Supporting Information (SI)

Practical Aqueous Reactions Leading to Skeletally Diverse Carbohydrate-derived Ketones

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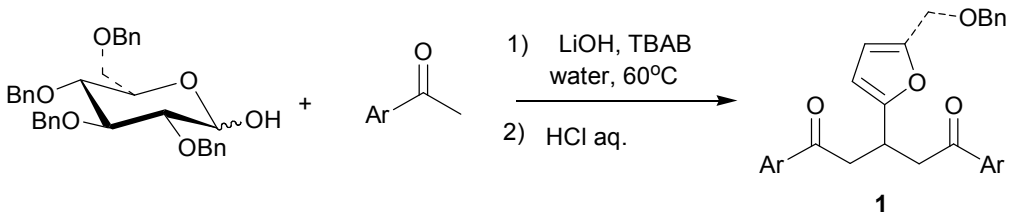
General experimental information:

All of the chemicals were obtained from commercial sources or prepared according to standard methods. NMR spectra were recorded with a 600 MHz spectrometer for ^{1}H NMR, 151 MHz for ^{13}C NMR using TMS as an internal standard. Chemical shifts (δ) are reported relative to TMS (^{1}H) or $CDCl_3$ (^{13}C). Multiplicities are reported as follows: singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), dd (doublet of doublets) and dt (doublet of triplets). Coupling constants were reported in Hertz (Hz). Melting points were recorded with a micro melting point apparatus. Optical rotations were determined using an Autopol IV automatic polarimeter. Infrared analyses (KBr pellet) were performed by FT-IR. High resolution spectra (HRMS) were recorded on a QTOF mass analyzer with electrospray ionization (ESI).

General procedure for all products

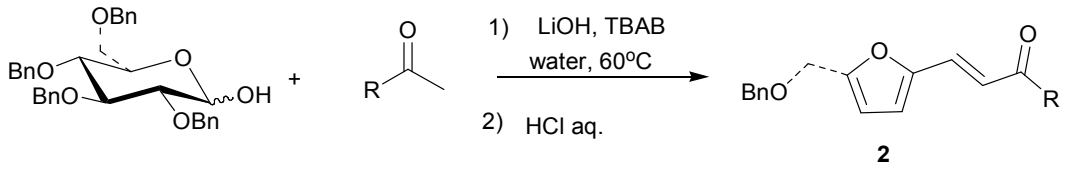
General procedure for the synthesis of furanyl-substituted diketone 1 and furanyl-substituted α,β-unsaturated ketones 2:



1

To a 10 mL test tube were added aldosyl hemiacetal (0.25 mmol), methyl ketone (6 equiv), LiOH (2 equiv), TBAB (1 equiv) and water (0.5 mL). The mixture was stirred and heated at 60 °C for 15 min and TLC indicated completion of the first step. Then 10% HCl aq. (2.5 equiv) was added to the test tube, which was kept at 60 °C until TLC indicated completion of the reaction (**1a-f** 8 h, **1g**, **1h** 32 h). The reaction was stopped and in-tube extracted with ethyl acetate (3 x 2 mL), dried over Na_2SO_4 and purified on a silica gel pad (eluted with petroleum ether/ethyl acetate) to give products **1a-1h**. Compounds **1a** and **1f** are known.[1]

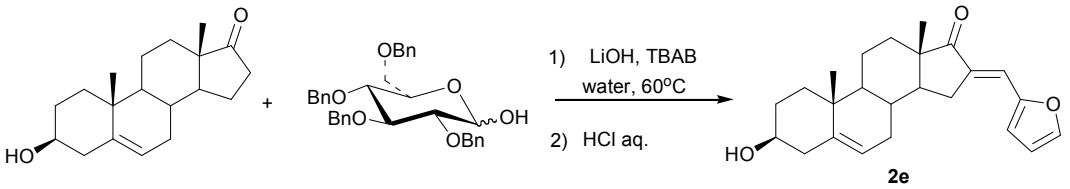
The synthesis of **1a** starting from 10 g of O-benzyl-protected D-xylosyl hemiacetal was performed in a 100 mL round-bottom flask in the same conditions yielding **1a** (6.5 g, 86%, t_1: 0.33 h, t_2: 9 h).



2

To a 10 mL test tube were added aldosyl hemiacetal (0.25 mmol), methyl ketone (3 equiv), LiOH (2 equiv), TBAB (1 equiv) and water (0.5 mL). The mixture was stirred and heated at 60 °C for 15 min and TLC indicated completion of the first step. Then 10% HCl aq. (2.5 equiv) was added to the test tube, which was kept at 60 °C until TLC indicated completion of the reaction (**2a, 2c** 2 h, **2b**, **2d** 20 h). The reaction was stopped and in-tube extracted with ethyl acetate (3 x 2 mL), dried over Na_2SO_4 and purified on a silica gel pad (eluted with petroleum ether/ethyl acetate) to give products **2a-2d**. Compounds **2a**[2] and **2c**[3] are known.

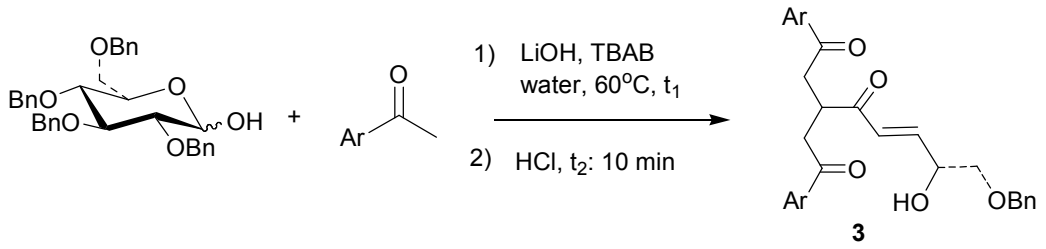
The synthesis of **2b** starting from 10 g of O-benzyl-protected D-glucosyl hemiacetal was performed in a 100 mL round-bottom flask in the same conditions yielding **2b** (4.63 g, 84%, t_1: 0.33 h, t_2: 22 h).



2e

To a 10 mL test tube were added 3β-hydroxyandrost-5-en-17-one (0.25 mmol), aldosyl hemiacetal (1.2 equiv), LiOH (2 equiv), TBAB (1 equiv) and water (0.5 mL). The mixture was stirred and heated at 60 °C for 1.5 h. Then more aldosyl hemiacetal (1 equiv) was added. After 0.5 h, TLC indicated completion of the first step. Then 10% HCl aq. (2.5 equiv) was added and the reaction was stirred at 60 °C until TLC indicated completion of the reaction (2 h). The reaction was stopped and in-tube extracted with ethyl acetate (3 x 2 mL), dried over Na_2SO_4 and purified on a silica gel pad (eluted with petroleum ether/ethyl acetate) to give product **2e**. Compound **2e** is known.[4]

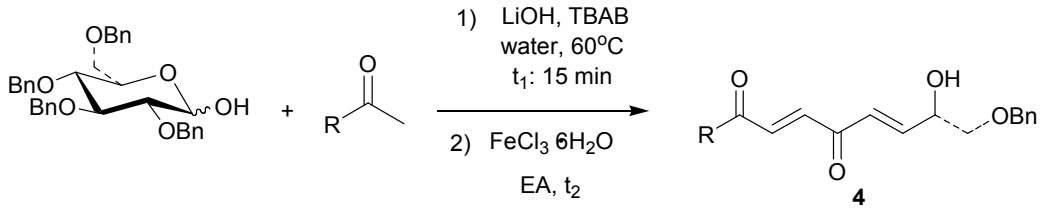
General procedure for the synthesis of enetriketone 3:



To a 10 mL test tube were added aldosyl hemiacetal (0.25 mmol), methyl ketone (6 equiv), LiOH (2 equiv), TBAB (1 equiv) and water (0.5 mL). The mixture was stirred and heated at 60 °C for 15 min and TLC indicated completion of the first step. Then 10% HCl aq. (2.1 equiv) was added to the test tube, which was kept at 60 °C for 10 min. The reaction was stopped and in-tube extracted with ethyl acetate (3 x 2 mL), dried over Na_2SO_4 and purified on a silica gel pad (eluted with petroleum ether/ethyl acetate) to give products **3a-3o**.

The synthesis of **3a** starting from 10 g of O-benzyl-protected D-xylosyl hemiacetal was performed in a 100 mL round-bottom flask in the same conditions yielding **3a** (7.04 g, 88%, t_1: 0.33 h, t_2: 0.25 h).

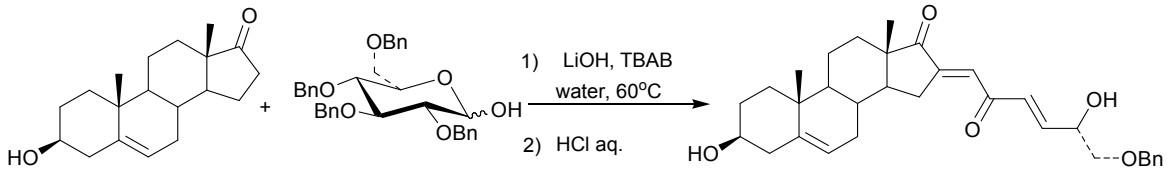
General procedure for the synthesis of dienediketone 4:



To a 10 mL test tube were added aldosyl hemiacetal (0.25 mmol), methyl ketone (3 equiv), LiOH (2 equiv), TBAB (1 equiv) and water (0.5 mL). The mixture was heated and stirred at 60 °C for 15 min and TLC indicated completion of the reaction. The reaction was in-tube extracted with ethyl acetate (3 x 2 mL), dried over Na_2SO_4. After concentration to about 2 mL, $FeCl_3$•$6H_2O$ (1.5 equiv for **4a**, **4c**, **4e**, **4g**, 1.0 equiv for **4b**, **4d**, **4f**) was added to the ethyl acetate solution, which was stirred at rt for a certain period (**4a** 1.5 h, **4b** 3.5 h, **4c** 2 h, **4d** 5 h, **4e** 1.5 h, **4f** 4 h, **4g** 0.25 h). The reaction was stopped by addition of Na_2CO_3 (5 equiv) under stirring. Then the solution was

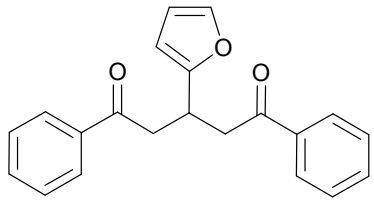
filtered and the filtrate was purified on a silica gel pad (eluted with petroleum ether/ethyl acetate) to give products **4a-4g**.

The synthesis of **4b** starting from 10 g of O-benzyl-protected D-glucosyl hemiacetal was performed in a 100 mL round-bottom flask in the same conditions yielding **4b** (5.09 g, 87%, t_1: 0.33 h, t_2: 4 h).



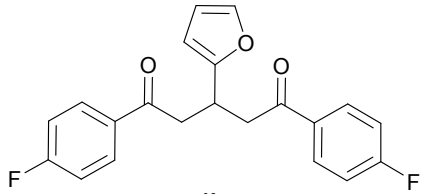
To a 10 mL test tube were added 3β-hydroxyandrost-5-en-17-one (0.25 mmol), aldosyl hemiacetal (1.2 equiv), LiOH (2 equiv), TBAB (1 equiv) and water (0.5 mL). The mixture was heated and stirred at 60 °C for a certain period (**4h** 1.5 h, **4i** 2 h), then more aldosyl hemiacetal (1 equiv) was added. After 0.5 h, TLC indicated completion of the reaction, which was in-tube extracted with ethyl acetate (3 x 2 mL), dried over Na_2SO_4. After concentration to about 2 mL, $FeCl_3$•$6H_2O$ (1.5 equiv for **4h**, 1.0 equiv for **4i**) was added to the ethyl acetate solution, which was stirred at rt for a certain period (**4h** 2 h, **4i** 4 h). The reaction was stopped by addition of Na_2CO_3 (5 equiv) under stirring. Then the solution was filtered and the filtrate was purified on a silica gel pad (eluted with petroleum ether/ethyl acetate) to give products **4h** and **4i**.

Spectral data for all products



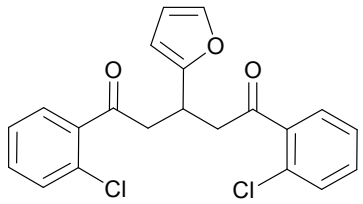
1a

3-(2-furyl)-1,5-diphenyl-1,5-pentanedione (1a): 66 mg; 83% yield; white solid; mp: 90–91 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.99-7.97 (m, 4H), 7.56 (t, *J* = 7.3 Hz, 2H), 7.46 (t, *J* = 7.7 Hz, 4H), 7.28 (d, *J* = 0.7 Hz, 1H), 6.24-6.23 (m, 1H), 6.06 (d, *J* = 2.9 Hz, 1H), 4.23-4.18 (m, 1H), 3.48-3.41 (m, 4H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 198.3, 156.4, 141.2, 136.7, 133.2, 128.7, 128.2, 110.3, 105.5, 42.2, 30.7; **IR** (KBr) ν: 3060, 2895, 1685, 1560, 1502, 1360, 1237, 1205, 975, 754, 736, 687, 501 cm^{-1}.



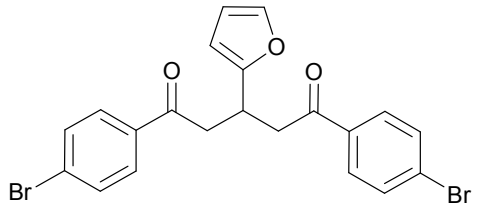
1b

3-(2-furyl)-1,5-bis(4-fluorophenyl)-1,5-pentanedione (1b): 73 mg; 83% yield; white solid; mp: 98–101 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.02-8.00 (m, 4H), 7.28 (s, 1H), 7.13 (t, *J* = 8.3 Hz, 4H), 6.24 (s, 1H), 6.06 (s, 1H), 4.18-4.14 (m, 1H), 3.41 (qd, *J* = 16.8, 6.7 Hz, 4H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 196.7, 166.7, 165.0, 156.1, 141.3, 133.1, 130.9, 130.8, 115.8, 115.7, 110.3, 105.6, 42.0, 30.8; **IR** (KBr) ν: 3117, 3070, 1692, 1676, 1595, 1506, 1413, 1356, 1264, 1225, 1159, 990, 840, 739 cm^{-1}. **HRMS** (ESI) found: m/z 377.0962 $[M+Na]^+$; calcd. for $C_{21}H_{16}F_2O_3Na^+$ 377.0960



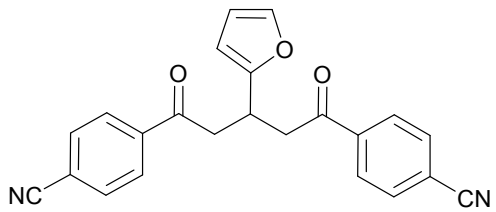
1c

3-(2-furyl)-1,5-bis(2-chlorophenyl)-1,5-pentanedione (1c): 84 mg; 87% yield; syrup; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.40-7.34 (m, 6H), 7.29 (td, *J* = 7.4, 1.2 Hz, 2H), 7.24 (m, 1H), 6.23 (dd, *J* = 3.0, 1.9 Hz, 1H), 6.05 (d, *J* = 3.2 Hz, 1H), 4.13-4.08 (m, 1H), 3.40 (d, *J* = 6.9 Hz, 4H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 201.1, 155.6, 141.3, 139.1, 131.8, 130.9, 130.5, 129.0, 126.9, 110.2, 105.9, 46.2, 30.9; **IR** (KBr) ν: 3066, 2916, 1697, 1589, 1470, 1433, 1356, 1163, 1037, 757, 733 cm^{-1}; **HRMS** (ESI) found: m/z 409.0370 $[M+Na]^+$; calcd. for $C_{21}H_{16}Cl_2O_3Na^+$ 409.0369.



1d

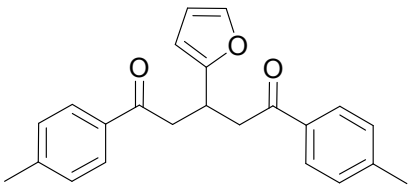
3-(2-furyl)-1,5-bis(4-bromophenyl)-1,5-pentanedione (1d): 105 mg; 82% yield; white solid; mp: 110–111 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.5 Hz, 4H), 7.60 (dd, *J* = 8.4, 1.5 Hz, 4H), 7.27 (d, *J* = 1.1 Hz, 1H), 6.23 (dd, *J* = 3.1, 1.8 Hz, 1H), 6.04 (d, *J* = 3.2 Hz, 1H), 4.16-4.12 (m, 1H), 3.43-3.34 (m, 4H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 197.2, 155.9, 141.3, 135.5, 132.0, 129.7, 128.4, 110.3, 105.6, 42.0, 30.8; **IR** (KBr) ν: 3094, 2902, 2357, 2320, 1686, 1582, 1397, 1361, 1234, 1069, 811, 733 cm^{-1}; **HRMS** (ESI) found: m/z 498.9334 $[M+Na]^+$; calcd. for $C_{21}H_{16}{}^{79}Br^{81}BrO_3Na^+$ 498.9338.



1e

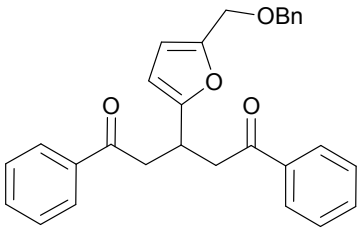
3-(2-furyl)-1,5-bis(4-cyanophenyl)-1,5-pentanedione (1e): 68 mg; 73% yield; white solid; mp: 157–159 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 4H), 7.77 (d, *J* = 8.4 Hz, 4H), 7.27 (s, 1H), 6.24 (dd, *J* = 3.1, 1.9 Hz, 1H), 6.06 (d, *J* = 3.2 Hz, 1H), 4.18-4.13 (m, 1H), 3.49-3.41 (m, 4H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 196.9, 155.3, 141.5, 139.5, 132.6, 128.5, 117.9,

116.6, 110.4, 105.9, 42.2, 30.6; **IR** (KBr) ν: 3048, 2904, 2230, 1691, 1404, 1361, 1291, 1210, 992, 828, 735 cm^{-1}; **HRMS** (ESI) found: m/z 391.1058 $[M+Na]^+$; calcd. for $C_{23}H_{16}N_2O_3Na^+$ 391.1053.



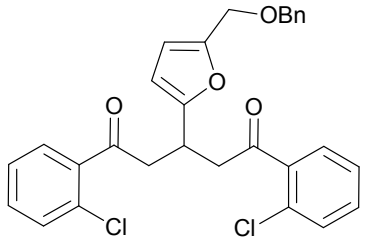
1f

3-(2-furyl)-1,5-bis(4-methylphenyl)-1,5-pentanedione (1f): 68 mg; in 78% yield; white solid; mp: 105–107 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.1 Hz, 4H), 7.27 (d, *J* = 1.0 Hz, 1H), 7.25 (d, *J* = 8.1 Hz, 4H), 6.23 (dd, *J* = 3.0, 1.8 Hz, 1H), 6.05 (d, *J* = 3.1 Hz, 1H), 4.20-4.15 (m, 1H), 3.44-3.37 (m, 4H), 2.40 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 198.0, 156.6, 144.0, 141.2, 134.3, 129.3, 128.3, 110.2, 105.4, 42.1, 30.9, 21.7; **IR** (KBr) ν: 3034, 2917, 1682, 1605, 1360,1238, 1174, 977, 806, 732, 508 cm^{-1}.



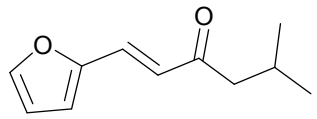
1g

3-(5-benzyloxymethyl-2-furyl)-1,5-diphenyl-1,5-pentanedione (1g): 83 mg; 76% yield; syrup; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.4 Hz, 4H), 7.53 (t, *J* = 7.4 Hz, 2H), 7.43 (t, *J* = 7.7 Hz, 4H), 7.32-7.24 (m, 5H), 6.16 (d, *J* = 3.1 Hz, 1H), 6.03 (d, *J* = 3.1 Hz, 1H), 4.46 (s, 2H), 4.39 (s, 2H), 4.21-4.17 (m. 1H), 3.48-3.41 (m, 4H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 198.3, 156.8, 150.4, 138.0, 136.9, 133.2, 128.6, 128.4, 128.2, 127.9, 127.7, 110.4, 106.4, 71.6, 64.0, 42.1, 31.0; **IR** (KBr) ν: 3053, 2905, 2856, 1684, 1448, 1359, 1274, 1216, 995, 758, 689 cm^{-1}; **HRMS** (ESI) found: m/z 461.1711 $[M+Na]^+$; calcd. for $C_{29}H_{26}O_4Na^+$ 461.1723.



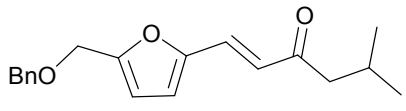
1h

3-(5-benzyloxymethyl-2-furyl)-1,5-bis(2-chlorophenyl)-1,5-pentanedione (1h): 92 mg; 73% yield; syrup; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 7.6, 1.2 Hz, 2H), 7.37 (d, *J* = 7.9 Hz, 2H), 7.35-7.29 (m, 7H), 7.24 (d, *J* = 7.5 Hz, 2H), 6.17 (d, *J* = 3.0 Hz, 1H), 6.03 (d, *J* = 3.0 Hz, 1H), 4.45 (s, 2H), 4.36 (s, 2H), 4.13-4.08 (m, 1H), 3.45-3.41 (m, 4H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 201.2, 156.0, 150.5, 139.1, 138.0, 131.8, 130.9, 130.5, 129.0, 128.4, 127.9, 127.7, 127.0, 110.4, 106.8, 71.6, 63.8, 46.1, 31.0; **IR** (KBr) ν: 3065, 2856, 1699, 1589, 1469, 1356, 1283, 1212, 1068, 988, 759 cm^{-1}; **HRMS** (ESI) found: m/z 529.0944 $[M+Na]^+$; calcd. for $C_{29}H_{24}Cl_2O_4Na^+$ 529.0944.



2a

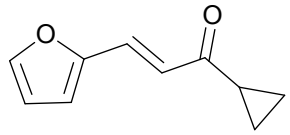
(*E*)-1-(2-furyl)-5-methyl-1-hexen-3-one (2a): 35 mg; 78% yield; syrup; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.32 (d, *J* = 15.8 Hz, 1H), 6.67-6.64 (m, 2H), 6.49 (dd, *J* = 3.3, 1.7 Hz, 1H), 2.48 (d, *J* = 7.0 Hz, 2H), 2.25-2.18 (m, 1H), 0.97 (d, *J* = 6.7 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 199.9, 151.1, 144.8, 128.5, 123.7, 115.6, 112.5, 50.4, 25.3, 22.7; **IR** (KBr) ν: 2925, 2856, 1747, 1613, 1460, 1378, 1254, 1157, 973, 746 cm^{-1}.



2b

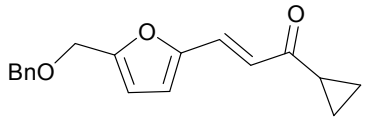
(*E*)-1-(5-benzyloxymethyl-2-furyl)-5-methyl-1-hexen-3-one (2b): 57 mg; 77% yield; syrup; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.37-7.31 (m, 5H), 7.28 (d, *J* = 15.8 Hz, 1H), 6.67 (d, *J* = 15.8 Hz, 1H), 6.62 (d, *J* = 3.2 Hz, 1H), 6.42 (d, *J* = 3.2 Hz, 1H), 4.59

(s, 2H), 4.51 (s, 2H), 2.47 (d, *J* = 7.0 Hz, 2H), 2.22 (tt, *J* = 13.4, 6.7 Hz, 1H), 0.96 (d, *J* = 6.6 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 199.9, 154.5, 151.3, 137.6, 128.5, 128.4, 127.95, 127.91, 123.8, 116.4, 112.0, 72.4, 64.0, 50.6, 25.3, 22.7; **IR** (KBr) ν: 3062, 2957, 2869, 1684, 1611, 1578, 1459, 1360, 1176, 1066, 912, 741 cm^{-1}; **HRMS** (ESI) found: m/z 321.1452 $[M+Na]^+$; calcd. for $C_{19}H_{22}O_3Na^+$ 321.1461.



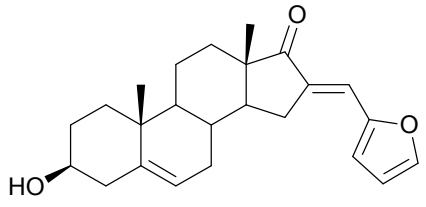
2c

(*E*)-1-cyclopropyl-3-(2-furyl)-2-propen-1-one (2c): 32mg; 81% yield; syrup; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.49 (d, *J* = 1.1 Hz, 1H), 7.36 (d, *J* = 15.7 Hz, 1H), 6.78 (d, *J* = 15.7 Hz, 1H), 6.66 (d, *J* = 3.3 Hz, 1H), 6.48 (dd, *J* = 3.3, 1.8 Hz, 1H), 2.18-2.13 (m, 1H), 1.14 (dt, *J* = 7.9, 3.8 Hz, 2H), 0.96 (dq, *J* = 7.2, 3.7 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 199.7, 151.3, 144.8, 128.1, 123.5, 115.6, 112.5, 20.2, 11.3; **IR** (KBr) ν: 3124, 3010, 1674, 1607, 1553, 1386, 1269, 1204, 1094, 1018, 973, 750 cm^{-1}.



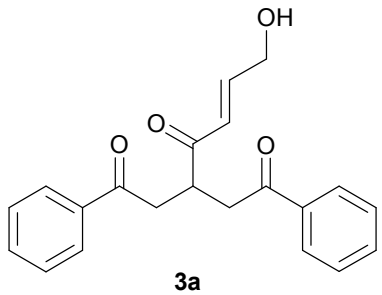
2d

(*E*)-3-(5-benzyloxymethyl-2-furyl)-1-cyclopropyl-2-propen-1-one (2d): 54 mg; 76% yield; syrup; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.37 (d, *J* = 4.4 Hz, 4H), 7.34-7.30 (m, 2H), 6.80 (d, *J* = 15.7 Hz, 1H), 6.61 (d, *J* = 3.3 Hz, 1H), 6.41 (d, *J* = 3.3 Hz, 1H), 4.59 (s, 2H), 4.51 (s, 2H), 2.17-2.13 (m, 1H), 1.16-1.13 (m, 2H), 0.96 (td, *J* = 7.1, 3.7 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 199.7, 154.4, 151.4, 137.6, 128.5, 128.0, 127.9, 123.5, 116.4, 112.0, 72.3, 64.0, 20.3, 11.3; **IR** (KBr) ν: 2924, 2855, 1673, 1609, 1578, 1446, 1387, 1201, 1088, 1019, 971, 797 cm^{-1}; **HRMS** (ESI) found: m/z 305.1150 $[M+Na]^+$; calcd. for $C_{18}H_{18}O_3Na^+$ 305.1150.



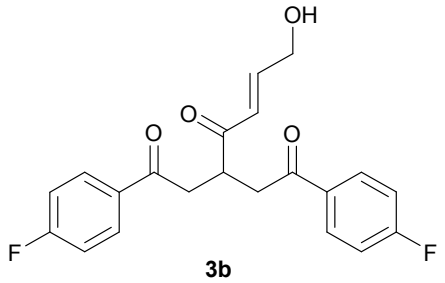
2e

(*E*)-16-furfuryliden-3β-hydroxy-5-androsten-17-one (2e): 87 mg; 95% yield; white solid; mp: 191–192 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.20 (s, 1H), 6.64 (d, *J* = 3.4 Hz, 1H), 6.50 (dd, *J* = 3.3, 1.7 Hz, 1H), 5.42-5.41 (m, 1H), 3.54 (ddd, *J* = 15.7, 11.0, 4.5 Hz, 1H), 3.02 (ddd, *J* = 16.6, 6.5, 1.3 Hz, 1H), 2.38-2.18 (m, 4H), 1.96 (ddd, *J* = 12.7, 3.8, 2.7 Hz, 1H), 1.90-1.85 (m, 2H), 1.82-1.65 (m, 4H), 1.61-1.49 (m, 3H), 1.43-1.25 (m, 4H), 1.17-1.05 (m, 6H), 0.95 (s, 3H), 0.89-0.83 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 209.8, 152.2, 144.8, 141.2, 133.5, 120.9, 119.6, 115.7, 112.4, 71.6, 50.4, 49.5, 47.5, 42.2, 37.2, 36.7, 31.6, 31.5, 31.2, 30.9, 29.0, 20.4, 19.5, 14.3; **IR** (KBr) ν: 2933, 2856, 2362, 1709, 1625, 1458, 1273, 1099, 1060, 913, 744, 650 cm^{-1}.



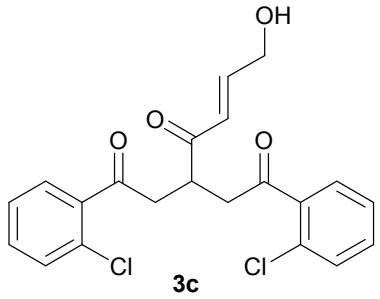
3a

(*E*)-7-hydroxy-3-(2-phenyl-2-ethanone)-1-phenyl-5-hepten-1,4-dione (3a): 71 mg; 86% yield; syrup; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.5 Hz, 4H), 7.54 (t, *J* = 7.4 Hz, 2H), 7.43 (t, *J* = 7.7 Hz, 4H), 7.06 (dt, *J* = 15.8, 3.8 Hz, 1H), 6.64 (dt, *J* = 15.7, 1.8 Hz, 1H), 4.37 (s, 2H), 4.06-4.02 (m, 1H), 3.47 (dd, *J* = 17.9, 7.0 Hz, 2H), 3.23 (dd, *J* = 17.9, 6.3 Hz, 2H), 2.78 (s, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 201.5, 197.9, 146.3, 136.4, 133.4, 128.7, 128.1, 126.8, 62.0, 40.2, 40.1; **IR** (KBr) ν: 3499, 3061, 2907, 1682, 1632, 1597, 1447, 1355, 1219, 996, 756, 691 cm^{-1}; **HRMS** (ESI) found: m/z 359.1258 $[M+Na]^+$; calcd. for $C_{21}H_{20}O_4Na^+$ 359.1254.



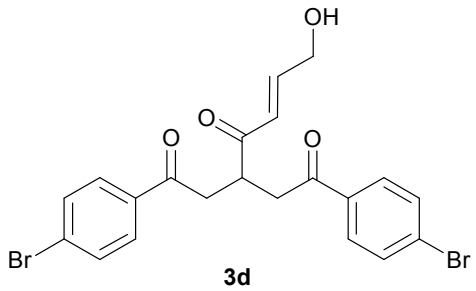
3b

(*E*)-1-(4-fluorophenyl)-3-(2-(4-fluorophenyl)-2-ethanone)-7-hydroxy-5-hepten-1,4-dione (3b): 79 mg; 84% yield; white solid; mp: 128–130 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.98-7.96 (m, 4H), 7.14-7.07 (m, 5H), 6.65 (dd, *J* = 15.8, 1.9 Hz, 1H), 4.42 (d, *J* = 1.9 Hz, 2H), 4.05-4.01 (m, 1H), 3.45 (dd, *J* = 17.9, 6.9 Hz, 2H), 3.21 (dd, *J* = 17.9, 6.3 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 201.2, 196.2, 166.8, 165.1, 146.2, 132.8, 130.8, 130.7, 126.8, 115.9, 115.7, 62.1, 40.2, 40.0; **IR** (KBr) ν: 3545, 3073, 2906, 1683, 1596, 1506, 1409, 1356, 1229, 1158, 991, 838 cm^{-1}; **HRMS** (ESI) found: m/z 395.1057 $[M+Na]^+$; calcd. for $C_{21}H_{18}F_2O_4Na^+$ 395.1065.



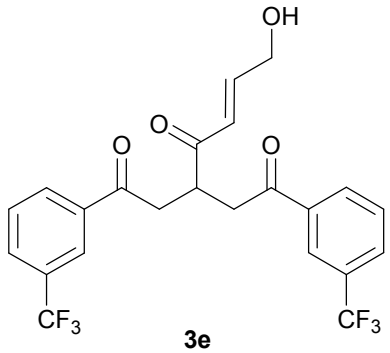
3c

(*E*)-1-(2-chlorophenyl)-3-(2-(2-chlorophenyl)-2-ethanone)-7-hydroxy-5-hepten-1,4-dione (3c): 84 mg; 84% yield; syrup; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.5 Hz, 2H), 7.39-7.27 (m, 6H), 7.06 (dd, *J* = 15.8, 3.5 Hz, 1H), 6.61 (d, *J* = 15.8 Hz, 1H), 4.39 (s, 2H), 4.04-4.01 (m, 1H), 3.44 (dd, *J* = 18.1, 7.0 Hz, 2H), 3.19 (dd, *J* = 18.1, 6.1 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 200.7, 200.5, 146.5, 138.5, 132.1, 131.0, 130.7, 129.2, 127.0, 126.4, 62.0, 43.9, 41.0; **IR** (KBr) ν: 3458, 3067, 2909, 1693, 1632, 1589, 1433, 1168, 1069, 989, 759 cm^{-1}; **HRMS** (ESI) found: m/z 427.0472 $[M+Na]^+$; calcd. for $C_{21}H_{18}Cl_2O_4Na^+$ 427.0474.



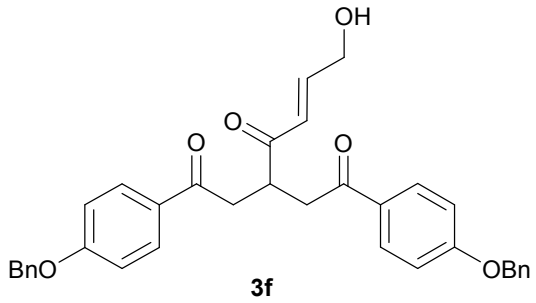
3d

(*E*)-1-(4-bromophenyl)-3-(2-(4-bromophenyl)-2-ethanone)-7-hydroxy-5-hepten-1,4-dione (3d): 102 mg; 83% yield; white solid; mp: 145–146 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.4 Hz, 4H), 7.60 (d, *J* = 8.3 Hz, 4H), 7.09 (dt, *J* = 15.7, 3.4 Hz, 1H), 6.65 (d, *J* = 15.8 Hz, 1H), 4.42 (s, 2H), 4.04-3.99 (m, 1H), 3.43 (dd, *J* = 18.0, 6.8 Hz, 2H), 3.19 (dd, *J* = 18.0, 6.3 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 201.2, 196.8, 146.6, 134.9, 132.0, 129.6, 128.8, 126.5, 62.1, 40.1, 39.9; **IR** (KBr) ν: 3396, 3053, 2894, 1680, 1623, 1584, 1399, 1232, 1071, 986, 812 cm^{-1}; **HRMS** (ESI) found: m/z 516.9440 $[M+Na]^+$; calcd. for $C_{21}H_{18}{}^{79}Br^{81}BrO_4Na^+$ 516.9444.



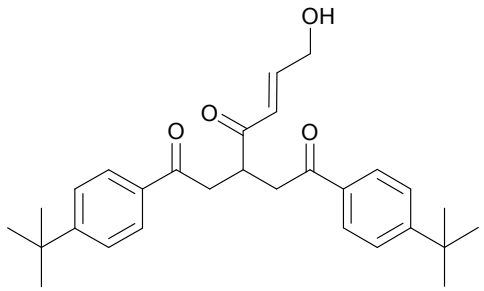
3e

(*E*)-1-(3-trifluoromethyl)-3-(2-(3-trifluoromethyl)-2-ethanone)-7-hydroxy-5-hepten-1,4-dione (3e): 96 mg; 81% yield; syrup; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.19 (s, 2H), 8.13 (d, *J* = 7.8 Hz, 2H), 7.83 (d, *J* = 7.8 Hz, 2H), 7.61 (t, *J* = 7.8 Hz, 2H), 7.10 (dt, *J* = 15.8, 3.8 Hz, 1H), 6.67 (dt, *J* = 15.8, 2.0 Hz, 1H), 4.43 (s, 2H), 4.11-4.07 (m, 1H), 3.52 (dd, *J* = 18.0, 6.9 Hz, 2H), 3.27 (dd, *J* = 18.0, 6.3 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 201.0, 196.5, 146.8, 136.8, 131.4, 131.2, 129.9, 129.8, 129.4, 126.5, 124.92, 124.90, 124.5, 122.7, 61.9, 40.0; **IR** (KBr) ν: 3453, 3074, 2920, 1691, 1632, 1439, 1329, 1208, 1127, 1073, 912, 805, 742, 695, 669 cm^{-1}; **HRMS** (ESI) found: m/z 495.1004 $[M+Na]^+$; calcd. for $C_{23}H_{18}F_6O_4Na^+$ 495.1001.



3f

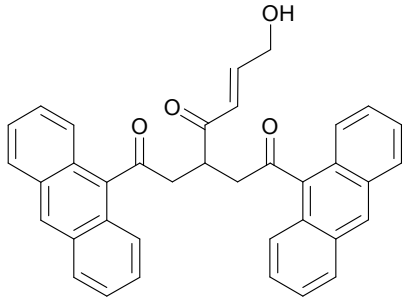
(*E*)-1-(4-benzyloxyphenyl)-3-(2-(4-benzyloxyphenyl)-2-ethanone)-7-hydroxy-5-hepten-1,4-dione (3f): 111 mg; 81% yield; syrup; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.8 Hz, 4H), 7.41 (dt, *J* = 14.9, 7.4 Hz, 8H), 7.34 (t, *J* = 7.0 Hz, 2H), 7.07 (dt, *J* = 15.8, 3.8 Hz, 1H), 6.98 (d, *J* = 8.8 Hz, 4H), 6.63 (d, *J* = 15.8 Hz, 1H), 5.12 (s, 4H), 4.39 (s, 2H), 4.03-3.98 (m, 1H), 3.40 (dd, *J* = 17.7, 7.1 Hz, 2H), 3.18 (dd, *J* = 17.6, 6.3 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 201.7, 196.4, 162.8, 145.9, 136.1, 130.4, 129.7, 128.7, 128.3, 127.5, 127.0, 114.7, 70.2, 62.1, 40.4, 39.9; **IR** (KBr) ν: 3474, 3036, 2919, 1672, 1599, 1508, 1313, 1256, 1171, 987, 832, 740 cm^{-1}; **HRMS** (ESI) found: m/z 571.2090 $[M+Na]^+$; calcd. for $C_{35}H_{32}O_6Na^+$ 571.2091.



3g

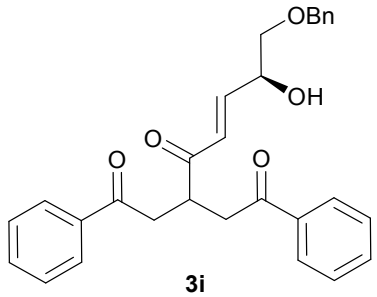
(*E*)-1-(4-*tert*-butylphenyl)-3-(2-(4-*tert*-butylphenyl)-2-ethanone)-7-hydroxy-5-hepten-1,4-dione (3g): 90 mg; 80% yield; syrup; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.5 Hz, 4H), 7.45 (d, *J* = 8.5 Hz, 4H), 7.07 (dt, *J* = 15.8, 3.9 Hz, 1H), 6.64 (dt, *J* = 15.8, 1.9 Hz, 1H), 4.39 (d, *J* = 1.0 Hz, 2H), 4.06-4.02 (m, 1H), 3.45 (dd, *J* = 17.7, 7.0 Hz, 2H), 3.21 (dd, *J* = 17.7, 6.3 Hz, 2H), 1.33 (s, 18H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 201.6, 197.5, 157.2, 146.0, 133.9, 128.1, 127.0, 125.6, 62.1, 40.3, 40.1, 35.1, 31.1; **IR** (KBr) ν: 3457, 2963, 1679, 1634, 1605, 1465, 1406, 1270, 1107, 991, 829, 730 cm^{-1}; **HRMS** (ESI) found: m/z 449.2674 $[M+H]^+$; calcd. for $[C_{29}H_{36}O_4+H]^+$

449.2686.



3h

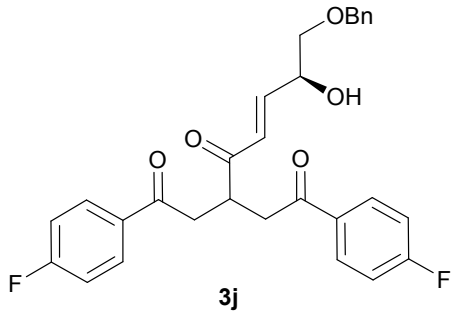
(*E*)-1-(9-anthracenyl)-3-(2-(9-anthracenyl)-2-ethanone)-7-hydroxy-5-hepten-1,4-dione (3h): 98 mg; 73% yield; white solid; mp: 178-180 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.50 (s, 2H), 8.03 (d, *J* = 8.3 Hz, 4H), 7.85 (d, *J* = 8.5 Hz, 4H), 7.53-7.47 (m, 8H), 7.22 (dt, *J* = 15.8, 3.8 Hz, 1H), 6.81 (dt, *J* = 15.8, 1.8 Hz, 1H) , 4.51-4.48 (m, 3H), 3.68 (dd, *J* = 19.3, 7.2 Hz, 2H), 3.39 (dd, *J* = 19.3, 6.1 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 207.7, 200.7 146.3, 135.1, 131.0, 128.8, 128.6, 127.14, 127.08, 127.04, 125.6, 124.1, 62.2, 47.3, 40.0; **IR** (KBr) ν: 3426, 3057, 1693, 1665, 1632, 1445, 1048, 1026, 913, 743 cm^{-1}; **HRMS** (ESI) found: m/z 559.1880 $[M+Na]^+$; calcd. for $C_{37}H_{28}O_4Na^+$ 559.1880.



3i

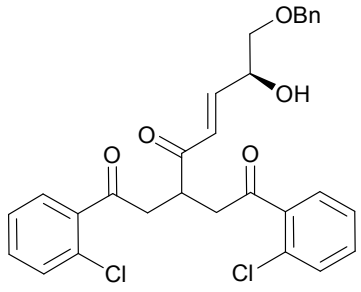
(*S*,*E*)-8-(benzyloxy)-7-hydroxy-1-phenyl-3-(2-phenyl-2-ethanone)-5-hepten-1,4-dione (3i): 92 mg; 81% yield; white solid; mp: 82–83 °C; $[\alpha]_D^{20}$ = - 7.4° (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.8 Hz, 4H), 7.56 (t, *J* = 7.4 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 4H), 7.35-7.28 (m, 5H), 6.92 (dd, *J* = 15.7, 4.1 Hz, 1H), 6.69 (dd, *J* = 15.7, 1.5 Hz, 1H), 4.58-4.56 (m, 3H), 4.05-4.00 (m, 1H), 3.63 (dt, *J* = 9.5, 3.0 Hz, 1H), 3.43 (m, 3H), 3.25-3.20 (m, 2H), 2.88-2.82 (m, 1H); **^{13}C NMR** (151 MHz,

$CDCl_3$) δ 201.3, 197.7, 144.44, 144.38, 137.5, 136.4, 133.5, 128.7, 128.6, 128.3, 128.1, 128.0, 127.9, 73.5, 73.0, 70.3, 40.4, 40.0, 39.9; **IR** (KBr) ν: 3480, 3061, 2904, 2361, 1682, 1633, 1450, 1357, 1272, 1103, 982, 753, 693 cm^{-1}; **HRMS** (ESI) found: m/z 479.1830 $[M+Na]^+$; calcd. for $C_{29}H_{28}O_5Na^+$ 479.1830.



3j

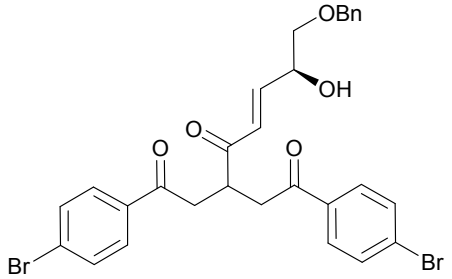
(*S,E*)-8-(benzyloxy)-1-(4-fluorophenyl)-3-(2-(4-fluorophenyl)-2-ethanone)-7-hydroxy-5-hepten-1,4-dione (3j): 98 mg; 80% yield; white solid; mp: 85–86 °C; $[\alpha]_D^{20}$ = - 9.4° (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 8.6, 5.4 Hz, 4H), 7.36-7.29 (m, 5H), 7.12 (t, *J* = 8.5 Hz, 4H), 6.92 (dd, *J* = 15.7, 4.1 Hz, 1H), 6.68 (dd, *J* = 15.7, 1.8 Hz, 1H), 4.58 (s, 3H), 4.02-3.98 (m, 1H), 3.65 (dd, *J* = 9.6, 3.4 Hz, 1H), 3.45-3.41 (m, 3H), 3.19 (ddd, *J* = 17.8, 6.3, 5.0 Hz, 2H), 2.72 (s, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 200.9, 196.0, 166.8, 165.1, 144.6, 137.5, 132.9, 130.8, 130.7, 128.5, 128.2, 128.0, 127.8, 115.9, 115.7, 73.5, 73.0, 70.2, 40.5, 39.8, 39.7; **IR** (KBr) ν: 3727, 3068, 2905, 1684, 1633, 1597, 1505, 1409, 1358, 1230, 1157, 986, 912, 838, 741 cm^{-1}; **HRMS** (ESI) found: m/z 515.1637 $[M+Na]^+$; calcd. for $C_{29}H_{26}F_2O_5Na^+$ 515.1641.



3k

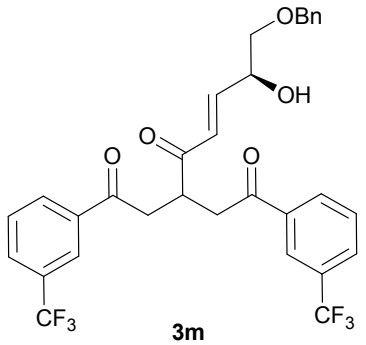
(*S,E*)-8-(benzyloxy)-1-(2-chlorophenyl)-3-(2-(2-chlorophenyl)-2-ethanone)-7-hydroxy-5-hepten-1,4-dione (3k): 106 mg; 81% yield; syrup; $[\alpha]_D^{20}$ = - 10.0° (*c* 1.0,

CH_2Cl_2); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.6 Hz, 2H), 7.40-7.27 (m, 11H), 6.91 (dd, *J* = 15.7, 4.1 Hz, 1H), 6.65 (dd, *J* = 15.7, 1.8 Hz, 1H), 4.57 (s, 3H), 4.03-3.99 (m, 1H), 3.63 (dd, *J* = 9.6, 3.5 Hz, 1H), 3.44-3.40 (m, 3H), 3.18 (ddd, *J* = 18.1, 6.3, 1.6 Hz, 2H), 2.80 (d, *J* = 3.5 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 200.52, 200.50, 200.2, 144.7, 138.6, 138.8, 137.5, 132.0, 131.0, 130.6, 129.2, 128.7, 128.0, 127.9, 127.0, 73.5, 73.1, 70.2, 43.8, 43.8, 41.3; **IR** (KBr) ν: 3454, 3065, 2903, 1695, 1633, 1589, 1469, 1274, 1105, 985, 759 cm^{-1}; **HRMS** (ESI) found: m/z 547.1050 $[M+Na]^+$; calcd. for $C_{29}H_{26}Cl_2O_4Na^+$ 547.1050.



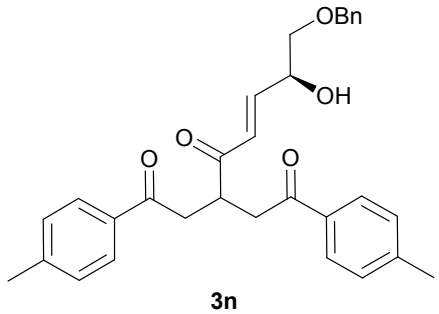
3l

(*S*,*E*)-8-(benzyloxy)-1-(4-bromophenyl)-3-(2-(4-bromophenyl)-2-ethanone)-7-hydroxy-5-hepten-1,4-dione (3l): 119 mg; 78% yield; white solid; mp: 97-98 °C; $[\alpha]_D^{20}$ = - 7.6° (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.5 Hz, 4H), 7.59 (d, *J* = 8.4 Hz, 4H), 7.37-7.28 (m, 5H), 6.91 (dd, *J* = 15.7, 4.1 Hz, 1H), 6.66 (dd, *J* = 15.7, 1.7 Hz, 1H), 4.57 (s, 3H), 4.01-3.96 (m, 1H), 3.64 (dd, *J* = 9.6, 3.5 Hz, 1H), 3.44-3.38 (m, 3H), 3.16 (ddd, *J* = 17.9, 6.3, 4.5 Hz, 2H), 2.70 (s, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 201.0, 196.7, 145.0, 137.5, 135.0, 132.0, 129.6, 128.7, 128.6, 128.04, 127.99, 127.9, 73.5, 73.0, 70.2, 40.4, 39.8, 39.7; **IR** (KBr) ν: 3444, 3090, 2897, 2362, 1680, 1626, 1583, 1398, 1336, 1235, 1072, 990, 817, 741 cm^{-1}; **HRMS** (ESI) found: m/z 637.0010 $[M+Na]^+$; calcd. for $C_{29}H_{26}{}^{79}Br^{81}BrO_5Na^+$ 637.0019.



3m

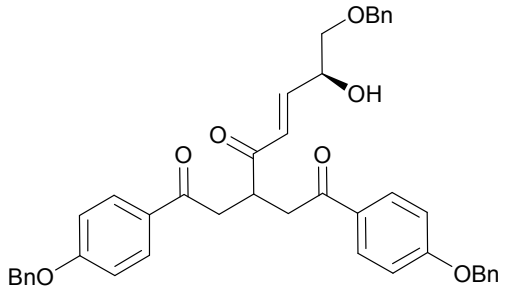
(*S*,*E*)-8-(benzyloxy)-1-(3-trifluoromethyl)-3-(2-(3-trifluoromethyl)-2-ethanone)-7-hydroxy-5-hepten-1,4-dione (3m): 113 mg; 76% yield; syrup; $[\alpha]_D^{20}$ = - 15.8° (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.19 (s, 2H), 8.12 (d, *J* = 7.8 Hz, 2H), 7.83 (d, *J* = 7.8 Hz, 2H), 7.60 (t, *J* = 7.8 Hz, 2H), 7.36-7.28 (m, 5H), 6.94 (dd, *J* = 15.7, 4.1 Hz, 1H), 6.70 (dd, *J* = 15.7, 1.8 Hz, 1H), 4.58 (s, 3H), 4.08-4.04 (m, 1H), 3.66 (dd, *J* = 9.6, 3.5 Hz, 1H), 3.50 (dd, *J* = 18.0, 6.7 Hz, 2H), 3.44 (dd, *J* = 9.5, 7.8 Hz, 1H), 3.25 (dt, *J* = 18.0, 6.3 Hz, 2H), 2.72 (d, *J* = 3.3 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 200.6, 196.2, 145.0, 137.5, 136.83, 136.81, 131.48, 131.46, 131.24, 129.86, 129.84, 129.80, 129.4, 128.55, 128.00, 127.85, 125.00, 124.98, 124.96, 124.93, 73.5, 73.0, 70.2, 40.3, 39.91, 39.86; **IR** (KBr) ν: 3366, 3070, 2911, 1690, 1633, 1328, 1208, 1127, 1073, 913, 805, 743, 695 cm^{-1}; **HRMS** (ESI) found: m/z 615.1579 $[M+Na]^+$; calcd. for $C_{31}H_{26}F_6O_5Na^+$ 615.1577.



3n

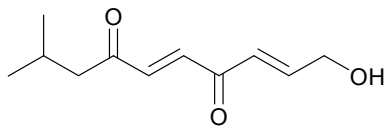
(*S*,*E*)-8-(benzyloxy)-1-(4-methylphenyl)-3-(2-(4-methylphenyl)-2-ethanone)-7-hydroxy-5-hepten-1,4-dione (3n): 96 mg; 79% yield; white solid; mp: 73–74 °C; $[\alpha]_D^{20}$ = - 5.4° (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.1 Hz, 4H), 7.34-7.27 (m, 5H), 7.22 (d, *J* = 8.0 Hz, 4H), 6.91 (dd, *J* = 15.8, 4.2 Hz, 1H), 6.67 (dd, *J* = 15.8, 1.7 Hz, 1H), 4.56 (s, 3H), 4.02-3.98 (m, 1H), 3.63 (dd, *J* = 9.6, 3.5 Hz,

1H), 3.44-3.40 (m, 3H), 3.18 (ddd, *J* = 17.7, 6.4, 3.8 Hz, 2H), 2.80 (s, 1H), 2.39 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 201.4, 197.3, 144.3, 144.2, 137.6, 134.0, 129.3, 128.54, 128.50, 128.2, 127.94, 127.86, 73.5, 73.1, 70.1, 40.5, 39.92, 39.86, 21.7; **IR** (KBr) ν: 3731, 3032, 2915, 2862, 1679, 1633, 1606, 1495, 1407, 1275, 1108, 981, 912, 811, 737 cm^{-1}; **HRMS** (ESI) found: m/z 507.2147 $[M+Na]^+$; calcd. for $C_{31}H_{32}O_5Na^+$ 507.2142.



3o

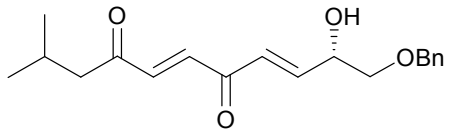
(*S,E*)-8-(benzyloxy)-1-(4-benzyloxy)-3-(2-(4-benzyloxy)-2-ethanone)-7-hydroxy-5-hepten-1,4-dione (3o): 130 mg; 78% yield; syrup; $[\alpha]_D^{20}$ = - 2.2° (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.6 Hz, 4H), 7.42-7.38 (m, 9H), 7.36-7.31 (m, 6H), 6.98 (d, *J* = 8.4 Hz, 4H), 6.90 (dd, *J* = 15.7, 4.2 Hz, 1H), 6.67 (dd, *J* = 15.7, 1.4 Hz, 1H), 5.11 (s, 4H), 4.56 (s, 3H), 4.00-3.96 (m, 1H), 3.63 (dd, *J* = 9.6, 3.4 Hz, 1H), 3.44-3.36 (m, 3H), 3.18-3.13 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 201.5, 196.2, 162.8, 144.2, 137.6, 136.2, 130.4, 129.80, 129.79, 128.7, 128.6, 128.5, 128.3, 128.0, 127.9, 127.5, 114.7, 73.5, 73.1, 70.3, 70.2, 40.6, 39.72, 39.65; **IR** (KBr) ν: 3456, 3064, 2919, 1672, 1599, 1508, 1256, 1225, 1171, 985, 832, 737, 698 cm^{-1} **HRMS** (ESI) found: m/z 691.2677 $[M+Na]^+$; calcd. for $C_{43}H_{40}O_7Na^+$ 691.2666.



4a

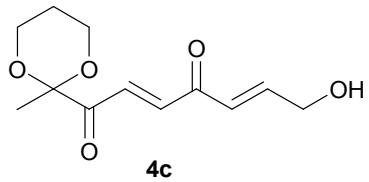
(*2E,5E*)-1-hydroxy-9-methyl-2,5-decadien-4,7-dione (4a): 74 mg; 76% yield; syrup; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.16 (dd, *J* = 15.9, 2.4 Hz, 1H), 7.10 (ddd, *J* = 15.8, 4.9, 2.3 Hz, 1H), 6.98 (dd, *J* = 15.9, 3.4 Hz, 1H), 6.70 (dd, *J* = 15.8, 2.1 Hz, 1H), 4.45

(s, 2H), 2.54 (d, *J* = 6.9 Hz, 2H), 2.23-2.16 (m, 1H), 0.96 (dd, *J* = 6.7, 2.7 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 200.5, 189.4, 148.6, 137.3, 135.2, 126.5, 61.9, 50.9, 24.8, 22.5; **IR** (KBr) ν: 3449, 3034, 2874, 1664, 1631, 1368, 1299, 1186, 1100, 980, 913, 744 cm^{-1}; **HRMS** (ESI) found: m/z 219.0992 $[M+Na]^+$; calcd. for $C_{11}H_{16}O_3Na^+$ 219.0992.



4b

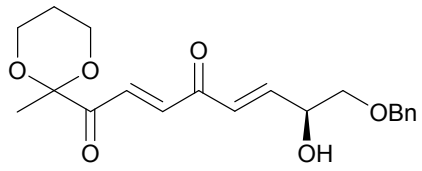
(*S,5E,8E*)-11-(benzyloxy)-10-hydroxy-2-methyl-5,8-undecadien-4,7-dione (4b): 134 mg; 85% yield; syrup; $[\alpha]_D^{20}$ = - 15.4° (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.37-7.30 (m, 5H), 7.12 (d, *J* = 16.0 Hz, 1H), 6.96 (d, *J* = 16.0 Hz, 1H), 6.93 (dd, *J* = 15.8, 3.9 Hz, 1H), 6.72 (dd, *J* = 15.7, 1.5 Hz, 1H), 4.57 (s, 3H), 3.64 (dd, *J* = 9.6, 3.5 Hz, 1H), 3.42 (dd, *J* = 9.5, 7.5 Hz, 1H), 2.94 (s, 1H), 2.52 (d, *J* = 6.9 Hz, 2H), 2.19 (tt, *J* = 13.4, 6.7 Hz, 1H), 0.95 (d, *J* = 6.7 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 200.2, 189.2, 146.7, 137.4, 137.3, 135.2, 128.6, 128.1, 128.0, 127.9, 73.6, 72.8, 70.2, 50.9, 24.8, 22.6; **IR** (KBr) ν: 3462, 3062, 2959, 2870, 1665, 1633, 1458, 1301, 1101, 983, 743, 700 cm^{-1}; **HRMS** (ESI) found: m/z 339.1571 $[M+Na]^+$; calcd. for $C_{19}H_{24}O_4Na^+$ 339.1567.



4c

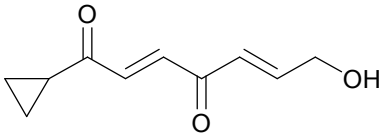
(*2E,5E*)-7-hydroxy-1-(2-methyl-1,3-dioxan-2-yl)-2,5-heptadien-1,4-dione (4c): 90 mg; 75% yield; syrup; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.44 (q, *J* = 15.7 Hz, 2H), 7.14 (dt, *J* = 15.8, 3.6 Hz, 1H), 6.71 (dt, *J* = 15.8, 1.9 Hz, 1H), 4.47 (dd, *J* = 3.4, 2.2 Hz, 2H), 4.01-3.98 (m, 2H), 3.77-3.73 (m, 2H), 2.12-2.04 (m, 1H), 1.43-1.40 (m, 4H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 199.4, 188.8, 148.6, 137.6, 132.2, 126.9, 100.9, 62.9, 61.9, 24.8, 24.1; **IR** (KBr) ν: 3482, 2968, 2930, 2880, 1710, 1662, 1631, 1289, 1201, 1139,

1076, 912, 744 cm^{-1}; **HRMS** (ESI) found: m/z 263.0892 $[M+Na]^+$; calcd. for $C_{12}H_{16}O_5Na^+$ 263.0890.



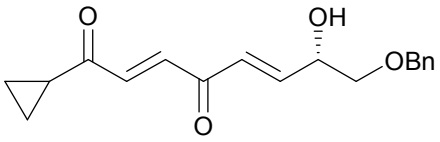
4d

(*S,2E,5E*)-8-(benzyloxy)-7-hydroxy-1-(2-methyl-1,3-dioxan-2-yl)-2,5-octadien-1,4-dione (4d): 149 mg; 83% yield; syrup; $[\alpha]_D^{20}$ = - 21.0° (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.42 (s, 2H), 7.38-7.36 (m, 2H), 7.33-7.31(m, 3H), 6.96 (dd, *J* = 15.8, 3.9 Hz, 1H), 6.74 (dd, *J* = 15.8, 1.7 Hz, 1H), 4.59 (s, 3H), 4.00-3.97 (m, 2H), 3.74 (dd, *J* = 11.8, 10.1 Hz, 2H), 3.66 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.44 (dd, *J* = 9.5, 7.5 Hz, 1H), 2.83 (s, 1H), 2.12-2.06 (m, 1H), 1.43-1.40 (m, 4H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 199.4, 188.7, 146.9, 137.6, 137.3, 132.4, 128.6, 128.4, 128.1, 127.9, 100.9, 73.6, 72.8, 70.2, 62.9, 24.9, 24.1; **IR** (KBr) ν: 3477, 2966, 2861, 1710, 1665, 1629, 1369, 1288, 1136, 1078, 981, 743 cm^{-1}; **HRMS** (ESI) found: m/z 383.1459 $[M+Na]^+$; calcd. for $C_{20}H_{24}O_6Na^+$ 383.1465.



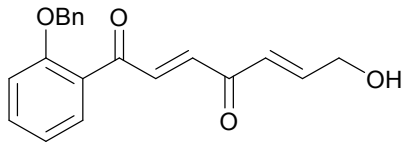
4e

(*2E,5E*)-1-cyclopropyl-7-hydroxy-2,5-heptadien-1,4-dione (4e): 66 mg; 73% yield; syrup; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.21 (d, *J* = 15.9 Hz, 1H), 7.12-7.08 (m, 2H), 6.70 (dt, *J* = 15.8, 2.0 Hz, 1H), 4.44 (s, 2H), 2.37 (s, 1H), 2.25-2.21 (m, 1H), 1.21-1.18 (m, 2H), 1.06 (td, *J* = 7.2, 3.8 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 200.6, 189.4, 148.6, 137.2, 134.9, 126.6, 61.9, 20.8, 12.6; **IR** (KBr) ν: 3449, 3012, 2903, 1658, 1631, 1442, 1391, 1286, 1195, 1089, 980, 905 cm^{-1}; **HRMS** (ESI) found: m/z 203.0677 $[M+Na]^+$; calcd. for $C_{10}H_{12}O_3Na^+$ 203.0679.



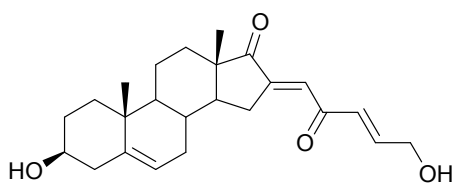
4f

(*S,2E,5E*)-8-(benzyloxy)-1-cyclopropyl-7-hydroxy-2,5-octadien-1,4-dione (4f): 121 mg; 81% yield; syrup; $[\alpha]_D^{20}$ = - 15.6° (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.37-7.31 (m, 5H), 7.17 (d, *J* = 15.9 Hz, 1H), 7.09 (d, *J* = 15.9 Hz, 1H), 6.93 (dd, *J* = 15.8, 4.0 Hz, 1H), 6.73 (dd, *J* = 15.8, 1.7 Hz, 1H), 4.57 (s, 3H), 3.64 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.42 (dd, *J* = 9.5, 7.5 Hz, 1H), 2.88-2.87 (m, 1H), 2.23-2.19 (m, 1H), 1.20-1.17 (m, 2H), 1.04 (td, *J* = 7.2, 3.7 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 200.2, 189.2, 146.6, 137.3, 134.8, 128.6, 128.2, 128.1, 127.9, 73.6, 72.9, 70.2, 20.8, 12.4; **IR** (KBr) ν: 3461, 3063, 2863, 1661, 1632, 1451, 1389, 1282, 1087, 983, 912, 744 cm^{-1}; **HRMS** (ESI) found: m/z 323.1261 $[M+Na]^+$; calcd. for $C_{18}H_{20}O_4Na^+$ 323.1254.



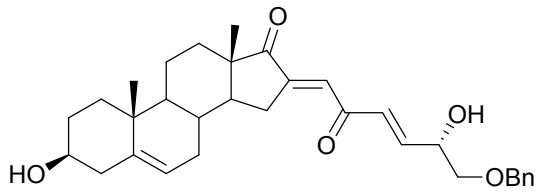
4g

(*2E,5E*)-1-(2-(benzyloxy)phenyl)-7-hydroxy-2,5-heptadien-1,4-dione (4g): 90 mg; 56% yield; syrup; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.73 (t, *J* = 12.4 Hz, 2H), 7.51 (t, *J* = 7.7 Hz, 1H), 7.42-7.30 (m, 5H), 7.18 (d, *J* = 15.7 Hz, 1H), 7.07-7.06 (m, 2H), 7.00 (d, *J* = 15.9 Hz, 1H), 6.56 (d, *J* = 15.8 Hz, 1H), 5.17 (s, 2H), 4.36 (s, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 192.0, 189.3, 158.1, 147.2, 139.1, 135.9, 134.7, 134.5, 131.0, 128.7, 128.2, 127.5, 126.5, 121.3, 112.9, 70.7, 62.1; **IR** (KBr) ν: 3445, 2922, 1652, 1598, 1483, 1450, 1384, 1309, 1234, 1013, 913, 748 cm^{-1}; **HRMS** (ESI) found: m/z 345.1102 $[M+Na]^+$; calcd. for $C_{20}H_{18}O_4Na^+$ 345.1097.



4h

(*E*)-16-((*E*)-5-hydroxy-2-oxo-3-penten-1-ylidene)-3β-hydroxy-5-androsten-17-one (4h): 85 mg; 89% yield; syrup; $[\alpha]_D^{20}$ = - 84.4° (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.15 (dd, *J* = 3.0, 2.0 Hz, 1H), 7.04 (dt, *J* = 15.9, 3.9 Hz, 1H), 6.57 (dt, *J* = 15.9, 1.9 Hz, 1H), 5.39-5.38 (m, 1H), 4.42 (d, *J* = 1.4 Hz, 2H), 3.53 (ddd, *J* = 15.7, 11.1, 4.5 Hz, 1H), 3.19 (ddd, *J* = 18.6, 6.5, 1.6 Hz, 1H), 2.40 (ddd, *J* = 18.5, 13.3, 3.3 Hz, 1H), 2.34-2.31 (m, 1H), 2.27-2.14 (m, 3H), 1.97 (dd, *J* = 9.6, 3.2 Hz, 1H), 1.88-1.72 (m, 6H), 1.67-1.48 (m, 4H), 1.40 (td, *J* = 13.1, 4.1 Hz, 1H), 1.32 (ddd, *J* = 13.2, 11.0, 6.6 Hz, 1H), 1.13-1.03 (m, 6H), 0.93 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 209.8, 190.7, 150.1, 146.8, 140.9, 129.5, 124.1, 120.9, 71.6, 61.9, 50.2, 48.8, 47.9, 42.2, 37.1, 36.7, 31.5, 31.4, 31.2, 30.8, 29.7, 20.4, 19.4, 14.0; **IR** (KBr) ν: 3389, 2934, 2900, 2859, 1726, 1663, 1456, 1369, 1221, 1054, 912, 734 cm^{-1}; **HRMS** (ESI) found: m/z 407.2197 $[M+Na]^+$; calcd. for $C_{24}H_{32}O_4Na^+$ 407.2193.



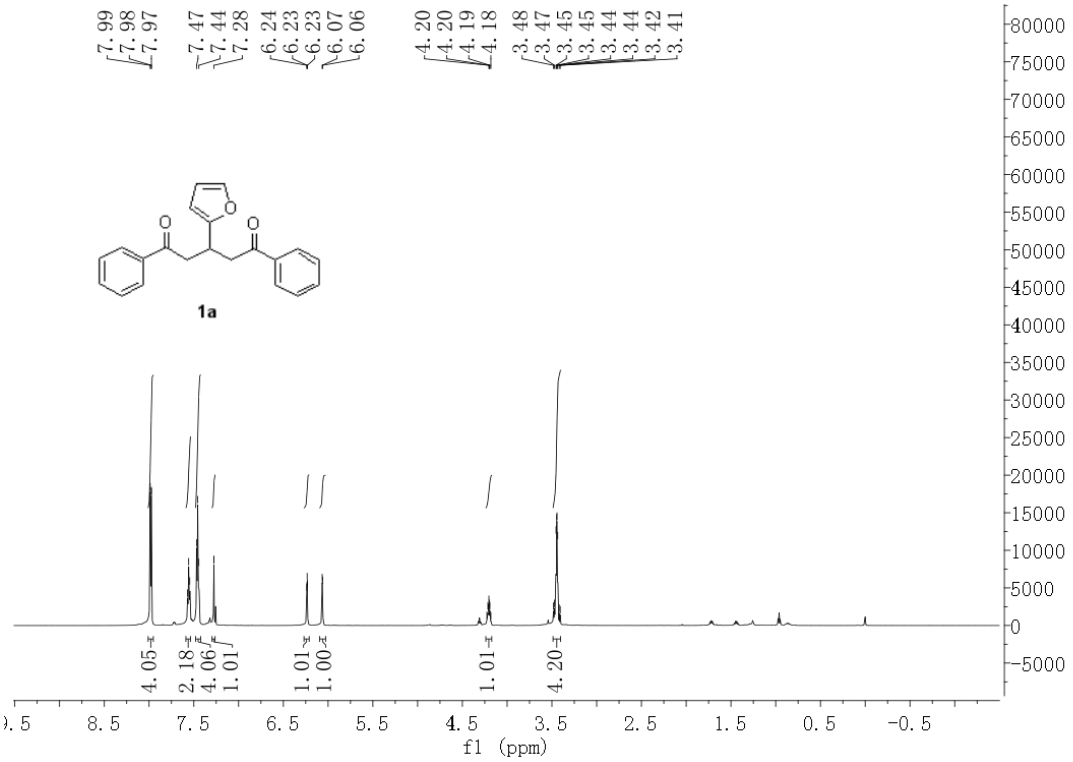
4i

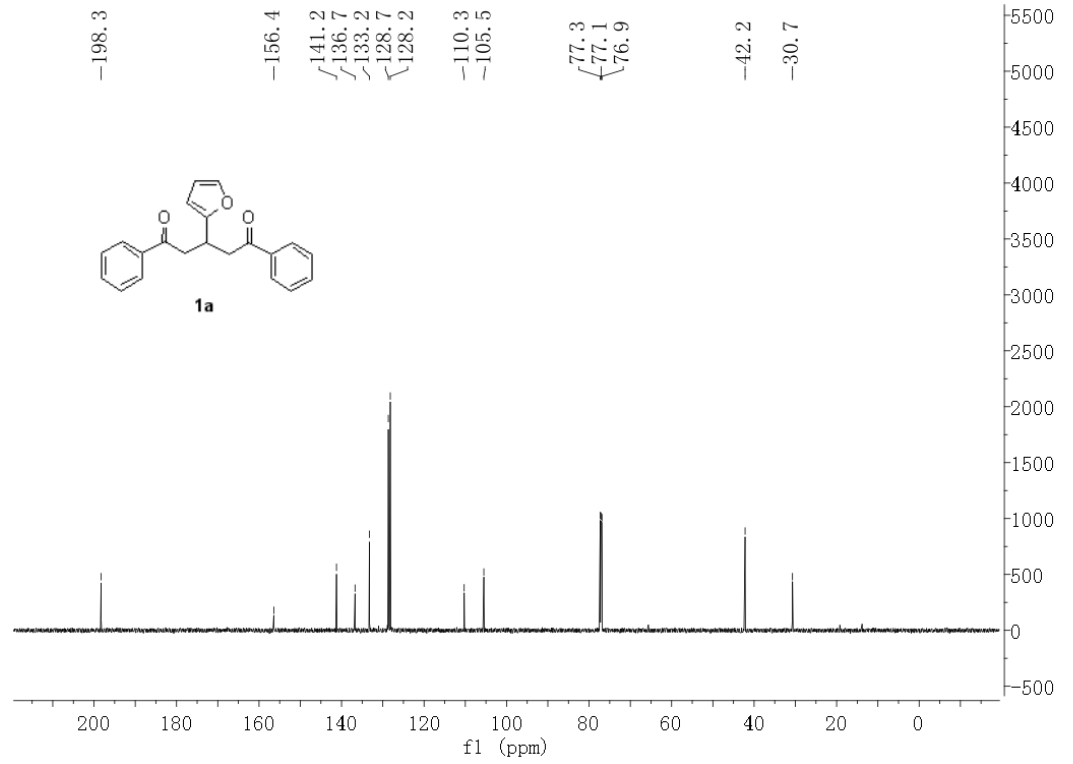
(*E*)-16-((*S*,*E*)-6-(benzyloxy)-5-hydroxy-2-oxo-3-hexen-1-ylidene)-3β-hydroxy-5-androsten-17-one (4i): 115 mg; 91% yield; syrup; $[\alpha]_D^{20}$ = - 65.2° (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.37-7.35 (m, 2H), 7.33-7.30 (m, 3H), 7.13-7.12 (m, 1H), 6.88 (dd, *J* = 15.9, 4.2 Hz, 1H), 6.60 (dd, *J* = 15.9, 0.9 Hz, 1H), 5.38 (d, *J* = 3.2 Hz, 1H), 4.57-4.56 (m, 3H), 3.65-3.62 (m, 1H), 3.54-3.50 (m, 1H), 3.43 (dd, *J* = 9.6, 7.4 Hz, 1H), 3.17 (dd, *J* = 18.6, 6.3 Hz, 1H), 2.41-2.36 (m, 1H), 2.33-2.30 (m, 1H), 2.24 (t, *J* = 12.1 Hz, 1H), 2.16 (d, *J* = 17.2 Hz, 1H), 1.97-1.95 (m, 1H), 1.87-1.85 (m, 3H), 1.78-1.72 (m, 3H), 1.66-1.47 (m, 4H), 1.42-1.24 (m, 4H), 1.11-1.02 (m, 6H), 0.92 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 209.7, 190.8, 150.2, 141.0, 137.4, 131.0, 128.6, 128.1, 127.9, 124.1, 120.9, 73.6, 73.0, 71.5, 70.1, 50.2, 48.8, 47.8, 42.1, 37.1, 36.7, 31.5, 31.4, 31.2, 30.8, 29.8, 20.4, 19.4, 14.0; **IR** (KBr) ν: 3441, 2933, 2860, 1725, 1662, 1455, 1357, 1269, 1220, 1103, 1059, 909,735 cm^{-1}; **HRMS** (ESI) found: m/z 527.2771 $[M+Na]^+$; calcd. for $C_{32}H_{40}O_5Na^+$ 527.2768.

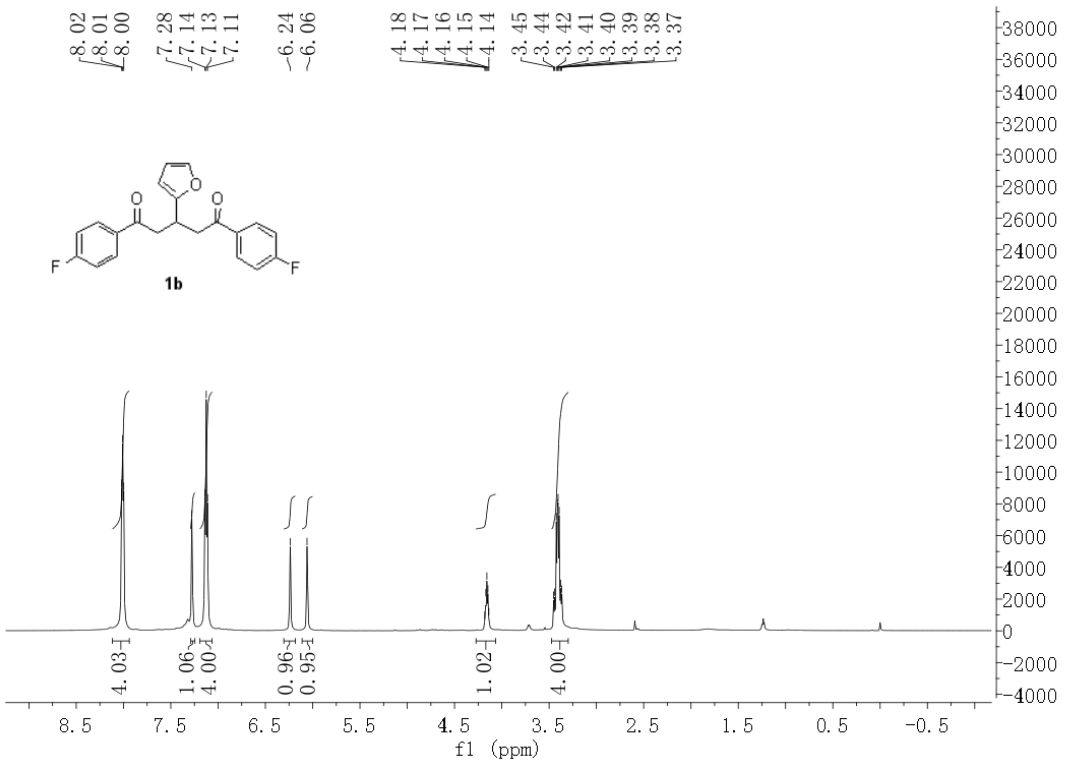
References

(1) X. Huang, Q. Feng, Y. Sun, Q. He and Y. Wang, *Lett. Org. Chem.*, 2012**, 9,** 280-286.
(2) J. Yang, N. Li, G. Li, W. Wang, A. Wang, X. Wang, Y. Cong and T. Zhang, *ChemSusChem*, 2013, **6**, 1149–1152.
(3) J. W. Hansen and C. C. Cassil, U.S. Patent 2470349, 1945.
(4) Stefanovic. *Tetrahedron Lett*., 1966, 3891-3894.

NMR spectra of the products:



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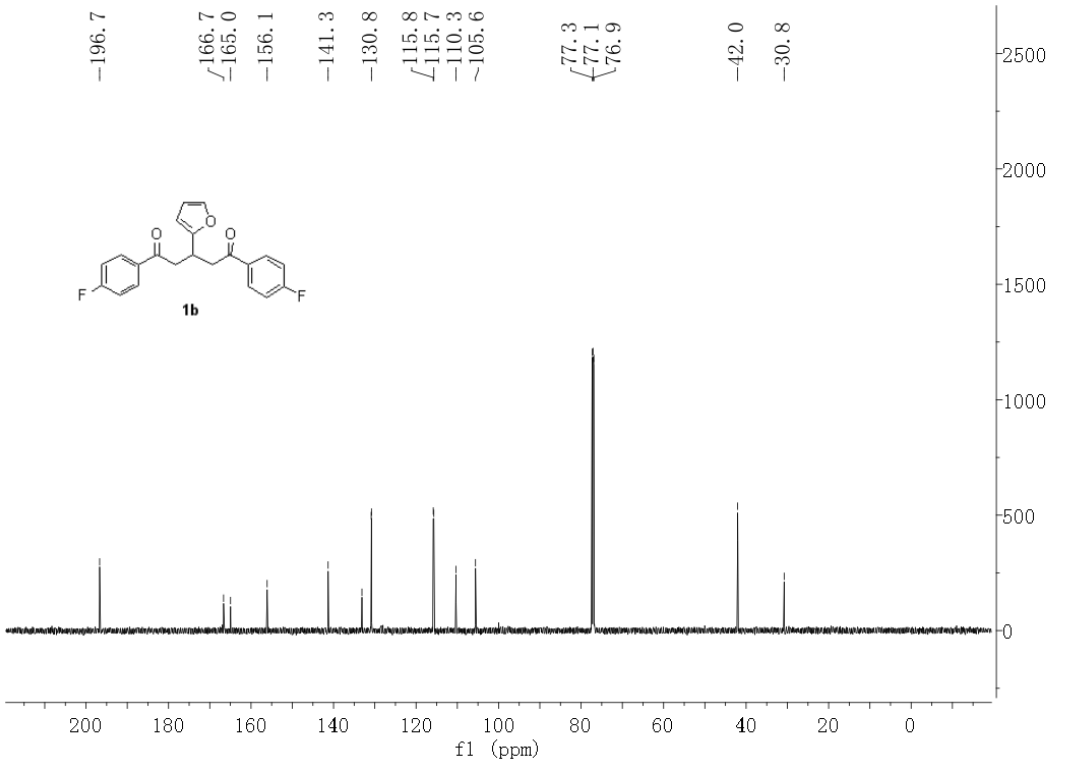
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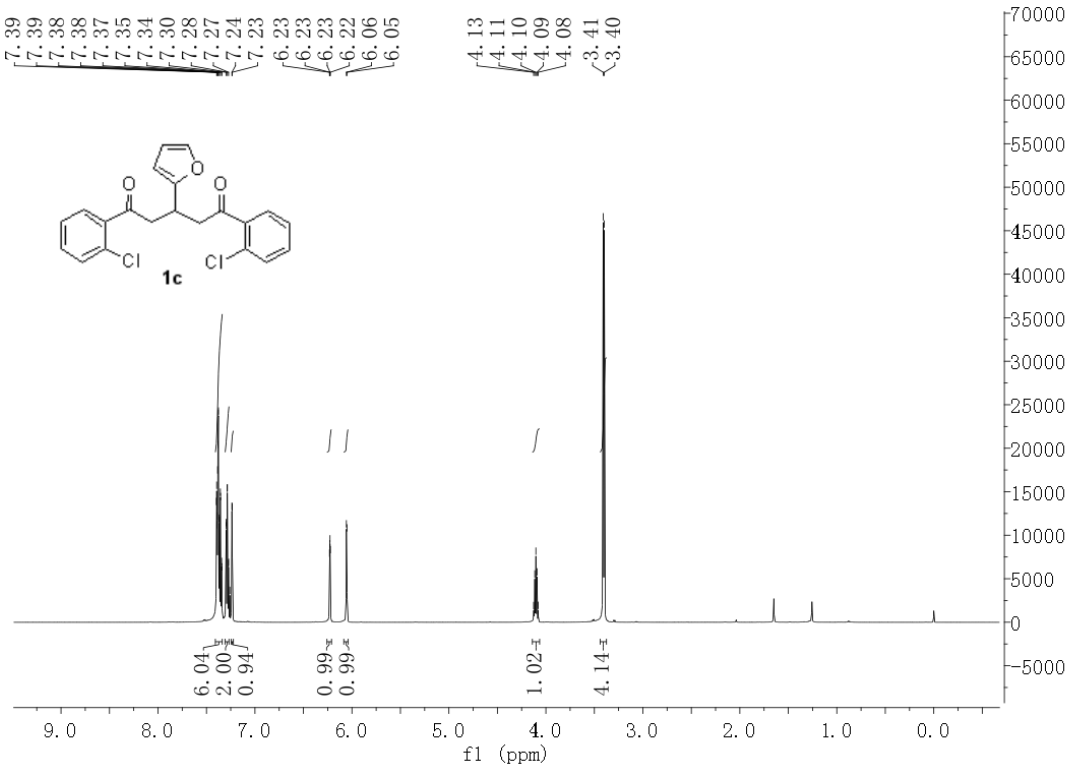
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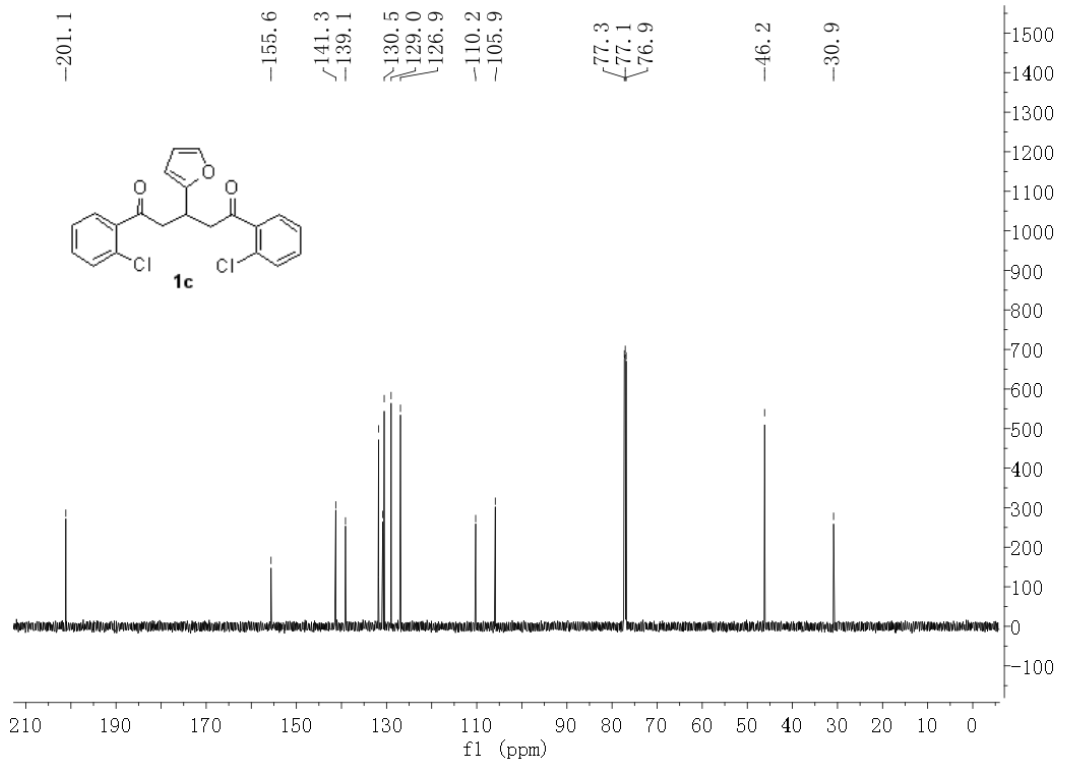
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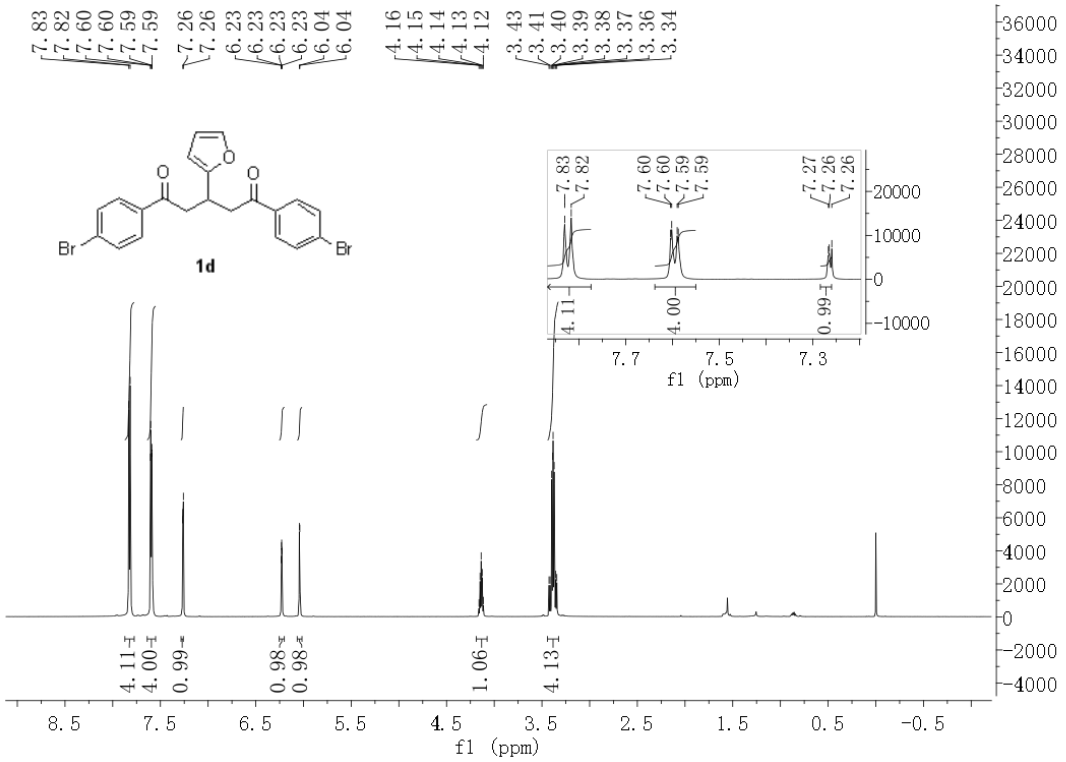
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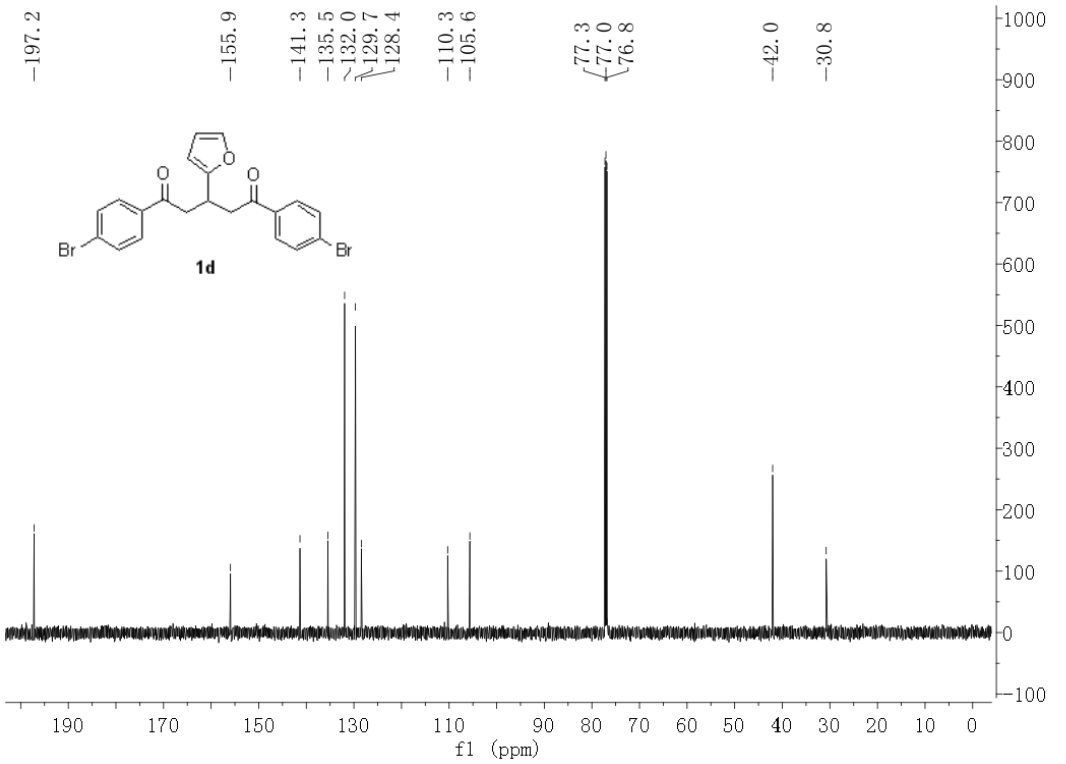
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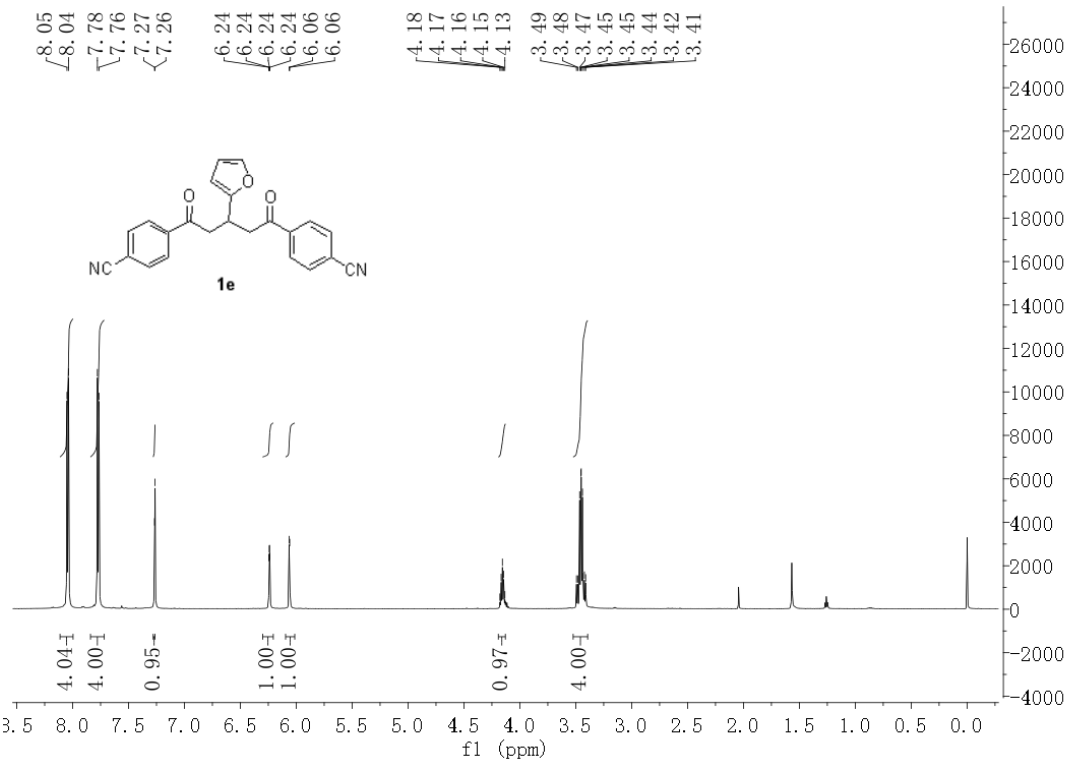
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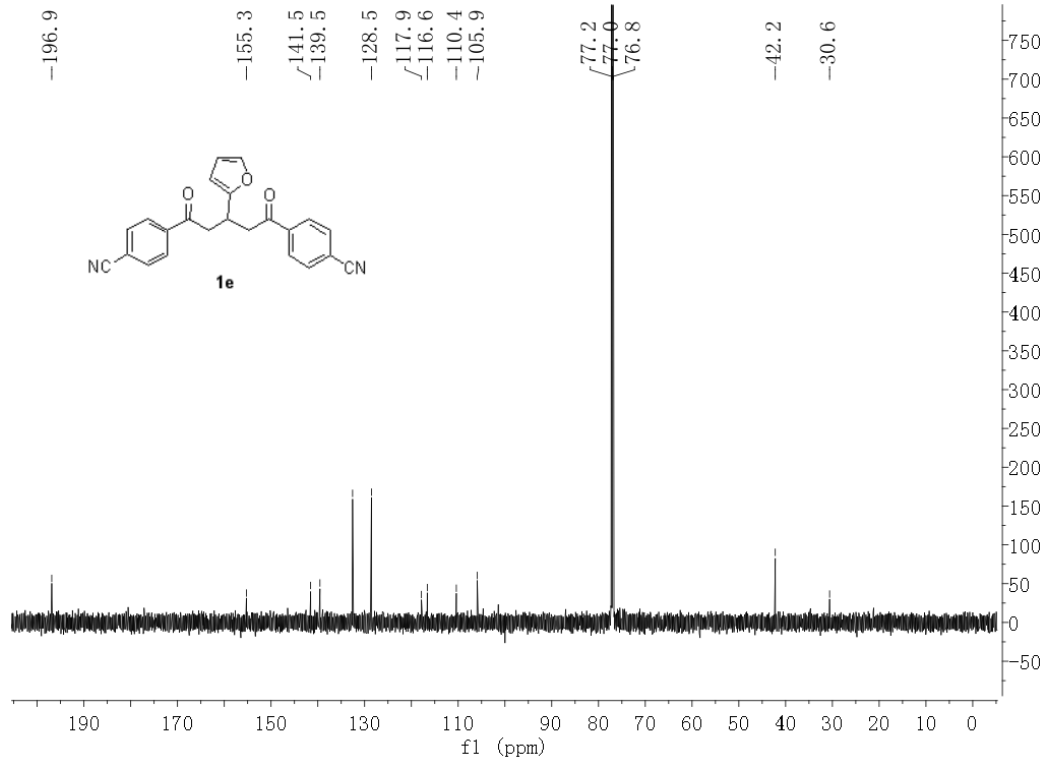
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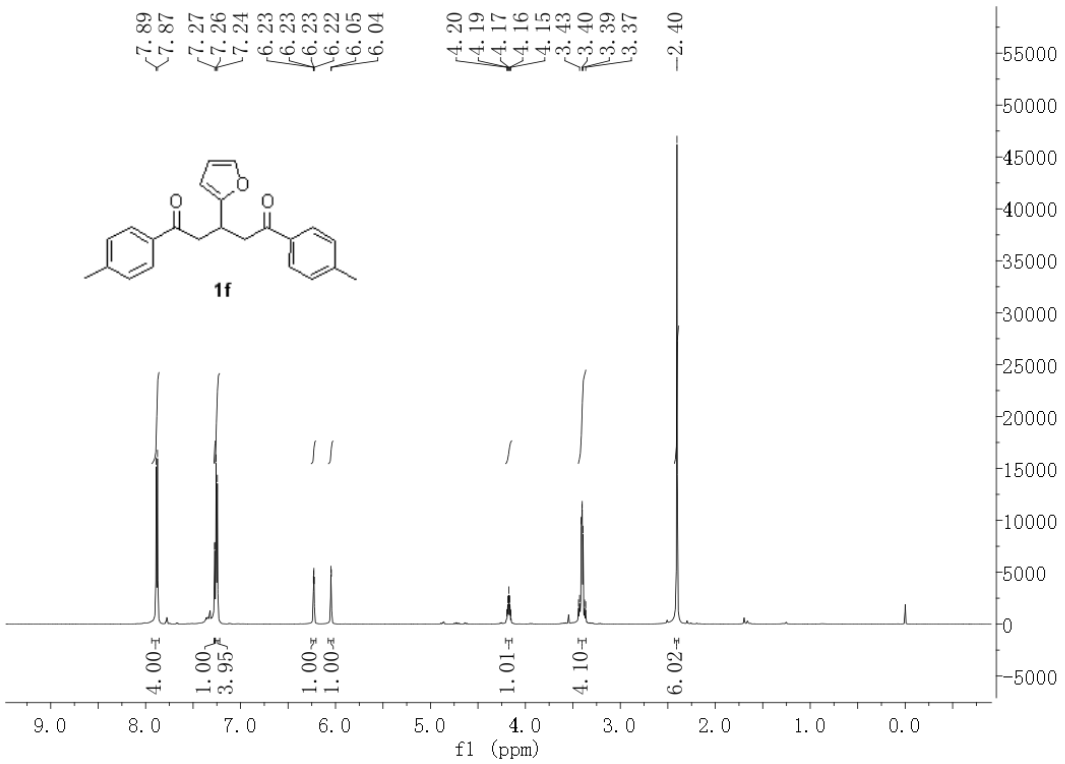
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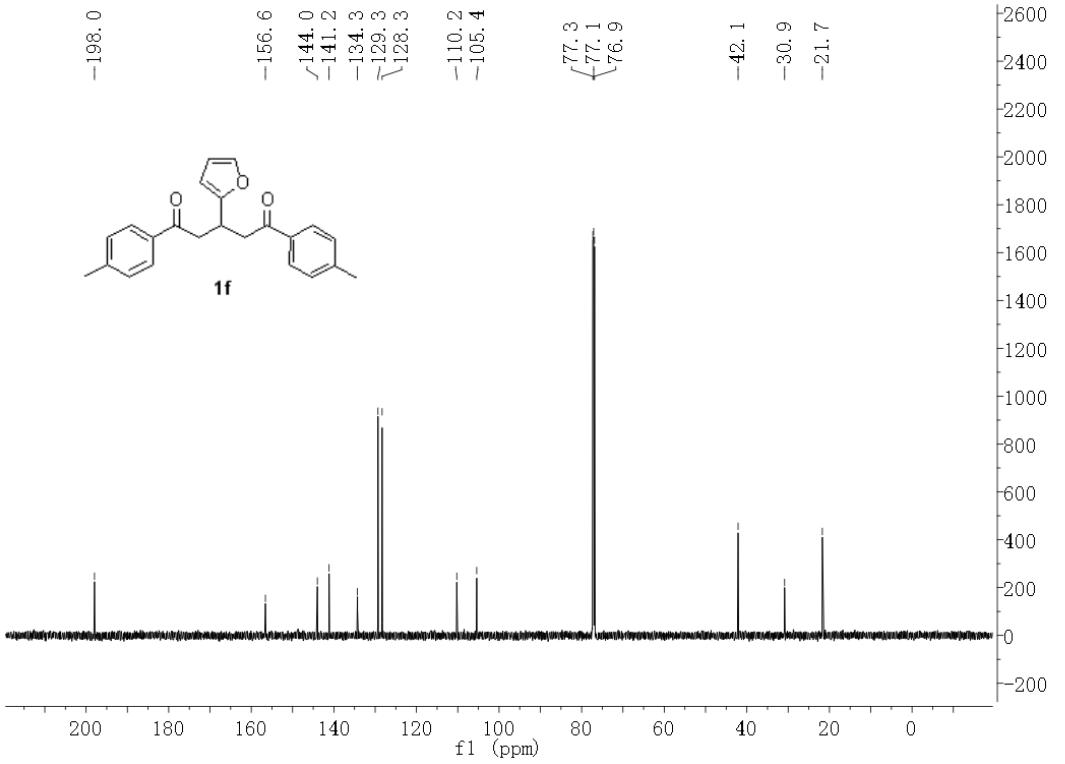
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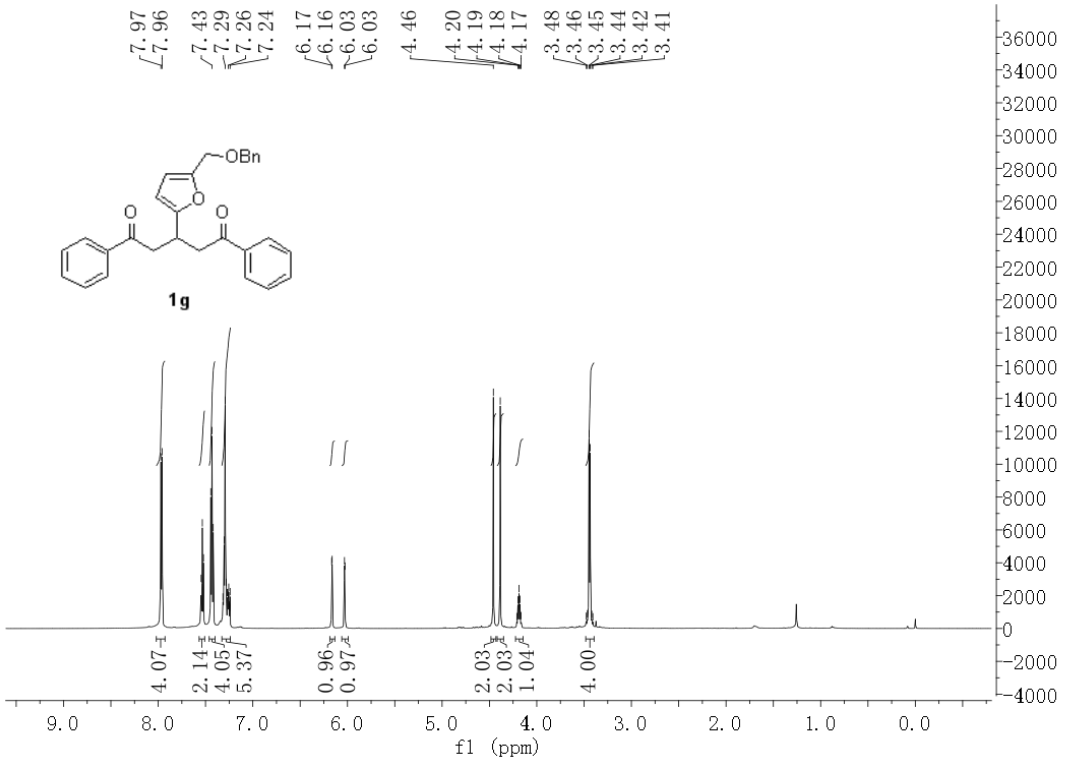
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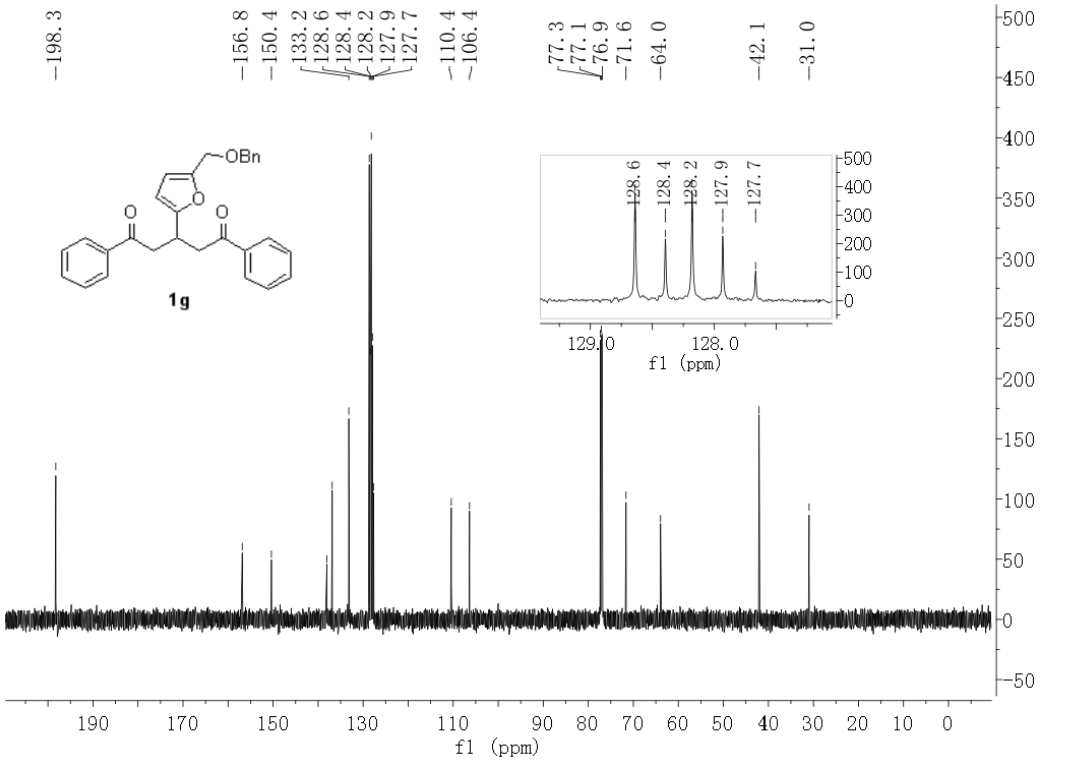
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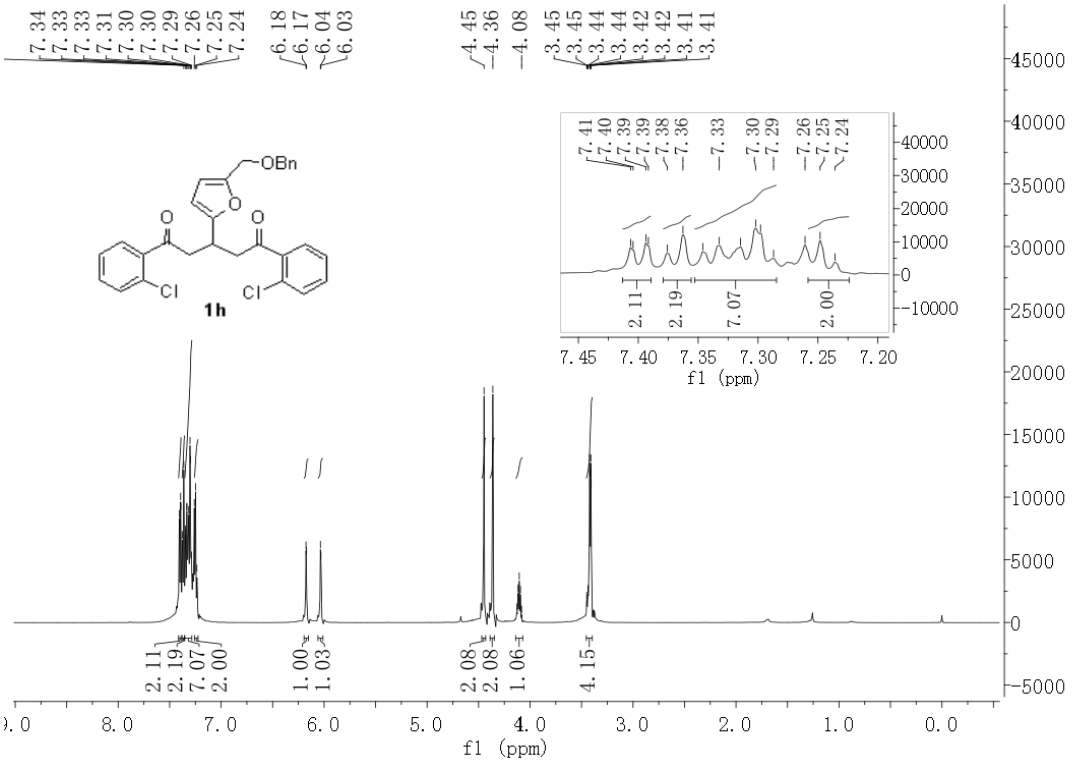
f1 (ppm)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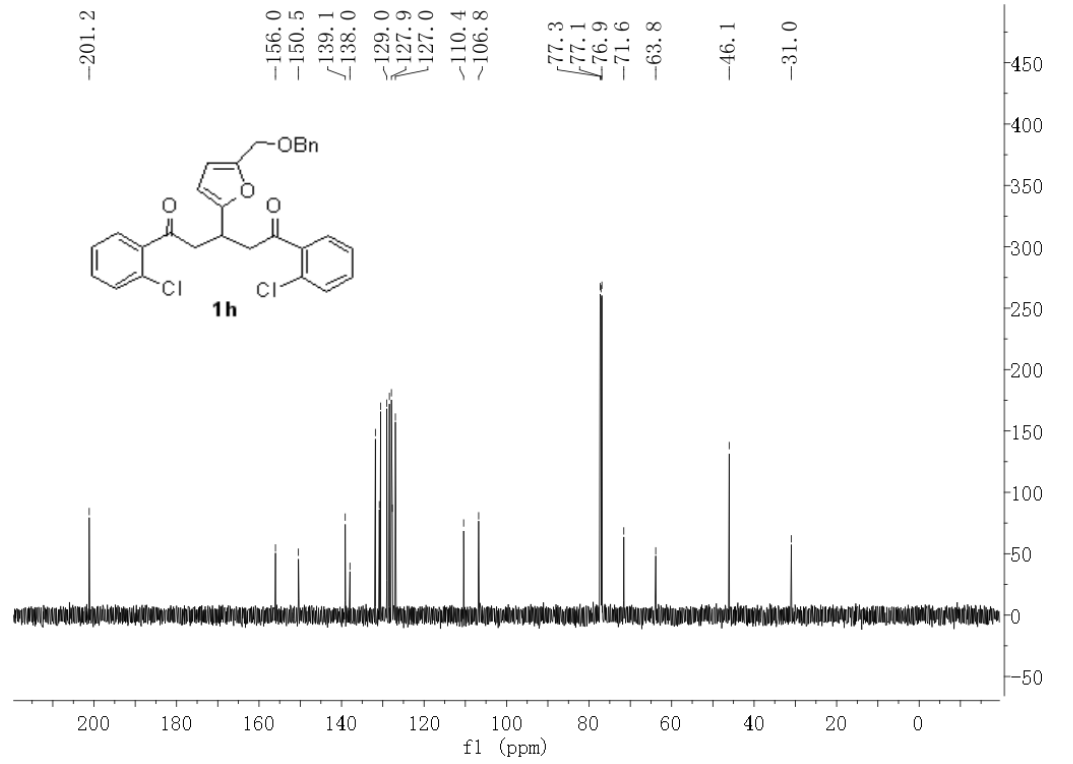
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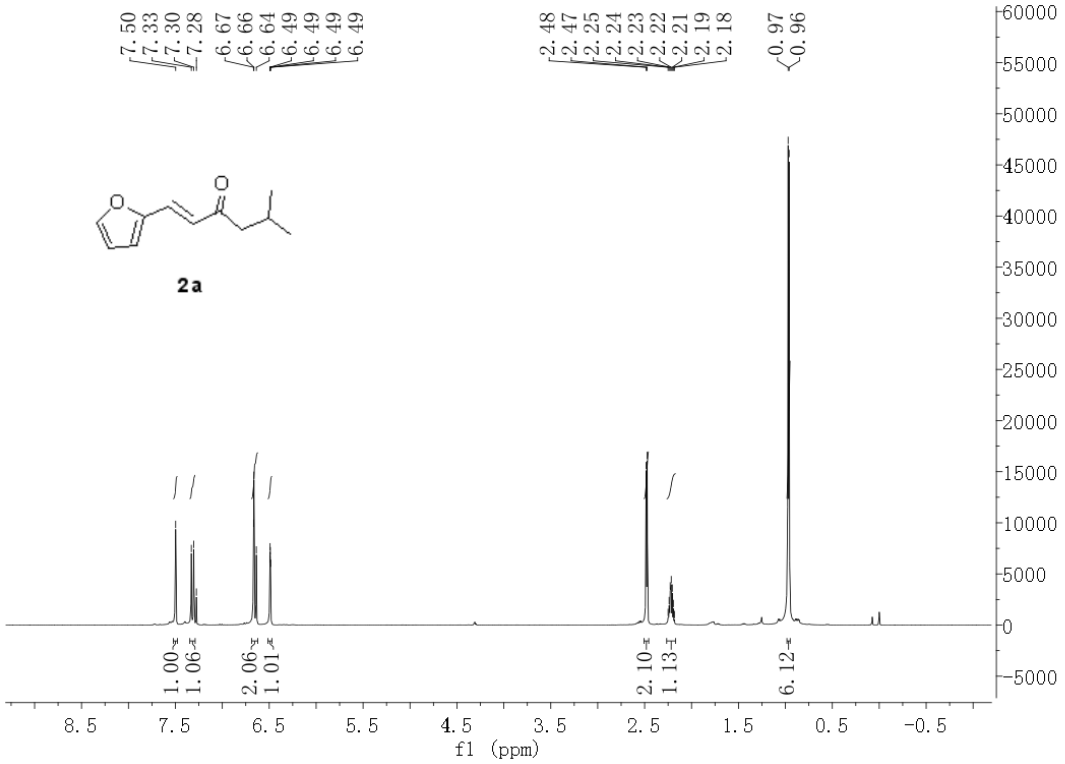
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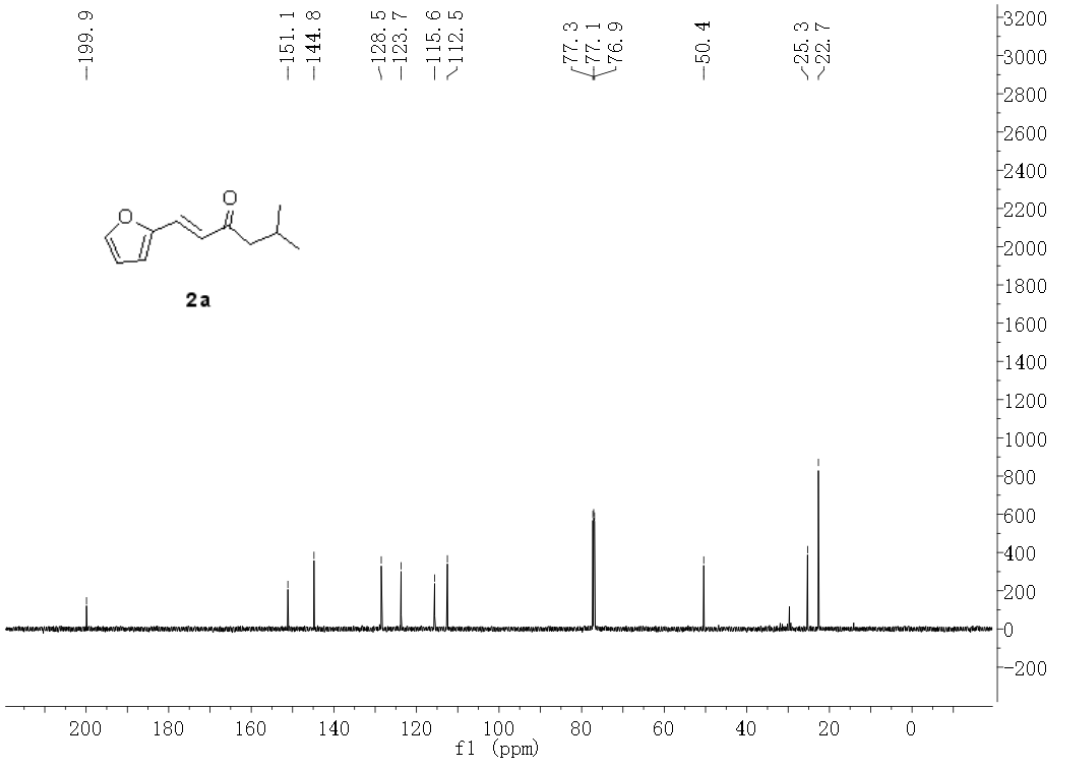
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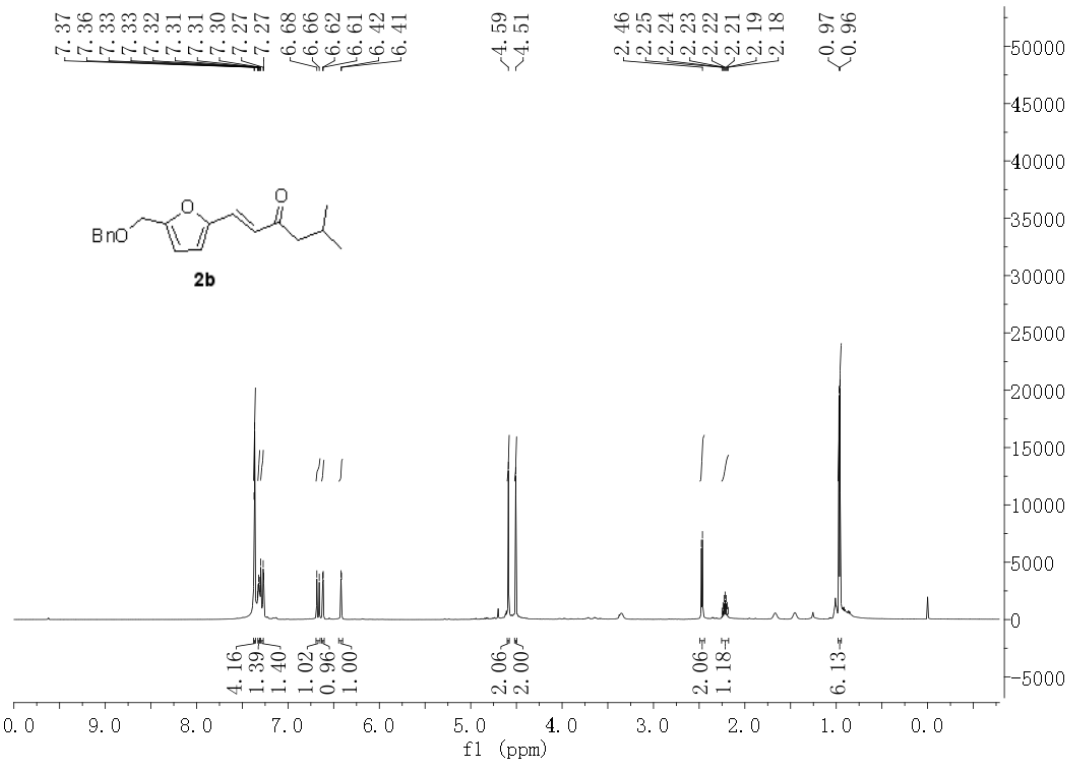
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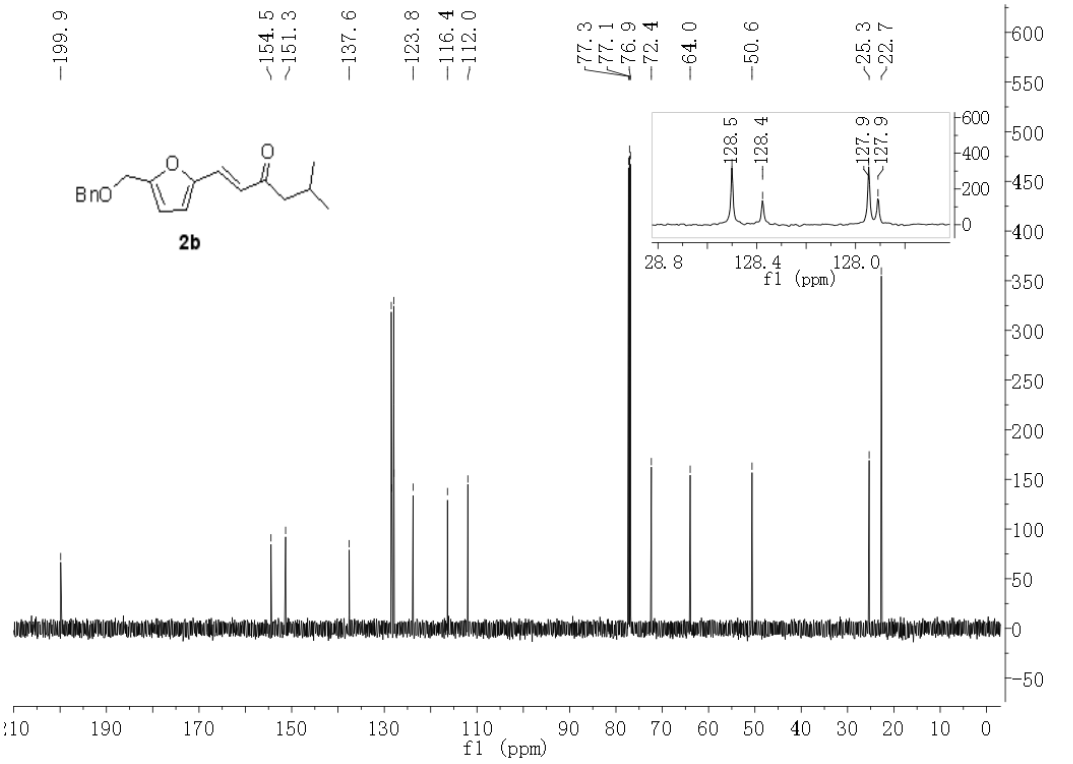
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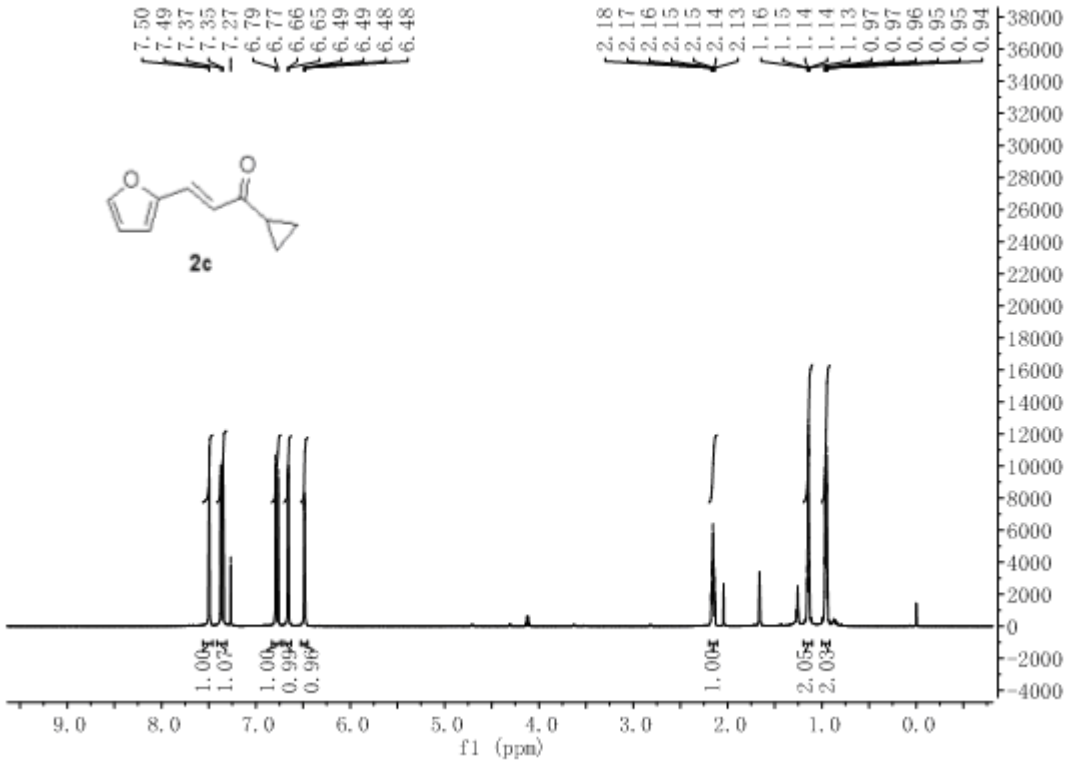
f1 (ppm)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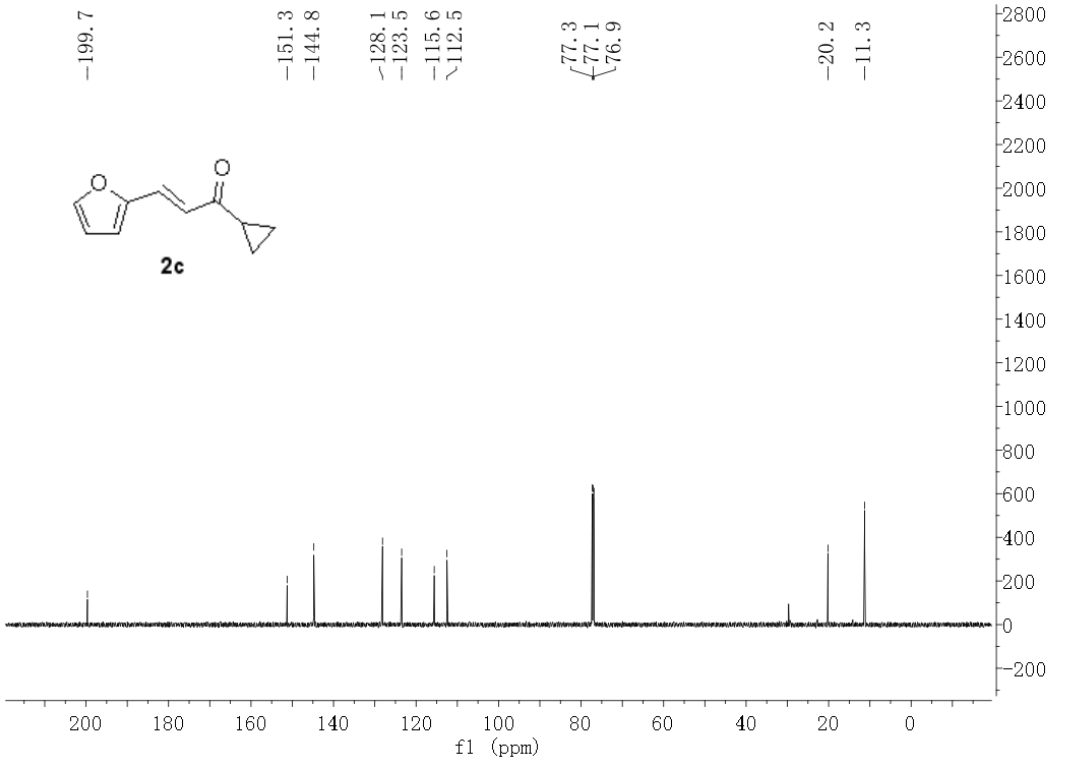
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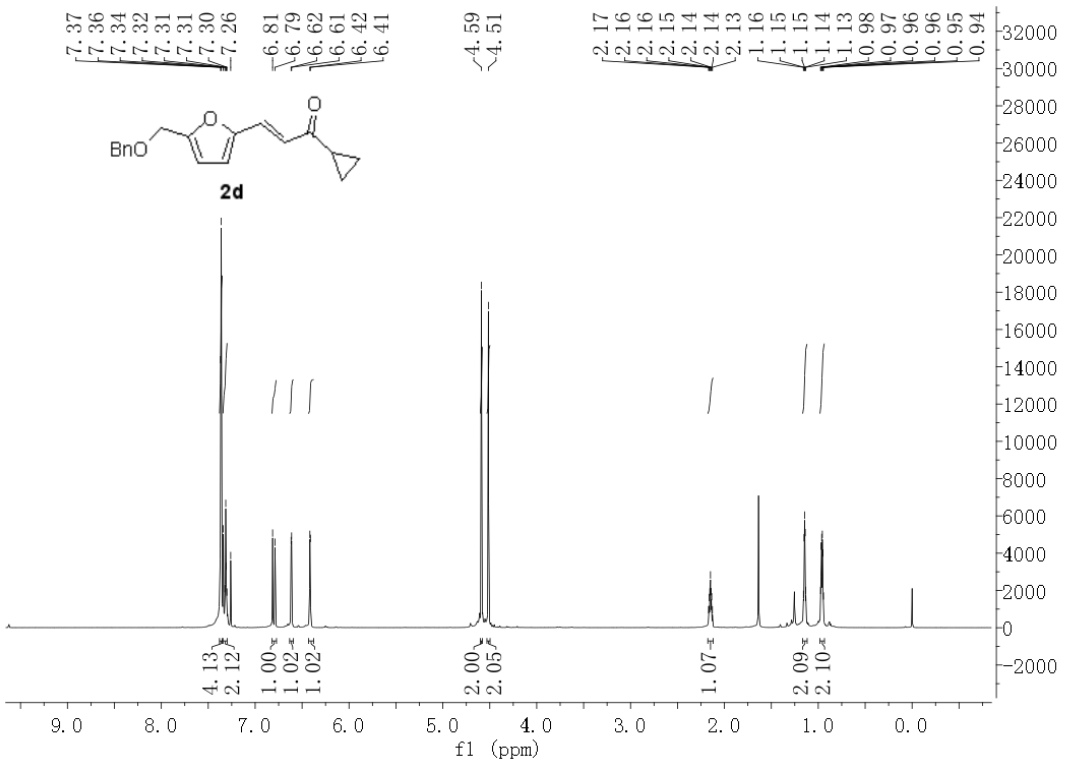
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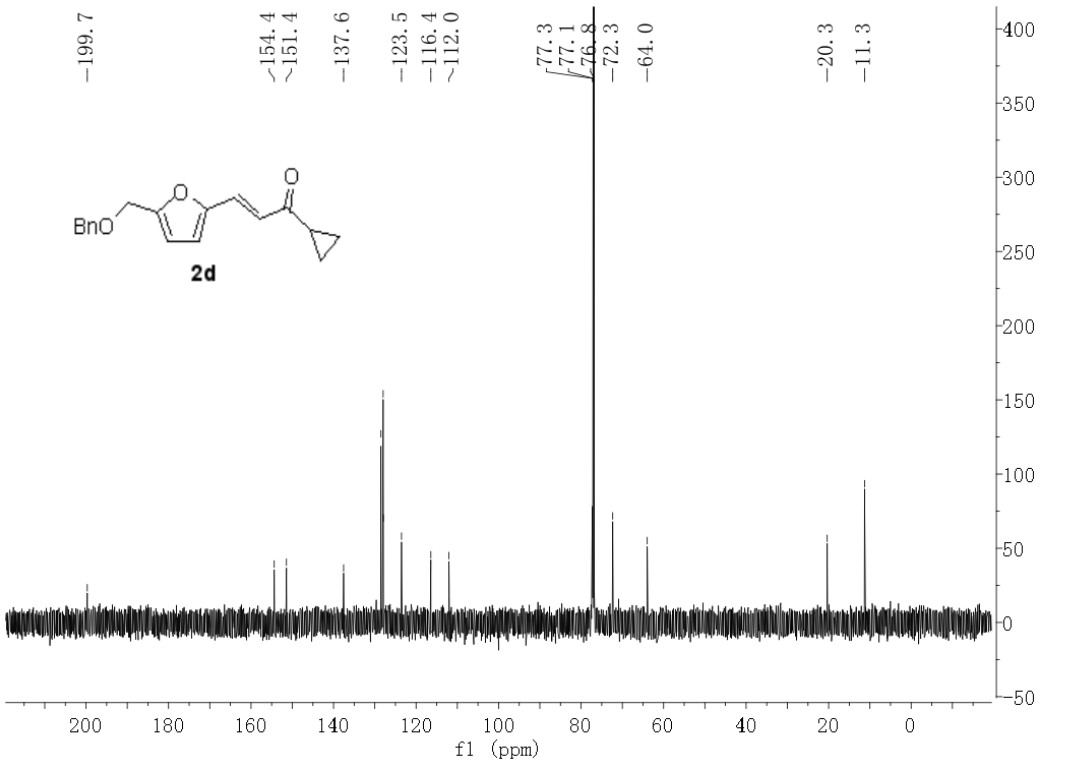
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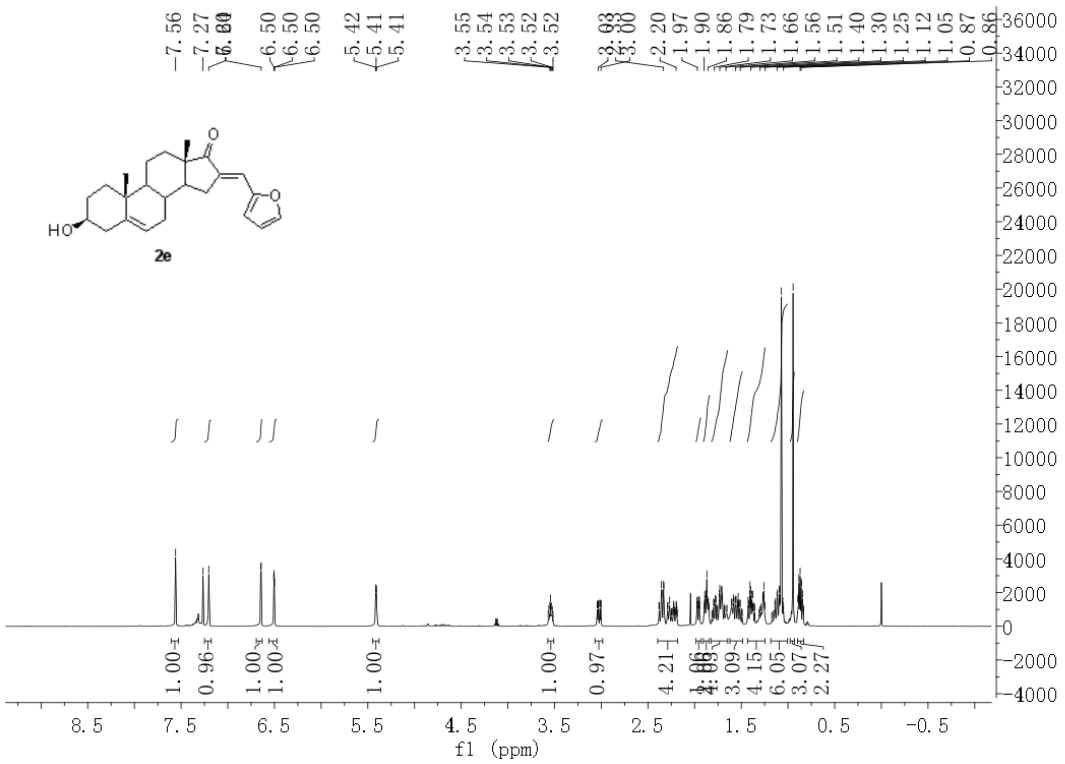
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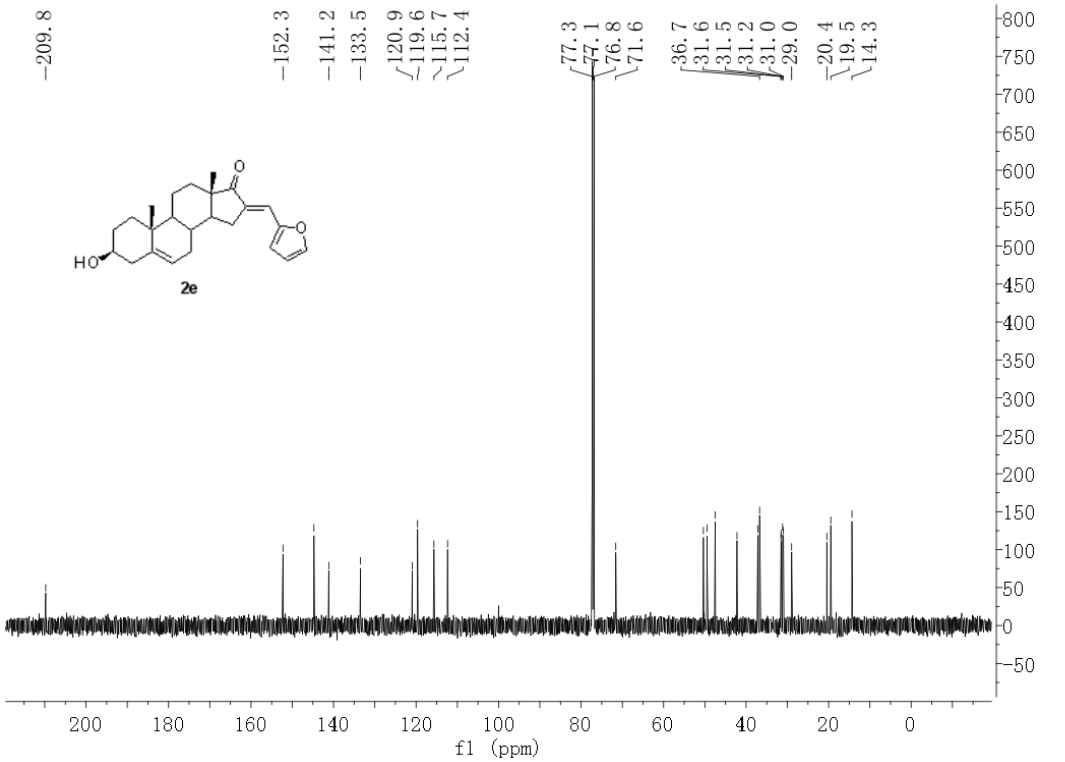
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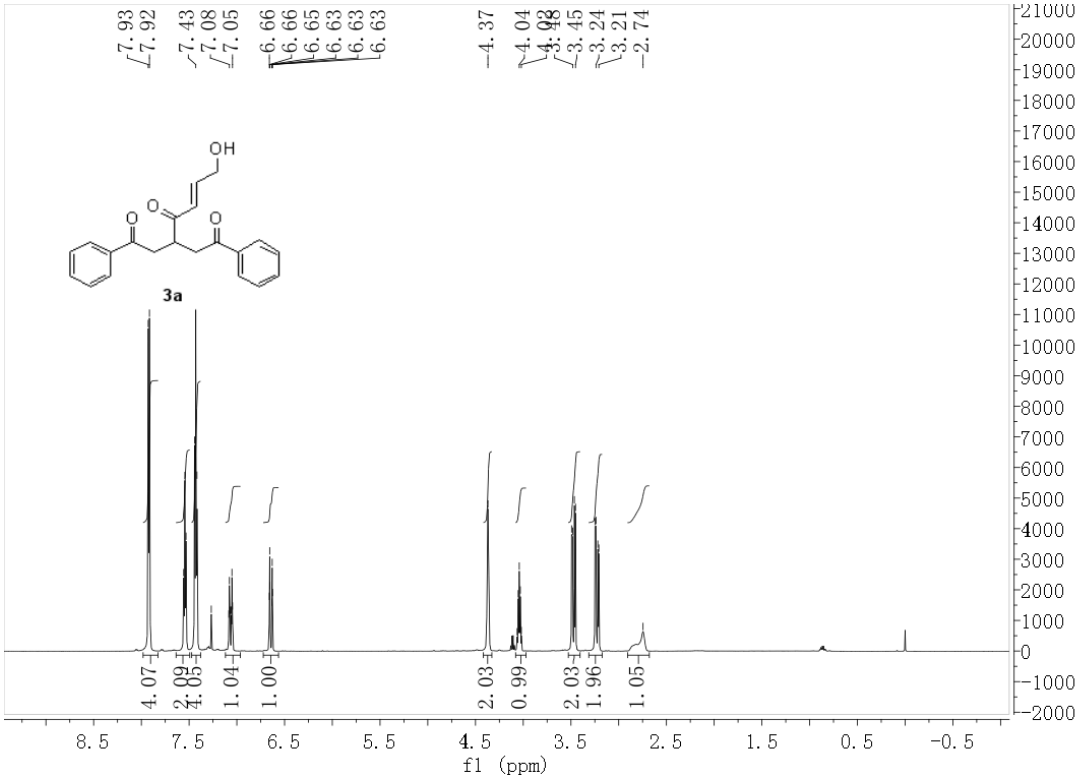
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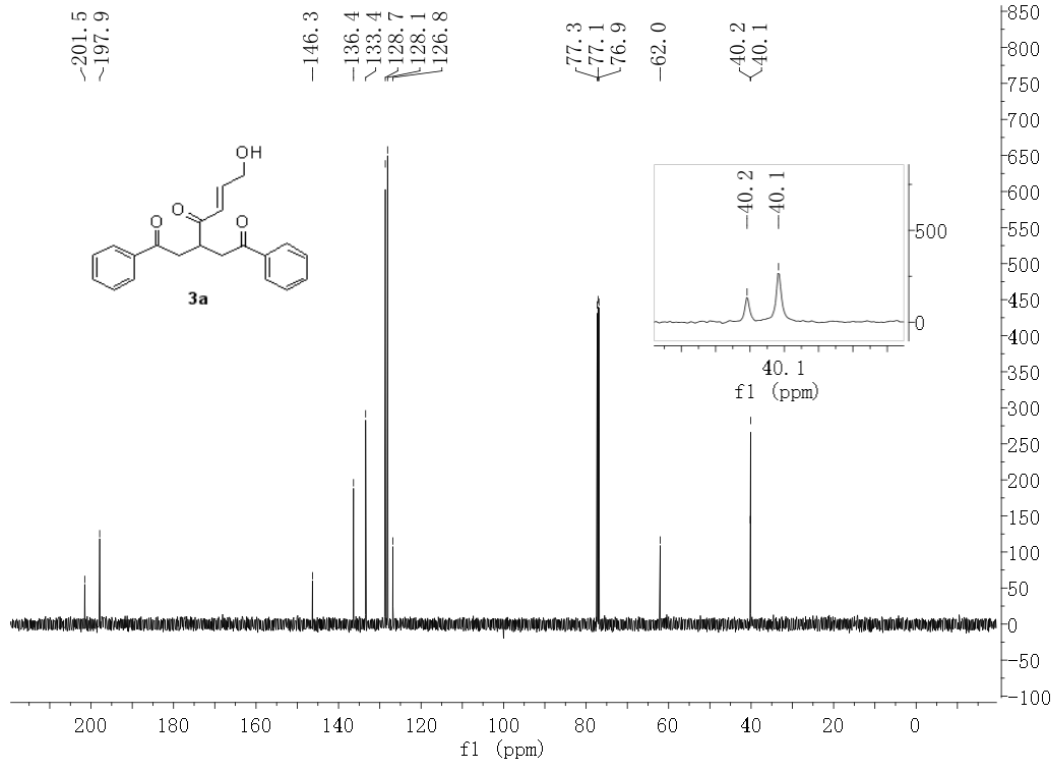
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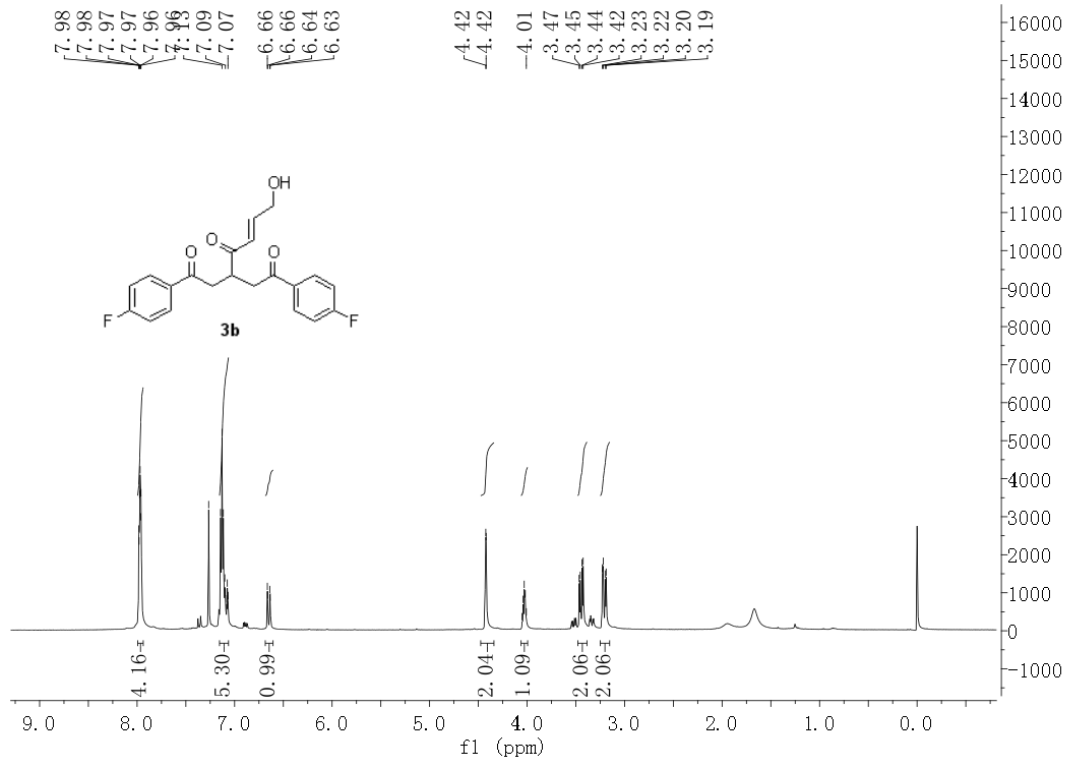
f1 (ppm)
f1 (ppm)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3.19
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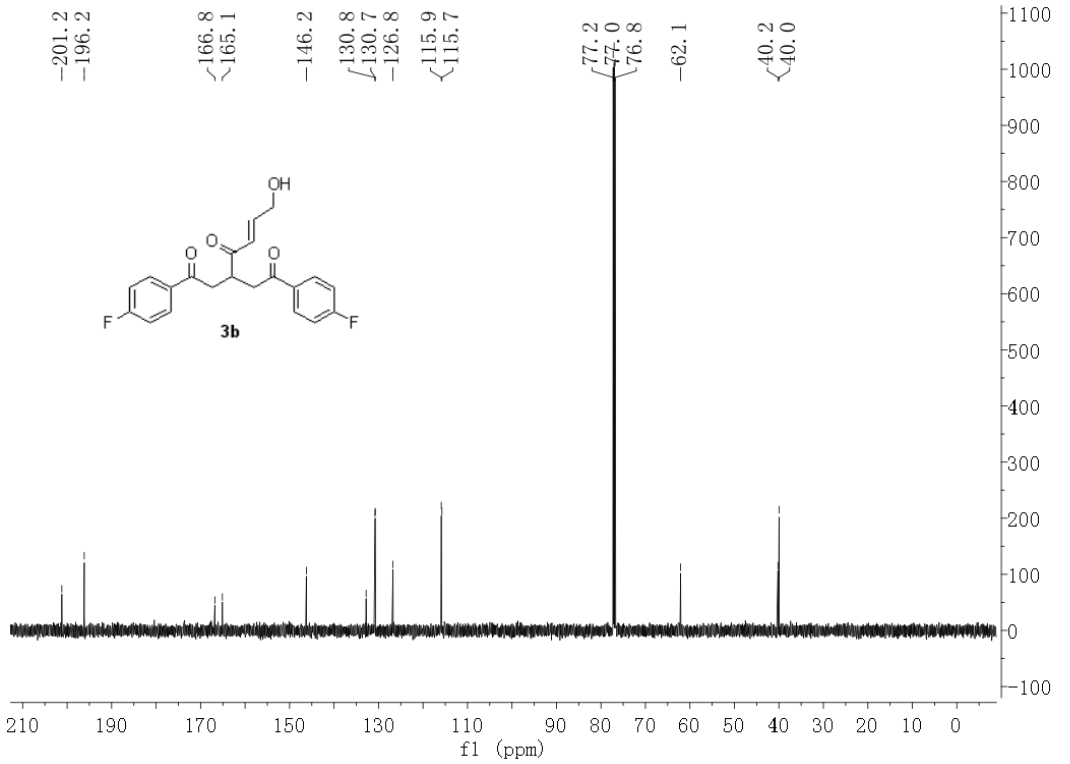
f1 (ppm)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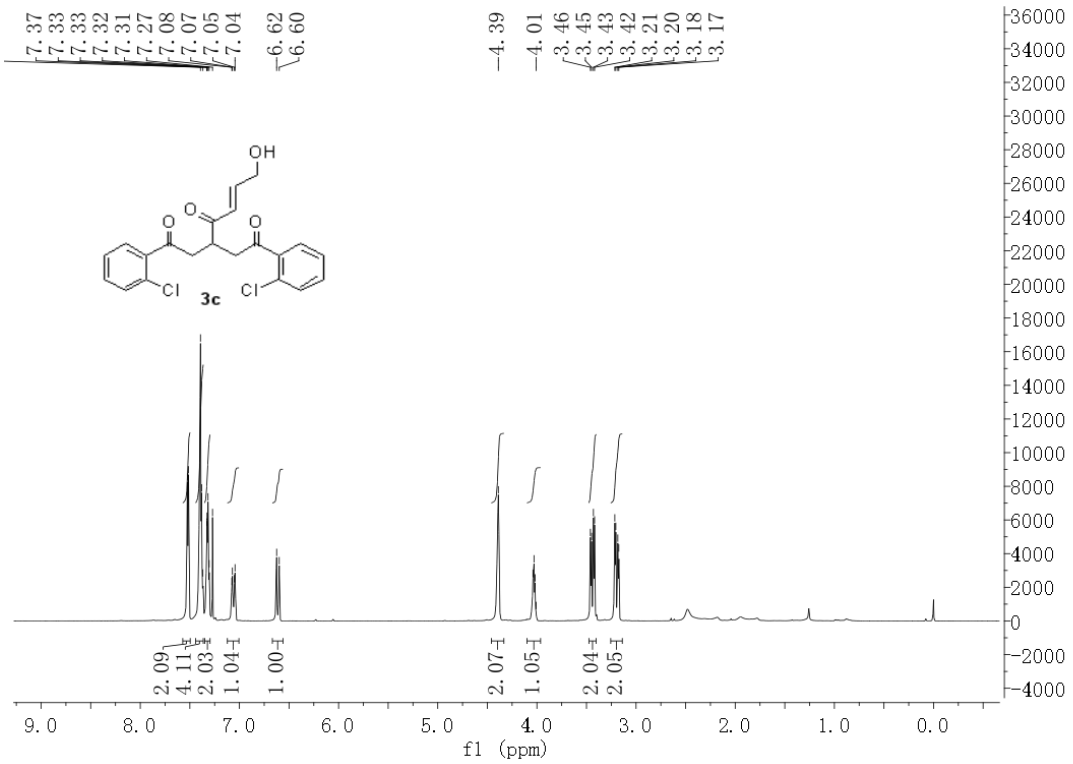
F
F
3b
f1 (ppm)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7.33
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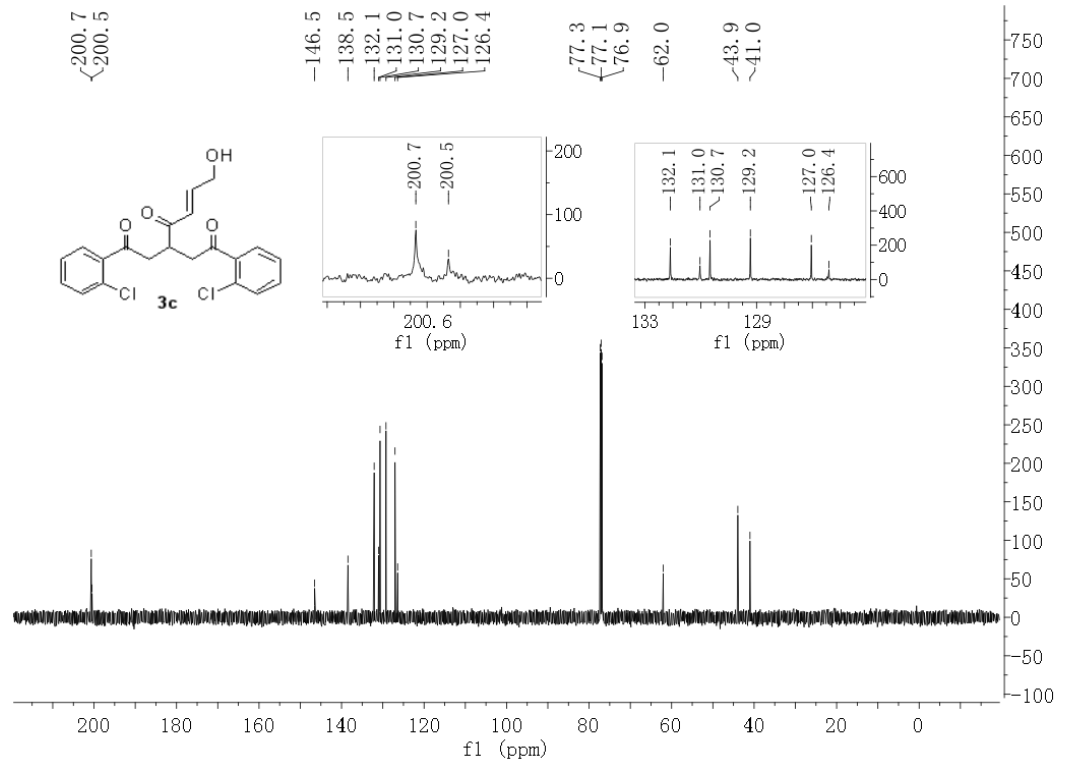
7.31
7.27
7.08
7.07
7.05
7.04
6.62
6.60
4.39
4.01
3.46
3.45
3.43
3.42
3.21
3.20
3.18
3.17
OH
O
O
O
Cl
Cl
3c
2.09
4.11
2.03
1.04
1.00
2.07
1.05
2.04
2.05
f1 (ppm)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200.5
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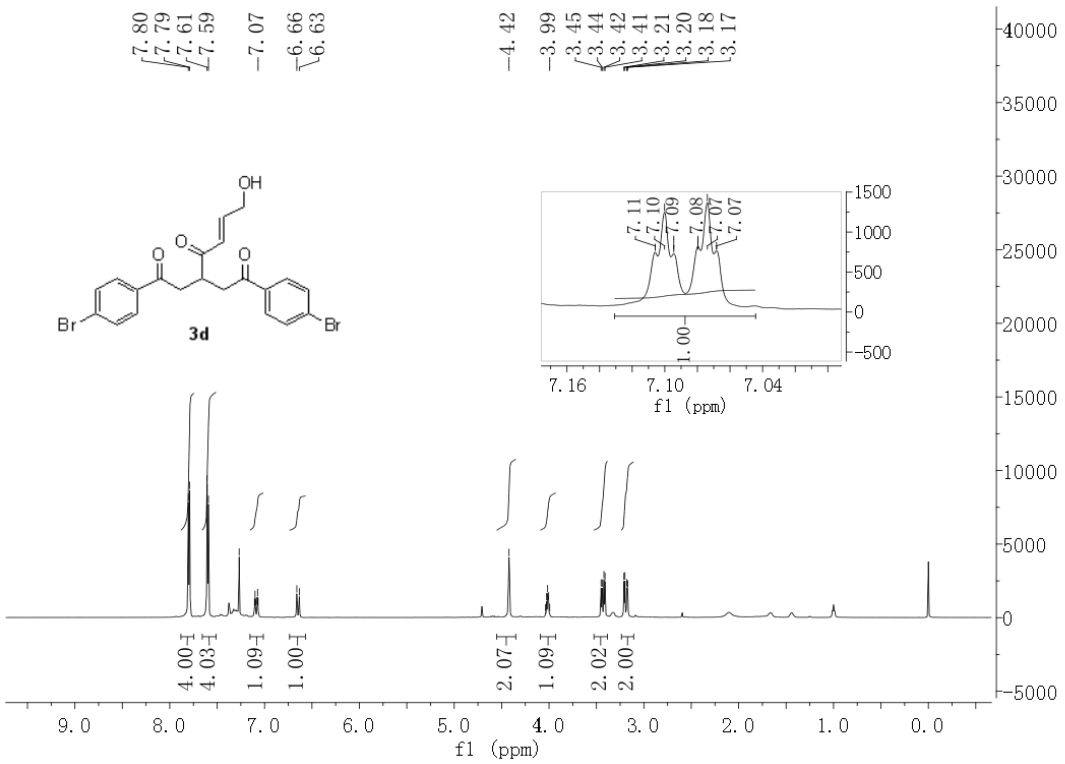
138.5
132.1
131.0
130.7
129.2
127.0
126.4
77.3
77.1
76.9
62.0
43.9
41.0
OH
O
O
O
Cl
Cl
3c
200.7
200.5
200.6
f1 (ppm)
132.1
131.0
130.7
129.2
127.0
126.4
133
129
f1 (ppm)
f1 (ppm)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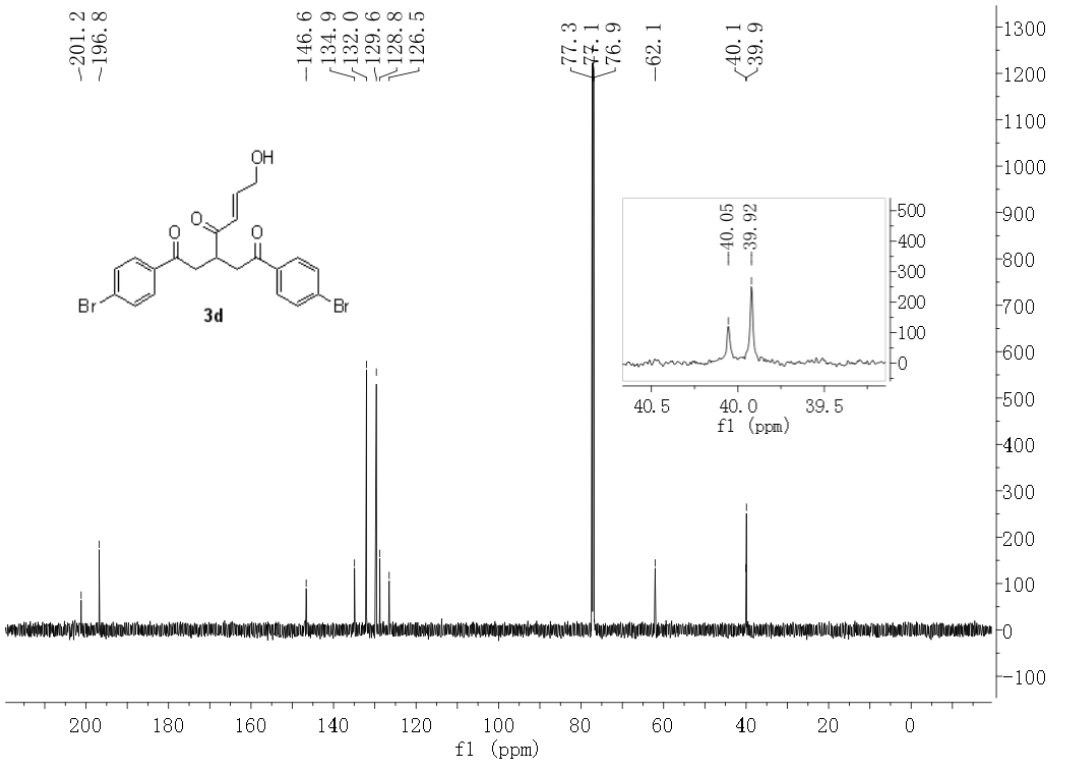
7.79
7.61
7.59
7.07
6.66
6.63
4.42
3.99
3.45
3.44
3.42
3.41
3.21
3.20
3.18
3.17
OH
O
O
O
Br
Br
3d
7.11
7.10
7.09
7.08
7.07
7.07
1.00
7.16
7.10
7.04
f1 (ppm)
4.00
4.03
1.09
1.00
2.07
1.09
2.02
2.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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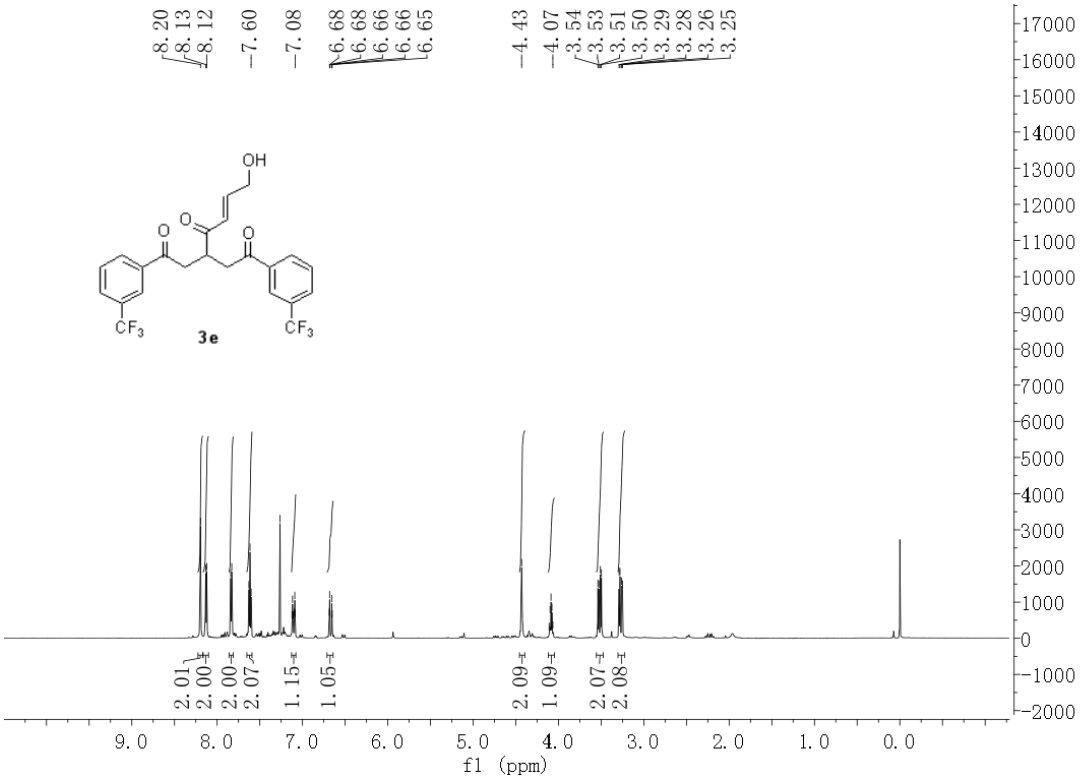
196.8
146.6
134.9
132.0
129.6
128.8
126.5
77.3
77.1
76.9
62.1
40.1
39.9
OH
O
O
O
Br
Br
3d
40.05
39.92
40.5
40.0
39.5
f1 (ppm)
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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8.13
8.12
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7.08
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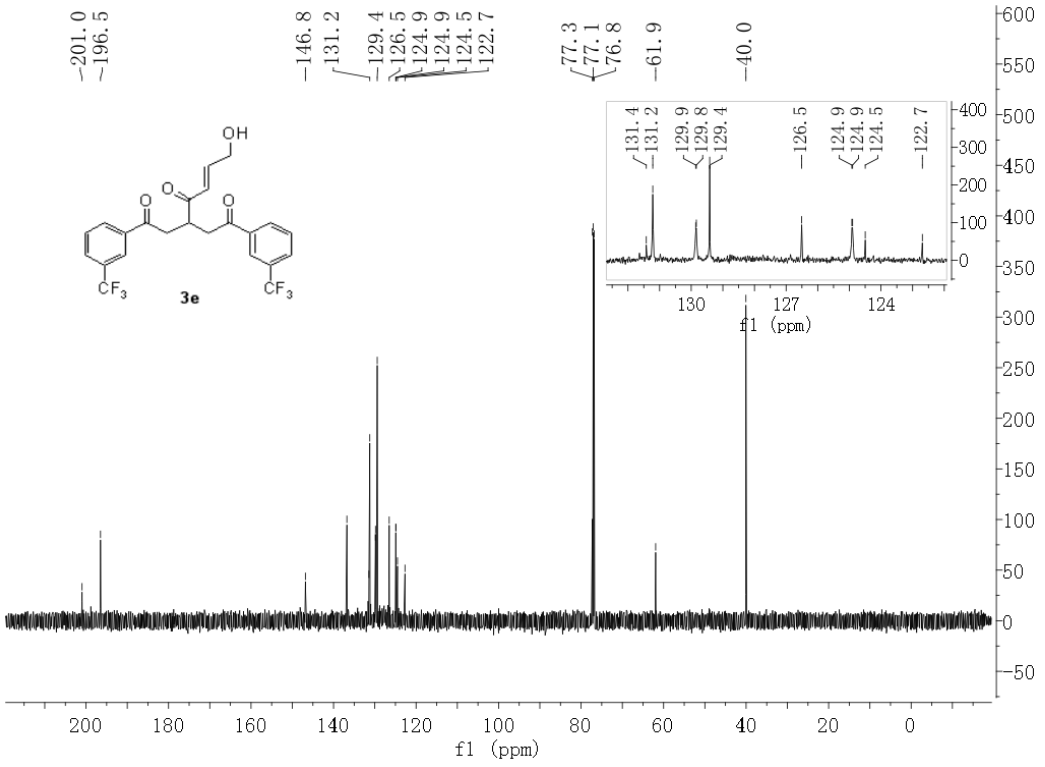
6.68
6.66
6.66
6.65
4.43
4.07
3.54
3.53
3.51
3.50
3.29
3.28
3.26
3.25
OH
O
O
O
CF3
CF3
3e
2.01
2.00
2.00
2.07
1.15
1.05
2.09
1.09
2.07
2.08
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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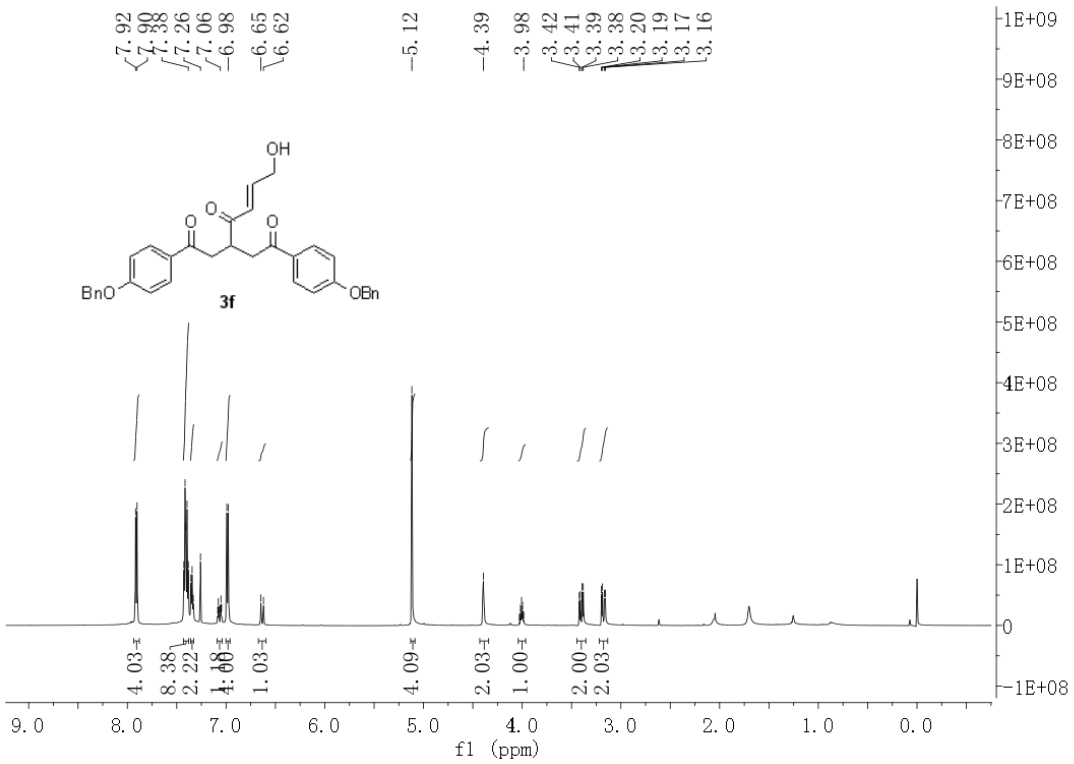
146.8
131.2
129.4
126.5
124.9
124.9
124.5
122.7
77.3
77.1
76.8
61.9
40.0
OH
O
O
O
CF3
CF3
3e
131.4
131.2
129.9
129.8
129.4
126.5
124.9
124.9
124.5
122.7
130
127
124
f1 (ppm)
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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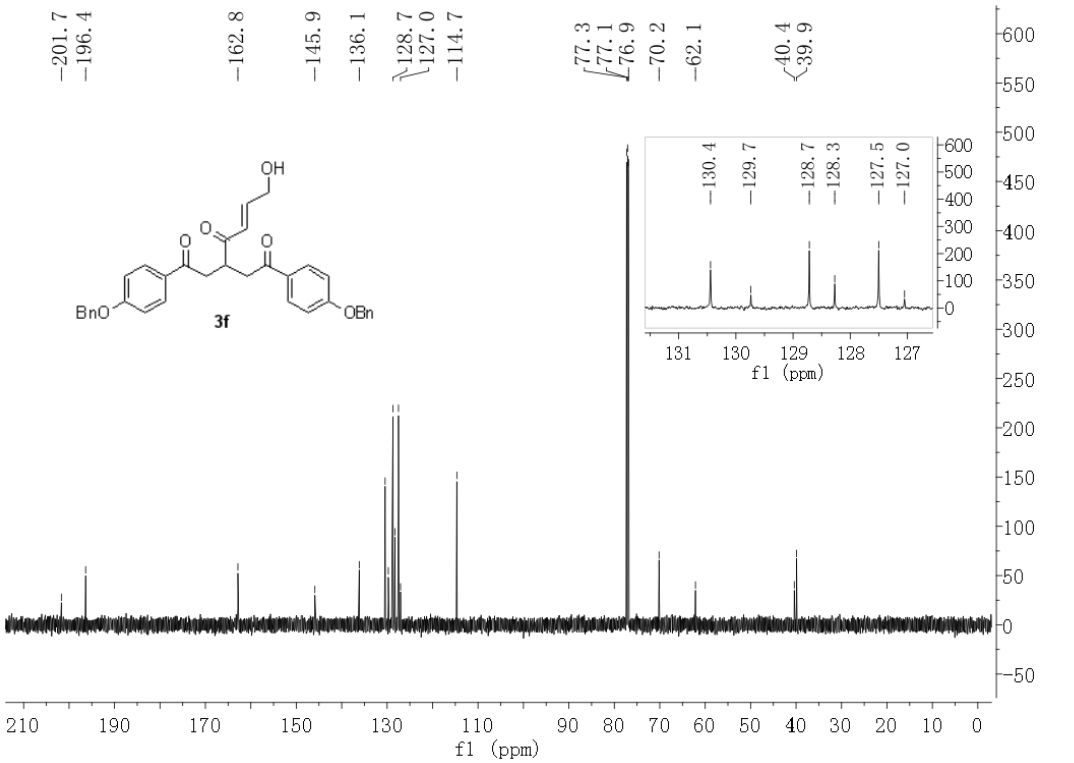
7.90
7.38
7.26
7.06
6.98
6.65
6.62
5.12
4.39
3.98
3.42
3.41
3.39
3.38
3.20
3.19
3.17
3.16
OH
O
O
O
BnO
OBn
3f
4.03
8.38
2.22
4.00
1.03
4.09
2.03
1.00
2.00
2.03
f1 (ppm)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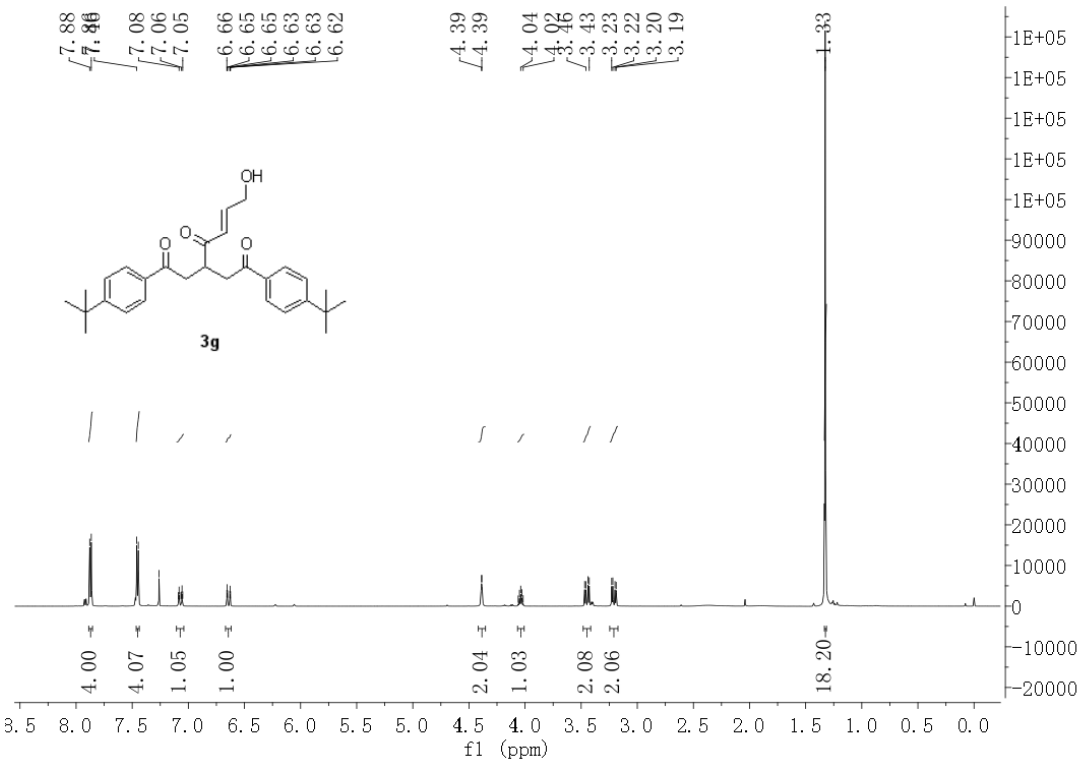
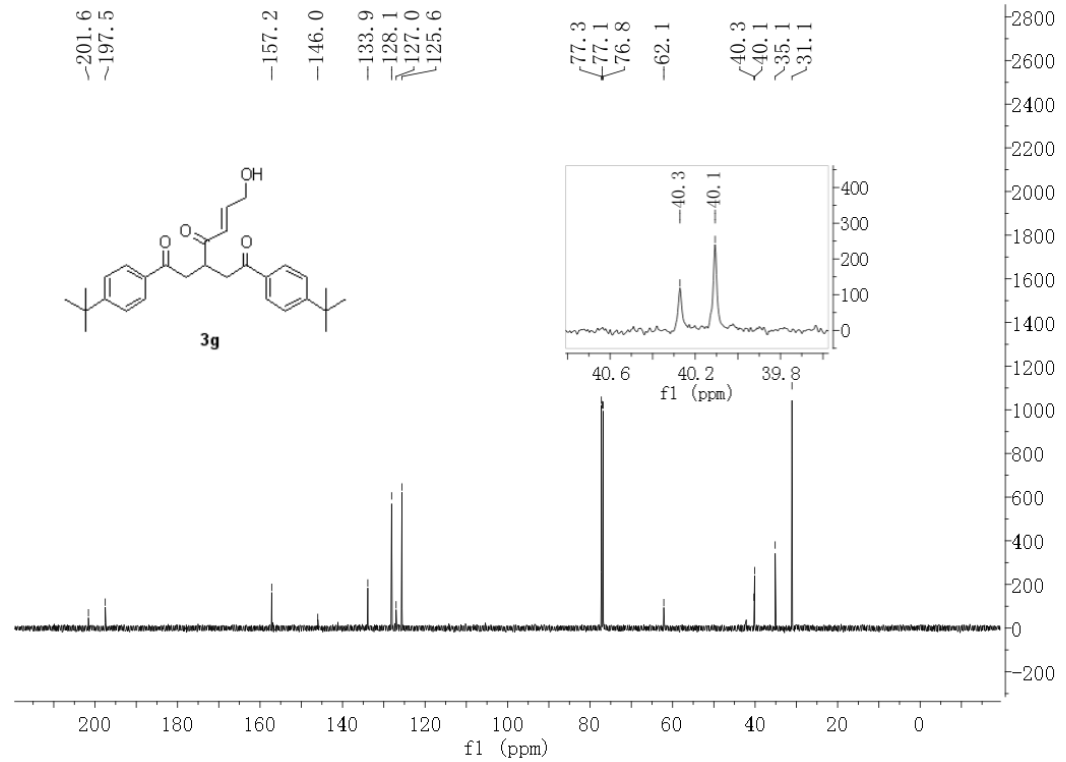
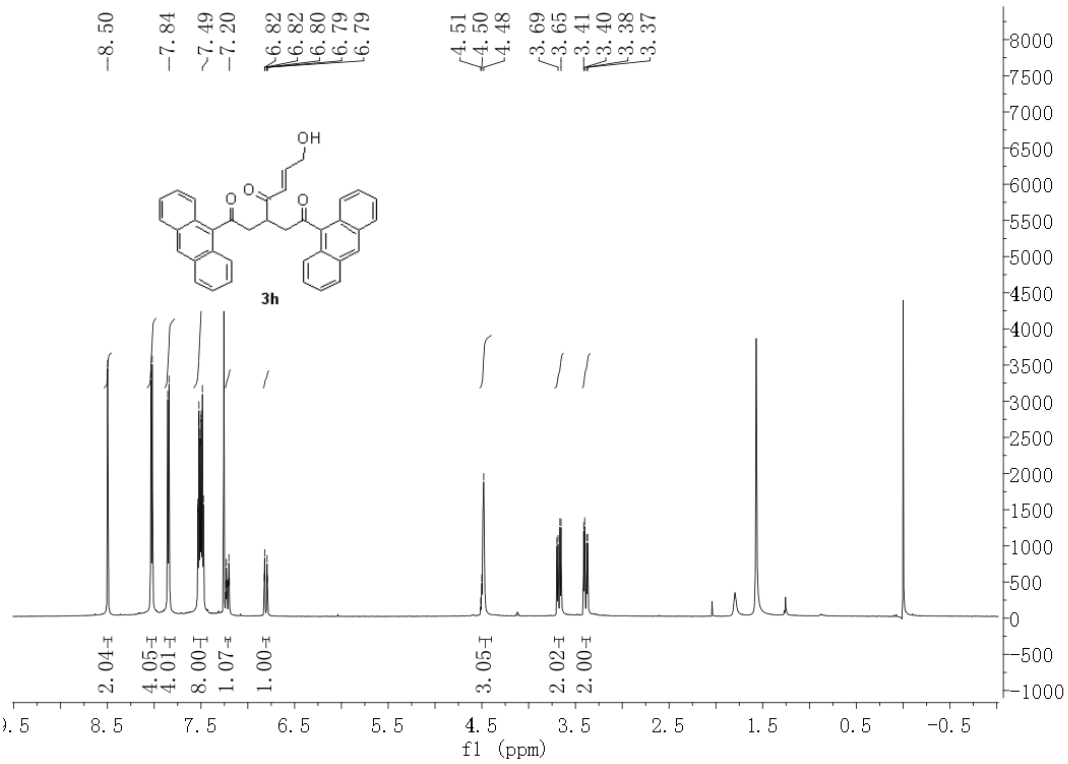
196.4
162.8
145.9
136.1
128.7
127.0
114.7
77.3
77.1
76.9
70.2
62.1
40.4
39.9
OH
O
O
O
BnO
OBn
3f
130.4
129.7
128.7
128.3
127.5
127.0
f1 (ppm)


7.88
7.86
7.08
7.06
7.05
6.66
6.65
6.65
6.63
6.63
6.62
4.39
4.39
4.04
4.02
3.46
3.43
3.23
3.22
3.20
3.19
1.33
OH
O
O
O
3g
4.00
4.07
1.05
1.00
2.04
1.03
2.08
2.06
18.20
f1 (ppm)


201.6
197.5
157.2
146.0
133.9
128.1
127.0
125.6
77.3
77.1
76.8
62.1
40.3
40.1
35.1
31.1
OH
O
O
O
3g
40.3
40.1
40.6
40.2
39.8
f1 (ppm)
f1 (ppm)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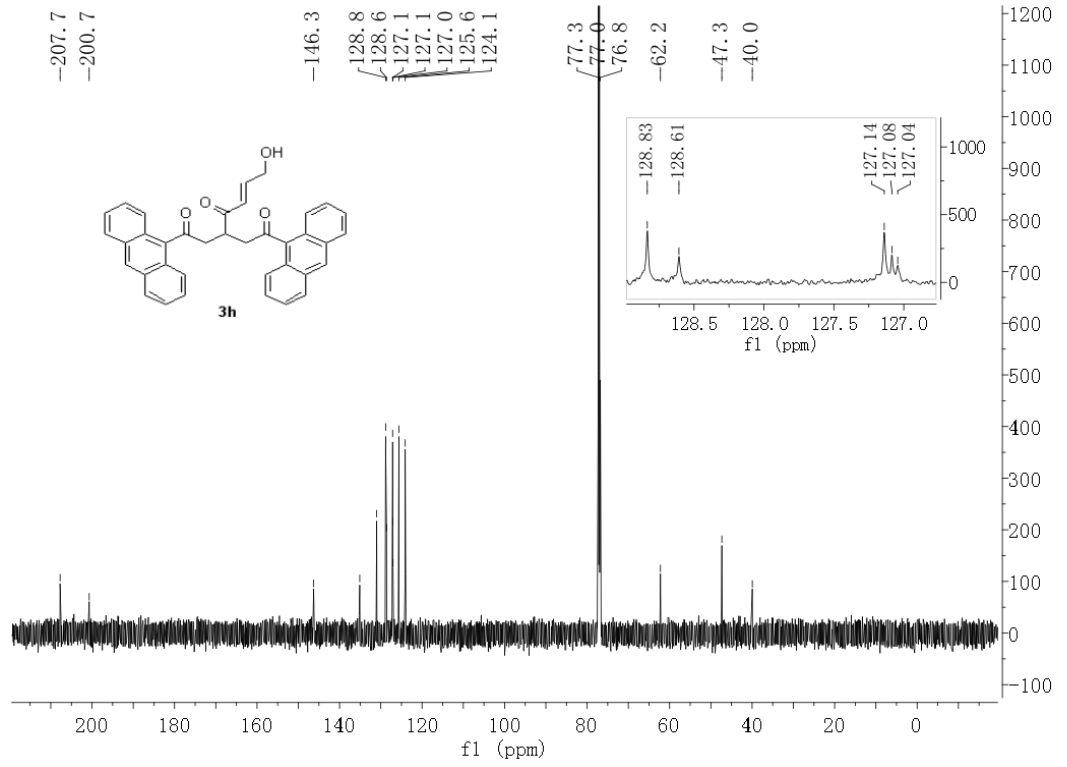
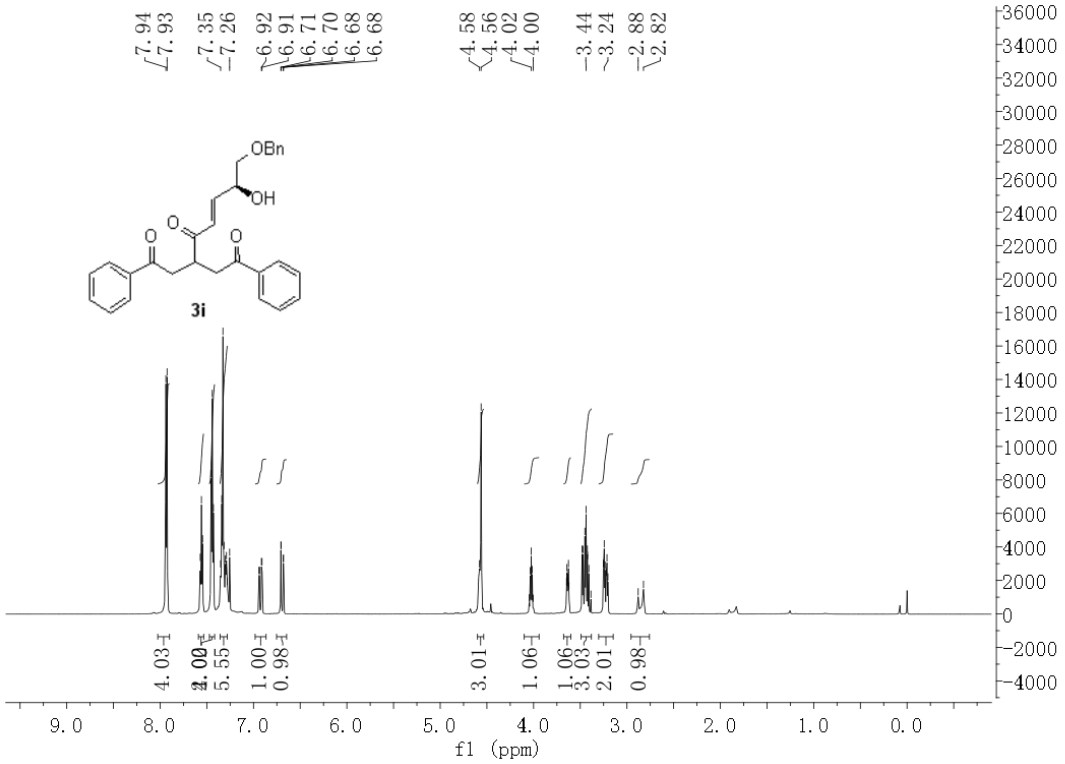
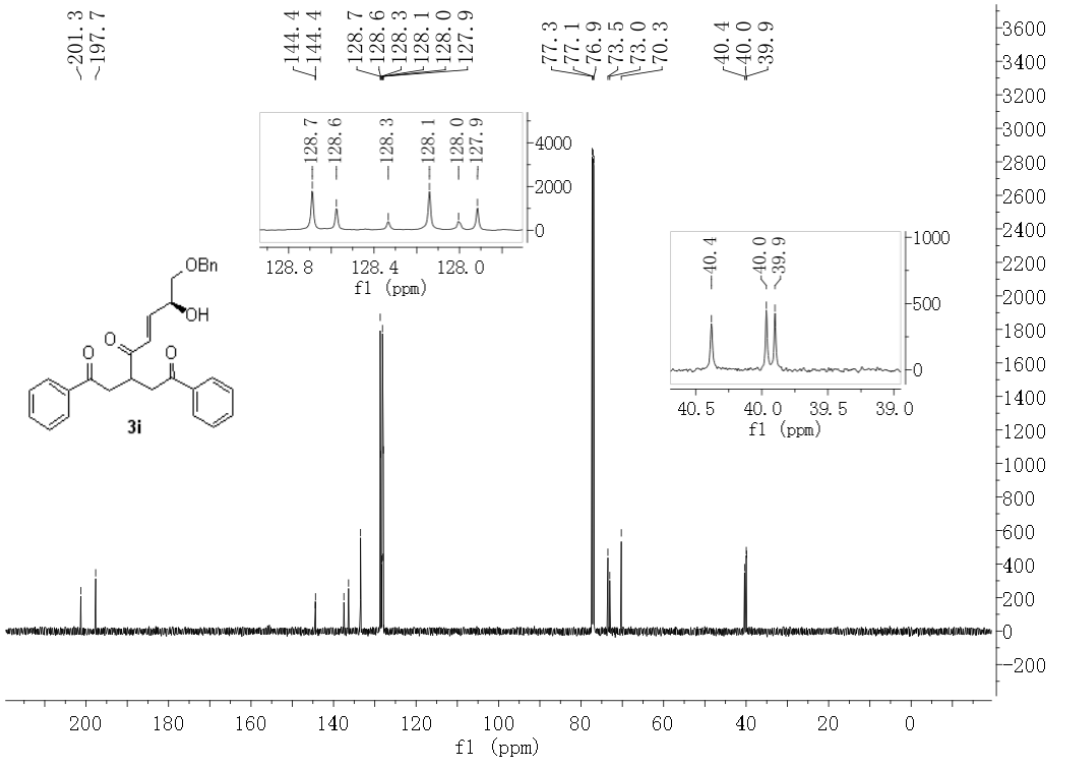
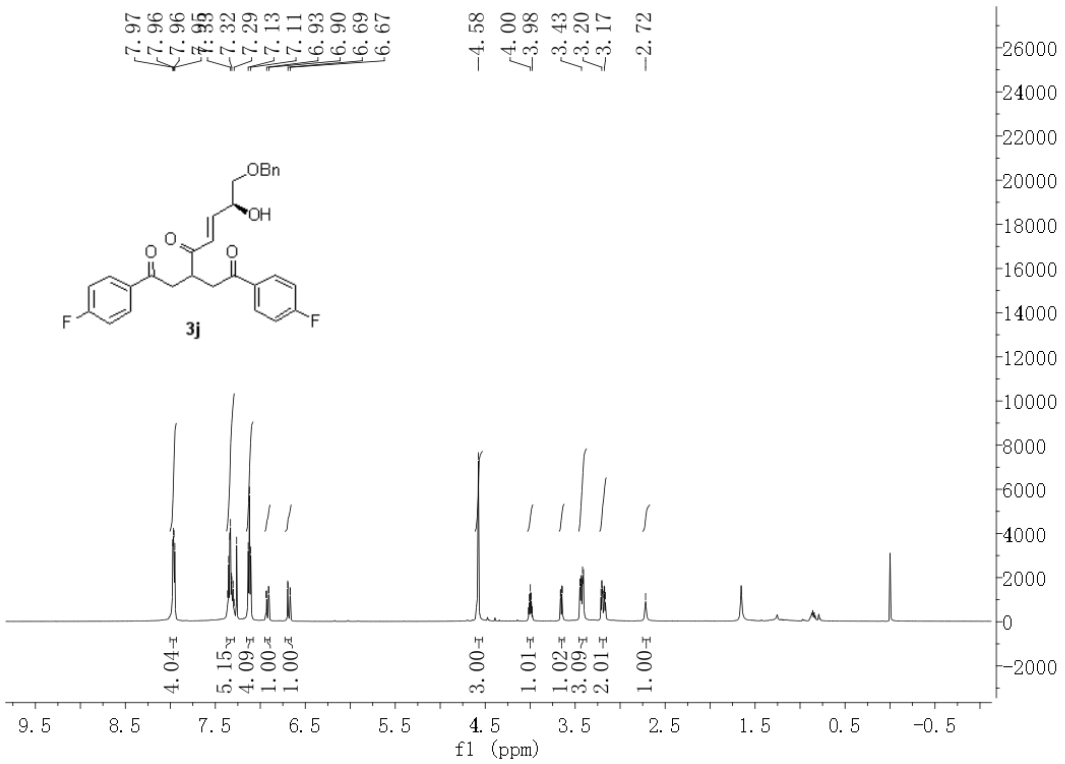
7.84
7.49
7.20
6.82
6.82
6.80
6.79
6.79
4.51
4.50
4.48
3.69
3.65
3.41
3.40
3.38
3.37
OH
O
O
O
3h
2.04
4.05
4.01
8.00
1.07
1.00
3.05
2.02
2.00
f1 (ppm)


207.7
200.7
146.3
128.8
128.6
127.1
127.1
127.0
125.6
124.1
77.3
77.0
76.8
62.2
47.3
40.0
OH
O
O
O
3h
128.83
128.61
127.14
127.08
127.04
f1 (ppm)
f1 (ppm)


7.94
7.93
7.35
7.26
6.92
6.91
6.71
6.70
6.68
6.68
4.58
4.56
4.02
4.00
3.44
3.24
2.88
2.82
OBn
OH
O
O
O
3i
4.03
2.00
5.55
1.00
0.98
3.01
1.06
1.06
3.03
2.01
0.98
f1 (ppm)


201.3
197.7
144.4
144.4
128.7
128.6
128.3
128.1
128.0
127.9
77.3
77.1
76.9
73.5
73.0
70.3
40.4
40.0
39.9
OBn
OH
O
O
O
3i
f1 (ppm)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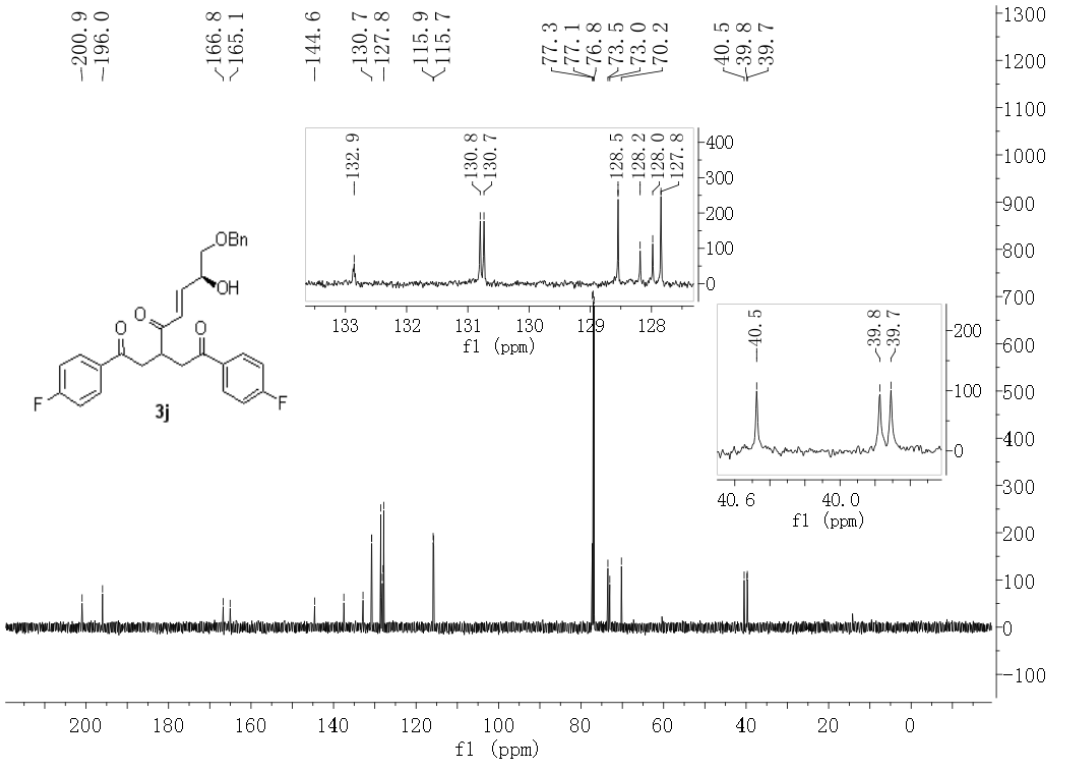
7.96
7.96
7.32
7.29
7.13
7.11
6.93
6.90
6.69
6.67
4.58
4.00
3.98
3.43
3.20
3.17
2.72
OBn
OH
O
O
O
F
F
3j
4.04
5.15
4.09
1.00
1.00
3.00
1.01
1.02
3.09
2.01
1.00
f1 (ppm)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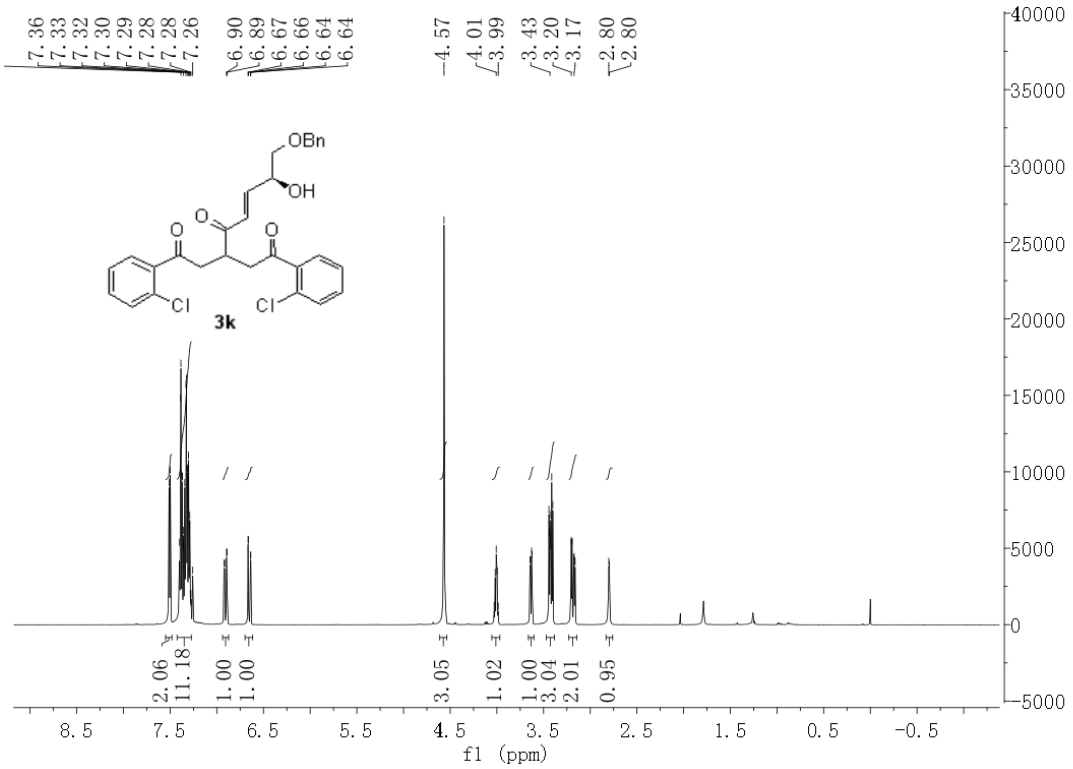
144.6
130.7
127.8
115.9
115.7
77.3
77.1
76.8
73.5
73.0
70.2
40.5
39.8
39.7
132.9
130.8
130.7
128.5
128.2
128.0
127.8
OBn
OH
3j
f1 (ppm)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7.26
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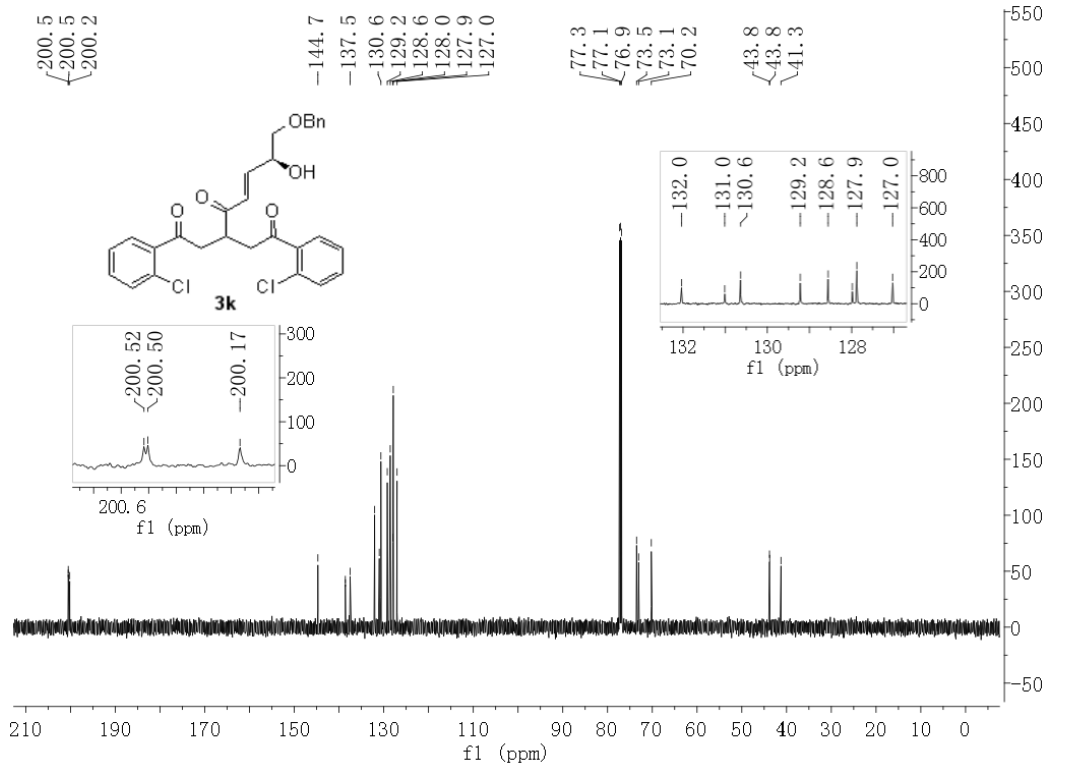
6.89
6.67
6.66
6.64
6.64
4.57
4.01
3.99
3.43
3.20
3.17
2.80
2.80
OBn
OH
O
O
O
Cl
Cl
3k
2.06
11.18
1.00
1.00
3.05
1.02
1.00
3.04
2.01
0.95
f1 (ppm)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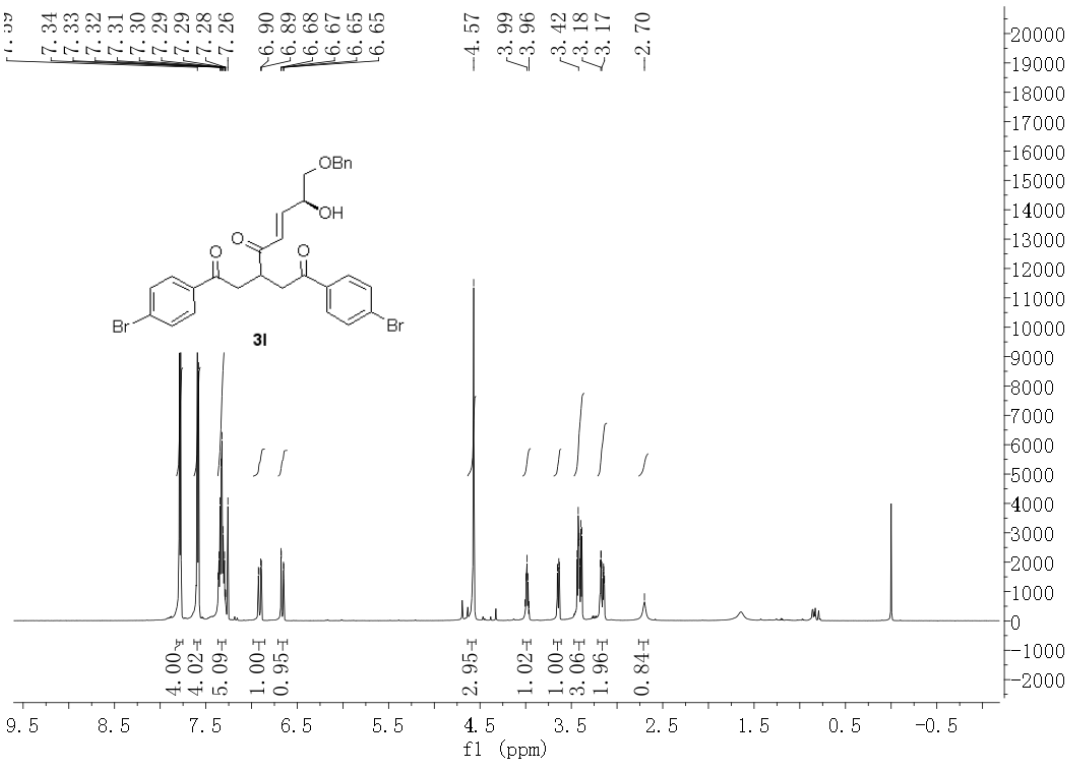
200.5
200.2
144.7
137.5
130.6
129.2
128.6
128.0
127.9
127.0
77.3
77.1
76.9
73.5
73.1
70.2
43.8
43.8
41.3
OBn
OH
O
O
O
Cl
Cl
3k
200.52
200.50
200.17
200.6
f1 (ppm)
132.0
131.0
130.6
129.2
128.6
127.9
127.0
132
130
128
f1 (ppm)
f1 (ppm)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7.32
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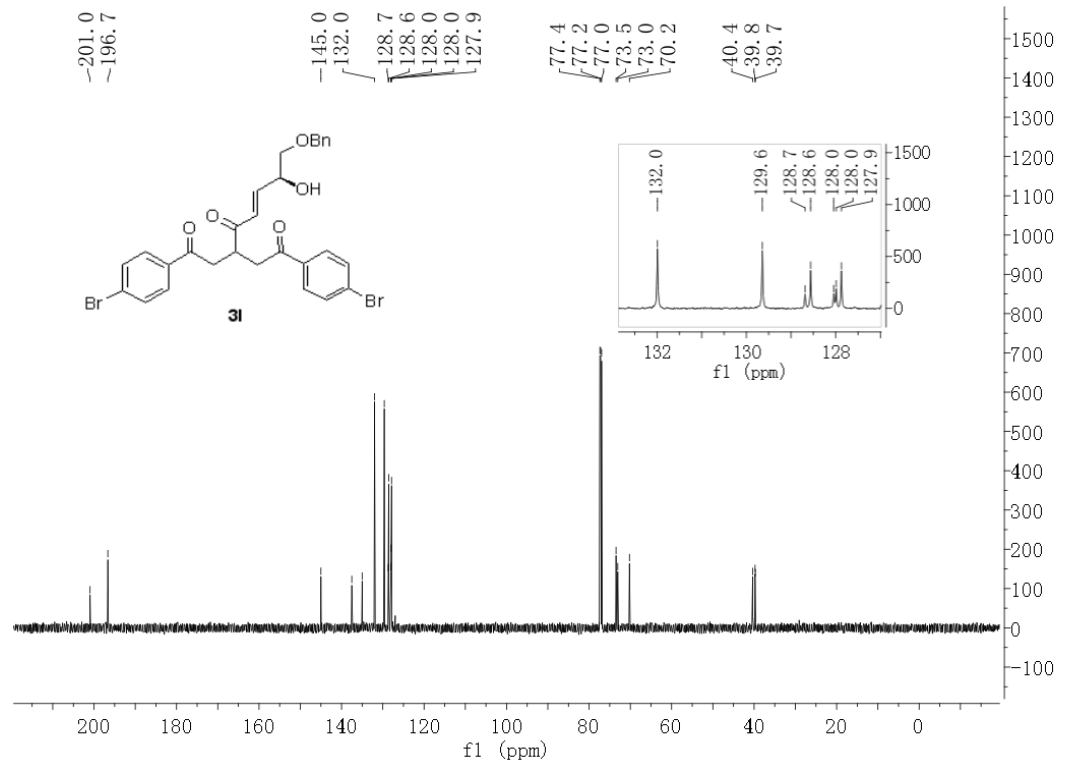
7.29
7.29
7.28
7.26
6.90
6.89
6.68
6.67
6.65
6.65
4.57
3.99
3.96
3.42
3.18
3.17
2.70
OBn
OH
O
O
O
Br
Br
3l
4.00
4.02
5.09
1.00
0.95
2.95
1.02
1.00
3.06
1.96
0.84
f1 (ppm)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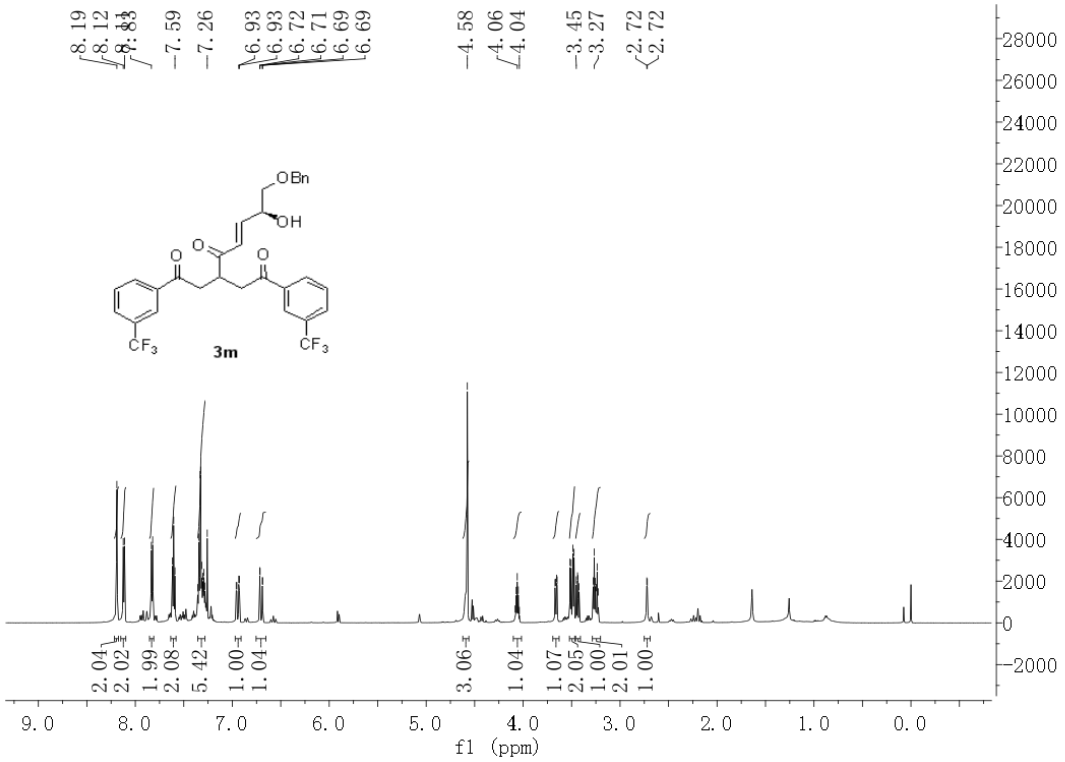
196.7
145.0
132.0
128.7
128.6
128.0
128.0
127.9
77.4
77.2
77.0
73.5
73.0
70.2
40.4
39.8
39.7
OBn
OH
O
O
O
Br
Br
3l
132.0
129.6
128.7
128.6
128.0
128.0
127.9
f1 (ppm)
f1 (ppm)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8.12
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7.26
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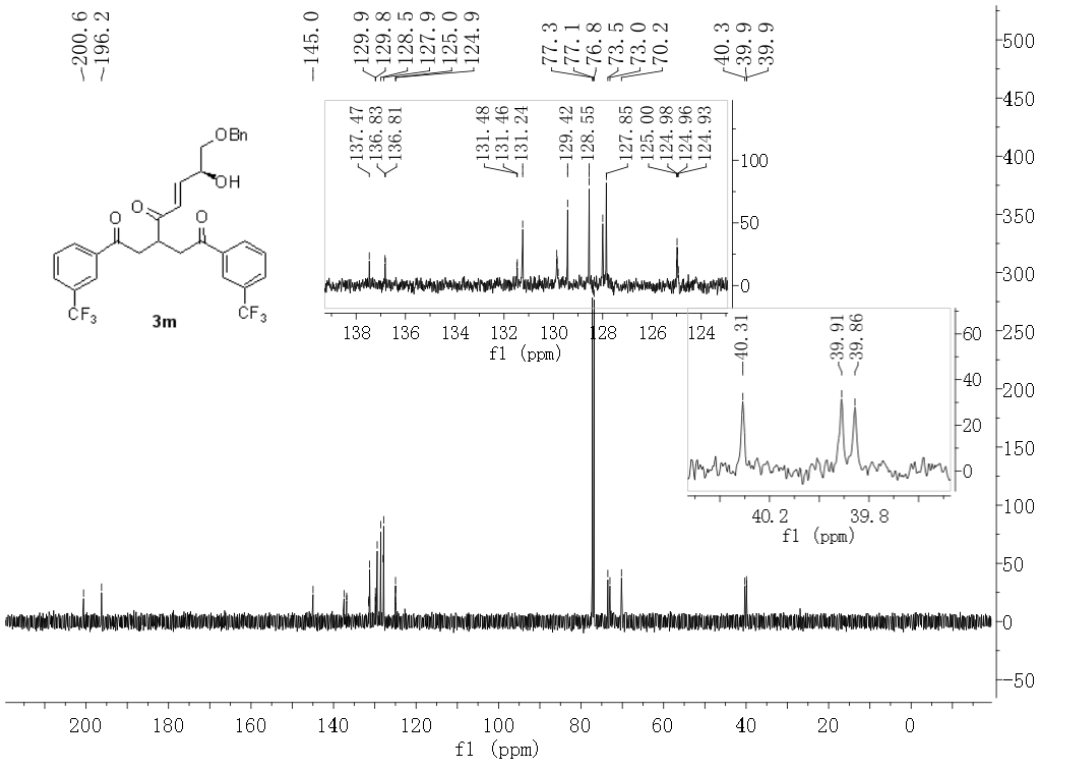
6.93
6.72
6.71
6.69
6.69
4.58
4.06
4.04
3.45
3.27
2.72
2.72
OBn
OH
O
O
O
CF3
CF3
3m
2.04
2.02
1.99
2.08
5.42
1.00
1.04
3.06
1.04
1.07
2.05
1.00
2.01
1.00
f1 (ppm)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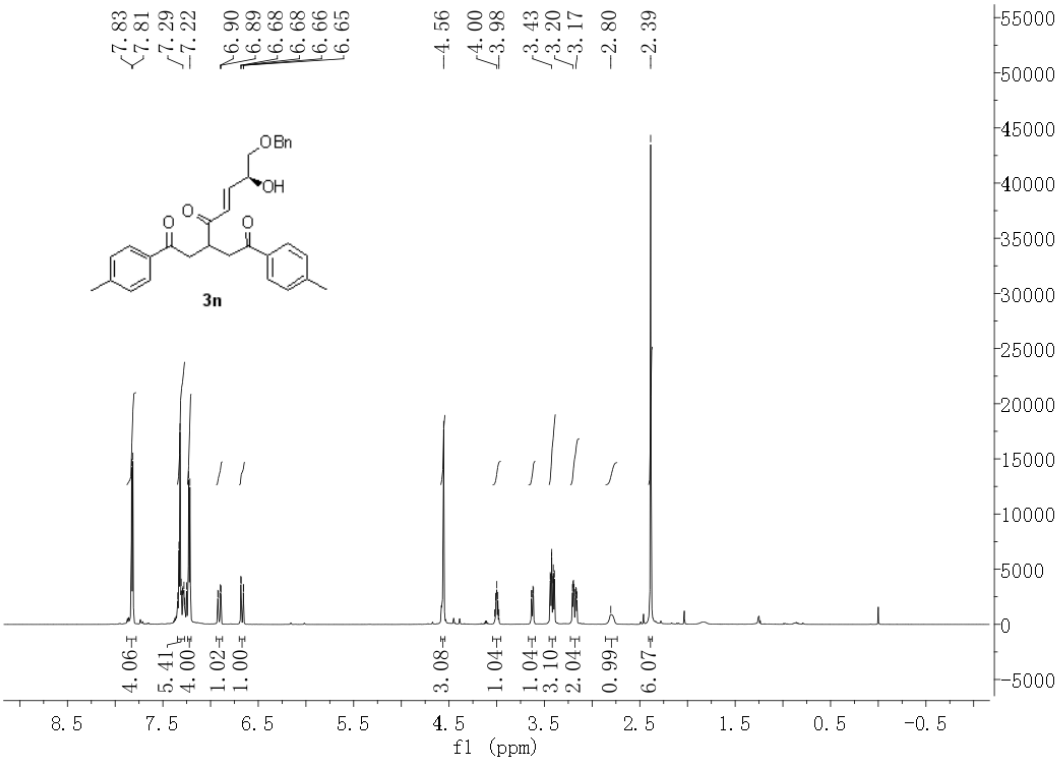
196.2
145.0
129.9
129.8
128.5
127.9
125.0
124.9
77.3
77.1
76.8
73.5
73.0
70.2
40.3
39.9
39.9
137.47
136.83
136.81
131.48
131.46
131.24
129.42
128.55
127.85
125.00
124.98
124.96
124.93
40.31
39.91
39.86
OBn
OH
O
O
O
CF3
CF3
3m
f1 (ppm)
f1 (ppm)
f1 (ppm)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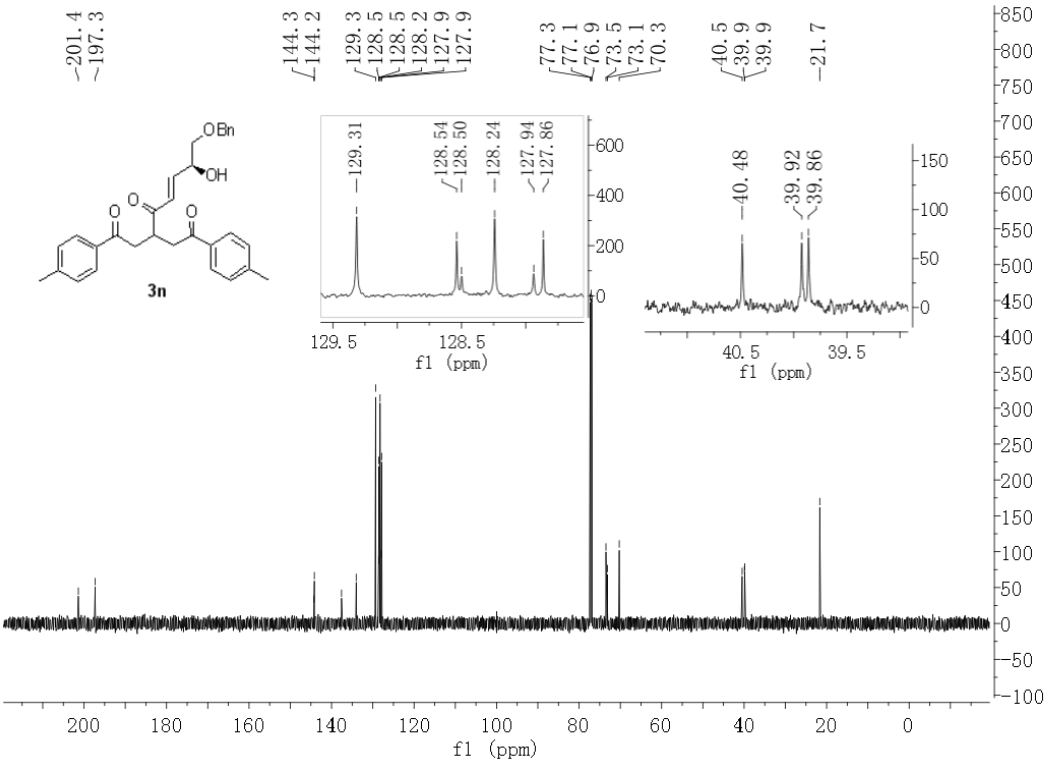
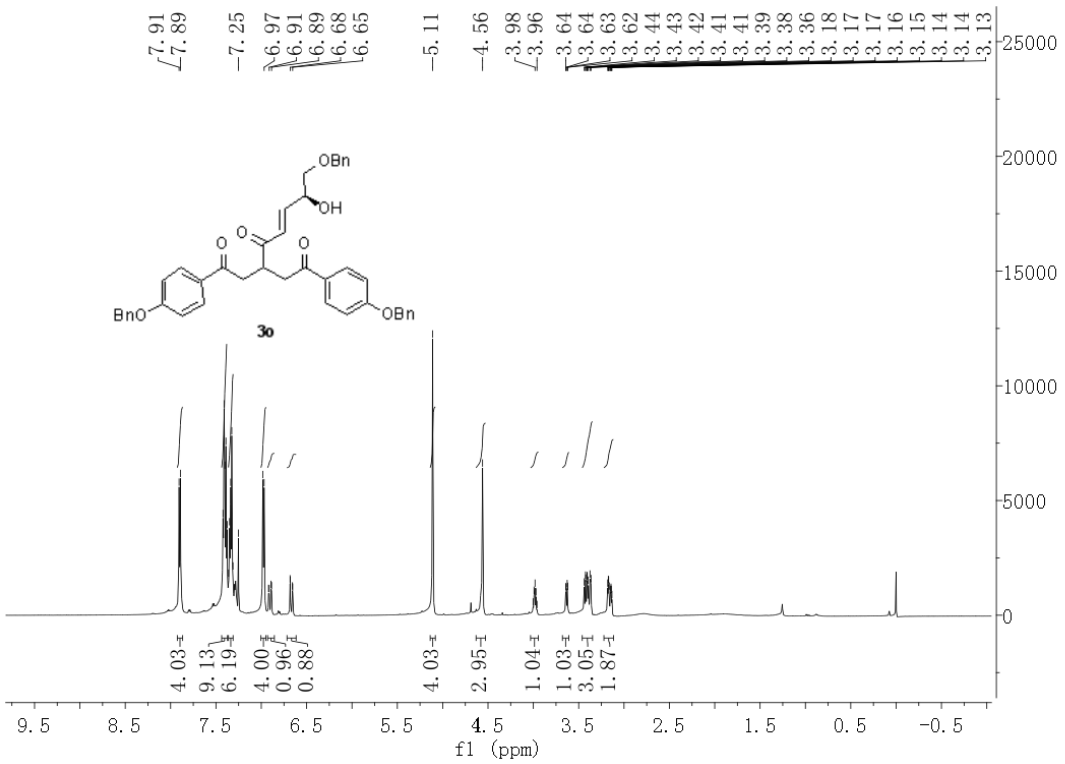
6.89
6.68
6.68
6.66
6.65
4.56
4.00
3.98
3.43
3.20
3.17
2.80
2.39
OBn
OH
O
O
O
3n
4.06
5.41
4.00
1.02
1.00
3.08
1.04
1.04
3.10
2.04
0.99
6.07
f1 (ppm)


201.4
197.3
144.3
144.2
129.3
128.5
128.5
128.2
127.9
127.9
77.3
77.1
76.9
73.5
73.1
70.3
40.5
39.9
39.9
21.7
OBn
OH
3n
129.31
128.54
128.50
128.24
127.94
127.86
40.48
39.92
39.86
f1 (ppm)


7.91
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6.89
6.68
6.65
5.11
4.56
3.98
3.96
3.64
3.64
3.63
3.62
3.44
3.43
3.42
3.41
3.41
3.39
3.38
3.36
3.18
3.17
3.17
3.16
3.15
3.14
3.14
3.13
OBn
OH
O
O
O
BnO
OBn
3o
4.03
9.13
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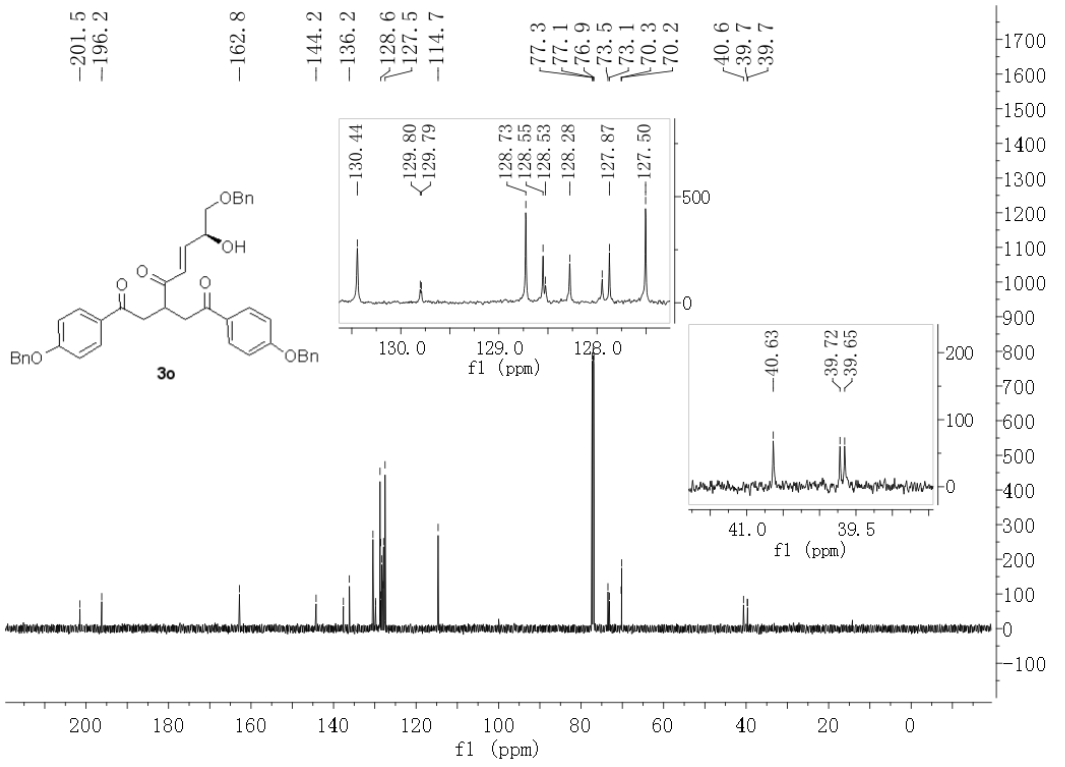
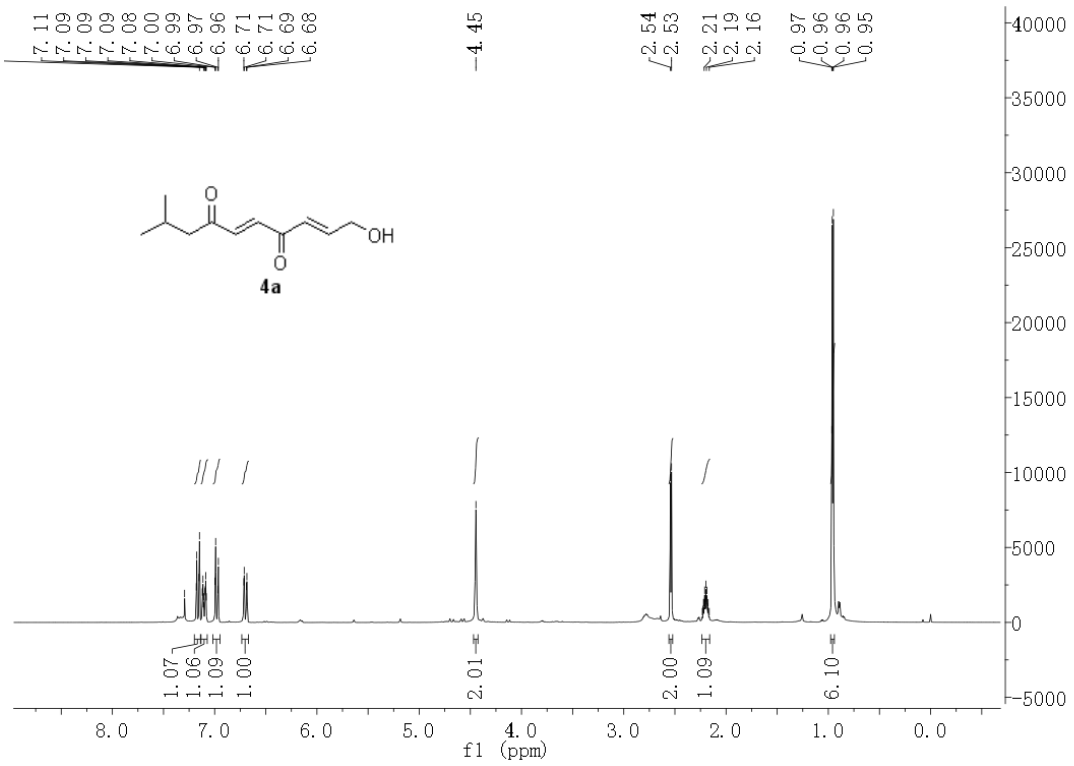
0.88
4.03
2.95
1.04
1.03
3.05
1.87
f1 (ppm)


201.5
196.2
162.8
144.2
136.2
128.6
127.5
114.7
77.3
77.1
76.9
73.5
73.1
70.3
70.2
40.6
39.7
39.7
130.44
129.80
129.79
128.73
128.55
128.53
128.28
127.87
127.50
40.63
39.72
39.65
OBn
OH
BnO
OBn
3o
f1 (ppm)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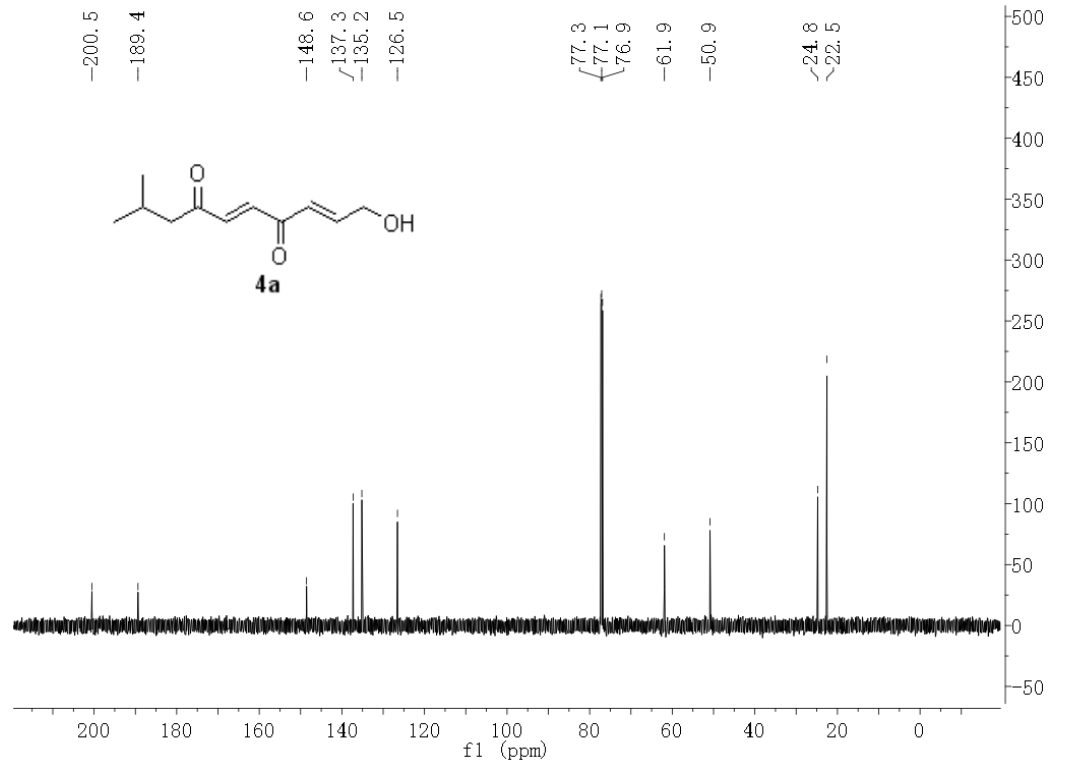
7.09
7.09
7.08
7.00
6.99
6.97
6.96
6.71
6.71
6.69
6.68
4.45
2.54
2.53
2.21
2.19
2.16
0.97
0.96
0.96
0.95
O
OH
O
4a
1.07
1.06
1.09
1.00
2.01
2.00
1.09
6.10
f1 (ppm)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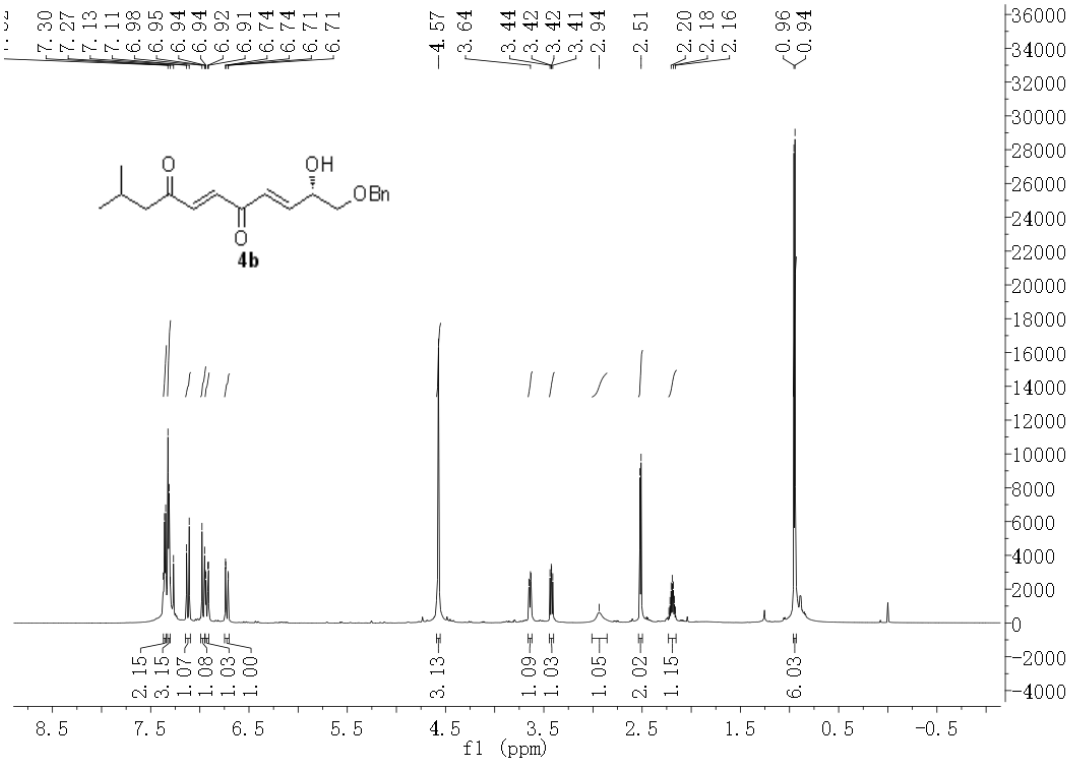
148.6
137.3
135.2
126.5
77.3
77.1
76.9
61.9
50.9
24.8
22.5
O
OH
O
4a
f1 (ppm)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7.13
7.11
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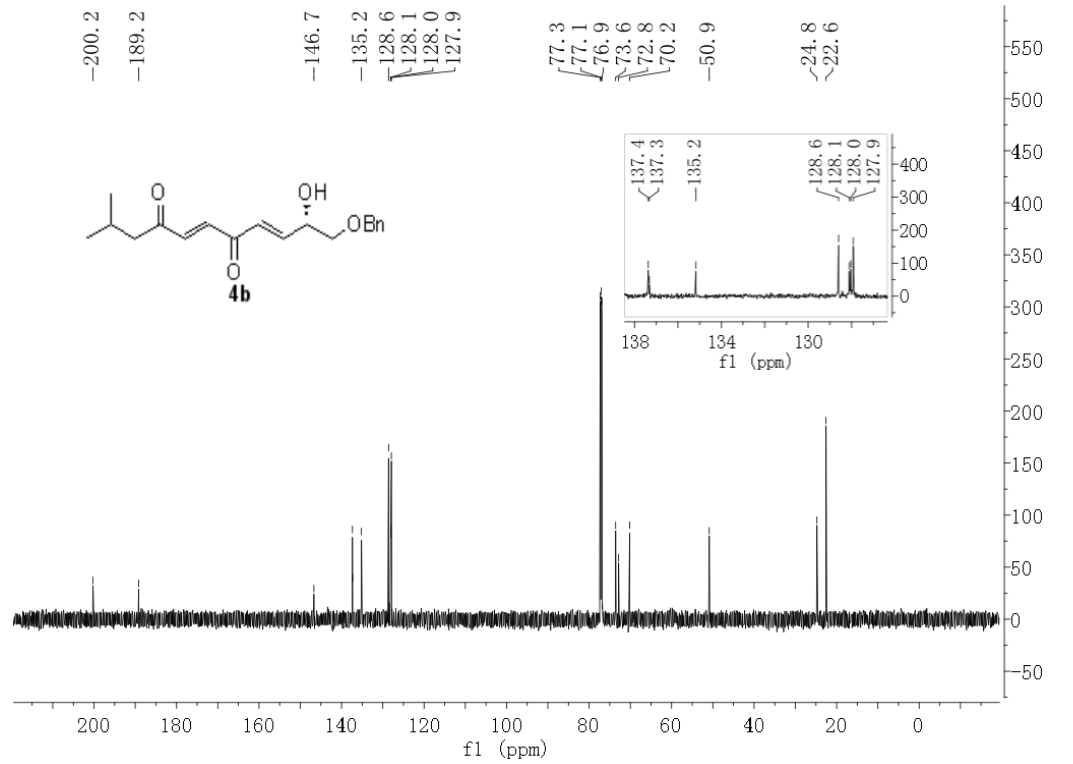
6.95
6.94
6.94
6.92
6.91
6.74
6.74
6.71
6.71
4.57
3.64
3.44
3.42
3.42
3.41
2.94
2.51
2.20
2.18
2.16
0.96
0.94
O
OH
OBn
O
4b
2.15
3.15
1.07
1.08
1.03
1.00
3.13
1.09
1.03
1.05
2.02
1.15
6.03
f1 (ppm)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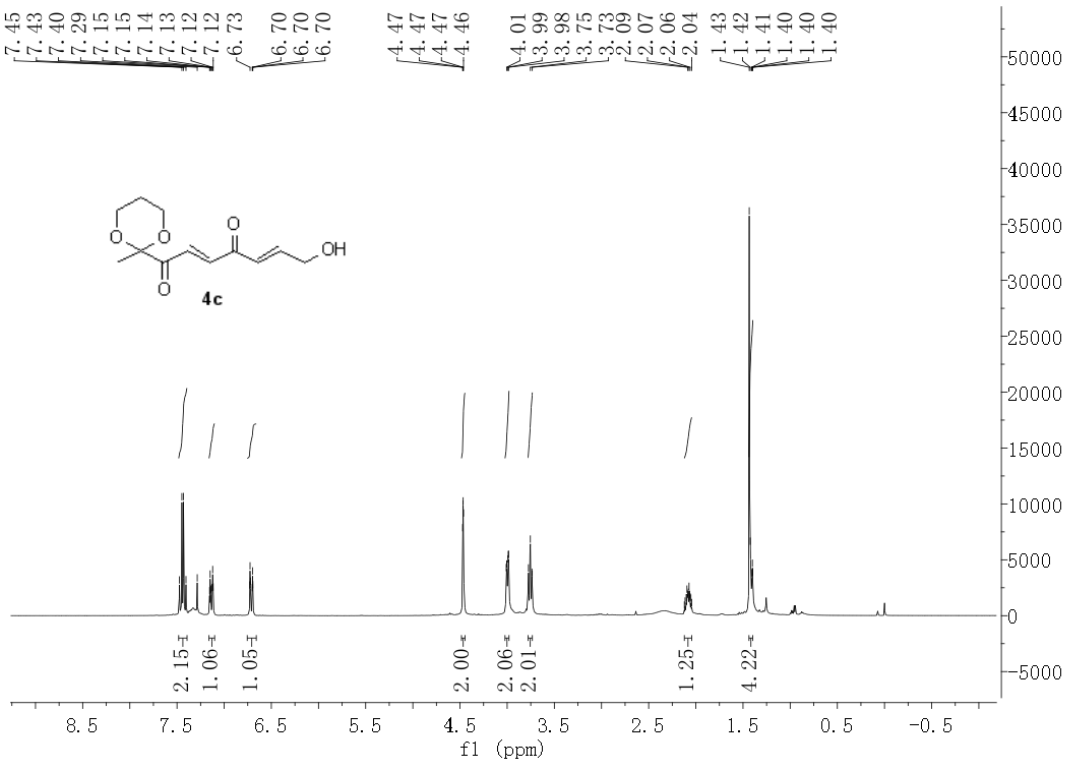
128.1
128.0
127.9
77.3
77.1
76.9
73.6
72.8
70.2
50.9
24.8
22.6
O
OH
OBn
O
4b
137.4
137.3
135.2
128.6
128.1
128.0
127.9
f1 (ppm)
f1 (ppm)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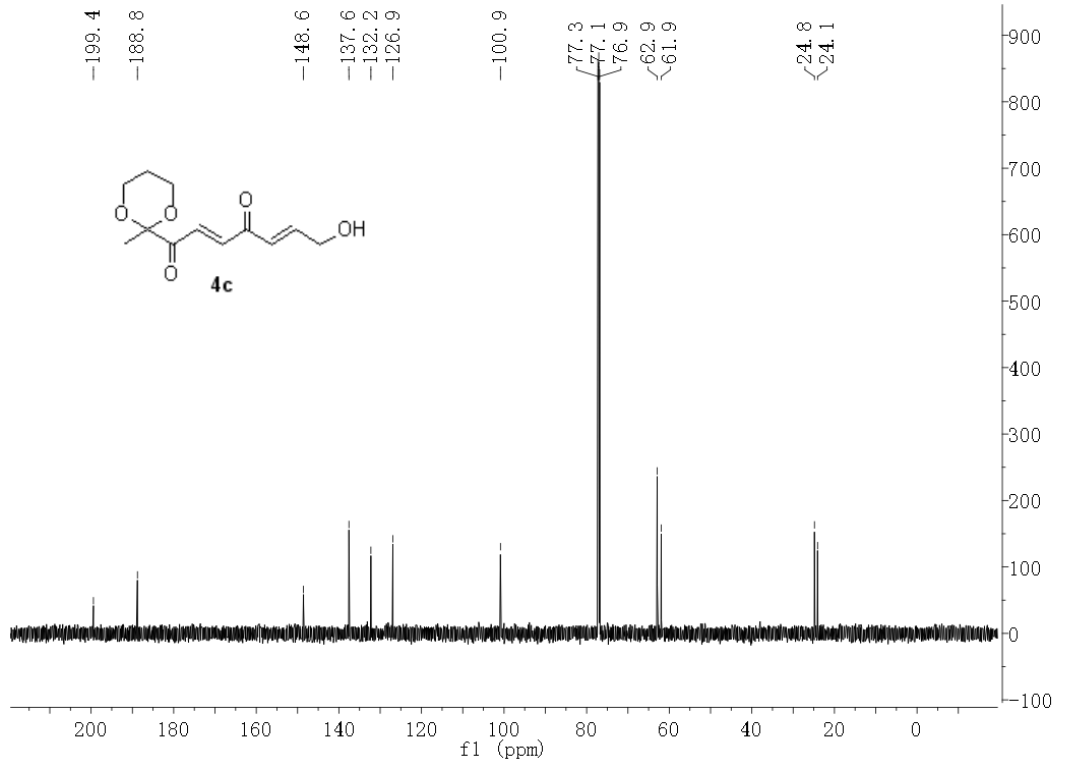
7.15
7.14
7.13
7.12
7.12
6.73
6.70
6.70
6.70
4.47
4.47
4.47
4.46
4.01
3.99
3.98
3.75
3.73
2.09
2.07
2.06
2.04
1.43
1.42
1.41
1.40
1.40
1.40
O
O
O
O
OH
4c
2.15
1.06
1.05
2.00
2.06
2.01
1.25
4.22
f1 (ppm)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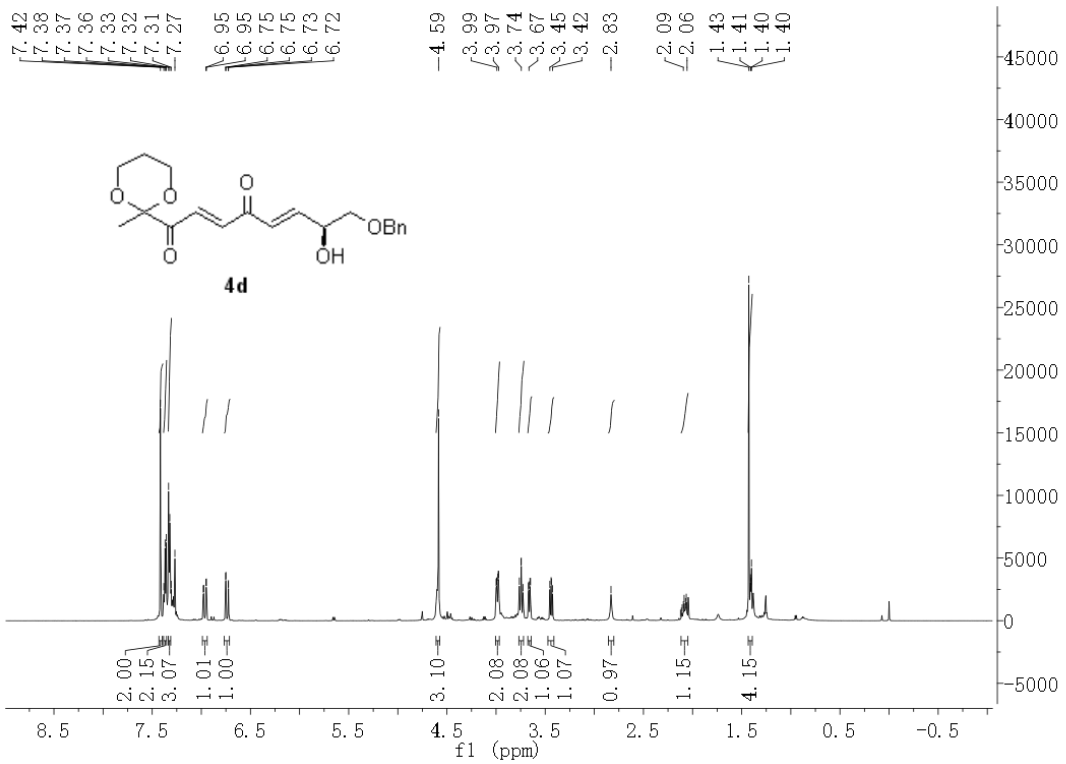
188.8
148.6
137.6
132.2
126.9
100.9
77.3
77.1
76.9
62.9
61.9
24.8
24.1
O
O
O
O
OH
4c
f1 (ppm)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7.32
7.31
7.27
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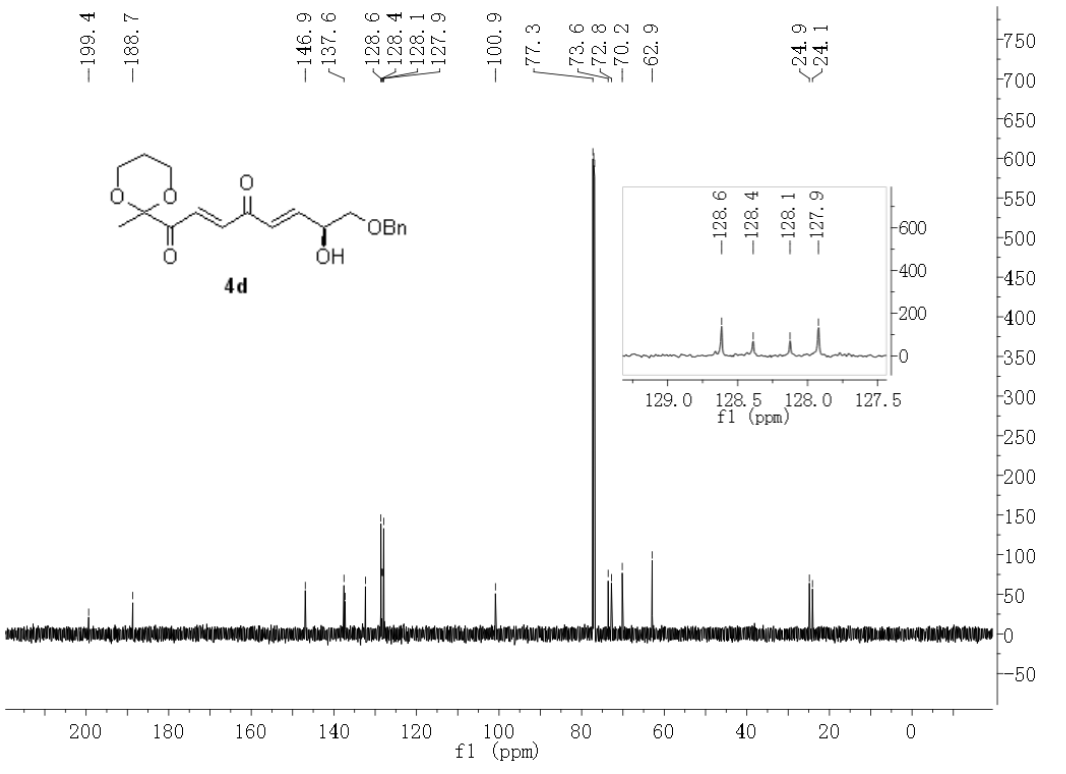
6.95
6.75
6.75
6.73
6.72
4.59
3.99
3.97
3.74
3.67
3.45
3.42
2.83
2.09
2.06
1.43
1.41
1.40
1.40
O
O
O
O
OBn
OH
4d
2.00
2.15
3.07
1.01
1.00
3.10
2.08
2.08
1.06
1.07
0.97
1.15
4.15
f1 (ppm)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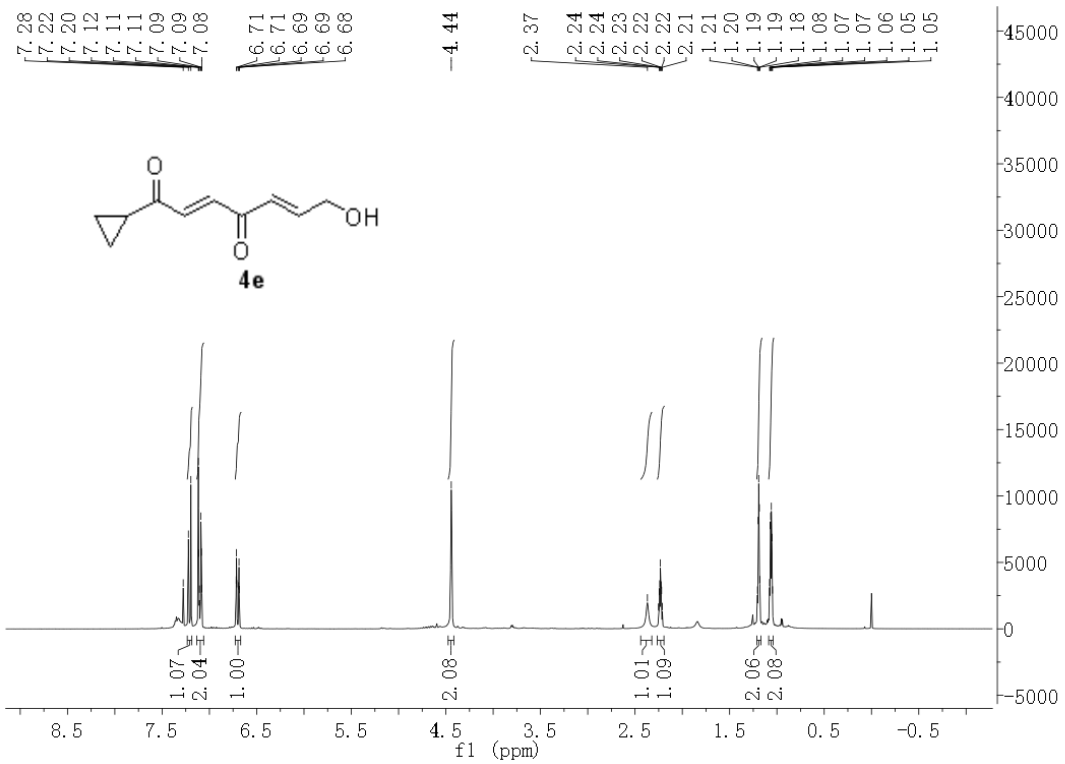
137.6
128.6
128.4
128.1
127.9
100.9
77.3
73.6
72.8
70.2
62.9
24.9
24.1
O
O
O
O
OBn
OH
4d
128.6
128.4
128.1
127.9
f1 (ppm)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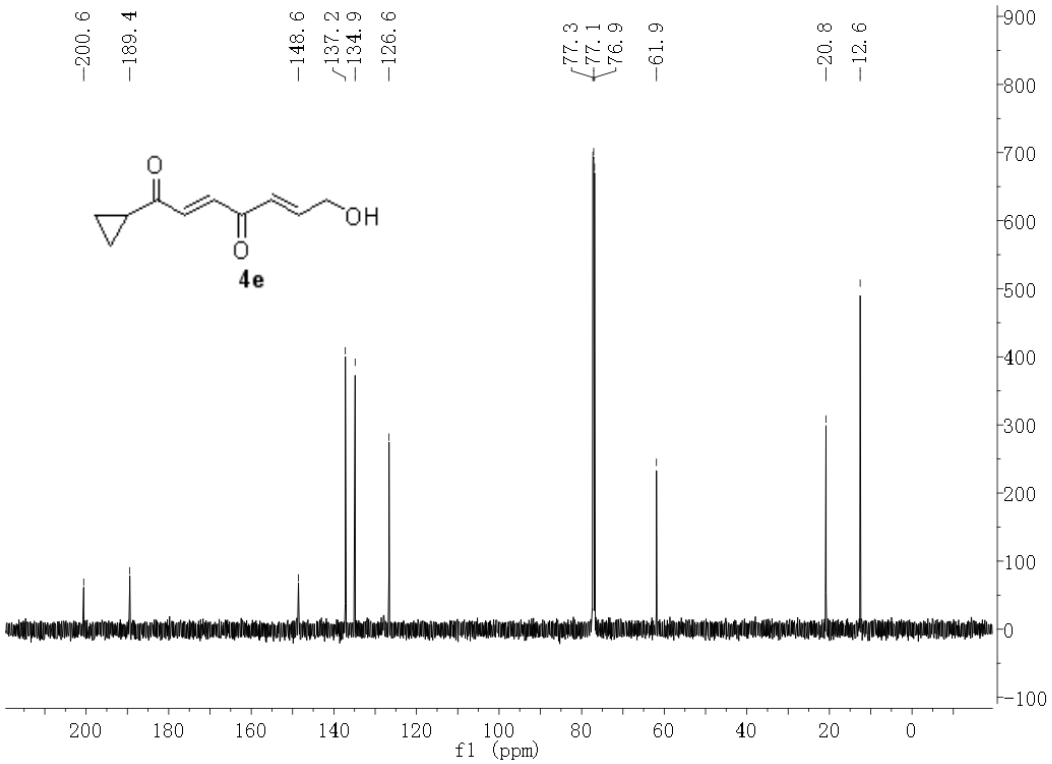
7.12
7.11
7.11
7.09
7.09
7.08
6.71
6.71
6.69
6.69
6.68
4.44
2.37
2.24
2.24
2.23
2.22
2.22
2.21
1.21
1.20
1.19
1.19
1.18
1.08
1.07
1.07
1.06
1.05
1.05
O
OH
O
4e
1.07
2.04
1.00
2.08
1.01
1.09
2.06
2.08
f1 (ppm)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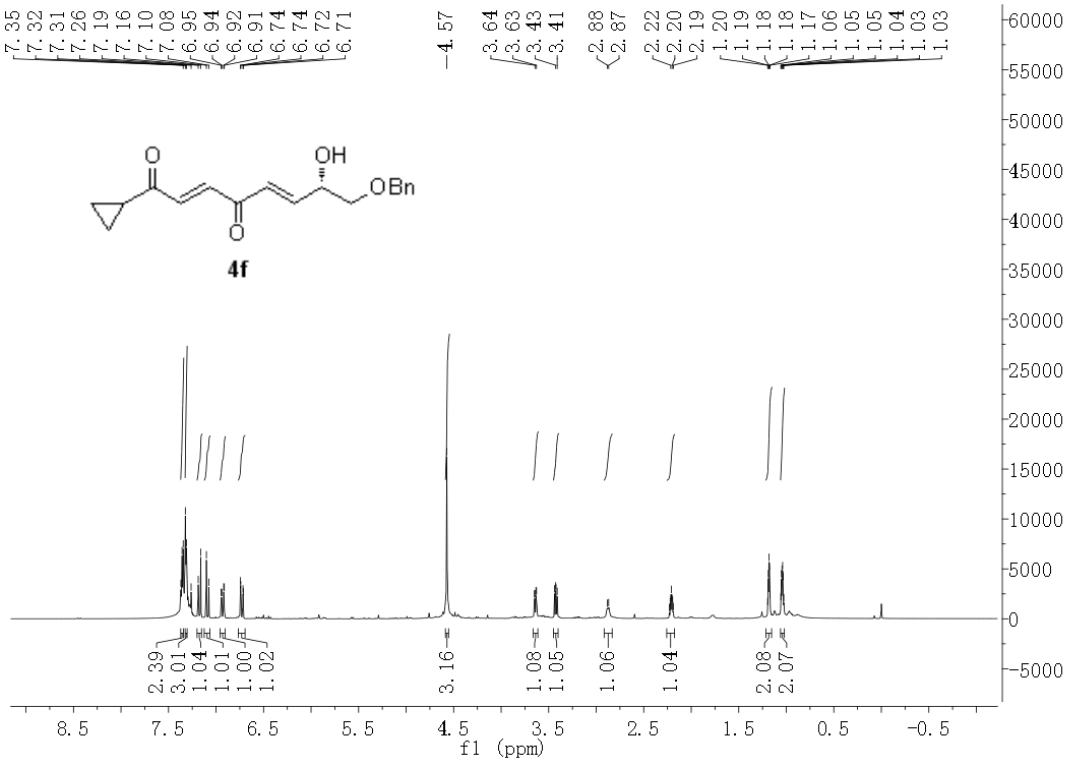
148.6
137.2
134.9
126.6
77.3
77.1
76.9
61.9
20.8
12.6
O
OH
O
4e
f1 (ppm)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7.32
7.31
7.26
7.19
7.16
7.10
7.08
6.95
6.94
6.92
6.91
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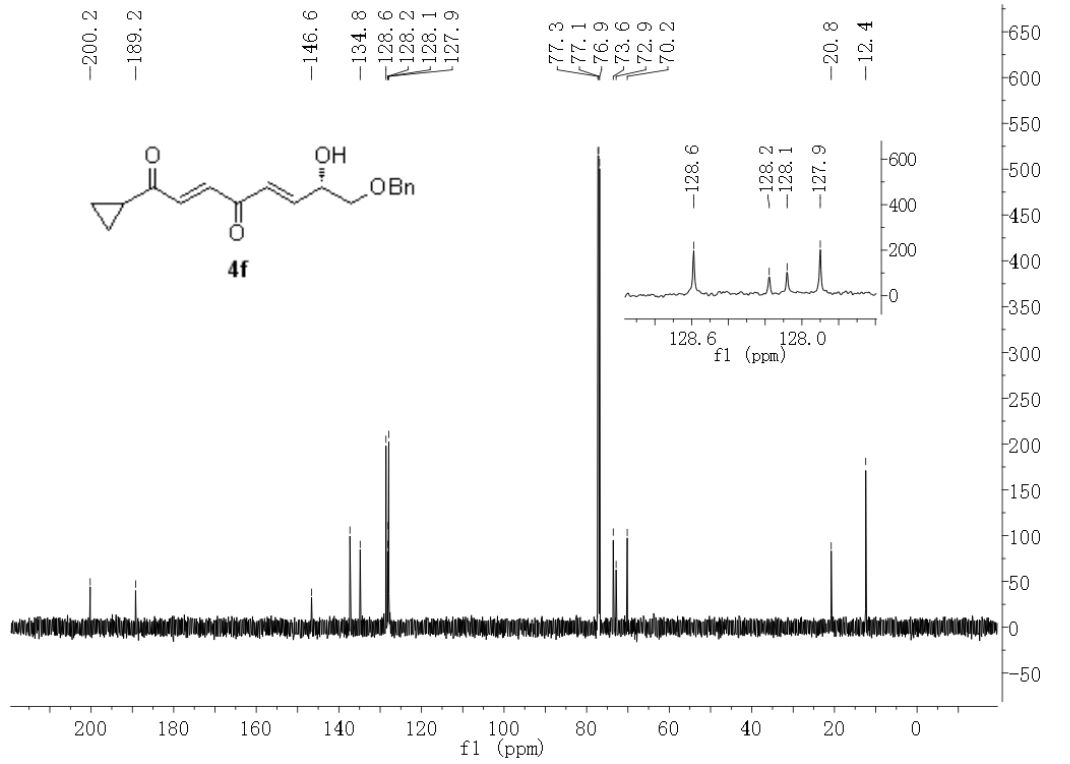
6.74
6.72
6.71
4.57
3.64
3.63
3.43
3.41
2.88
2.87
2.22
2.20
2.19
1.20
1.19
1.18
1.18
1.17
1.06
1.05
1.05
1.04
1.03
1.03
O
OH
OBn
O
4f
2.39
3.01
1.04
1.01
1.00
1.02
3.16
1.08
1.05
1.06
1.04
2.08
2.07
f1 (ppm)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146.6
134.8
128.6
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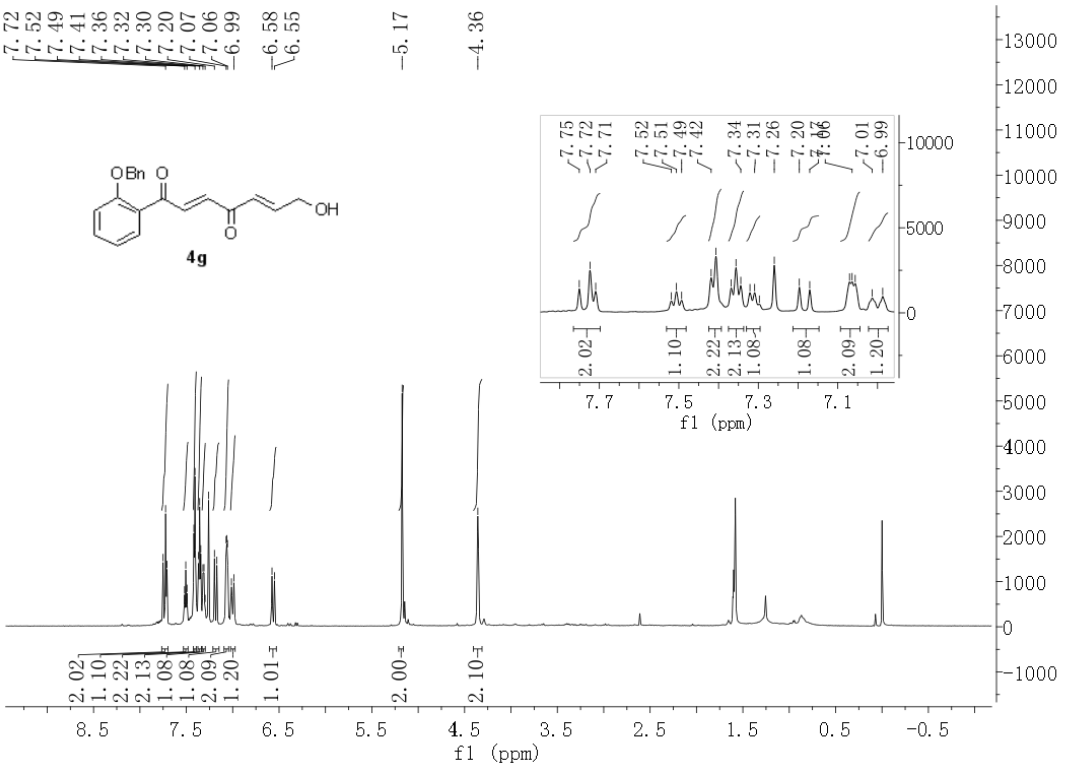
128.1
127.9
77.3
77.1
76.9
73.6
72.9
70.2
20.8
12.4
O
OH
OBn
O
4f
128.6
128.2
128.1
127.9
128.6
128.0
f1 (ppm)
f1 (ppm)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7.32
7.30
7.20
7.07
7.06
6.99
6.58
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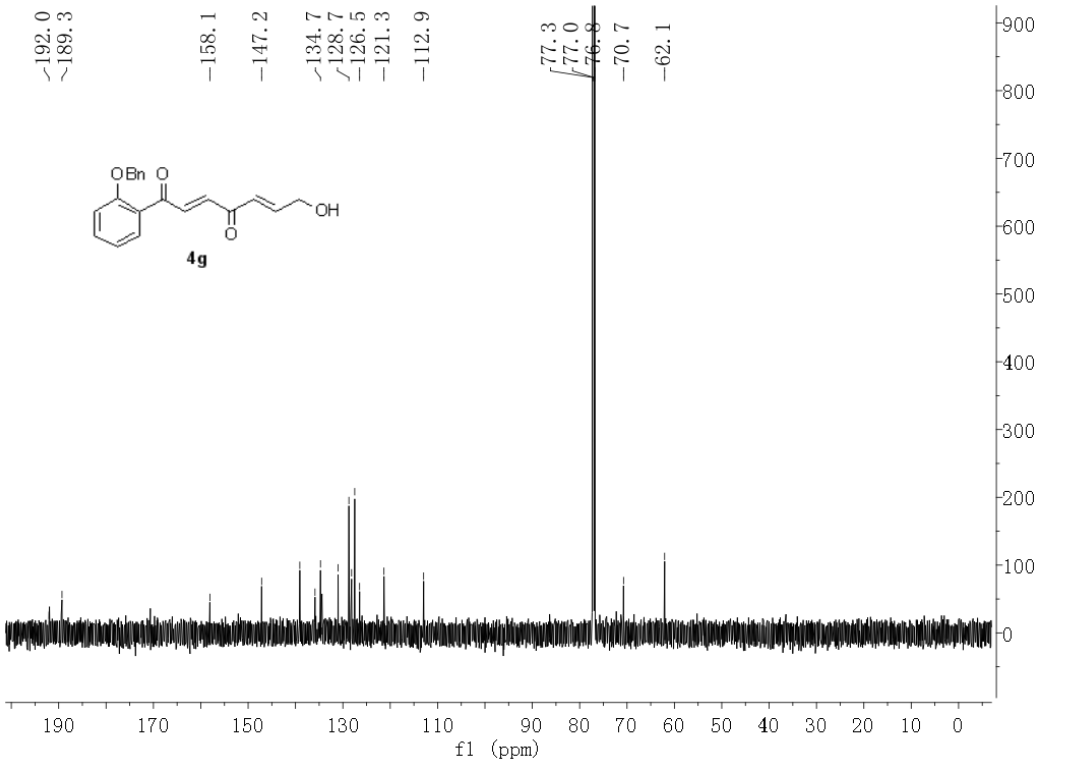
5.17
4.36
OBn
O
OH
O
4g
2.02
1.10
2.22
2.13
1.08
1.08
2.09
1.20
1.01
2.00
2.10
f1 (ppm)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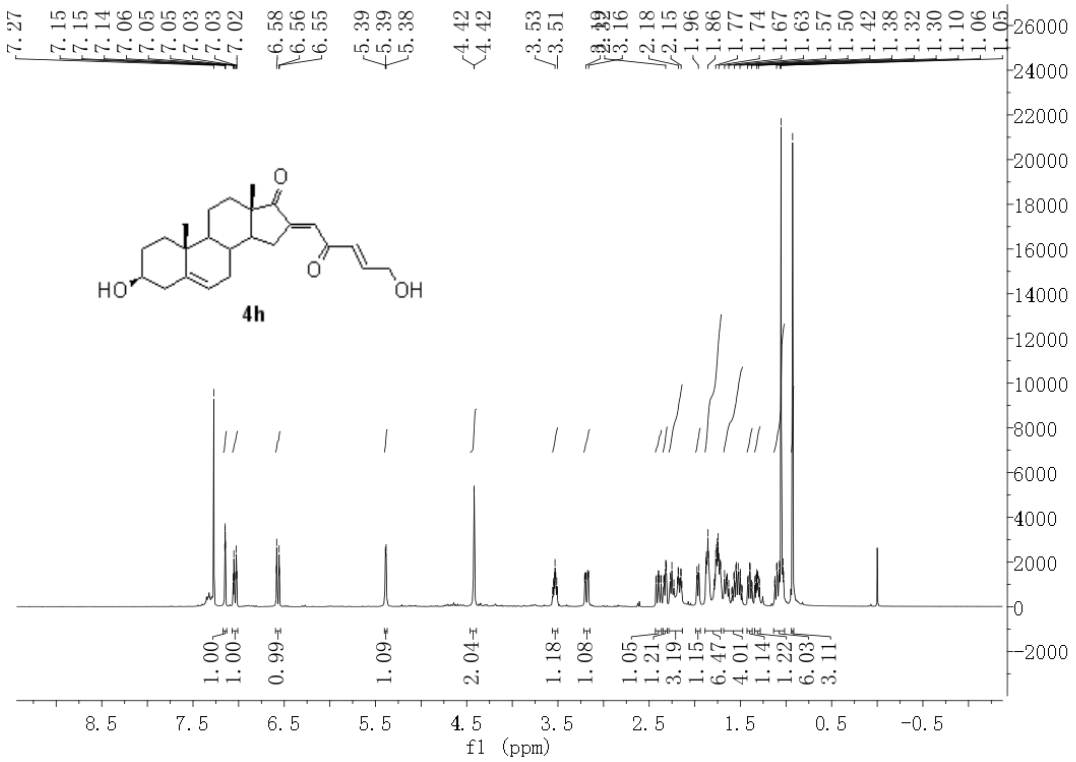
189.3
158.1
147.2
134.7
128.7
126.5
121.3
112.9
77.3
77.0
76.8
70.7
62.1
OBn
O
OH
O
4g
f1 (ppm)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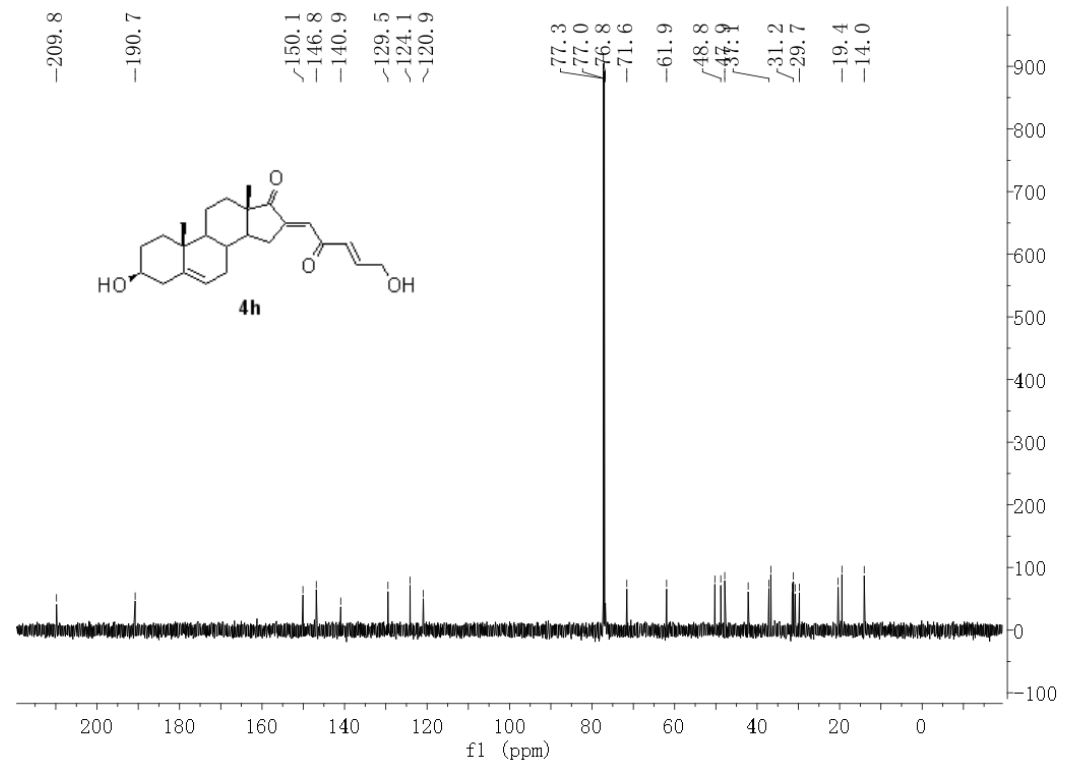
7.15
7.14
7.06
7.05
7.05
7.03
7.03
7.02
6.58
6.56
6.55
5.39
5.39
5.38
4.42
4.42
3.53
3.51
3.16
2.18
2.15
1.96
1.86
1.77
1.74
1.67
1.63
1.57
1.50
1.42
1.38
1.32
1.30
1.10
1.06
1.05
HO
O
O
OH
4h
1.00
1.00
0.99
1.09
2.04
1.18
1.08
1.05
1.21
3.19
1.15
6.47
4.01
1.14
1.22
6.03
3.11
f1 (ppm)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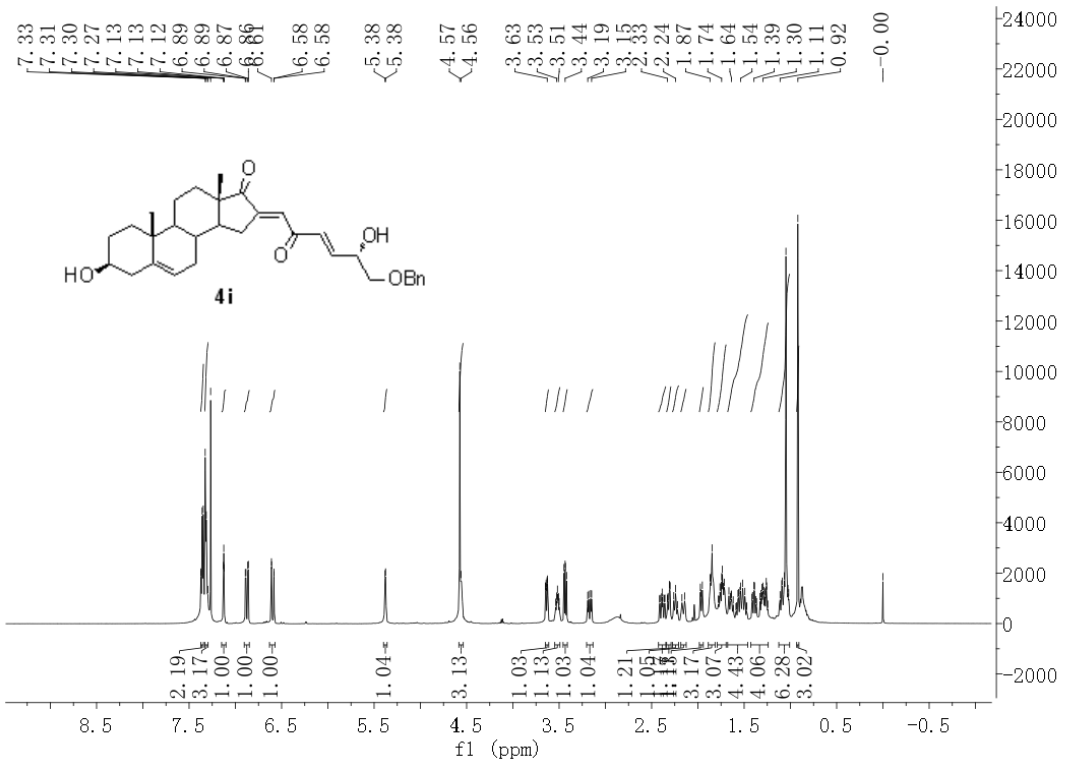
146.8
140.9
129.5
124.1
120.9
77.3
77.0
76.8
71.6
61.9
48.8
47.9
37.1
31.2
29.7
19.4
14.0
HO
O
O
OH
4h
f1 (ppm)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7.13
7.13
7.12
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6.89
6.87
6.86
6.61
6.58
6.58
5.38
5.38
4.57
4.56
3.63
3.53
3.51
3.44
3.19
3.15
2.33
2.24
1.87
1.74
1.64
1.54
1.39
1.30
1.11
0.92
-0.00
O
OH
HO
OBn
4i
2.19
3.17
1.00
1.00
1.00
1.04
3.13
1.03
1.13
1.03
1.04
1.21
3.17
3.07
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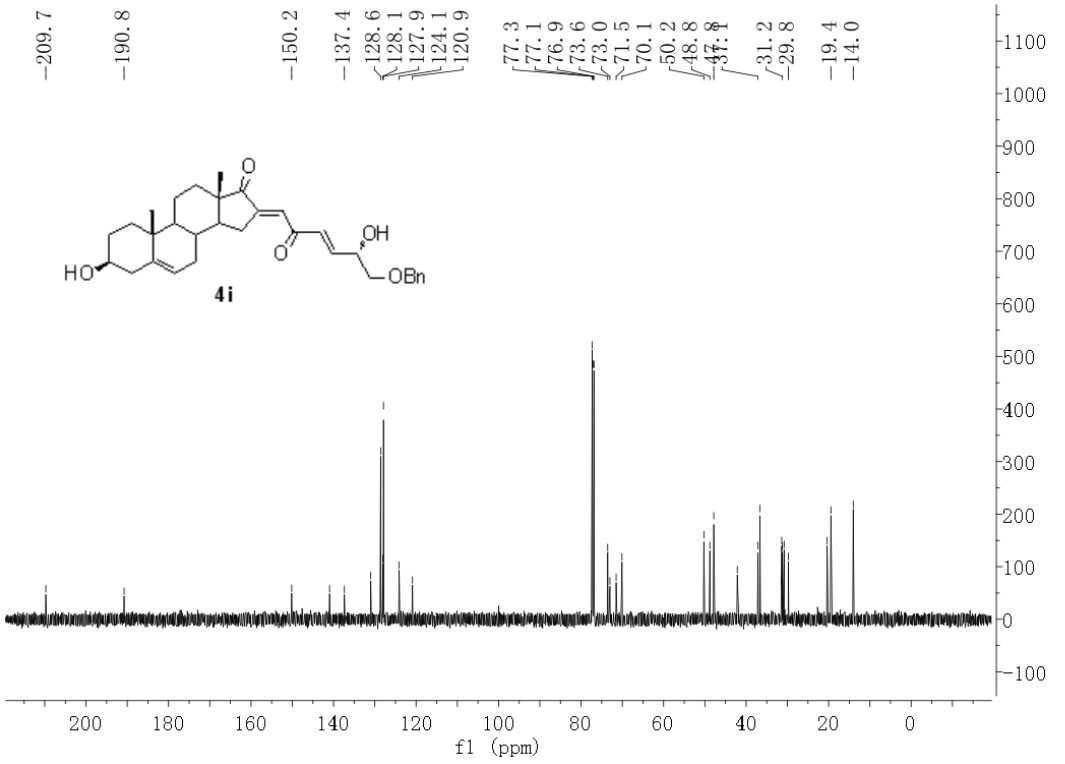
4.06
6.28
3.02
f1 (ppm)


209.7
190.8
150.2
137.4
128.6
128.1
127.9
124.1
120.9
77.3
77.1
76.9
73.6
73.0
71.5
70.1
50.2
48.8
47.8
37.1
31.2
29.8
19.4
14.0
O
OH
HO
OBn
4i
f1 (ppm)