Organocatalytic atroposelective synthesis of naphthoquinone thioglycosides from aryl-naphthoquinones and thiosugars

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Supplementary Information

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1. General Information

Nuclear magnetic resonance (NMR) spectra were recorded in DMSO-d_6 on Bruker 600 MHz, or JEOL 600 NMR instrument. Proton chemical shifts were reported in parts per million (δ scale). Spectral data were reported as follows: chemical shift (multiplicity [singlet (s), doublet (d), triplet (t), quartet (q), pentet (p), and multiplet (m)], coupling constants [Hz], integration). The ^{1}H NMR chemical shifts were reported in ppm with the residual non-deuterated solvents: DMSO-d_6 at 2.50 ppm as standard. The ^{13}C NMR chemical shifts were given using DMSO-d_6 as the internal standard (DMSO-d_6: δ = 39.5 ppm). High-resolution mass spectra (HRMS) were obtained using Agilent P/N G1969-90010 or Waters/Acquity UPLC-Synapt G2HDMS. High resolution mass spectra were reported for the molecular ion $[M+Na]^+$. Melting points were recorded on BUCHI Melting Point M-565 instrument. X-ray diffraction experiment was carried out on an Agilent Gemini or Agilent D8 QUEST, and the data obtained were deposited at the Cambridge Crystallographic Data Centre. Column chromatography was performed on silica gel (200-300 mesh) using an eluent of ethyl acetate (EA) and petroleum ether (PE). Large polar products were purified by Agilent semi-preparative liquid phase. TLC was performed on glass-backed silica plates; products were visualized using UV light (λ = 254 nm). Optical rotation values were measured with instruments operating at λ = 589 nm, corresponding to the sodium D line at 20 ℃. All reagents and solvents were obtained from commercial sources and used without further purification. Unless otherwise noted, reactions were run open to the air, and solvents were used without drying or degassing. [1,2'-binaphthalene]-1',4'-dione **1**[1,2], and glycosyl thiols **2**[3] were prepared according to the literature procedures.

Reference

(1) He, C.; Hou, M.; Zhu, Z.; Gu, Z. Enantioselective Synthesis of Indole-Based Biaryl Atropisomers via Palladium-Catalyzed Dynamic Kinetic Intramolecular C–H Cyclization. *ACS Catal.* **2017**, *7*, 5316-5320.

(2) Pan, C.; Zhu, Z.; Zhang, M.; Gu, Z. Palladium-Catalyzed Enantioselective Synthesis of 2-Aryl Cyclohex-2-enone Atropisomers: Platform Molecules for the Divergent Synthesis of Axially Chiral Biaryl Compounds. *Angew. Chem. Int. Ed.* **2017**, *56*, 4777-4781.

(3) Shu, P.; Zeng, J.; Tao, J.; Zhao, Y.; Yao, G.; Wan, Q. Selective S-deacetylation inspired by native chemical ligation: practical syntheses of glycosyl thiols and drug mercapto-analogues. *Green Chem.* **2015**, *17*, 2545-2551.

2. Optimizations of The Reaction Conditions

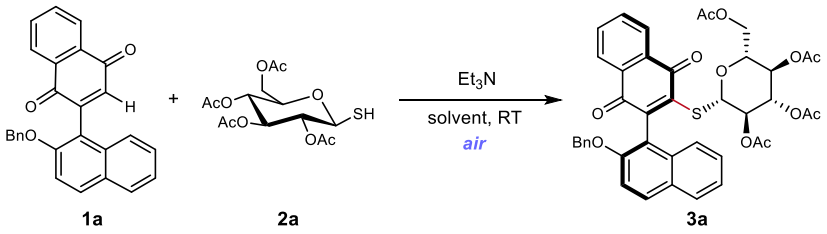


Table S1. Effect of solvents[a]

Entry	Solvent	Time (h)	Yield (%)[b]	dr[c]
1	DCM	24	90	3:1
2	THF	43	76	3:1
3	CH_3CN	43	88	1.4:1
4	DMF	1	93	1.5:1
5	DMSO	3	87	1.3:1
6	EtOH	3	95	2.2:1
7	n-hexane	96	trace	-

[a]Conditions: **1a** 20.0 mg (0.05 mmol), **2a** (1.20 eq.) and Et_3N (10 mol%) in Solvent (1.0 ml) at 25°C under air. [b]Yield of isolated product. [c]The dr value was determined by HPLC analysis.

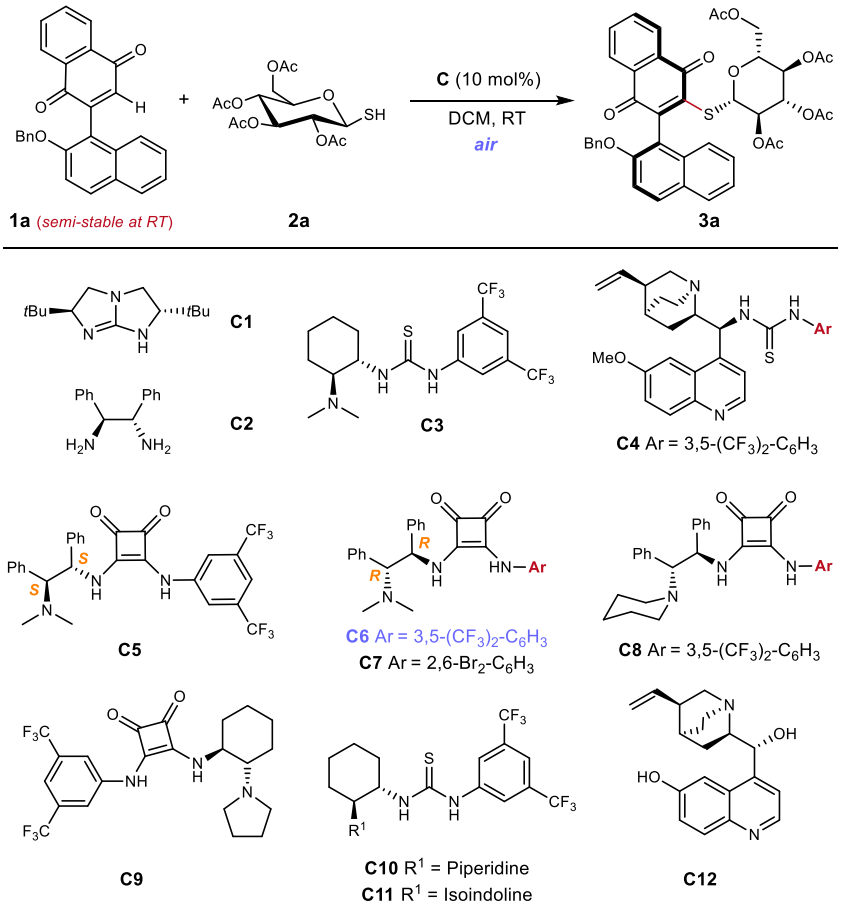


Table S2. Effect of catalysts[a]

Entry	Catlyst	Time (h)	Yield (%)[b]	dr[c]
1	none	-	trace	-
2	Et_3N	3	87	1.3:1
3	Et_3N	3	95	2.2:1
4	Et_3N	24	90	3:1
5	**C1**	50	73	1.8:1
6	**C2**	45	89	1.2:1
7	**C3**	48	61	1.3:1
8	**C4**	51	52	5.4:1
9	**C5**	33	82	5.4:1
10	**C6**	43	60	1:2.1
11	**C7**	43	22	2.4:1
12	**C8**	48	59	4.1:1
13	**C9**	43	68	1.6:1
14	**C10**	48	52	3:1
15	**C11**	51	49	1.7:1
16	**C12**	54	74	1.7:1

[a]Conditions: **1a** 20.0 mg (0.05 mmol), **2a** (1.20 eq.) and Catalyst (10 mol%) in DCM (1.0 ml) at 25℃ under air. [b]Yield of isolated product. [c]The dr value was determined by HPLC analysis.

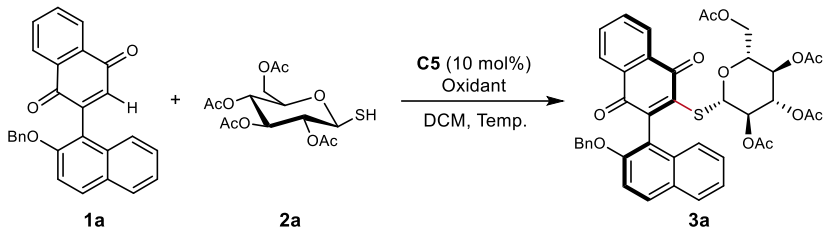
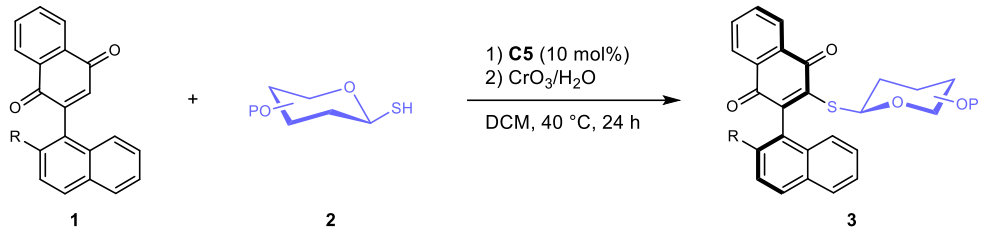


Table S3. Effect of temperature and oxidant[a]

Entry	Temp. (℃)	Oxidant	Time (h)	Yield (%)[e]	Dr[f]
1	25	none	33	82	5.4:1
2	40	none	24	83	13.3:1
3	60	none	17	98	9:1
4[b]	40	O_2	24	86	13.1:1
4[c]	40	O_2/$Cu(OAc)_2$	47	85	13.1:1
5[d]	40	CrO_3/H_2O	24	95	>19:1

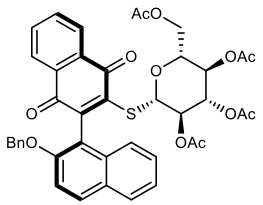
[a]Conditions: **1a** 20.0 mg (0.05 mmol), **2a** (1.20 eq.) and **C5** (10 mol%) in DCM (1.0 ml). [b]Under O_2 atmosphere. [c]$Cu(OAc)_2$ (20 mol%) was used. [d]CrO_3 (1.0 eq.) and H_2O (0.25 ml) was used. [e]Yield of isolated product. [f]The dr value was determined by HPLC analysis.

3. General Procedure for the Synthesis of 3 and Characterization Data



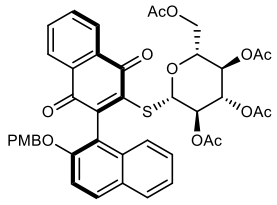
1 (0.10 mmol), **2** (1.20 eq.) and **C5** (10 mol%) were dissolved in dichloromethane (2.0 mL), and the mixture was stirred at 40 ℃ until complete consumption of the starting material. then, CrO_3 (1.0 eq.) and H_2O (0.5 ml) were added, the reaction mixture was stirred for 30 min. Anhydrous sodium sulfate was added to the reaction solution to remove water. Then, directly purified by flash column chromatography on silica gel using petroleum ether (PE) and EA (3/1 to 2/1 v/v) as eluents to afford the pure products **3**.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((2-(benzyloxy)-1',4'-dioxo-1',4'-dihydro-[1,2'-binaphthalen]-3'-yl)thio)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3a)



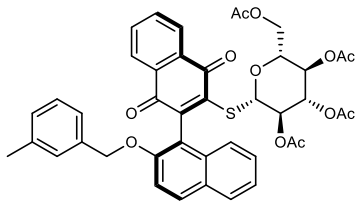
The residue was purified by a silica gel flash chromatography (PE/EA = 3/1) giving the product **3a** as a red-brown solid in 93% yield (70.0 mg), m.p. 97.1-98.3 °C. dr > 19:1, $[\alpha]_D^{20}$ = 134.5 (*c* = 0.50, dichloromethane). ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.17 (dd, *J* = 6.6, 1.2 Hz, 1H), 8.07 – 8.04 (m, 2H), 7.99 – 7.90 (m, 3H), 7.58 (d, *J* = 9.0 Hz, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.40 (t, *J* = 6.6 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.29 – 7.20 (m, 5H), 5.50 (d, *J* =10.2 Hz, 1H), 5.24 (d, *J* = 12.0 Hz, 1H), 5.20 (t, *J* = 9.6 Hz, 1H), 5.15 (d, *J* = 12.0 Hz, 1H), 4.74 (t, *J* = 10.2 Hz, 1H), 4.58 (t, *J* = 9.6 Hz, 1H), 4.05 (dd, *J* = 12.6, 5.4 Hz, 1H), 3.84 (dd, *J* = 12.6, 2.4 Hz, 1H), 3.79 (m, 1H), 1.94 (s, 3H), 1.88 (s, 3H), 1.79 (s, 3H), 1.74 (s, 3H) ^{13}C NMR (150 MHz, DMSO-d_6) δ 181.5, 180.8, 170.3, 169.9, 169.7, 169.4, 153.6, 146.9, 146.5, 137.4, 135.0, 134.8, 133.1, 132.2, 131.5, 131.5, 128.9, 128.8, 128.6, 128.24, 127.7, 127.4, 127.3, 126.9, 124.9, 124.4, 117.3, 115.2, 81.7, 75.1, 73.2, 71.3, 70.8, 68.2, 62.2, 20.8, 20.7, 20.6, 20.5. IR (cm^{-1}): 3060, 2940, 1757, 1667, 1588, 1370, 1274, 1221, 1047, 904, 809, 711, 601. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{41}H_{36}NaO_{12}S^+$ 775.1820, found 775.1822.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((2-((4-methoxybenzyl)oxy)-1',4'-dioxo-1',4'-dihydro-[1,2'-binaphthalen]-3'-yl)thio)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3b)



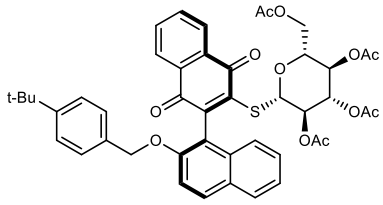
The residue was purified by a silica gel flash chromatography (PE/EA = 3/1) giving the product **3b** as a red-brown solid in 92% yield (71.8 mg), m.p. 66.5-67.8 °C. dr 14:1, $[\alpha]_D^{20}$ = 166.2 (*c* = 0.16, dichloromethane). ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.16 (dd, *J* = 7.8, 1.8 Hz, 1H), 8.07 – 8.02 (m, 2H), 7.99 – 7.87 (m, 3H), 7.58 (d, *J* = 9.0 Hz, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.35 (t, *J* = 8.4 Hz, 1H), 7.19 (d, *J* = 9.0 Hz, 2H), 6.78 (d, *J* = 9.0 Hz, 2H), 5.47 (d, *J* = 10.2 Hz, 1H), 5.19 (t, *J* = 9.0 Hz, 1H), 5.11 (dd, *J* = 65.9, 11.8 Hz, 2H), 4.74 (t, *J* = 10.2 Hz, 1H), 4.57 (t, *J* =9.6 Hz,1H), 4.04 (dd, *J* = 12.6, 5.4 Hz, 1H), 3.84 (dd, *J* = 12.6, 2.4 Hz, 1H), 3.78 (m, 1H), 3.68 (s, 3H), 1.94 (s, 3H), 1.88 (s, 3H), 1.81 (s, 3H), 1.73 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 181.5, 180.8, 170.3, 169.9, 169.7, 169.4, 159.4, 153.7, 146.7, 146.6, 135.0, 134.8, 133.0, 132.2, 131.5, 131.4, 129.5, 129.1, 128.9, 128.6, 127.4, 127.2, 127.0, 124.9, 124.4, 117.4, 115.4, 114.1, 81.7, 75.1, 73.2, 71.3, 70.7, 68.2, 62.2, 55.5, 20.8, 20.7, 20.6, 20.5. IR (cm^{-1}): 3057, 2926, 1748, 1664, 1588, 1507, 1367, 1274, 1232, 1042, 910, 812, 714, 599. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{42}H_{38}NaO_{13}S^+$ 805.1925, found 805.1922.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((2-((3-methylbenzyl)oxy)-1',4'-dioxo-1',4'-dihydro-[1,2'-binaphthalen]-3'-yl)thio)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3c)



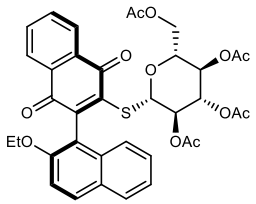
The residue was purified by a silica gel flash chromatography (PE/EA = 3/1) giving the product **3c** as a red-brown solid in 90% yield (69.1 mg), m.p. 70.6-71.5 °C. dr > 19:1, $[\alpha]_D^{20}$ = 152.2 (*c* = 0.50, dichloromethane). ^{1}H NMR (600 MHz, DMSO-*d*6) δ 8.18 (dd, *J* = 7.2, 1.8 Hz, 1H), 8.09 – 8.00 (m, 2H), 8.00 – 7.91 (m, 3H), 7.58 (d, *J* = 9.6 Hz, 1H), 7.54 (d, *J* = 9.0 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.37 (t, *J* = 8.4 Hz, 1H), 7.12 (t, *J* = 7.2 Hz, 1H), 7.05 (d, *J* = 7.2 Hz, 1H), 7.01 (d, *J* = 7.8 Hz, 2H), 5.48 (d, *J* = 10.2 Hz, 1H), 5.22 – 5.17 (m, 2H), 5.09 (d, *J* = 12.6 Hz, 1H), 4.75 (t, *J* = 9.6 Hz, 1H), 4.57 (t, *J* = 9.6 Hz, 1H), 4.06 (dd, *J* = 12.6, 5.4 Hz, 1H), 3.85 (dd, *J* = 12.0, 1.8 Hz, 1H), 3.78 (m, 1H), 2.10 (s, 3H), 1.95 (s, 3H), 1.88 (s, 3H), 1.79 (s, 3H), 1.75 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 181.4, 180.8, 170.3, 169.9, 169.7, 169.4, 153.6, 146.9, 146.7, 137.9, 137.2, 135.0, 134.8, 133.0, 132.2, 131.5, 131.5, 128.9, 128.8, 128.6, 128.6, 128.2, 127.4, 127.3, 126.9, 124.9, 124.7, 124.4, 117.4, 115.2, 81.7, 75.1, 73.2, 71.3, 70.8, 68.2, 62.2, 21.2, 20.8, 20.7, 20.6, 20.5. IR (cm^{-1}): 3060, 2942, 1754, 1664, 1588, 1370, 1274, 1224, 1047, 907, 812, 711, 601. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{42}H_{38}NaO_{12}S^+$ 789.1976, found 789.1976.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((2-((4-(tert-butyl)benzyl)oxy)-1',4'-dioxo-1',4'-dihydro-[1,2'-binaphthalen]-3'-yl)thio)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3d)



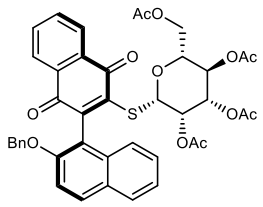
The residue was purified by a silica gel flash chromatography (PE/EA = 3/1) giving the product **3d** as a yellow solid in 80% yield (64.8 mg), m.p. 89.2-90.4 °C. dr > 19:1, $[\alpha]_D^{20}$ = 362.5 (*c* = 0.20, dichloromethane). ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ 8.17 (dd, *J* = 7.8, 1.8 Hz, 1H), 8.08 – 8.03 (m, 2H), 7.99 – 7.89 (m, 3H), 7.57 (d, *J* = 9.0 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.35 (t, *J* = 8.4 Hz, 1H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 7.8 Hz, 2H), 5.49 (d, *J* = 10.2 Hz, 1H), 5.23 – 5.17 (m, 2H), 5.11 (d, *J* = 12.6 Hz, 1H), 4.74 (t, *J* = 10.2 Hz, 1H), 4.58 (t, *J* = 9.6 Hz, 1H), 4.05 (dd, *J* = 12.0, 5.4 Hz, 1H), 3.84 (dd, *J* = 12.6, 2.4 Hz, 1H), 3.78 (m, 1H), 1.94 (s, 3H), 1.88 (s, 3H), 1.80 (s, 3H), 1.74 (s, 3H), 1.20 (s, 9H). ^{13}C NMR (150 MHz, DMSO-*d*$_6$) δ 181.5, 180.8, 170.3, 169.9, 169.7, 169.4, 153.7, 150.6, 146.8, 146.6, 134.9, 134.8, 134.3, 133.1, 132.2, 131.5, 131.4, 128.8, 128.6, 127.5, 127.4, 127.3, 127.0, 125.5, 124.9, 124.4, 117.3, 115.2, 81.8, 75.1, 73.2, 71.3, 70.6, 68.2, 62.2, 34.7, 31.5, 20.8, 20.7, 20.6, 20.5. IR (cm^{-1}): 3057, 2962, 1757, 1670, 1588, 1364, 1277, 1227, 1047, 915, 817, 716, 601. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{45}H_{44}NaO_{12}S^+$ 831.2446, found 831.2415.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((2-ethoxy-1',4'-dioxo-1',4'-dihydro-[1,2'-binaphthalen]-3'-yl)thio)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3e)



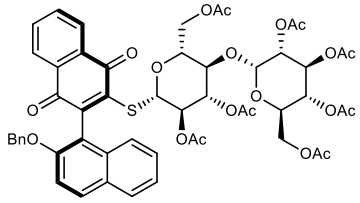
The residue was purified by preparing liquid phase (n-hexane/EA = 4/1) giving the product **3e** as a red-brown solid in 86% yield (59.7 mg), m.p. 68.5-69.6 °C. dr 2:1, $[\alpha]_D^{20}$ = −52.4 (*c* = 0.50, dichloromethane). ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ 8.19 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.06 (d, *J* = 9.0 Hz, 1H), 8.03 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.97 (td, *J* = 7.2, 1.2 Hz, 1H), 7.95 – 7.90 (m, 2H), 7.53 (d, *J* = 9.0 Hz, 1H), 7.46 (d, *J* = 9.6 Hz, 1H), 7.38 (td, *J* = 7.2, 1.8 Hz, 1H), 7.34 (td, *J* = 8.4, 1.8 Hz, 1H), 5.51 (d, *J* = 10.2 Hz, 1H), 5.22 (t, *J* = 9.6 Hz, 1H), 4.74 (t, *J* = 9.6 Hz, 1H), 4.58 (t, *J* = 9.0 Hz, 1H), 4.21 – 4.16 (m, 1H), 4.12 – 4.07 (m, 1H), 4.04 (dd, *J* = 12.6, 6.0 Hz, 1H), 3.86 (dd, *J* = 12.6, 2.4 Hz, 1H), 3.82 (m, 1H), 1.95 (s, 3H), 1.88 (s, 3H), 1.86 (s, 3H), 1.72 (s, 3H), 1.14 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, DMSO-*d*$_6$) δ 181.4, 180.8, 170.3, 169.9, 169.7, 169.4, 153.9, 146.7, 146.6, 135.1, 134.8, 133.1, 132.2, 131.5, 131.5, 128.8, 128.6, 127.4, 127.2, 126.9, 124.9, 124.2, 117.2, 115.1, 81.6, 75.0, 73.2, 71.3, 68.3, 65.0, 62.3, 20.8, 20.7, 20.6, 20.5, 15.2. IR (cm^{-1}): 3057, 2979, 2937, 1754, 1667, 1588, 1364, 1277, 1229, 1056, 910, 812, 711, 601. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{36}H_{34}NaO_{12}S^+$ 713.1663, found 713.1669.

(2*R*,3*R*,4*S*,5*S*,6*S*)-2-(acetoxymethyl)-6-((2-(benzyloxy)-1',4'-dioxo-1',4'-dihydro-[1,2'-binaphthalen]-3'-yl)thio)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3f)



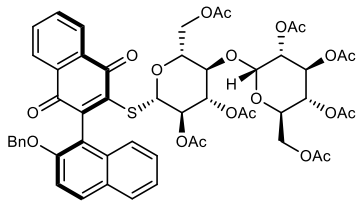
The residue was purified by a silica gel flash chromatography (PE/EA = 3/1) giving the product **3f** as a red-brown solid in 80% yield (60.3 mg), m.p. 97.8-98.7 °C. dr 3:1, $[\alpha]_D^{20}$ = 141.0 (*c* = 0.20, dichloromethane). ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.20 (dd, *J* = 7.8, 1.8 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 2H), 7.96 (td, *J* = 6.6, 0.6 Hz, 1H), 7.94 – 7.90 (m, 2H), 7.55 (d, J = 9.0 Hz, 1H), 7.52 (d, *J* = 9.0 Hz, 1H), 7.41 – 7.37 (m, 2H), 7.27 – 7.19 (m, 5H), 5.74 (d, *J* = 1.2 Hz, 1H), 5.55 (d, *J* = 3.6 Hz, 1H), 5.24 (d, *J* = 12.6 Hz, 1H), 5.20 – 5.15 (m, 2H), 4.87 (t, *J* = 9.6 Hz, 1H), 4.05 (dd, *J* = 12.6, 6.0 Hz, 1H), 3.81 – 3.74 (m, 2H), 1.98 (s, 3H), 1.90 (s, 3H), 1.78 (s, 3H), 1.72 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 181.5, 181.1, 170.3, 170.1, 169.9, 169.9, 153.7, 147.7, 146.1, 137.4, 135.1, 134.8, 132.9, 132.1, 131.3, 131.2, 128.9, 128.8, 128.7, 128.5, 128.1, 127.5, 127.5, 127.5, 127.2, 126.9, 125.1, 124.3, 117.5, 115.2, 81.6, 75.6, 71.3, 70.7, 70.7, 65.6, 62.5, 20.9, 20.7, 20.7, 20.3. IR (cm^{-1}): 3060, 2942, 1745, 1664, 1588, 1367, 1277, 1218, 1047, 969, 812, 711, 604. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{41}H_{36}NaO_{12}S^+$ 775.1820, found 775.1826.

(2*S*,3*S*,4*R*,5*S*,6*S*)-2-(acetoxymethyl)-6-(((2*S*,3*S*,4*R*,5*S*,6*R*)-4,5-diacetoxy-2-(acetoxymethyl)-6-((2-(benzyloxy)-1',4'-dioxo-1',4'-dihydro-[1,2'-binaphthalen]-3'-yl)thio)tetrahydro-2*H*-pyran-3-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3g)



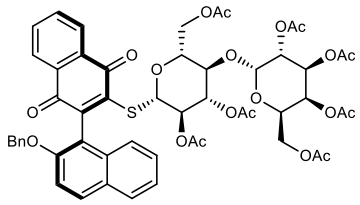
The residue was purified by a silica gel flash chromatography (PE/EA = 2/1) giving the product **3g** as a red-brown solid in 90% yield (93.5 mg), m.p. 72.8-73.4 °C. dr > 19:1, $[\alpha]_D^{20}$ = −227.0 (*c* = 0.20, dichloromethane). ^{1}H NMR (150 MHz, DMSO-d_6) δ 8.17 (dd, *J* = 7.2, 1.2 Hz, 1H), 8.05 (dd, *J* = 7.8, 1.8 Hz, 1H), 8.04 (d, *J* = 9.0 Hz, 1H), 7.97 (td, *J* = 7.8, 1.8 Hz, 1H), 7.96 – 7.91 (m, 2H), 7.56 (d, *J* = 9.6 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.38 (td, *J* = 7.5, 1.2 Hz, 1H), 7.35 (td, *J* = 8.4, 1.2 Hz, 1H), 7.29 – 7.20 (m, 5H), 5.57 (d, *J* = 10.2 Hz, 1H), 5.28 – 5.21 (m, 2H), 5.21 – 5.14 (m, 3H), 4.95 (t, *J* = 9.6 Hz, 1H), 4.82 (dd, *J* = 10.2, 3.6 Hz, 1H), 4.48 (t, *J* = 9.6 Hz, 1H), 4.20 (dd, *J* = 12.6, 2.4 Hz, 1H), 4.12 (dd, *J* = 12.6, 4.8 Hz, 1H), 4.06 (dd, *J* = 12.0, 4.8 Hz, 1H), 3.96 (dd, *J* = 12.0, 2.4 Hz, 1H), 3.91 (m, 1H), 3.83 – 3.74 (m, 2H), 1.99 (s, 3H), 1.98 (s, 3H), 1.96 (s, 3H), 1.94 (s, 3H), 1.88 (s, 3H), 1.77 (s, 3H), 1.74 (s, 3H). ^{13}C NMR (600 MHz, DMSO-d_6) δ 181.5, 180.7, 170.5, 170.4, 170.3, 170.0, 169.9, 169.6, 169.5, 153.6, 147.1, 146.6, 137.4, 135.0, 134.8, 133.1, 132.2, 131.5, 131.4, 128.9, 128.8, 128.6, 128.2, 127.7, 127.4, 127.2, 126.9, 124.9, 124.4, 117.3, 115.1, 95.8, 81.4, 75.8, 75.2, 74.2, 71.9, 70.8, 69.9, 69.3, 68.4, 68.2, 63.5, 61.9, 20.9, 20.9, 20.8, 20.8, 20.7, 20.6, 20.5. IR (cm^{-1}): 3060, 2948, 1748, 1664, 1591, 1372, 1271, 1232, 1039, 901, 814, 716, 604. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{53}H_{52}NaO_{20}S^+$ 1063.2665, found 1063.2662.

(2*S*,3*S*,4*R*,5*S*,6*R*)-2-(acetoxymethyl)-6-(((2*S*,3*S*,4*R*,5*S*,6*S*)-4,5-diacetoxy-2-(acetoxymethyl)-6-((2-(benzyloxy)-1',4'-dioxo-1',4'-dihydro-[1,2'-binaphthalen]-3'-yl)thio)tetrahydro-2*H*-pyran-3-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3h)



The residue was purified by a silica gel flash chromatography (PE/EA = 2/1) giving the product **3h** as a red-brown solid in 80% yield (83.4 mg), m.p. 96.5-96.9 °C. dr > 19:1, $[\alpha]_D^{20}$ = 103.0 (*c* = 0.30, dichloromethane). ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.16 (dd, *J* = 7.8, 1.8 Hz, 1H), 8.04 (d, *J* = 9.0 Hz, 1H), 7.96 (td, *J* = 7.2, 1.8 Hz, 1H), 7.95 – 7.90 (m, 2H), 7.56 (d, *J* = 9.0 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.34 (t, *J* = 8.4 Hz, 1H), 7.28 – 7.20 (m, 5H), 5.50 (d, *J* = 10.0 Hz, 1H), 5.23 (d, *J* = 12.0 Hz, 1H), 5.19 (t, *J* = 9.6 Hz, 1H), 5.16 (d, *J* = 12.0 Hz, 1H), 5.09 (t, *J* = 9.0 Hz, 1H), 4.84 (t, *J* = 9.6 Hz, 1H), 4.75 (d, *J* = 8.4 Hz, 1H), 4.61 (dd, *J* = 9.6, 7.8 Hz, 1H), 4.47 (t, *J* = 9.6 Hz, 1H), 4.20 – 4.14 (m, 2H), 3.99 – 3.91 (m, 2H), 3.90 (dd, *J* = 12.0, 2.4 Hz, 1H), 3.69 – 3.58 (m, 2H), 1.97 (s, 3H), 1.95 (s, 3H), 1.95 (s, 3H), 1.90 (s, 3H), 1.88 (s, 3H), 1.80 (s, 3H), 1.71 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 181.4, 180.6, 170.5, 170.5, 170.1, 169.8, 169.7, 169.5, 169.4, 153.6, 147.0, 146.8, 137.3, 135.1, 134.9, 133.0, 132.1, 131.5, 131.4, 128.9, 128.8, 128.6, 128.2, 127.7, 127.4, 127.2, 126.9, 124.9, 124.4, 117.4, 115.1, 99.9, 81.6, 76.6, 76.3, 73.2, 72.7, 71.6, 71.5, 70.9, 70.8, 68.1, 62.7, 61.9, 20.9, 20.8, 20.7, 20.7, 20.6, 20.5. IR (cm^{-1}): 3060, 2945, 1754, 1664, 1588, 1370, 1271, 1229, 1047, 907, 812, 714, 599. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{53}H_{52}NaO_{20}S^+$ 1063.2665, found 1063.2686.

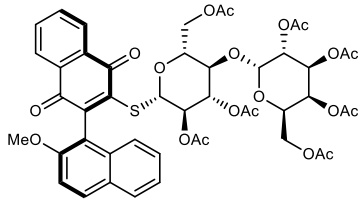
(2*S*,3*R*,4*R*,5*S*,6*R*)-2-(acetoxymethyl)-6-(((2*S*,3*S*,4*R*,5*S*,6*S*)-4,5-diacetoxy-2-(acetoxymethyl)-6-((2-(benzyloxy)-1',4'-dioxo-1',4'-dihydro-[1,2'-binaphthalen]-3'-yl)thio)tetrahydro-2*H*-pyran-3-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3i)



The residue was purified by a silica gel flash chromatography (PE/EA = 2/1) giving the product **3i** as a red-brown solid in 91% yield (95.0 mg), m.p. 97.0-98.3 °C. dr 12:1, $[\alpha]_D^{20}$ = 105.6 (*c* = 0.50, dichloromethane). ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.17 (d, *J* = 7.8 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 2H), 7.98 – 7.91 (m, 3H), 7.56 (d, *J* = 9.0 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.29 – 7.20 (m, 5H), 5.53 (d, *J* = 10.2 Hz, 1H), 5.24 (d, *J* = 12.0 Hz, 1H), 5.21 (d, *J* = 3.6 Hz, 1H), 5.16 (d, *J* = 12.0 Hz, 1H), 5.14 – 5.08 (m, 2H), 4.82 (dd, *J* = 10.2, 7.8 Hz, 1H), 4.69 (d, *J* = 7.8 Hz, 1H), 4.48 (t, *J* = 9.6 Hz, 1H), 4.18 – 4.13 (m, 2H), 4.00 – 3.93 (m, 3H), 3.67 – 3.63 (m, 2H), 2.08 (s, 3H), 1.98 (s, 3H), 1.96 (s, 3H), 1.91 (s, 3H), 1.89 (s, 3H), 1.80 (s, 3H), 1.71 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 181.4, 180.7, 170.5, 170.4, 170.3, 169.9, 169.7, 169.5, 153.6, 147.0, 146.8, 137.4, 135.0, 134.8, 133.0, 132.2, 131.5, 131.4, 128.9, 128.8, 128.6, 128.2, 127.7, 127.4,

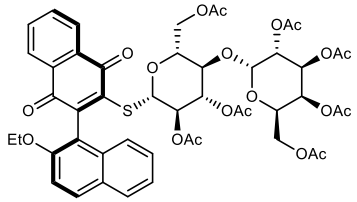
127.2, 126.9, 124.9, 124.4, 117.4, 115.1, 100.2, 81.5, 76.4, 76.3, 73.5, 71.7, 70.8, 70.8, 70.1, 69.3, 67.5, 62.8, 61.4, 20.9, 20.8, 20.8, 20.8, 20.8, 20.5, 20.5. IR (cm^{-1}): 3060, 2940, 1751, 1667, 1588, 1370, 1274, 1227, 1050, 907, 809, 714, 604. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{53}H_{52}NaO_{20}S^+$ 1063.2665, found 1063.2677.

(2*S*,3*R*,4*R*,5*S*,6*R*)-2-(acetoxymethyl)-6-(((2*S*,3*S*,4*R*,5*S*,6*S*)-4,5-diacetoxy-2-(acetoxymethyl)-6-((2-methoxy-1',4'-dioxo-1',4'-dihydro-[1,2'-binaphthalen]-3'-yl)thio)tetrahydro-2*H*-pyran-3-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3j)



The residue was purified by a silica gel flash chromatography (PE/EA = 2/1) giving the product **3j** as a red-brown solid in 81% yield (78.3 mg), m.p. 97.5-98.8 °C. dr > 19:1, $[\alpha]_D^{20}$ = 116.2 (*c* = 0.50, dichloromethane). ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.18 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.07 (d, *J* = 9.0 Hz, 1H), 8.02 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.96 (td, *J* = 7.8, 1.2 Hz, 1H), 7.96 – 7.89 (m, 2H), 7.54 (d, *J* = 9.0 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.38 (t, *J* = 8.4 Hz, 1H), 7.32 (t, *J* = 8.4 Hz, 1H), 5.55 (d, *J* = 10.2 Hz, 1H), 5.20 (d, *J* = 4.2 Hz, 1H), 5.13 – 5.07 (m, 2H), 4.81 (dd, *J* = 10.2, 7.8 Hz, 1H), 4.69 (d, *J* = 7.8 Hz, 1H), 4.47 (t, *J* = 9.6 Hz, 1H), 4.20 – 4.13 (m, 2H), 4.01 – 3.92 (m, 3H), 3.79 (s, 3H), 3.71 (td, 10.2, 1.8 Hz, 1H), 3.66 (q, *J* = 9.6 Hz, 1H), 2.08 (s, 3H), 1.98 (s, 3H), 1.96 (s, 3H), 1.90 (s, 3H), 1.88 (s, 3H), 1.84 (s, 3H), 1.71 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 181.3, 180.7, 170.5, 170.4, 170.3, 169.9, 169.7, 169.5, 169.5, 154.4, 147.1, 146.6, 135.1, 134.9, 133.1, 132.1, 131.5, 131.4, 128.7, 128.6, 127.4, 127.2, 126.9, 124.7, 124.2, 116.6, 113.8, 100.2, 81.2, 76.4, 76.3, 73.5, 71.9, 70.8, 70.1, 69.3, 67.5, 62.8, 61.3, 56.9, 20.9, 20.8, 20.8, 20.8, 20.6, 20.5. IR (cm^{-1}): 3063, 2942, 1754, 1667, 1594, 1367, 1274, 1227, 1053, 913, 814, 716, 601. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{47}H_{48}NaO_{20}S^+$ 987.2352, found 987.2369.

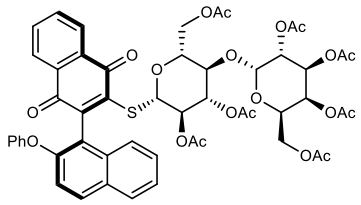
(2*S*,3*R*,4*R*,5*S*,6*R*)-2-(acetoxymethyl)-6-(((2*S*,3*S*,4*R*,5*S*,6*S*)-4,5-diacetoxy-2-(acetoxymethyl)-6-((2-ethoxy-1',4'-dioxo-1',4'-dihydro-[1,2'-binaphthalen]-3'-yl)thio)tetrahydro-2*H*-pyran-3-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3k)



The residue was purified by a silica gel flash chromatography (PE/EA = 2/1) giving the product **3k** as a red-brown solid in 83% yield (81.6 mg), m.p. 97.0-98.6 °C. dr > 19:1, $[\alpha]_D^{20}$ = 109.6 (*c* = 0.50, dichloromethane). ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.19 (dd, *J* = 7.8, 1.8 Hz, 1H), 8.04 (d, *J* = 9.0 Hz, 1H), 8.03 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.96 (td, *J* = 7.8, 1.8 Hz, 1H), 7.95 - 7.89 (m, 2H), 7.51 (d, *J* = 9.0 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.38 (t, *J* = 8.4 Hz, 1H), 7.32 (t, *J* = 8.4 Hz, 1H), 5.52 (d, *J* = 10.2 Hz, 1H), 5.20 (d, *J* = 4.2 Hz, 1H), 5.13 – 5.07 (m, 2H), 4.81 (dd, *J* = 10.2, 7.8 Hz, 1H), 4.69 (d, *J* = 7.8 Hz, 1H), 4.48 (t, *J* = 9.6 Hz, 1H), 4.20 – 4.12 (m,

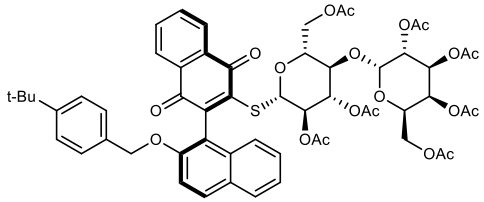
3H), 4.08 (dd, *J* = 9.6, 7.8 Hz, 1H), 4.01 – 3.92 (m, 3H), 3.70 – 3.61 (m, 2H), 2.08 (s, 3H), 1.97 (s, 3H), 1.96 (s, 3H), 1.91 (s, 3H), 1.88 (s, 3H), 1.85 (s, 3H), 1.69 (s, 3H), 1.13 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 181.4, 180.7, 170.4, 170.4, 170.3, 169.9, 169.7, 169.5, 169.5, 153.9, 146.9, 146.7, 135.1, 134.8, 133.0, 132.1, 131.4, 128.8, 128.6, 127.4, 127.1, 126.9, 124.8, 124.2, 117.2, 115.1, 100.2, 81.4, 76.4, 76.3, 73.5, 71.7, 70.8, 70.1, 69.3, 67.5, 65.0, 62.8, 61.3, 20.9, 20.8, 20.8, 20.7, 20.6, 20.4, 15.1. IR (cm^{-1}): 3057, 2979, 2934, 1745, 1667, 1588, 1370, 1277, 1229, 1058, 910, 812, 719, 604. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{48}H_{50}NaO_{20}S^+$ 1001.2508, found 1001.2543.

(2*S*,3*R*,4*R*,5*S*,6*R*)-2-(acetoxymethyl)-6-(((2*S*,3*S*,4*R*,5*S*,6*S*)-4,5-diacetoxy-2-(acetoxymethyl)-6-((1',4'-dioxo-2-phenoxy-1',4'-dihydro-[1,2'-binaphthalen]-3'-yl)thio)tetrahydro-2*H*-pyran-3-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3l)



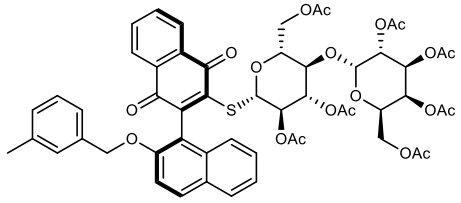
The residue was purified by a silica gel flash chromatography (PE/EA = 2/1) giving the product **3l** as a yellow solid in 80% yield (82.0 mg), m.p. 113.3-114.3 °C, dr 10:1, $[\alpha]_D^{20}$ = 68.5 (*c* = 0.20, dichloromethane). ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.15 (dd, *J* = 7.2, 1.2 Hz, 1H), 8.06 (d, *J* = 7.8 Hz, 1H), 8.00 (d, *J* = 7.2 Hz, 1H), 7.96 (dd, *J* = 6.6, 1.2 Hz, 1H), 7.94 (td, *J* = 6.6, 1.2 Hz, 1H), 7.88 (td, *J* = 6.6, 1.2 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.51 (t, *J* = 6.6 Hz, 1H), 7.40 (td, *J* = 6.0, 1.2 Hz, 1H), 7.30 (t, *J* = 7.2 Hz, 2H), 7.18 (d, *J* = 7.2 Hz, 1H), 7.07 (t, *J* = 6.6 Hz, 1H), 6.94 (dd, *J* = 7.8, 1.2 Hz, 2H), 5.59 (d, *J* = 8.4 Hz, 1H), 5.20 (d, *J* = 4.2 Hz, 1H), 5.16 (t, *J* = 7.2 Hz, 1H), 5.10 (dd, *J* = 8.4, 3.0 Hz, 1H), 4.81 (dd, *J* = 9.0, 6.6 Hz, 1H), 4.70 (d, *J* = 6.6 Hz, 1H), 4.53 (t, *J* = 8.4 Hz, 1H), 4.19 – 4.13 (m, 2H), 4.01 – 3.93 (m, 3H), 3.72 – 3.64 (m, 2H), 2.08 (s, 3H), 1.98 (s, 3H), 1.96 (s, 3H), 1.92 (s, 3H), 1.89 (s, 3H), 1.89 (s, 3H), 1.68 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 181.3, 180.3, 170.5, 170.4, 170.4, 170.0, 169.8, 169.6, 169.5, 157.1, 151.9, 147.5, 145.8, 135.1, 134.9, 132.9, 131.8, 131.8, 131.6, 130.4, 130.2, 128.8, 127.5, 127.5, 126.9, 125.7, 125.4, 124.1, 120.7, 119.0, 100.2, 81.3, 76.4, 76.3, 73.4, 71.8, 70.8, 70.1, 69.2, 67.5, 62.7, 61.3, 20.9, 20.8, 20.8, 20.8, 20.7, 20.5. IR (cm^{-1}): 3060, 2942, 1745, 1667, 1591, 1370, 1229, 1050, 904, 758, 714, 601. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{52}H_{50}NaO_{20}S^+$ 1049.2508, found 1049.2518.

(2*S*,3*R*,4*R*,5*S*,6*R*)-2-(acetoxymethyl)-6-(((2*S*,3*S*,4*R*,5*S*,6*S*)-4,5-diacetoxy-2-(acetoxymethyl)-6-((2-((4-(tert-butyl)benzyl)oxy)-1',4'-dioxo-1',4'-dihydro-[1,2'-binaphthalen]-3'-yl)thio)tetrahydro-2*H*-pyran-3-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3m)



The residue was purified by a silica gel flash chromatography (PE/EA = 2/1) giving the product **3m** as a red solid in 68% yield (74.5 mg), m.p. 117.0-117.9 °C, dr 9:1, $[\alpha]_D^{20}$ =99.0 (*c* = 0.30, dichloromethane). ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.16 (dd, *J* = 7.2, 1.2 Hz, 1H), 8.04 (dd, *J* = 6.0, 1.8 Hz, 1H), 8.03 (d, *J* = 6.0 Hz, 1H), 7.96 (td, *J* = 7.2, 1.2 Hz, 1H), 7.95 – 7.90 (m, 2H), 7.54 (d, *J* = 9.0 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.39 (t, *J* = 8.4 Hz, 1H), 7.33 (t, *J* = 8.4 Hz, 0H), 7.25 (d, *J* = 7.8 Hz, 2H), 7.19 (d, *J* = 7.8 Hz, 2H), 5.53 (d, *J* = 10.2 Hz, 1H), 5.20 (dd, *J* = 6.6, 3.0 Hz, 2H), 5.14 – 5.09 (m, 2H), 5.09 (dd, *J* = 7.2, 3.6 Hz, 1H), 4.81 (dd, *J* = 10.2, 7.8 Hz, 1H), 4.69 (d, *J* = 8.4 Hz, 1H), 4.48 (t, *J* = 9.6 Hz, 1H), 4.18 – 4.13 (m, 2H), 3.96 (m, 3H), 3.70 – 3.61 (m, 2H), 2.08 (s, 3H), 1.97 (s, 3H), 1.96 (s, 3H), 1.91 (s, 3H), 1.88 (s, 3H), 1.81 (s, 3H), 1.71 (s, 3H), 1.20 (s, 9H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 181.5, 180.7, 170.5, 170.4, 170.4, 169.9, 169.8, 169.5, 153.7, 150.6, 146.9, 146.8, 135.0, 134.8, 134.4, 133.1, 132.2, 131.5, 131.4, 128.9, 128.6, 127.5, 127.4, 127.3, 127.2, 127.0, 125.5, 125.4, 124.8, 124.3, 117.4, 115.2, 100.3, 81.5, 76.45, 76.3, 73.5, 71.7, 70.8, 70.6, 70.2, 69.3, 67.5, 62.8, 61.4, 34.7, 31.5, 20.9, 20.9, 20.8, 20.8, 20.6, 20.5. IR (cm^{-1}): 3060, 2962, 1754, 1664, 1591, 1364, 1271, 1227, 1050, 913, 820, 716, 599. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{57}H_{60}NaO_{20}S^+$ 1119.3291, found 1119.3291.

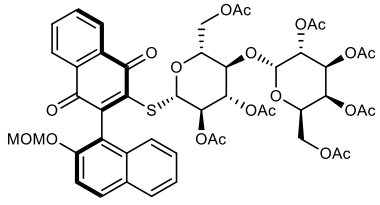
(2*S*,3*R*,4*R*,5*S*,6*R*)-2-(acetoxymethyl)-6-(((2*S*,3*S*,4*R*,5*S*,6*S*)-4,5-diacetoxy-2-(acetoxymethyl)-6-((2-((3-methylbenzyl)oxy)-1',4'-dioxo-1',4'-dihydro-[1,2'-binaphthalen]-3'-yl)thio)tetrahydro-2*H*-pyran-3-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3n)



The residue was purified by a silica gel flash chromatography (PE/EA = 2/1) giving the product **3n** as a red solid in 70% yield (74.8 mg), m.p.90.1-91.1°C, dr 10:1, $[\alpha]_D^{20}$ = 98.0 (*c* = 0.30, dichloromethane). ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.18 (d, *J* = 7.8 Hz, 1H), 8.05 (d, *J* = 9.0 Hz, 2H), 7.96 (t, *J* = 14.4 Hz, 1H), 7.96 – 7.89 (m, 2H), 7.56 (d, *J* = 9.0 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.34 (t, *J* = 8.4 Hz, 1H), 7.11 (t, *J* = 7.2 Hz, 1H), 7.04 (d, *J* = 7.8 Hz, 1H), 7.01 (d, *J* = 7.2 Hz, 2H), 5.51 (d, *J* = 10.2 Hz, 1H), 5.22 – 5.16 (m, 2H), 5.12 – 5.07 (m, 3H), 4.81 (dd, *J* = 10.2, 7.8 Hz, 1H), 4.69 (d, *J* = 7.8 Hz, 1H), 4.47 (t, *J* = 9.6 Hz, 1H), 4.18 – 4.13 (m, 2H), 4.01 – 3.93 (m, 3H), 3.66 – 3.63 (m, 2H), 2.10 (s, 3H), 2.08 (s, 3H), 1.98 (s, 3H), 1.96 (s, 3H), 1.90 (s, 3H), 1.89 (s, 3H), 1.80 (s, 3H), 1.72 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 181.4, 180.7, 170.5, 170.4, 170.4, 169.9, 169.7, 169.5, 169.5, 153.7, 147.1, 146.9, 137.9, 137.3, 135.1, 134.9, 133.0, 132.2,

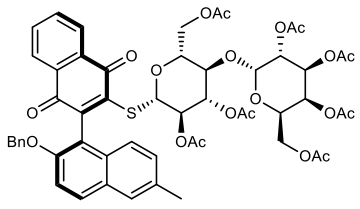
131.4, 131.4, 128.9, 128.8, 128.7, 128.6, 128.6, 128.1, 127.4, 127.2, 126.9, 124.9, 124.7, 124.4, 117.5, 115.2, 100.3, 81.5, 76.4, 76.3, 73.5, 71.7, 70.8, 70.8, 70.1, 69.3, 67.5, 62.8, 61.4, 21.3, 20.9, 20.8, 20.8, 20.5, 20.5. IR (cm^{-1}): 3057, 2937, 1748, 1670, 1585, 1367, 1274, 1227, 1053, 907, 812, 711, 607. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{54}H_{54}NaO_{20}S^+$ 1077.2821, found 1077.2821.

(2*R*,3*S*,4*S*,5*R*,6*R*)-2-(acetoxymethyl)-6-(((2*R*,3*R*,4*S*,5*R*,6*S*)-4,5-diacetoxy-2-(acetoxymethyl)-6-((2-(methoxymethoxy)-1',4'-dioxo-1',4'-dihydro-[1,2'-binaphthalen]-3'-yl)thio)tetrahydro-2*H*-pyran-3-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3o)



The residue was purified by a silica gel flash chromatography (PE/EA = 2/1) giving the product **3o** as a yellow solid in 90% yield (52.1 mg), m.p.61.3-61.8 °C, dr 12:1, $[\alpha]_D^{20}$ = 159.4 (*c* = 0.50, dichloromethane).^{1}H NMR (600 MHz, DMSO-d_6) δ 8.19 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.06 – 8.00 (m, 2H), 7.96 (td, *J* = 7.8, 1.8 Hz, 1H), 7.97 – 7.90 (m, 2H), 7.53 (d, *J* = 9.0 Hz, 1H), 7.45 (d, *J* = 9.0 Hz, 1H), 7.40 (td, *J* = 7.8, 1.2 Hz, 1H), 7.33 (td, *J* = 8.4, 1.2 Hz, 1H), 5.58 (d, *J* = 10.2 Hz, 1H), 5.23 (d, *J* = 7.2 Hz, 1H), 5.19 (dd, *J* = 3.6, 1.2 Hz, 1H), 5.16 (d, *J* = 7.2 Hz, 1H), 5.12 (t, *J* = 9.0 Hz, 1H), 5.09 (dd, *J* = 10.8, 3.6 Hz, 1H), 4.80 (dd, *J* = 10.2, 7.8 Hz, 1H), 4.68 (d, *J* = 7.8 Hz, 1H), 4.47 (dd, *J* = 10.2, 9.6 Hz, 1H), 4.15 (dd, *J* = 6.6, 5.4 Hz, 2H), 4.00 – 3.91 (m, 3H), 3.73 – 3.67 (m, 1H), 3.64 (t, *J* = 13.8 Hz, 1H), 3.24 (s, 3H), 2.08 (s, 3H), 1.97 (s, 3H), 1.96 (s, 3H), 1.90 (s, 3H), 1.88 (s, 3H), 1.86 (s, 3H), 1.68 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 181.3, 180.6, 170.4, 170.3, 170.3, 169.9, 169.7, 169.5, 169.4, 152.0, 147.1, 146.7, 135.1, 134.9, 133.0, 132.0, 131.4, 131.1, 129.2, 128.5, 127.4, 127.1, 126.9, 124.9, 124.6, 118.0, 116.0, 100.2, 94.6, 81.2, 76.4, 76.2, 73.4, 71.7, 70.7, 70.1, 69.2, 67.5, 62.8, 61.3, 56.2, 20.9, 20.8, 20.7, 20.6, 20.4. IR (cm^{-1}): 3063, 2948, 1748, 1667, 1591, 1370, 1274, 1224, 1042, 910, 812, 711, 601. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{48}H_{50}NaO_{21}S^+$ 1017.2458, found 1017.2458.

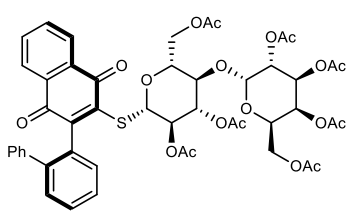
(2*R*,3*S*,4*S*,5*R*,6*R*)-2-(acetoxymethyl)-6-(((2*R*,3*R*,4*S*,5*R*,6*S*)-4,5-diacetoxy-2-(acetoxymethyl)-6-((2-(benzyloxy)-6-methyl-1',4'-dioxo-1',4'-dihydro-[1,2'-binaphthalen]-3'-yl)thio)tetrahydro-2*H*-pyran-3-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3p)



The residue was purified by a silica gel flash chromatography (PE/EA = 2/1) giving the product **3p** as a red-brown solid in 91% yield (47.7 mg), m.p.77.7-78.1 °C, dr 10:1, $[\alpha]_D^{20}$ = 84.5 (*c* = 0.20, dichloromethane) ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.16 (d, *J* = 6.6 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.98 – 7.89 (m, 3H), 7.70 (s, 1H), 7.51 (d, *J* = 9.0 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.28 – 7.19 (m, 5H), 7.18 (d, *J* = 7.2 Hz, 1H), 5.51 (d, *J* = 10.2 Hz, 1H), 5.20 (dd, *J* = 7.2, 3.6 Hz, 2H), 5.16 – 5.06 (m, 3H), 4.81 (dd, *J* = 10.2, 7.8 Hz, 1H), 4.69 (d, *J* = 8.4 Hz, 1H), 4.49 (t, *J* = 9.6 Hz,

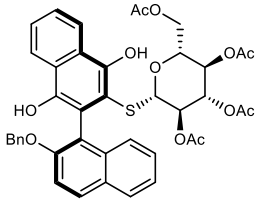
1H), 4.19 – 4.13 (m, 2H), 3.99 – 3.94 (m, 3H), 3.68 – 3.63 (m, 2H), 2.43 (s, 3H), 2.08 (s, 3H), 1.98 (s, 3H), 1.96 (s, 3H), 1.91 (s, 3H), 1.89 (s, 3H), 1.80 (s, 3H), 1.71 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 181.4, 180.6, 170.4, 170.3, 170.3, 169.9, 169.7, 169.5, 169.4, 153.0, 146.8, 137.4, 135.0, 134.8, 133.4, 133.0, 132.1, 130.6, 129.7, 129.4, 129.0, 128.7, 128.6, 128.1, 127.6, 127.3, 127.3, 126.9, 124.8, 117.3, 115.1, 100.2, 81.5, 76.3, 76.2, 73.4, 71.6, 70.8, 70.7, 70.1, 69.2, 67.5, 62.8, 61.3, 21.4, 20.8, 20.8, 20.8, 20.7, 20.5, 20.4. IR (cm^{-1}): 3024, 2940, 1748, 1667, 1593, 1370, 1276, 1229, 1056, 909, 813, 716, 602. HRMS (ESI-TOF) *m/z*: [M+Na]$^+$ Calcd for $C_{54}H_{54}NaO_{20}S^+$ 1077.2821, found 1077.2851.

(2*R*,3*S*,4*R*,5*R*,6*S*)-2-(((2*S*,3*S*,4*R*,5*S*,6*S*)-6-((3-([1,1'-biphenyl]-2-yl)-1,4-dioxo-1,4-dihydronaphthalen-2-yl)thio)-4,5-diacetoxy-2-(acetoxymethyl)tetrahydro-2*H*-pyran-3-yl)oxy)-6-(acetoxymethyl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3q)



The residue was purified by a silica gel flash chromatography (PE/EA = 2/1) giving the product **3q** as a red-brown solid in 70% yield (67.1 mg), m.p.106.7-107.6 °C, dr 3:1, $[\alpha]_D^{20}$ = 52.7 (*c* = 0.30, dichloromethane). ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.05 (dd, *J* = 6.6, 0.6 Hz, 1H), 7.84 (td, *J* = 6.0, 1.2 Hz, 1H), 7.75 (td, *J* = 6.6, 1.2 Hz, 1H), 7.66 (dd, *J* = 6.6, 1.2 Hz, 1H), 7.57 (td, *J* = 6.6, 1.2 Hz, 1H), 7.49 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.46 (td, *J* = 6.6, 1.2 Hz, 1H), 7.33 – 7.29 (m, 2H), 7.20 (dd, *J* = 6.6, 1.2 Hz, 1H), 7.16 – 7.12 (m, 3H), 5.74 (d, *J* = 9.0 Hz, 1H), 5.23 (dd, *J* = 2.4, 1.2 Hz, 1H), 5.10 (t, *J* = 6.0 Hz, 1H), 4.82 (dd, *J* = 9.0, 3.6 Hz, 1H), 4.74 (dd, *J* = 8.4, 6.6 Hz, 2H), 4.73 – 4.69 (m, 2H), 4.20 (dd, *J* = 10.2, 1.8 Hz, 1H), 4.17 (td, *J* =5.4, 1.2 Hz, 1H), 4.01 – 3.96 (m, 2H), 3.92 (dd, *J* = 10.2, 6.6 Hz, 1H), 3.78 (t, *J* = 7.8 Hz, 1H), 3.70 (td, *J* = 9.0, 1.8 Hz, 1H), 2.09 (s, 3H), 2.02 (s, 3H), 1.98 (s, 3H), 1.97 (s, 3H), 1.95 (s, 3H), 1.88 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 180.7, 180.4, 170.6, 170.4, 169.9, 169.8, 169.7, 169.5, 150.2, 145.1, 141.0, 140.9, 134.8, 134.5, 132.8, 132.7, 131.7, 130.9, 130.3, 129.9, 128.8, 128.3, 127.5, 127.4, 127.0, 126.5, 100.3, 80.9, 76.7, 76.3, 73.6, 71.9, 70.8, 70.2, 69.3, 67.5, 63.4, 61.4, 20.9, 20.9, 20.8, 20.8, 20.7, 20.1. IR (cm^{-1}): 3055, 2945, 1754, 1664, 1367, 1229, 1137, 1058, 910, 761, 716, 615. HRMS (ESI-TOF) *m/z*: [M+Na]$^+$ Calcd for $C_{48}H_{48}NaO_{19}S^+$ 983.2403, found 983.2429.

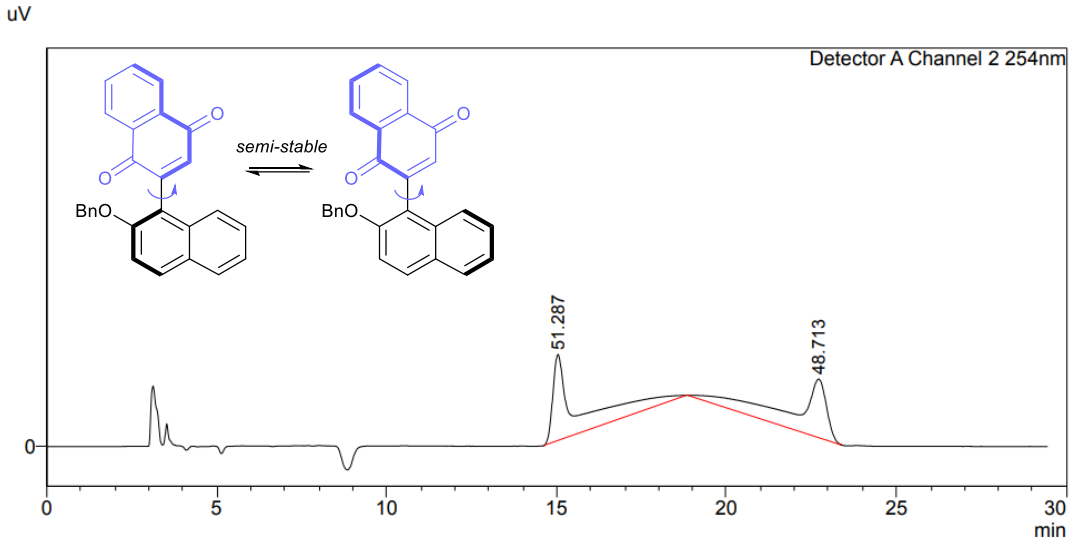
(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((2-(benzyloxy)-1',4'-dihydroxy-[1,2'-binaphthalen]-3'-yl)thio)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (5)



^{1}H NMR (600 MHz, DMSO-d_6) δ 8.30 (s, 1H), 8.28 (s, 1H), 8.25 (dd, *J* = 7.2, 2.4 Hz, 1H), 8.20 (dd, *J* = 7.2, 1.8 Hz, 1H), 7.99 (d, *J* = 9.0 Hz, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.61 (m, 2H), 7.56 (d, *J* = 9.0 Hz, 1H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.30 – 7.20 (m, 6H), 7.07 (d, *J* = 8.4 Hz, 1H), 5.33 – 5.24 (m, 2H), 4.94 (t, *J* = 9.6 Hz, 1H), 4.77 (t, *J* = 9.6 Hz, 1H), 4.73 (d, *J* = 10.8 Hz, 1H), 4.66 (dd, *J* = 10.2, 9.6 Hz, 1H), 3.98 (dd, *J* = 12.0, 6.0 Hz, 1H), 3.64 (dd, *J* = 12.0, 1.8 Hz, 1H),

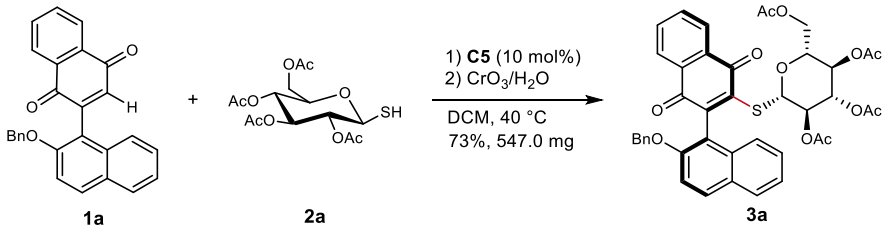
3.14 (m, 1H), 1.94 (s, 3H), 1.93 (s, 3H), 1.90 (s, 3H), 1.58 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 170.3, 169.9, 169.6, 169.3, 154.4, 149.7, 143.8, 138.1, 134.1, 129.7, 129.3, 128.8, 128.3, 127.9, 127.6, 127.3, 126.9, 126.8, 126.3, 124.9, 124.9, 123.8, 123.3, 122.9, 120.87, 115.8, 111.6, 87.2, 75.0, 73.1, 70.2, 69.6, 68.1, 62.1, 20.8, 20.7, 20.7, 20.6. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{41}H_{38}NaO_{12}S^+$ 777.1976, found 777.1930.

4. HPLC Analysis of Substrate 1a



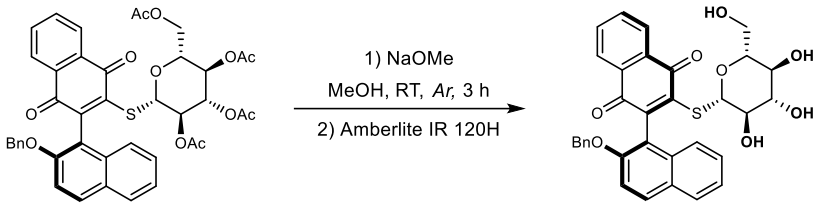
Conditions for HPLC: (Daicel Chiralpak IG, n-hexane/isopropanol = 90:10, 1.0 mL/min, at 254 nm): tR = 15.04 min, tR = 22.71 min.

5. Mmol-Scale Synthesis of Compound 3a



2-(benzyloxy)-[1,2'-binaphthalene]-1',4'-dione **1a** (1.0 mmol, 390.4 mg) and (2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-mercaptotetrahydro-2*H*-pyran-3,4,5-triyl triacetate **2a** (1.2 mmol, 437.2 mg), **C5** (10 mol%, 54.7 mg) were dissolved in dichloromethane (20 mL), and the mixture was stirred at 40 ℃ until complete consumption of the starting material. Then, CrO_3 (1.0 mmol, 99.9 mg) and H_2O (5 ml) were added, the reaction mixture was stirred for 30 min. 25 mL of water was added into the reaction mixture, and the solution mixture was extracted with DCM (30 mL). The combined organic phase was washed with saturated brine, then was dried over Na_2SO_4. After concentration, the residue was purified by flash column chromatography on silica gel using petroleum ether (PE) and EA (3/1 v/v) as eluents to afford the pure product **3a** as a red-brown solid in 73% yield (547.0 mg).

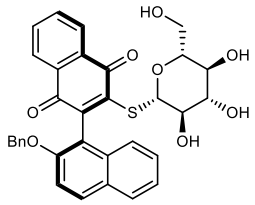
6. Synthesis of 4a and Characterization Data



3a **4a**, 90%, >19:1 dr

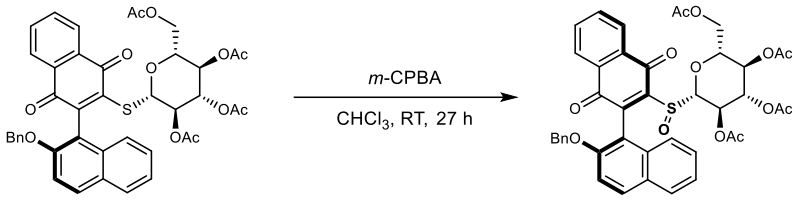
To a suspension of compound **3a** (80 mg, 0.10 mmol, 1.0 equiv.) in anhydrous methanol (4.0 mL), a solution of sodium methoxide in methanol (11.5 mg, 2.0 equiv.) was added. The solution was stirred at room temperature under argon for 3h. When TLC indicated complete consumption of the starting materials, Amberlite IR 120H ion exchange resin was added until the solution was neutralized. The resin was filtered, and the reaction mixture was concentrated under reduced pressure to give compound **4a** (57.6 mg, 90% yield) as a yellow solid.

2-(benzyloxy)-3'-(((2*S*,3*R*,4*S*,5*S*,6*R*)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yl)thio)-[1,2'-binaphthalene]-1',4'-dione (4a)



The residue was purified by preparing liquid phase (n-hexane/EA = 1/1) giving the product **4a** as a red-brown solid in 90% yield (56.2 mg), m.p. 42.1-43.0 °C. dr > 19:1, $[\alpha]_D^{20}$ = 272.5 (*c* = 0.16, dichloromethane). ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.10 (dd, *J* = 6.6, 1.8 Hz, 1H), 8.03 – 7.97 (m, 2H), 7.93 – 7.85 (m, 3H), 7.66 (dd, *J* = 6.6, 3.6 Hz, 1H), 7.53 (d, *J* = 9.0 Hz, 1H), 7.38 (dd, *J* = 6.0, 3.0 Hz, 2H), 7.30 (d, *J* = 6.6 Hz, 2H), 7.28 – 7.19 (m, 3H), 5.32 (d, *J* = 6.0 Hz, 1H), 5.27 – 5.16 (m, 3H), 5.02 (d, *J* = 4.8 Hz, 1H), 4.93 (d, *J* = 4.8 Hz, 1H), 4.31 (t, *J* = 5.4 Hz, 1H), 3.49 (dd, *J* = 11.4, 6.0 Hz, 1H), 3.35 - 3.28 (m, 1H), 3.11 – 3.05 (m, 1H), 2.99 – 2.91 (m, 2H), 2.74 – 2.66 (m, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 181.7, 181.2, 154.0, 150.3, 144.1, 137.6, 134.6, 134.4, 133.5, 132.3, 131.2, 130.9, 129.02 128.8, 128.4, 128.1, 127.5, 127.2, 127.2, 126.7, 125.6, 124.3, 117.8, 115.3, 83.6, 81.9, 78.4, 74.9, 70.7, 70.4, 61.4. IR (cm^{-1}): 3444, 3057, 2923, 1667, 1588, 1277, 1243, 1053, 809, 742, 714, 621. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{33}H_{28}NaO_8S^+$ 607.1397, found 607.1393.

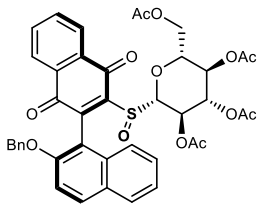
7. Synthesis of 4b and Characterization Data



3a **4b**, 74%, >19:1 dr

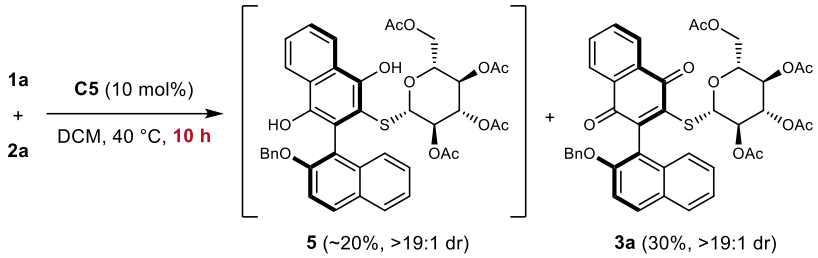
Add *m*-chloroperoxybenzoic acid (80.7 mg, 4.4 eq.) to the chloroform solution of compound **3a** (80 mg, 0.10 mmol, 1.0 equivalent), and stir the mixture at room temperature for 27 hours. The reaction was monitored by TLC. After the raw material was completely consumed, $NaHCO_3$ was added, and then extracted with dichloromethane and water 3 times. The organic layer was combined and concentrated. The concentrated solution was separated by column chromatography (eluent: petroleum ether/ethyl acetate, 3:1) to obtain compound **4b** (61.0 mg, 74% yield), as a yellow solid.

(2*R*,3*R*,4*S*,5*R*)-2-(acetoxymethyl)-6-((2-(benzyloxy)-1',4'-dioxo-1',4'-dihydro-[1,2'-binaphthalen]-3'-yl)sulfinyl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (4b)



The residue was purified by preparing liquid phase (n-hexane/EA = 1/1)giving the product **4a** as a red-brown solid in 74% yield, m.p. 50.2-50.9 °C, dr > 19:1, $[\alpha]_D^{20}$ = 134.5 (*c* = 0.20, dichloromethane). ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.21 (dd, *J* = 7.8, 1.8 Hz, 1H), 8.10 (d, *J* = 9.0 Hz, 1H), 8.07 (dd, *J* = 7.8, 1.8 Hz, 1H), 8.02 (td, *J* = 7.2, 1.2 Hz, 1H), 7.98 (td, *J* = 7.8, 1.2 Hz, 1H), 7.95 (d, *J* = 9.0 Hz, 1H), 7.59 (d, *J* = 9.0 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.39 (t, *J* = 8.4 Hz, 1H), 7.28 – 7.23 (m, 2H), 7.21 – 7.17 (m, 3H), 5.53 (d, *J* = 9.6 Hz, 1H), 5.48 (t, *J* = 9.0 Hz, 1H), 5.28 (d, *J* = 12.6 Hz, 1H), 5.20 (d, *J* = 12.6 Hz, 1H), 4.82 (t, *J* = 9.6 Hz, 1H), 4.71 (t, *J* = 9.6 Hz, 1H), 4.12 – 4.02 (m, 2H), 3.84 (d, *J* = 10.2 Hz, 1H), 1.98 (s, 3H), 1.89 (s, 3H), 1.83 (s, 3H), 1.45 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 182.8, 180.0, 170.1, 169.9, 169.8, 169.5, 153.2, 150.5, 146.6, 137.2, 135.7, 135.5, 133.3, 132.2, 132.1, 132.0, 128.7, 128.5, 128.5, 128.2, 127.6, 127.3, 127.2, 127.1, 124.7, 124.6, 115.0, 114.7, 90.2, 76.0, 72.6, 71.0, 70.5, 67.9, 62.0, 20.8, 20.6, 20.6, 20.1. IR (cm^{-1}): 3060, 2926, 1742, 1667, 1591, 1367, 1274, 1243, 1044, 806, 744, 716, 601. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{41}H_{36}NaO_{13}S^+$ 791.1769, found 791.1769.

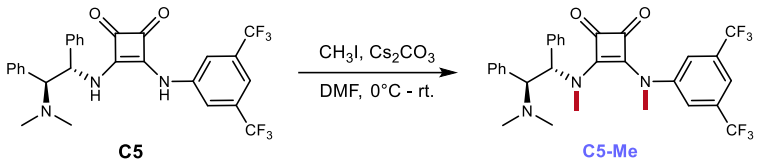
8. Identification of Intermediate 5



5 (~20%, >19:1 dr) **3a** (30%, >19:1 dr)

1a (20.0 mg, 0.05 mmol), **2a** (22.4 mg, 1.20 eq.) and **C5** (2.8 mg, 10 mol%) were dissolved in dichloromethane (2.0 mL), and the mixture was stirred at 40 ℃ for 10 h. When the concentration of naphthol product is the highest, quickly separated by a silica gel column (EA/n-hexane: 30/70) to obtain about 8.0 mg of product **5** (about 20% yield), followed immediately by NMR and MS detection.

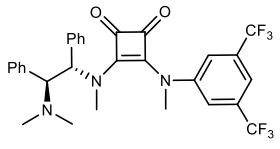
9. Synthesis of C5-Me and Characterization Data



C5 **C5-Me**

Added Cs_2CO_3 (89.3 mg, 3.0 eq.) to the DMF solution of compound **C5** (50.0 mg, 1.0 eq.), and cool the mixture to 0℃. Iodomethane (17 μl, 3.0 eq.) was added, the solution was stirred for 30 min. Then, warm the reaction mixture to rt and stirred for 3d. The reaction was monitored by TLC. After the material was consumed, extract it with ethyl acetate and water 3 times. The organic layer was combined and concentrated. The concentrated solution was separated by column chromatography (eluent: petroleum ether/ethyl acetate, 2:1) to obtain compound **C5-Me** (15.8 mg, 30% yield).

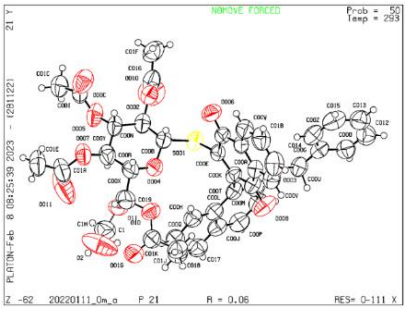
3-((3,5-bis(trifluoromethyl)phenyl)(methyl)amino)-4-(((1*S*,2*S*)-2-(dimethylamino)-1,2-diphenylethyl)(methyl)amino)cyclobut-3-ene-1,2-dione (C5-Me)



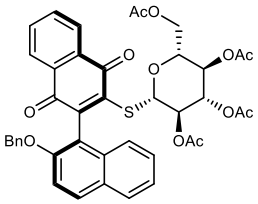
The residue was purified by preparing liquid phase (n-hexane/EA = 2/1) giving the product **C5-Me** in 30% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.71 (s, 1H), 7.62 (s, 2H), 7.41 – 7.36 (m, 2H), 7.27 (t, J = 7.8 Hz, 2H), 7.23 (t, J = 7.2 Hz, 2H), 7.20 – 7.13 (m, 4H), 6.52 (d, J = 11.2 Hz, 1H), 4.66 (d, J = 12.0 Hz, 1H), 3.58 (s, 3H), 2.66 (s, 3H), 2.09 (s, 6H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 189.5, 183.5, 165.8, 145.8, 136.9, 135.9, 132.4, 131.8, 131.6, 131.4, 131.2, 129.7, 129.7, 129.5, 128.9, 128.7, 128.4, 128.2, 127.7, 127.3, 124.4, 122.6, 119.7, 116.0, 63.8, 60.7, 40.8, 40.5, 39.3, 32.6. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{30}H_{27}F_6N_3NaO_2^+$ 598.1900, found 598.1904.

10. X-ray Crystal Data of 3a

To a 10 mL tube containing **3a** (15.0 mg) was added a mixture of solvent (MeOH/DCM=10:1) (2.2 mL). A clear solution was obtained through ultrasound treatment and was kept at room temperature and the crystals were obtained after the solvent evaporated, which were characterized by X-ray single crystal diffraction. X-ray diffraction experiment was carried out on an Agilent Gemini and the data obtained were deposited at the Cambridge Crystallographic Data Centre.



≡



3a

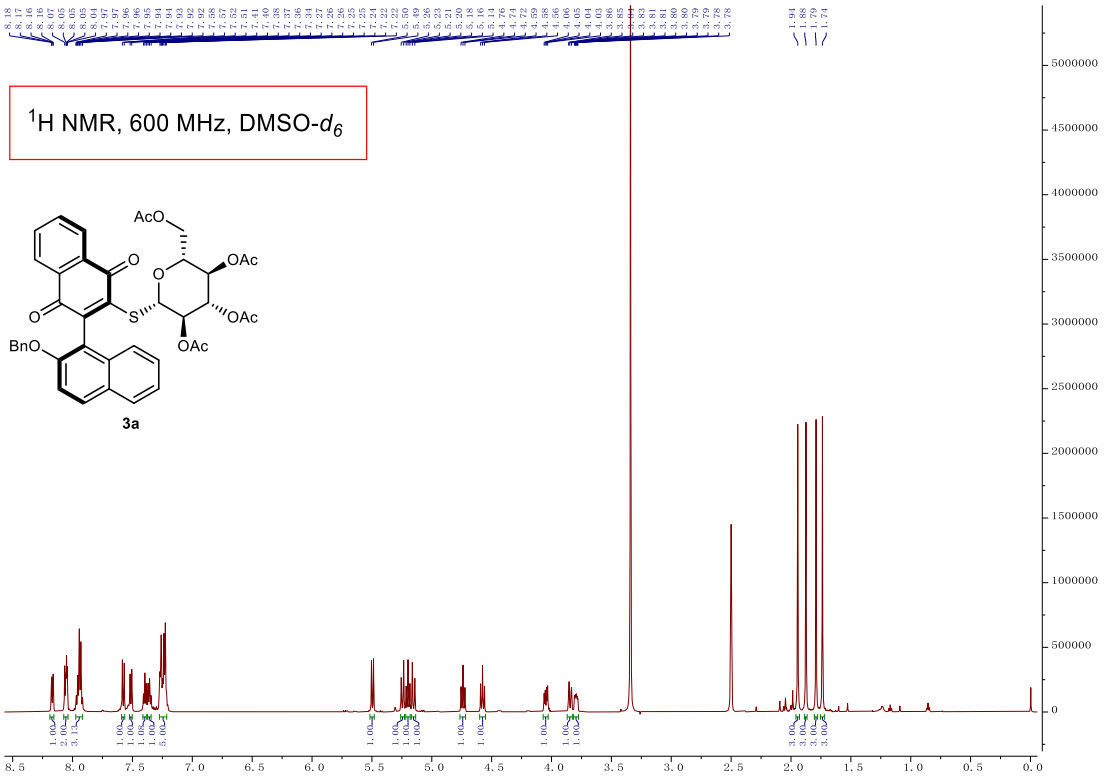
(Ellipsoid contour probability 50%)

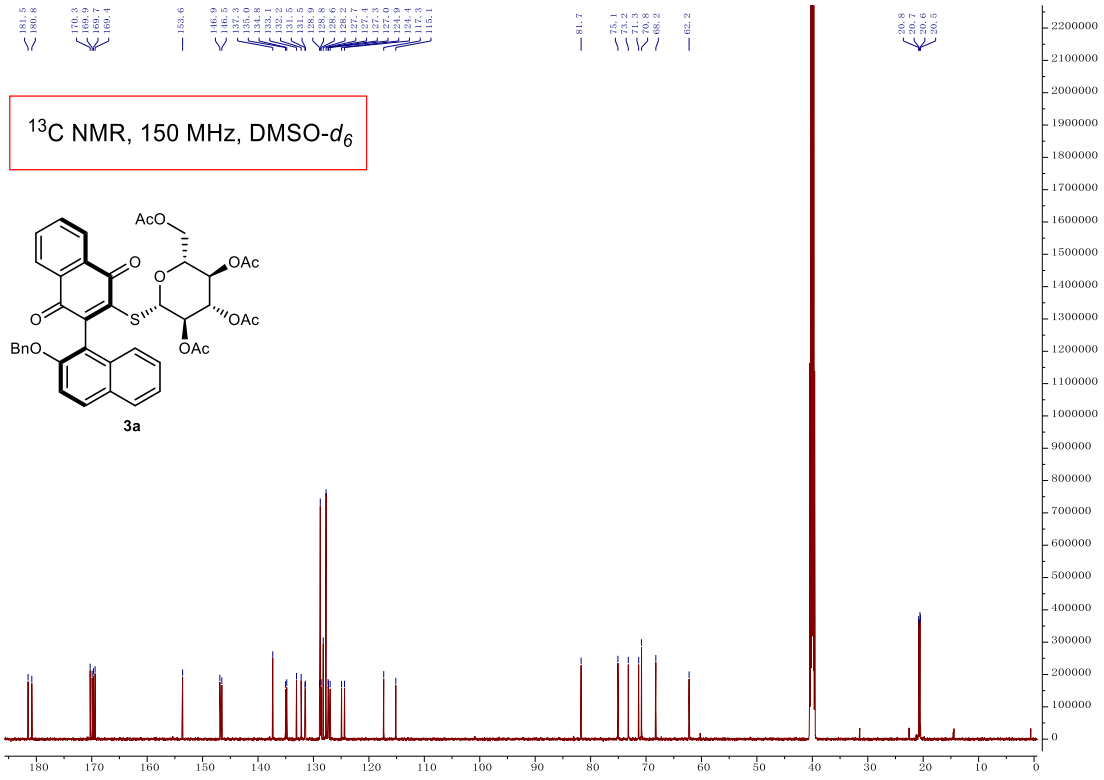
Chemical formula	$C_{41}H_{36}O_{12}S$	
Formula weight	750.74 g/mol	
Temperature	293(2) K	
Wavelength	1.54178 Å	
Crystal system	monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 11.2300(4) Å	α = 90°
	b = 7.3747(2) Å	β = 99.251(2)°
	c = 23.9590(7) Å	γ = 90°
Volume	1958.43(11) $Å^3$	
Z	2	
Density (calculated)	1.273 g/cm^3	
Absorption coefficient	1.259 mm^{-1}	
F(000)	784	

Theta range for data collection	3.74 to 68.67°

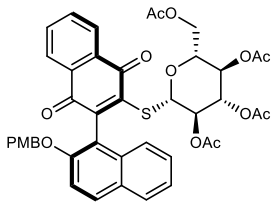
Index ranges	-13<=h<=13, -8<=k<=8, -28<=l<=28
Reflections collected	30569
Independent reflections	6931 [R(int) = 0.0570]
Coverage of independent reflections	98.9%
Absorption correction	Multi-Scan
Structure solution technique	direct methods
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2016/6 (Sheldrick, 2016)
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	6931 / 2 / 579
Goodness-of-fit on F2	0.986
Final R indices	5494 data; R1 = 0.0630, wR2 = 0.1785
	$I>2\sigma(I)$
	all data R1 = 0.0753, wR2 = 0.1986
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.1534P)^2+0.0106P]$
	where $P=(F_o^2+2F_c^2)/3$
Absolute structure parameter	0.058(11)
Largest diff. peak and hole	0.437 and -0.304 $eÅ^{-3}$
R.M.S. deviation from mean	0.067 $eÅ^{-3}$

11. NMR Spectra



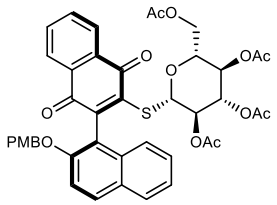


^{1}H NMR, 600 MHz, DMSO-d_6

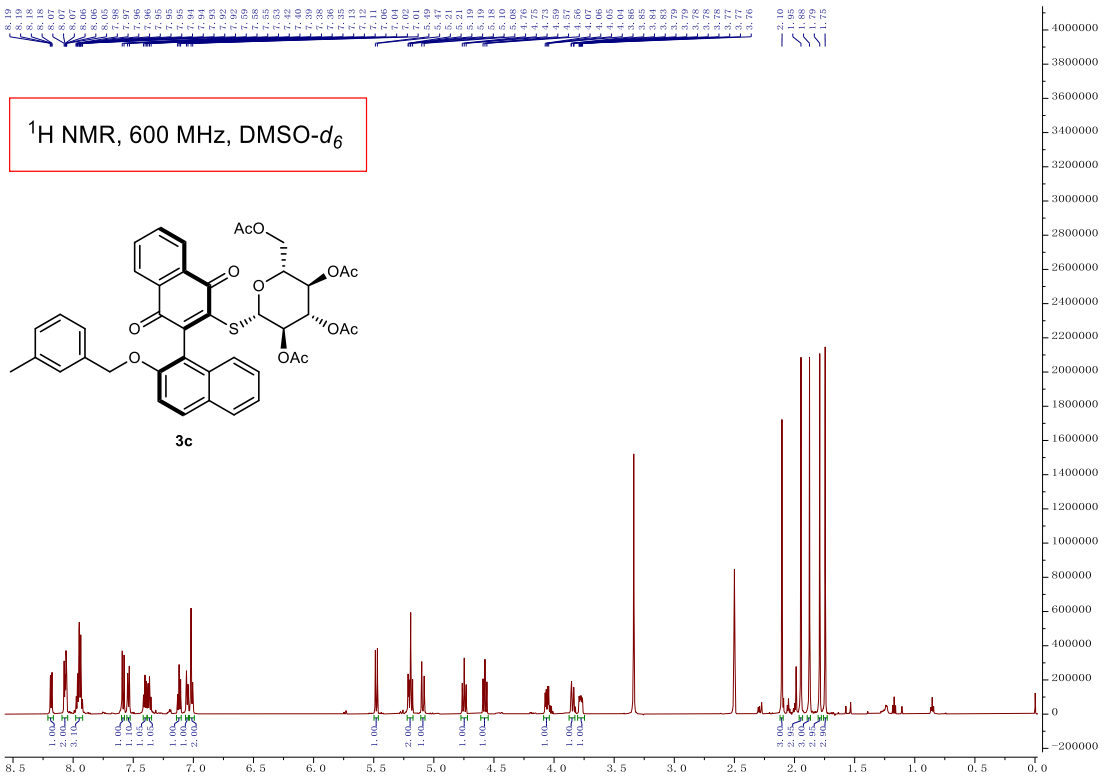


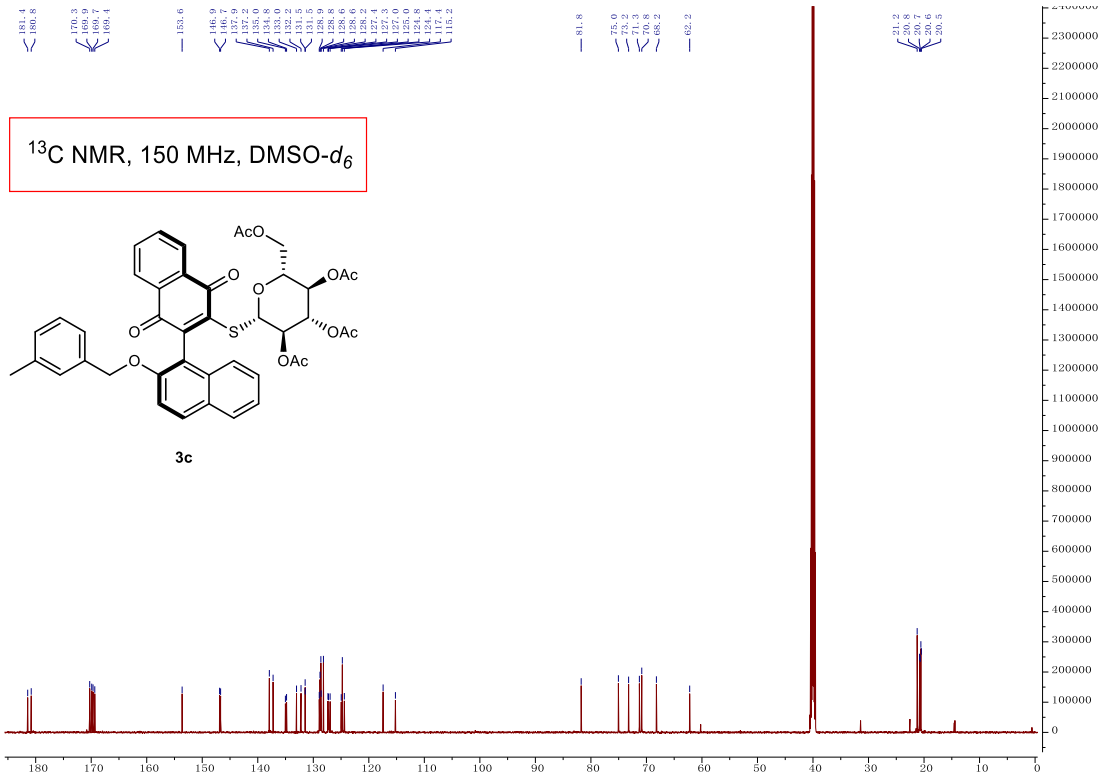
3b

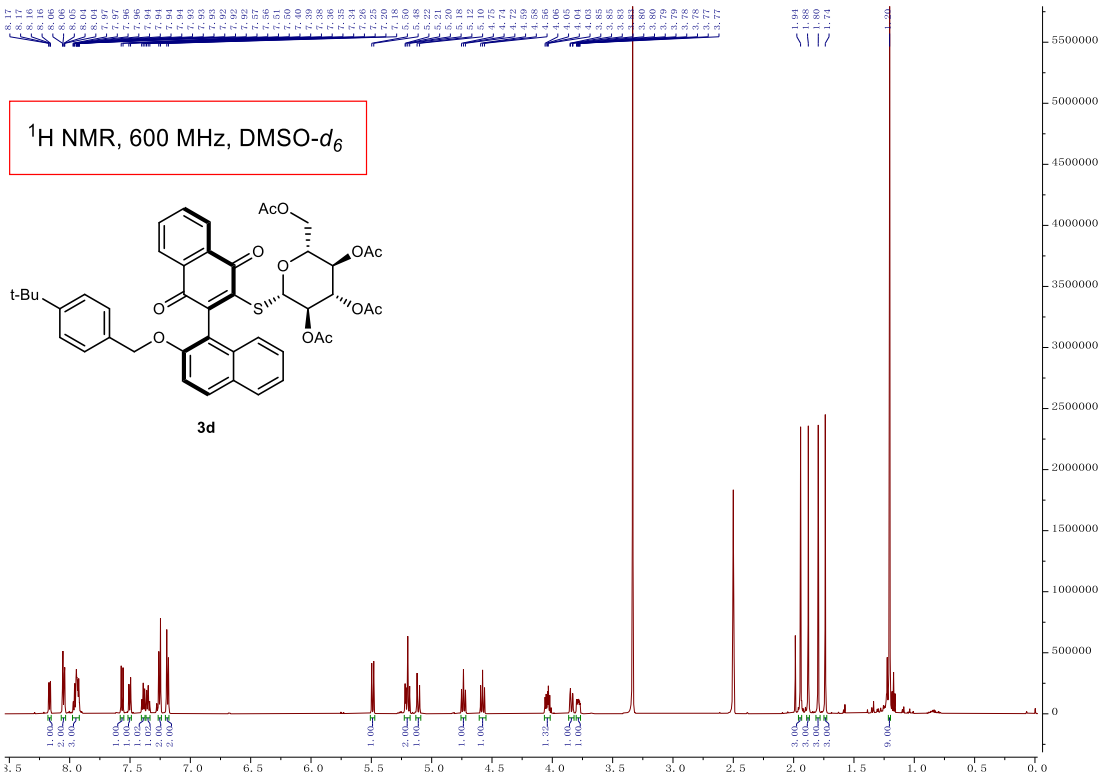
^{13}C NMR, 150 MHz, DMSO-d_6



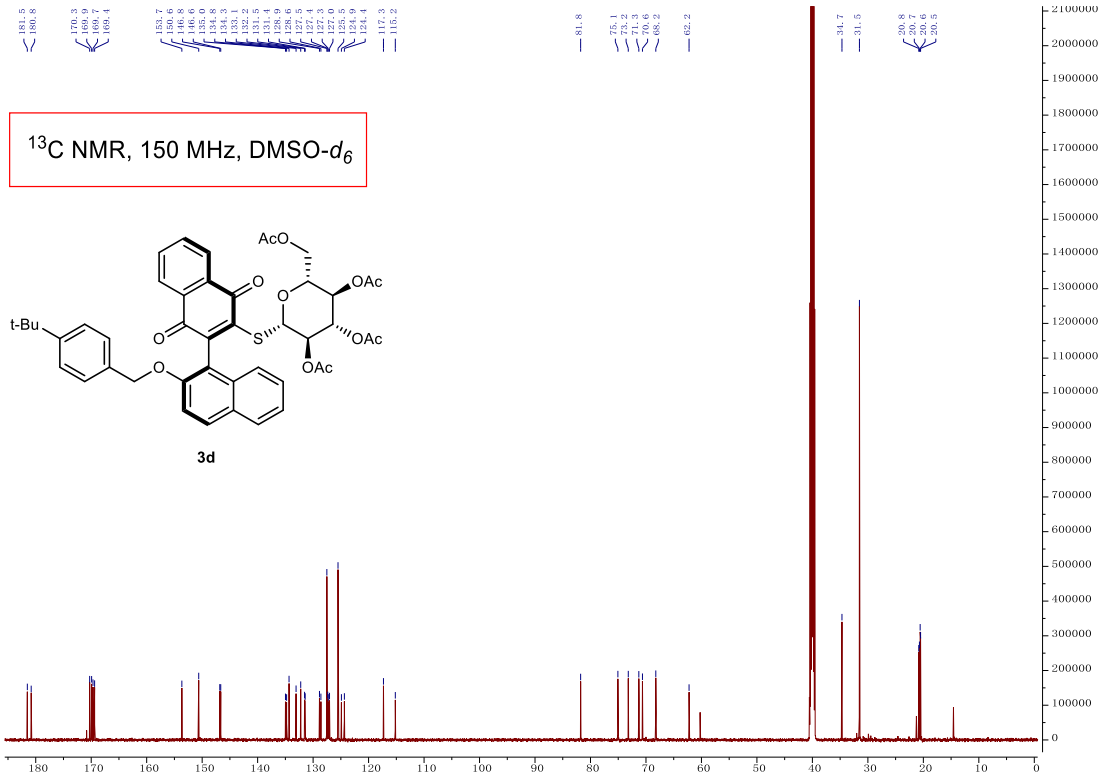
3b


^{1}H NMR, 600 MHz, DMSO-d_6
AcO
OAc
OAc
OAc
O
S
3c

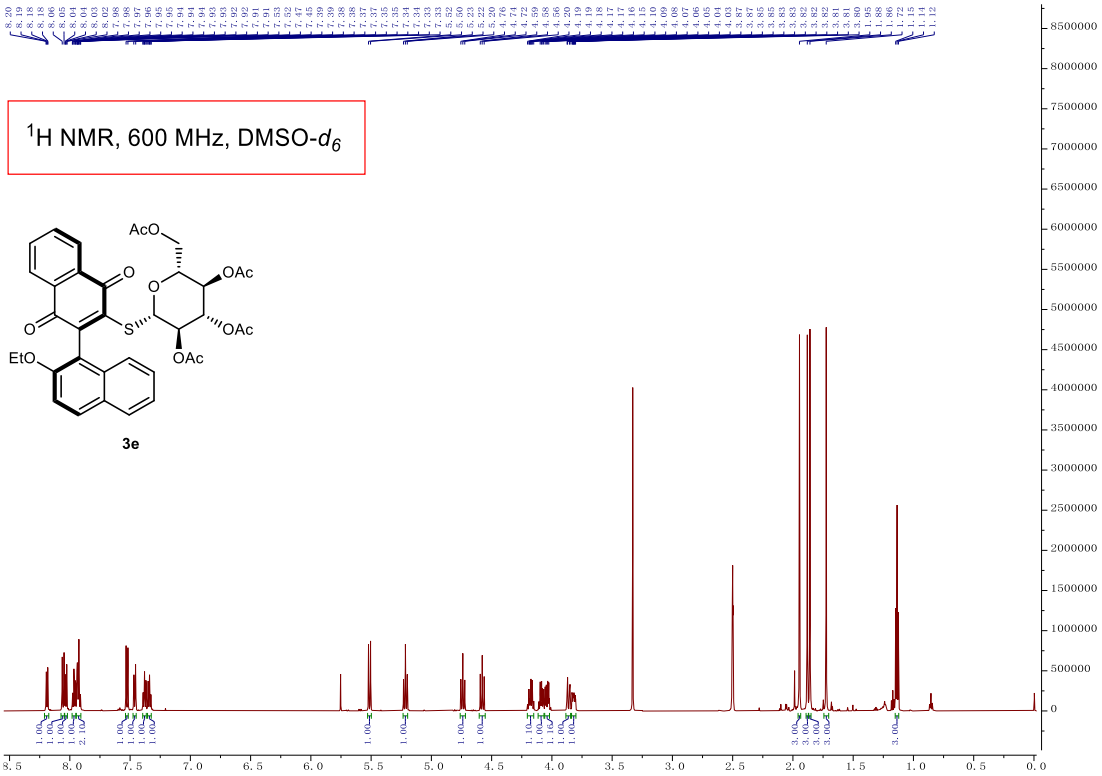

^{13}C NMR, 150 MHz, DMSO-d_6
AcO
OAc
OAc
OAc
O
S
3c


^{1}H NMR, 600 MHz, DMSO-d_6
AcO
OAc
OAc
OAc
t-Bu
O
O
O
O
S

3d

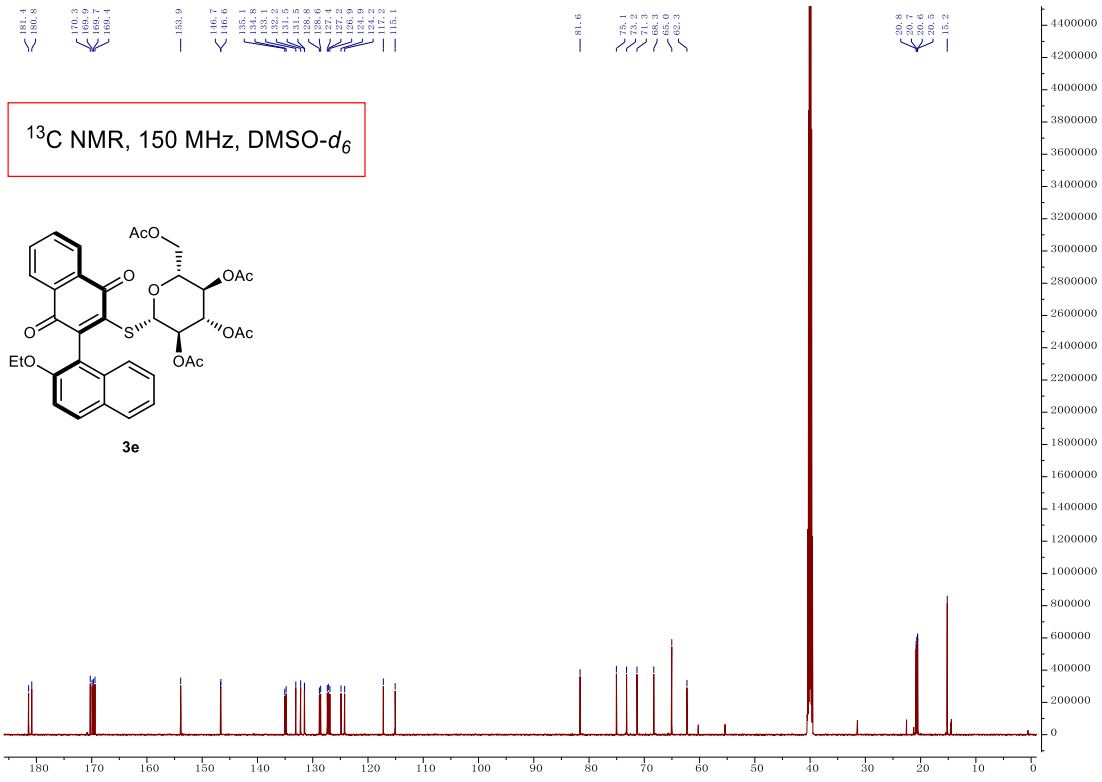

^{13}C NMR, 150 MHz, DMSO-d_6
AcO
OAc
OAc
OAc
t-Bu
O
O
O
O
S

3d



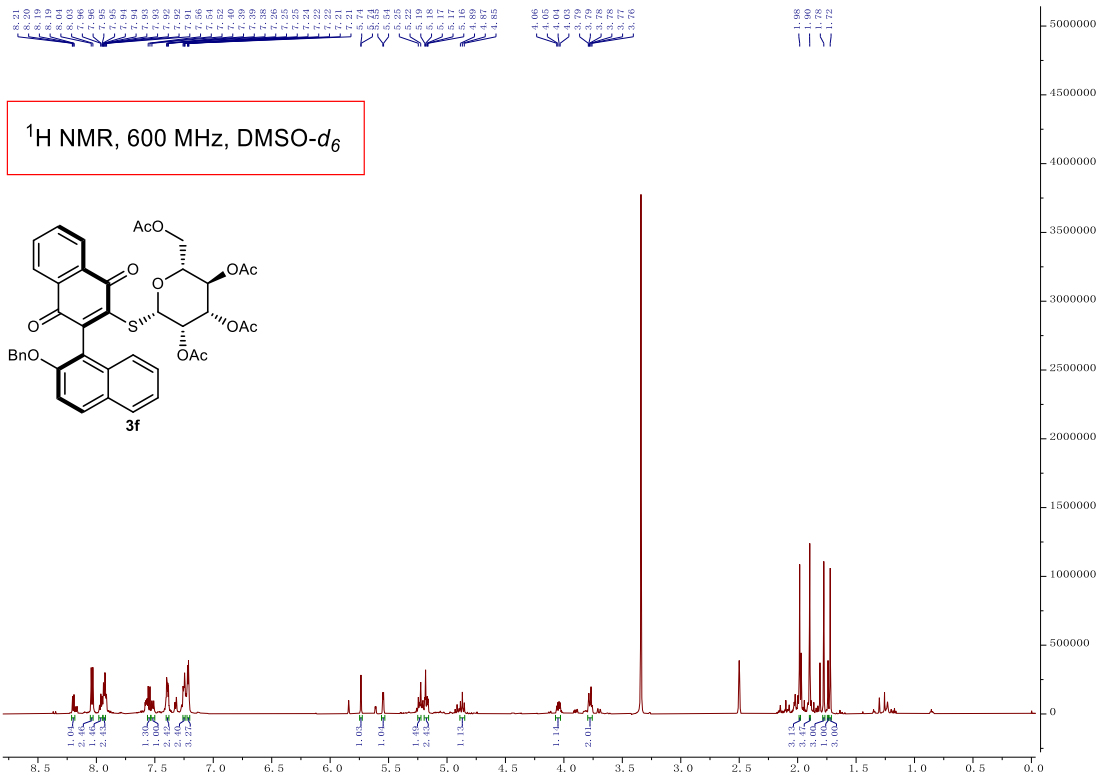
^{1}H NMR, 600 MHz, DMSO-d_6

3e



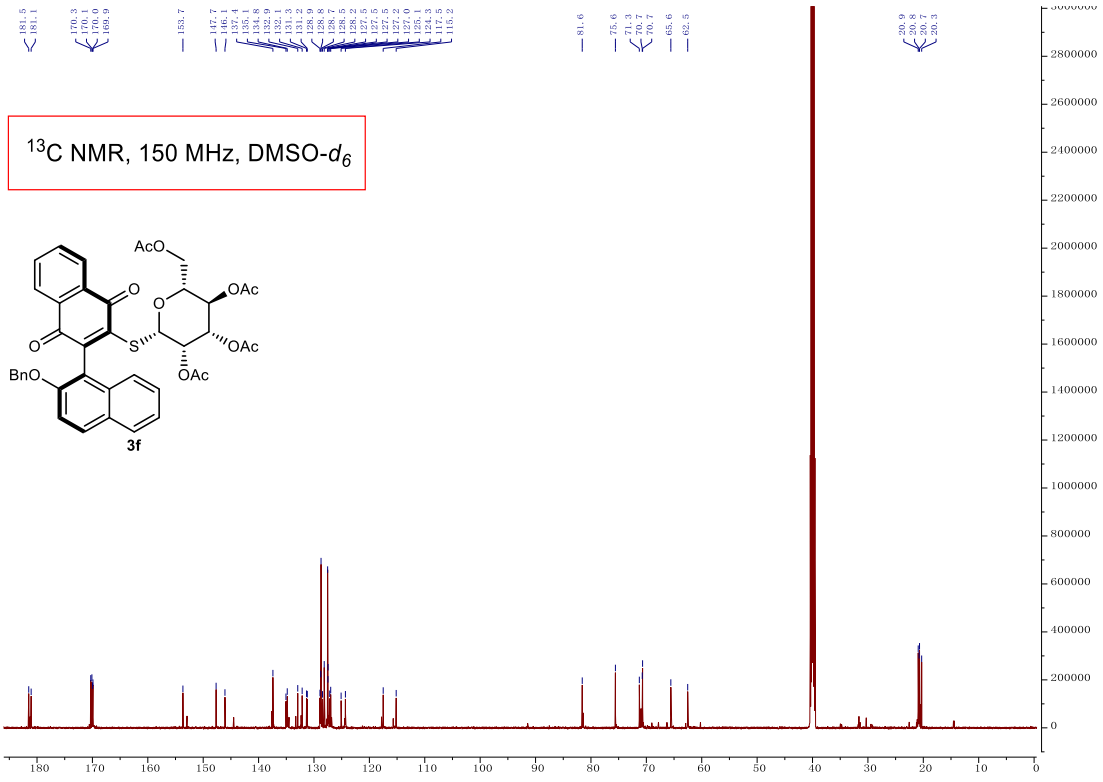
^{13}C NMR, 150 MHz, DMSO-d_6

3e



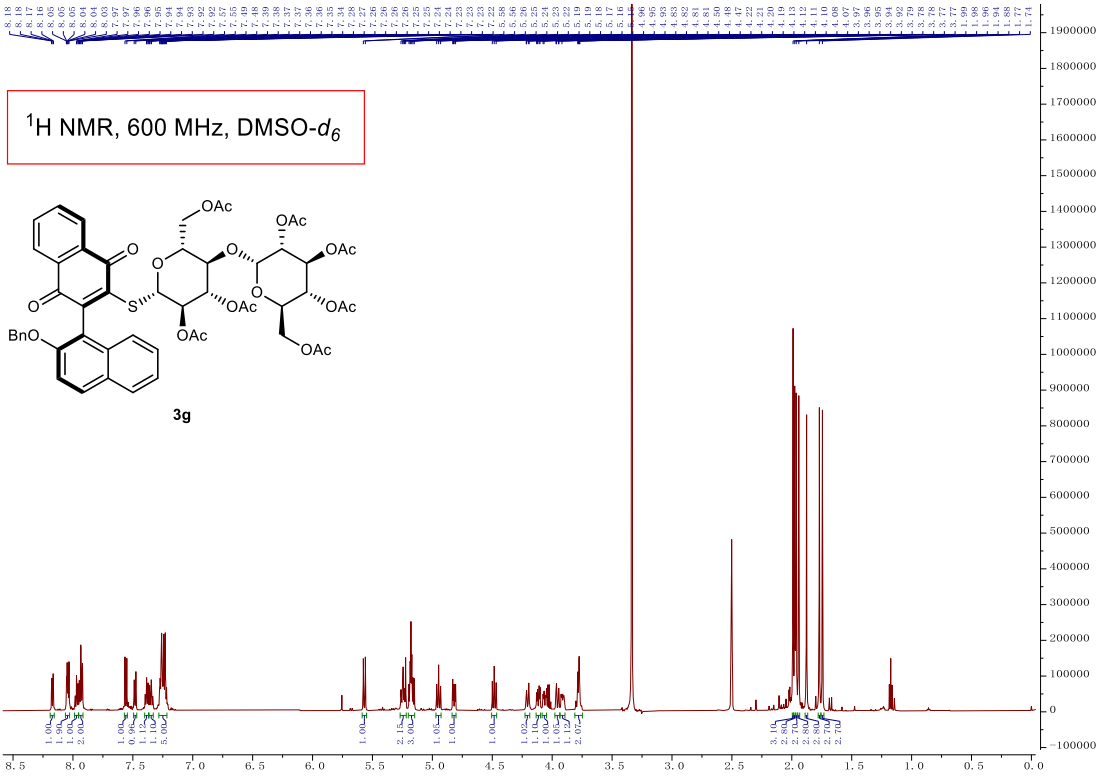
^{1}H NMR, 600 MHz, DMSO-d_6

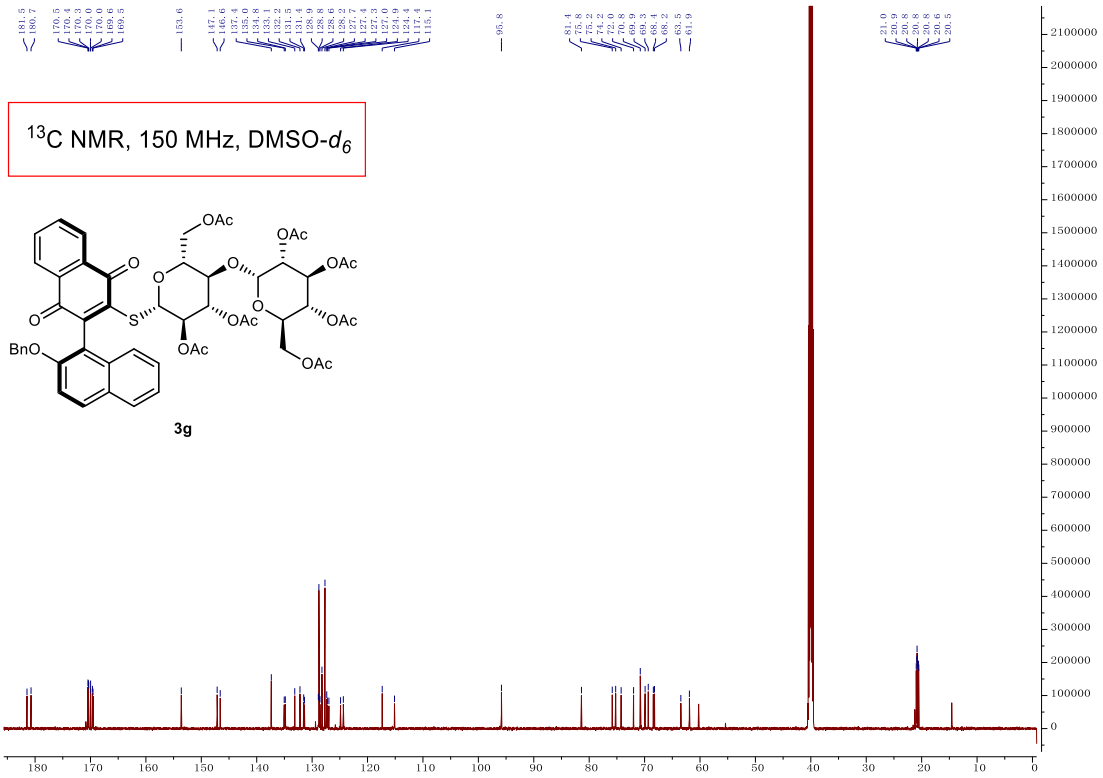
3f



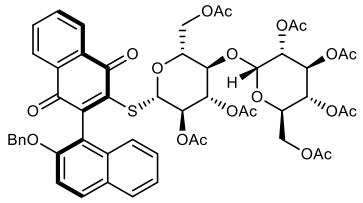
^{13}C NMR, 150 MHz, DMSO-d_6

3f


^{1}H NMR, 600 MHz, DMSO-d_6
OAc
OAc
OAc
OAc
OAc
OAc
OAc
O
O
O
S
BnO
3g

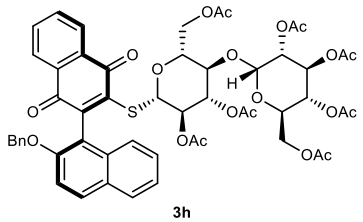

^{13}C NMR, 150 MHz, DMSO-d_6
OAc
OAc
OAc
OAc
OAc
OAc
OAc
O
O
O
S
BnO
3g

^{1}H NMR, 600 MHz, DMSO-d_6

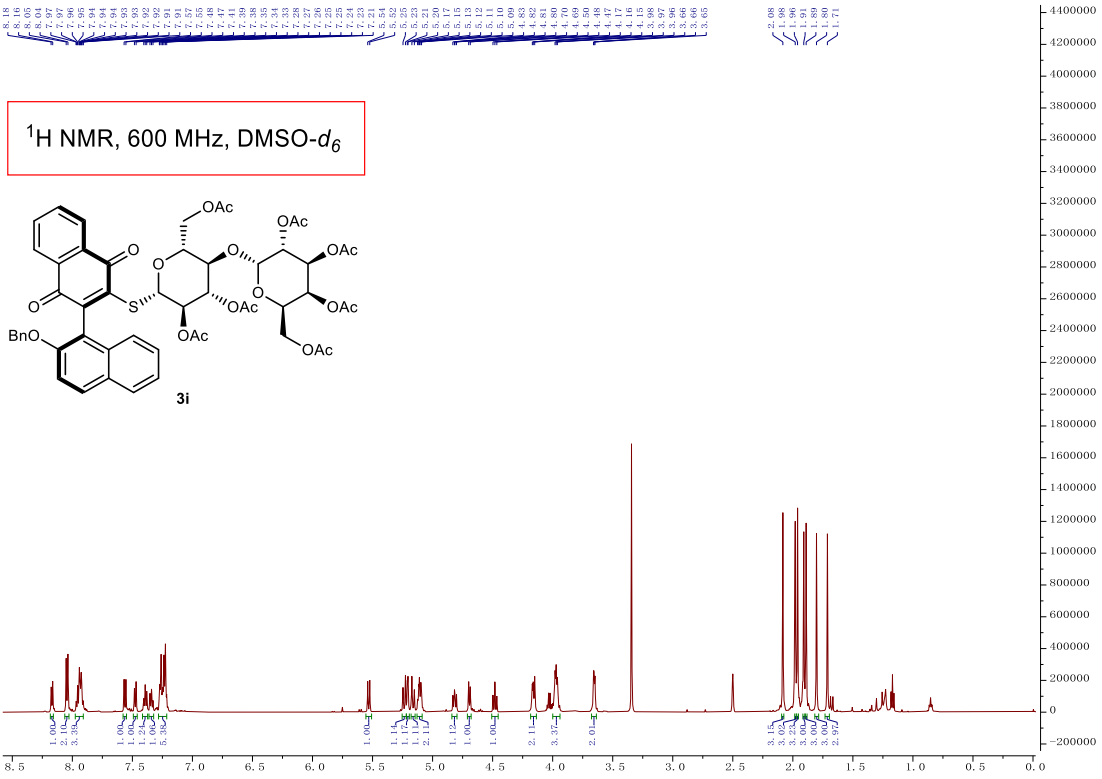


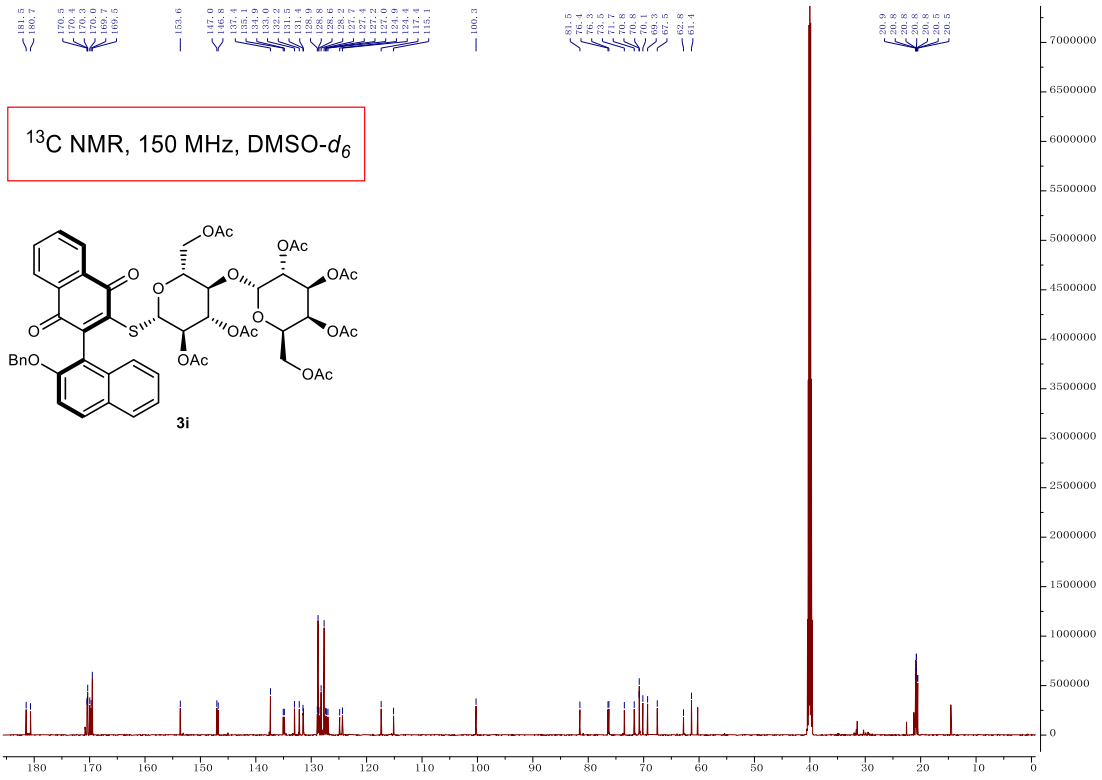
3h

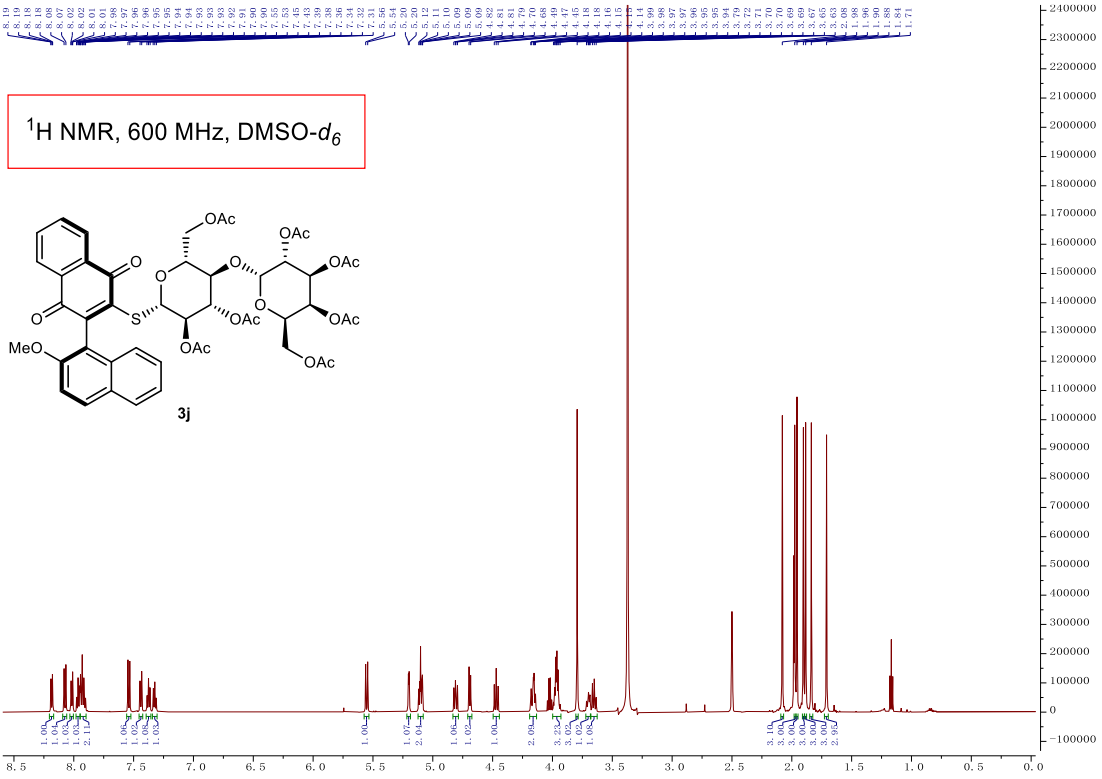
^{13}C NMR, 150 MHz, DMSO-d_6

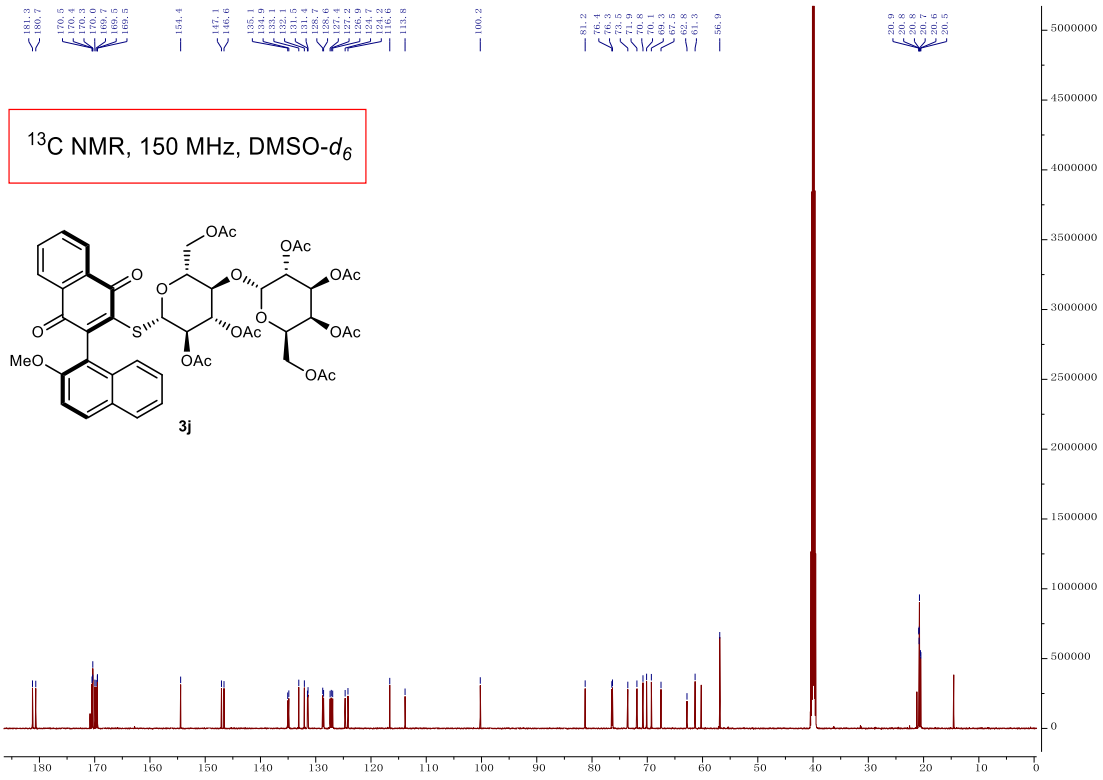


3h

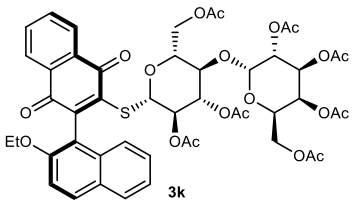

^{1}H NMR, 600 MHz, DMSO-d_6
OAc
OAc
OAc
OAc
OAc
OAc
OAc
O
O
O
O
S
BnO
3i


^{13}C NMR, 150 MHz, DMSO-d_6
OAc
OAc
OAc
OAc
OAc
OAc
OAc
O
O
O
O
S
BnO
3i


^{1}H NMR, 600 MHz, DMSO-d_6
OAc
OAc
OAc
OAc
OAc
OAc
OAc
O
O
O
O
S
MeO
3j

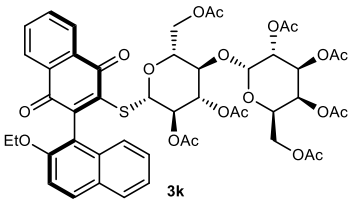

^{13}C NMR, 150 MHz, DMSO-d_6
OAc
OAc
OAc
OAc
OAc
OAc
OAc
O
O
O
O
S
MeO
3j

^{1}H NMR, 600 MHz, DMSO-d_6

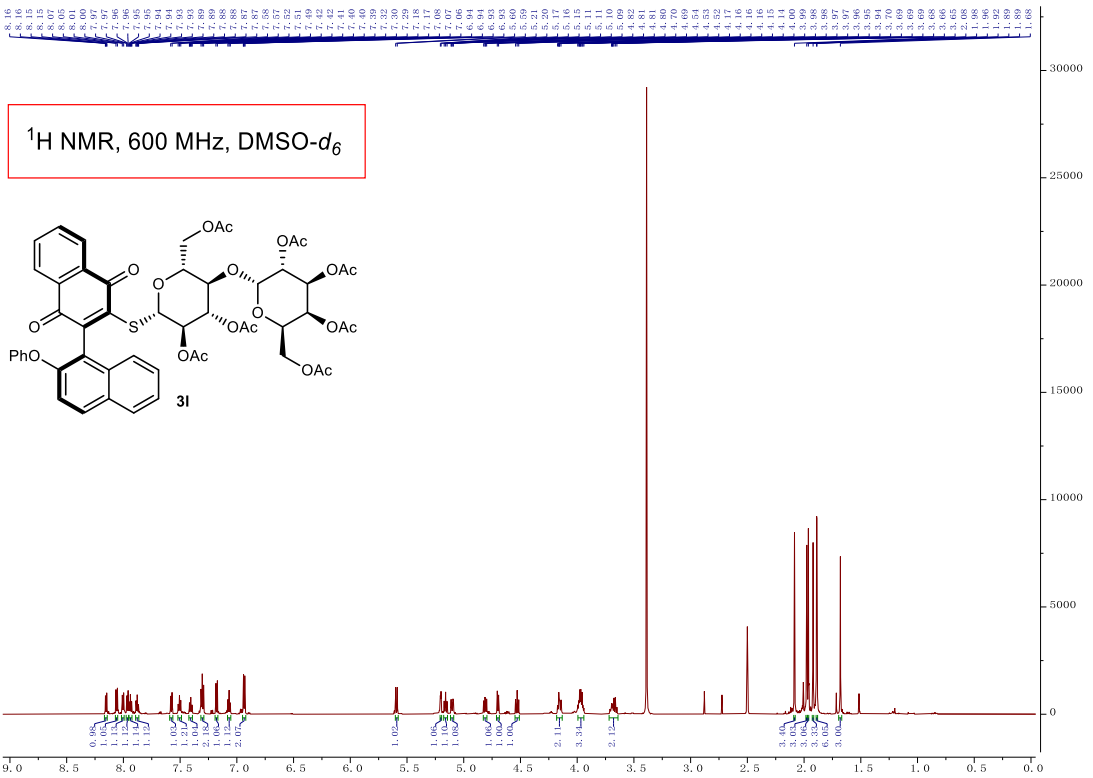


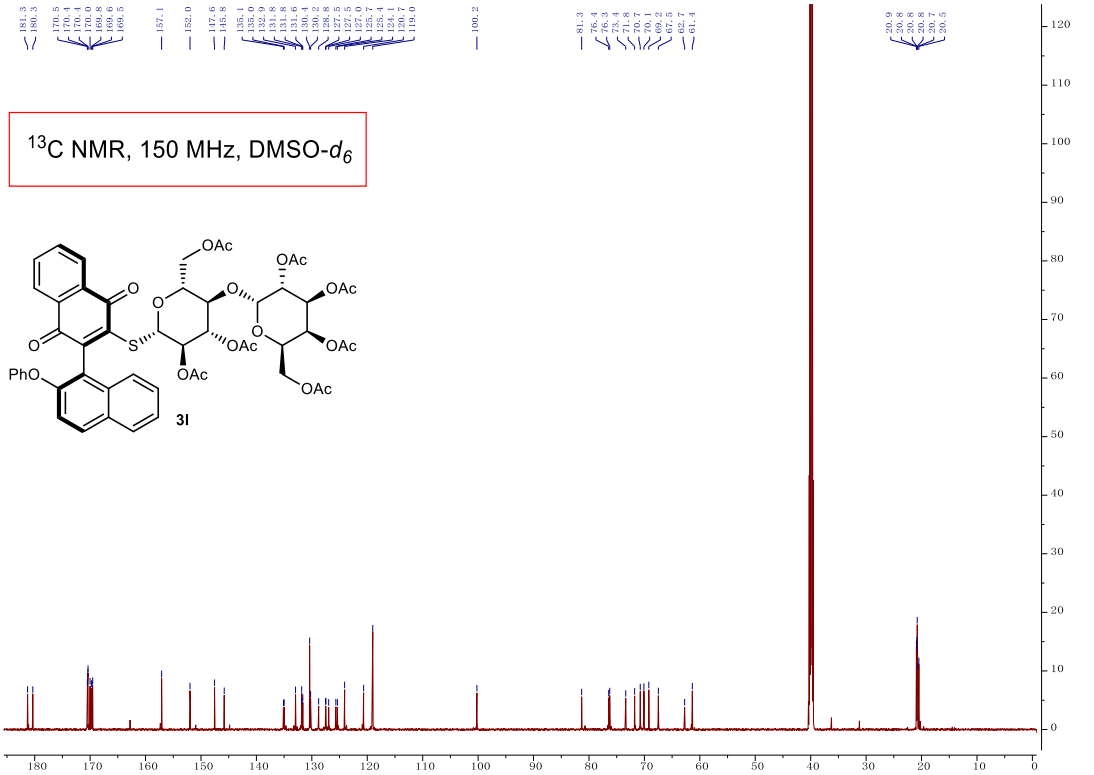
3k

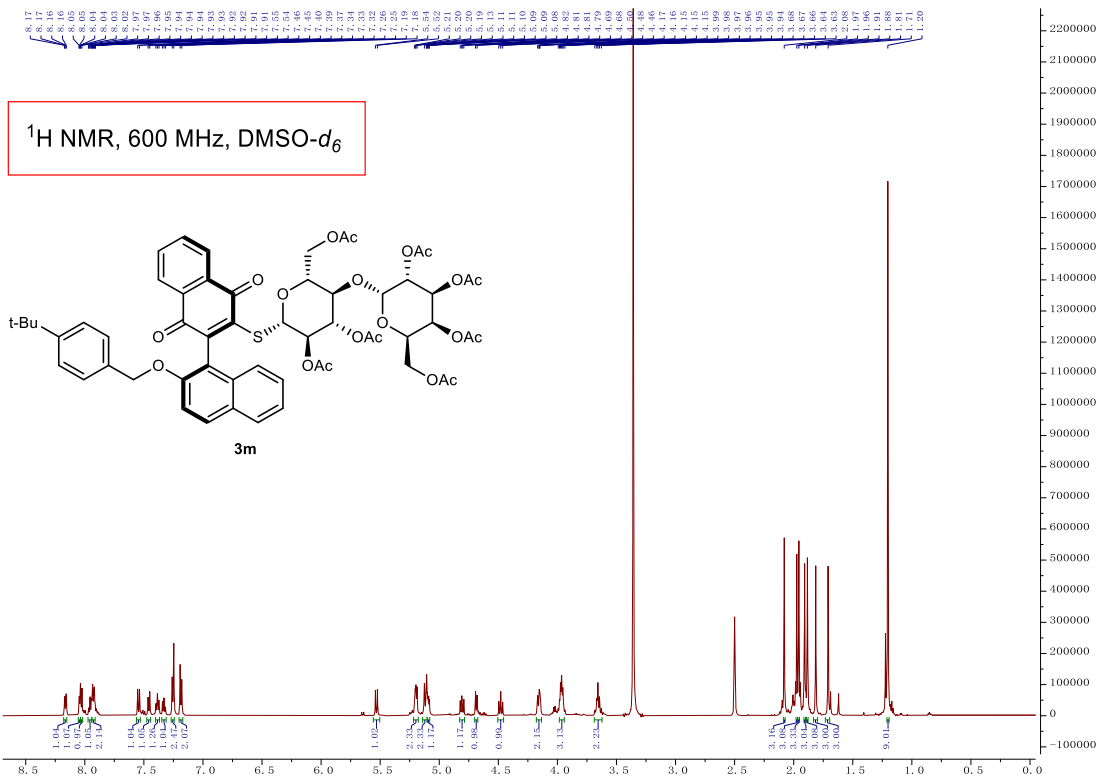
^{13}C NMR, 150 MHz, DMSO-d_6

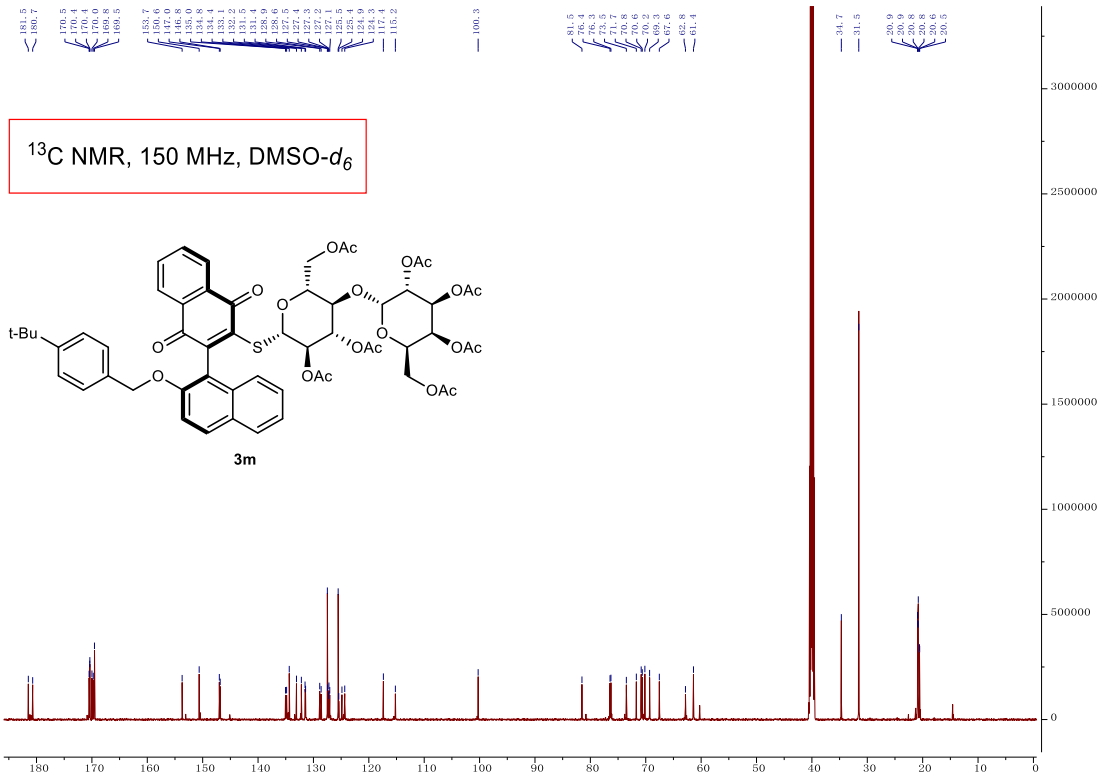


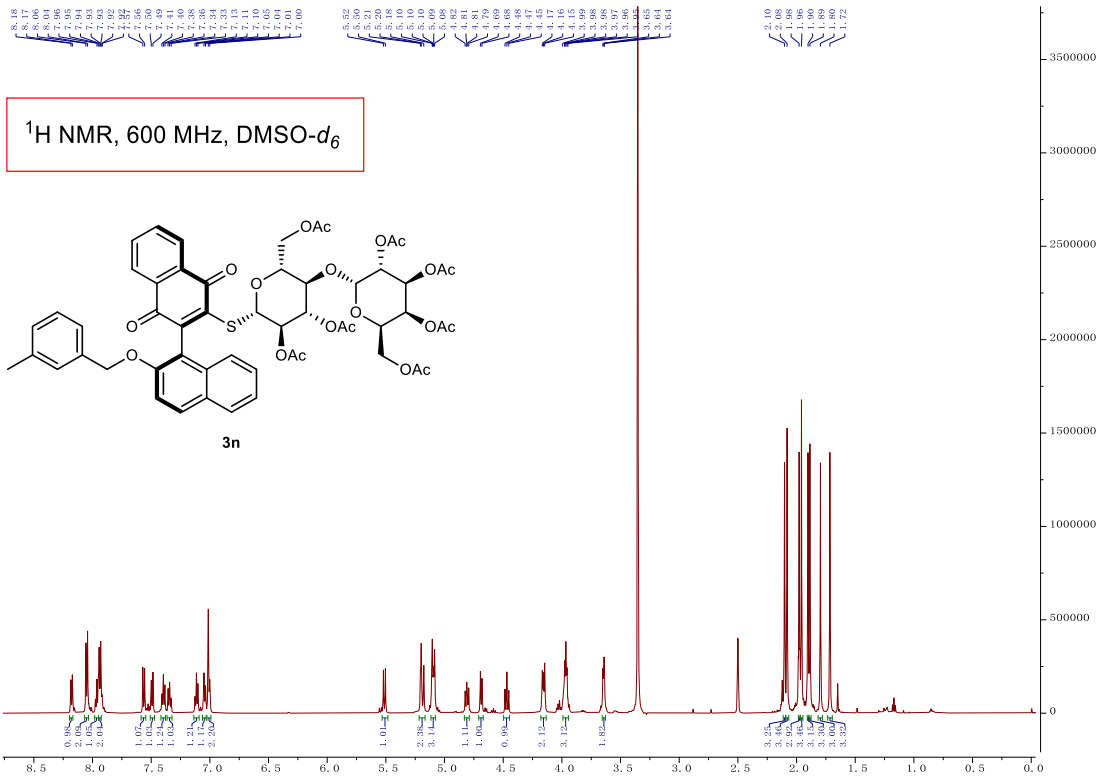
3k

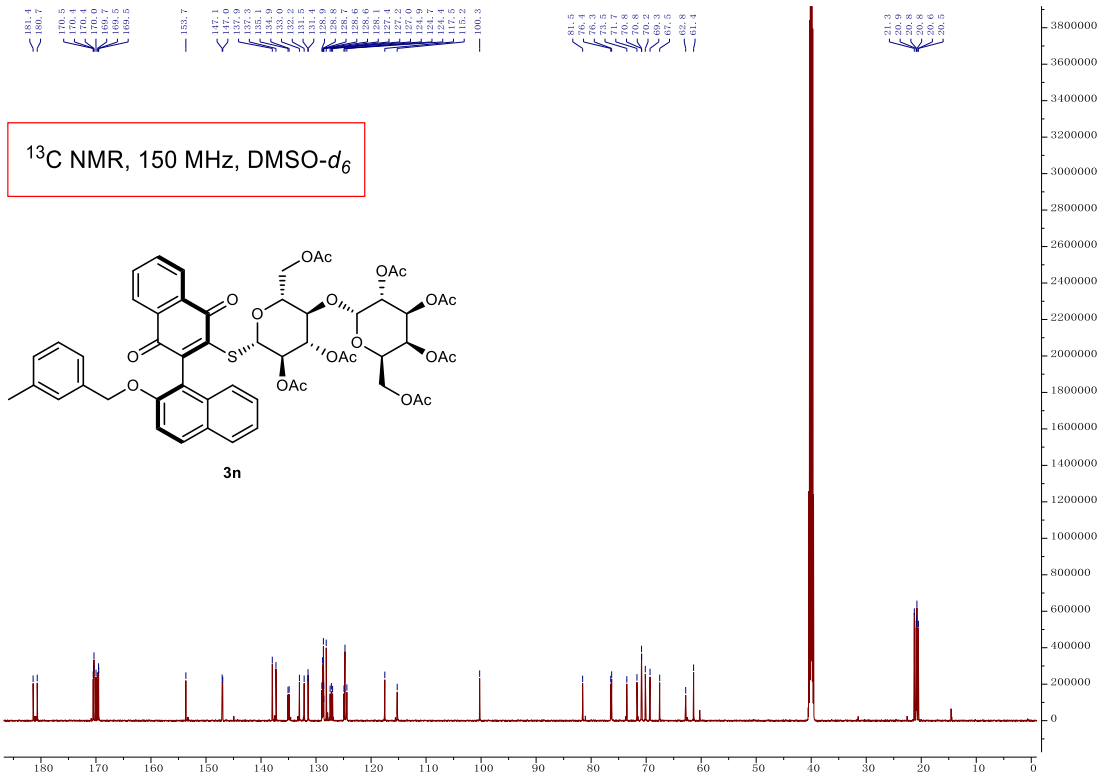

^{1}H NMR, 600 MHz, DMSO-d_6
OAc
OAc
OAc
OAc
OAc
OAc
OAc
O
O
O
O
S
PhO
3l

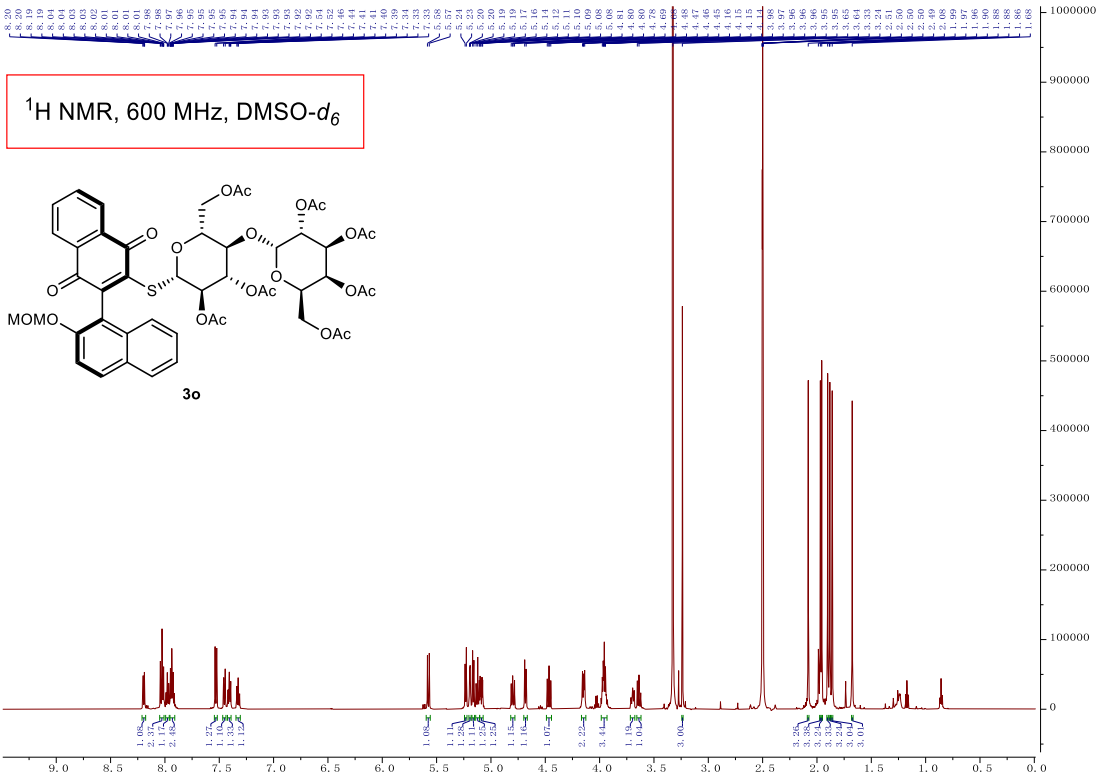

^{13}C NMR, 150 MHz, DMSO-d_6
OAc
OAc
OAc
OAc
OAc
OAc
OAc
O
O
O
O
S
PhO
3l

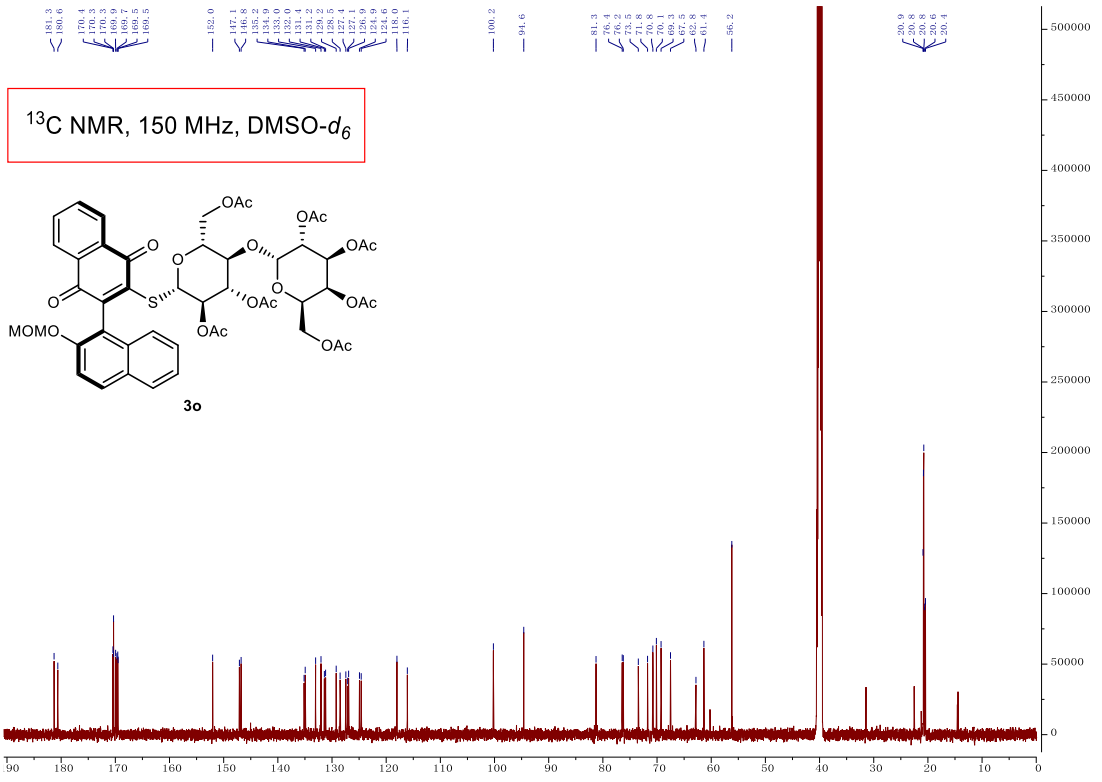

^{1}H NMR, 600 MHz, DMSO-d_6
t-Bu
OAc
S
3m


^{13}C NMR, 150 MHz, DMSO-d_6
t-Bu
OAc
S
3m

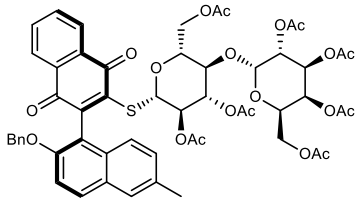

^{1}H NMR, 600 MHz, DMSO-d_6
OAc
O
S
3n


^{13}C NMR, 150 MHz, DMSO-d_6
OAc
O
S
3n


^{1}H NMR, 600 MHz, DMSO-d_6
OAc
OAc
OAc
OAc
OAc
OAc
OAc
OAc
O
O
O
O
O
S
MOMO
3o

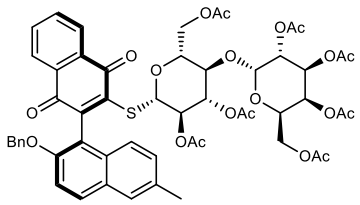

^{13}C NMR, 150 MHz, DMSO-d_6
OAc
OAc
OAc
OAc
OAc
OAc
OAc
OAc
O
O
O
O
O
S
MOMO
3o

^{1}H NMR, 600 MHz, DMSO-d_6

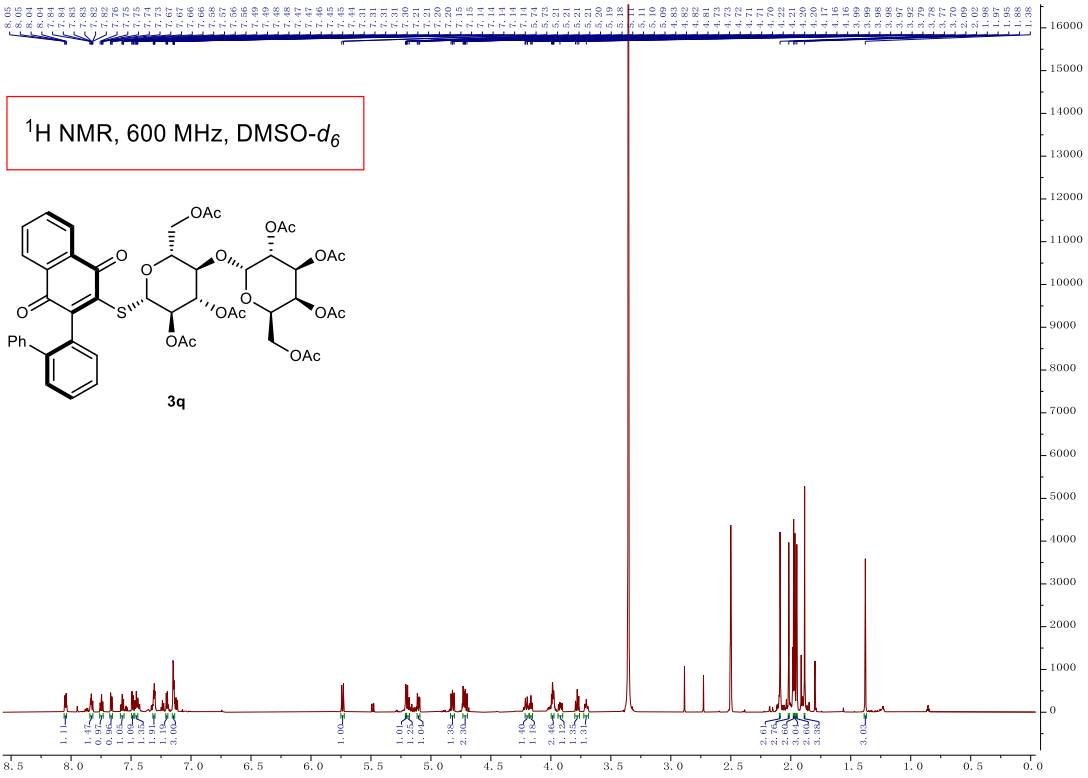


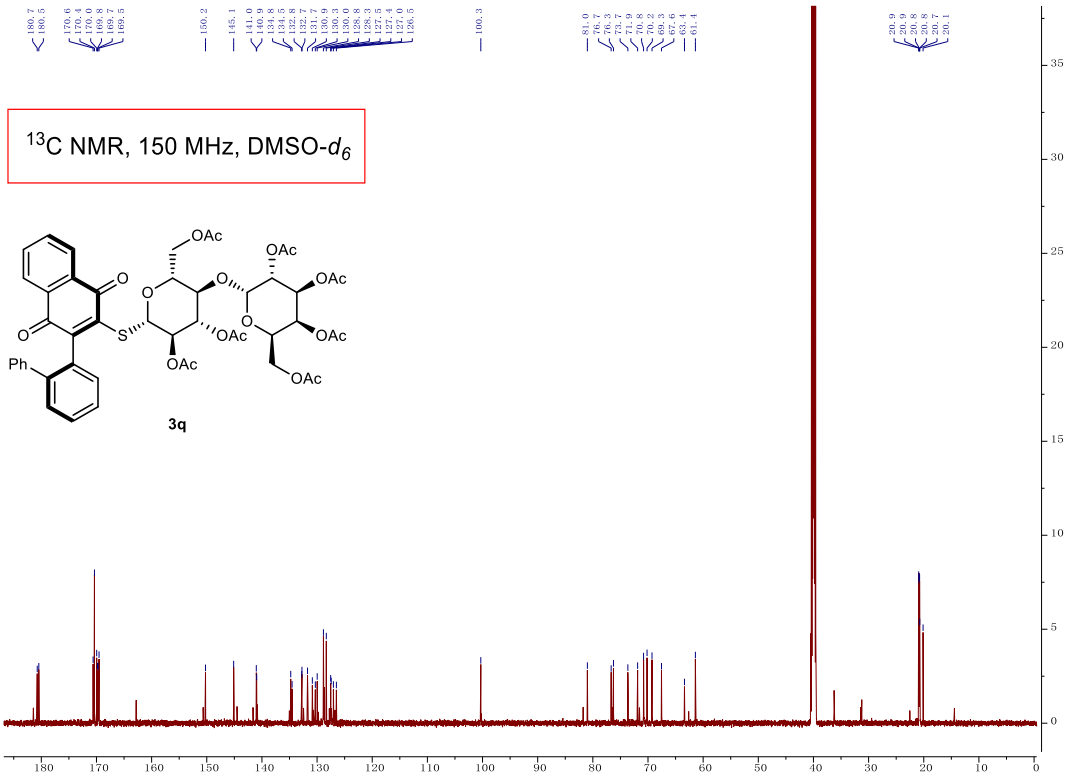
3p

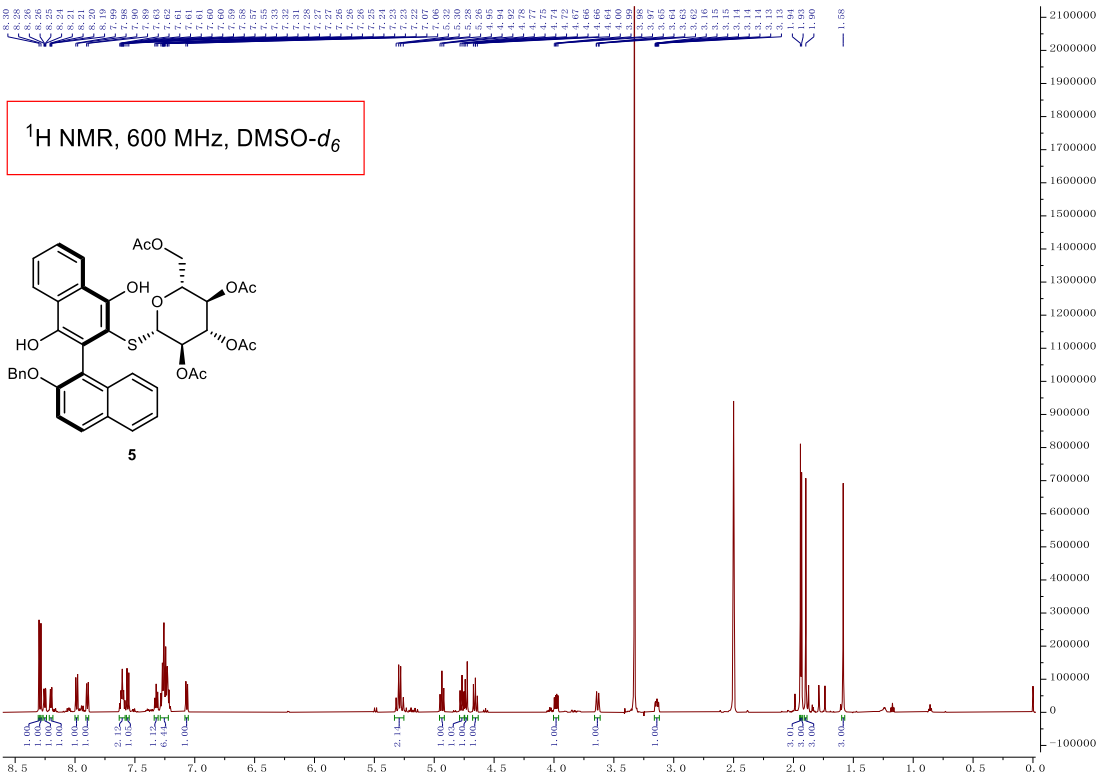
^{13}C NMR, 150 MHz, DMSO-d_6

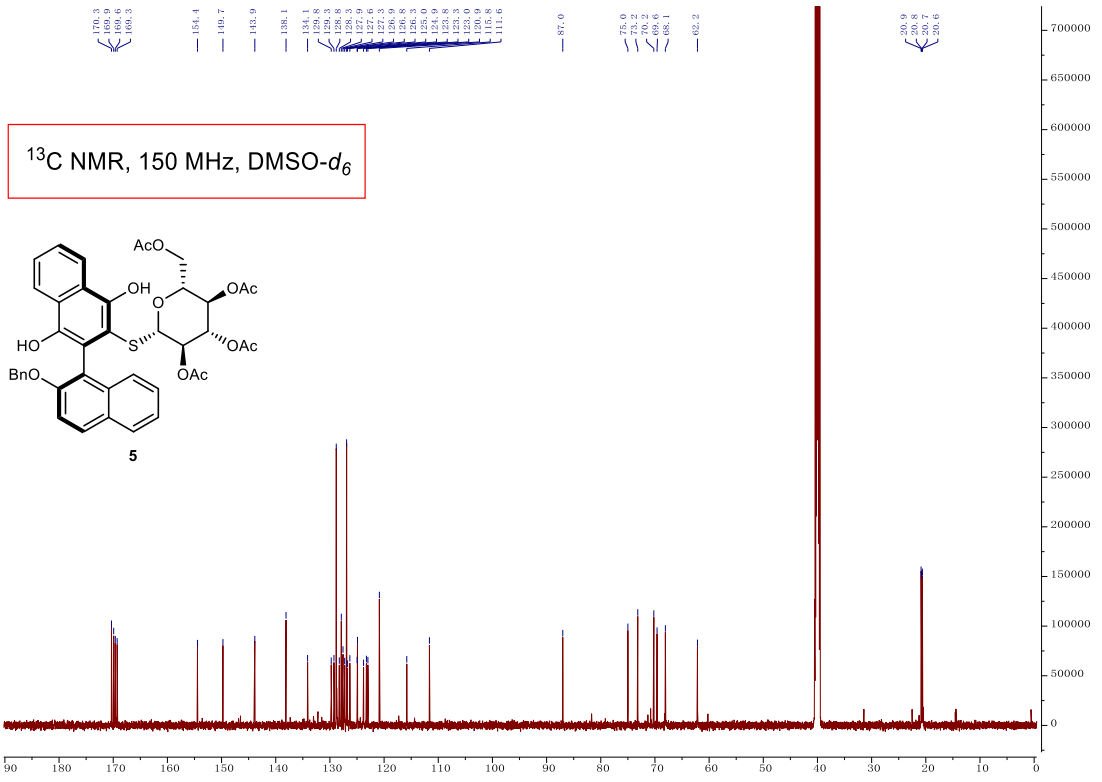


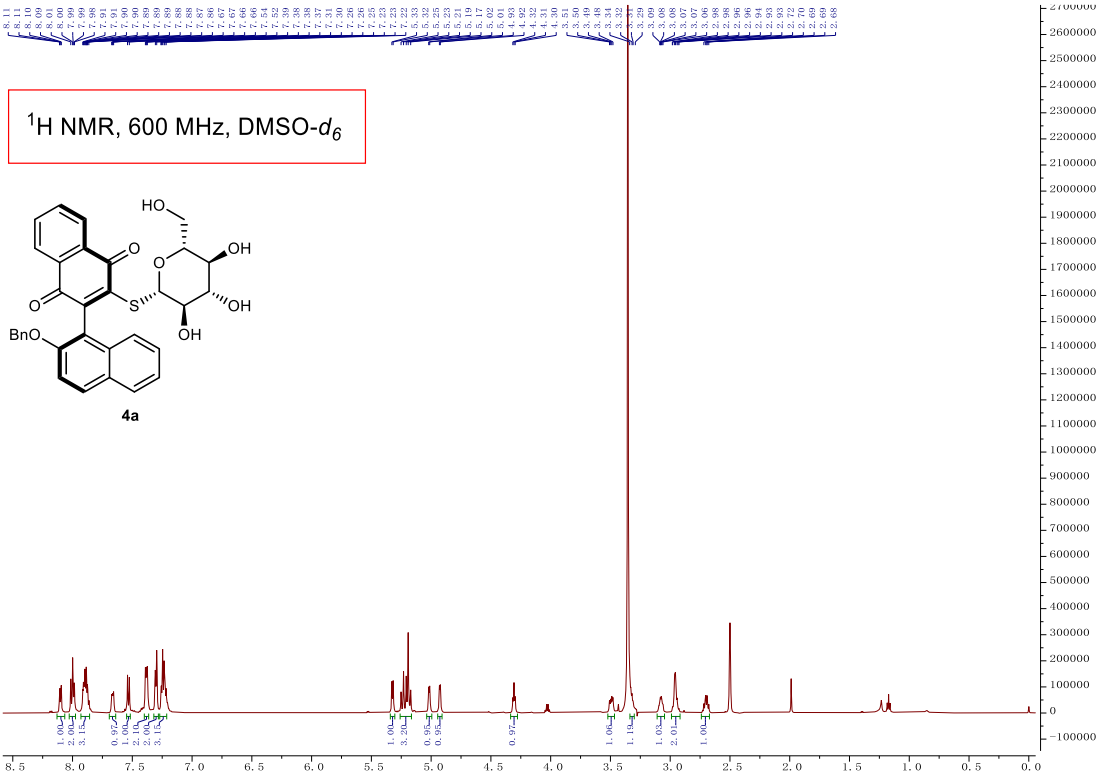
3p

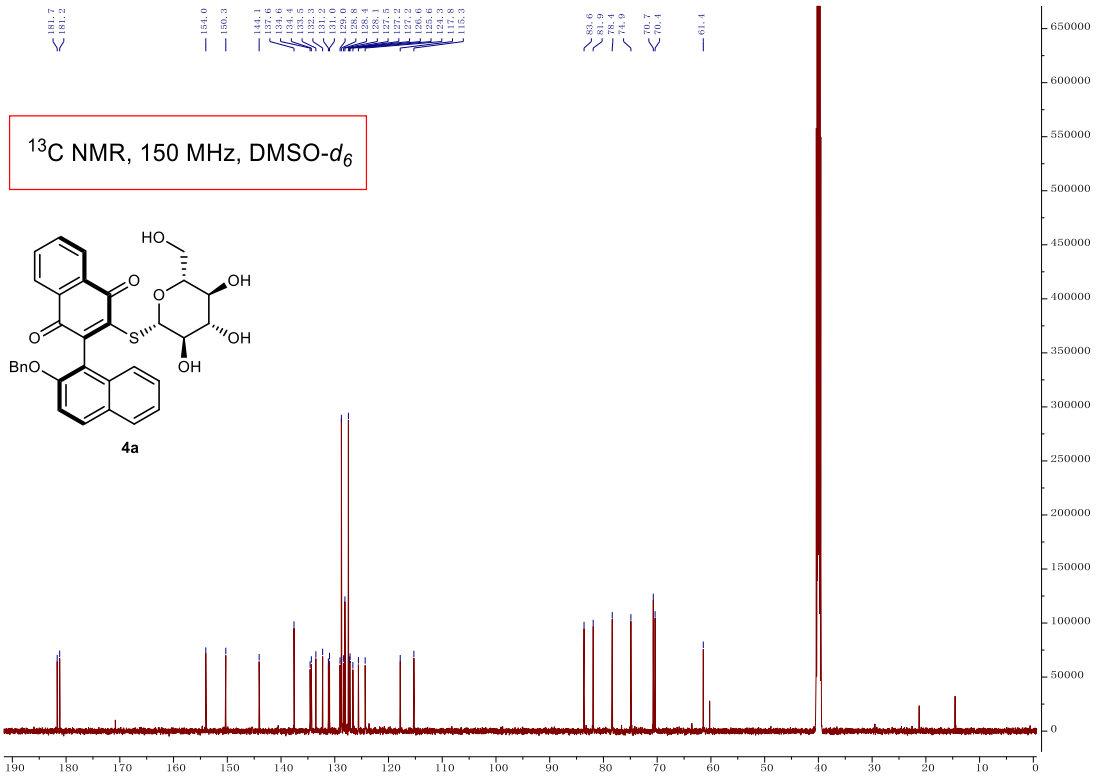

^{1}H NMR, 600 MHz, DMSO-d_6
OAc
OAc
OAc
OAc
OAc
OAc
OAc
O
O
O
O
O
S
Ph
3q

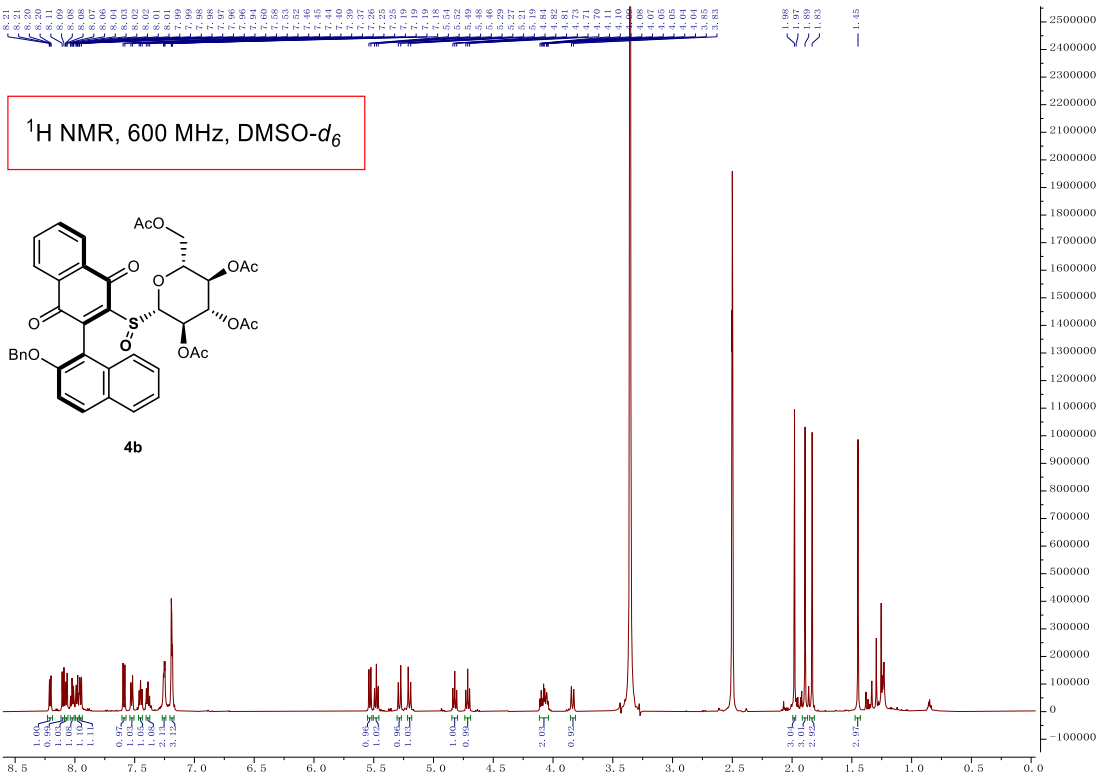

^{13}C NMR, 150 MHz, DMSO-d_6
OAc
OAc
OAc
OAc
OAc
OAc
OAc
O
O
O
O
O
S
Ph
3q

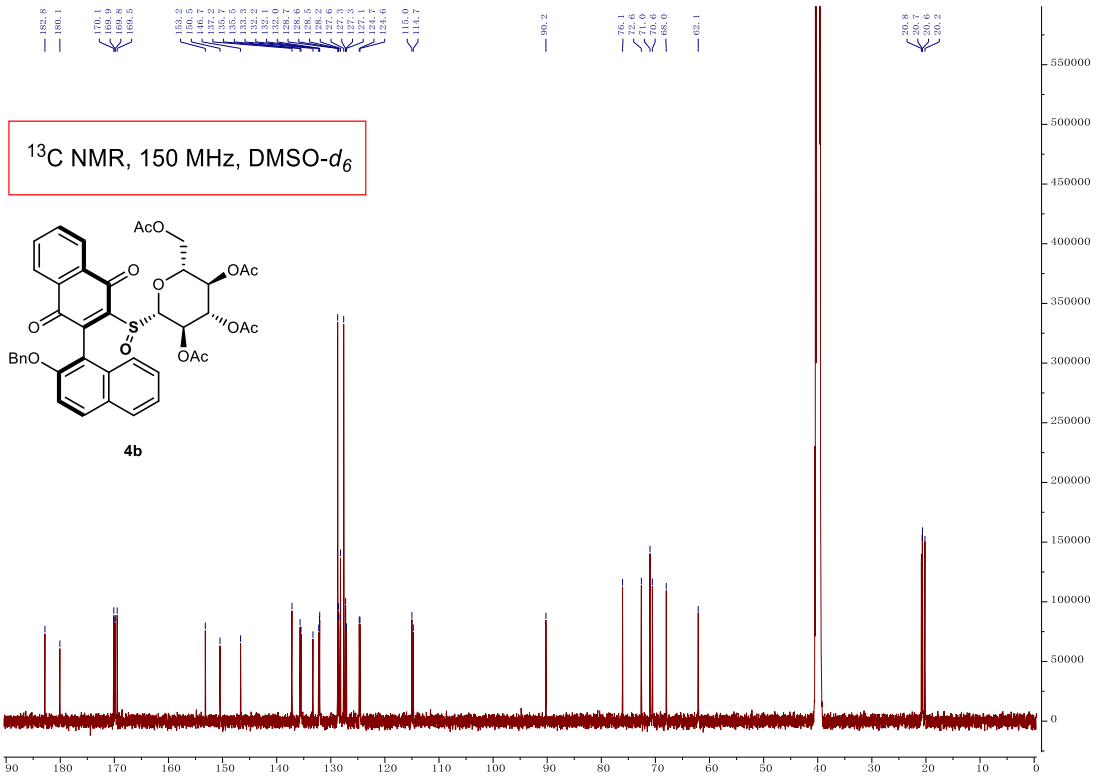

^{1}H NMR, 600 MHz, DMSO-d_6
AcO
OH
O
OAc
HO
S
OAc
BnO
OAc
5

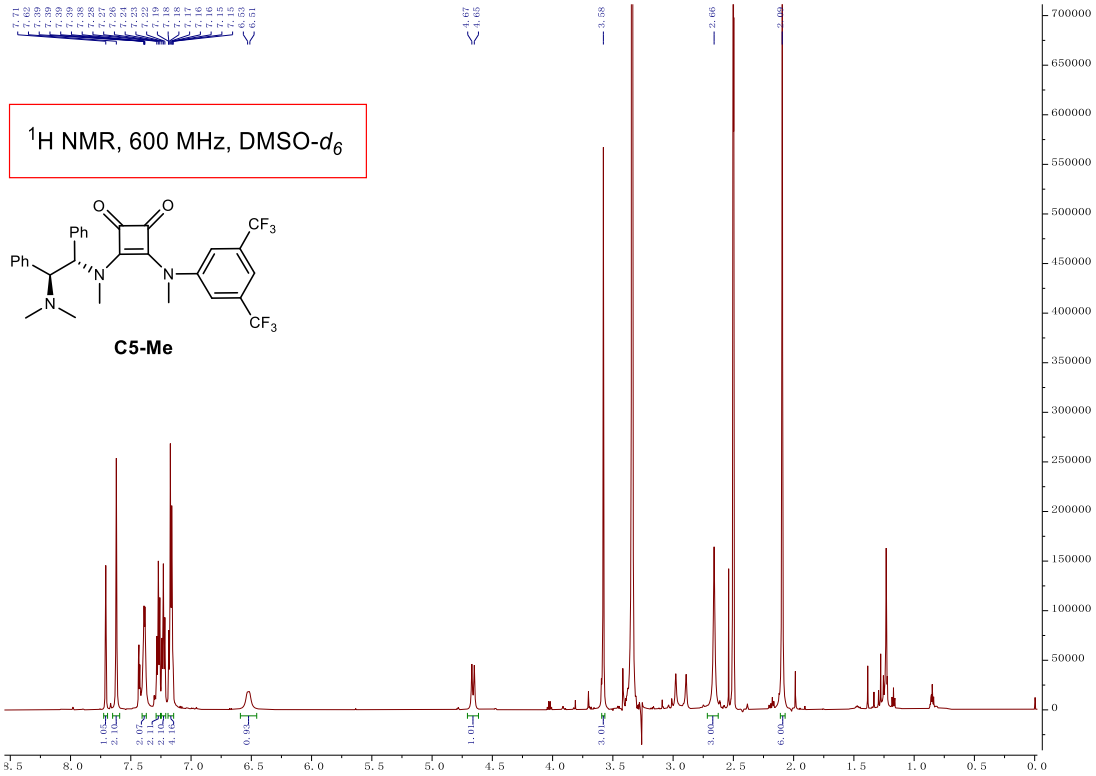

^{13}C NMR, 150 MHz, DMSO-d_6
AcO
OH
O
OAc
HO
S
OAc
BnO
OAc
5

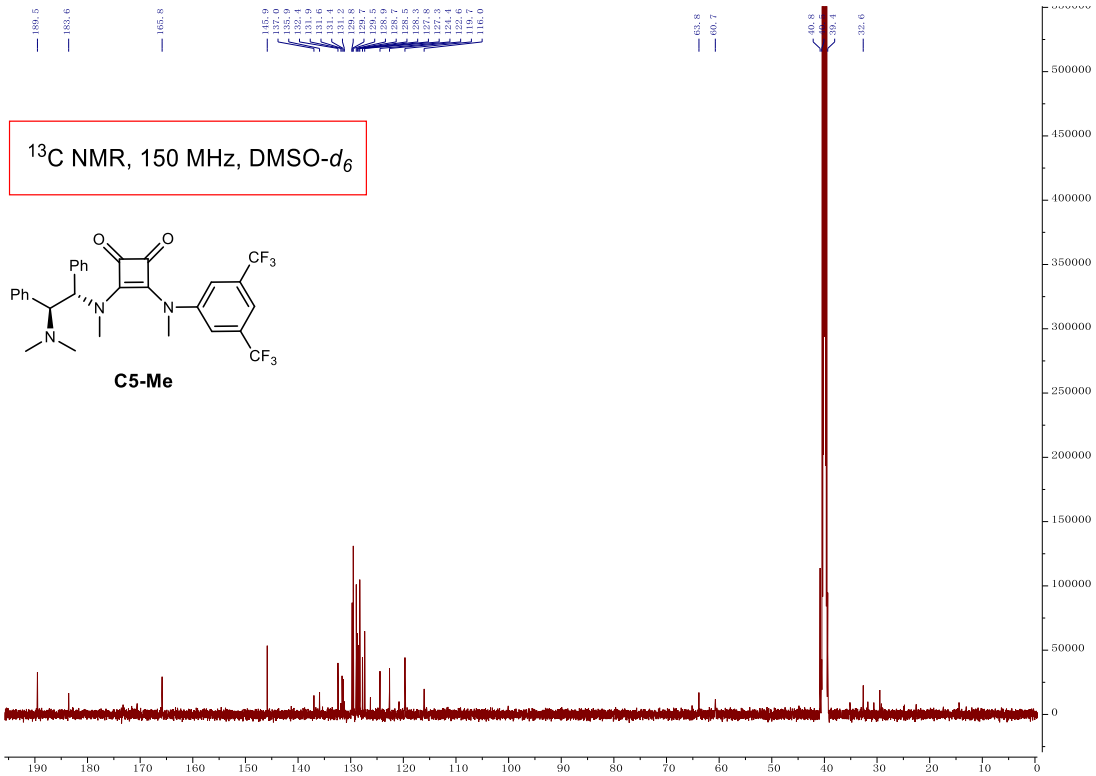

^{1}H NMR, 600 MHz, DMSO-d_6
HO
O
OH
O
O
S
OH
O
OH
BnO
4a


^{13}C NMR, 150 MHz, DMSO-d_6
HO
O
OH
O
O
S
OH
O
OH
BnO
4a


^{1}H NMR, 600 MHz, DMSO-d_6
AcO
OAc
OAc
OAc
BnO
4b


^{13}C NMR, 150 MHz, DMSO-d_6
AcO
OAc
OAc
OAc
BnO
4b


^{1}H NMR, 600 MHz, DMSO-d_6
C5-Me


^{13}C NMR, 150 MHz, DMSO-d_6
C5-Me