# Supporting Information

# Structural Elucidation and Total Synthesis of Three 9-Norlignans from *Curculigo capitulata*

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**Table S1. $^{1}H$ (500 MHz) and $^{13}C$ (125 MHz) NMR spectroscopic data for 1–3**

| | **1**[a] | | **2**[a] | | **3**[a] | |
|---|---|---|---|---|---|---|
| position | $\delta_H$ (multi, *J* in Hz) | $\delta_C$ | $\delta_H$ (multi, *J* in Hz) | $\delta_C$ | $\delta_H$ (multi, *J* in Hz) | $\delta_C$ |
| 1 | | 140.6 | | 140.6 | | 140.6 |
| 2 | | 166.4 | | 166.3 | | 166.3 |
| 3 | 5.69, s | 95.7 | 5.69, s | 95.7 | 5.69, s | 95.7 |
| 4 | | 169.4 | | 169.2 | | 169.2 |
| 5 | 4.52–4.60, m (2H) | 62.6 | 4.52–4.60, m (2H) | 62.6 | 4.54–4.62, m (2H) | 62.6 |
| 6 | 6.35, m | 127.4 | 6.34, m | 127.4 | 6.35, m | 127.4 |
| 7 | 2.95, dd (15.4, 7.1) | 35.6 | 2.95, dd (15.4, 7.1) | 35.6 | 2.95, dd (15.5, 7.1) | 35.6 |
| | 2.61, dd (15.4, 6.9) | | 2.61, dd (15.4, 6.9) | | 2.61, dd (15.5, 7.0) | |
| 8 | 4.62, p (6.7) | 82.7 | 4.62, p (6.7) | 82.7 | 4.62, p (6.8) | 82.6 |
| 9 | 2.76, m | 33.8 | 2.76, m | 33.8 | 2.76, dddd (15.3, 7.2, 6.6, 1.8) | 33.9 |
| | 2.65, m | | 2.65, m | | 2.67, dddd (15.3, 7.4, 6.3, 1.8) | |
| 1′ | | 129.4 | | 129.3 | | 130.3 |
| 2′ | 7.13, d (8.5) | 130.1 | 7.19, (8.6) | 129.9 | 6.84, d (2.0) | 114.7 |
| 3′ | 6.82, d (8.5) | 115.3 | 6.88, (8.6) | 113.8 | | 145.3 |
| 4′ | | 154.8 | | 158.7 | | 145.7 |
| 5′ | 6.82, d (8.5) | 115.3 | 6.88, (8.6) | 113.8 | 6.83, d (8.3) | 110.5 |
| 6′ | 7.13, d (8.5) | 130.1 | 7.19, (8.6) | 129.9 | 6.74, dd (8.3, 2.0) | 120.9 |
| 7′ | 6.55, dt (11.6, 1.8) | 132.1 | 6.56, dt (11.6, 1.8) | 132.1 | 6.55, ddd (11.6, 1.8, 1.8) | 132.2 |
| 8′ | 5.54, dt (11.6, 7.2) | 123.4 | 5.55, dt (11.6, 7.2) | 123.4 | 5.55, ddd (11.6, 7.4, 7.2) | 123.9 |
| OCH3 | | | 3.82, s | 55.3 | 3.90, s | 56.0 |
| 3′-OH | | | | | 5.61, s | |
| 4′-OH | 5.31, s | | | | | |

[a] Data were measured in $CDCl_3$.

**Table S2. Specific optical rotation of natural products and corresponding synthetic compounds.**

| No | C (g/100ml) | $[\alpha]$ | T (℃) | Solvent |
|---|---|---|---|---|
| **1** | 0.135 | -10.7 | 20 | Methanol |
| **1a** | 0.230 | -10.6 | 20 | Methanol |
| **1b** | 0.285 | +11.1 | 20 | Methanol |
| | | | | |
| **2** | 0.138 | -13.6 | 18 | Methanol |
| **2a** | 0.117 | -11.9 | 18 | Methanol |
| **2b** | 0.098 | +13.3 | 18 | Methanol |
| | | | | |
| **3** | 0.15 | -8.5 | 20 | Methanol |
| **3a** | 0.450 | -13.0 | 20 | Methanol |
| **3b** | 0.247 | +13.8 | 20 | Methanol |

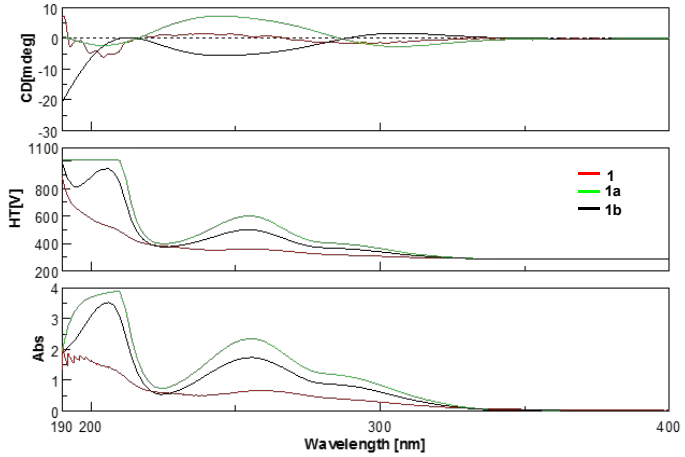



**Figure S1.** CD curves for compounds **1**, **1a**, and **1b.**

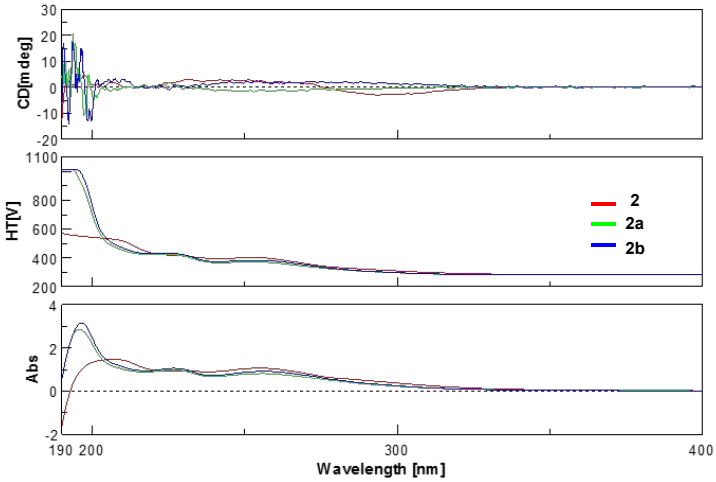



**Figure S2.** CD curves for compounds **2**, **2a**, and **2b.**

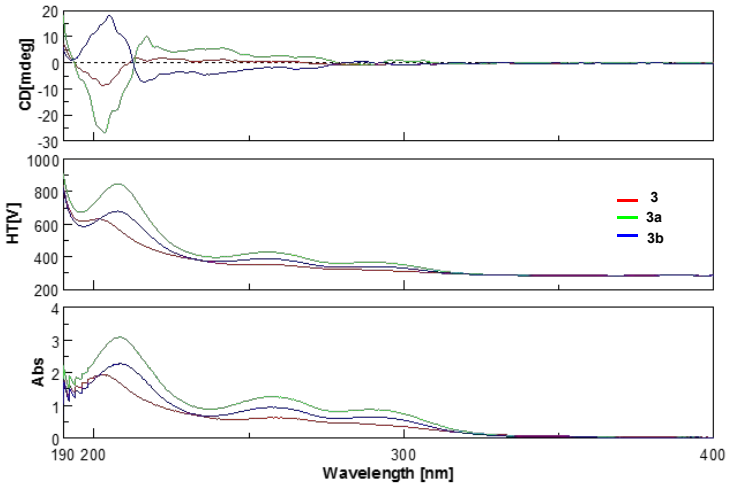



**Figure S3.** CD curves for compounds **3**, **3a**, and **3b.**

**Figure S4.** $^{1}H$ NMR spectrum of Capitulactone A (**1**) in $CDCl_3$

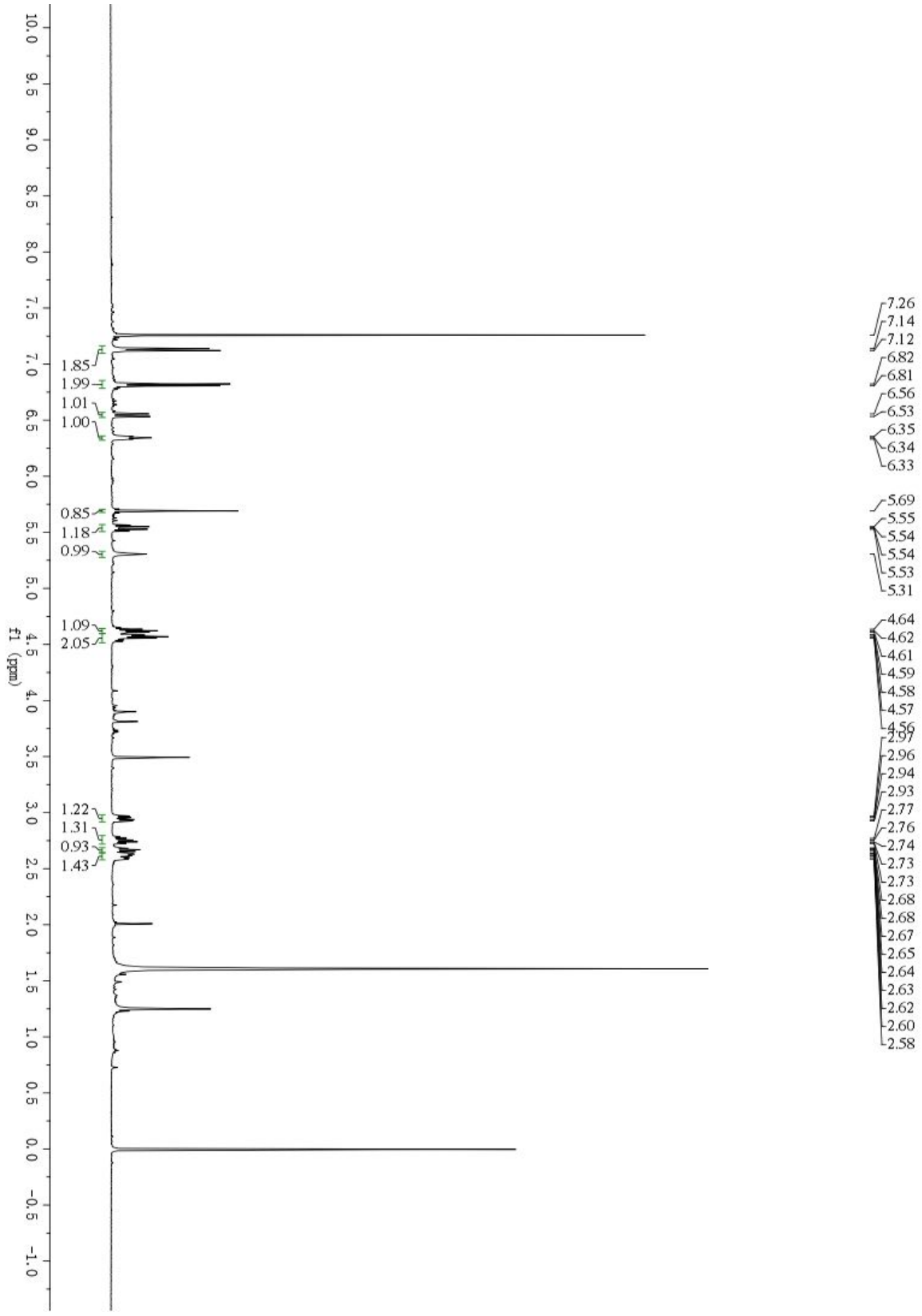


**Figure S5.** $^{13}C$ NMR spectrum of Capitulactone A (**1**) in $CDCl_3$

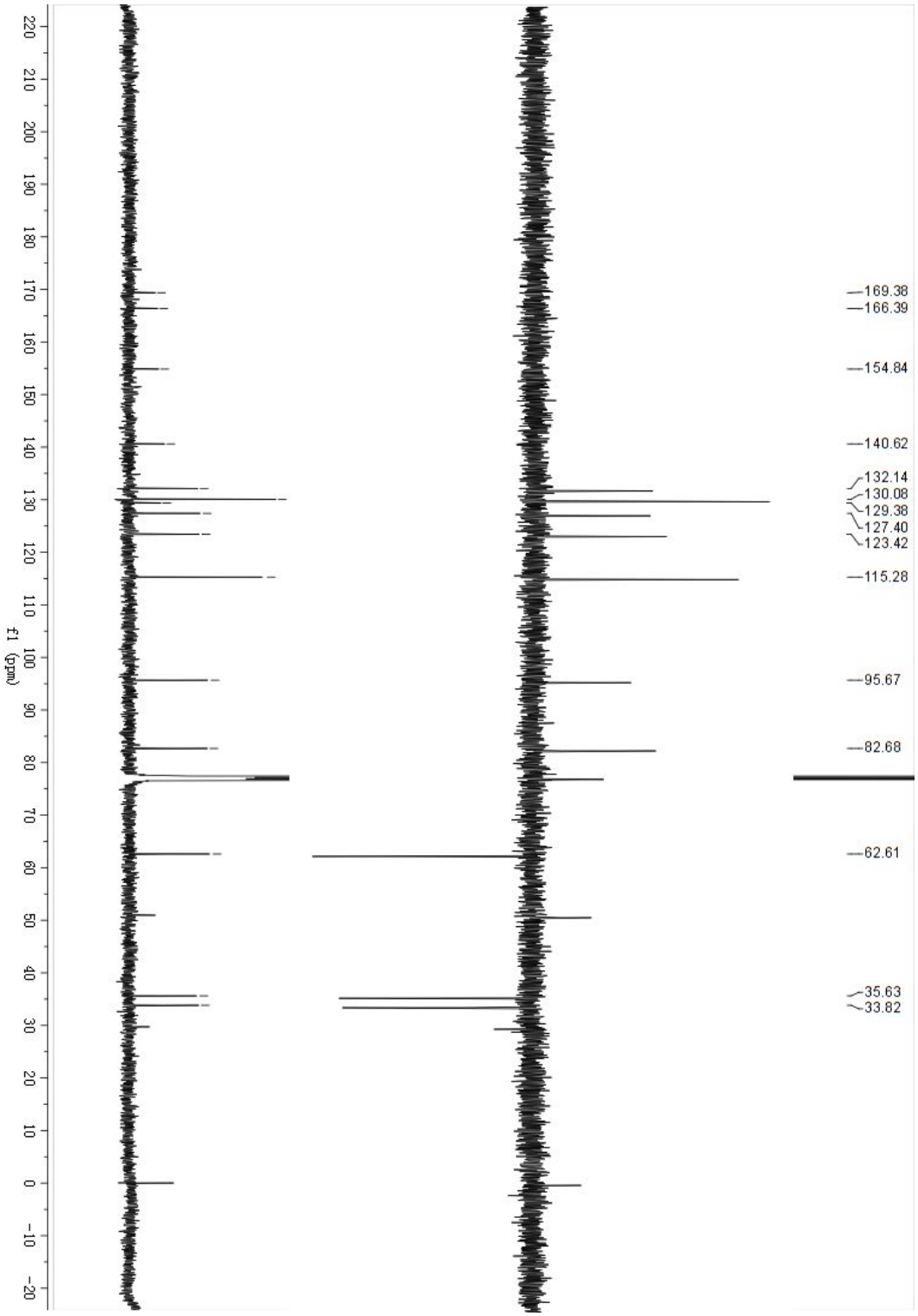


**Figure S6.** $^{1}H$-$^{1}H$ COSY spectrum of Capitulactone A (**1**) in $CDCl_3$

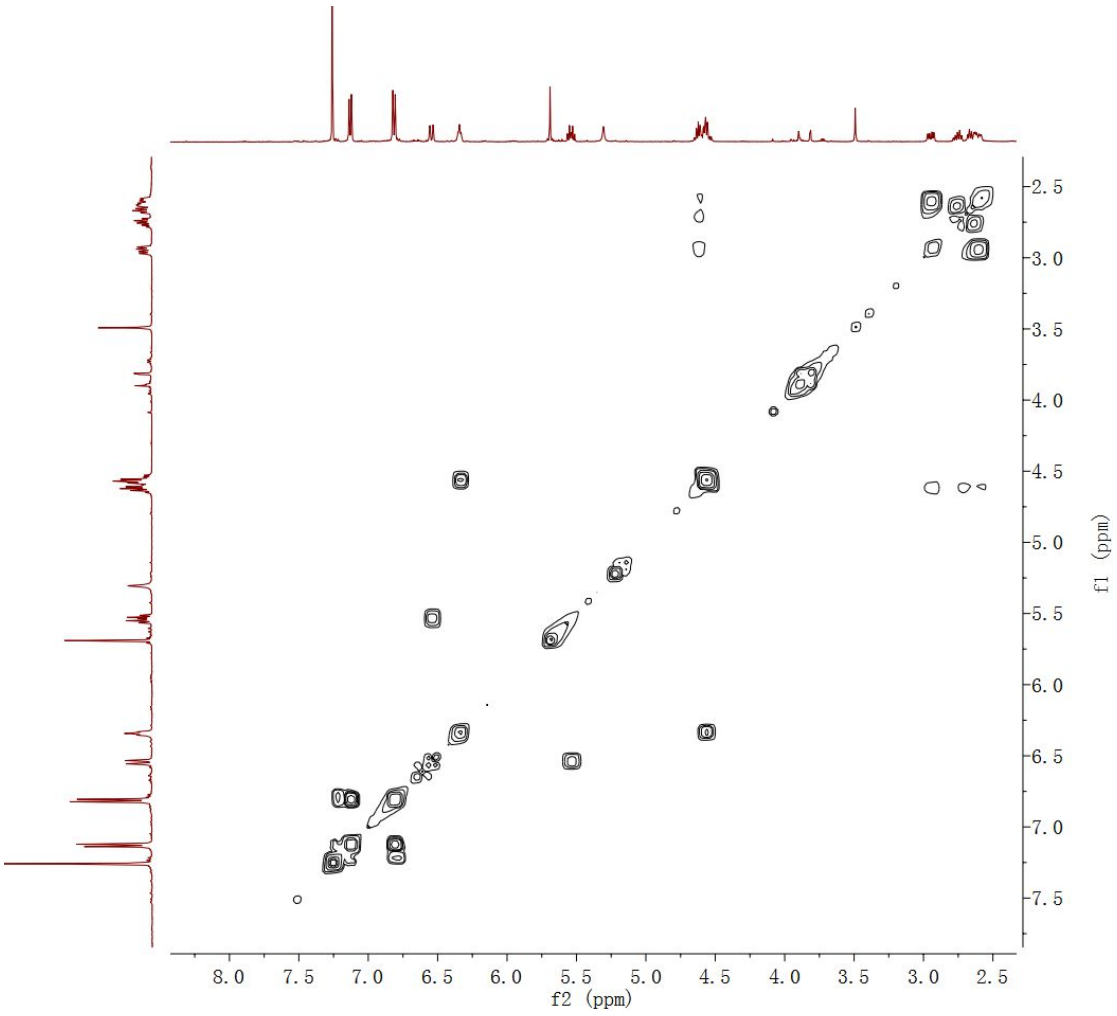


**Figure S7.** HSQC spectrum of Capitulactone A (**1**) in $CDCl_3$

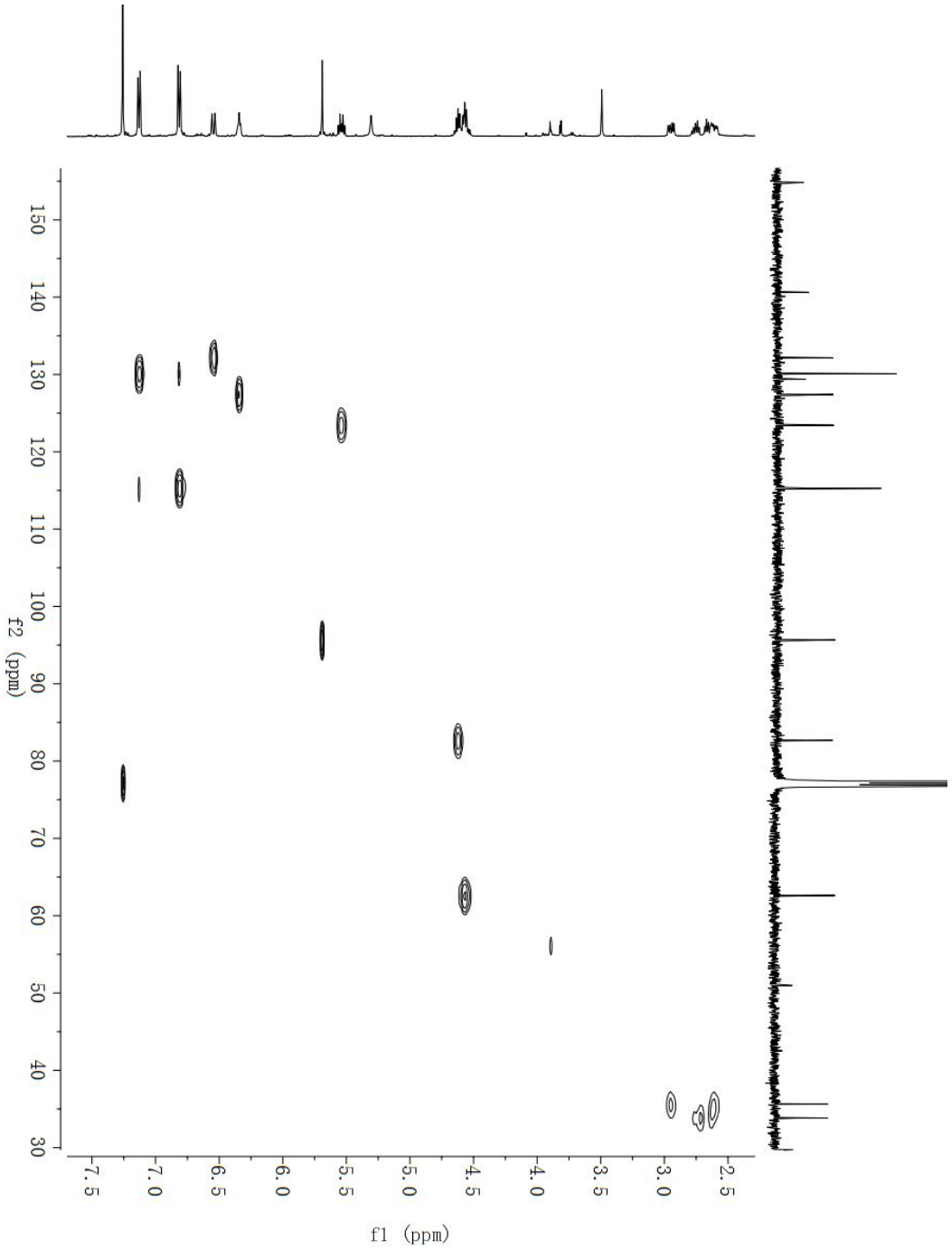


**Figure S8.** HMBC spectrum of Capitulactone A (**1**) in $CDCl_3$

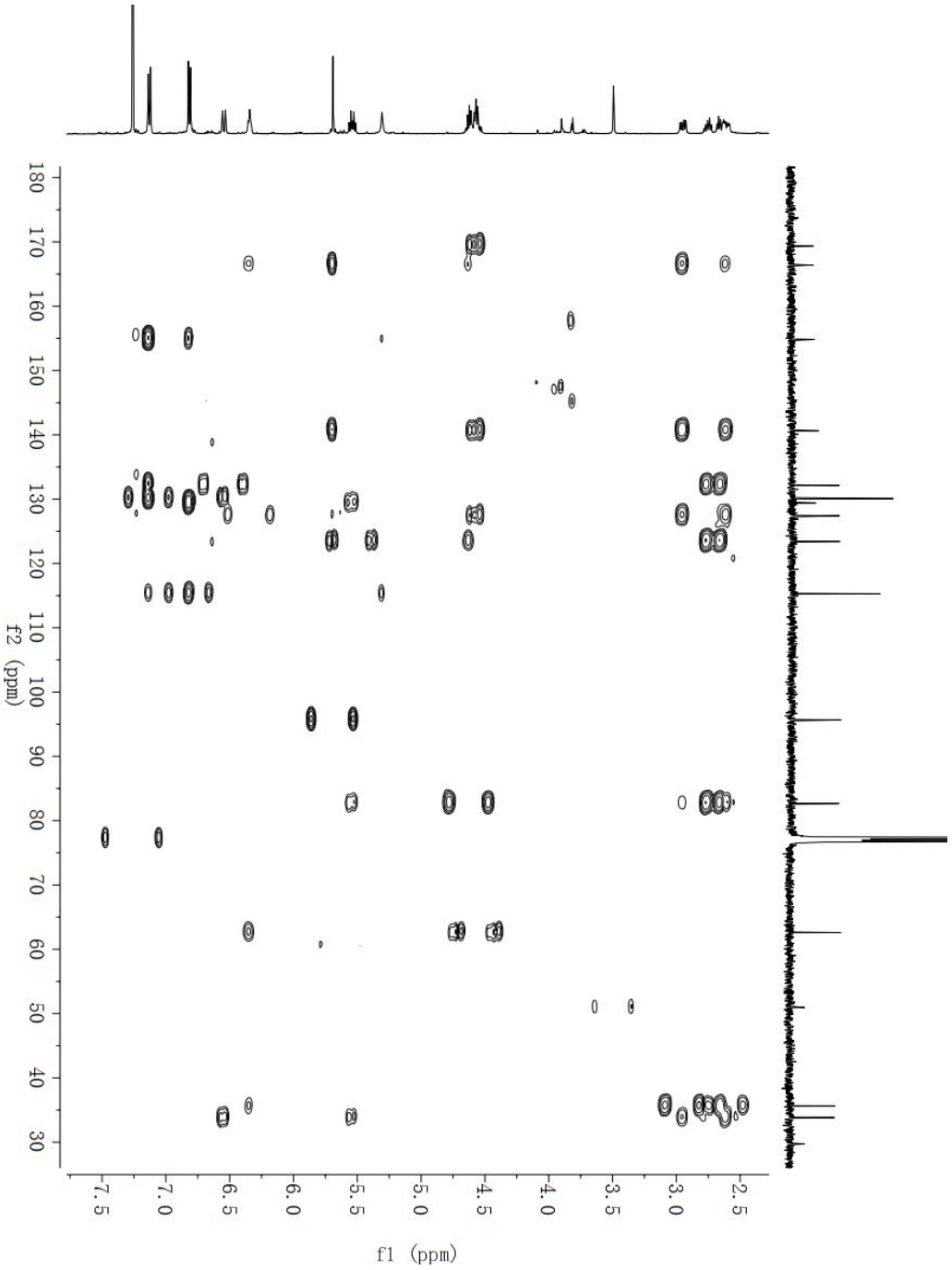


**Figure S9.** (+)-ESIMS spectrum of Capitulactone A (**1**)

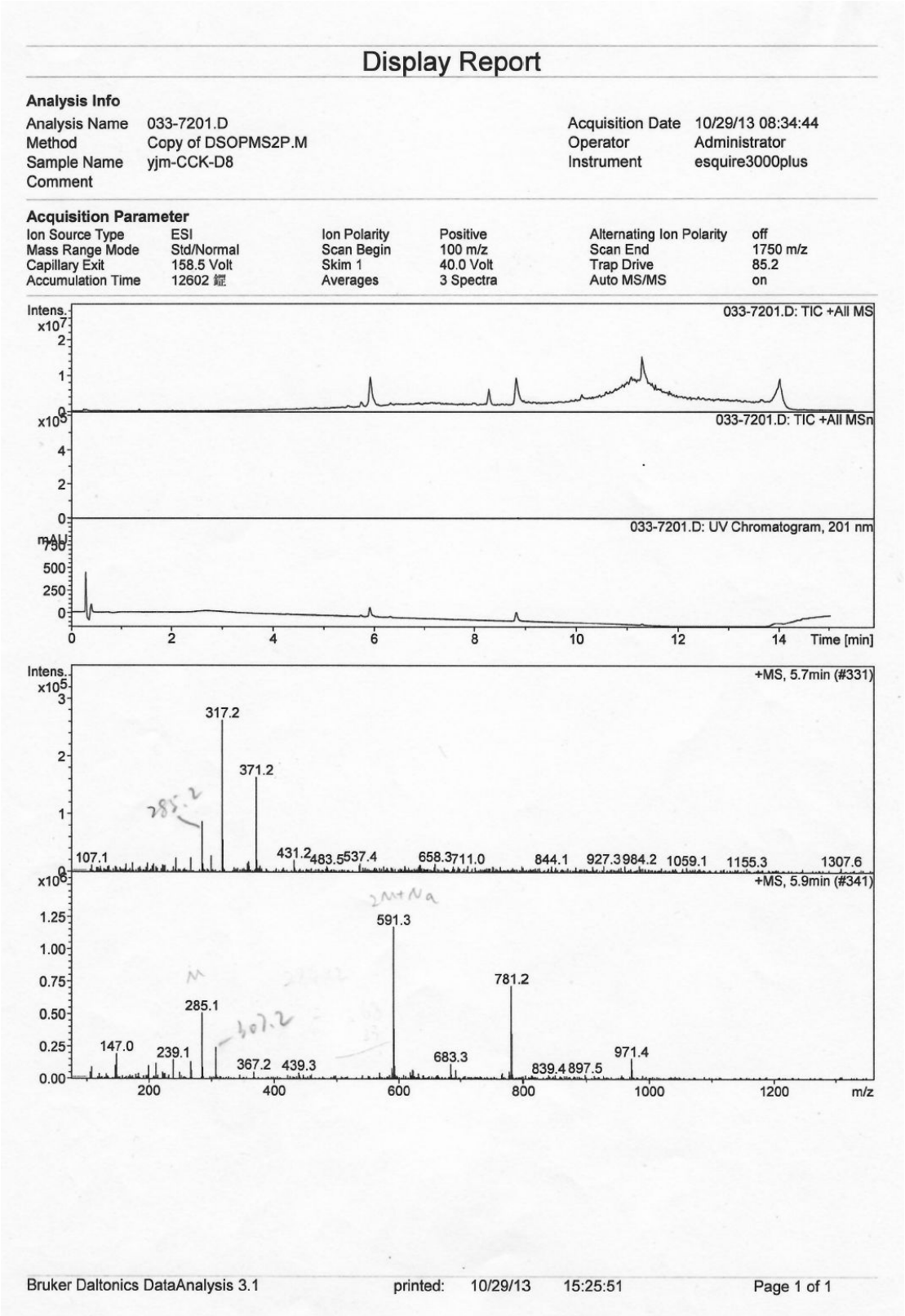


**Figure S10.** (−)-ESIMS spectrum of Capitulactone A (**1**).

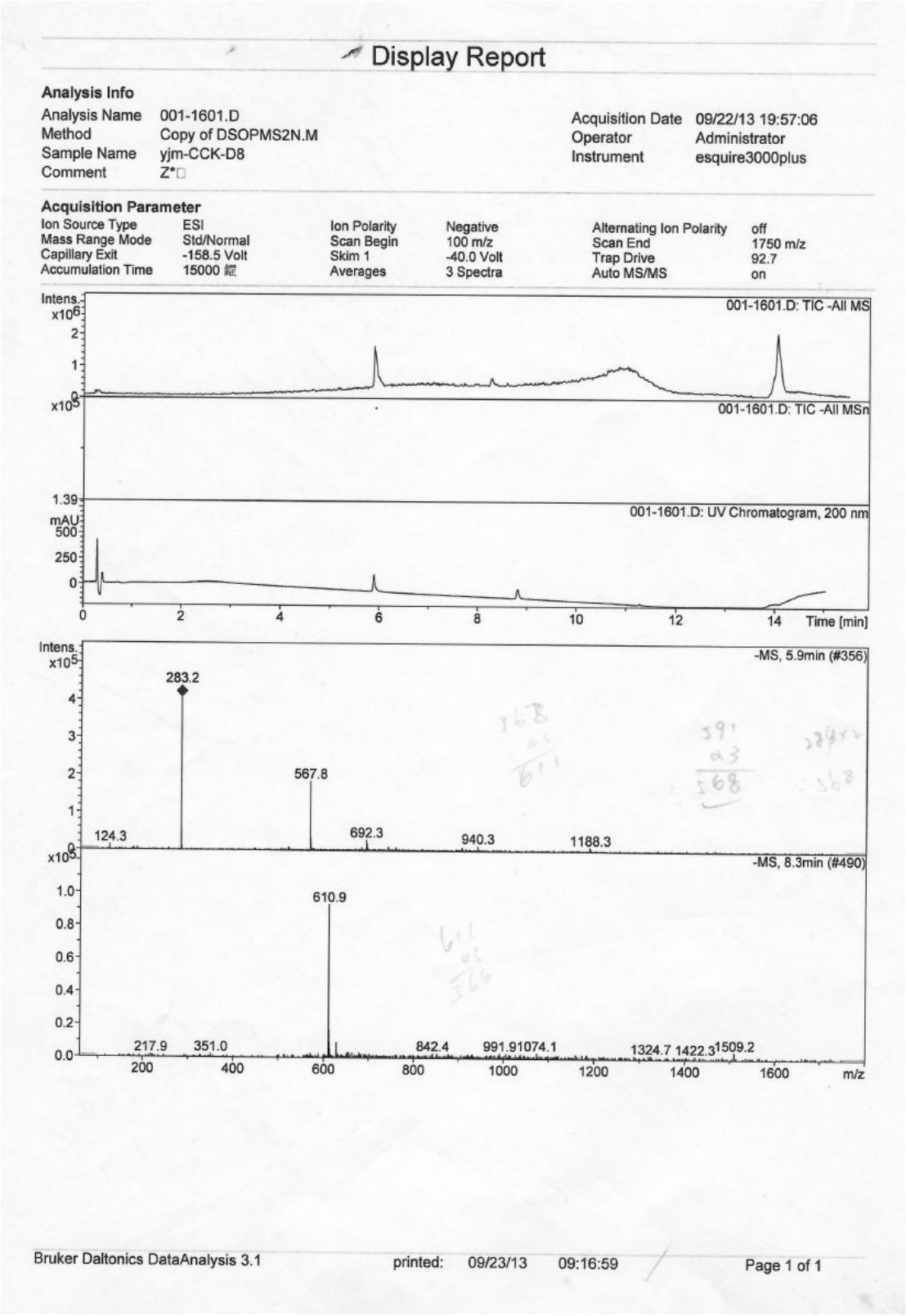


**Figure S11.** (−)-HRESIMS spectrum of Capitulactone A (**1**)

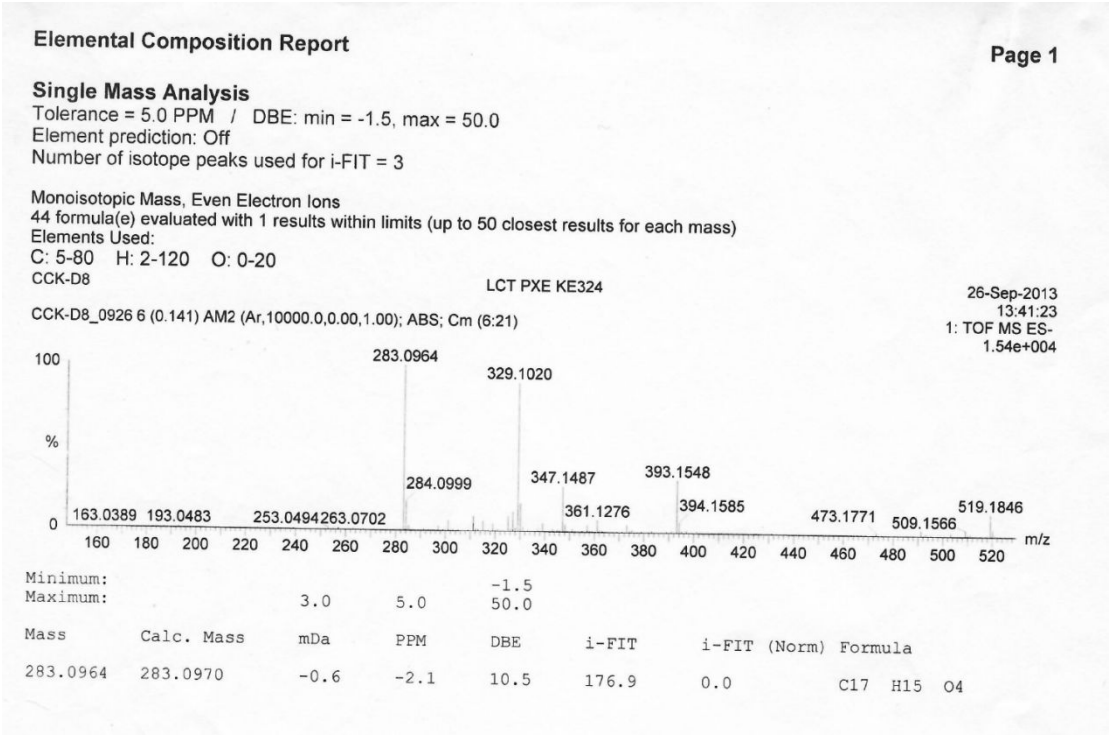


**Figure S12.** $^{1}H$ NMR spectrum of Capitulactone B (**2**) in $CDCl_3$

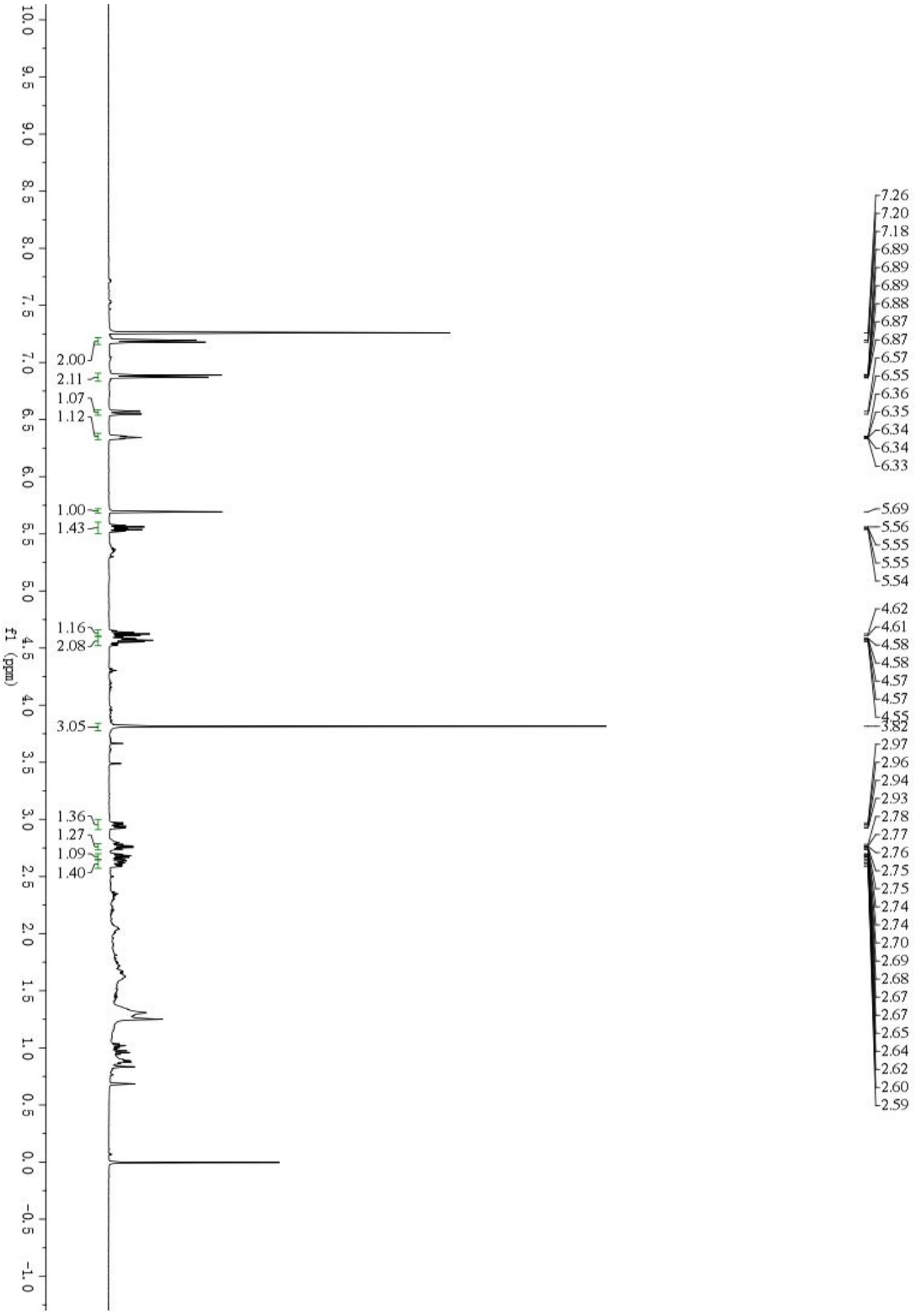


**Figure S13.** $^{13}C$ NMR spectrum of Capitulactone B (**2**) in $CDCl_3$

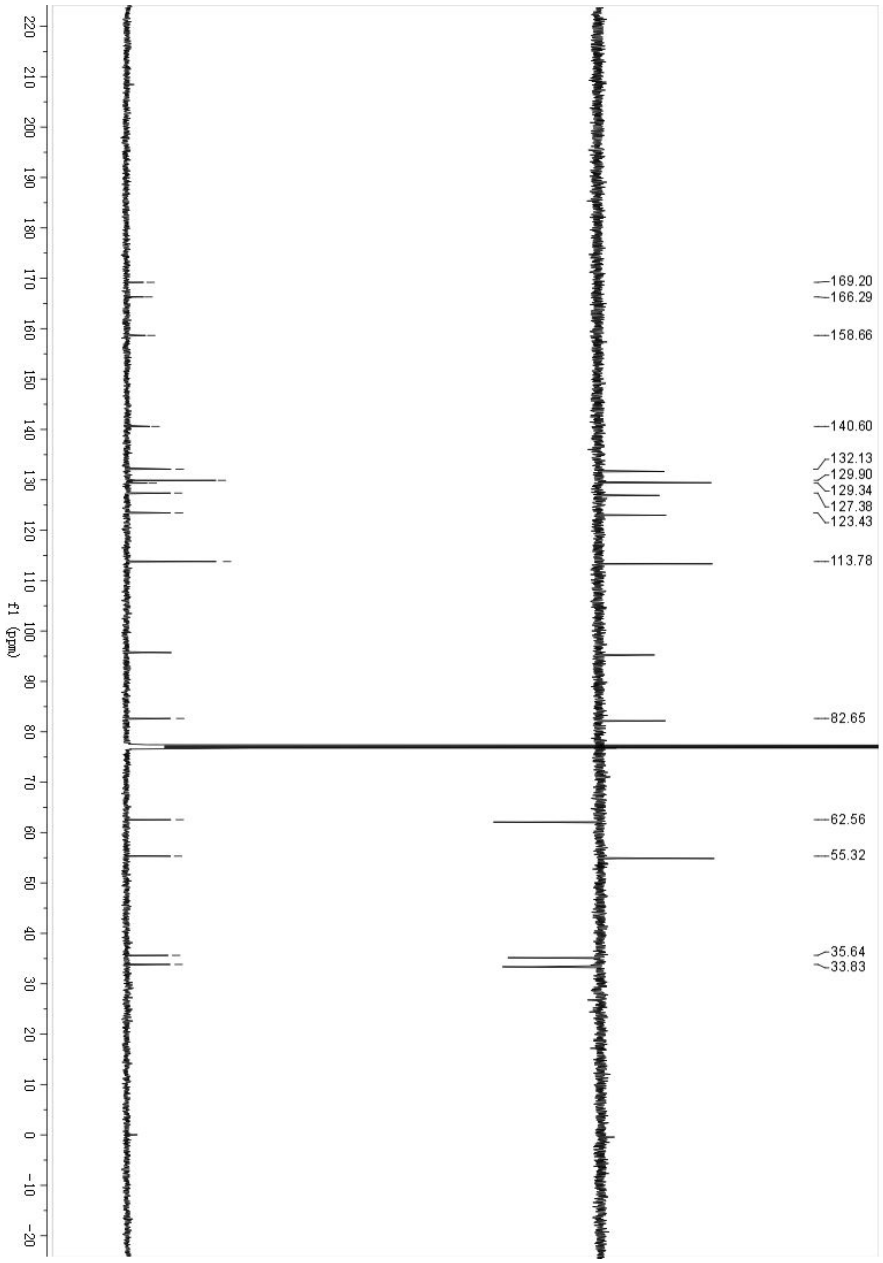


**Figure S14.** HSQC spectrum of Capitulactone B (**2**) in $CDCl_3$

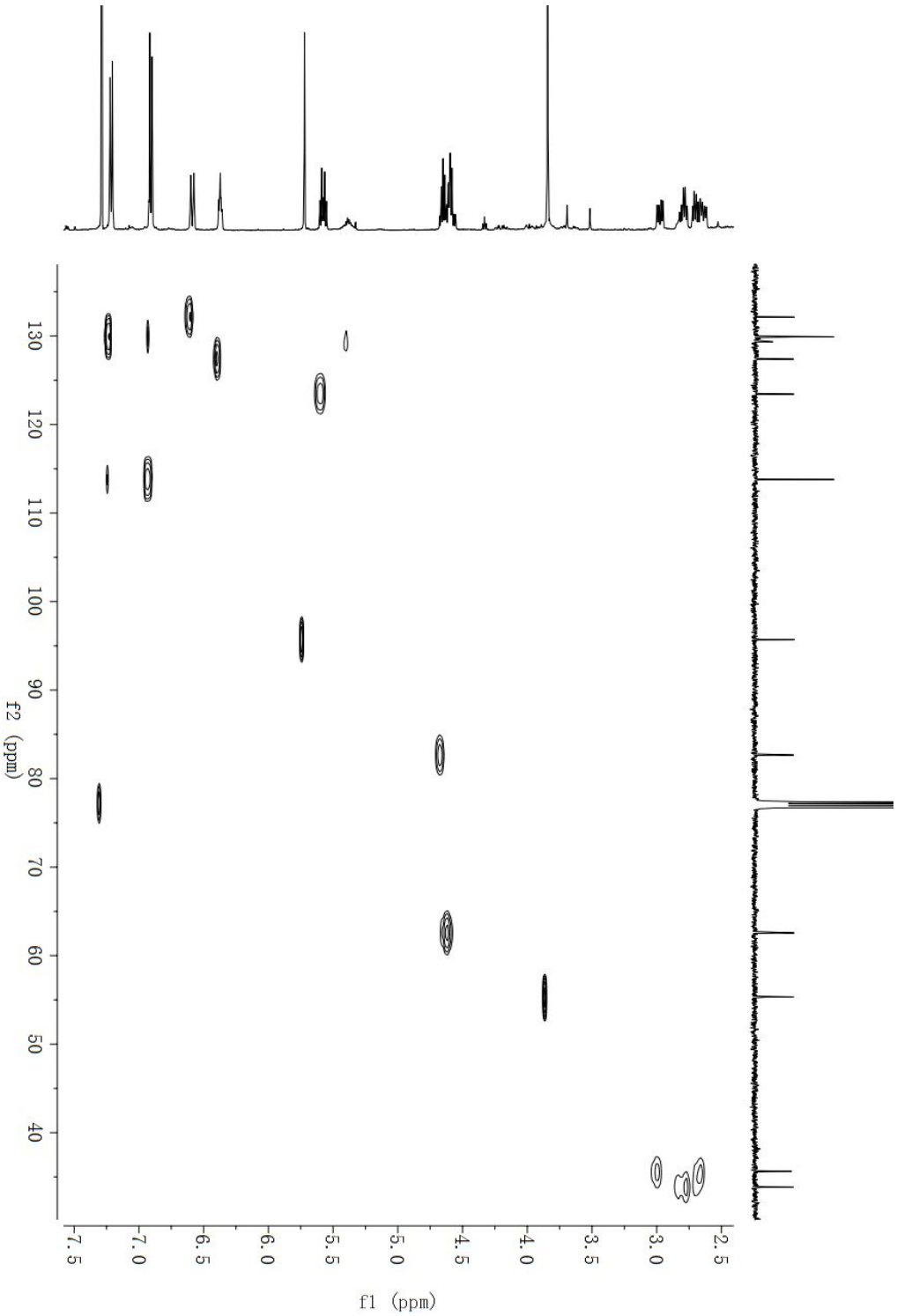


**Figure S15.** HMBC spectrum of Capitulactone B (**2**) in $CDCl_3$

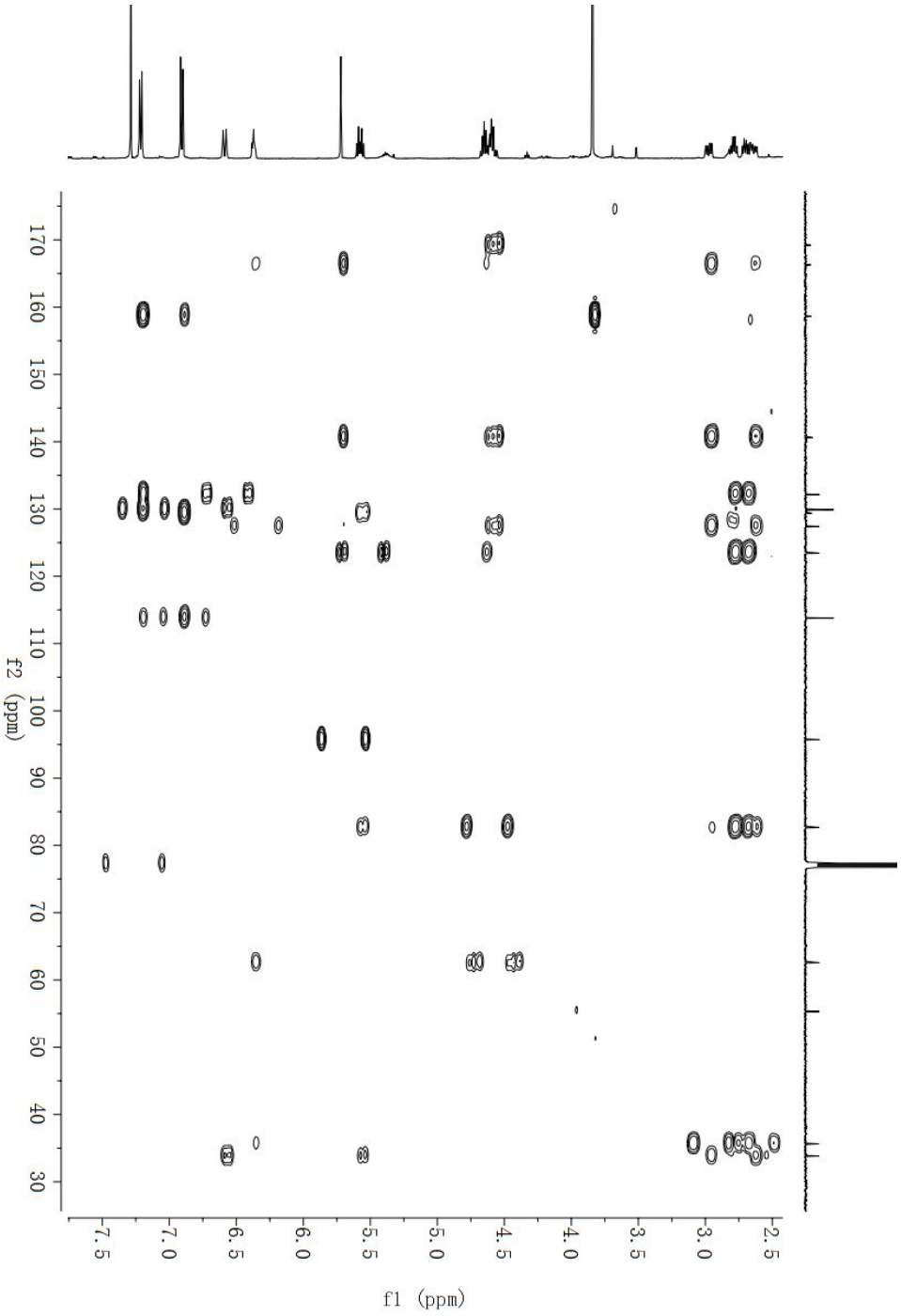


**Figure S16.** (+)-ESIMS spectrum of Capitulactone B (**2**)

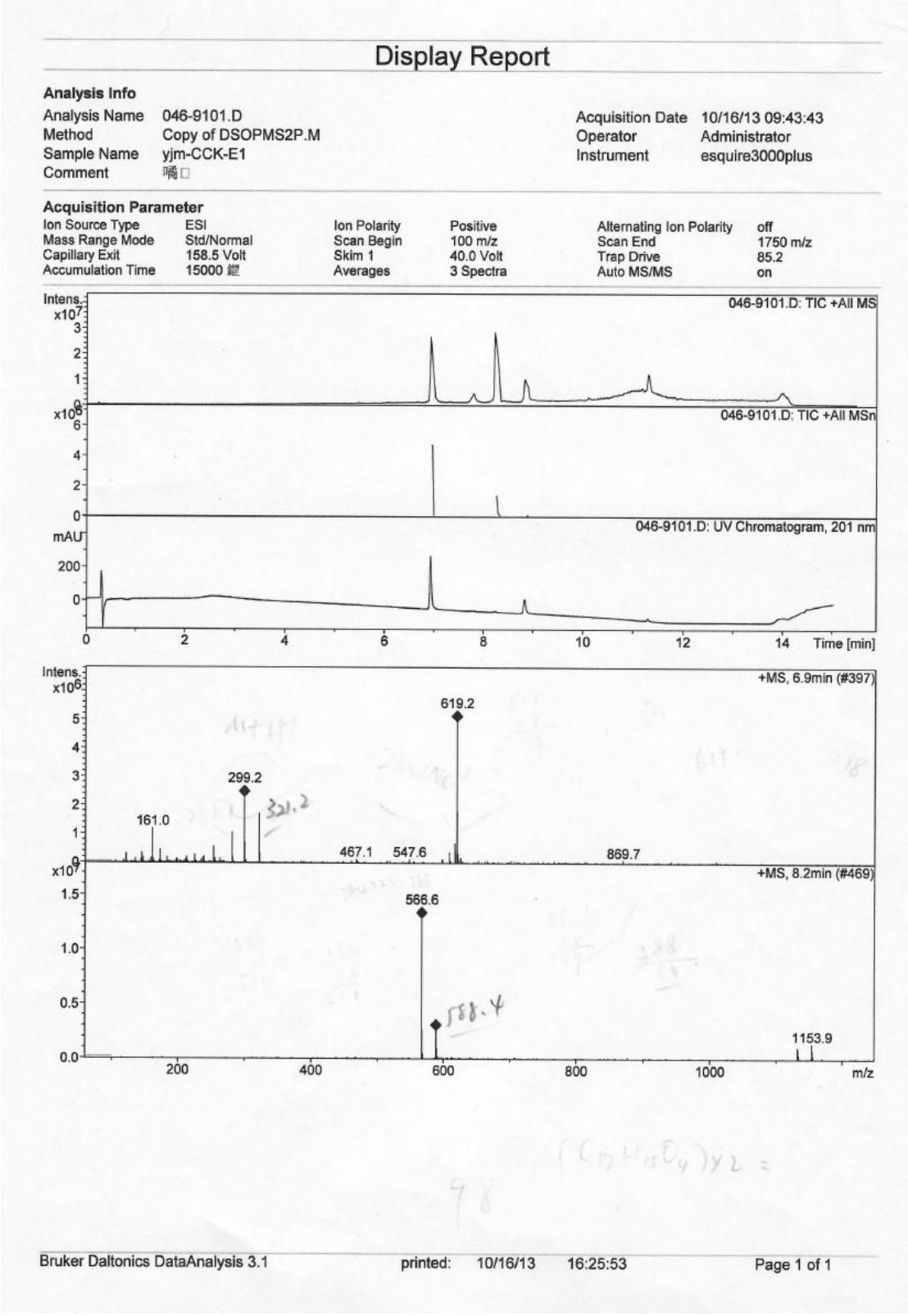


**Figure S17.** (+)-HRESIMS spectrum of Capitulactone B (**2**)

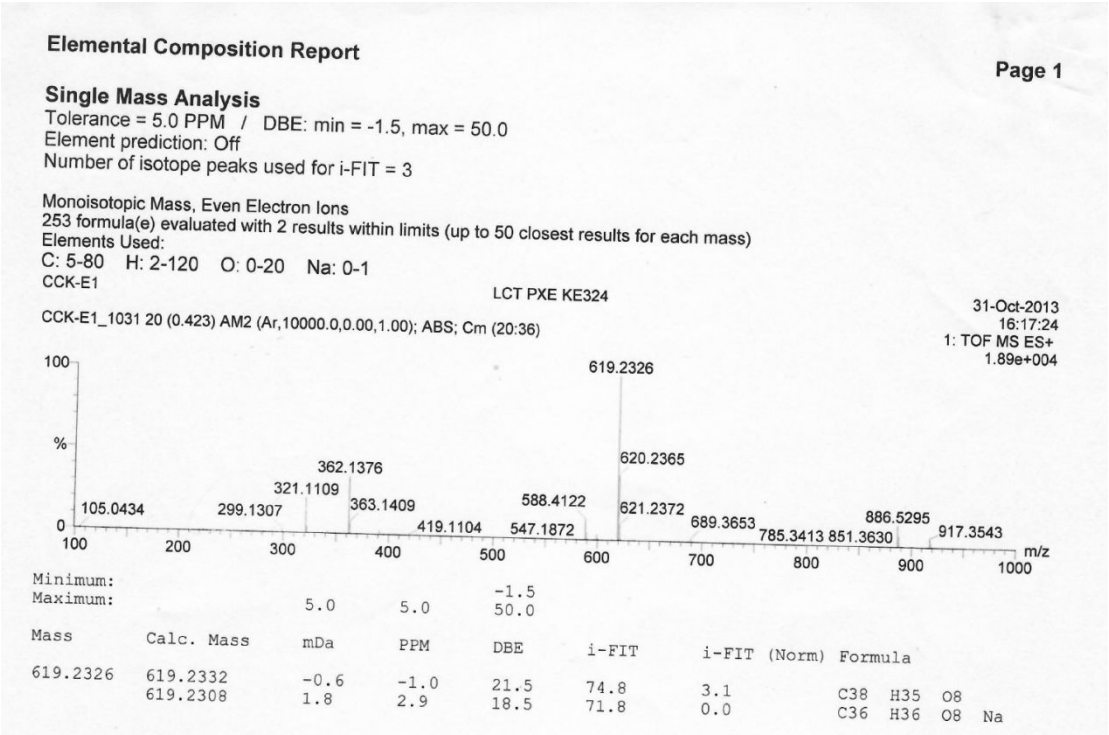


**Figure S18.** $^{1}H$ NMR spectrum of Capitulactone C (**3**) in $CDCl_3$

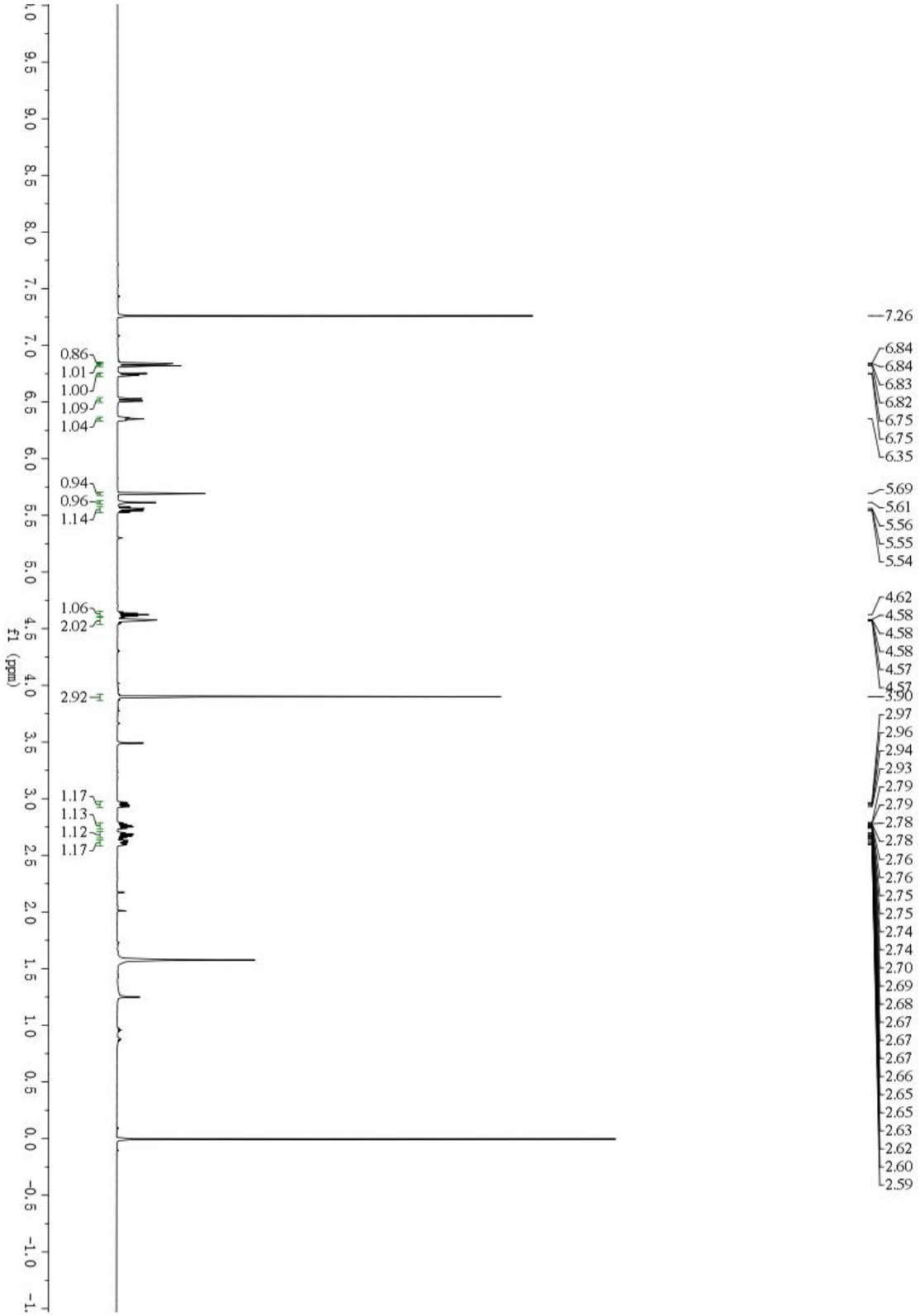


**Figure S19.** $^{13}C$ NMR spectrum of Capitulactone C (**3**) in $CDCl_3$

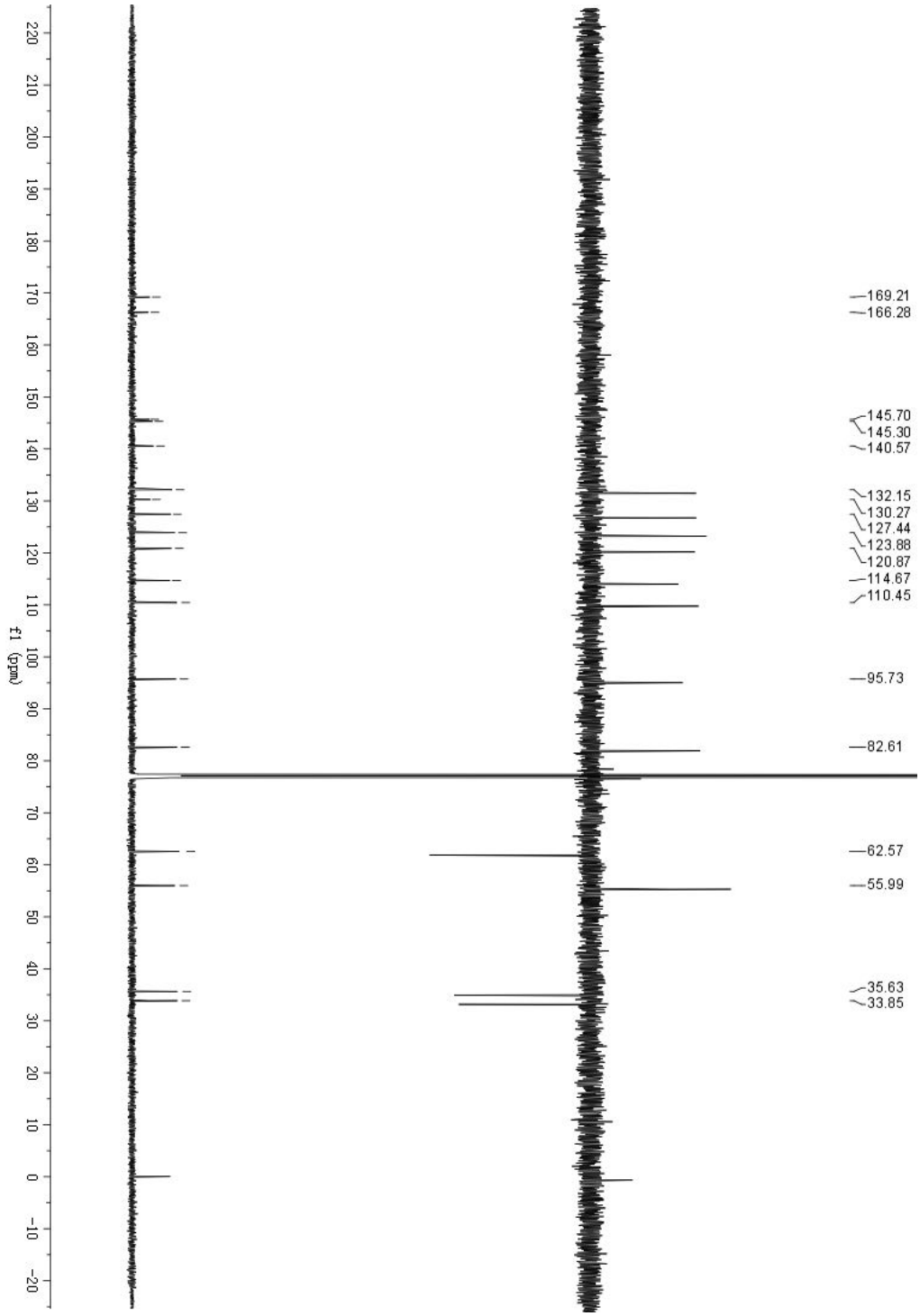


**Figure S20.** HMBC spectrum of Capitulactone C (**3**) in $CDCl_3$

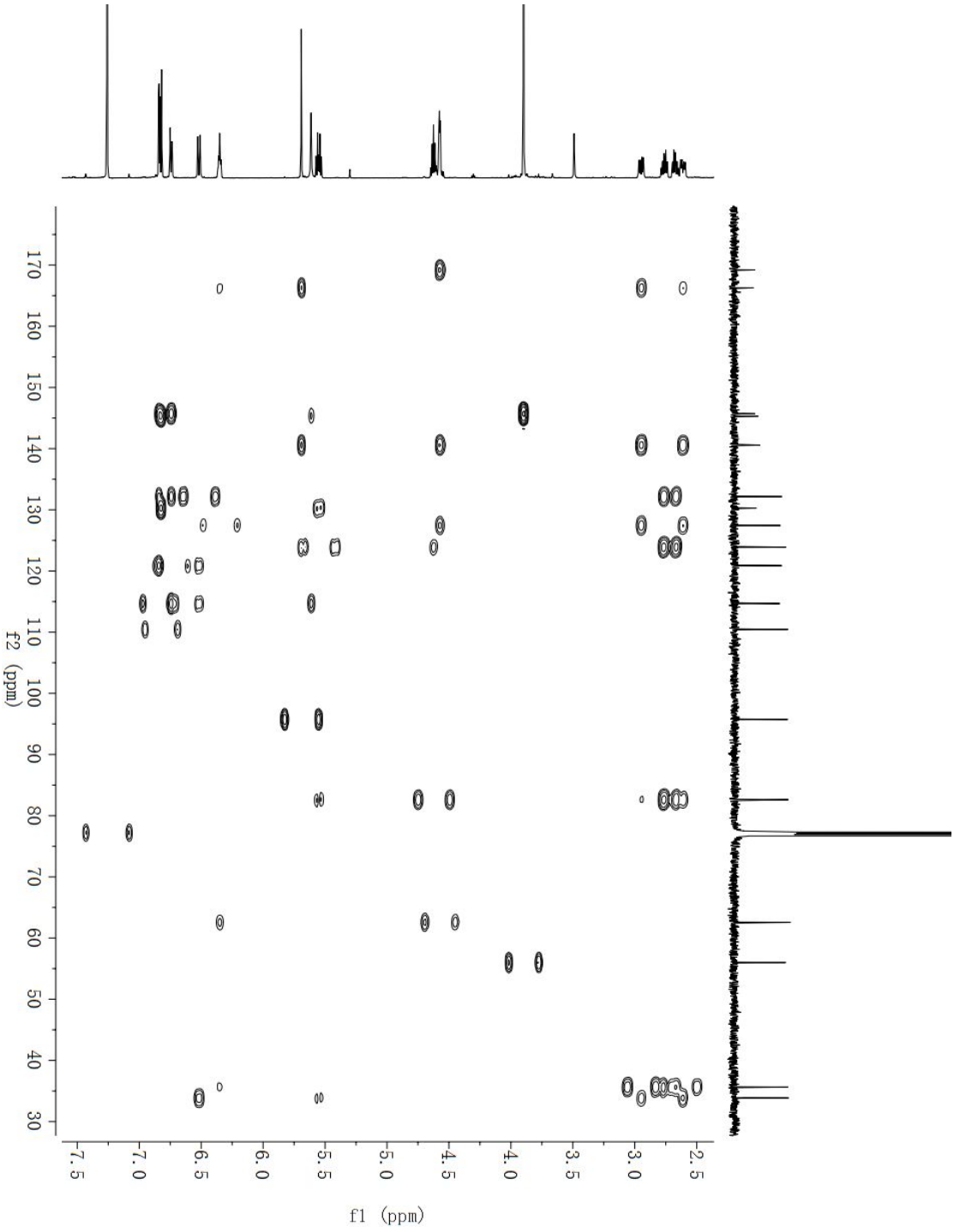


**Figure S21.** (+)-ESIMS spectrum of Capitulactone C (**3**)

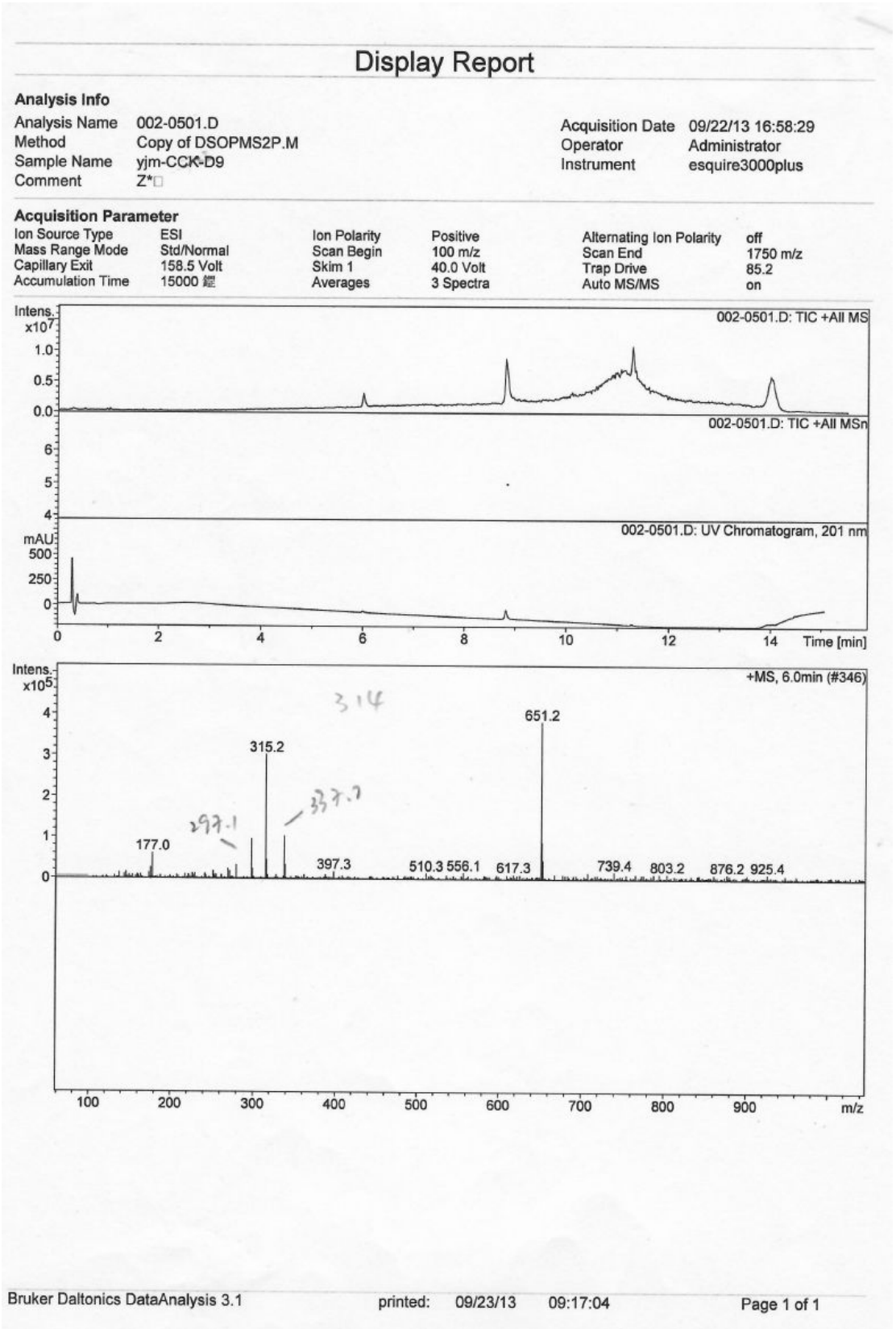


**Figure S22.** (−)-ESIMS spectrum of Capitulactone C (**3**)

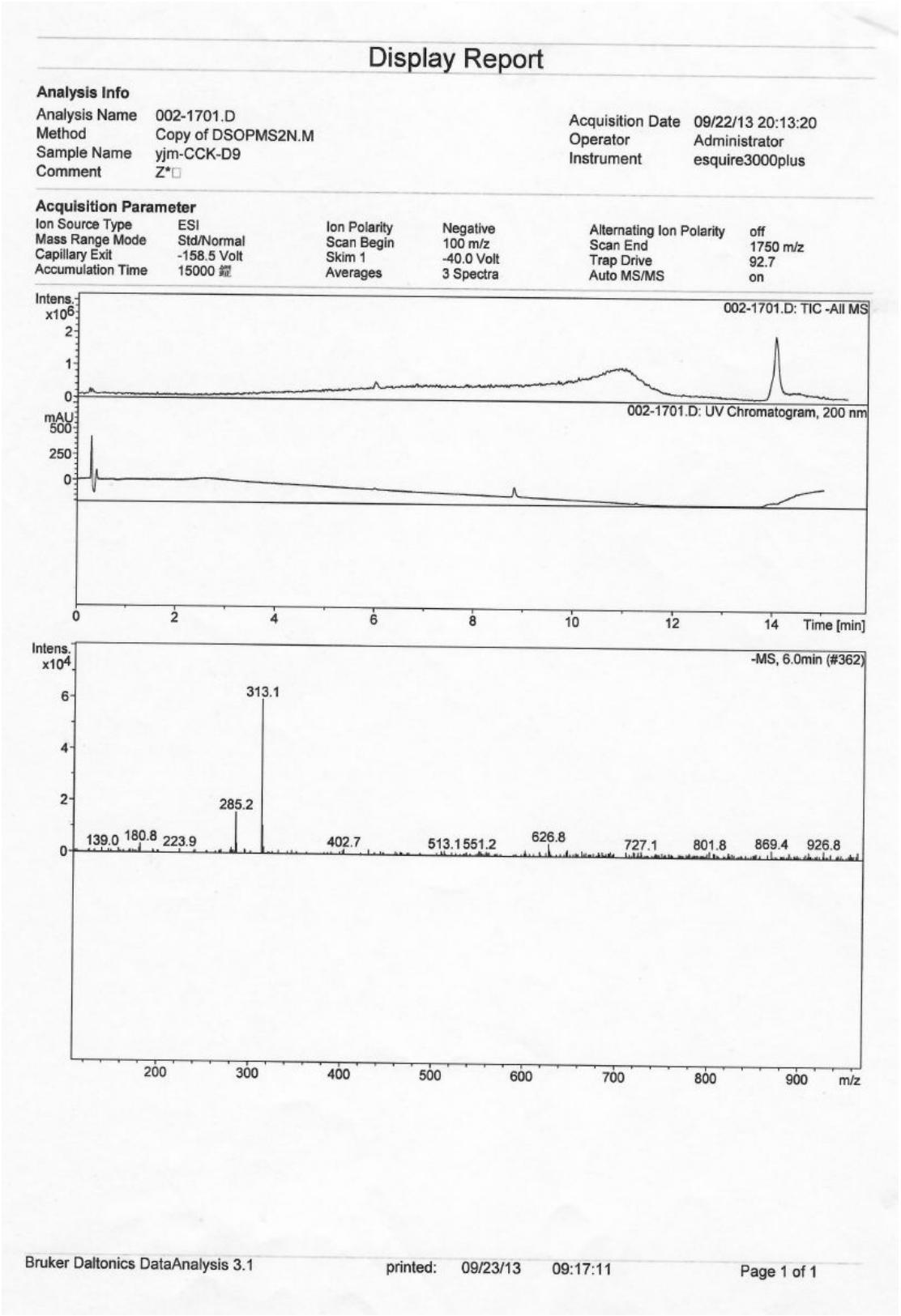
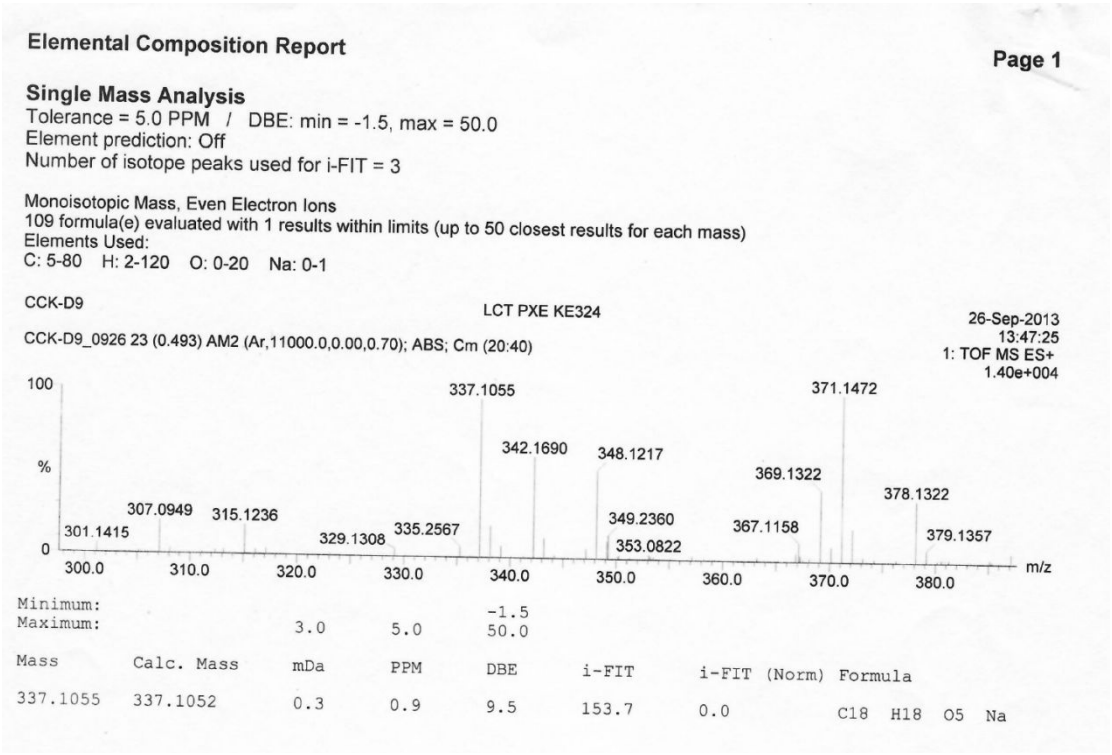


**Figure S23.** (+)-HRESIMS spectrum of Capitulactone C (**3**)



**Total syntheses of 1a, 1b, 3a and 3b**

**(*S*)-1-(2-Bromo-4,5-bis((tert-butyldimethylsilyl)oxy)phenyl)-5-(4-(methoxymethoxy)phenyl)pent-4-yn-2-ol ((*S*)-15a).** To a solution of **14** (3.1 g, 19.1 mmol) in dry THF (80 mL) under argon atmosphere was added *n*-BuLi (2.4 M, 9.6 mL, 23.0 mmol) at -78 °C. The mixture was stirred at -78 °C for 1 h, (*R*)-**7a** (9.1 g, 19.1 mmol) in anhydrous THF and $BF_3 \cdot OEt_2$ (2.4 mL, 19.1 mmol) was slowly added. After the completion of the reaction, the resulting solution was quenched with water (20 mL) and extracted with ethyl acetate (3 × 50 mL). The combined organic solution was washed with saturated aqueous NaCl (10 mL), dried over anhydrous $Na_2SO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (hexanes/EtOAc, 8:1) to give (*S*)-**15a** (11.2 g, 92%) as a colorless oil. $[\alpha]_D^{20}$ -38.0 (c 1.00, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.7 Hz, 2H), 7.01 (s, 1H), 6.96 (d, *J* = 8.7 Hz, 2H), 6.82 (s, 1H), 5.17 (s, 2H), 4.11 (m, 1H), 3.47 (s, 3H), 3.01 (dd, *J* = 13.7, 5.8 Hz, 1H), 2.87 (dd, *J* = 13.7, 7.3 Hz, 1H), 2.62 (m, 2H), 2.05 (d, *J* = 4.9 Hz, 1H), 0.99 (s, 9H), 0.97 (s, 9H), 0.20 (s, 6H), 0.19 (s, 6H). $^{13}$C {$^1$H}NMR (101 MHz, $CDCl_3$) δ 156.9, 146.4, 146.3, 133.0, 130.0, 124.9, 123.7, 116.7, 116.1, 114.8, 94.3, 84.5, 83.2, 69.7, 56.0, 42.0, 27.4, 25.9, 25.8, 18.43, 18.40, -4.11, -4.14, -4.18, -4.21. IR (KBr) $\nu_{max}$ 3451, 3043, 2955, 2930, 2897, 2858, 1606, 1508, 1442, 1385, 1256, 839, 783cm$^{-1}$; HRMS (ESI): calcd for $C_{31}H_{48}BrO_5Si_2$ $[M + H]^+$ 635.2218, found 635.2218.

**(*R*)-1-(2-Bromo-4,5-bis((tert-butyldimethylsilyl)oxy)phenyl)-5-(4-(methoxymethoxy)phenyl)pent-4-yn-2-ol ((*R*)-15b).** Prepared according to the above step. Colorless oil (11.0 g, 90%). $[\alpha]_D^{20}$ +34.0 (c 1.00, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.8 Hz, 2H), 7.01 (s, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.83 (s, 1H), 5.17 (s, 2H), 4.16 – 4.05 (m, 1H), 3.47 (s, 3H), 3.01 (dd, *J* = 13.7, 5.8 Hz, 1H), 2.88 (dd, *J* = 13.7, 7.3 Hz, 1H), 2.62 (m, 2H), 1.97 (br, 1H), 0.99 (s, 9H), 0.97 (s, 9H),

0.20 (s, 6H) , 0.19 (s, 6H). $^{13}C$ {$^{1}H$}NMR (101 MHz, $CDCl_3$) δ 156.9, 146.4, 146.3, 133.0, 130.1, 124.9, 123.7, 116.7, 116.1, 114.8, 94.3, 84.5, 83.2, 69.7, 56.0, 42.0, 27.4, 25.9, 25.8, 18.42, 18.39, -4.11, -4.14, -4.18, -4.21. IR (KBr) $\nu_{max}$ 3430，3054，2957，2931，2899，2859，1606，1508, 1422, 1385, 1265， 1201， 840,742$cm^{-1}$; HRMS (ESI): calcd for $C_{31}H_{48}BrO_5Si_2$ $[M + H]^+$ 635.2218, found 635.2220.

**(*S*)-((2-(3-(4-(Methoxymethoxy)phenyl)prop-2-yn-1-yl)-2,3-dihydrobenzofuran-5,6-diyl)bis(oxy))bis(tert-butyldimethylsilane) ((*S*)-16a).** To a solution of (*S*)-**15a** (4.5 g, 7.1 mmol) in dry toluene (100 mL) under argon atmosphere, NaH (60%) (348 mg, 8.7 mmol) was added. The mixture was stirred at 40 °C for 15 min. Then, the mixture was cooled to room temperature and CuCl (28 mg, 0.28 mmol) was added to the solution. The suspension was stirred for 6 h at reflux and after this time, the mixture was filtered through Celite®. Then, the mixture was purified by flash column chromatography (hexanes/EtOAc, 16:1) to give (*S*)-**16a** (3.7 g, 95%) as a colorless oil. $[\alpha]_D^{20}$ +37.0 (c 1.00, $CH_2Cl_2$); $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 6.66 (s, 1H), 6.36 (s, 1H), 5.16 (s, 2H), 4.94 (m, 1H), 3.46 (s, 3H), 3.30 (dd, *J* = 15.4, 8.9 Hz, 1H), 3.07 (dd, *J* = 15.4, 6.6 Hz, 1H), 2.82 (m, 2H), 1.00 (s, 9H), 0.99 (s, 9H), 0.21 (s, 6H), 0.18 (s, 3H), 0.17 (s, 3H). $^{13}C$ {$^{1}H$}NMR (101 MHz, $CDCl_3$) δ 156.8, 153.4, 146.2, 140.4, 132.9, 117.8, 116.9, 116.7, 115.9, 102.6, 94.1, 83.9, 82.0, 81.2, 55.9, 34.9, 26.5, 25.95, 25.92, 18.4, 18.3, -4.09, -4.12, -4.19, -4.21. IR (KBr) $\nu_{max}$ 3053, 2957, 2931, 2899, 2858, 1607, 1508, 1424, 1362, 1265, 1165, 839, 741$cm^{-1}$； HRMS (ESI): calcd for $C_{31}H_{46}NaO_5Si_2$ $[M + Na]^+$ 577.2776, found 577.2778.

**(*R*)-((2-(3-(4-(Methoxymethoxy)phenyl)prop-2-yn-1-yl)-2,3-dihydrobenzofuran-5,6-diyl)bis(oxy))bis(tert-butyldimethylsilane) ((*R*)-16b).** Prepared according to the above step. Colorless oil,

(3.6 g, 93%). $[\alpha]_D^{20}$ -34.0 (c 1.00, $CH_2Cl_2$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.7 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.64 (s, 1H), 6.34 (s, 1H), 5.16 (s, 2H), 4.93 (m, 1H), 3.47 (s, 3H), 3.29 (dd, *J* = 15.3, 9.0 Hz, 1H), 3.05 (dd, *J* = 15.3, 6.6 Hz, 1H), 2.81 (m, 2H), 0.98 (s, 9H), 0.97 (s, 9H), 0.19 (s, 6H), 0.163 (s, 3H), 0.159 (s, 3H). $^{13}C$ {$^1H$}NMR (101 MHz, $CDCl_3$) δ 156.9, 153.4, 146.3, 140.5, 133.0, 117.8, 116.9, 116.8, 116.1, 102.7, 94.3, 84.0, 82.0, 81.3, 56.0, 35.0, 26.5, 26.0, 18.5,18.4, -4.0, -4.07, -4.14. IR (KBr) $\nu_{max}$ 3052, 2957, 2930, 2898, 2858, 1607, 1508, 1424, 1361, 1265, 1165, 839, 740$cm^{-1}$； HRMS (ESI): calcd for $C_{31}H_{46}NaO_5Si_2$ $[M + Na]^+$ 577.2776, found 577.2776.

**(*S*)-2-(3-(4-(Methoxymethoxy)phenyl)prop-2-yn-1-yl)-2,3-dihydrofuro[2,3-d]oxepin-7(5H)-one ((*S*)-17a).** To a solution of (*S*)-**16a** (1.2 g, 2.2 mmol) in THF (50 mL) was added tetrabutylammonium fluoride (2 M in THF, 1.1 mL,), and the resultant mixture was stirred at 0 °C for 5 min. The reaction was quenched with saturated aqueous $NH_4Cl$ (10 mL), and the resultant mixture was extracted with ethyl acetate (3 × 20 mL). The organic extracts were washed with saturated aqueous NaCl (2 × 20 mL), dried over $Na_2SO_4$, filtered and concentrated under reduced pressure. The crude was dissolved in MeCN (20 mL), and Ceric ammonium nitrate (1.0 M in $H_2O$, 4.8 mL) was added dropwise at 0 °C. Ethyl acetate (10 mL) was added to the reaction immediately, and the resultant mixture was extracted with ethyl acetate (3 × 20 mL). The organic extracts were washed with saturated aqueous NaCl (2 × 20 mL), dried over $Na_2SO_4$, filtered and concentrated under reduced pressure to give the crude product benzoquinone. The benzoquinone was dissolved in anhydrous $CH_2Cl_2$ at 0 °C, *m*-CPBA (75%) (504 mg, 2.2 mmol) was added to the solution. After the completion of the reaction, the solvent was removed under reduced pressure. the residue was quickly purified through thin pad of silica gel (hexanes/EtOAc, 2:1) to give crude product

anhydride as a yellow oil. The crude product is used directly for the next step. The crude product anhydride was added to a solution of $NaBH_4$ (29 mg, 0.77 mmol) in 5 mL of dry THF at 0 °C. After the completion of the reaction, the reaction was treated by slow addition of 1.0 M HCl until all the solid had dissolved. The resulting solution was extracted with ethyl acetate (3 × 10 mL). The combined organic solution was washed with saturated aqueous NaCl (2 × 10 mL), dried over anhydrous $Na_2SO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (hexanes/EtOAc, 8:1) to give (*S*)-**17a** (148 mg, 21% for 4 steps) as a colorless oil. $[\alpha]_D^{20}$ +26.0 (c 1.00, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.7 Hz, 2H), 6.95 (d, *J* = 8.7 Hz, 2H), 6.43 – 6.37 (m, 1H), 5.72 (s, 1H), 5.16 (s, 2H), 4.80 – 4.72 (m, 1H), 4.54 (m, 2H), 3.46 (s, 3H), 3.08 (dd, *J* = 15.6, 7.3 Hz, 1H), 2.89 (dd, *J* = 15.6, 5.4 Hz, 1H), 2.79 (m, 2H). $^{13}$C {$^1$H}NMR (101 MHz, $CDCl_3$) δ 169.0, 166.2, 157.2, 140.2, 133.0, 127.5, 116.1, 95.9, 94.2, 83.2, 82.0, 80.5, 62.5, 56.1, 35.2, 25.9. IR (KBr) $\nu_{max}$ 3055, 2986, 2960, 2927, 2853, 1690, 1607, 1509, 1393, 1266, 1237, 1153, 838, 740cm$^{-1}$； HRMS (ESI): calcd for $C_{19}H_{19}O_5$ $[M + H]^+$ 327.1227, found 327.1227.

**(*R*)-2-(3-(4-(Methoxymethoxy)phenyl)prop-2-yn-1-yl)-2,3-dihydrofuro[2,3-d]oxepin-7(5H)-one ((*R*)-17b).** Prepared according to the above steps. Colorless oil (162 mg, 23% for 4 steps). $[\alpha]_D^{20}$ -43.0 (c 1.00, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.7 Hz, 2H), 6.95 (d, *J* = 8.7 Hz, 2H), 6.43 – 6.38 (m, 1H), 5.73 (s, 1H), 5.16 (s, 2H), 4.80 – 4.70 (m, 1H), 4.55 (m, 2H), 3.46 (s, 3H), 3.09 (dd, *J* = 15.7, 7.5 Hz, 1H), 2.90 (dd, *J* = 16.1, 5.6 Hz, 1H), 2.85 – 2.71 (m, 2H). $^{13}$C {$^1$H}NMR (101 MHz, $CDCl_3$) δ 169.0, 166.2, 157.2, 140.3, 133.0, 127.5, 116.2, 95.9, 94.3, 83.3, 82.0, 80.6, 62.6, 56.1, 35.2, 25.9. IR (KBr) $\nu_{max}$ 3055, 2986, 2958, 2926, 2853, 1690, 1608, 1509, 1393, 1265, 1237, 1153, 838, 739cm$^{-1}$； HRMS (ESI): calcd for $C_{19}H_{19}O_5$ $[M + H]^+$

327.1227, found 327.1227.

**(*S*)-2-(3-(4-Hydroxyphenyl)prop-2-yn-1-yl)-2,3-dihydrofuro[2,3-d]oxepin-7(5H)-one ((*S*)-18a).** Compound (*S*)-**17a** (105 mg, 0.32 mmol) was dissolved in acetonitrile/$H_2O$ = 5/0.1 (10 mL). $BiCl_3$ (31 mg, 0.10 mmol) was added to this solution. The mixture was stirred for 1 h at 50 °C. The reaction was treated by slow addition of 1.0 M HCl and extracted with ethyl acetate (3 × 10 mL), dried over anhydrous $Na_2SO_4$, filtered and concentrated under reduced pressure. The residue was purified by a flash column chromatography (hexanes/EtOAc, 2:1) to give (*S*)-**18a** (82 mg, 90%) as a colorless oil. $[\alpha]_D^{20}$ +44.0 (c 0.50, MeOH); $^1$H NMR (400 MHz, DMSO) δ 9.78 (s, 1H), 7.18 (d, *J* = 8.6 Hz, 2H), 6.72 (d, *J* = 8.7 Hz, 2H), 6.61 – 6.54 (m, 1H), 5.54 (s, 1H), 4.81 (m, 1H), 4.51 (m, 2H), 3.12 (dd, *J* = 15.8, 7.5 Hz, 1H), 2.89 – 2.74 (m, 3H). $^{13}$C {$^1$H}NMR (101 MHz, DMSO) δ 168.1, 166.4, 157.6, 139.9, 132.8, 128.6, 115.5, 112.8, 94.5, 82.82, 82.76, 80.8, 62.3, 34.4, 25.1. IR (KBr) $\nu_{max}$ 3361, 2974, 2893, 1668, 1611, 1513, 1453, 1328, 1272, 1187, 1049, 881, 837, 740cm$^{-1}$； HRMS (ESI): calcd for $C_{17}H_{15}O_4$ $[M + H]^+$ 283.0965, found 283.0966.

**(*R*)-2-(3-(4-Hydroxyphenyl)prop-2-yn-1-yl)-2,3-dihydrofuro[2,3-d]oxepin-7(5H)-one ((*R*)-18b).** Prepared according to the above step. Colorless oil (84 mg, 93%). $[\alpha]_D^{20}$ -46.0 (c 1.00, MeOH); $^1$H NMR (400 MHz, DMSO) δ 9.79 (s, 1H), 7.18 (d, *J* = 8.6 Hz, 2H), 6.72 (d, *J* = 8.7 Hz, 2H), 6.61 – 6.54 (m, 1H), 5.54 (s, 1H), 4.85 – 4.77 (m, 1H), 4.58 – 4.44 (m, 2H), 3.12 (dd, *J* = 15.8, 7.5 Hz, 1H), 2.88 – 2.75 (m, 3H). $^{13}$C {$^1$H}NMR (101 MHz, DMSO) δ 168.1, 166.4, 157.6, 140.0, 132.8, 128.6, 115.6, 112.8, 94.5, 82.83, 82.78, 80.8, 62.3, 34.4, 25.1. IR (KBr) $\nu_{max}$ 3373, 3055, 2975, 2923, 2894, 1670, 1611, 1513, 1449, 1382, 1267, 1186, 1048, 880, 839, 741cm$^{-1}$； HRMS (ESI): calcd for $C_{17}H_{15}O_4$ $[M + H]^+$ 283.0965, found 283.0968.

**(*S*, *Z*)-2-(3-(4-Hydroxyphenyl)allyl)-2,3-dihydrofuro[2,3-d]oxepin-7(5H)-one ((*S*)-1a).** To a

solution of (*S*)-**18a** (50 mg, 0.18 mmol) in ethyl acetate (5 mL ) was added quinoline (4.6 μL, 10% in weight) followed by Lindlar's catalyst (10.0 mg, 20% in weight). This solution was stirred under a balloon of hydrogen for 1.5 h. The reaction mixture was filtered through a plug of silica and the solvent removed in vacuo; purification by Silver nitrate silica gel column chromatography yielded (*S*)-**1a** (45 mg, 89%) as a white powder. $[\alpha]_D^{20}$ -10.6 (c 0.23, MeOH); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 6.55 (d, *J* = 11.4 Hz, 1H), 6.34 (m, 1H), 5.69 (s, 1H), 5.53 (dt, *J* = 11.7, 7.2 Hz, 1H), 4.62 (m, 1H), 4.59 – 4.52 (m, 2H), 2.95 (dd, *J* = 15.4, 7.1 Hz, 1H), 2.75 (dd, *J* = 14.1, 7.3 Hz, 1H), 2.64 (dt, *J* = 16.1, 7.8 Hz, 2H). $^{13}$C {$^1$H}NMR (101 MHz, $CDCl_3$) δ 169.3, 166.4, 154.8, 140.6, 132.1, 130.0, 129.4, 127.4, 123.4, 115.3, 112.3, 95.6, 82.6, 62.6, 35.6, 33.8. IR (KBr) $\nu_{max}$ 2986, 2853, 1652, 1609, 1516, 1402, 1197, 1026, 841 cm$^{-1}$; HRMS (ESI): calcd for $C_{17}H_{17}O_4$ $[M + H]^+$ 285.1121, found 285.1122.

**(*R*, *Z*)-2-(3-(4-Hydroxyphenyl)allyl)-2,3-dihydrofuro[2,3-d]oxepin-7(5H)-one ((*R*)-1b).** Prepared according to the above step. White powder (43 mg, 86%). $[\alpha]_D^{20}$ +11.1 (c 0.29, MeOH); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 6.55 (d, *J* = 11.7 Hz, 1H), 6.34 (m, 1H), 5.69 (s, 1H), 5.54 (dt, *J* = 11.7, 7.2 Hz, 1H), 5.39 (br, 1H), 4.62 (m, 1H), 4.59 – 4.52 (m, 2H), 2.95 (dd, *J* = 15.5, 7.0 Hz, 1H), 2.80 – 2.71 (m, 1H), 2.70 – 2.56 (m, 2H). $^{13}$C {$^1$H}NMR (101 MHz, $CDCl_3$) δ 169.4, 166.4, 154.9, 140.6, 132.2, 130.0, 129.3, 127.4, 123.3, 115.3, 95.6, 82.7, 62.6, 35.6, 33.8. IR (KBr) $\nu_{max}$ 3015, 2867, 1649, 1612, 1513, 1396, 1183, 1020, 841 cm$^{-1}$; HRMS (ESI): calcd for $C_{17}H_{17}O_4$ $[M + H]^+$ 285.1121, found 285.1123.

**5-Ethynyl-2-methoxyphenol (20).** To a solution of the aldehyde **19** (10 g, 0.066 mol) in dry $CH_2Cl_2$ (150 mL), triphenylphosphine (43.6 g, 0.13 mmol) was added under argon atmosphere. The resulting solution was cooled at 0 °C and a solution of carbon tetrabromide (69 g, 0.26 mmol)

in dry $CH_2Cl_2$ was added dropwise. The reaction mixture was stirred for 2 h and quenched adding water (100 mL). The organic layer was separated and washed with brine (2 × 50 mL), dried over anhydrous $Na_2SO_4$, filtered and concentrated under reduced pressure. The residue was purified by a flash column chromatography (hexanes/EtOAc, 4:1) to give dibromoethene derivative as a white solid. *n*-BuLi (2.4 M, 47.3 mL) was added slowly to a solution containing the dibromoethene derivative (10.6 g, 0.034 mol) in dry THF cooled at -78 °C. The resulting solution was stirred at -78 °C for 1h then warmed slowly to room temperature, after the completion of the reaction, the mixture was quenched with water (50 mL) and extracted with ethyl acetate (3 × 50 mL). The combined organic solution was washed with saturated aqueous $NH_4Cl$ (10 mL), dried over anhydrous $Na_2SO_4$, filtered and concentrated under reduced pressure. The residue was purified by a flash column chromatography (hexanes/EtOAc, 4:1) to give **20** (11.9 g，86%) as a white solid. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.05 (d, *J* = 1.9 Hz, 1H), 7.03 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.78 (d, *J* = 8.2 Hz, 1H), 5.60 (s, 1H), 3.90 (s, 3H), 2.97 (s, 1H). $^{13}$C {$^1$H}NMR (101 MHz, $CDCl_3$) δ 147.3, 145.3, 124.8, 118.1, 114.9, 110.4, 83.6, 75.6, 55.9. Consistent with the literature report.[1]

**4-Ethynyl-1-methoxy-2-(methoxymethoxy)benzene (21).** MOMCl (4.1 mL, 0.055 mmol) was added to a stirred solution of **20** (6.2 g, 0.042 mol) in $CH_2Cl_2$ (100 mL) at 0 °C. Diisopropylethyl amine (11.1 mL, 0.067 mmol) was slowly added to the reaction mixture. The ice bath was removed and the mixture was stirred at room temperature for 2 h. water (15 mL) was added in the reaction mixture, and the organic phase was separated and washed with 1 M of HCl, water, 1 M of NaOH, and brine. The organic phase was dried over anhydrous $Na_2SO_4$, filtered and concentrated under reduced pressure. The residue was purified by a flash column chromatography (hexanes/EtOAc, 8:1) to give **21** (7.9 g，98%) as a colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) δ

7.28 (d, $J$ = 1.9 Hz, 1H), 7.14 (dd, $J$ = 8.4, 1.9 Hz, 1H), 6.81 (d, $J$ = 8.4 Hz, 1H), 5.21 (s, 2H), 3.87 (s, 3H), 3.50 (s, 3H), 2.98 (s, 1H). $^{13}$C {$^{1}$H}NMR (101 MHz, $CDCl_3$) δ 150.5, 146.0, 126.9, 119.9, 114.3, 111.4, 95.4, 83.5, 75.7, 56.2, 55.8; IR (KBr) $\nu_{max}$ 3296, 3056, 2958, 2839, 2105, 1601, 1511, 1263, 1130, 925, 812, 738cm$^{-1}$； HRMS (ESI): calcd for $C_{11}H_{13}O_3$ $[M + H]^+$ 193.0859, found 193.0859.

**(*S*)-1-(2-Bromo-4,5-bis((tert-butyldimethylsilyl)oxy)phenyl)-5-(4-methoxy-3-(methoxymethoxy)phenyl)pent-4-yn-2-ol ((*S*)-22a).** To a solution of **21** (4.6 g, 24.0 mmol) in dry THF (80 mL) Under argon atmosphere was added *n*-BuLi (2.4 M, 12.0 mL, 28.8 mmol) at -78 °C. The mixture was stirred at -78 °C for 1 h, (*R*)**-7a** (11.3 g, 24.0 mmol) in anhydrous THF and $BF_3{\cdot}OEt_2$ (3.0 mL, 24.0 mmol) was slowly added. After the completion of the reaction, the resulting solution was quenched with water (50 mL) and extracted with ethyl acetate (3 × 50 mL). The combined organic solution was washed with saturated aqueous NaCl (10 mL), dried over anhydrous $Na_2SO_4$, filtered and concentrated under reduced pressure. The residue was purified by a flash column chromatography (hexanes/EtOAc, 8:1) to give (*S*)-**22a** (14.7 g，92%) as a colorless oil. $[\alpha]_D^{20}$ -49.0 (c 1.00, $CH_2Cl_2$); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, $J$ = 1.9 Hz, 1H), 7.08 (dd, $J$ = 8.4, 1.9 Hz, 1H), 7.00 (s, 1H), 6.82 (s, 1H), 6.80 (d, $J$ = 8.4 Hz, 1H), 5.21 (s, 2H), 4.15 – 4.04 (m, 1H), 3.87 (s, 3H), 3.51 (s, 3H), 3.01 (dd, $J$ = 13.7, 5.7 Hz, 1H), 2.86 (dd, $J$ = 13.7, 7.3 Hz, 1H), 2.61 (ddd, $J$ = 22.9, 16.8, 5.6 Hz, 2H), 2.01 (s, 1H), 0.98 (s, 9H), 0.97 (s, 9H), 0.21 – 0.18 (m, 12H). $^{13}$C {$^{1}$H}NMR (101 MHz, $CDCl_3$) δ 149.9, 146.4, 146.3, 146.1, 130.1, 126.3, 124.8, 123.7, 119.6, 115.7, 114.8, 111.4, 95.5, 84.2, 83.2, 69.7, 56.2, 55.9, 42.0, 27.4, 25.9, 25.8, 18.40, 18.36, -4.1, -4.15, -4.20, -4.24. IR (KBr) $\nu_{max}$ 3397, 3055, 2929, 2857, 1595, 1510, 1422, 1385, 1265, 846, 739cm$^{-1}$； HRMS (ESI): calcd for $C_{32}H_{50}BrO_6Si_2$ $[M + H]^+$ 665.2324, found 665.2323.

**(*R*)-1-(2-Bromo-4,5-bis((tert-butyldimethylsilyl)oxy)phenyl)-5-(4-methoxy-3-(methoxymethoxy)phenyl)pent-4-yn-2-ol ((*R*)-22b).** Prepared according to the above step. Colorless oil (14.3 g, 90%). $[\alpha]_D^{20}$ +47.0 (c 1.00, $CH_2Cl_2$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 1.8 Hz, 1H), 7.09 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.00 (s, 1H), 6.81 (d, 2H), 5.21 (s, 2H), 4.14 – 4.05 (m, 1H), 3.88 (s, 3H), 3.51 (s, 3H), 3.01 (dd, *J* = 13.7, 5.7 Hz, 1H), 2.86 (dd, *J* = 13.7, 7.4 Hz, 1H), 2.62 (qd, *J* = 16.7, 5.6 Hz, 2H), 1.79 (s, 1H), 0.98 (s, 9H), 0.97 (s, 9H), 0.20 (s, 6H), 0.19 (s, 6H). $^{13}C$ {$^1H$}NMR (101 MHz, $CDCl_3$) δ 150.0, 146.4, 146.3, 146.2, 130.1, 126.4, 124.9, 123.7, 119.7, 115.8, 114.8, 111.5, 95.6, 84.3, 83.2, 69.8, 56.2, 55.9, 42.0, 27.5, 25.89, 25.86, 18.44, 18.41, -4.1, -4.17, -4.20. IR (KBr) $\nu_{max}$ 3426, 3054, 2957, 2931, 2859, 1600, 1494, 1442, 1386, 1265, 842, 739$cm^{-1}$； HRMS (ESI): calcd for $C_{32}H_{50}BrO_6Si_2$ $[M + H]^+$ 665.2324, found 665.2325.

**(*S*)-((2-(3-(4-Methoxy-3-(methoxymethoxy)phenyl)prop-2-yn-1-yl)-2,3-dihydrobenzofuran-5,6-diyl)bis(oxy))bis(tert-butyldimethylsilane) ((*S*)-23a).** To a solution of (*S*)-**22a** (5.1 g, 7.66 mmol) in dry toluene (100 mL) under argon atmosphere, NaH (60%) (377 mg, 9.42 mmol) was added. The mixture was stirred at 40 °C for 15 min. Then, the mixture was cooled to rt and CuCl (30.3 mg, 0.31 mmol) was added to the solution.The suspension was stirred for at reflux and after this time, the mixture was filtered through Celite®. Then, the mixture was purified by flash column chromatography (hexanes/EtOAc, 16:1) to give (*S*)-**23a** (4.02 g，90%) as a colorless oil. $[\alpha]_D^{20}$ +32.0 (c 1.00, $CH_2Cl_2$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 1.9 Hz, 1H), 7.02 (dd, *J* = 8.4, 1.9 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 6.65 (s, 1H), 6.34 (s, 1H), 5.21 (s, 2H), 4.92 (tt, *J* = 8.8, 7.1 Hz, 1H), 3.87 (s, 3H), 3.51 (s, 3H), 3.29 (dd, *J* = 15.5, 8.8 Hz, 1H), 3.04 (dd, *J* = 15.6, 6.6 Hz, 1H), 2.80 (ddd, *J* = 24.1, 16.6, 6.4 Hz, 2H), 0.98 (s, 9H), 0.97 (s, 9H), 0.20 – 0.15 (m, 12H). $^{13}C$ {$^1H$}NMR (101 MHz, $CDCl_3$) δ 153.4, 149.9, 146.2, 146.1, 140.5, 126.4, 119.6, 117.8, 117.0,

115.8, 111.4, 102.7, 95.5, 83.8, 82.0, 81.3, 56.2, 55.9, 35.0, 26.5, 25.99, 25.96, 18.5, 18.4, -4.06, -4.08, -4.15, -4.2. IR (KBr) $\nu_{max}$ 3053, 2956, 2930, 2898, 2858, 1603, 1509, 1424, 1361, 1259, 1165, 839, 782, 739cm$^{-1}$； HRMS (ESI): calcd for $C_{32}H_{48}NaO_6Si_2$ $[M + Na]^+$ 607.2882, found 607.2881.

**(*R*)-((2-(3-(4-Methoxy-3-(methoxymethoxy)phenyl)prop-2-yn-1-yl)-2,3-dihydrobenzofuran-5, 6-diyl)bis(oxy))bis(tert-butyldimethylsilane) ((*R*)-23b).** Prepared according to the above step. Colorless oil (3.9 g, 87%). $[\alpha]_D^{20}$ -22.0 (c 1.00, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 1.8 Hz, 1H), 7.02 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 6.65 (s, 1H), 6.34 (s, 1H), 5.21 (s, 2H), 4.93 (dt, *J* = 14.1, 7.0 Hz, 1H), 3.86 (s, 3H), 3.51 (s, 3H), 3.29 (dd, *J* = 15.3, 8.9 Hz, 1H), 3.04 (dd, *J* = 15.3, 6.6 Hz, 1H), 2.80 (ddd, *J* = 24.0, 16.6, 6.4 Hz, 2H), 0.98 (s, 9H), 0.97 (s, 9H), 0.21 – 0.14 (m, 12H). $^{13}$C {$^1$H}NMR (101 MHz, $CDCl_3$) δ 153.4, 149.9, 146.2, 146.0, 140.5, 126.4, 119.5, 117.7, 116.9, 115.8, 111.4, 102.7, 95.5, 83.8, 82.0, 81.3, 56.2, 55.8, 35.0, 26.5, 26.0, 25.9, 18.44, 18.36, -4.07, -4.10, -4.16, -4.18. IR (KBr) $\nu_{max}$ 3054, 2956, 2930, 2899, 2858, 1603, 1511, 1424, 1361, 1262, 1165, 840, 783, 739cm$^{-1}$； HRMS (ESI): calcd for $C_{32}H_{48}NaO_6Si_2$ $[M + Na]^+$ 607.2882, found 607.2881.

**(*S*)-2-(3-(4-Methoxy-3-(methoxymethoxy)phenyl)prop-2-yn-1-yl)-2,3-dihydrofuro[2,3-d]oxepin-7(5H)-one ((*S*)-24a).** To a solution of (*S*)-**23a** (1.2 g, 2.1 mmol) in THF (50 mL) was added tetrabutylammonium fluoride (2 M in THF, 2.1 mL,), and the resultant mixture was stirred at 0 °C for 5 min. The reaction was quenched with saturated aqueous $NH_4Cl$ (10 mL), and the resultant mixture was extracted with ethyl acetate (3 × 20 mL). The organic extract was washed with saturated aqueous NaCl (2 × 20 mL), dried over $Na_2SO_4$, filtered and concentrated under reduced pressure. The crude was dissolved in MeCN (20 mL), and Ceric ammonium nitrate (1.0 M in $H_2O$,

4.6 mL) was added dropwise at 0 °C. Ethyl acetate (10 mL) was added to the reaction immediately, and the resultant mixture was extracted with ethyl acetate (3 × 20 mL). The organic extract was washed with saturated aqueous NaCl (2 × 20 mL), dried over $Na_2SO_4$, filtered and concentrated under reduced pressure to give the crude product benzoquinone. The benzoquinone was dissolved in anhydrous $CH_2Cl_2$ at 0 °C, *m*-CPBA (75%) (482 mg, 2.1 mmol) was added to the solution. After the completion of the reaction, the solvent was removed under reduced pressure. the residue was quickly purified through thin pad of silica gel (hexanes/EtOAc, 2:1) to give crude product anhydride as a yellow oil. The crude product is used directly for the next step. The crude product anhydride was added to a solution of $NaBH_4$ (25 mg, 0.66 mmol) in 5 mL of dry THF at 0 °C. After the completion of the reaction, the reaction was treated by slow addition of 1.0 M HCl until all the solid had dissolved. The resulting solution was extracted with ethyl acetate (3 × 10 mL). The combined organic solution was washed with saturated aqueous NaCl (2 × 10 mL), dried over anhydrous $Na_2SO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (hexanes/EtOAc, 8:1) to give (*S*)-**24a** (132 mg, 18% for 4 steps) as a colorless oil. $[\alpha]_D^{20}$ +18.0 (c 1.00, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, *J* = 1.9 Hz, 1H), 7.03 (dd, *J* = 8.4, 1.9 Hz, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 6.45 – 6.38 (m, 1H), 5.73 (s, 1H), 5.21 (s, 2H), 4.81 – 4.71 (m, 1H), 4.55 (d, *J* = 5.8 Hz, 2H), 3.87 (s, 3H), 3.51 (s, 3H), 3.10 (dd, *J* = 16.3, 7.2 Hz, 1H), 2.90 (dd, *J* = 15.7, 4.6 Hz, 1H), 2.79 (qd, *J* = 16.9, 5.7 Hz, 2H). $^{13}$C {$^1$H}NMR (101 MHz, $CDCl_3$) δ 169.0, 166.2, 150.1, 146.1, 140.2, 127.5, 126.3, 119.3, 115.1, 111.5, 95.9, 95.5, 83.2, 81.8, 80.5, 62.6, 56.3, 55.9, 35.2, 25.9. IR (KBr) $\nu_{max}$ 3055, 2987, 2928, 2854, 1691, 1603, 1512, 1422, 1394, 1265, 1183, 896, 740cm$^{-1}$； HRMS (ESI): calcd for $C_{20}H_{21}O_6$ $[M + H]^+$ 357.1333, found 357.1332.

**(*R*)-2-(3-(4-Methoxy-3-(methoxymethoxy)phenyl)prop-2-yn-1-yl)-2,3-dihydrofuro[2,3-d]oxepin-7(5H)-one ((*R*)-24b).** Prepared according to the above steps. Colorless oil (139 mg, 19% for 4 steps). $[\alpha]_D^{20}$ -17.0 (c 1.00, $CH_2Cl_2$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 1.9 Hz, 1H), 7.01 (dd, *J* = 8.4, 1.9 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 6.42 – 6.35 (m, 1H), 5.71 (s, 1H), 5.19 (s, 2H), 4.77 – 4.69 (m, 1H), 4.53 (d, *J* = 5.8 Hz, 2H), 3.86 (s, 3H), 3.49 (s, 3H), 3.13 – 3.02 (m, 1H), 2.92 – 2.84 (m, 1H), 2.83 – 2.69 (m, 2H). $^{13}C$ {$^1H$}NMR (101 MHz, $CDCl_3$) δ 168.9, 166.2, 150.1, 146.1, 140.2, 127.5, 126.3, 119.3, 115.1, 111.5, 95.8, 95.4, 83.2, 81.7, 80.4, 62.5, 56.2, 55.9, 35.2, 25.9. IR (KBr) $\nu_{max}$ 3055, 2978, 2927, 2848, 1689, 1618, 1512, 1442, 1394, 1265, 1183, 896, 739$cm^{-1}$； HRMS (ESI): calcd for $C_{20}H_{21}O_6$ $[M + H]^+$ 357.1333, found 357.1334.

**(*S*)-2-(3-(3-Hydroxy-4-methoxyphenyl)prop-2-yn-1-yl)-2,3-dihydrofuro[2,3-d]oxepin-7(5H)-one ((*S*)-25a).** Compound (*S*)-**24a** (66 mg, 0.19 mmol) was dissolved in acetonitrile/$H_2O$ = 5/0.1 (10 mL). $BiCl_3$ (17.5 mg, 0.057 mmol) was added to this solution. The mixture was stirred for 1 h at 50 °C. The reaction was treated by slow addition of 1.0 M HCl and extracted with ethyl acetate (3 × 10 mL), dried over anhydrous $Na_2SO_4$, filtered and concentrated under reduced pressure. The residue was purified by a flash column chromatography (hexanes/EtOAc, 2:1) to give (*S*)-**25a** (53 mg, 91%) in yield as a colorless oil. $[\alpha]_D^{20}$ +29.0 (c 1.00, $CH_2Cl_2$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 6.92 (d, *J* = 1.7 Hz, 1H), 6.92 – 6.88 (m, 1H), 6.76 (d, *J* = 8.3 Hz, 1H), 6.41 (m, 1H), 5.73 (s, 1H), 5.62 (s, 1H), 4.80 – 4.72 (m, 1H), 4.55 (m, 2H), 3.89 (s, 3H), 3.09 (dd, *J* = 15.8, 7.5 Hz, 1H), 2.90 (dd, *J* = 15.4, 6.1 Hz, 1H), 2.79 (qd, *J* = 16.9, 5.7 Hz, 2H). $^{13}C$ {$^1H$}NMR (101 MHz, $CDCl_3$) δ 169.0, 166.2, 147.0, 145.3, 140.3, 127.5, 124.2, 117.6, 115.6, 110.4, 95.9, 83.3, 81.6, 80.5, 62.6, 55.9, 35.2, 25.9. IR (KBr) $\nu_{max}$ 3404, 3055, 2918, 2849, 1688, 1618, 1511, 1442, 1394, 1266, 1183, 895, 845, 738$cm^{-1}$； HRMS (ESI): calcd for $C_{18}H_{17}O_5$ $[M + H]^+$ 313.1071, found 313.1071.

**(*R*)-2-(3-(3-Hydroxy-4-methoxyphenyl)prop-2-yn-1-yl)-2,3-dihydrofuro[2,3-d]oxepin-7(5H)-one ((*R*)-25b).** Prepared according to the above step. Colorless oil (51 mg, 89%). $[\alpha]_D^{20}$ -26.0 (c 1.00, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$) δ 6.92 (d, *J* = 1.9 Hz, 1H), 6.90 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.76 (d, *J* = 8.3 Hz, 1H), 6.43 – 6.38 (m, 1H), 5.73 (s, 1H), 5.62 (s, 1H), 4.83 – 4.72 (m, 1H), 4.61 – 4.51 (m, 2H), 3.89 (s, 3H), 3.09 (dd, *J* = 15.4, 7.5 Hz, 1H), 2.90 (dd, *J* = 15.8, 5.6 Hz, 1H), 2.78 (qd, *J* = 16.9, 5.7 Hz, 2H). $^{13}$C {$^1$H}NMR (101 MHz, $CDCl_3$) δ 169.0, 166.2, 147.0, 145.3, 140.3, 127.5, 124.2, 117.6, 115.6, 110.5, 96.0, 83.3, 81.6, 80.5, 62.6, 55.9, 35.2, 25.9. IR (KBr) $\nu_{max}$ 3375, 3055, 2926, 2849, 1689, 1618, 1512, 1442, 1394, 1266, 1183, 896, 845, 739cm$^{-1}$；HRMS (ESI): calcd for $C_{18}H_{17}O_5$ $[M + H]^+$ 313.1071, found 313.1072.

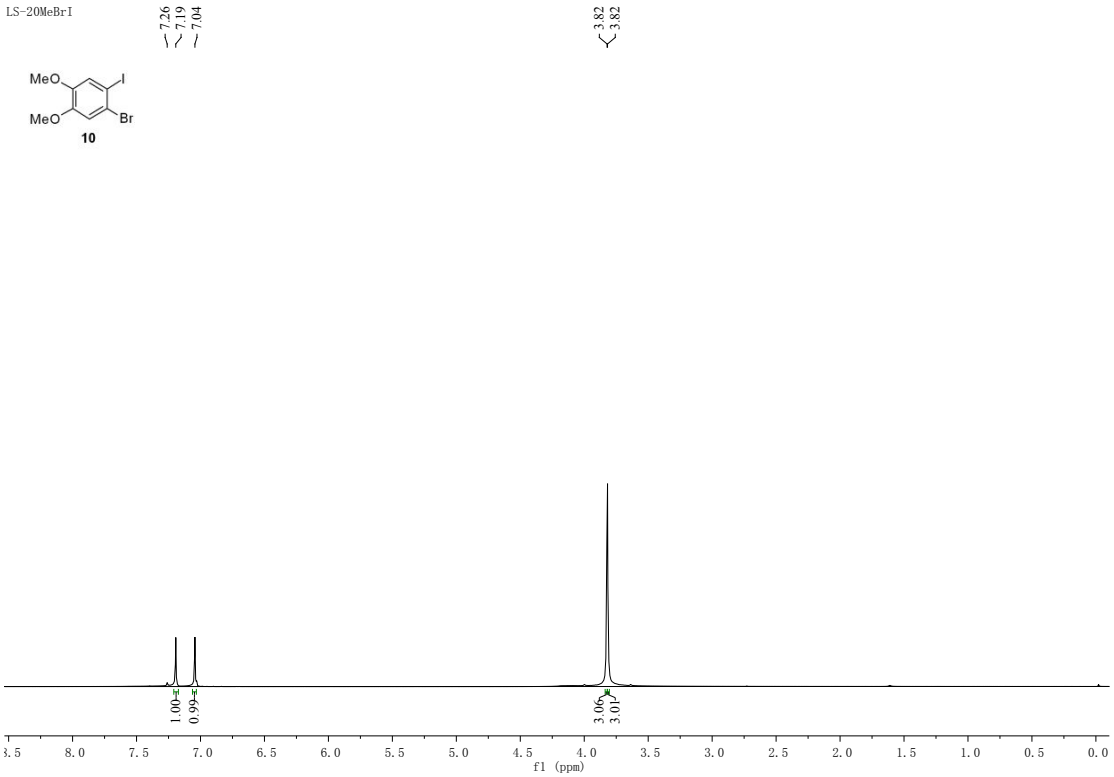
**(*S*, *Z*)-2-(3-(3-Hydroxy-4-methoxyphenyl)allyl)-2,3-dihydrofuro[2,3-d]oxepin-7(5H)-one ((*S*)-3a).** To a solution of (*S*)-**25a** (43 mg, 0.14 mmol) in ethyl acetate (2 mL ) was added quinoline (3.9 μL, 10% in weight) followed by Lindlar's catalyst (8.6 mg, 20% in weight). This solution was stirred under a balloon of hydrogen for 1.5 h. The reaction mixture was filtered through a plug of silica and the solvent removed in vacuo; purification by Silver nitrate silica gel column chromatography yielded (*S*)-**3a** (38 mg, 88%) as a white solid. $[\alpha]_D^{20}$ -13.0 (c 0.45, MeOH); $^1$H NMR (400 MHz, $CDCl_3$) δ 6.85 – 6.0 (m, 2H), 6.73 (dd, *J* = 8.3, 1.9 Hz, 1H), 6.51 (d, *J* = 11.6 Hz, 1H), 6.34 (ddd, *J* = 7.8, 5.7, 2.0 Hz, 1H), 5.68 (s, 1H), 5.54 (dt, *J* = 11.6, 7.2 Hz, 1H), 4.63 (m, 1H), 4.61 – 4.52 (m, 2H), 3.89 (s, 3H), 2.94 (dd, *J* = 15.5, 7.1 Hz, 1H), 2.80 – 2.71 (m, 1H), 2.70 – 2.56 (m, 2H). $^{13}$C {$^1$H}NMR (101 MHz, $CDCl_3$) δ 169.1, 166.2, 145.7, 145.3, 140.5, 132.2, 130.3, 127.4, 123.8, 120.8, 114.7, 110.5, 95.7, 82.6, 62.5, 56.0, 35.6, 33.8. IR (KBr) $\nu_{max}$ 3386, 3054, 2912, 1689, 1615, 1510, 1396, 1274, 1185, 1129, 1026 cm$^{-1}$；HRMS (ESI): calcd for $C_{18}H_{18}NaO_5$ $[M + H]^+$ 337.1046, found 337.1050.

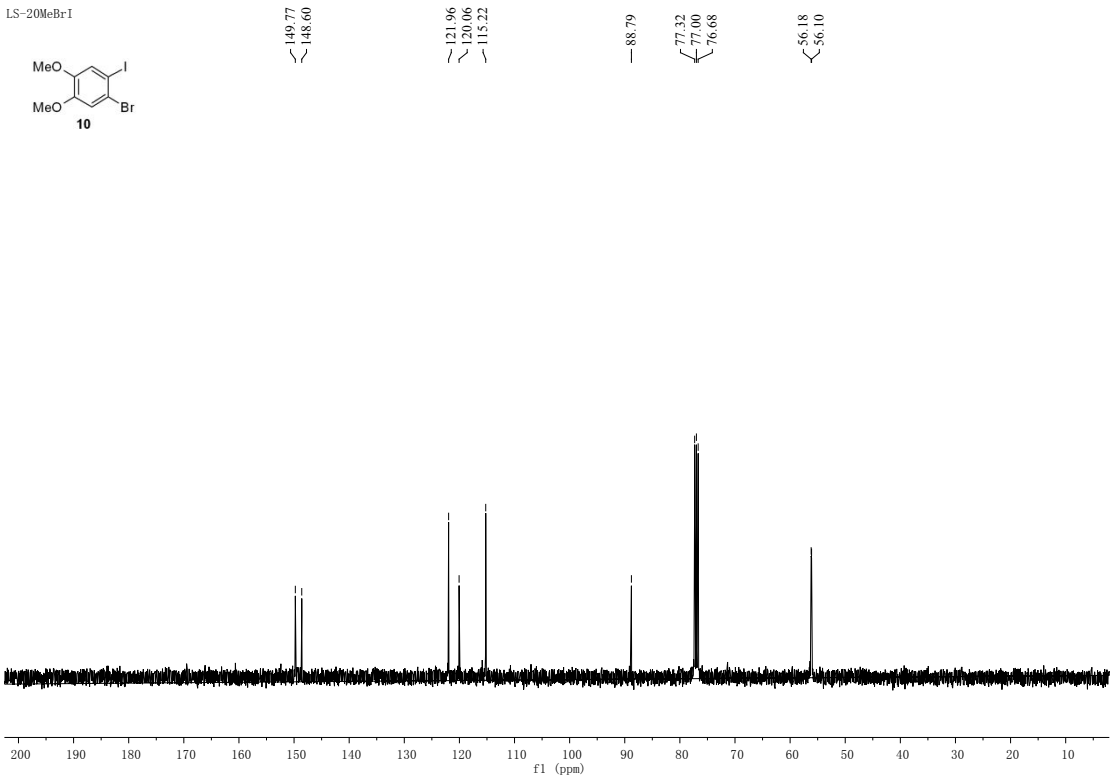
**(*R*, *Z*)-2-(3-(3-Hydroxy-4-methoxyphenyl)allyl)-2,3-dihydrofuro[2,3-d]oxepin-7(5H)-one ((*R*)-3b).** Prepared according to the above step. White solid (39 mg, 90%). $[\alpha]_D^{20}$ +13.8 (c 0.25, MeOH); $^1$H NMR (400 MHz, $CDCl_3$) δ 6.85 – 6.81 (m, 2H), 6.74 (dd, *J* = 8.3, 1.9 Hz, 1H), 6.52 (d, *J* = 11.6 Hz, 1H), 6.37 – 6.32 (m, 1H), 5.69 (s, 1H), 5.55 (dt, *J* = 11.6, 7.2 Hz, 1H), 4.62 (t, *J* = 6.5 Hz, 1H), 4.59 – 4.52 (m, 2H), 3.90 (s, 3H), 2.95 (dd, *J* = 15.4, 7.1 Hz, 1H), 2.80 – 2.71 (m, 1H), 2.71 – 2.57 (m, 2H). $^{13}$C {$^1$H}NMR (101 MHz, $CDCl_3$) δ 169.1, 166.2, 145.7, 145.3, 140.5, 132.2, 130.3, 127.4, 123.8, 120.8, 114.7, 110.5, 95.7, 82.6, 62.5, 56.0, 35.6, 33.8. IR (KBr) $\nu_{max}$ 3392, 2993, 2915, 1683, 1609, 1516, 1396, 1271, 1185, 1026 $cm^{-1}$； HRMS (ESI): calcd for $C_{18}H_{18}NaO_5$ $[M + H]^+$ 337.1046, found 337.1042.

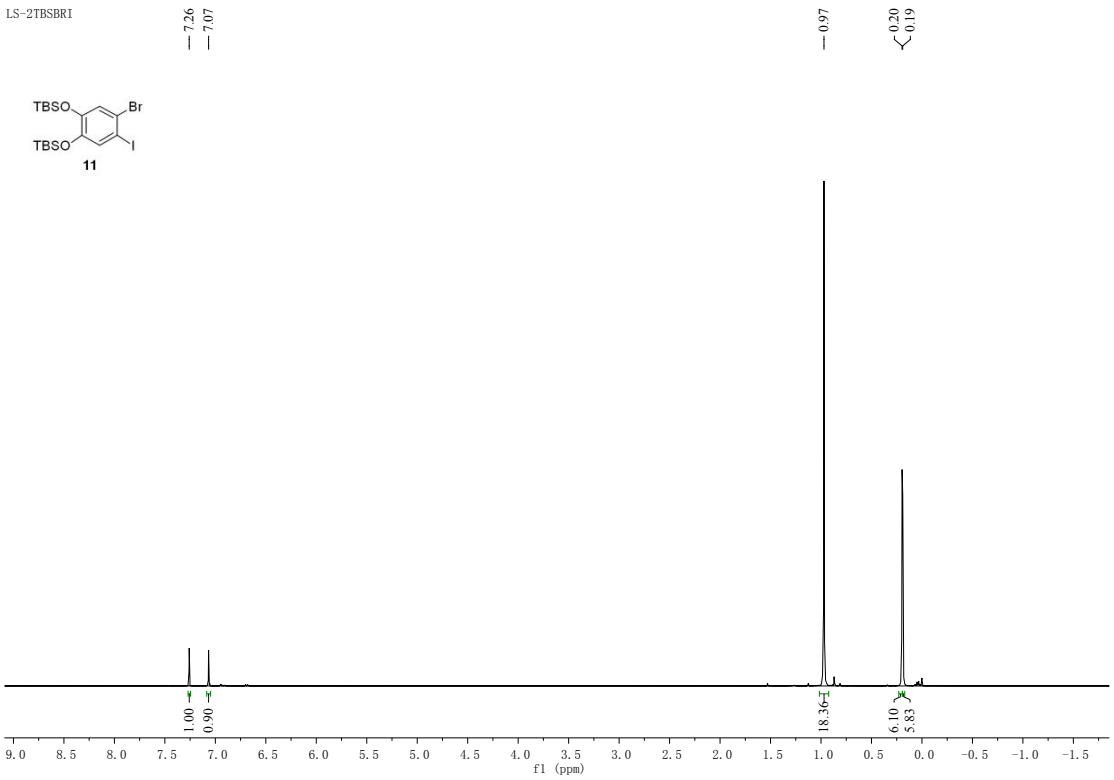
REFERENCES

(1) Pagliai, F.; Pirali, T.; Grosso, E. D.; Brisco, R. D.; Tron, G. C.; Sorba, G.; Genazzani, A. A. Rapid Synthesis of Triazole-Modified Resveratrol Analogues via Click Chemistry. *J. Med. Chem* . **2006**, *49*, 467-470.

# $^{1}H$ and $^{13}C$ NMR spectra of synthetic compounds

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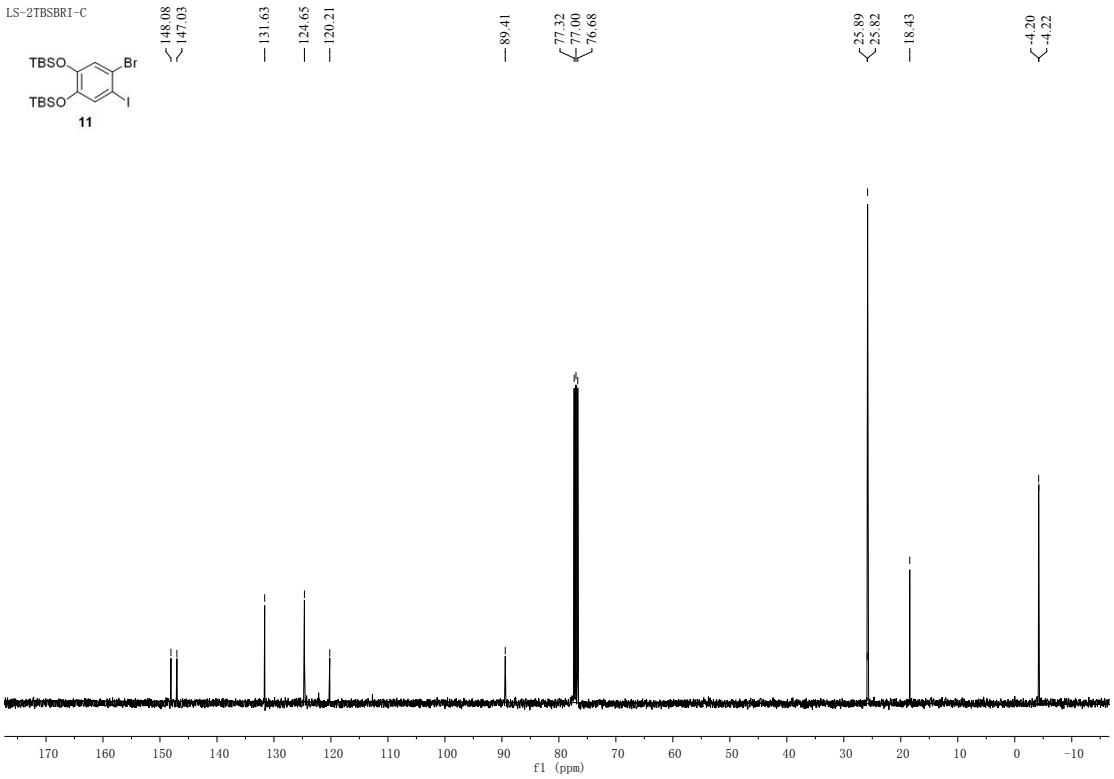
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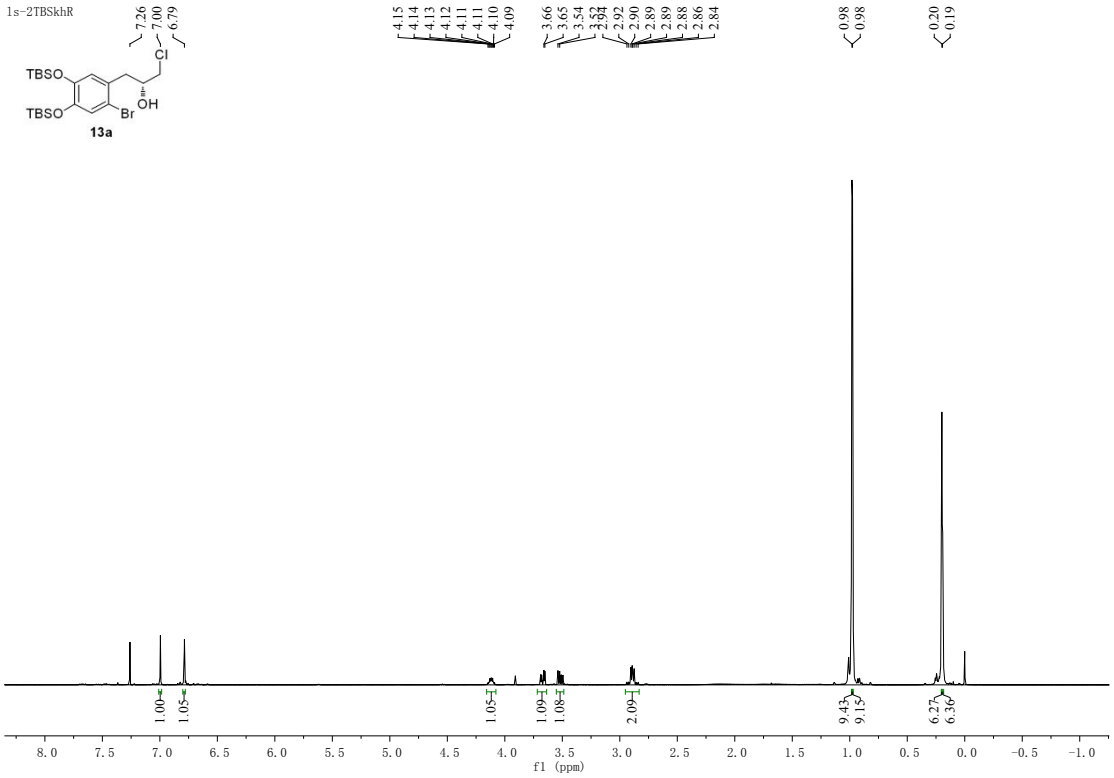
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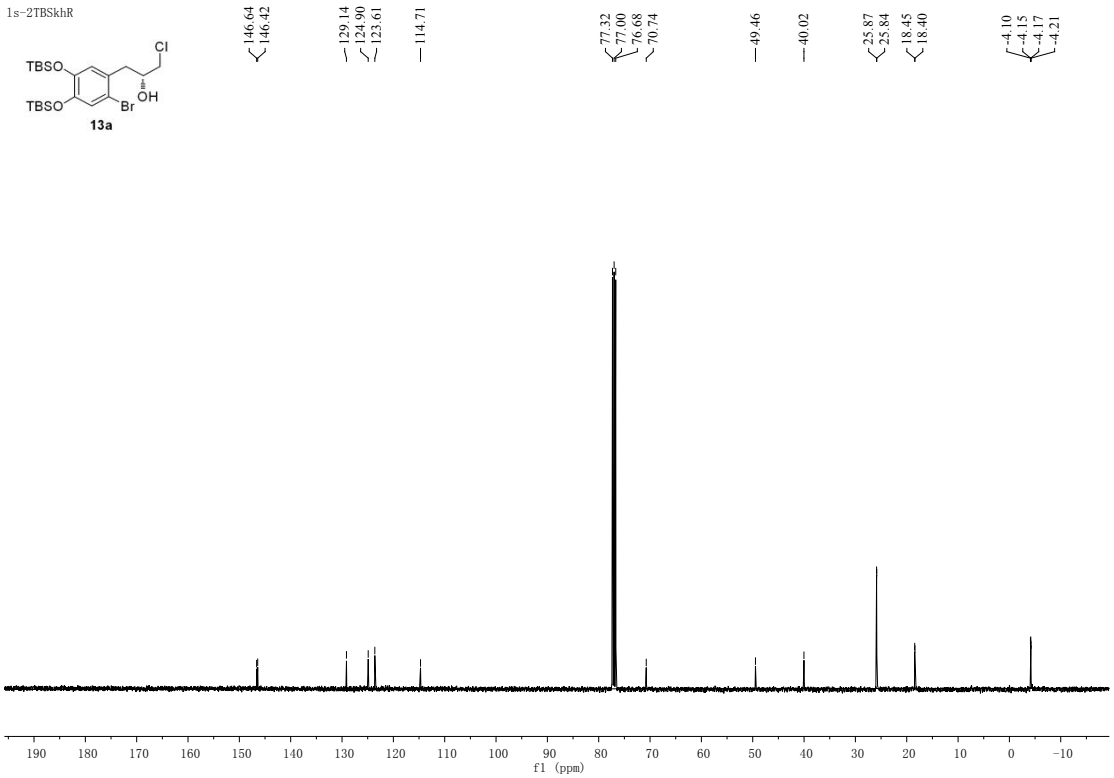
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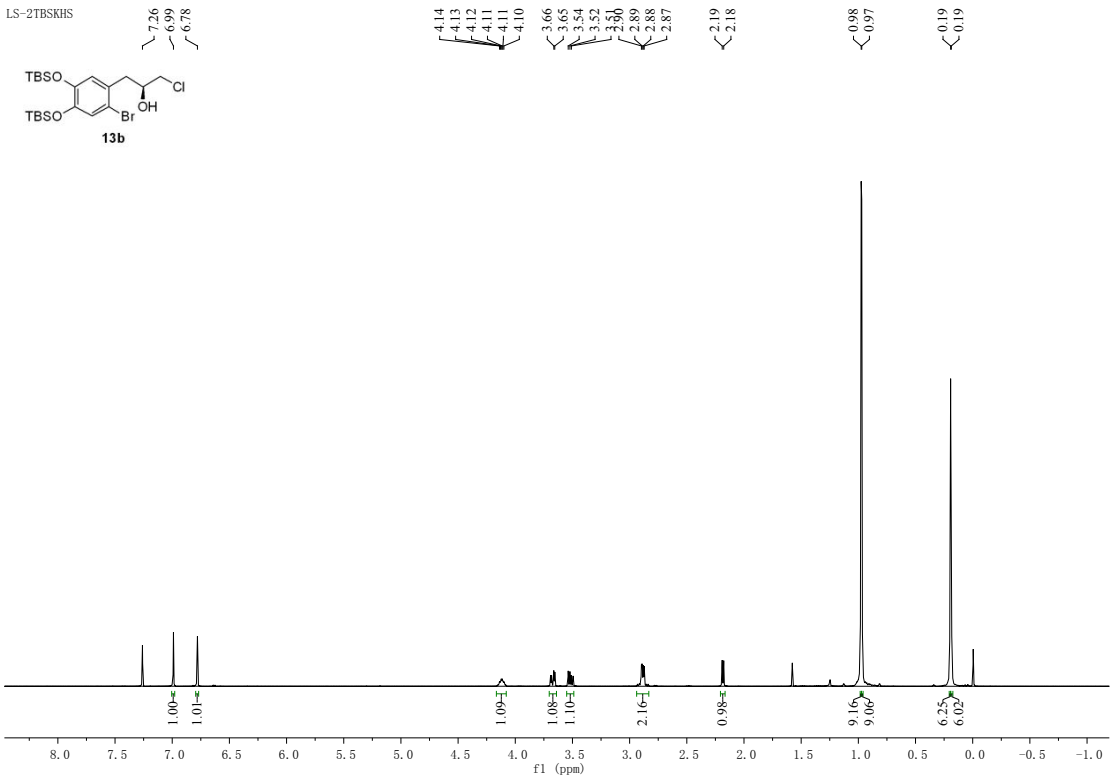
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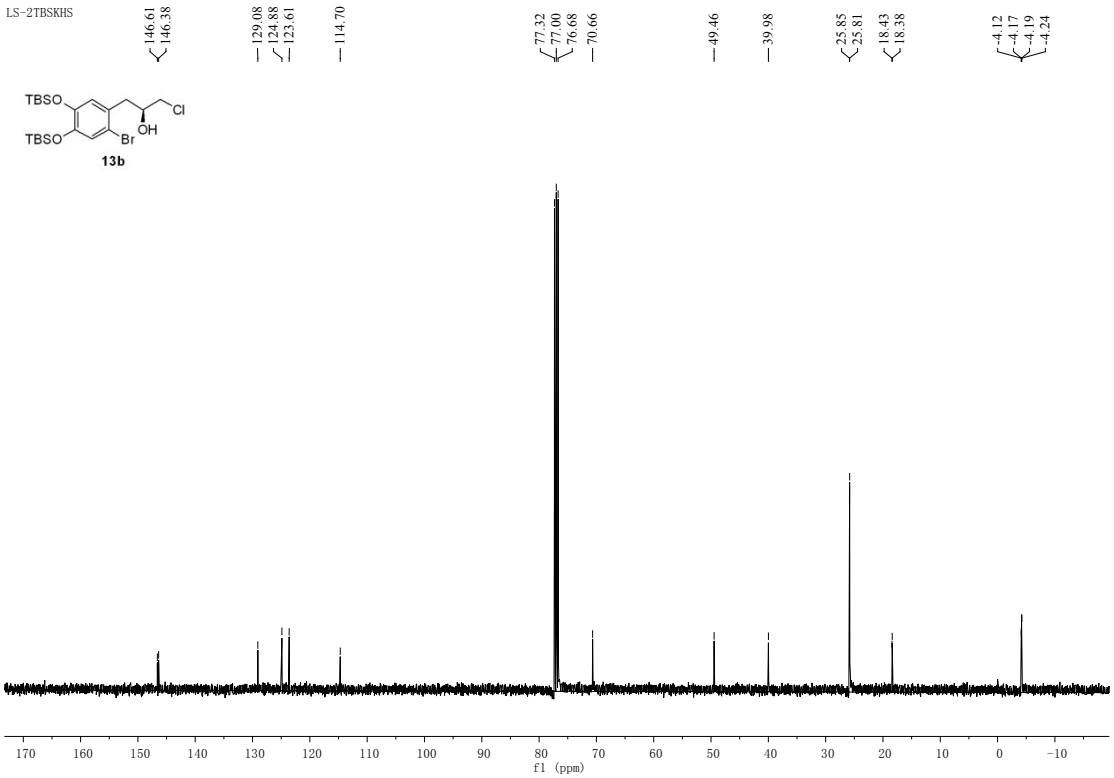
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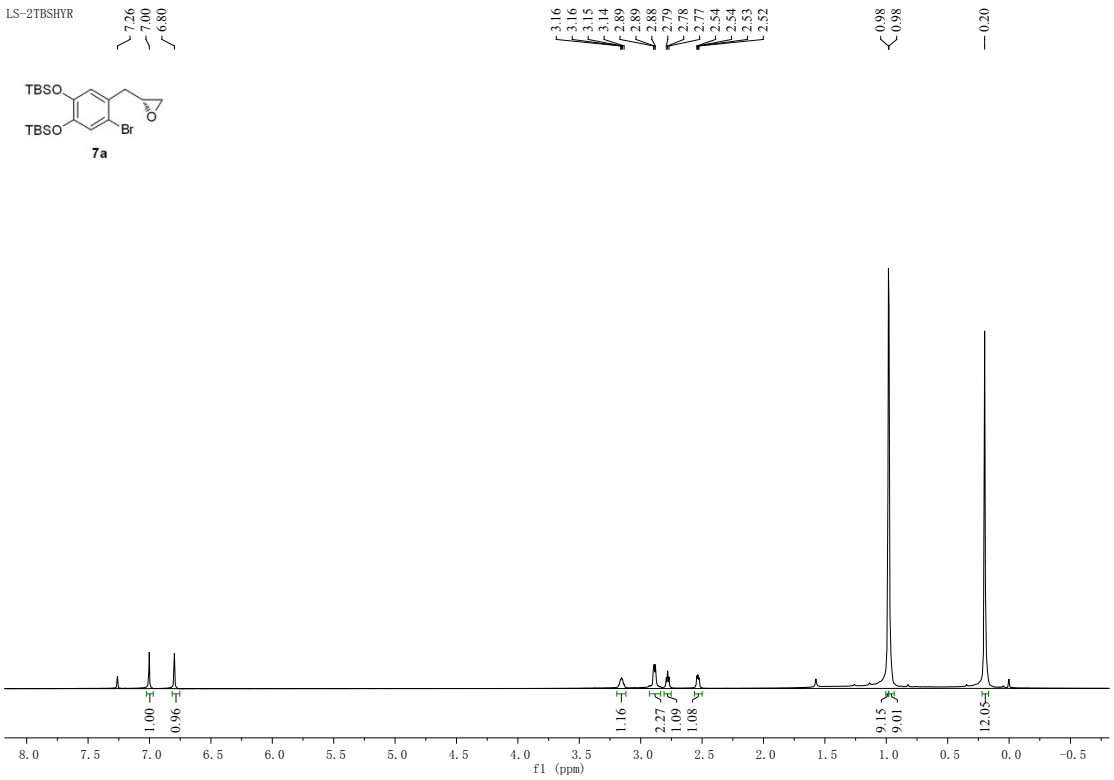
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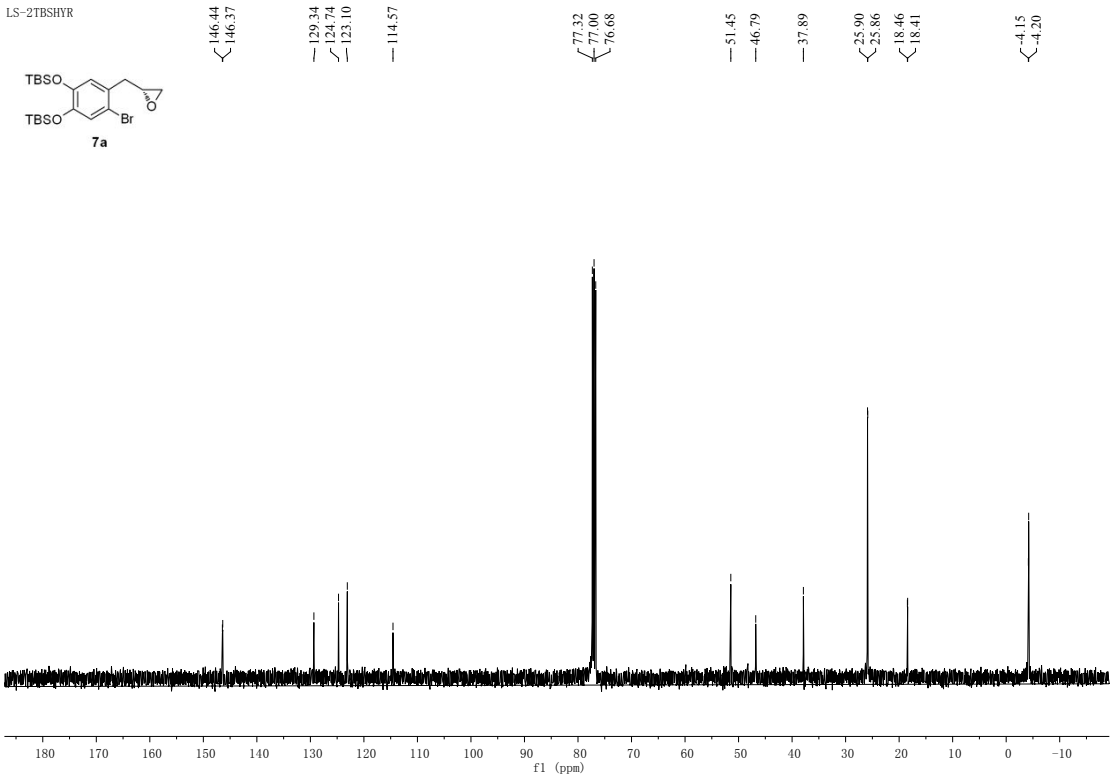
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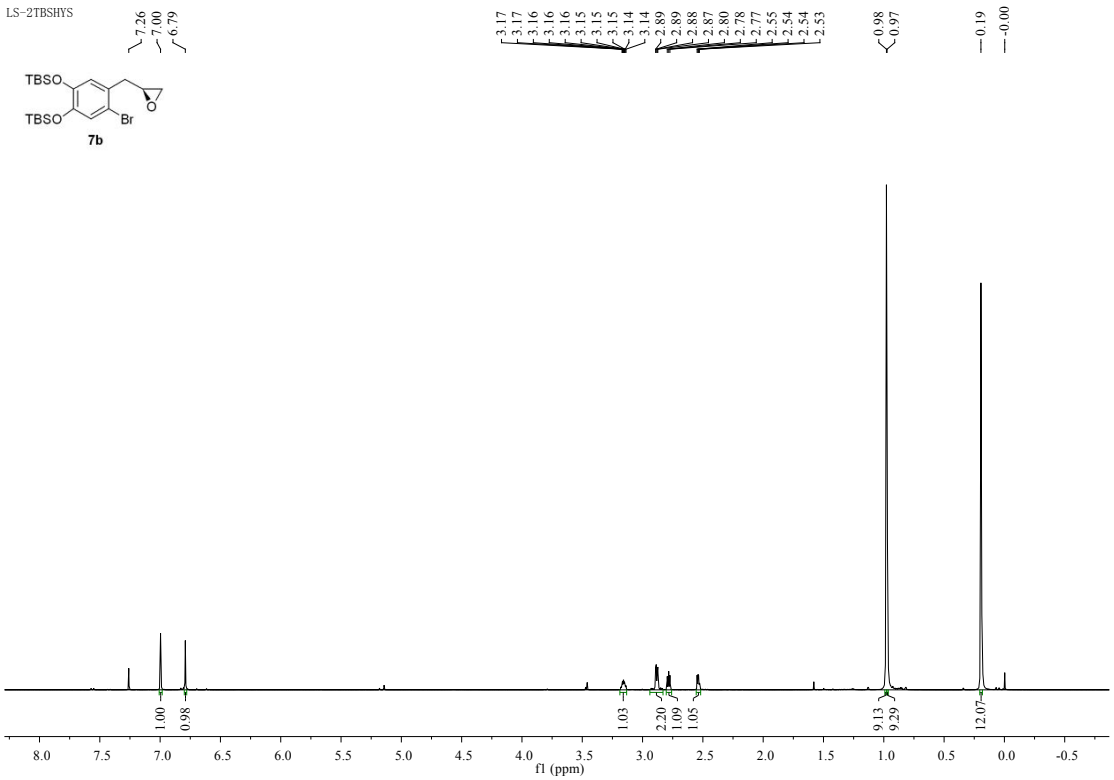
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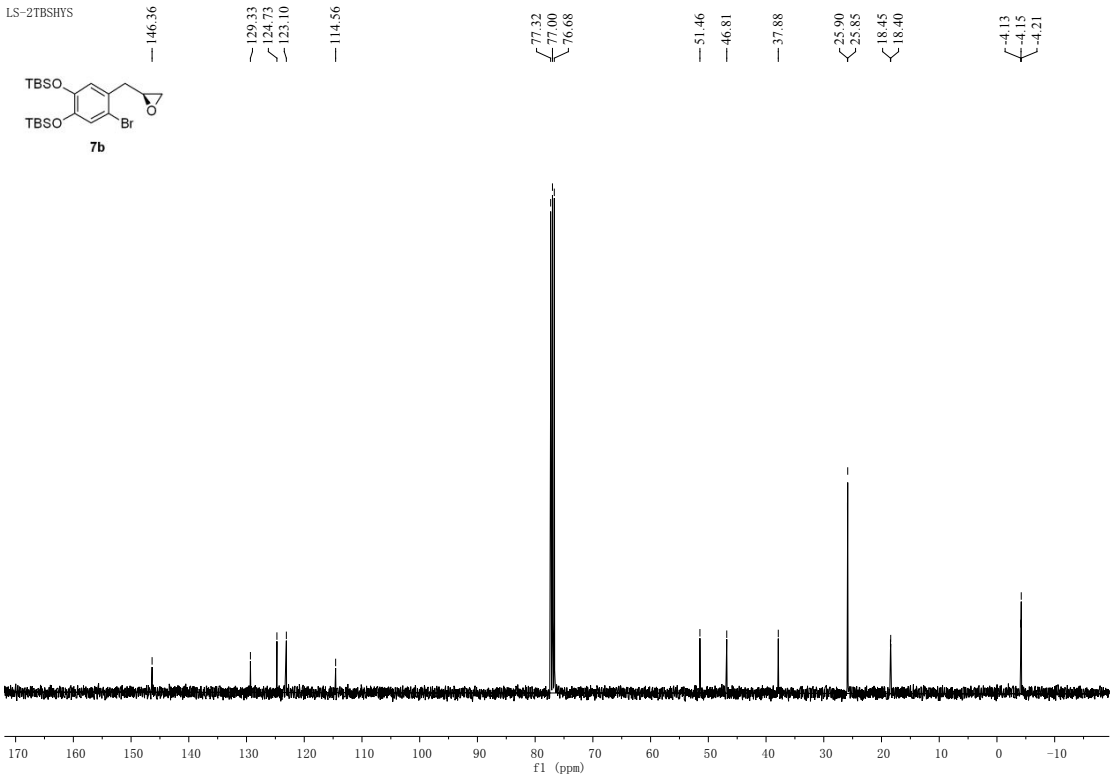
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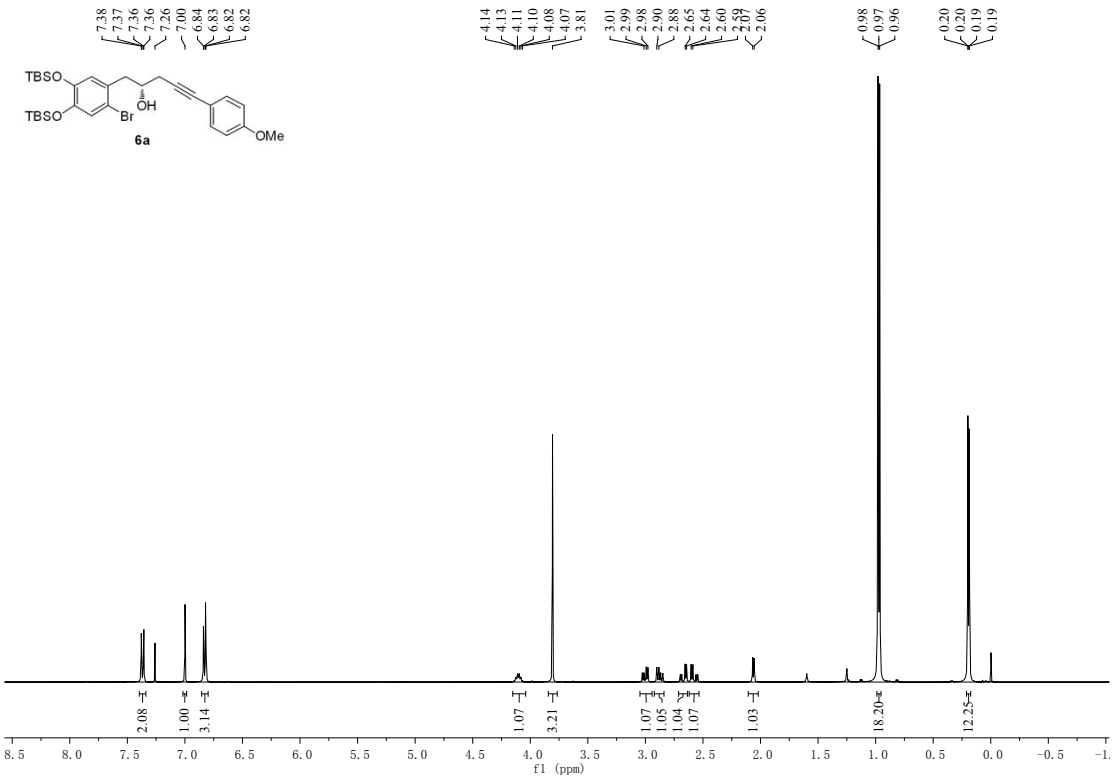
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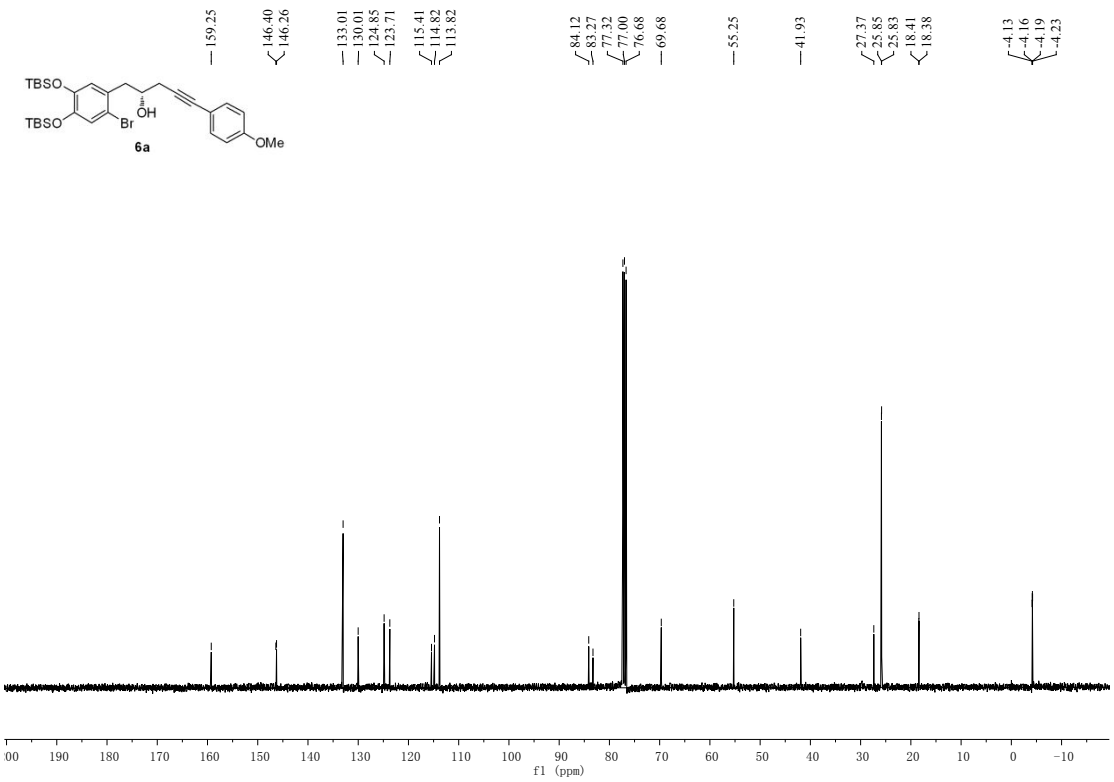
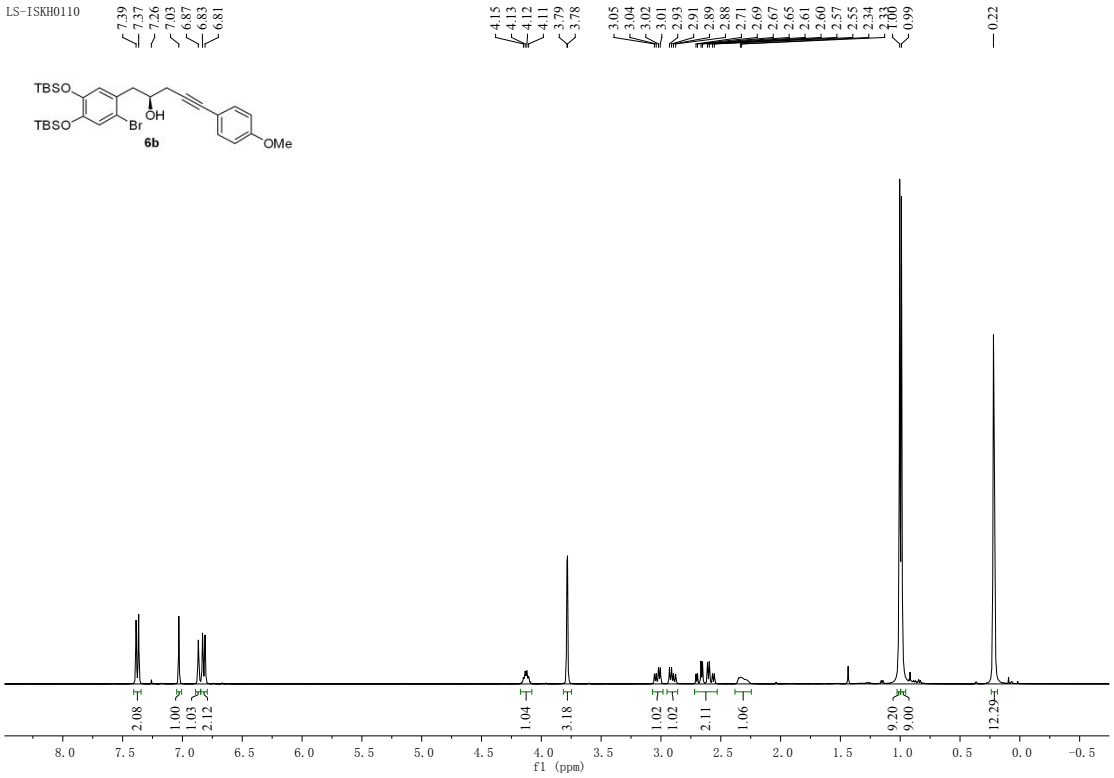
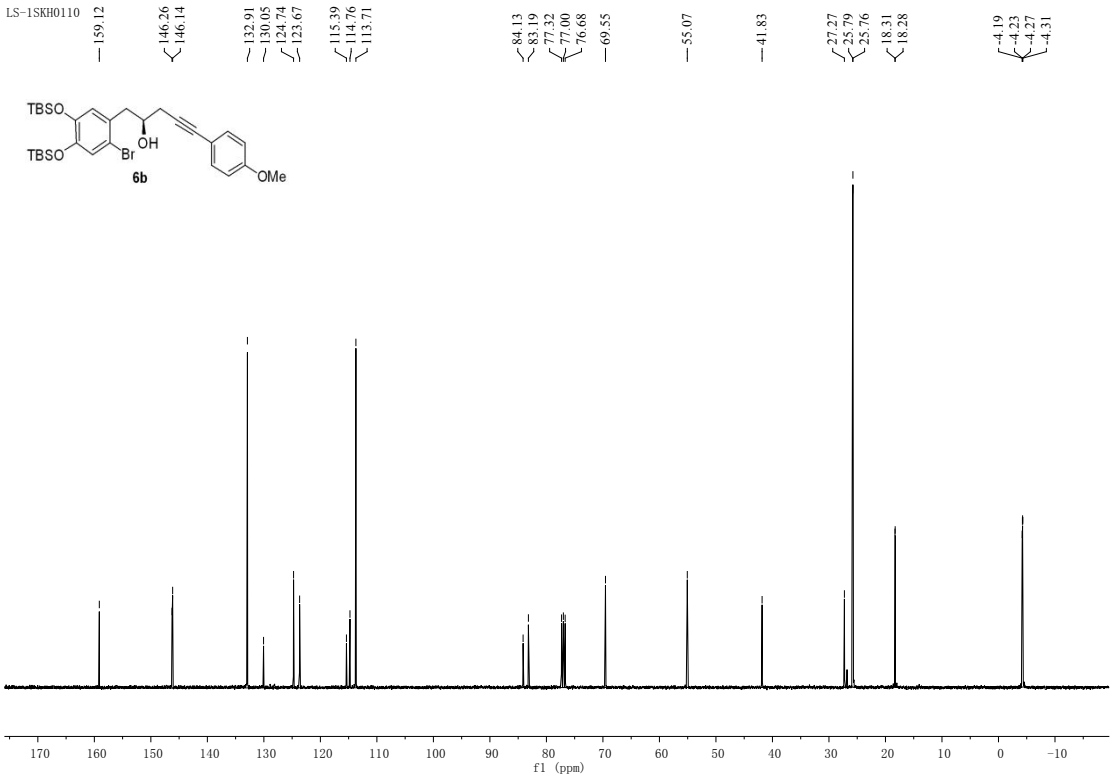
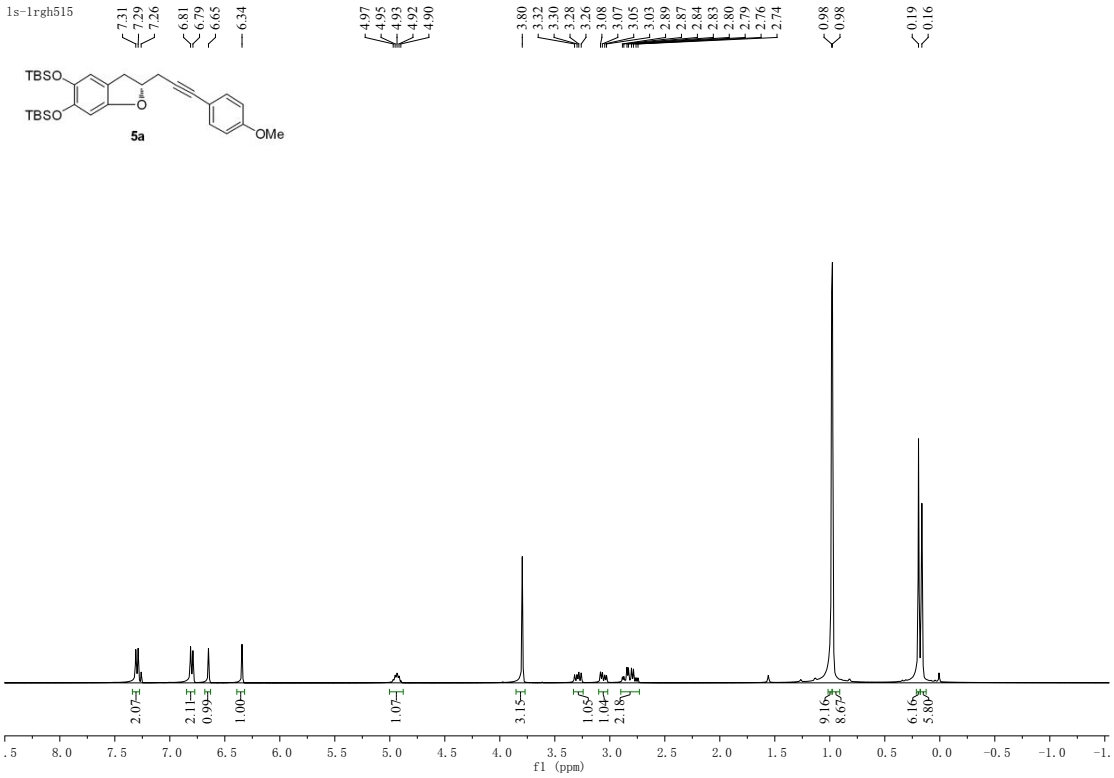
2.07
2.06
0.98
0.97
0.96
0.20
0.20
0.19
0.19
TBSO
TBSO
OH
Br
OMe
6a
2.08
1.00
3.14
1.07
3.21
1.07
1.05
1.04
1.07
1.03
18.20
12.25
f1 (ppm)


159.25
146.40
146.26
133.01
130.01
124.85
123.71
115.41
114.82
113.82
84.12
83.27
77.32
77.00
76.68
69.68
55.25
41.93
27.37
25.85
25.83
18.41
18.38
-4.13
-4.16
-4.19
-4.23
TBSO
TBSO
OH
Br
OMe
6a
f1 (ppm)


LS-1SKH0110
7.39
7.37
7.26
7.03
6.87
6.83
6.81
4.15
4.13
4.12
4.11
3.79
3.78
3.05
3.04
3.02
3.01
2.93
2.91
2.89
2.88
2.71
2.69
2.67
2.65
2.61
2.60
2.57
2.55
2.34
2.33
1.00
0.99
0.22
TBSO
TBSO
Br
OH
OMe
6b
2.08
1.00
1.03
2.12
1.04
3.18
1.02
1.02
2.11
1.06
9.20
9.00
12.29
f1 (ppm)


LS-1SKH0110
159.12
146.26
146.14
132.91
130.05
124.74
123.67
115.39
114.76
113.71
84.13
83.19
77.32
77.00
76.68
69.55
55.07
41.83
27.27
25.79
25.76
18.31
18.28
-4.19
-4.23
-4.27
-4.31
TBSO
TBSO
Br
OH
OMe
6b
f1 (ppm)


ls-lrgh515
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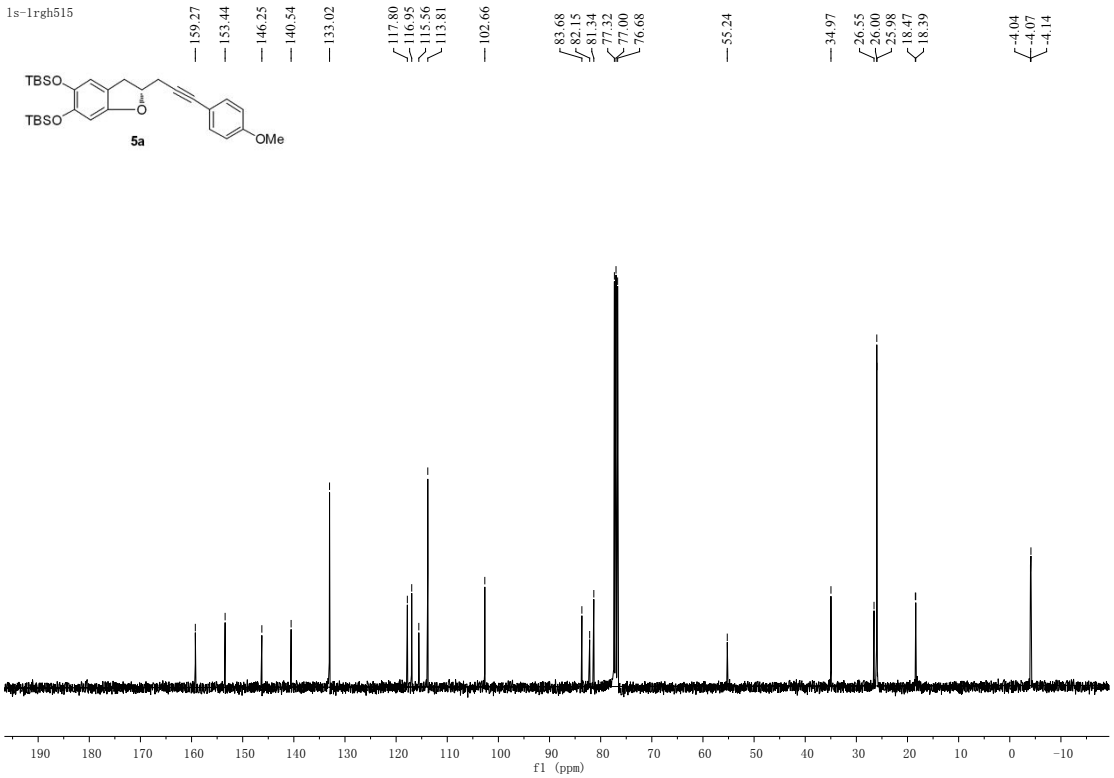
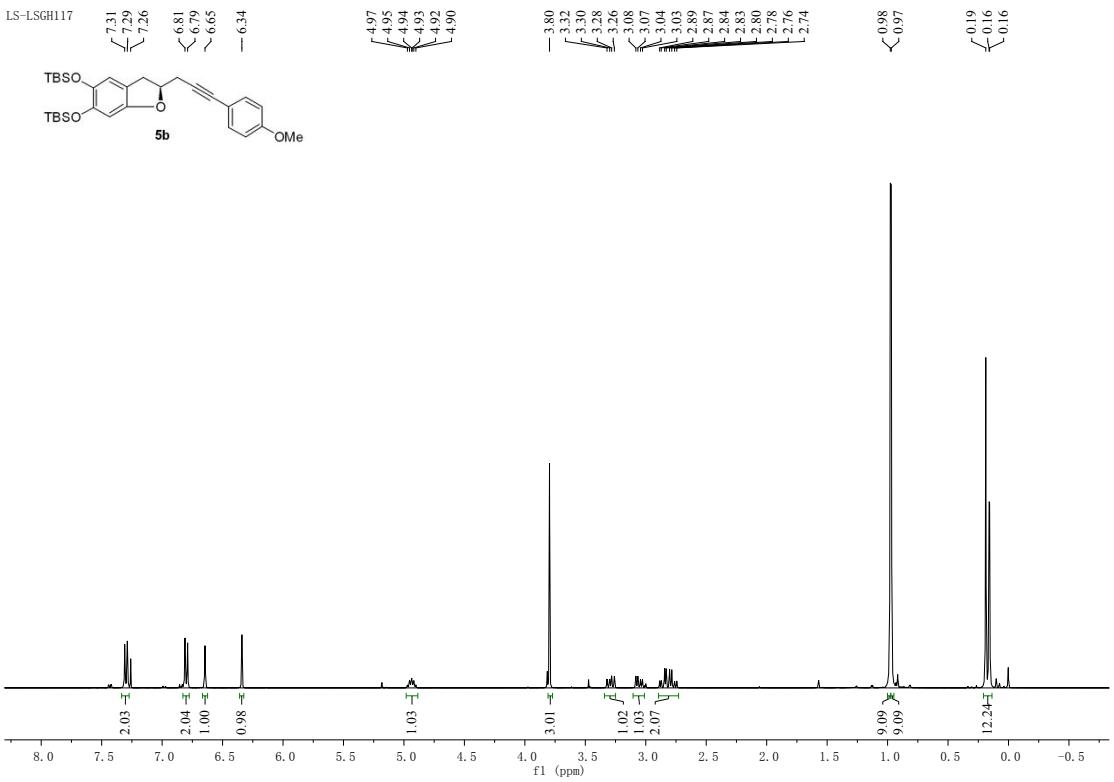
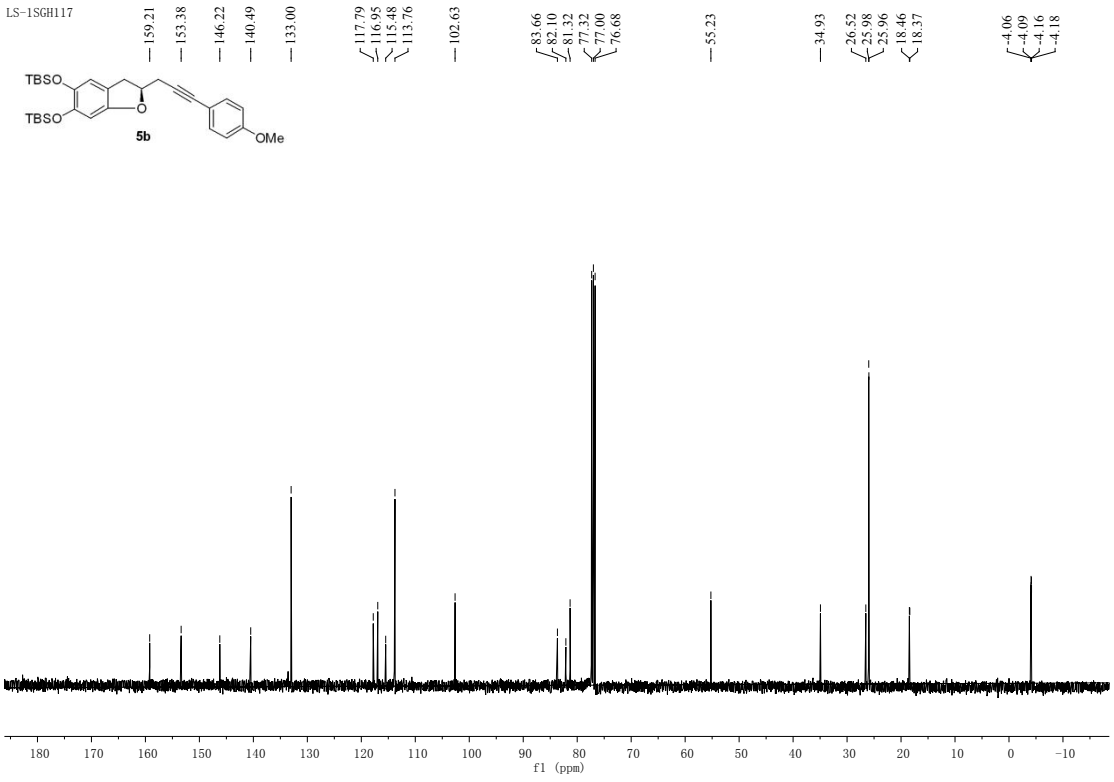
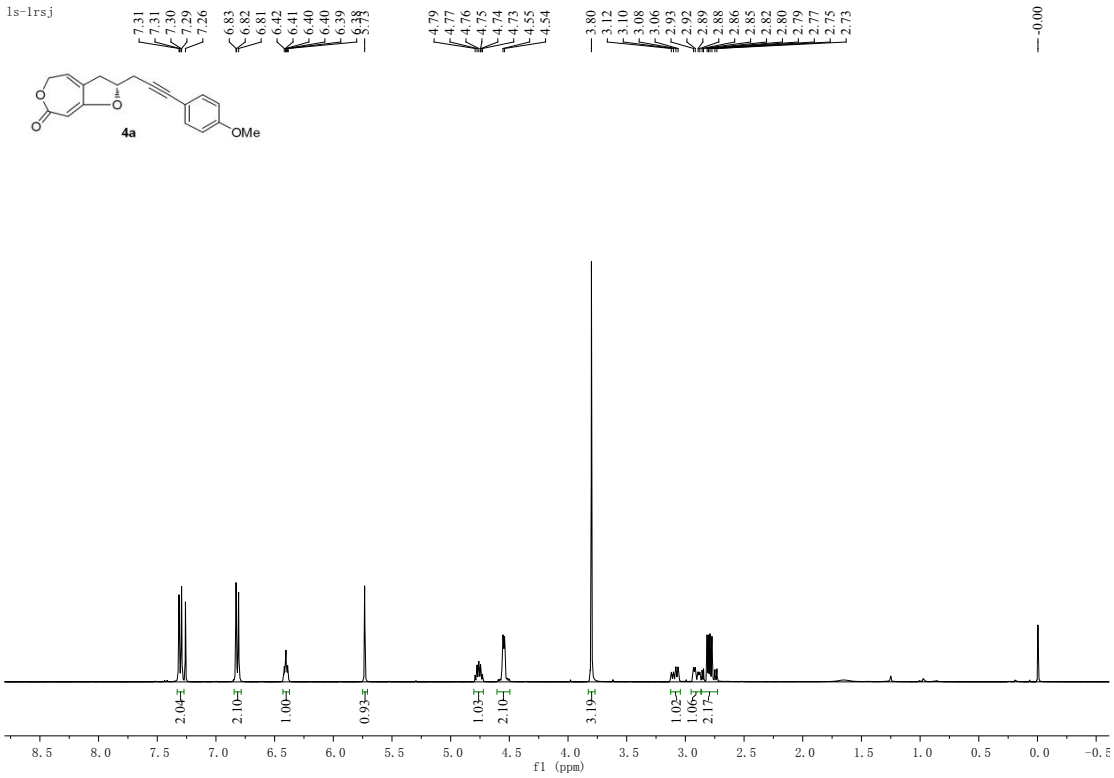
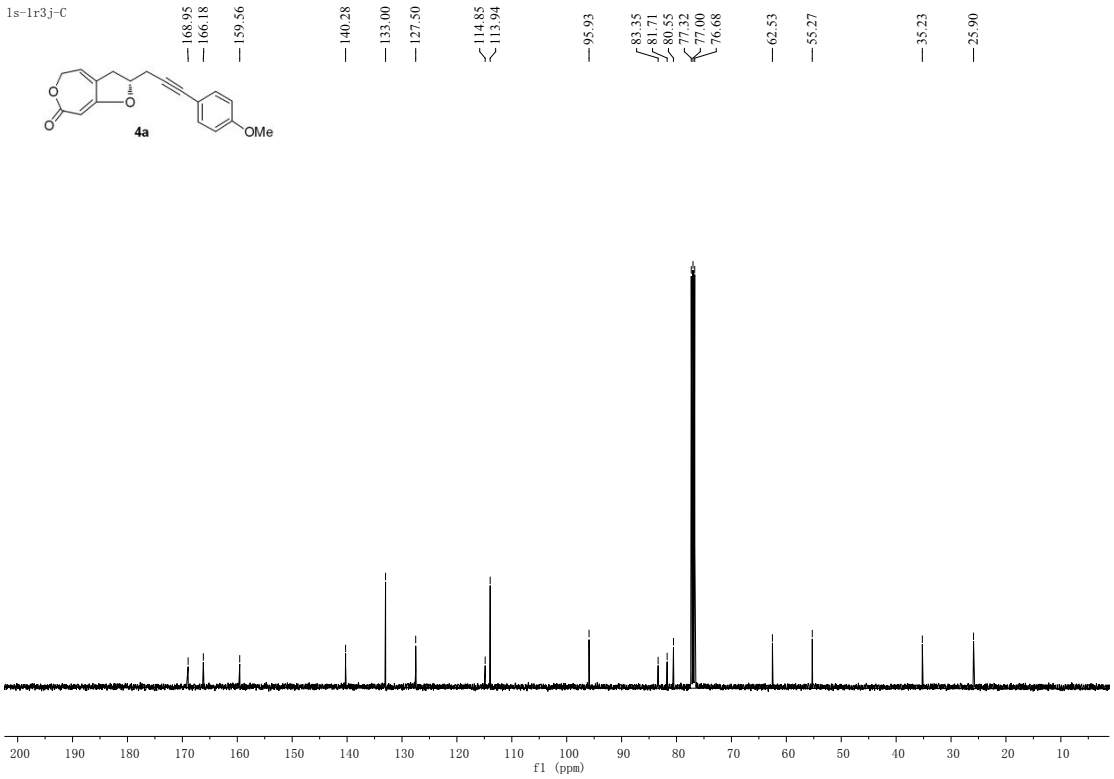
7.29
7.26
6.81
6.79
6.65
6.34
4.97
4.95
4.93
4.92
4.90
3.80
3.32
3.30
3.28
3.26
3.08
3.07
3.05
3.03
2.89
2.87
2.84
2.83
2.80
2.79
2.76
2.74
0.98
0.98
0.19
0.16
TBSO
TBSO
O
OMe
5a
2.07
2.11
0.99
1.00
1.07
3.15
1.05
1.04
2.18
9.16
8.67
6.16
5.80
f1 (ppm)

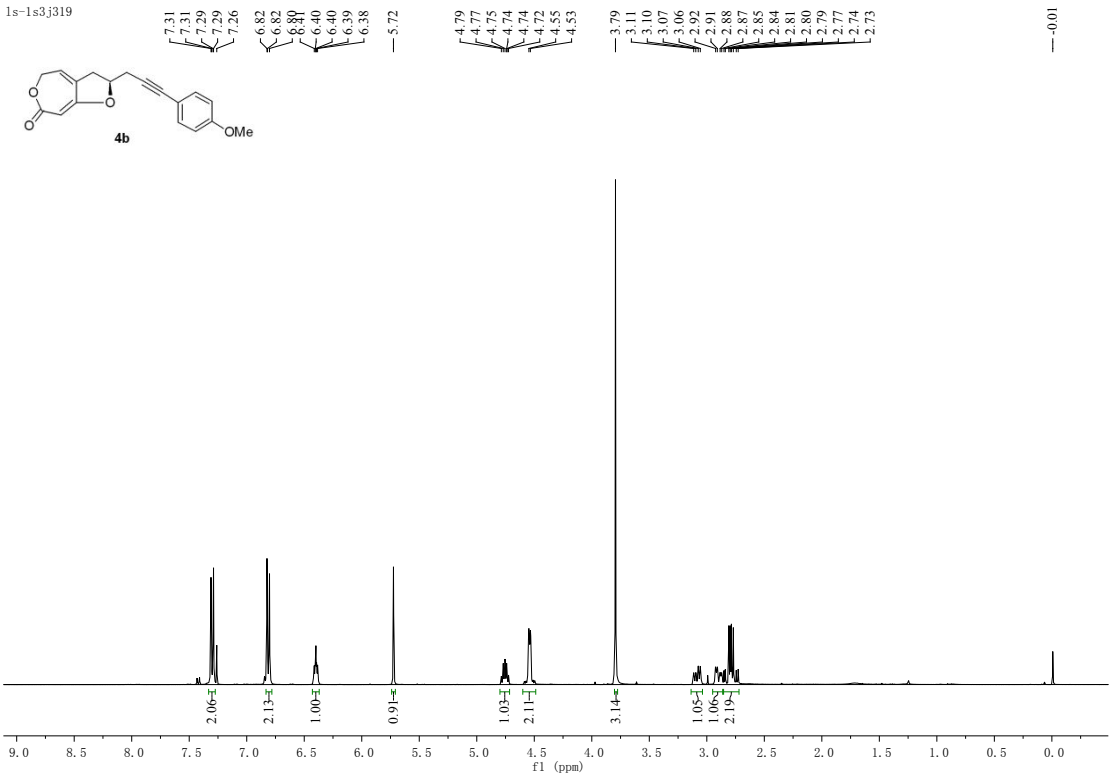

ls-lrgh515
159.27
153.44
146.25
140.54
133.02
117.80
116.95
115.56
113.81
102.66
83.68
82.15
81.34
77.32
77.00
76.68
55.24
34.97
26.55
26.00
25.98
18.47
18.39
-4.04
-4.07
-4.14
TBSO
TBSO
O
OMe
5a
f1 (ppm)

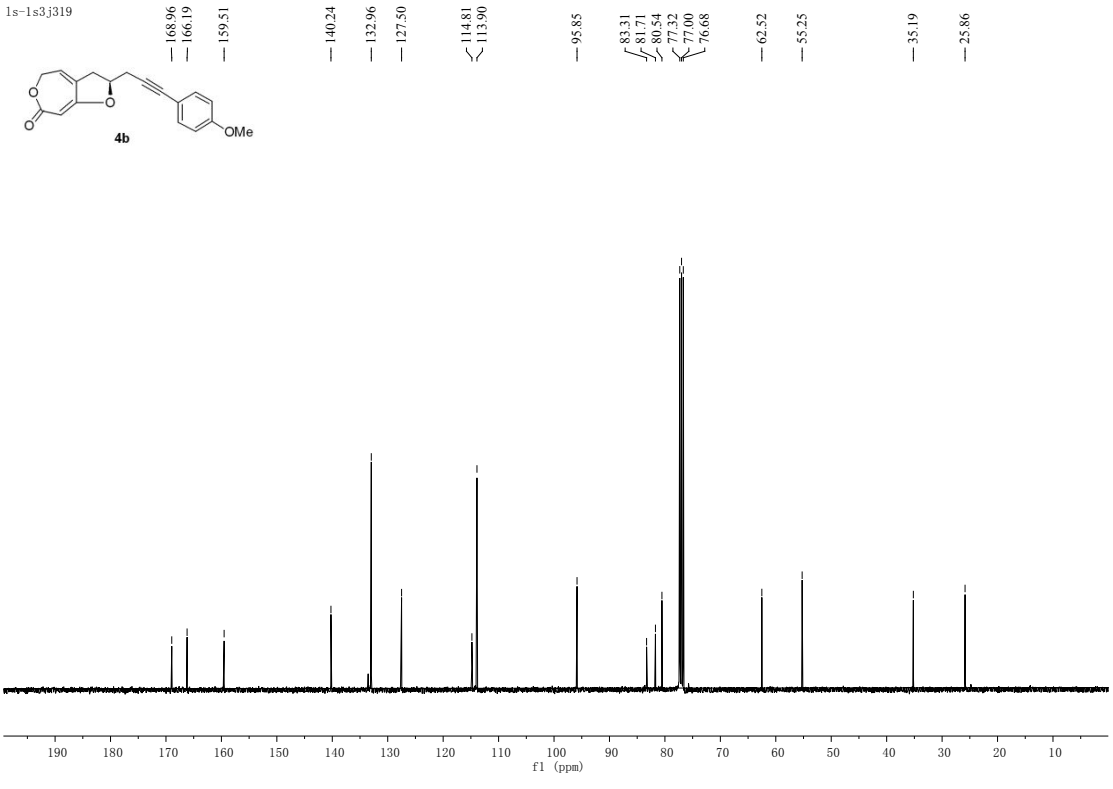

LS-LSGH117
7.31
7.29
7.26
6.81
6.79
6.65
6.34
4.97
4.95
4.94
4.93
4.92
4.90
3.80
3.32
3.30
3.28
3.26
3.08
3.07
3.04
3.03
2.89
2.87
2.84
2.83
2.80
2.78
2.76
2.74
0.98
0.97
0.19
0.16
0.16
TBSO
TBSO
O
OMe
5b
2.03
2.04
1.00
0.98
1.03
3.01
1.02
1.03
2.07
9.09
9.09
12.24
f1 (ppm)

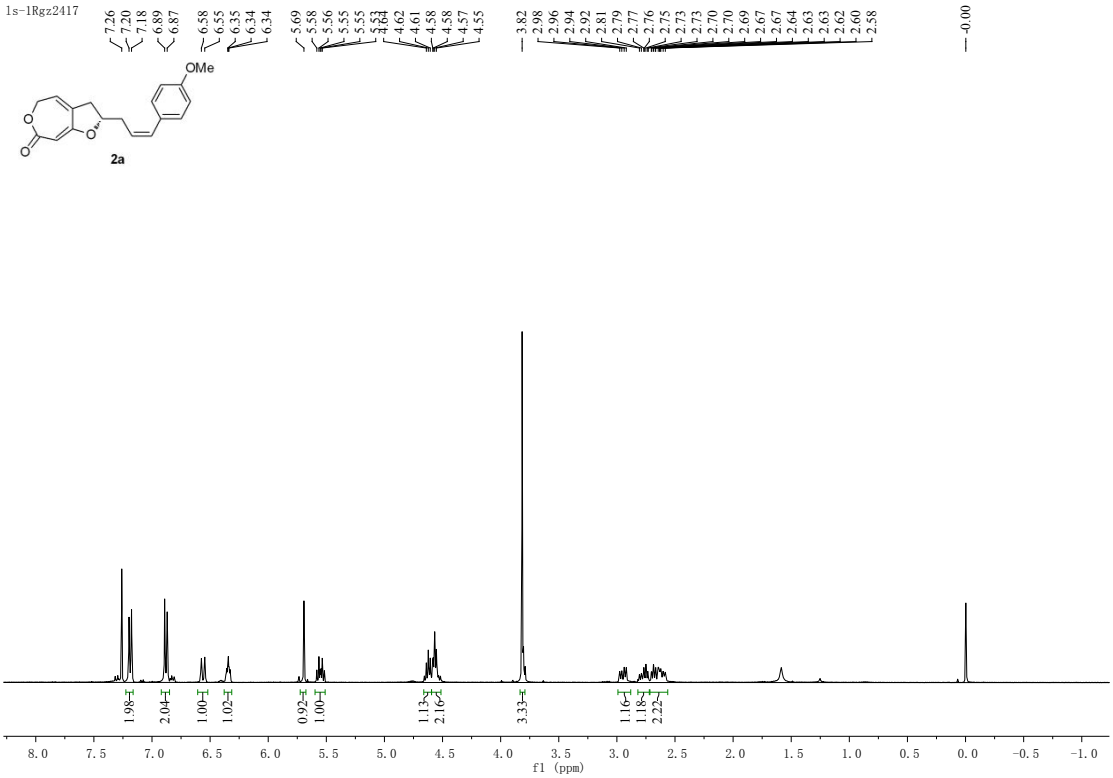

LS-1SGH117
159.21
153.38
146.22
140.49
133.00
117.79
116.95
115.48
113.76
102.63
83.66
82.10
81.32
77.32
77.00
76.68
55.23
34.93
26.52
25.98
25.96
18.46
18.37
-4.06
-4.09
-4.16
-4.18
TBSO
TBSO
O
OMe
5b
f1 (ppm)


1s-1rsj
7.31
7.31
7.30
7.29
7.26
6.83
6.82
6.81
6.42
6.41
6.40
6.40
6.39
4.79
4.77
4.76
4.75
4.74
4.73
4.55
4.54
3.80
3.12
3.10
3.08
3.06
2.93
2.92
2.89
2.88
2.86
2.85
2.82
2.80
2.79
2.77
2.75
2.73
0.00
4a
OMe
2.04
2.10
1.00
0.93
1.03
2.10
3.19
1.02
1.06
2.17
f1 (ppm)


1s-1r3j-C
168.95
166.18
159.56
140.28
133.00
127.50
114.85
113.94
95.93
83.35
81.71
80.55
77.32
77.00
76.68
62.53
55.27
35.23
25.90
4a
OMe
f1 (ppm)


1s-1s3j319
7.31
7.31
7.29
7.29
7.26
6.82
6.82
6.80
6.41
6.40
6.40
6.39
6.38
5.72
4.79
4.77
4.75
4.74
4.74
4.72
4.55
4.53
3.79
3.11
3.10
3.07
3.06
2.92
2.91
2.88
2.87
2.85
2.84
2.81
2.80
2.79
2.77
2.74
2.73
-0.01
O
O
O
OMe
4b
2.06
2.13
1.00
0.91
1.03
2.11
3.14
1.05
1.06
2.19
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


1s-1s3j319
168.96
166.19
159.51
140.24
132.96
127.50
114.81
113.90
95.85
83.31
81.71
80.54
77.32
77.00
76.68
62.52
55.25
35.19
25.86
O
O
O
OMe
4b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


1s-1Rgz2417
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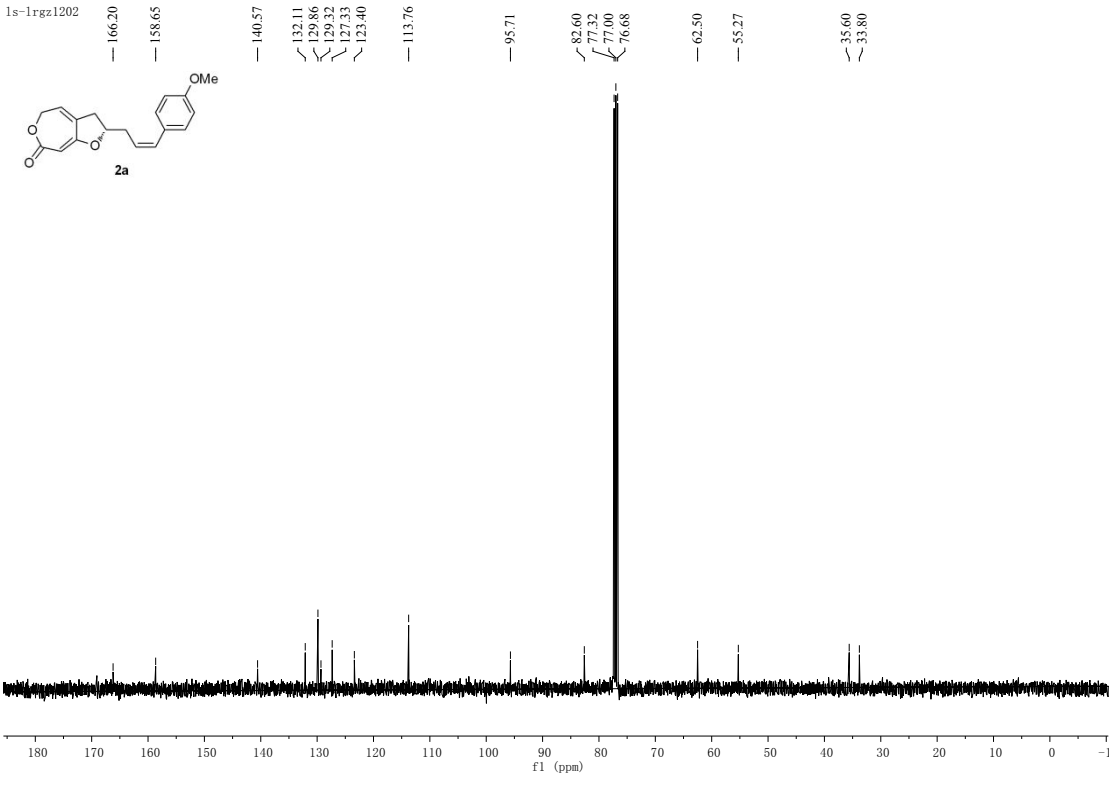
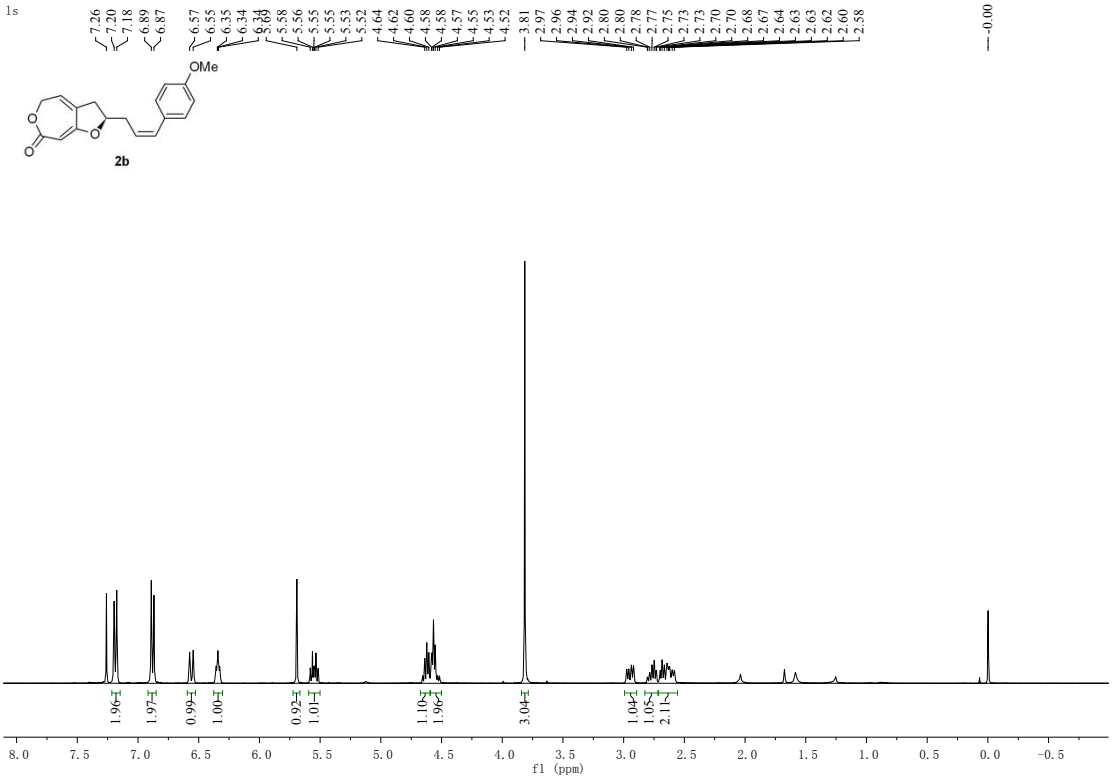
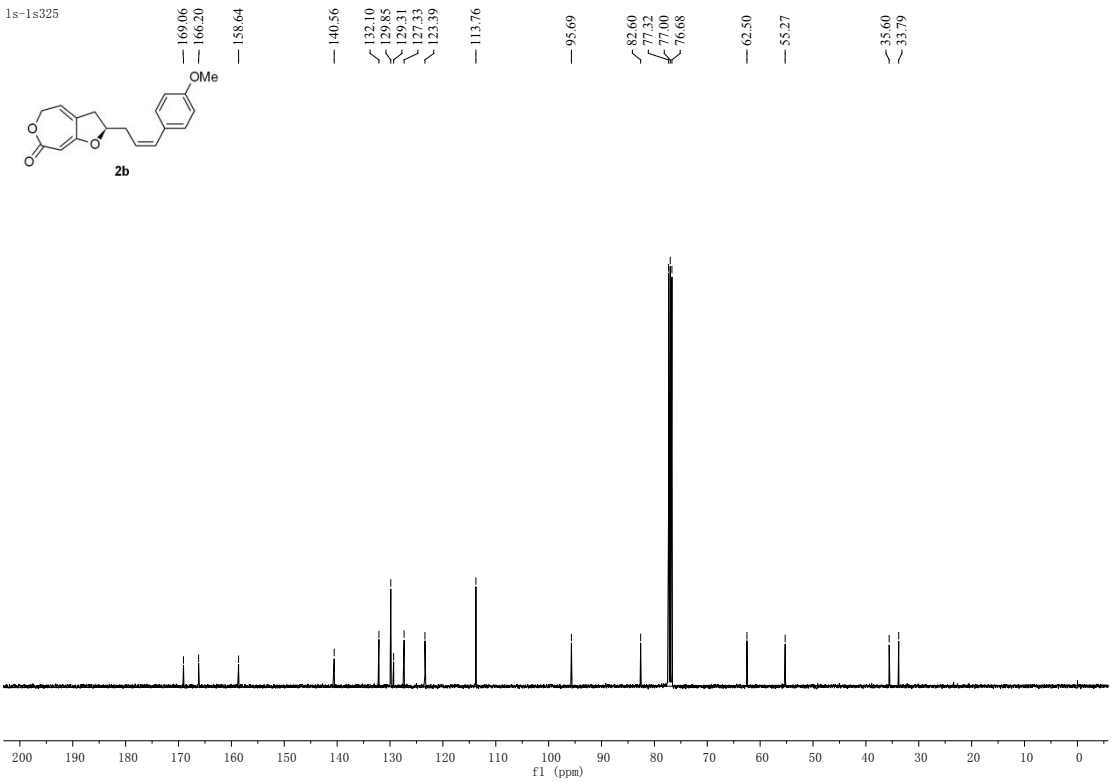
7.20
7.18
6.89
6.87
6.58
6.55
6.35
6.34
6.34
5.69
5.58
5.56
5.55
5.55
5.53
4.64
4.62
4.61
4.58
4.58
4.57
4.55
3.82
2.98
2.96
2.94
2.92
2.81
2.79
2.77
2.76
2.75
2.73
2.73
2.70
2.70
2.69
2.67
2.67
2.64
2.63
2.63
2.62
2.60
2.58
-0.00
OMe
2a
1.98
2.04
1.00
1.02
0.92
1.00
1.13
2.16
3.33
1.16
1.18
2.22
f1 (ppm)


1s-1rgz1202
166.20
158.65
140.57
132.11
129.86
129.32
127.33
123.40
113.76
95.71
82.60
77.32
77.00
76.68
62.50
55.27
35.60
33.80
OMe
2a
f1 (ppm)


1s
7.26
7.20
7.18
6.89
6.87
6.57
6.55
6.35
6.34
5.58
5.56
5.55
5.53
5.52
4.64
4.62
4.60
4.58
4.58
4.57
4.55
4.53
4.52
3.81
2.97
2.96
2.94
2.92
2.80
2.80
2.78
2.77
2.75
2.73
2.73
2.70
2.70
2.68
2.67
2.64
2.63
2.63
2.62
2.60
2.58
-0.00
OMe
2b
1.96
1.97
0.99
1.00
0.92
1.01
1.10
1.96
3.04
1.04
1.05
2.11
f1 (ppm)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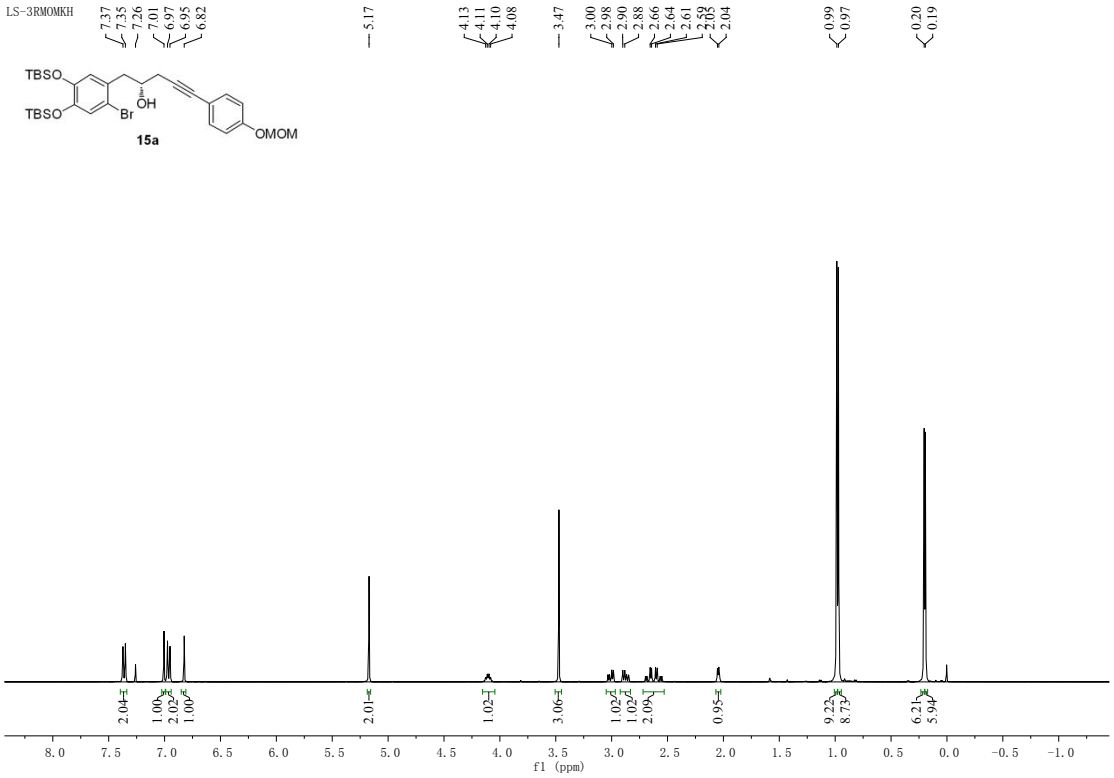
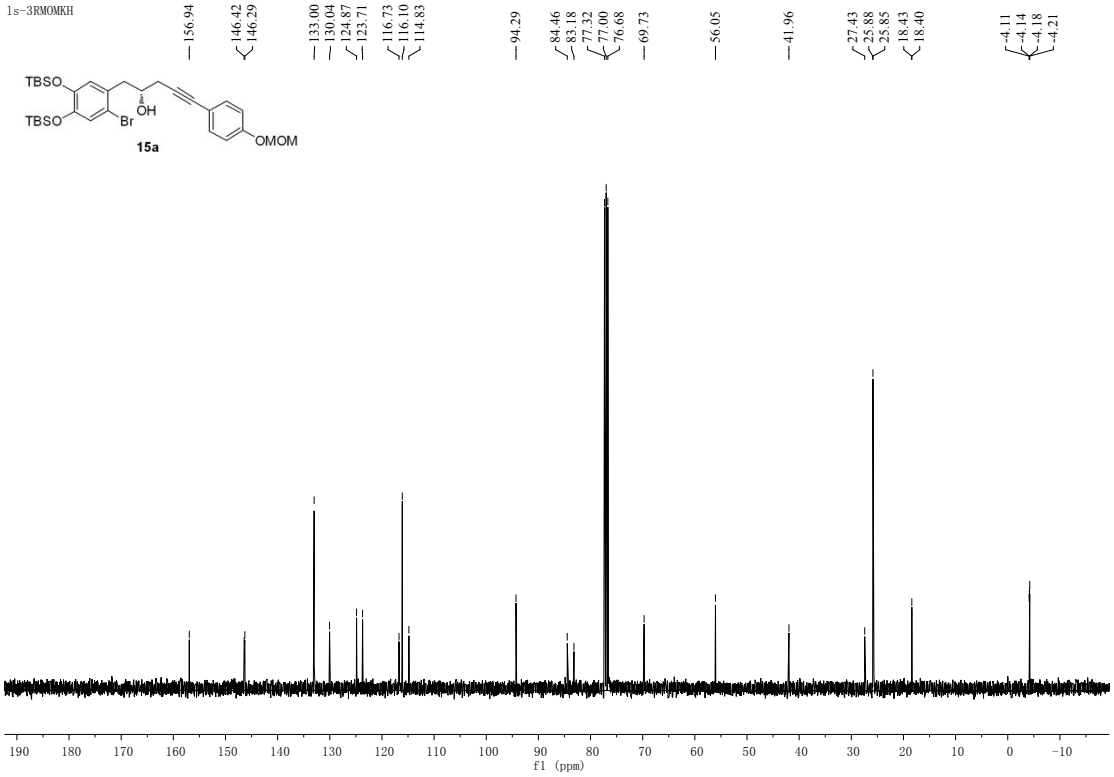
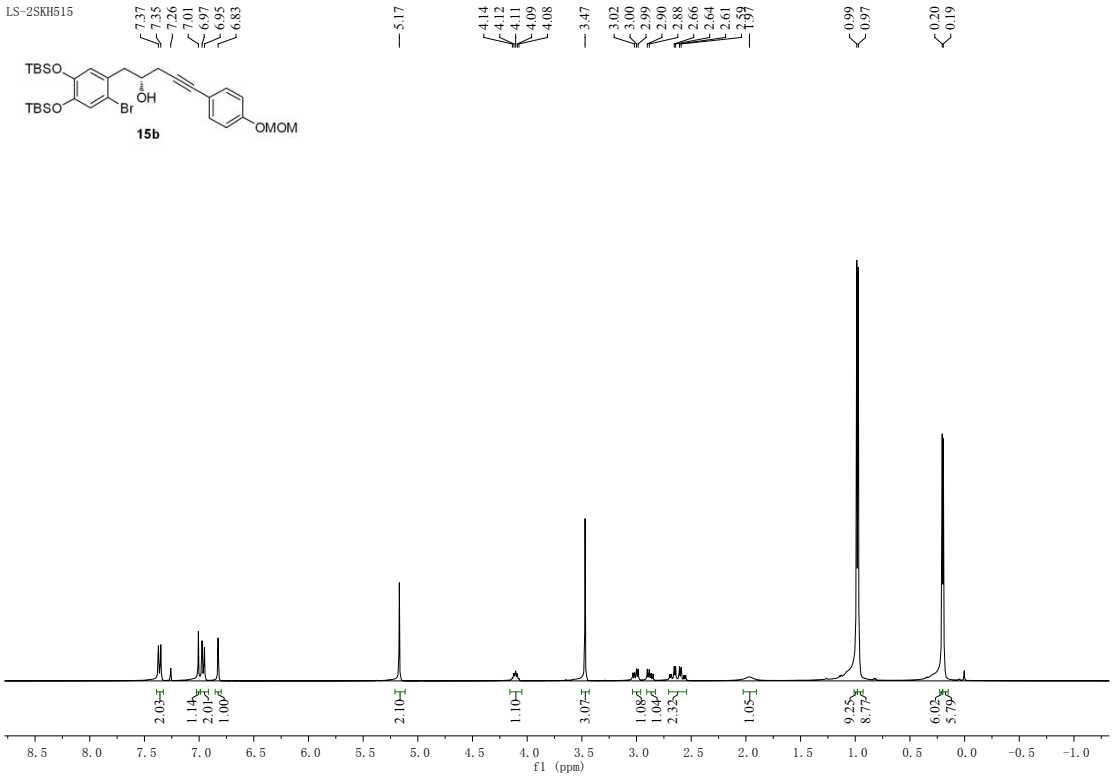
166.20
158.64
140.56
132.10
129.85
129.31
127.33
123.39
113.76
95.69
82.60
77.32
77.00
76.68
62.50
55.27
35.60
33.79
OMe
2b
f1 (ppm)


LS-3RMOMKH
7.37
7.35
7.26
7.01
6.97
6.95
6.82
5.17
4.13
4.11
4.10
4.08
3.47
3.00
2.98
2.90
2.88
2.66
2.64
2.61
2.59
2.05
2.04
0.99
0.97
0.20
0.19
TBSO
TBSO
OH
Br
OMOM
15a
2.04
1.00
2.02
1.00
2.01
1.02
3.06
1.02
1.02
2.09
0.95
9.22
8.73
6.21
5.94
f1 (ppm)


1s-3RMOMKH
156.94
146.42
146.29
133.00
130.04
124.87
123.71
116.73
116.10
114.83
94.29
84.46
83.18
77.32
77.00
76.68
69.73
56.05
41.96
27.43
25.88
25.85
18.43
18.40
-4.11
-4.14
-4.18
-4.21
TBSO
TBSO
OH
Br
OMOM
15a
f1 (ppm)


LS-2SKH515
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7.35
7.26
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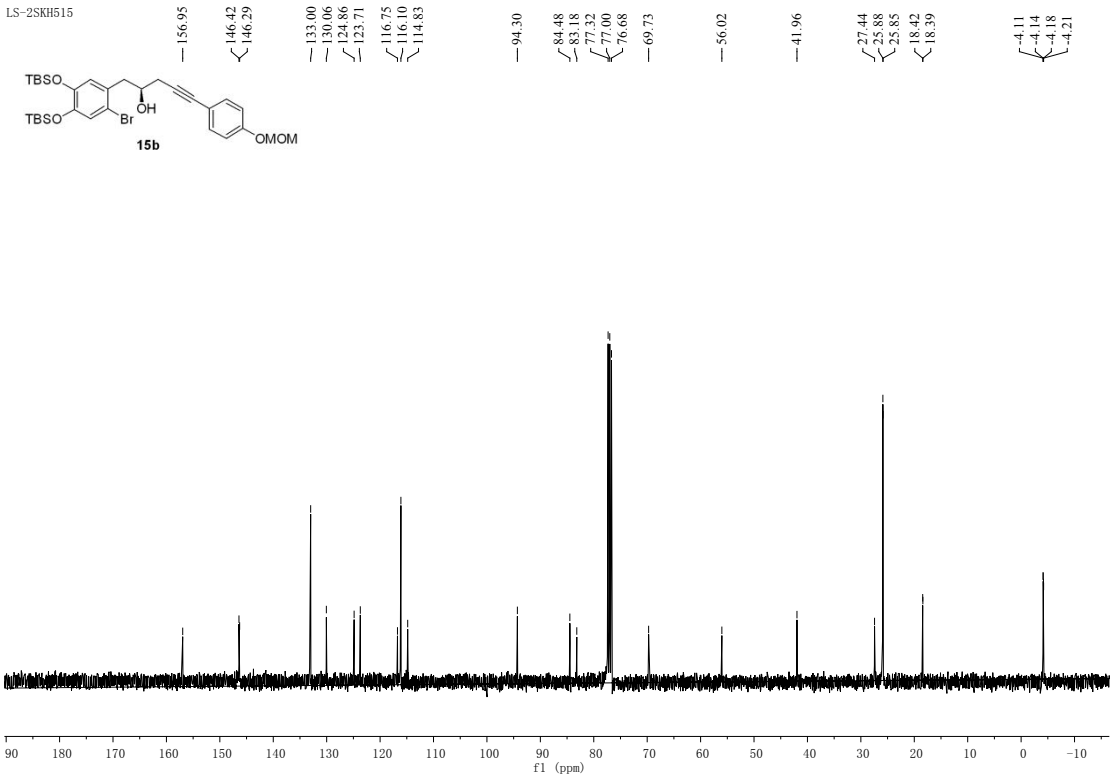
6.97
6.95
6.83
5.17
4.14
4.12
4.11
4.09
4.08
3.47
3.02
3.00
2.99
2.90
2.88
2.66
2.64
2.61
2.59
1.97
0.99
0.97
0.20
0.19
TBSO
TBSO
Br
OH
OMOM
15b
2.03
1.14
2.01
1.00
2.10
1.10
3.07
1.08
1.04
2.32
1.05
9.25
8.77
6.02
5.79
f1 (ppm)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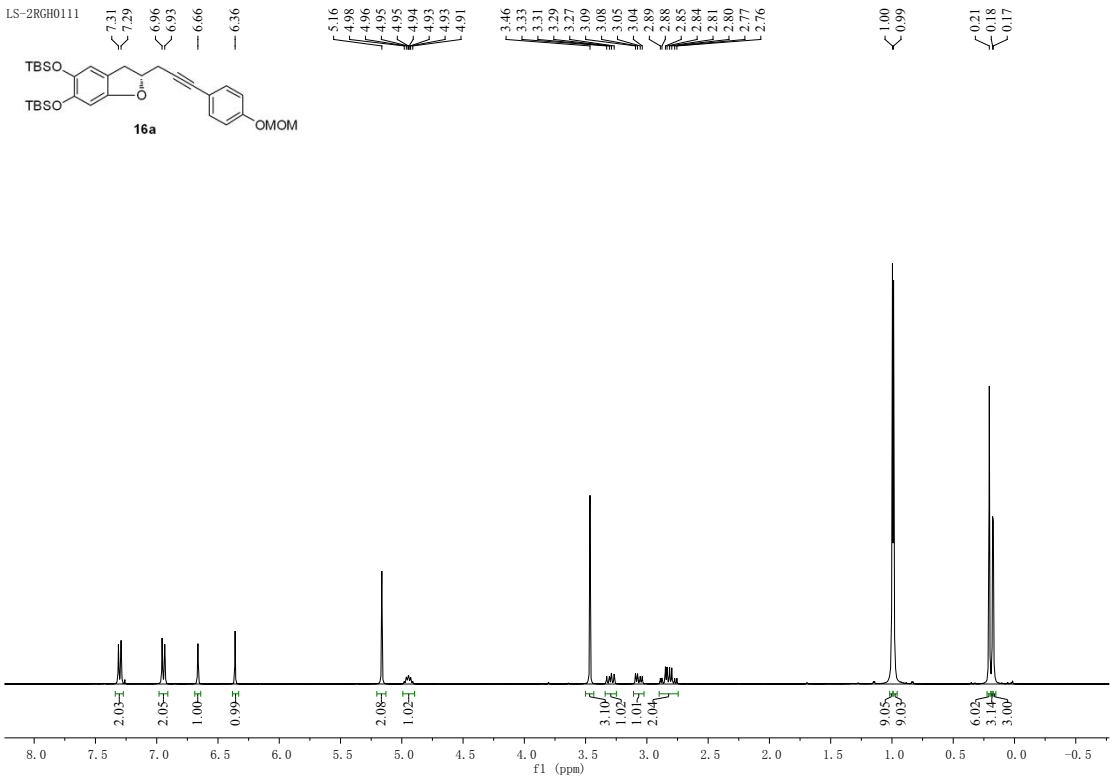
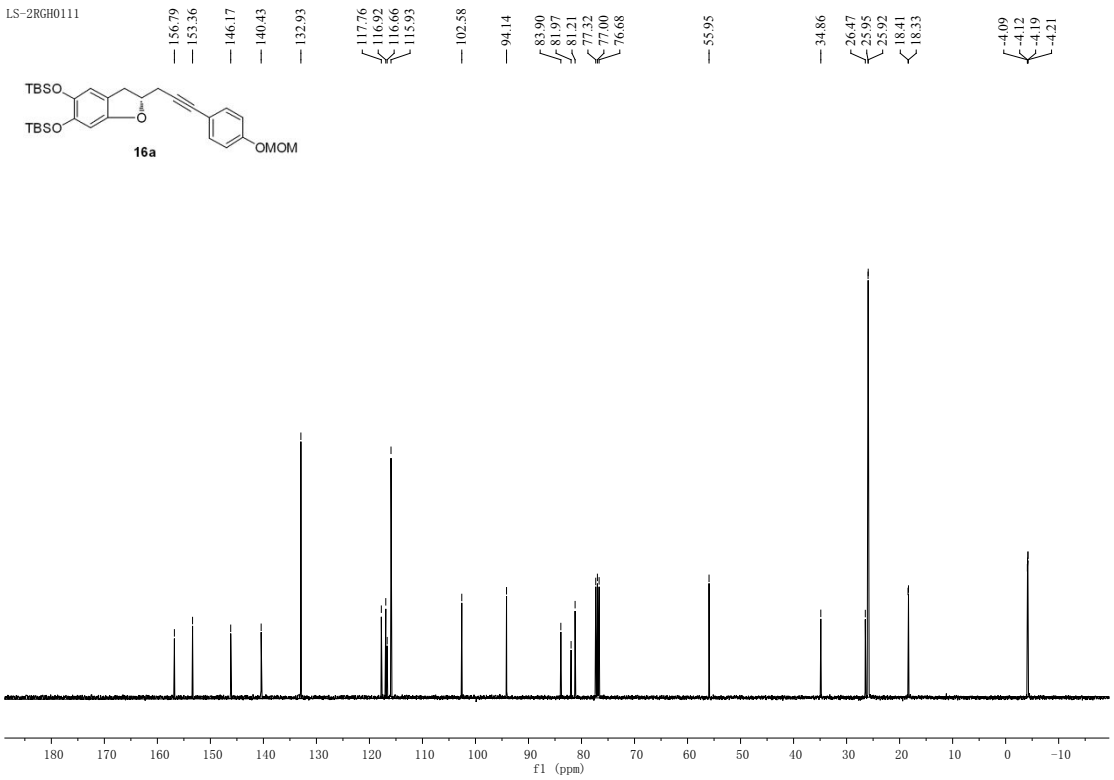
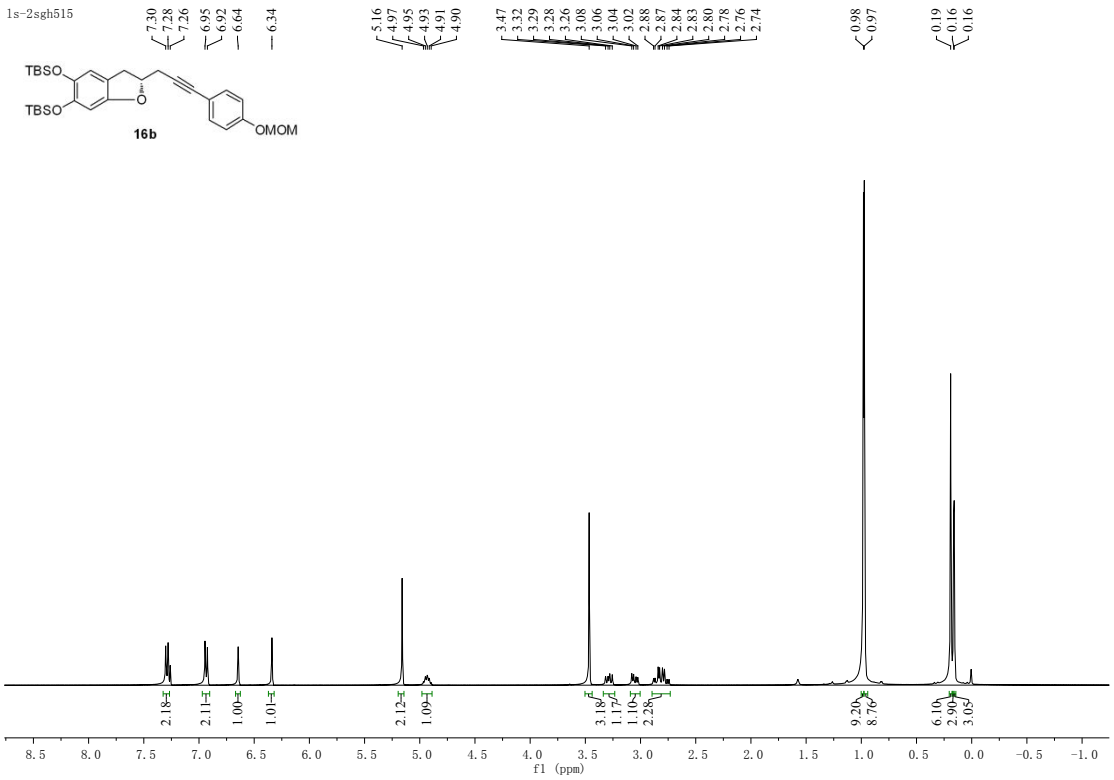
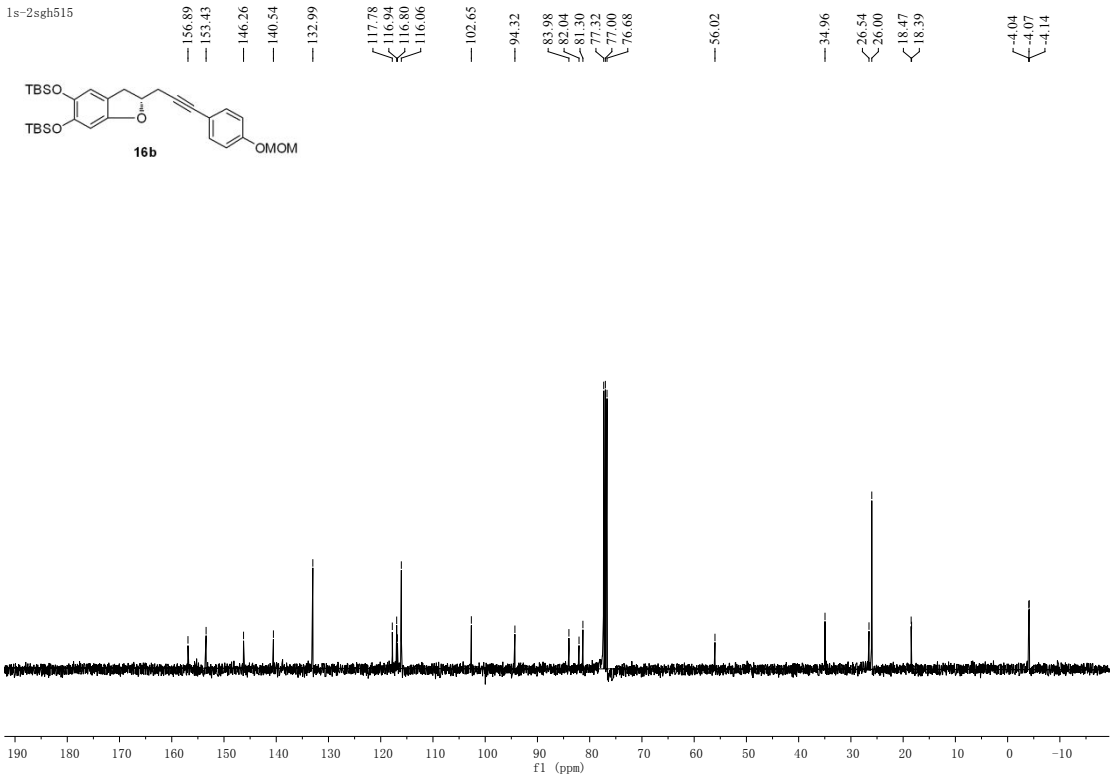
146.29
133.00
130.06
124.86
123.71
116.75
116.10
114.83
94.30
84.48
83.18
77.32
77.00
76.68
69.73
56.02
41.96
27.44
25.88
25.85
18.42
18.39
-4.11
-4.14
-4.18
-4.21
TBSO
TBSO
Br
OH
OMOM
15b
f1 (ppm)


LS-2RGH0111
TBSO
TBSO
O
OMOM
16a
f1 (ppm)


LS-2RGH0111
TBSO
TBSO
O
OMOM
16a
f1 (ppm)


1s-2sgh515
7.30
7.28
7.26
6.95
6.92
6.64
6.34
5.16
4.97
4.95
4.93
4.91
4.90
3.47
3.32
3.29
3.28
3.26
3.08
3.06
3.04
3.02
2.88
2.87
2.84
2.83
2.80
2.78
2.76
2.74
0.98
0.97
0.19
0.16
0.16
TBSO
TBSO
O
OMOM
16b
2.18
2.11
1.00
1.01
2.12
1.09
3.18
1.17
1.10
2.28
9.20
8.76
6.10
2.90
3.05
f1 (ppm)


1s-2sgh515
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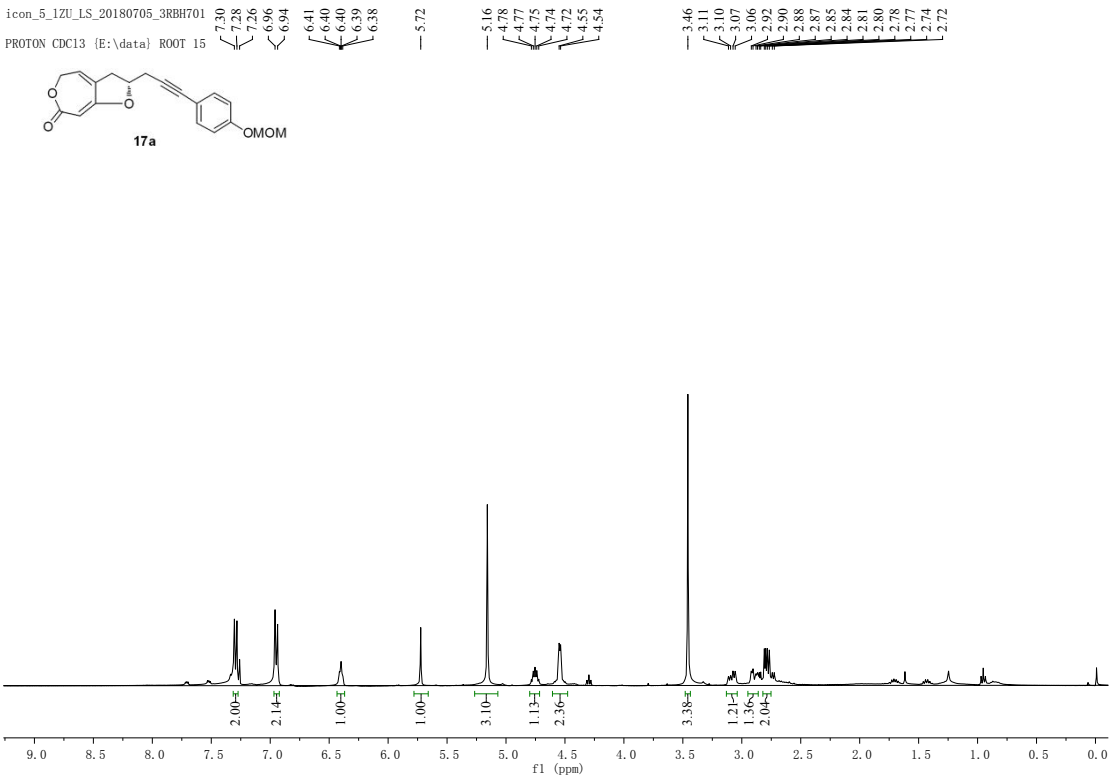
153.43
146.26
140.54
132.99
117.78
116.94
116.80
116.06
102.65
94.32
83.98
82.04
81.30
77.32
77.00
76.68
56.02
34.96
26.54
26.00
18.47
18.39
-4.04
-4.07
-4.14
TBSO
TBSO
O
OMOM
16b
f1 (ppm)


icon_5_1ZU_LS_20180705_3RBH701
PROTON CDC13 {E:\data} ROOT 15
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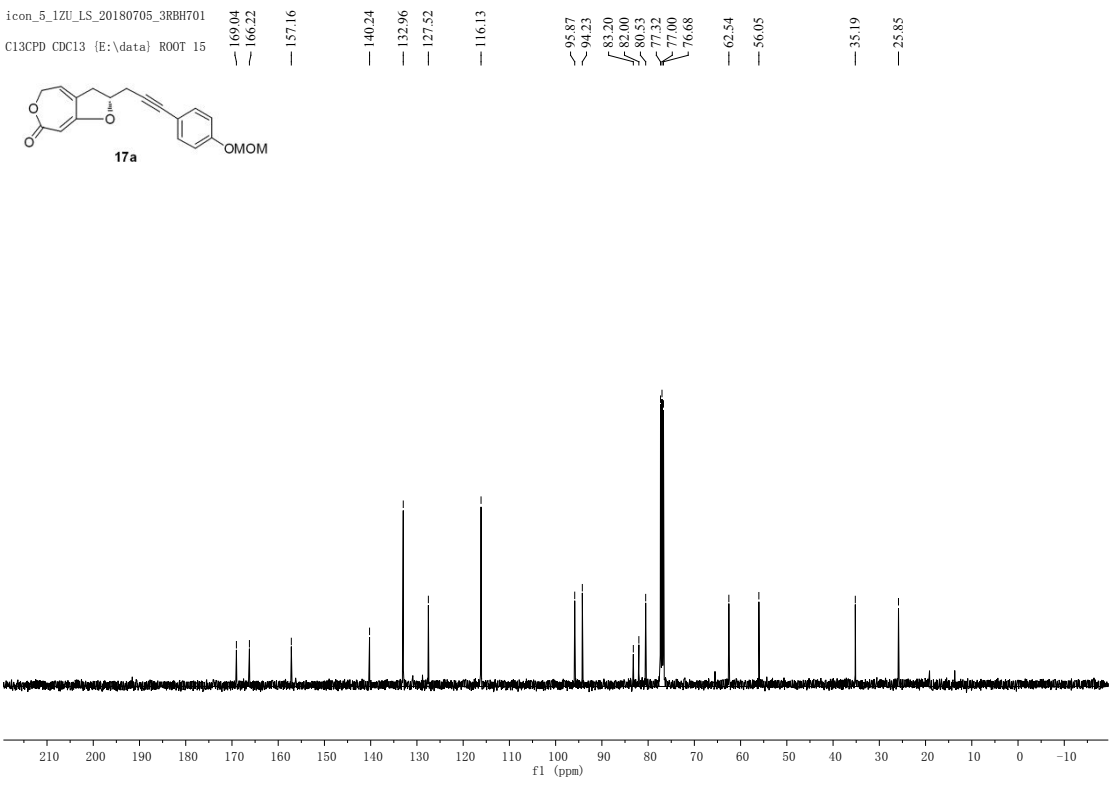
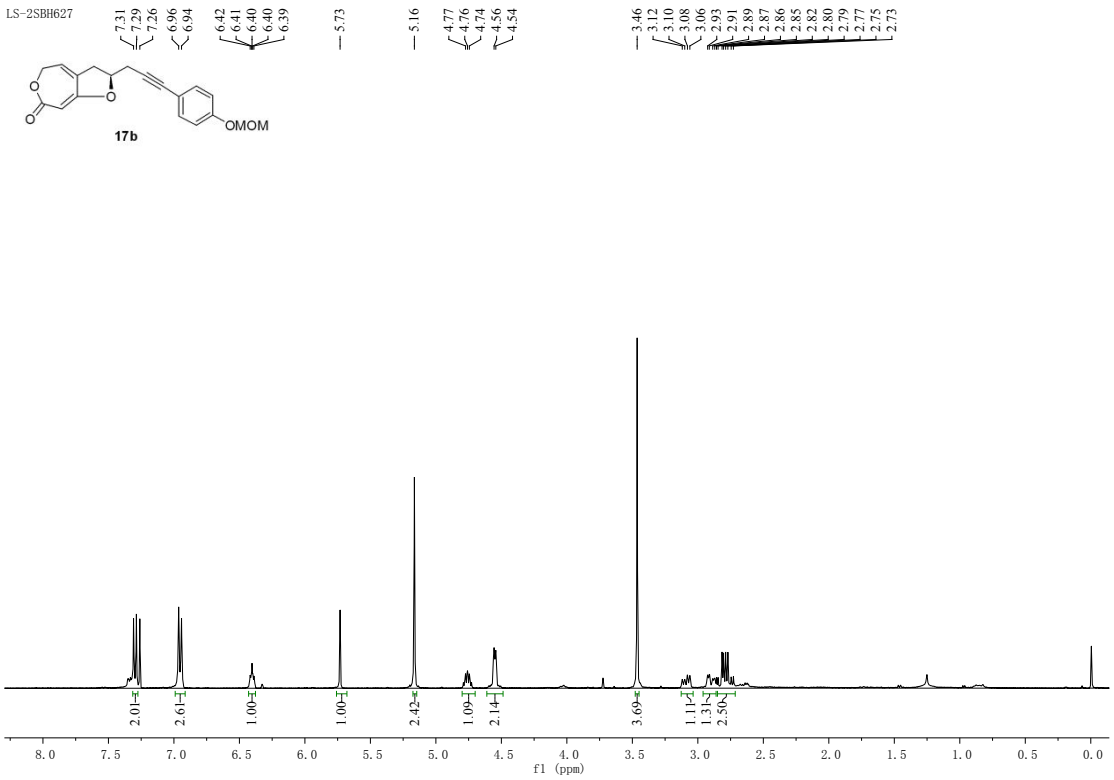
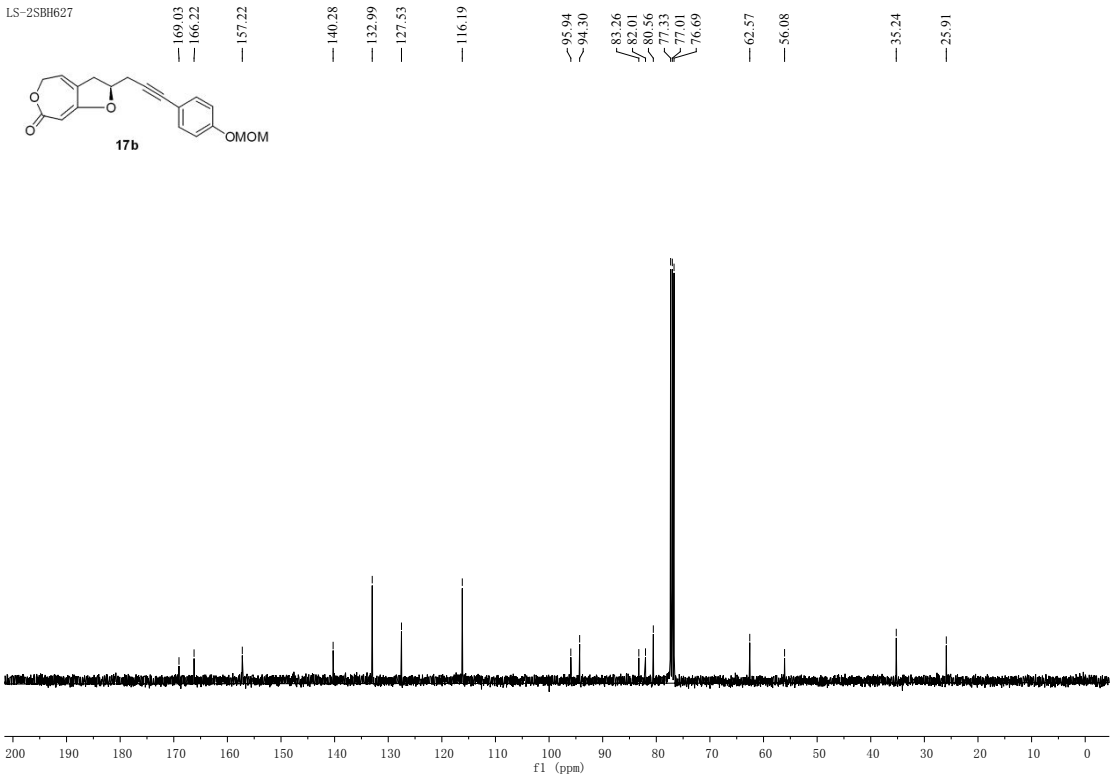
7.28
7.26
6.96
6.94
6.41
6.40
6.40
6.39
6.38
5.72
5.16
4.78
4.77
4.75
4.74
4.72
4.55
4.54
3.46
3.11
3.10
3.07
3.06
2.92
2.90
2.88
2.87
2.85
2.84
2.81
2.80
2.78
2.77
2.74
2.72
OMOM
17a
2.00
2.14
1.00
1.00
3.10
1.13
2.36
3.38
1.21
1.36
2.04
f1 (ppm)


icon_5_1ZU_LS_20180705_3RBH701
C13CPD CDC13 {E:\data} ROOT 15
169.04
166.22
157.16
140.24
132.96
127.52
116.13
95.87
94.23
83.20
82.00
80.53
77.32
77.00
76.68
62.54
56.05
35.19
25.85
OMOM
17a
f1 (ppm)


LS-2SBH627
7.31
7.29
7.26
6.96
6.94
6.42
6.41
6.40
6.40
6.39
5.73
5.16
4.77
4.76
4.74
4.56
4.54
3.46
3.12
3.10
3.08
3.06
2.93
2.91
2.89
2.87
2.86
2.85
2.82
2.80
2.79
2.77
2.75
2.73
OMOM
17b
2.01
2.61
1.00
1.00
2.42
1.09
2.14
3.69
1.11
1.31
2.50
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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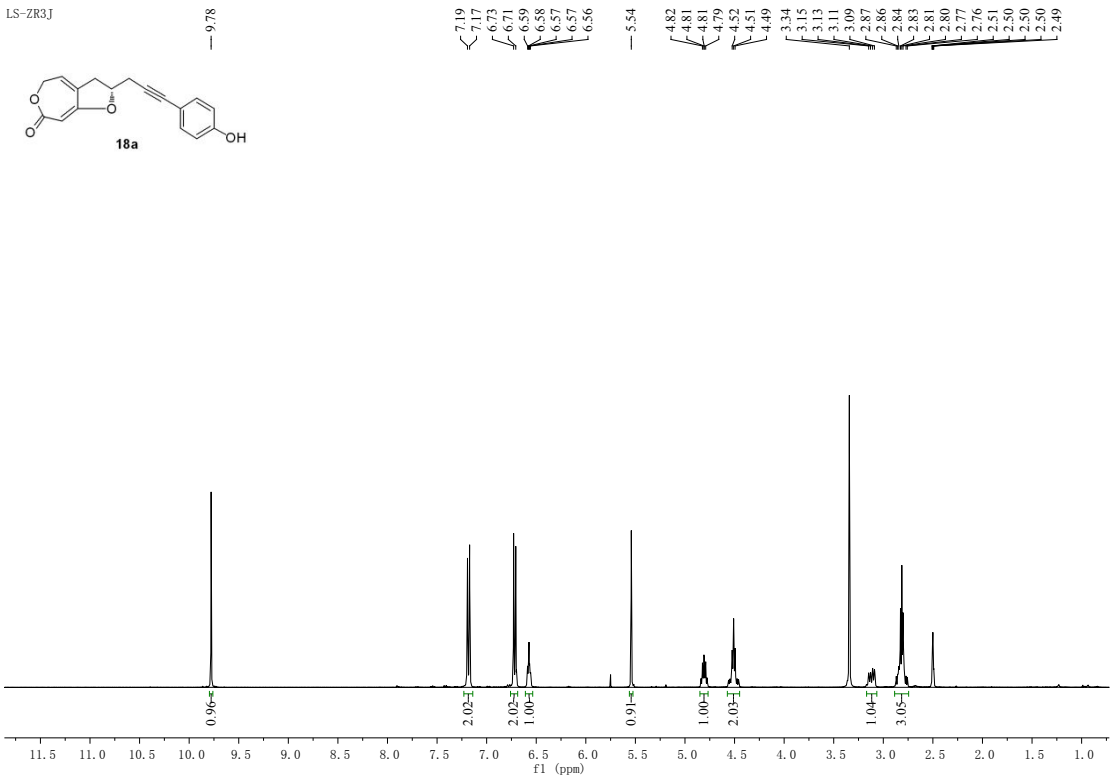
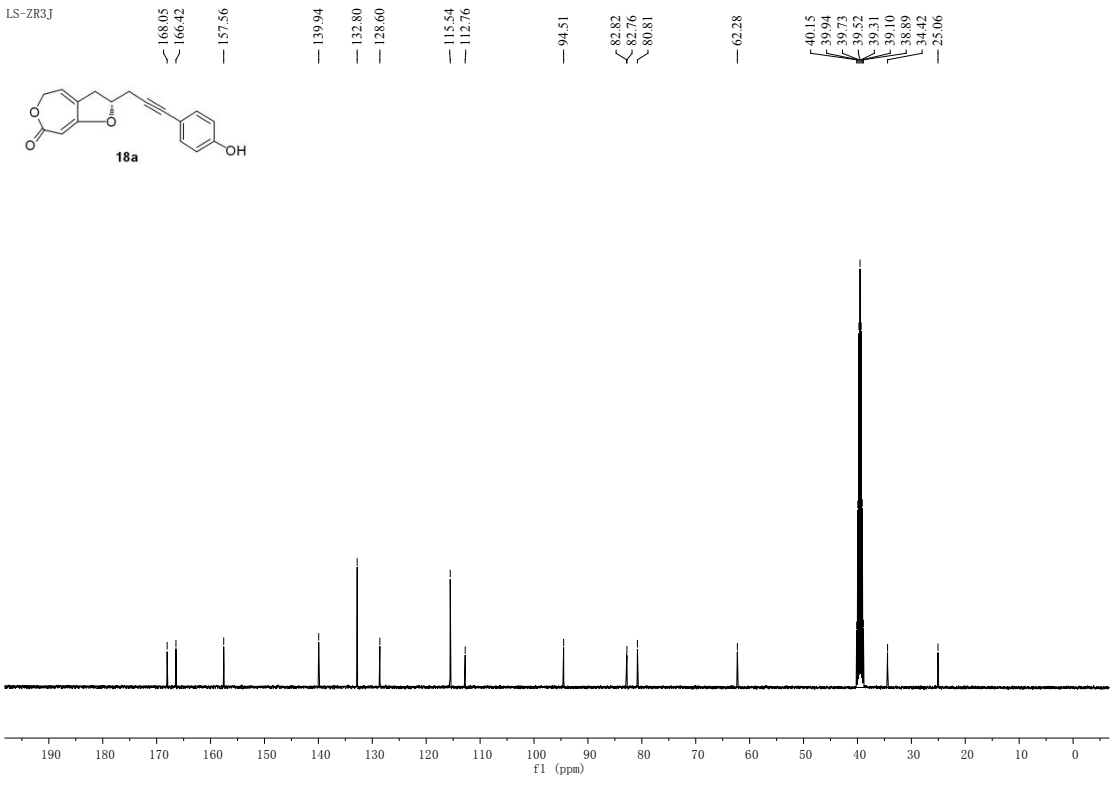
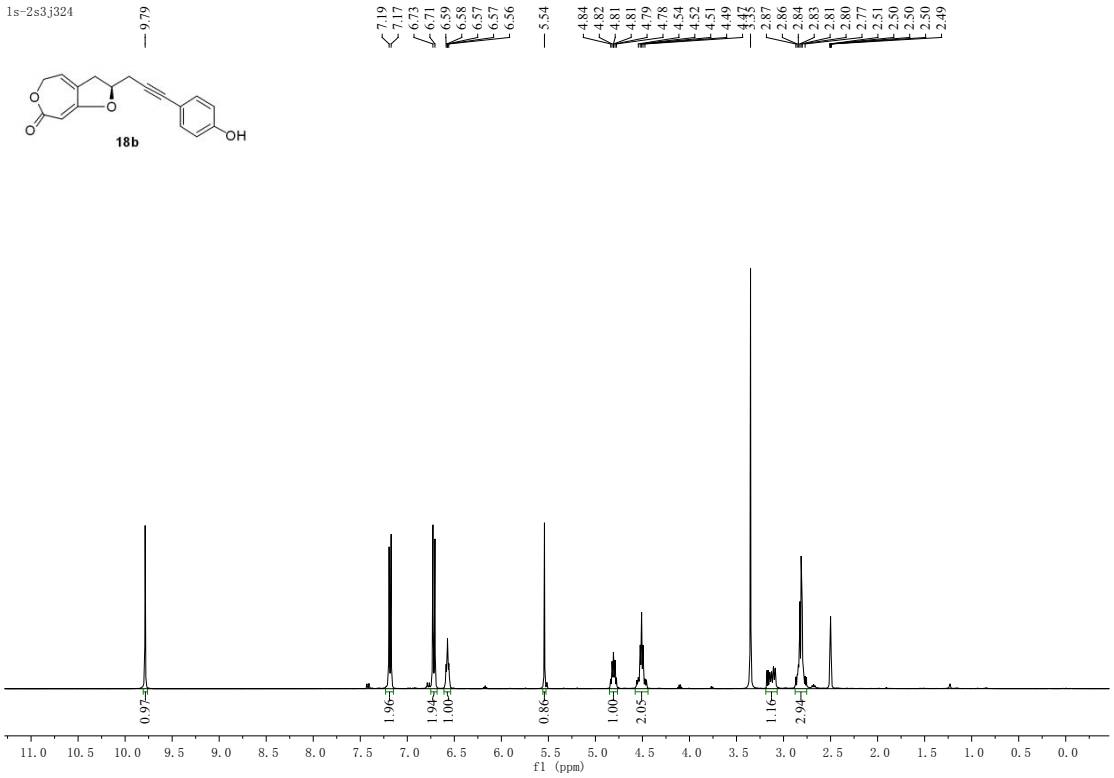
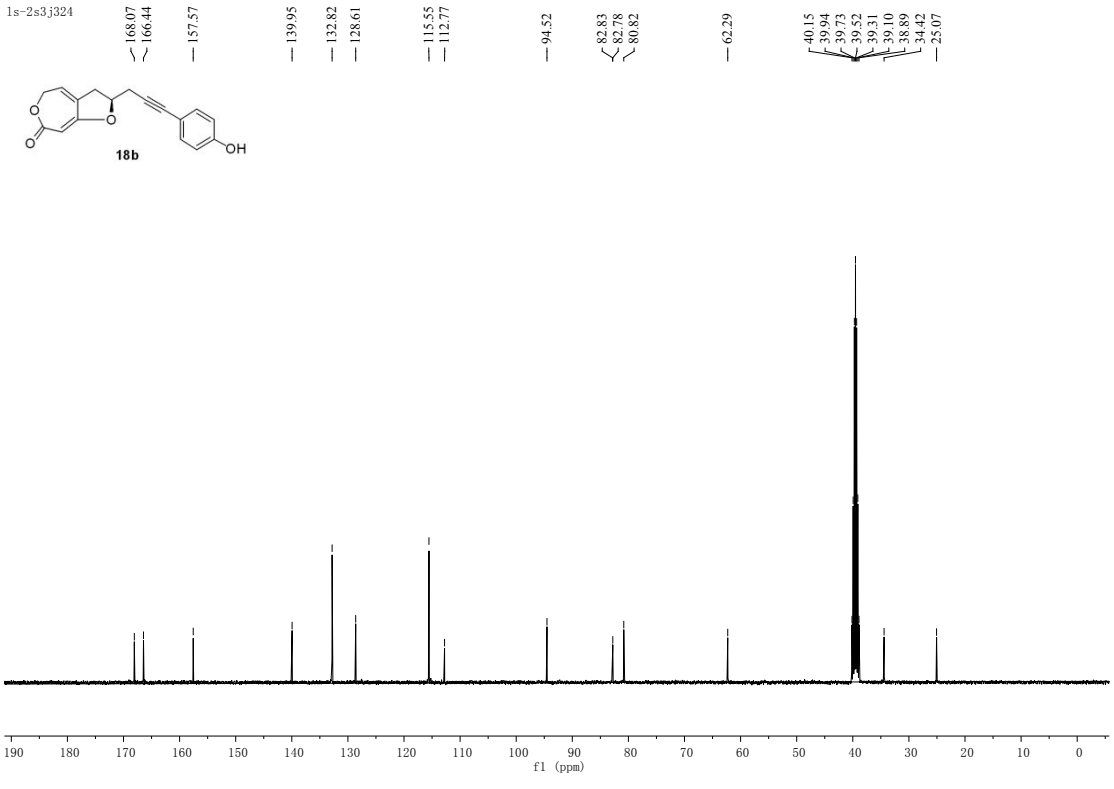
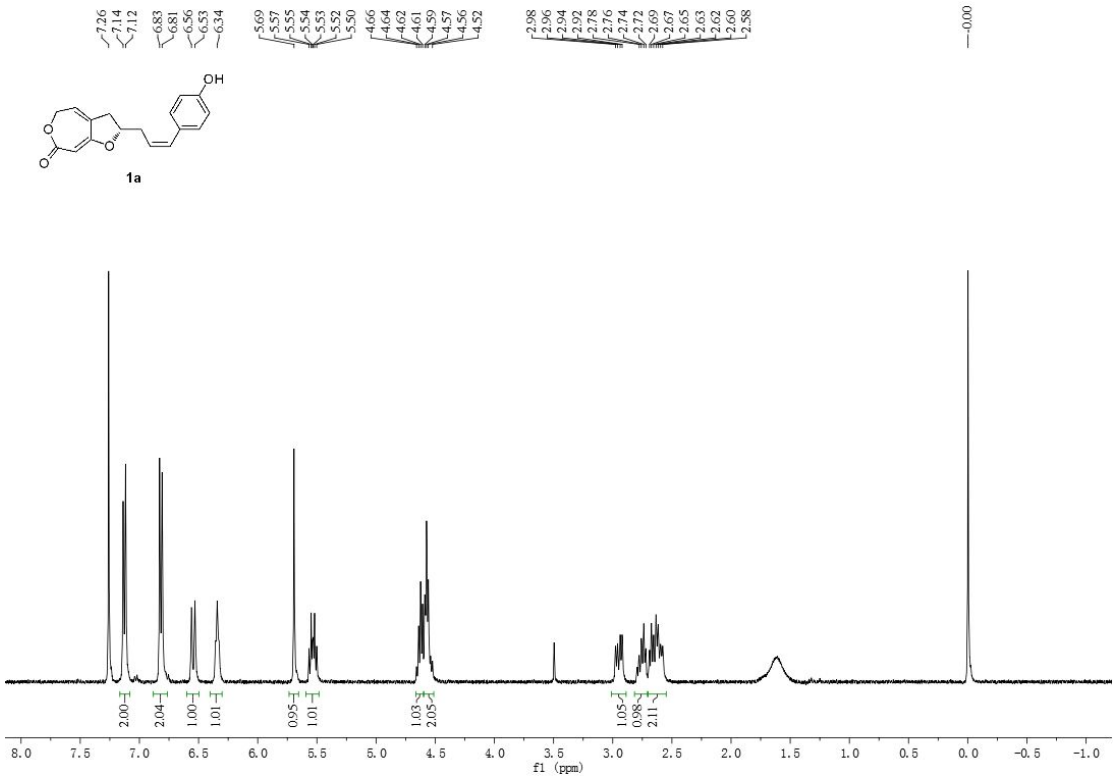
169.03
166.22
157.22
140.28
132.99
127.53
116.19
95.94
94.30
83.26
82.01
80.56
77.33
77.01
76.69
62.57
56.08
35.24
25.91
OMOM
17b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

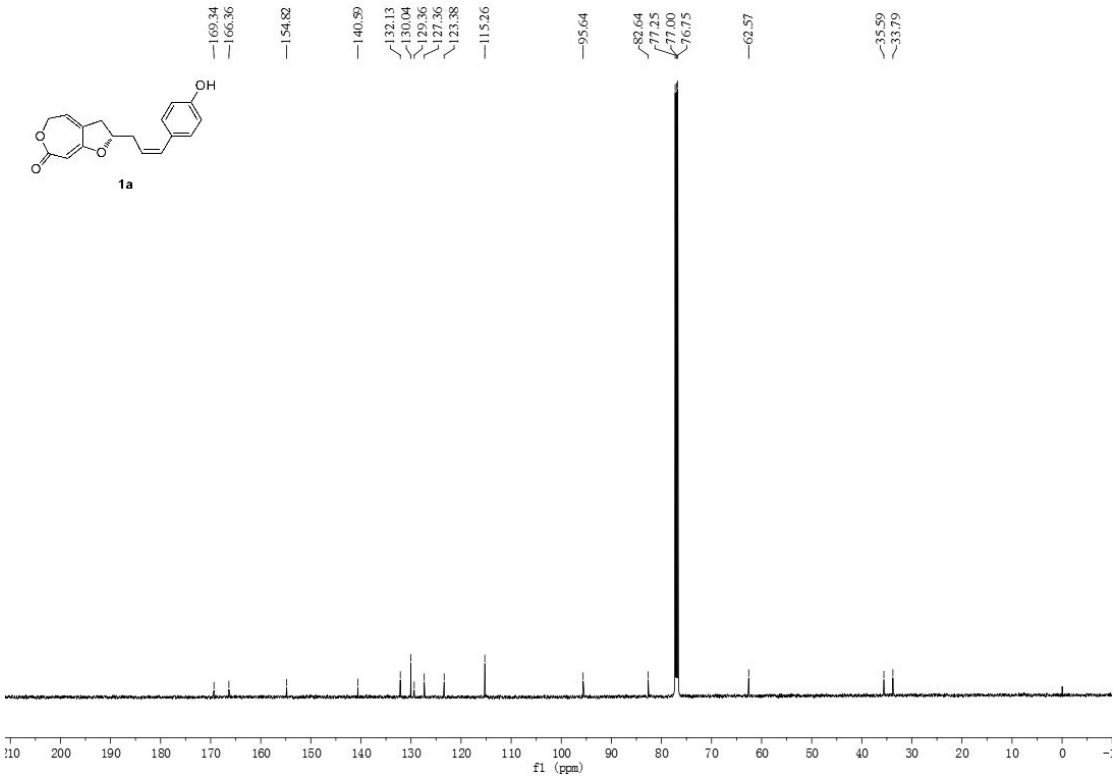

LS-ZR3J
9.78
7.19
7.17
6.73
6.71
6.59
6.58
6.57
6.57
6.56
5.54
4.82
4.81
4.81
4.79
4.52
4.51
4.49
3.34
3.15
3.13
3.11
3.09
2.87
2.86
2.84
2.83
2.81
2.80
2.77
2.76
2.51
2.50
2.50
2.50
2.49
18a
OH
0.96
2.02
2.02
1.00
0.91
1.00
2.03
1.04
3.05
f1 (ppm)

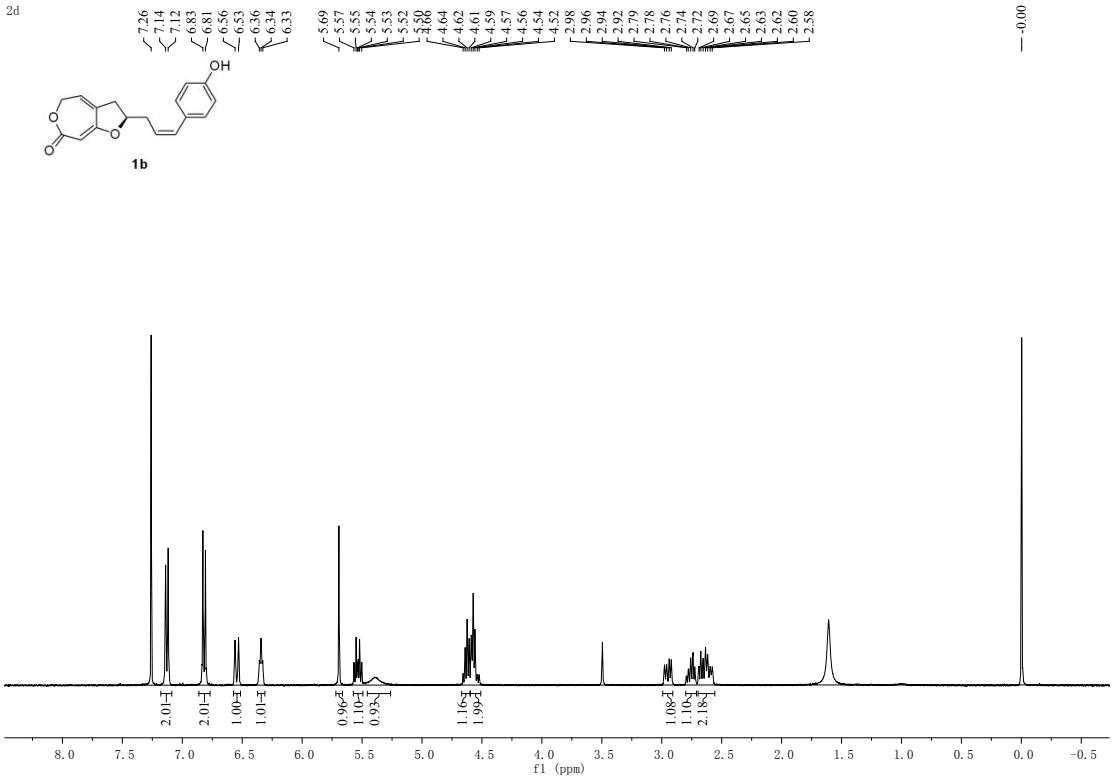

LS-ZR3J
168.05
166.42
157.56
139.94
132.80
128.60
115.54
112.76
94.51
82.82
82.76
80.81
62.28
40.15
39.94
39.73
39.52
39.31
39.10
38.89
34.42
25.06
18a
OH
f1 (ppm)

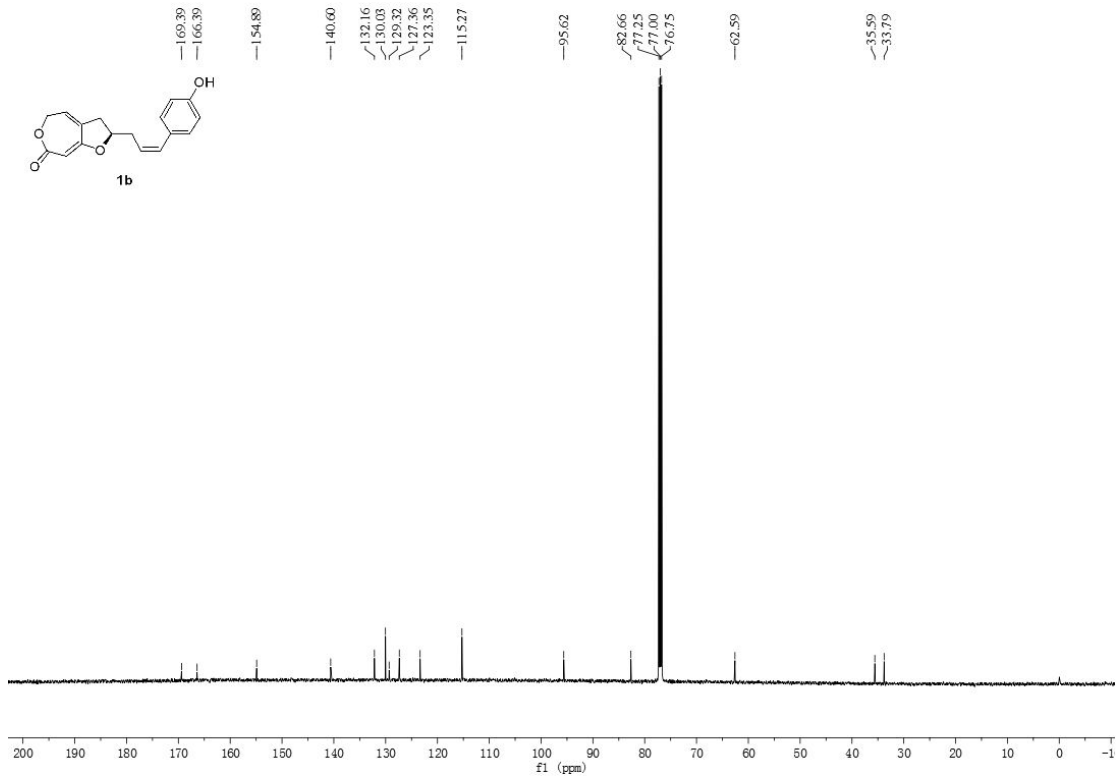

1s-2s3j324
9.79
7.19
7.17
6.73
6.71
6.59
6.58
6.57
6.57
6.56
5.54
4.84
4.82
4.81
4.81
4.79
4.78
4.54
4.52
4.51
4.49
3.47
3.35
2.87
2.86
2.84
2.83
2.81
2.80
2.77
2.51
2.50
2.50
2.50
2.49
O
O
O
OH
18b
0.97
1.96
1.94
1.00
0.86
1.00
2.05
1.16
2.94
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

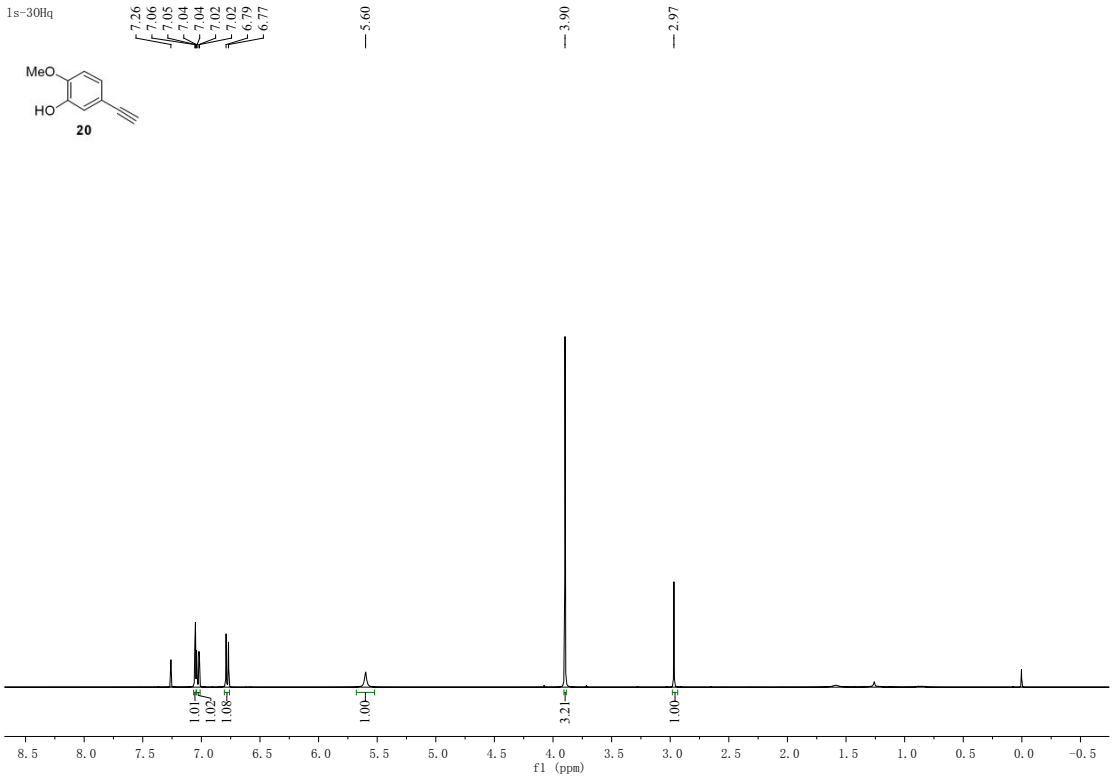

1s-2s3j324
168.07
166.44
157.57
139.95
132.82
128.61
115.55
112.77
94.52
82.83
82.78
80.82
62.29
40.15
39.94
39.73
39.52
39.31
39.10
38.89
34.42
25.07
O
O
O
OH
18b
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

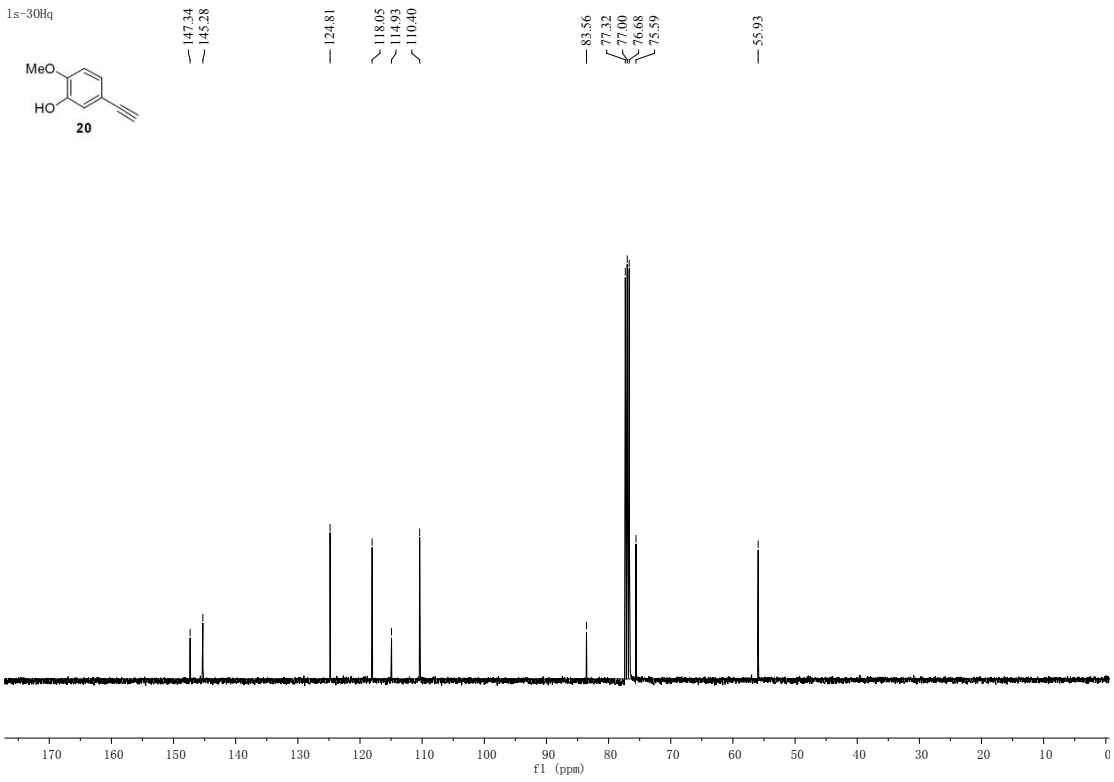

7.26
7.14
7.12
6.83
6.81
6.56
6.53
6.34
5.69
5.57
5.55
5.54
5.53
5.52
5.50
4.66
4.64
4.62
4.61
4.59
4.57
4.56
4.52
2.98
2.96
2.94
2.92
2.78
2.76
2.74
2.72
2.69
2.67
2.65
2.63
2.62
2.60
2.58
0.00
OH
1a
2.00
2.04
1.00
1.01
0.95
1.01
1.03
2.05
1.05
0.98
2.11
f1 (ppm)

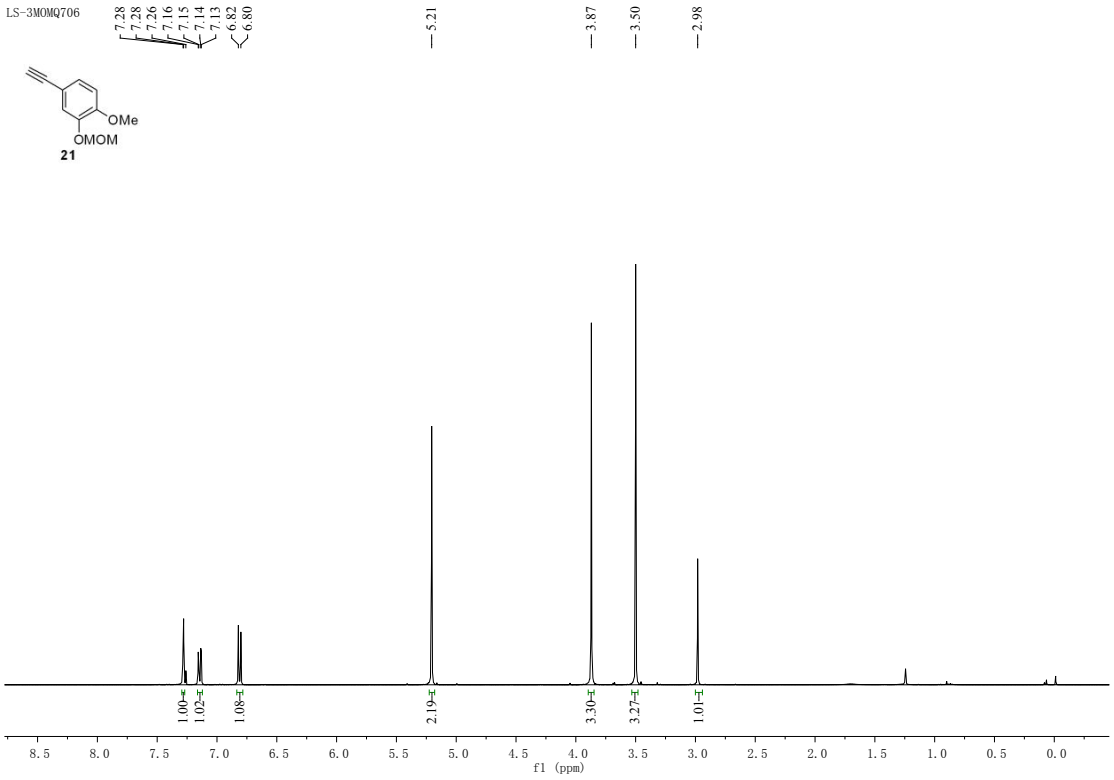

169.34
166.36
154.82
140.59
132.13
130.04
129.36
127.36
123.38
115.26
95.64
82.64
77.25
77.00
76.75
62.57
35.59
33.79
OH
1a
f1 (ppm)

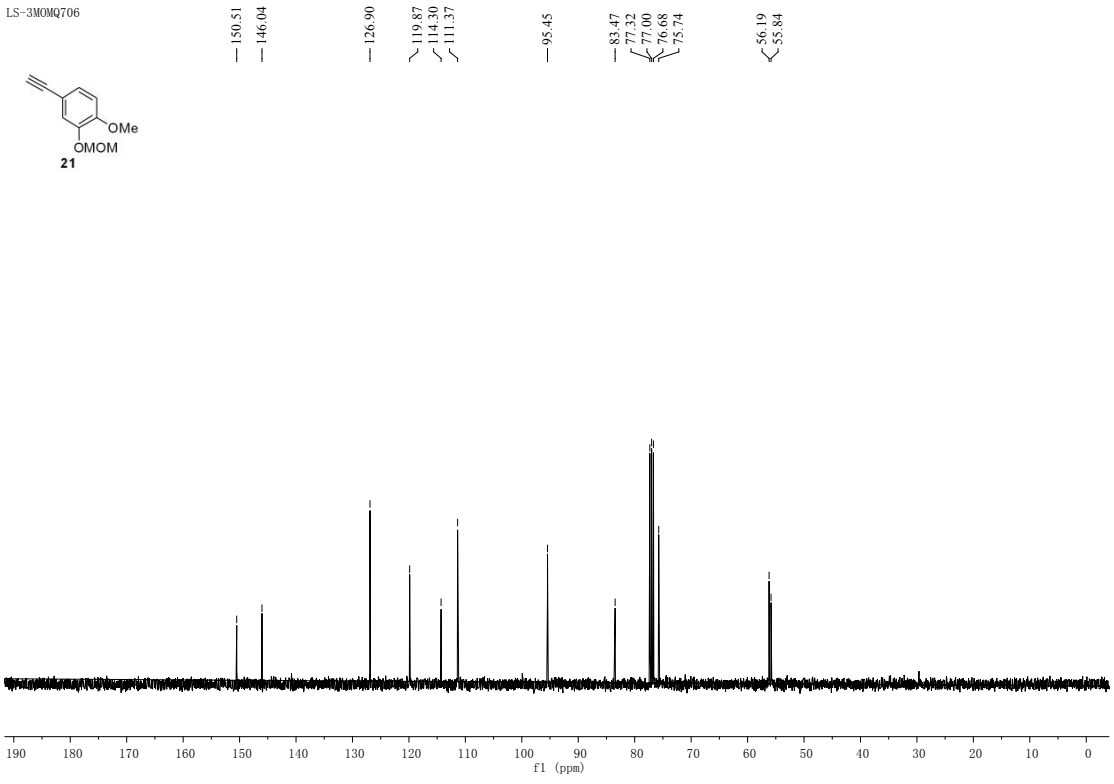

2d
7.26
7.14
7.12
6.83
6.81
6.56
6.53
6.36
6.34
6.33
5.69
5.57
5.55
5.54
5.53
5.52
5.50
4.66
4.64
4.62
4.61
4.59
4.57
4.56
4.54
4.52
2.98
2.96
2.94
2.92
2.79
2.78
2.76
2.74
2.72
2.69
2.67
2.65
2.63
2.62
2.60
2.58
-0.00
OH
O
O
O
1b
2.01
2.01
1.00
1.01
0.96
1.10
0.93
1.16
1.99
1.08
1.10
2.18
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

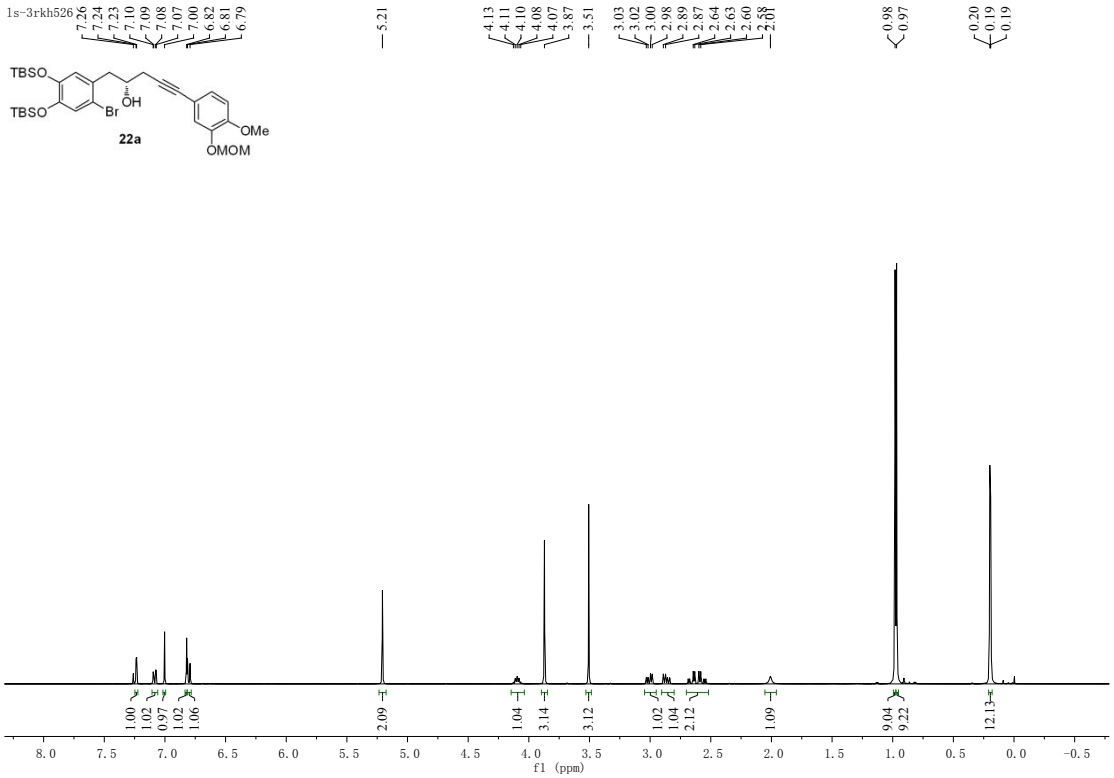

169.39
166.39
154.89
140.60
132.16
130.03
129.32
127.36
123.35
115.27
95.62
82.66
77.25
77.00
76.75
62.59
35.59
33.79
OH
O
O
O
1b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

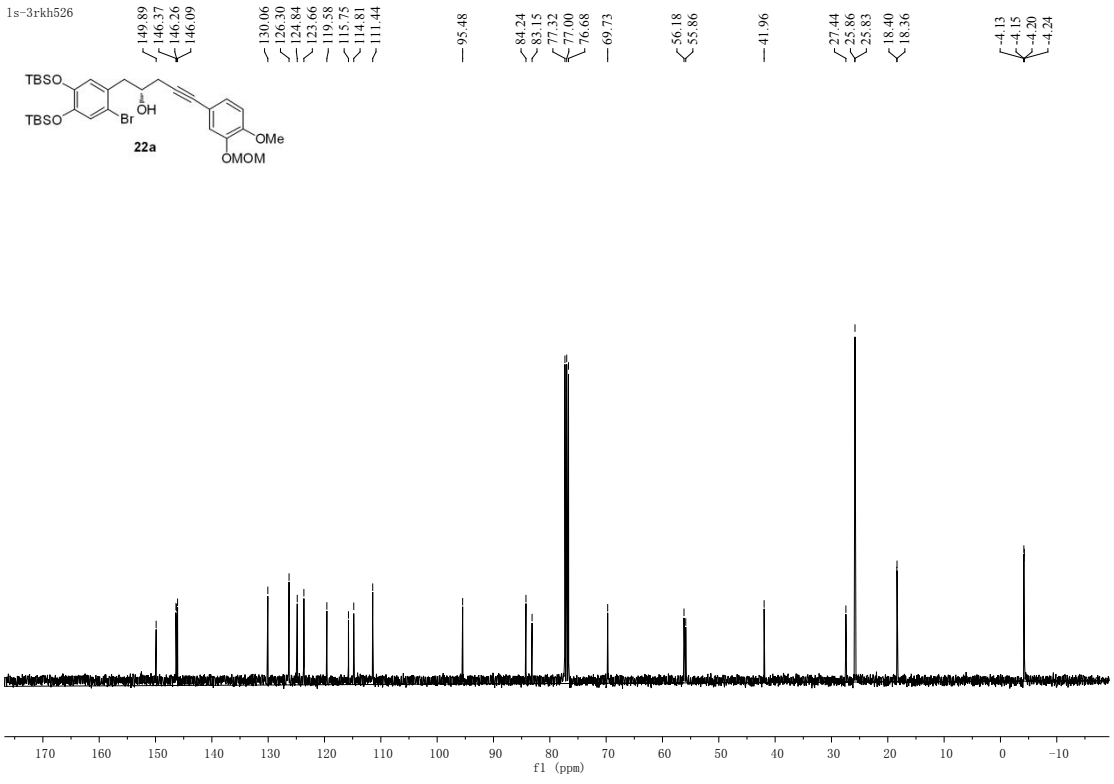

1s-30Hq
7.26
7.06
7.05
7.04
7.04
7.02
7.02
6.79
6.77
5.60
3.90
2.97
MeO
HO
20
1.01
1.02
1.08
1.00
3.21
1.00
f1 (ppm)

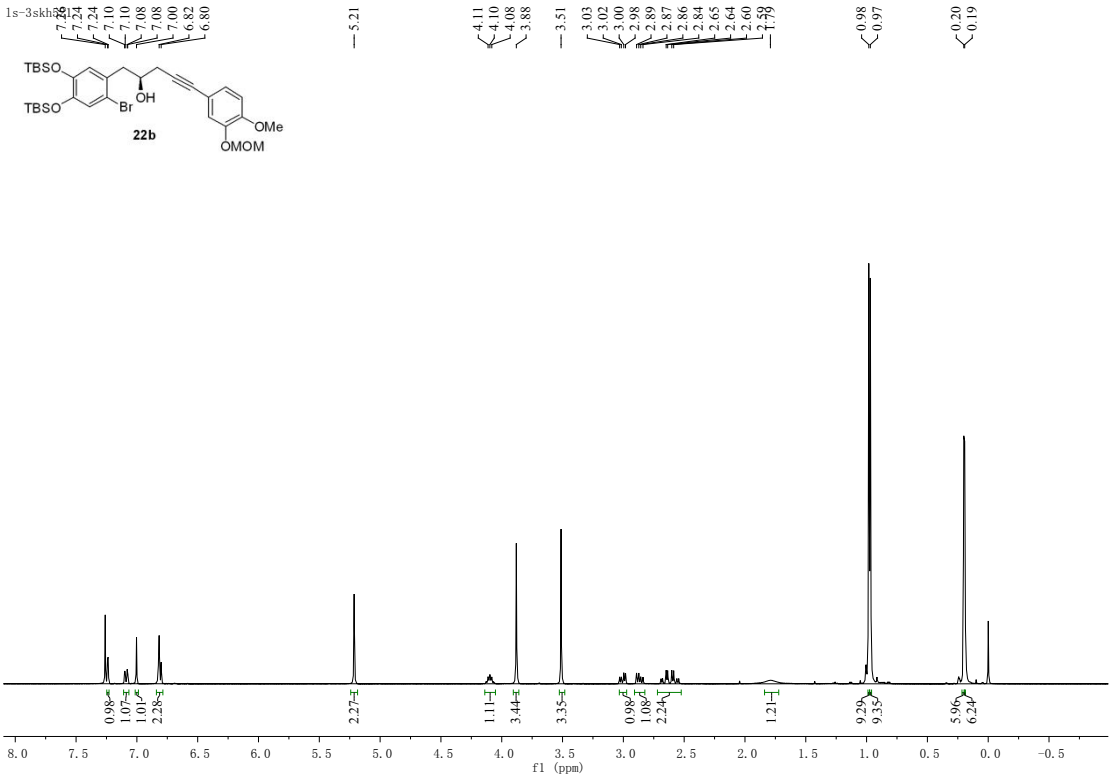

1s-30Hq
147.34
145.28
124.81
118.05
114.93
110.40
83.56
77.32
77.00
76.68
75.59
55.93
MeO
HO
20
f1 (ppm)

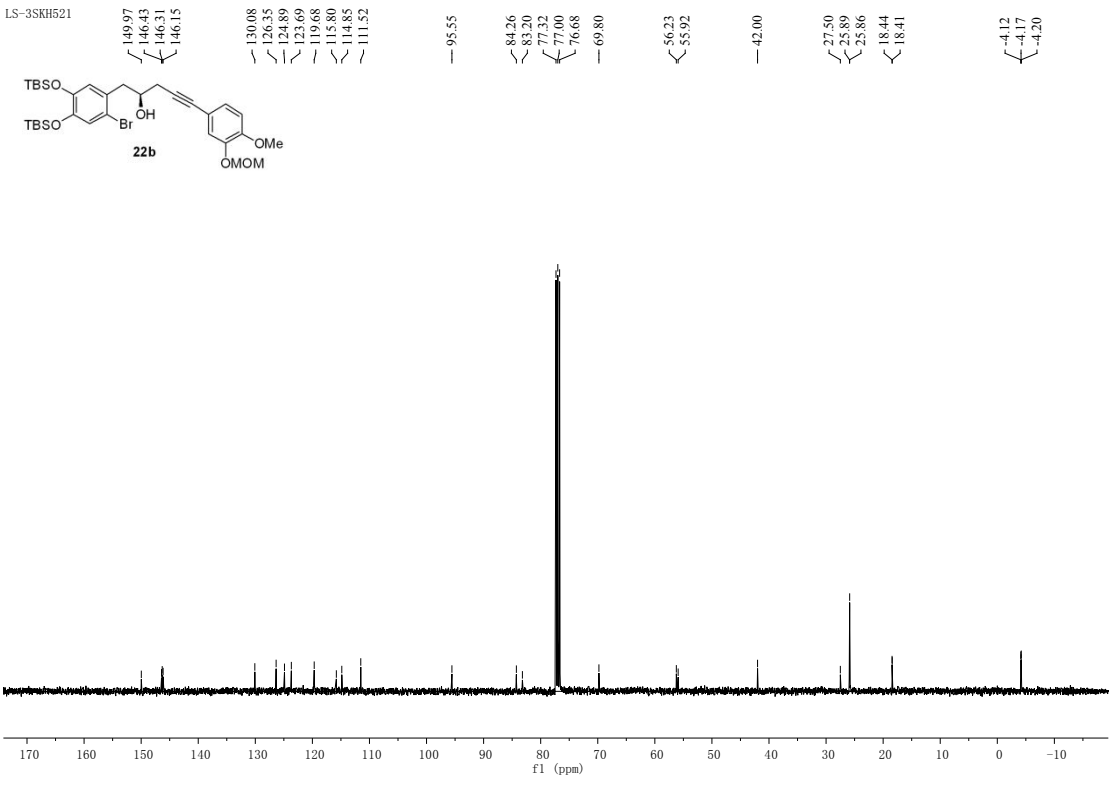

LS-3MOMQ706
7.28
7.28
7.26
7.16
7.15
7.14
7.13
6.82
6.80
5.21
3.87
3.50
2.98
OMe
OMOM
21
1.00
1.02
1.08
2.19
3.30
3.27
1.01
f1 (ppm)

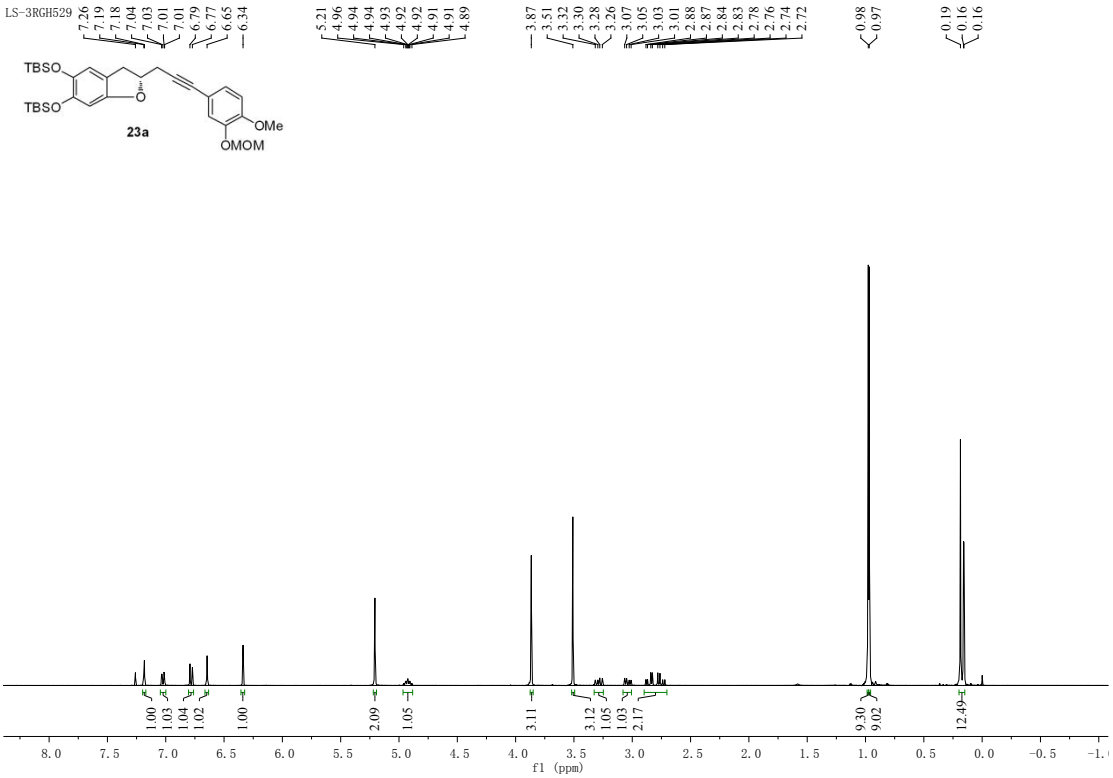

LS-3MOMQ706
150.51
146.04
126.90
119.87
114.30
111.37
95.45
83.47
77.32
77.00
76.68
75.74
56.19
55.84
OMe
OMOM
21
f1 (ppm)

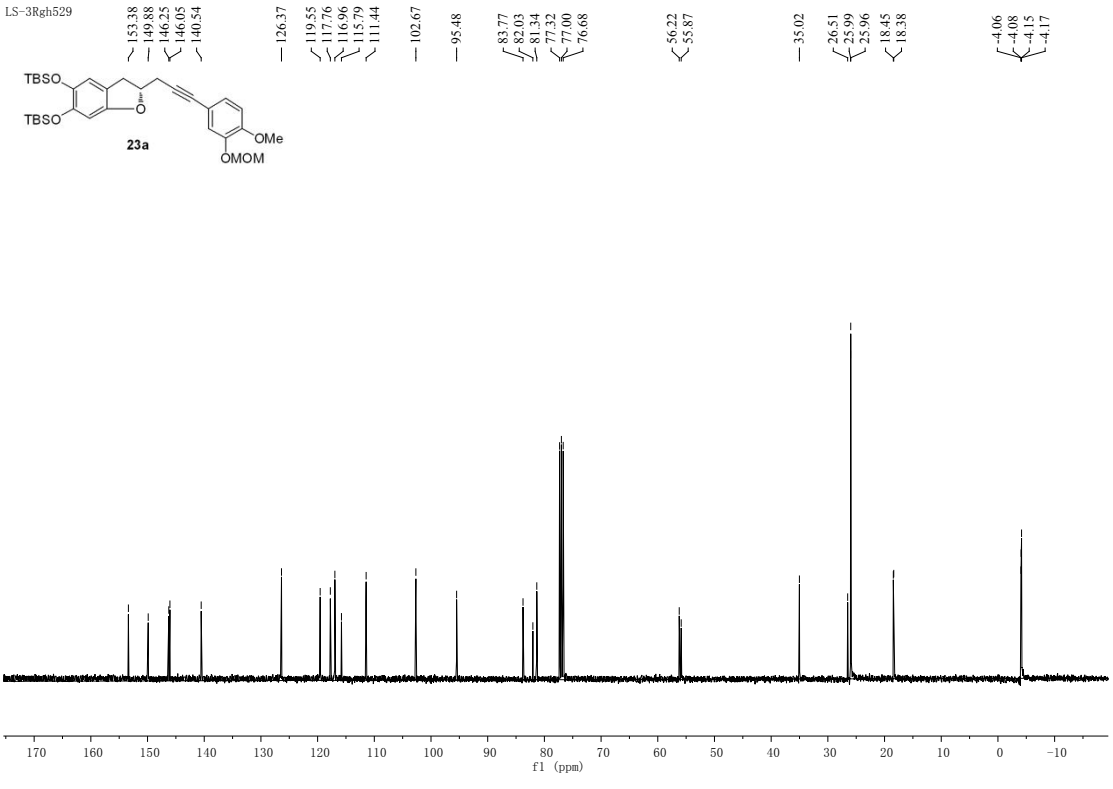

1s-3rkh526
7.26
7.24
7.23
7.10
7.09
7.08
7.07
7.00
6.82
6.81
6.79
5.21
4.13
4.11
4.10
4.08
4.07
3.87
3.51
3.03
3.02
3.00
2.98
2.89
2.87
2.64
2.63
2.60
2.58
2.01
0.98
0.97
0.20
0.19
0.19
TBSO
TBSO
Br
OH
OMe
OMOM
22a
1.00
1.02
0.97
1.02
1.06
2.09
1.04
3.14
3.12
1.02
1.04
2.12
1.09
9.04
9.22
12.13
f1 (ppm)

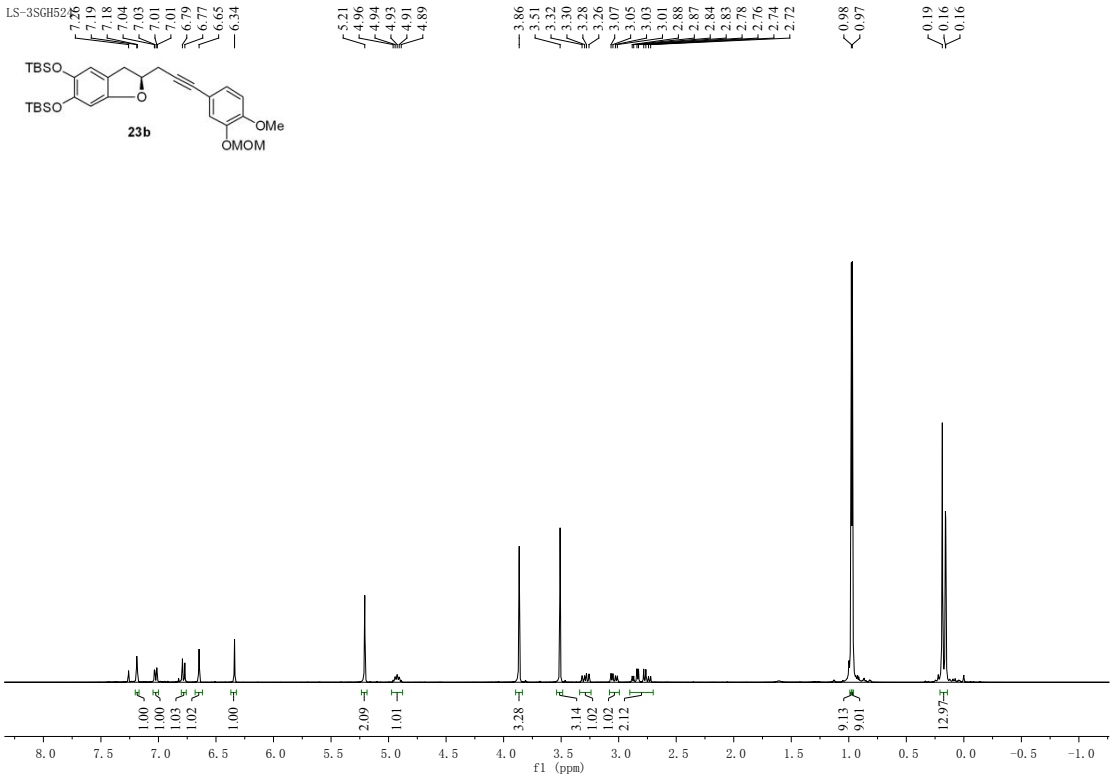

1s-3rkh526
149.89
146.37
146.26
146.09
130.06
126.30
124.84
123.66
119.58
115.75
114.81
111.44
95.48
84.24
83.15
77.32
77.00
76.68
69.73
56.18
55.86
41.96
27.44
25.86
25.83
18.40
18.36
-4.13
-4.15
-4.20
-4.24
TBSO
TBSO
Br
OH
OMe
OMOM
22a
f1 (ppm)

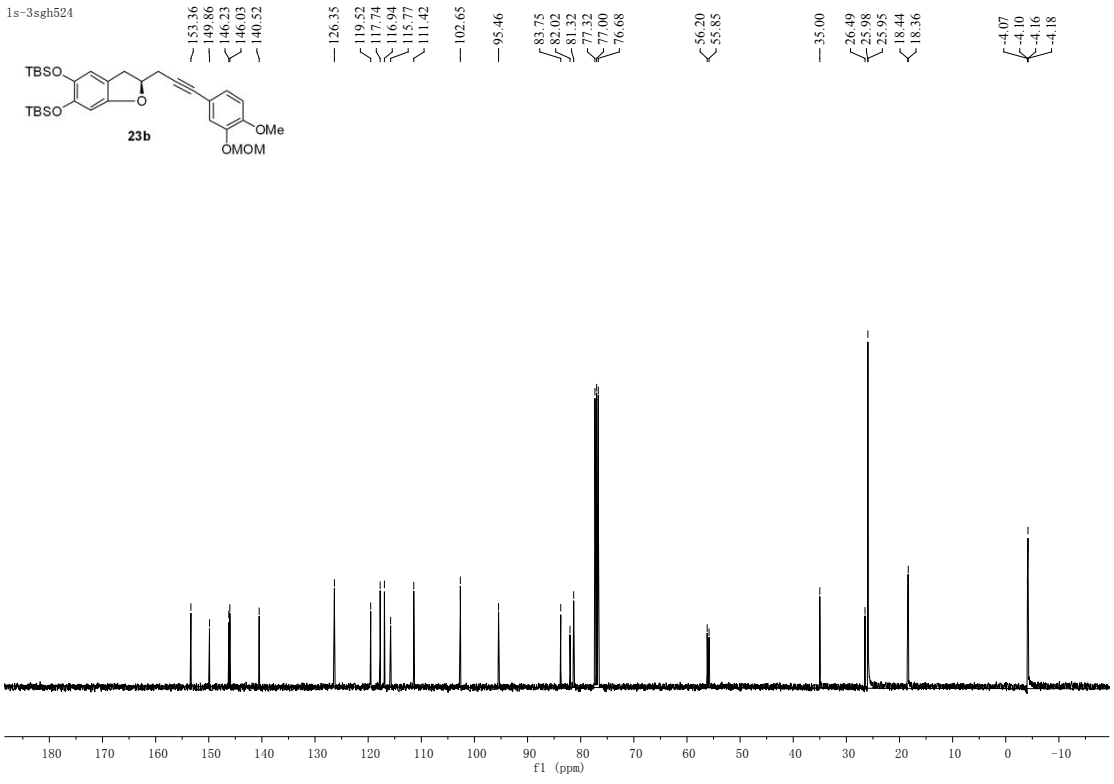

1s-3skh521
7.26
7.24
7.24
7.10
7.10
7.08
7.08
7.00
6.82
6.80
5.21
4.11
4.10
4.08
3.88
3.51
3.03
3.02
3.00
2.98
2.89
2.87
2.86
2.84
2.65
2.64
2.60
1.99
0.98
0.97
0.20
0.19
TBSO
TBSO
Br
OH
OMe
OMOM
22b
0.98
1.07
1.01
2.28
2.27
1.11
3.44
3.35
0.98
1.08
2.24
1.21
9.29
9.35
5.96
6.24
f1 (ppm)

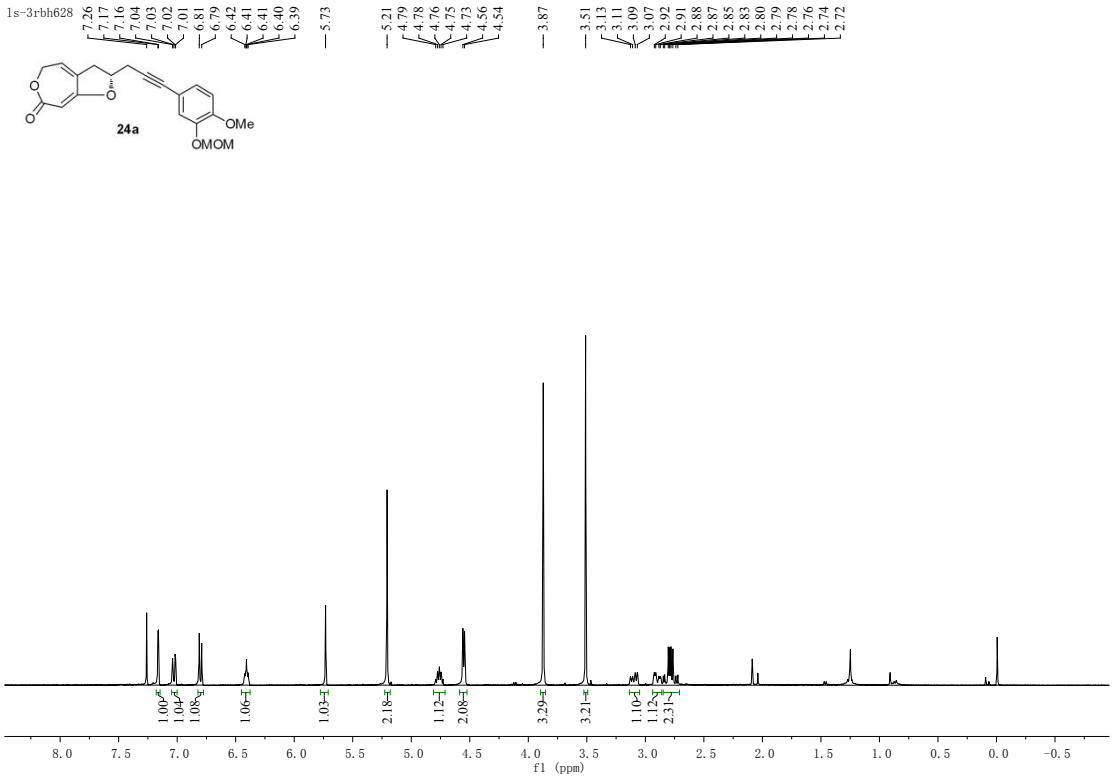

LS-3SKH521
149.97
146.43
146.31
146.15
130.08
126.35
124.89
123.69
119.68
115.80
114.85
111.52
95.55
84.26
83.20
77.32
77.00
76.68
69.80
56.23
55.92
42.00
27.50
25.89
25.86
18.44
18.41
-4.12
-4.17
-4.20
TBSO
TBSO
Br
OH
OMe
OMOM
22b
f1 (ppm)


LS-3RGH529
TBSO
TBSO
OMe
OMOM
23a
f1 (ppm)


LS-3Rgh529
TBSO
TBSO
OMe
OMOM
23a
f1 (ppm)


LS-3SGH524
7.26
7.19
7.18
7.04
7.03
7.01
7.01
6.79
6.77
6.65
6.34
5.21
4.96
4.94
4.93
4.91
4.89
3.86
3.51
3.32
3.30
3.28
3.26
3.07
3.05
3.03
3.01
2.88
2.87
2.84
2.83
2.78
2.76
2.74
2.72
0.98
0.97
0.19
0.16
0.16
TBSO
TBSO
O
OMe
OMOM
23b
1.00
1.00
1.03
1.02
1.00
2.09
1.01
3.28
3.14
1.02
1.02
2.12
9.13
9.01
12.97
f1 (ppm)


1s-3sgh524
153.36
149.86
146.23
146.03
140.52
126.35
119.52
117.74
116.94
115.77
111.42
102.65
95.46
83.75
82.02
81.32
77.32
77.00
76.68
56.20
55.85
35.00
26.49
25.98
25.95
18.44
18.36
-4.07
-4.10
-4.16
-4.18
TBSO
TBSO
O
OMe
OMOM
23b
f1 (ppm)


1s-3rbh628
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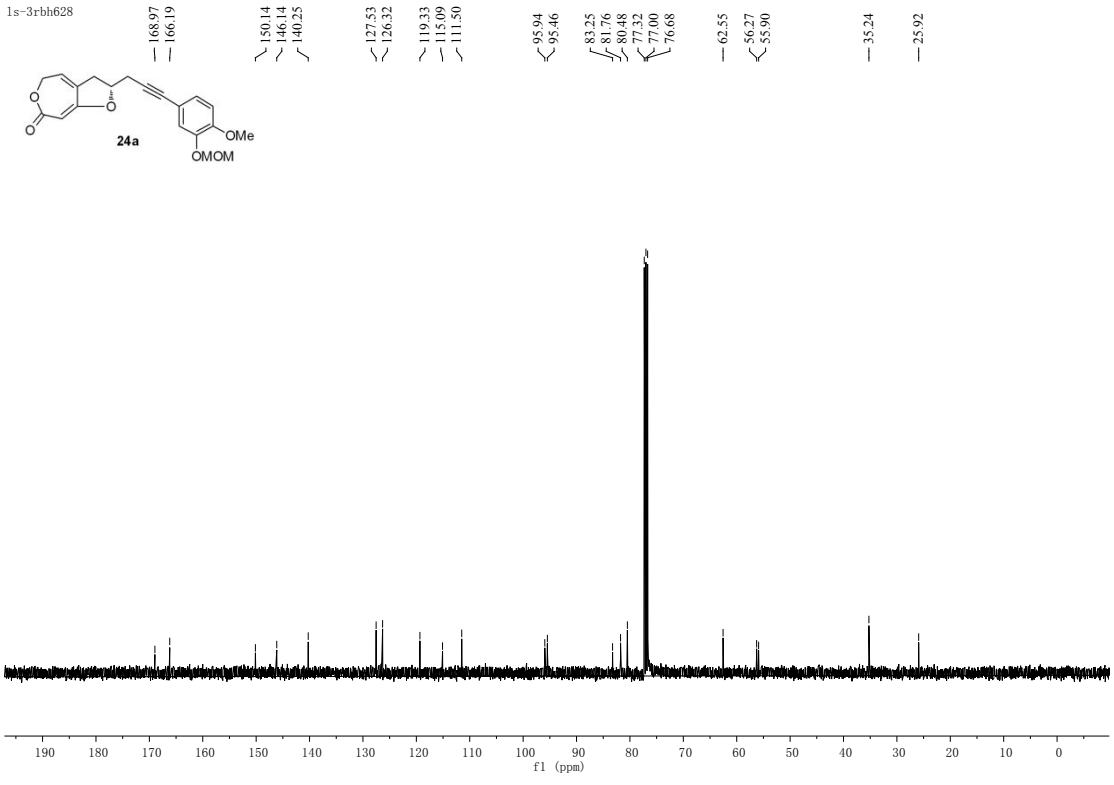
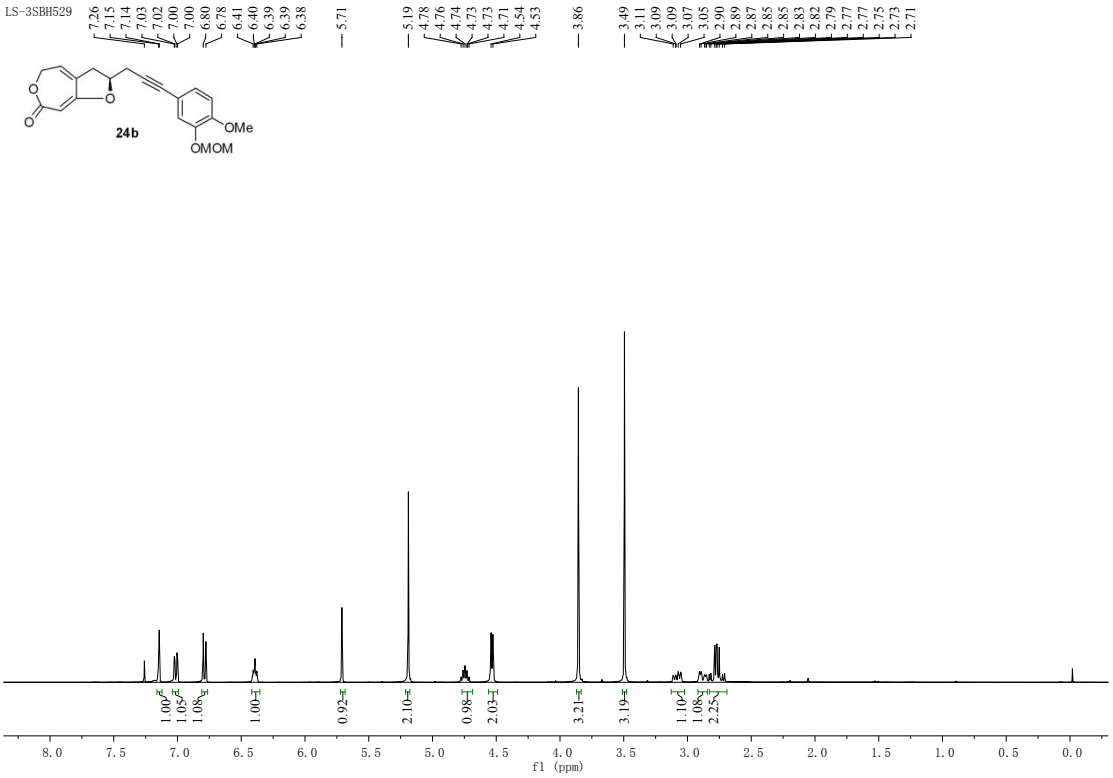
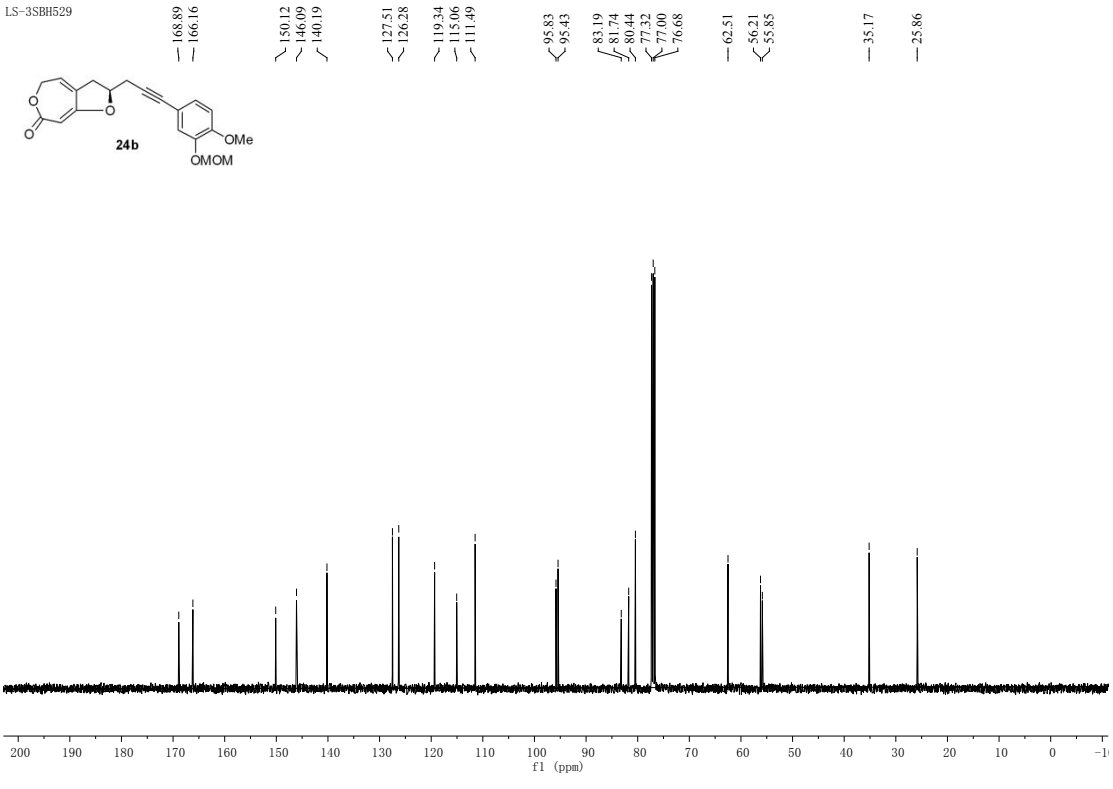
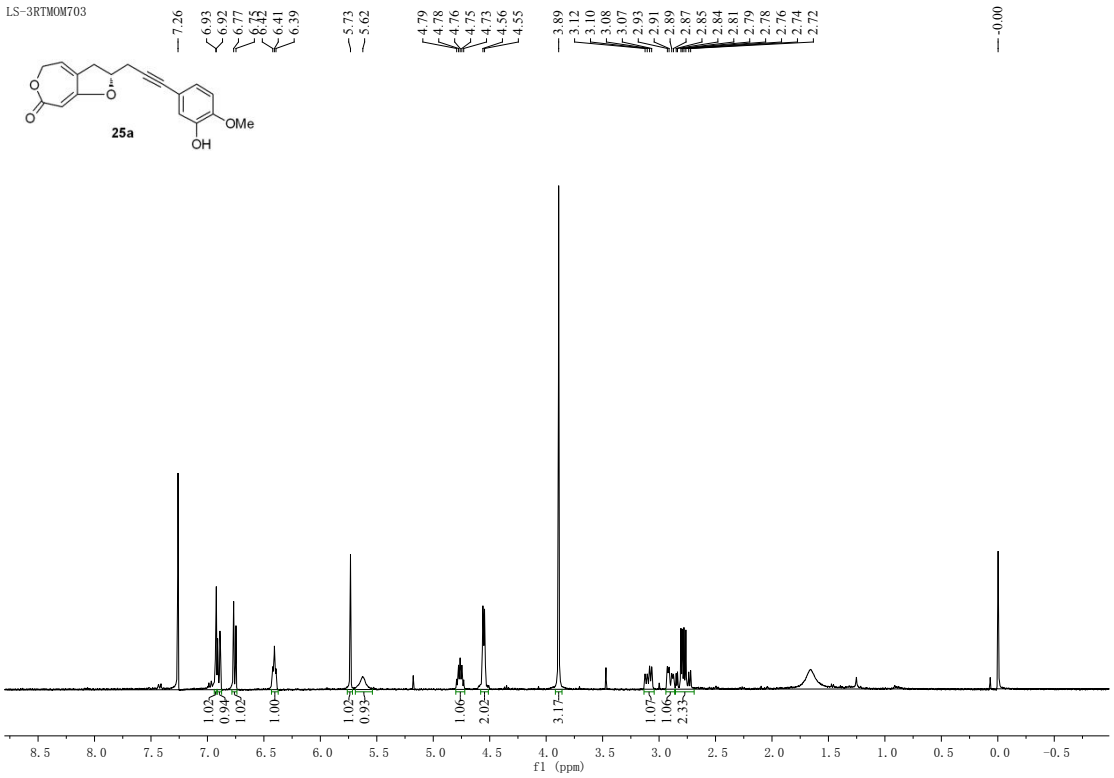
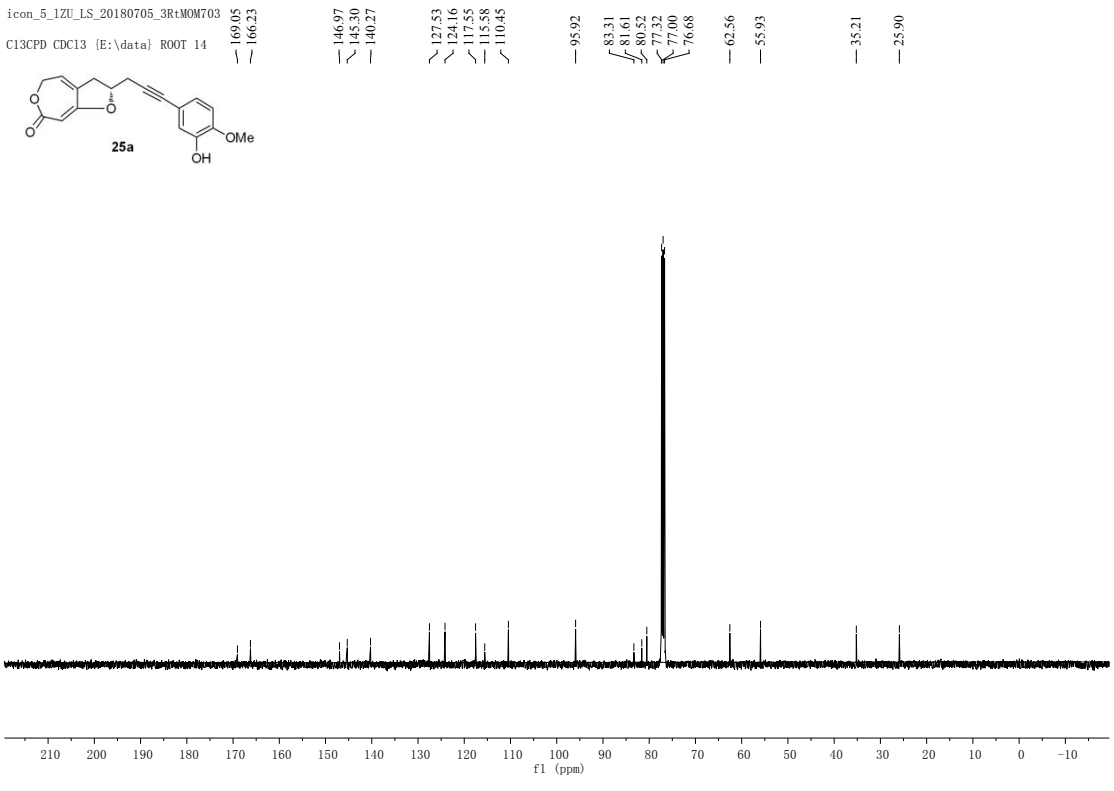
7.17
7.16
7.04
7.03
7.02
7.01
6.81
6.79
6.42
6.41
6.41
6.40
6.39
5.73
5.21
4.79
4.78
4.76
4.75
4.73
4.56
4.54
3.87
3.51
3.13
3.11
3.09
3.07
2.92
2.91
2.88
2.87
2.85
2.83
2.80
2.79
2.78
2.76
2.74
2.72
24a
OMe
OMOM
1.00
1.04
1.08
1.06
1.03
2.18
1.12
2.08
3.29
3.21
1.10
1.12
2.31
f1 (ppm)

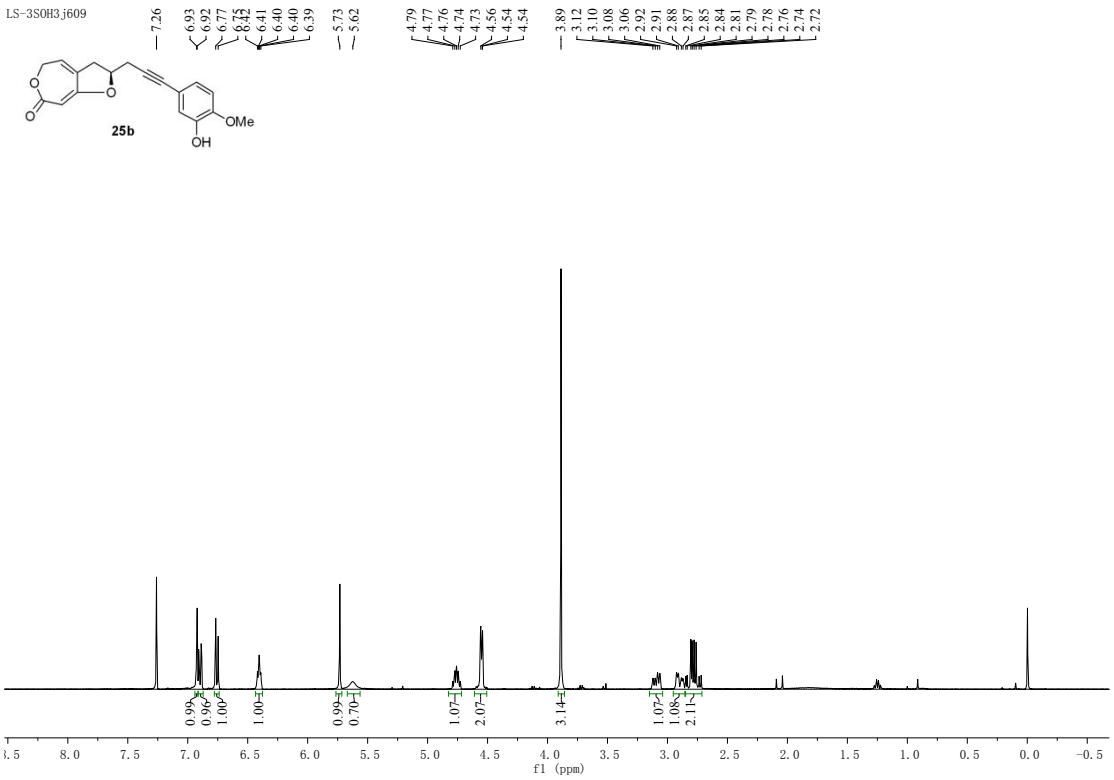

1s-3rbh628
168.97
166.19
150.14
146.14
140.25
127.53
126.32
119.33
115.09
111.50
95.94
95.46
83.25
81.76
80.48
77.32
77.00
76.68
62.55
56.27
55.90
35.24
25.92
24a
OMe
OMOM
f1 (ppm)

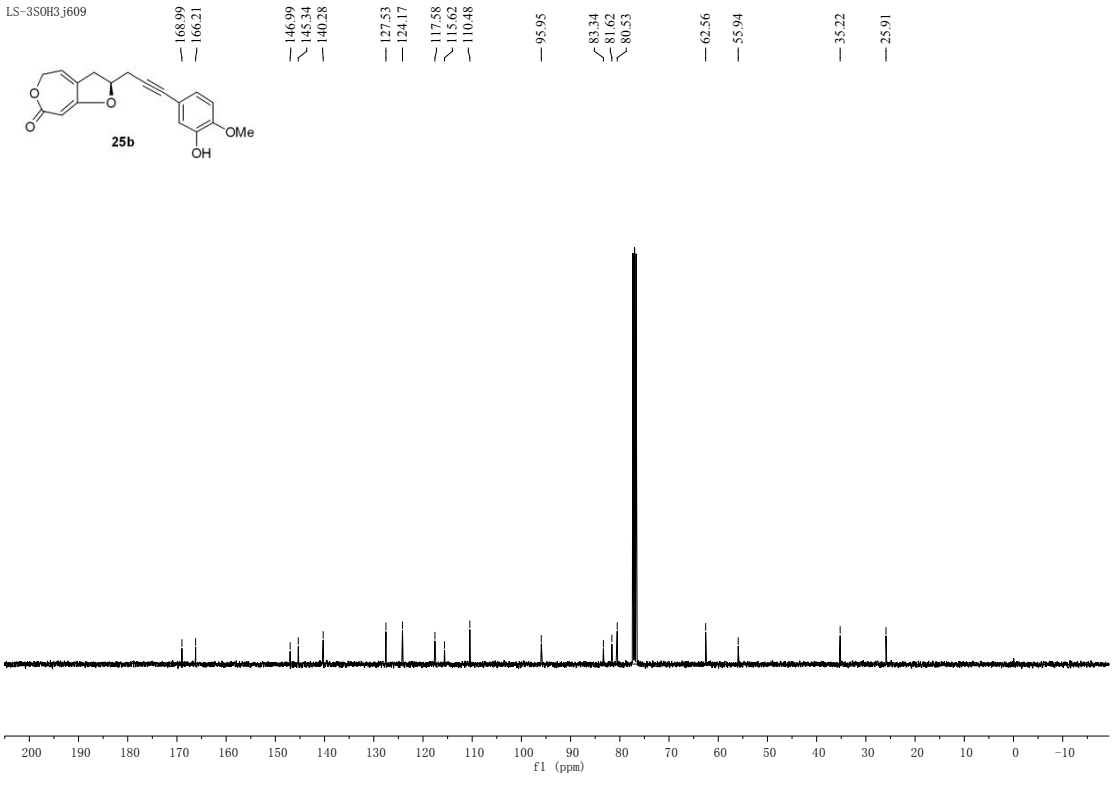

LS-3SBH529
7.26
7.15
7.14
7.03
7.02
7.00
7.00
6.80
6.78
6.41
6.40
6.39
6.39
6.38
5.71
5.19
4.78
4.76
4.74
4.73
4.73
4.71
4.54
4.53
3.86
3.49
3.11
3.09
3.09
3.07
3.05
2.90
2.89
2.87
2.85
2.85
2.83
2.82
2.79
2.77
2.77
2.75
2.73
2.71
24b
OMe
OMOM
1.00
1.05
1.08
1.00
0.92
2.10
0.98
2.03
3.21
3.19
1.10
1.08
2.25
f1 (ppm)

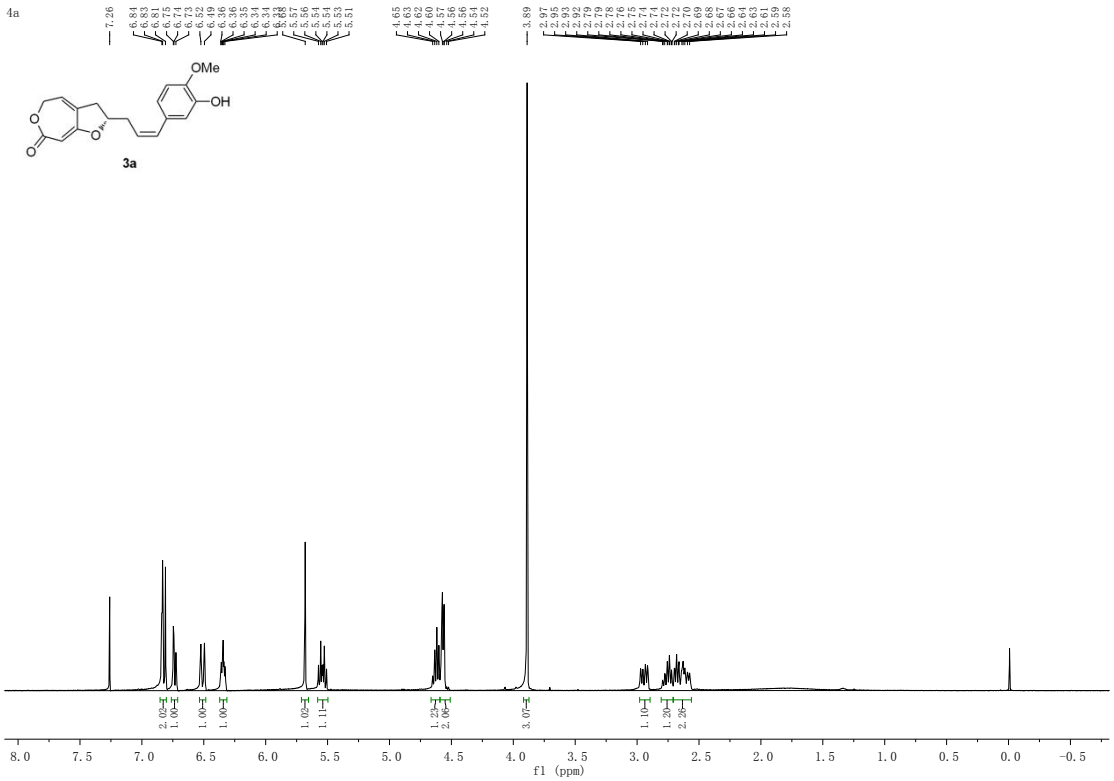

LS-3SBH529
168.89
166.16
150.12
146.09
140.19
127.51
126.28
119.34
115.06
111.49
95.83
95.43
83.19
81.74
80.44
77.32
77.00
76.68
62.51
56.21
55.85
35.17
25.86
24b
OMe
OMOM
f1 (ppm)

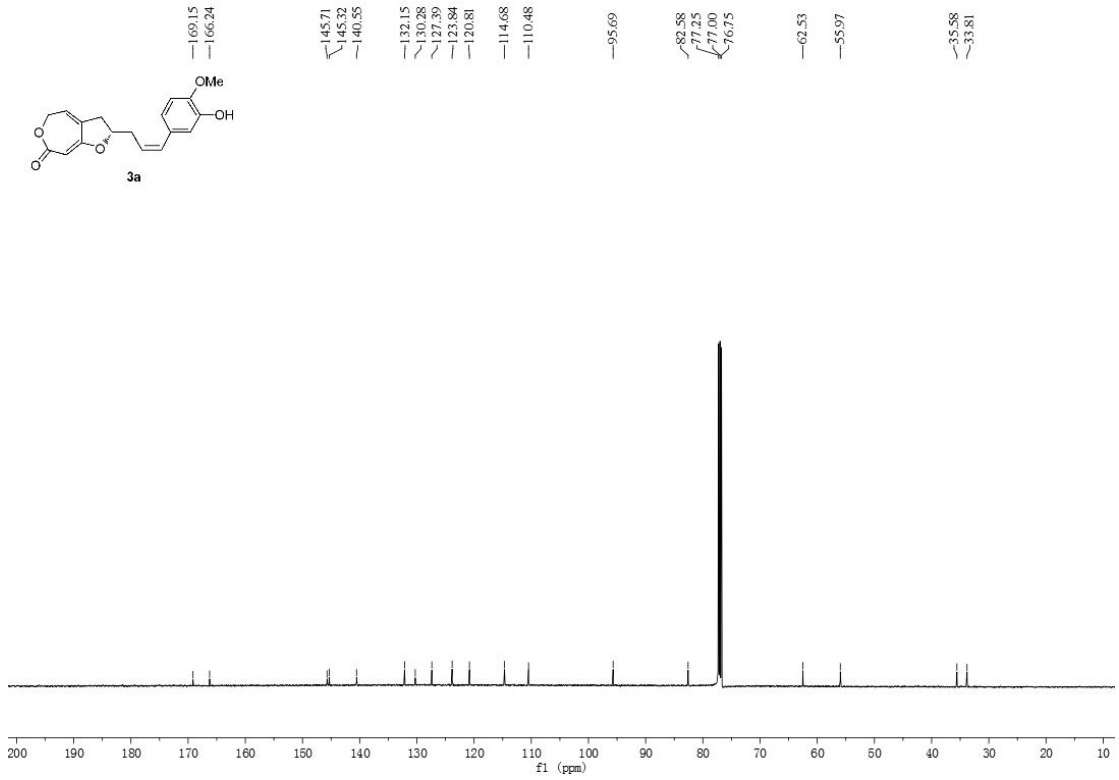

LS-3RTMOM703
7.26
6.93
6.92
6.77
6.75
6.42
6.41
6.39
5.73
5.62
4.79
4.78
4.76
4.75
4.73
4.56
4.55
3.89
3.12
3.10
3.08
3.07
2.93
2.91
2.89
2.87
2.85
2.84
2.81
2.79
2.78
2.76
2.74
2.72
0.00
OMe
OH
25a
1.02
0.94
1.02
1.00
1.02
0.93
1.06
2.02
3.17
1.07
1.06
2.33
f1 (ppm)

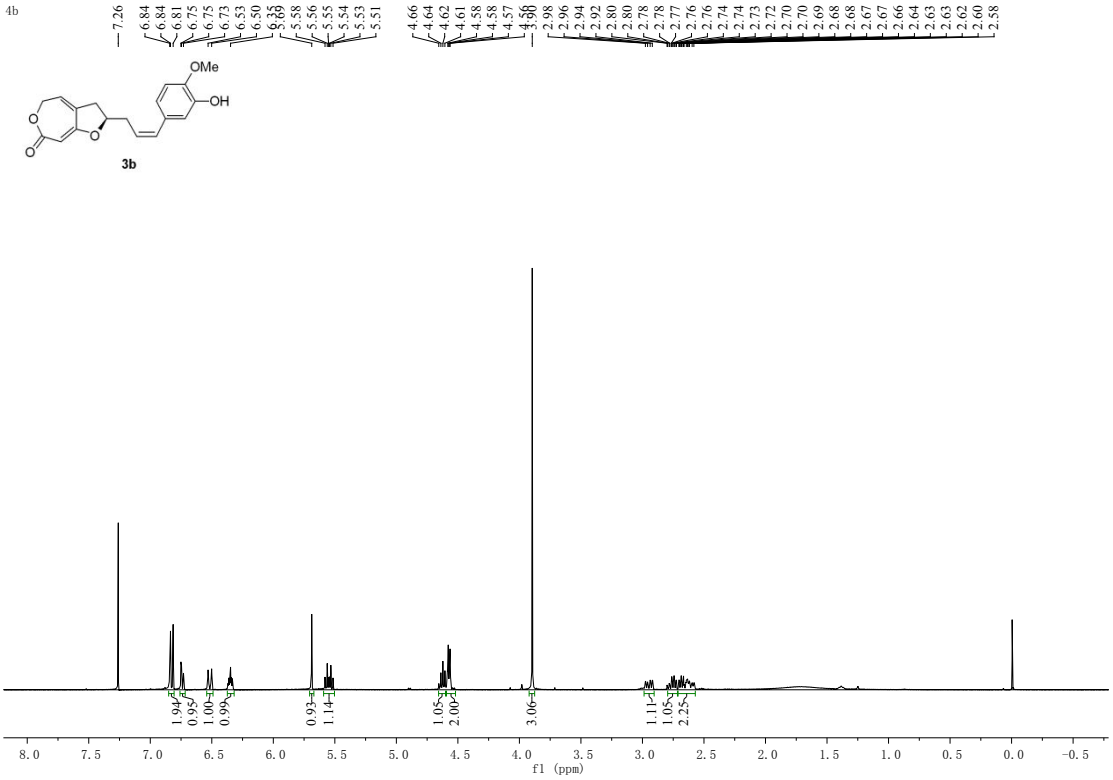

icon_5_1ZU_LS_20180705_3RtMOM703
C13CPD CDCl3 {E:\data} ROOT 14
169.05
166.23
146.97
145.30
140.27
127.53
124.16
117.55
115.58
110.45
95.92
83.31
81.61
80.52
77.32
77.00
76.68
62.56
55.93
35.21
25.90
OMe
OH
25a
f1 (ppm)

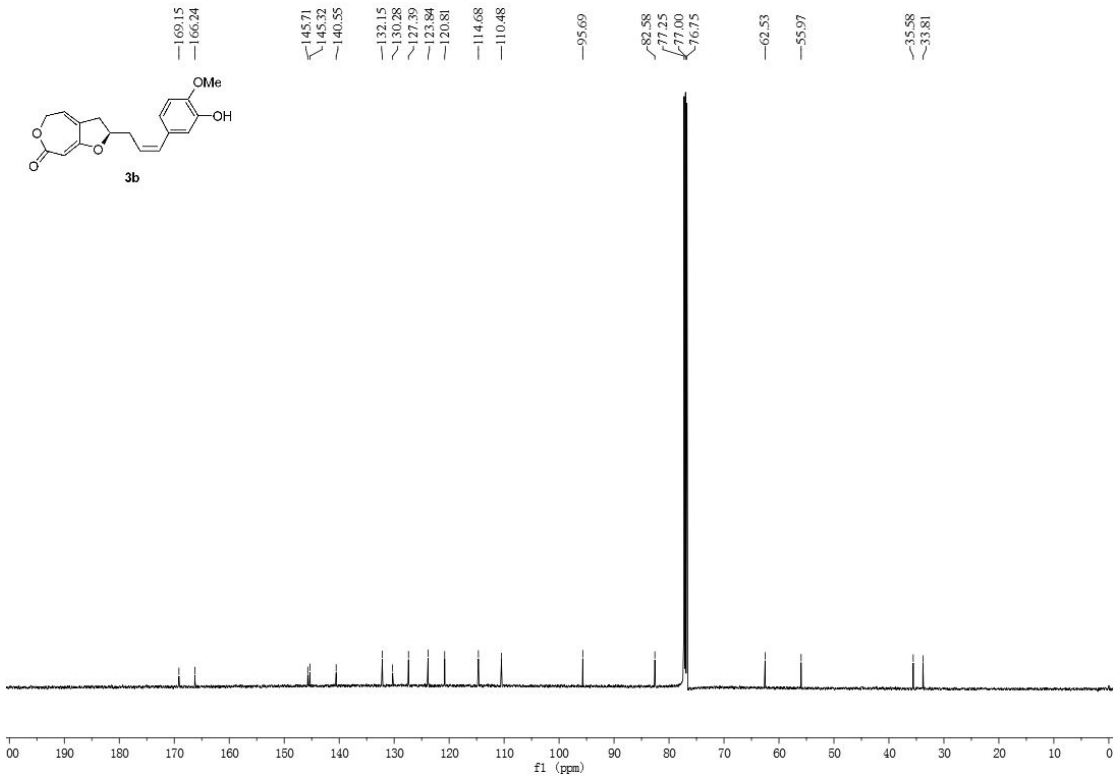

LS-3S0H3.j609
7.26
6.93
6.92
6.77
6.75
6.42
6.41
6.40
6.40
6.39
5.73
5.62
4.79
4.77
4.76
4.74
4.73
4.56
4.54
4.54
3.89
3.12
3.10
3.08
3.06
2.92
2.91
2.88
2.87
2.85
2.84
2.81
2.79
2.78
2.76
2.74
2.72
25b
OMe
OH
0.99
0.96
1.00
1.00
0.99
0.70
1.07
2.07
3.14
1.07
1.08
2.11
f1 (ppm)


LS-3S0H3.j609
168.99
166.21
146.99
145.34
140.28
127.53
124.17
117.58
115.62
110.48
95.95
83.34
81.62
80.53
62.56
55.94
35.22
25.91
25b
OMe
OH
f1 (ppm)


4a
OMe
OH
3a
f1 (ppm)


OMe
OH
3a
f1 (ppm)


4b
7.26
6.84
6.84
6.81
6.75
6.75
6.73
6.53
6.50
5.58
5.56
5.55
5.54
5.53
5.51
4.66
4.64
4.62
4.61
4.58
4.58
4.57
2.98
2.96
2.94
2.92
2.80
2.80
2.78
2.78
2.77
2.76
2.76
2.74
2.74
2.73
2.72
2.70
2.70
2.69
2.68
2.68
2.67
2.67
2.66
2.64
2.63
2.63
2.62
2.60
2.58
OMe
OH
3b
1.94
0.95
1.00
0.99
0.93
1.14
1.05
2.00
3.06
1.11
1.05
2.25
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


169.15
166.24
145.71
145.32
140.55
132.15
130.28
127.39
123.84
120.81
114.68
110.48
95.69
82.58
77.25
77.00
76.75
62.53
55.97
35.58
33.81
OMe
OH
3b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)