Electronic Supplementary Information

Phosphine-Catalyzed (3+3) Annulation of Cinnamaldehyde-Derived Morita-Baylis-Hillman Carbonates with Dinucleophiles

Yue Ren, Wangyu Shi, Yi Tang, and Hongchao Guo*

Department of Chemistry and Innovation Center of Pesticide Research, China Agricultural University, Beijing 100193, China

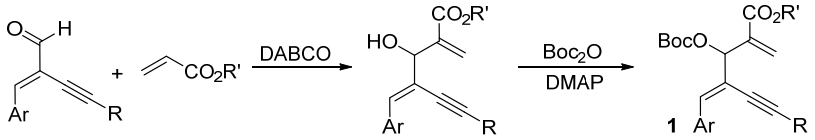
E-mail: *hchguo@cau.edu.cn*

Contents

General Information

All reactions were performed under Ar atmospheres in oven-dried glassware with magnetic stirring. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All solvents were purified and dried according to standard methods before use. Organic solutions were concentrated under reduced pressure on a rotary evaporator or an oil pump. Reactions were monitored through thin-layer chromatography (TLC) on silica gel–precoated glass plates. Chromatograms were visualized by fluorescence quenching with UV light at 254 nm. Flash column chromatography was performed using Qingdao Haiyang flash silica gel (200–300 mesh). Infrared spectra were recorded using a Bruker Optics TENSOR 27 instrument. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ using a 500 MHz NMR instrument (referenced internally to Me_4Si). ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet; d = doublet; q = quartet; m = multiplet; br = broad), coupling constant (Hz), and integral. Data for ^{13}C NMR spectra are reported in terms of chemical shift. Optical rotation was obtained on an Autopol VI automatic polarimeter. Accurate mass measurements were performed using an Agilent instrument with the ESI-MS technique. X-ray crystallographic data were collected using an MM007HF Saturn724+. HPLC analysis was performed on Agilent 1100 or 1200 series, UV detection monitored at 254 nm, using Chiralpak RC-OD column with hexane and *i*-PrOH as the eluent. All reactions requiring heating are heated with an oil bath.

General Procedure for Preparation of γ-Alkynyl-Substituted Cinnamic Aldehyde-Derived MBH Carbonates 1a–1x



The α-alkynyl cinnamaldehyde (prepared according to the literature[1]) (5.0 mmol, 1.0 equiv.), acrylate (7.5 mmol, 1.5 equiv.), and DABCO (0.56 g, 5.0 mmol, 1.0 equiv.) were stirred at rt for 24 h. The resulting reaction mixture was diluted with water and extracted by DCM. The organic layer was dried over Na_2SO_4, filtered, concentrated and simply purified by flash column to give the crude MBH alcohol.

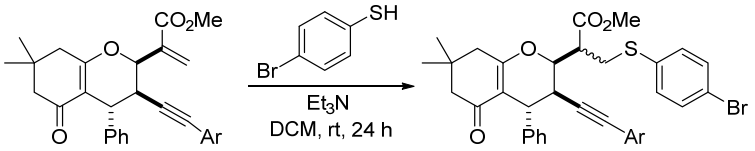
The mixture of dibutyldicarbonate (0.79 g, 3.6 mmol, 1.2 equiv.), and 4-dimethylaminopyridine (0.12 g, 0.3 mmol, 0.1 equiv.) in DCM (10 mL) was slowly added (10 min) to the solution of MBH alcohol (3.0 mmol, 1.0 equiv.) in DCM (10 mL). The mixture was stirred at 0 °C for 30 min. The resulting reaction mixture was quenched and washed with 1 N of aqueous HCl, saturated aqueous $NaHCO_3$, and brine. The organic layer was dried over Na_2SO_4, filtered, concentrated, and purified by flash column to provide Morita-Baylis-Hillman carbonates **1a**–**1x**.

[1] M. Kamlar, S. Hybelbauerová, I. Císařovác, J. Veselý, *Org. Biomol. Chem.* **2014**, *12*, 5071.

General Procedure for the Phosphine-Catalyzed (3+3) Annulation of γ-Substituted Cinnamic Aldehyde-Derived MBH Carbonates 1 with Cyclodiones 2

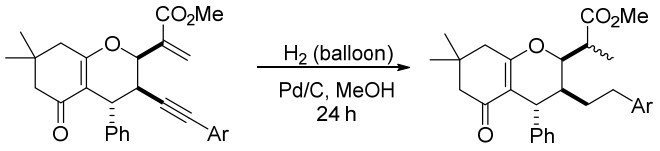
To a stirred solution of γ-substituted cinnamic aldehyde-derived MBH carbonates **1** (0.10 mmol, 1.0 equiv.) and cyclodiones **2** (0.15 mmol, 1.5 equiv.) in 1 mL of DCM was added PPh_3 (5.2 mg, 0.02 mmol, 0.2 equiv.) under Ar atmosphere. The mixture was kept at room temperature and stirred until MBH carbonates **1** were fully consumed (detected by TLC). Then the mixture was concentrated under vacuum and purified by silica gel column chromatography to provide products **3aa**–**3ax** and **3ba**–**3fa**.

Further Elaboration of the Products



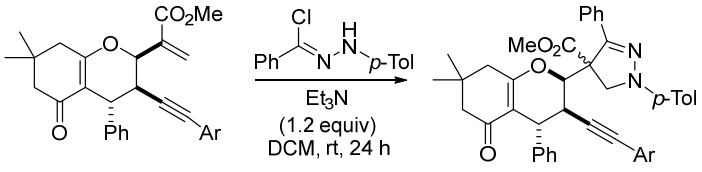
3aa, Ar = 4-ClC_6H_4 **4**, 73%, 1:1 dr

An oven-dried 10 mL of Schlenk tube was charged with **3aa** (47.5 mg, 0.1 mmol) and 4-bromothiophenol (22.7 mg, 0.12 mmol) in 1 mL of DCM at rt and the resulting mixture was stirred for 24 h. Once the starting material was completely consumed (monitored by TLC), the mixture was concentrated to dryness. The residue was purified by flash column chromatography to afford product **4** (48.5 mg, 73% yield, 1:1 dr).



3aa, Ar = 4-ClC_6H_4 **5**, 80%, >20:1 dr

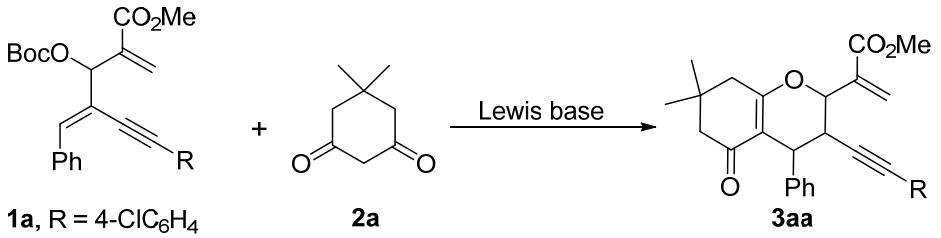
An oven-dried 10 mL of Schlenk tube was charged with **3aa** (47.5 mg, 0.1 mmol) and Pd/C catalyst (2.1 mg, 10.0 wt% palladium on carbon), and then the reactor was evacuated/filled with H_2 (balloon) for three times. After that, MeOH (3 mL) was added and the reaction mixture was stirred under H_2 atmosphere (balloon) for 24 h at rt, and monitored by TLC. The reaction mixture was filtered through Celite. The solvent in the filtrate was concentrated to dryness. The residue was purified by flash chromatography to afford the pure product **5** (38.4 mg, 80% yield, >20:1 dr).



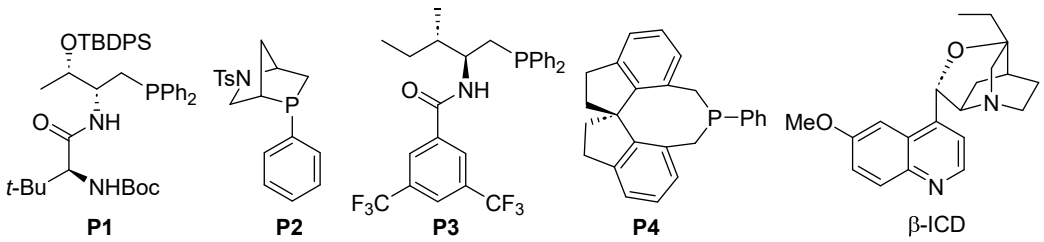
3aa (>20:1 dr), Ar = 4-ClC_6H_4 **6**, 64%, >20:1 dr

An oven-dried 10 mL of Schlenk tube was charged with **3aa** (47.5 mg, 0.1 mmol) and N-(*p*-tolyl)benzohydrazonoyl chloride (29.4 mg, 0.12 mmol) in 1 mL of DCM at rt and the resulting mixture was stirred for 24 h. Once the starting material was completely consumed (monitored by TLC), the mixture was concentrated to dryness. The residue was purified by flash column chromatography to afford product **6** (43.8 mg, 64% yield, >20:1 dr).

Attempt on Asymmetric (3+3) Annulation



1a, R = 4-ClC$_6$H$_4$ **2a** **3aa**



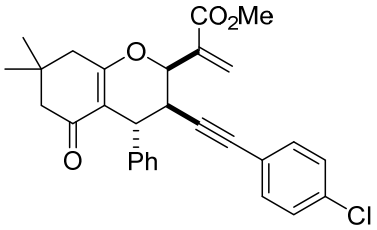
P1 **P2** **P3** **P4** β-ICD

entry	catalyst	yield[b]	dr[c]	ee (%)[d]
1	**P1**	62	>20:1	50
2	**P2**	38	11:1	–50
3	**P3**	31	10:1	–54
4	**P4**	34	5:1	75
5	quinine	NR	-	-
6	hydroquinidine	NR	-	-
7	β-ICD	19	10:1	25

[a]Unless otherwise stated, the reactions were carried out with the use of **1a** (0.06 mmol), **2a** (0.05 mmol), and catalyst (0.01 mmol) at 25 °C in 0.5 mL of DCM under Ar. [b]Isolated yield. [c]Determined by ^{1}H NMR analysis. [d]Determined by chiral HPLC.

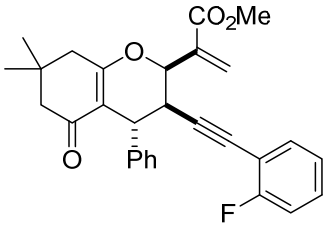
Characterization Data of New Compounds

Methyl 2-(3-((4-chlorophenyl)ethynyl)-7,7-dimethyl-5-oxo-4-phenyl-3,4,5,6,7,8-hexahydro-2H-chromen-2-yl)acrylate (3aa)



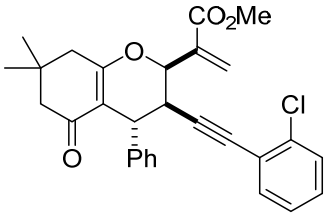
Prepared according to the general procedure as described above from the substrate **1aa** (0.1 mmol, 45.2 mg) and **2a** (0.12 mmol, 16.4 mg) and purified by flash chromatography (PE/EtOAc 10:1). White solid, 85% yield (40.4 mg), 6:1 dr; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.5 Hz, 2H), 7.24 (td, *J* = 10.2, 7.6 Hz, 5H), 7.10 (d, *J* = 7.7 Hz, 2H), 6.56 (s, 1H), 6.18 (s, 1H), 4.83 (s, 1H), 4.44 (s, 1H), 3.62 (s, 3H), 3.44 (s, 1H), 2.65 (d, *J* = 17.2 Hz, 1H), 2.50 – 2.38 (m, 2H), 2.32 (d, *J* = 16.3 Hz, 1H), 1.21 (s, 3H), 1.15 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.1, 170.0, 165.0, 142.1, 136.3, 134.1, 132.8, 128.6, 127.9, 127.7, 127.0, 121.5, 110.14, 87.3, 83.3, 70.9, 51.9, 50.9, 42.4, 40.6, 37.1, 32.7, 29.8, 26.8; HRMS (ESI) calculated for $C_{29}H_{28}ClO_4^+$ $[M+H]^+$ 475.1671, found 475.1661.

Methyl 2-(3-((2-fluorophenyl)ethynyl)-7,7-dimethyl-5-oxo-4-phenyl-3,4,5,6,7,8-hexahydro-2H-chromen-2-yl)acrylate (3ab)



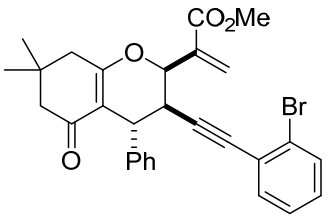
Prepared according to the general procedure as described above from the substrate **1b** (0.1 mmol, 43.7 mg) and **2a** (0.12 mmol, 16.4 mg) and purified by flash chromatography (PE/EtOAc 10:1). white solid, 60% yield (28.3 mg), 6:1 dr; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 3H), 7.26 – 7.15 (m, 4H), 7.08 – 6.98 (m, 2H), 6.54 (d, *J* = 1.1 Hz, 1H), 6.20 (d, *J* = 1.4 Hz, 1H), 4.83 (s, 1H), 4.43 (s, 1H), 3.59 (s, 3H), 3.46 (t, *J* = 2.0 Hz, 1H), 2.60 (d, *J* = 17.2 Hz, 1H), 2.52 – 2.36 (m, 2H), 2.29 (dd, *J* = 16.0, 1.5 Hz, 1H), 1.19 (s, 3H), 1.09 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.1, 170.1, 165.1, 162.9 (d, *J* = 251.3 Hz), 142.1, 135.9, 133.4, 129.7 (d, *J* = 7.9 Hz), 128.5, 128.3, 128.0, 127.0, 123.8 (d, *J* = 3.7 Hz), 115.4 (d, *J* = 20.9 Hz), 111.5 (d, *J* = 15.8 Hz), 110.0, 91.7 (d, *J* = 3.3 Hz) 77.6, 70.8, 51.9, 50.9, 42.4, 40.6, 37.4, 32.5, 29.7, 26.9; HRMS (ESI) calculated for $C_{29}H_{28}FO_4^+$ $[M+H]^+$ 459.1966, found 459.1966.

Methyl 2-(3-((2-chlorophenyl)ethynyl)-7,7-dimethyl-5-oxo-4-phenyl-3,4,5,6,7,8-hexahydro-2H-chromen-2-yl)acrylate (3ac)



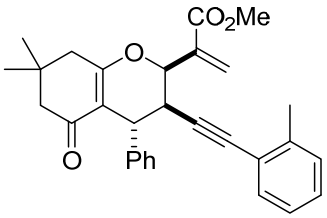
Prepared according to the general procedure as described above from the substrate **1c** (0.1 mmol, 45.2 mg) and **2a** (0.12 mmol, 16.4 mg) and purified by flash chromatography (PE/EtOAc 8:1). yellow solid, 74% yield (36.2 mg), 6:1 dr; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (ddd, *J* = 14.6, 7.9, 4.5 Hz, 4H), 7.25 – 7.14 (m, 5H), 6.55 (s, 1H), 6.24 (s, 1H), 4.83 (s, 1H), 4.45 (s, 1H), 3.59 (s, 3H), 3.49 (t, *J* = 2.0 Hz, 1H), 2.59 (d, *J* = 17.2 Hz, 1H), 2.48 (d, *J* = 17.3 Hz, 1H), 2.43 – 2.26 (m, 2H), 1.19 (s, 3H), 1.10 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.1, 170.0, 165.1, 142.2, 135.9, 135.7, 133.4, 129.2, 129.1, 128.6, 128.5, 128.0, 127.0, 126.4, 122.9, 110.1, 91.8, 81.0, 70.9, 51.9, 50.9, 42.4, 40.7, 37.5, 32.5, 29.5, 27.4; HRMS (ESI) calculated for $C_{29}H_{28}ClO_4^+$ $[M+H]^+$ 475.1671, found 475.1669.

Methyl 2-(3-((2-bromophenyl)ethynyl)-7,7-dimethyl-5-oxo-4-phenyl-3,4,5,6,7,8-hexahydro-2H-chromen-2-yl)acrylate (3ad)



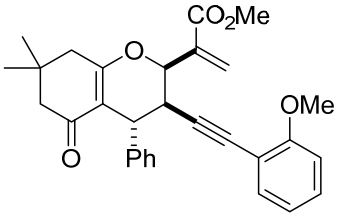
Prepared according to the general procedure as described above from the substrate **1d** (0.1 mmol, 49.6 mg) and **2a** (0.12 mmol, 16.4 mg) and purified by flash chromatography (PE/EtOAc 8:1). white solid, 70% yield (37.5 mg), 8:1 dr; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.30 – 7.24 (m, 3H), 7.18 – 7.11 (m, 4H), 7.05 (td, *J* = 7.7, 1.7 Hz, 1H), 6.48 (d, *J* = 1.2 Hz, 1H), 6.19 (t, *J* = 1.3 Hz, 1H), 4.77 (s, 1H), 4.38 (s, 1H), 3.52 (s, 3H), 3.42 (t, *J* = 2.1 Hz, 1H), 2.55 – 2.39 (m, 2H), 2.32 (d, *J* = 16.0 Hz, 1H), 2.22 (dd, *J* = 15.9, 1.2 Hz, 1H), 1.12 (s, 3H), 1.04 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.1, 169.0, 164.1, 141.2, 134.8, 132.5, 131.3, 128.2, 127.6, 127.5, 127.0, 126.0, 125.9, 124.3, 124.1, 109.2, 90.2, 81.7, 69.9, 50.9, 49.9, 41.4, 39.7, 36.5, 31.4, 28.4, 26.6. HRMS (ESI) calculated for $C_{29}H_{27}BrO_4^+$ $[M+H]^+$ 519.1165, found 519.1160.

Methyl 2-(7,7-dimethyl-5-oxo-4-phenyl-3-(*o*-tolylethynyl)-3,4,5,6,7,8-hexahydro-2H-chromen-2-yl)acrylate (3ae)



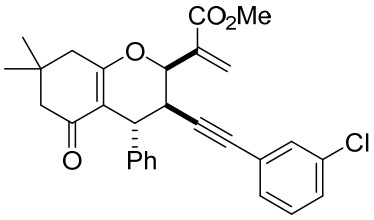
Prepared according to the general procedure as described above from the substrate **1e** (0.1 mmol, 43.2 mg) and **2a** (0.12 mmol, 16.4 mg) and purified by flash chromatography (PE/EtOAc 8:1). white solid, 72% yield (33.7 mg), 6:1 dr; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.7 Hz, 2H), 7.30 – 7.26 (m, 1H), 7.23 (dd, *J* = 7.6, 5.4 Hz, 3H), 7.19 – 7.13 (m, 2H), 7.09 (td, *J* = 7.2, 1.9 Hz, 1H), 6.53 (d, *J* = 1.4 Hz, 1H), 6.15 (d, *J* = 1.5 Hz, 1H), 4.83 (d, *J* = 2.2 Hz, 1H), 4.43 (s, 1H), 3.59 (s, 3H), 3.49 (t, *J* = 2.1 Hz, 1H), 2.59 (d, *J* = 17.2 Hz, 1H), 2.48 – 2.42 (m, 1H), 2.40 (d, *J* = 16.0 Hz, 1H), 2.32 (s, 3H), 2.28 (dd, *J* = 16.0, 1.4 Hz, 1H), 1.19 (s, 3H), 1.10 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.1, 169.9, 165.1, 142.4, 139.9, 136.3, 132.0, 129.3, 128.6, 128.1, 128.0, 127.8, 127.0, 125.5, 122.8, 110.3, 90.1, 83.1, 71.1, 51.9, 50.9, 42.4, 40.9, 37.4, 32.5, 29.5, 27.5, 20.8; HRMS (ESI) calculated for $C_{30}H_{31}O_4^+$ $[M+H]^+$ 455.2217, found 455.2216.

Methyl 2-(3-((2-methoxyphenyl)ethynyl)-7,7-dimethyl-5-oxo-4-phenyl-3,4,5,6,7,8-hexahydro-2H-chromen-2-yl)acrylate (3af)



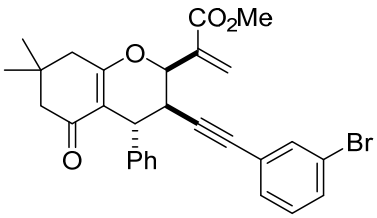
Prepared according to the general procedure as described above from the substrate **1f** (0.1 mmol, 44.8 mg) and **2a** (0.12 mmol, 16.4 mg) and purified by flash chromatography (PE/EtOAc 8:1). white solid, 80% yield (38.7 mg), 7:1 dr; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.6 Hz, 2H), 7.25 – 7.20 (m, 4H), 6.87 – 6.80 (m, 2H), 6.54 (s, 1H), 6.22 (d, *J* = 1.4 Hz, 1H), 4.83 (s, 1H), 4.45 (s, 1H), 3.82 (s, 3H), 3.57 (s, 3H), 3.45 (t, *J* = 2.0 Hz, 1H), 2.60 (d, *J* = 17.2 Hz, 1H), 2.48 – 2.37 (m, 2H), 2.28 (dd, *J* = 16.0, 1.5 Hz, 1H), 1.18 (s, 3H), 1.09 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.1, 170.1, 165.1, 160.1, 142.4, 136.1, 133.6, 129.4, 128.5, 128.3, 128.0, 126.9, 120.3, 112.3, 110.6, 110.2, 90.2, 80.5, 71.0, 55.6, 51.8, 50.9, 42.4, 40.7, 37.5, 32.5, 29.7, 26.9; HRMS (ESI) calculated for $C_{30}H_{31}O_5^+$ $[M+H]^+$ 471.2166, found 471.2166.

Methyl 2-(3-((3-chlorophenyl)ethynyl)-7,7-dimethyl-5-oxo-4-phenyl-3,4,5,6,7,8-hexahydro-2H-chromen-2-yl)acrylate (3ag)



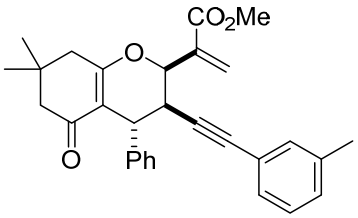
Prepared according to the general procedure as described above from the substrate **1g** (0.1 mmol, 45.2 mg) and **2a** (0.12 mmol, 16.4 mg) and purified by flash chromatography (PE/EtOAc 8:1). yellow solid, 72% yield (35.2 mg), 6:1 dr; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.26 (m, 3H), 7.26 – 7.09 (m, 6H), 6.54 (s, 1H), 6.14 (d, *J* = 1.5 Hz, 1H), 4.81 (s, 1H), 4.41 (s, 1H), 3.60 (s, 3H), 3.44 (t, *J* = 2.0 Hz, 1H), 2.63 (d, *J* = 17.2 Hz, 1H), 2.47 – 2.39 (m, 2H), 2.30 (dd, *J* = 16.1, 1.6 Hz, 1H), 1.19 (s, 3H), 1.12 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.1, 169.9, 165.0, 142.1, 136.3, 134.0, 131.5, 129.8, 129.5, 128.6, 128.4, 127.9, 127.8, 127.0, 124.7, 110.1, 87.7, 83.0, 70.9, 51.9, 50.9, 42.4, 40.6, 37.1, 32.7, 29.8, 26.8; HRMS (ESI) calculated for $C_{29}H_{28}ClO_4^+$ $[M+H]^+$ 475.1671, found 475.1669.

Methyl 2-(3-((3-bromophenyl)ethynyl)-7,7-dimethyl-5-oxo-4-phenyl-3,4,5,6,7,8-hexahydro-2H-chromen-2-yl)acrylate (3ah)



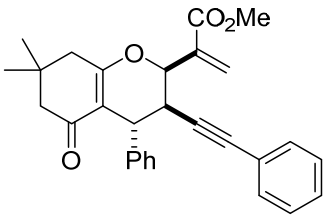
Prepared according to the general procedure as described above from the substrate **1h** (0.1 mmol, 49.6 mg) and **2a** (0.12 mmol, 16.4 mg) and purified by flash chromatography (PE/EtOAc 8:1). Pale yellow hemi solid, 69% yield (36.7 mg), 5:1 dr; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.38 (m, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.22 (dt, *J* = 8.7, 7.2 Hz, 4H), 7.13 (t, *J* = 7.8 Hz, 1H), 6.54 (s, 1H), 6.14 (d, *J* = 1.5 Hz, 1H), 4.81 (d, *J* = 2.2 Hz, 1H), 4.41 (s, 1H), 3.60 (s, 3H), 3.44 (s, 1H), 2.63 (d, *J* = 17.2 Hz, 1H), 2.46 – 2.39 (m, 2H), 2.30 (dd, *J* = 16.1, 1.6 Hz, 1H), 1.19 (s, 3H), 1.12 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.1, 169.9, 165.0, 142.1, 136.3, 134.4, 131.3, 130.2, 129.7, 128.6, 127.9, 127.8, 127.1, 125.0, 122.0, 110.1, 87.8, 82.9, 70.9, 51.9, 50.9, 42.4, 40.6, 37.1, 32.7, 29.8, 26.8; HRMS (ESI) calculated for $C_{29}H_{28}BrO_4^+$ $[M+H]^+$ 519.1165, found 519.1159.

Methyl 2-(7,7-dimethyl-5-oxo-4-phenyl-3-(m-tolylethynyl)-3,4,5,6,7,8-hexahydro-2H-chromen-2-yl)acrylate (3ai)



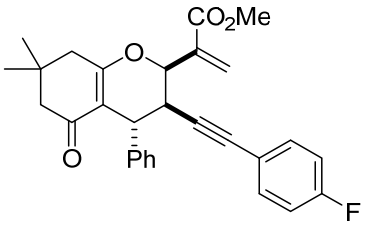
Prepared according to the general procedure as described above from the substrate **1i** (0.1 mmol, 43.2 mg) and **2a** (0.12 mmol, 16.4 mg) and purified by flash chromatography (PE/EtOAc 8:1). White solid, 73% yield (34.2 mg), 7:1 dr; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.5 Hz, 2H), 7.24 – 7.19 (m, 3H), 7.17 – 7.07 (m, 4H), 6.54 (t, *J* = 1.1 Hz, 1H), 6.15 (d, *J* = 1.5 Hz, 1H), 4.81 (s, 1H), 4.41 (s, 1H), 3.59 (s, 3H), 3.41 (t, *J* = 2.1 Hz, 1H), 2.62 (d, *J* = 17.2 Hz, 1H), 2.46 – 2.31 (m, 3H), 2.30 (s, 3H), 1.19 (s, 3H), 1.13 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.1, 170.0, 165.1, 142.3, 137.9, 136.3, 132.2, 128.9, 128.7, 128.5, 128.1, 128.0, 127.9, 126.9, 122.9, 110.2, 85.8, 84.5, 71.0, 51.9, 50.9, 42.5, 40.7, 37.1, 32.6, 29.8, 26.9, 21.2; HRMS (ESI) calculated for $C_{30}H_{31}O_4^+$ $[M+H]^+$ 455.2217, found 455.2215.

Methyl 2-(7,7-dimethyl-5-oxo-4-phenyl-3-(phenylethynyl)-3,4,5,6,7,8-hexahydro-2H-chromen-2-yl)acrylate (3aj)



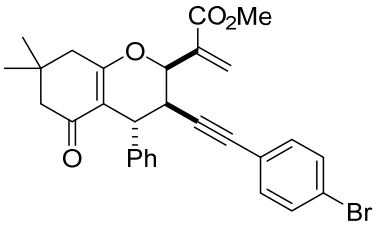
Prepared according to the general procedure as described above from the substrate **1j** (0.1 mmol, 41.8 mg) and **2a** (0.12 mmol, 16.4 mg) and purified by flash chromatography (PE/EtOAc 8:1). Yellow hemi solid, 80% yield (36.7 mg), 7:1 dr; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.26 (m, 6H), 7.25 – 7.17 (m, 4H), 6.53 (s, 1H), 6.15 (d, *J* = 1.5 Hz, 1H), 4.81 (s, 1H), 4.42 (s, 1H), 3.59 (s, 3H), 3.43 (t, *J* = 2.0 Hz, 1H), 2.62 (d, *J* = 17.2 Hz, 1H), 2.48 – 2.37 (m, 2H), 2.29 (dd, *J* = 16.1, 1.6 Hz, 1H), 1.19 (s, 3H), 1.12 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.1, 170.0, 165.1, 142.3, 136.3, 131.6, 128.5, 128.2, 128.1, 128.0, 127.8, 126.9, 123.0, 110.2, 86.2, 84.3, 71.0, 51.9, 50.9, 42.4, 40.6, 37.1, 32.6, 29.8, 29.7, 26.9; HRMS (ESI) calculated for $C_{29}H_{29}O_4^+$ $[M+H]^+$ 441.2060, found 441.2060.

Methyl 2-(3-((4-fluorophenyl)ethynyl)-7,7-dimethyl-5-oxo-4-phenyl-3,4,5,6,7,8-hexahydro-2H-chromen-2-yl)acrylate (3ak)



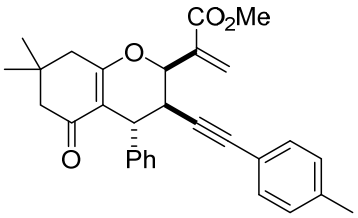
Prepared according to the general procedure as described above from the substrate **1k** (0.1 mmol, 43.6 mg) and **2a** (0.12 mmol, 16.4 mg) and purified by flash chromatography (PE/EtOAc 8:1). White solid, 71% yield (33.5 mg), 5:1 dr; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.26 (m, 4H), 7.21 (dd, *J* = 8.6, 7.1 Hz, 3H), 6.96 (t, *J* = 8.7 Hz, 2H), 6.53 (d, *J* = 1.2 Hz, 1H), 6.14 (d, *J* = 1.5 Hz, 1H), 4.80 (d, *J* = 2.1 Hz, 1H), 4.41 (s, 1H), 3.59 (s, 3H), 3.42 (t, *J* = 2.0 Hz, 1H), 2.63 (d, *J* = 17.2 Hz, 1H), 2.45 – 2.38 (m, 2H), 2.30 (dd, *J* = 16.0, 1.6 Hz, 1H), 1.19 (s, 3H), 1.11 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.1, 169.9, 162.3 (d, *J* = 249.2 Hz), 142.2, 136.4, 133.44 (d, *J* = 8.4 Hz), 128.6, 127.9, 127.7, 127.0, 119.1 (d, *J* = 3.4 Hz), 115.5 (d, *J* = 22.1 Hz), 110.2, 85.9, 83.3, 71.0, 51.9, 50.9, 42.4, 40.6, 37.1, 32.7, 29.8, 26.8; HRMS (ESI) calculated for $C_{29}H_{28}FO_4^+$ $[M+H]^+$ 459.1966, found 459.1965.

Methyl 2-(3-((4-bromophenyl)ethynyl)-7,7-dimethyl-5-oxo-4-phenyl-3,4,5,6,7,8-hexahydro-2H-chromen-2-yl)acrylate (3al)



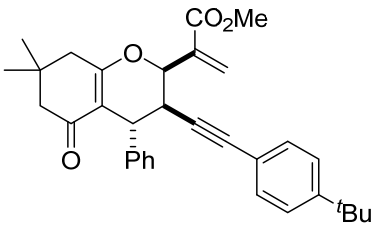
Prepared according to the general procedure as described above from the substrate **1l** (0.1 mmol, 49.6 mg) and **2a** (0.12 mmol, 16.4 mg) and purified by flash chromatography (PE/EtOAc 8:1). yellow solid, 74% yield (39.5 mg), 6:1 dr; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.4 Hz, 2H), 7.26 (t, *J* = 7.6 Hz, 2H), 7.14 (dd, *J* = 9.7, 8.1 Hz, 3H), 7.10 – 7.05 (m, 2H), 6.46 (s, 1H), 6.05 (d, *J* = 1.5 Hz, 1H), 4.73 (d, *J* = 2.1 Hz, 1H), 4.34 (s, 1H), 3.52 (s, 3H), 3.35 (d, *J* = 2.1 Hz, 1H), 2.56 (d, *J* = 17.2 Hz, 1H), 2.34 (d, *J* = 16.0 Hz, 2H), 2.22 (dd, *J* = 16.0, 1.6 Hz, 1H), 1.12 (s, 3H), 1.03 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.0, 168.9, 164.0, 141.1, 135.3, 132.0, 130.5, 127.5, 126.9, 126.7, 126.0, 121.2, 120.9, 109.1, 86.5, 82.3, 69.9, 50.9, 49.9, 41.4, 39.5, 36.1, 31.6, 28.8, 25.8; HRMS (ESI) calculated for $C_{29}H_{28}BrO_4^+$ $[M+H]^+$ 519.1165, found 519.1163.

Methyl 2-(7,7-dimethyl-5-oxo-4-phenyl-3-(*p*-tolylethynyl)-3,4,5,6,7,8-hexahydro-2H-chromen-2-yl)acrylate (3am)



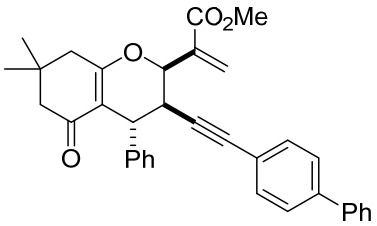
Prepared according to the general procedure as described above from the substrate **1m** (0.1 mmol, 43.2 mg) and **2a** (0.12 mmol, 16.4 mg) and purified by flash chromatography (PE/EtOAc 8:1). White solid, 85% yield (39.8 mg), 7:1 dr; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (t, *J* = 7.5 Hz, 2H), 7.17 – 7.08 (m, 5H), 6.99 (d, *J* = 7.9 Hz, 2H), 6.46 (s, 1H), 6.07 (d, *J* = 1.5 Hz, 1H), 4.73 (s, 1H), 4.34 (s, 1H), 3.51 (s, 3H), 3.34 (t, *J* = 2.1 Hz, 1H), 2.54 (d, *J* = 17.2 Hz, 1H), 2.38 – 2.30 (m, 2H), 2.25 (s, 3H), 2.22 (dd, *J* = 16.0, 1.6 Hz, 1H), 1.11 (s, 3H), 1.05 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.1, 169.0, 164.1, 141.3, 137.1, 135.3, 130.5, 127.9, 127.5, 126.9, 126.8, 125.9, 118.9, 109.1, 84.4, 83.4, 70.0, 50.8, 49.9, 41.4, 39.7, 36.1, 31.6, 28.8, 25.8, 20.4; HRMS (ESI) calculated for $C_{30}H_{31}O_4^+$ $[M+H]^+$ 455.2217, found 455.2216.

Methyl 2-(3-((4-(*tert*-butyl)phenyl)ethynyl)-7,7-dimethyl-5-oxo-4-phenyl-3,4,5,6,7,8-hexahydro-2H-chromen-2-yl)acrylate (3an)



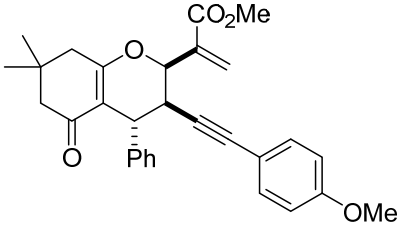
Prepared according to the general procedure as described above from the substrate **1n** (0.1 mmol, 47.4 mg) and **2a** (0.12 mmol, 16.4 mg) and purified by flash chromatography (PE/EtOAc 8:1). Pale yellow solid, 61% yield (31.1 mg), 6:1 dr; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.26 (m, 4H), 7.25 – 7.17 (m, 5H), 6.52 (d, *J* = 1.2 Hz, 1H), 6.14 (t, *J* = 1.4 Hz, 1H), 4.81 (d, *J* = 2.1 Hz, 1H), 4.41 (s, 1H), 3.59 (s, 3H), 3.41 (t, *J* = 2.0 Hz, 1H), 2.61 (d, *J* = 17.2 Hz, 1H), 2.46 – 2.36 (m, 2H), 2.29 (dd, *J* = 15.9, 1.5 Hz, 1H), 1.29 (s, 9H), 1.19 (s, 3H), 1.14 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.1, 170.0, 165.1, 151.3, 142.3, 136.3, 131.3, 128.5, 128.0, 127.9, 126.9, 125.2, 120.0, 110.2, 85.4, 84.3, 71.0, 51.9, 50.9, 42.4, 40.7, 37.2, 34.7, 32.6, 31.2, 29.8, 27.0; HRMS (ESI) calculated for $C_{33}H_{37}O_4^+$ $[M+H]^+$ 497.2686, found 497.2685.

Methyl 2-(3-([1,1'-biphenyl]-4-ylethynyl)-7,7-dimethyl-5-oxo-4-phenyl-3,4,5,6,7,8-hexahydro-2H-chromen-2-yl)acrylate (3ao)



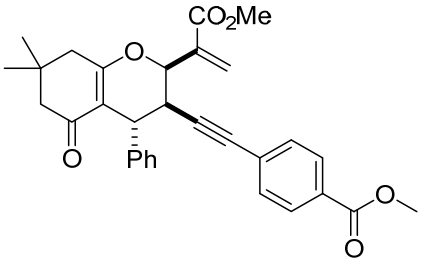
Prepared according to the general procedure as described above from the substrate **1o** (0.1 mmol, 49.4 mg) and **2a** (0.12 mmol, 16.4 mg) and purified by flash chromatography (PE/EtOAc 8:1). White solid, 77% yield (40.8 mg), 5:1 dr; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.55 (m, 2H), 7.52 – 7.48 (m, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.38 – 7.31 (m, 5H), 7.25 – 7.20 (m, 3H), 6.55 (s, 1H), 6.17 (d, *J* = 1.5 Hz, 1H), 4.83 (d, *J* = 2.2 Hz, 1H), 4.44 (s, 1H), 3.60 (s, 3H), 3.45 (t, *J* = 2.1 Hz, 1H), 2.63 (d, *J* = 17.2 Hz, 1H), 2.47 – 2.40 (m, 2H), 2.31 (dd, *J* = 16.1, 1.6 Hz, 1H), 1.19 (s, 3H), 1.14 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.2, 170.0, 165.1, 142.3, 140.9, 140.3, 136.3, 132.1, 128.9, 128.6, 128.0, 127.9, 127.6, 127.01, 126.99, 126.9, 122.0, 110.2, 86.9, 84.2, 71.0, 51.9, 50.9, 42.5, 40.7, 37.2, 32.7, 29.8, 26.9; HRMS (ESI) calculated for $C_{35}H_{33}O_4^+$ $[M+H]^+$ 517.2373, found 517.2372.

Methyl 2-(3-((4-methoxyphenyl)ethynyl)-7,7-dimethyl-5-oxo-4-phenyl-3,4,5,6,7,8-hexahydro-2H-chromen-2-yl)acrylate (3ap)



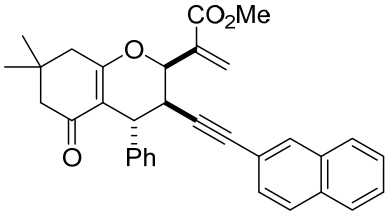
Prepared according to the general procedure as described above from the substrate **1p** (0.1 mmol, 44.8 mg) and **2a** (0.12 mmol, 16.4 mg) and purified by flash chromatography (PE/EtOAc 8:1). White solid, 73% yield (35.3 mg), 6:1 dr; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (t, *J* = 7.6 Hz, 2H), 7.18 – 7.11 (m, 5H), 6.72 (d, *J* = 8.7 Hz, 2H), 6.45 (s, 1H), 6.07 (d, *J* = 1.5 Hz, 1H), 4.73 (s, 1H), 4.33 (s, 1H), 3.72 (s, 3H), 3.51 (s, 3H), 3.33 (t, *J* = 2.0 Hz, 1H), 2.54 (d, *J* = 17.2 Hz, 1H), 2.39 – 2.30 (m, 2H), 2.22 (dd, *J* = 16.1, 1.6 Hz, 1H), 1.11 (s, 3H), 1.05 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.1, 169.0, 164.1, 158.4, 141.3, 135.3, 132.0, 127.5, 126.9, 126.8, 125.9, 114.2, 112.8, 109.2, 83.6, 83.1, 70.0, 54.3, 50.8, 49.9, 41.4, 39.7, 36.1, 31.6, 28.8, 25.8; HRMS (ESI) calculated for $C_{30}H_{31}O_5^+$ $[M+H]^+$ 471.2166, found 471.2167.

Methyl 4-((2-(3-methoxy-3-oxoprop-1-en-2-yl)-7,7-dimethyl-5-oxo-4-phenyl-3,4,5,6,7,8-hexahydro-2H-chromen-3-yl)ethynyl)benzoate (3aq)



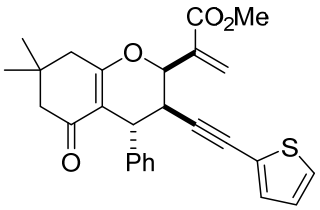
Prepared according to the general procedure as described above from the substrate **1q** (0.1 mmol, 47.6 mg) and **2a** (0.12 mmol, 16.4 mg) and purified by flash chromatography (PE/EtOAc 8:1). White solid, 64% yield (32.9 mg), 7:1 dr; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.1 Hz, 2H), 7.37 – 7.30 (m, 4H), 7.26 – 7.19 (m, 3H), 6.54 (s, 1H), 6.15 (d, *J* = 1.5 Hz, 1H), 4.82 (d, *J* = 2.1 Hz, 1H), 4.43 (s, 1H), 3.91 (s, 3H), 3.60 (s, 3H), 3.47 (t, *J* = 2.1 Hz, 1H), 2.64 (d, *J* = 17.2 Hz, 1H), 2.47 – 2.37 (m, 2H), 2.30 (dd, *J* = 16.0, 1.5 Hz, 1H), 1.19 (s, 3H), 1.10 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.1, 170.0, 166.5, 165.0, 142.0, 136.3, 131.6, 129.4, 128.6, 127.9, 127.8, 127.7, 127.1, 110.1, 89.6, 83.7, 70.9, 52.2, 52.0, 50.9, 42.4, 40.6, 37.2, 32.7, 29.8, 26.8; HRMS (ESI) calculated for $C_{31}H_{31}O_6^+$ $[M+H]^+$ 499.2115, found 499.2113.

Methyl 2-(7,7-dimethyl-3-(naphthalen-2-ylethynyl)-5-oxo-4-phenyl-3,4,5,6,7,8-hexahydro-2H-chromen-2-yl)acrylate (3ar)



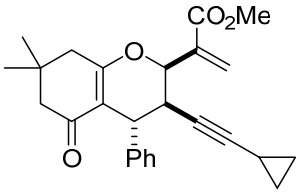
Prepared according to the general procedure as described above from the substrate **1r** (0.1 mmol, 46.8 mg) and **2a** (0.12 mmol, 16.4 mg) and purified by flash chromatography (PE/EtOAc 8:1). Pale yellow hemi solid, 78% yield (39.3 mg), 6:1 dr; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 – 7.71 (m, 4H), 7.50 – 7.44 (m, 2H), 7.37 – 7.31 (m, 3H), 7.23 (d, *J* = 7.8 Hz, 3H), 6.58 (d, *J* = 1.2 Hz, 1H), 6.21 (t, *J* = 1.4 Hz, 1H), 4.84 (s, 1H), 4.47 (s, 1H), 3.61 (s, 3H), 3.48 (t, *J* = 2.0 Hz, 1H), 2.64 (d, *J* = 17.2 Hz, 1H), 2.48 – 2.39 (m, 2H), 2.31 (dd, *J* = 16.0, 1.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.1, 170.0, 165.1, 142.3, 136.4, 132.9, 132.7, 131.3, 128.6, 128.5, 128.0, 127.89, 127.87, 127.7, 127.6, 127.0, 126.6, 126.5, 120.3, 110.2, 86.6, 84.7, 71.0, 51.9, 50.9, 42.5, 40.7, 37.2, 32.7, 29.8, 26.9; HRMS (ESI) calculated for $C_{33}H_{31}O_4^+$ $[M+H]^+$ 491.2217, found 491.2215.

Methyl 2-(7,7-dimethyl-5-oxo-4-phenyl-3-(thiophen-2-ylethynyl)-3,4,5,6,7,8-hexahydro-2H-chromen-2-yl)acrylate (3as)



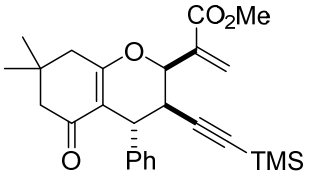
Prepared according to the general procedure as described above from the substrate **1s** (0.1 mmol, 42.4 mg) and **2a** (0.12 mmol, 16.4 mg) and purified by flash chromatography (PE/EtOAc 8:1). Pale yellow hemi solid, 69% yield (31.7 mg), 7:1 dr; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.6 Hz, 2H), 7.25 – 7.16 (m, 4H), 7.05 (dd, *J* = 3.7, 1.2 Hz, 1H), 6.92 (dd, *J* = 5.2, 3.7 Hz, 1H), 6.53 (t, *J* = 1.1 Hz, 1H), 6.14 (d, *J* = 1.4 Hz, 1H), 4.80 (s, 1H), 4.41 (s, 1H), 3.59 (s, 3H), 3.44 (t, *J* = 2.0 Hz, 1H), 2.63 (d, *J* = 17.2 Hz, 1H), 2.45 – 2.39 (m, 2H), 2.32 (d, *J* = 1.6 Hz, 1H), 1.19 (s, 3H), 1.14 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.1, 170.0, 165.0, 142.1, 136.1, 131.6, 128.6, 128.0, 127.9, 127.0, 126.8, 126.6, 123.0, 110.1, 90.2, 70.9, 51.9, 50.9, 42.4, 40.5, 37.4, 32.7, 29.9, 26.8; HRMS (ESI) calculated for $C_{27}H_{27}O_4S^+$ $[M+H]^+$ 447.1625, found 447.1626.

Methyl 2-(3-(cyclopropylethynyl)-7,7-dimethyl-5-oxo-4-phenyl-3,4,5,6,7,8-hexahydro-2H-chromen-2-yl)acrylate (3at)



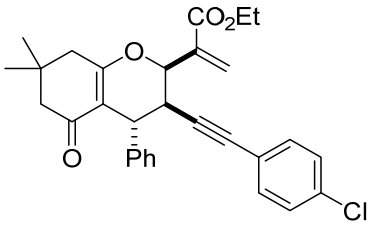
Prepared according to the general procedure as described above from the substrate **1t** (0.1 mmol, 38.2 mg) and **2a** (0.12 mmol, 16.4 mg) and purified by flash chromatography (PE/EtOAc 8:1). Yellow hemi solid, 69% yield (28.9 mg), 7:1 dr; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (t, *J* = 7.6 Hz, 2H), 7.12 (t, *J* = 7.4 Hz, 1H), 7.10 – 7.05 (m, 2H), 6.41 (s, 1H), 5.97 (d, *J* = 1.5 Hz, 1H), 4.61 (s, 1H), 4.17 (s, 1H), 3.49 (s, 3H), 3.05 (d, *J* = 2.0 Hz, 1H), 2.53 (d, *J* = 17.1 Hz, 1H), 2.36 – 2.28 (m, 2H), 2.21 (dd, *J* = 16.0, 1.7 Hz, 1H), 1.12 (s, 3H), 1.07 (s, 3H), 0.64 – 0.58 (m, 2H), 0.43 (ddt, *J* = 7.0, 4.5, 2.0 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.8, 170.5, 165.7, 143.1, 137.0, 129.1, 128.6, 128.2, 127.4, 110.8, 88.3, 72.2, 71.7, 52.4, 51.5, 43.1, 41.5, 37.1, 33.3, 30.5, 27.4, 8.9, 8.8; HRMS (ESI) calculated for $C_{26}H_{29}O_4^+$ $[M+H]^+$ 405.2060, found 405.2061.

Methyl 2-(7,7-dimethyl-5-oxo-4-phenyl-3-((trimethylsilyl)ethynyl)-3,4,5,6,7,8-hexahydro-2H-chromen-2-yl)acrylate (3au)



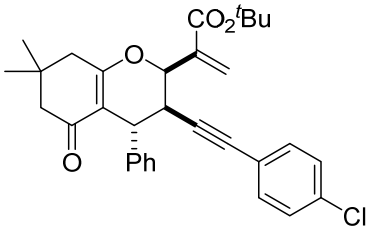
Prepared according to the general procedure as described above from the substrate **1u** (0.1 mmol, 41.4 mg) and **2a** (0.12 mmol, 16.4 mg) and purified by flash chromatography (PE/EtOAc 8:1). Pale yellow hemi solid, 67% yield (30.2 mg), 6:1 dr; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.6 Hz, 2H), 7.14 – 7.05 (m, 3H), 6.42 (t, *J* = 1.1 Hz, 1H), 5.97 (t, *J* = 1.5 Hz, 1H), 4.63 (d, *J* = 2.1 Hz, 1H), 4.25 (s, 1H), 3.48 (s, 3H), 3.10 (t, *J* = 2.0 Hz, 1H), 2.54 (d, *J* = 17.2 Hz, 1H), 2.35 – 2.24 (m, 2H), 2.19 (dd, *J* = 15.9, 1.8 Hz, 1H), 1.10 (s, 3H), 1.05 (s, 3H), -0.00 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.0, 169.9, 165.0, 142.2, 136.0, 128.5, 127.9, 127.7, 126.9, 110.0, 102.8, 88.7, 70.7, 51.8, 50.9, 42.4, 40.4, 37.5, 32.6, 30.0, 26.7, 0.0; HRMS (ESI) calculated for $C_{26}H_{33}O_4Si^+$ $[M+H]^+$ 437.2143, found 437.2142.

Ethyl 2-(3-((4-chlorophenyl)ethynyl)-7,7-dimethyl-5-oxo-4-phenyl-3,4,5,6,7,8-hexahydro-2H-chromen-2-yl)acrylate (3av)



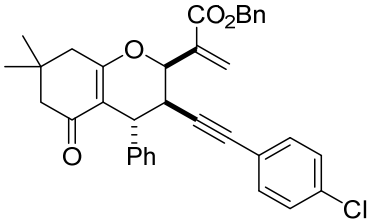
Prepared according to the general procedure as described above from the substrate **1v** (0.1 mmol, 46.6 mg) and **2a** (0.12 mmol, 16.4 mg) and purified by flash chromatography (PE/EtOAc 8:1). White solid, 60% yield (29.3 mg), 7:1 dr; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.6 Hz, 2H), 7.22 (dq, *J* = 7.1, 2.5 Hz, 7H), 6.55 (s, 1H), 6.10 (t, *J* = 1.5 Hz, 1H), 4.84 (s, 1H), 4.41 (s, 1H), 4.09 – 3.94 (m, 2H), 3.39 (t, *J* = 2.0 Hz, 1H), 2.62 (d, *J* = 17.2 Hz, 1H), 2.48 – 2.37 (m, 2H), 2.29 (dd, *J* = 16.0, 1.6 Hz, 1H), 1.19 (s, 3H), 1.11 (s, 3H), 0.98 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.1, 170.0, 164.4, 142.3, 136.5, 134.1, 132.8, 128.58, 128.57, 128.0, 127.8, 127.0, 121.5, 110.0, 87.3, 83.2, 70.8, 60.9, 50.9, 42.4, 40.7, 37.3, 32.6, 29.8, 26.8, 13.7; HRMS (ESI) calculated for $C_{30}H_{30}ClO_4^+$ $[M+H]^+$ 489.1827, found 489.1826.

***tert*-butyl 2-(3-((4-chlorophenyl)ethynyl)-7,7-dimethyl-5-oxo-4-phenyl-3,4,5,6,7,8-hexahydro-2H-chromen-2-yl)acrylate (3aw)**



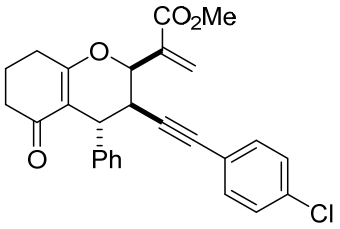
Prepared according to the general procedure as described above from the substrate **1w** (0.1 mmol, 49.4 mg) and **2a** (0.12 mmol, 16.4 mg) and purified by flash chromatography (PE/EtOAc 8:1). Pale yellow hemi solid, 64% yield (33.1 mg), 8:1 dr; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.6 Hz, 2H), 7.25 – 7.18 (m, 7H), 6.50 (d, *J* = 1.5 Hz, 1H), 6.02 (d, *J* = 1.6 Hz, 1H), 4.87 (s, 1H), 4.39 (s, 1H), 3.27 (t, *J* = 2.0 Hz, 1H), 2.61 (d, *J* = 17.2 Hz, 1H), 2.47 – 2.35 (m, 2H), 2.27 (dd, *J* = 16.0, 1.6 Hz, 1H), 1.18 (s, 3H), 1.16 (s, 9H), 1.10 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.1, 170.0, 163.5, 142.7, 138.0, 134.1, 132.8, 128.7, 128.6, 128.1, 127.4, 127.0, 121.5, 109.9, 87.4, 83.3, 81.6, 70.8, 50.9, 42.5, 41.0, 37.4, 32.6, 29.7, 27.7, 26.9; HRMS (ESI) calculated for $C_{32}H_{34}ClO_4^+$ $[M+H]^+$ 517.2140, found 517.2151.

Benzyl 2-(3-((4-chlorophenyl)ethynyl)-7,7-dimethyl-5-oxo-4-phenyl-3,4,5,6,7,8-hexahydro-2H-chromen-2-yl)acrylate (3ax)



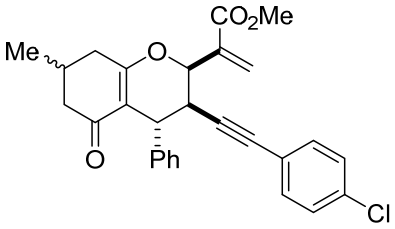
Prepared according to the general procedure as described above from the substrate **1x** (0.1 mmol, 52.9 mg) and **2a** (0.12 mmol, 16.4 mg) and purified by flash chromatography (PE/EtOAc 8:1). White solid, 65% yield (35.8 mg), 7:1 dr; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 5H), 7.25 – 7.16 (m, 7H), 7.11 (dd, *J* = 6.6, 3.0 Hz, 2H), 6.59 (d, *J* = 1.2 Hz, 1H), 6.15 (d, *J* = 1.5 Hz, 1H), 5.04 (d, *J* = 2.2 Hz, 2H), 4.90 – 4.77 (m, 1H), 4.40 (s, 1H), 3.41 (t, *J* = 2.0 Hz, 1H), 2.61 (d, *J* = 17.2 Hz, 1H), 2.44 – 2.38 (m, 2H), 2.28 (dd, *J* = 16.1, 1.6 Hz, 1H), 1.18 (s, 3H), 1.10 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.0, 169.8, 164.3, 142.1, 136.5, 135.3, 134.1, 132.8, 128.6, 128.6, 128.4, 128.3, 128.2, 127.9, 127.0, 121.4, 110.1, 87.3, 83.3, 70.8, 66.6, 50.9, 42.4, 40.6, 37.1, 32.6, 29.8, 26.8; HRMS (ESI) calculated for $C_{35}H_{32}ClO_4^+$ $[M+H]^+$ 551.1984, found 551.1984.

Methyl 2-(3-((4-chlorophenyl)ethynyl)-5-oxo-4-phenyl-3,4,5,6,7,8-hexahydro-2H-chromen-2-yl)acrylate (3ba)



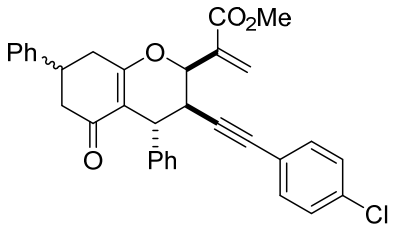
Prepared according to the general procedure as described above from the substrate **1a** (0.1 mmol, 45.2 mg) and **2b** (0.12 mmol, 13.4 mg) and purified by flash chromatography (PE/EtOAc 8:1). White solid, 75% yield (33.5 mg), 7:1 dr; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.14 (m, 7H), 6.53 (d, *J* = 1.2 Hz, 1H), 6.13 (t, *J* = 1.5 Hz, 1H), 4.80 (d, *J* = 2.3 Hz, 1H), 4.39 (s, 1H), 3.59 (s, 3H), 3.43 (t, *J* = 2.1 Hz, 1H), 2.74 – 2.61 (m, 2H), 2.48 (dt, *J* = 7.2, 5.4 Hz, 2H), 2.19 – 2.03 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.2, 171.5, 165.0, 142.2, 136.3, 134.1, 132.9, 128.6, 127.9, 127.7, 127.0, 121.6, 111.2, 87.3, 83.3, 70.8, 51.9, 40.5, 37.2, 37.1, 29.7, 28.7, 21.2; HRMS (ESI) calculated for $C_{27}H_{24}ClO_4^+$ $[M+H]^+$ 447.1358, found 447.1356.

Methyl 2-(3-((4-chlorophenyl)ethynyl)-7-methyl-5-oxo-4-phenyl-3,4,5,6,7,8-hexahydro-2H-chromen-2-yl)acrylate (3ca)



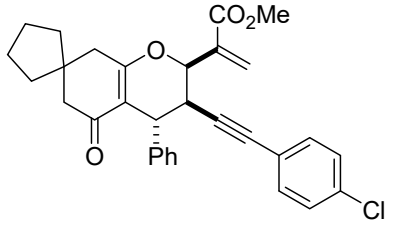
Prepared according to the general procedure as described above from the substrate **1a** (0.1 mmol, 45.2 mg) and **2c** (0.12 mmol, 15.1 mg) and purified by flash chromatography (PE/EtOAc 8:1). Pale yellow hemi solid, 71% yield (32.7 mg), 7:1 dr; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (td, *J* = 7.7, 1.9 Hz, 2H), 7.26 – 7.14 (m, 7H), 6.53 (dt, *J* = 2.6, 1.1 Hz, 1H), 6.13 (dt, *J* = 4.3, 1.5 Hz, 1H), 4.79 (s, 1H), 4.39 (d, *J* = 11.9 Hz, 1H), 3.59 (d, *J* = 6.7 Hz, 3H), 3.42 (dt, *J* = 14.9, 2.1 Hz, 1H), 2.65 (ddd, *J* = 27.2, 9.9, 3.7 Hz, 1H), 2.54 – 2.38 (m, 2H), 2.25 – 2.16 (m, 1H), 1.14 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.3, 197.0, 170.84, 170.76, 165.01, 164.98, 142.2, 142.0, 136.3, 134.1, 132.90, 132.87, 128.6, 127.88, 127.85, 127.70, 127.67, 127.00, 126.98, 121.6, 121.5, 110.9, 110.7, 87.3, 87.2, 83.27, 83.25, 70.9, 70.8, 51.9, 45.6, 44.9, 40.7, 40.3, 37.2, 37.0, 36.7, 36.5, 29.1, 28.3, 21.2, 20.5; HRMS (ESI) calculated for $C_{28}H_{26}ClO_4^+$ $[M+H]^+$ 461.1514, found 461.1513.

Methyl 2-(3-((4-chlorophenyl)ethynyl)-5-oxo-4,7-diphenyl-3,4,5,6,7,8-hexahydro-2H-chromen-2-yl)acrylate (3da)



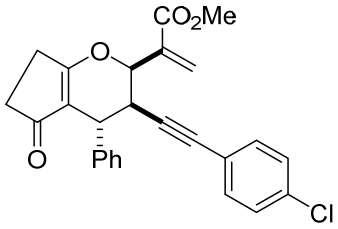
Prepared according to the general procedure as described above from the substrate **1a** (0.1 mmol, 45.2 mg) and **2d** (0.12 mmol, 22.6 mg) and purified by flash chromatography (PE/EtOAc 8:1). Pale yellow hemi solid, 63% yield (32.9 mg), 6:1 dr; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.32 (m, 3H), 7.30 – 7.23 (m, 9H), 7.22 – 7.18 (m, 2H), 6.54 (dt, *J* = 2.3, 1.1 Hz, 1H), 6.13 (dt, *J* = 6.1, 1.5 Hz, 1H), 4.85 (dd, *J* = 18.4, 2.2 Hz, 1H), 4.44 (d, *J* = 5.2 Hz, 1H), 3.60 (d, *J* = 8.4 Hz, 3H), 3.48 – 3.44 (m, 1H), 2.99 – 2.88 (m, 2H), 2.82 – 2.64 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.4, 196.0, 170.6, 170.3, 165.0, 164.9, 142.7, 142.5, 142.1, 142.0, 136.3, 136.2, 134.2, 134.1, 133.0, 132.9, 128.8, 128.8, 128.62, 128.59, 128.56, 127.9, 127.8, 127.7, 127.10, 127.05, 127.0, 126.7, 121.53, 121.46, 111.21, 111.19, 87.19, 87.16, 83.44, 83.40, 71.1, 71.0, 51.94, 51.93, 44.2, 43.8, 40.8, 40.4, 39.2, 38.6, 37.3, 37.0, 36.0, 35.8; HRMS (ESI) calculated for $C_{33}H_{28}ClO_4^+$ $[M+H]^+$ 523.1671, found 523.1669.

Methyl 2-(3-((4-chlorophenyl)ethynyl)-5-oxo-4-phenyl-2,3,4,5,6,8-hexahydrospiro[chromene-7,1'-cyclopentan]-2-yl)acrylate (3ea)



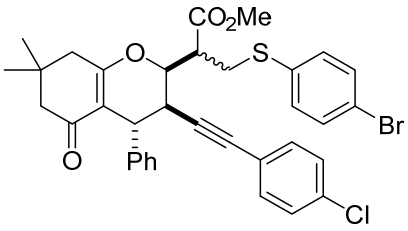
Prepared according to the general procedure as described above from the substrate **1a** (0.1 mmol, 45.2 mg) and **2e** (0.12 mmol, 19.9 mg) and purified by flash chromatography (PE/EtOAc 8:1). White solid, 66% yield (33.1 mg), 2:1 dr; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (q, *J* = 8.3 Hz, 2H), 7.19 – 7.09 (m, 6H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.47 (d, *J* = 3.9 Hz, 1H), 6.08 (dd, *J* = 9.4, 1.5 Hz, 1H), 4.69 (d, *J* = 14.5 Hz, 1H), 4.19 (d, *J* = 15.6 Hz, 1H), 3.53 (dd, *J* = 17.7, 1.3 Hz, 3H), 3.38 – 3.25 (m, 1H), 3.03 – 2.89 (m, 2H), 2.26 – 2.05 (m, 2H), 2.04 – 1.81 (m, 2H), 1.80 – 1.56 (m, 2H), 1.52 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.2, 199.9, 176.8, 164.0, 163.9, 141.4, 140.7, 135.3, 135.2, 133.2, 133.1, 131.9, 131.7, 127.7, 127.59, 127.57, 127.55, 126.9, 126.8, 126.7, 126.6, 126.02, 125.99, 120.5, 120.4, 106.2, 106.1, 86.1, 86.0, 82.3, 81.9, 70.3, 70.1, 50.92, 50.89, 48.8, 48.5, 40.9, 40.8, 39.0, 38.6, 38.1, 36.7, 36.5, 35.5, 29.2, 28.6, 25.8, 24.9; HRMS (ESI) calculated for $C_{31}H_{30}ClO_4^+$ $[M+H]^+$ 501.1827, found 501.1825.

Methyl 2-(3-((4-chlorophenyl)ethynyl)-5-oxo-4-phenyl-2,3,4,5,6,7-hexahydrocyclopenta[b]pyran-2-yl)acrylate (3fa)



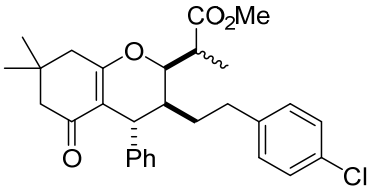
Prepared according to the general procedure as described above from the substrate **1a** (0.1 mmol, 45.2 mg) and **2f** (0.12 mmol, 17.7 mg) and purified by flash chromatography (PE/EtOAc 8:1). Yellow hemi solid, 65% yield (28.1 mg), 8:1 dr; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.6 Hz, 2H), 7.25 – 7.13 (m, 7H), 6.53 (t, *J* = 1.2 Hz, 1H), 6.13 (t, *J* = 1.4 Hz, 1H), 4.80 (d, *J* = 2.2 Hz, 1H), 4.39 (s, 1H), 3.59 (s, 3H), 3.42 (t, *J* = 2.0 Hz, 1H), 2.67 (d, *J* = 17.0 Hz, 1H), 2.57 – 2.50 (m, 2H), 2.39 (dd, *J* = 16.0, 1.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.3, 170.7, 165.0, 142.1, 136.3, 134.1, 132.8, 128.6, 128.5, 127.9, 127.7, 127.0, 121.5, 110.7, 87.3, 83.2, 70.9, 51.9, 49.4, 43.4, 41.2, 40.6, 39.0, 37.5, 37.1, 24.3, 24.2. HRMS (ESI) calculated for $C_{26}H_{22}ClO_4^+$ $[M+H]^+$ 433.1201, found 433.1201.

Methyl 3-((4-bromophenyl)thio)-2-(3-((4-chlorophenyl)ethynyl)-7,7-dimethyl-5-oxo-4-phenyl-3,4,5,6,7,8-hexahydro-2H-chromen-2-yl)propanoate (4)



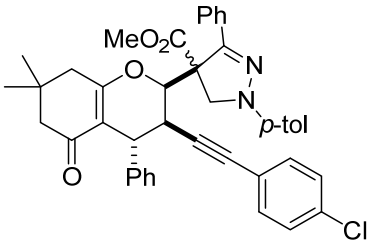
Prepared according to the general procedure as described above from the substrate **3aa** (0.10 mmol, 47.5 mg) and 4-bromothiophenol (0.12 mmol, 22.7 mg) and purified by flash chromatography (PE/EtOAc 8:1). Yellow oil, 73% yield (48.5 mg), 1:1 dr; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 6H), 7.31 – 7.28 (m, 7H), 7.27 – 7.24 (m, 7H), 7.22 – 7.19 (m, 2H), 7.06 – 6.96 (m, 4H), 6.60 (s, 1H), 6.48 (s, 1H), 5.82 (dd, *J* = 9.8, 1.4 Hz, 1H), 5.76 (dd, *J* = 9.8, 1.4 Hz, 1H), 5.39 (d, *J* = 3.8 Hz, 2H), 3.95 (tt, *J* = 10.9, 8.0 Hz, 2H), 3.70 (s, 3H), 3.69 (s, 3H), 3.39 (ddd, *J* = 13.8, 8.7, 6.7 Hz, 2H), 3.02 (ddd, *J* = 27.0, 13.8, 8.1 Hz, 2H), 2.47 – 2.33 (m, 4H), 2.31 (d, *J* = 5.5 Hz, 3H), 1.10 – 1.08 (m, 8H), 1.07 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.9, 196.8, 172.2, 172.0, 171.2, 171.0, 138.9, 138.7, 135.2, 135.0, 134.87, 134.85, 134.3, 134.1, 132.70, 132.67, 132.12, 132.08, 131.69, 131.67, 129.2, 129.1, 128.9, 128.8, 128.4, 128.3, 127.43, 127.41, 120.7, 120.64, 120.57, 114.5, 114.3, 95.1, 95.0, 87.1, 87.0, 52.5, 52.4, 50.4, 46.8, 45.4, 45.2, 43.43, 43.37, 36.1, 35.6, 31.9, 31.8, 28.7, 28.5, 27.8, 27.7; HRMS (ESI) calculated for $C_{35}H_{33}BrClO_4S^+$ $[M+H]^+$ 663.0966, found 663.0960.

Methyl 2-(3-(4-chlorophenethyl)-7,7-dimethyl-5-oxo-4-phenyl-3,4,5,6,7,8-hexahydro-2H-chromen-2-yl)propanoate (5)



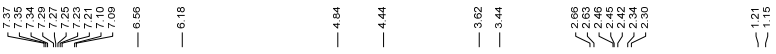
Prepared according to the general procedure as described above from the substrate **3aa** (0.10 mmol, 47.5 mg) and **Pd-C** (10.0 wt% palladium on carbon, 2.1 mg) and purified by flash chromatography (PE/EtOAc 8:1). White soild, 80% yield (38.4 mg), >20:1 dr; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.22 (m, 4H), 7.18 – 7.14 (m, 1H), 7.08 – 7.04 (m, 2H), 4.10 (s, 1H), 4.02 (dd, *J* = 10.6, 2.0 Hz, 1H), 3.69 (s, 3H), 2.97 (ddd, *J* = 13.6, 8.5, 5.0 Hz, 1H), 2.76 – 2.63 (m, 2H), 2.50 – 2.21 (m, 4H), 1.80 (dq, *J* = 10.6, 2.1 Hz, 1H), 1.70 (dtd, *J* = 14.0, 8.3, 2.5 Hz, 1H), 1.41 (dddd, *J* = 13.7, 10.6, 8.3, 5.1 Hz, 1H), 1.15 (s, 3H), 1.07 (s, 3H), 0.68 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.4, 175.10, 170.05, 144.3, 141.4, 128.6, 128.53, 128.48, 127.9, 126.27, 126.25, 109.6, 51.9, 51.0, 42.2, 41.1, 38.4, 37.7, 33.4, 32.3, 29.6, 27.6, 27.4, 12.8; HRMS (ESI) calculated for $C_{29}H_{33}ClNaO_4^+$ $[M+Na]^+$ 503.1960, found 503.1959.

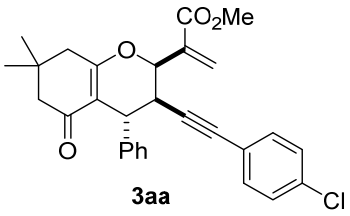
Methyl 4-(3-((4-chlorophenyl)ethynyl)-7,7-dimethyl-5-oxo-4-phenyl-3,4,5,6,7,8-hexahydro-2H-chromen-2-yl)-3-phenyl-1-(*p*-tolyl)-4,5-dihydro-1H-pyrazole-4-carboxylate (6)



Prepared according to the general procedure as described above from the substrate **3aa** (0.10 mmol, 47.5 mg) and N-(*p*-tolyl)benzohydrazonoyl chloride (0.12 mmol, 29.4 mg) and purified by flash chromatography (PE/EtOAc 8:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 – 7.65 (m, 2H), 7.40 – 7.33 (m, 3H), 7.31 – 7.26 (m, 6H), 7.23 (d, *J* = 7.2 Hz, 1H), 7.05 (dd, *J* = 7.0, 1.8 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 6.90 – 6.85 (m, 2H), 4.74 (d, *J* = 1.8 Hz, 1H), 4.33 (s, 1H), 4.26 (d, *J* = 17.1 Hz, 1H), 3.71 (d, *J* = 17.1 Hz, 1H), 3.56 (t, *J* = 1.9 Hz, 1H), 3.45 (s, 3H), 2.44 (d, *J* = 17.3 Hz, 1H), 2.30 (s, 3H), 2.29 – 2.15 (m, 3H), 1.07 (s, 3H), 1.01 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.9, 170.02, 169.95, 147.8, 142.2, 141.2, 134.5, 132.6, 132.30, 132.28, 129.2, 128.81, 128.79, 128.6, 128.5, 127.9, 127.1, 125.8, 121.3, 119.4, 110.2, 88.5, 84.1, 75.2, 70.7, 52.5, 50.8, 42.4, 42.1, 38.7, 33.7, 32.6, 29.6, 26.7, 20.8; HRMS (ESI) calculated for $C_{43}H_{40}ClN_2O_4^+$ $[M+H]^+$ 683.2671, found 683.2668.

^{1}H and ^{13}C NMR Spectra of New Substrates and All Products

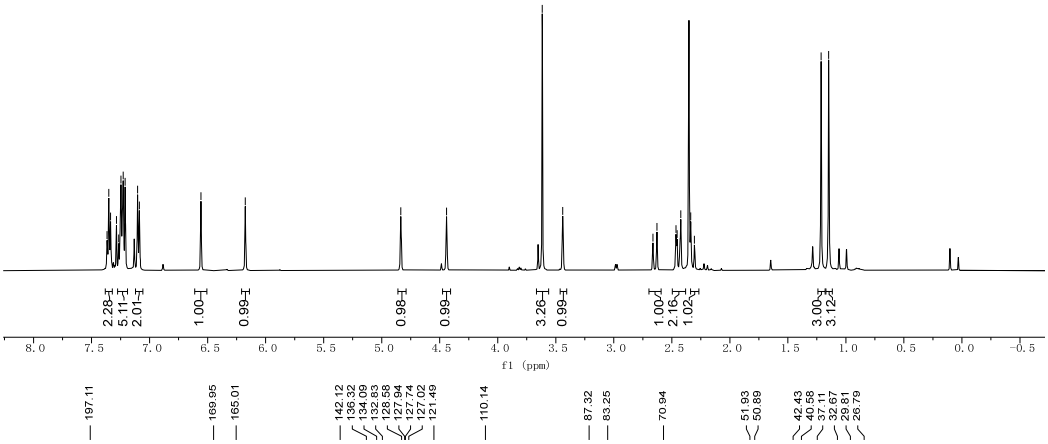


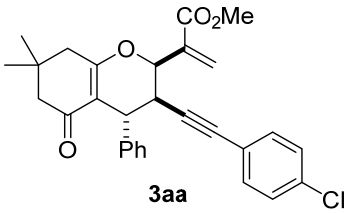


3aa

^{1}H NMR of **3aa**

$CDCl_3$, 500 MHz

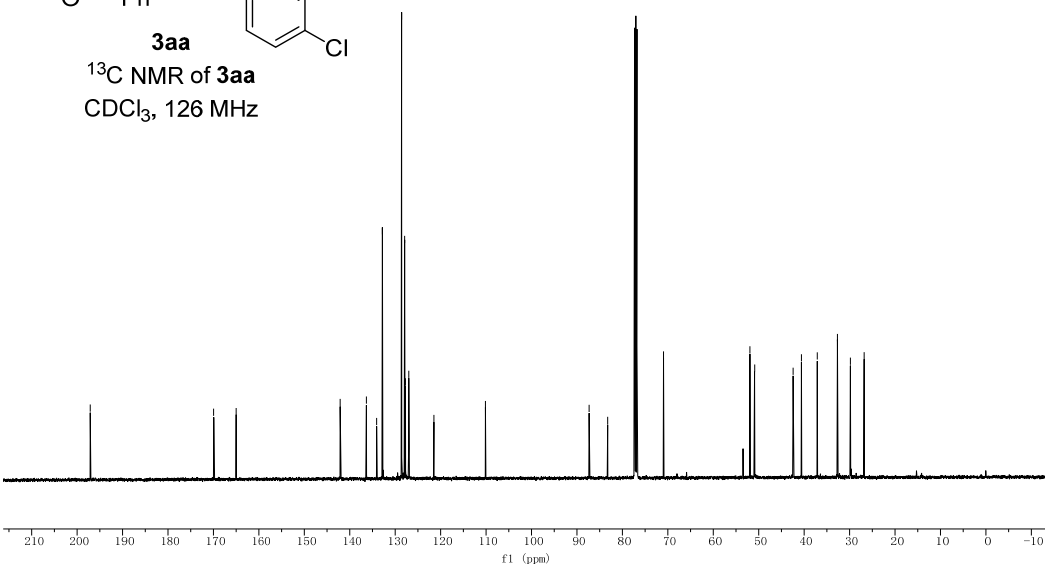


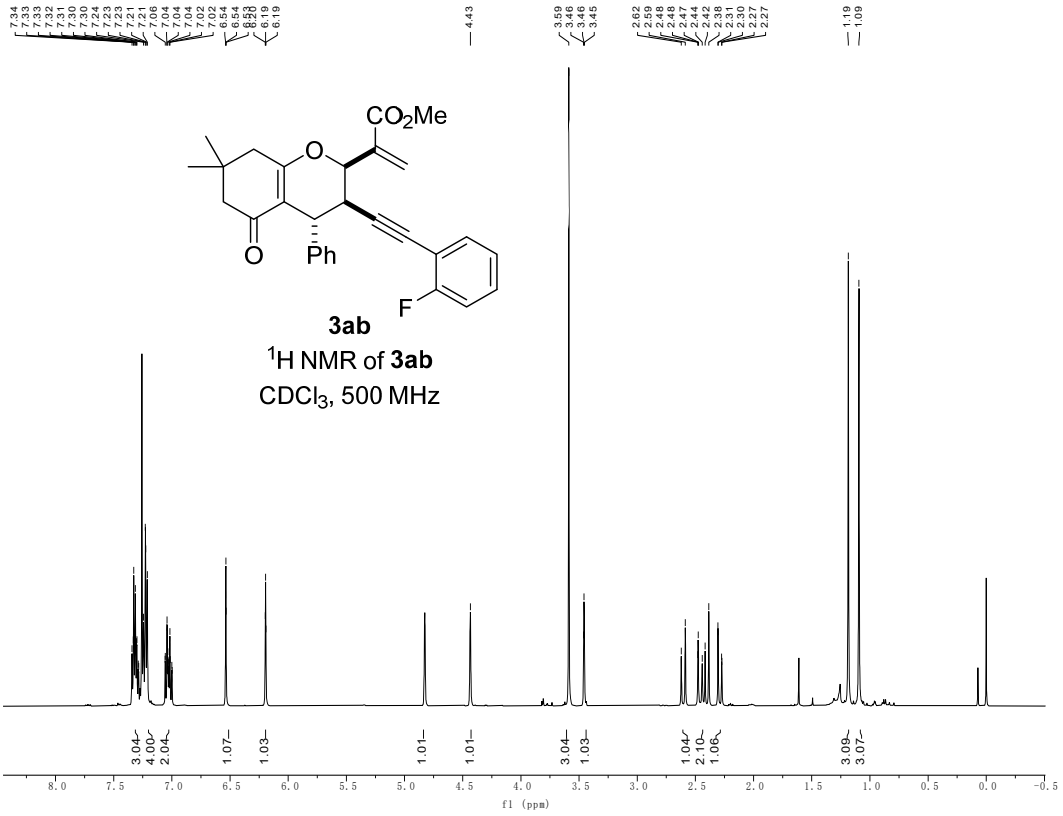


3aa

^{13}C NMR of **3aa**

$CDCl_3$, 126 MHz

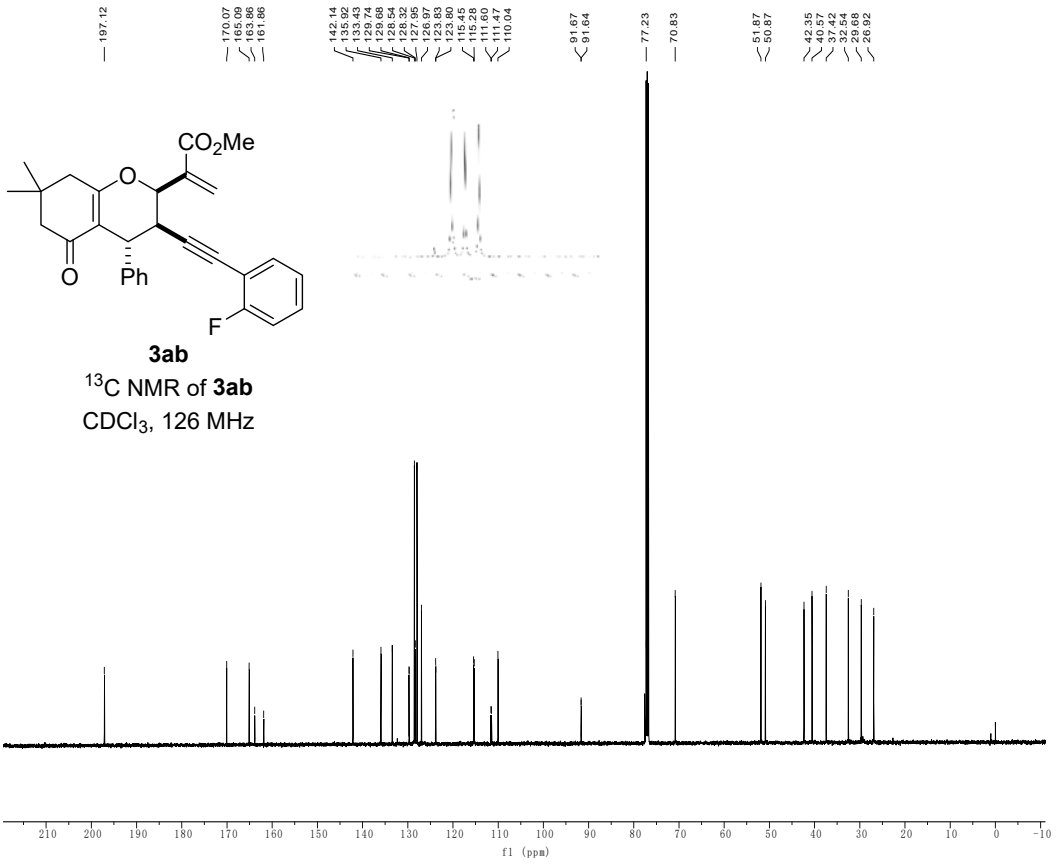




3ab

^{1}H NMR of **3ab**

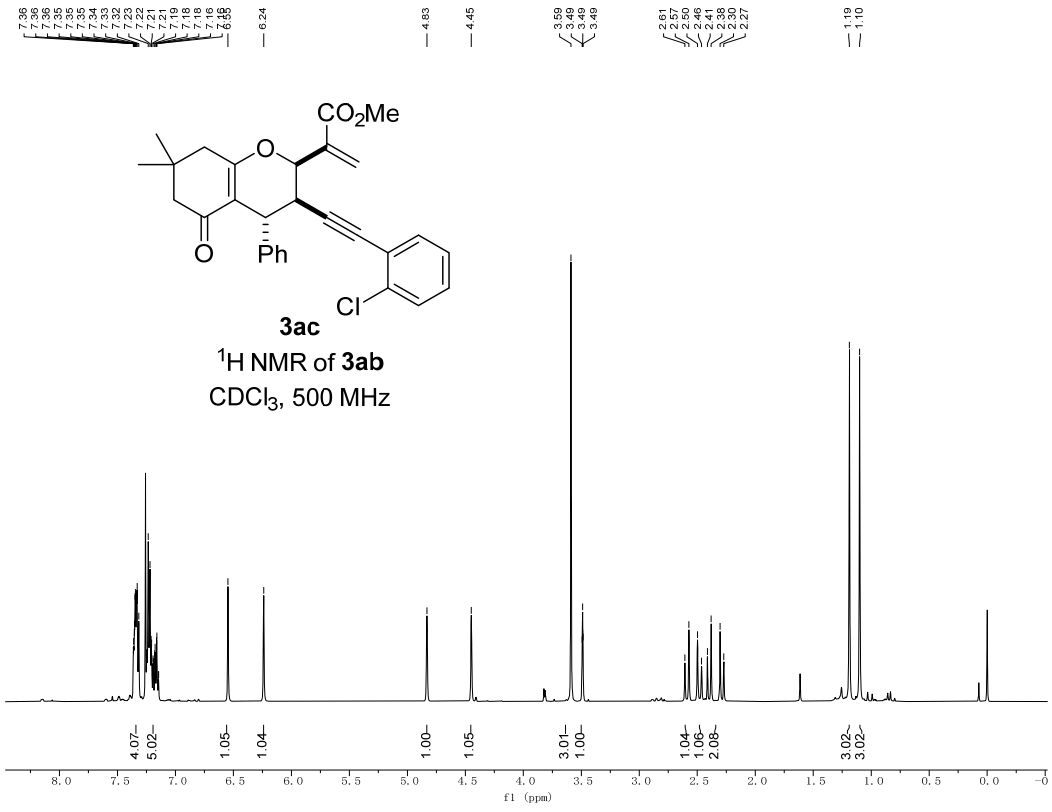
$CDCl_3$, 500 MHz



3ab

^{13}C NMR of **3ab**

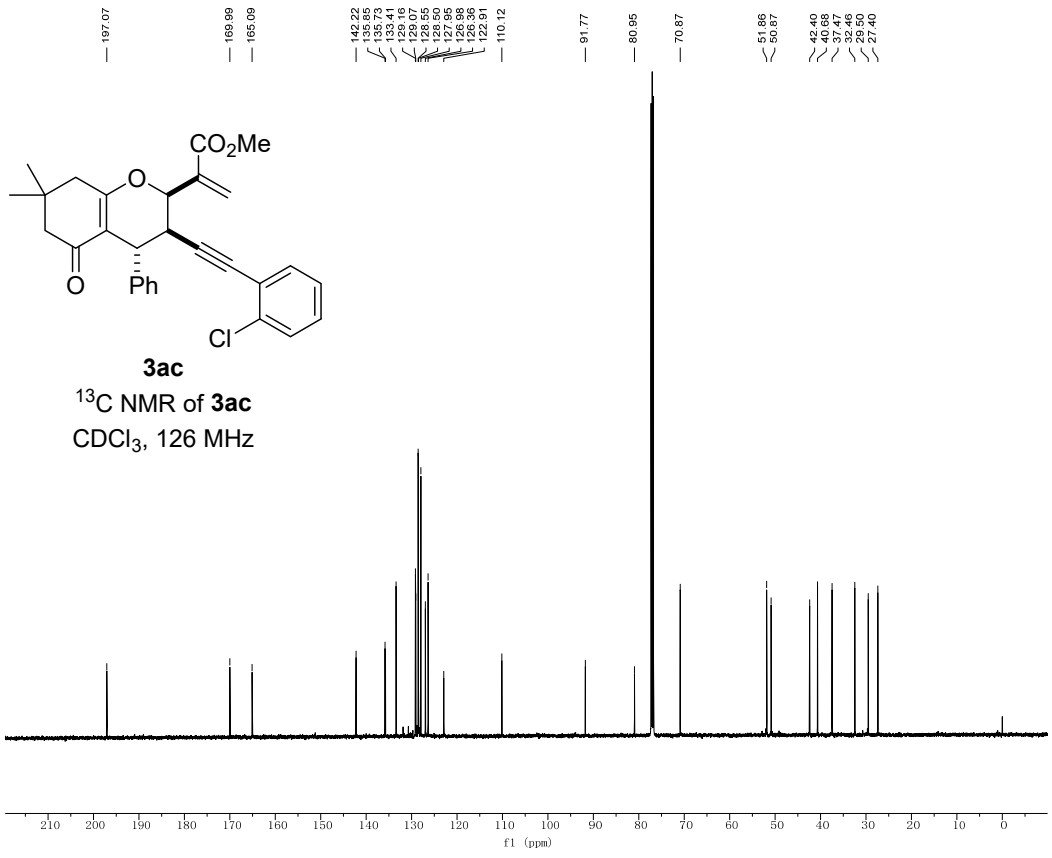
$CDCl_3$, 126 MHz



3ac

^{1}H NMR of **3ab**

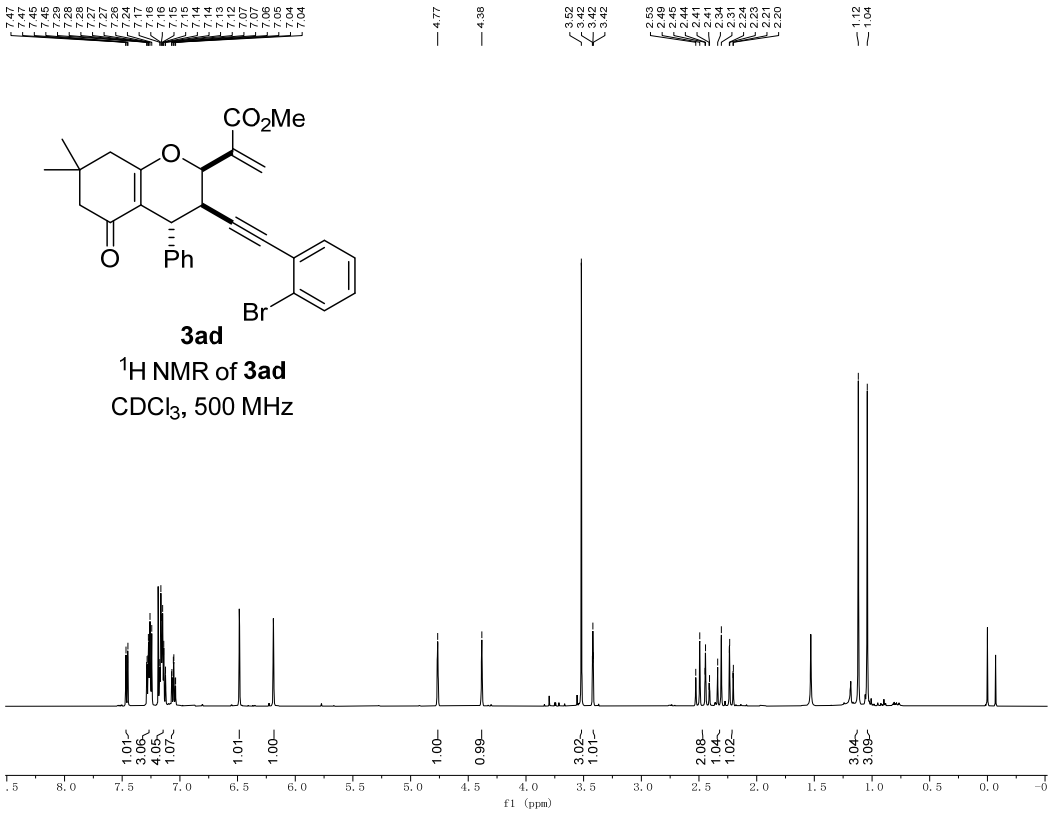
$CDCl_3$, 500 MHz



3ac

^{13}C NMR of **3ac**

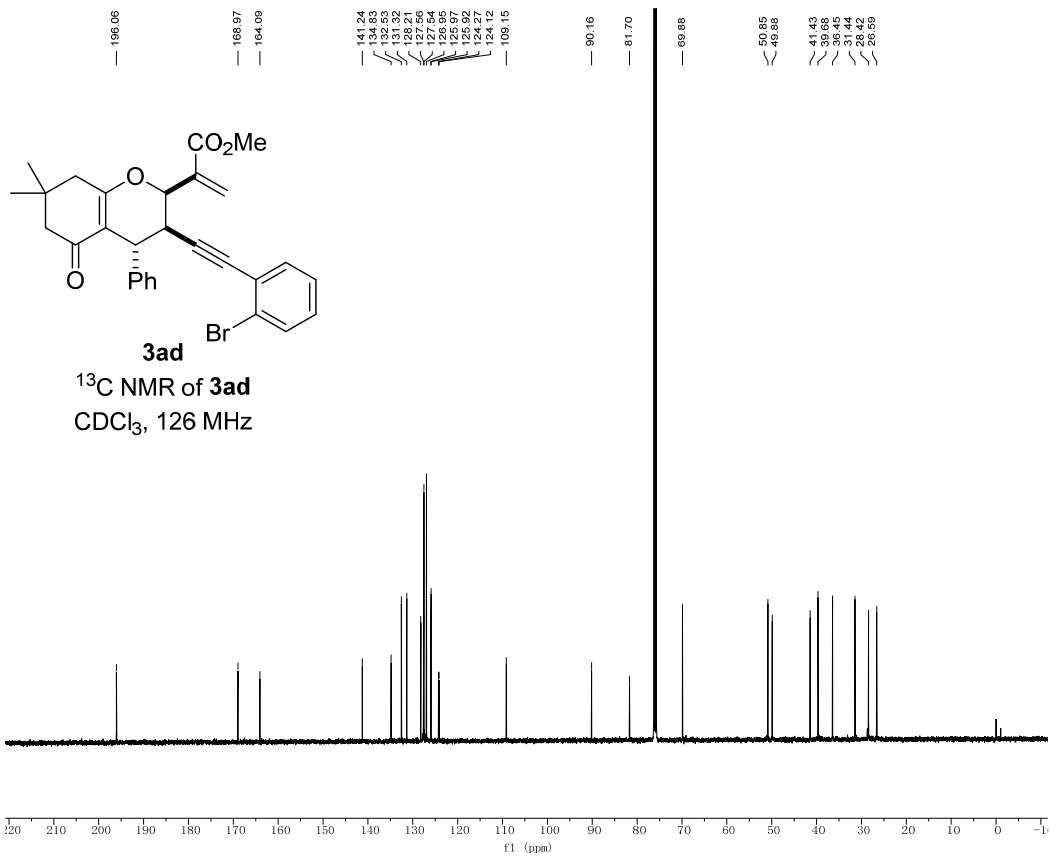
$CDCl_3$, 126 MHz



3ad

^{1}H NMR of **3ad**

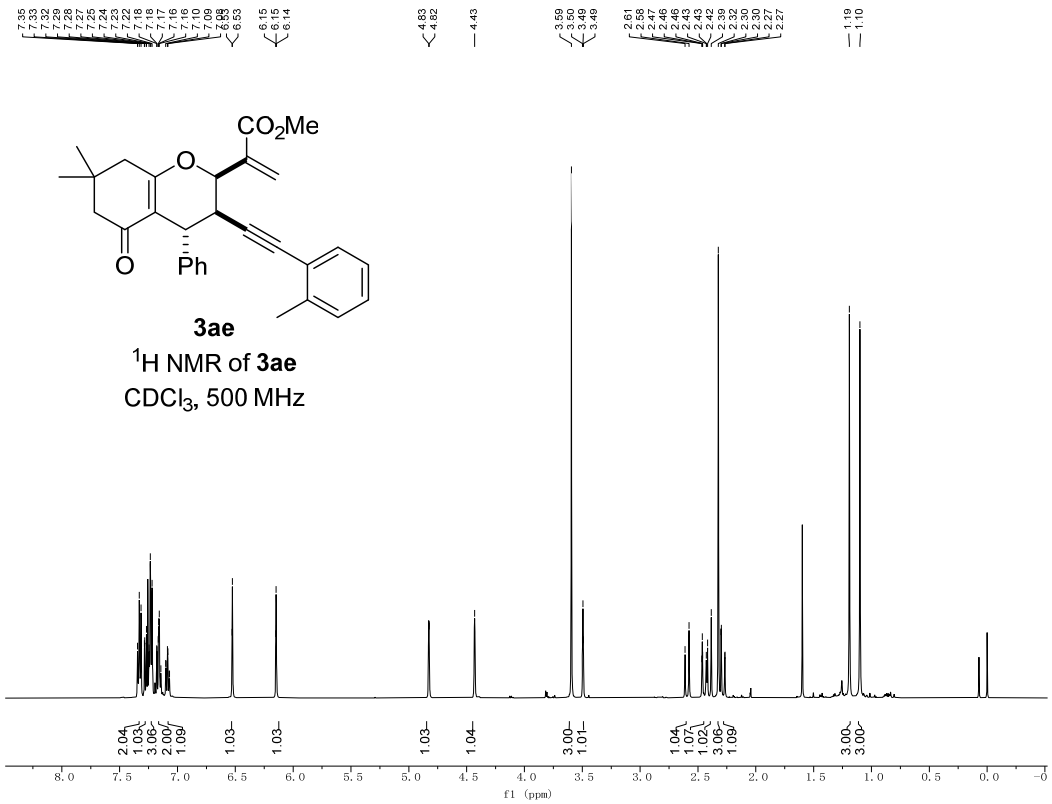
$CDCl_3$, 500 MHz

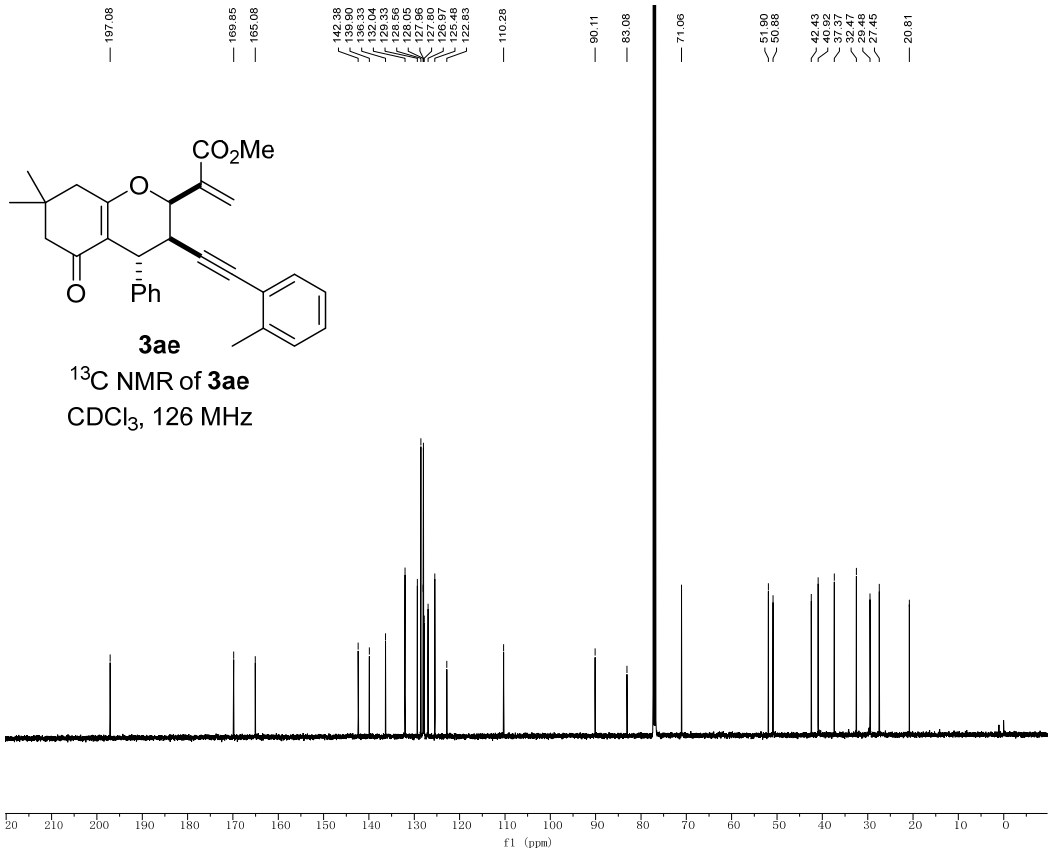


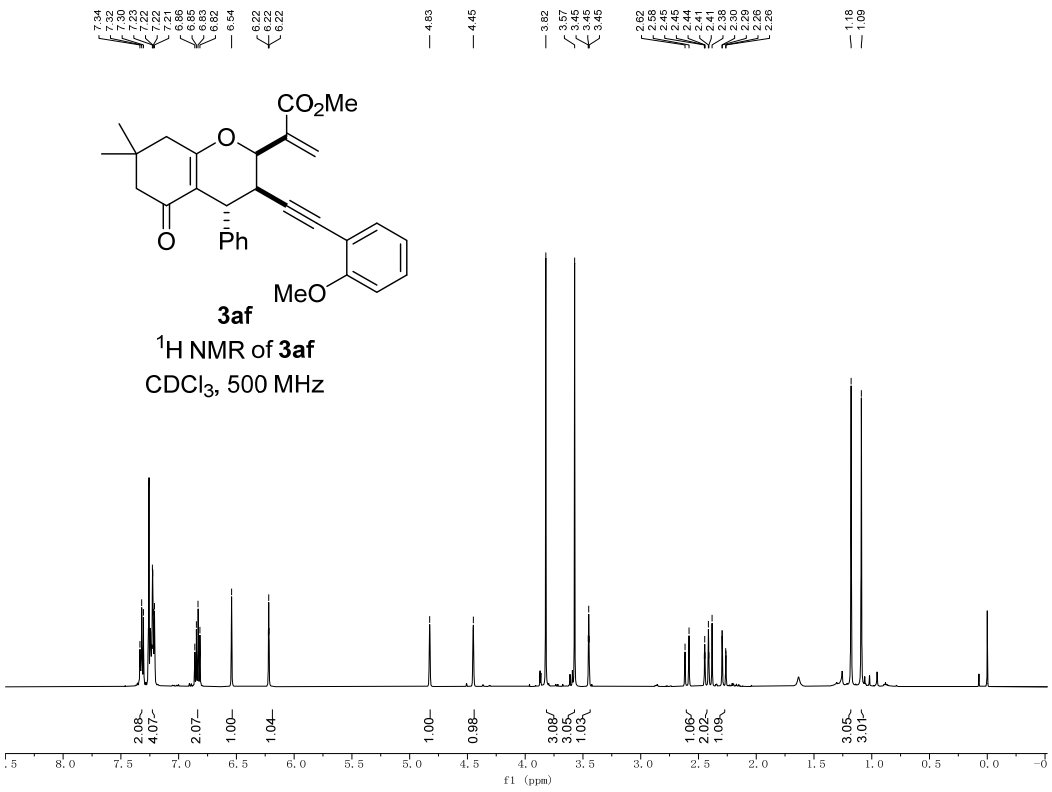
3ad

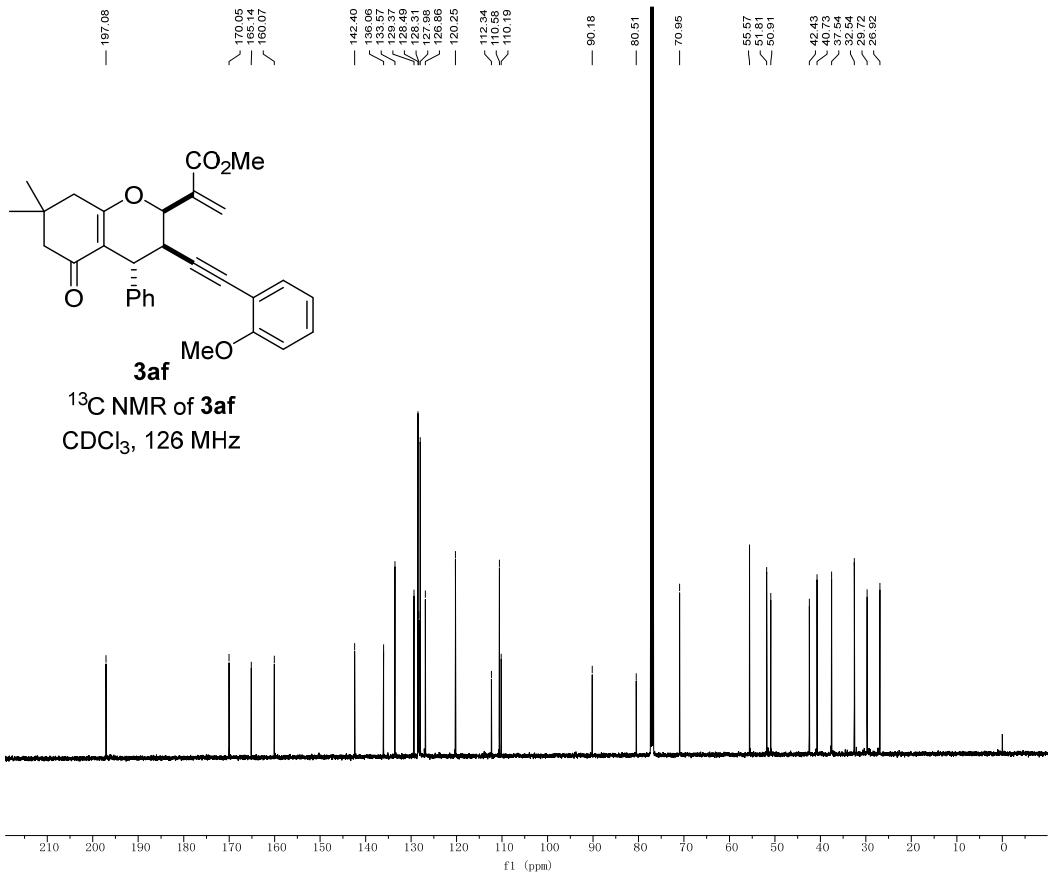
^{13}C NMR of **3ad**

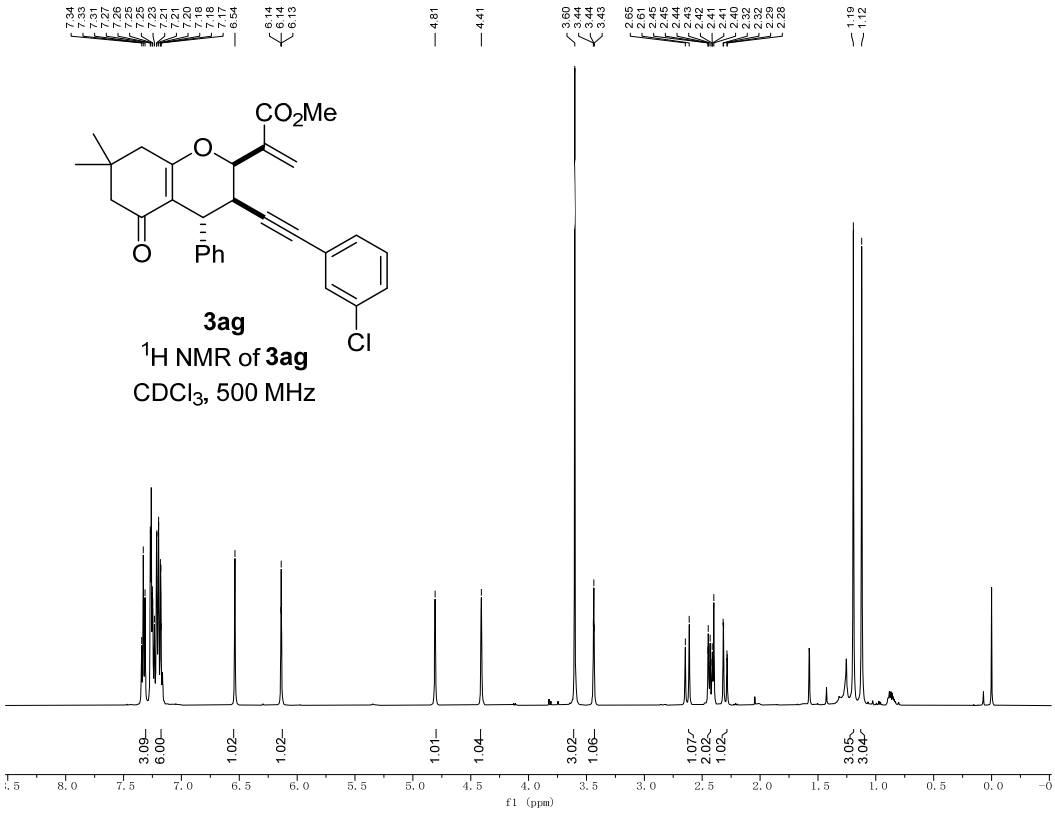
$CDCl_3$, 126 MHz


CO2Me
O
O
Ph
3ae
1H NMR of 3ae
CDCl3, 500 MHz
f1 (ppm)


CO2Me
O
O
Ph
3ae
13C NMR of 3ae
CDCl3, 126 MHz
f1 (ppm)


CO2Me
O
O
Ph
MeO
3af
1H NMR of 3af
CDCl3, 500 MHz
f1 (ppm)

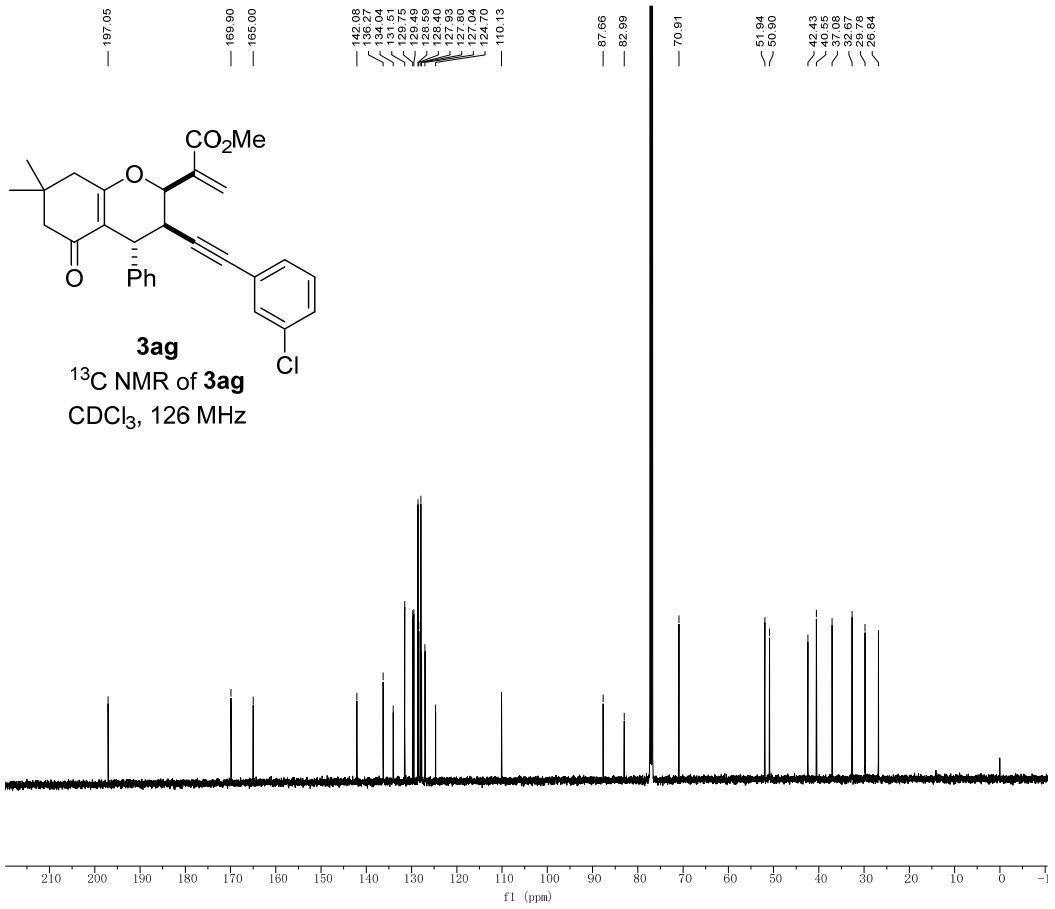

CO2Me
O
O
Ph
MeO
3af
13C NMR of 3af
CDCl3, 126 MHz
f1 (ppm)



3ag

^{1}H NMR of **3ag**

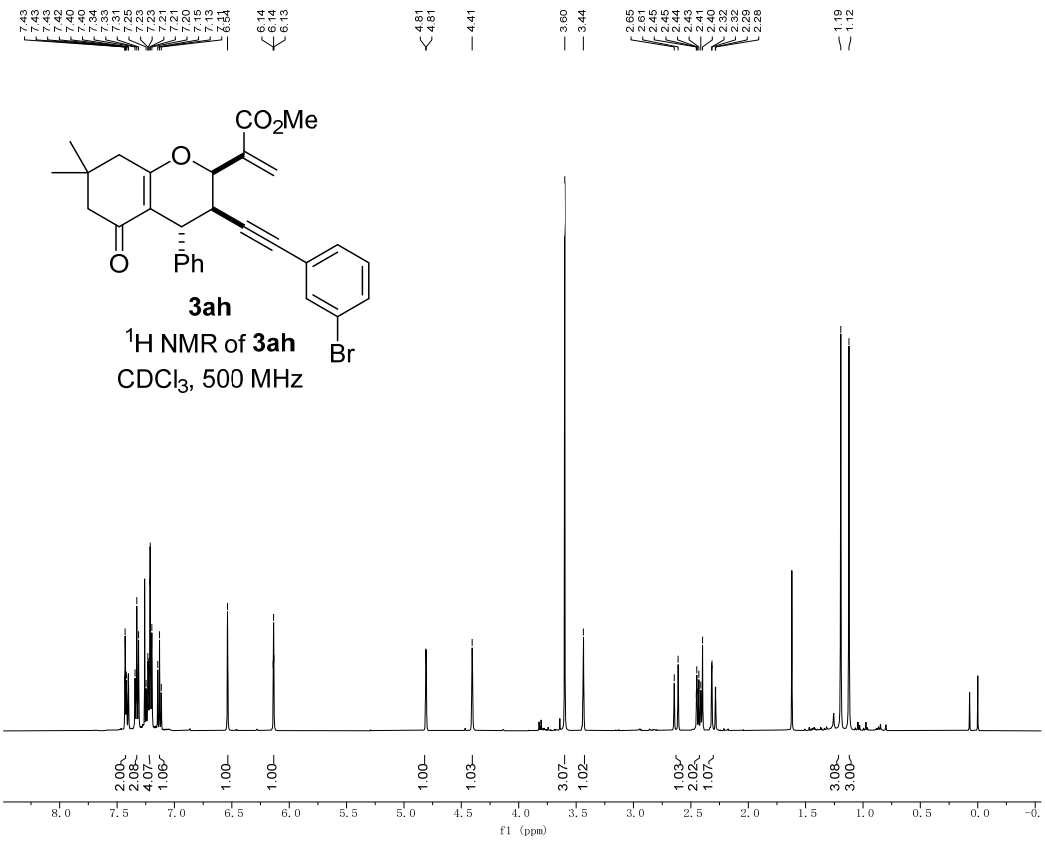
$CDCl_3$, 500 MHz

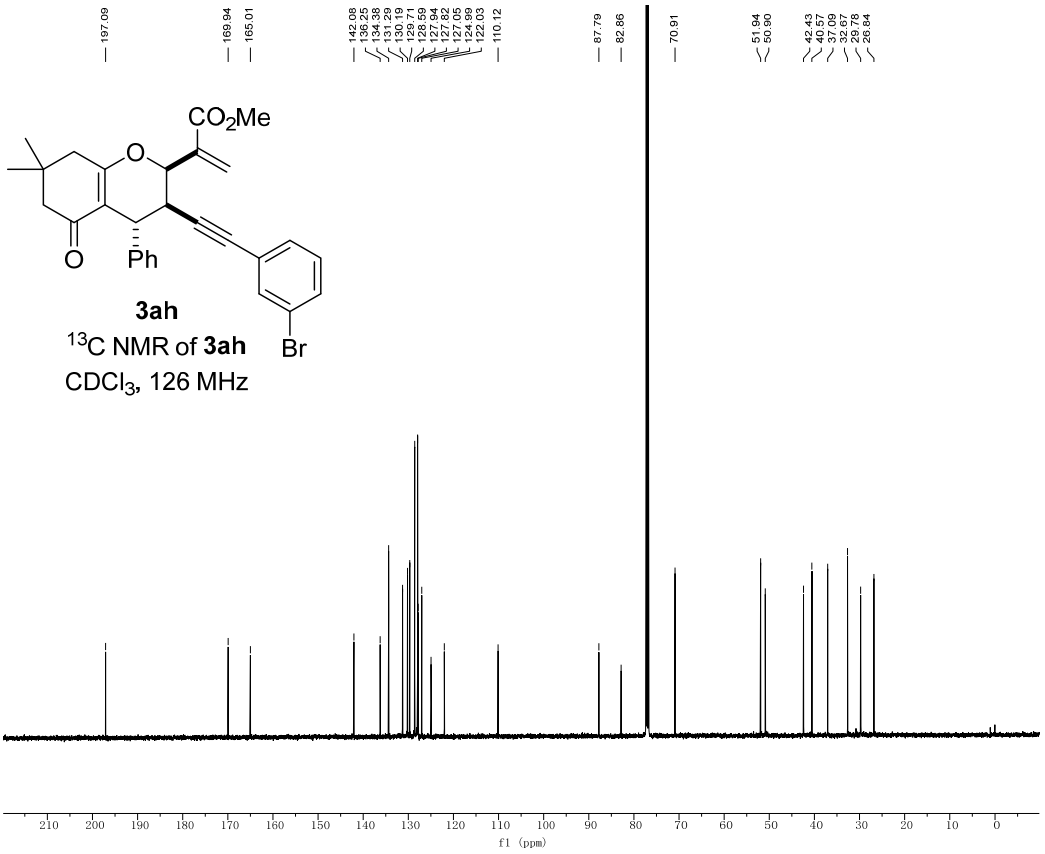


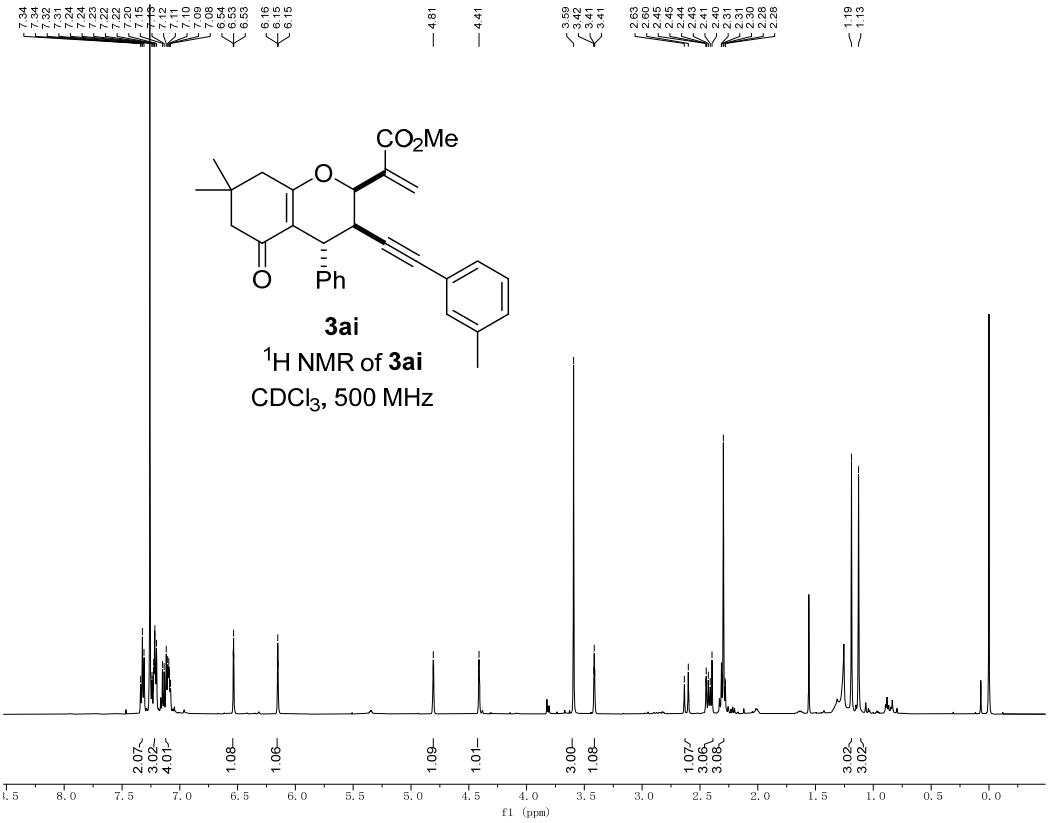
3ag

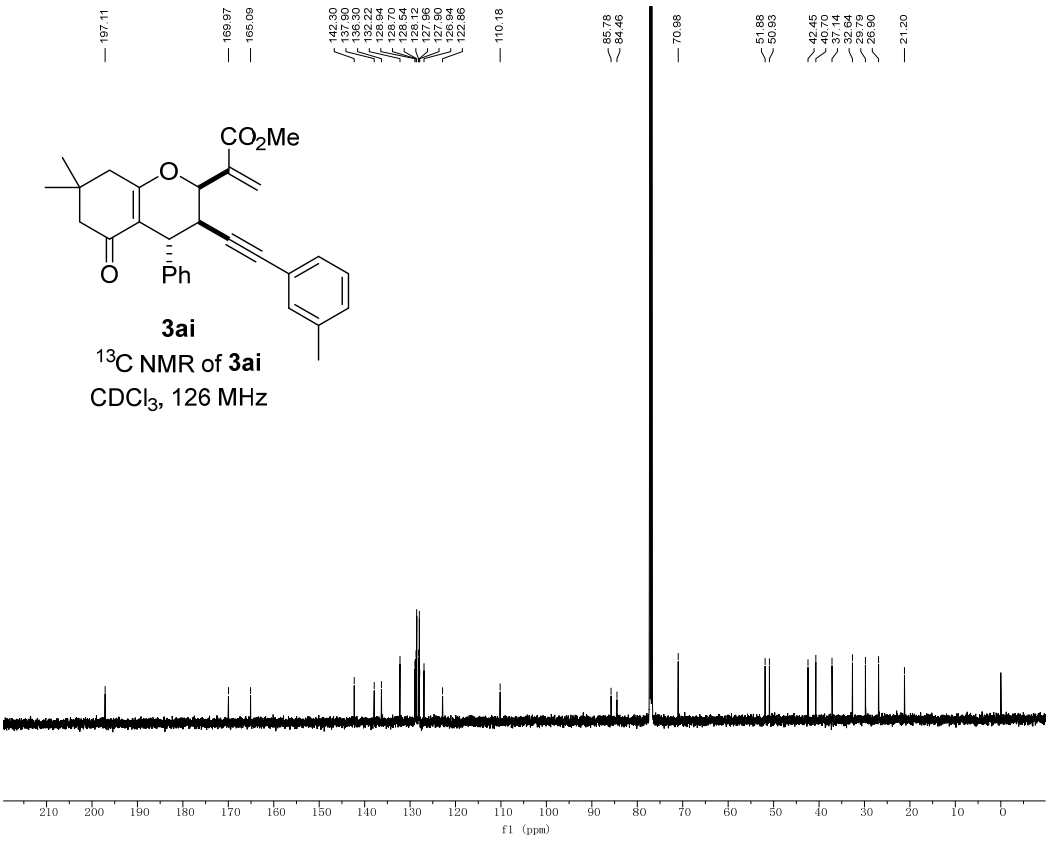
^{13}C NMR of **3ag**

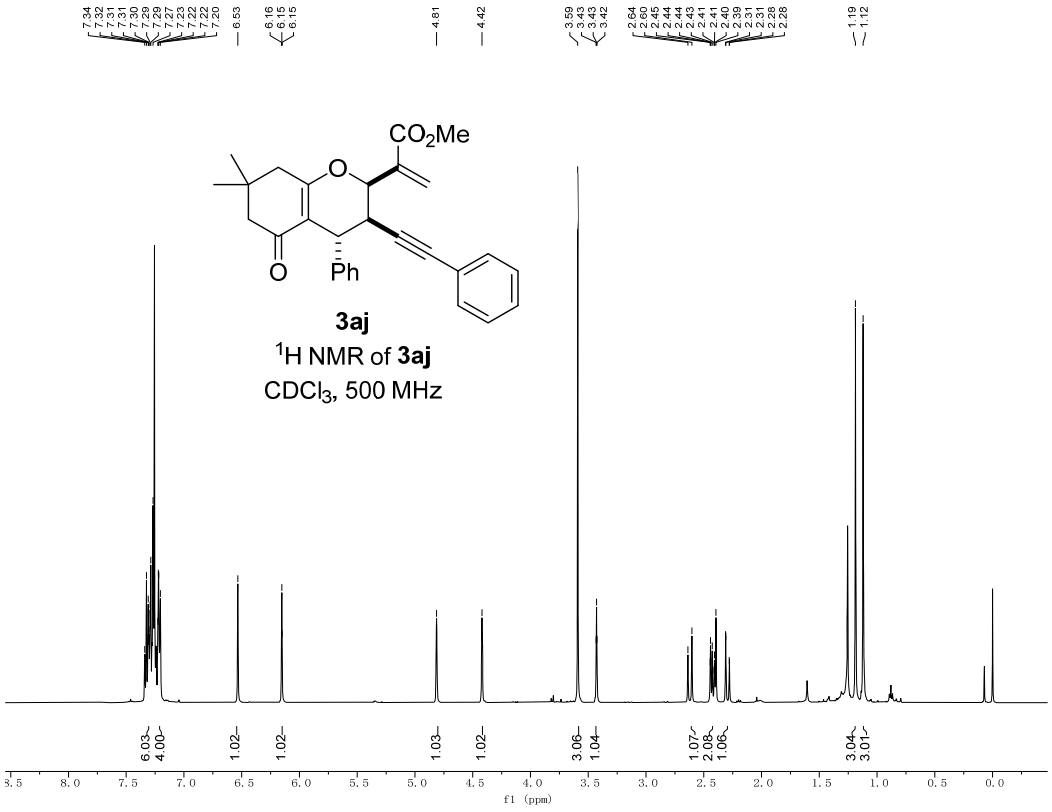
$CDCl_3$, 126 MHz


CO2Me
O
O
Ph
Br
3ah
1H NMR of 3ah
CDCl3, 500 MHz
f1 (ppm)


CO2Me
O
O
Ph
Br
3ah
13C NMR of 3ah
CDCl3, 126 MHz
f1 (ppm)


CO2Me
O
O
Ph
3ai
1H NMR of 3ai
CDCl3, 500 MHz
f1 (ppm)

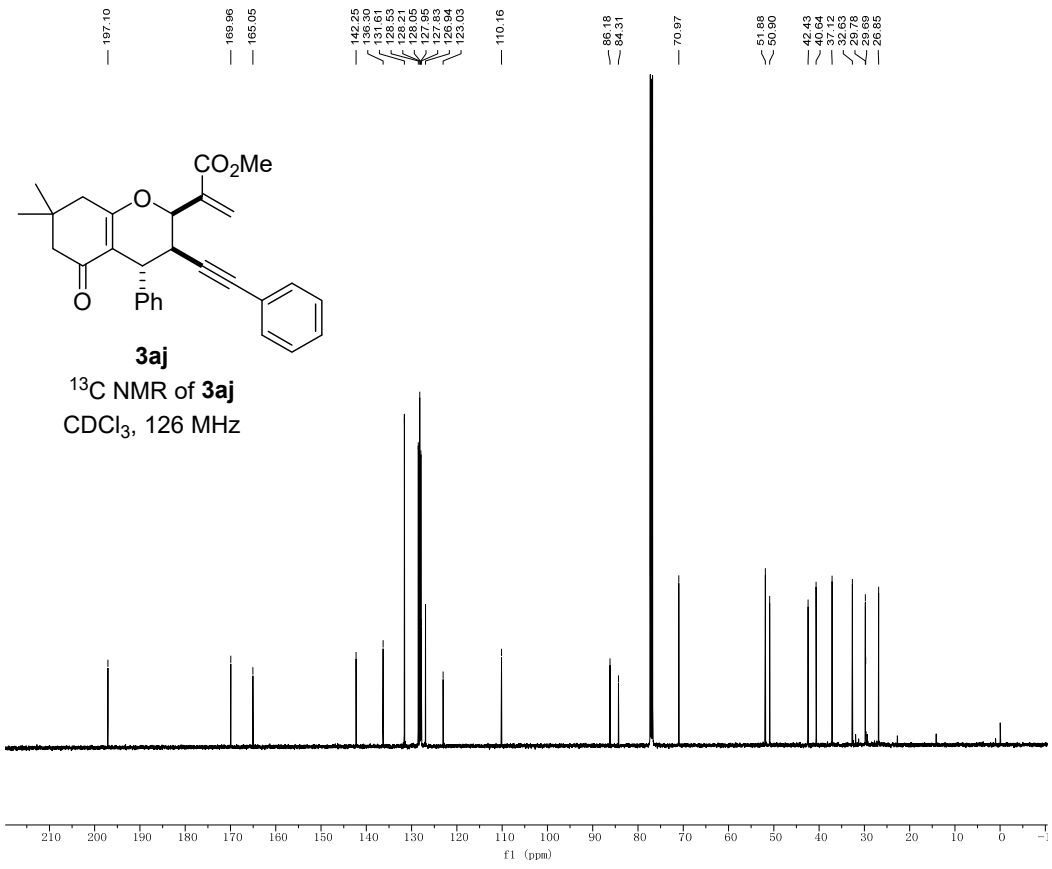

CO2Me
O
O
Ph
3ai
13C NMR of 3ai
CDCl3, 126 MHz
f1 (ppm)



3aj

^{1}H NMR of **3aj**

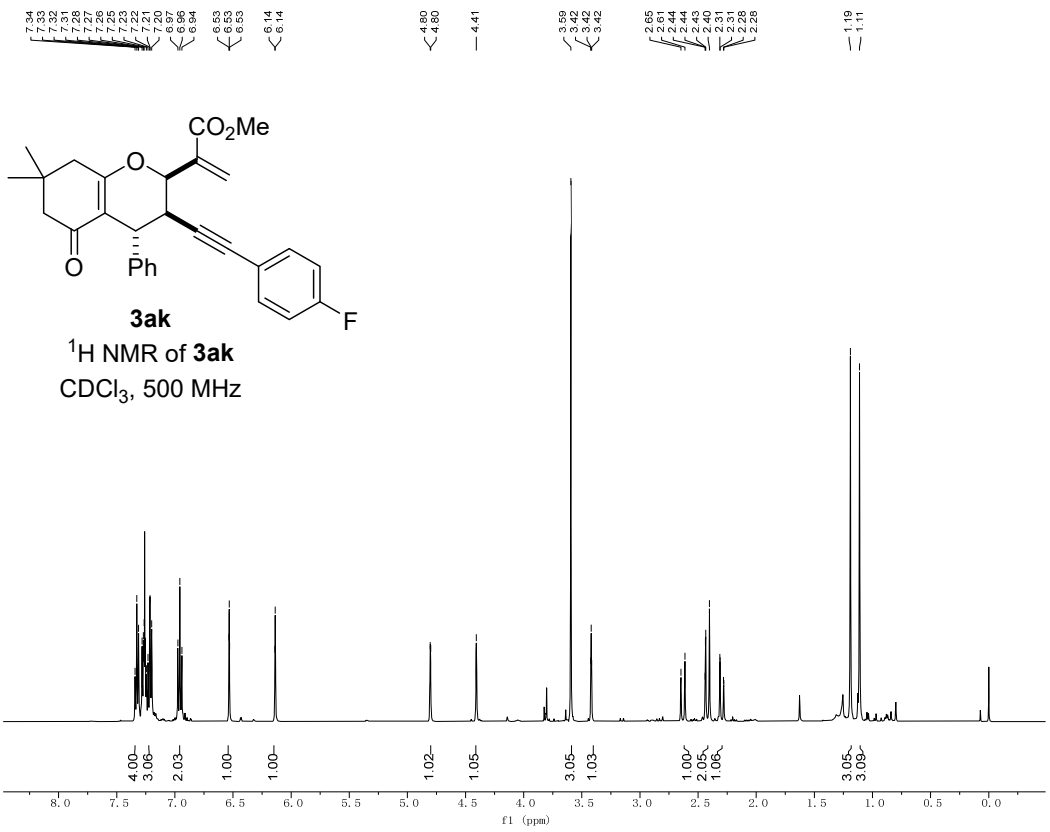
$CDCl_3$, 500 MHz

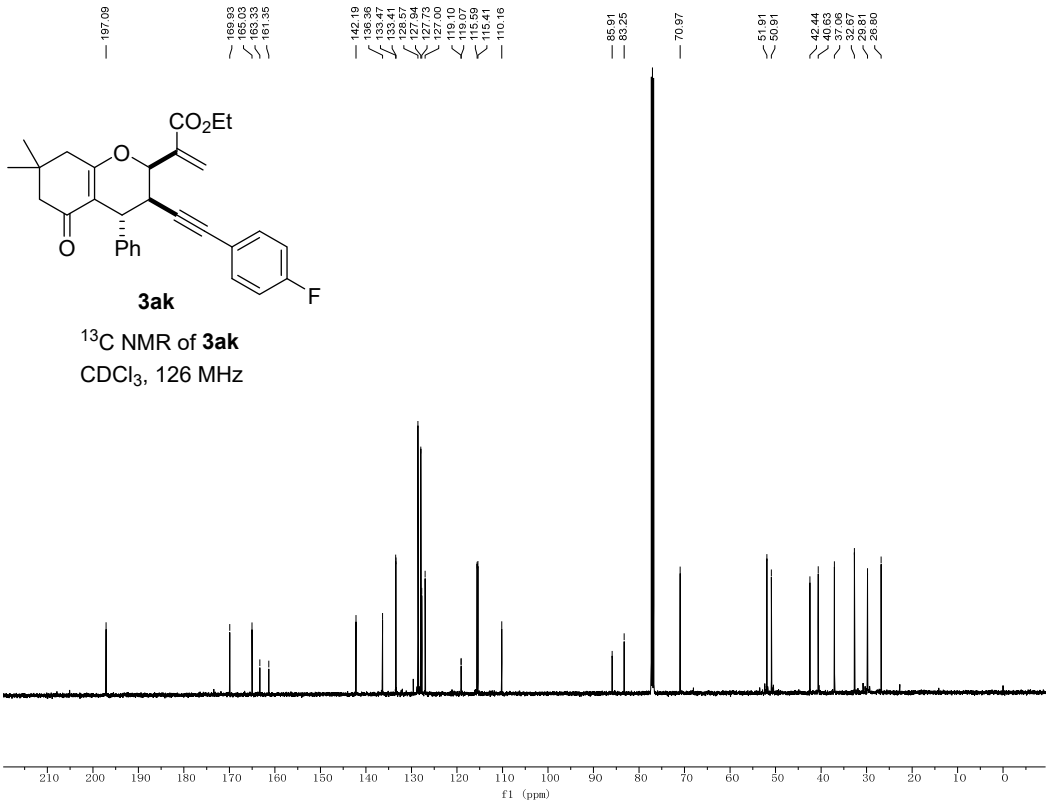


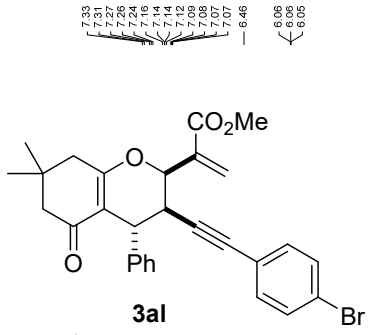
3aj

^{13}C NMR of **3aj**

$CDCl_3$, 126 MHz


CO2Me
O
O
Ph
F
3ak
1H NMR of 3ak
CDCl3, 500 MHz
f1 (ppm)

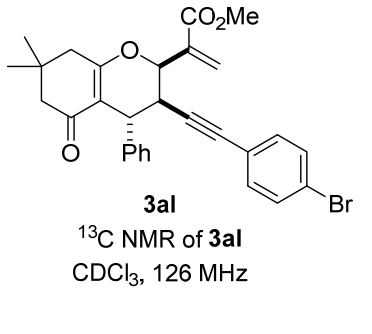

CO2Et
O
O
Ph
F
3ak
13C NMR of 3ak
CDCl3, 126 MHz
f1 (ppm)



3al

^{1}H NMR of **3al**

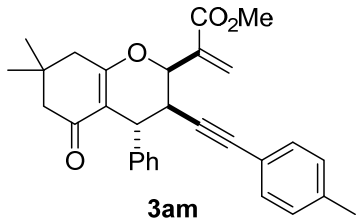
$CDCl_3$, 500 MHz



3al

^{13}C NMR of **3al**

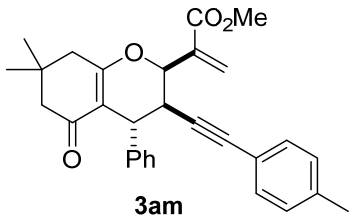
$CDCl_3$, 126 MHz



3am

^{1}H NMR of **3am**

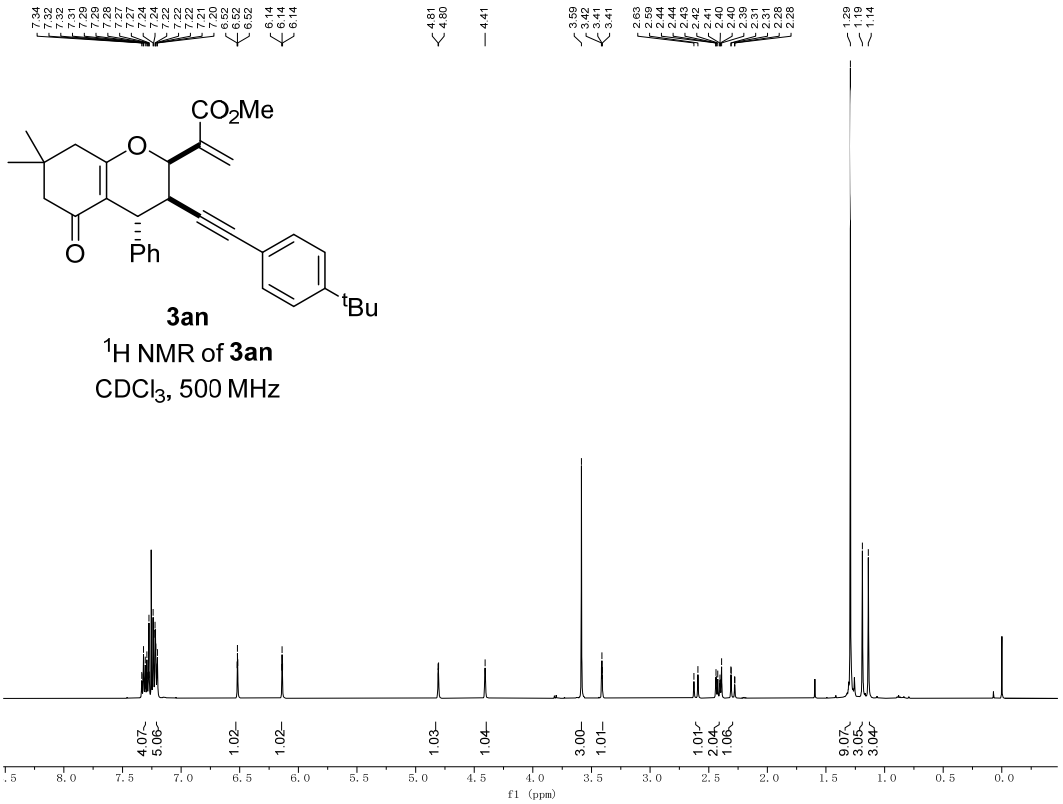
$CDCl_3$, 500 MHz



3am

^{13}C NMR of **3am**

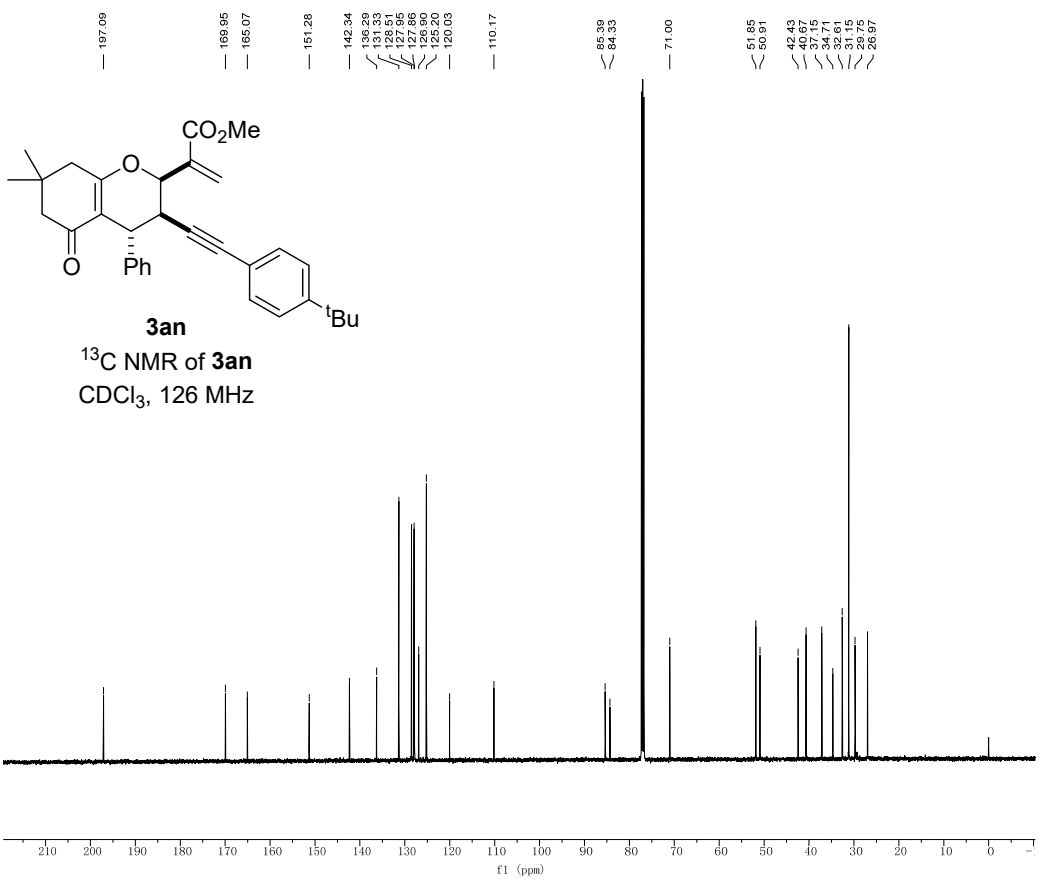
$CDCl_3$, 126 MHz



3an

^{1}H NMR of **3an**

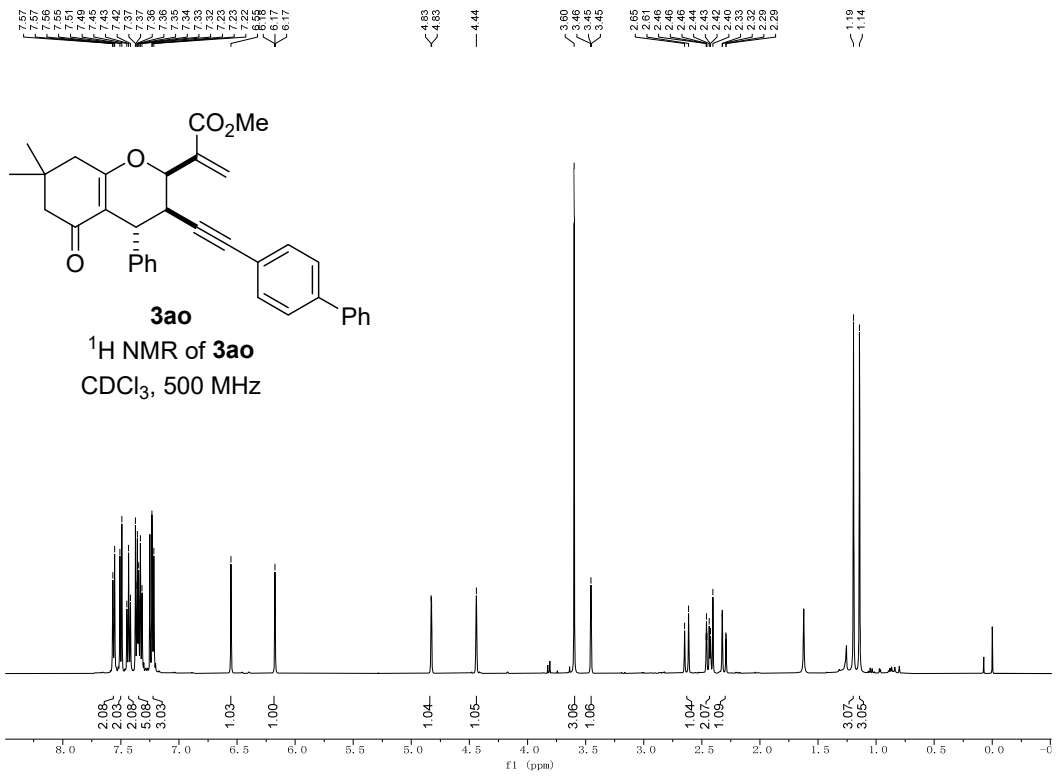
$CDCl_3$, 500 MHz



3an

^{13}C NMR of **3an**

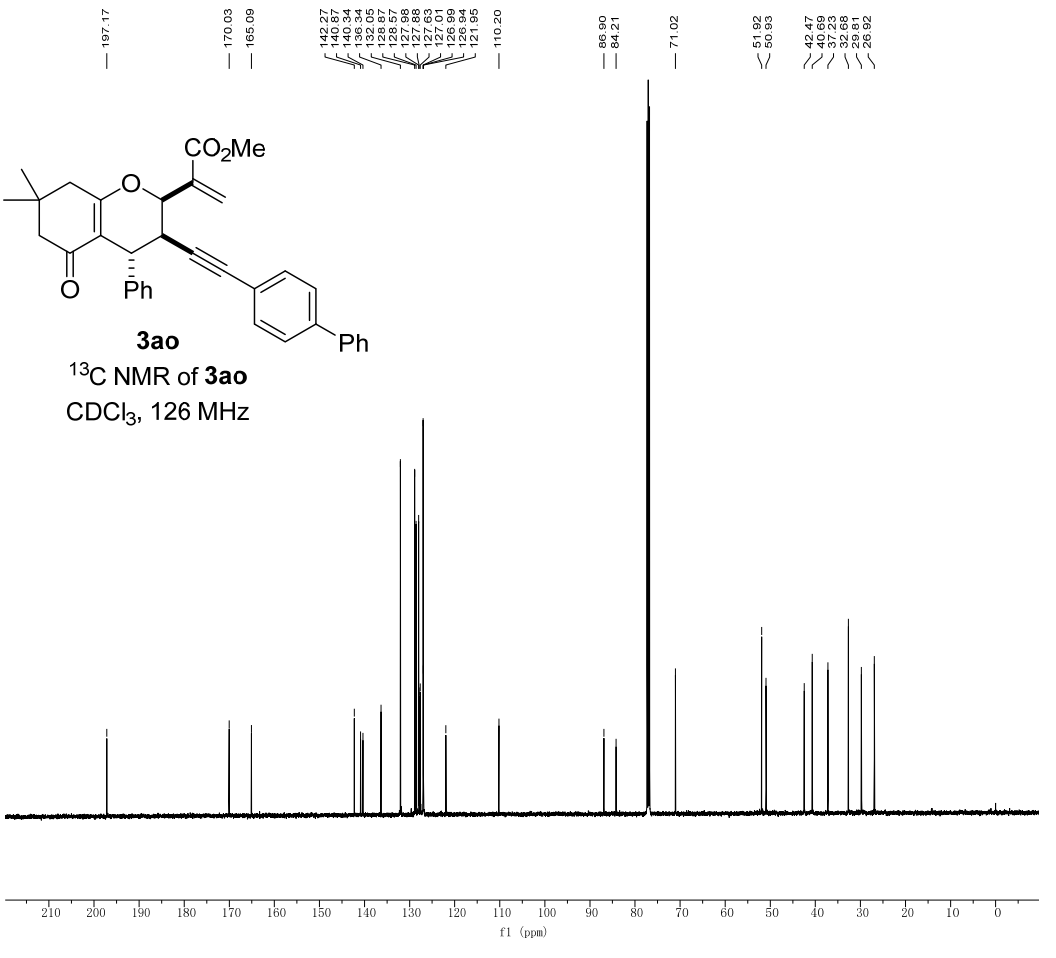
$CDCl_3$, 126 MHz



3ao

^{1}H NMR of **3ao**

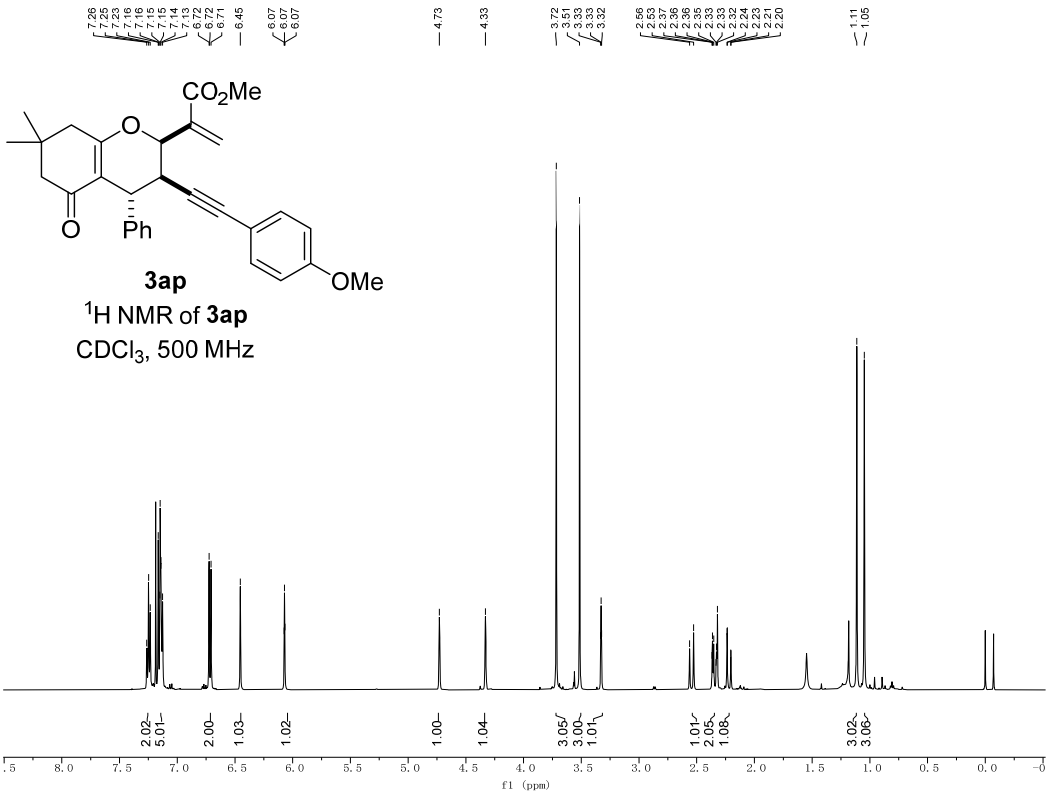
$CDCl_3$, 500 MHz



3ao

^{13}C NMR of **3ao**

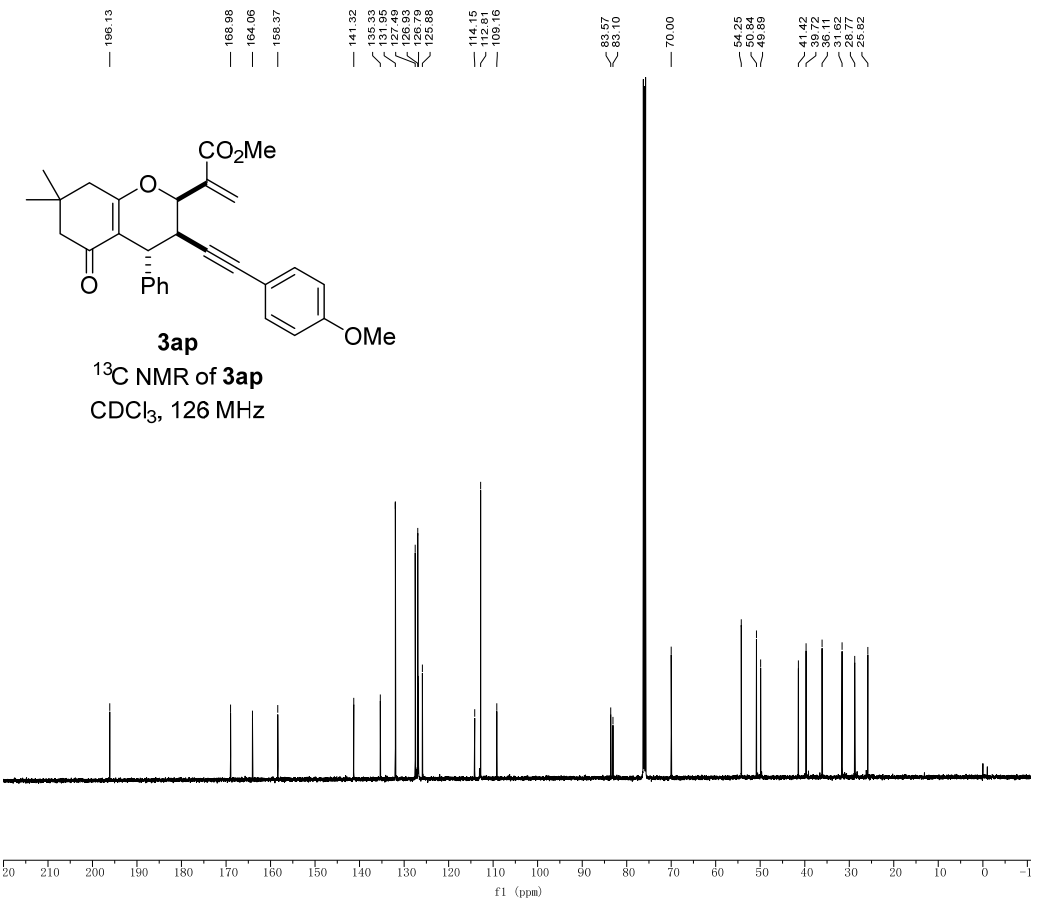
$CDCl_3$, 126 MHz



3ap

^{1}H NMR of **3ap**

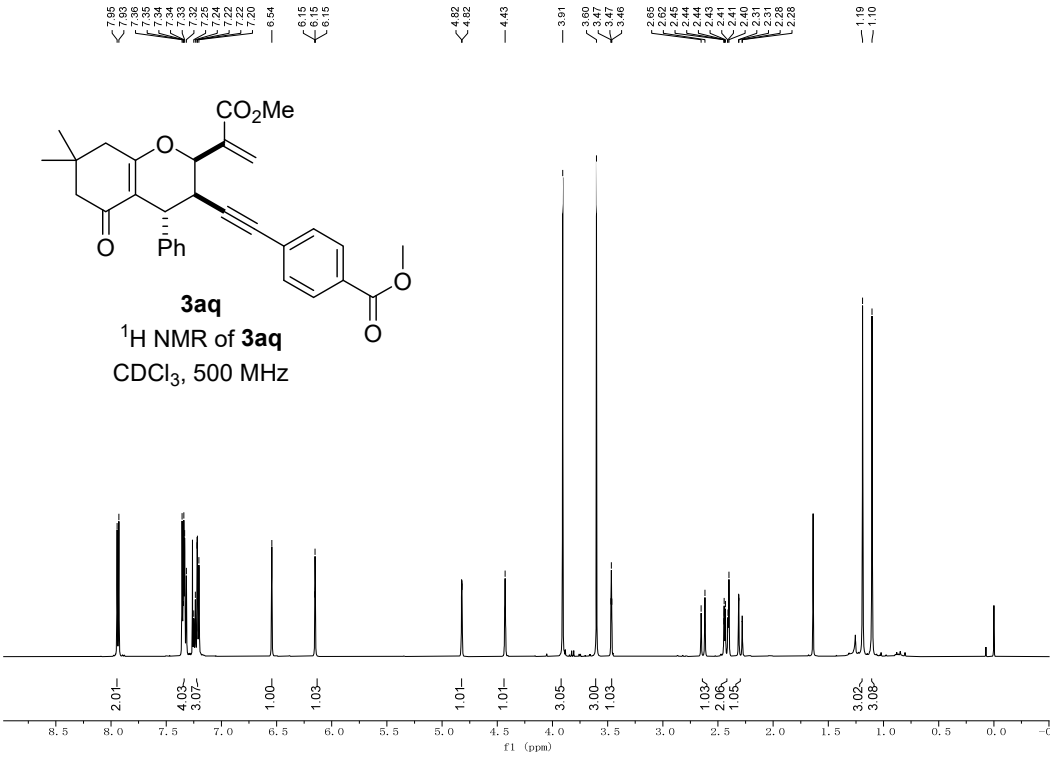
$CDCl_3$, 500 MHz



3ap

^{13}C NMR of **3ap**

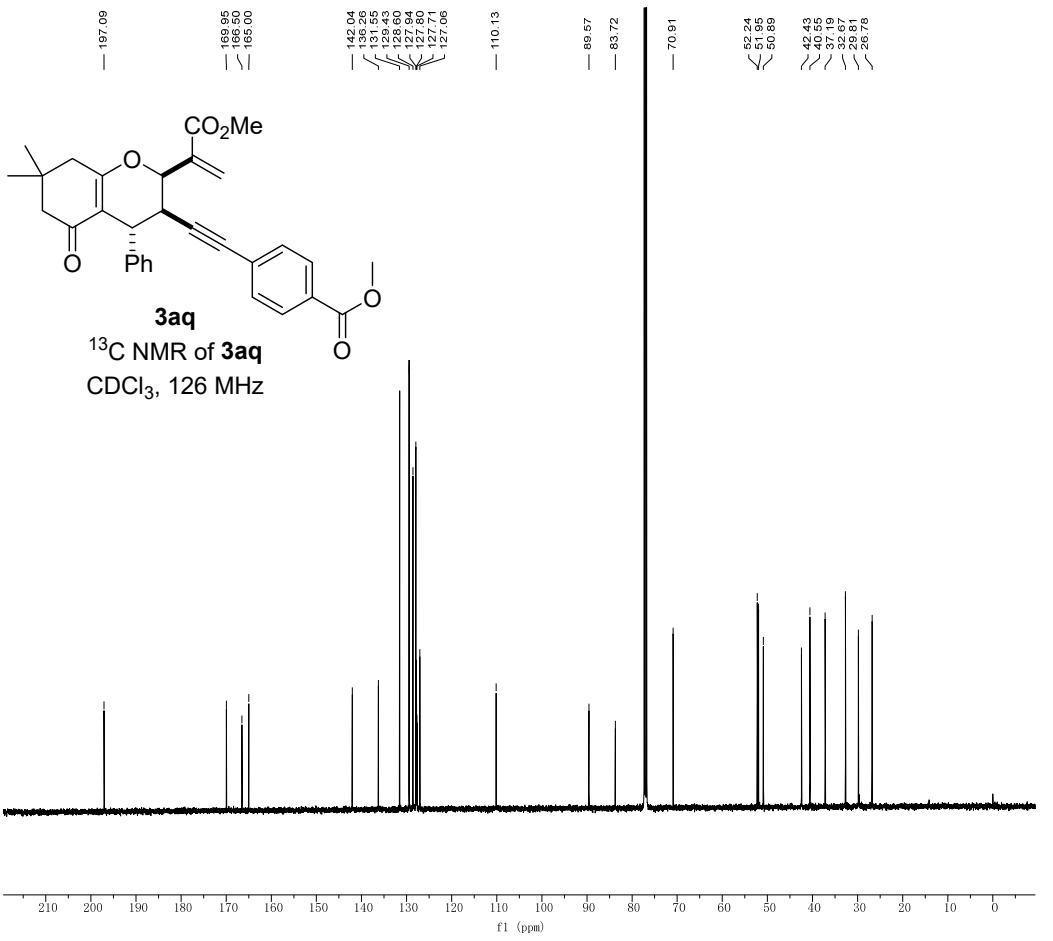
$CDCl_3$, 126 MHz



3aq

^{1}H NMR of **3aq**

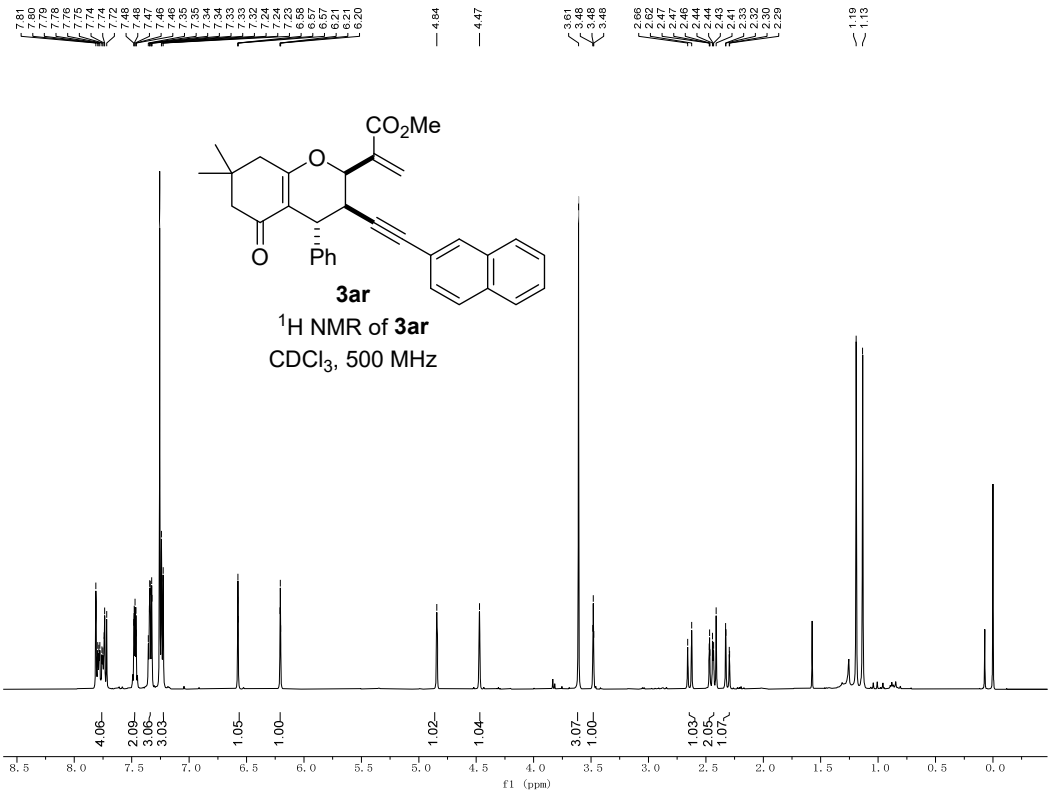
$CDCl_3$, 500 MHz

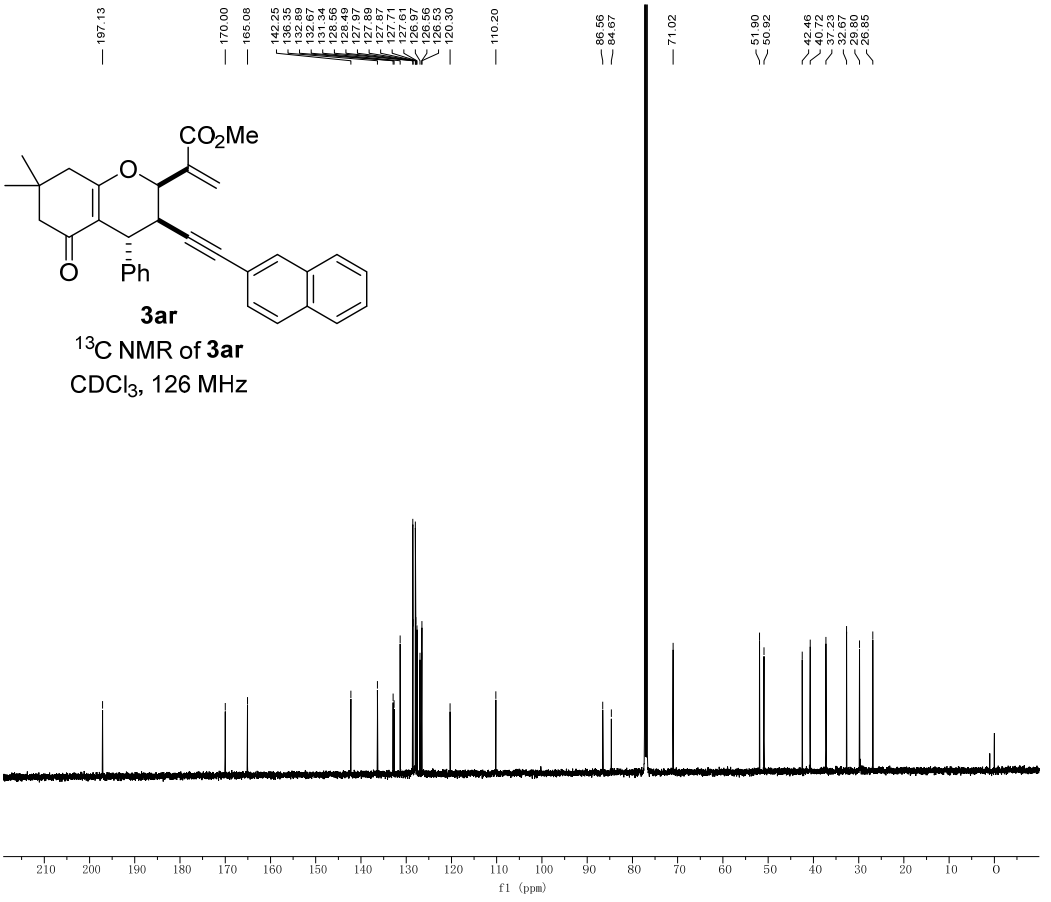


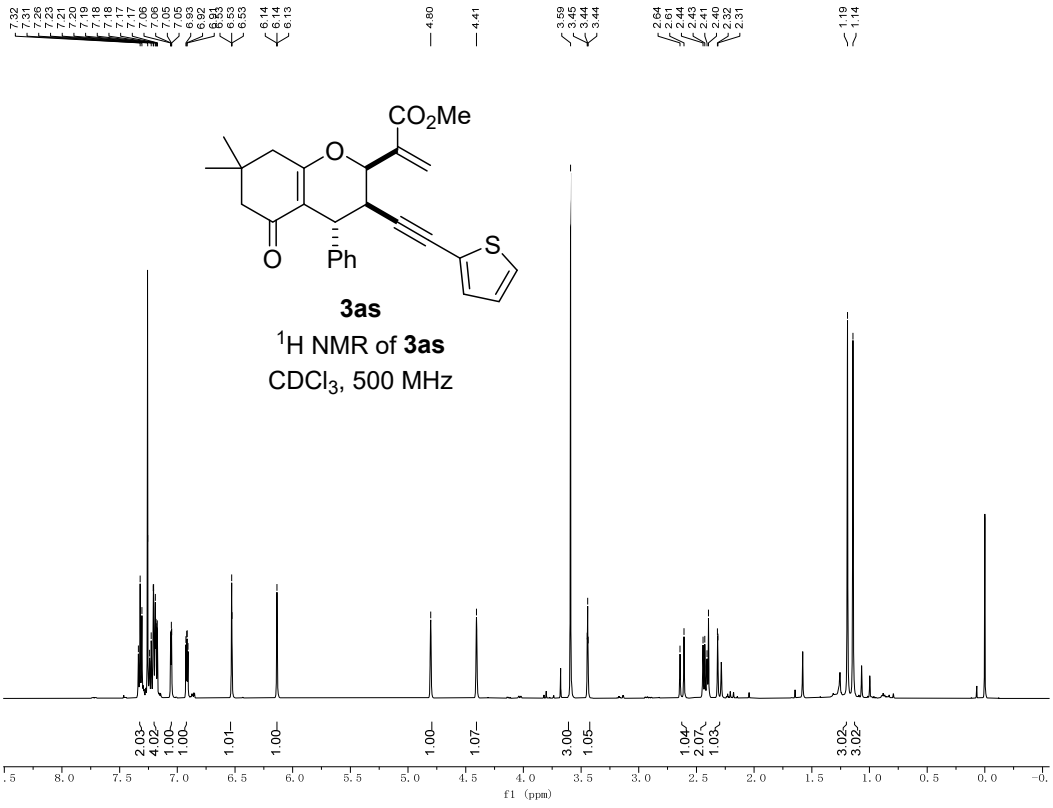
3aq

^{13}C NMR of **3aq**

$CDCl_3$, 126 MHz


7.81
7.80
7.79
7.78
7.76
7.75
7.74
7.74
7.72
7.48
7.48
7.47
7.47
7.46
7.46
7.45
7.35
7.34
7.34
7.33
7.33
7.32
7.24
7.24
7.23
6.58
6.57
6.57
6.21
6.21
6.20
4.84
4.47
3.61
3.48
3.48
3.46
2.66
2.62
2.47
2.47
2.46
2.44
2.44
2.43
2.41
2.33
2.32
2.30
2.29
1.19
1.13
CO2Me
O
O
Ph
3ar
1H NMR of 3ar
CDCl3, 500 MHz
4.06
2.09
3.06
3.03
1.05
1.00
1.02
1.04
3.07
1.00
1.03
2.05
1.07
f1 (ppm)

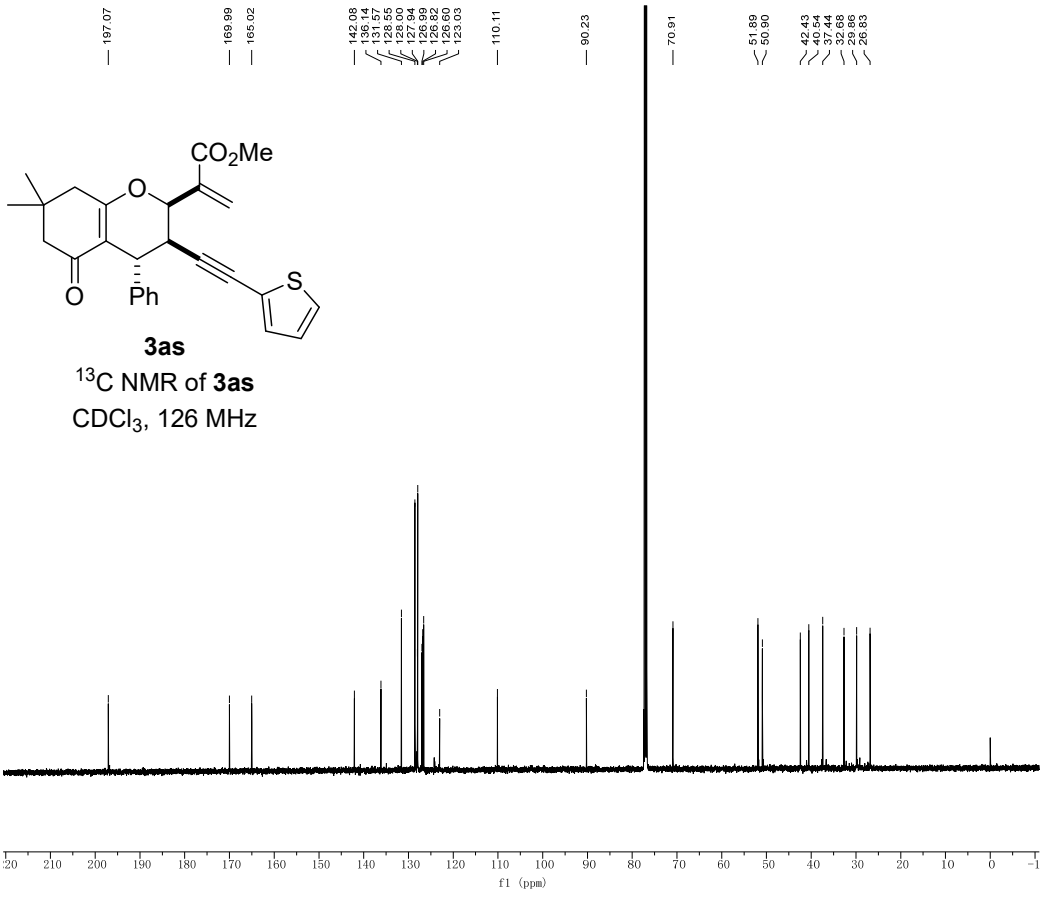

197.13
170.00
165.08
142.25
136.35
132.89
132.67
131.94
128.56
128.49
127.97
127.89
127.77
127.71
127.61
126.97
126.56
126.53
120.30
110.20
86.56
84.67
71.02
51.90
50.92
42.46
40.72
37.23
33.67
28.80
28.85
CO2Me
O
O
Ph
3ar
13C NMR of 3ar
CDCl3, 126 MHz
f1 (ppm)



3as

^{1}H NMR of **3as**

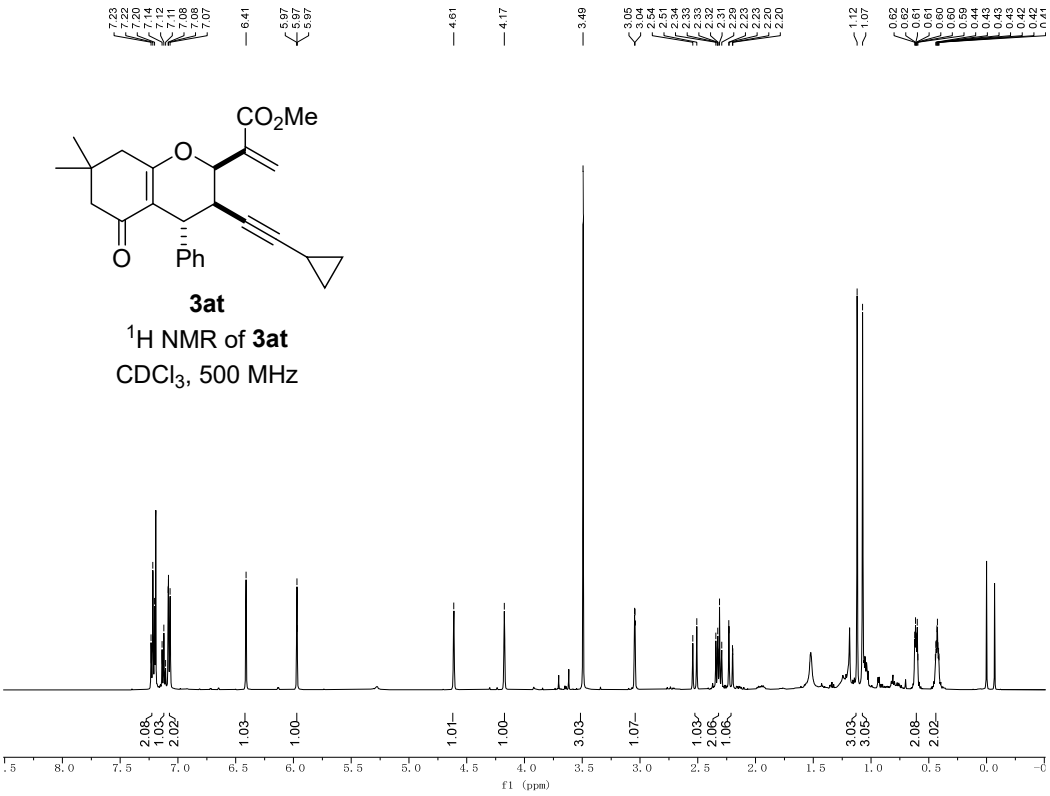
$CDCl_3$, 500 MHz



3as

^{13}C NMR of **3as**

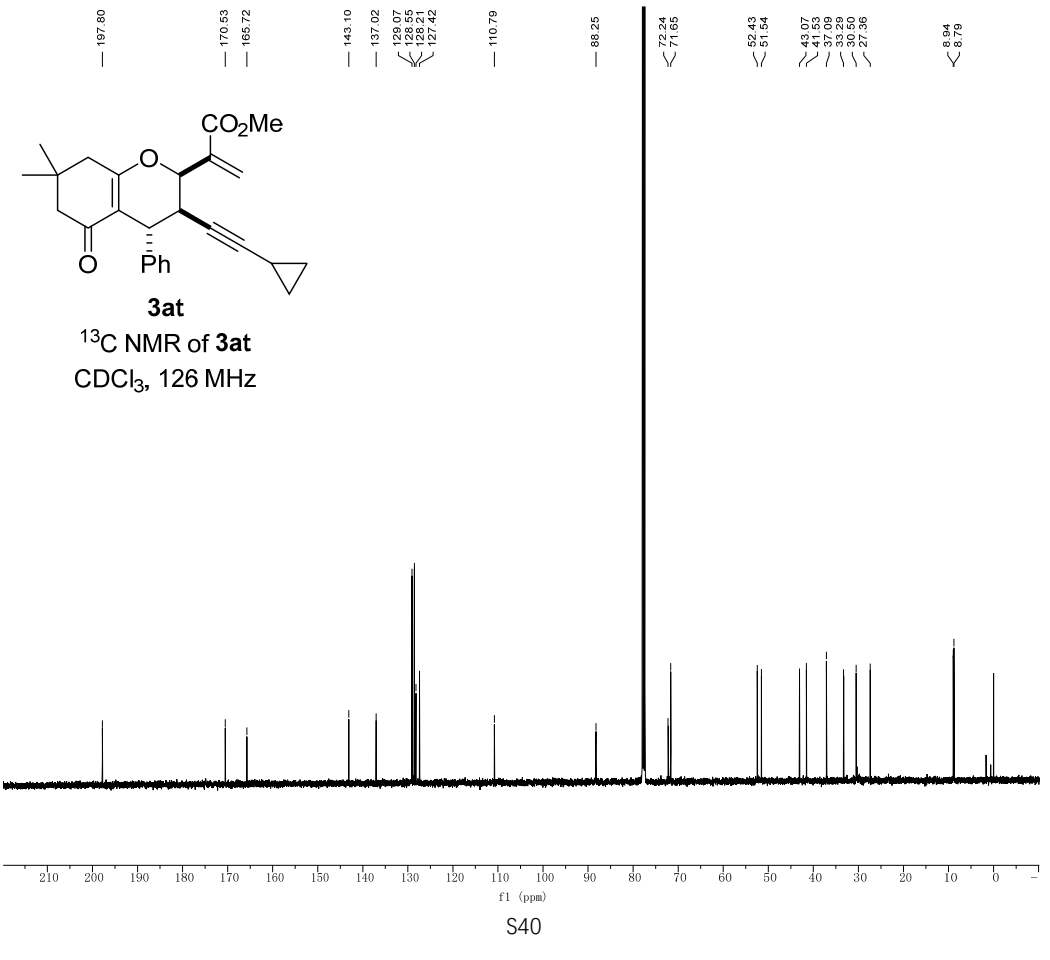
$CDCl_3$, 126 MHz



3at

^{1}H NMR of **3at**

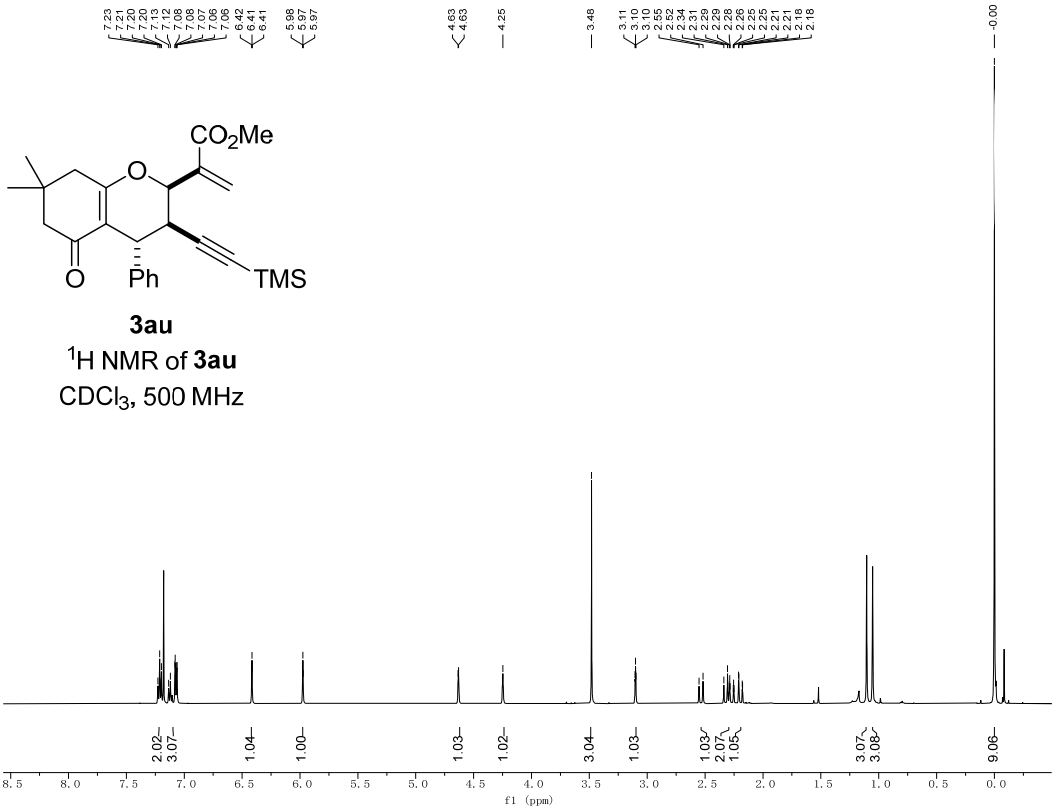
$CDCl_3$, 500 MHz



3at

^{13}C NMR of **3at**

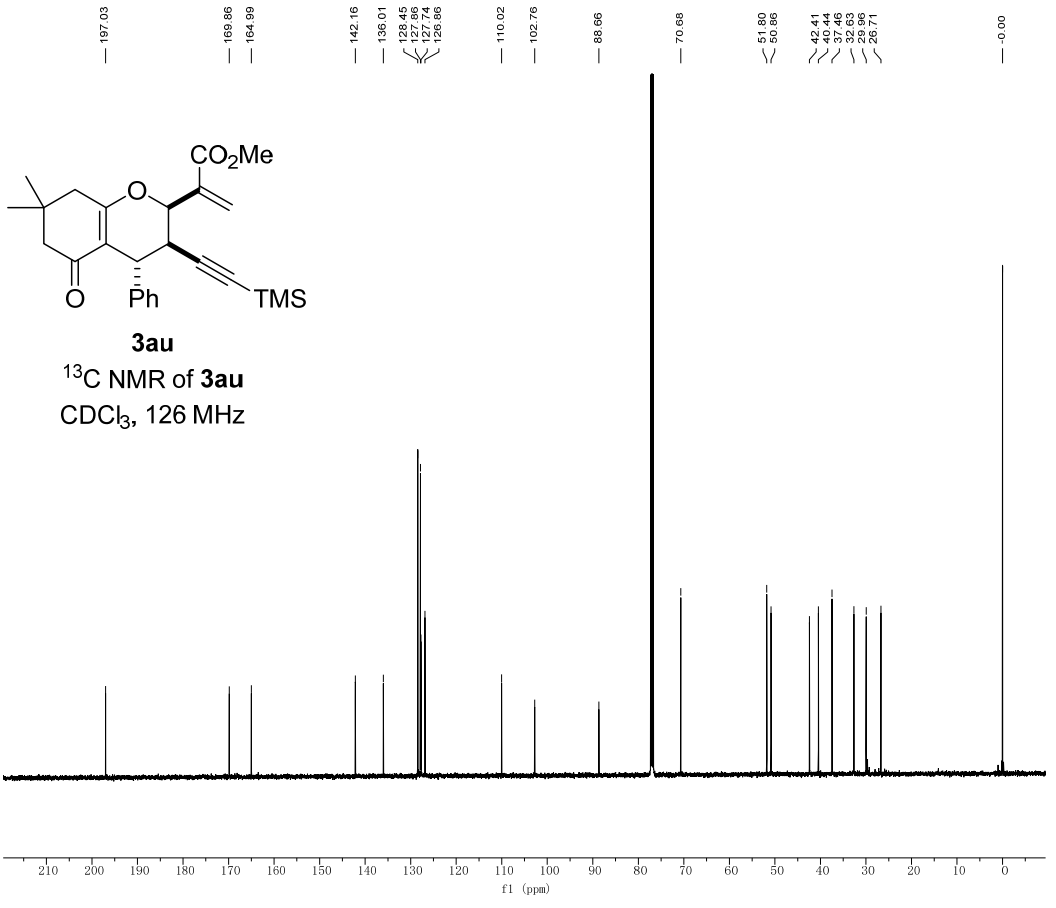
$CDCl_3$, 126 MHz



3au

^{1}H NMR of **3au**

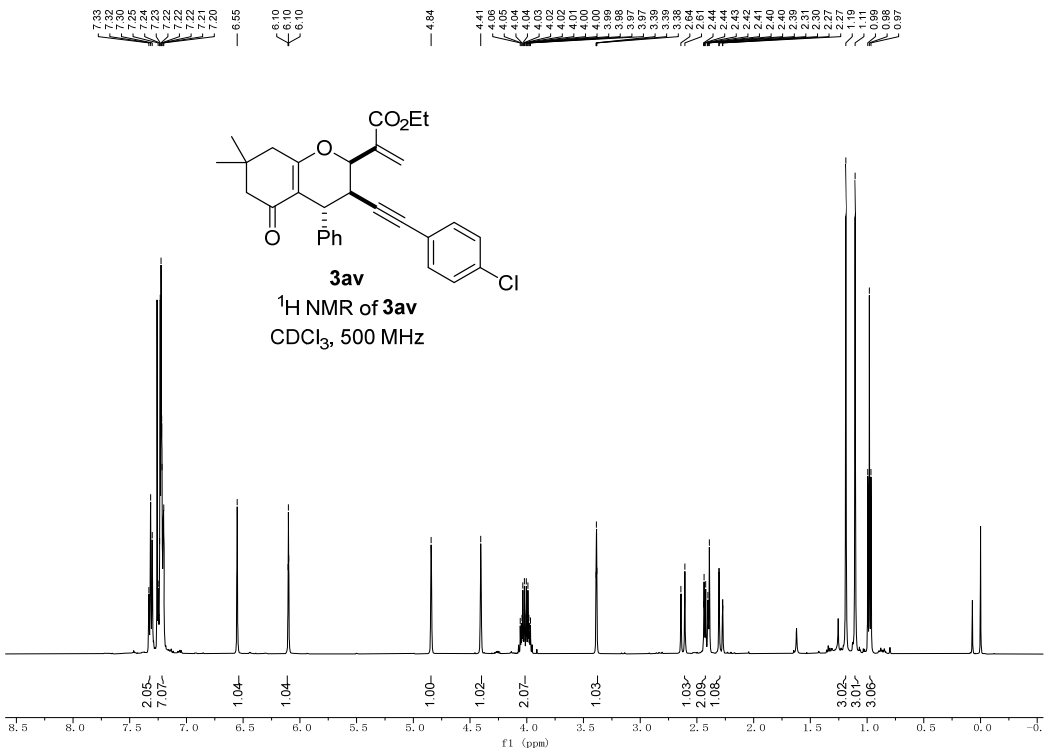
$CDCl_3$, 500 MHz

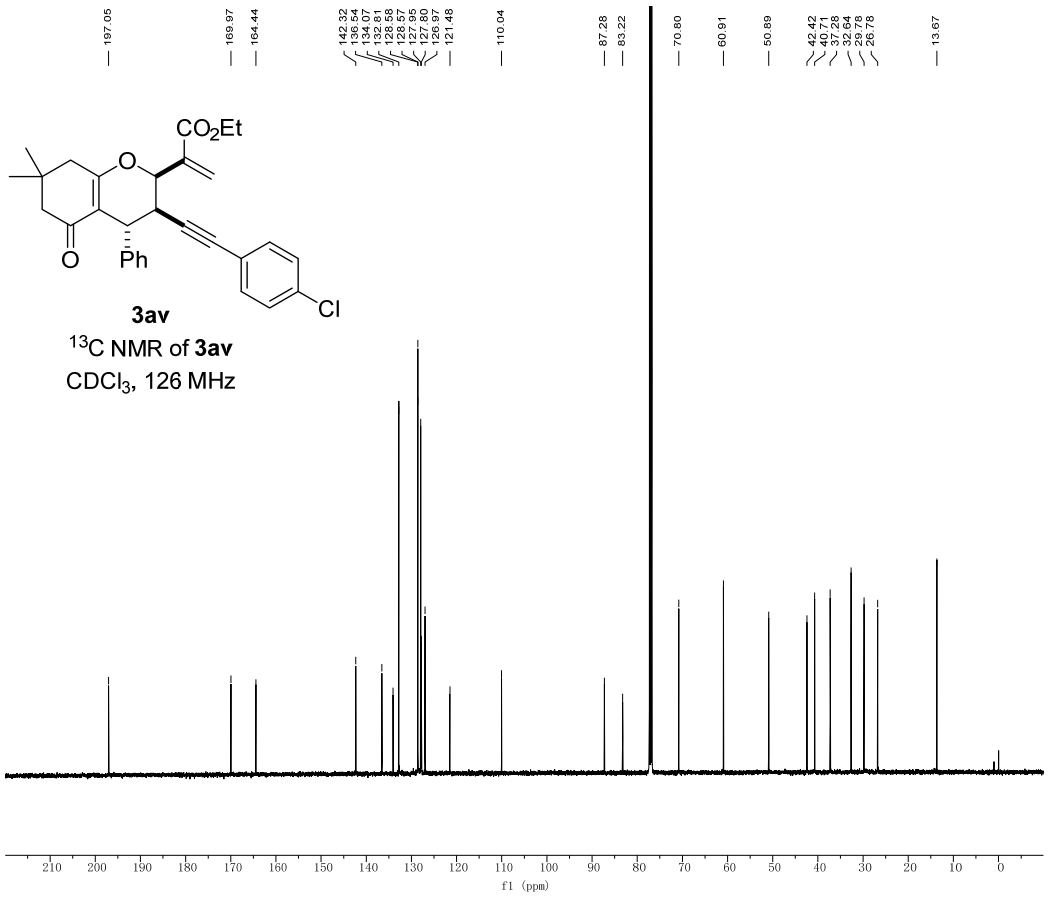


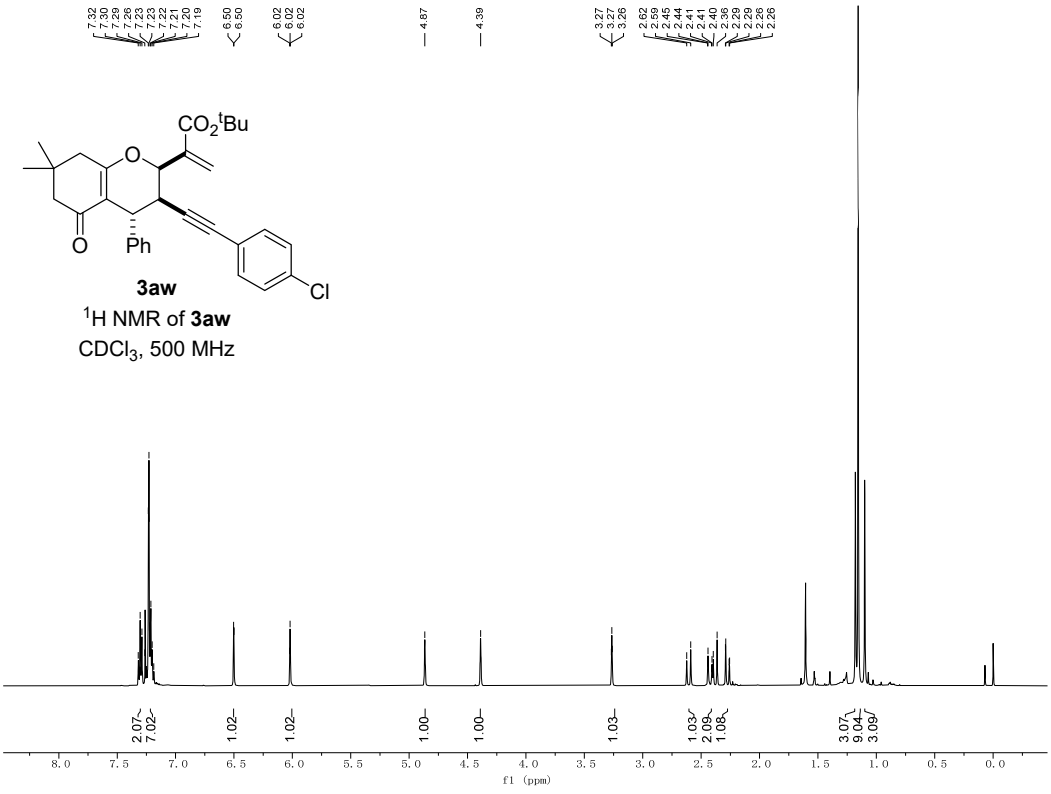
3au

^{13}C NMR of **3au**

$CDCl_3$, 126 MHz


CO2Et
O
O
Ph
Cl
3av
1H NMR of 3av
CDCl3, 500 MHz
f1 (ppm)

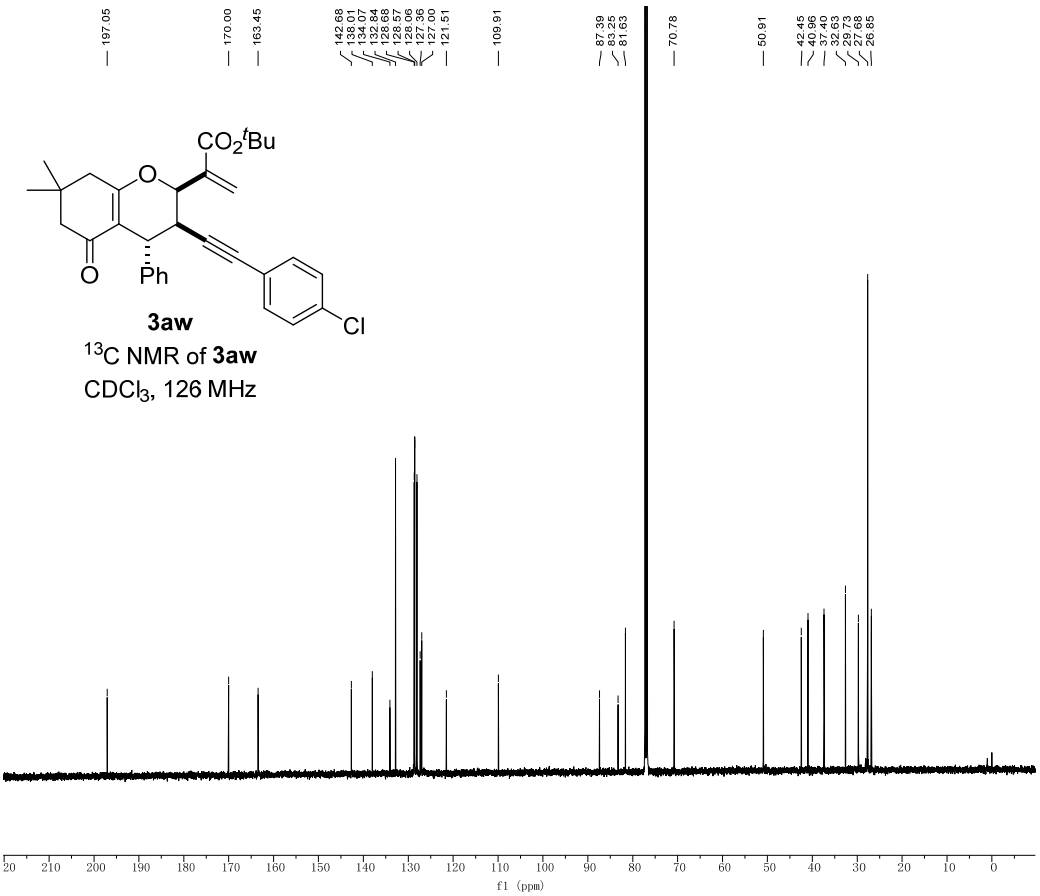

CO2Et
O
O
Ph
Cl
3av
13C NMR of 3av
CDCl3, 126 MHz
f1 (ppm)



3aw

^{1}H NMR of **3aw**

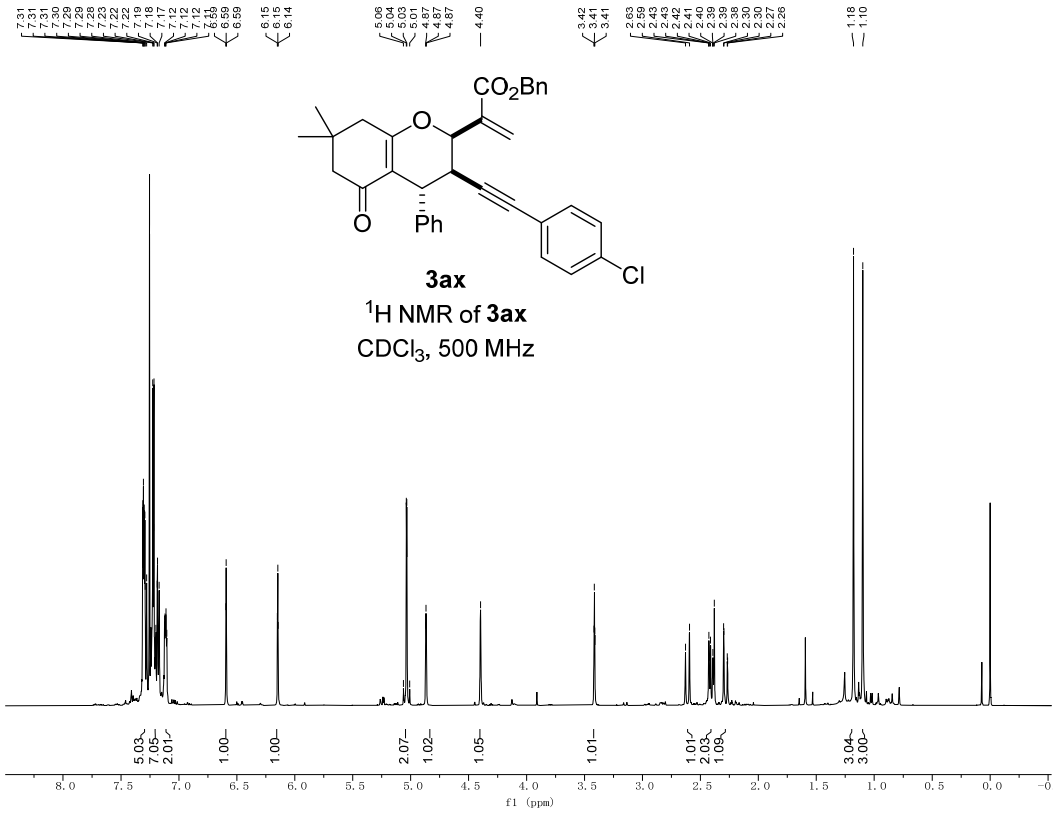
$CDCl_3$, 500 MHz

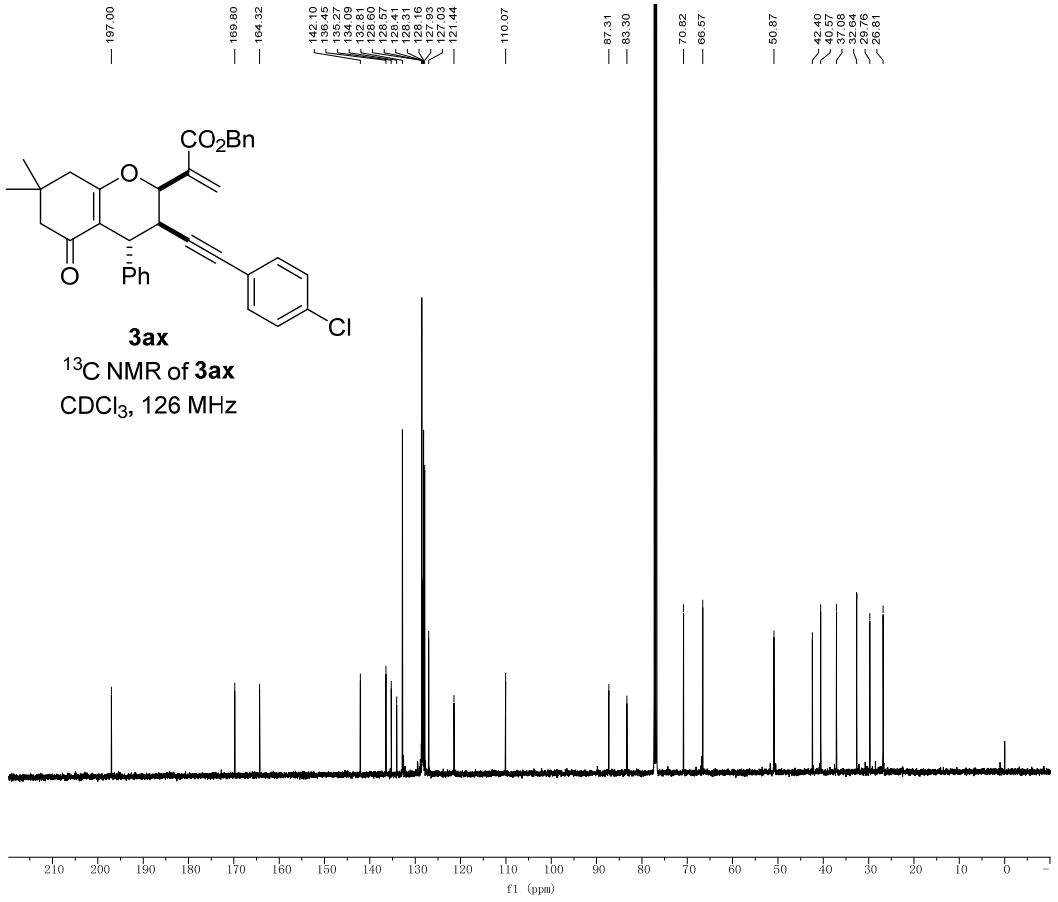


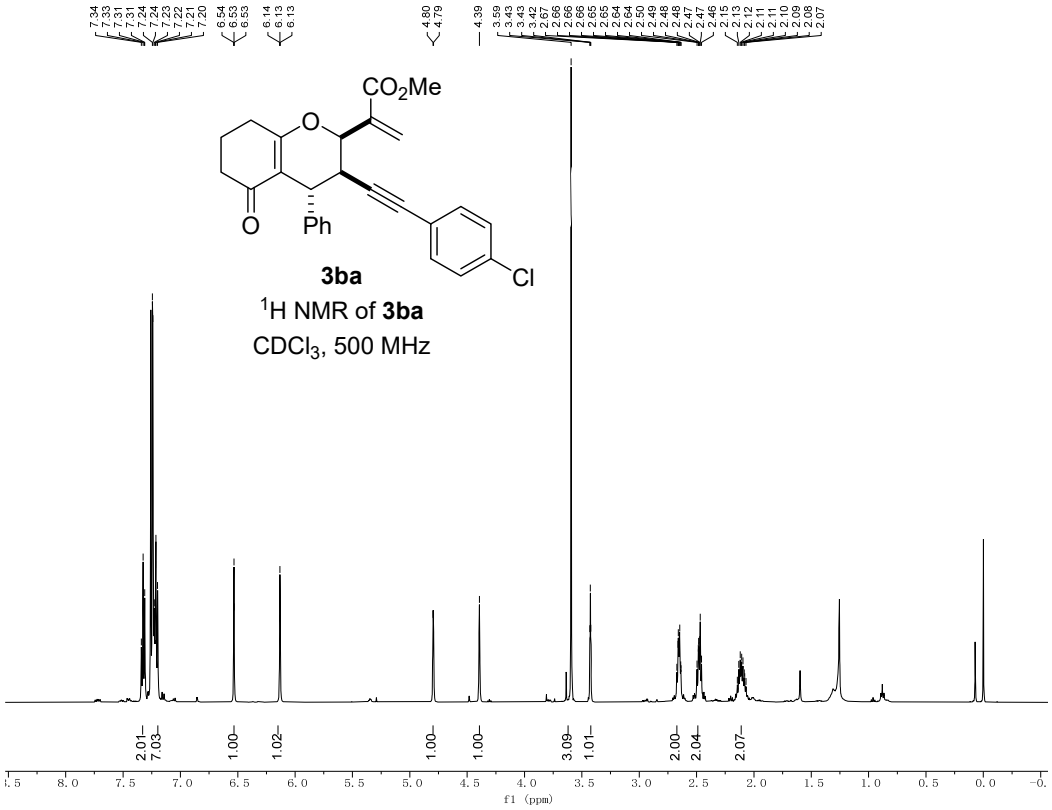
3aw

^{13}C NMR of **3aw**

$CDCl_3$, 126 MHz


CO2Bn
O
O
Ph
Cl
3ax
1H NMR of 3ax
CDCl3, 500 MHz
f1 (ppm)

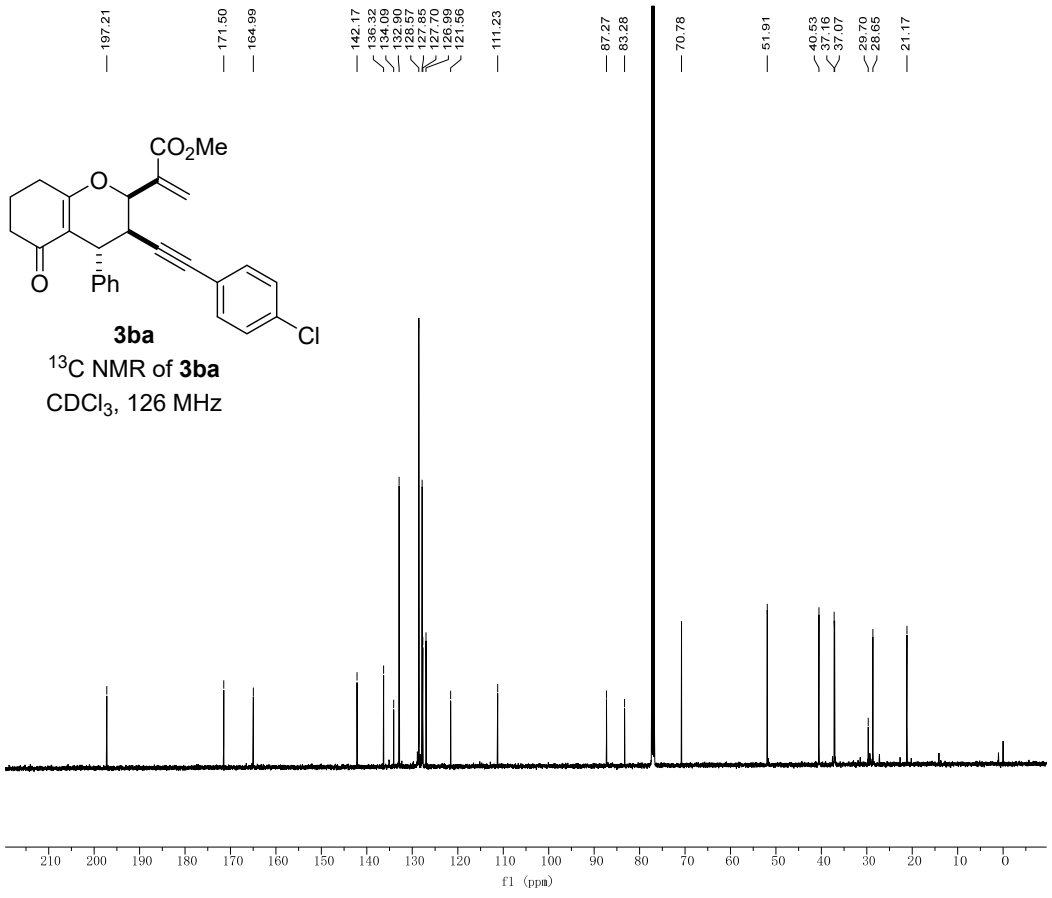

CO2Bn
O
O
Ph
Cl
3ax
13C NMR of 3ax
CDCl3, 126 MHz
f1 (ppm)



3ba

^{1}H NMR of **3ba**

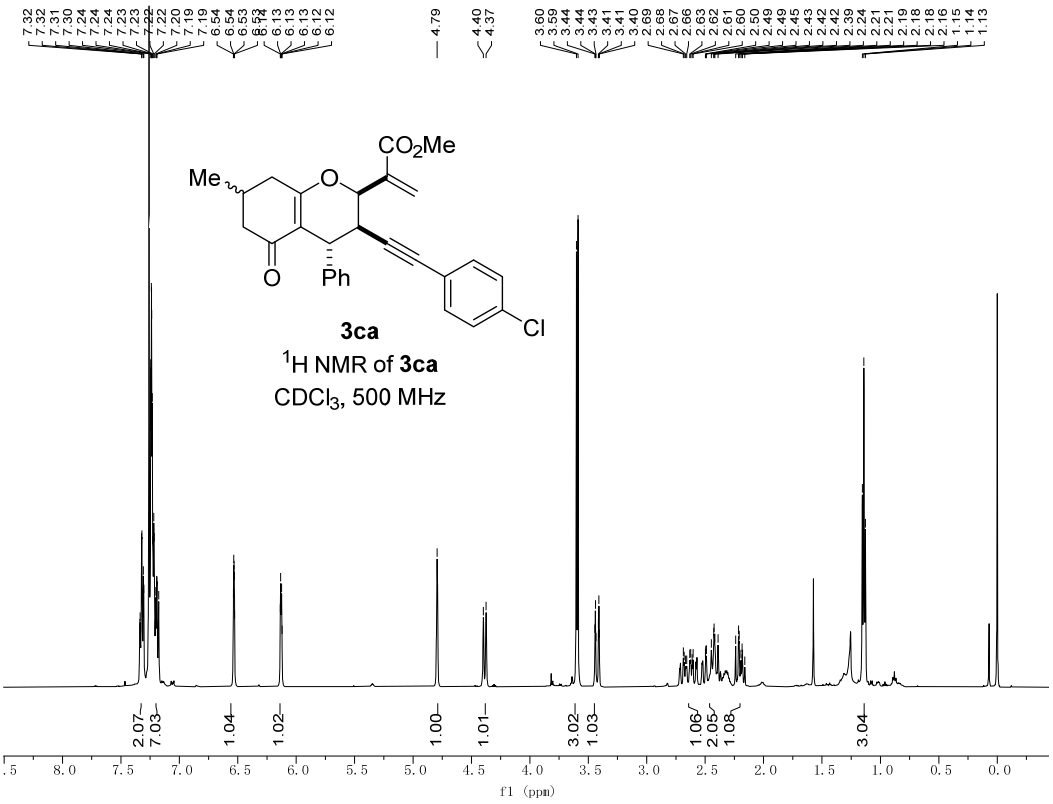
$CDCl_3$, 500 MHz



3ba

^{13}C NMR of **3ba**

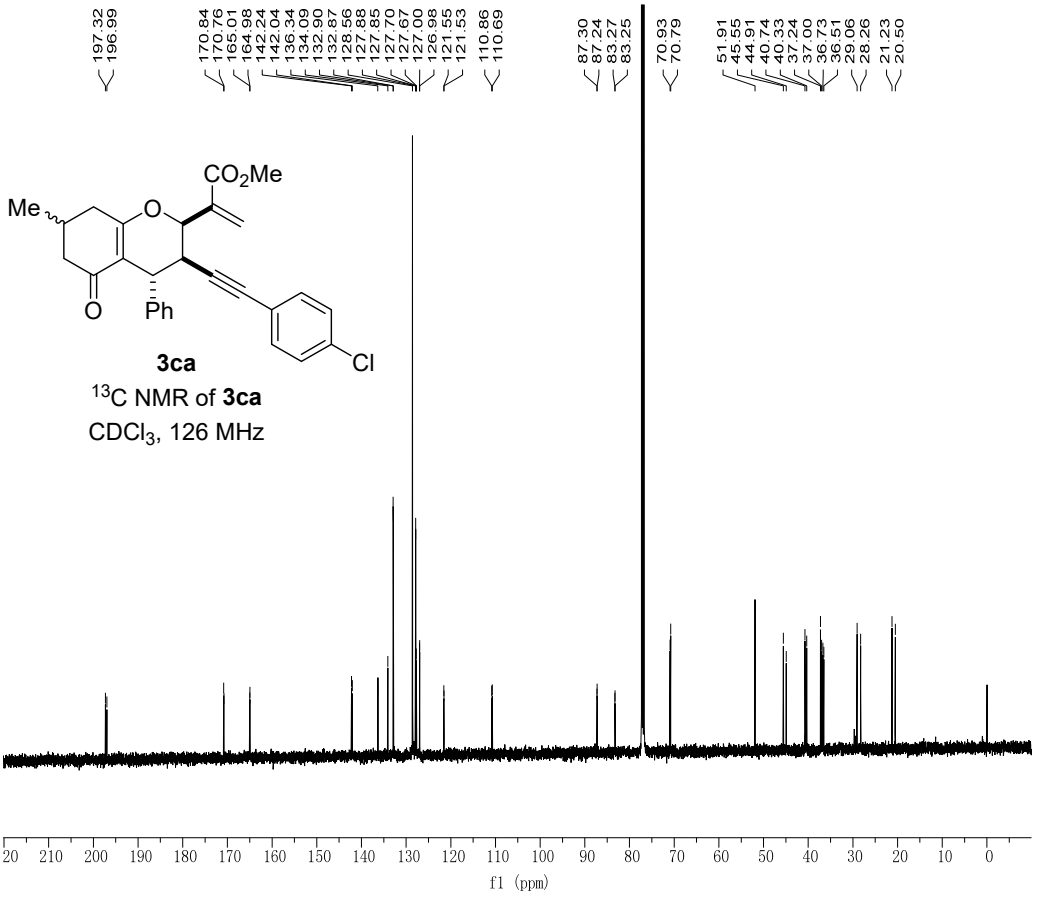
$CDCl_3$, 126 MHz



3ca

^{1}H NMR of **3ca**

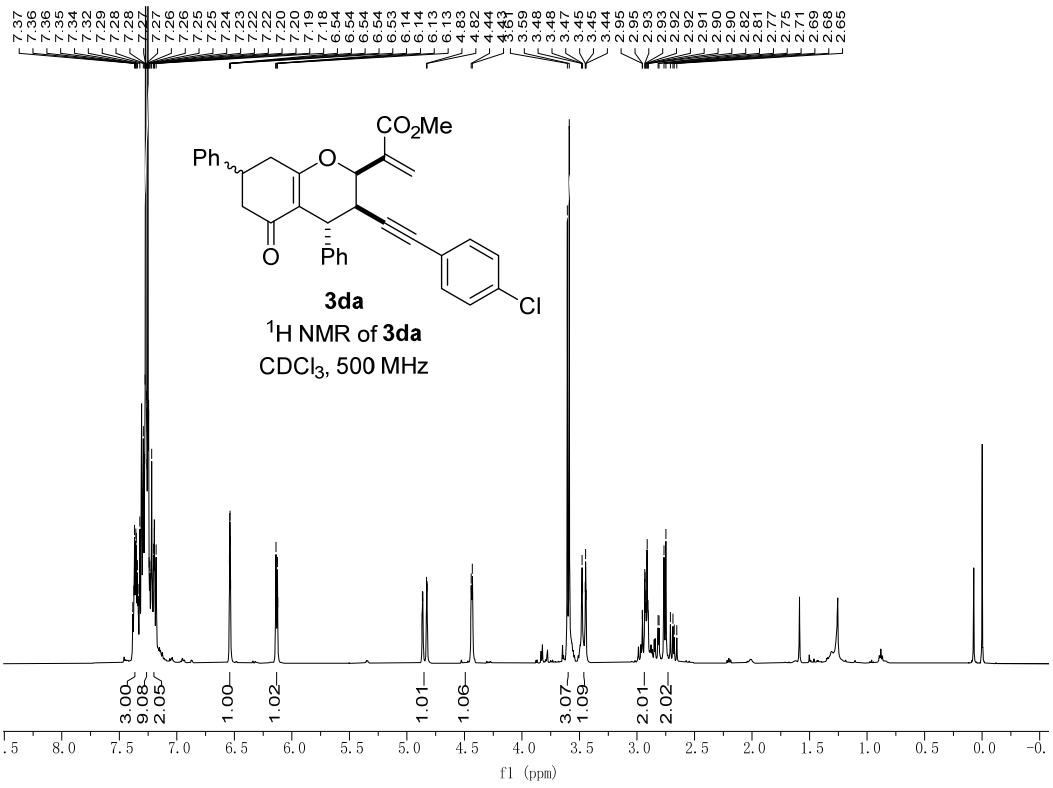
$CDCl_3$, 500 MHz

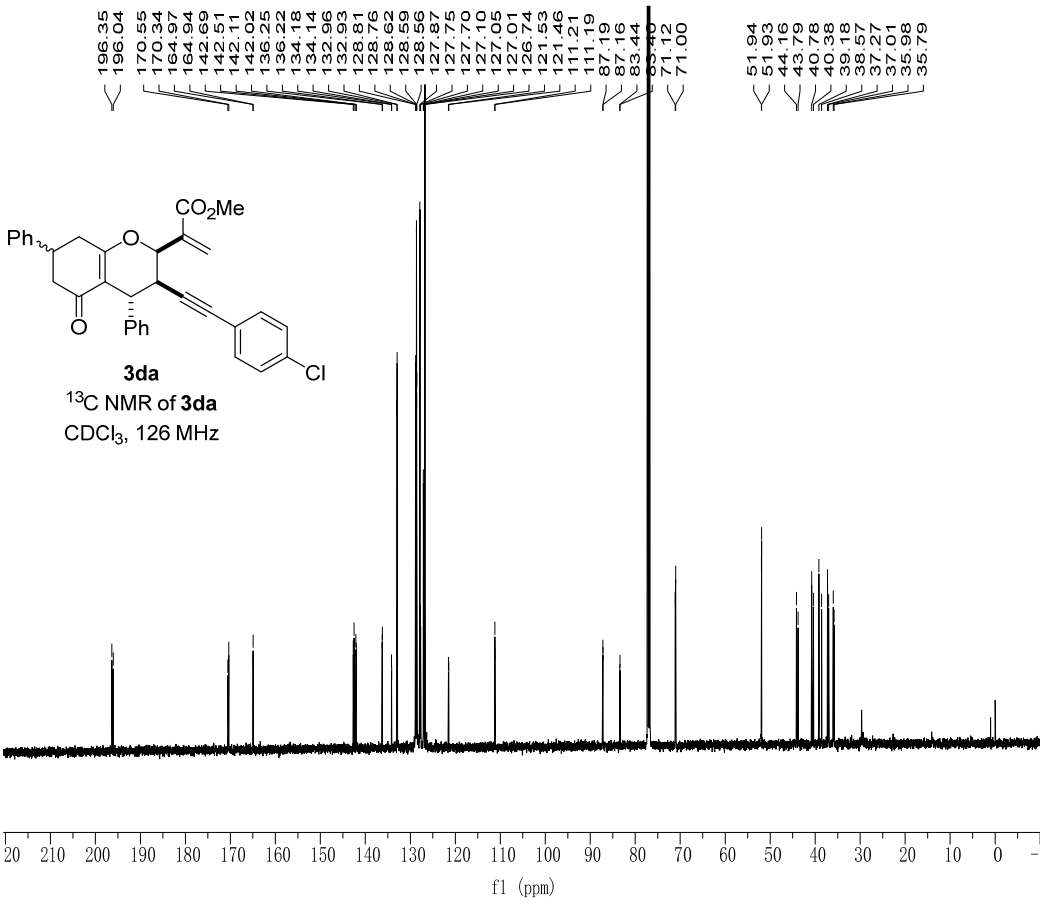


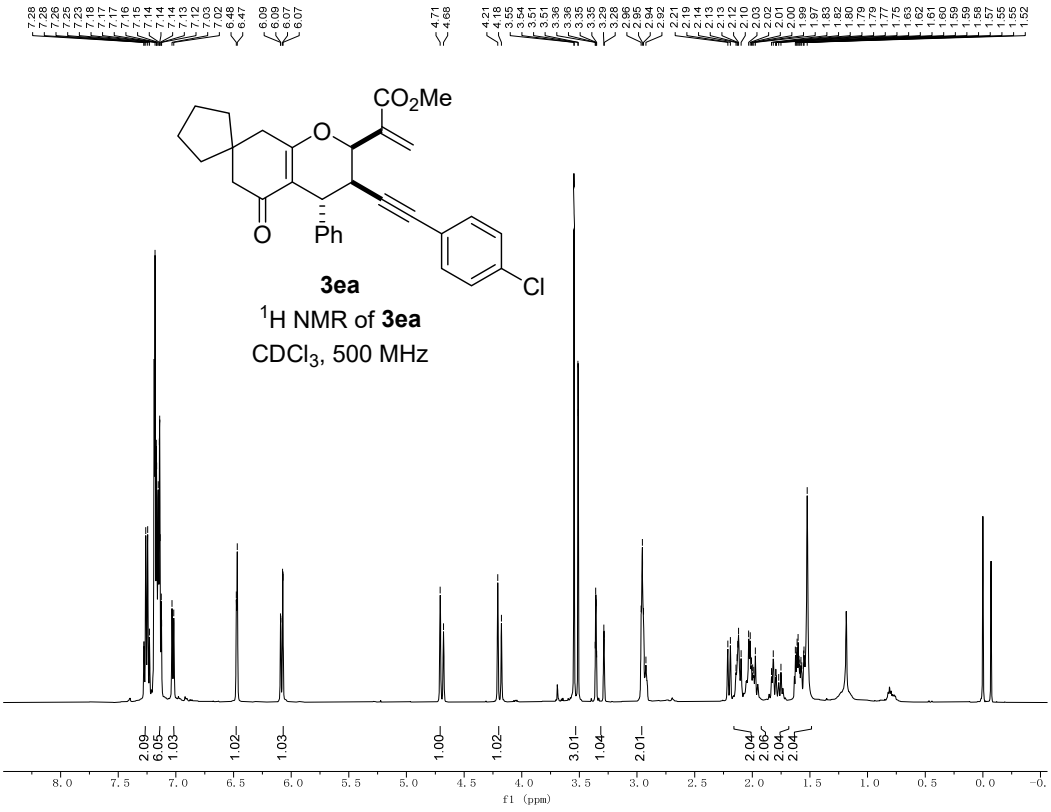
3ca

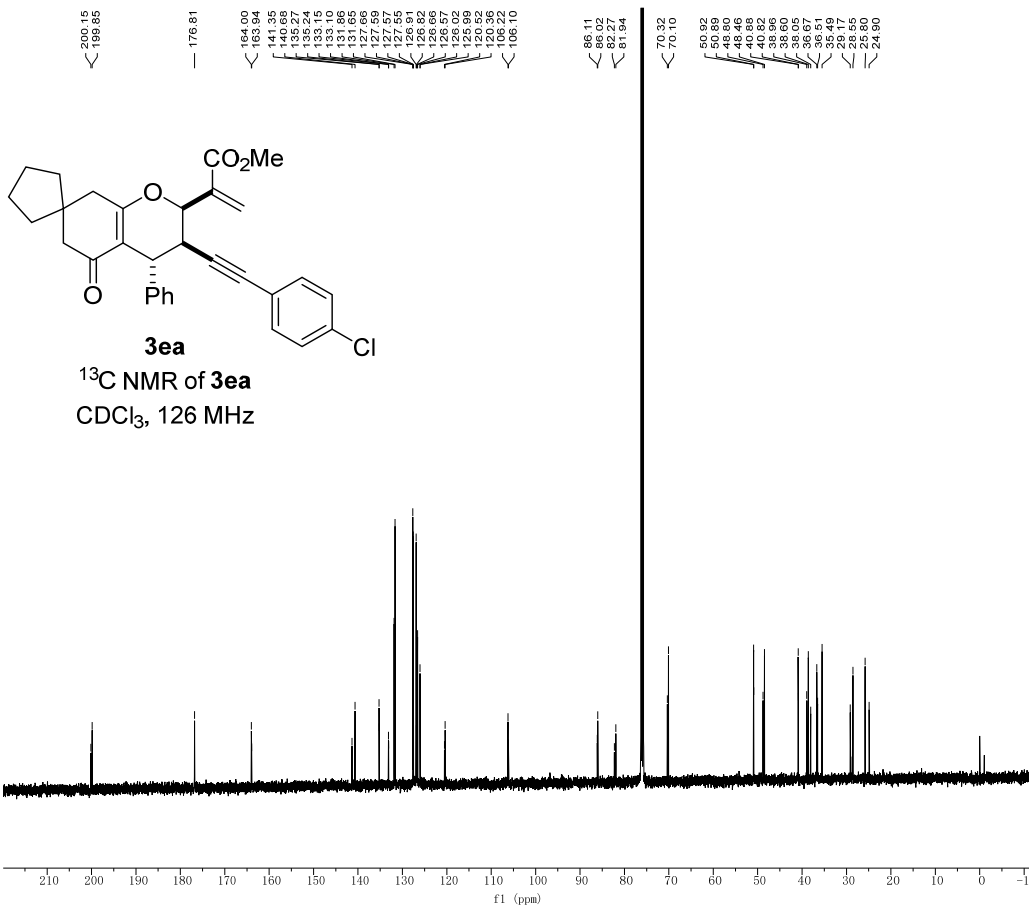
^{13}C NMR of **3ca**

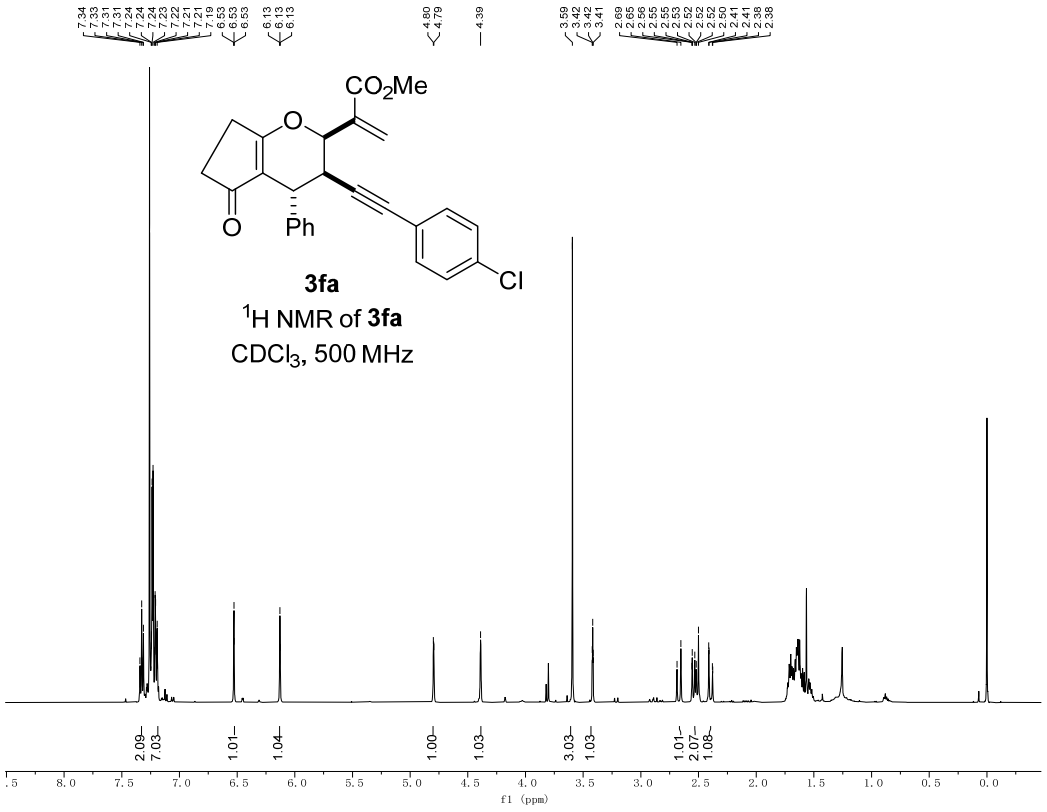
$CDCl_3$, 126 MHz

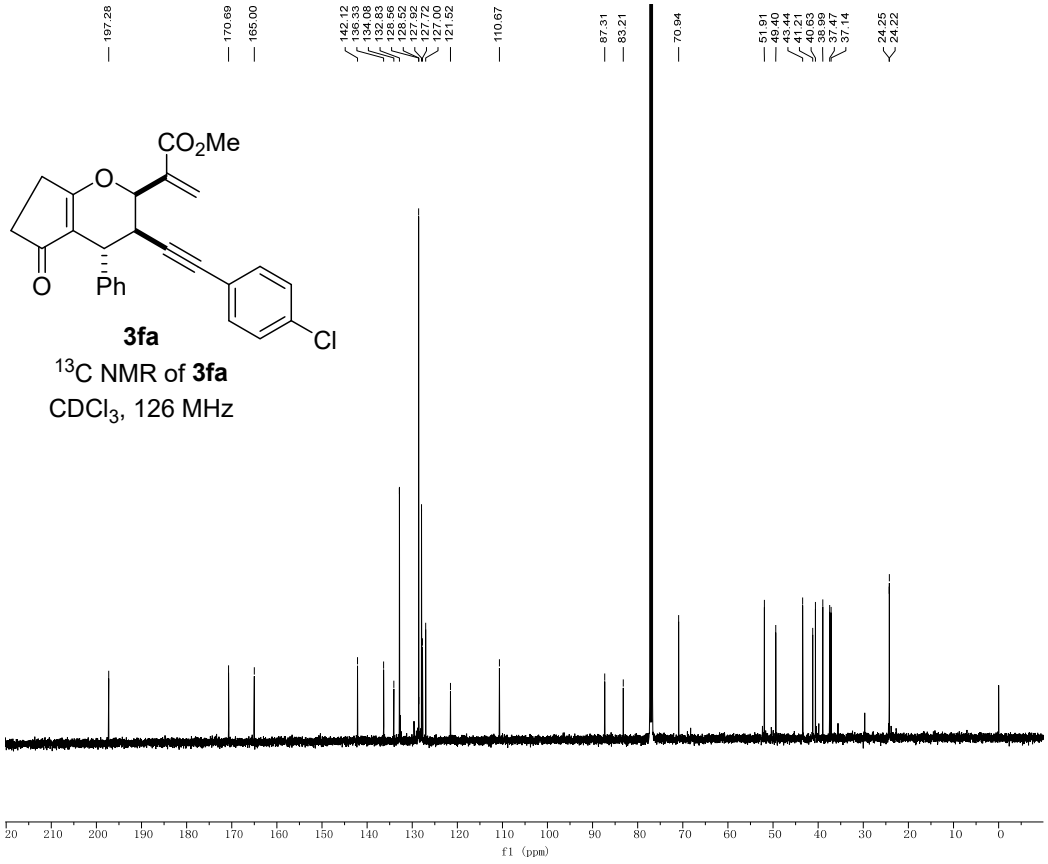

7.37 7.36 7.36 7.35 7.34 7.32 7.29 7.28 7.28 7.27 7.27 7.26 7.26 7.25 7.24 7.23 7.22 7.20 7.20 7.19 7.18 6.54 6.54 6.54 6.54 6.53 6.14 6.13 6.13 4.83 4.82 4.44 4.43 4.41 3.59 3.48 3.48 3.47 3.45 3.45 3.44 2.95 2.93 2.93 2.92 2.92 2.91 2.90 2.90 2.82 2.81 2.77 2.75 2.71 2.69 2.68 2.65
CO2Me
Ph
O
O
Ph
Cl
3da
1H NMR of 3da
CDCl3, 500 MHz
3.00 9.08 2.05 1.00 1.02 1.01 1.06 3.07 1.09 2.01 2.02
f1 (ppm)

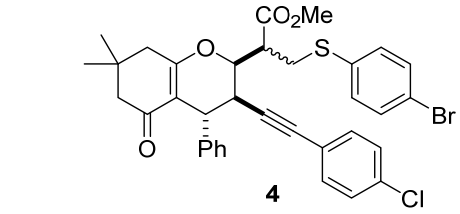

196.35 196.04 170.55 170.34 164.97 164.94 142.69 142.51 142.11 142.02 136.25 136.22 134.18 134.14 132.96 132.93 128.81 128.76 128.62 128.59 128.56 127.87 127.75 127.70 127.10 127.05 127.01 126.74 121.53 121.46 111.21 111.19 87.19 87.16 83.44 83.40 71.12 71.00 51.94 51.93 44.16 43.79 40.78 40.38 39.18 38.57 37.27 37.01 35.98 35.79
CO2Me
Ph
O
O
Ph
Cl
3da
13C NMR of 3da
CDCl3, 126 MHz
f1 (ppm)


CO2Me
O
O
Ph
Cl
3ea
1H NMR of 3ea
CDCl3, 500 MHz
f1 (ppm)


CO2Me
O
O
Ph
Cl
3ea
13C NMR of 3ea
CDCl3, 126 MHz
f1 (ppm)


CO2Me
O
O
Ph
Cl
3fa
1H NMR of 3fa
CDCl3, 500 MHz
f1 (ppm)

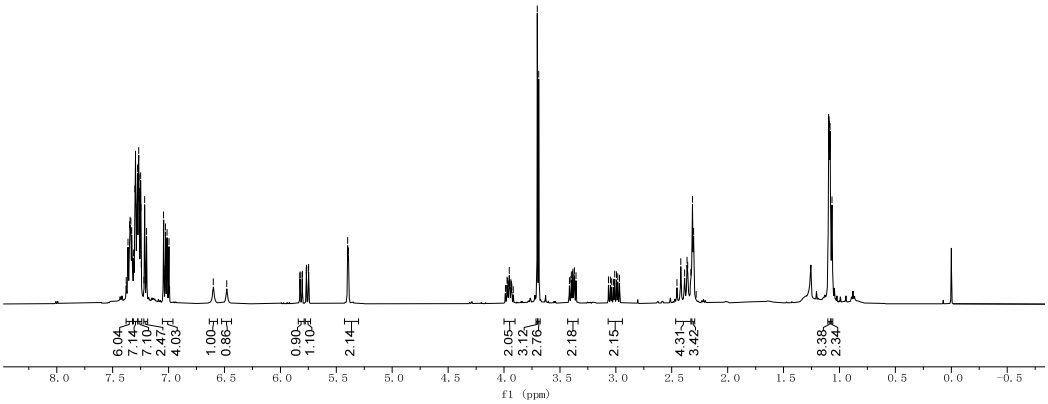

CO2Me
O
O
Ph
Cl
3fa
13C NMR of 3fa
CDCl3, 126 MHz
f1 (ppm)

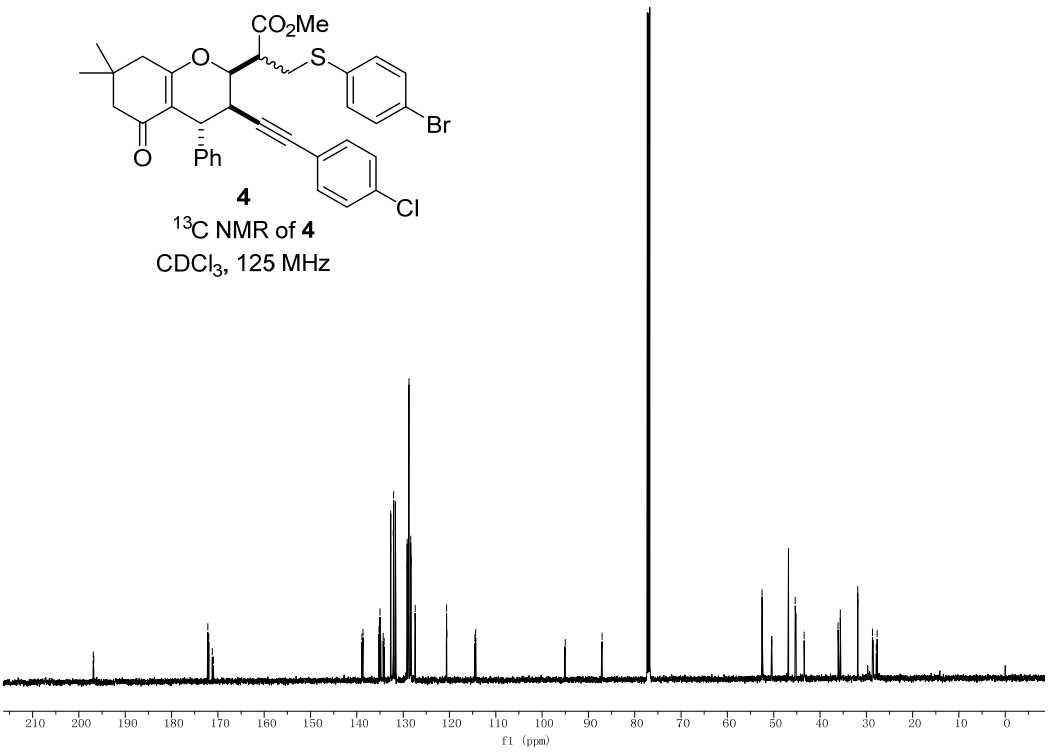


4

^{1}H NMR of **4**

$CDCl_3$, 500 MHz

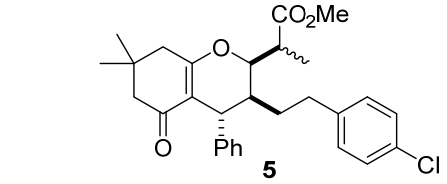




4

^{13}C NMR of **4**

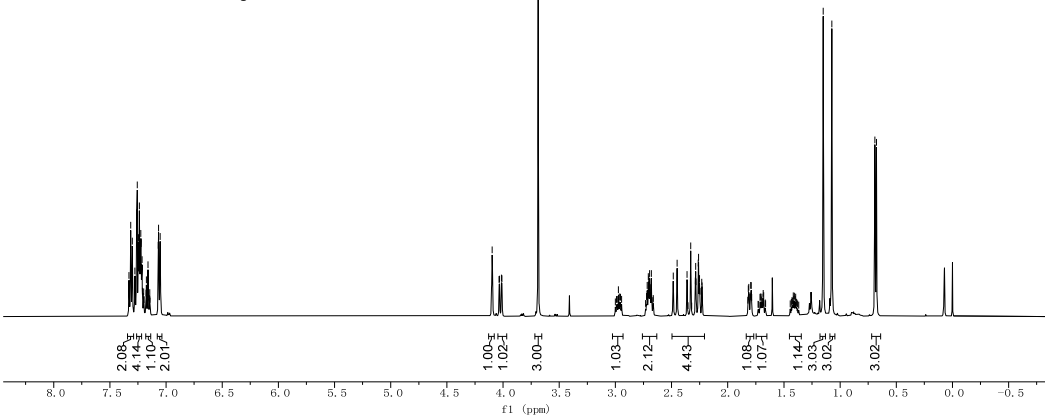
$CDCl_3$, 125 MHz

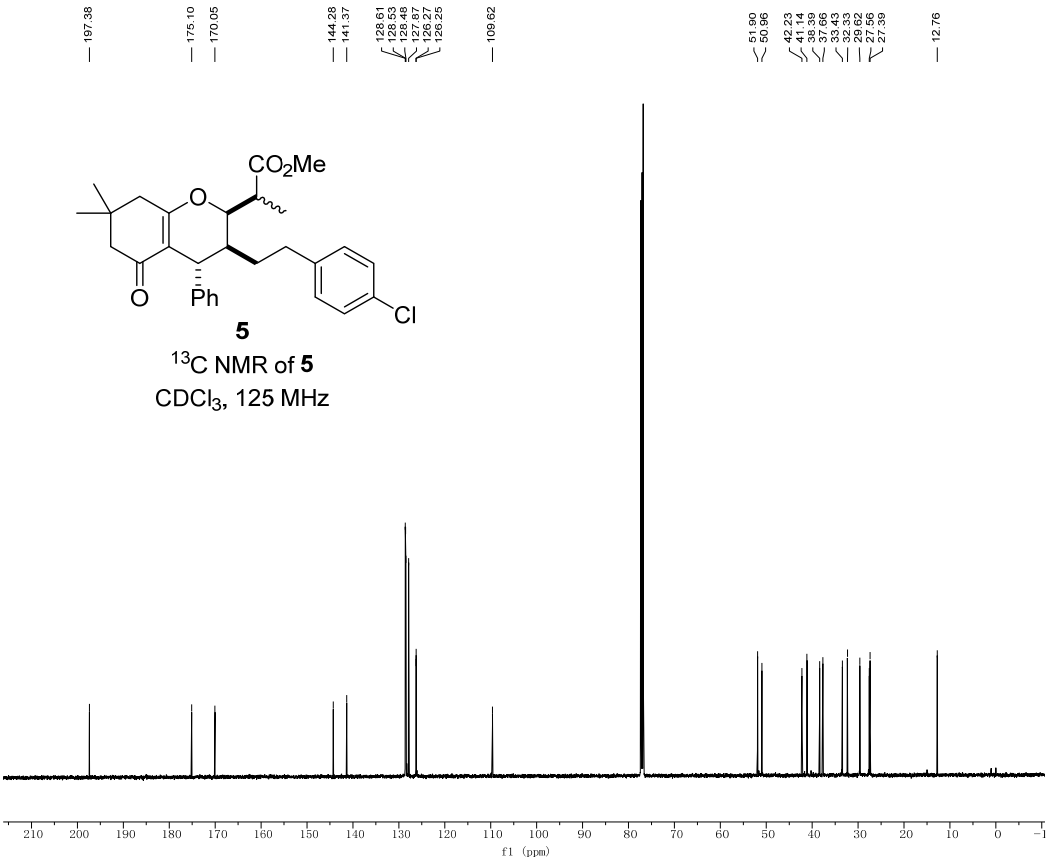


5

^{1}H NMR of **5**

$CDCl_3$, 500 MHz

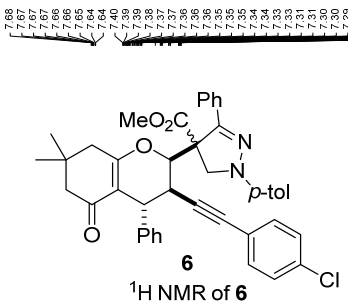




5

^{13}C NMR of **5**

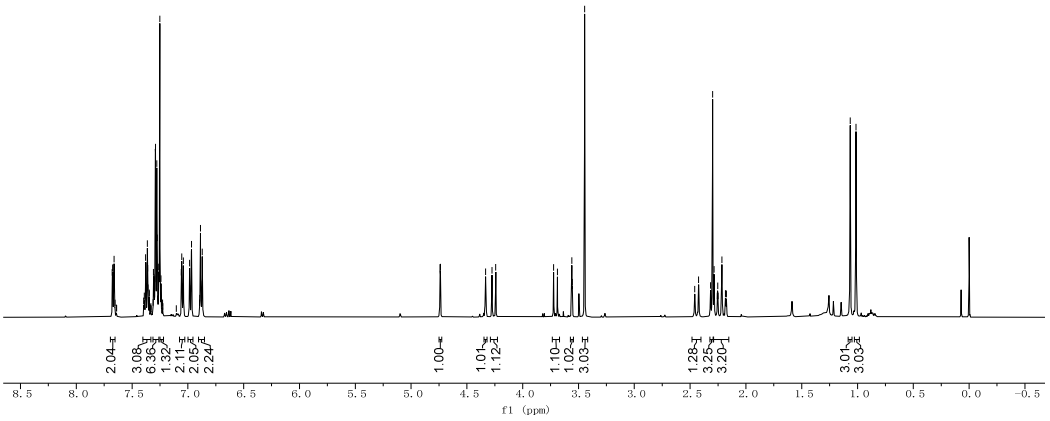
$CDCl_3$, 125 MHz

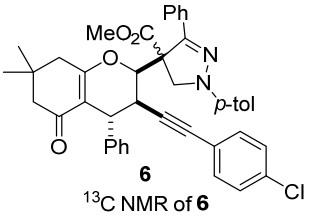


6

^{1}H NMR of **6**

$CDCl_3$, 500 MHz





6

^{13}C NMR of **6**

$CDCl_3$, 125 MHz

X-ray crystallographic data

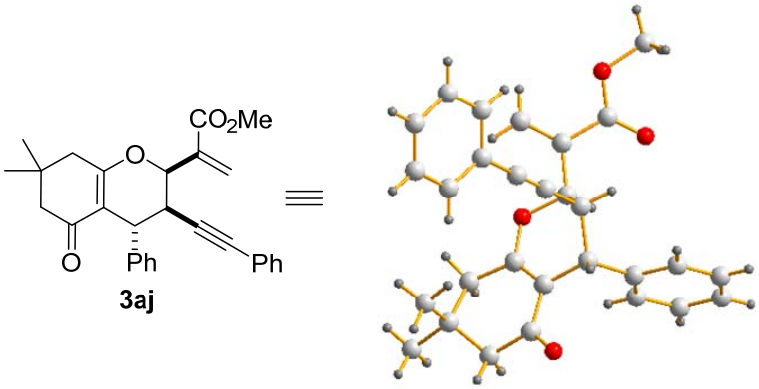


Table S1. Crystal Data and Structure Refinement for 3aj

Identification code	**3aj**
Empirical formula	$C_{29}H_{28}O_4$
Formula weight	440.51
Temperature/K	295(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	19.9766(15)
b/Å	15.8235(11)
c/Å	15.6346(12)
α/°	90
β/°	93.935(3)
γ/°	90
Volume/Å^3	4930.4(6)
Z	8
ρ_{calc}g/cm^3	1.187
μ/mm^{-1}	0.078
F(000)	1872
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.03 to 27.37
Index ranges	$-25 \le h \le 23$, $-20 \le k \le 20$, $-20 \le l \le 20$
Reflections collected	31095
Independent reflections	5661 [R_{int} = 0.0462, R_{sigma} = 0.0308
Data/restraints/parameters	5661/264/301
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0581 wR_2 = 0.1433
Final R indexes [all data]	R_1 = 0.0857 wR_2 = 0.1597