

Supporting Information for

Highly Efficient Synthesis of Flavonol 5-O-glycosides with Glycosyl ortho-Akynylbenzoates as Donors

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Contents

S1-S3 List of the Contents

S5-S16 Experimental Section and Characterization Data for New Compounds

S4	3,7,3',4'-Tetra- <i>O</i> -tert-butyldimethylsilyl-quercetin (3)
S4	3,7,4'-Tri- <i>O</i> -hexanoyl-kaempferol (5)
S5	3,7,4'-Tri- <i>O</i> -tert-butyldimethylsilyl-5- <i>O</i> -(2",3",4",6"-tetra- <i>O</i> -benzoyl- β-D-glucopyranosyl)-kaempferol (10)
S5	3,7,4'-Tri- <i>O</i> -tert-butyldimethylsilyl-5- <i>O</i> -(2",3",4"-tri- <i>O</i> -benzoyl-6- <i>O</i> -te rt-butyldiphenylsilyl-β-D-glucopyranosyl)-kaempferol (11)
S6	3,7,4'-Tri- <i>O</i> -tert-butyldimethylsilyl-5- <i>O</i> -(2",3",4",6"-tetra- <i>O</i> -benzoyl-β -D-galactopyranosyl)-kaempferol (12)
S6	3,7,4'-Tri- <i>O</i> -tert-butyldimethylsilyl-5- <i>O</i> -(2",3",4"-tri- <i>O</i> -benzoyl-α-L-r hamnopyranosyl)-kaempferol (13)
S7	3,7,3',4'-Tetra- <i>O</i> -tert-butyldimethylsilyl-5- <i>O</i> -(2",3",4",6"-tetra- <i>O</i> -benz oyl-β-D-glucopyranosyl)-quercetin (14)
S7	3,7,3',4'-Tetra- <i>O</i> -tert-butyldimethylsilyl-5- <i>O</i> -(2",3",4"-tri- <i>O</i> -benzoyl-6- <i>O</i> -tert-butyldiphenylsilyl-β-D-glucopyranosyl)-quercetin (15)
S8	3,7,3',4'-Tetra- <i>O</i> -tert-butyldimethylsilyl-5- <i>O</i> -(2",3",4",6"-tetra- <i>O</i> -benz oyl-β-D-galactopyranosyl)-quercetin (16)
S8	3,7,3',4'-Tetra- <i>O</i> -tert-butyldimethylsilyl-5- <i>O</i> -(2",3",4"-tri- <i>O</i> -benzoyl-α

	-L-rhamnopyranosyl)-quercetin (17)
S9	3,7,4'-Tri-O-benzyl-5-O-(2",3",4",6"-tetra-O-benzoyl-β-D-glucopyranosyl)-kaempferol (18)
S9	3,7,4'-Tri-O-benzyl-5-O-(2",3",4"-tri-O-benzoyl-6-O-tert-butyldiphenylsilyl-β-D-glucopyranosyl)-kaempferol (19)
S10	3,7,4'-Tri-O-benzyl-5-O-(2",3",4",6"-tetra-O-benzoyl-β-D-galactopyranosyl)-kaempferol (20)
S10	3,7,4'-Tri-O-benzyl-2",3",4"-tri-O-benzoyl-α-L-rhamnopyranosyl)-kaempferol (21)
S11	3,7,4'-Tri-O-hexanoyl-5-O-(2",3",4",6"-tetra-O-benzoyl-β-D-glucopyranosyl)-kaempferol (22)
S11	3,7,4'-Tri-O-hexanoyl-5-O-(2",3",4"-tri-O-benzoyl-6-O-tert-butyldiphenylsilyl-β-D-glucopyranosyl)-kaempferol (23)
S12	3,7,4'-Tri-O-hexanoyl-5-O-(2",3",4",6"-tetra-O-benzoyl-β-D-galactopyranosyl)-kaempferol (24)
S12	3,7,4'-Tri-O-hexanoyl-2",3",4"-tri-O-benzoyl-α-L-rhamnopyranosyl)-kaempferol (25)
S13	3,7,4'-Tri-O-hexanoyl-5-O-(2",3",4"-tri-O-benzoyl-β-D-glucopyranosyl)-kaempferol (26)
S14	3,7,4'-Tri-O-hexanoyl-5-O-[2",3",4"-tri-O-benzoyl-6"-O-(2",3",4"-tri-O-benzoyl-α-L-rhamnopyranonyl)-β-D-glucopyranosyl]-kaempferol (27)
S14	3,7,4'-Tri-O-benzyl-5-O-(2",3",4"-tri-O-benzoyl-β-D-glucopyranosyl)-kaempferol (29)
S14	3,7,4'-Tri-O-benzyl-5-O-[2",3",4"-tri-O-benzoyl-6"-O-(2",3",4"-tri-O-benzoyl-α-L-rhamnopyranonyl)-β-D-glucopyranosyl]-kaempferol (30)
S15	3,7,4'-Tri-O-acetyl-5-O-[2",3",4"-tri-O-acetyl-6"-O-(2",3",4"-tri-O-acetyl-α-L-rhamnopyranonyl)-β-D-glucopyranosyl]-kaempferol (28)

S16	Key 2D correlations in compound (28)
S17-S81 ^1H , ^{13}C NMR, and 2D spectra	
S17-20	1D and 2 D spectra for compound 2
S21-22	^1H and ^{13}C NMR spectra for compound 3
S23-27	1D and 2D spectra for compound 4
S28-32	1D and 2D spectra for compound 5
S33-36	1D and 2D spectra for compound 10
S37-38	^1H and ^{13}C NMR spectra for compound 11
S39-40	^1H and ^{13}C NMR spectra for compound 12
S41-42	^1H and ^{13}C NMR spectra for compound 13
S43-44	^1H and ^{13}C NMR spectra for compound 14
S45-46	^1H and ^{13}C NMR spectra for compound 15
S47-48	^1H and ^{13}C NMR spectra for compound 16
S49-50	^1H and ^{13}C NMR spectra for compound 17
S51-52	^1H and ^{13}C NMR spectra for compound 18
S53-54	^1H and ^{13}C NMR spectra for compound 19
S55-56	^1H and ^{13}C NMR spectra for compound 20
S57-58	^1H and ^{13}C NMR spectra for compound 21
S59-60	^1H and ^{13}C NMR spectra for compound 22
S61-62	^1H and ^{13}C NMR spectra for compound 23
S63-64	^1H and ^{13}C NMR spectra for compound 24
S65-66	^1H and ^{13}C NMR spectra for compound 25
S67-68	^1H and ^{13}C NMR spectra for compound 26
S69-70	^1H and ^{13}C NMR spectra for compound 27
S71-72	^1H and ^{13}C NMR spectra for compound 29
S73-74	^1H and ^{13}C NMR spectra for compound 30
S75-81	1D and 2D spectra for compound 28

3,7,3',4'-Tetra-O-*tert*-butyldimethylsilyl-quercetin (3)

To a suspension of quercetin (1 g, 3.3 mmol) in dry CH₂Cl₂ (10 mL) was added TBSCl (2.80g, 19 mmol) and DBU (3 mL, 20 mmol) at room temperature. Then the reaction mixture was stirred for another 5 h, at which time TLC showed that all starting material was consumed. Ethyl acetate (100 mL) was added to dilute the reaction mixture, and the mixture was washed successively with water, saturated NaCl solution and dried over Na₂SO₄. Filtration and concentration under reduced pressure to afford the crude product, which was further purified by silica gel chromatography (eluent system: PE : EA = 15 : 1) to afford the fully TBS protected quercetin.

The above obtained intermediate was dissolved in CH₂Cl₂/H₂O (v/v = 10 : 1, 10 mL), to which catalytic amount I₂ was added. Then the reaction mixture was heated to reflux for 3 hours, at which time TLC showed that all starting material was consumed. General procedure was adopted to get **3** (1.8 g, 70 %) as light-yellow solid: ¹H NMR (400 MHz, CDCl₃) δ 12.68 (s, 1 H), 7.46 (m, 1 H), 7.35 (m, 1 H), 6.91 (d, *J* = 8.4 Hz, 1 H), 1.01 (s, 9 H), 1.00 (s, 9 H), 0.99 (s, 9 H), 0.84 (s, 9 H), 0.26 (s, 6 H), 0.23 (s, 6 H), 0.21 (s, 6 H), 0.12 (s, 6 H); ¹³C NMR (100 MHz, CDCl₃) δ 178.2, 161.8 (2 C), 156.4, 153.2, 149.2, 146.8, 135.6, 124.4, 123.2, 121.8, 120.8, 106.1, 102.9, 98.2, 25.9 (2 C), 25.7, 25.6, 18.6, 18.4, 18.3, -4.0, -4.1, -4.2, -4.4; HRMS (ESI) calcd for C₃₉H₆₇O₇Si₄ [M+H]⁺ 759.3958, found 759.3959.

3,7,4'-Tri-O-hexanoyl-kaempferol (5)

To a suspension of kaempferol (2.3 g, 8 mmol) and Et₃N (3.7 mL) in dry acetone (100 mL) was added hexanoyl chloride (3.66 mL, 26.4 mmol) dropwise at 0 °C. After hexanoyl chloride addition completed, the temperature was raised to rt, and the stirring was continued for another 3 h. Ice water (10 mL) was added to quench the reaction and the acetone was removed under reduced pressure, the resultant reaction mixture was diluted with ethyl acetate and washed with 1 N HCl, saturated Na₂CO₃ and NaCl successively, then dried over Na₂SO₄. Filtration and concentration under reduced pressure afforded the crude product which was further purified by silica gel chromatography (eluent system: PE : EA = 13 : 1) to give **5** (3.1 g, 68%) as light-yellow solid: ¹H NMR (400 MHz, CDCl₃) δ 12.17 (s, 1 H), 7.88 (dd, *J* = 2.0, 6.8

Hz, 2 H), 7.26 (dd, J = 2.0, 6.8 Hz, 2 H), 6.84 (d, J = 2.0 Hz, 1 H), 6.58 (d, J = 2.0 Hz, 1 H), 2.63-2.56 (m, 6 H), 1.80-1.74 (m, 6 H), 1.41-1.33 (m, 12 H), 0.96-0.88 (m, 9 H); ^{13}C NMR (100 MHz, CDCl_3) δ 176.3, 171.7, 171.1, 170.6, 161.7, 156.5, 156.4, 156.0, 153.2, 132.0, 129.7, 126.7, 122.0, 108.7, 105.4, 101.0, 34.3, 33.7, 31.2, 31.1, 31.0, 24.5, 24.4 (2 C), 22.3, 22.2 (2 C), 13.9, 13.8; HRMS (ESI) calcd for $\text{C}_{33}\text{H}_{40}\text{O}_9\text{Na}$ $[\text{M}+\text{Na}]^+$ 603.2565, found 603.2562.

3,7,4'-Tri-O-*tert*-butyldimethylsilyl-5-O-(2'',3'',4'',6''-tetra-O-benzoyl- β -D-glucopyranosyl)-kaempferol (10)

To a suspension of acceptor **2** (63 mg, 0.1 mmol), donor **6** (115 mg, 0.15 mmol), and activated powdered 4 Å MS in dry CH_2Cl_2 (3 mL) was added $\text{PPh}_3\text{AuNTf}_2$ (22 mg, 0.03 mmol) under the protection of N_2 . The reaction mixture was then stirred at 30 °C overnight. Filtration and concentration under reduced pressure gave the crude product which was further purified by silica gel chromatography (eluent system: PE : EA = 15 : 1) to furnish **10** (103 mg, 90%), as a white solid: $[\alpha]^{28}\text{D}$ 6.0 (c 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.07 (d, J = 7.2 Hz, 2 H), 7.93-7.87 (m, 6 H), 7.82 (d, J = 8.8 Hz, 2 H), 7.52-7.28 (m, 12 H), 6.91 (d, J = 8.8 Hz, 2 H), 6.62 (d, J = 2.4 Hz, 1 H), 6.61 (d, J = 2.4 Hz, 1 H), 6.04-5.95 (m, 2 H), 5.86 (t, J = 9.2 Hz, 1 H), 5.71 (d, J = 6.8 Hz, 1 H), 4.61 (dd, J = 3.1, 12.4 Hz, 1 H), 4.50 (dd, J = 4.7, 12.0 Hz, 1 H), 4.23 (m, 1 H), 1.00 (s, 9 H), 0.95 (s, 9 H), 0.75 (s, 9 H), 0.23 (s, 6 H), 0.22 (s, 3 H), 0.21 (s, 3 H), 0.01 (d, J = 4.0 Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.5, 166.0, 165.8, 165.2, 165.1, 159.3, 157.6, 157.1, 155.9, 149.5, 137.7, 133.4, 133.1, 133.0, 132.8, 130.1, 129.8 (2 C), 129.7, 129.6, 129.5, 128.9, 128.8, 128.4, 128.3, 128.1, 124.6, 119.8, 110.8, 109.6, 103.9, 99.9, 73.1, 72.4, 72.0, 69.6, 65.5, 63.0, 25.8, 25.6, 25.5, 18.7, 18.3, 18.2, 1.0, -3.9, -4.0, -4.4; HRMS (ESI) calcd for $\text{C}_{67}\text{H}_{78}\text{O}_{15}\text{Si}_3\text{Na}$ $[\text{M}+\text{Na}]^+$ 1229.4541, found 1229.4542.

3,7,4'-Tri-O-*tert*-butyldimethylsilyl-5-O-(2'',3'',4''-tri-O-benzoyl-6-O-*tert*-butyldiphenylsilyl- β -D-glucopyranosyl)-kaempferol (11)

Similar procedure as that used for the synthesis of **10** was adopted to give **11** (121 mg, 90%) as a white solid: $[\alpha]^{28}\text{D}$ -0.1 (c 2.7, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.08 (d, J = 8.0 Hz, 2 H), 7.91-7.88 (m, 4 H), 7.84 (d, J = 8.8 Hz, 2 H), 7.62 (d, J =

8.0 Hz, 2 H), 7.56-7.19 (m, 15 H), 7.14 (t, J = 7.6 Hz, 2 H), 6.92 (d, J = 8.8 Hz, 2 H), 6.67 (d, J = 2.4 Hz, 1 H), 6.64 (d, J = 2.4 Hz, 1 H), 6.01-5.86 (m, 3 H), 5.69 (d, J = 7.2 Hz, 1 H), 3.93-3.89 (m, 1 H), 3.83 (d, J = 2.8 Hz, 2 H), 1.01 (s, 9 H), 0.98 (s, 9 H), 0.94 (s, 9 H), 0.75 (s, 9 H), 0.23 (s, 6 H), 0.19 (s, 3 H), 0.18 (s, 3 H), 0.07 (s, 3 H), -0.04 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.6, 166.0, 165.2, 164.9, 159.4, 157.6, 157.0, 156.4, 149.4, 137.7, 135.6, 135.4, 133.1, 133.0, 132.9, 132.7, 132.6, 130.2, 129.8 (2 C), 129.5, 129.4, 129.3, 129.1, 128.3, 128.2, 128.1, 127.6, 127.5, 124.6, 119.8, 110.8, 109.3, 103.5, 100.1, 75.2, 73.6, 72.0, 68.9, 62.2, 26.5, 25.8, 25.7, 25.5, 19.0, 18.7, 18.3, 18.2, -4.0 (2 C), -4.4 (3 C); HRMS (ESI) calcd for $\text{C}_{76}\text{H}_{92}\text{O}_{14}\text{Si}_4\text{Na}^+$ [M+Na]⁺ 1363.5456, found 1363.5458.

3,7,4'-Tri-O-*tert*-butyldimethylsilyl-5-O-(2",3",4",6"-tetra-O-benzoyl- β -D-galactopyranosyl)-kaempferol (12)

Similar procedure as that used for the synthesis of **10** was adopted to give **12** (120 mg, 99%) as a white solid: $[\alpha]^{28}\text{D}$ 47.6 (*c* 1.6, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.14 (d, J = 7.2 Hz, 2 H), 8.06 (d, J = 7.2 Hz, 2 H), 7.94 (d, J = 7.6 Hz, 2 H), 7.84 (d, J = 7.2 Hz, 2 H), 7.82 (d, J = 8.8 Hz, 2 H), 7.65 (t, J = 7.2 Hz, 1 H), 7.54-7.24 (m, 11 H), 6.91 (d, J = 8.8 Hz, 2 H), 6.70 (d, J = 2.2 Hz, 1 H), 6.63 (d, J = 2.2 Hz, 1 H), 6.27 (dd, J = 8.0, 10.4 Hz, 1 H), 6.08 (d, J = 3.2 Hz, 1 H), 5.70 (dd, J = 3.8, 10.4 Hz, 1 H), 5.65 (d, J = 8.0 Hz, 1 H), 4.68-4.62 (m, 1 H), 4.44-4.38 (m, 2 H), 1.00 (s, 9 H), 0.98 (s, 9 H), 0.74 (s, 9 H), 0.26 (s, 6 H), 0.22 (s, 6 H), 0.07 (s, 3 H), -0.10 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.5, 165.9, 165.6, 165.3, 159.4, 157.6, 157.1, 156.4, 149.4, 137.7, 133.5, 133.2 (2 C), 132.8, 130.2, 130.1, 129.8, 129.7, 129.3, 129.1, 128.8, 128.6, 128.4 (2 C), 128.2, 128.1, 124.6, 119.8, 110.7, 109.6, 103.8, 100.6, 71.9, 71.6, 69.4, 68.0, 61.7, 25.8, 25.7, 25.6, 18.7, 18.3, 18.2, -3.9, -4.1, -4.3 (2 C), -4.4; HRMS (ESI) calcd for $\text{C}_{67}\text{H}_{78}\text{O}_{15}\text{Si}_3\text{Na}^+$ [M+H]⁺ 1207.4721, found 1207.4726.

3,7,4'-Tri-O-*tert*-butyldimethylsilyl-5-O-(2",3",4"-tri-O-benzoyl- α -L-rhamnopyranosyl)-kaempferol (13)

Similar procedure as that used for the synthesis of **10** was adopted to give **13** (73 mg, 72%) as a white solid: $[\alpha]^{28}\text{D}$ 17.9 (*c* 1.5, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.17 (d, J = 7.2 Hz, 2 H), 8.05 (d, J = 7.2 Hz, 2 H), 7.93 (d, J = 8.8 Hz, 2 H), 7.89 (d,

J = 7.2 Hz, 2 H), 7.63 (t, *J* = 7.2 Hz, 1 H), 7.54-7.50 (m, 3 H), 7.44-7.36 (m, 3 H), 7.29-7.25 (m, 2 H), 6.95 (d, *J* = 8.8 Hz, 2 H), 6.62 (d, *J* = 2.0 Hz, 1 H), 6.54 (d, *J* = 2.0 Hz, 1 H), 6.53 (dd, *J* = 3.4, 10.0 Hz, 1 H), 6.13-6.12 (m, 1 H), 5.89 (s, 1 H), 5.81 (t, *J* = 10.0 Hz, 1 H), 4.55-4.51 (m, 1 H), 1.33 (d, *J* = 6.4 Hz, 3 H), 1.01 (s, 9 H), 1.007 (s, 9 H), 0.36 (s, 3 H), 0.31 (s, 3 H), 0.294 (s, 3 H), 0.291 (s, 3 H), 0.24 (s, 6 H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.7, 166.0, 165.5, 164.9, 159.7, 157.9, 157.1, 155.5, 149.1, 138.0, 133.4, 133.2, 132.8, 130.1, 130.0, 129.9, 129.7, 129.6, 129.5, 129.4, 128.6, 128.3, 128.2, 124.6, 119.8, 110.2, 105.3, 102.6, 96.1, 72.0, 70.7, 69.7, 68.2, 26.0, 25.7 (2 C), 25.6, 19.0, 18.3, 18.2, 17.6, -3.4 (2 C), -4.3, -4.4 (2 C). HRMS (MALDI) calcd for $\text{C}_{60}\text{H}_{75}\text{O}_{13}\text{Si}_3$ [$\text{M}+\text{H}$] $^+$ 1087.4783, found 1087.4510.

3,7,3',4'-Tetra-*O*-tert-butyldimethylsilyl-5-*O*-(2",3",4",6"-tetra-*O*-benzoyl- β -D-glucopyranosyl)-quercetin (14)

Similar procedure as that used for the synthesis of **10** was adopted to give **14** (125 mg, 93%) as a white solid: $[\alpha]^{28}\text{D}$ 7.3 (*c* 1.7, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.08 (d, *J* = 7.2 Hz, 2 H), 7.92 (d, *J* = 6.5 Hz, 2 H), 7.88 (d, *J* = 7.2 Hz, 2 H), 7.52-7.41 (m, 5 H), 7.37-7.26 (m, 9 H), 6.88 (d, *J* = 8.4 Hz, 2 H), 6.62 (d, *J* = 2.2 Hz, 1 H), 6.56 (d, *J* = 2.2 Hz, 1 H), 6.04-5.93 (m, 2 H), 5.85 (t, *J* = 9.6 Hz, 1 H), 5.71 (d, *J* = 7.2 Hz, 1 H), 4.96 (dd, *J* = 3.2, 12.0 Hz, 1 H), 4.49 (dd, *J* = 4.8, 12.0 Hz, 1 H), 4.22-4.17 (m, 1 H), 1.00 (s, 9 H), 0.99 (s, 9 H), 0.94 (s, 9 H), 0.73 (s, 9 H), 0.223 (s, 3 H), 0.218 (s, 3 H), 0.21 (s, 3 H), 0.20 (s, 6 H), 0.198 (s, 3 H), -0.01 (s, 3 H), -0.02 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.6, 166.0, 165.8, 165.2, 165.1, 159.3, 157.5, 155.9, 159.6, 148.6, 146.6, 137.6, 133.3, 133.1, 133.0, 132.8, 130.1, 129.8 (2 C), 129.7, 129.6, 129.5, 128.9, 128.8, 128.3, 128.2, 128.1, 124.7, 123.0, 121.4, 120.7, 110.9, 109.9, 103.8, 100.0, 73.1, 72.4, 72.0, 69.6, 62.9, 25.9, 25.7, 25.5, 15.6, 18.5, 18.4, 18.2, -4.0, -4.1 (2 C), -4.2 (3 C), -4.4 (2 C); HRMS (ESI) calcd for $\text{C}_{73}\text{H}_{92}\text{O}_{16}\text{Si}_4\text{Na}$ [$\text{M}+\text{Na}$] $^+$ 1359.5355, found 1359.5361.

3,7,3',4'-Tetra-*O*-tert-butyldimethylsilyl-5-*O*-(2",3",4"-tri-*O*-benzoyl-6-*O*-tert-butyldiphenylsilyl- β -D-glucopyranosyl)-quercetin (15)

Similar procedure as that used for the synthesis of **10** was adopted to give **15** (121 mg, 90%) as a white solid: $[\alpha]^{28}\text{D}$ -0.1 (*c* 2.7, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ

8.08 (d, $J = 7.6$ Hz, 2 H), 7.90 (d, $J = 8.0$ Hz, 4 H), 7.61 (d, $J = 6.8$ Hz, 2 H), 7.55-7.24 (m, 15 H), 7.20 (t, $J = 7.2$ Hz, 2 H), 7.15 (t, $J = 7.6$ Hz, 2 H), 6.89 (d, $J = 8.4$ Hz, 1 H), 6.67 (d, $J = 2.1$ Hz, 1 H), 6.60 (d, $J = 2.1$ Hz, 1 H), 5.99-5.92 (m, 2 H), 5.88 (t, $J = 9.2$ Hz, 1 H), 5.69 (d, $J = 7.2$ Hz, 1 H), 3.91 (m, 1 H), 3.82 (d, $J = 2.5$ Hz, 1 H), 1.00 (s, 9 H), 0.99 (s, 9 H), 0.97 (s, 9 H), 0.94 (s, 9 H), 0.74 (s, 9 H), 0.22 (s, 6 H), 0.20 (s, 6 H), 0.19 (s, 3 H), 0.188 (s, 3 H), 0.04 (s, 3 H), -0.05 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.6, 166.0, 165.2, 164.9, 159.4, 157.6, 156.4, 149.5, 148.6, 146.6, 137.7, 135.6, 135.4, 133.1, 133.0 (2 C), 132.7, 132.6, 130.2, 129.8 (3 C), 129.5, 129.4 (2 C), 129.1, 128.3, 128.2, 128.0, 127.6, 127.5, 124.8, 123.0, 121.4, 120.7, 110.9, 109.5, 103.5, 100.2, 75.2, 73.6, 72.1, 69.0, 62.2, 26.5, 25.9, 25.8, 25.5, 19.0, 18.7, 18.6, 18.4, 18.2, -4.1 (3 C), -4.2, -4.3, -4.4; HRMS (ESI) calcd for $\text{C}_{76}\text{H}_{92}\text{O}_{14}\text{Si}_4\text{Na} [\text{M}+\text{Na}]^+$ 1363.5456, found 1363.5458.

3,7,3'4'-Tetra-O-*tert*-butyldimethylsilyl-5-O-(2'',3'',4'',6''-tetra-O-benzoyl- β -D-galactopyranosyl)-quercetin (16)

Similar procedure as that used for the synthesis of **10** was adopted to give **16** (87 mg, 70%) as a white solid: $[\alpha]^{28}\text{D}$ 41.7 (c 1.5, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.13 (d, $J = 7.2$ Hz, 2 H), 8.06 (d, $J = 7.2$ Hz, 2 H), 7.94 (d, $J = 7.2$ Hz, 2 H), 7.84 (d, $J = 7.2$ Hz, 2 H), 7.64 (t, $J = 7.2$ Hz, 1 H), 7.54-7.24 (m, 13 H), 6.88 (d, $J = 8.4$ Hz, 1 H), 6.70 (d, $J = 2.2$ Hz, 1 H), 6.58 (d, $J = 2.2$ Hz, 1 H), 6.25 (dd, $J = 8.0, 10.4$ Hz, 1 H), 6.07 (d, $J = 3.3$ Hz, 1 H), 5.70 (dd, $J = 3.4, 10.4$ Hz, 1 H), 5.65 (d, $J = 8.0$ Hz, 1 H), 4.66-4.61 (m, 1 H), 4.44-4.37 (m, 1 H), 1.00 (s, 9 H), 0.998 (s, 9 H), 0.990 (s, 9 H), 0.98 (s, 9 H), 0.72 (s, 9 H), 0.26 (d, $J = 1.8$ Hz, 6 H), 0.22 (s, 6 H), 0.20 (s, 6 H), 0.03 (s, 3 H), -0.12 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.6, 165.9, 165.6, 165.3, 159.4, 157.6, 156.3, 149.6, 148.6, 146.6, 137.7, 133.5, 133.2 (2 C), 132.8, 130.1, 130.0, 129.8 (2 C), 129.7, 129.3, 129.2, 129.1, 128.8, 128.6, 128.5, 128.4 (2 C), 128.3 (2 C), 128.1, 126.3, 124.7, 123.0, 121.4, 120.7, 110.8, 109.3, 103.7, 100.6, 71.9, 71.6, 69.5, 68.0, 61.7, 25.9, 25.7, 25.6, 18.7, 18.6, 18.4, 18.3, -4.1, -4.2 (2 C), -4.3 (2 C); HRMS (ESI) calcd for $\text{C}_{73}\text{H}_{93}\text{O}_{16}\text{Si}_4 [\text{M}+\text{H}]^+$ 1338.5560, found 1338.5561.

3,7,3',4'-Tetra-O-*tert*-butyldimethylsilyl-5-O-(2'',3'',4''-tri-O-benzoyl- α -L-rhamnopyranosyl)-quercetin (17)

Similar procedure as that used for the synthesis of **10** was adopted to give **17** (120 mg, 99%) as a white solid: $[\alpha]^{28}_D$ 7.7 (*c* 1.9, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 8.17 (d, *J* = 7.2 Hz, 2 H), 8.04 (d, *J* = 7.2 Hz, 2 H), 7.88 (d, *J* = 7.2 Hz, 2 H), 7.64 (t, *J* = 7.2 Hz, 1 H), 7.56-7.49 (m, 4 H), 7.43-7.36 (m, 4 H), 7.28 (t, *J* = 8.0 Hz, 2 H), 6.92 (d, *J* = 8.4 Hz, 1 H), 6.58 (d, *J* = 2.0 Hz, 1 H), 6.54 (d, *J* = 2.0 Hz, 1 H), 6.52 (dd, *J* = 3.4, 10.0 Hz, 1 H), 6.12 (m, 1 H), 5.88 (bs, 1 H), 5.80 (t, *J* = 6.0 Hz, 1 H), 4.56-4.52 (m, 1 H), 1.02 (s, 9 H), 1.01 (s, 18 H), 0.83 (s, 9 H), 0.33 (s, 3 H), 0.29 (s, 6 H), 0.28 (s, 3 H), 0.24 (s, 6 H), 0.23 (s, 6 H); ¹³C NMR (100 MHz, CDCl₃) δ 172.8, 166.0, 165.5, 164.9, 159.7, 157.9, 155.6, 149.2, 148.6, 146.6, 138.0, 133.4, 133.2, 132.8, 130.0 (2 C), 129.7, 129.6 (2 C), 129.4, 128.6, 128.3, 128.1, 124.8, 123.0, 121.3, 120.7, 110.2, 105.2, 96.1, 72.0, 70.7, 69.7, 68.2, 26.0, 25.9, 25.6, 19.0, 18.6, 18.5, 18.3, 17.6, -3.5, -3.6, -4.0 (2 C), -4.1, -4.2, -4.3, -4.4; HRMS (ESI) calcd for C₆₆H₈₉O₁₄Si₄Na [M+Na]⁺ 1217.5324, found 1217.5314.

3,7,4'-Tri-O-benzyl-5-O-(2'',3'',4'',6''-tetra-O-benzoyl- β -D-glucopyranosyl)-kaempferol (18)

Similar procedure as that used for the synthesis of **10** was adopted to give **18** (108 mg, 87%) as a white solid: $[\alpha]^{28}_D$ 9.0 (*c* 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 8.08 (d, *J* = 7.2 Hz, 2 H), 7.98-7.89 (m, 6 H), 7.53-7.20 (m, 29 H), 6.99 (d, *J* = 12.8 Hz, 2 H), 6.84 (d, *J* = 2.3 Hz, 1 H), 6.64 (d, *J* = 2.3 Hz, 1 H), 6.07 (t, *J* = 9.2 Hz, 1 H), 6.00 (dd, *J* = 7.2, 9.2 Hz, 1 H), 5.86 (t, *J* = 9.6 Hz, 1 H), 5.70 (d, *J* = 7.2 Hz, 1 H), 5.12 (s, 2 H), 5.06 (s, 2 H), 4.77 (d, *J* = 10.8 Hz, 1 H), 4.72 (dd, *J* = 2.9, 12.0 Hz, 1 H), 4.70 (d, *J* = 10.8 Hz, 1 H), 4.52 (dd, *J* = 5.6, 12.0 Hz, 1 H), 4.31-4.26 (m, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 172.6, 166.0, 165.8, 165.3, 165.2, 162.0, 160.2, 157.8, 156.6, 153.3, 139.2, 137.0, 136.4, 135.6, 133.4, 133.1, 132.9, 132.7, 130.1, 130.0, 129.8 (2 C), 129.6, 129.4, 128.9, 128.8, 128.7, 128.6, 128.4, 128.3, 128.2 (2 C), 128.1, 128.0 (2 C), 127.8, 127.4 (2 C), 123.4, 114.5, 111.0, 104.7, 100.2, 97.6, 73.3, 72.8, 72.6, 71.8, 70.4, 70.0, 69.5, 62.8. HRMS (MALDI) calcd for C₇₀H₅₅O₁₅ [M+H]⁺ 1135.1688, found 1135.3535.

3,7,4'-Tri-O-benzyl-5-O-(2'',3'',4''-tri-O-benzoyl-6-O-tert-butyldiphenylsilyl- β -D-glucopyranosyl)-kaempferol (19)

Similar procedure as that used for the synthesis of **10** was adopted to give **19** (87 mg, 69%) as a white solid: $[\alpha]^{28}_D$ 6.1 (*c* 1.4, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 8.09 (d, *J* = 7.6 Hz, 2 H), 7.93 (dd, *J* = 8.0, 8.4 Hz, 6 H), 7.65 (d, *J* = 7.2 Hz, 2 H), 7.56 (d, *J* = 7.2 Hz, 3 H), 7.46-7.13 (m, 29 H), 6.99 (d, *J* = 8.9 Hz, 2 H), 6.92 (d, *J* = 1.8 Hz, 1 H), 6.71 (d, *J* = 1.8 Hz, 1 H), 6.02-5.95 (m, 2 H), 5.81 (t, *J* = 9.6 Hz, 1 H), 5.65 (d, *J* = 6.8 Hz, 1 H), 5.12 (s, 2 H), 5.02 (s, 2 H), 4.74 (AB, 2 H), 3.98 (m, 1 H), 3.89-3.82 (m, 2 H), 0.97 (s, 9 H); ¹³C NMR (100 MHz, CDCl₃) δ 172.6, 165.9, 165.4, 164.9, 162.2, 160.2, 158.0, 157.1, 153.2, 139.3, 137.1, 136.5, 135.6, 135.5, 135.4, 133.2, 133.0, 132.9, 132.8, 132.6, 130.1, 130.0, 129.9, 129.8, 129.5, 129.2, 129.1, 128.8, 128.6, 128.3, 128.2, 128.1, 128.0 (2 C), 127.8, 127.6 (2 C), 127.4, 123.5, 114.5, 111.2, 105.3, 100.7, 97.2, 75.5, 73.3, 71.9, 70.4, 70.0, 69.1, 62.5, 26.5, 19.0; HRMS (ESI) calcd for C₇₉H₆₈O₁₄SiNa [M+Na]⁺ 1291.4271, found 1291.4280.

3,7,4'-Tri-*O*-benzyl-5-*O*-(2",3",4",6"-tetra-*O*-benzoyl- β -D-galactopyranosyl)-kaempferol (20)

Similar procedure as that used for the synthesis of **10** was adopted to give **20** (123 mg, 99%) as a white solid: $[\alpha]^{28}_D$ 70.8 (*c* 1.8, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 8.15 (d, *J* = 7.2 Hz, 2 H), 8.05 (d, *J* = 7.2 Hz, 2 H), 8.00 (d, *J* = 7.2 Hz, 2 H), 7.91 (d, *J* = 8.8 Hz, 2 H), 7.86 (d, *J* = 7.2 Hz, 2 H), 7.64 (t, *J* = 7.4 Hz, 1 H), 7.51-7.14 (m, 22 H), 6.98 (d, *J* = 9.0 Hz, 2 H), 6.95 (d, *J* = 2.3 Hz, 1 H), 6.68 (d, *J* = 2.3 Hz, 1 H), 6.34 (dd, *J* = 8.0, 10.4 Hz, 1 H), 6.09 (d, *J* = 2.9 Hz, 1 H), 5.74 (dd, *J* = 3.4, 10.4 Hz, 1 H), 5.60 (d, *J* = 8.0 Hz, 1 H), 5.11 (s, 2 H), 5.09 (s, 2 H), 4.71 (dd, *J* = 4.2, 11.2 Hz, 1 H), 4.62 (AB, 2 H), 4.52-4.45 (m, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 172.6, 166.0, 165.6, 165.4, 162.1, 160.1, 157.9, 157.3, 153.2, 139.3, 137.0, 136.4, 135.6, 133.6, 133.2, 133.1, 132.6, 130.0 (2 C), 129.9, 129.8, 129.7, 129.3, 128.9, 128.7 (2 C), 128.6, 128.3, 128.2, 128.1, 128.0, 127.8, 127.4, 123.4, 114.5, 111.0, 104.6, 101.3, 97.3, 73.2, 71.9, 70.4, 70.0, 69.2, 68.1, 62.4; HRMS (ESI) calcd for C₇₀H₅₄O₁₅ [M+H]⁺ 1135.3535, found 1135.3527.

3,7,4'-Tri-*O*-benzyl-2",3",4"-tri-*O*-benzoyl- α -L-rhamnopyranosyl)-kaempferol (21)

Similar procedure as that used for the synthesis of **10** was adopted to give **21** (100 mg,

99%) as a white solid: $[\alpha]^{28}_D$ 22.3 (*c* 0.6, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 8.17 (d, *J* = 7.6 Hz, 2 H), 8.05 (d, *J* = 7.6 Hz, 2 H), 8.00 (d, *J* = 8.4 Hz, 2 H), 7.89 (d, *J* = 7.6 Hz, 2 H), 7.64 (t, *J* = 7.2 Hz, 1 H), 7.53-7.26 (m, 23 H), 7.03 (d, *J* = 8.4 Hz, 2 H), 6.80 (s, 1 H), 6.72 (s, 1 H), 6.43 (dd, *J* = 3.4, 10.4 Hz, 1 H), 6.14 (s, 1 H), 5.92 (s, 1 H), 5.84 (t, *J* = 10.0 Hz, 1 H), 5.22-5.10 (m, 6 H), 4.61-4.58 (m, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 173.2, 166.0, 165.4, 165.2, 162.4, 160.2, 158.4, 156.2, 153.7, 139.6, 137.0, 136.5, 135.7, 133.4, 133.2, 132.9, 130.2, 030.0, 129.9, 129.7, 129.5, 129.4, 129.3, 129.1, 128.7, 128.6 (2 C), 128.4, 128.2, 128.1, 127.9, 127.5 (2 C), 123.5, 114.6, 110.7, 101.4, 96.6, 96.5, 74.0, 71.9, 70.7, 70.5, 70.0, 69.9, 68.4; HRMS (ESI) calcd for C₆₃H₅₀O₁₃Na [M+Na]⁺ 1037.3144, found 1037.3140.

3,7,4'-Tri-O-hexanoyl-5-O-(2",3",4",6"-tetra-O-benzoyl-β-D-glucopyranosyl)-kaempferol (22)

Similar procedure as that used for the synthesis of **10** was adopted to give **22** (115 mg, 99%) as a white solid: $[\alpha]^{28}_D$ 11 (*c* 1.3, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 8.01-7.90 (m, 8 H), 7.80 (d, *J* = 8.8 Hz, 2 H), 7.54-7.43 (m, 4 H), 7.40-7.30 (m, 8 H), 7.21 (d, *J* = 8.8 Hz, 2 H), 7.08 (d, *J* = 2.1 Hz, 1 H), 6.96 (d, *J* = 2.1 Hz, 1 H); 6.03 (t, *J* = 9.2 Hz, 1 H), 5.94 (dd, *J* = 7.2, 8.8 Hz, 1 H), 5.82 (t, *J* = 9.2 Hz, 1 H), 5.64 (d, *J* = 7.2 Hz, 1 H), 4.73 (dd, *J* = 3.2, 12.0 Hz, 1 H), 4.50 (dd, *J* = 5.6, 12.4 Hz, 1 H), 4.33 (m, 1 H), 2.60 (t, *J* = 7.6 Hz, 2 H), 2.46-2.41 (m, 4 H), 1.79-1.60 (m, 6 H), 1.43-1.28 (m, 12 H), 0.95-0.88 (m, 9 H); ¹³C NMR (100 MHz, CDCl₃) δ 171.7, 170.9, 170.4, 169.4, 166.0, 165.8, 165.3, 165.1, 157.1, 156.5, 154.2, 153.3, 152.7, 134.1, 133.4, 133.2, 133.0, 132.7, 130.0, 129.9, 129.8, 129.7, 129.5, 129.4, 128.9, 128.8, 128.4, 128.3 (2 C), 128.0, 127.1, 121.8, 113.8, 109.5, 106.5, 100.0, 72.7, 71.7, 69.4, 62.9, 34.3, 34.2, 33.7, 31.2, 31.1, 24.5, 24.3, 24.2, 22.3, 13.9; HRMS (ESI) calcd for C₆₇H₆₆O₁₈Na [M+Na]⁺ 1181.4141, found 1181.4148.

3,7,4'-Tri-O-hexanoyl-5-O-(2",3",4"-tri-O-benzoyl-6-O-tert-butyldiphenylsilyl-β-D-glucopyranosyl)-kaempferol (23)

Similar procedure as that used for the synthesis of **10** was adopted to give **23** (127 mg, 98%) as a white solid: $[\alpha]^{28}_D$ 14.7 (*c* 1.36, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, *J* = 7.2 Hz, 2 H), 7.90-7.86 (m, 4 H), 7.81 (d, *J* = 8.8 Hz, 2 H), 7.57-7.27 (m,

14 H), 7.25-7.18 (m, 5 H), 7.16 (d, J = 2.2 Hz, 1 H), 7.03 (d, J = 2.2 Hz, 1 H), 5.95-5.93 (m, 2 H), 5.78-5.73 (m, 1 H), 5.61 (d, J = 7.2 Hz, 1 H), 4.05-4.01 (m, 1 H), 6.90-3.82 (m, 2 H), 2.60 (t, J = 3.4 Hz, 2 H), 2.46-2.40 (m, 4 H), 1.81-1.74 (m, 2 H), 1.70-1.60 (m, 4 H), 1.42-1.26 (m, 12 H), 0.96-0.86 (m, 9 H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.7, 170.9, 170.4, 169.4, 165.9, 165.4, 164.9, 157.2, 157.1, 154.2, 153.2, 152.7, 135.5, 135.4, 134.1, 133.2, 133.0, 132.8, 132.5, 130.0, 129.9 (2 C), 129.8, 129.6, 129.4, 129.2, 129.0, 128.3, 128.2, 128.0, 127.6, 127.1, 121.8, 113.8, 109.3, 106.4, 100.5, 73.1, 71.7, 68.9, 62.5, 34.3 (2 C), 33.7, 31.2 (2 C), 31.1, 26.6, 24.5, 24.2, 22.2 (2 C), 19.1, 13.9, 13.8 (2 C); HRMS (MALDI) calcd for $\text{C}_{76}\text{H}_{80}\text{O}_{17}\text{Si}_3\text{Na}$ $[\text{M}+\text{Na}]^+$ 1315.5062, found 1315.5057.

3,7,4'-Tri-*O*-hexanoyl-5-*O*-(2",3",4",6"-tetra-*O*-benzoyl- β -D-galactopyranosyl)-k aempferol (24)

Similar procedure as that used for the synthesis of **10** was adopted to give **24** (115 mg, 99%) as a white solid: $[\alpha]^{28}\text{D}$ 66.3 (c 2.4, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.13 (d, J = 7.2 Hz, 2 H), 8.01 (dd, J = 7.2, 8.8 Hz, 4 H), 7.85 (d, J = 7.2 Hz, 2 H), 7.79 (d, J = 8.8 Hz, 2 H), 7.64 (t, J = 7.6 Hz, 1 H), 7.58-7.25 (m, 11 H), 7.20 (d, J = 8.8 Hz, 2 H), 7.12 (d, J = 2.1 Hz, 1 H), 7.03 (d, J = 2.0 Hz, 1 H), 6.27 (dd, J = 8.0, 10.3 Hz, 1 H), 6.07 (d, J = 3.2 Hz, 1 H), 4.68 (dd, J = 6.8, 11.1 Hz, 1 H), 4.55-4.47 (m, 2 H), 2.59 (t, J = 7.6 Hz, 2 H), 2.44-2.37 (m, 4 H), 1.78-1.57 (m, 6 H), 1.40-1.28 (m, 12 H), 0.95-0.88 (m, 9 H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.7, 171.0, 170.4, 169.3, 166.0, 165.6, 165.5, 157.1 (2 C), 154.2, 153.3, 152.7, 134.1, 133.6, 133.2 (2 C), 132.6, 130.1, 130.0, 129.8 (2 C), 129.4, 128.9, 128.7, 128.6, 128.4, 128.3, 128.0, 127.0, 121.8, 113.7, 109.1, 106.6, 101.0, 71.9, 71.6, 69.1, 68.0, 62.2, 34.3, 34.2, 33.6, 31.2 (2 C), 31.1, 24.5, 24.2 (2 C), 22.2, 13.4; HRMS (ESI) calcd for $\text{C}_{67}\text{H}_{66}\text{O}_{18}\text{Na}$ $[\text{M}+\text{Na}]^+$ 1181.4146, found 1181.4140.

3,7,4'-Tri-*O*-hexanoyl-2",3",4"-tri-*O*-benzoyl- α -L-rhamnopyranosyl)-kaempferol (25)

Similar procedure as that used for the synthesis of **10** was adopted to give **25** (85 mg, 82%) as a white solid: $[\alpha]^{28}\text{D}$ 15.9 (c 0.9, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.15 (d, J = 7.2 Hz, 2 H), 8.04 (d, J = 7.6 Hz, 2 H), 7.90 (t, J = 5.8, 8.4 Hz, 4 H), 7.64

(t, $J = 7.4$ Hz, 1 H), 7.54-7.49 (m, 3 H), 7.44-7.37 (m, 3 H), 7.29-7.24 (m, 4 H), 7.10 (d, $J = 1.8$ Hz, 1 H), 6.94 (d, $J = 1.8$ Hz, 1 H), 6.36 (dd, $J = 3.3, 10.1$ Hz, 1 H), 6.05 (s, 1 H), 5.89 (s, 1 H), 5.81 (t, $J = 10.0$ Hz, 1 H), 4.44-4.38 (m, 1 H), 2.68 (t, $J = 7.2$ Hz, 2 H), 2.62 (td, $J = 3.3, 7.6$ Hz, 4 H), 1.80 (dd, $J = 7.2, 14.4$ Hz, 6 H), 1.41-1.39 (m, 12 H), 1.35 (d, $J = 6.2$ Hz, 3 H), 0.96 (dd, $J = 6.8, 13.0$ Hz, 6 H), 0.86 (t, $J = 6.8$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.7, 171.0 (2 C), 165.9, 165.4, 165.0, 157.6, 156.1, 154.6, 153.6, 152.8, 134.2, 133.5, 133.2, 132.8, 129.9, 129.7, 129.5, 129.4, 129.3 (2 C), 128.6, 128.3, 128.2, 127.1, 121.9, 113.1, 105.7, 105.4, 96.3, 71.6, 70.6, 69.7, 68.3, 34.3, 33.9, 31.2 (2 C), 31.1, 24.5, 24.4 (2 C), 22.3, 22.2, 17.6, 13.8 (3 C); HRMS (ESI) calcd for $\text{C}_{60}\text{H}_{62}\text{O}_{16}\text{Na} [\text{M}+\text{Na}]^+$ 1061.3934, found 1061.3930.

3,7,4'-Tri-O-hexanoyl-5-O-(2'',3'',4''-tri-O-benzoyl- β -D-glucopyranosyl)-kaempferol (26)

To a solution of 23 (70 mg, 0.06 mmol) in THF (2 mL) was added HOAc (0.02 mL, 0.36 mmol) and TBAF (1 mmol/ml in THF, 0.18 mL, 0.18 mmol) at 0 °C. Then the reaction mixture was warmed to room temperature and stirred overnight. Ethly acetate (20 mL) was added and the solution was washed with water, saturated NaHCO_3 and brine successively, and then dried over Na_2SO_4 . Filtration and concentration under reduced pressure to afford the crude product which was further purified by silica gel chromatography (eluent system: PE : EA = 4 : 1) to afford **26** (32 mg, 57%) as a white solide: $[\alpha]^{28}\text{D} -9.6$ (c 1.1, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.01 (d, $J = 7.2$ Hz, 2 H), 7.99 (d, $J = 7.6$ Hz, 2 H), 7.90 (d, $J = 8.4$ Hz, 2 H), 7.81 (d, $J = 8.4$ Hz, 2 H), 7.55-7.28 (m, 9 H), 7.22 (d, $J = 8.4$ Hz, 2 H), 7.08 (d, $J = 2.1$ Hz, 1 H), 7.03 (d, $J = 2.1$ Hz, 1 H), 6.05 (t, $J = 9.2$ Hz, 1 H), 5.95 (dd, $J = 7.2, 9.6$ Hz, 1 H), 5.62 (d, $J = 7.6$ Hz, 1 H), 5.62 (dd, $J = 7.6, 9.6$ Hz, 1 H), 3.98-3.95 (m, 1 H), 3.88-3.80 (m, 2 H), 2.60 (t, $J = 7.6$ Hz, 4 H), 2.48 (t, $J = 7.6$ Hz, 2 H), 1.79-1.72 (m, 4 H), 1.69-1.62 (m, 2 H), 1.40-1.29 (m, 12 H), 0.95-0.89 (m, 9 H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.7, 171.2, 170.5, 169.6, 165.8, 165.7, 165.2, 157.2, 156.3, 154.1, 153.4, 152.8, 134.1, 133.5, 133.2, 132.7, 129.9 (2 C), 129.8, 129.7, 129.4, 128.9, 128.7, 128.4, 128.2, 128.0, 127.0, 121.8, 76.0, 72.5, 71.7, 69.8, 61.7, 34.3 (2 C), 33.7, 31.2, 31.1, 24.4, 24.3, 24.2, 22.2, 13.9, 13.8. HRMS (MALDI) calcd for $\text{C}_{60}\text{H}_{63}\text{O}_{17} [\text{M}+\text{H}]^+$ 1055.4040, found

1055.4060.

**3,7,4'-Tri-O-hexanoyl-5-O-[2'',3'',4''-tri-O-benzoyl-6''-O-(2'',3'',4''-tri-O-benzo
yl- α -L-rhamnopyranonyl)- β -D-glucopyranosyl]-kaempferol (27)**

Similar procedure as that used for the synthesis of **10** was adopted to give **27** (36 mg, 82%) as a white solid: $[\alpha]^{28}_D$ 33.0 (*c* 0.57, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 8.03 (dd, *J* = 7.2, 7.6 Hz, 6 H), 7.95 (t, *J* = 8.0 Hz, 4 H), 7.78 (d, *J* = 8.8 Hz, 4 H), 7.59 (t, *J* = 7.2 Hz, 1 H), 7.52-7.30 (m, 15 H), 7.23-7.17 (m, 4 H), 7.08 (d, *J* = 1.8 Hz, 1 H), 7.05 (s, 1 H), 6.05 (t, *J* = 9.2 Hz, 1 H), 5.94 (dd, *J* = 7.2, 9.2 Hz, 1 H), 5.72-5.54 (m, 5 H), 4.98 (s, 1 H), 4.30 (t, *J* = 6.8 Hz, 1 H), 4.10-3.90 (m, 3 H), 2.60 (t, *J* = 7.6 Hz, 2 H), 2.46-2.39 (m, 4 H), 1.81-1.73 (m, 2 H), 1.67-1.53 (m, 4 H), 1.43-1.18 (m, 15 H), 0.96-0.88 (m, 6 H), 0.82 (t, *J* = 7.2 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 171.8, 171.1, 170.4, 169.5, 165.7, 165.3, 165.1 (2 C), 157.2, 156.4, 154.3, 153.3, 152.7, 134.1, 133.5, 133.3, 133.2, 133.1, 132.9, 132.7, 130.0, 129.9, 129.8, 129.7, 129.6, 129.5, 129.3, 128.9, 128.8, 128.5 (2 C), 128.4, 128.3, 128.2, 128.0, 127.2, 121.8, 113.8, 109.8, 106.8, 100.2, 98.1, 74.4, 72.5, 71.7 (2 C), 70.4, 69.9, 69.7, 67.2, 66.9, 34.4, 34.1, 33.7, 31.2, 31.0, 29.7, 24.5, 24.2 (2 C), 22.3, 22.2, 17.5, 13.9 (2 C), 13.8. HRMS (MALDI) calcd for C₈₇H₈₅O₂₄ [M+H]⁺ 1513.5419, found 1513.5425.

**3,7,4'-Tri-O-benzyl-5-O-(2'',3'',4''-tri-O-benzoyl- β -D-glucopyranosyl)-kaempfero
l (29)**

Similar procedure as that used for the synthesis of **26** was adopted to give **29** (130 mg, 99%) as a white solid: $[\alpha]^{28}_D$ 4.7 (*c* 1.2, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 8.06 (t, *J* = 7.6 Hz, 4 H), 7.96 (dd, *J* = 6.4, 8.0 Hz, 4 H), 7.60 (t, *J* = 7.2 Hz, 1 H), 7.46-7.24 (m, 23 H), 7.01 (d, *J* = 8.4 Hz, 2 H), 6.87 (s, 1 H), 6.68 (d, *J* = 10.4 Hz, 1 H), 6.09-6.02 (m, 2 H), 5.76-5.69 (m, 2 H), 5.13 (s, 4 H), 4.74 (s, 2 H), 4.03 (s, 1 H), 3.94 (s, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 172.7, 165.9, 165.6, 165.0, 162.3, 160.0, 157.6, 157.4, 152.9, 139.2, 136.9, 136.4, 135.8, 133.3, 133.0, 132.6, 129.9, 129.8 (2 C), 129.0, 128.9, 128.8, 128.5, 128.3, 128.2, 128.1, 128.0, 127.9, 127.7, 127.6, 127.3, 123.2, 114.3, 110.3, 102.1, 100.5, 97.0, 76.7, 76.0, 73.3, 73.0, 71.6, 70.4, 69.8, 69.7, 61.5; HRMS (ESI) calcd for C₆₃H₅₀O₁₄Na [M+Na]⁺ 1053.3093, found 1053.3104.

3,7,4'-Tri-O-benzyl-5-O-[2'',3'',4''-tri-O-benzoyl-6''-O-(2'',3'',4''-tri-O-benzoyl

- α -L-rhamnopyranonyl]- β -D-glucopyranosyl]-kaempferol (30)

Similar procedure as that used for the synthesis of **10** was adopted to give **27** (106 mg, 67%) as a white solide: $[\alpha]^{28}_D$ 21.5 (*c* 1.2, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 8.1 (d, *J* = 7.2 Hz, 2 H), 8.03 (dd, *J* = 7.6, 8.4 Hz, 4 H), 7.94 (d, *J* = 7.6 Hz, 4 H), 7.87 (d, *J* = 8.8 Hz, 2 H), 7.87 (d, *J* = 7.2 Hz, 2 H), 7.57-7.18 (m, 33 H), 6.97 (d, *J* = 8.8 Hz, 2 H), 6.91 (d, *J* = 2.0 Hz, 1 H), 6.49 (d, *J* = 2.0 Hz, 1 H), 6.09 (t, *J* = 9.2 Hz, 1 H), 6.00 (dd, *J* = 7.2, 9.2 Hz, 1 H), 5.75-5.54 (m, 5 H), 5.11 (s, 2 H), 5.10 (AB, 2 H), 4.99 (s, 1 H), 4.80 (AB, 2 H), 4.31-4.25 (m, 1 H), 4.11-4.02 (m, 1 H), 4.02-3.91 (m, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 172.7, 165.7, 165.3, 165.1, 162.1, 160.1, 157.8, 156.4, 153.3, 139.2, 137.0, 136.4, 135.8, 133.4, 133.2 (2 C), 133.1, 132.8, 132.7, 130.1, 130.0, 129.9 (2 C), 129.8, 129.7, 129.6, 129.4, 129.2, 128.9, 128.8, 128.7, 128.6 (2 C), 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 127.4, 127.3, 123.4, 114.4, 111.1, 105.2, 100.2, 98.0, 97.7, 74.4, 73.3, 72.6, 71.8, 71.7, 70.4, 69.9, 69.8 (2 C), 66.9 (2 C); HRMS (ESI) calcd for C₉₀H₇₃O₂₁ [M+H]⁺ 1489.4639, found 1489.4647.

3,7,4'-Tri-O-acetyl-5-O-[2'',3'',4''-tri-O-acetyl-6''-O-(2'',3'',4''-tri-O-acetyl- α -L-rhamnopyranonyl]- β -D-glucopyranosyl]-kaempferol (28)

To a solution of **30** in MeOH (5 mL) and THF (5 mL) was added NaOMe (in MeOH solution). The reaction mixture was stirred at room temperature for 6 hours, then ¹H resin was added to quench the reaction. Filtration and concentration to get the crude deacylated intermediate which was not purified for the next hydrogenolysis step.

The above obtained intermediate was dissolved in ethyl acetate (2 mL) and ethanol (2 mL), to which 10% Pd/C was added. The reaction flask was evacuate and then refilled with H₂. After repeating this process three times, the mixture was stirred at room temperature for another 24 hours. Filtration and concentration yield the crude **28a** which was put directly to next acetylation step.

To a solution of **28a** in dry pyridine (1 mL) was added Ac₂O (1 mL) dropwise at 0 °C. Then the addition was completed, the temperature was raised to room temperature. The stirring was continued for another 36 hours, at which time TLC showed that the starting material disappeared and one new compound was formed. Ethyl acetate (30 mL) was added to dilute the reaction mixture, the solution was washed with 1 N HCl,

saturated NaHCO_3 , and brine successively and then dried over Na_2SO_4 . Filtration and concentration under reduced pressure to give the crude product which was further purified by silica gel chromatography (eluent system: PE : EA = 2 : 1) to afford **30** (20 mg, 99%) as a white solid: $[\alpha]^{28}_{\text{D}} -129.0$ (*c* 0.25, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.86 (d, *J* = 8.8 Hz, 2 H), 7.25 (d, *J* = 8.8 Hz, 2 H), 7.15 (d, *J* = 2.0 Hz, 1 H), 6.92 (d, *J* = 2.0 Hz, 1 H), 5.43 (dd, *J* = 7.8, 9.4 Hz, 1 H), 5.32 (dd, *J* = 9.3, 11.0 Hz, 1 H), 5.24-5.21 (m, 2 H), 5.15 (d, *J* = 7.7 Hz, 1 H), 5.13 (t, *J* = 10.0 Hz, 1 H), 5.06 (t, *J* = 9.8 Hz, 1 H), 4.74 (s, 1 H), 3.93-3.89 (m, 1 H), 3.85 (dd, *J* = 5.6, 9.7 Hz, 1 H), 3.80 (d, *J* = 11.4 Hz, 1 H), 3.71 (dd, *J* = 6.0, 11.6 Hz, 1 H), 2.34 (s, 3 H), 2.33 (s, 3 H), 2.31 (s, 3 H), 2.10 (s, 3 H), 2.07 (s, 3 H), 2.06 (s, 3 H), 2.05 (s, 3 H), 2.04 (s, 3 H), 1.97 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.3, 170.0, 169.8 (2 C), 169.5, 169.4, 168.9, 168.2, 167.9, 157.4, 157.2, 154.4, 153.3, 152.7, 134.3, 129.5, 127.1, 122.0, 113.3, 107.8, 106.2, 100.5, 98.0, 77.2, 73.5, 72.4, 70.8, 70.5, 69.3, 69.1, 69.0, 66.6, 21.1, 20.8, 20.7, 20.6 (2 C), 17.3; HRMS (ESI) calcd for $\text{C}_{45}\text{H}_{49}\text{O}_{24} [\text{M}+\text{H}]^+$ 973.2613, found 973.2626.

Key correlations in compound **28**:

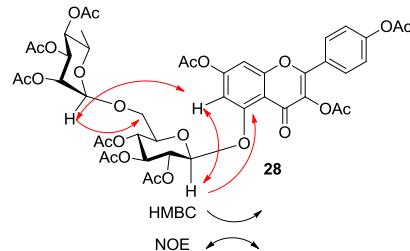


Figure 1. Key HMBC and NOE correlations in **28**

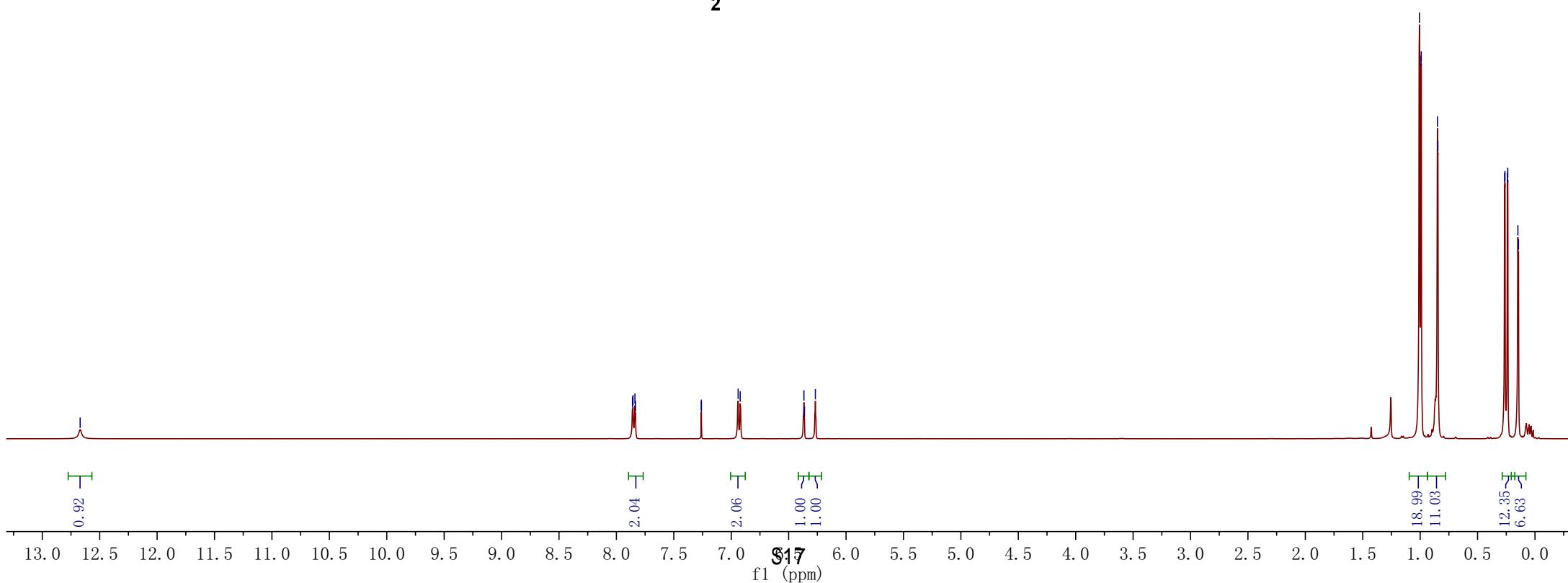
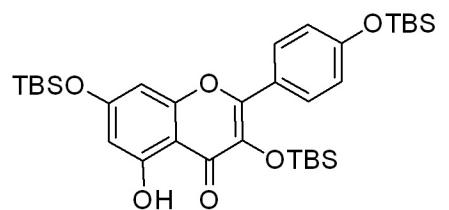
— 12.6701

Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	400.13
Nucleus	¹ H

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7.8555
7.8386
7.8338
7.2603
7.2600
6.9398
6.9218
6.3669
6.3619
6.2673

1.0060
0.9928
0.9906
0.8194
0.8457
0.2642
0.2615
0.2396
0.2370
0.1490
0.1436

∫ ∫ ∫



—178.1089

—161.7759

—157.6340

—156.4440

—153.1346

—135.6366

—130.4737

—124.2763

—119.9756

—106.0847

—102.9773

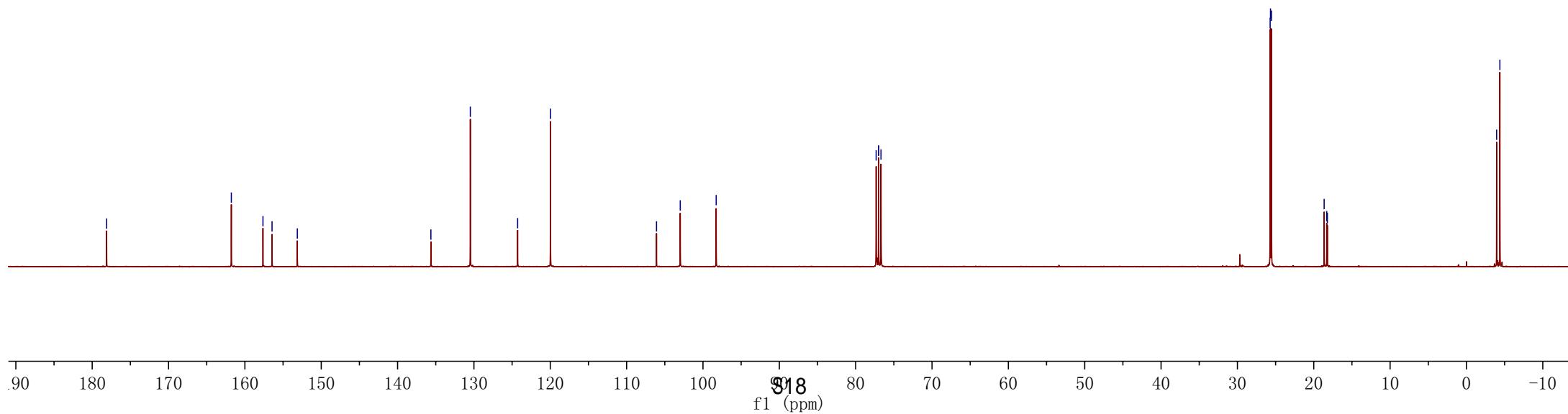
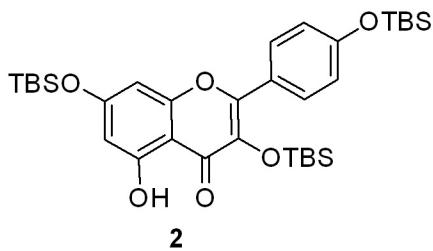
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77.3174
77.0000
76.9998
76.6820

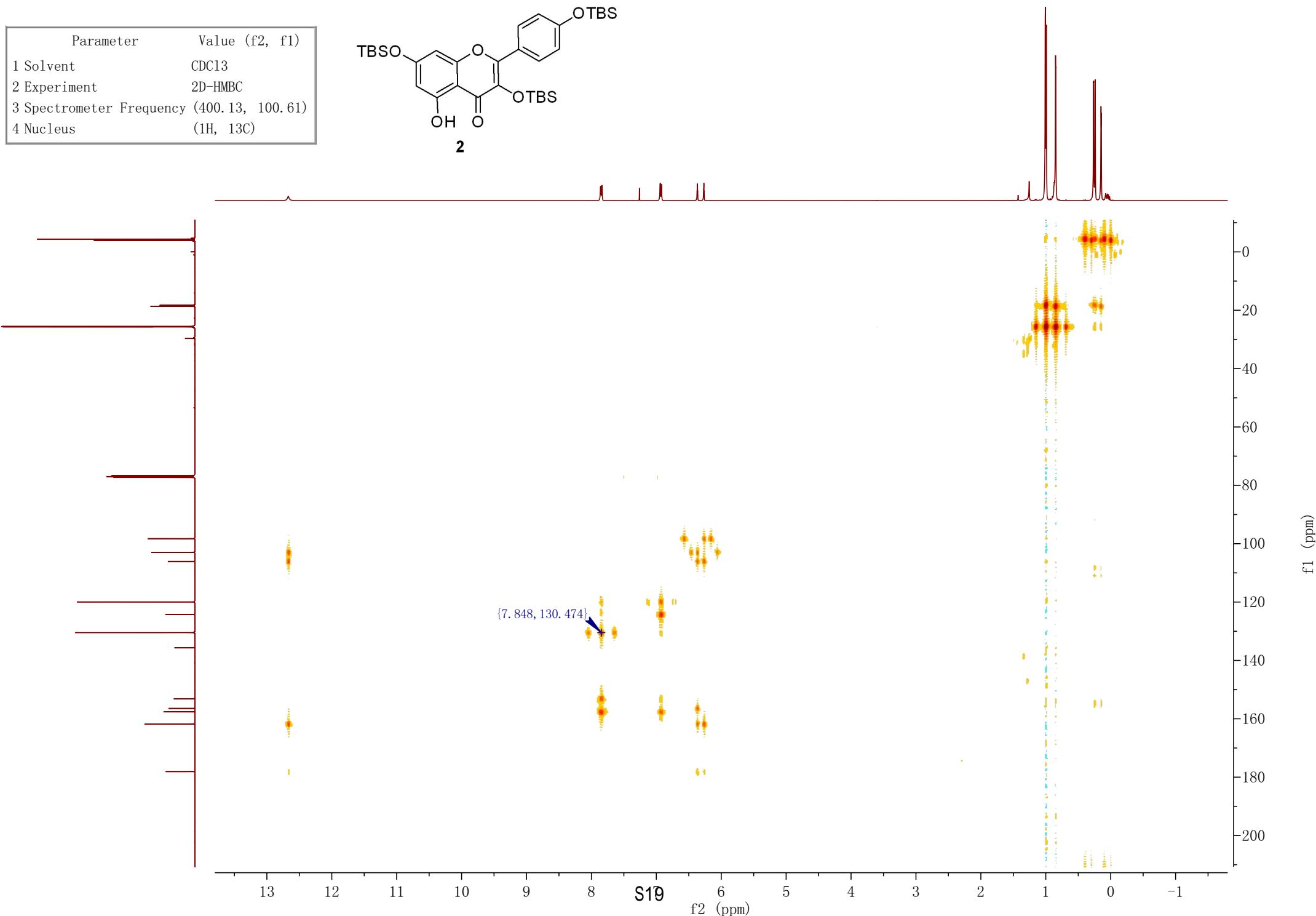
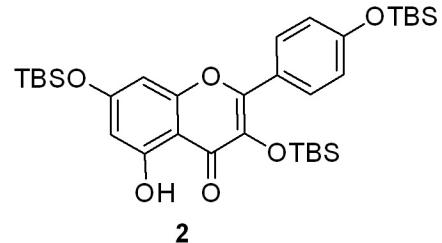
25.7130
25.6673
25.5328
18.6393
18.3048
18.2167

-3.9543
-4.3787

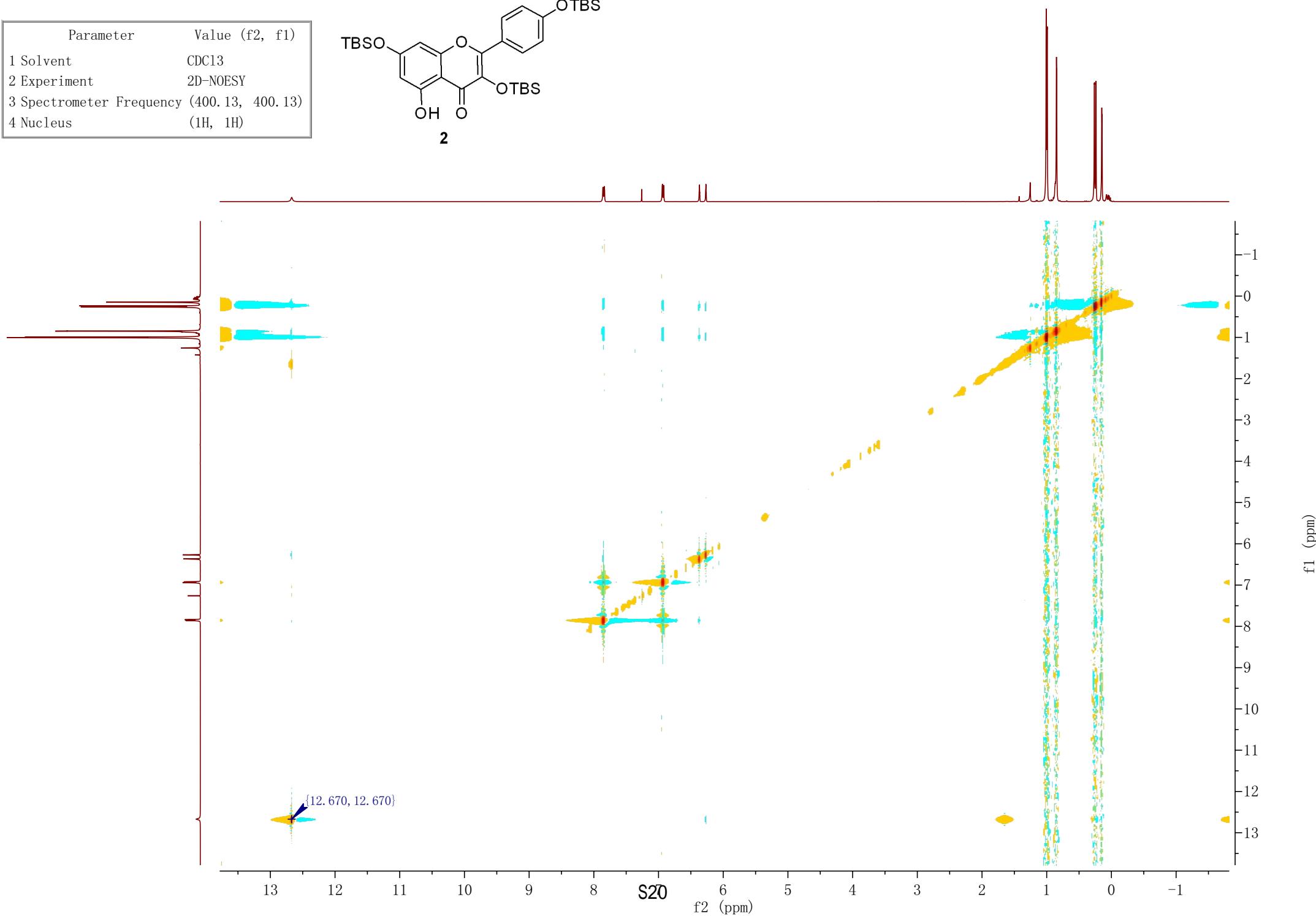
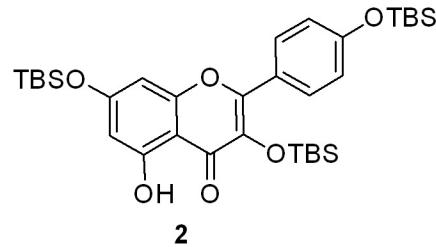
Parameter	Value
Solvent	CDCl ₃
Experiment	1D
Spectrometer Frequency	100.61
Nucleus	¹³ C



Parameter	Value (f2, f1)
1 Solvent	CDCl ₃
2 Experiment	2D-HMBC
3 Spectrometer Frequency	(400.13, 100.61)
4 Nucleus	(¹ H, ¹³ C)



Parameter	Value (f2, f1)
1 Solvent	CDC13
2 Experiment	2D-NOESY
3 Spectrometer Frequency	(400.13, 400.13)
4 Nucleus	(1H, 1H)

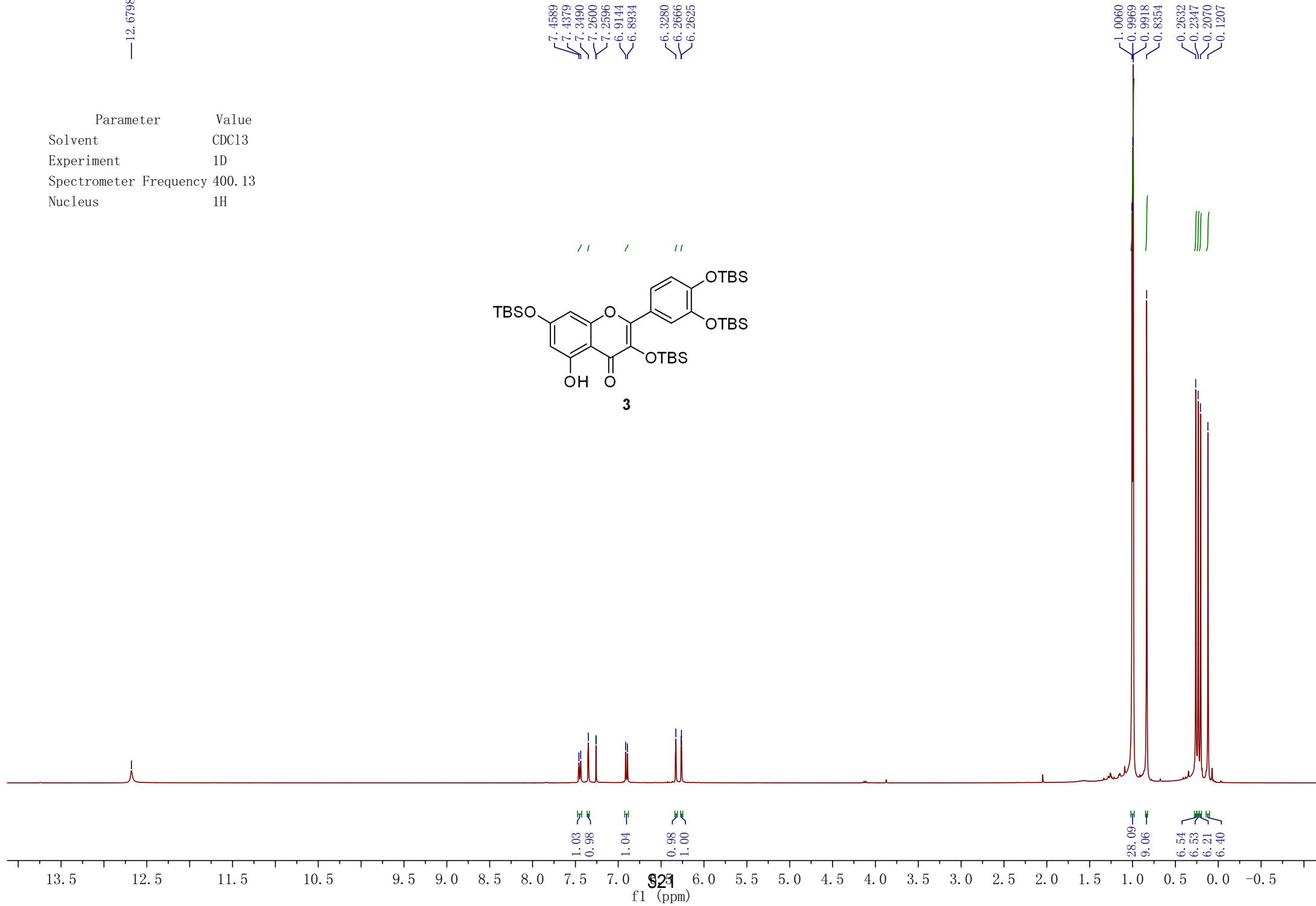
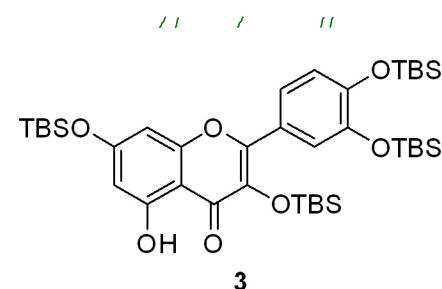


— 12.6798

Parameter	Value
Solvent	CDCl ₃
Experiment	1D
Spectrometer Frequency	400.13
Nucleus	¹ H

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7.3490
7.2600
7.2596
6.9144
6.8934
6.3280
6.2666
6.2625

1.0060
0.9969
0.9918
0.8354
0.2632
0.2347
0.2070
0.1207



— 178.2293

— 161.8045
— 161.7582
— 156.4417
— 153.2640
— 149.2328
— 146.7606

— 135.6150

— 124.4348
— 123.1953
— 121.7663
— 120.8029

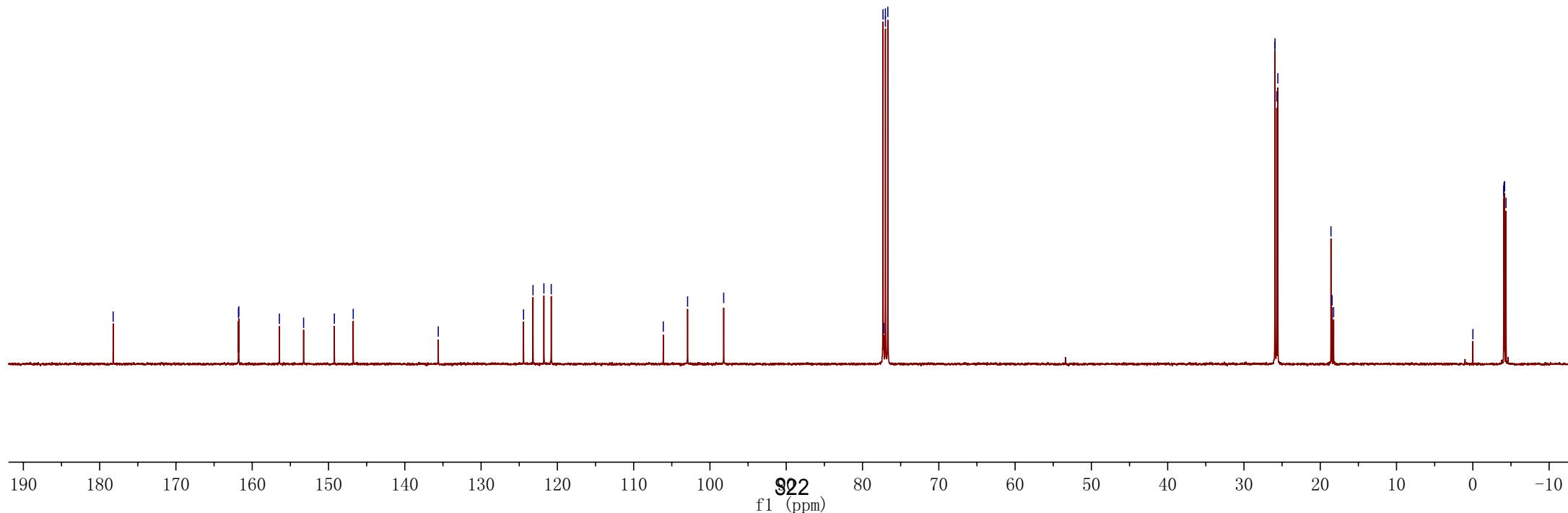
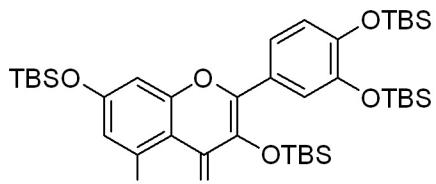
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— 102.9309
— 98.1965

— 77.3176
— 77.2034
— 77.0000
— 76.9999
— 76.6827

— 25.9431
— 25.9223
— 25.6942
— 25.5563
— 18.5937
— 18.4488
— 18.2449

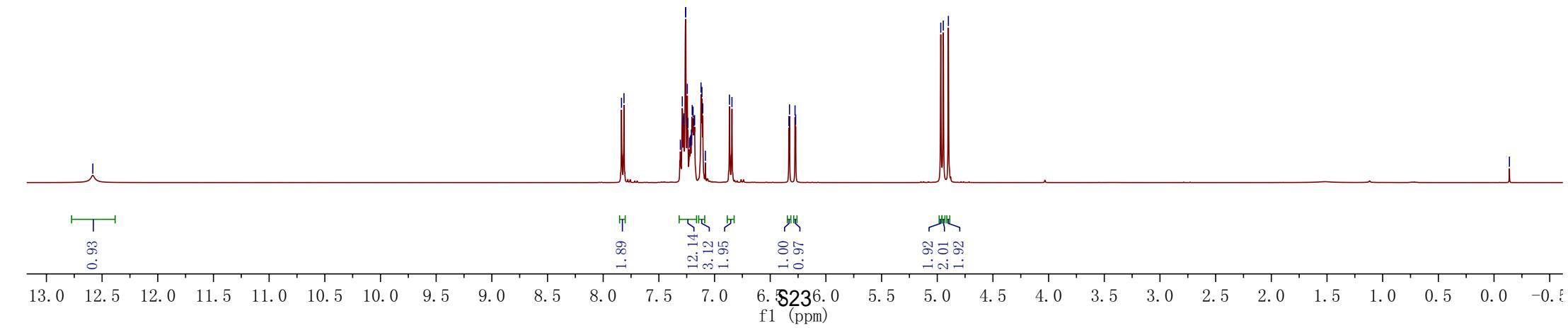
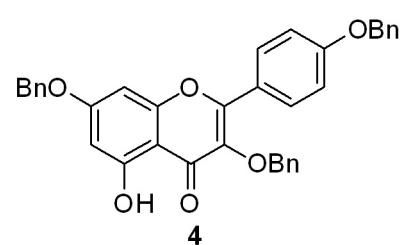
— 0.0130
— 4.0464
— 4.0959
— 4.1695
— 4.3525

Parameter	Value
Solvent	CDCl ₃
Experiment	1D
Spectrometer Frequency	100.61
Nucleus	¹³ C



—12. 5834

Parameter	Value
Solvent	CDCl ₃
Experiment	1D
Spectrometer	Frequency 400.13
Nucleus	1H



—178.7165

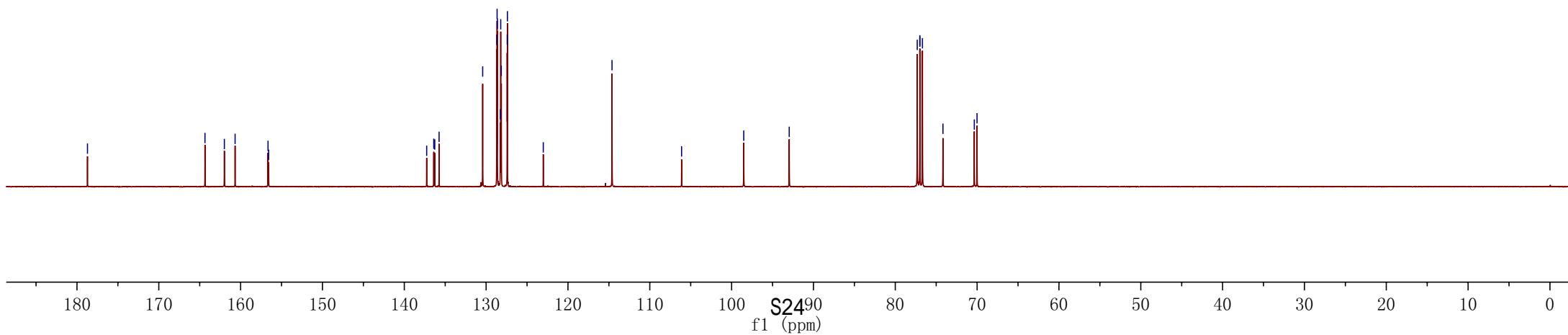
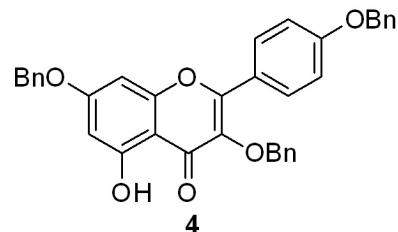
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—161.9884
—160.6761
—156.6516
—156.5730

137.2647
136.3981
136.2768
135.7474
128.6602
128.6241
128.2158
127.3986

—114.6156
—106.1129
—98.5190
—92.9603

77.3170
77.0000
76.9997
76.6815
74.1755
70.3446
70.0101

Parameter	Value
Solvent	CDCl ₃
Experiment	1D
Spectrometer Frequency	100.61
Nucleus	¹³ C



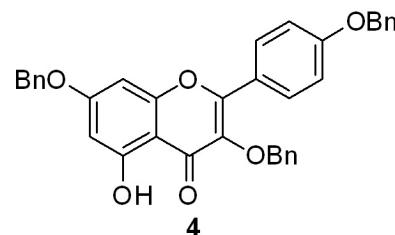
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128.1516
127.4318
127.4051

—114.6087

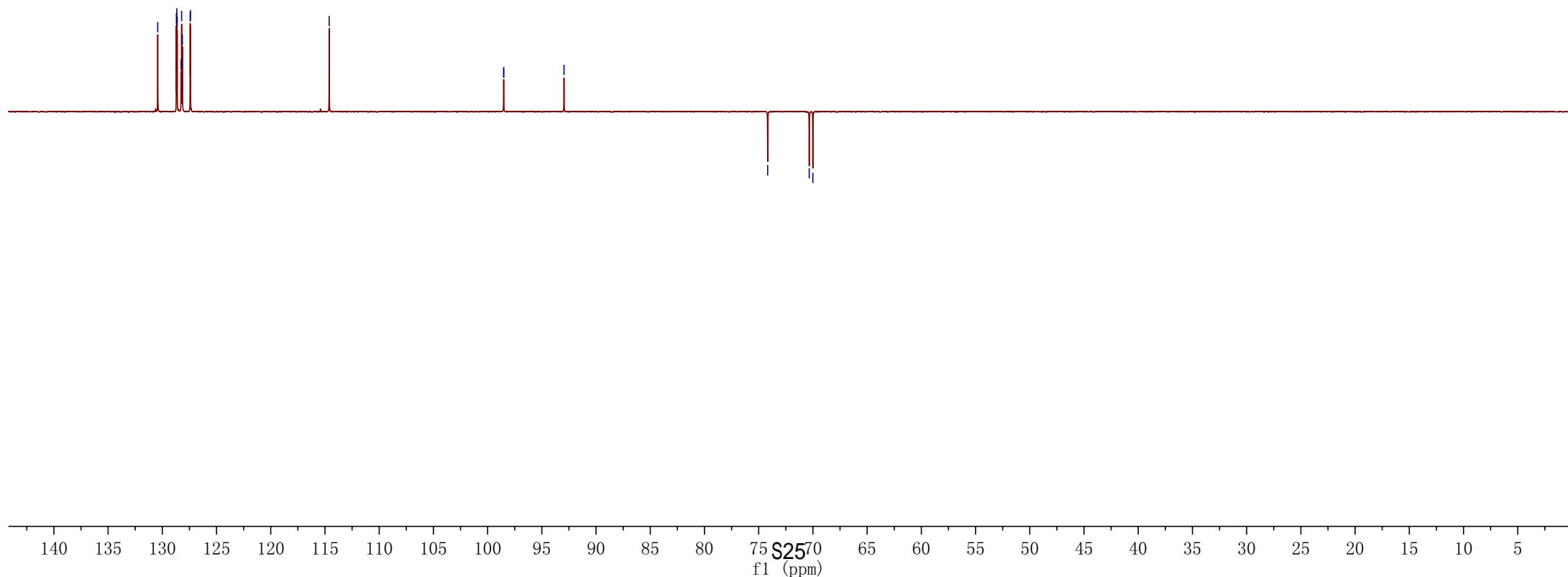
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98.5186

—92.9542

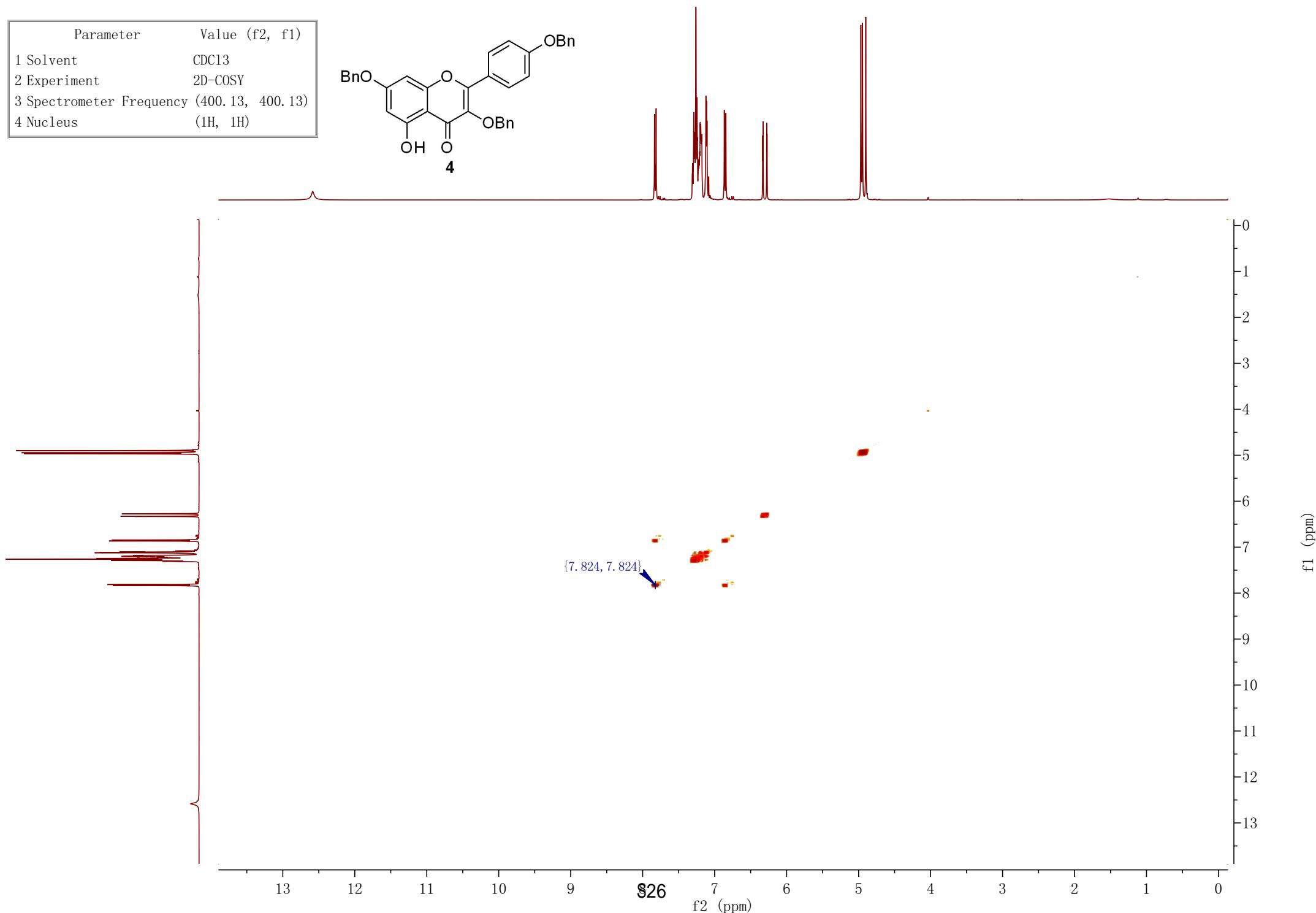
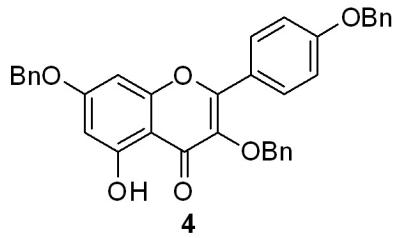
—74.1730
—70.3404
—70.0043



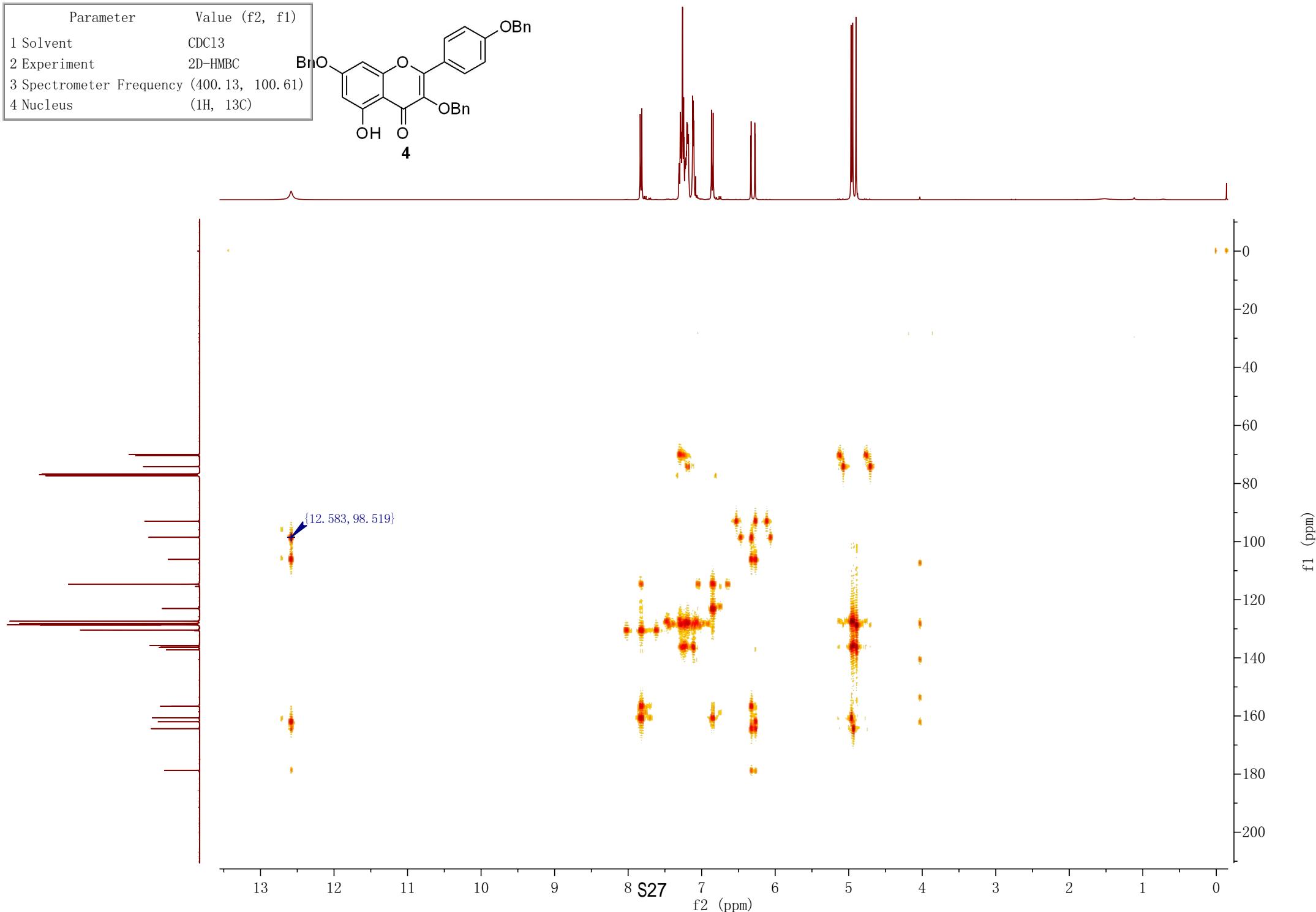
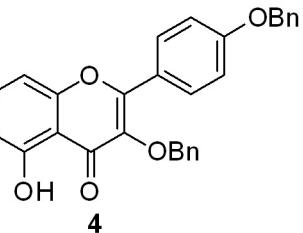
Parameter	Value
Solvent	CDCl ₃
Experiment	1D-DEPT-135
Spectrometer Frequency	100.61
Nucleus	¹³ C



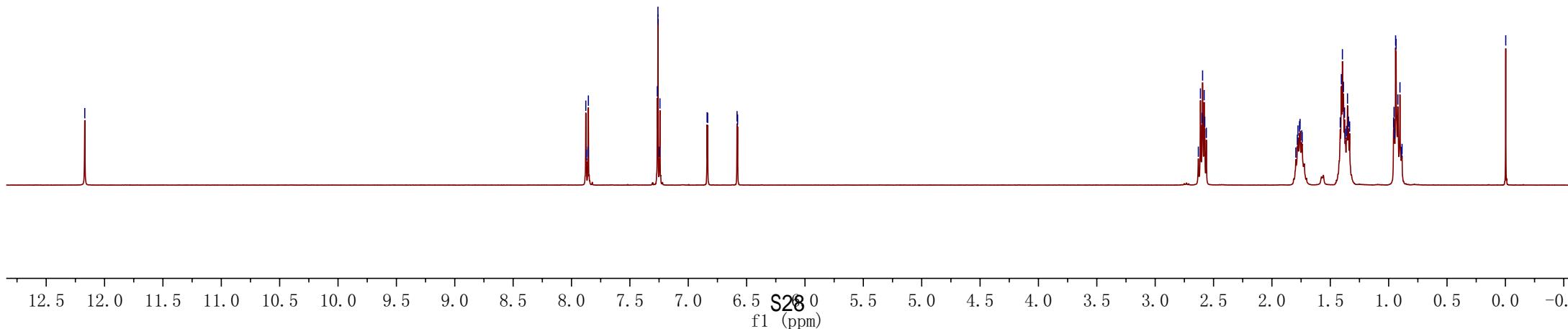
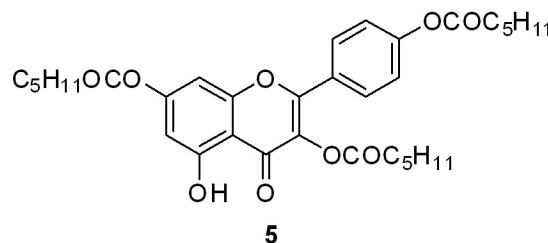
Parameter	Value (f2, f1)
1 Solvent	CDCl ₃
2 Experiment	2D-COSY
3 Spectrometer Frequency	(400.13, 400.13)
4 Nucleus	(¹ H, ¹ H)



Parameter	Value (f2, f1)
1 Solvent	CDCl ₃
2 Experiment	2D-HMBC
3 Spectrometer Frequency	(400.13, 100.61)
4 Nucleus	(¹ H, ¹³ C)



Parameter	Value
Solvent	CDCl ₃
Experiment	1D
Spectrometer Frequency	400.13
Nucleus	¹ H



— 176.2979
 ↘ 171.6853
 ↙ 171.1172
 ↙ 170.6086

— 161.6678
 ↗ 156.4841
 ↗ 156.3663
 ↗ 155.9748
 ↗ 153.2083

Parameter	Value
Solvent	CDCl ₃
Experiment	1D
Spectrometer Frequency	100.61
Nucleus	¹³ C

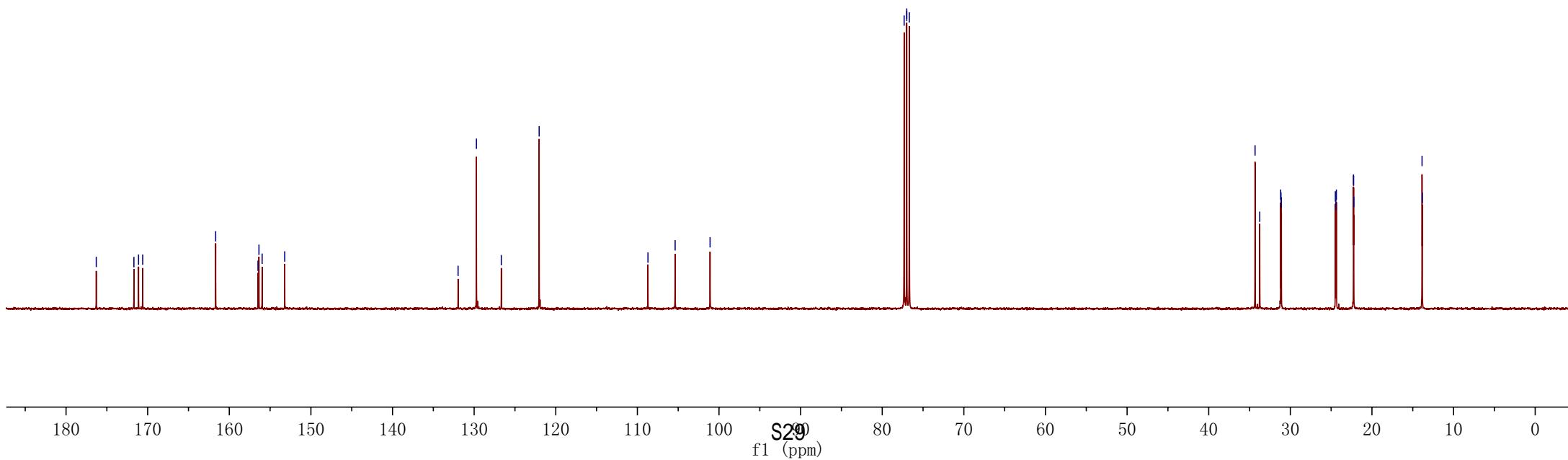
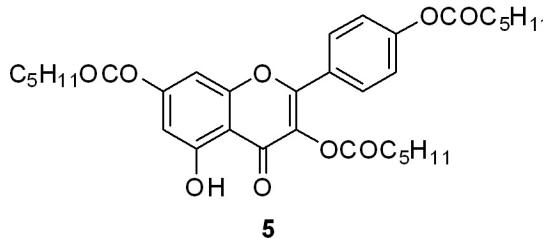
↗ 131.9675
 ↗ 129.7215
 ↗ 126.6709

— 122.0326

— 108.7036
 — 105.3739
 — 101.0953

↗ 77.3167
 ↗ 77.0000
 ↗ 76.9995
 ↗ 76.6813

↗ 34.3225
 ↗ 33.7486
 ↗ 31.1887
 ↗ 31.1449
 ↗ 31.0974
 ↗ 24.4826
 ↗ 24.4188
 ↗ 24.3587
 ↗ 22.2650
 ↗ 22.2508
 ↗ 22.2250
 ↗ 13.8625
 ↗ 13.8298



Parameter Value
Solvent CDCl₃
Experiment 1D-DEPT-135
Spectrometer Frequency 100.61
Nucleus ¹³C

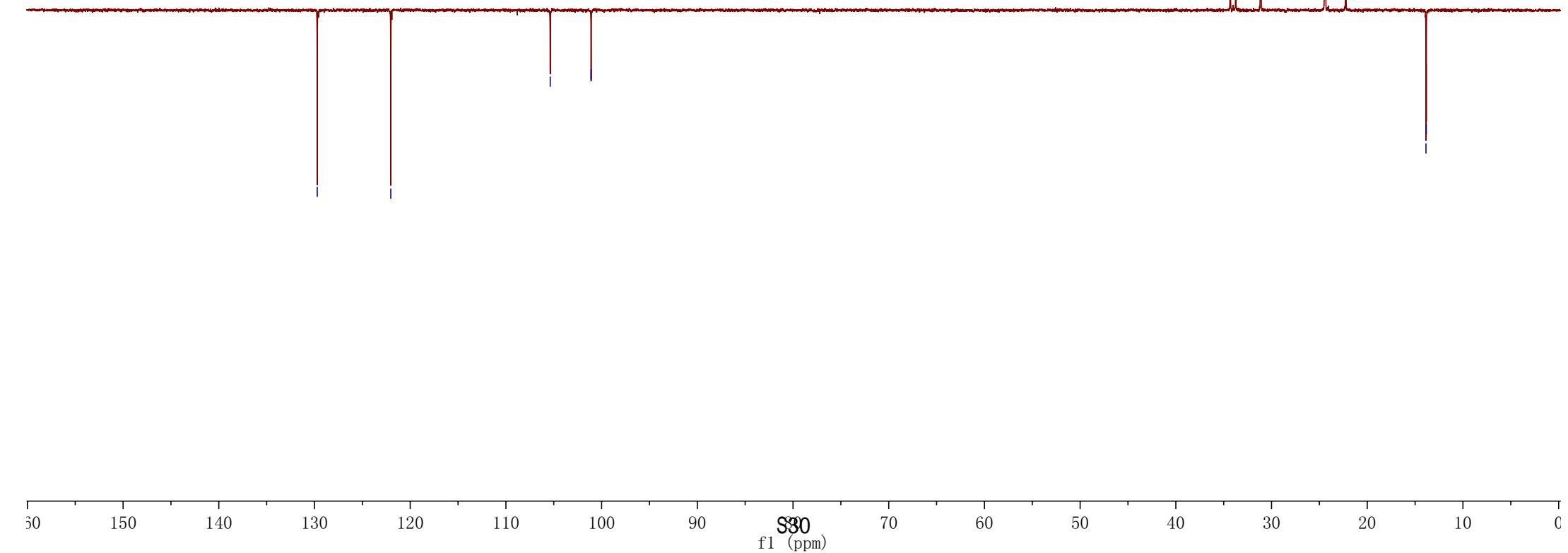
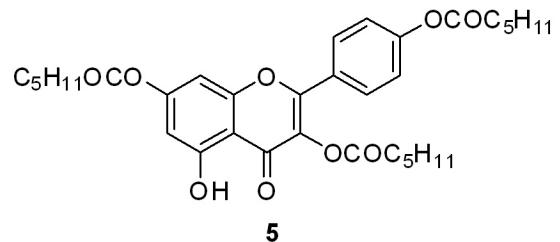
— 122.030

— 105.369

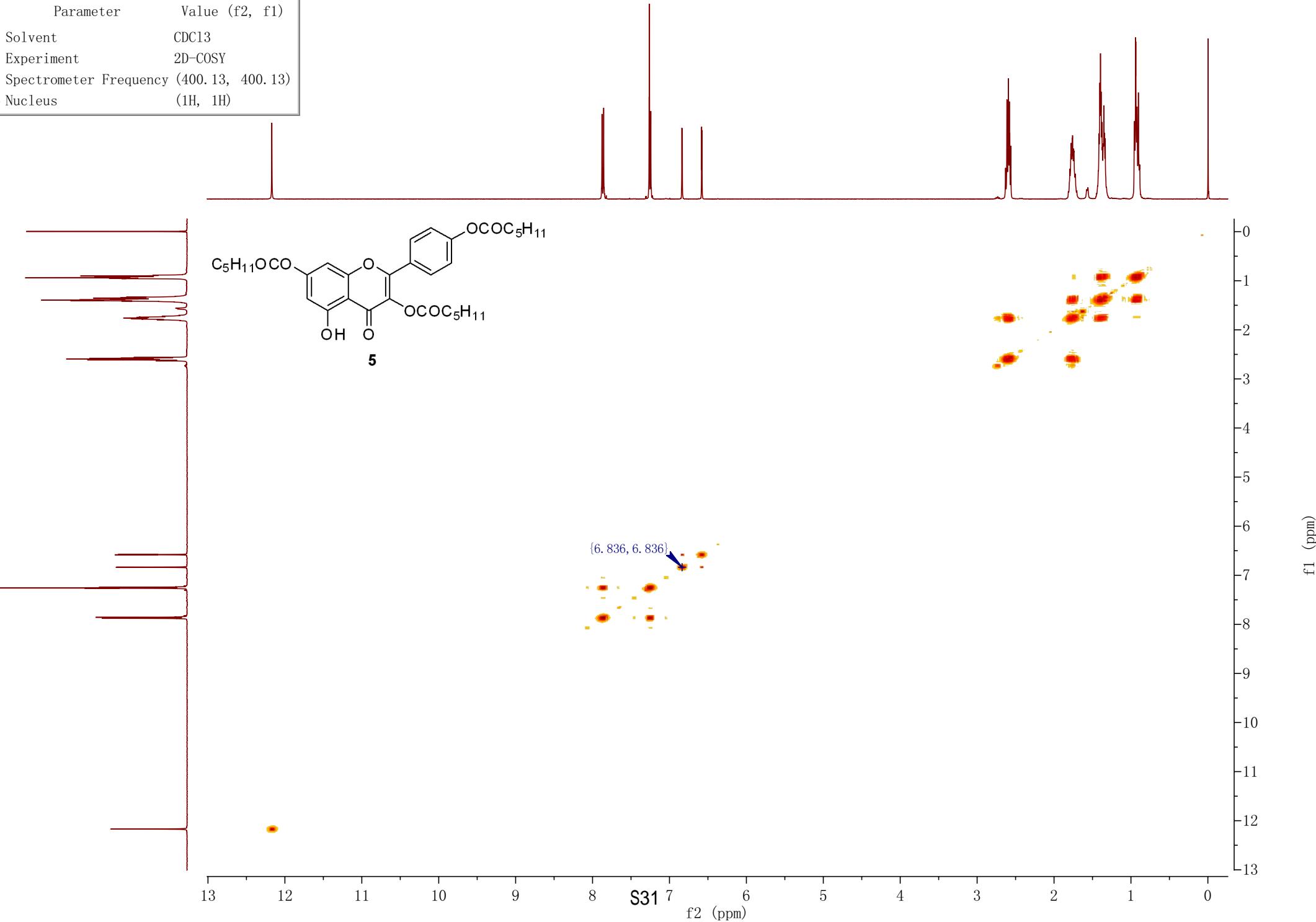
— 101.096

34.312
33.739
31.179
31.135
31.089
24.475
24.411
24.350
22.263
22.245
22.221

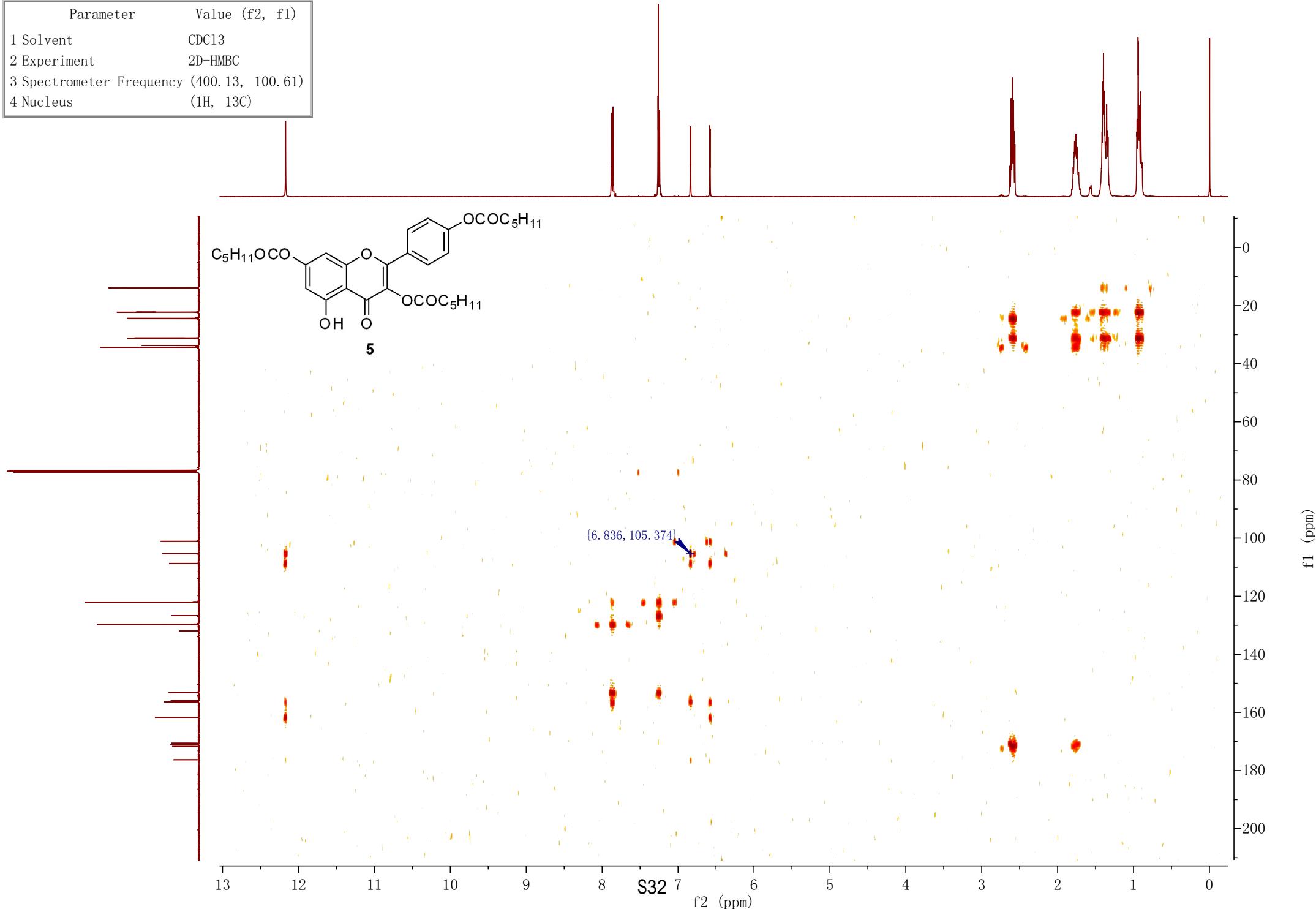
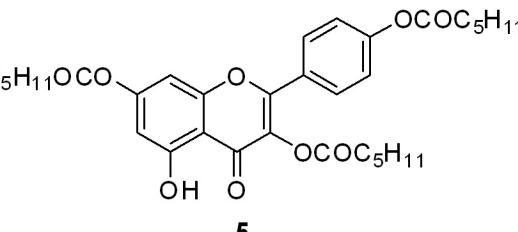
13.862
13.829



Parameter	Value (f2, f1)
1 Solvent	CDC13
2 Experiment	2D-COSY
3 Spectrometer Frequency	(400.13, 400.13)
4 Nucleus	(1H, 1H)

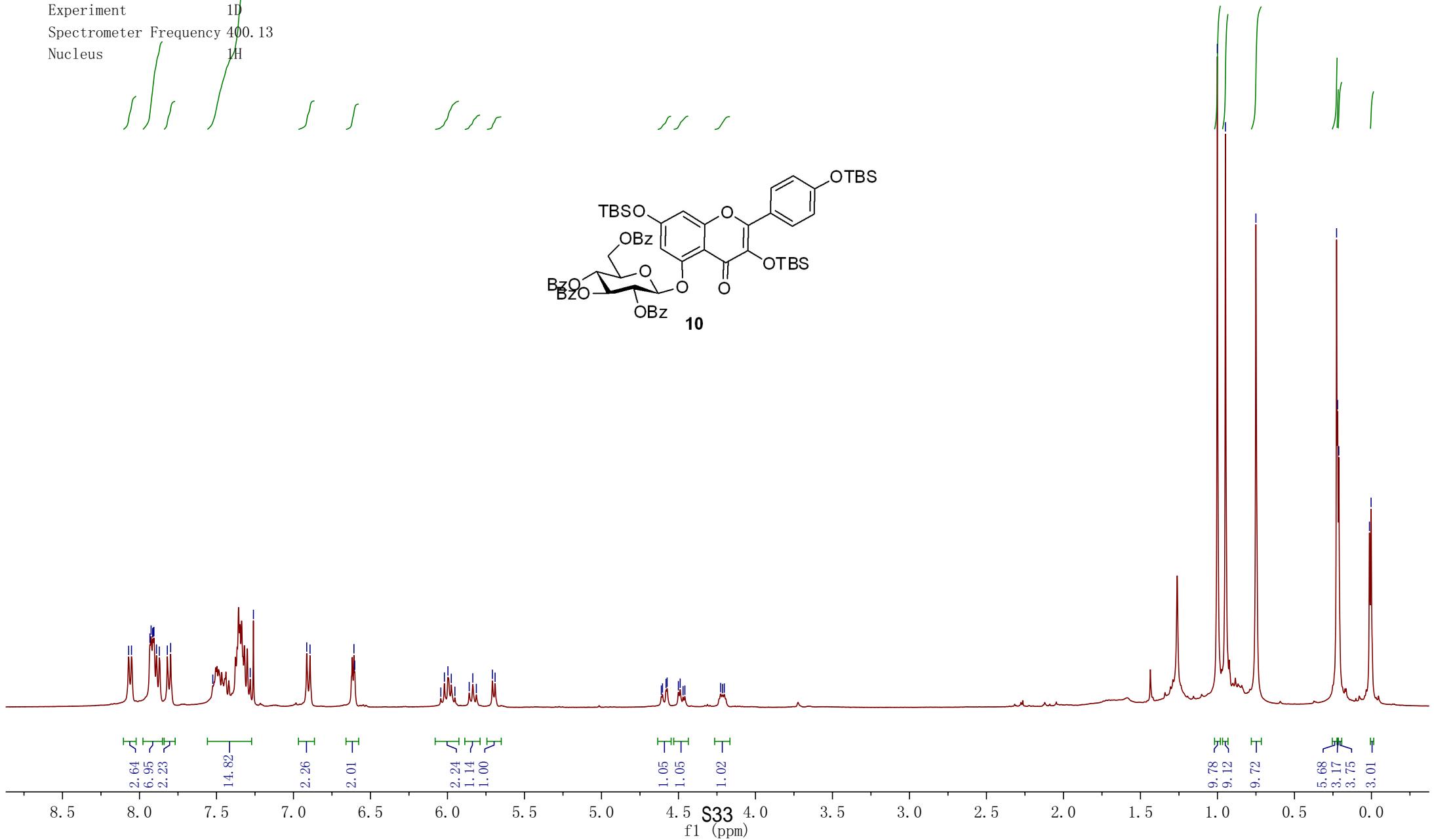
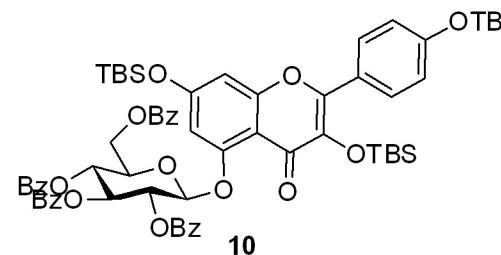


Parameter	Value (f2, f1)
1 Solvent	CDCl ₃
2 Experiment	2D-HMBC
3 Spectrometer Frequency	(400.13, 100.61)
4 Nucleus	(¹ H, ¹³ C)





Parameter	Value
Solvent	CDCl ₃
Experiment	1D
Spectrometer Frequency	400.13
Nucleus	¹ H



—172.5182

166.0122
165.8121
165.2161
165.1202
159.3297
157.5692
157.0806
155.8864

—149.4758

—137.6914
132.9745
130.1471
129.8314
129.8054
129.6741
128.3526
128.2669
119.8695

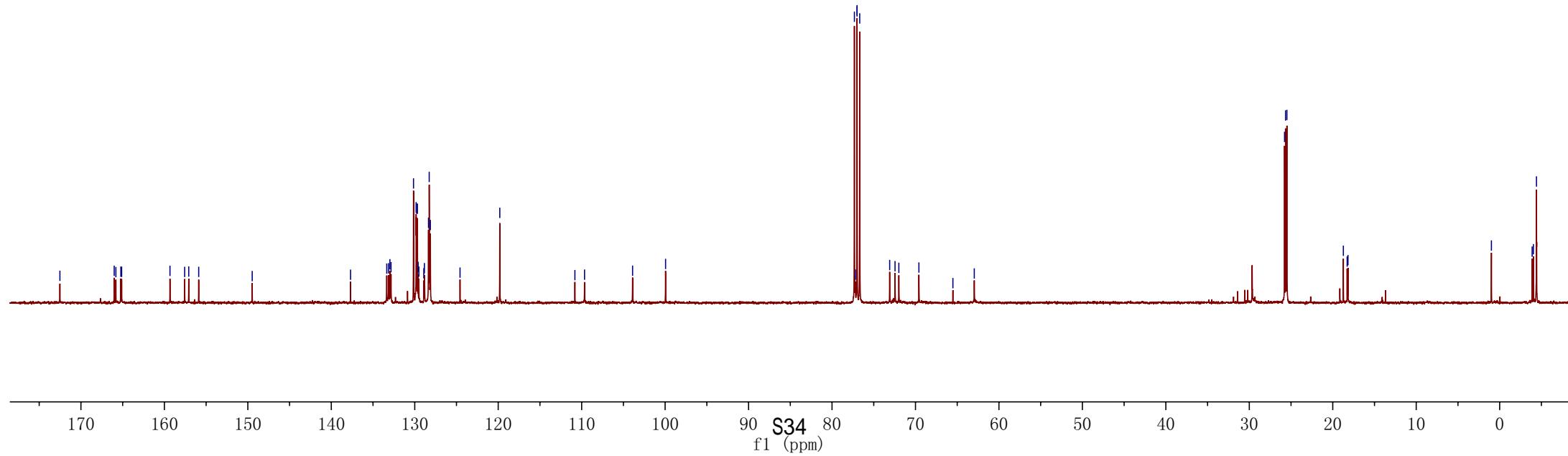
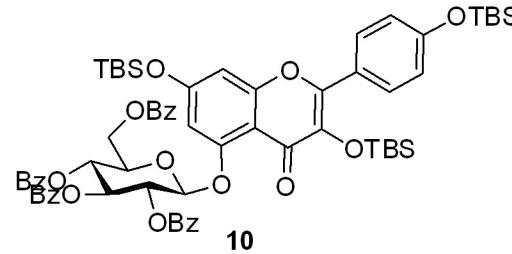
—110.8096
—109.6529
—103.8974
—99.9438

77.3186
77.2031
77.0005
77.0000
76.6831
73.0916
72.4497
71.9934
69.5894
65.5167
—62.9548

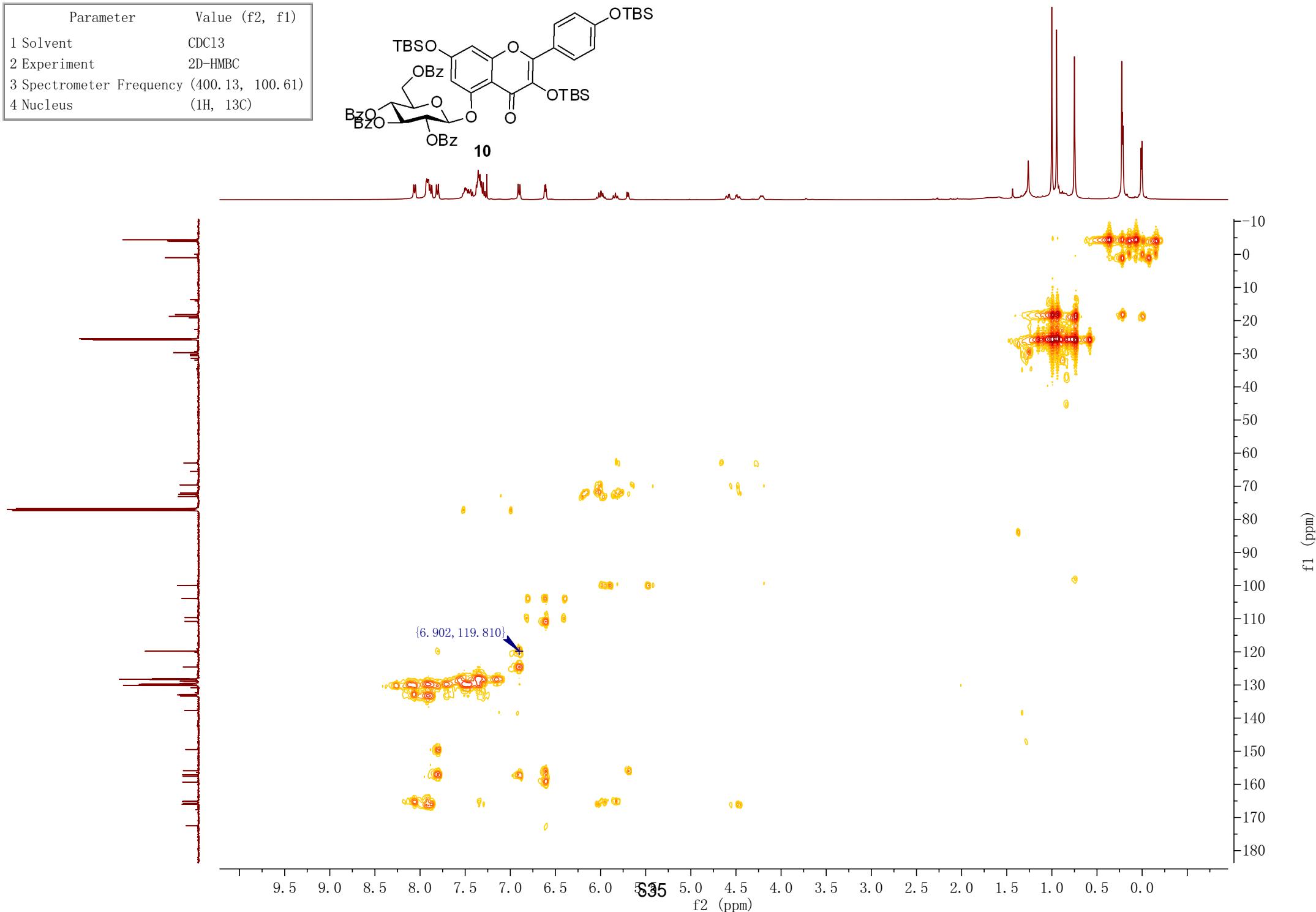
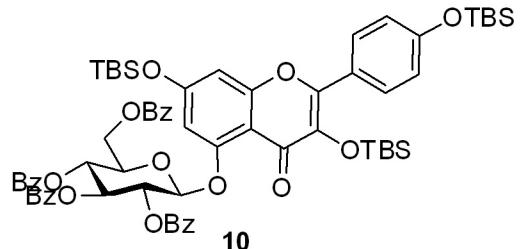
25.7767
25.6592
25.4987
18.7295
18.2750
18.1753

—0.9890
—3.8894
—4.0439
—4.4099

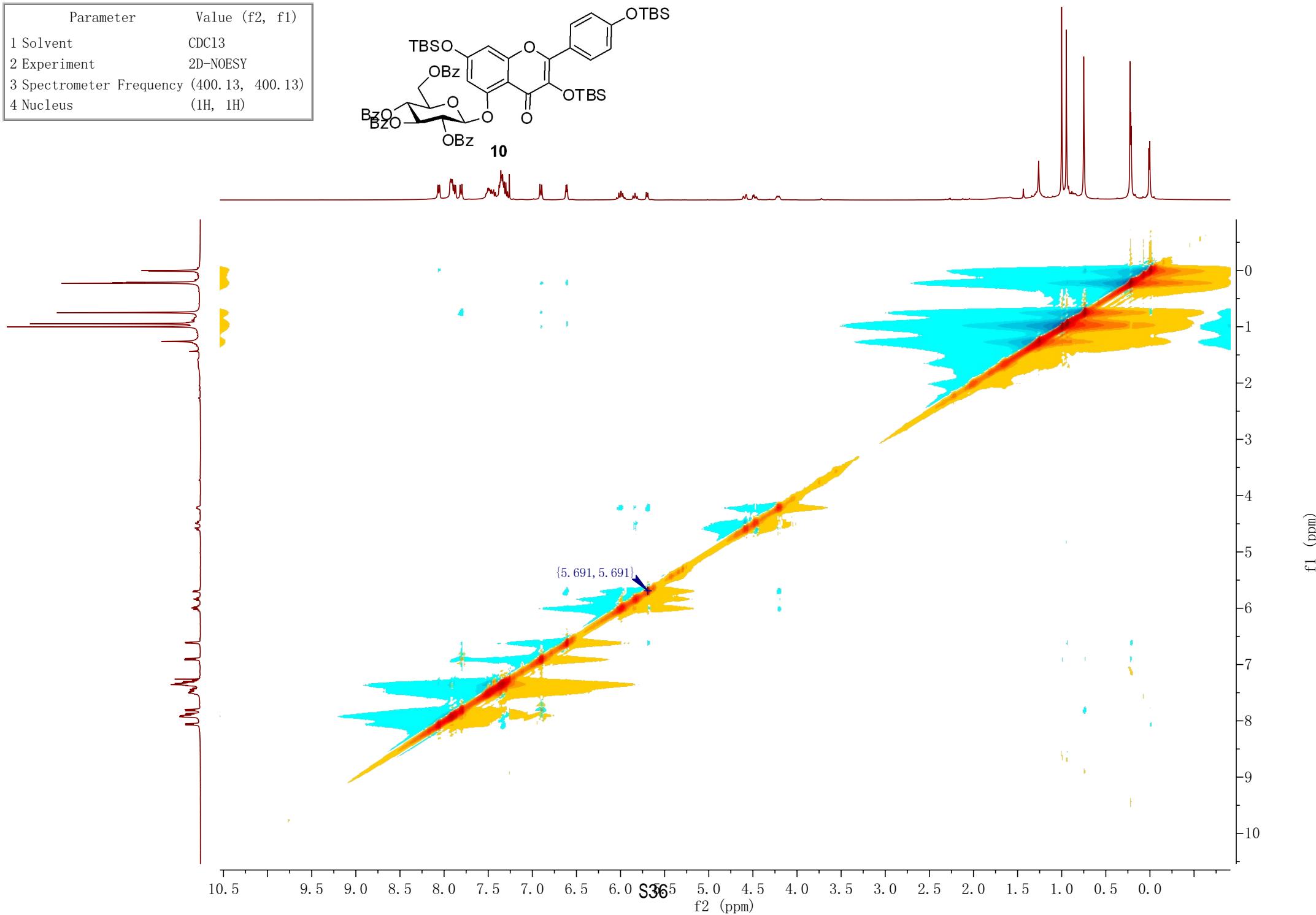
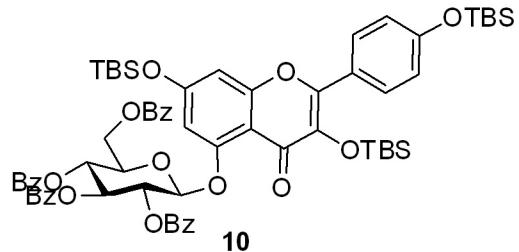
Parameter	Value
Solvent	CDCl ₃
Experiment	1D
Spectrometer Frequency	100.61
Nucleus	¹³ C



Parameter	Value (f2, f1)
1 Solvent	CDCl ₃
2 Experiment	2D-HMBC
3 Spectrometer Frequency (400.13, 100.61)	(¹ H, ¹³ C)
4 Nucleus	



Parameter	Value (f2, f1)
1 Solvent	CDCl ₃
2 Experiment	2D-NOESY
3 Spectrometer Frequency	(400.13, 400.13)
4 Nucleus	(¹ H, ¹ H)



8.0814
 8.0634
 8.0604
 7.9143
 7.9050
 7.8964
 7.8831
 7.8871
 7.8840
 7.8364
 7.8146
 7.6195
 7.6028
 7.1453
 7.1264
 6.9237
 6.9019
 6.8936
 6.6639
 6.6444
 6.6387
 5.6698
 5.6125
 5.5982
 5.5973
 5.9490
 5.9256
 5.9020
 5.8781
 5.8552
 5.6877
 5.6698

3.9310
 3.9239
 3.9164
 3.9003
 3.8932
 3.8276
 3.8207

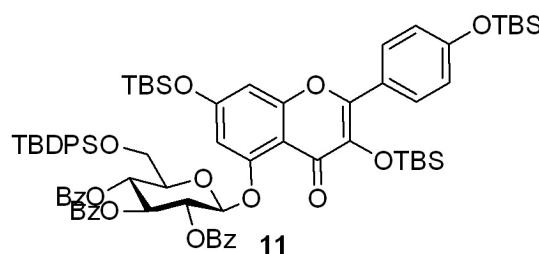
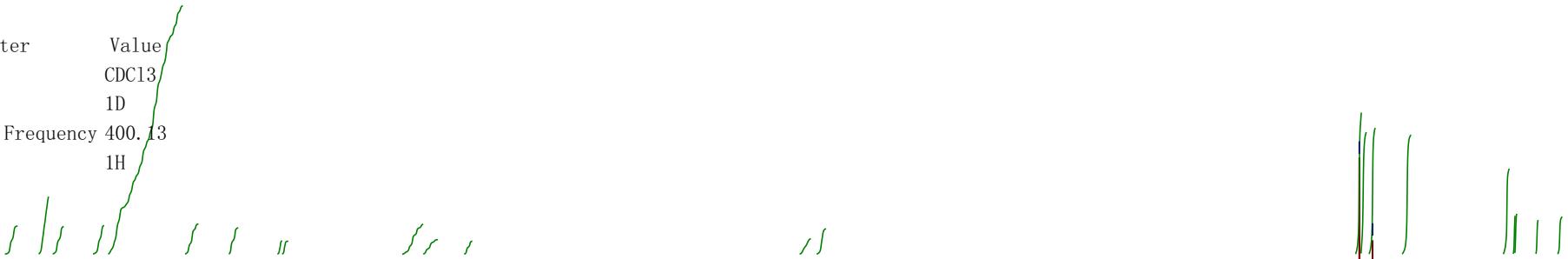
1.0060
 0.9851
 0.9358
 0.7542

0.2315
 0.1920
 0.1854
 0.0847
 0.0738
 -0.0455

Parameter

Value

Solvent CDCl₃
 Experiment 1D
 Spectrometer Frequency 400.13
 Nucleus 1H



9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 -0.5

f1 S374.0

2.18
 4.43
 2.14
 2.22
 19.12
 2.32
 2.03
 1.04
 1.00
 2.31
 1.12
 1.00
 1.20
 1.96
 10.89
 9.39
 9.72
 9.18
 6.57
 2.95
 3.11
 2.63
 2.88

—172.5546

—165.9693
—165.2147
—164.8751
—159.4050
—157.6240
—157.0435
—156.4351

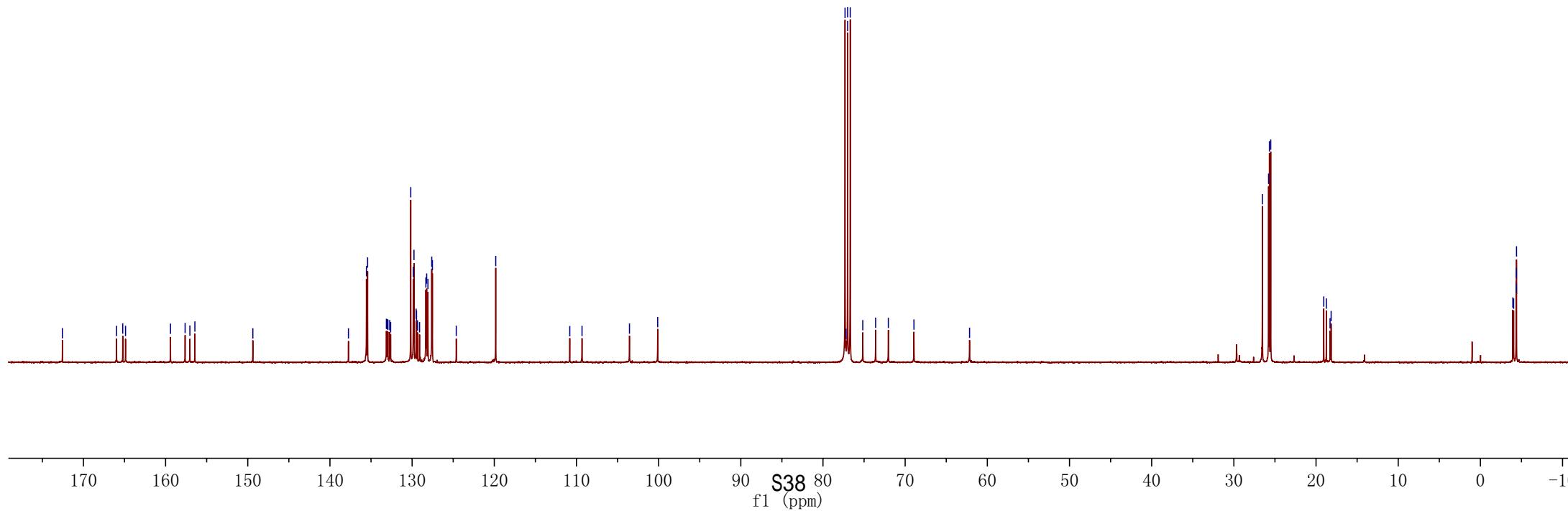
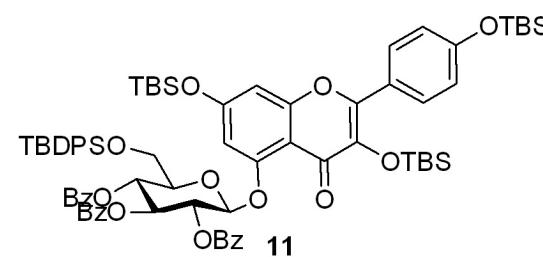
—149.3830
—135.5580
—135.4155
—133.1299
—133.0157
—130.1649
—129.8585
—129.7720
—129.5160
—129.4639
—128.3255
—128.2276
—128.0733
—127.6129
—127.5294

—110.8140

—109.3231
—103.5495
—100.1166

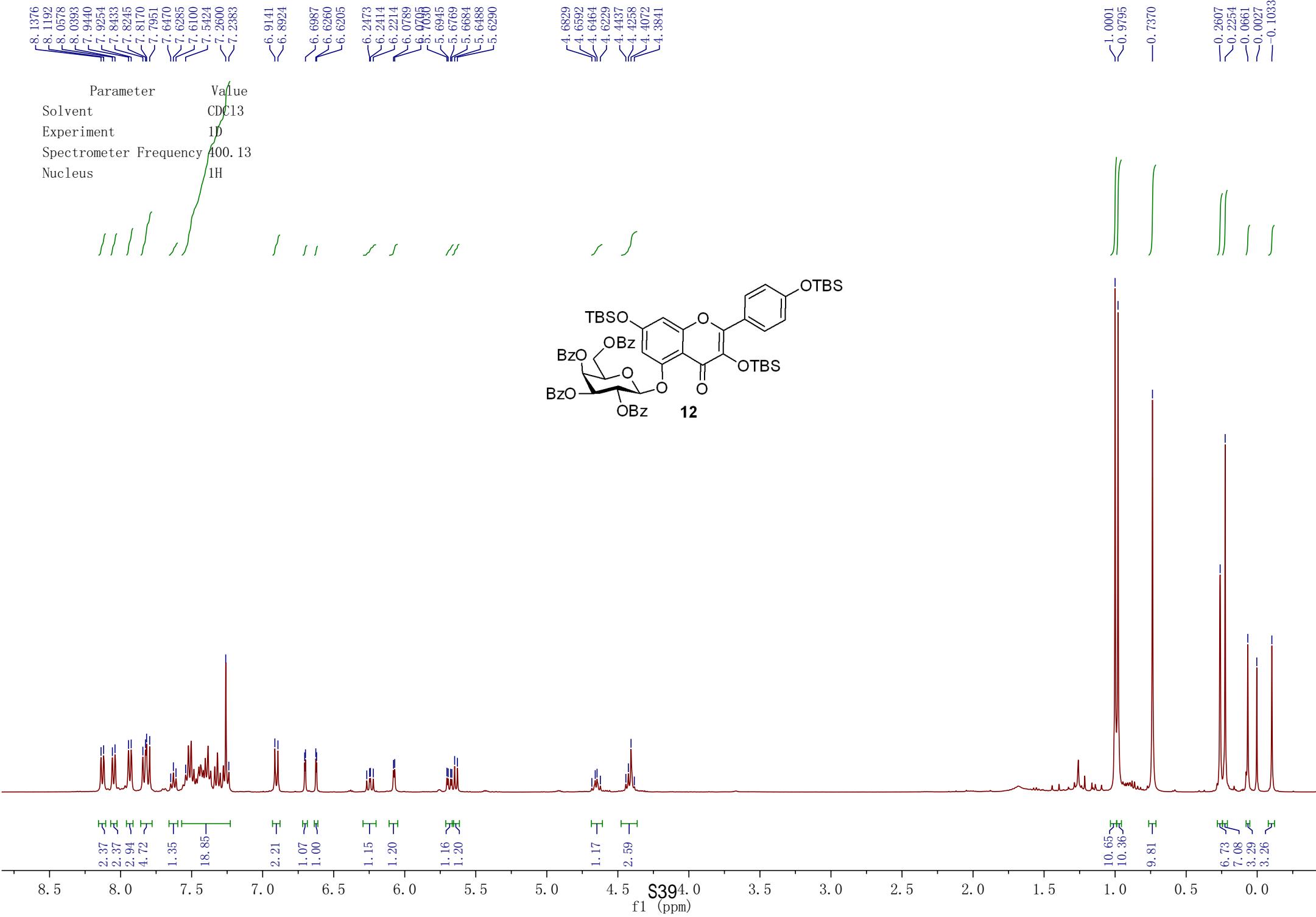
—62.1626

Parameter	Value
Solvent	CDCl ₃
Experiment	1D
Spectrometer Frequency	100.61
Nucleus	¹³ C



—26.5261
—25.7757
—25.6726
—25.5122
—19.0589
—18.7455
—18.2924
—18.1614

—3.9505
—4.0471
—4.3523
—4.3834
—4.3981



—172.5240

—165.9407
—165.6217
—165.2987
—159.4066
—157.6073
—157.0754
—156.3541

—149.4567

—137.7299
—130.1611
—130.0836
—129.8242
—129.7341
—128.6140
—128.4020
—128.2583
—118.8174

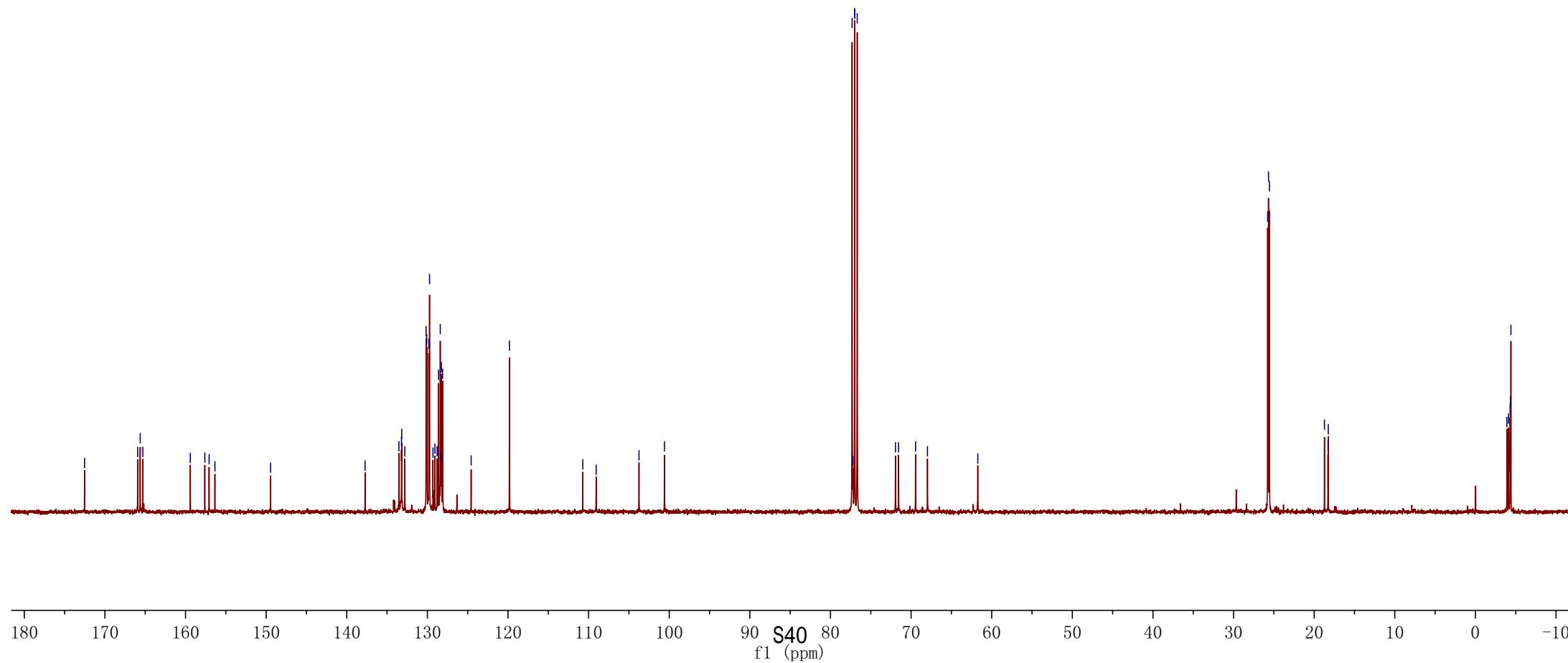
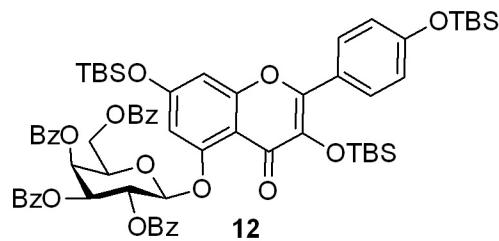
—110.7243
—109.0590
—103.7510
—100.5911

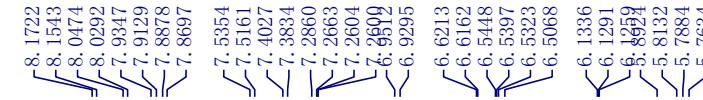
—61.7251
—77.3176
—77.2037
—77.0003
—77.0000
—76.6824
—71.9379
—71.5563
—69.4448
—67.9722

—25.7706
—25.6674
—25.5576
—18.7253
—18.2864
—18.2553

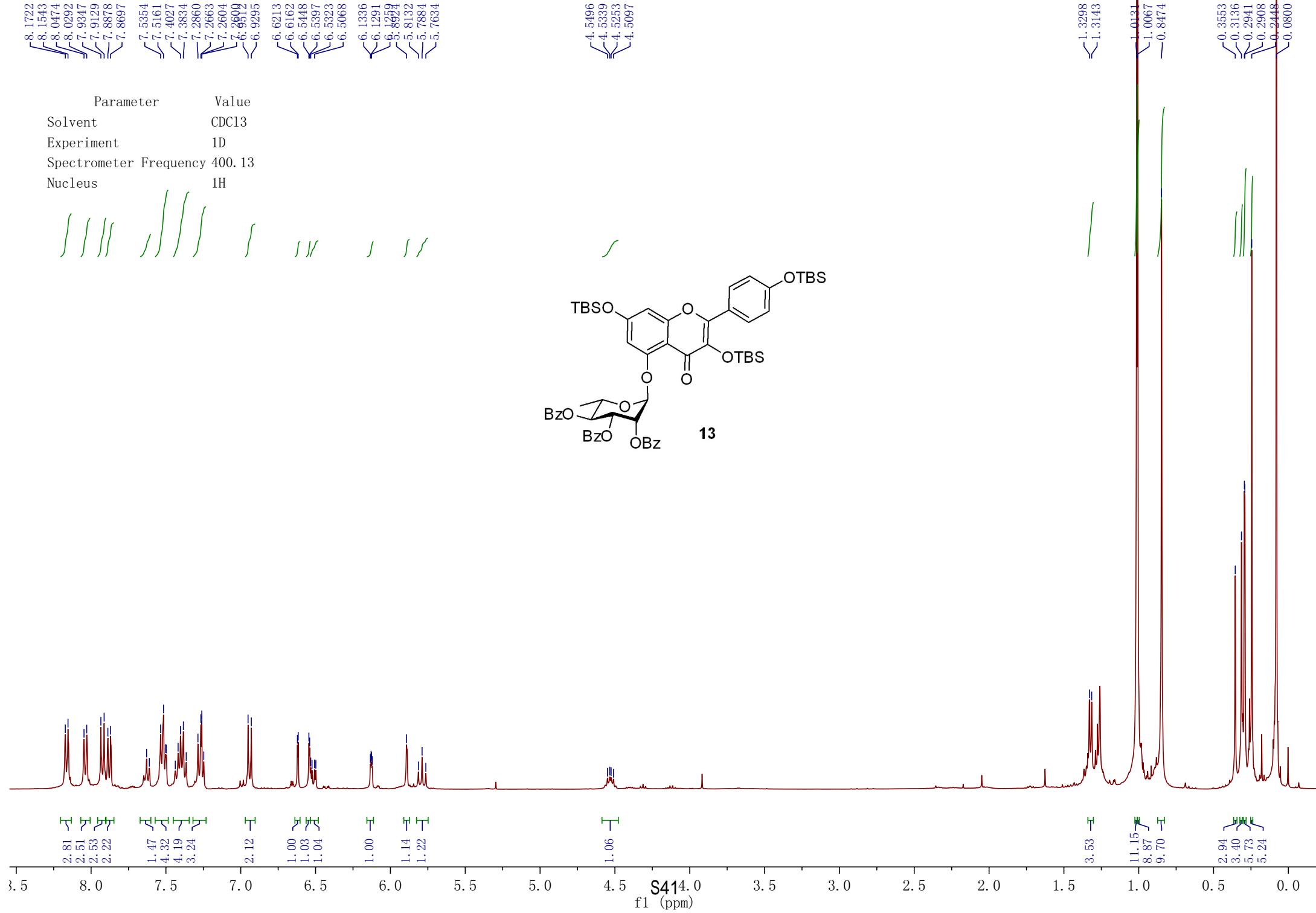
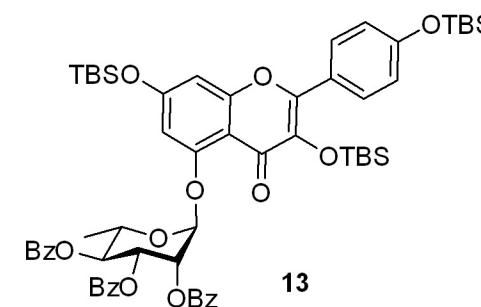
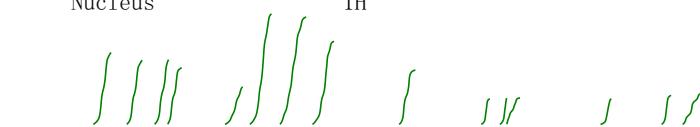
—3.9032
—4.1095
—4.3098
—4.3396
—4.4044

Parameter	Value
Solvent	CDCl ₃
Experiment	1D
Spectrometer Frequency	100.61
Nucleus	¹³ C





Parameter Value
 Solvent CDCl_3
 Experiment 1D
 Spectrometer Frequency 400.13
 Nucleus ^1H



—172.7287

165.9621
165.4809
164.9201
159.7063
157.9198
157.0669
155.4782

—149.0835

—138.0220
130.1206
129.9673
129.8918
129.7323
129.5278
128.5641
128.3026
118.8389

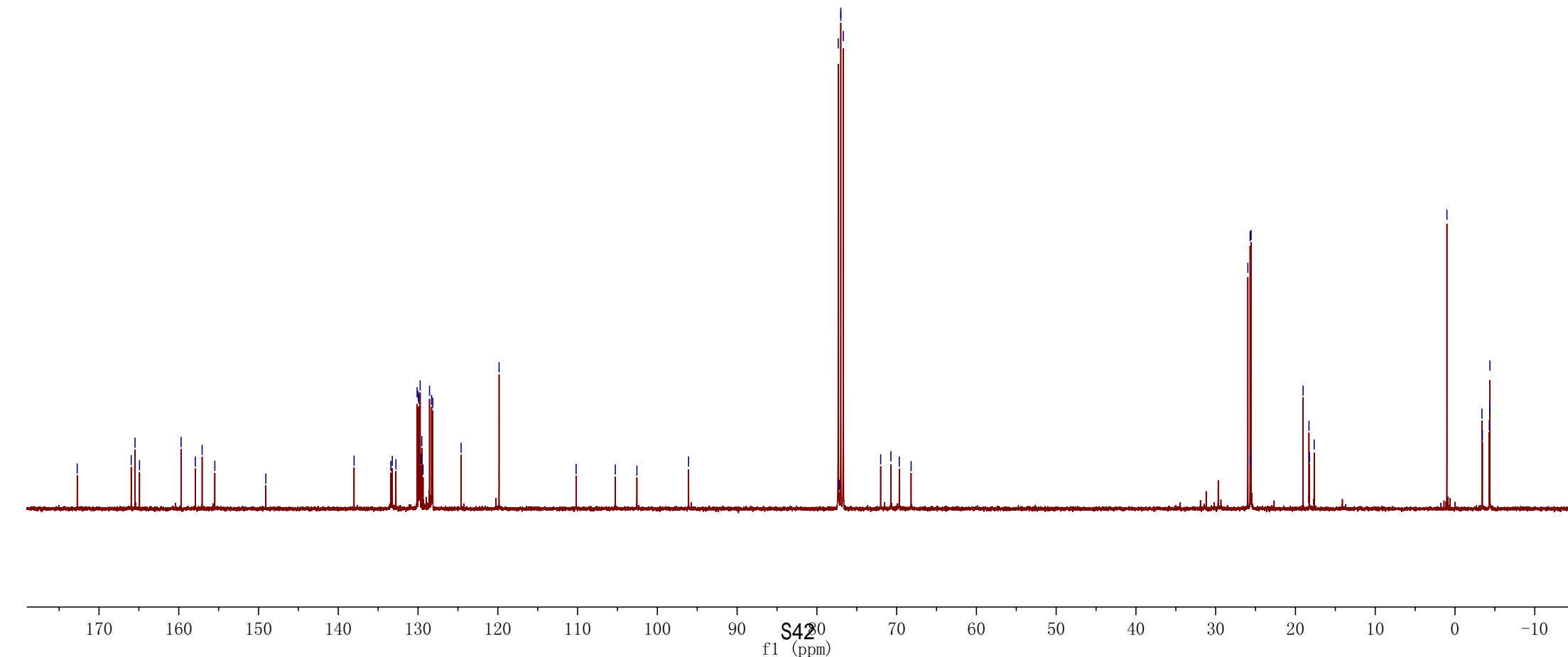
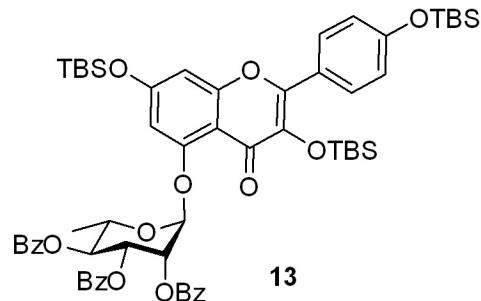
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—105.2709

—102.5634

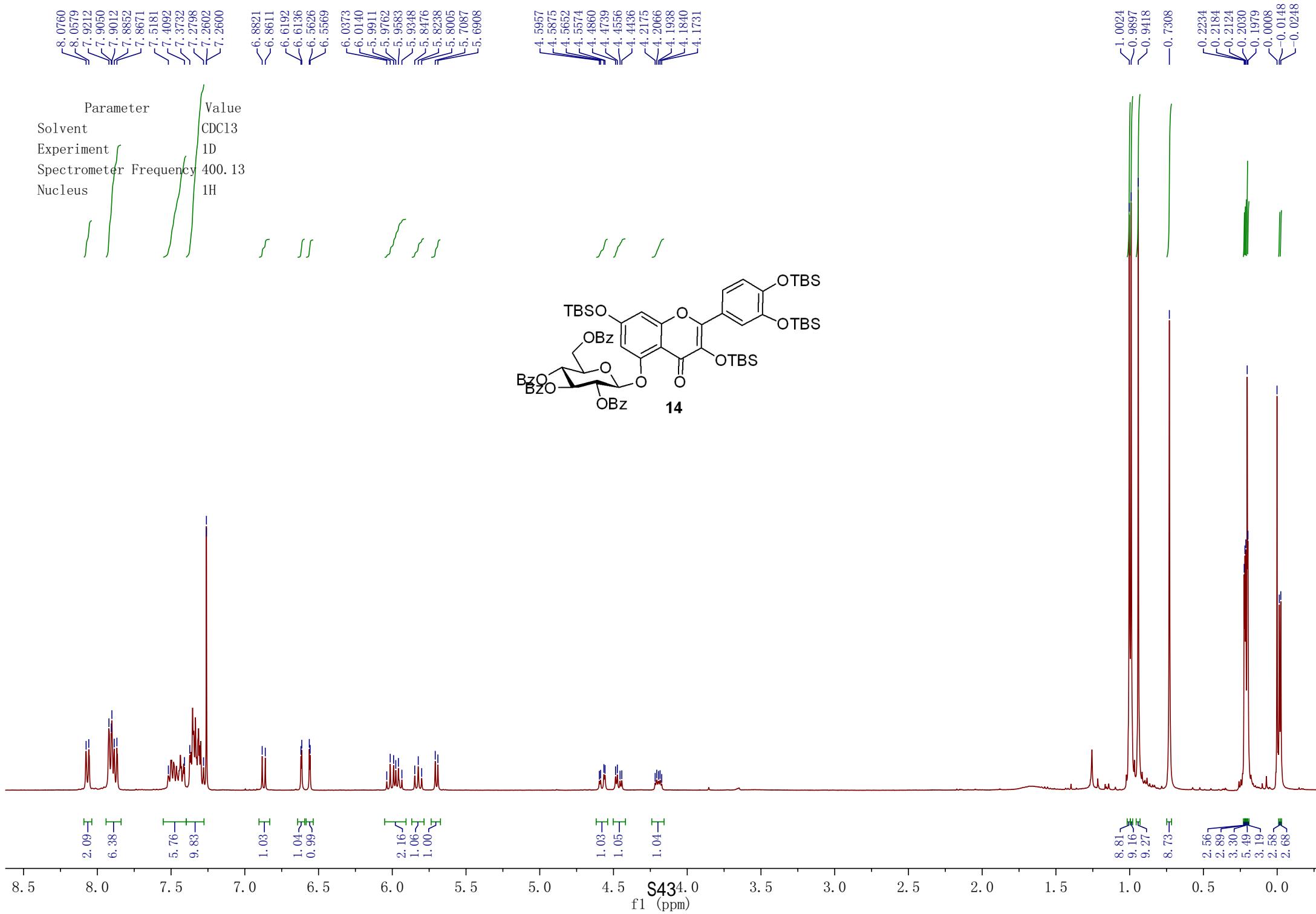
—96.0846

Parameter	Value
Solvent	CDCl ₃
Experiment	1D
Spectrometer Frequency	100.61
Nucleus	¹³ C



25.9687
25.6844
25.6640
25.5617
19.0429
18.3064
18.2416
17.6521

—1.0108
—3.3778
—3.4353
—4.3035
—4.3622
—4.3812



—172.6151
 ↘166.0082
 ↙165.8018
 ↗165.2496
 —165.1221
 —159.2897
 —157.5365
 —155.8641
 —149.6337
 ↗148.6240
 ↗146.5785

—137.6591
 ↗132.9639
 ↗130.1343
 ↗129.8262
 ↗129.7987
 ↗129.6660
 ↗129.6027
 ↗128.3480
 ↗128.2536
 ↗128.1242
 ↗123.0082
 ↗121.4447
 ↗110.8691
 —109.9027

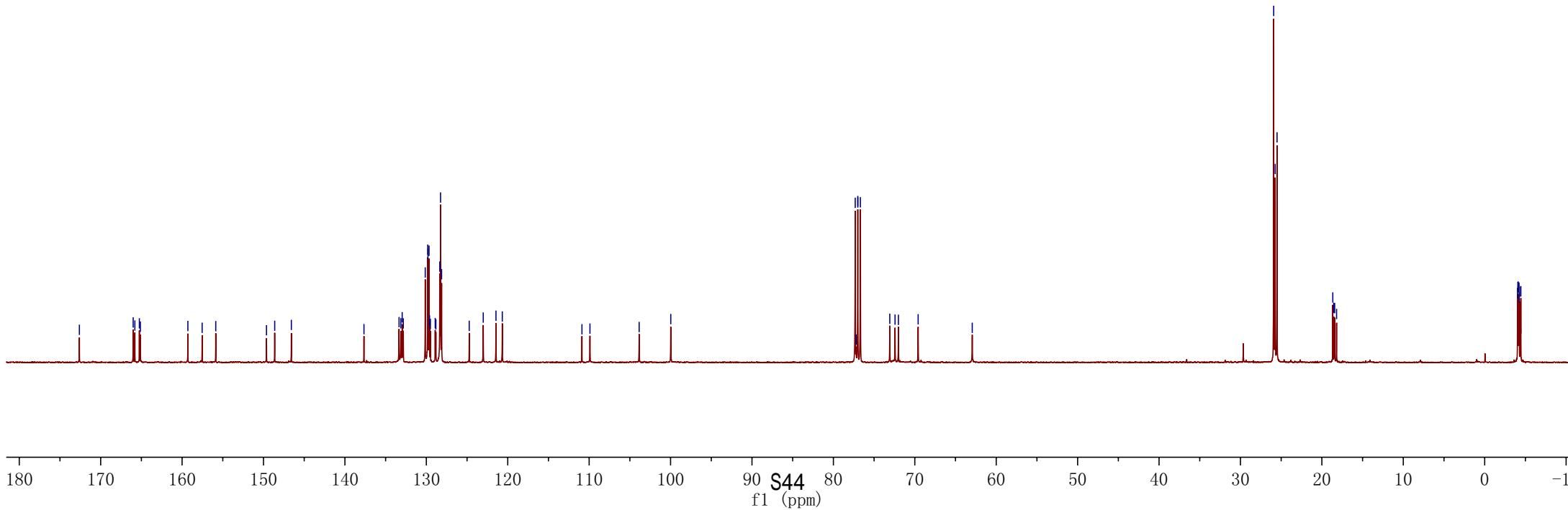
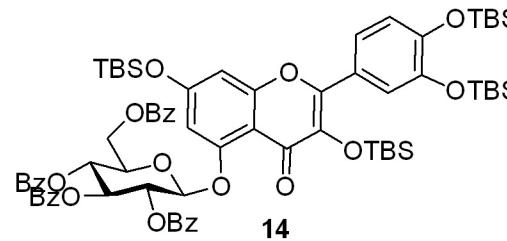
—103.8578
 —99.9744

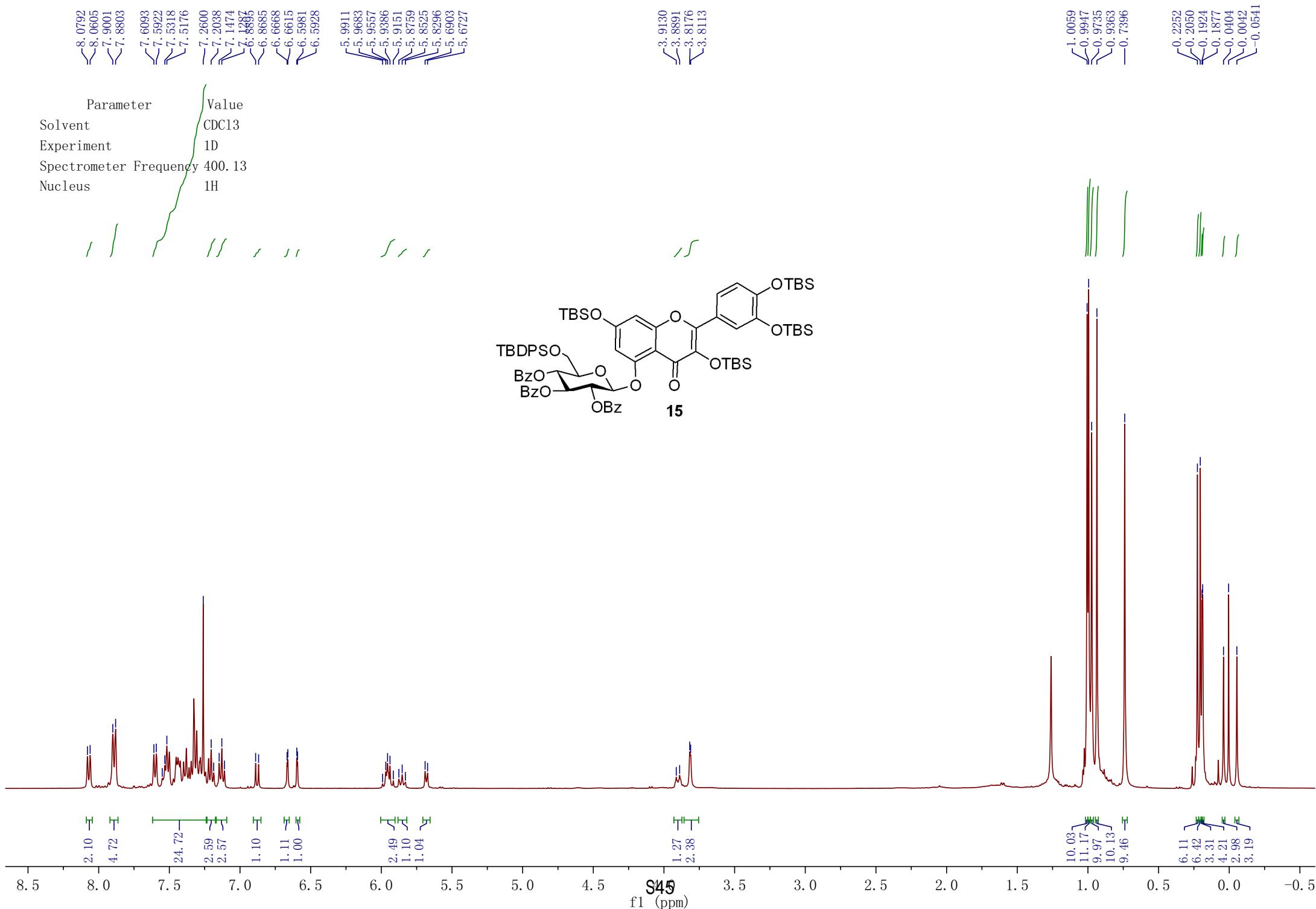
↗77.3178
 ↗77.2022
 ↗77.0003
 ↗76.6824
 ↗73.0729
 ↗72.4270
 ↗72.0141
 ↗69.5898
 —62.9436

↗25.9188
 ↗25.7361
 ↗25.5051
 ↗18.6587
 ↗18.5456
 ↗18.4274
 ↗18.1937

—4.0343
 —4.0706
 —4.1121
 —4.1812
 —4.2117
 —4.2467
 —4.4081
 —4.4410

Parameter	Value
Solvent	CDCl ₃
Experiment	1D
Spectrometer Frequency	100.61
Nucleus	¹³ C





—172.6408
—165.9638
—165.2497
—164.8952
—159.3881
—157.6158
—156.4546

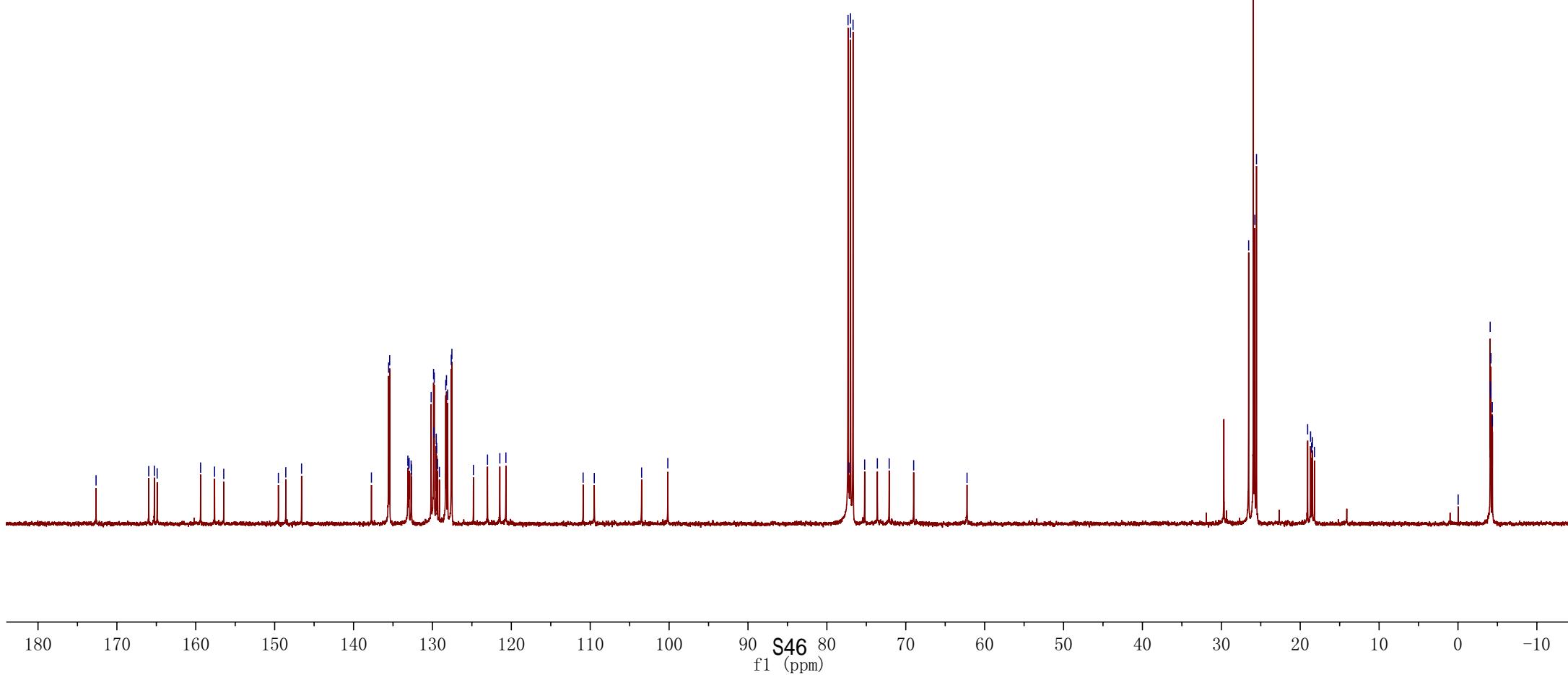
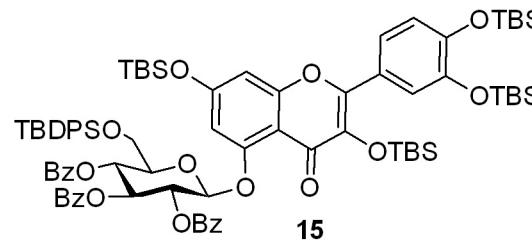
—149.5288
—148.5895
—146.5905

—135.5538
—135.4199
—130.1639
—129.8561
—129.8149
—129.7711
—129.5163
—129.4656
—128.3149
—128.2202
—128.0699
—127.6139
—127.5329
—123.0193
—121.4556
—120.9875
—109.4846

—103.4861
—100.1645

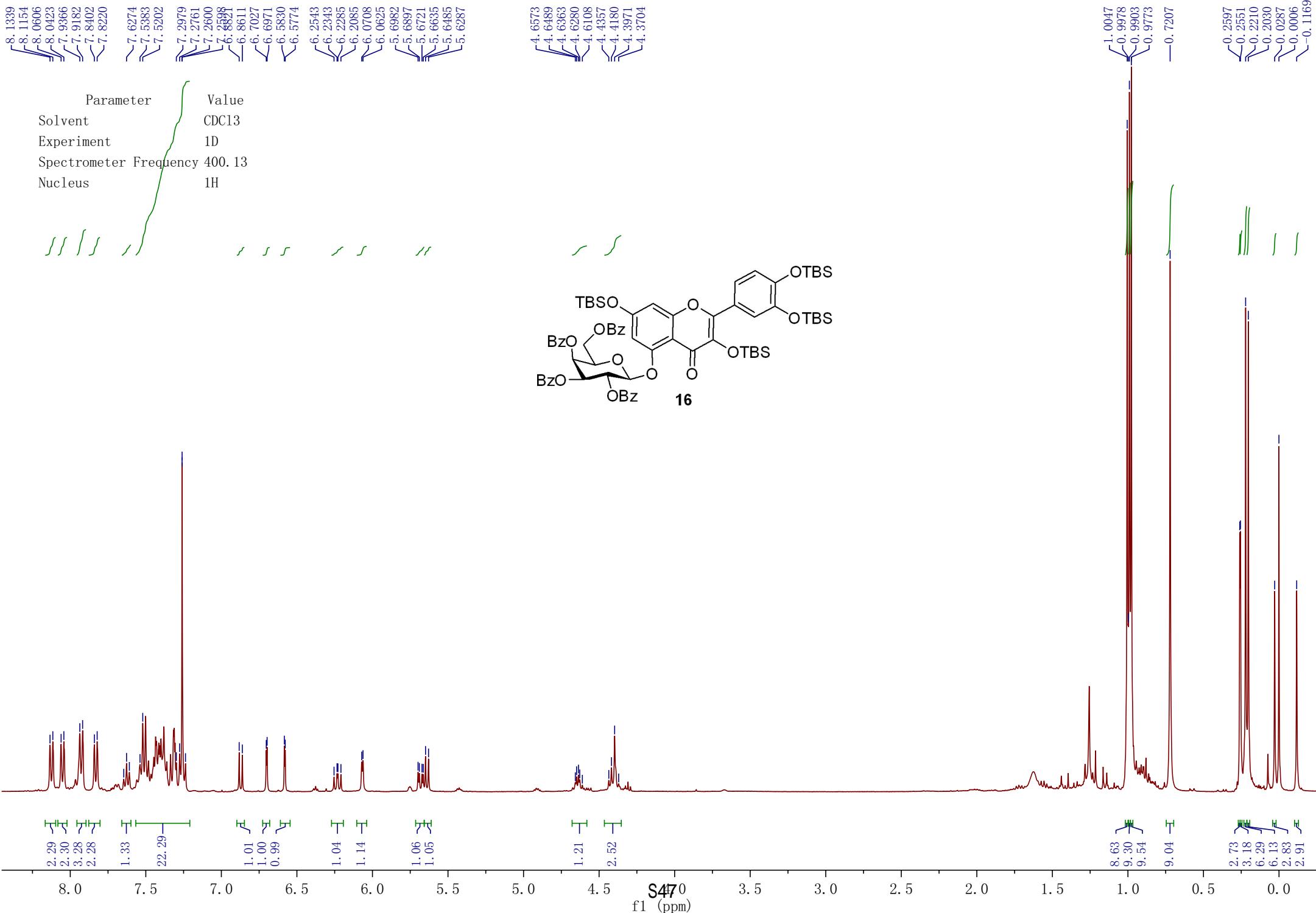
—62.2331

Parameter	Value
Solvent	CDCl ₃
Experiment	1D
Spectrometer Frequency	100.61
Nucleus	¹³ C



—26.5334
—25.9370
—25.7539
—25.5415
—19.0553
—18.6853
—18.5607
—18.4486
—18.1939

—0.0220
—4.0806
—4.1124
—4.1471
—4.1793
—4.3450
—4.3703



—172.6131
 <—165.9490
 <—165.6339
 —>—165.3427
 —>—159.3708
 —>—157.5817
 —>—156.3495
 —>—149.6037
 —>—148.6226
 —>—146.3953

—>—137.7118
 <—133.2105
 <—133.1775
 <—130.0957
 —>—130.0725
 —>—129.8323
 —>—129.7848
 —>—129.7401
 —>—128.6192
 —>—128.3993
 —>—128.3582
 —>—128.2625
 —>—128.1148
 —>—118.8766
 —>—109.3012

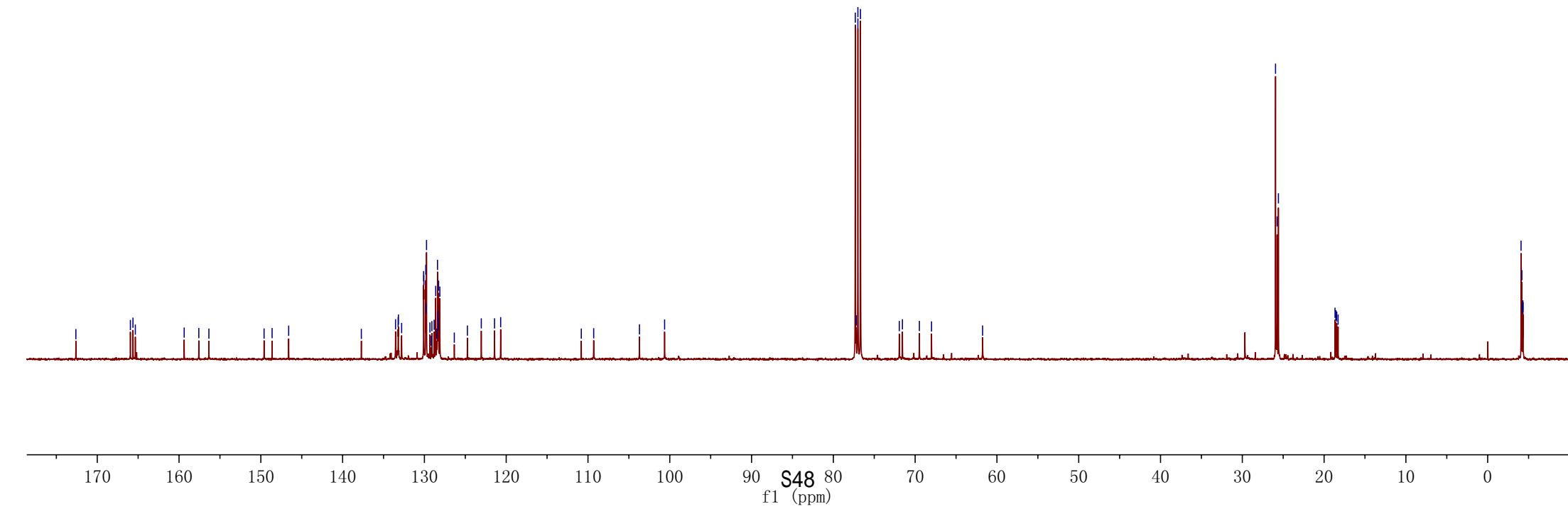
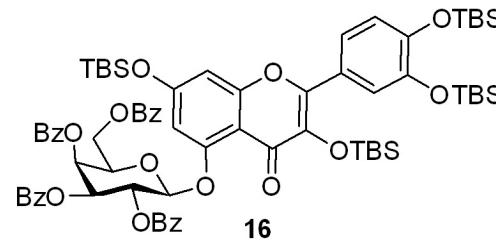
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 —>—100.6323

—>—61.7503

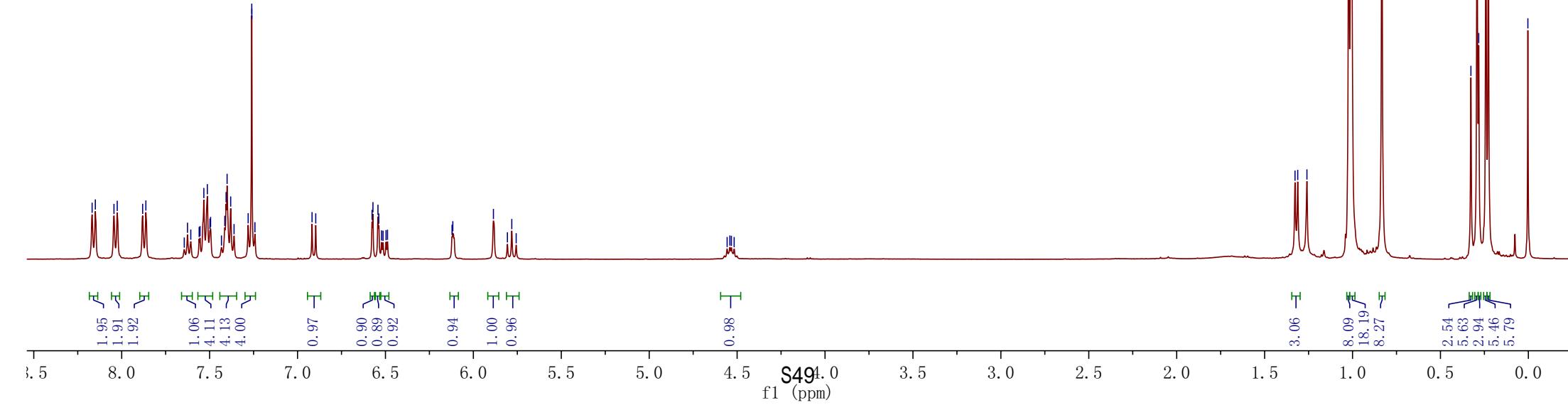
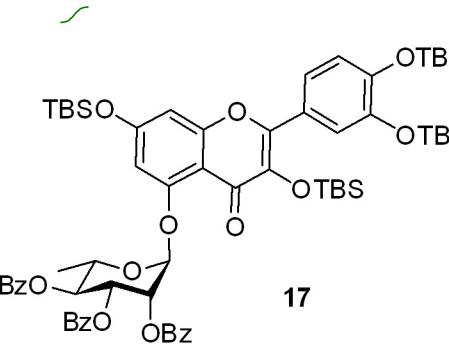
<—25.9360
 <—25.7418
 <—25.5837
 —>—18.6650
 <—18.5642
 <—18.4538
 <—18.2873

—>—4.0817
 —>—4.1853
 —>—4.2295
 —>—4.3029
 —>—4.3327

Parameter	Value
Solvent	CDCl ₃
Experiment	1D
Spectrometer Frequency	100.61
Nucleus	¹³ C



Parameter	Value
Solvent	CDCl ₃
Experiment	1D
Spectrometer Frequency	400.13
Nucleus	1H



—172.8146

≤165.9662
≤165.9809
≤164.9270

—159.6899

—157.9067

—155.5571

≤149.2280
≤148.6012

~146.6189

—138.0285

≤133.3929
≤133.2127

≤129.9675
≤129.8904

≤129.7312

≤129.6364

≤129.4041

≤128.5575

≤128.2981

≤128.1432

≤123.0182

≤121.3123

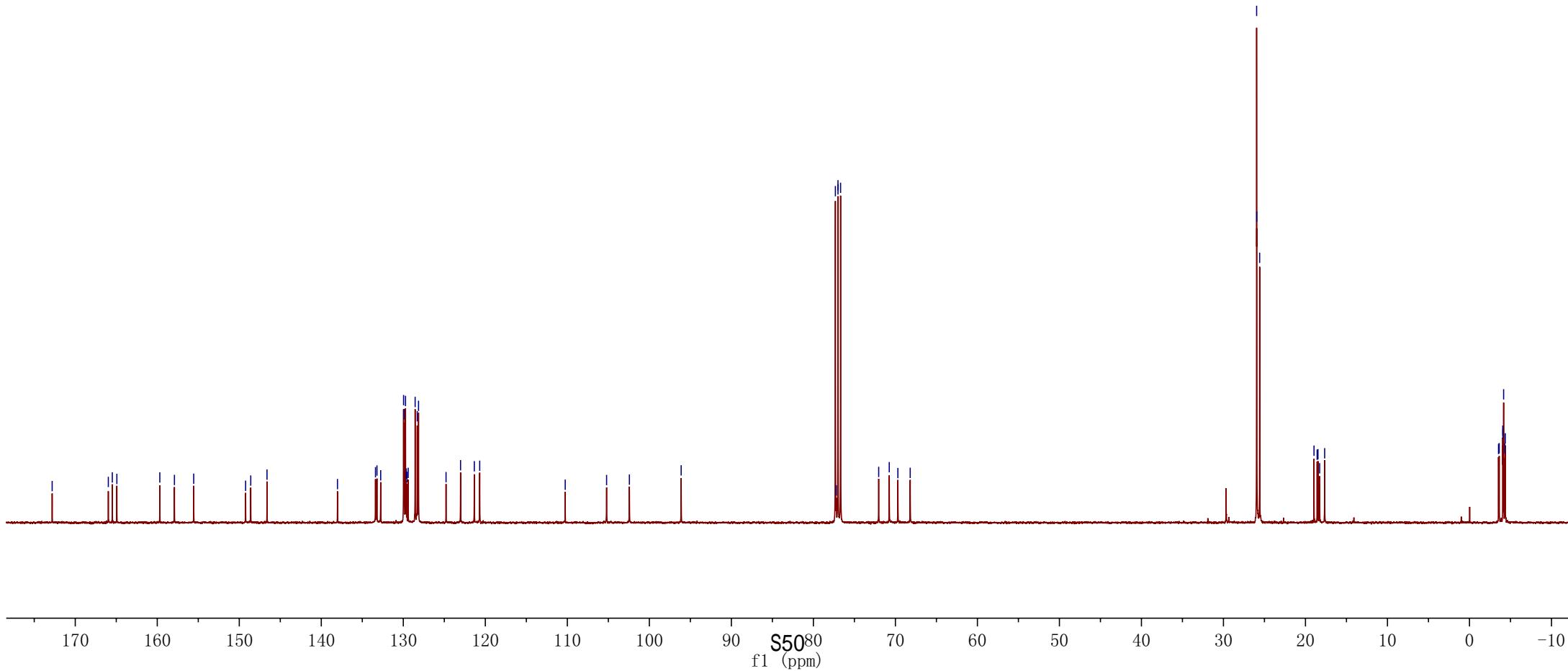
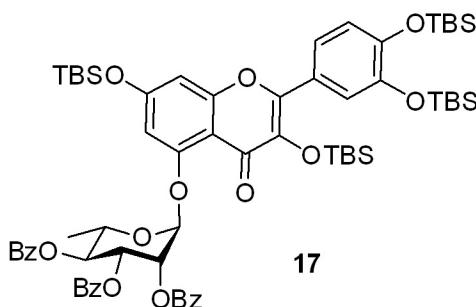
≤118.2844

—105.2136

—102.4329

—96.1218

77.3169
77.2026
77.0000
76.9997
76.6818
72.0360
≤70.7484
~69.6958
~68.1949



—3.5395
—3.6239
—4.0554
—4.0738
—4.1633
—4.3062
—4.3613

≤25.9536
≤25.9359
≤25.5846
≤18.9573
≤18.5769
≤18.4747
≤18.2687
≤17.6584

8.0882
8.0697
7.9840
7.9665
7.9494
7.9389
7.9211
7.9107
7.8884

7.4367
7.3817
7.3625
7.2600
7.2599
6.9508
6.9682
6.8373
6.8316
6.6364
6.6307

6.0687
6.0459
6.0232
6.0007
5.9829
5.9600
5.8603
5.8367
5.8133
5.6952
5.6775

5.1196
5.0658
4.7731
4.7462
4.7207
4.7134
4.6903
4.6831
4.6699
4.6429
4.5201
4.3032
4.2974
4.2875
4.2789
4.2733
4.2657

Parameter

Solvent

Experiment

Spectrometer Frequency

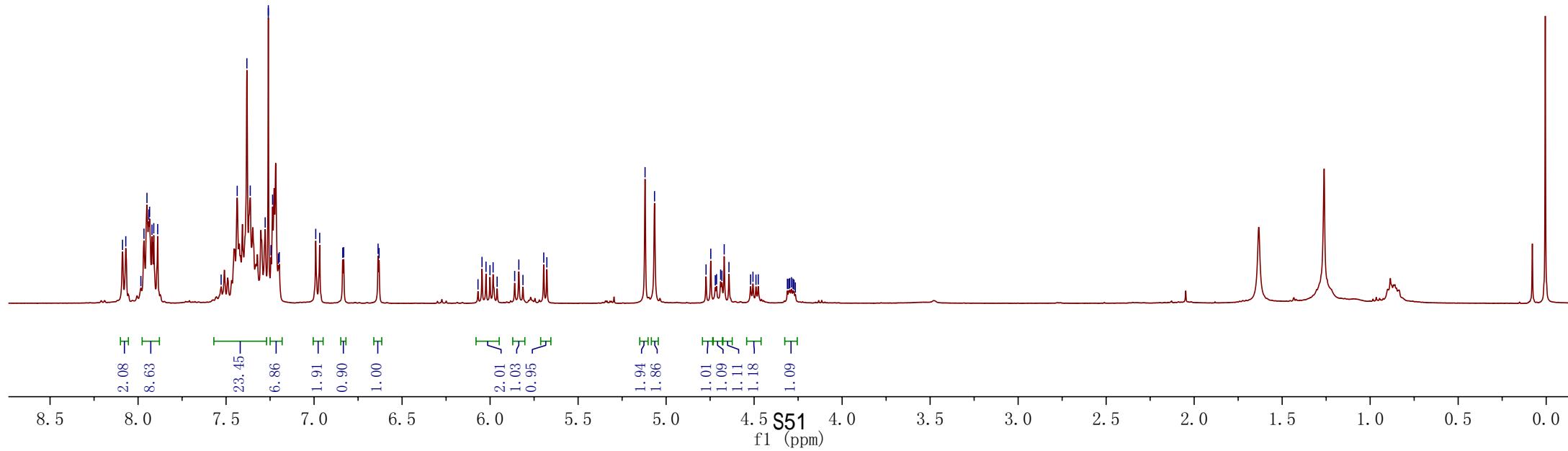
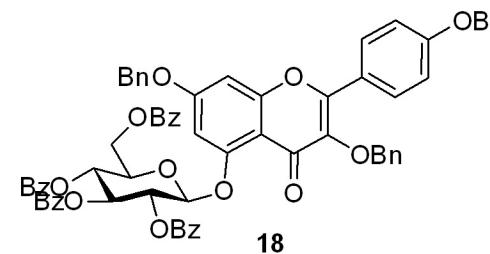
Nucleus

Value

CDCl₃

10

1H



—172.6858

166.0315
165.8040
165.2922
165.1604
162.0217
160.1797
157.8092
156.6317
153.3034

130.0682
129.8577
129.6467
128.7536
128.6718
128.6001
128.3669
128.2885
128.2508
128.2220
128.0328
128.0006
127.4377
123.3898

—114.4864

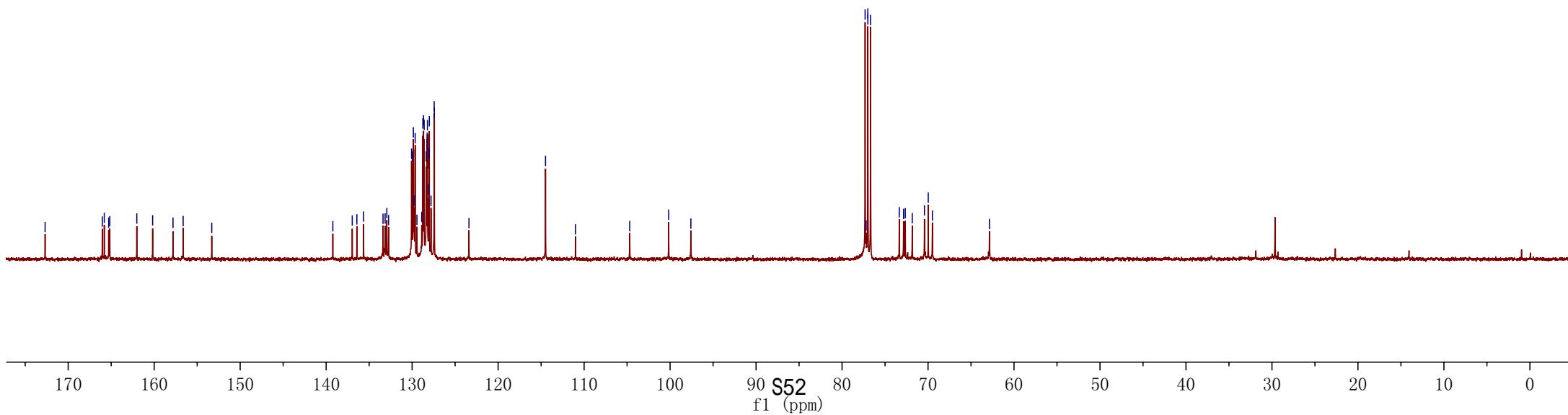
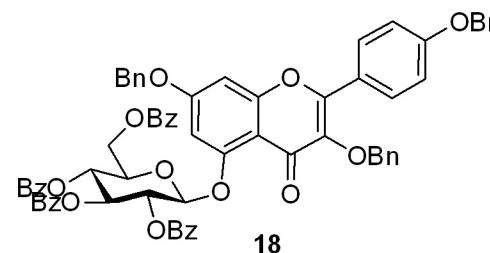
—111.0033

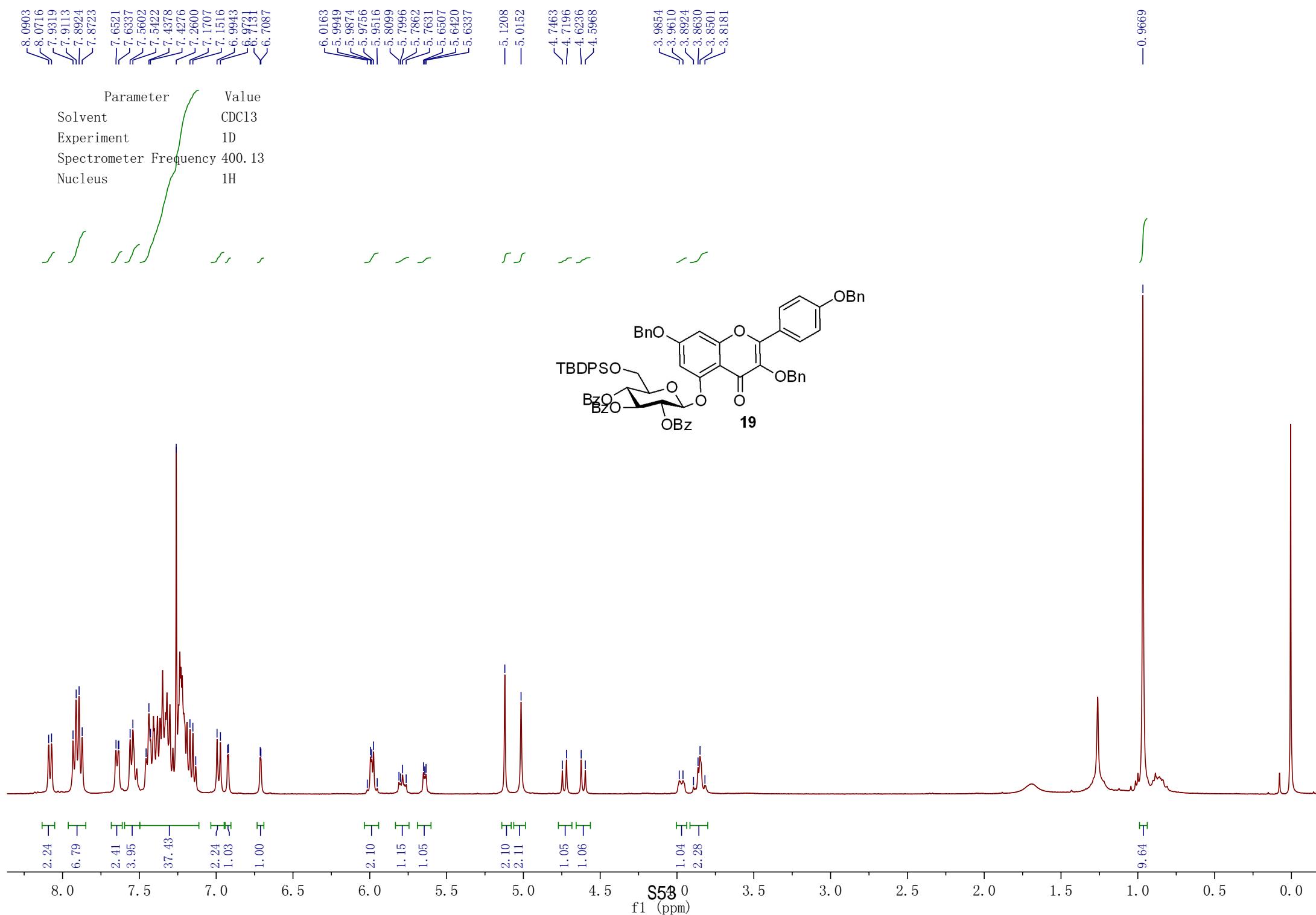
—104.6963

—100.1622

—97.5793

Parameter	Value
Solvent	CDCl ₃
Experiment	1D
Spectrometer Frequency	100.61
Nucleus	¹³ C





— 172.6515

— 165.9300
— 165.3902
— 164.9474
— 162.1567
— 160.1708
— 157.9617
— 157.1163
— 153.2009

— 135.5491
— 135.4379
— 130.0754
— 130.0160
— 129.8840
— 129.7734
— 128.7817
— 128.6409
— 128.3205
— 128.2284
— 128.0191
— 127.9736
— 127.6196
— 127.5913
— 123.4876

— 114.5119

— 111.2304

— 105.3417

— 100.7454

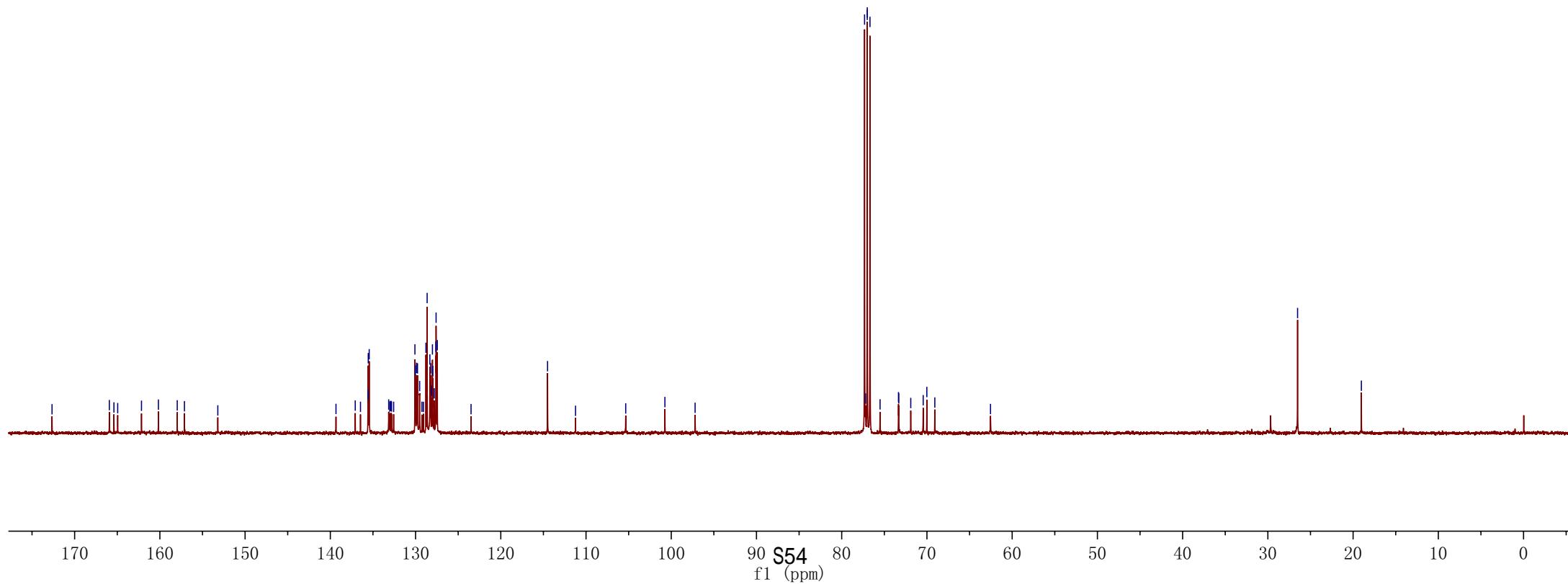
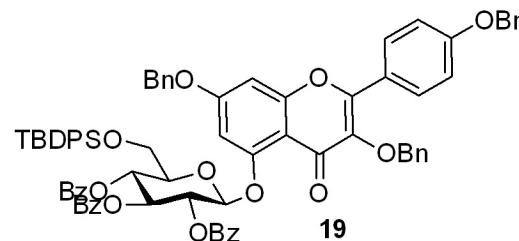
— 97.2017

Parameter	Value
Solvent	CDCl ₃
Experiment	1D
Spectrometer Frequency	100.61
Nucleus	¹³ C

— 77.3182
— 77.2034
— 77.0001
— 77.0000
— 76.6830
— 75.5003
— 73.3393
— 73.3033
— 71.8981
— 70.4399
— 70.0113
— 69.0747
— 62.5409

— 26.5140

— 19.0259



8.1462
8.1280
8.0541
8.0358
7.9982
7.9807
7.9097
7.8874
7.8622
7.8439

7.6229
7.6043
7.2068
7.1429
6.9819
6.9594
6.9521
6.9464

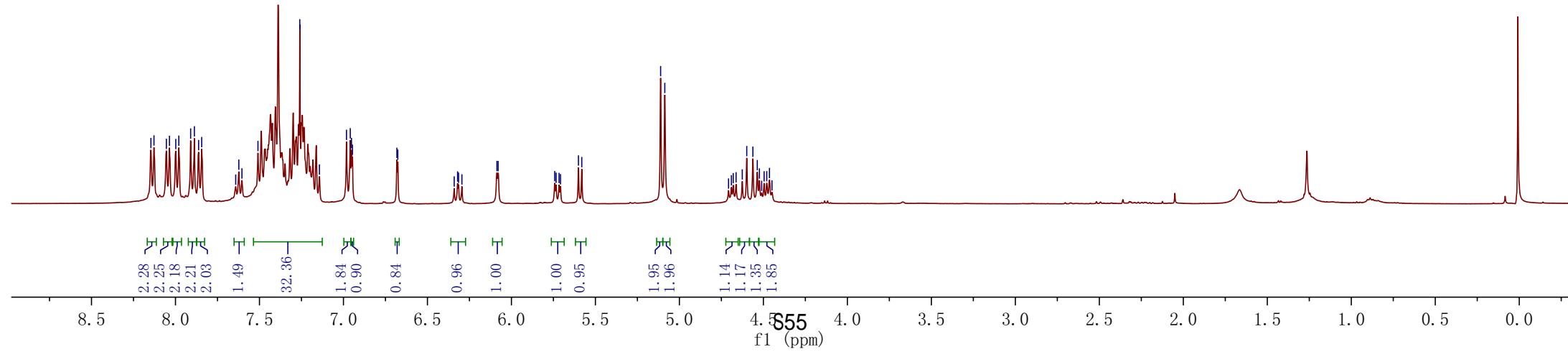
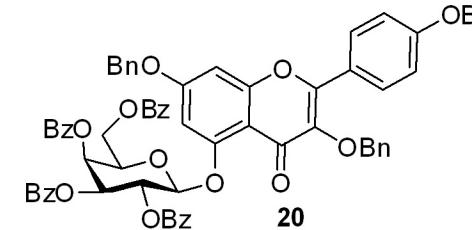
6.6820
6.6763
6.3406
6.3205
6.3148
6.2947
6.0864
6.0791

5.7424

5.7340
5.7163
5.7078
5.6010
5.5811

Parameter
Solvent
Experiment
Spectrometer Frequency
Nucleus

Value
CDCl₃
1D
400.13
1H

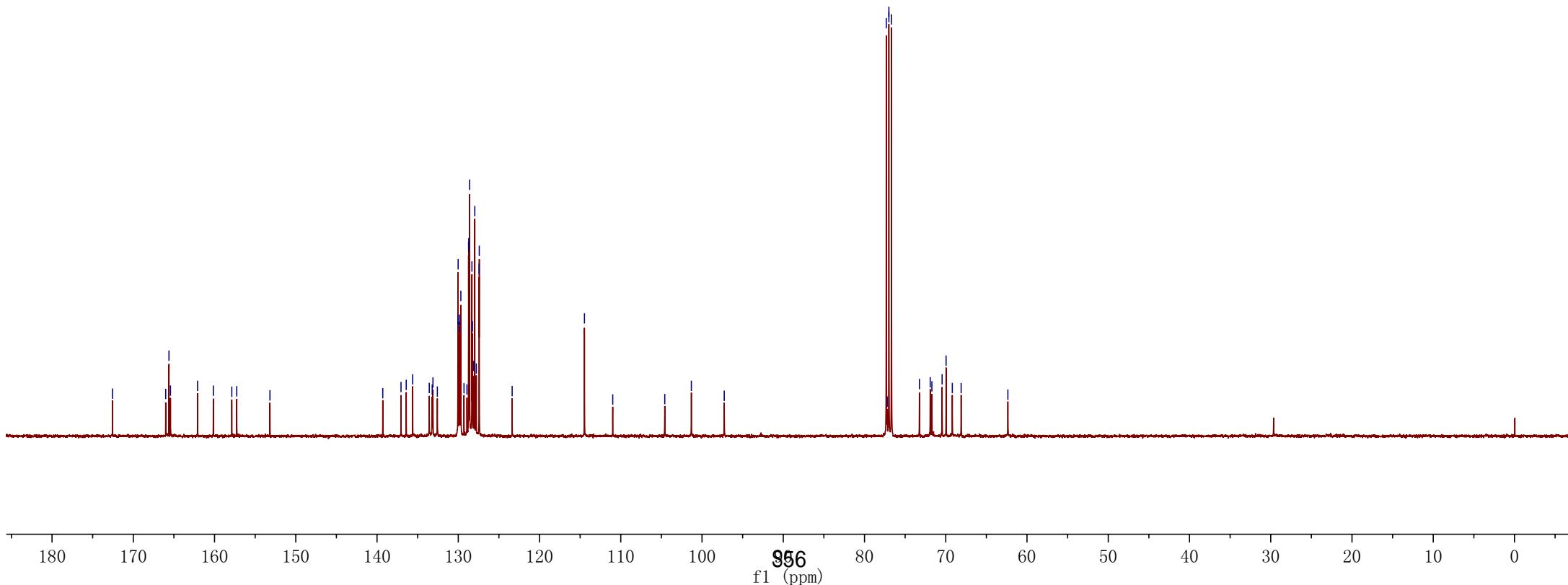
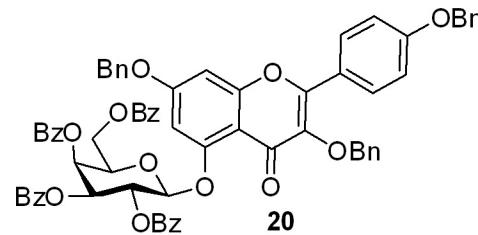


— 172.5536

166.0108
165.6068
165.4217
162.0846
160.1461
157.8746
157.2657
153.1796

130.0445
130.0175
129.8698
129.8199
129.6827
128.7320
128.7125
128.6007
128.3188
128.2583
128.0947
127.9667
127.4368
123.3676

Parameter	Value
Solvent	CDCl ₃
Experiment	1D
Spectrometer Frequency	100.61
Nucleus	¹³ C



8.1685

8.1497

8.0511

8.0324

7.9966

7.9757

7.8927

7.8739

7.6262

7.6087

7.5348

7.2900

7.2600

7.0345

7.0134

6.8050

6.7237

> 6.4219

> 6.3962

> 6.1351

> 5.9193

> 5.8401

> 5.8155

> 5.7907

> 5.2169

> 5.1901

> 5.1643

> 5.1492

> 5.1286

> 5.1015

> 4.6141

> 4.5990

> 4.5753

< 1.3644

< 1.3497

Parameter

Solvent

Experiment

Spectrometer Frequency

Nucleus

value

CDCl₃

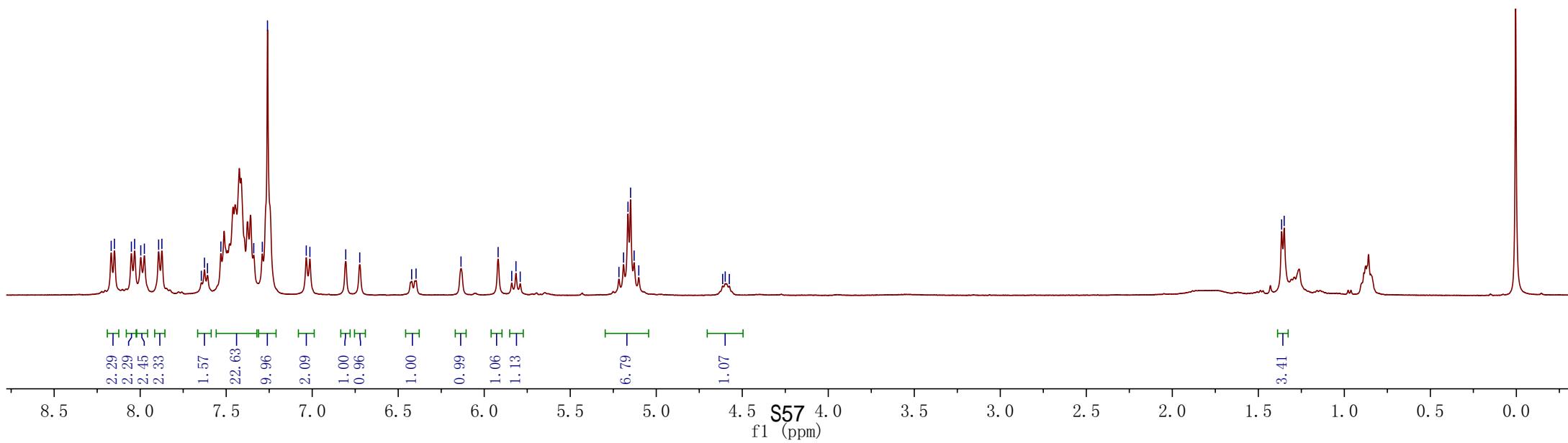
1D

400.13

1H



21



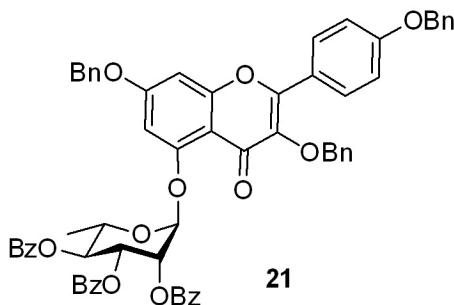
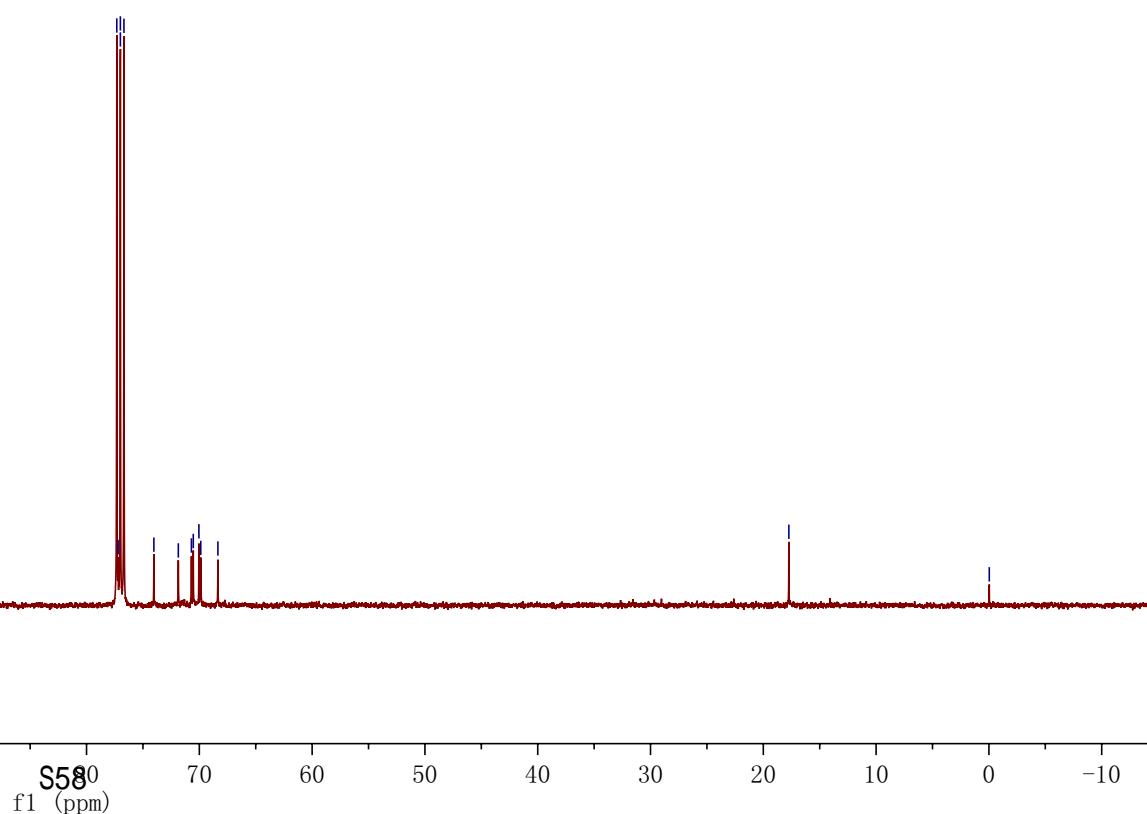
—173.2490

165.9896
165.5460
165.1921
162.4278
160.2437
158.4089
156.2124
153.7032
130.2217
129.9701
129.8728
129.7359
129.1104
128.7221
128.6473
128.5784
128.3682
128.1884
128.1091
127.8918
127.5172
123.4614

—114.5598

—110.7163

—101.3711
96.6392
96.4740



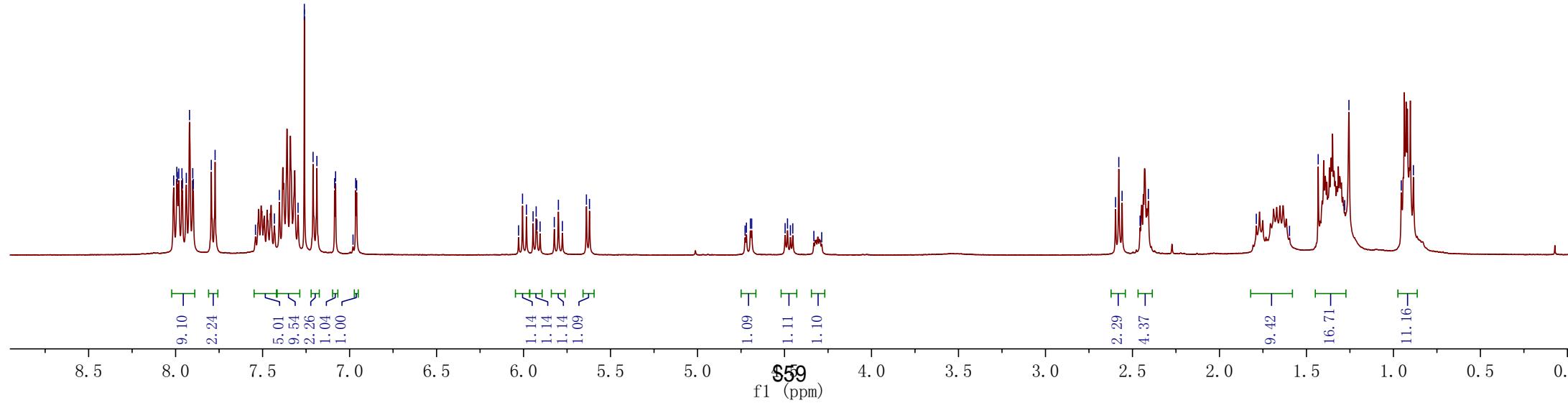
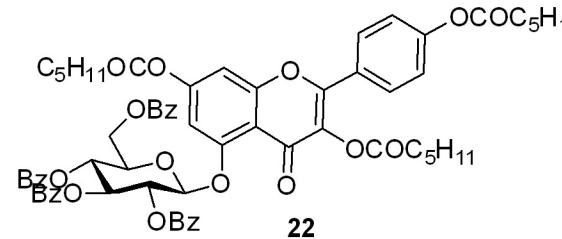
Parameter	Value
Solvent	CDCl ₃
Experiment	1D
Spectrometer Frequency	100.61
Nucleus	¹³ C

—0.0331

—17.7350

8. 0111	$\sqrt{7.9931}$
7. 9899	$\sqrt{7.9899}$
7. 9817	$\sqrt{7.9817}$
7. 9636	$\sqrt{7.9636}$
7. 9605	$\sqrt{7.9605}$
7. 9523	$\sqrt{7.9523}$
7. 9202	$\sqrt{7.9202}$
7. 9014	$\sqrt{7.9014}$
7. 8894	$\sqrt{7.8894}$
7. 7950	$\sqrt{7.7950}$
7. 7777	$\sqrt{7.7777}$
7. 5410	$\sqrt{7.5410}$
7. 4321	$\sqrt{7.4321}$
7. 4037	$\sqrt{7.4037}$
7. 2961	$\sqrt{7.2961}$
7. 2600	$\sqrt{7.2600}$
7. 2099	$\sqrt{7.2099}$
7. 0858	$\sqrt{7.0858}$
7. 0806	$\sqrt{7.0806}$
6. 9803	$\sqrt{6.9803}$
6. 9648	$\sqrt{6.9648}$

Parameter	Value
Solvent	CDCl ₃
Experiment	1D
Spectrometer Frequency	400.13
Nucleus	1H



171.7411
 170.9494
 170.4085
 169.3605
 165.3845
 165.7500
 165.2762
 165.1392
 157.1188
 156.5234
 154.1883
 153.2690
 152.7383

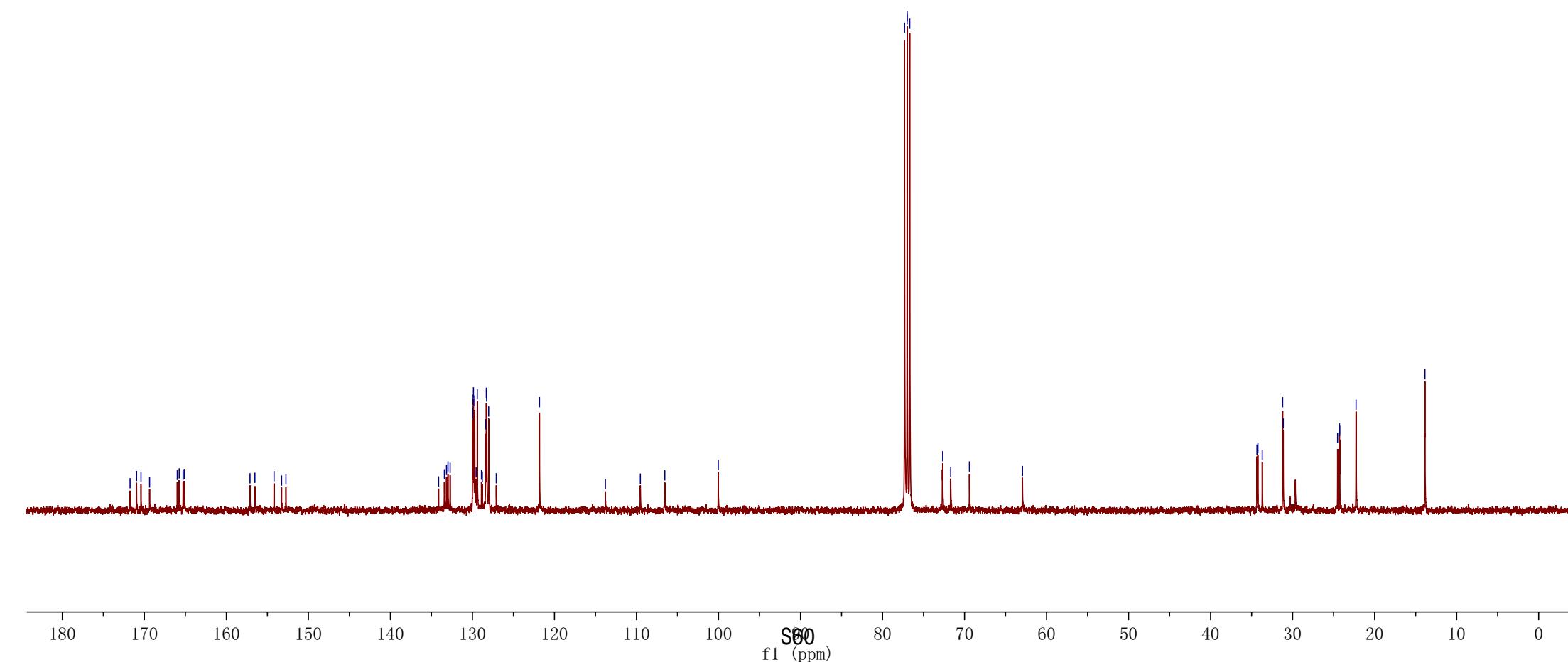
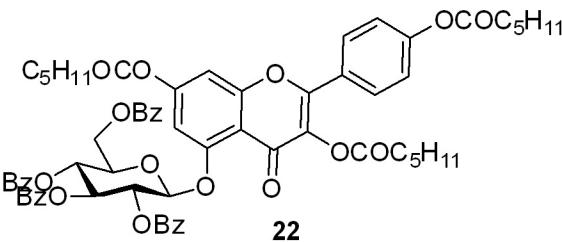
133.4165
 133.1589
 132.9809
 132.7188
 129.9807
 129.9142
 129.8771
 129.7220
 129.5491
 129.4111
 128.3936
 128.3067
 128.2686
 128.8244

—113.7952
 —109.5280
 —106.5482
 —100.0287

77.3168
 77.0000
 76.9996
 76.6816
 72.6642
 71.6855
 69.4073

—62.9365

Parameter	Value
Solvent	CDCl ₃
Experiment	1D
Spectrometer Frequency	100.61
Nucleus	¹³ C



—13.8658

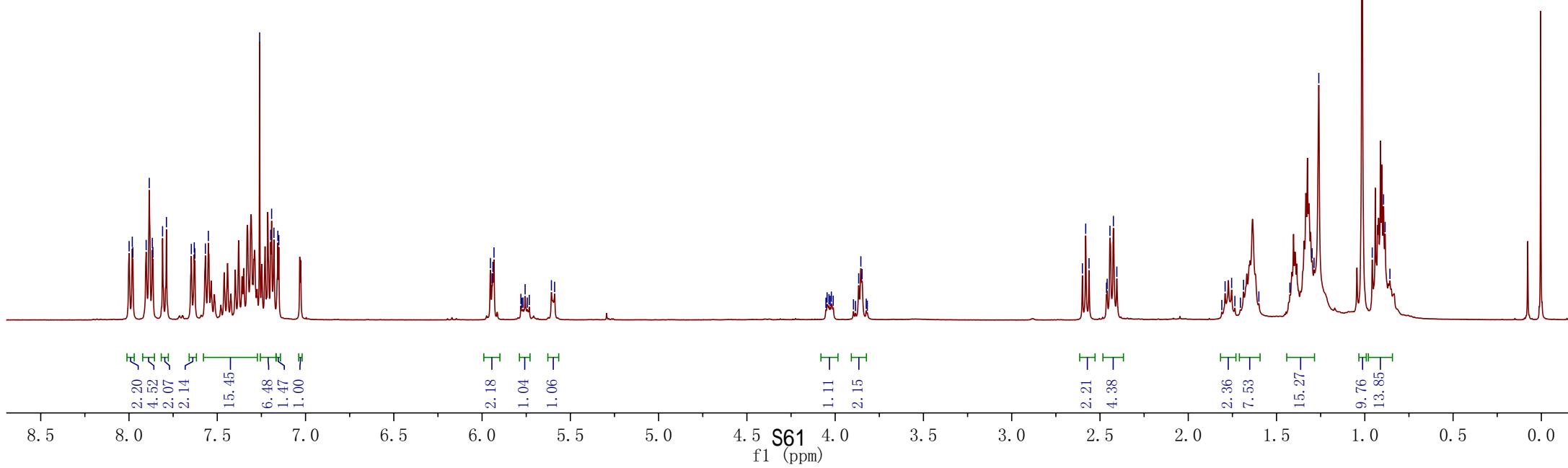
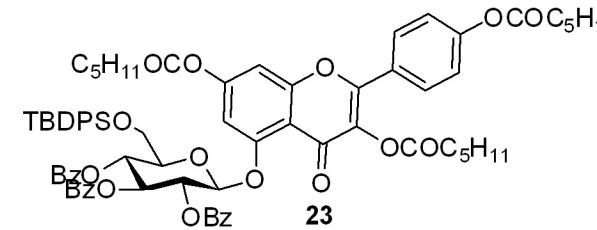
7.9993
7.9813
7.9783
7.9028
7.8852
7.6470
7.6272
7.5674
7.5504
7.2600
7.1973
7.1921
7.1790
7.1568
7.1513

5.9528
5.9435
5.9387
5.9326
5.7800
5.7749
5.7684
5.7562
5.7440
5.7327
5.6073
5.5891

4.0523
4.0458
4.0352
4.0284
4.0216
4.0110
3.8964
3.8850
3.8668
3.8546
3.8476
3.8241
3.8180

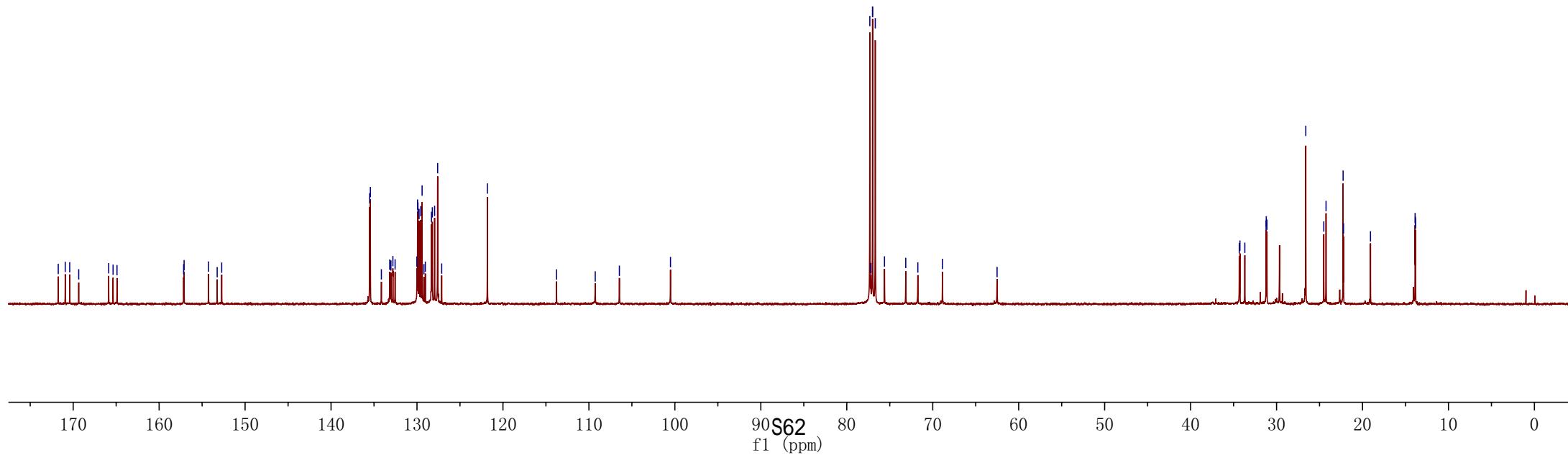
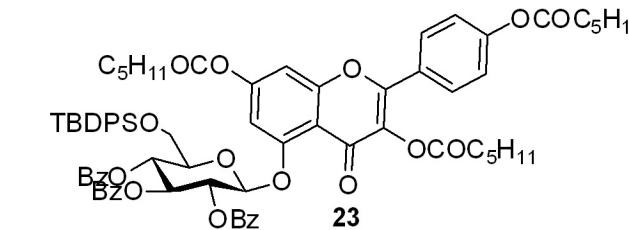
2.5995
2.5809
2.5621
2.4630
2.4593
2.4436
2.4240
2.4046
1.8099
1.7914
1.7543
1.7359
1.7047
1.6869
1.6601
1.4243
1.2985
1.2875
1.2606
1.0155
0.9579
0.8936
0.8850
0.8577

Parameter	value
Solvent	CDCl ₃
Experiment	1D
Spectrometer Frequency	400.13
Nucleus	1H



171.7372
 170.4021
 169.3550
 165.8678
 165.3581
 164.9009
 157.1500
 157.0941
 154.2566
 153.2461
 152.7201
 135.5069
 135.4255
 133.1733
 132.8061
 132.5472
 130.0146
 129.9336
 129.8896
 129.7602
 129.5575
 129.4065
 128.3171
 128.2165
 127.9509
 127.8105⁴

Parameter	Value
Solvent	CDCl ₃
Experiment	1D
Spectrometer Frequency	100.61
Nucleus	¹³ C



34.3365
 34.2602
 33.6914
 31.2201
 31.1980
 31.1163
 26.5986
 24.5040
 24.2421
 22.2582
 22.2117
 19.0712
 13.8799
 13.8522
 13.8300

8.1279
8.1096
8.0115
7.9930
7.9893
7.9676
7.8480
7.8298
7.7894
7.7675
7.2685
7.2600
7.6431
7.6244
7.6058
7.5955
7.0278

6.2743
6.2545
6.2486
6.2288
6.0780
6.0703
5.7072
5.6988
5.6812
5.6728
5.5403

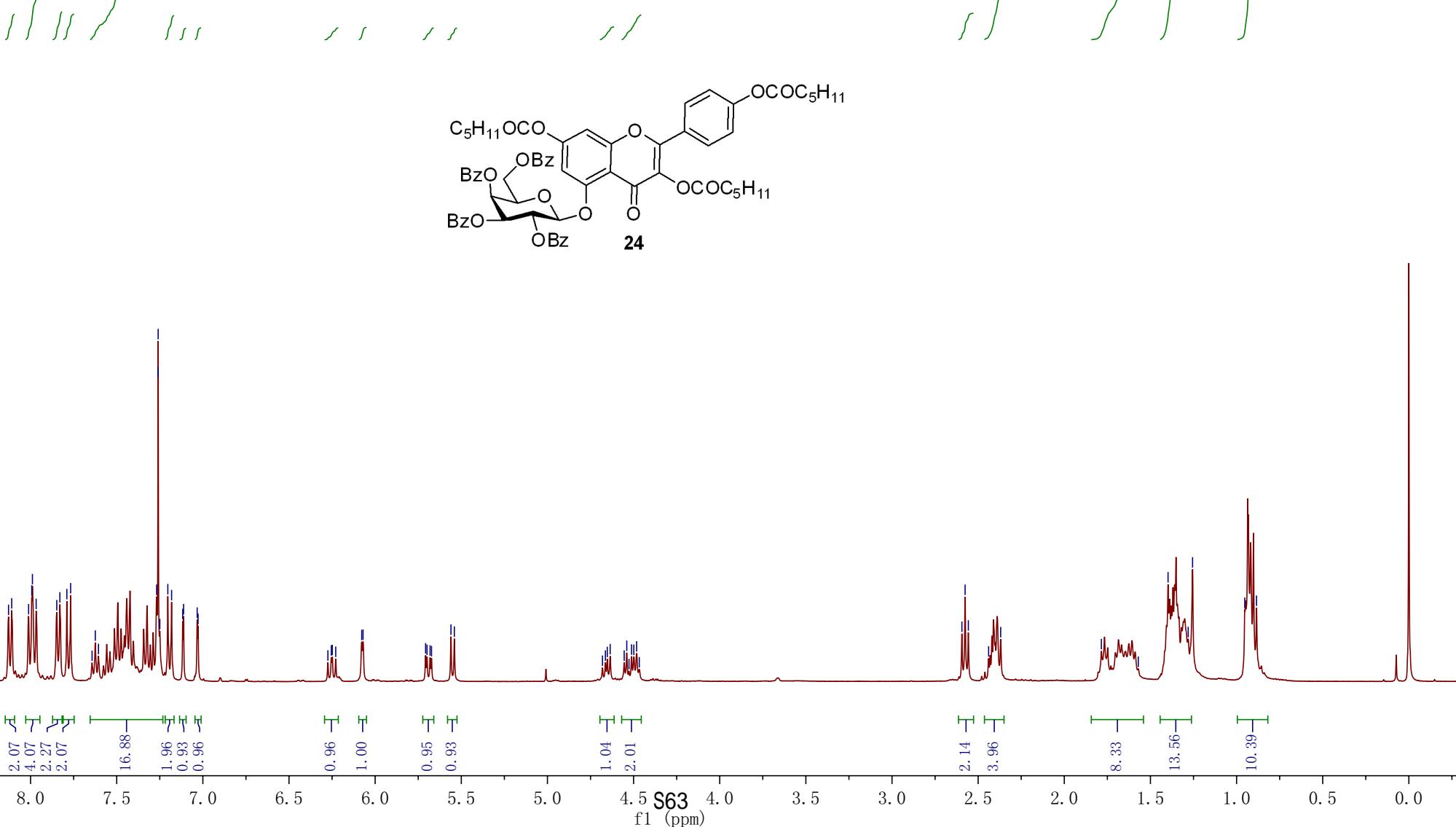
4.6805
4.6635
4.6527
4.6359
4.5545
4.5395
4.5266
4.5117
4.4987
4.4824
4.4670

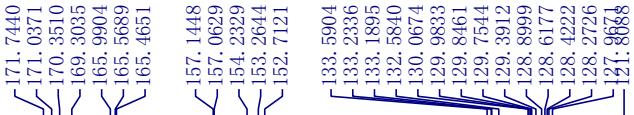
2.5943
2.5757
2.5569
2.4392
2.3691

-1.7848
-1.5705
-1.3977
-1.2808
-1.2554

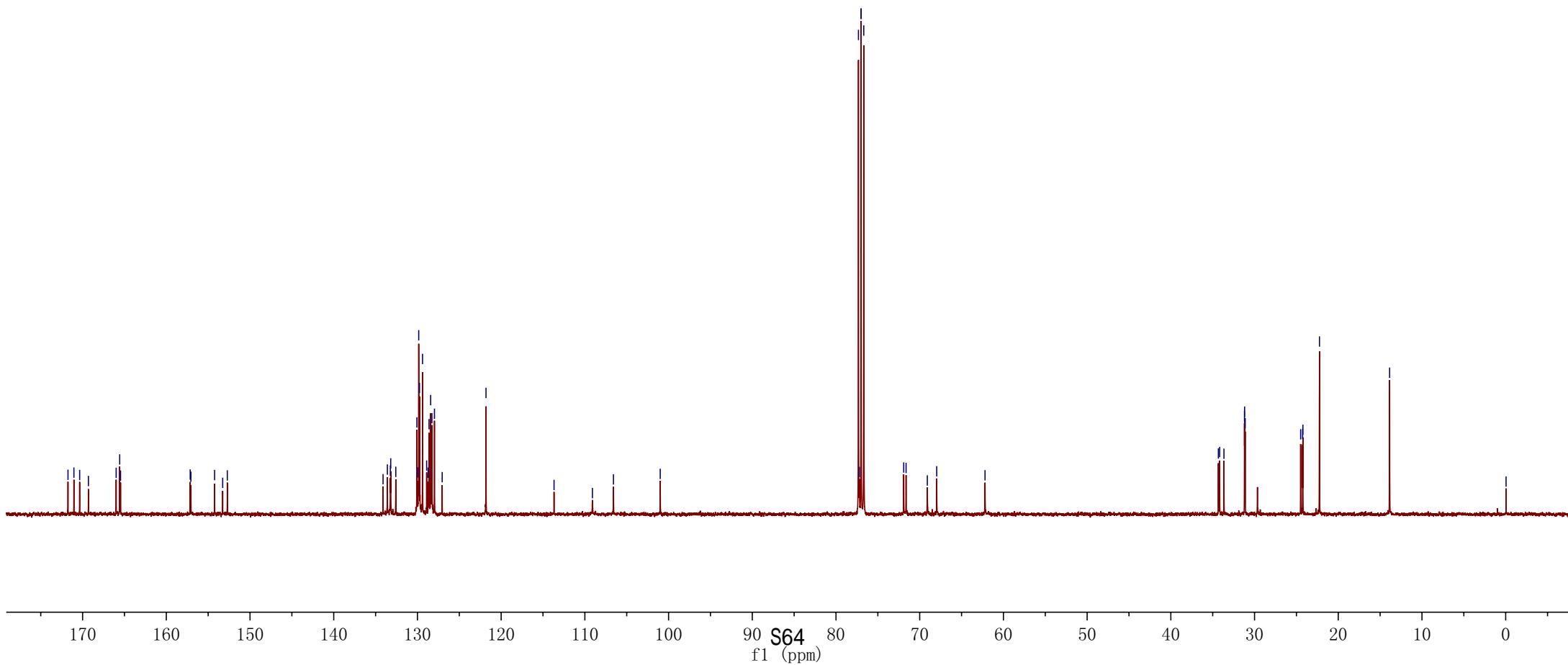
-0.9524
-0.8841

Parameter Value
Solvent CDCl₃
Experiment 1D
Spectrometer Frequency 400.13
Nucleus 1H





Parameter	Value
Solvent	CDCl ₃
Experiment	1D
Spectrometer Frequency	100.61
Nucleus	¹³ C



8.1521
8.1337
8.0459
8.0272
7.8963
7.8751
7.8607

7.6244
7.6059
7.5359
7.4879
7.4405
7.3749
7.2863
7.2600
7.2597
7.2379
7.1025
7.0980
6.9414
6.9374
6.3531
6.3361
6.3278
6.0470
5.8954
5.8130
5.7881
5.7631

Parameter	Value
Solvent	CDCl ₃
Experiment	1D
Spectrometer Frequency	400.13
Nucleus	¹ H

4.4454
4.4304
4.4148
4.4060
4.3904
4.3750

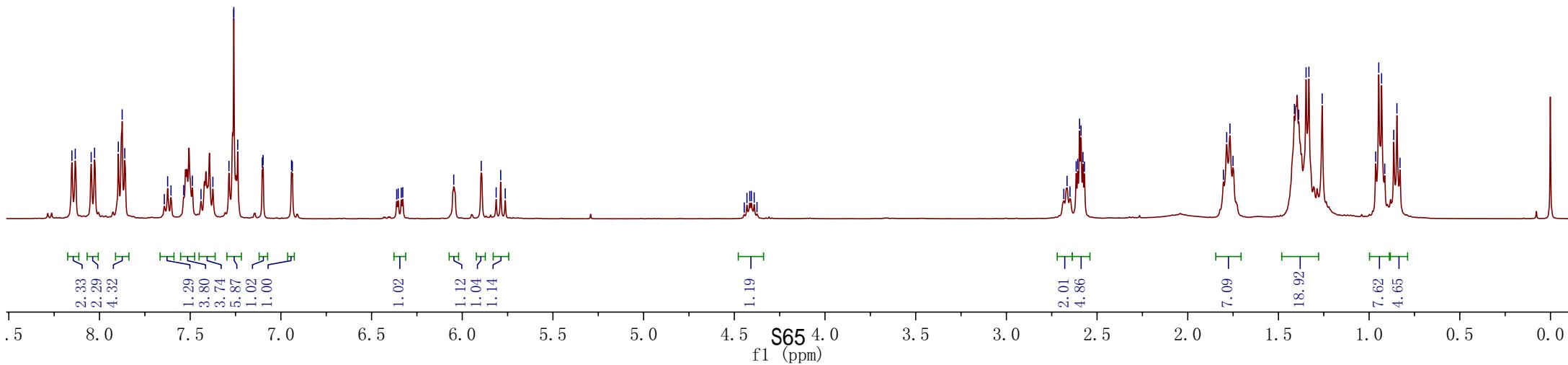
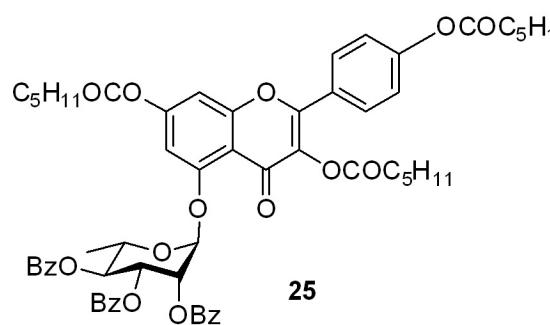
2.6834
2.6654
2.6494
2.6151
2.6069
2.5964
2.5884
2.5778
2.5696

1.8034
1.7852
1.7673
1.7505

1.4120
1.3882
1.3477
1.3321

1.2587
0.9638
0.9469
0.9313

0.9140
0.8641
0.8468
0.8297



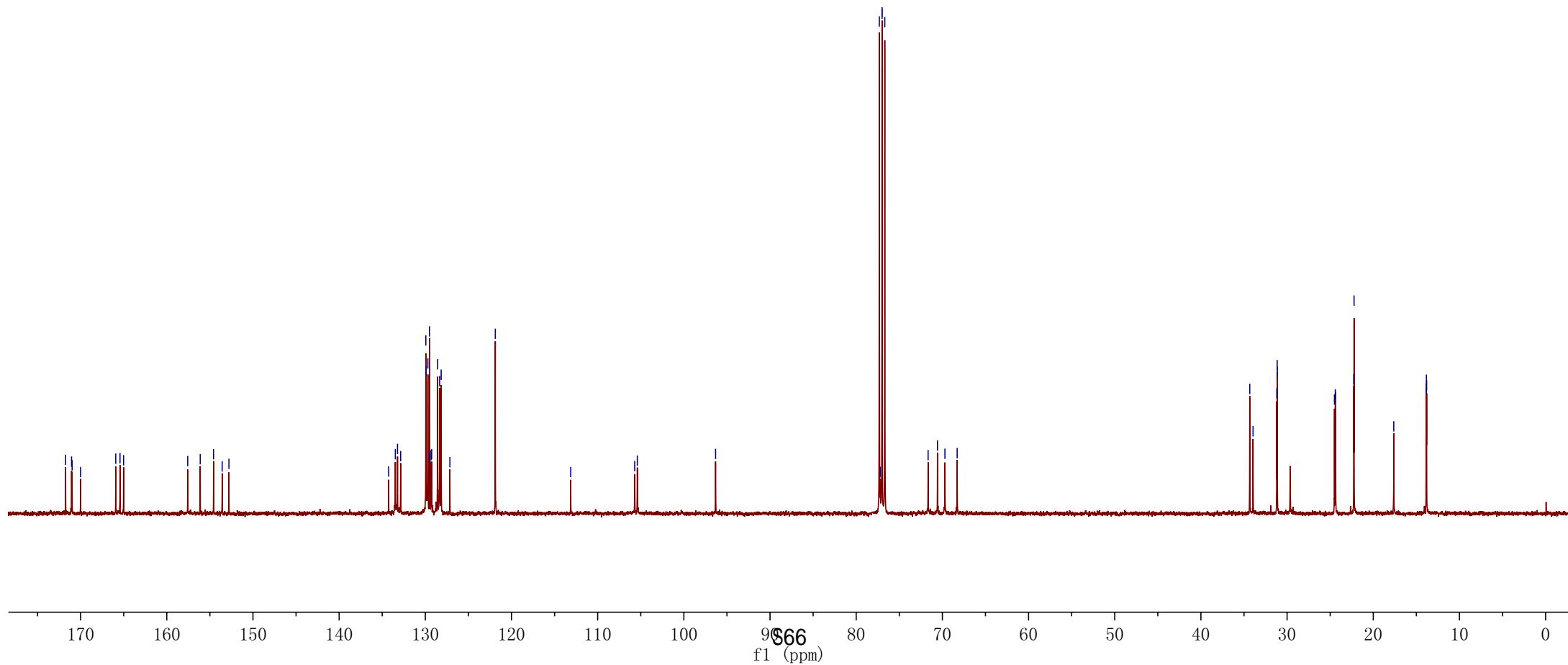
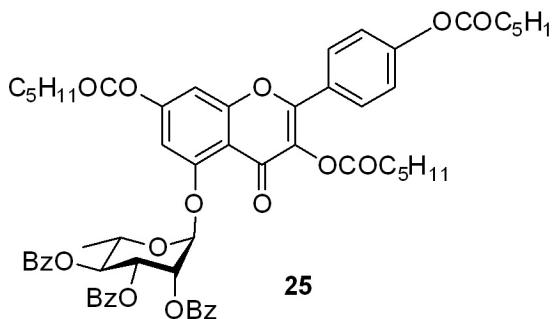
171.7405
 171.0458
 170.9825
 169.9995
 165.9218
 165.4273
 165.0125
 157.5725
 156.1173
 154.5703
 153.5722
 152.7870
 134.2525
 133.4794
 133.2239
 132.8584
 129.9380
 129.9001
 129.7029
 129.5178
 129.4560
 129.3285
 129.2614
 128.5658
 128.3365
 128.1594
 127.1473
 -121.8774

-113.1250
 -105.7013
 -105.3991
 -96.3186

77.3180
 77.2016
 77.0000
 76.9999
 76.6825
 71.6557
 70.5670
 69.7039
 68.2894

34.3325
 33.9498
 31.1964
 31.1511
 31.1380
 24.5036
 24.4071
 24.3672
 22.2635
 22.2301
 -17.6190
 -13.8569
 -13.8334
 -13.8065

Parameter	Value
Solvent	CDCl ₃
Experiment	1D
Spectrometer Frequency	100.61
Nucleus	¹³ C



8.0141
7.9961
7.9739
7.9559
7.9011
7.8832
7.8127
7.7908
7.5281
7.5095
7.3035
7.2845
7.2600
7.2194
7.1975
7.0757
7.0705
7.0345
7.0295

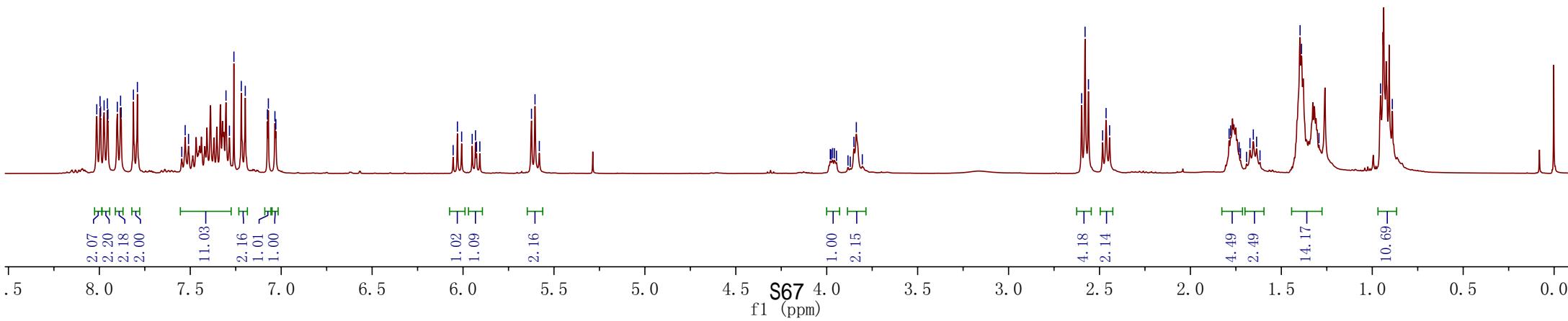
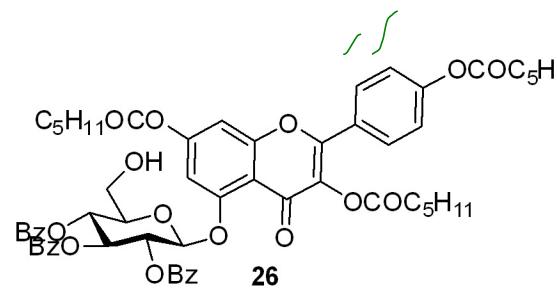
6.0544
6.0309
6.0076
5.9497
5.9316
5.9259
5.9076
5.6236
5.6043
5.5805

3.9803
3.9760
3.9678
3.9578
3.9464
3.8831
3.8705
3.8504
3.8373
3.8043

2.5981
2.5793
2.5606
2.4826
2.4637
2.4444
1.7872
1.7789
1.7321
1.7248
1.6913
1.6726
1.6541
1.6361
1.6174
1.3970
1.3890
1.2932

-0.9545
-0.8895

Parameter Value
Solvent CDCl₃
Experiment 1D
Spectrometer Frequency 400.13
Nucleus 1H



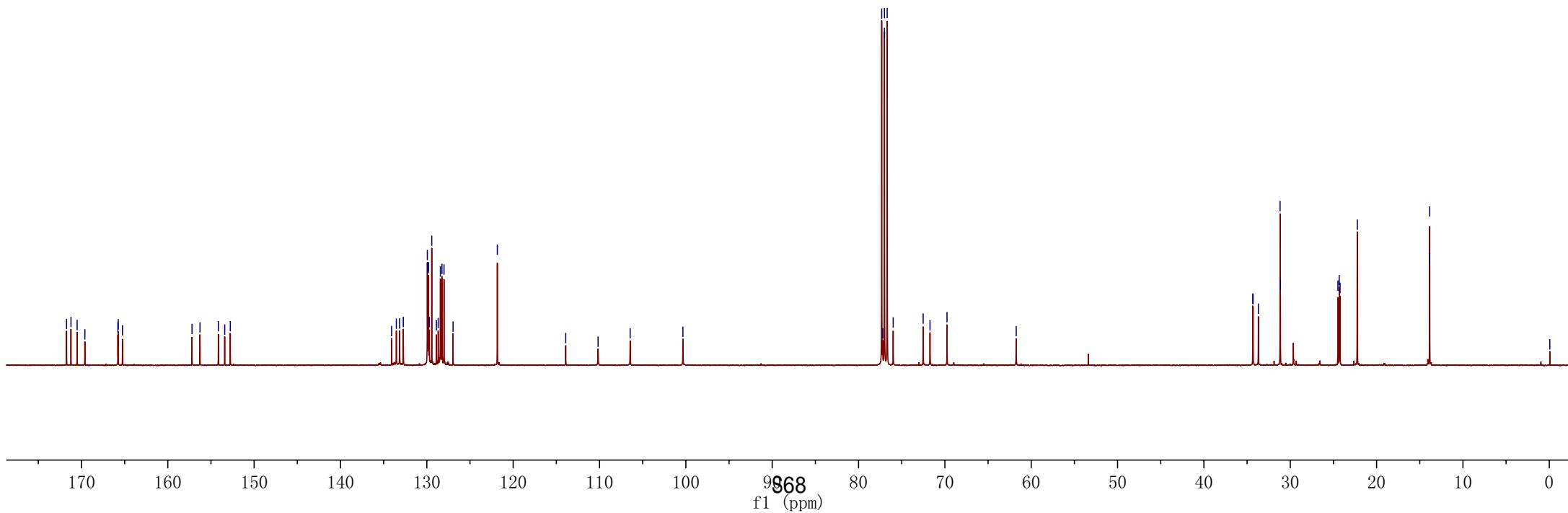
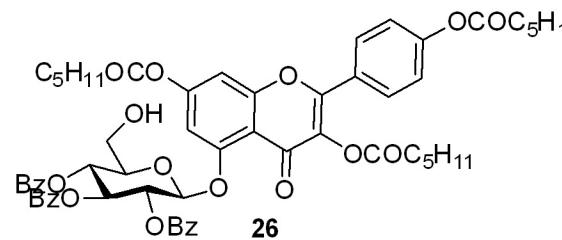
171.7250
 171.2147
 170.5001
 169.6044
 165.7806
 165.7392
 165.2463

157.1954
 156.2732
 154.1433
 153.4089
 152.7605
 134.0788
 133.5320
 133.1536
 132.7243
 129.9392
 129.8920
 129.8058
 129.7066
 129.4286
 128.8918
 128.6824
 128.4298
 128.2529
 128.0109
 126.9633
 121.8342

113.9139
 110.1672
 106.4510
 100.3416

—61.7404

Parameter	Value
Solvent	CDCl ₃
Experiment	1D
Spectrometer Frequency	100.61
Nucleus	¹³ C



—0.0580

8.0348
 8.0156
 7.9981
 7.9517
 7.9319
 7.9124
 7.5761
 7.5574
 7.7798
 7.7754
 7.7577
 7.5945
 7.5574
 7.3218
 7.3020
 7.2600
 7.2598
 7.2342
 7.1945
 7.1727
 7.0757
 7.0713
 7.0545

6.0522
 6.0295
 6.0068
 5.9405
 5.9226
 5.8997

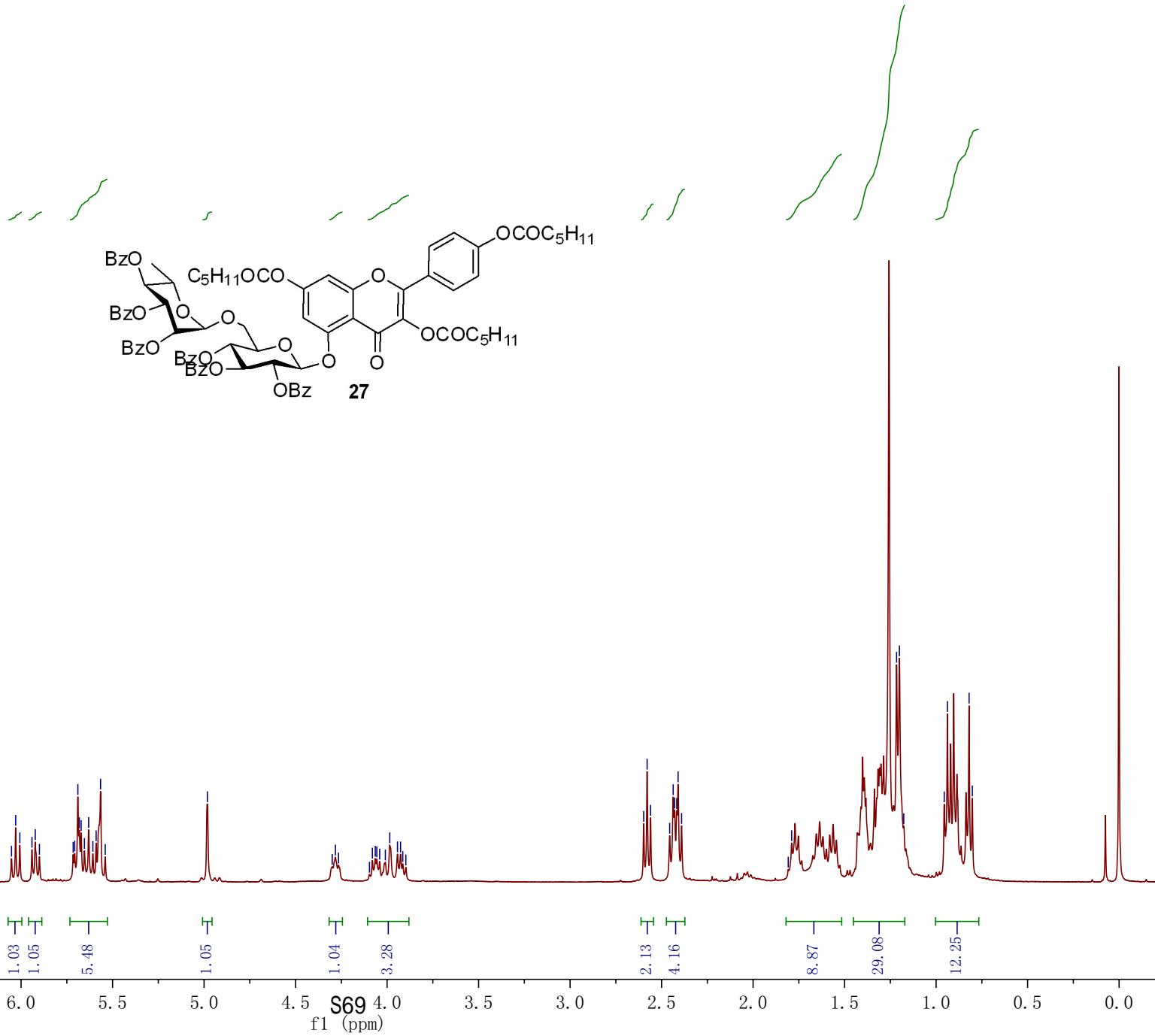
5.7069
 5.6896
 5.6817
 5.6718
 5.6537
 5.6307
 5.5897
 5.5626

4.2999
 4.2823
 4.2654
 4.0961
 4.0802
 4.0646
 4.0561
 4.0405
 4.0094
 3.9853
 3.9432
 3.9264
 3.9143
 3.8975

2.5978
 2.5792
 2.5603
 2.4558
 2.4366
 2.4288
 2.4171
 2.4098
 2.3907

1.8079
 1.2004
 1.1768
 0.9556
 0.9382
 0.8197
 0.8021

Parameter Value
 Solvent CDC13
 Experiment 1D
 Spectrometer Frequency 400.13
 Nucleus 1H



171.7526
 171.0713
 170.3930
 169.4976
 165.7403
 165.2869
 165.1303
 165.0734
 156.4302
 154.3023
 153.3050
 152.6766

133.2364
 130.0320
 129.9341
 129.8512
 129.7403
 129.6292
 129.4610
 129.2814
 128.4811
 128.4641
 128.3606
 128.2794
 128.1760
 128.9681

113.7832
 109.8452
 106.7533
 100.1736
 98.1445

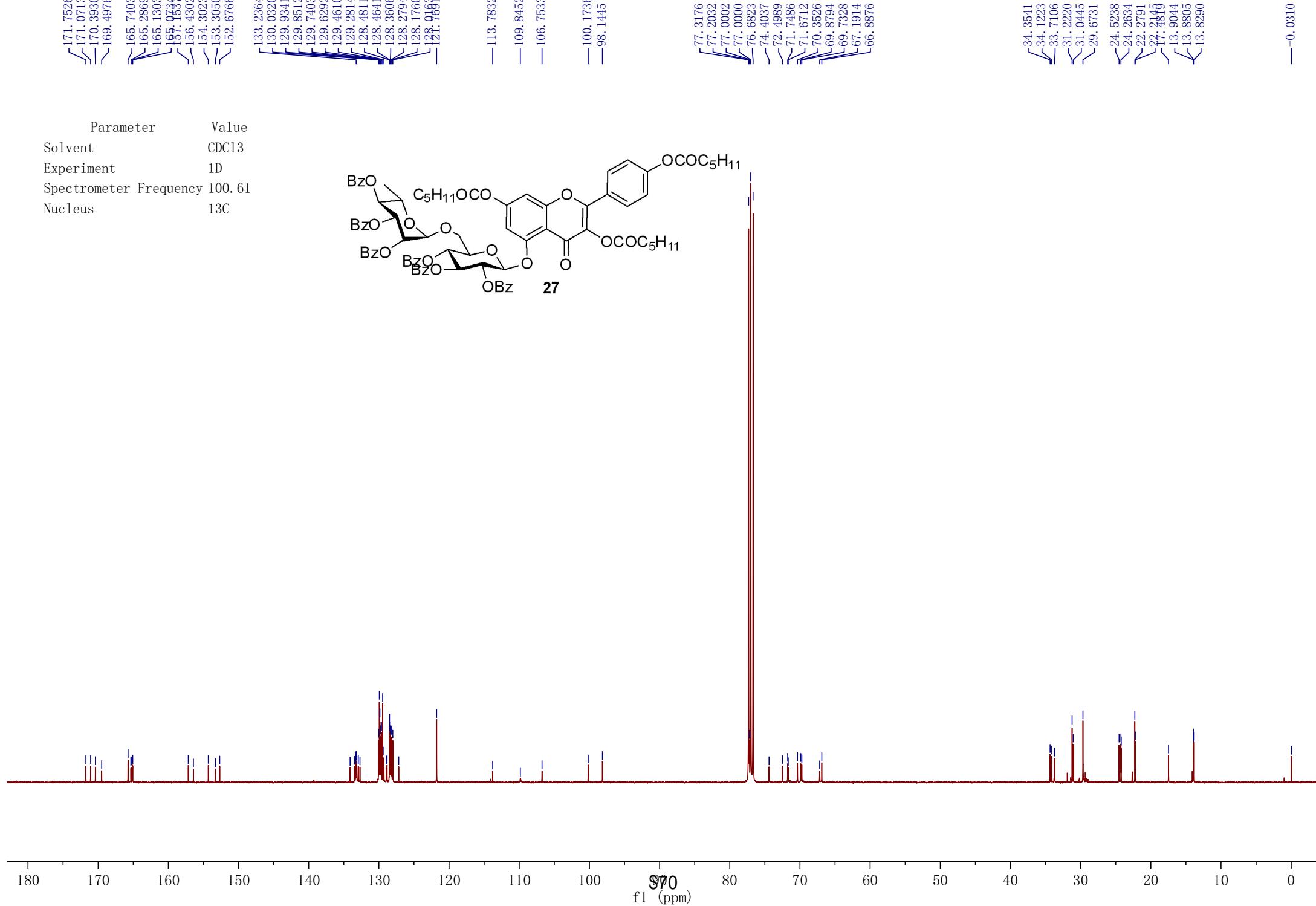
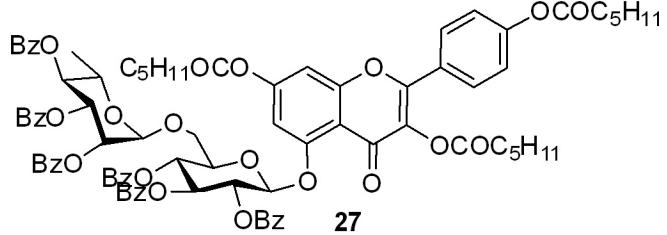
77.3176
 77.2032
 77.0002
 77.0000
 76.6823
 74.4037
 72.4989
 71.7486
 71.6712
 70.3526
 69.8794
 68.7328
 67.1914
 66.8876

34.3541
 34.1223
 33.7106
 31.2220
 31.0445
 29.6731

24.5238
 24.2634
 22.2791
 17.4845
 13.9044
 13.8805
 13.8290

-0.0310

Parameter	Value
Solvent	CDCl ₃
Experiment	1D
Spectrometer Frequency	100.61
Nucleus	¹³ C



8.0618
8.0427
8.0240
7.9605
7.9447
7.9243

7.4638
7.4449
7.4259
7.2984
7.2600
7.2595
7.0699
6.9869
6.8676
6.6759
6.6494

6.0881
6.0642
6.0457
6.0215
5.7603
5.7382
5.7138
5.6956

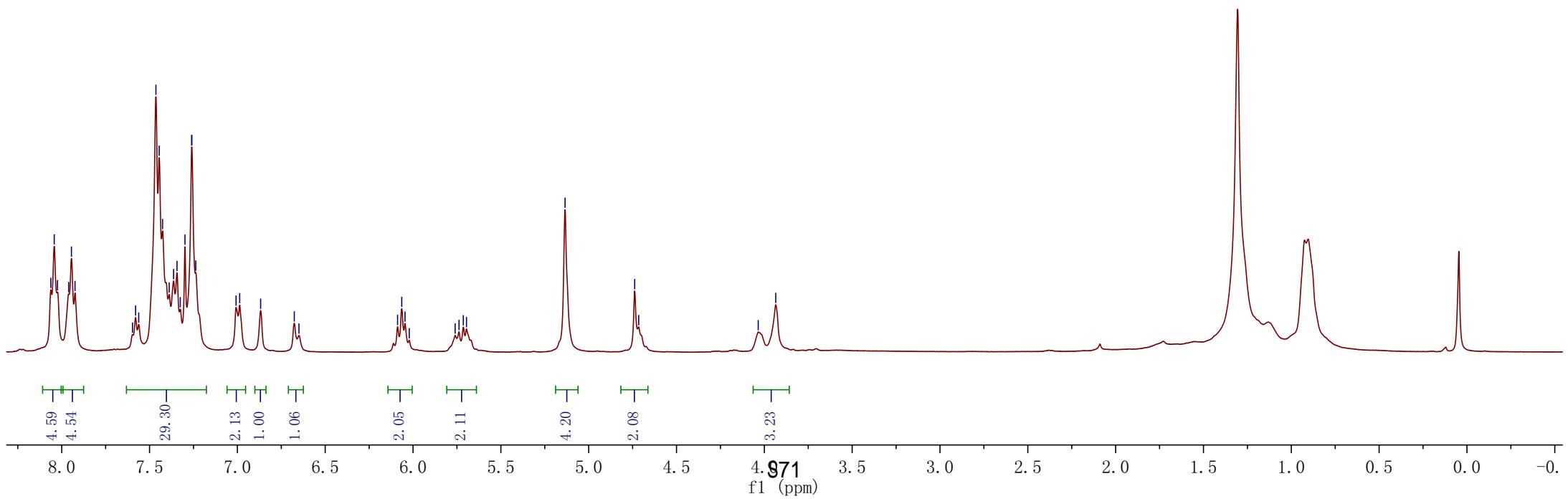
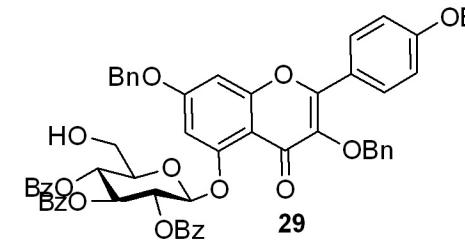
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4.7381
4.7152

-4.0348
-3.9350

Parameter
Solvent
Experiment
Spectrometer
Nucleus

Value
CDCl₃
1D
Frequency 400.13
1H



—172.6957

—165.8647
—165.6030
—165.0464
—162.2862
—160.0508
—157.6589
—157.3715

—152.8791
—139.1770
—136.8842
—136.3779
—135.8555
—133.3375
—133.0271
—129.9181
—129.8258
—129.7875
—128.9662
—128.8861
—128.7976
—128.5149
—128.3391
—128.1897
—128.1126
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—127.9294
—127.7417
—127.6310
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—114.3120

—110.2843

—102.0678

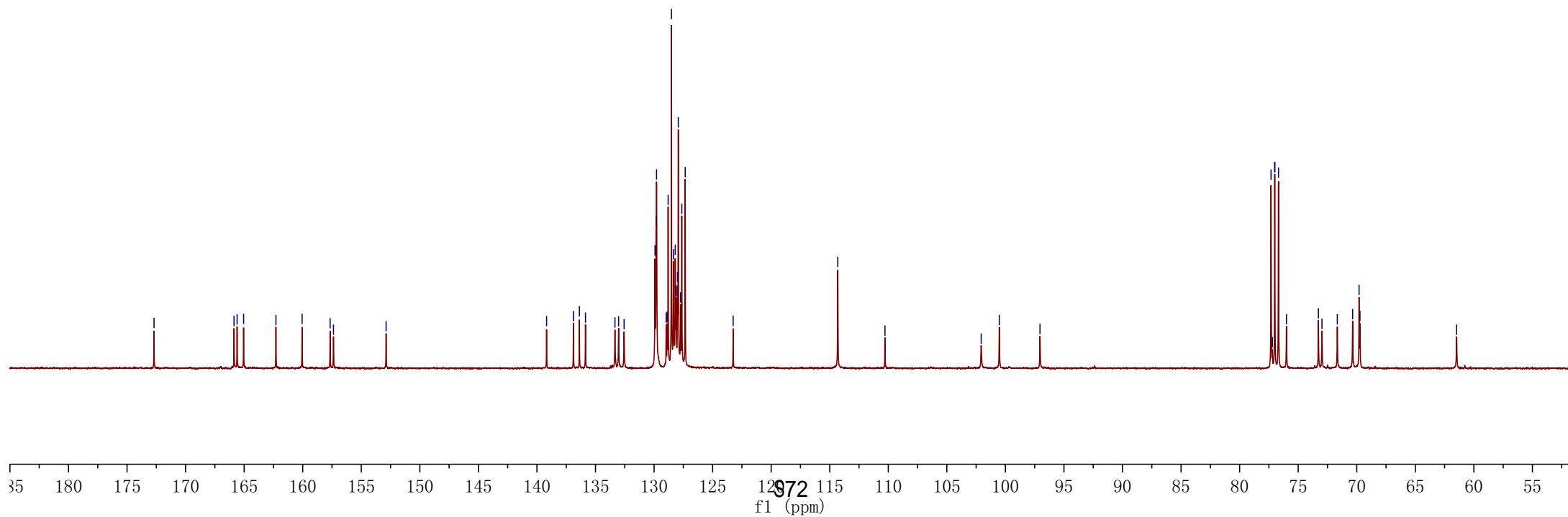
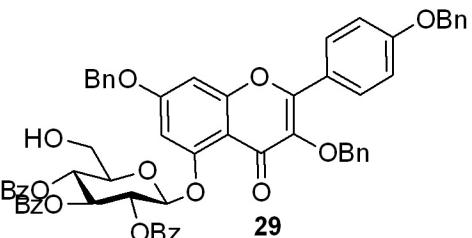
—100.5206

—97.0460

—77.3181
—77.2025
—77.0000
—76.9999
—76.6817
—76.0008
—73.2737
—72.9685
—71.6586
—70.3508
—69.8023
—69.7257

—61.4706

Parameter	Value
Solvent	CDCl ₃
Experiment	1D
Spectrometer Frequency	100.61
Nucleus	¹³ C

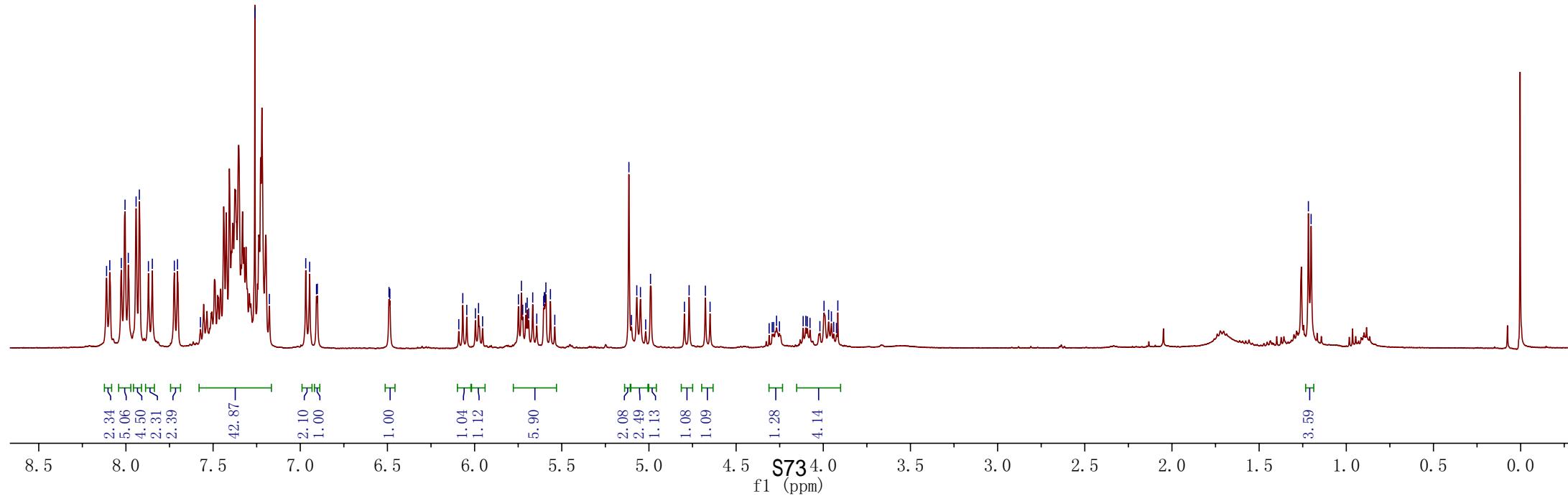
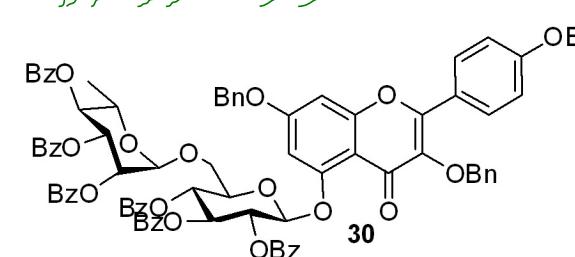


Parameter	Value
Solvent	CDCl3
Experiment	1D
Spectrometer Frequency	400.13
Nucleus	1H

6. 4909
6. 4860
6. 0908
6. 0677
6. 0448
5. 9953
5. 9774
5. 9541

5.7313	5.6666	5.5911	5.5650
5.6002	5.5486	5.4989	5.4677
5.5600	5.5086	5.4605	5.4295
5.5200	5.4686	5.4195	5.3884
5.4800	5.4166	5.3675	5.3364
5.4400	5.3866	5.3375	5.3064
5.4000	5.3486	5.2995	5.2684
5.3600	5.3086	5.2595	5.2284
5.3200	5.2686	5.2195	5.1884
5.2800	5.2286	5.1795	5.1484
5.2400	5.1886	5.1395	5.1084
5.2000	5.1486	5.0995	5.0684
5.1600	5.1086	5.0595	5.0284
5.1200	5.0686	5.0195	4.9884
5.0800	5.0286	4.9795	4.9484
5.0400	4.9886	4.9395	4.9084
5.0000	4.9486	4.8995	4.8684
4.9600	4.9086	4.8595	4.8284
4.9200	4.8686	4.8195	4.7884
4.8800	4.8286	4.7795	4.7484
4.8400	4.7886	4.7395	4.7084
4.8000	4.7486	4.6995	4.6684
4.7600	4.7086	4.6595	4.6284
4.7200	4.6686	4.6195	4.5884
4.6800	4.6286	4.5795	4.5484
4.6400	4.5886	4.5395	4.5084
4.6000	4.5486	4.4995	4.4684
4.5600	4.5086	4.4595	4.4284
4.5200	4.4686	4.4195	4.3884
4.4800	4.4286	4.3795	4.3484
4.4400	4.3886	4.3395	4.3084
4.4000	4.3486	4.2995	4.2684
4.3600	4.3086	4.2595	4.2284
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4.2800	4.2286	4.1795	4.1484
4.2400	4.1886	4.1395	4.1084
4.2000	4.1486	4.0995	4.0684
4.1600	4.1086	4.0595	4.0284
4.1200	4.0686	4.0195	3.9884
4.0800	4.0286	3.9795	3.9484
4.0400	3.9886	3.9395	3.9084
4.0000	3.9486	3.8995	3.8684
3.9600	3.9086	3.8595	3.8284
3.9200	3.8686	3.8195	3.7884
3.8800	3.8286	3.7795	3.7484
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3.8000	3.7486	3.6995	3.6684
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3.2800	3.2286	3.1795	3.1484
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3.1600	3.1086	3.0595	3.0284
3.1200	3.0686	3.0195	2.9884
3.0800	3.0286	2.9795	2.9484
3.0400	2.9886	2.9395	2.9084
3.0000	2.9486	2.8995	2.8684
2.9600	2.9086	2.8595	2.8284
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2.0400	1.9886	1.9395	1.9084
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1.9200	1.8686	1.8195	1.7884
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1.8400	1.7886	1.7395	1.7084
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1.7600	1.7086	1.6595	1.6284
1.7200	1.6686	1.6195	1.5884
1.6800	1.6286	1.5795	1.5484
1.6400	1.5886	1.5395	1.5084
1.6000	1.5486	1.4995	1.4684
1.5600	1.5086	1.4595	1.4284
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1.2400	1.1886	1.1395	1.1084
1.2000	1.1486	1.0995	1.0684
1.1600	1.1086	1.0595	1.0284
1.1200	1.0686	1.0195	0.9884
1.0800	1.0286	0.9795	0.9484
1.0400	0.9886	0.9395	0.9084
1.0000	0.9486	0.8995	0.8684
0.9600	0.9086	0.8595	0.8284
0.9200	0.8686	0.8195	0.7884
0.8800	0.8286	0.7795	0.7484
0.8400	0.7886	0.7395	0.7084
0.8000	0.7486	0.6995	0.6684
0.7600	0.7086	0.6595	0.6284
0.7200	0.6686	0.6195	0.5884
0.6800	0.6286	0.5795	0.5484
0.6400	0.5886	0.5395	0.5084
0.6000	0.5486	0.4995	0.4684
0.5600	0.5086	0.4595	0.4284
0.5200	0.4686	0.4195	0.3884
0.4800	0.4286	0.3795	0.3484
0.4400	0.3886	0.3395	0.3084
0.4000	0.3486	0.2995	0.2684
0.3600	0.3086	0.2595	0.2284
0.3200	0.2686	0.2195	0.1884
0.2800	0.2286	0.1795	0.1484
0.2400	0.1886	0.1395	0.1084
0.2000	0.1486	0.0995	0.0684
0.1600	0.1086	0.0595	0.0284
0.1200	0.0686	0.0195	-0.0284
0.0800	0.0286	-0.0395	-0.0684
0.0400	-0.0186	-0.0795	-0.1084
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-1- 2174



—172.7394

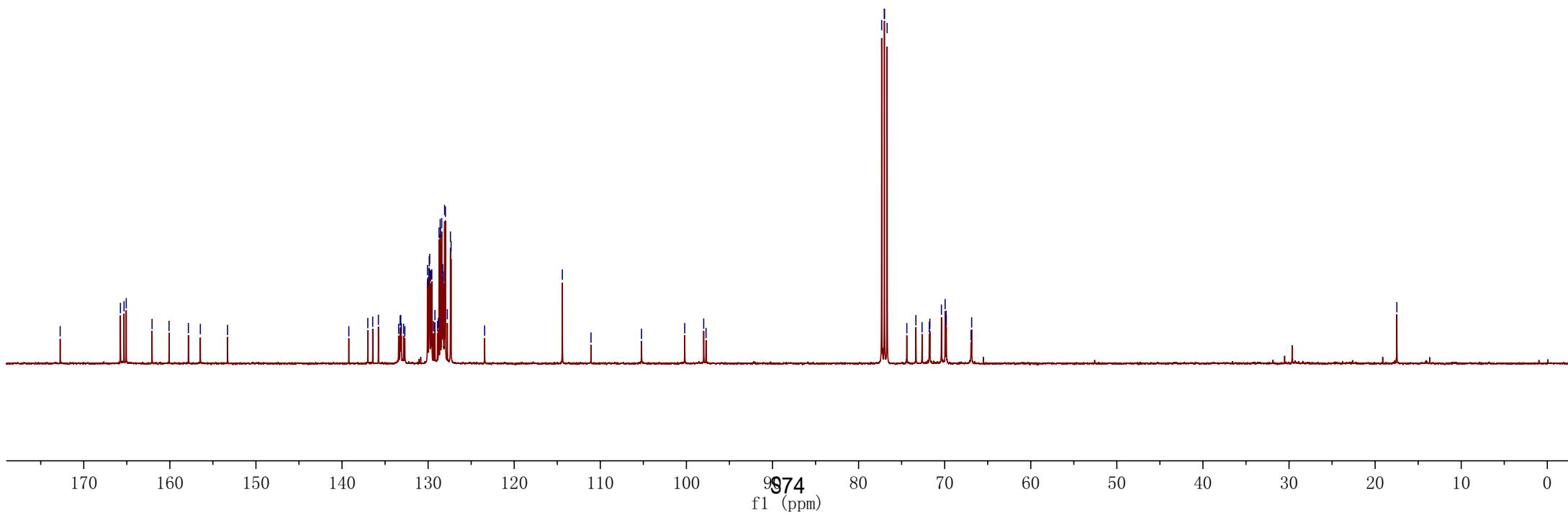
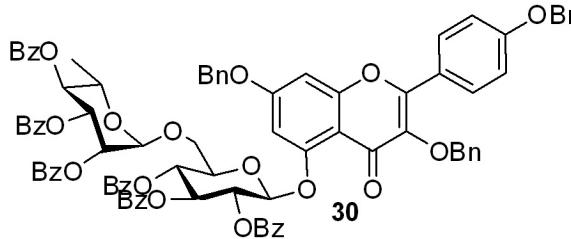
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129.6994
129.5704
128.7310
128.5980
128.5665
128.4197
128.3088
128.0852
127.9891
127.4068
123.2348

Parameter	Value
Solvent	CDCl ₃
Experiment	1D
Spectrometer Frequency	100.61
Nucleus	¹³ C

—114.4094
—111.0813
—105.2124
—100.1942
—97.9898
—97.7162

77.3183
77.0001
77.0000
76.6823
74.3950
73.3397
72.6249
71.7868
71.7184
70.3764
69.9483
69.8386
69.8112
66.9328
66.8666

—17.4748



7.8595

7.8376

7.2600
7.2595
7.2484
7.2265
7.1468
7.1419
6.9171
6.9123

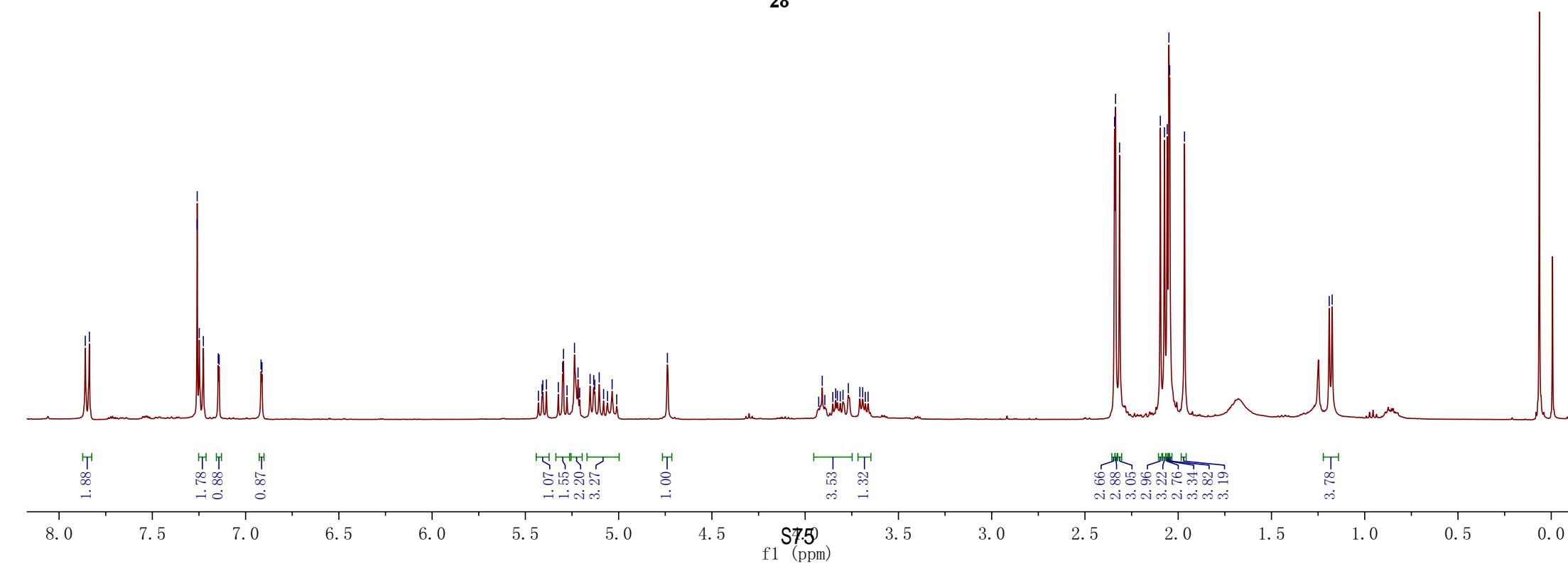
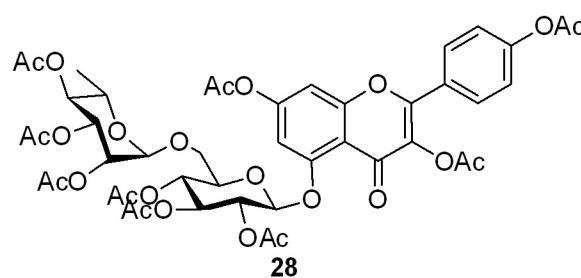
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5.2957
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5.2367
5.2178
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5.1336
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5.1041
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5.0595
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4.7385

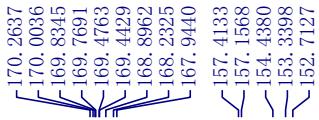
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3.8118
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3.6915
3.6775
3.6627

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2.0455
1.9661

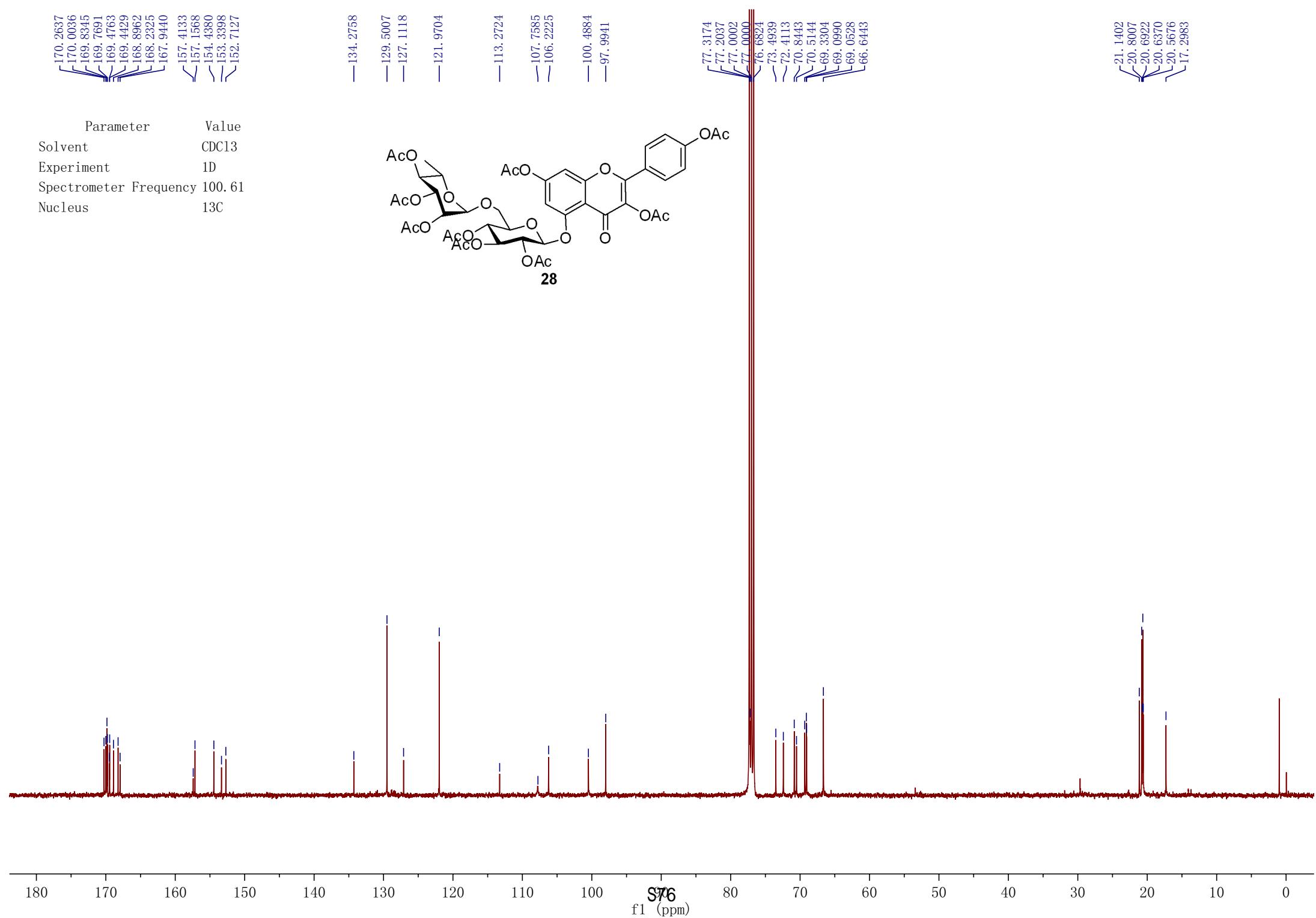
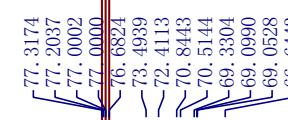
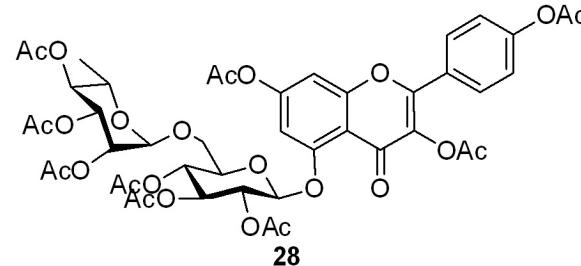
1.1902
1.1746

Parameter	Value
Solvent	CDCl ₃
Experiment	1D
Spectrometer Frequency	400.13
Nucleus	¹ H





Parameter	Value
Solvent	CDCl ₃
Experiment	1D
Spectrometer Frequency	100.61
Nucleus	¹³ C



—129.5010

—121.9733

—106.2254

—100.4856

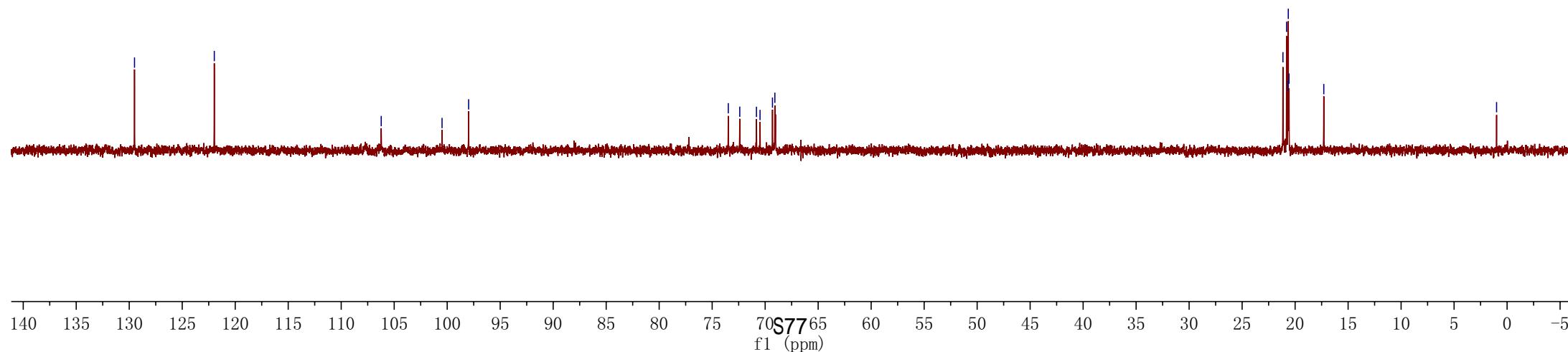
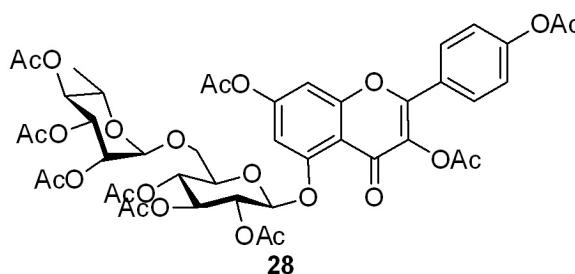
—97.9785

Parameter	Value
Solvent	CDCl ₃
Experiment	1D-DEPT-135
Spectrometer Frequency	100.61
Nucleus	¹³ C

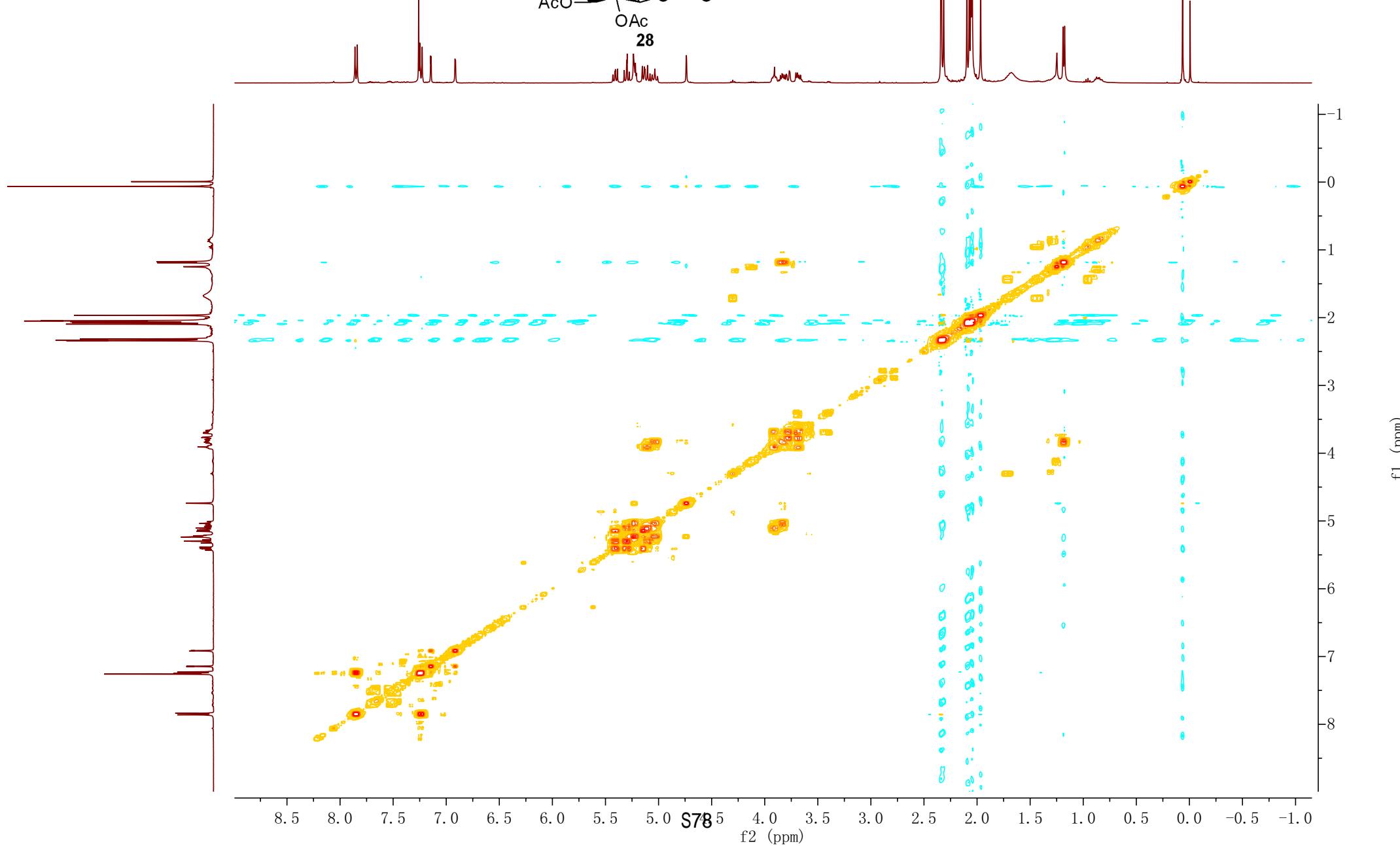
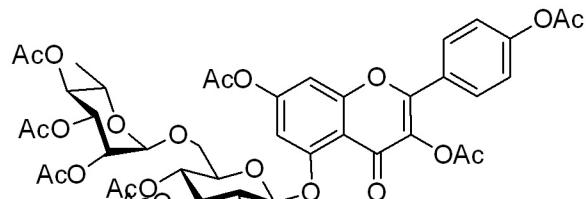
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69.0852

21.1489
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—17.2940

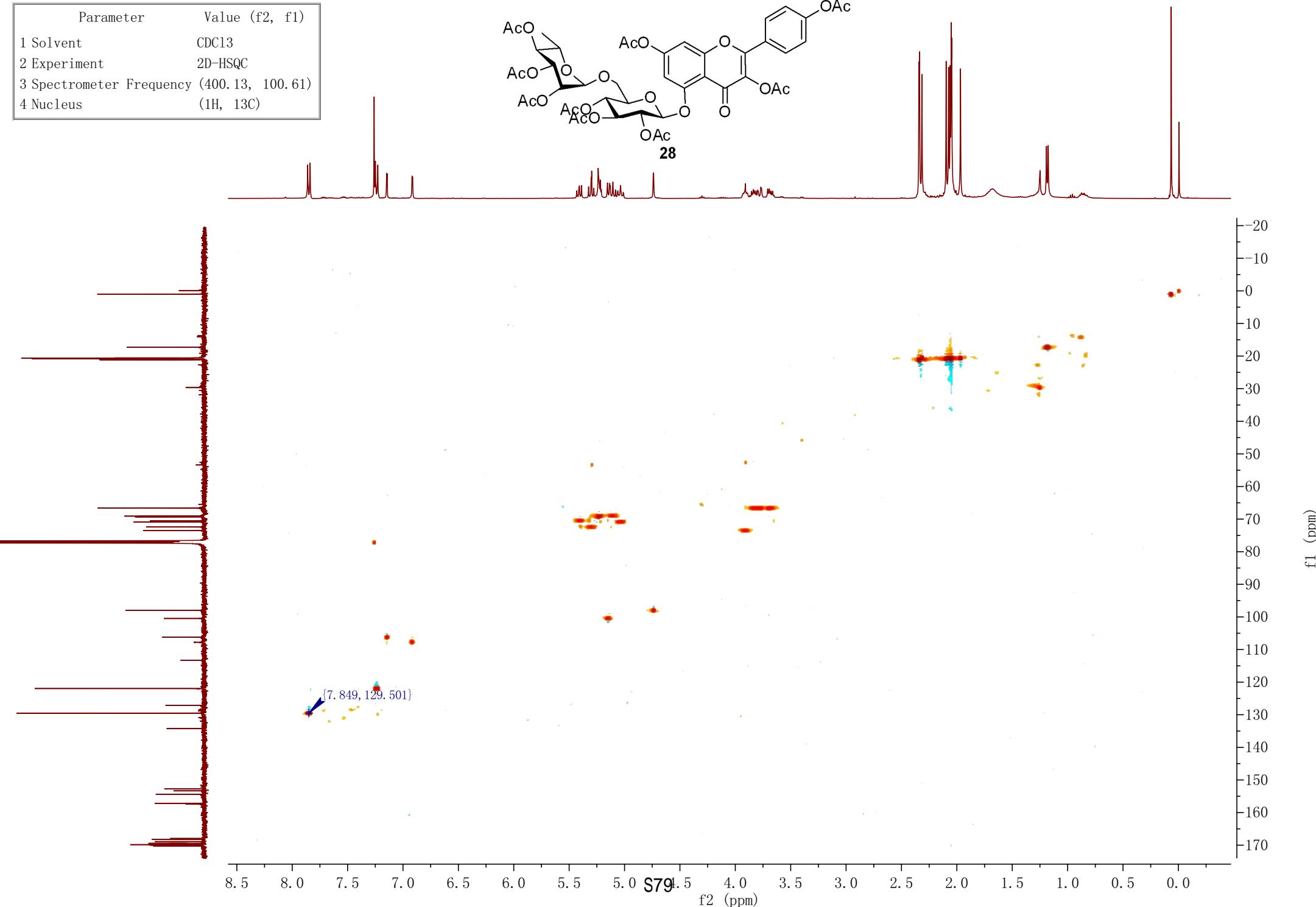
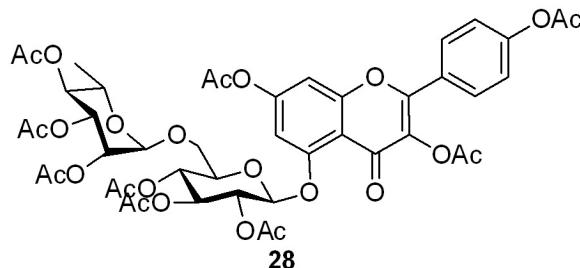
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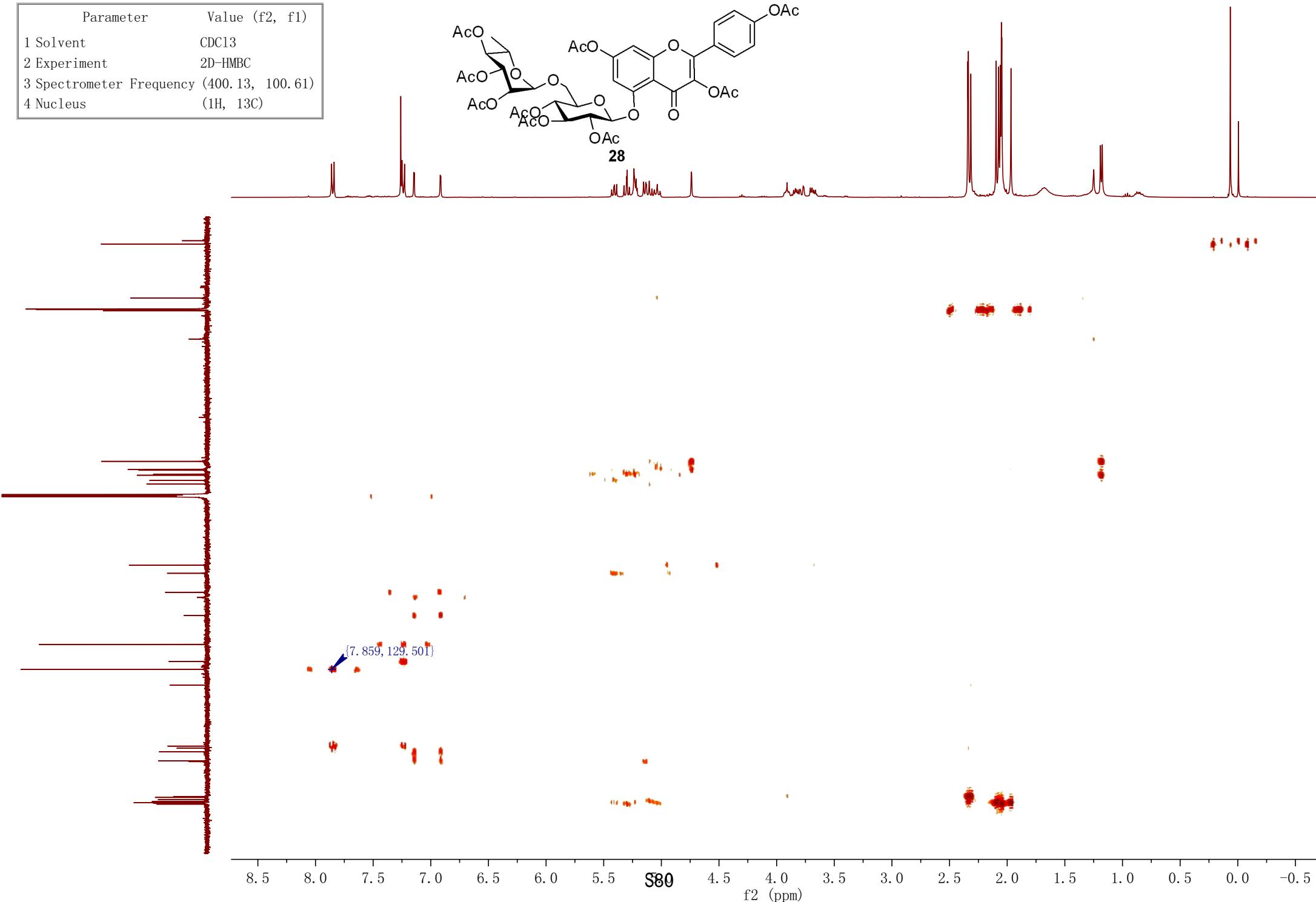
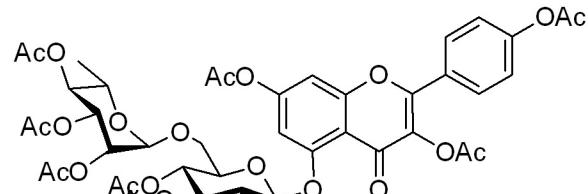
Parameter	Value (f2, f1)
1 Solvent	CDCl ₃
2 Experiment	2D-COSY
3 Spectrometer Frequency	(400.13, 400.13)
4 Nucleus	(¹ H, ¹ H)



Parameter	Value (f2, f1)
1 Solvent	CDCl ₃
2 Experiment	2D-HSQC
3 Spectrometer Frequency (400.13, 100.61)	(¹ H, ¹³ C)
4 Nucleus	



Parameter	Value (f2, f1)
1 Solvent	CDCl ₃
2 Experiment	2D-HMBC
3 Spectrometer Frequency (400.13, 100.61)	(¹ H, ¹³ C)
4 Nucleus	



Parameter	Value (f2, f1)
1 Solvent	CDCl ₃
2 Experiment	2D-NOESY
3 Spectrometer Frequency	(400.13, 400.13)
4 Nucleus	(¹ H, ¹ H)

