Supporting Information

Photosensitizer-Free, Harnessing Sunlight for Highly Efficient Consecutive [3+2]/[4+2] Annulation to Fused Benzobicyclic Skeletons

Nengneng Zhou, [a] Yixiang Cheng, [a] Jin Xie*,[a] and Chengjian Zhu*,[a,b]

([a] State Key Laboratory of Coordination Chemistry, Jiangsu Key Laboratory of Advanced Organic Material, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, P. R. China; E-mail: xie@nju.edu.cn or cjzhu@nju.edu.cn
[b] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Shanghai, 200032, P. R. China)

Table of Contents

General Information: All reactions were carried out under Ar atmosphere unless otherwise noted. All catalysts and solvents were obtained from commercial suppliers. Reactions were monitored by TLC on silica gel plates (GF254), and the analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gel plates. ^{1}H NMR, ^{13}C NMR spectra and ^{19}F NMR spectra were recorded on 400 MHz spectrometer at room temperature. Chemical shifts (δ) are reported in ppm downfield from tetramethylsilane. High resolution mass spectra were obtained on a high–resolution mass spectrometer in the ESI mode.

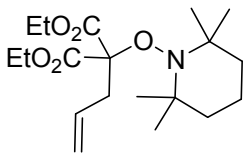
General procedure for sunlight-promoted cascade annulation of unsaturated α-bromocarbonyls with o-alkynylanilines

An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, **1** (0.1 mmol), **2** (2 equiv, 0.2 mmol), K_2CO_3 (2 equiv, 0.2 mmol). The flask was evacuated and backfilled with Ar for 3 times. 1 mL CH_3CN was added with syringe under Ar. The tube was placed exposed to sun light at room temperature for 2-3 h. After the reaction was finished, the solvent was concentrated in vacuo and the residue was purified by chromatography on silica gel to afford the corresponding products **3**.

Trapping experiment with TEMPO

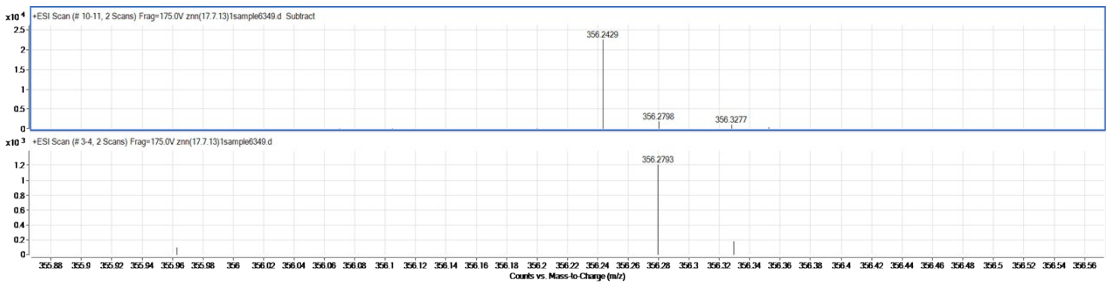
An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, **1** (0.1 mmol), **2** (2 equiv, 0.2 mmol), K_2CO_3 (2 equiv, 0.2 mmol), TEMPO (2 equiv). The flask was evacuated and backfilled with Ar for 3 times. 1 mL CH_3CN was added with syringe under Ar. The tube was placed exposed to sunlight at room temperature. However, products **3a** could not be detected, the corresponding alkylfragment of the halides were formed. Which suggests that the initiation of this radical chain is best achieved via photoinduction.

The HRMS (ESI) for the important intermediate 10



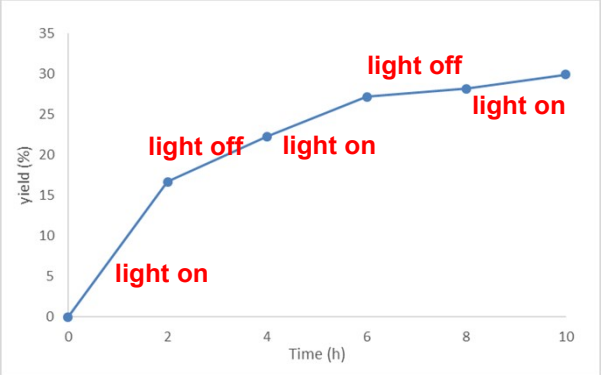
10

HRMS [**5** + H]$^{+}$： Calcd：356.2431；Found: 356.2429.



The light on/off experiments

An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, **1** (0.1 mmol), **2** (2 equiv, 0.2 mmol), K_2CO_3 (2 equiv, 0.2 mmol). The flask was evacuated and backfilled with Ar for 3 times. 1 mL CH_3CN was added with syringe under Ar. The tube was placed at a distance (app.5 cm) from 33 W fluorescent light bulb, and the resulting solution was stirred at ambient temperature under visible-light irradiation. After the indicated reaction time, 50 μL of the reaction mixture aliquot was collected at different points. The ^1H NMR analysis was calculated using 4,4'-dimethylbenzophenone as the internal standard.



UV/Vis measurement

The corresponding NK salts generated in situ from **1a** and KH occurred bathochromic shift from the UV-vis absorption, which showed much stronger absorption range from 325-375 nm than any of **1a, 2a** and product **3aa**.

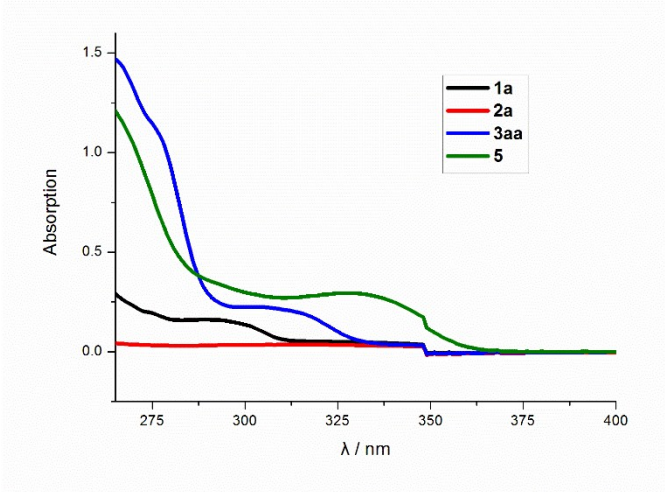
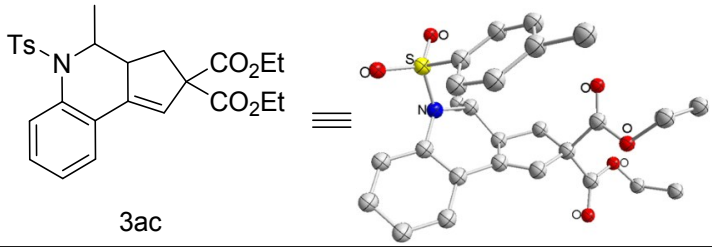


Figure 1: Absorption spectra of the reagents of the model reaction (c = 10^{-4} mol/L, recorded in MeCN in 1 mm path length quartz cuvettes using a Shimadzu UV-3600 UV-visible spectrophotometer).

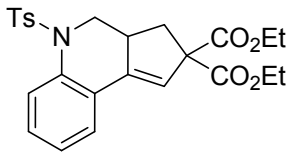
The crystallographic data

CCDC **1569256**



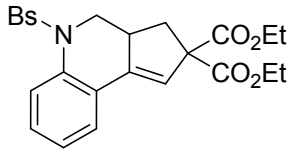
Identification code	**3ac**
Empirical formula	C26 H29 N O6 S
Formula weight	483.56
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	triclinic, *P*-1
Unit cell dimensions	a = 9.8833(13) Å alpha = 61.578(2)
	b = 12.3066(16) Å beta = 71.152(2)
	c = 12.4078(15) Å gamma = 72.508(2)
Volume	1236.4(3) Å ^{3}
Z, Calculated density	2, 1.299 g/cm^3
Absorption coefficient	0.172 mm^{-1}
F(000)	512
Limiting indices	-11<=h<=11, -14<=k<=14, -13<=l<=14
Data / parameters	4328 /311
Goodness-of-fit on F^2	0.982
Final R indices [I>2sigma(I)]	R1 = 0.058, wR2 = 0.198

Characterization of products

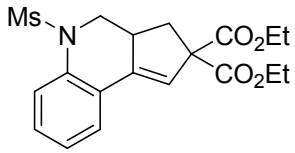


*diethyl 5-tosyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2,2-dicarboxylate(**3aa**).* Yellow solid; (41.7 mg, 89%); mp: 145-146 ^{o}C; R_f = 0.32 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (dd, *J* = 8.4 Hz, *J* = 1.2 Hz, 1H), 7.59-7.55 (m, 3H), 7.28-7.21 (m, 3H), 7.14-7.10 (m, 1H), 6.15 (d, *J* = 2.4 Hz, 1H), 4.61 (dd, *J* = 13.2 Hz, *J* = 4.8 Hz, 1H), 4.24-4.08 (m, 4H), 3.04 (m, 1H), 2.82-2.78 (m, 2H), 2.37 (s, 3H), 1.82-1.76 (m, 1H), 1.28-1.19 (m, 6H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 170.8, 169.8, 143.9, 142.2, 137.0, 135.9, 129.8, 129.2, 127.0, 125.7, 125.0, 124.4, 123.4, 121.1, 65.3, 61.7, 61.6, 51.4, 39.6, 37.2, 21.5, 14.1, 14.0 ppm. HRMS

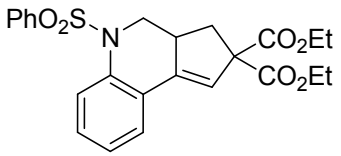
(ESI): m/z Calcd for $C_{25}H_{28}NO_6S$ [M+H$^+$] :470.1632, found 470.1635.



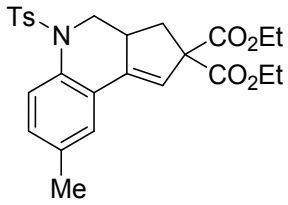
*diethyl 5-((4-bromophenyl)sulfonyl)-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2,2-dicarboxylate(**3ba**)*. Yellow solid; (43.2 mg, 81%); mp: 123-125 ^{o}C; R_f = 0.35 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (dd, *J* = 8.4 Hz, *J* = 1.2 Hz, 1H), 7.61-7.50 (m, 5H), 7.30-7.26 (m, 1H), 7.17-7.13 (m, 1H), 6.18 (d, *J* = 1.6 Hz, 1H), 4.60 (dd, *J* = 13.2 Hz, *J* = 4.4 Hz, 1H), 4.23-4.08 (m, 4H), 3.07 (t, *J* = 13.2 Hz, 1H), 2.83-2.78 (m, 2H), 1.83-1.76 (m, 1H), 1.28-1.20 (m, 6H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 170.7, 169.7, 141.8, 138.9, 135.4, 132.4, 129.3, 128.5, 128.1, 125.9, 125.4, 124.4, 123.7, 121.7, 65.3, 61.80, 61.77, 51.5, 39.7, 37.2, 14.06 ppm. HRMS (ESI): m/z Calcd for $C_{24}H_{24}BrNO_6S$ [M+H$^+$]: 534.0580, found 534.0582.



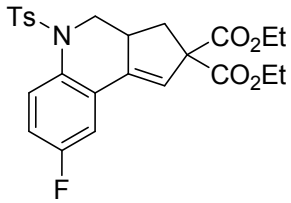
*diethyl 5-(methylsulfonyl)-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2,2-dicarboxylate(**3ca**)* . Yellow solid; (30.7 mg, 78%); mp: 146-148 ^{o}C; R_f = 0.38 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (dd, *J* = 8.4 Hz, *J* = 1.2 Hz, 1H), 7.69 (dd, *J* = 8.0 Hz, *J* = 1.6 Hz, 1H), 7.30 (dd, *J* = 7.2 Hz, *J* = 1.6 Hz, 1H), 7.18-7.14 (m, 1H), 6.30 (d, *J* = 2.4 Hz, 1H), 4.60 (dd, *J* = 13.2 Hz, *J* = 4.8 Hz, 1H), 4.28-4.13 (m, 4H), 3.32-3.23 (m, 1H), 3.06-2.96 (m, 2H), 2.94 (s, 3H), 1.90 (dd, *J* = 13.2 Hz, *J* = 8.8 Hz, 1H), 1.31-1.26 (m, 6H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 170.7, 170.0, 142.1, 135.8, 129.6, 126.2, 125.0, 123.1, 121.7, 65.4, 61.9, 61.8, 51.1, 40.8, 39.9, 37.2, 14.1 ppm. HRMS (ESI): m/z Calcd for $C_{19}H_{23}NO_6S$ [M+H$^+$]: 394.1319, found 394.1317.



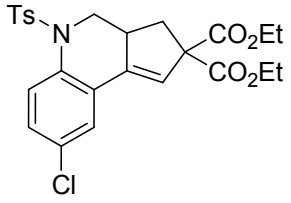
*diethyl 5-(phenylsulfonyl)-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2,2-dicarboxylate(**3da**)* . Yellow oil; (38.7 mg, 85%); R_f = 0.35 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (dd, *J* = 8.4 Hz, *J* = 1.2 Hz, 1H), 7.69-7.67 (m, 2H), 7.59-7.51 (m, 2H), 7.45-7.41 (m, 2H), 7.29-7.25 (m, 1H), 7.15-7.11 (m, 1H), 6.15 (d, *J* = 1.6 Hz, 1H), 4.61 (dd, *J* = 13.2 Hz, *J* = 4.0 Hz, 1H), 4.23-4.05 (m, 4H), 3.06 (m, 1H), 2.82-2.74 (m, 2H), 1.82-1.76 (m, 1H), 1.27-1.19 (m, 6H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 170.8, 169.8, 142.1, 140.0, 135.7, 133.0, 129.2, 126.9, 125.8, 125.1, 124.4, 123.5, 121.3, 65.3, 61.7, 51.4, 39.6, 37.2, 14.04 ppm. HRMS (ESI): m/z Calcd for $C_{24}H_{25}NO_6S$ [M+H$^+$]:456.1475, found 456.1476.



*diethyl 8-methyl-5-tosyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2,2-dicarboxylate(**3ea**)* . Yellow solid; (42.1 mg, 87%); mp: 133-135 °C; R_f = 0.33 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 8.8 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.38 (d, *J* = 1.6 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.08 (dd, *J* = 8.4 Hz, *J* = 1.6 Hz, 1H), 6.12 (d, *J* = 1.6 Hz, 1H), 4.57 (dd, *J* = 13.2 Hz, *J* = 4.4 Hz, 1H), 4.22-4.05 (m, 4H), 3.02 (t, *J* = 13.2 Hz, 1H), 2.79-2.68 (m, 2H), 2.37 (s, 3H), 2.31 (s, 3H), 1.80-1.73 (m, 1H), 1.27-1.19 (m, 6H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 170.8, 169.9, 143.8, 142.4, 137.0, 134.7, 133.5, 130.1, 129.7, 127.0, 125.9, 124.4, 123.2, 120.9, 65.3, 61.7, 61.6, 51.5, 39.5, 37.2, 21.5, 20.8, 14.1, 14.0 ppm. HRMS (ESI): m/z Calcd for $C_{26}H_{29}NO_6S$ [M+H$^+$]:484.1788, found 484.1790.

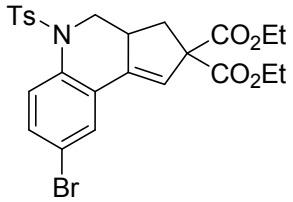


*diethyl 8-fluoro-5-tosyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2,2-dicarboxylate(**3fa**).* Yellow solid; (39.0 mg, 80%); mp: 113-115 °C; R_f = 0.33 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7. 81 (dd, *J* = 9.2 Hz, *J* = 5.2 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.25-7.22 (m, 3H), 7.04-6.96 (m, 1H), 6.14 (d, *J* = 2.4 Hz, 1H), 4.53 (dd, *J* = 13.2 Hz, *J* = 4.8 Hz, 1H), 4.26-4.05 (m, 4H), 3.01 (t, *J* = 13.2 Hz, 1H), 2.77 (dd, *J* = 12.8 Hz, *J* = 6.8 Hz, 1H), 2.73-2.64 (m, 1H), 2.38 (s, 3H), 1.77 (dd, *J* = 12.8 Hz, *J* = 9.2 Hz, 1H), 1.27-1.19 (m, 6H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 170.5, 169.5, 159.9 (d, *J* = 243.6 Hz), 144.1, 141.6 (d, *J* = 2.3 Hz), 136.7,131.9 (d, *J* = 2.7 Hz), 129.8, 127.0, 126.8 (d, *J* = 8.2 Hz), 125.4 (d, *J* = 8.2 Hz), 122.8, 116.4, 116.2, 111.7, 111.4, 65.3, 61.8, 61.7, 52.3, 39.0, 37.2, 21.5, 14.04, 13.98 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): -116.86 ppm. HRMS (ESI): m/z Calcd for $C_{25}H_{26}FNO_6S$ [M+H$^+$]:488.1538, found 488.1536.

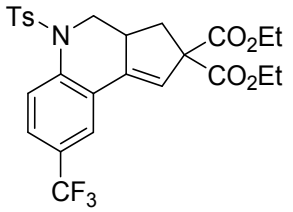


*diethyl 8-chloro-5-tosyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2,2-dicarboxylate(**3ga**).* Yellow solid; (41.7 mg, 83%); mp: 133-135 °C; R_f = 0.33 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 9.2 Hz, 1H), 7.56-7.53 (m, 3H), 7.25-7.20 (m, 3H), 6.17 (d, *J* = 2.4 Hz, 1H), 4.58 (dd, *J* = 13.6 Hz, *J* = 4.8 Hz, 1H), 4.24-4.06 (t, *J* = 13.6 Hz, 4H), 3.00 (m, 1H), 2.79 (dd, *J* = 12.8 Hz, *J* = 7.6 Hz, 1H), 2.74-2.65 (m, 1H), 2.38 (s, 3H), 1.80-1.73 (m, 1H), 1.79 (dd, *J* = 12.8 Hz, *J* = 8.8 Hz, 1H), 1.28-1.19 (m, 6H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 170.5, 169.6, 144.2, 141.2, 136.6, 134.4, 130.6, 129.9, 129.0, 127.0, 125.8, 125.4, 124.9, 122.6,

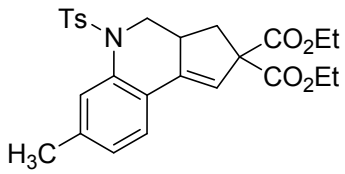
65.3, 61.83, 61.76, 51.2, 39.2, 37.1, 21.5, 14.1, 14.0 ppm. HRMS (ESI): m/z Calcd for $C_{25}H_{26}ClNO_6S$ [M+H$^+$]:504.1242, found 504.1244.



*diethyl 8-bromo-5-tosyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2,2-dicarboxylate(**3ha**).* Yellow solid; (42.7 mg, 78%); mp: 123-124 ^{o}C; R_f = 0.31 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73-7.69 (m, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.36 (dd, *J* = 8.8 Hz, *J* = 2.4 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.16 (d, *J* = 2.4 Hz, 1H), 4.58 (dd, *J* = 13.6 Hz, *J* = 4.8 Hz, 1H), 4.23-4.06 (m, 4H), 3.00 (t, *J* = 12.8 Hz, 1H), 2.79 (dd, *J* = 12.8 Hz, *J* = 7.6 Hz, 1H), 2.73-2.65 (m, 1H), 2.39 (s, 3H), 1.80-1.73 (m, 1H), 1.79 (dd, *J* = 12.8 Hz, *J* = 9.2 Hz, 1H), 1.28-1.19 (m, 6H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 170.5, 169.6, 144.2, 141.1, 136.6, 134.9, 131.9, 129.9, 128.4, 127.0, 126.0, 125.2, 122.6, 118.3, 65.3, 61.83, 61.77, 51.2, 39.2, 37.1, 21.5, 14.1, 14.0 ppm. HRMS (ESI): m/z Calcd for $C_{25}H_{26}BrNO_6S$ [M+H$^+$]:548.0737, found 548.0709.

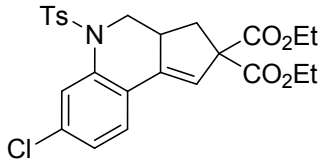


*diethyl 5-tosyl-8-(trifluoromethyl)-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2,2-dicarboxylate(**3ia**)* . Yellow solid; (39.2 mg, 73%); mp: 178-181 ^{o}C; R_f = 0.31 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 8.8 Hz, 1H), 7.82 (d, *J* = 2.0 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.47 (dd, *J* = 8.8 Hz, *J* = 8.8 Hz, 1H), 7.26 (d, *J* = 8.4 Hz, 2H), 6.26 (d, *J* = 2.4 Hz, 1H), 4.65 (dd, *J* = 13.2 Hz, *J* = 4.8 Hz, 1H), 4.24-4.08 (m, 4H), 3.03 (t, *J* = 18.8 Hz, 1H), 2.89-2.77 (m, 2H), 2.40 (s, 3H), 1.87-1.81 (m, 1H), 1.79-1.73 (m, 1H), 1.29-1.21 (m, 6H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 170.5, 169.6, 144.4, 141.1, 138.6, 136.5, 130.0, 127.0, 126.6 (q, *J* = 33 Hz), 125.6 (q, *J* = 3.6 Hz), 123.9, 123.8 (q, *J* = 270.1 Hz), 123.2, 123.0 (q, *J* = 3.7 Hz), 122.8, 65.4, 61.9, 51.2, 39.6, 37.0, 21.6, 14.06, 14.00 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): --62.55 ppm. HRMS (ESI): m/z Calcd for $C_{26}H_{26}F_3NO_6S$ [M+H$^+$]: 538.1506, found 538.1508.

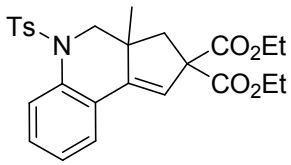


*diethyl 7-methyl-5-tosyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2,2-dicarboxylate(**3ja**)* . Yellow solid; (42.0 mg, 87%); mp: 167-169 ^{o}C; R_f = 0.38 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (s, 1H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.22

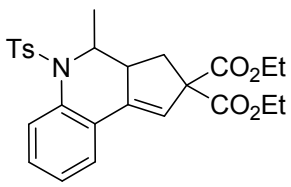
(dd, *J* = 8.4 Hz, *J* = 0.8 Hz, 2H), 6.94 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H), 6.07 (d, *J* = 2.4 Hz, 1H), 4.57 (dd, *J* = 13.2 Hz, *J* = 4.0 Hz, 1H), 4.22-4.07 (m, 4H), 3.04-2.98 (m, 1H), 2.79-2.74 (m, 2H), 2.37 (s, 3H), 2.35 (s, 3H), 1.79-1.73 (m, 1H), 1.27-1.18 (m, 6H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 170.9, 170.0, 143.8, 142.3, 139.4, 137.1, 135.8, 129.7, 127.0, 126.1, 125.5, 124.8, 120.8, 120.0, 65.3, 61.7, 61.6, 51.5, 39.6, 37.2, 21.7, 21.5, 14.1, 14.0 ppm. HRMS (ESI): m/z Calcd for $C_{26}H_{29}NO_6S$ [M+H$^+$]:484.1788, found 484.1786.



*diethyl 7-chloro-5-tosyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2,2-dicarboxylate(**3ka**)* . Yellow solid; (44.8 mg, 89%); mp: 142-144 °C; R_f = 0.39 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (d, *J* = 2.0 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 9.6 Hz, 2H), 7.09 (dd, *J* = 8.4 Hz, *J* = 2.0 Hz, 1H), 6.13 (d, *J* = 2.4 Hz, 1H), 4.59 (dd, *J* = 13.2 Hz, *J* = 4.8 Hz, 1H), 4.23-4.06 (m, 4H), 3.03-2.96 (m, 1H), 2.83-2.71 (m, 2H), 2.39 (s, 3H), 1.82-1.79 (m, 1H), 1.77-1.73 (m, 1H), 1.28-1.19 (m, 6H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 170.6, 169.7, 144.3, 141.3, 136.7, 136.5, 134.7, 129.9, 127.0, 126.7, 125.2, 124.0, 121.7, 121.6, 65.3, 61.8, 61.7, 51.2, 39.5, 37.0, 21.6, 14.05, 14.00 ppm. HRMS (ESI): m/z Calcd for $C_{25}H_{27}ClNO_6S$ [M+H$^+$]:504.1242, found 504. 1243.

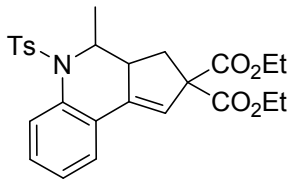


*diethyl 3a-methyl-5-tosyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2,2-dicarboxylate (**3ab**).* Yellow solid; (43.0 mg, 89%); mp: 145-146 °C; R_f = 0.32 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 7.6 Hz, 2H), 7.59-7.52 (m, 2H), 7.31-7.29 (m, 2H), 7.17-7.12 (m, 2H), 7.01-6.91 (m, 1H), 6.00 (s, 1H), 4.61 (d, *J* = 8.0 Hz, 1H), 4.32-4.18 (m, 4H), 3.21 (d, *J* = 8.0 Hz, 1H), 2.74 (d, *J* = 5.6 Hz, 1H), 2.41 (s, 3H), 2.46 (d, *J* = 13.6 Hz, 1H), 2.26 (d, *J* = 13.6 Hz, 1H), 1.31-1.25 (m, 6H), 1.23 (s, 3H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 171.1, 170.8, 146.8, 143.9, 137.9, 135.6, 129.9, 129.1, 126.9, 126.7, 123.1，120.6, 119.2, 118.9, 65.0, 61.88, 61.85, 57.5, 43.6, 43.4, 22.6, 21.5, 14.1 ppm. HRMS (ESI): m/z Calcd for $C_{26}H_{29}NO_6S$ [M+H$^+$]:484.1788, found 484.1789.

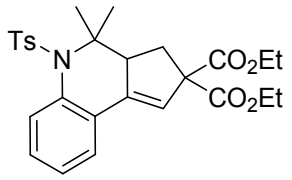


*diethyl 4-methyl-5-tosyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2,2-dicarboxylate (**3ac**).* Yellow solid; (10 mg, 21%); mp: 145-146 °C; R_f = 0.33 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 7.6 Hz, 1H), 7.38-7.33 (m, 1H), 7.26-7.18 (m, 4H), 7.04 (d, *J* = 8.0 Hz, 1H), 5.57 (d, *J* = 2.8 Hz, 1H), 4.24 (dd, *J* = 7.2 Hz, *J* = 3.6 Hz, 1H), 4.22-4.08 (m,

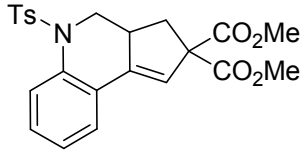
4H), 2.84-2.77 (m, 2H), 2.34 (s, 3H), 1.85-1.78 (m, 1H), 1.42 (d, *J* = 6.4Hz, 3H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.21 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 170.0, 169.8, 143.5, 142.1, 135.6, 130.2, 129.2, 129.1, 128.6, 127.1, 126.6, 125.2, 120.4, 66.2, 61.7, 61.4, 60.0, 52.1, 40.2, 24.1, 21.5, 14.1, 14.0 ppm. HRMS (ESI): m/z Calcd for $C_{26}H_{29}NO_6S$ [M+H$^+$]:484.1788, found 484.1790.



*diethyl 4-methyl-5-tosyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2,2-dicarboxylate (**3ac'**)*. Yellow solid; (30 mg, 62%); mp: 145-146 °C; R_f = 0.32 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (dd, *J* = 8.4 Hz, *J* = 1.2 Hz, 1H), 7.60-7.54 (m, 3H), 7.30-7.26 (m, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.15-7.11 (m, 1H), 6.20 (d, *J* = 2.4 Hz, 1H), 4.73-4.67 (m, 1H), 4.24-4.05 (m, 4H), 2.94-2.88 (m, 1H), 2.64 (dd, *J* = 13.2 Hz, *J* = 7.6 Hz, 1H), 2.37 (s, 3H), 1.94 (dd, *J* = 13.2 Hz, *J* = 8.4 Hz, 1H), 1.27-1.19 (m, 6H), 0.98 (d, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 170.9, 170.0, 143.7, 139.7, 137.2, 133.5, 129.7, 129.3，127.0, 125.9, 125.3, 124.9, 123.5, 122.3, 65.5, 61.7, 61.6, 53.1, 43.7, 35.3, 21.5, 14.05, 14.00, 13.4 ppm. HRMS (ESI): m/z Calcd for $C_{26}H_{29}NO_6S$ [M+H$^+$]:484.1788, found 484.1786.

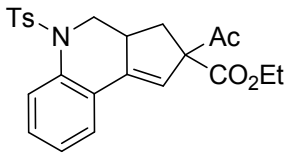


*diethyl 4,4-dimethyl-5-tosyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2,2-dicarboxylate (**3ae**)*. Yellow solid; (43.3 mg, 87%); mp: 145-146 °C; R_f = 0.32 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.26-7.22 (m, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 4.0 Hz, 1H), 5.62 (s, 1H), 4.43-4.38 (m, 1H), 4.37-4.15 (m, 4H), 3.38 (d, *J* = 16.4 Hz, 1H), 3.02 (d, *J* = 16.4 Hz, 1H), 2.36 (s, 3H), 1.68 (s, 3H), 1.36 (t, *J* = 6.8 Hz, 3H), 1.28 (t, *J* = 6.8 Hz, 3H), 0.89 (s, 3H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 171.4, 169.9, 144.4, 143.6, 136.5, 134.5, 133.8, 133.2, 129.4, 129.3, 129.1, 128.8, 128.2, 127.4, 123.8, 119.3, 63.2, 62.4, 61.9, 38.3, 23.7, 21.5, 19.6, 14.2, 14.1 ppm. HRMS (ESI): m/z Calcd for $C_{27}H_{31}NO_6S$ [M+H$^+$]:498.1945, found 498.1947.

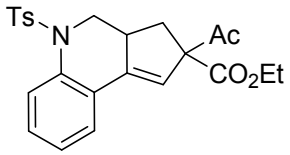


*dimethyl 5-tosyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2,2-dicarboxylate (**3af**)*. Yellow solid; (37.0 mg, 84%); mp: 145-146 °C; R_f = 0.32 (petroleum ether/ethyl acetate 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (dd, *J* = 8.4 Hz, *J* = 1.2 Hz, 1H), 7.58-7.55 (m, 3H), 7.28-7.21 (m, 3H), 7.14-7.10 (m, 1H), 6.14 (d, *J* = 2.0 Hz, 1H), 4.60 (dd, *J* = 13.2 Hz, *J* = 4.0 Hz, 1H), 3.75 (s,

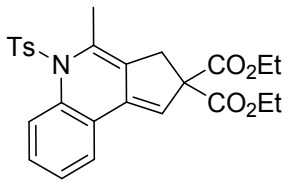
3H), 3.68 (s, 3H), 3.04 (t, J = 12.8, 1H), 2.84-2.77 (m, 2H), 2.38 (s, 3H), 1.83-1.77 (m, 1H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 171.2, 170.3, 143.9, 142.4, 137.0, 135.9, 129.8, 129.3, 127.0, 125.7, 125.0, 124.4, 123.3, 120.8, 65.1, 52.9, 52.8, 51.3, 42.6, 40.3, 39.7, 37.3, 21.5 ppm. HRMS (ESI): m/z Calcd for $C_{23}H_{23}NO_6S$ [M+H$^+$]:442.1319, found 442.1317.



ethyl 2-acetyl-5-tosyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate ***(3ag)***. Yellow solid; (10 mg, 22%); mp: 145-146 °C; R_f = 0.35 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (dd, J = 8.4 Hz, J = 1.2 Hz, 1H), 7.58-7.53 (m, 3H), 7.29-7.25 (m, 1H), 7.22 (d, J = 8.0 Hz, 2H), 7.15-7.11 (m, 1H), 6.20 (d, J = 2.8 Hz, 1H), 4.58 (dd, J = 13.2 Hz, J = 4.8 Hz, 1H), 4.20 (q, J = 7.2 Hz, 2H), 3.05 (t, J = 13.2 Hz, 1H), 2.77 (dd, J = 12.8 Hz, J = 6.8 Hz, 1H), 2.67-2.58 (m, 1H), 2.37 (s, 3H), 2.11 (s, 3H), 1.94 (dd, J = 12.8 Hz, J = 5.2 Hz, 1H), 1.27 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 201.3, 171.2, 144.0, 143.0, 136.9, 136.0, 129.8, 129.3, 127.0, 125.6, 125.0, 124.6, 123.3, 120.8, 72.2, 61.8, 51.4, 39.4, 35.8, 26.6, 21.5, 14.1 ppm. HRMS (ESI): m/z Calcd for $C_{24}H_{25}NO_5S$ [M+H$^+$]:440.1526, found 440.1528.

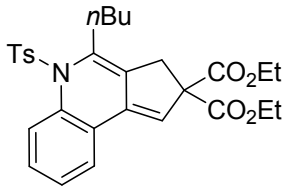


ethyl 2-acetyl-5-tosyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate ***(3ag')***. Yellow solid; (30 mg, 67%); mp: 145-146 °C; R_f = 0.32 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (dd, J = 8.4 Hz, J = 1.2 Hz, 1H), 7.60-7.55 (m, 3H), 7.28-7.21 (m, 3H), 7.15-7.11 (m, 1H), 6.17 (d, J = 2.0 Hz, 1H), 4.60 (dd, J = 13.2 Hz, J = 4.0 Hz, 1H), 4.20-4.07 (m, 2H), 3.05-2.99 (m, 1H), 2.85-2.77 (m, 2H), 2.38 (s, 3H), 2.20 (s, 3H), 1.68-1.61 (m, 1H), 1.22 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 203.6, 170.3, 143.9, 142.4, 137.0, 135.9, 129.8, 129.2, 127.0, 125.7, 125.0, 124.4, 123.3, 120.8, 71.9, 61.8, 51.4, 39.7, 36.6, 26.7, 21.5, 14.0 ppm. HRMS (ESI): m/z Calcd for $C_{24}H_{25}NO_5S$ [M+H$^+$]:440.1526, found 440.1528.

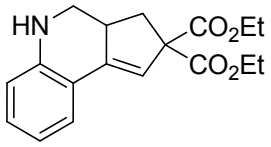


diethyl 4-methyl-5-tosyl-2H-cyclopenta[c]quinoline-2,2(3H,5H)-dicarboxylate ***(3ah)***. Yellow solid; (39.0 mg, 81%); mp: 145-146 °C; R_f = 0.32 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (dd, J = 8.4 Hz, J = 1.2 Hz, 1H), 7.65 (d, J = 8.4 Hz, 2H), 7.31-7.26 (m, 1H), 7.21 (d, J = 8.4 Hz, 2H), 7.07-6.99 (m, 2H), 5.92 (s, 1H), 4.45-4.17 (m, 4H), 3.54-3.49 (m, 1H), 3.15-3.11 (m, 1H), 2.38 (s, 3H), 1.37 (t, J = 3.2 Hz, 3H), 1.32 (s, 3H), 1.29 (t, J = 3.2 Hz, 3H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 170.9, 168.9, 143.9，141.8, 139.3, 137.9, 136.5, 134.7, 129.6, 129.5, 129.4, 127.3, 126.3, 124.1, 120.2, 119.9, 62.9, 62.1, 43.1, 24.7, 21.6，14.2,

14.1 ppm. HRMS (ESI): m/z Calcd for $C_{26}H_{27}NO_6S$ [M+H$^+$]:482.1632, found 482.1635.

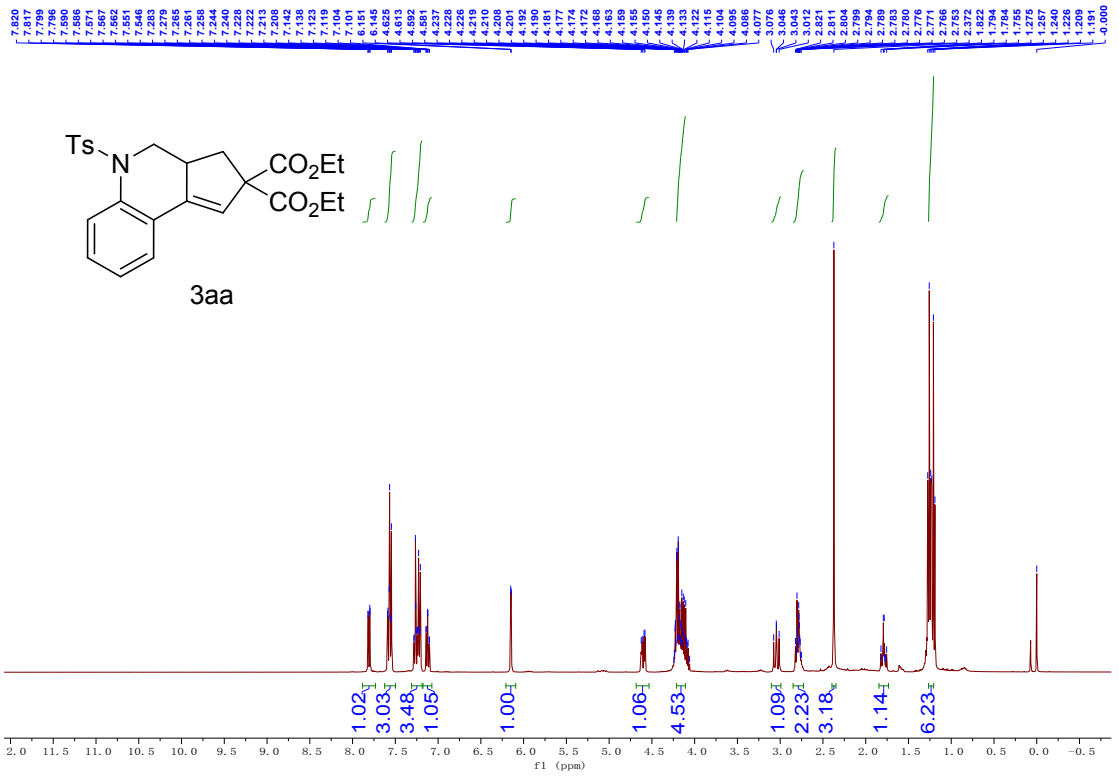


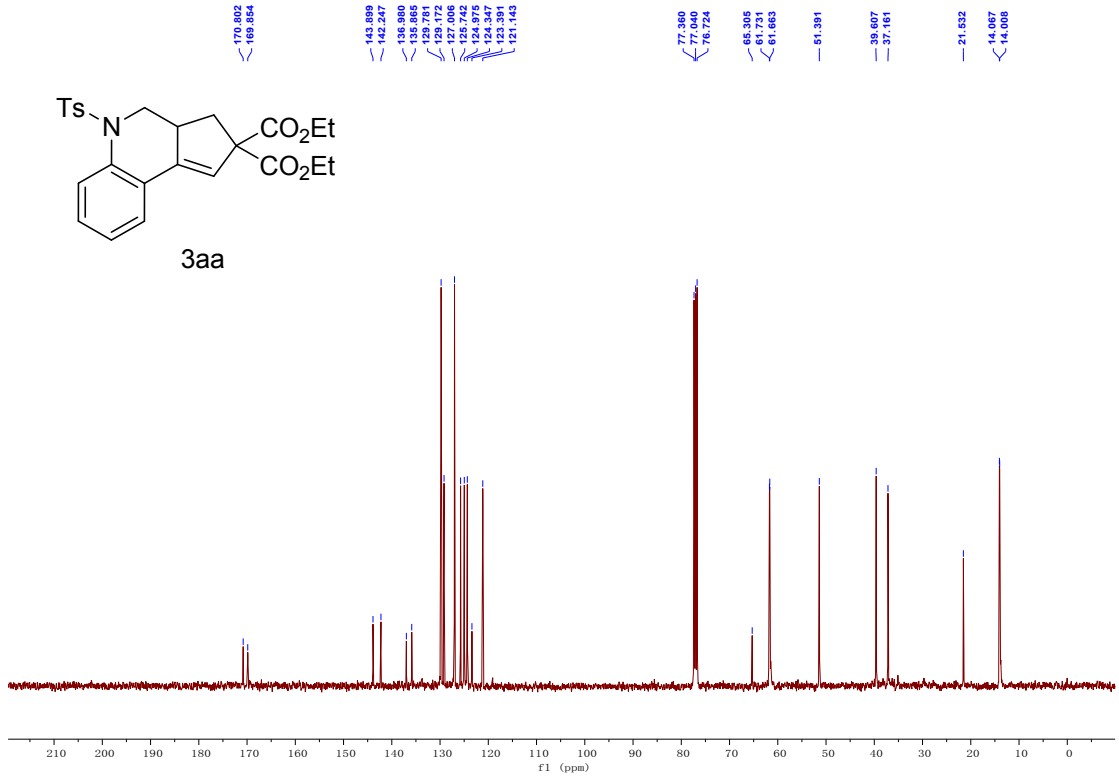
diethyl 4-butyl-5-tosyl-2H-cyclopenta[c]quinoline-2,2(3H,5H)-dicarboxylate. Yellow solid (***3ai***); (40.8 mg, 78%); mp: 145-146 ^oC; R_f = 0.32 (petroleum ether/ethyl acetate 10:1); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.4 Hz,, 2H), 7.31-7.26 (m, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.03-7.00 (m, 2H), 5.82 (s, 1H), 4.45-4.17 (m, 4H), 3.50 (d, *J* = 17.6 Hz, 1H), 3.14 (d, *J* = 17.6 Hz, 1H), 2.37 (s, 3H), 1.56-1.48 (m, 1H), 1.38-1.27 (m, 6H), 1.06-0.98 (m, 1H), 0.90-0.70 (m, 4H), 0.57 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 170.9, 169.0, 143.9, 141.8, 139.0, 138.0, 136.5, 134.8, 129.6, 129.5, 128.9, 127.4, 127.1, 126.2, 123.8, 119.5, 62.8, 62.7, 62.1,43.2, 36.4, 31.0, 21.9, 21.5, 14.2, 14.1, 13.4 ppm. HRMS (ESI): m/z Calcd for $C_{29}H_{33}NO_6S$ [M+H$^+$]:524.2101, found 524.2103.

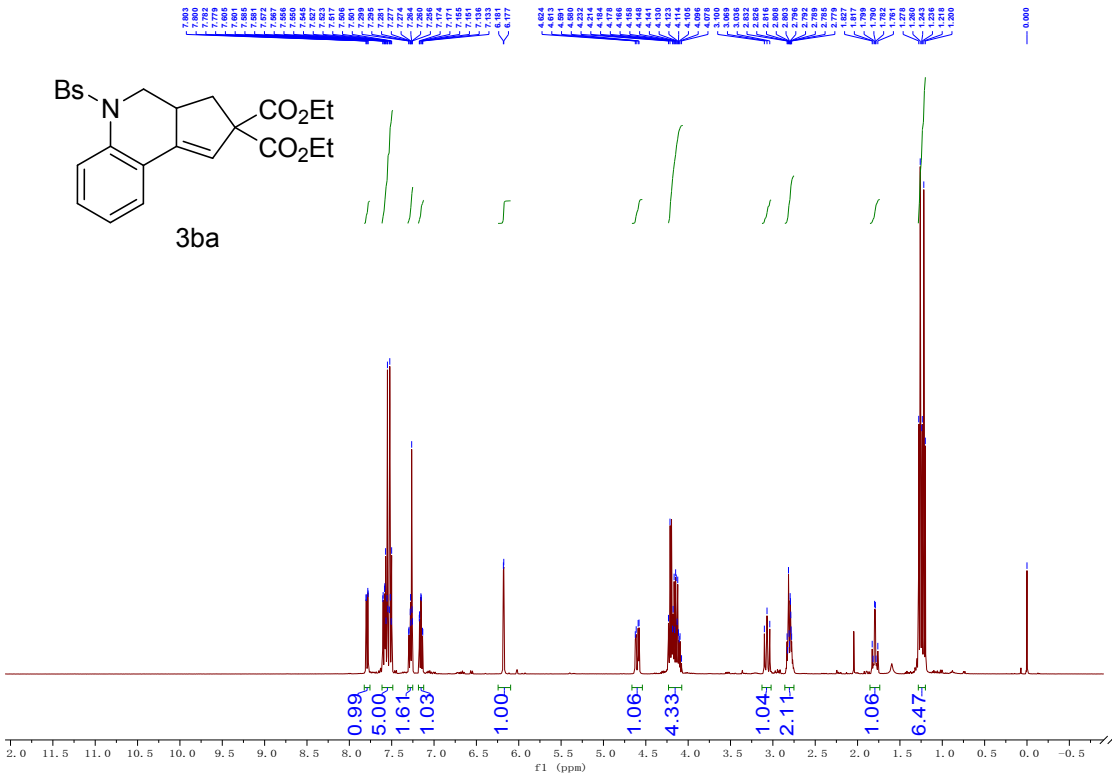


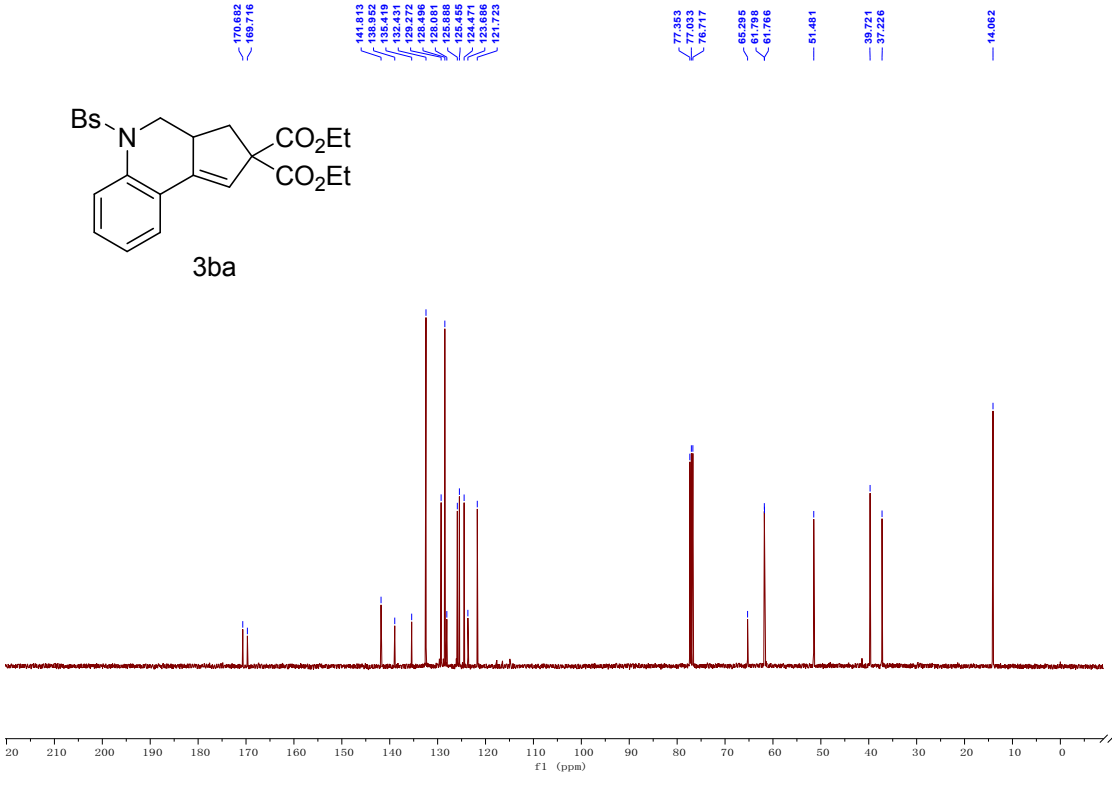
*diethyl 3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2,2-dicarboxylate(**4**)* . Yellow solid; (26.8 mg, 85%); mp: 166-168 ^oC; R_f = 0.38 (petroleum ether/ethyl acetate 10:1); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.45 (dd, *J* = 7.6 Hz, *J* = 1.6 Hz, 1H), 7.07-7.03 (m, 1H), 6.69-6.65 (m, 1H), 6.56 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H), 6.02 (d, *J* = 2.8 Hz, 1H), 4.25-4.14 (m, 4H), 4.10 (s, 1H), 3.53 (dd, *J* = 10.4 Hz, *J* = 5.2 Hz, 1H), 3.25-3.16 (m, 1H), 2.97-2.91 (m, 2H), 1.89 (dd, *J* = 13.2 Hz, *J* = 9.2 Hz, 1H), 1.30-1.24 (m, 6H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 171.6, 170.8, 144.7, 143.7, 129.6, 126.1, 117.6, 116.4, 114.9, 65.8, 61.6, 61.5, 48.0, 41.4, 37.2, 14.13, 14.10 ppm. HRMS (ESI): m/z Calcd for $C_{18}H_{21}NO_4$ [M+H$^+$]:316.1543, found 316.1545.

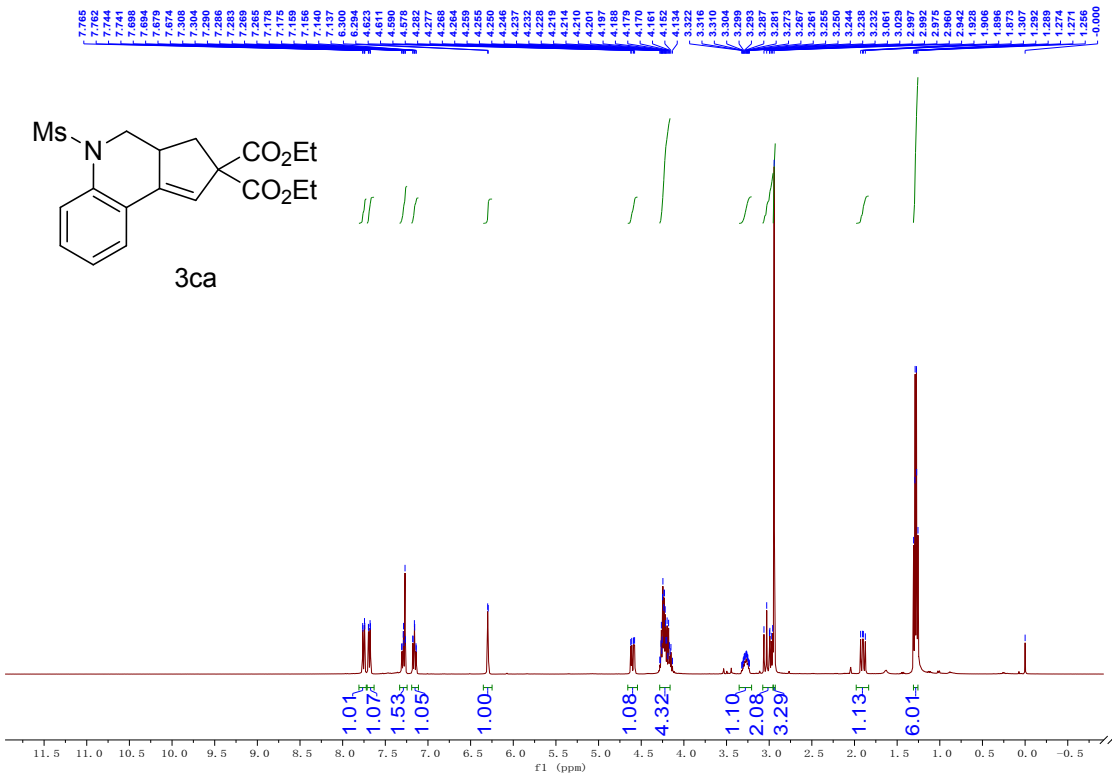
Copies of ^{1}H NMR, ^{13}C NMR, ^{19}F NMR

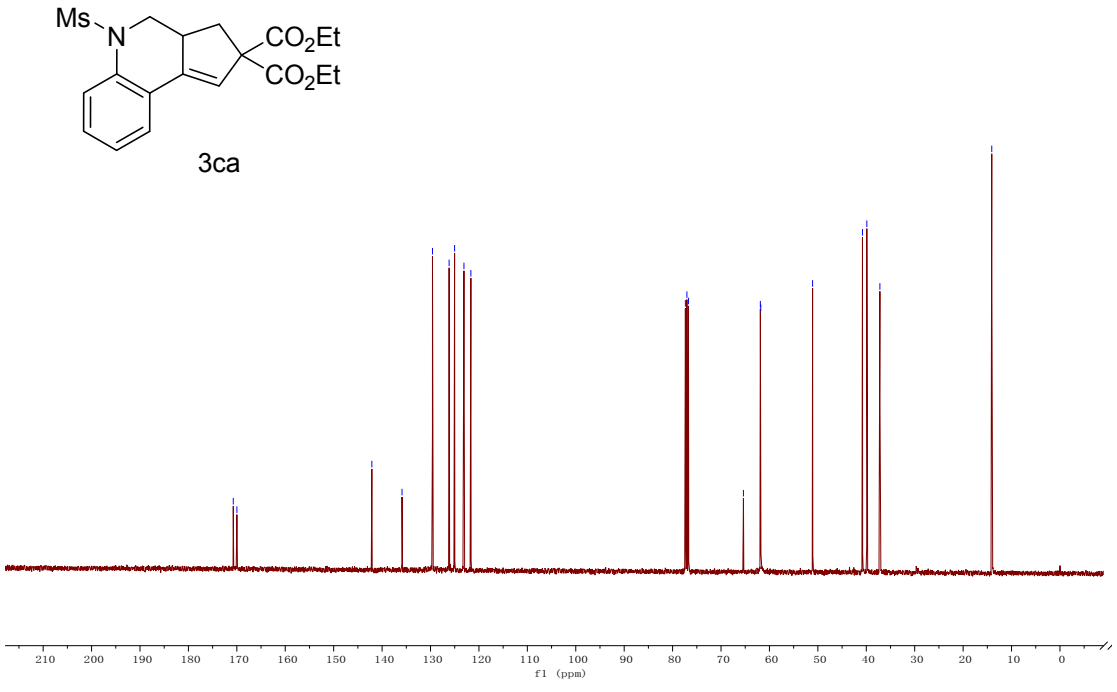


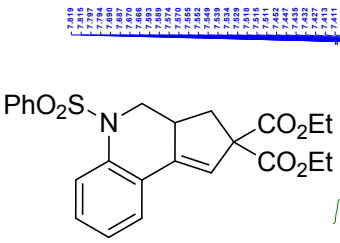



Bs
N
CO2Et
CO2Et
3ba
0.99
5.00
1.61
1.03
1.00
1.06
4.33
1.04
2.11
1.06
6.47
f1 (ppm)

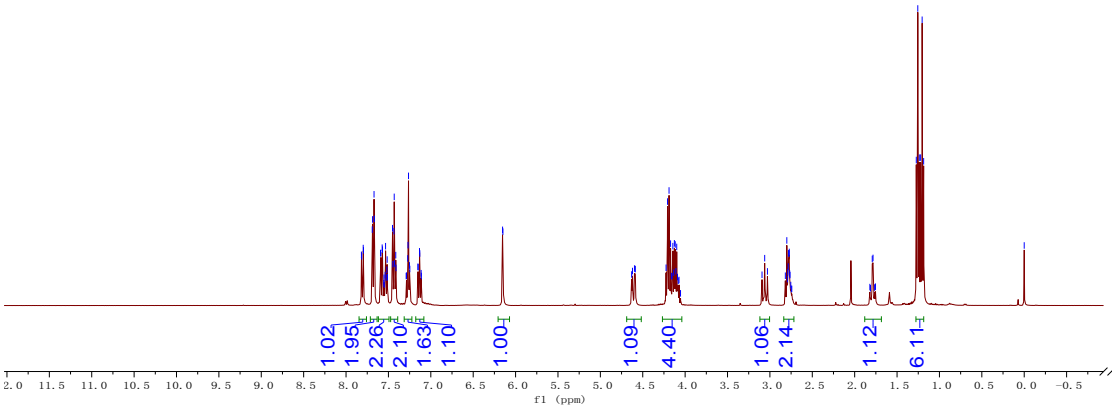

Bs
N
CO2Et
CO2Et
3ba
f1 (ppm)

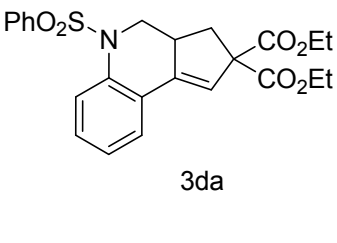

Ms
N
CO2Et
CO2Et
3ca
1.01
1.07
1.53
1.05
1.00
1.08
4.32
1.10
2.08
3.29
1.13
6.01
f1 (ppm)


Ms
N
CO2Et
CO2Et
3ca
f1 (ppm)

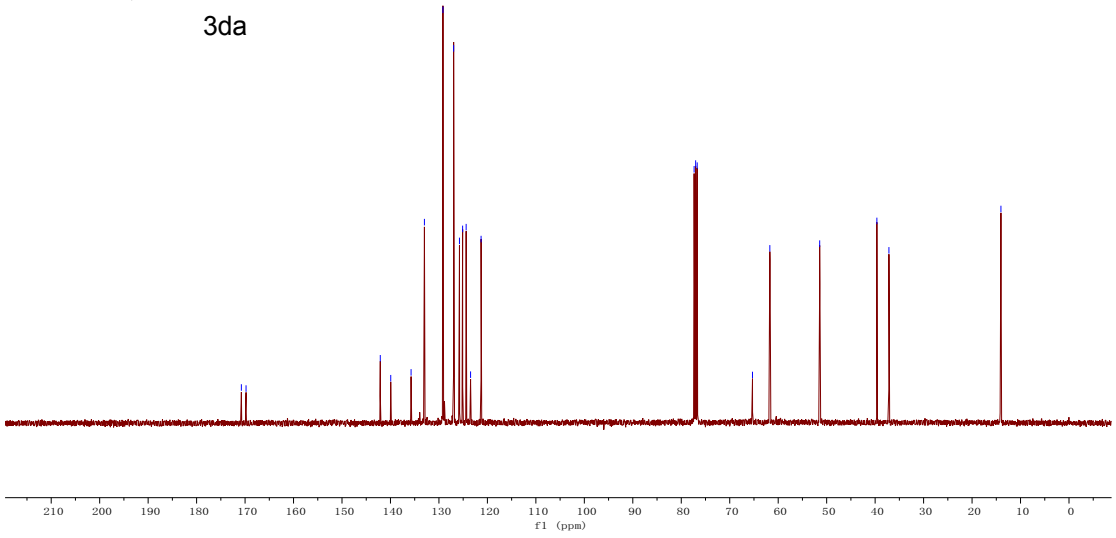

PhO2S
N
CO2Et
CO2Et

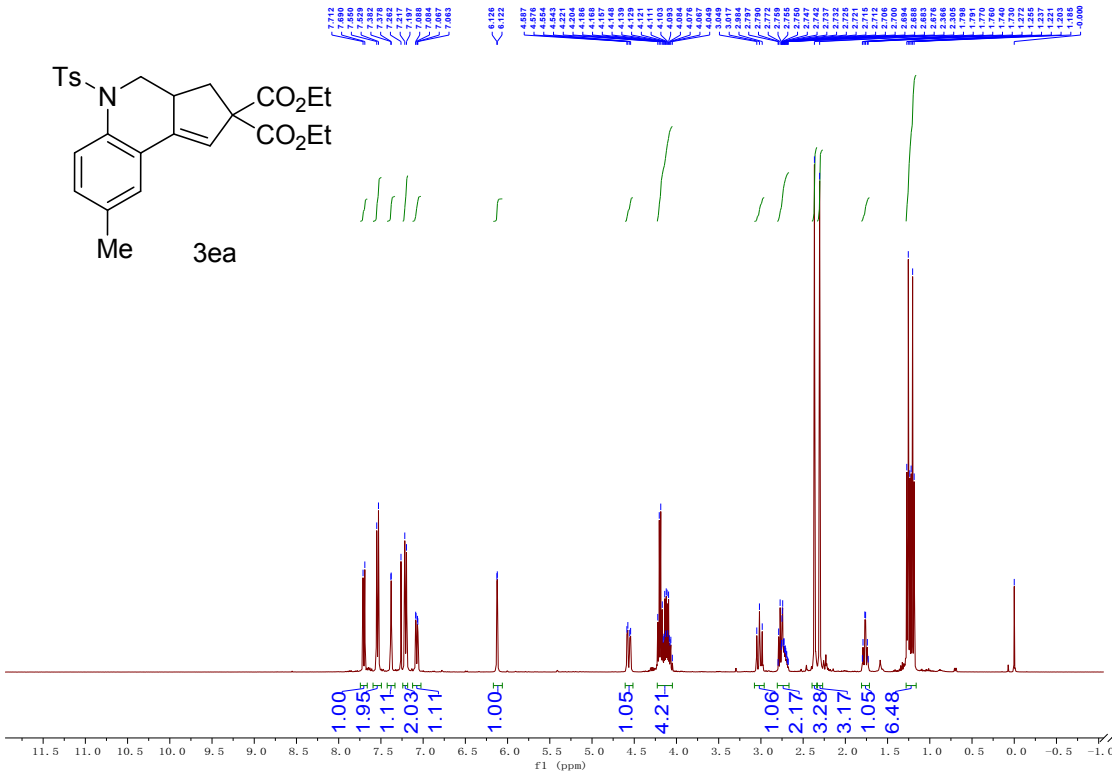
3da

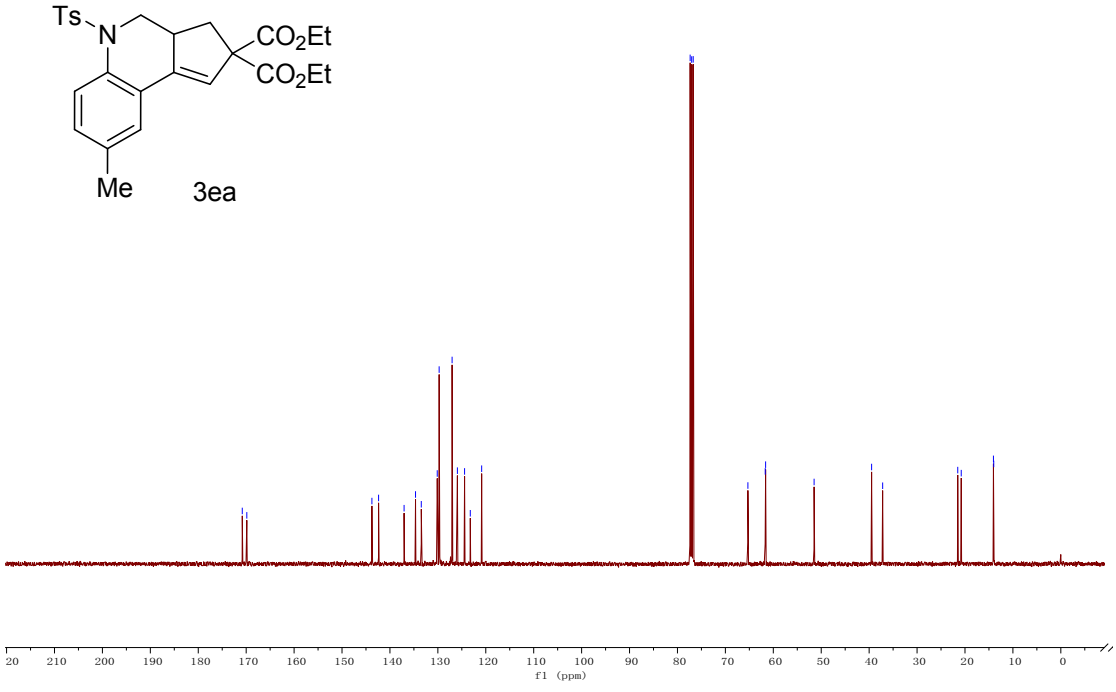

1.02
1.95
2.26
2.10
1.63
1.10
1.00
1.09
4.40
1.06
2.14
1.12
6.11
f1 (ppm)

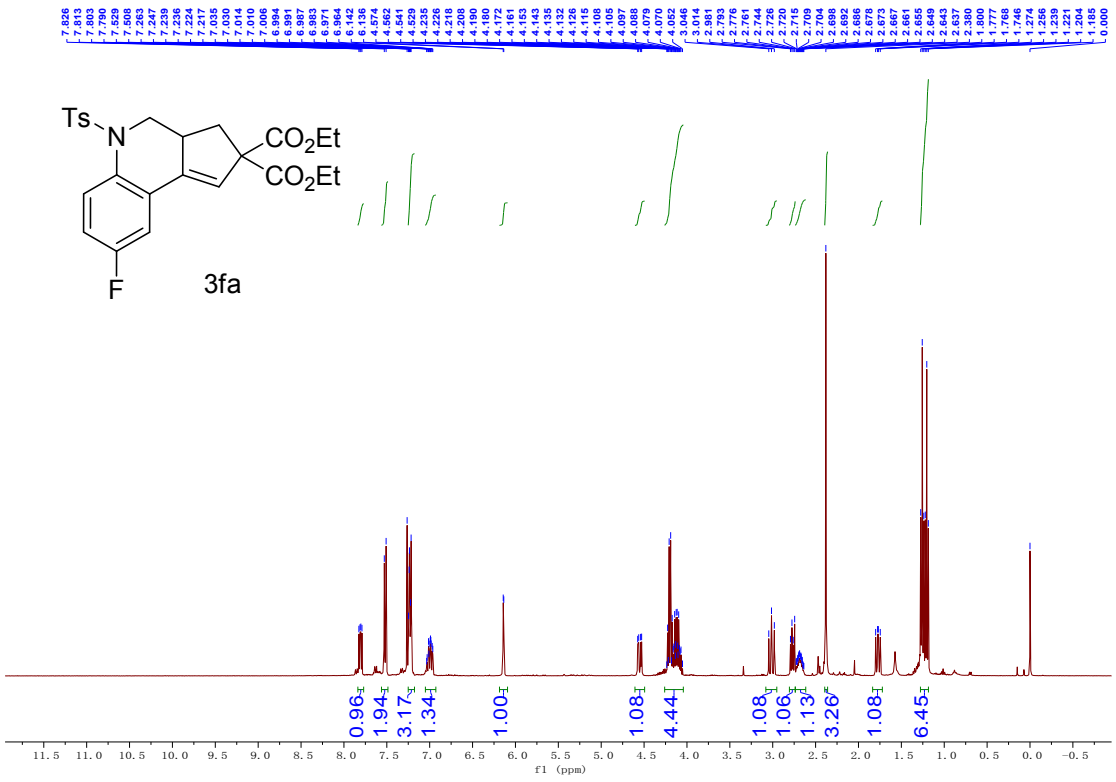

PhO2S
N
CO2Et
CO2Et

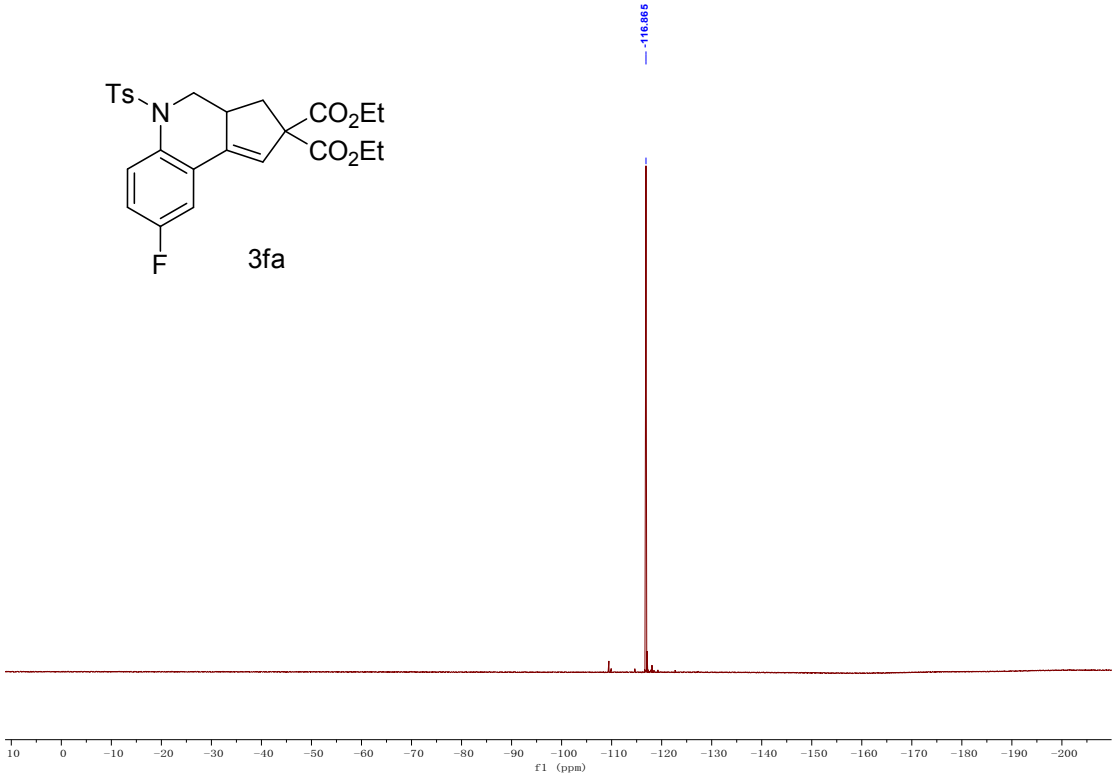
3da

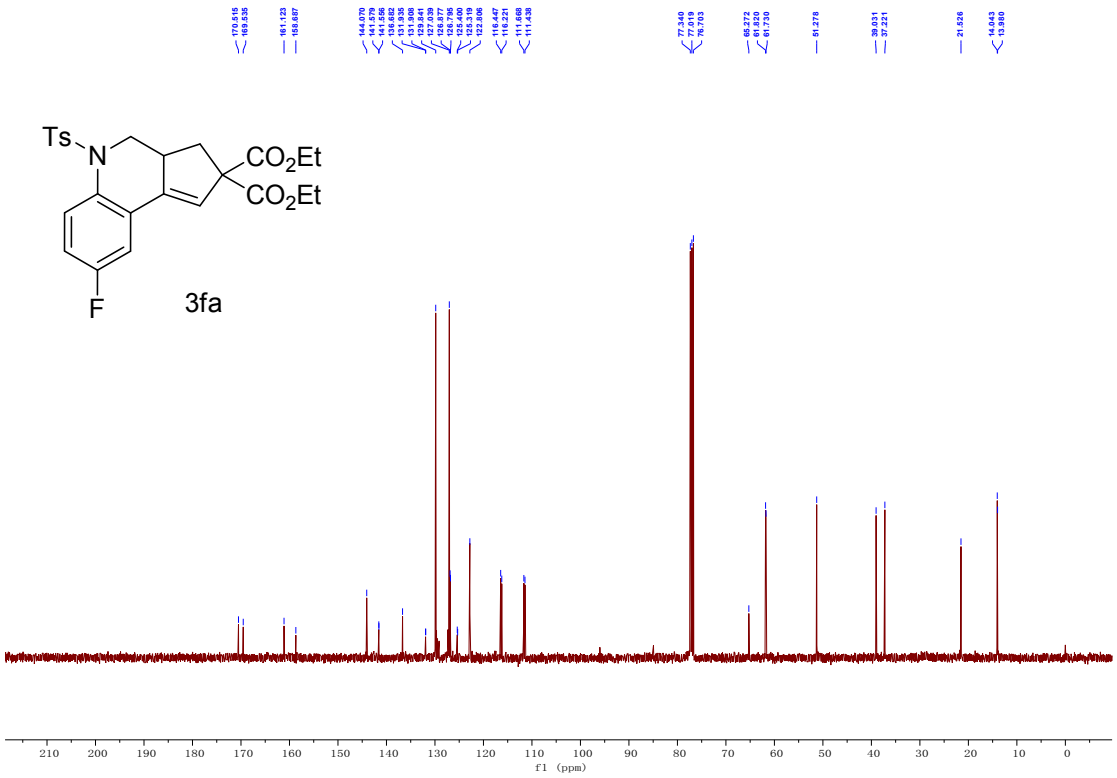

f1 (ppm)

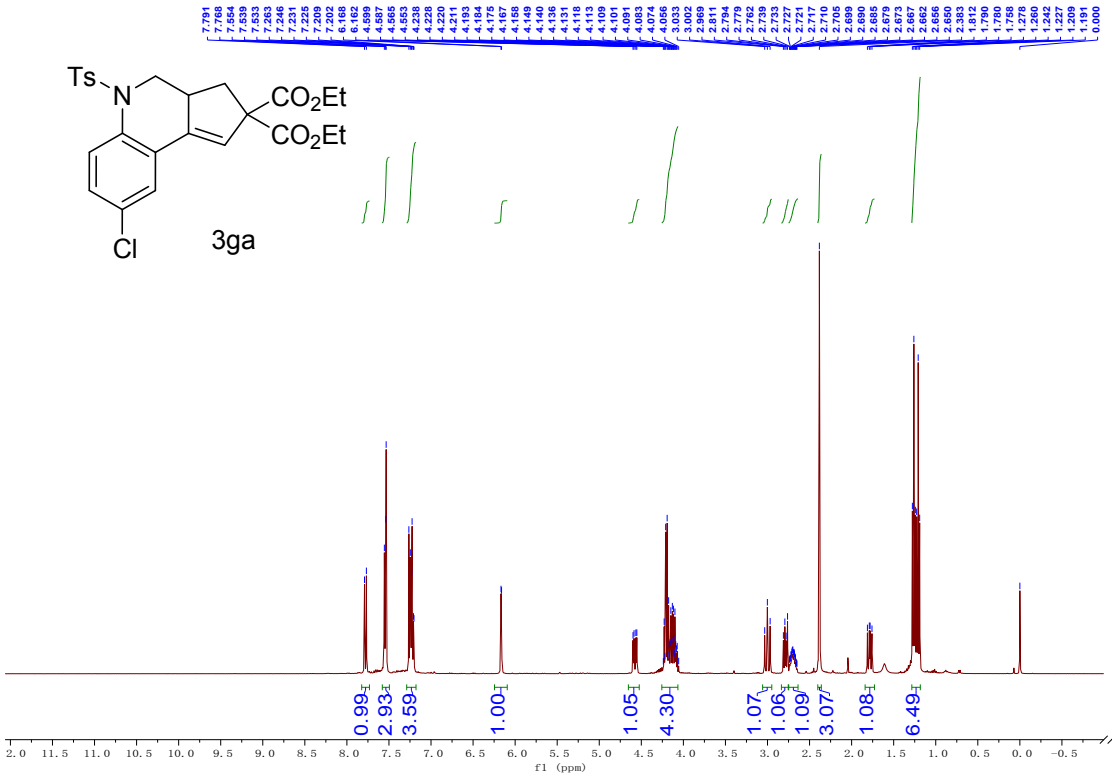

Ts
N
CO2Et
CO2Et
Me
3ea
1.00
1.95
1.11
2.03
1.11
1.00
1.05
4.21
1.06
2.17
3.28
3.17
1.05
6.48
f1 (ppm)

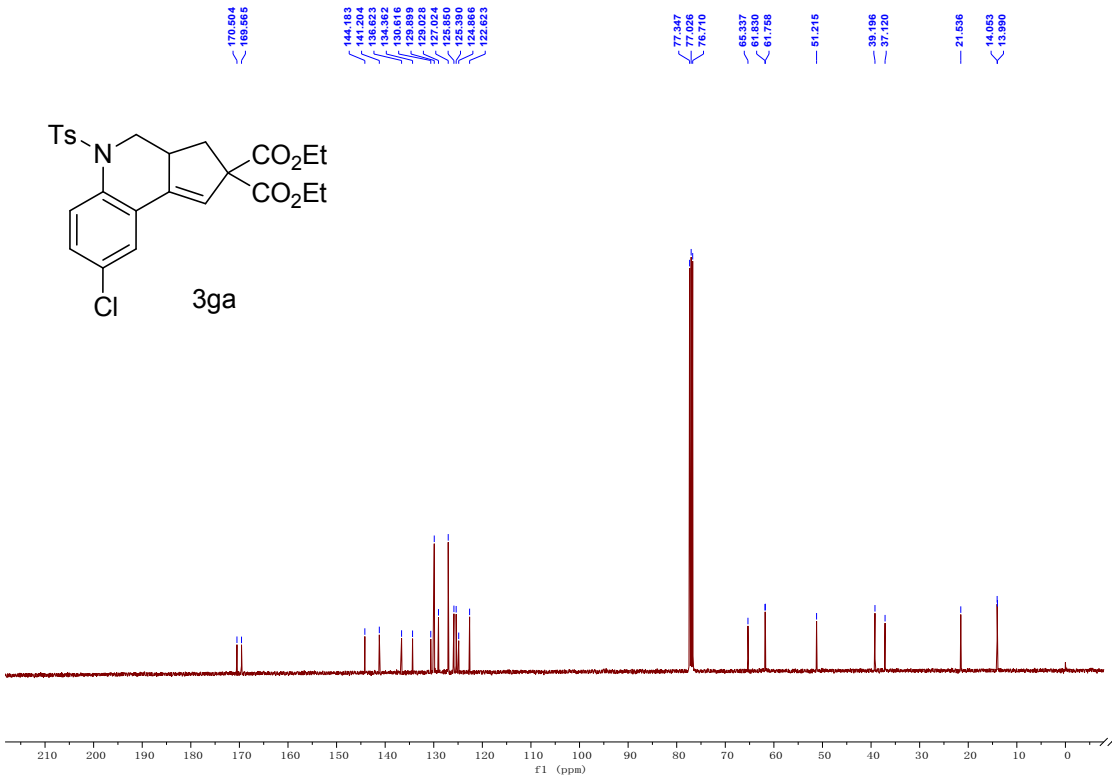

Ts
N
CO2Et
CO2Et
Me
3ea
f1 (ppm)

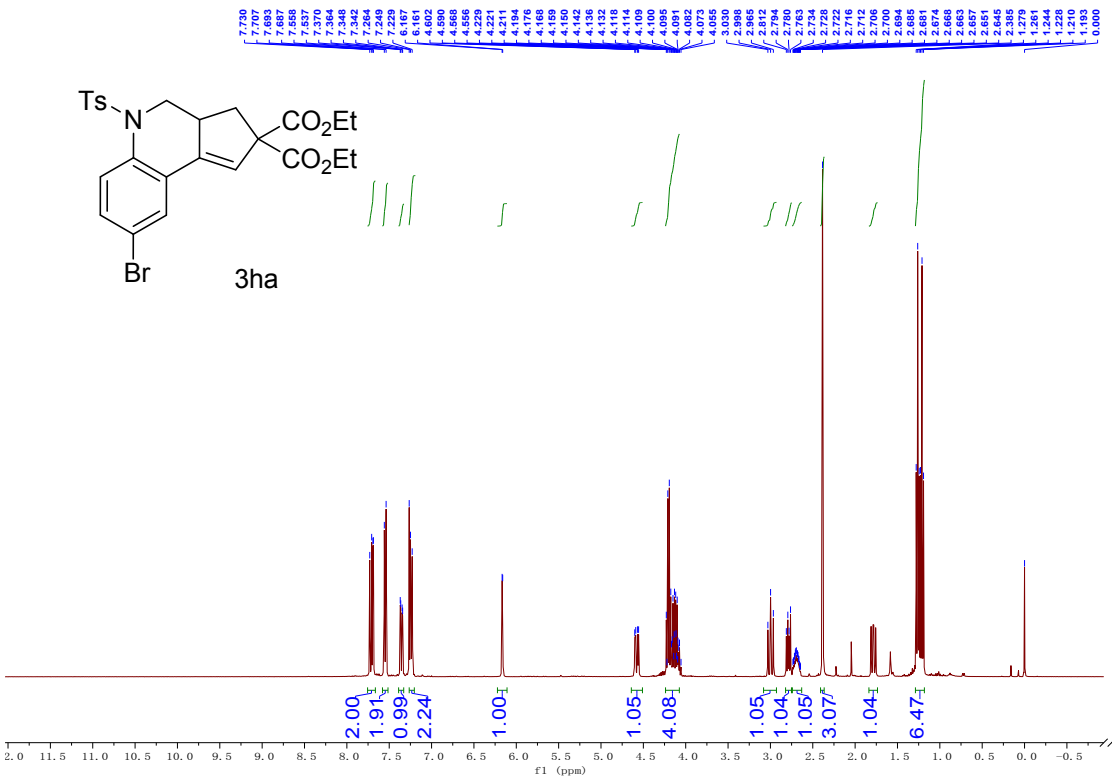

Ts
N
CO2Et
CO2Et
F
3fa
0.96
1.94
3.17
1.34
1.00
1.08
4.44
1.08
1.06
1.13
3.26
1.08
6.45
f1 (ppm)

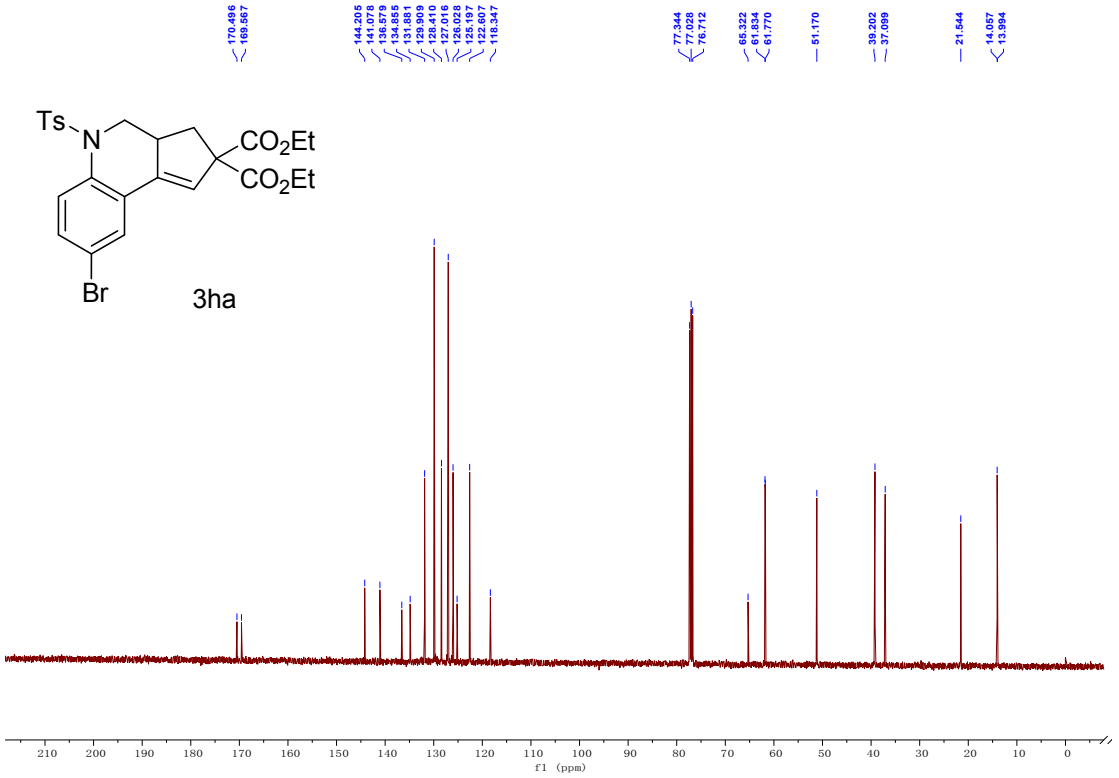

-116.665
Ts
N
CO2Et
CO2Et
F
3fa
f1 (ppm)

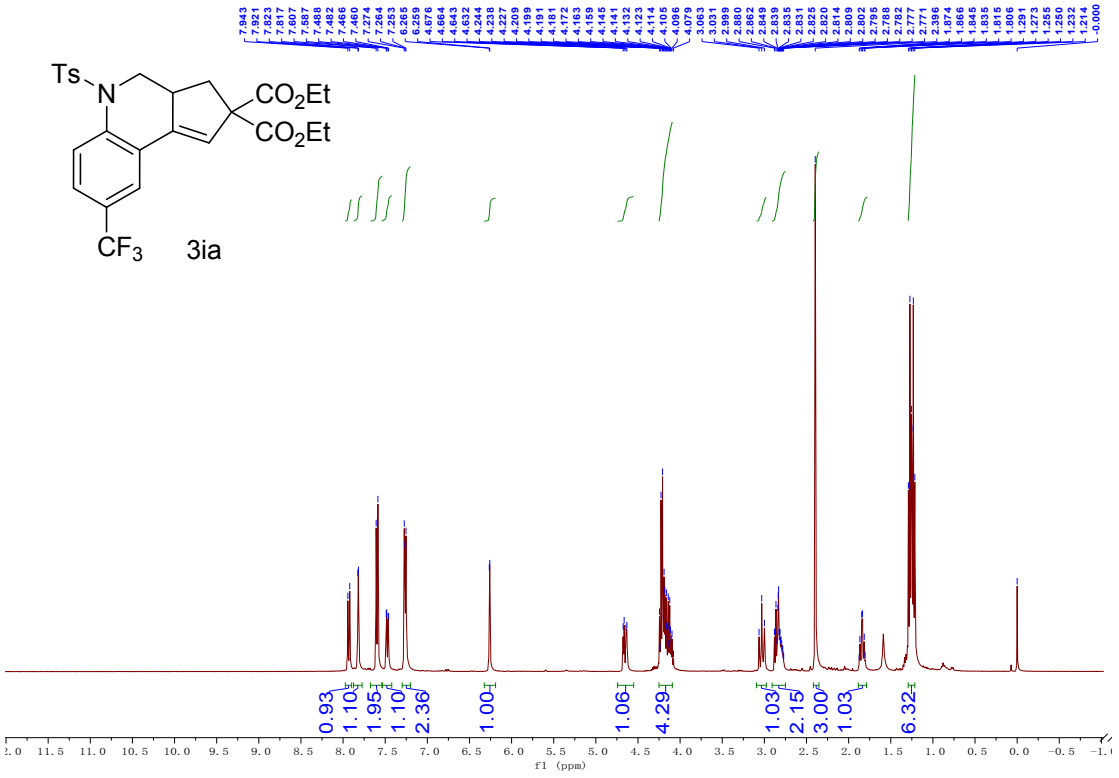

Ts
N
CO2Et
CO2Et
F
3fa
f1 (ppm)

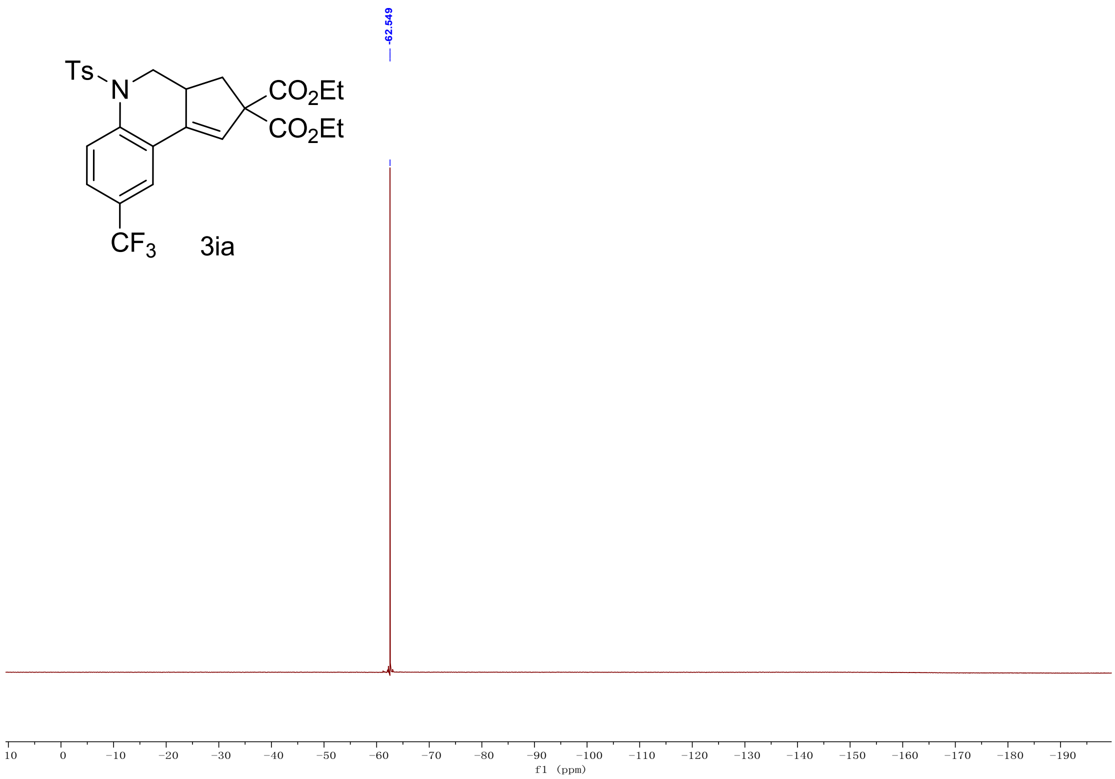

Ts
N
CO2Et
CO2Et
Cl
3ga
0.99
2.93
3.59
1.00
1.05
4.30
1.07
1.06
1.09
3.07
1.08
6.49
f1 (ppm)

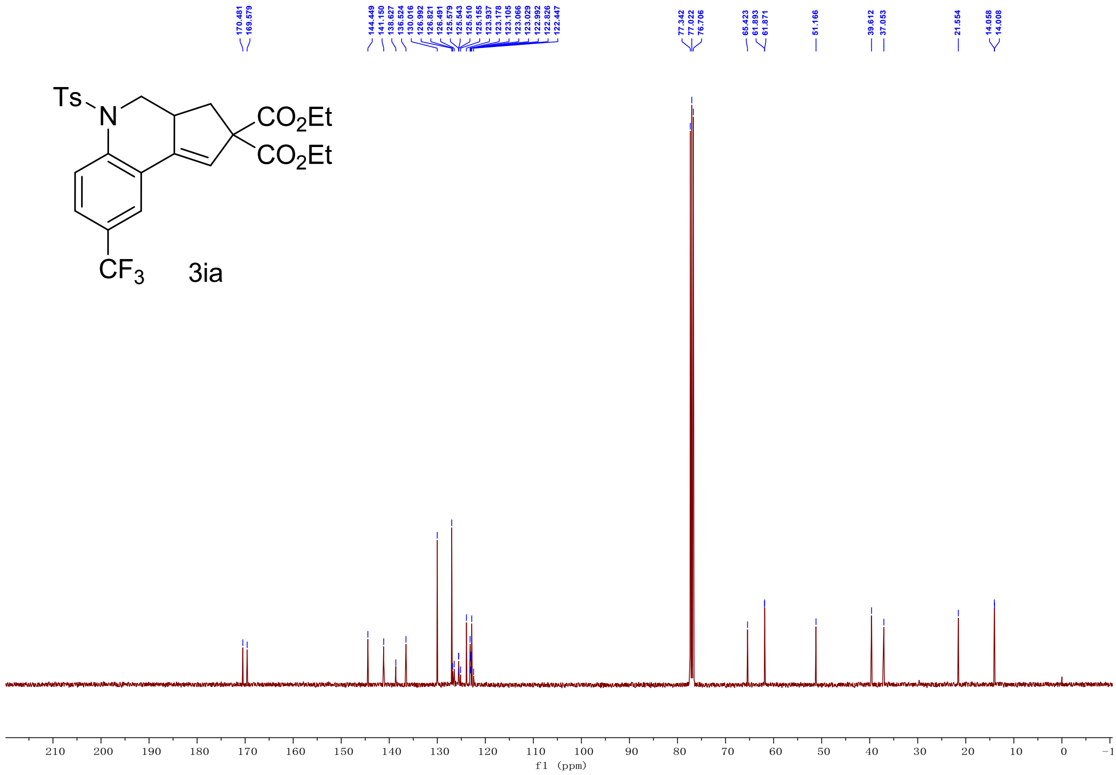

170.504
169.565
144.183
141.204
136.623
134.362
130.616
129.899
129.028
127.024
125.390
124.866
122.623
77.347
77.026
76.710
65.337
61.930
61.798
51.215
39.196
37.120
21.536
14.053
13.990
Ts
N
CO2Et
CO2Et
Cl
3ga
f1 (ppm)

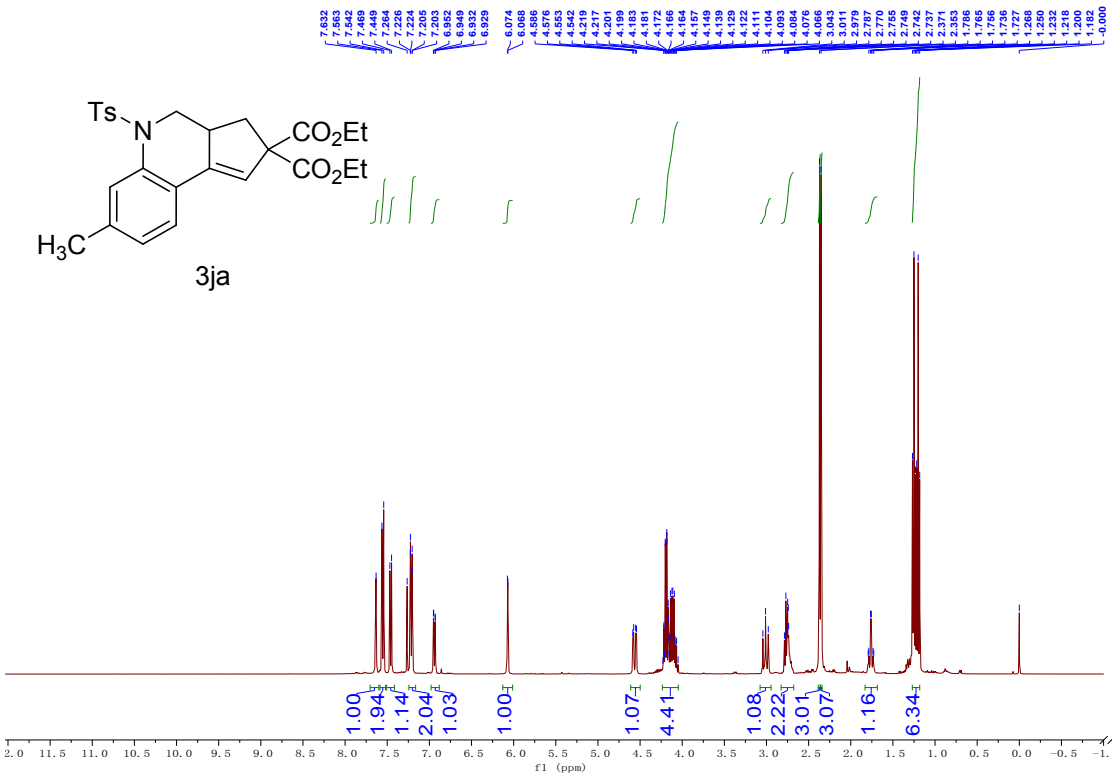

Ts
N
CO2Et
CO2Et
Br
3ha
2.00
1.91
0.99
2.24
1.00
1.05
4.08
1.05
1.04
1.05
3.07
1.04
6.47
f1 (ppm)

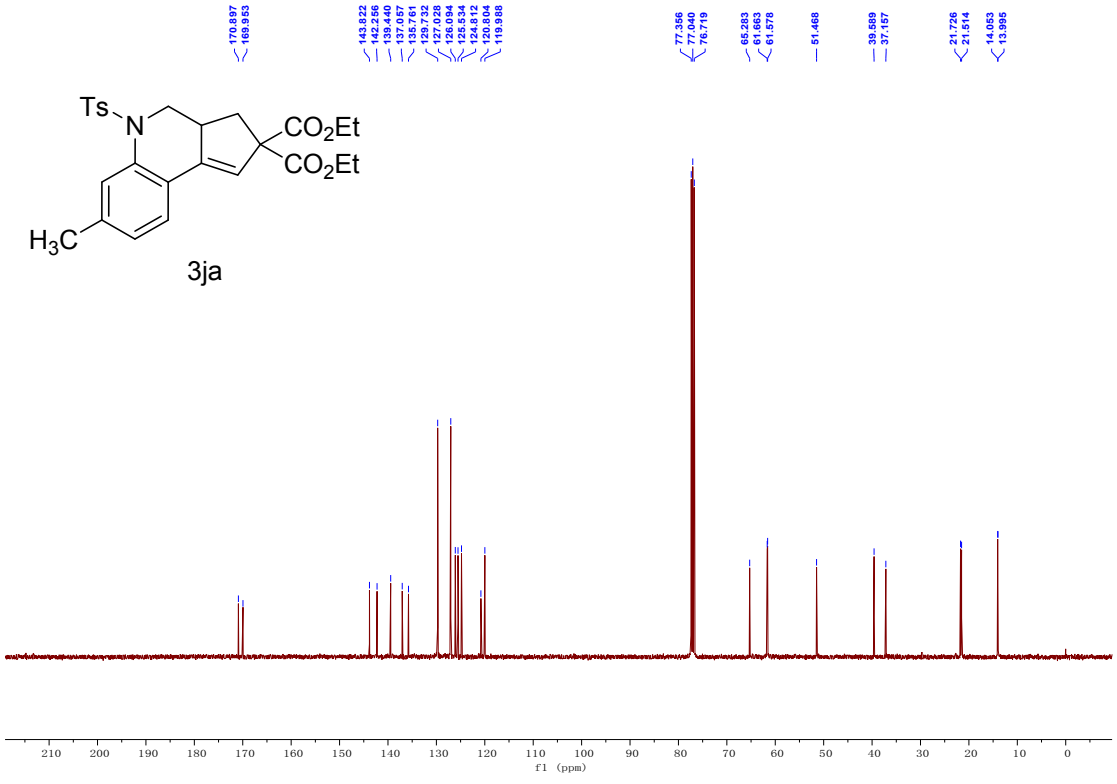

Ts
N
CO2Et
CO2Et
Br
3ha
f1 (ppm)

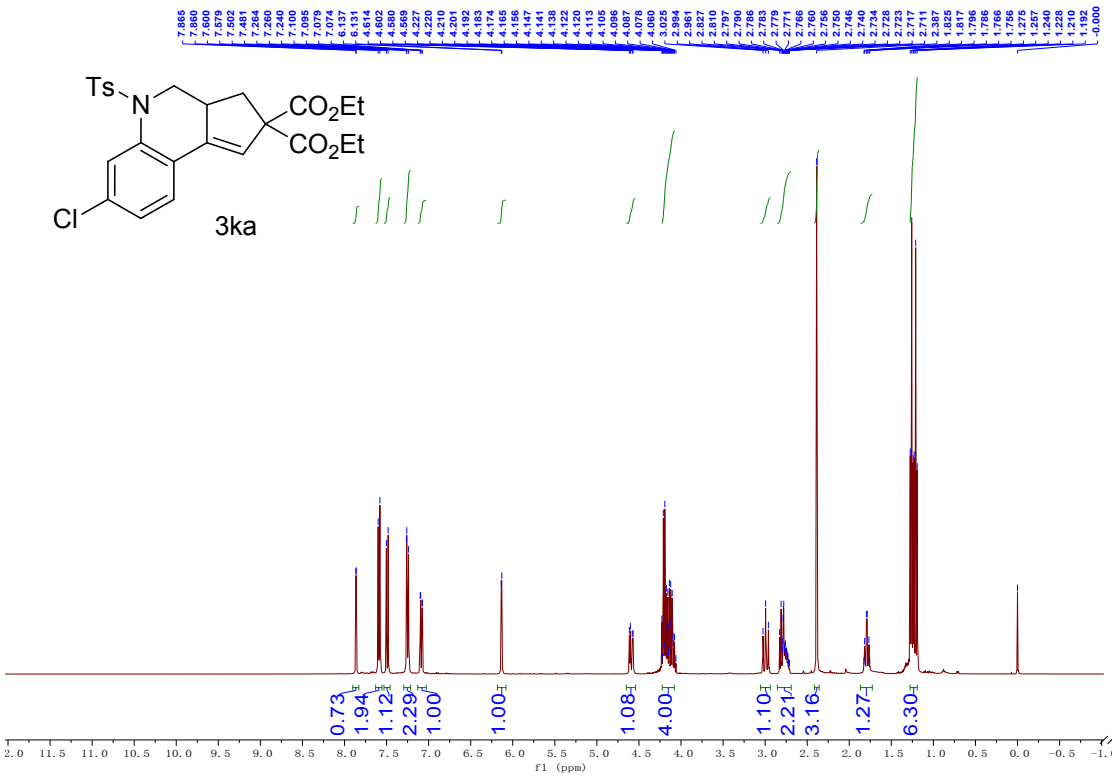

Ts
N
CO2Et
CO2Et
CF3
3ia
0.93
1.10
1.95
1.10
2.36
1.00
1.06
4.29
1.03
2.15
3.00
1.03
6.32
f1 (ppm)

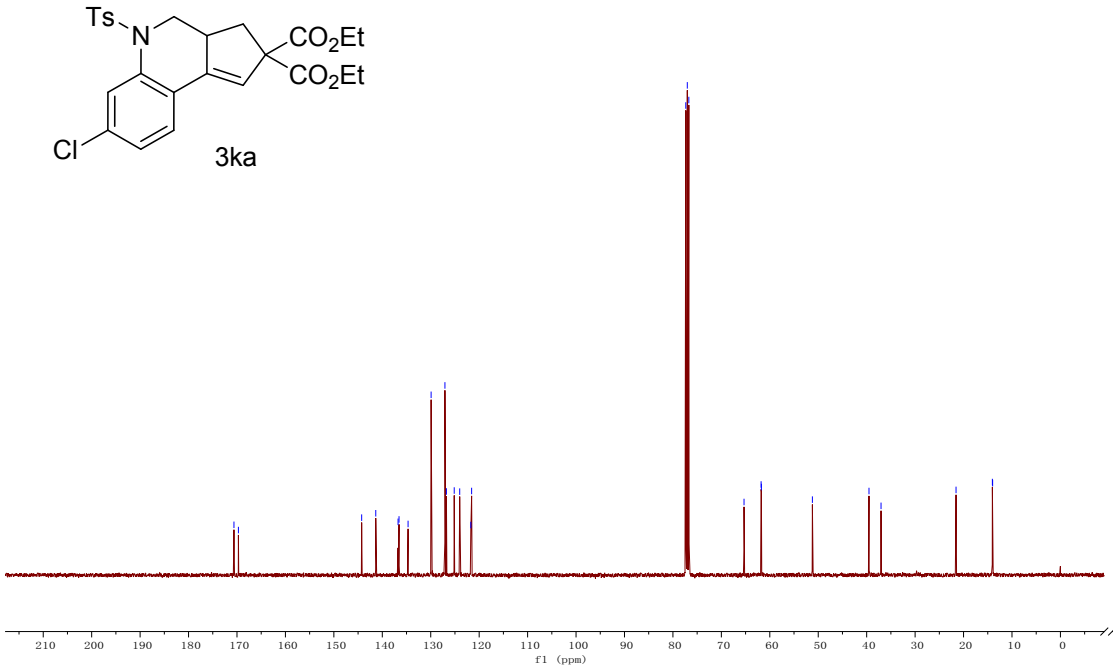

Ts
N
CO2Et
CO2Et
CF3
3ia
-62.549
f1 (ppm)

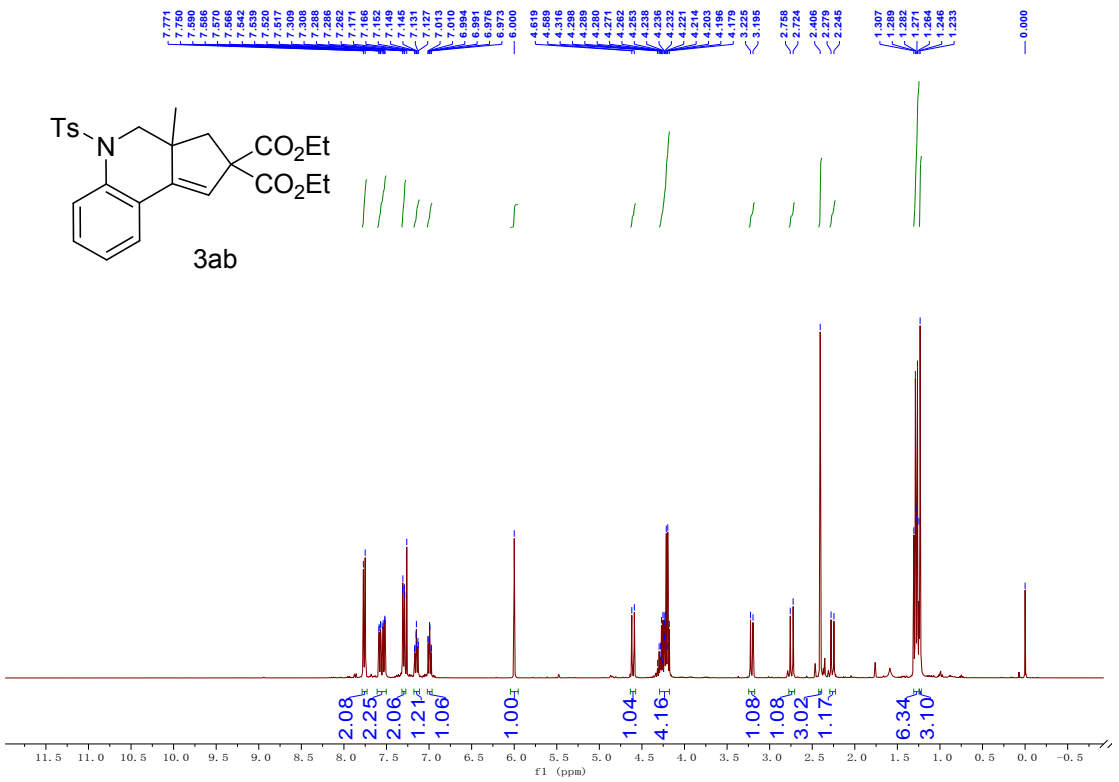

170.481
169.579
144.449
141.150
138.627
136.524
130.016
126.992
126.621
126.491
125.579
125.543
125.510
125.155
123.937
123.178
123.105
123.066
123.029
122.992
122.826
122.447
77.342
77.022
76.706
65.423
61.893
61.871
51.166
39.612
37.053
21.554
14.058
14.008
Ts
N
CO2Et
CO2Et
CF3
3ia
f1 (ppm)

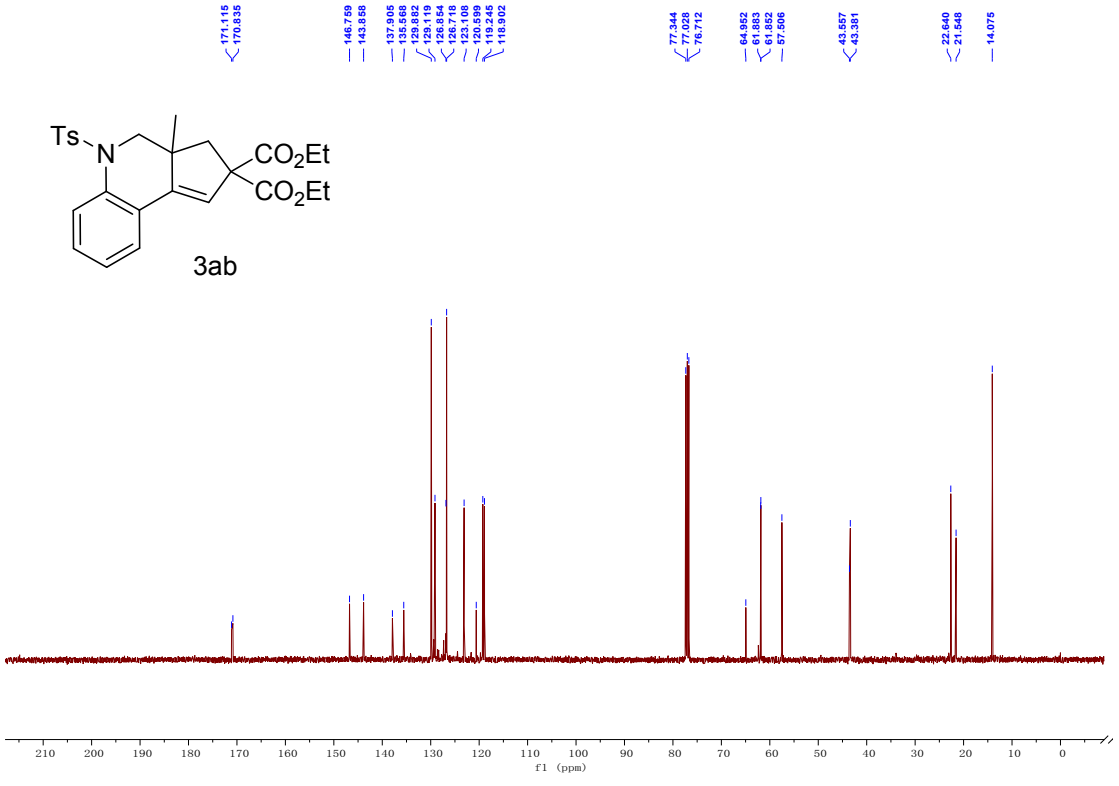

Ts
N
CO2Et
CO2Et
H3C
3ja
f1 (ppm)

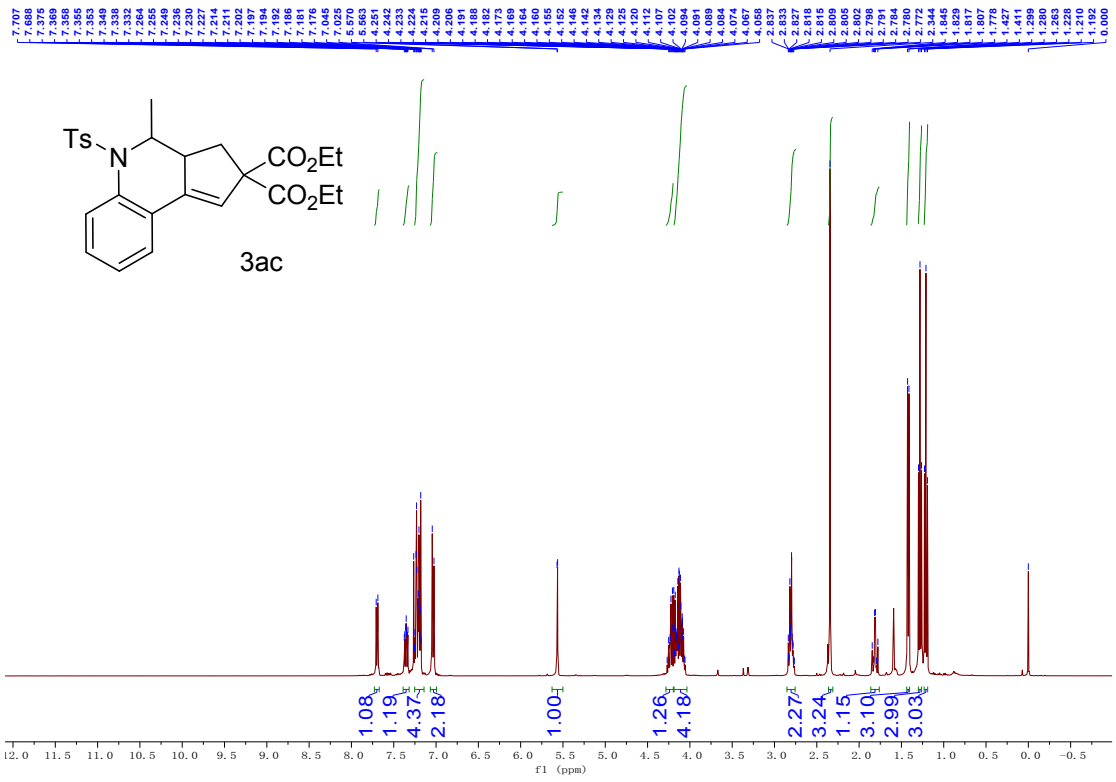

Ts
N
CO2Et
CO2Et
H3C
3ja
f1 (ppm)

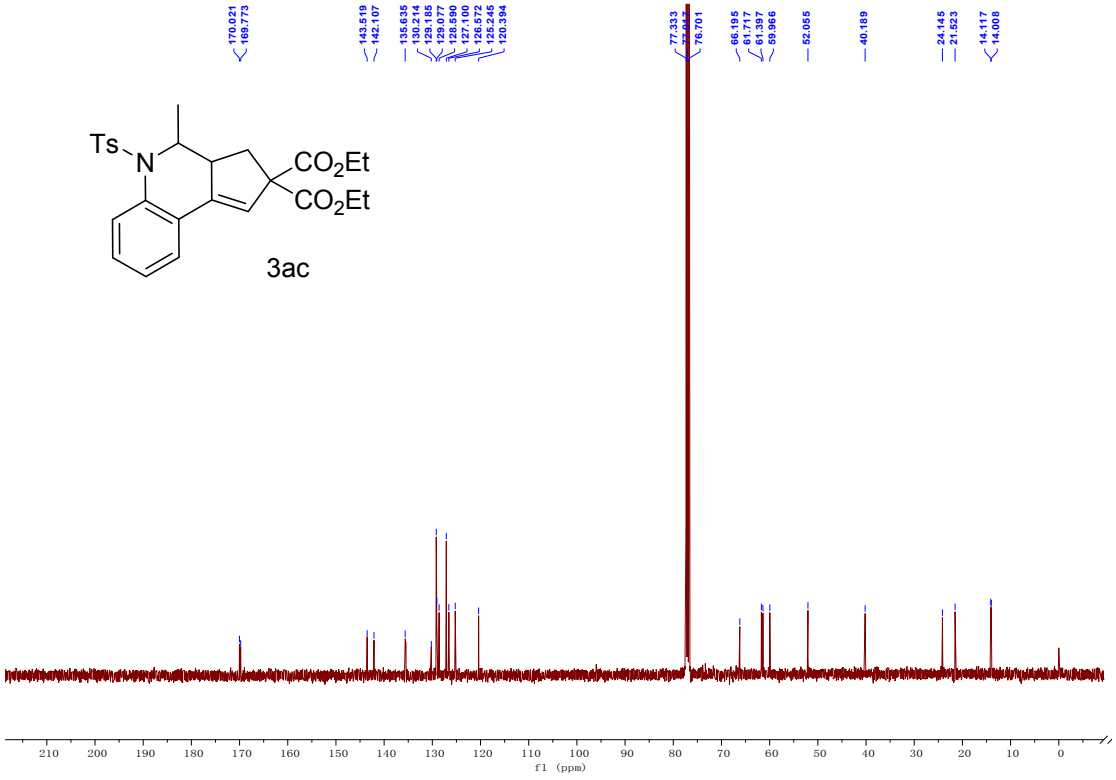

Ts
N
CO2Et
CO2Et
Cl
3ka
0.73
1.94
1.12
2.29
1.00
1.00
1.08
4.00
1.10
2.21
3.16
1.27
6.30
f1 (ppm)

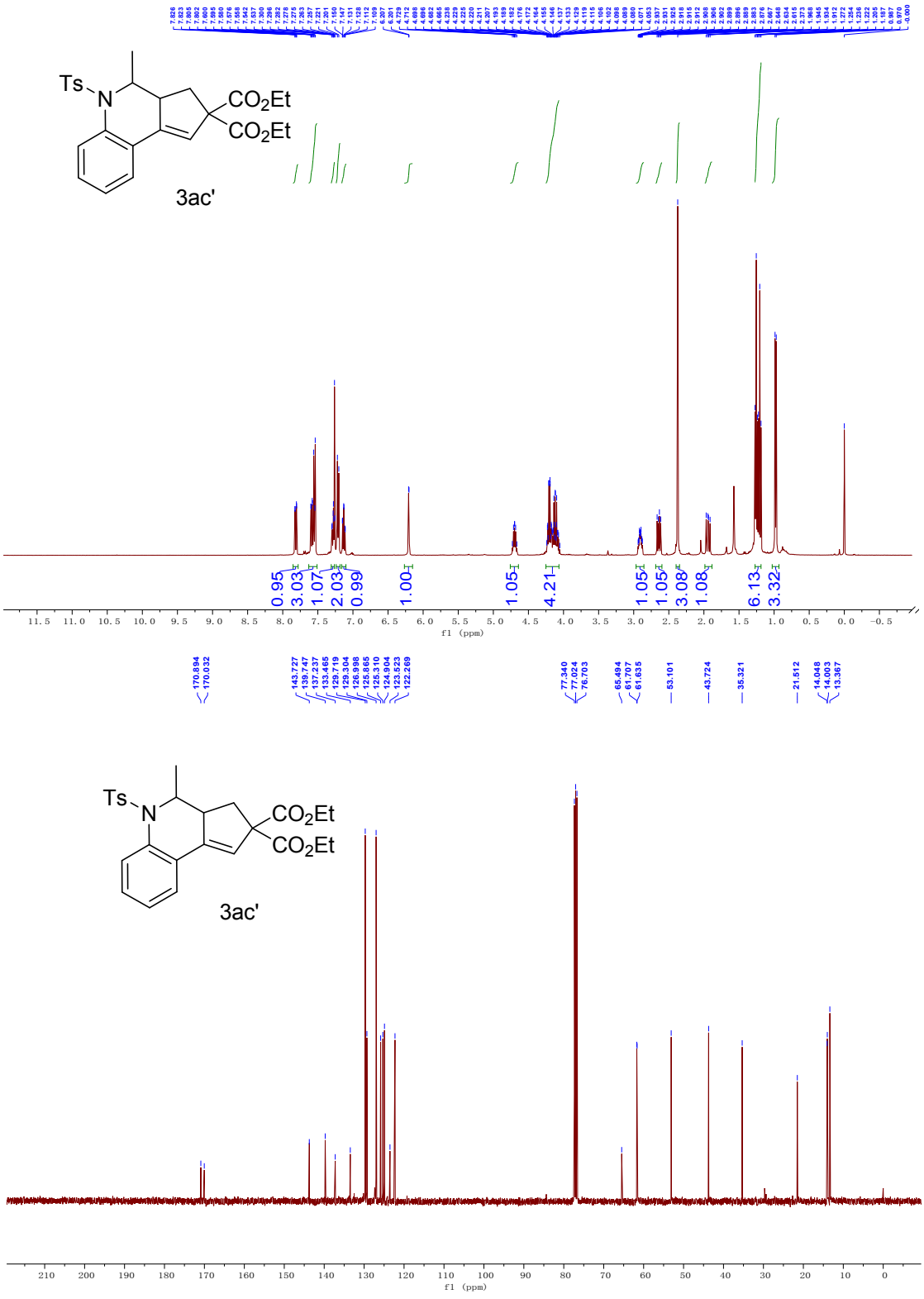

Ts
N
CO2Et
CO2Et
Cl
3ka
f1 (ppm)

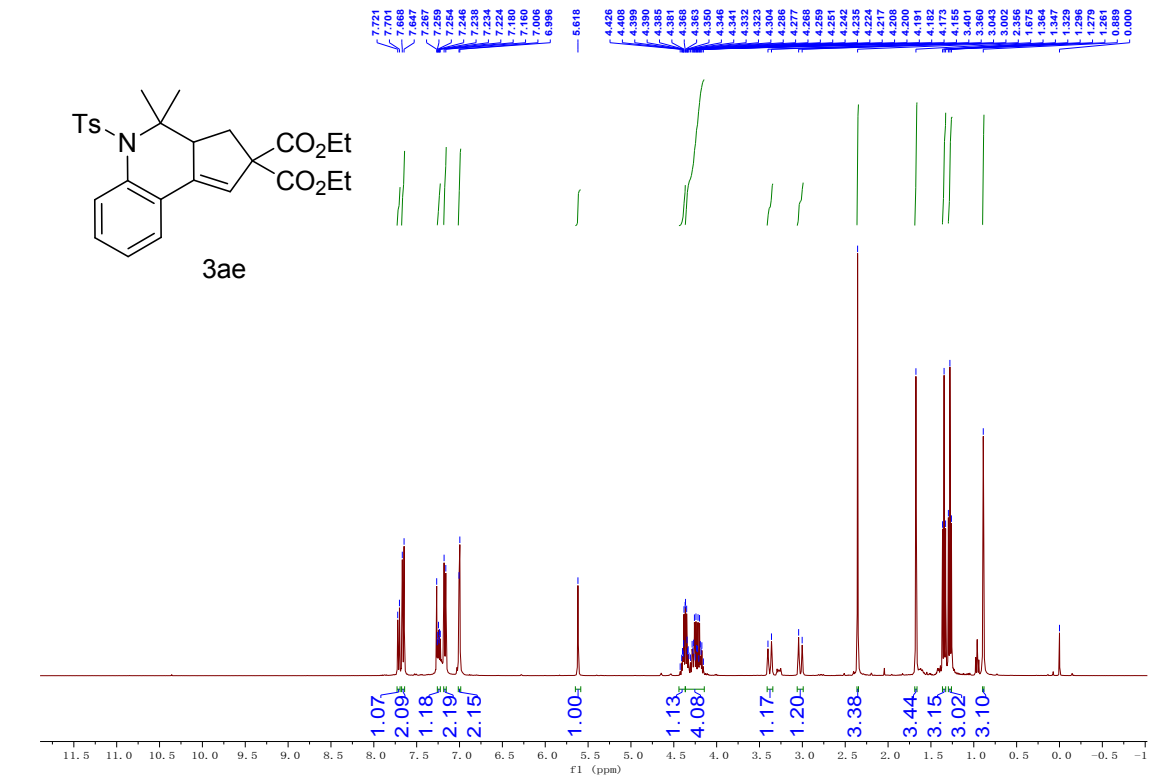

Ts
N
CO2Et
CO2Et
3ab
2.08
2.25
2.06
1.21
1.06
1.00
1.04
4.16
1.08
1.08
3.02
1.17
6.34
3.10
f1 (ppm)

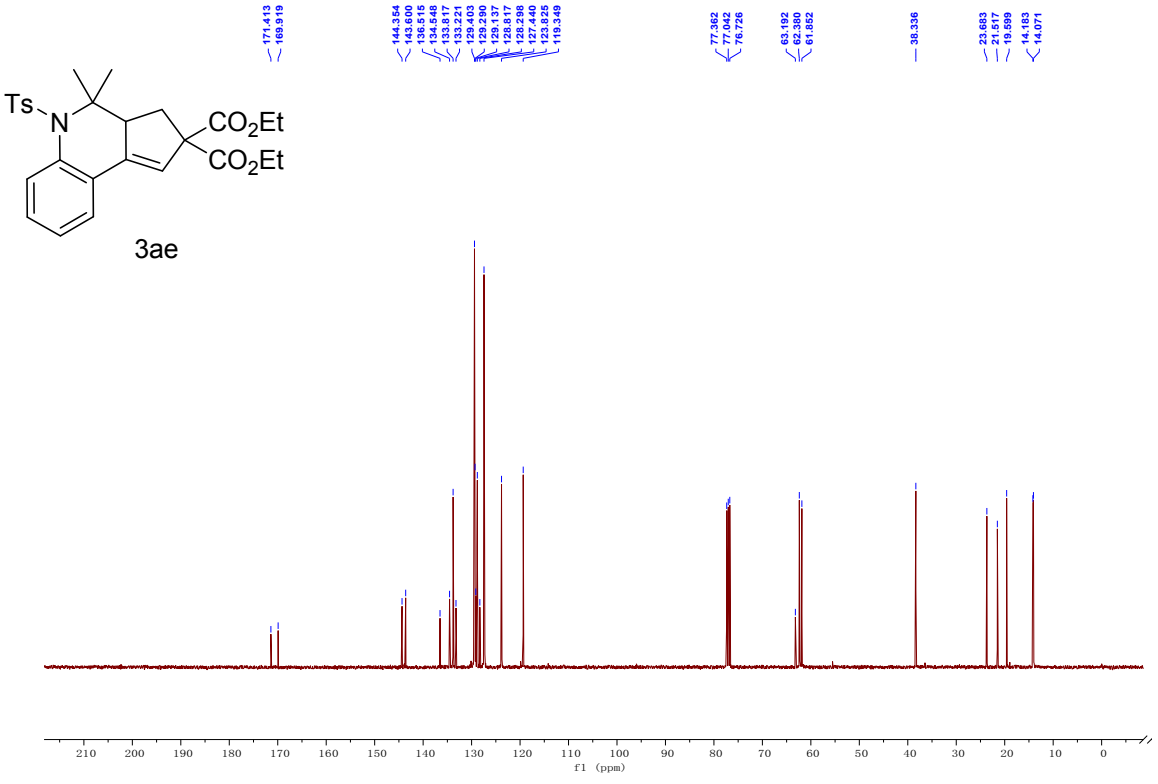

Ts
N
CO2Et
CO2Et
3ab
f1 (ppm)

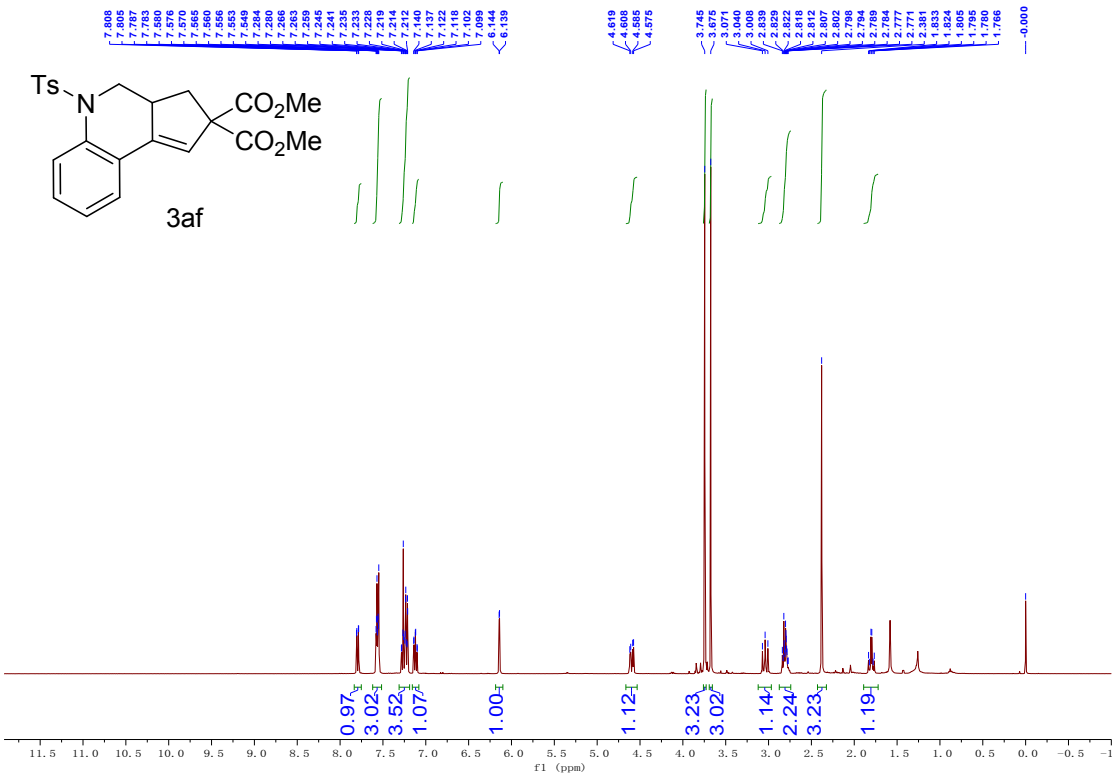

Ts
N
CO2Et
CO2Et
3ac
1.08
1.19
4.37
2.18
1.00
1.26
4.18
2.27
3.24
1.15
3.10
2.99
3.03
f1 (ppm)

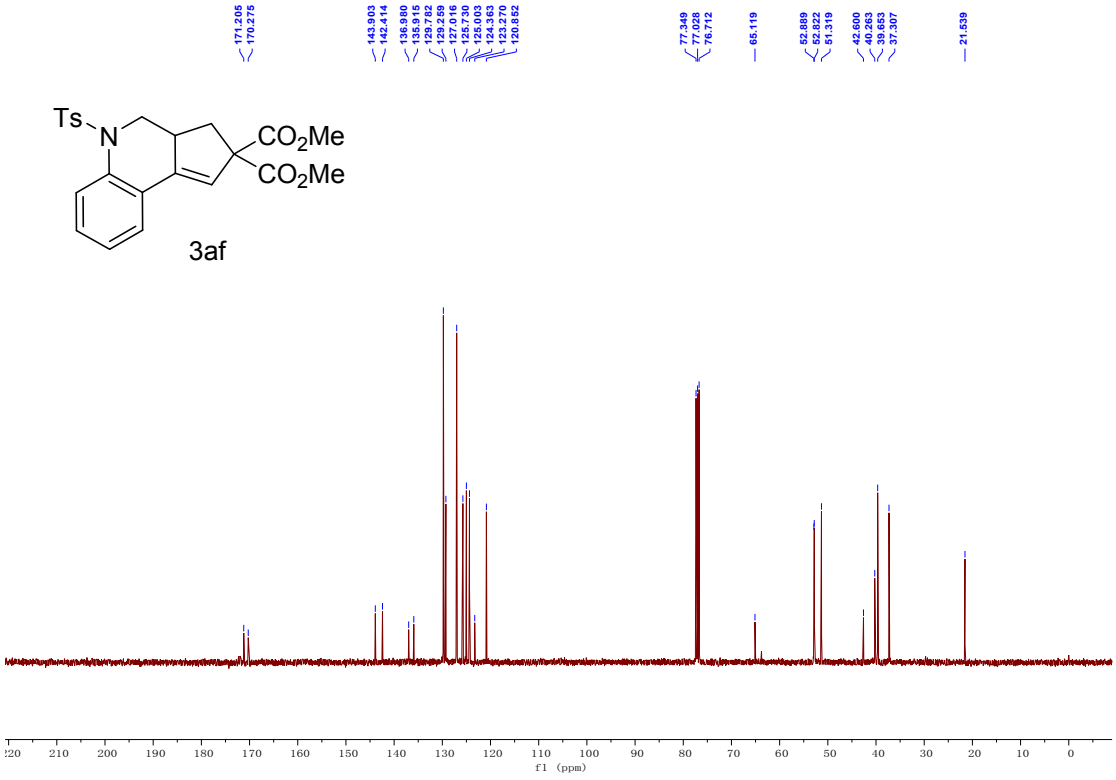

Ts
N
CO2Et
CO2Et
3ac
f1 (ppm)

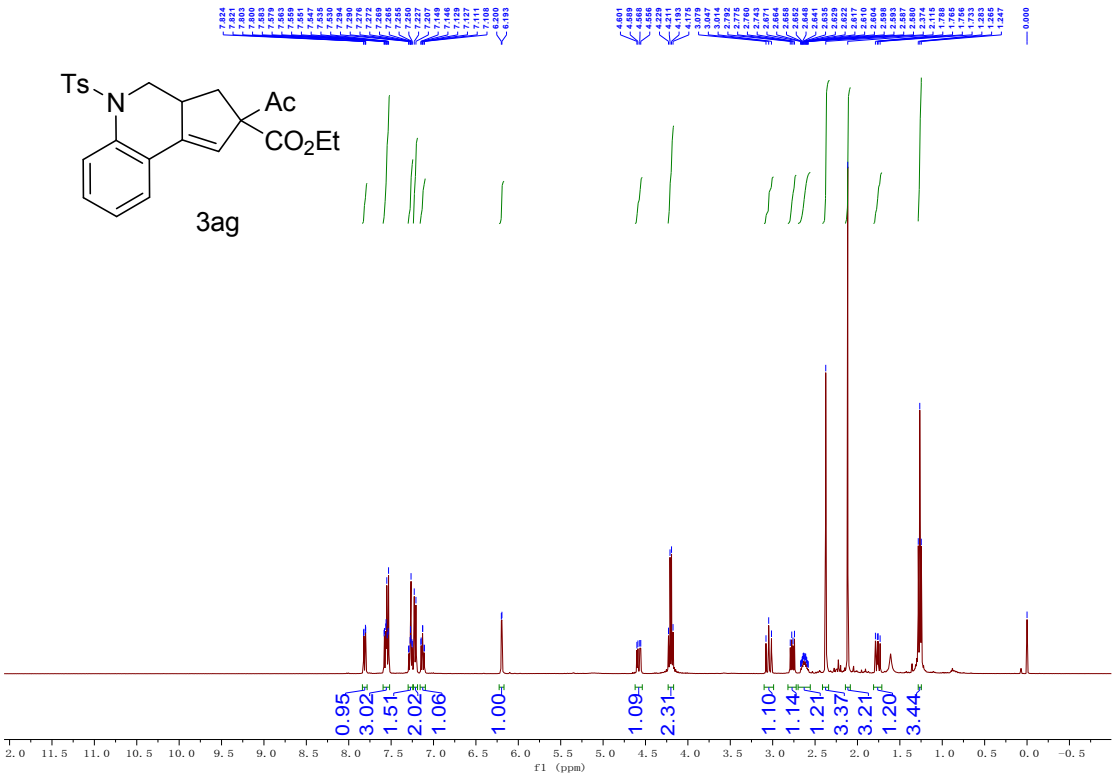

Ts
N
CO2Et
CO2Et
3ac'
0.95
3.03
1.07
2.03
0.99
1.00
1.05
4.21
1.05
1.05
3.08
1.08
6.13
3.32
f1 (ppm)
Ts
N
CO2Et
CO2Et
3ac'
f1 (ppm)

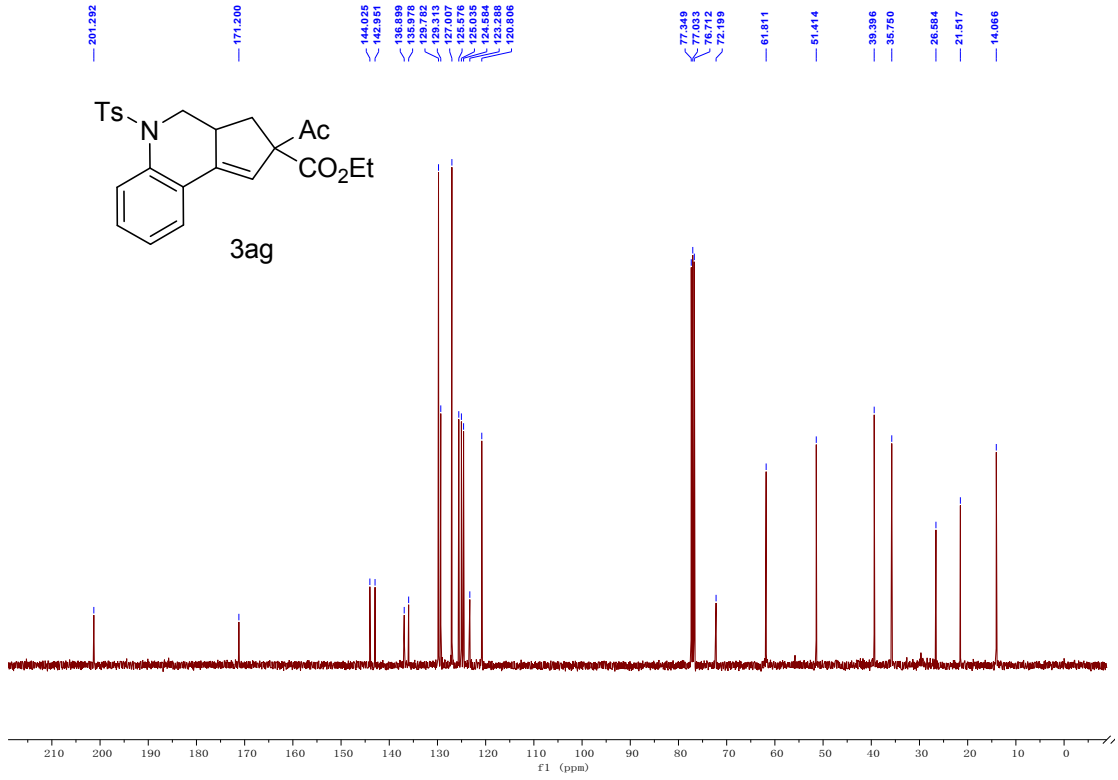

Ts
N
CO2Et
CO2Et
3ae
1.07
2.09
1.18
2.19
2.15
1.00
1.13
4.08
1.17
1.20
3.38
3.44
3.15
3.02
3.10
f1 (ppm)

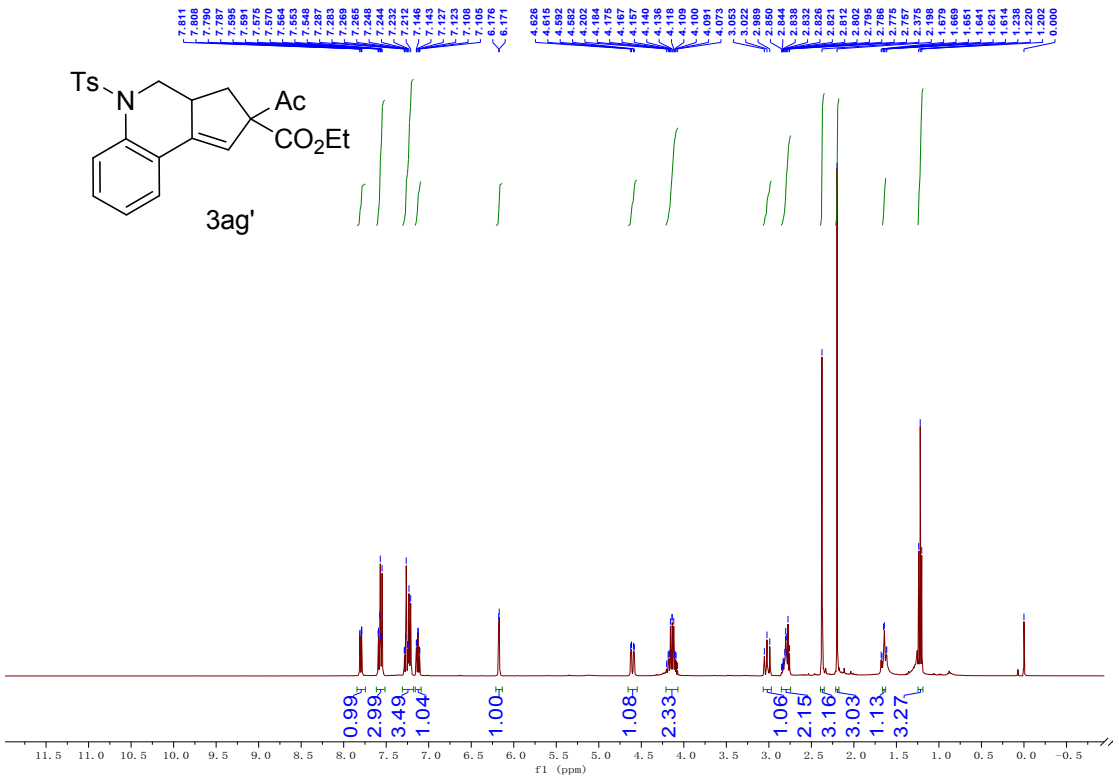

Ts
N
CO2Et
CO2Et
3ae
f1 (ppm)

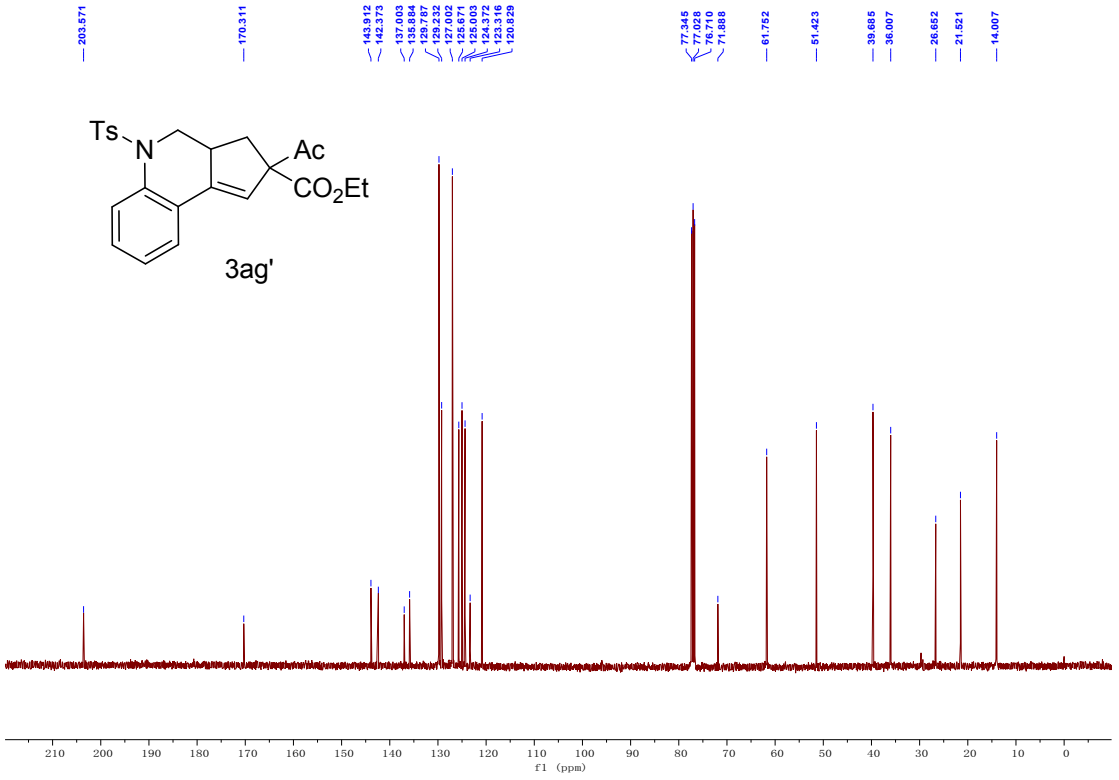

Ts
N
CO2Me
CO2Me
3af
f1 (ppm)

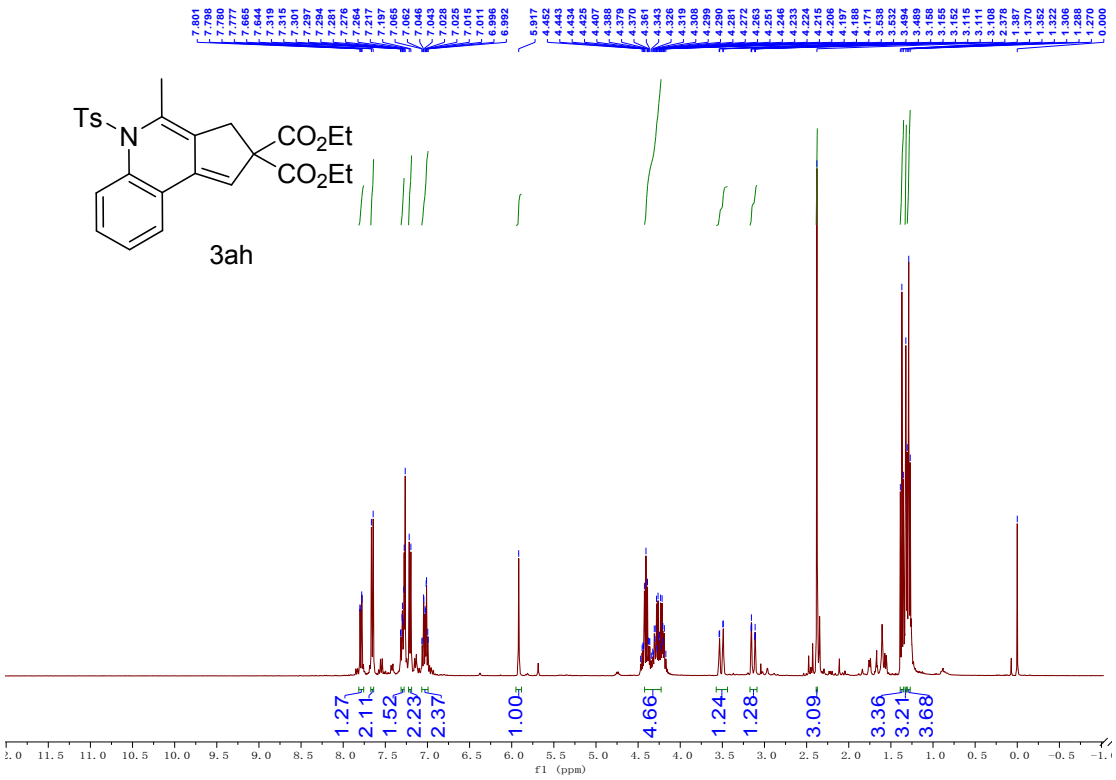

Ts
N
CO2Me
CO2Me
3af
f1 (ppm)

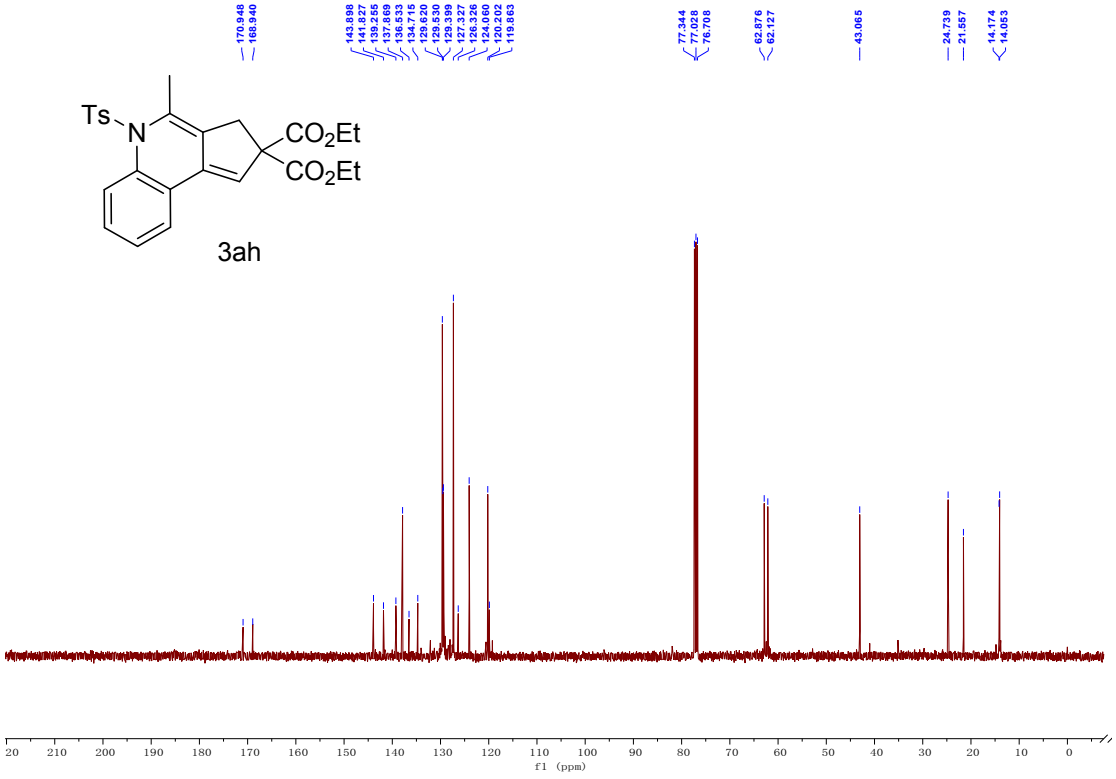

Ts
N
Ac
CO2Et
3ag
0.95
3.02
1.51
2.02
1.06
1.00
1.09
2.31
1.10
1.14
1.21
3.37
3.21
1.20
3.44
f1 (ppm)

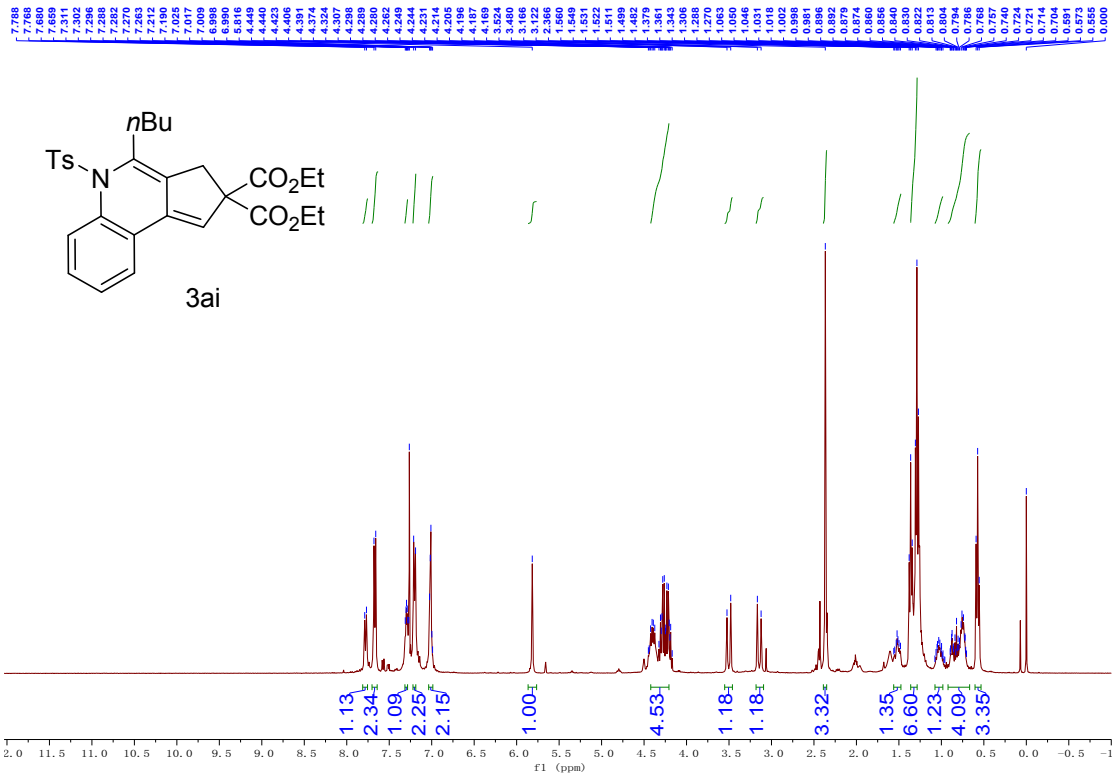

Ts
N
Ac
CO2Et
3ag
f1 (ppm)

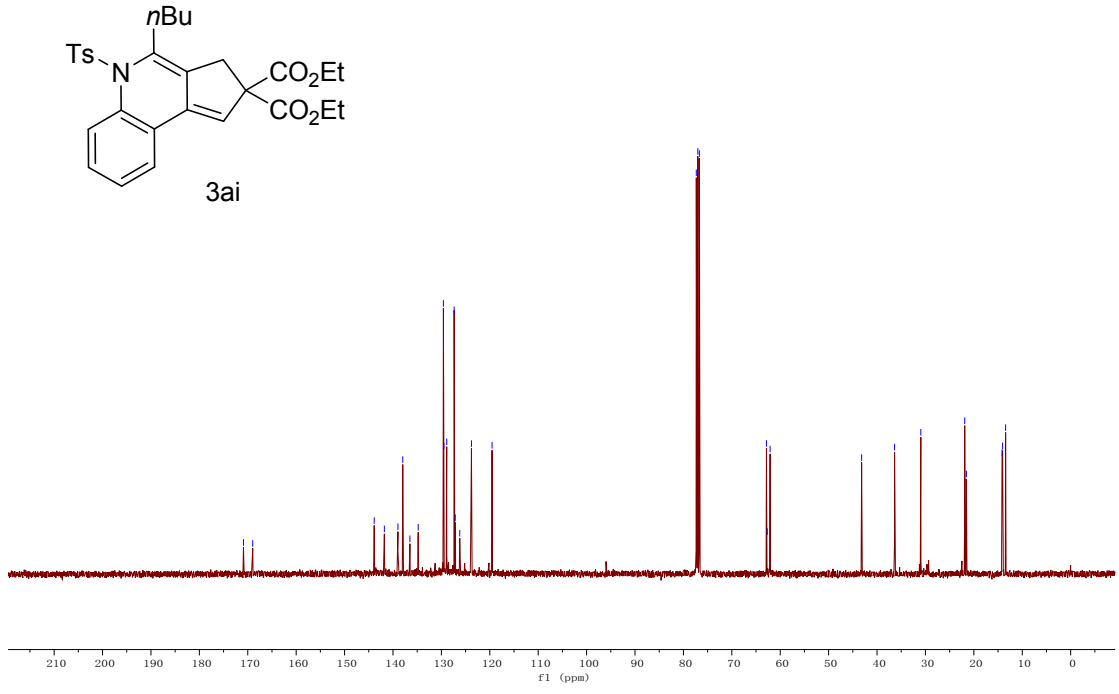

Ts
N
Ac
CO2Et
3ag'
0.99
2.99
3.49
1.04
1.00
1.08
2.33
1.06
2.15
3.16
3.03
1.13
3.27
f1 (ppm)

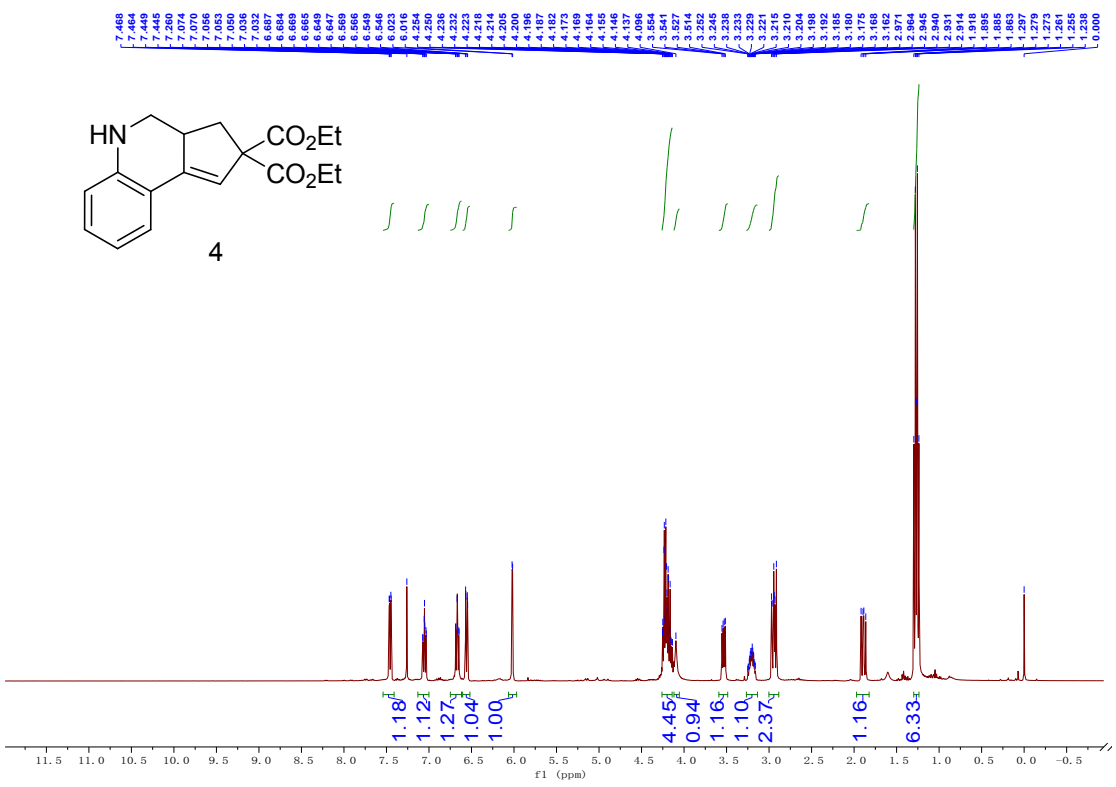

Ts
N
Ac
CO2Et
3ag'
f1 (ppm)

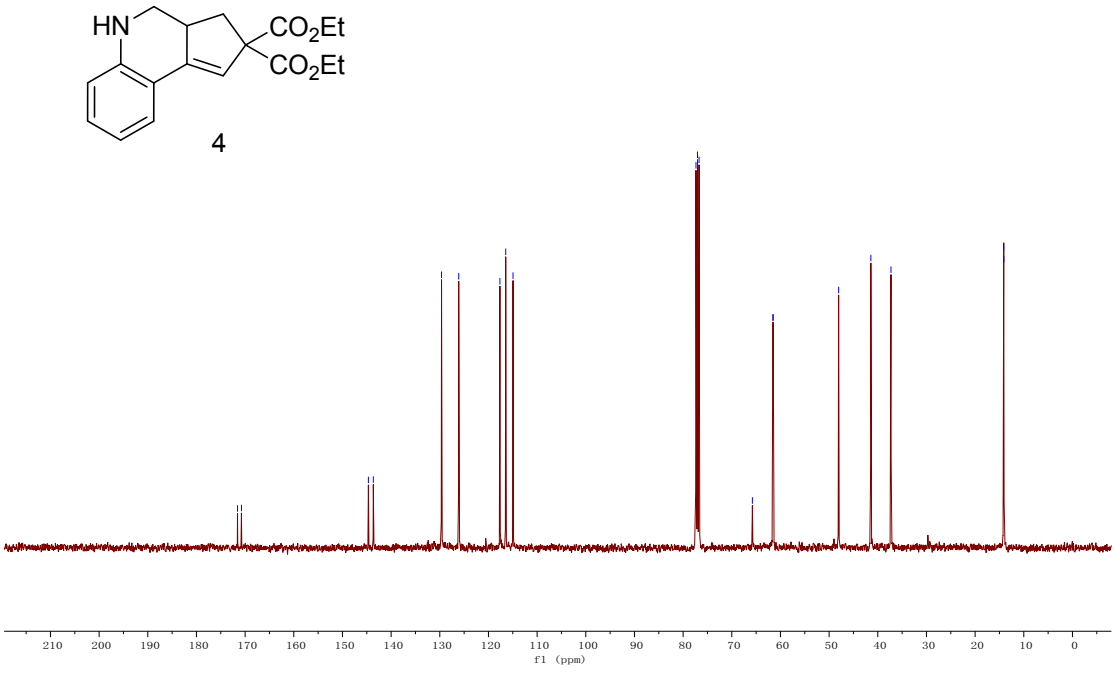

Ts
N
CO2Et
CO2Et
3ah
1.27
2.11
1.52
2.23
2.37
1.00
4.66
1.24
1.28
3.09
3.36
3.21
3.68
f1 (ppm)


Ts
N
CO2Et
CO2Et
3ah
f1 (ppm)


nBu
Ts
N
CO2Et
CO2Et
3ai
1.13
2.34
1.09
2.25
2.15
1.00
4.53
1.18
1.18
3.32
1.35
6.60
1.23
4.09
3.35
f1 (ppm)


nBu
Ts
N
CO2Et
CO2Et
3ai
f1 (ppm)


HN
CO2Et
CO2Et
4
1.18
1.12
1.27
1.04
1.00
4.45
0.94
1.16
1.10
2.37
1.16
6.33
f1 (ppm)


HN
CO2Et
CO2Et
4
f1 (ppm)