Supporting Information

Hydroalkynylative Cyclization of 1,6-Enynes with Terminal Alkynes

*Qi Teng, Nuligonda Thirupathi, Chen-Ho Tung and Zhenghu Xu**

xuzh@sdu.edu.cn

CONTENT:

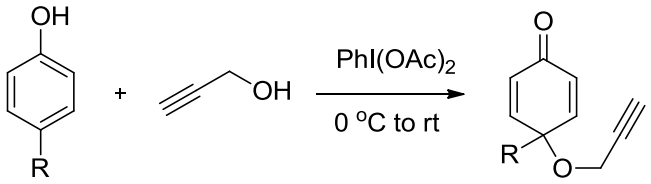
1. General Information.....S2
2. Preparation of Starting Materials.....S2
3. Preparation and Characterization of Compound 3.....S4
4. Preparation and Characterization of Compound 4 to 9.....S32
5. Scale up Experiment.....S39
6. Deuterium‐Labeling Experiments.....S40
7. X-ray Crystallography.....S42
8. NMR and HRMS Spectra of All Compounds.....S43
9. References.....S107

1. General Information

Unless otherwise noted, analytic grade solvents were used for the chromatography, and all the reagents were obtained commercially and used without further purification. All reactions were performed under nitrogen atmosphere and in a flame-dried or oven-dried glassware with magnetic stirring. Reactions were monitored by TLC. Solvents were dried with CaH_2. All NMR spectra were recorded on Bruker-500 MHz spectrometer. The chemical shifts (δ) and coupling constants (*J*) were expressed in ppm and Hz respectively. HRMS were measured on the Q-TOF6510 instruments.

2. Preparation of Starting Materials

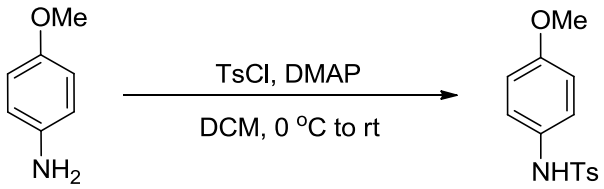
(1) General procedure for the synthesis of *O*-Tethered Alkynes



The meso-1,6-dienyne substrates **1** were prepared from commercially available 4-substituted phenols **S1** and propargyl alcohol using standard procedures[1] as following:

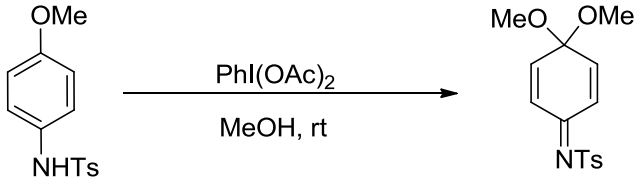
To a stirred solution of 4-substituted phenol **S1** (1.0 mmol) in 1 mL of propargyl alcohol was added $PhI(OAc)_2$ (PIDA, 1.2 eq, 1.2 mmol) in several portions at 0 ℃. The resulting reaction mixture was stirred at room temperature for overnight. Then the reaction mixture was diluted with water (10 mL) and extracted with ethyl acetate (15 mL × 3). The combined organic solvent was washed with brine (15 mL), dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography (EtOAc/hexane) to give the desired products **1a-1d**.

(2) General procedure for the synthesis of *N*-Tethered Alkyne[2]



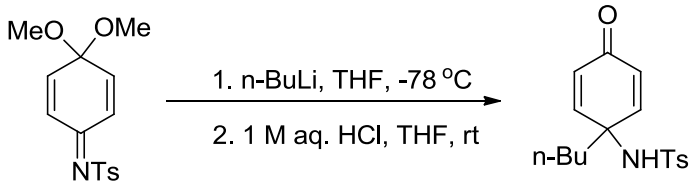
S2 **S3**

To a solution of 4-methoxyaniline **S2** (10 mmol, 1.0 equiv.) and DMAP (1 mmol, 0.1 equiv) in DCM (40 mL) was added the TsCl (11 mmol, 1.1 equiv.) at 0 ℃. The reaction was allowed to stir at 0 ℃ for 0.5 h and gradually warmed at room temperature. After the reaction was complete, the mixture was added saturated NH_4Cl. The aqueous layer was extracted with DCM for 3 times (20 mL × 3). Then the organic phase was combined and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by a silica gel column chromatography to give **S3** as a white solid.



S3 **S4**

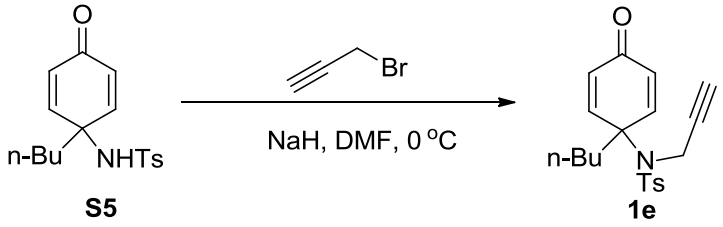
To a solution of Ts-protected 4-methoxyaniline **S3** (10 mmol, 1.0 equiv) and MeOH (40mL), $PhI(OAc)_2$ (12 mmol, 1.2 equiv.) was added to this solution over 5 minutes, and keep the stirring for 0.5 hour. The reaction was continued until completion of starting material monitored by TLC. Then, the mixture was quenched by sat. aqueous solution of $NaHCO_3$ and extracted with DCM three times. The extract was dried over Na_2SO_4 and concentrated under reduced pressure to give the residue which was purified by a silica gel column chromatography to give **S4**.



S4 **S5**

To a solution of substrate **S4** (1 equiv) in dry THF (0.3 M) was added n-BuLi (1.2 equiv) slowly at -78 ℃ under inert atmosphere. The resulting mixture was stirred at same temperature for 2 h. The reaction mixture was quenched with cold water (20

mL) and extracted with EtOAc (3 times). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in *vacuo*. Later, the crude reaction mixture in THF (1 M) was added 1M HCl (0.5 mL for 1 mmol) at room temperature and stirred for overnight. The reaction mixture was quenched by saturated aqueous $NaHCO_3$, extracted with EtOAc (40 mL× 3), dried over anhydrous Na_2SO_4, filtered and concentrated in *vacuo*. The residue was purified by flash column chromatography to give the pure cyclohexadienone **S5**.

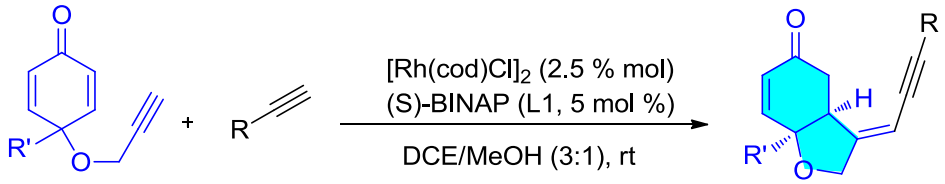


S5 **1e**

To a well-stirred solution of substrate **S5** (1 equiv) in DMF (0.5 M) was added NaH (2.0 equiv) portionwise at 0 ℃ under inert atmosphere. The resulting reaction mixture was added 3-bromopropyne (1.5 equiv) at 0 ℃ and stirred for 30 min. The reaction mixture was quenched by saturated aqueous NH_4Cl and extracted with 1:1 ratio of hexanes/EtOAc (3 times). The combined organic solvent was dried over Na_2SO_4, filtered, and evaporated under reduced pressure. The residue was purified by flash column chromatography (EtOAc/Hexane) to afford **1e**.

3. **Preparation and Characterization of Compound 3**

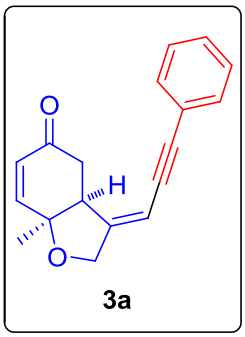
General Procedure for Rhodium-Catalyzed Enantioselective Cross-dimerization of Alkynes with Enynes



1 **2** **3**

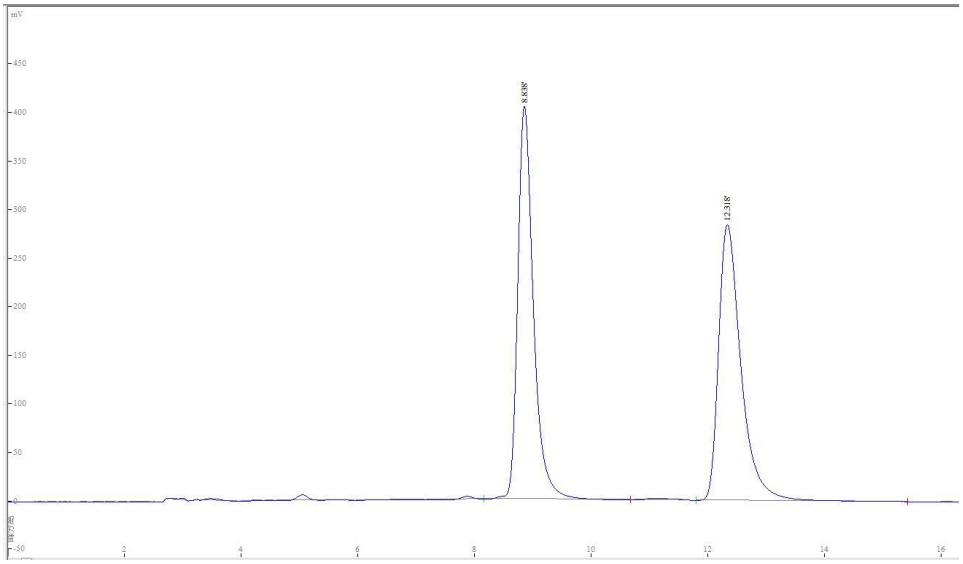
To a mixture of **1** (0.2 mmol, 1 equiv), $[Rh(cod)Cl]_2$ (0.005 mmol, 2.5 mmol%), and (S)-BINAP (0.010 mmol, 5.0 mol %), 1.5 mL DCE was added under nitrogen atmosphere . Then, to the stirred solution above, **2** (0.4 mmol, 2.0 equiv) and 0.5 ml MeOH was added quikly. The reaction system was stirred at room temperature

overnight. After the reaction was completed (determined by TLC analysis), the solvent was evaporated under reduced pressure, and purified by column chromatography (silica gel, Petroleum ether/ EtOAc: 10/1 to 3/1) to afford the desired product **3**.

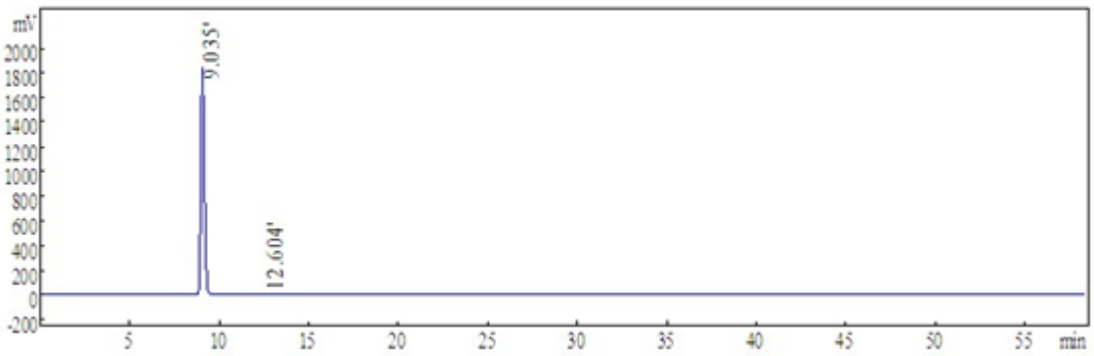


3a

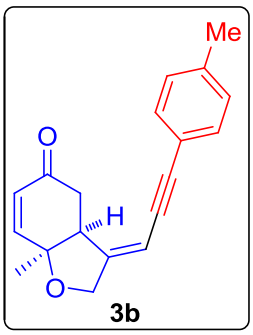
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 6.5, 3.2 Hz, 2H), 7.33 (dd, *J* = 5.0, 1.9 Hz, 3H), 6.54 (dd, *J* = 10.3, 1.4 Hz, 1H), 6.03 (d, *J* = 10.3 Hz, 1H), 5.73 (d, *J* = 2.5 Hz, 1H), 4.50 (d, *J* = 14.4 Hz, 1H), 4.31 (dt, *J* = 14.3, 2.5 Hz, 1H), 3.72 – 3.57 (m, 1H), 3.27 – 3.16 (m, 1H), 2.68 (dd, *J* = 17.0, 6.1 Hz, 1H), 1.55 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.66, 153.7, 150.3, 131.3, 130.1, 128.4, 128.4, 123.1, 102.2, 95.6, 84.7, 80.5, 70.4, 47.9, 36.2, 23.4. HRMS (ESI, m/z) calcd for $C_{18}H_{16}O_2$ $[M+H]^+$ 265.1229, found 265.1229. $[\alpha]^{27}_D$ = -242.9 ° (c 0.46, $CHCl_3$); 99% ee; Chiral HPLC analysis of the product: Phenomenex 00G-4457-E0 250X4.6 mm 5u column; hexane/2-propanol =85/15, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 9.0 min (major), 12.6 min (minor).



Peak#	Ret.Time	Area	Area %
1	8.838	7597408	50.06
2	12.318	7577711	49.94
Total		15175119	100

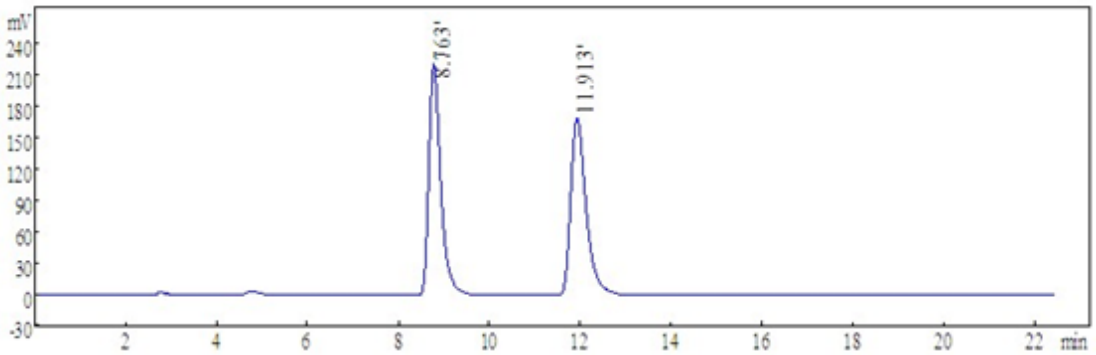


Peak#	Ret.Time	Area	Area %
1	9.035	25399662	99.44
2	12.604	143451	0.5616
Total		25543113	100



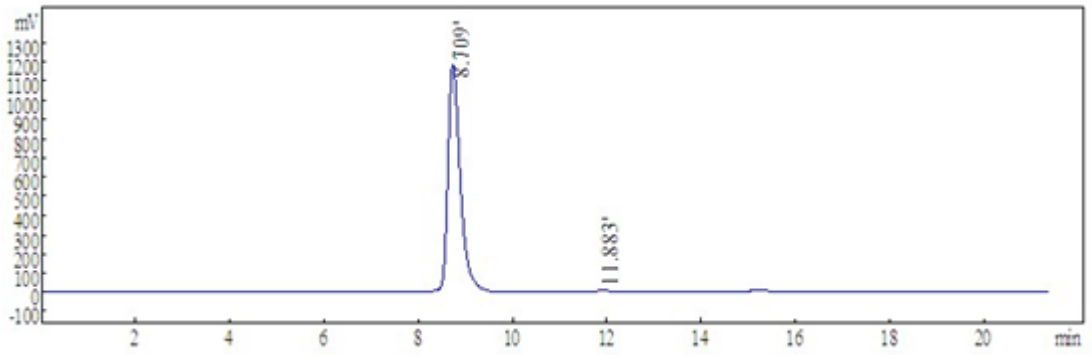
3b

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.53 (dd, *J* = 10.3, 1.2 Hz, 1H), 6.02 (d, *J* = 10.3 Hz, 1H), 5.71 (q, 2.2 Hz, 1H), 4.48 (d, *J* = 14.4 Hz, 1H), 4.30 (dt, *J* = 14.3, 2.5 Hz, 1H), 3.62 (dd, *J* = 17.0, 3.4 Hz, 1H), 3.29 – 3.13 (m, 1H), 2.67 (dd, *J* = 17.0, 6.1 Hz, 1H), 2.35 (s, 3H), 1.54 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.7, 153.2, 150.3, 138.6, 131.2, 130.1, 129.1, 120.0, 102.4, 95.9, 84.19, 80.5, 70.4, 47.9, 36.2, 23.4, 21.5. HRMS (ESI, m/z) calcd for $C_{19}H_{18}O_2$ $[M+H]^+$ 279.1380, found 279.1384. $[\alpha]^{29}_D$ = -212.7 ° (c 0.58, $CHCl_3$); 98% ee; Chiral HPLC analysis of the product: Phenomenex 00G-4457-E0 250X4.6 mm 5u column; hexane/2-propanol = 90/10, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 8.7 min (major), 11.9 min (minor).

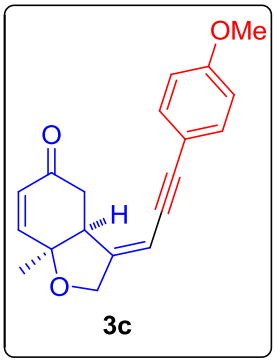


Peak#	Ret.Time	Area	Area %
1	8.763	4083202	50.14

2	11.913	4060320	49.86
Total		8143522	100

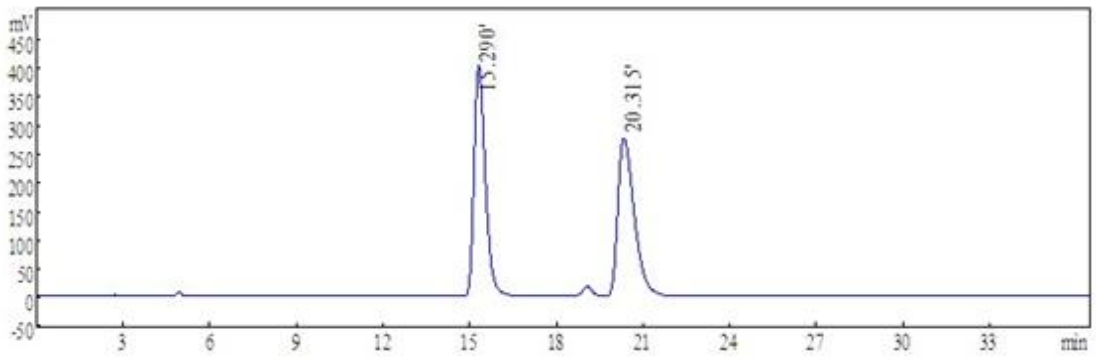


Peak#	Ret.Time	Area	Area %
1	8.709	21951938	98.91
2	11.883	240423	1.093
Total		22192361	100

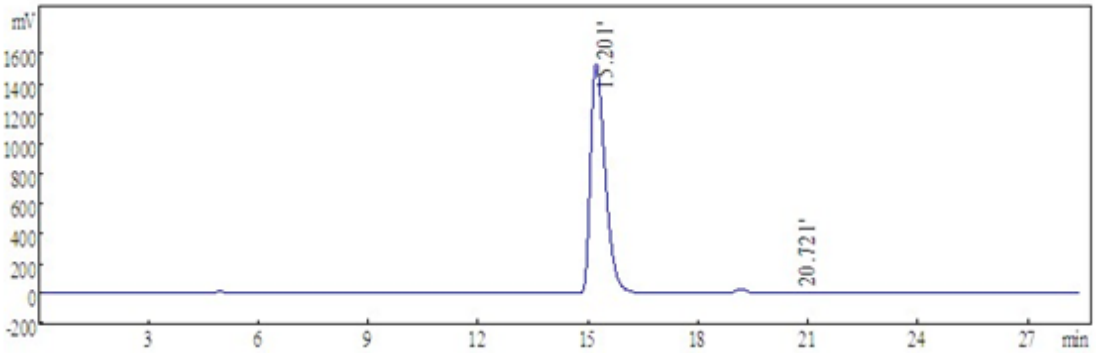


3c

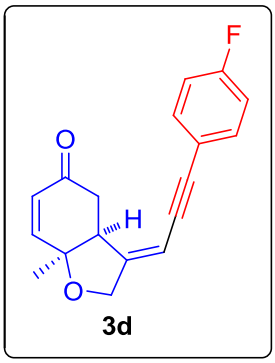
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.9 Hz, 2H), 6.85 (d, *J* = 8.9 Hz, 2H), 6.53 (dd, *J* = 10.3, 1.4 Hz, 1H), 6.02 (dd, *J* = 10.3, 0.8 Hz, 1H), 5.71 (dd, *J* = 4.9, 2.3 Hz, 1H), 4.48 (ddd, *J* = 14.2, 1.6, 1.0 Hz, 1H), 4.30 (dt, *J* = 14.2, 2.6 Hz, 1H), 3.81 (s, 3H), 3.62 (ddd, *J* = 16.9, 3.6, 0.8 Hz, 1H), 3.26 – 3.17 (m, 1H), 2.66 (dd, *J* = 17.0, 6.1 Hz, 1H), 1.54 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.8, 159.8, 152.7, 150.3, 132.8, 130.1, 115.3, 114.1, 102.4, 95.7, 83.5, 80.5, 70.4, 55.3, 47.9, 36.2, 23.4. HRMS (ESI, m/z) calcd for $C_{19}H_{19}O_3$ $[M+H]^+$ 295.1334, found 295.1334. $[\alpha]^{29}_D$ = -195.2 °(c 0.61, $CHCl_3$); 98% ee; Chiral HPLC analysis of the product: Phenomenex 00G-4457-E0 250X4.6 mm 5μ column; hexane/2-propanol = 90/10, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 15.2 min (major), 20.7 min (minor).



Peak#	Ret.Time	Area	Area %
1	15.290	11037956	50.13
2	20.315	10978556	49.87
Total		22016512	100



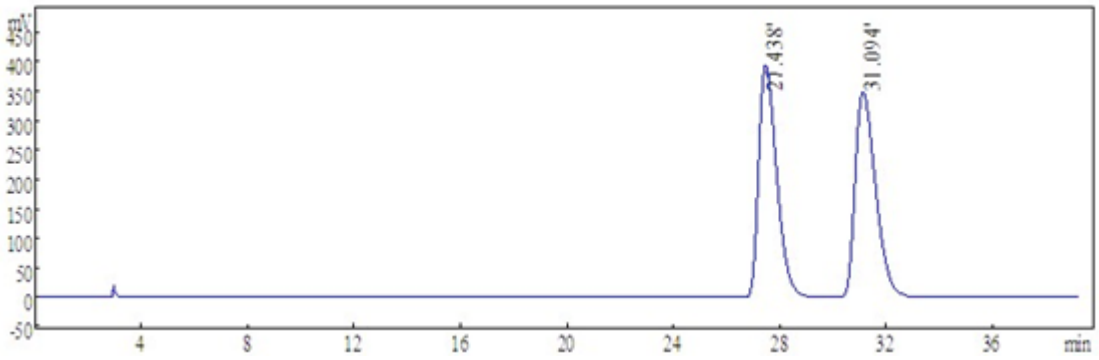
Peak#	Ret.Time	Area	Area %
1	15.201	42994717	99.11
2	20.721	386220	0.8903
Total		43380937	100



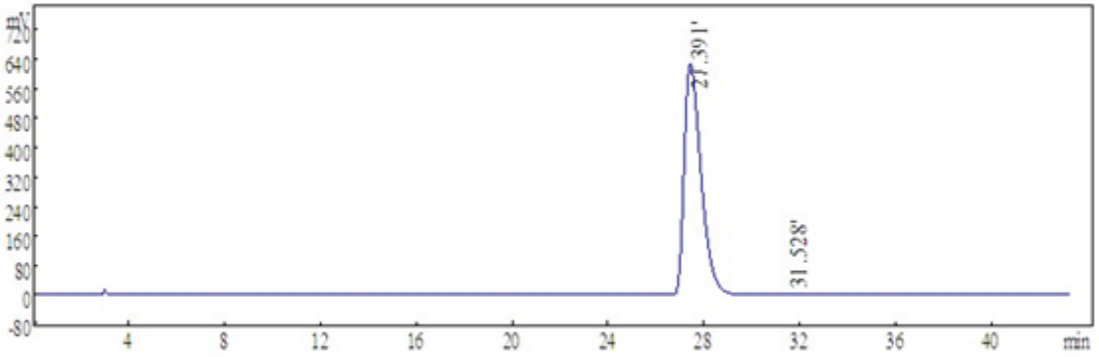
3d

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.41 (m, 2H), 7.06 – 6.98 (m, 2H), 6.53 (dd, *J* = 10.3, 1.5 Hz, 1H), 6.02 (dd, *J* = 10.3, 0.9 Hz, 1H), 5.70 (dd, *J* = 4.8, 2.3 Hz, 1H), 4.49 (ddd, *J* = 14.4, 1.7, 1.0 Hz, 1H), 4.30 (dt, *J* = 14.4, 2.6 Hz, 1H), 3.60 (ddd, *J* = 16.9, 3.5, 0.9 Hz, 1H), 3.28 – 3.12 (m, 1H), 2.67 (dd, *J* = 16.9, 6.0 Hz, 1H), 1.54 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.67, 162.6 (d, *J* = 249.5 Hz), 153.8, 150.4, 133.2 (d, *J* = 8.3 Hz), 130.1, 119.2 (d, *J* = 3.5 Hz), 115.7 (d, *J* = 22.7 Hz), 102.0, 94.5, 84.42 (d, *J* = 1.3 Hz), 80.6, 70.4, 47.9, 36.2, 23.3. HRMS (ESI, m/z) calcd for $C_{18}H_{15}FO_2$

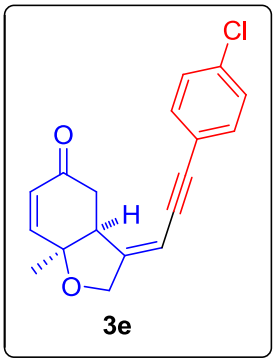
$[M+H]^+$ 283.1134, found 283.1122. $[\alpha]^{26}_D$ = -220.2 °(c 1.06, $CHCl_3$); >99% ee; Chiral HPLC analysis of the product: Phenomenex 00G-4457-E0 250X4.6 mm 5u column; hexane/2-propanol = 98/2, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 27.4 min (major), 31.5 min (minor).



Peak#	Ret.Time	Area	Area %
1	27.438	18709666	49.78
2	31.094	18874670	50.22
Total		37584336	100



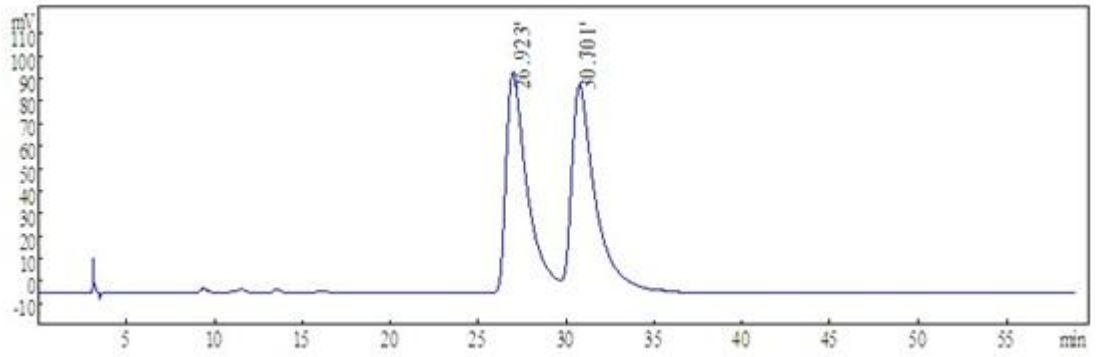
Peak#	Ret.Time	Area	Area %
1	27.391	30972749	99.75
2	31.528	79437	0.2558
Total		31052186	100



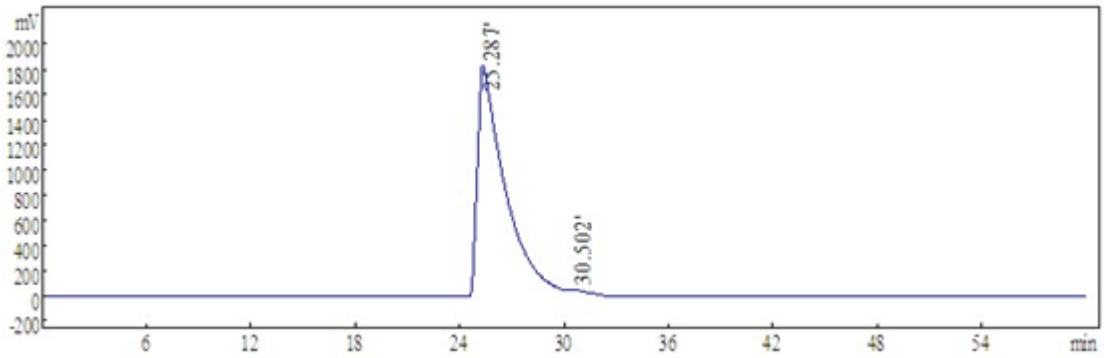
3e

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 2H), 7.25 – 7.21 (m, 2H), 6.47 (dd, *J* = 10.3, 1.5 Hz, 1H), 5.96 (dd, *J* = 10.3, 0.9 Hz, 1H), 5.64 (dd, *J* = 4.9, 2.3 Hz, 1H), 4.42 (ddd, *J* = 14.5, 1.8, 1.0 Hz, 1H), 4.23 (dt, *J* = 14.4, 2.6 Hz, 1H), 3.52 (ddd, *J* = 16.9,

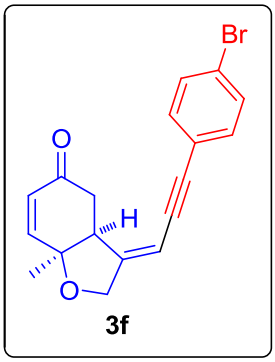
3.5, 0.9 Hz, 1H), 3.17 – 3.08 (m, 1H), 2.60 (dd, *J* = 16.9, 6.0 Hz, 1H), 1.48 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.7, 153.17, 149.47, 133.47, 131.57, 129.07, 127.77, 120.57, 100.97, 93.47, 84.67, 79.6, 69.4, 47.0, 35.20, 22.3. HRMS (ESI, m/z) calcd for $C_{18}H_{15}ClO_2$ $[M+H]^+$ 299.0833, found 299.0838. $[\alpha]^{27}_D$ = -196.8 ° (c 1.06, $CHCl_3$); >99% ee; Chiral HPLC analysis of the product: Daicel Chiralpak OJ-H 250X4.6 mm 5u column; hexane/2-propanol = 95/5, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 25.3 min (major), 30.5 min (minor).



Peak#	Ret.Time	Area	Area %
1	26.923	7533778	50
2	30.701	7533254	50
Total		15067032	100

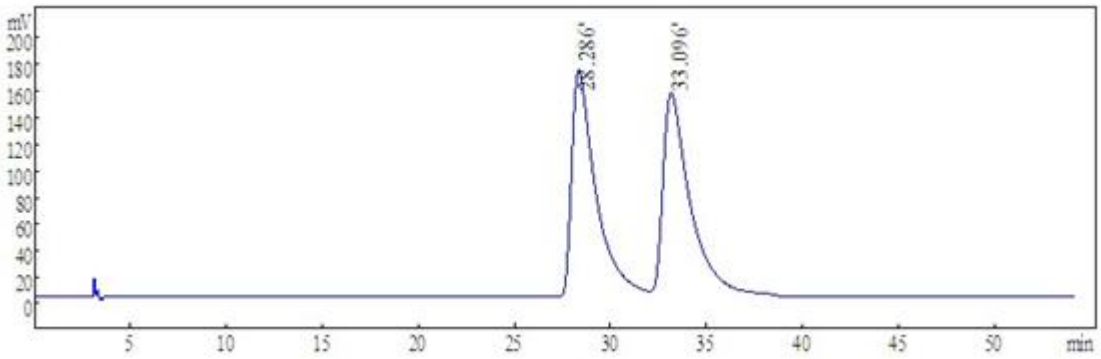


Peak#	Ret.Time	Area	Area %
1	25.287	195594816	99.74
2	30.502	524139	0.2673
Total		196118955	100

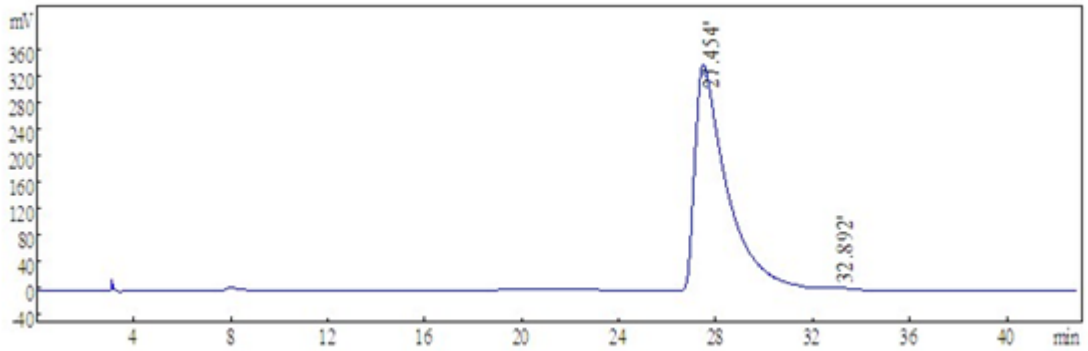


3f

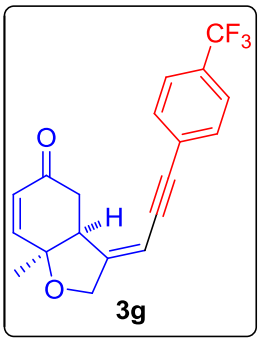
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.43 (m, 2H), 7.36 – 7.29 (m, 2H), 6.54 (dd, *J* = 10.3, 1.5 Hz, 1H), 6.03 (dd, *J* = 10.3, 0.8 Hz, 1H), 5.70 (dd, *J* = 4.9, 2.3 Hz, 1H), 4.49 (ddd, *J* = 14.4, 1.7, 0.9 Hz, 1H), 4.30 (dt, *J* = 14.5, 2.6 Hz, 1H), 3.59 (ddd, *J* = 16.9, 3.5, 0.9 Hz, 1H), 3.28 – 3.14 (m, 1H), 2.67 (dd, *J* = 16.9, 6.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.5, 154.3, 150.4, 132.8, 131.7, 130.1, 122.7, 122.0, 101.9, 94.5, 85.8, 80.6, 70.4, 48.0, 36.2, 23.4. HRMS (ESI, m/z) calcd for $C_{18}H_{15}BrO_2$ $[M+Na]^+$ 365.0153, found 365.0151. $[\alpha]^{26}_D$ = -170.0 ° (c 1.26, $CHCl_3$); >99% ee; Chiral HPLC analysis of the product: Daicel Chiralpak OJ-H 250X4.6 mm 5u column; hexane/2-propanol = 95/5, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 27.5 min (major), 32.9 min (minor).



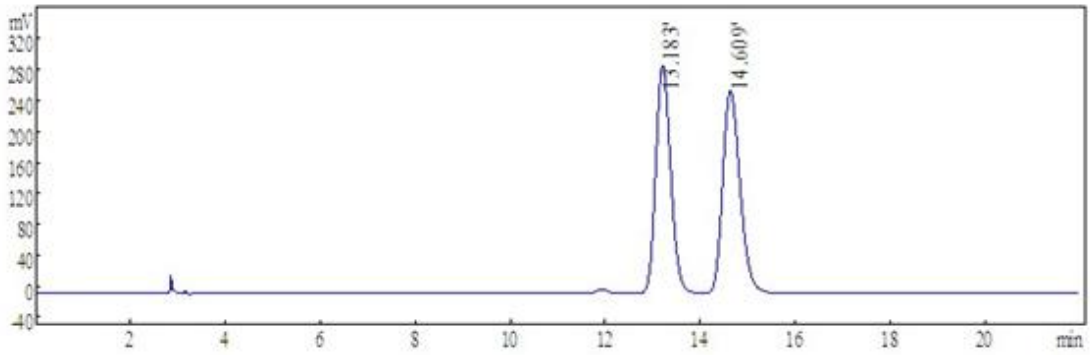
Peak#	Ret.Time	Area	Area %
1	28.286	14444146	50.34
2	33.096	14246797	49.66
Total		28690943	100



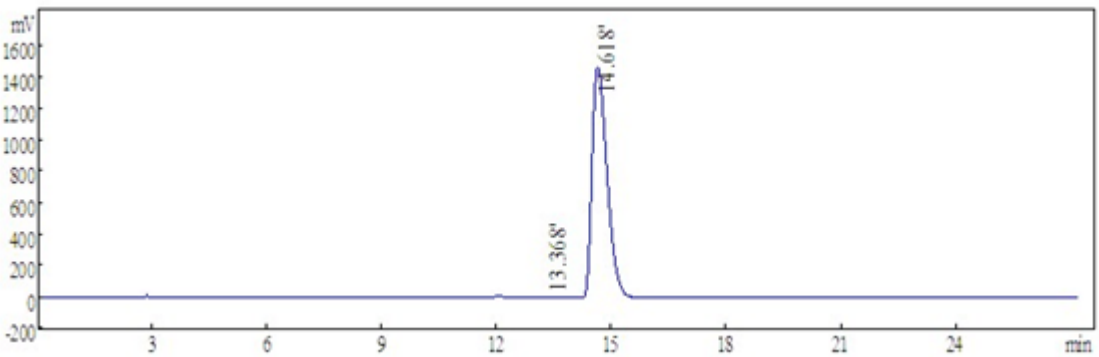
Peak#	Ret.Time	Area	Area %
1	27.454	30728422	99.79
2	32.892	65411	0.2124
Total		30793833	100



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 – 7.43 (m, 4H), 6.47 (dd, *J* = 10.3, 1.4 Hz, 1H), 5.96 (d, *J* = 10.2 Hz, 1H), 5.66 (dd, *J* = 4.7, 2.2 Hz, 1H), 4.45 (d, *J* = 14.6 Hz, 1H), 4.25 (dt, *J* = 14.6, 2.5 Hz, 1H), 3.53 (dd, *J* = 16.9, *J* = 3.2, 1H), 3.22 – 3.07 (m, 1H), 2.62 (dd, *J* = 16.9, 6.0 Hz, 1H), 1.49 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.5, 155.2, 150.4, 131.6, 130.16, 126.9, 125.3 (q, *J* = 3.8 Hz), 125.0, 122.8, 101.7, 94.1, 87.0, 80.7, 70.4, 48.1, 36.3, 23.3. HRMS (ESI, m/z) calcd for $C_{19}H_{15}F_3O_2$ $[M+H]^+$ 333.1102, found 333.1107. $[\alpha]^{26}_D$ = -316.7 ° (c 0.72, $CHCl_3$); 99% ee; Chiral HPLC analysis of the product: Phenomenex 00G-4457-E0 250X4.6 mm 5u column; hexane/2-propanol = 95/5, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 13.4 min (minor), 14.6 min (major).

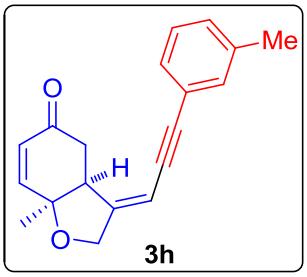


Peak#	Ret.Time	Area	Area %
1	13.183	6425727	49.18
2	14.609	6640352	50.82
Total		13066079	100



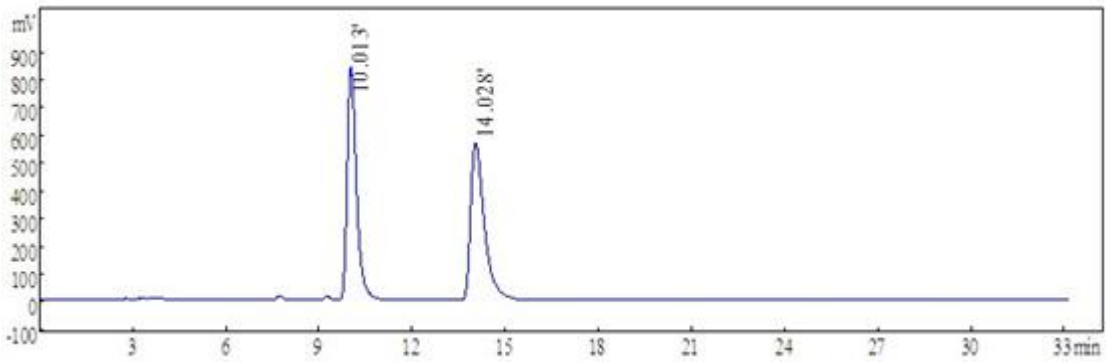
Peak#	Ret.Time	Area	Area %
1	13.368	279214	0.6856

2	14.618	40445606	99.32
Total		40724820	100

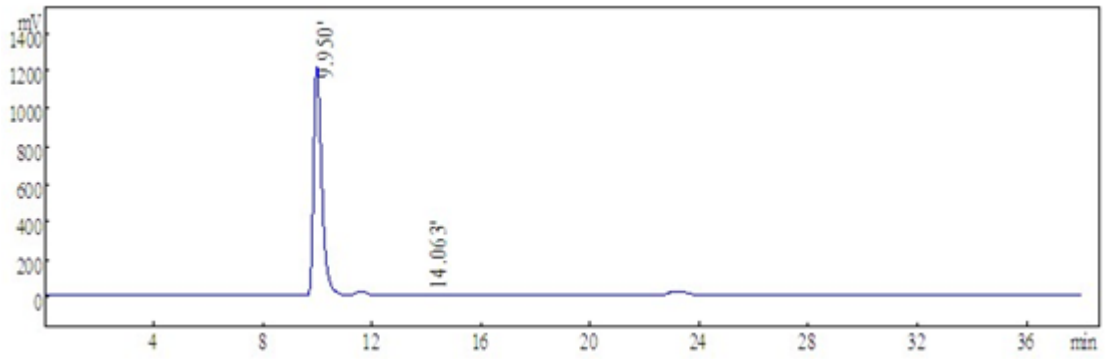


3h

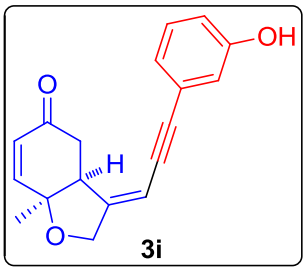
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.8 Hz, 2H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.06 (d, *J* = 7.6 Hz, 1H), 6.46 (dd, *J* = 10.3, 1.4 Hz, 1H), 5.95 (dd, *J* = 10.3, 0.7 Hz, 1H), 5.64 (q, *J* = 2.4 Hz, 1H), 4.41 (d, *J* = 14.3 Hz, 1H), 4.23 (dt, *J* = 14.3, 2.5 Hz, 1H), 3.55 (ddd, *J* = 16.9, 3.6, 0.7 Hz, 1H), 3.26 – 3.00 (m, 1H), 2.60 (dd, *J* = 17.0, 6.1 Hz, 1H), 2.26 (s, 3H), 1.47 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.7, 153.5, 150.3, 138.0, 131.8, 130.1, 129.3, 128.5, 128.3, 122.9, 102.3, 95.9, 84.4, 80.5, 70.4, 47.9, 36.2, 23.4, 21.2. HRMS (ESI, m/z) calcd for $C_{19}H_{18}O_2$ $[M+Na]^+$ 301.1199, found 301.1203. $[\alpha]^{26}_D$ = -254.2 ° (c 1.05, $CHCl_3$); 99% ee; Chiral HPLC analysis of the product: Phenomenex 00G-4457-E0 250X4.6 mm 5u column; hexane/2-propanol = 90/10, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 10.0 min (major), 14.1 min (minor).



Peak#	Ret.Time	Area	Area %
1	10.013	17436931	49.75
2	14.028	17612576	50.25
Total		35049507	100

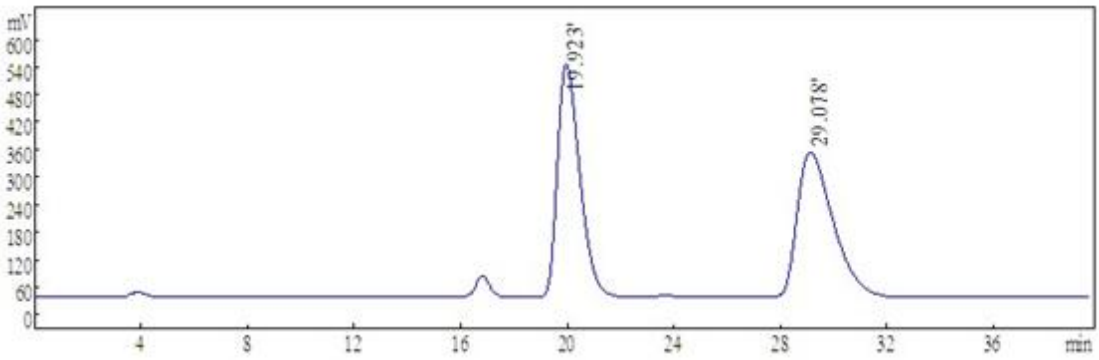


Peak#	Ret.Time	Area	Area %
1	9.950	25340474	99.3
2	14.063	178126	0.698
Total		25518600	100

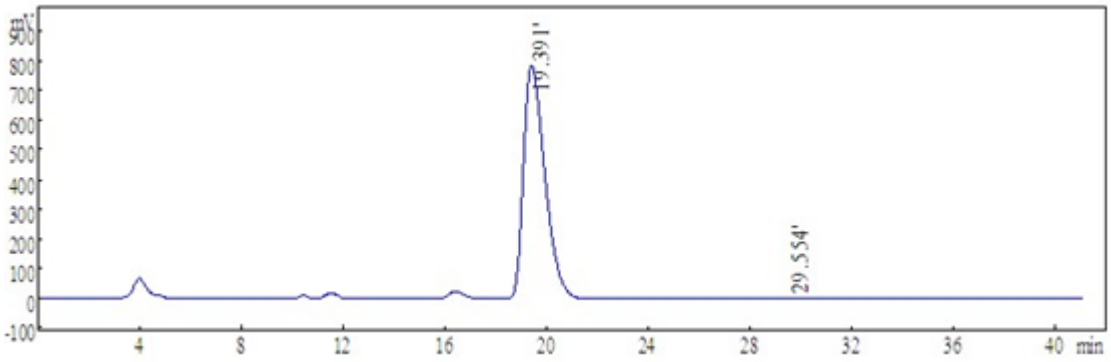


3i

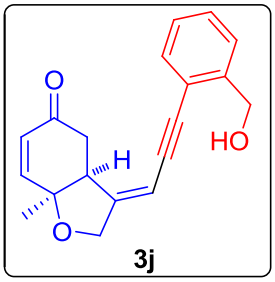
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 (t, *J* = 7.9 Hz, 1H), 6.99 – 6.94 (m, 2H), 6.88 – 6.78 (m, 1H), 6.74 (s, 1H), 6.58 (dd, *J* = 10.2, 1.3 Hz, 1H), 6.06 (d, *J* = 10.2 Hz, 1H), 5.71 (d, *J* = 2.4 Hz, 1H), 4.50 (d, *J* = 14.5 Hz, 1H), 4.30 (dt, *J* = 14.4, 2.5 Hz, 1H), 3.70 (dd, *J* = 17.1, 2.9 Hz, 1H), 3.26 – 3.11 (m, 1H), 2.69 (dd, *J* = 17.1, 6.0 Hz, 1H), 1.55 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.9, 154.9, 152.3, 150.3, 128.9, 128.5, 123.0, 122.40, 117.1, 115.0, 101.3, 94.7, 83.4, 79.6, 69.4, 46.8, 35.1, 22.2. HRMS (ESI, m/z) calcd for $C_{18}H_{16}O_3$ $[M+H]^+$ 281.1178, found 281.1167. $[\alpha]^{26}_D$ = -366.1 °(c 0.90, $CHCl_3$); 99% ee; Chiral HPLC analysis of the product: Daicel Chiralpak AS-H 250X4.6 mm 5u column; hexane/2-propanol = 80/20, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 19.4 min (major), 29.6 min (minor).



Peak#	Ret.Time	Area	Area %
1	19.923	29782384	49.87
2	29.078	29943200	50.13
Total		59725584	100

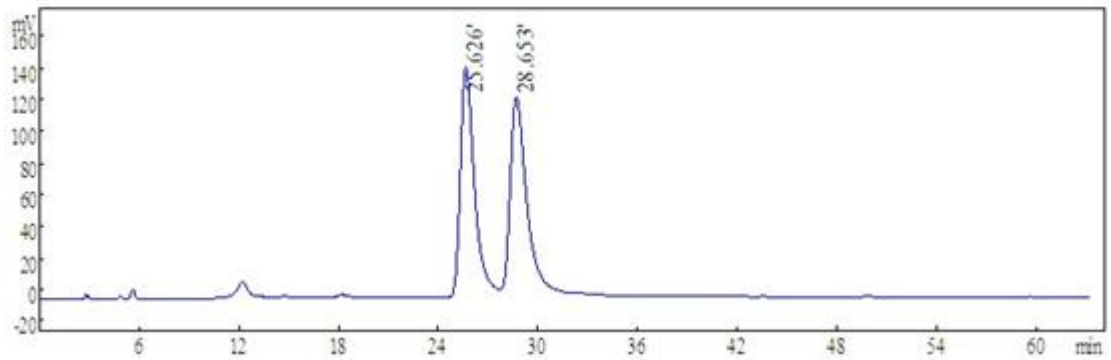


Peak#	Ret.Time	Area	Area %
1	19.391	46507158	99.36
2	29.554	302970	0.6473
Total		46810128	100



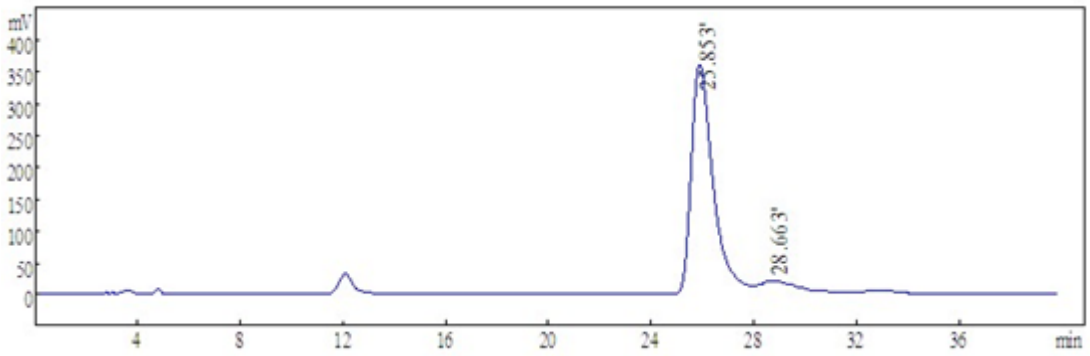
3j

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 – 7.40 (m, 2H), 7.33 (td, *J* = 7.5, 1.3 Hz, 1H), 7.26 (td, *J* = 7.5, 1.2 Hz, 1H), 6.55 (dd, *J* = 10.2, 1.5 Hz, 1H), 6.02 (dd, *J* = 10.2, 0.9 Hz, 1H), 5.77 (dd, *J* = 5.0, 2.3 Hz, 1H), 4.86 (dd, *J* = 12.5, 3.7 Hz, 1H), 4.76 (dd, *J* = 12.4, 2.5 Hz, 1H), 4.57 – 4.42 (m, 1H), 4.30 (dt, *J* = 14.5, 2.6 Hz, 1H), 3.75 (ddd, *J* = 16.8, 3.4, 0.9 Hz, 1H), 3.25 – 3.10 (m, 2H), 2.67 (dd, *J* = 16.8, 5.8 Hz, 1H), 1.55 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.6, 153.5, 151.0, 142.3, 132.4, 129.9, 128.8, 128.3, 127.6, 121.8, 102.0, 93.4, 88.6, 80.8, 70.5, 63.7, 48.1, 36.2, 23.1. HRMS (ESI, m/z) calcd for $C_{19}H_{18}O_3$ $[M+Na]^+$ 317.1154, found 317.1162. $[\alpha]^{18}_D$ = -249.6 °(c 0.20, $CHCl_3$); 92% ee; Chiral HPLC analysis of the product: Phenomenex 00G-4457-E0 250X4.6 mm 5u column; hexane/2-propanol = 85/15, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 25.9 min (major), 28.7 min (minor).

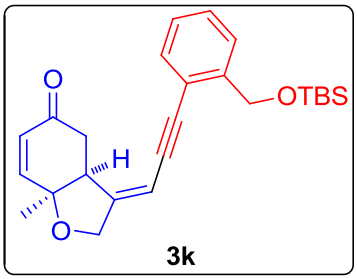


Peak#	Ret.Time	Area	Area %
1	25.626	8158973	49.86
2	28.653	8205902	50.14

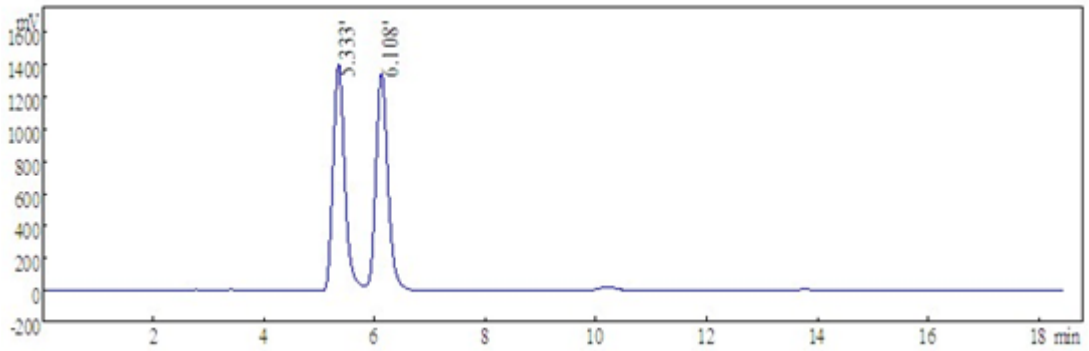
Total		16364875	100



Peak#	Ret.Time	Area	Area %
1	25.853	20304504	96.23
2	28.663	796585	3.775
Total		21101089	100

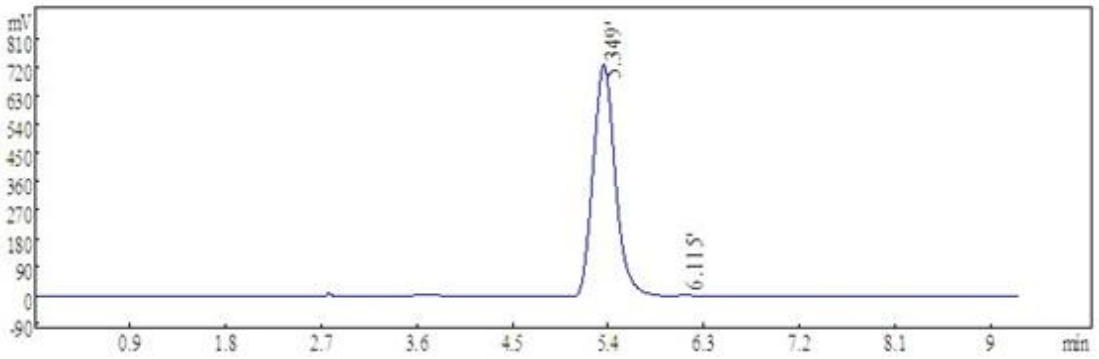


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.7 Hz, 1H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.40 (dd, *J* = 10.3, 1.3 Hz, 1H), 5.90 (d, *J* = 10.3 Hz, 1H), 5.70 – 5.51 (m, 1H), 4.77 (s, 2H), 4.36 (d, *J* = 14.3 Hz, 1H), 4.19 (dt, *J* = 14.3, 2.5 Hz, 1H), 3.47 (dd, *J* = 16.8, 3.6 Hz, 1H), 3.17 – 2.95 (m, 1H), 2.53 (dd, *J* = 16.8, 6.1 Hz, 1H), 1.42 (s, 3H), 0.83 (s, 9H), -0.00 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.4, 153.5, 150.1, 142.9, 131.7, 130.1, 128.7, 126.5, 125.8, 119.8, 102.3, 93.3, 89.3, 80.5, 70.4, 63.3, 48.0, 36.3, 26.0, 23.5, 18.4, -5.3. HRMS (ESI, m/z) calcd for $C_{25}H_{32}O_3Si$ $[M+H]^+$ 409.2193, found 409.2195. $[\alpha]^{29}_D$ = -167.0 ° (c 0.66, $CHCl_3$); >99% ee; Chiral HPLC analysis of the product: Phenomenex 00G-4457-E0 250X4.6 mm 5u column; hexane/2-propanol = 90/10, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 5.3 min (major), 6.1 min (minor).

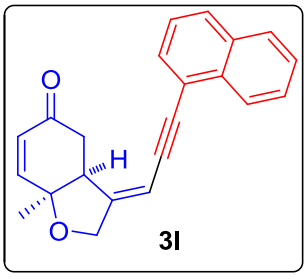


Peak#	Ret.Time	Area	Area %

1	5.333	19883960	50.55
2	6.108	19455030	49.45
Total		39338990	100

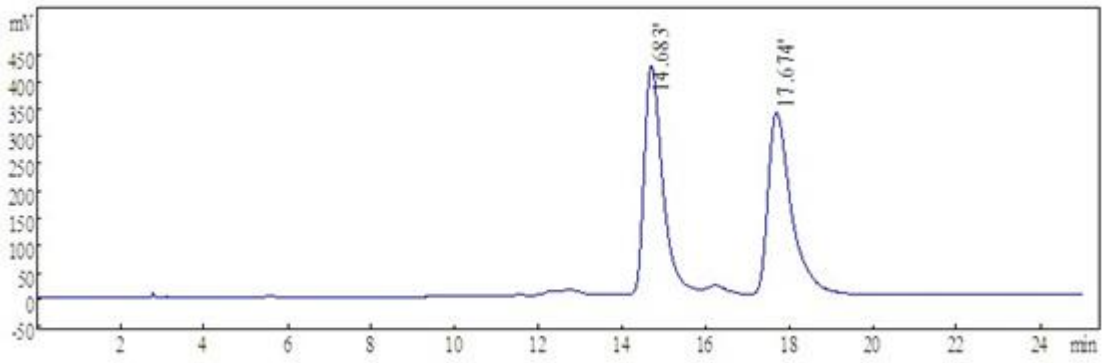


Peak#	Ret.Time	Area	Area %
1	5.349	10606755	99.63
2	6.115	38816	0.3646
Total		10645571	100

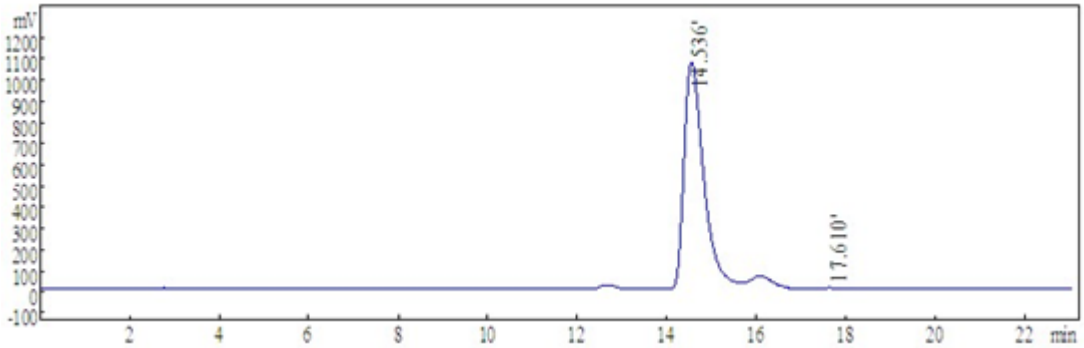


3l

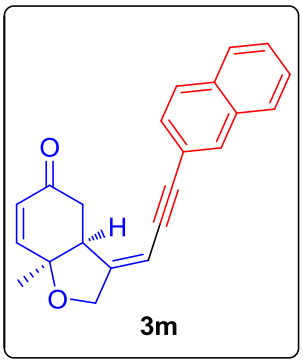
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.3 Hz, 1H), 7.88 – 7.81 (m, 2H), 7.72 (d, *J* = 7.0 Hz, 1H), 7.60 (dd, *J* = 11.1, 4.1 Hz, 1H), 7.52 (t, *J* = 7.1 Hz, 1H), 7.48 – 7.41 (m, 1H), 6.55 (dd, *J* = 10.3, 1.3 Hz, 1H), 6.06 (d, *J* = 10.3 Hz, 1H), 5.89 (dd, *J* = 4.7, 2.3 Hz, 1H), 4.54 (d, *J* = 14.4 Hz, 1H), 4.36 (dt, *J* = 14.4, 2.5 Hz, 1H), 3.73 (dd, *J* = 16.9, 3.6 Hz, 1H), 3.29 (d, *J* = 2.2 Hz, 1H), 2.72 (dd, *J* = 16.9, 6.1 Hz, 1H), 1.57 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.7, 153.8, 150.3, 133.2, 133.1, 130.4, 130.2, 128.9, 128.3, 126.9, 126.5, 126.2, 125.3, 120.8, 102.4, 93.9, 89.4, 80.6, 70.5, 48.0, 36.4, 23.4. HRMS (ESI, m/z) calcd for $C_{22}H_{18}O_2$ $[M+H]^+$ 315.1380, found 315.1383. $[\alpha]^{18}_D$ = -263.4 ° (c 1.30, $CHCl_3$); 99% ee; Chiral HPLC analysis of the product: Phenomenex 00G-4457-E0 250X4.6 mm 5u column; hexane/2-propanol = 90/10, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 14.5 min (major), 17.6 min (minor).



Peak#	Ret.Time	Area	Area %
1	14.683	12431003	49.19
2	17.674	12840881	50.81
Total		25271884	100

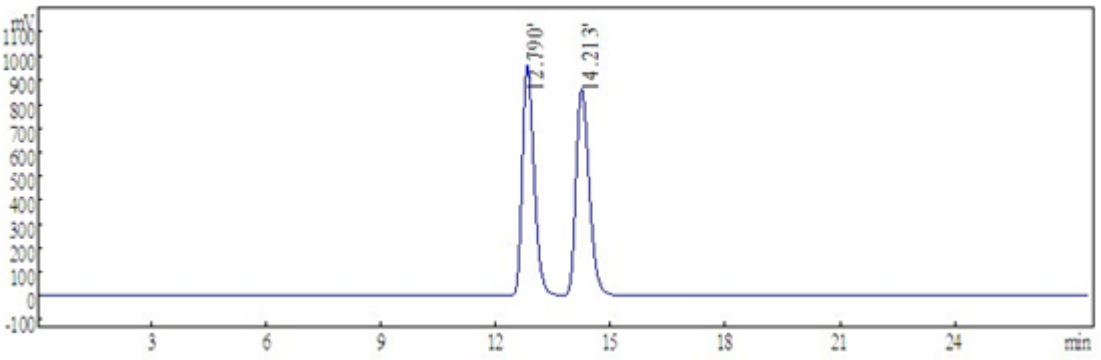


Peak#	Ret.Time	Area	Area %
1	14.536	31478195	99.29
2	17.610	227469	0.7175
Total		31705664	100

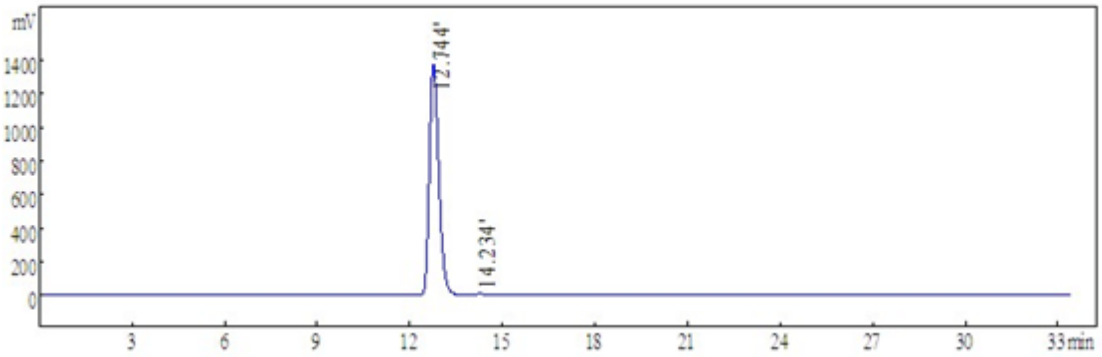


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 0.6 Hz, 1H), 7.85 – 7.73 (m, 3H), 7.55 – 7.43 (m, 3H), 6.55 (dd, *J* = 10.3, 1.4 Hz, 1H), 6.05 (dd, *J* = 10.3, 0.8 Hz, 1H), 5.77 (dd, *J* = 4.9, 2.3 Hz, 1H), 4.51 (ddd, *J* = 14.4, 1.7, 0.9 Hz, 1H), 4.33 (dt, *J* = 14.3, 2.6 Hz, 1H), 3.69 (ddd, *J* = 17.0, 3.6, 0.9 Hz, 1H), 3.31 – 3.22 (m, 1H), 2.72 (dd, *J* = 17.0, 6.1 Hz, 1H), 1.56 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.8, 153.8, 150.4, 133.0, 132.9, 131.2, 130.2, 128.1, 128.1, 127.8, 128.8, 126.8, 126.68, 120.48, 102.3, 96.1, 85.1, 80.6, 70.4, 48.0, 36.3, 23.4. HRMS (ESI, m/z) calcd for $C_{22}H_{18}O_2$ $[M+H]^+$

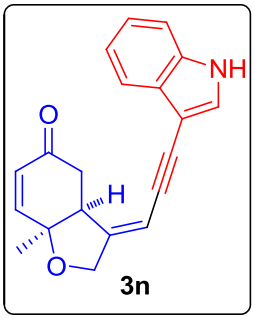
315.1385, found 315.1392. $[\alpha]^{29}_{D}$ = -348.9 ° (c 1.16, $CHCl_3$); 98% ee; Chiral HPLC analysis of the product: Phenomenex 00G-4457-E0 250X4.6 mm 5u column; hexane/2-propanol = 90/10, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 12.7 min (major), 14.2 min (minor).



Peak#	Ret.Time	Area	Area %
1	12.790	20604024	49.89
2	14.213	20692331	50.11
Total		41296355	100

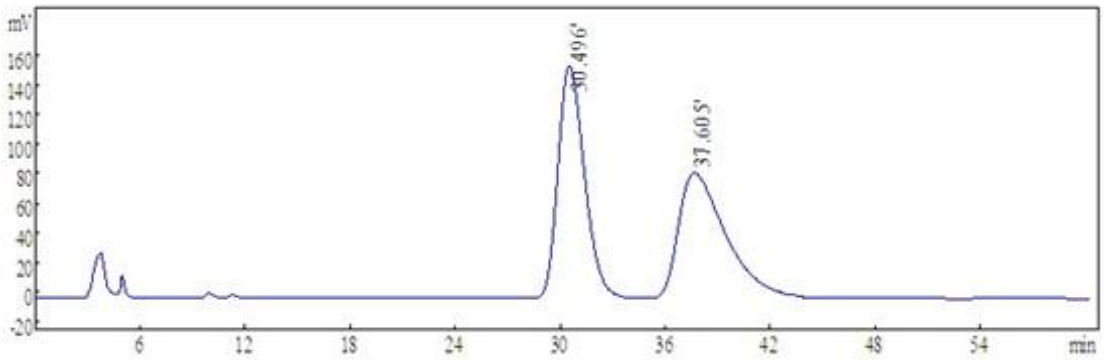


Peak#	Ret.Time	Area	Area %
1	12.744	29399446	99.22
2	14.234	231573	0.7815
Total		29631019	100

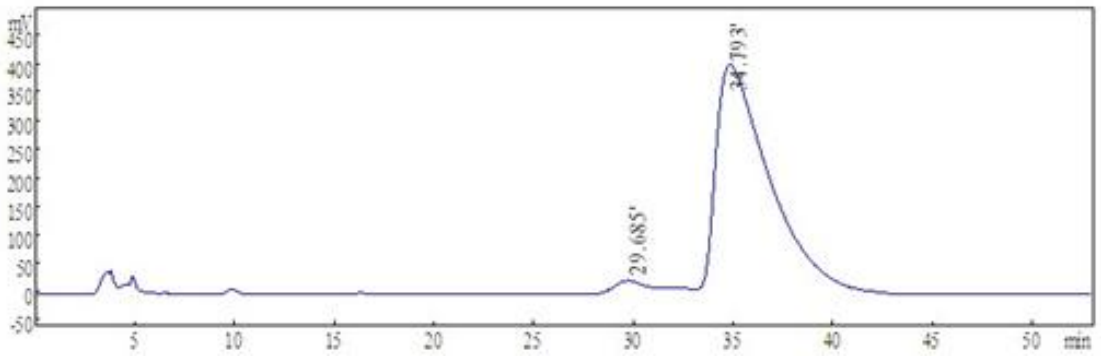


^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.77 (d, *J* = 7.5 Hz, 1H), 7.37 (dd, *J* = 8.2, 1.9 Hz, 2H), 7.26 – 7.17 (m, 2H), 6.56 (dd, *J* = 10.2, 1.4 Hz, 1H), 6.05 (d, *J* = 10.2 Hz, 1H), 5.81 (d, *J* = 2.5 Hz, 1H), 4.51 (d, *J* = 14.2 Hz, 1H), 4.33 (dt, *J* = 14.1, 2.6 Hz, 1H), 3.91 – 3.67 (m, 1H), 3.42 – 3.17 (m, 1H), 2.71 (dd, *J* = 16.9, 6.1 Hz, 1H), 1.57 (s,

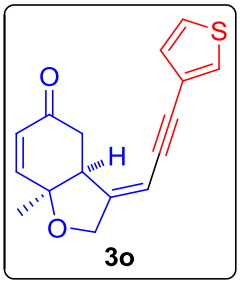
3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.2, 151.4, 150.6, 135.3, 130.1, 128.3, 128.0, 123.1, 120.8, 120.0, 111.4, 102.9, 98.6, 89.7, 86.3, 80.6, 70.4, 47.9, 36.3, 23.4. HRMS (ESI, m/z) calcd for $C_{20}H_{17}NO_2$ $[M+H]^+$ 304.1332, found 304.1328. $[\alpha]^{19}_D$ = -170 °(c 0.02, $CHCl_3$); 96% ee; Chiral HPLC analysis of the product: Daicel Chiralpak AS-H 250X4.6 mm 5u column; hexane/2-propanol = 75/25, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 29.7min (minor), 34.8 min (major).



Peak#	Ret.Time	Area	Area %
1	30.496	16659046	50.5
2	37.605	16331592	49.5
Total		32990638	100



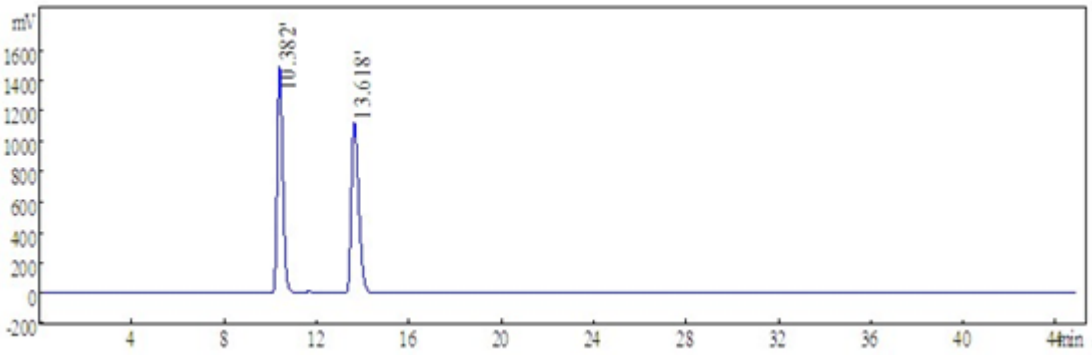
Peak#	Ret.Time	Area	Area %
1	29.685	1552651	2.075
2	34.793	73266342	97.93
Total		74266342	100



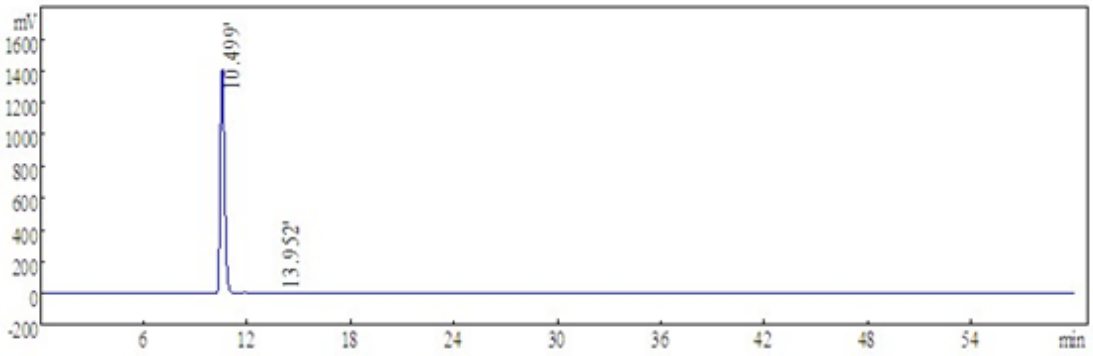
3o

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 2.9, 0.9 Hz, 1H), 7.24 – 7.17 (m, 1H), 7.07 (dd, *J* = 5.0, 1.1 Hz, 1H), 6.46 (dd, *J* = 10.3, 1.4 Hz, 1H), 5.95 (dd, *J* = 10.3, 0.7 Hz, 1H), 5.62 (dd, *J* = 4.8, 2.3 Hz, 1H), 4.41 (d, *J* = 14.5 Hz, 1H), 4.22 (dt, *J* = 14.3,

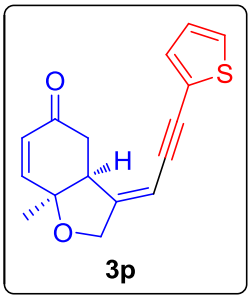
2.5 Hz, 1H), 3.52 (ddd, *J* = 17.0, 3.6, 0.7 Hz, 1H), 3.20 – 3.06 (m, 1H), 2.59 (dd, *J* = 17.0, 6.1 Hz, 1H), 1.47 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.7, 153.5, 150.4, 130.1, 129.6, 128.6, 125.5, 122.1, 102.1, 90.8, 84.3, 80.5, 70.4, 47.9, 36.2, 23.4. HRMS (ESI, m/z) calcd for $C_{16}H_{14}O_2S$ $[M+H]^+$ 271.0793, found 271.0800. $[\alpha]^{29}_D$ = -312.7 °(c 1.56, $CHCl_3$); >99% ee; Chiral HPLC analysis of the product: Phenomenex 00G-4457-E0 250X4.6 mm 5u column; hexane/2-propanol = 90/10, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 10.5 min (major), 14.0 min (minor).



Peak#	Ret.Time	Area	Area %
1	10.382	25119749	49.95
2	13.618	25174278	50.05
Total		50294027	100



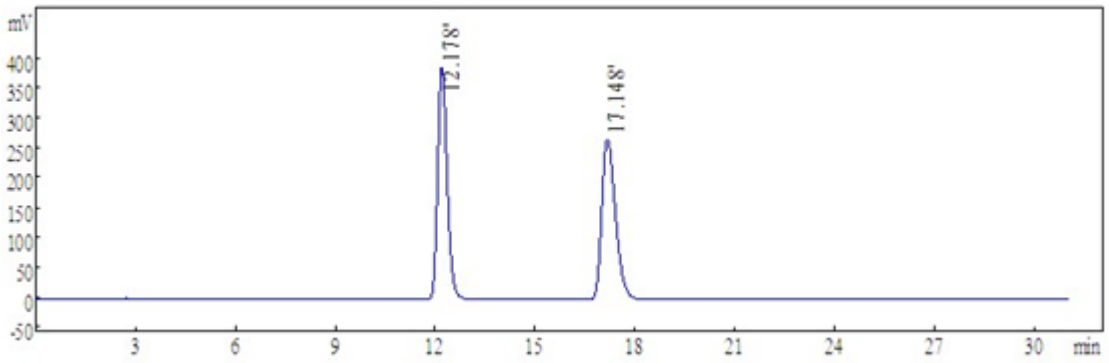
Peak#	Ret.Time	Area	Area %
1	10.499	24628270	99.51
2	13.952	120877	0.4884
Total		24749147	100



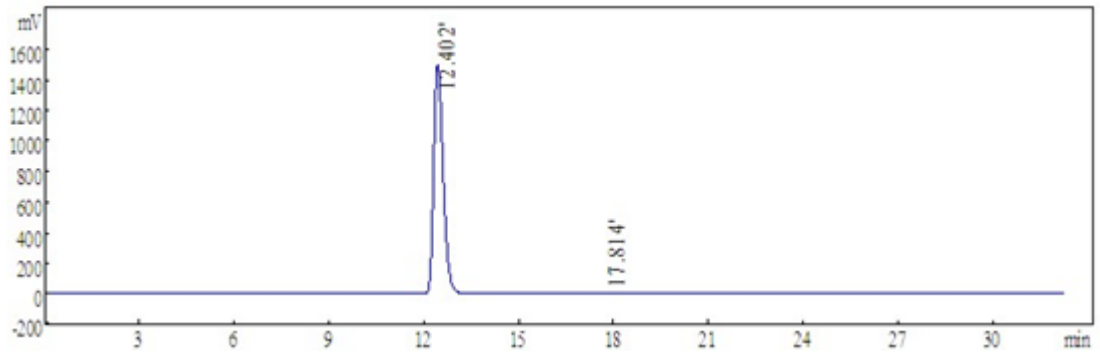
3p

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 5.8 Hz, 1H), 7.23 (d, *J* = 3.5 Hz, 1H), 6.99

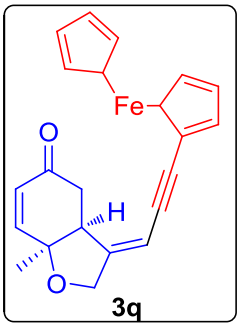
(dd, *J* = 4.9, 3.8 Hz, 1H), 6.53 (d, *J* = 10.3 Hz, 1H), 6.02 (d, *J* = 10.3 Hz, 1H), 5.72 (d, *J* = 2.1 Hz, 1H), 4.48 (d, *J* = 14.5 Hz, 1H), 4.30 (d, *J* = 14.4 Hz, 1H), 3.53 (dd, *J* = 17.0, 3.5 Hz, 1H), 3.26 – 3.11 (m, 1H), 2.67 (dd, *J* = 17.0, 6.1 Hz, 1H), 1.54 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.6, 154.0, 150.2, 131.8, 130.1, 127.5, 127.2, 123.0, 101.9, 88.8, 88.5, 80.5, 70.4, 48.0, 36.3, 23.4. HRMS (ESI, m/z) calcd for $C_{16}H_{14}O_2S$ $[M+H]^+$ 271.0793, found 271.0792. $[\alpha]^{30}_D$ = -356.5 ° (c 1.05, $CHCl_3$); 99% ee; Chiral HPLC analysis of the product: Phenomenex 00G-4457-E0 250X4.6 mm 5u column; hexane/2-propanol = 90/10, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 12.4 min (major), 17.8 min (minor).



Peak#	Ret.Time	Area	Area %
1	12.178	7724198	49.84
2	17.148	7774286	50.16
Total		15498484	100

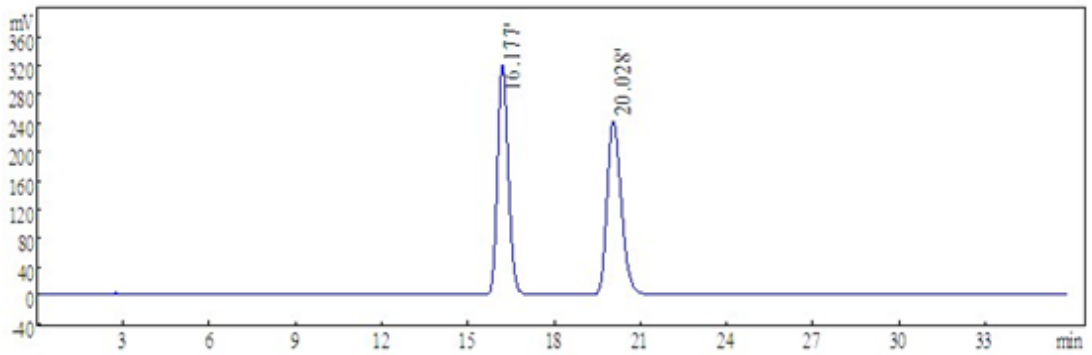


Peak#	Ret.Time	Area	Area %
1	12.402	31403862	99.27
2	17.814	230790	0.7296
Total		31634652	100

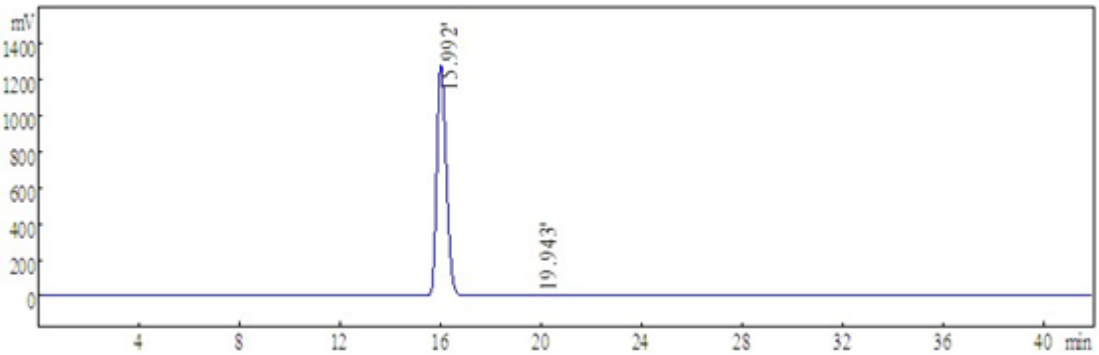


3q

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.51 (dd, *J* = 10.3, 1.5 Hz, 1H), 6.01 (dd, *J* = 10.3, 0.5 Hz, 1H), 5.60 (dd, *J* = 4.9, 2.3 Hz, 1H), 4.54 – 4.37 (m, 3H), 4.26 (s, 5H), 4.24 – 4.19 (m, 2H), 3.66 (ddd, *J* = 16.9, 3.3, 0.6 Hz, 1H), 3.28 – 3.05 (m, 1H), 2.65 (dd, *J* = 16.9, 6.0 Hz, 1H), 1.54 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.7, 151.9, 150.4, 130.1, 102.7, 95.0, 81.3, 80.6, 71.2, 71.1, 70.4, 70.0, 68.9, 68.9, 65.0, 48.0, 36.10, 23.4. HRMS (ESI, m/z) calcd for $C_{22}H_{20}FeO_2$ $[M+H]^+$ 373.0891, found 373.0910. Very dark solid, light rays can't pass through; >99% ee; Chiral HPLC analysis of the product: Phenomenex 00G-4457-E0 250X4.6 mm 5u column; hexane/2-propanol = 90/10, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 16.0 min (major), 19.9 min (minor).

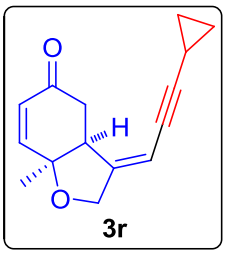


Peak#	Ret.Time	Area	Area %
1	16.177	8379750	49.9
2	20.028	8414606	50.1
Total		16794356	100



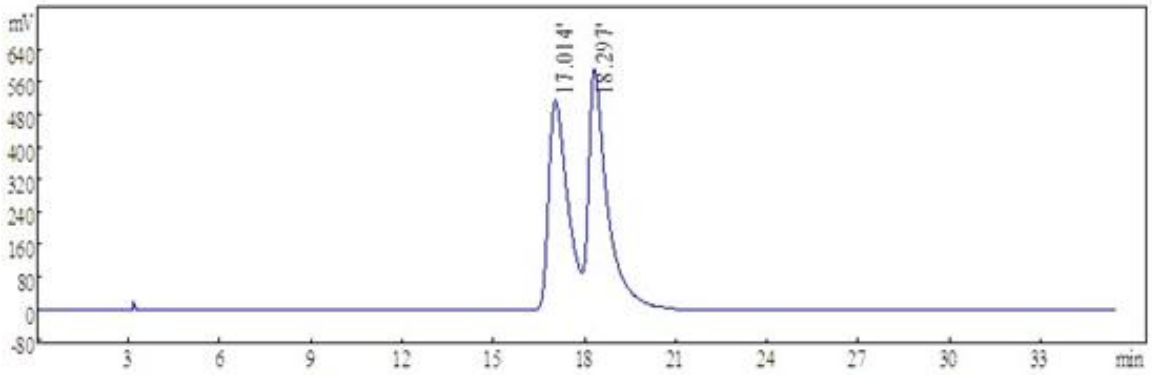
Peak#	Ret.Time	Area	Area %
1	15.992	33767203	99.66
2	19.943	115259	0.3402

Total		33882462	100

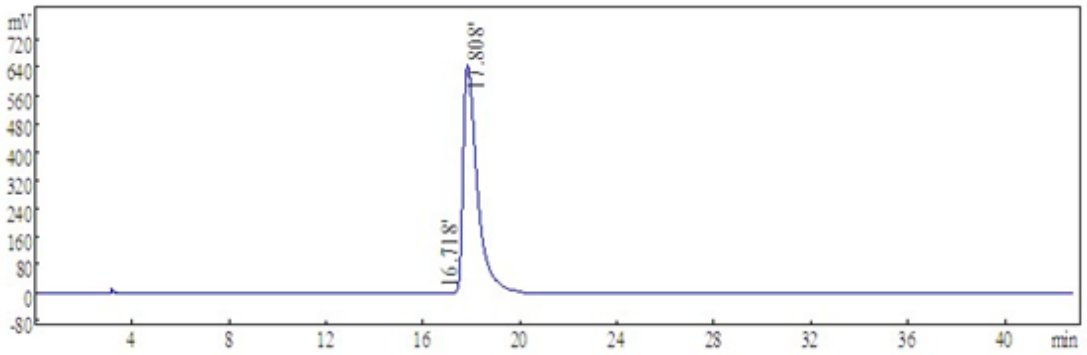


3r

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.43 (dd, *J* = 10.3, 1.4 Hz, 1H), 5.92 (dd, *J* = 10.3, 0.9 Hz, 1H), 5.40 – 5.27 (m, 1H), 4.33 (d, *J* = 14.1 Hz, 1H), 4.16 (dt, *J* = 14.0, 2.3 Hz, 1H), 3.42 (ddd, *J* = 16.9, 3.6, 0.9 Hz, 1H), 3.08 – 3.00 (m, 1H), 2.52 (dd, *J* = 16.9, 6.1 Hz, 1H), 1.44 (s, 3H), 0.80 – 0.75 (m, 2H), 0.72 – 0.63 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.6, 151.6, 150.0, 129.6, 102.2, 99.7, 80.0, 70.8, 69.8, 47.2, 35.8, 23.0, 8.3, 8.2. HRMS (ESI, m/z) calcd for $C_{15}H_{16}O_2$ $[M+H]^+$ 229.1229, found 229.1231. $[\alpha]^{26}_D$ = -75.6 ° (c 0.35, $CHCl_3$); >99% ee; Chiral HPLC analysis of the product: Daicel Chiralpak OJ-H 250X4.6 mm 5u column; hexane/2-propanol = 97/3, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 16.7 min (minor), 17.8 min (major).

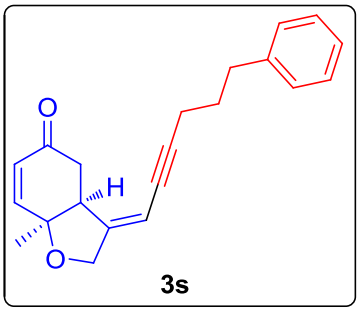


Peak#	Ret.Time	Area	Area %
1	17.014	18184405	49.43
2	18.297	18607157	50.57
Total		36791562	100



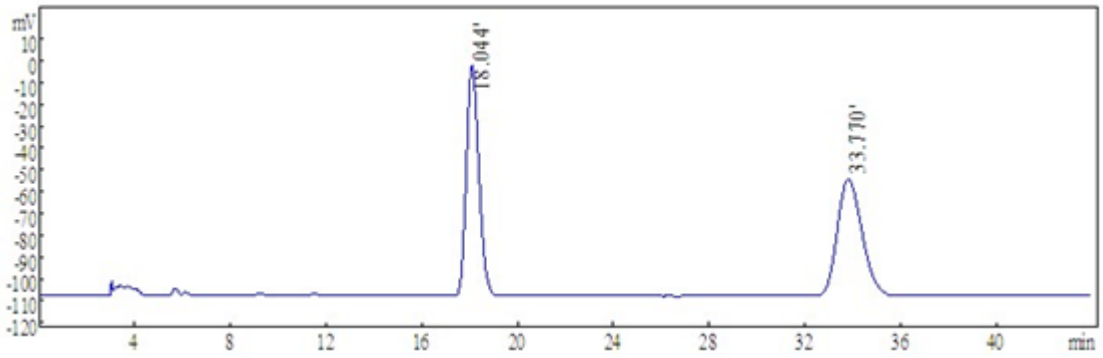
Peak#	Ret.Time	Area	Area %

1	16.718	72876	0.2716
2	17.808	26758698	99.73
Total		26831574	100

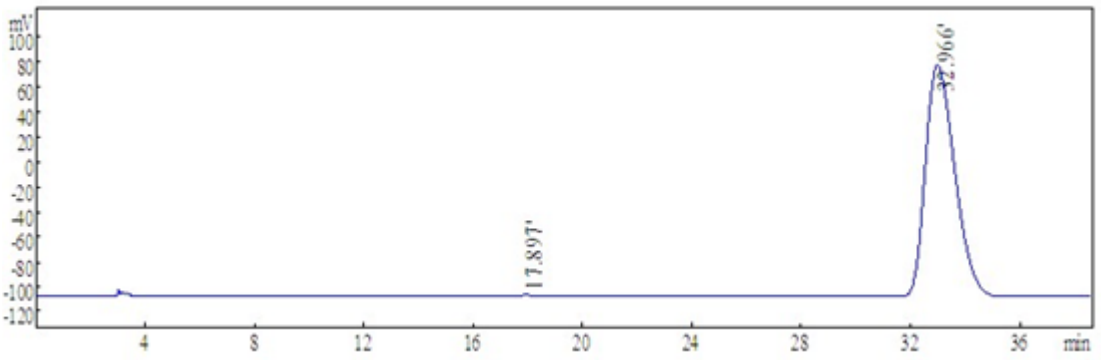


3s

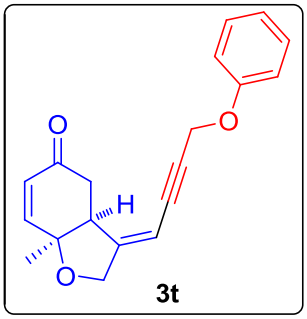
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.15 (m, 5H), 6.51 (dd, *J* = 10.3, 1.4 Hz, 1H), 6.01 (dd, *J* = 10.3, 0.7 Hz, 1H), 5.61 – 5.26 (m, 1H), 4.42 (d, *J* = 14.6 Hz, 1H), 4.25 (dt, *J* = 14.2, 2.4 Hz, 1H), 3.55 (ddd, *J* = 16.9, 3.6, 0.7 Hz, 1H), 3.12 (s, 1H), 2.78 – 2.70 (m, 2H), 2.60 (dd, *J* = 16.9, 6.1 Hz, 1H), 2.38 (td, *J* = 6.9, 1.4 Hz, 2H), 1.93 – 1.81 (m, 2H), 1.52 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.0, 151.9, 150.4, 141.6, 130.0, 128.6, 128.4, 125.9, 102.6, 96.6, 80.4, 76.4, 70.2, 47.6, 36.2, 35.0, 30.3, 23.4, 19.1. HRMS (ESI, m/z) calcd for $C_{21}H_{22}O_2$ $[M+Na]^+$ 329.1517, found 329.1519. $[\alpha]^{26}_D$ = -148.5 ° (c 0.21, $CHCl_3$); >99% ee; Chiral HPLC analysis of the product: Daicel Chiralpak AS-H 250X4.6 mm 5u column; hexane/2-propanol = 90/10, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 17.9 min (minor), 33.0 min (major).



Peak#	Ret.Time	Area	Area %
1	18.044	3893656	49.89
2	33.770	3910254	50.11
Total		7803910	100

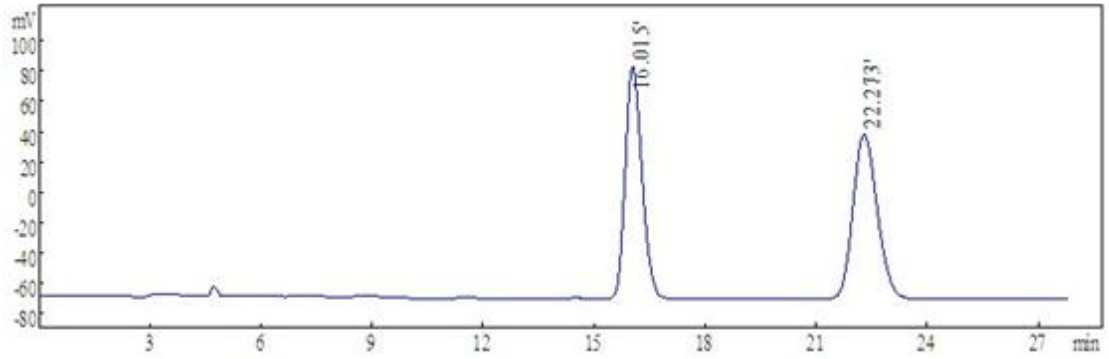


Peak#	Ret.Time	Area	Area %
1	17.897	69310	99.5
2	32.966	13949554	0.4944
Total		14018864	100



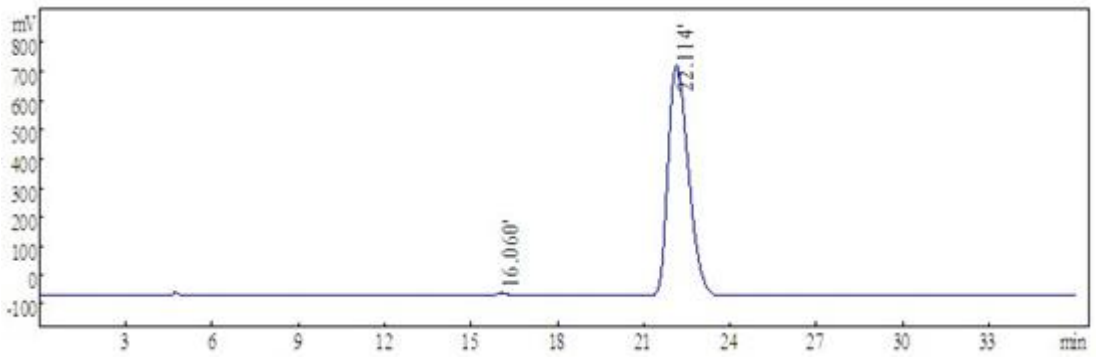
3t

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 2H), 6.99 (d, *J* = 7.9 Hz, 3H), 6.49 (dd, *J* = 10.3, 1.3 Hz, 1H), 5.99 (d, *J* = 10.3 Hz, 1H), 5.60 – 5.45 (m, 1H), 4.87 (s, 2H), 4.41 (d, *J* = 14.6 Hz, 1H), 4.24 (d, *J* = 14.4 Hz, 1H), 3.36 (dd, *J* = 16.9, 3.4 Hz, 1H), 3.04 (s, 1H), 2.51 (dd, *J* = 17.0, 6.1 Hz, 1H), 1.48 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.7, 157.6, 155.1, 150.1, 130.1, 129.5, 121.5, 115.1, 101.4, 90.4, 82.5, 80.4, 70.2, 56.5, 47.7, 36.1, 23.4. HRMS (ESI, m/z) calcd for $C_{19}H_{18}O_3[M+H]^+$ 295.1329, found 295.1328. $[\alpha]^{18}_D$ = -240.5 ° (c 0.84, $CHCl_3$); 98% ee; Chiral HPLC analysis of the product: Daicel Chiralpak AS-H 250X4.6 mm 5u column; hexane/2-propanol = 80/20, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 16.1 min (minor), 22.1 min (major).

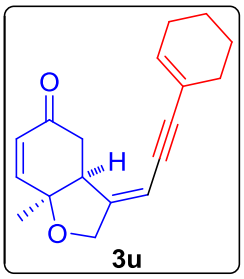


Peak#	Ret.Time	Area	Area %
1	16.015	4874806	49.14
2	22.273	5046206	50.86

Total		9921012	100

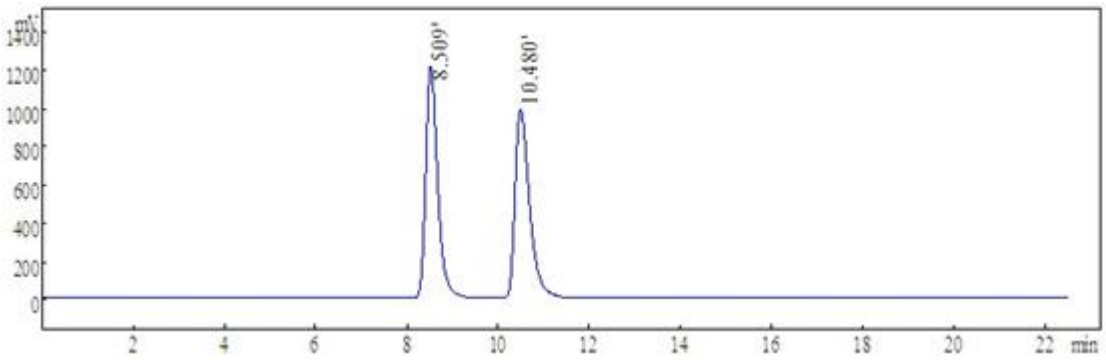


Peak#	Ret.Time	Area	Area %
1	16.060	332535	0.8436
2	22.114	39084205	99.15
Total		39416740	100



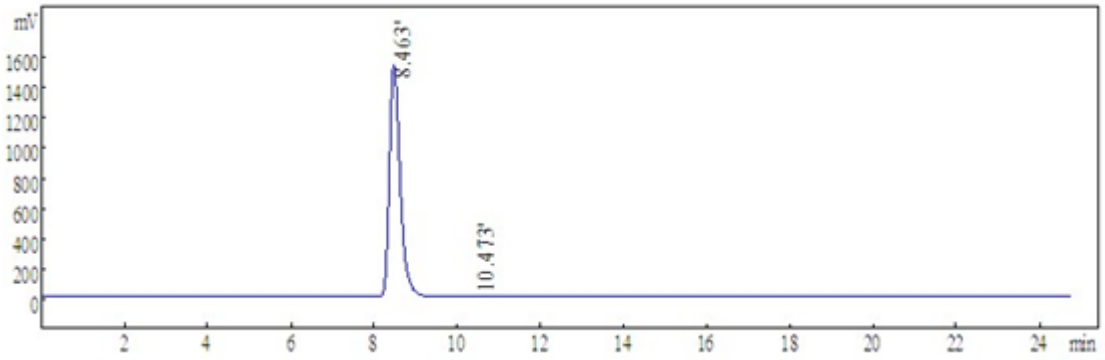
3u

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.44 (dd, *J* = 10.3, 1.3 Hz, 1H), 6.11 – 6.02 (m, 1H), 5.93 (d, *J* = 10.2 Hz, 1H), 5.61 – 5.45 (m, 1H), 4.36 (d, *J* = 14.3 Hz, 1H), 4.19 (dt, *J* = 14.2, 2.5 Hz, 1H), 3.47 (dd, *J* = 17.0, 3.5 Hz, 1H), 3.12 – 2.97 (m, 1H), 2.54 (dd, *J* = 17.0, 6.1 Hz, 1H), 2.17 – 1.99 (m, 4H), 1.61 – 1.56 (m, 2H), 1.55 – 1.49 (m, 2H), 1.45 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.8, 152.2, 150.3, 135.1, 130.0, 120.7, 102.5, 97.7, 82.2, 80.4, 70.3, 47.8, 36.1, 29.0, 25.7, 23.4, 22.3, 21.5. HRMS (ESI, m/z) calcd for $C_{18}H_{20}O_2$ $[M+H]^+$ 269.1542, found 269.1536. $[\alpha]^{27}_D$ = -289.6 ° (c 1.40, $CHCl_3$); >99% ee; Chiral HPLC analysis of the product: Phenomenex 00G-4457-E0 250X4.6 mm 5u column; hexane/2-propanol = 90/10, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 8.5 min (major), 10.5 min (minor).

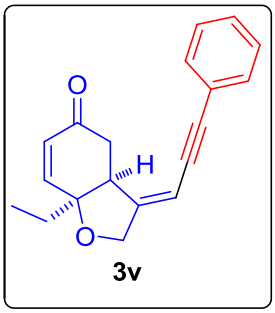


Peak#	Ret.Time	Area	Area %
1	8.509	22054958	50.27

2	10.480	21814411	49.73
Total		43869369	100

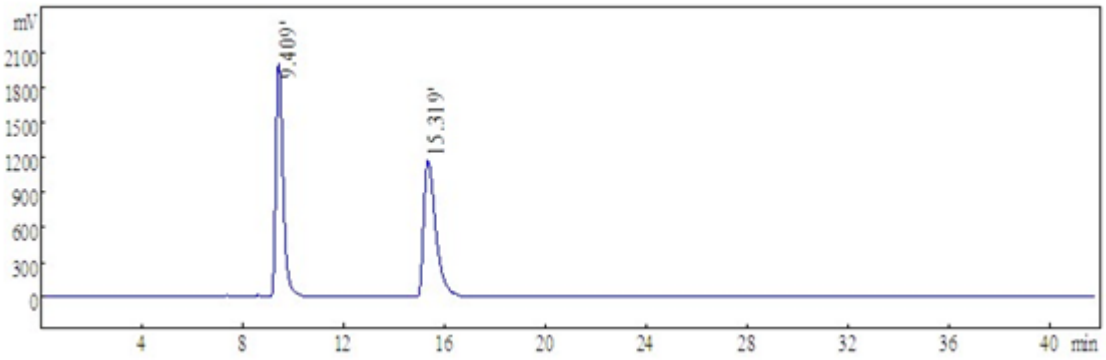


Peak#	Ret.Time	Area	Area %
1	8.463	27896128	99.69
2	10.473	85095	0.3041
Total		27981223	100

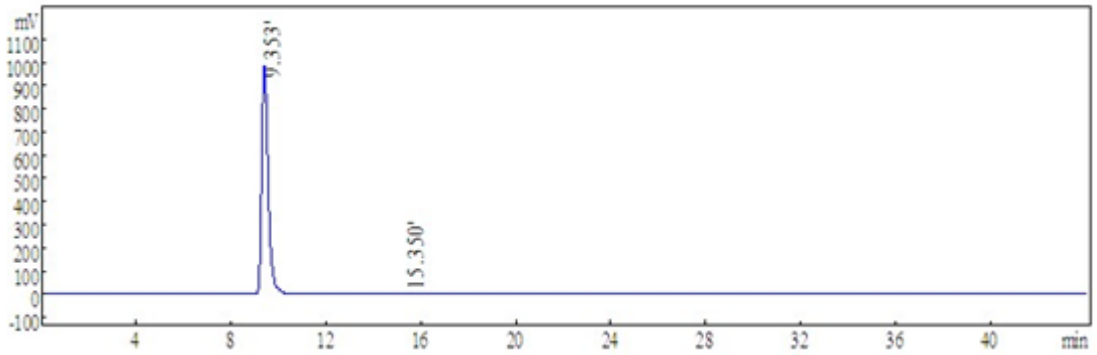


3v

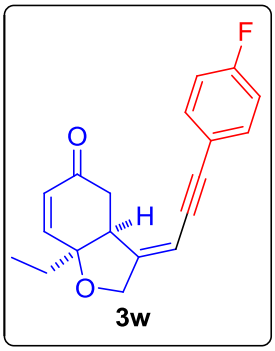
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.42 (m, 2H), 7.36 – 7.29 (m, 3H), 6.57 (dd, *J* = 10.3, 1.3 Hz, 1H), 6.10 (dd, *J* = 10.3, 0.5 Hz, 1H), 5.77 – 5.63 (m, 1H), 4.51 – 4.42 (m, 1H), 4.31 (dt, *J* = 14.3, 2.5 Hz, 1H), 3.60 (ddd, *J* = 17.1, 3.4, 0.6 Hz, 1H), 3.34 – 3.23 (m, 1H), 2.67 (dd, *J* = 17.1, 6.3 Hz, 1H), 1.97 – 1.78 (m, 2H), 1.06 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.9, 154.2, 149.6, 131.3, 130.9, 128.4, 128.4, 123.1, 102.1, 95.7, 84.8, 82.9, 70.2, 45.5, 36.6, 30.1, 8.1. HRMS (ESI, m/z) calcd for $C_{19}H_{18}O_2$ $[M+H]^+$ 279.1385, found 279.1382. $[\alpha]^{26}_D$ = -384.4 °(c 1.18, $CHCl_3$); >99% ee; Chiral HPLC analysis of the product: Phenomenex 00G-4457-E0 250X4.6 mm 5u column; hexane/2-propanol = 90/10, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 9.4 min (major), 15.4 min (minor).



Peak#	Ret.Time	Area	Area %
1	9.409	40252848	50.3
2	15.319	39772822	49.7
Total		80025670	100

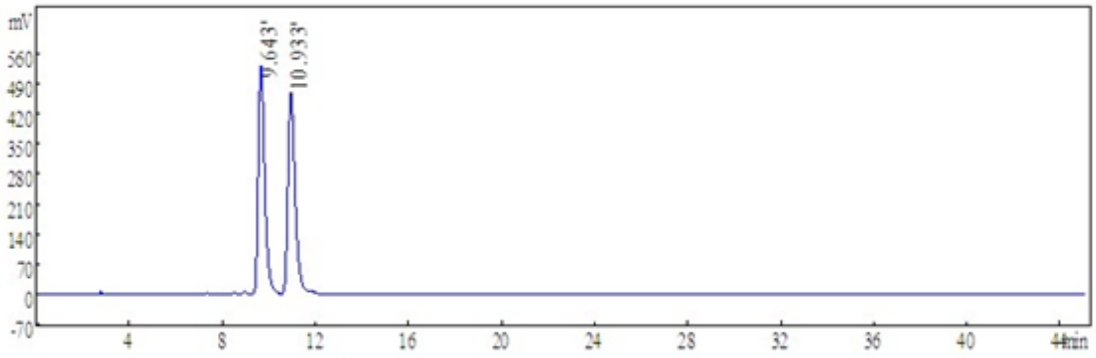


Peak#	Ret.Time	Area	Area %
1	9.353	18949392	99.57
2	15.350	80658	0.4238
Total		19030050	100

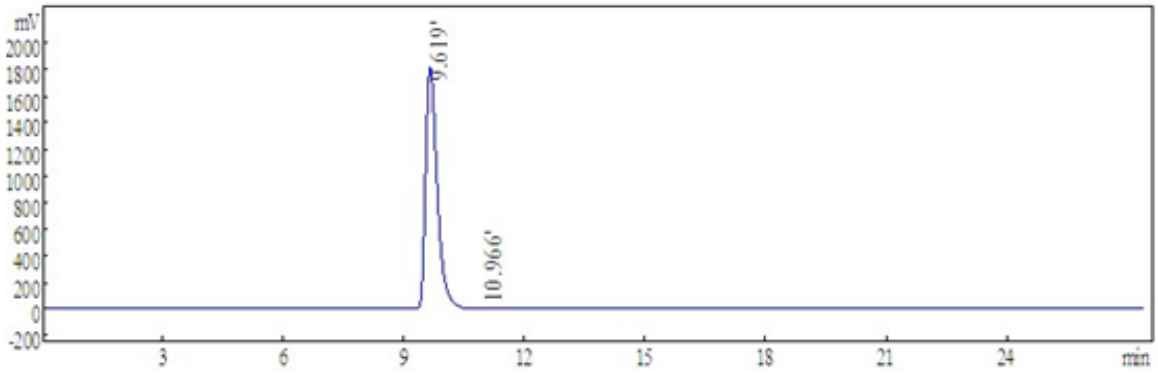


3w

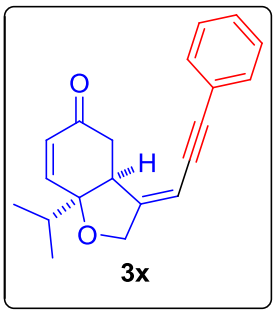
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 – 7.39 (m, 2H), 7.08 – 6.95 (m, 2H), 6.56 (dd, *J* = 10.3, 1.4 Hz, 1H), 6.08 (dd, *J* = 10.3, 0.7 Hz, 1H), 5.69 (dd, *J* = 4.7, 2.3 Hz, 1H), 4.46 (dd, *J* = 14.3, 0.8 Hz, 1H), 4.29 (dt, *J* = 14.3, 2.5 Hz, 1H), 3.57 (ddd, *J* = 17.1, 3.4, 0.8 Hz, 1H), 3.32 – 3.20 (m, 1H), 2.65 (dd, *J* = 17.1, 6.3 Hz, 1H), 1.97 – 1.77 (m, 2H), 1.05 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.9, 162.6 (d, *J* = 250.7 Hz), 154.3, 149.7, 133.2 (d, *J* = 8.4 Hz), 130.8, 119.2 (d, *J* = 3.5 Hz), 115.7 (d, *J* = 22.7 Hz), 101.9, 94.6, 84.5 (d, *J* = 1.4 Hz), 82.9, 70.2, 45.6, 36.6, 30.0, 8.1. HRMS (ESI, m/z) calcd for $C_{19}H_{17}FO_2$ $[M+K]^+$ 335.0850, found 335.0849. $[\alpha]^{26}_D$ = -443.3 ° (c 0.71, $CHCl_3$); >99% ee; Chiral HPLC analysis of the product: Phenomenex 00G-4457-E0 250X4.6 mm 5u column; hexane/2-propanol = 90/10, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 9.6 min (major), 11.0 min (minor).



Peak#	Ret.Time	Area	Area %
1	9.643	10326406	51.17
2	10.933	9853984	48.83
Total		20180290	100



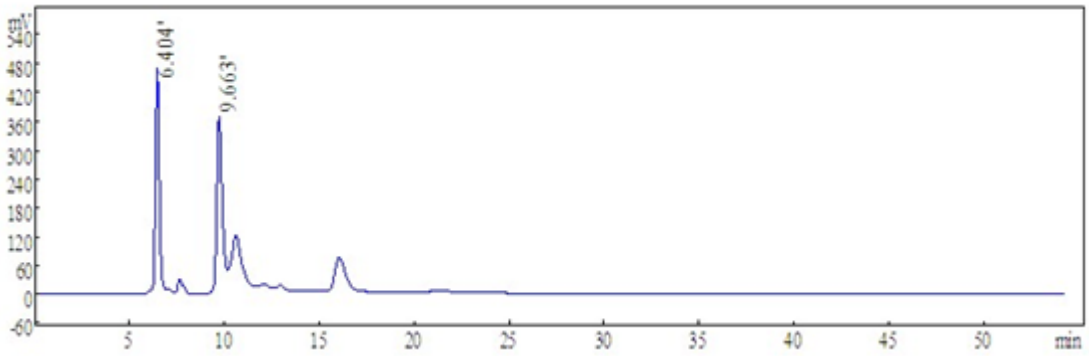
Peak#	Ret.Time	Area	Area %
1	9.619	36493523	99.56
2	10.966	159432	0.435
Total		36652955	100



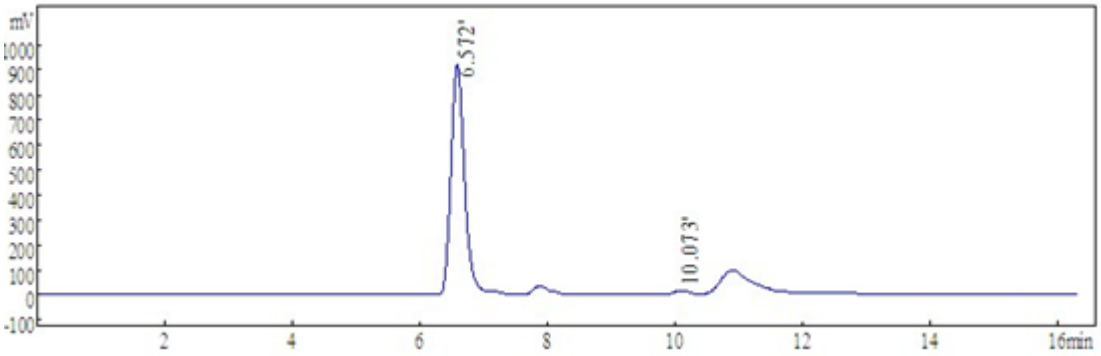
3x

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.42 (m, 2H), 7.36 – 7.31 (m, 3H), 6.57 (dd, *J* = 10.4, 1.3 Hz, 1H), 6.18 (d, *J* = 10.5 Hz, 1H), 5.76 – 5.73 (m, 1H), 4.43 (dd, *J* = 14.1, 1.5 Hz, 1H), 4.27 (dt, *J* = 14.1, 2.5 Hz, 1H), 3.56 (dd, *J* = 17.4, 2.7 Hz, 1H), 3.41 – 3.29 (m, 1H), 2.69 (dd, *J* = 17.3, 6.8 Hz, 1H), 2.13 – 2.10 (m, 1H), 1.07 (dd, *J* = 8.7, 7.0 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.3, 155.1, 148.5, 131.7, 131.4, 128.4, 128.4, 123.1, 101.9, 96.0, 85.0, 84.8, 69.9, 43.4, 37.6, 35.2, 17.5, 17.0. HRMS (ESI, m/z) calcd for $C_{20}H_{20}O_2$ $[M+Na]^+$ 315.1356, found 315.1355. $[\alpha]^{29}_D$ = -275.4 °(c 2.52,

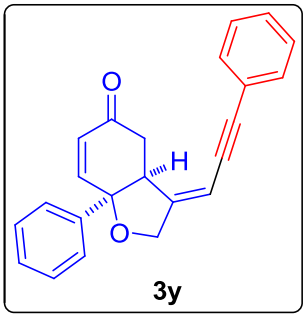
$CHCl_3$); 97% ee; Chiral HPLC analysis of the product: Phenomenex 00G-4457-E0 Phenomenex 00G-4457-E0 250X4.6 mm 5u column; hexane/2-propanol = 90/10, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 6.6 min (major), 10.1 min (minor).



Peak#	Ret.Time	Area	Area %
1	6.404	6246729	49.82
2	9.663	6292222	50.18
Total		12538951	100

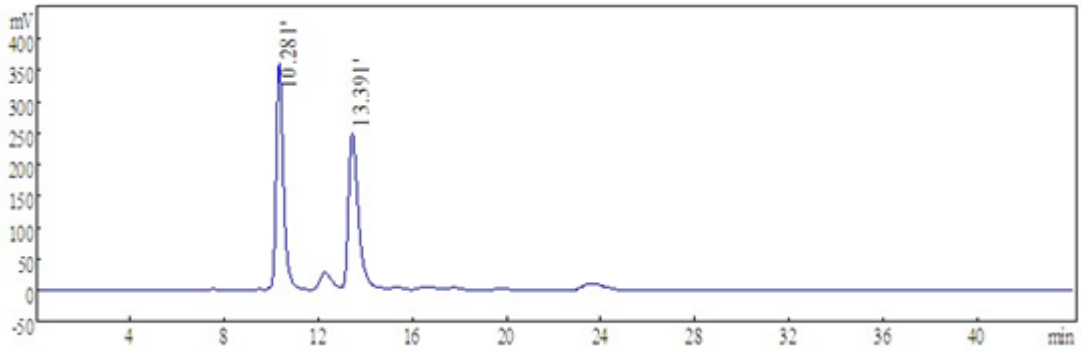


Peak#	Ret.Time	Area	Area %
1	6.572	13803278	98.28
2	10.073	241342	1.718
Total		14044620	100

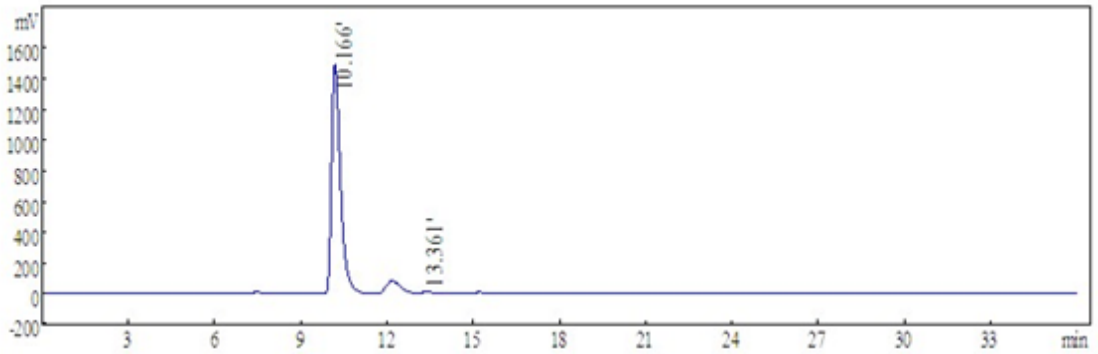


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.48 (m, 2H), 7.45 – 7.33 (m, 6H), 7.31 – 7.29 (m, 2H), 6.64 (dd, *J* = 10.2, 1.5 Hz, 1H), 6.28 (dd, *J* = 10.2, 0.7 Hz, 1H), 5.77 – 5.63 (m, 1H), 4.72 (ddd, *J* = 14.3, 1.7, 0.9 Hz, 1H), 4.50 (dt, *J* = 14.3, 2.6 Hz, 1H), 3.62 (ddd, *J* = 17.0, 3.6, 0.8 Hz, 1H), 3.50 – 3.38 (m, 1H), 2.74 (dd, *J* = 17.0, 6.0 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 196.9, 153.2, 148.1, 140.2, 131.3, 131.2, 128.8, 128.5, 128.4, 128.3, 125.3, 123.0, 102.2, 956.0, 84.6, 84.2, 70.8, 50.1, 35.8. HRMS (ESI, m/z) calcd for $C_{23}H_{18}O_2$ $[M+H]^+$ 327.1380, found 327.1391. $[\alpha]^{27}_D$ = -168.3 °(c 1.27, $CHCl_3$); 99% ee; Chiral HPLC analysis of the product: Phenomenex 00G-4457-E0 250X4.6 mm 5u column; hexane/2-propanol = 90/10, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 10.2 min (major), 13.4 min (minor).

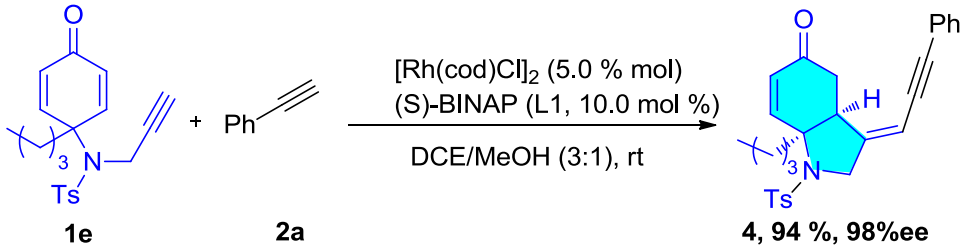


Peak#	Ret.Time	Area	Area %
1	10.281	7649156	52.14
2	13.391	7020674	47.86
Total		14669830	100

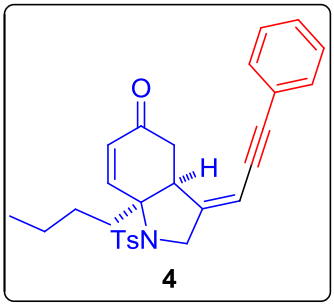


Peak#	Ret.Time	Area	Area %
1	10.166	32355379	99.34
2	13.361	212626	0.6528
Total		32568005	100

4. **Preparation and Characterization of Compound 4 to 9**

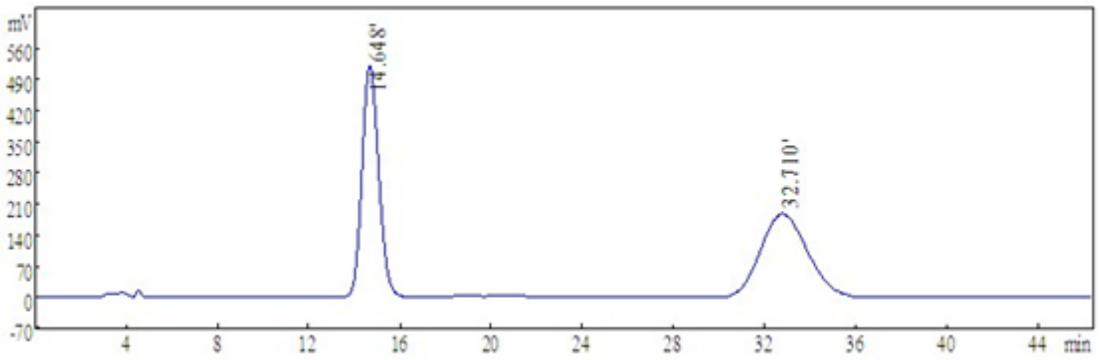


To a mixture of **1e** (0.2 mmol, 1 equiv), $[Rh(cod)Cl]_2$ (0.010 mmol, 5.0 mmol%), and (S)-BINAP (0.020 mmol, 10.0 mol %), 1.5 mL DCE was added under nitrogen atmosphere . Then, to the stirred solution above, **2a** (0.4 mmol, 2.0 equiv) and 0.5 ml MeOH was added quikly. The reaction system was stirred at room temperature overnight. After the reaction was completed (determined by TLC analysis), the solvent was evaporated under reduced pressure, and purified by column chromatography (silica gel, Petroleum ether/ EtOAc: 15/1) to afford the desired product **4**.



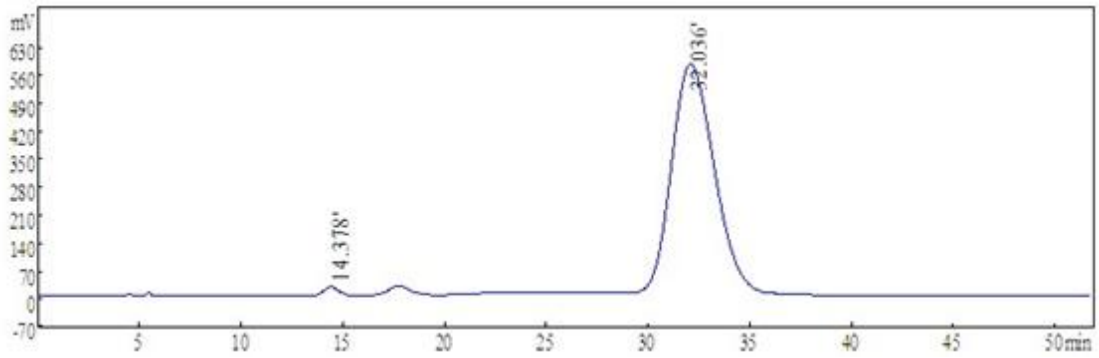
4

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 – 7.63 (d, *J* = 8.3 Hz, 2H), 7.41 – 7.35 (m, 2H), 7.43 – 7.36 (m, 3H), 7.28 (s, 1H), 7.22 (d, *J* = 10.4 Hz, 1H), 6.10 (d, *J* = 10.4 Hz, 1H), 5.74 – 5.66 (m, 1H), 4.24 (dd, *J* = 15.5, 1.9 Hz, 1H), 4.20 – 4.13 (m, 1H), 3.52 (dd, *J* = 11.8, 5.5 Hz, 1H), 2.56 (dd, *J* = 16.3, 5.6 Hz, 1H), 2.41 (s, 3H), 2.09 (dd, *J* = 16.2, 11.8 Hz, 1H), 2.02 – 1.93 (m, 1H), 1.87 – 1.77 (m, 1H), 1.63 (s, 1H), 1.37 – 1.27 (m, 4H), 0.90 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.9, 148.5, 147.8, 143.9, 137.0, 131.5, 129.8, 129.7, 128.6, 128.4, 127.1, 122.7, 104.4, 94.9, 84.4, 67.2, 51.6, 47.6, 38.8, 37.4, 26.9, 22.9, 21.5, 13.9. HRMS (ESI, m/z) calcd for $C_{28}H_{29}NO_3S$ $[M+H]^+$ 460.1941, found 460.1948. $[\alpha]^{30}_D$ = -78.2 ° (c 0.64, $CHCl_3$); 98% ee; Chiral HPLC analysis of the product: Daicel Chiralpak AS-H 250X4.6 mm 5u column; hexane/2-propanol = 80/20, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 14.4 min (minor), 32.0 min (major).

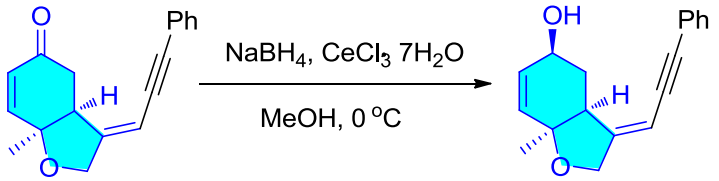


Peak#	Ret.Time	Area	Area %
1	14.648	26423853	49.03
2	32.710	27469174	50.97

Total		53893027	100

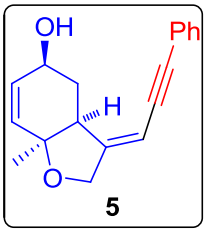


Peak#	Ret.Time	Area	Area %
1	14.378	1043798	1.218
2	32.036	84652589	98.78
Total		85696387	100



3a **5, 93%, dr = 5:1, ee = 98 %**

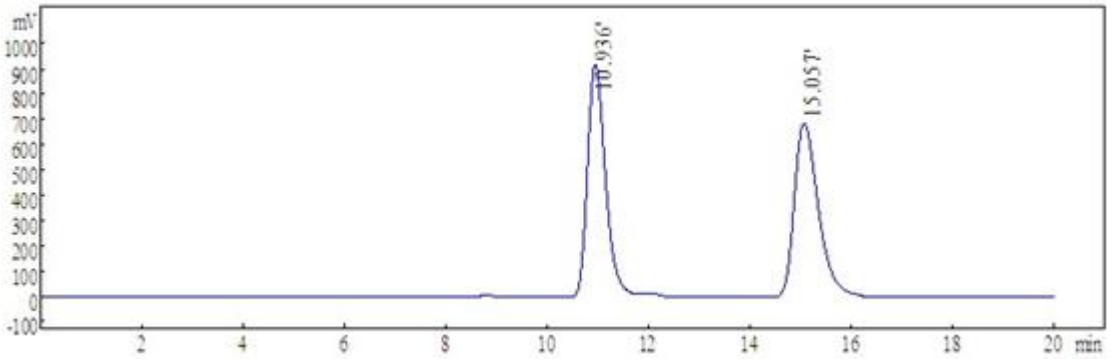
To a mixture of **3a** (0.2 mmol), and $CeCl_3 \cdot 7H_2O$ (0.22 mmol, 1.1 equiv), 2 mL MeOH was added. Then, to the stirred solution above, $NaBH_4$ (0.22 mmol, 1.1 equiv) was added. The reaction system was stirred at 0 ℃ for 10 min. After the reaction was completed (determined by TLC analysis), the reaction mixture was filtered and evaporated under reduced pressure, and purified by column chromatography (silica gel, Petroleum ether/ EtOAc: 5/1) to afford the desired product **5**.[3] HRMS (ESI, m/z) calcd for $C_{28}H_{29}NO_3S$ $[M+H]^+$ 460.1941, found 460.1948.



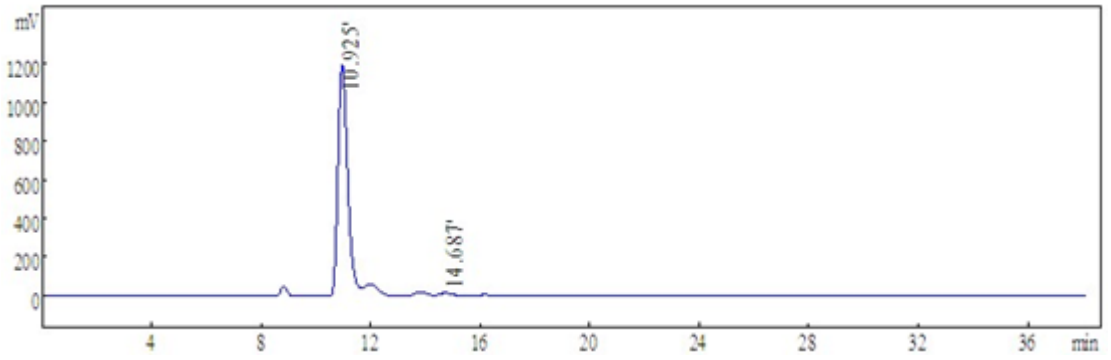
5

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 2H), 7.30 – 7.32 (m, 3H), 5.90 (dd, *J* = 10.1, 1.3 Hz, 1H), 5.69 (dd, *J* = 10.1, 1.8 Hz, 1H), 5.63 (q, *J* = 2.0 Hz, 1H), 4.57 (dt, *J* = 14.8, 2.1 Hz, 1H), 4.44 (dd, *J* = 14.8, 1.7 Hz, 1H), 4.28 – 4.18 (m, 1H), 2.98 – 2.85 (m, 1H), 2.49 (s, 1H), 2.29 (dt, *J* = 12.1, 4.6 Hz, 1H), 1.80 – 1.74 (m, 1H), 1.25 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.6, 134.0, 131.3, 130.7, 128.4, 128.2, 123.4, 100.9, 93.7, 86.0, 79.6, 69.1, 66.1, 46.5, 32.8, 25.3. HRMS (ESI, m/z) calcd for

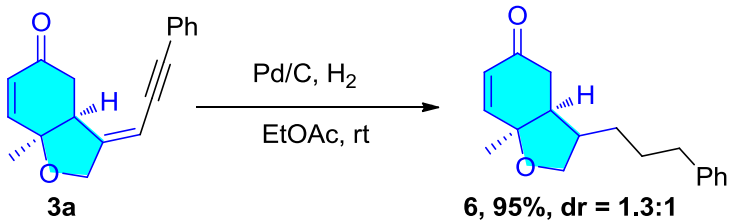
$C_{18}H_{18}O_2$ $[M+Na]^+$ 289.1199, found 289.1200. $[\alpha]^{18}_D$ = -417.6 °(c 0.52, $CHCl_3$); 98% ee; Chiral HPLC analysis of the product: Phenomenex 00G-4457-E0 250X4.6 mm 5u column; hexane/2-propanol = 85/15, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 10.9 min (minor), 14.7 min (major).



Peak#	Ret.Time	Area	Area %
1	10.936	22328238	49.19
2	15.057	23062210	50.81
Total		45390448	100



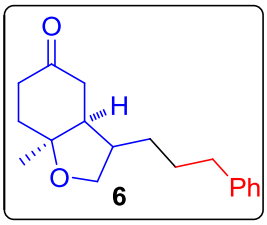
Peak#	Ret.Time	Area	Area %
1	10.925	28347546	98.85
2	14.687	327742	1.143
Total		28675288	100



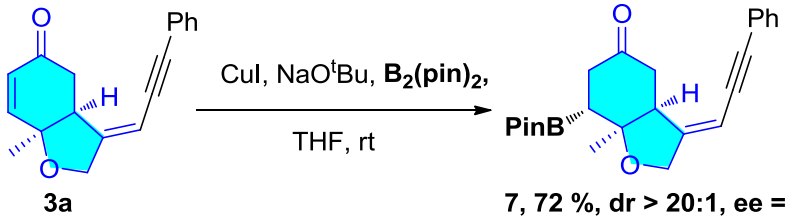
3a **6, 95%, dr = 1.3:1**

A mixture of 3ab (0.264 g, 1.0 mmol) and Pd/C (5% w/w, 0.053 g) in ethyl acetate (15 mL) was stirred overnight at ambient temperature under a hydrogen atmosphere. The solid was filtered out. The filtrate was concentrated in vacuo and the residue was purified by column chromatography (silica gel, Petroleum ether/ EtOAc:

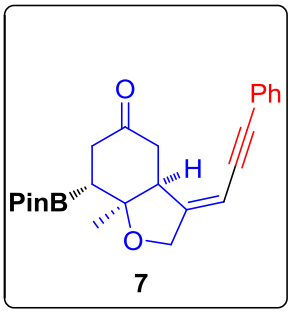
10/1) to afford **6** as colorless oil.[1b]



(major) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (t, *J* = 7.5 Hz, 2H), 7.30 -7.10 (m, 3H), 3.98 (dd, *J* = 8.8, 7.1 Hz, 1H), 3.33 (dd, *J* = 10.0, 9.0 Hz, 1H), 2.64 – 2.53 (m, 2H), 2.47 (dd, *J* = 15.9, 6.2 Hz, 1H), 2.42 – 2.30 (m, 2H), 2.20 (dt, *J* = 18.6, 4.7 Hz, 1H), 1.97 (dt, *J* = 14.4, 5.0 Hz, 1H), 1.90 – 1.80 (m, 1H), 1.81 – 1.70 (m, 2H), 1.60 – 1.49 (m, 3H), 1.31 (s, 3H), 1.29 – 1.23 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 212.5, 141.9, 128.4, 128.4, 125.9, 80.7, 70.6, 49.5, 47.5, 41.3, 36.1, 34.9, 33.0, 31.8, 30.1, 27.2. (minor) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.4 Hz, 2H), 7.22 – 7.10 (m, 3H), 4.06 – 3.99 (m, 1H), 3.46 (dd, *J* = 10.3, 8.7 Hz, 1H), 2.61 (t, *J* = 7.7 Hz, 2H), 2.59 – 2.41 (m, 2H), 2.32 – 2.19 (m, 3H), 2.17 – 2.05 (m, 2H), 1.98 (dt, *J* = 18.7, 6.6 Hz, 1H), 1.66 – 1.50 (m, 2H), 1.40 – 1.30 (m, 2H), 1.28 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 213.3, 142.0, 128.4, 128.3, 125.9, 81.9, 71.2, 45.3, 42.4, 37.8, 36.1, 35.8, 34.3, 30.4, 27.5, 26.9. HRMS (ESI, m/z) calcd for $C_{18}H_{24}O_2$ $[M+H]^+$ 273.1849, found 273.1847.

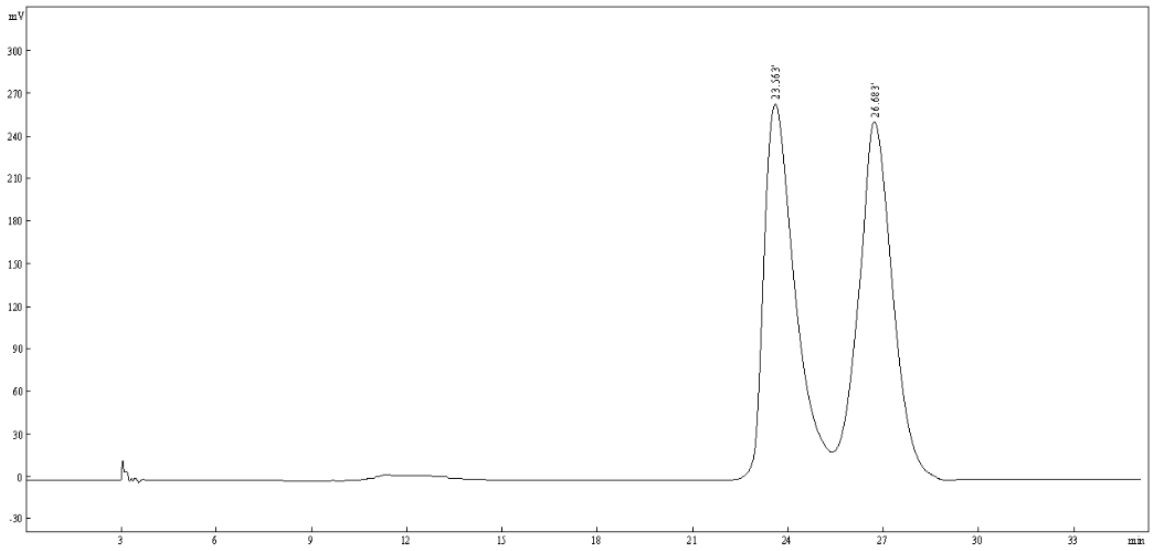


To a mixture of **3a** (0.2 mmol), CuI (0.02 mmol, 10 mmol%), NaO^{t}Bu (0.4 mmol, 2.0 equiv), $B_2(pin)_2$ (0.48 mmol, 2.4 equiv), 2 mL THF was added. The reaction system was stirred at rt for 2 hours. After the reaction was completed (determined by TLC analysis), the reaction mixture was filtered and evaporated under reduced pressure, and purified quickly by TLC to afford the desired product **7**.[4]

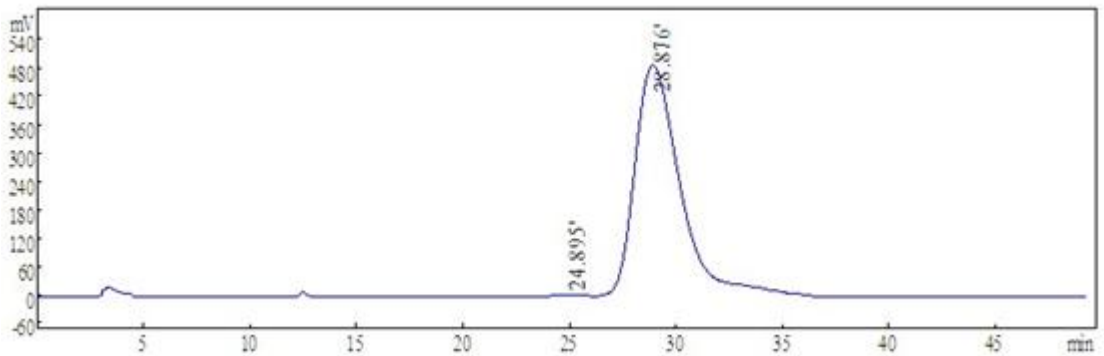


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.38 (m, 2H), 7.36 – 7.27 (m, 3H), 5.72 – 5.58 (m, 1H), 4.60 (d, *J* = 15.1 Hz, 1H), 4.50 (d, *J* = 15.1 Hz, 1H), 3.21 (t, *J* = 7.4 Hz, 1H),

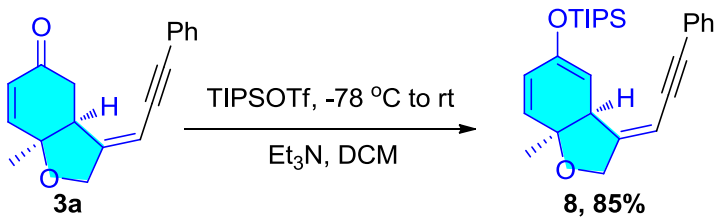
2.90 (dd, *J* = 15.5, 7.5 Hz, 1H), 2.63 (dd, *J* = 17.9, 6.1 Hz, 1H), 2.49 (dd, *J* = 15.5, 7.7 Hz, 1H), 2.24 (dd, *J* = 17.9, 7.5 Hz, 1H), 1.94 (t, *J* = 6.8 Hz, 1H), 1.35 (s, 3H), 1.27 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 212.1, 157.6, 131.3, 128.4, 128.3, 123.3, 101.4, 94.0, 85.8, 84.0, 83.9, 69.0, 48.3, 41.1, 37.3, 24.8, 24.7, 24.1. HRMS (ESI, m/z) calcd for $C_{24}H_{29}BO_4$ $[M+H]^+$ 393.2232, found 393.2236. $[\alpha]^{19}_D$ = -12.3 ° (c 0.28, $CHCl_3$); >99% ee; Chiral HPLC analysis of the product: Daicel Chiralpak AS-H 250X4.6 mm 5u column; hexane/2-propanol = 95/5, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 24.9 min (minor), 28.9 min (major).



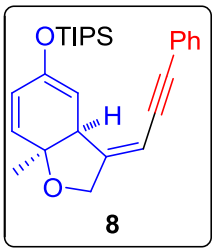
Peak#	Ret.Time	Area	Area %
1	23.563	16220048	49.09
2	26.683	16821995	50.91
Total		33042043	100



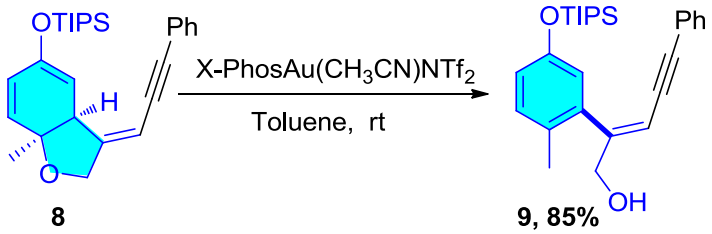
Peak#	Ret.Time	Area	Area %
1	24.895	334897	0.4576
2	28.876	72846413	99.54
Total		73181310	100



To a mixture of **3a** (0.2 mmol), and Et_3N (0.6 mmol, 3.0 equiv), 1 mL DCM was added at rt. And then, TIPSOTf (0.26 mmol, 1.3 equiv) was added at -78 ℃. And the the reaction system was stirred at the same temperature for 15 min, and stirred at rt for 1 h. After the reaction was completed (determined by TLC analysis), the reaction mixture was filtered and evaporated under reduced pressure, and purified by column chromatography (silica gel, Petroleum ether/ EtOAc: 100/1) to afford the desired product **8**.[5]

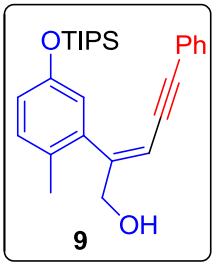


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 2H), 7.34 – 7.28 (m, 3H), 5.81 (dd, *J* = 10.0, 2.2 Hz, 1H), 5.66 – 5.59 (m, 2H), 5.45 (dd, *J* = 5.4, 1.9 Hz, 1H), 4.41 (dd, *J* = 13.8, 1.6 Hz, 1H), 4.19 (dt, *J* = 13.8, 2.4 Hz, 1H), 3.44 (dt, *J* = 5.1, 2.4 Hz, 1H), 1.37 (s, 3H), 1.14 (dd, *J* = 9.8, 5.3 Hz, 3H), 1.01 (dd, *J* = 7.4, 2.6 Hz, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.0, 146.6, 132.0, 131.3, 128.3, 128.1, 127.2, 123.6, 101.4, 99.7, 93.7, 86.5, 81.0, 69.7, 48.3, 26.4, 17.87 (d, *J* = 4.9 Hz), 12.5. HRMS (ESI, m/z) calcd for $C_{27}H_{36}O_2Si$ $[M+H]^+$ 421.2557, found 421.2535.



To a mixture of **8** (0.2 mmol), and X-PhosAu(CH_3CN)NTf_2 (0.01 mmol, 5.0 mmol%), 1 mL toluene was added under nitrogen atmosphere at rt. Then, to the stirred solution above, 100 μl MeOH was added quikly. And the the reaction system was stirred at the same temperature for 15 min. After the reaction was completed (determined by TLC analysis), the reaction mixture was filtered and evaporated under

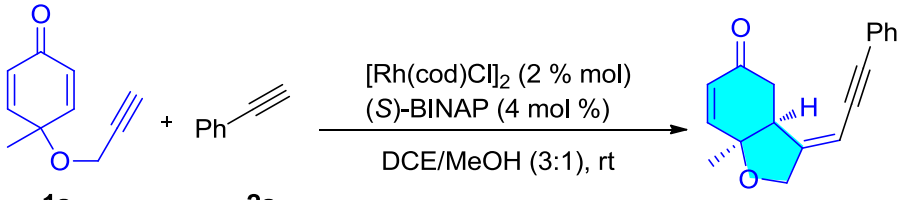
reduced pressure, and purified by column chromatography (silica gel, Petroleum ether/ EtOAc: 20/1) to afford the desired product **9**.



9

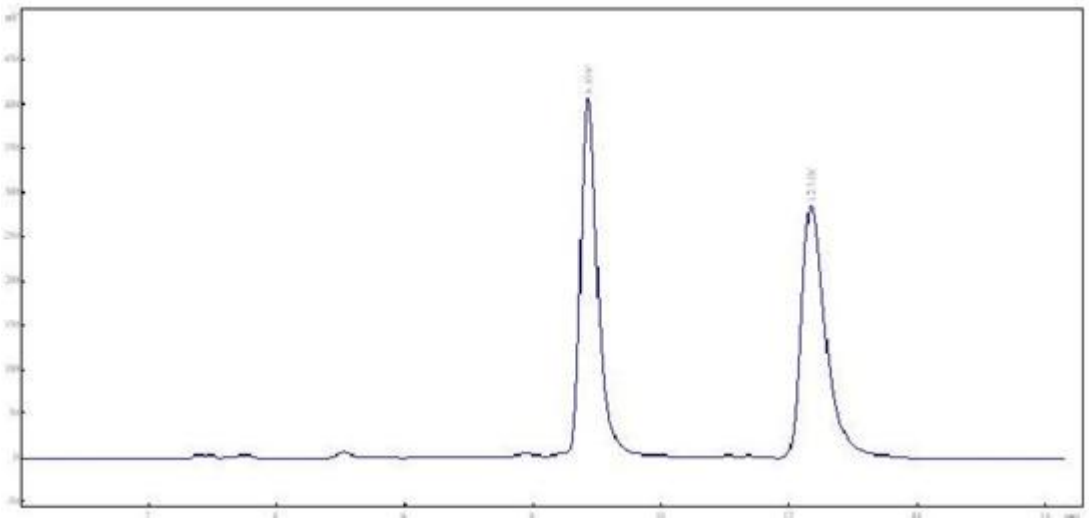
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 – 7.15 (m, 3H), 7.15 – 7.10 (m, 2H), 7.08 (d, *J* = 8.3 Hz, 1H), 6.77 (dd, *J* = 8.3, 2.6 Hz, 1H), 6.68 (d, *J* = 2.6 Hz, 1H), 6.09 (t, *J* = 1.8 Hz, 1H), 4.37 (s, 2H), 2.25 (s, 3H), 1.69 (s, 1H), 1.24 – 1.19 (m, 3H), 1.06 (d, *J* = 7.3 Hz, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.7, 153.0, 138.2, 131.4, 130.9, 128.5, 128.0, 127.8, 123.6, 119.8, 119.4, 106.9, 93.0, 86.9, 66.3, 18.5, 17.9, 12.6. HRMS (ESI, m/z) calcd for $C_{27}H_{36}O_2Si$ $[M+NH_4]^+$ 438.2823, found 438.2827.

5. **Scale up Experiment**

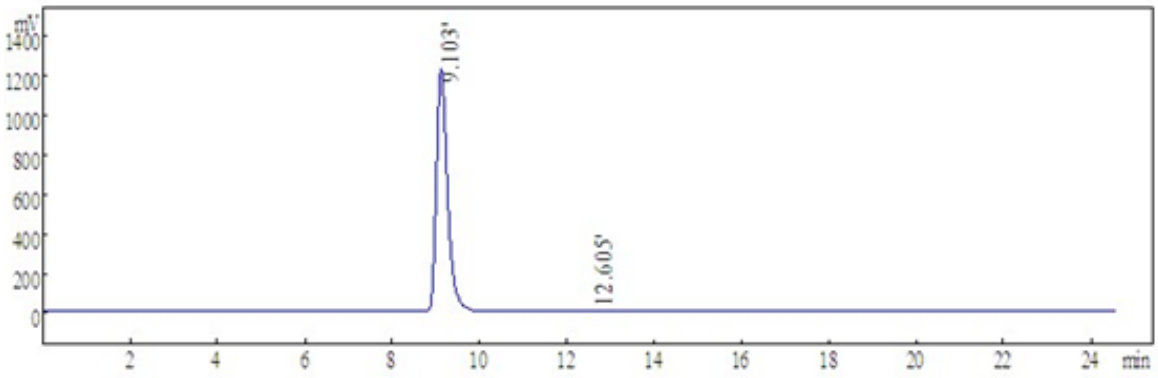


1a **2a** **3a, 86 %, 1.14 g, 99%ee**

To a mixture of **1a** (5 mmol, 1 equiv), $[Rh(cod)Cl]_2$ (0.1 mmol, 2.0 mmol%), and (S)-BINAP (0.2 mmol, 4.0 mol %), 15 mL DCE was added under nitrogen atmosphere . Then, to the stirred solution above, **2** (10 mmol, 2.0 equiv) and 5 ml MeOH was added quikly. The reaction system was stirred at room temperature overnight. After the reaction was completed (determined by TLC analysis), the solvent was evaporated under reduced pressure, and purified by column chromatography (silica gel, Petroleum ether/ EtOAc: 10/1) to afford the desired product **3a**. 99% ee; Chiral HPLC analysis of the product: Phenomenex 00G-4457-E0 250X4.6 mm 5u column; hexane/2-propanol =85/15, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 9.1 min (major), 12.6 min (minor).

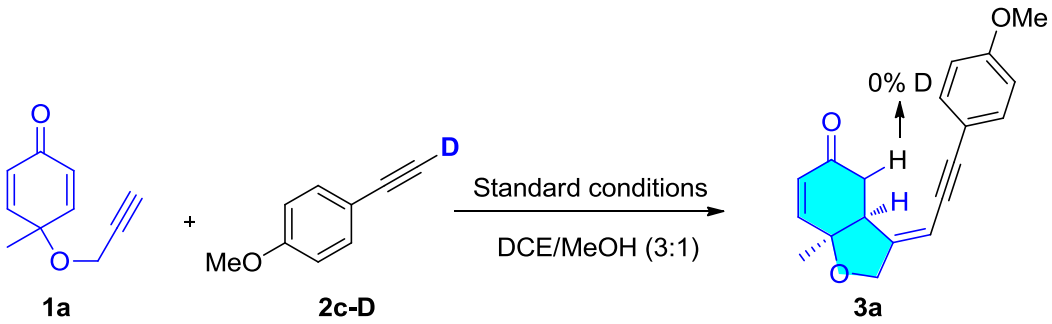


Peak#	Ret.Time	Area	Area %
1	8.838	7597408	50.06
2	12.318	7577711	49.94
Total		15175119	100

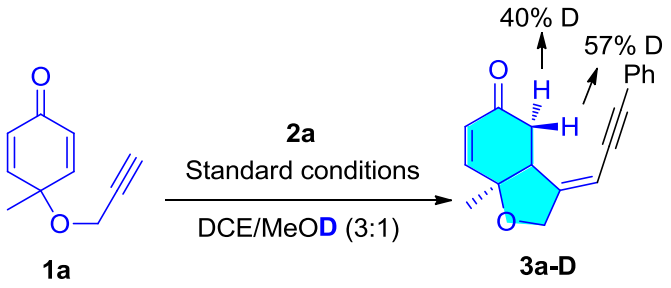


Peak#	Ret.Time	Area	Area %
1	9.103	21859675	99.56
2	12.605	96794	0.4408
Total		21956469	100

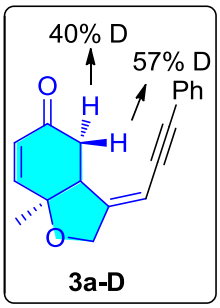
6. **Deuterium - Labeling Experiments**



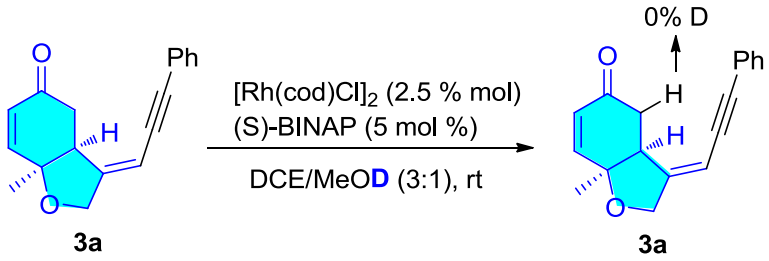
To a mixture of **1a** (0.2 mmol, 1 equiv), $[Rh(cod)Cl]_2$ (0.005 mmol, 2.5 mmol%), and (S)-BINAP (0.010 mmol, 5.0 mol %), 1.5 mL DCE was added under nitrogen atmosphere . Then, to the stirred solution above, **2c-D** (0.4 mmol, 2.0 equiv) and 0.5 ml MeOH was added quikly. The reaction system was stirred at room temperature overnight. After the reaction was completed (determined by TLC analysis), the solvent was evaporated under reduced pressure, and purified by column chromatography (silica gel, Petroleum ether/ EtOAc: 10/1) to afford product **3a**.



To a mixture of **1a** (0.2 mmol, 1 equiv), $[Rh(cod)Cl]_2$ (0.005 mmol, 2.5 mmol%), and (S)-BINAP (0.010 mmol, 5.0 mol %), 1.5 mL DCE was added under nitrogen atmosphere . Then, to the stirred solution above, **2a** (0.4 mmol, 2.0 equiv) and 0.5 ml MeO**D** was added quikly. The reaction system was stirred at room temperature overnight. After the reaction was completed (determined by TLC analysis), the solvent was evaporated under reduced pressure, and purified by column chromatography (silica gel, Petroleum ether/ EtOAc: 10/1) to afford the desired product **3a-D**.



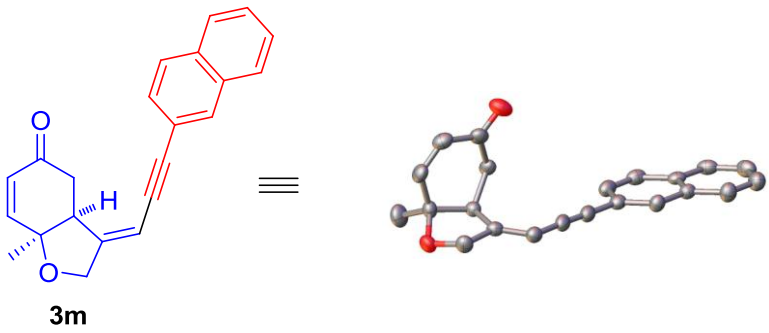
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 6.5, 3.2 Hz, 2H), 7.33 (dd, *J* = 5.0, 1.8 Hz, 3H), 6.54 (dt, *J* = 10.3, 1.8 Hz, 1H), 6.03 (dd, *J* = 10.3, 1.0 Hz, 1H), 5.73 (dd, *J* = 4.9, 2.3 Hz, 1H), 4.54 – 4.44 (m, 1H), 4.34 – 4.28 (m, 1H), 3.63 – 3.56 (m, 1H), 3.26 – 3.16 (m, 1H), 2.66 (dd, *J* = 6.0, 1.0 Hz, 1H), 1.55 (d, *J* = 1.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.81 (d, *J* = 5.1 Hz), 153.65 (d, *J* = 2.7 Hz), 150.39 (d, *J* = 4.2 Hz), 131.4, 130.1, 128.4, 128.4, 123.1, 102.2, 95.6, 84.7, 80.5, 70.4, 47.9, 36.0 (dd, *J* = 38.4, 19.4 Hz), 23.41 (d, *J* = 6.9 Hz). HRMS (ESI, m/z) calcd for $C_{18}H_{15}DO_2$ $[M+Na]^+$ 288.1105, found 288.1111.

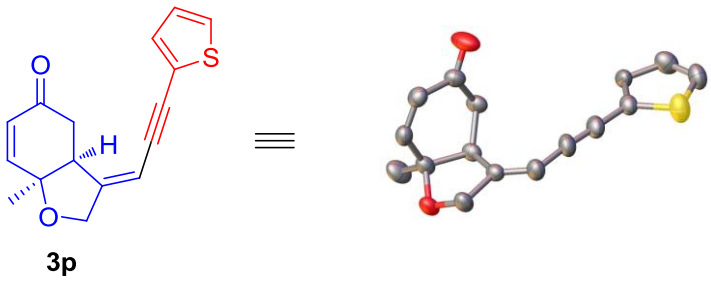


To a mixture of **3a** (0.2 mmol, 1 equiv), $[Rh(cod)Cl]_2$ (0.005 mmol, 2.5 mmol%), and (S)-BINAP (0.010 mmol, 5.0 mol %), 1.5 mL DCE was added under nitrogen atmosphere . Then, to the stirred solution above, **2a** (0.4 mmol, 2.0 equiv) and 0.5 ml MeO**D** was added quikly. The reaction system was stirred at room temperature overnight. After the reaction was completed (determined by TLC analysis), the solvent was evaporated under reduced pressure, and purified by column chromatography (silica gel, Petroleum ether/ EtOAc: 10/1) to afford product **3a**.

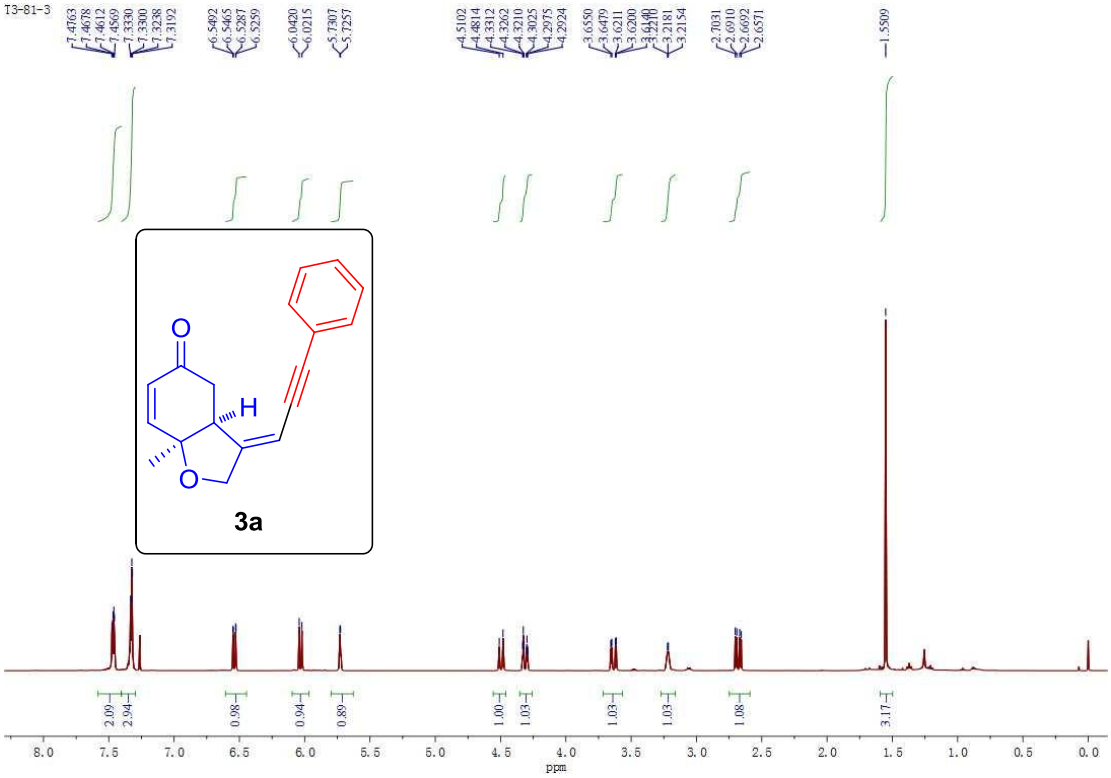
7. X-ray Crystallography

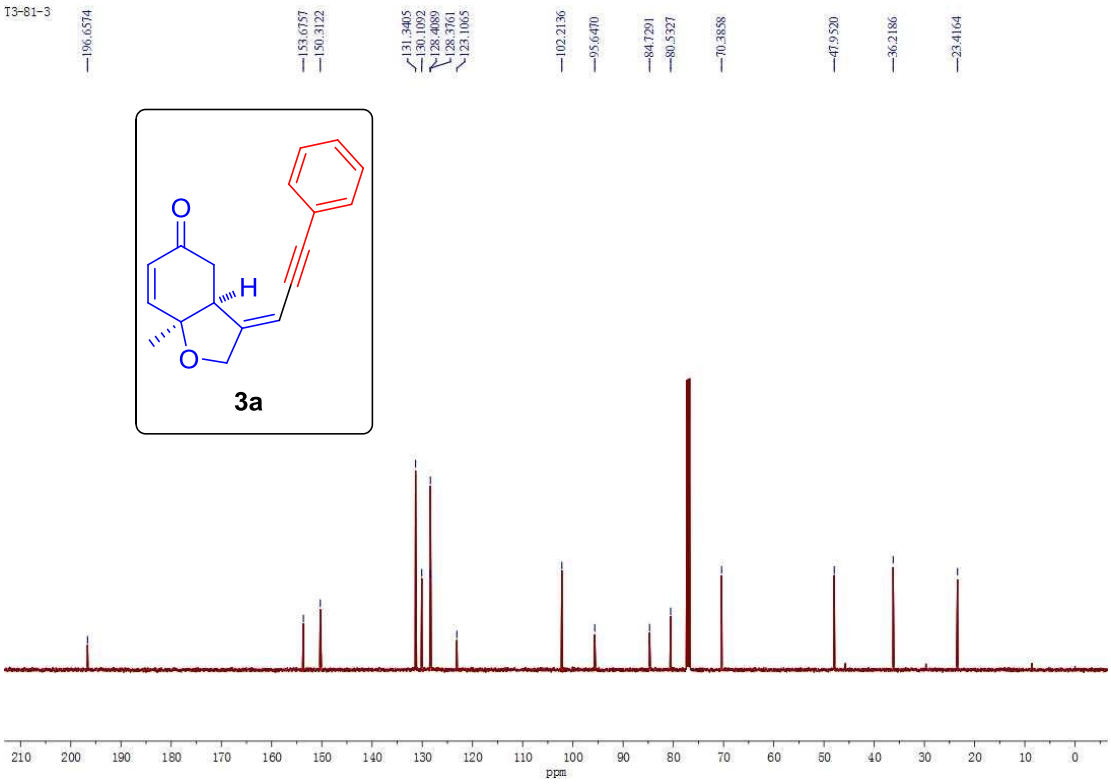
The crystal of **3m** and **3p** suitable for XRD analysis was prepared by recrystallization from a mixed solvent of DCM and petroleum ether. CCDC 1845186 (**3m**) and CCDC 1847564 (**3p**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

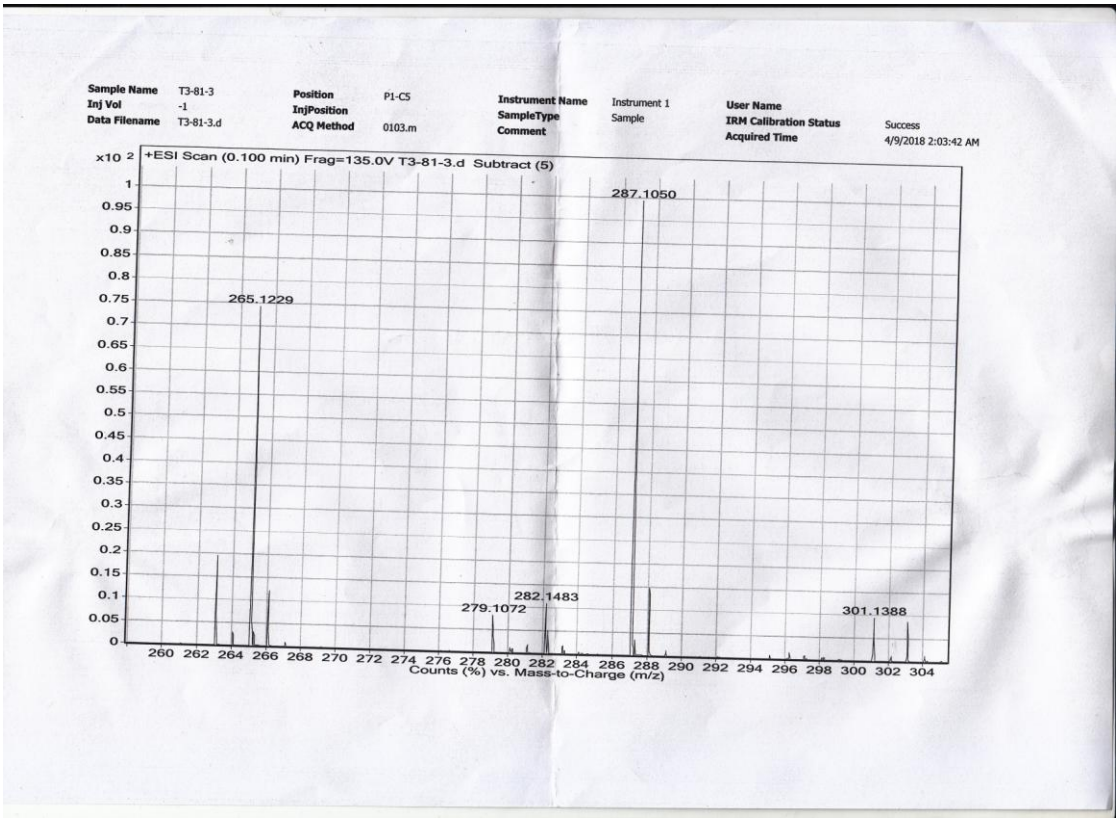


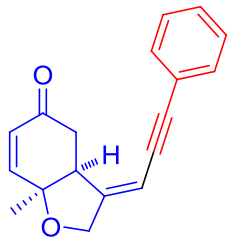


8. **NMR and HRMS Spectra of All Compounds**





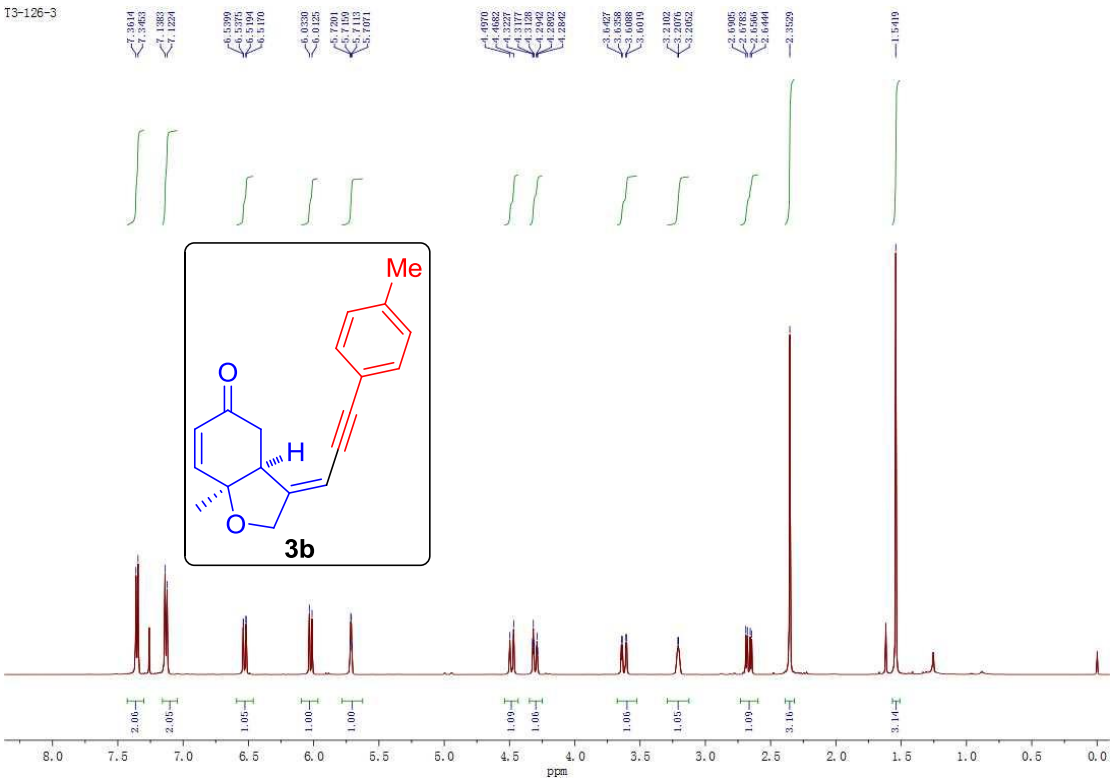


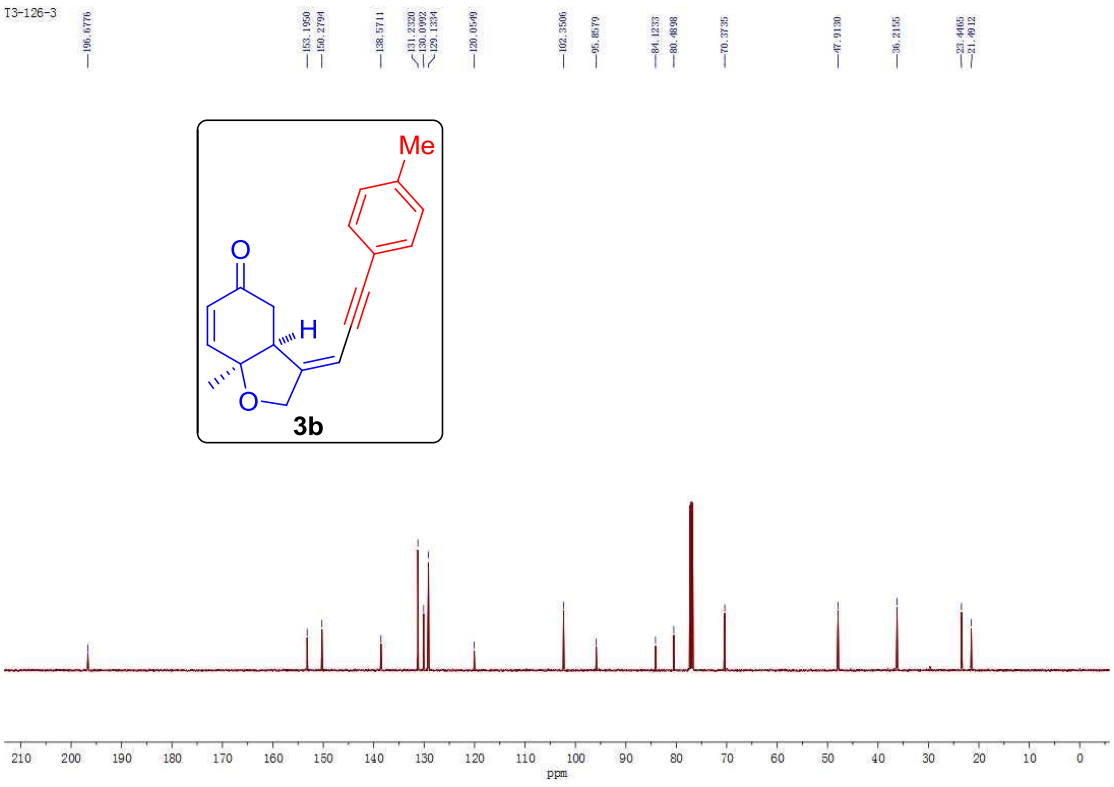


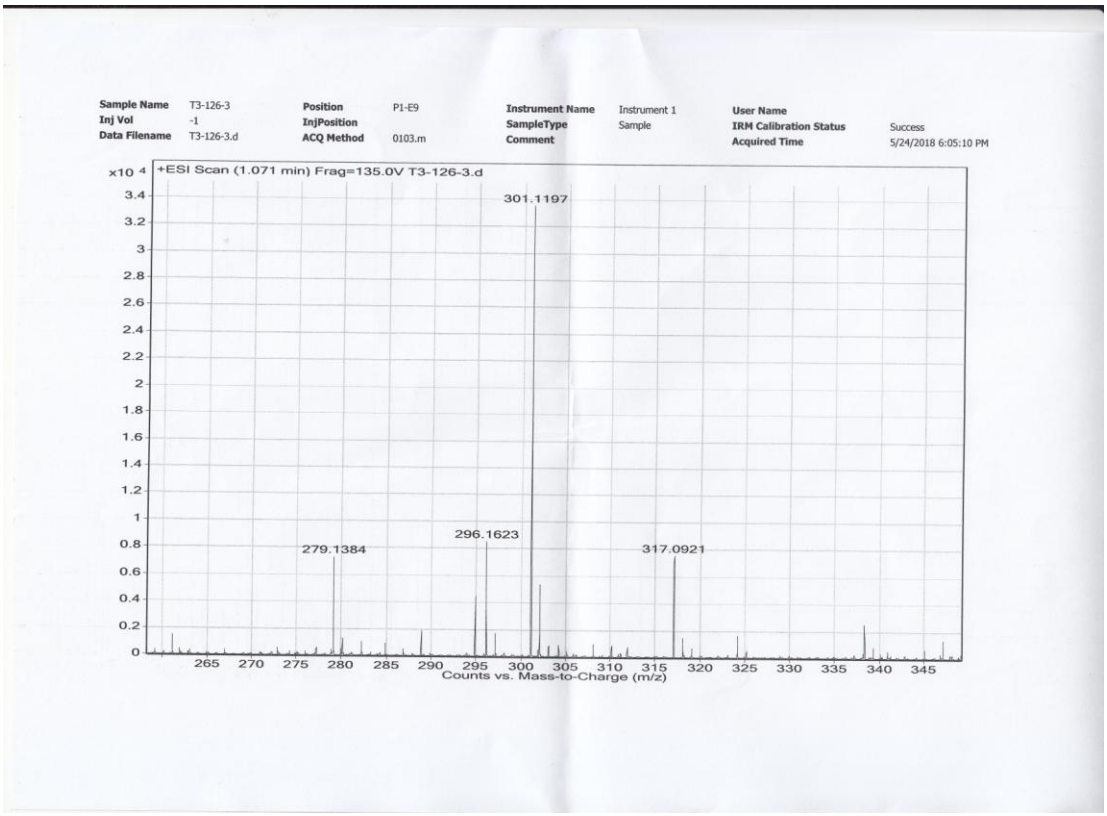
3a

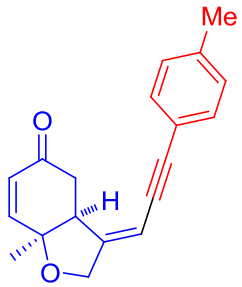
Chemical Formula: $C_{18}H_{16}O_2$
Exact Mass: 264.1150
Molecular Weight: 264.3184
m/z: 264.1150 (100.0%), 265.1184 (19.5%), 266.1217 (1.8%)

HRMS (ESI, m/z) calcd for $C_{18}H_{16}O_2$ $[M+H]^+$ 265.1229, found 265.1229.


T3-126-3
Me
O
H
O
3b
ppm


T3-126-3
Me
O
H
O
3b
ppm

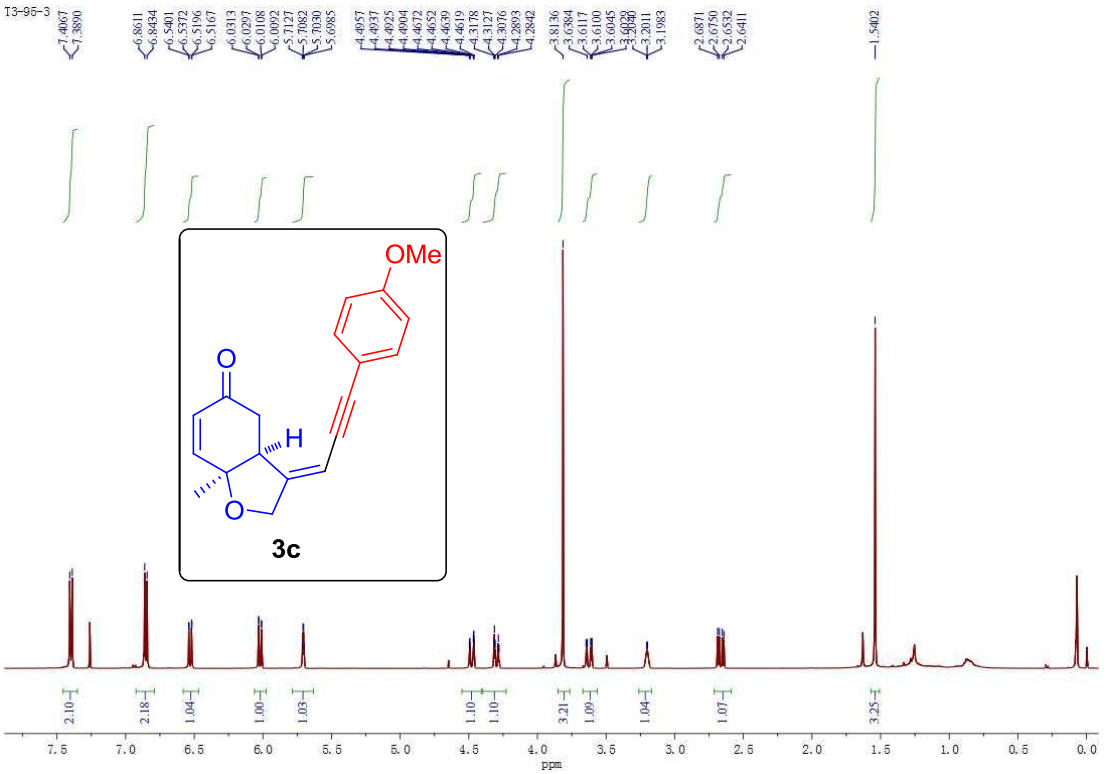


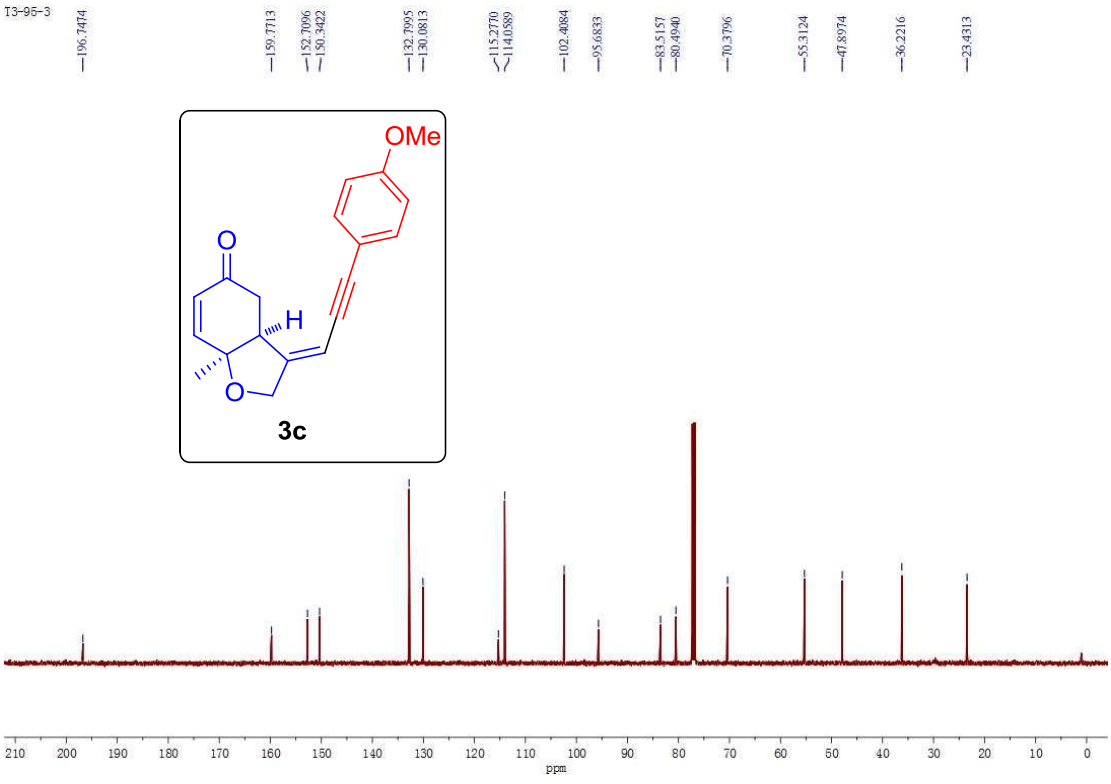


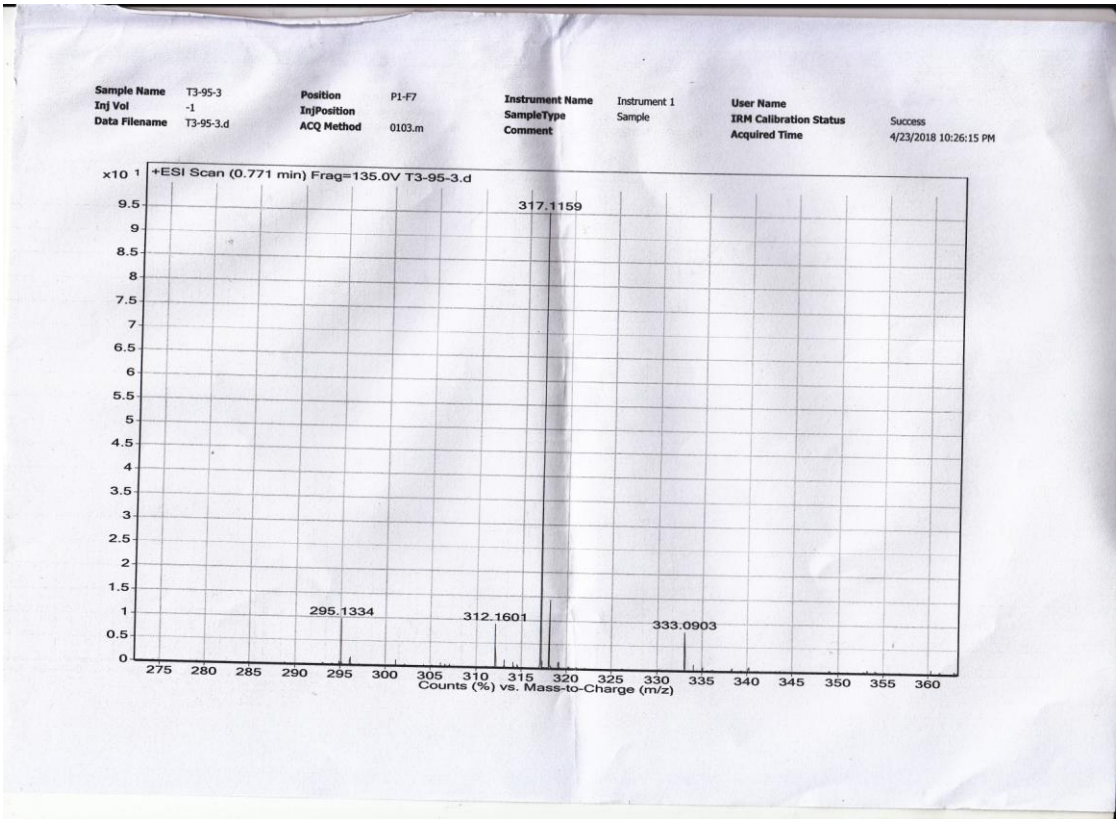
3b

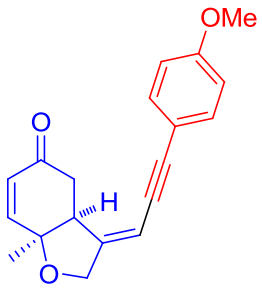
Chemical Formula: $C_{19}H_{18}O_2$
Exact Mass: 278.1307
Molecular Weight: 278.3450
m/z: 278.1307 (100.0%), 279.1340 (20.5%), 280.1374 (2.0%)

HRMS (ESI, m/z) calcd for $C_{19}H_{18}O_2$ $[M+H]^+$ 279.1380, found 279.1384.


T3-95-3
OMe
O
H
O
3c
ppm


T3-95-3
OMe
O
H
O
3c
ppm

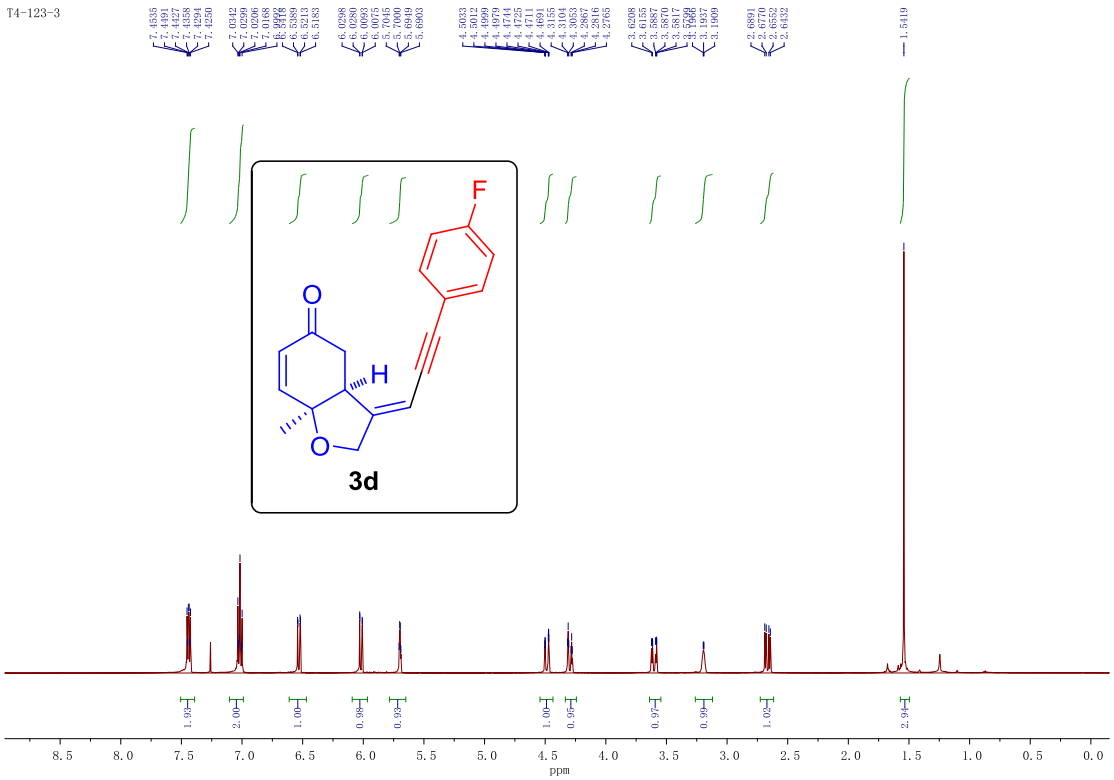


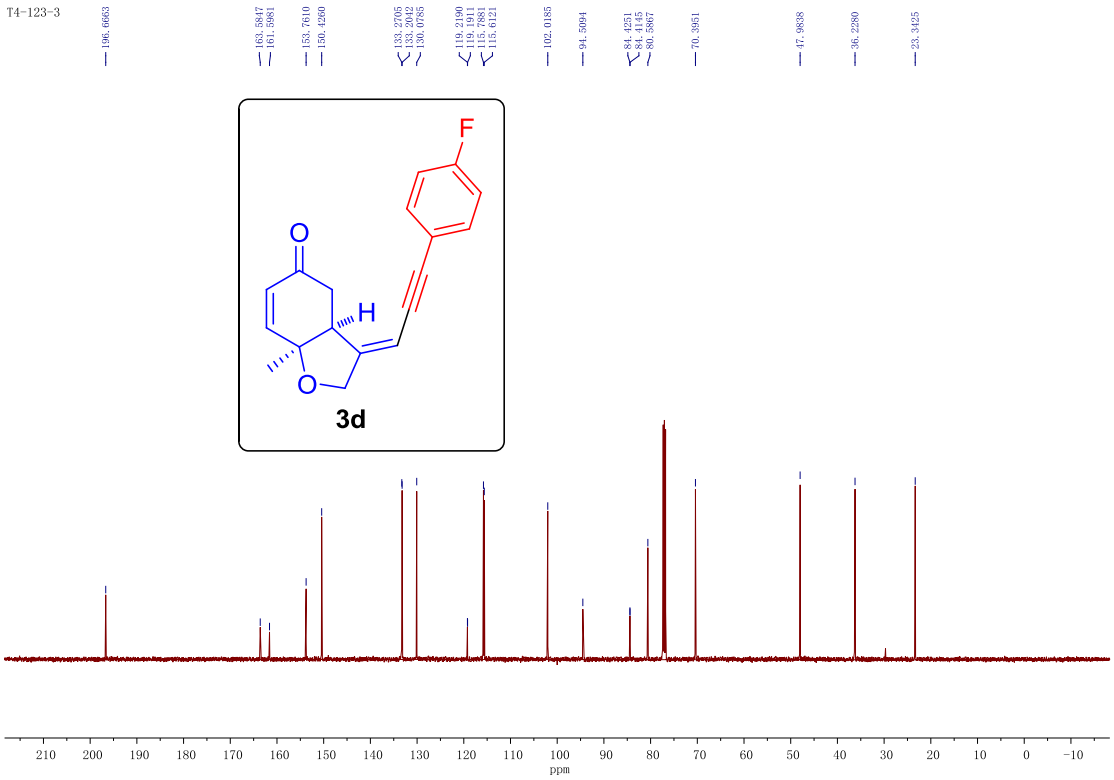


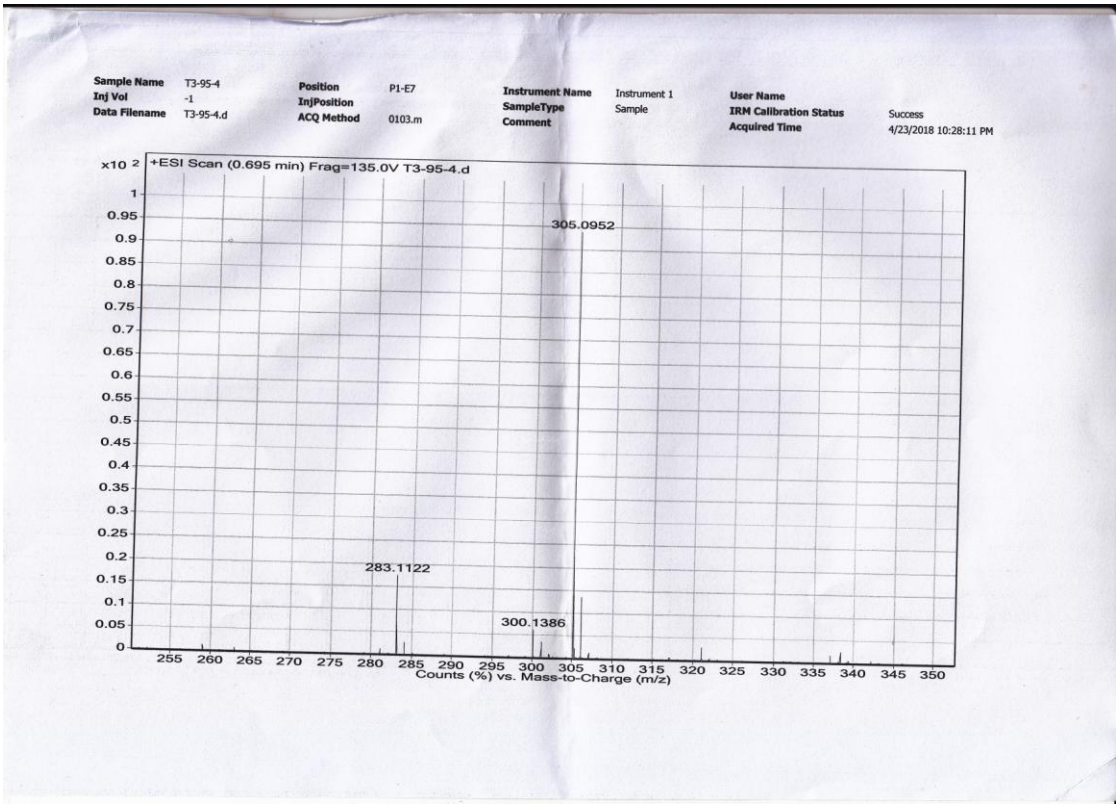
3c

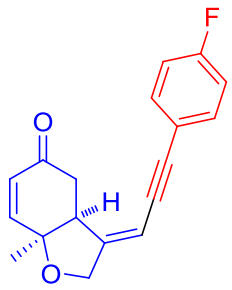
Chemical Formula: $C_{19}H_{18}O_3$
Exact Mass: 294.1256
Molecular Weight: 294.3444
m/z: 294.1256 (100.0%), 295.1289 (20.5%), 296.1323 (2.0%)

HRMS (ESI, m/z) calcd for $C_{19}H_{19}O_3$ $[M+H]^+$ 295.1334, found 295.1334.


T4-123-3
F
O
H
O
3d
ppm


T4-123-3
F
O
H
O
3d
ppm

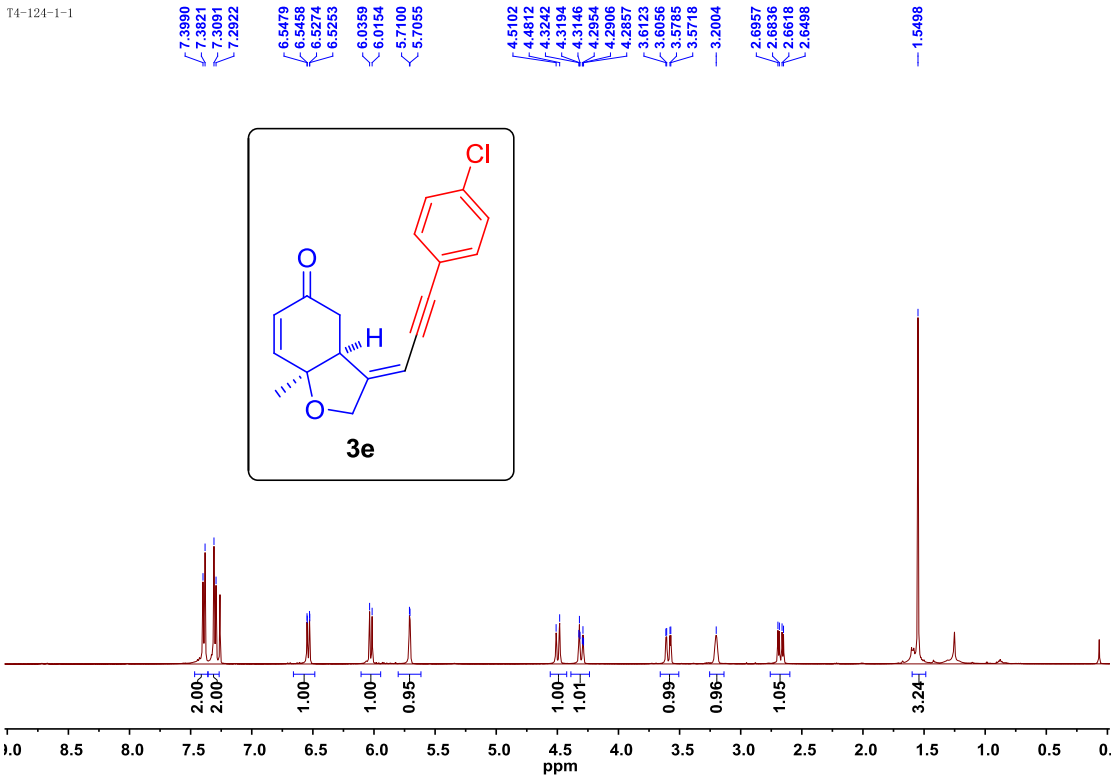


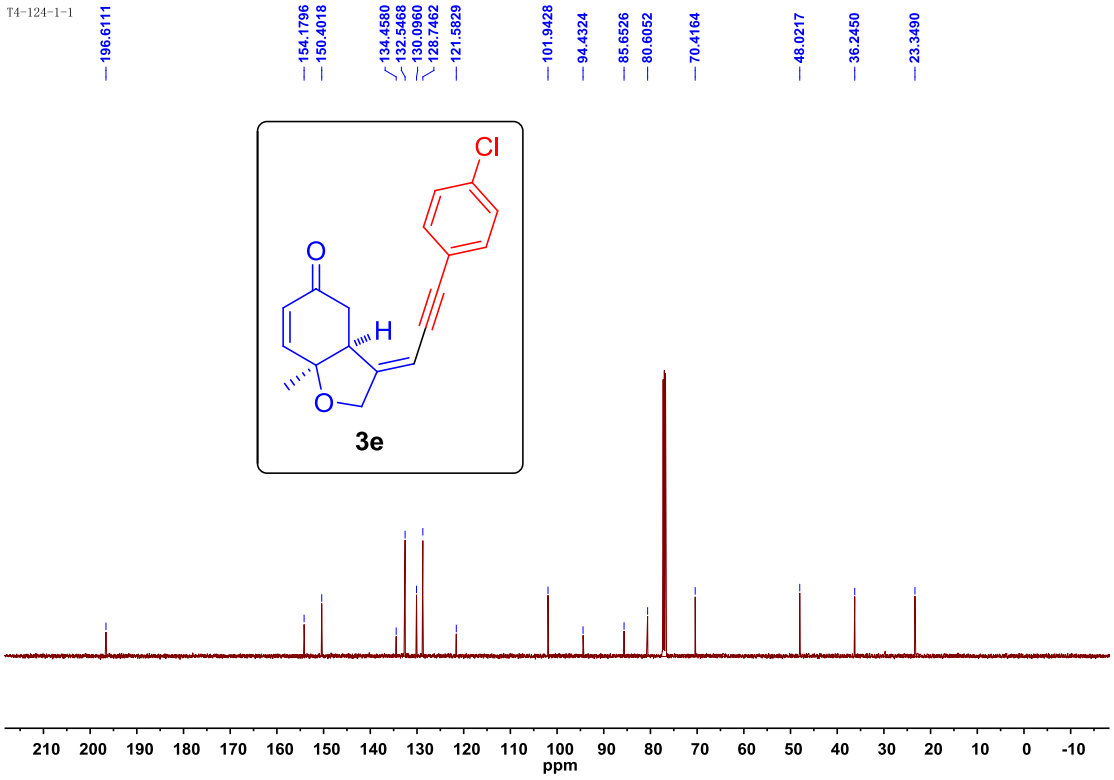


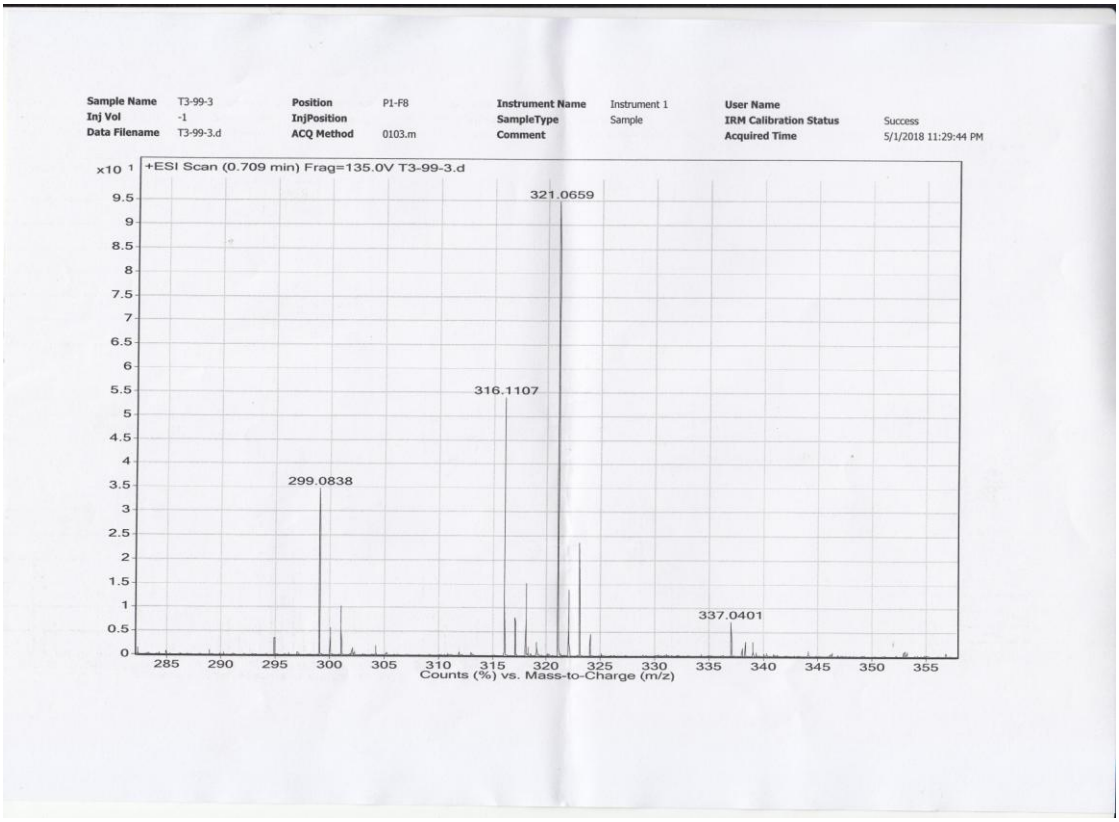
3d

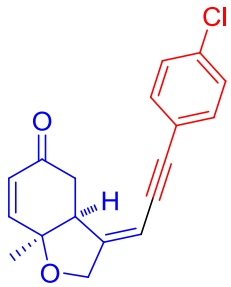
Chemical Formula: $C_{18}H_{15}FO_2$
Exact Mass: 282.1056
Molecular Weight: 282.3089
m/z: 282.1056 (100.0%), 283.1090 (19.5%), 284.1123 (1.8%)

HRMS (ESI, m/z) calcd for $C_{18}H_{15}FO_2$ $[M+H]^+$ 283.1134, found 283.1122.


T4-124-1-1
7.3990
7.3821
7.3091
7.2922
6.5479
6.5458
6.5274
6.5253
6.0359
6.0154
5.7100
5.7055
4.5102
4.4812
4.3242
4.3194
4.3146
4.2954
4.2906
4.2857
3.6123
3.6056
3.5785
3.5718
3.2004
2.6957
2.6836
2.6618
2.6498
1.5498
Cl
O
H
O
3e
2.00
2.00
1.00
1.00
0.95
1.00
1.01
0.99
0.96
1.05
3.24
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
ppm


T4-124-1-1
196.6111
154.1796
150.4018
134.4580
132.5468
130.0960
128.7462
121.5829
101.9428
94.4324
85.6526
80.6052
70.4164
48.0217
36.2450
23.3490
Cl
O
H
O
3e
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

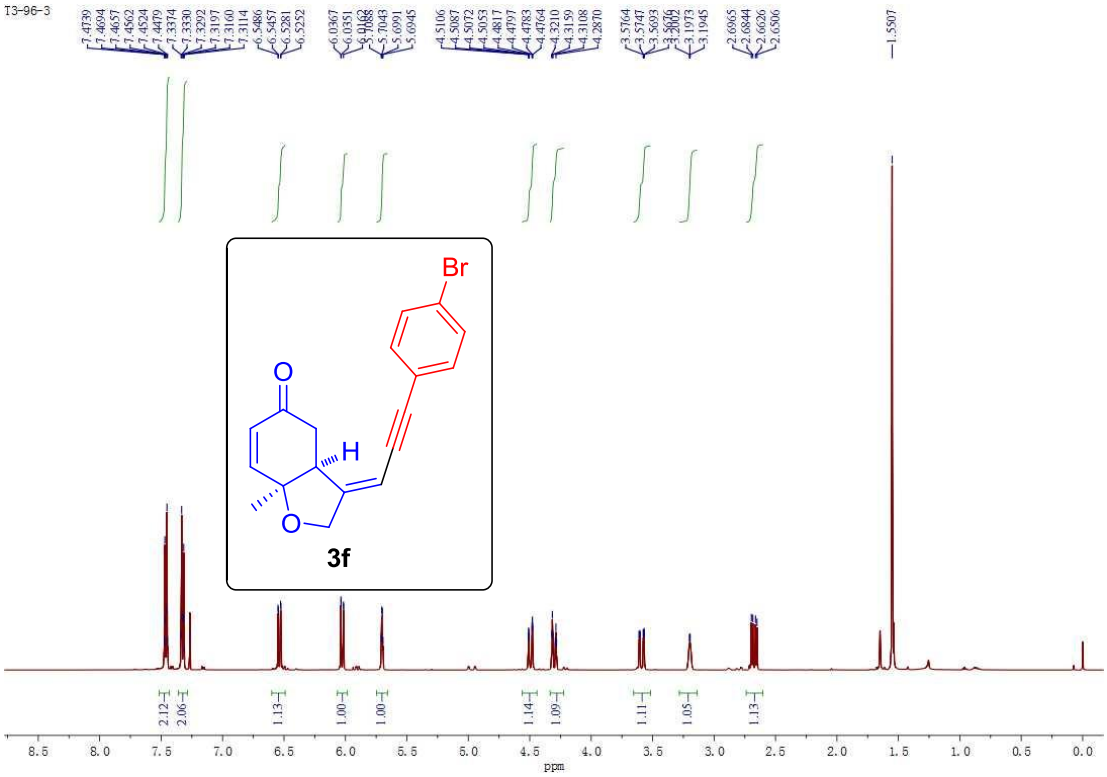


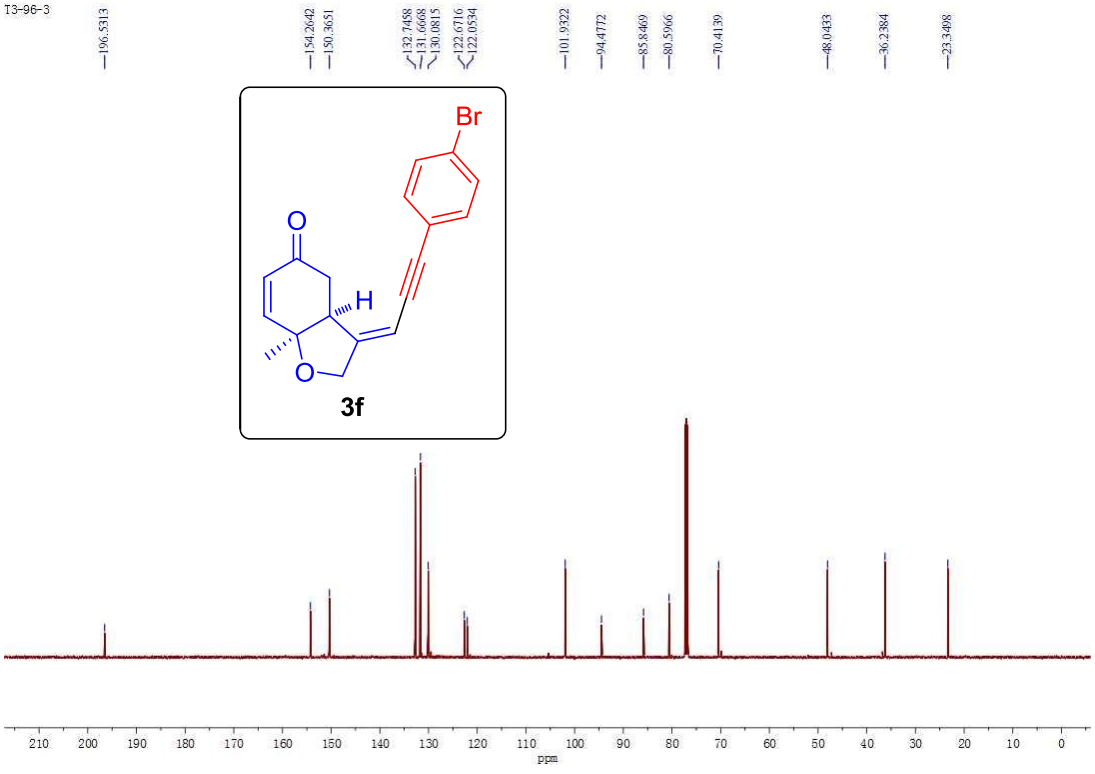


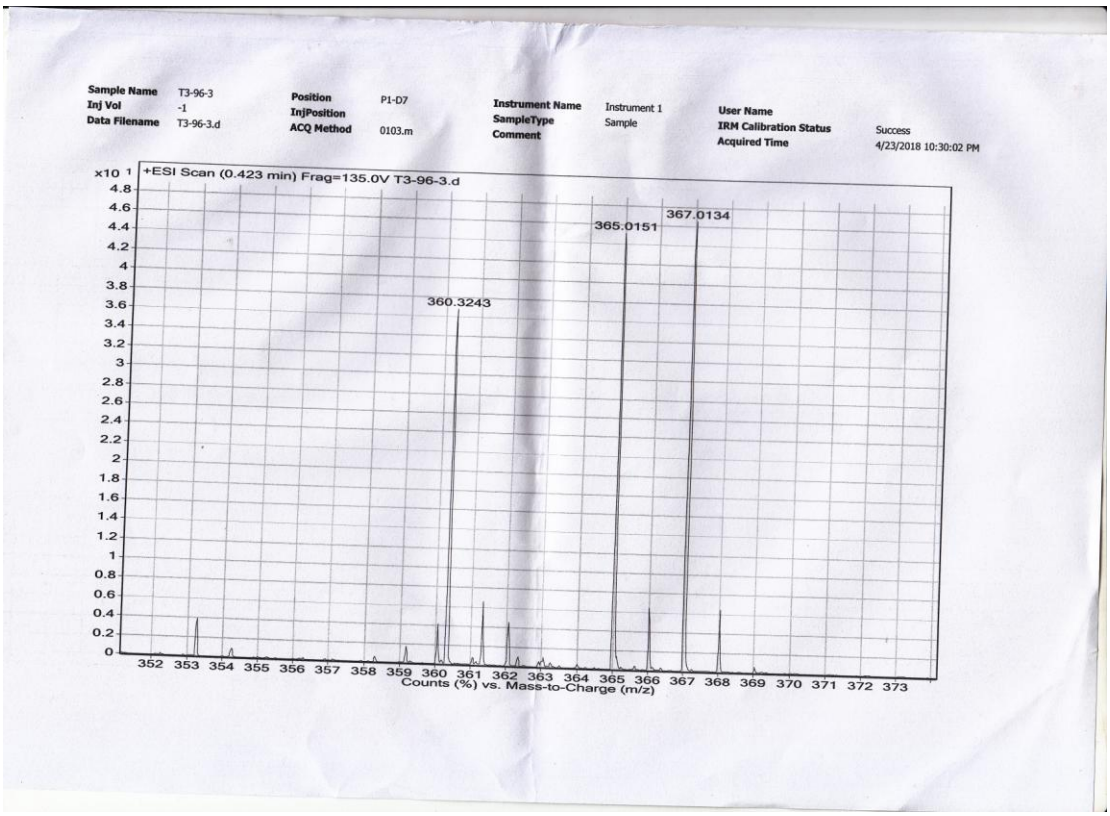
3e

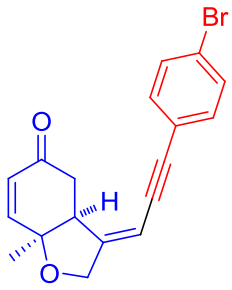
Chemical Formula: $C_{18}H_{15}ClO_2$
Exact Mass: 298.0761
Molecular Weight: 298.7635
m/z: 298.0761 (100.0%), 300.0731 (32.0%), 299.0794 (19.5%), 301.0765 (6.2%), 300.0828 (1.8%)

HRMS (ESI, m/z) calcd for $C_{18}H_{15}ClO_2$ $[M+H]^+$ 299.0833, found 299.0838.


T3-96-3
Br
O
H
O
3f
ppm


T3-96-3
Br
O
H
O
3f
ppm

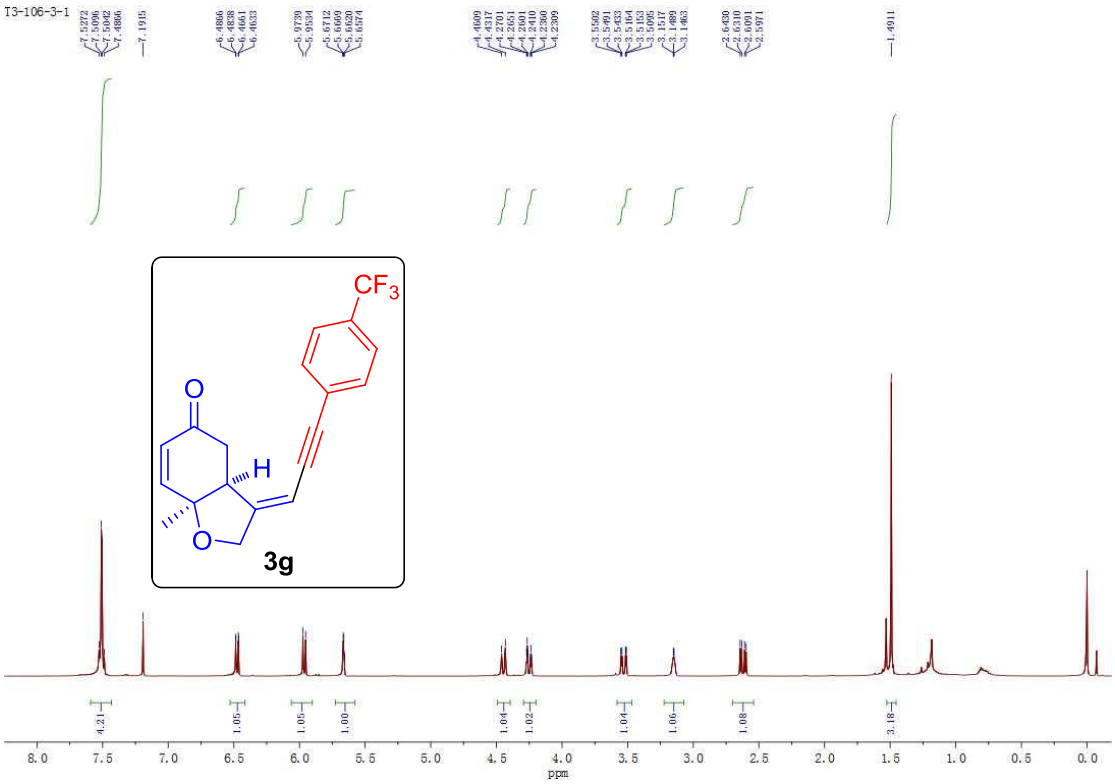


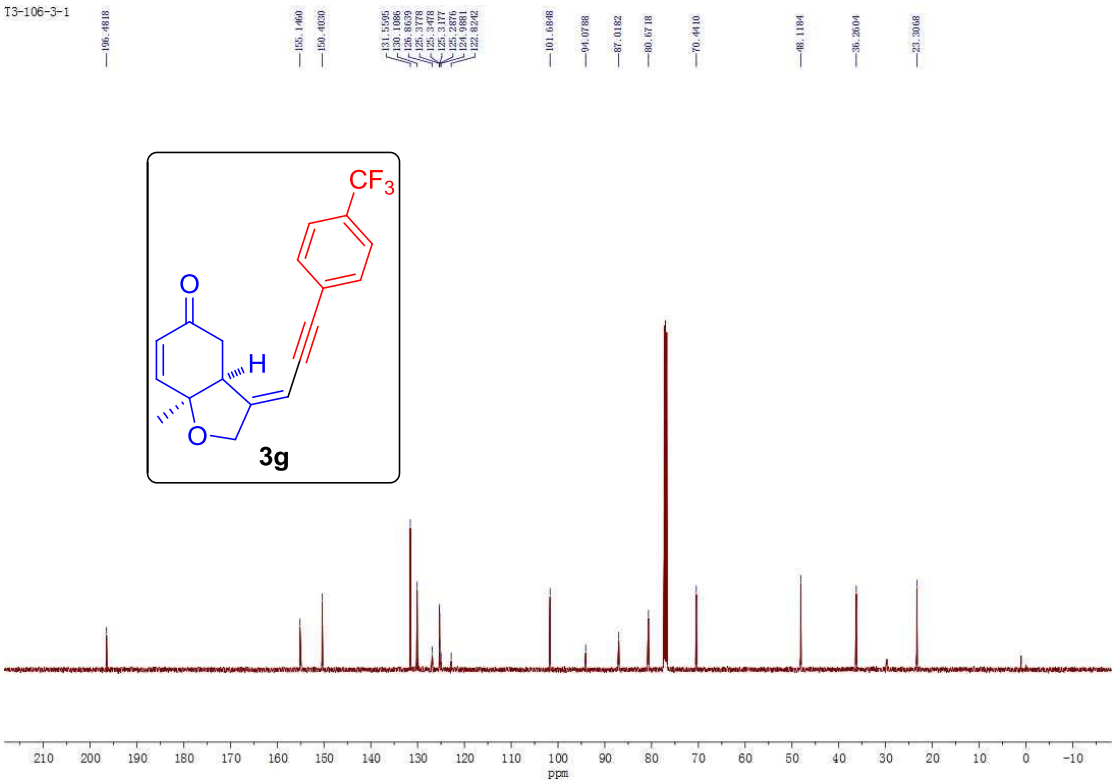


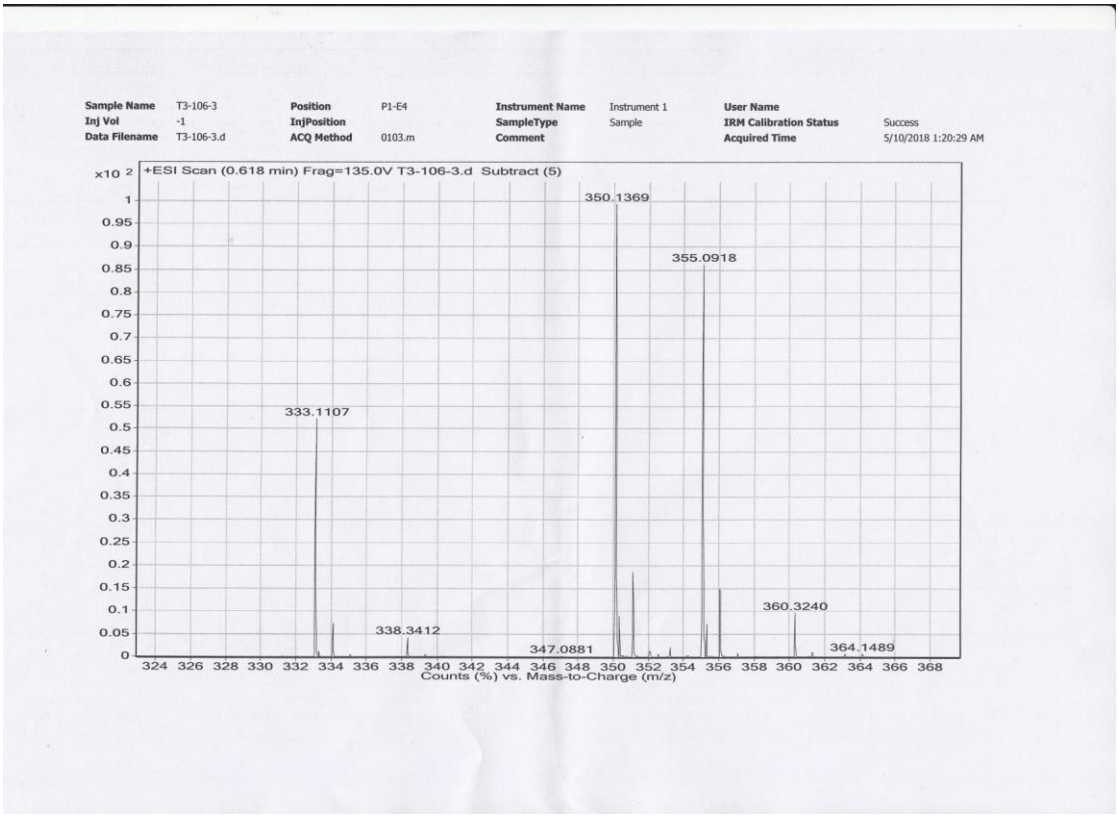
3f

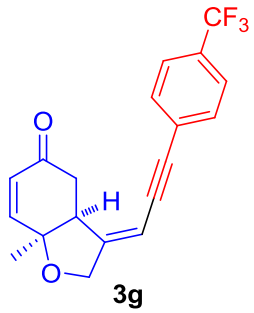
Chemical Formula: $C_{18}H_{15}BrO_2$
Exact Mass: 342.0255
Molecular Weight: 343.2145
m/z: 342.0255 (100.0%), 344.0235 (97.3%), 343.0289 (19.5%), 345.0269 (18.9%), 344.0323 (1.8%), 346.0302 (1.7%)

HRMS (ESI, m/z) calcd for $C_{18}H_{15}BrO_2$ $[M+Na]^+$ 365.0153, found 365.0151.


T3-106-3-1
CF3
O
H
O
3g
ppm


T3-106-3-1
CF3
O
H
O
3g
ppm

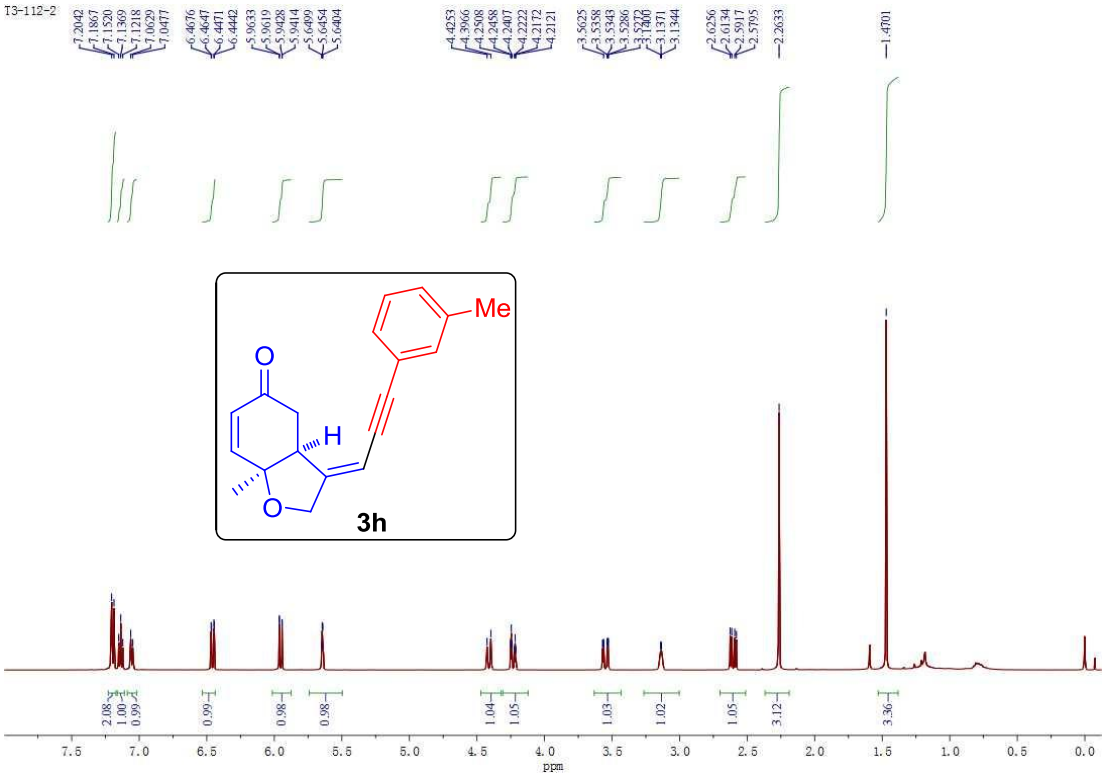


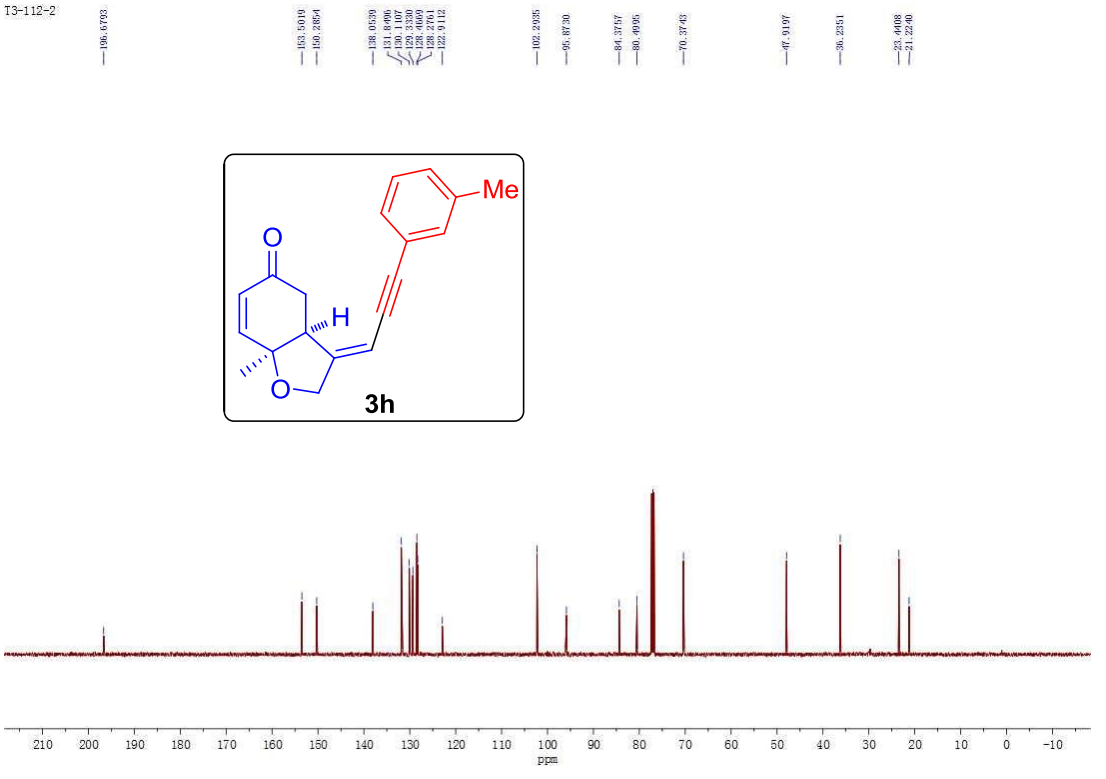


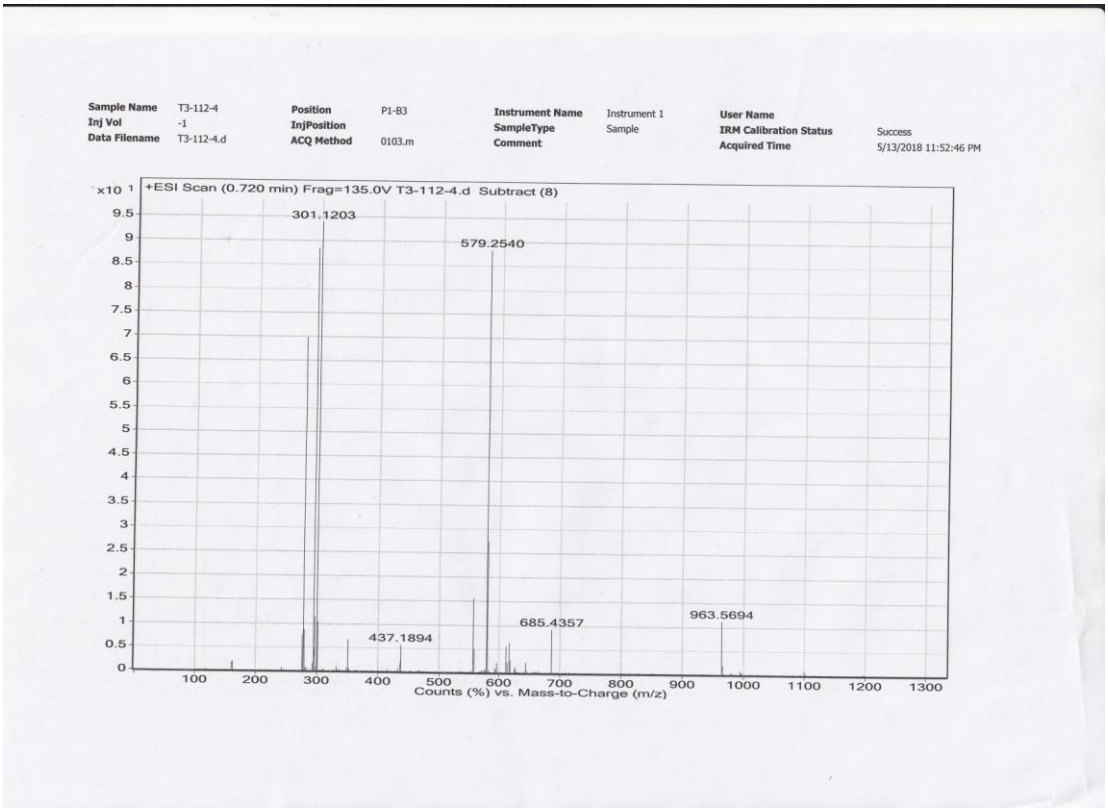
3g

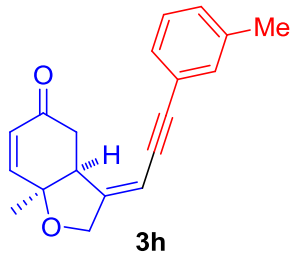
Chemical Formula: $C_{19}H_{15}F_3O_2$
Exact Mass: 332.1024
Molecular Weight: 332.3164
m/z: 332.1024 (100.0%), 333.1058 (20.5%), 334.1091 (2.0%)

HRMS (ESI, m/z) calcd for $C_{19}H_{15}F_3O_2$ $[M+H]^+$ 333.1102, found 333.1107.


T3-112-2
Me
O
H
O
3h
ppm


T3-112-2
Me
O
H
O
3h
ppm

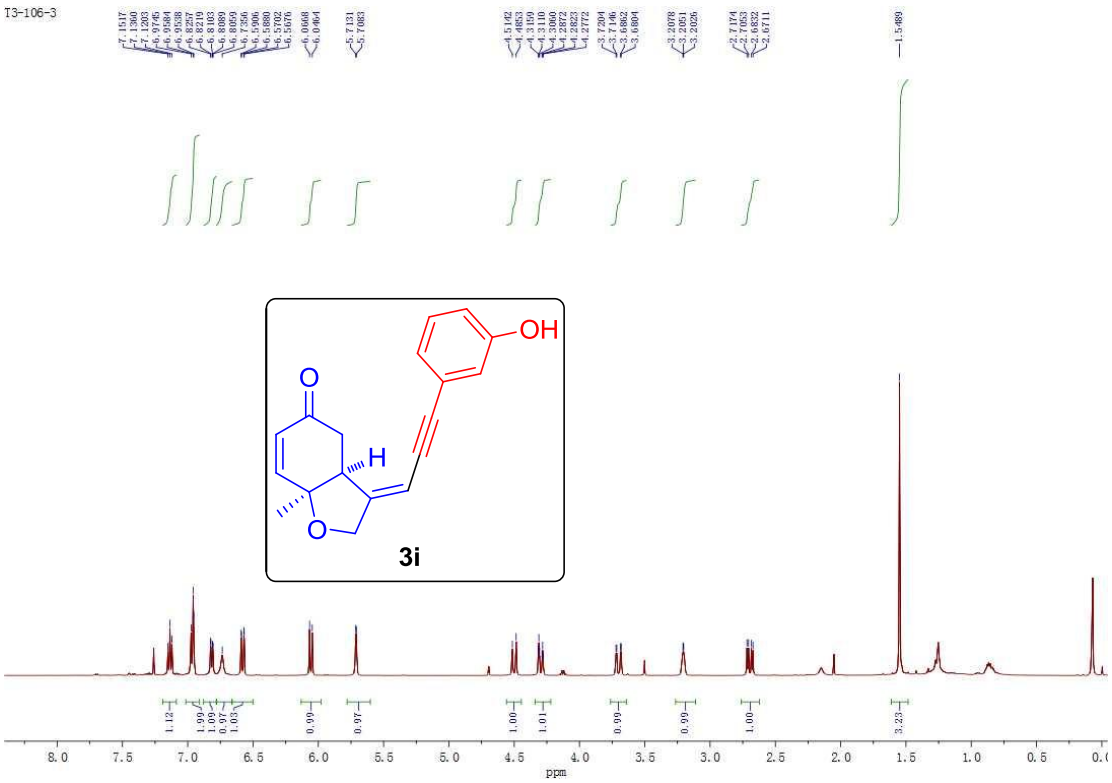


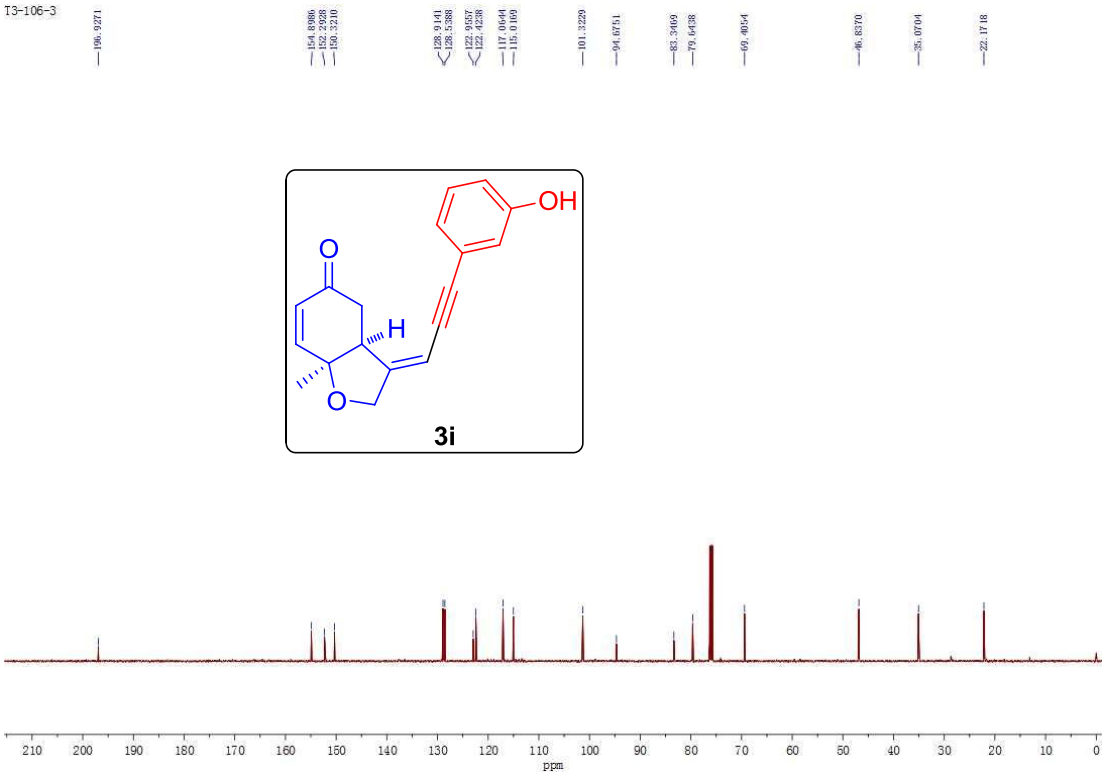


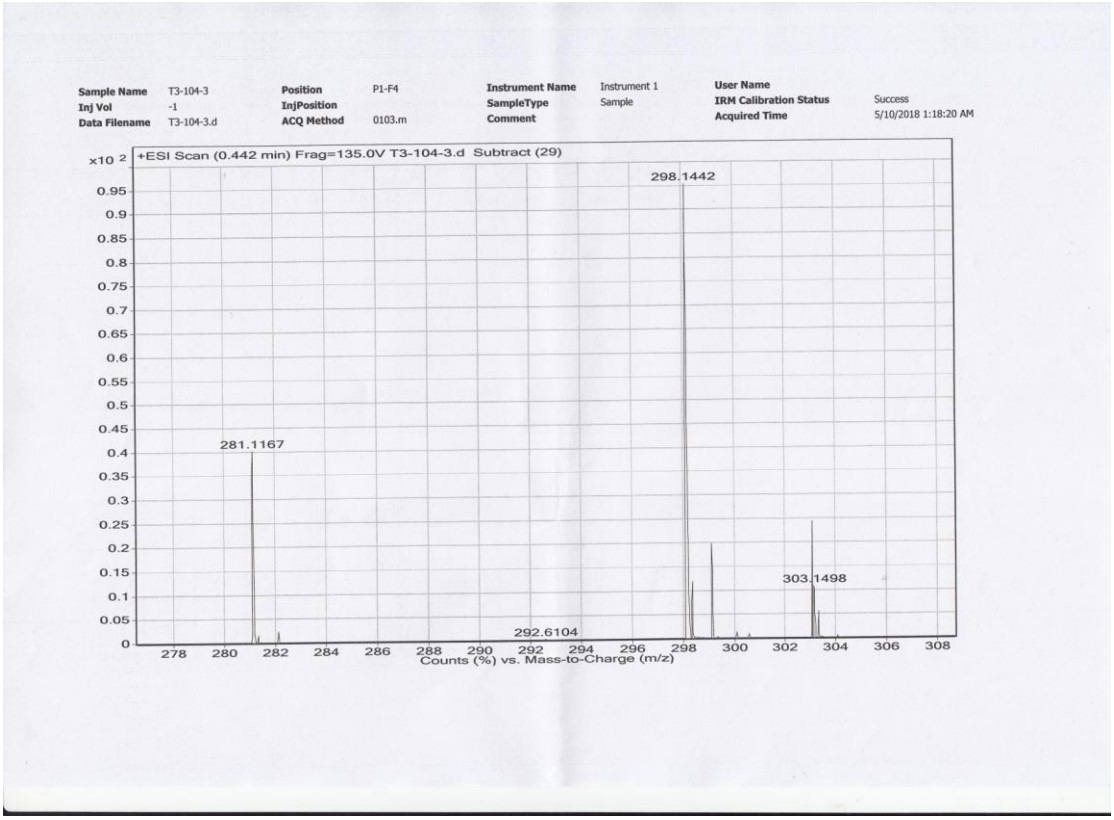
3h

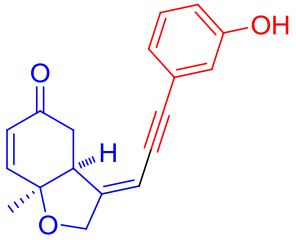
Chemical Formula: $C_{19}H_{18}O_2$
Exact Mass: 278.1307
Molecular Weight: 278.3450
m/z: 278.1307 (100.0%), 279.1340 (20.5%), 280.1374 (2.0%)

HRMS (ESI, m/z) calcd for $C_{19}H_{18}O_2$ $[M+Na]^+$ 301.1199, found 301.1203.


T3-106-3
OH
O
H
O
3i
ppm


T3-106-3
OH
O
H
O
3i
ppm

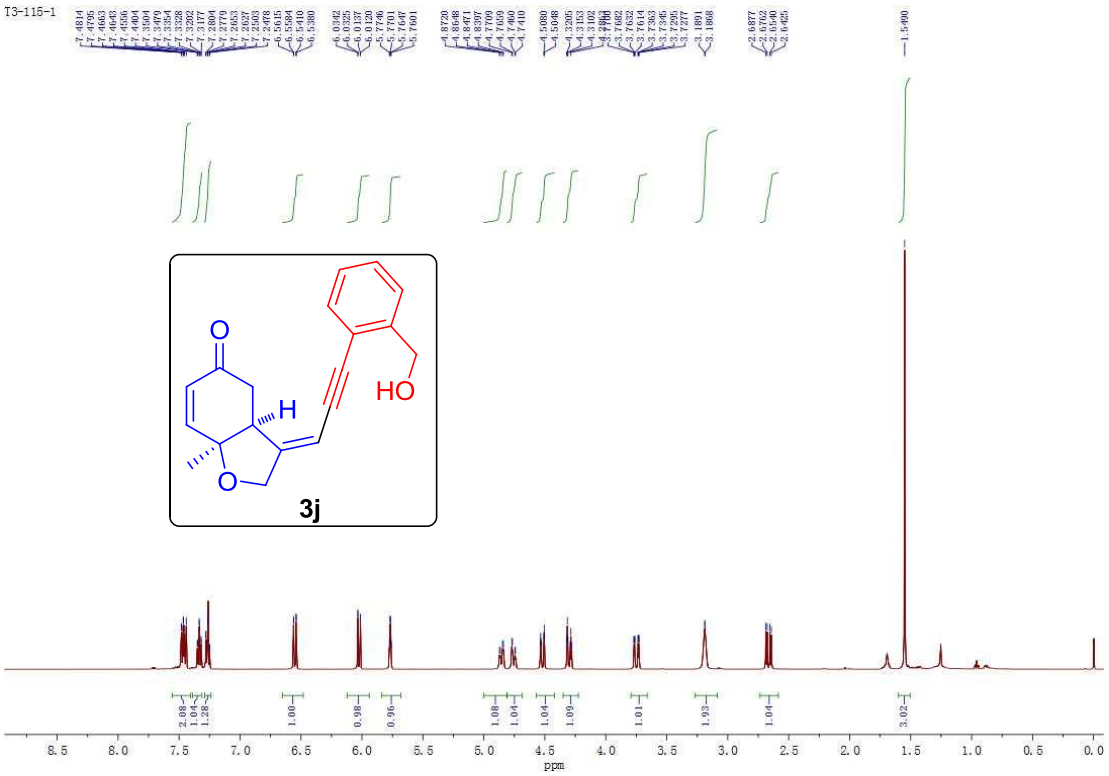


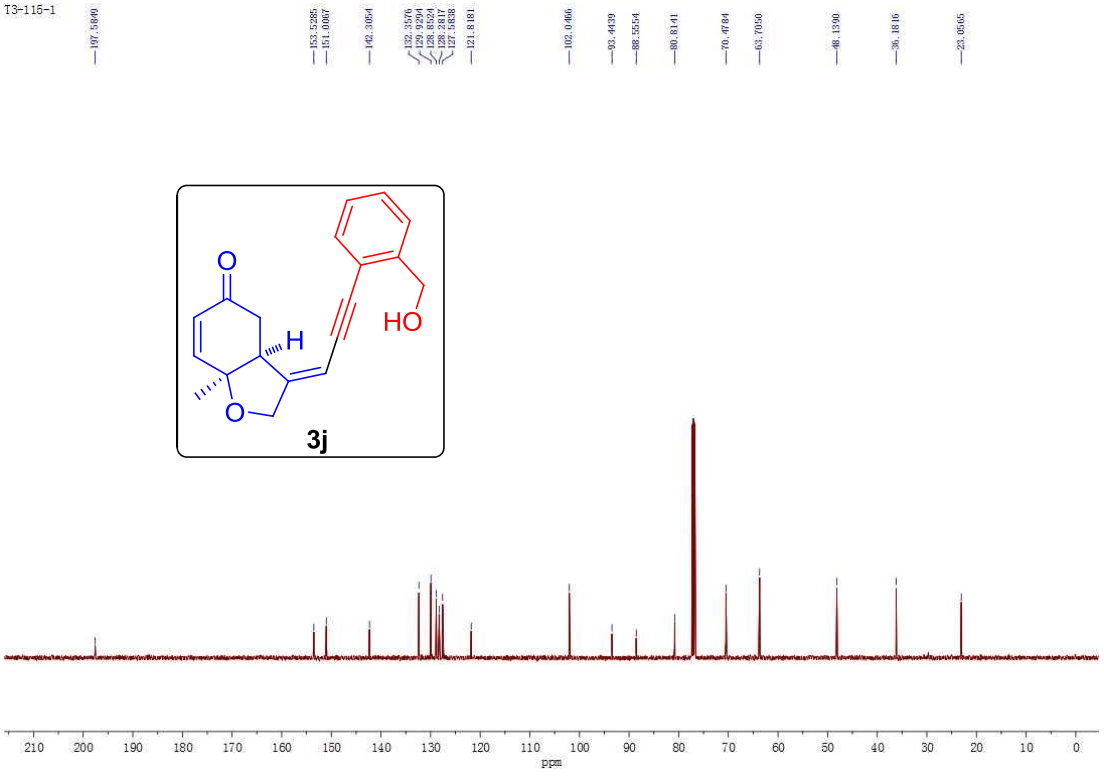


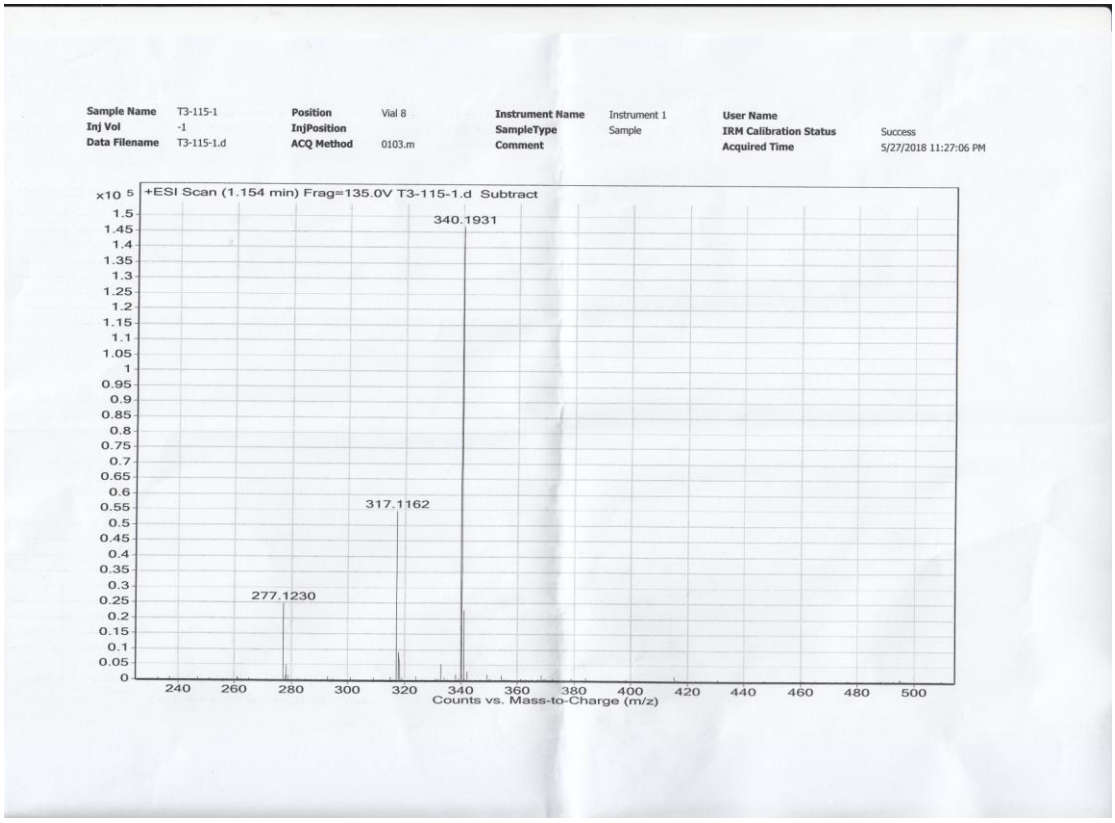
3i

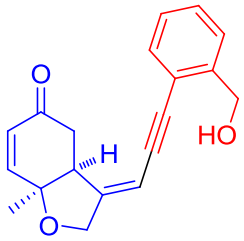
Chemical Formula: $C_{18}H_{16}O_3$
Exact Mass: 280.1099
Molecular Weight: 280.3178
m/z: 280.1099 (100.0%), 281.1133 (19.5%), 282.1167 (1.8%)

HRMS (ESI, m/z) calcd for $C_{18}H_{16}O_3$ $[M+H]^+$ 281.1178, found 281.1167.


T3-115-1
O
H
O
HO
3j
2.08
1.04
1.28
1.00
0.98
0.96
1.08
1.04
1.04
1.09
1.01
1.93
1.04
3.02
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
ppm


T3-115-1
197.5890
153.5285
151.0067
142.3054
132.3576
129.9294
128.8524
128.2817
127.5838
121.8181
102.0466
93.4439
88.5554
80.8141
70.4784
63.7050
48.1390
26.1816
23.0565
O
H
O
HO
3j
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

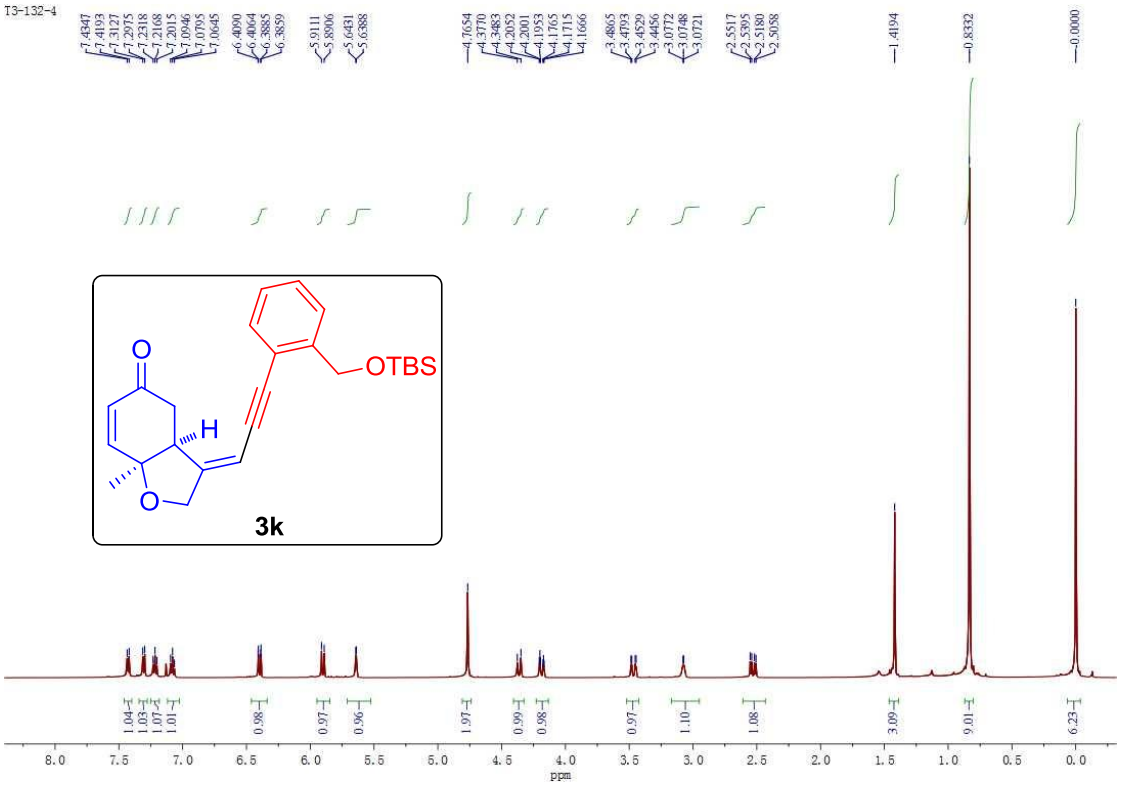


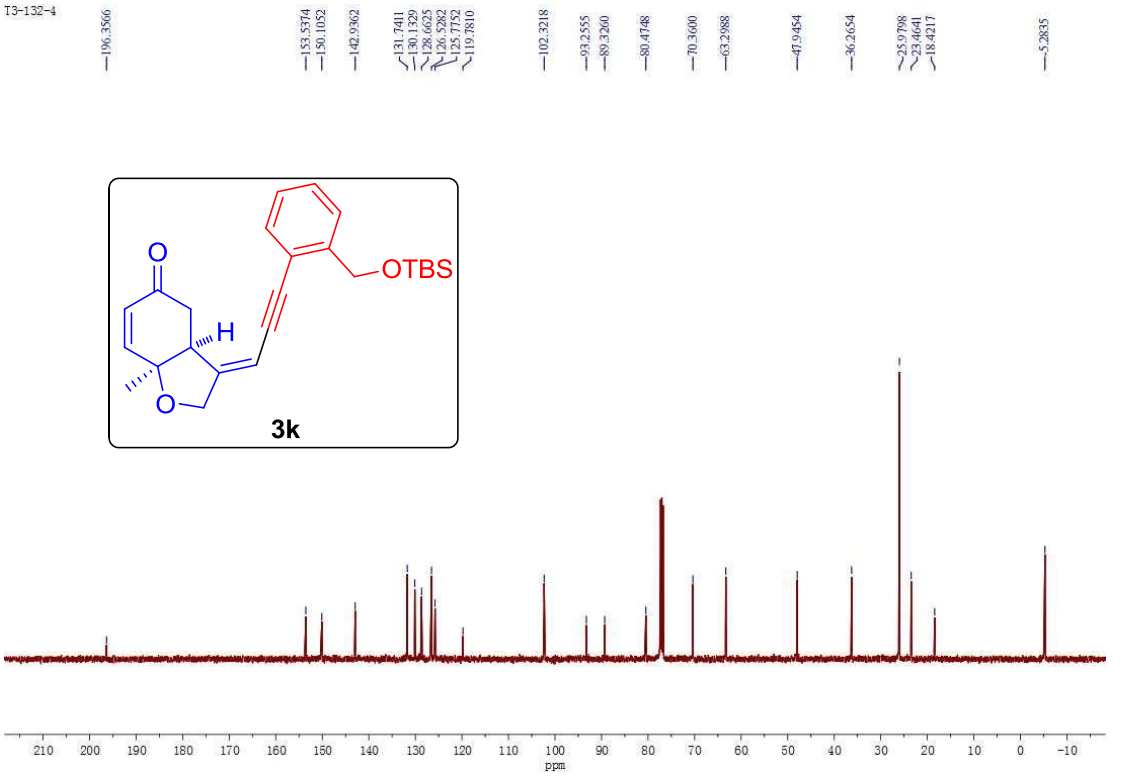


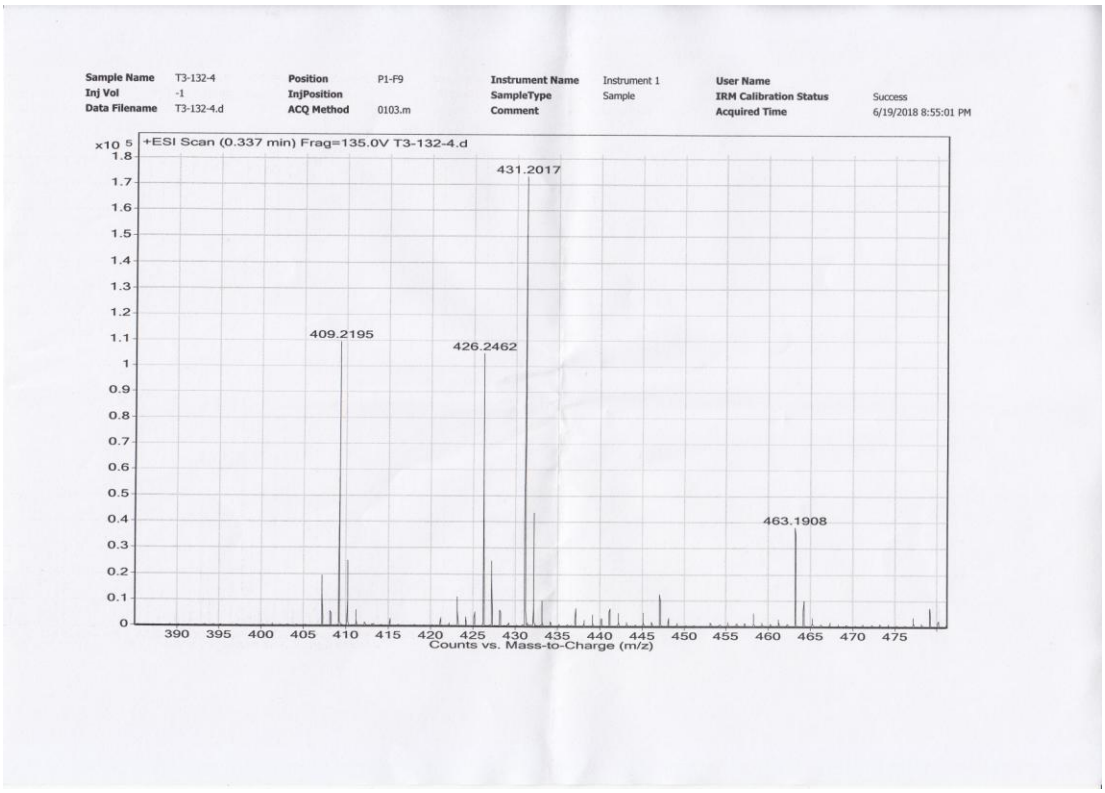
3j

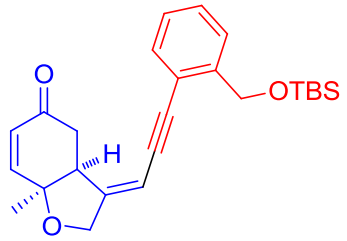
Chemical Formula: $C_{19}H_{18}O_3$
Exact Mass: 294.1256
Molecular Weight: 294.3444
m/z: 294.1256 (100.0%), 295.1289 (20.5%), 296.1323 (2.0%)

HRMS (ESI, m/z) calcd for $C_{19}H_{18}O_3$ $[M+Na]^+$ 317.1154, found 317.1162.


T3-132-4
OTBS
H
O
O
3k


T3-132-4
OTBS
H
O
O
3k

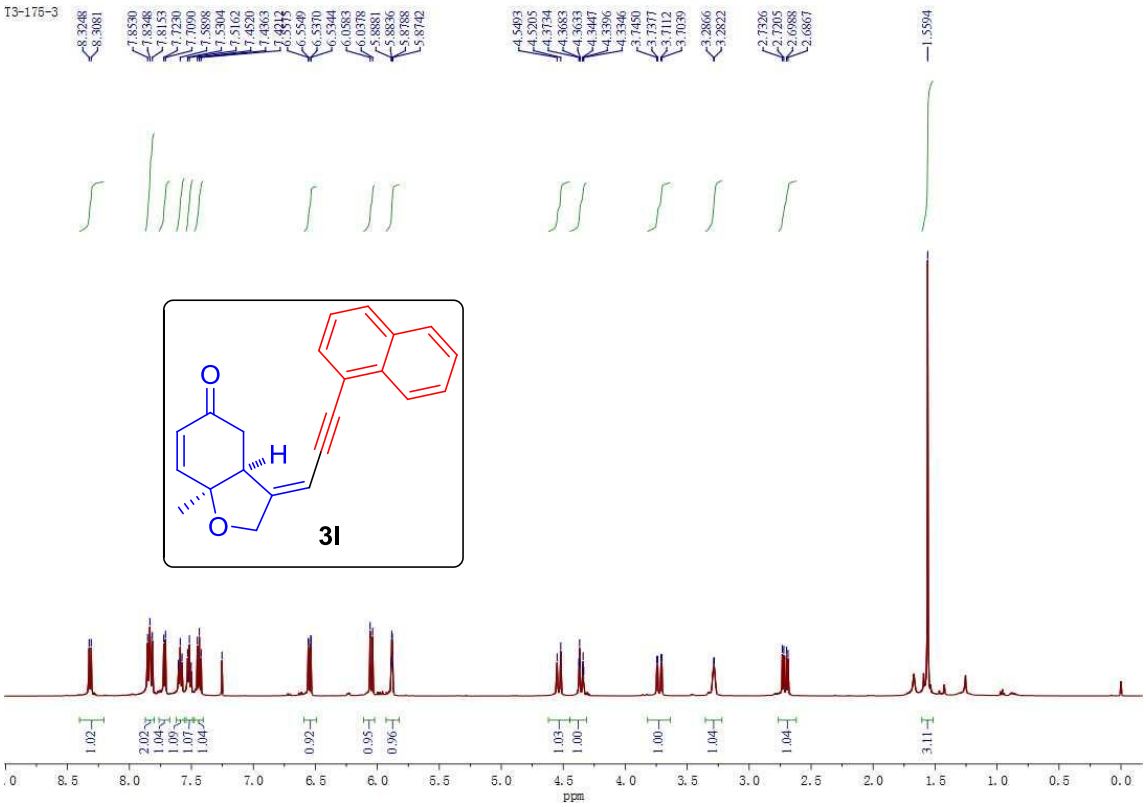


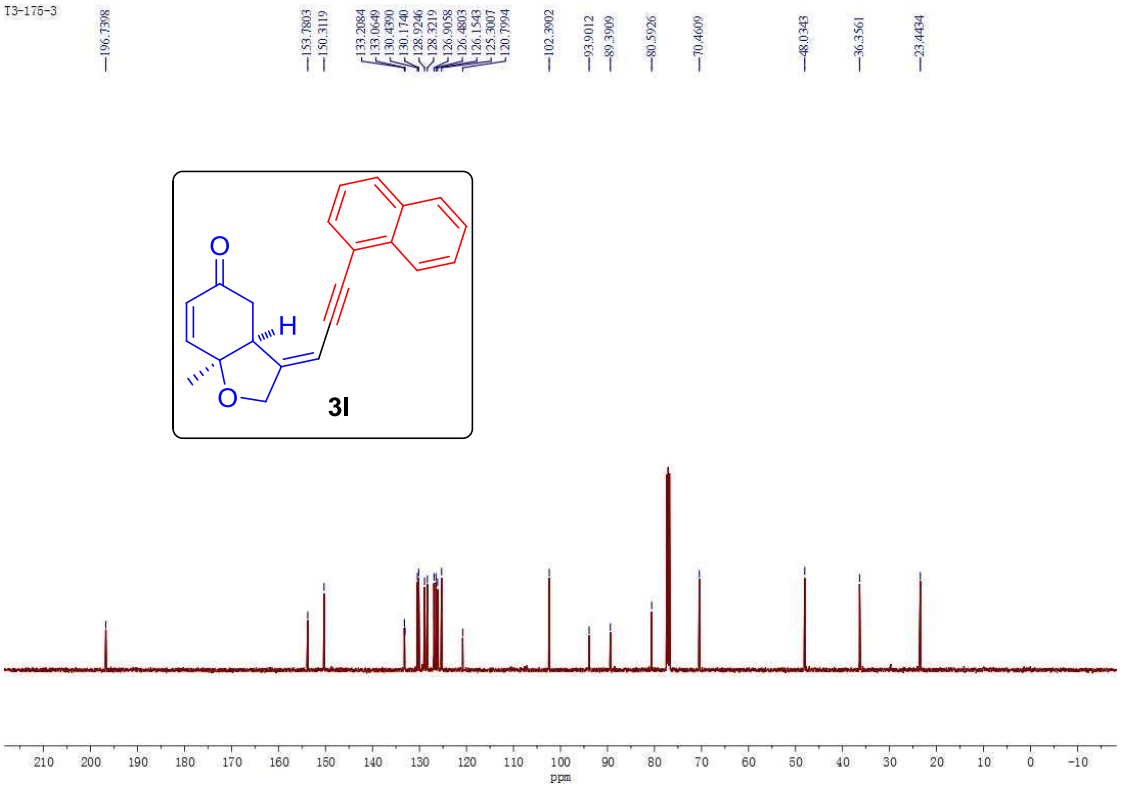


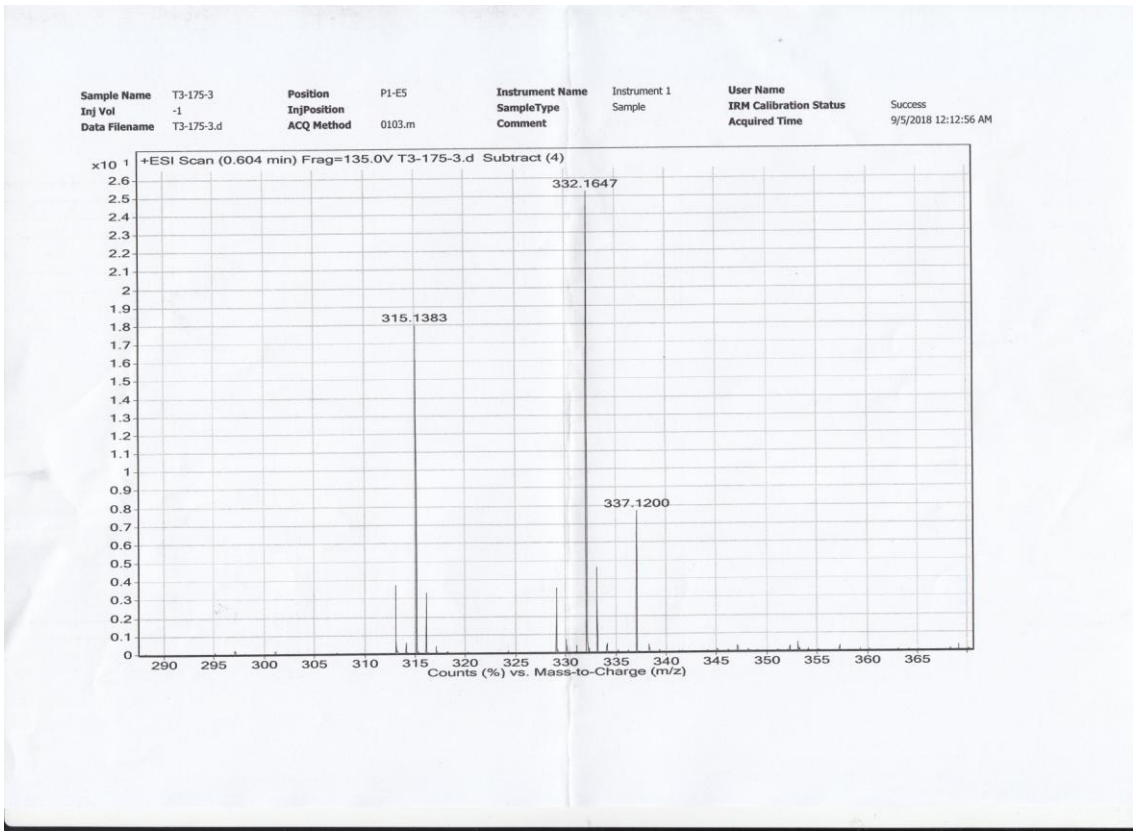
3k

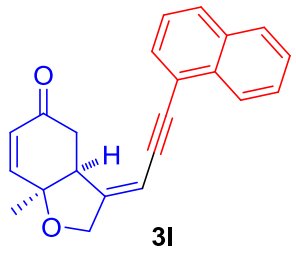
Chemical Formula: $C_{25}H_{32}O_3Si$
Exact Mass: 408.2121
Molecular Weight: 408.6053
m/z: 408.2121 (100.0%), 409.2154 (27.0%), 409.2116 (5.1%),
410.2188 (3.5%), 410.2089 (3.3%), 410.2150 (1.4%)

HRMS (ESI, m/z) calcd for $C_{25}H_{32}O_3Si$ $[M+H]^+$ 409.2193, found 409.2195.


T3-176-3
8.3248
8.3081
7.8530
7.8348
7.8153
7.7230
7.7090
7.5898
7.5304
7.5162
7.4520
7.4363
7.4212
6.5515
6.5549
6.5370
6.5344
6.0583
6.0378
5.8881
5.8836
5.8788
5.8742
4.5493
4.5205
4.3734
4.3683
4.3633
4.3447
4.3396
4.3346
3.7450
3.7377
3.7112
3.7039
3.2866
3.2822
2.7326
2.7205
2.6988
2.6867
1.5594
O
H
O
3l
1.02
2.02
1.04
1.09
1.07
1.04
0.92
0.95
0.96
1.03
1.00
1.00
1.04
1.04
3.11
ppm


T3-176-3
196.7398
153.7803
150.3119
133.2084
133.0649
130.4390
130.1740
128.9246
128.3219
126.9058
126.4803
126.1543
125.3007
120.7994
102.3902
93.9012
89.3909
80.5926
70.4609
48.0343
36.3561
23.4434
O
H
O
3l
ppm

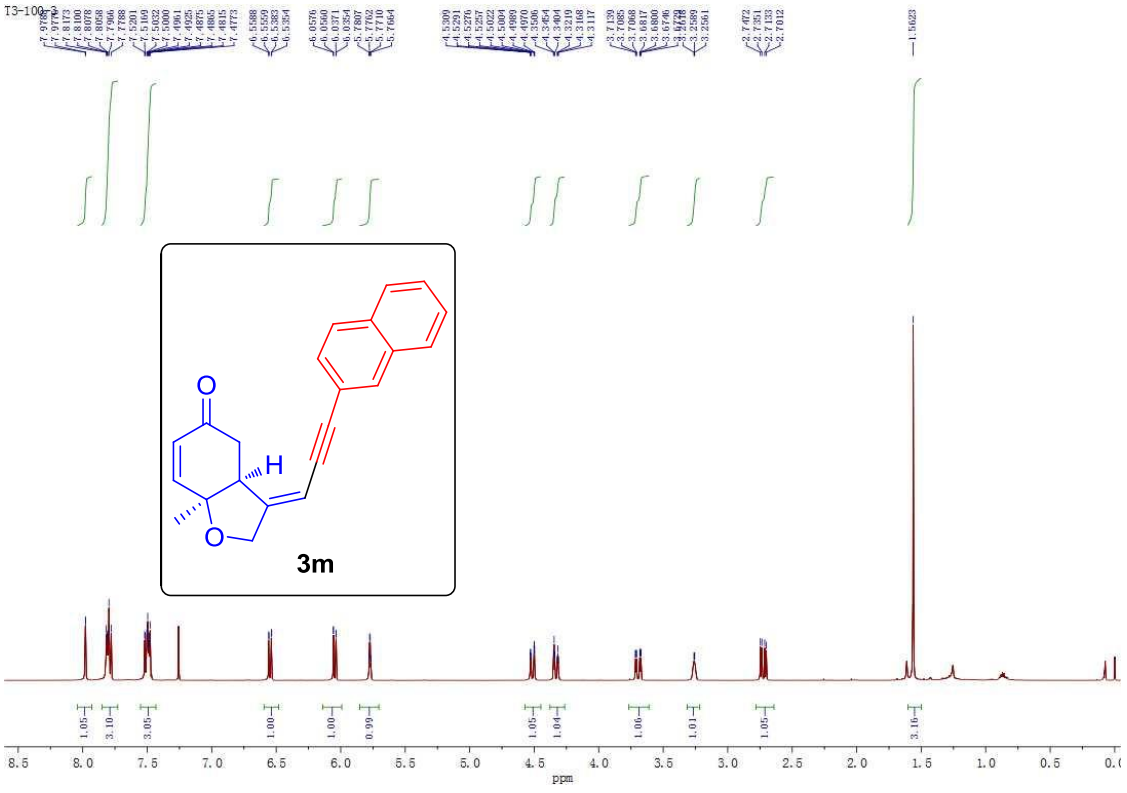


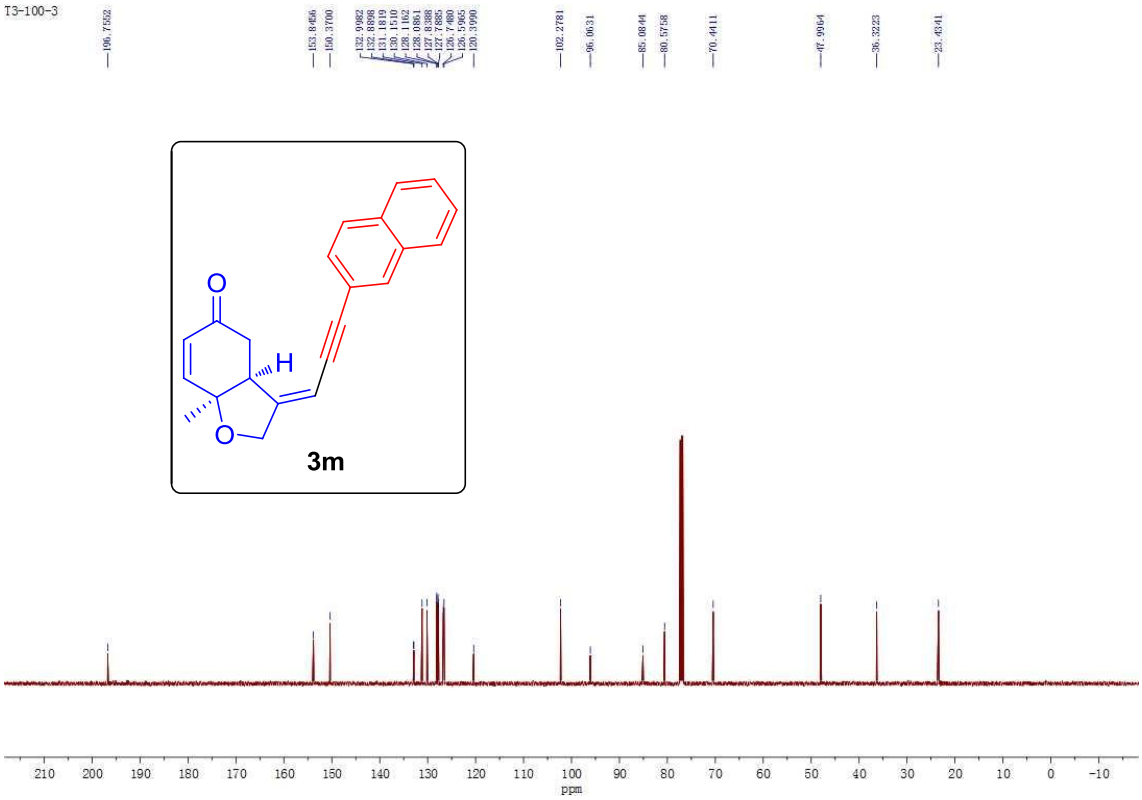


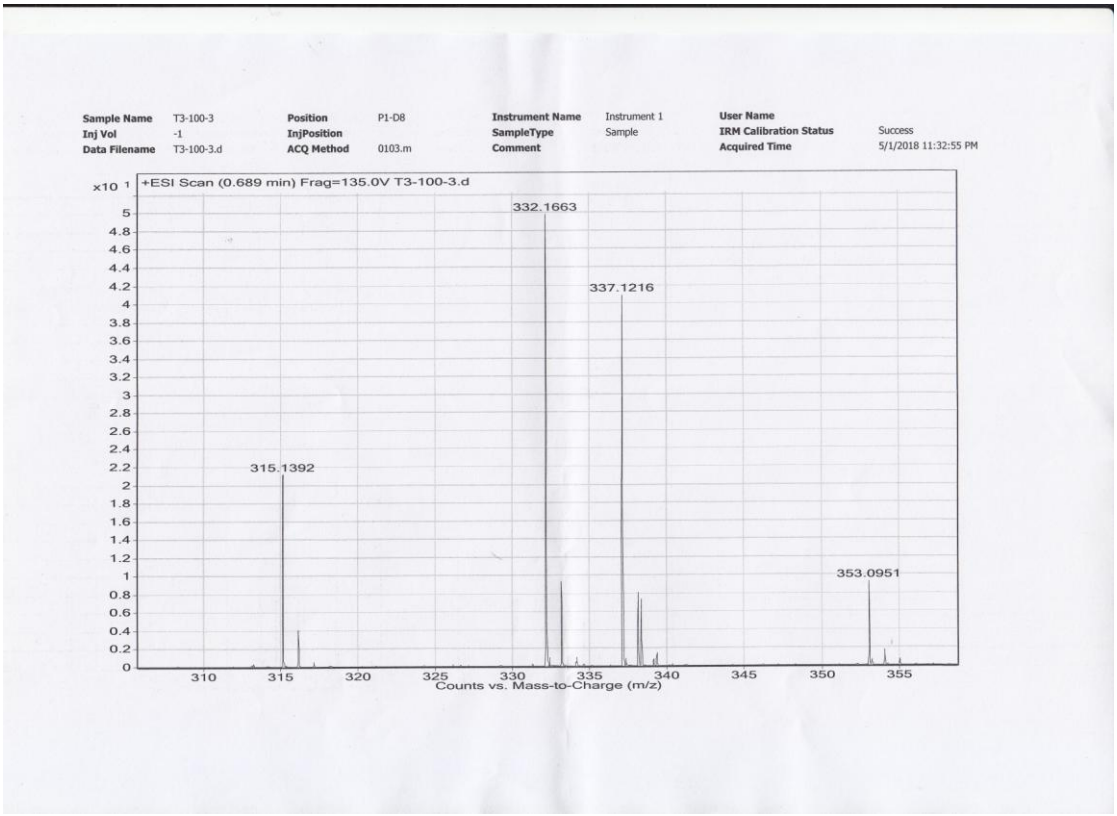
3l

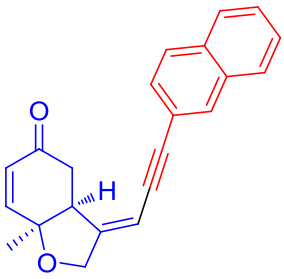
Chemical Formula: $C_{22}H_{18}O_2$
Exact Mass: 314.1307
Molecular Weight: 314.3771
m/z: 314.1307 (100.0%), 315.1340 (23.8%), 316.1374 (2.7%)

HRMS (ESI, m/z) calcd for $C_{22}H_{18}O_2$ $[M+H]^+$ 315.1380, found 315.1383.


T3-100-2
O
H
O
3m
ppm


T3-100-3
O
H
O
3m
ppm

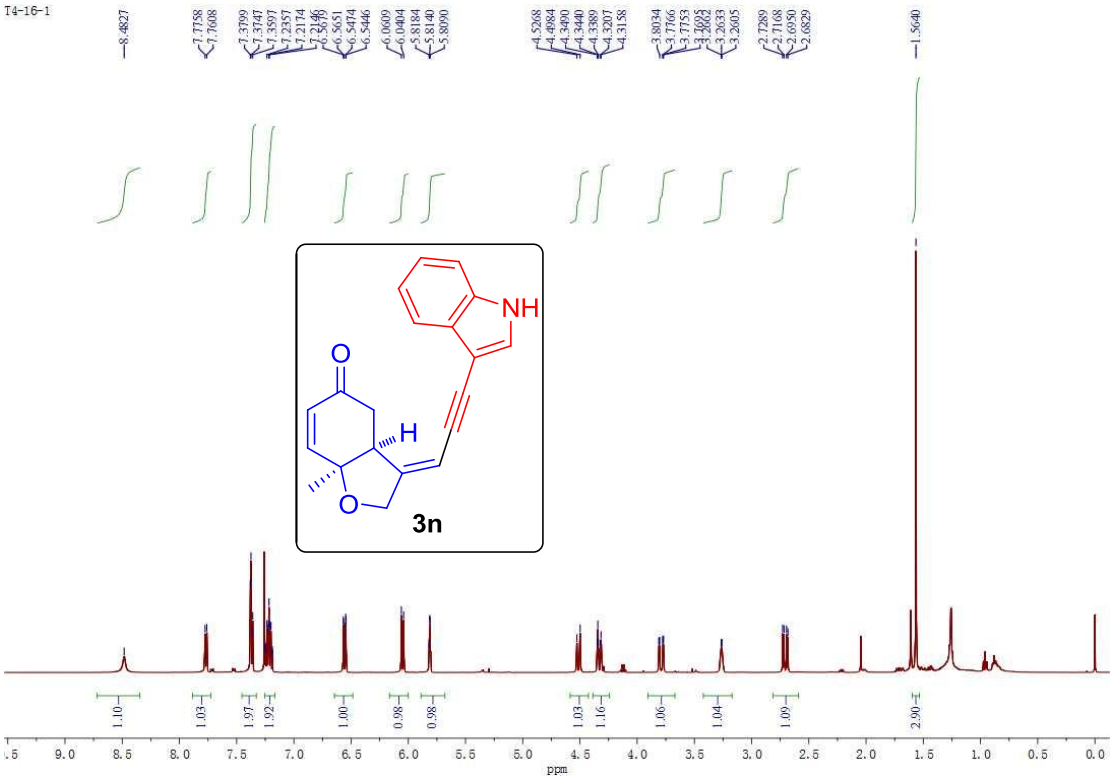


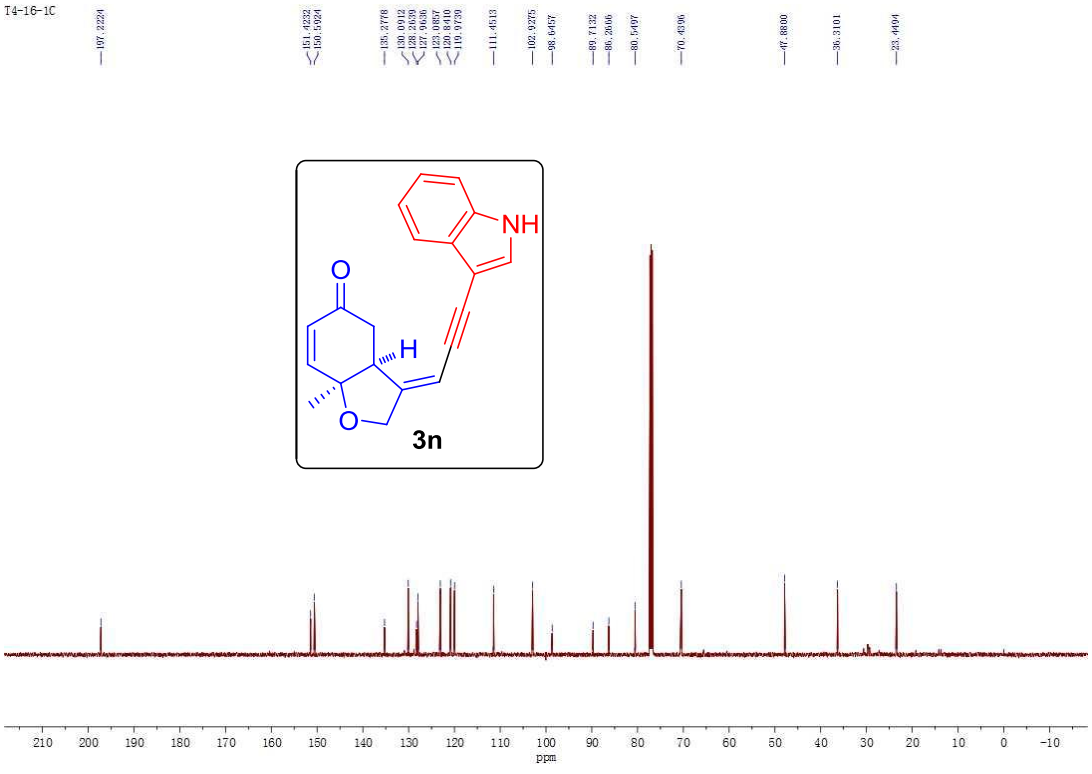


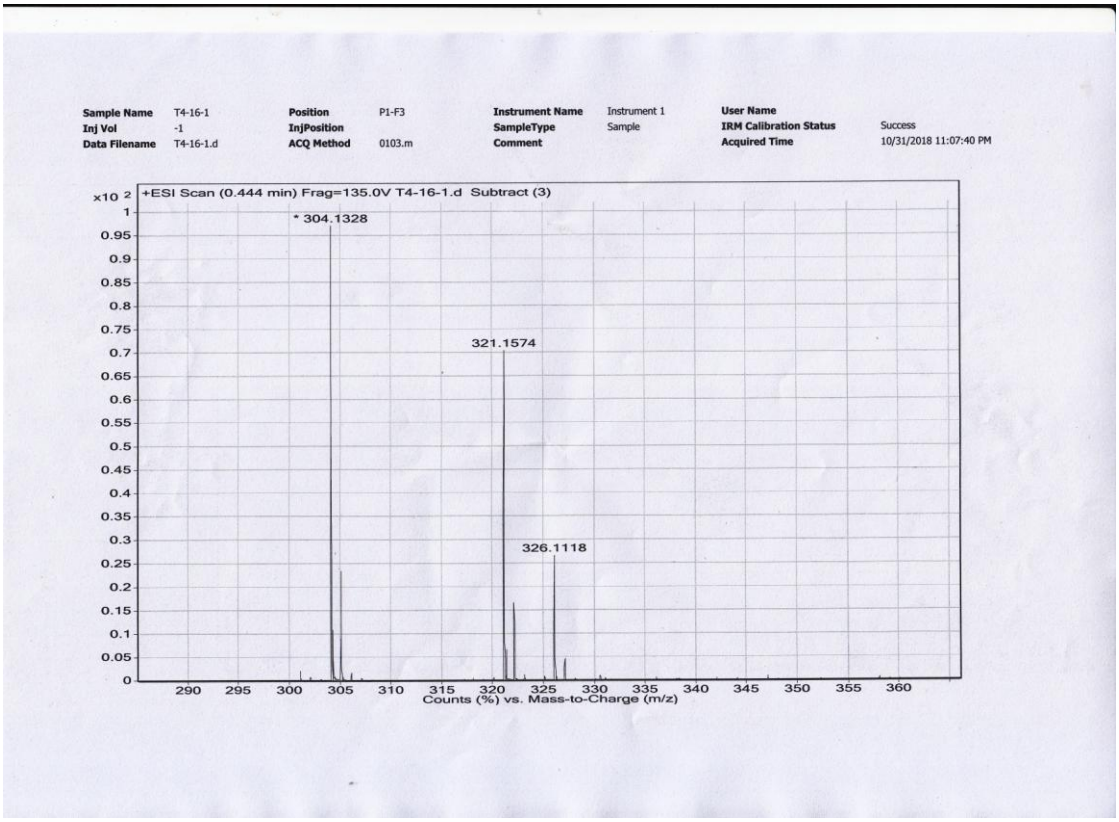
3m

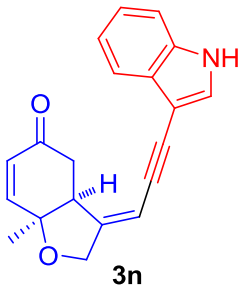
Chemical Formula: $C_{22}H_{18}O_2$
Exact Mass: 314.1307
Molecular Weight: 314.3771
m/z: 314.1307 (100.0%), 315.1340 (23.8%), 316.1374 (2.7%)

HRMS (ESI, m/z) calcd for $C_{22}H_{18}O_2$ $[M+H]^+$ 315.1385, found 315.1392.


T4-16-1
NH
O
H
O
3n
ppm


T4-16-1C
NH
O
H
O
3n
ppm

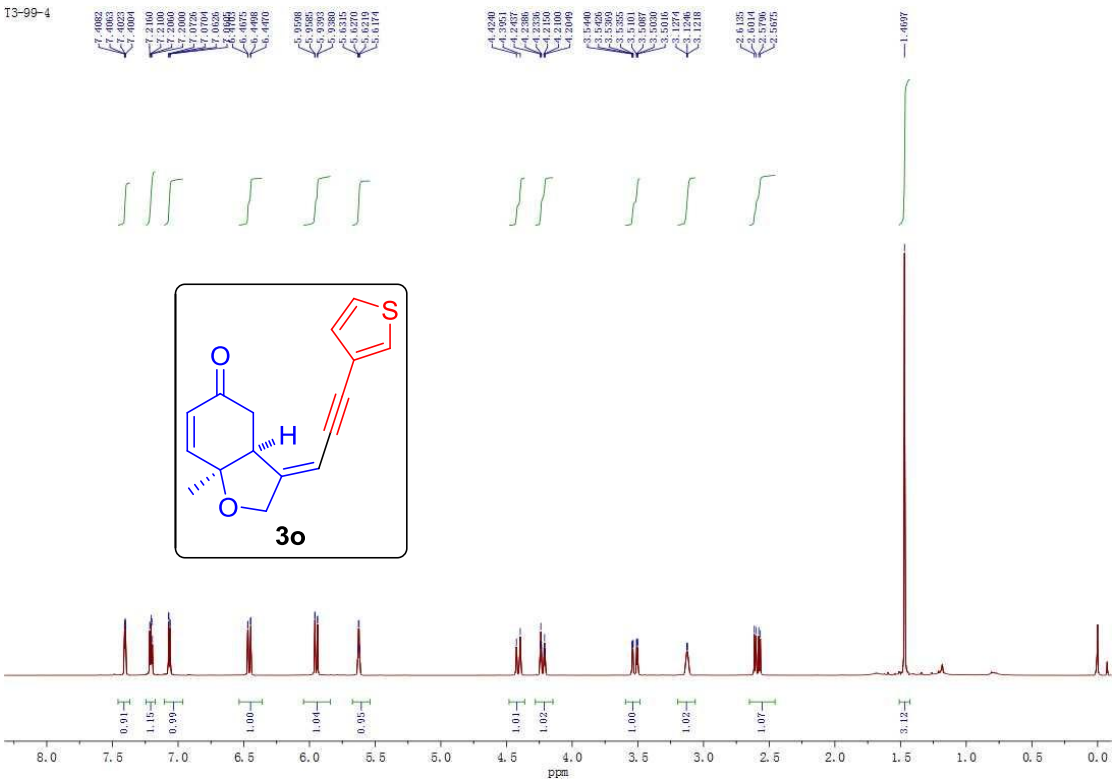


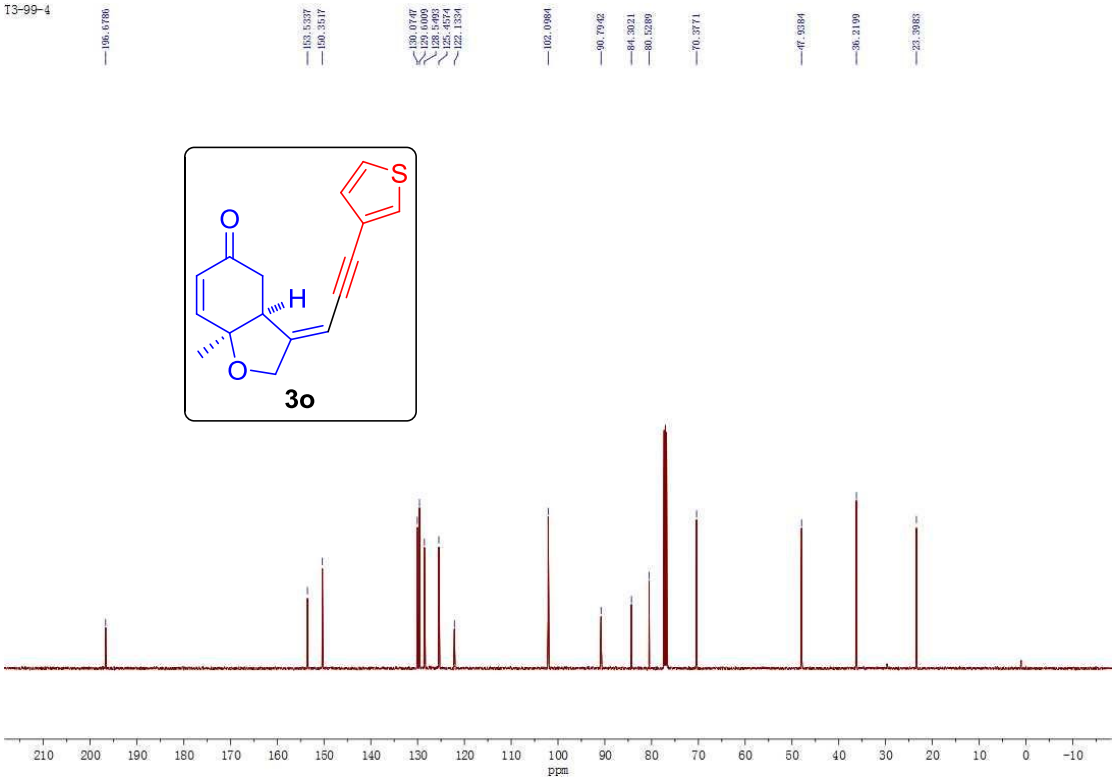


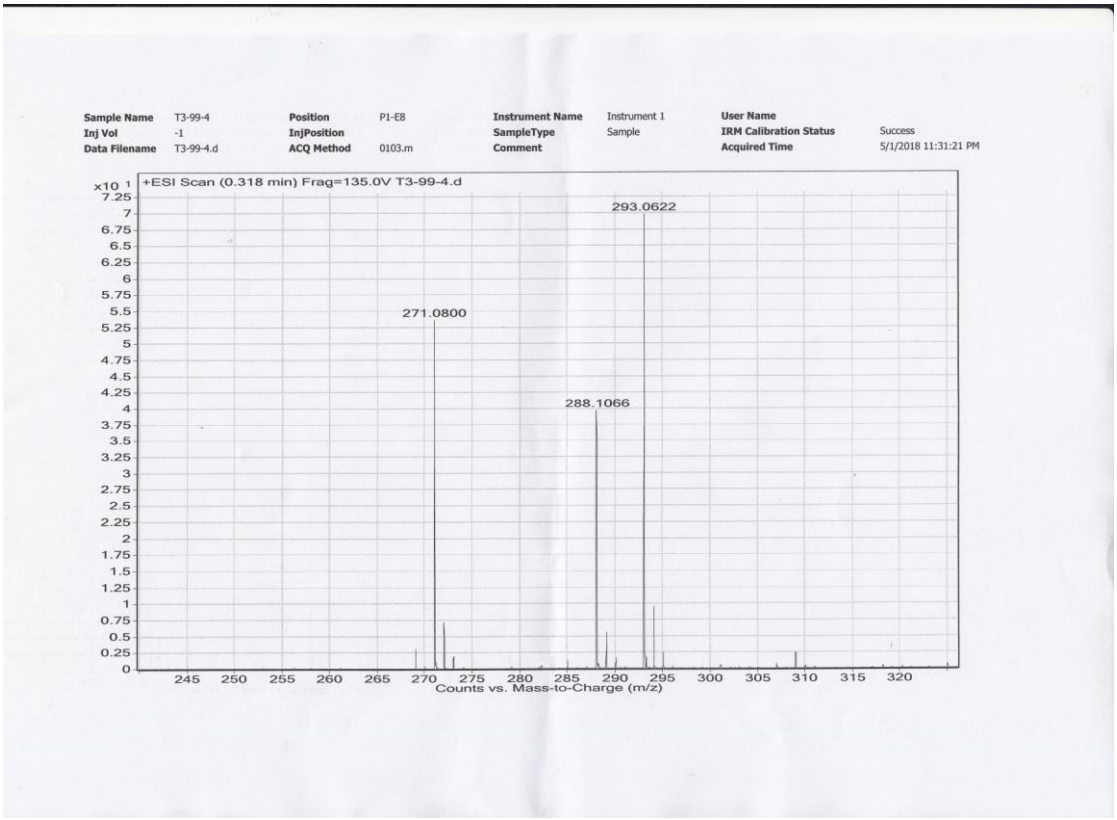
3n

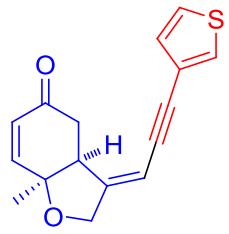
Chemical Formula: $C_{20}H_{17}NO_2$
Exact Mass: 303.1259
Molecular Weight: 303.3545
m/z: 303.1259 (100.0%), 304.1293 (21.6%), 305.1326 (2.2%)

HRMS (ESI, m/z) calcd for $C_{20}H_{17}NO_2$ $[M+H]^+$ 304.1332, found 304.1328.


T3-99-4
O
H
O
S
3o
ppm


T3-99-4
O
H
O
S
3o
ppm

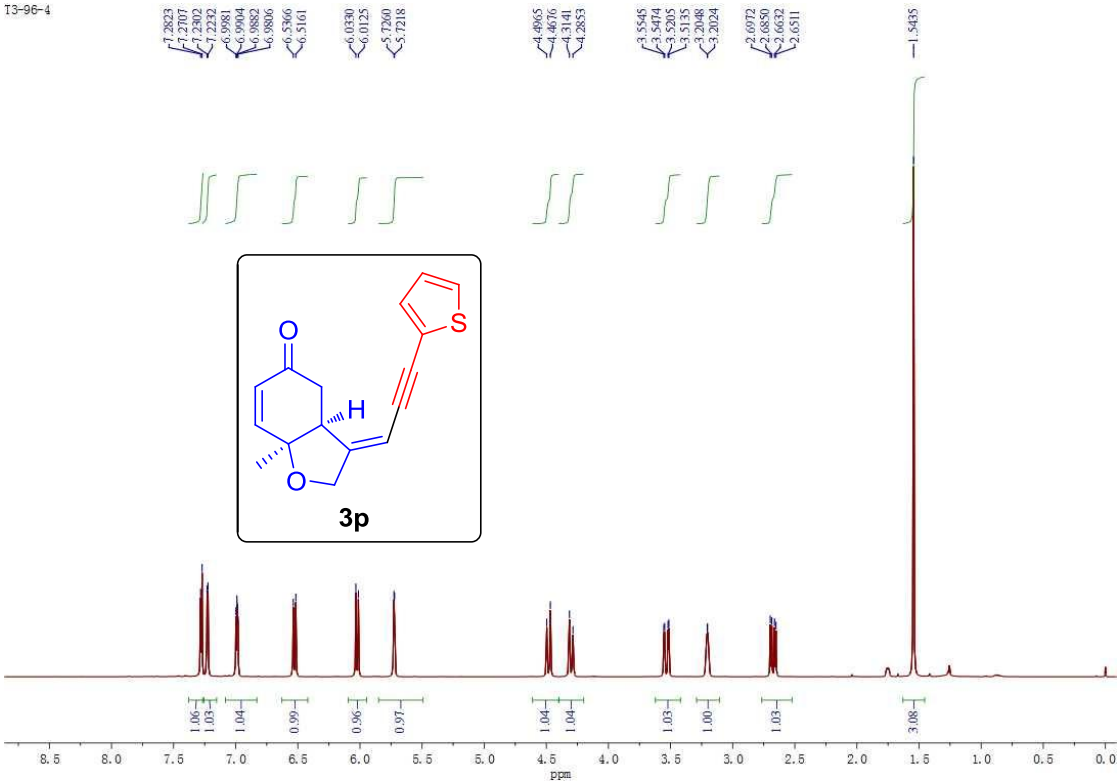


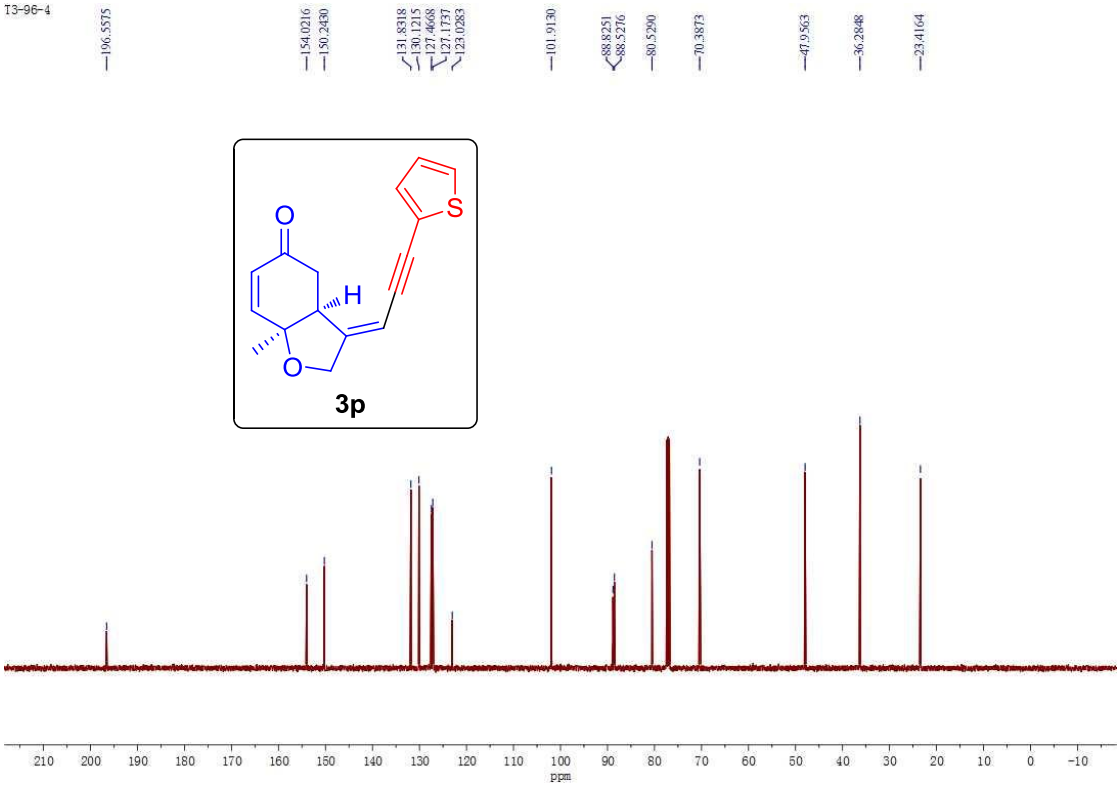


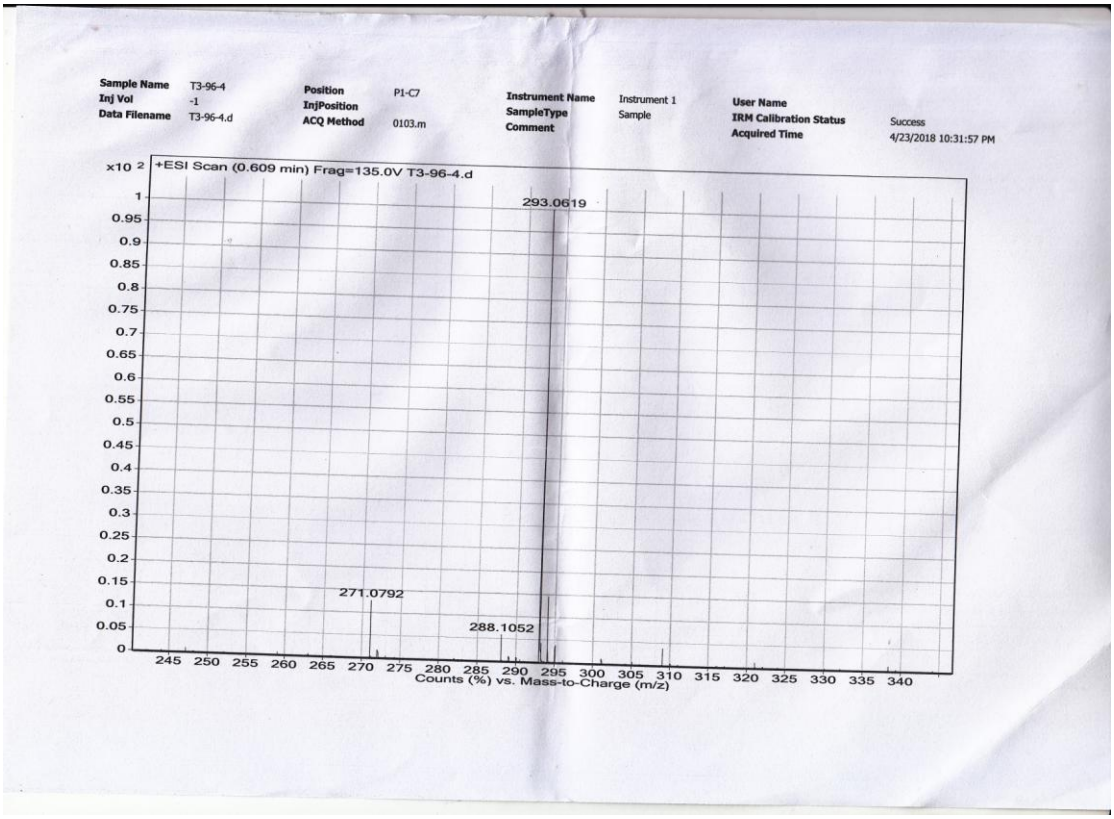
3o

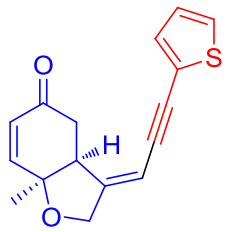
Chemical Formula: $C_{16}H_{14}O_2S$
Exact Mass: 270.0715
Molecular Weight: 270.3462
m/z: 270.0715 (100.0%), 271.0748 (17.3%), 272.0672 (4.5%), 272.0782 (1.4%)

HRMS (ESI, m/z) calcd for $C_{16}H_{14}O_2S$ $[M+H]^+$ 271.0793, found 271.0800.


T3-96-4
7.2923
7.2707
7.2302
7.2232
6.9981
6.9904
6.9882
6.9806
6.5366
6.5161
6.0330
6.0125
5.7260
5.7218
4.4965
4.4676
4.3141
4.2853
3.5545
3.5474
3.5205
3.5135
3.2048
3.2024
2.6972
2.6850
2.6632
2.6511
1.5435
O
H
O
S
3p
1.06
1.03
1.04
0.99
0.96
0.97
1.04
1.04
1.03
1.00
1.03
3.08
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
ppm


T3-96-4
196.5575
154.0216
150.2430
131.8318
130.1215
127.4668
127.1737
123.0283
101.9130
88.8251
88.5276
80.5290
70.3873
47.9563
36.2848
23.4164
O
H
O
S
3p
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

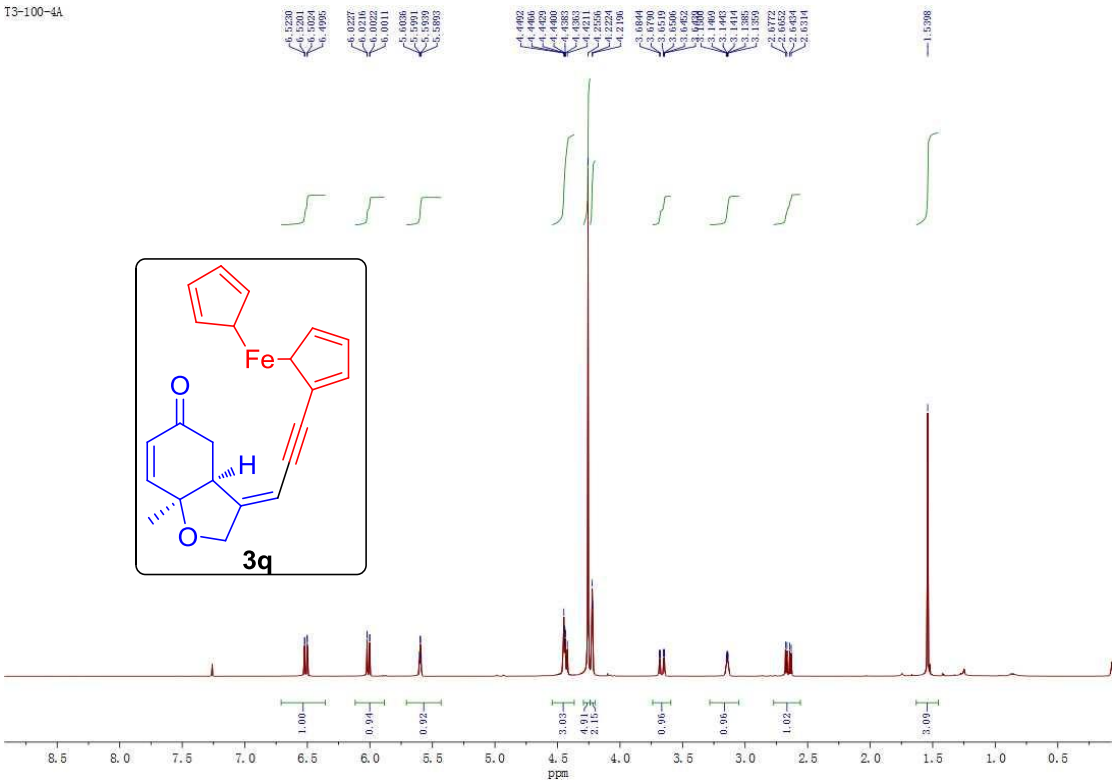


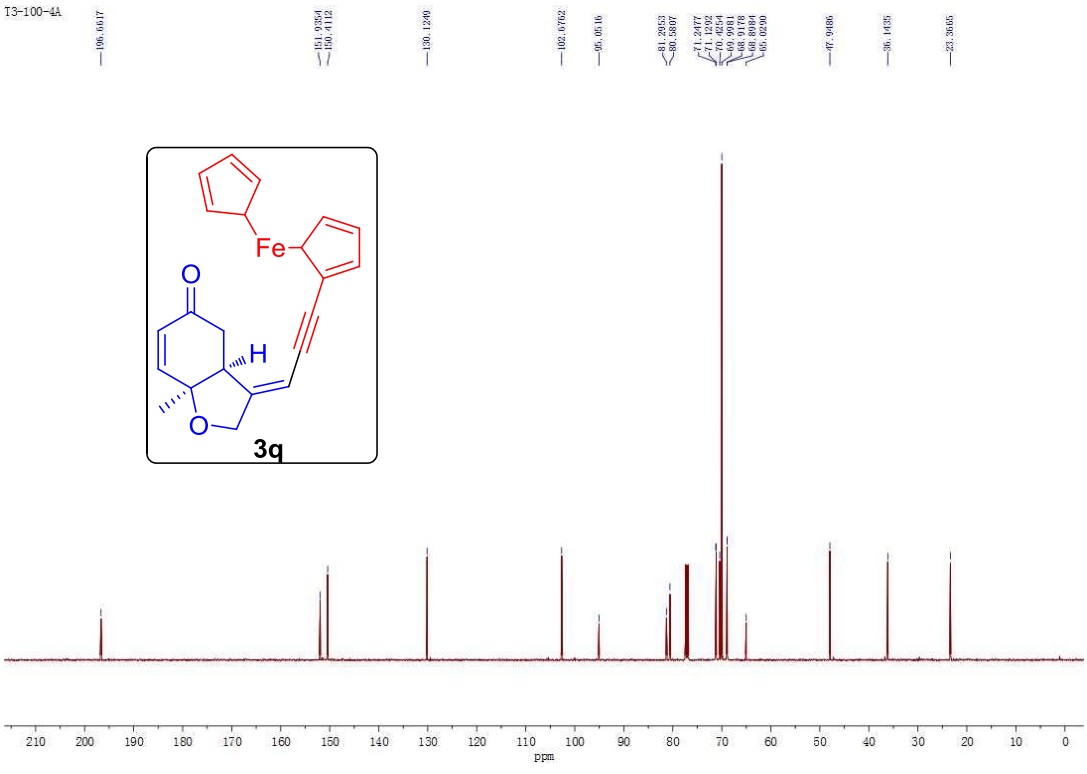


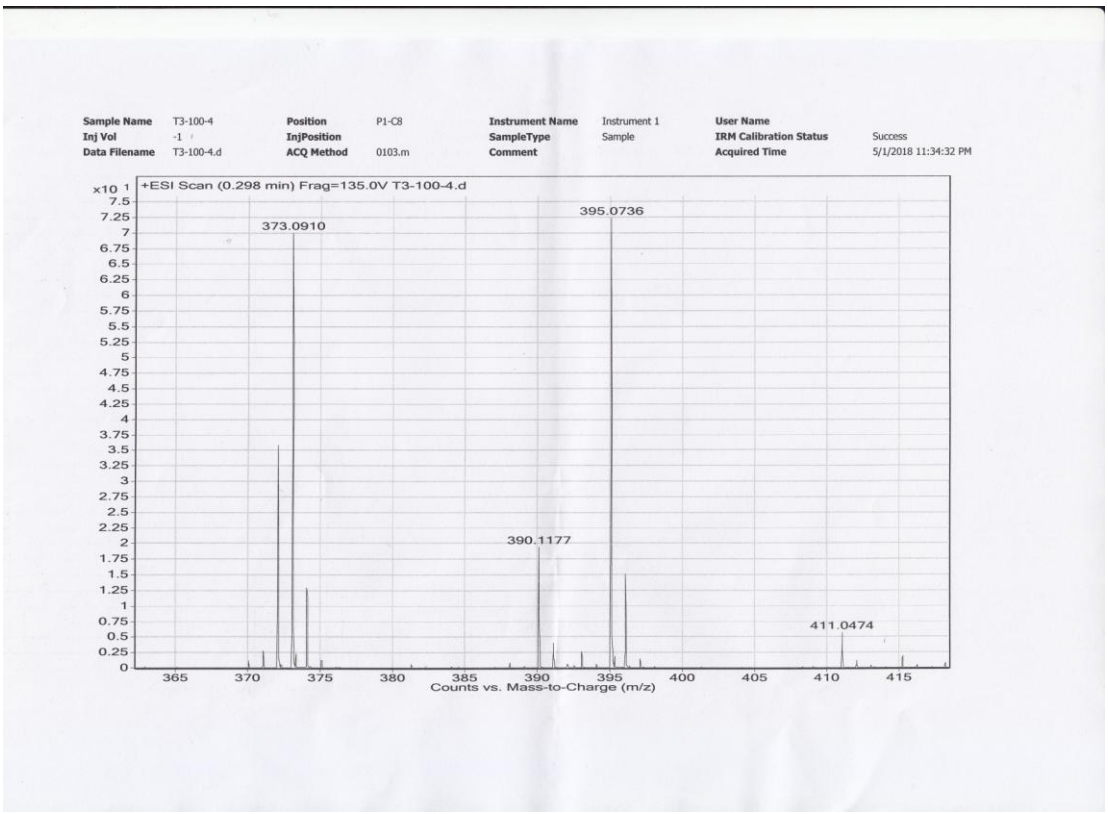
3p

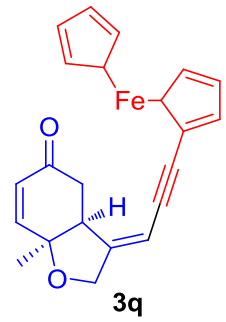
Chemical Formula: $C_{16}H_{14}O_2S$
Exact Mass: 270.0715
Molecular Weight: 270.3462
m/z: 270.0715 (100.0%), 271.0748 (17.3%), 272.0672 (4.5%), 272.0782 (1.4%)

HRMS (ESI, m/z) calcd for $C_{16}H_{14}O_2S$ $[M+H]^+$ 271.0793, found 271.0792.


T3-100-4A
Fe
O
H
O
3q
ppm


T3-100-4A
Fe
O
H
O
3q
ppm

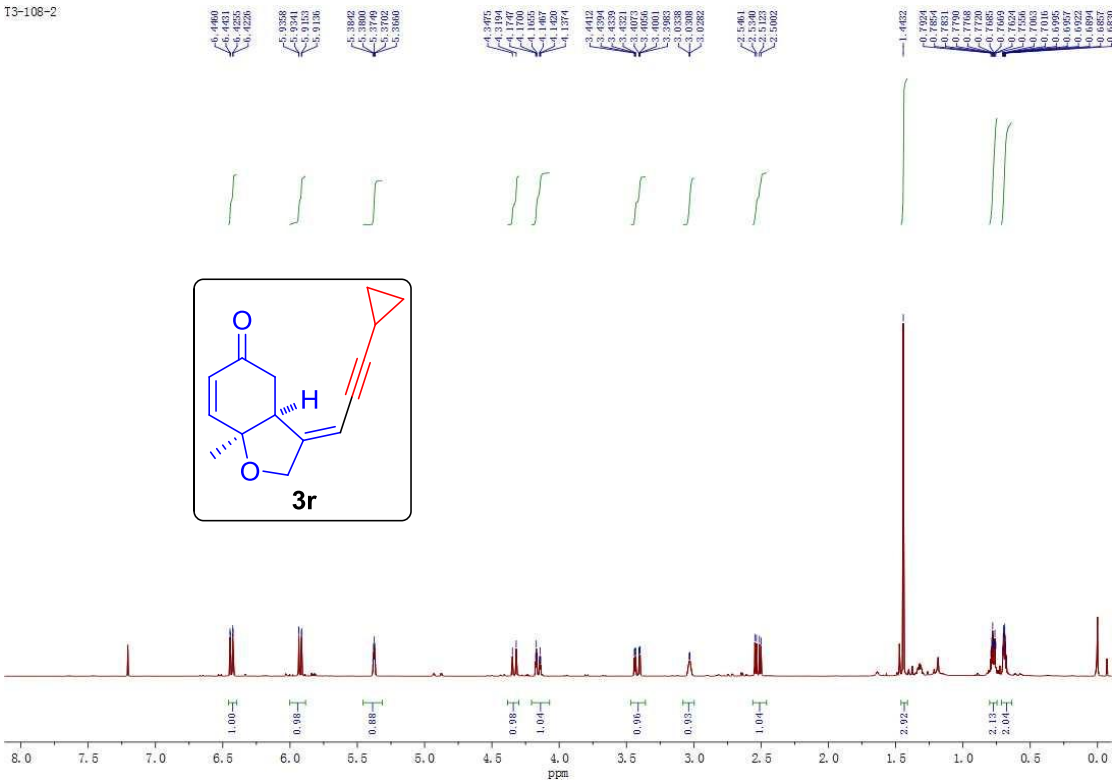


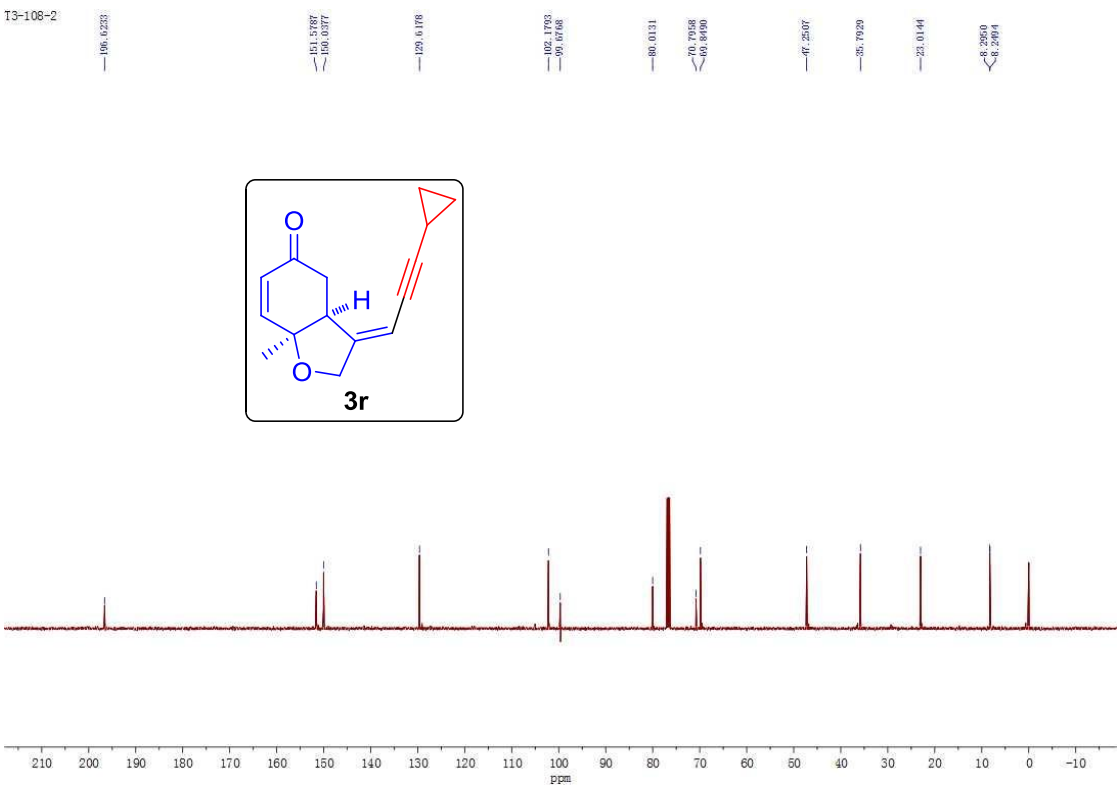


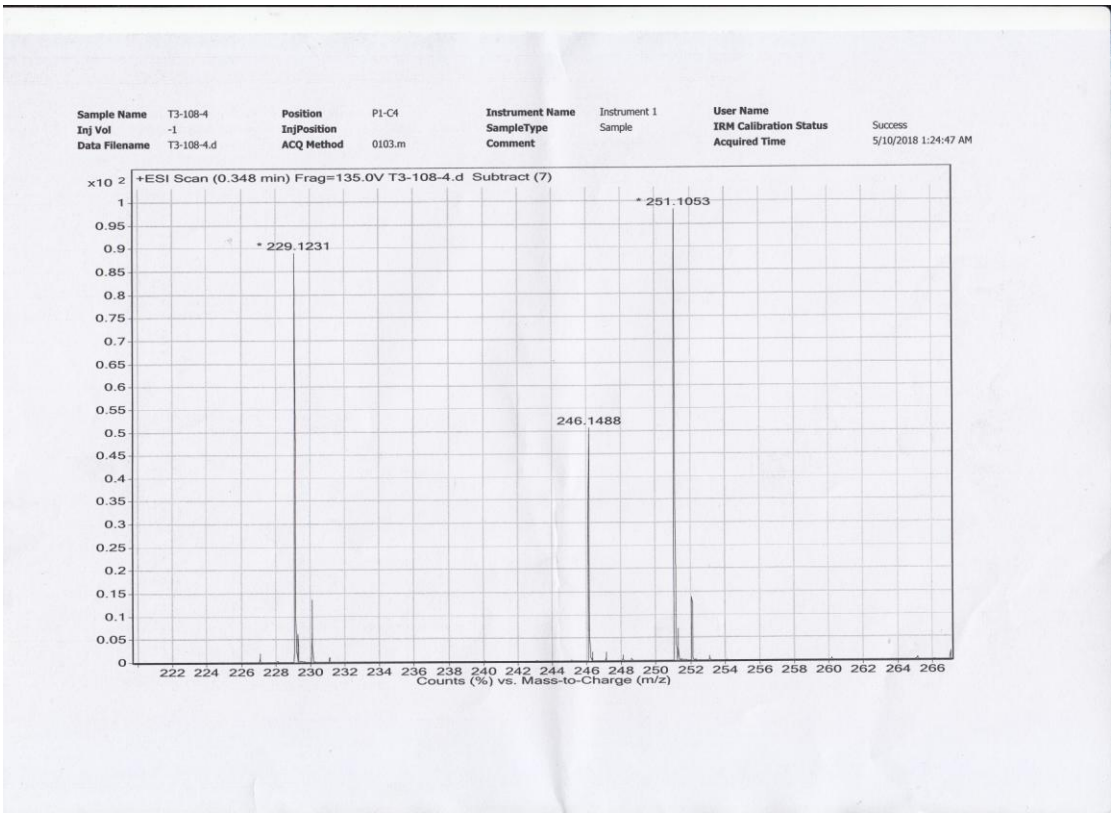
3q

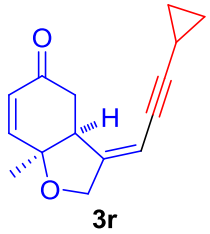
Chemical Formula: $C_{22}H_{20}FeO_2$
Exact Mass: 372.0813
Molecular Weight: 372.2380
m/z: 372.0813 (100.0%), 373.0846 (23.8%), 370.0859 (6.4%),
374.0880 (2.7%), 373.0817 (2.3%), 371.0893 (1.5%)

HRMS (ESI, m/z) calcd for $C_{22}H_{20}FeO_2$ $[M+H]^+$ 373.0891, found 373.0910.


T3-108-2
3r
ppm


T3-108-2
3r
ppm

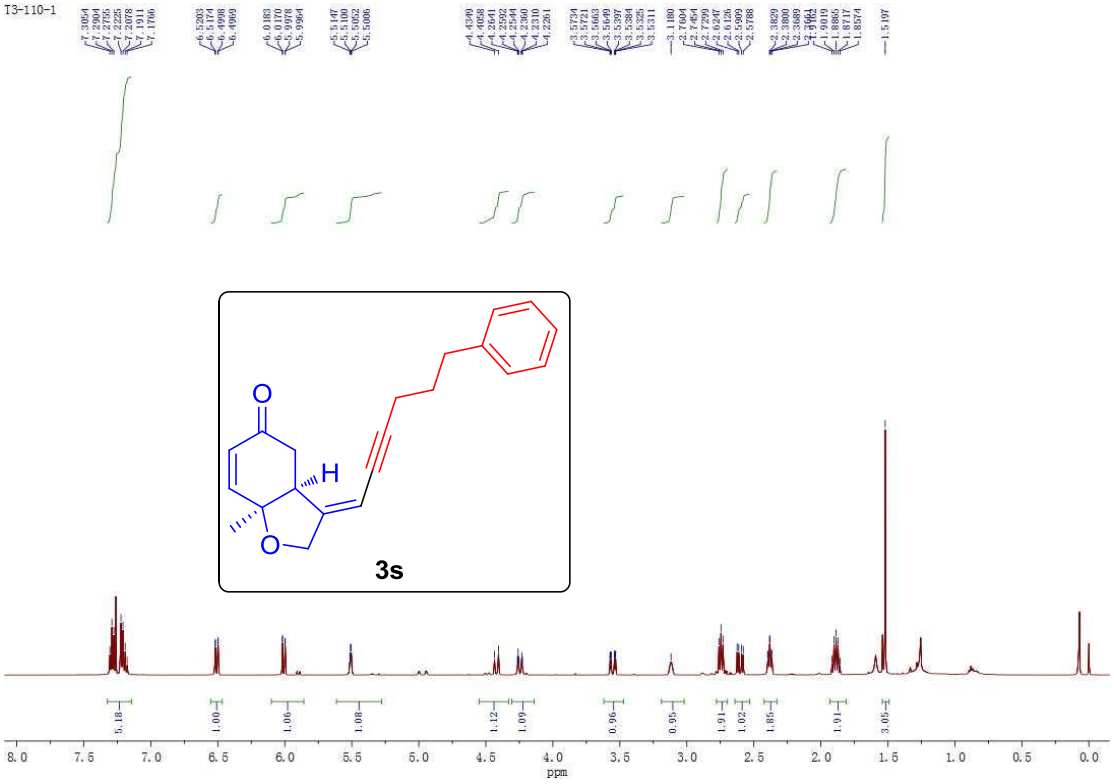


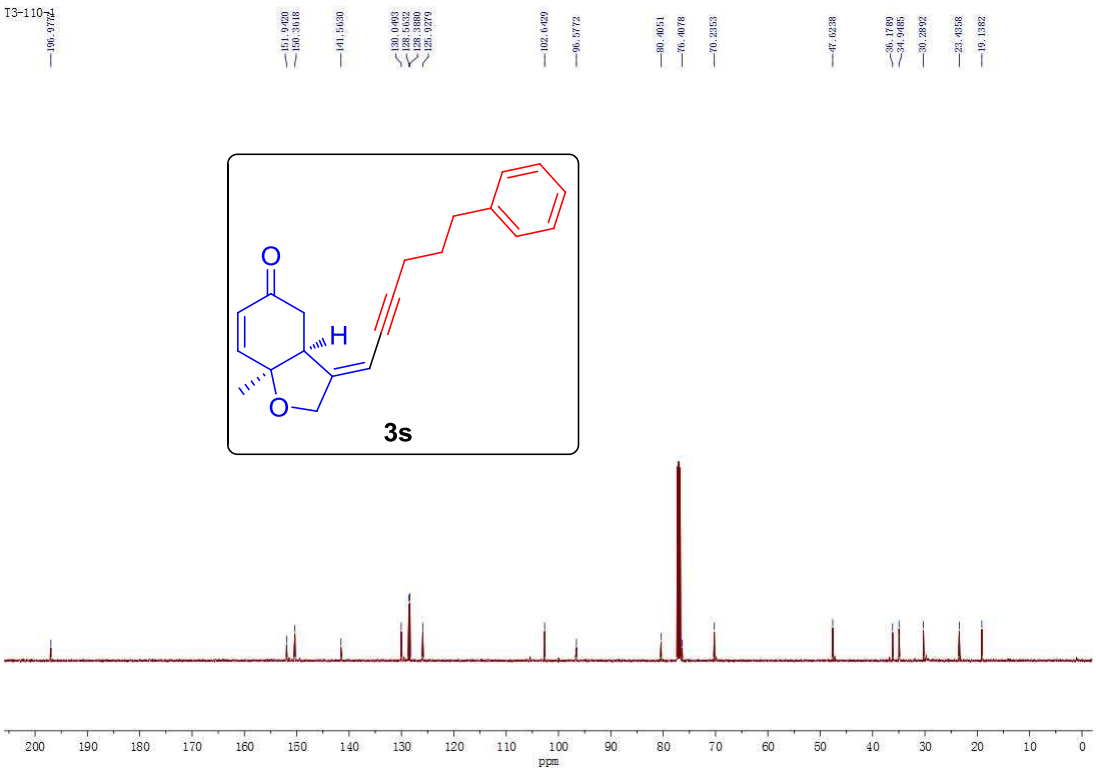


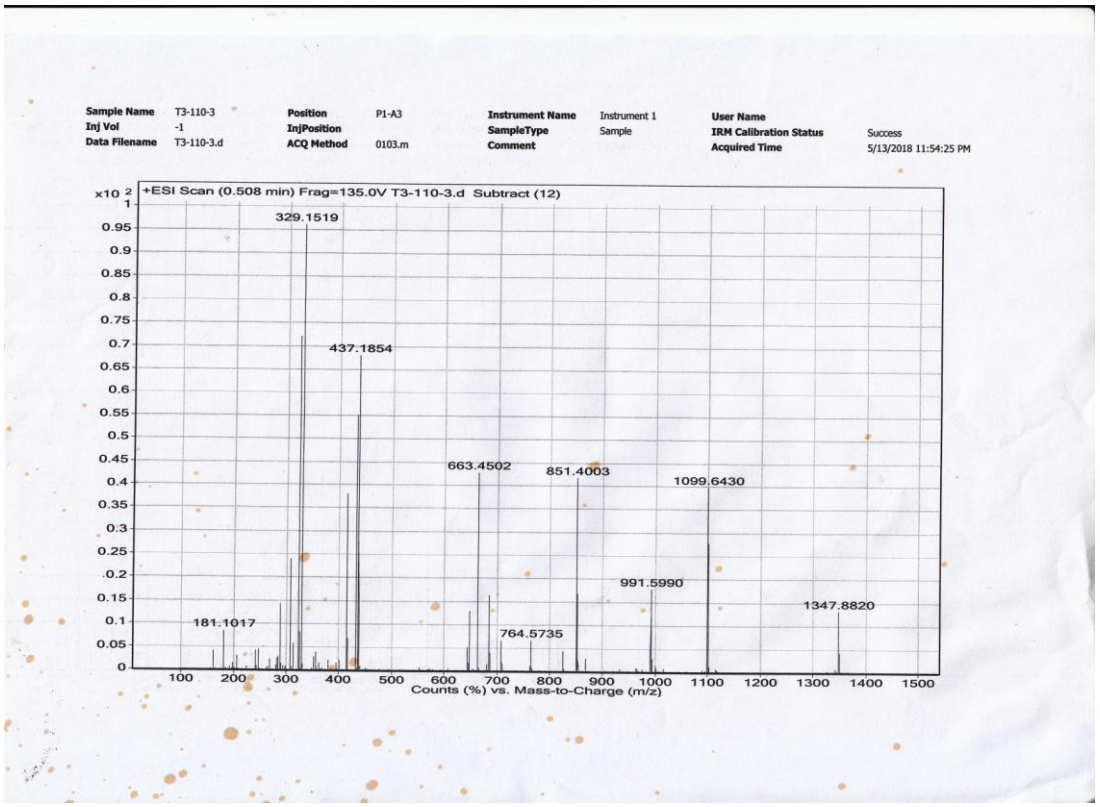
3r

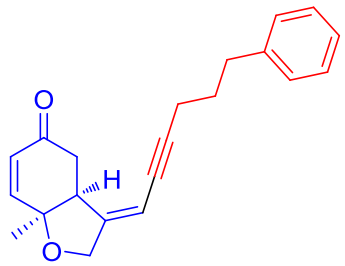
Chemical Formula: $C_{15}H_{16}O_2$
Exact Mass: 228.1150
Molecular Weight: 228.2863
m/z: 228.1150 (100.0%), 229.1184 (16.2%), 230.1217 (1.2%)

HRMS (ESI, m/z) calcd for $C_{15}H_{16}O_2$ $[M+H]^+$ 229.1229, found 229.1231.


T3-110-1
3s
ppm


T3-110-1
3s
ppm

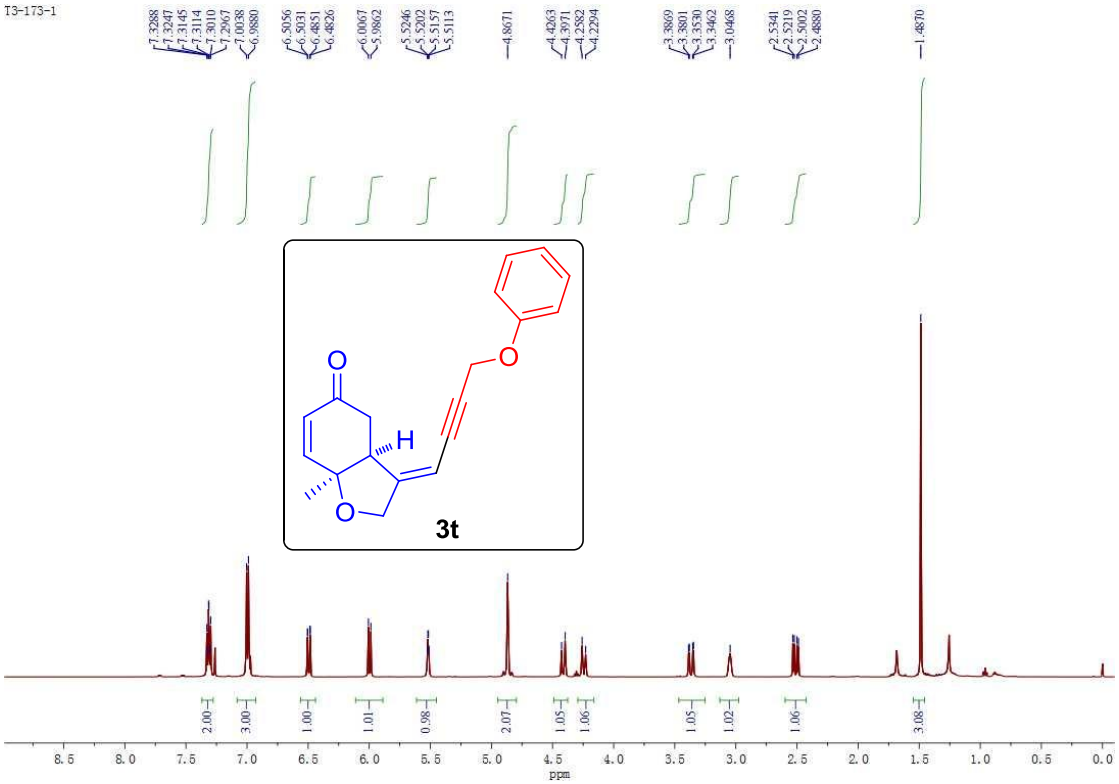


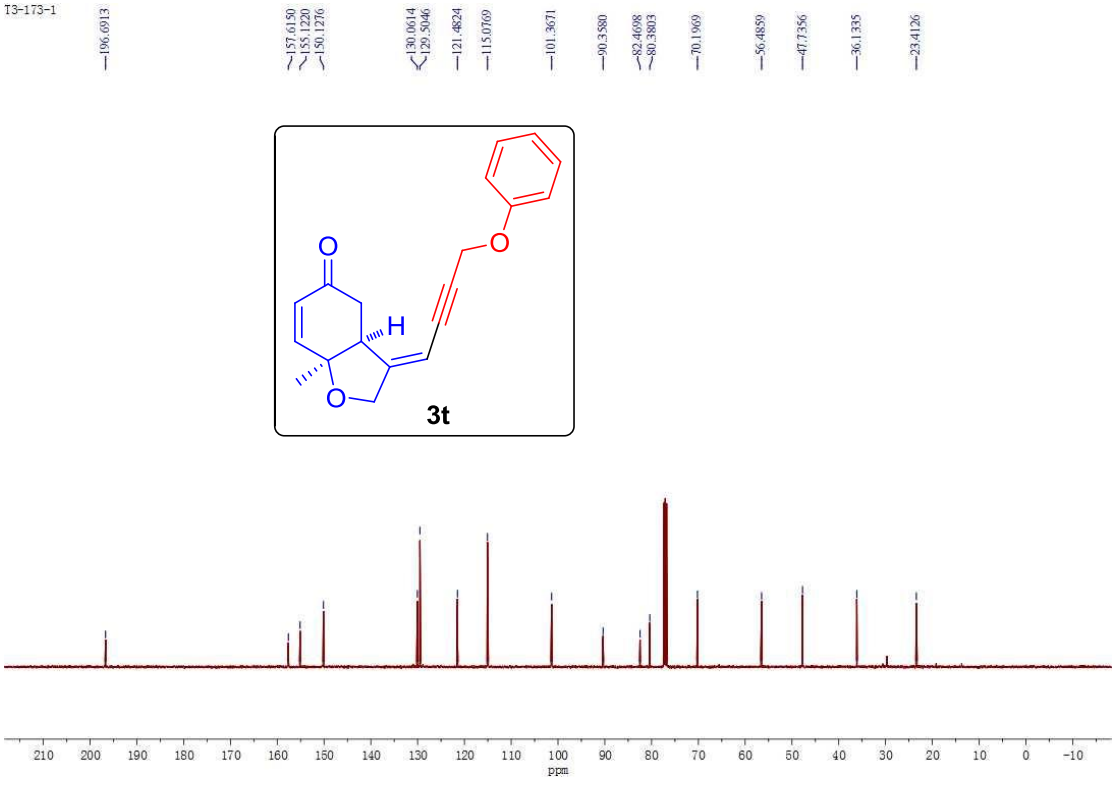


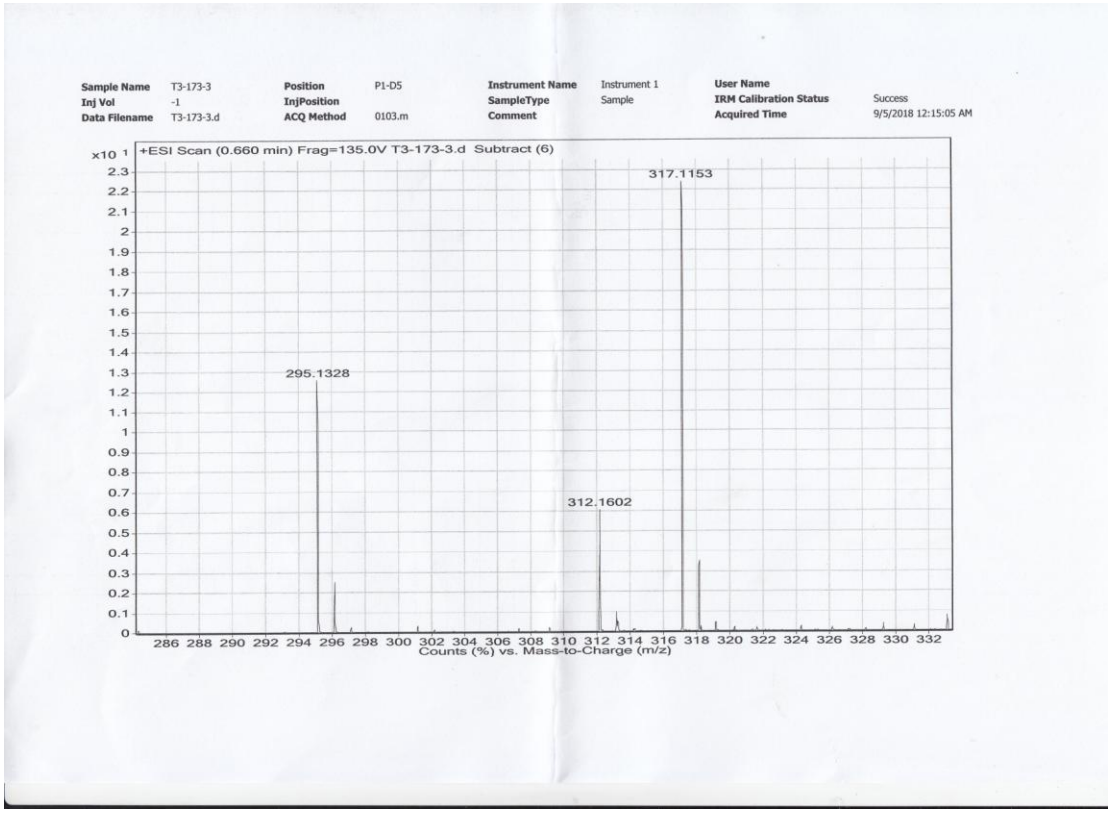
3s

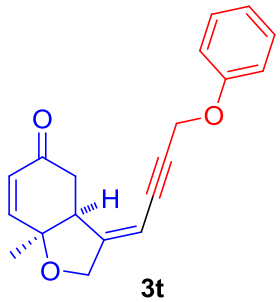
Chemical Formula: $C_{21}H_{22}O_2$
Exact Mass: 306.1620
Molecular Weight: 306.3982
m/z: 306.1620 (100.0%), 307.1653 (22.7%), 308.1687 (2.5%)

HRMS (ESI, m/z) calcd for $C_{21}H_{22}O_2$ $[M+Na]^+$ 329.1517, found 329.1519.


T3-173-1
7.3288
7.3247
7.3145
7.3114
7.3010
7.2967
7.0038
6.9880
6.5056
6.5031
6.4851
6.4826
6.0067
5.9862
5.5246
5.5202
5.5157
5.5113
4.8671
4.4263
4.3971
4.2582
4.2294
3.3869
3.3801
3.3530
3.3462
3.0468
2.5341
2.5219
2.5002
2.4880
1.4870
O
O
H
O
3t
2.00
3.00
1.00
1.01
0.98
2.07
1.05
1.06
1.05
1.02
1.06
3.08
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
ppm


T3-173-1
196.6913
157.6150
155.1220
150.1276
130.0614
129.5046
121.4824
115.0769
101.3671
90.3580
82.4698
80.3803
70.1969
56.4859
47.7356
36.1335
23.4126
O
O
H
O
3t
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

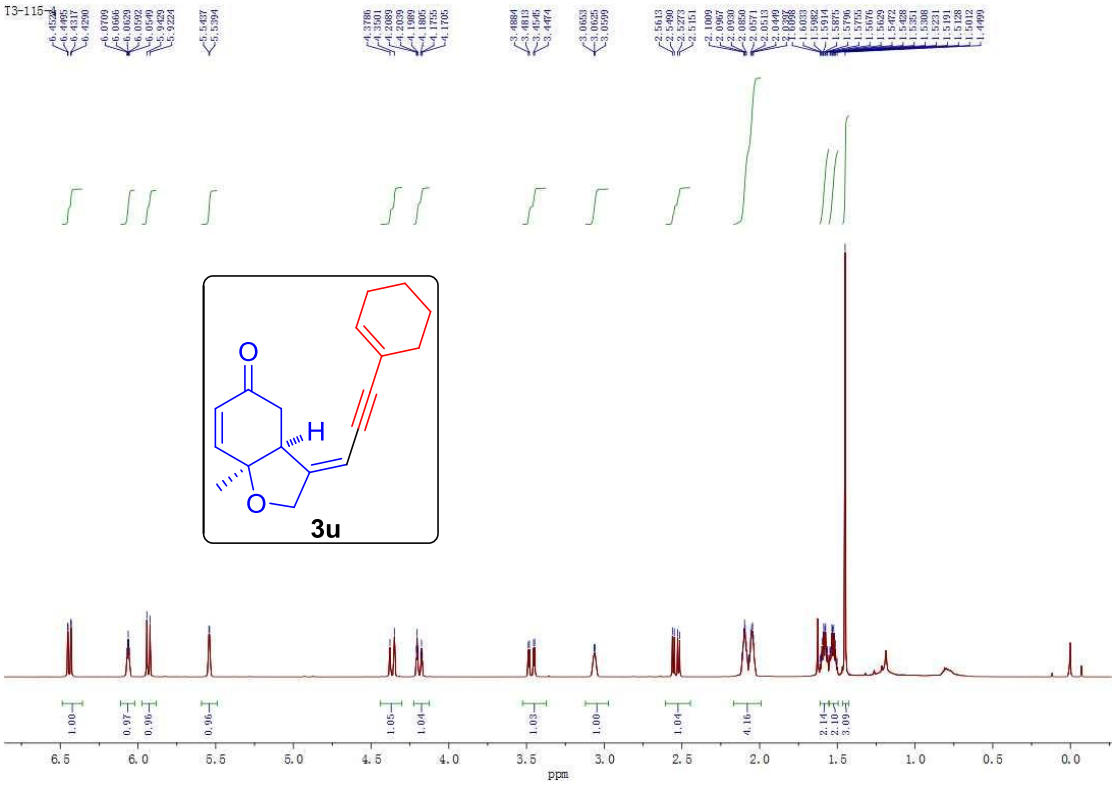


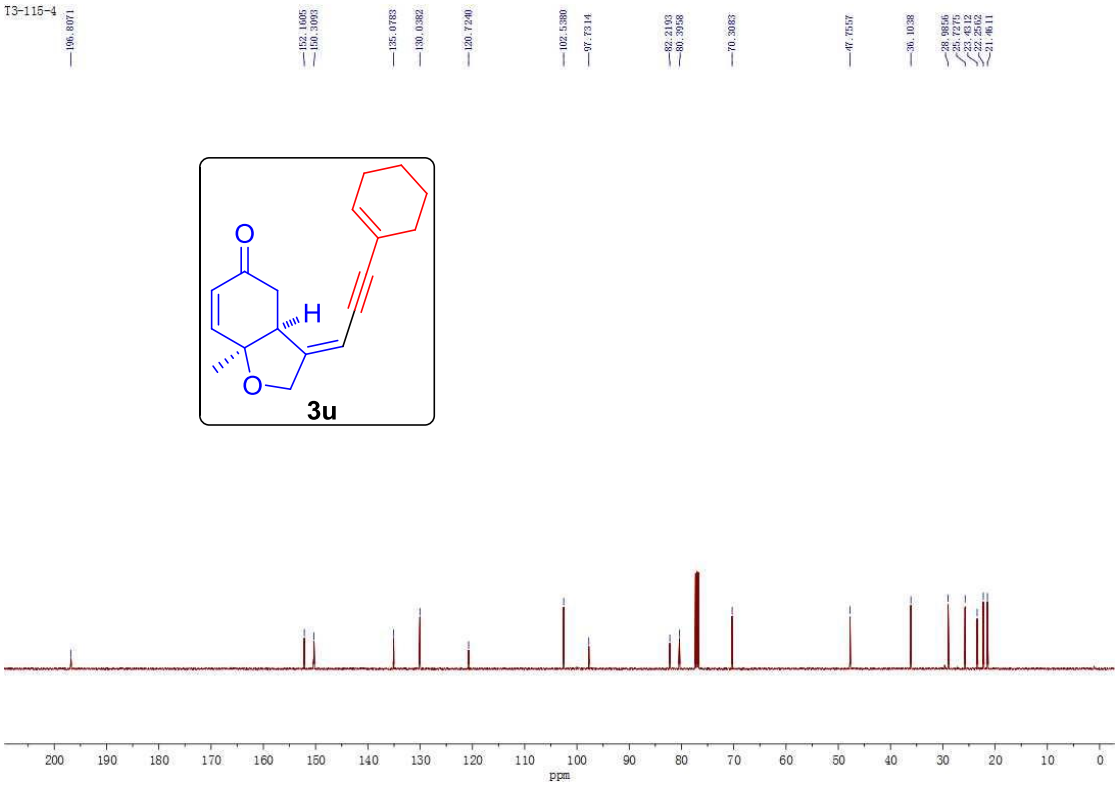


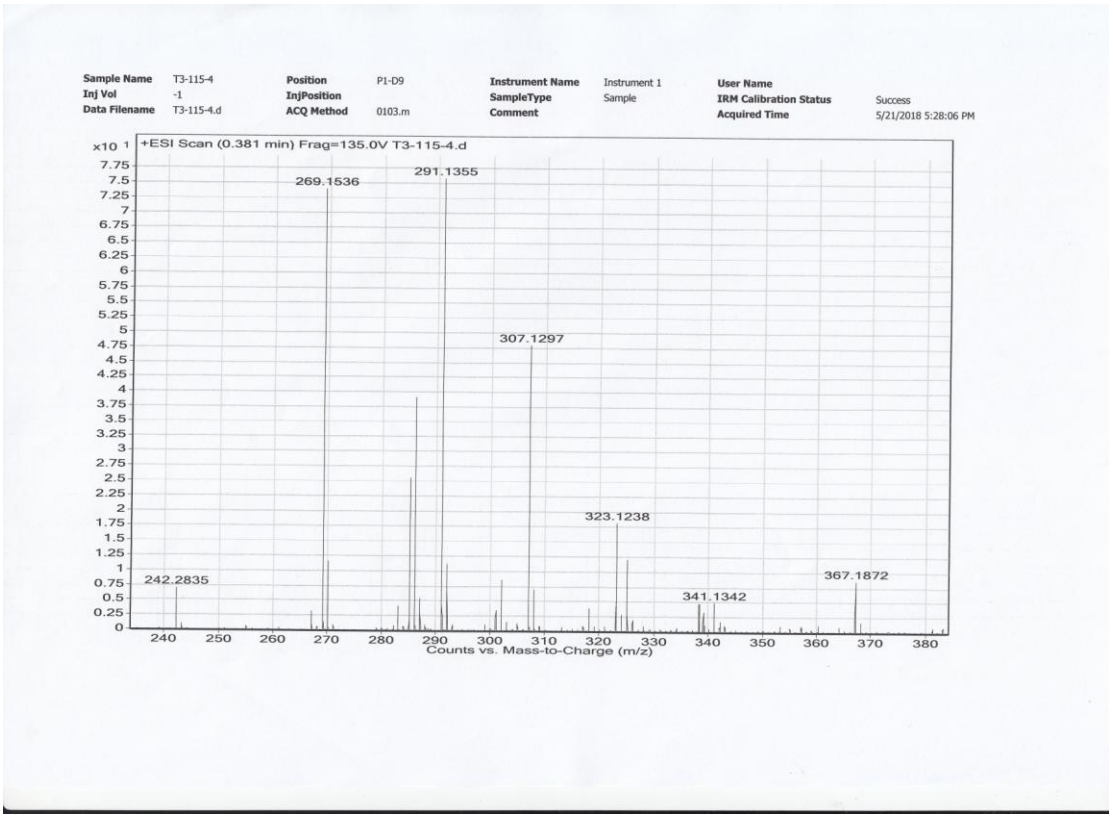
3t

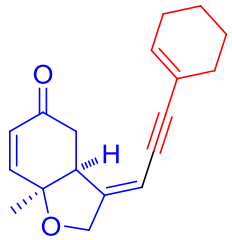
Chemical Formula: $C_{19}H_{18}O_3$
Exact Mass: 294.1256
Molecular Weight: 294.3444
m/z: 294.1256 (100.0%), 295.1289 (20.5%), 296.1323 (2.0%)

HRMS (ESI, m/z) calcd for $C_{19}H_{18}O_3[M+H]^+$ 295.1329, found 295.1328.


T3-115-4
O
H
O
3u
1.00
0.97
0.96
0.96
1.05
1.04
1.03
1.00
1.04
4.16
2.14
2.10
3.09
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
ppm


T3-115-4
O
H
O
3u
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

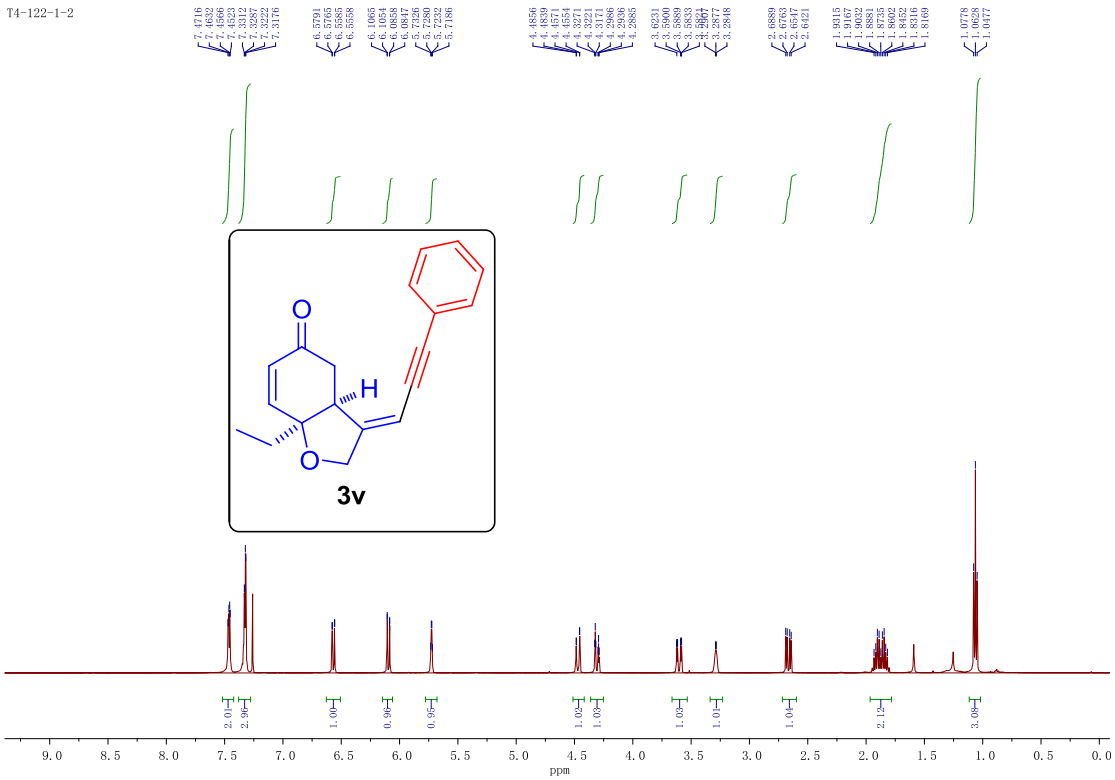


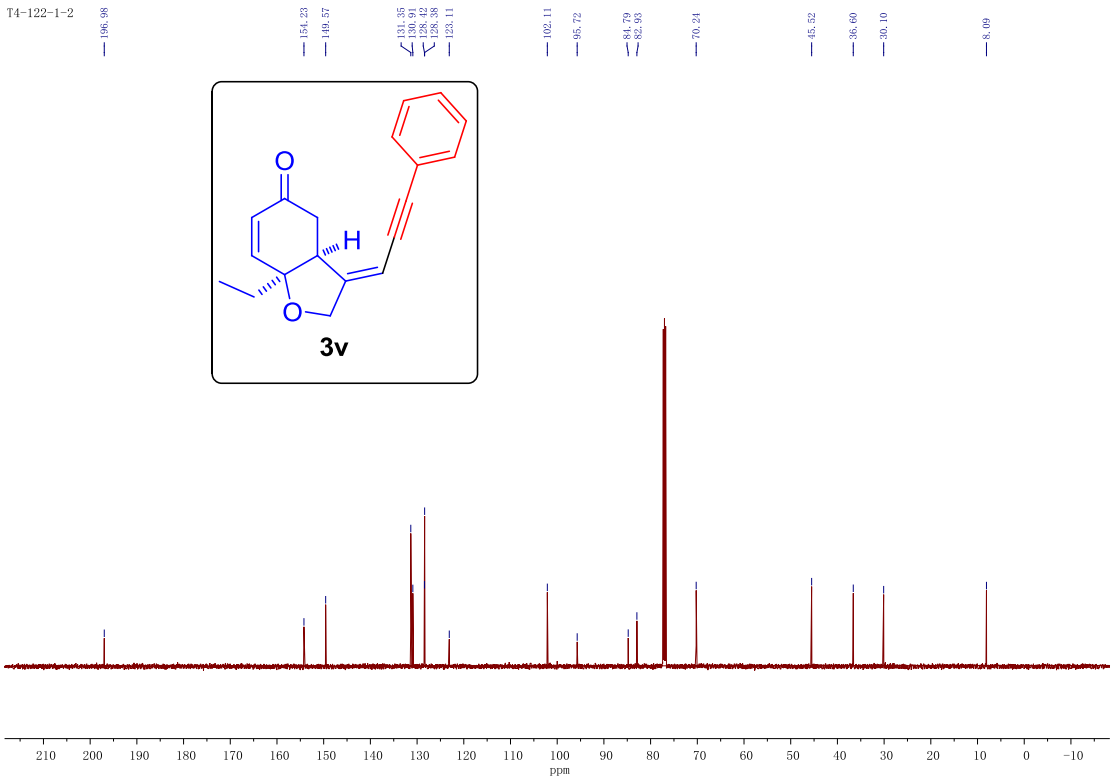


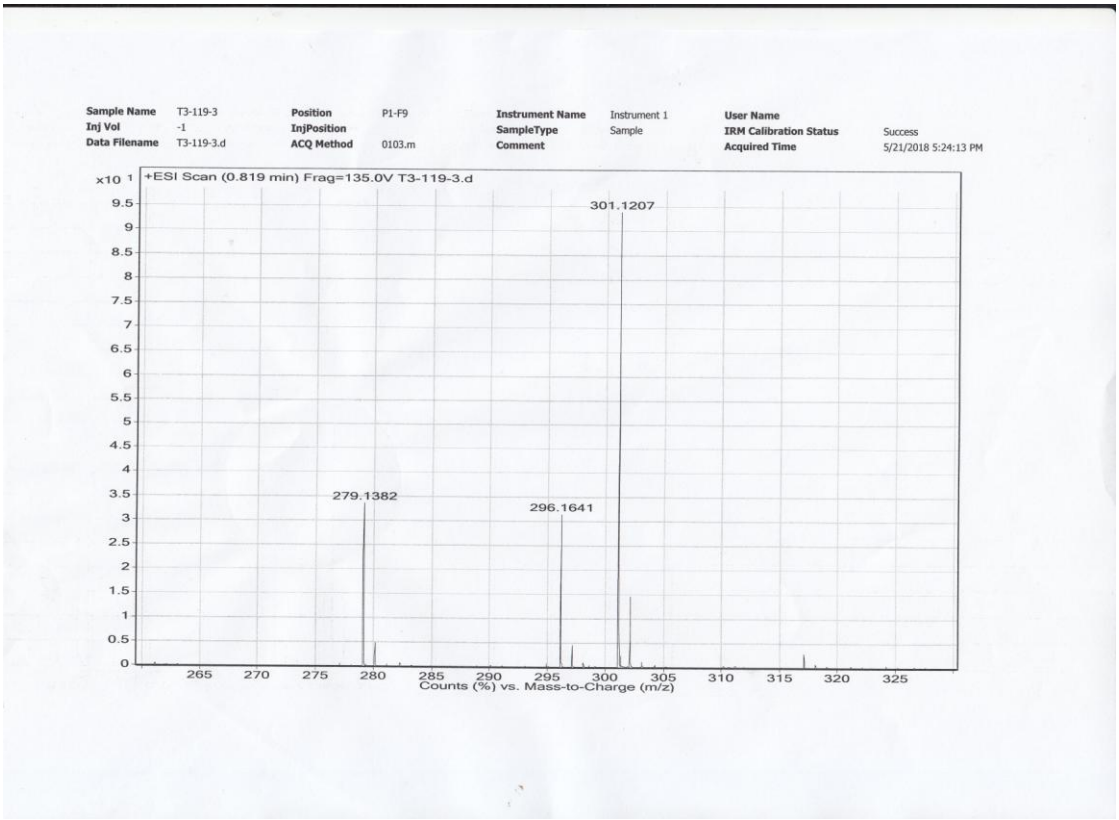
3u

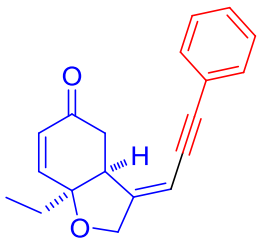
Chemical Formula: $C_{18}H_{20}O_2$
Exact Mass: 268.1463
Molecular Weight: 268.3502
m/z: 268.1463 (100.0%), 269.1497 (19.5%), 270.1530 (1.8%)

HRMS (ESI, m/z) calcd for $C_{18}H_{20}O_2$ $[M+H]^+$ 269.1542, found 269.1536.


T4-122-1-2
7.4716
7.4632
7.4566
7.4523
7.3812
7.3595
7.2222
7.3176
6.5791
6.5765
6.5585
6.5398
6.1065
6.1054
6.0998
6.0847
5.7326
5.7280
5.7232
5.7186
4.4856
4.4839
4.4571
4.4554
4.3271
4.3222
4.3171
4.2986
4.2936
4.2885
3.6231
3.5900
3.5889
3.5833
3.5821
3.5807
3.5757
3.5848
2.6889
2.6763
2.6547
2.6421
1.9315
1.9167
1.9032
1.8961
1.8735
1.8602
1.8452
1.8316
1.8169
1.0778
1.0628
1.0477
O
H
O
3v
2.01
2.96
1.00
0.96
0.96
1.02
1.03
1.03
1.01
1.04
2.13
3.08
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
ppm


T4-122-1-2
196.98
154.23
149.57
131.35
130.91
128.42
126.98
123.11
102.11
95.72
84.79
82.93
70.24
45.52
36.60
30.10
8.09
O
H
O
3v
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

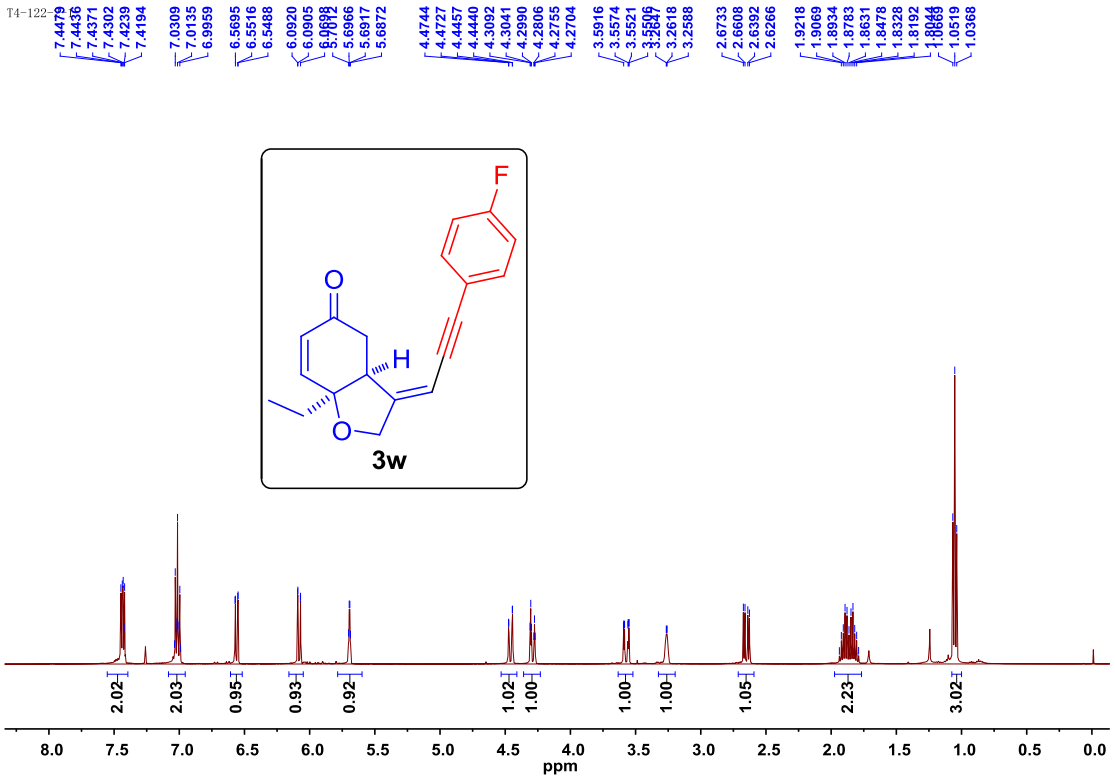


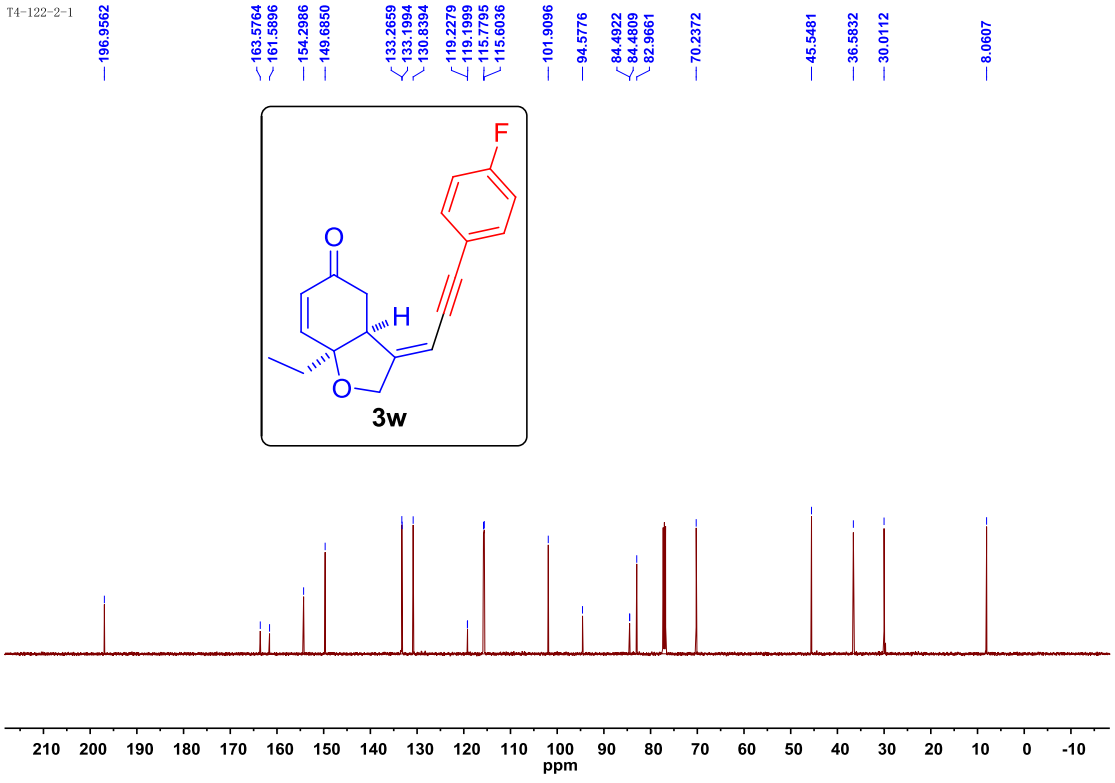


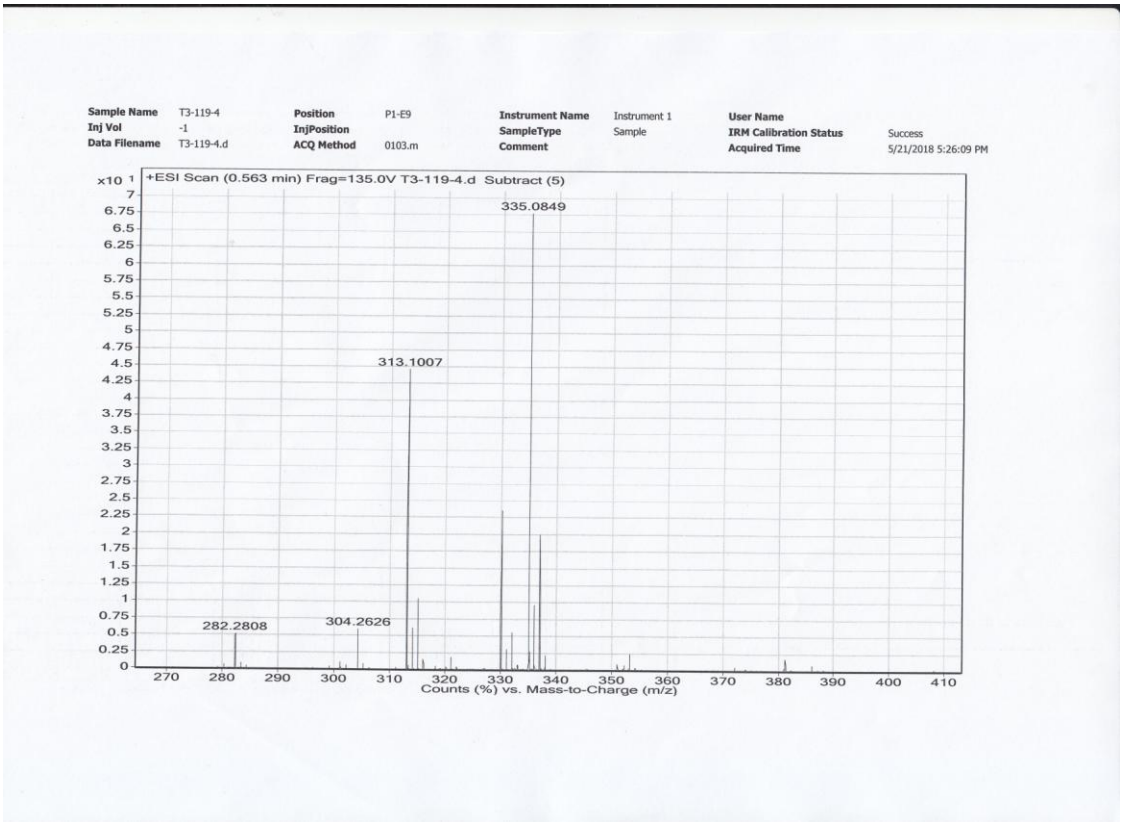
3v

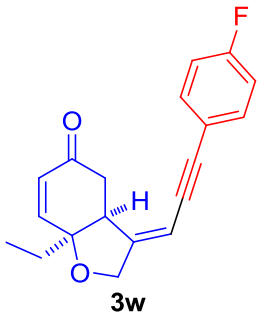
Chemical Formula: $C_{19}H_{18}O_2$
Exact Mass: 278.1307
Molecular Weight: 278.3450
m/z: 278.1307 (100.0%), 279.1340 (20.5%), 280.1374 (2.0%)

HRMS (ESI, m/z) calcd for $C_{19}H_{18}O_2$ $[M+H]^+$ 279.1385, found 279.1382.


T4-122-
7.4479
7.4436
7.4371
7.4302
7.4239
7.4194
7.0309
7.0135
6.9959
6.5695
6.5516
6.5488
6.0920
6.0905
5.6966
5.6917
5.6872
4.4744
4.4727
4.4457
4.4440
4.3092
4.3041
4.2990
4.2806
4.2755
4.2704
3.5916
3.5574
3.5521
3.2618
3.2588
2.6733
2.6608
2.6392
2.6266
1.9218
1.9069
1.8934
1.8783
1.8631
1.8478
1.8328
1.8192
1.0519
1.0368
F
O
H
O
3w
2.02
2.03
0.95
0.93
0.92
1.02
1.00
1.00
1.00
1.05
2.23
3.02
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
ppm


T4-122-2-1
196.9562
163.5764
161.5896
154.2986
149.6850
133.2659
133.1994
130.8394
119.2279
119.1999
115.7795
115.6036
101.9096
94.5776
84.4922
84.4809
82.9661
70.2372
45.5481
36.5832
30.0112
8.0607
F
O
H
O
3w
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

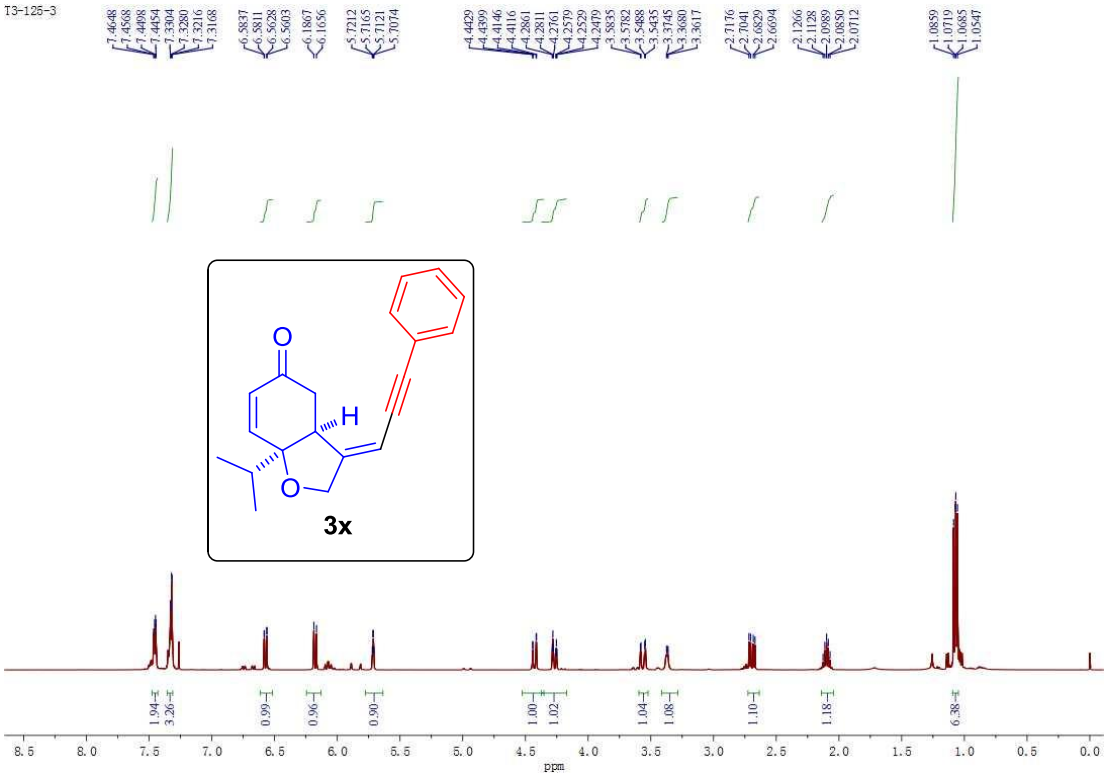


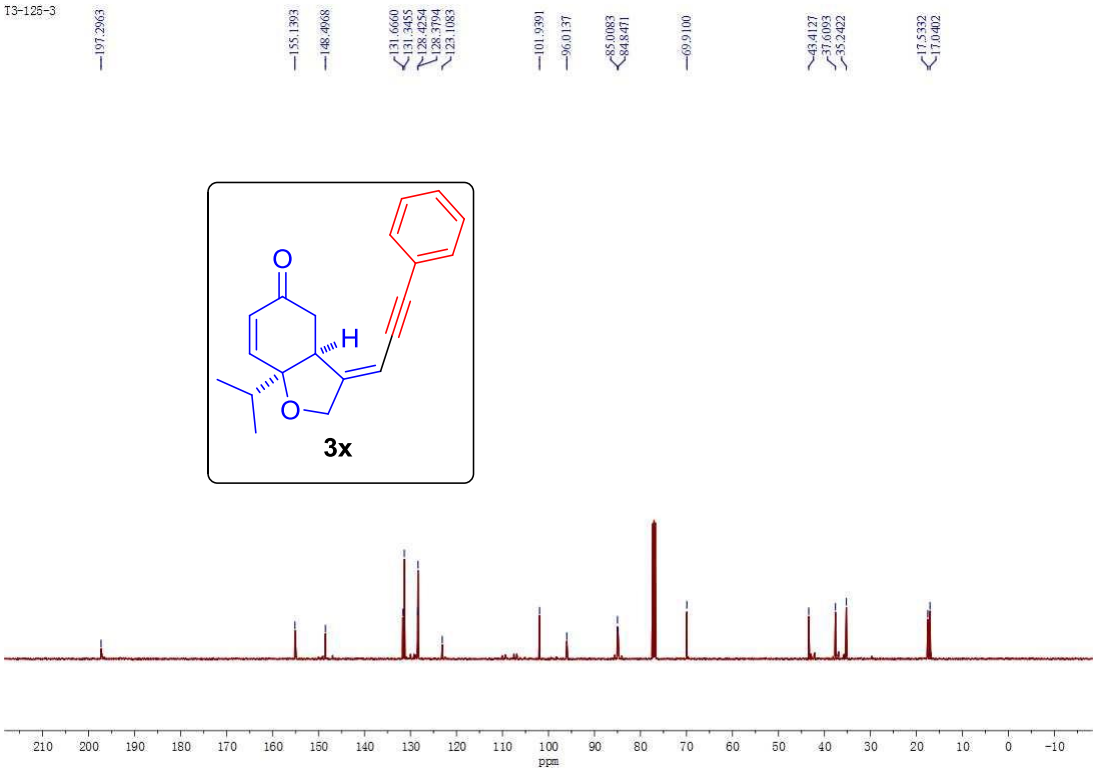


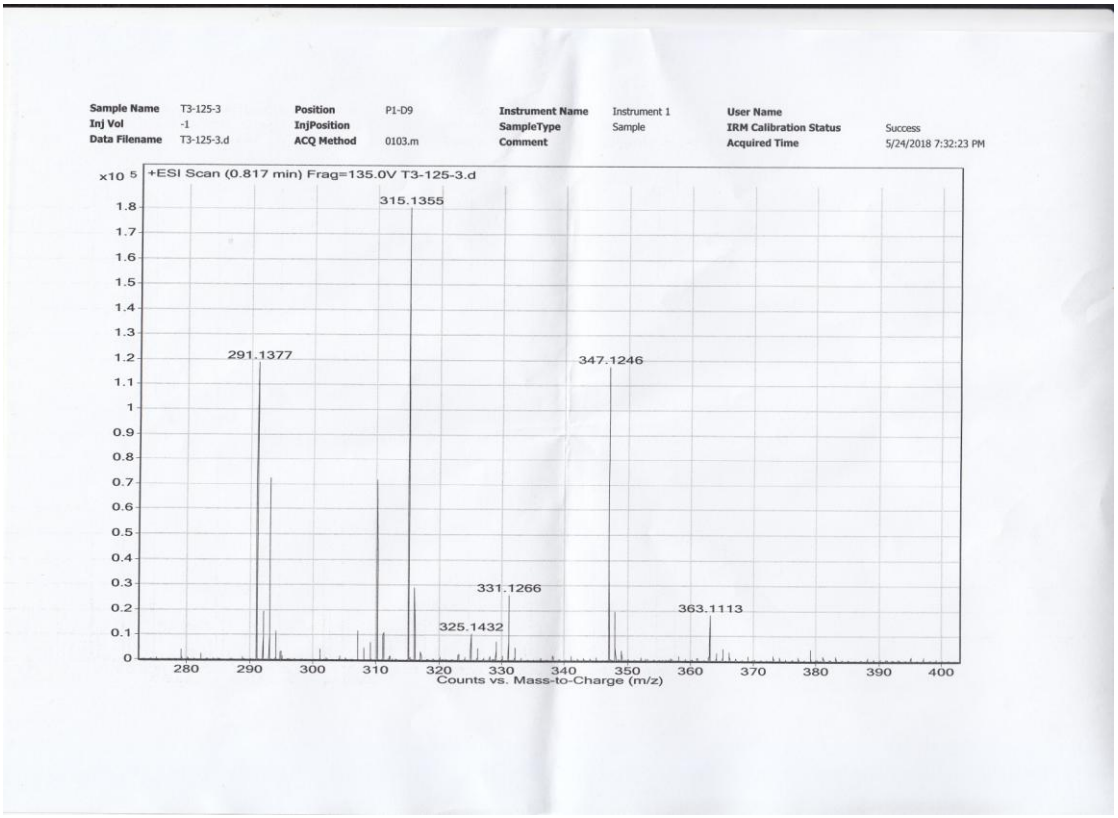
3w

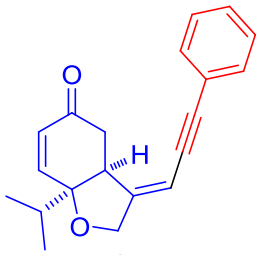
Chemical Formula: $C_{19}H_{17}FO_2$
Exact Mass: 296.1213
Molecular Weight: 296.3355
m/z: 296.1213 (100.0%), 297.1246 (20.5%), 298.1280 (2.0%)

HRMS (ESI, m/z) calcd for $C_{19}H_{17}FO_2$ $[M+K]^+$ 335.0850, found 335.0849.


T3-125-3
7.4648
7.4568
7.4498
7.4454
7.3304
7.3280
7.3216
7.3168
6.5837
6.5811
6.5628
6.5603
6.1867
6.1656
5.7212
5.7165
5.7121
5.7074
4.4429
4.4399
4.4146
4.4116
4.2861
4.2811
4.2761
4.2579
4.2529
4.2479
3.5835
3.5782
3.5488
3.5435
3.3745
3.3680
3.3617
2.7176
2.7041
2.6829
2.6694
2.1266
2.1128
2.0989
2.0850
2.0712
1.0859
1.0719
1.0685
1.0547
O
H
O
3x
1.94
3.26
0.99
0.96
0.90
1.00
1.02
1.04
1.08
1.10
1.18
6.38
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
ppm


T3-125-3
197.2963
155.1393
148.4968
131.6660
131.3455
128.4254
128.3794
123.1083
101.9391
96.0137
85.0083
84.8471
69.9100
43.4127
37.6093
35.2422
17.5332
17.0402
O
H
O
3x
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

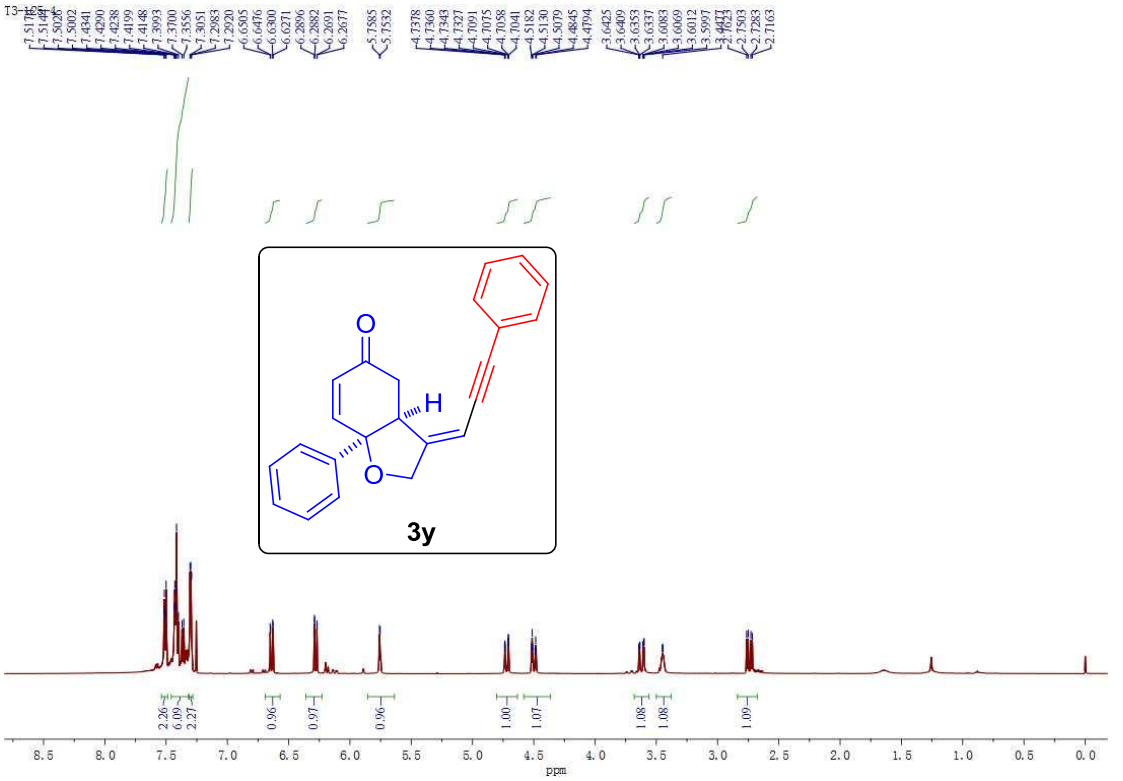


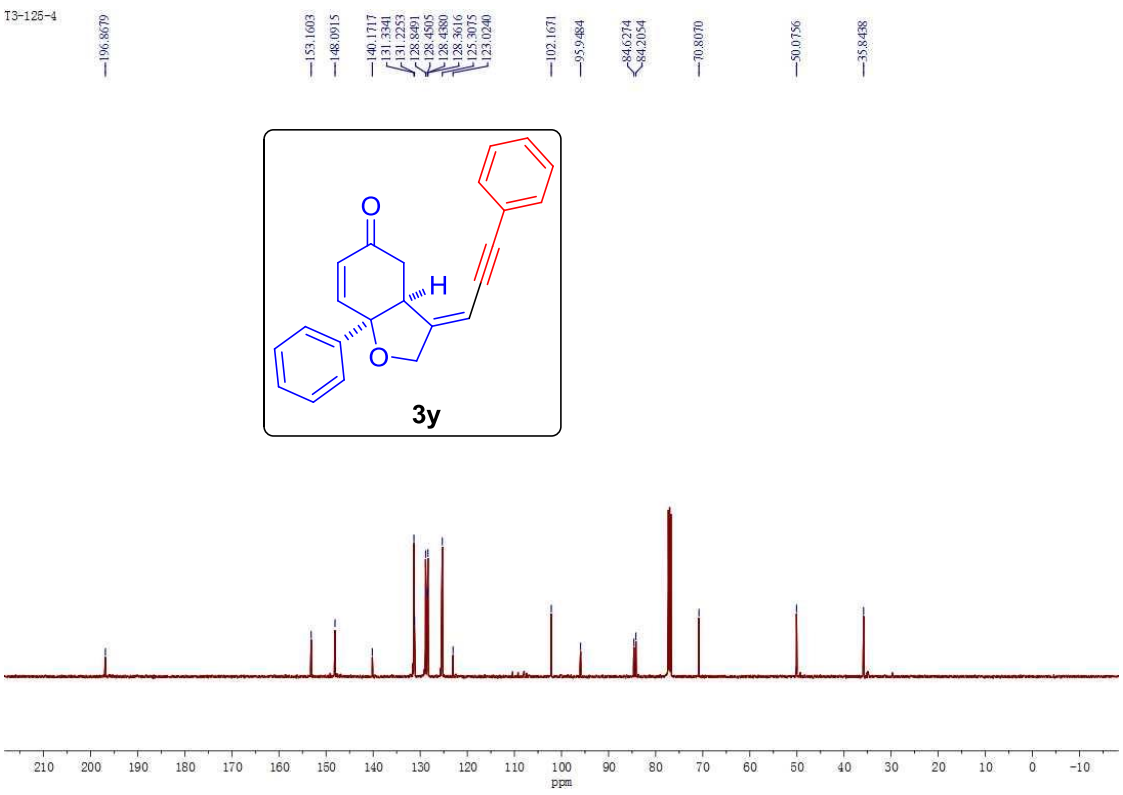


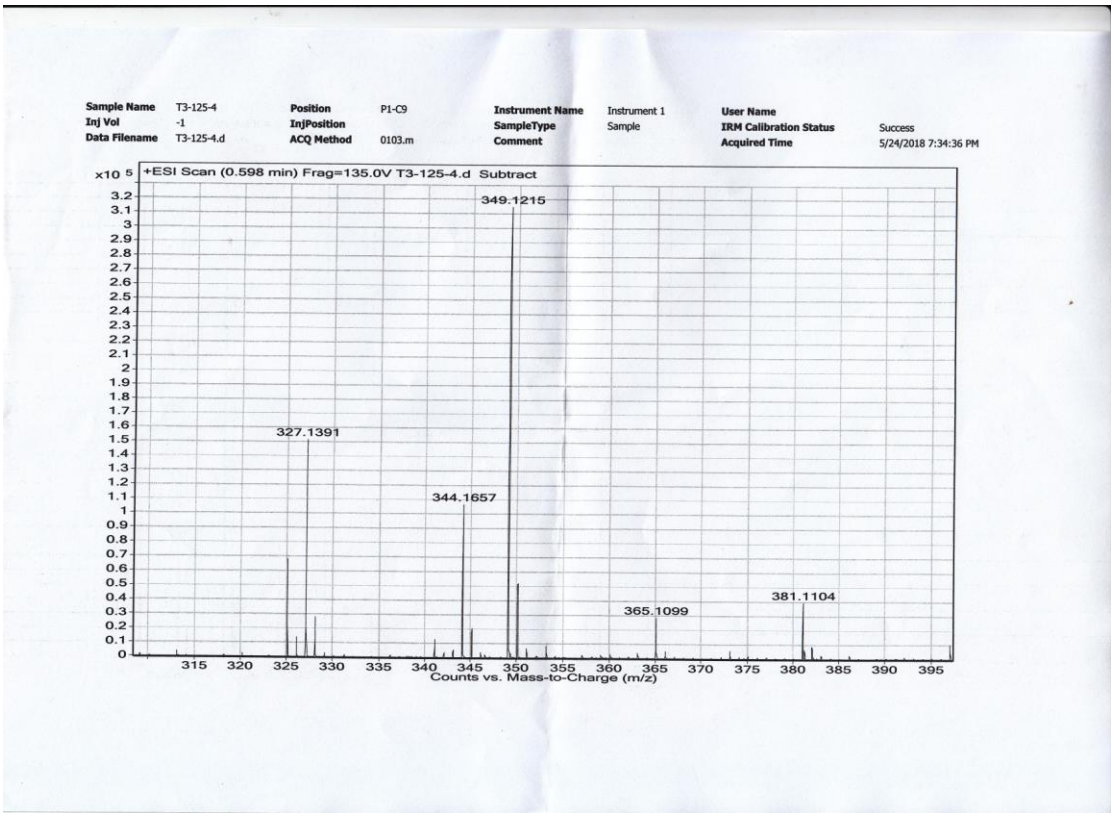
3x

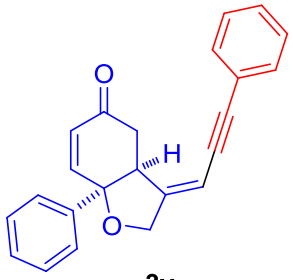
Chemical Formula: $C_{20}H_{20}O_2$
Exact Mass: 292.1463
Molecular Weight: 292.3716
m/z: 292.1463 (100.0%), 293.1497 (21.6%), 294.1530 (2.2%)

HRMS (ESI, m/z) calcd for $C_{20}H_{20}O_2$ $[M+Na]^+$ 315.1356, found 315.1355.


O
H
O
3y
2.26
6.09
2.27
0.96
0.97
0.96
1.00
1.07
1.08
1.08
1.09
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
ppm


O
H
O
3y
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

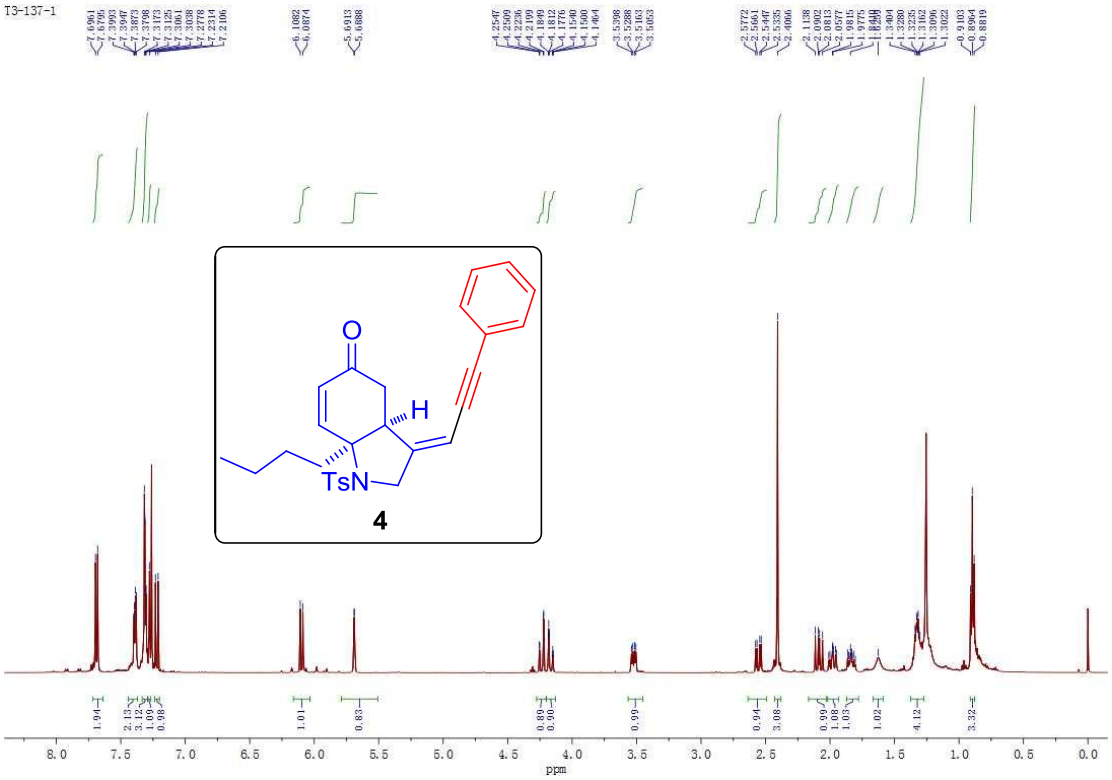


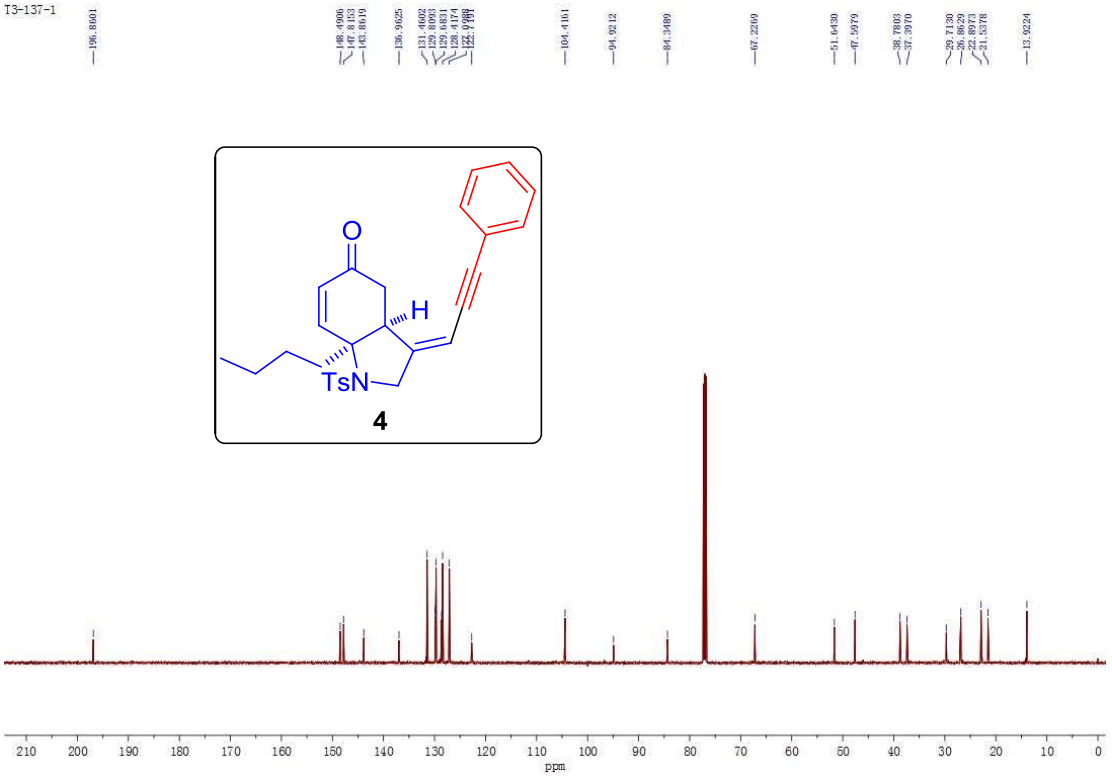


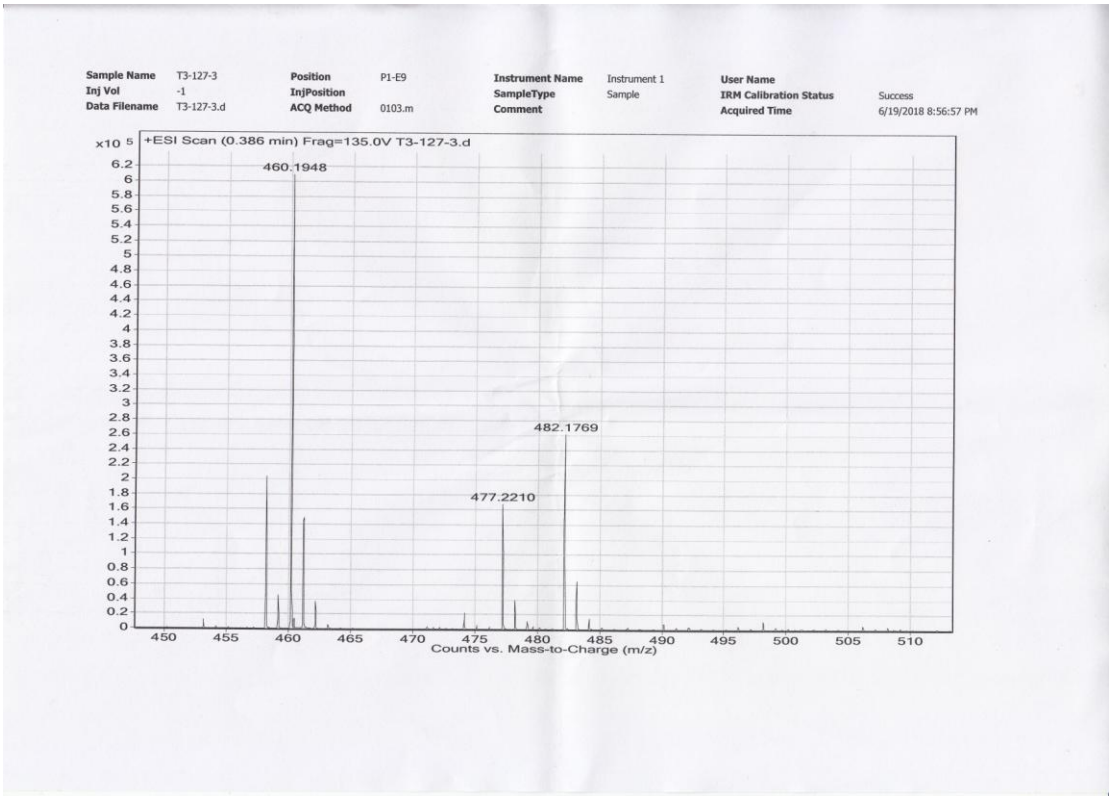
3y

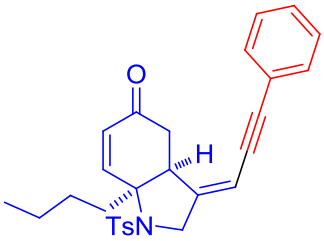
Chemical Formula: $C_{23}H_{18}O_2$
Exact Mass: 326.1307
Molecular Weight: 326.3878
m/z: 326.1307 (100.0%), 327.1340 (24.9%), 328.1374 (3.0%)

HRMS (ESI, m/z) calcd for $C_{23}H_{18}O_2$ $[M+H]^+$ 327.1380, found 327.1391.


T3-137-1
O
H
TsN
4
ppm


T3-137-1
O
H
TsN
4
ppm

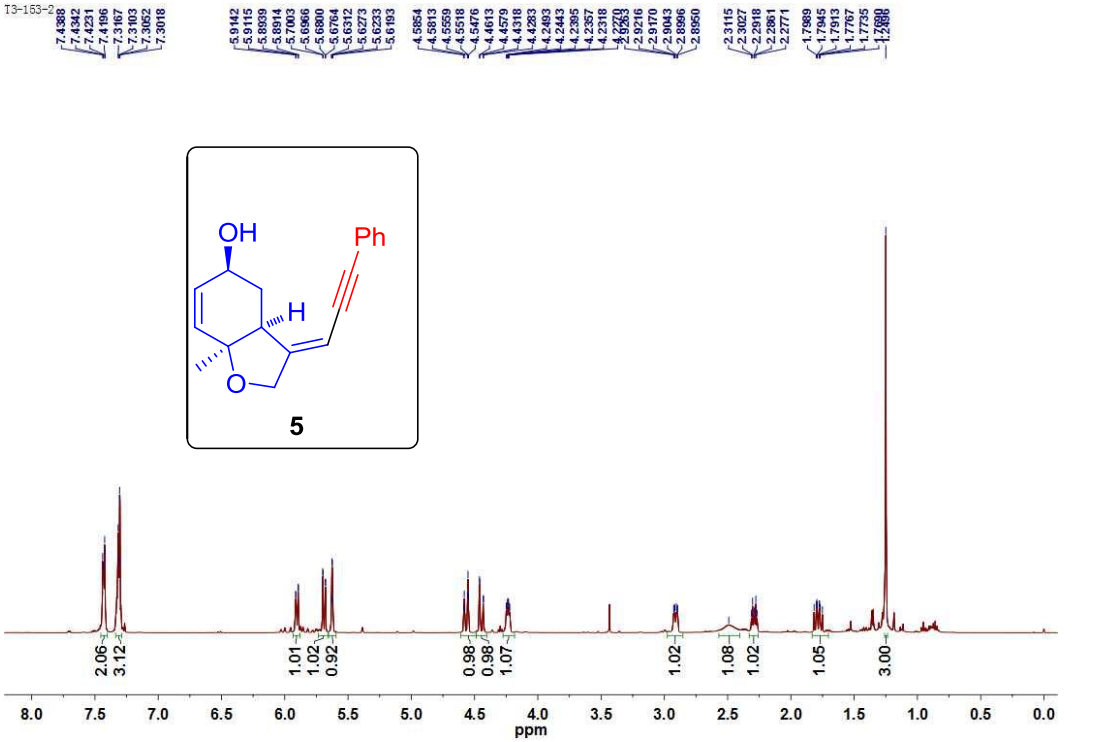


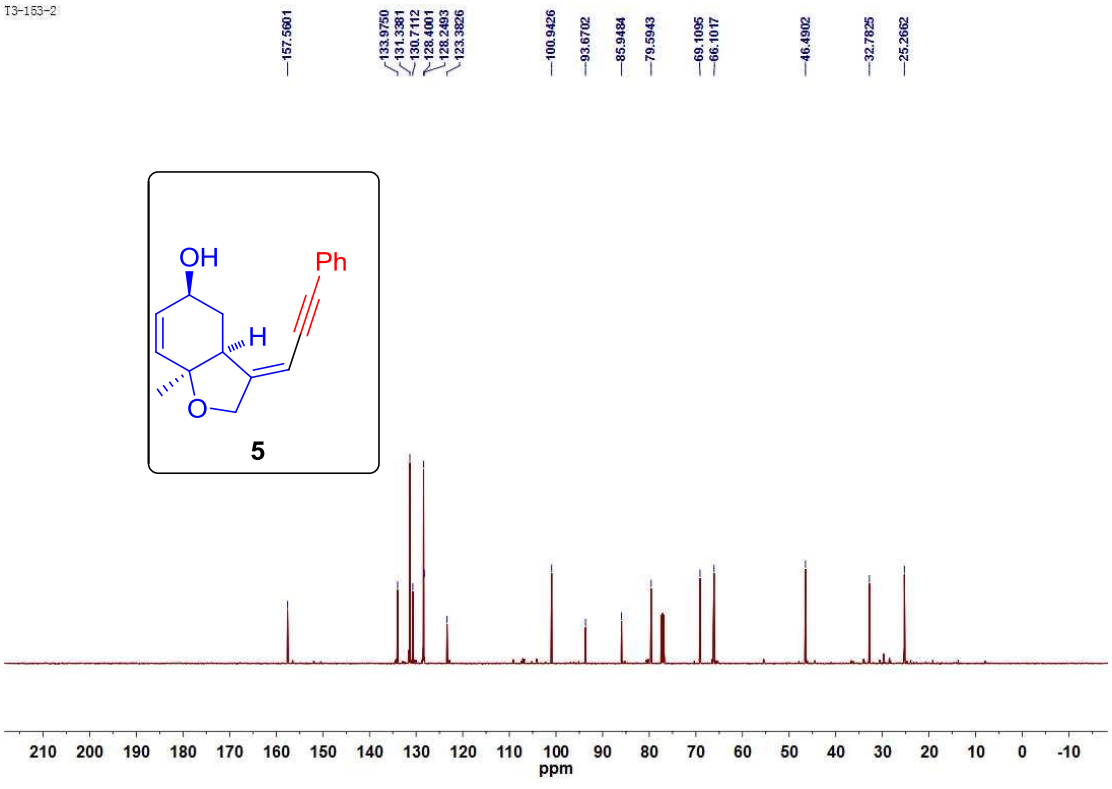


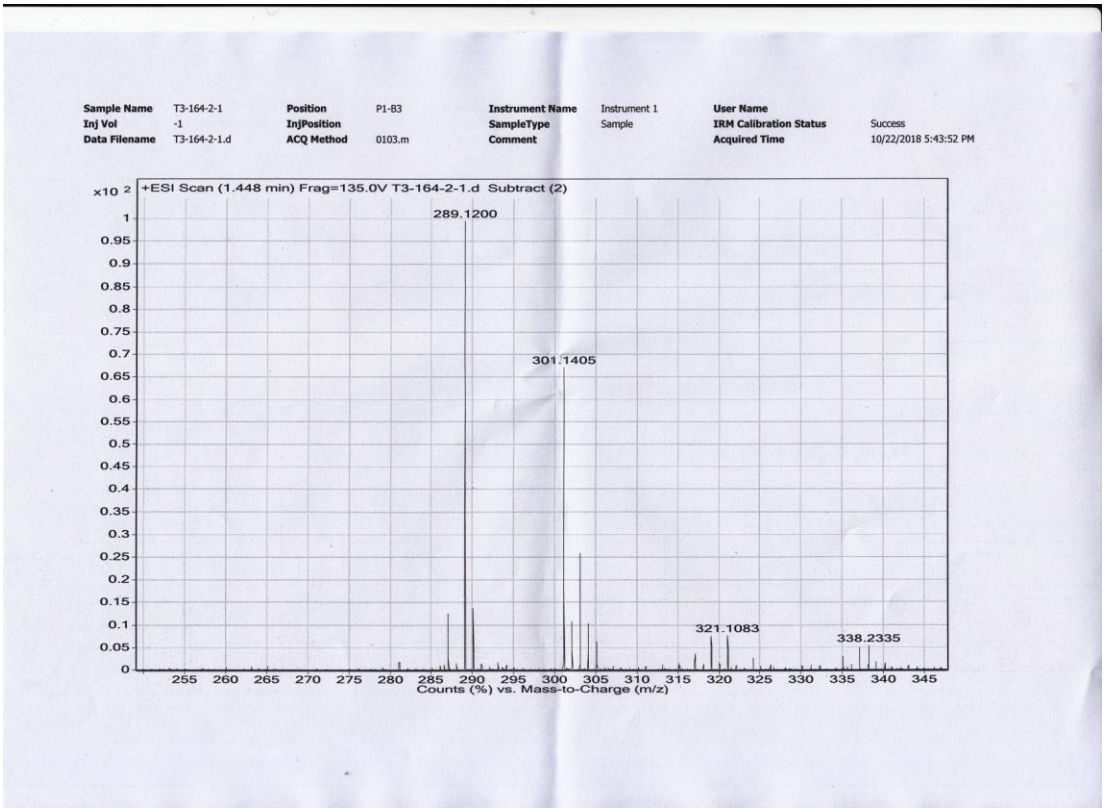
4

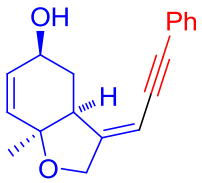
Chemical Formula: $C_{28}H_{29}NO_3S$
Exact Mass: 459.1868
Molecular Weight: 459.5998
m/z: 459.1868 (100.0%), 460.1902 (30.3%), 461.1826 (4.5%), 461.1935 (4.4%), 462.1860 (1.4%)

HRMS (ESI, m/z) calcd for $C_{28}H_{29}NO_3S$ $[M+H]^+$ 460.1941, found 460.1948.


T3-153-2
OH
Ph
H
O
5
2.06
3.12
1.01
1.02
0.92
0.98
0.98
1.07
1.02
1.08
1.02
1.05
3.00
ppm


T3-153-2
157.5601
133.9750
131.3381
130.7112
128.4001
128.2493
123.3826
100.9426
93.6702
85.9484
79.5943
69.1095
66.1017
46.4902
32.7825
25.2662
OH
Ph
H
O
5
ppm



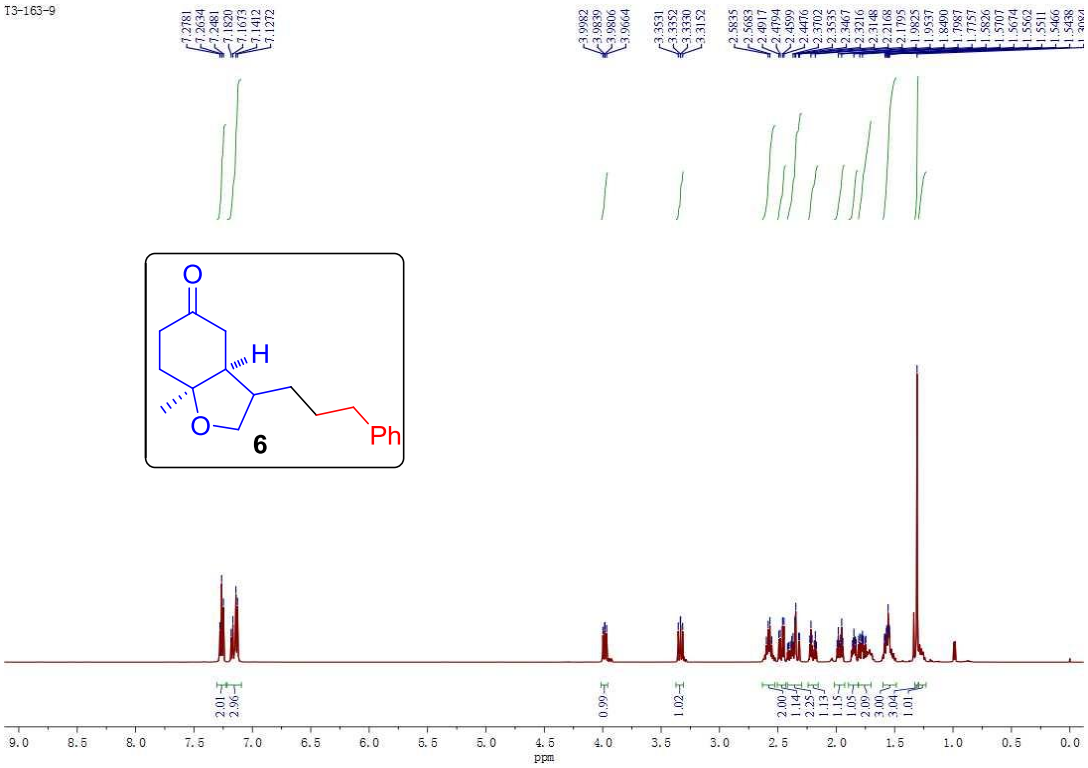


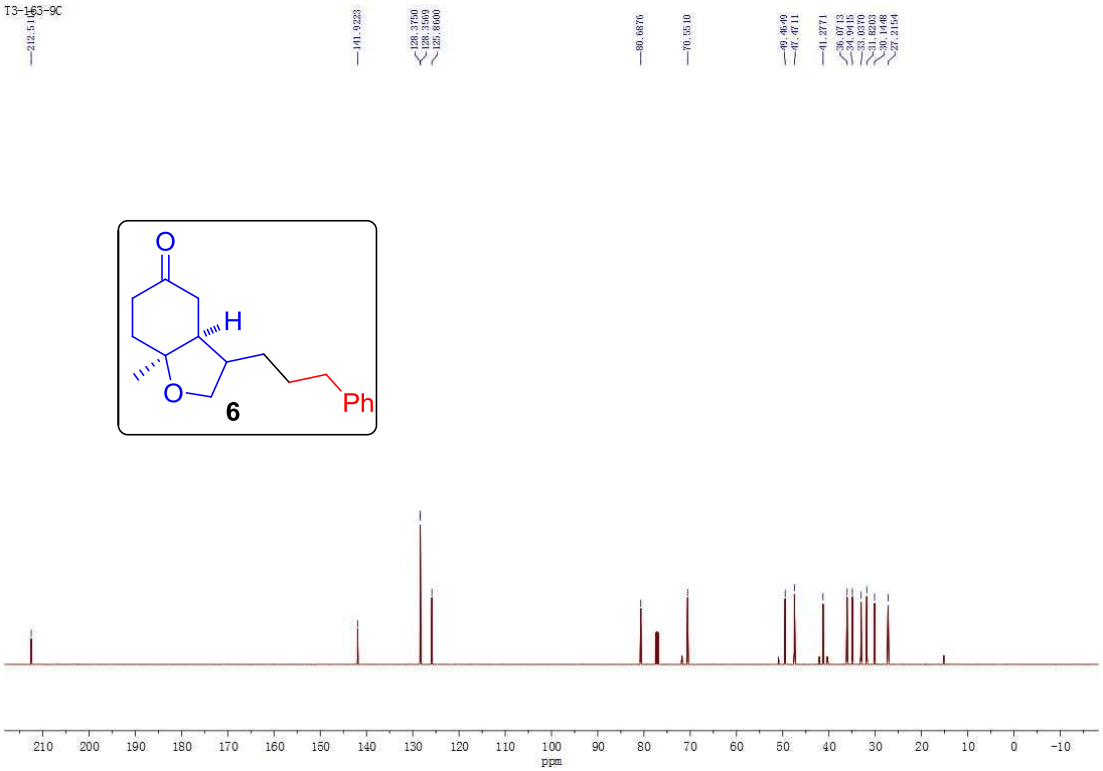
5

Chemical Formula: $C_{18}H_{18}O_2$
Exact Mass: 266.1307
Molecular Weight: 266.3343
m/z: 266.1307 (100.0%), 267.1340 (19.5%), 268.1374 (1.8%)

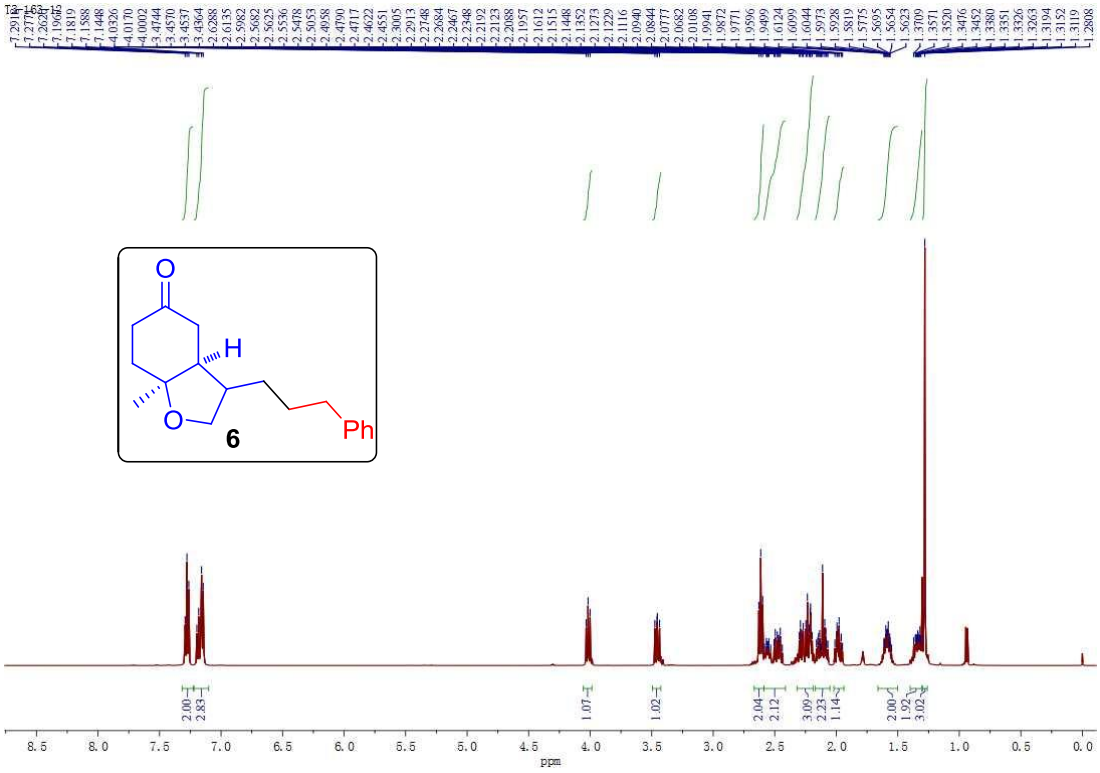
HRMS (ESI, m/z) calcd for $C_{18}H_{18}O_2$ $[M+Na]^+$ 289.1199, found 289.1200.

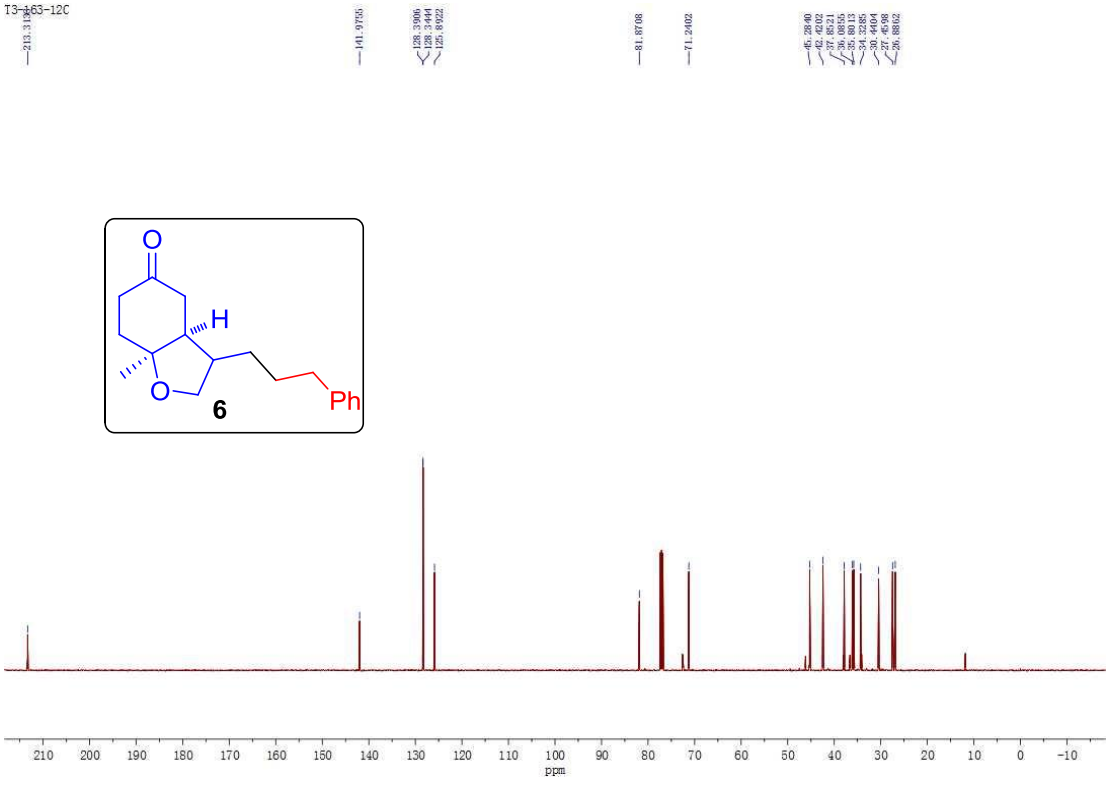
Major

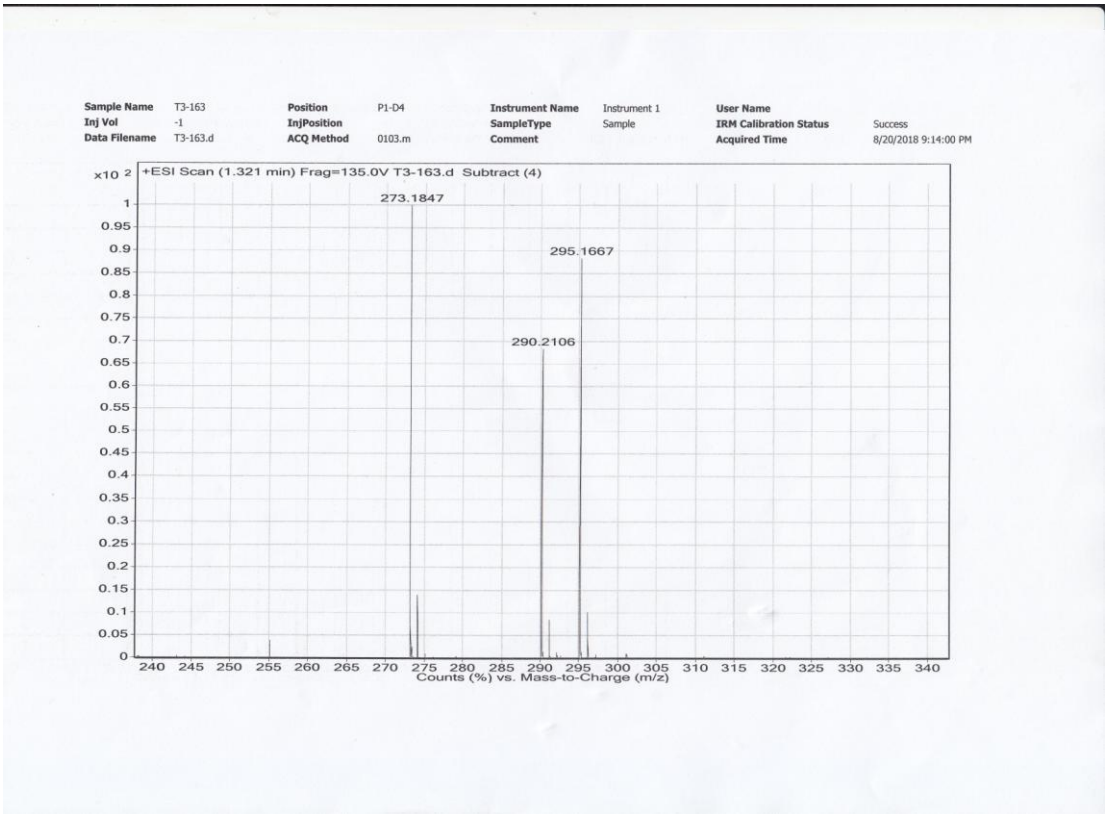


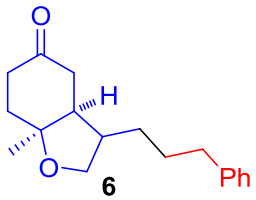


Minor


O
H
O
Ph
6
2.00
2.83
1.07
1.02
2.04
2.12
3.09
2.23
1.14
2.00
1.92
3.02
ppm


O
H
O
Ph
6
ppm

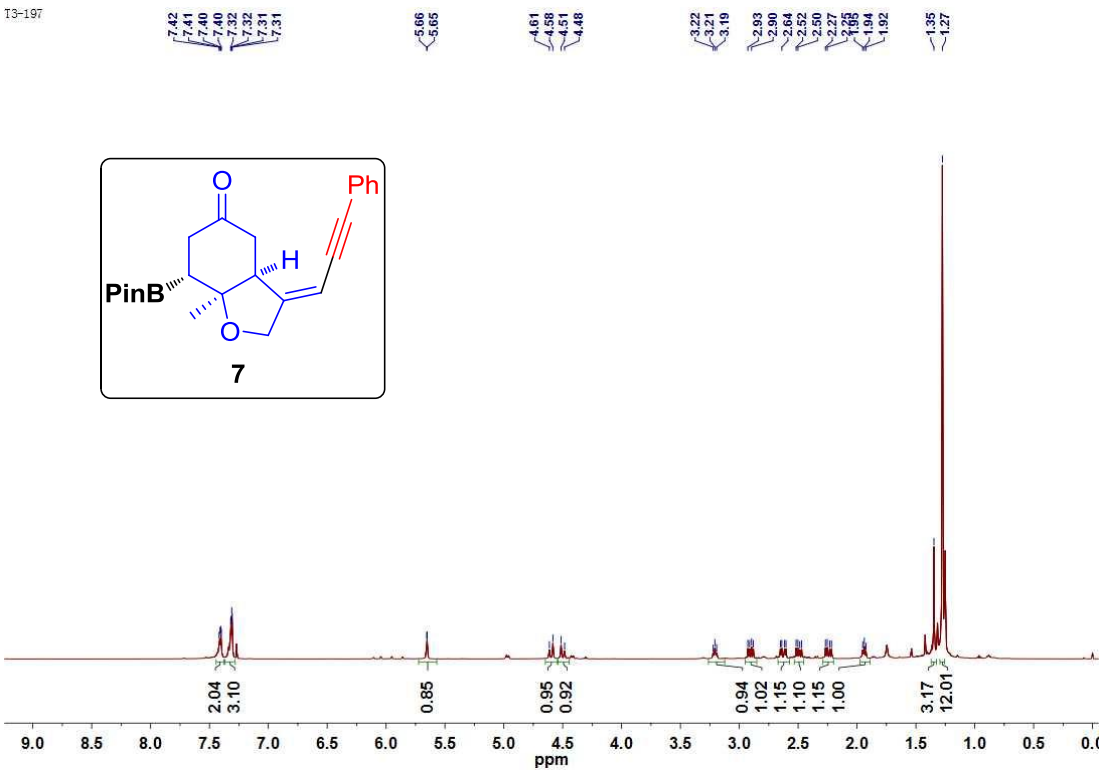


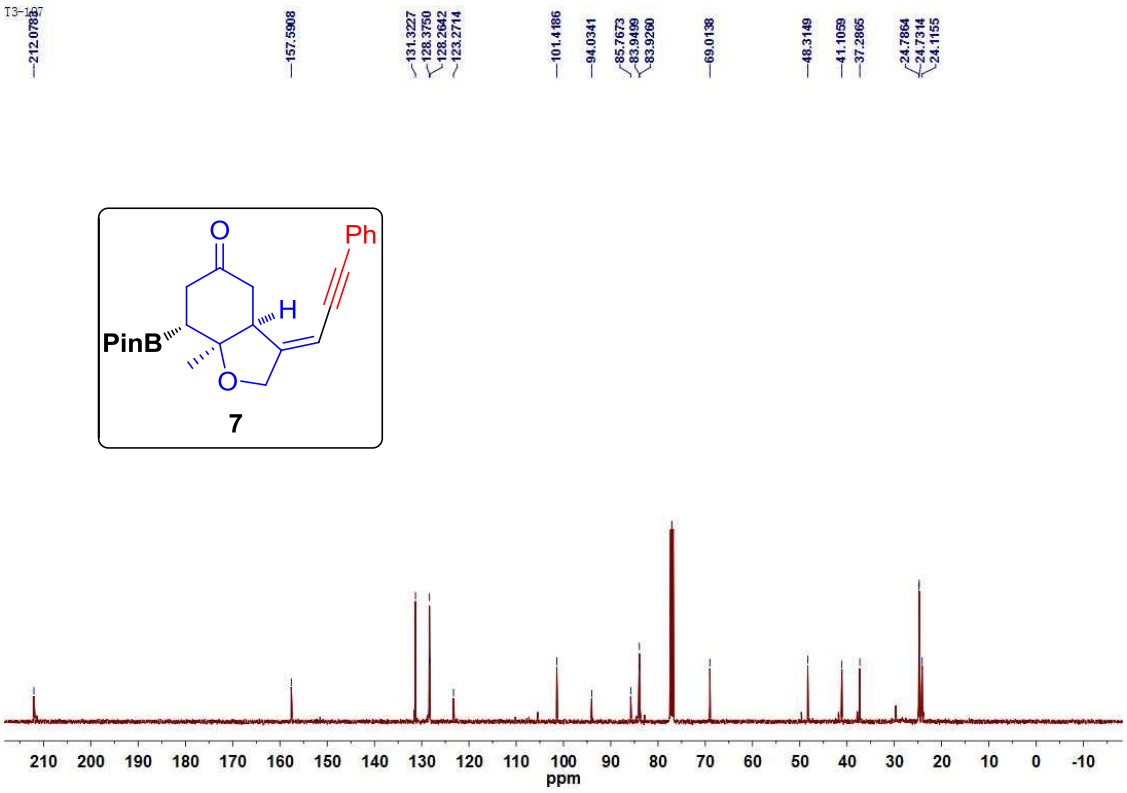


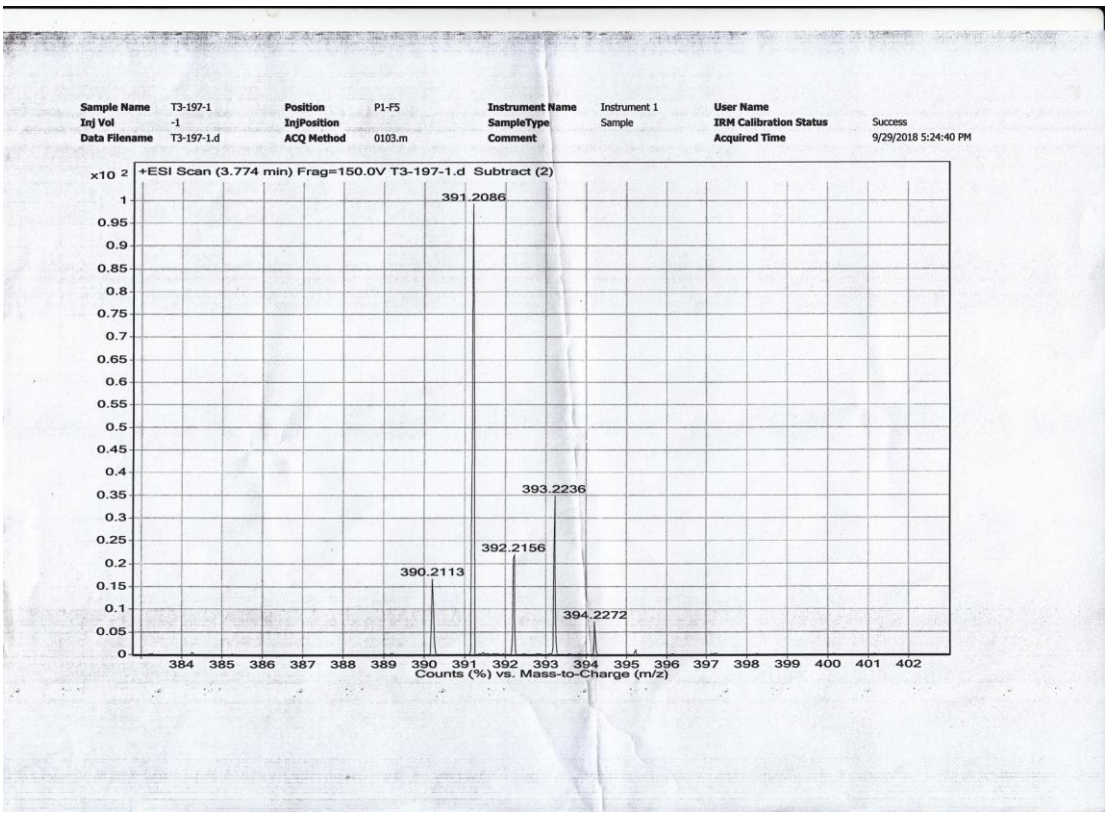
6

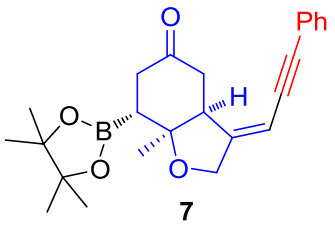
Chemical Formula: $C_{18}H_{24}O_2$
Exact Mass: 272.1776
Molecular Weight: 272.3820
m/z: 272.1776 (100.0%), 273.1810 (19.5%), 274.1843 (1.8%)

HRMS (ESI, m/z) calcd for $C_{18}H_{24}O_2$ $[M+H]^+$ 273.1849, found 273.1847.


T3-197
7.42
7.41
7.40
7.40
7.32
7.32
7.31
7.31
5.66
5.65
4.61
4.58
4.51
4.48
3.22
3.21
3.19
2.93
2.90
2.64
2.52
2.50
2.27
1.94
1.92
1.35
1.27
O
Ph
H
PinB
O
7
2.04
3.10
0.85
0.95
0.92
0.94
1.02
1.15
1.10
1.15
1.00
3.17
12.01
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
ppm


T3-197
212.0782
157.5908
131.3227
128.3750
128.2642
123.2714
101.4186
94.0341
85.7673
83.9489
83.9260
69.0138
48.3149
41.1059
37.2865
24.7864
24.7314
24.1155
O
Ph
H
PinB
O
7
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

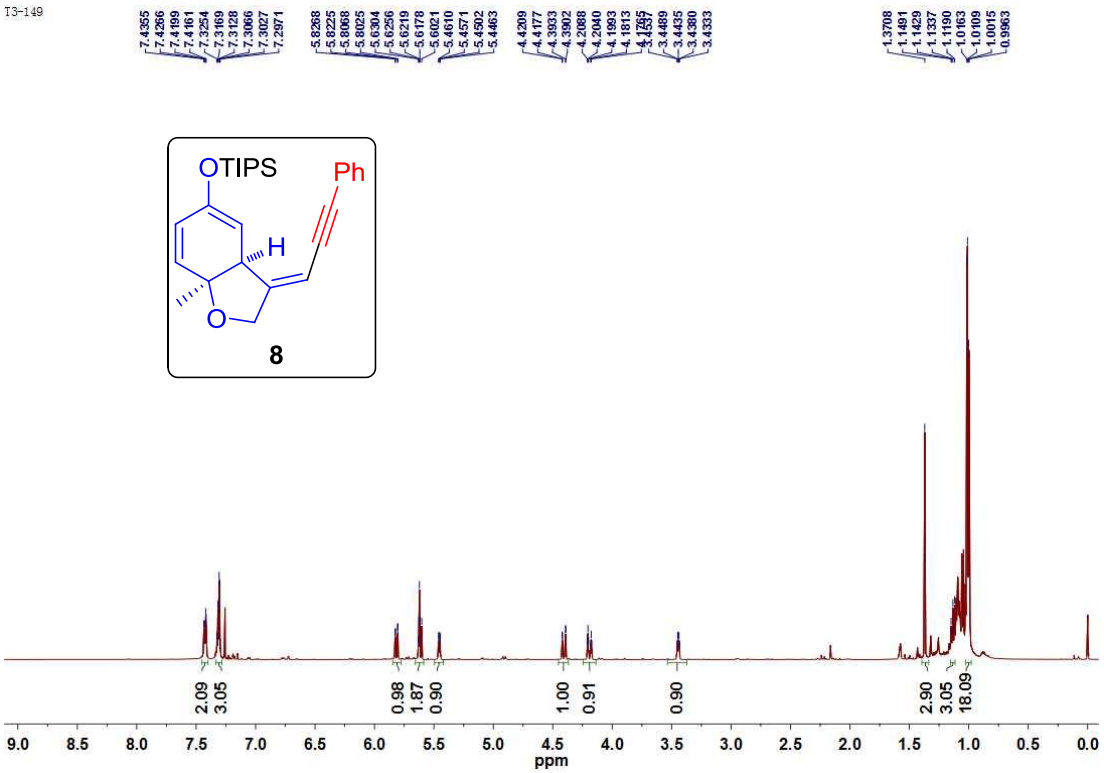


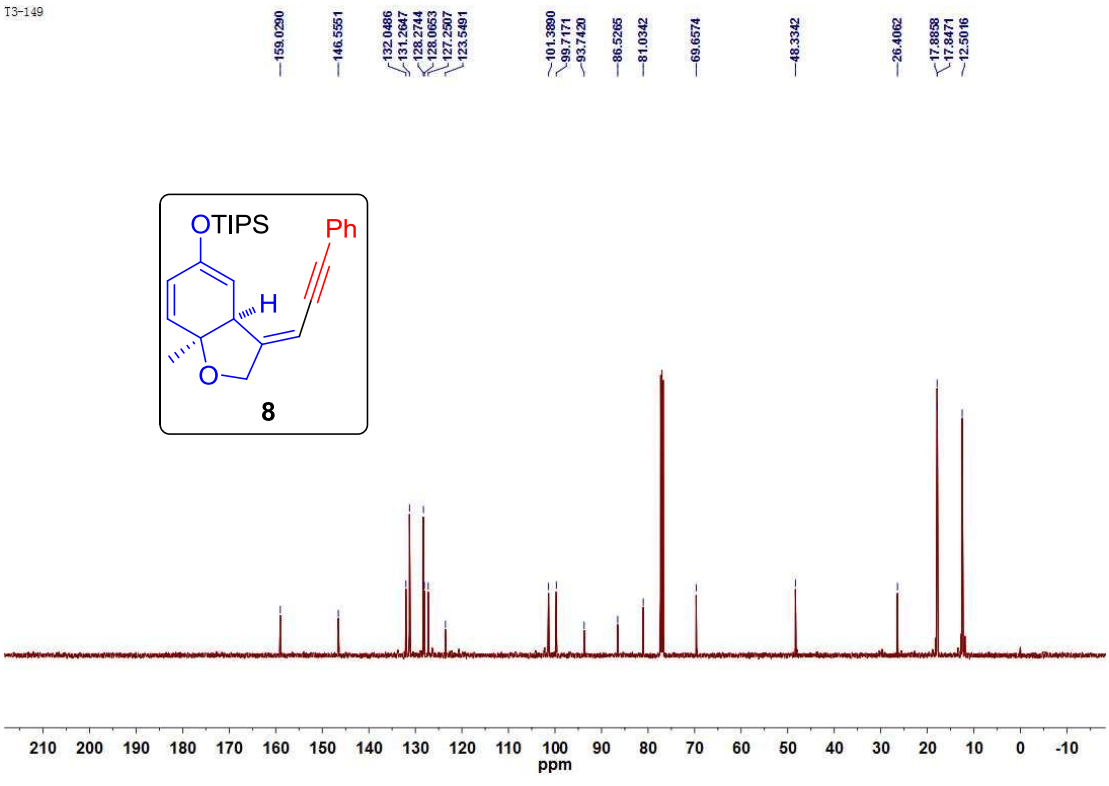


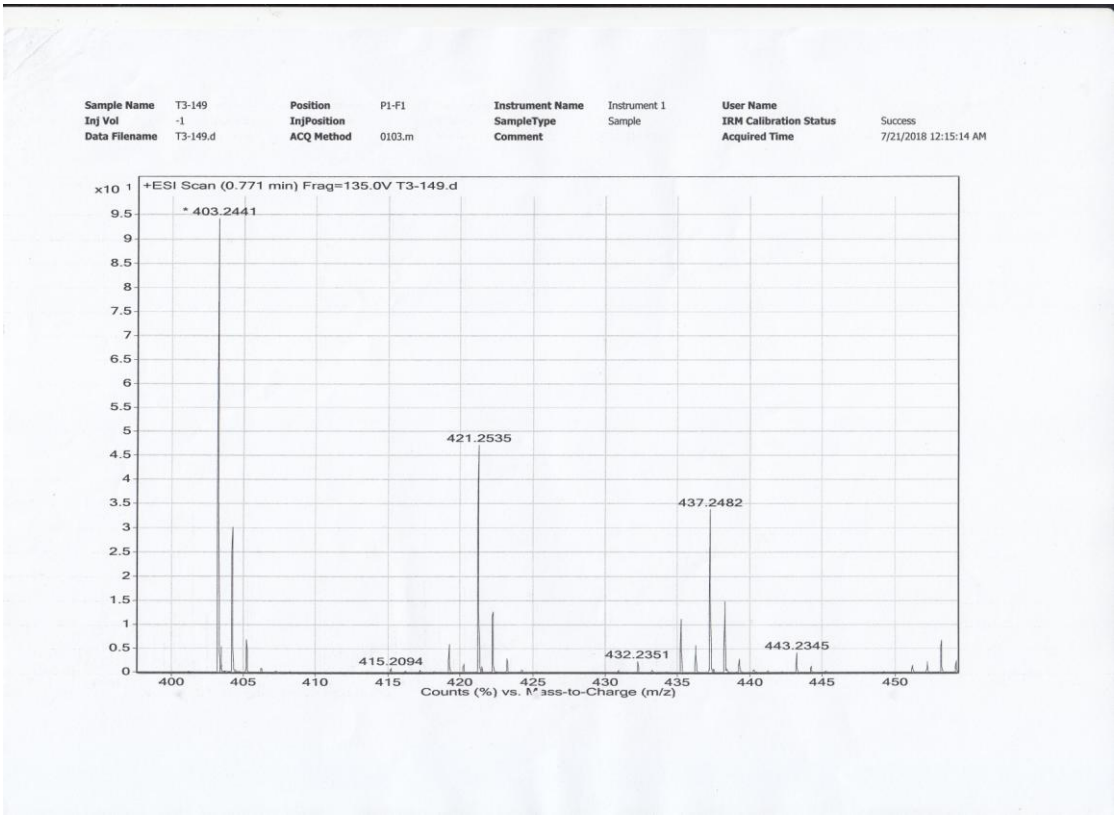
7

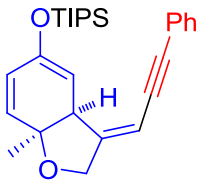
Chemical Formula: $C_{24}H_{29}BO_4$
Exact Mass: 392.2159
Molecular Weight: 392.2957
m/z: 392.2159 (100.0%), 393.2192 (26.0%), 391.2195 (24.8%), 392.2229 (6.4%), 394.2226 (3.2%)

HRMS (ESI, m/z) calcd for $C_{24}H_{29}BO_4$ $[M+H]^+$ 393.2232, found 393.2236.


T3-149
OTIPS
Ph
H
O
8
2.09
3.05
0.98
1.87
0.90
1.00
0.91
0.90
2.90
3.05
18.09
ppm


T3-149
OTIPS
Ph
H
O
8
ppm

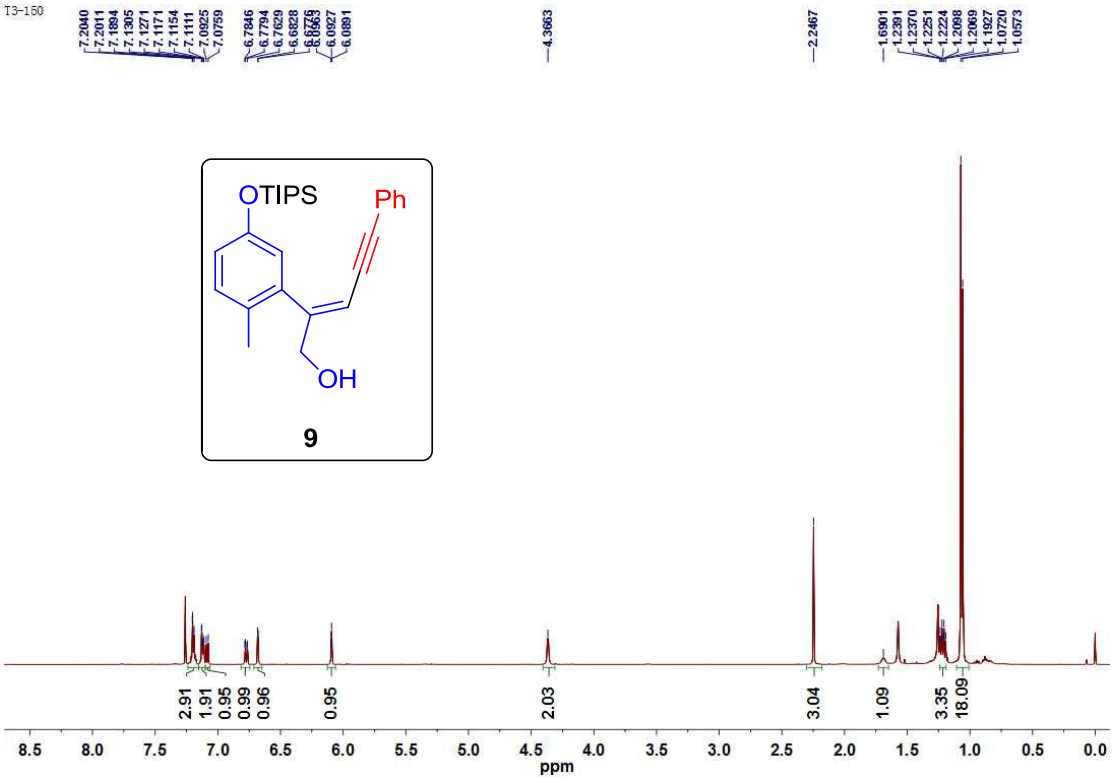


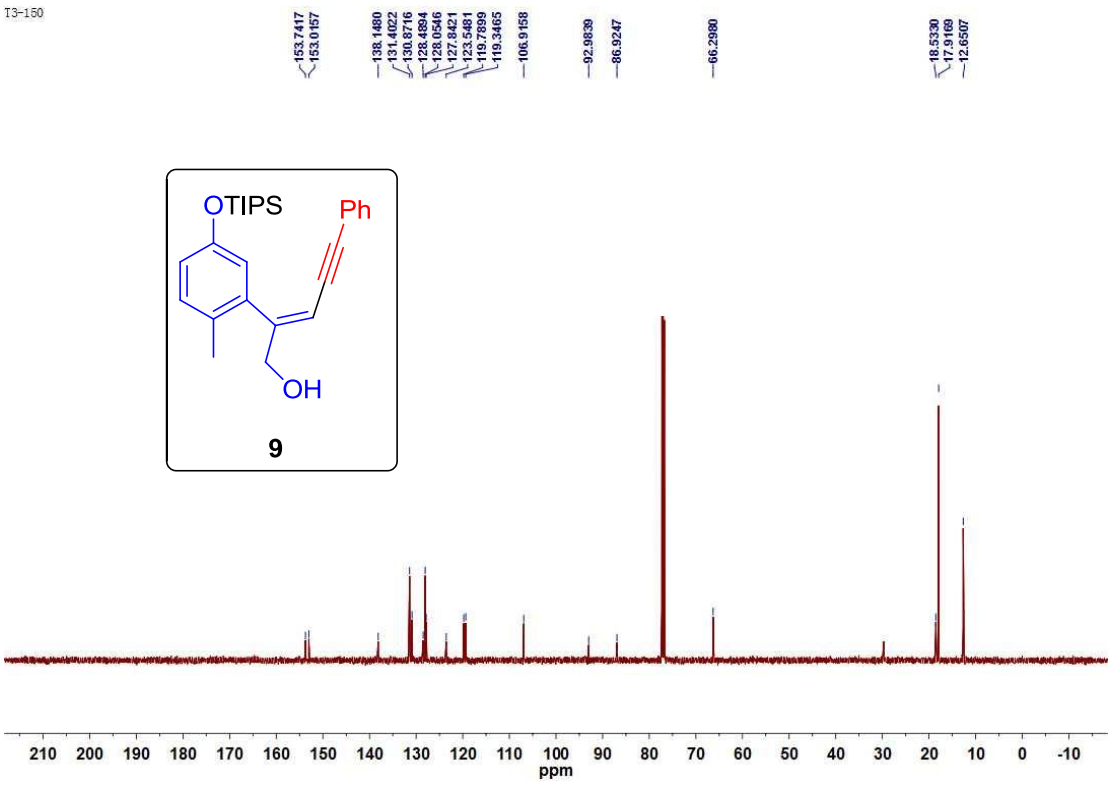


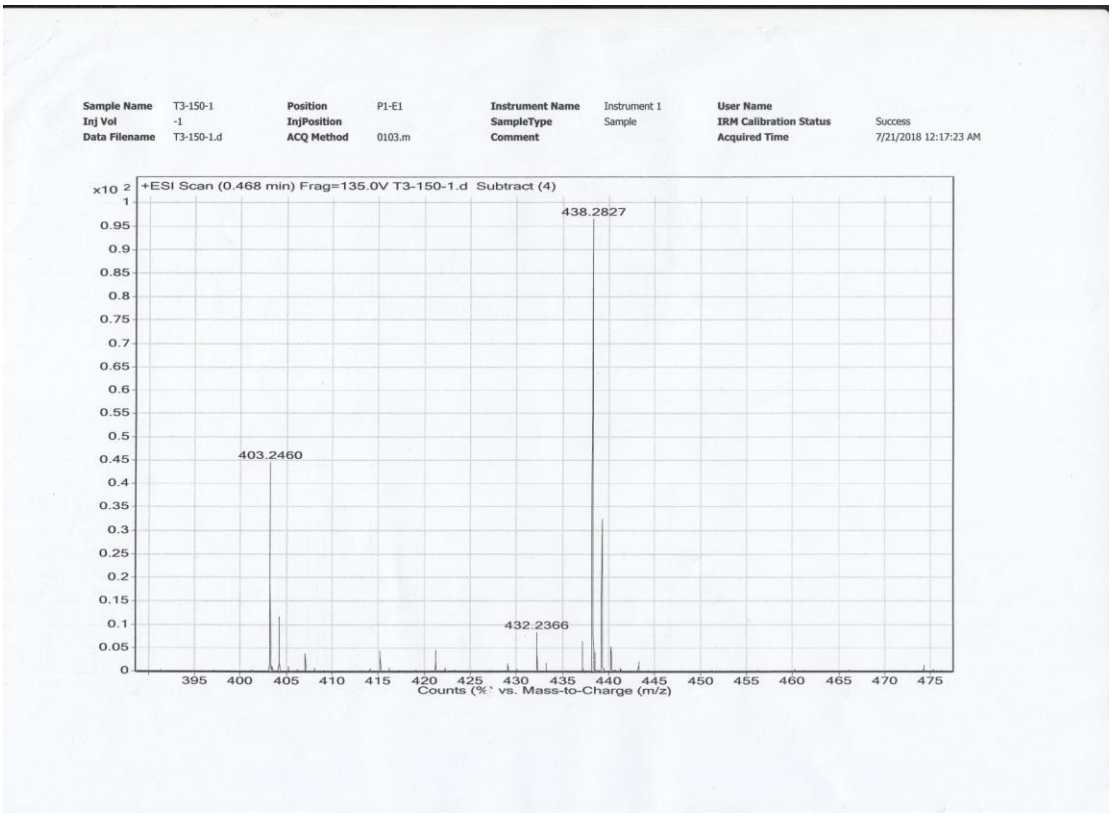
8

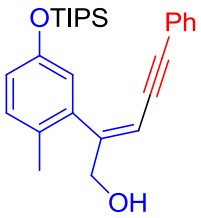
Chemical Formula: $C_{27}H_{36}O_2Si$
Exact Mass: 420.2485
Molecular Weight: 420.6590
m/z: 420.2485 (100.0%), 421.2518 (29.2%), 421.2480 (5.1%),
422.2552 (4.1%), 422.2453 (3.3%), 422.2514 (1.5%)

HRMS (ESI, m/z) calcd for $C_{27}H_{36}O_2Si$ $[M+H]^+$ 421.2557, found 421.2535.


T3-150
OTIPS
Ph
OH
9
ppm


T3-150
OTIPS
Ph
OH
9
ppm

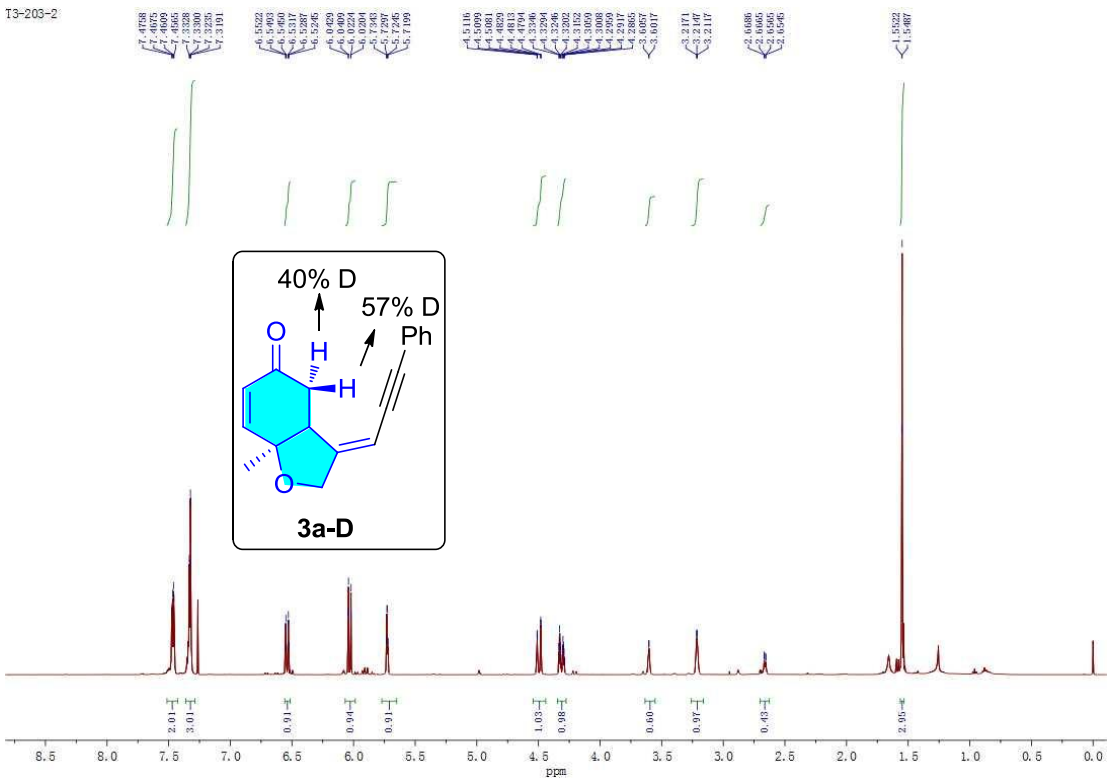


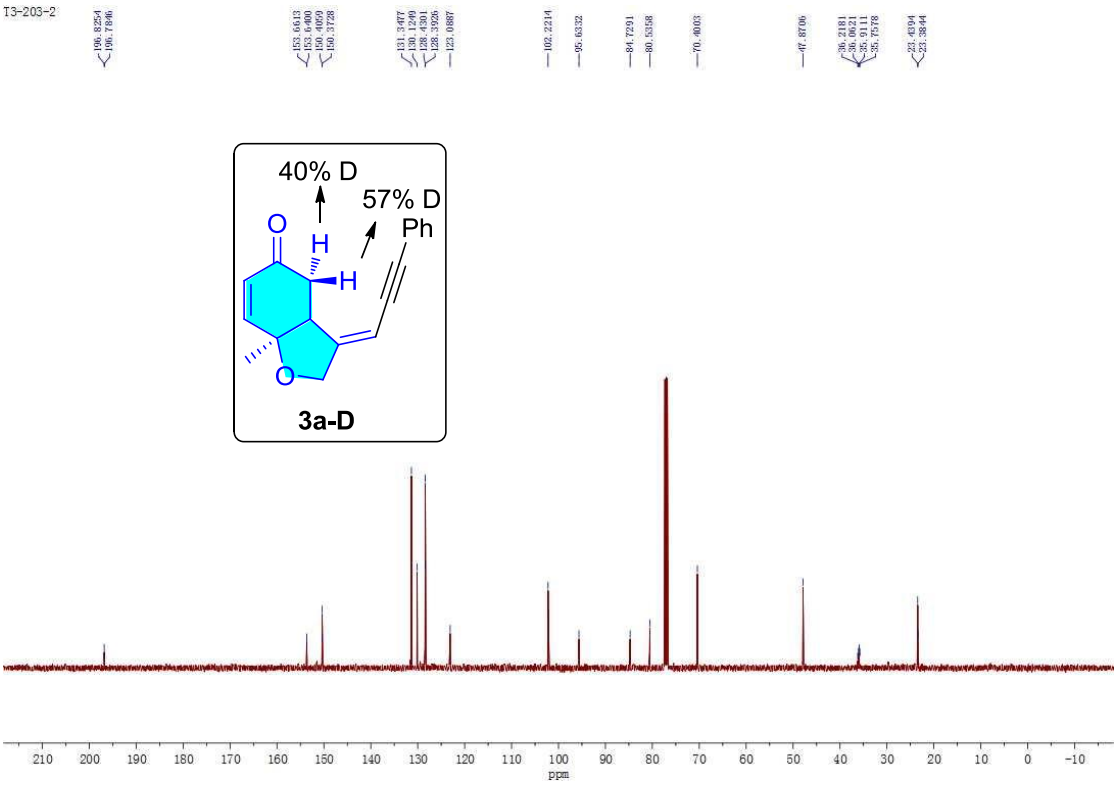


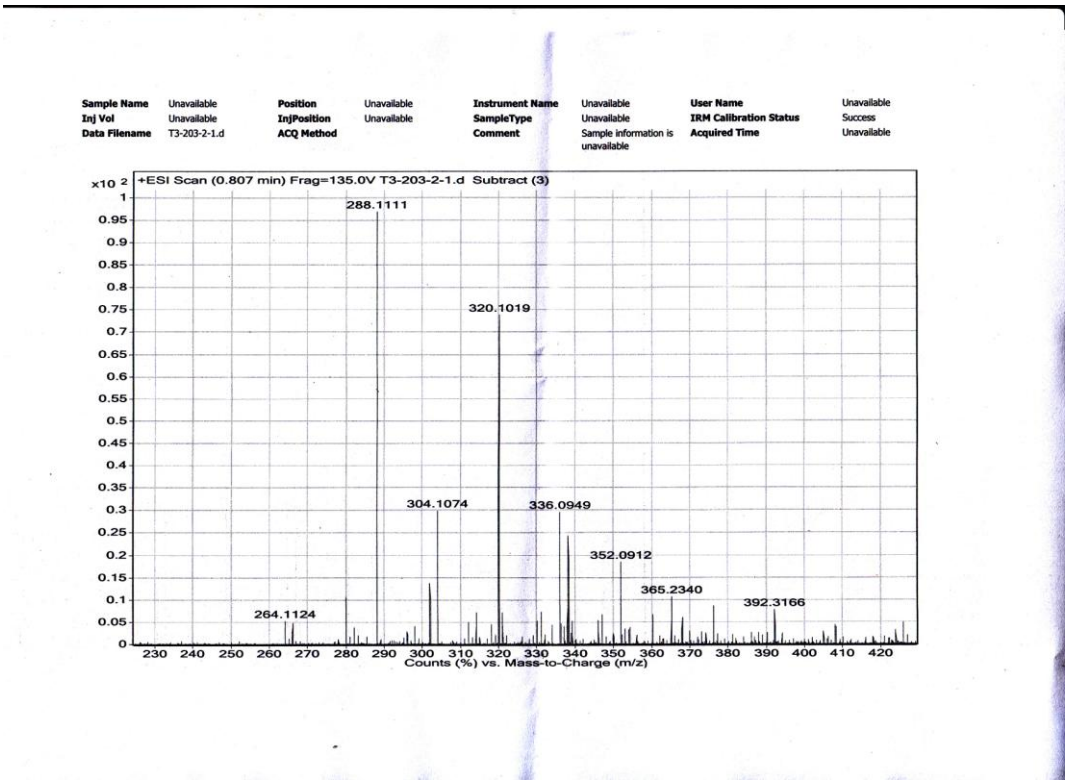
9

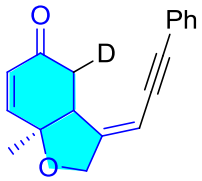
Chemical Formula: $C_{27}H_{36}O_2Si$
Exact Mass: 420.2485
Molecular Weight: 420.6590
m/z: 420.2485 (100.0%), 421.2518 (29.2%), 421.2480 (5.1%),
422.2552 (4.1%), 422.2453 (3.3%), 422.2514 (1.5%)

HRMS (ESI, m/z) calcd for $C_{27}H_{36}O_2Si$ $[M+NH_4]^+$ 438.2823, found 438.2827.


T3-203-2
40% D
57% D
Ph
O
H
H
O
3a-D
ppm


T3-203-2
40% D
57% D
Ph
O
H
H
O
3a-D
ppm





3a-D

Chemical Formula: $C_{18}H_{15}DO_2$
Exact Mass: 265.1213
Molecular Weight: 265.3246
m/z: 265.1213 (100.0%), 266.1247 (19.5%), 267.1280 (1.8%)

HRMS (ESI, m/z) calcd for $C_{18}H_{15}DO_2$ $[M+Na]^+$ 288.1105, found 288.1111.

9. References

[1] a) Y. Fukui, P. Liu, Q. Liu, Z.-T. He, N.-Y. Wu, P. Tian, G.-Q. Lin, *J. Am. Chem. Soc.* **2014**, *136*, 15607; b) Z.-T. He, B. Tian, Y. Fukui, X. Tong, P. Tian, G.-Q. Lin, *Angew. Chem., Int. Ed.* **2013**, *52*, 5314.

[2] a) K. K. Gollapelli, S. Donikela, N. Manjula, R. Chegondi, *ACS Catal.* **2018**, *8*, 1440; b) Q. Teng, J. Qi, L. Zhou, Z. Xu, C.-H. Tung, *Org. Chem. Front.*, **2014**, *5*, 990.

[3] R. Tello-Aburto, A. M. Harned, *Org. Lett.* **2009**, *11*, 3998.

[4] S. Mun, J.-E. Lee, J. Yun, *Org. Lett.* **2006**, *8*, 4887.

[5] K. C. Nicolaou, G. S. Tria, D. J. Edmonds, M. Kar, *J. Am. Chem. Soc.* **2009**, *131*, 15909.