Supporting Information

Phosphine Sequential Catalyzed Domino 1, 6-Addition/Annulation: Access to Functionalized Chromans and Tetrahydroquinolines with an Ethynyl-Substituted All-Carbon Quaternary Center

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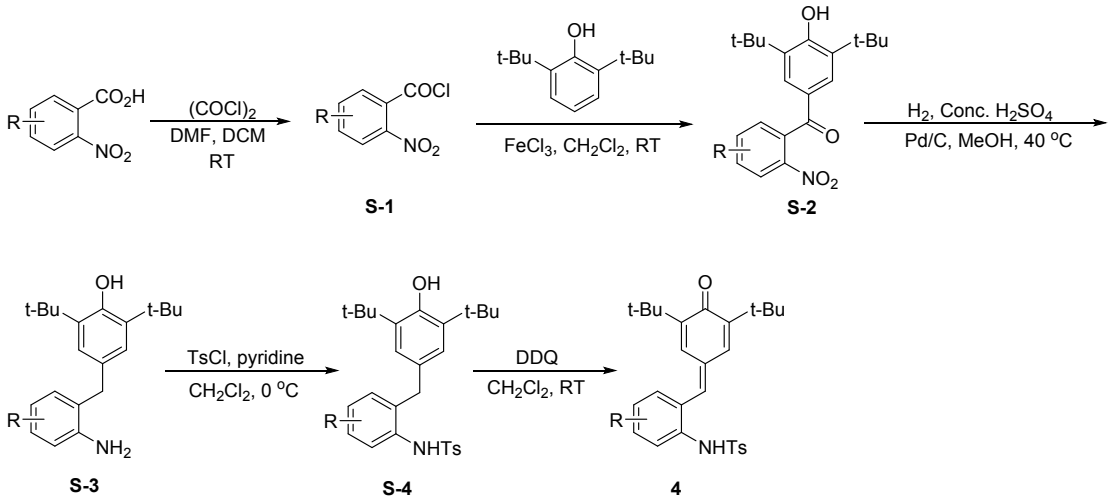
1. General information

All the solvents were used without further purification. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) were recorded on a Bruker AV 400 (400 MHz) spectrometer with $CDCl_3$ as solvent. Chemical shifts were recorded in parts per million (ppm) relative to tetramethylsilane as an internal reference. All shifts are reported in ppm as downfield from TMS as standard. Multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), m (multiplet). Coupling constants J are reported in Hz. HRMS were obtained on an VG ZAB-HS mass spectrometer with ESI resource. Melting points were measured on a RY-I apparatus and are reported uncorrected. IR spectra were recorded as KBr disks on a Nicolet 380 FT-IR spectrometer. Column chromatography was performed on silica gel 200-300 mesh. The *para*-quinone methides (*p*-QMs) **1a-1x, 7**[1] and allenoates **2a-2k**[2] were prepared according to the known methods.

2. General procedures

2.1. Preparation of the *para*-quinone methides (*p*-QMs) 4



The Synthesis of S-1: 2-nitrobenzoic acid (30 mmol) was dissolved in CH_2Cl_2 (100 mL) at room temperature, then $(COCl)_2$ (60 mmol) was added in one portion and stirred at room temperature for 12 h. The solvent was removed under reduced pressure, giving the crude product **S-1**, which was used for the next step without further purification.

The Synthesis of S-2: $FeCl_3$ (15 mmol) and 2, 6-di-tert-butylphenol (10 mmol) were added to the solution of **S-1** (10 mmol) in CH_2Cl_2 (50 mL), the mixture was stirred at room temperature for 20 min, then was quenched by NH_4Cl, the resulting residue was extracted with CH_2Cl_2, the organic phase was washed with brine, then dried over Na_2SO_4, filtered and concentrated. The crude product was purified by column chromatography on silica gel eluting with petroleum ether/EtOAc (5:1), giving the corresponding product **S-2**.

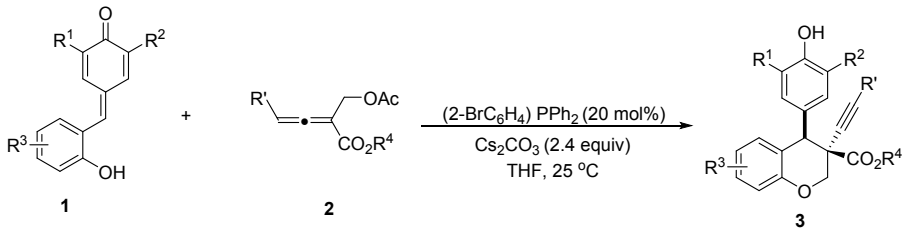
The Synthesis of S-3: After three vacuum/H_2 cycles to replace air in the reaction flask, the mixture of **S-2** (5 mmol), Pd/C (10% wt of the substrate), and concentrated sulfuric acid (543 μL, 10 mmol) in MeOH (20 mL) was vigorously stirred at room temperature and detected by TLC analysis. The reaction

mixture was filtered with celite, and the filtrate was concentrated and purified by column chromatography with petroleum ether/EtOAc (10:1) to provide **S-3**.

The Synthesis of S-4: To a solution of **S-3** (3 mmol) and pyridine (360 μL, 4.5 mmol) in CH_2Cl_2 (20 mL) was added TsCl (4.5 mmol) at 0 °C, and then the mixture was stirred for 24 h at room temperature. The reaction was diluted with CH_2Cl_2 and washed with 1N HCl and brine. The organic layer was dried over Na_2SO_4 , filtered and concentrated. The residue was chromatographed with petroleum ether/EtOAc (4:1) to give **S-4**.

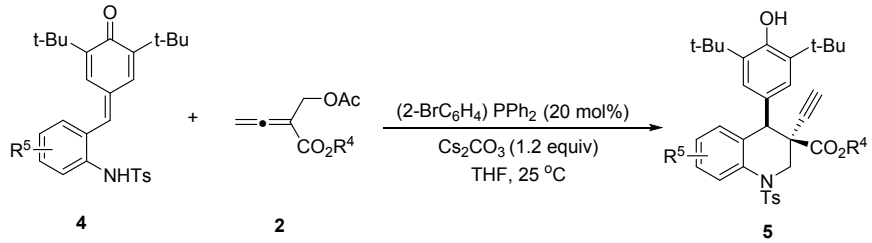
The Synthesis of 4: DDQ (680 mg, 3 mmol) was added to a solution of **S-4** (2.5 mmol) in CH_2Cl_2 (50 mL).The mixture was stirred at room temperature for 30 min and then directly purified by column chromatography with petroleum ether/EtOAc (3:1) to afford the crude product **4** which was recrystallized from CH_2Cl_2 and n-hexane (CH_2Cl_2: n-pentane = 10:90) afforded the analytically pure product as a yellow solid.

2.2 General procedure for the synthesis of 4-aryl-chroman derivatives 3



ortho-Hydroxyphenyl-substituted *para*-quinone methides **1** (0.1 mmol), $(2\text{-}BrC_6H_4)PPh_2$ (20 mol %) , Cs_2CO_3 (2.4 equiv) and THF (1.0 mL) were added to a dry flask at the temperature of 25 °C. Then α-substituted allenoates **2** (0.15 mmol) was added. This solution was stirred at 25 °C until the complete consumption of the starting materials monitored by TLC. After the removal of the solvent, the residue was purified by flash column chromatography (petroleum ether: EtOAc = 10:1) to afford product **3.**

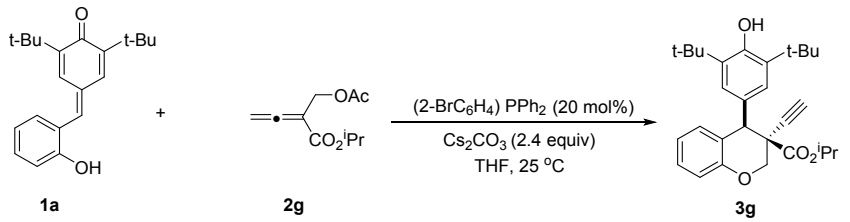
2.3 General procedure for the synthesis of 4-aryl-tetrahydroquinoline derivatives 5



ortho-Aminophenyl-substituted *para*-quinone methides **4** (0.1 mmol), $(2\text{-}BrC_6H_4)PPh_2$ (20 mol %) , Cs_2CO_3 (1.2 equiv) and THF (1.0 mL) were added to a dry flask at the temperature of 25 °C. Then α-substituted allenoates **2** (0.15 mmol) was added. This solution was stirred at 25 °C until the complete consumption of the starting materials monitored by TLC. After the removal of the solvent, the residue

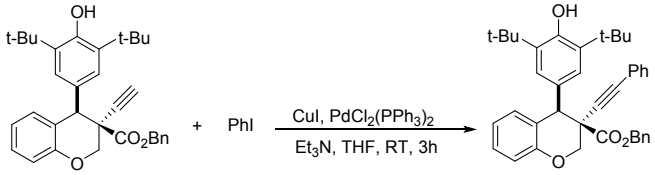
was purified by flash column chromatography (petroleum ether: EtOAc = 5:1) to afford product **5.**

2.4 Gram scale reaction and synthetic transformations of 3



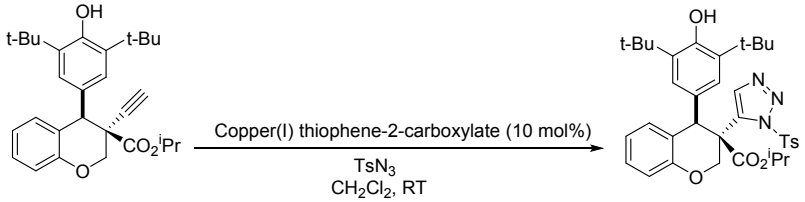
1a **2g** **3g**

A 50 mL flask equipped with a stirring bar was charged with *p*-QMs **1a** (0.775 g, 2.50 mmol, 1.0 equiv), α-substituted allenoates **2g** (0.923 g, 3.75 mmol, 1.5 equiv), $(2\text{-}BrC_6H_4)PPh_2$ (170 mg, 0.5 mmol, 20 mol %) and THF (25.0 mL). The resulting solution of the reaction mixture is stirred at room temperature for 30 min. The solvent was evaporated to give the crude product, which was directly purified by flash chromatography (petroleum ether: EtOAc = 10:1) to provide the desired product **3h** as a white solid (1.22 g, 85% yield, > 20:1 dr). The analytical data of the gram scale reaction of **3h** are consistent with those of the 0.1 mmol scale experiment.



3a **6a**

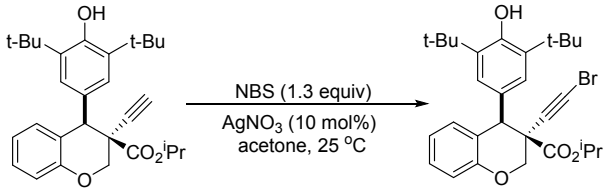
A mixture of **3a** (0.1 mmol), $PdCl_2(PPh_3)_2$ (5 mol %), PhI (0.2 mmol), CuI (5 mol %) and Et_3N (2.5 equiv.) in dry THF was stirred at room temperature for the desired time until complete consumption of starting material as monitored by TLC. After the mixture was washed with water, extracted with CH_2Cl_2, and evaporated, the residue was purified by column chromatography on silica gel (petroleum ether: EtOAc = 10:1) to afford coupled product **6a** (37 mg, 64% yield, > 20:1 dr).



3g **7g**

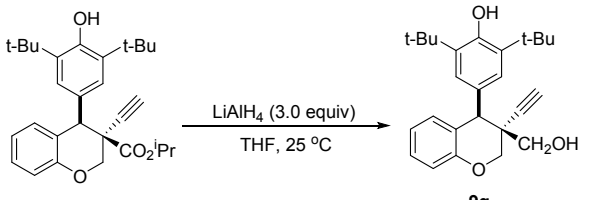
82% yield, >20:1 d.r.

To a stirred solution of **3g** (0.1 mmol, 1.0 equiv) in 1 mL CH_2Cl_2 was added copper(I)-thiophene-2-carboxylate (CuTc, 0.01mmol, 10 mol %). The solution was treated dropwise with a solution of 0.15 mmol TsN_3 in 1 mL CH_2Cl_2. Then, the reaction mixture was stirred a further 3 h, monitored by TLC. After reaction, it was diluted with 10 mL saturated NH_4Cl and extracted with CH_2Cl_2 (10 mL×3). The combined organics were washed with brine, dried with Na_2SO_4 and concentrated in vacuo. The crude product was then purified by flash chromatography (petroleum ether: EtOAc = 5:1) to afford coupled product **7g** (53 mg, 82% yield, > 20:1 dr).



3g **8g**

To a stirred solution of **3g** (0.1 mmol, 1.0 equiv) in 2 mL acetone was added silver nitrate (0.01mmol, 10 mol %). After stirring for 5 minutes, N-bromosuccinimide (0.13 mmol, 1.3 equiv) was added in one portion. The reaction mixture was stirred at room temperature, and monitored by TLC. Upon the complete consumption of **3g**, the reaction mixture was filtered over a celite pad and washed with acetone. The filtrate was concentrated in vacuum. The residue was purified by column chromatography on silica gel (petroleum ether: EtOAc = 5:1) to afford the corresponding product **8g** (37 mg, 71% yield, >20:1 dr) as a white solid.

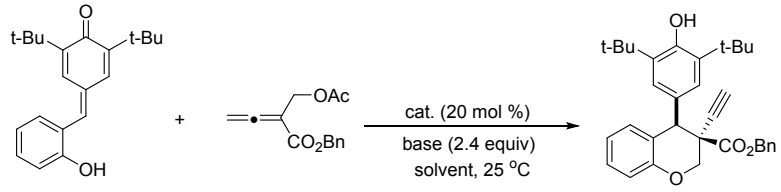


3g **9g**
76% yield, >20:1 d.r.

To a suspension of lithium aluminium tetrahydride (0.3 mmol) in THF (4 mL) was added **3g** (0.1 mmol) in one portion, mixture was stirred 15 min at 25 °C. NH_4Cl (aq) was added in small portions. Then, extracted with CH_2Cl_2, and dried with Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether: EtOAc = 5:1) to afford product **9g** (30 mg, 76% yield, > 20:1 dr).

3. Optimization of reaction conditions

Table S1. Optimization of the reaction conditions[a]



1a **2a** **3a**

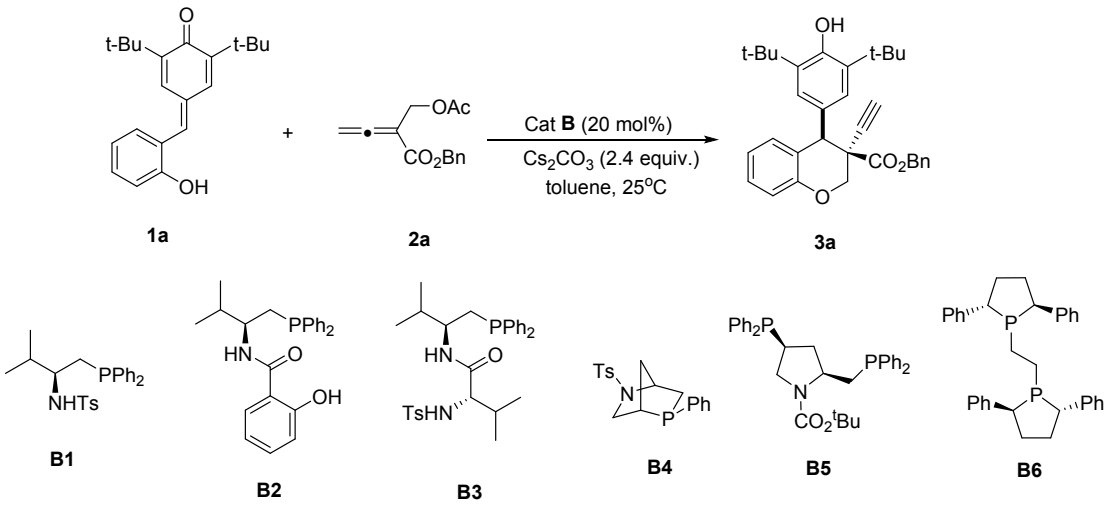
entry	cat.	base	solvent	yield (%)[c]	dr[d]
1[b]	PPh_3	Na_2CO_3	THF	trace	-
2	PPh_3	Na_2CO_3	THF	41	2:1
3	PPh_3	K_2CO_3	THF	35	2:1
4	PPh_3	Cs_2CO_3	THF	75	2:1
5	PPh_3	K_3PO_4	THF	47	2:1
6	PPh_3	NaOEt	THF	-	-
7	Ph_2PEt	Cs_2CO_3	THF	53	2:1

8	$PhPEt_2$	Cs_2CO_3	THF	52	2:1
9	PBu_3	Cs_2CO_3	THF	36	1:1
10	$P(4\text{-}OMeC_6H_4)_3$	Cs_2CO_3	THF	72	1:1
11	$P(4\text{-}FC_6H_4)_3$	Cs_2CO_3	THF	86	2:1
12	$(2\text{-}OMeC_6H_4)\ PPh_2$	Cs_2CO_3	THF	73	2:1
13	$(2\text{-}BrC_6H_4)\ PPh_2$	Cs_2CO_3	THF	96	2:1
14	$(2\text{-}BrC_6H_4)\ PPh_2$	Cs_2CO_3	THF	72	5:3
15	$(2\text{-}BrC_6H_4)\ PPh_2$	Cs_2CO_3	THF	76	2:1
16	$(2\text{-}BrC_6H_4)\ PPh_2$	Cs_2CO_3	THF	48	1:1
17	$(2\text{-}BrC_6H_4)\ PPh_2$	Cs_2CO_3	$CHCl_3$	72	2:1
18	$(2\text{-}BrC_6H_4)\ PPh_2$	Cs_2CO_3	Toluene	39	2:1
19	$(2\text{-}BrC_6H_4)\ PPh_2$	Cs_2CO_3	isopropanol	42	2:1
20	$(2\text{-}BrC_6H_4)\ PPh_2$	Cs_2CO_3	acetone	94	1:1

[a] Unless otherwise specified, all reactions were carried out with: **1a** (0.1 mmol), **2a** (0.15 mmol), catalyst (20 mol %), base (0.24 mmol) and 1.0 mL indicated solvent at 25 °C for 1 h. [b] 1.2 equiv. Na_2CO_3 was used. [c] Isolated yield. [d] Determined by ^1H NMR analysis.

4. Primary asymmetric study

Table S2. Primary asymmetric study [a]



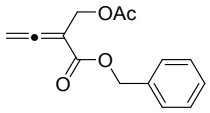
entry	cat. (20 mol %)	time (h)	yield (%)[b]	dr[c]	ee (%)[d]
1	**B1**	1.5	29	2:1	<5
2	**B2**	1	54	2:1	<5
3	**B3**	6.5	49	2:1	14
4	**B4**	2	54	2:1	<5
5	**B5**	1	23	2:1	<5
6	**B6**	1	47	2:1	<5

[a] reactions were carried out with: **1a** (0.1 mmol), **2a** (0.15 mmol), catalyst **B** (20 mol%), Cs_2CO_3 (0.24

mmol) and 1.0 mL toluene at 25 °C. [b] Isolated yield. [c] Determined by ^{1}H NMR analysis. [d] Determined by HPLC.

5. Spectral Data

benzyl 2-(acetoxymethyl)buta-2,3-dienoate **(2a)**



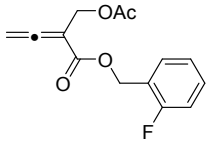
Colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.24 (m, 5H), 5.31 (q, *J* = 2.0 Hz, 2H), 5.22 (d, *J* = 1.4 Hz, 2H), 4.81 (q, *J* = 2.0 Hz, 2H), 2.05 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 214.86, 170.53, 165.16, 135.73, 128.54, 128.24, 127.99, 96.81, 80.61, 66.84, 60.91, 20.89.

HRMS (ESI): m/z calcd for $C_{14}H_{18}NO_4$ ($[M+NH_4]^+$): 264.1230; found: 264.1228.

2-fluorobenzyl 2-(acetoxymethyl)buta-2,3-dienoate (**2b**)



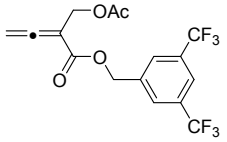
White solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (td, *J* = 7.5, 1.8 Hz, 1H), 7.32 (tdd, *J* = 7.5, 5.2, 1.8 Hz, 1H), 7.14 (td, *J* = 7.6, 1.2 Hz, 1H), 7.07 (ddd, *J* = 9.7, 8.3, 1.1 Hz, 1H), 5.31 (t, *J* = 2.2 Hz, 2H), 5.28 (d, *J* = 1.1 Hz, 2H), 4.80 (t, *J* = 2.2 Hz, 2H), 2.06 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 214.89, 170.51, 165.03, 162.08, 159.61, 131.27 – 129.43 (m), 124.14 (d, *J* = 4.0 Hz), 122.91 (d, *J* = 14.5 Hz), 115.44 (d, *J* = 20.9 Hz), 96.69, 80.65, 60.87, 60.83, 20.86.

HRMS (ESI): m/z calcd for $C_{14}H_{17}FNO_4$ ($[M+NH_4]^+$): 282.1136; found: 282.1139.

3,5-bis(trifluoromethyl)benzyl 2-(acetoxymethyl)buta-2,3-dienoate (**2c**)



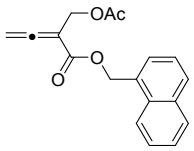
White solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.82 (s, 1H), 5.38 (t, *J* = 2.1 Hz, 2H), 5.32 (s, 2H), 4.82 (t, *J* = 2.1 Hz, 2H), 2.07 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 215.24, 170.49, 164.82, 138.36, 131.96 (q, *J* = 33.5 Hz), 127.70, 122.23 – 122.07 (m), 96.43, 80.78, 64.96, 60.76, 20.80.

HRMS (ESI): m/z calcd for $C_{16}H_{16}F_6NO_4$ ($[M+NH_4]^+$): 400.0978; found: 400.0981.

naphthalen-1-ylmethyl 2-(acetoxymethyl)buta-2,3-dienoate (**2d**)



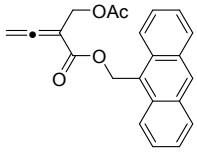
White solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.90 – 7.86 (m, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.61 – 7.48 (m, 3H), 7.44 (dd, *J* = 8.2, 7.0 Hz, 1H), 5.67 (s, 2H), 5.26 (t, *J* = 2.2 Hz, 2H), 4.79 (t, *J* = 2.2 Hz, 2H), 2.00 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 214.97, 170.49, 165.18, 133.70, 131.56, 131.23, 129.29, 128.70, 127.24, 126.52, 125.95, 125.28, 123.59, 96.89, 80.58, 65.29, 60.92, 20.83.

HRMS (ESI): m/z calcd for $C_{18}H_{20}NO_4$ ($[M+NH_4]^+$): 314.1387; found: 314.1390.

anthracen-9-ylmethyl 2-(acetoxymethyl)buta-2,3-dienoate (**2e**)



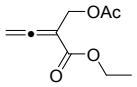
White solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 8.35 (dd, *J* = 8.9, 1.1 Hz, 2H), 8.00 (d, *J* = 8.6 Hz, 2H), 7.55 (ddd, *J* = 8.9, 6.5, 1.4 Hz, 2H), 7.47 (ddd, *J* = 7.8, 6.5, 1.1 Hz, 2H), 6.23 (s, 2H), 5.15 (t, *J* = 2.2 Hz, 2H), 4.75 (t, *J* = 2.2 Hz, 2H), 1.94 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 214.92, 170.47, 165.49, 131.35, 131.11, 129.30, 129.06, 126.62, 125.99, 125.11, 124.08, 96.85, 80.58, 60.94, 59.75, 20.79.

HRMS (ESI): m/z calcd for $C_{14}H_{18}NO_4$ ($[M+NH_4]^+$): 264.1230; found: 264.1227.

ethyl 2-(acetoxymethyl)buta-2,3-dienoate (**2f**)



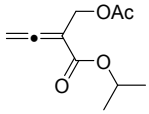
Colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.29 (t, *J* = 2.3 Hz, 2H), 4.78 (t, *J* = 2.2 Hz, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.07 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 214.56, 170.54, 165.29, 96.92, 80.41, 61.34, 60.91, 20.88, 14.18.

HRMS (ESI): m/z calcd for $C_9H_{16}NO_4$ ($[M+NH_4]^+$): 202.1074; found: 202.1077.

isopropyl 2-(acetoxymethyl)buta-2,3-dienoate (**2g**)



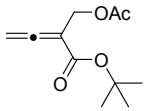
Colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.29 (t, *J* = 2.4 Hz, 2H), 5.16 – 4.98 (m, 1H), 4.78 (d, *J* = 2.4 Hz, 2H), 2.07 (d, *J* = 2.2 Hz, 3H), 1.27 (d, *J* = 2.1 Hz, 3H), 1.26 (d, *J* = 2.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 214.39, 170.47, 164.75, 97.27, 80.31, 68.81, 60.89, 21.74, 20.85.

HRMS (ESI): m/z calcd for $C_{10}H_{18}NO_4$ ($[M+NH_4]^+$): 216.1230; found: 216.1229.

tert-butyl 2-(acetoxymethyl)buta-2,3-dienoate (**2h**)



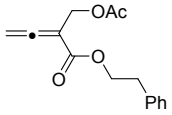
Colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.23 (t, *J* = 2.3 Hz, 2H), 4.74 (t, *J* = 2.3 Hz, 2H), 2.06 (s, 3H), 1.47 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 214.28, 170.51, 164.38, 98.21, 81.63, 79.99, 60.92, 28.01, 20.90.

HRMS (ESI): m/z calcd for $C_{11}H_{20}NO_4$ ($[M+NH_4]^+$): 230.1387; found: 230.1393.

phenethyl 2-(acetoxymethyl)buta-2,3-dienoate (**2i**)



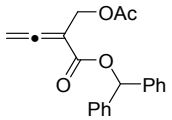
White solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 2H), 7.25 – 7.19 (m, 3H), 5.29 (t, *J* = 2.2 Hz, 2H), 4.77 (t, *J* = 2.2 Hz, 2H), 4.37 (t, *J* = 7.0 Hz, 2H), 2.97 (t, *J* = 7.0 Hz, 2H), 2.05 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 214.84, 170.53, 165.22, 137.67, 129.04, 128.46, 126.60, 96.83, 80.42, 65.84, 60.87, 35.09, 20.91.

HRMS (ESI): m/z calcd for $C_{15}H_{20}NO_4$ ($[M+NH_4]^+$): 278.1387; found: 278.1391.

benzhydryl 2-(acetoxymethyl)buta-2,3-dienoate (**2j**)



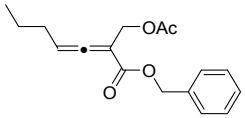
White solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.38 (m, 5H), 7.38 – 7.35 (m, 2H), 7.35 – 7.27 (m, 3H), 6.99 (s, 1H), 5.41 (t, *J* = 2.1 Hz, 2H), 4.87 (t, *J* = 2.1 Hz, 2H), 2.08 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 215.15, 170.57, 164.34, 140.10, 128.55, 127.99, 127.00, 97.04, 80.60, 77.56, 60.92, 20.90.

HRMS (ESI): m/z calcd for $C_{20}H_{19}O_4$ ($[M+H]^+$): 323.1278; found: 323.1279.

benzyl 2-(acetoxymethyl)hepta-2,3-dienoate (**2k**)



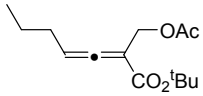
Colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.29 (m, 5H), 5.69 (tt, *J* = 7.1, 2.0 Hz, 1H), 5.33 – 5.14 (m, 2H), 4.79 (d, *J* = 2.0 Hz, 2H), 2.12 (q, *J* = 7.2 Hz, 2H), 2.04 (s, 3H), 1.54 – 1.41 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 211.28, 170.59, 165.67, 135.94, 128.27, 128.12, 127.92, 96.76, 96.55, 66.62, 61.48, 29.63, 22.00, 20.94, 13.51.

HRMS (ESI): m/z calcd for $C_{17}H_{24}NO_4$ ($[M+NH_4]^+$): 306.1700; found: 306.1709.

tert-butyl 2-(acetoxymethyl)hepta-2,3-dienoate (**2l**)



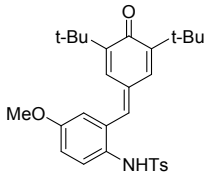
Colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.62 (tt, J = 7.2, 2.1 Hz, 1H), 4.73 (dd, J = 2.1, 0.8 Hz, 2H), 2.11 (q, J = 7.2 Hz, 2H), 2.06 (s, 3H), 1.52 – 1.49 (m, 2H), 1.47 (s, 9H), 0.96 (t, J = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 210.57, 170.57, 164.96, 98.15, 95.89, 81.21, 61.48, 29.66, 28.07, 20.96, 13.50.

HRMS (ESI): m/z calcd for $C_{14}H_{26}NO_4$ ($[M+NH_4]^+$): 272.1856; found: 272.1858.

N-(2-((3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (**4a**)



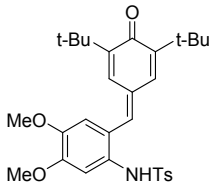
Yellow solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.8 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 2.4 Hz, 1H), 6.91 (dd, *J* = 8.8, 2.9 Hz, 1H), 6.76 (d, *J* = 2.9 Hz, 1H), 6.72 (d, *J* = 2.4 Hz, 1H), 6.68 (s, 1H), 6.62 (s, 1H), 3.80 (s, 3H), 2.30 (s, 3H), 1.31 (s, 9H), 1.26 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 186.42, 158.16, 149.37, 147.86, 144.05, 137.03, 136.19, 134.72, 133.30, 133.19, 129.73, 129.60, 127.47, 127.35, 127.33, 116.04, 116.02, 55.57, 35.43, 35.00, 29.60, 29.50, 21.64.

HRMS (ESI): m/z calcd for $C_{29}H_{39}N_2O_4S$ ($[M+NH_4]^+$): 511.2625; found: 511.2627.

N-(2-((3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl)-4,5-dimethoxyphenyl)-4-methylbenzenesulfonamide (**4b**)



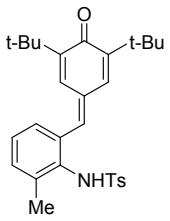
Yellow solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.3 Hz, 2H), 7.16 (dd, *J* = 5.4, 2.9 Hz, 3H), 7.01 (s, 1H), 6.75 (s, 1H), 6.70 (dd, *J* = 7.3, 2.7 Hz, 2H), 6.60 (s, 1H), 3.90 (s, 3H), 3.85 (s, 3H), 2.29 (s, 3H), 1.30 (s, 9H), 1.27 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 186.24, 150.36, 149.10, 147.66, 147.44, 144.21, 136.88, 135.87, 134.87, 133.74, 131.94, 130.02, 129.76, 128.58, 127.44, 127.35, 124.12, 113.23, 111.24, 56.20, 56.00, 35.43, 34.96, 29.66, 29.50, 29.02, 21.62.

HRMS (ESI): m/z calcd for $C_{30}H_{41}N_2O_5S$ ($[M+NH_4]^+$): 541.2731; found: 541.2732.

N-(2-((3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl)-6-methylphenyl)-4-methylbenzene sulfonamide (**4c**)



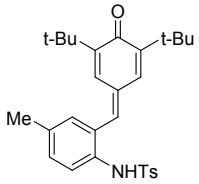
Yellow solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.39 – 7.26 (m, 2H), 7.14 (dd, *J* = 8.8, 4.7 Hz, 4H), 6.72 (s, 1H), 6.57 (d, *J* = 2.4 Hz, 1H), 6.44 (d, *J* = 5.8 Hz, 1H), 2.44 (s, 3H), 2.28 (s, 3H), 1.32 (s, 9H), 1.29 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 186.50, 148.79, 147.06, 144.05, 139.72, 139.09, 136.83, 135.14, 135.10, 133.27, 132.43, 132.04, 130.03, 129.84, 127.99, 127.90, 127.40, 68.18, 35.37, 34.92, 29.59, 29.57, 21.70, 19.14.

HRMS (ESI): m/z calcd for $C_{29}H_{39}N_2O_3S$ ($[M+NH_4]^+$): 495.2676; found: 495.2676.

N-(2-((3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl)-4-methylphenyl)-4-methylbenzene sulfonamide **(4d**)



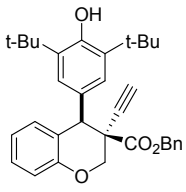
Yellow solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.59 (m, 2H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.21 – 7.14 (m, 3H), 7.09 (d, *J* = 2.3 Hz, 1H), 7.05 (d, *J* = 2.0 Hz, 1H), 6.77 (d, *J* = 2.4 Hz, 1H), 6.73 (s, 2H), 2.34 (s, 3H), 2.31 (s, 3H), 1.31 (s, 9H), 1.25 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 186.42, 149.22, 147.88, 144.10, 136.87, 136.38, 136.27, 134.56, 133.34, 132.34, 132.24, 130.84, 130.62, 129.76, 127.60, 127.28, 126.18, 35.39, 35.01, 29.50, 21.63, 20.97.

HRMS (ESI): m/z calcd for $C_{29}H_{39}N_2O_3S$ ($[M+NH_4]^+$): 495.2676; found: 495.2677.

benzyl 4-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-ethynylchromane-3-carboxylate (**3a**)



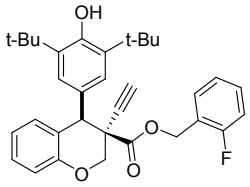
White solid, 48 mg, 96% yield

mp: 123-125 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ (major) 7.28 (d, *J* = 1.4 Hz, 1H), 7.27 (d, *J* = 2.3 Hz, 2H), 7.18 (ddd, *J* = 8.5, 7.2, 1.8 Hz, 1H), 7.07 (dd, *J* = 7.0, 2.6 Hz, 1H), 7.02 (d, *J* = 3.2 Hz, 2H), 6.98 (d, *J* = 1.1 Hz, 2H), 6.88 (s, 2H), 5.17 (s, 1H), 4.91 (d, *J* = 12.6 Hz, 1H), 4.84 (d, *J* = 12.5 Hz, 1H), 4.63 (s, 1H), 4.40 (d, *J* = 11.2 Hz, 1H), 4.27 (d, *J* = 11.1 Hz, 1H), 2.29 (s, 1H), 1.33 (s, 18H).

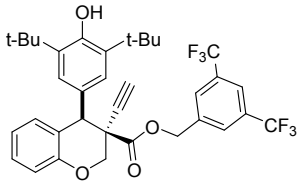
^{13}C NMR (101 MHz, $CDCl_3$) δ (major) 168.62, 153.26, 153.20, 135.41, 134.71, 131.08, 130.36, 128.53, 128.28, 127.52, 126.73, 122.01, 121.07, 116.37, 81.82, 72.75, 67.27, 64.28, 50.51, 46.21, 34.29, 30.30.
IR (KBr, cm^{-1}): 3629, 3284, 2958, 2360, 1739, 1488, 1455, 1436, 1236, 1120, 1024, 754, 737, 697, 653.
HRMS (ESI): m/z calcd for $C_{33}H_{40}NO_4$ ($[M+NH_4]^+$): 514.2952; found: 514.2952.

2-fluorobenzyl 4-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-ethynylchromane-3-carboxylate (**3b**)



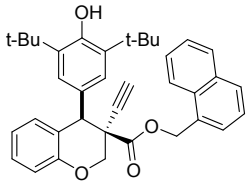
White solid, 45 mg, 87% yield
mp: 117-119 ℃
^{1}H NMR (400 MHz, $CDCl_3$) δ (major) 7.29 – 7.22 (m, 1H), 7.17 (ddd, *J* = 8.6, 7.2, 1.7 Hz, 1H), 7.07 – 6.96 (m, 5H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.87 (s, 2H), 5.19 (s, 1H), 5.01 (d, *J* = 13.0 Hz, 1H), 4.91 (d, *J* = 13.0 Hz, 1H), 4.62 (s, 1H), 4.41 (d, *J* = 11.2 Hz, 1H), 4.28 (dd, *J* = 10.9, 3.2 Hz, 1H), 2.29 (s, 1H), 1.33 (s, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ (major) 168.44, 161.61, 159.17, 153.17, 135.42, 131.09, 130.35, 130.10 (d, *J* = 8.1 Hz), 129.84, 129.45 (t, *J* = 4.0 Hz), 128.28, 126.67, 124.21 (t, *J* = 4.1 Hz), 122.68, 122.10 (d, *J* = 14.2 Hz), 121.99, 121.09, 116.37, 115.37 (d, *J* = 20.9 Hz), 81.70, 72.81, 64.30, 61.01 (d, *J* = 4.9 Hz), 50.49, 46.18, 34.28, 30.27.
IR (KBr, cm^{-1}): 3630, 3284, 2959, 1741, 1586, 1489, 1456, 1435, 1234, 1229, 1155, 1037, 757, 653.
HRMS (ESI): m/z calcd for $C_{33}H_{39}FNO_4$ ($[M+NH_4]^+$): 532.2858; found: 532.2861.

3,5-bis(trifluoromethyl)benzyl 4-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-ethynylchromane-3-carboxylate **(3c)**



White solid, 61 mg, 96% yield
mp: 112-114 ℃
^{1}H NMR (400 MHz, $CDCl_3$) δ (major) 7.84 (s, 1H), 7.75 (s, 2H), 7.20 (t, *J* = 7.8 Hz, 1H), 7.03 – 6.97 (m, 2H), 6.92 – 6.80 (m, 3H), 5.16 (s, 1H), 5.13 (d, *J* = 8.2 Hz, 1H), 4.99 (d, *J* = 13.4 Hz, 1H), 4.62 (s, 1H), 4.41 (d, *J* = 11.2 Hz, 1H), 4.30 (d, *J* = 11.2 Hz, 1H), 2.36 (s, 1H), 1.33 (s, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ (major) 167.98, 153.18 (d, *J* = 19.8 Hz), 137.79, 135.44, 132.06 (q, *J* = 33.5 Hz), 130.84 (d, *J* = 22.5 Hz), 128.36, 127.22, 126.51, 124.42, 122.24 (d, *J* = 4.2 Hz), 121.72 (d, *J* = 3.3 Hz), 121.20, 116.42, 81.36, 73.14, 65.01, 64.60, 50.31, 45.98, 34.24, 30.25.
IR (KBr, cm^{-1}): 3641, 3309, 2961, 1747, 1586, 1436, 1361, 1280, 1229, 1179, 1139, 1040, 888, 755, 682.
HRMS (ESI): m/z calcd for $C_{35}H_{38}F_6NO_4$ ($[M+NH_4]^+$): 650.2700; found: 650.2703.

naphthalen-1-ylmethyl 4-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-ethynylchromane-3-carboxylate **(3d)**



White solid, 52 mg, 95% yield

mp: 147-150 ℃

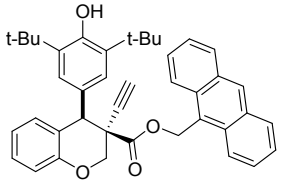
^{1}H NMR (400 MHz, $CDCl_3$) δ (major) 7.85 (dd, *J* = 6.5, 3.2 Hz, 1H), 7.81 (d, *J* = 8.5 Hz, 1H), 7.73 (dd, *J* = 6.4, 3.4 Hz, 1H), 7.48 (dd, *J* = 6.4, 3.2 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 7.0 Hz, 1H), 7.22 – 7.14 (m, 1H), 7.04 – 6.96 (m, 2H), 6.90 (s, 2H), 6.85 (d, *J* = 7.6 Hz, 1H), 5.41 (d, *J* = 12.8 Hz, 1H), 5.29 (d, *J* = 12.8 Hz, 1H), 5.18 (s, 1H), 4.65 (s, 1H), 4.39 (d, *J* = 11.2 Hz, 1H), 4.26 (dd, *J* = 11.4, 1.7 Hz, 1H), 2.27 (s, 1H), 1.33 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (major) 168.62, 153.24, 153.18, 135.39, 133.57, 131.21, 131.05, 130.31, 129.28, 128.69, 128.25, 126.79, 126.63, 126.56, 125.96, 125.21, 123.23, 122.06, 121.04, 116.33, 81.83, 72.80, 65.63, 64.36, 50.41, 46.24, 34.30, 30.33.

IR (KBr, cm^{-1}): 3629, 3285, 2957, 1734, 1488, 1456, 1435, 1361, 1237, 1158, 1122, 1016, 890, 755, 734, 650.

HRMS (ESI): m/z calcd for $C_{37}H_{42}NO_4$ ($[M+NH_4]^+$): 564.3108; found: 564.3112.

anthracen-9-ylmethyl 4-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-ethynylchromane-3-carboxylate **(3e)**



White solid, 51 mg, 87% yield

mp: 202-204 ℃

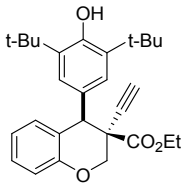
^{1}H NMR (400 MHz, $CDCl_3$) δ (major) 8.46 (s, 1H), 8.13 (d, *J* = 8.6 Hz, 1H), 7.96 (d, *J* = 9.6 Hz, 3H), 7.49 – 7.40 (m, 3H), 7.15 (t, *J* = 7.9 Hz, 1H), 7.01 (d, *J* = 7.8 Hz, 1H), 6.95 (s, 2H), 6.91 (d, *J* = 8.3 Hz, 1H), 6.84 (q, *J* = 8.9, 8.4 Hz, 2H), 6.18 (s, 1H), 5.55 (d, *J* = 12.5 Hz, 1H), 5.29 (s, 1H), 4.68 (s, 1H), 4.27 (d, *J* = 11.3 Hz, 1H), 4.09 (d, *J* = 11.8 Hz, 1H), 2.19 (s, 1H), 1.39 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (major) 169.08, 153.29, 135.36, 131.23, 131.04, 129.47, 129.07, 128.25, 127.12, 126.88, 125.09, 123.68, 122.12, 120.98, 116.28, 81.84, 72.74, 64.16, 60.31, 50.49, 46.46, 34.41, 30.44.

IR (KBr, cm^{-1}): 3629, 3285, 2957, 1734, 1488, 1456, 1435, 1361, 1237, 1158, 1122, 1016, 890, 755, 734, 650.

HRMS (ESI): m/z calcd for $C_{41}H_{44}NO_4$ ($[M+NH_4]^+$): 614.3265; found: 614.3267.

ethyl 4-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-ethynylchromane-3-carboxylate **(3f)**



White solid, 40 mg, 92% yield

mp: 130-132 ℃

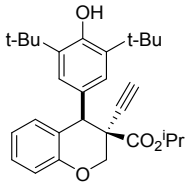
^{1}H NMR (400 MHz, $CDCl_3$) δ (major) 7.41 (ddd, *J* = 8.7, 7.1, 1.7 Hz, 1H), 7.23 (d, *J* = 4.4 Hz, 2H), 7.18 – 7.13 (m, 1H), 7.08 (s, 2H), 5.38 (s, 1H), 4.79 (s, 1H), 4.64 (d, *J* = 11.2 Hz, 1H), 4.56 – 4.45 (m, 1H), 4.27 – 4.18 (m, 1H), 4.15 – 4.07 (m, 1H), 2.52 (s, 1H), 1.59 (s, 18H), 1.28 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (major) 168.58, 153.13, 135.26, 131.13, 130.32, 128.18, 126.57, 122.12, 121.04, 116.34, 82.06, 72.44, 64.35, 61.56, 50.39, 45.92, 34.24, 30.25, 13.65.

IR (KBr, cm^{-1}): 3629, 3279, 2958, 1734, 1488, 1456, 1436, 1369, 1231, 1119, 1043, 755, 651.

HRMS (ESI): m/z calcd for $C_{28}H_{38}NO_4$ ($[M+NH_4]^+$): 452.2795; found: 452.2800.

isopropyl 4-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-ethynylchromane-3-carboxylate **(3g)**



White solid, 39 mg,88% yield

mp: 100-102 ℃

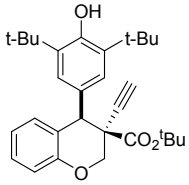
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (t, *J* = 7.8 Hz, 1H), 7.02 – 6.94 (m, 2H), 6.90 – 6.75 (m, 3H), 5.13 (d, *J* = 2.0 Hz, 1H), 4.65 (hept, 1H), 4.54 (s, 1H), 4.42 (dd, *J* = 11.1, 1.9 Hz, 1H), 4.26 (d, *J* = 11.3 Hz, 1H), 2.27 (s, 1H), 1.35 (d, *J* = 2.0 Hz, 18H), 1.13 (d, *J* = 5.6 Hz, 3H), 0.71 (d, *J* = 5.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.15, 153.13, 153.06, 135.18, 131.36, 131.18, 128.11, 126.80, 122.28, 121.02, 116.35, 82.32, 72.28, 69.35, 64.26, 50.51, 46.29, 34.24, 30.22, 21.63, 21.05.

IR (KBr, cm^{-1}): 3618, 3283, 2958, 2360, 1733, 1489, 1456, 1436, 1243, 1231, 1105, 1020, 754, 652.

HRMS (ESI): m/z calcd for $C_{29}H_{40}NO_4$ ($[M+NH_4]^+$): 466.2952; found: 466.2953.

tert-butyl 4-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-ethynylchromane-3-carboxylate **(3h)**



White solid, 38 mg, 82% yield

mp: 123-125 ℃

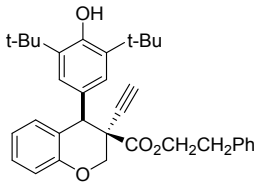
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (ddd, *J* = 8.5, 7.2, 1.7 Hz, 1H), 6.97 (t, *J* = 2.0 Hz, 1H), 6.95 (d, *J* = 2.1 Hz, 1H), 6.94 (s, 2H), 6.83 (td, *J* = 7.4, 1.3 Hz, 1H), 5.11 (s, 1H), 4.49 (s, 1H), 4.46 (d, *J* = 11.3 Hz, 1H), 4.32 (dd, *J* = 11.4, 1.7 Hz, 1H), 2.26 (s, 1H), 1.36 (s, 18H), 1.16 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.35, 152.83, 135.12, 131.49, 131.21, 127.88, 127.13, 122.85, 120.97, 116.41, 82.96, 82.27, 71.76, 64.92, 50.30, 46.40, 34.22, 30.21, 27.63.

IR (KBr, cm^{-1}): 3629, 3283, 2958, 1732, 1488, 1456, 1435, 1369, 1277, 1238, 1160, 1119, 1016, 753, 651.

HRMS (ESI): m/z calcd for $C_{30}H_{42}NO_4$ ($[M+NH_4]^+$): 480.3108; found: 480.3111.

phenethyl 4-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-ethynylchromane-3-carboxylate **(3i)**



White solid, 47 mg, 92% yield

mp: 165-168 ℃

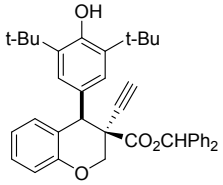
^{1}H NMR (400 MHz, $CDCl_3$) δ (major) 7.35 – 7.24 (m, 3H), 7.24 – 7.20 (m, 1H), 7.16 – 7.06 (m, 2H), 7.04 – 6.96 (m, 2H), 6.95 – 6.88 (m, 1H), 6.88 – 6.76 (m, 2H), 5.14 (d, *J* = 1.4 Hz, 1H), 4.56 (s, 1H), 4.38 (d, *J* = 11.2 Hz, 1H), 4.26 – 4.17 (m, 1H), 4.11 (ddd, *J* = 10.7, 7.6, 6.1 Hz, 1H), 3.99 (dt, *J* = 10.6, 7.3 Hz, 1H), 2.90 – 2.55 (m, 2H), 2.28 (d, *J* = 1.8 Hz, 1H), 1.34 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (major) 168.45, 153.16, 153.13, 137.20, 135.32, 131.11, 130.37, 128.90, 128.50, 128.22, 127.26, 126.63, 122.05, 121.06, 116.34, 81.89, 72.56, 66.03, 64.31, 50.42, 46.09, 34.67, 34.24, 30.29.

IR (KBr, cm^{-1}): 3648, 3283, 2956, 2359, 1735, 1488, 1473, 1420, 1262, 1235, 1021, 751, 700, 651.

HRMS (ESI): m/z calcd for $C_{34}H_{42}NO_4$ ($[M+NH_4]^+$): 528.3108; found: 528.3102.

benzhydryl 4-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-ethynylchromane-3-carboxylate **(3j)**



White solid, 50 mg, 87% yield

mp: 157-159 ℃

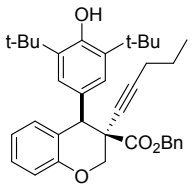
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 4.3 Hz, 4H), 7.22 – 7.16 (m, 1H), 7.13 – 7.01 (m, 4H), 6.95 – 6.87 (m, 2H), 6.82 (dd, *J* = 7.0, 2.5 Hz, 2H), 6.79 – 6.71 (m, 3H), 6.47 (s, 1H), 5.00 (s, 1H), 4.56 (s, 1H), 4.40 (d, *J* = 11.2 Hz, 1H), 4.21 (dd, *J* = 11.2, 1.7 Hz, 1H), 2.20 (s, 1H), 1.13 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.44, 153.23, 153.19, 139.81, 139.68, 135.34, 130.89, 130.74, 128.71, 128.67, 128.53, 128.39, 128.22, 128.09, 127.73, 127.36, 126.94, 126.82, 126.57, 126.24, 122.38, 120.95, 116.30, 81.88, 78.17, 72.85, 64.78, 50.47, 46.28, 34.18, 30.19.

IR (KBr, cm^{-1}): 3629, 3284, 2957, 1733, 1488, 1456, 1436, 1230, 1141, 1023, 754, 739, 699, 650.

HRMS (ESI): m/z calcd for $C_{39}H_{44}NO_4$ ($[M+NH_4]^+$): 590.3265; found: 590.3264.

benzyl 4-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-(pent-1-yn-1-yl)chromane-3-carboxylate (**3k**)



White solid, 47 mg, 88% yield

mp: 146-148 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ (major) 7.37 – 7.22 (m, 3H), 7.19 – 7.09 (m, 1H), 7.06 – 6.98 (m, 2H), 6.99 – 6.92 (m, 2H), 6.88 (s, 2H), 6.86 – 6.79 (m, 1H), 5.13 (s, 1H), 4.95 (d, *J* = 12.6 Hz, 1H), 4.82 (d,

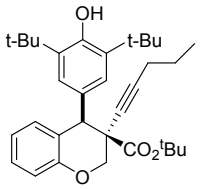
J = 12.6 Hz, 1H), 4.55 (d, *J* = 1.6 Hz, 1H), 4.39 (d, *J* = 11.1 Hz, 1H), 4.20 (dd, *J* = 11.1, 1.8 Hz, 1H), 2.08 (t, *J* = 6.9 Hz, 2H), 1.42 – 1.26 (m, 20H), 0.76 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (major) 169.51, 153.36, 153.05, 135.24, 134.99, 131.62, 130.99, 128.43, 128.12, 127.93, 127.47, 126.73, 122.53, 120.67, 116.12, 85.05, 78.10, 66.87, 64.77, 50.96, 46.12, 34.26, 30.30, 21.93, 20.73, 13.06.

IR (KBr, cm^{-1}): 3918, 3629, 2959, 1743, 1559, 1497, 1457, 1436, 1369, 1236, 1171, 1022, 752, 696.

HRMS (ESI): m/z calcd for $C_{36}H_{46}NO_4$ ($[M+NH_4]^+$): 556.3421; found: 556.3431.

tert-butyl 4-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-(pent-1-yn-1-yl)chromane-3-carboxylate (**3l**)



White solid, 38 mg, 75% yield

mp: 135-137 ℃

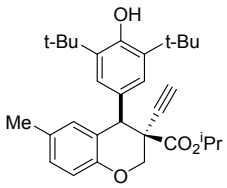
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.06 (m, 1H), 7.01 – 6.88 (m, 3H), 6.80 (t, *J* = 7.4 Hz, 1H), 5.09 (d, *J* = 3.9 Hz, 1H), 4.45 (d, *J* = 11.3 Hz, 1H), 4.42 (s, 1H), 4.31 – 4.20 (m, 1H), 2.08 (t, *J* = 6.8 Hz, 2H), 1.41 – 1.31 (m, 20H), 1.17 (s, 9H), 0.79 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.30, 153.01, 152.84, 134.96, 131.95, 131.12, 127.55, 127.11, 123.38, 120.57, 116.18, 84.02, 81.67, 79.25, 65.45, 50.71, 46.25, 34.21, 30.23, 27.70, 22.00, 20.74, 13.05.

IR (KBr, cm^{-1}): 3918, 3630, 2958, 1743, 1559, 1497, 1457, 1436, 1369, 1277, 1236, 1171, 1159, 1022, 752, 696.

HRMS (ESI): m/z calcd for $C_{33}H_{48}NO_4$ ($[M+NH_4]^+$): 522.3578; found: 522.3575.

isopropyl 4-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-ethynyl-6-methylchromane-3-carboxylate **(3m)**



White solid, 42 mg, 91% yield

mp: 124-126 ℃

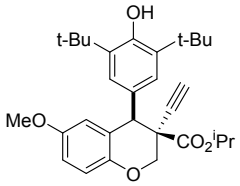
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.91 – 6.84 (m, 3H), 6.78 (d, *J* = 2.1 Hz, 1H), 5.14 (s, 1H), 4.71 – 4.56 (m, 1H), 4.49 (s, 1H), 4.39 (d, *J* = 11.2 Hz, 1H), 4.22 (dd, *J* = 11.2, 1.8 Hz, 1H), 2.28 (s, 1H), 2.19 (s, 3H), 1.36 (s, 18H), 1.13 (d, *J* = 6.3 Hz, 3H), 0.69 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.24, 153.12, 150.87, 135.13, 131.46, 131.27, 130.08, 129.04, 126.80, 121.65, 116.03, 82.45, 72.16, 69.29, 64.11, 50.55, 46.37, 34.32, 34.25, 30.23, 21.63, 21.05, 20.56.

IR (KBr, cm^{-1}): 3629, 3283, 2956, 2360, 1739, 1521, 1472, 1457, 1239, 1122, 1029, 815, 737, 697, 652.

HRMS (ESI): m/z calcd for $C_{30}H_{42}NO_4$ ($[M+NH_4]^+$): 480.3108; found: 480.3110.

isopropyl 4-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-ethynyl-6-methoxychromane-3-carboxylate **(3n)**



White solid, 43 mg, 90% yield

mp: 126-128 ℃

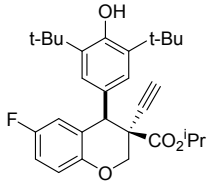
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.91 (d, *J* = 8.9 Hz, 1H), 6.87 (s, 2H), 6.76 (dd, *J* = 8.9, 3.0 Hz, 1H), 6.48 (d, *J* = 3.0 Hz, 1H), 5.14 (s, 1H), 4.72 – 4.58 (m, 1H), 4.49 (s, 1H), 4.39 (d, *J* = 11.2 Hz, 1H), 4.22 (dd, *J* = 11.2, 1.7 Hz, 1H), 3.69 (s, 3H), 2.29 (s, 1H), 1.35 (s, 19H), 1.12 (d, *J* = 6.2 Hz, 3H), 0.70 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.20, 153.63, 153.15, 147.17, 135.13, 131.11, 126.74, 122.64, 117.04, 115.12, 114.74, 82.40, 72.21, 69.34, 64.22, 55.64, 50.82, 46.35, 34.23, 30.21, 21.62, 21.03.

IR (KBr, cm^{-1}): 3630, 3284, 2957, 2360, 1739, 1497, 1456, 1435, 1211, 1121, 1033, 889, 738, 699, 653.

HRMS (ESI): m/z calcd for $C_{30}H_{39}O_5$ ($[M+H]^+$): 479.2792; found: 479.2792.

isopropyl 4-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-ethynyl-6-fluorochromane-3-carboxylate **(3o)**



White solid, 45 mg, 97% yield

mp: 116-118 ℃

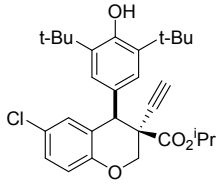
^{1}H NMR (400 MHz, $CDCl_3$) δ (major) 6.94 – 6.89 (m, 1H), 6.87 (dd, *J* = 7.9, 3.0 Hz, 1H), 6.84 (s, 2H), 6.67 (dd, *J* = 8.9, 2.9 Hz, 1H), 5.14 (s, 1H), 4.70 – 4.54 (m, 1H), 4.47 (s, 1H), 4.37 (d, *J* = 11.3 Hz, 1H), 4.23 (dd, *J* = 11.3, 1.8 Hz, 1H), 2.28 (s, 1H), 1.34 (s, 18H), 1.10 (d, *J* = 6.3 Hz, 3H), 0.70 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (major)167.91, 158.27, 155.89, 153.29, 149.14, 135.34, 130.67, 126.71, 123.40 (d, *J* = 7.5 Hz), 117.41 (d, *J* = 7.8 Hz), 116.74 (d, *J* = 22.8 Hz), 115.30 (d, *J* = 23.1 Hz), 82.08, 72.46, 69.47, 64.44, 50.63, 46.08, 34.24, 30.18, 21.59, 21.03.

IR (KBr, cm^{-1}): 3619, 3288, 2958, 2343, 1734, 1494, 1436, 1236, 1153, 1029, 738, 701, 652.

HRMS (ESI): m/z calcd for $C_{29}H_{39}FNO_4$ ($[M+NH_4]^+$): 484.2858; found: 484.2856.

isopropyl 6-chloro-4-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-ethynylchromane-3-carboxylate **(3p)**



White solid, 45 mg, 95% yield

mp: 140-142 ℃

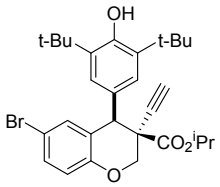
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.90 – 6.83 (m, 3H), 6.78 (d, *J* = 2.1 Hz,

1H), 5.14 (s, 1H), 4.71 – 4.57 (m, 1H), 4.52 – 4.47 (m, 1H), 4.39 (d, *J* = 11.2 Hz, 1H), 4.22 (dd, *J* = 11.2, 1.8 Hz, 1H), 2.28 (s, 1H), 2.19 (s, 3H), 1.36 (s, 18H), 1.13 (d, *J* = 6.3 Hz, 3H), 0.69 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.24 , 153.12 , 150.87 , 135.13 , 131.46 , 131.27 , 130.08 , 129.04 , 126.80 , 121.65 , 116.03 , 72.16 , 69.29 , 64.11 , 50.55 , 46.37 , 34.25 , 30.23 , 21.63 , 21.05 , 20.56 .

HRMS (ESI): m/z calcd for $C_{29}H_{39}ClNO_4$ ($[M+NH_4]^+$): 500.2562; found: 500.2559.

isopropyl 6-bromo-4-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-ethynylchromane-3-carboxylate **(3q)**



White solid, 43 mg, 81% yield

mp: 141-143 ℃

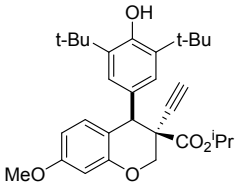
^{1}H NMR (400 MHz, $CDCl_3$) δ (major) 7.43 – 7.35 (m, 1H), 7.24 (d, *J* = 2.4 Hz, 1H), 7.00 (d, *J* = 8.8 Hz, 1H), 6.96 (s, 2H), 5.29 (s, 1H), 4.78 (hept, *J* = 6.3 Hz, 1H), 4.60 (d, *J* = 1.7 Hz, 1H), 4.53 (d, *J* = 11.3 Hz, 1H), 4.38 (dd, *J* = 11.3, 1.8 Hz, 1H), 2.41 (s, 1H), 1.48 (s, 18H), 1.26 (d, *J* = 6.3 Hz, 3H), 0.84 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (major) 167.74, 153.35, 152.24, 135.38, 133.41, 131.17, 130.48, 126.70, 124.44, 118.24, 112.99, 81.89, 72.61, 69.54, 64.42, 50.34, 45.91, 34.25, 30.18, 21.61, 21.04.

IR (KBr, cm^{-1}): 3629, 3290, 2957, 2360, 1734, 1480, 1456, 1436, 1234, 1122, 1029, 813, 738, 696, 650.

HRMS (ESI): m/z calcd for $C_{29}H_{39}BrNO_4$ ($[M+NH_4]^+$): 544.2057; found: 544.2047.

isopropyl 4-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-ethynyl-7-methoxychromane-3-carboxylate **(3r)**



White solid, 42 mg, 88% yield

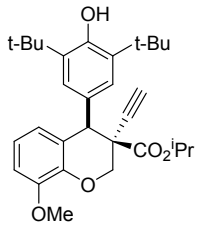
mp: 119-121 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85 (d, *J* = 8.1 Hz, 3H), 6.50 (d, *J* = 2.5 Hz, 1H), 6.44 (dd, *J* = 8.5, 2.6 Hz, 1H), 5.10 (s, 1H), 4.70 – 4.54 (m, 1H), 4.46 (s, 1H), 4.37 (d, *J* = 11.2 Hz, 1H), 4.21 (dd, *J* = 11.3, 1.7 Hz, 1H), 3.77 (s, 3H), 2.27 (s, 1H), 1.33 (s, 18H), 1.10 (d, *J* = 6.2 Hz, 3H), 0.67 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.19, 159.45, 153.83, 153.09, 135.14, 131.71, 131.51, 126.69, 114.52, 108.53, 100.56, 82.43, 72.06, 69.31, 64.29, 55.23, 50.01, 46.45, 34.22, 30.21, 21.61, 21.03.

HRMS (ESI): m/z calcd for $C_{30}H_{39}O_5$ ($[M+H]^+$): 479.2792; found: 479.2799.

isopropyl 4-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-ethynyl-8-methoxychromane-3-carboxylate **(3s)**



White solid, 41 mg, 85% yield

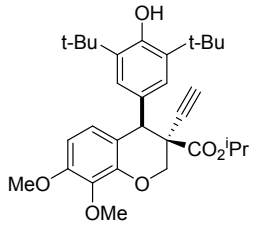
mp: 144-146 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ (major) 7.10 (s, 2H), 7.05 – 6.97 (m, 2H), 6.81 (dd, *J* = 7.1, 2.2 Hz, 1H), 5.35 (s, 1H), 4.94 – 4.82 (m, 1H), 4.75 (s, 1H), 4.67 (d, *J* = 11.2 Hz, 1H), 4.60 (dd, *J* = 11.2, 1.7 Hz, 1H), 4.15 (s, 3H), 2.48 (s, 1H), 1.57 (s, 18H), 1.34 (d, *J* = 6.3 Hz, 3H), 0.93 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (major) 168.09, 153.15, 147.96, 142.81, 135.22, 131.23, 126.76, 122.94, 120.40, 109.49, 82.05, 72.37, 69.36, 64.55, 55.92, 50.44, 46.28, 34.22, 30.23, 21.58, 21.01.

HRMS (ESI): m/z calcd for $C_{30}H_{42}NO_5$ ($[M+NH_4]^+$): 496.3057; found: 496.3060.

isopropyl 4-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-ethynyl-7,8-dimethoxychromane-3-carboxylate **(3t)**



White solid, 41 mg, 81% yield

mp: 122-124 ℃

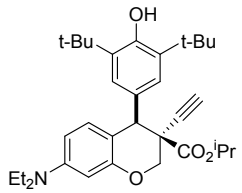
^{1}H NMR (400 MHz, $CDCl_3$) δ (major) 7.09 (s, 1H), 6.92 (d, *J* = 8.6 Hz, 0H), 6.72 (d, *J* = 8.6 Hz, 0H), 5.36 (s, 0H), 4.94 – 4.85 (m, 0H), 4.72 (d, *J* = 1.6 Hz, 1H), 4.66 (d, *J* = 11.2 Hz, 0H), 4.59 (dd, *J* = 11.1, 1.7 Hz, 1H), 4.14 (s, 1H), 4.07 (s, 1H), 2.47 (s, 0H), 1.58 (s, 9H), 1.37 (d, *J* = 6.2 Hz, 2H), 0.95 (d, *J* = 6.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (major)168.97, 168.13, 153.08, 151.97, 151.89, 147.16, 147.05, 136.69, 136.60, 135.19, 134.76, 131.33, 130.90, 129.95, 128.83, 127.13, 126.58, 125.25, 124.50, 117.11, 116.52, 105.16, 104.77, 82.12, 72.24, 69.36, 64.40, 60.88, 55.98, 50.07, 46.15, 34.22, 30.20, 21.61, 21.04.

IR (KBr, cm^{-1}): 3629, 3281, 2958, 2360, 1739, 1614, 1499, 1472, 1435, 1241, 1119, 1068, 736, 698, 657.

HRMS (ESI): m/z calcd for $C_{31}H_{40}NO_6$ ($[M+NH_4]^+$): 526.3163; found: 526.3171.

isopropyl 4-(3,5-di-tert-butyl-4-hydroxyphenyl)-7-(diethylamino)-3-ethynylchromane-3-carboxylate **(3u)**



White solid, 48mg, 92% yield

mp: 170-172 ℃

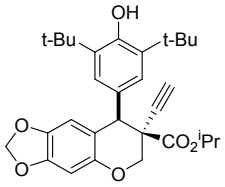
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (s, 2H), 6.74 (d, *J* = 8.7 Hz, 1H), 6.24 (s, 2H), 5.07 (s, 1H), 4.74 – 4.55 (m, 1H), 4.41 (s, 1H), 4.37 (d, *J* = 11.7 Hz, 1H), 4.19 (d, *J* = 11.1 Hz, 1H), 3.29 (q, *J* = 7.4 Hz, 4H), 2.27 (s, 1H), 1.34 (s, 18H), 1.13 (t, *J* = 7.0 Hz, 6H), 1.08 (d, *J* = 6.3 Hz, 3H), 0.66 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.49, 153.90, 152.94, 148.08, 134.99, 132.15, 131.44, 126.69, 109.46, 106.43, 98.55, 82.88, 71.79, 69.11, 64.34, 49.96, 46.80, 44.28, 34.22, 30.26, 21.59, 21.03, 12.67, 1.03.

IR (KBr, cm^{-1}): 3629, 3279, 2964, 2360, 1739, 1624, 1560, 1515, 1435, 1264, 1123, 1029, 736, 685.

HRMS (ESI): m/z calcd for $C_{33}H_{46}NO_4$ ($[M+H]^+$): 520.3421; found: 520.3427.

isopropyl
8-(3,5-di-tert-butyl-4-hydroxyphenyl)-7-ethynyl-7,8-dihydro-6H-[1,3]dioxolo[4,5-g]chromene-7-carboxylate **(3v)**



White solid, 38 mg, 81% yield

mp: 178-180 ℃

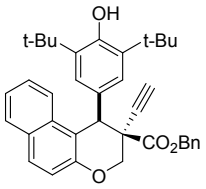
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (s, 2H), 6.51 (s, 1H), 6.38 (s, 1H), 5.87 (d, *J* = 5.1 Hz, 2H), 5.14 (s, 1H), 4.71 – 4.55 (m, 1H), 4.39 (s, 1H), 4.35 (d, *J* = 11.2 Hz, 1H), 4.26 – 4.16 (m, 1H), 2.31 (s, 1H), 1.36 (s, 18H), 1.11 (d, *J* = 6.2 Hz, 3H), 0.68 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.15, 153.18, 147.81, 147.27, 142.04, 135.19, 131.24, 126.67, 113.71, 109.34, 101.05, 97.86, 82.48, 71.95, 69.32, 64.19, 50.59, 46.31, 34.24, 30.21, 21.60, 21.00.

IR (KBr, cm^{-1}): 3853, 3769, 3629, 2955, 2360, 1733, 1716, 1652, 1558, 1507, 1457, 1156, 1068, 752, 699, 652.

HRMS (ESI): m/z calcd for $C_{30}H_{40}NO_6$ ($[M+NH_4]^+$): 510.2850; found: 510.2848.

benzyl
1-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-ethynyl-2,3-dihydro-1H-benzo[f]chromene-2-carboxylate **(3w)**



White solid, 43 mg, 86% yield

mp: 179-181 ℃

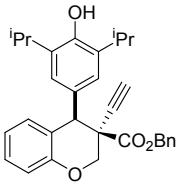
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.68 (m, 2H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.41 – 7.24 (m, 5H), 7.20 (d, *J* = 8.9 Hz, 1H), 7.08 – 6.94 (m, 4H), 5.13 (s, 2H), 4.94 (d, *J* = 12.5 Hz, 1H), 4.88 (d, *J* = 12.5 Hz, 1H), 4.55 (d, *J* = 11.1 Hz, 1H), 4.34 (dd, *J* = 11.2, 1.9 Hz, 1H), 2.20 (s, 1H), 1.31 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.81, 153.31, 150.81, 135.60, 134.64, 132.73, 130.55, 129.58, 129.27, 128.54, 128.45, 128.33, 127.65, 126.56, 126.17, 123.22, 122.77, 118.24, 113.08, 81.87, 77.36, 77.05, 76.73, 72.34, 67.43, 63.90, 47.68, 45.92, 34.27, 30.30.

IR (KBr, cm^{-1}): 3629, 3288, 2958, 2360, 1737, 1635, 1498, 1488, 1436, 1233, 1122, 1027, 807, 740, 697.

HRMS (ESI): m/z calcd for $C_{37}H_{42}NO_4$ ($[M+NH_4]^+$): 564.3108; found: 564.3107.

benzyl 3-ethynyl-4-(4-hydroxy-3,5-diisopropylphenyl)chromane-3-carboxylate **(3x)**



White solid, 42 mg, 90% yield

mp: 117-119 ℃

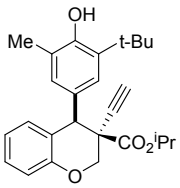
^1H NMR (400 MHz, $CDCl_3$) δ (major) 7.34 – 7.27 (m, 3H), 7.19 (t, *J* = 7.8 Hz, 1H), 7.08 (dd, *J* = 6.1, 3.0 Hz, 2H), 7.01 – 6.95 (m, 2H), 6.86 (t, *J* = 7.3 Hz, 1H), 6.75 (s, 2H), 5.00 (d, *J* = 12.6 Hz, 1H), 4.86 (d, *J* = 12.6 Hz, 1H), 4.75 (s, 1H), 4.62 (s, 1H), 4.42 (d, *J* = 11.2 Hz, 1H), 4.30 (d, *J* = 11.4 Hz, 1H), 3.11 – 2.96 (m, 2H), 2.30 (s, 1H), 1.17 (d, *J* = 6.9 Hz, 6H), 1.11 (d, *J* = 7.7 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (major) 168.43, 153.15, 149.54, 134.84, 133.26, 132.33, 130.99, 128.49, 128.28, 128.22, 127.44, 125.28, 122.01, 121.10, 116.42, 81.74, 72.74, 67.11, 64.37, 50.28, 46.07, 27.21, 22.69, 22.63.

IR (KBr, cm^{-1}): 3527, 3285, 2962, 1735, 1585, 1489, 1457, 1267, 1229, 1126, 1038, 753, 737, 697, 667.

HRMS (ESI): m/z calcd for $C_{31}H_{36}NO_4$ ($[M+NH_4]^+$): 486.2639; found: 486.2637.

isopropyl 4-(3-(tert-butyl)-4-hydroxy-5-methylphenyl)-3-ethynylchromane-3-carboxylate **(3y)**



White solid, 36 mg, 88% yield

mp: 78-80 ℃

^1H NMR (400 MHz, $CDCl_3$) δ 7.10 (ddd, *J* = 8.6, 7.1, 1.7 Hz, 1H), 6.89 (ddd, *J* = 9.8, 7.9, 1.4 Hz, 1H), 6.82 (d, *J* = 2.3 Hz, 1H), 6.78 (td, *J* = 7.4, 1.3 Hz, 0H), 6.58 (d, *J* = 2.2 Hz, 1H), 4.76 – 4.60 (m, 1H), 4.43 (s, 0H), 4.36 (d, *J* = 11.3 Hz, 1H), 4.20 (dd, *J* = 11.2, 1.8 Hz, 1H), 2.18 (s, 0H), 2.05 (s, 2H), 1.26 (s, 5H), 1.11 (d, *J* = 6.3 Hz, 2H), 0.81 (d, *J* = 6.2 Hz, 2H).

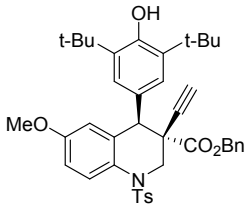
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.13, 153.07, 152.09, 135.01, 131.78, 131.02, 129.97, 128.12, 127.20, 122.52, 122.35, 121.02, 116.43, 82.24, 72.25, 69.54, 64.40, 50.00, 45.91, 34.44, 29.66, 21.68, 21.12, 16.00.

IR (KBr, cm^{-1}): 3675, 3285, 2955, 2360, 1734, 1488, 1489, 1456, 1265, 1226, 1168, 1039, 754, 737, 697, 658.

HRMS (ESI): m/z calcd for $C_{26}H_{31}O_4$ ($[M+NH_4]^+$): 407.2217; found: 407.2219.

benzyl
(3S,4S)-4-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-ethynyl-6-methoxy-1-tosyl-1,2,3,4-tetrahydroquinolin

e-3-carboxylate **(5aa)**



White solid, 34 mg, 50% yield (95% total yield with **5ab**)

mp: 176-178 ℃

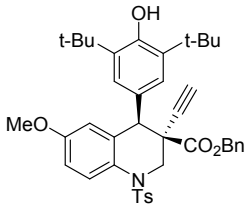
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 9.0 Hz, 1H), 7.33 – 7.24 (m, 3H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.05 – 6.97 (m, 2H), 6.93 (s, 2H), 6.76 (dd, *J* = 8.9, 3.0 Hz, 1H), 6.36 (dd, *J* = 3.0, 0.9 Hz, 1H), 5.16 (s, 1H), 4.91 (d, *J* = 12.5 Hz, 1H), 4.86 (d, *J* = 12.5 Hz, 1H), 4.52 (d, *J* = 12.4 Hz, 1H), 4.08 (d, *J* = 12.5 Hz, 1H), 3.66 (s, 1H), 3.65 (s, 3H), 2.38 (s, 3H), 2.28 (s, 1H), 1.34 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.54, 156.44, 153.33, 143.58, 136.78, 135.30, 134.85, 132.90, 129.60, 128.84, 128.46, 128.21, 127.76, 127.14, 126.69, 124.14, 114.23, 112.85, 80.96, 75.77, 67.81, 55.25, 53.68, 51.21, 50.84, 34.33, 30.35, 21.64.

IR (KBr, cm^{-1}): 3629, 3286, 2957, 2360, 1735, 1496, 1436, 1351, 1230, 1167, 1038, 813, 736, 697, 652, 567, 544.

HRMS (ESI): m/z calcd for C41H49N2O6S ([M+NH4]+): 697.3306; found: 697.3315.

benzyl
(3R,4S)-4-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-ethynyl-6-methoxy-1-tosyl-1,2,3,4-tetrahydroquinolin
e-3-carboxylate **(5ab)**



White solid, 31 mg, 45% yield (95% total yield with **5aa**)

mp: 167-169 ℃

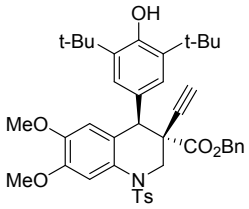
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 9.3 Hz, 1H), 7.29 – 7.15 (m, 5H), 6.96 (dd, *J* = 6.5, 2.9 Hz, 2H), 6.70 (s, 2H), 6.63 (dd, *J* = 9.2, 3.0 Hz, 1H), 6.49 (d, *J* = 3.0 Hz, 1H), 5.10 (s, 1H), 4.92 (d, *J* = 12.5 Hz, 1H), 4.80 (d, *J* = 12.5 Hz, 1H), 4.53 (dd, *J* = 13.1, 1.5 Hz, 1H), 4.46 (s, 1H), 3.86 (d, *J* = 13.1 Hz, 1H), 3.59 (s, 3H), 2.33 (s, 2H), 2.12 (s, 1H), 1.23 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.68, 155.12, 153.32, 143.68, 138.25, 135.51, 134.62, 130.20, 129.74, 129.44, 128.54, 128.31, 127.89, 127.60, 127.07, 126.39, 119.59, 116.03, 113.49, 81.81, 73.67, 67.49, 55.36, 52.86, 46.61, 46.48, 34.26, 30.24, 21.59.

IR (KBr, cm^{-1}): 3629, 3282, 2957, 2359, 1741, 1498, 1456, 1435, 1347, 1237, 1166, 1037, 813, 737, 697, 647, 543.

HRMS (ESI): m/z calcd for $C_{41}H_{49}N_2O_6S$ ($[M+NH_4]^+$): 697.3306; found: 697.3314.

benzyl
(3R,4S)-4-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-ethynyl-6,7-dimethoxy-1-tosyl-1,2,3,4-tetrahydroquin
oline-3-carboxylate **(5ba)**



White solid, 30 mg, 43% yield (79% total yield with **5bb**)

mp: 163-166 ℃

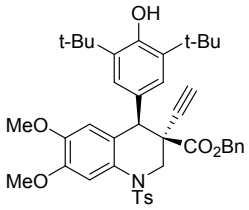
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 2.0 Hz, 1H), 7.69 (d, *J* = 2.0 Hz, 1H), 7.34 – 7.20 (m, 5H), 7.15 (d, *J* = 1.9 Hz, 1H), 7.01 (dd, *J* = 6.3, 2.9 Hz, 2H), 6.95 (d, *J* = 1.9 Hz, 2H), 6.33 (s, 1H), 5.17 (d, *J* = 1.9 Hz, 2H), 4.97 (d, *J* = 12.4 Hz, 1H), 4.91 (d, *J* = 12.4 Hz, 1H), 4.48 (d, *J* = 12.3 Hz, 1H), 4.04 (dd, *J* = 12.3, 2.0 Hz, 1H), 3.85 (s, 3H), 3.81 (d, *J* = 1.9 Hz, 3H), 2.40 (s, 3H), 2.29 (s, 1H), 1.35 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.53, 153.30, 147.77, 145.44, 143.77, 136.98, 135.15, 134.88, 129.65, 128.91, 128.40, 128.20, 127.75, 127.45, 127.19, 126.82, 121.83, 111.68, 105.85, 80.69, 75.80, 67.73, 55.85, 55.78, 52.44, 50.49, 50.35, 34.33, 30.34, 21.64.

IR (KBr, cm^{-1}): 3629, 3275, 2956, 2404, 1733, 1653, 1507, 1464, 1436, 1362, 1227, 1166, 1002, 737, 697, 577, 526.

HRMS (ESI): m/z calcd for $C_{42}H_{51}N_2O_7S$ ($[M+NH_4]^+$): 727.3411; found: 727.3418.

benzyl (3R,4S)-4-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-ethynyl-6,7-dimethoxy-1-tosyl-1,2,3,4-tetrahydroquinoline-3-carboxylate **(5bb)**



White solid, 26 mg, 36% yield (79% total yield with **5ba**)

mp: 153-155 ℃

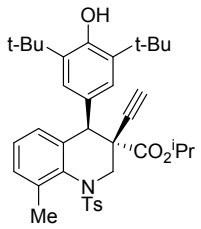
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.34 – 7.22 (m, 6H), 7.03 (dd, *J* = 6.6, 2.9 Hz, 2H), 6.78 (s, 2H), 6.46 (s, 1H), 5.18 (s, 1H), 4.98 (d, *J* = 12.5 Hz, 1H), 4.87 (d, *J* = 12.5 Hz, 1H), 4.60 (dd, *J* = 13.1, 1.6 Hz, 1H), 4.50 (d, *J* = 1.4 Hz, 1H), 3.87 (d, *J* = 13.1 Hz, 1H), 3.77 (s, 3H), 3.71 (s, 3H), 2.42 (s, 3H), 2.18 (s, 1H), 1.31 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.75, 153.32, 147.83, 144.92, 143.90, 138.22, 135.47, 134.58, 130.46, 129.72, 129.28, 128.52, 128.32, 127.63, 127.23, 126.37, 117.92, 113.45, 102.50, 81.89, 73.40, 67.51, 56.02, 55.75, 52.33, 46.58, 46.12, 34.26, 30.25, 21.59.

IR (KBr, cm^{-1}): 3629, 3276, 2957, 2404, 1734, 1653, 1508, 1437, 1436, 1362, 1227, 1002, 737, 697, 576, 526.

HRMS (ESI): m/z calcd for $C_{42}H_{51}N_2O_7S$ ($[M+NH_4]^+$): 727.3411; found: 727.3417.

isopropyl (3S,4S)-4-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-ethynyl-8-methyl-1-tosyl-1,2,3,4-tetrahydroquinoline-3-carboxylate **(5ca)**



White solid, 29 mg, 47% yield (75% total yield with **5cb**)

mp: 197-199 ℃

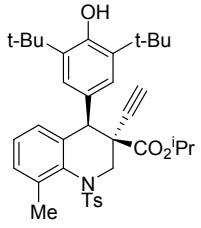
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 2.2 Hz, 1H), 7.56 (d, *J* = 7.9 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 1H), 7.29 – 7.23 (m, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.57 (d, *J* = 7.6 Hz, 1H), 5.97 (d, *J* = 2.2 Hz, 1H), 5.10 (s, 1H), 4.81 (d, *J* = 13.2 Hz, 1H), 4.58 (m, *J* = 6.2 Hz, 1H), 3.91 (d, *J* = 13.1 Hz, 1H), 2.92 (s, 1H), 2.62 (s, 3H), 2.43 (s, 3H), 2.07 (s, 1H), 1.36 (s, 9H), 1.33 (s, 9H), 0.90 (d, *J* = 6.3 Hz, 3H), 0.67 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.07, 153.21, 143.66, 138.39, 138.32, 136.09, 135.20, 135.06, 134.20, 130.21, 129.45, 128.30, 127.69, 126.50, 125.76, 125.30, 124.74, 83.04, 74.19, 69.66, 57.58, 54.98, 50.65, 34.56, 33.96, 30.33, 30.27, 21.80, 21.20, 20.91, 19.81.

IR (KBr, cm^{-1}): 3648, 3277, 2957, 1733, 1567, 1507, 1436, 1252, 1166, 1090, 693, 578.

HRMS (ESI): m/z calcd for $C_{37}H_{49}N_2O_5S$ ($[M+NH_4]^+$): 633.3357; found: 633.3361.

benzyl (3R,4S)-4-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-ethynyl-8-methyl-1-tosyl-1,2,3,4-tetrahydroquinoline-3-carboxylate **(5cb)**



White solid, 17 mg, 28% yield (75% total yield with **5ca**)

mp: 165-167 ℃

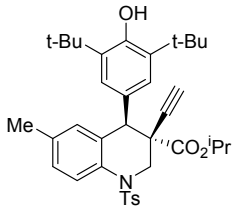
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.8 Hz, 2H), 7.40 – 7.20 (m, 3H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.56 (s, 2H), 5.13 (s, 1H), 4.71 (d, *J* = 14.8 Hz, 1H), 4.68 – 4.59 (m, 1H), 4.01 (d, *J* = 14.5 Hz, 1H), 3.13 (s, 1H), 2.58 (s, 3H), 2.44 (s, 3H), 2.35 (s, 1H), 1.37 (s, 18H), 0.93 (d, *J* = 6.1 Hz, 3H), 0.78 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.61, 153.12, 143.85, 137.74, 137.07, 136.60, 135.45, 134.88, 129.93, 129.62, 128.23, 126.63, 124.84, 124.74, 83.84, 74.40, 69.13, 56.96, 53.75, 52.12, 34.24, 30.37, 21.80, 21.30, 20.95, 19.54.

IR (KBr, cm^{-1}): 3619, 3278, 2958, 1733, 1437, 1352, 1213, 1166, 1103, 738, 661, 582, 546.

HRMS (ESI): m/z calcd for $C_{37}H_{49}N_2O_5S$ ($[M+NH_4]^+$): 633.3357; found: 633.3366.

isopropyl (3S,4S)-4-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-ethynyl-6-methyl-1-tosyl-1,2,3,4-tetrahydroquinoline-3-carboxylate **(5da)**



White solid, 29 mg, 47% yield (86% total yield with **5db**)

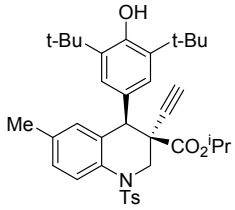
mp: 142-145 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.68 (m, 2H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.35 – 7.20 (m, 2H), 7.09 – 6.89 (m, 3H), 6.70 (s, 1H), 5.15 (d, *J* = 1.6 Hz, 1H), 4.86 – 4.70 (m, 1H), 4.47 (d, *J* = 12.0 Hz, 1H), 3.95 (t, *J* = 6.1 Hz, 2H), 2.42 (s, 3H), 2.29 (d, *J* = 1.6 Hz, 1H), 2.17 (s, 3H), 1.37 (d, *J* = 1.7 Hz, 18H), 1.07 (d, *J* = 6.1 Hz, 3H), 0.87 (d, *J* = 5.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.90, 153.19, 143.62, 137.31, 135.01, 133.33, 133.31, 129.88, 129.73, 129.51, 128.29, 127.72, 127.04, 126.91, 121.02, 81.10, 75.31, 69.88, 51.88, 50.65, 49.68, 34.32, 30.31, 21.62, 21.31, 21.05, 20.73.

HRMS (ESI): m/z calcd for $C_{37}H_{49}N_2O_5S$ ($[M+NH_4]^+$): 633.3357; found: 633.3363.

isopropyl
(3R,4S)-4-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-ethynyl-6-methyl-1-tosyl-1,2,3,4-tetrahydroquinoline-3-carboxylate **(5db)**



White solid, 24 mg, 39% yield (86% total yield with **5da**)

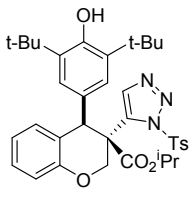
mp: 119-121 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.6 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 6.90 (dd, *J* = 8.7, 2.1 Hz, 1H), 6.83 (d, *J* = 2.1 Hz, 1H), 6.78 (s, 2H), 5.14 (s, 1H), 4.76 – 4.67 (m, 1H), 4.59 (dd, *J* = 13.0, 1.7 Hz, 1H), 4.51 (d, *J* = 1.6 Hz, 1H), 3.97 (d, *J* = 13.0 Hz, 1H), 2.41 (s, 3H), 2.15 (d, *J* = 2.0 Hz, 4H), 1.33 (s, 18H), 1.21 (d, *J* = 6.2 Hz, 3H), 0.78 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.22, 153.17, 143.68, 138.28, 135.31, 133.27, 132.12, 131.81, 130.81, 129.71, 129.68, 128.31, 127.10, 126.47, 126.06, 117.76, 82.36, 73.07, 69.73, 52.63, 46.27, 46.15, 34.24, 30.18, 21.67, 21.57, 21.14, 20.40.

HRMS (ESI): m/z calcd for $C_{37}H_{49}N_2O_5S$ ($[M+NH_4]^+$): 633.3357; found: 633.3358.

Isopropyl
4-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-(1-tosyl-1H-1,2,3-triazol-5-yl)chromane-3-carboxylate (**6g**)



White solid, 53 mg, 82% yield

mp: 189-191 ℃

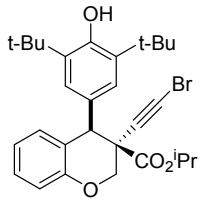
^{1}H NMR (400 MHz, $CDCl_3$) δ (major) 7.78 (s, 1H), 7.74 (d, J = 8.1 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 7.01 (t, J = 7.8 Hz, 1H), 6.93 (d, J = 7.5 Hz, 1H), 6.83 (s, 2H), 6.75 (t, J = 7.2 Hz, 1H), 6.65 (d, J = 8.3 Hz, 1H), 5.06 (s, 1H), 4.67 – 4.59 (m, 2H), 4.56 (s, 1H), 4.54 – 4.48 (m, 1H), 2.35 (s, 3H), 1.28 (s, 18H), 1.00 (d, J = 6.2 Hz, 3H), 0.56 (d, J = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (major) 169.27, 153.05, 152.97, 147.30, 147.08, 135.20, 133.00, 131.57, 130.75, 130.33, 128.54, 128.20, 126.93, 122.88, 122.05, 121.20, 116.32, 69.08, 63.86, 49.41, 47.95, 34.25, 30.22, 21.82, 21.62, 21.05.

IR (KBr, cm^{-1}): 3618, 2965, 2958, 2869, 2360, 1733, 1675, 1489, 1456, 1436, 1243, 1231, 1105, 1020, 898, 754, 652.

HRMS (ESI): m/z calcd for $C_{36}H_{44}N_3O_6S$ ($[M+H]^+$): 646.2945; found: 646.2949.

isopropyl 3-(bromoethynyl)-4-(3,5-di-tert-butyl-4-hydroxyphenyl)chromane-3-carboxylate (**7g**)



White solid, 37 mg, 71% yield

mp: 96-98 ℃

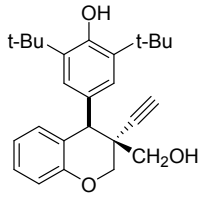
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (s, 1H), 7.16 (t, *J* = 7.8 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 2H), 6.86 (s, 2H), 5.12 (s, 1H), 4.70 – 4.59 (m, 1H), 4.51 (s, 1H), 4.39 (d, *J* = 11.2 Hz, 1H), 4.24 (dd, *J* = 11.3, 1.7 Hz, 1H), 1.34 (s, 18H), 1.12 (d, *J* = 6.2 Hz, 3H), 0.71 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.84, 153.11, 153.07, 135.15, 131.24, 131.10, 128.03, 126.84, 122.22, 120.98, 116.38, 69.39, 65.58, 64.37, 50.28, 47.47, 43.72, 34.23, 30.20, 21.63, 21.08.

IR (KBr, cm^{-1}): 3620, 2958, 2359, 1733, 1489, 1456, 1436, 1243, 1231, 1105, 1020, 754, 652.

HRMS (ESI): m/z calcd for $C_{29}H_{36}BrO_4$ ($[M+H]^+$): 527.1791; found: 527.1794.

2,6-di-tert-butyl-4-(3-ethynyl-3-(hydroxymethyl)chroman-4-yl)phenol (**8g**)



Colorless oil, 30 mg, 76% yield

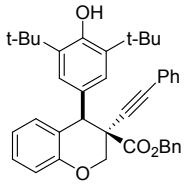
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (t, J = 7.7 Hz, 1H), 7.25 (d, J = 7.7 Hz, 1H), 7.23 – 7.15 (m, 3H), 7.11 (t, J = 7.5 Hz, 1H), 5.43 (s, 1H), 4.63 (s, 1H), 4.54 (d, J = 10.8 Hz, 1H), 4.40 (d, J = 10.7 Hz, 1H), 3.74 – 3.50 (m, 2H), 2.53 (s, 1H), 1.98 (s, 1H), 1.64 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.18, 152.96, 135.32, 130.82, 129.81, 127.96, 126.84, 122.99, 120.89, 116.52, 85.06, 72.95, 67.17, 63.67, 49.48, 40.90, 34.29, 30.33.

IR (KBr, cm^{-1}): 3637, 3618, 3283, 2958, 2360, 1489, 1456, 1436, 1243, 1225, 1105, 1020, 749, 654.

HRMS (ESI): m/z calcd for $C_{26}H_{33}O_3$ ($[M+H]^+$): 393.2424; found: 393.2425.

benzyl 4-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-(phenylethynyl)chromane-3-carboxylate **(9a)**



White solid, 37 mg, 64% yield

mp: 202-204 ℃

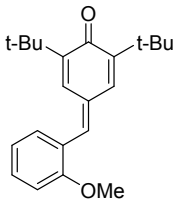
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.21 (m, 8H), 7.22 – 7.12 (m, 1H), 7.11 – 7.06 (m, 2H), 7.00 (dd, *J* = 18.5, 8.1 Hz, 2H), 6.93 (s, 2H), 6.85 (t, *J* = 7.5 Hz, 1H), 5.16 (s, 1H), 5.03 (d, *J* = 12.6 Hz, 1H), 4.87 (d, *J* = 12.6 Hz, 1H), 4.70 (s, 1H), 4.48 (d, *J* = 11.1 Hz, 1H), 4.34 (d, *J* = 11.2 Hz, 1H), 1.34 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.90, 153.40, 153.17, 135.32, 134.98, 131.87, 131.32, 130.99, 128.49, 128.22, 128.18, 128.11, 128.04, 127.44, 126.79, 122.63, 122.30, 120.82, 116.22, 87.29, 84.56, 66.98, 64.69, 50.70, 46.73, 34.29, 30.31.

IR (KBr, cm^{-1}): 3635, 2958, 2360, 1739, 1488, 1455, 1445, 1369, 1436, 1236, 1158, 1122, 1024, 754, 737, 697, 653.

HRMS (ESI): m/z calcd for $C_{39}H_{44}NO_4$ ($[M+NH_4]^+$): 590.3265; found: 590.3268.

2,6-di-tert-butyl-4-(2-methoxybenzylidene)cyclohexa-2,5-dien-1-one (**10**)



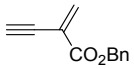
Yellow solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 2.5, 0.8 Hz, 1H), 7.41 (d, *J* = 1.1 Hz, 1H), 7.39 (s, 1H), 7.37 (s, 1H), 7.08 (dd, *J* = 2.4, 0.6 Hz, 1H), 7.03 (td, *J* = 7.6, 0.9 Hz, 1H), 6.98 – 6.93 (m, 1H), 3.89 (s, 3H), 1.34 (s, 9H), 1.29 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 186.67, 158.27, 148.92, 147.34, 138.75, 135.30, 131.80, 131.58, 130.85, 128.31, 124.92, 120.55, 110.78, 55.57, 35.39, 34.99, 29.56, 29.53.

HRMS (ESI): m/z calcd for $C_{22}H_{29}O_2$ ($[M+H]^+$): 325.2162; found: 325.2166.

benzyl 2-methylenebut-3-ynoate (**11a**)



Light yellow oil

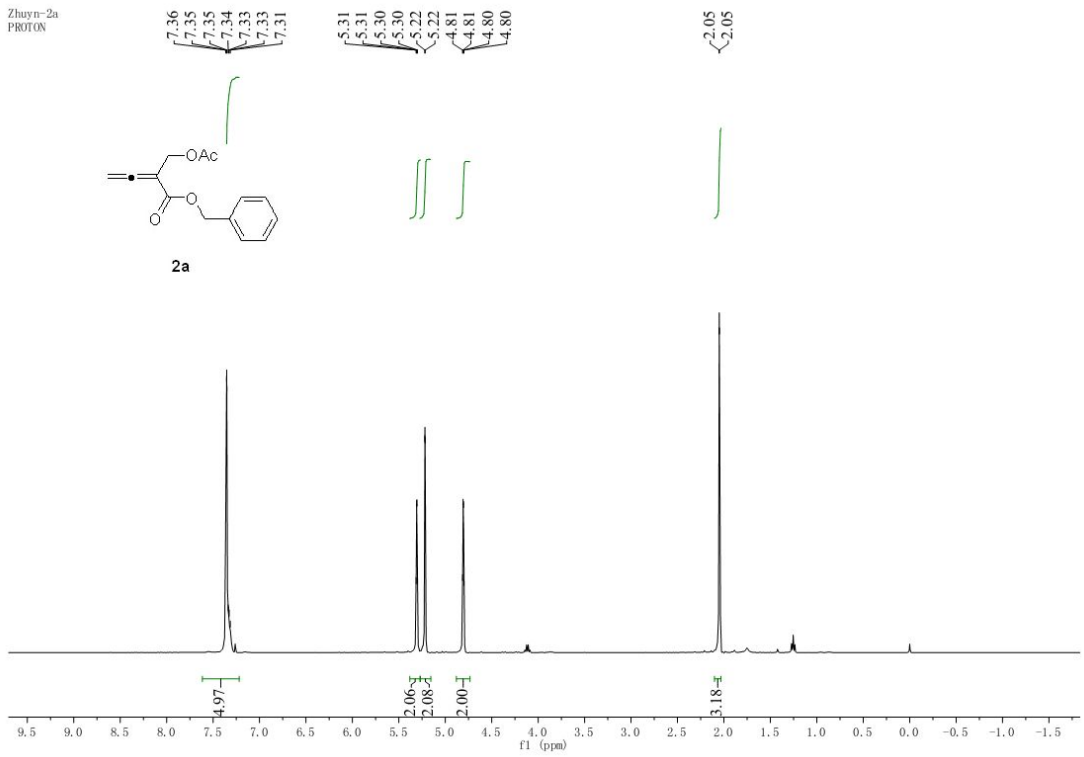
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.11 (m, 5H), 6.61 (s, 1H), 6.12 (s, 1H), 5.18 (s, 2H), 3.04 (s, 1H).

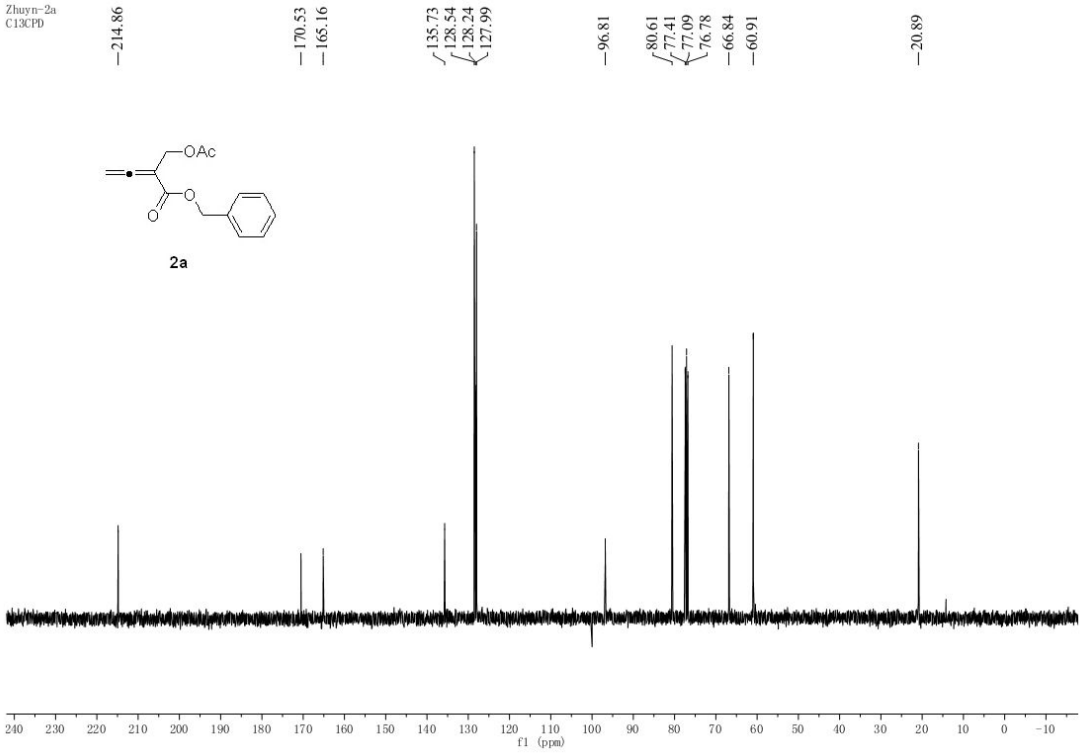
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.59, 136.14, 135.48, 128.58, 128.33, 128.08, 123.36, 80.58, 78.64, 67.31.

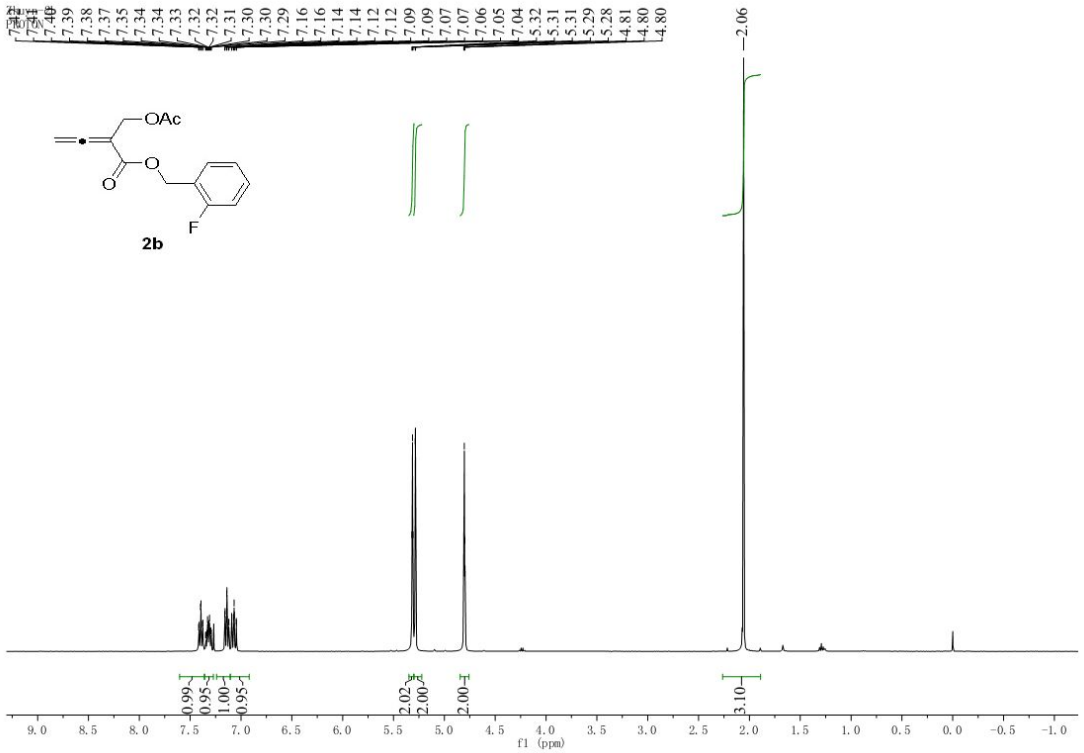
IR (KBr, cm^{-1}): 3326, 3284, 3055, 2957, 1711, 1588, 1459, 1436, 737, 658.

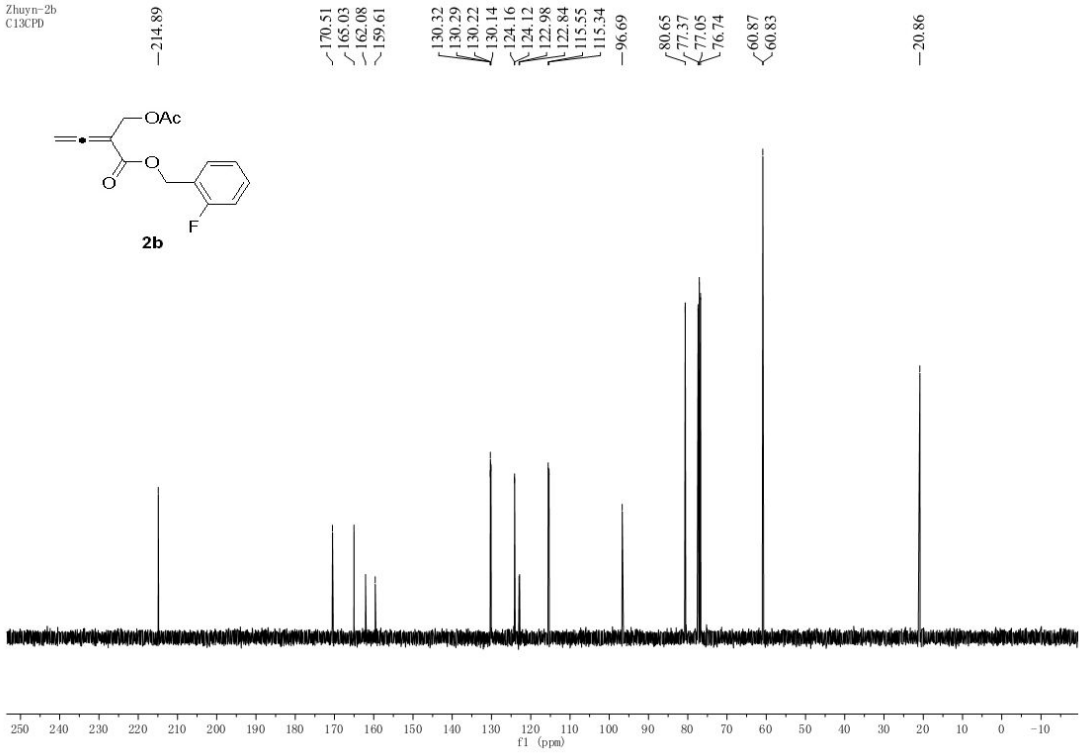
HRMS (ESI): m/z calcd for $C_{12}H_{11}O_2$ ($[M+H]^+$): 187.0754; found: 187.0759.

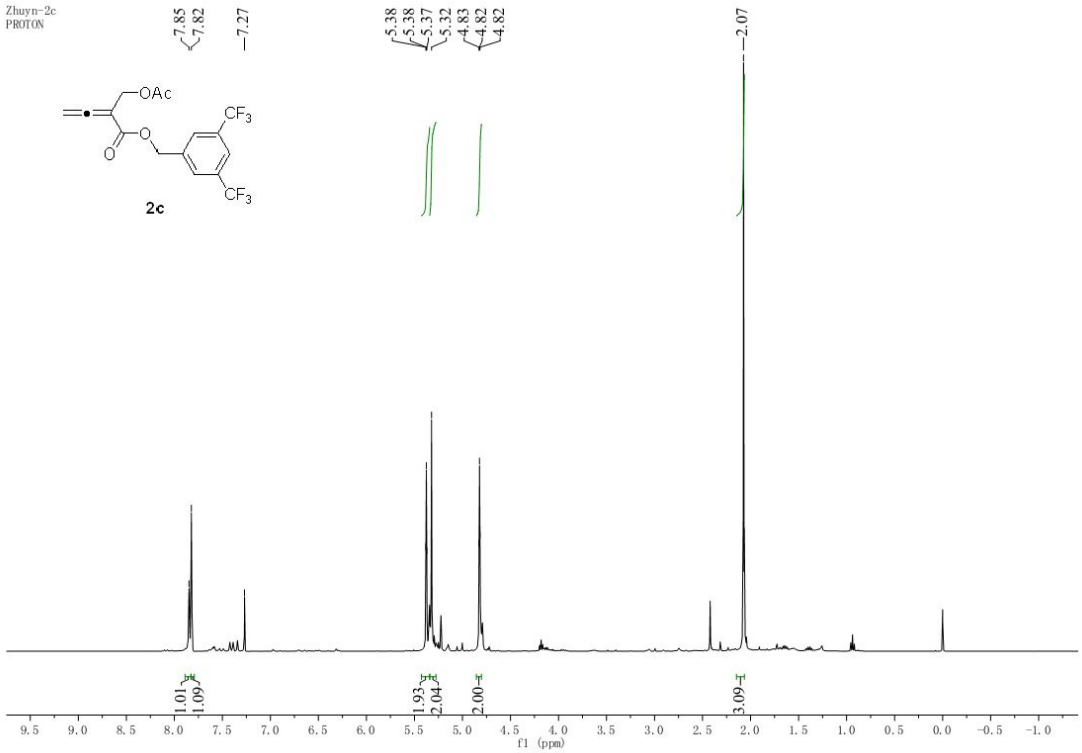
6. ^{1}H- and ^{13}C-NMR Spectra

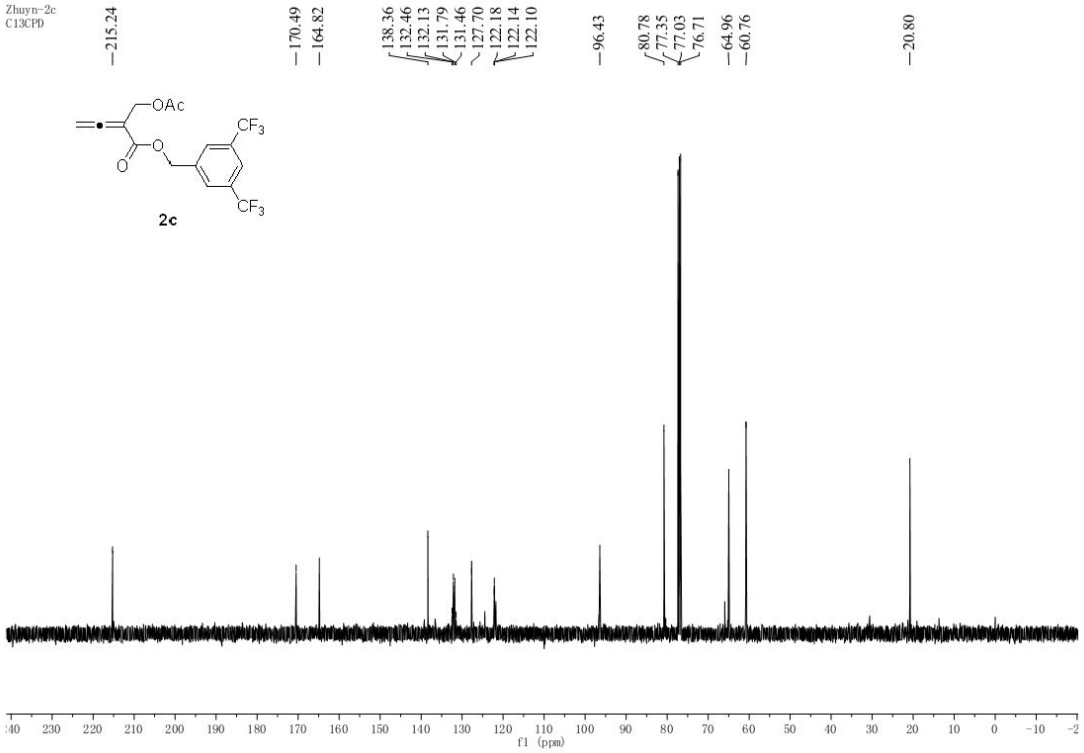


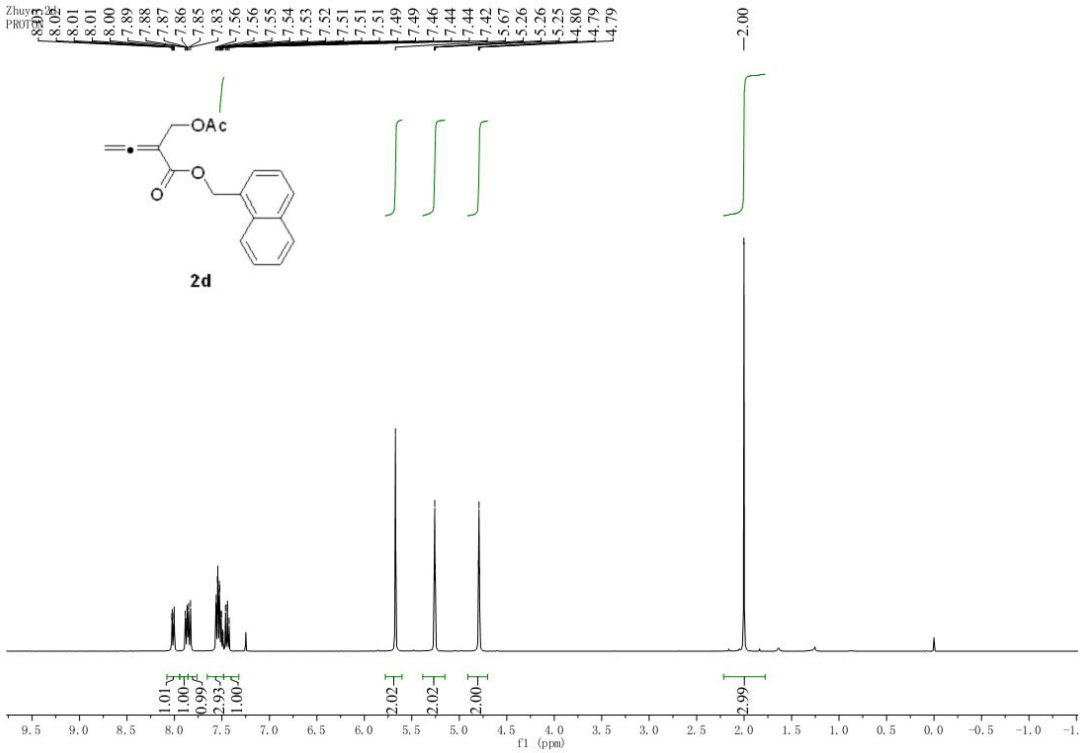

Zhuyn-2a
C13CPD
214.86
170.53
165.16
135.73
128.54
128.24
127.99
96.81
80.61
77.41
77.09
76.78
66.84
60.91
20.89
OAc
O
O
2a
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

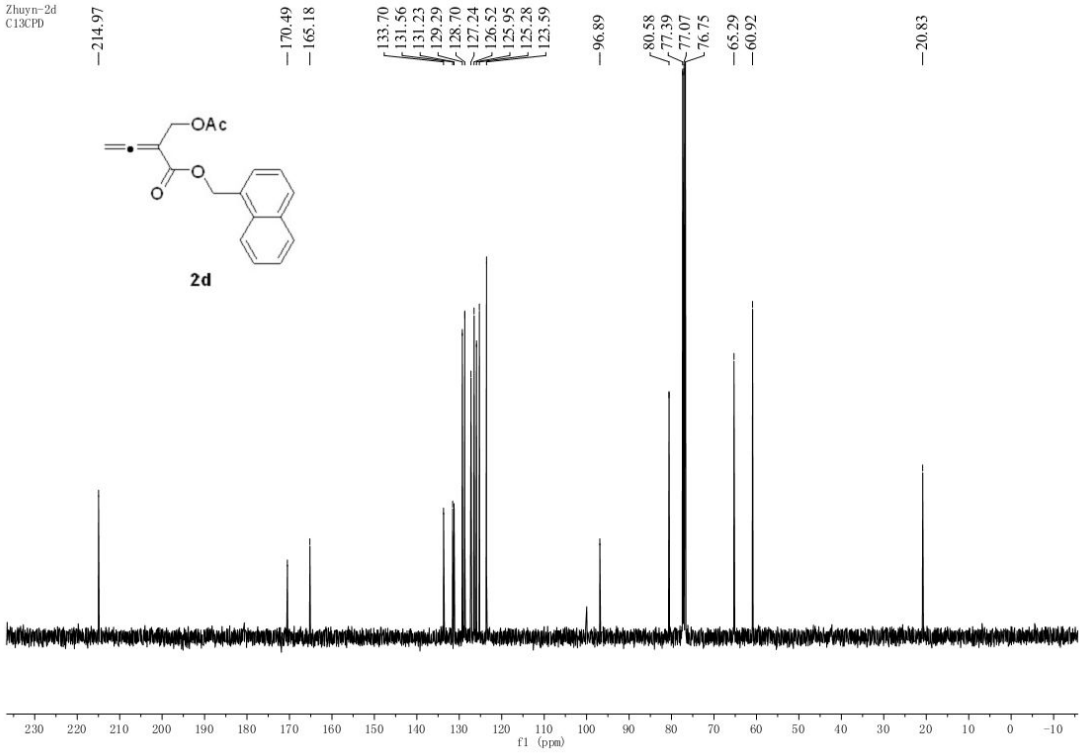

7.39
7.38
7.37
7.35
7.34
7.34
7.33
7.32
7.32
7.31
7.30
7.30
7.29
7.16
7.16
7.14
7.14
7.12
7.12
7.09
7.09
7.07
7.07
7.06
7.05
7.04
5.32
5.31
5.31
5.29
5.28
4.81
4.80
4.80
2.06
OAc
O
O
F
2b
0.99
0.95
1.00
0.95
2.02
2.00
2.00
3.10
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

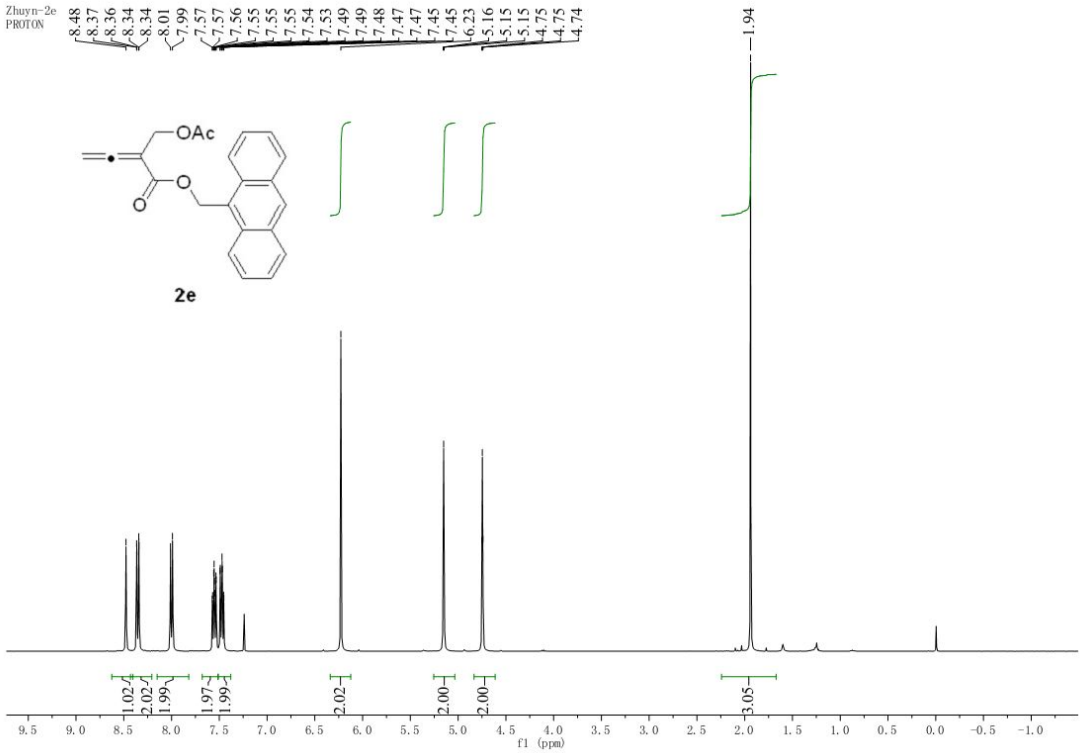

Zhuyn-2b
C13CPD
214.89
170.51
165.03
162.08
159.61
130.32
130.29
130.22
130.14
124.16
124.12
122.98
122.84
115.55
115.34
96.69
80.65
77.37
77.05
76.74
60.87
60.83
20.86
OAc
O
O
F
2b
f1 (ppm)

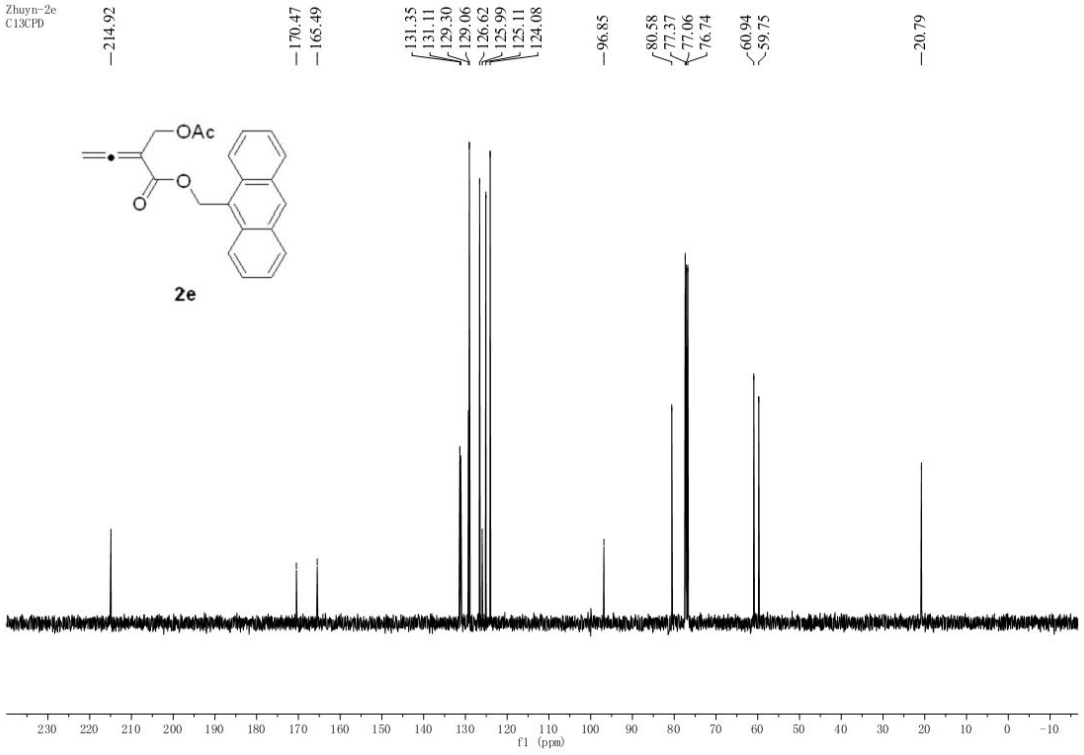

Zhuyn-2c
PROTON
7.85
7.82
7.27
5.38
5.38
5.37
5.32
4.83
4.82
4.82
2.07
OAc
O
O
CF3
CF3
2c
1.01
1.09
1.93
2.04
2.00
3.09
f1 (ppm)

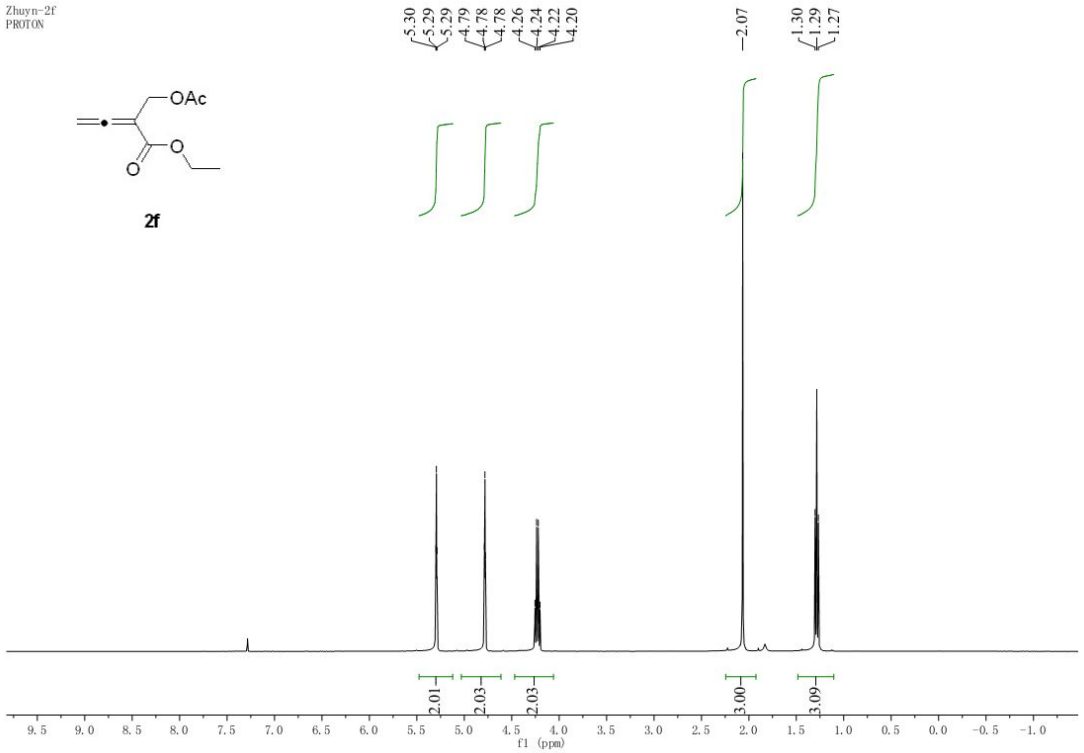

Zhuyn-2c
C13CPD
215.24
170.49
164.82
138.36
132.46
132.13
131.79
131.46
127.70
122.18
122.14
122.10
96.43
80.78
77.35
77.03
76.71
64.96
60.76
20.80
OAc
CF3
CF3
O
O
2c
f1 (ppm)

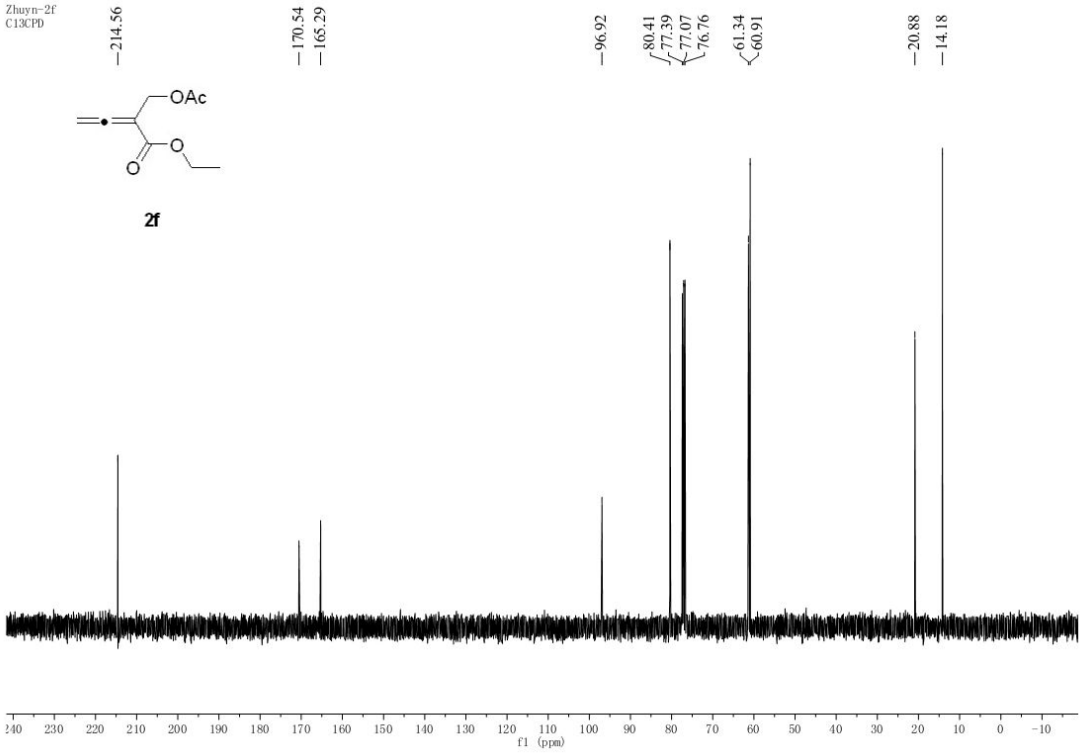

8.02
8.01
8.01
8.00
7.89
7.88
7.87
7.86
7.85
7.83
7.56
7.56
7.55
7.54
7.53
7.52
7.51
7.51
7.51
7.49
7.49
7.46
7.44
7.44
7.42
5.67
5.26
5.25
4.80
4.79
4.79
2.00
OAc
O
O
2d
1.01
1.00
0.99
2.93
1.00
2.02
2.02
2.00
2.99
f1 (ppm)

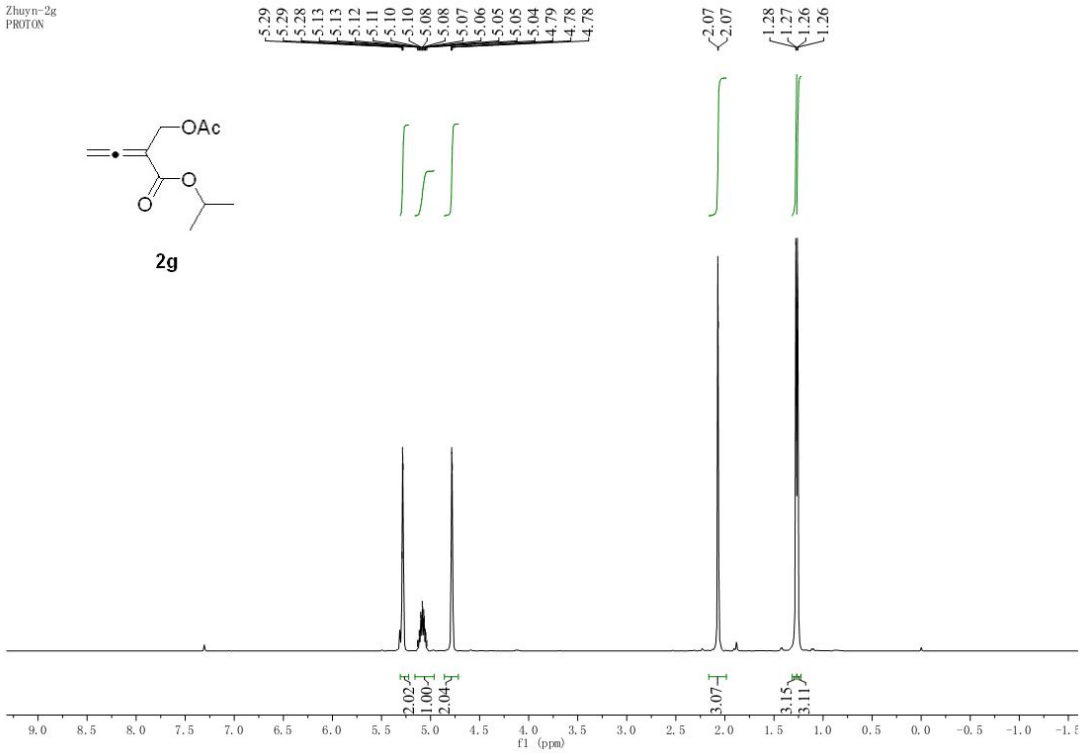

Zhuyn-2d
C13CPD
214.97
170.49
165.18
133.70
131.56
131.23
129.29
128.70
127.24
126.52
125.95
125.28
123.59
96.89
80.58
77.39
77.07
76.75
65.29
60.92
20.83
OAc
O
O
2d
f1 (ppm)

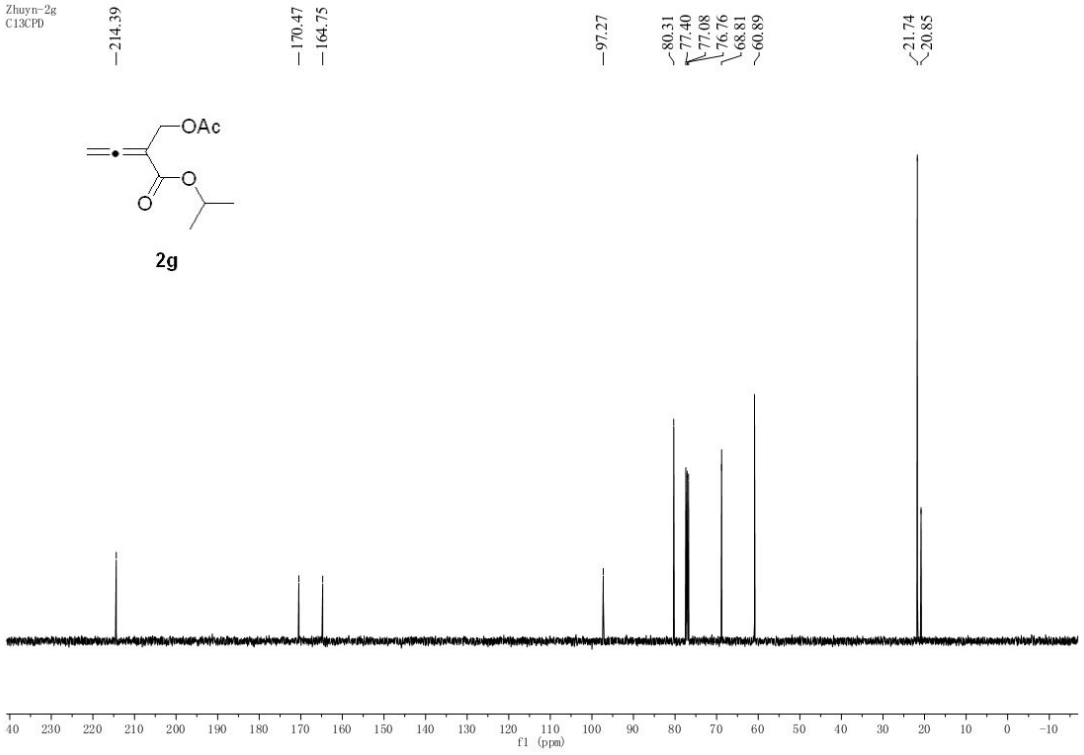

Zhuyn-2e
PROTON
8.48
8.37
8.36
8.34
8.34
8.01
7.99
7.57
7.57
7.56
7.55
7.55
7.55
7.54
7.53
7.49
7.49
7.48
7.47
7.47
7.45
7.45
6.23
5.16
5.15
5.15
4.75
4.75
4.74
1.94
OAc
O
O
2e
1.02
2.02
1.99
1.97
1.99
2.02
2.00
2.00
3.05
f1 (ppm)

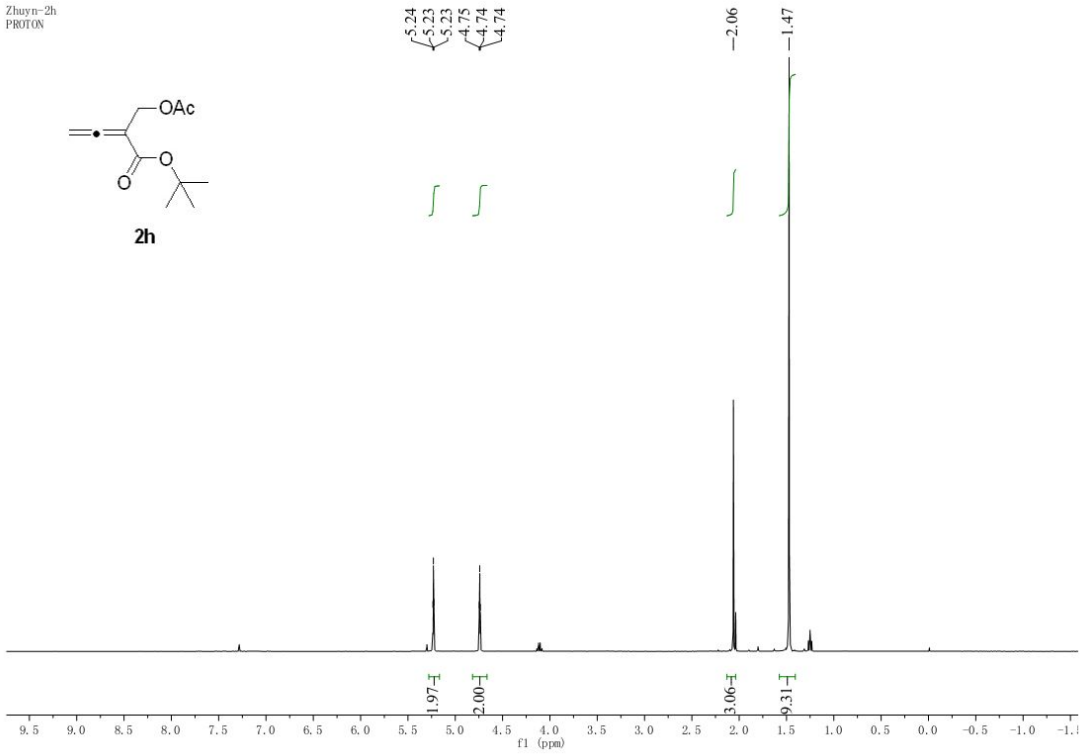

Zhuyn-2e
C13CPD
214.92
170.47
165.49
131.35
131.11
129.30
129.06
126.62
125.99
125.11
124.08
96.85
80.58
77.37
77.06
76.74
60.94
59.75
20.79
OAc
O
O
2e
f1 (ppm)

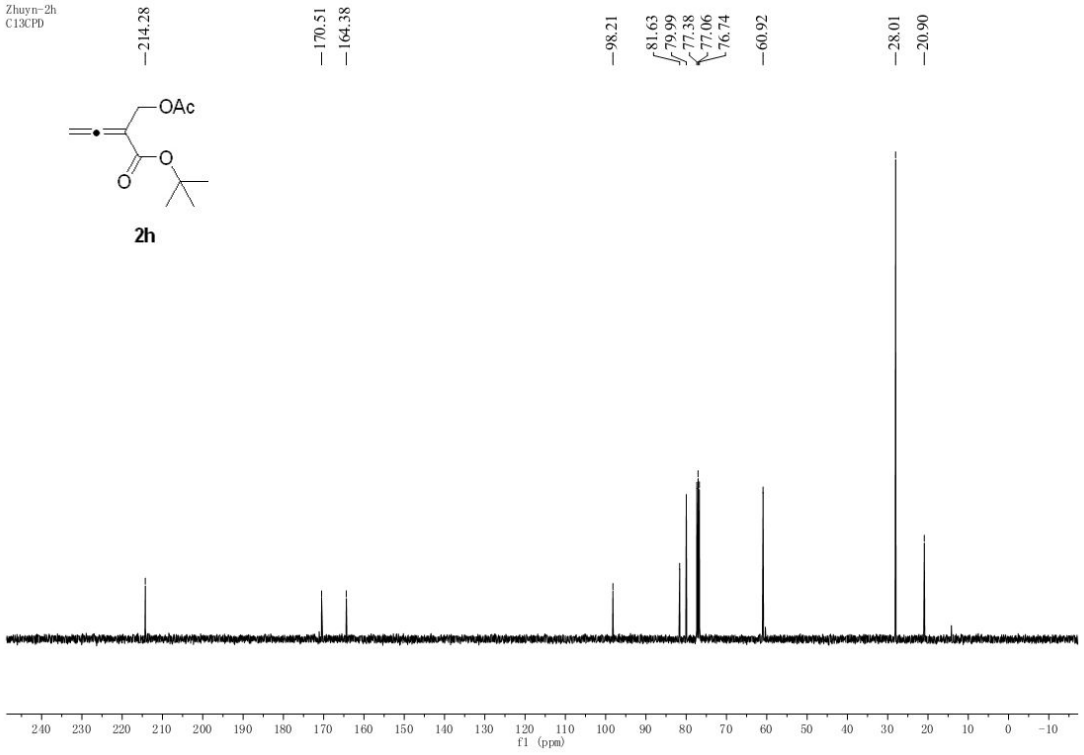

Zhuyn-2f
PROTON
5.30
5.29
5.29
4.79
4.78
4.78
4.26
4.24
4.22
4.20
2.07
1.30
1.29
1.27
OAc
O
O
2f
2.01
2.03
2.03
3.00
3.09
f1 (ppm)

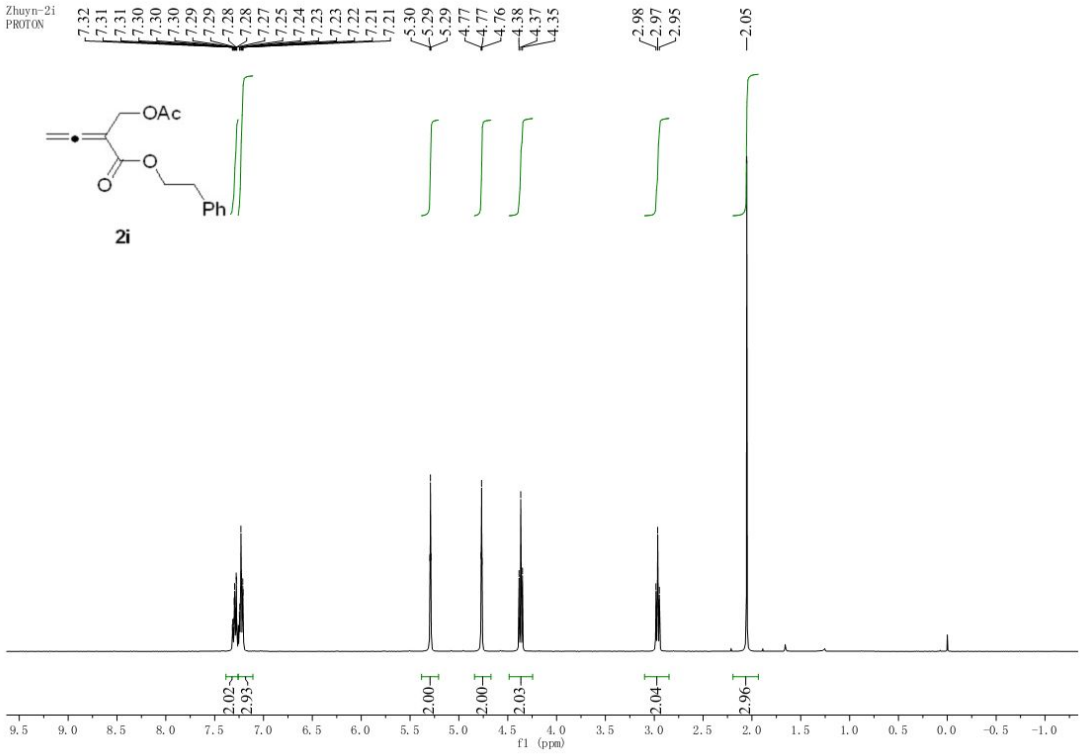

Zhuyn-2f
C13CPD
214.56
170.54
165.29
96.92
80.41
77.39
77.07
76.76
61.34
60.91
20.88
14.18
OAc
O
O
2f
f1 (ppm)

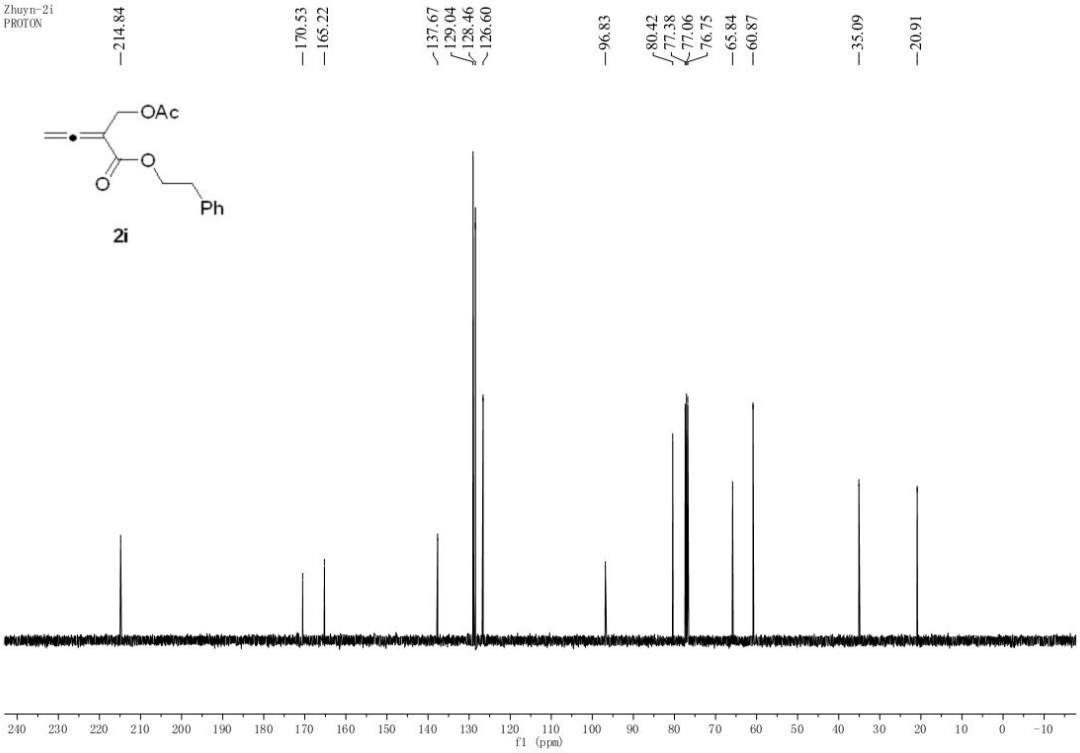

Zhuyn-2g
PROTON
5.29
5.29
5.28
5.13
5.13
5.12
5.11
5.10
5.10
5.08
5.08
5.07
5.06
5.05
5.05
5.04
4.79
4.78
4.78
2.07
2.07
1.28
1.27
1.26
1.26
OAc
O
O
2g
2.02
1.00
2.04
3.07
3.15
3.11
f1 (ppm)

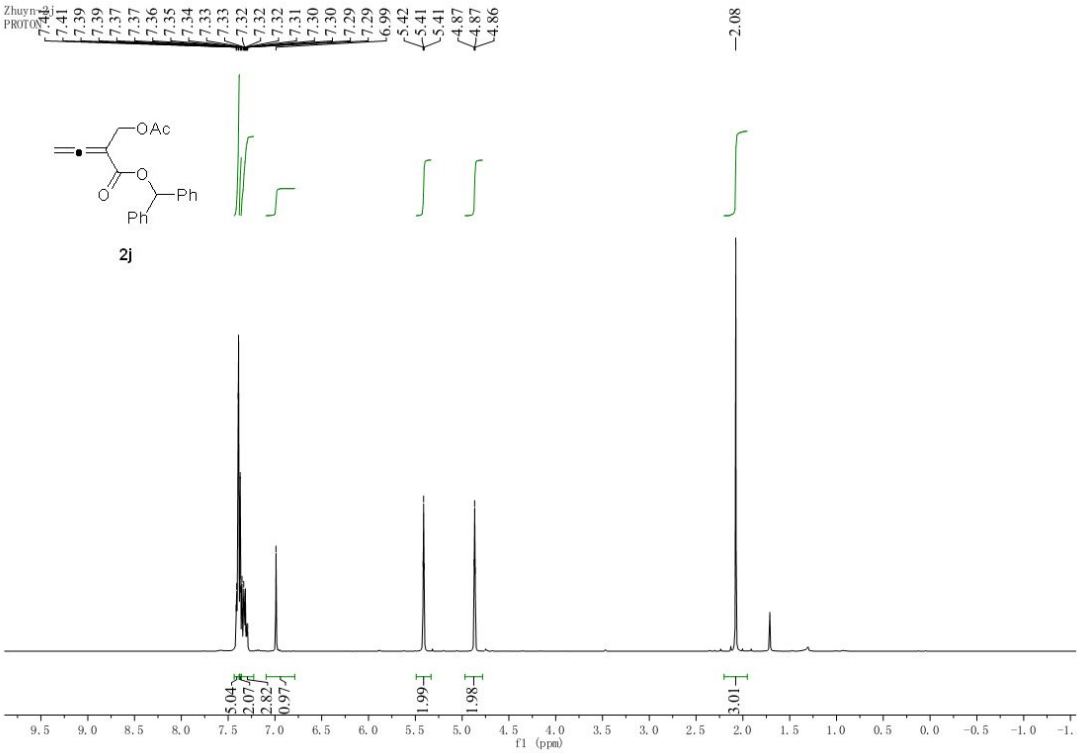

Zhuyn-2g
C13CPD
214.39
170.47
164.75
97.27
80.31
77.40
77.08
76.76
68.81
60.89
21.74
20.85
OAc
O
O
2g
f1 (ppm)

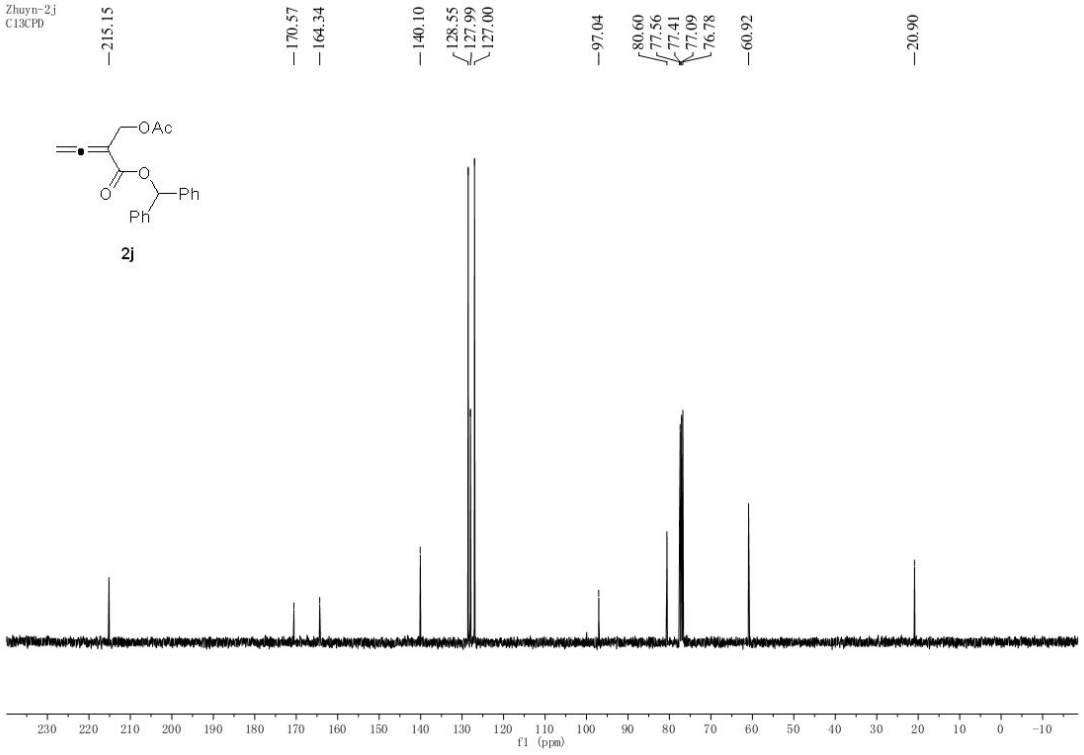

Zhuyn-2h
PROTON
5.24
5.23
5.23
4.75
4.74
4.74
2.06
1.47
OAc
O
O
2h
1.97
2.00
3.06
9.31
f1 (ppm)

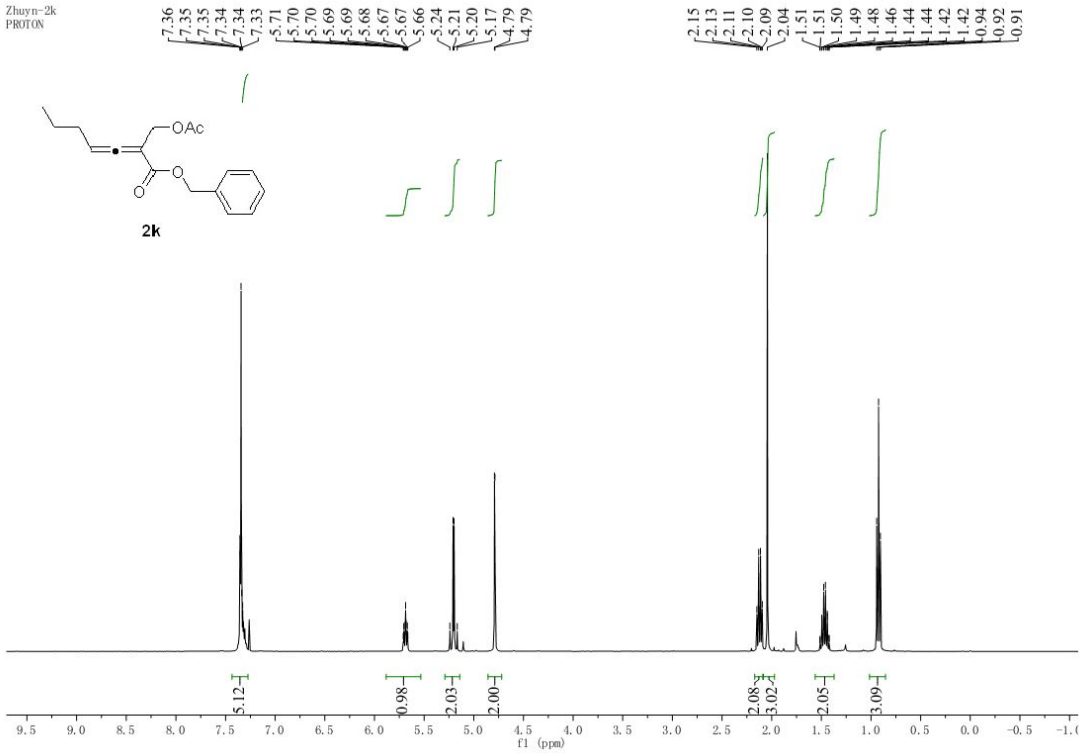

Zhuyn-2h
C13CPD
214.28
170.51
164.38
98.21
81.63
79.99
77.38
77.06
76.74
60.92
28.01
20.90
OAc
O
O
2h
f1 (ppm)

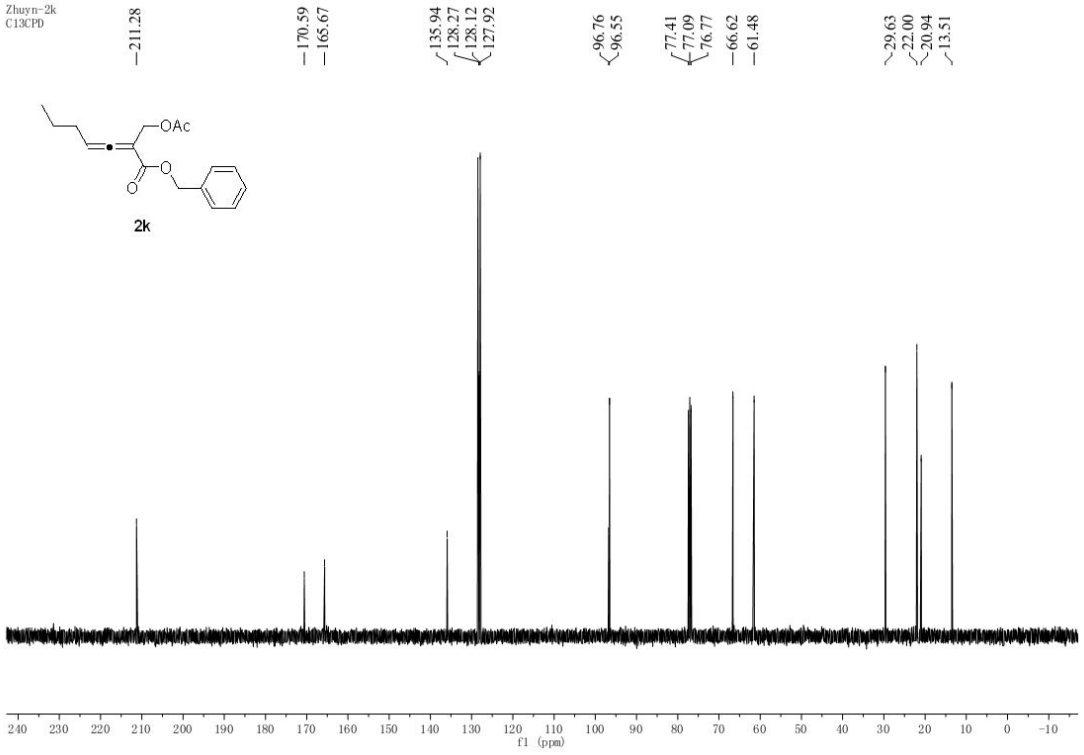

Zhuyn-2i
PROTON
7.32
7.31
7.31
7.30
7.30
7.30
7.29
7.29
7.28
7.28
7.27
7.25
7.24
7.23
7.23
7.22
7.21
7.21
5.30
5.29
5.29
4.77
4.77
4.76
4.38
4.37
4.35
2.98
2.97
2.95
2.05
OAc
O
O
Ph
2i
2.02
2.93
2.00
2.00
2.03
2.04
2.96
f1 (ppm)

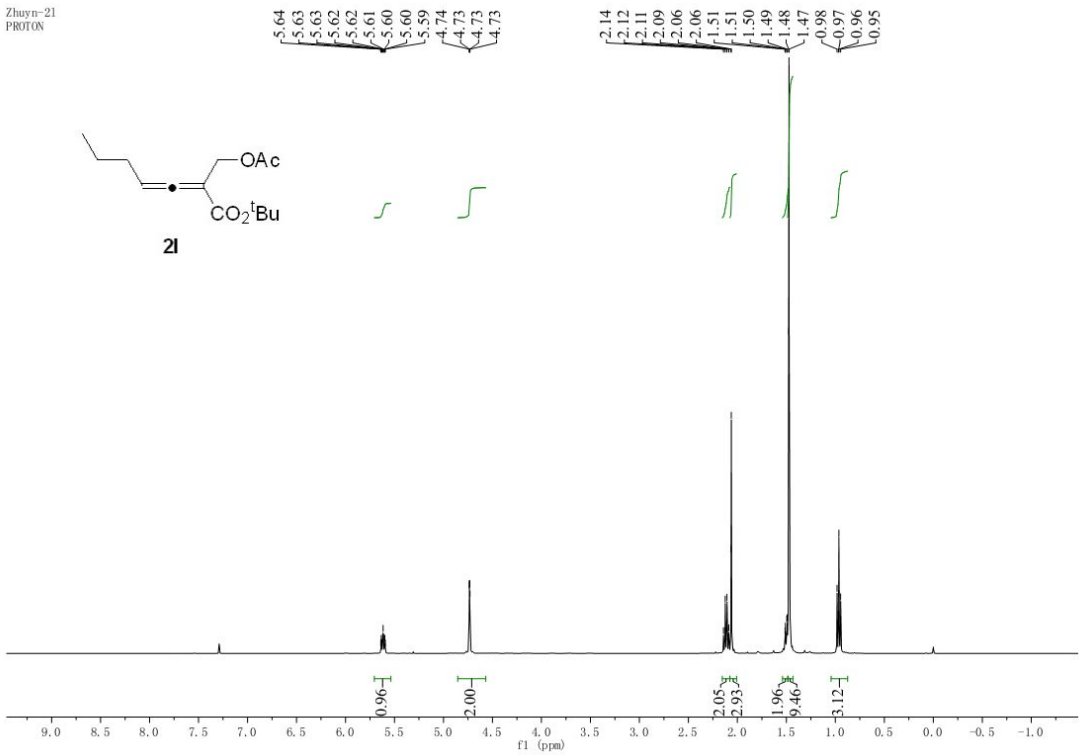

Zhuyn-2i
PROTON
214.84
170.53
165.22
137.67
129.04
128.46
126.60
96.83
80.42
77.38
77.06
76.75
65.84
60.87
35.09
20.91
OAc
O
O
Ph
2i
f1 (ppm)

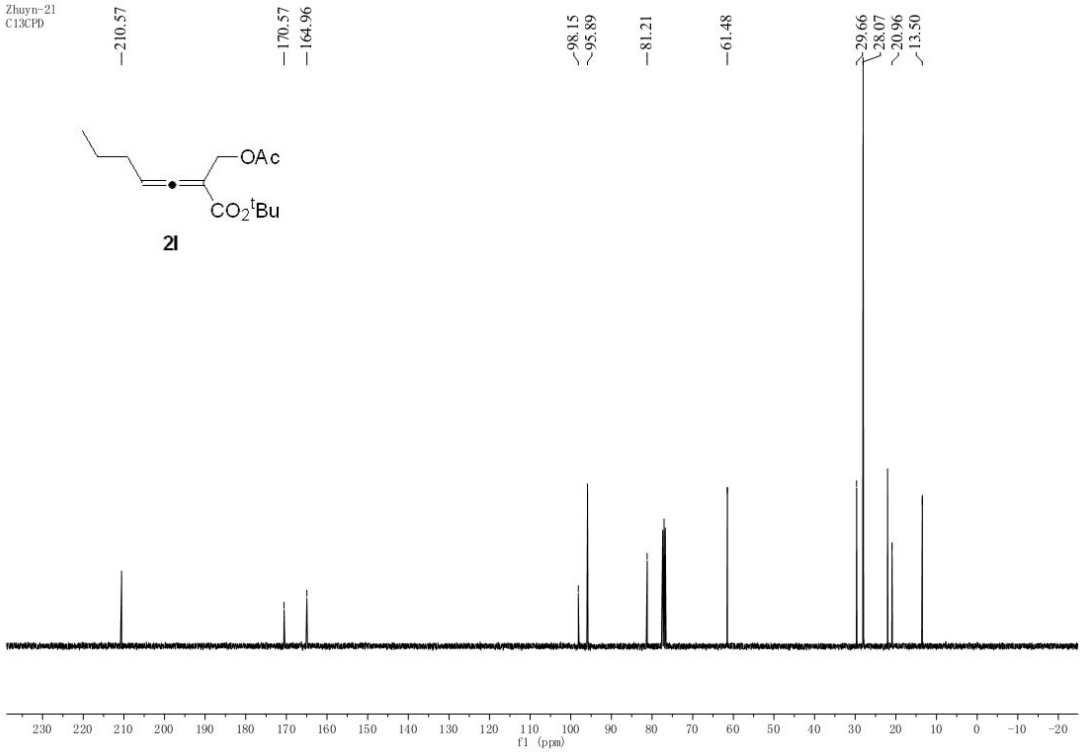

Zhuyn-4c
PROTON
7.41
7.39
7.39
7.37
7.37
7.36
7.35
7.34
7.33
7.32
7.32
7.32
7.31
7.30
7.30
7.29
7.29
6.99
5.42
5.41
5.41
4.87
4.87
4.86
2.08
OAc
O
O
Ph
Ph
2j
5.04
2.07
2.82
0.97
1.99
1.98
3.01
f1 (ppm)

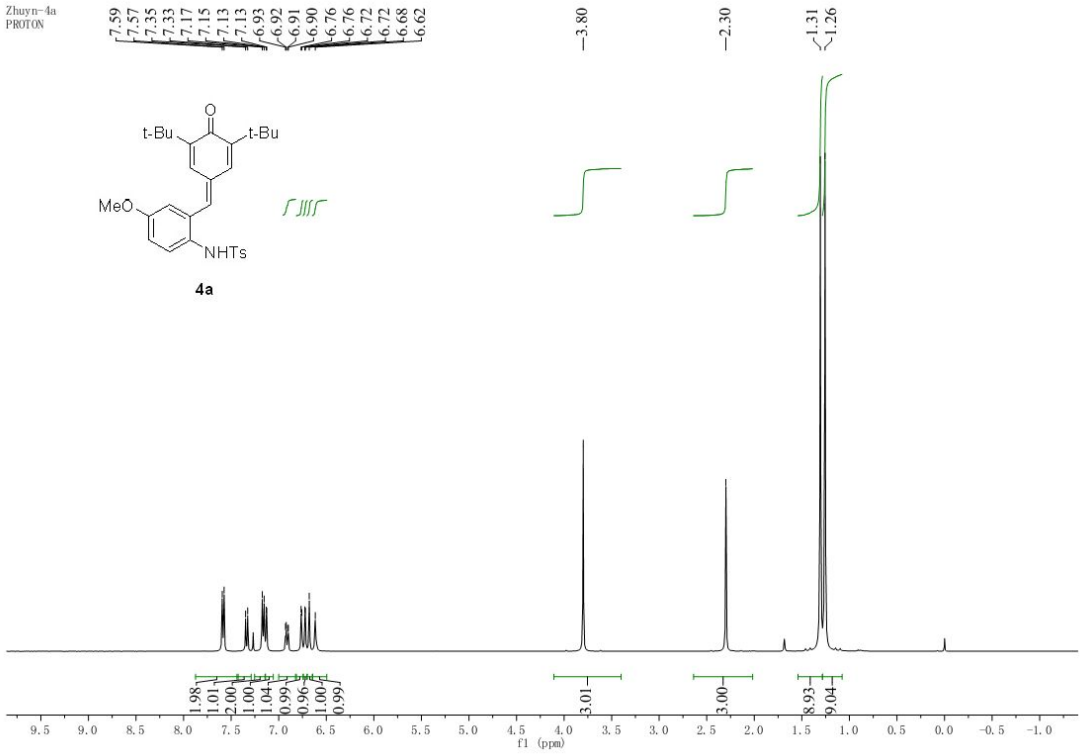

Zhuyn-2j
C13CPD
215.15
170.57
164.34
140.10
128.55
127.99
127.00
97.04
80.60
77.56
77.41
77.09
76.78
60.92
20.90
OAc
O
O
Ph
Ph
2j
f1 (ppm)

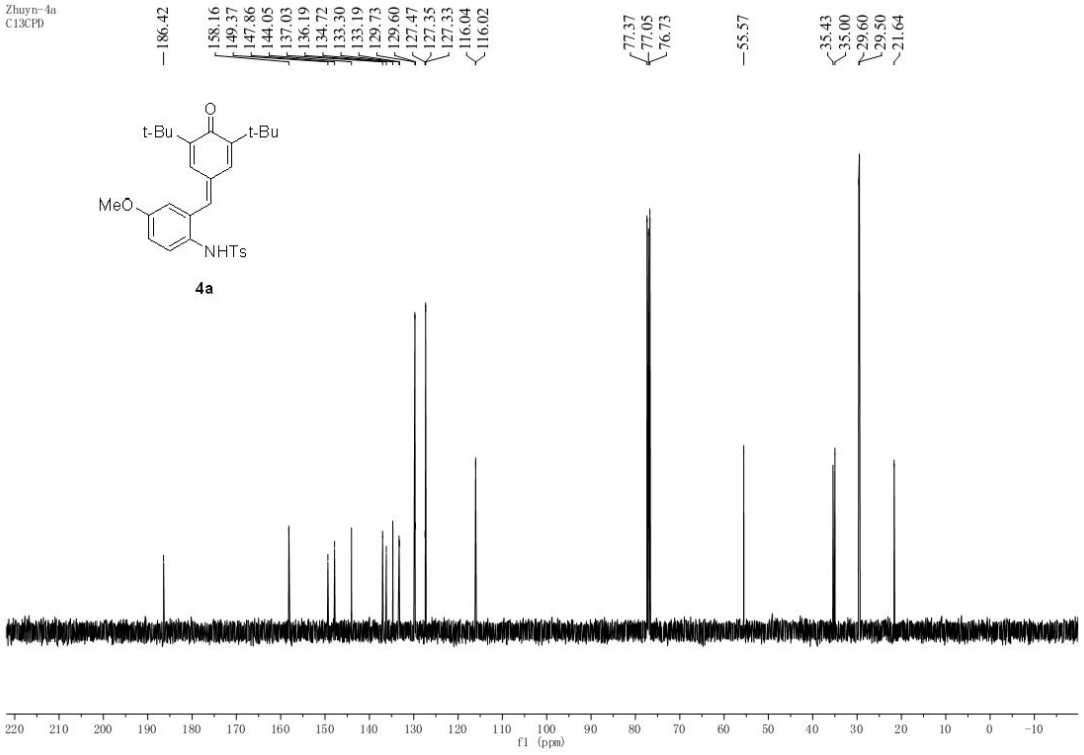

Zhuyn-2k
PROTON
7.36
7.35
7.35
7.34
7.34
7.33
5.71
5.70
5.70
5.69
5.69
5.68
5.67
5.67
5.66
5.24
5.21
5.20
5.17
4.79
4.79
2.15
2.13
2.11
2.10
2.09
2.04
1.51
1.51
1.50
1.49
1.48
1.46
1.44
1.44
1.42
1.42
0.94
0.92
0.91
OAc
O
O
2k
5.12
0.98
2.03
2.00
2.08
3.02
2.05
3.09
f1 (ppm)

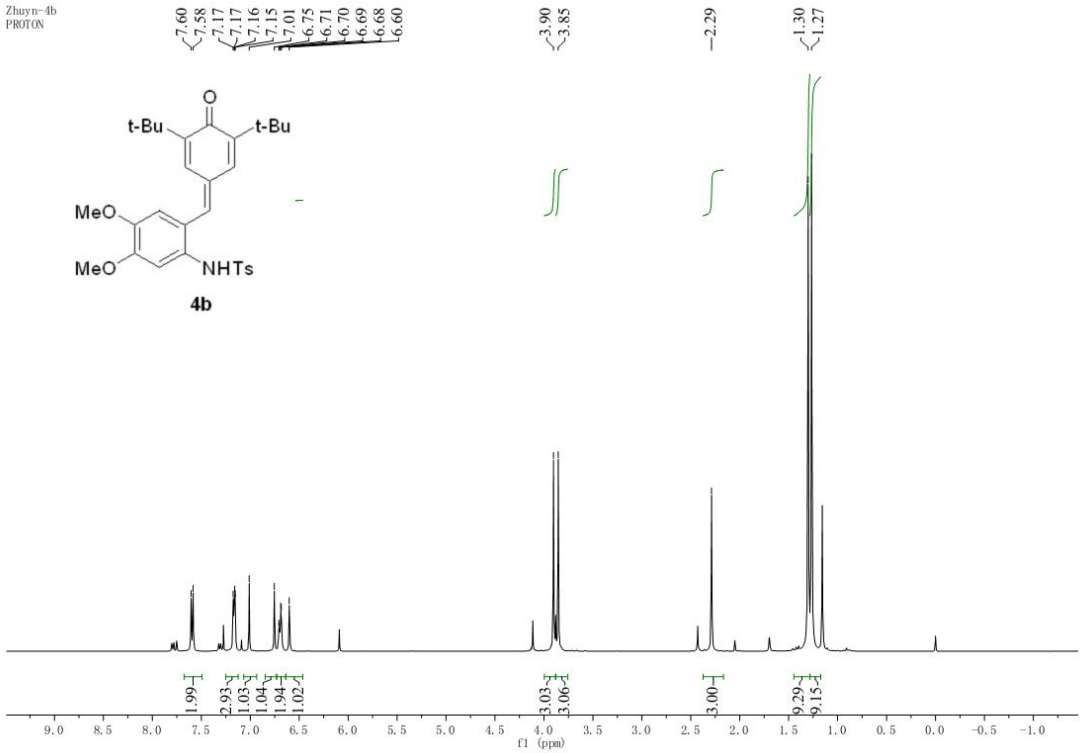

Zhuyn-2k
C13CPD
211.28
170.59
165.67
135.94
128.27
128.12
127.92
96.76
96.55
77.41
77.09
76.77
66.62
61.48
29.63
22.00
20.94
13.51
OAc
O
O
2k
f1 (ppm)

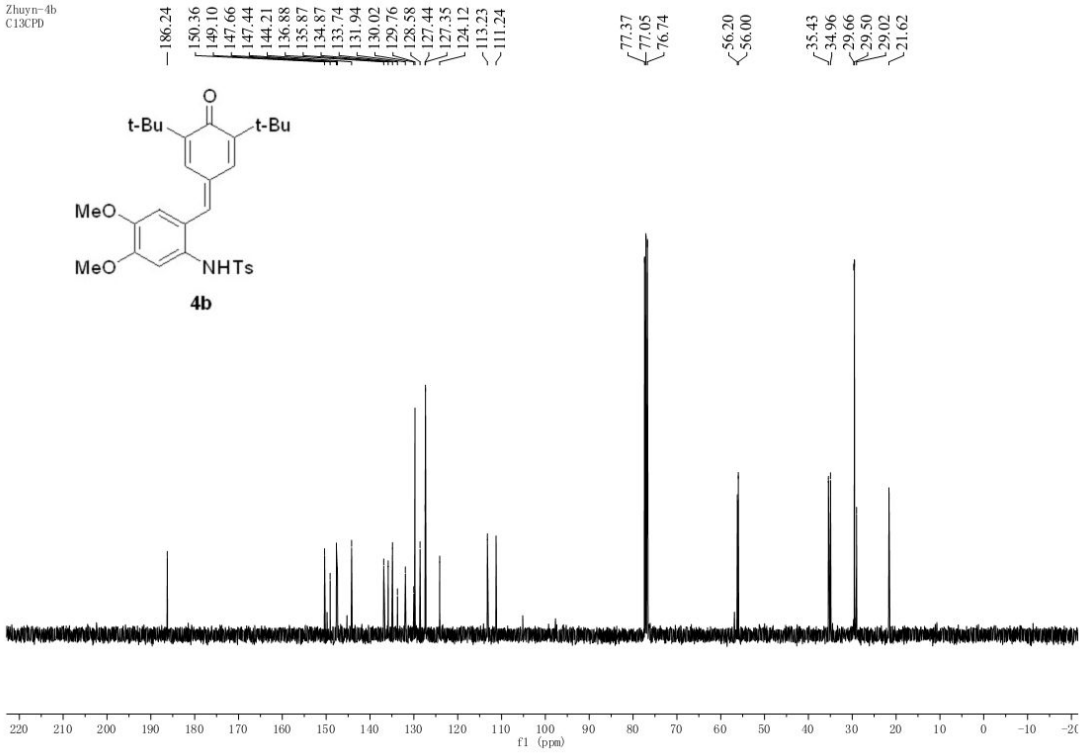

Zhuyn-21
PROTON
5.64
5.63
5.63
5.62
5.62
5.61
5.60
5.60
5.59
4.74
4.73
4.73
4.73
2.14
2.12
2.11
2.09
2.06
2.06
1.51
1.51
1.50
1.49
1.48
1.47
0.98
0.97
0.96
0.95
OAc
CO2tBu
2l
0.96
2.00
2.05
2.93
1.96
9.46
3.12
f1 (ppm)

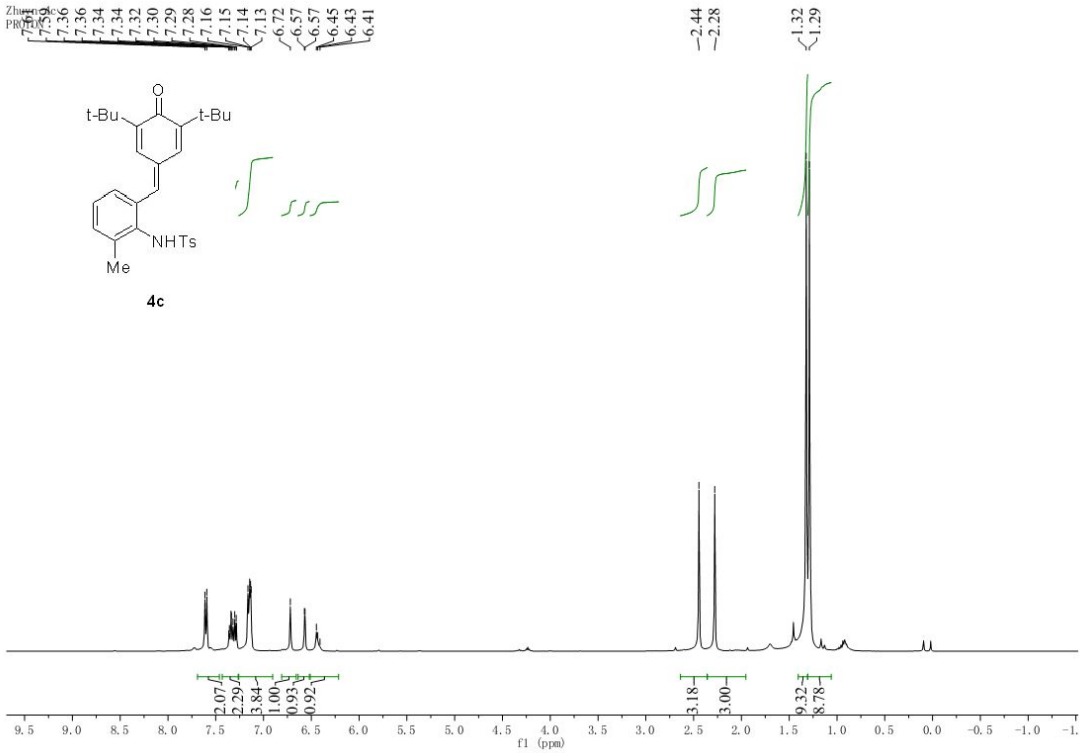

Zhuyn-21
C13CPD
210.57
170.57
164.96
98.15
95.89
81.21
61.48
29.66
28.07
20.96
13.50
OAc
CO2tBu
2l
f1 (ppm)

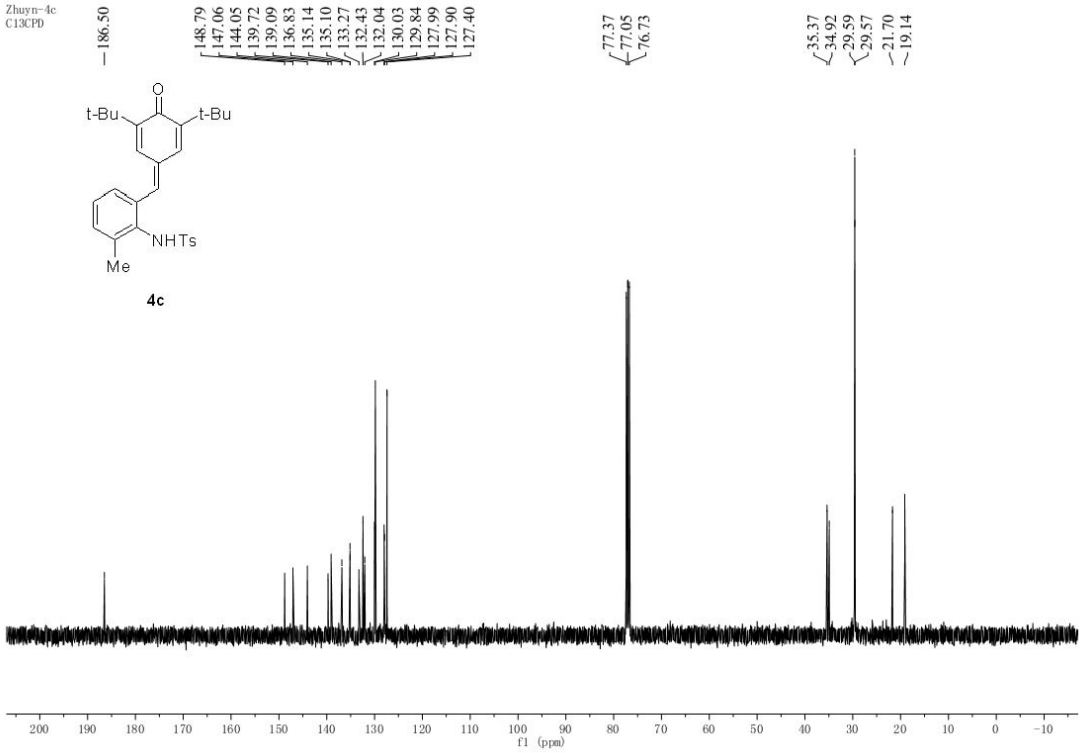

Zhuyn-4a
PROTON
7.59
7.57
7.35
7.33
7.17
7.15
7.13
7.13
6.93
6.92
6.91
6.90
6.76
6.76
6.72
6.72
6.68
6.62
3.80
2.30
1.31
1.26
t-Bu
t-Bu
MeO
NHTs
4a
1.98
1.01
2.00
1.00
1.04
0.99
0.96
1.00
0.99
3.01
3.00
8.93
9.04
f1 (ppm)

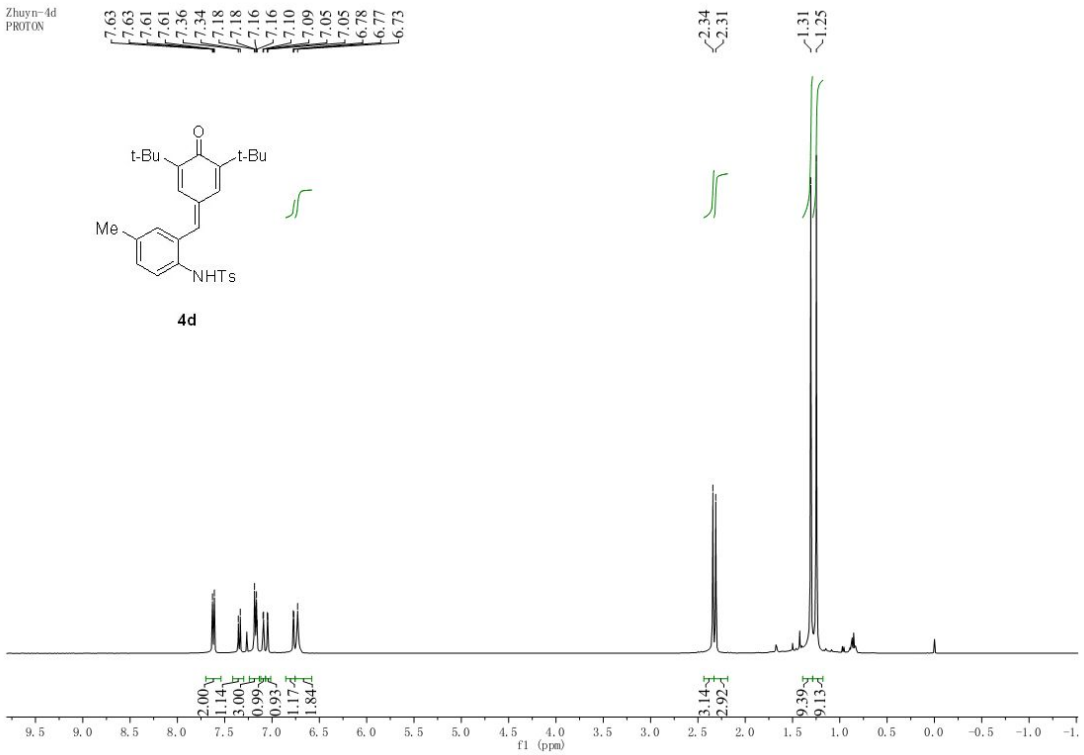

Zhuyn-4a
C13CPD
186.42
158.16
149.37
147.86
144.05
137.03
136.19
134.72
133.30
133.19
129.73
129.60
127.47
127.35
127.33
116.04
116.02
77.37
77.05
76.73
55.57
35.43
35.00
29.60
29.50
21.64
t-Bu
t-Bu
MeO
NHTs
4a
f1 (ppm)

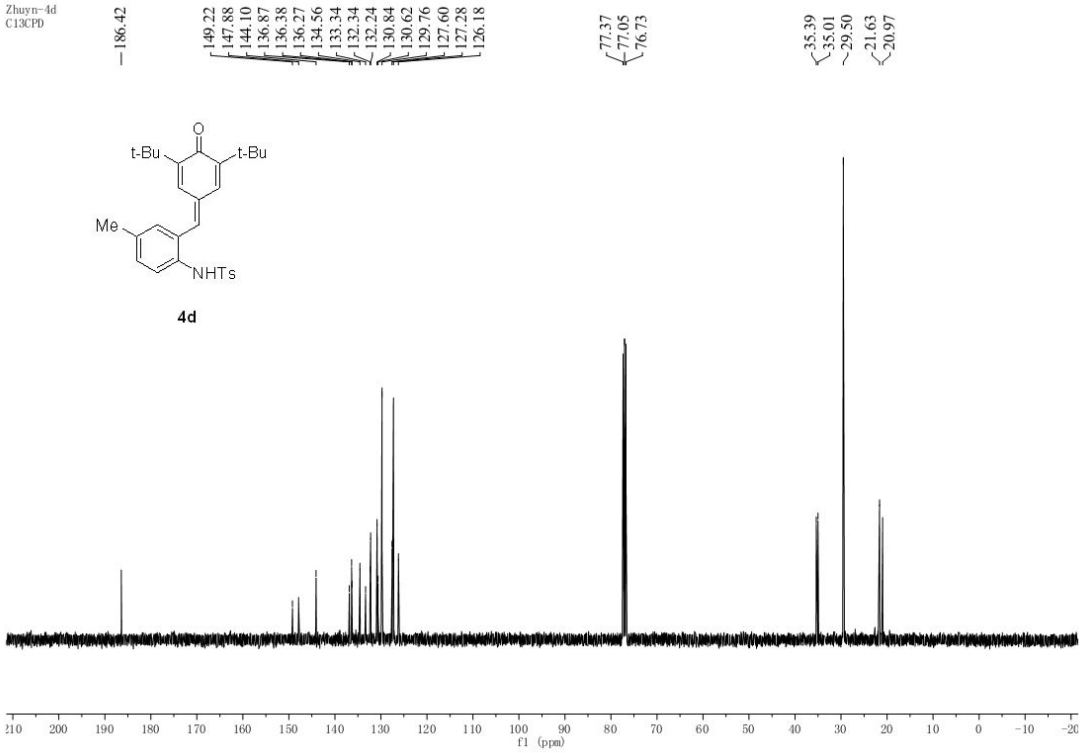

Zhuyn-4b
PROTON
7.60
7.58
7.17
7.17
7.16
7.15
7.01
6.75
6.71
6.70
6.69
6.68
6.60
3.90
3.85
2.29
1.30
1.27
t-Bu
t-Bu
MeO
MeO
NHTs
4b
1.99
2.93
1.03
1.04
1.94
1.02
3.03
3.06
3.00
9.29
9.15
f1 (ppm)

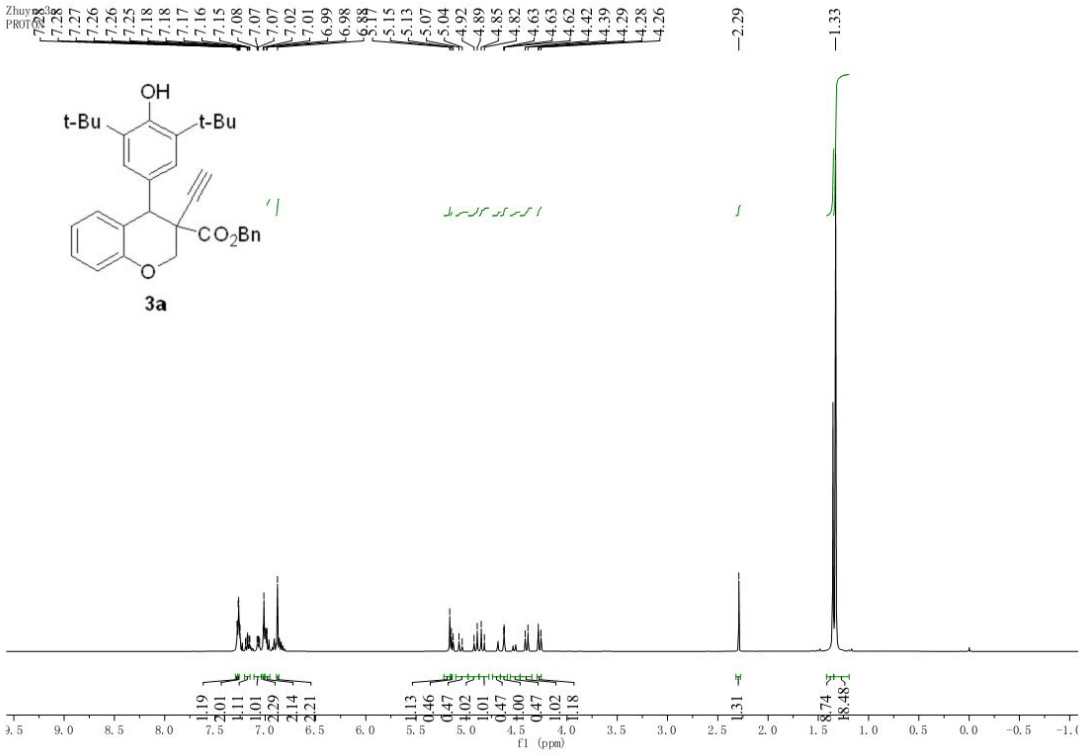

Zhuyn-4b
C13CPD
186.24
150.36
149.10
147.66
147.44
144.21
136.88
135.87
134.87
133.74
131.94
130.02
129.76
128.58
127.44
127.35
124.12
113.23
111.24
77.37
77.05
76.74
56.20
56.00
35.43
34.96
29.66
29.50
29.02
21.62
t-Bu
t-Bu
MeO
MeO
NHTs
4b
f1 (ppm)

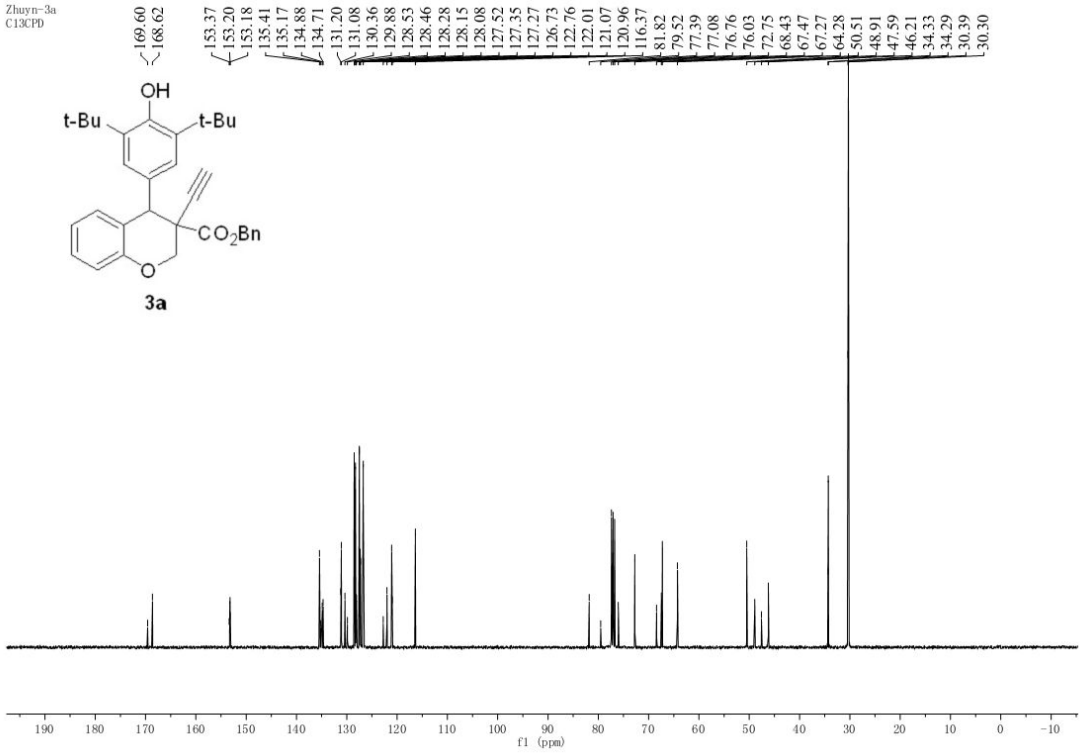

7.36
7.34
7.32
7.30
7.29
7.28
7.16
7.15
7.14
7.13
6.72
6.57
6.57
6.45
6.43
6.41
2.44
2.28
1.32
1.29
t-Bu
t-Bu
NHTs
Me
4c
2.07
2.29
3.84
1.00
0.93
0.92
3.18
3.00
9.32
8.78
f1 (ppm)

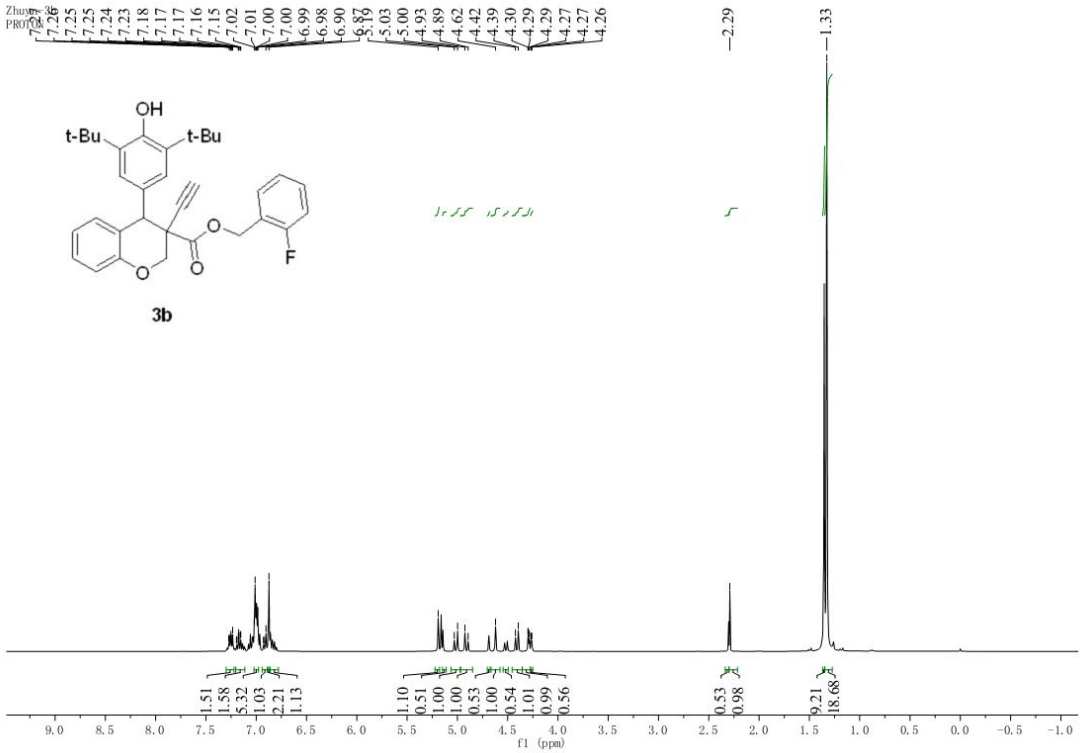

Zhuyn-4c
C13CPD
186.50
148.79
147.06
144.05
139.72
139.09
136.83
135.14
135.10
133.27
132.43
132.04
130.03
129.84
127.99
127.90
127.40
77.37
77.05
76.73
35.37
34.92
29.59
29.57
21.70
19.14
t-Bu
t-Bu
NHTs
Me
4c
f1 (ppm)

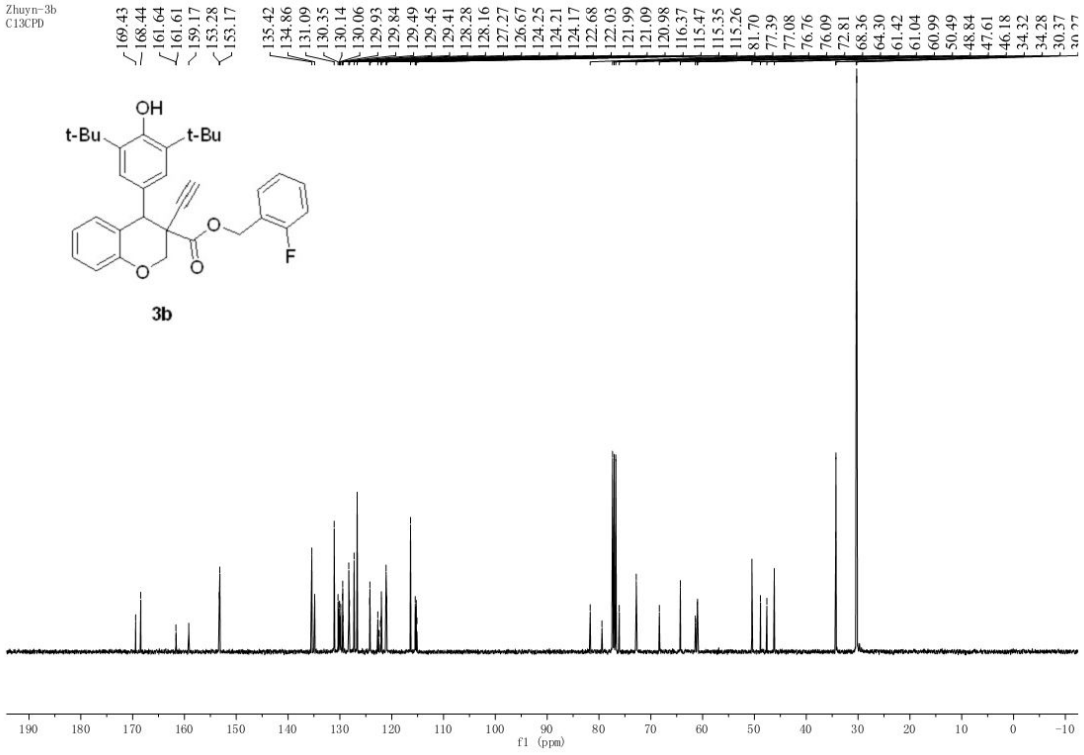

Zhuyn-4d
PROTON
7.63
7.63
7.61
7.61
7.36
7.34
7.18
7.18
7.16
7.16
7.10
7.09
7.05
7.05
6.78
6.77
6.73
2.34
2.31
1.31
1.25
t-Bu
t-Bu
Me
NHTs
4d
2.00
1.14
3.00
0.99
0.93
1.17
1.84
3.14
2.92
9.39
9.13
f1 (ppm)

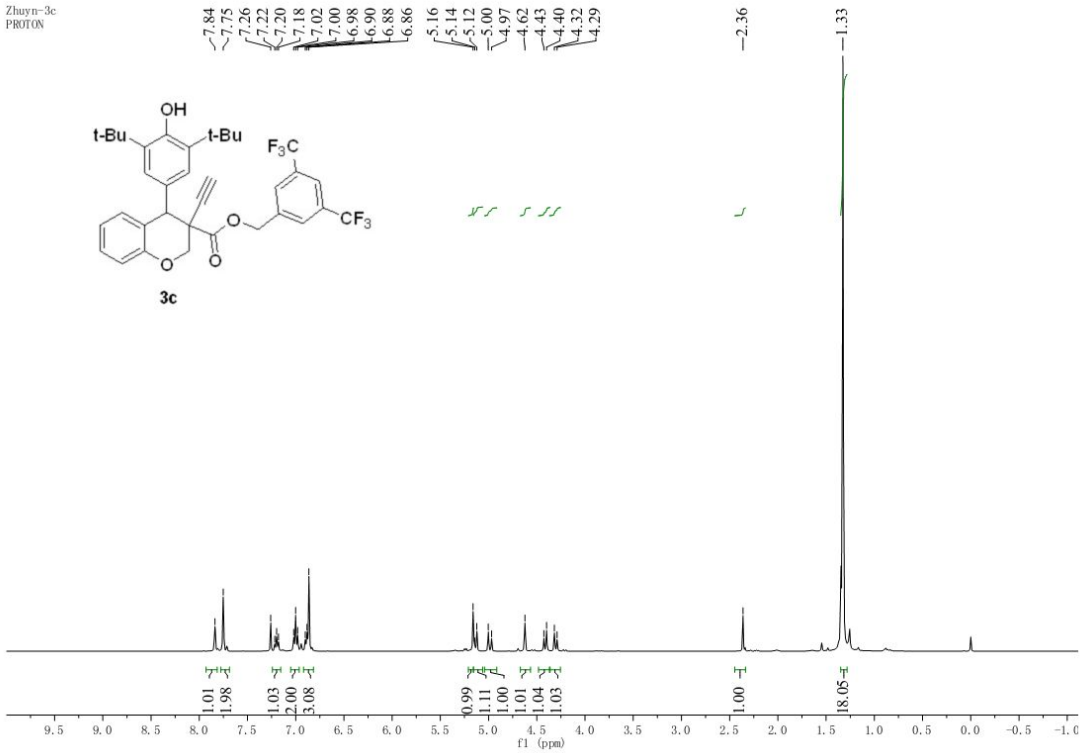

Zhuyn-4d
C13CPD
186.42
149.22
147.88
144.10
136.87
136.38
136.27
134.56
133.34
132.34
132.24
130.84
130.62
129.76
127.60
127.28
126.18
77.37
77.05
76.73
35.39
35.01
29.50
21.63
20.97
t-Bu
t-Bu
Me
NHTs
4d
f1 (ppm)

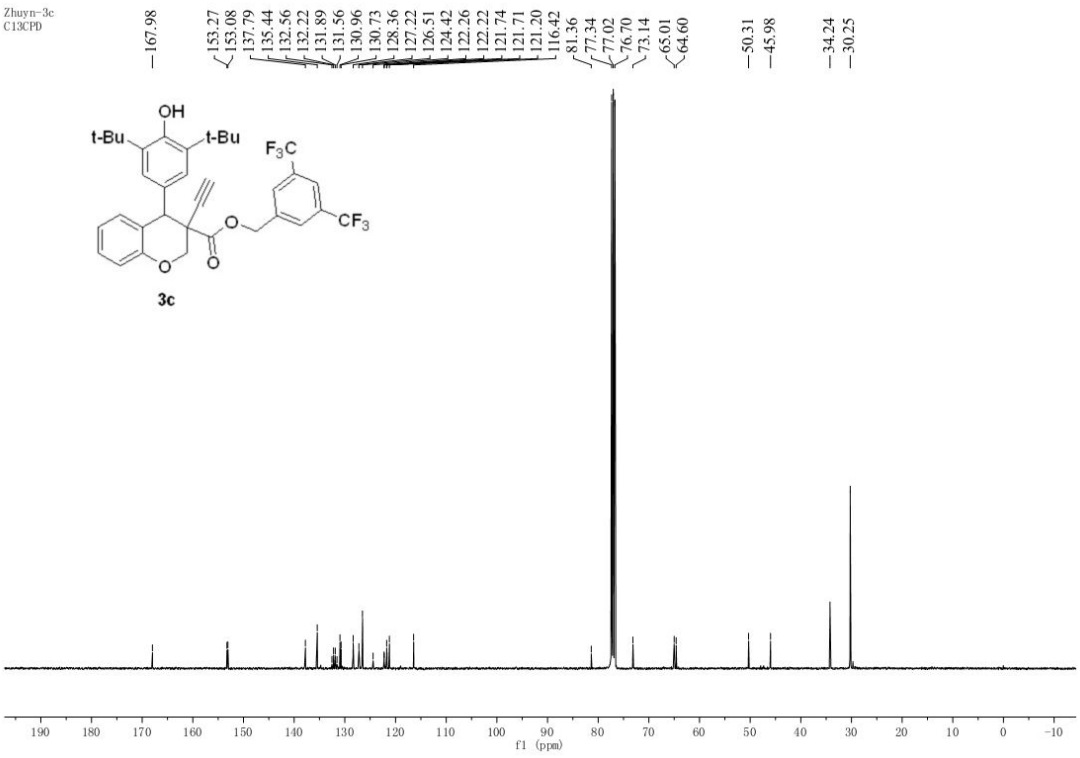

7.28
7.27
7.26
7.25
7.18
7.17
7.16
7.15
7.08
7.07
7.02
7.01
6.99
6.98
5.15
5.13
5.07
5.04
4.92
4.89
4.85
4.82
4.63
4.62
4.42
4.39
4.29
4.28
4.26
2.29
1.33
OH
t-Bu
t-Bu
CO2Bn
O
3a
1.19
2.01
1.11
1.01
2.29
2.14
2.21
1.13
0.46
0.47
4.02
1.01
0.47
1.00
0.47
1.02
1.18
1.31
8.74
18.48
f1 (ppm)

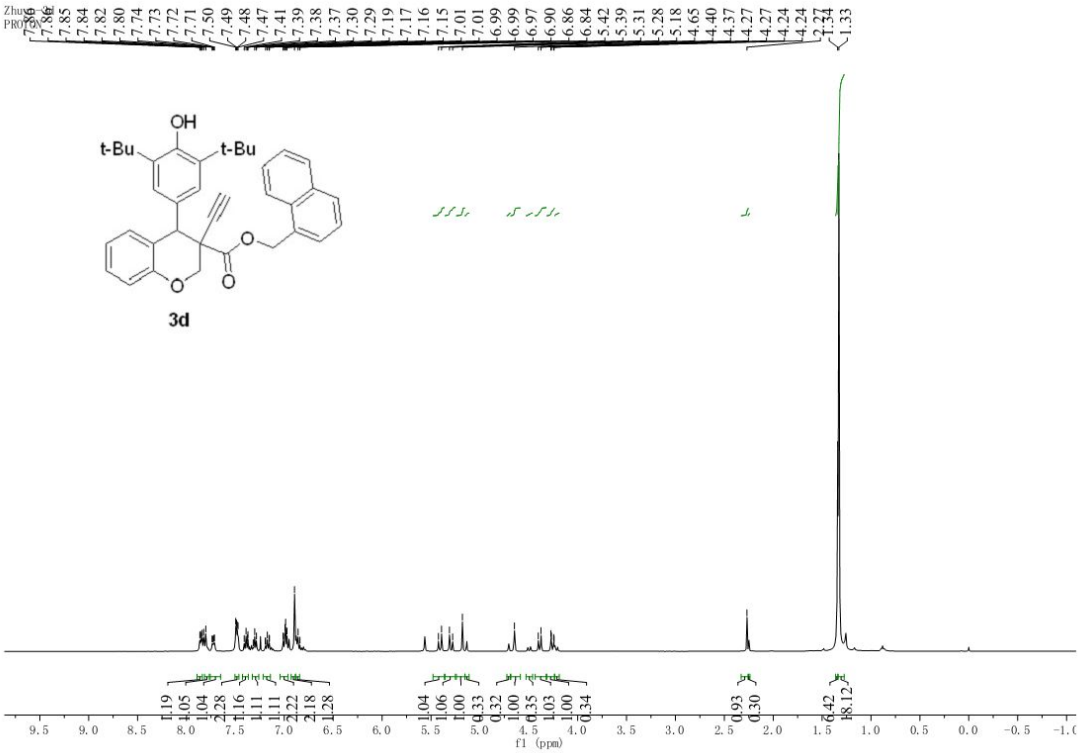

Zhuyn-3a
C13CPD
169.60
168.62
153.37
153.20
153.18
135.41
135.17
134.88
134.71
131.20
131.08
130.36
129.88
128.53
128.46
128.28
128.15
128.08
127.52
127.35
127.27
126.73
122.76
122.01
121.07
120.96
116.37
81.82
79.52
77.39
77.08
76.76
76.03
72.75
68.43
67.47
67.27
64.28
50.51
48.91
47.59
46.21
34.33
34.29
30.39
30.30
OH
t-Bu
t-Bu
CO2Bn
O
3a
f1 (ppm)

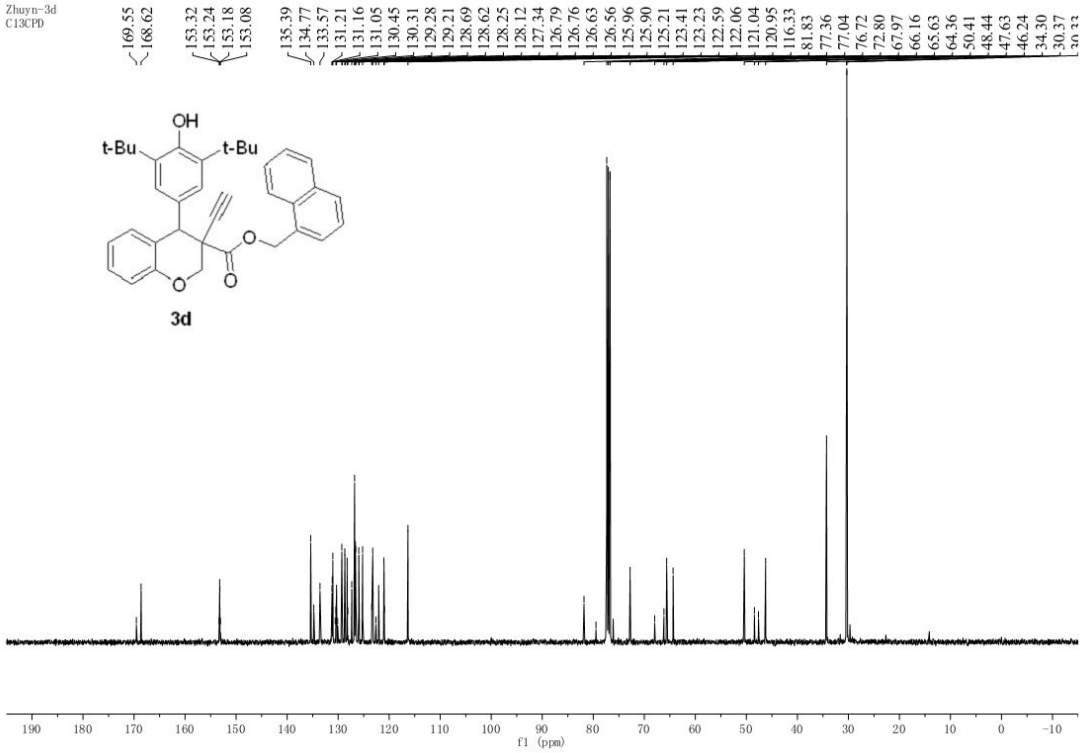

7.26
7.25
7.24
7.23
7.18
7.17
7.16
7.15
7.02
7.01
7.00
6.99
6.98
6.90
5.03
5.00
4.93
4.89
4.62
4.42
4.39
4.30
4.29
4.27
4.26
2.29
1.33
OH
t-Bu
t-Bu
O
F
3b
1.51
1.58
5.32
1.03
2.21
1.13
1.10
0.51
1.00
1.00
0.53
1.00
0.54
1.01
0.99
0.56
0.53
0.98
9.21
18.68
f1 (ppm)

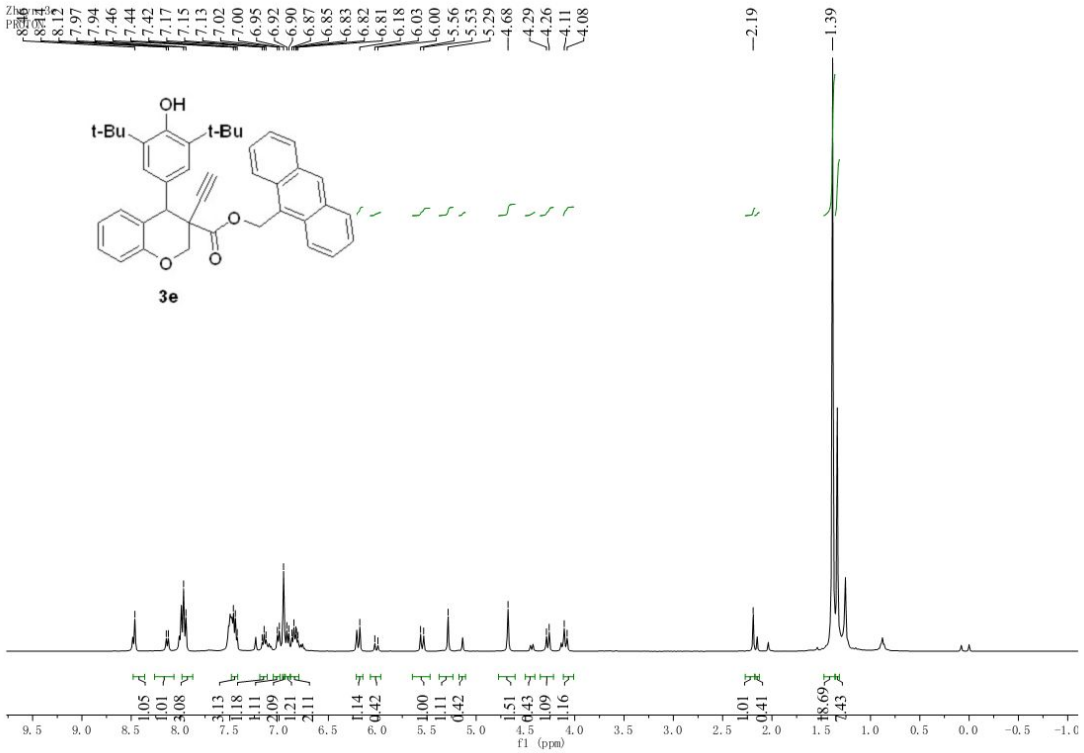

Zhuyn-3b
C13CPD
169.43
168.44
161.64
161.61
159.17
153.28
153.17
135.42
134.86
131.09
130.35
130.14
130.06
129.93
129.84
129.49
129.45
129.41
128.28
128.16
127.27
126.67
124.25
124.21
124.17
122.68
122.03
121.99
121.09
120.98
116.37
115.47
115.35
115.26
81.70
77.39
77.08
76.76
76.09
72.81
68.36
64.30
61.42
61.04
60.99
50.49
48.84
47.61
46.18
34.32
34.28
30.37
OH
t-Bu
t-Bu
O
O
O
F
3b
f1 (ppm)

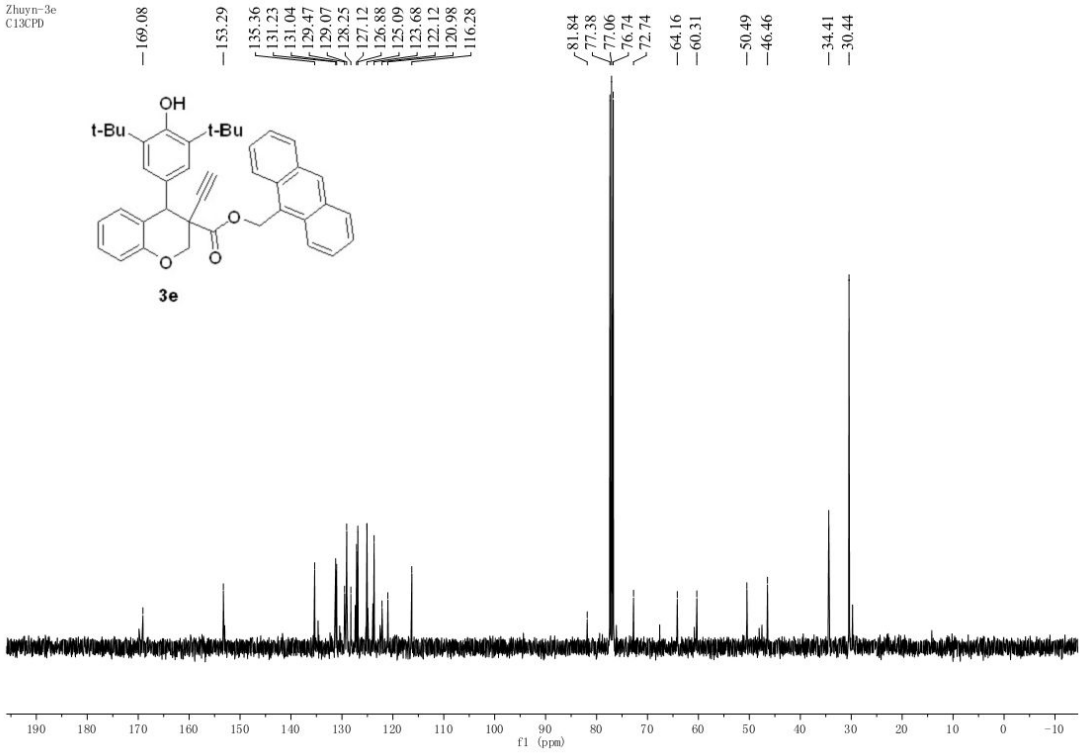

Zhuyn-3c
PROTON
7.84
7.75
7.26
7.22
7.20
7.18
7.02
7.00
6.98
6.90
6.88
6.86
5.16
5.14
5.12
5.00
4.97
4.62
4.43
4.40
4.32
4.29
2.36
1.33
OH
t-Bu
t-Bu
F3C
CF3
O
O
O
3c
1.01
1.98
1.03
2.00
3.08
0.99
1.11
1.00
1.01
1.04
1.03
1.00
18.05
f1 (ppm)

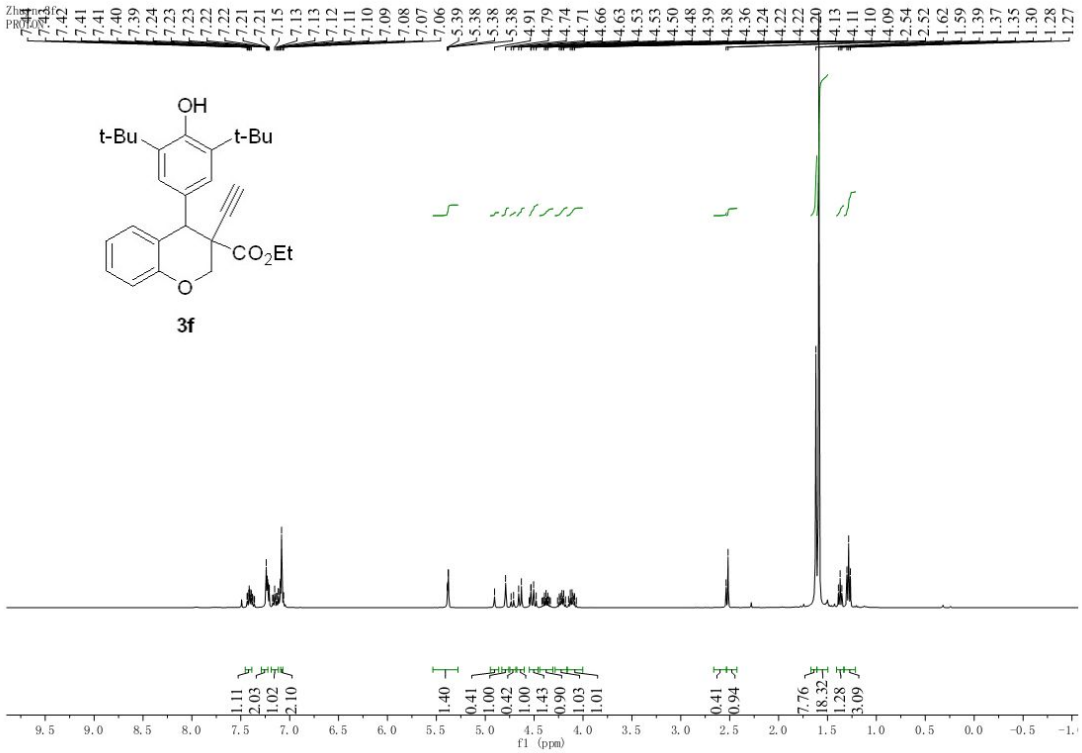

Zhuyn-3c
C13CPD
167.98
153.27
153.08
137.79
135.44
132.56
132.22
131.89
131.56
130.96
130.73
128.36
127.22
126.51
124.42
122.26
122.22
121.74
121.71
121.20
116.42
81.36
77.34
77.02
76.70
73.14
65.01
64.60
50.31
45.98
34.24
30.25
OH
t-Bu
t-Bu
F3C
CF3
O
O
O
3c
f1 (ppm)

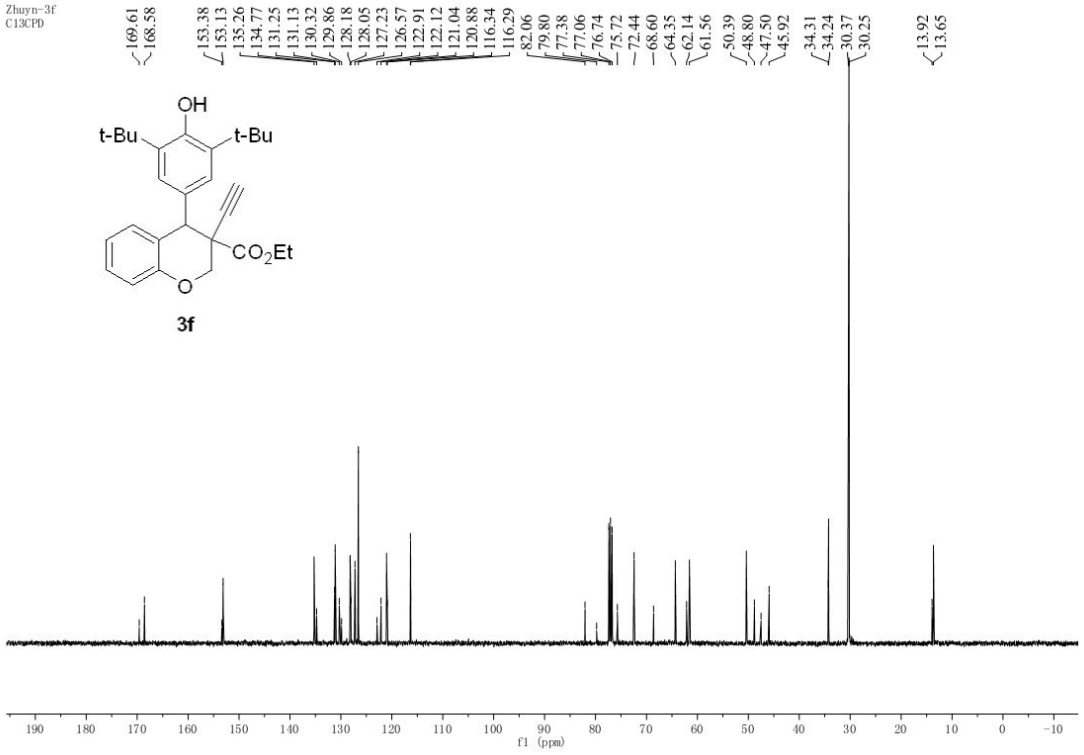

7.86
7.85
7.84
7.82
7.80
7.74
7.73
7.72
7.71
7.50
7.49
7.48
7.47
7.41
7.39
7.38
7.37
7.30
7.29
7.19
7.17
7.16
7.15
7.01
7.01
6.99
6.99
6.97
6.90
6.86
6.84
5.42
5.39
5.31
5.28
5.18
4.65
4.40
4.37
4.27
4.27
4.24
4.24
2.27
1.34
1.33
OH
t-Bu
t-Bu
O
O
O
3d
1.19
1.05
1.04
2.28
1.16
1.11
1.11
2.22
2.18
1.28
1.04
1.06
1.00
0.33
0.32
1.00
0.35
1.03
1.00
0.34
0.93
0.30
6.42
18.12
f1 (ppm)

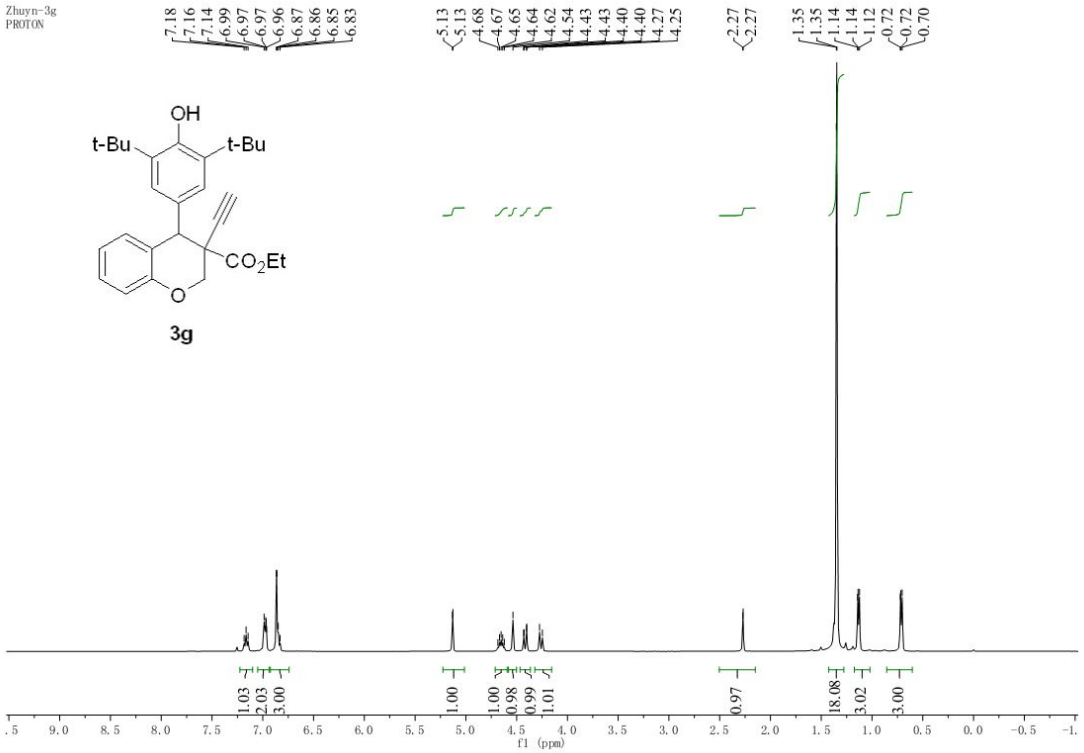

Zhuyn-3d
C13CPD
OH
t-Bu
t-Bu
O
O
O
3d
f1 (ppm)

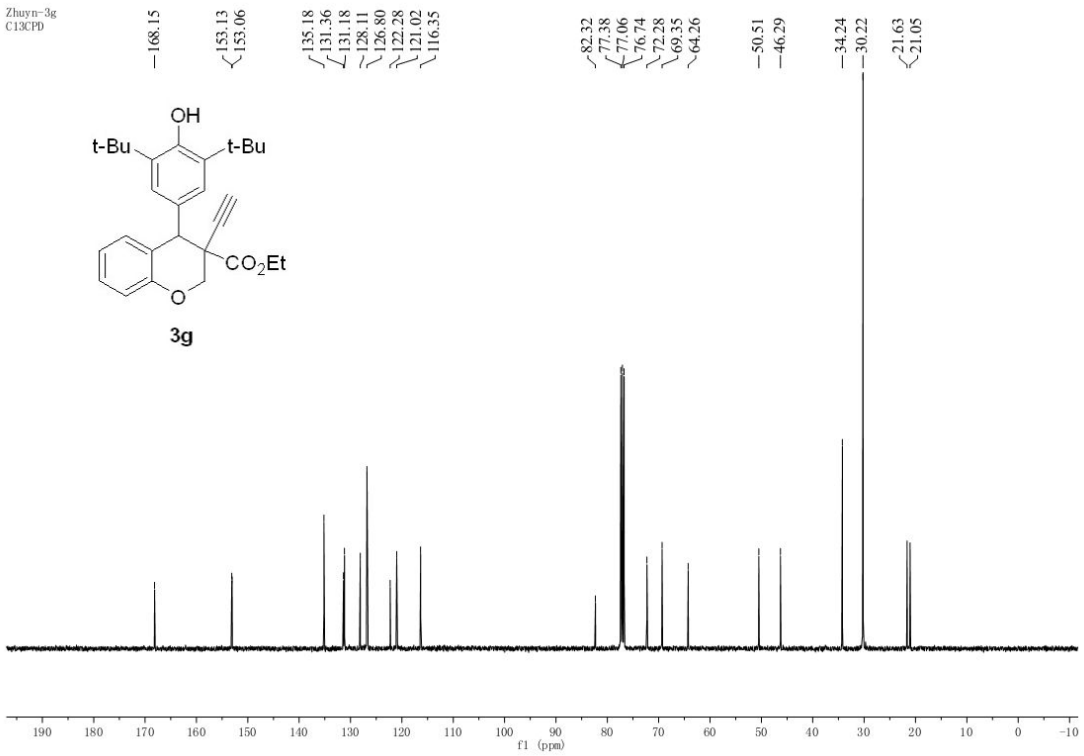

OH
t-Bu
t-Bu
O
O
O
3e
f1 (ppm)

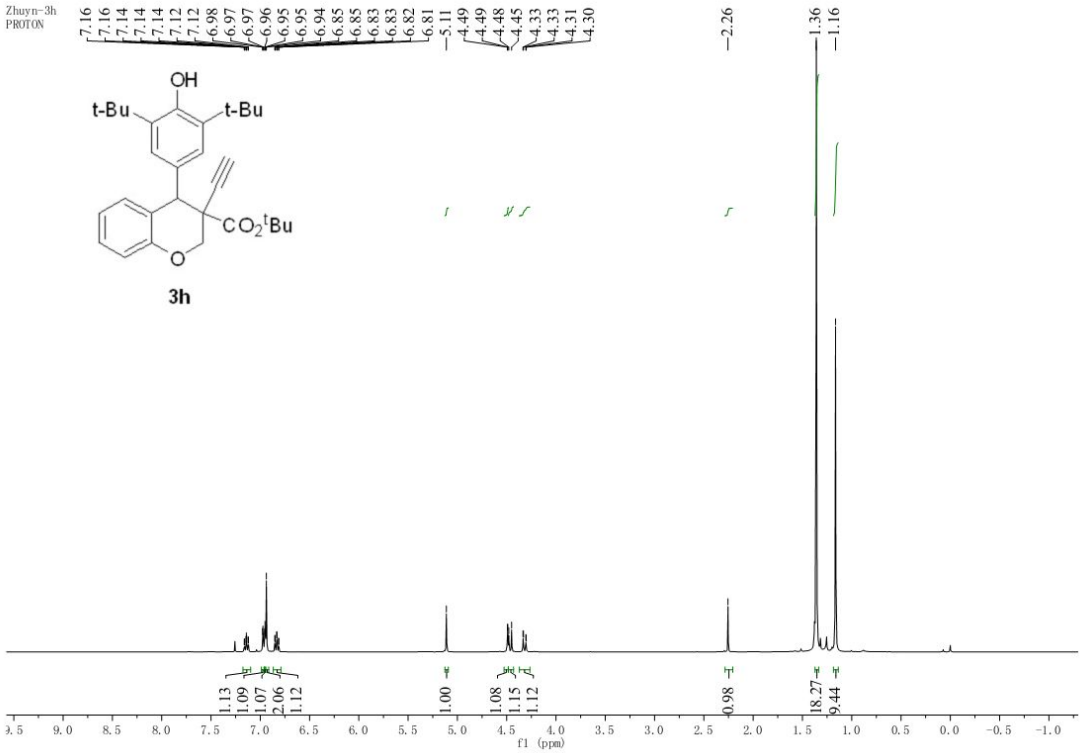

Zhuyn-3e
C13CPD
169.08
153.29
135.36
131.23
131.04
129.47
129.07
128.25
127.12
126.88
125.09
123.68
122.12
120.98
116.28
81.84
77.38
77.06
76.74
72.74
64.16
60.31
50.49
46.46
34.41
30.44
OH
t-Bu
t-Bu
O
O
O
3e
f1 (ppm)

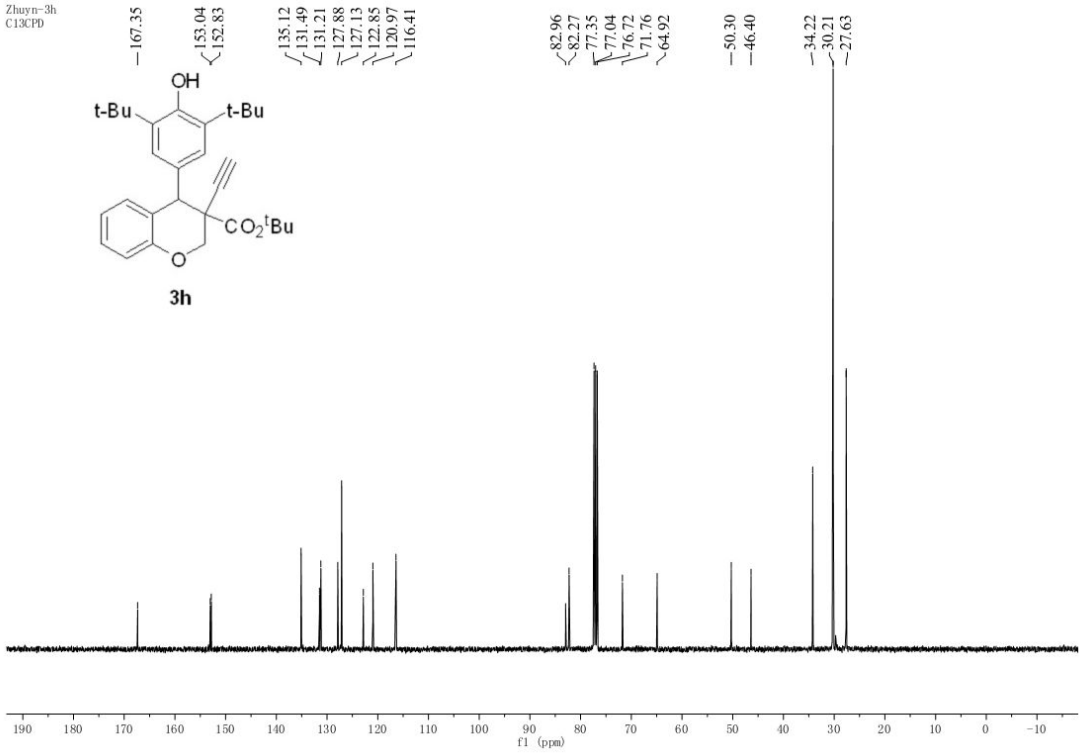

OH
t-Bu
t-Bu
CO2Et
O
3f
1.11
2.03
1.02
2.10
1.40
0.41
1.00
0.42
1.00
1.43
0.90
1.03
1.01
0.41
0.94
7.76
18.32
1.28
3.09
f1 (ppm)

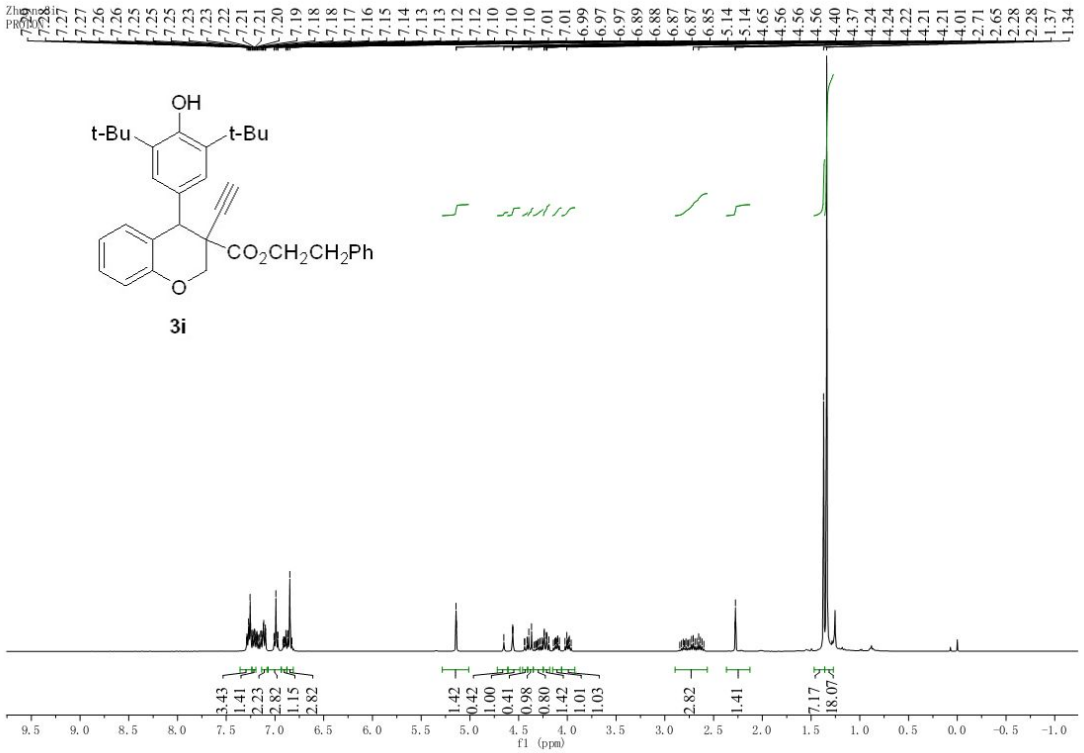

Zhuyn-3f
C13CPD
169.61
168.58
153.38
153.13
135.26
134.77
131.25
131.13
130.32
129.86
128.18
128.05
127.23
126.57
122.91
122.12
121.04
120.88
116.34
116.29
82.06
79.80
77.38
77.06
76.74
75.72
72.44
68.60
64.35
62.14
61.56
50.39
48.80
47.50
45.92
34.31
34.24
30.37
30.25
13.92
13.65
OH
t-Bu
t-Bu
CO2Et
O
3f
f1 (ppm)

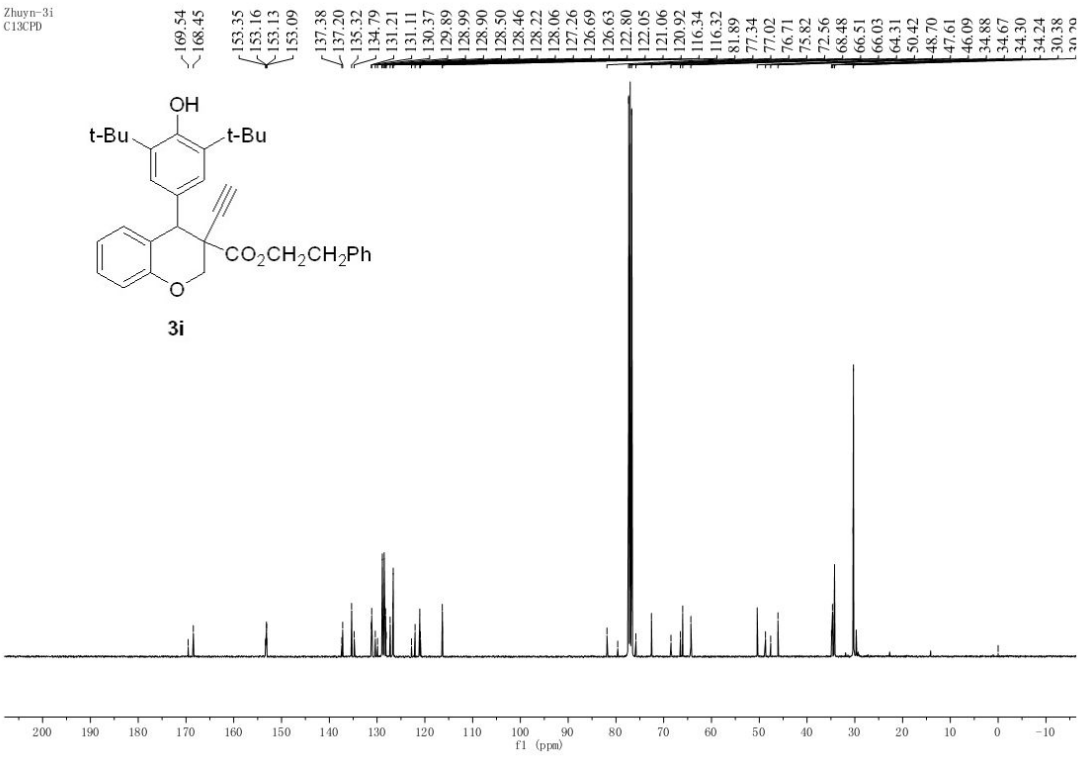

Zhuyn-3g
PROTON
7.18
7.16
7.14
6.99
6.97
6.97
6.96
6.87
6.86
6.85
6.83
5.13
5.13
4.68
4.67
4.65
4.64
4.62
4.54
4.43
4.43
4.40
4.40
4.27
4.25
2.27
2.27
1.35
1.35
1.14
1.14
1.12
0.72
0.72
0.70
OH
t-Bu
t-Bu
CO2Et
O
3g
1.03
2.03
3.00
1.00
1.00
0.98
0.99
1.01
0.97
18.08
3.02
3.00
f1 (ppm)

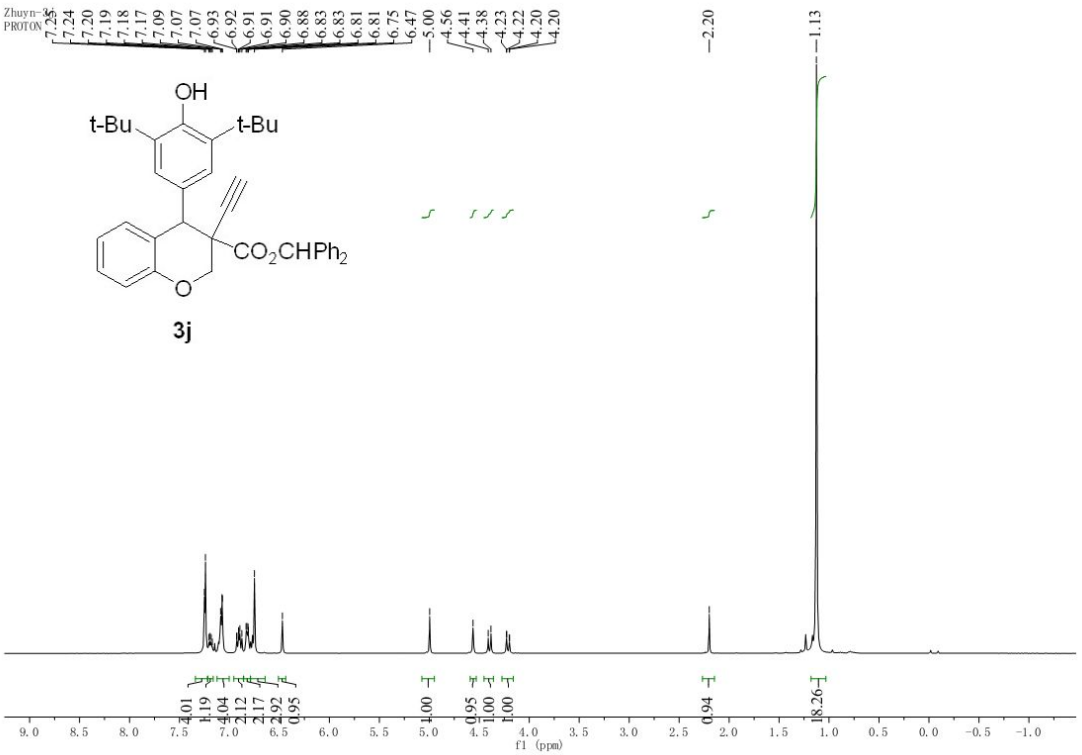

Zhuyn-3g
C13CPD
168.15
153.13
133.06
135.18
131.36
131.18
128.11
126.80
122.28
121.02
116.35
82.32
77.38
77.06
76.74
72.28
69.35
64.26
50.51
46.29
34.24
30.22
21.63
21.05
OH
t-Bu
t-Bu
CO2Et
O
3g
f1 (ppm)

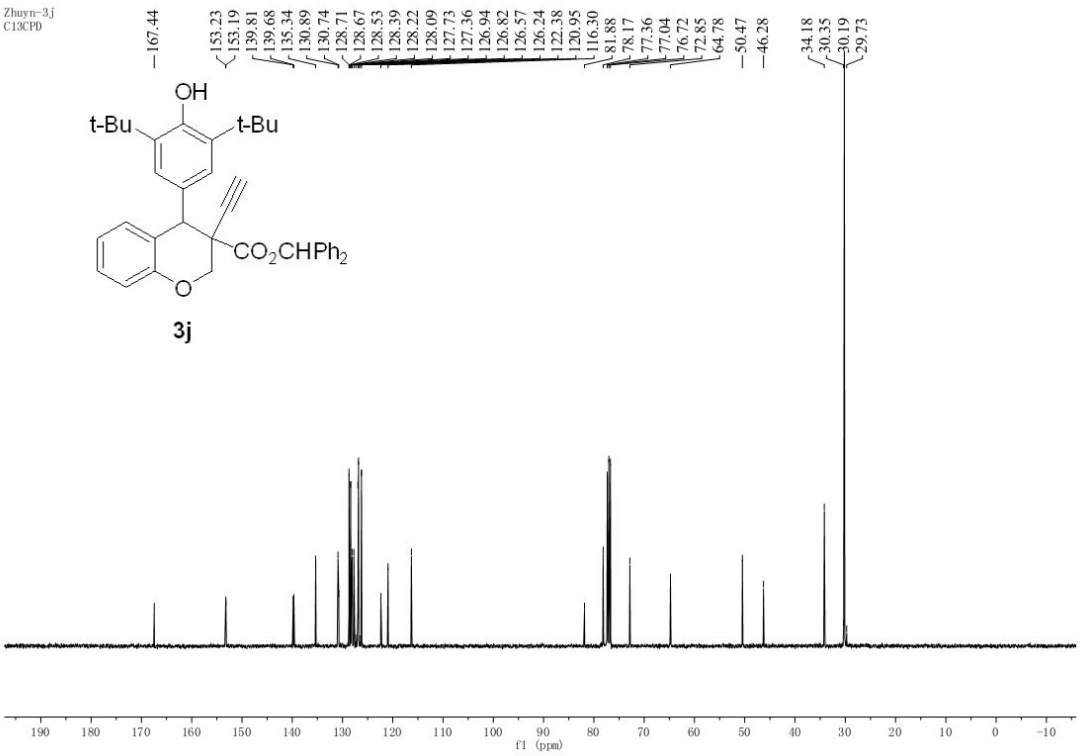

Zhuyn-3h
PROTON
7.16
7.16
7.14
7.14
7.14
7.12
7.12
6.98
6.97
6.97
6.96
6.95
6.95
6.94
6.85
6.85
6.83
6.83
6.82
6.81
5.11
4.49
4.49
4.48
4.45
4.33
4.33
4.31
4.30
2.26
1.36
1.16
OH
t-Bu
t-Bu
CO2tBu
O
3h
1.13
1.09
1.07
2.06
1.12
1.00
1.08
1.15
1.12
0.98
18.27
9.44
f1 (ppm)

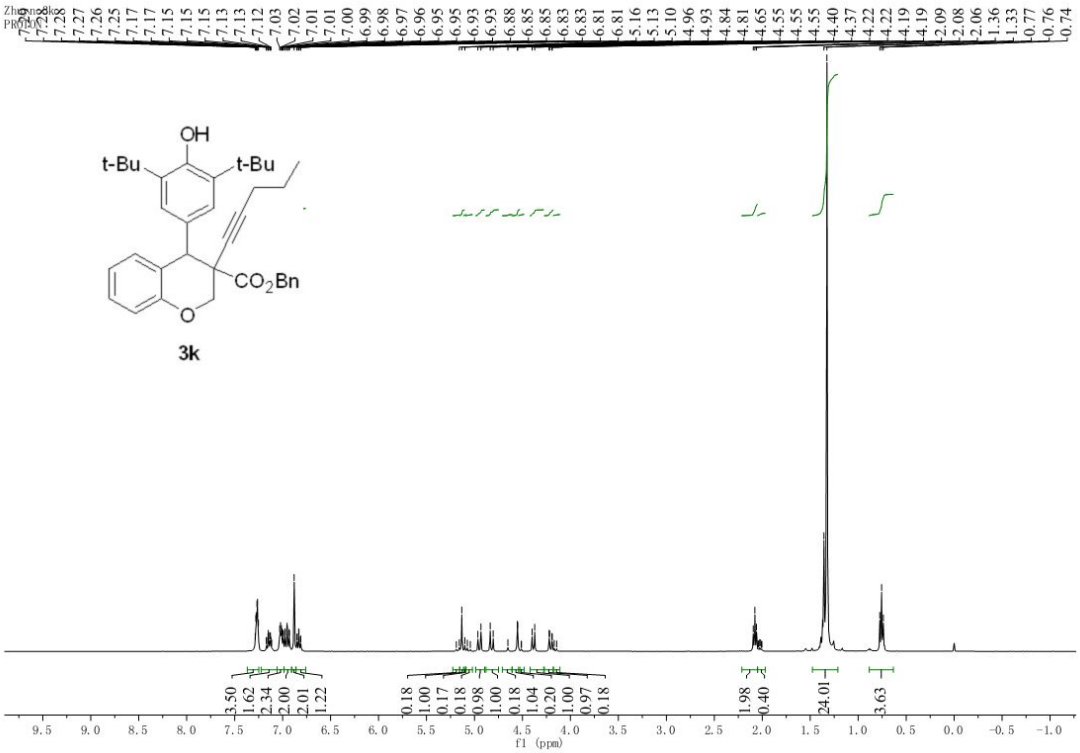

Zhuyn-3h
C13CPD
167.35
153.04
152.83
135.12
131.49
131.21
127.88
127.13
122.85
120.97
116.41
82.96
82.27
77.35
77.04
76.72
71.76
64.92
50.30
46.40
34.22
30.21
27.63
OH
t-Bu
t-Bu
CO2tBu
O
3h
f1 (ppm)

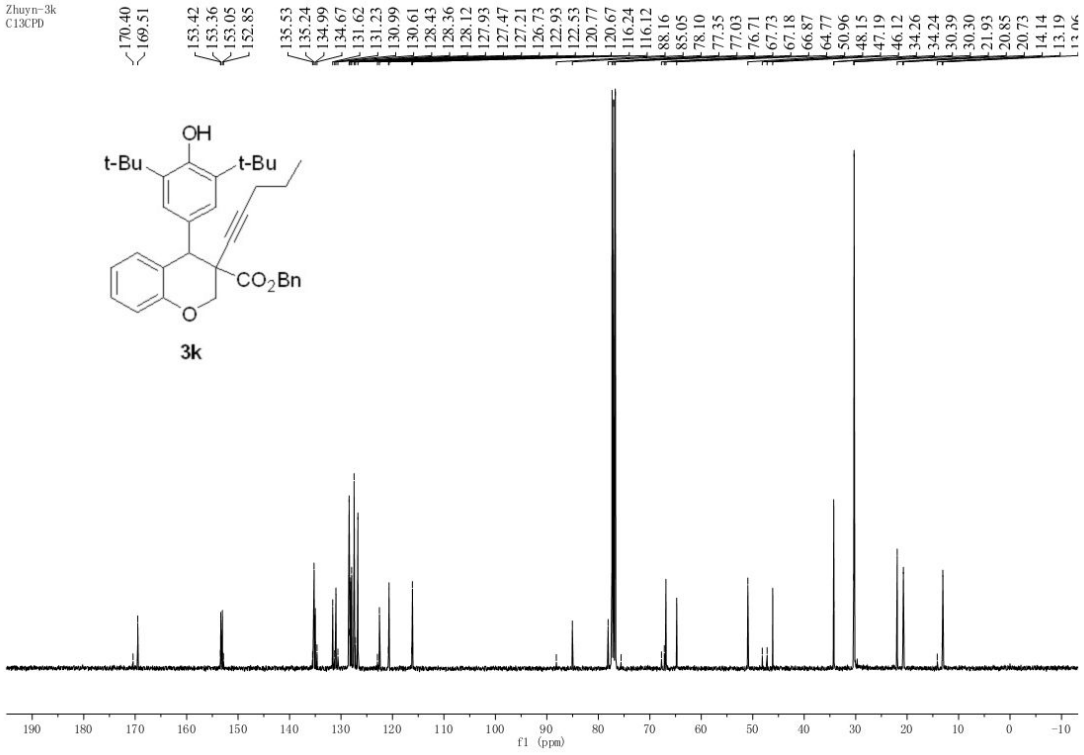

OH
t-Bu
t-Bu
CO2CH2CH2Ph
O
3i
3.43
1.41
2.23
2.82
1.15
2.82
1.42
0.42
1.00
0.41
0.98
0.80
1.42
1.01
1.03
2.82
1.41
7.17
18.07
f1 (ppm)

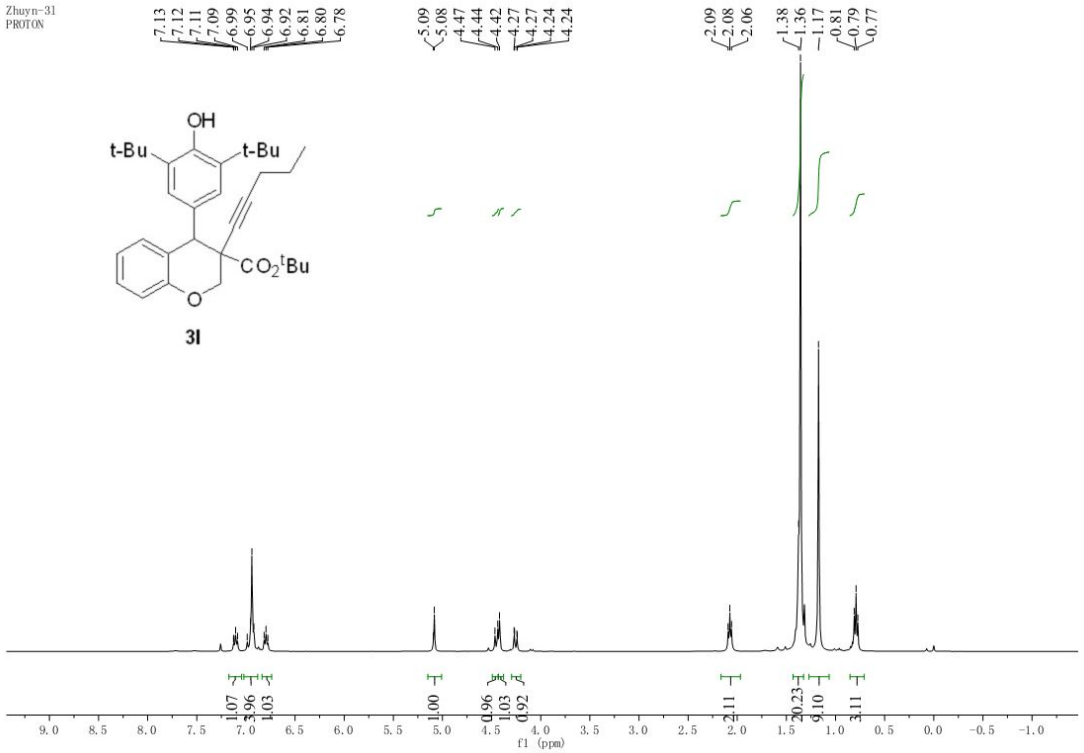

Zhuyn-3i
C13CPD
OH
t-Bu
t-Bu
CO2CH2CH2Ph
O
3i
f1 (ppm)

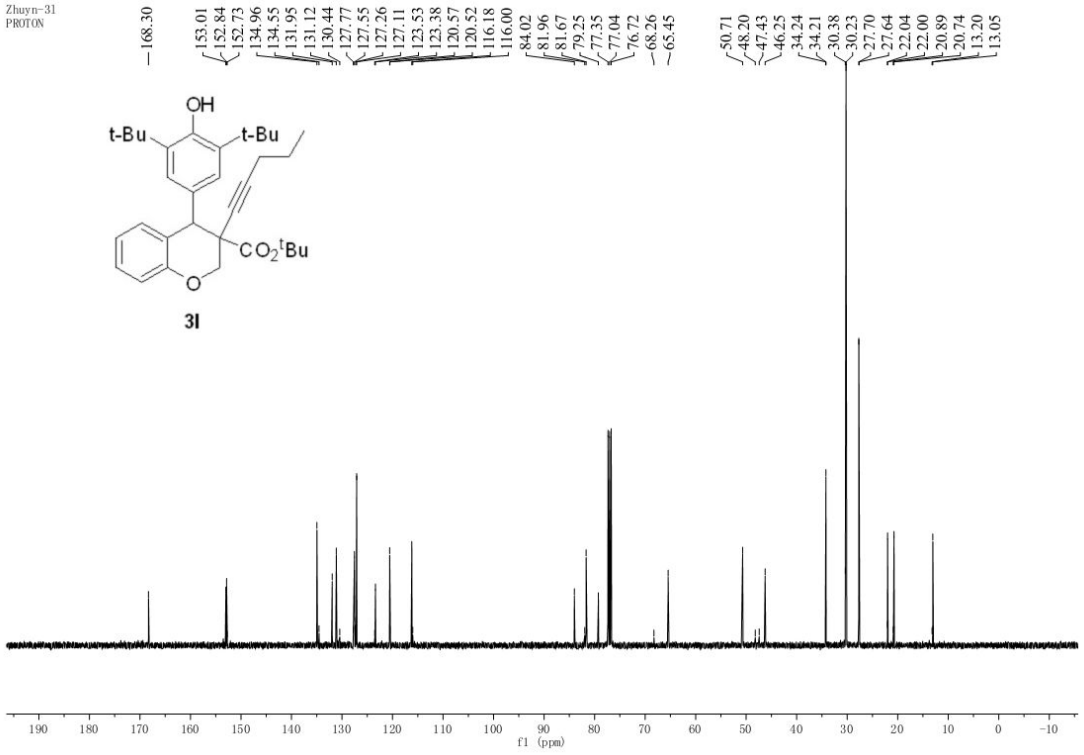

Zhuyn-3j
PROTON
OH
t-Bu
t-Bu
CO2CHPh2
O
3j
f1 (ppm)

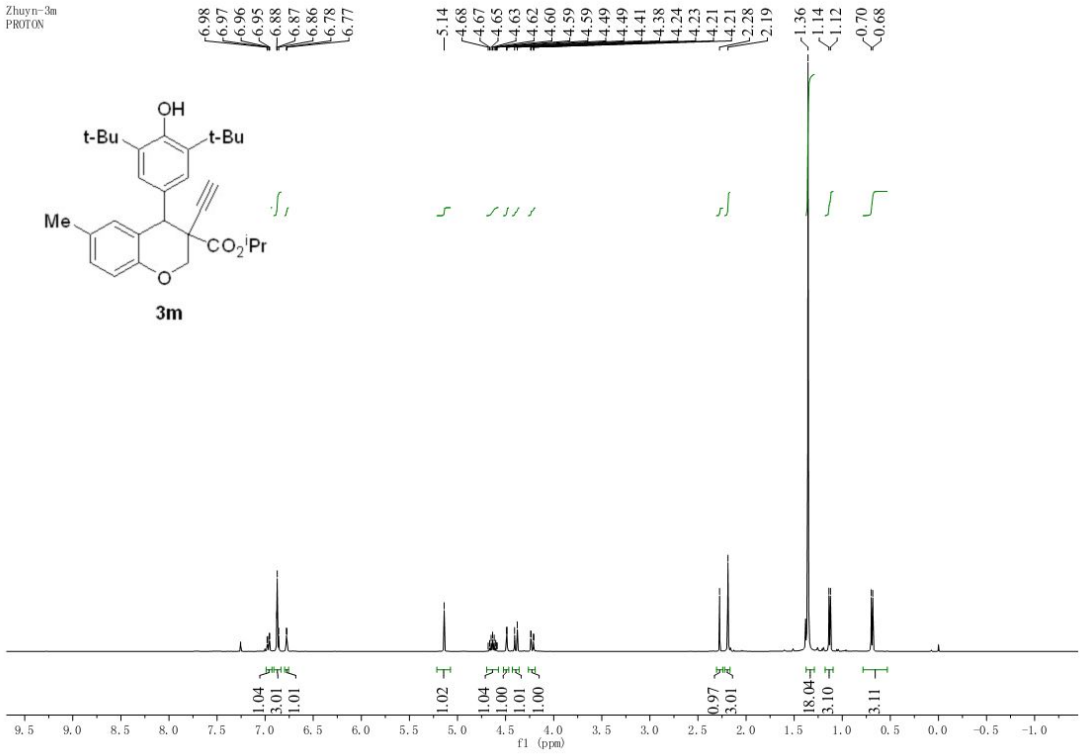

Zhuyn-3j
C13CPD
167.44
153.23
153.19
139.81
139.68
135.34
130.89
130.74
128.71
128.67
128.53
128.39
128.22
128.09
127.73
127.36
126.94
126.82
126.57
126.24
122.38
120.95
116.30
81.88
78.17
77.36
77.04
76.72
72.85
64.78
50.47
46.28
34.18
30.35
30.19
29.73
OH
t-Bu
t-Bu
CO2CHPh2
O
3j
f1 (ppm)

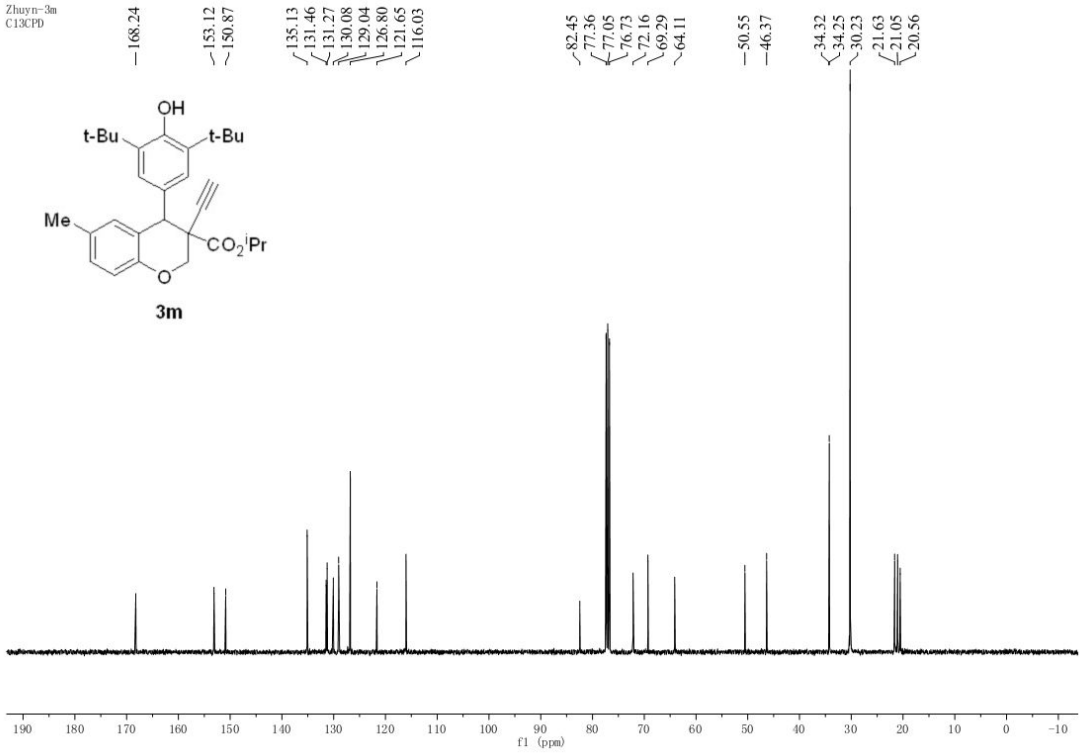

OH
t-Bu
t-Bu
CO2Bn
O
3k
3.50
1.62
2.34
2.00
2.01
1.22
0.18
1.00
0.17
0.18
0.98
1.00
0.18
1.04
0.20
1.00
0.97
0.18
1.98
0.40
24.01
3.63
f1 (ppm)

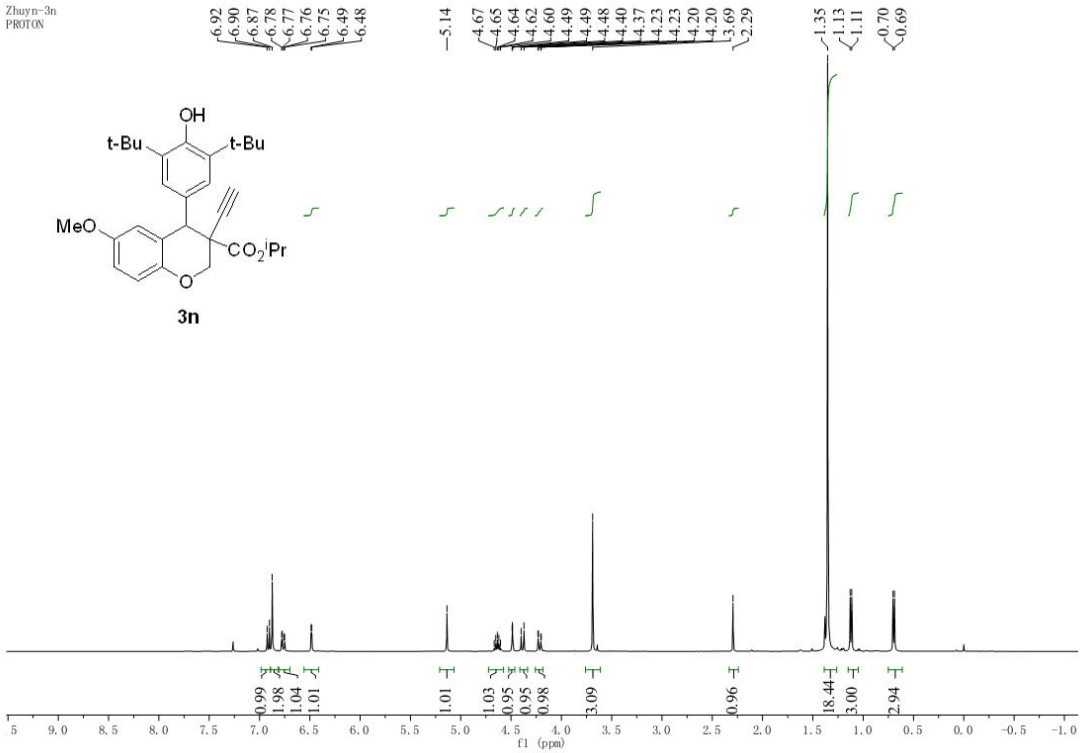

Zhuyn-3k
C13CPD
OH
t-Bu
t-Bu
CO2Bn
O
3k
f1 (ppm)

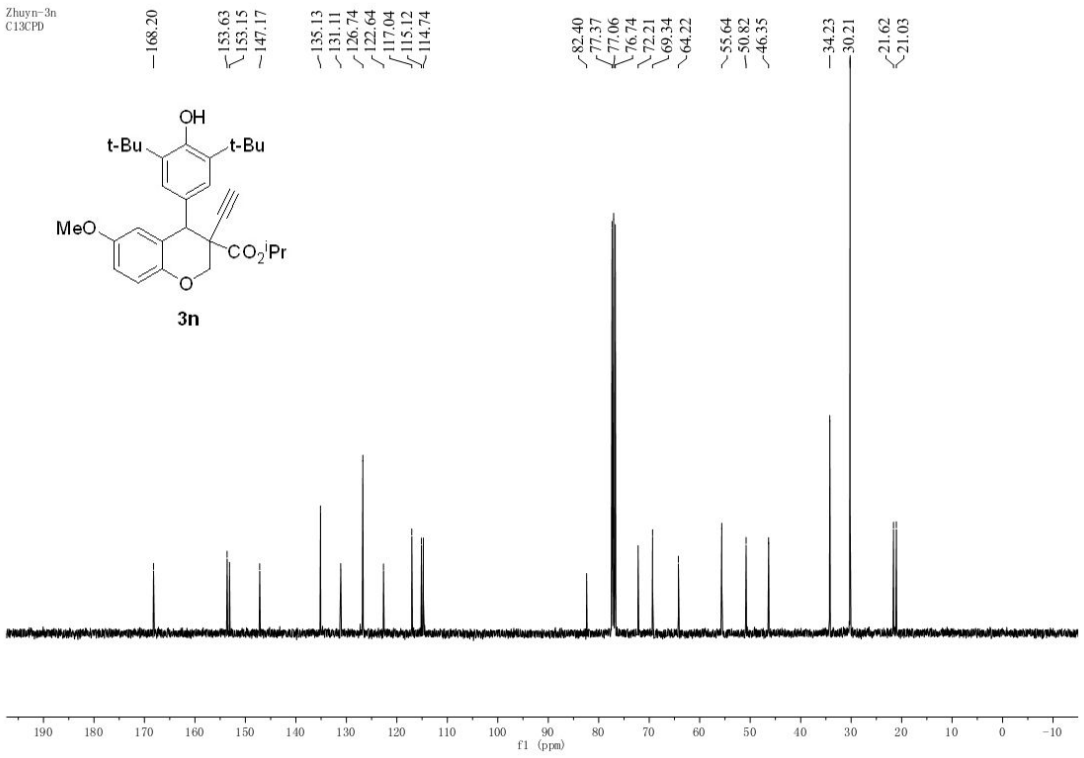

Zhuyn-31
PROTON
OH
t-Bu
t-Bu
CO2tBu
O
3l
f1 (ppm)

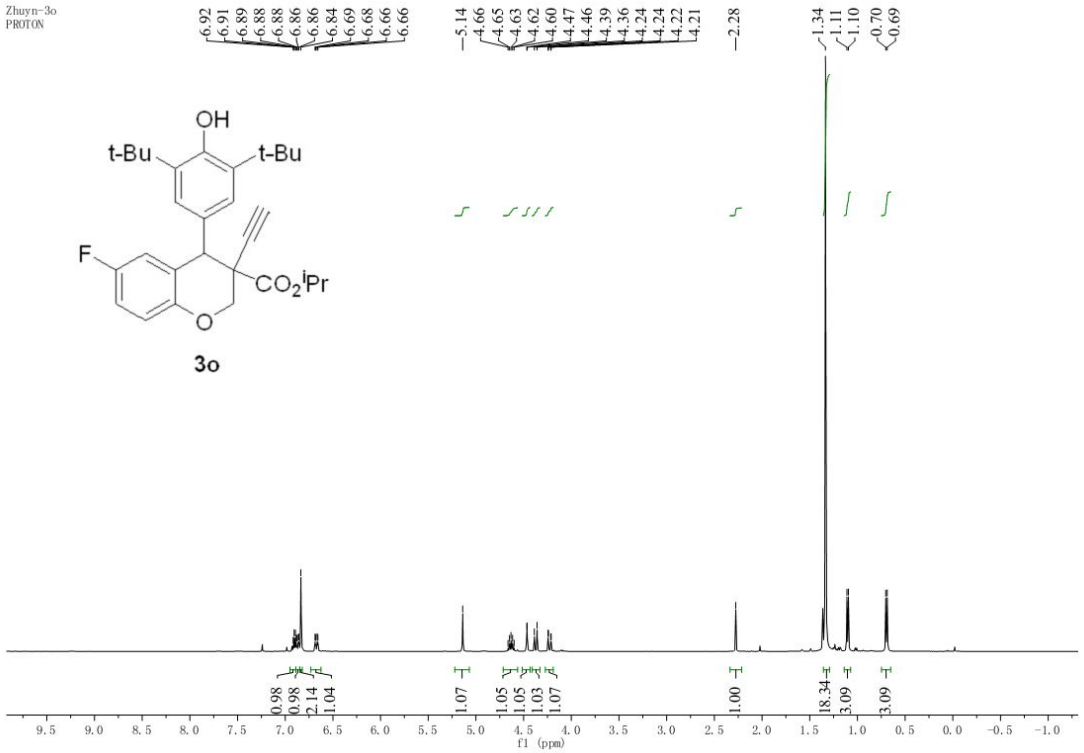

Zhuyn-3l
PROTON
168.30
153.01
152.84
152.73
134.96
134.55
131.95
131.12
130.44
127.77
127.55
127.26
127.11
123.53
123.38
120.57
120.52
116.18
116.00
84.02
81.96
81.67
79.25
77.35
77.04
76.72
68.26
65.45
50.71
48.20
47.43
46.25
34.24
34.21
30.38
30.23
27.70
27.64
22.04
22.00
20.89
20.74
13.20
13.05
OH
t-Bu
t-Bu
CO2tBu
O
3l
f1 (ppm)

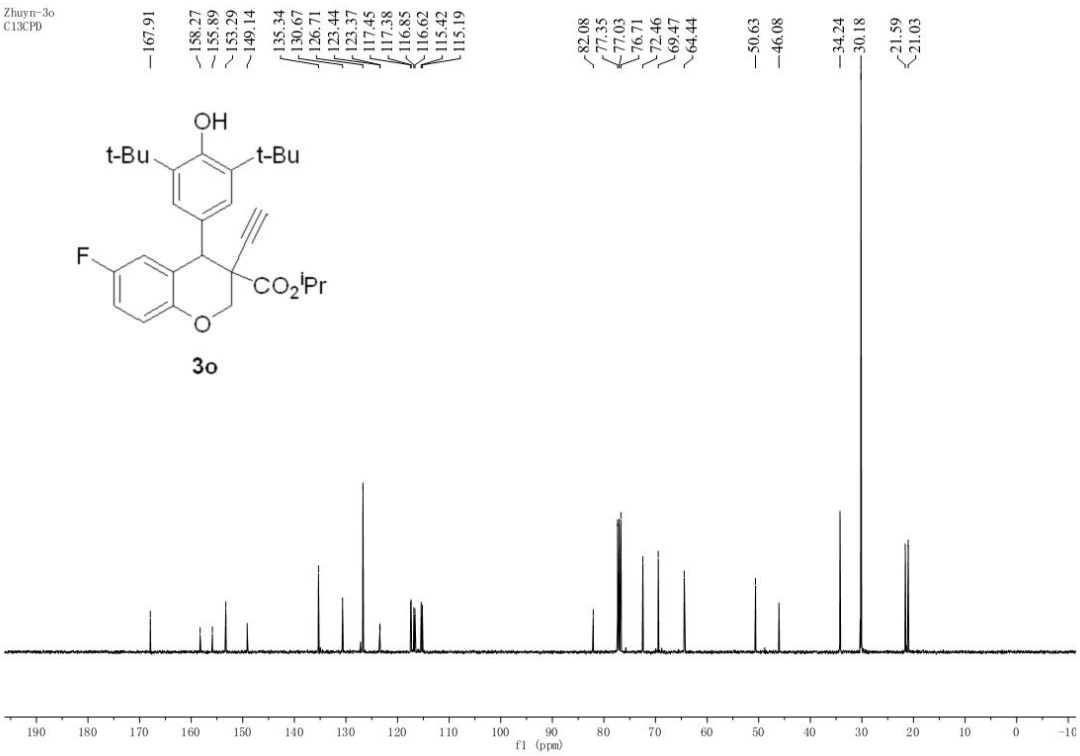

Zhuyn-3m
PROTON
6.98
6.97
6.96
6.95
6.88
6.87
6.86
6.78
6.77
5.14
4.68
4.67
4.65
4.63
4.62
4.60
4.59
4.59
4.49
4.49
4.41
4.38
4.24
4.23
4.21
4.21
2.28
2.19
1.36
1.14
1.12
0.70
0.68
OH
t-Bu
t-Bu
Me
CO2iPr
O
3m
1.04
3.01
1.01
1.02
1.04
1.00
1.01
1.00
0.97
3.01
18.04
3.10
3.11
f1 (ppm)

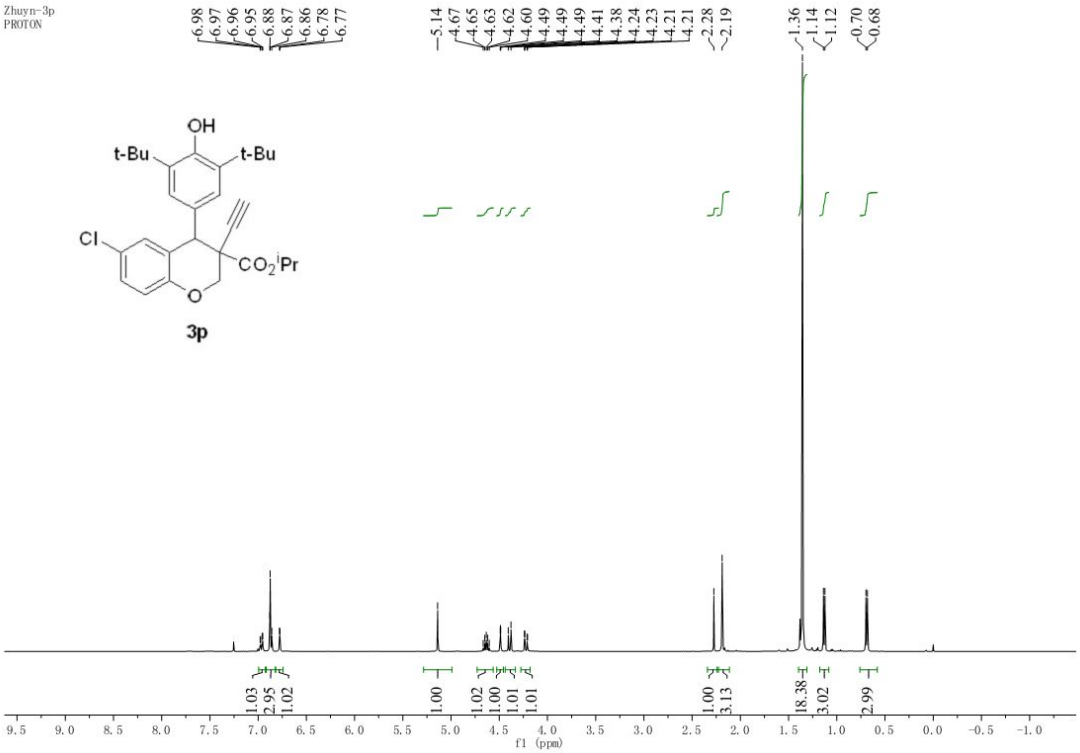

Zhuyn-3m
C13CPD
168.24
153.12
150.87
135.13
131.46
131.27
130.08
129.04
126.80
121.65
116.03
82.45
77.36
77.05
76.73
72.16
69.29
64.11
50.55
46.37
34.32
34.25
30.23
21.63
21.05
20.56
OH
t-Bu
t-Bu
Me
CO2iPr
O
3m
f1 (ppm)

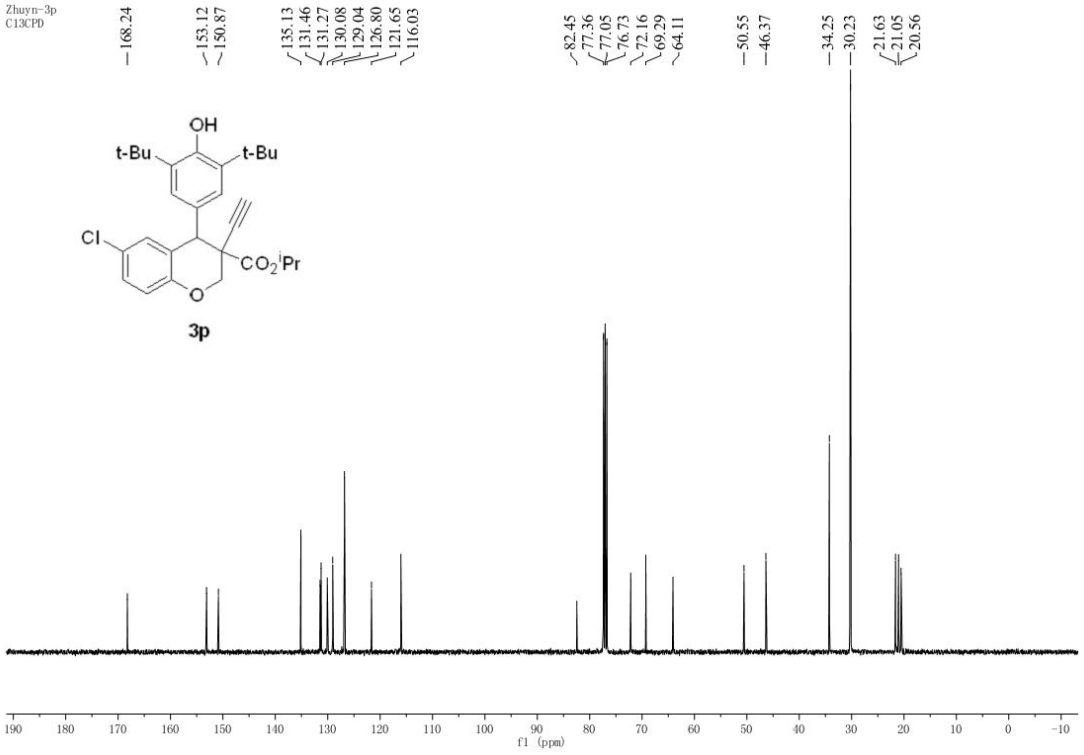

Zhuyn-3n
PROTON
6.92
6.90
6.87
6.78
6.77
6.76
6.75
6.49
6.48
5.14
4.67
4.65
4.64
4.62
4.60
4.49
4.49
4.48
4.40
4.37
4.23
4.23
4.20
4.20
3.69
2.29
1.35
1.13
1.11
0.70
0.69
OH
t-Bu
t-Bu
MeO
CO2iPr
O
3n
0.99
1.98
1.04
1.01
1.01
1.03
0.95
0.95
0.98
3.09
0.96
18.44
3.00
2.94
f1 (ppm)

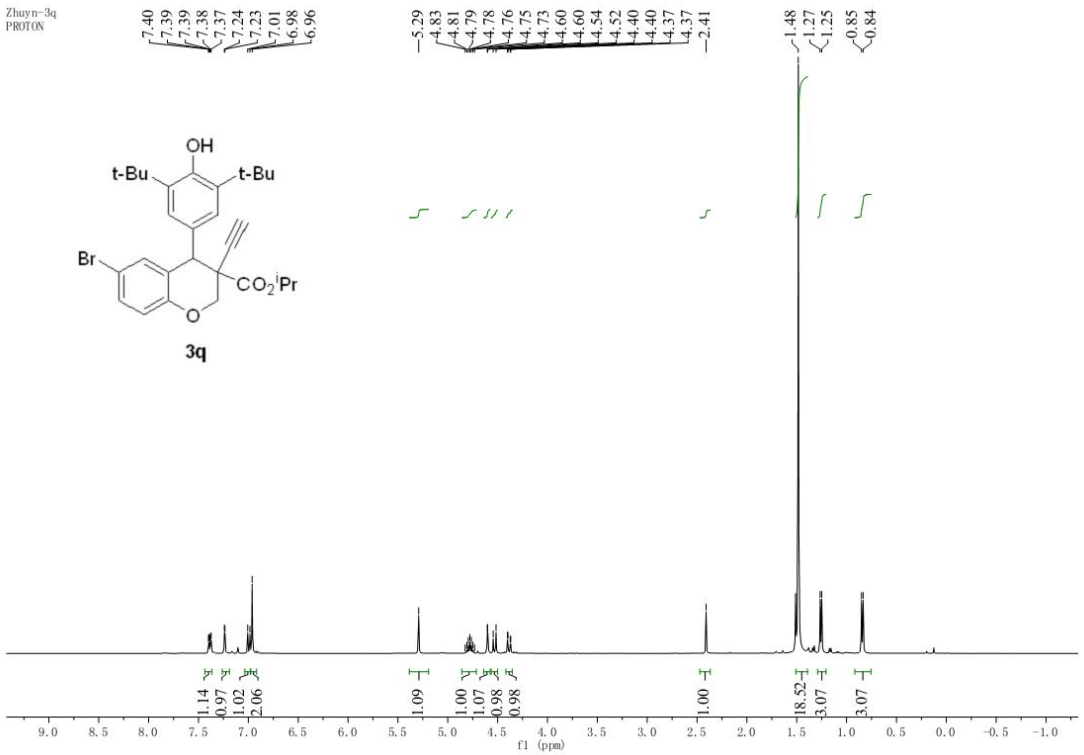

Zhuyn-3n
C13CPD
168.20
153.63
153.15
147.17
135.13
131.11
126.74
122.64
117.04
115.12
114.74
82.40
77.37
77.06
76.74
72.21
69.34
64.22
55.64
50.82
46.35
34.23
30.21
21.62
21.03
OH
t-Bu
t-Bu
MeO
CO2iPr
O
3n
f1 (ppm)

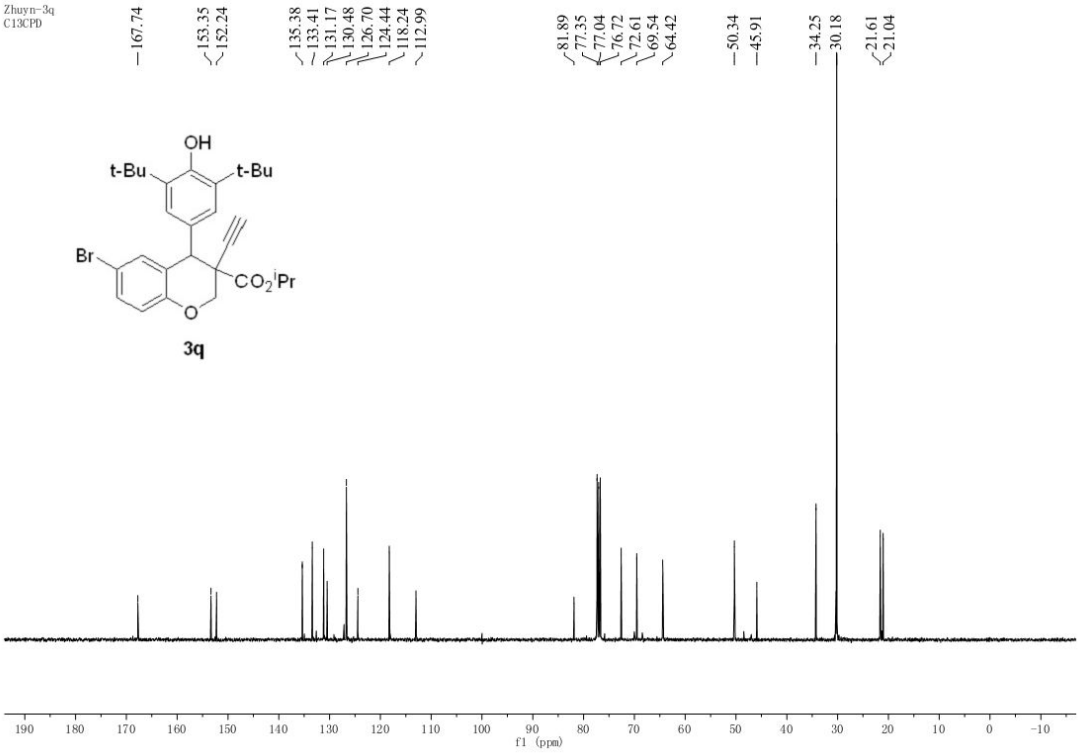

Zhuyn-3o
PROTON
6.92
6.91
6.89
6.88
6.88
6.86
6.86
6.84
6.69
6.68
6.66
6.66
5.14
4.66
4.65
4.63
4.62
4.60
4.47
4.46
4.39
4.36
4.24
4.24
4.22
4.21
2.28
1.34
1.11
1.10
0.70
0.69
OH
t-Bu
t-Bu
F
CO2iPr
O
3o
0.98
0.98
2.14
1.04
1.07
1.05
1.05
1.03
1.07
1.00
18.34
3.09
3.09
f1 (ppm)

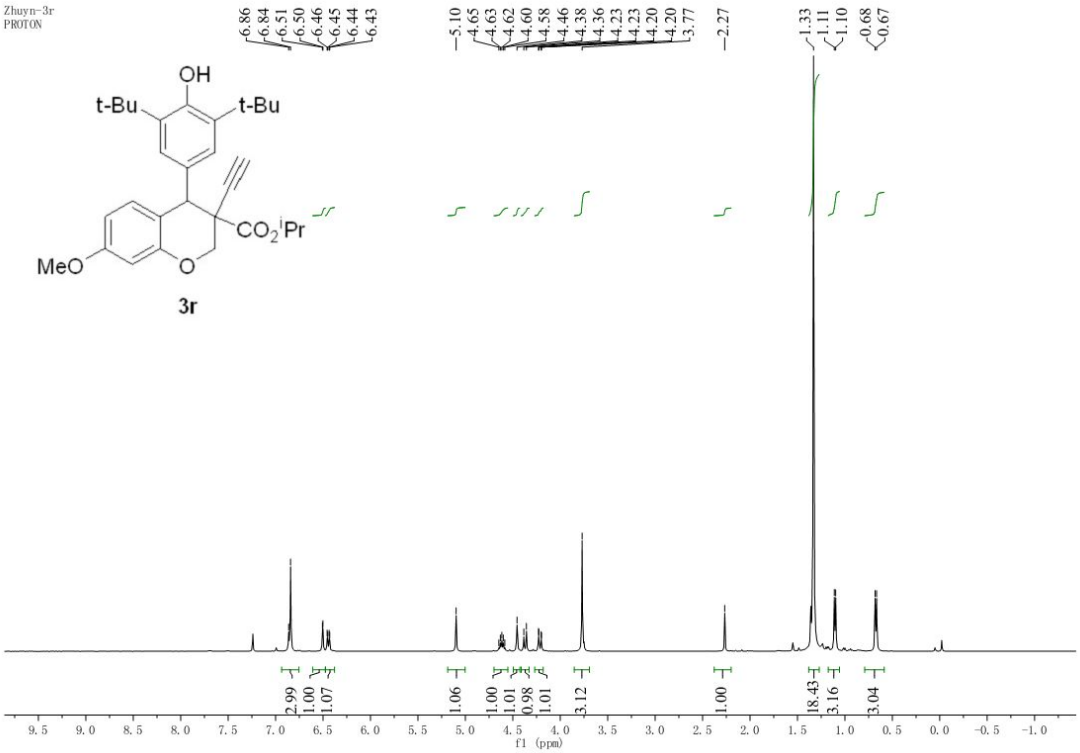

Zhuyn-3o
C13CPD
167.91
158.27
155.89
153.29
149.14
135.34
130.67
126.71
123.44
123.37
117.45
117.38
116.85
116.62
115.42
115.19
82.08
77.35
77.03
76.71
72.46
69.47
64.44
50.63
46.08
34.24
30.18
21.59
21.03
OH
t-Bu
t-Bu
F
CO2iPr
O
3o
f1 (ppm)

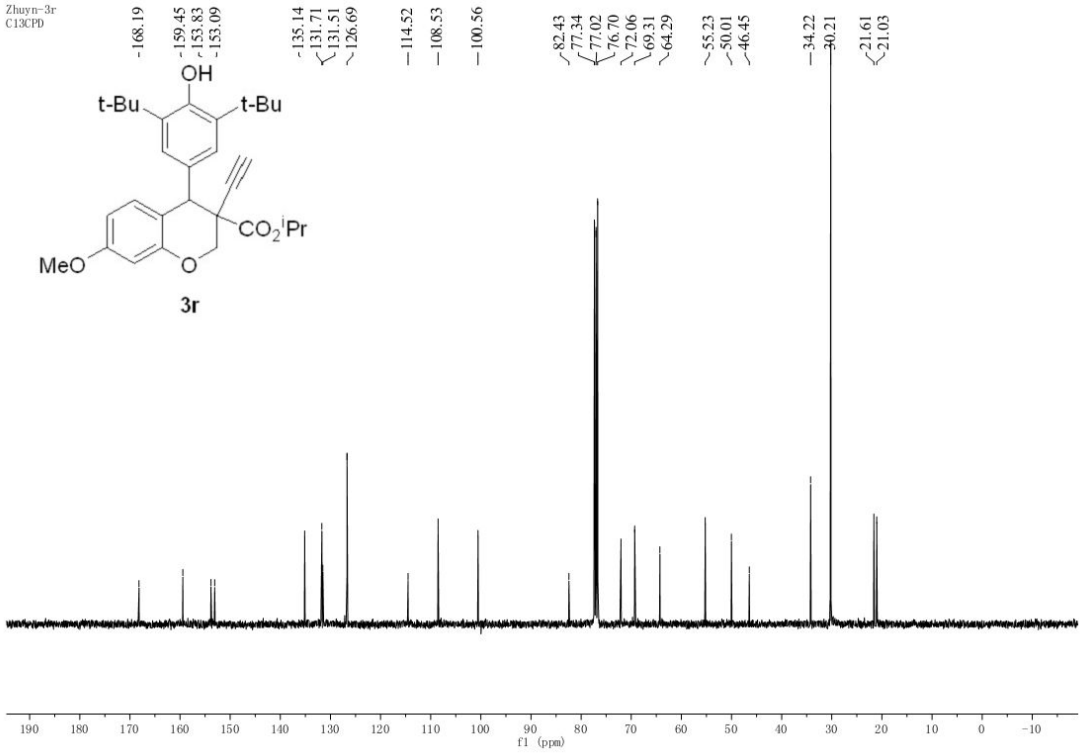

Zhuyn-3p
PROTON
6.98
6.97
6.96
6.95
6.88
6.87
6.86
6.78
6.77
5.14
4.67
4.65
4.63
4.62
4.60
4.49
4.49
4.49
4.41
4.38
4.24
4.23
4.21
4.21
2.28
2.19
1.36
1.14
1.12
0.70
0.68
OH
t-Bu
t-Bu
Cl
CO2iPr
O
3p
1.03
2.95
1.02
1.00
1.02
1.00
1.01
1.01
1.00
3.13
18.38
3.02
2.99
f1 (ppm)

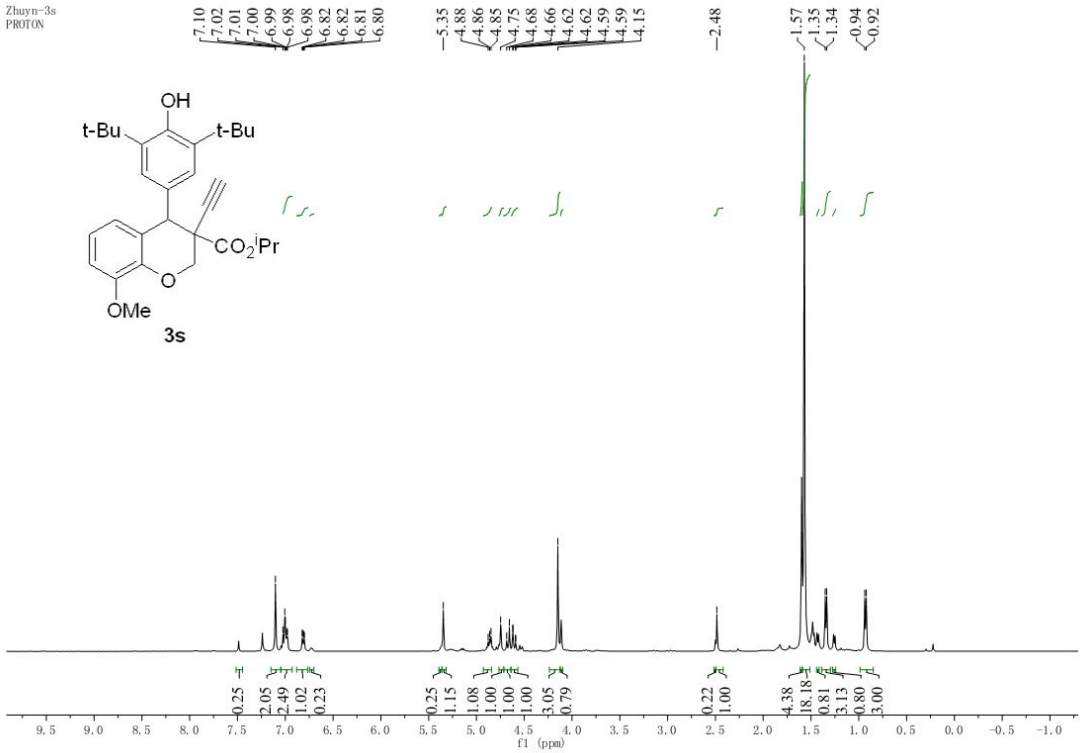

Zhuyn-3p
C13CPD
168.24
153.12
150.87
135.13
131.46
131.27
130.08
129.04
126.80
121.65
116.03
82.45
77.36
77.05
76.73
72.16
69.29
64.11
50.55
46.37
34.25
30.23
21.63
21.05
20.56
OH
t-Bu
t-Bu
Cl
CO2iPr
O
3p
f1 (ppm)

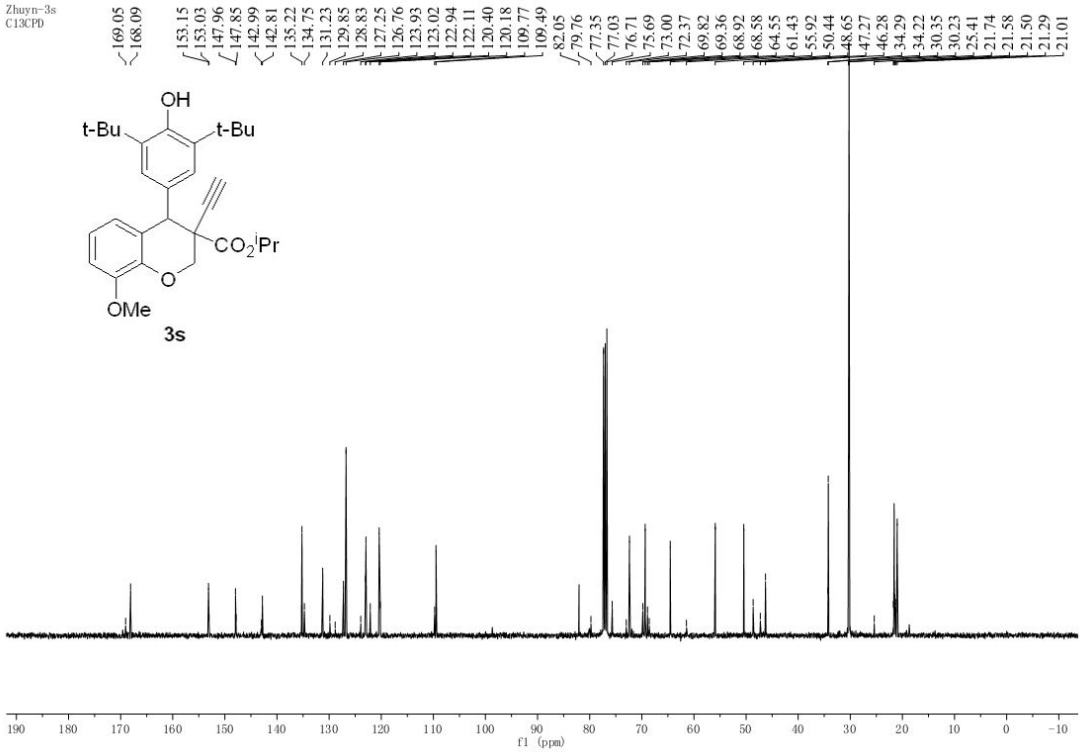

Zhuyn-3q
PROTON
7.40
7.39
7.39
7.38
7.37
7.24
7.23
7.01
6.98
6.96
5.29
4.83
4.81
4.79
4.78
4.76
4.75
4.73
4.60
4.60
4.54
4.52
4.40
4.40
4.37
4.37
2.41
1.48
1.27
1.25
0.85
0.84
OH
t-Bu
t-Bu
Br
CO2iPr
O
3q
1.14
0.97
1.02
2.06
1.09
1.00
1.07
0.98
0.98
1.00
18.52
3.07
3.07
f1 (ppm)

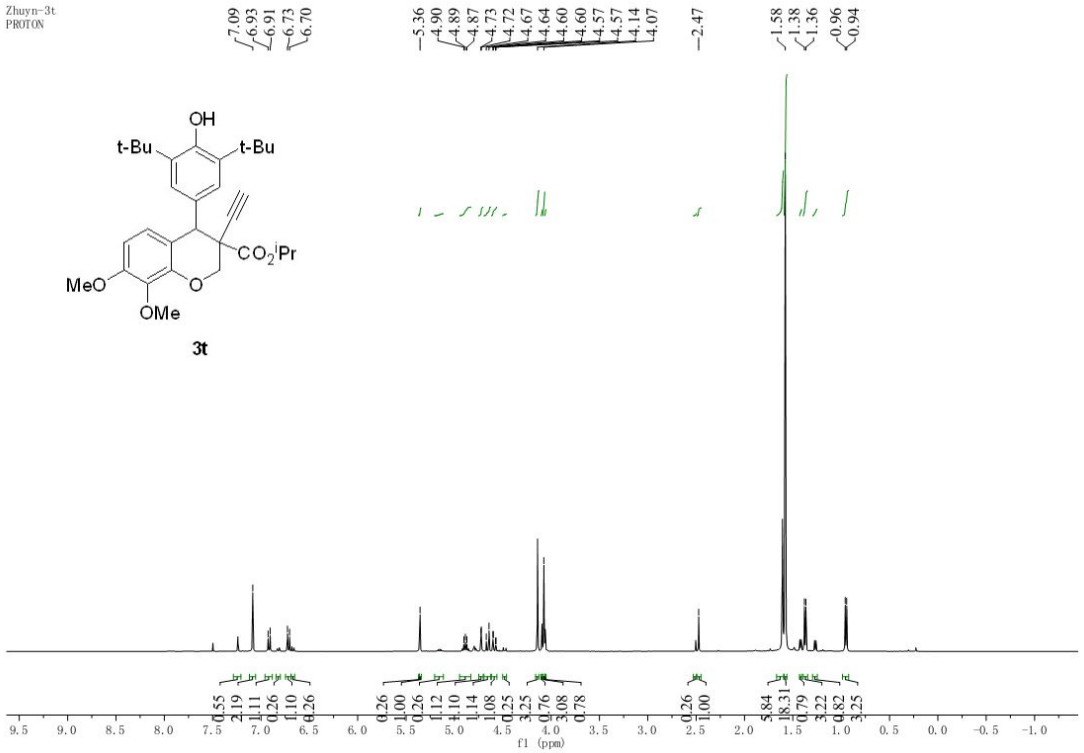

Zhuyn-3q
C13CPD
167.74
153.35
152.24
135.38
133.41
131.17
130.48
126.70
124.44
118.24
112.99
81.89
77.35
77.04
76.72
72.61
69.54
64.42
50.34
45.91
34.25
30.18
21.61
21.04
OH
t-Bu
t-Bu
Br
CO2iPr
O
3q
f1 (ppm)

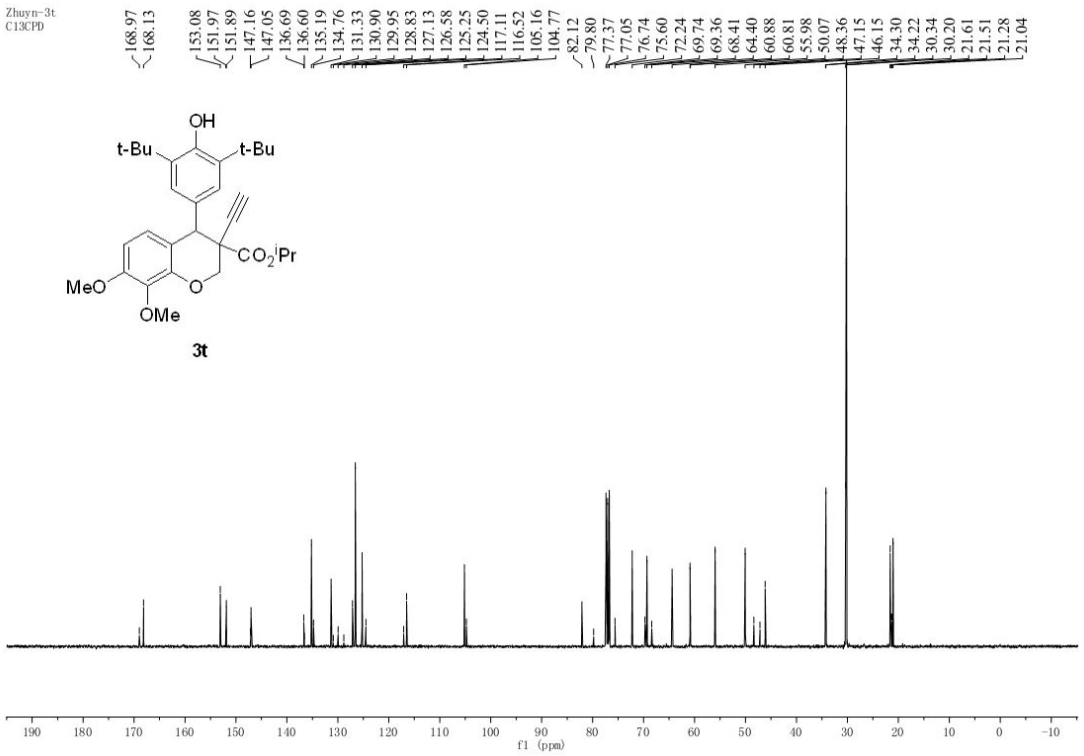

Zhuyn-3r
PROTON
6.86
6.84
6.51
6.50
6.46
6.45
6.44
6.43
5.10
4.65
4.63
4.62
4.60
4.58
4.46
4.38
4.36
4.23
4.23
4.20
4.20
3.77
2.27
1.33
1.11
1.10
0.68
0.67
OH
t-Bu
t-Bu
CO2iPr
MeO
O
3r
2.99
1.00
1.07
1.06
1.00
1.01
0.98
1.01
3.12
1.00
18.43
3.16
3.04
f1 (ppm)

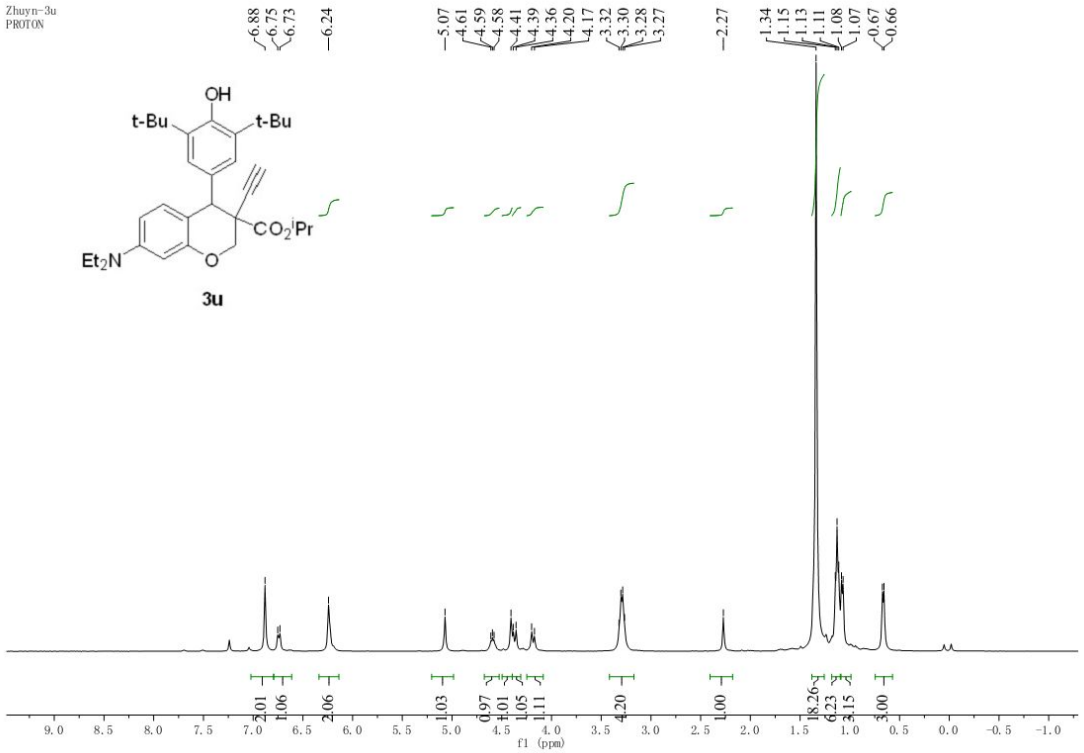

Zhuyn-3r
C13CPD
168.19
159.45
153.83
153.09
135.14
131.71
131.51
126.69
114.52
108.53
100.56
82.43
77.34
77.02
76.70
72.06
69.31
64.29
55.23
50.01
46.45
34.22
30.21
21.61
21.03
OH
t-Bu
t-Bu
CO2iPr
MeO
O
3r
f1 (ppm)

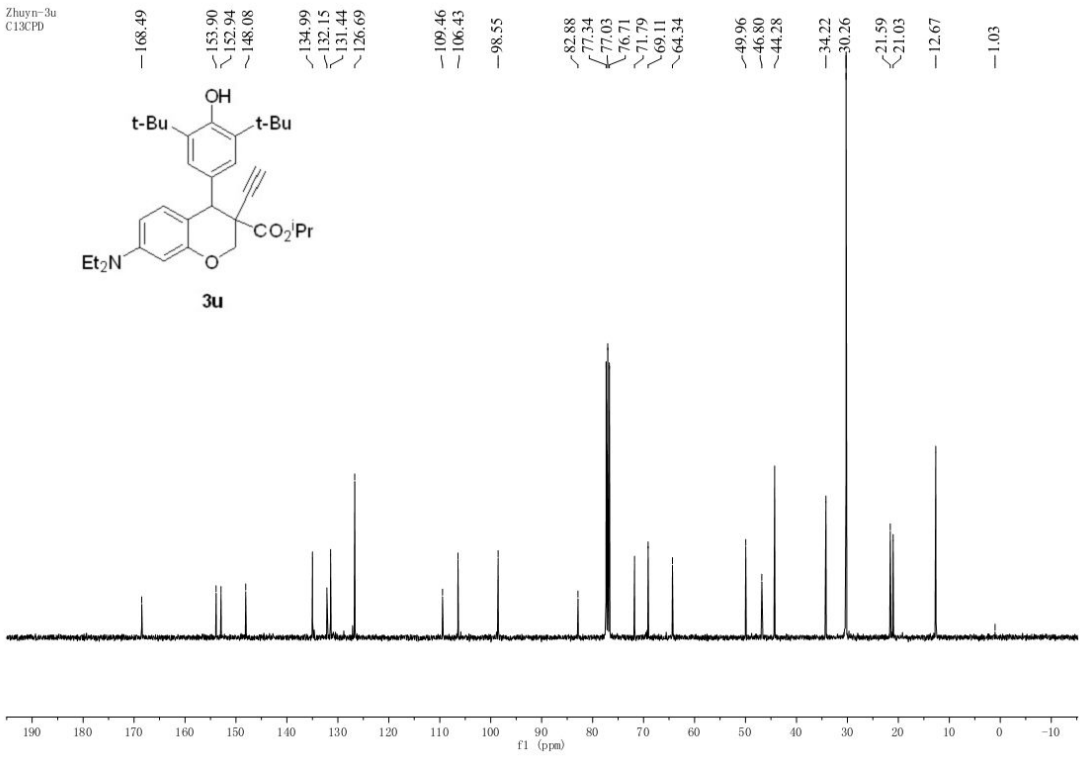

Zhuyn-3s
PROTON
7.10
7.02
7.01
7.00
6.99
6.98
6.98
6.82
6.82
6.81
6.80
5.35
4.88
4.86
4.85
4.75
4.68
4.66
4.62
4.62
4.59
4.59
4.15
2.48
1.57
1.35
1.34
0.94
0.92
OH
t-Bu
t-Bu
CO2iPr
O
OMe
3s
0.25
2.05
2.49
1.02
0.23
0.25
1.15
1.08
1.00
1.00
1.00
3.05
0.79
0.22
1.00
4.38
18.18
0.81
3.13
0.80
3.00
f1 (ppm)

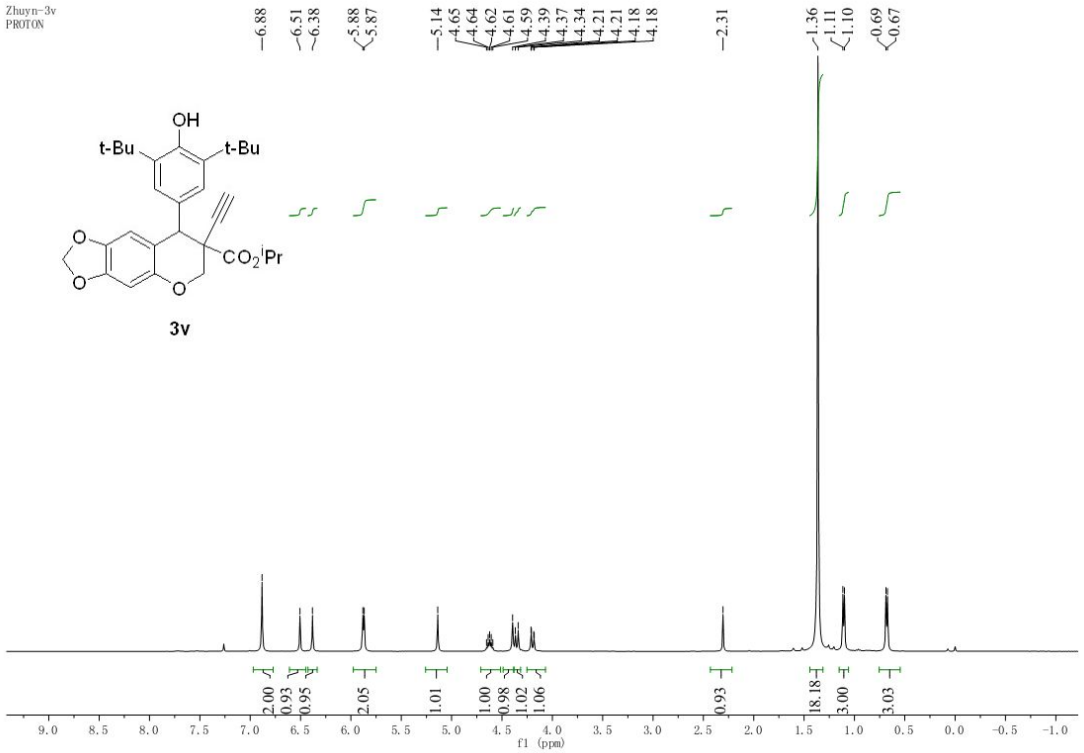

Zhuyn-3s
C13CPD
169.05
168.09
153.15
153.03
147.96
147.85
142.99
142.81
135.22
134.75
131.23
129.85
128.83
127.25
126.76
123.93
123.02
122.94
122.11
120.40
120.18
109.77
109.49
82.05
79.76
77.35
77.03
76.71
75.69
73.00
72.37
69.82
69.36
68.92
68.58
64.55
61.43
55.92
50.44
48.65
47.27
46.28
34.29
34.22
30.35
30.23
25.41
21.74
21.58
21.50
21.29
21.01
OH
t-Bu
t-Bu
CO2iPr
O
OMe
3s
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

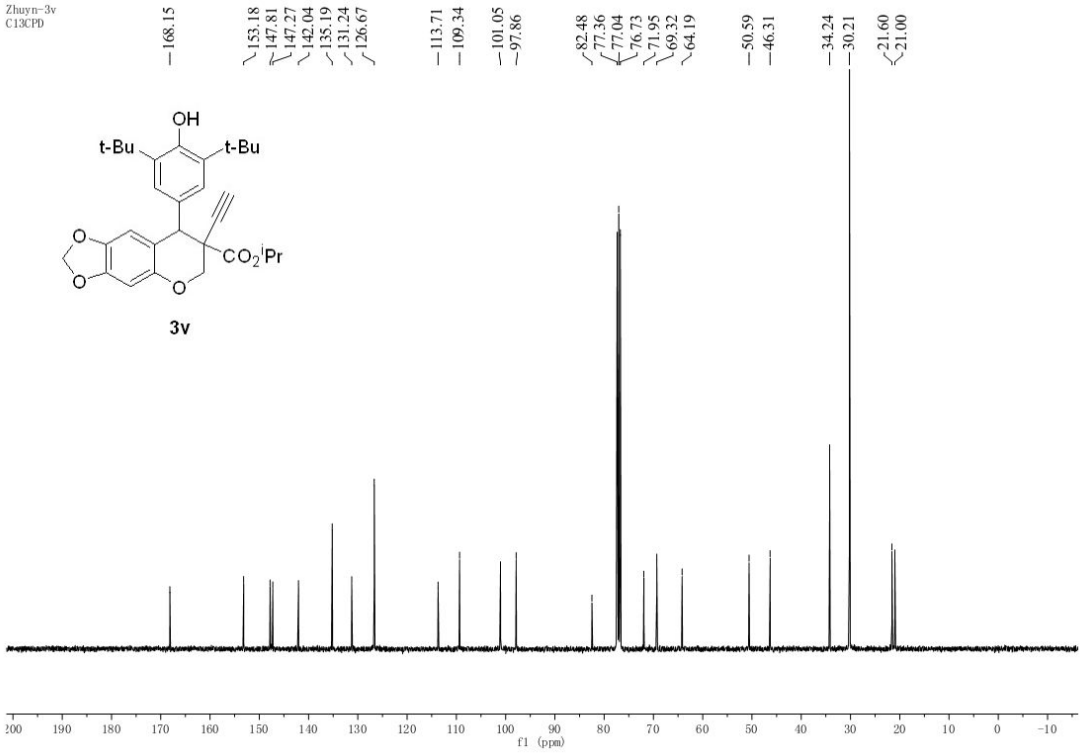

Zhuyn-3t
PROTON
7.09
6.93
6.91
6.73
6.70
5.36
4.90
4.89
4.87
4.73
4.72
4.67
4.64
4.60
4.60
4.57
4.57
4.14
4.07
2.47
1.58
1.38
1.36
0.96
0.94
OH
t-Bu
t-Bu
CO2iPr
MeO
O
OMe
3t
0.55
2.19
1.11
0.26
1.10
0.26
0.26
1.00
0.26
1.12
1.10
1.14
1.08
0.25
3.25
0.76
3.08
0.78
0.26
1.00
5.84
18.31
0.79
3.22
0.82
3.25
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

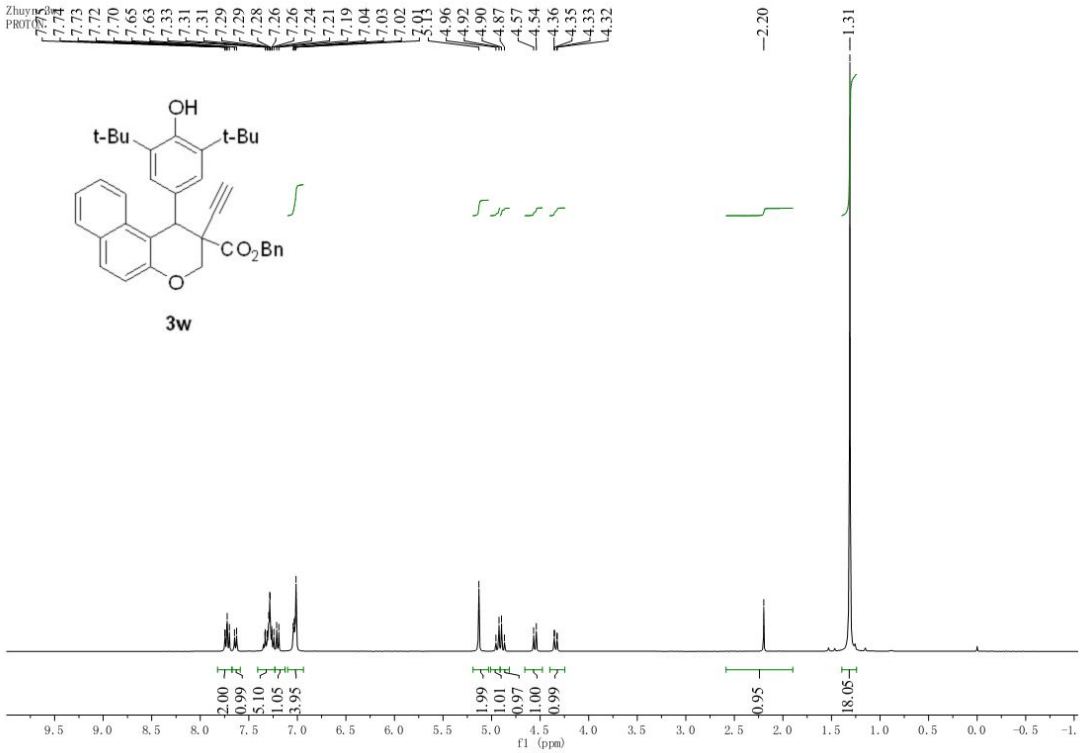

Zhuyn-3t
C13CPD
168.97
168.13
153.08
151.97
151.89
147.16
147.05
136.60
136.69
135.19
134.76
131.33
130.90
129.95
128.83
127.13
126.58
125.25
124.50
117.11
116.52
105.16
104.77
82.12
79.80
77.37
77.05
76.74
75.60
72.24
69.74
69.36
68.41
64.40
60.88
60.81
55.98
50.07
48.36
47.15
46.15
34.30
34.22
30.34
30.20
21.61
21.51
21.28
21.04
OH
t-Bu
t-Bu
CO2iPr
MeO
OMe
O
3t
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

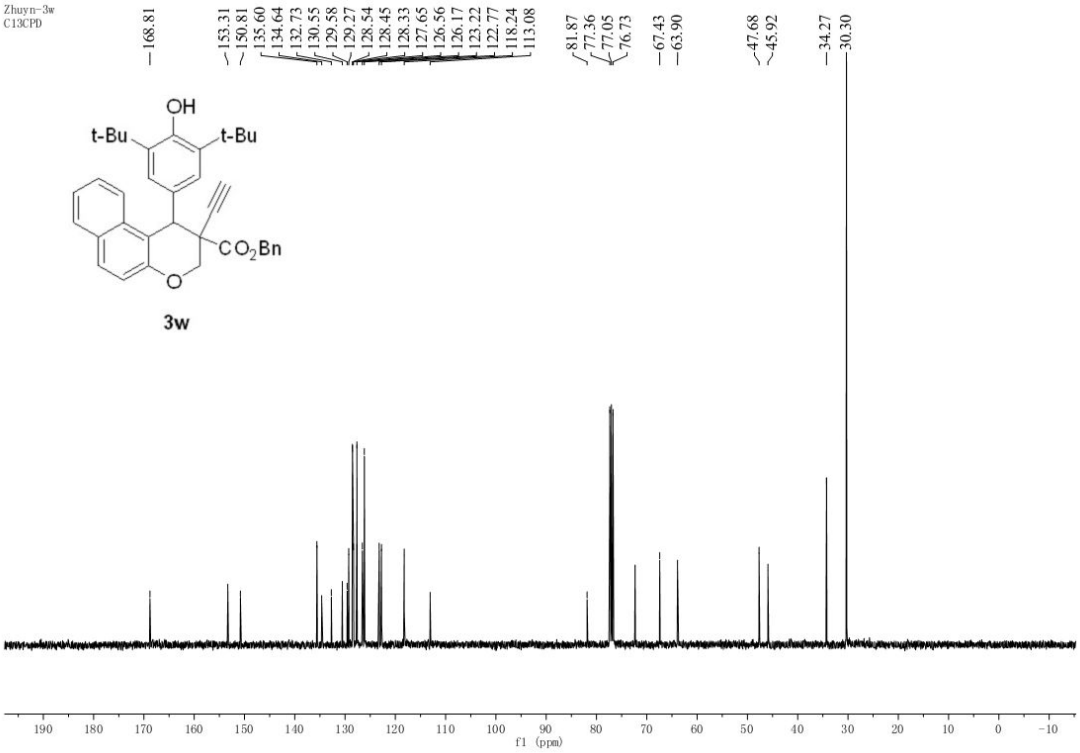

Zhuyn-3u
PROTON
6.88
6.75
6.73
6.24
5.07
4.61
4.59
4.58
4.41
4.39
4.36
4.20
4.17
3.32
3.30
3.28
3.27
2.27
1.34
1.15
1.13
1.11
1.08
1.07
0.67
0.66
OH
t-Bu
t-Bu
CO2iPr
Et2N
O
3u
2.01
1.06
2.06
1.03
0.97
1.01
1.05
1.11
4.20
1.00
18.26
6.23
3.15
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

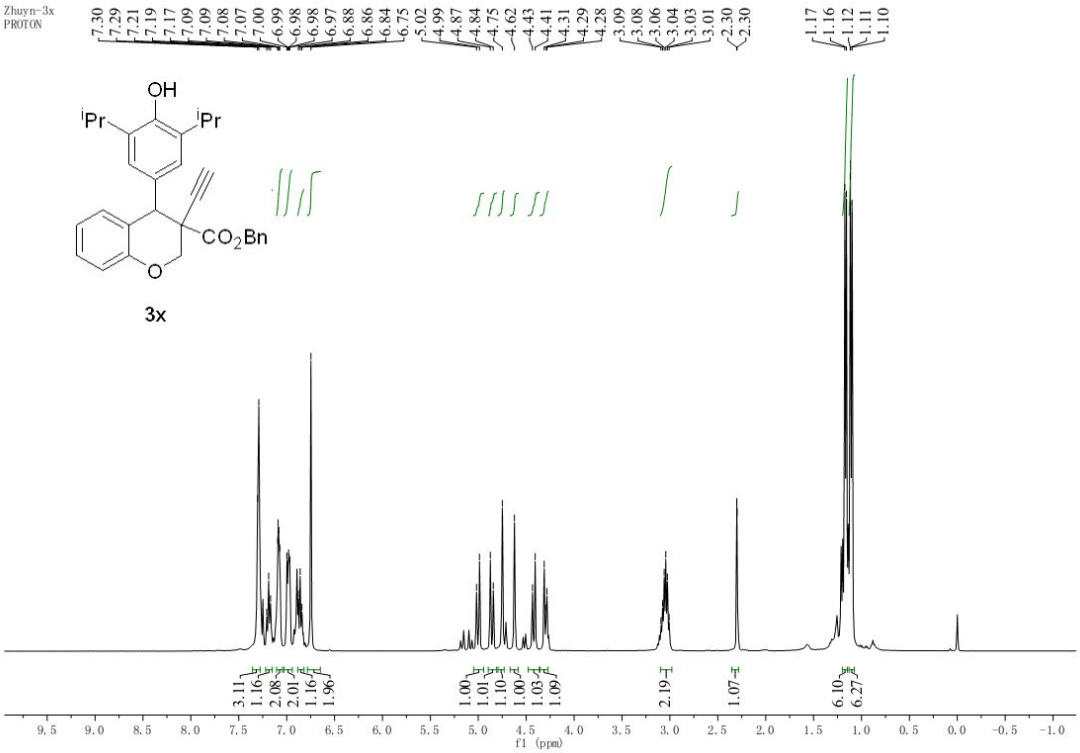

Zhuyn-3u
C13CPD
168.49
153.90
152.94
148.08
134.99
132.15
131.44
126.69
109.46
106.43
98.55
82.88
77.34
77.03
76.71
71.79
69.11
64.34
49.96
46.80
44.28
34.22
30.26
21.59
21.03
12.67
1.03
OH
t-Bu
t-Bu
CO2iPr
Et2N
O
3u
f1 (ppm)

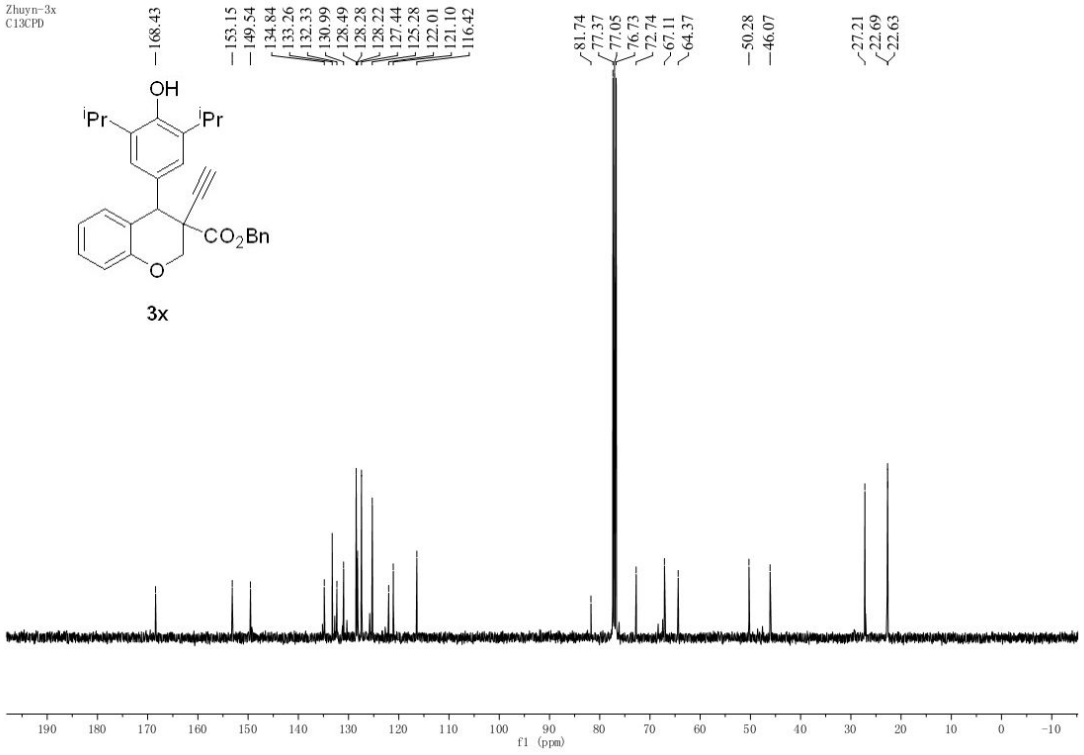

Zhuyn-3v
PROTON
6.88
6.51
6.38
5.88
5.87
5.14
4.65
4.64
4.62
4.61
4.59
4.39
4.37
4.34
4.21
4.21
4.18
4.18
2.31
1.36
1.11
1.10
0.69
0.67
OH
t-Bu
t-Bu
O
O
O
CO2iPr
3v
2.00
0.93
0.95
2.05
1.01
1.00
0.98
1.02
1.06
0.93
18.18
3.00
3.03
f1 (ppm)

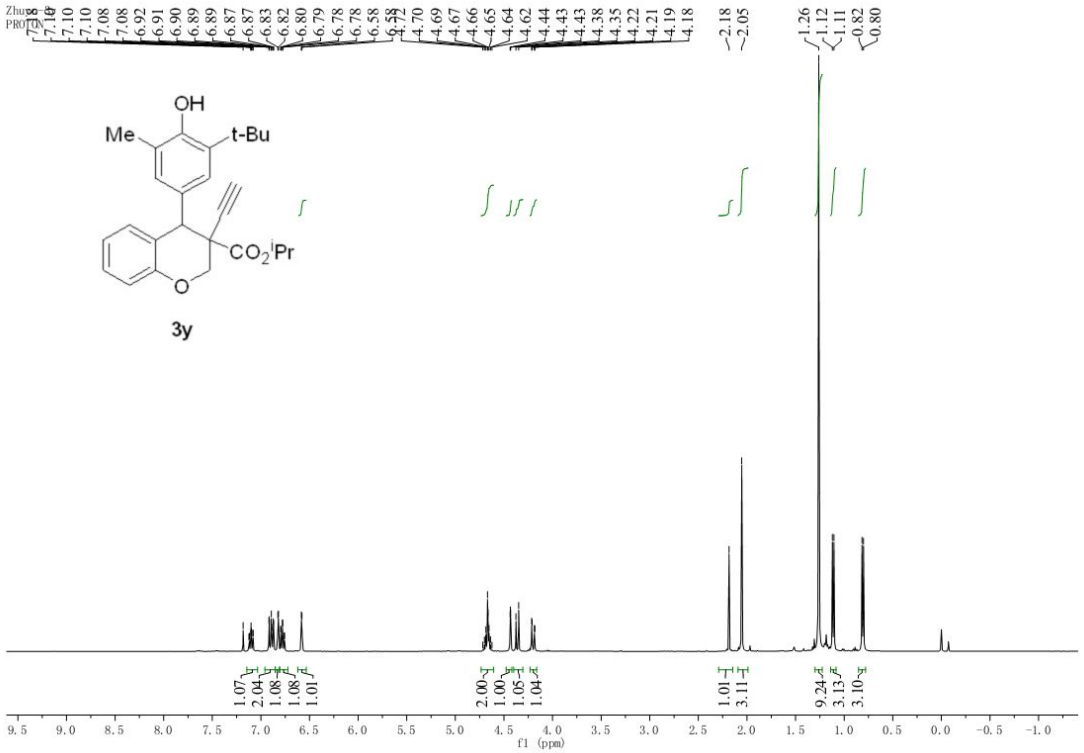

Zhuyn-3v
C13CPD
168.15
153.18
147.81
147.27
142.04
135.19
131.24
126.67
113.71
109.34
101.05
97.86
82.48
77.36
77.04
76.73
71.95
69.32
64.19
50.59
46.31
34.24
30.21
21.60
21.00
OH
t-Bu
t-Bu
O
O
O
CO2iPr
3v
f1 (ppm)

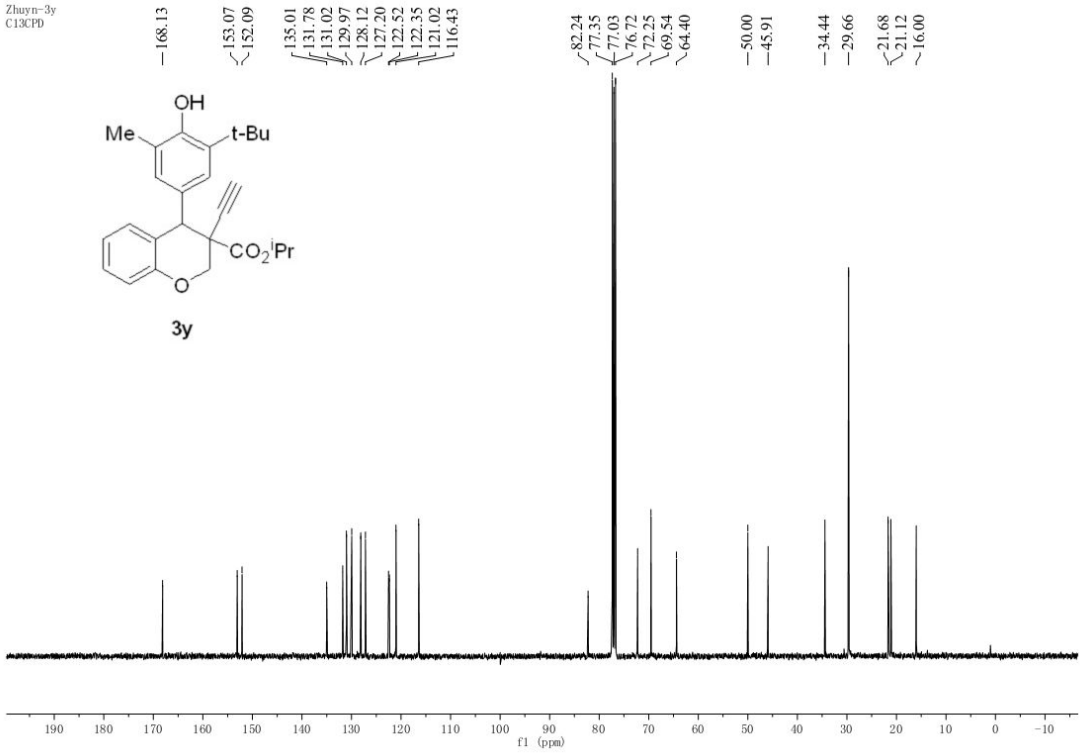

7.74
7.73
7.72
7.70
7.65
7.63
7.33
7.31
7.31
7.29
7.29
7.28
7.26
7.26
7.24
7.21
7.19
7.04
7.03
7.02
7.01
5.13
4.96
4.92
4.90
4.87
4.57
4.54
4.36
4.35
4.33
4.32
2.20
1.31
OH
t-Bu
t-Bu
O
CO2Bn
3w
2.00
0.99
5.10
1.05
3.95
1.99
1.01
0.97
1.00
0.99
0.95
18.05
f1 (ppm)

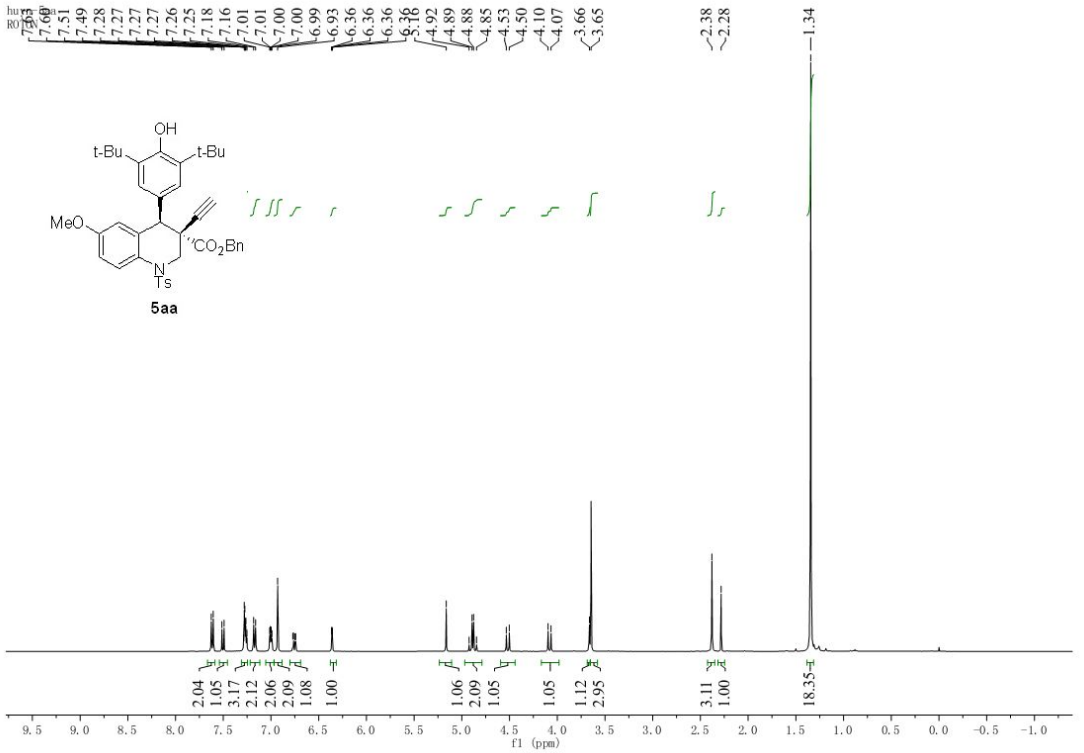

Zhuyn-3w
C13CPD
168.81
153.31
150.81
135.60
134.64
132.73
130.55
129.58
129.27
128.54
128.45
128.33
127.65
126.56
126.17
123.22
122.77
118.24
113.08
81.87
77.36
77.05
76.73
67.43
63.90
47.68
45.92
34.27
30.30
OH
t-Bu
t-Bu
CO2Bn
O
3w
f1 (ppm)

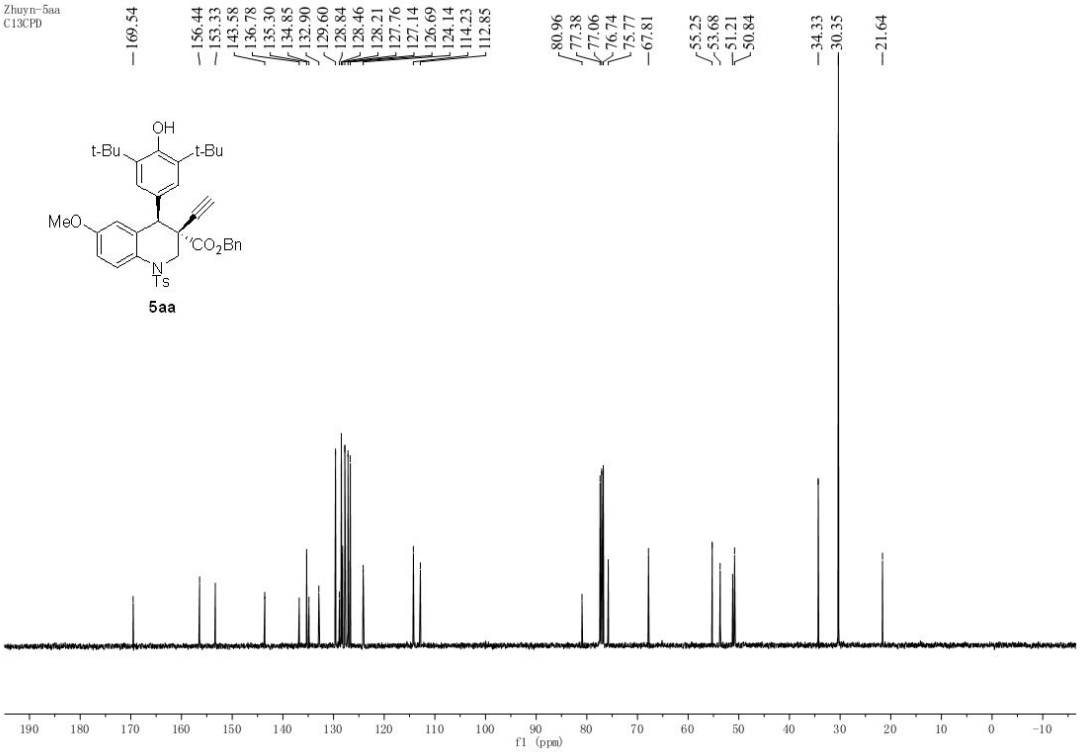

Zhuyn-3x
PROTON
7.30
7.29
7.21
7.19
7.17
7.09
7.09
7.08
7.07
7.00
6.99
6.98
6.98
6.97
6.88
6.86
6.84
6.75
5.02
4.99
4.87
4.84
4.75
4.62
4.43
4.41
4.31
4.29
4.28
3.09
3.08
3.06
3.04
3.03
3.01
2.30
2.30
1.17
1.16
1.12
1.11
1.10
OH
iPr
iPr
CO2Bn
O
3x
3.11
1.16
2.08
2.01
1.16
1.96
1.00
1.01
1.10
1.00
1.03
1.09
2.19
1.07
6.10
6.27
f1 (ppm)

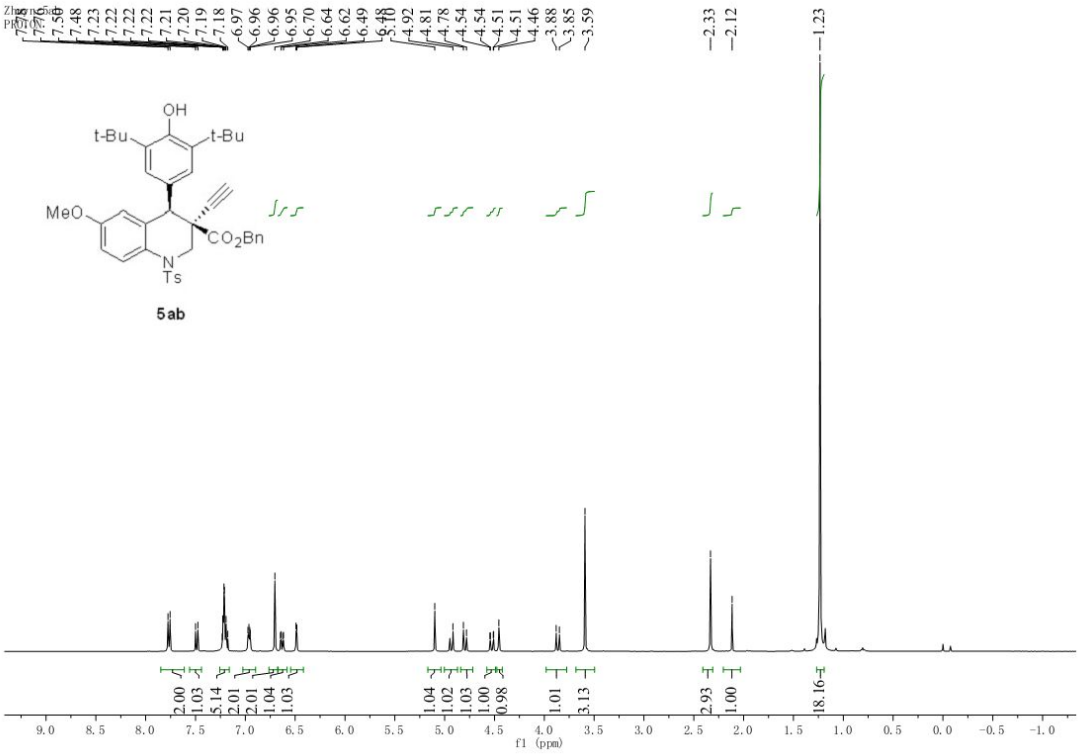

Zhuyn-3x
C13CPD
168.43
153.15
149.54
134.84
133.26
132.33
130.99
128.49
128.28
128.22
127.44
125.28
122.01
121.10
116.42
81.74
77.37
77.05
76.73
72.74
67.11
64.37
50.28
46.07
27.21
22.69
22.63
OH
iPr
iPr
CO2Bn
O
3x
f1 (ppm)

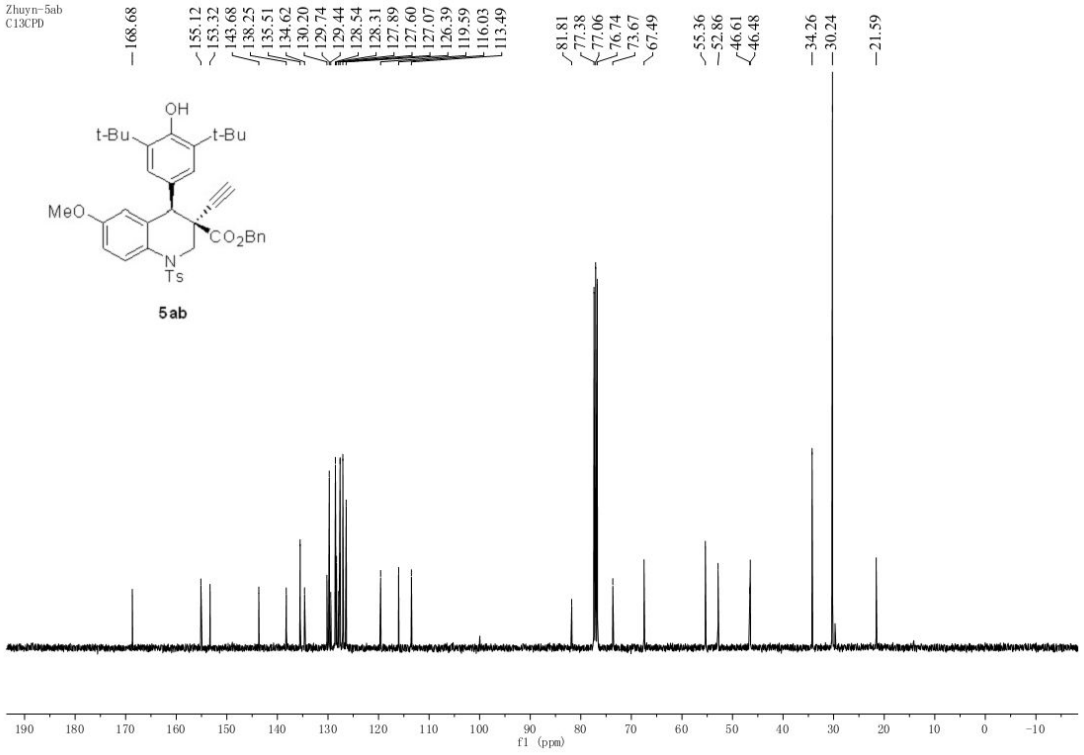

7.18
7.10
7.08
6.92
6.91
6.90
6.89
6.87
6.83
6.82
6.80
6.79
6.78
6.58
4.70
4.69
4.67
4.66
4.65
4.64
4.62
4.44
4.43
4.38
4.35
4.22
4.21
4.19
4.18
2.18
2.05
1.26
1.12
1.11
0.82
0.80
OH
Me
t-Bu
CO2iPr
O
3y
1.07
2.04
1.08
1.08
1.01
2.00
1.00
1.05
1.04
1.01
3.11
9.24
3.13
3.10
f1 (ppm)

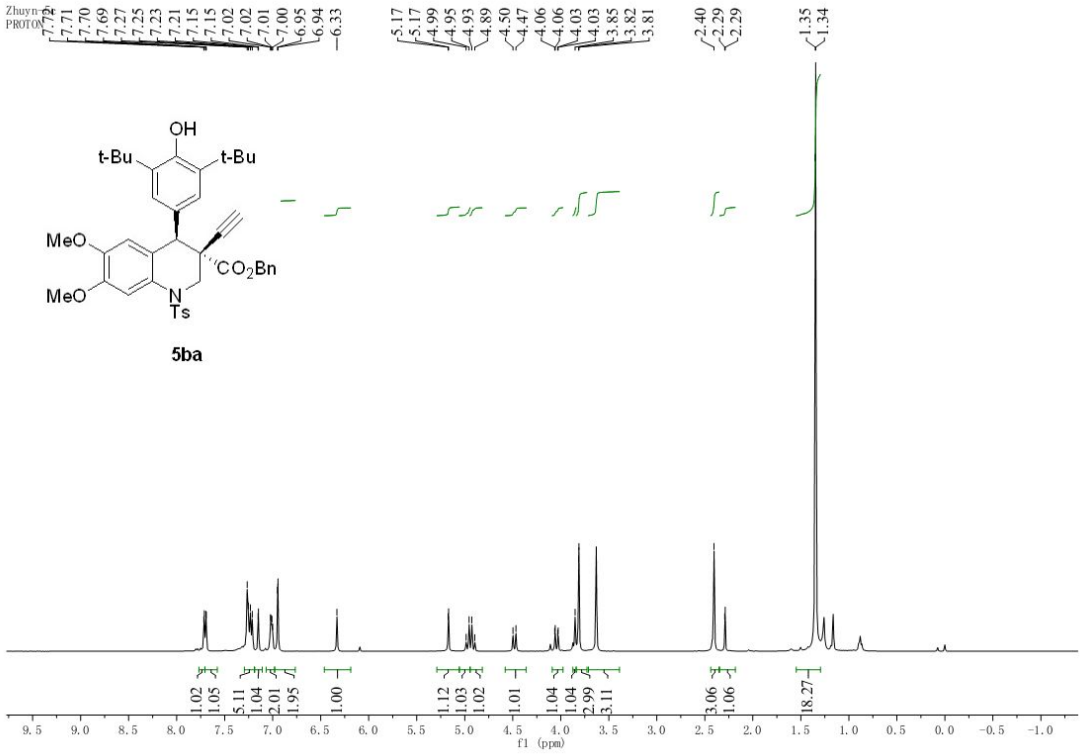

Zhuyn-3y
C13CPD
168.13
153.07
152.09
135.01
131.78
131.02
129.97
128.12
127.20
122.52
122.35
121.02
116.43
82.24
77.35
77.03
76.72
72.25
69.54
64.40
50.00
45.91
34.44
29.66
21.68
21.12
16.00
OH
Me
t-Bu
CO2iPr
O
3y
f1 (ppm)

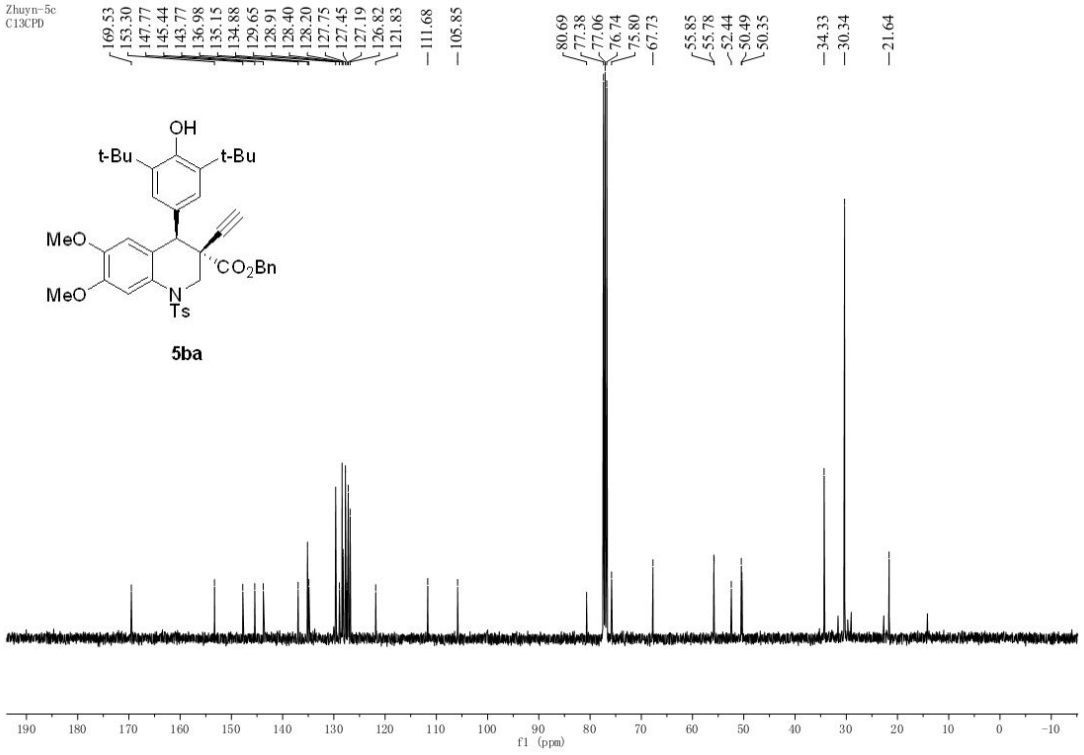

7.51
7.49
7.28
7.27
7.27
7.27
7.26
7.25
7.18
7.16
7.01
7.01
7.00
7.00
6.99
6.93
6.36
6.36
6.36
6.35
5.16
4.92
4.89
4.88
4.85
4.53
4.50
4.10
4.07
3.66
3.65
2.38
2.28
1.34
OH
t-Bu
t-Bu
MeO
CO2Bn
N
Ts
5aa
2.04
1.05
3.17
2.12
2.06
2.09
1.08
1.00
1.06
2.09
1.05
1.05
1.12
2.95
3.11
1.00
18.35
f1 (ppm)

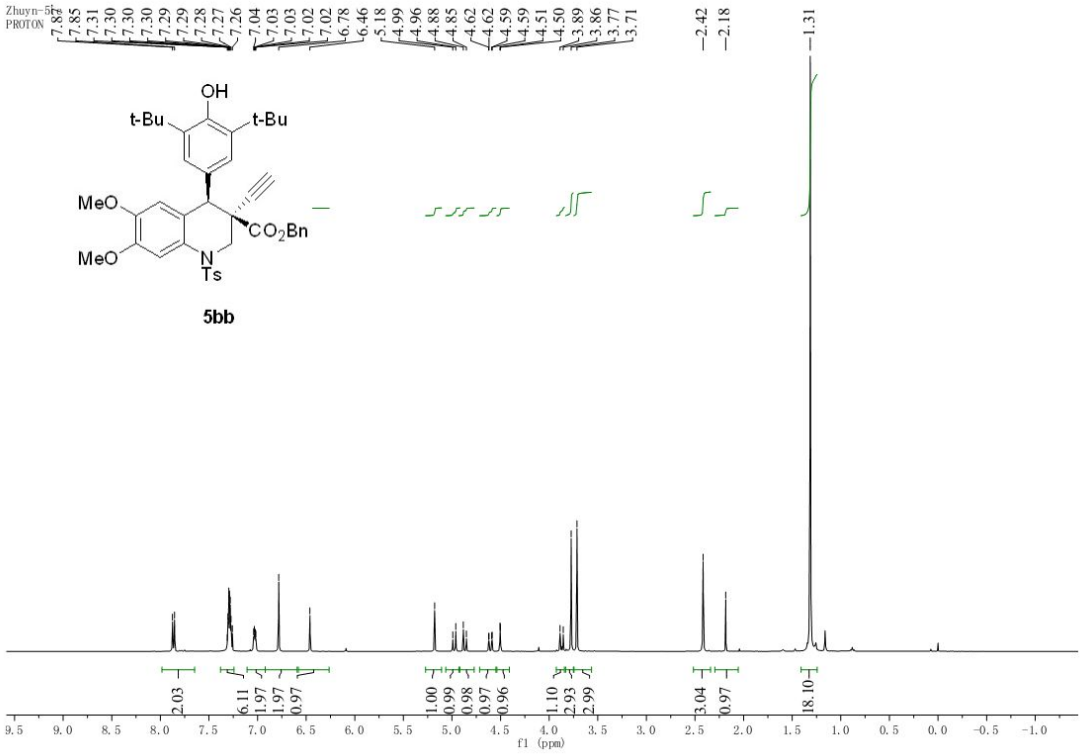

Zhuyn-5aa
C13CPD
169.54
156.44
153.33
143.58
136.78
135.30
134.85
132.90
129.60
128.84
128.46
128.21
127.76
127.14
126.69
124.14
114.23
112.85
80.96
77.38
77.06
76.74
75.77
67.81
55.25
53.68
51.21
50.84
34.33
30.35
21.64
OH
t-Bu
t-Bu
MeO
CO2Bn
N
Ts
5aa
f1 (ppm)

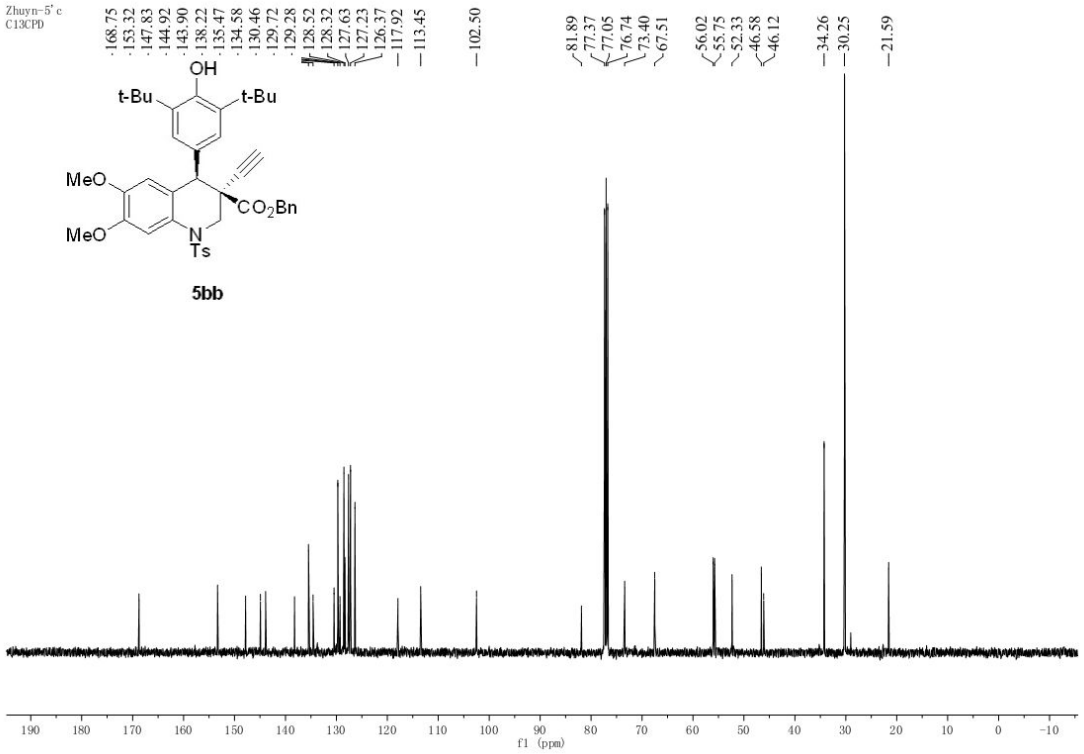

7.58
7.56
7.48
7.23
7.22
7.22
7.22
7.21
7.20
7.19
7.18
6.97
6.96
6.96
6.95
6.70
6.64
6.62
6.49
4.92
4.81
4.78
4.54
4.54
4.51
4.51
4.46
3.88
3.85
3.59
2.33
2.12
1.23
OH
t-Bu
t-Bu
MeO
CO2Bn
N
Ts
5ab
2.00
1.03
5.14
2.01
2.01
1.04
1.03
1.04
1.02
1.03
1.00
0.98
1.01
3.13
2.93
1.00
18.16
f1 (ppm)

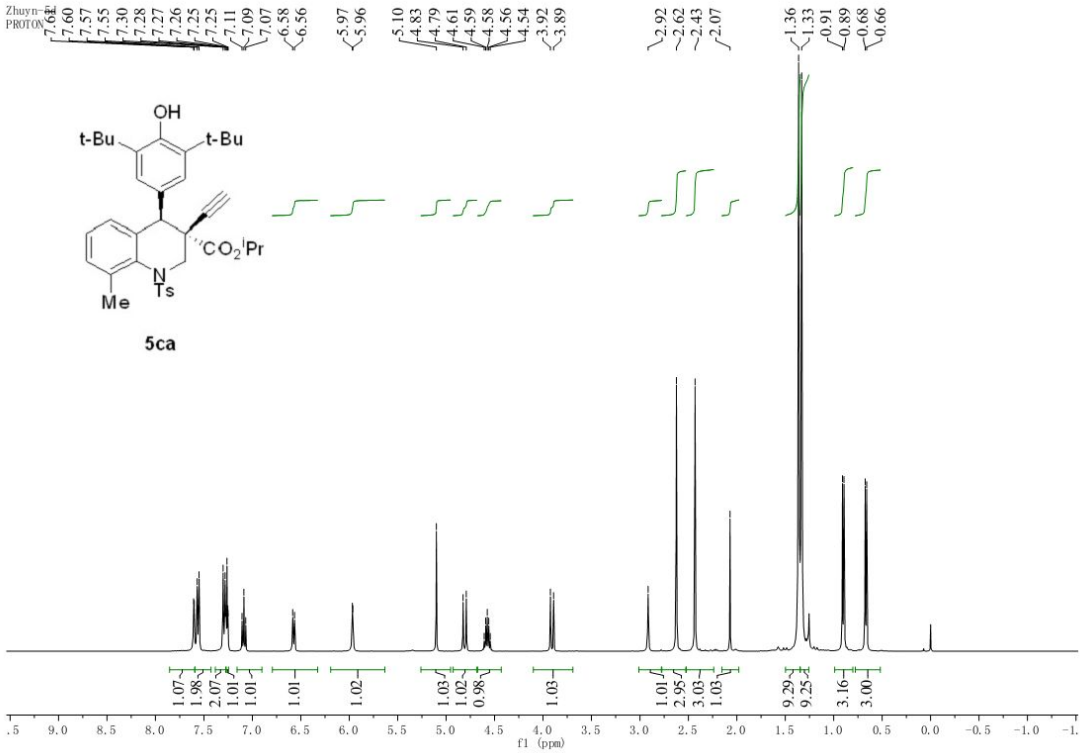

Zhuyn-5ab
C13CPD
168.68
155.12
153.32
143.68
138.25
135.51
134.62
130.20
129.74
129.44
128.54
128.31
127.89
127.60
127.07
126.39
119.59
116.03
113.49
81.81
77.38
77.06
76.74
73.67
67.49
55.36
52.86
46.61
46.48
34.26
30.24
21.59
OH
t-Bu
t-Bu
MeO
CO2Bn
N
Ts
5ab
f1 (ppm)

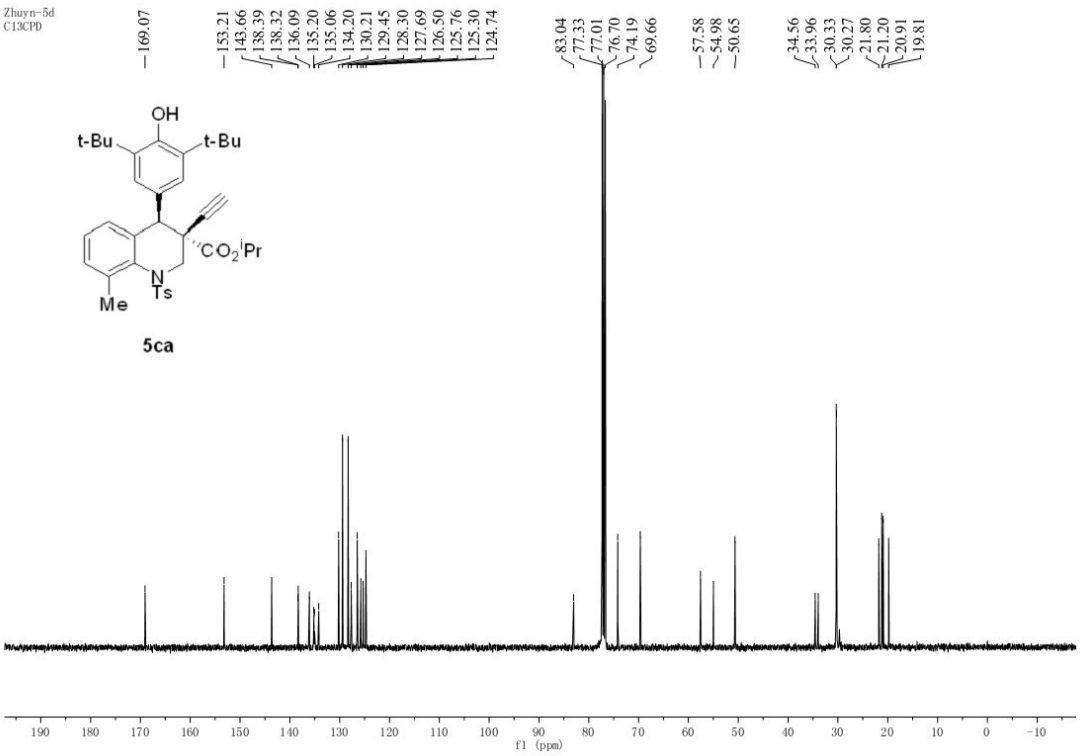

Zhuyn-5
PROTON
7.72
7.71
7.70
7.69
7.27
7.25
7.23
7.21
7.15
7.15
7.02
7.02
7.01
7.00
6.95
6.94
6.33
5.17
5.17
4.99
4.95
4.93
4.89
4.50
4.47
4.06
4.06
4.03
4.03
3.85
3.82
3.81
2.40
2.29
2.29
1.35
1.34
OH
t-Bu
t-Bu
MeO
MeO
CO2Bn
N
Ts
5ba
1.02
1.05
5.11
1.04
2.01
1.95
1.00
1.12
1.03
1.02
1.01
1.04
1.04
2.99
3.11
3.06
1.06
18.27
f1 (ppm)

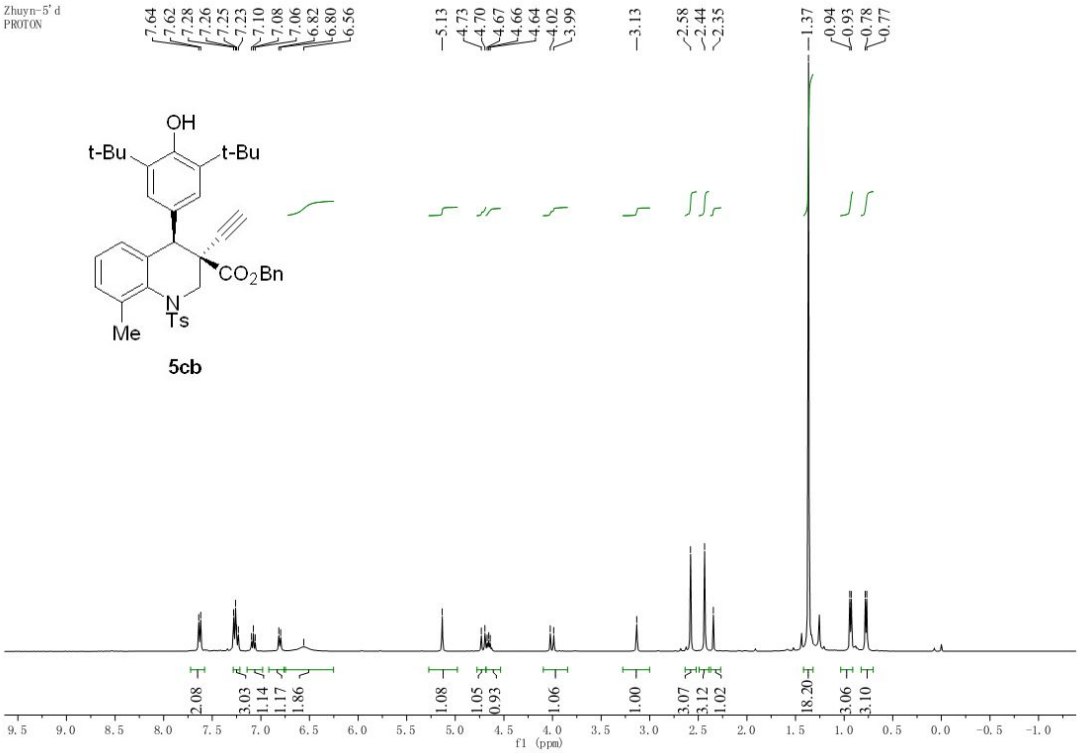

Zhuyn-5c
C13CPD
169.53
153.30
147.77
145.44
143.77
136.98
135.15
134.88
129.65
128.91
128.40
128.20
127.75
127.45
127.19
126.82
121.83
111.68
105.85
80.69
77.38
77.06
76.74
75.80
67.73
55.85
55.78
52.44
50.49
50.35
34.33
30.34
21.64
OH
t-Bu
t-Bu
MeO
MeO
CO2Bn
N
Ts
5ba
f1 (ppm)

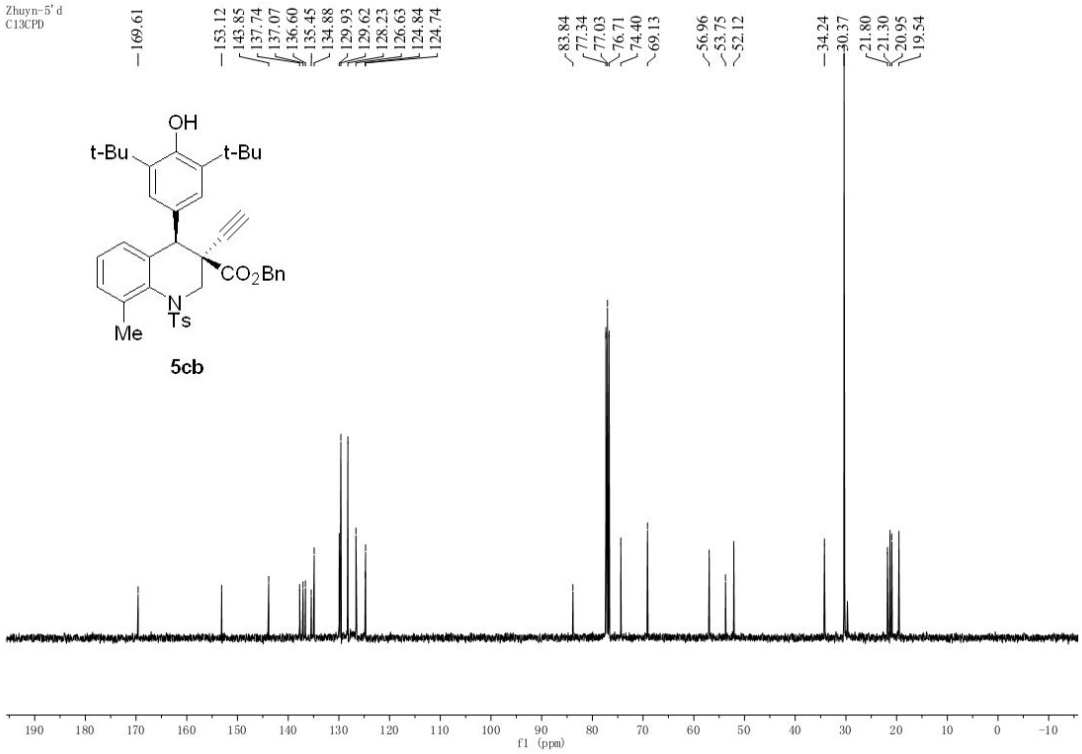

Zhuyn-5b
PROTON
7.88
7.85
7.31
7.30
7.30
7.30
7.29
7.29
7.28
7.27
7.26
7.04
7.03
7.03
7.02
7.02
6.78
6.46
5.18
4.99
4.96
4.88
4.85
4.62
4.62
4.59
4.59
4.51
4.50
3.89
3.86
3.77
3.71
2.42
2.18
1.31
OH
t-Bu
t-Bu
MeO
MeO
CO2Bn
N
Ts
5bb
2.03
6.11
1.97
1.97
0.97
1.00
0.99
0.98
0.97
0.96
1.10
2.93
2.99
3.04
0.97
18.10
f1 (ppm)

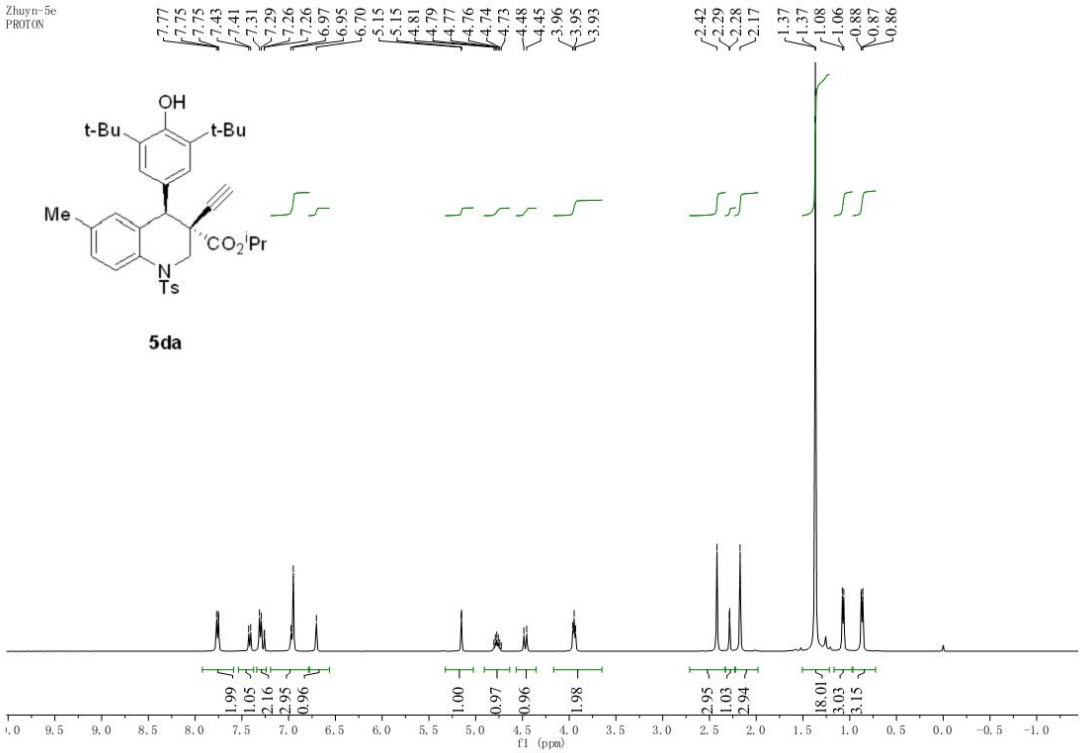

Zhuyn-5'c
C13CPD
168.75
153.32
147.83
144.92
143.90
138.22
135.47
134.58
130.46
129.72
129.28
128.52
128.32
127.63
127.23
126.37
117.92
113.45
102.50
81.89
77.37
77.05
76.74
73.40
67.51
56.02
55.75
52.33
46.58
46.12
34.26
30.25
21.59
OH
t-Bu
t-Bu
MeO
MeO
CO2Bn
N
Ts
5bb
f1 (ppm)

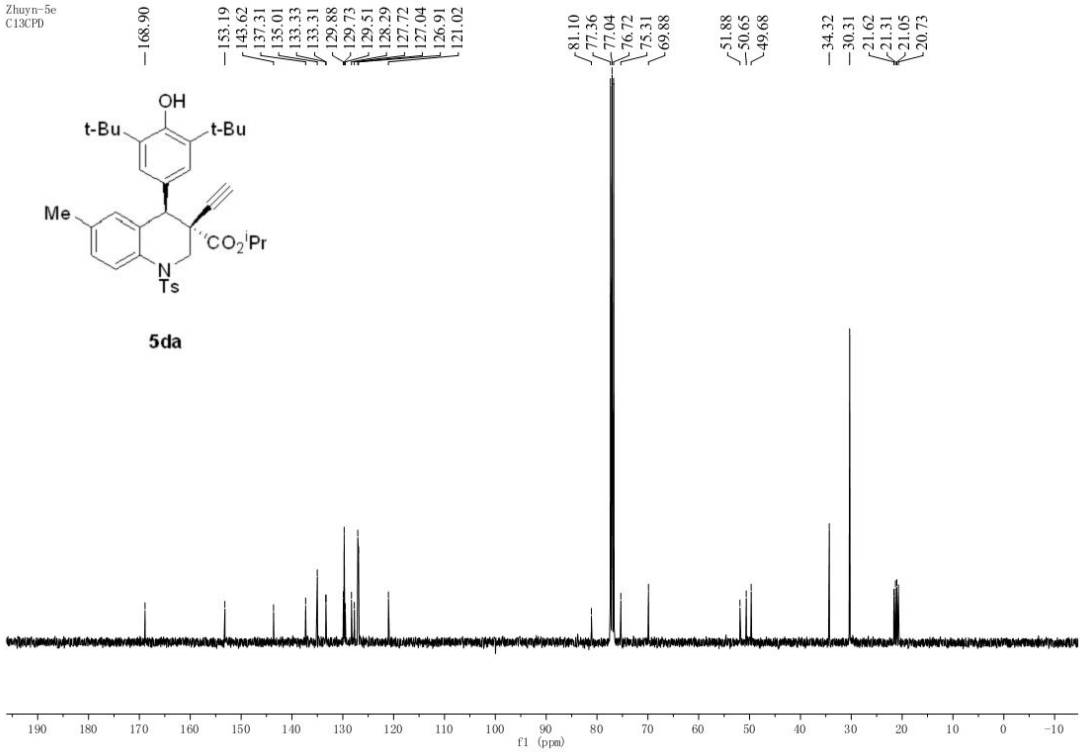

Zhuyn-
PROTON
7.61
7.60
7.57
7.55
7.30
7.28
7.27
7.26
7.25
7.25
7.11
7.09
7.07
6.58
6.56
5.97
5.96
5.10
4.83
4.79
4.61
4.59
4.58
4.56
4.54
3.92
3.89
2.92
2.62
2.43
2.07
1.36
1.33
0.91
0.89
0.68
0.66
OH
t-Bu
t-Bu
CO2iPr
N
Ts
Me
5ca
1.07
1.98
2.07
1.01
1.01
1.01
1.02
1.03
1.02
0.98
1.03
1.01
2.95
3.03
1.03
9.29
9.25
3.16
3.00
f1 (ppm)

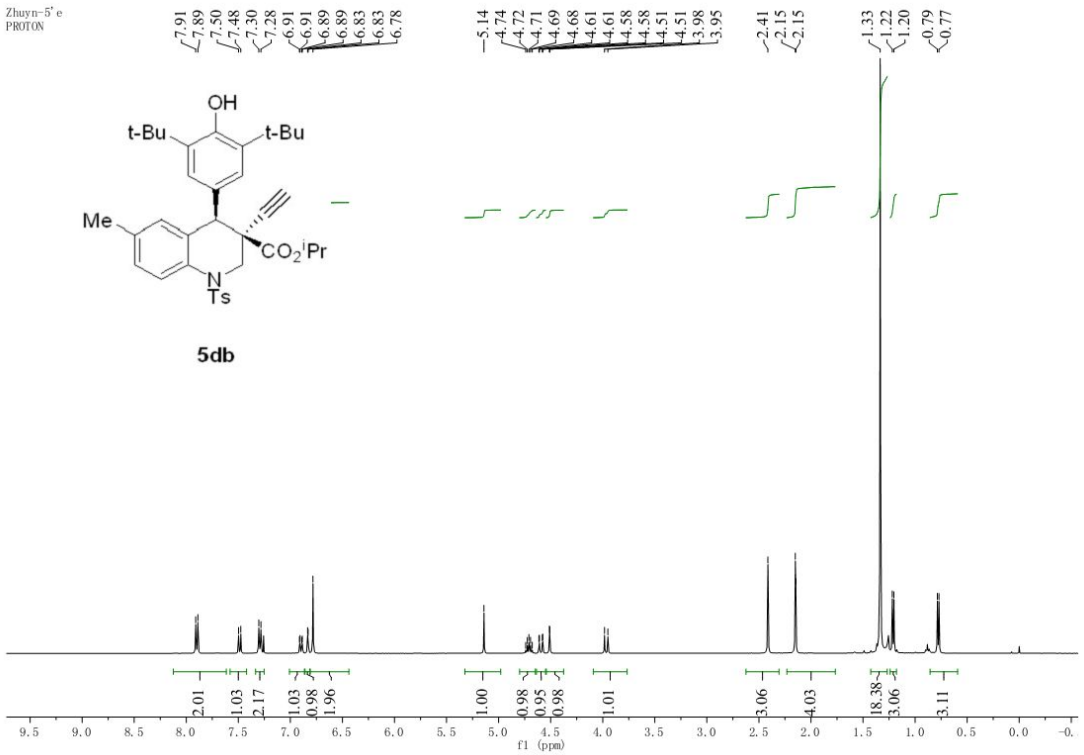

Zhuyn-5d
C13CPD
169.07
153.21
143.66
138.39
138.32
136.09
135.20
135.06
134.20
130.21
129.45
128.30
127.69
126.50
125.76
125.30
124.74
83.04
77.33
77.01
76.70
74.19
69.66
57.58
54.98
50.65
34.56
33.96
30.33
30.27
21.80
21.20
20.91
19.81
OH
t-Bu
t-Bu
CO2iPr
N
Ts
Me
5ca
f1 (ppm)

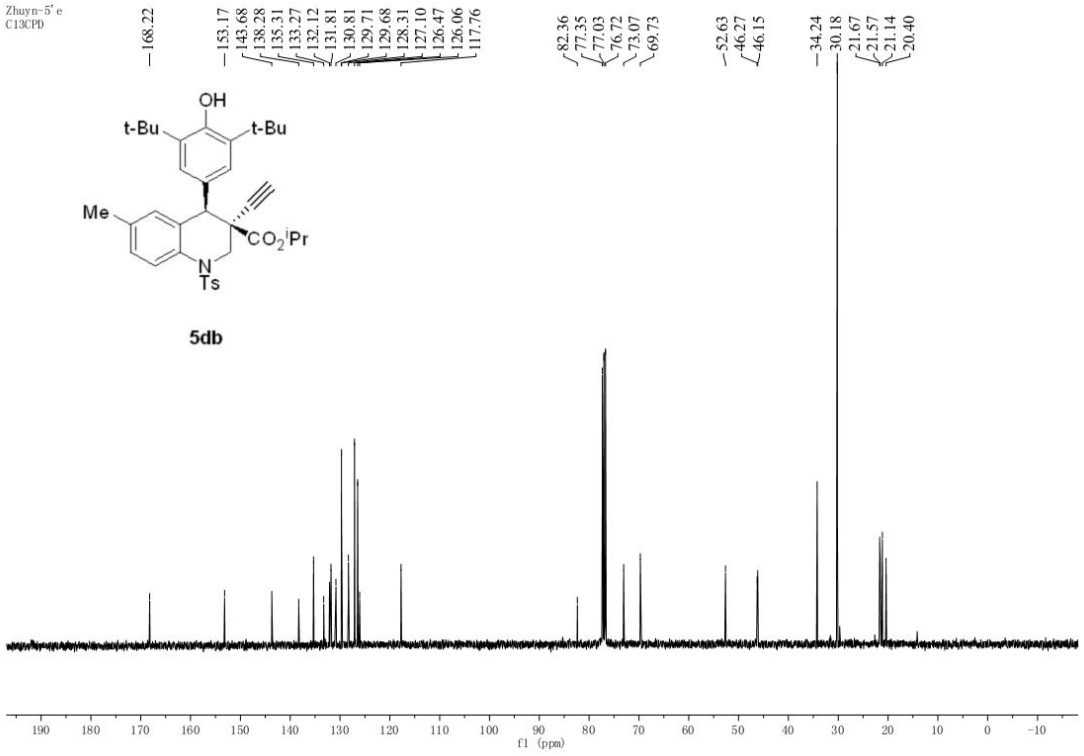

Zhuyn-5'd
PROTON
7.64
7.62
7.28
7.26
7.25
7.23
7.10
7.08
7.06
6.82
6.80
6.56
5.13
4.73
4.70
4.67
4.66
4.64
4.02
3.99
3.13
2.58
2.44
2.35
1.37
0.94
0.93
0.78
0.77
OH
t-Bu
t-Bu
CO2Bn
N
Ts
Me
5cb
2.08
3.03
1.14
1.17
1.86
1.08
1.05
0.93
1.06
1.00
3.07
3.12
1.02
18.20
3.06
3.10
f1 (ppm)

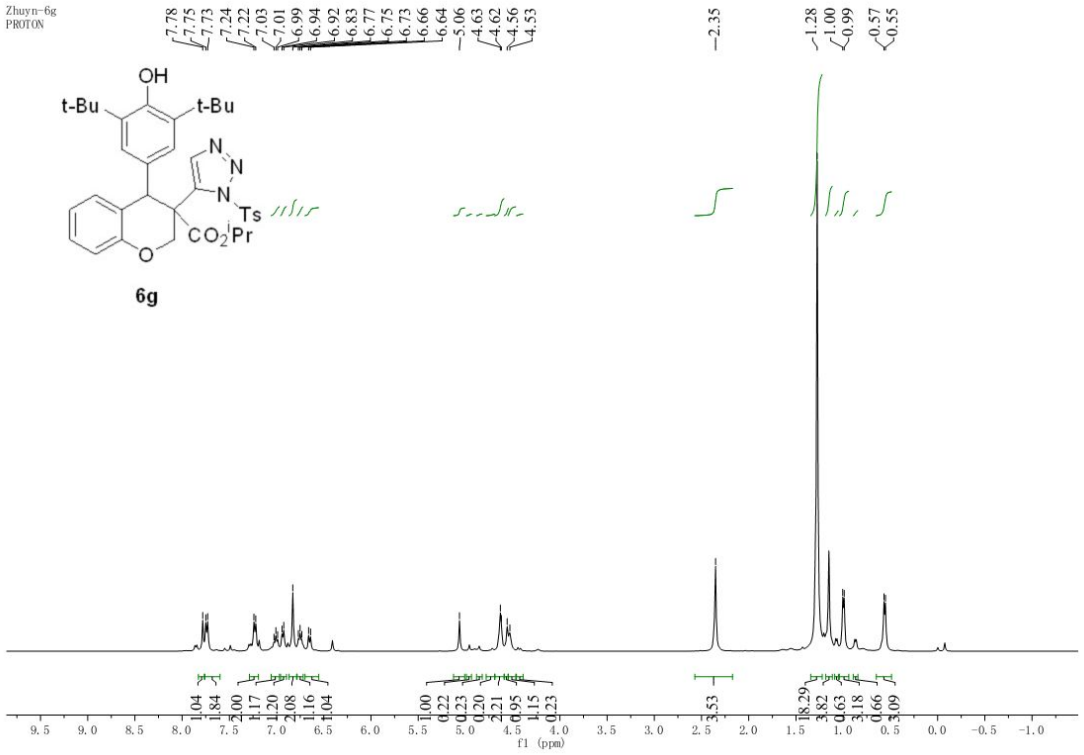

Zhuyn-5'd
C13CPD
169.61
153.12
143.85
137.74
137.07
136.60
135.45
134.88
129.93
129.62
128.23
126.63
124.84
124.74
83.84
77.34
77.03
76.71
74.40
69.13
56.96
53.75
52.12
34.24
30.37
21.80
21.30
20.95
19.54
OH
t-Bu
t-Bu
CO2Bn
N
Ts
Me
5cb
f1 (ppm)

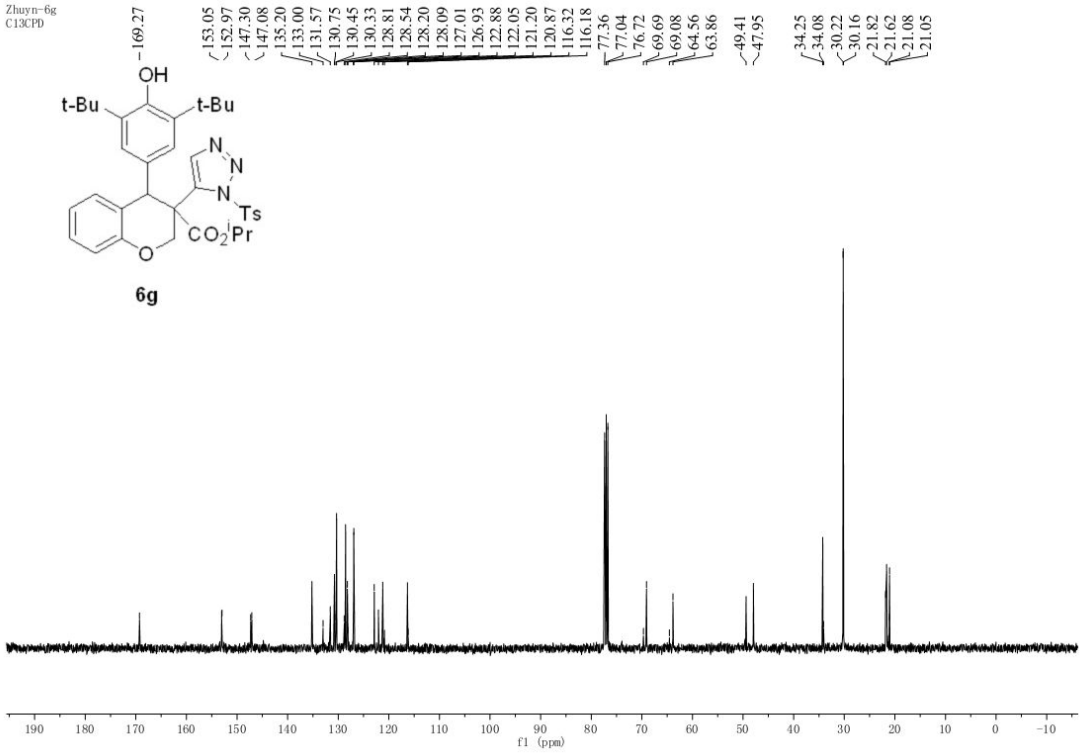

Zhuyn-5e
PROTON
7.77
7.75
7.75
7.43
7.41
7.31
7.29
7.26
7.26
6.97
6.95
6.70
5.15
5.15
4.81
4.79
4.77
4.76
4.74
4.73
4.48
4.45
3.96
3.95
3.93
2.42
2.29
2.28
2.17
1.37
1.37
1.08
1.06
0.88
0.87
0.86
OH
t-Bu
t-Bu
Me
CO2iPr
N
Ts
5da
1.99
1.05
2.16
2.95
0.96
1.00
0.97
0.96
1.98
2.95
1.03
2.94
18.01
3.03
3.15
f1 (ppm)

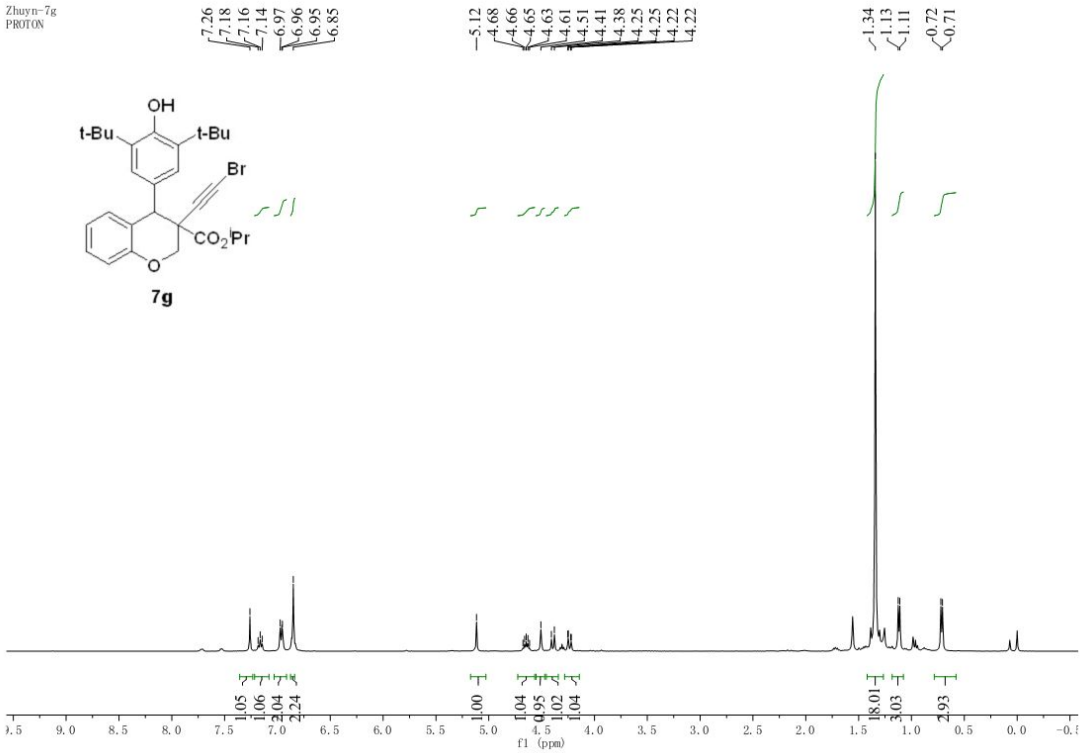

Zhuyn-5e
C13CPD
168.90
153.19
143.62
137.31
135.01
133.33
133.31
129.88
129.73
129.51
128.29
127.72
127.04
126.91
121.02
81.10
77.36
77.04
76.72
75.31
69.88
51.88
50.65
49.68
34.32
30.31
21.62
21.31
21.05
20.73
OH
t-Bu
t-Bu
Me
CO2iPr
N
Ts
5da
f1 (ppm)

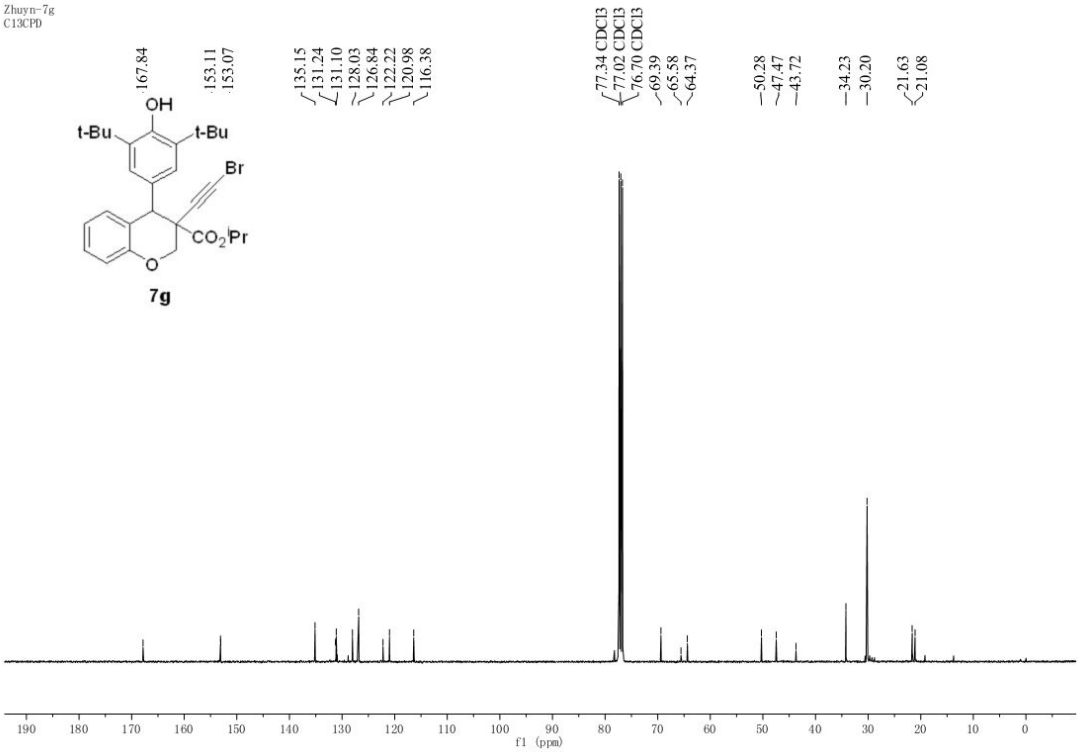

Zhuyn-5'e
PROTON
7.91
7.89
7.50
7.48
7.30
7.28
6.91
6.91
6.89
6.89
6.83
6.83
6.78
5.14
4.74
4.72
4.71
4.69
4.68
4.61
4.61
4.58
4.58
4.51
4.51
3.98
3.95
2.41
2.15
2.15
1.33
1.22
1.20
0.79
0.77
OH
t-Bu
t-Bu
Me
CO2iPr
N
Ts
5db
2.01
1.03
2.17
1.03
0.98
1.96
1.00
0.98
0.95
0.98
1.01
3.06
4.03
18.38
3.06
3.11
f1 (ppm)

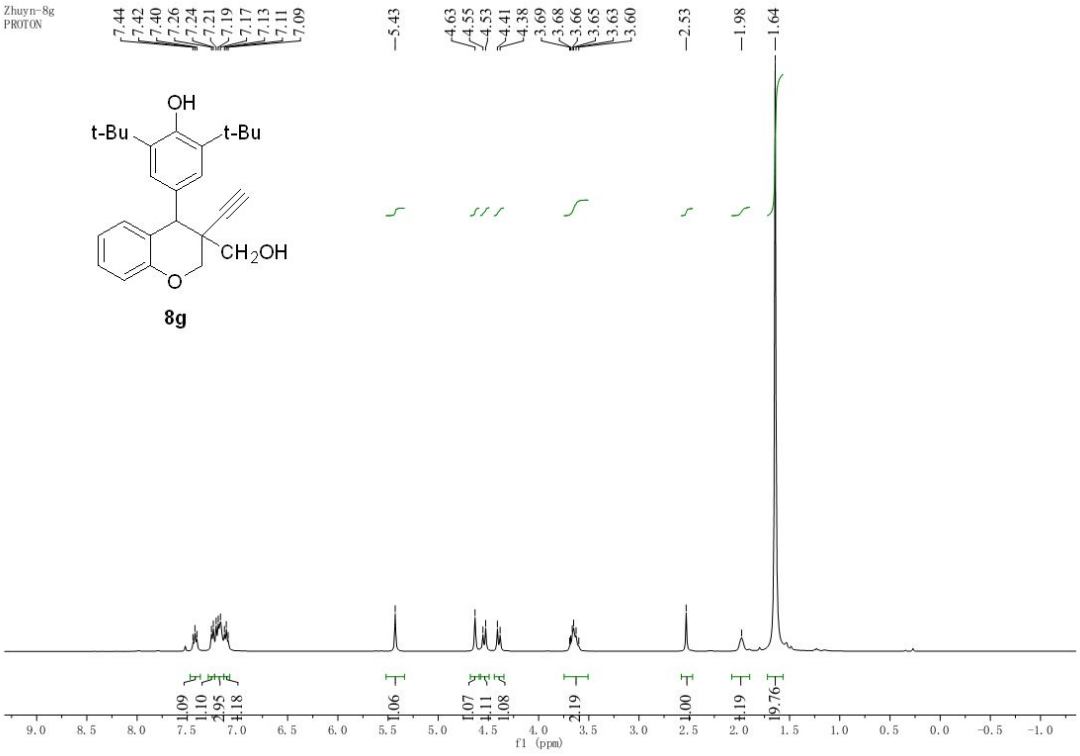

Zhuyn-5'e
C13CPD
168.22
153.17
143.68
138.28
135.31
133.27
132.12
131.81
130.81
129.71
129.68
128.31
127.10
126.47
126.06
117.76
82.36
77.35
77.03
76.72
73.07
69.73
52.63
46.27
46.15
34.24
30.18
21.67
21.57
21.14
20.40
OH
t-Bu
t-Bu
Me
CO2iPr
N
Ts
5db
f1 (ppm)

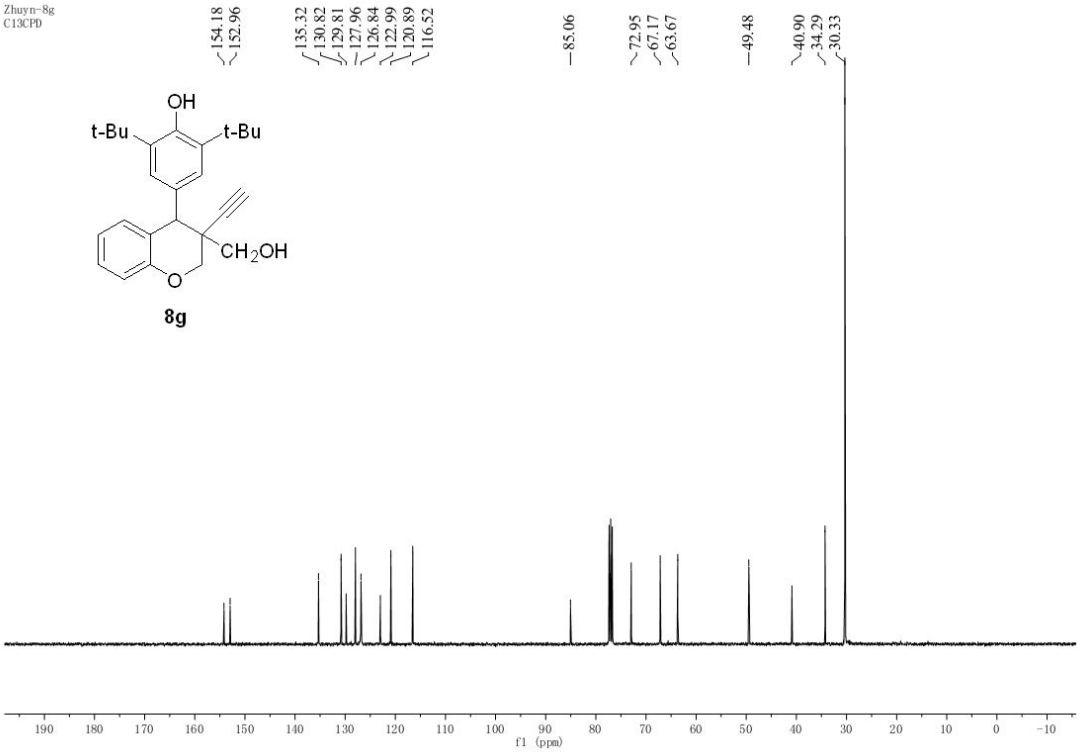

Zhuyn-6g
PROTON
7.78
7.75
7.73
7.24
7.22
7.03
7.01
6.99
6.94
6.92
6.83
6.77
6.75
6.73
6.66
6.64
5.06
4.63
4.62
4.56
4.53
2.35
1.28
1.00
0.99
0.57
0.55
OH
t-Bu
t-Bu
N
N
N
Ts
CO2iPr
O
6g
1.04
1.84
2.00
1.17
1.20
2.08
1.16
1.04
1.00
0.22
0.23
0.20
2.21
0.95
1.15
0.23
3.53
18.29
3.82
0.63
3.18
0.66
3.09
f1 (ppm)

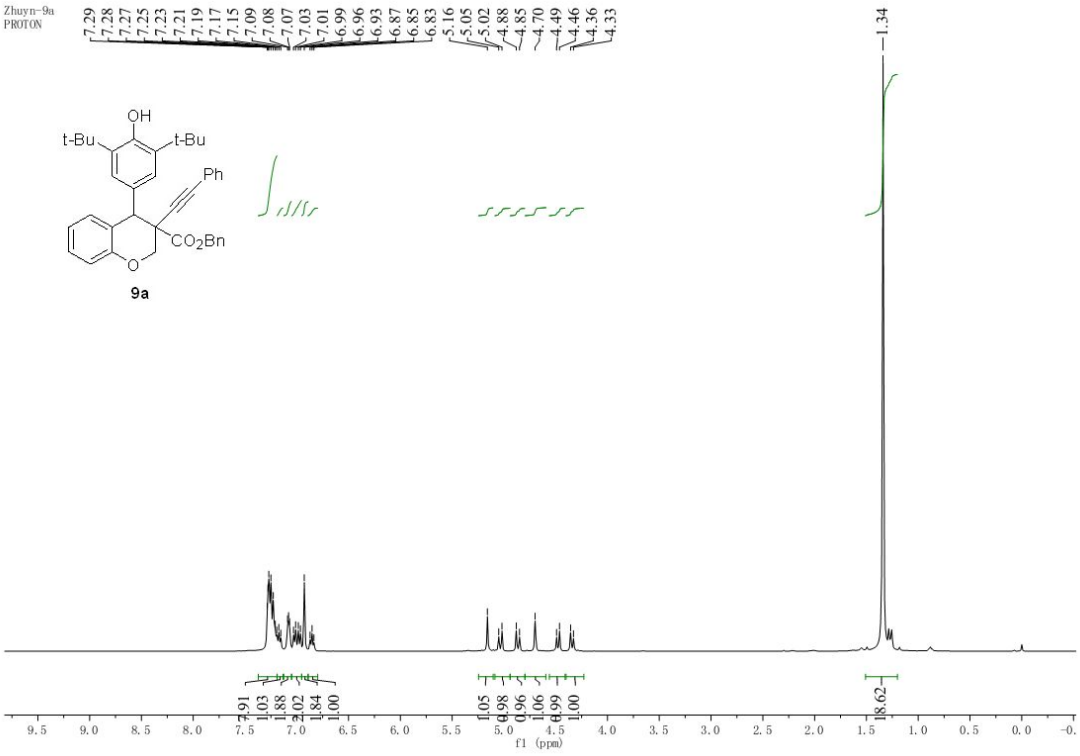

Zhuyn-6g
C13CPD
169.27
153.05
152.97
147.30
147.08
135.20
133.00
131.57
130.75
130.45
130.33
128.81
128.54
128.20
128.09
127.01
126.93
122.88
122.05
121.20
120.87
116.32
116.18
77.36
77.04
76.72
69.69
69.08
64.56
63.86
49.41
47.95
34.25
34.08
30.22
30.16
21.82
21.62
21.08
21.05
OH
t-Bu
t-Bu
N
N
N
Ts
CO2iPr
O
6g
f1 (ppm)

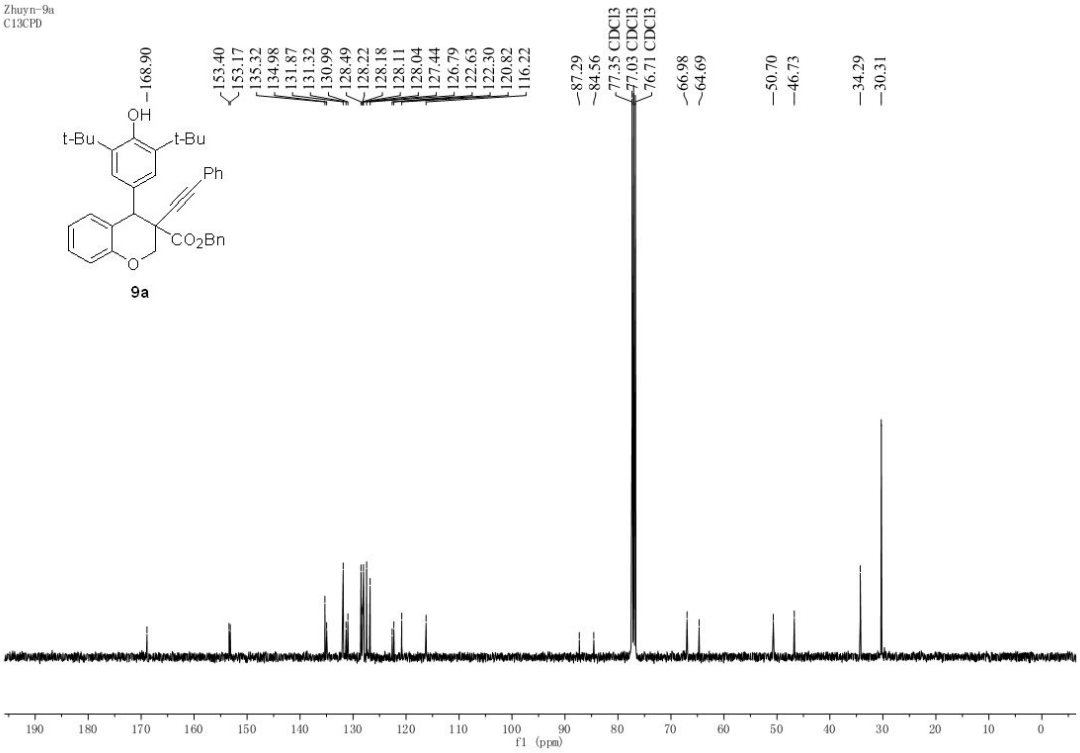

Zhuyn-7g
PROTON
7.26
7.18
7.16
7.14
6.97
6.96
6.95
6.85
5.12
4.68
4.66
4.65
4.63
4.61
4.51
4.41
4.38
4.25
4.25
4.22
4.22
1.34
1.13
1.11
0.72
0.71
OH
t-Bu
t-Bu
Br
CO2iPr
O
7g
1.05
1.06
2.04
2.24
1.00
1.04
0.95
1.02
1.04
18.01
3.03
2.93
f1 (ppm)

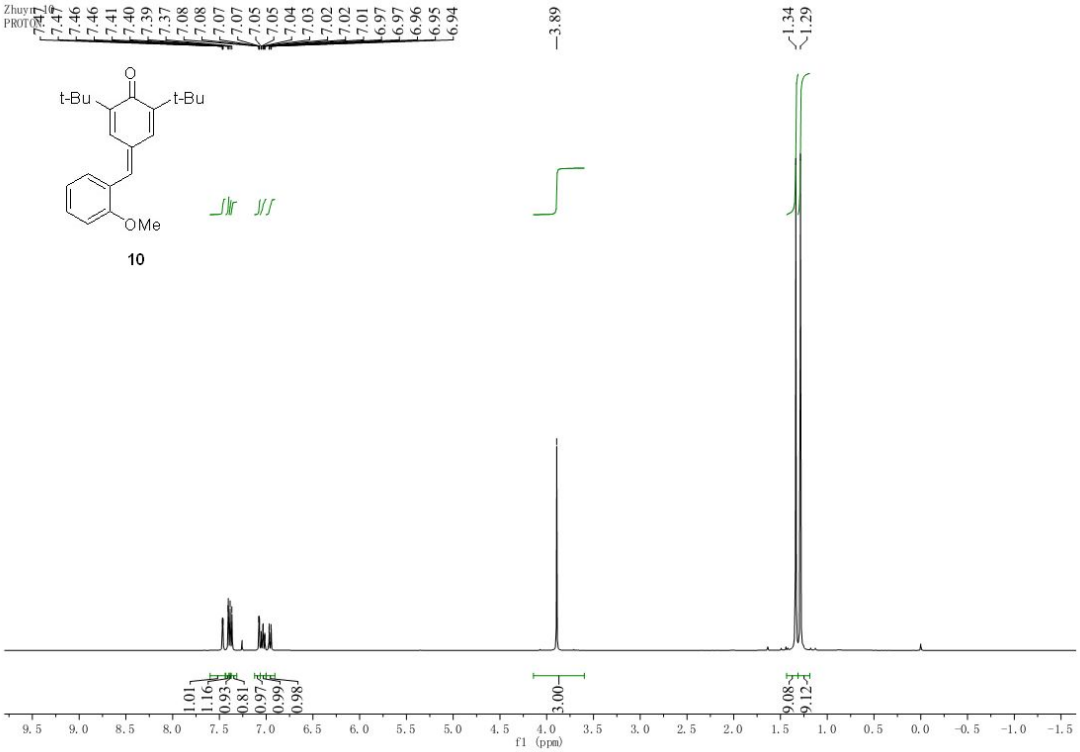

Zhuyn-7g
C13CPD
167.84
153.11
153.07
135.15
131.24
131.10
128.03
126.84
122.22
120.98
116.38
77.34 CDCl3
77.02 CDCl3
76.70 CDCl3
69.39
65.58
64.37
50.28
47.47
43.72
34.23
30.20
21.63
21.08
OH
t-Bu
t-Bu
Br
CO2iPr
O
7g
f1 (ppm)

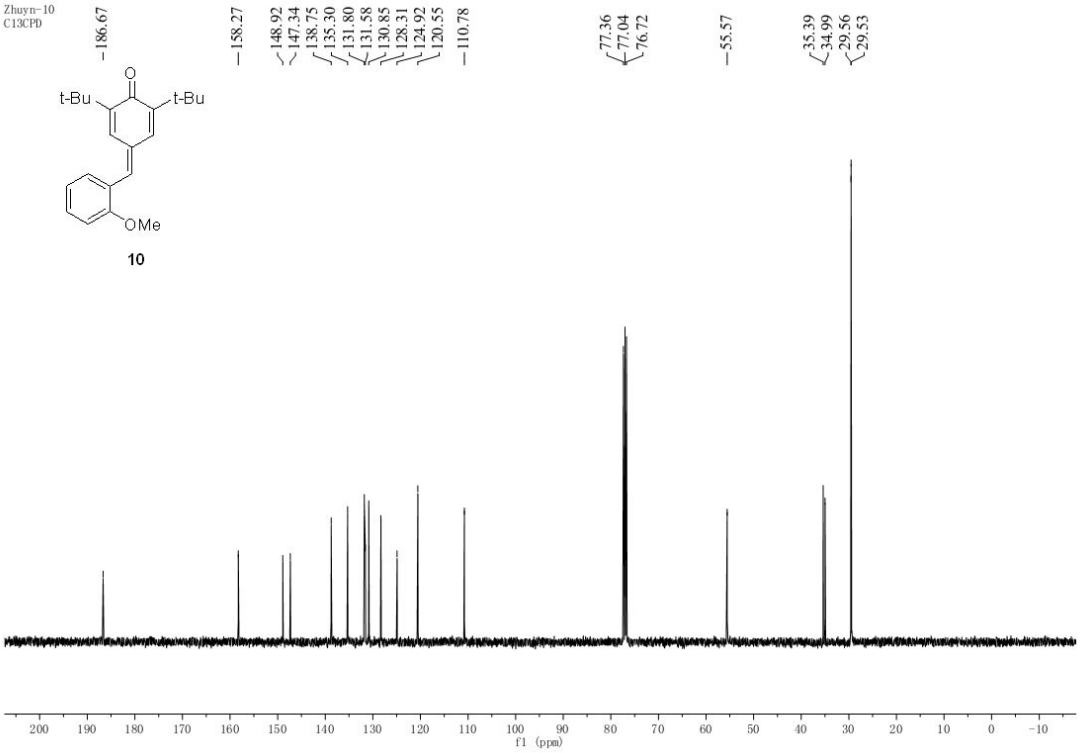

Zhuyn-8g
PROTON
7.44
7.42
7.40
7.26
7.24
7.21
7.19
7.17
7.13
7.11
7.09
5.43
4.63
4.55
4.53
4.41
4.38
3.69
3.68
3.66
3.65
3.63
3.60
2.53
1.98
1.64
OH
t-Bu
t-Bu
CH2OH
O
8g
1.09
1.10
2.95
1.18
1.06
1.07
1.11
1.08
2.19
1.00
1.19
19.76
f1 (ppm)

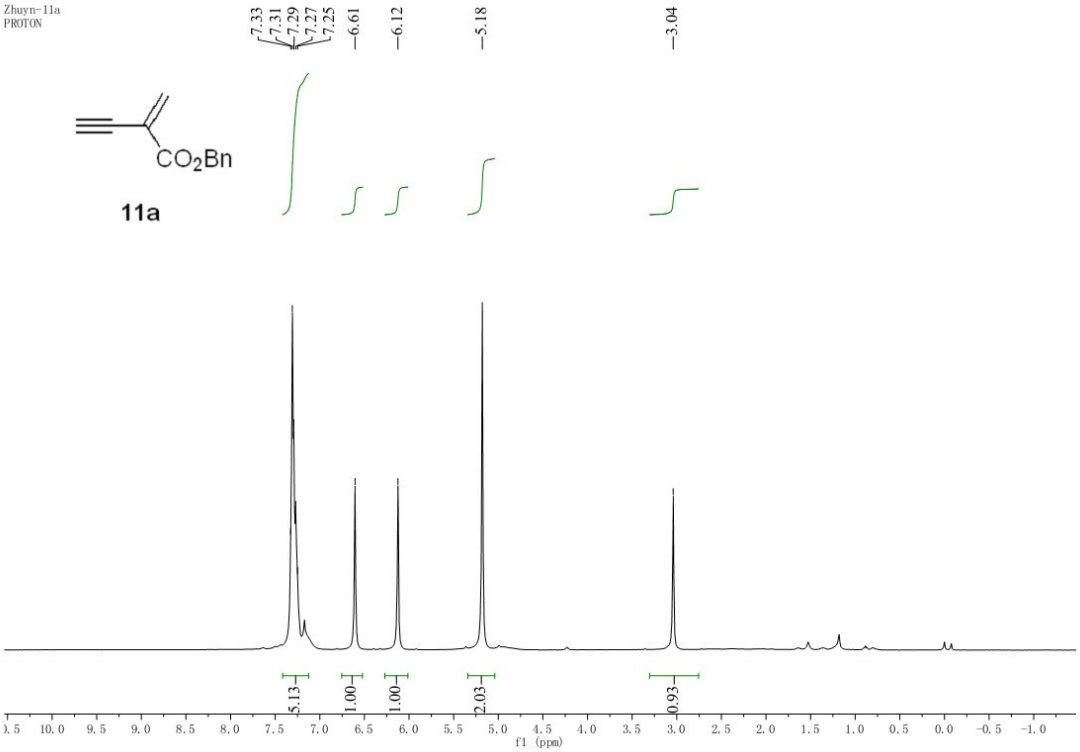

Zhuyn-8g
C13CPD
154.18
152.96
135.32
130.82
129.81
127.96
126.84
122.99
120.89
116.52
85.06
72.95
67.17
63.67
49.48
40.90
34.29
30.33
OH
t-Bu
t-Bu
CH2OH
O
8g
f1 (ppm)

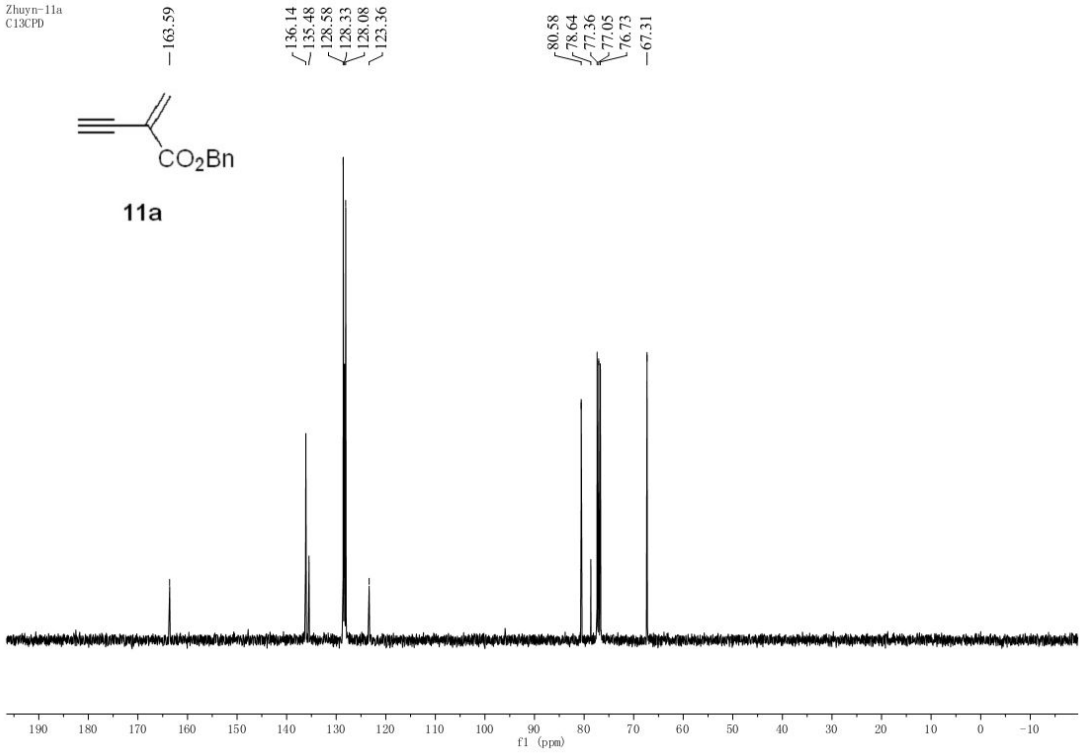

Zhuyn-9a
PROTON
7.29
7.28
7.27
7.25
7.23
7.21
7.19
7.17
7.15
7.09
7.08
7.07
7.03
7.01
6.99
6.96
6.93
6.87
6.85
6.83
5.16
5.05
5.02
4.88
4.85
4.70
4.49
4.46
4.36
4.33
1.34
OH
t-Bu
t-Bu
Ph
CO2Bn
O
9a
7.91
1.03
1.88
2.02
1.84
1.00
1.05
0.98
0.96
1.06
0.99
1.00
18.62
f1 (ppm)


Zhuyn-9a
C13CPD
168.90
153.40
153.17
135.32
134.98
131.87
131.32
130.99
128.49
128.22
128.18
128.11
128.04
127.44
126.79
122.63
122.30
120.82
116.22
87.29
84.56
77.35 CDCl3
77.03 CDCl3
76.71 CDCl3
66.98
64.69
50.70
46.73
34.29
30.31
OH
t-Bu
t-Bu
Ph
CO2Bn
O
9a
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

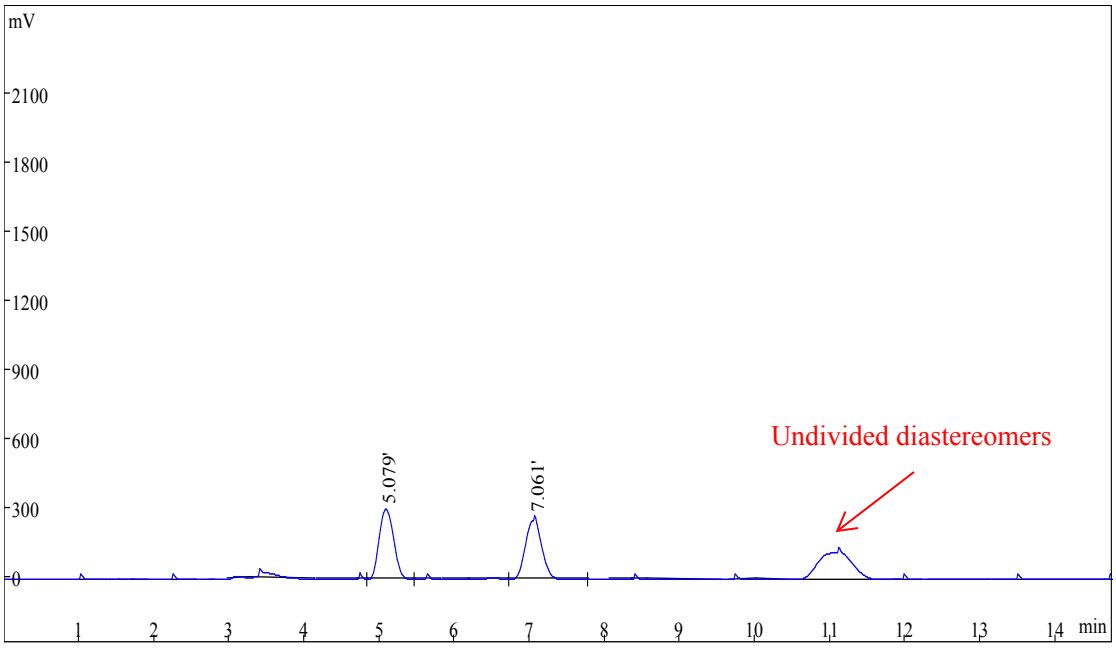

7.47
7.46
7.46
7.41
7.40
7.39
7.37
7.08
7.08
7.07
7.07
7.05
7.05
7.04
7.03
7.02
7.02
7.01
6.97
6.97
6.96
6.95
6.94
3.89
1.34
1.29
O
t-Bu
t-Bu
OMe
10
1.01
1.16
0.93
0.81
0.97
0.99
0.98
3.00
9.08
9.12
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0 −1.5
f1 (ppm)


Zhuyn-10
C13CPD
186.67
158.27
148.92
147.34
138.75
135.30
131.80
131.58
130.85
128.31
124.92
120.55
110.78
77.36
77.04
76.72
55.57
35.39
34.99
29.56
29.53
t-Bu
t-Bu
OMe
10
f1 (ppm)


Zhuyn-11a
PROTON
7.33
7.31
7.29
7.27
7.25
6.61
6.12
5.18
3.04
CO2Bn
11a
5.13
1.00
1.00
2.03
0.93
f1 (ppm)



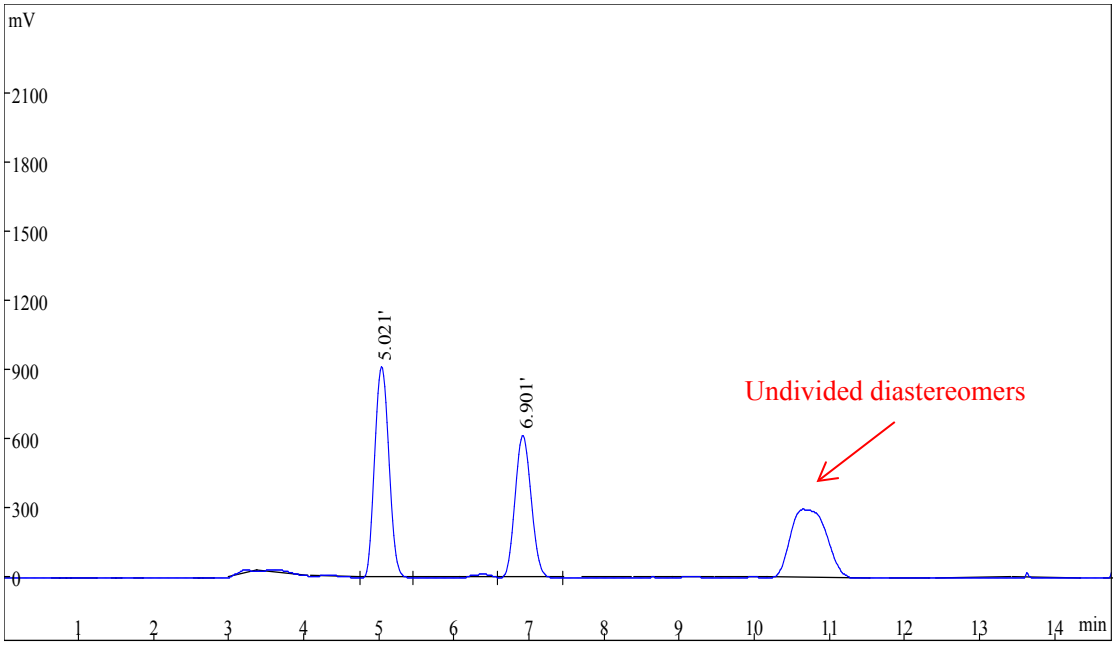
7. Chiral HPLC analysis of 3a



Rank	Time (min)	Area%	Area	Peak height
1	5.079	50.62	4105148	304640
2	7.061	49.38	4004020	283550

Total		100	8109168	588190

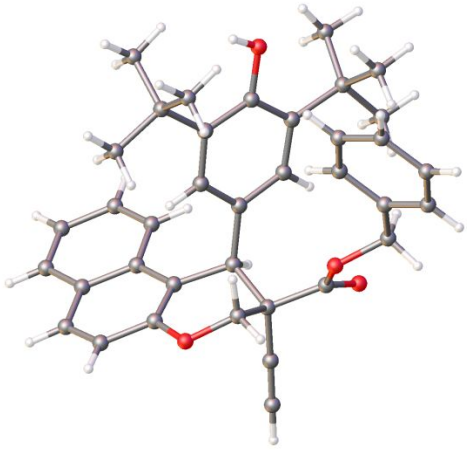
Racemic **3a**

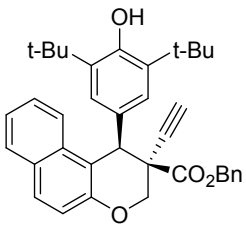


Rank	Time (min)	Area%	Area	Peak height
1	5.021	56.82	12147629	918519
2	6.901	43.18	9231633	618824
Total		100	21379262	1537343

Enantiomerically enriched **3a**

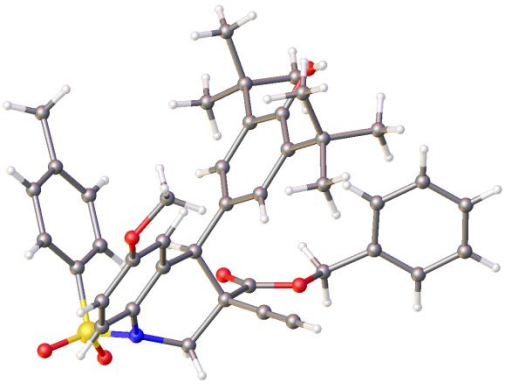
8. X-Ray Crystallography Data

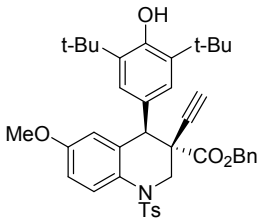




3w

The product **3w** was recrystallized from a mixture solvent of ethyl acetate and n-hexane. CCDC: 1831405.





5aa

The product **5aa** was recrystallized from a mixture solvent of ethyl acetate and n-hexane. CCDC: 1831406.

9. References

1. Zhao, K.; Zhi, Y.; Shu, T.; Valkonen, A.; Rissanen, K.; Enders, D. *Angew. Chem. Int. Ed.* **2016**, *55*, 12104.

2. Ziegler, D. T.; Riesgo, L.; Ikeda, T.; Fujiwara, Y.; Fu, G. C. *Angew. Chem. Int. Ed.* **2014**, *53*, 13183.