Supporting Information

Phosphine Mediated Sequential Annulation Process of 2-Tosylaminochalcones with MBH Carbonates to Construct Functionalized Aza-Benzobicyclo[4.3.0] Derivatives

Qinglong Zhang,[a] Yannan Zhu,[a] Hongxing Jin[a] and You Huang*[a,b,c]

a State Key Laboratory and Institute of Elemento-Organic Chemistry, College of Chemistry, Nankai University, Tianjin 300071, China

b Collaborative Innovation Center of Chemical Science and Engineering (Tianjin)

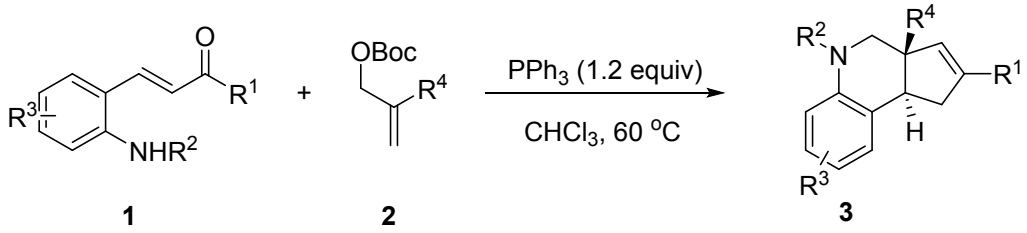
c Key Laboratory of Bioorganic Phosphorus Chemistry and Chemical Biology (Ministry of Education), Department of Chemistry, Tsinghua University, Beijing 100084 (China)

E-mail: hyou@nankai.edu.cn

I. General information

All reactions were carried out with the use of argon atmospheres. All the solvents were used without further purification. Yields refer to isolated compounds. Reactions were monitored by TLC using a UV lamp as a visualizing agent. All ^{1}H NMR, ^{13}C NMR were recorded in $CDCl_3$. The ^{1}H NMR was recorded at 400MHz, ^{13}C NMR was recorded at 101MHz. ^{19}F NMR was recorded at 376 MHz. All shifts are reported in ppm as downfield from TMS as standard. Multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Coupling constants J are reported in Hz. HRMS were obtained on an IonSpec FT-ICR mass spectrometer with ESI resource. Melting points were measured on a RY-I apparatus and are reported uncorrected. 2'-AminoChalcone **1** [1] and MBH carbonates [2] were prepared according to the known methods

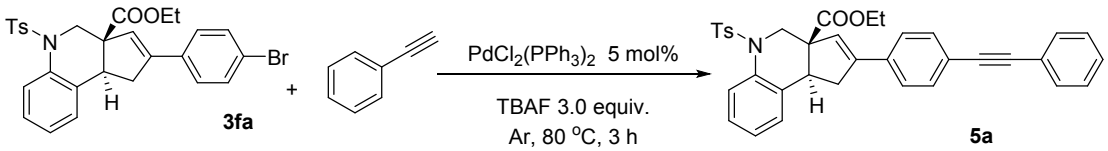
II. General procedure for the synthesis of Benzobicyclo[4.3.0] derivatives



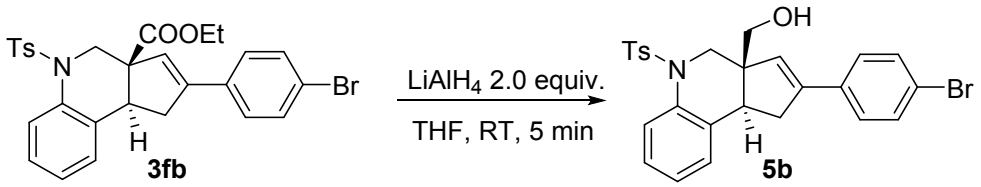
1 **2** **3**

2'- AminoChalcone **1** (0.1 mmol) , MBH carbonates **2** (0.1 mmol) and $CHCl_3$ (1.5 ml) were added to a dry flask, at the temperature of 60℃. Then PPh_3 (0.12 mmol) was added. This solution was stirred at 60℃ until the complete consumption of the starting materials monitored by TLC. After the removal of the solvent, the residue was subjected to chromatography on a silicagel (200-300 mesh) column using petroleum ether/dichloromethane (8:1-5:1) as eluent to afford product **3**.

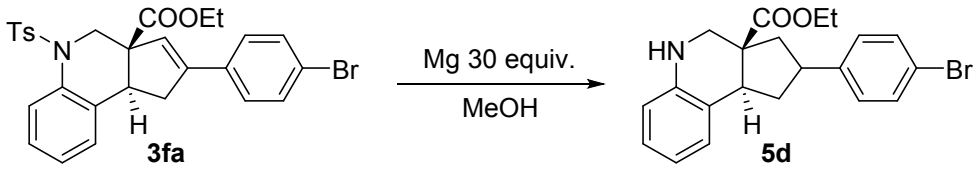
III Synthetic Transformation of 3fa



A mixture of **3fa** (0.1 mmol), alkyne (0.15 mmol), $PdCl_2(PPh_3)_2$ (5 mol%), and $TBAF{\cdot}3H_2O$ (3 eq) was stirred under Ar at 80 °C for the desired time until complete consumption of starting material as monitored by TLC. After the mixture was washed with water, extracted with CH_2Cl_2, and evaporated, the residue was purified by column chromatography on silica gel (gradient eluant: petroleum ether/ethyl acetate 5:1) to afford coupled product **5a**.(57.3 mg, yield: 96%)

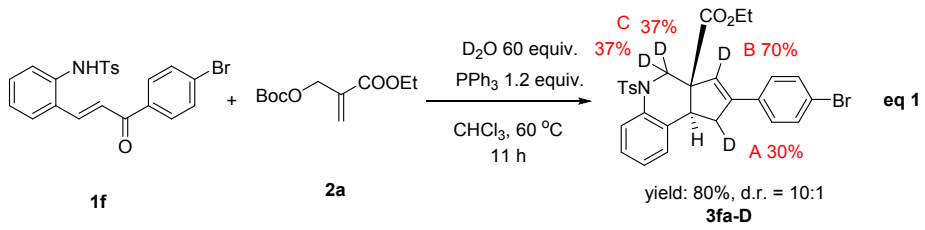


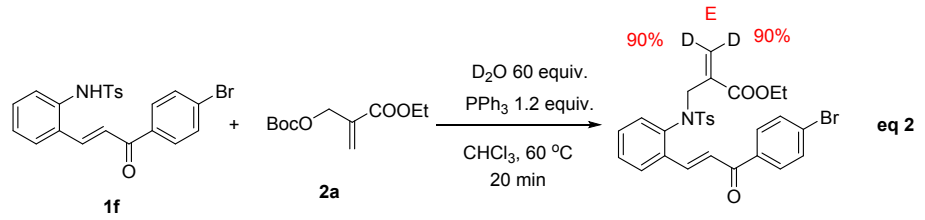
To a suspension of lithium aluminium tetrahydride (0.2 mmol) in THF (5 mL) was added **3fb** (0.1 mmol) in one portion, mixture was stirred 5 min at rt. NH_4Cl (aq) was added in small portions. Then, extracted with CH_2Cl_2, and dried with Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (gradient eluant: petroleum ether/ethyl acetate 4:1) to afford coupled product **5b.** 36 mg, yield: 70%)

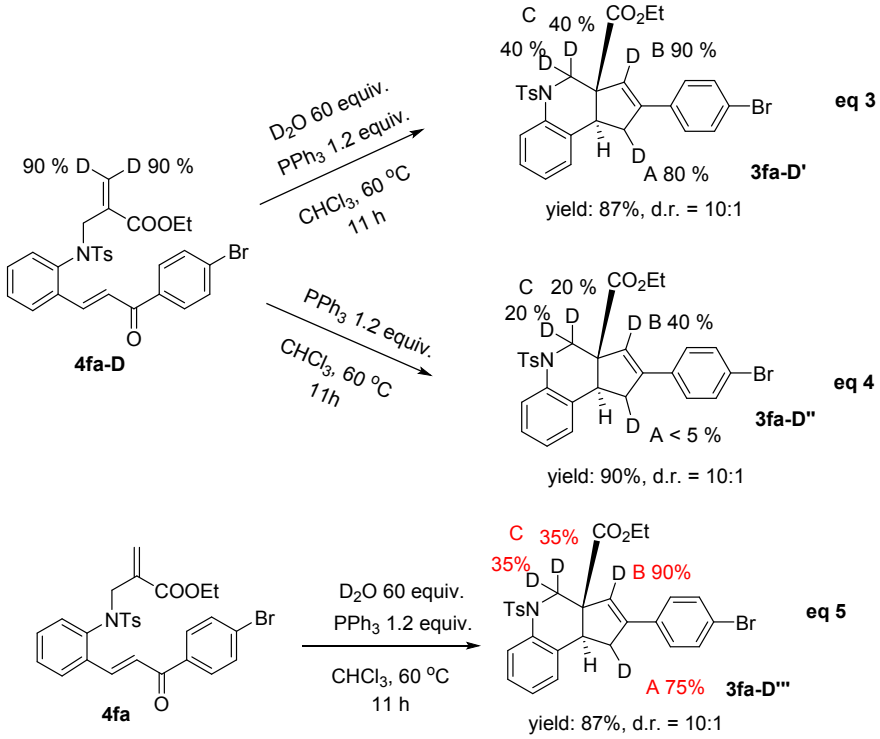


The substrate **3fa** (0.4 mmol) was dissolved in a methanol (5 ml) . Then Mg-powder (30 equiv.) was added and the mixture ultrasonicated (300W, 40 KHz) for 3 h, whereby the mixture warms slightly. When reduction was normally complete (TLC), the mixture was poured into 25 mL of dilute hydrochloric acid and ice and extracted with ethyl acetate, the extracts were washed well with dilute KOH and brine and dried over $MgSO_4$, and then the solvent was removed. The crude product was purified by column chromatography on silica gel (gradient eluant: petroleum ether/ethyl acetate 6:1) to afford product **5d (**30 mg, yield: 75%)

IV. Analytical Data for The deuterated experimental

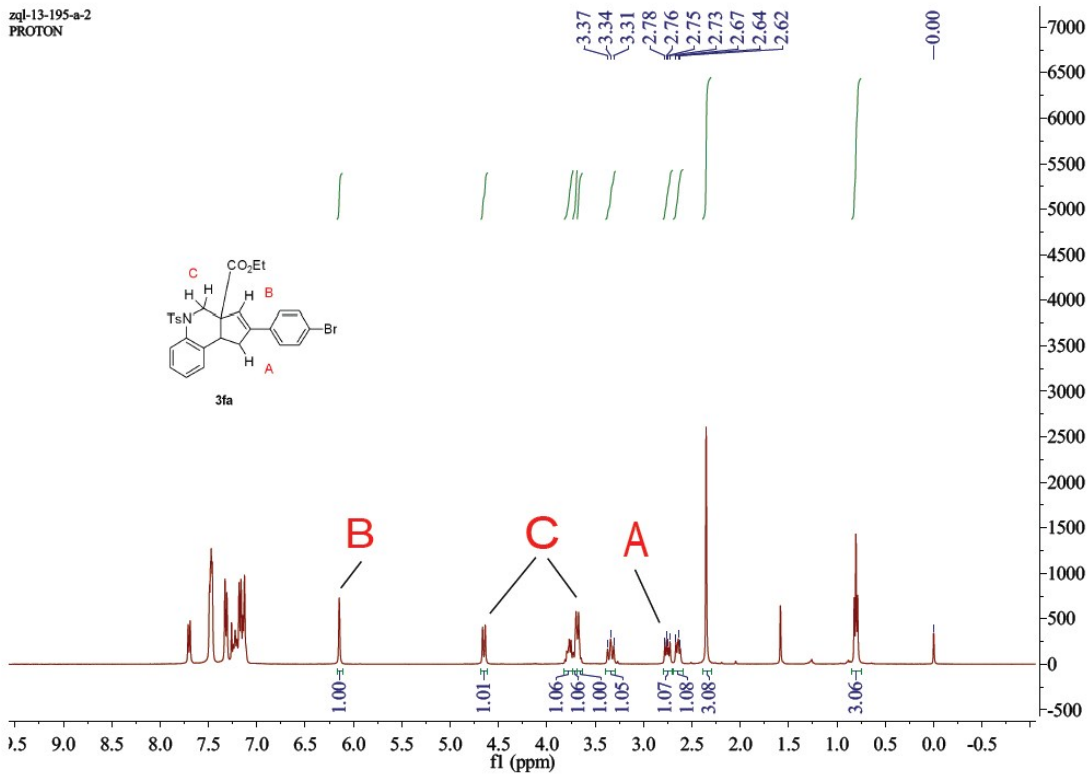


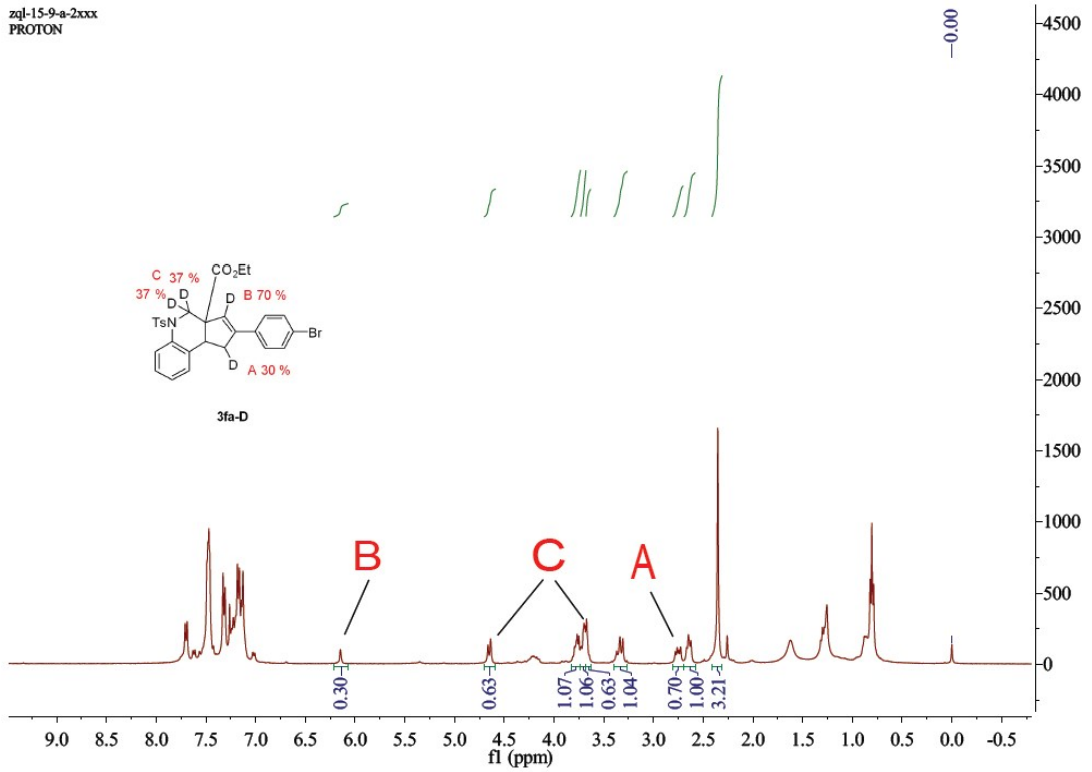


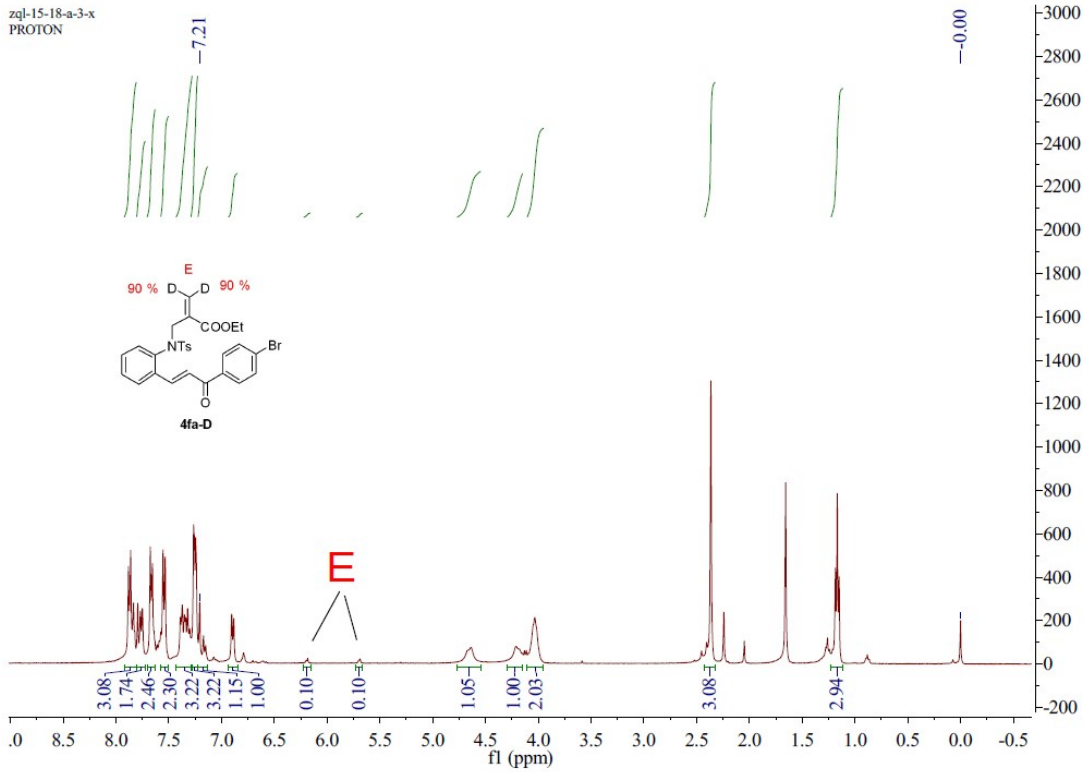


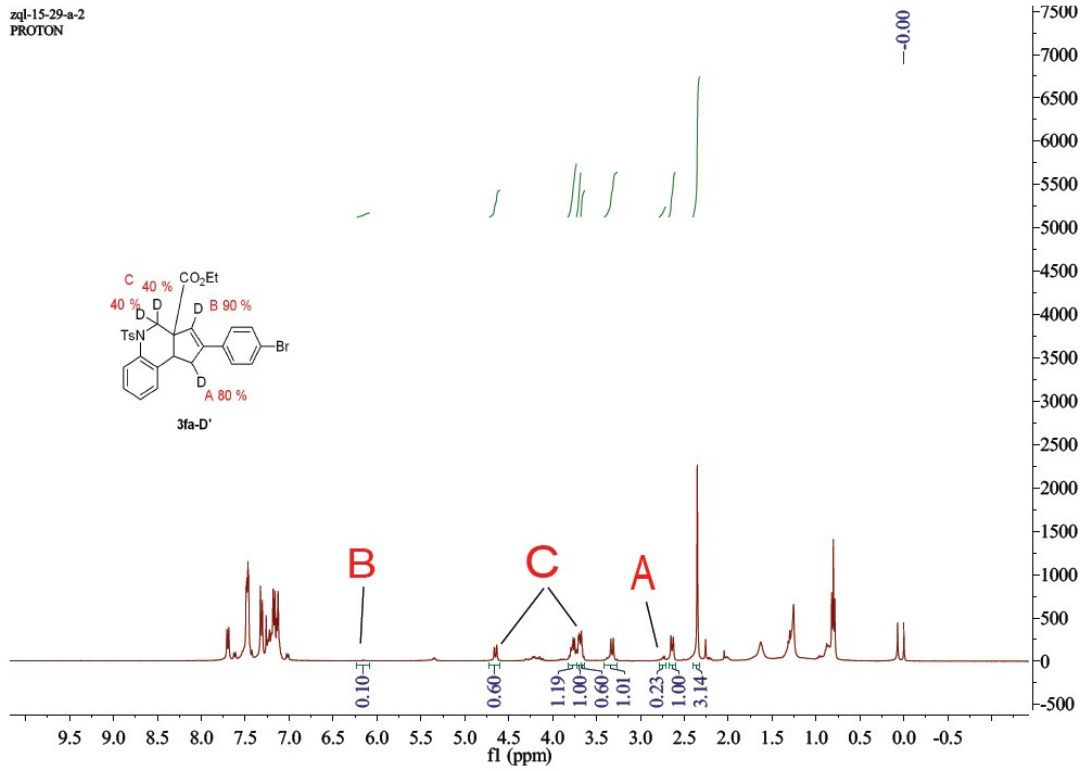
The deuterium labeling experiment of 2-tosyl-aminochalcones **1f** with **2a** in D2O at standerd condtion provided the desired product **3fa-D** in 80% yield with 30% exchange of **D** at the $\mathbf{C_A}$ position, 70% at the $\mathbf{C_B}$ position, 37% at the $\mathbf{C_C}$ position (**eq 1**). If we conducted **1f** with **2a** in D2O and stop the reaction in 20 min, the intermediate **4fa-D** was obtained in 82% yield with 90% exchange of **D** at the $\mathbf{C_E}$ position and 0% at the $\mathbf{C_C}$ position (**eq 2**). Then, **4fa-D** was used in D2O at standerd condtion, provided the desired product **3fa-D'** in 87% yield with $\mathbf{C_A}$ (80% D), $\mathbf{C_B}$ (90% D), $\mathbf{C_C}$ (40% D). If **4fa-D** was used in standerd condtion, provided the desired product **3fa-D"** in 90% yield with $\mathbf{C_A}$ (< 5%

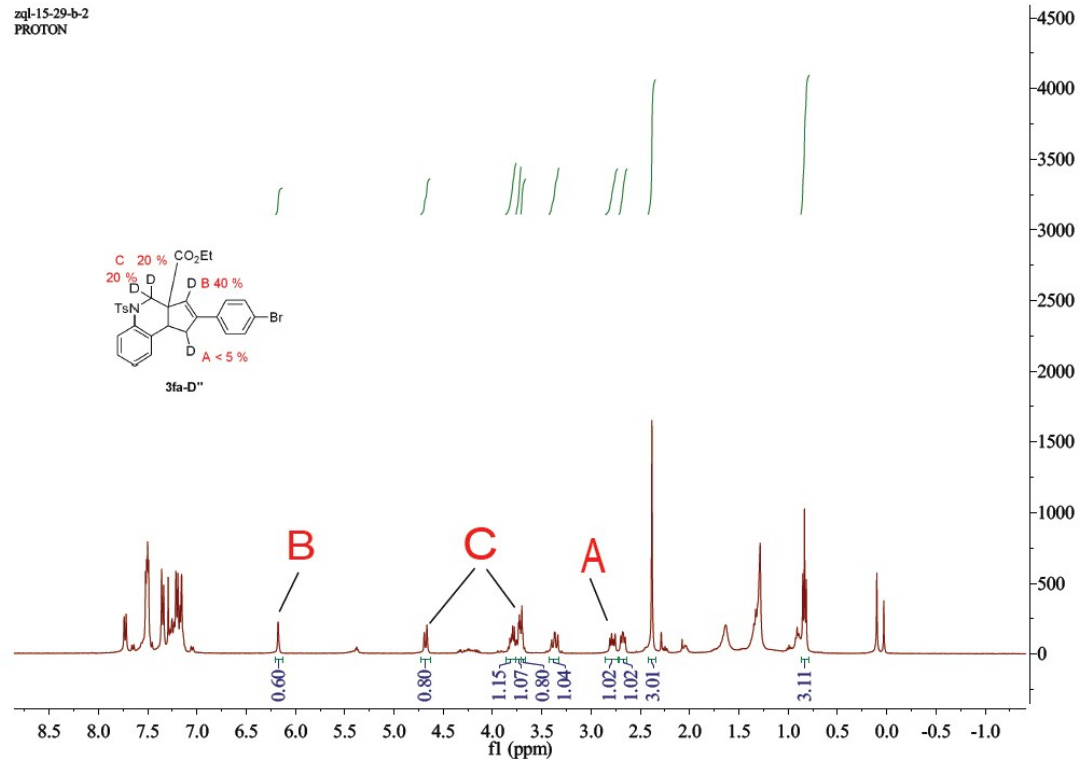
D), $\mathbf{C_B}$ (40% D), $\mathbf{C_C}$ (20% D). **3fa-D'''** was obtained in 87% yield with $\mathbf{C_A}$ (75% D), $\mathbf{C_B}$ (90% D), $\mathbf{C_C}$ (35% D) from 4fa in D2O at standerd condtion.






zql-15-18-a-3-x
PROTON
7.21
0.00
E
90 %
D
D
90 %
COOEt
NTs
Br
O
4fa-D
E
3.08
1.74
2.46
2.30
3.22
3.22
1.15
1.00
0.10
0.10
1.05
1.00
2.03
3.08
2.94
fl (ppm)


zql-15-29-a-2
PROTON
0.00
C
40 %
CO2Et
40 %
D
D
D
B 90 %
TsN
Br
D
A 80 %
3fa-D'
B
C
A
0.10
0.60
1.19
1.00
0.60
1.01
0.23
1.00
3.14
fl (ppm)


zql-15-29-b-2
PROTON
C 20 %
20 %
D
D
CO2Et
D B 40 %
TsN
Br
D
A < 5 %
3fa-D''
B
C
A
0.60
0.80
1.15
1.07
0.80
1.04
1.02
1.02
3.01
3.11
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
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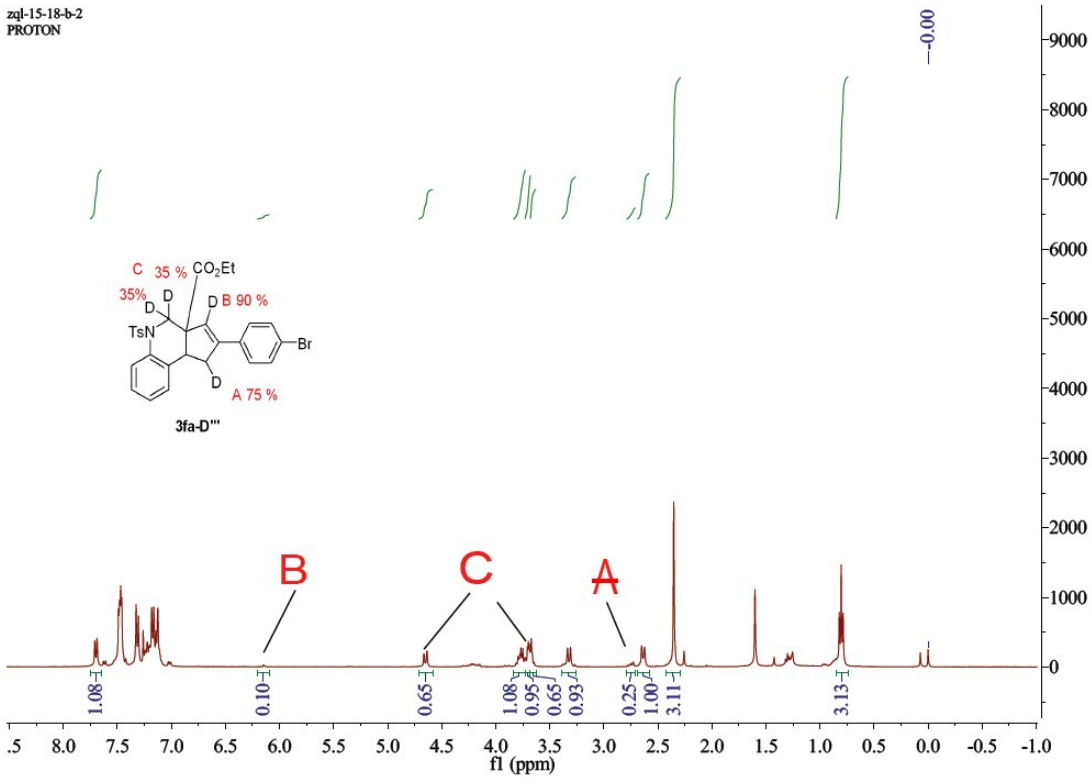
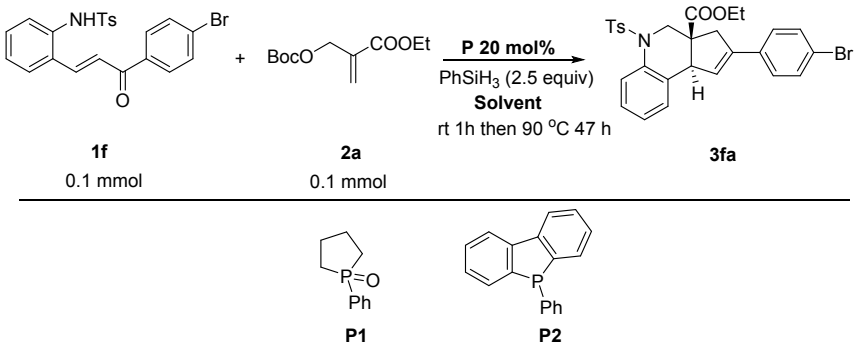
4000
3500
3000
2500
2000
1500
1000
500
0


zql-15-18-b-2
PROTON
-0.00
C 35 %
35%
D
D
CO2Et
D B 90 %
TsN
Br
D
A 75 %
3fa-D'''
B
C
A
1.08
0.10
0.65
1.08
0.95
0.65
0.93
0.25
1.00
3.11
3.13
.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
9000
8000
7000
6000
5000
4000
3000
2000
1000
0

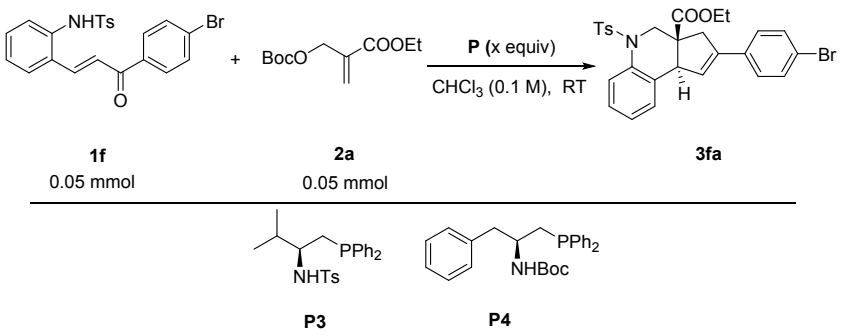
V. Catalytic Reaction study.



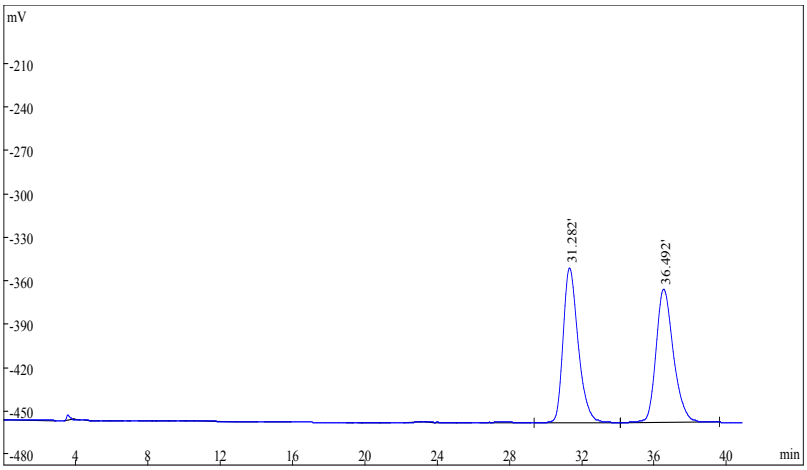
entry	**P** (x equiv)	Solvent	T(°C)	T(h)	Yield(%)	d.r.
1	**PBu_3** (0.1)	toluene	rt-125 °C	48 h	30	5:1
2	**PPh_3** (0.1)	toluene	rt-125 °C	48 h	< 5%	-
3	**P1** (0.2)	toluene	rt-90 °C	48 h	trace	-
4	**P1** (0.2)	$CHCl_3$	rt-80 °C	48 h	trace	-
5	**P1** (0.2) + **PPh_3** (0.1)	toluene	rt-90 °C	48 h	27%	5:1
6	**P2** (0.2)	toluene	rt-90 °C	48 h	15%	5:1

When PBu_3(0.1 equiv) was used in the reaction, 30% yield of **3fa** was isolated. **PPh_3** was used, 5% yield of **3fa** indicated that it is hard to make **O=PPh_3** transfer to **PPh_3** using this condition. When **P1**(V) was used, bad result was also obtained. Due to the first step from **1f** to produce **4fa** rapidly. Initially, the reaction was prevented without the presence of trivalent phosphonie. Meanwhile high temperature makes the reaction complexed before the formation of **4fa**. The formation of **4fa** is essential to the reaction. The existence of trivalent phosphine is crucial. Actually, when PPh_3 plus **P1** or **P2** were used, that still could not get a better result in this time.

VI. Enantioselective Reaction study.

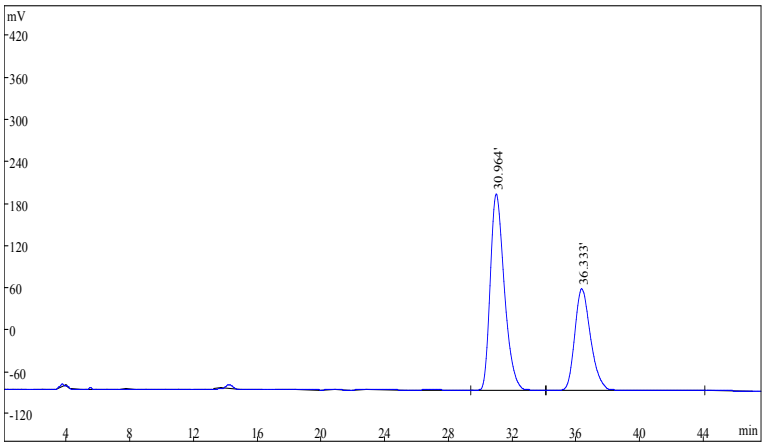


entry	**P** (x equiv)	t(h)	Yield(%)	d.r.	ee value of major diastereomer **3fa** (%)
1	**P3** (0.2)	24 h	trace	-	-
2	**P3** (1.2)	24 h	trace	-	-
3	**P4** (0.2)	24 h	10	5:1	25.7
4	**P4** (1.2)	24 h	75	5:1	25.7



序号	保留时间	浓度	峰面积	峰高
1	31.282	49.95	6231782	107545
2	36.492	50.05	6244198	92846
总计		100	12475980	200391

Racemic **3fa**

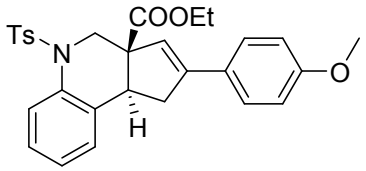


序号	保留时间	浓度	峰面积	峰高
1	30.964	62.84	17417270	281172
2	36.333	37.16	10298215	146301
总计		100	27715485	427473

Enantiomerically enriched **3fa**

VII. Analytical Data for Compounds Benzobicyclo[4.3.0] derivatives(3).

Ethyl 2-(4-methoxyphenyl)-5-tosyl-1,4,5,9b-tetrahydro-3aH-cyclopenta[c]quinolone-3a-carboxylate (3aa)



3aa

Yield: 52%; White solid; m.p. 159-160 °C

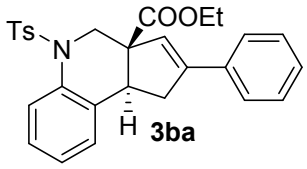
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 1H), 7.46 (dd, *J* = 22.9, 8.5 Hz, 4H), 7.28 – 7.21 (m, 1H), 7.18 (dd, *J* = 11.7, 6.3 Hz, 4H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.04 (s, 1H), 4.69 (dd, *J* = 10.6, 1.1 Hz, 1H), 3.86 (s, 3H), 3.71 (s, 2H), 3.70 – 3.64 (m, 1H), 3.41 – 3.27 (m, 1H), 2.80 (dd, *J* = 14.3, 7.4 Hz, 1H), 2.70 – 2.59 (m, 1H), 2.38 (s, 3H), 0.83 (t, *J* = 7.1 Hz, 3H)..

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.07, 159.86, 148.98, 143.51, 135.89, 133.21, 129.60, 128.04, 127.26, 126.99, 126.81, 125.38, 124.99, 124.17, 121.82, 113.95, 62.45, 60.85, 55.39, 55.25, 48.20, 32.86, 21.56, 13.73.

IR (KBr, ν_{max},cm^{-1}): 3128, 2980, 2958, 2964, 2838, 1721, 1606, 1512, 1484, 1457, 1400, 1350, 1306, 1256, 1201, 1165, 1090, 1024, 943, 822, 757, 672, 593, 566, 546

HRMS (ESI): found: 504.1864 for $C_{29}H_{30}NO_5S$ ($[M+H]^+$): 504.1839

Ethyl 2-phenyl-5-tosyl-1,4,5,9b-tetrahydro-3aH-cyclopenta[c]quinoline-3a-carboxylate(3ba)



3ba

Yield: 74%; White solid; m.p. 139-140 °C

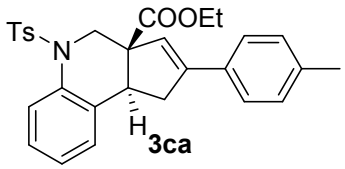
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 7.1 Hz, 4H), 7.41 – 7.29 (m, 3H), 7.25 – 7.19 (m, 1H), 7.19 – 7.09 (m, 3H), 6.15 (s, 1H), 4.67 (d, *J* = 10.5 Hz, 1H), 3.87 – 3.55 (m, 3H), 3.36 (t, *J* = 11.7 Hz, 1H), 2.79 (dd, *J* = 14.3, 7.4 Hz, 1H), 2.69 – 2.56 (m, 1H), 2.35 (s, 3H), 0.81 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.89, 149.61, 143.58, 136.05, 135.80, 135.28, 133.13, 129.63, 128.61, 128.53, 127.06, 126.80, 125.93, 125.48, 125.08, 124.19, 124.00, 62.51, 60.94, 55.10, 48.21, 32.80, 21.58, 13.74.

IR (KBr, ν_{max},cm^{-1}): 3143, 2979, 2924, 2854, 1721, 1485, 1453, 1400, 1350, 1199, 1166, 1089, 1021, 941, 843, 813, 753, 719, 663, 593, 566, 546

HRMS (ESI): found: 474.1744 for $C_{28}H_{28}NO_4S$ ($[M+H]^+$): 474.1734

Ethyl 2-(p-tolyl)-5-tosyl-1,4,5,9b-tetrahydro-3aH-cyclopenta[c]quinoline-3a-carboxylate(3ca)



Yield: 64%; White solid; m.p. 120-122 °C

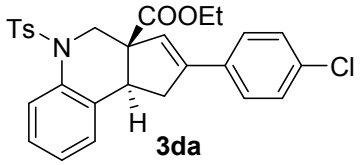
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 7.5 Hz, 2H), 7.36 (d, *J* = 7.4 Hz, 2H), 7.24 – 7.19 (m, 1H), 7.19 – 7.09 (m, 6H), 6.09 (s, 1H), 4.66 (d, *J* = 10.6 Hz, 1H), 3.71 (dd, *J* = 35.1, 8.7 Hz, 3H), 3.31 (dd, *J* = 28.1, 15.0 Hz, 1H), 2.77 (dd, *J* = 14.2, 7.4 Hz, 1H), 2.61 (d, *J* = 9.6 Hz, 1H), 2.35 (d, *J* = 2.3 Hz, 6H), 0.80 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.00, 149.45, 143.53, 138.54, 136.06, 135.84, 133.22, 132.50, 129.61, 129.27, 127.01, 126.80, 125.85, 125.45, 125.04, 124.18, 122.99, 62.47, 60.88, 55.17, 48.18, 32.79, 21.56, 21.27, 13.73.

IR (KBr, ν_{max},cm^{-1}):3055,3030,1980,2923,2860,1723,1600,1512,1484,1456,1351,1305,1202, 1166,1090,1022,943,813,756,737,723,704,673,593,565,546,466

HRMS (ESI): found: 488.1896 for $C_{29}H_{30}NO_4S$ ([M+H]$^+$): 488.1890

Ethyl 2-(4-chlorophenyl)-5-tosyl-1,4,5,9b-tetrahydro-3aH-cyclopenta[c]quinoline-3a-carboxylate(3da)



Yield: 79%; White solid; m.p.142-143 °C

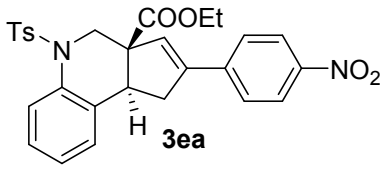
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.1 Hz, 1H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.38 (dd, *J* = 24.7, 8.5 Hz, 4H), 7.28 – 7.23 (m, 1H), 7.18 (dd, *J* = 15.1, 7.3 Hz, 4H), 6.16 (s, 1H), 4.68 (d, *J* = 10.6 Hz, 1H), 3.87 – 3.64 (m, 3H), 3.35 (dd, *J* = 26.5, 13.3 Hz, 1H), 2.79 (dd, *J* = 14.1, 7.4 Hz, 1H), 2.73 – 2.61 (m, 1H), 2.38 (s, 3H), 0.84 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.68, 148.55, 143.58, 136.08, 135.90, 134.27, 133.77, 132.80, 129.63, 128.75, 127.21, 127.14, 126.81, 125.33, 125.05, 124.63, 124.13, 62.54, 61.02, 54.94, 48.28, 32.85, 21.57, 13.72.

IR (KBr, ν_{max},cm^{-1}):3065, 2955, 2925, 2858,1722, 1646, 1599, 1488, 1456, 1401, 1350, 1201, 1165, 1090, 1013, 939, 816, 757, 721, 670, 593, 568, 546

HRMS (ESI): found: 508.1351 for $C_{28}H_{27}ClNO_4S$ ([M+H]$^+$): 508.1344

ethyl 2-(4-nitrophenyl)-5-tosyl-1,4,5,9b-tetrahydro-3aH-cyclopenta[c]quinoline-3a-carboxylate(3ea)



3ea

Yield: 89%; White solid; m.p. 175-176 °C

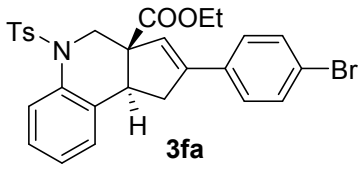
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.9 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 7.9 Hz, 2H), 7.49 (d, *J* = 7.6 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 1H), 7.17 (dd, *J* = 13.7, 7.5 Hz, 4H), 6.35 (s, 1H), 4.67 (d, *J* = 10.6 Hz, 1H), 3.84 – 3.66 (m, 3H), 3.48 – 3.35 (m, 1H), 2.83 (dd, *J* = 14.1, 7.5 Hz, 1H), 2.77 – 2.65 (m, 1H), 2.36 (s, 3H), 0.81 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.15, 147.97, 147.41, 143.69, 141.51, 136.08, 135.89, 132.30, 129.67, 128.69, 127.35, 126.81, 126.66, 125.30, 125.14, 124.11, 123.92, 62.75, 61.26, 54.59, 48.37, 32.93, 21.58, 13.72.

IR (KBr, ν_{max},cm^{-1}): 3125, 2981, 2925, 2854, 1722, 1596, 1516, 1486, 1455, 1399, 1342, 1201, 1165, 1090, 1014, 940, 856, 843, 813, 749, 720, 669, 593, 568, 546

HRMS (ESI): found: 519.1597 for $C_{28}H_{27}N_2O_6S$ ($[M+H]^+$): 519.1584

Ethyl 2-(4-bromophenyl)-5-tosyl-1,4,5,9b-tetrahydro-3aH-cyclopenta[c]quinoline-3a-carboxylate(3fa)



3fa

Yield: 94%; White solid; m.p. 122-123 °C

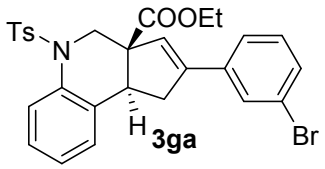
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.1 Hz, 1H), 7.47 (dd, *J* = 6.7, 4.4 Hz, 4H), 7.32 (d, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.15 (dd, *J* = 14.9, 7.3 Hz, 4H), 6.15 (s, 1H), 4.65 (d, *J* = 10.5 Hz, 1H), 3.83 – 3.61 (m, 3H), 3.32 (dd, *J* = 27.1, 14.6 Hz, 1H), 2.75 (dd, *J* = 14.2, 7.4 Hz, 1H), 2.70 – 2.57 (m, 1H), 2.35 (s, 3H), 0.80 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.64, 148.61, 143.60, 136.06, 135.87, 134.20, 132.79, 131.70, 129.64, 127.50, 127.14, 126.80, 125.34, 125.06, 124.75, 124.14, 122.45, 62.56, 61.03, 54.91, 48.27, 32.80, 21.58, 13.73.

IR (KBr, ν_{max},cm^{-1}): 3064, 2980, 2934, 2863, 1723, 1599, 1486, 1456, 1398, 1351, 1201, 1166, 1090, 1022, 1010, 944, 815, 757, 736, 722, 669, 593, 568, 546

HRMS (ESI): found: 552.0844 for $C_{28}H_{27}BrNO_4S$ ($[M+H]^+$): 552.0839

Ethyl 2-(3-bromophenyl)-5-tosyl-1,4,5,9b-tetrahydro-3aH-cyclopenta[c]quinoline-3a-carboxylate(3ga)



3ga

Yield: 9o%; White solid; m.p. 156-157 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 1H), 7.61 (s, 1H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.44 (dd, *J* = 18.7, 8.0 Hz, 2H), 7.31 – 7.26 (m, 2H), 7.19 (dt, *J* = 13.6, 8.3 Hz, 5H), 6.19 (s, 1H), 4.68 (d, *J* =

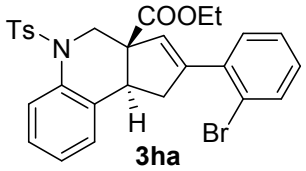
10.6 Hz, 1H), 3.86 – 3.66 (m, 3H), 3.36 (dd, *J* = 18.4, 6.8 Hz, 1H), 2.78 (dd, *J* = 14.3, 7.3 Hz, 1H), 2.71 – 2.61 (m, 1H), 2.39 (s, 3H), 0.84 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.59, 148.37, 143.62, 137.39, 136.03, 135.78, 132.79, 131.31, 130.10, 129.65, 129.04, 127.17, 126.79, 125.51, 125.47, 125.13, 124.48, 124.13, 122.81, 62.53, 61.07, 54.87, 48.24, 32.80, 21.59, 13.74.

IR (KBr, ν_{max},cm^{-1}): 3064, 2979, 2957, 2926, 2861, 1723, 1594, 1557, 1483, 1457, 1351, 1304, 1201, 1166, 1090, 1022, 945, 813, 774, 757, 670, 594, 570, 545

HRMS (ESI): found: 552.0849 for $C_{28}H_{27}BrNO_4S$ ($[M+H]^+$): 552.0839

Ethyl 2-(2-bromophenyl)-5-tosyl-1,4,5,9b-tetrahydro-3aH-cyclopenta[c]quinoline-3a-carboxylate(3ha)



3ha

Yield: 63%; White solid; m.p. 98-99 °C

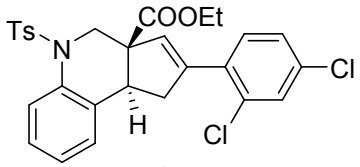
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.33 – 7.24 (m, 3H), 7.24 – 7.03 (m, 6H), 5.91 (d, *J* = 1.7 Hz, 1H), 4.61 (d, *J* = 10.8 Hz, 1H), 3.91 – 3.69 (m, 3H), 3.50 – 3.25 (m, 1H), 2.79 – 2.55 (m, 2H), 2.38 (s, 3H), 0.87 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.66, 150.64, 143.57, 138.11, 136.21, 135.85, 133.19, 132.94, 129.72, 129.61, 129.47, 129.28, 127.33, 127.13, 126.85, 125.71, 125.18, 124.01, 121.96, 62.68, 60.97, 54.57, 48.67, 35.52, 21.58, 13.83.

IR (KBr, ν_{max},cm^{-1}): 3065, 2979, 2929, 2902, 2860, 1723, 1599, 1483, 1464, 1352, 1201, 1167, 1090, 1023, 944, 813, 755, 668, 593, 567, 545

HRMS (ESI): found: 552.0844 for $C_{28}H_{27}BrNO_4S$ ($[M+H]^+$): 552.0839

Ethyl 2-(2,4-dichlorophenyl)-5-tosyl-1,4,5,9b-tetrahydro-3aH-cyclopenta[c]quinoline-3a-carboxylate(3ia)



3ia

Yield: 92%; White solid; m.p. 149-150 °C

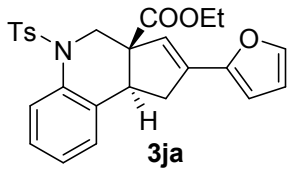
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 7.1 Hz, 4H), 7.37 (dt, *J* = 22.1, 7.0 Hz, 3H), 7.28 – 7.23 (m, 1H), 7.23 – 7.12 (m, 4H), 6.18 (s, 1H), 4.70 (d, *J* = 10.5 Hz, 1H), 3.90 – 3.62 (m, 3H), 3.39 (t, *J* = 11.7 Hz, 1H), 2.82 (dd, *J* = 14.3, 7.4 Hz, 1H), 2.74 – 2.59 (m, 1H), 2.38 (s, 3H), 0.84 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.89, 149.61, 143.58, 136.05, 135.28, 133.13, 129.63, 128.61, 128.53, 127.06, 126.80, 125.93, 125.48, 125.08, 124.19, 124.00, 62.51, 60.94, 55.10, 48.21, 32.80, 21.58, 13.74.

IR (KBr, ν_{max},cm^{-1}): 3067, 2980, 2961, 2930, 2862, 1724, 1599, 1582, 1548, 1473, 1352, 1201, 1167, 1090, 1022, 944, 814, 756, 668, 594, 569, 547

HRMS (ESI): found: 542.0964 for $C_{28}H_{26}Cl_2NO_4S$ ($[M+H]^+$): 542.0954

Ethyl 2-(furan-2-yl)-5-tosyl-1,4,5,9b-tetrahydro-3aH-cyclopenta[c]quinoline-3a-carboxylate(3ja)



3ja

Yield: 67%; White solid; m.p. 133-134 °C

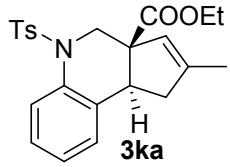
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 1H), 7.63 – 7.55 (m, 2H), 7.50 (dd, *J* = 16.9, 8.0 Hz, 3H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 8.3 Hz, 1H), 7.18 – 7.07 (m, 2H), 6.14 (s, 1H), 4.66 (dd, *J* = 10.6, 1.2 Hz, 1H), 3.82 – 3.62 (m, 3H), 3.32 (ddd, *J* = 21.9, 12.0, 6.5 Hz, 1H), 2.73 (dd, *J* = 14.3, 7.4 Hz, 1H), 2.64 – 2.53 (m, 1H), 0.80 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.73, 150.89, 143.57, 142.96, 139.07, 136.04, 135.77, 132.78, 129.64, 127.11, 126.79, 125.46, 125.07, 124.16, 122.15, 111.45, 108.96, 62.39, 60.99, 55.01, 48.35, 32.02, 21.58, 13.72.

IR (KBr, ν_{max},cm^{-1}): 3066, 2980, 2930, 2861, 1803, 1722, 1599, 1484, 1456, 1351, 1229, 1202, 1166, 1089, 1022, 944, 814, 739, 673, 594, 568, 546

HRMS (ESI): found: 464.1533 for $C_{26}H_{26}NO_5S$ ($[M+H]^+$): 464.1526

Ethyl 2-methyl-5-tosyl-1,4,5,9b-tetrahydro-3aH-cyclopenta[c]quinoline-3a-carboxylate(3ka)



3ka

Yield: 31%; White oil;

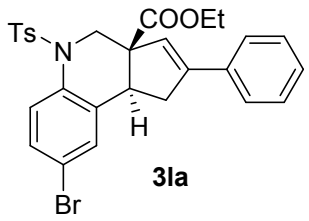
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 3H), 7.08 (t, *J* = 7.2 Hz, 1H), 7.03 (t, *J* = 6.0 Hz, 1H), 5.39 (s, 1H), 4.54 (dd, *J* = 10.5, 1.2 Hz, 1H), 3.80 – 3.63 (m, 2H), 3.58 (d, *J* = 10.5 Hz, 1H), 3.03 – 2.85 (m, 1H), 2.63 – 2.48 (m, 1H), 2.37 (s, 3H), 2.22 (dd, *J* = 14.7, 7.3 Hz, 1H), 1.82 (s, 3H), 0.81 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.49, 147.95, 142.38, 135.02, 132.22, 128.61, 128.51, 125.97, 125.77, 123.97, 123.78, 123.28, 123.11, 61.27, 59.59, 54.21, 48.01, 35.06, 20.52, 16.56, 12.68.

IR (KBr, ν_{max},cm^{-1}): 3066, 3041, 2964, 2855, 1724, 1599, 1485, 1455, 1352, 1306, 1262, 1234, 1202, 1167, 1090, 1022, 944, 815, 757, 720, 677, 661, 591, 574, 560, 544

HRMS (ESI): found: 412.1590 for $C_{23}H_{26}NO_4S$ ($[M+H]^+$): 412.1577

Ethyl 8-bromo-2-phenyl-5-tosyl-1,4,5,9b-tetrahydro-3aH-cyclopenta[c]quinoline-3a-carboxylate(3la)



3la

Yield: 80%; White solid; m.p. 172-173 °C

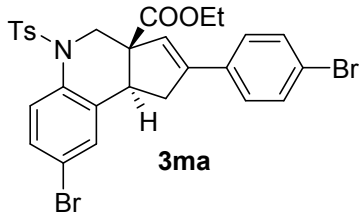
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.7 Hz, 1H), 7.52 – 7.44 (m, 4H), 7.32 (dd, *J* = 14.3, 8.5 Hz, 3H), 7.20 (d, *J* = 7.9 Hz, 2H), 6.14 (s, 1H), 4.64 (d, *J* = 10.6 Hz, 1H), 3.85 (dt, *J* = 14.0, 7.0 Hz, 1H), 3.72 (dt, *J* = 18.5, 7.6 Hz, 1H), 3.64 (d, *J* = 10.5 Hz, 1H), 3.37 – 3.26 (m, 1H), 2.75 (dd, *J* = 14.1, 7.4 Hz, 1H), 2.64 – 2.55 (m, 1H), 2.37 (s, 3H), 0.85 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.35, 148.47, 143.94, 135.50, 135.15, 134.87, 133.91, 131.76, 130.05, 129.81, 127.48, 127.39, 126.83, 126.79, 124.42, 122.64, 118.51, 62.42, 61.23, 54.92, 47.90, 32.73, 21.61, 13.75.

IR (KBr, ν_{max},cm^{-1}): 3063, 2979, 2926, 2856, 1724, 1595, 1480, 1413, 1352, 1201, 1165, 1088, 1023, 1010, 939, 924, 815, 742, 672, 597, 575, 546

HRMS (ESI): found: 552.0842 for $C_{28}H_{27}BrNO_4S$ ($[M+H]^+$): 552.0839

Ethyl 8-bromo-2-(4-bromophenyl)-5-tosyl-1,4,5,9b-tetrahydro-3aH-cyclopenta[c] quinoline-3a-carboxylate(3ma)



3ma

Yield: 65%; White solid; m.p. 188-190 °C

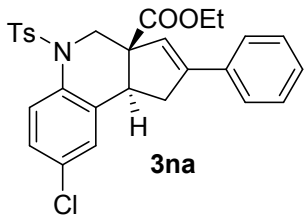
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.7 Hz, 1H), 7.46 (t, *J* = 6.8 Hz, 4H), 7.34 (td, *J* = 14.0, 7.3 Hz, 4H), 7.28 (s, 1H), 7.19 (d, *J* = 7.9 Hz, 2H), 6.14 (s, 1H), 4.65 (d, *J* = 10.6 Hz, 1H), 3.86 (dq, *J* = 14.1, 7.1 Hz, 1H), 3.77 – 3.66 (m, 1H), 3.64 (d, *J* = 10.6 Hz, 1H), 3.33 (t, *J* = 12.6 Hz, 1H), 2.78 (dd, *J* = 14.3, 7.4 Hz, 1H), 2.63 – 2.54 (m, 1H), 2.36 (s, 3H), 0.85 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.60, 149.48, 143.92, 135.47, 135.22, 135.17, 135.01, 129.96, 129.80, 128.68, 128.67, 127.42, 126.97, 126.79, 125.92, 123.69, 118.55, 62.38, 61.14, 55.10, 47.87, 32.74, 21.61, 13.76.

IR (KBr, ν_{max},cm^{-1}): 3061, 2980, 2934, 2866, 1723, 1596, 1477, 1352, 1201, 1166, 1088, 1023, 940, 924, 814, 758, 742, 722, 667, 597, 574, 546

HRMS (ESI): found: 629.9949 for $C_{28}H_{26}Br_2NO_4S$ ($[M+H]^+$): 629.9944

Ethyl 8-chloro-2-phenyl-5-tosyl-1,4,5,9b-tetrahydro-3aH-cyclopenta[c]quinoline-3a-carboxylate(3na)



3na

Yield: 75%; White solid; m.p. 187-188 °C

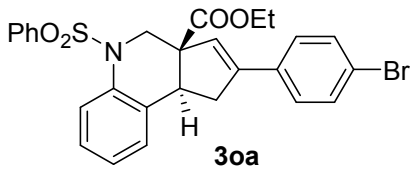
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.7 Hz, 1H), 7.52 – 7.40 (m, 4H), 7.34 (dt, *J* = 20.2, 7.0 Hz, 3H), 7.19 (d, *J* = 7.8 Hz, 3H), 7.13 (s, 1H), 6.13 (s, 1H), 4.65 (d, *J* = 10.6 Hz, 1H), 3.85 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.71 (ddd, *J* = 14.3, 10.8, 7.1 Hz, 1H), 3.64 (d, *J* = 10.6 Hz, 1H), 3.32 (dd, *J* = 18.3, 7.0 Hz, 1H), 2.78 (dd, *J* = 14.3, 7.4 Hz, 1H), 2.61 – 2.49 (m, 1H), 2.36 (s, 3H), 0.85 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.61, 149.47, 143.90, 135.45, 135.01, 134.98, 134.60, 133.66, 130.71, 129.79, 128.67, 127.00, 126.79, 126.72, 125.92, 124.53, 123.72, 62.40, 61.12, 55.08, 47.91, 32.72, 21.61, 13.75.

IR (KBr, ν_{max},cm^{-1}): 3062, 2980, 2927, 2857, 1723, 1597, 1478, 1417, 1352, 1201, 1166, 1089, 1023, 945, 926, 814, 760, 746, 724, 669, 600, 576, 546

HRMS (ESI): found: 508.1347 for $C_{28}H_{27}ClNO_4S$ ($[M+H]^+$): 508.1344

Ethyl 2-(4-bromophenyl)-5-(phenylsulfonyl)-1,4,5,9b-tetrahydro-3aH-cyclopenta[c]quinoline-3a-carboxylate(3oa)



3oa

Yield: 87%; White solid; m.p. 174-175 °C

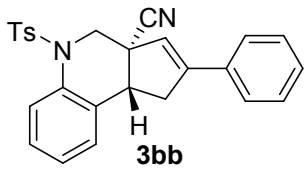
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 1H), 7.62 – 7.55 (m, 2H), 7.50 (dd, *J* = 16.9, 8.0 Hz, 3H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 7.26 – 7.20 (m, 1H), 7.19 – 7.08 (m, 2H), 6.14 (d, *J* = 1.4 Hz, 1H), 4.66 (dd, *J* = 10.6, 1.2 Hz, 1H), 3.77 (ddd, *J* = 14.2, 10.8, 7.1 Hz, 1H), 3.73 – 3.63 (m, 2H), 3.37 – 3.27 (m, 1H), 2.73 (dd, *J* = 14.3, 7.4 Hz, 1H), 2.62 – 2.53 (m, 1H), 0.80 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.63, 148.64, 138.62, 135.93, 134.14, 132.90, 132.88, 131.69, 129.03, 127.51, 127.20, 126.74, 125.45, 125.24, 124.65, 124.16, 122.47, 62.59, 61.06, 54.96, 48.24, 32.76, 13.74.

IR (KBr, ν_{max},cm^{-1}): 3065, 2980, 2936, 2862, 1722, 1586, 1485, 1447, 1352, 1201, 1168, 1090, 1073, 1017, 1010, 939, 816, 738, 727, 689, 589, 558

HRMS (ESI): found: 538.0692 for $C_{27}H_{25}BrNO_4S$ ($[M+H]^+$): 538.0682

2-phenyl-5-tosyl-1,4,5,9b-tetrahydro-3aH-cyclopenta[c]quinoline-3a-carbonitrile(3bb)



3bb

Yield: 59%; White solid; m.p. 166-167 °C

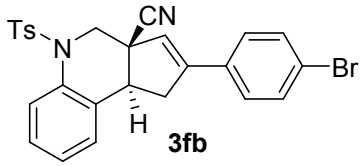
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.1 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 4H), 7.42 – 7.32 (m, 4H), 7.30 – 7.22 (m, 1H), 7.21 – 7.11 (m, 3H), 6.23 (s, 1H), 4.36 (d, *J* = 11.4 Hz, 1H), 3.83 (d, *J* = 11.4 Hz, 1H), 3.10 – 2.94 (m, 2H), 2.51 – 2.42 (m, 1H), 2.35 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.37, 144.14, 135.55, 135.21, 134.04, 131.22, 129.82, 129.35, 128.80, 128.52, 126.85, 126.10, 126.02, 124.35, 121.14, 118.68, 54.20, 53.07, 48.91, 32.38, 21.60.

IR (KBr, ν_{max},cm^{-1}): 3064, 2954, 2924, 2897, 2849, 2230, 1716, 1598, 1486, 1453, 1351, 1166, 1090, 1023, 935, 814, 757, 736, 689, 657, 596, 573, 547, 534, 517

HRMS (ESI): found: 449.1303 for $C_{26}H_{22}N_2O_2SNa$ ([M+Na]$^+$): 449.1300

2-(4-bromophenyl)-5-tosyl-1,4,5,9b-tetrahydro-3aH-cyclopenta[c]quinoline-3a-carbonitrile(3fb)



3fb

Yield: 67%; White solid; m.p. 219-220 °C

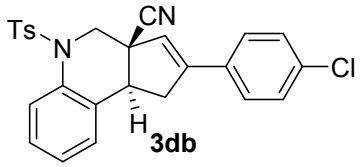
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.1 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.25 (dd, *J* = 9.0, 5.7 Hz, 1H), 7.17 (dd, *J* = 15.2, 7.7 Hz, 3H), 6.23 (s, 1H), 4.35 (d, *J* = 11.4 Hz, 1H), 3.84 (d, *J* = 11.4 Hz, 1H), 3.08 – 2.88 (m, 2H), 2.49 (dd, *J* = 10.6, 6.9 Hz, 1H), 2.36 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.34, 144.16, 135.53, 135.25, 132.94, 131.96, 130.91, 129.82, 128.59, 127.63, 126.86, 126.00, 125.87, 124.32, 123.45, 121.85, 118.43, 54.04, 53.08, 48.92, 32.39, 21.60.

IR (KBr, ν_{max},cm^{-1}): 3066, 2954, 2897, 2230, 1715, 1698, 1597, 1486, 1455, 1399, 1351, 1225, 1166, 1090, 1023, 1010, 934, 812, 760, 737, 708, 669, 598, 572, 546, 534

HRMS (ESI): found: 522.0848 for $C_{26}H_{25}BrN_3O_2S$ ([M+NH_4]$^+$): 522.0845

2-(4-chlorophenyl)-5-tosyl-1,4,5,9b-tetrahydro-3aH-cyclopenta[c]quinoline-3a-carbonitrile(3db)



3db

Yield: 69%; White solid; m.p. 193-195 °C

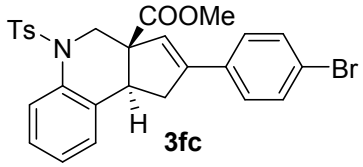
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.2 Hz, 1H), 7.45 (d, *J* = 7.9 Hz, 2H), 7.37 (q, *J* = 8.5 Hz, 5H), 7.25 (dd, *J* = 8.6, 6.3 Hz, 1H), 7.17 (dd, *J* = 14.5, 7.7 Hz, 3H), 6.22 (s, 1H), 4.35 (d, *J* = 11.4 Hz, 1H), 3.84 (d, *J* = 11.4 Hz, 1H), 3.08 – 2.89 (m, 2H), 2.50 (dd, *J* = 10.6, 6.9 Hz, 1H), 2.36 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.24, 144.19, 135.52, 135.19, 132.50, 130.96, 129.84, 128.99, 128.58, 127.40, 126.85, 126.02, 125.87, 124.35, 121.73, 118.53, 54.08, 53.07, 48.92, 32.44, 21.62.

IR (KBr, ν_{max},cm^{-1}): 3079, 2956, 2230, 1730, 1714, 1698, 1596, 1553, 1489, 1455, 1351, 1166, 1090, 1023, 1014, 936, 813, 759, 740, 672, 600, 571, 547, 535

HRMS (ESI): found:483.0909 for $C_{26}H_{21}ClN_2O_2SNa$ ([M+Na]$^+$): 483.0910

Methyl 2-(4-bromophenyl)-5-tosyl-1,4,5,9b-tetrahydro-3aH-cyclopenta[c]quinoline-3a-carboxylate(3fc)



3fc

Yield: 80%; White solid; m.p. 179-181 °C

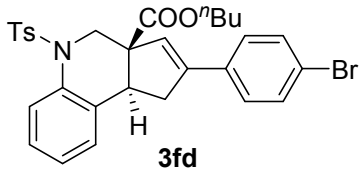
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.1 Hz, 1H), 7.47 (t, *J* = 6.3 Hz, 4H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.25 – 7.20 (m, 1H), 7.20 – 7.08 (m, 4H), 6.15 (s, 1H), 4.64 (d, *J* = 10.6 Hz, 1H), 3.69 (d, *J* = 10.6 Hz, 1H), 3.40 – 3.29 (m, 1H), 3.27 (s, 3H), 2.76 (dd, *J* = 14.2, 7.4 Hz, 1H), 2.71 – 2.57 (m, 1H), 2.35 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.13, 148.70, 143.63, 135.96, 135.81, 134.11, 132.69, 131.71, 129.65, 127.52, 127.19, 126.81, 125.34, 125.18, 124.55, 123.95, 122.51, 62.66, 54.85, 51.99, 48.32, 32.70, 21.59.

IR (KBr, ν_{max},cm^{-1}): 3064, 2950, 2924, 2861, 1729, 1598, 1486, 1455, 1399, 1350, 1210, 1166, 1089, 1010, 932, 815, 795, 757, 736, 722, 669, 593, 568, 546

HRMS (ESI): found: 538.0693 for $C_{27}H_{25}BrNO_4S$ ($[M+H]^+$): 538.0688

Butyl 2-(4-bromophenyl)-5-tosyl-1,4,5,9b-tetrahydro-3aH-cyclopenta[c]quinoline-3a-carboxylate(3fd)



3fd

Yield: 78%; White solid; m.p. 136-138 °C

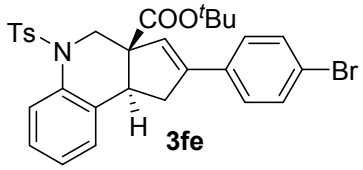
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.1 Hz, 1H), 7.48 (dd, *J* = 8.3, 4.5 Hz, 4H), 7.31 (d, *J* = 8.5 Hz, 2H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.20 – 7.08 (m, 4H), 6.15 (s, 1H), 4.65 (dd, *J* = 10.5, 1.0 Hz, 1H), 3.68 (dd, *J* = 12.6, 6.2 Hz, 3H), 3.40 – 3.28 (m, 1H), 2.76 (dd, *J* = 14.2, 7.4 Hz, 1H), 2.69 – 2.60 (m, 1H), 2.35 (s, 3H), 1.24 – 1.14 (m, 2H), 1.09 (dt, *J* = 15.8, 7.9 Hz, 2H), 0.76 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.75, 148.62, 143.58, 136.02, 135.87, 134.22, 132.72, 131.71, 129.63, 127.47, 127.13, 126.82, 125.30, 125.07, 124.87, 124.06, 122.45, 64.91, 62.64, 54.89, 48.23, 32.85, 30.29, 21.57, 18.99, 13.56.

IR (KBr, ν_{max},cm^{-1}): 3065, 2959, 2932, 2871, 1723, 1598, 1486, 1456, 1351, 1227, 1199, 1166, 1089, 1010, 946, 815, 756, 721, 669, 593, 568, 546, 530

HRMS (ESI): found: 580.1161 for $C_{30}H_{31}BrNO_4S$ ($[M+H]^+$): 580.1157

tert-butyl 2-(4-bromophenyl)-5-tosyl-1,4,5,9b-tetrahydro-3aH-cyclopenta[c]quinoline-3a-carboxylate(3fe)



3fe

Yield: 60%; White solid; m.p. 165-166 °C

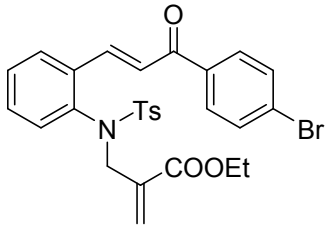
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.1 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 4H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.23 (t, *J* = 7.7 Hz, 1H), 7.15 (dd, *J* = 17.3, 8.1 Hz, 4H), 6.14 (s, 1H), 4.62 (d, *J* = 10.4 Hz, 1H), 3.63 (d, *J* = 10.4 Hz, 1H), 3.30 (t, *J* = 12.5 Hz, 1H), 2.72 (dd, *J* = 14.0, 7.5 Hz, 1H), 2.67 – 2.58 (m, 1H), 2.35 (s, 3H), 0.99 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.63, 148.35, 143.52, 136.27, 135.92, 134.42, 133.18, 131.70, 129.61, 127.44, 127.06, 126.80, 125.44, 125.10, 124.93, 124.25, 122.32, 81.68, 63.18, 55.09, 48.19, 32.92, 27.38, 21.57.

IR (KBr, ν_{max},cm^{-1}): 3064, 2977, 2929, 2866, 1718, 1598, 1485, 1456, 1396, 1351, 1232, 1166, 1090, 1010, 944, 841, 815, 756, 737, 723, 668, 594, 568, 547

HRMS (ESI): found: 580.1143 for $C_{30}H_{31}BrNO_4S$ ($[M+H]^+$): 580.1157

Ethyl (E)-2-(((N-(2-(3-(4-bromophenyl)-3-oxoprop-1-en-1-yl)phenyl)-4-methylphenyl)sulfonamido)methyl)acrylate(4fa)



4fa

Yield: 82%; White solid; m.p. 145-147 °C

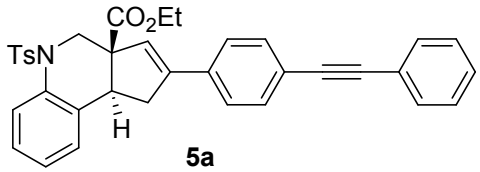
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.2 Hz, 2H), 7.82 (d, *J* = 16.1 Hz, 1H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.54 (d, *J* = 7.9 Hz, 2H), 7.35 (dt, *J* = 15.1, 7.4 Hz, 3H), 7.28 – 7.19 (m, 3H), 6.89 (d, *J* = 7.7 Hz, 1H), 6.20 (s, 1H), 5.70 (s, 1H), 4.66 (d, *J* = 12.6 Hz, 1H), 4.19 (d, *J* = 12.2 Hz, 1H), 4.03 (s, 2H), 2.36 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.32, 165.58, 144.04, 141.16, 139.09, 136.63, 135.92, 135.18, 134.79, 131.91, 130.72, 130.41, 129.99, 129.67, 129.58, 128.84, 128.11, 127.77, 127.34, 124.21, 61.18, 52.31, 21.57, 14.02.

IR (KBr, ν_{max},cm^{-1}): 3065, 2982, 2928, 2871, 1719, 1665, 1642, 1602, 1482, 1451, 1397, 1349, 1330, 1278, 1214, 1162, 1091, 1069, 1027, 1008, 815, 759, 738, 680, 651, 565, 541

HRMS (ESI): found: 568.0793 for $C_{28}H_{27}BrNO_5S$ ($[M+H]^+$): 568.0793

Ethyl 2-(4-(phenylethynyl)phenyl)-5-tosyl-1,4,5,9b-tetrahydro-3aH-cyclopenta[c] quinoline-3a-carboxylate(5a)



5a

Yield: 96%; Yellow solid; m.p. 119-121 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 1H), 7.59 – 7.49 (m, 4H), 7.45 (t, *J* = 9.4 Hz, 4H), 7.40 – 7.32 (m, 3H), 7.22 (d, *J* = 8.3 Hz, 1H), 7.16 (dd, *J* = 11.5, 6.8 Hz, 4H), 6.19 (s, 1H), 4.67 (d, *J* =

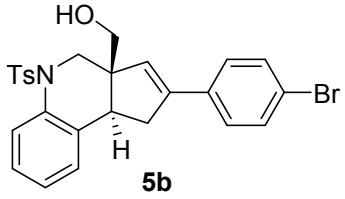
10.5 Hz, 1H), 3.84 – 3.62 (m, 3H), 3.36 (t, *J* = 12.5 Hz, 1H), 2.80 (dd, *J* = 14.1, 7.4 Hz, 1H), 2.69 – 2.59 (m, 1H), 2.36 (s, 3H), 0.81 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.71, 149.03, 143.61, 136.06, 135.84, 135.01, 132.93, 131.75, 131.64, 129.65, 128.47, 128.42, 127.12, 126.81, 125.91, 125.41, 125.08, 124.94, 124.18, 123.31, 123.06, 90.72, 89.16, 77.38, 77.06, 76.74, 62.55, 61.03, 55.01, 48.24, 32.75, 21.58, 13.74.

IR (KBr, ν_{max},cm^{-1}): 3062, 2980, 2934, 2868, 2315, 1722, 1597, 1552, 1512, 1485, 1455, 1351, 1200, 1166, 1090, 1022, 1015, 944, 815, 755, 716, 691, 670, 593, 566, 545, 526, 435, 419

HRMS (ESI): found: 574.2052 for $C_{36}H_{32}NO_4S$ ($[M+H]^+$): 574.2047

(2-(4-bromophenyl)-5-tosyl-1,4,5,9b-tetrahydro-3aH-cyclopenta[c]quinolin-3a-yl)methanol(5b)



5b

Yield: 70%; White solid; m.p. 154-155 °C

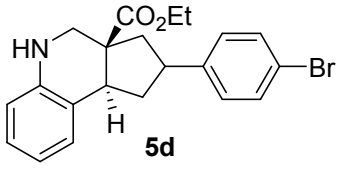
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.1 Hz, 1H), 7.46 (t, *J* = 7.9 Hz, 4H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.32 – 7.27 (m, 2H), 7.16 (t, *J* = 6.8 Hz, 3H), 7.09 (d, *J* = 7.4 Hz, 1H), 6.33 (s, 1H), 4.08 (d, *J* = 11.0 Hz, 1H), 3.64 (d, *J* = 10.9 Hz, 1H), 3.11 (d, *J* = 11.0 Hz, 1H), 3.00 (d, *J* = 11.1 Hz, 1H), 2.98 – 2.89 (m, 1H), 2.74 (dd, *J* = 14.7, 7.3 Hz, 1H), 2.47 (dd, *J* = 10.8, 7.5 Hz, 1H), 2.34 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.02, 143.62, 136.77, 135.72, 135.49, 132.26, 129.62, 128.59, 128.16, 127.84, 127.17, 126.86, 125.71, 125.33, 125.18, 123.98, 64.53, 55.06, 53.80, 46.80, 31.92, 21.58.

IR (KBr, ν_{max},cm^{-1}): 3545, 3061, 2944, 2886, 2856, 1599, 1485, 1453, 1348, 1164, 1090, 1040, 1020, 931, 845, 814, 758, 711, 695, 671, 654, 609, 572, 554

HRMS (ESI): found: 510.0732 for $C_{26}H_{25}BrNO_3S$ ($[M+H]^+$): 510.0733

Ethyl 2-(4-bromophenyl)-1,2,3,4,5,9b-hexahydro-3aH-cyclopenta[c]quinoline-3a-carboxylate(5d)



5d

Yield:75%; White solid; m.p. 105-106 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 6.8 Hz, 2H), 7.28 (s, 1H), 7.21 (s, 1H), 7.02 – 6.87 (m, 2H), 6.63 (d, *J* = 7.2 Hz, 1H), 6.46 (d, *J* = 7.5 Hz, 1H), 4.08 – 3.84 (m, 4H), 3.64 (dd, *J* = 18.7, 11.0 Hz, 1H), 3.37 (dd, *J* = 28.7, 10.1 Hz, 2H), 2.80 (dd, *J* = 23.9, 12.1 Hz, 1H), 2.58 (dd, *J* = 12.6, 7.9 Hz, 1H), 2.26 (dd, *J* = 12.0, 9.1 Hz, 1H), 1.68 (t, *J* = 11.3 Hz, 1H), 1.03 (t, *J* = 5.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.18, 147.33, 143.22, 128.66, 127.07, 126.87, 126.08, 125.13, 123.76, 116.87, 112.47, 60.37, 52.30, 52.16, 48.35, 44.39, 43.50, 34.44, 13.97.

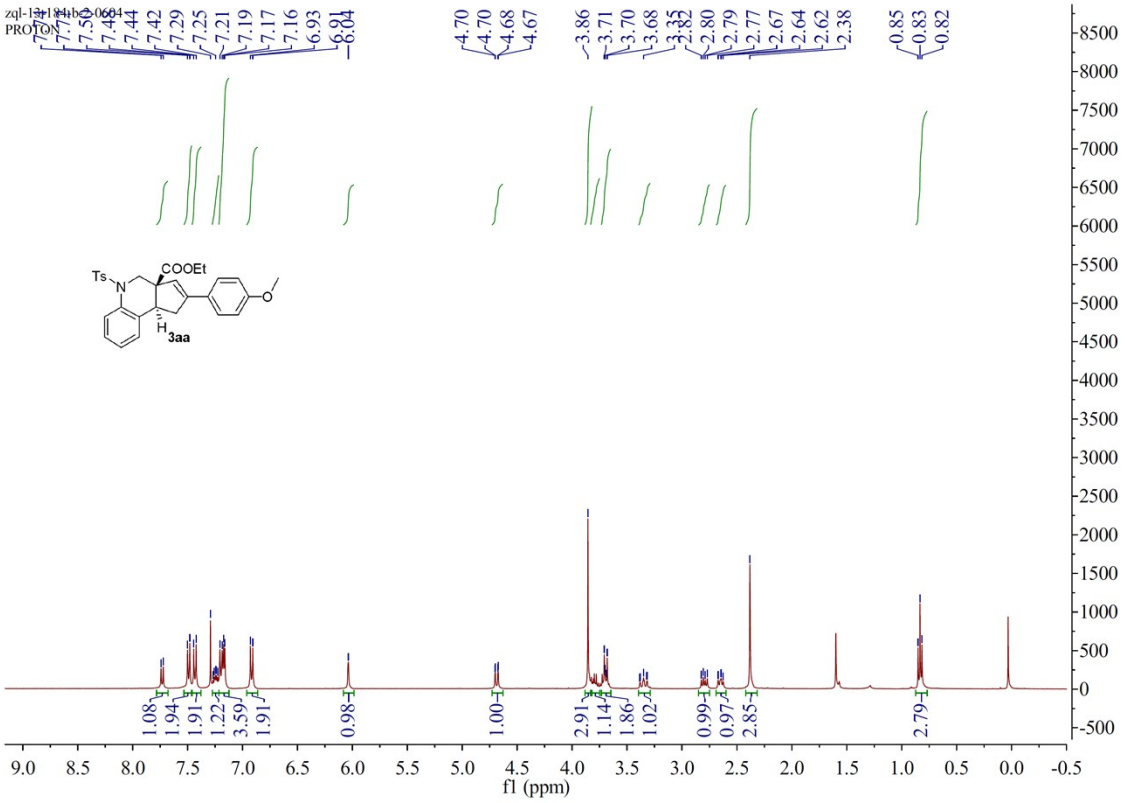
IR (KBr, ν_{max},cm^{-1}):3412,3056,3025,2961,2866,1716,1608,1582,1494,1469,1449,1370,1349,1314, 1279,1209,1152,1020,745,700

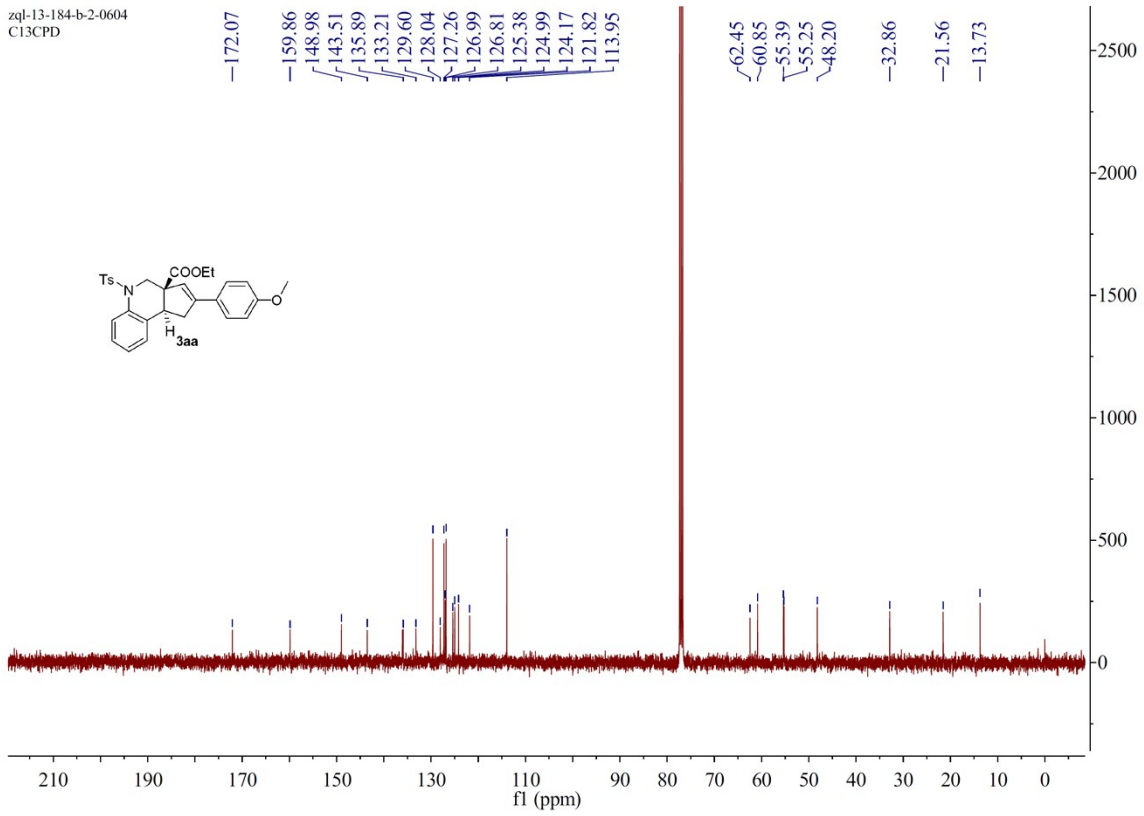
HRMS (ESI): found: 400.0907 for $C_{21}H_{23}BrNO_2$ ($[M+H]^+$): 400.0912

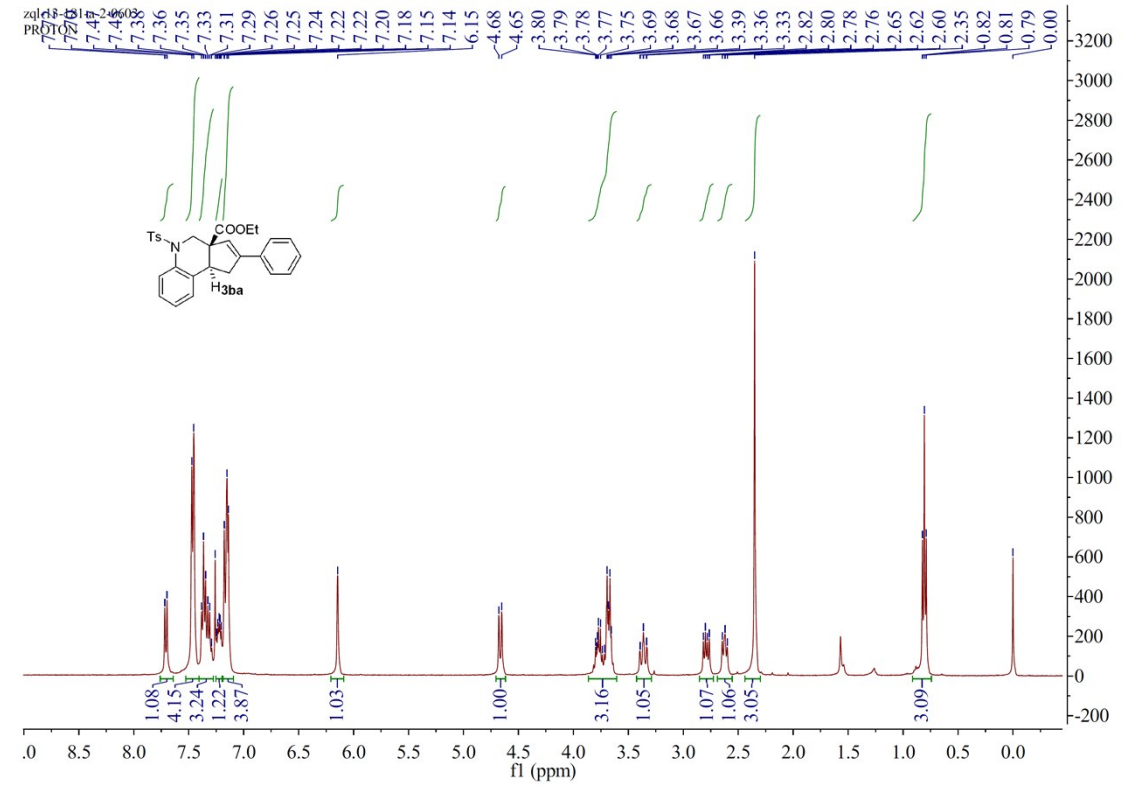
VIII. References

[1] Yang ,W.; Du, D. M. *Chem. Commun.,* 2013, **49**, 8842-8844; Huang, Y.; Zheng, C.; Zhao, G. *RSC Adv.,* **2013**, *3,* 16999–17002; Kim, S., Kang, K., Kim, S.G. *Tetrahedron.* **2014**, *70*, 5114-5121.
[2] Xie, P.; Huang,Y.; Chen, R. *Org. Lett.,* **2010**, *12*, 3768–3771

IX. NMR spectra for Benzobicyclo[4.3.0] derivatives (3).



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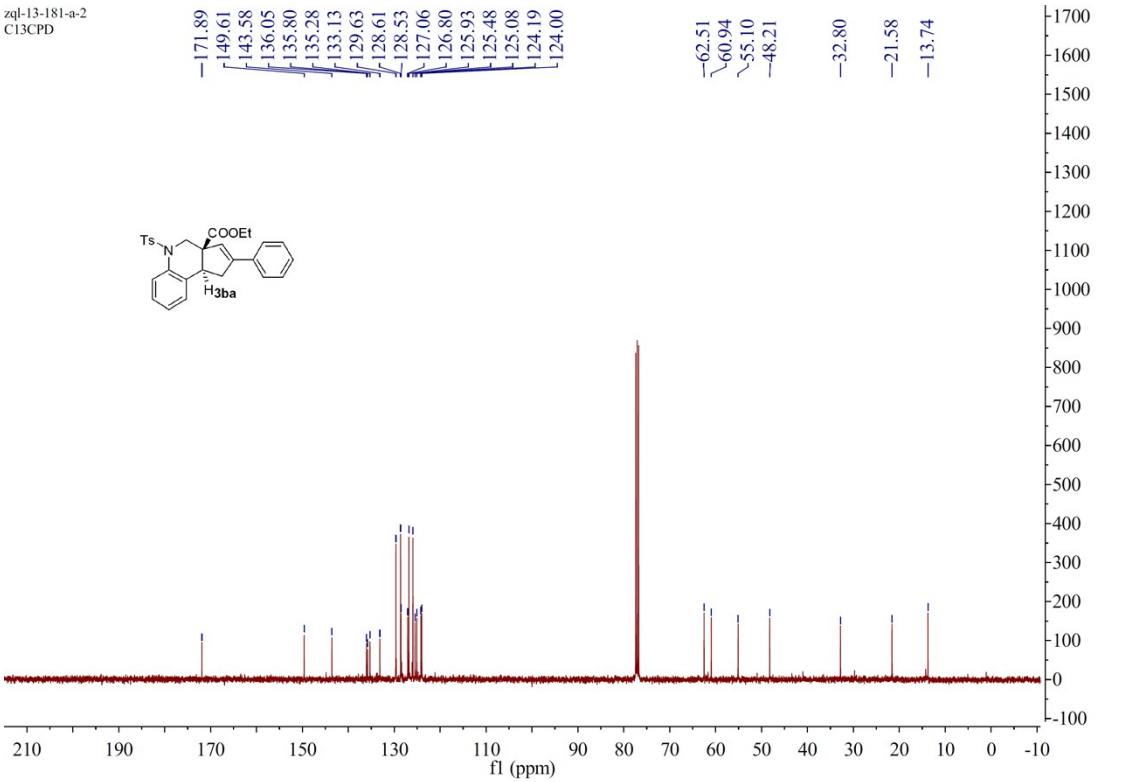
Ts
N
COOEt
H
3ba
1.08 4.15 3.24 1.22 3.87 1.03 1.00 3.16 1.05 1.07 1.06 3.05 3.09
fl (ppm)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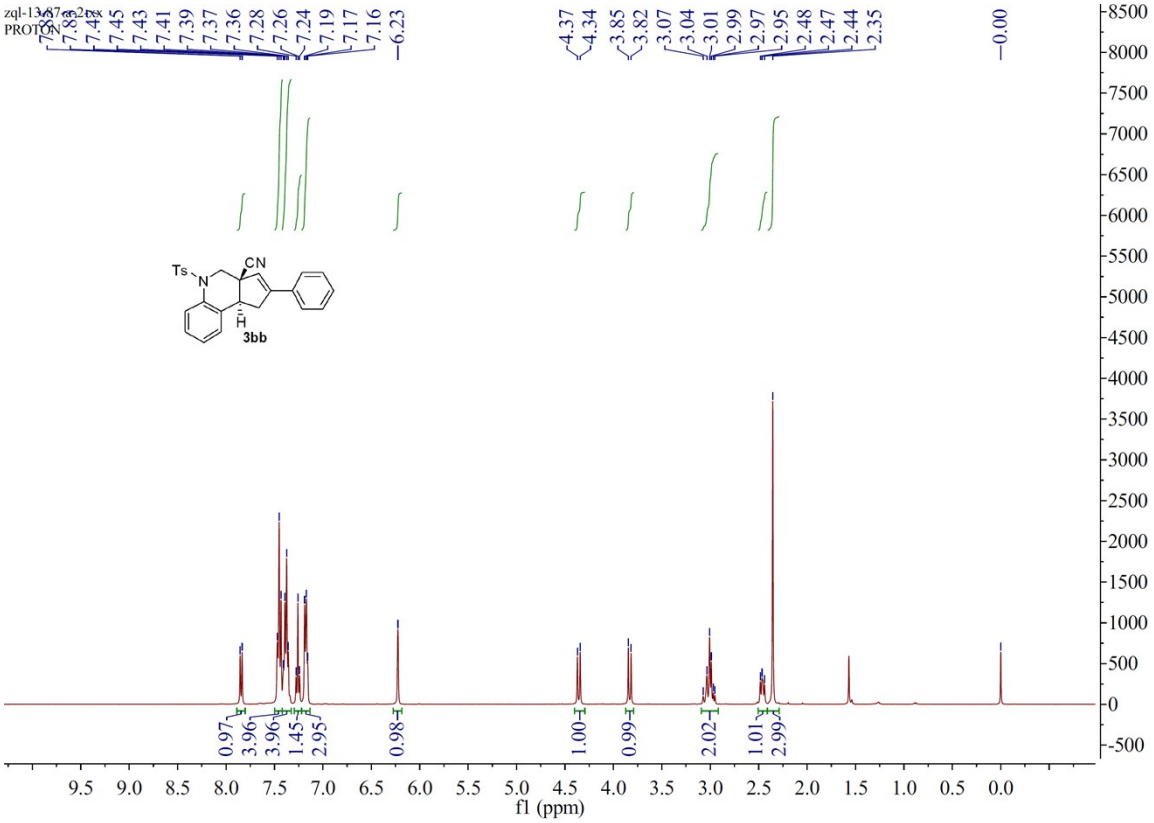
Ts
N
COOEt
H
3ba
fl (ppm)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7.39
7.37
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7.26
7.24
7.19
7.17
7.16
6.23
4.37
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3.01
2.99
2.97
2.95
2.48
2.47
2.44
2.35
0.00
Ts
N
CN
H
3bb
0.97
3.96
3.96
1.45
2.95
0.98
1.00
0.99
2.02
1.01
2.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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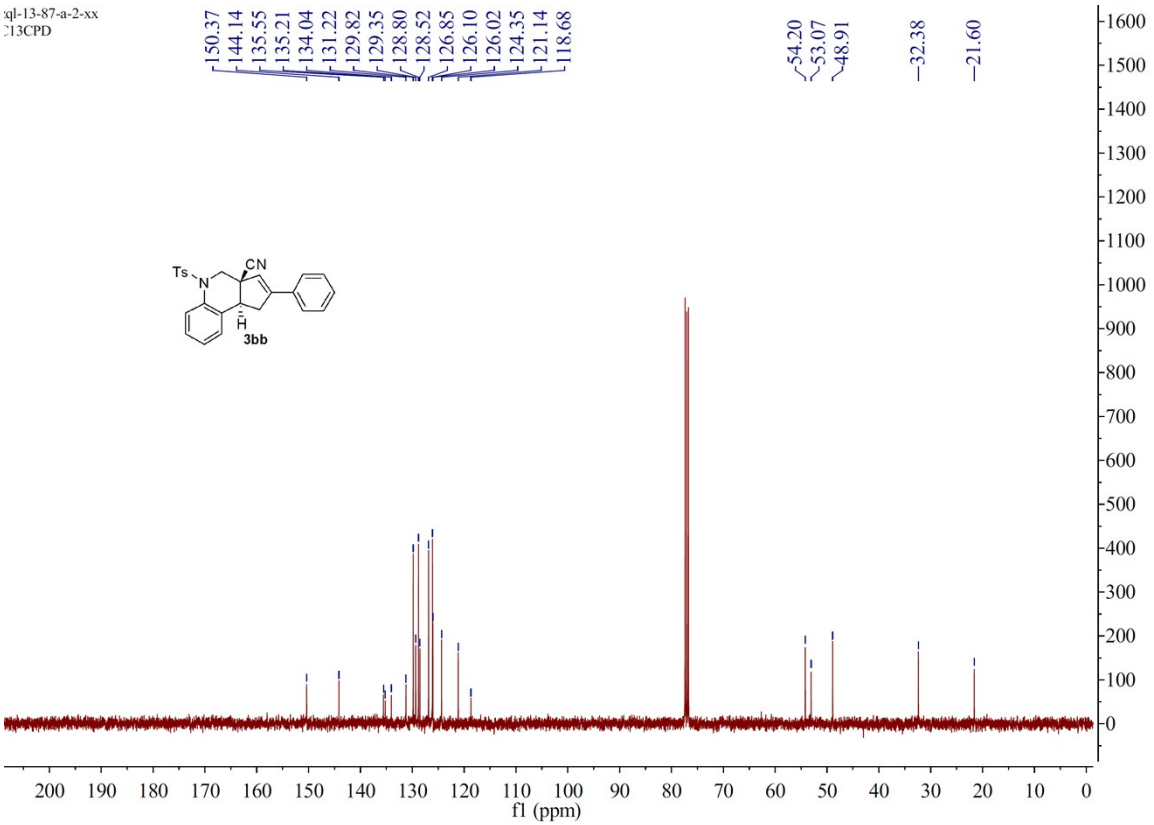
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C13CPD
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144.14
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129.82
129.35
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128.52
126.85
126.10
126.02
124.35
121.14
118.68
54.20
53.07
48.91
32.38
21.60
Ts
N
CN
H
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200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
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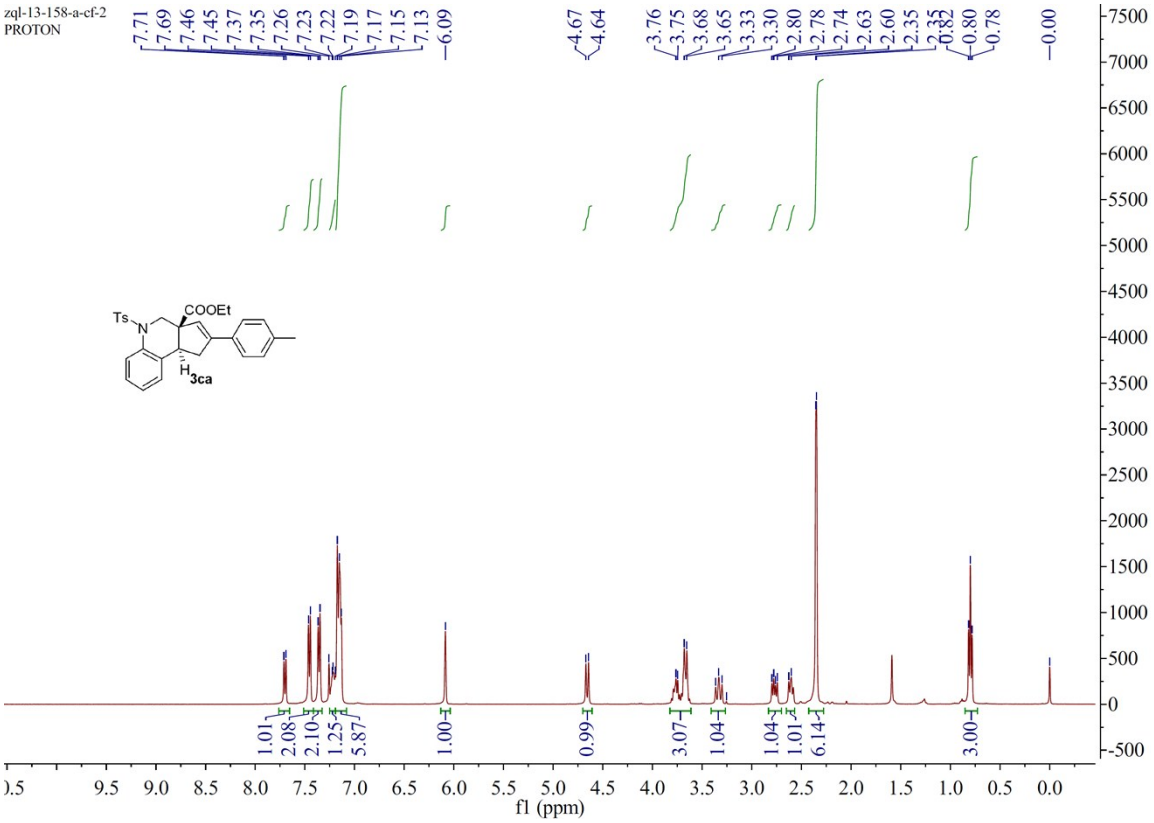
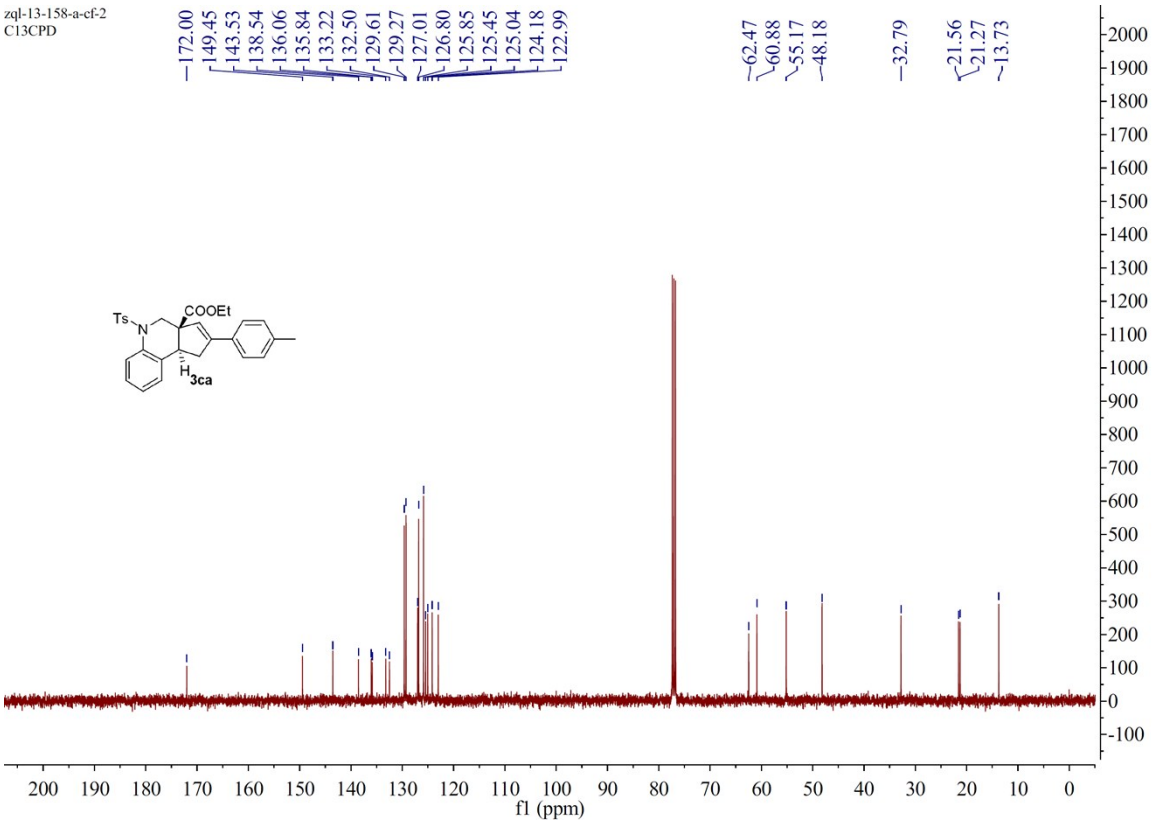
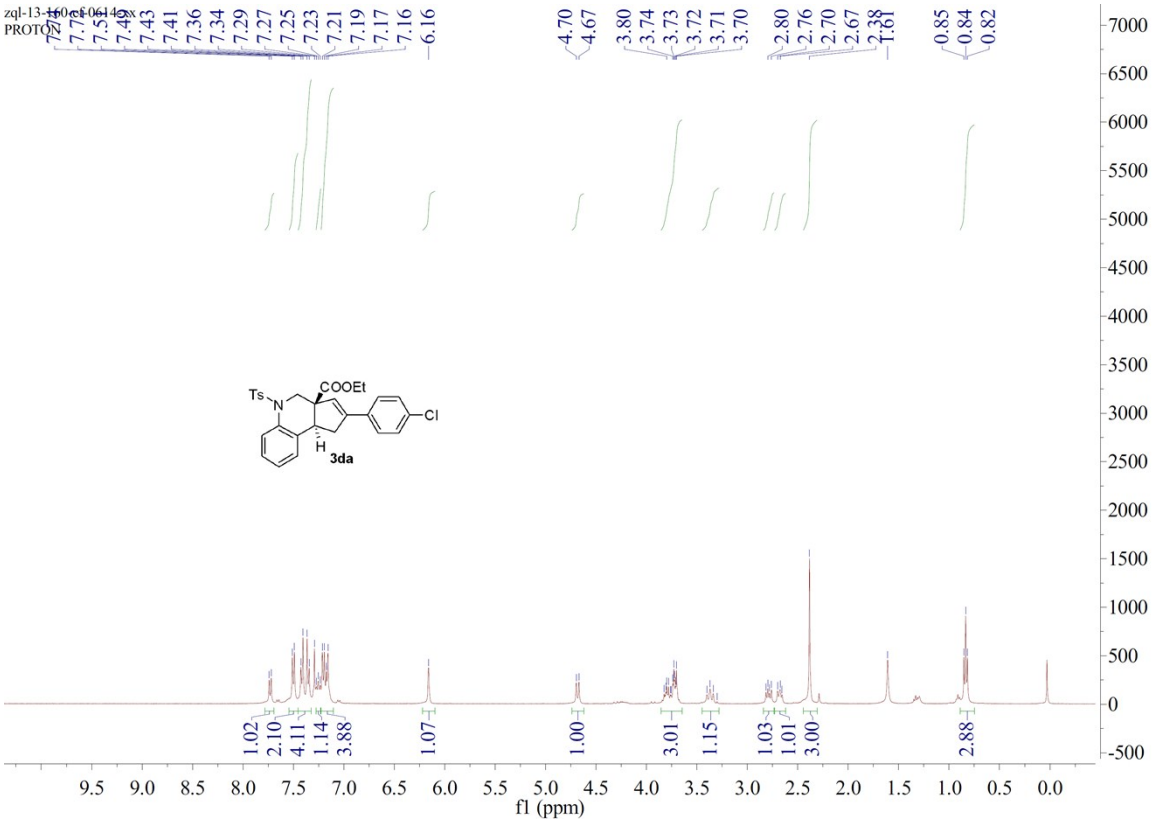
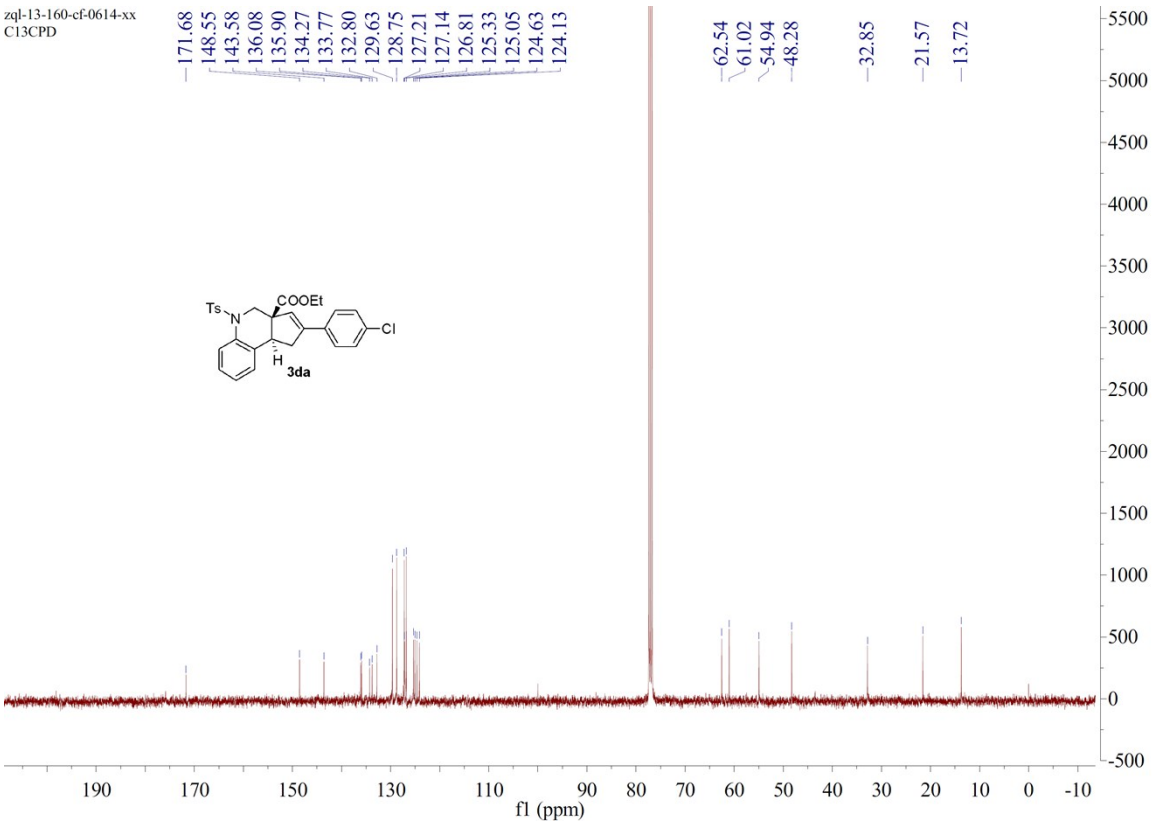
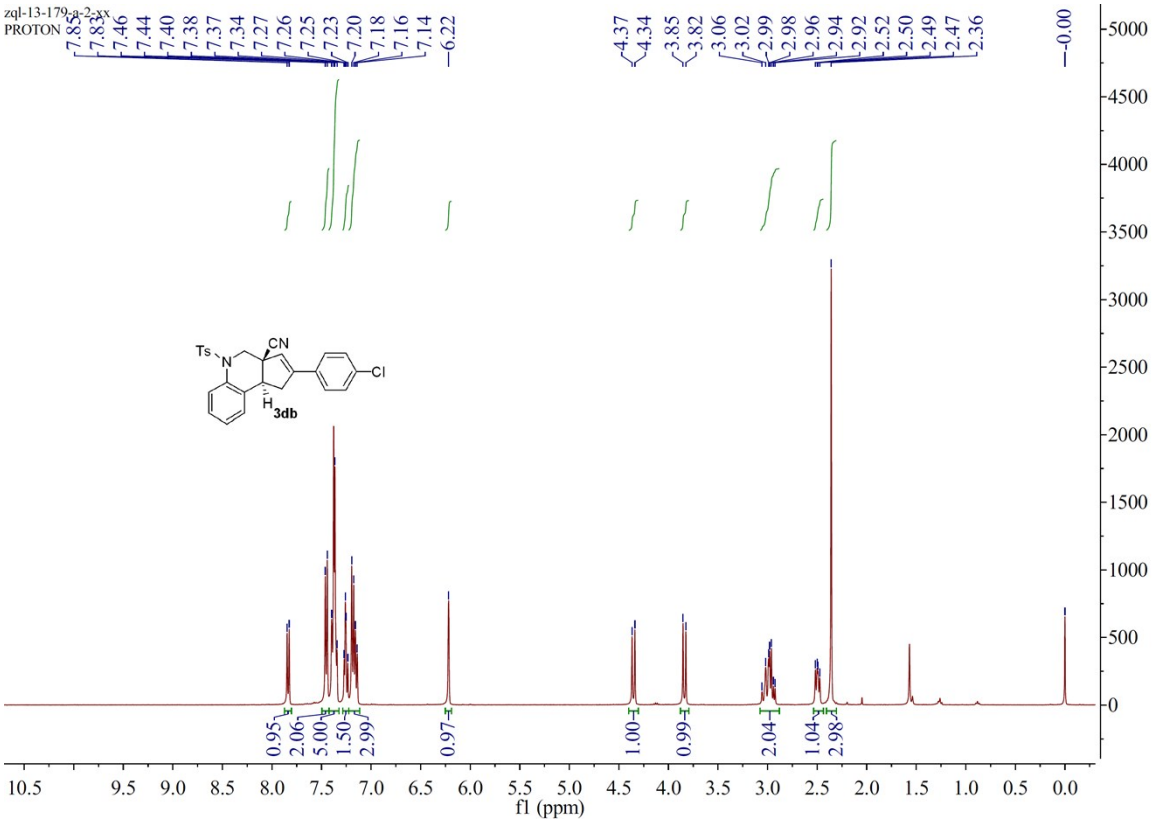
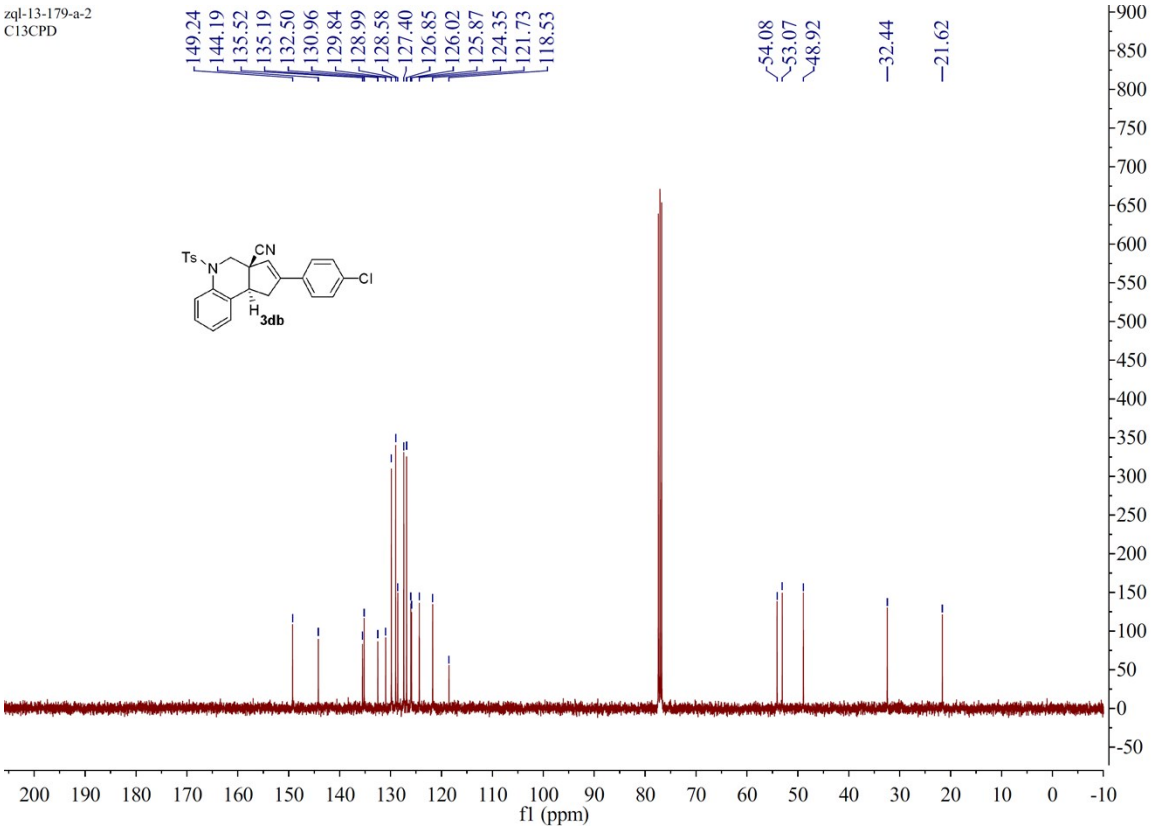

zql-13-158-a-cf-2
PROTON
7.71
7.69
7.46
7.45
7.37
7.35
7.26
7.23
7.22
7.19
7.17
7.15
7.13
6.09
4.67
4.64
3.76
3.75
3.68
3.65
3.33
3.30
2.80
2.78
2.74
2.63
2.60
2.35
2.35
0.82
0.80
0.78
0.00
COOEt
Ts
N
H3ca
1.01
2.08
2.10
1.25
5.87
1.00
0.99
3.07
1.04
1.04
1.01
6.14
3.00
f1 (ppm)

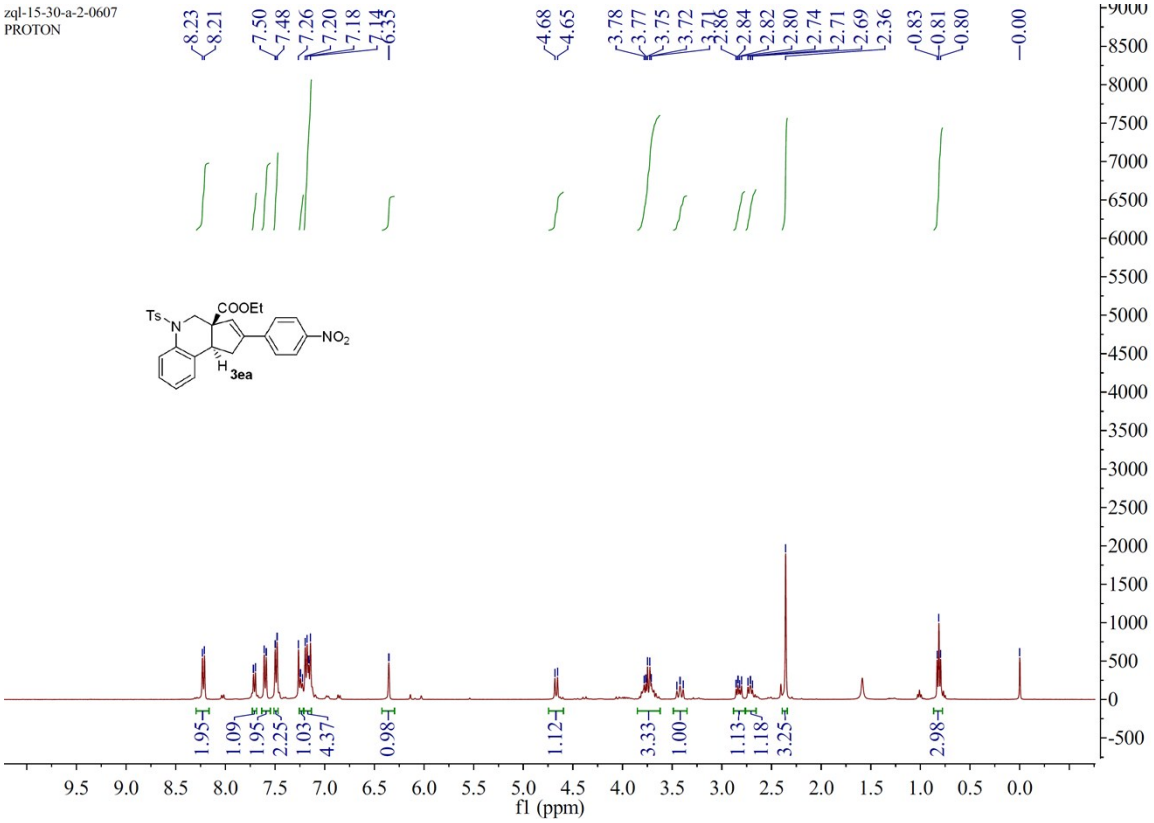

zql-13-158-a-cf-2
C13CPD
172.00
149.45
143.53
138.54
136.06
135.84
133.22
132.50
129.61
129.27
127.01
126.80
125.85
125.45
125.04
124.18
122.99
62.47
60.88
55.17
48.18
32.79
21.56
21.27
13.73
COOEt
Ts
N
H3ca
f1 (ppm)

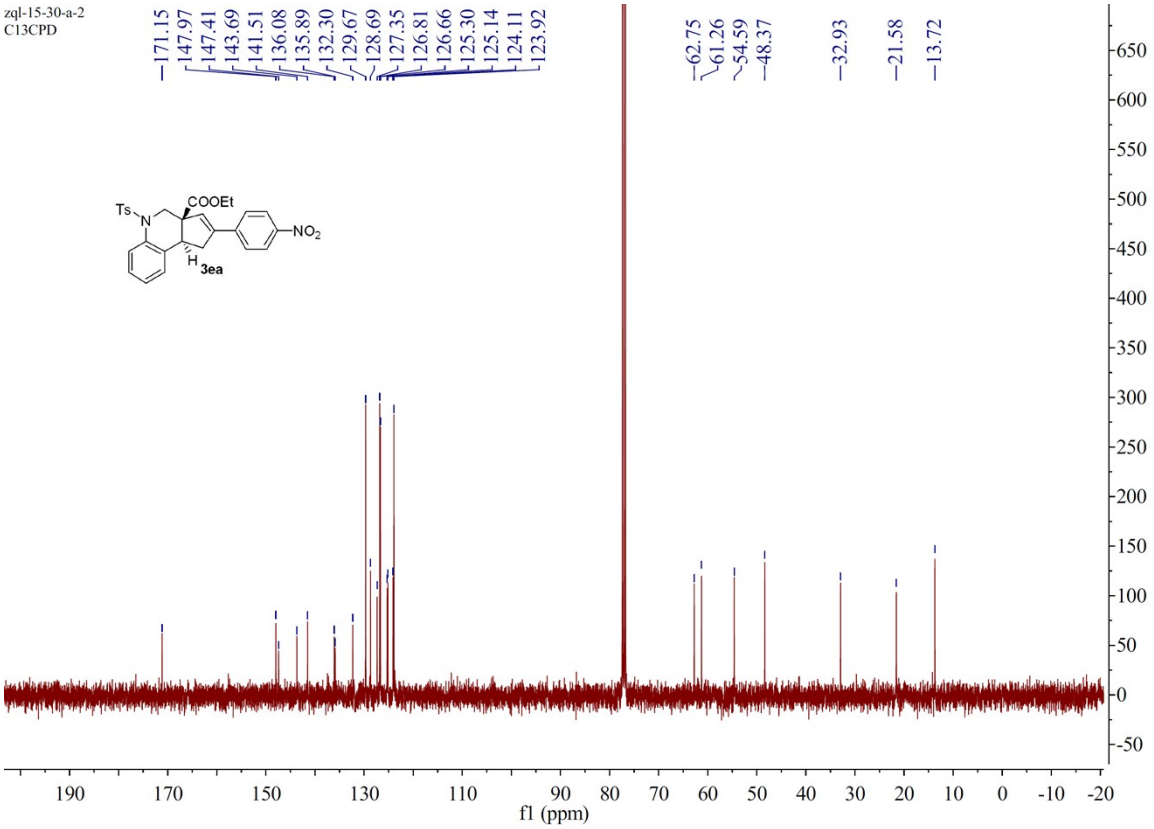

zql-13-160-cf-0614-xx
PROTON
7.77
7.75
7.48
7.43
7.41
7.36
7.34
7.29
7.27
7.25
7.23
7.21
7.19
7.17
7.16
6.16
4.70
4.67
3.80
3.74
3.73
3.72
3.71
3.70
2.80
2.76
2.70
2.67
2.38
1.61
0.85
0.84
0.82
COOEt
Ts
N
Cl
H
3da
1.02
2.10
4.11
1.14
3.88
1.07
1.00
3.01
1.15
1.03
1.01
3.00
2.88
fl (ppm)

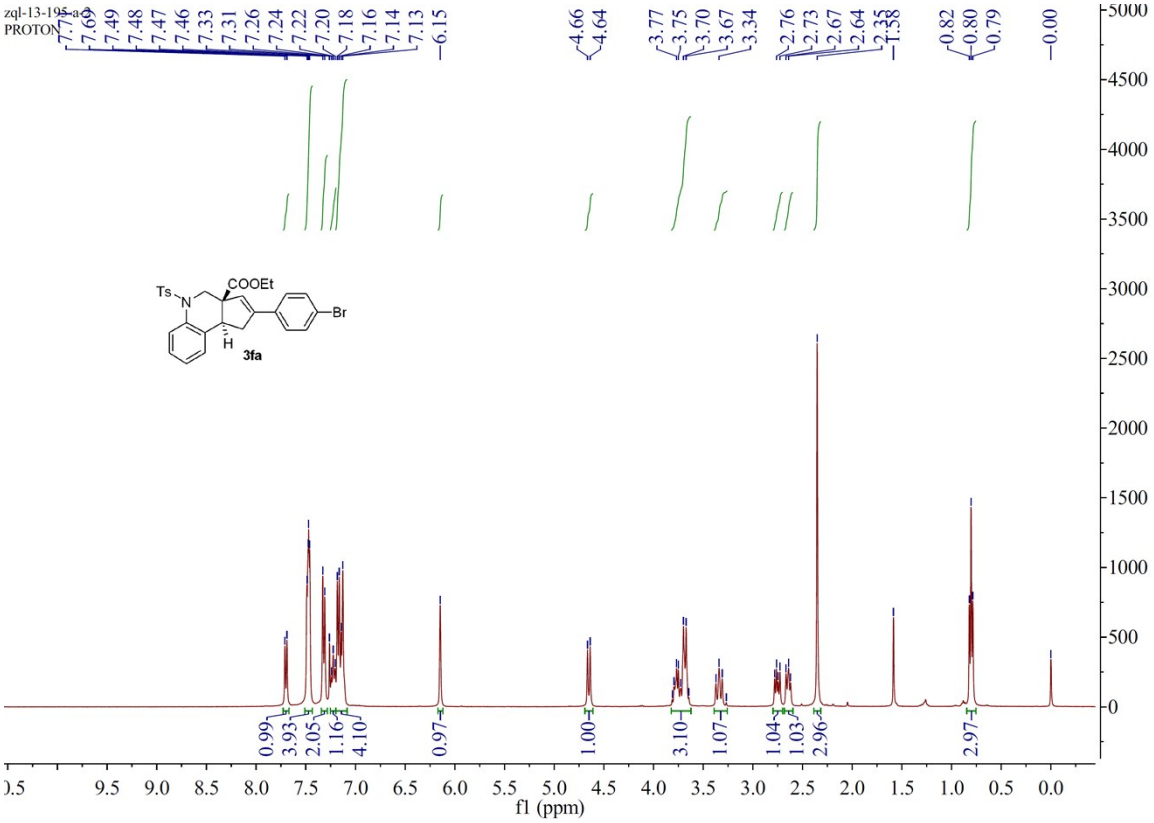

zql-13-160-cf-0614-xx
C13CPD
171.68
148.55
143.58
136.08
135.90
134.27
133.77
132.80
129.63
128.75
127.21
127.14
126.81
125.33
125.05
124.63
124.13
62.54
61.02
54.94
48.28
32.85
21.57
13.72
COOEt
Ts
N
Cl
H
3da
fl (ppm)

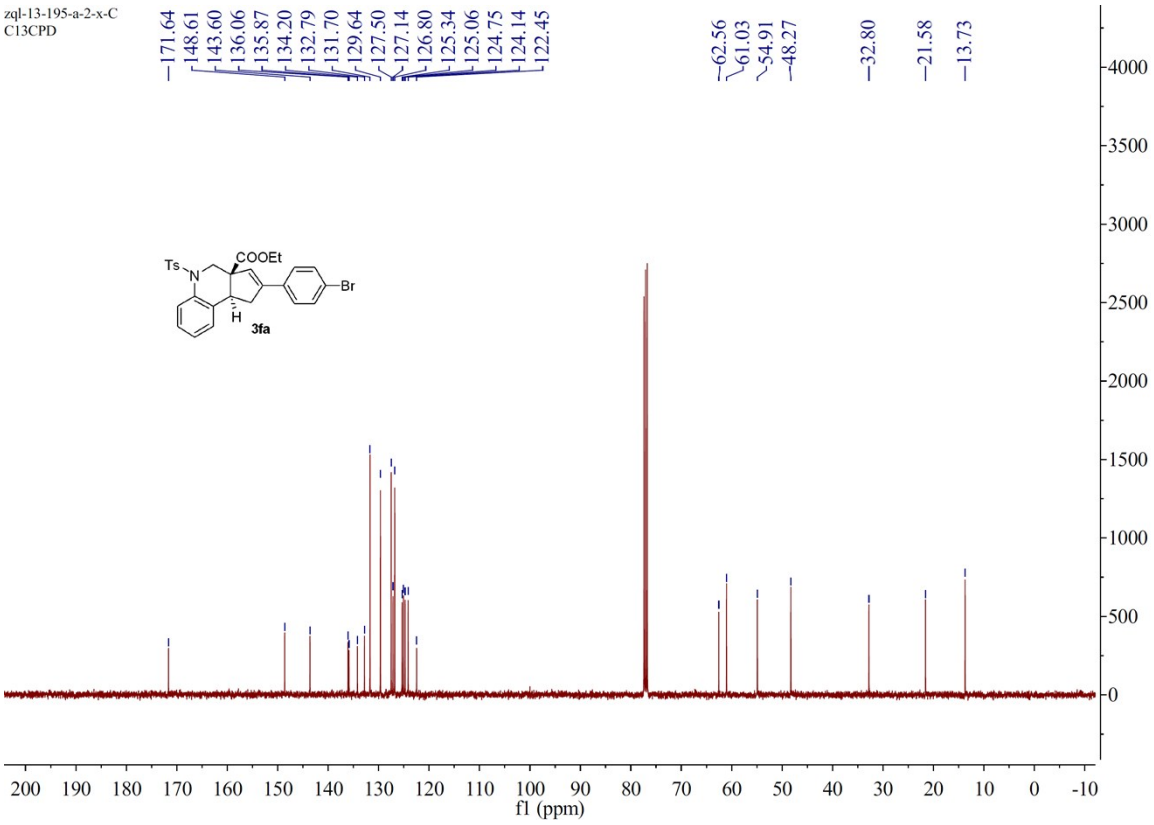

zql-13-179-a-2-xx
PROTON
7.85
7.83
7.46
7.44
7.40
7.38
7.37
7.34
7.27
7.26
7.25
7.23
7.20
7.18
7.16
7.14
6.22
4.37
4.34
3.85
3.82
3.06
3.02
2.99
2.98
2.96
2.94
2.92
2.52
2.50
2.49
2.47
2.36
0.00
Ts
N
CN
Cl
H
3db
0.95
2.06
5.00
1.50
2.99
0.97
1.00
0.99
2.04
1.04
2.98
fl (ppm)

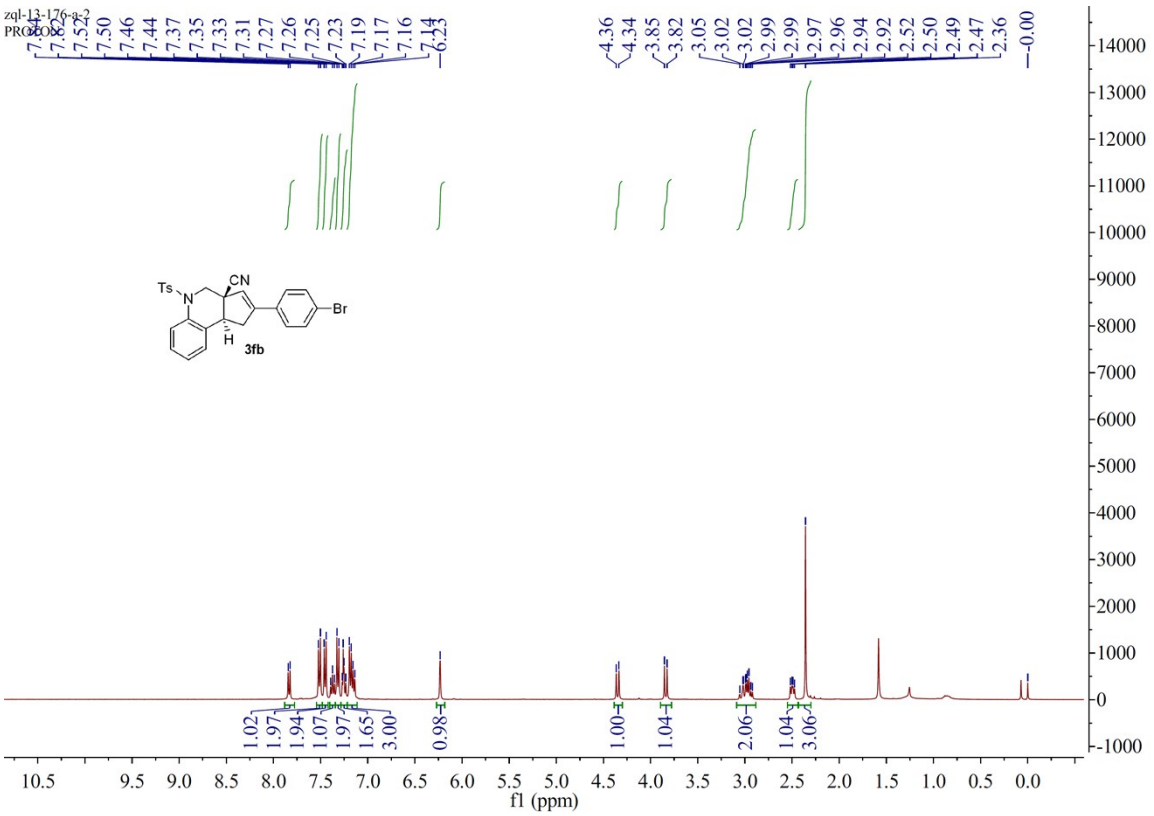

zql-13-179-a-2
C13CPD
149.24
144.19
135.52
135.19
132.50
130.96
129.84
128.99
128.58
127.40
126.85
126.02
125.87
124.35
121.73
118.53
54.08
53.07
48.92
32.44
21.62
Ts
N
CN
Cl
H
3db
fl (ppm)

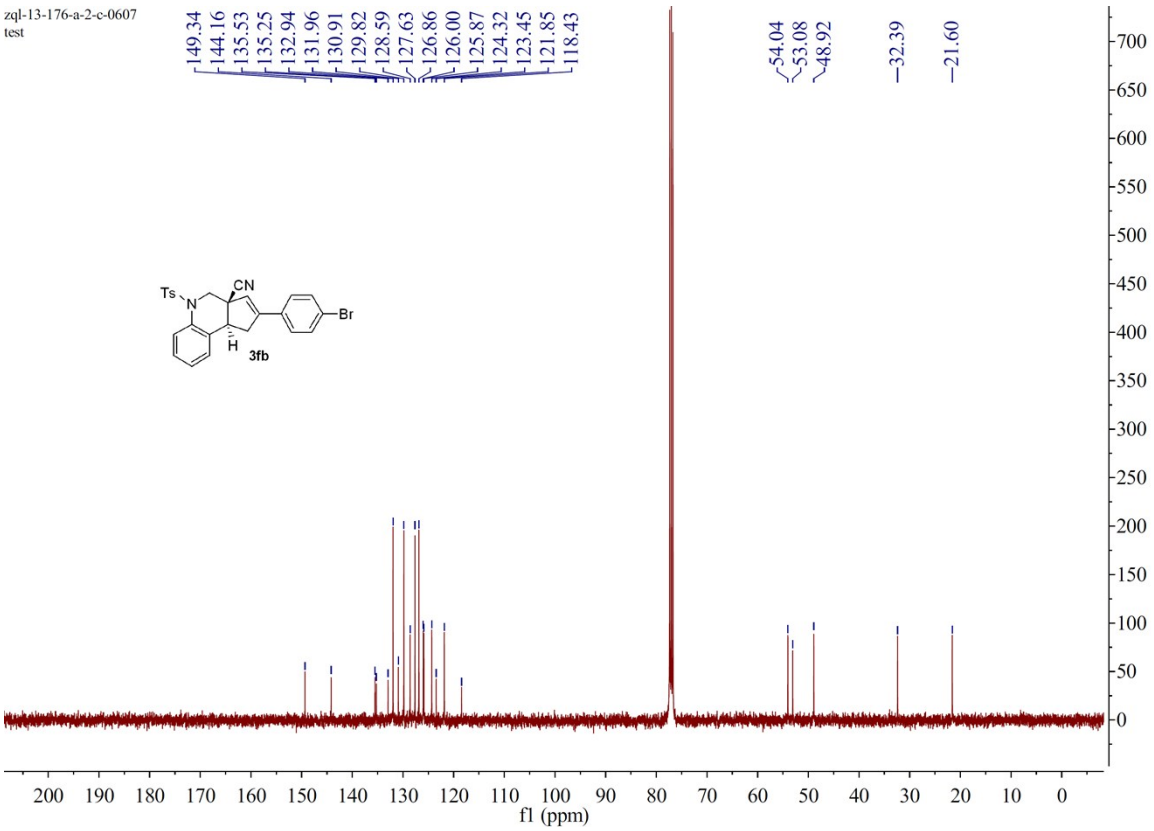

zql-15-30-a-2-0607
PROTON
8.23
8.21
7.50
7.48
7.26
7.20
7.18
7.14
6.35
4.68
4.65
3.78
3.77
3.75
3.72
3.71
2.86
2.84
2.82
2.80
2.74
2.71
2.69
2.36
0.83
0.81
0.80
0.00
Ts
N
COOEt
NO2
H
3ea
1.95
1.09
1.95
2.25
1.03
4.37
0.98
1.12
3.33
1.00
1.13
1.18
3.25
2.98
f1 (ppm)

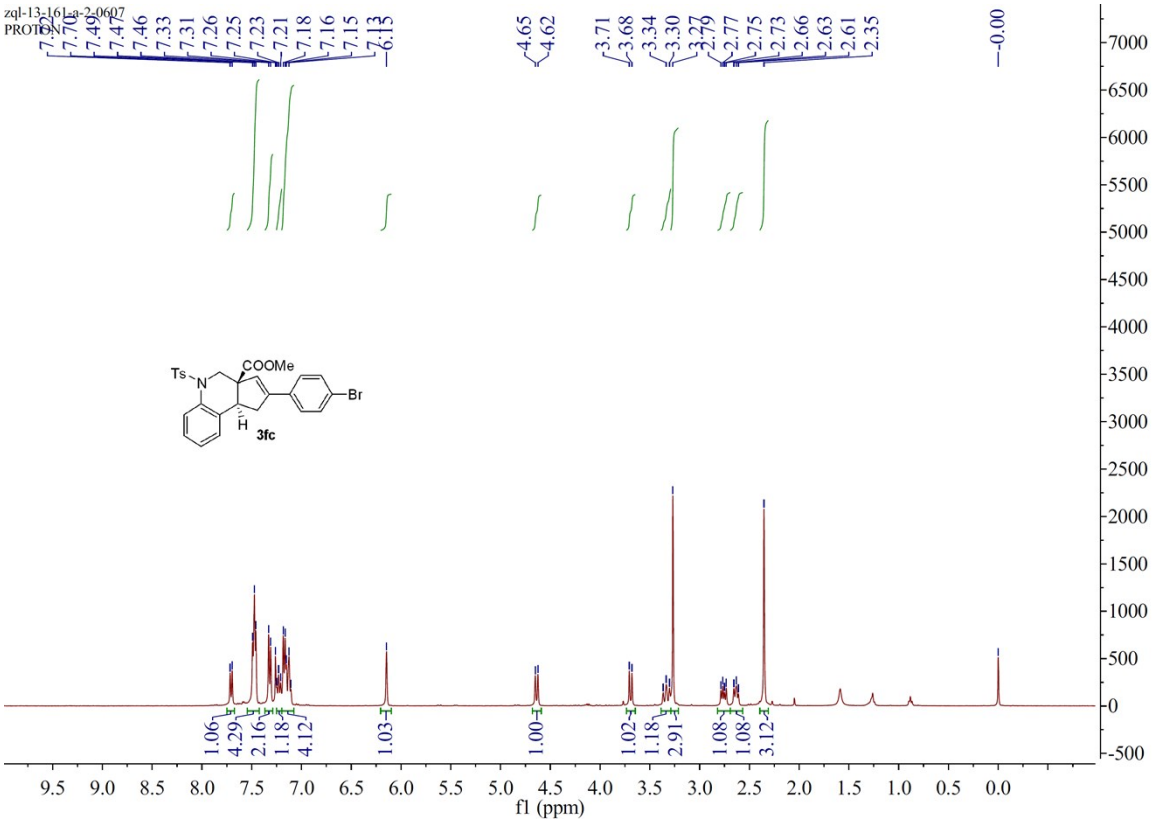

zql-15-30-a-2
C13CPD
171.15
147.97
147.41
143.69
141.51
136.08
135.89
132.30
129.67
128.69
127.35
126.81
126.66
125.30
125.14
124.11
123.92
62.75
61.26
54.59
48.37
32.93
21.58
13.72
Ts
N
COOEt
NO2
H
3ea
f1 (ppm)

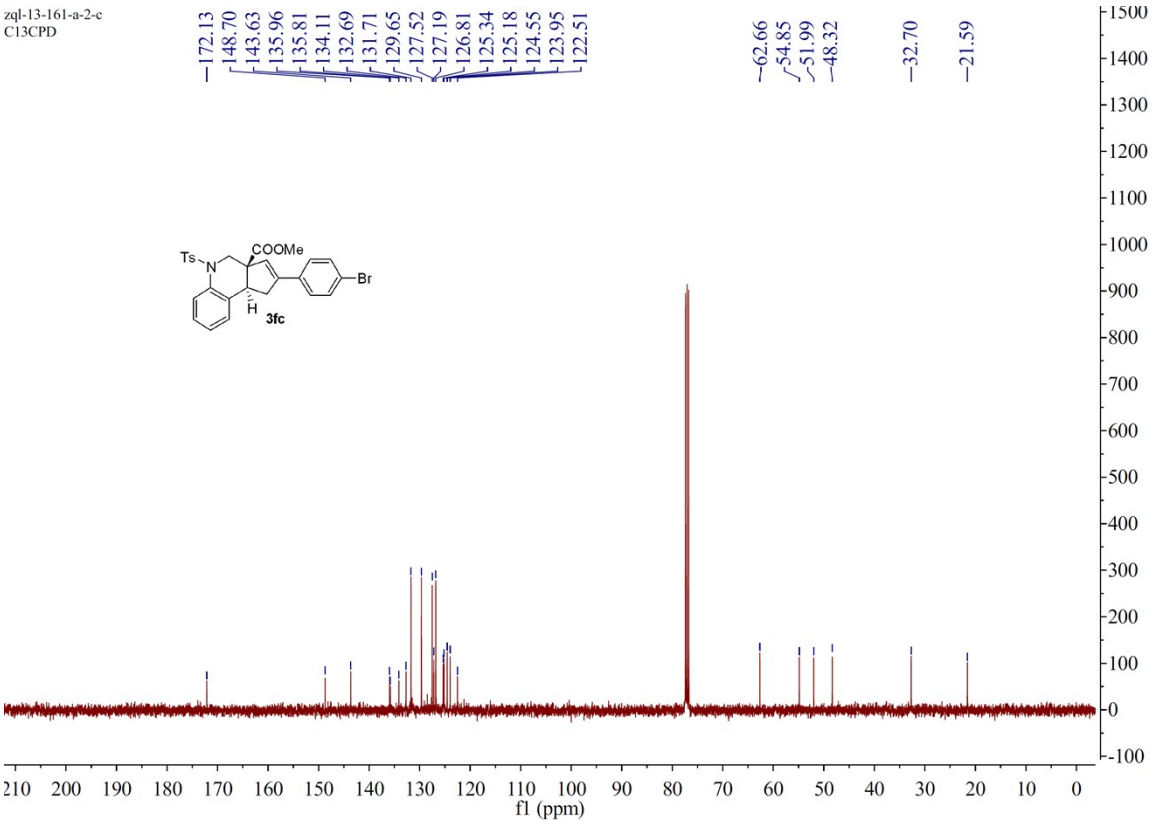

zql-13-195-a-2
PROTON
7.71
7.69
7.49
7.48
7.47
7.46
7.33
7.31
7.26
7.24
7.22
7.20
7.18
7.16
7.14
7.13
6.15
4.66
4.64
3.77
3.75
3.70
3.67
3.34
2.76
2.73
2.67
2.64
2.35
1.58
0.82
0.80
0.79
0.00
COOEt
Ts
N
H
Br
3fa
0.99
3.93
2.05
1.16
4.10
0.97
1.00
3.10
1.07
1.04
1.03
2.96
2.97
f1 (ppm)

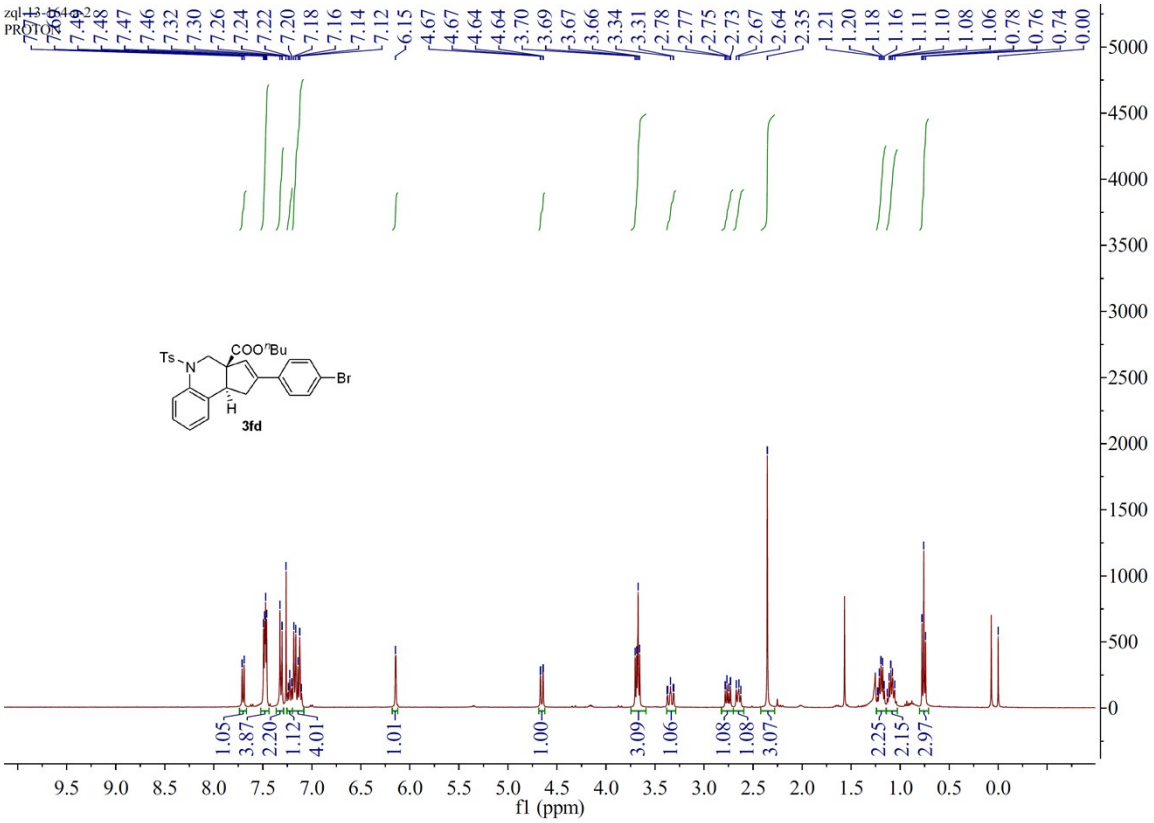

zql-13-195-a-2-x-C
C13CPD
171.64
148.61
143.60
136.06
135.87
134.20
132.79
131.70
129.64
127.50
127.14
126.80
125.34
125.06
124.75
124.14
122.45
62.56
61.03
54.91
48.27
32.80
21.58
13.73
COOEt
Ts
N
H
Br
3fa
f1 (ppm)

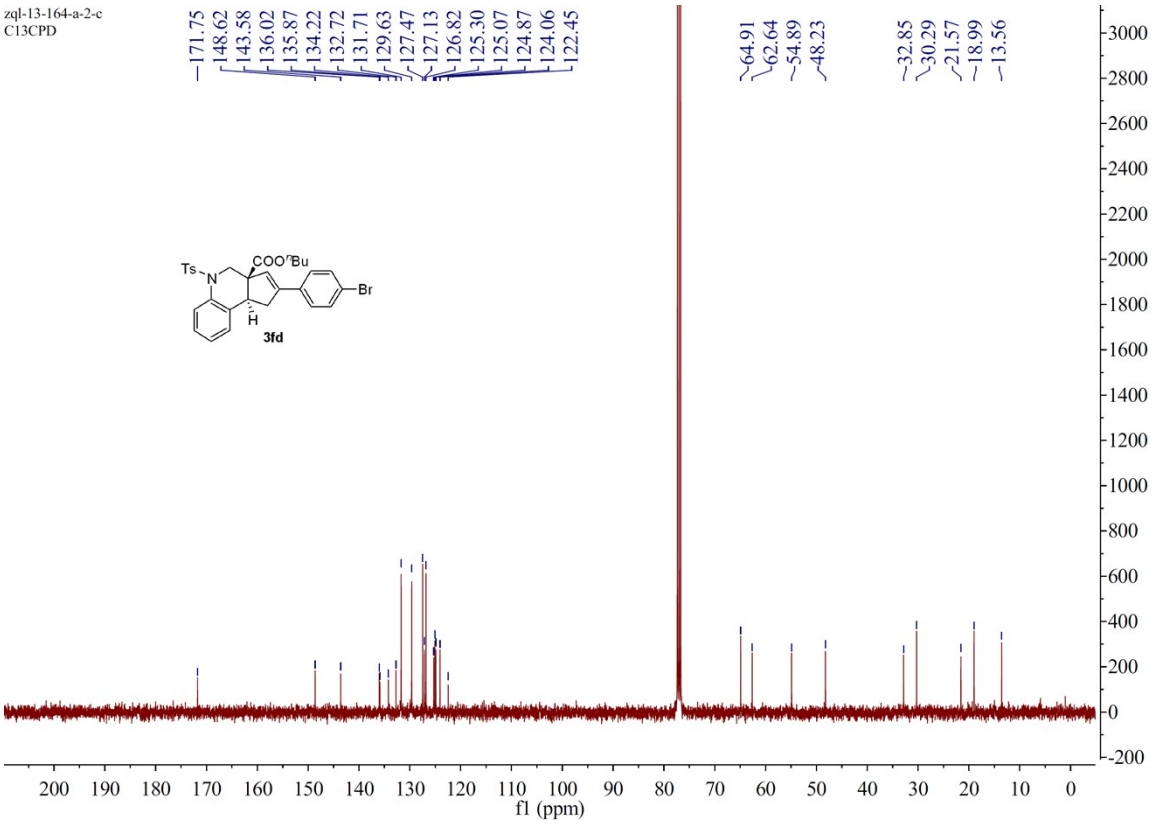

zql-13-176-a-2
PROTON
7.54
7.52
7.50
7.46
7.44
7.37
7.35
7.33
7.31
7.27
7.26
7.25
7.23
7.19
7.17
7.16
7.14
6.23
4.36
4.34
3.85
3.82
3.05
3.02
3.02
2.99
2.99
2.97
2.96
2.94
2.92
2.52
2.50
2.49
2.47
2.36
0.00
Ts
N
CN
Br
H
3fb
1.02
1.97
1.94
1.07
1.97
1.65
3.00
0.98
1.00
1.04
2.06
1.04
3.06
fl (ppm)

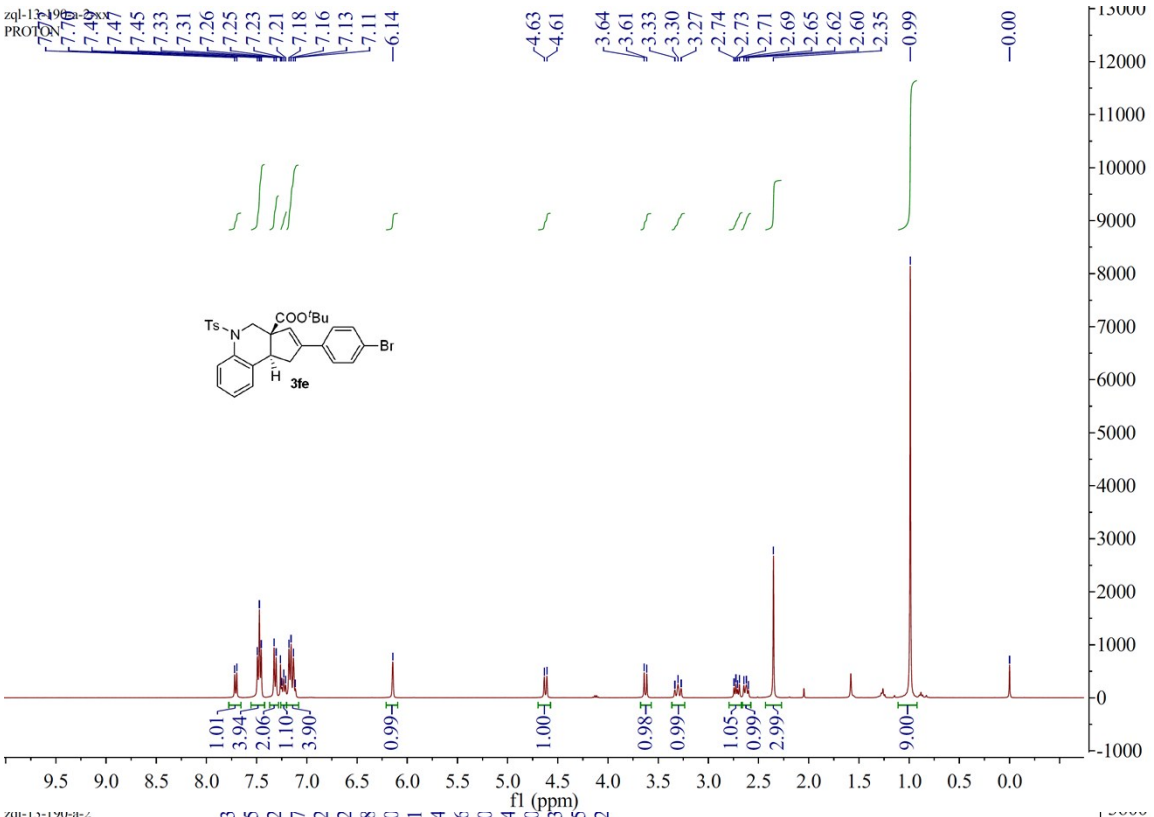

zql-13-176-a-2-c-0607
test
149.34
144.16
135.53
135.25
132.94
131.96
130.91
129.82
128.59
127.63
126.86
126.00
125.87
124.32
123.45
121.85
118.43
54.04
53.08
48.92
32.39
21.60
Ts
N
CN
Br
H
3fb
fl (ppm)

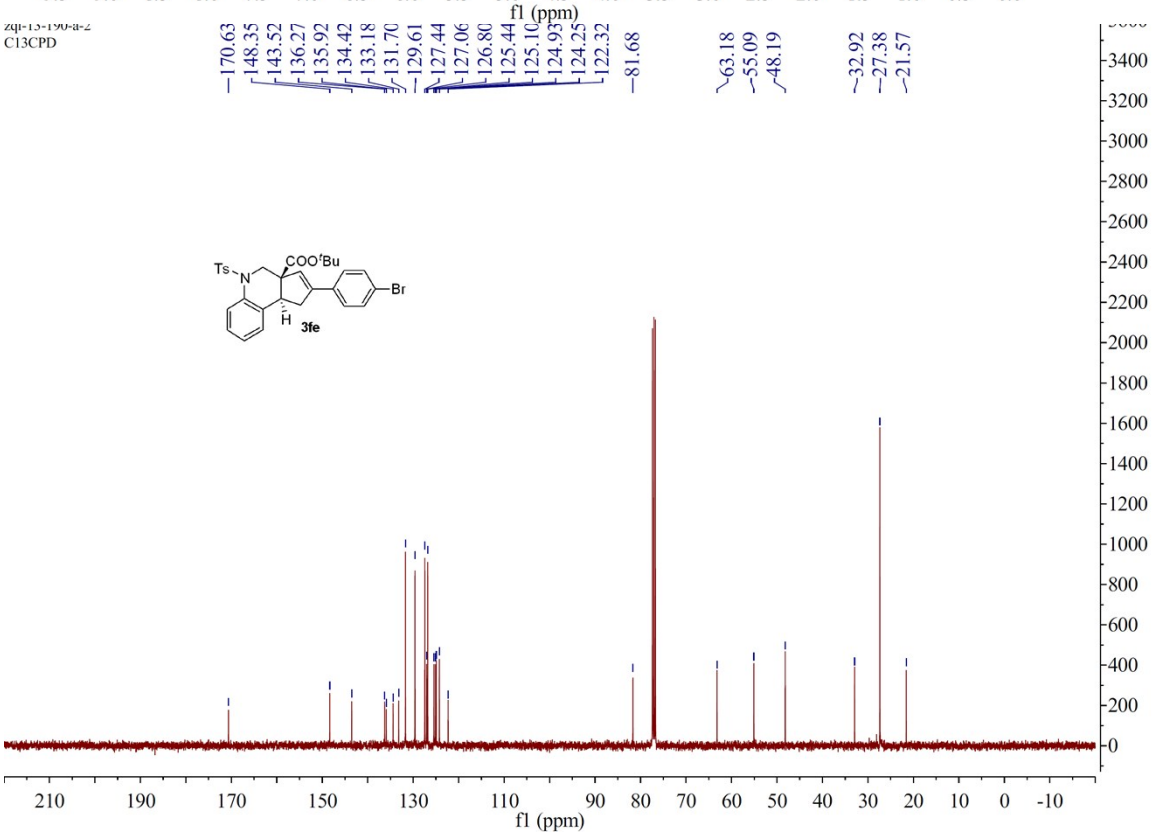

zql-13-161-a-2-0607
PROTON
7.72
7.70
7.49
7.47
7.46
7.33
7.31
7.26
7.25
7.23
7.21
7.18
7.16
7.15
7.13
6.15
4.65
4.62
3.71
3.68
3.34
3.30
3.27
2.79
2.77
2.75
2.73
2.66
2.63
2.61
2.35
0.00
COOMe
Ts
N
Br
H
3fc
1.06
4.29
2.16
1.18
4.12
1.03
1.00
1.02
1.18
2.91
1.08
1.08
3.12
f1 (ppm)

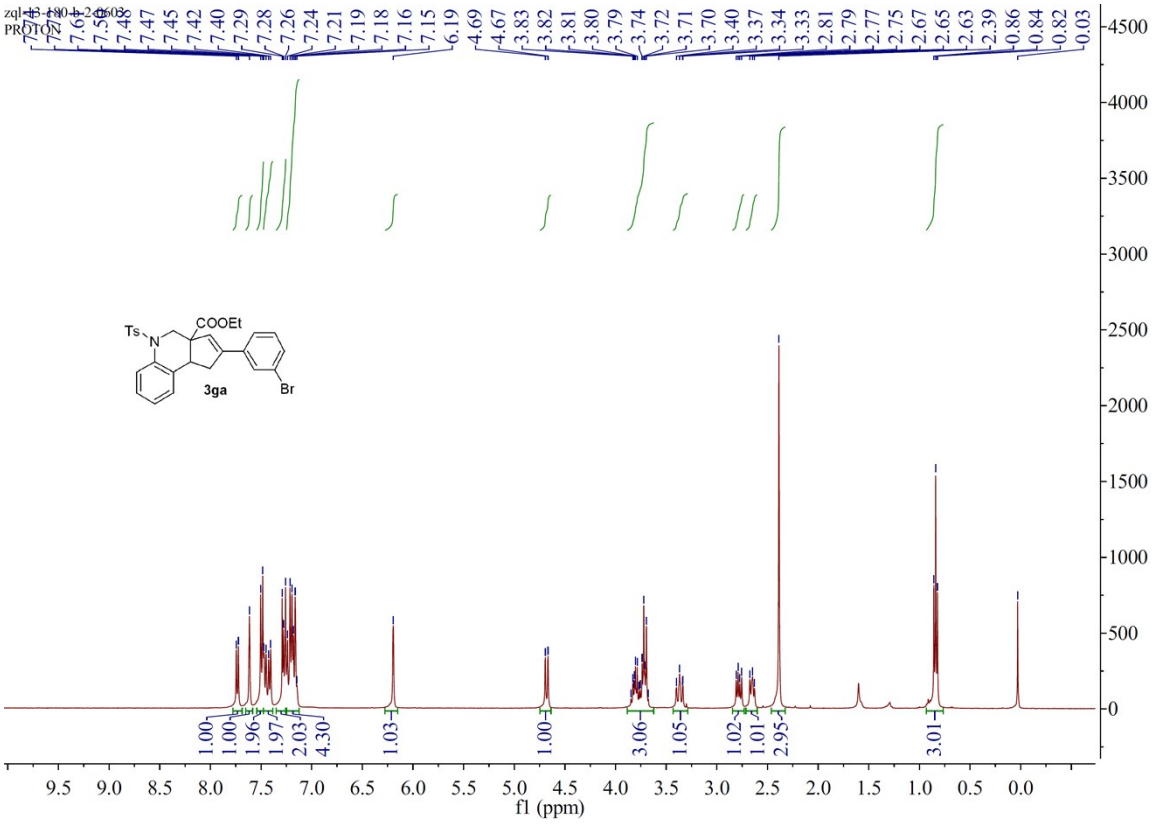

zql-13-161-a-2-c
C13CPD
172.13
148.70
143.63
135.96
135.81
134.11
132.69
131.71
129.65
127.52
127.19
126.81
125.34
125.18
124.55
123.95
122.51
62.66
54.85
51.99
48.32
32.70
21.59
COOMe
Ts
N
Br
H
3fc
f1 (ppm)

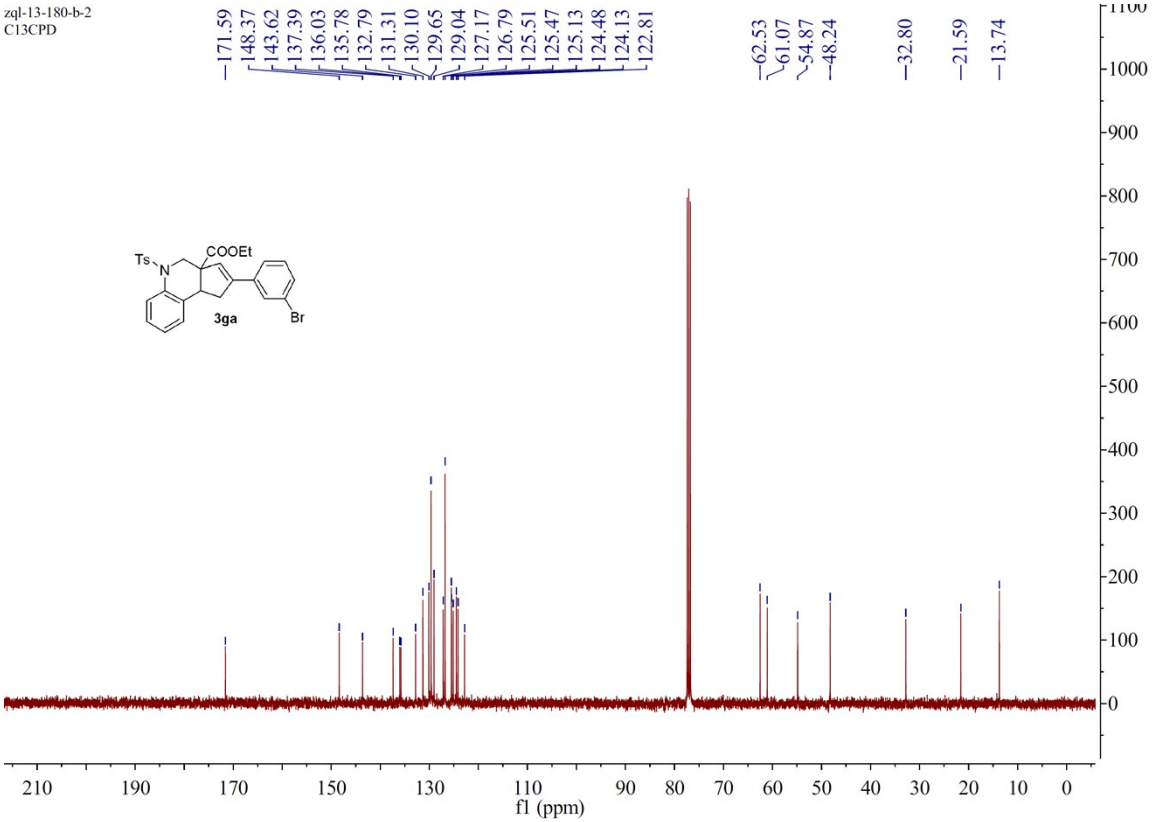

zql-13-164-a-2-c
PROTON
7.71
7.69
7.49
7.48
7.47
7.46
7.32
7.30
7.26
7.24
7.22
7.20
7.18
7.16
7.14
7.12
6.15
4.67
4.67
4.64
4.64
3.70
3.69
3.67
3.66
3.34
3.31
2.78
2.77
2.75
2.73
2.67
2.64
2.35
1.21
1.20
1.18
1.16
1.11
1.10
1.08
1.06
0.78
0.76
0.74
0.00
Ts
N
COO^{n}Bu
H
Br
3fd
1.05
3.87
2.20
1.12
4.01
1.01
1.00
3.09
1.06
1.08
1.08
3.07
2.25
2.15
2.97
fl (ppm)

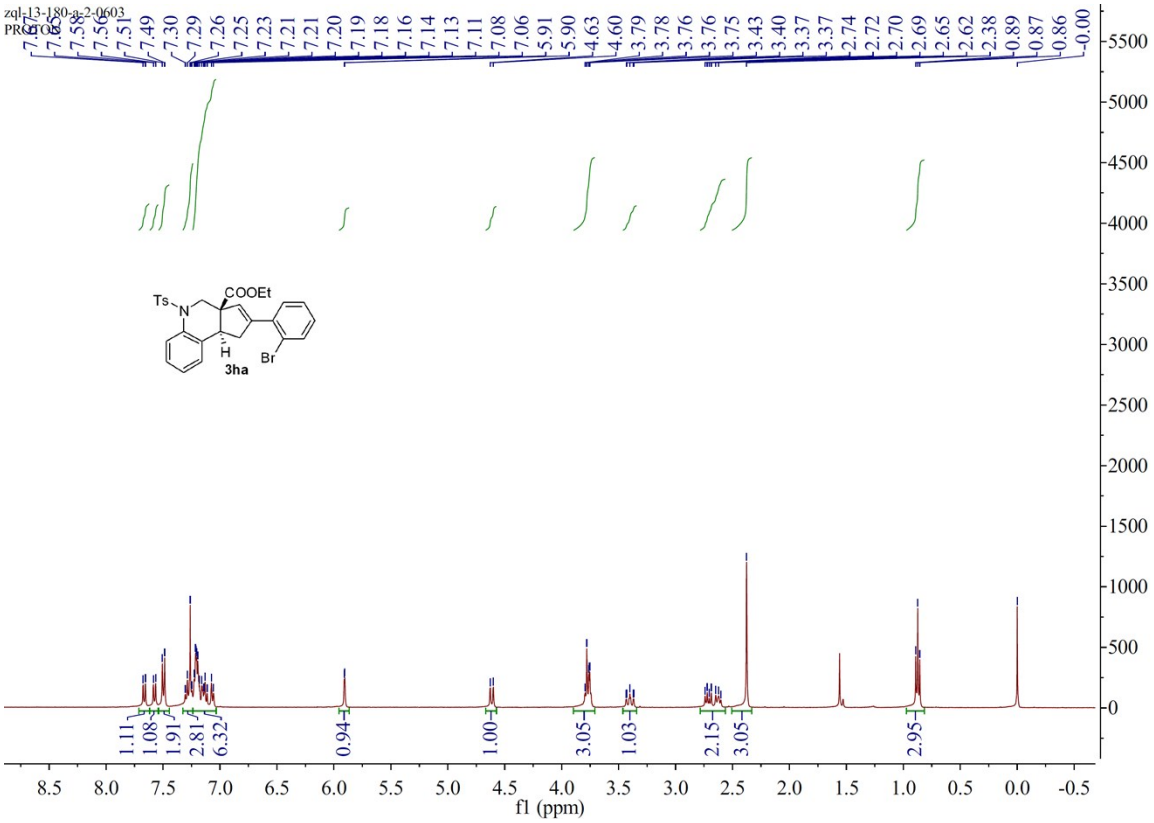

zql-13-164-a-2-c
C13CPD
171.75
148.62
143.58
136.02
135.87
134.22
132.72
131.71
129.63
127.47
127.13
126.82
125.30
125.07
124.87
124.06
122.45
64.91
62.64
54.89
48.23
32.85
30.29
21.57
18.99
13.56
Ts
N
COO^{n}Bu
H
Br
3fd
fl (ppm)

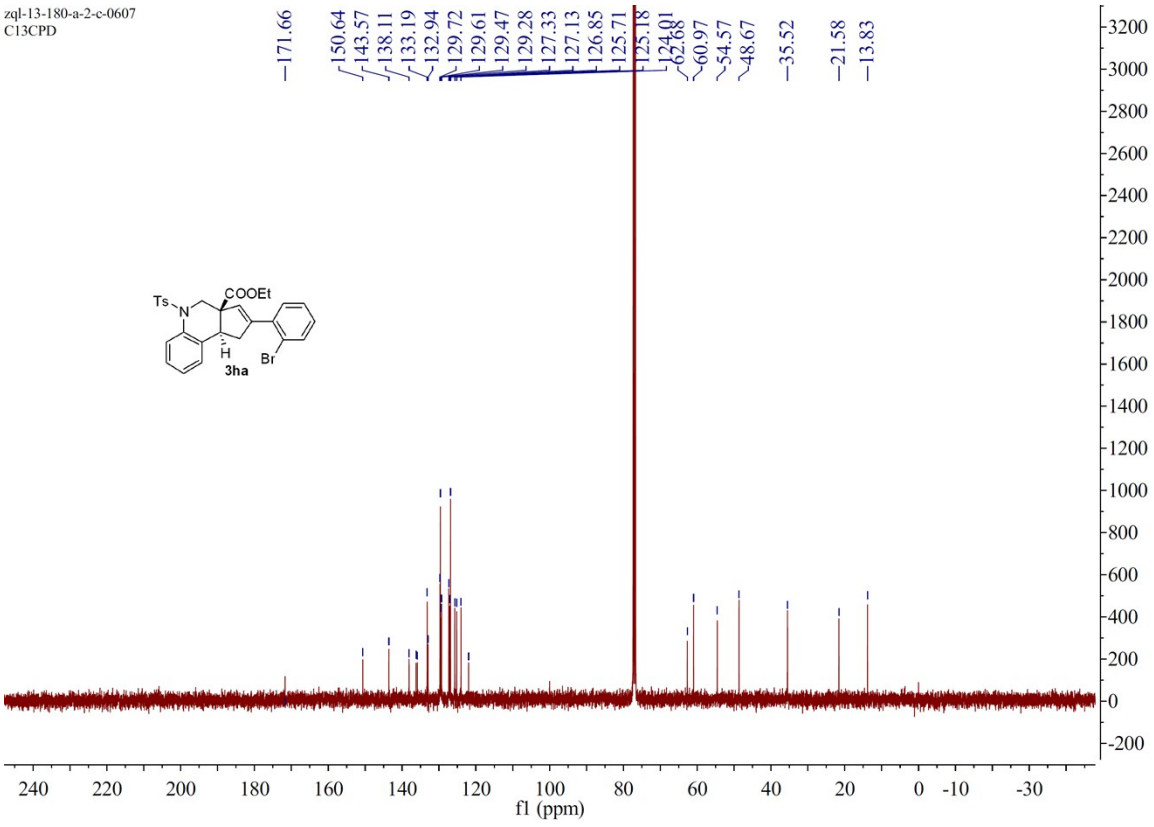

PROTON
7.76
7.49
7.47
7.45
7.33
7.31
7.26
7.25
7.23
7.21
7.18
7.16
7.13
7.11
6.14
4.63
4.61
3.64
3.61
3.33
3.30
3.27
2.74
2.73
2.71
2.69
2.65
2.62
2.60
2.35
0.99
0.00
COO^{t}Bu
Ts
N
H
Br
3fe
1.01
3.94
2.06
1.10
3.90
0.99
1.00
0.98
0.99
1.05
0.99
2.99
9.00
f1 (ppm)

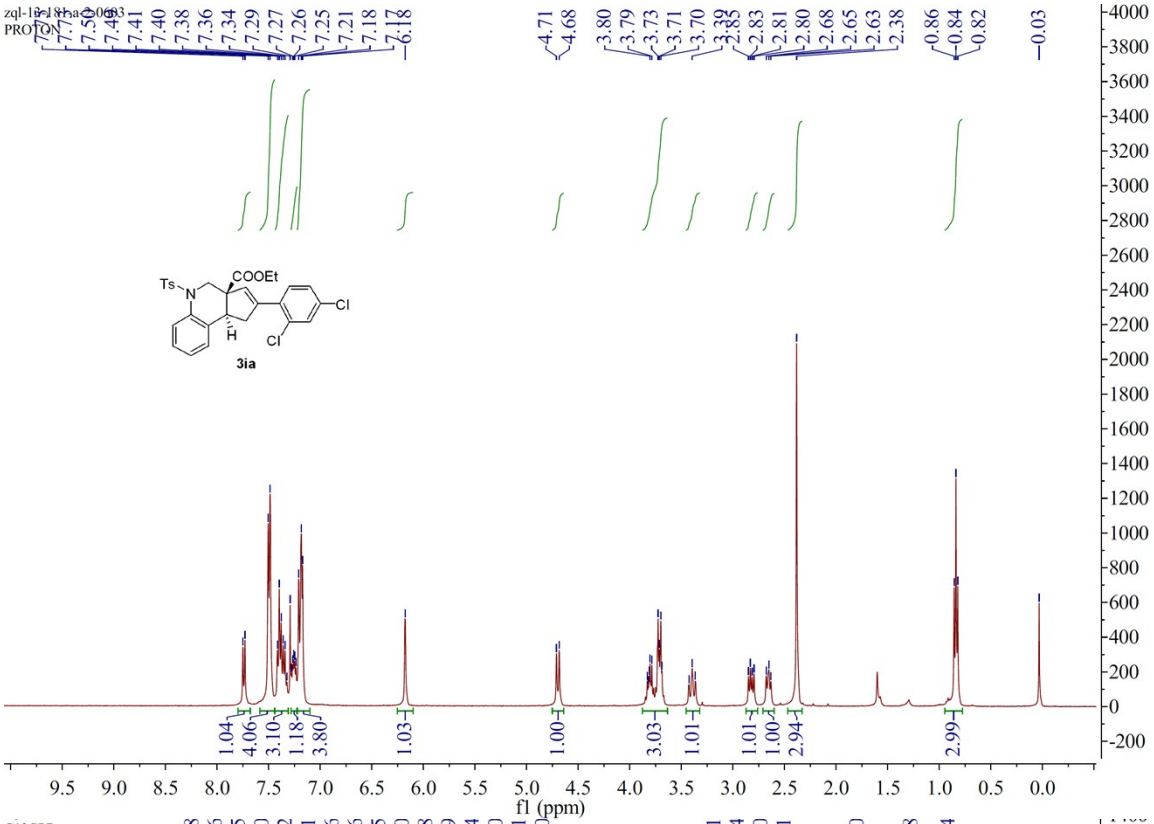

C13CPD
170.63
148.35
143.52
136.27
135.92
134.42
133.18
131.70
129.61
127.44
127.06
126.80
125.44
125.10
124.93
124.25
122.32
81.68
63.18
55.09
48.19
32.92
27.38
21.57
COO^{t}Bu
Ts
N
H
Br
3fe
f1 (ppm)

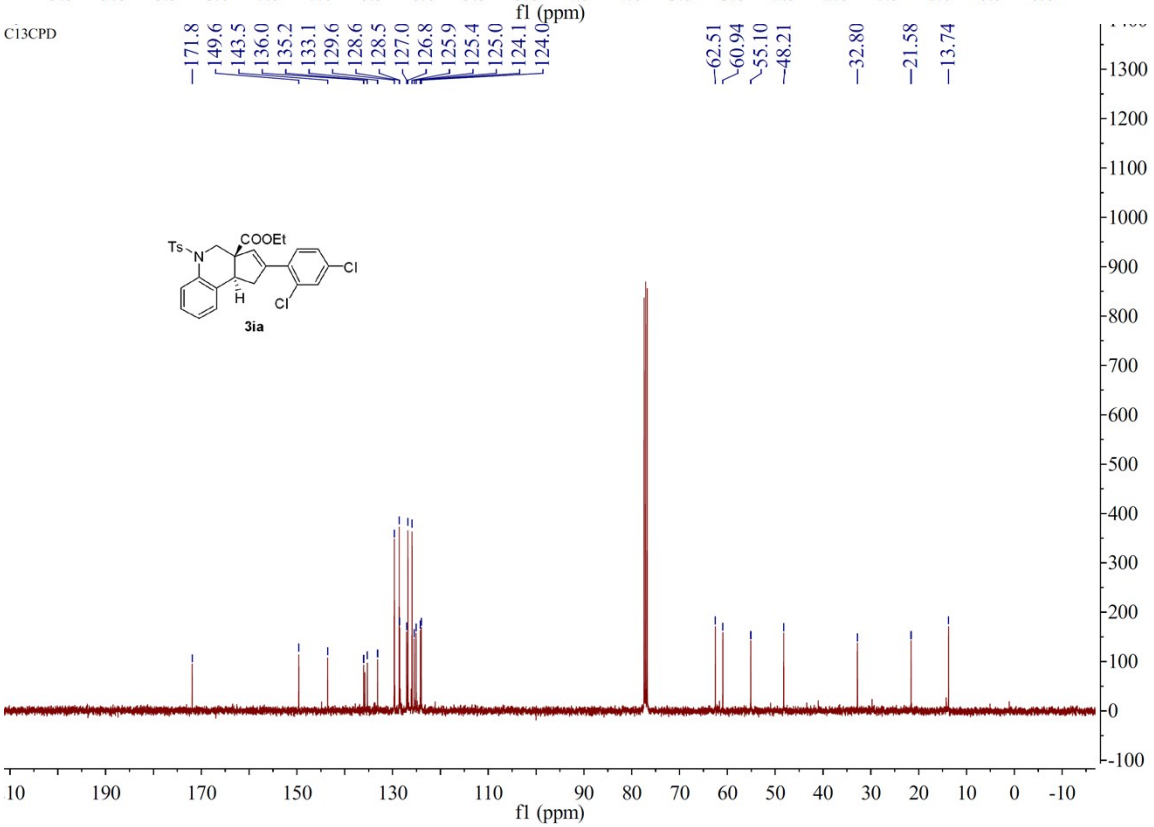

zql-13-180-b-2-1603
PROTON
7.72
7.69
7.55
7.48
7.47
7.45
7.42
7.40
7.29
7.28
7.26
7.24
7.21
7.19
7.18
7.16
7.15
6.19
4.69
4.67
3.83
3.82
3.81
3.80
3.79
3.74
3.72
3.71
3.70
3.40
3.37
3.34
3.33
2.81
2.79
2.77
2.75
2.67
2.65
2.63
2.39
0.86
0.84
0.82
0.03
COOEt
Ts
N
3ga
Br
1.00
1.00
1.96
1.97
2.03
4.30
1.03
1.00
3.06
1.05
1.02
1.01
2.95
3.01
fl (ppm)

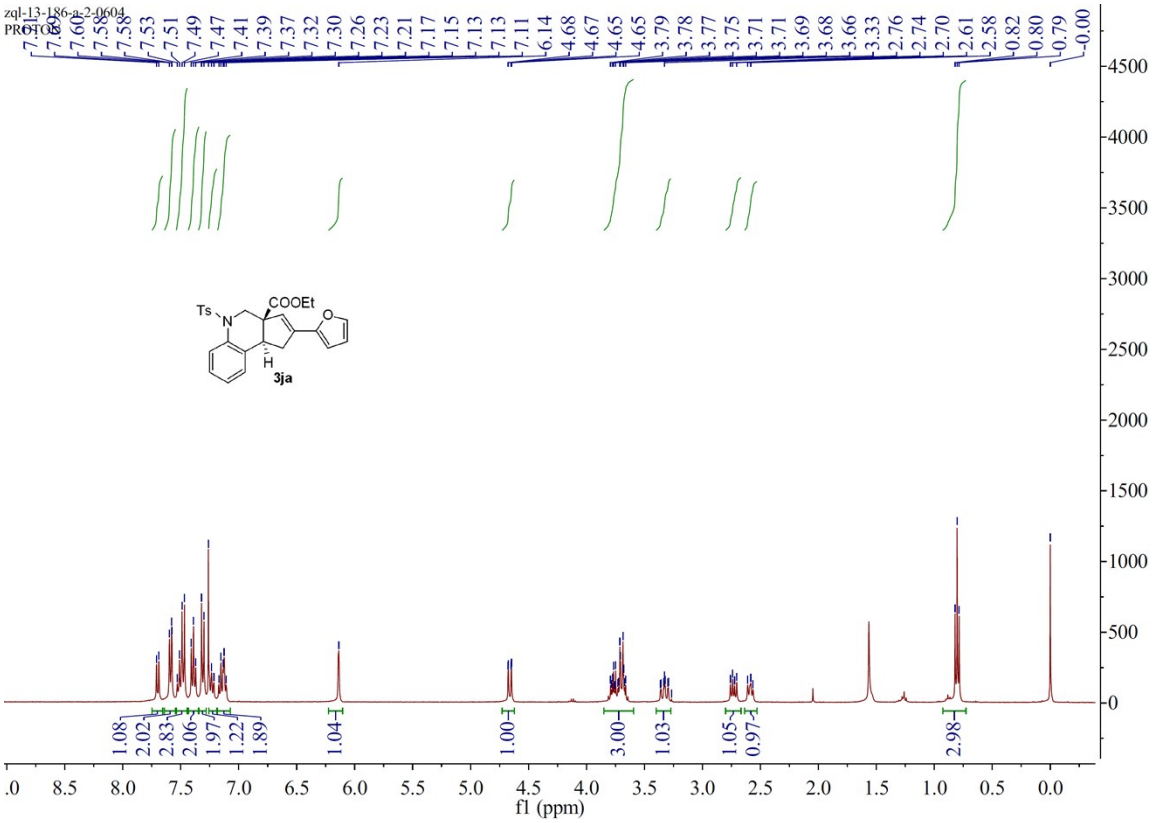

zql-13-180-b-2
C13CPD
171.59
148.37
143.62
137.39
136.03
135.78
132.79
131.31
130.10
129.65
129.04
127.17
126.79
125.51
125.47
125.13
124.48
124.13
122.81
62.53
61.07
54.87
48.24
32.80
21.59
13.74
COOEt
Ts
N
3ga
Br
fl (ppm)

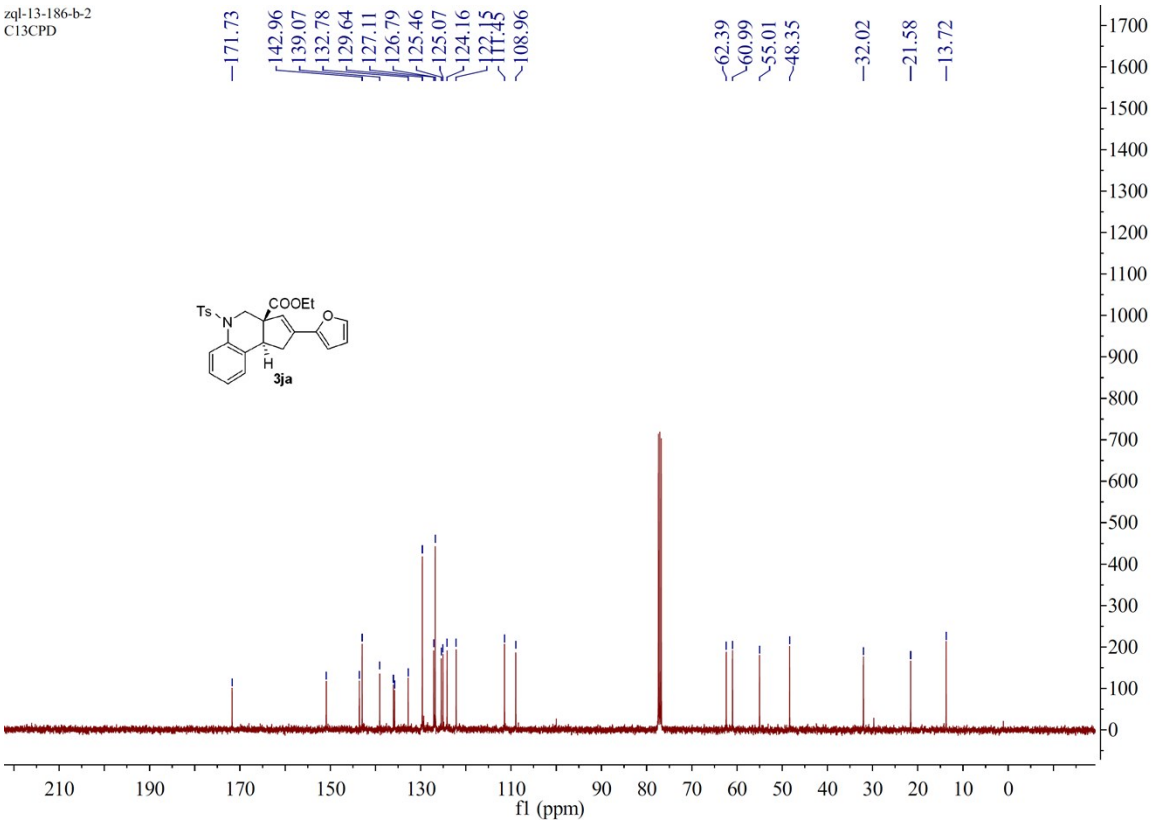

zql-13-180-a-2-0603
PROTON
7.77
7.58
7.56
7.51
7.49
7.30
7.29
7.26
7.25
7.23
7.21
7.21
7.20
7.19
7.18
7.16
7.14
7.13
7.11
7.08
7.06
5.91
5.90
4.63
4.60
3.79
3.78
3.76
3.76
3.75
3.43
3.40
3.37
3.37
2.74
2.72
2.70
2.69
2.65
2.62
2.38
0.89
0.87
0.86
0.00
Ts
N
COOEt
H
Br
3ha
1.11
1.08
1.91
2.81
6.32
0.94
1.00
3.05
1.03
2.15
3.05
2.95
fl (ppm)

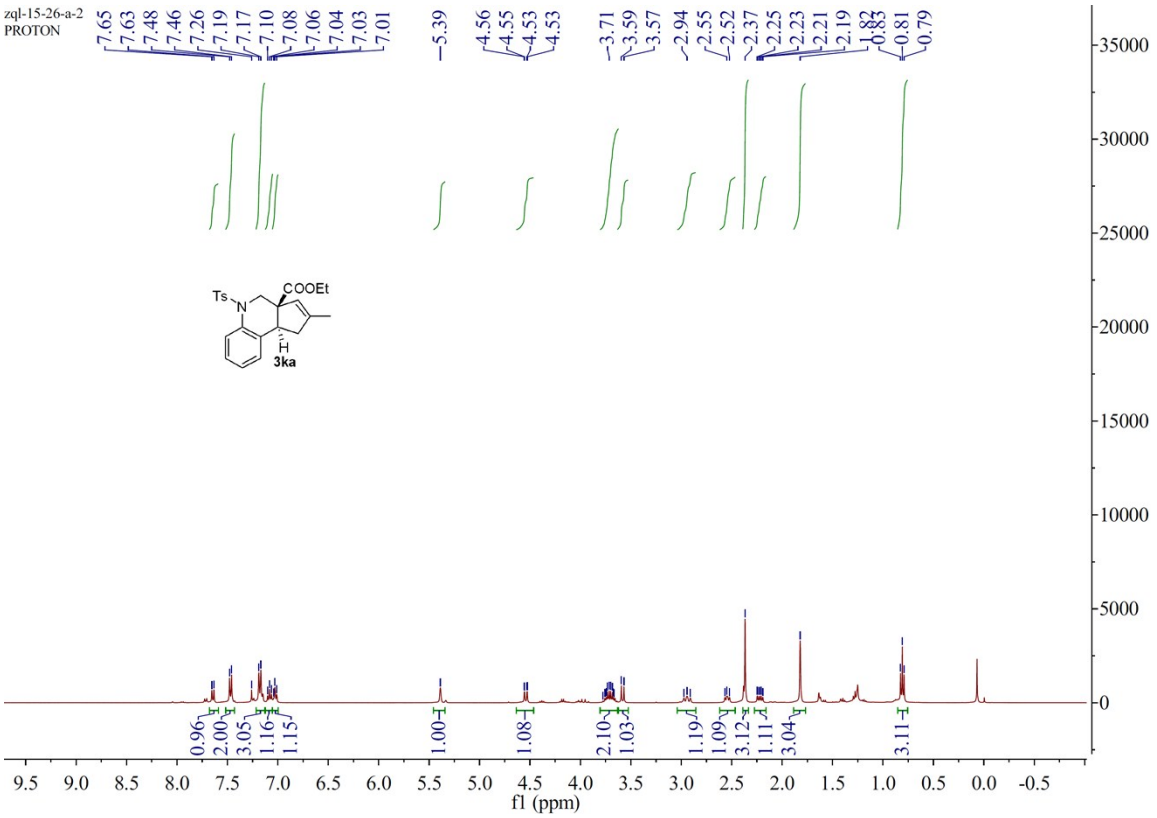

zql-13-180-a-2-c-0607
C13CPD
171.66
150.64
143.57
138.11
133.19
132.94
129.72
129.61
129.47
129.28
127.33
127.13
126.85
125.71
125.18
124.01
62.68
60.97
54.57
48.67
35.52
21.58
13.83
Ts
N
COOEt
H
Br
3ha
fl (ppm)

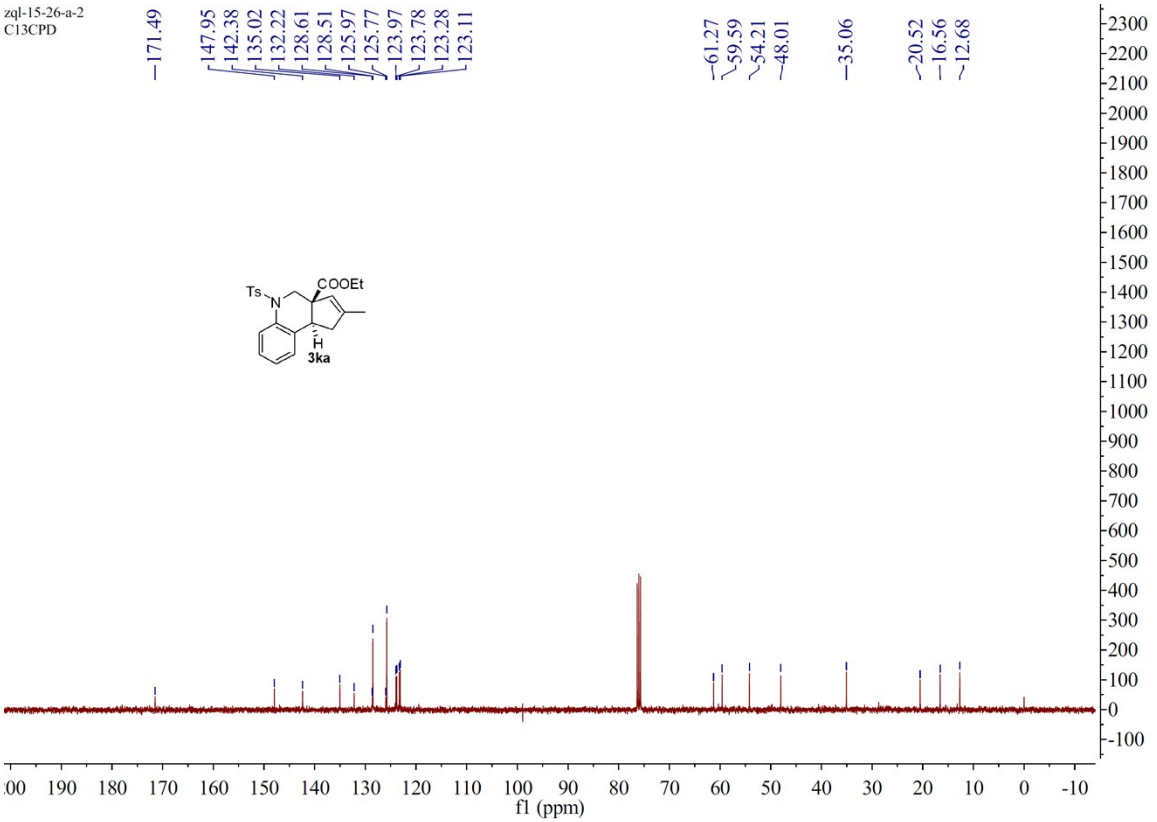

PROTON
7.77
7.54
7.49
7.41
7.40
7.38
7.36
7.34
7.29
7.27
7.26
7.25
7.21
7.18
7.17
6.18
4.71
4.68
3.80
3.79
3.73
3.71
3.70
2.85
2.83
2.81
2.80
2.68
2.65
2.63
2.38
0.86
0.84
0.82
0.03
Ts
N
COOEt
H
Cl
Cl
3ia
1.04
4.06
3.10
1.18
3.80
1.03
1.00
3.03
1.01
1.01
1.00
2.94
2.99
f1 (ppm)

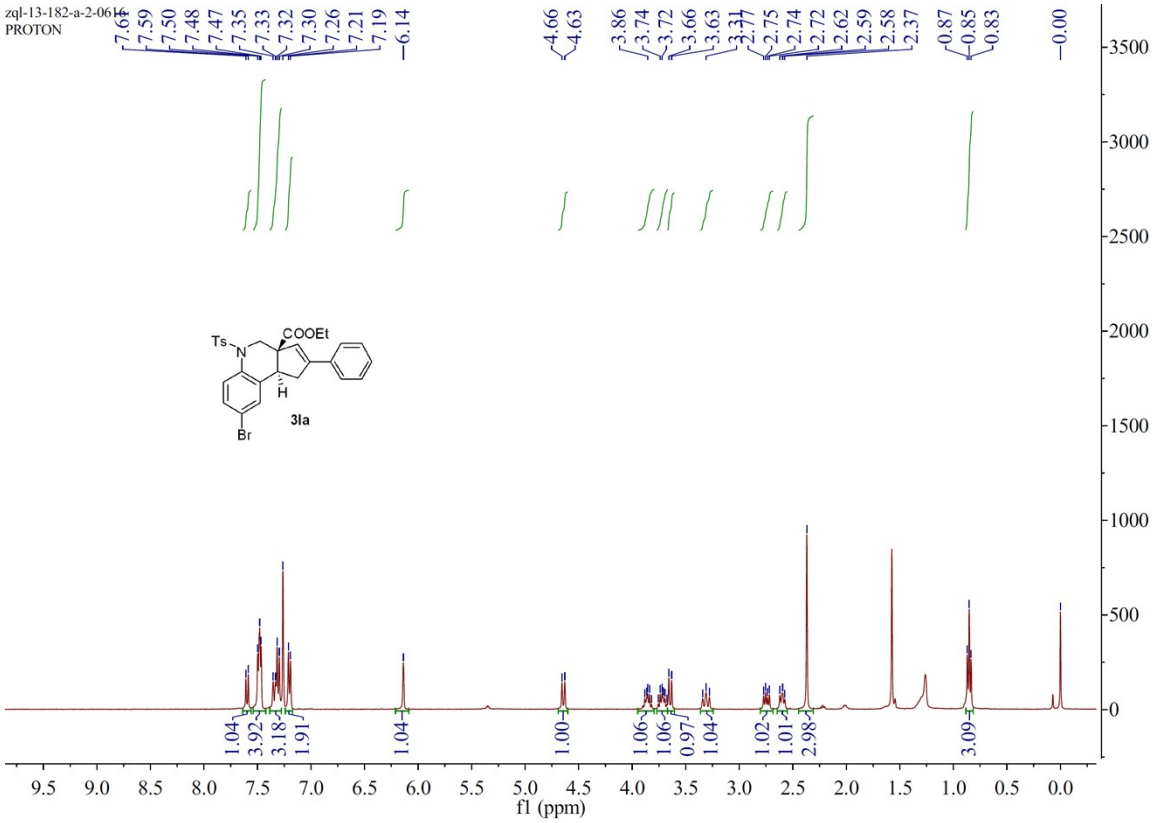

C13CPD
171.8
149.6
143.5
136.0
135.2
133.1
129.6
128.6
128.5
127.0
126.8
125.9
125.4
125.0
124.1
124.0
62.51
60.94
55.10
48.21
32.80
21.58
13.74
Ts
N
COOEt
H
Cl
Cl
3ia
f1 (ppm)

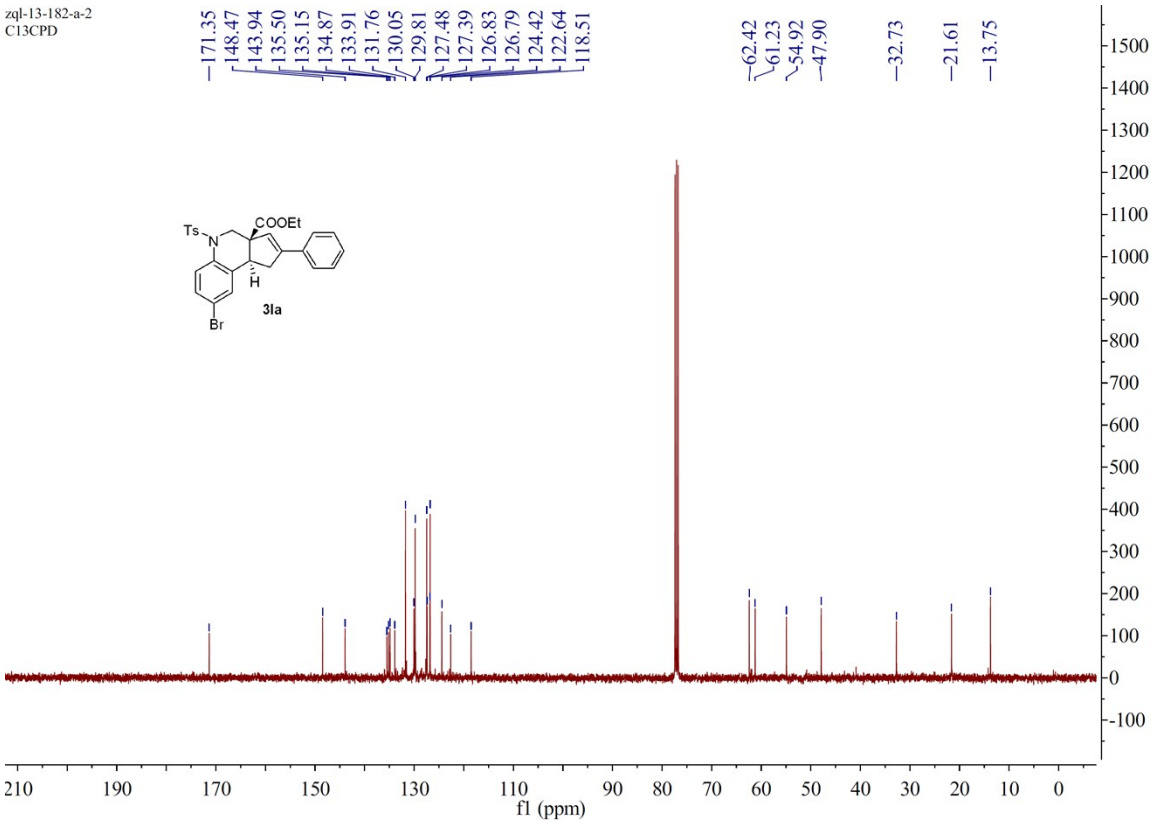

zql-13-186-a-2-0604
PROTON
7.72
7.60
7.58
7.56
7.53
7.51
7.49
7.47
7.41
7.39
7.37
7.32
7.30
7.26
7.23
7.21
7.17
7.15
7.13
7.13
7.11
6.14
4.68
4.67
4.65
4.65
3.79
3.78
3.77
3.75
3.71
3.71
3.69
3.68
3.66
3.33
2.76
2.74
2.70
2.61
2.58
0.82
0.80
0.79
0.00
COOEt
Ts
N
O
H
3ja
1.08
2.02
2.83
2.06
1.97
1.22
1.89
1.04
1.00
3.00
1.03
1.05
0.97
2.98
fl (ppm)

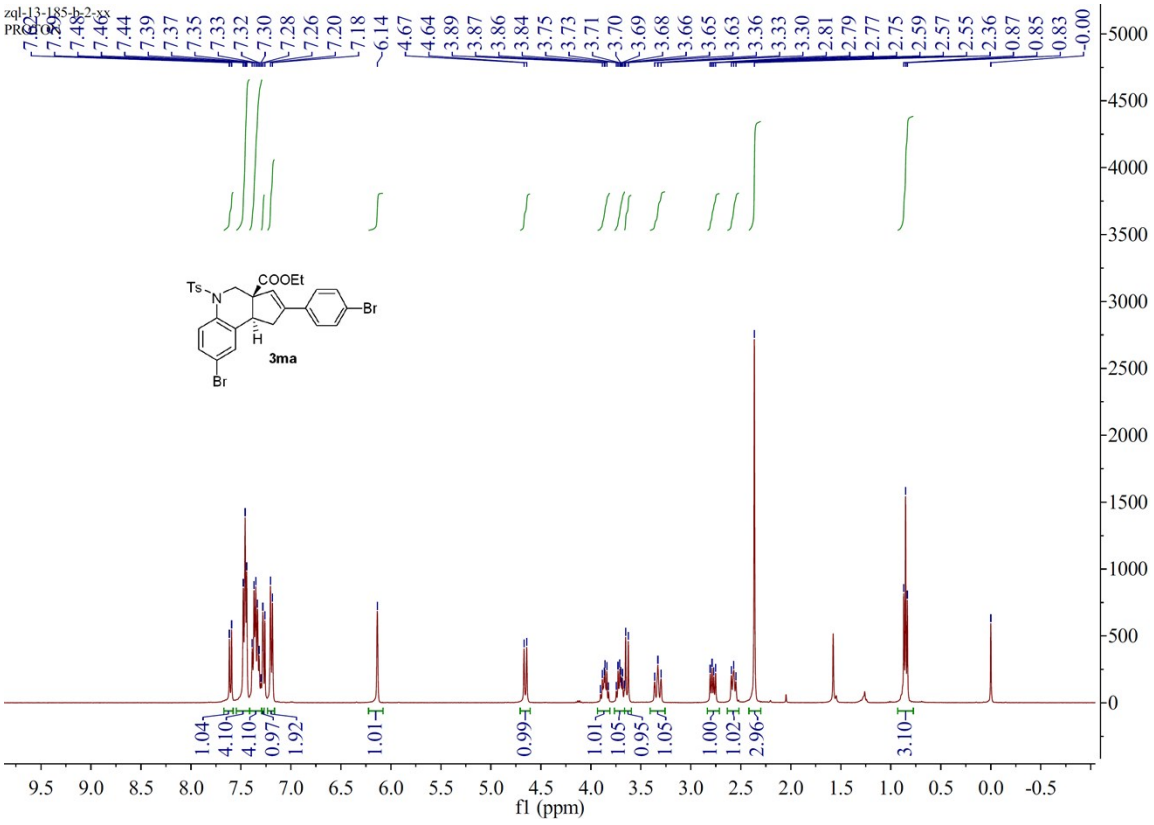

zql-13-186-b-2
C13CPD
171.73
142.96
139.07
132.78
129.64
127.11
126.79
125.46
125.07
124.16
111.45
108.96
62.39
60.99
55.01
48.35
32.02
21.58
13.72
COOEt
Ts
N
O
H
3ja
fl (ppm)

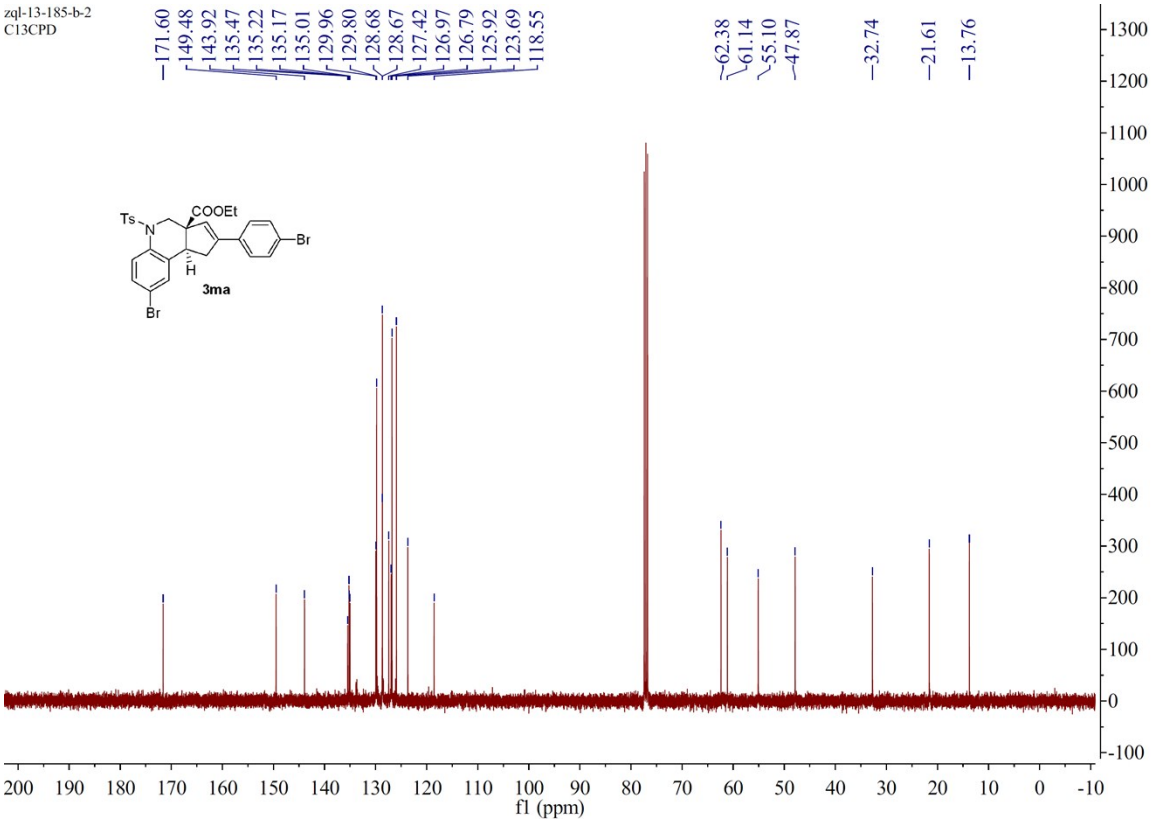

zql-15-26-a-2
PROTON
7.65
7.63
7.48
7.46
7.26
7.19
7.17
7.10
7.08
7.06
7.04
7.03
7.01
5.39
4.56
4.55
4.53
4.53
3.71
3.59
3.57
2.94
2.55
2.52
2.37
2.25
2.23
2.21
2.19
1.82
0.83
0.81
0.79
Ts
N
COOEt
H
3ka
0.96
2.00
3.05
1.16
1.15
1.00
1.08
2.10
1.03
1.19
1.09
3.12
1.11
3.04
3.11
f1 (ppm)

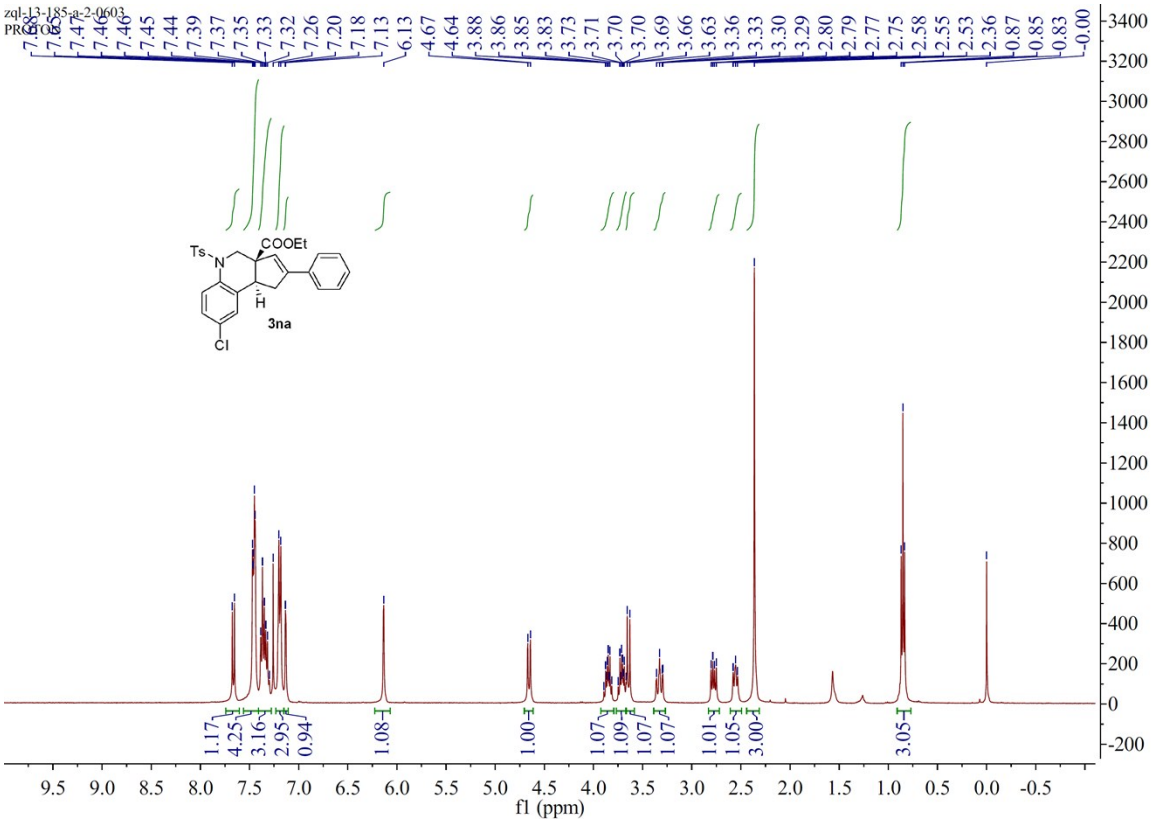

zql-15-26-a-2
C13CPD
171.49
147.95
142.38
135.02
132.22
128.61
128.51
125.97
125.77
123.97
123.78
123.28
123.11
61.27
59.59
54.21
48.01
35.06
20.52
16.56
12.68
Ts
N
COOEt
H
3ka
f1 (ppm)

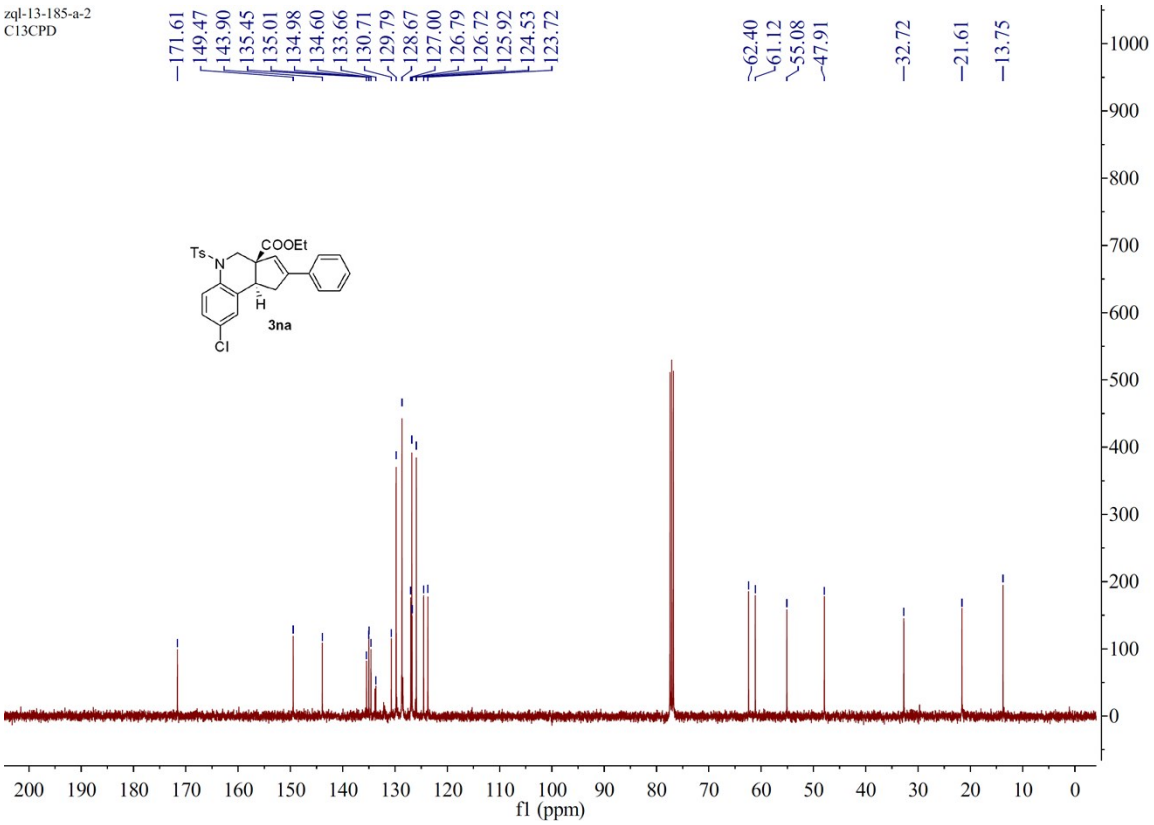

zql-13-182-a-2-06H
PROTON
7.61
7.59
7.50
7.48
7.47
7.35
7.33
7.32
7.30
7.26
7.21
7.19
6.14
4.66
4.63
3.86
3.74
3.72
3.66
3.63
3.31
2.77
2.75
2.74
2.72
2.62
2.59
2.58
2.37
0.87
0.85
0.83
0.00
Ts
N
COOEt
H
Br
3la
1.04
3.92
3.18
1.91
1.04
1.00
1.06
1.06
0.97
1.04
1.02
1.01
2.98
3.09
fl (ppm)

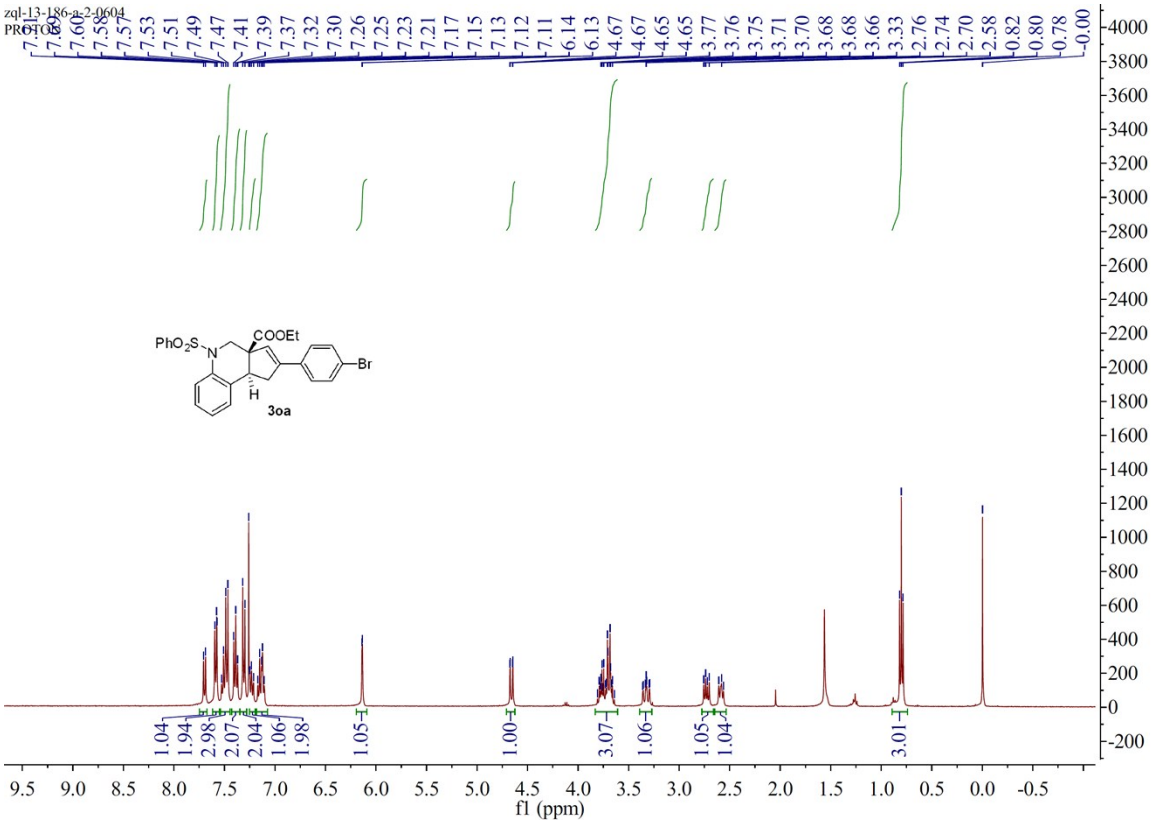

zql-13-182-a-2
C13CPD
171.35
148.47
143.94
135.50
135.15
134.87
133.91
131.76
130.05
129.81
127.48
127.39
126.83
126.79
124.42
122.64
118.51
62.42
61.23
54.92
47.90
32.73
21.61
13.75
Ts
N
COOEt
H
Br
3la
fl (ppm)

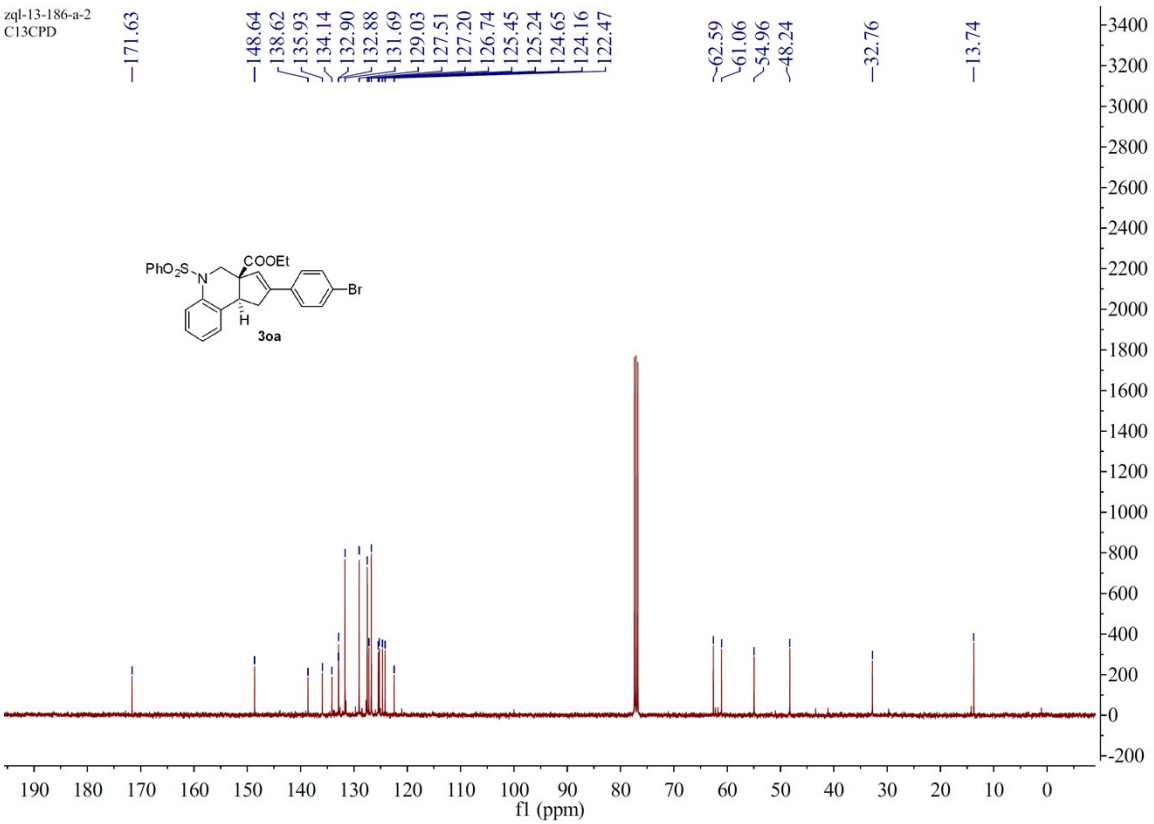

zql-13-185-b-2-yx
PROTON
7.48
7.46
7.44
7.39
7.37
7.35
7.33
7.32
7.30
7.28
7.26
7.20
7.18
6.14
4.67
4.64
3.89
3.87
3.86
3.84
3.75
3.73
3.71
3.70
3.69
3.68
3.66
3.65
3.63
3.36
3.33
3.30
2.81
2.79
2.77
2.75
2.59
2.57
2.55
2.36
0.87
0.85
0.83
0.00
COOEt
Ts
N
Br
H
3ma
Br
1.04
4.10
4.10
0.97
1.92
1.01
0.99
1.01
1.05
0.95
1.05
1.00
1.02
2.96
3.10
fl (ppm)

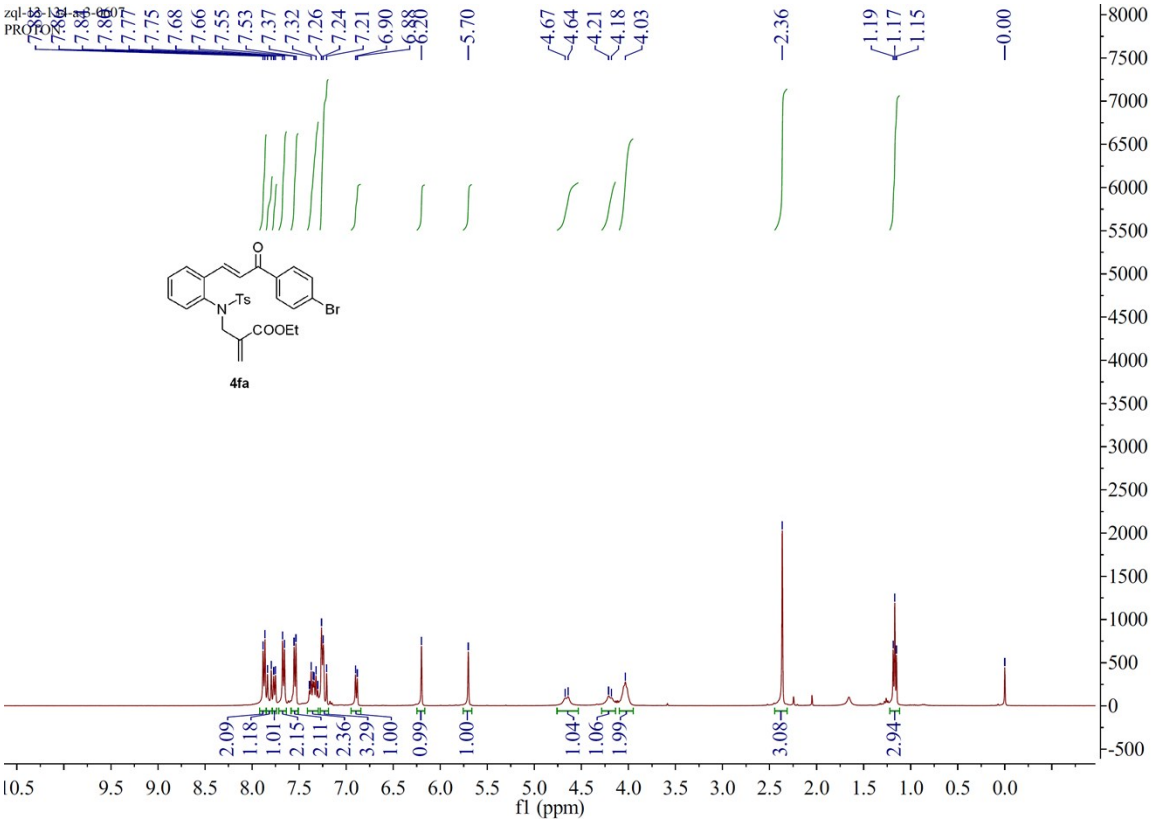

zql-13-185-b-2
C13CPD
171.60
149.48
143.92
135.47
135.22
135.17
135.01
129.96
129.80
128.68
128.67
127.42
126.97
126.79
125.92
123.69
118.55
62.38
61.14
55.10
47.87
32.74
21.61
13.76
COOEt
Ts
N
Br
H
3ma
Br
fl (ppm)

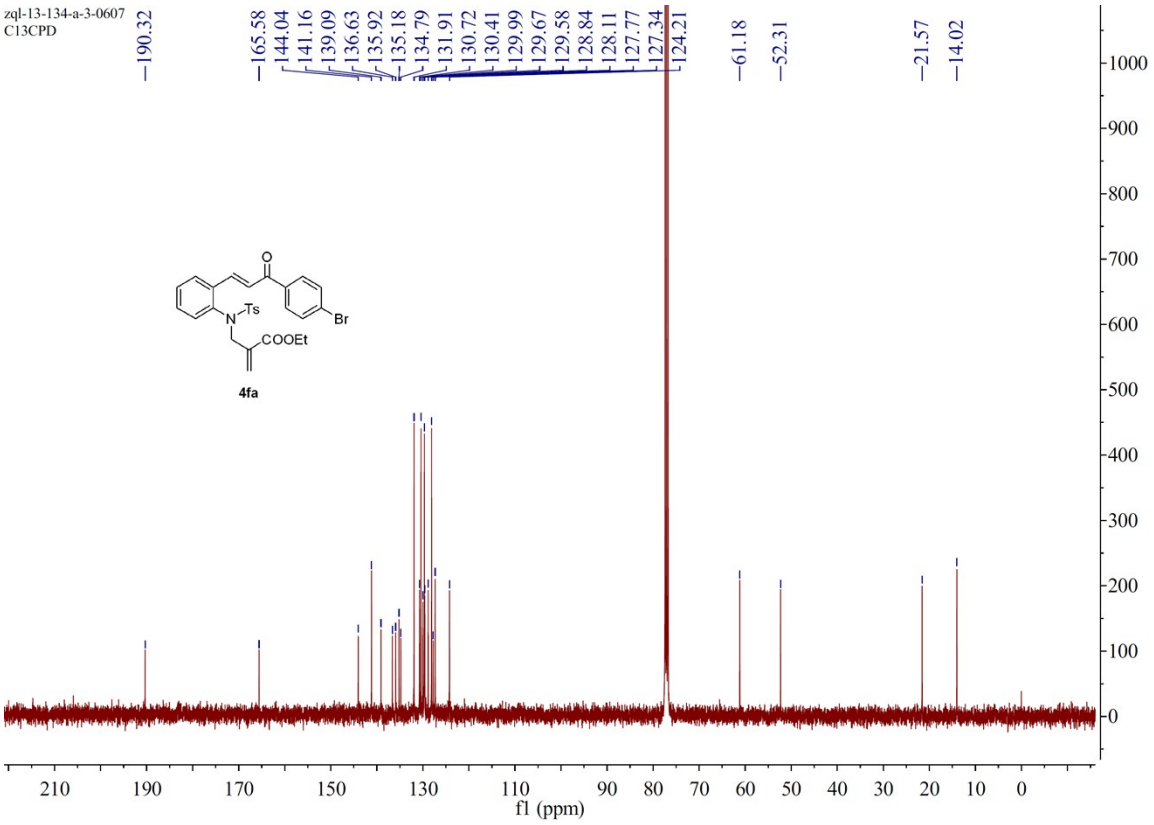

zql-13-185-a-2-0603
PROTON
7.68
7.67
7.47
7.46
7.46
7.45
7.44
7.39
7.37
7.35
7.33
7.32
7.26
7.20
7.18
7.13
6.13
4.67
4.64
3.88
3.86
3.85
3.83
3.73
3.71
3.70
3.70
3.69
3.66
3.63
3.36
3.33
3.30
3.29
2.80
2.79
2.77
2.75
2.58
2.55
2.53
2.36
0.87
0.85
0.83
0.00
COOEt
Ts
N
H
Cl
3na
1.17
4.25
3.16
2.95
0.94
1.08
1.00
1.07
1.09
1.07
1.07
1.01
1.05
3.00
3.05
f1 (ppm)

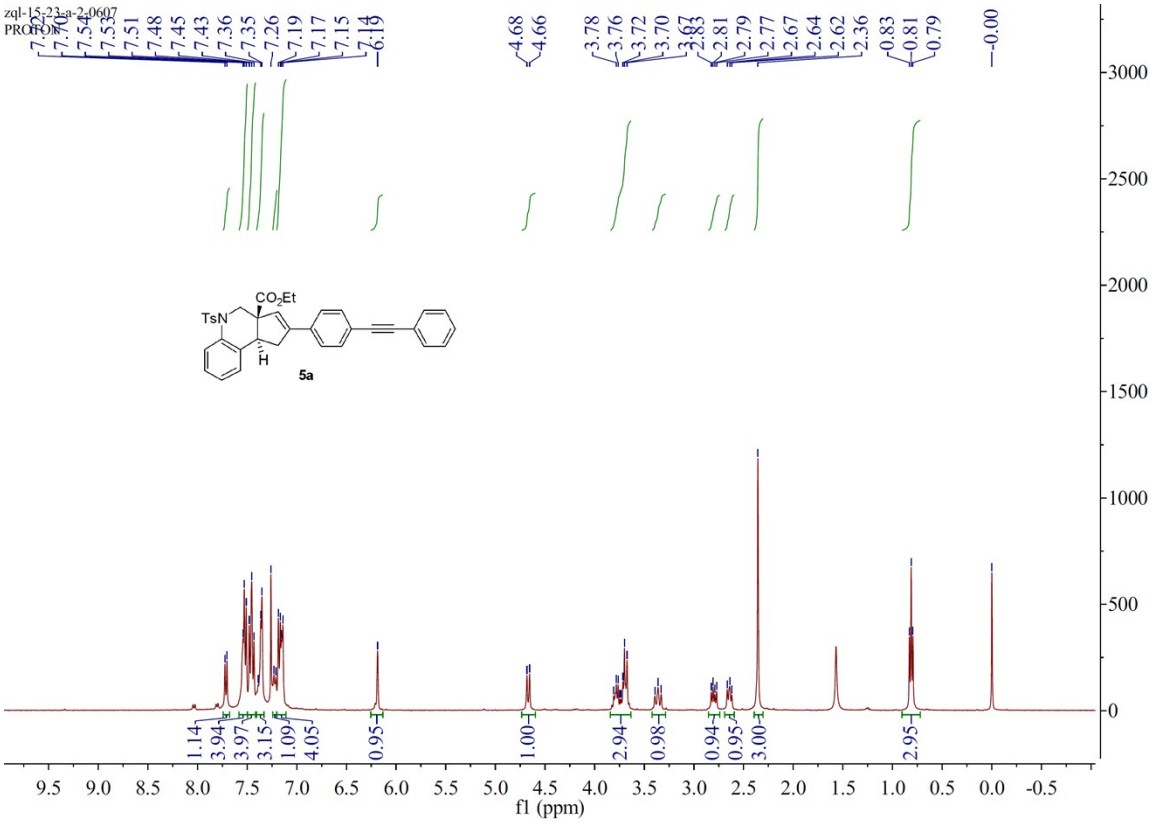

zql-13-185-a-2
C13CPD
171.61
149.47
143.90
135.45
135.01
134.98
134.60
133.66
130.71
129.79
128.67
127.00
126.79
126.72
125.92
124.53
123.72
62.40
61.12
55.08
47.91
32.72
21.61
13.75
COOEt
Ts
N
H
Cl
3na
f1 (ppm)

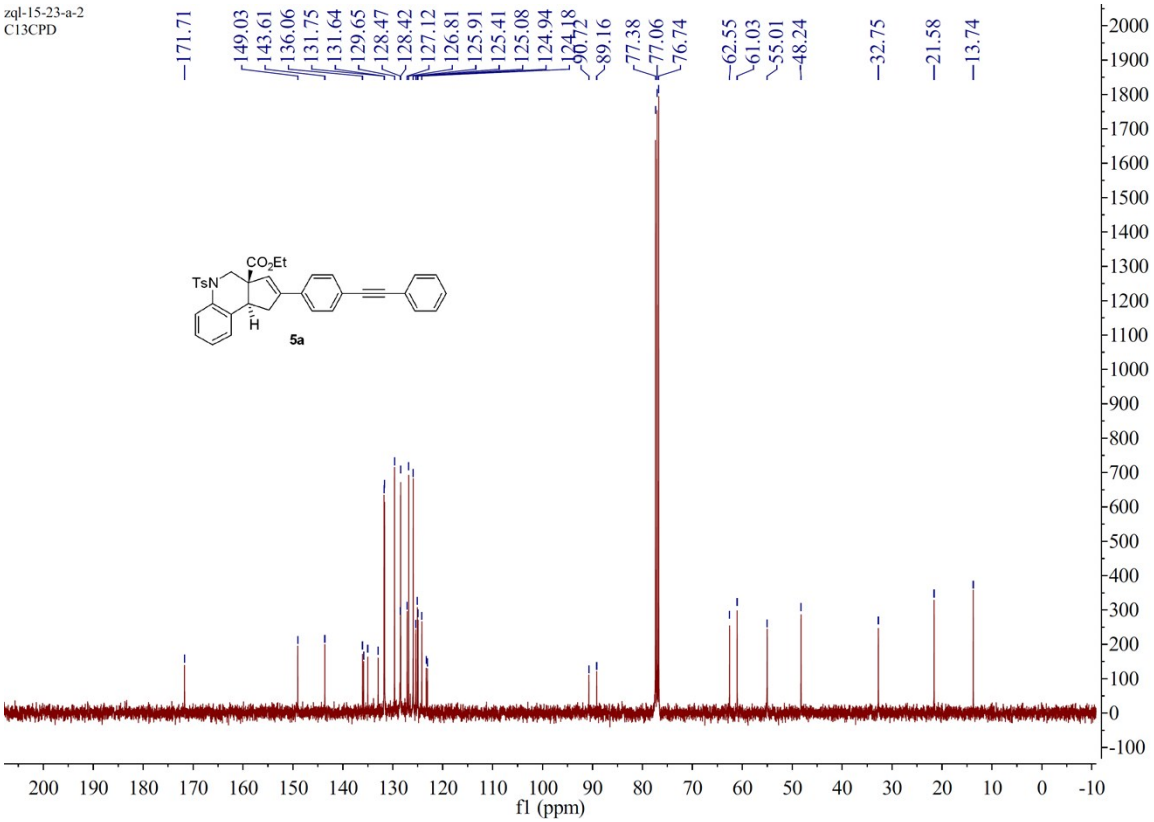

zql-13-186-a-2-0604
PROTON
7.72
7.60
7.58
7.57
7.53
7.51
7.49
7.47
7.41
7.39
7.37
7.32
7.30
7.26
7.25
7.23
7.21
7.17
7.15
7.13
7.12
7.11
6.14
6.13
4.67
4.67
4.65
4.65
3.77
3.76
3.75
3.71
3.70
3.68
3.68
3.66
3.33
2.76
2.74
2.70
2.58
0.82
0.80
0.78
0.00
PhO2S
N
COOEt
Br
H
3oa
1.04
1.94
2.98
2.07
2.04
1.06
1.98
1.05
1.00
3.07
1.06
1.05
1.04
3.01
f1 (ppm)

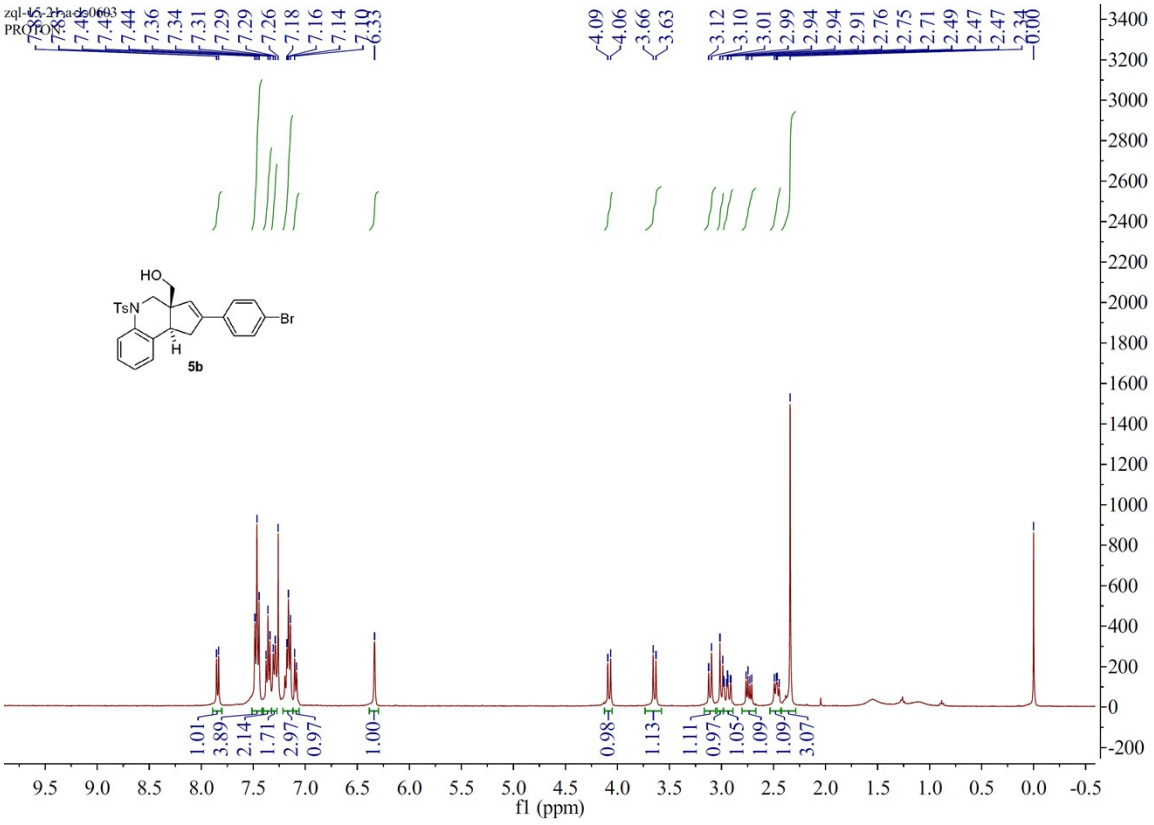

zql-13-186-a-2
C13CPD
171.63
148.64
138.62
135.93
134.14
132.90
132.88
131.69
129.03
127.51
127.20
126.74
125.45
125.24
124.65
124.16
122.47
62.59
61.06
54.96
48.24
32.76
13.74
PhO2S
N
COOEt
Br
H
3oa
f1 (ppm)

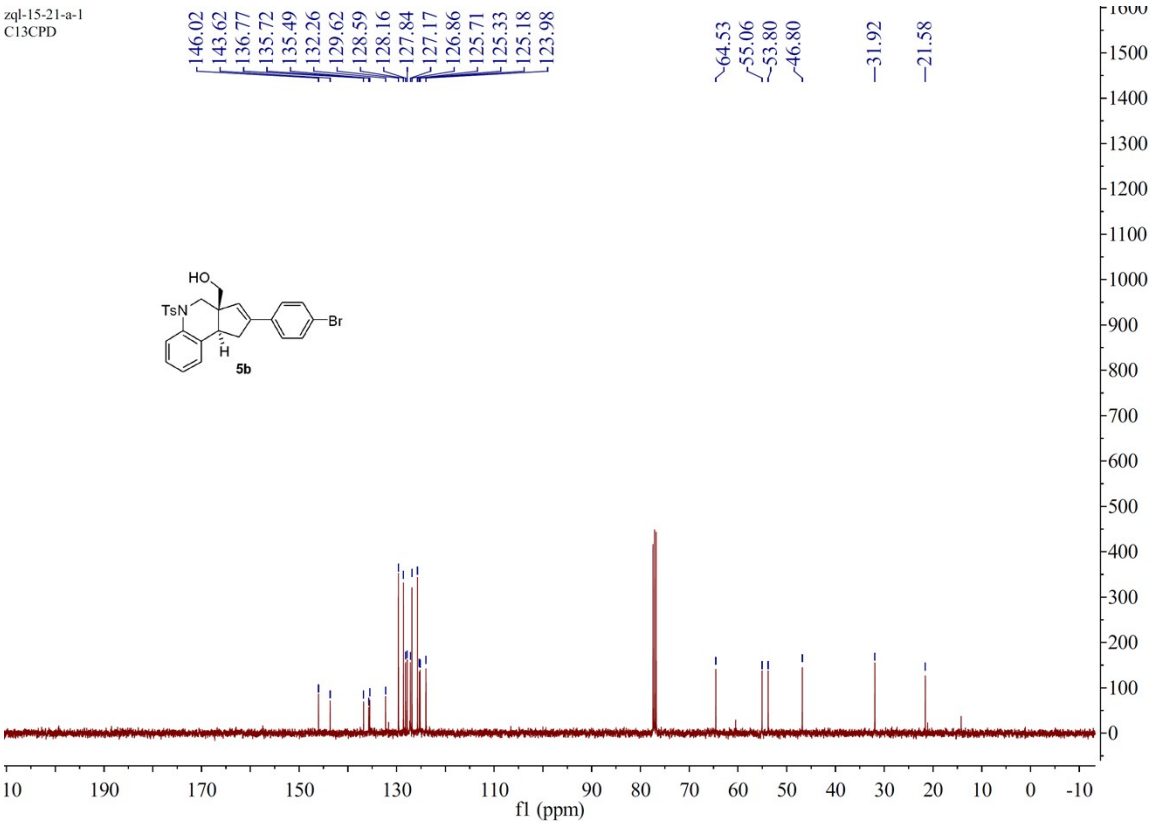

zql-13-134-a-3-0607
PROTON
7.84
7.83
7.77
7.75
7.68
7.66
7.55
7.53
7.37
7.32
7.26
7.24
7.21
6.90
6.88
6.20
5.70
4.67
4.64
4.21
4.18
4.03
2.36
1.19
1.17
1.15
0.00
Ts
N
Br
COOEt
4fa
2.09
1.18
1.01
2.15
2.11
2.36
3.29
1.00
0.99
1.00
1.04
1.06
1.99
3.08
2.94
f1 (ppm)

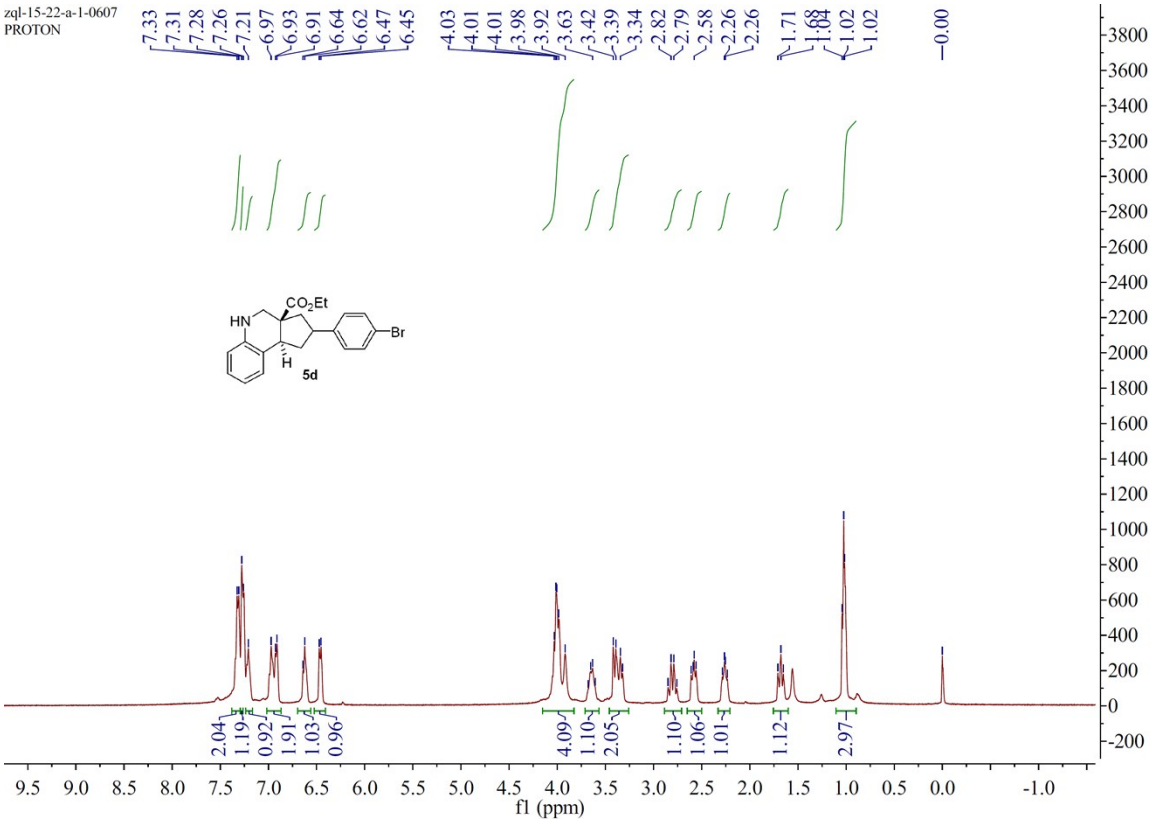

zql-13-134-a-3-0607
C13CPD
190.32
165.58
144.04
141.16
139.09
136.63
135.92
135.18
134.79
131.91
130.72
130.41
129.99
129.67
129.58
128.84
128.11
127.77
127.34
124.21
61.18
52.31
21.57
14.02
Ts
N
Br
COOEt
4fa
f1 (ppm)

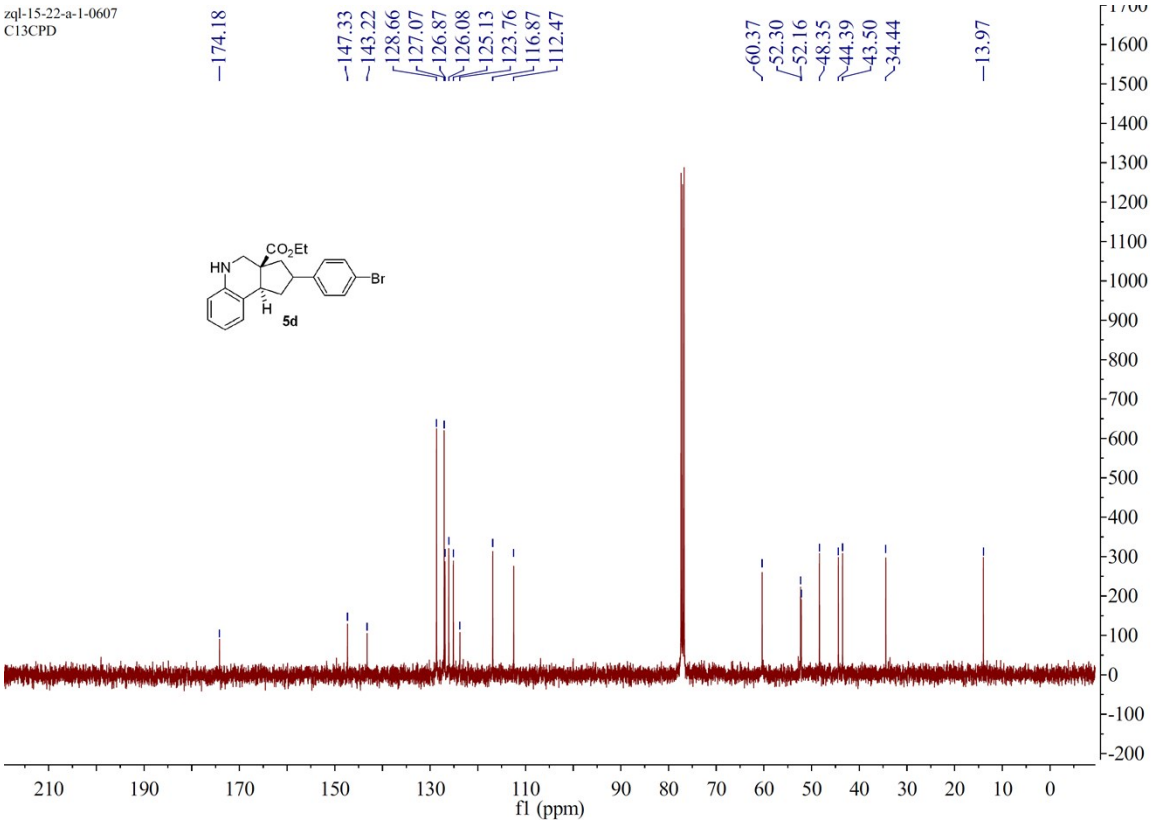

zql-15-23-a-2-0607
PROTON
7.72
7.70
7.54
7.53
7.51
7.48
7.45
7.43
7.36
7.35
7.26
7.19
7.17
7.15
7.14
6.13
4.68
4.66
3.78
3.76
3.72
3.70
3.67
2.83
2.81
2.79
2.77
2.67
2.64
2.62
2.36
0.83
0.81
0.79
-0.00
CO2Et
TsN
H
5a
1.14
3.94
3.97
3.15
1.09
4.05
0.95
1.00
2.94
0.98
0.94
0.95
3.00
2.95
fl (ppm)


zql-15-23-a-2
C13CPD
171.71
149.03
143.61
136.06
131.75
131.64
129.65
128.47
128.42
127.12
126.81
125.91
125.41
125.08
124.94
124.18
90.72
89.16
77.38
77.06
76.74
62.55
61.03
55.01
48.24
32.75
21.58
13.74
CO2Et
TsN
H
5a
fl (ppm)


zql-15-21-a-d-20603
PROTON
7.48
7.45
7.44
7.36
7.34
7.31
7.29
7.29
7.26
7.18
7.16
7.14
7.10
6.33
4.09
4.06
3.66
3.63
3.12
3.10
3.01
2.99
2.94
2.94
2.91
2.76
2.75
2.71
2.49
2.47
2.47
2.34
0.00
HO
TsN
Br
H
5b
1.01
3.89
2.14
1.71
2.97
0.97
1.00
0.98
1.13
1.11
0.97
1.05
1.09
1.09
3.07
fl (ppm)

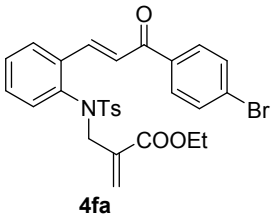

zql-15-21-a-1
C13CPD
146.02
143.62
136.77
135.72
135.49
132.26
129.62
128.59
128.16
127.84
127.17
126.86
125.71
125.33
125.18
123.98
64.53
55.06
53.80
46.80
31.92
21.58
HO
TsN
Br
H
5b
fl (ppm)


zql-15-22-a-1-0607
PROTON
7.33
7.31
7.28
7.26
7.21
6.97
6.93
6.91
6.64
6.62
6.47
6.45
4.03
4.01
4.01
3.98
3.92
3.63
3.42
3.39
3.34
2.82
2.79
2.58
2.26
2.26
1.71
1.68
1.02
1.02
0.00
CO2Et
HN
Br
H
5d
2.04
1.19
0.92
1.91
1.03
0.96
4.09
1.10
2.05
1.10
1.06
1.01
1.12
2.97
fl (ppm)

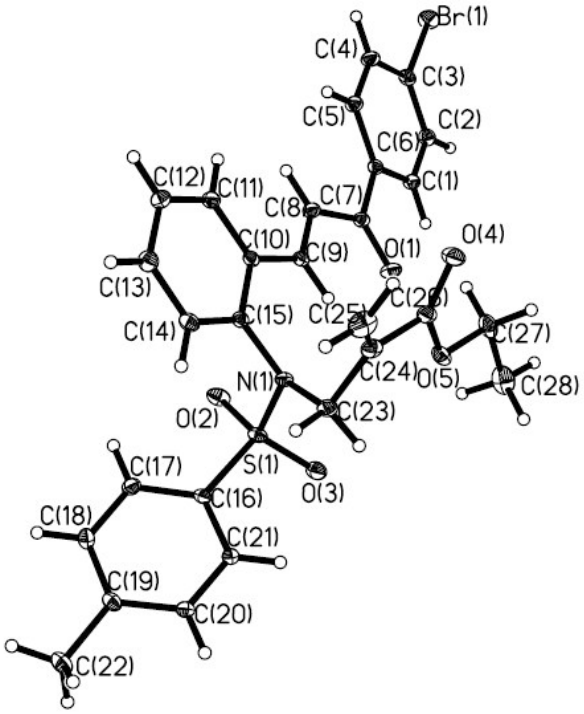

zql-15-22-a-1-0607
C13CPD
174.18
147.33
143.22
128.66
127.07
126.87
126.08
125.13
123.76
116.87
112.47
60.37
52.30
52.16
48.35
44.39
43.50
34.44
13.97
CO2Et
HN
Br
H
5d
fl (ppm)

X. X-ray crystal structure of 4fa and 3ba

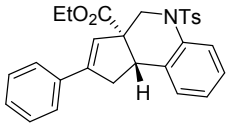
4fa (CCDC 1485460)



4fa



3ba (CCDC 1448208)



3ba