# Supporting Information

# for

# Access to Tetrahydrocarbazoles and Pyrrolo[3,4-*b*]carbazoles through Sequential Reactions of Triazoles and Indoles

Cong Chen,[a] Hongjian Jiao,[a] Di Chen,[a] Tao Tang,[a] Ze-Feng Xu,[a] Shengguo Duan,*[a] and Chuan-Ying Li* [a]

[a] Department of Chemistry, Key Laboratory of Surface & Interface Science of Polymer Materials of Zhejiang Province, Zhejiang Sci-Tech University, Hangzhou, 310018, China

E-mail: dsg@zstu.edu.cn; licy@zstu.edu.cn

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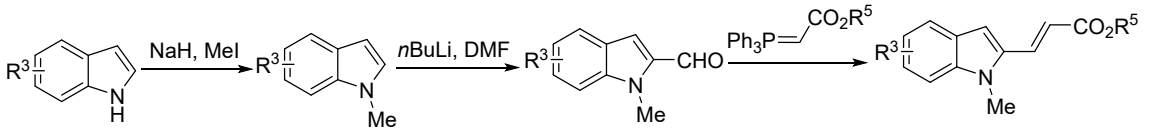
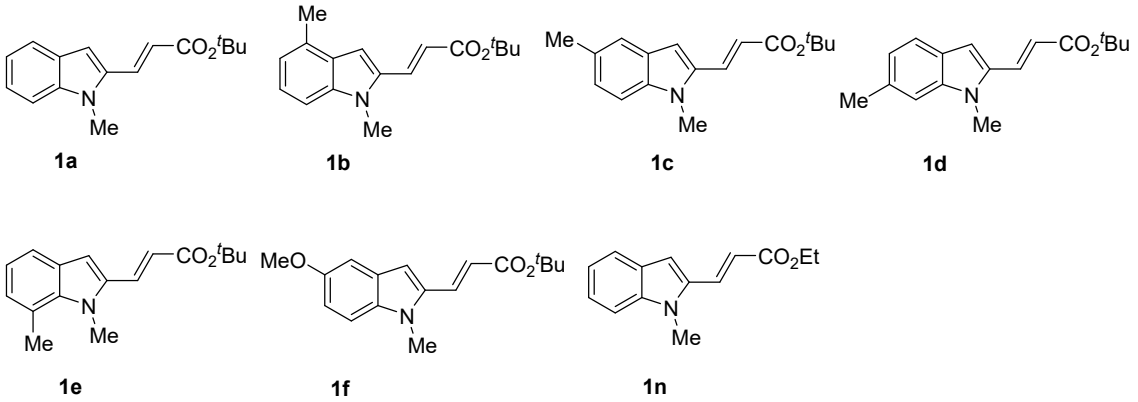
## 1 General information

All reactions were conducted in oven-dried glassware under an inert atmosphere of dry nitrogen unless otherwise noted. All commercial reagents were used without further purification unless otherwise noted. All solvents were freshly distilled prior to use in synthesis unless otherwise noted. Analytical thin layer chromatography (TLC) was performed using silica gel HSGF254 pre-coated plates. Flash column chromatography was performed using silica gel (200-300 mesh). $^{1}H$, $^{13}C$ NMR spectra were measured on Brucker Avance IIDMX 400MHz spectrometers (400 MHz for $^{1}H$ NMR, 101 MHz for $^{13}C$ NMR). Chemical shifts are reported as δ values relative to internal tetramethylsilane (TMS: 0.00 ppm) or deuterated solvent (chloroform-d: 7.26 ppm, 77.16 ppm; DMSO-$d_6$:2.50 ppm, 39.52 ppm; Acetone-$d_6$: 2.05 ppm, 206.26 ppm; Methanol-$d_4$: 3.31 ppm, 49.00 ppm). Abbreviations for signal couplings are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet and br, broad. Coupling constants (*J*) were taken from the spectra directly and are uncorrected. Melting points are uncorrected. High resolution mass spectra (HRMS) were recorded on a Waters TOFMS GCT Premier using ESI ionization.

## 2 Preparation of indoles

Indole **1a-f**, **1n** were prepared by the same procedure as shown below:




**Typical procedure (1a):**

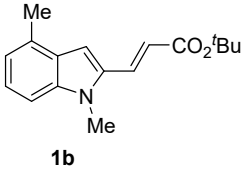
To a solution of indole (0.48 mL, 5.0 mmol) in anhydrous DMF (10 mL) was added NaH (60% in oil, 240 mg, 6.0 mmol) at 0 °C under $N_2$. After 30 min, iodomethane (0.37 mL, 6.0 mmol) was added to the mixture drop wise and then the mixture was warmed to room temperature stirred for 1 h. The reaction was quenched with $NH_4Cl$ (sat.) and diluted with ethyl acetate (100 mL). The organic layer was washed with water (20 mL × 2) and brine (20 mL × 3), dried with $Na_2SO_4$, filtered and concentrated. The crude was purified by silica gel column (PE : EtOAc = 20 : 1 to 15 : 1) to afford *N*-methyl indole (590 mg, 90% yield) as a yellow oil.

To a solution of *N*-methyl indole (590 mg, 4.5 mmol) in anhydrous THF (10 mL) was added *n*BuLi (2.4 M in hexane, 2.3 mL, 5.4 mmol) drop wise at 0 °C under $N_2$. After 30 min, anhydrous DMF (0.52 mL, 6.75 mmol) was added to the mixture drop wise and then the mixture was warmed to room temperature stirred for 1 h. The reaction was quenched with $NH_4Cl$ (sat.) and extracted with ethyl acetate. The organic layers were combined, washed with brine, dried with $Na_2SO_4$, filtered and concentrated. The crude was purified by silica gel column (PE : EtOAc = 50 : 1 to 30 : 1) to afford the aldehyde (537 mg, 75% yield) as a yellow solid.

The mixture of the aldehyde (537 mg, 3.38 mmol), $Ph_3P{=}CHCO_2{}^t$Bu (1.91 g, 5.06 mmol) in anhydrous DCM (30 mL) was stirred at room temperature for 1 h. The mixture was concentrated in vacuo and the residue was purified by silica gel column (PE : EtOAc = 50 : 1 to 30 : 1) to afford **1a** (782 mg, 90% yield) as a yellow solid.

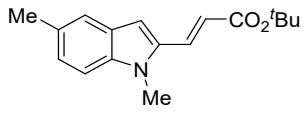
The spectra data of **1a** and **1n** were consistent with literature reported.[1a]

The spectral data of compounds **1b-f** were shown below.



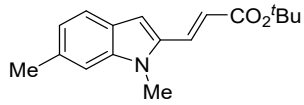

**1b**

*tert*-butyl (*E*)-3-(1,4-dimethyl-1*H*-indol-2-yl)acrylate (**1b**): yellow solid, m.p. 108 – 109 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 15.7 Hz, 1H), 7.19 – 7.10 (m, 2H), 6.95 (s, 1H), 6.89 (d, *J* = 6.2 Hz, 1H), 6.44 (d, *J* = 15.7 Hz, 1H), 3.79 (s, 3H), 2.53 (s, 3H), 1.55 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 166.62, 138.94, 134.74, 131.88, 131.03, 127.70, 123.74, 120.54, 120.02, 107.32, 102.14, 80.66, 30.27, 28.38, 18.70; ESI-HRMS *m/z* calcd for $C_{17}H_{22}NO_2^+$ $[M + H]^+$ 272.1645, found 272.1651.



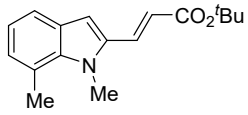

**1c**

*tert*-butyl (*E*)-3-(1,5-dimethyl-1*H*-indol-2-yl)acrylate (**1c**): yellow solid, m.p. 88 – 89 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 15.8 Hz, 1H), 7.35 (s, 1H), 7.15 (d, *J* = 8.4 Hz, 1H), 7.09 – 7.01 (m, 1H), 6.80 (s, 1H), 6.38 (d, *J* = 15.7 Hz, 1H), 3.72 (s, 3H), 2.41 (s, 3H), 1.54 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 166.56, 137.58, 135.17, 131.89, 129.64, 127.80, 125.31, 120.78, 119.83, 109.34, 102.89, 80.58, 30.03, 28.33, 21.44; ESI-HRMS *m/z* calcd for $C_{17}H_{22}NO_2^+$ $[M + H]^+$ 272.1645, found 272.1652.



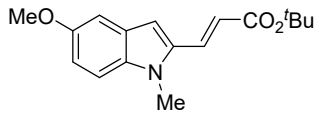

**1d**

*tert*-butyl (*E*)-3-(1,6-dimethyl-1*H*-indol-2-yl)acrylate (**1d**): yellow solid, m.p. 105 – 106 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 15.7 Hz, 1H), 7.47 (d, *J* = 8.1 Hz, 1H), 7.08 (s, 1H), 6.97 – 6.91 (m, 1H), 6.87 (s, 1H), 6.38 (d, *J* = 15.7 Hz, 1H), 3.75 (s, 3H), 2.48 (s, 3H), 1.54 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 166.69, 139.55, 134.75, 133.64, 131.98, 125.52, 122.45, 121.06, 119.49, 109.56, 103.56, 80.62, 30.04, 28.37, 22.23; ESI-HRMS *m/z* calcd for $C_{17}H_{22}NO_2^+$ $[M + H]^+$ 272.1645, found 272.1656.




**1e**

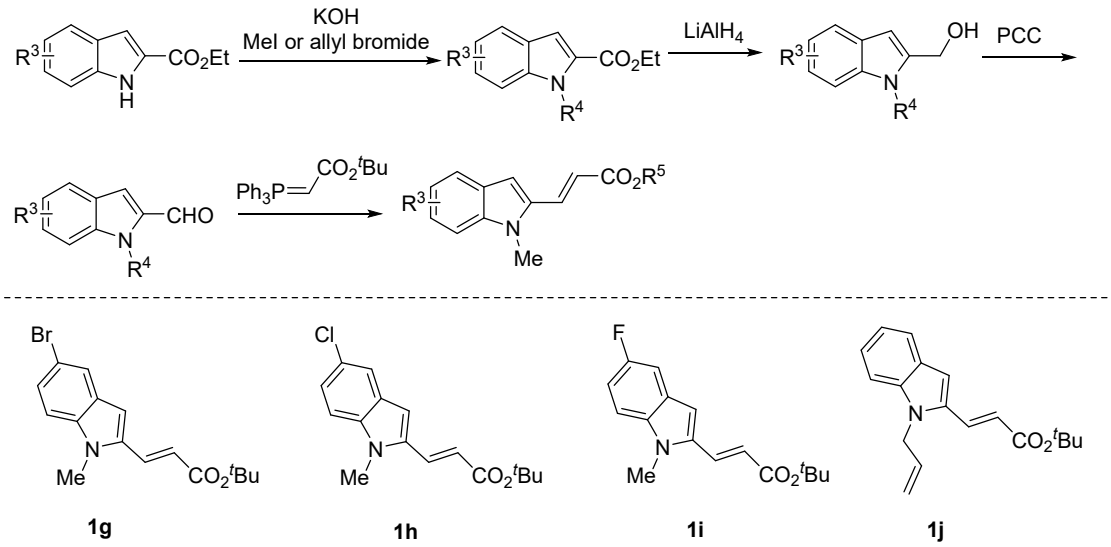
*tert*-butyl (*E*)-3-(1,7-dimethyl-1*H*-indol-2-yl)acrylate (**1e**): yellow solid, m.p. 124 – 125 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 15.7 Hz, 1H), 7.46 – 7.37 (m, 1H), 7.00 – 6.90 (m, 2H), 6.88 (s, 1H), 6.38 (d, *J* = 15.7 Hz, 1H), 4.04 (s, 3H), 2.76 (s, 3H), 1.55 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 166.56, 138.21, 135.94, 132.01, 128.49, 126.57, 121.42, 120.56, 120.53, 119.61, 104.01, 80.71, 33.09, 28.37, 20.66; ESI-HRMS *m/z* calcd for $C_{17}H_{22}NO_2^+$ $[M + H]^+$ 272.1645, found 272.1647.




**1f**

*tert*-butyl (*E*)-3-(5-methoxy-1-methyl-1*H*-indol-2-yl)acrylate (**1f**): yellow solid, m.p. 137 – 138 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 15.7 Hz, 1H), 7.18 (d, *J* = 9.0 Hz, 1H), 7.01 (d, *J* = 2.4 Hz, 1H), 6.95 – 6.88 (m, 1H), 6.83 (s, 1H), 6.38 (d, *J* = 15.8 Hz, 1H), 3.83 (s, 3H), 3.76 (s, 3H), 1.55 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 166.61, 154.72, 135.60, 134.64, 131.79, 127.90, 119.93, 114.64, 110.55, 102.84, 102.00, 80.69, 55.88, 30.20, 28.37; ESI-HRMS *m/z* calcd for $C_{17}H_{22}NO_3^+$ $[M + H]^+$ 288.1594, found 288.1613.

Indole **1g-j** were prepared by the same procedure as shown below:




**Typical procedure (1g):**

To a solution of ethyl 5-bromo-1*H*-indole-2-carboxylate (1.34 g, 5.0 mmol) in anhydrous DMF (10 mL) was added KOH (561 mg, 10.0 mmol) under $N_2$. After 30 min, iodomethane (0.46 mL, 7.5 mmol) was added to the mixture drop wise and then the mixture stirred for 1 hour at room temperature. The reaction was quenched with $NH_4Cl$ (sat.) and diluted with ethyl acetate (100 mL). The organic layer was washed with water (20 mL × 2) and brine (20 mL × 3), dried with $Na_2SO_4$, filtered and concentrated. The crude was purified by silica gel column (PE : EtOAc = 20 : 1 to 15 : 1) to afford *N*-methyl indole (1.24 g, 88% yield) as a yellow solid.

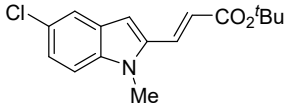
To a solution of $LiAlH_4$ (334 mg, 8.8 mmol) in anhydrous THF (20 mL) was added drop wise the solution of above mentioned *N*-methyl indole (1.24 g, 4.4 mmol) in anhydrous THF (10 mL) at 0 °C. Then the mixture was warmed to room temperature stirred for 1 h. The reaction was quenched with methanol (5 mL). Silica gel was added to the mixture and the solvent was evaporated in vacuo. The crude was purified by silica gel column (PE : EtOAc = 6 : 1 to 5 : 1) to afford the alcohol (856 mg, 81% yield) as a yellow solid.

To the solution of above mentioned alcohol (856 mg, 3.56 mmol), neutral alumina (3 g) in anhydrous DCM (30 mL) was added PCC (1.54 g, 7.12 mmol). The mixture was stirred at room temperature for 3 hours. Then the solvent was evaporated in vacuo and the crude was purified by silica gel column (PE : EtOAc = 50 : 1 to 30 : 1) to afford the aldehyde (424 mg, 50% yield) as a yellow solid.

The mixture of the above mentioned aldehyde (424 mg, 1.78 mmol), $Ph_3P{=}CHCO_2{}^tBu$ (1.00 g, 2.67 mmol) in anhydrous DCM (20 mL) was stirred at room temperature for 1 h. The mixture was concentrated in vacuo and the residue was purified by silica gel column (PE : EtOAc = 50 : 1 to 30 : 1) to afford **1g** (539 mg, 90% yield) as a yellow solid.

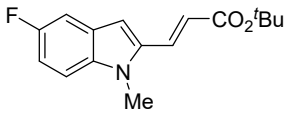
The spectra data of **1g** was consistent with literature reported.[1b]

The spectral data of compounds **1h-j** was shown below.



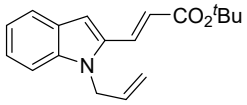

**1h**

*tert*-butyl (*E*)-3-(5-chloro-1-methyl-1*H*-indol-2-yl)acrylate (**1h**): yellow solid, m.p. 95 – 96 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 15.8 Hz, 1H), 7.50 – 7.45 (m, 1H), 7.16 – 7.08 (m, 2H), 6.76 (s, 1H), 6.35 (d, *J* = 15.8 Hz, 1H), 3.71 (s, 3H), 1.47 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 166.29, 137.33, 136.49, 131.27, 128.44, 126.12, 123.72, 121.45, 120.52, 110.74, 102.52, 80.96, 30.31, 28.34; ESI-HRMS *m/z* calcd for $C_{16}H_{19}ClNO_2^+$ $[M + H]^+$ 292.1099, found 292.1089.



**1i**

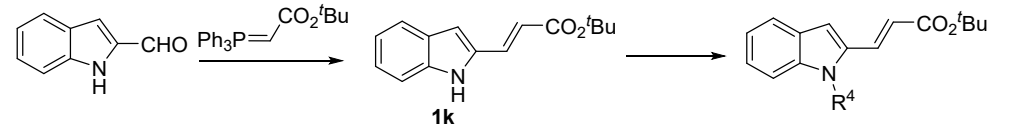
*tert*-butyl (*E*)-3-(5-fluoro-1-methyl-1*H*-indol-2-yl)acrylate (**1i**): $^1$H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 15.7 Hz, 1H), 7.21 – 7.07 (m, 2H), 6.96 – 6.87 (m, 1H), 6.77 (s, 1H), 6.34 (d, *J* = 15.7 Hz, 1H), 3.70 (s, 3H), 1.47 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 166.35, 158.25 (d, *J* = 236.3 Hz), 136.66, 135.67, 131.39, 127.66 (d, *J* = 10.1 Hz), 121.15, 112.11 (d, *J* = 26.3 Hz), 110.44 (d, *J* = 10.1 Hz), 105.69 (d, *J* = 23.2 Hz), 102.91 (d, *J* = 6.1 Hz), 80.90, 30.30, 28.33; ESI-HRMS *m/z* calcd for $C_{16}H_{19}FNO_2^+$ $[M + H]^+$ 276.1394, found 276.1398.



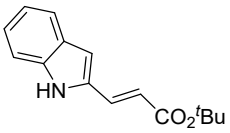
**1j**

*tert*-butyl (*E*)-3-(1-allyl-1*H*-indol-2-yl)acrylate (**1j**): white solid, m.p. 86 – 87 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.57 (m, 2H), 7.30 – 7.19 (m, 2H), 7.15 – 7.08 (m, 1H), 6.94 (s, 1H), 6.41 (d, *J* = 15.7 Hz, 1H), 6.03 – 5.88 (m, 1H), 5.20 – 5.12 (m, 1H), 4.93 – 4.85 (m, 1H), 4.85 – 4.76 (m, 2H), 1.54 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 166.47, 138.53, 134.98, 133.06, 131.76, 127.73, 123.58, 121.46, 120.61, 120.59, 116.89, 109.90, 103.63, 80.71, 45.60, 28.35; ESI-HRMS *m/z* calcd for $C_{18}H_{22}NO_3^+$ $[M + H]^+$ 284.1645, found 284.1659.

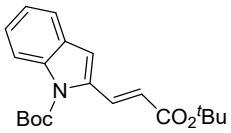
Indole **1k**-**m** were prepared by the same procedure as shown below:



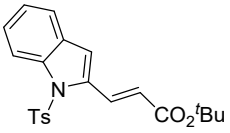
**1k**



**1k**



**1l**

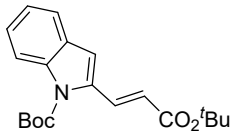


**1m**

The mixture of 1*H*-indole-2-carbaldehyde (726 mg, 5.0 mmol), $Ph_3P{=}CHCO_2{}^t$Bu (2.82 g, 7.5 mmol) in anhydrous DCM (25 mL) was stirred at room temperature for 1 h. The mixture was concentrated in vacuo and the residue was purified by silica gel column (PE : EtOAc = 30 : 1 to 10 : 1) to afford **1k** (1.13 g, 93% yield) as a faint yellow solid.

The spectra data of **1k** was consistent with literature reported.[1b]

To the mixture of **1k** (243 mg, 1.0 mmol), $Et_3N$ (0.42 mL, 3.0 mmol), and DMAP (24.4 mg, 0.20 mmol) in DCM (10 mL) was added $Boc_2O$ (261.9 mg, 1.2 mmol) at room temperature. After 1 hour later, the mixture was concentrated in vacuo and the residue was purified by silica gel column (PE : EtOAc = 50 : 1 to 30 : 1) to afford **1l** (337 mg, 98% yield) as a yellow solid.

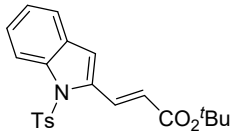


**1l**

*tert*-butyl (*E*)-2-(3-(*tert*-butoxy)-3-oxoprop-1-en-1-yl)-1*H*-indole-1-carboxylate (**1l**): yellow solid, m.p. 58 – 59 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.00 (m, 2H), 7.46 (d, *J* = 7.7 Hz, 1H), 7.30 – 7.21 (m, 1H), 7.18 – 7.12 (m, 1H), 6.83 (s, 1H), 6.21 (d, *J* = 15.8 Hz, 1H), 1.62 (s, 9H), 1.46 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 166.00, 150.20, 137.71, 136.35, 135.57, 128.86, 125.54, 123.37, 121.38, 121.12, 115.86, 109.97, 84.83, 80.67, 28.35 (one carbon missed); ESI-HRMS *m/z*

calcd for $C_{20}H_{26}NO_4^+$ $[M + H]^+$ 344.1856, found 344.1845.

To the solution of **1k** (243 mg, 1.0 mmol) in anhydrous THF (10 mL) was added NaH (60% in oil, 60 mg, 1.5 mmol) at 0 °C. Then the mixture was warmed to room temperature and TsCl (285 mg, 1.5 mmol) was added to the mixture after 30 min later. The reaction was quenched with $NH_4Cl$ (sat.) after 2 hours. The mixture was extracted with EtOAc twice, washed with brine, dried with $Na_2SO_4$, filtered and concentrated. The residue was purified by silica gel column (PE : EtOAc = 30 : 1 to 10 : 1) to afford **1m** (291 mg, 73% yield) as a yellow oil.

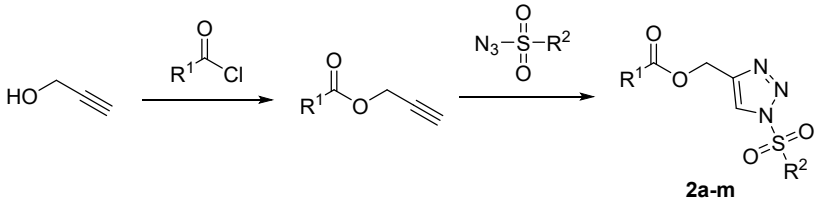



**1m**

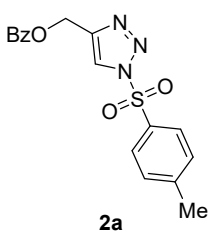
*tert*-butyl (*E*)-3-(1-tosyl-1*H*-indol-2-yl)acrylate (**1m**): yellow oil; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 15.8 Hz, 1H), 8.15 (d, *J* = 8.5 Hz, 1H), 7.60 – 7.55 (m, 2H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.32 – 7.25 (m, 1H), 7.19 – 7.15 (m, 1H), 7.10 (d, *J* = 8.1 Hz, 2H), 6.87 (s, 1H), 6.22 (d, *J* = 15.8 Hz, 1H), 2.25 (s, 3H), 1.50 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 165.61, 145.20, 138.12, 136.61, 135.46, 133.15, 129.93, 129.45, 126.79, 126.09, 124.29, 123.09, 121.51, 115.32, 111.73, 81.03, 28.35, 21.71; ESI-HRMS *m/z* calcd for $C_{22}H_{24}NO_4S^+$ $[M + H]^+$ 398.4965, found 398.4976.

## 3 Preparation of triazoles

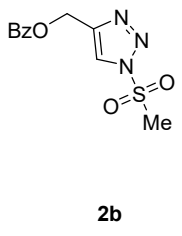
All triazoles were synthesized according to known procedure.[2]



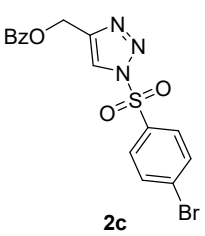
**2a-m**



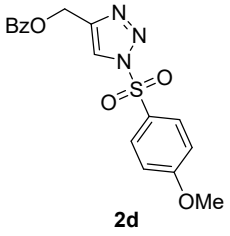
**2a**



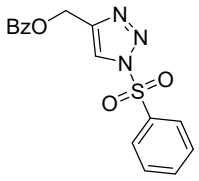
**2b**



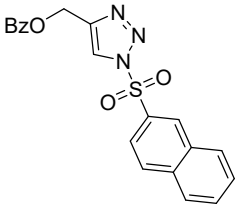
**2c**



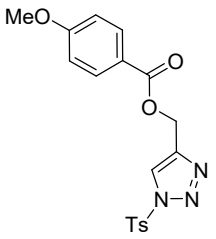
**2d**



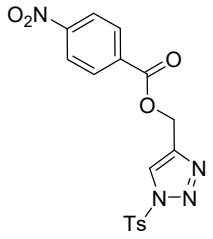
**2e**



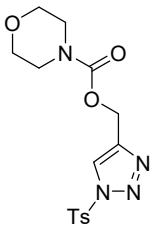
**2f**



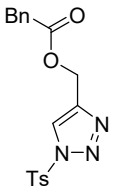
**2g**



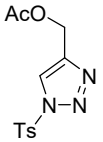
**2h**



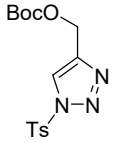
**2i**



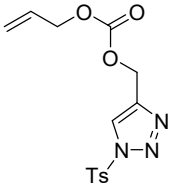
**2j**



**2k**



**2l**



**2m**

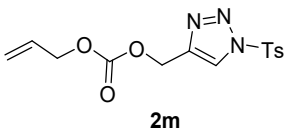
**Typical procedure (2m):**[2]

To a 100 mL flask containing propargyl alcohol (0.35 mL, 6.0 mmol), $Et_3N$ (0.83 mL, 6.0 mmol), and DMAP (122 mg, 1.0 mmol) in DCM (20 mL) was added allyl chloroformate (0.55 mL, 5.0 mmol) at 0 °C dropwise. Then the mixture was warmed up to room temperature and stirred for 3 hrs. The reaction was quenched by water and extracted with DCM three times. The organic phases were combined, washed with brine, dried with $Na_2SO_4$, filtered and concentrated. The crude was purified by silica gel column to give alkyne (680 mg, 97% yield) as oil.

To a flask charged with copper(I) thiophene-2-carboxylate (92 mg, 0.49 mmol) and above-mentioned alkyne (680 mg, 4.85 mmol) was added dry toluene (15 mL). The reaction mixture was cooled in an ice-brine bath and then the $TsN_3$ (5.8 mmol, 1.2 equiv) was added slowly (Caution: Sulfonyl azides are potentially explosive materials and must be handled with caution.). The reaction mixture was allowed to warm to room temperature and stirred until TLC analysis showed that alkyne was completely consumed. The reaction mixture filtered through a short plug of silica gel and the filtrate was concentrated in vacuo. The crude was purified by recrystallization to give **2m** (1.31 g, 80% yield) as a white solid.

The $^1$H NMR spectra of **2a**,[2a] **2b**,[2a] **2c**,[2b] **2d**,[2c] **2e**,[2c] **2f**,[2b] **2g**,[2c] **2h**,[2a] **2i**,[2a] **2j**,[2a] **2k**[2a] and **2l**[2a] were consistent with references.

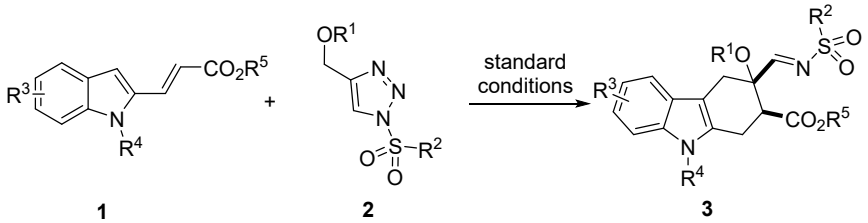
The spectral data of compounds **2m** was shown below.



**2m**

allyl ((1-tosyl-1*H*-1,2,3-triazol-4-yl)methyl) carbonate (**2m**): white solid, m.p. 58 – 59 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 8.04 – 7.96 (m, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 5.97 – 5.84 (m, 1H), 5.40 – 5.31 (m, 1H), 5.30 – 5.24 (m, 3H), 4.67 – 4.61 (m, 2H), 2.46 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 154.71, 147.71, 142.12, 132.82, 131.24, 130.63, 128.92, 123.71, 119.42, 69.05, 60.34, 21.97; ESI-HRMS *m/z* calcd for $C_{14}H_{16}N_3O_5S^+$ $[M + H]^+$ 338.0805, found 338.0815.

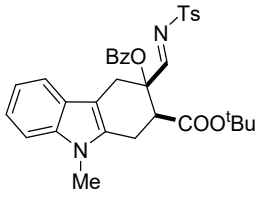
## 4 General procedure for synthesis of tetrahydrocarbazoles




1 2 3

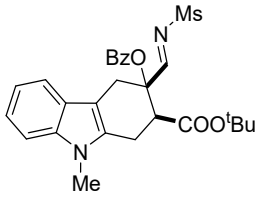
**Typical procedure (3aa):**

To the solution of **1a** (51.5 mg, 0.20 mmol) and $Rh_2(OAc)_4$ (1.8 mg, 2 mol %) in anhydrous DCE (2 mL) was added the solution of **2a** (100.1 mg, 0.28 mmol) in anhydrous DCE (2 mL) via syringe pump for 3 hours at 80 °C under $N_2$. After 1 hour, the reaction was cooled to room temperature and the solvent was evaporated in vacuo. The residue was purified by silica gel column chromatography (PE : EtOAc = 4 : 1 to 3 : 1) to give **3aa** as a yellow solid.



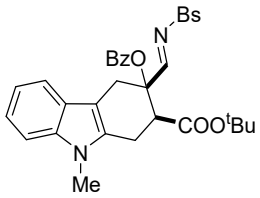

**3aa**

*tert*-butyl 3-(benzoyloxy)-9-methyl-3-((*E*)-(tosylimino)methyl)-2,3,4,9-tetrahydro-1*H*-carbazole-2-carboxylate (**3aa**): yellow solid, m.p. 52 – 53 °C; 113 mg, 96% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.22 (s, 1H), 7.83 – 7.70 (m, 4H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.28 – 7.21 (m, 3H), 7.18 (t, *J* = 7.8 Hz, 1H), 7.07 (t, *J* = 7.4 Hz, 1H), 3.89 (t, *J* = 5.1 Hz, 1H), 3.71 – 3.56 (m, 5H), 3.29 (dd, *J* = 16.5, 4.6 Hz, 1H), 3.16 (dd, *J* = 16.4, 5.8 Hz, 1H), 2.38 (s, 3H), 1.38 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 178.92, 169.45, 165.21, 144.54, 137.59, 134.54, 133.71, 132.03, 129.90, 129.64, 128.96, 128.45, 128.33, 126.68, 121.29, 119.08, 118.04, 108.90, 104.76, 83.38, 80.10, 48.98, 29.46, 28.59, 28.04, 22.58, 21.74; ESI-HRMS *m/z* calcd for $C_{33}H_{34}N_2NaO_6S^+$ $[M + Na]^+$ 609.2030, found 609.2052.




**3ab**

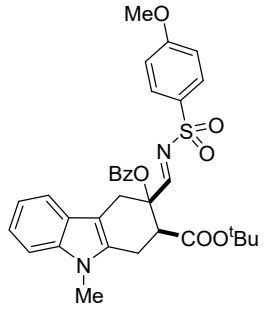
*tert*-butyl 3-(benzoyloxy)-9-methyl-3-((*E*)-((methylsulfonyl)imino)methyl)-2,3,4,9-tetrahydro-1*H*-carbazole-2-carboxylate (**3ab**): yellow solid, m.p. 43 – 44 °C; 100 mg, 98% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.18 (s, 1H), 7.96 – 7.90 (m, 2H), 7.59 – 7.53 (m, 1H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 1H), 7.23 – 7.17 (m, 1H), 7.13 – 7.06 (m, 1H), 3.88 (t, *J* = 5.5 Hz, 1H), 3.76 (d, *J* = 16.7 Hz, 1H), 3.69 (s, 3H), 3.60 (d, *J* = 16.8 Hz, 1H), 3.34 (dd, *J* = 16.4, 5.3 Hz, 1H), 3.21 (dd, *J* = 16.4, 5.7 Hz, 1H), 2.96 (s, 3H), 1.42 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 180.61, 169.41, 165.39, 137.65, 133.92, 131.94, 130.02, 128.98, 128.65, 126.61, 121.41, 119.16, 118.02, 108.99, 104.65, 83.53, 80.28, 49.31, 39.96, 29.53, 28.93, 28.07, 22.72; ESI-HRMS *m/z* calcd for $C_{27}H_{31}N_2O_6S^+$ $[M + H]^+$ 511.1897, found 511.1911.




**3ac**

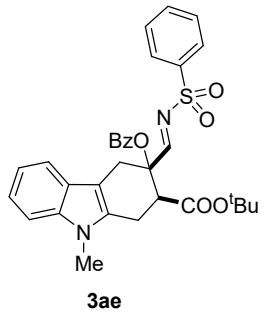
*tert*-butyl 3-(benzoyloxy)-3-((*E*)-(((4-bromophenyl)sulfonyl)imino)methyl)-9-methyl-2,3,4,9-tetrahydro-1*H*-carbazole-2-

carboxylate (**3ac**): yellow oil; 129 mg, 99% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.26 (s, 1H), 7.81 – 7.76 (m, 2H), 7.73 – 7.68 (m, 2H), 7.57 – 7.50 (m, 3H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 1H), 7.22 – 7.15 (m, 1H), 7.07 (t, *J* = 7.4 Hz, 1H), 3.87 (t, *J* = 5.2 Hz, 1H), 3.72 – 3.54 (m, 5H), 3.28 (dd, *J* = 16.6, 4.9 Hz, 1H), 3.17 (dd, *J* = 16.4, 5.8 Hz, 1H), 1.39 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 180.27, 169.47, 165.31, 137.63, 136.83, 133.86, 132.29, 131.93, 129.89, 129.78, 128.83, 128.80, 128.56, 126.64, 121.40, 119.17, 118.04, 108.93, 104.73, 83.47, 80.17, 49.30, 29.46, 28.73, 28.05, 22.64; ESI-HRMS *m/z* calcd for $C_{32}H_{32}BrN_2O_6S^+$ $[M + H]^+$ 651.1159, found 651.1161.



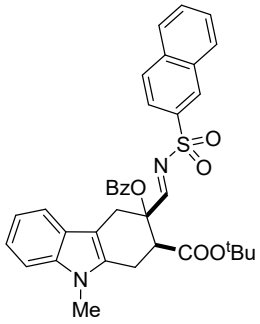

**3ad**

*tert*-butyl 3-(benzoyloxy)-3-((*E*)-(((4-methoxyphenyl)sulfonyl)imino)methyl)-9-methyl-2,3,4,9-tetrahydro-1*H*-carbazole-2-carboxylate (**3ad**): yellow solid, m.p. 56 – 57 °C; 99 mg, 82% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.19 (s, 1H), 7.82 – 7.76 (m, 4H), 7.53 – 7.47 (m, 1H), 7.44 – 7.39 (m, 1H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.28 – 7.24 (m, 1H), 7.20 – 7.14 (m, 1H), 7.09 – 7.03 (m, 1H), 6.92 – 6.85 (m, 2H), 3.89 (t, *J* = 5.1 Hz, 1H), 3.81 (s, 3H), 3.70 – 3.57 (m, 5H), 3.29 (dd, *J* = 16.5, 4.6 Hz, 1H), 3.16 (dd, *J* = 16.4, 5.7 Hz, 1H), 1.39 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 178.30, 169.46, 165.20, 163.70, 137.61, 133.68, 132.05, 130.54, 129.89, 129.04, 128.99, 128.46, 126.71, 121.29, 119.08, 118.04, 114.23, 108.89, 104.81, 83.33, 80.15, 55.70, 48.97, 29.44, 28.63, 28.05, 22.60; ESI-HRMS *m/z* calcd for $C_{33}H_{35}N_2O_7S^+$ $[M + H]^+$ 603.2159, found 603.2158.



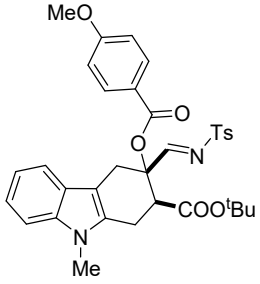

**3ae**

*tert*-butyl 3-(benzoyloxy)-9-methyl-3-((*E*)-((phenylsulfonyl)imino)methyl)-2,3,4,9-tetrahydro-1*H*-carbazole-2-carboxylate (**3ae**): yellow oil; 113 mg, 99% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.26 (s, 1H), 7.89 – 7.84 (m, 2H), 7.82 – 7.76 (m, 2H), 7.57 – 7.47 (m, 2H), 7.46 – 7.40 (m, 3H), 7.34 (t, *J* = 7.8 Hz, 2H), 7.28 – 7.25 (m, 1H), 7.21 – 7.15 (m, 1H), 7.10 – 7.04 (m, 1H), 3.89 (t, *J* = 5.2 Hz, 1H), 3.72 – 3.56 (m, 5H), 3.28 (dd, *J* = 16.4, 4.8 Hz, 1H), 3.21 – 3.12 (m, 1H), 1.38 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 179.55, 169.46, 165.23, 137.71, 137.62, 133.74, 133.55, 132.01, 129.90, 128.98, 128.94, 128.49, 128.25, 126.69, 121.34, 119.12, 118.05, 108.91, 104.78, 83.40, 80.14, 49.12, 29.45, 28.69, 28.06, 22.62; ESI-HRMS *m/z* calcd for $C_{32}H_{32}N_2NaO_6S^+$ $[M + Na]^+$ 595.1873, found 595.1888.



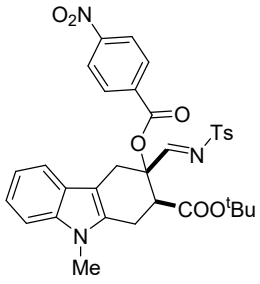

**3af**

*tert*-butyl 3-(benzoyloxy)-9-methyl-3-((*E*)-((naphthalen-2-ylsulfonyl)imino)methyl)-2,3,4,9-tetrahydro-1*H*-carbazole-2-carboxylate (**3af**): yellow solid, m.p. 49 – 50 °C; 123 mg, 99% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.32 (s, 1H), 8.46 (s, 1H), 7.90 – 7.78 (m, 4H), 7.74 – 7.68 (m, 2H), 7.65 – 7.53 (m, 2H), 7.48 – 7.42 (m, 1H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.29 – 7.22 (m, 3H), 7.20 – 7.14 (m, 1H), 7.09 – 7.02 (m, 1H), 3.89 (t, *J* = 5.2 Hz, 1H), 3.69 (d, *J* = 16.8 Hz, 1H), 3.64 – 3.55 (m, 4H), 3.26 (dd, *J* = 16.4, 4.8 Hz, 1H), 3.14 (dd, *J* = 16.4, 5.7 Hz, 1H), 1.37 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 179.58, 169.48, 165.24, 137.60, 135.31, 134.63, 133.66, 132.14, 131.98, 130.00, 129.83, 129.56, 129.18, 128.86, 128.41, 127.96, 127.48, 126.67, 123.05, 121.31, 119.10, 118.05, 108.90, 104.80, 83.39, 80.19, 49.17, 29.40, 28.73, 28.03, 22.61 (one carbon missed); ESI-HRMS *m/z* calcd for $C_{36}H_{35}N_2O_6S^+$ $[M + H]^+$ 623.2210, found 623.2209.




**3ag**

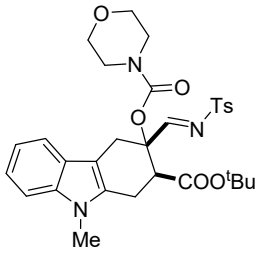
*tert*-butyl 3-((4-methoxybenzoyl)oxy)-9-methyl-3-((*E*)-(tosylimino)methyl)-2,3,4,9-tetrahydro-1*H*-carbazole-2-carboxylate (**3ag**): yellow solid, m.p. 46 – 47 °C; 122 mg, 99% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.21 (s, 1H), 7.79 – 7.71 (m, 4H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.28 – 7.20 (m, 3H), 7.20 – 7.14 (m, 1H), 7.09 – 7.03 (m, 1H), 6.83 – 6.77 (m, 2H), 3.87 (t, *J* = 5.3 Hz, 1H), 3.80 (s, 3H), 3.69 – 3.52 (m, 5H), 3.26 (dd, *J* = 16.4, 4.8 Hz, 1H), 3.13 (dd, *J* = 16.4, 5.7 Hz, 1H), 2.37 (s, 3H), 1.38 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 179.11, 169.54, 164.93, 163.96, 144.44, 137.59, 134.67, 132.05, 129.75, 129.60, 128.28, 126.71, 126.51, 121.24, 119.04, 118.03, 113.71, 108.87, 104.93, 83.24, 79.78, 55.55, 48.95, 29.41, 28.76, 28.03, 22.60, 21.71; ESI-HRMS *m/z* calcd for $C_{34}H_{37}N_2O_7S^+$ $[M + H]^+$ 617.2316, found 617.2300.




**3ah**

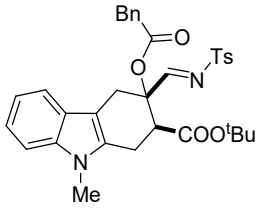
*tert*-butyl 9-methyl-3-((4-nitrobenzoyl)oxy)-3-((*E*)-(tosylimino)methyl)-2,3,4,9-tetrahydro-1*H*-carbazole-2-carboxylate (**3ah**): orange solid, m.p. 46 – 47 °C; 121 mg, 96% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.18 (s, 1H), 8.20 – 8.15 (m, 2H), 7.98 – 7.93 (m, 2H), 7.77 – 7.72 (m, 2H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.29 – 7.23 (m, 3H), 7.22 – 7.17 (m, 1H), 7.11 – 7.05 (m, 1H), 3.92 – 3.85 (m, 1H), 3.72 – 3.60 (m, 5H), 3.33 (dd, *J* = 16.6, 4.6 Hz, 1H), 3.16 (dd, *J* = 16.5, 5.9 Hz, 1H), 2.40 (s, 3H), 1.38 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 177.84, 169.16, 163.30, 150.87, 144.79, 137.67, 134.53, 134.41, 131.82,

131.01, 129.71, 128.40, 126.57, 123.61, 121.58, 119.29, 118.03, 109.02, 104.41, 83.63, 81.31, 49.19, 29.51, 28.49, 28.05, 22.67, 21.79; ESI-HRMS *m/z* calcd for $C_{33}H_{34}N_3O_8S^+$ $[M + H]^+$ 632.2061, found 632.2081.



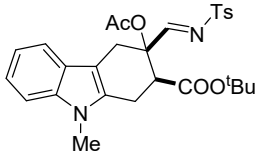

**3ai**

2-(*tert*-butoxycarbonyl)-9-methyl-3-((*E*)-(tosylimino)methyl)-2,3,4,9-tetrahydro-1*H*-carbazol-3-yl morpholine-4-carboxylate (**3ai**): yellow oil; 102 mg, 86% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.11 (s, 1H), 7.82 – 7.76 (m, 2H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.31 – 7.25 (m, 3H), 7.21 – 7.15 (m, 1H), 7.11 – 7.04 (m, 1H), 3.73 (t, *J* = 5.1 Hz, 1H), 3.63 (s, 3H), 3.56 – 3.14 (m, 11H), 2.99 (dd, *J* = 16.4, 5.8 Hz, 1H), 2.41 (s, 3H), 1.38 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 179.94, 169.42, 153.41, 144.48, 137.59, 134.93, 132.04, 129.57, 128.45, 126.74, 121.29, 119.09, 118.07, 108.89, 104.95, 83.28, 79.38, 66.36, 49.24, 44.78, 43.83, 29.43, 28.89, 28.04, 22.56, 21.75 (one carbon missed); ESI-HRMS *m/z* calcd for $C_{31}H_{38}N_3O_7S^+$ $[M + H]^+$ 596.2425, found 596.2425.



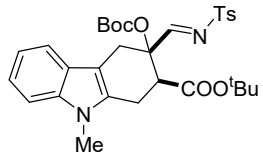

**3aj**

*tert*-butyl 9-methyl-3-(2-phenylacetoxy)-3-((*E*)-(tosylimino)methyl)-2,3,4,9-tetrahydro-1*H*-carbazole-2-carboxylate (**3aj**): yellow oil; 114 mg, 95% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.11 (s, 1H), 7.78 – 7.73 (m, 2H), 7.39 (d, *J* = 7.8 Hz, 1H), 7.28 – 7.24 (m, 3H), 7.22 – 7.16 (m, 1H), 7.15 – 7.00 (m, 4H), 6.88 – 6.83 (m, 2H), 3.66 (dd, *J* = 6.1, 3.1 Hz, 1H), 3.59 – 3.49 (m, 4H), 3.47 – 3.33 (m, 3H), 3.17 (dd, *J* = 16.5, 3.1 Hz, 1H), 2.79 (dd, *J* = 16.5, 6.1 Hz, 1H), 2.42 (s, 3H), 1.35 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 178.96, 170.20, 169.19, 144.62, 137.54, 134.47, 133.07, 132.17, 129.74, 129.03, 128.43, 128.39, 127.05, 126.77, 121.23, 119.05, 117.93, 108.82, 104.21, 83.45, 79.56, 48.51, 40.94, 29.35, 28.02, 27.59, 22.18, 21.81; ESI-HRMS *m/z* calcd for $C_{34}H_{37}N_2O_6S^+$ $[M + H]^+$ 601.2367, found 601.2367.



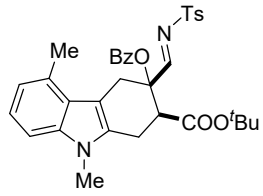

**3ak**

*tert*-butyl 3-acetoxy-9-methyl-3-((*E*)-(tosylimino)methyl)-2,3,4,9-tetrahydro-1*H*-carbazole-2-carboxylate (**3ak**): yellow oil; 92 mg, 88% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.08 (s, 1H), 7.80 – 7.74 (m, 2H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.32 – 7.25 (m, 3H), 7.21 – 7.15 (m, 1H), 7.10 – 7.04 (m, 1H), 3.70 (dd, *J* = 5.8, 3.8 Hz, 1H), 3.63 (s, 3H), 3.50 (s, 2H), 3.23 (dd, *J* = 16.4, 3.9 Hz, 1H), 3.11 – 3.02 (m, 1H), 2.42 (s, 3H), 1.87 (s, 3H), 1.35 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 179.11, 169.87, 169.41, 144.66, 137.54, 134.52, 132.16, 129.70, 128.39, 126.70, 121.30, 119.09, 117.97, 108.89, 104.54, 83.26, 79.44, 48.83, 29.39, 28.00, 22.37, 21.77, 20.87 (one carbon missed); ESI-HRMS *m/z* calcd for $C_{28}H_{32}N_2NaO_6S^+$ $[M + Na]^+$ 547.1873, found 547.1852.



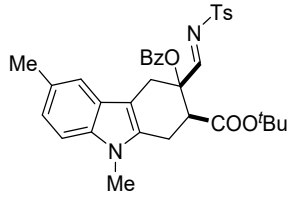

**3al**

*tert*-butyl 3-((*tert*-butoxycarbonyl)oxy)-9-methyl-3-((*E*)-(tosylimino)methyl)-2,3,4,9-tetrahydro-1*H*-carbazole-2-carboxylate (**3al**): yellow solid, m.p. 122 – 123 °C; 99 mg, 85% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.09 (s, 1H), 7.81 (d, *J* = 8.1 Hz, 2H), 7.43 (d, *J* = 7.9 Hz, 1H), 7.31 – 7.26 (m, 3H), 7.21 – 7.15 (m, 1H), 7.10 – 7.05 (m, 1H), 3.71 (dd, *J* = 5.8, 3.6 Hz, 1H), 3.63 (s, 3H), 3.60 – 3.46 (m, 2H), 3.23 (dd, *J* = 16.4, 3.6 Hz, 1H), 3.09 (dd, *J* = 16.4, 5.9 Hz, 1H), 2.41 (s, 3H), 1.35 (s, 9H), 1.24 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 179.53, 169.42, 152.01, 144.64, 137.57, 134.69, 132.36, 129.73, 128.57, 126.86, 121.22, 119.03, 117.99, 108.87, 104.39, 83.62, 83.37, 79.68, 49.13, 29.41, 28.03, 27.97, 27.54, 22.35, 21.74; ESI-HRMS *m/z* calcd for $C_{31}H_{39}N_2O_7S^+$ $[M + H]^+$ 583.2472, found 583.2470.



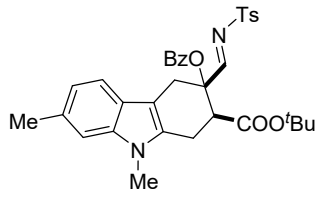

**3ba**

*tert*-butyl 3-(benzoyloxy)-5,9-dimethyl-3-((*E*)-(tosylimino)methyl)-2,3,4,9-tetrahydro-1*H*-carbazole-2-carboxylate (**3ba**): yellow solid, m.p. 90 – 91 °C; 115 mg, 99% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.21 (s, 1H), 7.83 – 7.72 (m, 4H), 7.54 – 7.48 (m, 1H), 7.38 – 7.31 (m, 2H), 7.24 – 7.21 (m, 2H), 7.12 – 7.01 (m, 2H), 6.81 – 6.75 (m, 1H), 3.89 (s, 2H), 3.88 – 3.83 (m, 1H), 3.61 (s, 3H), 3.26 (dd, *J* = 16.4, 4.5 Hz, 1H), 3.14 (dd, *J* = 16.4, 5.9 Hz, 1H), 2.61 (s, 3H), 2.38 (s, 3H), 1.38 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 179.06, 169.50, 165.18, 144.51, 137.64, 134.64, 133.69, 131.44, 130.29, 129.93, 129.63, 129.04, 128.45, 128.35, 125.81, 121.34, 120.45, 106.71, 105.15, 83.29, 80.14, 48.41, 30.78, 29.46, 28.06, 22.52, 21.73, 20.11; ESI-HRMS *m/z* calcd for $C_{34}H_{36}N_2NaO_6S^+$ $[M + Na]^+$ 623.2186, found 623.2197.




**3ca**

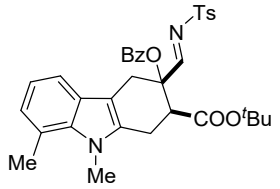
*tert*-butyl 3-(benzoyloxy)-6,9-dimethyl-3-((*E*)-(tosylimino)methyl)-2,3,4,9-tetrahydro-1*H*-carbazole-2-carboxylate (**3ca**): yellow oil; 114 mg, 95% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.21 (s, 1H), 7.82 – 7.71 (m, 4H), 7.54 – 7.47 (m, 1H), 7.34 (t, *J* = 7.8 Hz, 2H), 7.24 – 7.20 (m, 3H), 7.14 (d, *J* = 8.3 Hz, 1H), 7.02 – 6.97 (m, 1H), 3.91 – 3.83 (m, 1H), 3.67 – 3.53 (m, 5H), 3.27 (dd, *J* = 16.4, 4.5 Hz, 1H), 3.17 – 3.08 (m, 1H), 2.42 (s, 3H), 2.38 (s, 3H), 1.38 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 178.95, 169.48, 165.20, 144.49, 136.07, 134.67, 133.67, 132.10, 129.92, 129.64, 129.08, 128.45, 128.36, 126.94, 122.76, 117.89, 108.60, 104.26, 83.33, 80.17, 49.02, 29.49, 28.62, 28.07, 22.63, 21.75, 21.51 (one carbon missed); ESI-HRMS *m/z* calcd for $C_{34}H_{36}N_2NaO_6S^+$ $[M + Na]^+$ 623.2186, found 623.2203.




**3da**

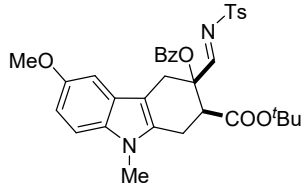
*tert*-butyl 3-(benzoyloxy)-7,9-dimethyl-3-((*E*)-(tosylimino)methyl)-2,3,4,9-tetrahydro-1*H*-carbazole-2-carboxylate (**3da**):

yellow oil; 114 mg, 95% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.21 (s, 1H), 7.81 – 7.72 (m, 4H), 7.53 – 7.47 (m, 1H), 7.37 – 7.28 (m, 3H), 7.24 – 7.20 (m, 2H), 7.05 (s, 1H), 6.92 – 6.87 (m, 1H), 3.87 (t, *J* = 5.1 Hz, 1H), 3.67 – 3.53 (m, 5H), 3.27 (dd, *J* = 16.4, 4.6 Hz, 1H), 3.13 (dd, *J* = 16.4, 5.7 Hz, 1H), 2.47 (s, 3H), 2.37 (s, 3H), 1.38 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 178.93, 169.49, 165.21, 144.49, 138.04, 134.63, 133.66, 131.34, 131.13, 129.90, 129.62, 129.04, 128.43, 128.33, 124.59, 120.70, 117.72, 109.03, 104.58, 83.30, 80.17, 48.95, 29.35, 28.67, 28.04, 22.59, 21.98, 21.72; ESI-HRMS *m/z* calcd for $C_{34}H_{36}N_2NaO_6S^+$ $[M + Na]^+$ 623.2186, found 623.2173.



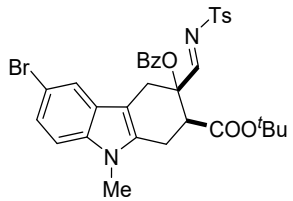

**3ea**

*tert*-butyl 3-(benzoyloxy)-8,9-dimethyl-3-((*E*)-(tosylimino)methyl)-2,3,4,9-tetrahydro-1*H*-carbazole-2-carboxylate (**3ea**): yellow oil; 106 mg, 88% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.21 (s, 1H), 7.81 – 7.72 (m, 4H), 7.54 – 7.48 (m, 1H), 7.34 (t, *J* = 7.8 Hz, 2H), 7.25 – 7.21 (m, 3H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.86 (d, *J* = 7.1 Hz, 1H), 3.92 – 3.85 (m, 4H), 3.65 – 3.52 (m, 2H), 3.26 (dd, *J* = 16.4, 4.6 Hz, 1H), 3.11 (dd, *J* = 16.3, 5.8 Hz, 1H), 2.75 (s, 3H), 2.38 (s, 3H), 1.39 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 178.90, 169.47, 165.22, 144.51, 136.50, 134.63, 133.68, 132.42, 129.92, 129.64, 129.04, 128.45, 128.36, 127.54, 124.44, 120.89, 119.27, 116.06, 105.02, 83.40, 80.12, 49.09, 32.54, 28.56, 28.08, 22.89, 21.74, 20.24; ESI-HRMS *m/z* calcd for $C_{34}H_{36}N_2NaO_6S^+$ $[M + Na]^+$ 623.2186, found 623.2171.




**3fa**

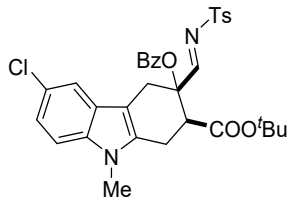
*tert*-butyl 3-(benzoyloxy)-6-methoxy-9-methyl-3-((*E*)-(tosylimino)methyl)-2,3,4,9-tetrahydro-1*H*-carbazole-2-carboxylate (**3fa**): yellow solid, m.p. 68 – 69 °C; 122 mg, 99% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.20 (s, 1H), 7.83 – 7.78 (m, 2H), 7.77 – 7.72 (m, 2H), 7.55 – 7.49 (m, 1H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.8 Hz, 1H), 6.87 (d, J = 2.4 Hz, 1H), 6.82 (dd, *J* = 8.8, 2.5 Hz, 1H), 3.87 (t, *J* = 5.2 Hz, 1H), 3.82 (s, 3H), 3.68 – 3.51 (m, 5H), 3.25 (dd, *J* = 16.5, 4.8 Hz, 1H), 3.13 (dd, *J* = 16.4, 5.8 Hz, 1H), 2.38 (s, 3H), 1.39 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 178.79, 169.48, 165.27, 153.93, 144.53, 134.63, 133.72, 132.88, 132.59, 129.92, 129.64, 129.04, 128.47, 128.35, 126.93, 111.21, 109.59, 104.44, 100.17, 83.34, 80.26, 56.00, 49.05, 29.57, 28.78, 28.06, 22.72, 21.74; ESI-HRMS *m/z* calcd for $C_{34}H_{37}N_2O_7S^+$ $[M + H]^+$ 617.2316, found 617.2307.




**3ga**

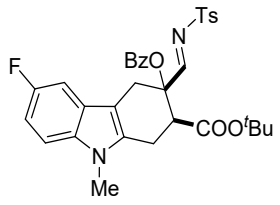
*tert*-butyl 3-(benzoyloxy)-6-bromo-9-methyl-3-((*E*)-(tosylimino)methyl)-2,3,4,9-tetrahydro-1*H*-carbazole-2-carboxylate (**3ga**): yellow solid, m.p. 87 – 88 °C; 109 mg, 82% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.18 (s, 1H), 7.83 – 7.77 (m, 2H), 7.76 – 7.71 (m, 2H), 7.55 – 7.49 (m, 2H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.25 – 7.21 (m, 3H), 7.11 (d, *J* = 8.6 Hz, 1H), 3.87 (t, *J* = 5.3 Hz, 1H), 3.64 – 3.47 (m, 5H), 3.25 (dd, *J* = 16.5, 4.9 Hz, 1H), 3.14 (dd, *J* = 16.5, 5.7 Hz, 1H), 2.38 (s, 3H), 1.39 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 178.47, 169.33, 165.17, 144.60, 136.31, 134.54, 133.78, 133.46, 129.91, 129.67, 128.94, 128.50, 128.32, 124.03, 120.67, 112.43, 110.37, 104.58, 83.51, 80.03, 48.93, 29.63, 28.54, 28.05, 22.66, 21.75 (one carbon

missed); ESI-HRMS *m/z* calcd for $C_{33}H_{34}BrN_2O_6S^+$ $[M + H]^+$ 665.1315, found 665.1329.



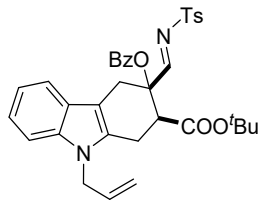

**3ha**

*tert*-butyl (*Z*)-3-(benzoyloxy)-6-chloro-9-methyl-3-((tosylimino)methyl)-2,3,4,9-tetrahydro-1*H*-carbazole-2-carboxylate (**3ha**): faint yellow oil; 98 mg, 79% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.11 (s, 1H), 7.75 – 7.70 (m, 2H), 7.68 – 7.63 (m, 2H), 7.47 – 7.41 (m, 1H), 7.30 – 7.24 (m, 3H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.07 (d, *J* = 8.6 Hz, 1H), 7.02 (dd, *J* = 8.6, 1.9 Hz, 1H), 3.79 (t, *J* = 5.3 Hz, 1H), 3.57 – 3.40 (m, 5H), 3.17 (dd, *J* = 16.5, 4.9 Hz, 1H), 3.06 (dd, *J* = 16.5, 5.8 Hz, 1H), 2.30 (s, 3H), 1.31 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 178.52, 169.34, 165.16, 144.60, 136.01, 134.52, 133.77, 133.58, 129.90, 129.66, 128.92, 128.50, 128.30, 127.63, 124.90, 121.44, 117.57, 109.89, 104.61, 83.48, 80.03, 48.94, 29.63, 28.53, 28.03, 22.67, 21.74; ESI-HRMS *m/z* calcd for $C_{33}H_{34}ClN_2O_6S^+$ $[M + H]^+$ 621.1821, found 621.1834.



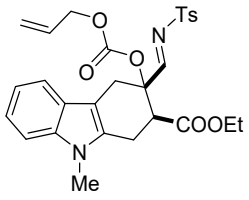

**3ia**

*tert*-butyl (*Z*)-3-(benzoyloxy)-6-fluoro-9-methyl-3-((tosylimino)methyl)-2,3,4,9-tetrahydro-1*H*-carbazole-2-carboxylate (**3ia**): yellow solid, m.p. 53 – 54 °C; 119 mg, 98% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.11 (s, 1H), 7.76 – 7.70 (m, 2H), 7.68 – 7.64 (m, 2H), 7.47 – 7.41 (m, 1H), 7.27 (t, *J* = 7.8 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.07 (dd, *J* = 8.8, 4.2 Hz, 1H), 6.96 (dd, *J* = 9.5, 2.5 Hz, 1H), 6.82 (td, *J* = 9.1, 2.5 Hz, 1H), 3.79 (t, *J* = 5.3 Hz, 1H), 3.57 – 3.40 (m, 5H), 3.18 (dd, *J* = 16.5, 4.9 Hz, 1H), 3.07 (dd, *J* = 16.5, 5.7 Hz, 1H), 2.30 (s, 3H), 1.31 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 178.60, 169.38, 165.19, 157.74 (d, *J* = 235.3 Hz), 144.58, 134.54, 134.20, 133.81, 133.76, 129.91, 129.65, 128.95, 128.49, 128.31, 126.83 (d, *J* = 10.1 Hz), 109.43 (d, *J* = 2.0 Hz), 109.25 (d, *J* = 18.2 Hz), 104.86 (d, *J* = 5.1 Hz), 103.17 (d, *J* = 23.2 Hz), 83.44, 80.11, 48.98, 29.66, 28.61, 28.03, 22.73, 21.73; ESI-HRMS *m/z* calcd for $C_{33}H_{34}FN_2O_6S^+$ $[M + H]^+$ 605.2116, found 605.2107.




**3ja**

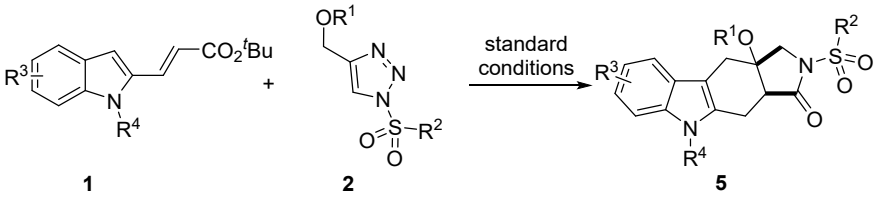
*tert*-butyl 9-allyl-3-(benzoyloxy)-3-((*E*)-(tosylimino)methyl)-2,3,4,9-tetrahydro-1*H*-carbazole-2-carboxylate (**3ja**): yellow solid, m.p. 149 – 150 °C; 113 mg, 92% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.22 (s, 1H), 7.80 – 7.74 (m, 4H), 7.53 – 7.47 (m, 1H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.25 – 7.20 (m, 3H), 7.18 – 7.13 (m, 1H), 7.10 – 7.04 (m, 1H), 5.97 – 5.84 (m, 1H), 5.10 – 5.03 (m, 1H), 4.77 – 4.69 (m, 1H), 4.69 – 4.63 (m, 2H), 3.92 – 3.84 (m, 1H), 3.71 – 3.56 (m, 2H), 3.26 (dd, *J* = 16.5, 4.2 Hz, 1H), 3.20 – 3.06 (m, 1H), 2.38 (s, 3H), 1.37 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 178.92, 169.49, 165.14, 144.53, 137.06, 134.57, 133.70, 133.30, 131.78, 129.89, 129.66, 129.00, 128.44, 128.39, 126.89, 121.45, 119.27, 118.13, 116.23, 109.21, 105.30, 83.25, 80.00, 48.81, 45.23, 28.39, 28.02, 22.49, 21.73; ESI-HRMS *m/z* calcd for $C_{35}H_{37}N_2O_6S^+$ $[M + H]^+$ 613.2367, found 613.2347.




**3nm**

ethyl 3-(((allyloxy)carbonyl)oxy)-9-methyl-3-((*E*)-(tosylimino)methyl)-2,3,4,9-tetrahydro-1*H*-carbazole-2-carboxylate (**3nm**): yellow oil; 84 mg, 78% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.04 (s, 1H), 7.82 – 7.77 (m, 2H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.27 – 7.25 (m, 1H), 7.22 – 7.15 (m, 1H), 7.10 – 7.05 (m, 1H), 5.77 – 5.64 (m, 1H), 5.25 – 5.14 (m, 2H), 4.45 – 4.33 (m, 2H), 4.05 (qt, *J* = 6.9, 3.5 Hz, 2H), 3.76 (dd, *J* = 6.0, 3.8 Hz, 1H), 3.60 (d, *J* = 12.4 Hz, 5H), 3.26 (dd, *J* = 16.6, 3.9 Hz, 1H), 3.22 – 3.13 (m, 1H), 2.43 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 178.45, 170.24, 153.25, 144.78, 137.59, 134.36, 131.78, 130.92, 129.72, 128.57, 126.64, 121.45, 119.63, 119.20, 117.96, 108.95, 104.27, 80.69, 69.14, 62.01, 48.35, 29.43, 27.68, 22.33, 21.78, 14.04; ESI-HRMS *m/z* calcd for $C_{28}H_{30}N_2NaO_7S^+$ $[M + Na]^+$ 561.1666, found 561.1686.

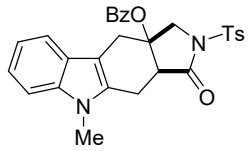
## 5 General procedure for synthesis of pyrrolo[3,4-*b*]carbazoles




**1** **2** **5**

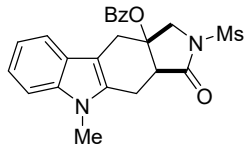
**General procedure:**

To the solution of **1a** (51.5 mg, 0.20 mmol) and $Rh_2(OAc)_4$ (1.8 mg, 2 mol %) in anhydrous DCE (2 mL) was added the solution of **2a** (100.1 mg, 0.28 mmol) in anhydrous DCE (2 mL) via syringe pump for 3 hours at 80 °C under $N_2$. After 1 hour, the reaction was cooled to 0 °C and the methanol (2 mL) was added to the mixture. $NaBH_4$ (7.6 mg, 0.20 mmol) was added to the mixture and stirred at 0 °C for 10 min. Then water (1 mL) was added to the mixture to quench the reaction. After 10 minutes, the mixture was dried with anhydrous $Na_2SO_4$ (5 g), filtered with a pad of silica gel, washed with ethyl acetate. The combined filter was concentrated in vacuo and the residue was dissolved in DCE (2 mL). To the mixture was added $TsOH{\cdot}H_2O$ (19.0 mg, 0.10 mmol) and the reaction was stirred at 80 °C for 0.5 hour. The solvent was evaporated in vacuo and the crude was purified by silica gel column chromatography (PE : EtOAc = 3 : 1 to 2 : 1) to give **5aa** as a yellow solid.



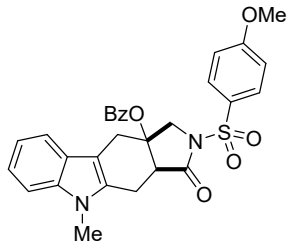
**5aa**

5-methyl-3-oxo-2-tosyl-2,3,3a,4,5,10-hexahydropyrrolo[3,4-*b*]carbazol-10a(1*H*)-yl benzoate (**5aa**): yellow solid, m.p. 72 – 73 °C; 96 mg, 93% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.78 (m, 4H), 7.57 – 7.50 (m, 1H), 7.40 – 7.32 (m, 3H), 7.24 – 7.21 (m, 1H), 7.19 – 7.11 (m, 3H), 7.08 – 7.01 (m, 1H), 4.55 (d, *J* = 11.1 Hz, 1H), 4.34 (d, *J* = 11.1 Hz, 1H), 3.61 (s, 4H), 3.42 (dd, *J* = 7.7, 4.2 Hz, 1H), 3.28 – 3.08 (m, 3H), 2.29 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 171.12, 165.60, 145.44, 137.58, 134.89, 133.66, 130.97, 129.86, 129.80, 129.49, 128.51, 127.82, 126.32, 121.62, 119.27, 117.83, 108.94, 104.55, 80.16, 55.90, 48.38, 29.42, 27.40, 21.76, 19.03; ESI-HRMS *m/z* calcd for $C_{29}H_{27}N_2O_5S^+$ $[M + H]^+$ 515.1635, found 515.1633.



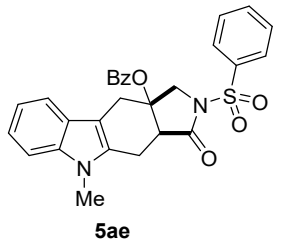
**5ab**

5-methyl-2-(methylsulfonyl)-3-oxo-2,3,3a,4,5,10-hexahydropyrrolo[3,4-*b*]carbazol-10a(1*H*)-yl benzoate (**5ab**): yellow solid, m.p. 68 – 69 °C; 83 mg, 95% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.91 (m, 2H), 7.58 – 7.52 (m, 1H), 7.45 – 7.38 (m, 3H), 7.29 – 7.25 (m, 1H), 7.22 – 7.16 (m, 1H), 7.10 – 7.04 (m, 1H), 4.59 (d, *J* = 10.7 Hz, 1H), 4.24 (d, *J* = 10.7 Hz, 1H), 3.82 – 3.74 (m, 1H), 3.69 (s, 3H), 3.64 – 3.57 (m, 1H), 3.42 – 3.33 (m, 1H), 3.32 – 3.18 (m, 5H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 172.06, 165.72, 137.72, 133.79, 131.12, 129.88, 129.58, 128.63, 126.42, 121.80, 119.43, 117.90, 109.04, 104.58, 79.84, 55.77, 48.48, 41.14, 29.51, 27.89, 18.75; ESI-HRMS *m/z* calcd for $C_{23}H_{23}N_2O_5S^+$ $[M + H]^+$ 439.1322, found 439.1333.



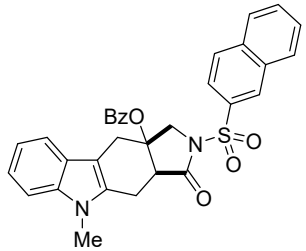

**5ad**

2-((4-methoxyphenyl)sulfonyl)-5-methyl-3-oxo-2,3,3a,4,5,10-hexahydropyrrolo[3,4-*b*]carbazol-10a(1*H*)-yl benzoate (**5ad**): yellow solid, m.p. 59 – 60 °C; 93 mg, 88% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.81 (m, 4H), 7.56 – 7.50 (m, 1H), 7.39 – 7.33 (m, 3H), 7.24 – 7.21 (m, 1H), 7.19 – 7.14 (m, 1H), 7.08 – 7.02 (m, 1H), 6.83 – 6.76 (m, 2H), 4.54 (d, *J* = 11.1 Hz, 1H), 4.33 (d, *J* = 11.1 Hz, 1H), 3.75 (s, 3H), 3.64 – 3.56 (m, 4H), 3.43 (dd, *J* = 7.7, 4.2 Hz, 1H), 3.28 – 3.11 (m, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 171.16, 165.62, 164.14, 137.59, 133.65, 131.03, 130.13, 129.78, 129.52, 129.28, 128.50, 126.33, 121.62, 119.27, 117.83, 114.37, 108.95, 104.58, 80.23, 55.91, 55.67, 48.39, 29.42, 27.45, 19.08; ESI-HRMS *m/z* calcd for $C_{29}H_{27}N_2O_6S^+$ $[M + H]^+$ 531.1584, found 531.1591.



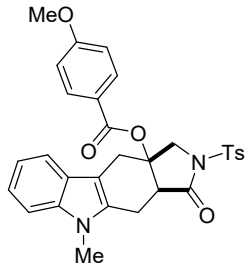

**5ae**

5-methyl-3-oxo-2-(phenylsulfonyl)-2,3,3a,4,5,10-hexahydropyrrolo[3,4-*b*]carbazol-10a(1*H*)-yl benzoate (**5ae**): yellow solid, m.p. 46 – 47 °C; 70 mg, 70% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.91 (m, 2H), 7.86 – 7.80 (m, 2H), 7.56 – 7.51 (m, 1H), 7.50 – 7.44 (m, 1H), 7.40 – 7.32 (m, 5H), 7.24 – 7.20 (m, 1H), 7.20 – 7.13 (m, 1H), 7.08 – 7.01 (m, 1H), 4.56 (d, *J* = 11.1 Hz, 1H), 4.34 (d, *J* = 11.0 Hz, 1H), 3.64 – 3.57 (m, 4H), 3.44 (dd, *J* = 7.6, 4.1 Hz, 1H), 3.28 – 3.06 (m, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 171.15, 165.63, 137.84, 137.59, 134.25, 133.69, 130.97, 129.81, 129.48, 129.22, 128.54, 127.76, 126.31, 121.65, 119.31, 117.83, 108.98, 104.53, 80.10, 56.01, 48.41, 29.41, 27.46, 19.05; ESI-HRMS *m/z* calcd for $C_{28}H_{25}N_2O_5S^+$ $[M + H]^+$ 501.1479, found 501.1479.



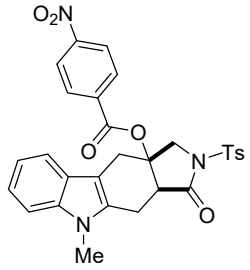

**5af**

5-methyl-2-(naphthalen-2-ylsulfonyl)-3-oxo-2,3,3a,4,5,10-hexahydropyrrolo[3,4-*b*]carbazol-10a(1*H*)-yl benzoate (**5af**): white solid, m.p. 71 – 72 °C; 76 mg, 69% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.87 – 7.81 (m, 1H), 7.80 – 7.67 (m, 4H), 7.66 – 7.53 (m, 2H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.35 – 7.25 (m, 3H), 7.21 – 7.10 (m, 2H), 7.02 (t, *J* = 7.3 Hz, 1H), 4.59 (d, *J* = 11.2 Hz, 1H), 4.41 (d, *J* = 11.1 Hz, 1H), 3.62 – 3.50 (m, 4H), 3.46 – 3.39 (m, 1H), 3.27 – 3.13 (m, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 171.39, 165.62, 137.57, 135.53, 134.65, 133.63, 131.94, 130.95, 130.02, 129.73, 129.69, 129.66, 129.48, 129.36, 128.44, 128.08, 127.79, 126.28, 122.03, 121.64, 119.30, 117.82, 108.96, 104.60, 80.29, 56.00, 48.48, 29.36, 27.55, 19.28; ESI-HRMS *m/z* calcd for $C_{32}H_{27}N_2O_5S^+$ $[M + H]^+$ 551.1635, found 551.1636.



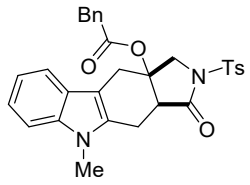

**5ag**

5-methyl-3-oxo-2-tosyl-2,3,3a,4,5,10-hexahydropyrrolo[3,4-*b*]carbazol-10a(1*H*)-yl 4-methoxybenzoate (**5ag**): yellow solid, m.p. 154 – 155 °C; 71 mg, 65% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.76 (m, 4H), 7.37 – 7.33 (m, 1H), 7.24 – 7.20 (m, 1H), 7.19 – 7.12 (m, 3H), 7.07 – 7.02 (m, 1H), 6.86 – 6.80 (m, 2H), 4.53 (d, *J* = 11.0 Hz, 1H), 4.33 (d, *J* = 11.0 Hz, 1H), 3.83 (s, 3H), 3.64 – 3.54 (m, 4H), 3.41 (dd, *J* = 7.8, 4.0 Hz, 1H), 3.27 – 3.05 (m, 3H), 2.30 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 171.27, 165.37, 163.99, 145.35, 137.66, 135.05, 131.94, 131.09, 129.83, 127.86, 126.43, 121.97, 121.62, 119.29, 117.87, 113.80, 108.94, 104.78, 79.89, 56.07, 55.59, 48.53, 29.39, 27.60, 21.72, 19.13; ESI-HRMS *m/z* calcd for $C_{30}H_{29}N_2O_6S^+$ $[M + H]^+$ 545.1741, found 545.1759.



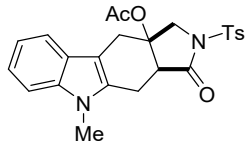

**5ah**

5-methyl-3-oxo-2-tosyl-2,3,3a,4,5,10-hexahydropyrrolo[3,4-*b*]carbazol-10a(1*H*)-yl 4-nitrobenzoate (**5ah**): yellow solid, m.p. 153 – 154 °C; 56 mg, 50% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.23 – 8.17 (m, 2H), 8.04 – 7.98 (m, 2H), 7.87 – 7.81 (m, 2H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.21 – 7.14 (m, 3H), 7.09 – 7.02 (m, 1H), 4.56 (d, *J* = 11.1 Hz, 1H), 4.33 (d, *J* = 11.1 Hz, 1H), 3.65 – 3.56 (m, 4H), 3.47 (dd, *J* = 7.9, 3.8 Hz, 1H), 3.30 – 3.08 (m, 3H), 2.32 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.67, 163.74, 150.89, 145.62, 137.60, 134.87, 134.82, 130.97, 130.92, 129.91, 127.91, 126.20, 123.64, 121.80, 119.41, 117.77, 109.04, 104.17, 81.27, 55.75, 48.27, 29.46, 27.37, 21.76, 18.97; ESI-HRMS *m/z* calcd for $C_{29}H_{25}N_3NaO_7S^+$ $[M + Na]^+$ 582.1305, found 582.1307.



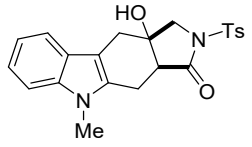

**5aj**

5-methyl-3-oxo-2-tosyl-2,3,3a,4,5,10-hexahydropyrrolo[3,4-*b*]carbazol-10a(1*H*)-yl 2-phenylacetate (**5aj**): yellow oil; 59 mg, 56% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.79 (m, 2H), 7.30 (d, J = 7.8 Hz, 1H), 7.24 – 7.20 (m, 3H), 7.20 – 7.14 (m, 4H), 7.13 – 7.02 (m, 3H), 4.45 (d, *J* = 10.8 Hz, 1H), 4.08 (d, *J* = 10.8 Hz, 1H), 3.57 (s, 3H), 3.52 – 3.43 (m, 3H), 3.30 – 3.23 (m, 1H), 3.20 – 3.11 (m, 1H), 2.97 (dd, *J* = 17.1, 8.5 Hz, 1H), 2.83 – 2.74 (m, 1H), 2.36 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 171.06, 170.49, 145.55, 137.49, 134.94, 133.21, 131.15, 129.91, 129.09, 128.71, 127.93, 127.37, 126.35, 121.53, 119.24, 117.78, 108.89, 104.27, 79.43, 56.11, 48.03, 41.54, 29.34, 26.99, 21.78, 18.27; ESI-HRMS *m/z* calcd for $C_{30}H_{29}N_2O_5S^+$ $[M + H]^+$ 529.1792, found 529.1798.



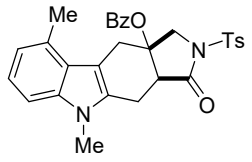

**5ak**

5-methyl-3-oxo-2-tosyl-2,3,3a,4,5,10-hexahydropyrrolo[3,4-*b*]carbazol-10a(1*H*)-yl acetate (**5ak**): yellow solid, m.p. 48 – 49 °C; 57 mg, 63% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.82 (m, 2H), 7.36 – 7.32 (m, 1H), 7.28 – 7.21 (m, 3H), 7.20 – 7.14 (m, 1H), 7.09 – 7.02 (m, 1H), 4.50 (d, *J* = 10.8 Hz, 1H), 4.11 (d, *J* = 10.8 Hz, 1H), 3.60 (s, 3H), 3.52 (d, *J* = 17.1 Hz, 1H), 3.31 – 3.25 (m, 1H), 3.23 – 3.14 (m, 1H), 3.07 – 2.97 (m, 1H), 2.87 – 2.78 (m, 1H), 2.38 (s, 3H), 1.95 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.57, 170.41, 145.57, 137.48, 135.00, 131.13, 129.94, 127.96, 126.36, 121.57, 119.24, 117.80, 108.93, 104.37, 79.00, 56.20, 48.17, 29.38, 26.95, 21.81, 21.61, 18.25; ESI-HRMS *m/z* calcd for $C_{24}H_{25}N_2O_5S^+$ $[M + H]^+$ 453.1479, found 453.1471.



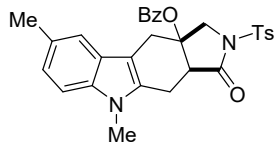

**6al**

10a-hydroxy-5-methyl-2-tosyl-1,3a,4,5,10,10a-hexahydropyrrolo[3,4-*b*]carbazol-3(2*H*)-one (**6al**): yellow solid, m.p. 79 – 80 °C; 29 mg, 35% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.07 (t, *J* = 7.4 Hz, 1H), 3.94 (d, *J* = 9.8 Hz, 1H), 3.83 (d, *J* = 9.8 Hz, 1H), 3.58 (s, 3H), 3.10 (d, *J* = 15.2 Hz, 1H), 3.03 – 2.91 (m, 3H), 2.74 (d, *J* = 16.4 Hz, 1H), 2.39 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 171.99, 145.53, 137.61, 135.12, 131.44, 129.94, 128.03, 126.67, 121.63, 119.31, 117.70, 109.00, 104.22, 72.67, 57.06, 49.00, 30.78, 29.39, 21.81, 17.78; ESI-HRMS *m/z* calcd for $C_{22}H_{23}N_2O_4S^+$ $[M + H]^+$ 411.1373, found 411.1386.




**5ba**

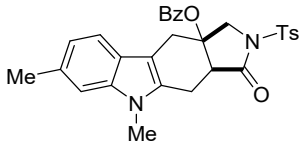
5,9-dimethyl-3-oxo-2-tosyl-2,3,3a,4,5,10-hexahydropyrrolo[3,4-*b*]carbazol-10a(1*H*)-yl benzoate (**5ba**): yellow solid, m.p. 55 – 56 °C; 86 mg, 81% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.79 (m, 4H), 7.57 – 7.51 (m, 1H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 2H), 7.08 – 6.99 (m, 2H), 6.78 – 6.74 (m, 1H), 4.52 (d, *J* = 11.1 Hz, 1H), 4.33 (d, *J* = 11.1 Hz, 1H), 3.84 (d, *J* = 17.0 Hz, 1H), 3.57 (s, 3H), 3.43 – 3.32 (m, 2H), 3.25 – 3.11 (m, 2H), 2.54 (s, 3H), 2.30 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 171.17, 165.58, 145.43, 137.59, 134.89, 133.66, 130.48, 129.97, 129.83, 129.52, 128.51, 127.80, 125.30, 121.57, 120.74, 106.79, 104.94, 80.27, 55.97, 47.99, 29.67, 29.42, 21.75, 20.13, 19.03 (one carbon missed); ESI-HRMS *m/z* calcd for $C_{30}H_{29}N_2O_5S^+$ $[M + H]^+$ 529.1792, found 529.1810.




**5ca**

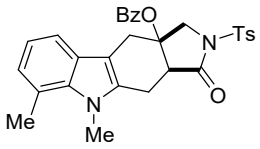
5,8-dimethyl-3-oxo-2-tosyl-2,3,3a,4,5,10-hexahydropyrrolo[3,4-*b*]carbazol-10a(1*H*)-yl benzoate (**5ca**): white solid, m.p. 110 – 111 °C; 88 mg, 83% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.79 (m, 4H), 7.57 – 7.50 (m, 1H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.16 – 7.08 (m, 4H), 7.01 – 6.96 (m, 1H), 4.53 (d, *J* = 11.1 Hz, 1H), 4.34 (d, *J* = 11.1 Hz, 1H), 3.61 – 3.51 (m, 4H), 3.40 (dd, *J* = 7.5, 4.4 Hz, 1H), 3.26 – 3.06 (m, 3H), 2.40 (s, 4H), 2.29 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 171.23,

165.58, 145.40, 136.01, 134.92, 133.62, 130.98, 129.85, 129.79, 129.53, 128.49, 127.81, 126.55, 126.52, 123.08, 117.63, 108.63, 103.99, 80.25, 55.86, 48.40, 29.42, 27.40, 21.73, 21.48, 19.10; ESI-HRMS *m/z* calcd for $C_{30}H_{29}N_2O_5S^+$ $[M + H]^+$ 529.1792, found 529.1790.



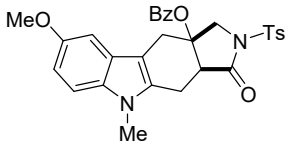

**5da**

5,7-dimethyl-3-oxo-2-tosyl-2,3,3a,4,5,10-hexahydropyrrolo[3,4-*b*]carbazol-10a(1*H*)-yl benzoate (**5da**): yellow solid, m.p. 50 – 51 °C; 93 mg, 88% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.79 (m, 4H), 7.56 – 7.50 (m, 1H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.13 (d, *J* = 8.1 Hz, 2H), 7.02 (s, 1H), 6.91 – 6.86 (m, 1H), 4.52 (d, *J* = 11.1 Hz, 1H), 4.34 (d, *J* = 11.1 Hz, 1H), 3.60 – 3.50 (m, 4H), 3.40 (dd, *J* = 7.2, 4.8 Hz, 1H), 3.24 – 3.08 (m, 3H), 2.45 (s, 3H), 2.29 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 171.29, 165.60, 145.40, 138.02, 134.92, 133.62, 131.46, 130.22, 129.84, 129.80, 129.53, 128.49, 127.82, 124.21, 120.91, 117.51, 109.05, 104.36, 80.32, 55.82, 48.40, 29.33, 27.46, 21.98, 21.75, 19.13; ESI-HRMS *m/z* calcd for $C_{30}H_{29}N_2O_5S^+$ $[M + H]^+$ 529.1792, found 529.1774.



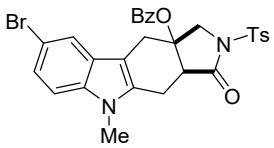

**5ea**

5,6-dimethyl-3-oxo-2-tosyl-2,3,3a,4,5,10-hexahydropyrrolo[3,4-*b*]carbazol-10a(1*H*)-yl benzoate (**5ea**): yellow oil; 95 mg, 90% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.79 (m, 4H), 7.56 – 7.50 (m, 1H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.19 – 7.11 (m, 3H), 6.91 (t, *J* = 7.4 Hz, 1H), 6.85 (d, *J* = 7.1 Hz, 1H), 4.55 (d, *J* = 11.1 Hz, 1H), 4.33 (d, *J* = 11.1 Hz, 1H), 3.87 (s, 3H), 3.55 (d, *J* = 17.1 Hz, 1H), 3.42 (dd, *J* = 7.8, 4.0 Hz, 1H), 3.25 – 3.04 (m, 3H), 2.72 (s, 3H), 2.29 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 171.10, 165.59, 145.44, 136.44, 134.93, 133.64, 131.25, 129.86, 129.80, 129.49, 128.50, 127.84, 127.13, 124.74, 120.94, 119.43, 115.82, 104.74, 80.07, 55.85, 48.49, 32.50, 27.30, 21.75, 20.18, 19.27; ESI-HRMS *m/z* calcd for $C_{30}H_{29}N_2O_5S^+$ $[M + H]^+$ 529.1792, found 529.1775.




**5fa**

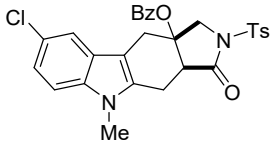
8-methoxy-5-methyl-3-oxo-2-tosyl-2,3,3a,4,5,10-hexahydropyrrolo[3,4-*b*]carbazol-10a(1*H*)-yl benzoate (**5fa**): yellow solid, m.p. 54 – 55 °C; 59 mg, 54% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.79 (m, 4H), 7.58 – 7.52 (m, 1H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.17 – 7.10 (m, 3H), 6.85 – 6.80 (m, 2H), 4.54 (d, *J* = 11.1 Hz, 1H), 4.35 (d, *J* = 11.1 Hz, 1H), 3.81 (s, 3H), 3.61 – 3.51 (m, 4H), 3.41 (dd, *J* = 7.5, 4.6 Hz, 1H), 3.25 – 3.14 (m, 3H), 2.30 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 171.24, 165.66, 154.01, 145.46, 134.85, 133.70, 132.82, 131.52, 129.86, 129.81, 129.46, 128.53, 127.83, 126.53, 111.49, 109.68, 104.15, 99.98, 80.30, 77.48, 56.01, 55.85, 48.47, 29.55, 27.53, 21.78, 19.22; ESI-HRMS *m/z* calcd for $C_{30}H_{29}N_2O_6S^+$ $[M + H]^+$ 545.1741, found 545.1741.




**5ga**

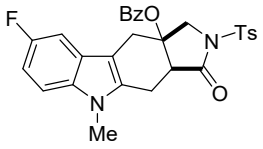
8-bromo-5-methyl-3-oxo-2-tosyl-2,3,3a,4,5,10-hexahydropyrrolo[3,4-*b*]carbazol-10a(1*H*)-yl benzoate (**5ga**): yellow solid, m.p. 150 – 151 °C; 77 mg, 65% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.79 (m, 4H), 7.57 – 7.50 (m, 1H), 7.43 (s, 1H),

7.37 (t, *J* = 7.6 Hz, 2H), 7.24 – 7.19 (m, 1H), 7.16 (d, *J* = 8.1 Hz, 2H), 7.07 (d, *J* = 8.6 Hz, 1H), 4.55 (d, *J* = 11.0 Hz, 1H), 4.29 (d, *J* = 11.0 Hz, 1H), 3.59 (s, 3H), 3.53 (d, *J* = 17.1 Hz, 1H), 3.43 (dd, *J* = 8.1, 3.3 Hz, 1H), 3.28 – 3.20 (m, 1H), 3.15 (dd, *J* = 17.3, 8.1 Hz, 1H), 2.99 (d, *J* = 17.2 Hz, 1H), 2.32 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.77, 165.57, 145.61, 136.27, 134.86, 133.76, 132.46, 129.93, 129.84, 129.40, 128.56, 127.97, 127.85, 124.33, 120.51, 112.56, 110.39, 104.25, 79.75, 56.05, 48.29, 29.62, 27.29, 21.82, 18.87; ESI-HRMS *m/z* calcd for $C_{29}H_{25}BrN_2NaO_5S^+$ $[M + Na]^+$ 615.0560, found 615.0577.



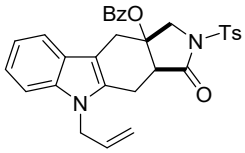

**5ha**

8-chloro-5-methyl-3-oxo-2-tosyl-2,3,3a,4,5,10-hexahydropyrrolo[3,4-*b*]carbazol-10a(1*H*)-yl benzoate (**5ha**): white solid, m.p. 189 – 190 °C; 74 mg, 67% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.72 (m, 4H), 7.50 – 7.44 (m, 1H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.21 (d, *J* = 1.8 Hz, 1H), 7.09 (d, *J* = 8.1 Hz, 2H), 7.07 – 6.99 (m, 2H), 4.48 (d, *J* = 11.1 Hz, 1H), 4.23 (d, *J* = 11.1 Hz, 1H), 3.53 (s, 3H), 3.46 (d, *J* = 17.1 Hz, 1H), 3.36 (dd, *J* = 8.1, 3.4 Hz, 1H), 3.17 (dd, *J* = 17.2, 3.4 Hz, 1H), 3.08 (dd, *J* = 17.4, 8.0 Hz, 1H), 2.97 – 2.88 (m, 1H), 2.24 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.80, 165.56, 145.58, 135.97, 134.83, 133.74, 132.59, 129.90, 129.82, 129.39, 128.55, 127.82, 127.29, 125.04, 121.73, 117.40, 109.92, 104.29, 79.77, 56.02, 48.28, 29.62, 27.29, 21.79, 18.90; ESI-HRMS *m/z* calcd for $C_{29}H_{26}ClN_2O_5S^+$ $[M + H]^+$ 549.1245, found 549.1258.




**5ia**

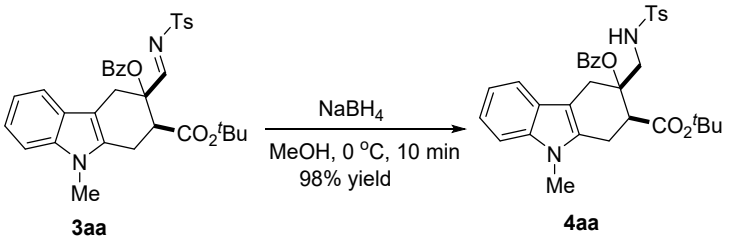
8-fluoro-5-methyl-3-oxo-2-tosyl-2,3,3a,4,5,10-hexahydropyrrolo[3,4-*b*]carbazol-10a(1*H*)-yl benzoate (**5ia**): white solid, m.p. 182 – 183 °C; 86 mg, 81% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.71 (m, 4H), 7.49 – 7.43 (m, 1H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.10 – 7.01 (m, 3H), 6.89 (dd, *J* = 9.4, 2.5 Hz, 1H), 6.82 (td, *J* = 9.1, 2.5 Hz, 1H), 4.48 (d, *J* = 11.0 Hz, 1H), 4.24 (d, *J* = 11.1 Hz, 1H), 3.53 (s, 3H), 3.45 (d, *J* = 17.1 Hz, 1H), 3.35 (dd, *J* = 7.9, 3.7 Hz, 1H), 3.20 – 3.04 (m, 2H), 3.01 – 2.92 (m, 1H), 2.23 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.92, 165.58, 157.78 (d, *J* = 235.3 Hz), 145.53, 134.84, 134.15, 133.72, 132.82, 129.88, 129.81, 129.41, 128.54, 127.82, 126.9 (d, *J* = 10.1 Hz), 109.64 (d, *J* = 23.2 Hz), 109.46 (d, *J* = 6.1 Hz), 104.55 (d, *J* = 4.0 Hz), 103.00 (d, *J* = 23.2 Hz), 79.92, 55.99, 48.34, 29.64, 27.40, 21.76, 19.05; ESI-HRMS *m/z* calcd for $C_{29}H_{26}FN_2O_5S^+$ $[M + H]^+$ 533.1541, found 533.1530.




**5ja**

5-allyl-3-oxo-2-tosyl-2,3,3a,4,5,10-hexahydropyrrolo[3,4-*b*]carbazol-10a(1*H*)-yl benzoate (**5ja**): yellow solid, m.p. 56 – 57 °C; 81 mg, 75% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.79 (m, 4H), 7.56 – 7.50 (m, 1H), 7.40 – 7.33 (m, 3H), 7.21 (d, *J* = 8.1 Hz, 1H), 7.18 – 7.10 (m, 3H), 7.05 (t, *J* = 7.4 Hz, 1H), 5.95 – 5.81 (m, 1H), 5.16 – 5.07 (m, 1H), 4.87 – 4.77 (m, 1H), 4.71 – 4.49 (m, 3H), 4.35 (d, *J* = 11.1 Hz, 1H), 3.58 (d, *J* = 17.0 Hz, 1H), 3.39 (t, *J* = 6.0 Hz, 1H), 3.25 – 3.10 (m, 3H), 2.28 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 171.15, 165.55, 145.44, 137.04, 134.82, 133.66, 133.20, 130.77, 129.86, 129.76, 129.46, 128.51, 127.79, 126.44, 121.75, 119.44, 117.89, 116.62, 109.28, 105.02, 80.19, 55.82, 48.41, 45.41, 27.45, 21.76, 18.96; ESI-HRMS *m/z* calcd for $C_{31}H_{29}N_2O_5S^+$ $[M + H]^+$ 541.1792, found 541.1776.

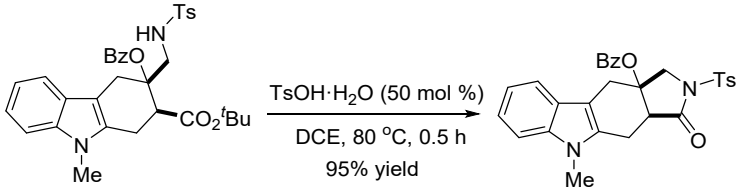
## 6 Large scale reaction and further transformation




**3aa** **4aa**

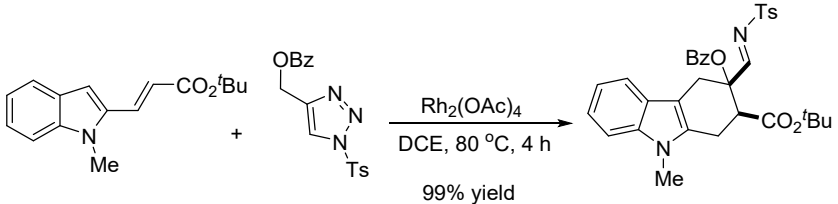
To the solution of **3aa** (117 mg, 0.20 mmol) in methanol (2 mL) was added $NaBH_4$ (7.6 mg, 0.20 mmol) at 0 °C. After 10 min, the reaction was quenched with water and extracted with ethyl acetate. The combined organic layer was washed with brine, dried with $Na_2SO_4$, filtered and concentrated. The residual was purified by silica gel column chromatography (PE : EtOAc = 3 : 1 to 2 : 1) to give the desired product **4aa** in 98% yield.

*tert*-butyl 3-(benzoyloxy)-9-methyl-3-(((4-methylphenyl)sulfonamido)methyl)-2,3,4,9-tetrahydro-1*H*-carbazole-2-carboxylate (**4aa**): yellow solid, m.p. 129 – 130 °C; 115 mg, 98% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.8 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.43 – 7.35 (m, 3H), 7.23 – 7.21 (m, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.11 – 7.03 (m, 3H), 5.49 (t, *J* = 6.8 Hz, 1H), 3.97 (t, *J* = 7.0 Hz, 1H), 3.72 (d, *J* = 6.7 Hz, 2H), 3.62 – 3.52 (m, 4H), 3.33 (d, *J* = 15.8 Hz, 1H), 3.13 – 2.96 (m, 2H), 2.33 (s, 3H), 1.35 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 171.35, 165.80, 143.29, 137.71, 136.94, 133.38, 131.56, 130.64, 129.89, 129.65, 128.50, 127.17, 126.68, 121.28, 119.11, 118.12, 108.82, 105.59, 83.53, 82.34, 46.29, 46.22, 29.38, 28.66, 27.98, 23.75, 21.61; ESI-HRMS *m/z* calcd for $C_{33}H_{37}N_2O_6S^+$ $[M + H]^+$ 589.2367, found 589.2354.



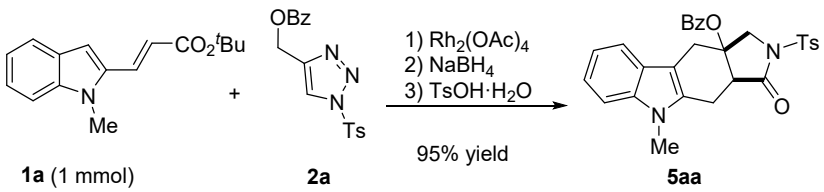

**4aa** **5aa**

The mixture of **4aa** (118 mg, 0.20 mmol) and $TsOH·H_2O$ (19 mg, 0.10 mmol) in anhydrous DCE (2 mL) was stirred at 80 °C for 0.5 hrs. After completed, the solvent was evaporated in vacuo and the residual was purified by silica gel column chromatography (PE : EtOAc = 3 : 1 to 2 : 1) to give the desired product **5aa** in 95% yield (98 mg).




**1a** (1 mmol) **2a** **3aa**

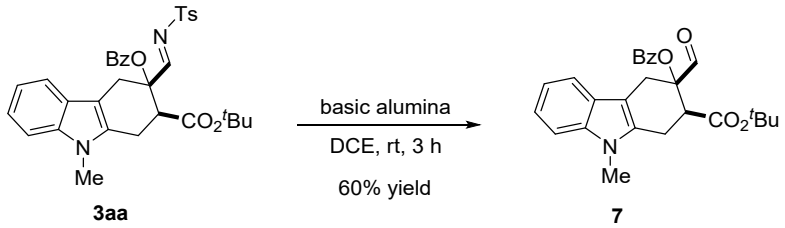
To the solution of **1a** (257 mg, 1.00 mmol) and $Rh_2(OAc)_4$ (8.8 mg, 2 mol %) in anhydrous DCE (10 mL) was added the solution of **2a** (500 mg, 1.40 mmol) in anhydrous DCE (10 mL) via syringe pump for 3 hours at 80 °C under $N_2$. After 1 hour, the reaction was cooled to room temperature and the solvent was evaporated in vacuo. The residue was purified by silica gel column chromatography (PE : EtOAc = 4 : 1 to 3 : 1) to give **3aa** (581 mg, 99% yield) as a yellow solid.




**1a** (1 mmol) **2a** **5aa**

To the solution of **1a** (257 mg, 1.00 mmol) and $Rh_2(OAc)_4$ (8.8 mg, 2 mol %) in anhydrous DCE (10 mL) was added the solution of **2a** (500 mg, 1.40 mmol) in anhydrous DCE (10 mL) via syringe pump for 3 hours at 80 °C under $N_2$. After 1

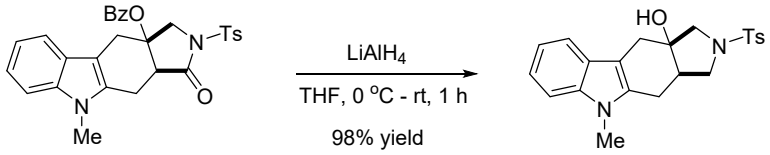
hour, the reaction was cooled to 0 °C and the methanol (5 mL) was added to the mixture. $NaBH_4$ (38 mg, 1.00 mmol) was added to the mixture and stirred at 0 °C for 10 min. Then water (5 mL) was added to the mixture to quench the reaction. After 10 minutes, the mixture was dried with anhydrous $Na_2SO_4$ (25 g), filtered with a pad of silica gel, washed with ethyl acetate. The combined filter was concentrated in vacuo and the residue was dissolved in DCE (10 mL). To the mixture was added $TsOH \cdot H_2O$ (95 mg, 0.50 mmol) and the reaction was stirred at 80 °C for 0.5 hour. The solvent was evaporated in vacuo and the crude was purified by silica gel column chromatography (PE : EtOAc = 3 : 1 to 2 : 1) to give **5aa** (489 mg, 95% yield) as a yellow solid.




**3aa** **7**

The mixture of **3aa** (117 mg, 0.20 mmol) and basic alumina (100 mg) in DCE (2 mL) was stirred at room temperature for 3 hrs. After completed, the solvent was evaporated in vacuo and the residual was purified by silica gel column chromatography (PE : EtOAc = 4 : 1 to 3 : 1) to give the desired product **7** in 60% yield.

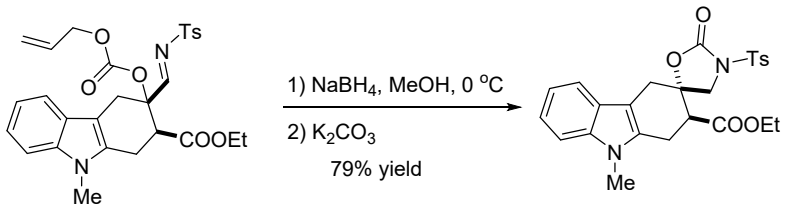
*tert*-butyl 3-(benzoyloxy)-3-formyl-9-methyl-2,3,4,9-tetrahydro-1*H*-carbazole-2-carboxylate (**7**): white solid, m.p. 184 – 185 °C; 52 mg, 60% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 10.11 (s, 1H), 7.98 – 7.91 (m, 2H), 7.58 – 7.52 (m, 1H), 7.46 (d, *J* = 7.9 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.29 – 7.26 (m, 1H), 7.21 – 7.16 (m, 1H), 7.11 – 7.05 (m, 1H), 3.80 – 3.73 (m, 2H), 3.69 (s, 3H), 3.46 (d, *J* = 16.8 Hz, 1H), 3.32 (dd, *J* = 16.3, 5.1 Hz, 1H), 3.22 (dd, *J* = 16.3, 5.6 Hz, 1H), 1.40 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 197.68, 170.08, 165.59, 137.69, 133.77, 132.15, 130.06, 129.11, 128.59, 126.80, 121.36, 119.15, 118.07, 108.95, 104.96, 83.01, 82.15, 48.17, 29.50, 28.09, 26.65, 22.66; ESI-HRMS *m/z* calcd for $C_{26}H_{27}NNaO_5S^+$ $[M + H]^+$ 456.1781, found 456.1799.




**5aa** **8**

To the solution of **5aa** (103 mg, 0.20 mmol) in anhydrous THF (2 mL) was added $LiAlH_4$ (23 mg, 0.60 mmol) at 0 °C. The mixture was warmed to room temperature and stirred for 1 hour. After completed, the reaction was quenched with $NH_4Cl$ (sat.) and extracted with ethyl acetate. The combined organic layer was washed with brine, dried with $Na_2SO_4$, filtered and concentrated. The residual was purified by silica gel column chromatography (PE : EtOAc = 1 : 2 to 1 : 3) to give the desired product **8** in 98% yield.

5-methyl-2-tosyl-2,3,3a,4,5,10-hexahydropyrrolo[3,4-*b*]carbazol-10a(1*H*)-ol (**8**): yellow solid, m.p. 168 – 169 °C; 78 mg, 98% yield; 1H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.9 Hz, 2H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.25 – 7.21 (m, 3H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.06 (t, *J* = 7.4 Hz, 1H), 5.40 (s, 1H), 4.00 – 3.90 (m, 1H), 3.74 – 3.65 (m, 1H), 3.59 (s, 3H), 3.27 (d, *J* = 12.9 Hz, 1H), 3.03 – 2.93 (m, 1H), 2.93 – 2.70 (m, 3H), 2.70 – 2.59 (m, 1H), 2.56 – 2.47 (m, 1H), 2.39 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 143.71, 137.65, 136.58, 132.98, 129.94, 127.15, 126.81, 121.25, 119.12, 117.90, 108.89, 73.62, 63.72, 48.35, 43.34, 32.58, 29.44, 22.57, 21.66 (one carbon missed); ESI-HRMS *m/z* calcd for $C_{22}H_{25}N_2O_3S^+$ $[M + H]^+$ 397.1580, found 397.1587.




**3nm** **9**

To the solution of **3nm** (108 mg, 0.20 mmol) in methanol (2 mL) was added $NaBH_4$ (7.6 mg, 0.20 mmol) at 0 °C. After 10 min, the mixture was warmed to room temperature and $K_2CO_3$ (28 mg, 0.20 mmol) was added. After 1 hour, the solvent was evaporated in vacuo and the residual was purified by silica gel column chromatography (PE : EtOAc = 4 : 1 to 3 : 1) to give the desired product **9** in 79% yield.

ethyl 9-methyl-2'-oxo-3'-tosyl-1,2,4,9-tetrahydrospiro[carbazole-3,5'-oxazolidine]-2-carboxylate (**9**): white solid, m.p. 70 – 71 °C; 76 mg, 79% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.91 (m, 2H), 7.37 (t, *J* = 7.7 Hz, 3H), 7.28 – 7.25 (m, 1H), 7.23 – 7.18 (m, 1H), 7.13 – 7.07 (m, 1H), 4.40 (d, *J* = 9.5 Hz, 1H), 4.06 (q, *J* = 7.2 Hz, 2H), 3.88 – 3.81 (m, 1H), 3.62 (s, 3H), 3.30 (dd, *J* = 8.7, 6.0 Hz, 1H), 3.26 – 3.07 (m, 4H), 2.46 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.79, 150.91, 145.72, 137.83, 134.26, 131.39, 129.91, 128.49, 126.39, 121.92, 119.58, 117.92, 109.12, 104.28, 80.00, 61.78, 51.87, 46.39, 33.70, 29.54, 23.36, 21.85, 14.08; ESI-HRMS *m/z* calcd for $C_{25}H_{27}N_2O_6S^+$ $[M + H]^+$ 483.1584, found 483.1600.

## 7 References


1. (a) A. Maehara, H. Tsurugi, T. Satoh and M. Miura, *Org. Lett.*, 2008, **10**, 1159-1162; (b) Y. J. Wang, C. H. Yuan, D. Z. Chu and L. Jiao, *Chem. Sci.*, 2020, **11**, 11042-11054.
2. (a) S. Yu, Y. An, W. Wang, Z.-F. Xu and C.-Y. Li, *Adv. Synth. Catal.*, 2018, **360**, 2125-2130; (b) Z.-F. Xu, Y. An, Y. Chen and S. Duan, *Tetrahedron Lett.*, 2019, **60**, 1849-1853; (c) S. Duan, W. Zhang, Y. Hu, Z.-F. Xu and C.-Y. Li, *Adv. Synth. Catal.*, 2020, **362**, 3570-3575.

## 8 Copies of NMR spectra

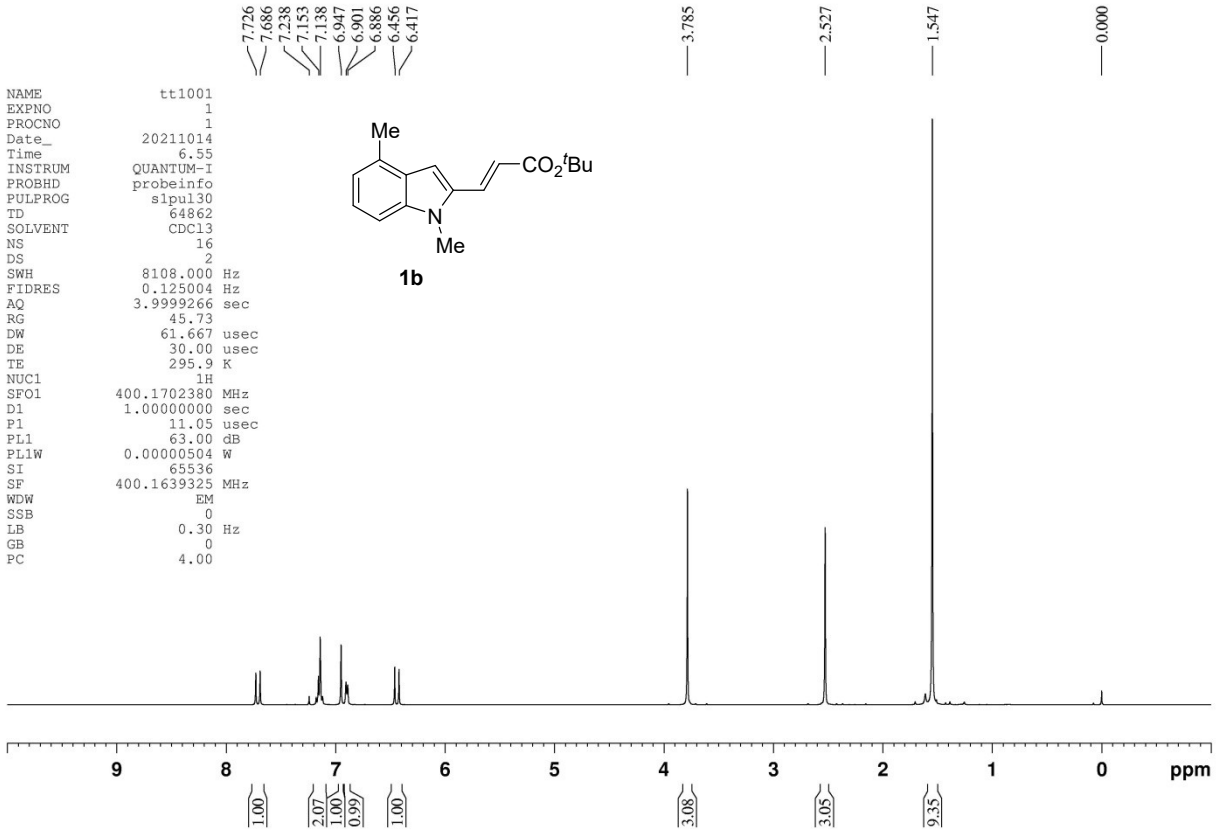



**Figure S8-1. $^{1}$H NMR of 1b ($CDCl_3$, 400 MHz)**

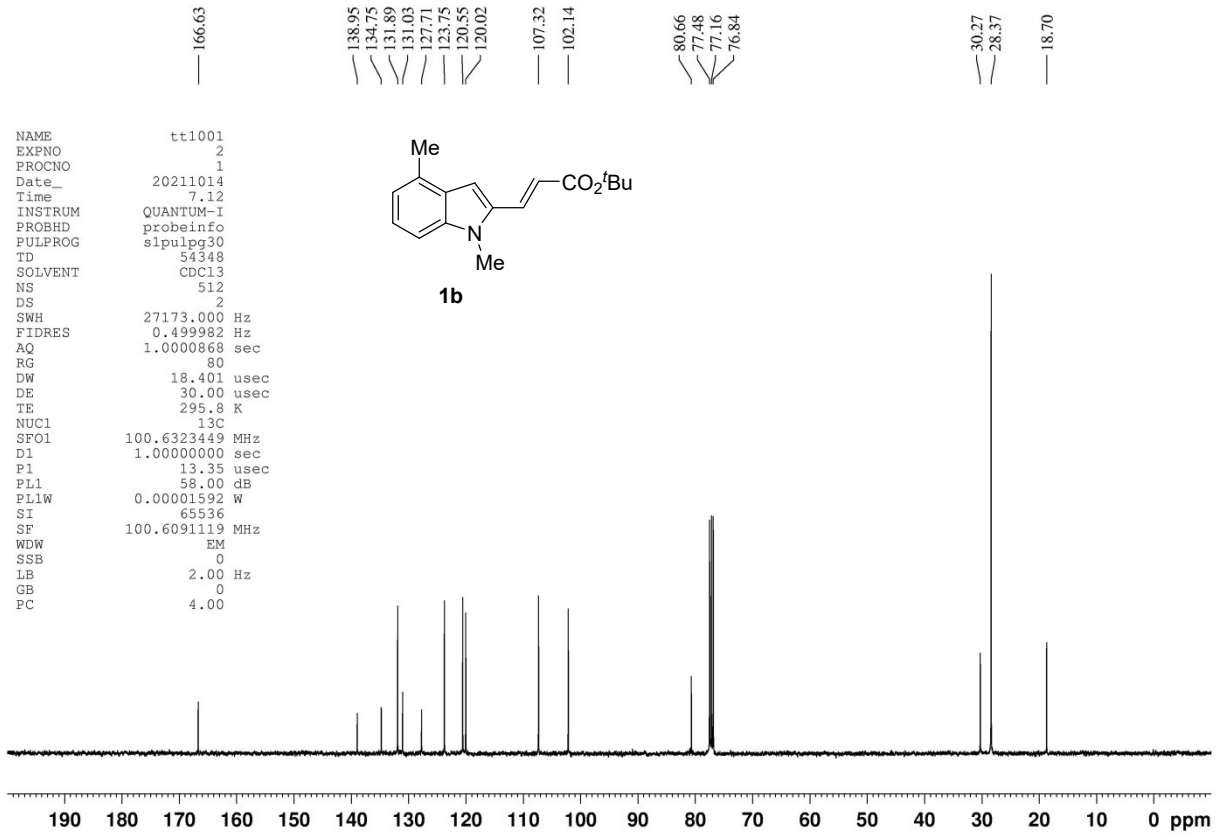



**Figure S8-2. $^{13}$C NMR of 1b ($CDCl_3$, 101 MHz)**

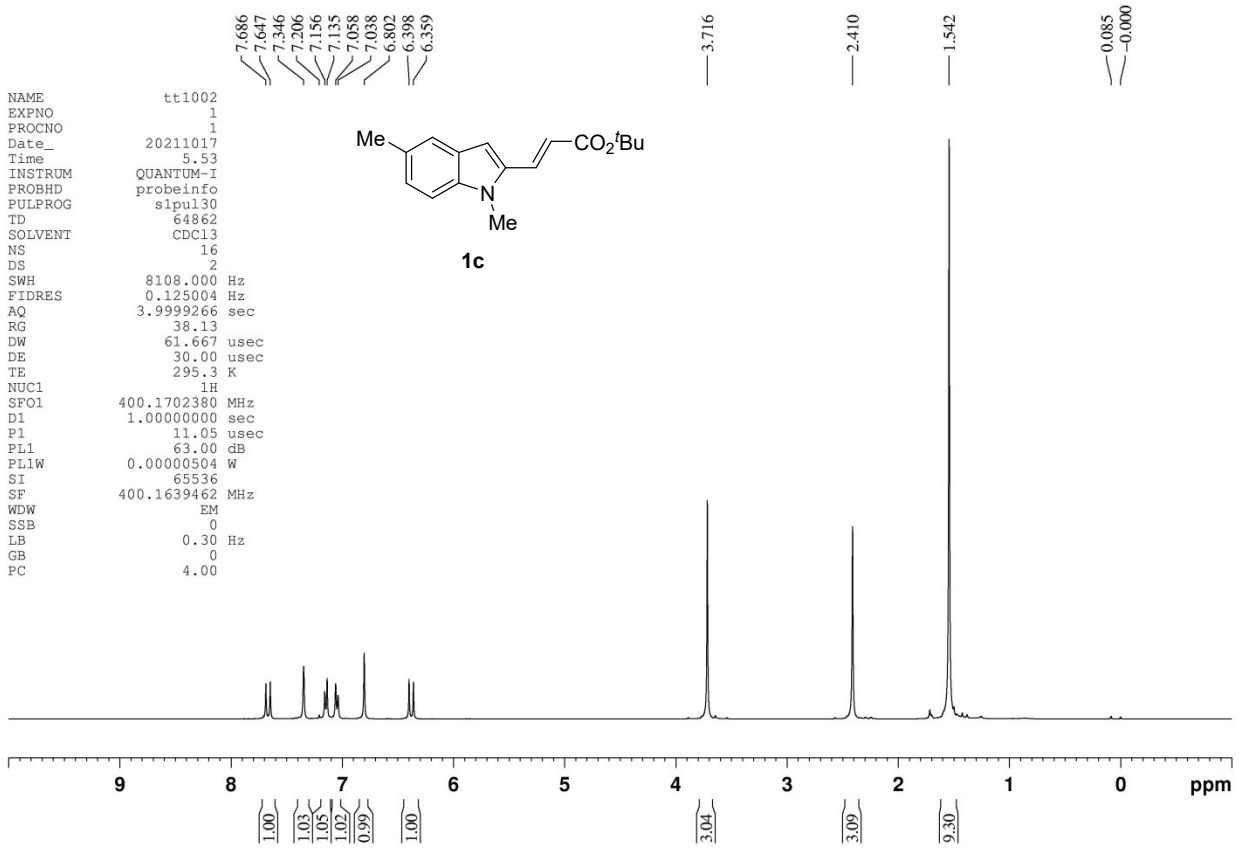



**Figure S8-3. $^{1}$H NMR of 1c ($CDCl_3$, 400 MHz)**

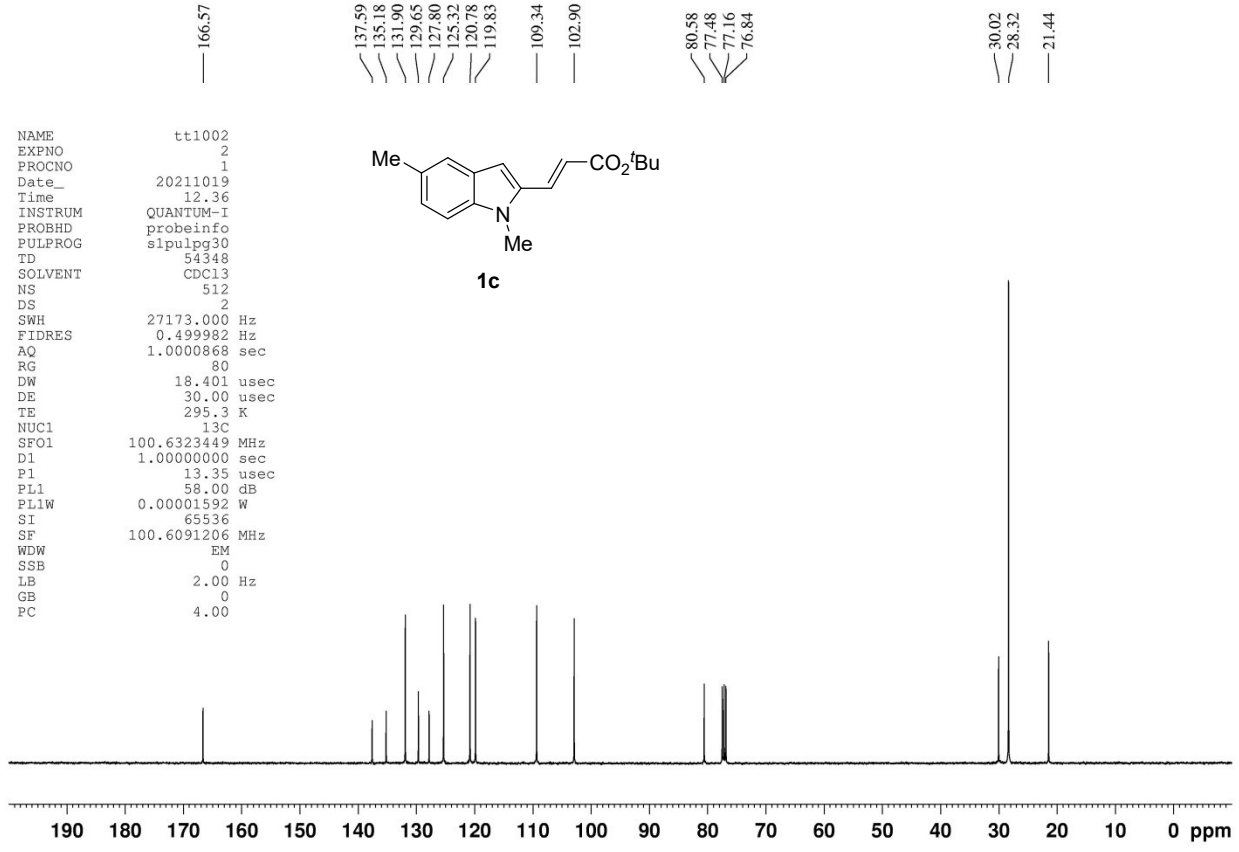



**Figure S8-4. $^{13}$C NMR of 1c ($CDCl_3$, 101 MHz)**

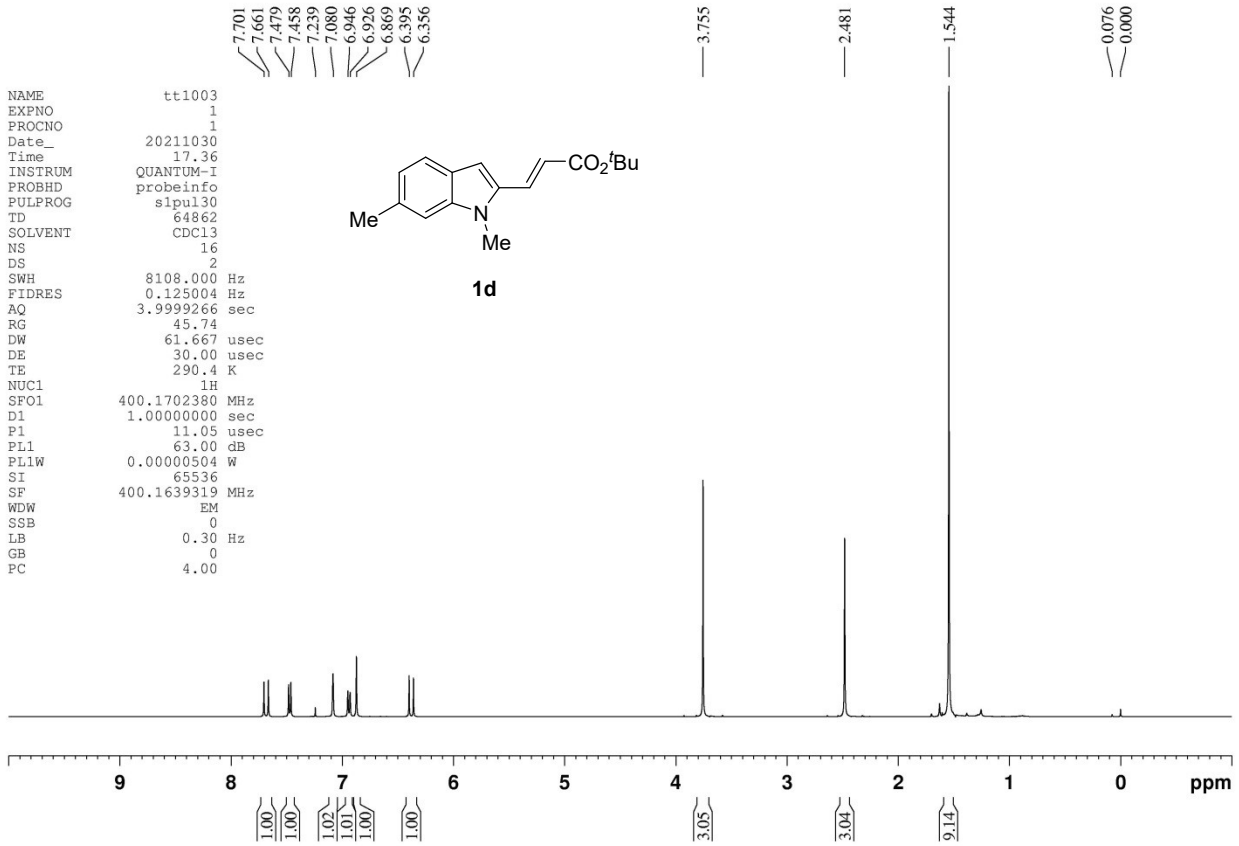



**Figure S8-5. $^{1}$H NMR of 1d ($CDCl_3$, 400 MHz)**

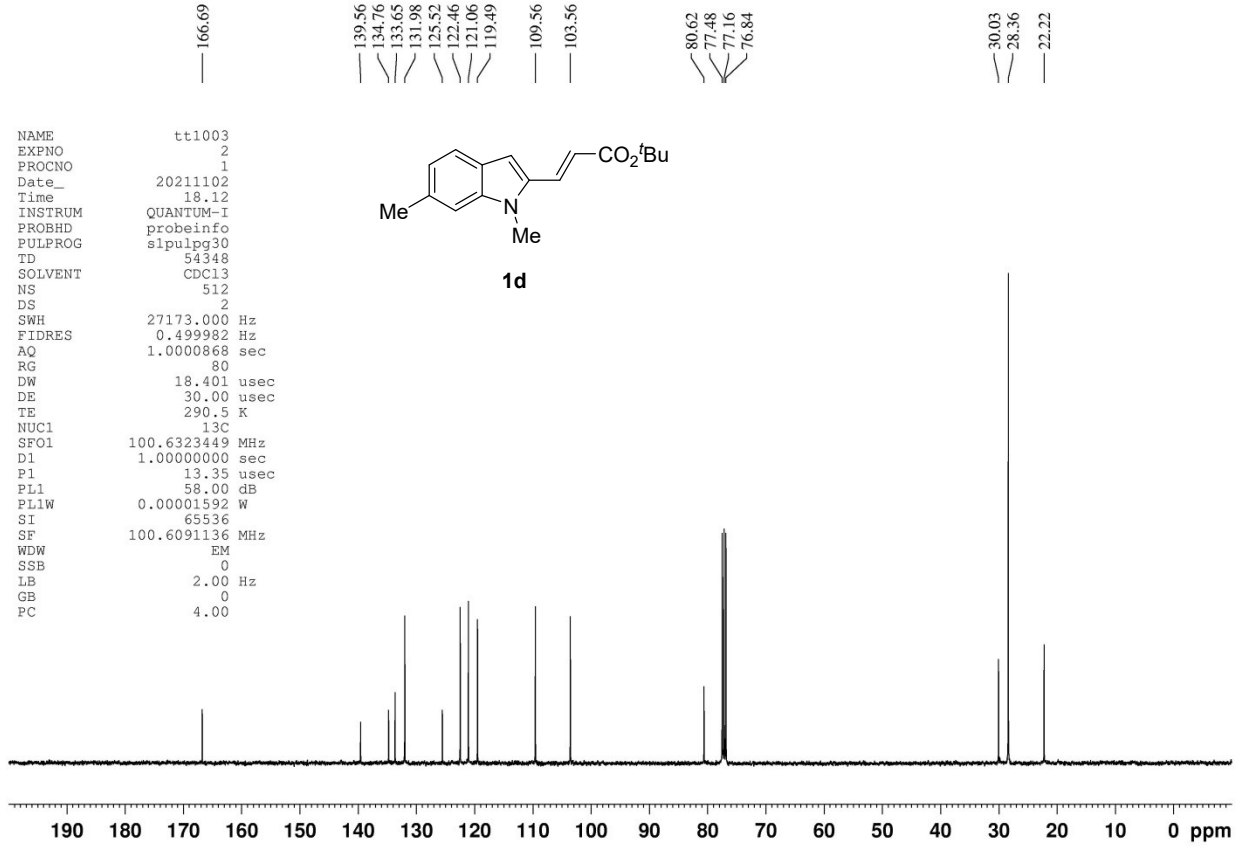



**Figure S8-6. $^{13}$C NMR of 1d ($CDCl_3$, 101 MHz)**

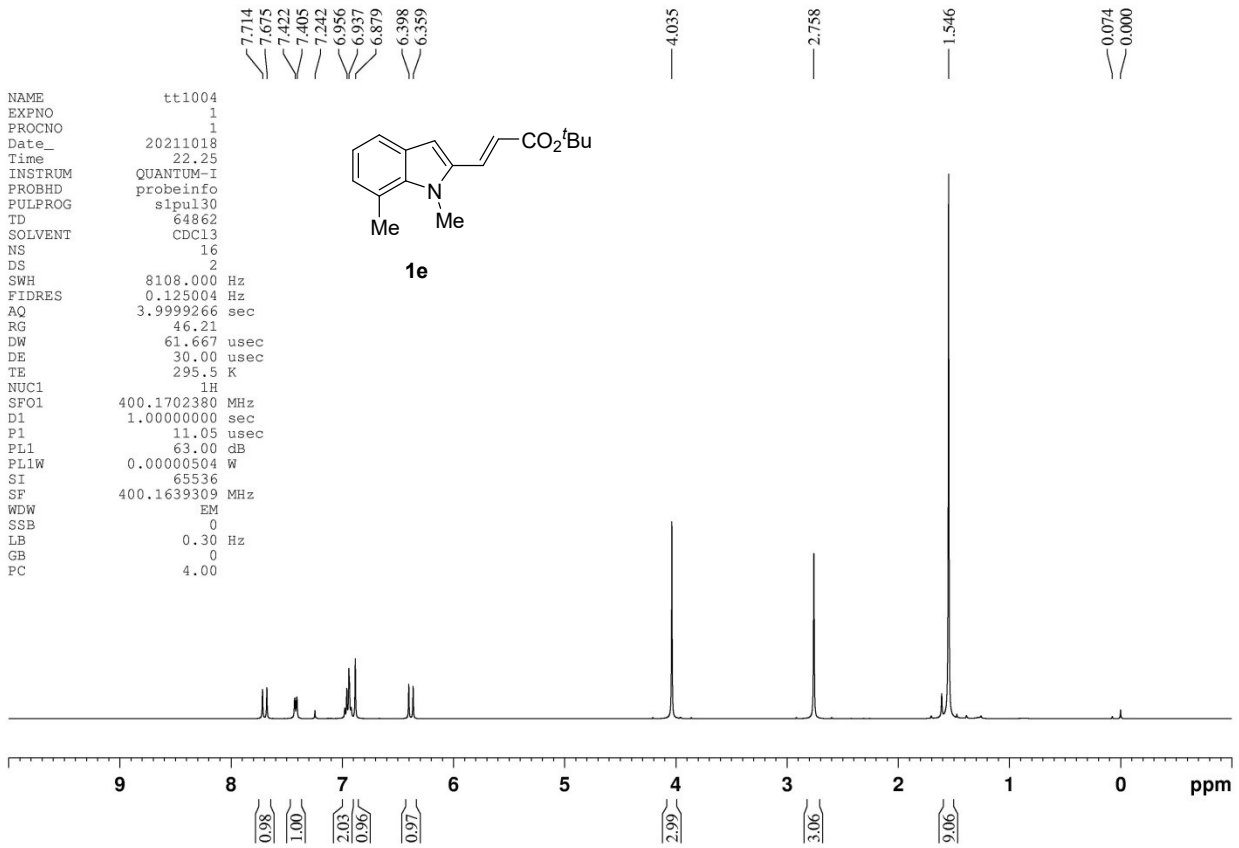



**Figure S8-7. $^{1}$H NMR of 1e ($CDCl_3$, 400 MHz)**

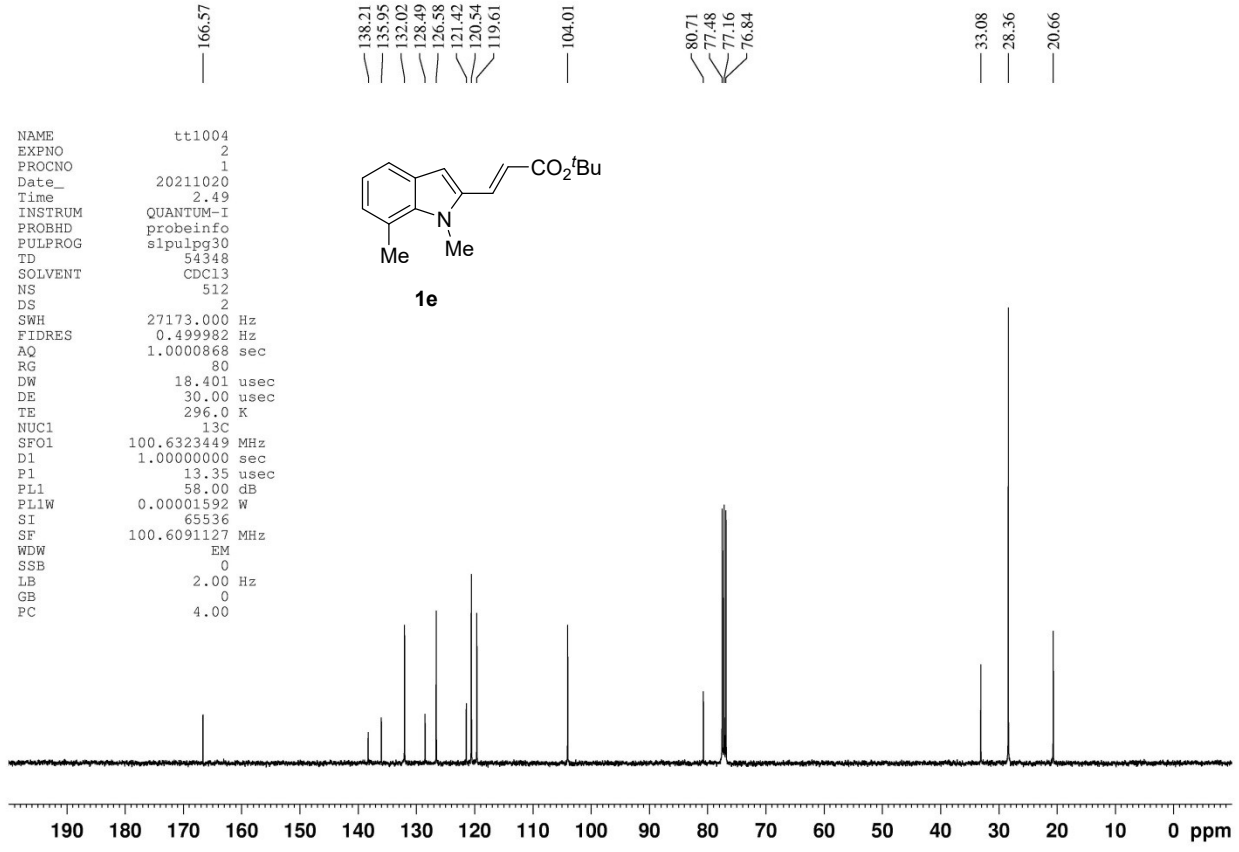



**Figure S8-8. $^{13}$C NMR of 1e ($CDCl_3$, 101 MHz)**

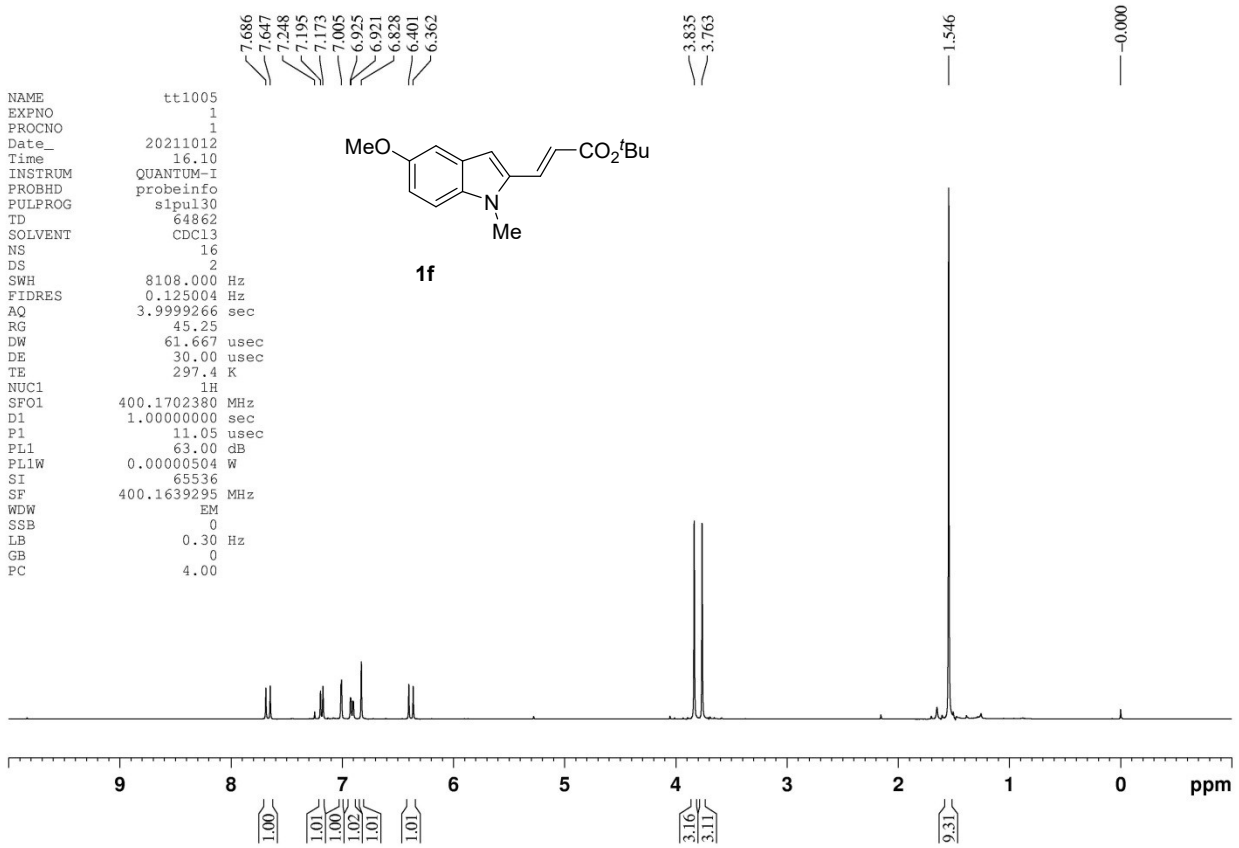



**Figure S8-9. $^{1}$H NMR of 1f ($CDCl_3$, 400 MHz)**

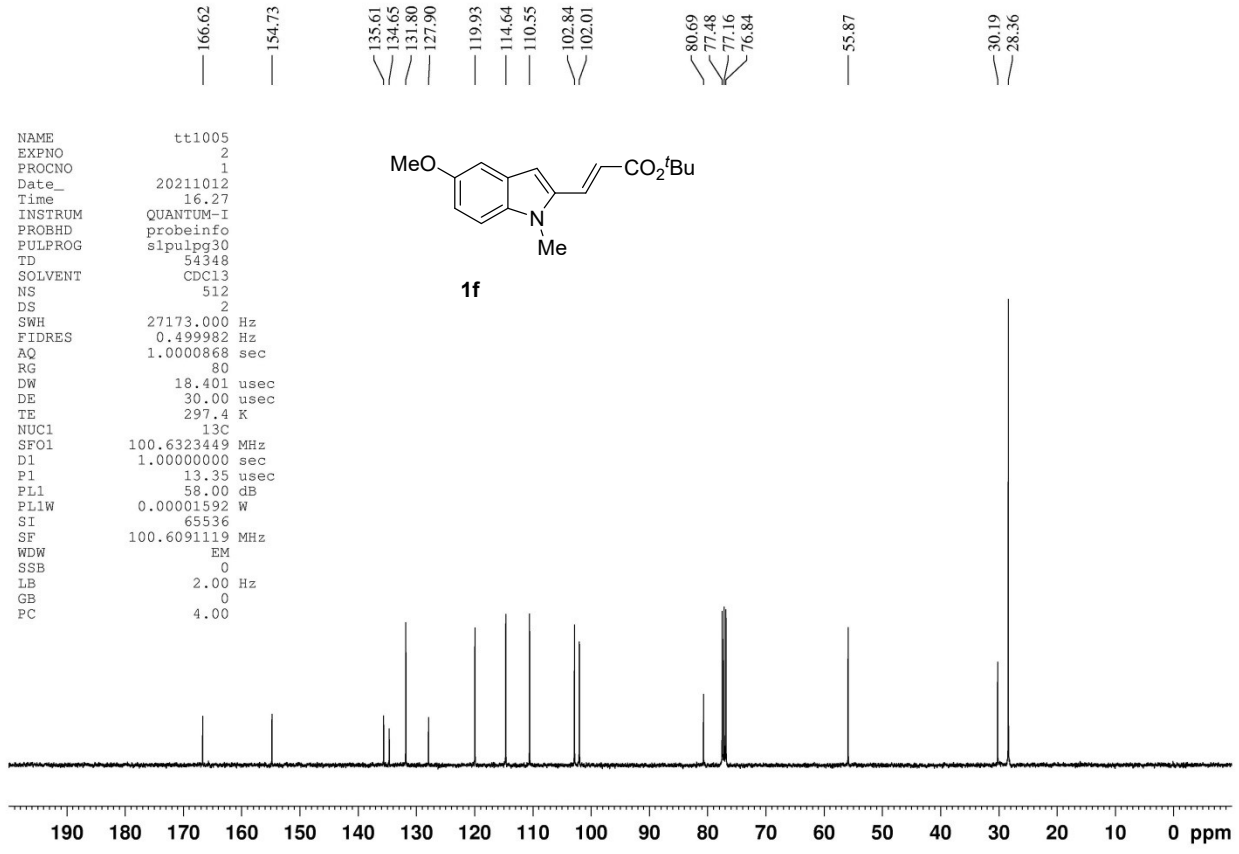



**Figure S8-10. $^{13}$C NMR of 1f ($CDCl_3$, 101 MHz)**

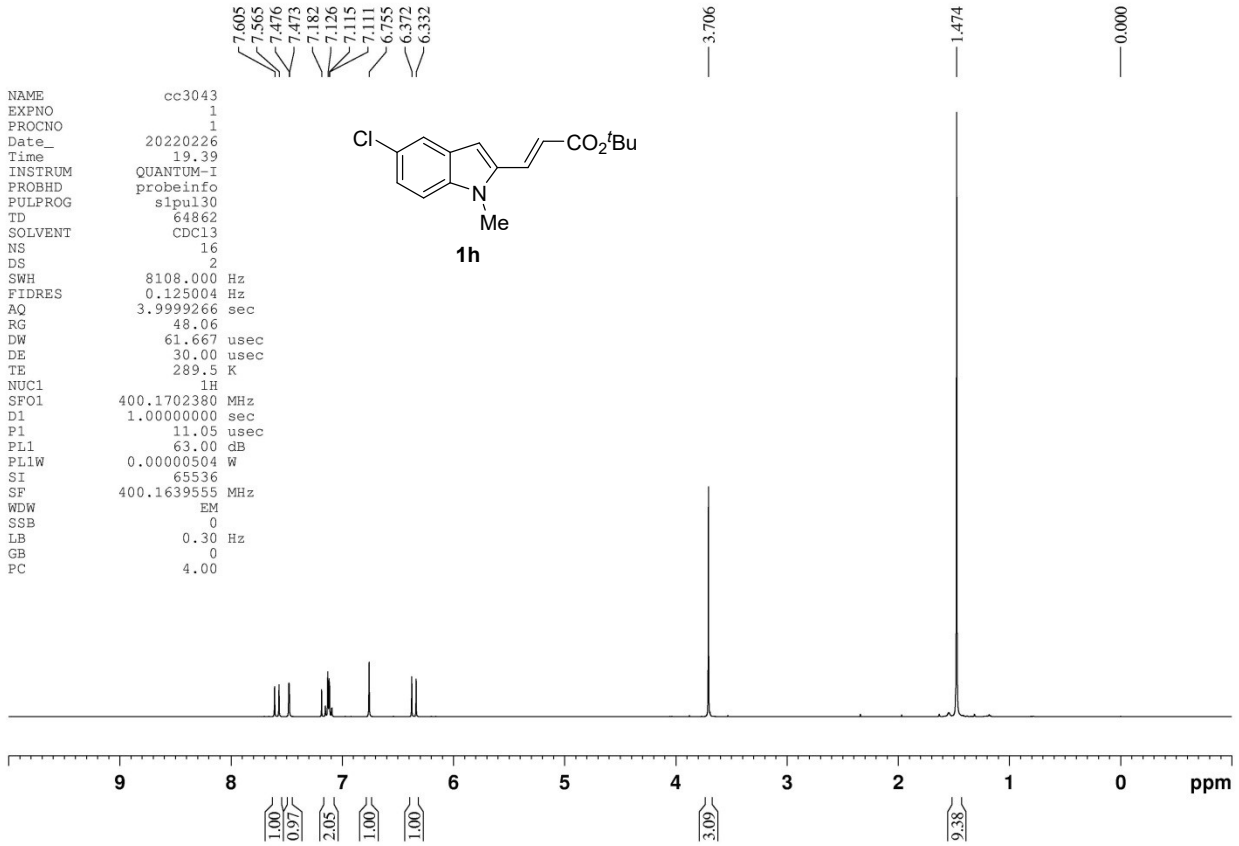



**Figure S8-11. $^{1}$H NMR of 1h ($CDCl_3$, 400 MHz)**

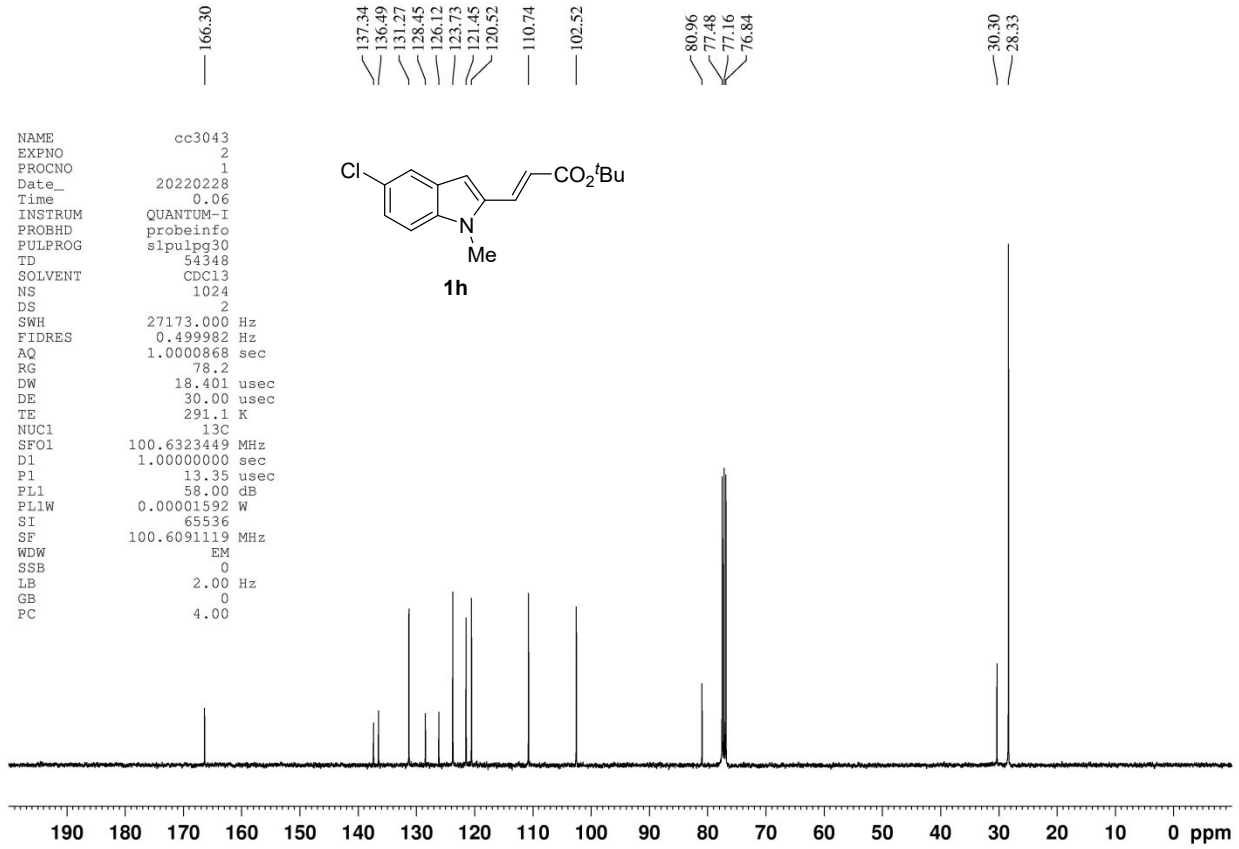



**Figure S8-12. $^{13}$C NMR of 1h ($CDCl_3$, 101 MHz)**

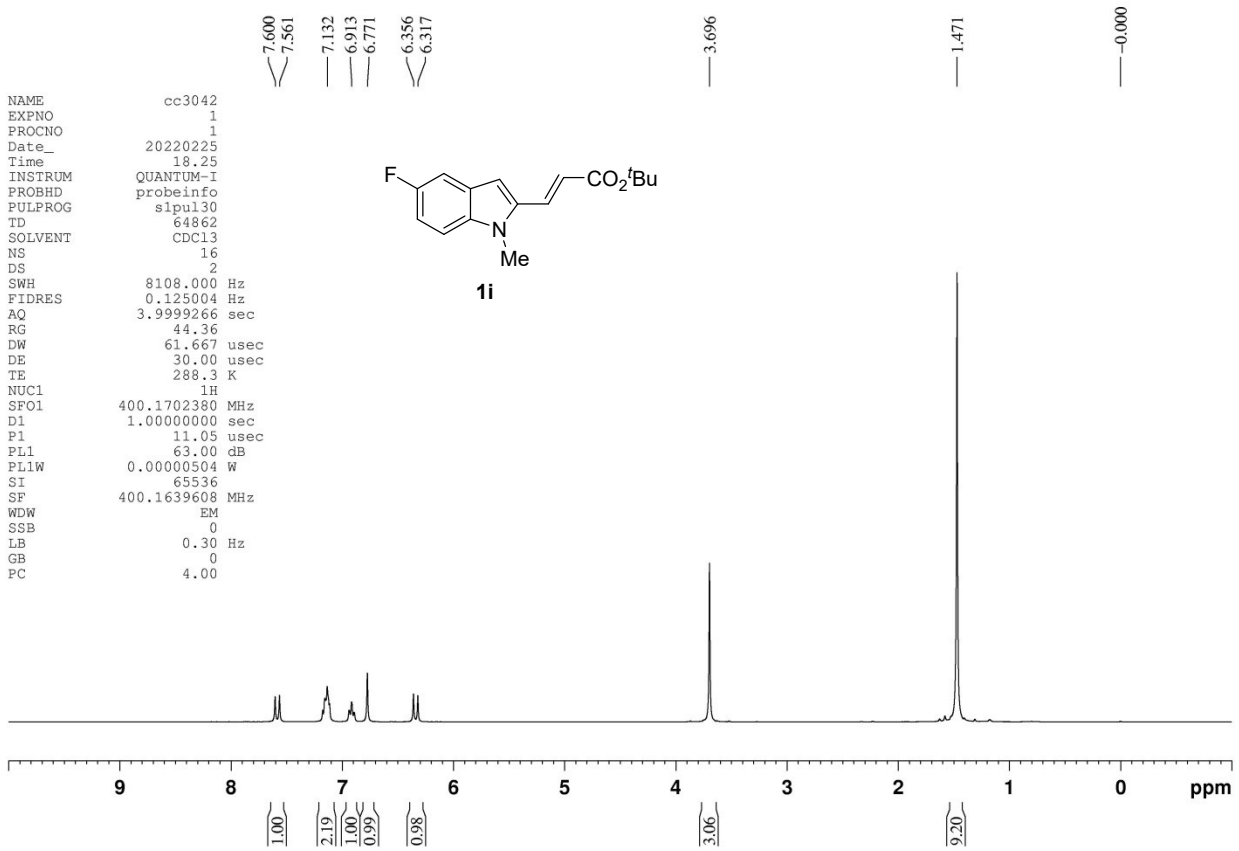



**Figure S8-13. $^{1}$H NMR of 1i ($CDCl_3$, 400 MHz)**

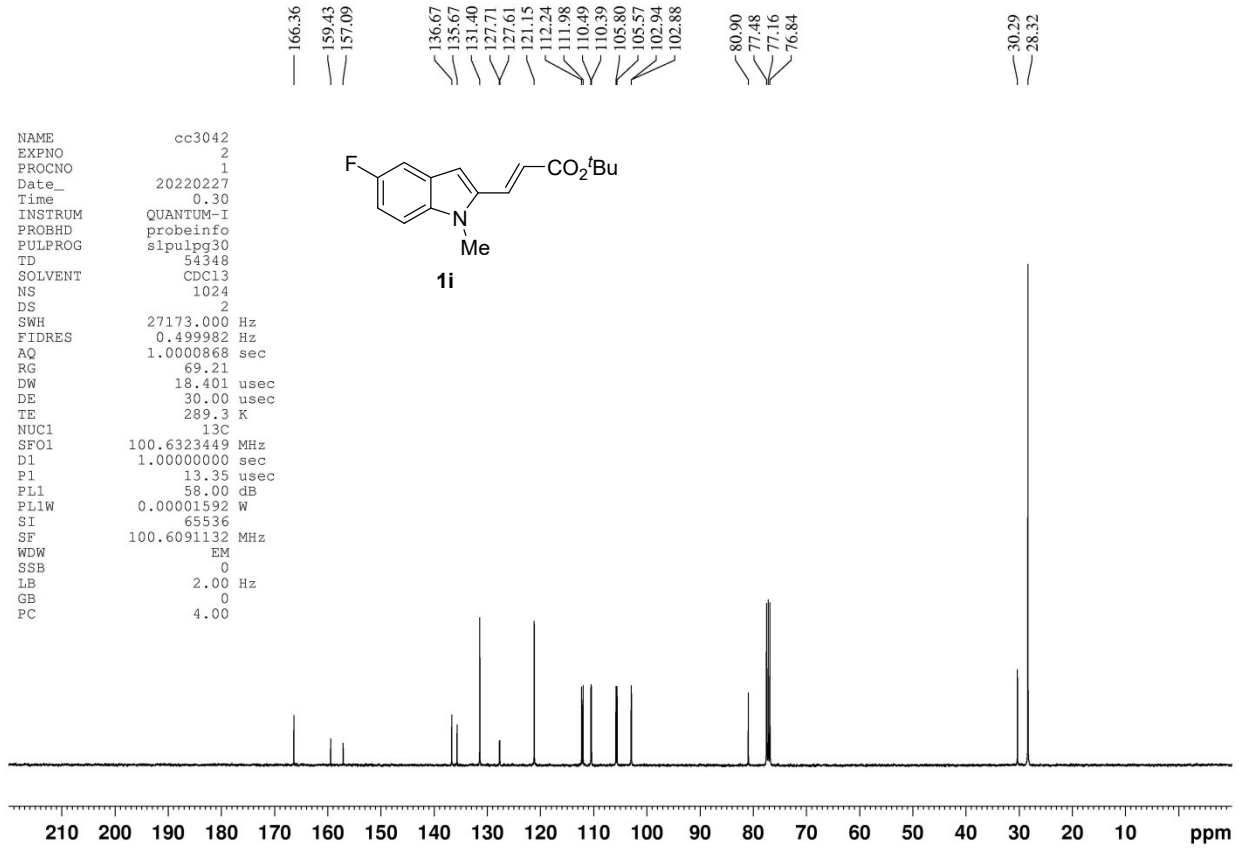



**Figure S8-14. $^{13}$C NMR of 1i ($CDCl_3$, 101 MHz)**

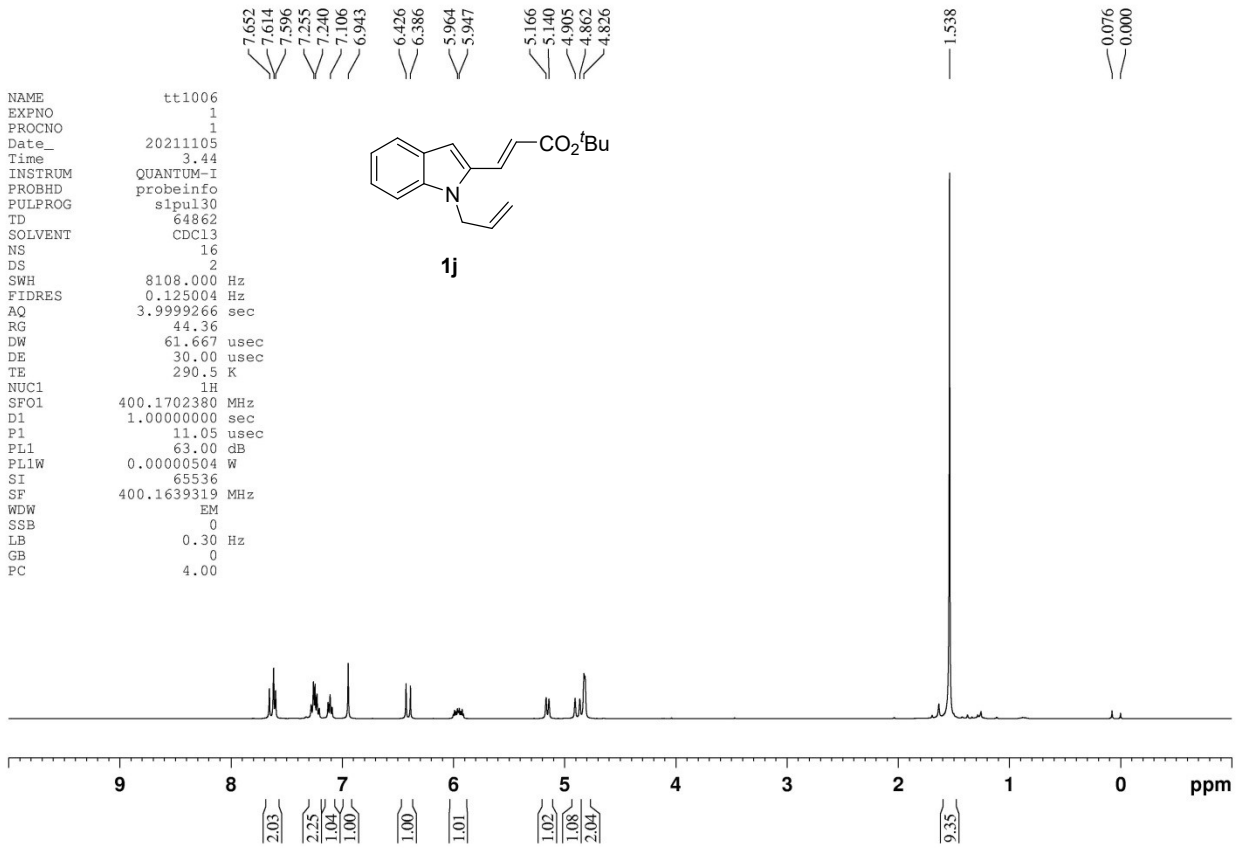



**Figure S8-15. $^{1}$H NMR of 1j ($CDCl_3$, 400 MHz)**

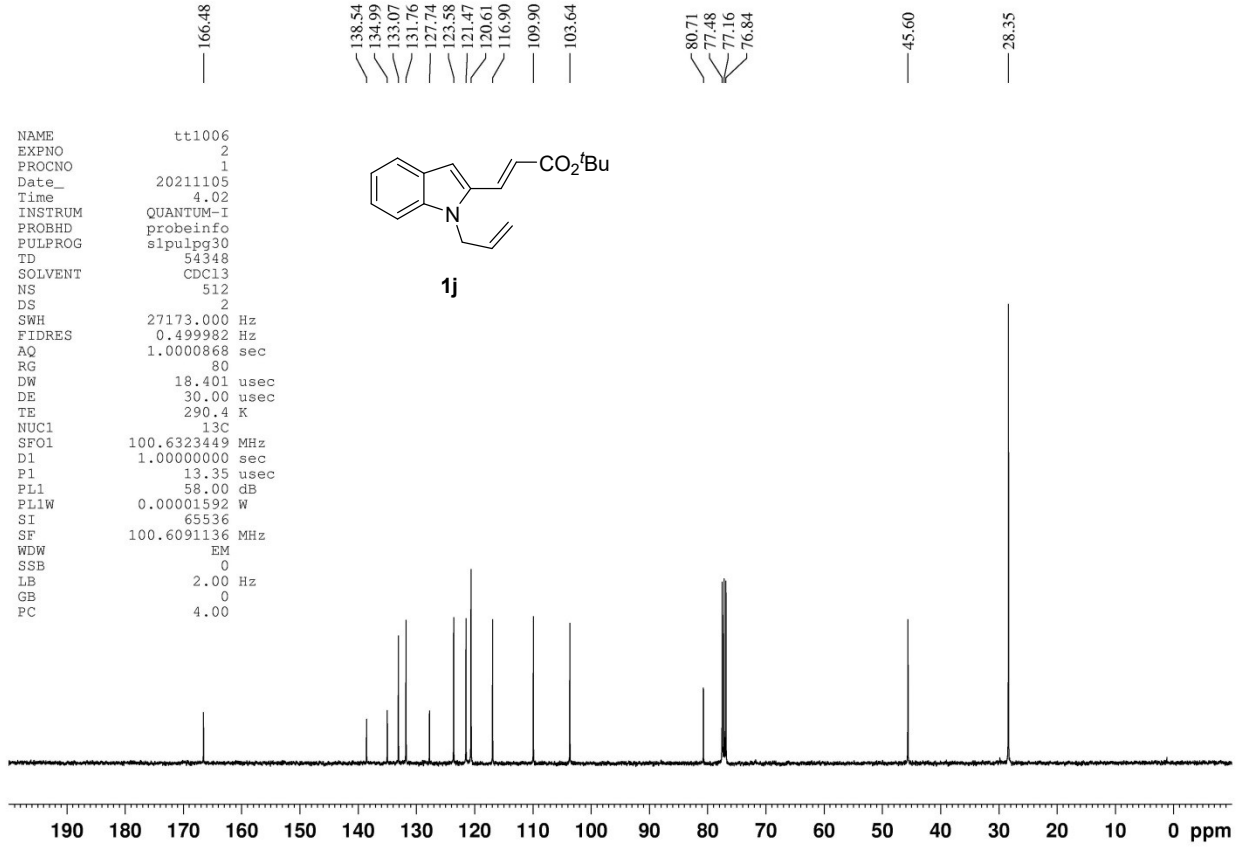



**Figure S8-16. $^{13}$C NMR of 1j ($CDCl_3$, 101 MHz)**

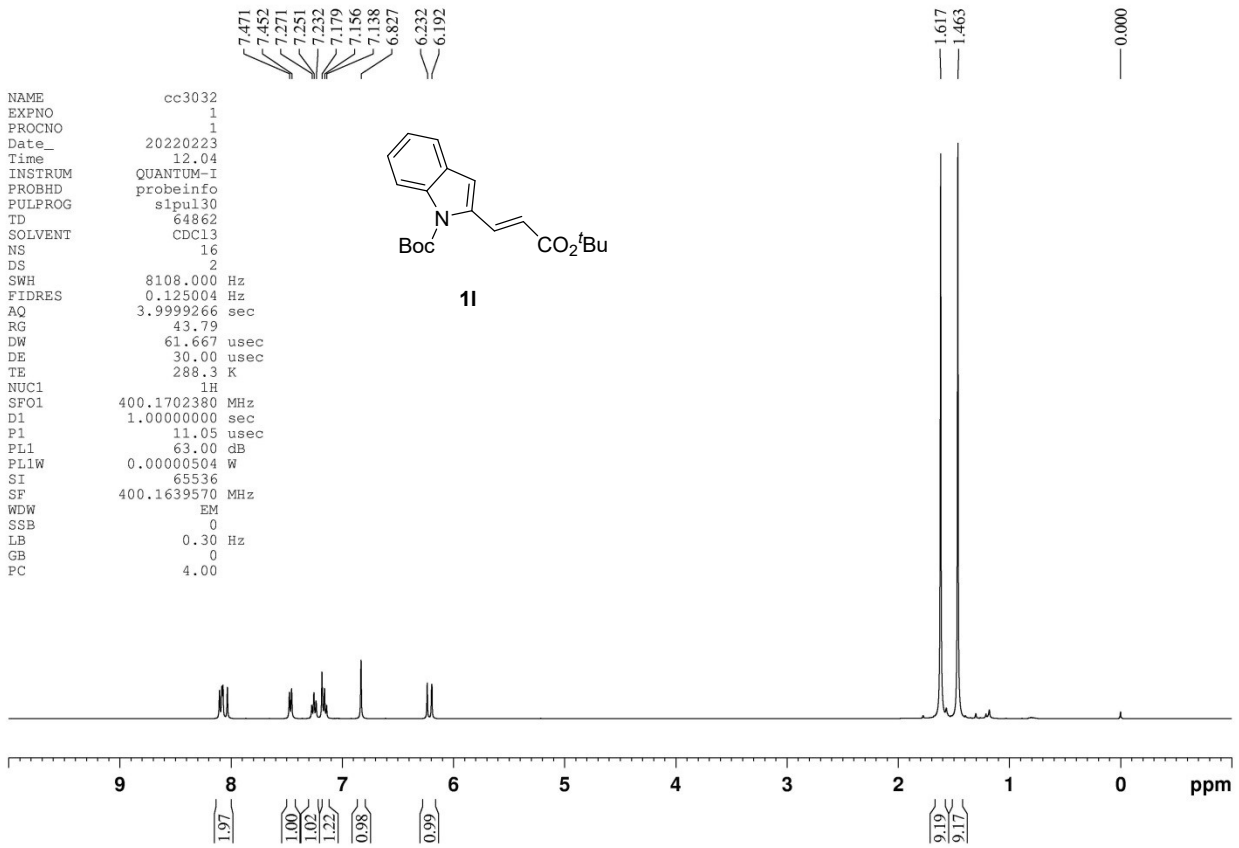



**Figure S8-17. $^{1}$H NMR of 1l ($CDCl_3$, 400 MHz)**

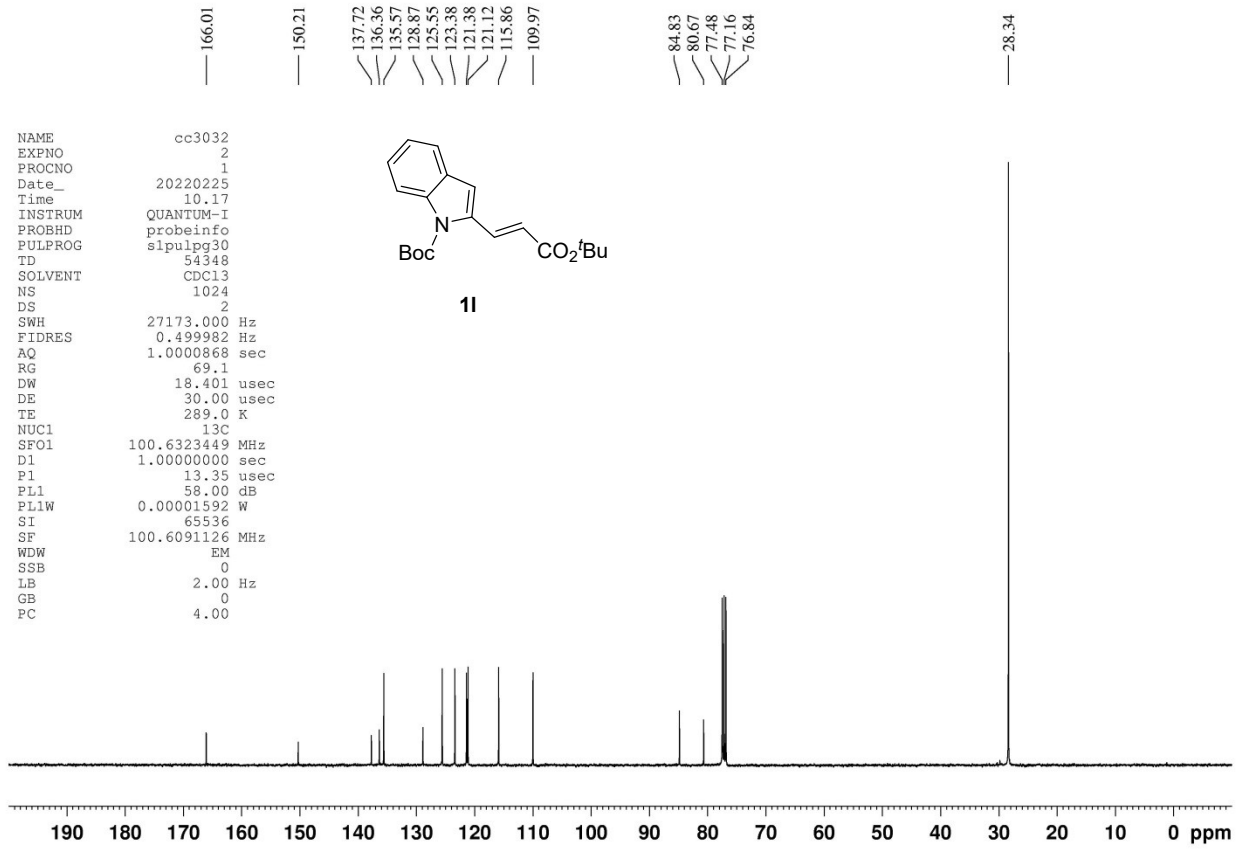



**Figure S8-18. $^{13}$C NMR of 1l ($CDCl_3$, 101 MHz)**

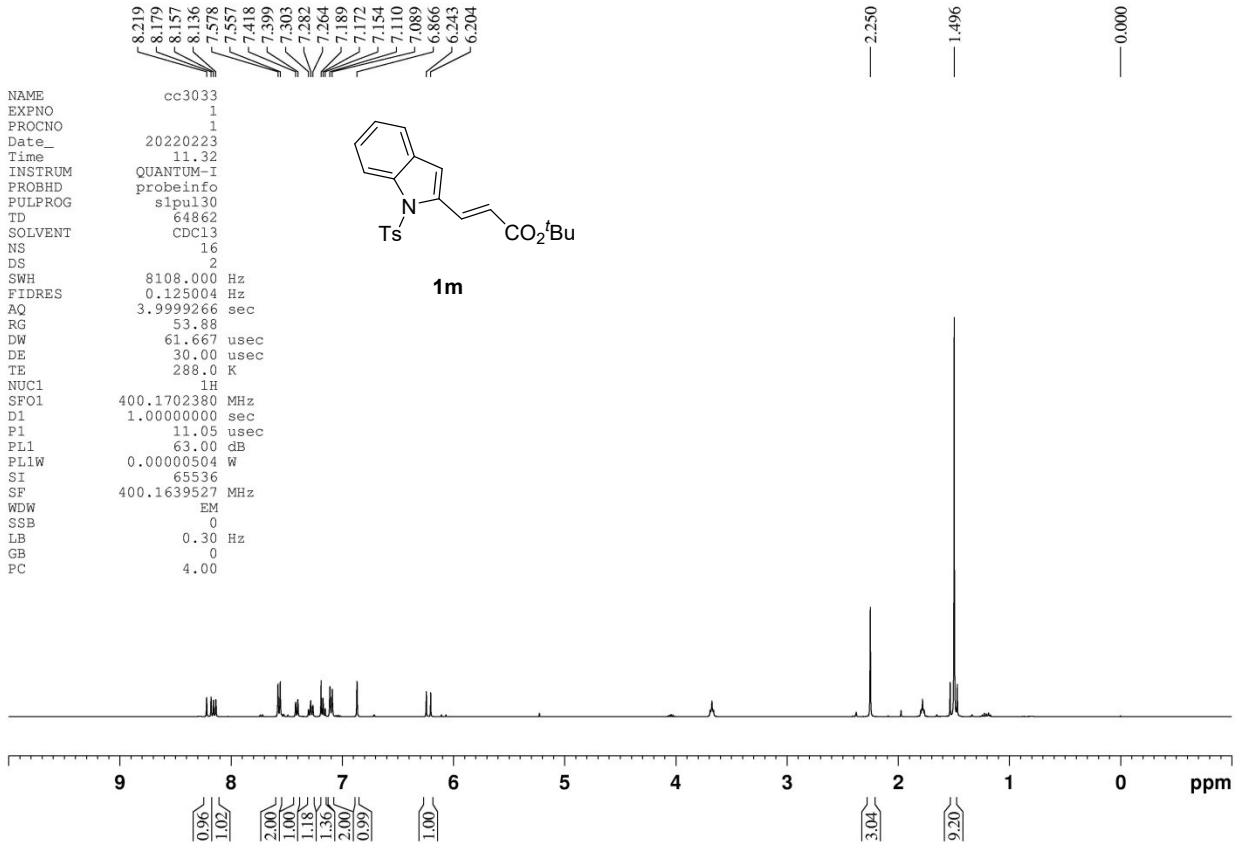



**Figure S8-19. $^{1}$H NMR of 1m ($CDCl_3$, 400 MHz)**

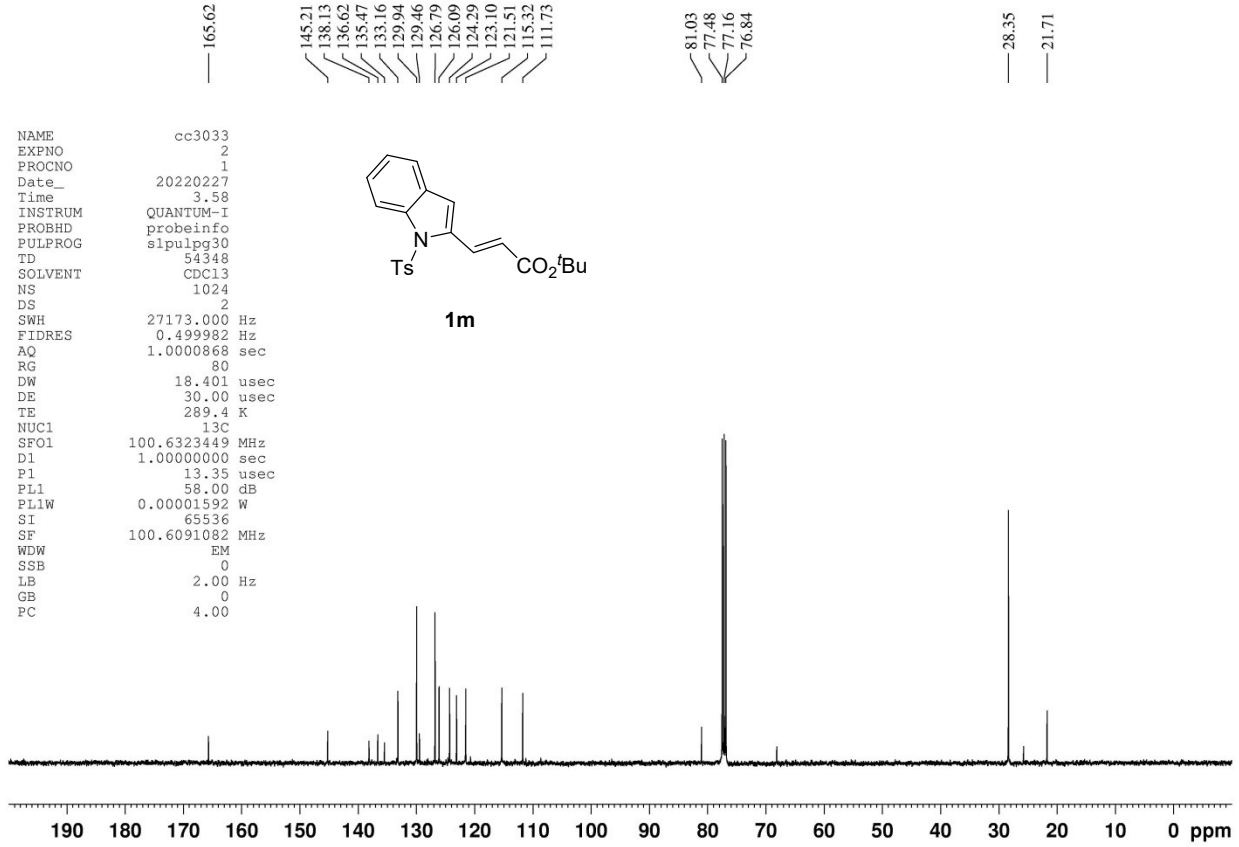



**Figure S8-20. $^{13}$C NMR of 1m ($CDCl_3$, 101 MHz)**

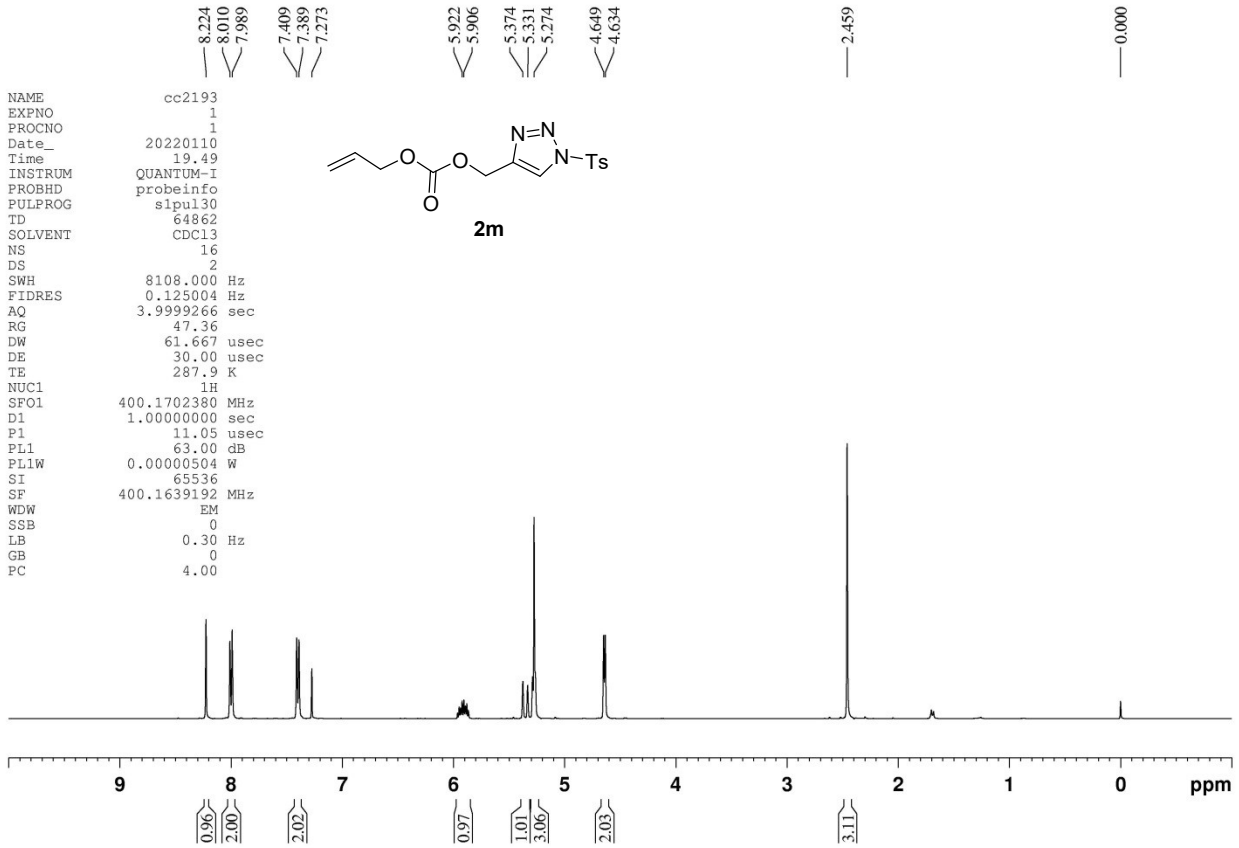



**Figure S8-21. $^{1}$H NMR of 2m ($CDCl_3$, 400 MHz)**

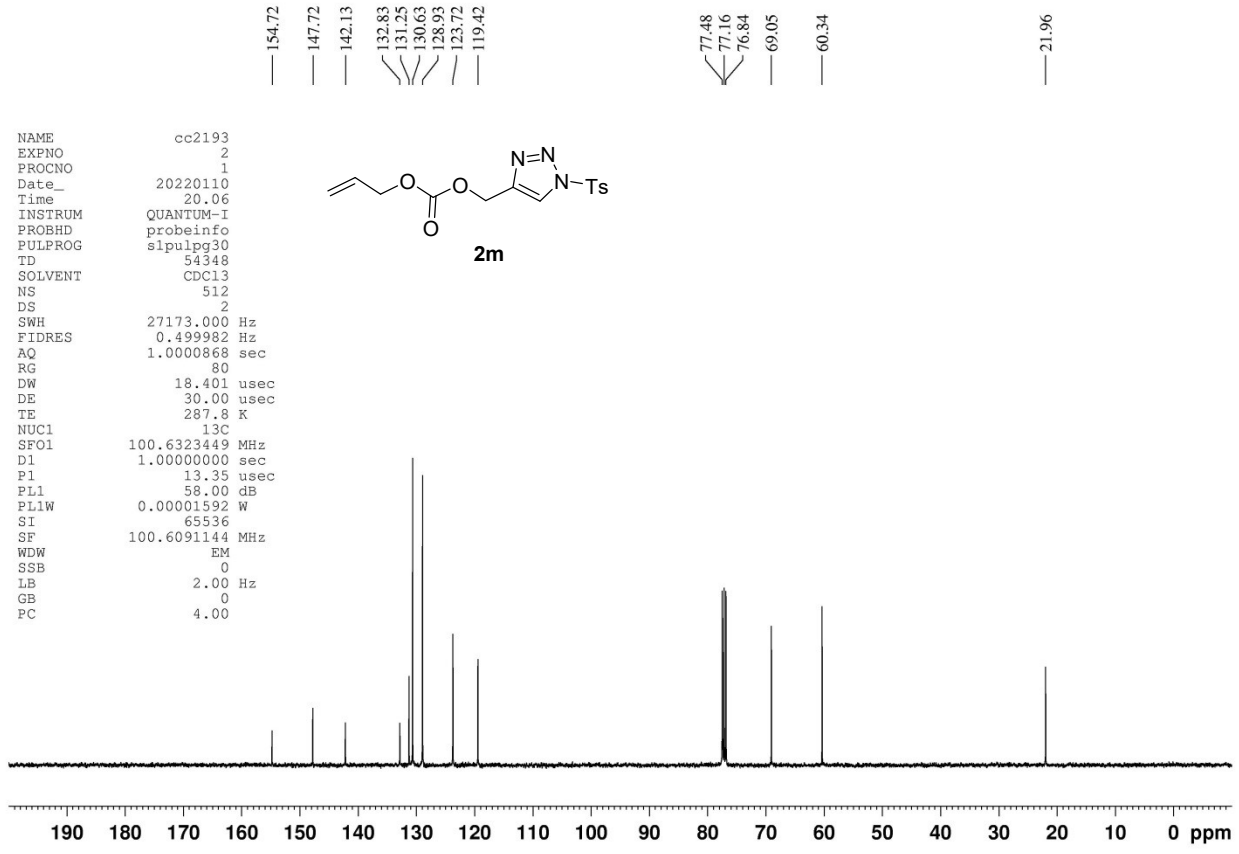



**Figure S8-22. $^{13}$C NMR of 2m ($CDCl_3$, 101 MHz)**

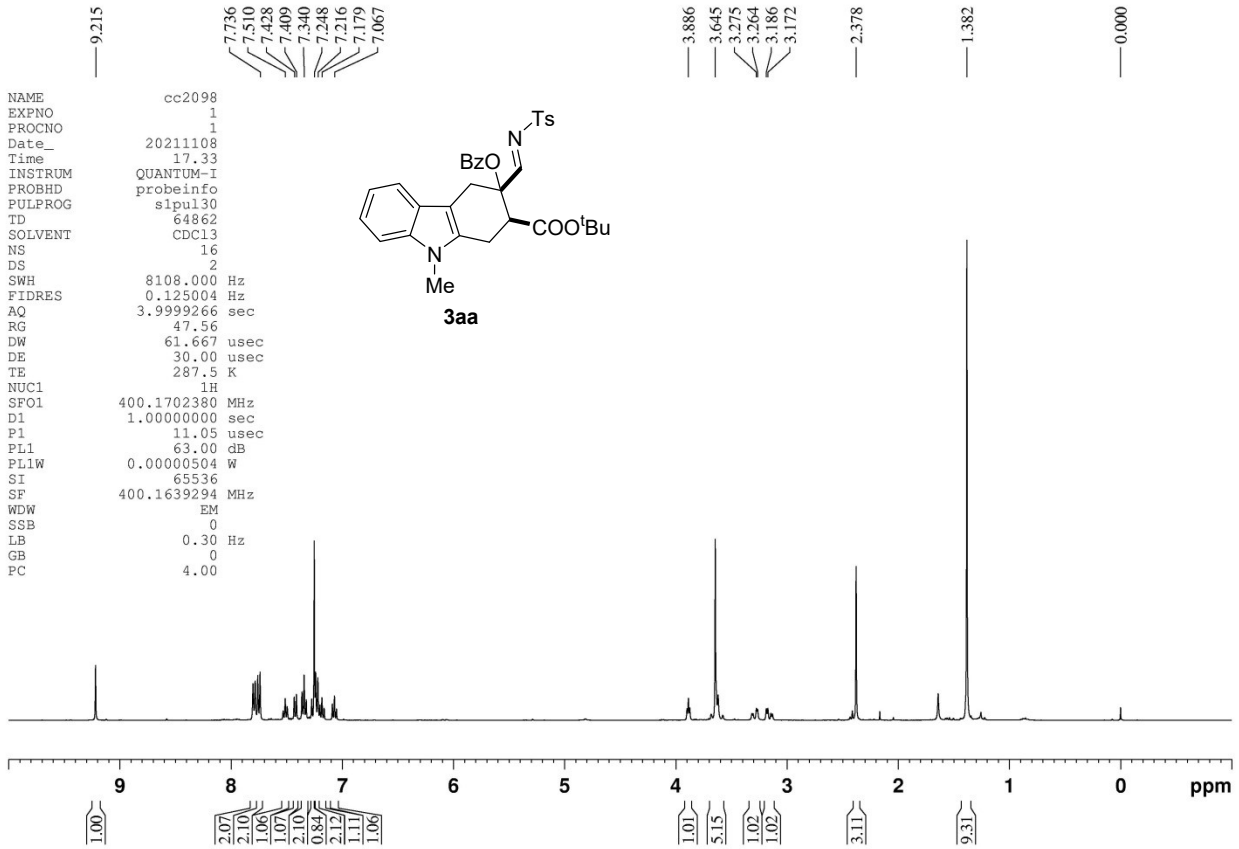



**Figure S8-23. $^{1}$H NMR of 3aa ($CDCl_3$, 400 MHz)**

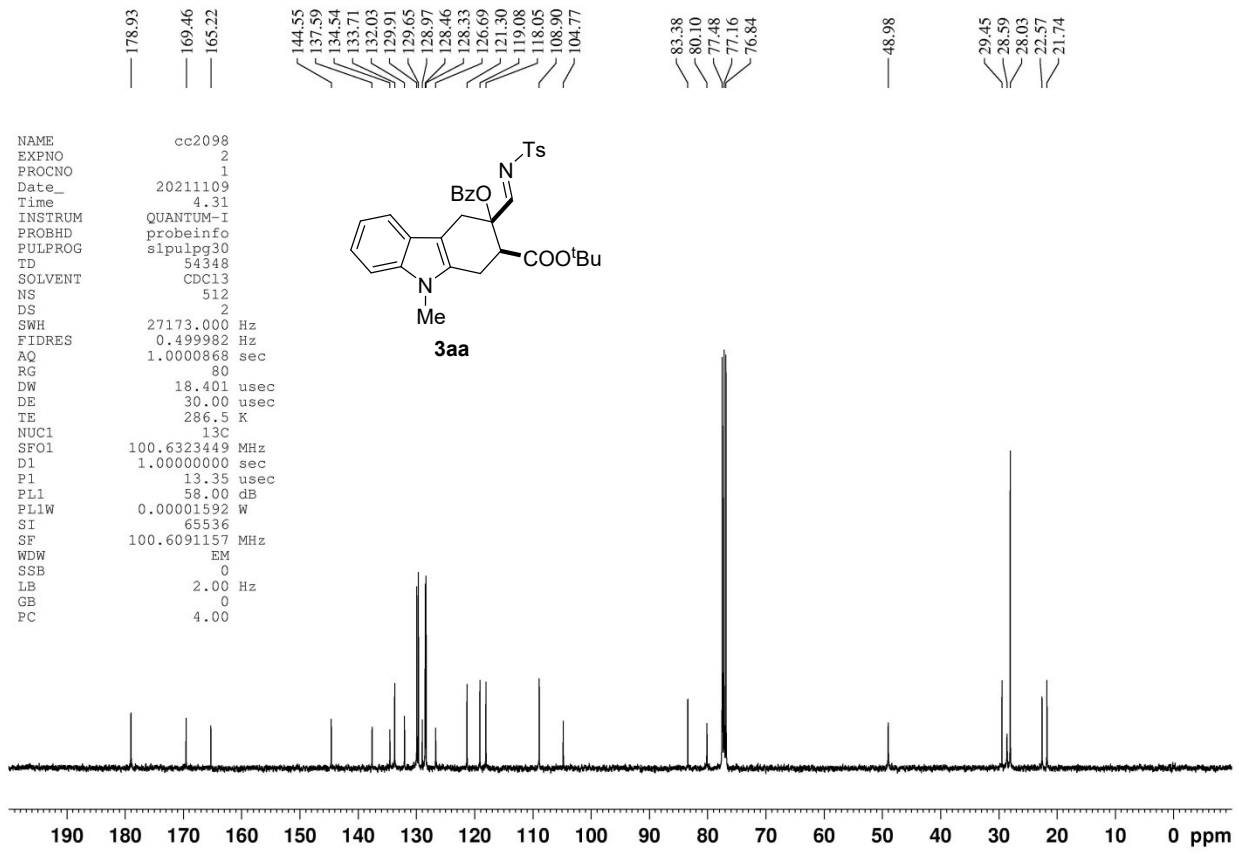



**Figure S8-24. $^{13}$C NMR of 3aa ($CDCl_3$, 101 MHz)**

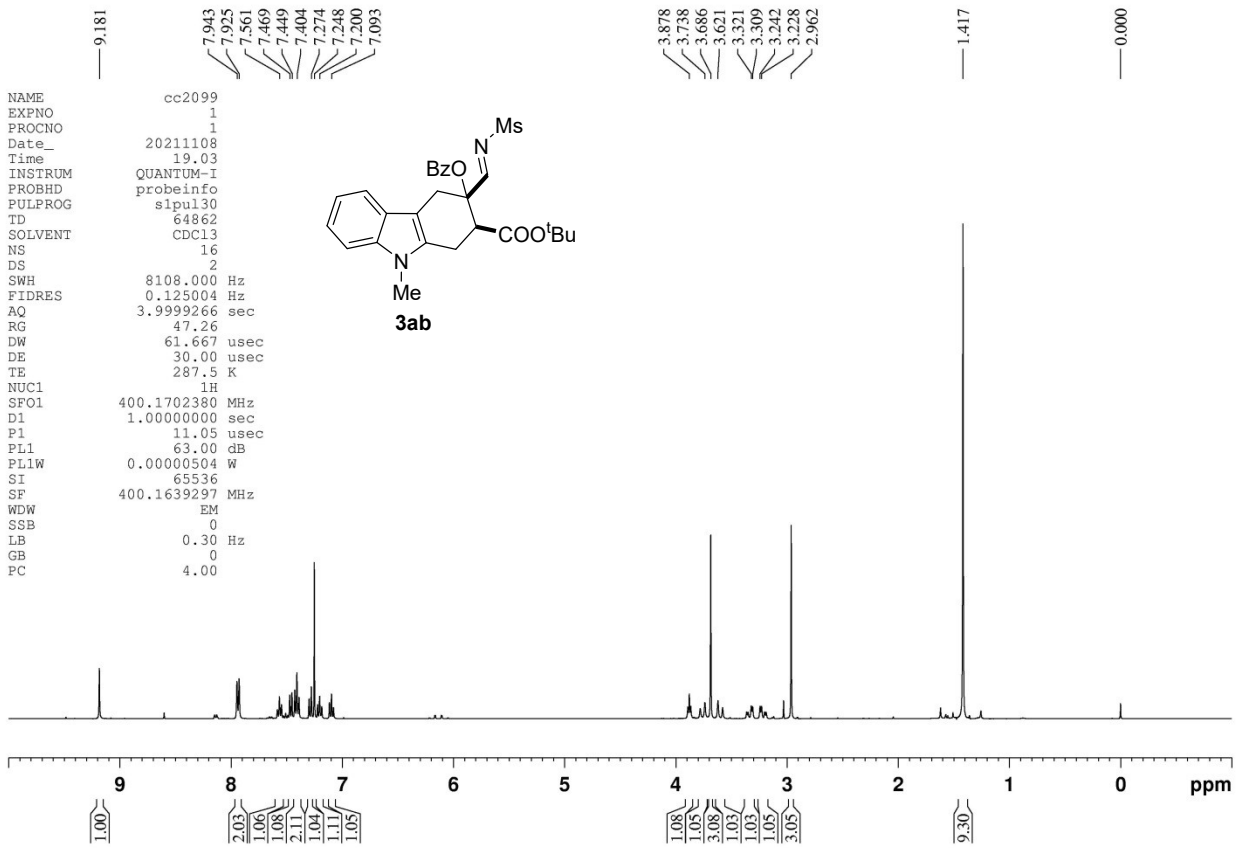



**Figure S8-25. $^{1}$H NMR of 3ab ($CDCl_3$, 400 MHz)**

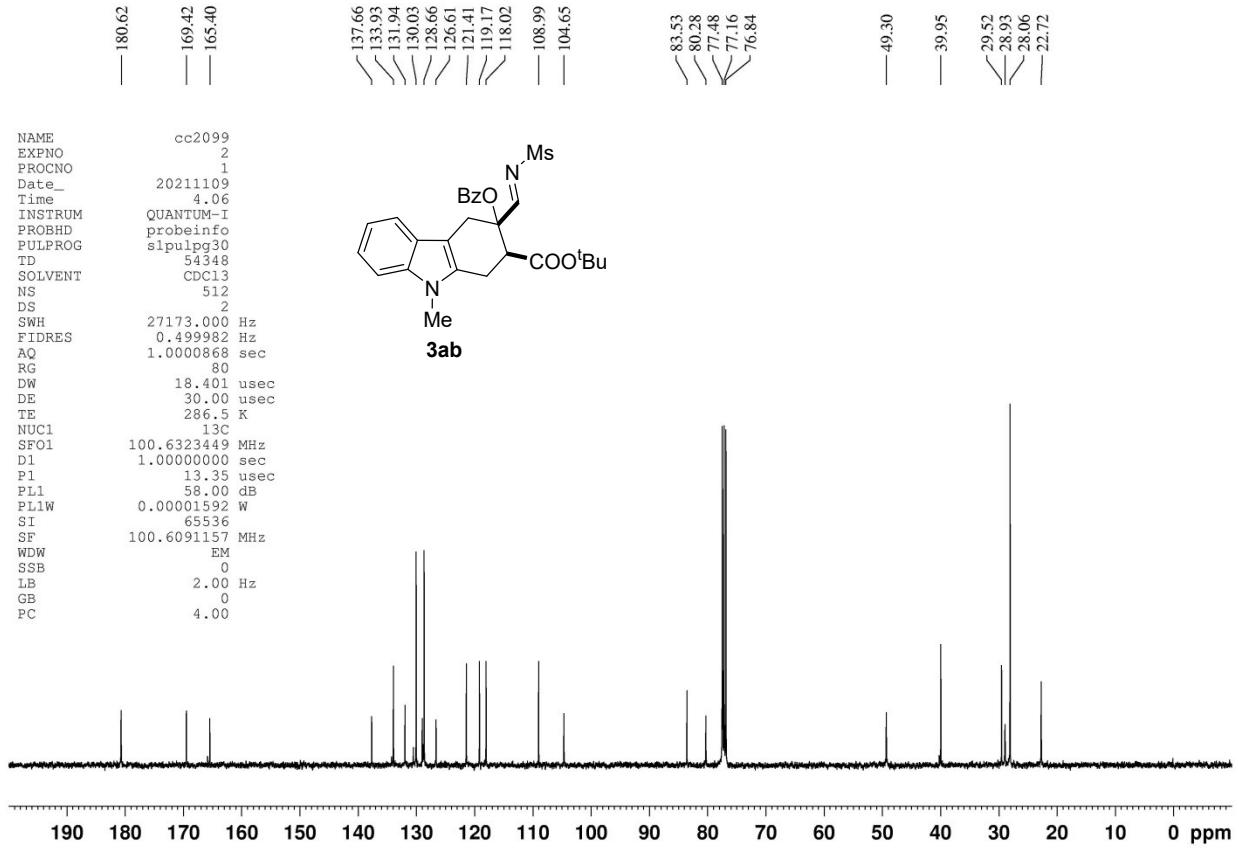



**Figure S8-26. $^{13}$C NMR of 3ab ($CDCl_3$, 101 MHz)**

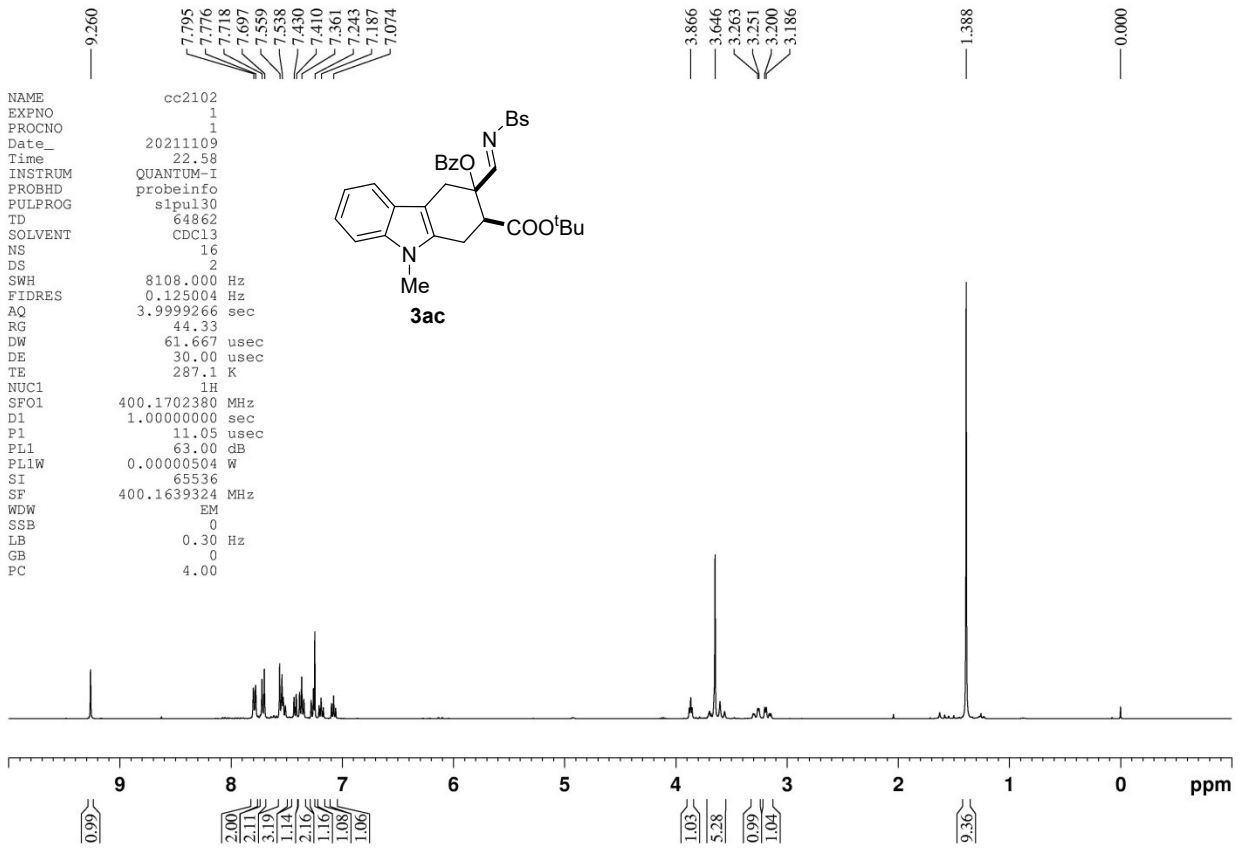



**Figure S8-27. $^{1}$H NMR of 3ac ($CDCl_3$, 400 MHz)**

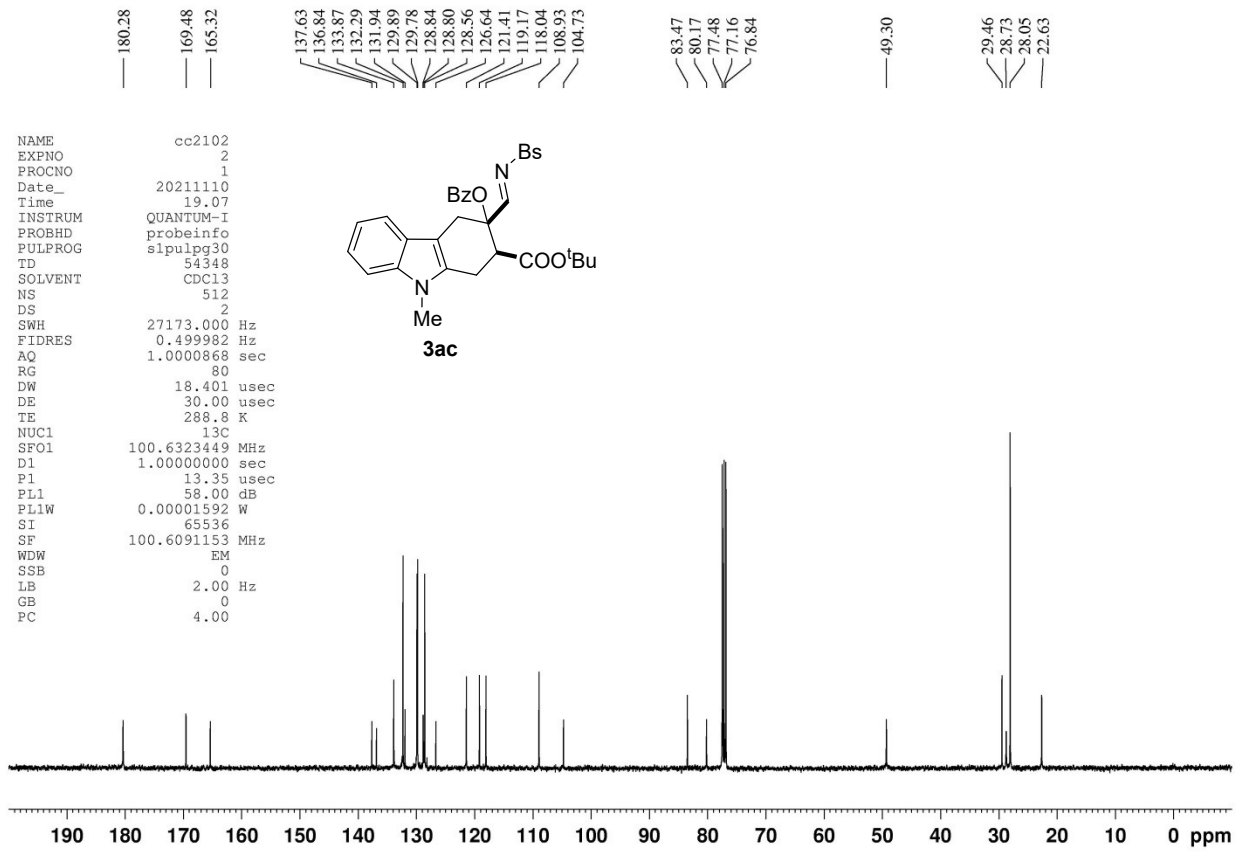



**Figure S8-28. $^{13}$C NMR of 3ac($CDCl_3$, 101 MHz)**

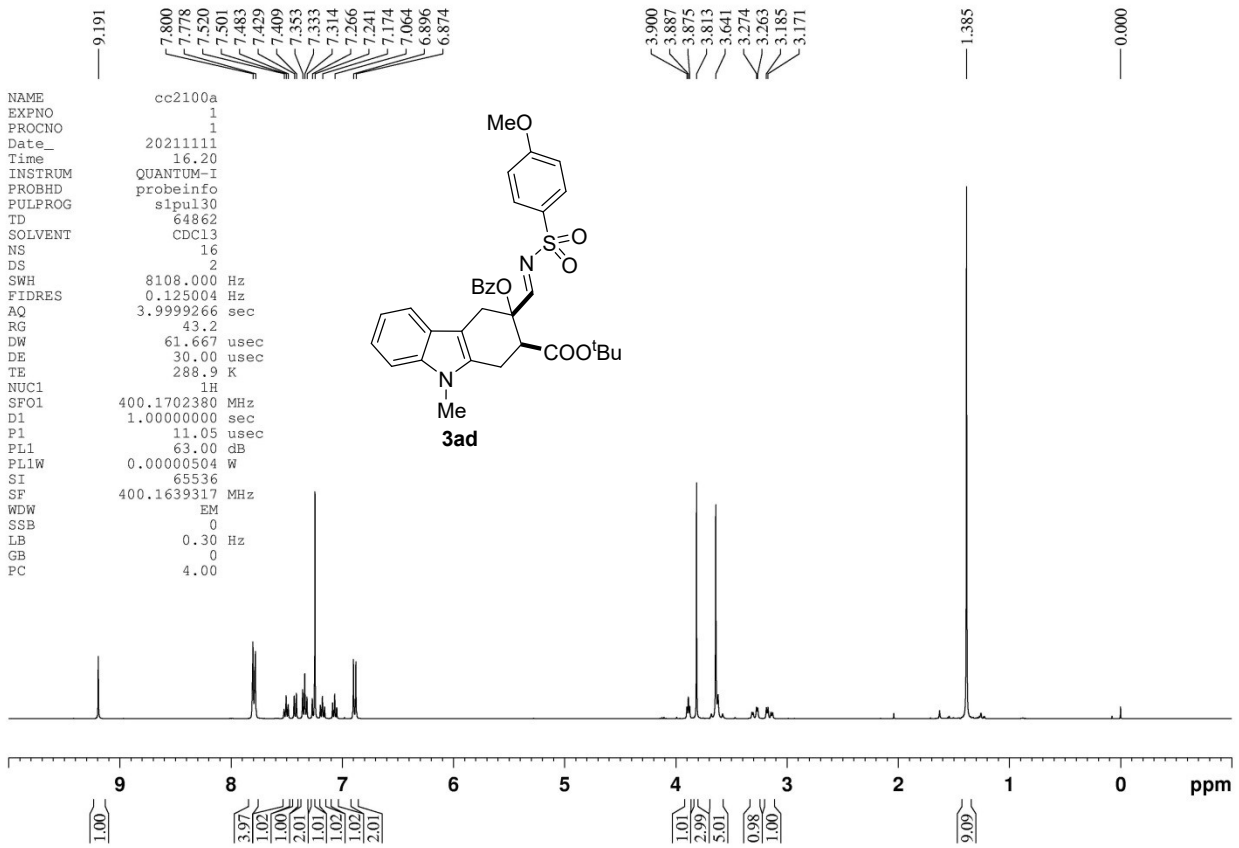



**Figure S8-29. $^{1}$H NMR of 3ad ($CDCl_3$, 400 MHz)**

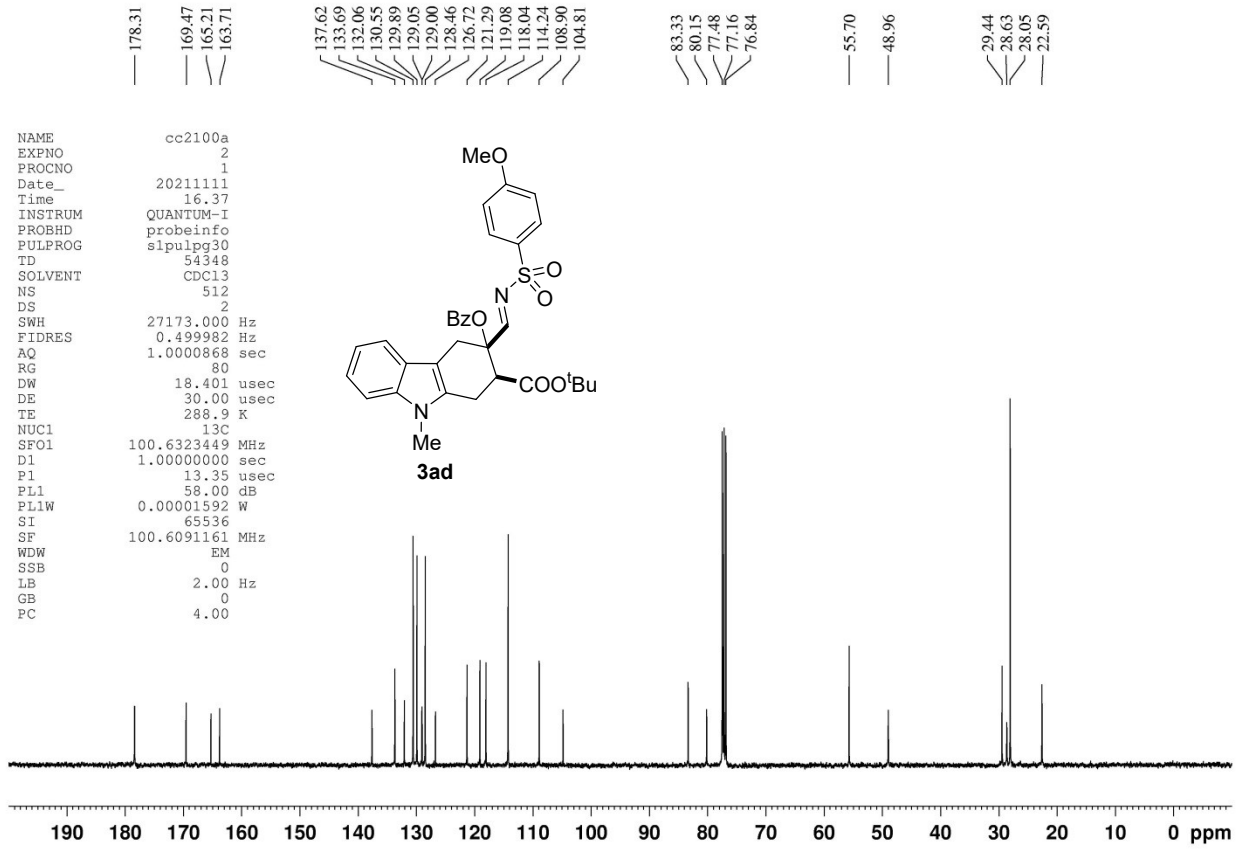



**Figure S8-30. $^{13}$C NMR of 3ad ($CDCl_3$, 101 MHz)**

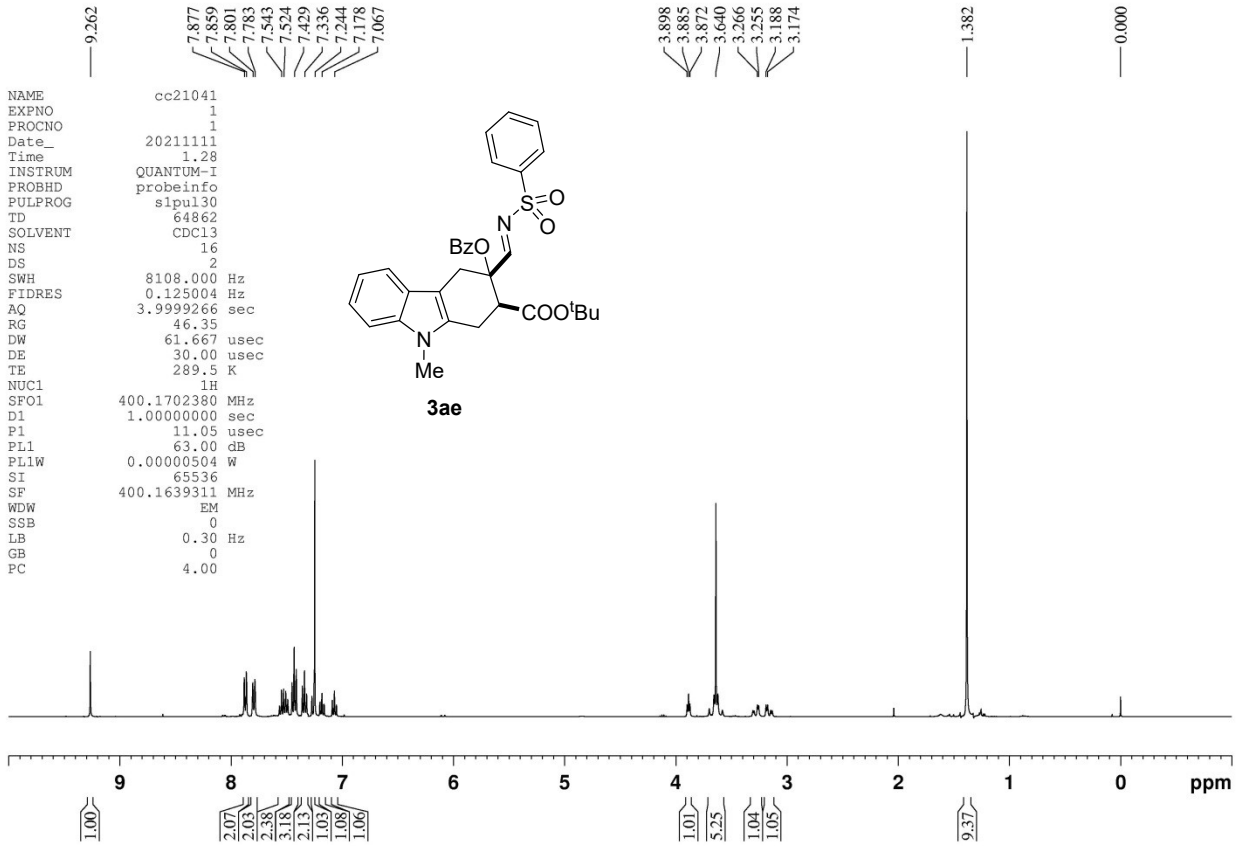



**Figure S8-31. $^{1}$H NMR of 3ae ($CDCl_3$, 400 MHz)**

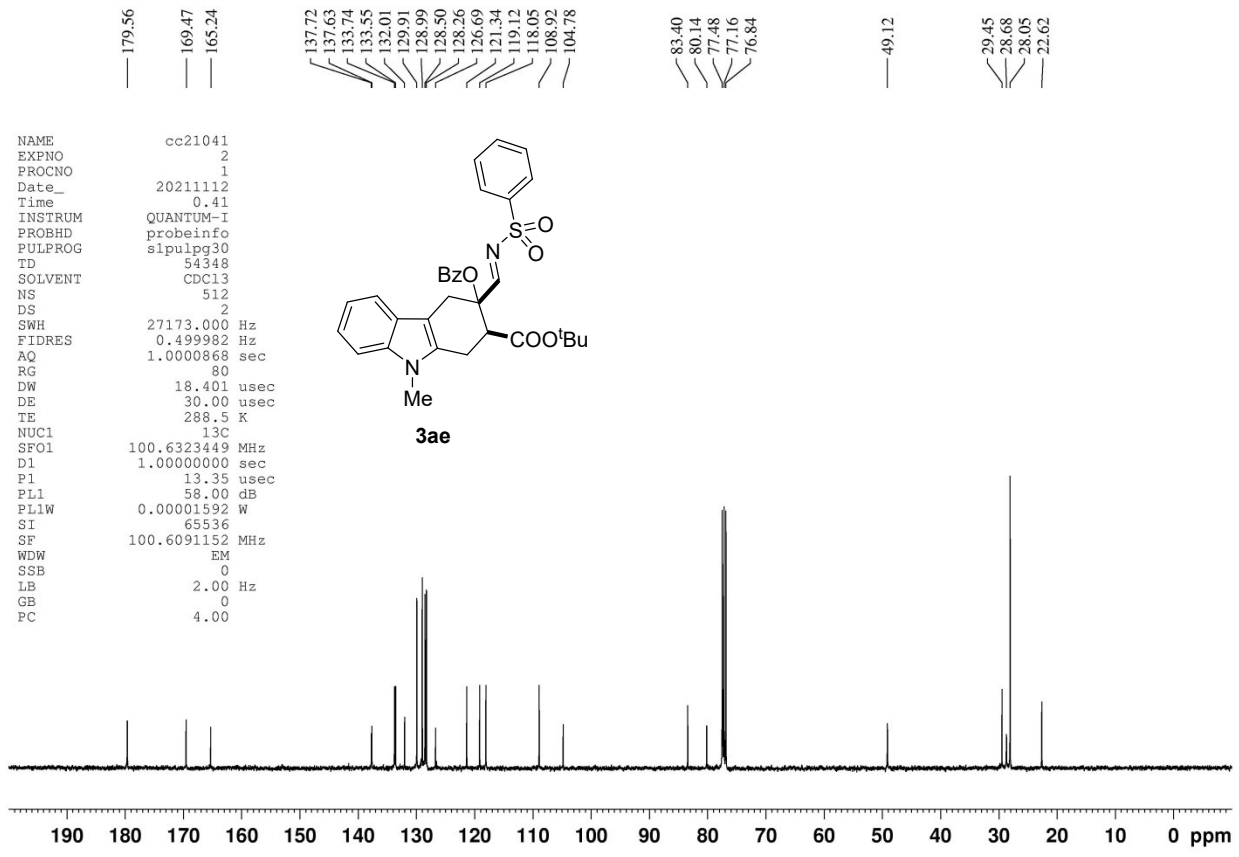



**Figure S8-32. $^{13}$C NMR of 3ae ($CDCl_3$, 101 MHz)**

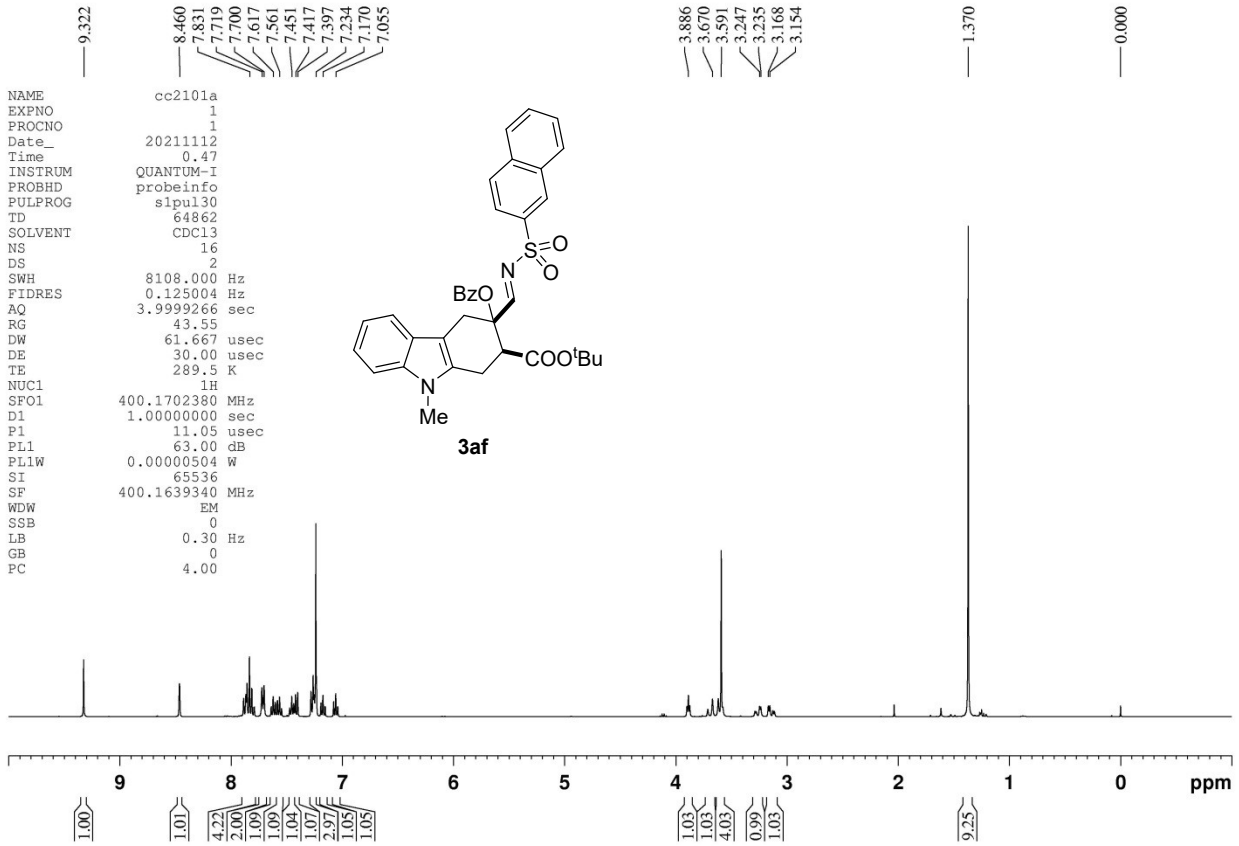



**Figure S8-33. $^{1}$H NMR of 3af ($CDCl_3$, 400 MHz)**

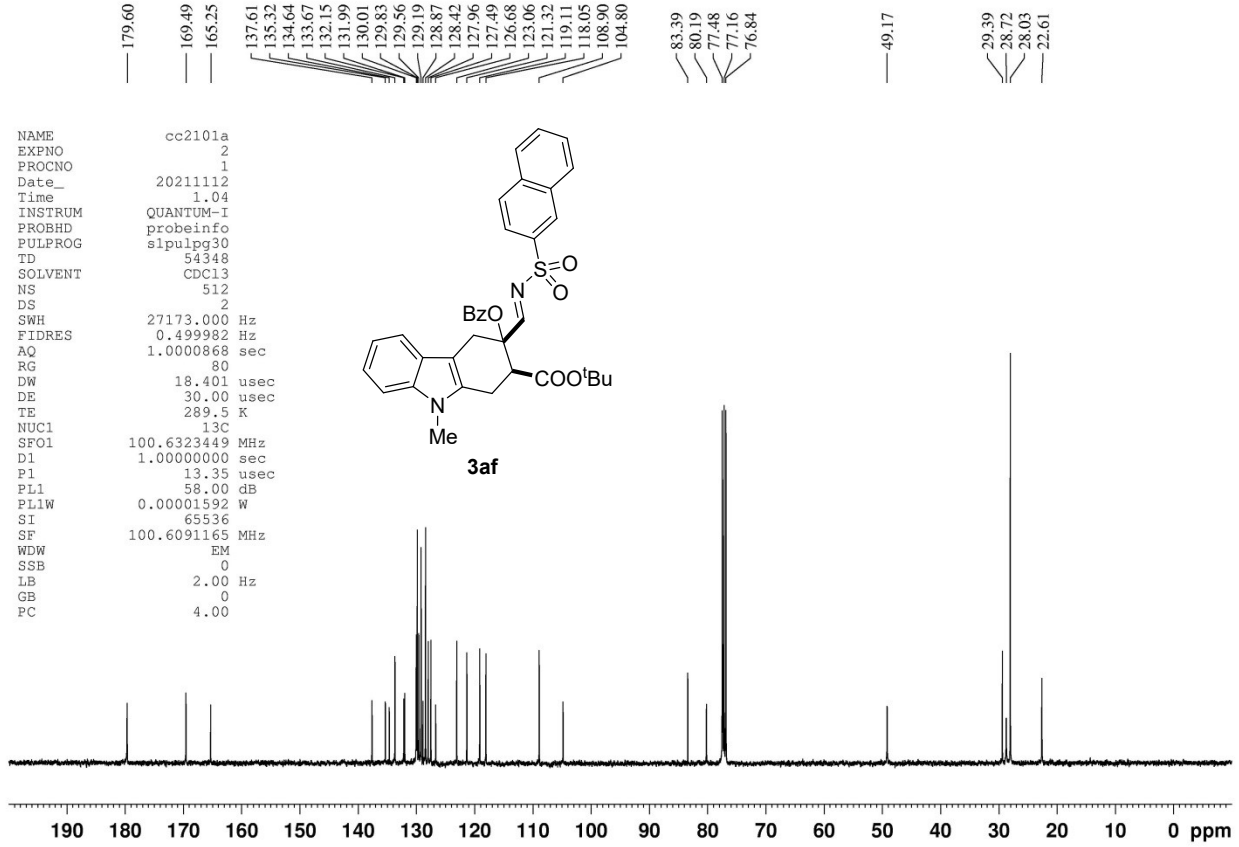



**Figure S8-34. $^{13}$C NMR of 3af ($CDCl_3$, 101 MHz)**

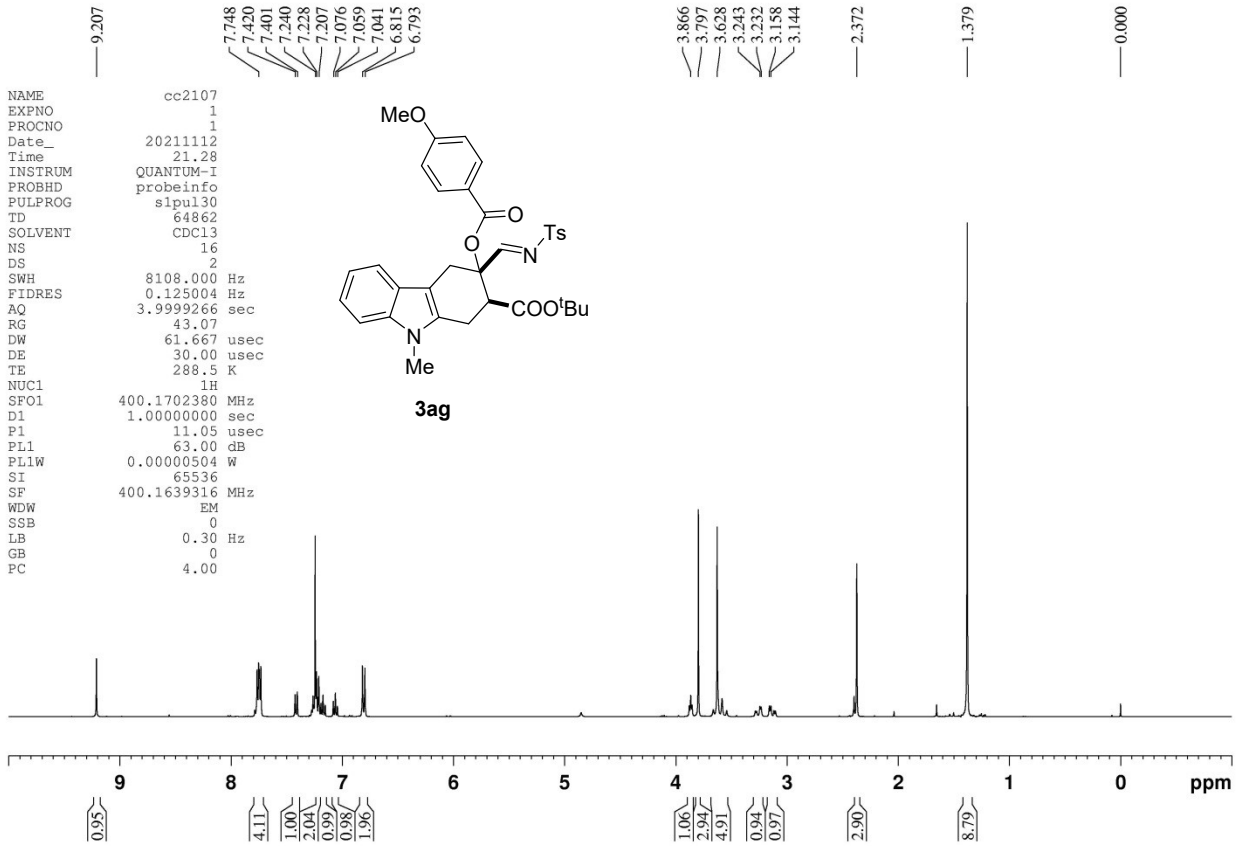



**Figure S8-35. $^{1}$H NMR of 3ag ($CDCl_3$, 400 MHz)**

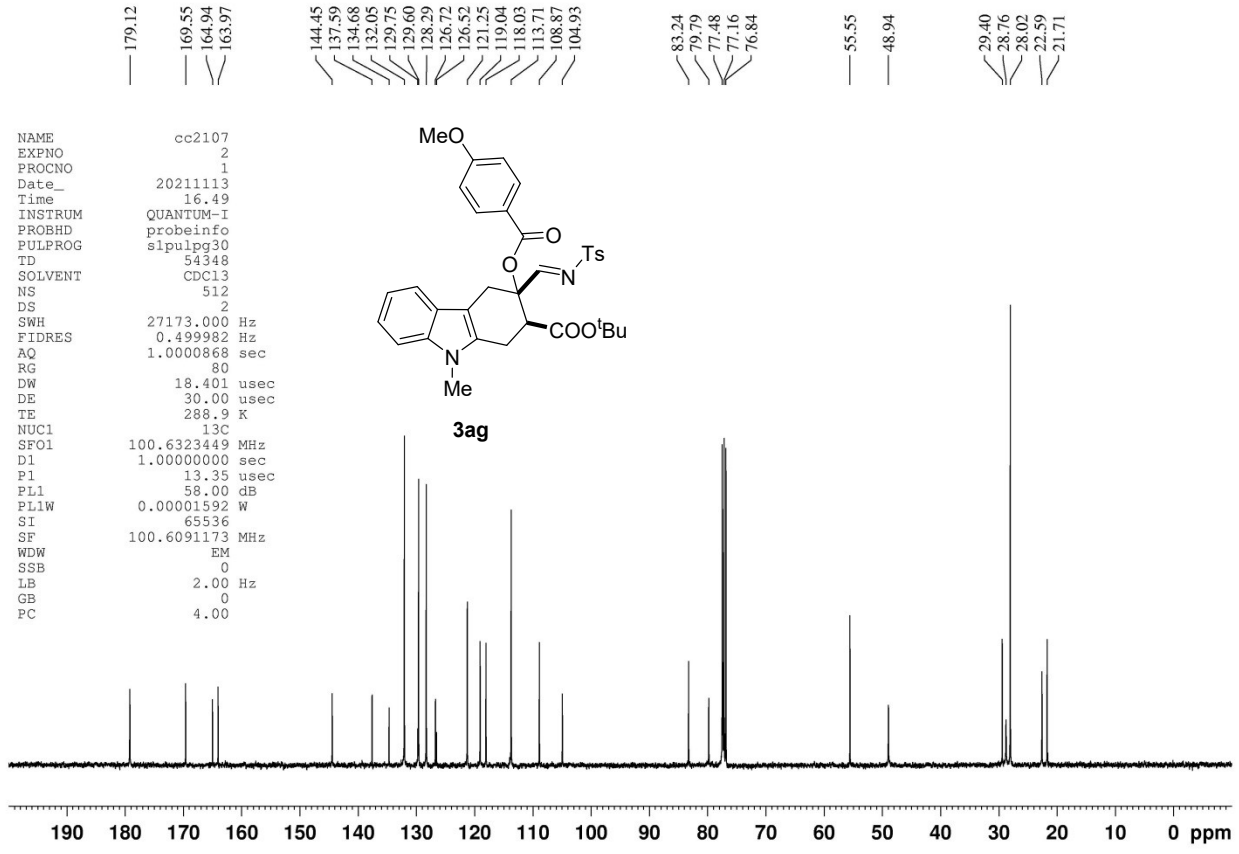



**Figure S8-36. $^{13}$C NMR of 3ag ($CDCl_3$, 101 MHz)**

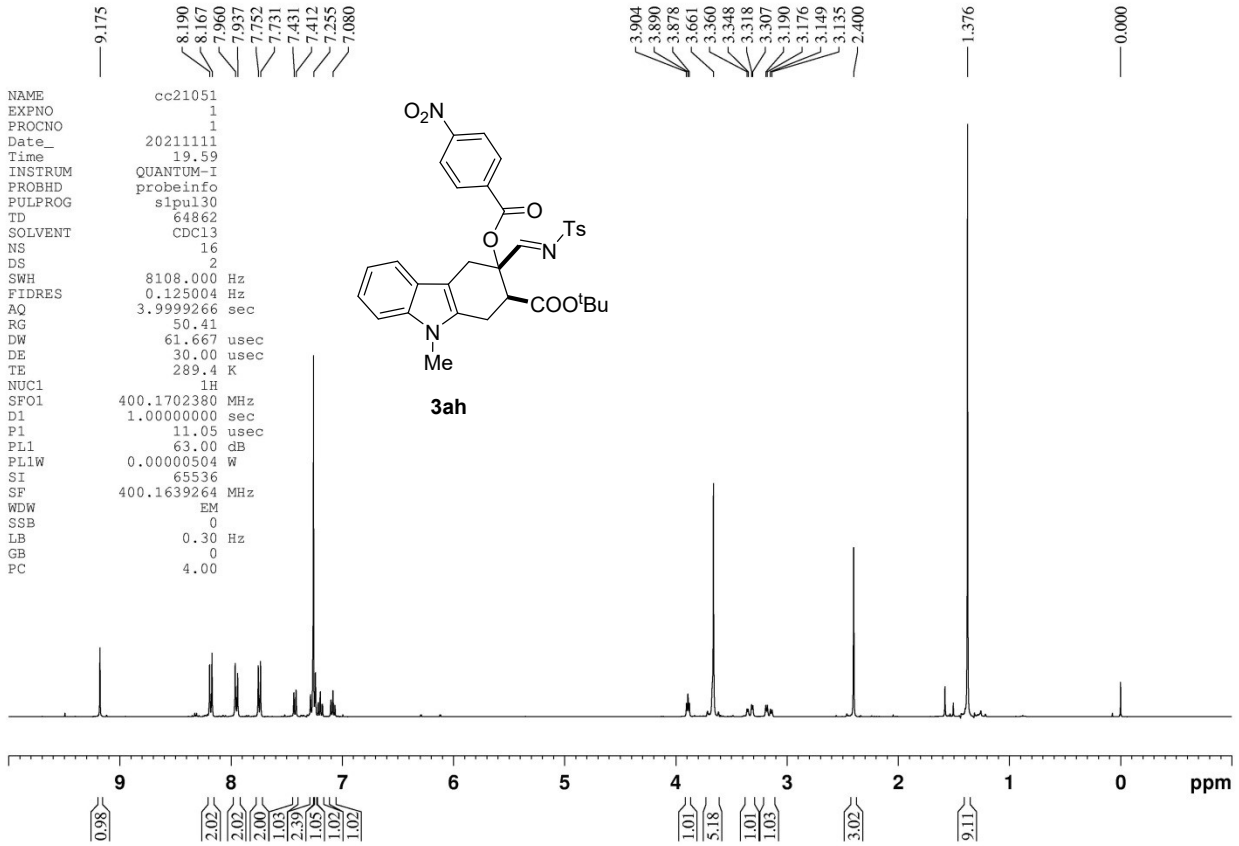



**Figure S8-37. $^{1}$H NMR of 3ah ($CDCl_3$, 400 MHz)**

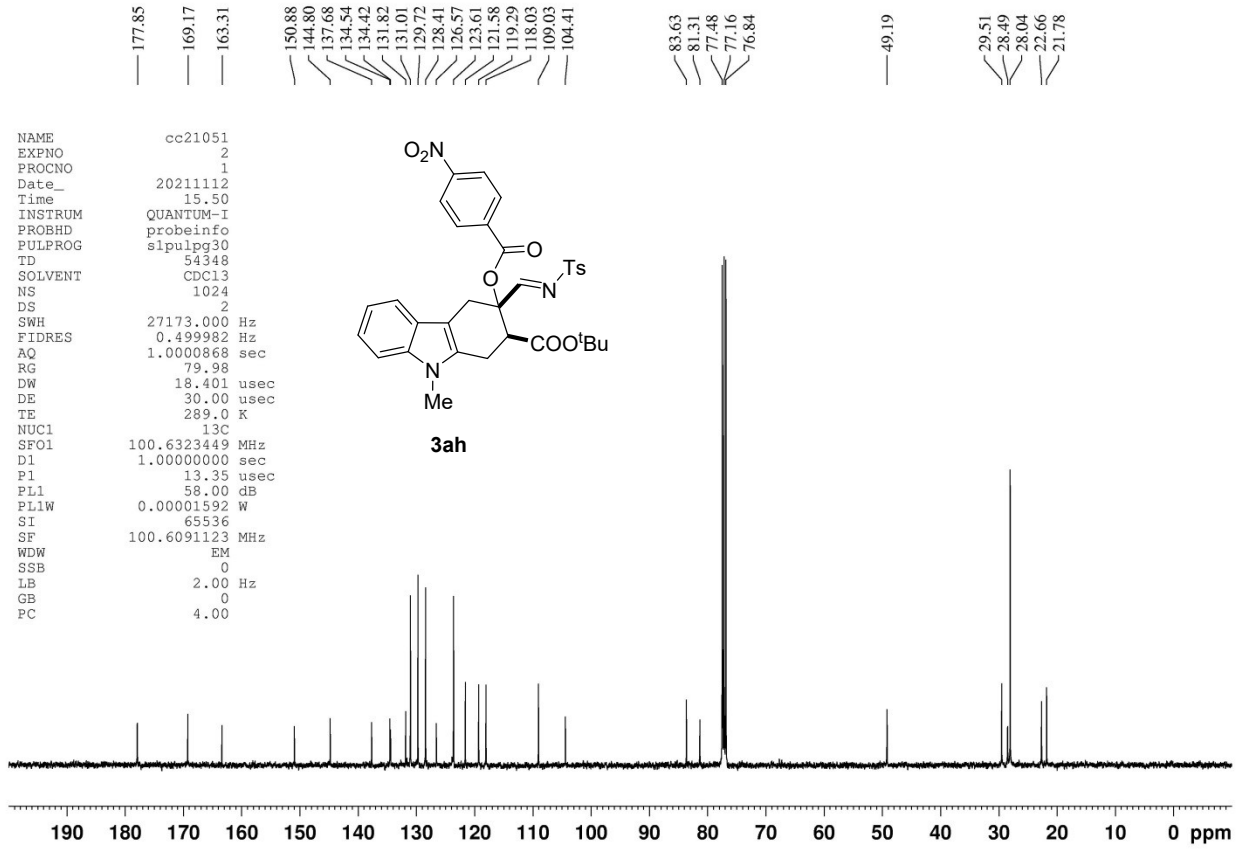



**Figure S8-38. $^{13}$C NMR of 3ah ($CDCl_3$, 101 MHz)**

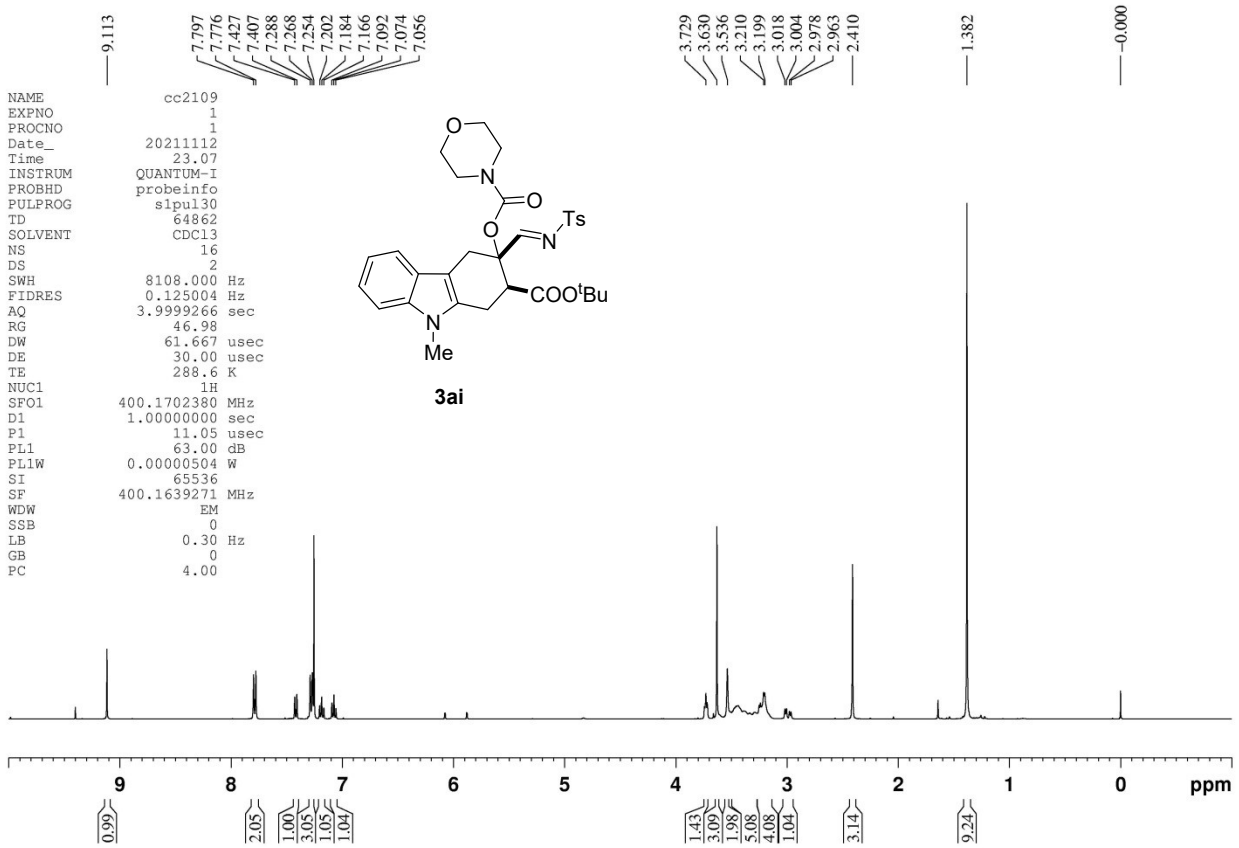



**Figure S8-39. $^{1}$H NMR of 3ai ($CDCl_3$, 400 MHz)**

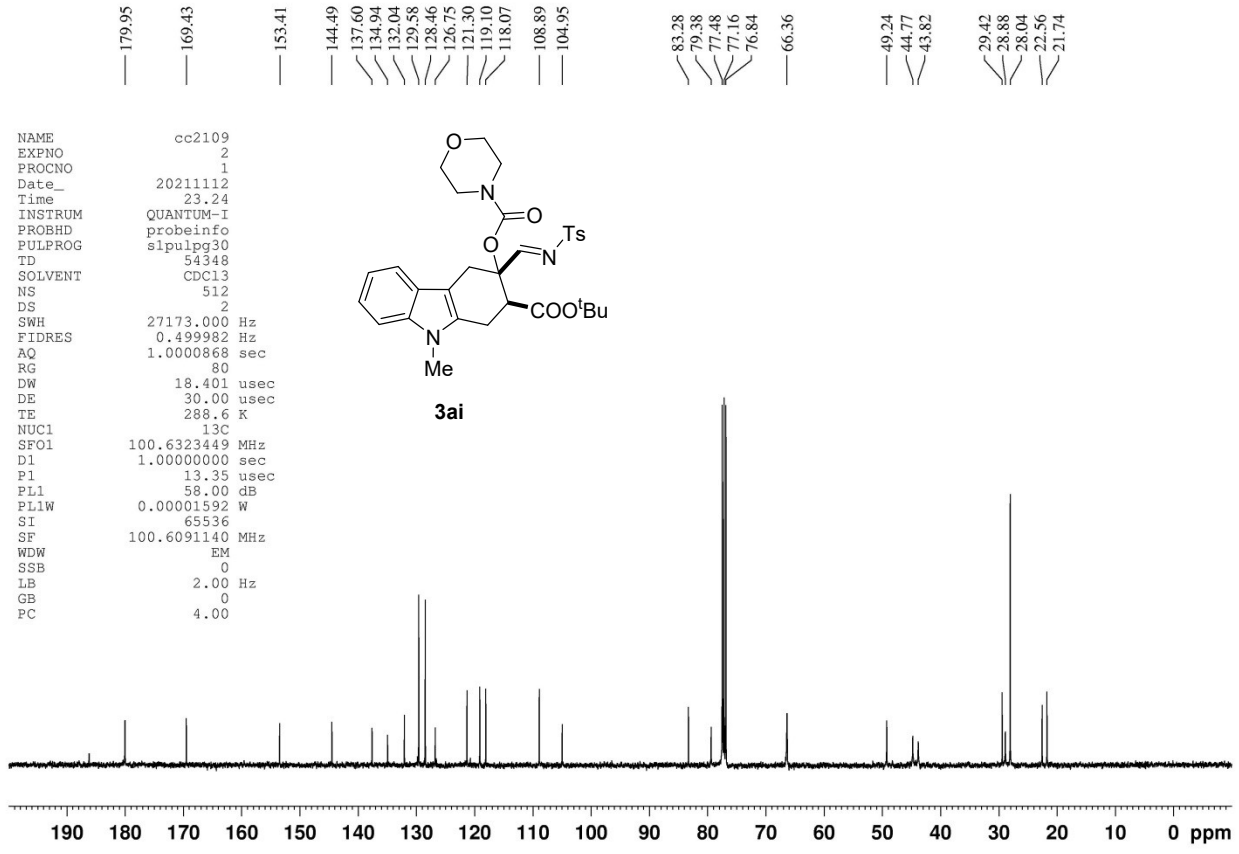



**Figure S8-40. $^{13}$C NMR of 3ai ($CDCl_3$, 101 MHz)**

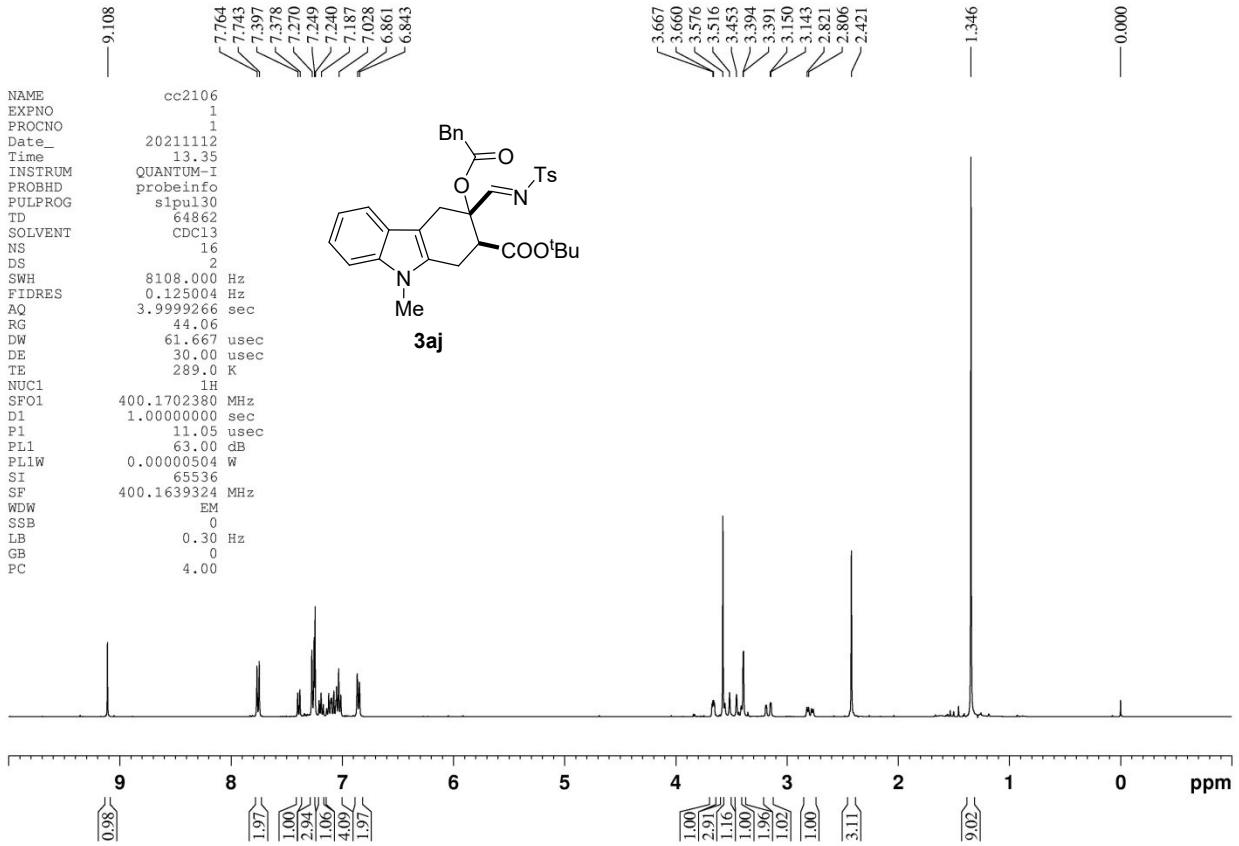



**Figure S8-41. $^{1}$H NMR of 3aj ($CDCl_3$, 400 MHz)**

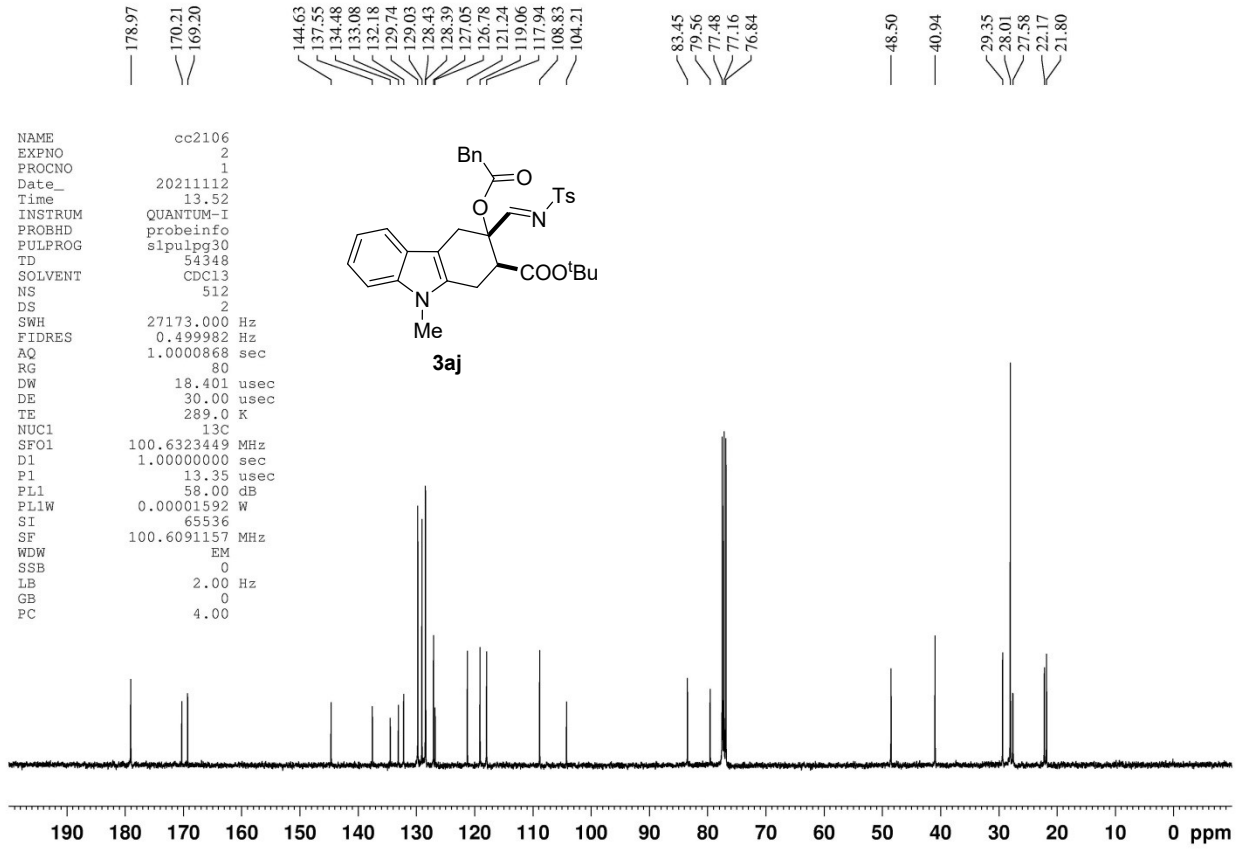



**Figure S8-42. $^{13}$C NMR of 3aj ($CDCl_3$, 101 MHz)**

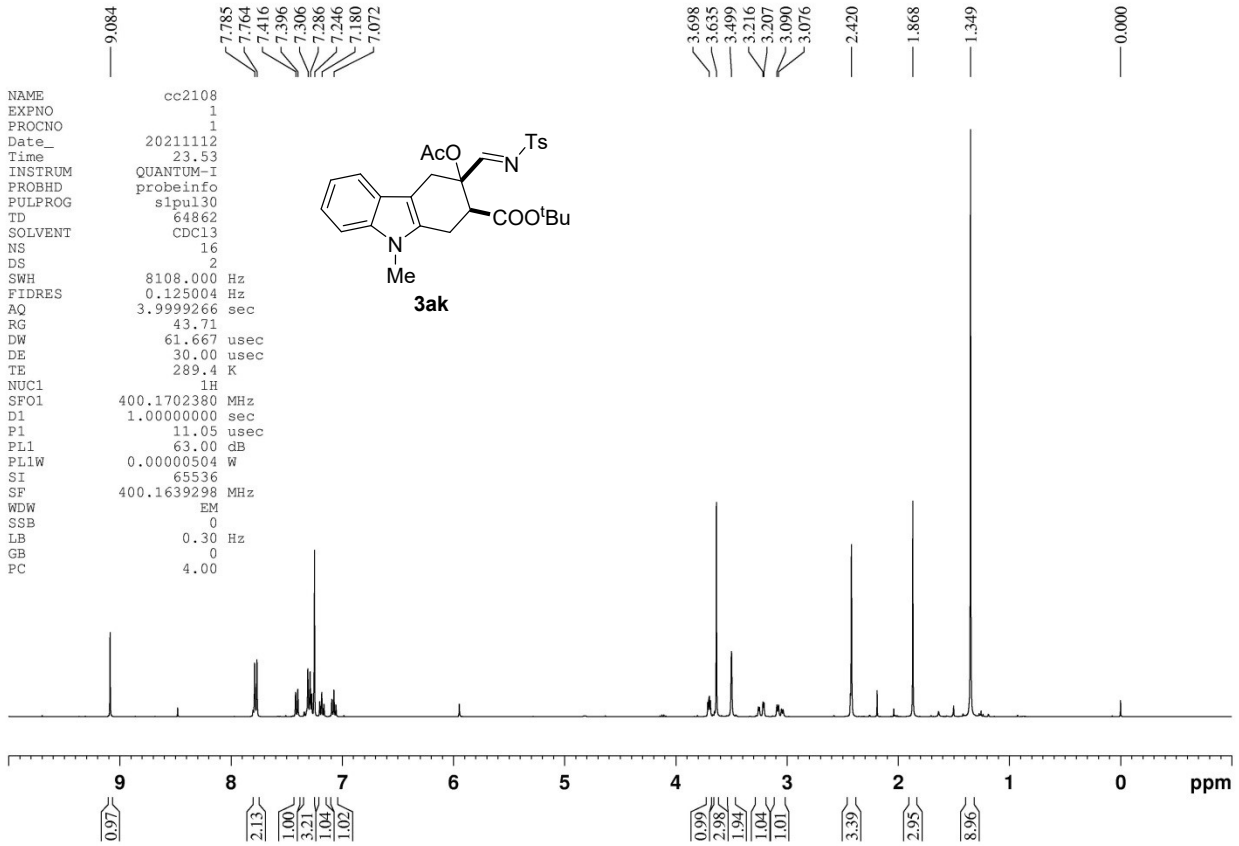



**Figure S8-43. $^{1}$H NMR of 3ak ($CDCl_3$, 400 MHz)**

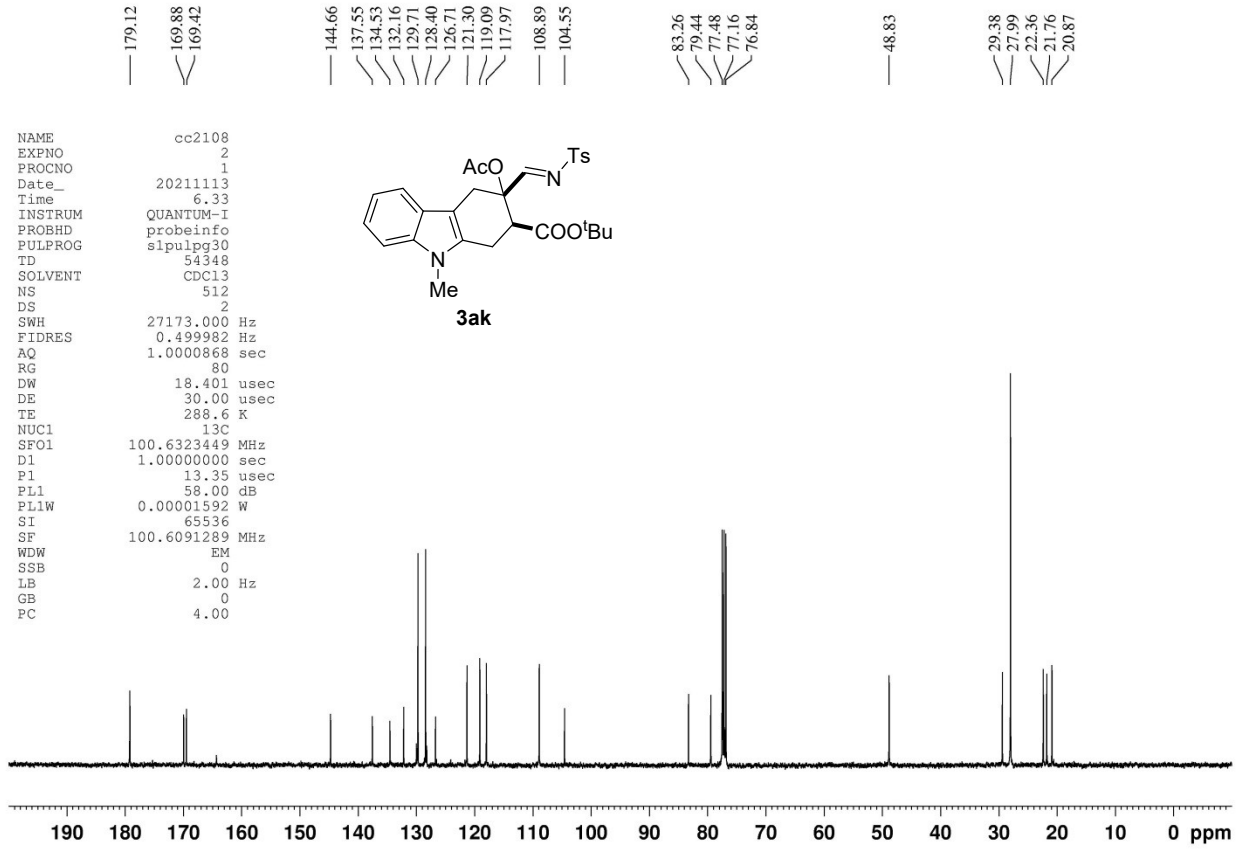



**Figure S8-44. $^{13}$C NMR of 3ak ($CDCl_3$, 101 MHz)**

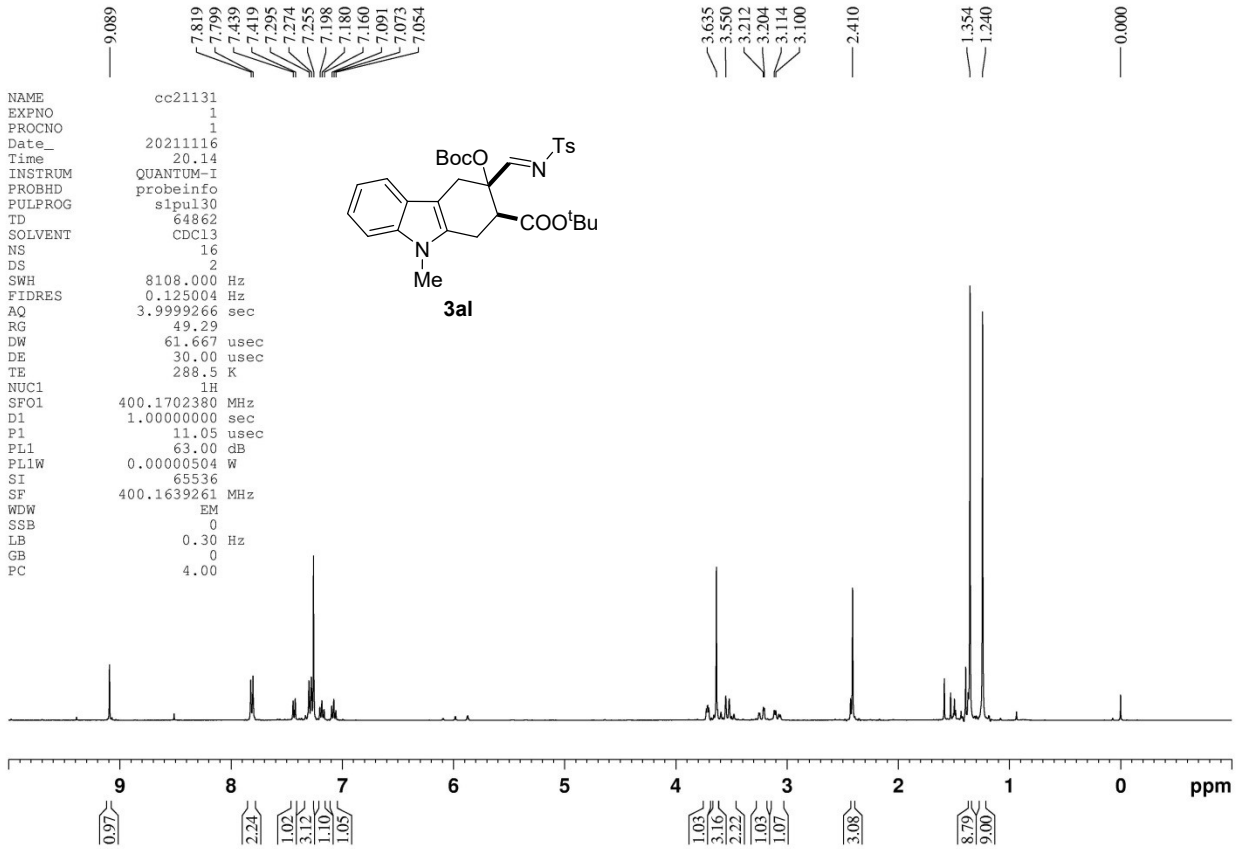



**Figure S8-45. $^{1}$H NMR of 3al ($CDCl_3$, 400 MHz)**

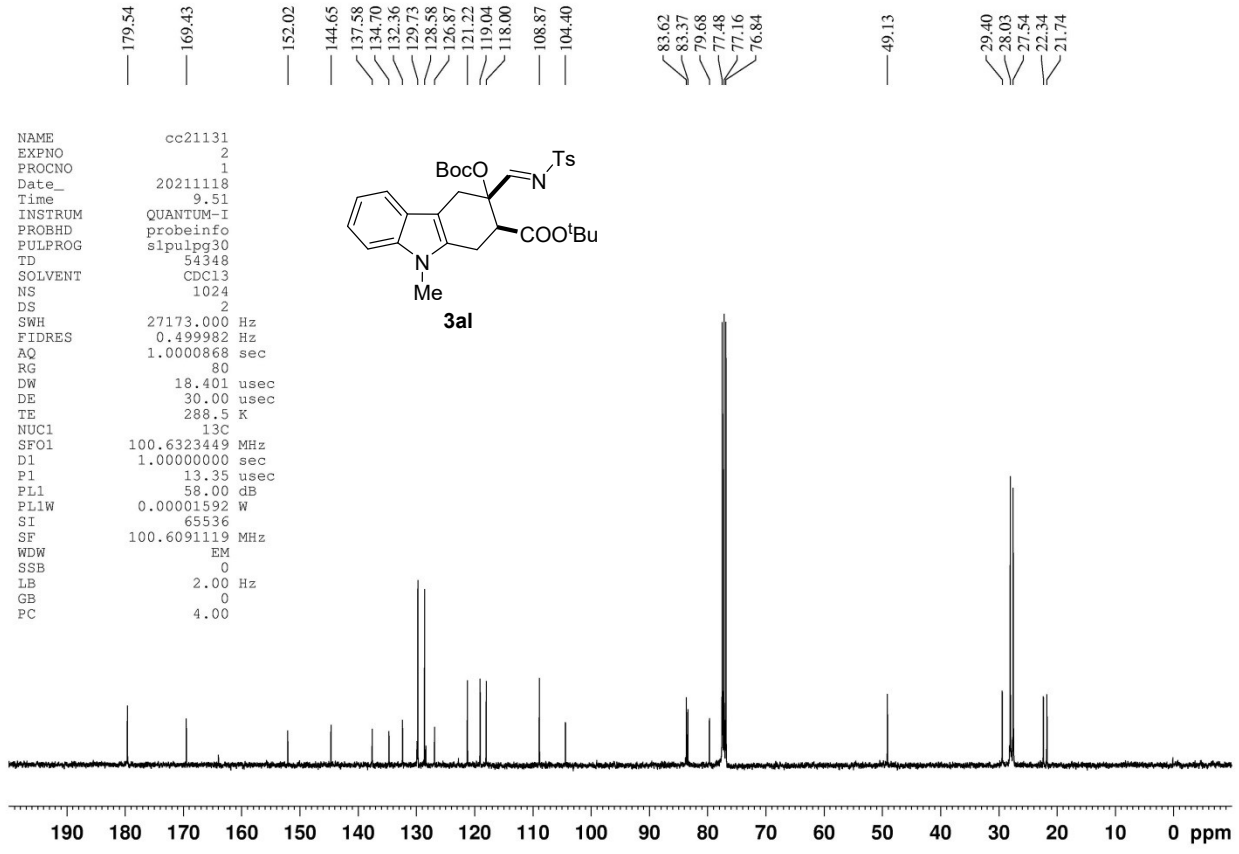



**Figure S8-46. $^{13}$C NMR of 3al ($CDCl_3$, 101 MHz)**

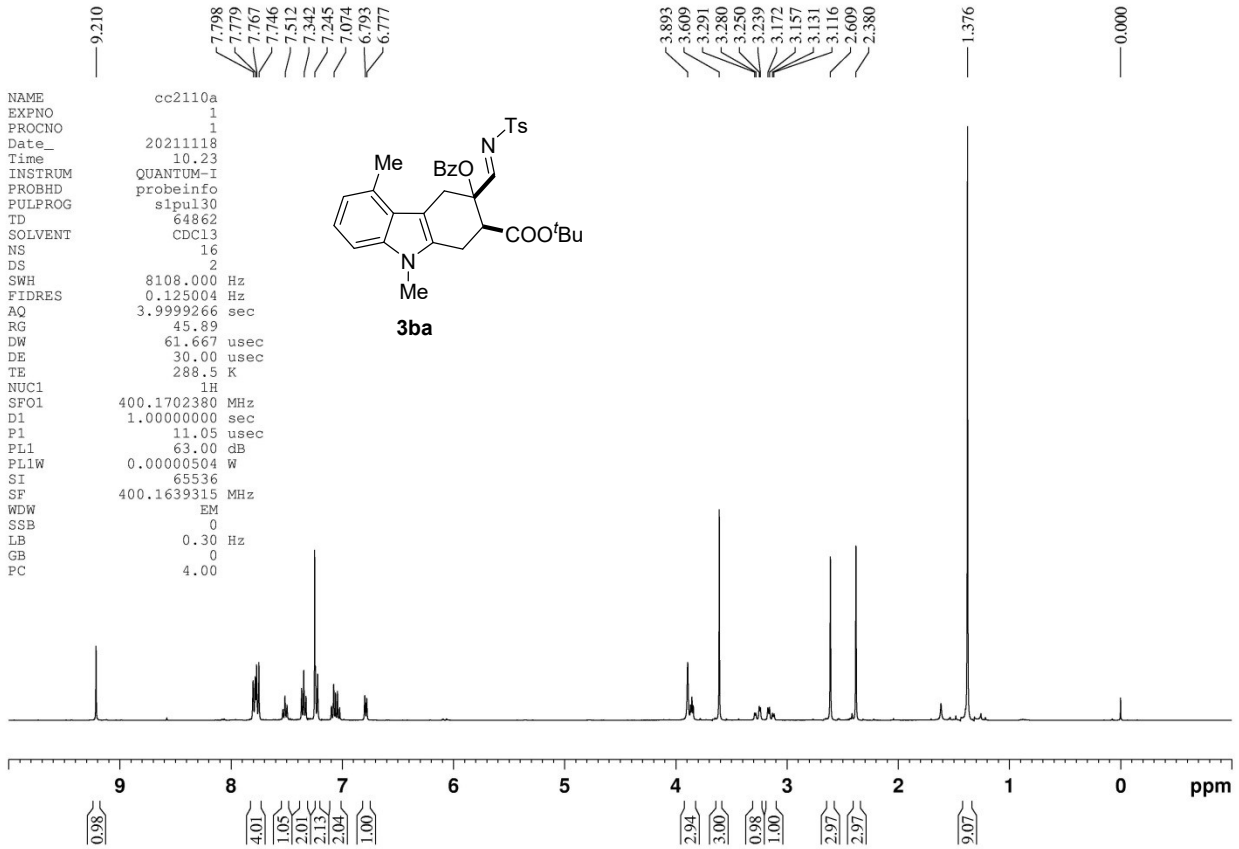



**Figure S8-47. $^{1}$H NMR of 3ba ($CDCl_3$, 400 MHz)**

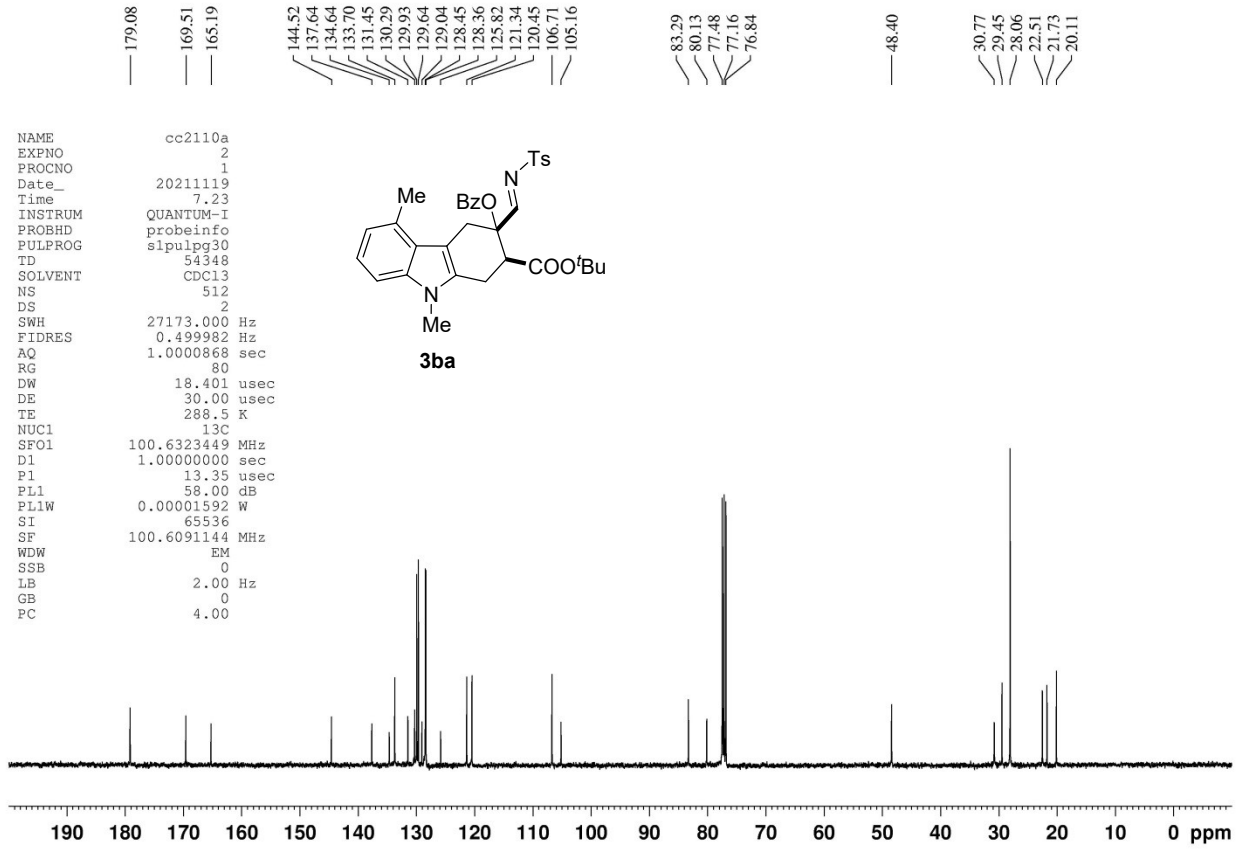



**Figure S8-48. $^{13}$C NMR of 3ba ($CDCl_3$, 101 MHz)**

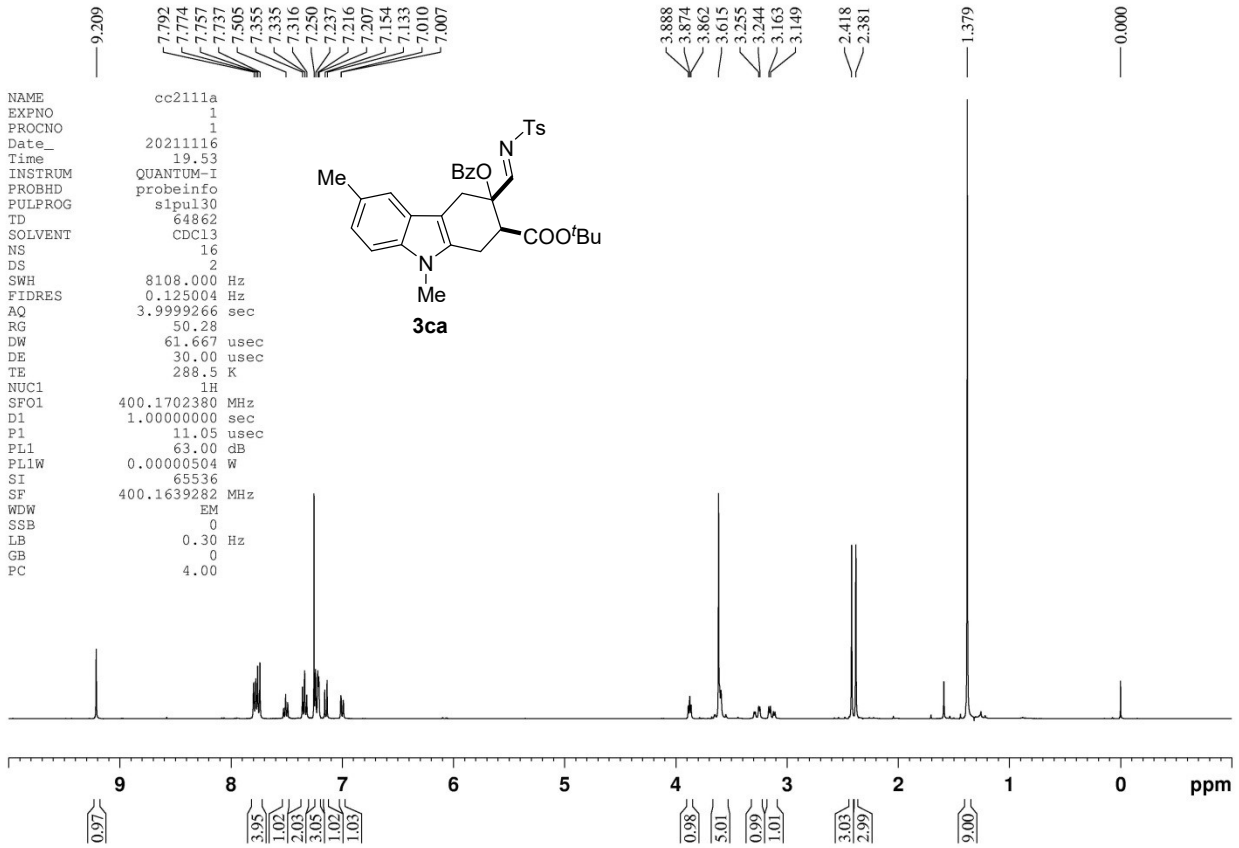



**Figure S8-49. $^{1}$H NMR of 3ca ($CDCl_3$, 400 MHz)**

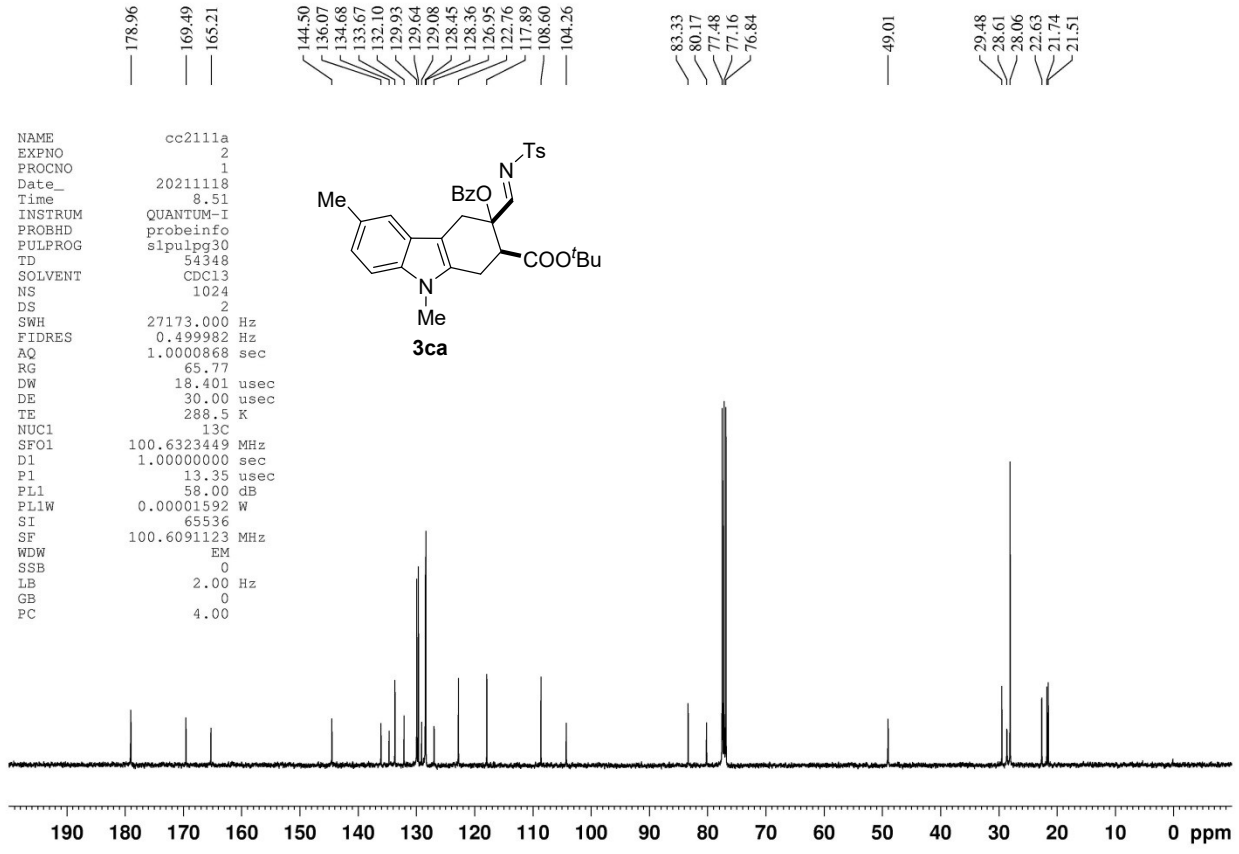



**Figure S8-50. $^{13}$C NMR of 3ca ($CDCl_3$, 101 MHz)**

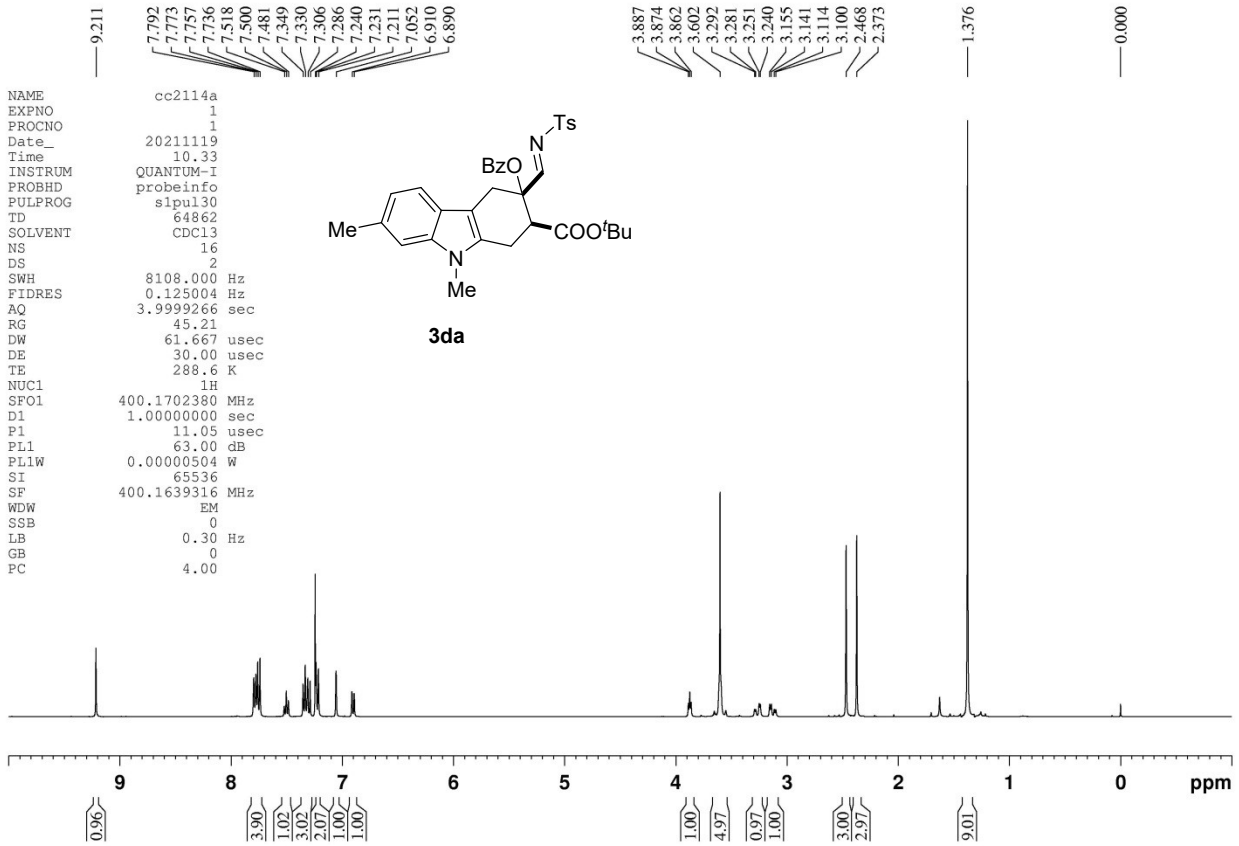



**Figure S8-51. $^{1}$H NMR of 3da ($CDCl_3$, 400 MHz)**

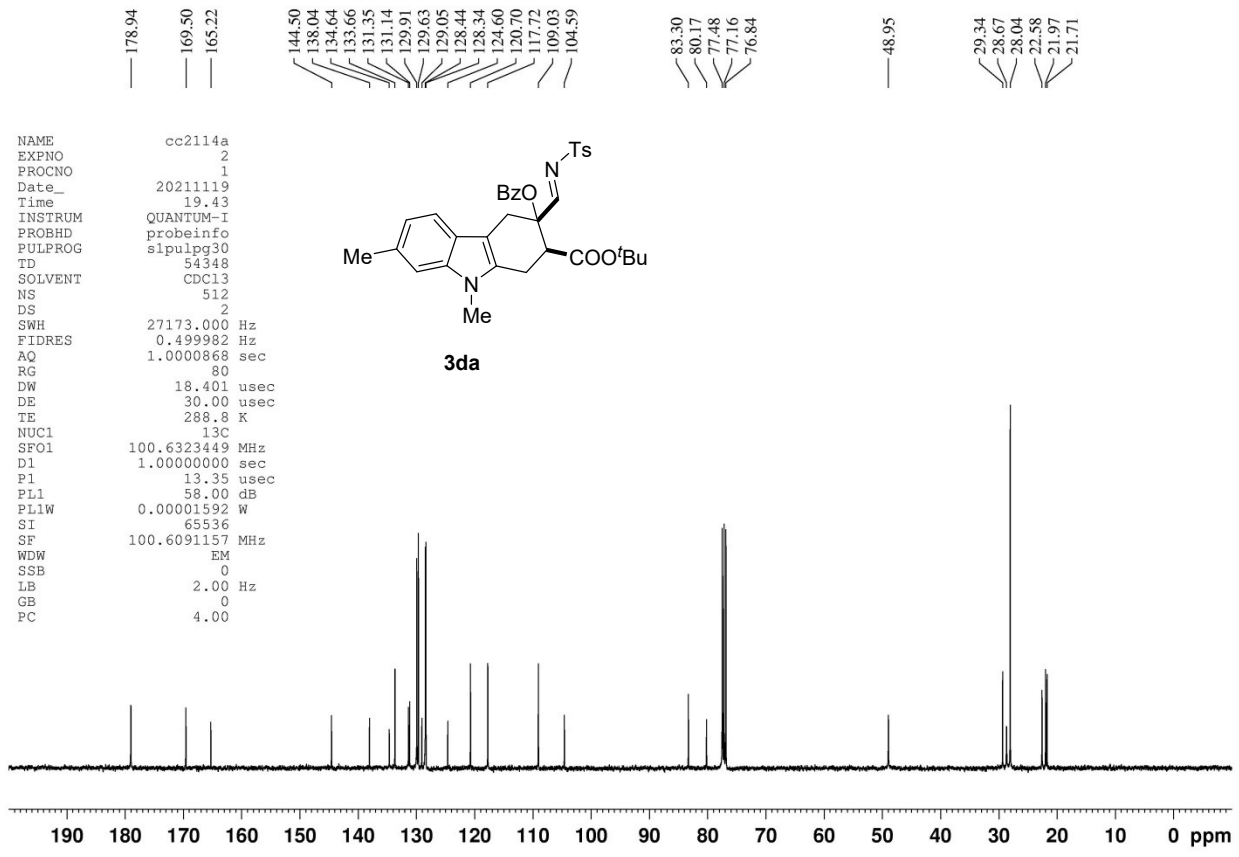



**Figure S8-52. $^{13}$C NMR of 3da ($CDCl_3$, 101 MHz)**

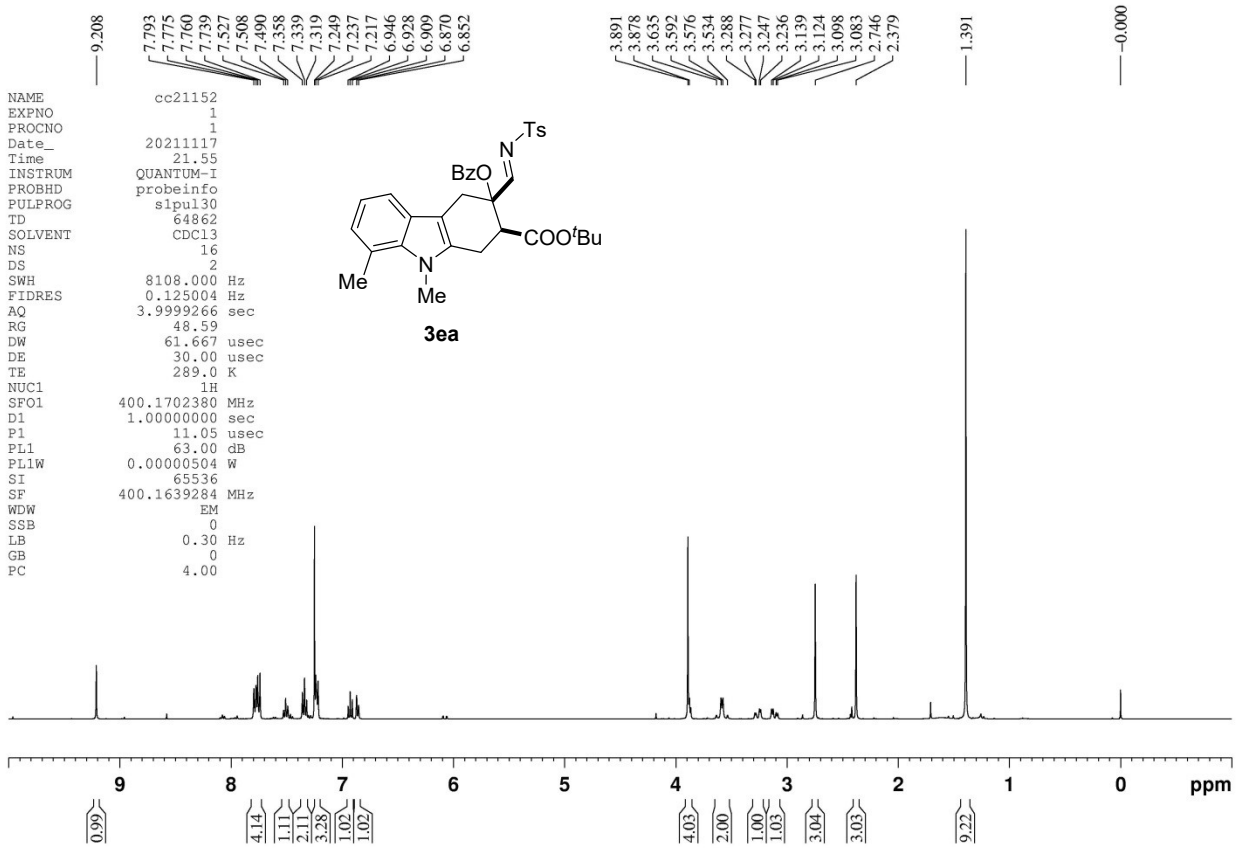



**Figure S8-53. $^{1}$H NMR of 3ea ($CDCl_3$, 400 MHz)**

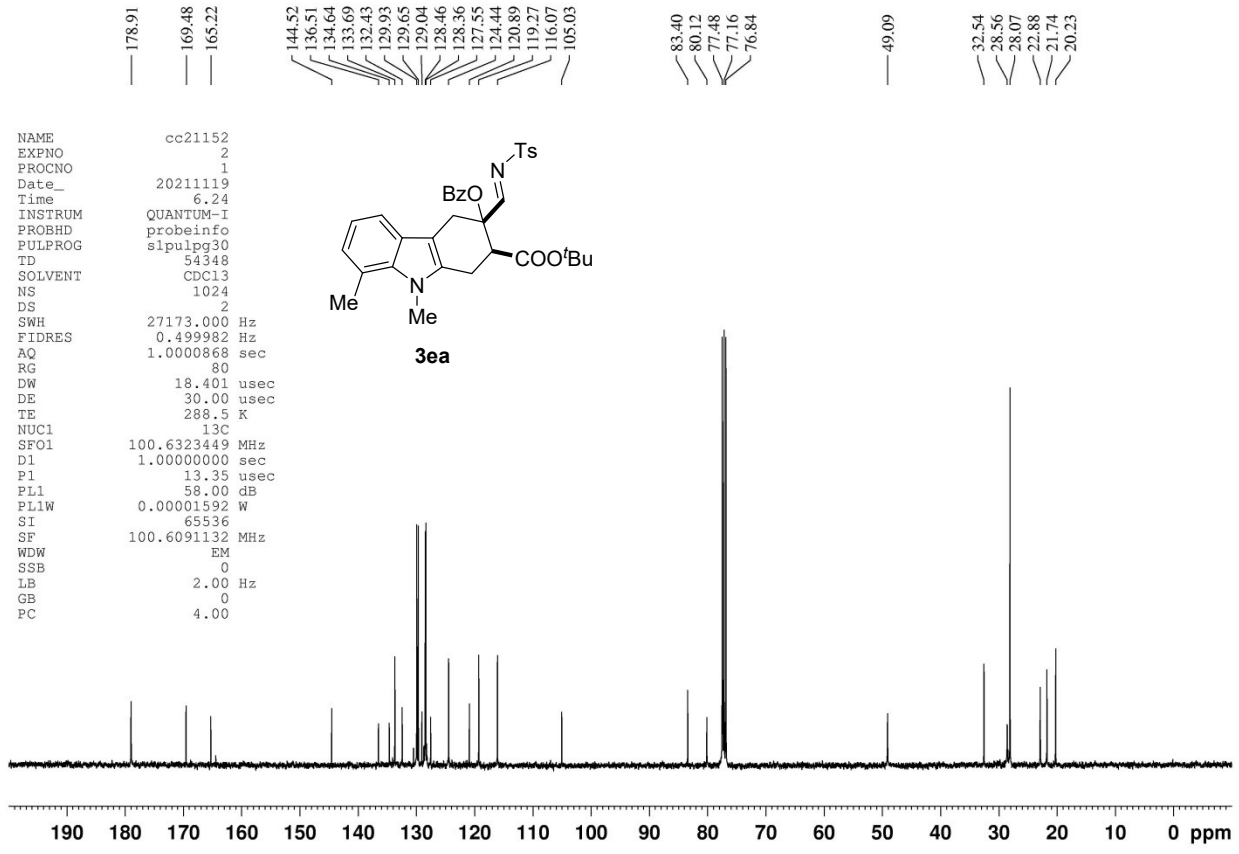



**Figure S8-54. $^{13}$C NMR of 3ea ($CDCl_3$, 101 MHz)**

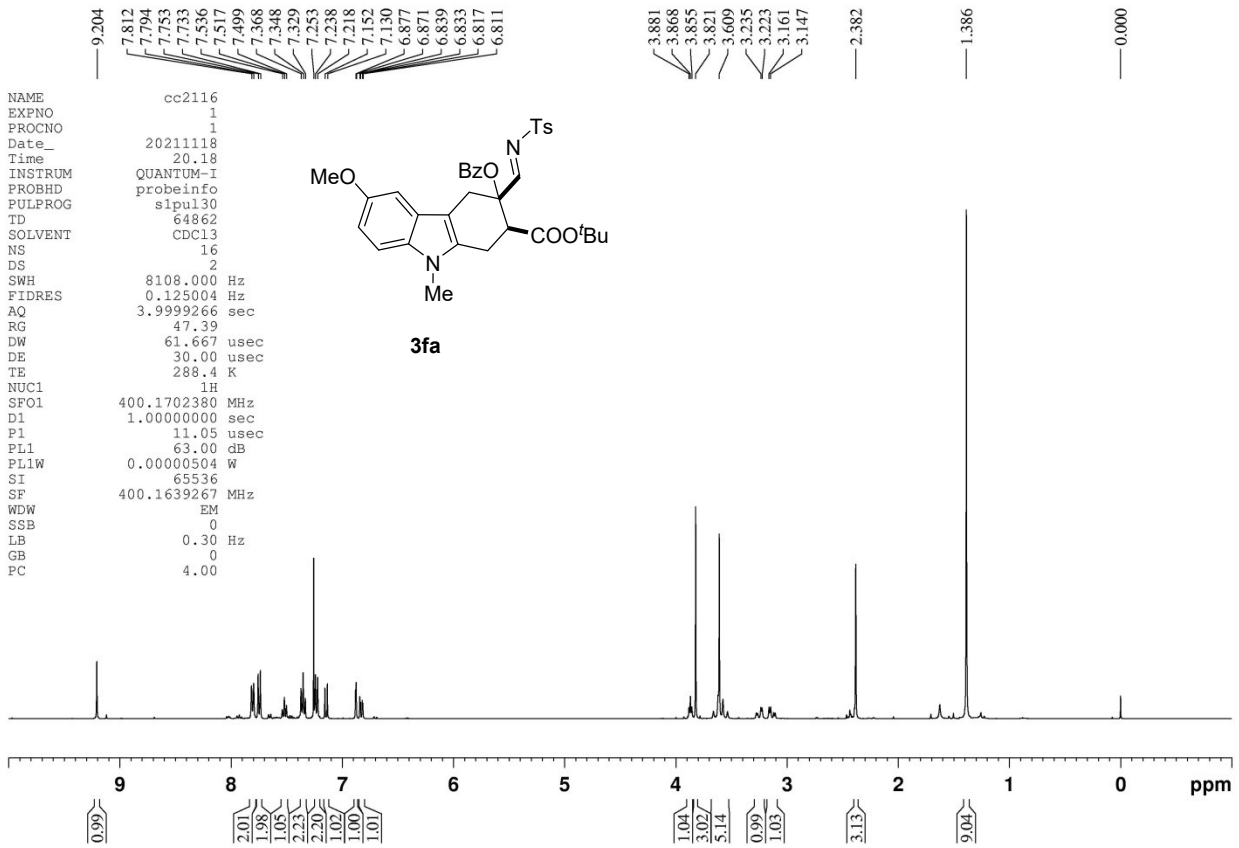



**Figure S8-55. $^{1}$H NMR of 3fa ($CDCl_3$, 400 MHz)**

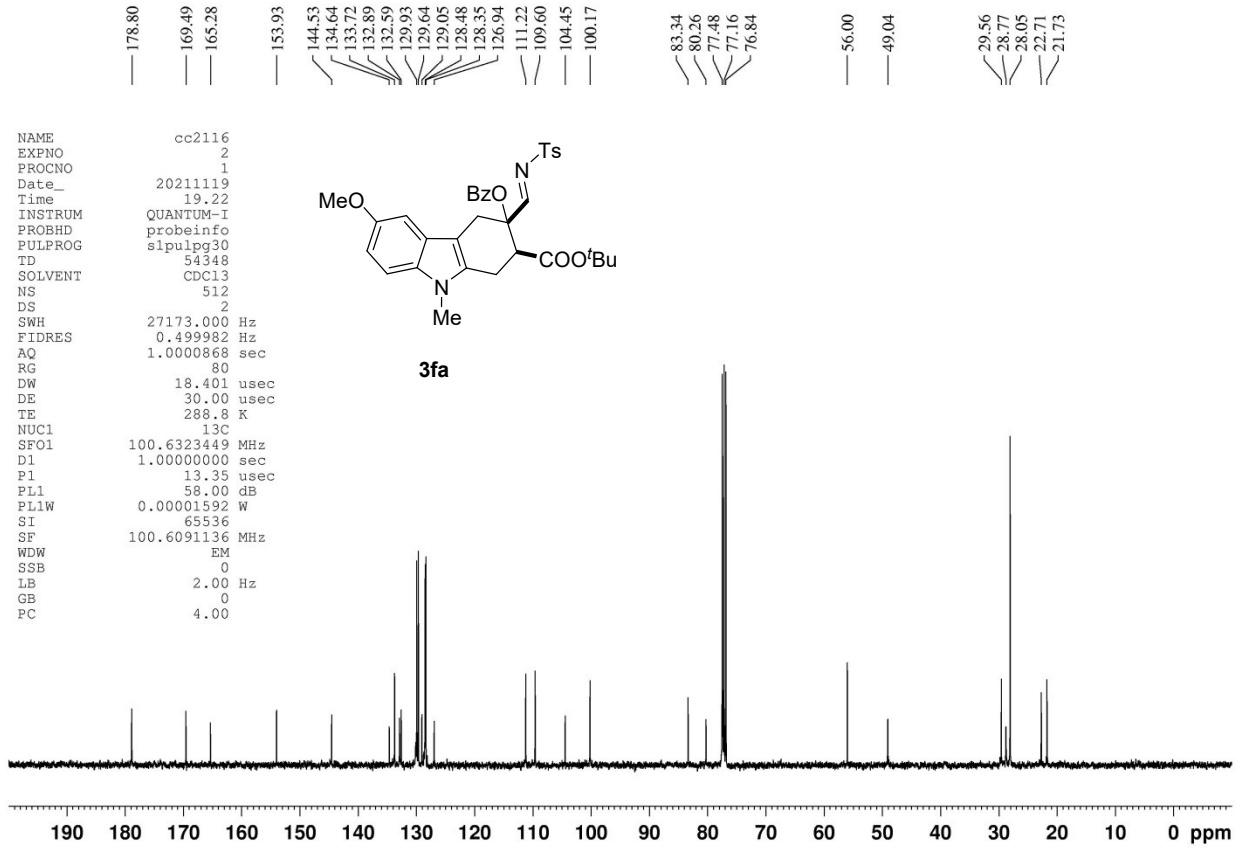



**Figure S8-56. $^{13}$C NMR of 3fa ($CDCl_3$, 101 MHz)**

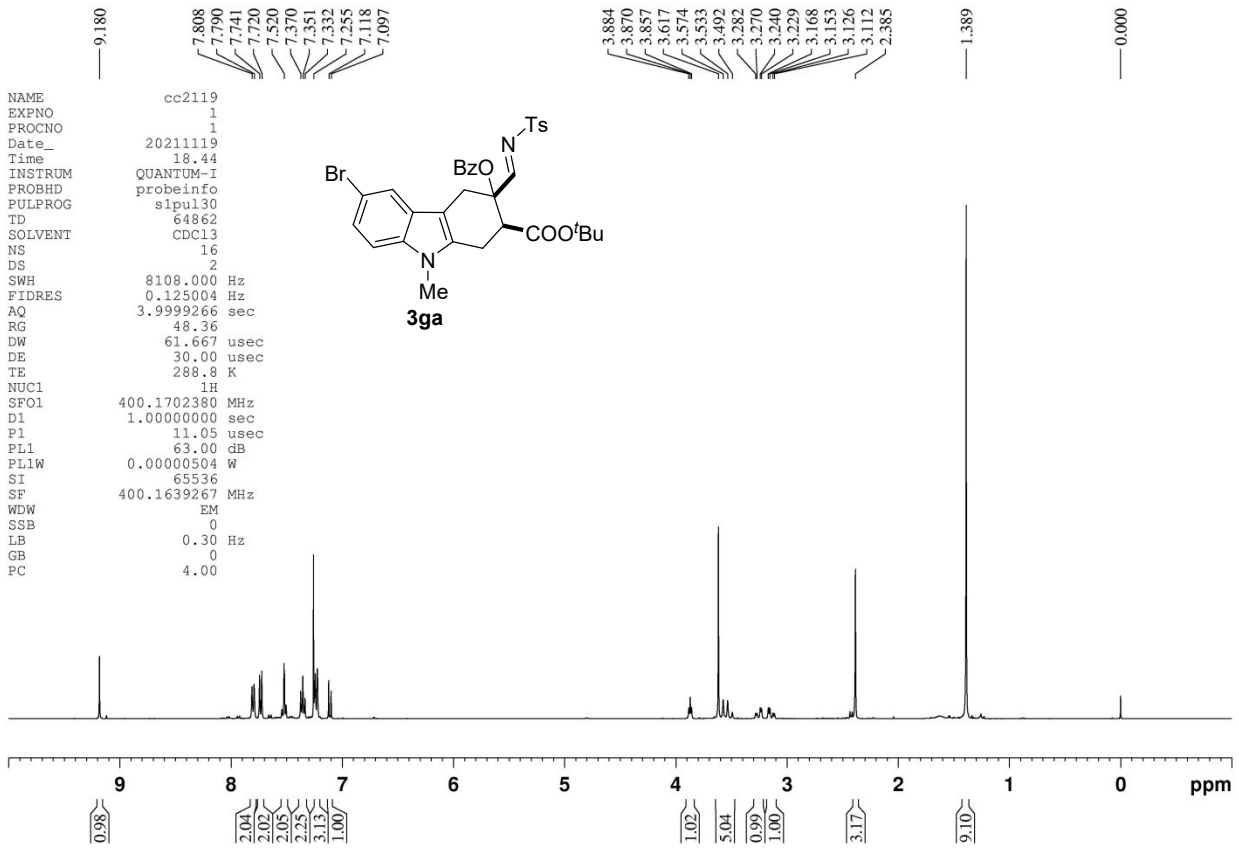



**Figure S8-57. $^{1}$H NMR of 3ga ($CDCl_3$, 400 MHz)**

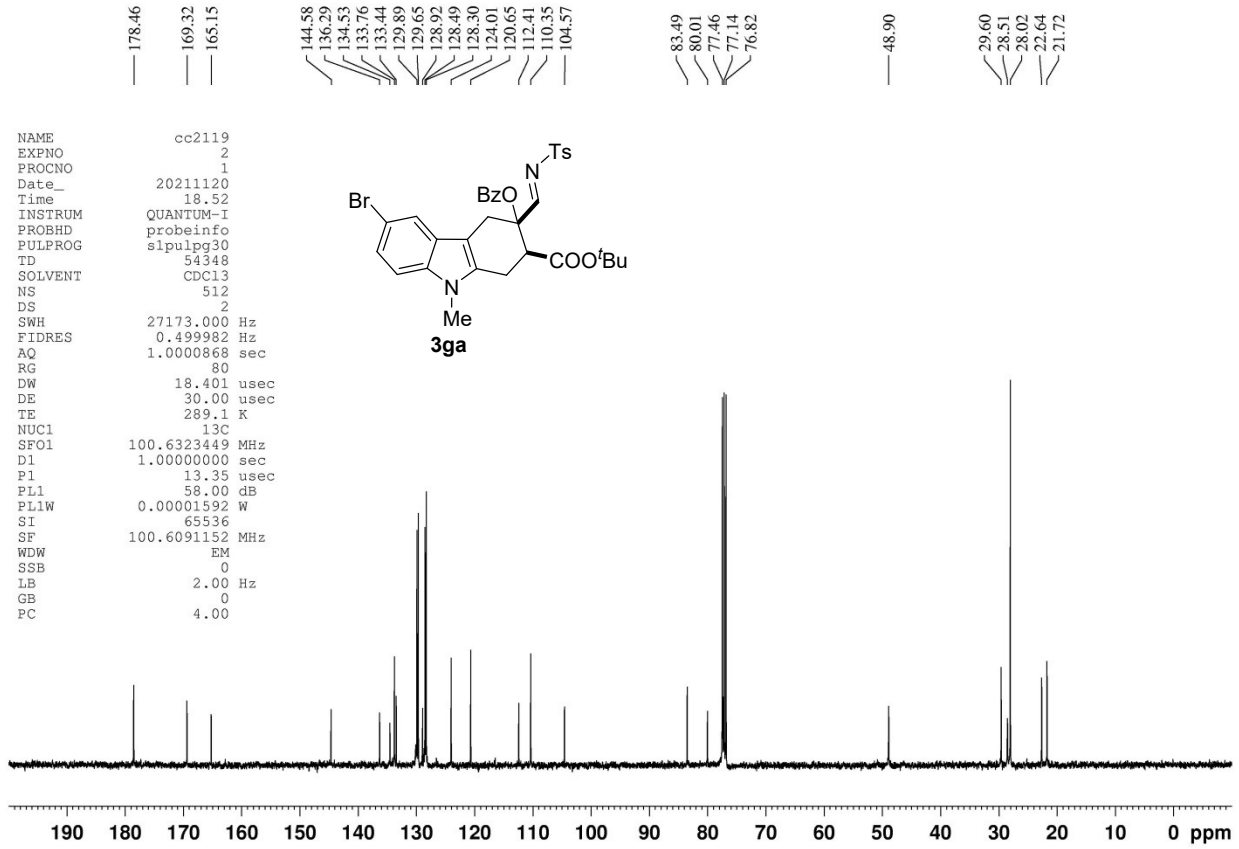



**Figure S8-58. $^{13}$C NMR of 3ga ($CDCl_3$, 101 MHz)**

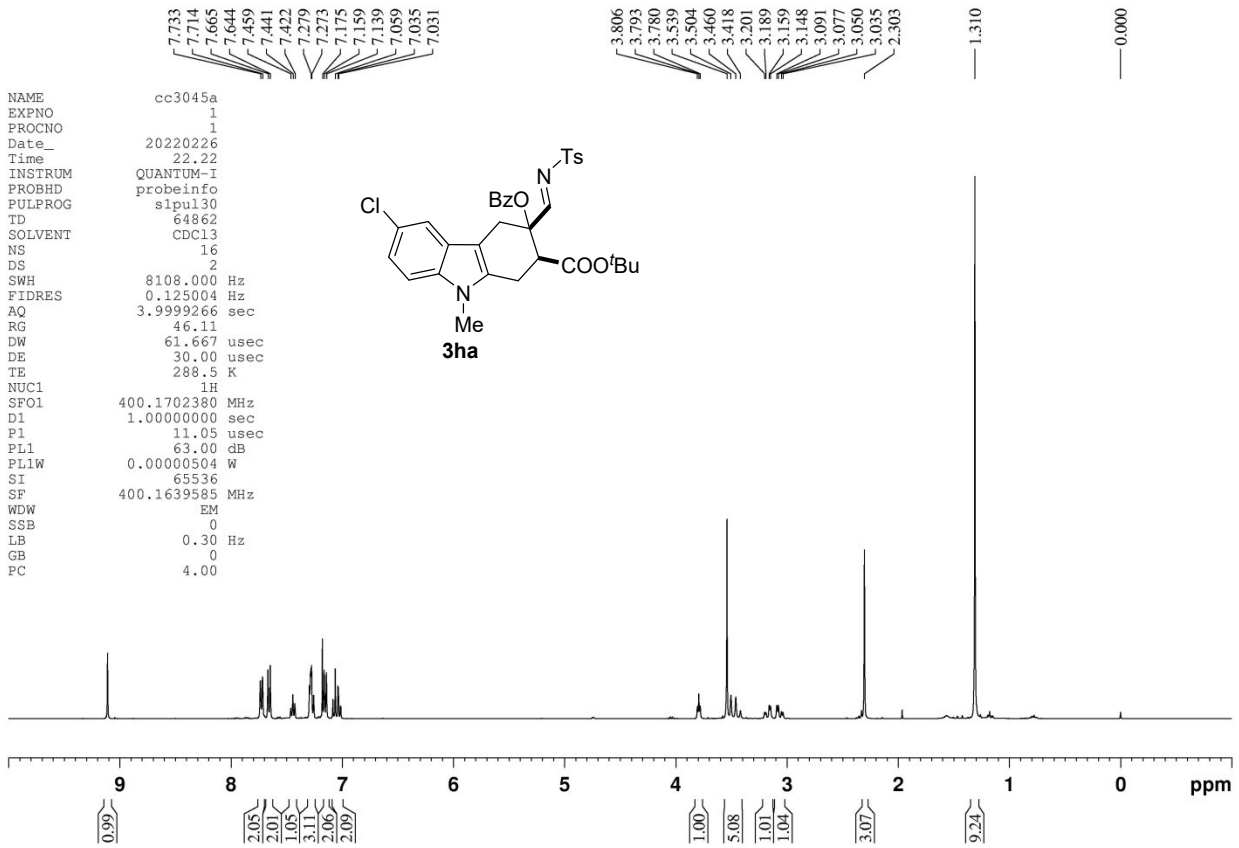



**Figure S8-59. $^{1}$H NMR of 3ha ($CDCl_3$, 400 MHz)**

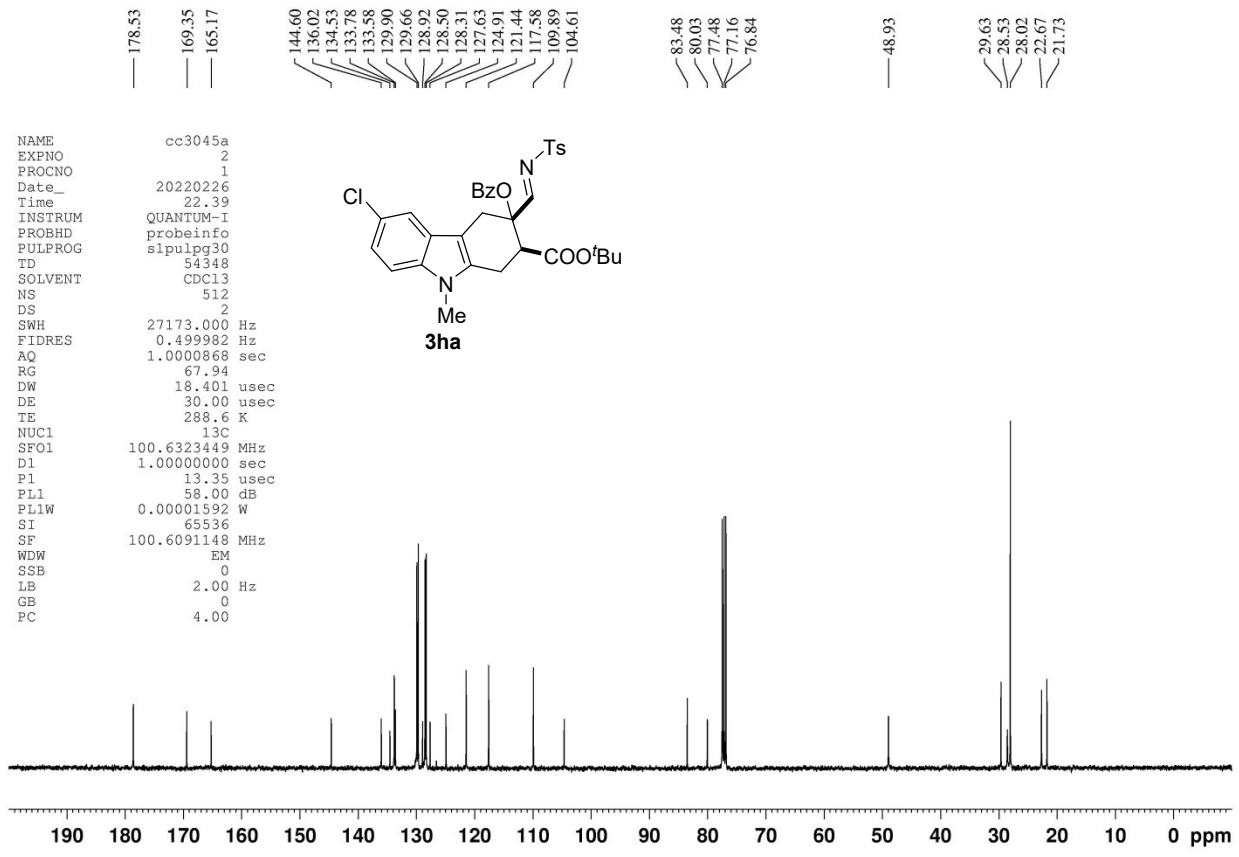



**Figure S8-60. $^{13}$C NMR of 3ha ($CDCl_3$, 101 MHz)**

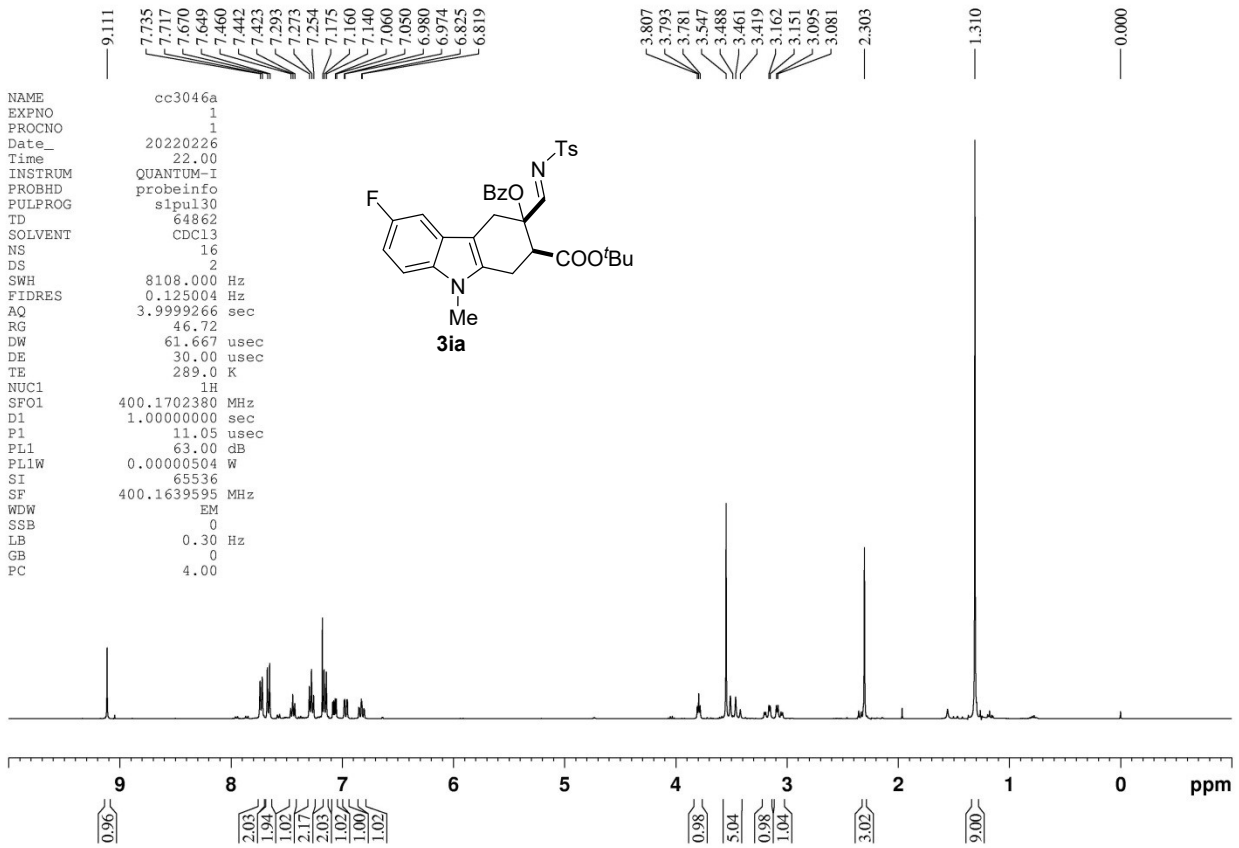



**Figure S8-61. $^{1}$H NMR of 3ia ($CDCl_3$, 400 MHz)**

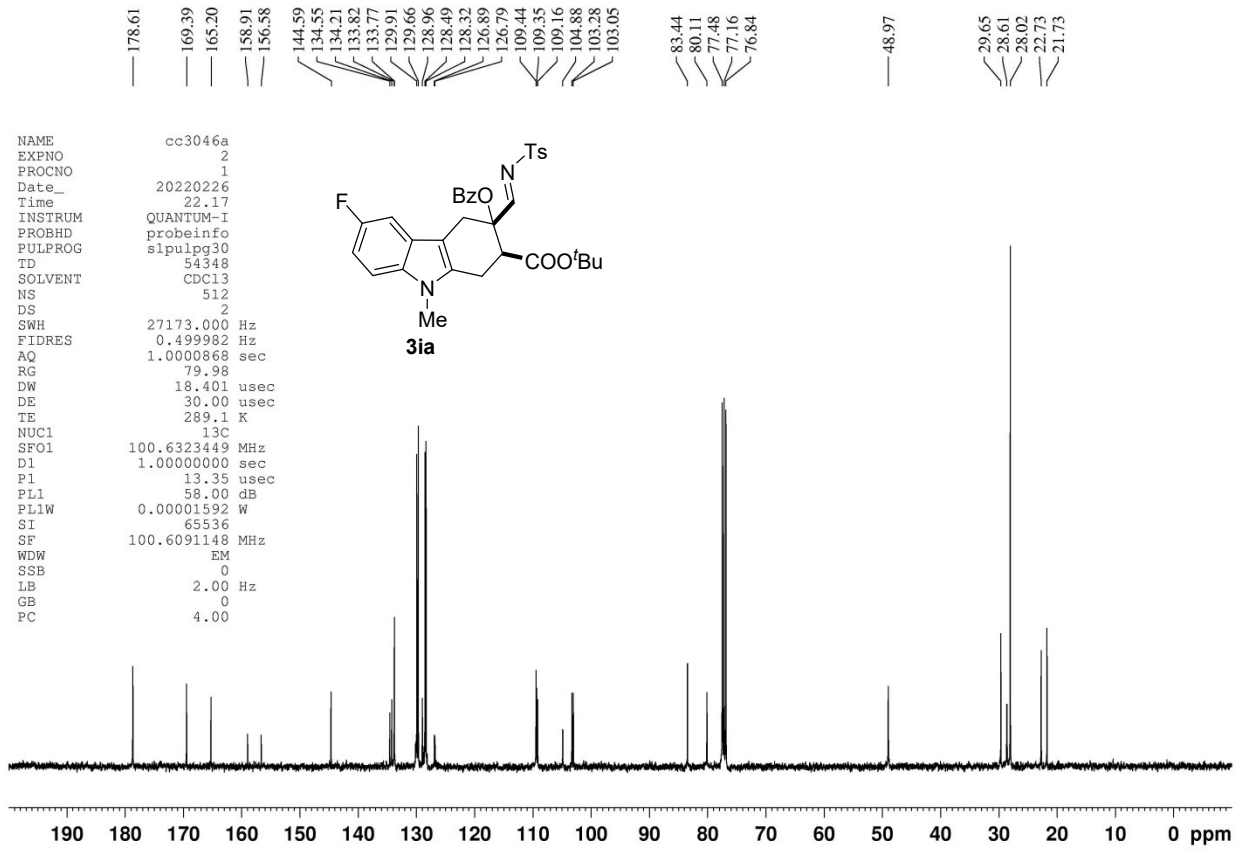



**Figure S8-62. $^{13}$C NMR of 3ia ($CDCl_3$, 101 MHz)**

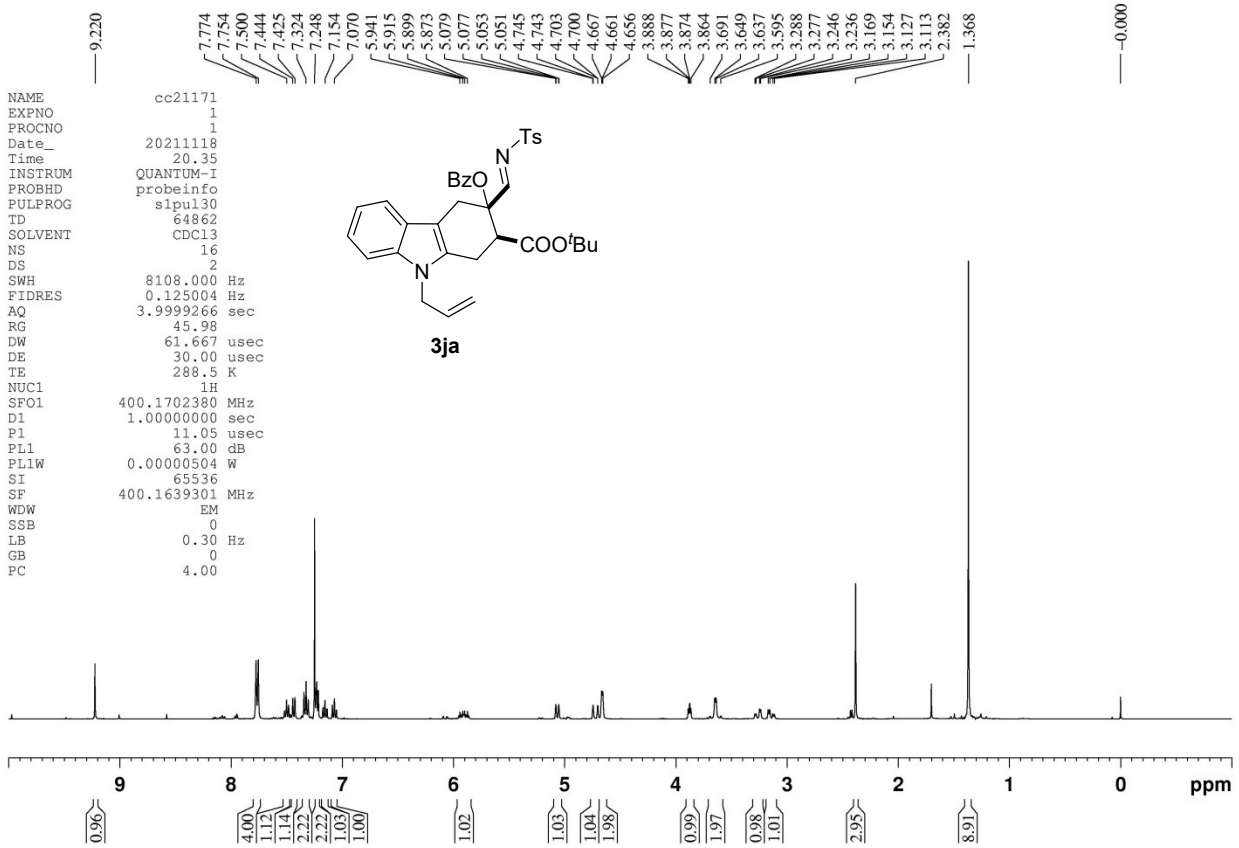



**Figure S8-63. $^{1}$H NMR of 3ja ($CDCl_3$, 400 MHz)**

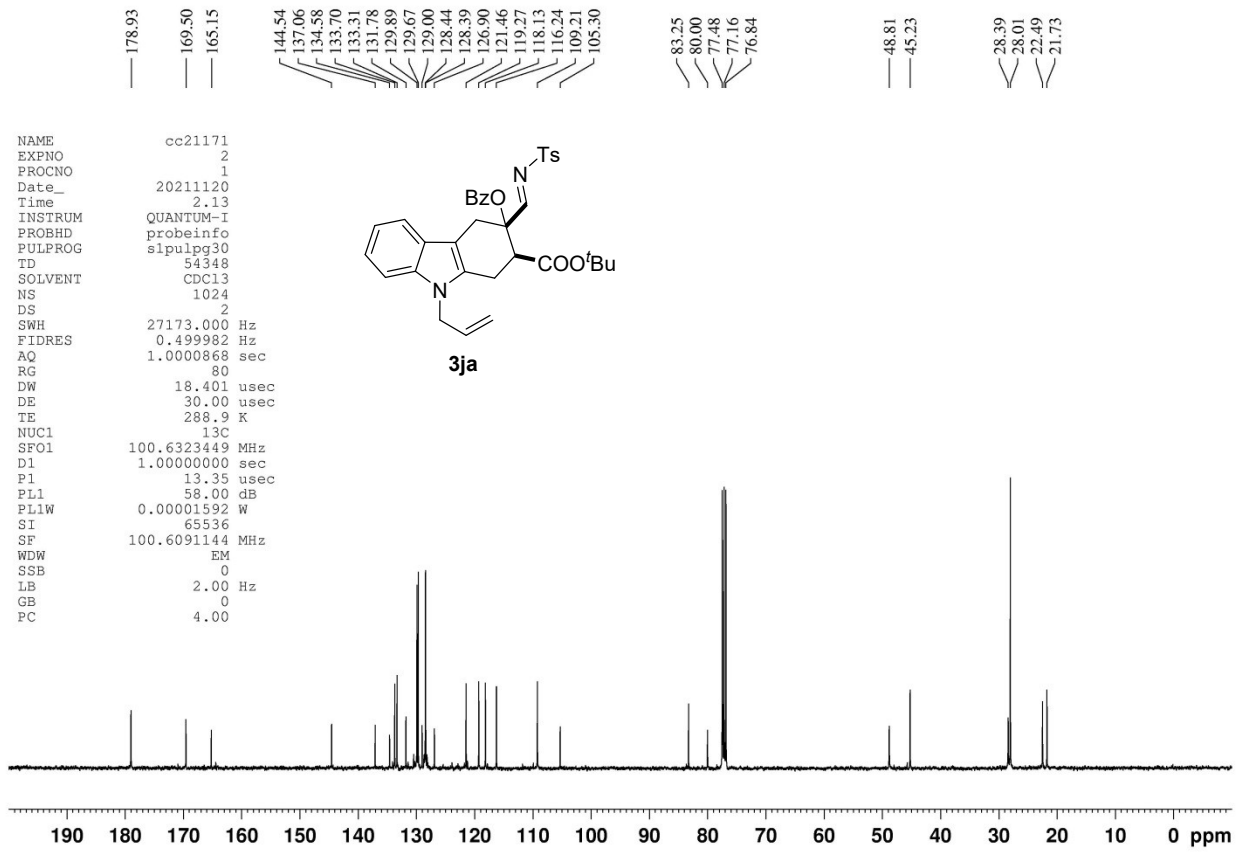



**Figure S8-64. $^{13}$C NMR of 3ja ($CDCl_3$, 101 MHz)**

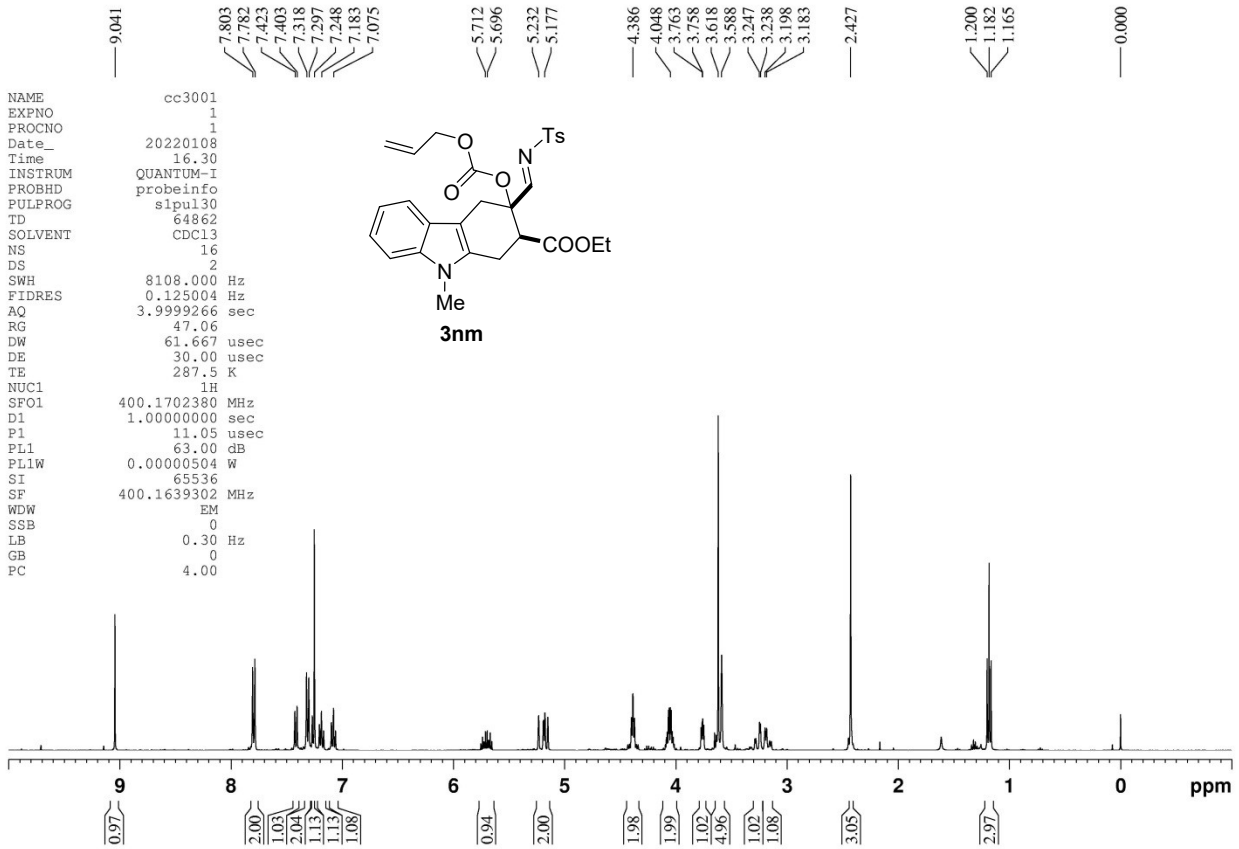



**Figure S8-65. $^{1}$H NMR of 3nm ($CDCl_3$, 400 MHz)**

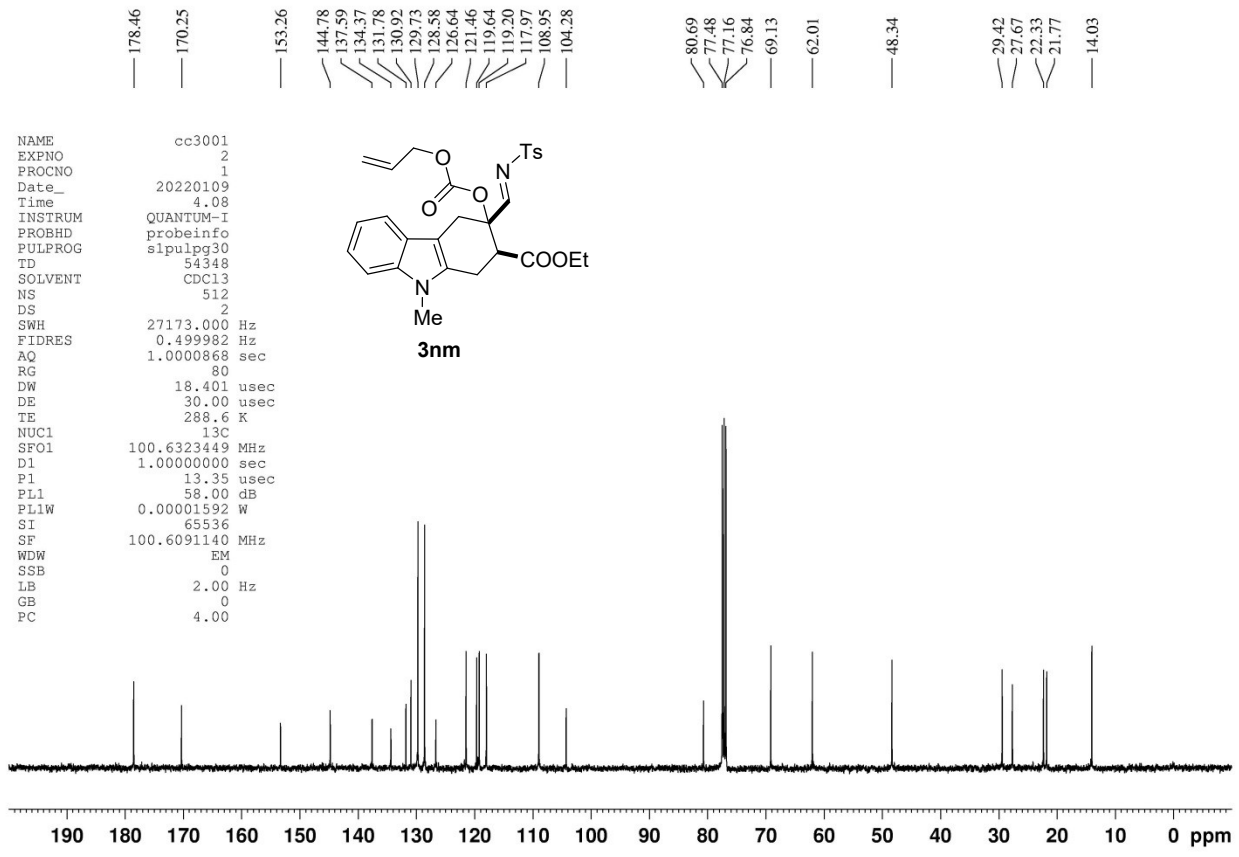



**Figure S8-66. $^{13}$C NMR of 3nm ($CDCl_3$, 101 MHz)**

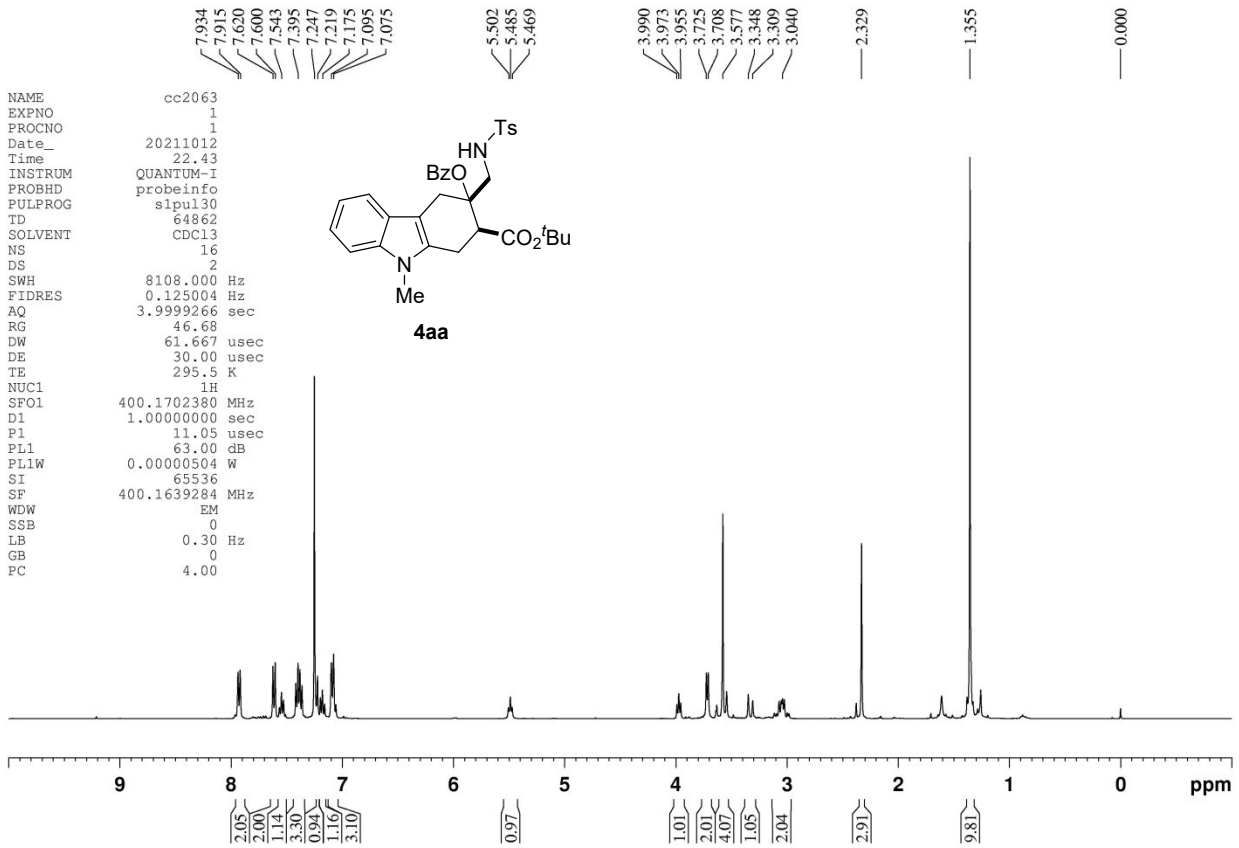



**Figure S8-67. $^{1}$H NMR of 4aa ($CDCl_3$, 400 MHz)**

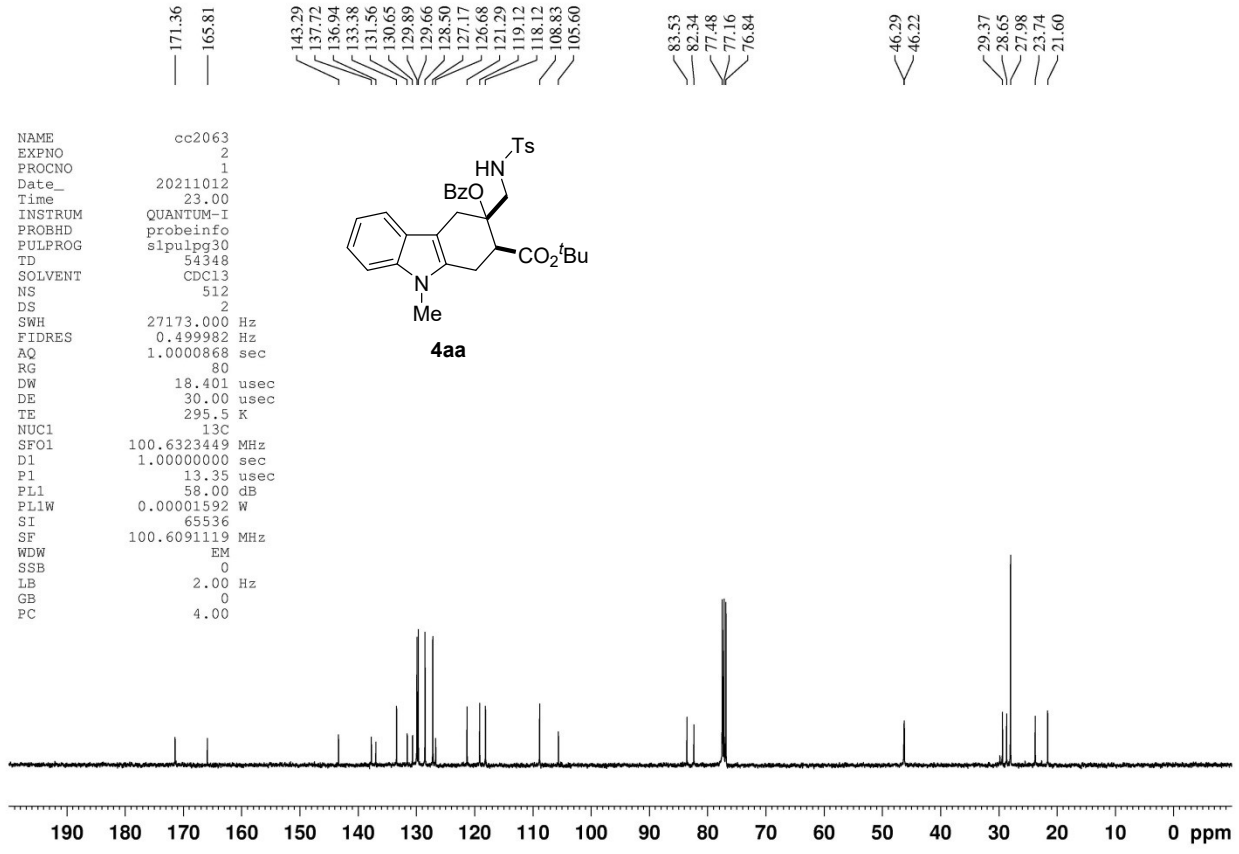



**Figure S8-68. $^{13}$C NMR of 4aa ($CDCl_3$, 101 MHz)**

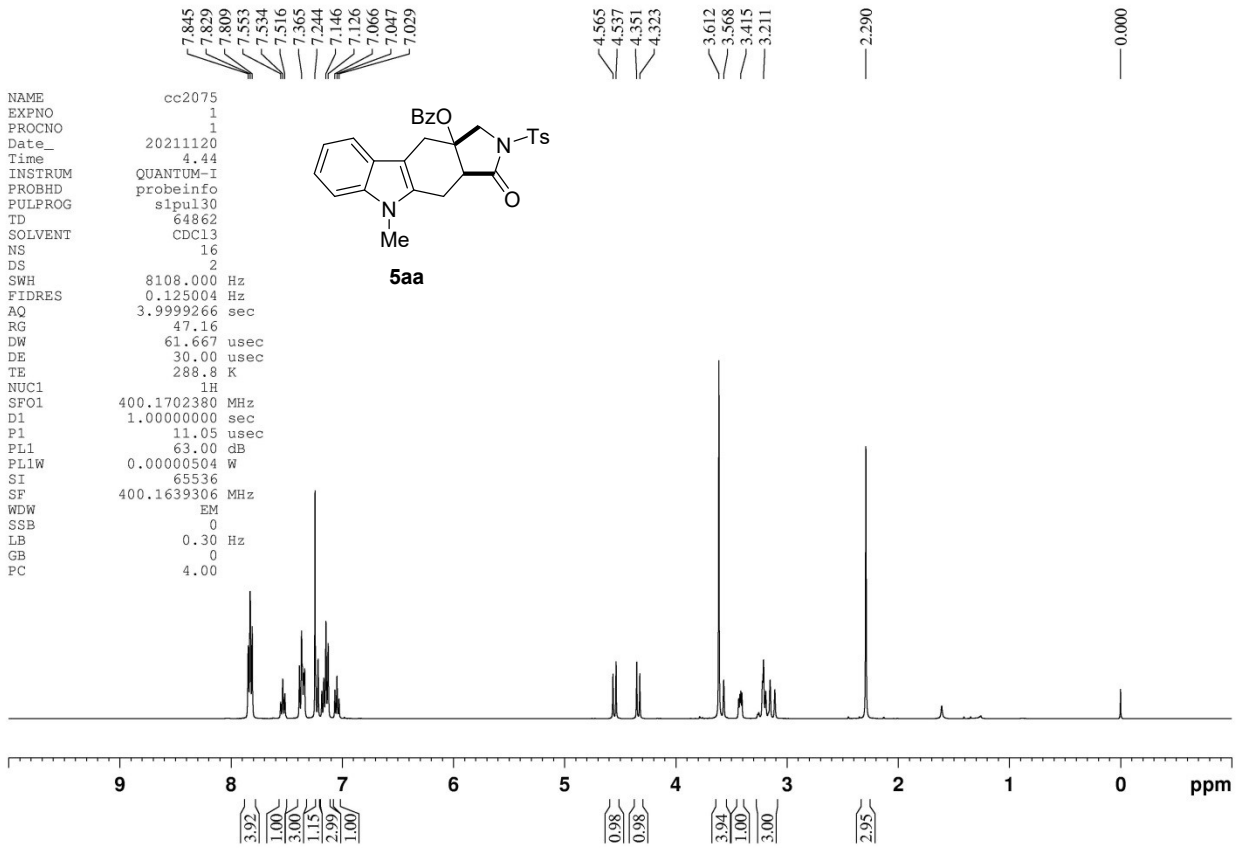



**Figure S8-69. $^{1}$H NMR of 5aa ($CDCl_3$, 400 MHz)**

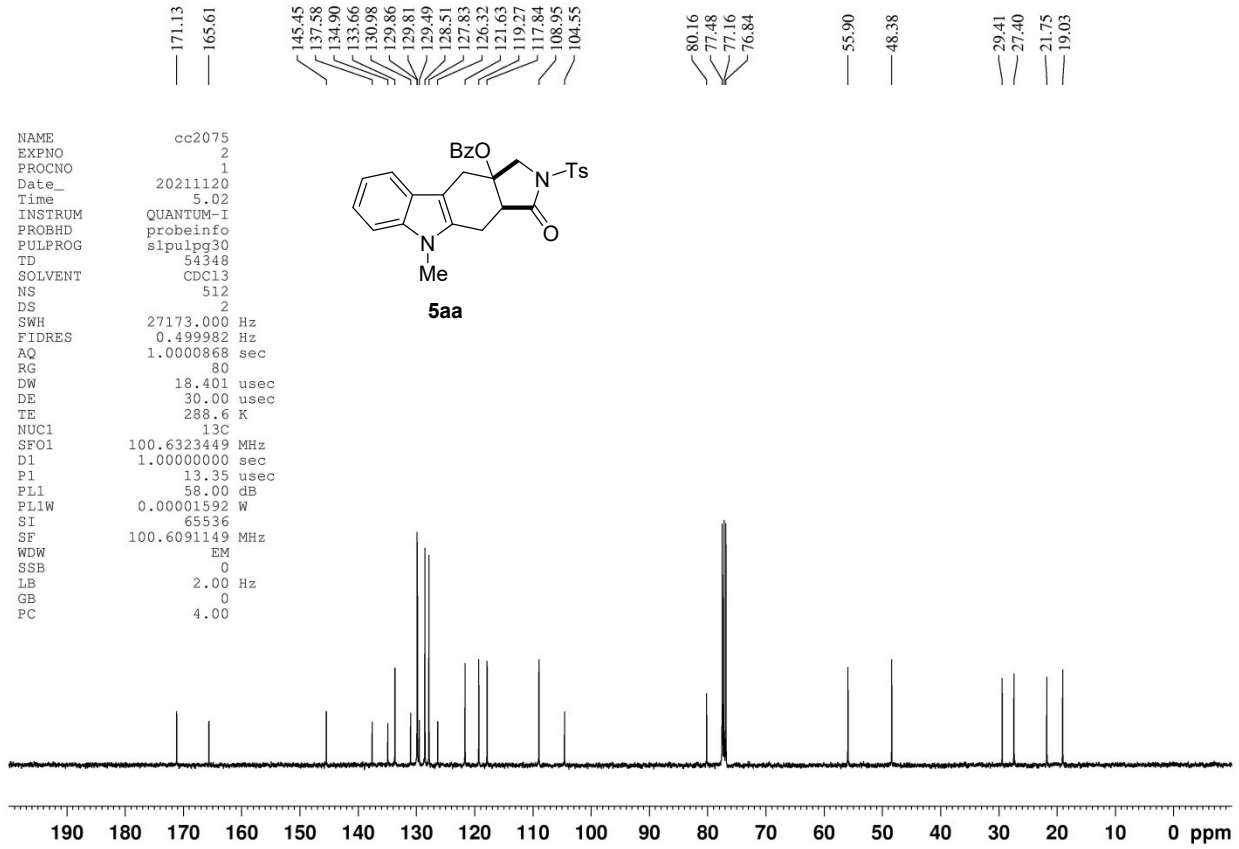



**Figure S8-70. $^{13}$C NMR of 5aa ($CDCl_3$, 101 MHz)**

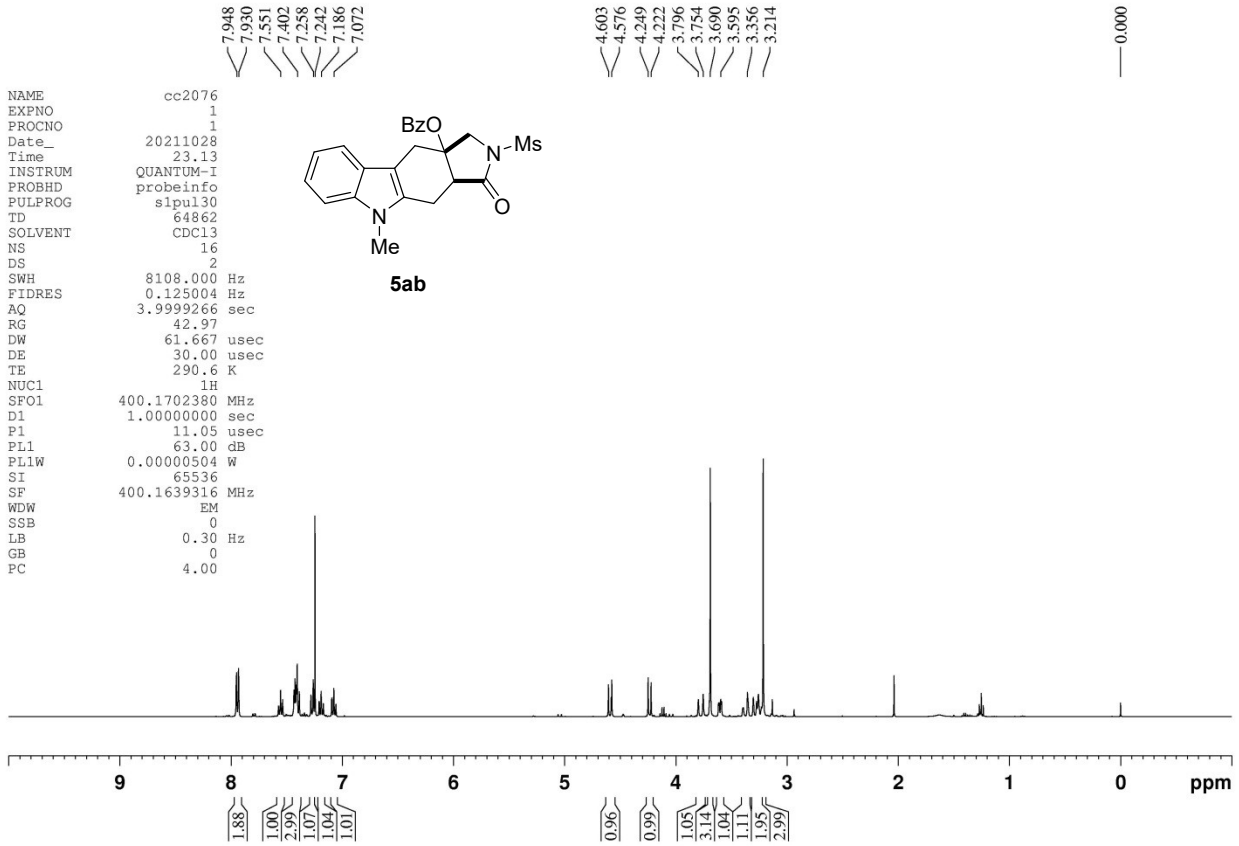



**Figure S8-71. $^{1}$H NMR of 5ab ($CDCl_3$, 400 MHz)**

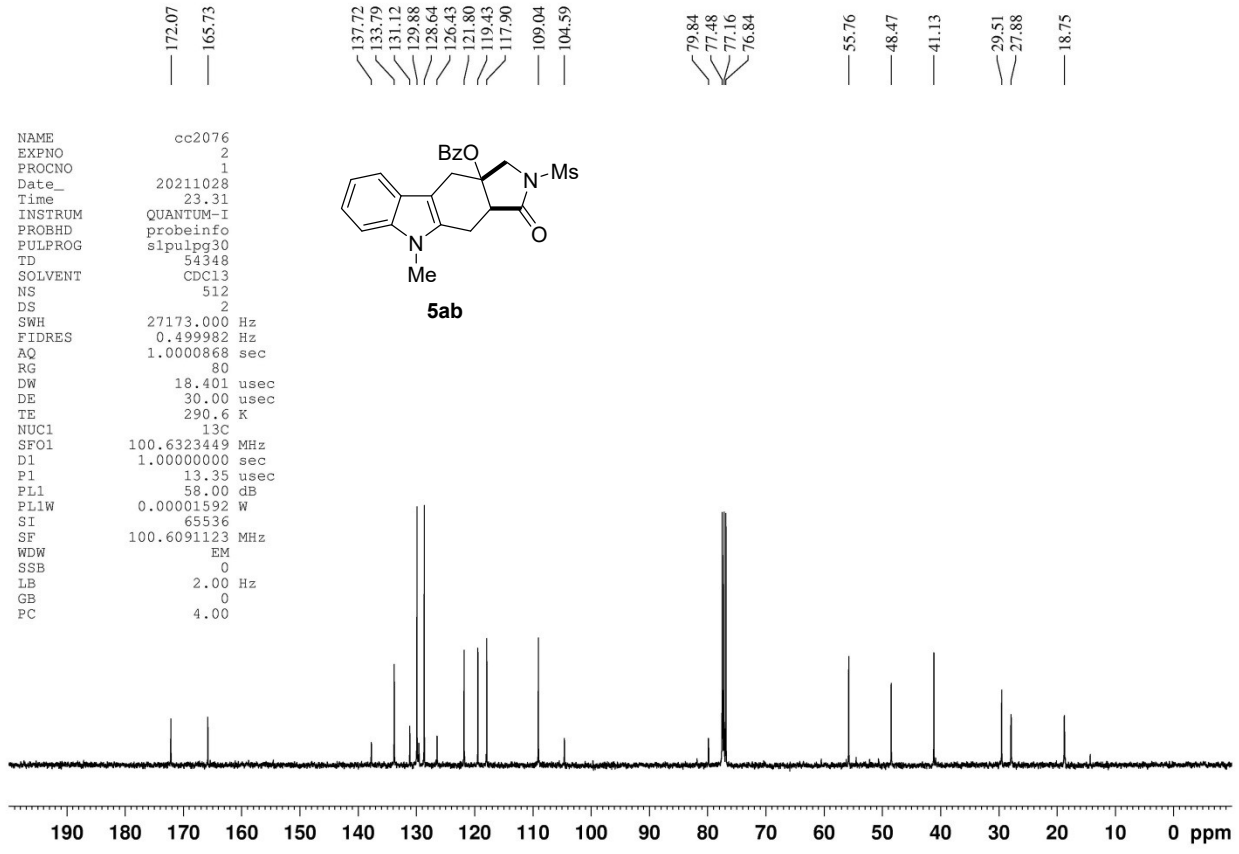



**Figure S8-72. $^{13}$C NMR of 5ab ($CDCl_3$, 101 MHz)**

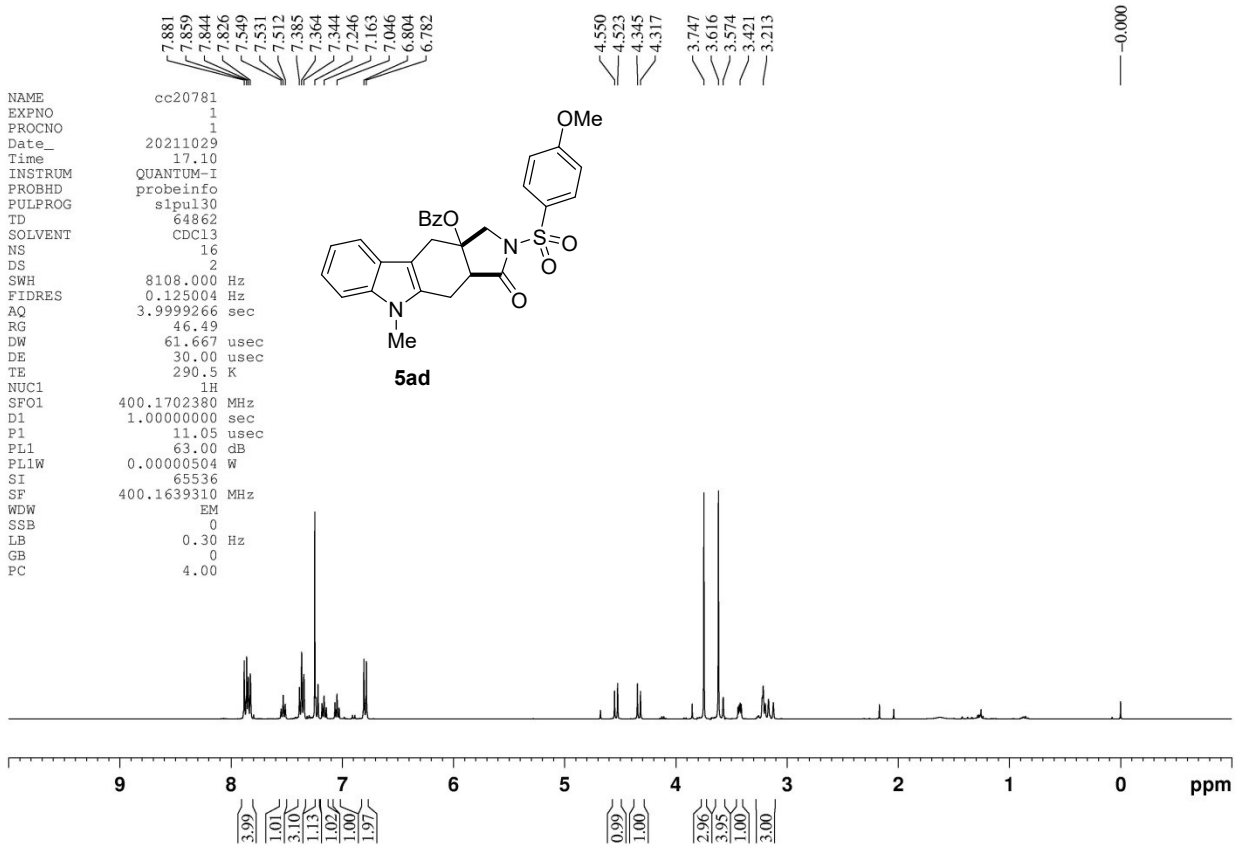



**Figure S8-73. $^{1}$H NMR of 5ad ($CDCl_3$, 400 MHz)**

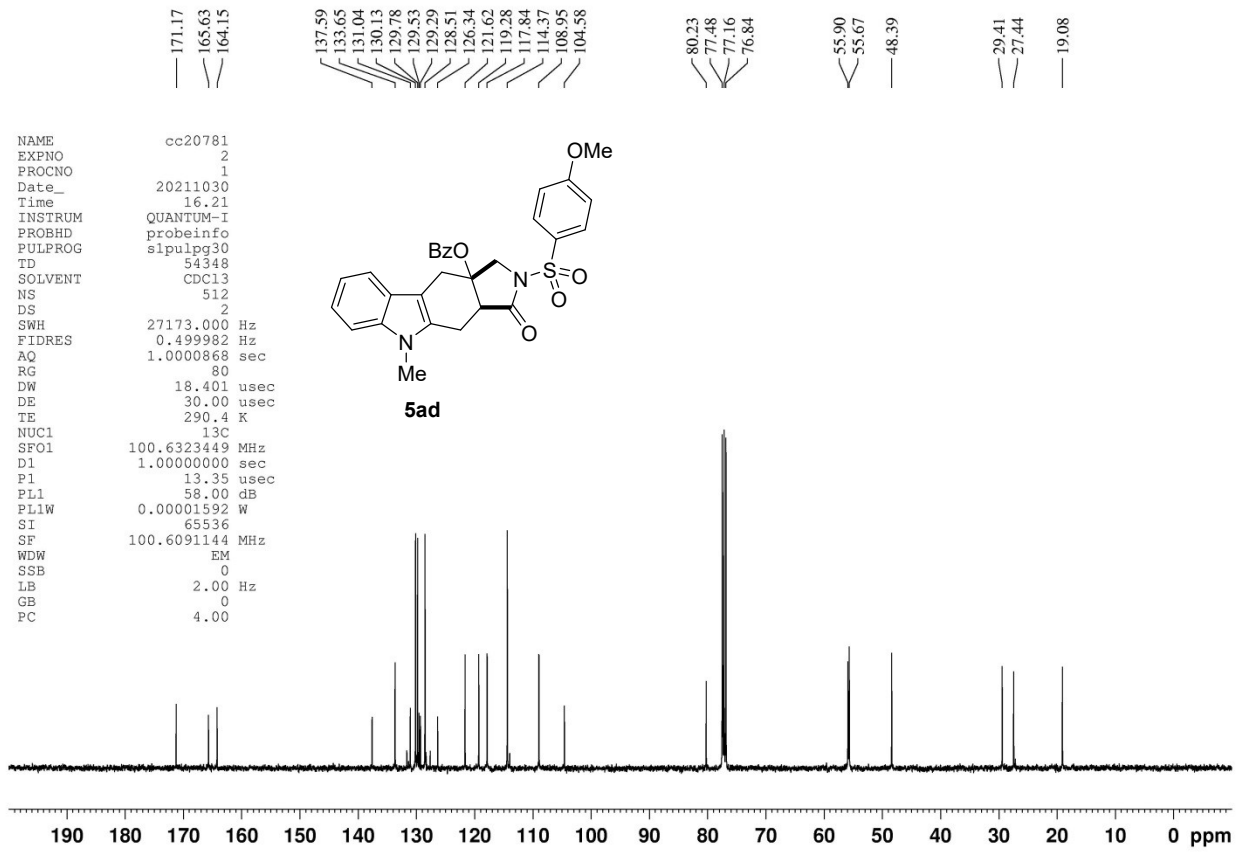



**Figure S8-74. $^{13}$C NMR of 5ad ($CDCl_3$, 101 MHz)**

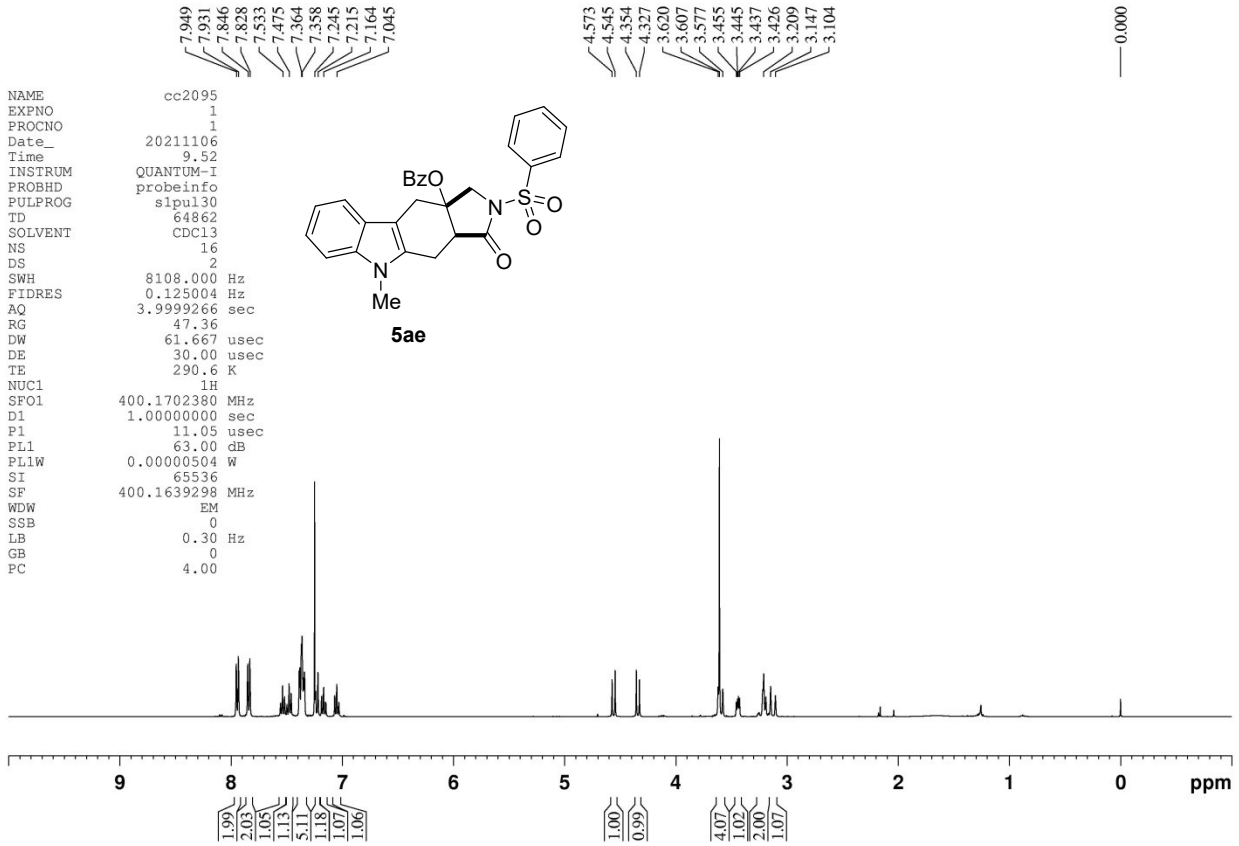



**Figure S8-75. $^{1}$H NMR of 5ae ($CDCl_3$, 400 MHz)**

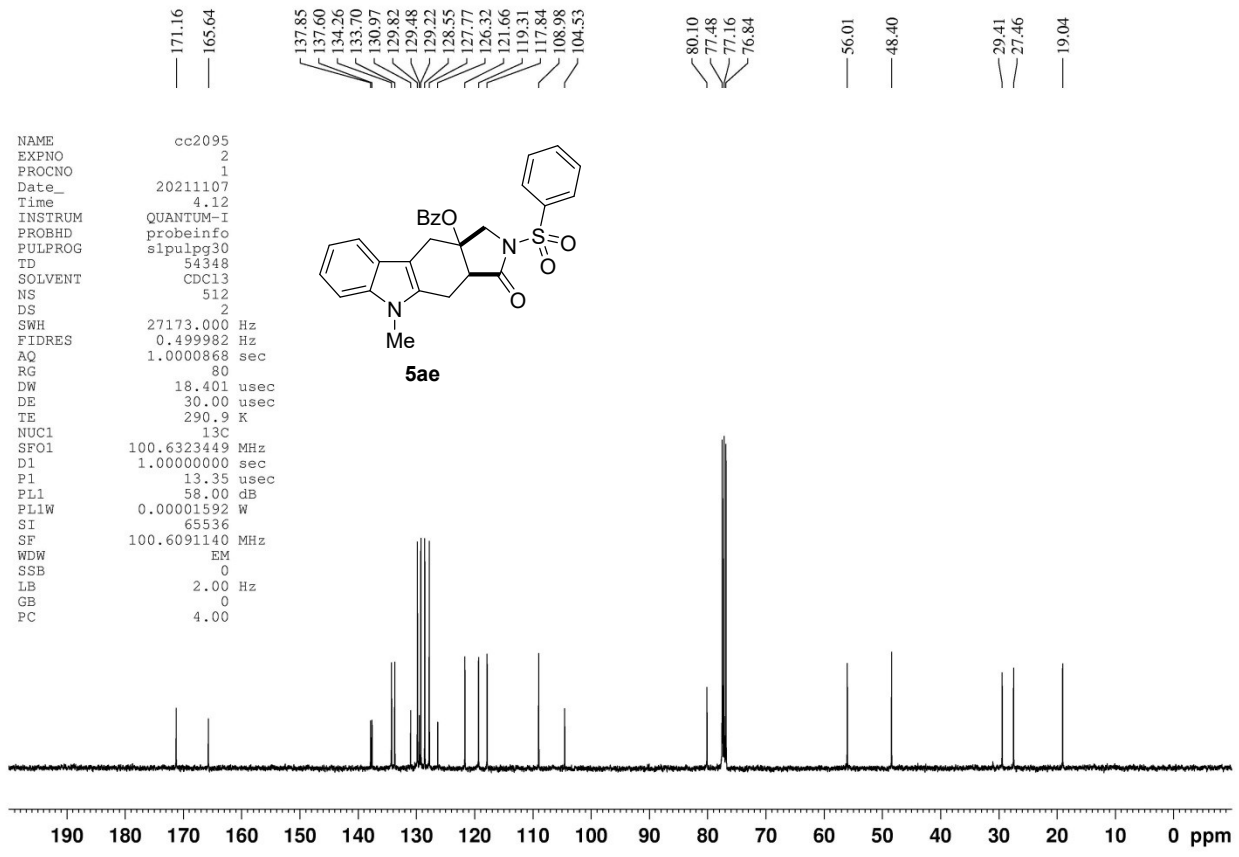



**Figure S8-76. $^{13}$C NMR of 5ae ($CDCl_3$, 101 MHz)**

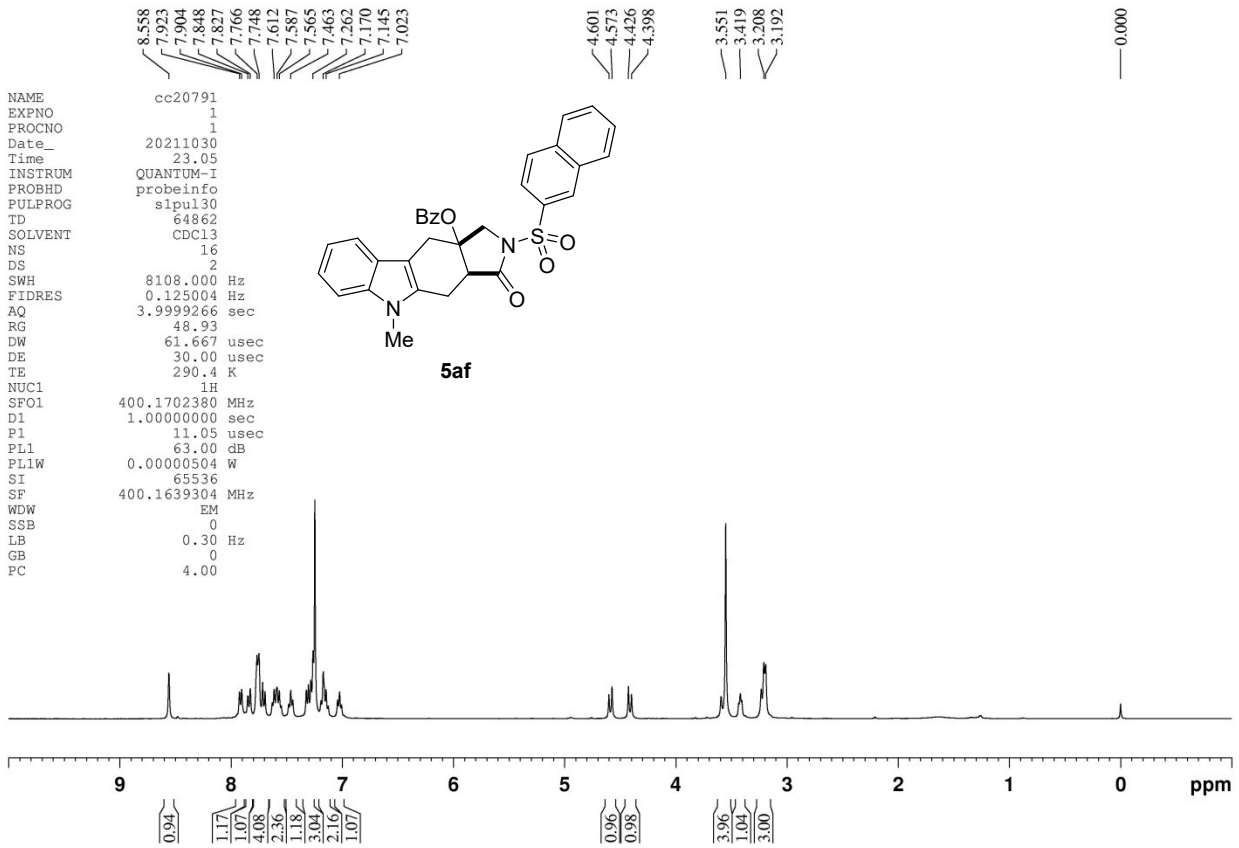



**Figure S8-77. $^{1}$H NMR of 5af ($CDCl_3$, 400 MHz)**

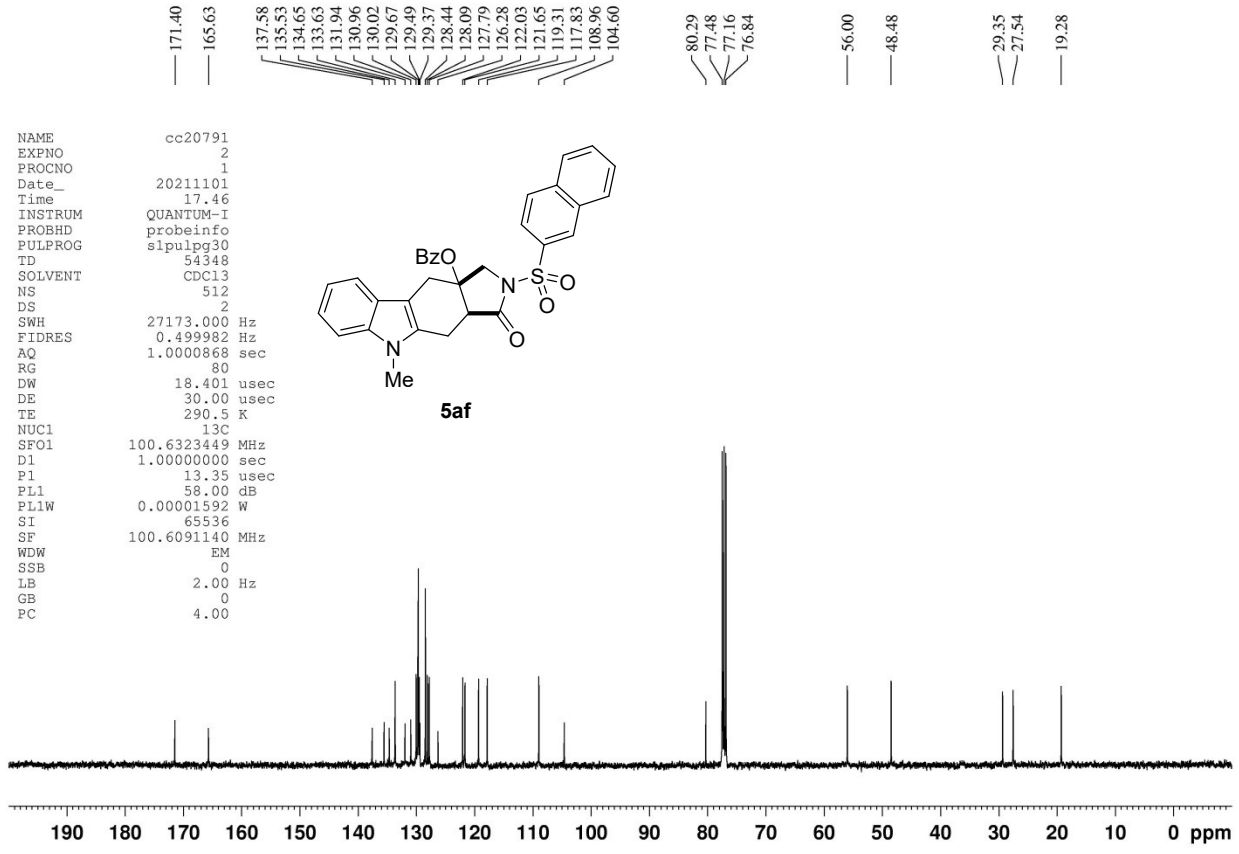



**Figure S8-78. $^{13}$C NMR of 5af ($CDCl_3$, 101 MHz)**

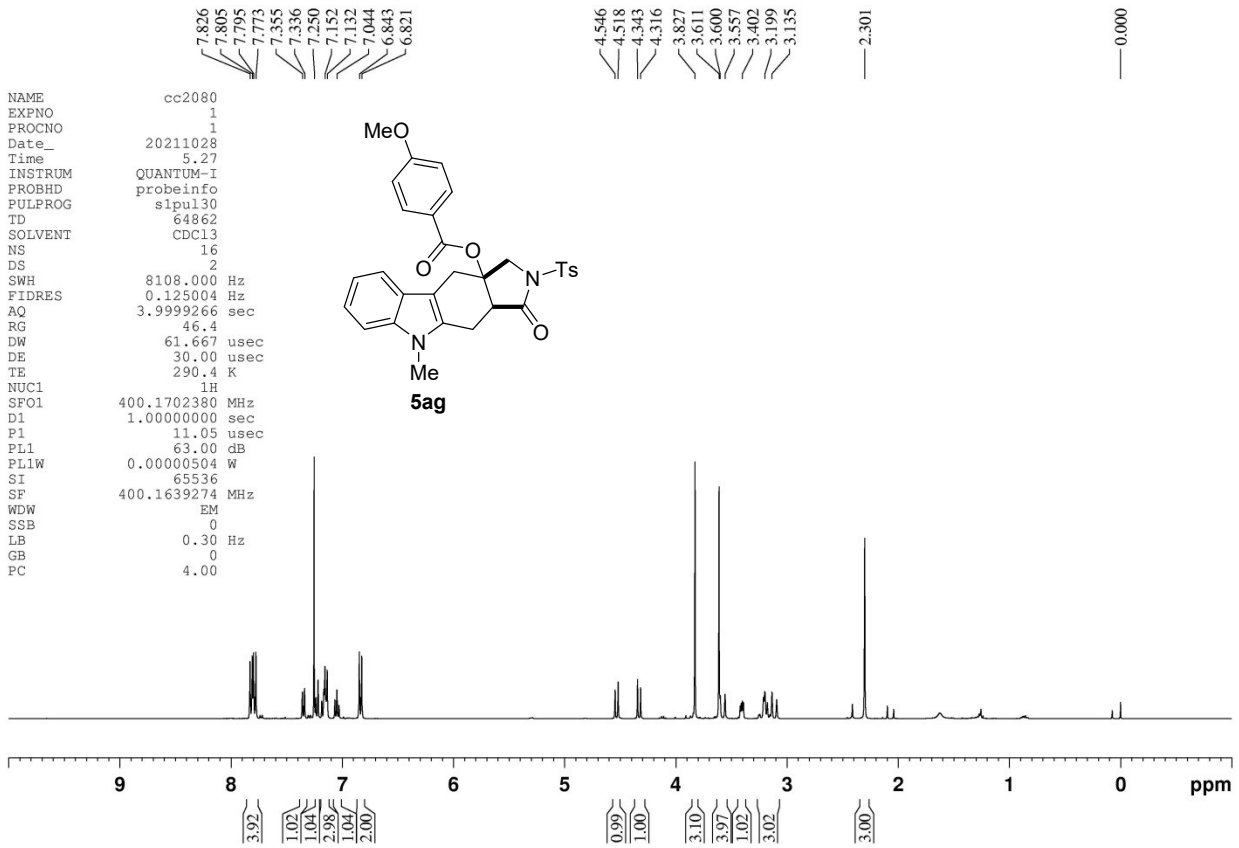



**Figure S8-79. $^{1}$H NMR of 5ag ($CDCl_3$, 400 MHz)**

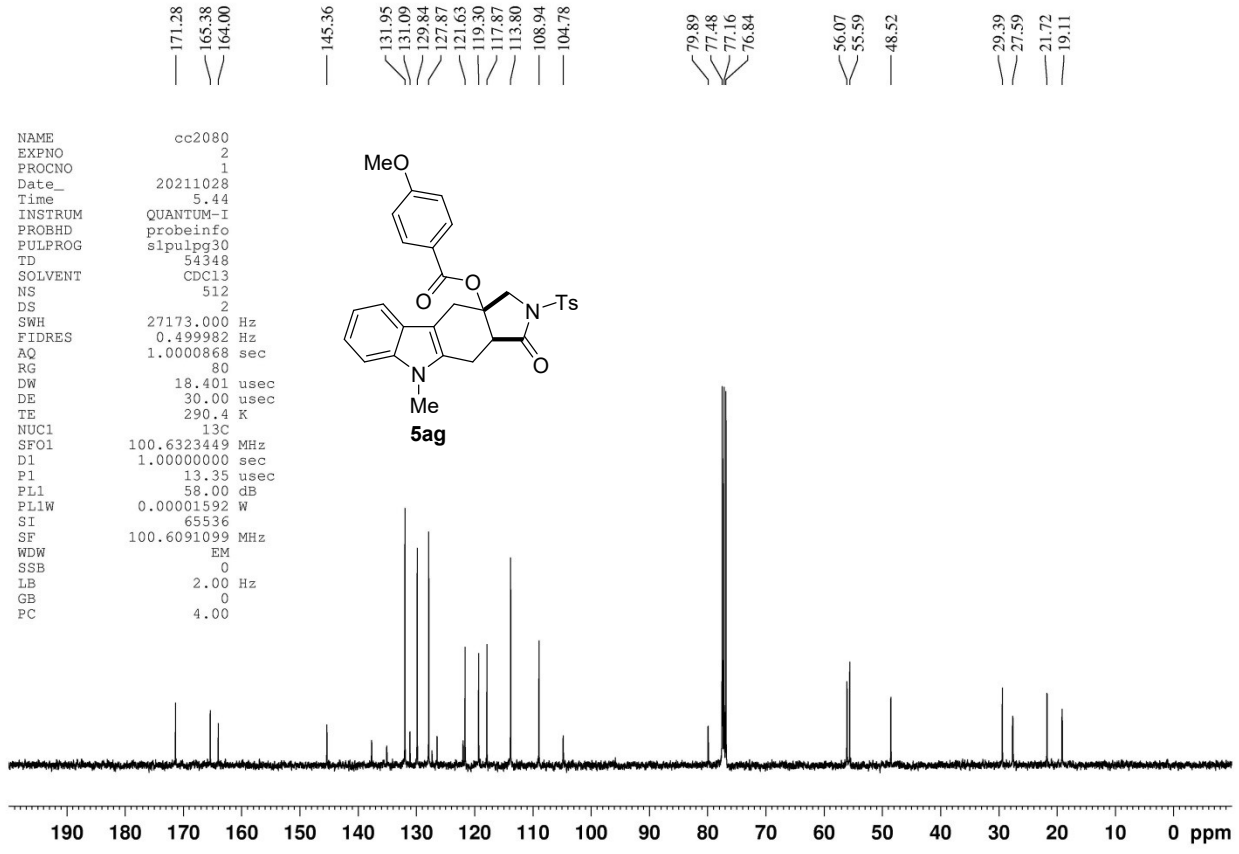



**Figure S8-80. $^{13}$C NMR of 5ag ($CDCl_3$, 101 MHz)**

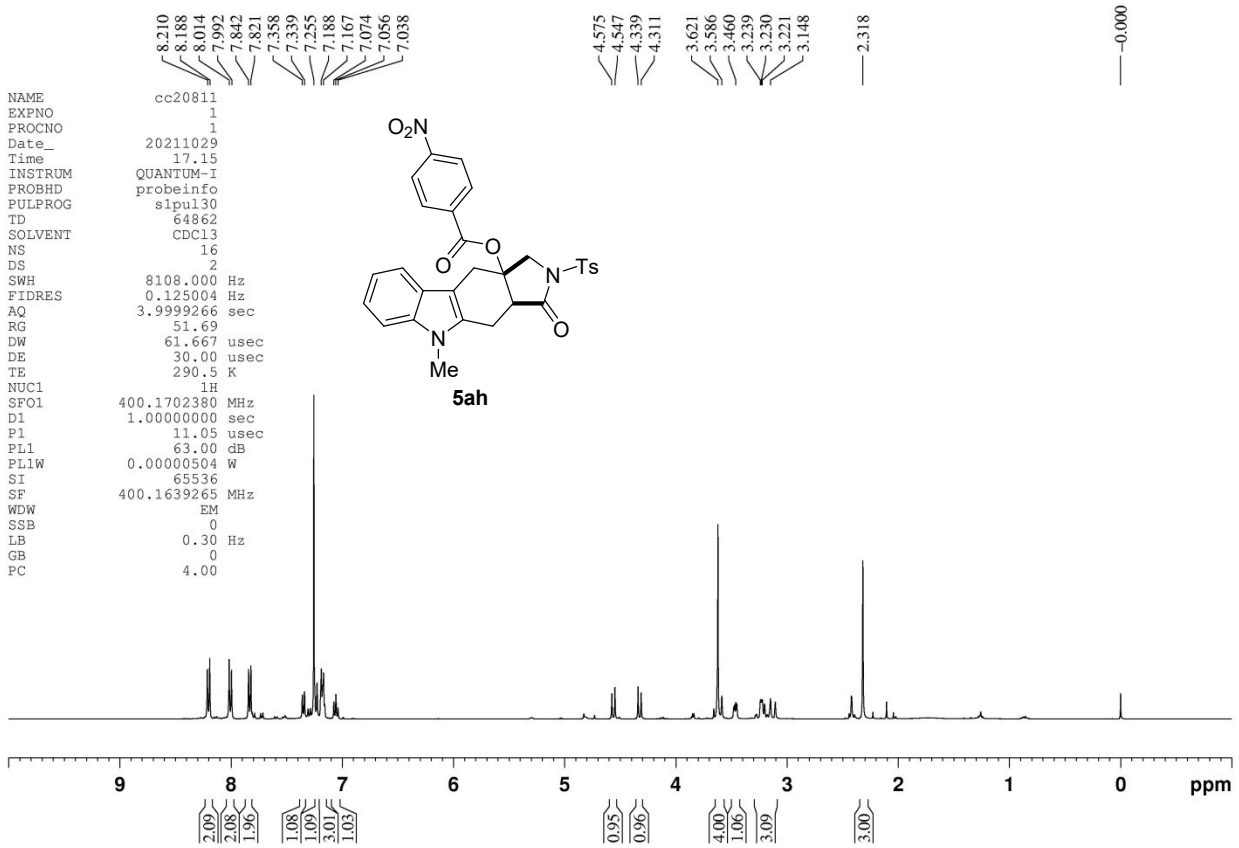



**Figure S8-81. $^{1}$H NMR of 5ah ($CDCl_3$, 400 MHz)**

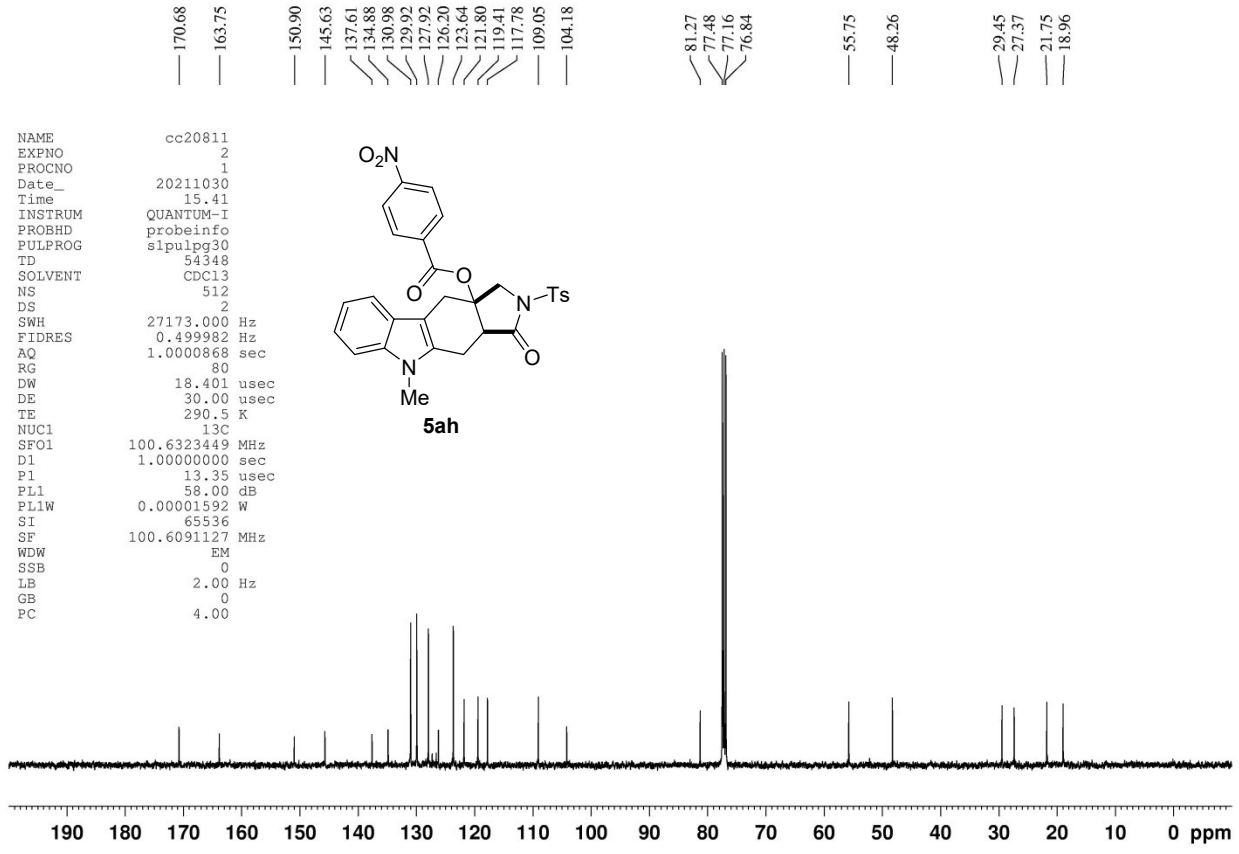



**Figure S8-82. $^{13}$C NMR of 5ah ($CDCl_3$, 101 MHz)**

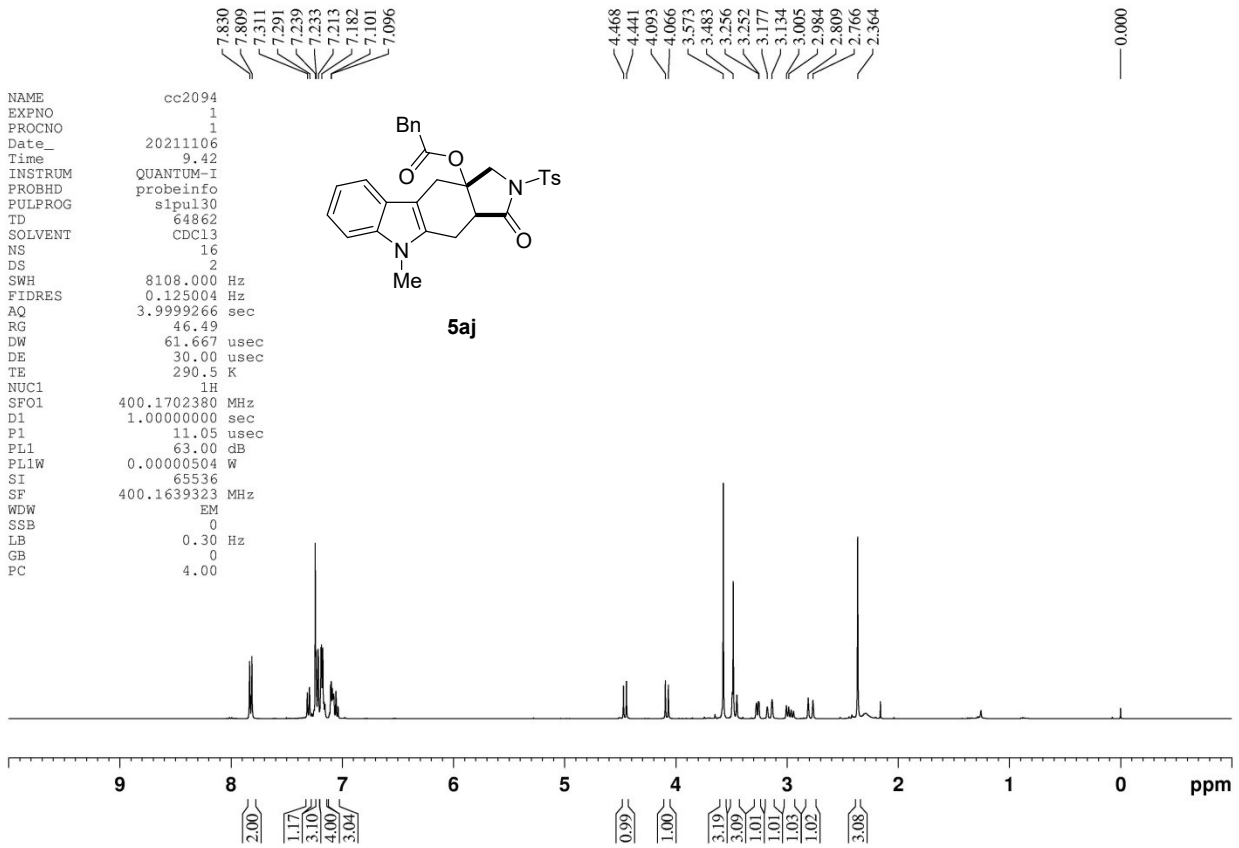



**Figure S8-83. $^{1}$H NMR of 5aj ($CDCl_3$, 400 MHz)**

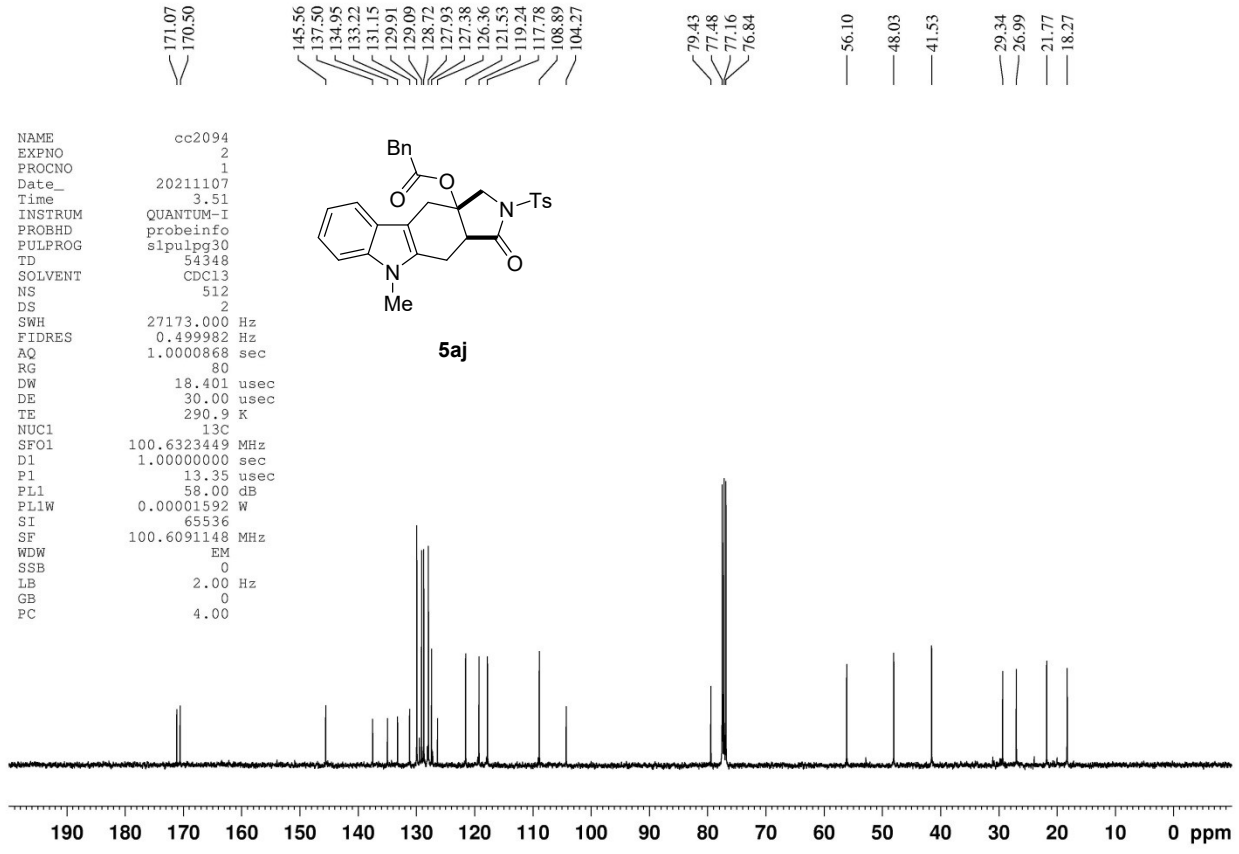



**Figure S8-84. $^{13}$C NMR of 5aj ($CDCl_3$, 101 MHz)**

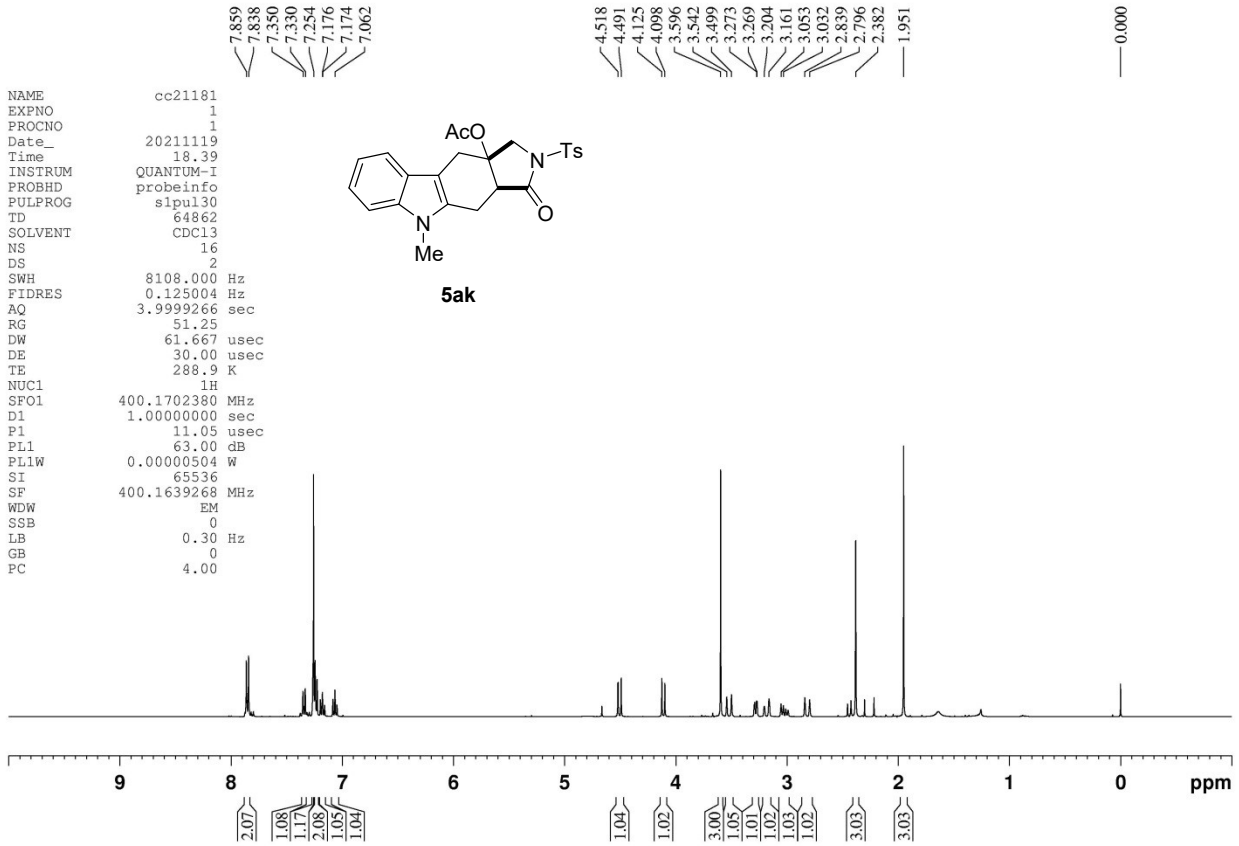



**Figure S8-85. $^{1}$H NMR of 5ak ($CDCl_3$, 400 MHz)**

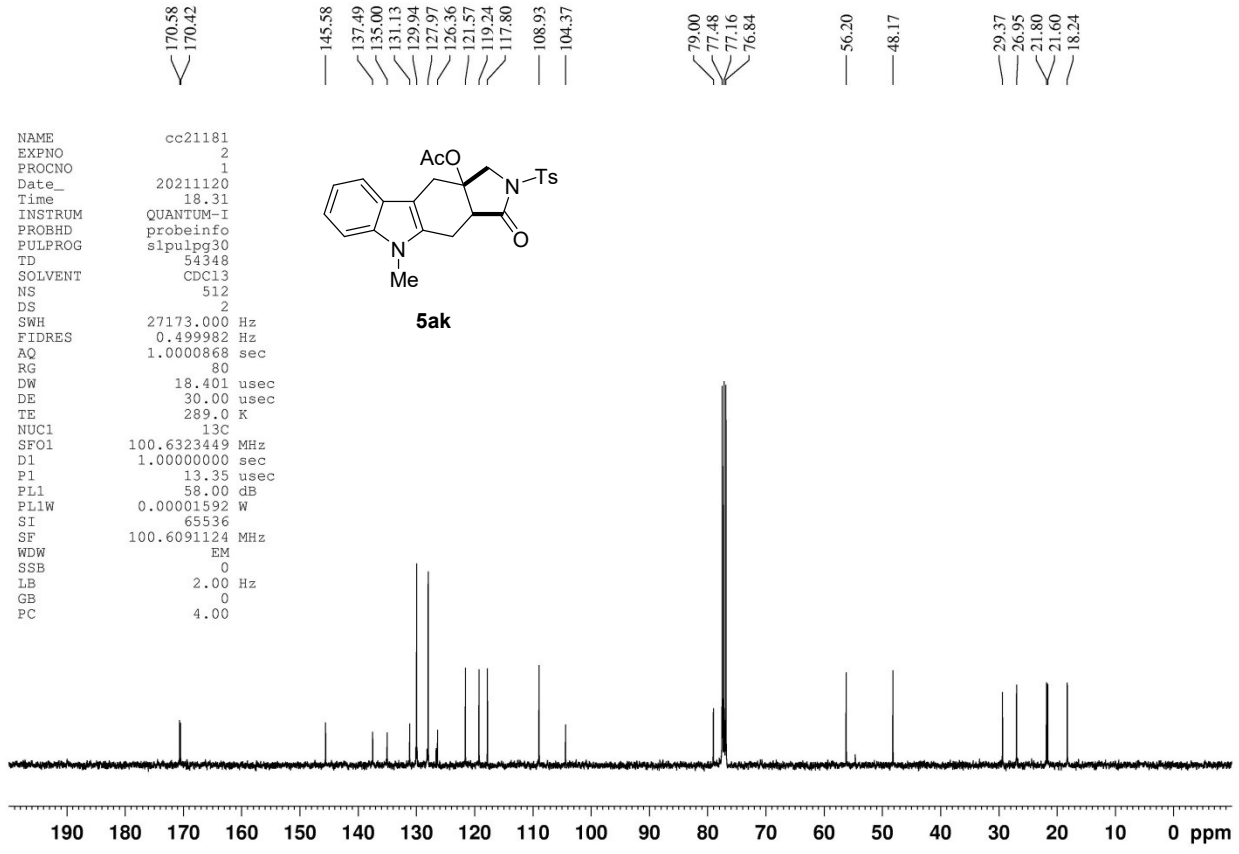



**Figure S8-86. $^{13}$C NMR of 5ak ($CDCl_3$, 101 MHz)**

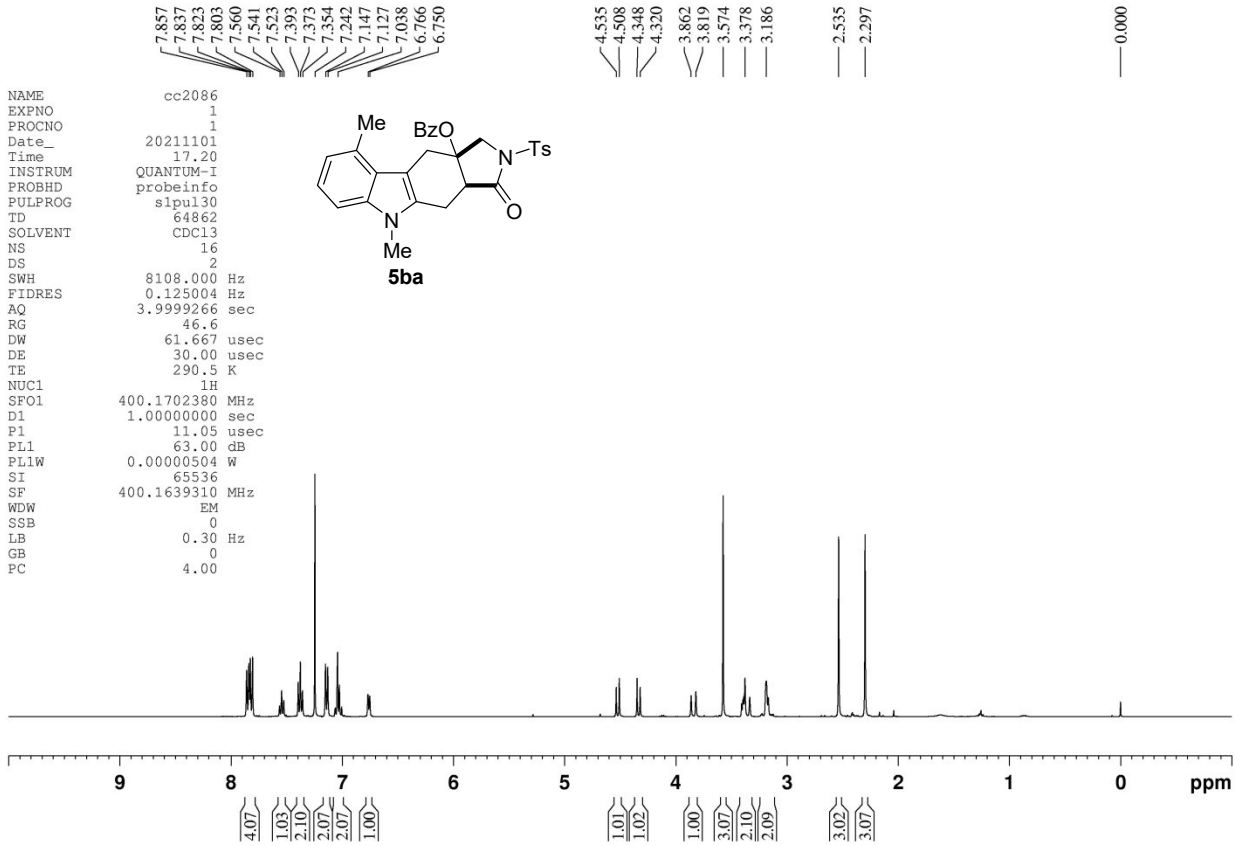



**Figure S8-87. $^{1}$H NMR of 5ba ($CDCl_3$, 400 MHz)**

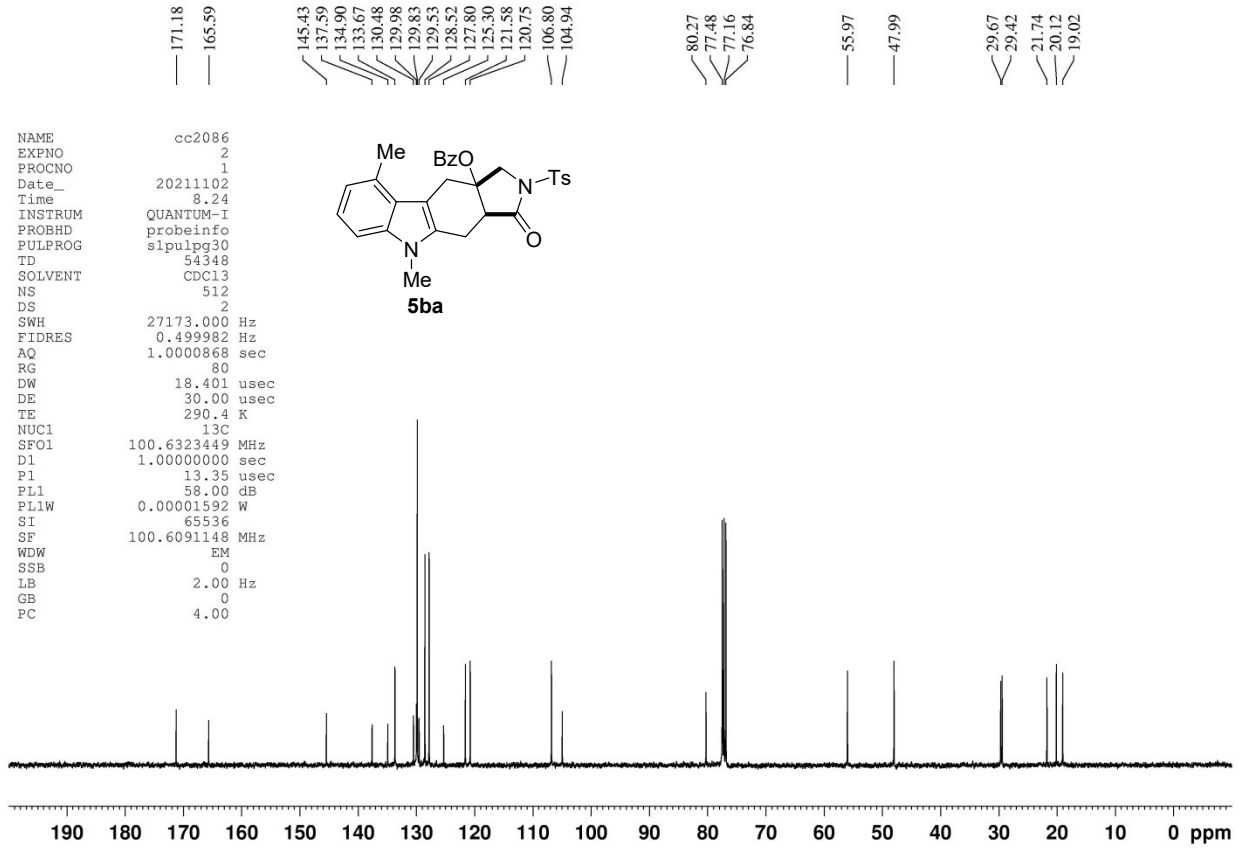



**Figure S8-88. $^{13}$C NMR of 5ba ($CDCl_3$, 101 MHz)**

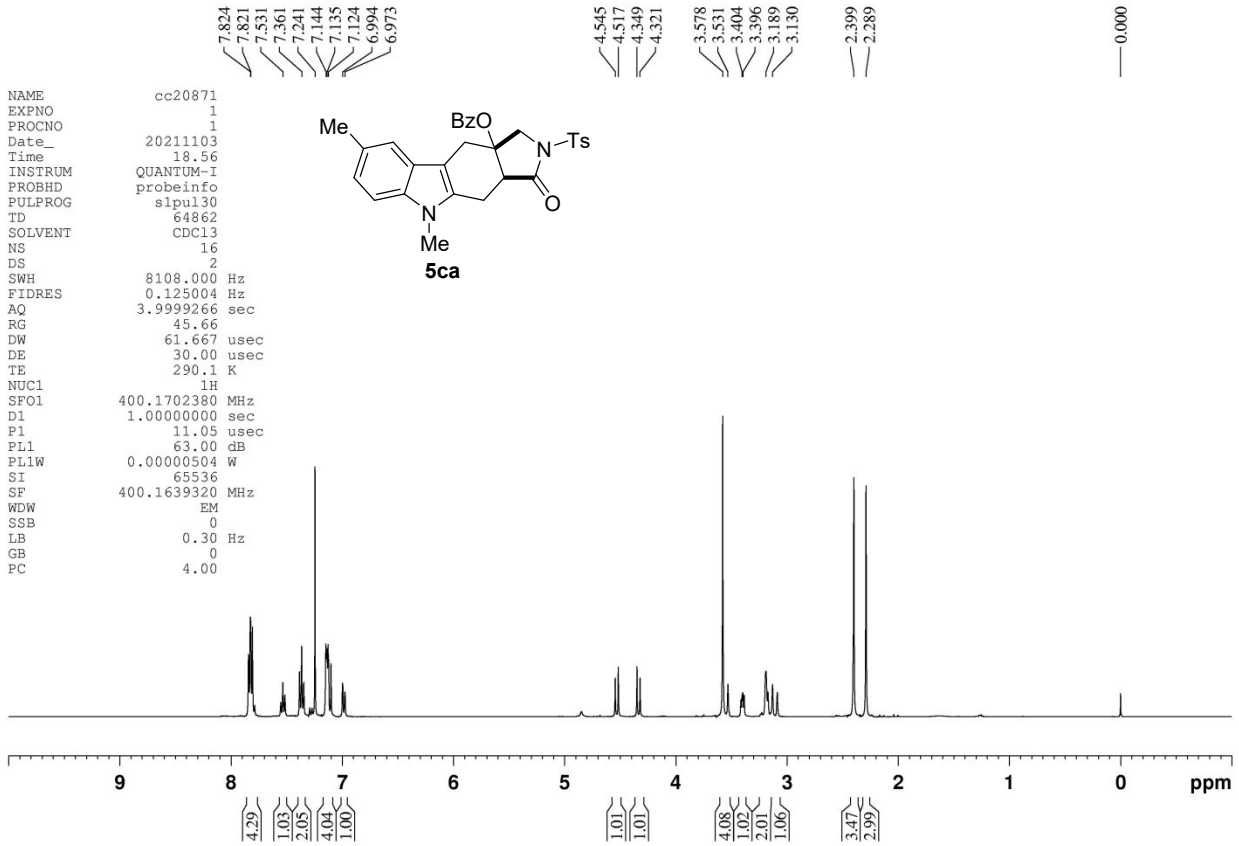



**Figure S8-89. $^{1}$H NMR of 5ca ($CDCl_3$, 400 MHz)**

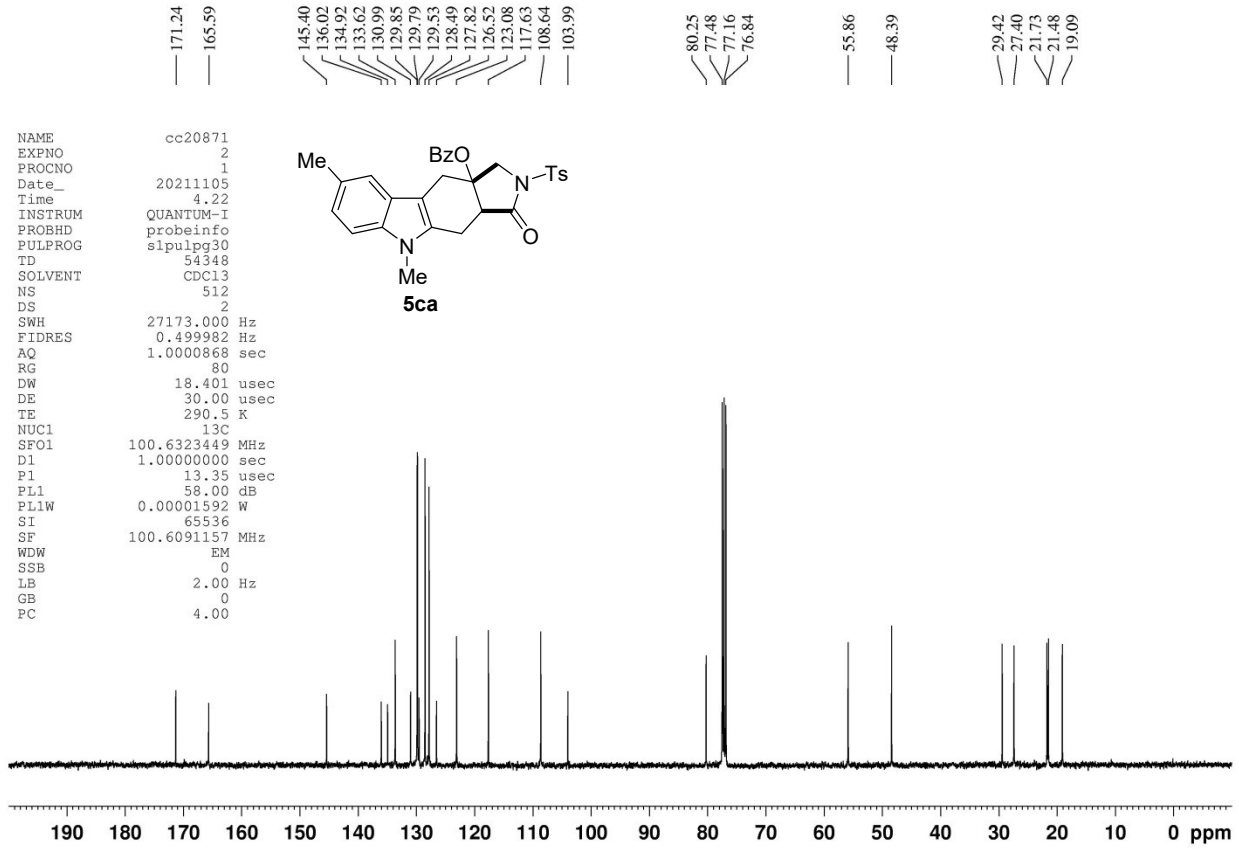



**Figure S8-90. $^{13}$C NMR of 5ca ($CDCl_3$, 101 MHz)**

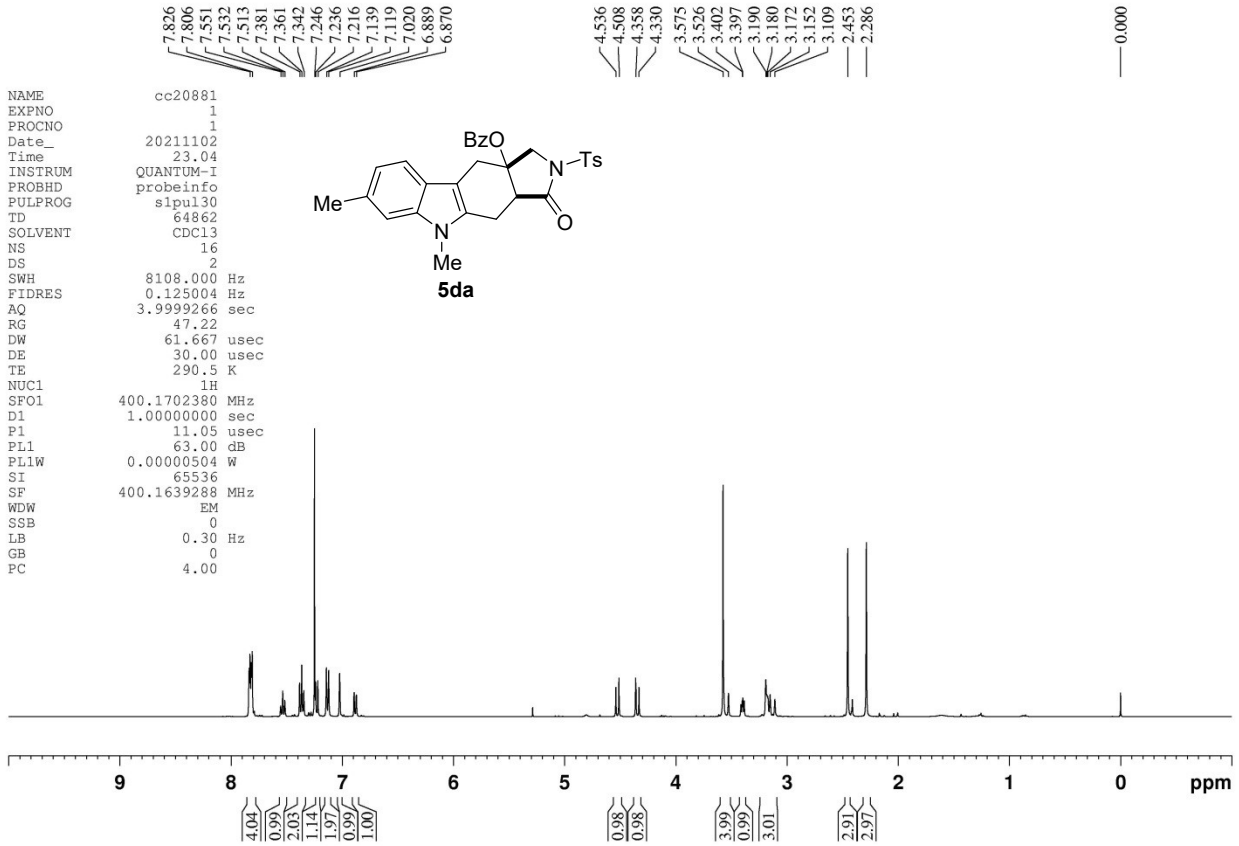



**Figure S8-91. $^{1}$H NMR of 5da ($CDCl_3$, 400 MHz)**

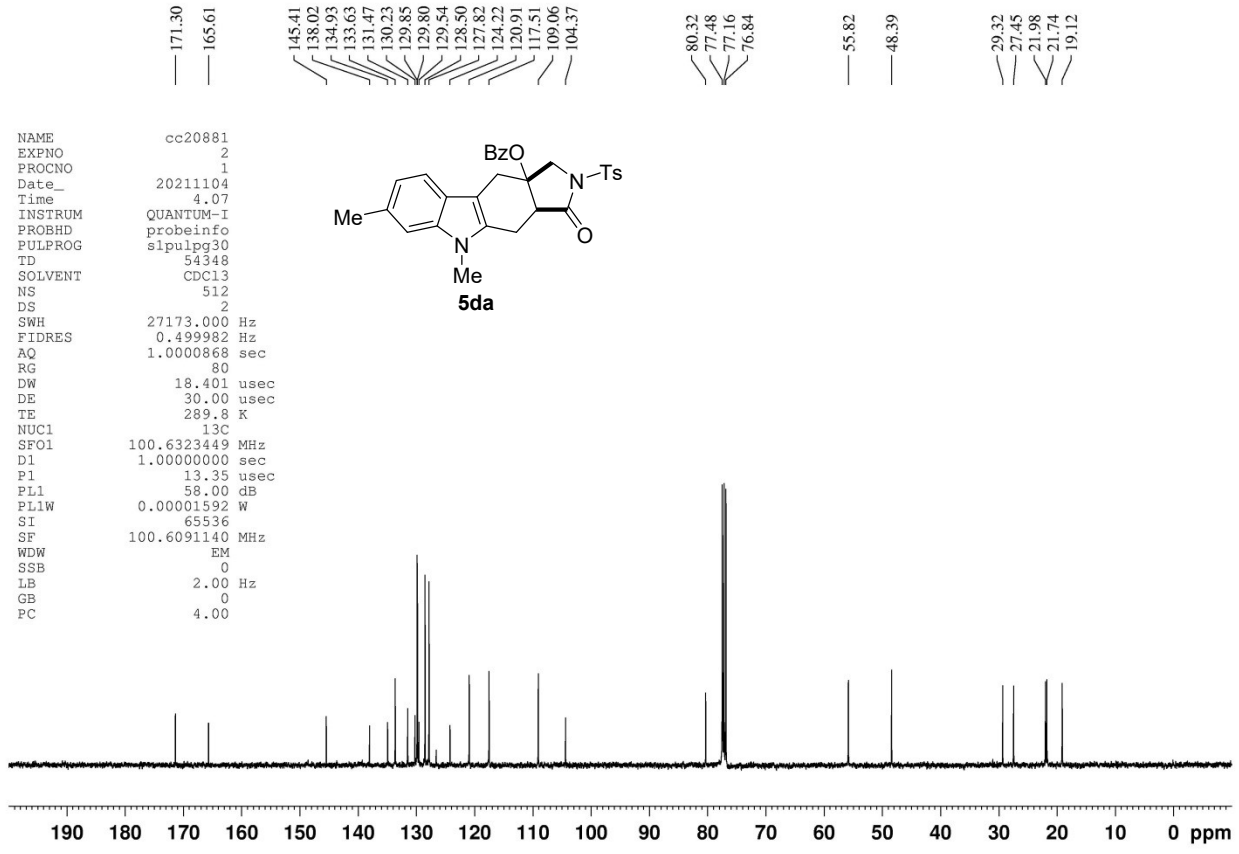



**Figure S8-92. $^{13}$C NMR of 5da ($CDCl_3$, 101 MHz)**

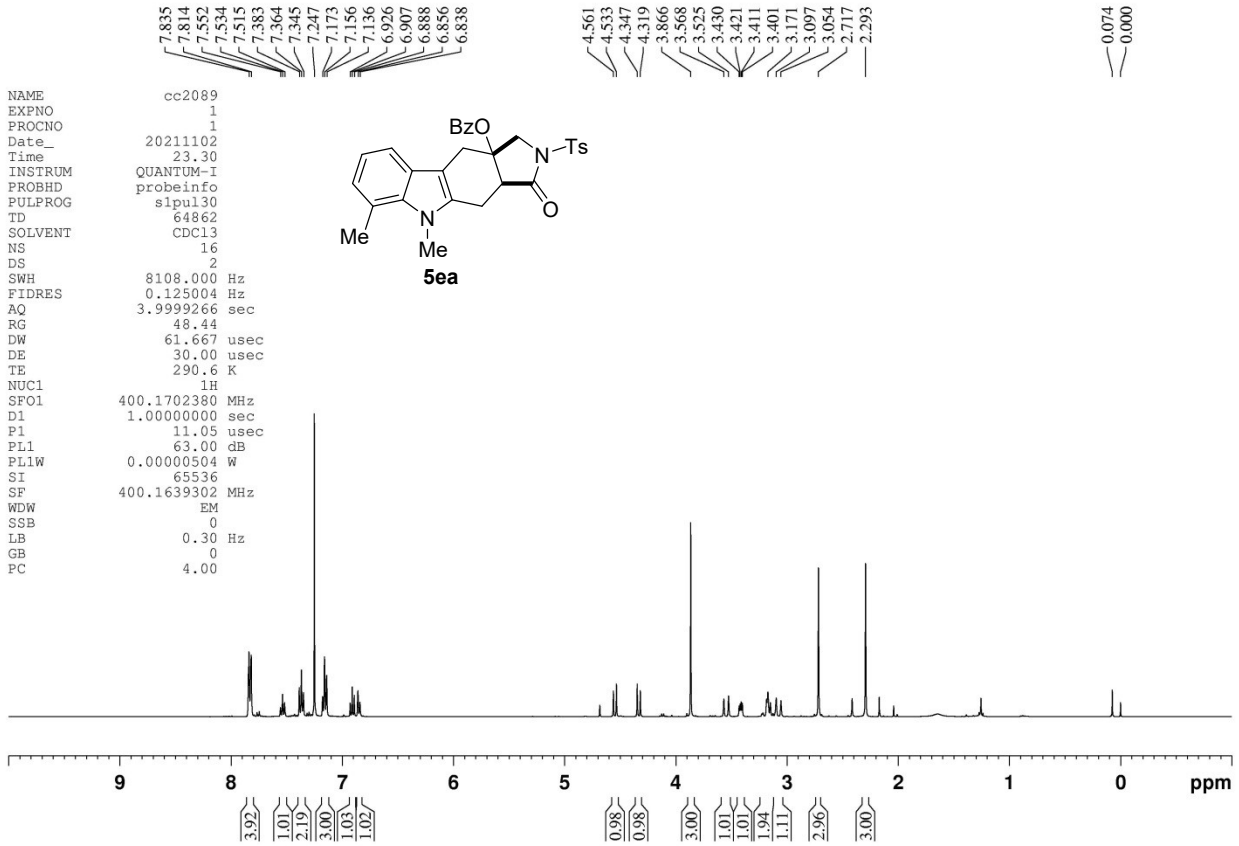



**Figure S8-93. $^{1}$H NMR of 5ea ($CDCl_3$, 400 MHz)**

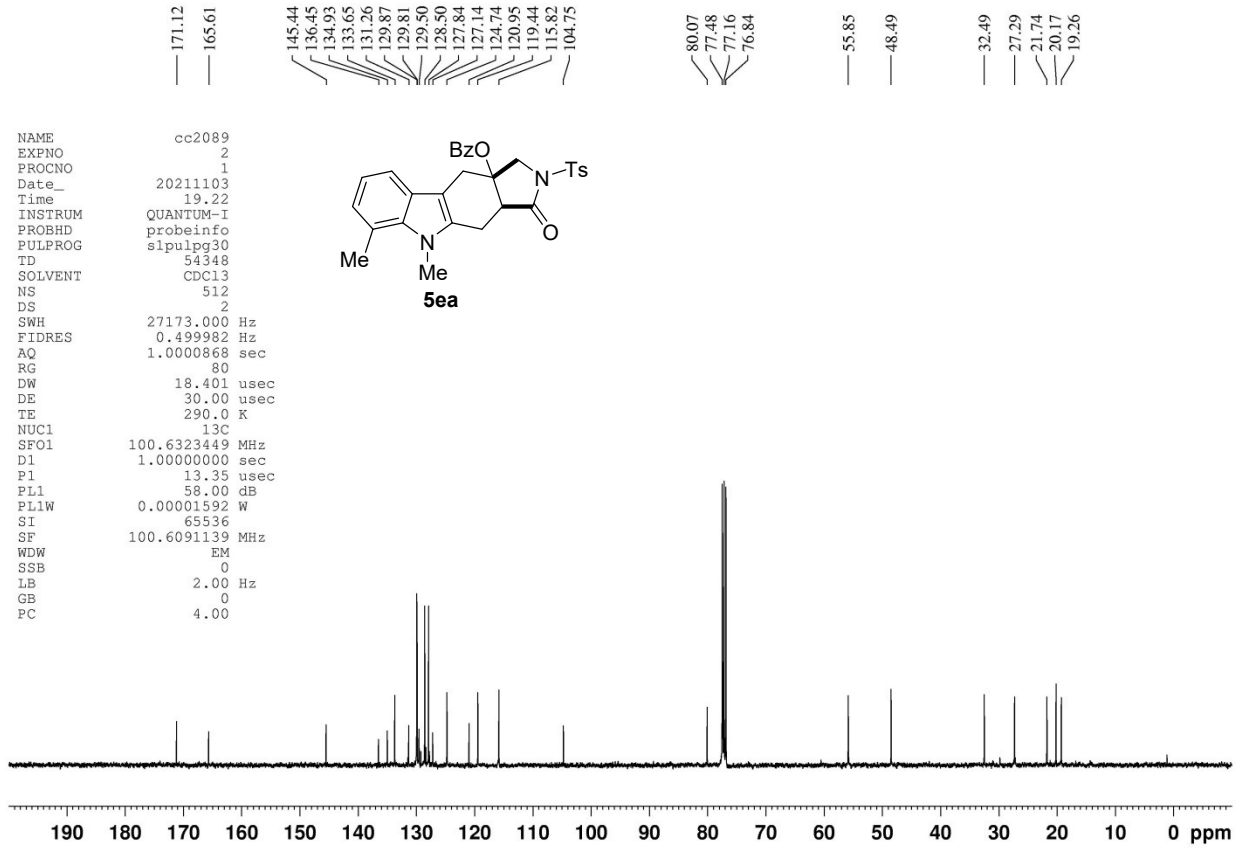



**Figure S8-94. $^{13}$C NMR of 5ea ($CDCl_3$, 101 MHz)**

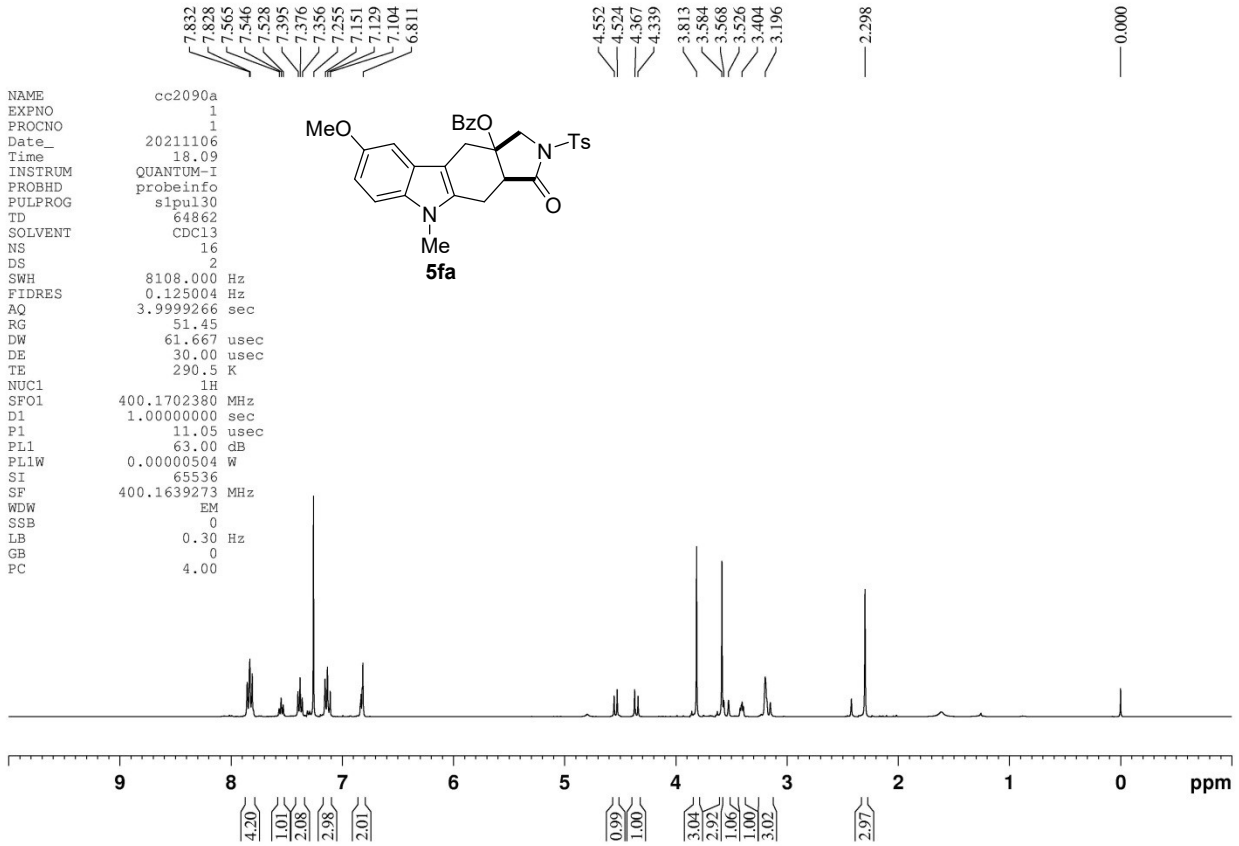



**Figure S8-95. $^{1}$H NMR of 5fa ($CDCl_3$, 400 MHz)**

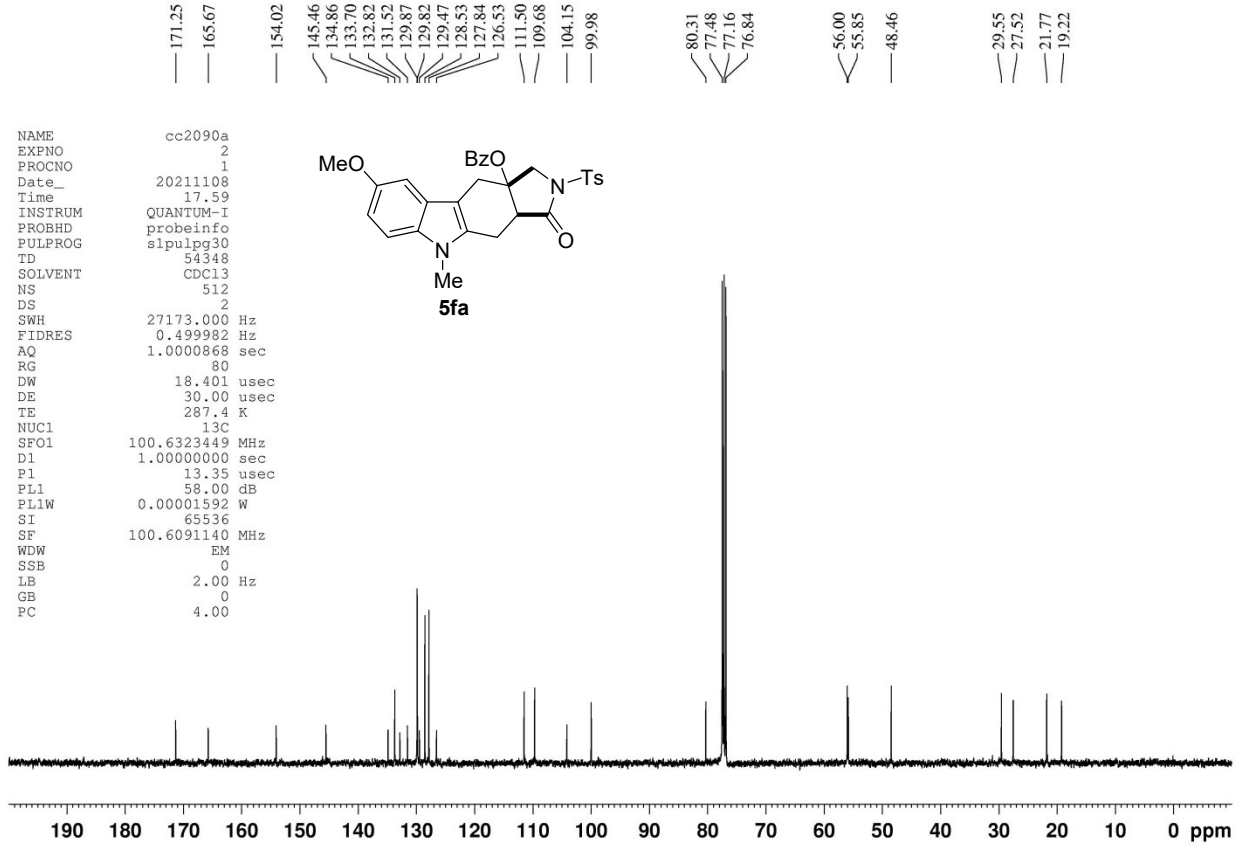



**Figure S8-96. $^{13}$C NMR of 5fa ($CDCl_3$, 101 MHz)**

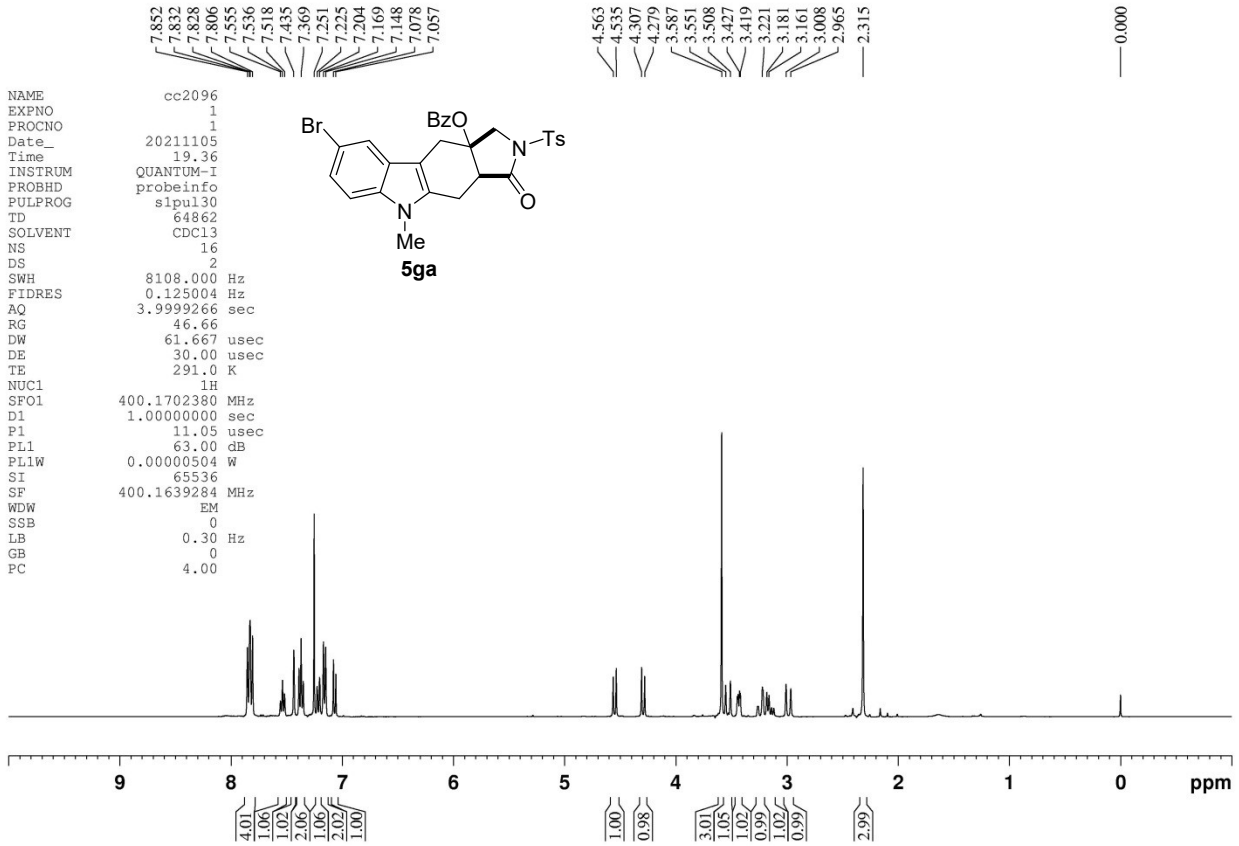



**Figure S8-97. $^{1}$H NMR of 5ga ($CDCl_3$, 400 MHz)**

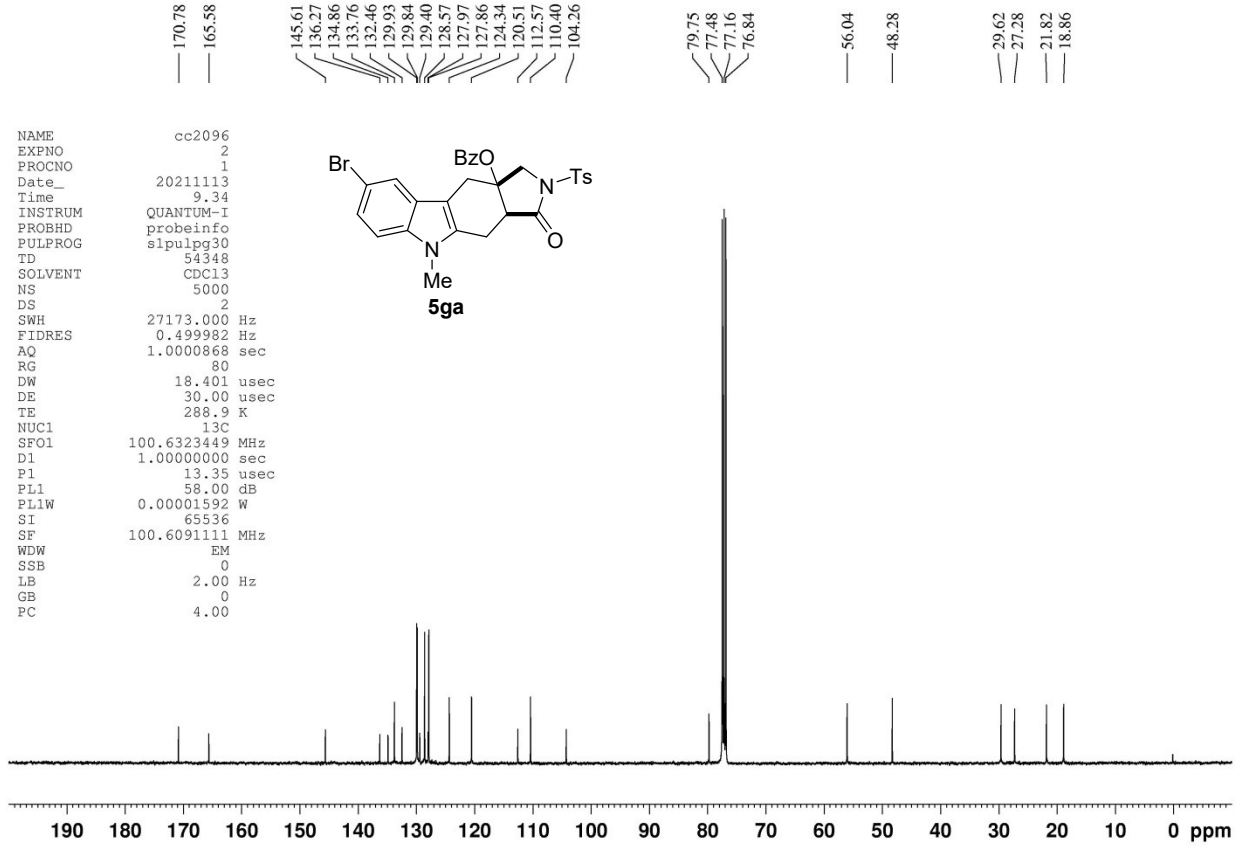



**Figure S8-98. $^{13}$C NMR of 5ga ($CDCl_3$, 101 MHz)**

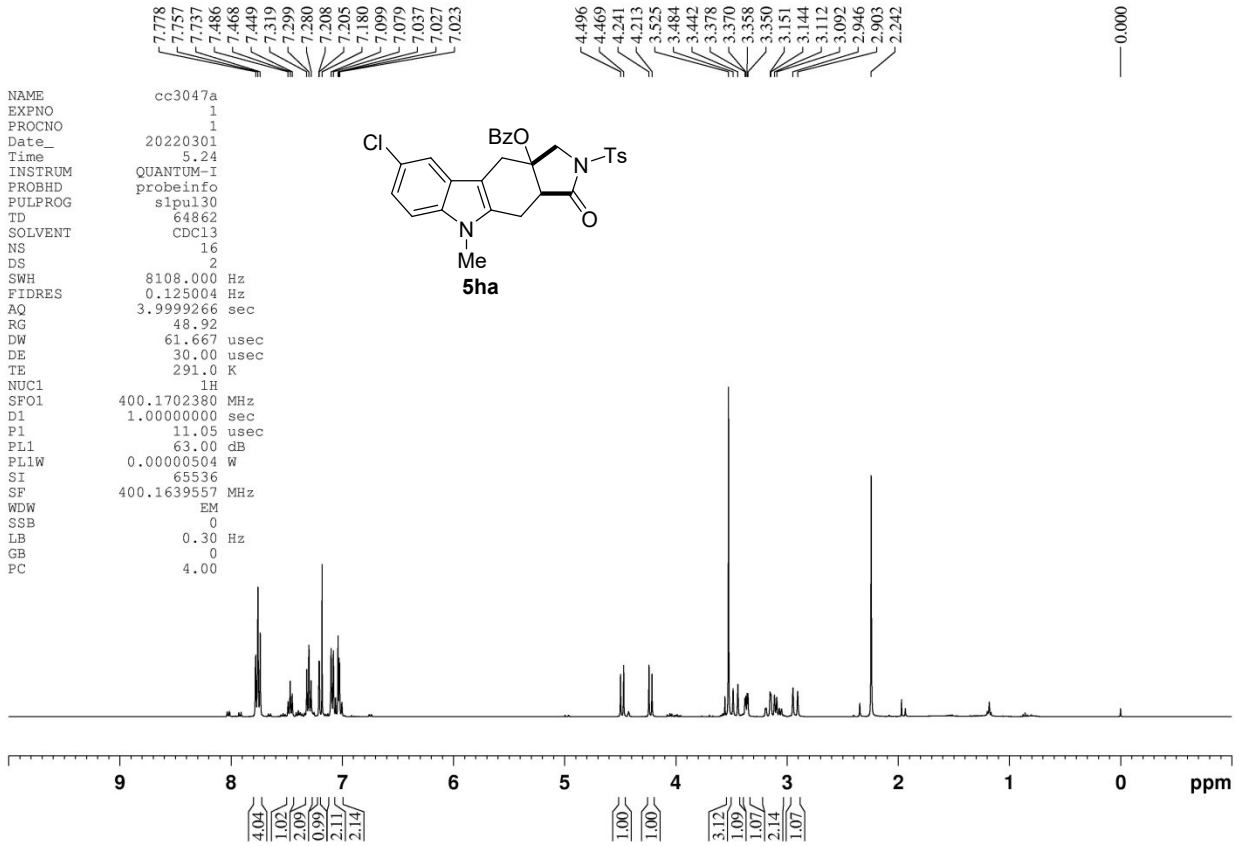



**Figure S8-99. $^{1}$H NMR of 5ha ($CDCl_3$, 400 MHz)**

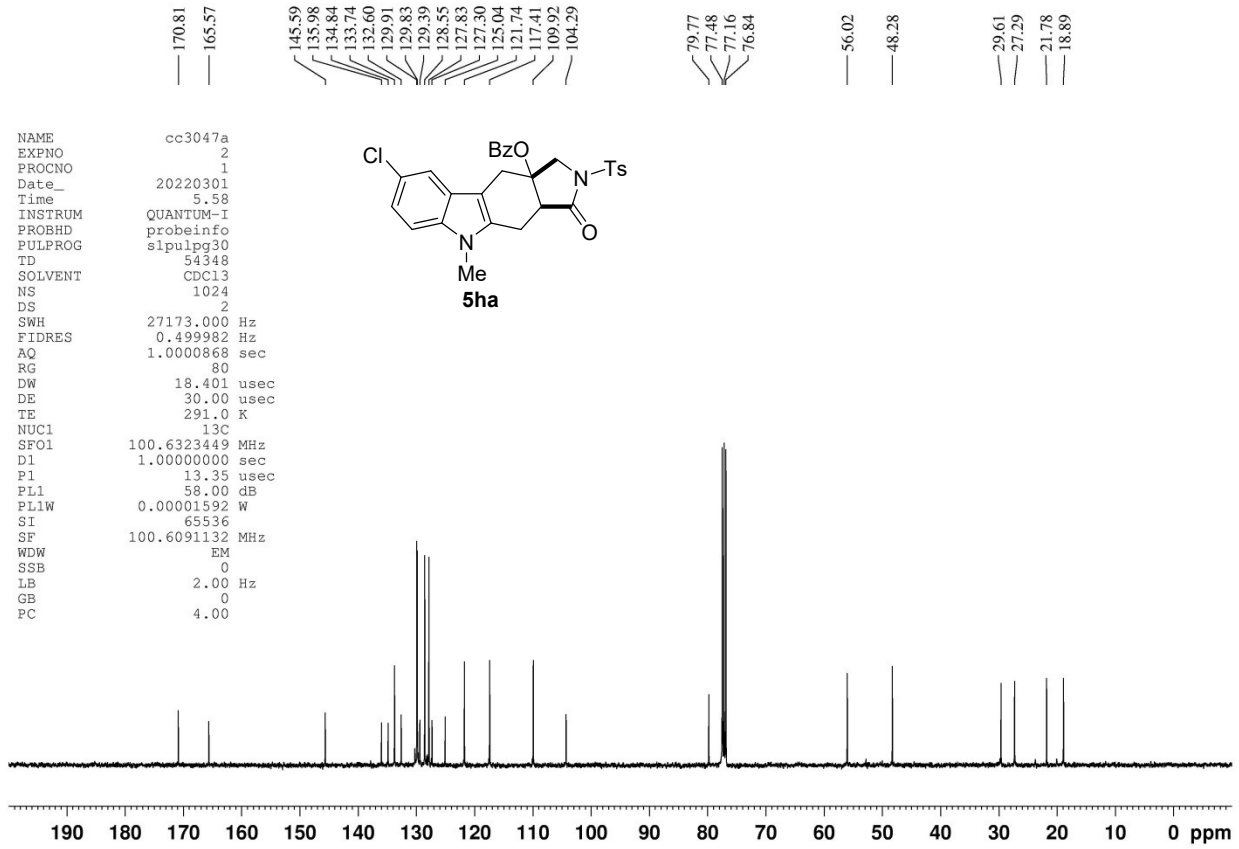



**Figure S8-100. $^{13}$C NMR of 5ha ($CDCl_3$, 101 MHz)**

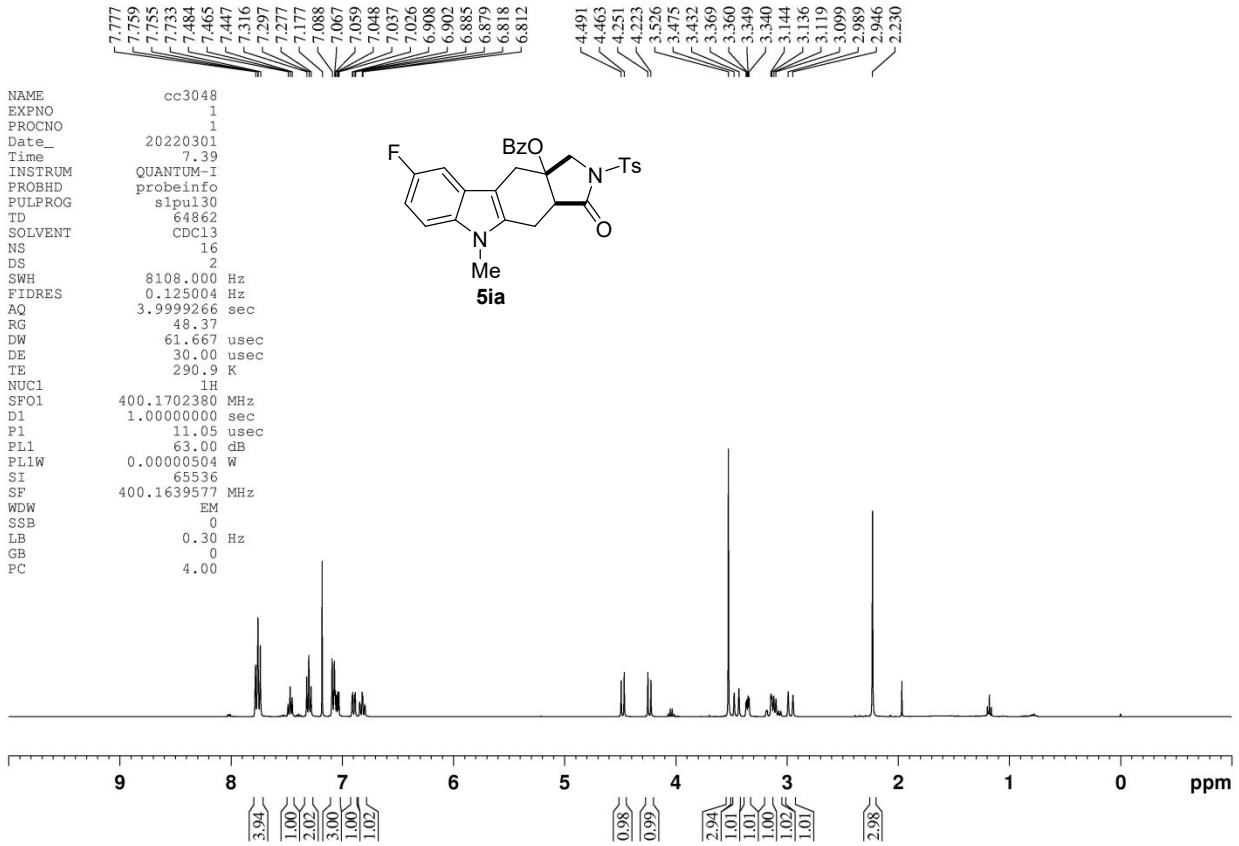



**Figure S8-101. $^{1}$H NMR of 5ia ($CDCl_3$, 400 MHz)**

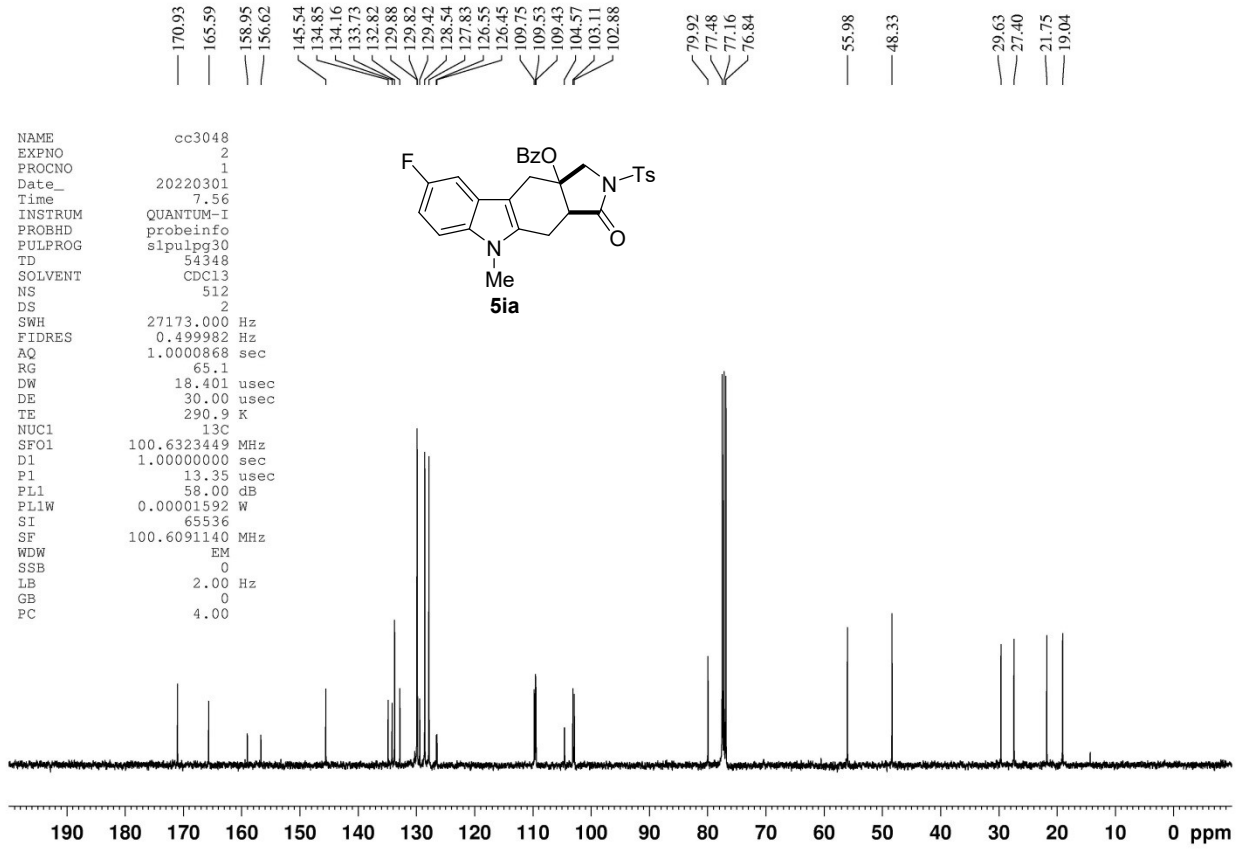



**Figure S8-102. $^{13}$C NMR of 5ia ($CDCl_3$, 101 MHz)**

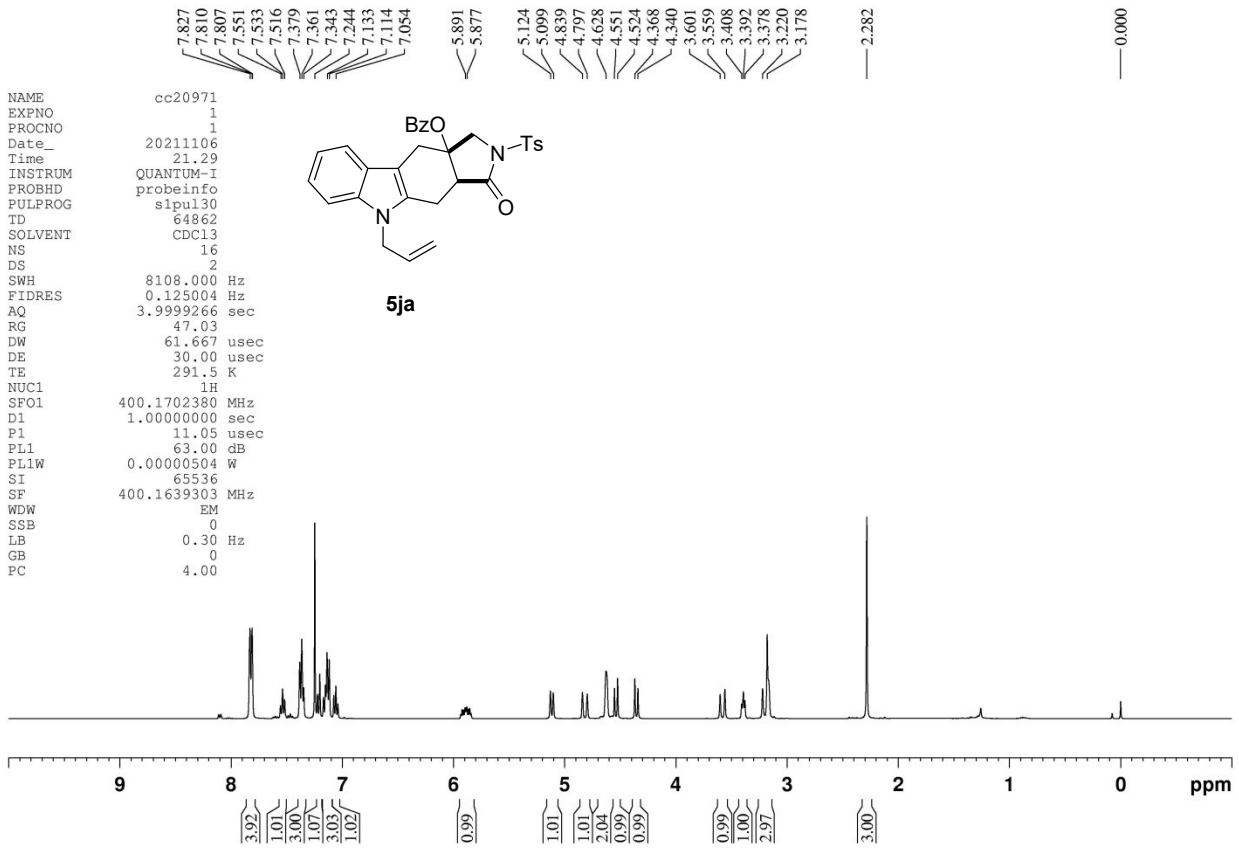



**Figure S8-103. $^{1}$H NMR of 5ja ($CDCl_3$, 400 MHz)**

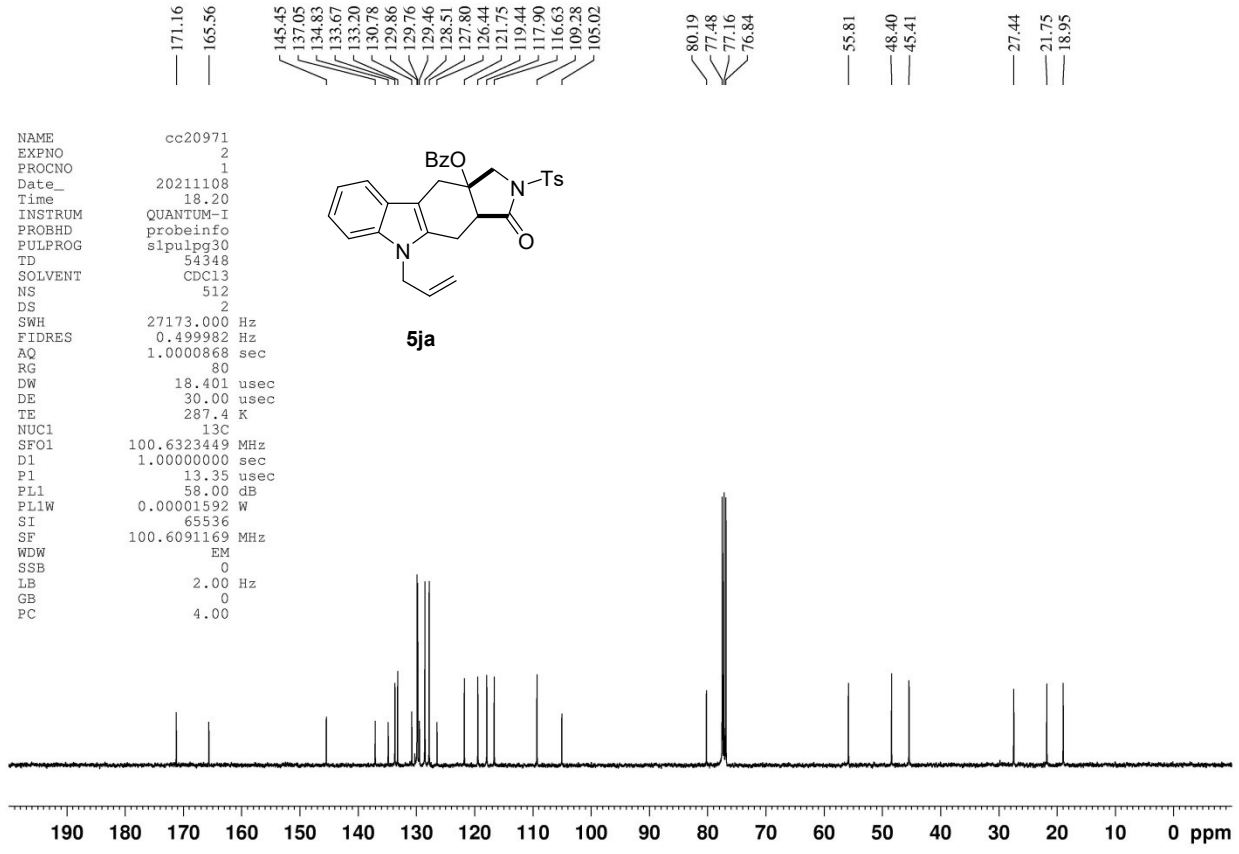



**Figure S8-104. $^{13}$C NMR of 5ja ($CDCl_3$, 101 MHz)**

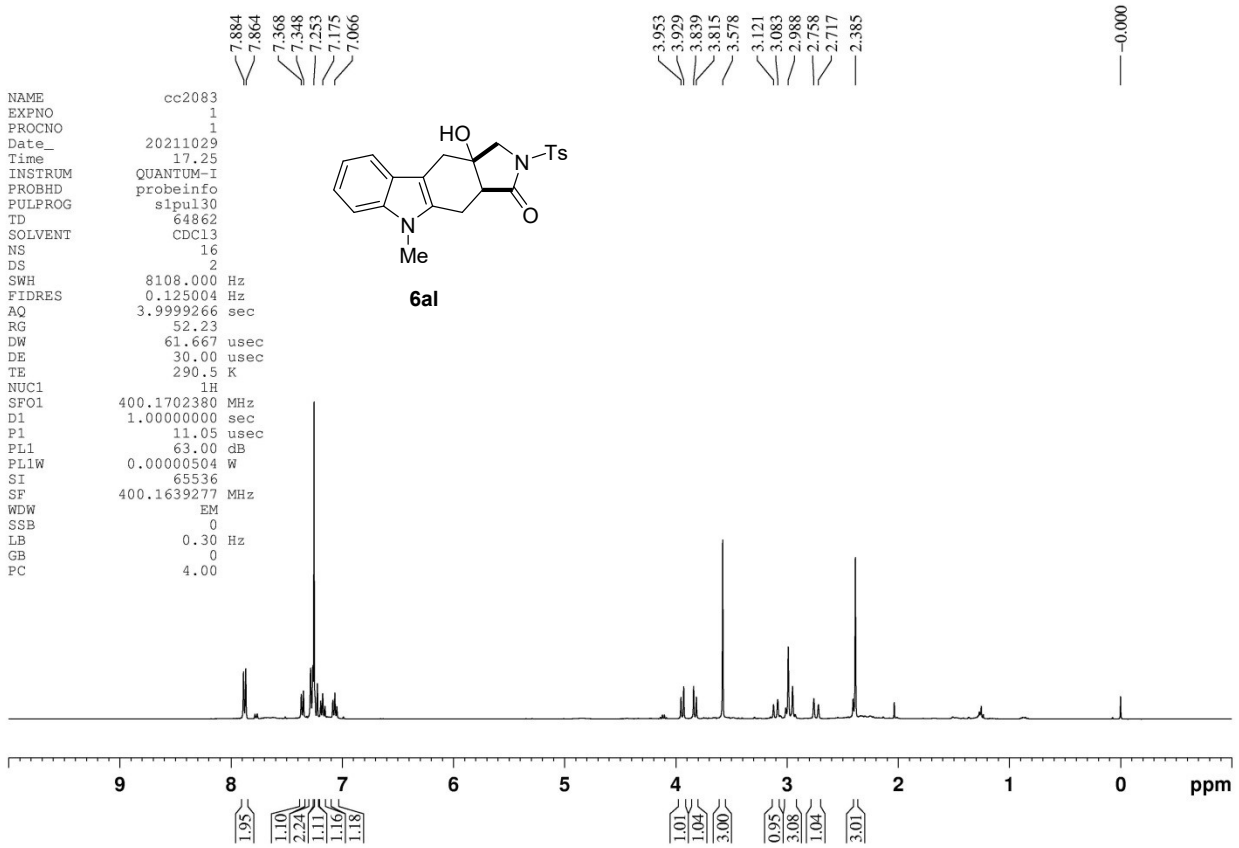



**Figure S8-105. $^{1}$H NMR of 6al ($CDCl_3$, 400 MHz)**

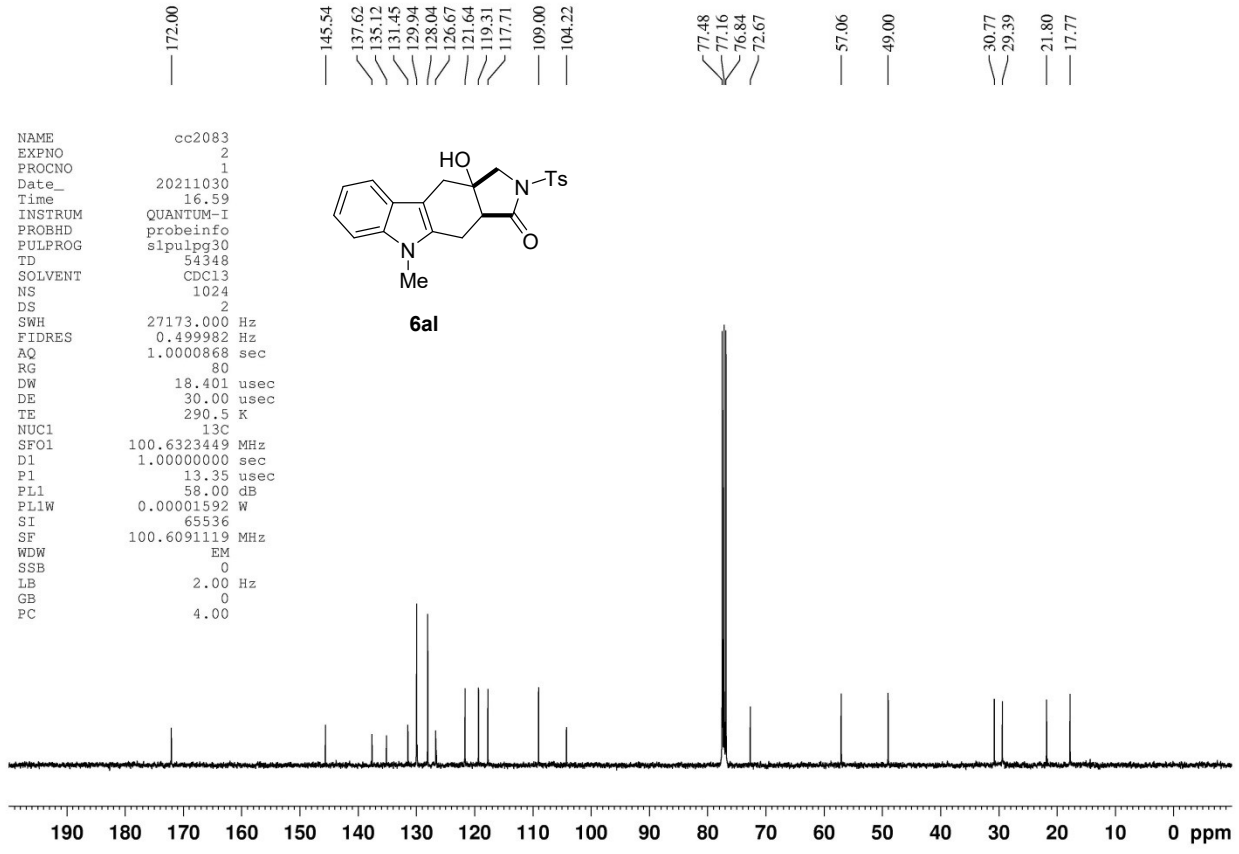



**Figure S8-106. $^{13}$C NMR of 6al ($CDCl_3$, 101 MHz)**

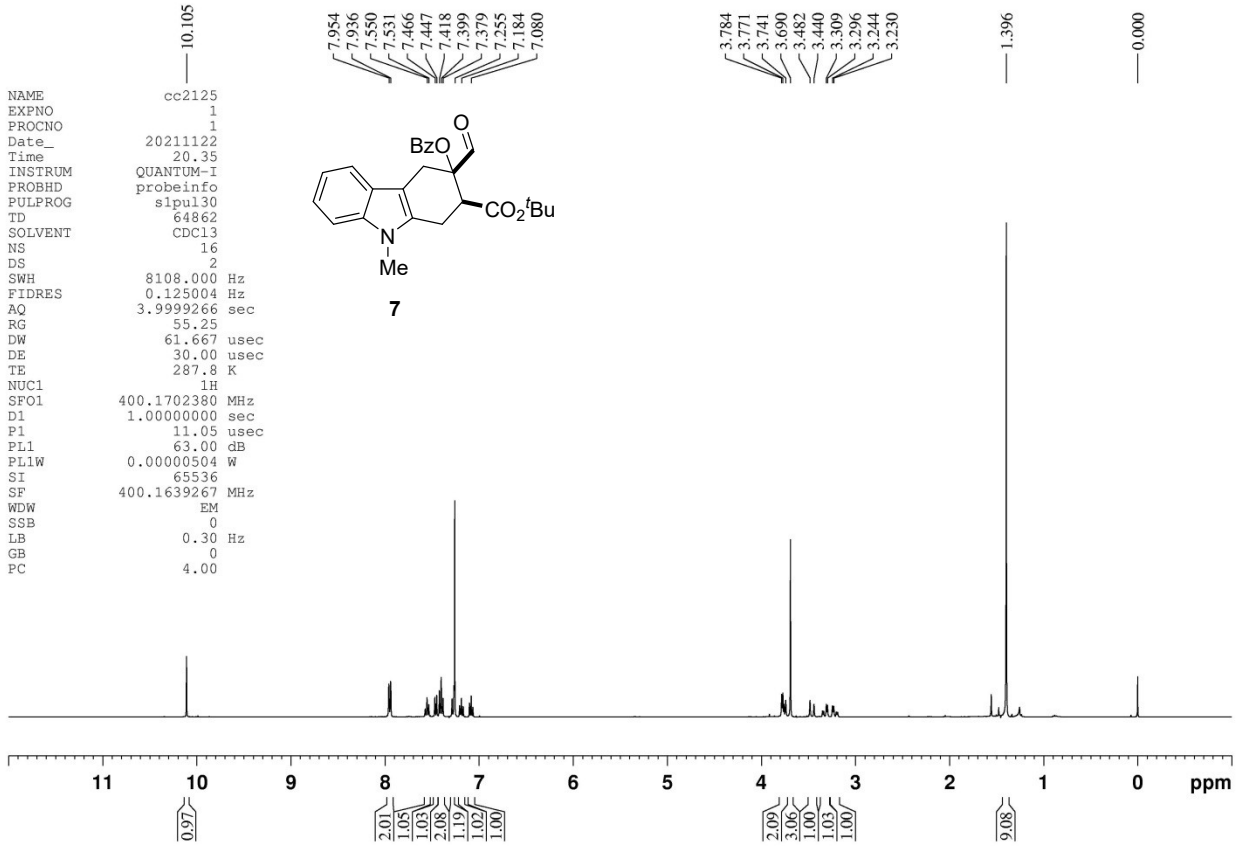



**Figure S8-107. $^{1}$H NMR of 7 ($CDCl_3$, 400 MHz)**

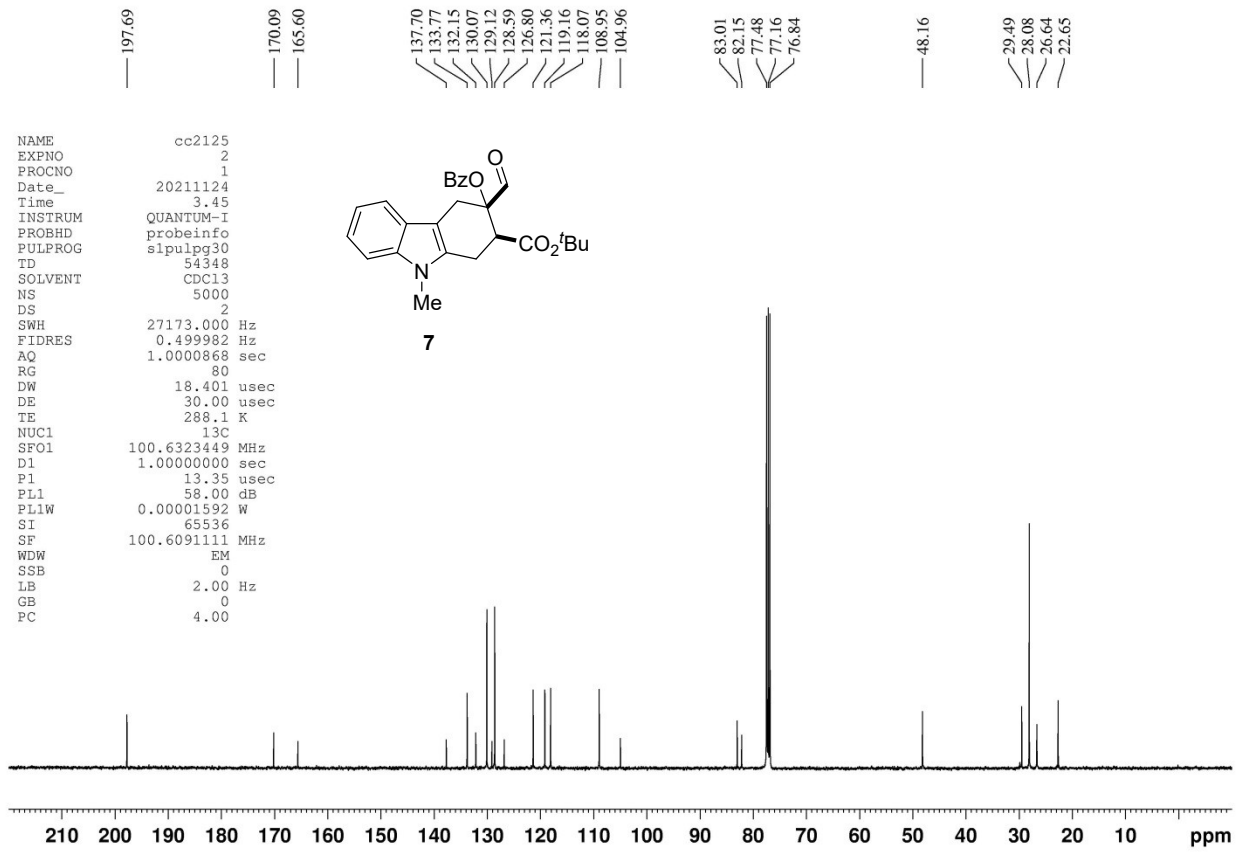



**Figure S8-108. $^{13}$C NMR of 7 ($CDCl_3$, 101 MHz)**

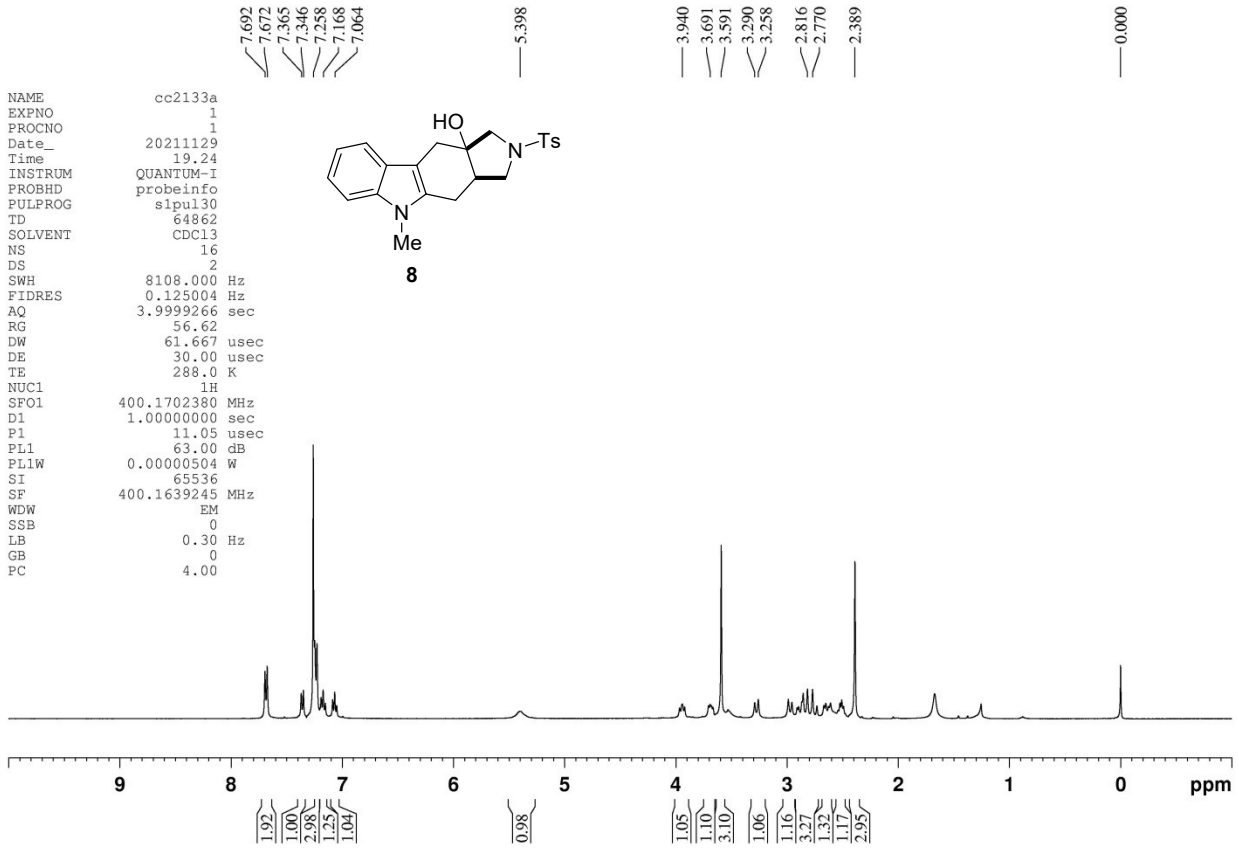



**Figure S8-109. $^{1}$H NMR of 8 ($CDCl_3$, 400 MHz)**

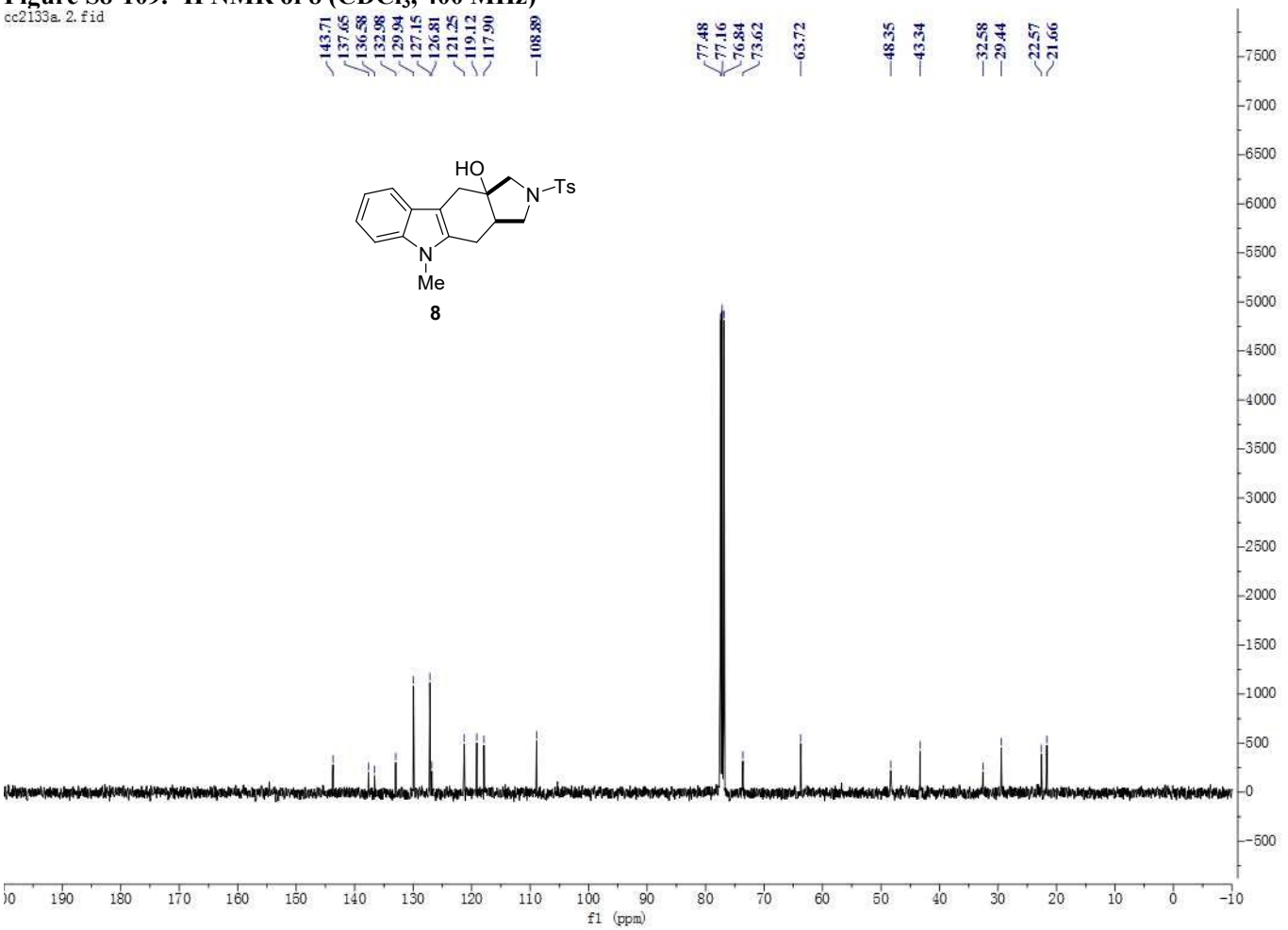



**Figure S8-110. $^{13}$C NMR of 8 ($CDCl_3$, 101 MHz)**

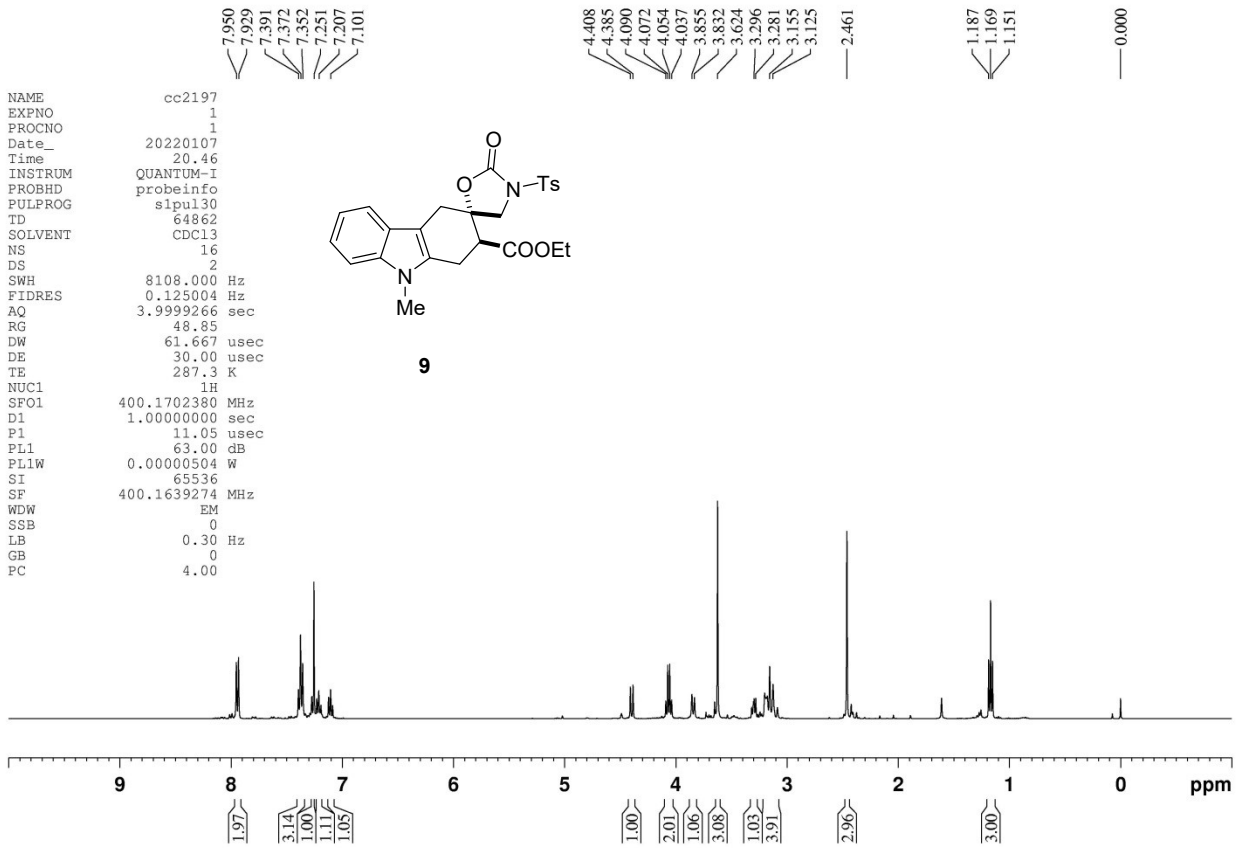



**Figure S8-111. $^{1}$H NMR of 9 ($CDCl_3$, 400 MHz)**

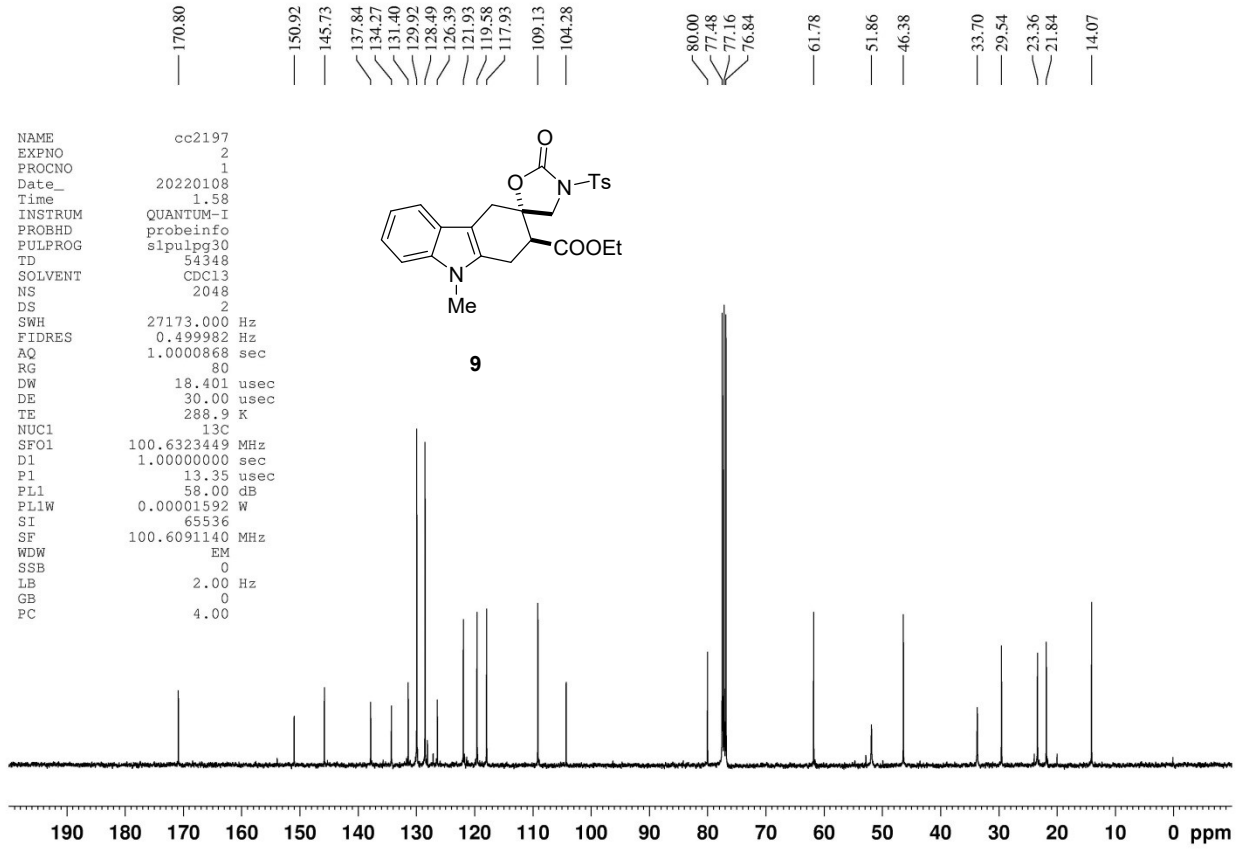
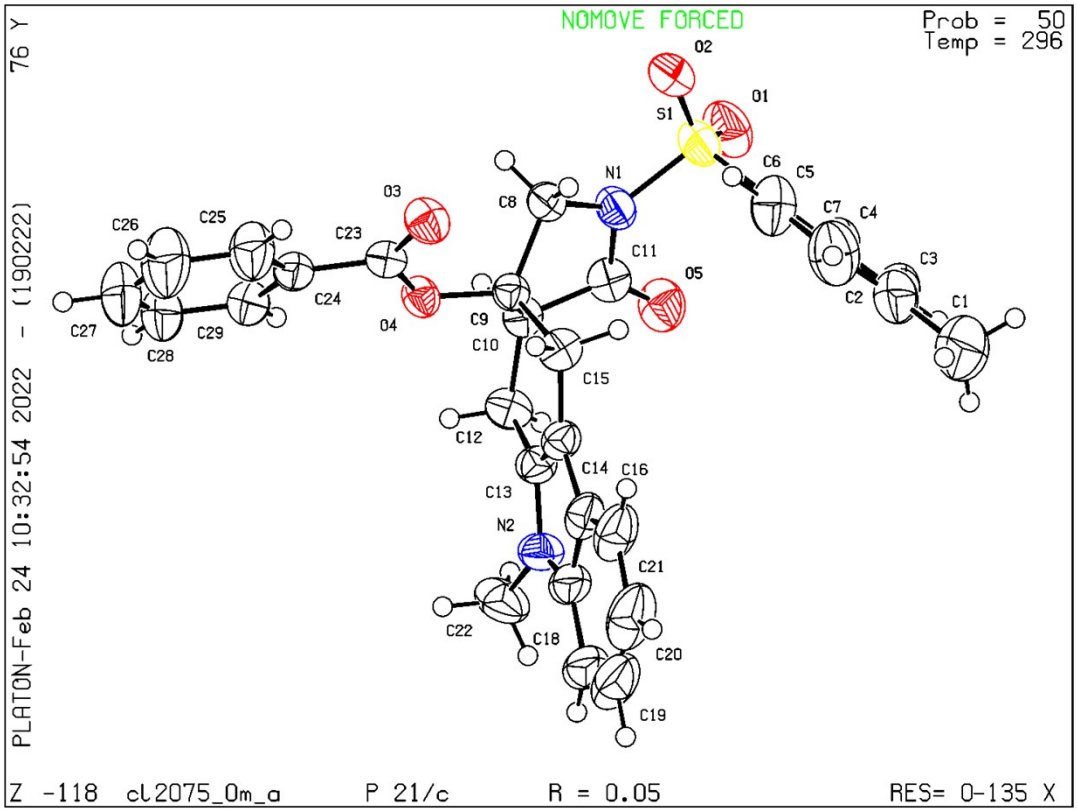



**Figure S8-112. $^{13}$C NMR of 9 ($CDCl_3$, 101 MHz)**

**9 X-ray data for compound 5aa**




# Datablock: cl2075_0m_a

Bond precision: C-C = 0.0039 A Wavelength=0.71073
Cell: a=6.8606(10) b=23.625(3) c=15.712(2)
alpha=90 beta=97.065(2) gamma=90
Temperature: 296 K
Calculated Reported
Volume 2527.3(6) 2527.3(6)
Space group P 21/c P 21/c
Hall group -P 2ybc -P 2ybc
Moiety formula C29 H26 N2 O5 S ?
Sum formula C29 H26 N2 O5 S C29 H26 N2 O5 S
Mr 514.58 514.58
Dx,g cm-3 1.352 1.352
Z 4 4
Mu (mm-1) 0.171 0.171
F000 1080.0 1080.0
F000' 1080.99
h,k,lmax 8,30,20 8,30,20
Nref 5834 5806
Tmin,Tmax 0.968,0.973
Tmin' 0.968
Correction method= Not given
Data completeness= 0.995 Theta(max)= 27.565
R(reflections)= 0.0532( 3582)
wR2(reflections)=
0.1750( 5806)

S = 0.966 Npar= 336