Supporting Information

Phosphine-catalyzed sequential [4+1]/[2+3] annulation of *o*-amino arylaldimines with Morita–Baylis–Hillman (MBH) carbonates

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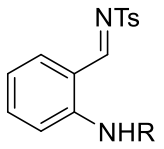
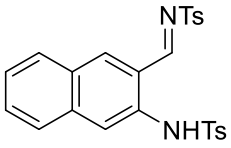
I. General Information

Unless otherwise specified, **all reactions** were carried out under a nitrogen atmosphere. **All solvents** were purified according to the standard procedures. **All chemicals** which are commercially available were employed without further purification. **Thin-layer chromatography (TLC)** was performed on silica gel plates (GF254) using UV-light (254 and 365 nm). **Flash chromatography** was conducted on silica gel (200–300 mesh). **^{1}H** and **^{13}C{^{1}H} NMR** spectra were recorded on a Bruker 400 MHz spectrometer. **Chemical shifts** were reported in parts per million (ppm). The **^{1}H NMR** (400 MHz) chemical shifts were measured relative to residual non-deuterated solvent resonance ($CDCl_3$: δ = 7.260 ppm). The **^{13}C{^{1}H} NMR** (100 MHz) chemical shifts were given using $CDCl_3$ as the internal standard ($CDCl_3$: δ = 77.00 ppm). **All high-resolution mass spectra (HR-MS)** were obtained on a Bruker microTOFQ II (ESI). **Crystal measurement** was performed by Bruker D8 Venture X-ray diffractionmeter. *o*-Amino arylaldimines **1**[1] and MBH carbonates **2**[2] were synthesized according to modified literature-reported procedure. **1a**[1], **1e**[1], **1h**[1],**1s**[1] and **2**[2] have been reported earlier. **1b-1d**, **1f-1g**, and **1i-1r** are new compounds.

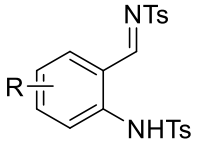
II. Substrate Scope of 1 and 2



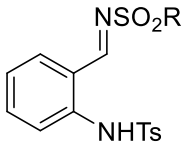
1a, R = Ts
1s, R = Cbz



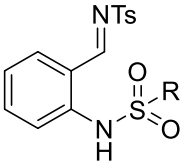
1h



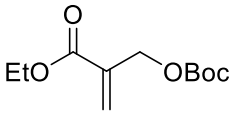
1b: R = 3-Cl
1c: R = 3-Me
1d: R = 4-Cl
1e: R = 4-Me
1f: R = 5-Br
1g: R = 5-Me



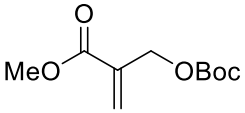
1i: R = 4-^{t}BuC$_6$H$_4$
1j: R = 4-OMeC$_6$H$_4$
1k: R = ^{t}Bu



1l: R = 2-ClC$_6$H$_4$
1m:R = 2-BrC$_6$H$_4$
1n: R = 2-MeC$_6$H$_4$
1o: R = 3-ClC$_6$H$_4$
1p: R = 3-MeC$_6$H$_4$
1q: R = 4-BrC$_6$H$_4$
1r: R = 4-OMeC$_6$H$_4$



2a



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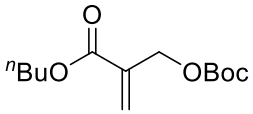

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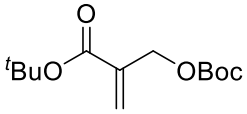

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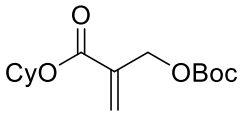

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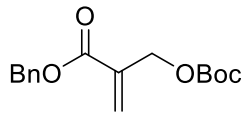
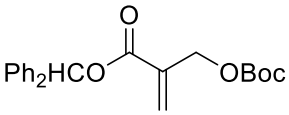
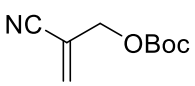


2f

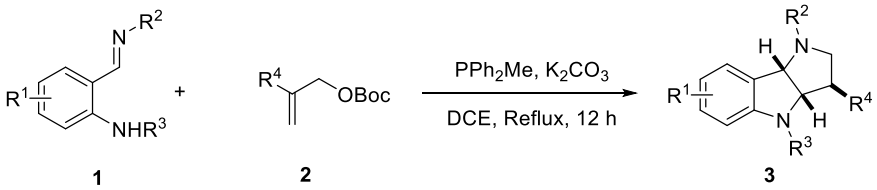


2g



2h

III. Representative Procedure of the Reaction

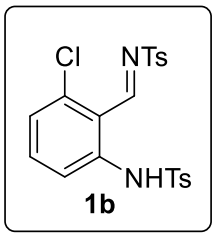


1 2 3

To a stirred solution of *o*-amino arylaldimines **1** (0.1 mmol), Morita-Baylis-Hillman carbonates **2** (0.12 mmol, 1.2 equiv) and K_2CO_3 (0.12 mmol, 1.2 equiv) in DCE (2.0 mL) was added PPh_2Me (4.0 mg, 20 mol%). The reaction mixture was stirred at reflux for 12 h. The reaction mixture was concentrated under reduce vacuum, and the residue was purified by flash column chromatography on silica gel (PE: EA = 10:1) to afford the compounds **3**.

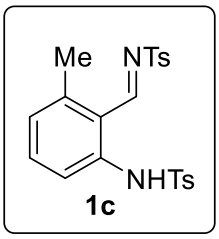
IV. Analytical Data

(E)-N-(3-Chloro-2-((tosylimino)methyl)phenyl)-4-methylbenzenesulfonamide (1b)



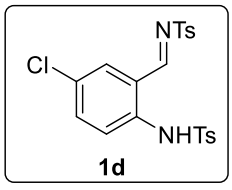
A white amorphous solid. **M.p**.: 175-176 ℃ **^{1}H NMR (400 MHz, $CDCl_3$)** δ 11.46 (s, 1H), 9.59 (s, 1H), 7.96 (d, J = 8.4 Hz, 2H), 7.63 (dt, J = 8.5, 0.8 Hz, 1H), 7.52 (d, J = 8.4 Hz, 2H), 7.47 – 7.41 (m, 2H), 7.38 (t, J = 8.3 Hz, 1H), 7.12 (td, J = 8.0, 1.0 Hz, 3H), 2.49 (s, 3H), 2.35 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 167.3, 145.5, 144.4, 142.8, 140.7, 136.3, 135.9, 134.6, 130.2, 129.8, 128.2, 127.2, 124.7, 117.2, 115.3, 21.7, 21.5. **HRMS (ESI)** m/z: calcd. for $C_{21}H_{20}ClN_2O_4S_2^+$ $[M + H]^+$: 463.0548, found: 463.0557.

(E)-4-Methyl-N-(3-methyl-2-((tosylimino)methyl)phenyl)benzenesulfonamide (1c)



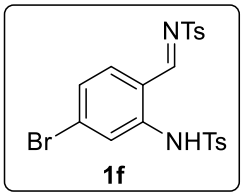
A white amorphous solid. **M.p**.: 118-119 ℃ **^{1}H NMR (400 MHz, $CDCl_3$)** δ 11.43 (s, 1H), 9.37 (s, 1H), 7.98 – 7.92 (m, 2H), 7.53 (dd, J = 10.6, 8.3 Hz, 3H), 7.43 (d, J = 8.1 Hz, 2H), 7.34 (t, J = 8.0 Hz, 1H), 7.11 (d, J = 8.1 Hz, 2H), 6.89 (d, J = 7.5 Hz, 1H), 2.52 (s, 3H), 2.48 (s, 3H), 2.33 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 167.1, 145.2, 144.5, 144.0, 141.7, 136.3, 136.1, 135.1, 130.1, 129.6, 128.0, 127.2, 125.8, 116.8, 116.5, 21.7, 21.5, 20.0. **HRMS (ESI)** m/z: calcd. for $C_{22}H_{23}N_2O_4S_2^+$ $[M + H]^+$: 443.1094, found: 443.1095.

(E)-N-(5-Chloro-2-((4-methylphenyl)sulfonamido)benzylidene)-4-methylbenzenesulfonamide (1d)



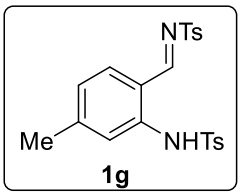
A white amorphous solid. **M.p**.: 119-120 ℃ **^{1}H NMR (400 MHz, $CDCl_3$)** δ 10.76 (s, 1H), 8.87 (s, 1H), 7.93 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.9 Hz, 1H), 7.51 (d, J = 8.4 Hz, 2H), 7.48 – 7.41 (m, 4H), 7.11 (d, J = 8.1 Hz, 2H), 2.49 (s, 3H), 2.34 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 168.9, 145.5, 144.4, 139.3, 136.0, 135.8, 135.6, 134.5, 130.2, 129.8, 128.8, 128.2, 127.1, 120.4, 119.7, 21.8, 21.5. **HRMS (ESI)** m/z: calcd. for $C_{21}H_{20}ClN_2O_4S_2^+$ $[M + H]^+$: 463.0548, found: 463.0556.

(E)-N-(4-Bromo-2-((4-methylphenyl)sulfonamido)benzylidene)-4-methylbenzenesulfonamide (1f)



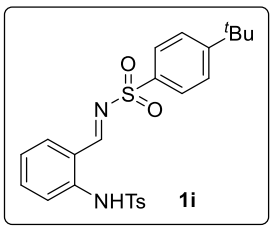
A white amorphous solid. **M.p**.: 188-189 ℃**^{1}H NMR (400 MHz, $CDCl_3$)** δ 10.97 (s, 1H), 8.90 (s, 1H), 7.95 – 7.88 (m, 3H), 7.59 – 7.54 (m, 2H), 7.43 (d, J = 8.1 Hz, 2H), 7.35 – 7.28 (m, 2H), 7.15 (d, J = 8.1 Hz, 2H), 2.49 (s, 3H), 2.35 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 169.2, 145.4, 144.5, 143.6, 141.6, 139.1, 138.0, 135.8, 134.8, 131.7, 130.2, 129.8, 129.7, 128.1, 127.2, 126.8, 126.5, 121.6, 117.1, 21.7, 21.6. **HRMS (ESI)** m/z: calcd. for $C_{21}H_{20}BrN_2O_4S_2^+$ $[M + H]^+$: 507.0042, found: 507.0049.

(E)-4-Methyl-N-(4-methyl-2-((4-methylphenyl)sulfonamido)benzylidene)benzenesulfonamide (1g)



A white amorphous solid. **M.p**.: 120-121 ℃ **^{1}H NMR (400 MHz, $CDCl_3$)** δ 10.88 (s, 1H), 8.89 (s, 1H), 7.92 (d, J = 8.1 Hz, 2H), 7.58 – 7.50 (m, 3H), 7.41 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 7.9 Hz, 1H), 7.11 (d, J = 8.0 Hz, 2H), 6.93 (d, J = 7.9 Hz, 1H), 2.48 (s, 3H), 2.37 (s, 3H), 2.33 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 169.8, 148.1, 145.1, 144.1, 140.9, 137.4, 136.2, 135.2, 130.1, 129.7, 129.6, 128.0, 127.2, 126.5, 124.6, 119.3, 116.2, 22.4, 21.7, 21.5. **HRMS (ESI)** m/z: calcd. for $C_{22}H_{23}N_2O_4S_2^+$ $[M + H]^+$: 443.1094, found: 443.1101.

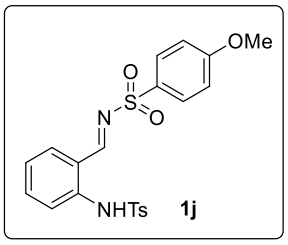
(E)-4-(Tert-butyl)-N-(2-((4-methylphenyl)sulfonamido)benzylidene)benzenesulfonamide (1i)



A white amorphous solid. **M.p**.: 146-147 ℃ **^{1}H NMR (400 MHz, $CDCl_3$)** δ 10.89 (s, 1H), 8.96 (s, 1H), 7.98 (d, J = 8.6 Hz, 2H), 7.73 – 7.69 (m, 1H), 7.63 (d, J = 8.6 Hz, 2H), 7.57 – 7.46 (m, 5H), 7.11 – 7.07 (m, 2H), 2.32 (s, 3H), 1.37 (s, 9H).

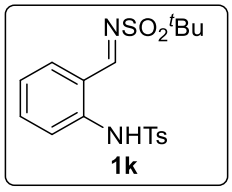
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.3, 158.2, 144.1, 140.9, 137.4, 136.1, 136.0, 134.8, 129.6, 127.9, 127.2, 126.6, 126.3, 126.1, 123.4, 118.8, 118.5, 35.4, 31.0, 21.5. **HRMS (ESI)** m/z: calcd. for $C_{24}H_{27}N_2O_4S_2^+$ $[M + H]^+$: 471.1407, found: 471.1416.

(E)-4- Methoxy -N-(2-((4-methylphenyl)sulfonamido)benzylidene)benzenesulfonamide (1j)



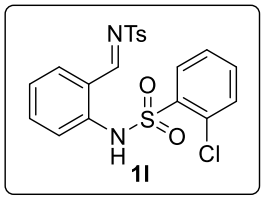
A white amorphous solid. **M.p**.: 174-175 ℃ **^1H NMR (400 MHz, $CDCl_3$)** δ 10.90 (s, 1H), 8.93 (s, 1H), 7.98 (d, J = 8.9 Hz, 2H), 7.70 (d, J = 8.6 Hz, 1H), 7.62 – 7.45 (m, 4H), 7.18 – 7.03 (m, 5H), 3.90 (s, 3H), 2.32 (s, 3H). **$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)** δ 169.6, 164.1, 144.1, 140.8, 137.3, 136.1, 135.9, 130.2, 129.6, 129.2, 127.1, 123.4, 118.7, 118.4, 114.7, 55.8, 21.5. **HRMS (ESI)** m/z: calcd. for $C_{21}H_{21}N_2O_5S_2^+$ $[M + H]^+$: 445.0886, found: 445.0895.

(E)-N-(2-(((tert-butylsulfonyl)imino)methyl)phenyl)-4-methylbenzenesulfonamide (1k)



A white amorphous solid. **M.p**.: 145-146 ℃ **^1H NMR (400 MHz, $CDCl_3$)** δ 11.08 (s, 1H), 9.00 (s, 1H), 7.79 (d, J = 8.3 Hz, 2H), 7.68 (d, J = 8.7 Hz, 1H), 7.53 (dd, J = 11.7, 8.0 Hz, 2H), 7.27 (s, 1H), 7.25 (s, 1H), 7.14 (t, J = 7.6 Hz, 1H), 2.37 (s, 3H), 1.55 (s, 9H). **$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)** δ 173.0, 144.4, 141.0, 137.5, 136.2, 136.1, 129.9, 127.3, 123.1, 118.1, 117.7, 58.7, 24.0, 21.5. **HRMS (ESI)** m/z: calcd. for $C_{18}H_{23}N_2O_4S_2^+$ $[M + H]^+$: 395.1094, found: 395.1102.

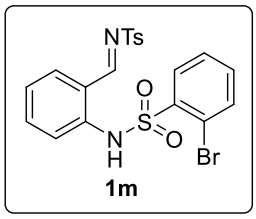
(E)-2-Chloro-N-(2-((tosylimino)methyl)phenyl)benzenesulfonamide (1l)



A white amorphous solid. **M.p**.: 134-135 ℃ **^1H NMR (400 MHz, $CDCl_3$)** δ 11.52 (s, 1H), 9.04 (s, 1H), 8.21 (dd, J = 7.7, 1.8 Hz, 1H), 7.94 (d, J = 8.2 Hz, 2H), 7.63 – 7.51 (m, 2H), 7.48 – 7.32 (m, 6H), 7.09 (td, J = 7.6, 1.1 Hz, 1H), 2.47 (s, 3H). **$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)** δ 169.7, 145.2, 140.2, 137.6, 136.0, 134.7, 134.4,

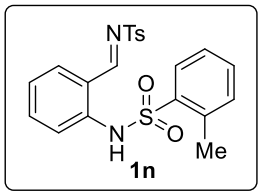
132.4, 132.1, 132.0, 130.1, 128.1, 126.8, 122.8, 117.6, 116.3, 21.7. **HRMS (ESI)** m/z: calcd. for $C_{20}H_{18}ClN_2O_4S_2^+$ $[M + H]^+$: 449.0391, found: 449.0396.

(E)-2-Bromo-N-(2-((tosylimino)methyl)phenyl)benzenesulfonamide (1m)



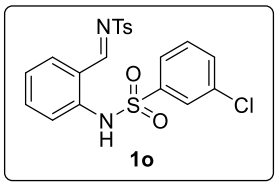
A white amorphous solid. **M.p**.: 173-174 ℃ **^{1}H NMR (400 MHz, $CDCl_3$)** δ 11.56 (s, 1H), 9.05 (s, 1H), 8.27 (dd, J = 7.9, 1.7 Hz, 1H), 7.98 – 7.90 (m, 2H), 7.56 (dt, J = 7.9, 1.4 Hz, 2H), 7.49 (d, J = 1.0 Hz, 1H), 7.45 (d, J = 1.3 Hz, 1H), 7.40 (d, J = 8.1 Hz, 3H), 7.35 (d, J = 1.7 Hz, 1H), 7.09 (td, J = 7.5, 1.2 Hz, 1H), 2.47 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 169.7, 145.3, 140.2, 137.6, 136.0, 135.5, 134.3, 132.4, 130.2, 129.7, 128.2, 127.4, 126.5, 122.8, 120.6, 117.6, 116.2, 21.7. **HRMS (ESI)** m/z: calcd. for $C_{20}H_{18}BrN_2O_4S_2^+$ $[M + H]^+$: 492.9886, found: 492.9893.

(E)-2-Methyl-N-(2-((tosylimino)methyl)phenyl)benzenesulfonamide (1n)



A white amorphous solid. **M.p**.: 180-181 ℃ **^{1}H NMR (400 MHz, $CDCl_3$)** δ 11.19 (s, 1H), 9.03 (s, 1H), 8.08 (dd, J = 7.9, 1.4 Hz, 1H), 7.92 (d, J = 8.3 Hz, 2H), 7.53 (dd, J = 7.8, 1.7 Hz, 2H), 7.46 – 7.37 (m, 4H), 7.30 (td, J = 7.7, 1.4 Hz, 1H), 7.19 (d, J = 7.6 Hz, 1H), 7.08 (td, J = 7.6, 1.0 Hz, 1H), 2.47 (s, 3H), 2.38 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 170.2, 145.2, 140.8, 137.6, 137.5, 136.9, 136.2, 134.9, 133.5, 132.8, 130.2, 130.1, 128.0, 126.1, 122.6, 117.2, 116.6, 21.7, 19.7. **HRMS (ESI)** m/z: calcd. for $C_{21}H_{21}N_2O_4S_2^+$ $[M + H]^+$: 492.0937, found: 429.0945.

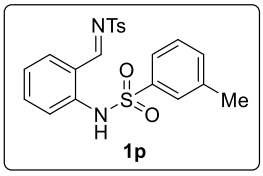
(E)-3-Chloro-N-(2-((tosylimino)methyl)phenyl)benzenesulfonamide (1o)



A white amorphous solid. **M.p**.: 128-129 ℃ **^{1}H NMR (400 MHz, $CDCl_3$)** δ 11.02 (s, 1H), 8.97 (s, 1H), 7.94 (d, J = 8.2 Hz, 2H), 7.81 (d, J = 8.1 Hz, 2H), 7.70 (d, J = 8.7 Hz, 1H), 7.56 – 7.53 (m, 2H), 7.43 (d, J = 7.9 Hz, 2H), 7.33 – 7.29 (m, 2H), 7.18 (t, J = 7.5 Hz, 1H), 2.43 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 170.1, 145.4, 143.6, 140.7, 140.3, 137.5, 136.1, 135.2, 134.8, 133.4, 130.4, 130.2,

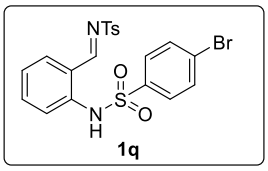
129.7, 128.0, 127.2, 126.5, 125.3, 123.9, 118.7, 21.8. **HRMS (ESI)** m/z: calcd. for $C_{20}H_{18}ClN_2O_4S_2^+$ $[M + H]^+$: 449.0391, found: 449.0398.

(E)-3-Methyl-N-(2-((tosylimino)methyl)phenyl)benzenesulfonamide (1p)



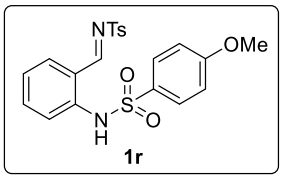
A white amorphous solid. **M.p**.: 129-130 °C **^{1}H NMR (400 MHz, $CDCl_3$)** δ 10.94 (s, 1H), 8.96 (s, 1H), 7.94 (d, J = 8.3 Hz, 2H), 7.69 (d, J = 7.8 Hz, 1H), 7.55 (s, 1H), 7.52 – 7.46 (m, 3H), 7.42 (d, J = 8.2 Hz, 2H), 7.28 (d, J = 7.6 Hz, 1H), 7.21 (t, J = 7.7 Hz, 1H), 7.13 (td, J = 7.5, 1.1 Hz, 1H), 2.47 (s, 3H), 2.29 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 170.1, 145.2, 140.8, 139.4, 138.9, 137.4, 136.0, 134.9, 134.1, 130.1, 128.8, 128.0, 127.5, 124.3, 123.4, 118.6, 118.4, 21.7, 21.2. **HRMS (ESI)** m/z: calcd. for $C_{21}H_{21}N_2O_4S_2^+$ $[M + H]^+$: 492.0937, found: 429.0945.

(E)-4-Bromo-N-(2-((tosylimino)methyl)phenyl)benzenesulfonamide (1q)



A white amorphous solid. **M.p**.: 191-192 °C **^{1}H NMR (400 MHz, $CDCl_3$)** δ 10.89 (s, 1H), 8.95 (s, 1H), 7.93 (d, J = 8.1 Hz, 2H), 7.72 (d, J = 8.7 Hz, 1H), 7.56 – 7.46 (m, 4H), 7.46 – 7.38 (m, 4H), 7.22 – 7.15 (m, 1H), 2.50 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 170.2, 145.4, 140.3, 138.1, 137.5, 136.1, 134.8, 132.3, 130.2, 129.7, 128.6, 128.3, 128.1, 126.5, 124.0, 119.2, 118.8, 21.7. **HRMS (ESI)** m/z: calcd. for $C_{20}H_{18}BrN_2O_4S_2^+$ $[M + H]^+$: 492.9886, found: 492.9894.

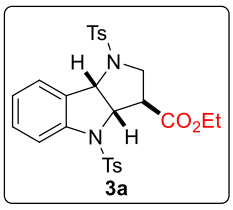
(E)-4-Methoxy-N-(2-((tosylimino)methyl)phenyl)benzenesulfonamide (1r)



A white amorphous solid. **M.p**.: 138-139 °C **^{1}H NMR (400 MHz, $CDCl_3$)** δ 10.84 (s, 1H), 8.95 (s, 1H), 7.94 (d, J = 8.1 Hz, 2H), 7.70 (d, J = 8.7 Hz, 1H), 7.59 (d, J = 8.9 Hz, 2H), 7.53 – 7.47 (m, 2H), 7.42 (d, J = 8.1 Hz, 2H), 7.13 (t, J = 7.5 Hz, 1H), 6.76 (d, J = 8.9 Hz, 2H), 3.79 (s, 3H), 2.48 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 170.2, 163.2, 145.2, 140.9, 137.4, 136.0, 135.0, 130.6, 130.1, 129.4, 128.1, 123.4, 118.8, 118.5,

114.2, 55.5, 21.7. **HRMS (ESI)** m/z: calcd. for $C_{21}H_{21}N_2O_5S_2^+$ $[M + H]^+$: 445.0886, found: 445.0892.

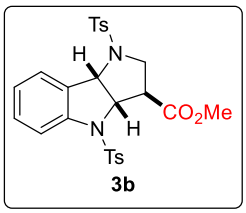
Ethyl-1,4-ditosyl-1,2,3,3a,4,8b-hexahydropyrrolo[3,2-b]indole-3-carboxylate (3a)



3a

The **3a** was prepared according to the general procedure as described above using **1a** (42.8 mg, 0.1 mmol), **2a** (27.6 mg, 0.12 mmol), K_2CO_3 (16.6 mg, 0.12 mmol) and PPh_2Me (4.0 mg, 20 mol%) and isolated as a yellow oil (46.6 mg, 86% yield, >20:1 *d.r.*) after flash column chromatography on silica gel (PE: EA = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.71 (d, J = 8.2 Hz, 1H), 7.65 – 7.57 (m, 5H), 7.36 – 7.30 (m, 1H), 7.28 (d, J = 8.1 Hz, 2H), 7.21 (d, J = 8.1 Hz, 2H), 7.10 (td, J = 7.5, 1.0 Hz, 1H), 5.26 (d, J = 8.3 Hz, 1H), 4.81 (dd, J = 8.3, 2.3 Hz, 1H), 4.02 (dd, J = 10.7, 7.1 Hz, 1H), 3.88 (dd, J = 10.7, 7.2 Hz, 1H), 3.77 – 3.70 (m, 1H), 3.57 – 3.50 (m, 2H), 2.43 (s, 3H), 2.38 (s, 3H), 1.23 (t, J = 7.2 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 170.6, 144.8, 143.8, 141.6, 135.8, 133.0, 130.2, 129.8, 129.71, 129.67, 127.54, 127.47, 125.1, 115.6, 67.3, 63.6, 61.6, 51.0, 48.9, 21.6, 21.5, 13.9. **HRMS (ESI)** m/z: calcd. for $C_{27}H_{29}N_2O_6S_2^+$ $[M + H]^+$: 541.1462, found: 541.1456.

Methyl-1,4-ditosyl-1,2,3,3a,4,8b-hexahydropyrrolo[3,2-b]indole-3-carboxylate (3b)

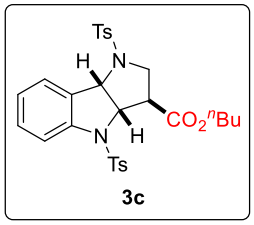


3b

The **3b** was prepared according to the general procedure as described above using **1a** (42.8 mg, 0.1 mmol), **2b** (25.9 mg, 0.12 mmol), K_2CO_3 (16.6 mg, 0.12 mmol) and PPh_2Me (4.0 mg, 20 mol%) and isolated as a yellow oil (38.6 mg, 73% yield, >20:1 *d.r.*) after flash column chromatography on silica gel (PE: EA = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.75 – 7.69 (m, 1H), 7.68 – 7.54 (m, 5H), 7.36 – 7.27 (m, 3H), 7.24 – 7.19 (m, 2H), 7.10 (td, J = 7.5, 1.0 Hz, 1H), 5.36 – 5.23 (m, 1H), 4.81 (dd, J = 8.2, 2.2 Hz, 1H), 3.77 – 3.69 (m, 1H), 3.59 – 3.51 (m, 5H), 2.44 (s, 3H), 2.38 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 171.1, 144.8, 143.9, 141.5, 135.7, 132.9, 130.2, 129.9, 129.8, 129.7, 127.52, 127.47, 125.2, 115.5, 67.3, 63.5, 52.5, 50.8, 48.9,

21.6, 21.5. **HRMS (ESI)** m/z: calcd. for $C_{26}H_{26}N_2O_6S_2Na^+$ $[M + Na]^+$: 549.1124, found: 549.1126.

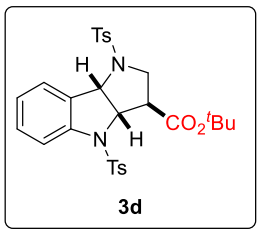
Butyl-1,4-ditosyl-1,2,3,3a,4,8b-hexahydropyrrolo[3,2-b]indole-3-carboxylate (3c)



3c

The **3c** was prepared according to the general procedure as described above using **1a** (42.8 mg, 0.1 mmol), **2c** (31.0 mg, 0.12 mmol), K_2CO_3 (16.6 mg, 0.12 mmol) and PPh_2Me (4.0 mg, 20 mol%) and isolated as a yellow oil (45.4 mg, 80% yield, >20:1 *d.r.*) after flash column chromatography on silica gel (PE: EA = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.71 (d, J = 8.2 Hz, 1H), 7.65 – 7.57 (m, 5H), 7.33 (td, J = 7.9, 1.3 Hz, 1H), 7.28 (d, J = 8.2 Hz, 2H), 7.20 (d, J = 8.1 Hz, 2H), 7.10 (td, J = 7.5, 1.0 Hz, 1H), 5.26 (d, J = 8.3 Hz, 1H), 4.81 (dd, J = 8.3, 2.0 Hz, 1H), 3.98 – 3.90 (m, 1H), 3.84 – 3.70 (m, 2H), 3.58 – 3.49 (m, 2H), 2.42 (s, 3H), 2.37 (s, 3H), 1.60 – 1.53 (m, 2H), 1.40 – 1.32 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 170.7, 144.8, 143.8, 141.5, 135.7, 132.8, 130.1, 129.8, 129.72, 129.66, 127.5, 127.4, 125.1, 115.5, 67.3, 65.6, 63.5, 51.0, 48.9, 30.3, 21.6, 21.5, 19.1, 13.7. **HRMS (ESI)** m/z: calcd. for $C_{29}H_{32}N_2O_6S_2Na^+$ $[M + Na]^+$: 591.1594, found: 591.1595.

Tert-butyl-1,4-ditosyl-1,2,3,3a,4,8b-hexahydropyrrolo[3,2-b]indole-3-carboxylate (3d)

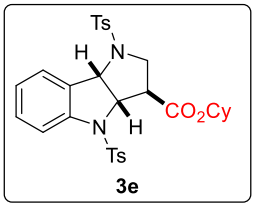


3d

The **3d** was prepared according to the general procedure as described above using **1a** (42.8 mg, 0.1 mmol), **2d** (31.0 mg, 0.12 mmol), K_2CO_3 (16.6 mg, 0.12 mmol) and PPh_2Me (4.0 mg, 20 mol%) and isolated as a yellow oil (46.1 mg, 81% yield, >20:1 *d.r.*) after flash column chromatography on silica gel (PE: EA = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.69 (d, J = 8.2 Hz, 1H), 7.60 (d, J = 8.3 Hz, 2H), 7.55 (dd, J = 8.6, 2.1 Hz, 3H), 7.31 (td, J = 7.9, 1.4 Hz, 1H), 7.28 – 7.26 (m, 1H), 7.25 (s, 1H), 7.21 – 7.17 (m, 2H), 7.07 (td, J = 7.6, 1.0 Hz, 1H), 5.17 (d, J = 8.3 Hz, 1H), 4.75 (dd, J = 8.3, 3.2 Hz, 1H), 3.67 – 3.60 (m, 1H), 3.50 – 3.41 (m, 2H), 2.41 (s, 3H), 2.37

(s, 3H), 1.43 (s, 9H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 169.6, 144.7, 143.9, 141.4, 135.5, 133.0, 130.1, 130.0, 129.8, 129.7, 127.5, 127.4, 127.3, 125.1, 116.0, 82.4, 67.5, 63.4, 51.6, 49.0, 28.0, 27.9, 21.6, 21.5. **HRMS (ESI)** m/z: calcd. for $C_{29}H_{32}N_2O_6S_2Na^+$ $[M + Na]^+$: 591.1594, found: 591.1586.

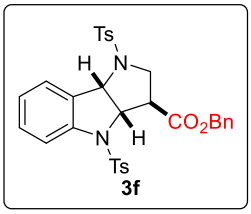
Cyclohexyl-1,4-ditosyl-1,2,3,3a,4,8b-hexahydropyrrolo[3,2-b]indole-3-carboxylate (3e)



3e

The **3e** was prepared according to the general procedure as described above using **1a** (42.8 mg, 0.1 mmol), **2e** (34.1 mg, 0.12 mmol), K_2CO_3 (16.6 mg, 0.12 mmol) and PPh_2Me (4.0 mg, 20 mol%) and isolated as a yellow oil (44,3 mg, 75% yield, >20:1 *d.r.*) after flash column chromatography on silica gel (PE: EA = 10:1).**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.70 (d, J = 8.2 Hz, 1H), 7.64 – 7.55 (m, 5H), 7.32 (td, J = 7.9, 1.4 Hz, 1H), 7.28 (s, 1H), 7.26 (s, 1H), 7.20 (d, J = 8.1 Hz, 2H), 7.09 (td, J = 7.5, 1.0 Hz, 1H), 5.26 (d, J = 8.3 Hz, 1H), 4.81 (d, J = 8.2 Hz, 1H), 4.54 (dq, J = 9.0, 5.2, 4.2 Hz, 1H), 3.74 – 3.67 (m, 1H), 3.56 – 3.48 (m, 2H), 2.42 (s, 3H), 2.38 (s, 3H), 1.84 (d, J = 12.3 Hz, 1H), 1.75 – 1.68 (m, 3H), 1.54 (dd, J = 11.1, 4.9 Hz, 1H), 1.41 – 1.24 (m, 5H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 170.1, 144.7, 143.8, 141.6, 135.7, 132.8, 130.1, 129.8, 129.6, 127.5, 127.4, 125.1, 115.6, 74.3, 67.3, 63.6, 51.2, 49.0, 31.3, 31.2, 25.2, 23.72, 23.65, 21.57, 21.55. **HRMS (ESI)** m/z: calcd. for $C_{31}H_{34}N_2O_6S_2Na^+$ $[M + Na]^+$: 617.1750, found: 617.1752.

Benzyl-1,4-ditosyl-1,2,3,3a,4,8b-hexahydropyrrolo[3,2-b]indole-3-carboxylate (3f)

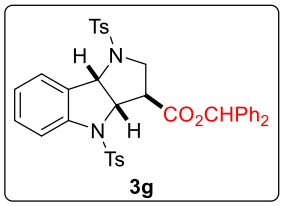


3f

The **3f** was prepared according to the general procedure as described above using **1a** (42.8 mg, 0.1 mmol), **2f** (34.1 mg, 0.12 mmol), K_2CO_3 (16.6 mg, 0.12 mmol) and PPh_2Me (4.0 mg, 20 mol%) and isolated as a yellow oil (27.7 mg, 46% yield, >20:1 *d.r.*) after flash column chromatography on silica gel (PE: EA = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.71 (d, J = 8.2 Hz, 1H), 7.63 (d, J = 8.3 Hz, 2H), 7.61 – 7.58 (m, 1H), 7.55 (d, J = 8.3 Hz, 2H), 7.44 – 7.36 (m, 3H), 7.32 (dd, J = 7.6, 1.9 Hz,

3H), 7.26 (d, J = 1.2 Hz, 1H), 7.25 – 7.24 (m, 1H), 7.20 – 7.15 (m, 2H), 7.10 (td, J = 7.5, 1.0 Hz, 1H), 5.30 (d, J = 8.3 Hz, 1H), 4.96 (d, J = 12.3 Hz, 1H), 4.89 (d, J = 12.3 Hz, 1H), 4.84 (dd, J = 8.3, 2.6 Hz, 1H), 3.81 (dd, J = 11.4, 3.3 Hz, 1H), 3.62 (dt, J = 6.3, 3.0 Hz, 1H), 3.53 (dd, J = 11.5, 6.9 Hz, 1H), 2.41 (s, 3H), 2.37 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 170.4, 144.8, 143.9, 141.6, 135.7, 135.0, 132.8, 130.2, 129.8, 129.7, 129.6, 128.7, 128.5, 128.1, 127.6, 127.5, 127.4, 125.1, 115.4, 67.4, 67.3, 63.5, 51.1, 48.9, 21.6, 21.5. **HRMS (ESI)** m/z: calcd. for $C_{32}H_{30}N_2O_6S_2Na^+$ [M + Na]$^+$: 625.1437, found: 625.1438.

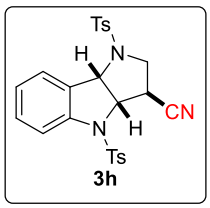
Benzhydryl-1,4-ditosyl-1,2,3,3a,4,8b-hexahydropyrrolo[3,2-b]indole-3-carboxylate (3g)



3g

The **3g** was prepared according to the general procedure as described above using **1a** (42.8 mg, 0.1 mmol), **2g** (44.2 mg, 0.12 mmol), K_2CO_3 (16.6 mg, 0.12 mmol) and PPh_2Me (4.0 mg, 20 mol%) and isolated as a yellow oil (44.2 mg, 65% yield, >20:1 *d.r.*) after flash column chromatography on silica gel (PE: EA = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.71 (d, J = 8.2 Hz, 1H), 7.59 (d, J = 7.6 Hz, 1H), 7.53 – 7.49 (m, 4H), 7.43 – 7.37 (m, 3H), 7.36 – 7.33 (m, 5H), 7.32 – 7.28 (m, 3H), 7.12 (dd, J = 8.3, 2.4 Hz, 4H), 7.08 (d, J = 7.5 Hz, 1H), 6.63 (s, 1H), 5.23 (d, J = 8.3 Hz, 1H), 4.82 (dd, J = 8.3, 2.6 Hz, 1H), 3.82 (dd, J = 11.4, 3.5 Hz, 1H), 3.71 (dt, J = 6.5, 3.1 Hz, 1H), 3.56 (dd, J = 11.4, 7.1 Hz, 1H), 2.39 (s, 3H), 2.35 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 169.6, 144.7, 143.7, 141.6, 139.51, 139.46, 135.4, 132.7, 130.2, 129.8, 129.7, 129.6, 129.5, 128.64, 128.59, 128.13, 128.11, 127.5, 127.4, 127.1, 126.9, 125.1, 115.5, 78.4, 67.4, 63.5, 51.3, 48.8, 21.6. **HRMS (ESI)** m/z: calcd. for $C_{38}H_{34}N_2O_6S_2Na^+$ [M + Na]$^+$: 701.1750, found: 701.1752.

1,4-Ditosyl-1,2,3,3a,4,8b-hexahydropyrrolo[3,2-b]indole-3-carbonitrile (3h)

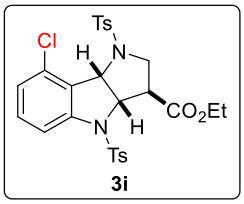


3h

The **3h** was prepared according to the general procedure as described above using **1a** (42.8 mg, 0.1 mmol), **2h** (22.0 mg, 0.12

mmol), K_2CO_3 (16.6 mg, 0.12 mmol) and PPh_2Me (4.0 mg, 20 mol%) and isolated as a yellow oil (28.7 mg, 58% yield, >20:1 *d.r.*) after flash column chromatography on silica gel (PE: EA = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.71 (dd, J = 12.0, 8.3 Hz, 3H), 7.61 (t, J = 7.5 Hz, 3H), 7.34 (dd, J = 8.2, 7.0 Hz, 3H), 7.24 (d, J = 8.2 Hz, 2H), 7.16 – 7.11 (m, 1H), 5.37 (d, J = 8.1 Hz, 1H), 4.54 (dd, J = 8.0, 2.2 Hz, 1H), 3.77 (dd, J = 11.9, 2.7 Hz, 1H), 3.68 (dt, J = 5.3, 2.5 Hz, 1H), 3.53 (dd, J = 11.9, 6.0 Hz, 1H), 2.44 (s, 3H), 2.39 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 145.4, 144.7, 141.1, 135.1, 132.2, 130.7, 130.1, 128.5, 127.6, 127.5, 125.6, 117.4, 115.2, 68.8, 63.1, 48.4, 37.2, 21.6. **HRMS (ESI)** m/z: calcd. for $C_{25}H_{23}N_3O_4S_2Na^+$ $[M + Na]^+$: 516.1022, found: 516.1023.

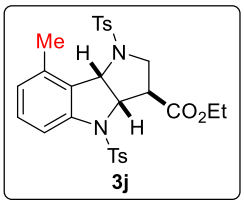
Ethyl-8-chloro-1,4-ditosyl-1,2,3,3a,4,8b-hexahydropyrrolo[3,2-b]indole-3-carboxylate (3i)



3i

The **3i** was prepared according to the general procedure as described above using **1b** (46.2 mg, 0.1 mmol), **2a** (27.6 mg, 0.12 mmol), K_2CO_3 (16.6 mg, 0.12 mmol) and PPh_2Me (4.0 mg, 20 mol%) and isolated as a yellow oil (40.2 mg, 70% yield, >20:1 *d.r.*) after flash column chromatography on silica gel (PE: EA = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.71 (d, J = 8.3 Hz, 2H), 7.64 (dd, J = 8.4, 1.8 Hz, 3H), 7.27 (d, J = 7.0 Hz, 3H), 7.25 – 7.21 (m, 2H), 6.99 (dd, J = 8.0, 0.8 Hz, 1H), 5.92 (d, J = 8.2 Hz, 1H), 5.12 (d, J = 8.2 Hz, 1H), 4.25 (p, J = 7.1 Hz, 2H), 4.21 – 4.14 (m, 1H), 3.56 (d, J = 6.9 Hz, 1H), 3.25 (dd, J = 13.2, 7.1 Hz, 1H), 2.41 (d, J = 3.8 Hz, 6H), 1.36 (t, J = 7.2 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 170.3, 145.2, 143.9, 143.6, 137.3, 132.9, 132.7, 131.4, 130.1, 129.4, 127.42, 127.39, 126.5, 125.5, 113.3, 66.8, 63.9, 61.9, 53.2, 49.8, 21.6, 21.5, 14.1. **HRMS (ESI)** m/z: calcd. for $C_{27}H_{28}ClN_2O_6S_2^+$ $[M + H]^+$: 575.1072, found: 575.1075.

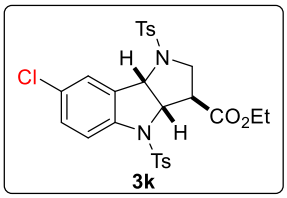
Ethyl-8-methyl-1,4-ditosyl-1,2,3,3a,4,8b-hexahydropyrrolo[3,2-b]indole-3-carboxylate (3j)



3j

The **3j** was prepared according to the general procedure as described above using **1c** (44.2 mg, 0.1 mmol), **2a** (27.6 mg, 0.12 mmol), K_2CO_3 (16.6 mg, 0.12 mmol) and PPh_2Me (4.0 mg, 20 mol%) and isolated as a yellow oil (42.3 mg, 76% yield, >20:1 *d.r.*) after flash column chromatography on silica gel (PE: EA = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.64 – 7.58 (m, 4H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.22 (dd, *J* = 17.8, 8.0 Hz, 3H), 6.84 (d, *J* = 7.6 Hz, 1H), 5.72 (d, *J* = 8.0 Hz, 1H), 4.96 (dd, *J* = 8.1, 1.9 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 4.02 (dd, *J* = 13.2, 1.8 Hz, 1H), 3.46 (dt, *J* = 7.8, 2.0 Hz, 1H), 3.28 (dd, *J* = 13.2, 7.8 Hz, 1H), 2.43 (s, 3H), 2.40 (s, 3H), 2.29 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 170.4, 144.7, 144.0, 142.0, 137.6, 136.3, 133.3, 130.2, 129.8, 129.7, 127.39, 127.35, 127.0, 126.8, 113.2, 66.5, 64.2, 61.7, 52.8, 49.3, 21.61, 21.55, 18.7, 14.1. **HRMS (ESI)** m/z: calcd. for $C_{28}H_{31}N_2O_6S_2^+$ $[M + H]^+$: 555.1618, found: 555.1607.

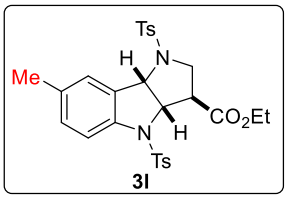
Ethyl-7-chloro-1,4-ditosyl-1,2,3,3a,4,8b-hexahydropyrrolo[3,2-b]indole-3-carboxylate (3k)



3k

The **3k** was prepared according to the general procedure as described above using **1d** (46.2 mg, 0.1 mmol), **2a** (27.6 mg, 0.12 mmol), K_2CO_3 (16.6 mg, 0.12 mmol) and PPh_2Me (4.0 mg, 20 mol%) and isolated as a yellow oil (45.0 mg, 78% yield, >20:1 *d.r.*) after flash column chromatography on silica gel (PE: EA = 10:1).**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.63 (d, *J* = 8.4 Hz, 3H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 2.3 Hz, 1H), 7.31 (s, 1H), 7.30 – 7.26 (m, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 5.19 (d, *J* = 8.3 Hz, 1H), 4.84 – 4.80 (m, 1H), 4.02 (dd, *J* = 10.7, 7.2 Hz, 1H), 3.89 (dd, *J* = 10.7, 7.2 Hz, 1H), 3.80 – 3.73 (m, 1H), 3.57 – 3.49 (m, 2H), 2.44 (s, 3H), 2.40 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 170.4, 145.1, 144.1, 140.2, 135.5, 132.5, 131.5, 130.4, 130.3, 130.0, 129.8, 127.52, 127.50, 116.6, 67.7, 63.1, 61.7, 50.9, 49.0, 21.6, 21.5, 13.9. **HRMS (ESI)** m/z: calcd. for $C_{27}H_{27}ClN_2O_6S_2Na^+$ $[M + Na]^+$: 597.0891, found: 597.0902.

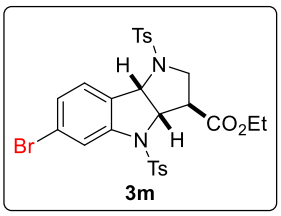
Ethyl-7-methyl-1,4-ditosyl-1,2,3,3a,4,8b-hexahydropyrrolo[3,2-b]indole-3-carboxylate (3l)



3l

The **3l** was prepared according to the general procedure as described above using **1e** (44.2 mg, 0.1 mmol), **2a** (27.6 mg, 0.12 mmol), K_2CO_3 (16.6 mg, 0.12 mmol) and PPh_2Me (4.0 mg, 20 mol%) and isolated as a yellow oil (45.8 mg, 83% yield, >20:1 *d.r.*) after flash column chromatography on silica gel (PE: EA = 10:1).**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.63 (d, J = 8.3 Hz, 2H), 7.56 (dd, J = 8.3, 5.4 Hz, 3H), 7.36 – 7.31 (m, 1H), 7.28 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 8.1 Hz, 2H), 7.12 (dd, J = 8.4, 1.8 Hz, 1H), 5.17 (d, J = 8.2 Hz, 1H), 4.77 (dd, J = 8.2, 2.5 Hz, 1H), 4.06 – 3.98 (m, 1H), 3.88 (dd, J = 10.7, 7.2 Hz, 1H), 3.77 – 3.70 (m, 1H), 3.57 – 3.47 (m, 2H), 2.43 (s, 3H), 2.37 (s, 3H), 2.28 (s, 3H), 1.23 (t, J = 7.2 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 170.6, 144.6, 143.8, 139.1, 135.7, 135.1, 132.8, 130.8, 129.9, 129.8, 129.6, 127.6, 127.5, 115.5, 67.4, 63.6, 61.6, 50.9, 48.9, 21.54, 21.48, 20.9, 13.9. **HRMS (ESI)** m/z: calcd. for $C_{28}H_{31}N_2O_6S_2^+$ $[M + H]^+$: 555.1618, found: 555.1616.

Ethyl-6-bromo-1,4-ditosyl-1,2,3,3a,4,8b-hexahydropyrrolo[3,2-b]indole-3-carboxylate (3m)

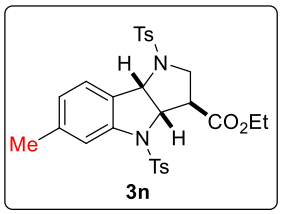


3m

The **3m** was prepared according to the general procedure as described above using **1f** (50.6 mg, 0.1 mmol), **2a** (27.6 mg, 0.12 mmol), K_2CO_3 (16.6 mg, 0.12 mmol) and PPh_2Me (4.0 mg, 20 mol%) and isolated as a yellow oil (50.8 mg, 82% yield, >20:1 *d.r.*) after flash column chromatography on silica gel (PE: EA = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.89 (d, J = 1.7 Hz, 1H), 7.64 – 7.59 (m, 4H), 7.46 (d, J = 8.2 Hz, 1H), 7.29 (t, J = 1.1 Hz, 1H), 7.27 (d, J = 2.2 Hz, 2H), 7.25 (s, 1H), 7.22 (dd, J = 8.1, 1.8 Hz, 1H), 5.21 (d, J = 8.3 Hz, 1H), 4.84 – 4.80 (m, 1H), 4.05 – 3.95 (m, 1H), 3.84 (dd, J = 10.7, 7.2 Hz, 1H), 3.76 – 3.70 (m, 1H), 3.53 (d, J = 8.0 Hz, 2H), 2.43 (s, 3H), 2.40 (s, 3H), 1.22 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 170.5, 145.2, 144.0, 142.9, 135.5, 132.5, 130.0, 129.7, 128.73, 128.70, 128.2,

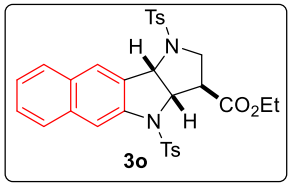
127.50, 127.47, 124.1, 118.4, 67.7, 63.0, 61.7, 50.9, 48.9, 21.6, 21.5, 13.9. **HRMS (ESI)** m/z: calcd. for $C_{27}H_{27}BrN_2O_6S_2Na^+$ $[M + Na]^+$: 641.0386, found: 641.0383.

Ethyl-6-methyl-1,4-ditosyl-1,2,3,3a,4,8b-hexahydropyrrolo[3,2-b]indole-3-carboxylate (3n)



The **3n** was prepared according to the general procedure as described above using **1g** (44.2 mg, 0.1 mmol), **2a** (27.6 mg, 0.12 mmol), K_2CO_3 (16.6 mg, 0.12 mmol) and PPh_2Me (4.0 mg, 20 mol%) and isolated as a yellow oil (46.3 mg, 84% yield, >20:1 *d.r.*) after flash column chromatography on silica gel (PE: EA = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.65 – 7.61 (m, 2H), 7.60 – 7.56 (m, 2H), 7.53 (s, 1H), 7.45 (d, J = 7.8 Hz, 1H), 7.28 (d, J = 8.2 Hz, 2H), 7.21 (d, J = 8.1 Hz, 2H), 6.91 (dt, J = 7.9, 1.0 Hz, 1H), 5.21 (d, J = 8.2 Hz, 1H), 4.79 (dd, J = 8.3, 2.4 Hz, 1H), 4.07 – 3.96 (m, 1H), 3.87 (dd, J = 10.7, 7.2 Hz, 1H), 3.73 – 3.67 (m, 1H), 3.54 – 3.48 (m, 2H), 2.43 (s, 3H), 2.39 (s, 3H), 2.38 (s, 3H), 1.22 (t, J = 7.2 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 170.7, 144.7, 143.8, 141.7, 140.6, 135.7, 132.9, 129.8, 129.6, 127.50, 127.46, 127.0, 126.1, 116.0, 67.5, 63.3, 61.6, 50.9, 48.8, 21.8, 21.6, 21.5, 13.9. **HRMS (ESI)** m/z: calcd. for $C_{28}H_{30}N_2O_6S_2Na^+$ $[M + Na]^+$: 577.1437, found: 577.1447.

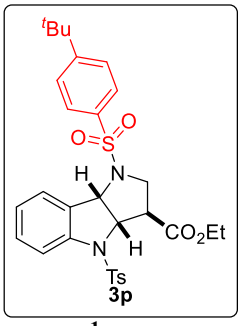
Ethyl-1,4-ditosyl-1,2,3,3a,4,10b-hexahydrobenzo[f]pyrrolo[3,2-b]indole-3-carboxylate (3o)



The **3o** was prepared according to the general procedure as described above using **1h** (47.8 mg, 0.1 mmol), **2a** (27.6 mg, 0.12 mmol), K_2CO_3 (16.6 mg, 0.12 mmol) and PPh_2Me (4.0 mg, 20 mol%) and isolated as a yellow oil (48.0 mg, 81% yield, >20:1 *d.r.*) after flash column chromatography on silica gel (PE: EA = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.05 (d, J = 16.8 Hz, 2H), 7.85 (d, J = 8.2 Hz, 1H), 7.76 (d, J = 8.1 Hz, 1H), 7.64 (dd, J = 11.2, 8.3 Hz, 4H), 7.52 – 7.47 (m, 1H), 7.41 (ddd, J = 8.2, 6.9, 1.2 Hz, 1H), 7.28 (d, J = 8.1 Hz, 2H), 7.17 (d, J = 8.1 Hz, 2H), 5.40 (d, J = 8.1 Hz, 1H), 4.91 (dd, J

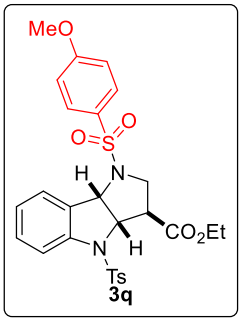
= 8.1, 2.2 Hz, 1H), 4.05 (dd, *J* = 10.7, 7.1 Hz, 1H), 3.91 (dd, *J* = 10.7, 7.2 Hz, 1H), 3.82 – 3.73 (m, 1H), 3.58 (d, *J* = 8.4 Hz, 2H), 2.42 (s, 3H), 2.34 (s, 3H), 1.24 (d, *J* = 7.3 Hz, 3H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** *δ* 170.6, 144.9, 143.9, 139.3, 135.8, 134.5, 133.0, 131.3, 130.0, 129.9, 129.7, 128.3, 127.7, 127.53, 127.48, 127.2, 127.0, 125.2, 112.0, 67.7, 62.9, 61.7, 51.0, 49.1, 21.6, 21.5, 13.9. **HRMS (ESI)** m/z: calcd. for $C_{31}H_{31}N_2O_6S_2^+$ $[M + H]^+$: 591.1618, found: 591.1611.

Ethyl-1-((4-(tert-butyl)phenyl)sulfonyl)-4-tosyl-1,2,3,3a,4,8b-hexahydropyrrolo[3,2-b]indole-3-carboxylate (3p)



The **3p** was prepared according to the general procedure as described above using **1i** (47.0 mg, 0.1 mmol), **2a** (27.6 mg, 0.12 mmol), K_2CO_3 (16.6 mg, 0.12 mmol) and PPh_2Me (4.0 mg, 20 mol%) and isolated as a yellow oil (49.7 mg, 85% yield, >20:1 *d.r.*) after flash column chromatography on silica gel (PE: EA = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** *δ* 7.69 (dd, *J* = 14.7, 8.4 Hz, 3H), 7.62 – 7.56 (m, 3H), 7.50 – 7.47 (m, 2H), 7.33 (td, *J* = 7.9, 1.4 Hz, 1H), 7.23 – 7.18 (m, 2H), 7.09 (td, *J* = 7.6, 1.0 Hz, 1H), 5.30 (d, *J* = 8.2 Hz, 1H), 4.84 (dd, *J* = 8.3, 2.0 Hz, 1H), 3.98 (dd, *J* = 10.7, 7.2 Hz, 1H), 3.86 – 3.73 (m, 2H), 3.55 (d, *J* = 8.7 Hz, 2H), 2.37 (s, 3H), 1.34 (s, 9H), 1.21 (t, *J* = 7.2 Hz, 3H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** *δ* 170.6, 156.7, 144.7, 141.7, 135.9, 133.0, 130.1, 129.83, 129.78, 127.53, 127.48, 127.4, 126.1, 125.1, 115.5, 67.4, 63.6, 61.5, 51.0, 48.9, 35.2, 31.1, 21.5, 13.9. **HRMS (ESI)** m/z: calcd. for $C_{30}H_{35}N_2O_6S_2^+$ $[M + H]^+$: 583.1931, found: 583.1930.

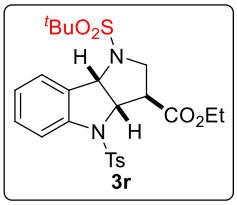
Ethyl-1-((4-methoxyphenyl)sulfonyl)-4-tosyl-1,2,3,3a,4,8b-hexahydropyrrolo[3,2-b]indole-3-carboxylate (3q)



The **3q** was prepared according to the general procedure as described above using **1j** (44.4 mg, 0.1 mmol), **2a** (27.6 mg, 0.12 mmol), K_2CO_3 (16.6 mg, 0.12 mmol) and PPh_2Me (4.0 mg, 20 mol%) and isolated as a yellow oil (40.7 mg, 73% yield, >20:1

d.r.) after flash column chromatography on silica gel (PE: EA = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.69 (t, *J* = 8.7 Hz, 3H), 7.59 (dd, *J* = 8.4, 1.9 Hz, 3H), 7.33 (ddd, *J* = 8.4, 7.6, 1.4 Hz, 1H), 7.23 – 7.18 (m, 2H), 7.10 (td, *J* = 7.5, 1.0 Hz, 1H), 6.99 – 6.90 (m, 2H), 5.24 (d, *J* = 8.3 Hz, 1H), 4.87 – 4.78 (m, 1H), 4.06 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.98 – 3.91 (m, 1H), 3.87 (s, 3H), 3.78 – 3.68 (m, 1H), 3.58 – 3.45 (m, 2H), 2.38 (s, 3H), 1.24 (t, *J* = 7.2 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 170.7, 163.2, 144.8, 141.6, 132.9, 130.2, 130.1, 129.9, 129.8, 129.7, 127.5, 127.4, 125.1, 115.6, 114.2, 67.3, 63.5, 61.7, 55.7, 51.0, 48.9, 21.6, 14.0. **HRMS (ESI)** m/z: calcd. for $C_{27}H_{29}N_2O_7S_2^+$ $[M + H]^+$: 557.1411, found: 557.1420.

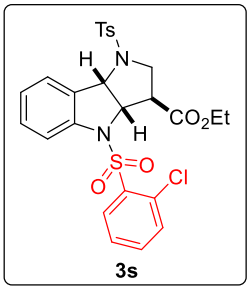
Ethyl-1-(tert-butylsulfonyl)-4-tosyl-1,2,3,3a,4,8b-hexahydropyrrolo[3,2-b]indole-3-carboxylate (3r)



3r

The **3r** was prepared according to the general procedure as described above using **1k** (39.4 mg, 0.1 mmol), **2a** (27.6 mg, 0.12 mmol), K_2CO_3 (16.6 mg, 0.12 mmol) and PPh_2Me (4.0 mg, 20 mol%) and isolated as a yellow oil (26.7 mg, 53% yield, >20:1 *d.r.*) after flash column chromatography on silica gel (PE: EA = 10:1).**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.75 (d, *J* = 8.4 Hz, 1H), 7.67 – 7.62 (m, 2H), 7.41 (d, *J* = 7.7 Hz, 1H), 7.34 – 7.29 (m, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.04 (td, *J* = 7.5, 1.0 Hz, 1H), 5.67 (d, *J* = 7.9 Hz, 1H), 4.90 (d, *J* = 7.9 Hz, 1H), 4.27 (dt, *J* = 7.1, 3.5 Hz, 2H), 4.05 – 3.98 (m, 1H), 3.75 (d, *J* = 6.3 Hz, 1H), 3.46 (dd, *J* = 11.9, 6.5 Hz, 1H), 2.37 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H), 1.29 (s, 9H). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 171.1, 144.9, 142.4, 132.5, 130.1, 130.0, 129.9, 129.5, 128.0, 127.6, 127.4, 124.4, 115.0, 67.2, 64.5, 61.8, 60.8, 52.1, 51.4, 24.5, 21.6, 14.1. **HRMS (ESI)** m/z: calcd. for $C_{24}H_{30}N_2O_6S_2Na^+$ $[M + Na]^+$: 529.1437, found: 529.1444.

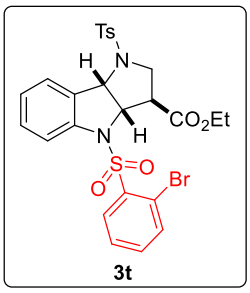
Ethyl-4-((2-chlorophenyl)sulfonyl)-1-tosyl-1,2,3,3a,4,8b-hexahydropyrrolo[3,2-b]indole-3-carboxylate (3s)



3s

The **3s** was prepared according to the general procedure as described above using **1l** (44.8 mg, 0.1 mmol), **2a** (27.6 mg, 0.12 mmol), K_2CO_3 (16.6 mg, 0.12 mmol) and PPh_2Me (4.0 mg, 20 mol%) and isolated as a yellow oil (42.4 mg, 76% yield, >20:1 *d.r.*) after flash column chromatography on silica gel (PE: EA = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.09 (dd, J = 7.9, 1.6 Hz, 1H), 7.75 – 7.69 (m, 3H), 7.52 – 7.42 (m, 2H), 7.40 – 7.28 (m, 4H), 7.20 (td, J = 7.8, 1.3 Hz, 1H), 7.08 (td, J = 7.5, 1.1 Hz, 1H), 5.51 (d, J = 8.5 Hz, 1H), 5.17 (dd, J = 8.6, 5.2 Hz, 1H), 4.12 – 3.95 (m, 2H), 3.61 – 3.55 (m, 2H), 3.39 (td, J = 6.9, 5.1 Hz, 1H), 2.45 (s, 3H), 1.24 (d, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 170.4, 144.2, 140.1, 135.53, 134.51, 134.4, 133.0, 132.2, 132.0, 129.9, 129.7, 129.6, 127.7, 127.3, 127.1, 124.9, 114.8, 67.4, 63.7, 61.7, 50.5, 49.3, 21.6, 13.9. **HRMS (ESI)** m/z: calcd. for $C_{26}H_{25}ClN_2O_6S_2Na^+$ $[M + Na]^+$: 583.0735, found: 583.0730.

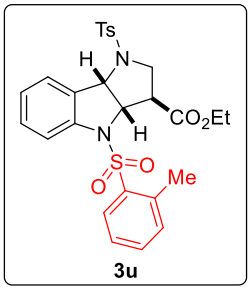
Ethyl-4-((2-bromophenyl)sulfonyl)-1-tosyl-1,2,3,3a,4,8b-hexahydropyrrolo[3,2-b]indole-3-carboxylate (3t)



3t

The **3t** was prepared according to the general procedure as described above using **1m** (49.2 mg, 0.1 mmol), **2a** (27.6 mg, 0.12 mmol), K_2CO_3 (16.6 mg, 0.12 mmol) and PPh_2Me (4.0 mg, 20 mol%) and isolated as a yellow oil (50.9 mg, 84% yield, >20:1 *d.r.*) after flash column chromatography on silica gel (PE: EA = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.09 (dd, J = 7.7, 1.9 Hz, 1H), 7.75 – 7.65 (m, 4H), 7.45 – 7.37 (m, 2H), 7.36 – 7.30 (m, 3H), 7.23 – 7.19 (m, 1H), 7.09 (t, J = 7.5 Hz, 1H), 5.53 (d, J = 8.5 Hz, 1H), 5.20 (dd, J = 8.5, 5.3 Hz, 1H), 4.10 – 3.94 (m, 2H), 3.57 (dd, J = 7.3, 1.6 Hz, 2H), 3.39 (dd, J = 7.0, 5.3 Hz, 1H), 2.45 (s, 3H), 1.23 (t, J = 7.2 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 170.4, 144.2, 140.2, 137.4, 135.9, 134.5, 134.3, 133.1, 129.9, 129.7, 129.6, 127.7, 127.6, 127.3, 124.9, 120.1, 114.9, 67.6, 63.7, 61.7, 50.3, 49.3, 21.6, 13.9. **HRMS (ESI)** m/z: calcd. for $C_{26}H_{25}BrN_2O_6S_2Na^+$ $[M + Na]^+$: 627.0230, found: 627.0238.

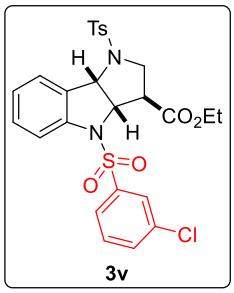
Ethyl-4-(o-tolylsulfonyl)-1-tosyl-1,2,3,3a,4,8b-hexahydropyrrolo[3,2-b]indole-3-carboxylate (3u)



3u

The **3u** was prepared according to the general procedure as described above using **1n** (42.8 mg, 0.1 mmol), **2a** (27.6 mg, 0.12 mmol), K_2CO_3 (16.6 mg, 0.12 mmol) and PPh_2Me (4.0 mg, 20 mol%) and isolated as a yellow oil (44.6 mg, 83% yield, >20:1 *d.r.*) after flash column chromatography on silica gel (PE: EA = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.74 (dd, J = 7.9, 1.3 Hz, 1H), 7.67 (dd, J = 8.4, 2.0 Hz, 3H), 7.51 (d, J = 8.2 Hz, 1H), 7.44 (td, J = 7.5, 1.4 Hz, 1H), 7.33 – 7.27 (m, 3H), 7.23 (d, J = 7.2 Hz, 1H), 7.12 (td, J = 7.5, 1.0 Hz, 1H), 5.41 (d, J = 8.4 Hz, 1H), 4.87 (dd, J = 8.4, 4.0 Hz, 1H), 4.03 – 3.84 (m, 2H), 3.63 (dd, J = 11.2, 5.2 Hz, 1H), 3.52 (dd, J = 11.2, 7.2 Hz, 1H), 3.46 – 3.34 (m, 1H), 2.49 (s, 3H), 2.44 (s, 3H), 1.19 (t, J = 7.2 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 170.4, 144.0, 141.5, 138.2, 136.1, 135.2, 133.3, 133.1, 130.0, 129.8, 129.60, 129.55, 127.6, 127.3, 126.4, 125.1, 115.7, 66.7, 63.8, 61.7, 50.6, 49.1, 21.5, 21.0, 13.9. **HRMS (ESI)** m/z: calcd. for $C_{27}H_{29}N_2O_6S_2^+$ $[M + H]^+$: 541.1462, found: 541.1468.

Ethyl-4-((3-chlorophenyl)sulfonyl)-1-tosyl-1,2,3,3a,4,8b-hexahydropyrrolo[3,2-b]indole-3-carboxylate (3v)

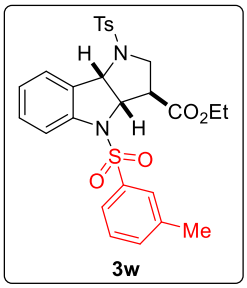


3v

The **3v** was prepared according to the general procedure as described above using **1o** (44.8 mg, 0.1 mmol), **2a** (27.6 mg, 0.12 mmol), K_2CO_3 (16.6 mg, 0.12 mmol) and PPh_2Me (4.0 mg, 20 mol%) and isolated as a yellow oil (43.5 mg, 78% yield, >20:1 *d.r.*) after flash column chromatography on silica gel (PE: EA = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.72 – 7.67 (m, 2H), 7.67 – 7.62 (m, 3H), 7.58 – 7.53 (m, 2H), 7.39 – 7.33 (m, 2H), 7.32 – 7.28 (m, 2H), 7.14 (td, J = 7.6, 1.0 Hz, 1H), 5.26 (d, J = 8.3 Hz, 1H), 4.80 (dd, J = 8.3, 2.9 Hz, 1H), 4.03 (dd, J = 10.7, 7.2 Hz, 1H), 3.95 – 3.85 (m, 1H), 3.74 – 3.67 (m, 1H), 3.59 – 3.46 (m, 2H), 2.43 (s, 3H), 1.23 (t, J = 7.2 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 170.4, 144.0, 140.9, 137.5, 135.5, 135.3, 133.9, 130.5, 130.3, 129.9, 129.8, 127.6, 127.52, 127.46, 125.7,

125.5, 115.5, 67.3, 63.5, 61.8, 50.8, 48.9, 21.5, 13.9. **HRMS (ESI)** m/z: calcd. for $C_{26}H_{25}ClN_2O_6S_2Na^+$ $[M + Na]^+$: 583.0735, found: 583,0743.

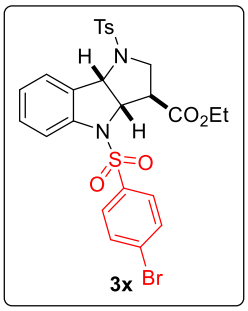
Ethyl-4-(m-tolylsulfonyl)-1-tosyl-1,2,3,3a,4,8b-hexahydropyrrolo[3,2-b]indole-3-carboxylate (3w)



3w

The **3w** was prepared according to the general procedure as described above using **1p** (42.8 mg, 0.1 mmol), **2a** (27.6 mg, 0.12 mmol), K_2CO_3 (16.6 mg, 0.12 mmol) and PPh_2Me (4.0 mg, 20 mol%) and isolated as a yellow oil (47.7 mg, 88% yield, >20:1 *d.r.*) after flash column chromatography on silica gel (PE: EA = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.71 (d, J = 8.2 Hz, 1H), 7.62 (dd, J = 13.7, 7.9 Hz, 3H), 7.52 – 7.46 (m, 2H), 7.41 – 7.33 (m, 2H), 7.29 (t, J = 8.5 Hz, 3H), 7.10 (td, J = 7.6, 1.0 Hz, 1H), 5.24 (d, J = 8.3 Hz, 1H), 4.82 (dd, J = 8.3, 2.4 Hz, 1H), 4.03 (dd, J = 10.7, 7.2 Hz, 1H), 3.90 (dd, J = 10.7, 7.2 Hz, 1H), 3.71 (q, J = 7.1 Hz, 1H), 3.57 – 3.48 (m, 2H), 2.43 (s, 3H), 2.33 (s, 3H), 1.23 (t, J = 7.2 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 170.6, 143.9, 141.4, 139.5, 135.8, 135.6, 134.5, 130.1, 129.9, 129.7, 129.0, 127.8, 127.5, 127.4, 125.2, 124.6, 115.6, 67.3, 63.5, 61.6, 50.9, 48.9, 21.5, 21.3, 13.9. **HRMS (ESI)** m/z: calcd. for $C_{27}H_{28}N_2O_6S_2Na^+$ $[M + Na]^+$: 563.1281, found: 563.1284.

ethyl-4-((4-bromophenyl)sulfonyl)-1-tosyl-1,2,3,3a,4,8b-hexahydropyrrolo[3,2-b]indole-3-carboxylate (3x)

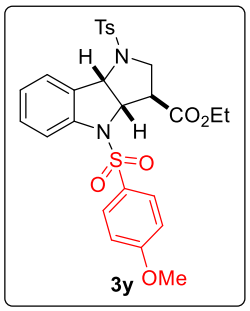


3x

The **3x** was prepared according to the general procedure as described above using **1q** (49.2 mg, 0.1 mmol), **2a** (27.6 mg, 0.12 mmol), K_2CO_3 (16.6 mg, 0.12 mmol) and PPh_2Me (4.0 mg, 20 mol%) and isolated as a yellow oil (52.3 mg, 87% yield, >20:1 *d.r.*) after flash column chromatography on silica gel (PE: EA = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.71 – 7.62 (m, 4H), 7.56 (s, 4H), 7.36 – 7.32 (m, 1H), 7.29 (d, J = 8.1 Hz, 2H), 7.13 (td, J = 7.6, 1.0 Hz, 1H), 5.26 (d, J = 8.3 Hz, 1H), 4.77 (dd, J = 8.4, 2.4 Hz, 1H), 4.09 – 3.96 (m, 1H), 3.89 (dd, J = 10.7,

7.1 Hz, 1H), 3.77 – 3.68 (m, 1H), 3.60 – 3.46 (m, 2H), 2.43 (s, 3H), 1.22 (t, J = 7.1 Hz, 3H). **$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)** δ 170.5, 144.0, 141.1, 135.5, 134.8, 132.6, 130.3, 129.8, 129.7, 129.1, 128.9, 127.7, 127.6, 125.5, 115.4, 67.3, 63.5, 61.7, 50.9, 48.9, 21.5, 13.9. **HRMS (ESI)** m/z: calcd. for $C_{26}H_{26}BrN_2O_6S_2^+$ $[M + H]^+$: 605.0410, found: 605.0421.

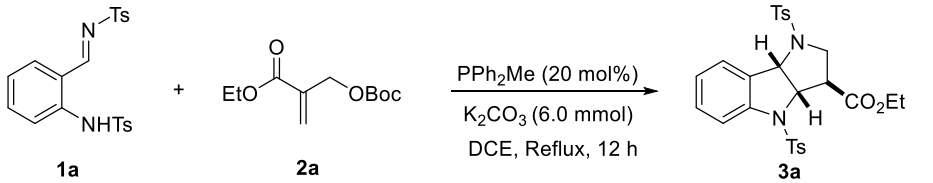
ethyl-4-((4-methoxyphenyl)sulfonyl)-1-tosyl-1,2,3,3a,4,8b-hexahydropyrrolo[3,2-b]indole-3-carboxylate (3y)



The **3y** was prepared according to the general procedure as described above using **1r** (44.4 mg, 0.1 mmol), **2a** (27.6 mg, 0.12 mmol), K_2CO_3 (16.6 mg, 0.12 mmol) and PPh_2Me (4.0 mg, 20 mol%) and isolated as a yellow oil (45.3 mg, 81% yield, >20:1 *d.r.*) after flash column chromatography on silica gel (PE: EA = 10:1). **^1H NMR (400 MHz, $CDCl_3$)** δ 7.70 (d, J = 8.3 Hz, 1H), 7.66 – 7.58 (m, 5H), 7.35 – 7.30 (m, 1H), 7.30 – 7.26 (m, 2H), 7.12 – 7.07 (m, 1H), 6.89 – 6.85 (m, 2H), 5.27 (d, J = 8.2 Hz, 1H), 4.80 (dd, J = 8.3, 2.2 Hz, 1H), 4.01 (dd, J = 10.7, 7.2 Hz, 1H), 3.91 – 3.84 (m, 1H), 3.82 (s, 3H), 3.77 – 3.71 (m, 1H), 3.58 – 3.51 (m, 2H), 2.43 (s, 3H), 1.23 (t, J = 7.1 Hz, 3H). **$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)** δ 170.7, 163.7, 143.8, 141.7, 135.7, 130.1, 129.8, 129.7, 127.50, 127.46, 127.3, 125.1, 115.5, 114.4, 67.3, 63.6, 61.6, 55.6, 50.9, 48.9, 21.5, 13.9. **HRMS (ESI)** m/z: calcd. for $C_{27}H_{29}N_2O_7S_2^+$ $[M + H]^+$: 557.1411, found: 557.1405.

V. Gram-Scale and Synthetic Manipulations

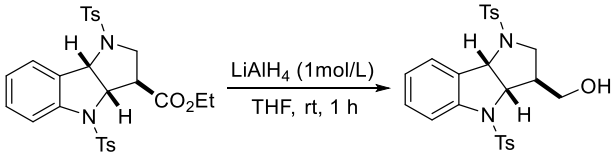
(a) Synthesis of 3a on Gram-Scale



To a stirred solution of *o*-amino arylaldimine **1a** (2.14 g, 5.0 mmol), Morita-Baylis-Hillman carbonates **2a** (1.38 g, 6.0 mmol, 1.2 equiv) and K_2CO_3 (0.83 g, 6.0 mmol, 1.2 equiv) in DCE (50.0 mL) was added PPh_2Me (0.20 g, 20 mol%). The reaction mixture was stirred at reflux for 12 h. The reaction mixture was concentrated under reduce vacuum, and the residue was purified by flash column chromatography on silica gel (PE: EA = 10:1) to afford the compounds **3a** (1.87 g, 69% yield, >20:1 *d.r.*).

(b) Synthetic Manipulations of 3a

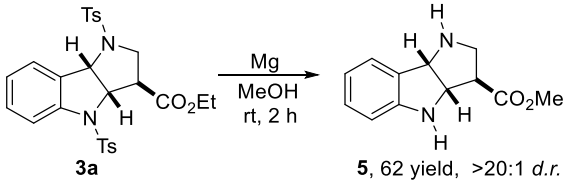
(1,4-Ditosyl-1,2,3,3a,4,8b-hexahydropyrrolo[3,2-b]indol-3-yl)methanol (4)



To a suspension of lithium aluminum tetrahydride (0.11mmol, 1.1 equiv.) in THF (5 mL) was added **3a** (54.0 mg, 0.1 mmol) in one portion, mixture was stirred 1 h at rt. NH_4Cl (aq.) was added in small portions. Then, extracted with CH_2Cl_2 (3 x 10 mL), and dried with Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (PE: EA = 5:1) to give desired compound **4** (45.0 mg, 90% yield, > 20:1 *d.r.*) as an oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.70 – 7.61 (m, 4H), 7.52 – 7.47 (m, 2H), 7.36 – 7.28 (m, 3H), 7.20 – 7.11 (m, 3H), 5.04 (d, J = 8.5 Hz, 1H), 4.30 (dd, J = 8.6, 5.5 Hz, 1H), 3.73 – 3.66 (m, 1H), 3.53 – 3.46 (m, 1H), 3.35 (dd, J = 10.6, 6.9 Hz, 1H), 3.20 – 3.13 (m, 1H), 2.74 – 2.65 (m, 1H), 2.45 (s, 3H), 2.39 (s, 3H), 2.13 (s, 1H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 144.7, 144.1, 140.8, 134.9, 133.3, 131.7, 129.9, 129.8, 127.5, 127.22, 127.20, 125.7, 116.8, 66.0,

63.2, 60.8, 48.4, 47.7, 21.6. **HRMS (ESI)** m/z: calcd. for $C_{25}H_{27}N_2O_5S_2^+$ $[M + H]^+$: 499.1356, found: 499.1356.

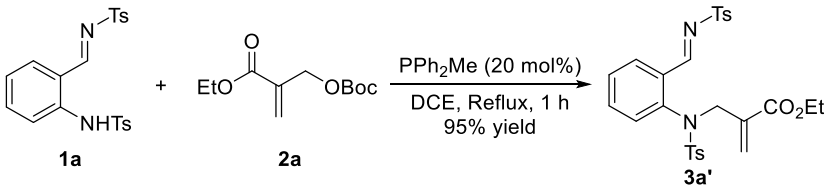
Methyl-1,2,3,3a,4,8b-hexahydropyrrolo[3,2-b]indole-3-carboxylate (5)



To a stirred solution of substrate **3a** (54.0 mg, 0.1 mmol) in MeOH (4.0 mL) was added Magnesium powder (145.9 mg, 6.0 mmol). The reaction mixture at room temperature for 2 h. Filtered, and concentrated under reduced pressure. Saturated NH_4Cl was added and the mixture was stirred for 30 min. Then it was extracted with EA (3 x 10 mL). The combined organic extracts were dried over dry Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (EA) to afford the desired product **5** (13.6 mg, 62 yield, > 20:1 *d.r.*) as an oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.27 (s, 1H), 7.16 – 7.08 (m, 1H), 6.80 – 6.73 (m, 1H), 6.59 (d, J = 7.8 Hz, 1H), 5.04 (d, J = 8.0 Hz, 1H), 4.55 (dd, J = 8.0, 2.4 Hz, 1H), 4.12 (s, 1H), 3.74 (s, 3H), 3.23 (dd, J = 12.1, 3.9 Hz, 1H), 3.04 (dd, J = 12.1, 6.4 Hz, 1H), 2.93 (dq, J = 6.2, 2.7 Hz, 1H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 174.0, 150.5, 129.2, 128.5, 125.8, 119.3, 109.4, 66.7, 66.6, 55.1, 52.0, 49.4. **HRMS (ESI)** m/z: calcd. for $C_{12}H_{15}N_2O_2^+$ $[M + H]^+$: 219.1134, found: 219.1135.

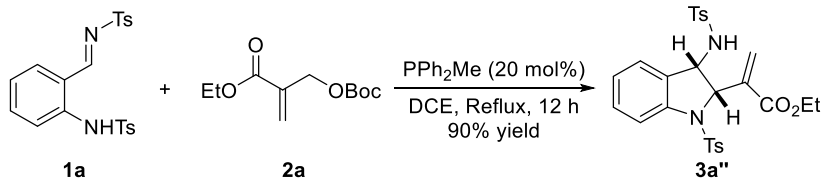
VI. Mechanistic Studies

***The reaction of 1a and 2a for the synthesis of* 3a'**



To a stirred solution of *o*-amino arylaldimine **1a** (0.1 mmol) and Morita-Baylis-Hillman carbonates **2a** (0.12 mmol, 1.2 equiv) in DCE (2.0 mL) was added PPh_2Me (4.0 mg, 20 mol%). The reaction mixture was stirred at reflux for 1 h. The reaction mixture was concentrated under reduce vacuum, and the residue was purified by flash column chromatography on silica gel (PE: EA = 5:1) to afford the compounds **3a'** (51.3 mg, 95% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.24 (s, 1H), 8.19 (dd, J = 7.8, 1.7 Hz, 1H), 7.94 – 7.87 (m, 2H), 7.47 – 7.42 (m, 3H), 7.36 (dd, J = 15.5, 7.5 Hz, 3H), 7.28 (s, 2H), 6.75 (dd, J = 8.0, 1.2 Hz, 1H), 6.26 (s, 1H), 5.78 – 5.71 (m, 1H), 4.76 (d, J = 14.5 Hz, 1H), 4.20 – 4.08 (m, 3H), 2.44 (s, 3H), 2.42 (s, 3H), 1.23 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 167.6, 165.4, 144.50, 144.47, 142.3, 135.0, 134.5, 134.4, 133.6, 133.1, 130.3, 129.8, 129.71, 129.67, 129.4, 128.6, 128.5, 128.1, 127.9, 61.5, 51.9, 21.63, 21.60, 14.0. **HRMS (ESI)** m/z: calcd. for $C_{27}H_{28}N_2O_6S_2Na^+$ $[M + Na]^+$: 563.1281, found: 563.1281.

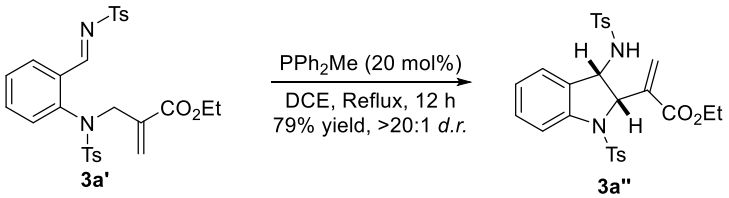
***The reaction of 1a and 2a for the synthesis of* 3a''**



To a stirred solution of *o*-amino arylaldimine **1a** (0.1 mmol) and Morita-Baylis-Hillman carbonates **2a** (0.12 mmol, 1.2 equiv) in DCE (2.0 mL) was added PPh_2Me (4.0 mg, 20 mol%). The reaction mixture was stirred at reflux for 12 h. The reaction mixture was concentrated under reduce vacuum, and the residue was purified by flash column chromatography on silica gel (PE: EA = 5:1) to afford the compounds **3a''** (48.6 mg, 90% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.73 (d, J = 8.2 Hz, 1H), 7.65

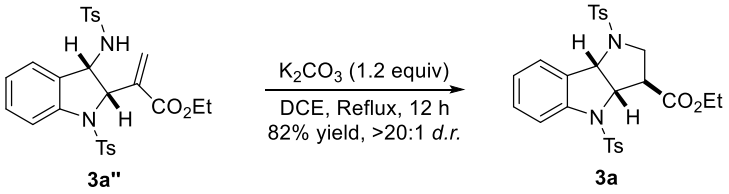
(d, *J* = 8.3 Hz, 2H), 7.58 – 7.52 (m, 2H), 7.38 – 7.29 (m, 3H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.03 (td, *J* = 7.5, 1.0 Hz, 1H), 6.90 – 6.86 (m, 1H), 6.24 (s, 1H), 5.75 (s, 1H), 4.80 – 4.75 (m, 1H), 4.50 (dd, *J* = 8.8, 2.1 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.39 (d, *J* = 8.8 Hz, 1H), 2.46 (s, 3H), 2.38 (s, 3H), 1.15 (t, *J* = 7.1 Hz, 3H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 164.8, 145.1, 143.8, 141.8, 137.7, 137.4, 133.7, 130.34, 130.26, 129.9, 129.6, 128.1, 127.3, 127.2, 125.9, 125.5, 117.1, 69.9, 61.1, 59.6, 21.6, 13.9. **HRMS (ESI)** m/z: calcd. for $C_{27}H_{28}N_2O_6S_2Na^+$ $[M + Na]^+$: 563.1281, found: 563.1281.

***The reaction of 3a' for the synthesis of* 3a''**



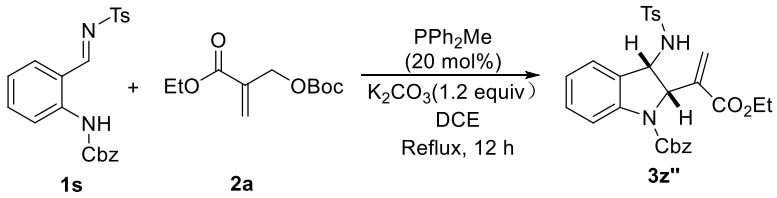
To a stirred solution of **3a'** (0.1 mmol) in DCE (2.0 mL) was added PPh_2Me (4.0 mg, 20 mol%). The reaction mixture was stirred at reflux for 12 h. The reaction mixture was concentrated under reduce vacuum, and the residue was purified by flash column chromatography on silica gel (PE: EA = 8:1) to afford the compounds **3a''** (42.6 mg, 79% yield).

***The reaction of 3a'' for the synthesis of* 3a**



To a stirred solution of **3a''** (0.1 mmol) in DCE (2.0 mL) was added K_2CO_3 (16.6mg, 0.12 mmol, 1.2 equiv). The reaction mixture was stirred at reflux for 12 h. The reaction mixture was concentrated under reduce vacuum, and the residue was purified by flash column chromatography on silica gel (PE: EA = 10:1) to afford the compounds **3a** (44.3 mg, 82% yield).

The reaction of 1s and 2a for the synthesis of 3z''



To a stirred solution of *o*-amino arylaldimine **1s** (0.1 mmol) and Morita-Baylis-Hillman carbonates **2a** (0.12 mmol, 1.2 equiv) in DCE (2.0 mL) was added PPh_2Me (4.0 mg, 20 mol%). The reaction mixture was stirred at reflux for 12 h. The reaction mixture was concentrated under reduce vacuum, and the residue was purified by flash column chromatography on silica gel (PE: EA = 5:1) to afford the compounds **3z''** (38.0 mg, 73% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.76 – 7.72 (m, 2H), 7.42 – 7.31 (m, 5H), 7.28 (d, J = 8.1 Hz, 5H), 6.90 (t, J = 7.4 Hz, 1H), 6.12 (s, 1H), 5.35 (s, 1H), 5.16 – 5.13 (m, 1H), 5.13 – 5.07 (m, 2H), 4.71 – 4.63 (m, 1H), 4.11 (q, J = 7.2 Hz, 2H), 2.43 (s, 3H), 1.13 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 165.0, 143.6, 138.0, 130.2, 129.7, 129.6, 128.5, 128.3, 128.0, 127.7, 127.2, 127.1, 123.6, 115.2, 61.12, 61.11, 44.6, 21.5, 14.1, 13.8. **HRMS (ESI)** m/z: calcd. for $C_{28}H_{28}N_2O_6Na^+$ $[M + Na]^+$: 543.1566, found: 543.1567.

VII. X-Ray Crystallographic Analysis

Crystal Growth Method: 15.1 mg of **3b** was added in a HPLC vial and dissolved by 1.0 mL EA, closed the lid. Then put it in a large bottle, added petroleum ether to the same level of the liquid in the HPLC vial, tighten the lid, put it in a fumehood and waited for growth.

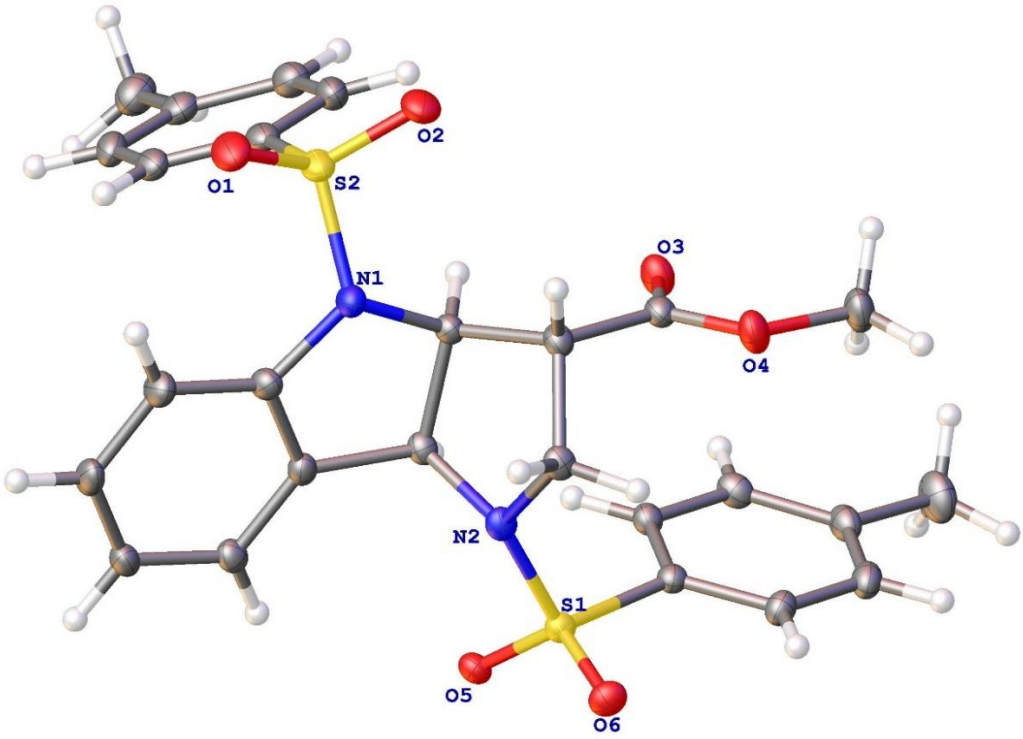


Figure S1. X-ray structure of **3b** (ellipsoid contour at 50% probability CCDC 2516957)

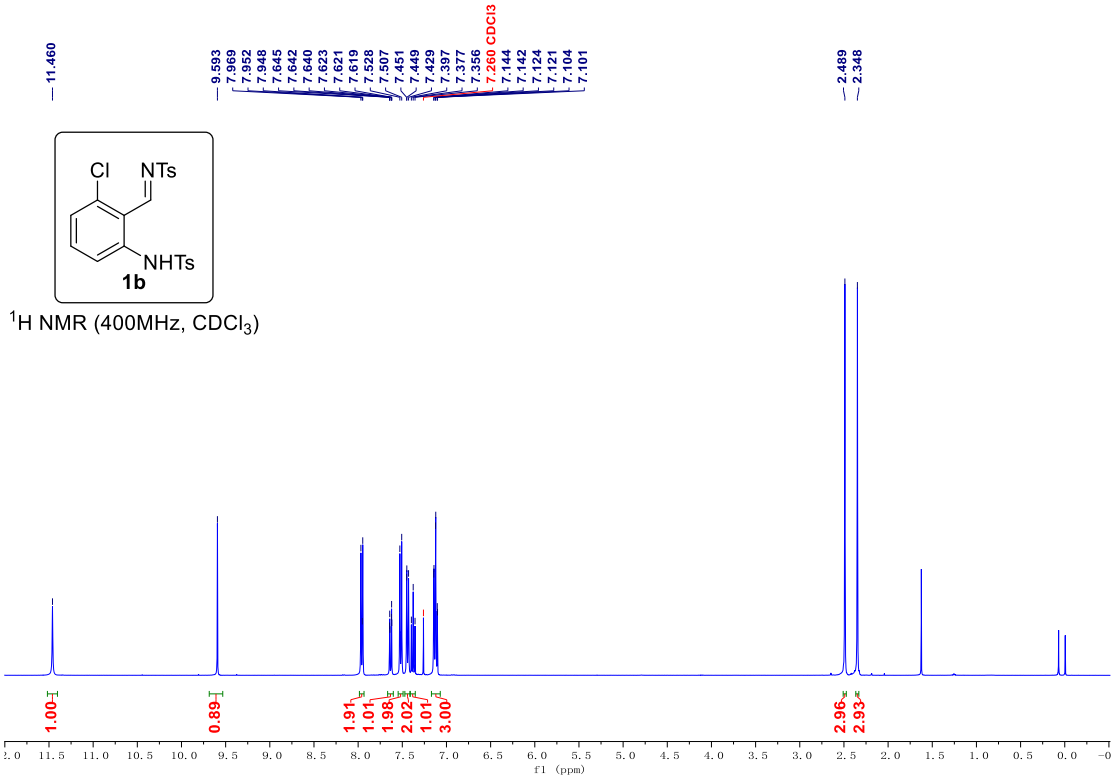
Table S1 Crystal data and structure refinement for 3b.

Identification code	**3b**
Empirical formula	$C_{26}H_{26}N_2O_6S_2$
Formula weight	526.61
Temperature/K	169.99(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	9.2302(3)
b/Å	25.9843(8)
c/Å	10.4917(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2516.33(13)
Z	4
ρ_{calc}g/cm^3	1.390
μ/mm^{-1}	2.299
F(000)	1104.0
Crystal size/mm^3	0.15 × 0.13 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.804 to 147.238
Index ranges	$-8 \le h \le 11$, $-31 \le k \le 32$, $-12 \le l \le 12$
Reflections collected	18700
Independent reflections	5018 [R_{int} = 0.0716, R_{sigma} = 0.0484]
Data/restraints/parameters	5018/0/328
Goodness-of-fit on F^2	1.066
Final R indexes [I>=2σ (I)]	R_1 = 0.0648, wR_2 = 0.1683
Final R indexes [all data]	R_1 = 0.0693, wR_2 = 0.1732
Largest diff. peak/hole / e Å^{-3}	0.46/-0.32

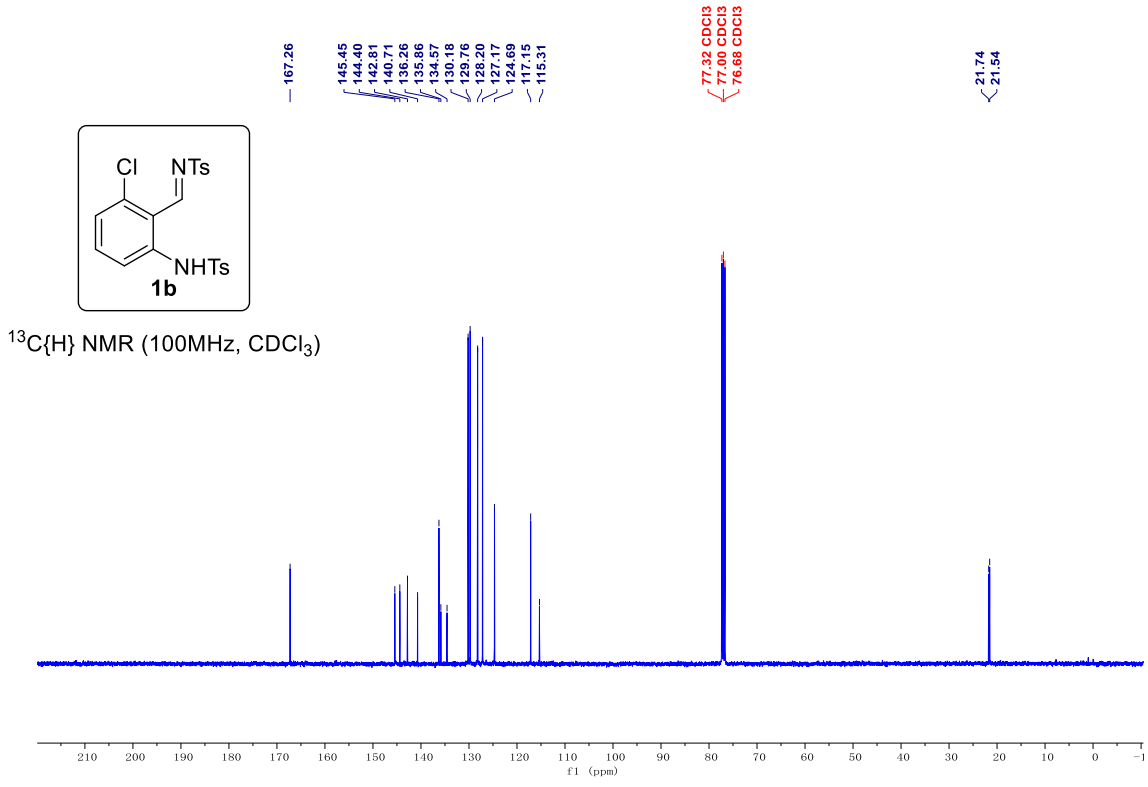
VIII. References

1. Zhu, J.-X.; Chen, Z.-C.; Du W.; Chen Y.-C. Asymmetric Auto-Tandem Palladium Catalysis for 2,4-Dienyl Carbonates: Ligand-Controlled Divergent Synthesis. *Angew. Chem. Int. Ed*. **2022**, *61*, e202200880.
2. Li, B.; Hu, X.; Yao, H.; Li, Y.; Xu, D.; Huang, N.; Wang, N. Pyridine-Catalyzed Chemoselective Four-Component Cascade Reaction of Aromatic Aldehydes, Malononitrile/Cyanoacetates, MBH Carbonates, and Alcohols. *Org. Lett*. **2024**, *26*, 7576–7583.

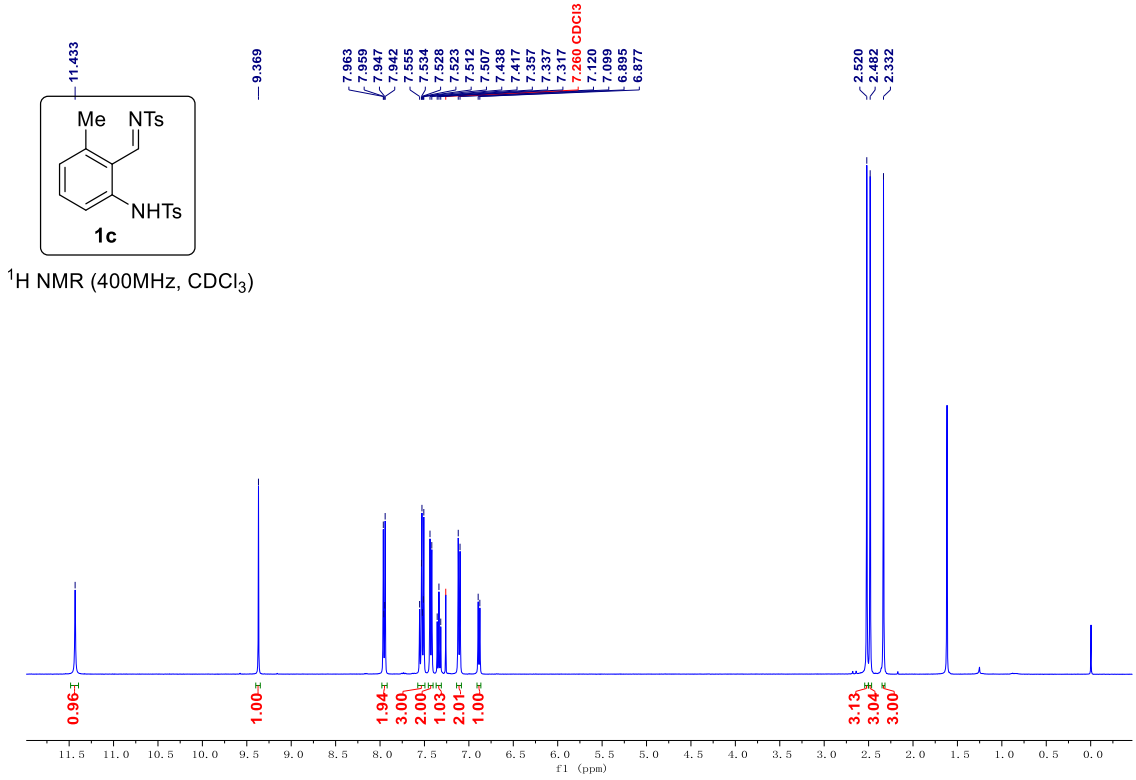
IX. Copies of ^{1}H and $^{13}C\{^{1}H\}$ NMR Spectra



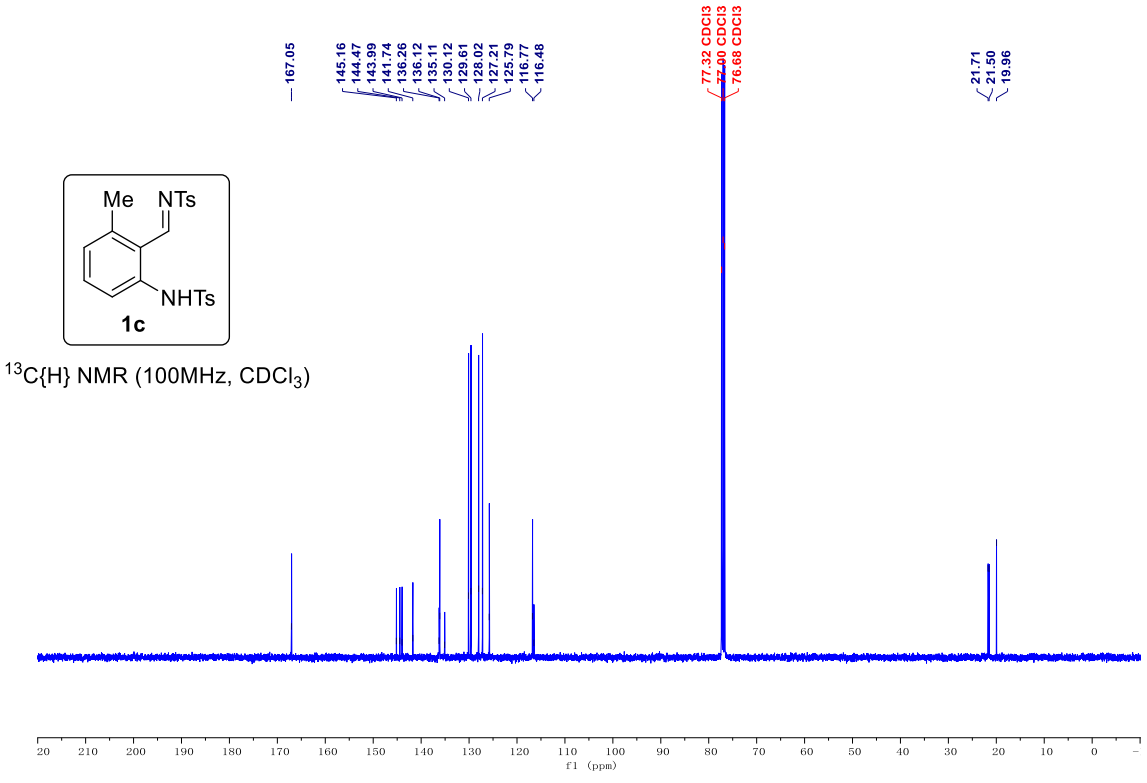
^{1}H NMR (400MHz, $CDCl_3$)



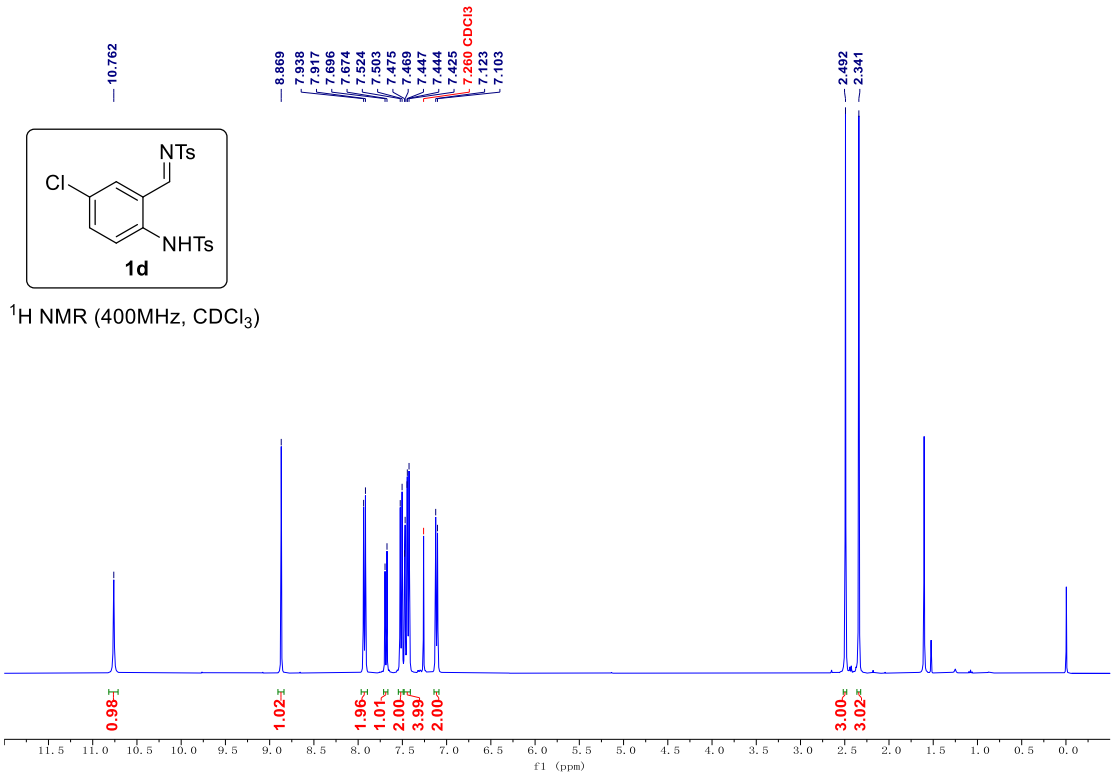
$^{13}C\{H\}$ NMR (100MHz, $CDCl_3$)



^{1}H NMR (400MHz, $CDCl_3$)



^{13}C{H} NMR (100MHz, $CDCl_3$)



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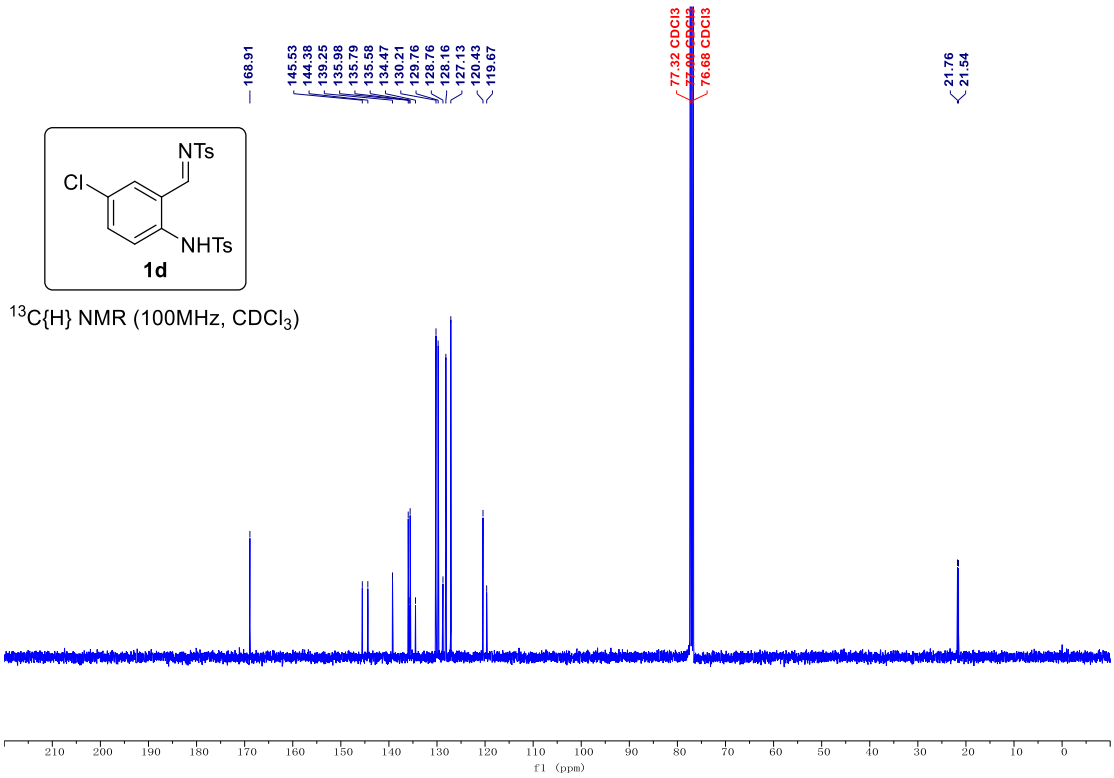

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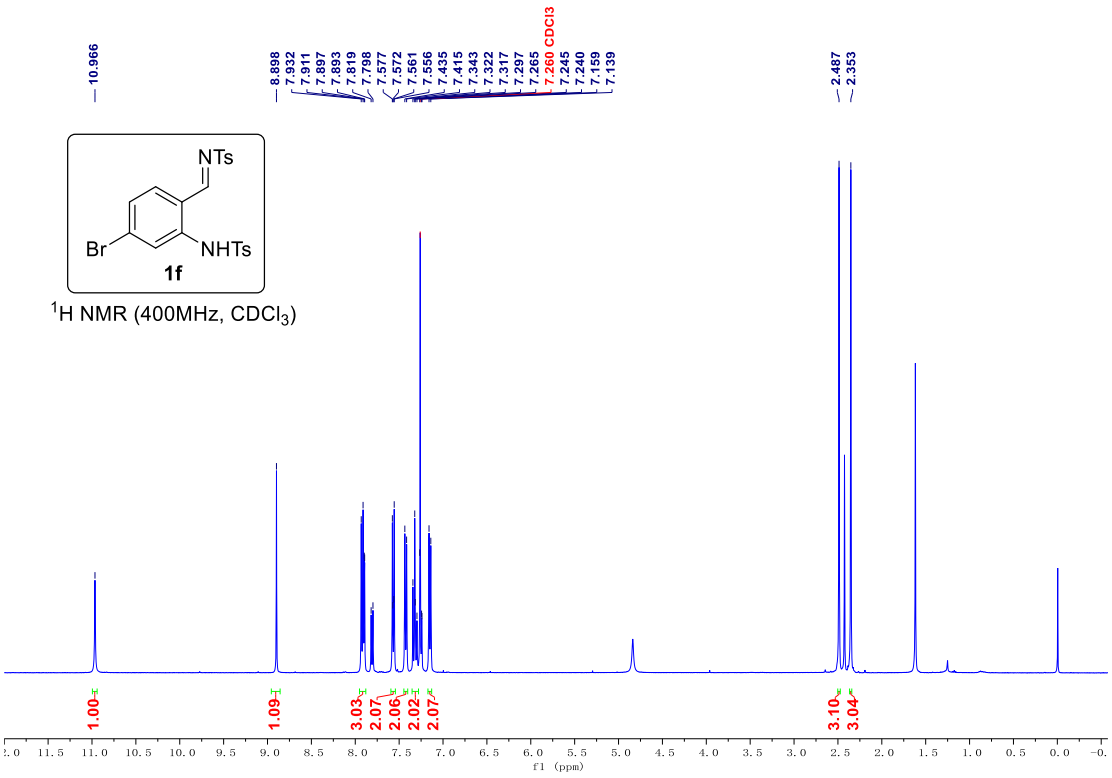
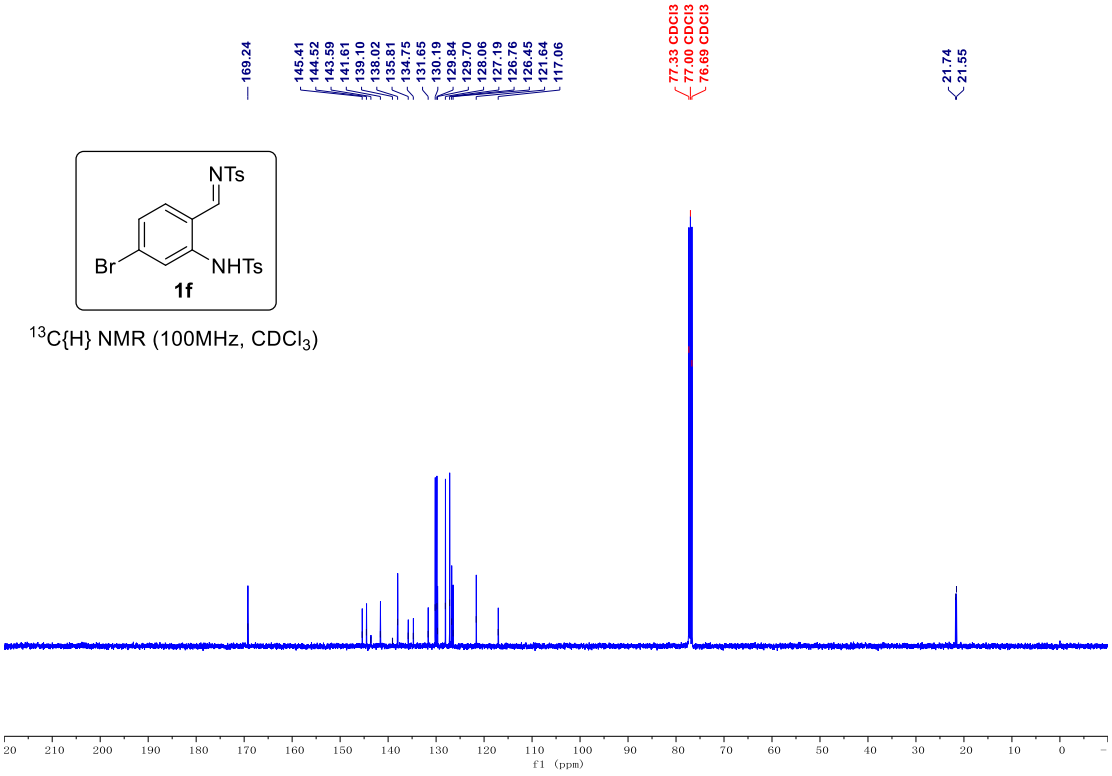
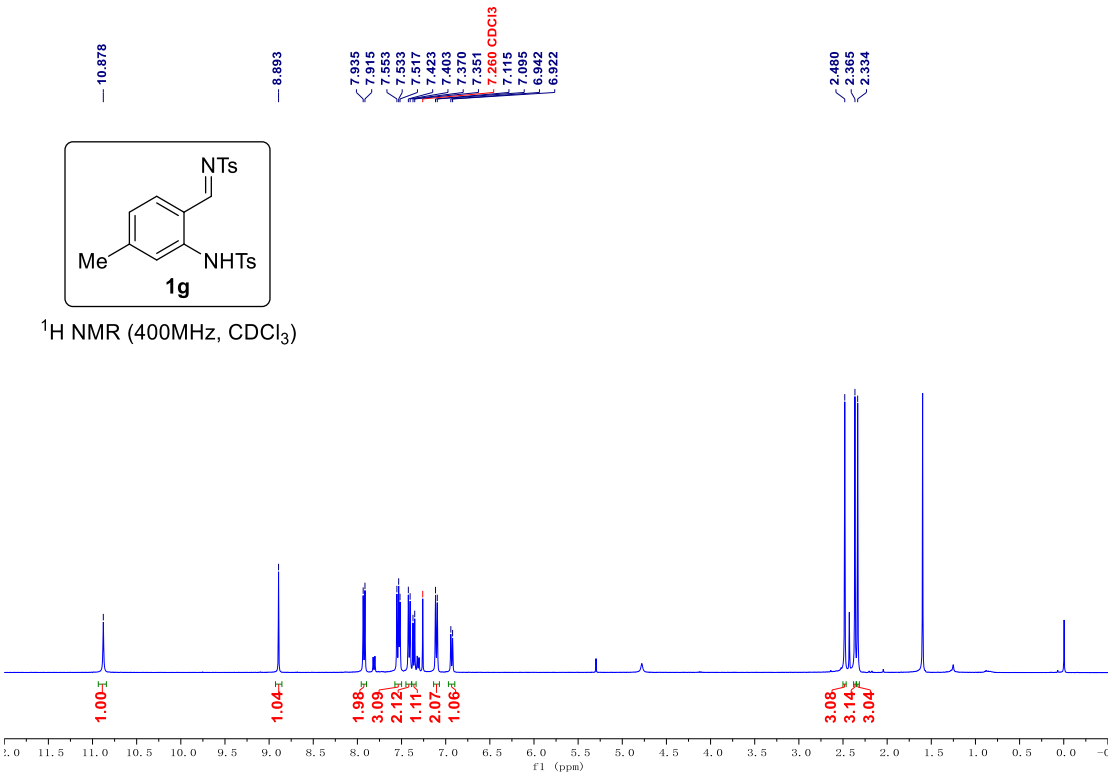


^{1}H NMR (400MHz, $CDCl_3$)



^{13}C{H} NMR (100MHz, $CDCl_3$)



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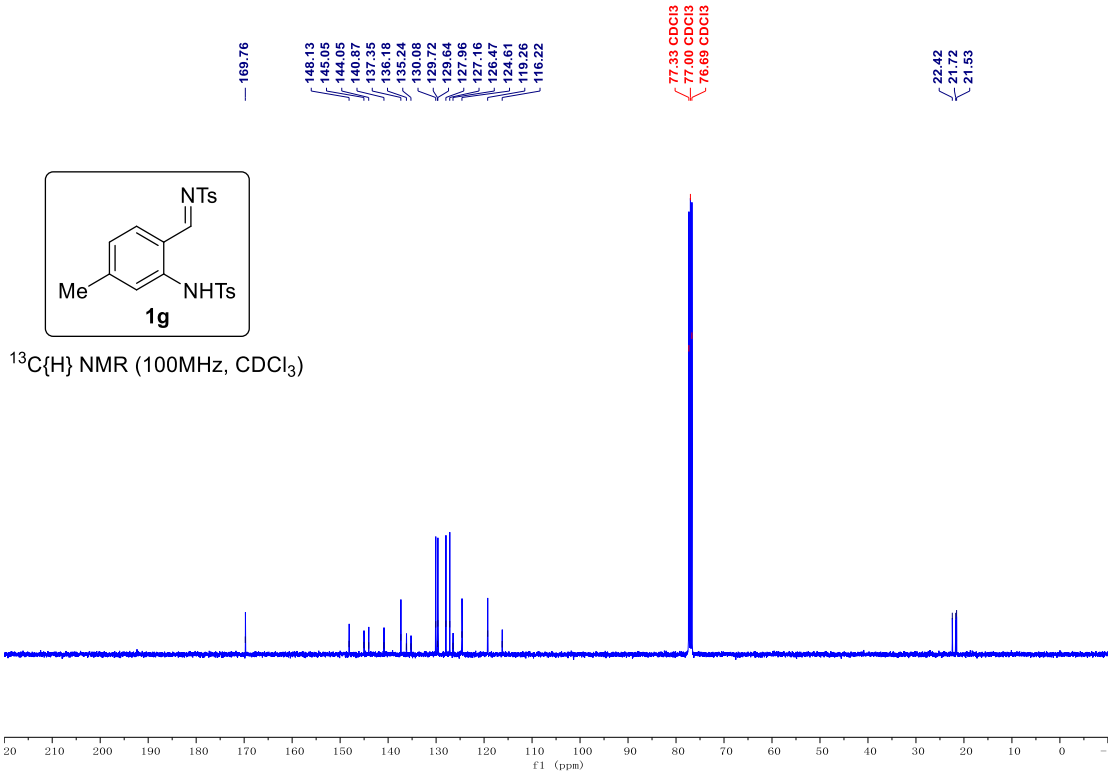
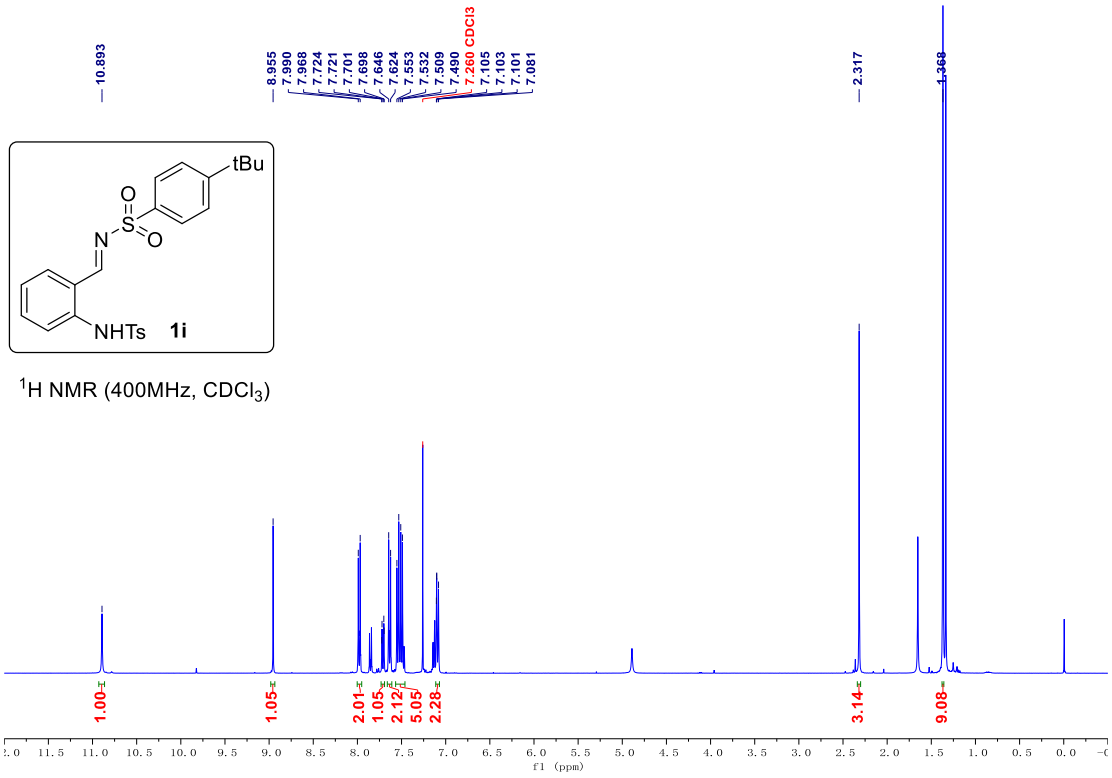


^{13}C{H} NMR (100MHz, $CDCl_3$)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7.990
7.968
7.724
7.721
7.701
7.698
7.646
7.624
7.553
7.532
7.509
7.490
7.260 CDCl3
7.105
7.103
7.101
7.081
2.317
1.368
tBu
O
S
O
N
NHTs
1i
1H NMR (400MHz, CDCl3)
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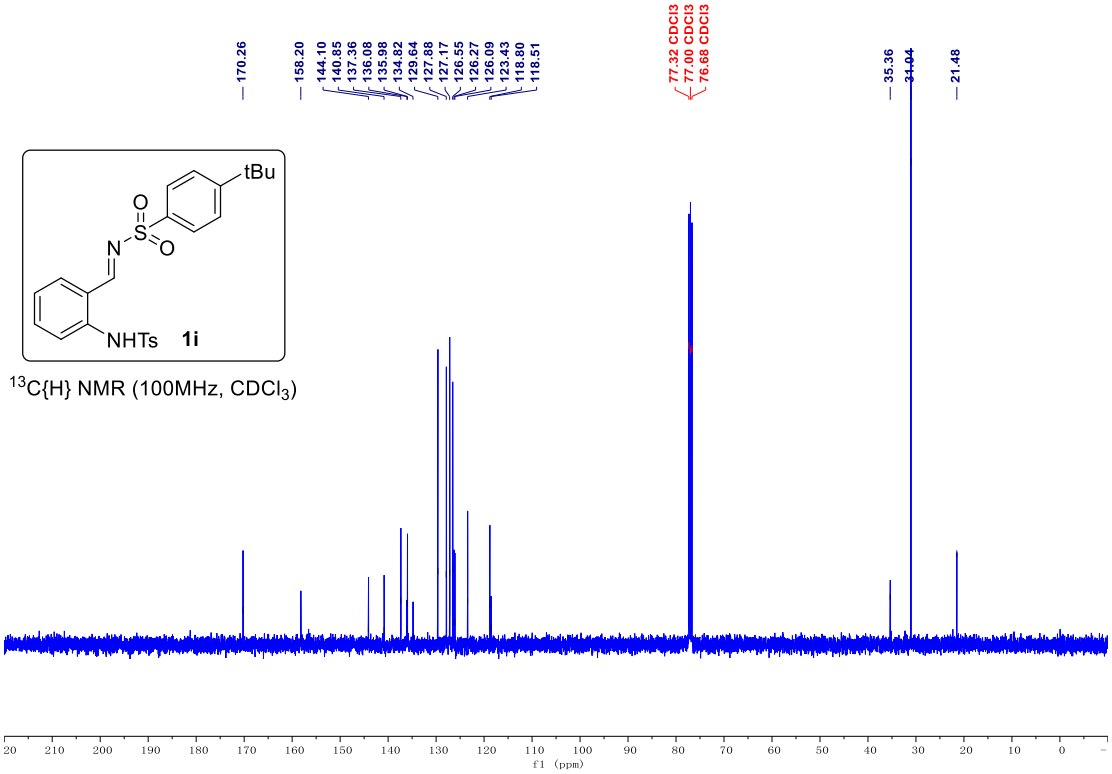
1.05
2.01
1.05
2.12
5.05
2.28
3.14
9.08
f1 (ppm)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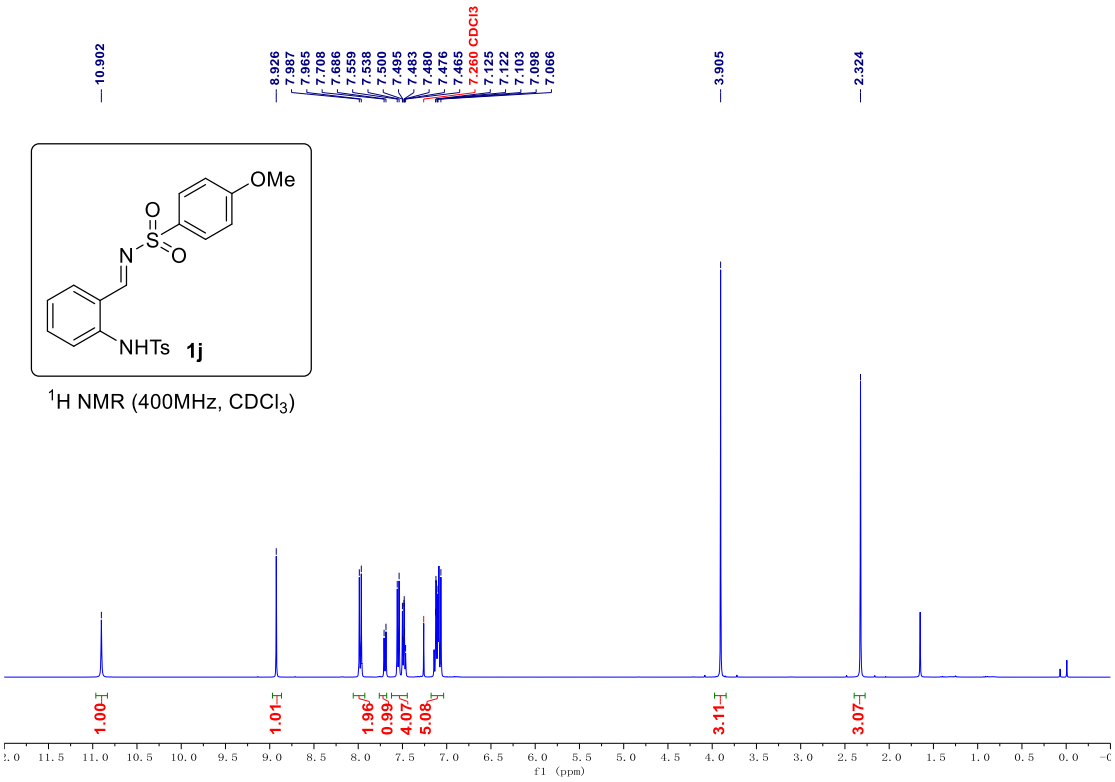
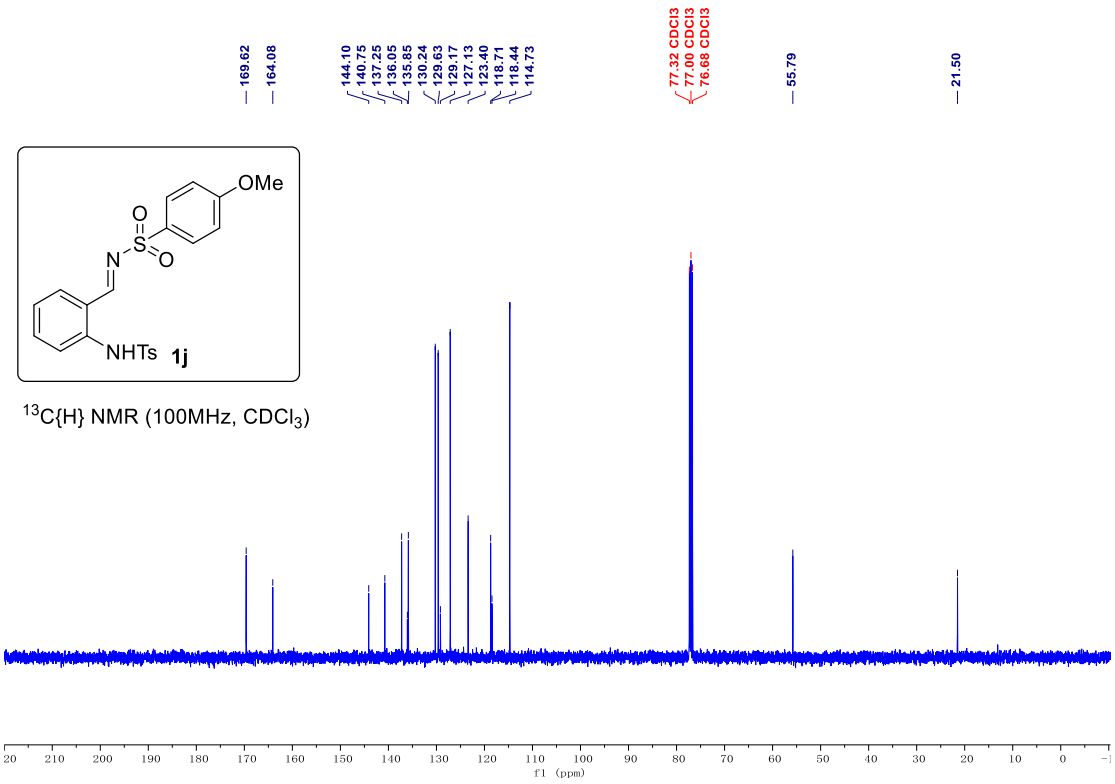
140.85
137.36
136.08
135.98
134.82
129.64
127.88
127.17
126.55
126.27
126.09
123.43
118.80
118.51
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
35.36
31.04
21.48
tBu
O
S
O
N
NHTs
1i
13C{H} NMR (100MHz, CDCl3)
f1 (ppm)



^{1}H NMR (400MHz, $CDCl_3$)



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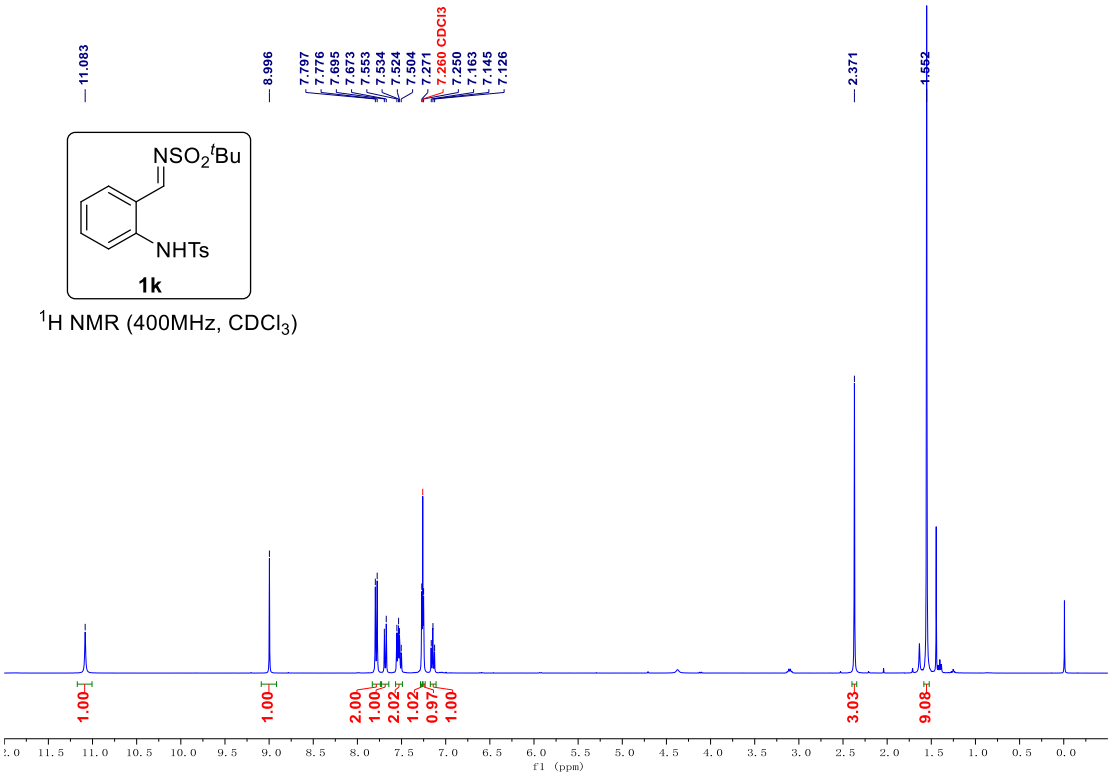
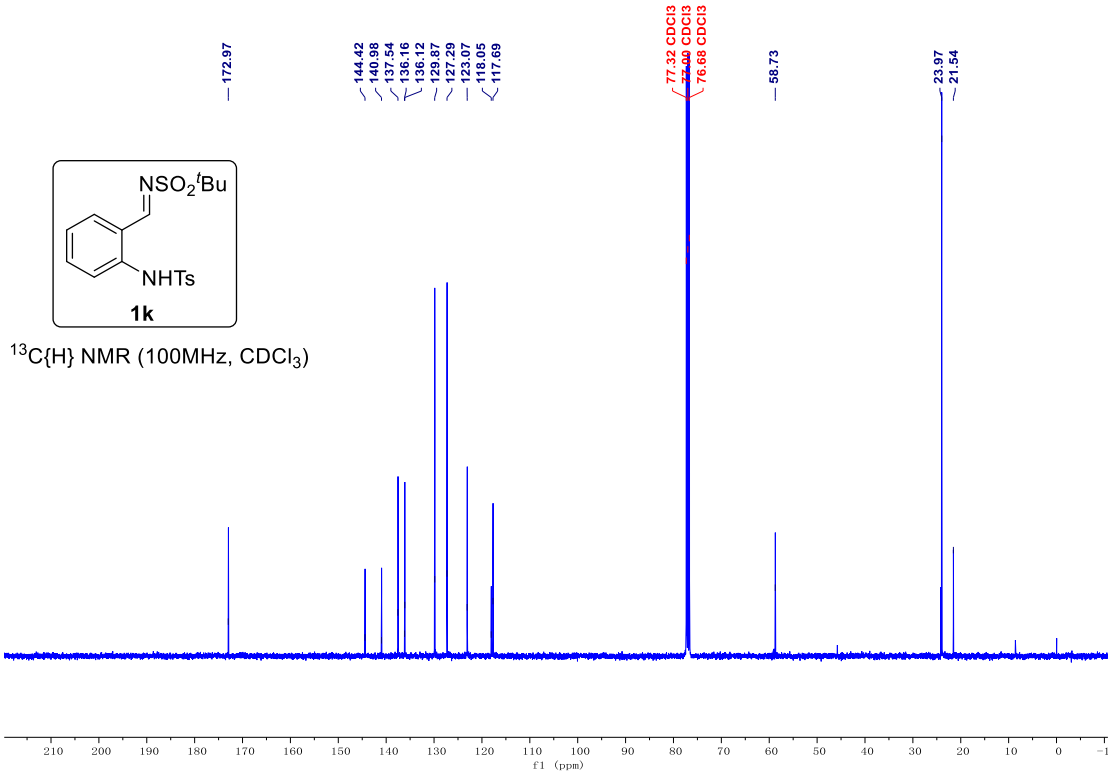
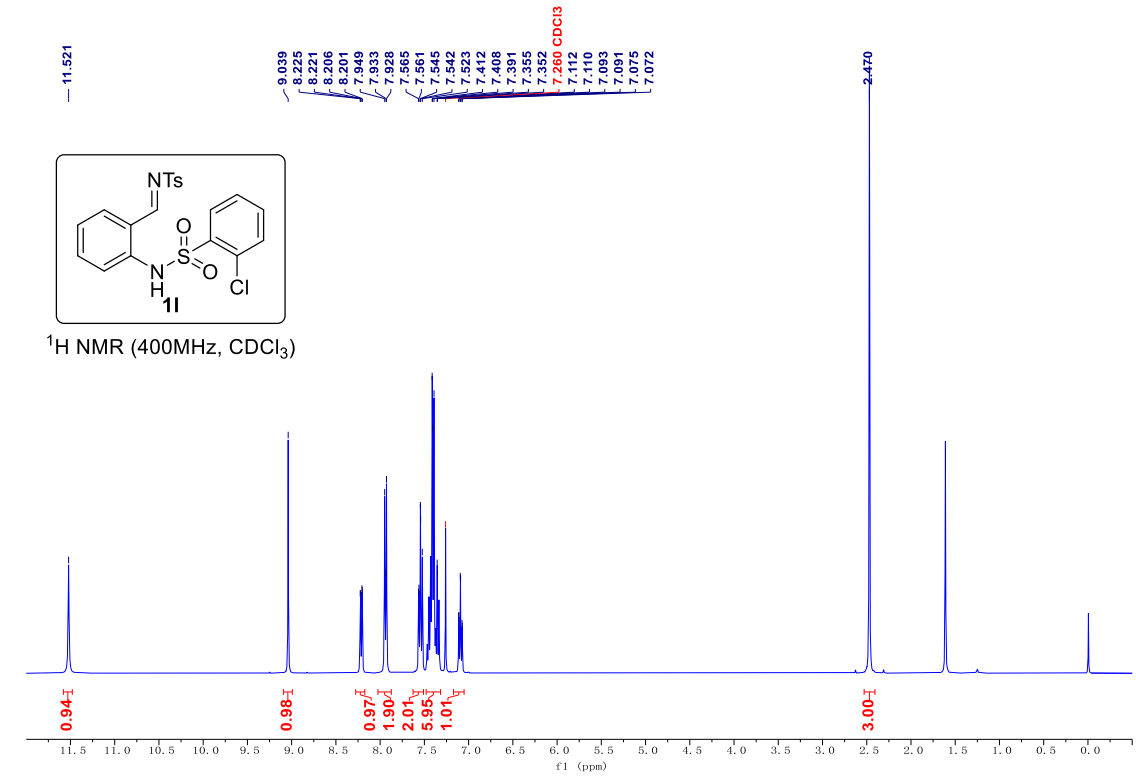


^{1}H NMR (400MHz, $CDCl_3$)



^{13}C{H} NMR (100MHz, $CDCl_3$)



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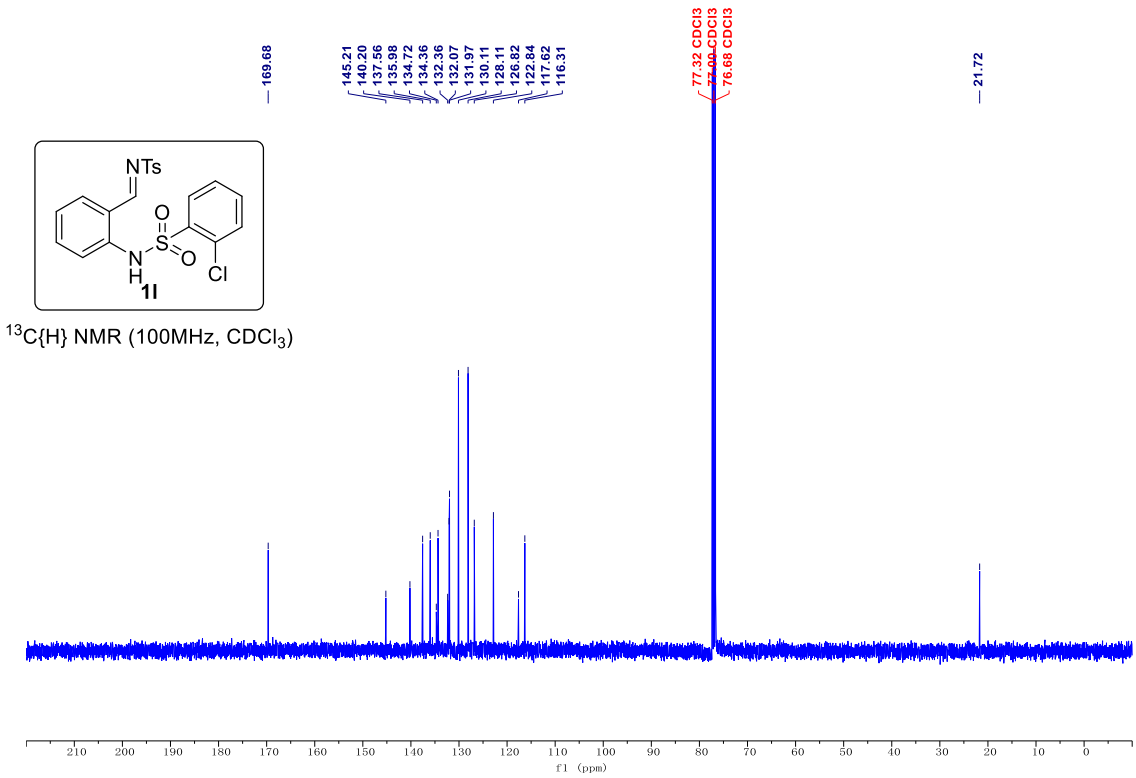

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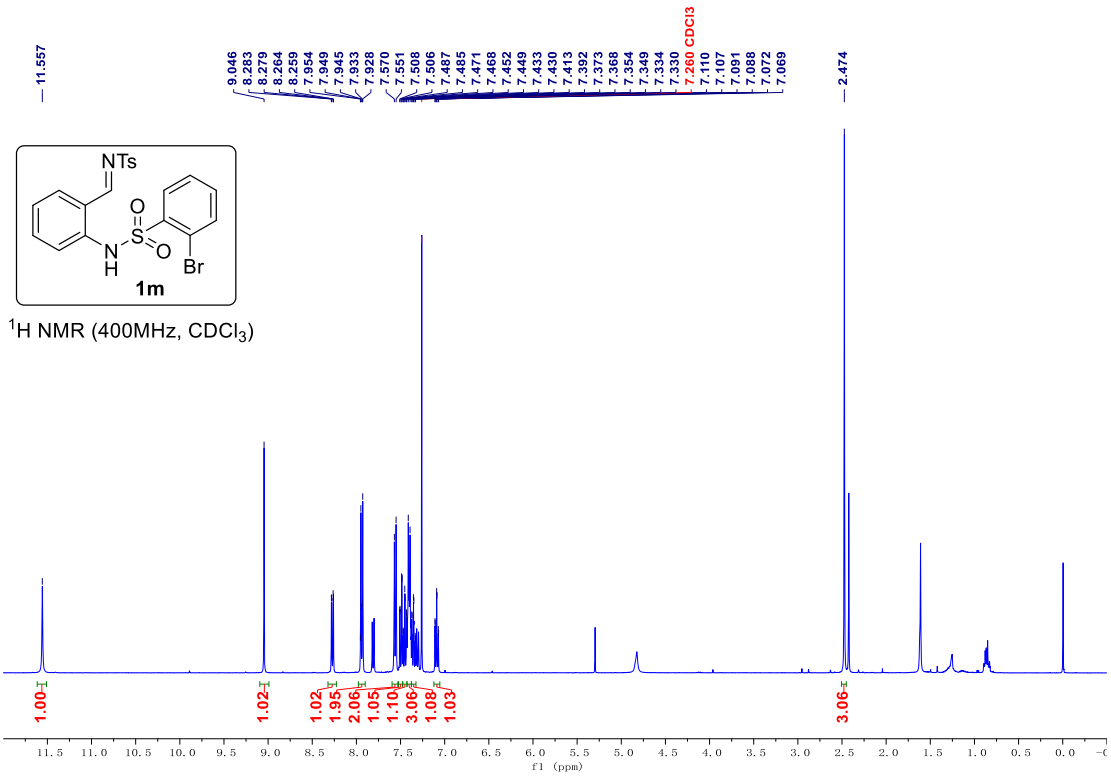
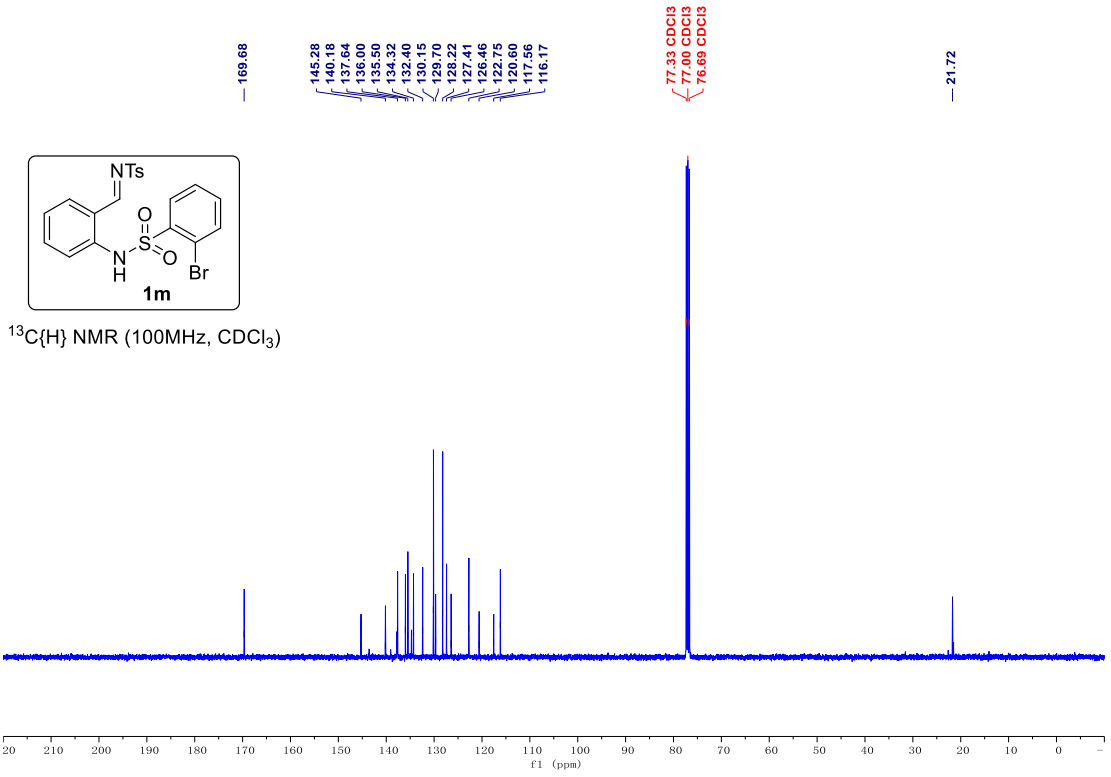
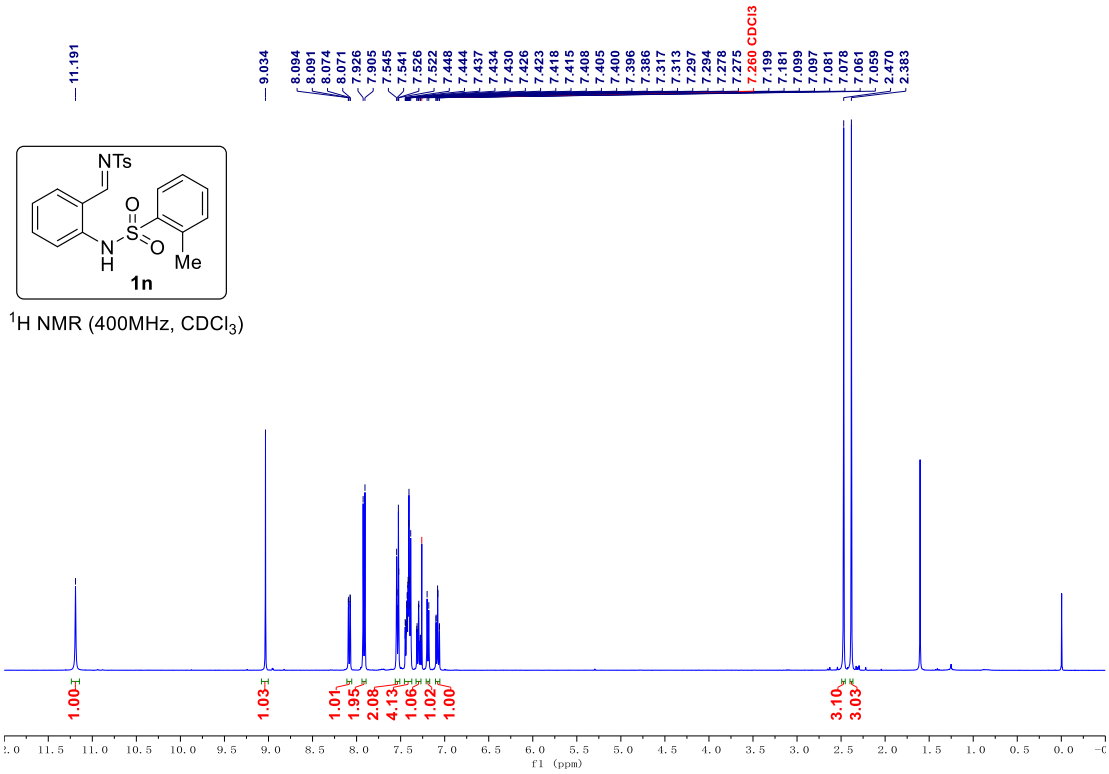


^{1}H NMR (400MHz, $CDCl_3$)



^{13}C{H} NMR (100MHz, $CDCl_3$)



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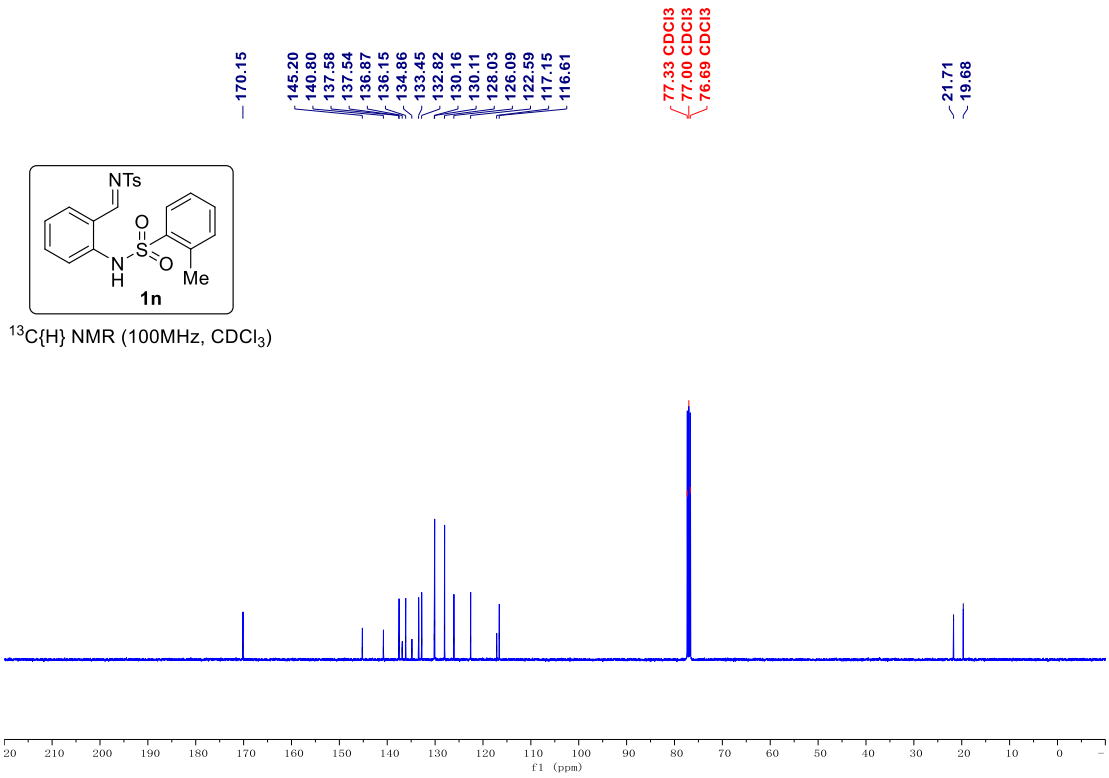
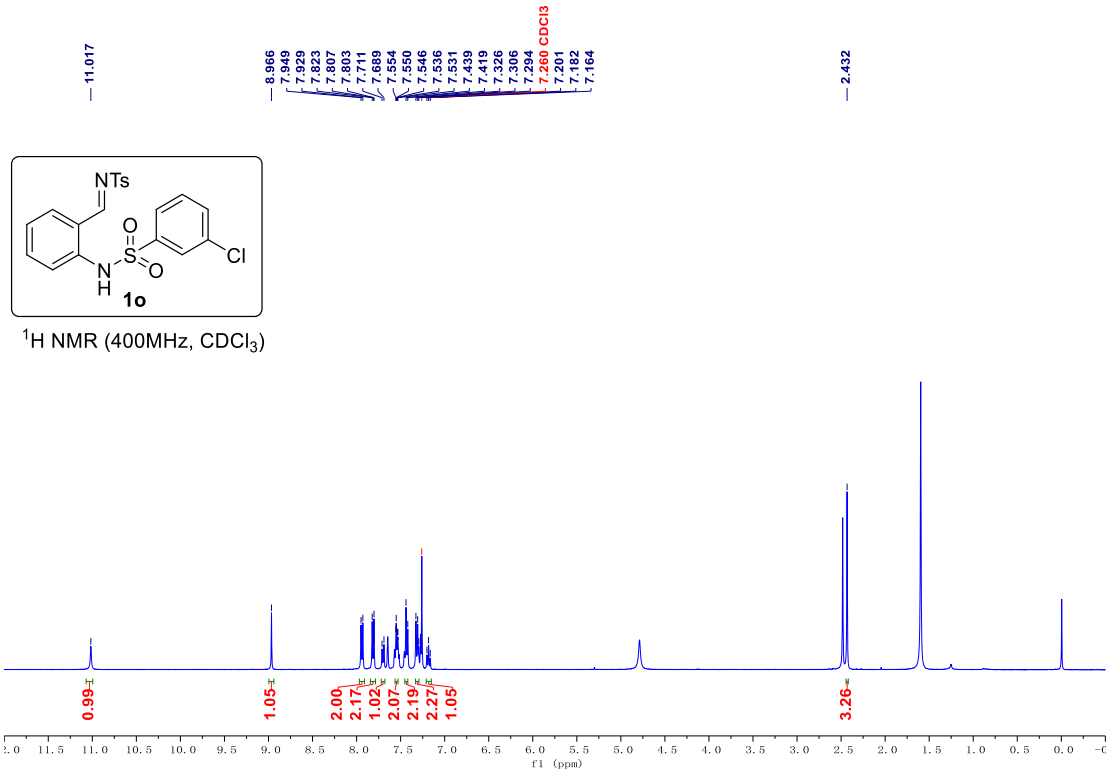
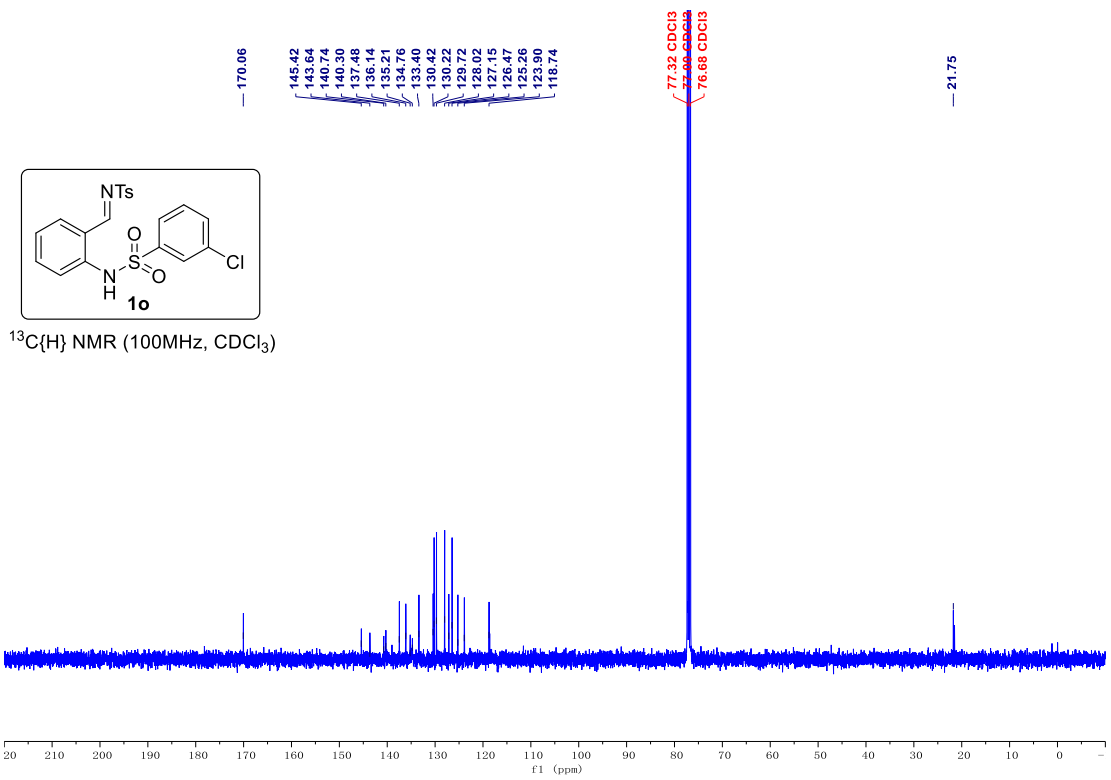


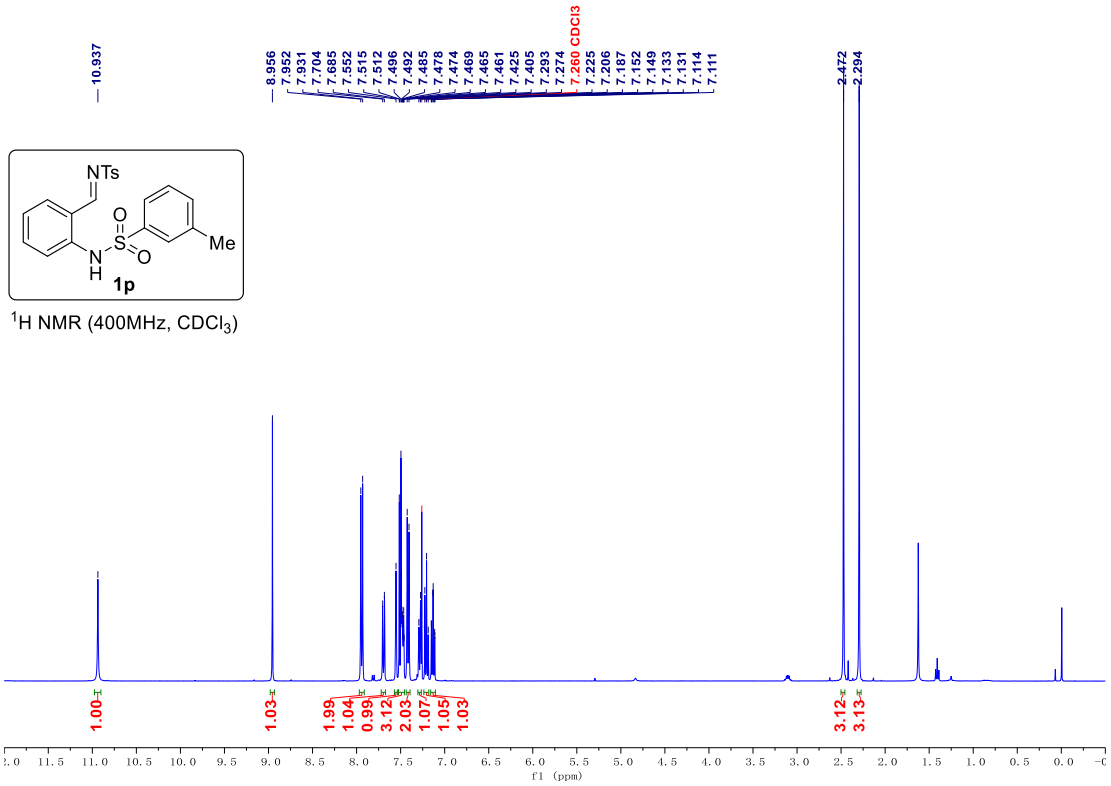
^{13}C{H} NMR (100MHz, $CDCl_3$)



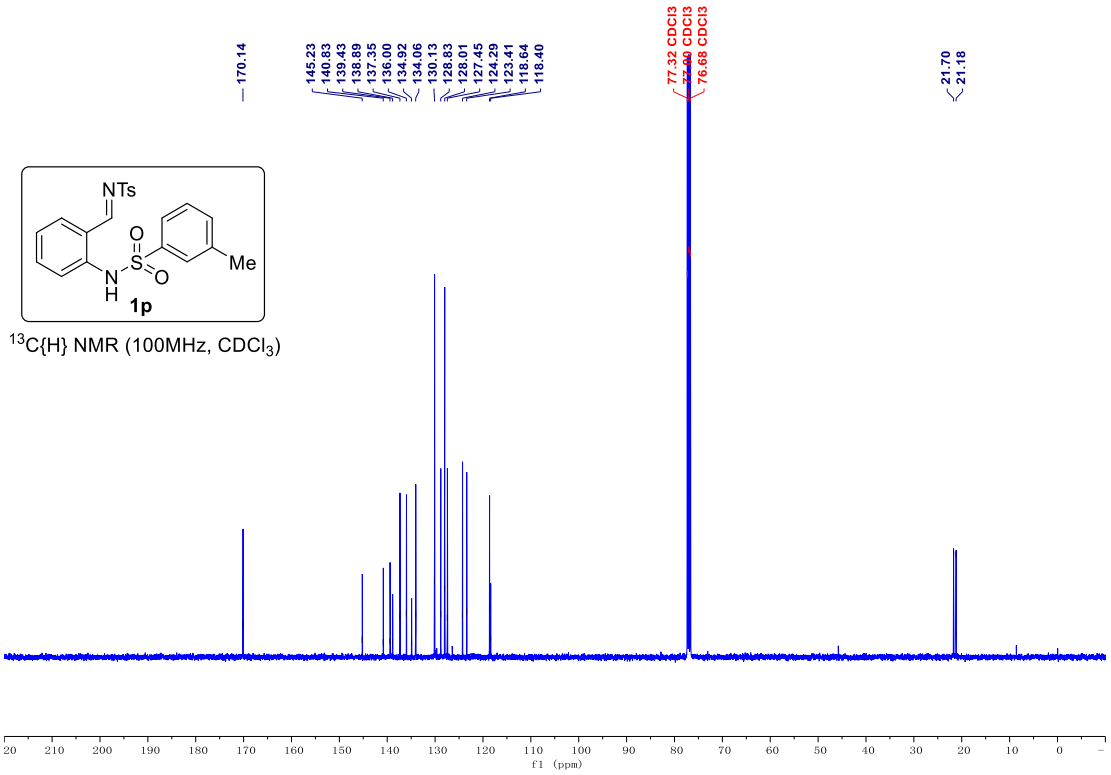
^{1}H NMR (400MHz, $CDCl_3$)



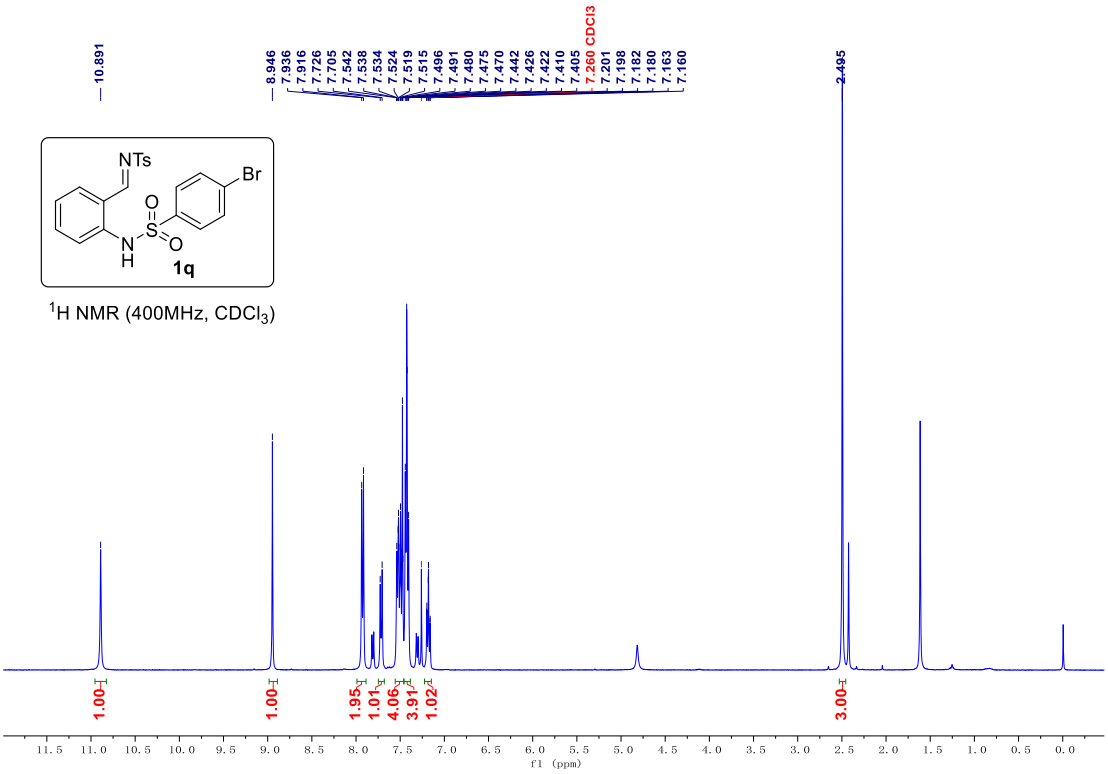
^{13}C{H} NMR (100MHz, $CDCl_3$)



^{1}H NMR (400MHz, $CDCl_3$)



^{13}C{H} NMR (100MHz, $CDCl_3$)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7.480
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7.470
7.442
7.426
7.422
7.410
7.405
7.260 CDCl3
7.201
7.198
7.182
7.180
7.163
7.160
2.495
NTs
Br
O
S
O
N
H
1q
1H NMR (400MHz, CDCl3)
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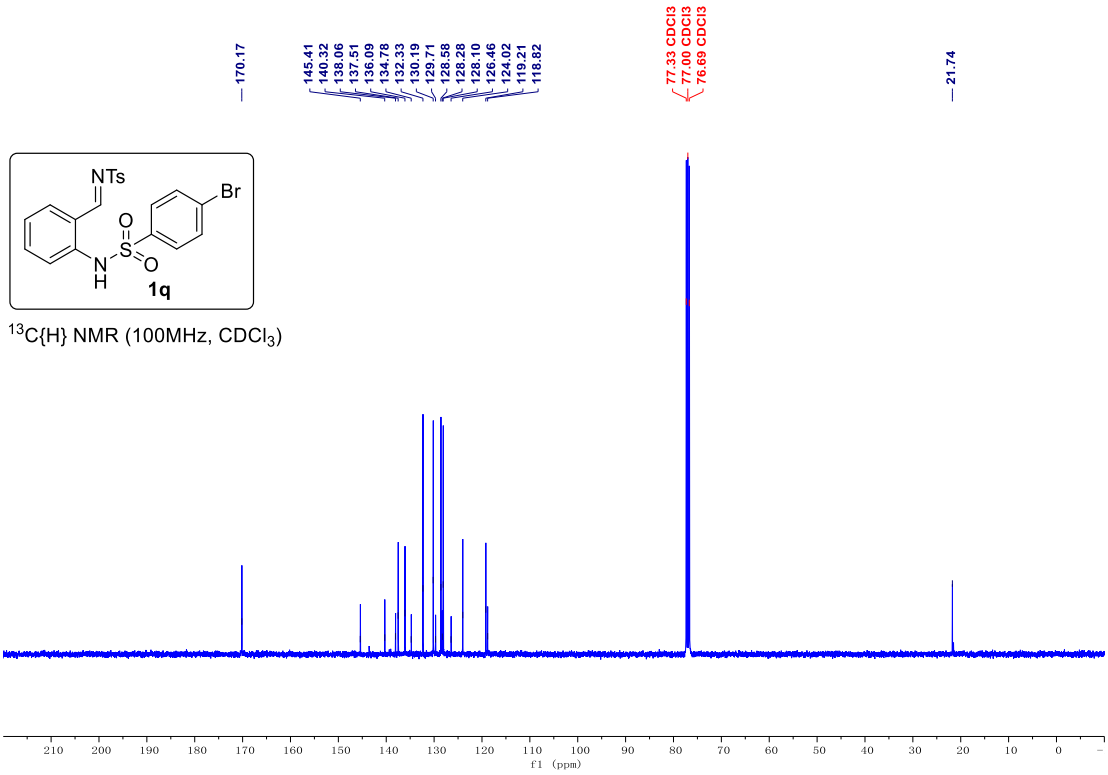
3.00
f1 (ppm)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129.71
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126.46
124.02
119.21
118.82
77.33 CDCl3
77.00 CDCl3
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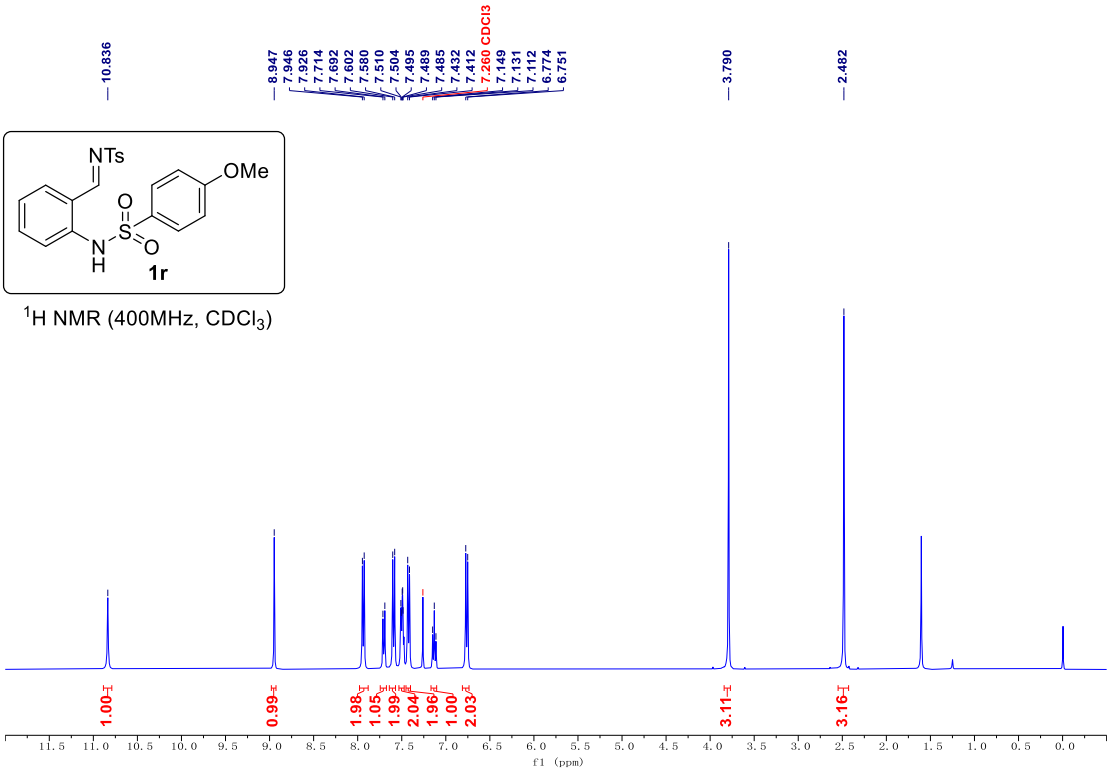
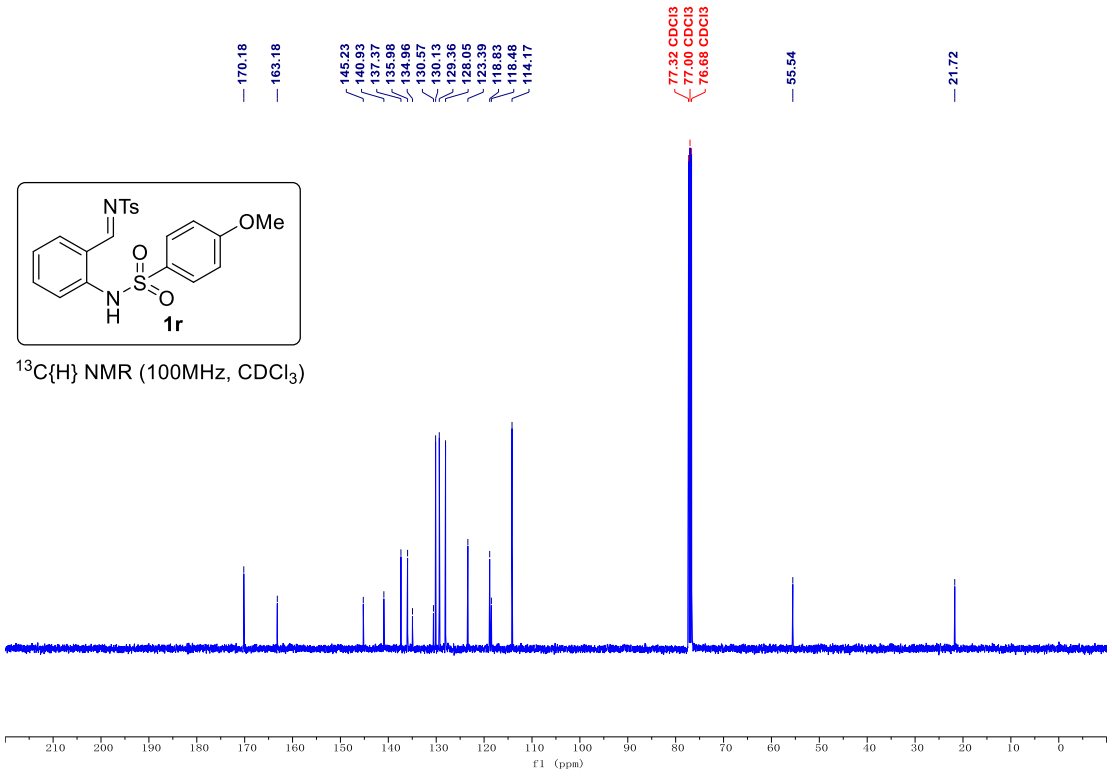
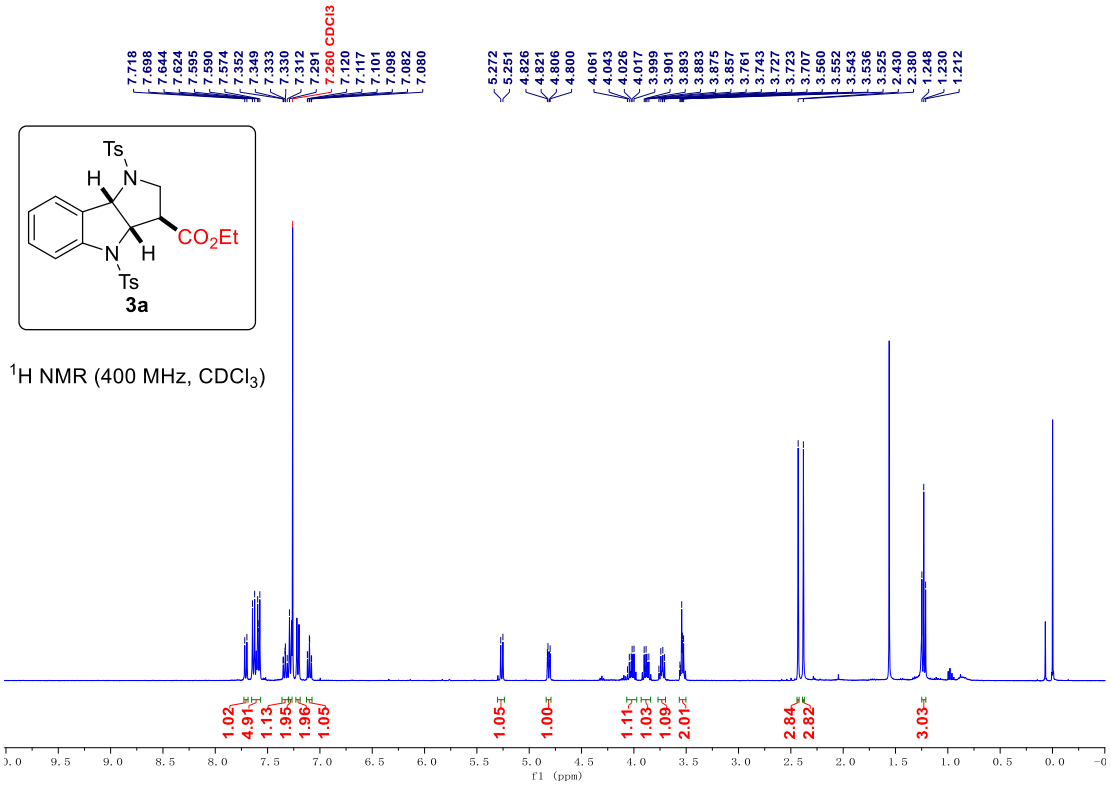
H
1q
13C{H} NMR (100MHz, CDCl3)
f1 (ppm)



^{1}H NMR (400MHz, $CDCl_3$)



^{13}C{H} NMR (100MHz, $CDCl_3$)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7.291
7.260 CDCl3
7.120
7.117
7.101
7.098
7.082
7.080
5.272
5.251
4.826
4.821
4.806
4.800
4.061
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3.857
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3.707
3.560
3.552
3.543
3.536
3.525
2.430
2.380
1.248
1.230
1.212
Ts
H
N
CO2Et
N
H
Ts
3a
1H NMR (400 MHz, CDCl3)
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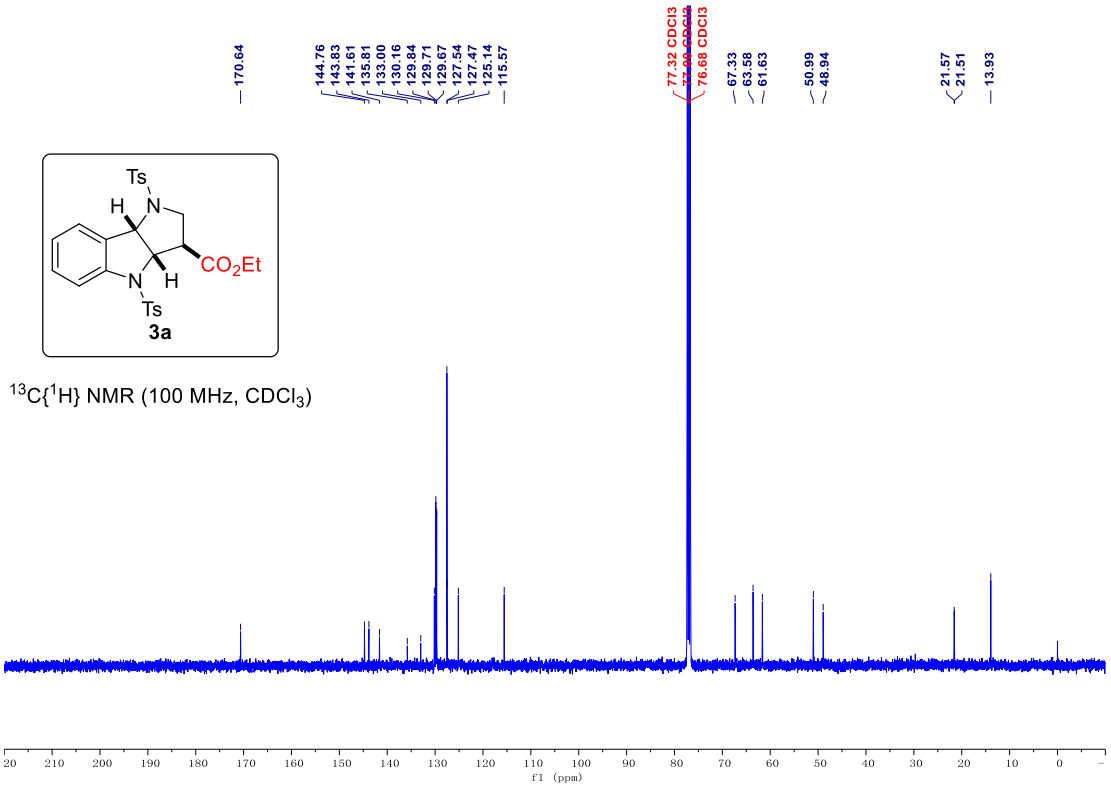
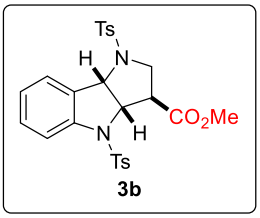
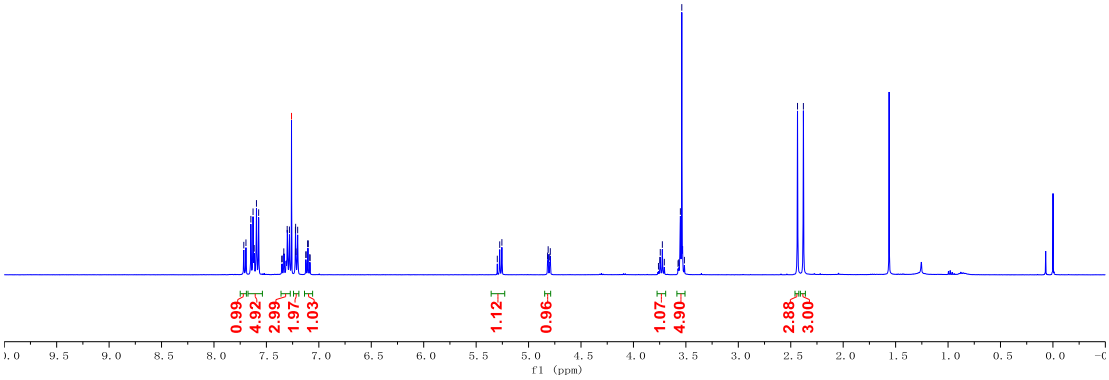
4.91
1.13
1.95
1.96
1.05
1.05
1.00
1.11
1.03
1.09
2.01
2.84
2.82
3.03
f1 (ppm)

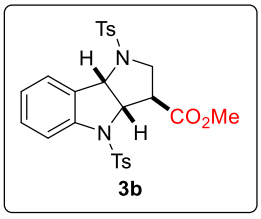

170.64
144.76
143.83
141.61
135.81
133.00
130.16
129.84
129.71
129.67
127.54
127.47
125.14
115.57
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
67.33
63.58
61.63
50.99
48.94
21.57
21.51
13.93
Ts
H
N
CO2Et
N
H
Ts
3a
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)



3b

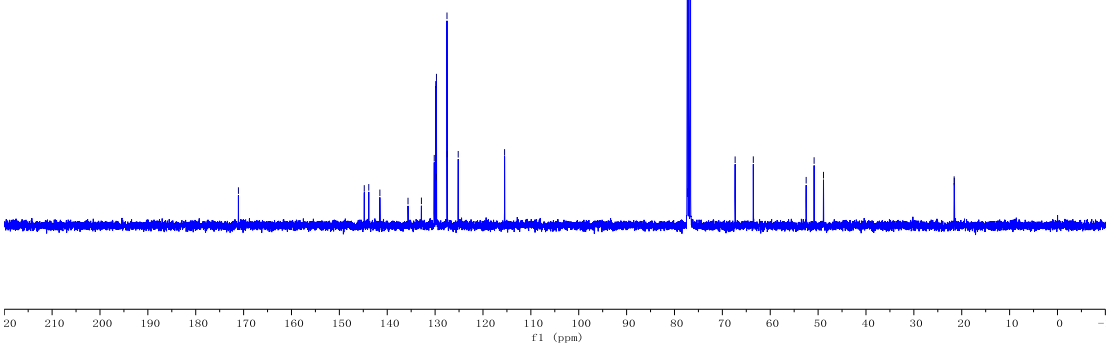
^{1}H NMR (400 MHz, $CDCl_3$)

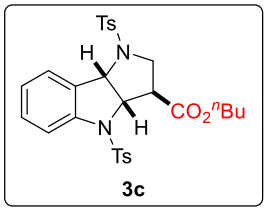




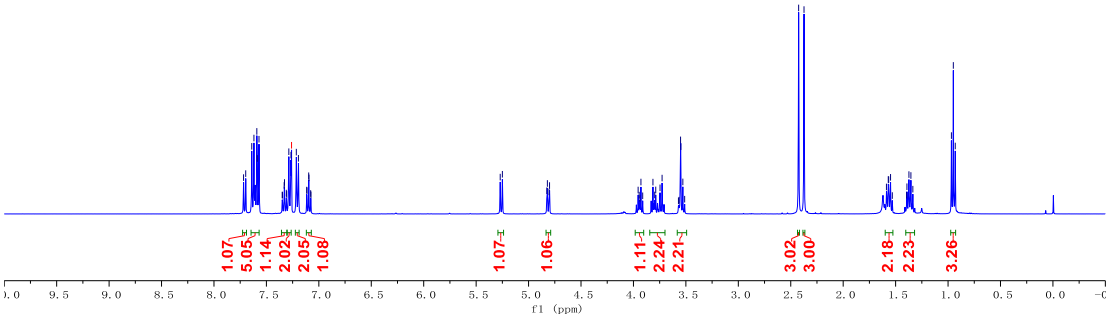
3b

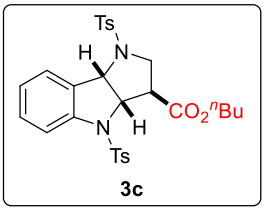
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



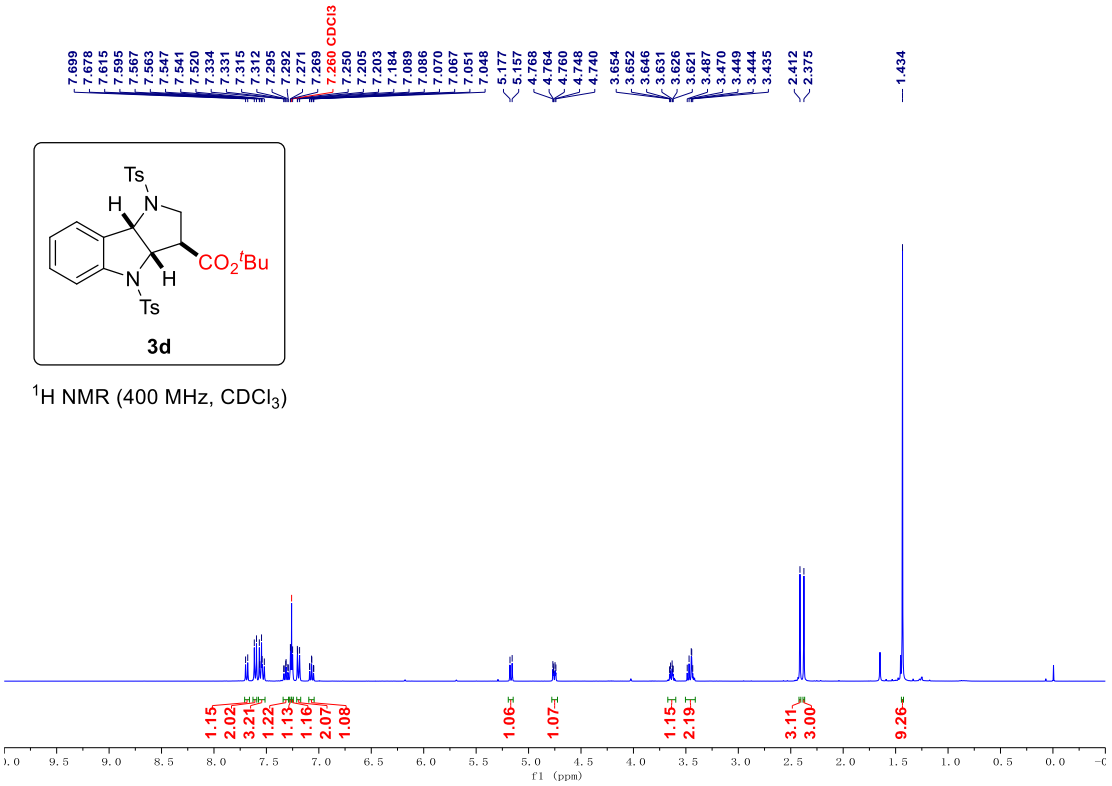


^{1}H NMR (400 MHz, $CDCl_3$)

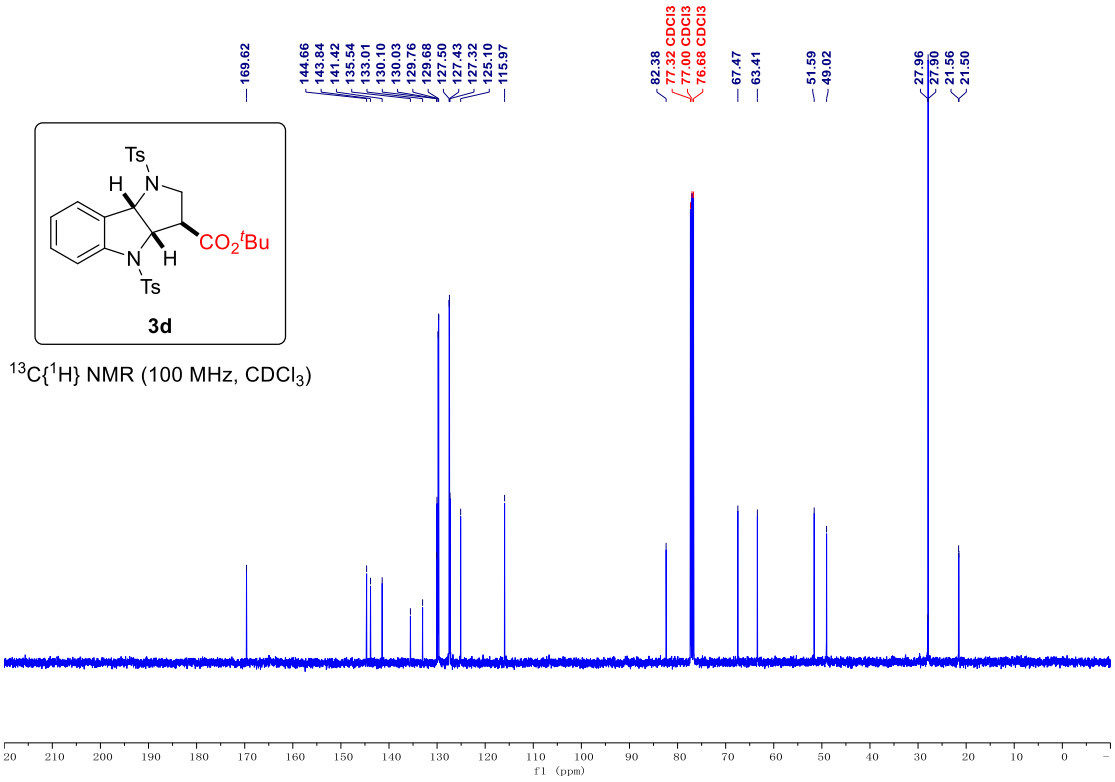




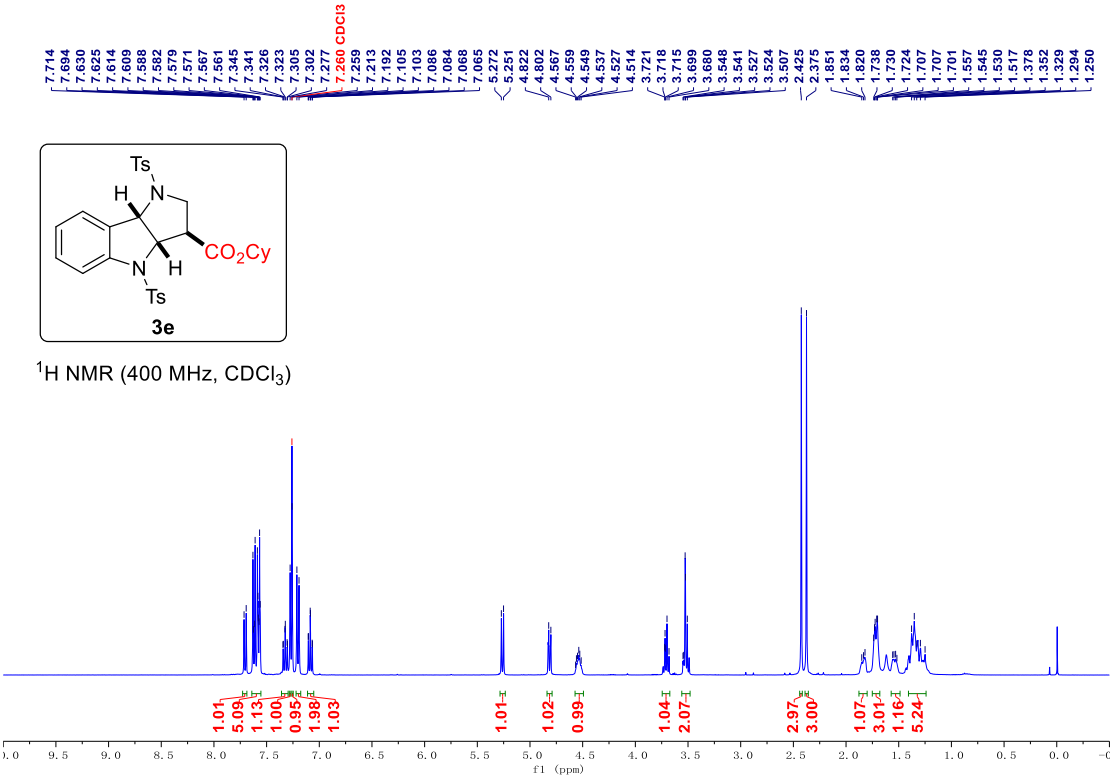
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

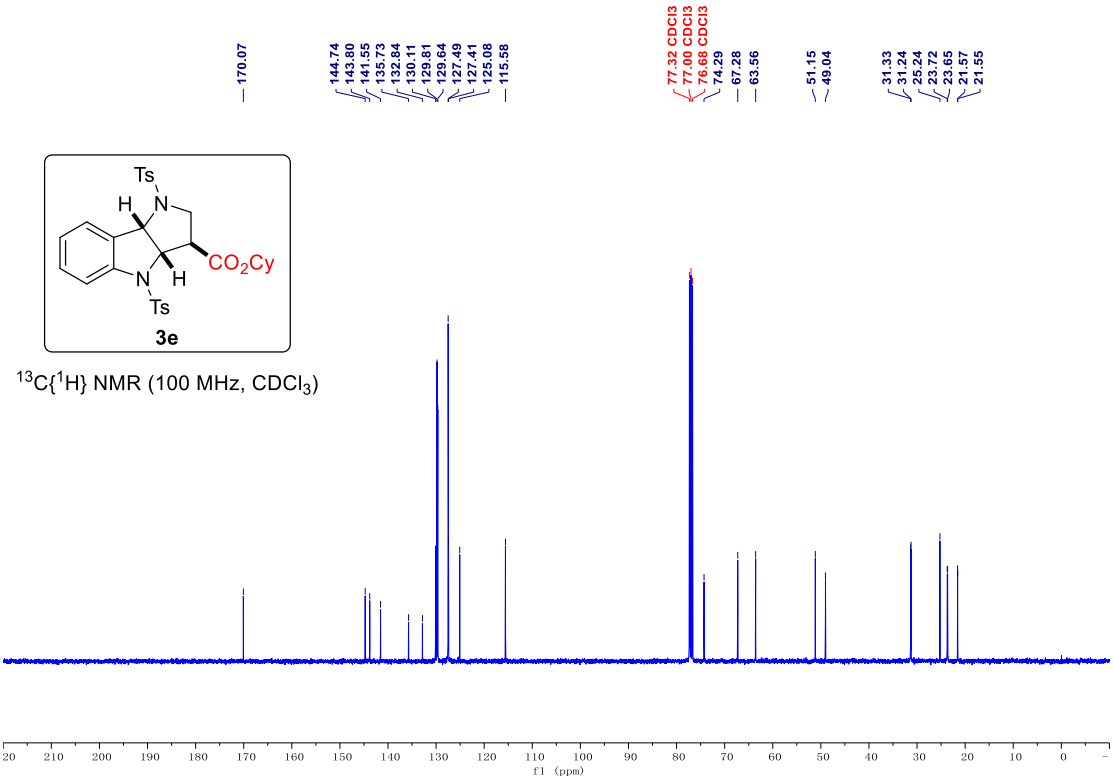


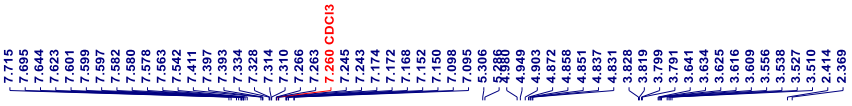
^{1}H NMR (400 MHz, $CDCl_3$)

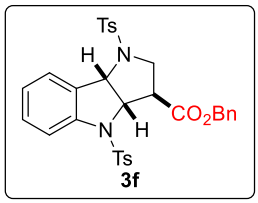


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)


7.714
7.694
7.630
7.625
7.614
7.609
7.588
7.582
7.579
7.571
7.567
7.561
7.345
7.341
7.326
7.323
7.305
7.302
7.277
7.260 CDCl3
7.259
7.213
7.192
7.105
7.103
7.086
7.084
7.068
7.065
5.272
5.251
4.822
4.802
4.567
4.559
4.549
4.537
4.527
4.514
3.721
3.718
3.715
3.699
3.680
3.548
3.541
3.527
3.524
3.507
2.425
2.375
1.851
1.834
1.820
1.738
1.730
1.724
1.707
1.707
1.701
1.557
1.545
1.530
1.517
1.378
1.352
1.329
1.294
1.250
Ts
H
N
CO2Cy
N
H
Ts
3e
1H NMR (400 MHz, CDCl3)
1.01
5.09
1.13
1.00
0.95
1.98
1.03
1.01
1.02
0.99
1.04
2.07
2.97
3.00
1.07
3.01
1.16
5.24
f1 (ppm)

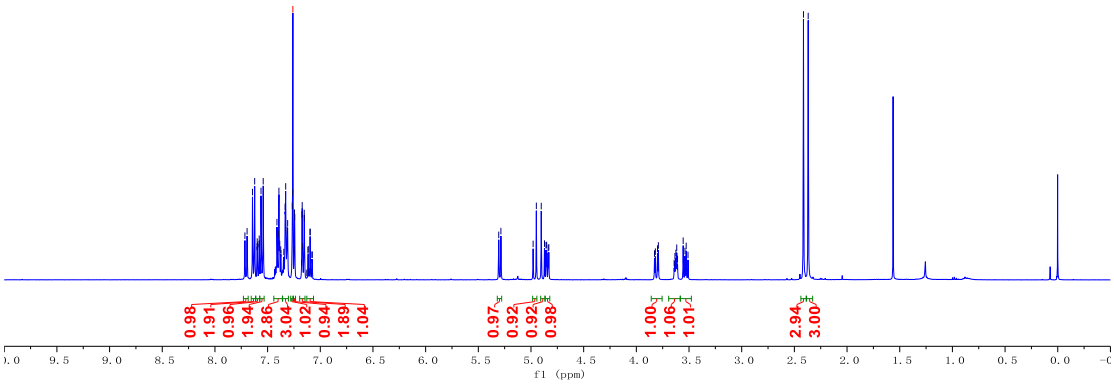

170.07
144.74
143.80
141.55
135.73
132.84
130.11
129.81
129.64
127.49
127.41
125.08
115.58
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
74.29
67.28
63.56
51.15
49.04
31.33
31.24
25.24
23.72
23.65
21.57
21.55
Ts
H
N
CO2Cy
N
H
Ts
3e
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)

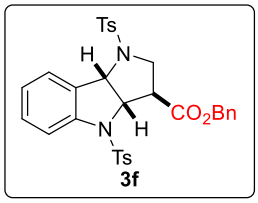




3f

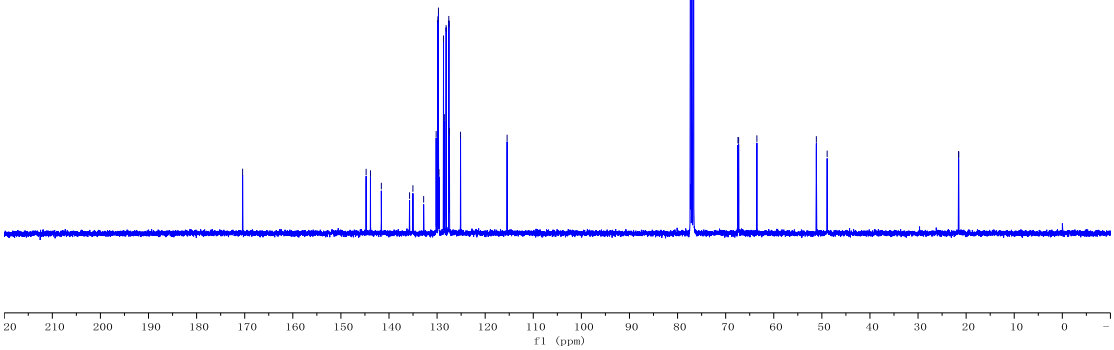
^{1}H NMR (400 MHz, $CDCl_3$)

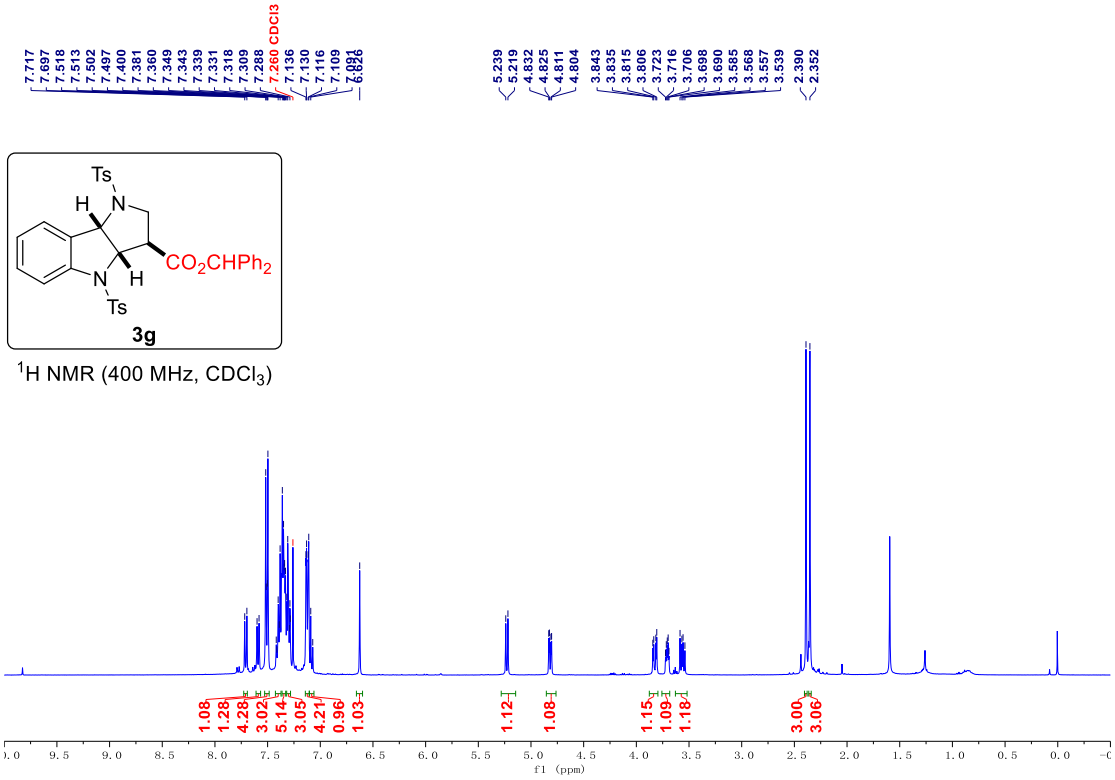


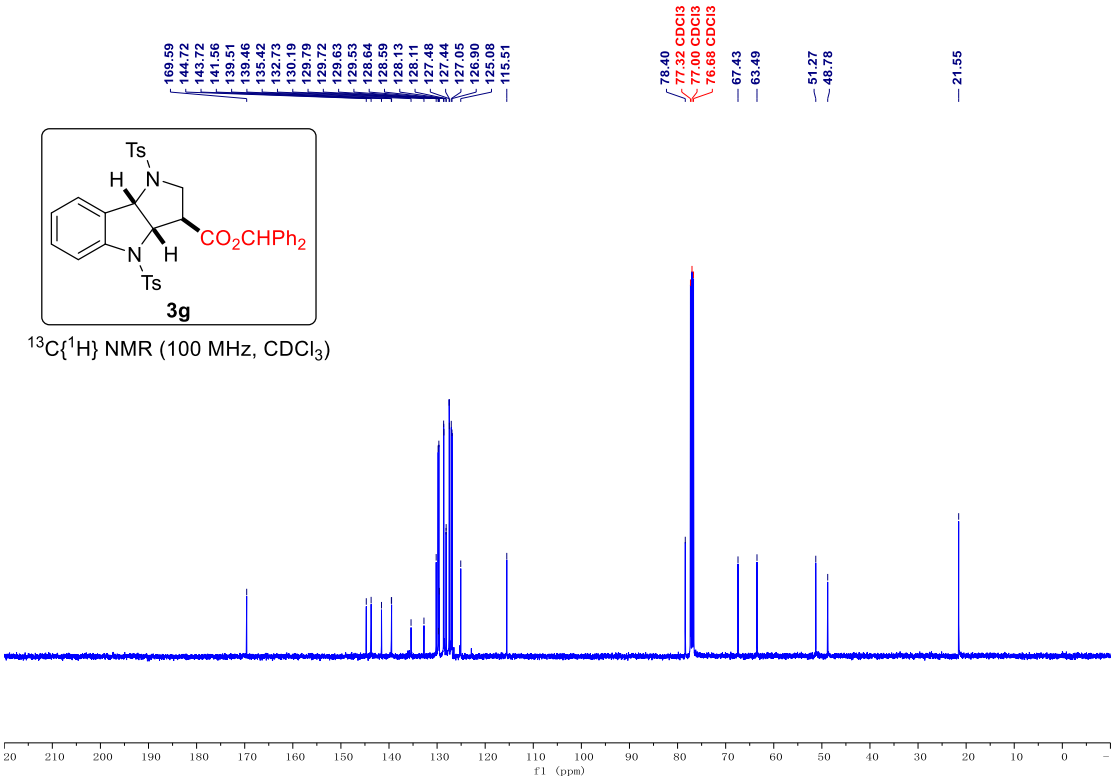


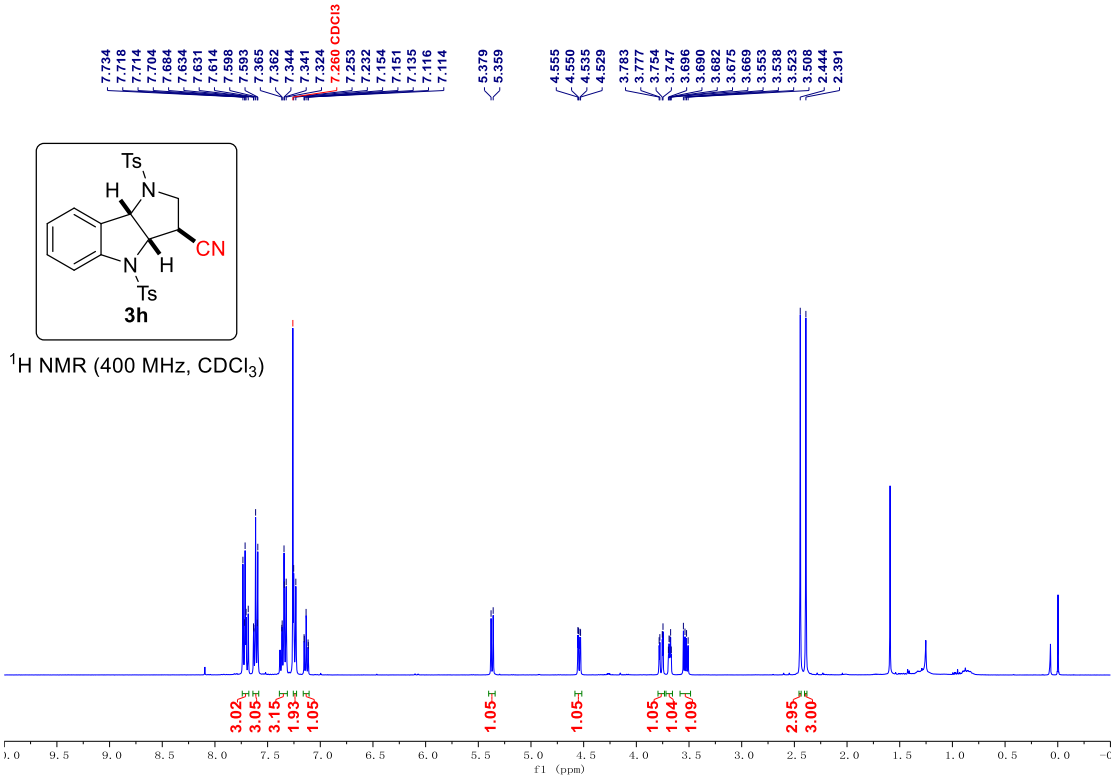
3f

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

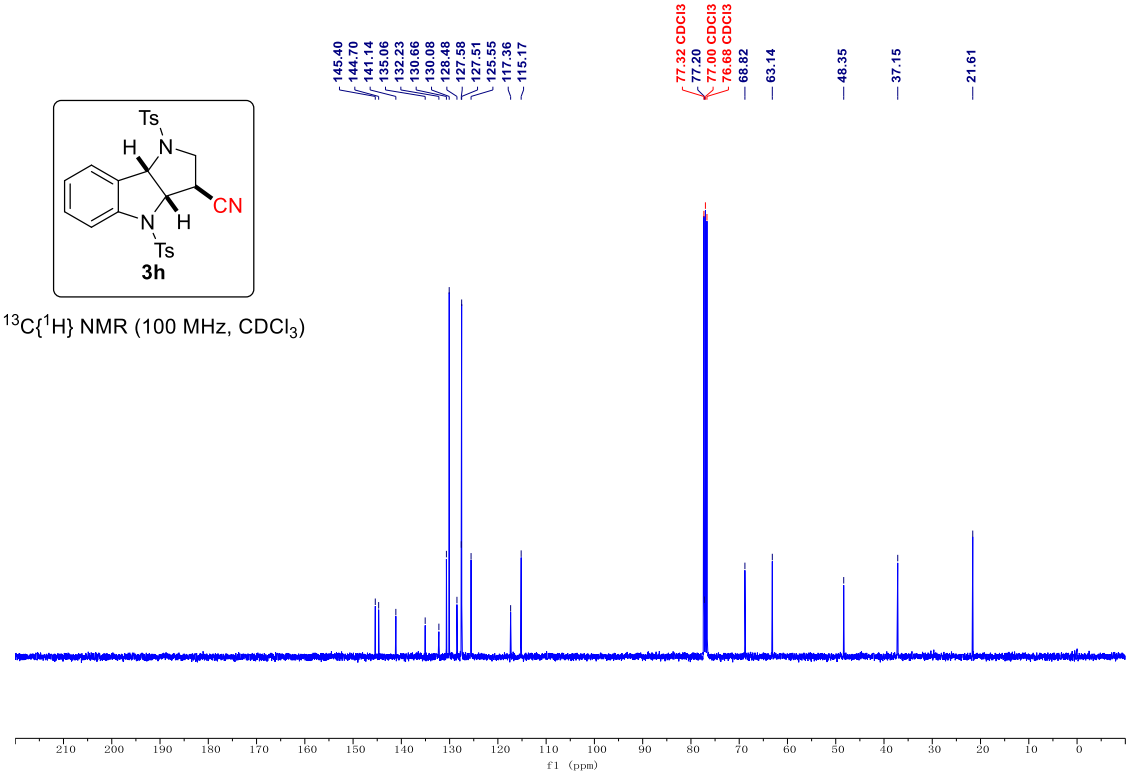



7.717
7.697
7.518
7.513
7.502
7.497
7.400
7.381
7.360
7.349
7.343
7.339
7.331
7.318
7.309
7.288
7.260 CDCl3
7.136
7.130
7.116
7.109
7.091
6.826
5.239
5.219
4.832
4.825
4.811
4.804
3.843
3.835
3.815
3.806
3.723
3.716
3.706
3.698
3.690
3.585
3.568
3.557
3.539
2.390
2.352
Ts
H
N
CO2CHPh2
N
H
Ts
3g
1H NMR (400 MHz, CDCl3)
1.08
1.28
4.28
3.02
5.14
3.05
4.21
0.96
1.03
1.12
1.08
1.15
1.09
1.18
3.00
3.06
f1 (ppm)

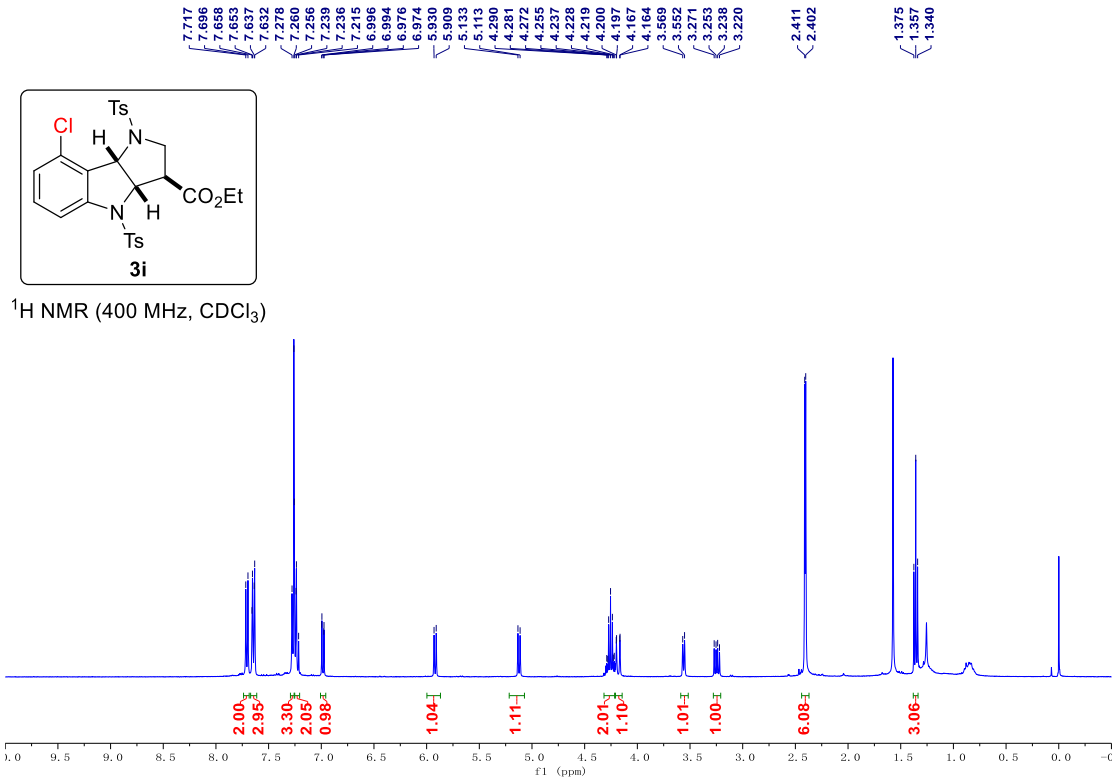

169.59
144.72
143.72
141.56
139.51
139.46
135.42
132.73
130.19
129.79
129.72
129.63
129.53
128.64
128.59
128.13
128.11
127.48
127.44
127.05
126.90
125.08
115.51
78.40
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
67.43
63.49
51.27
48.78
21.55
Ts
H
N
CO2CHPh2
N
H
Ts
3g
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)



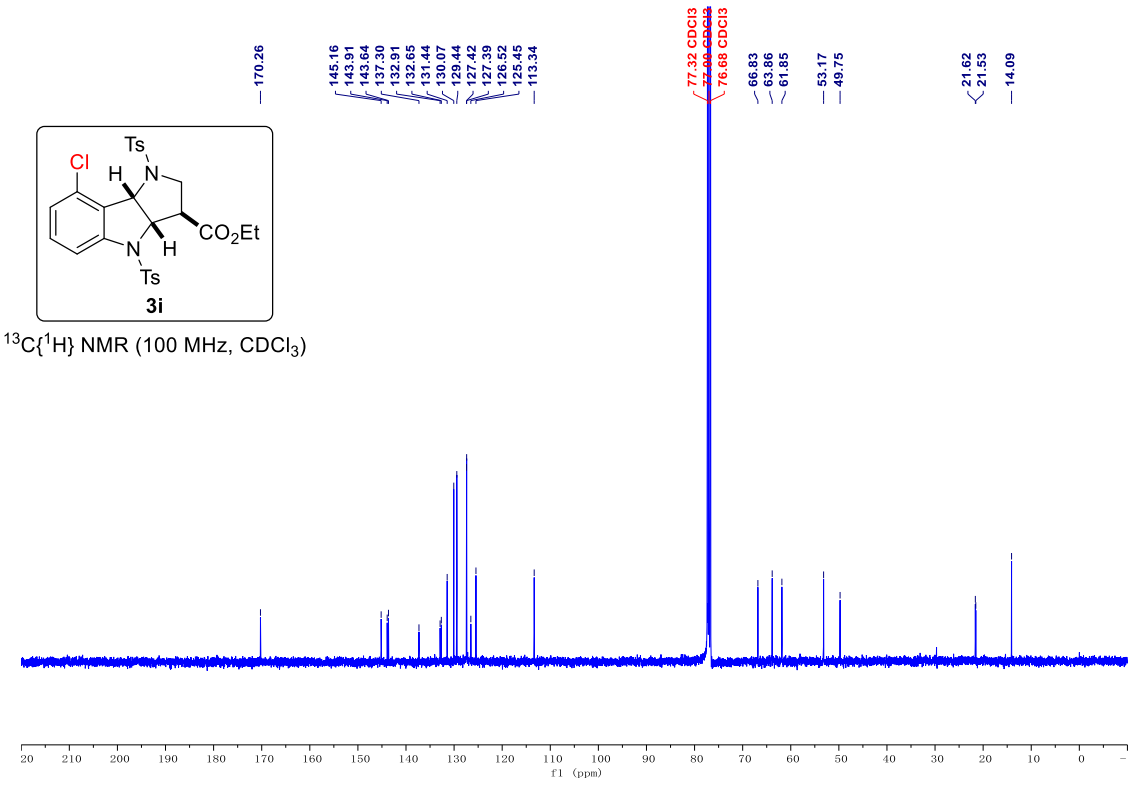
^{1}H NMR (400 MHz, $CDCl_3$)



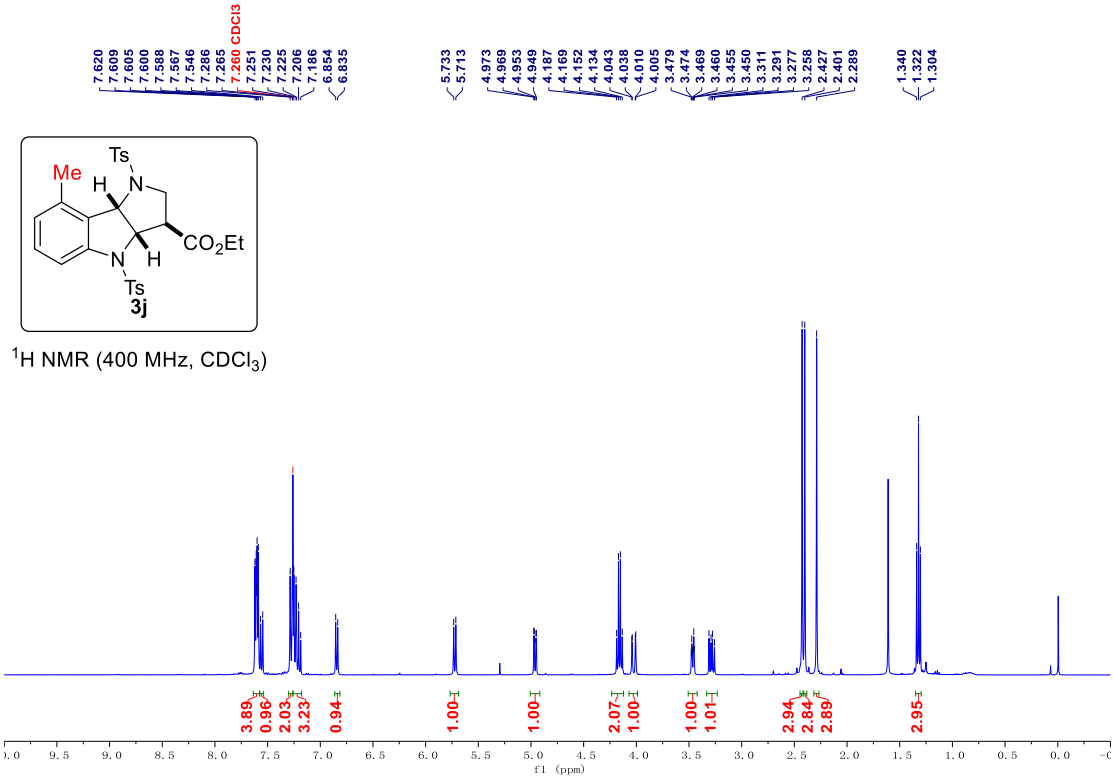
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



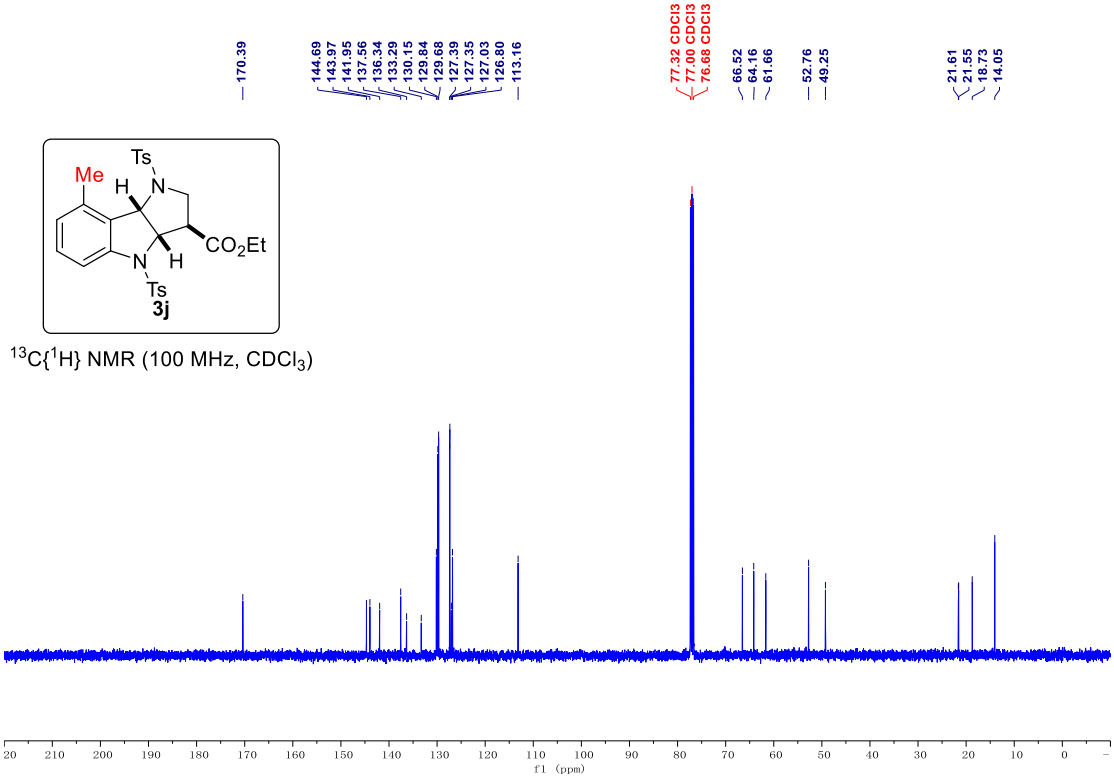
^{1}H NMR (400 MHz, $CDCl_3$)



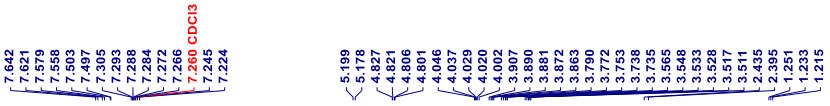
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

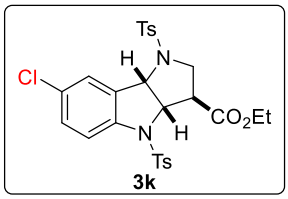


^{1}H NMR (400 MHz, $CDCl_3$)

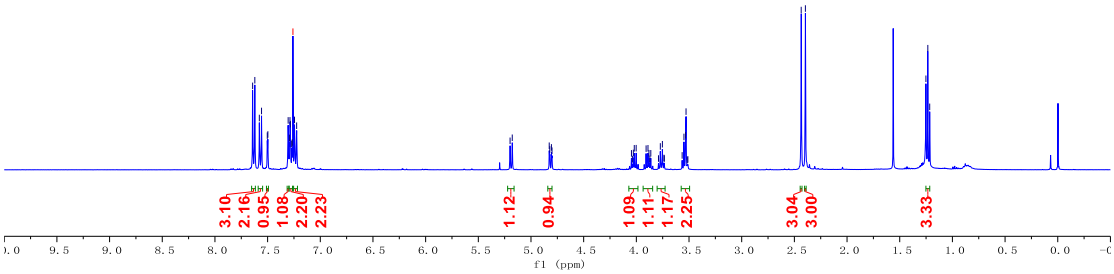


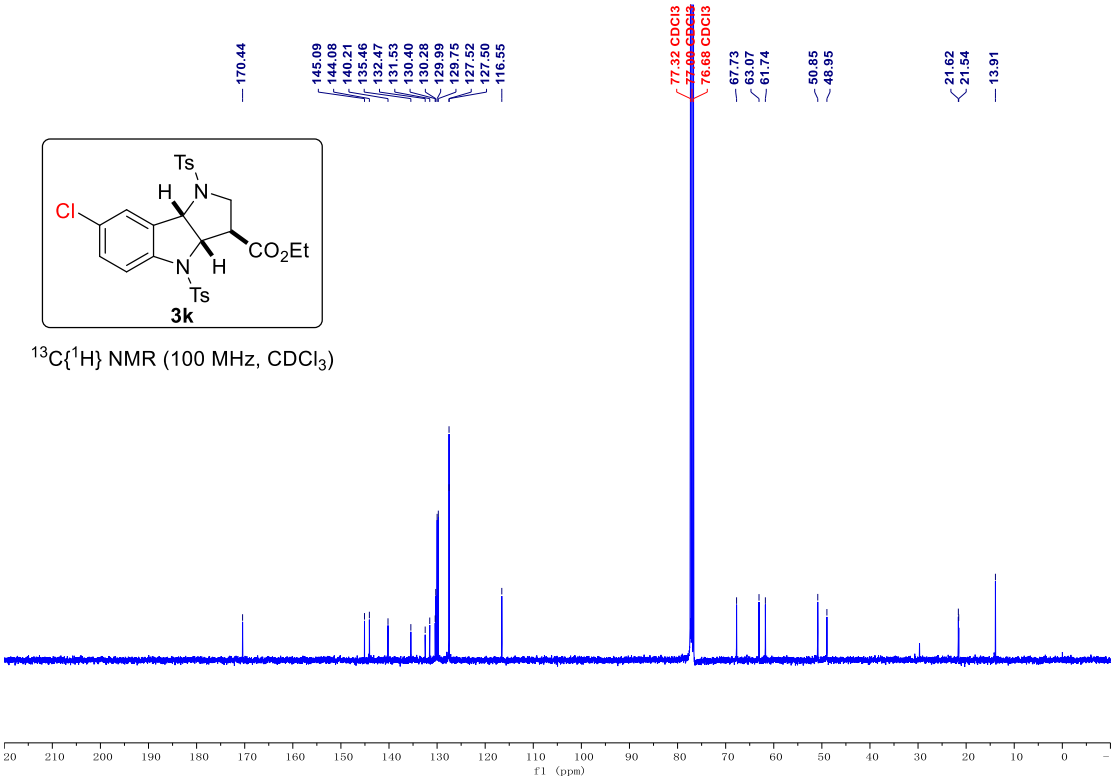
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



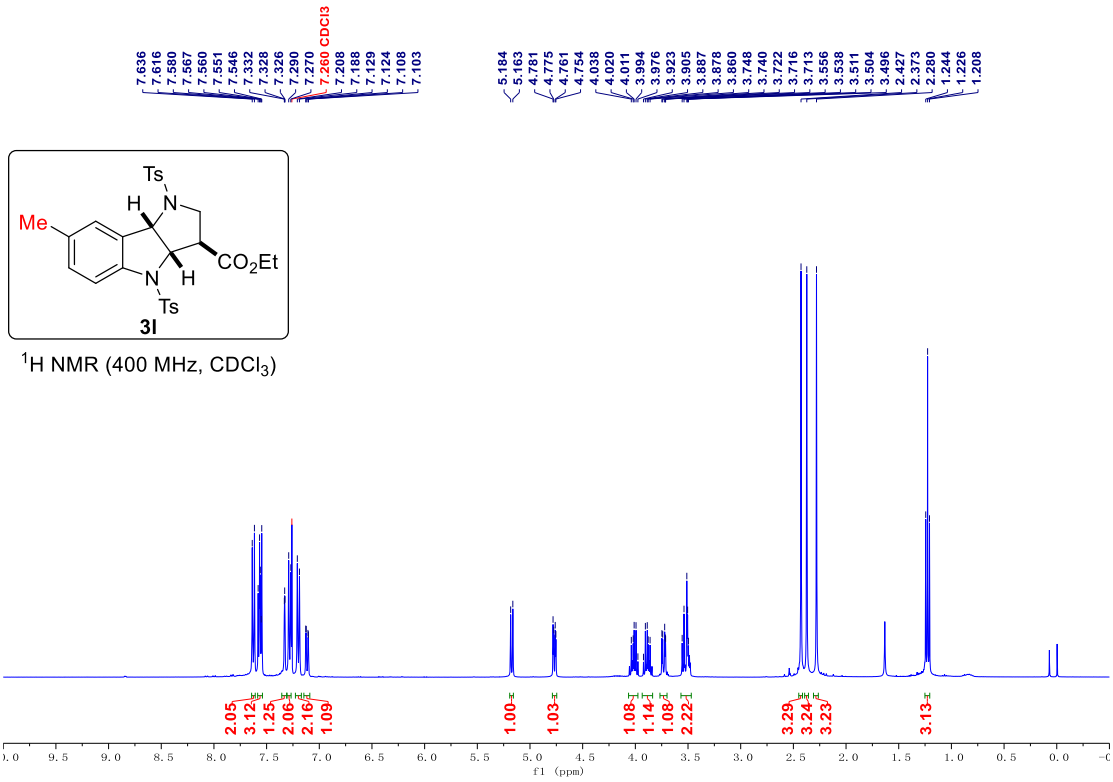


^{1}H NMR (400 MHz, $CDCl_3$)

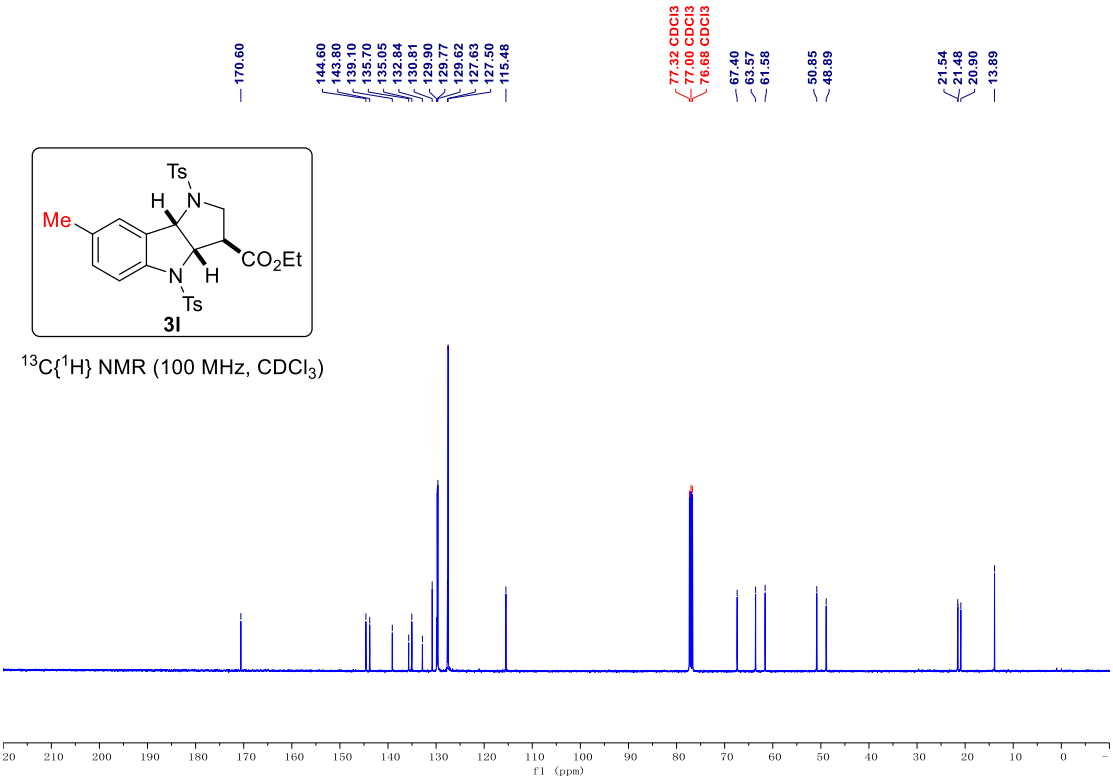




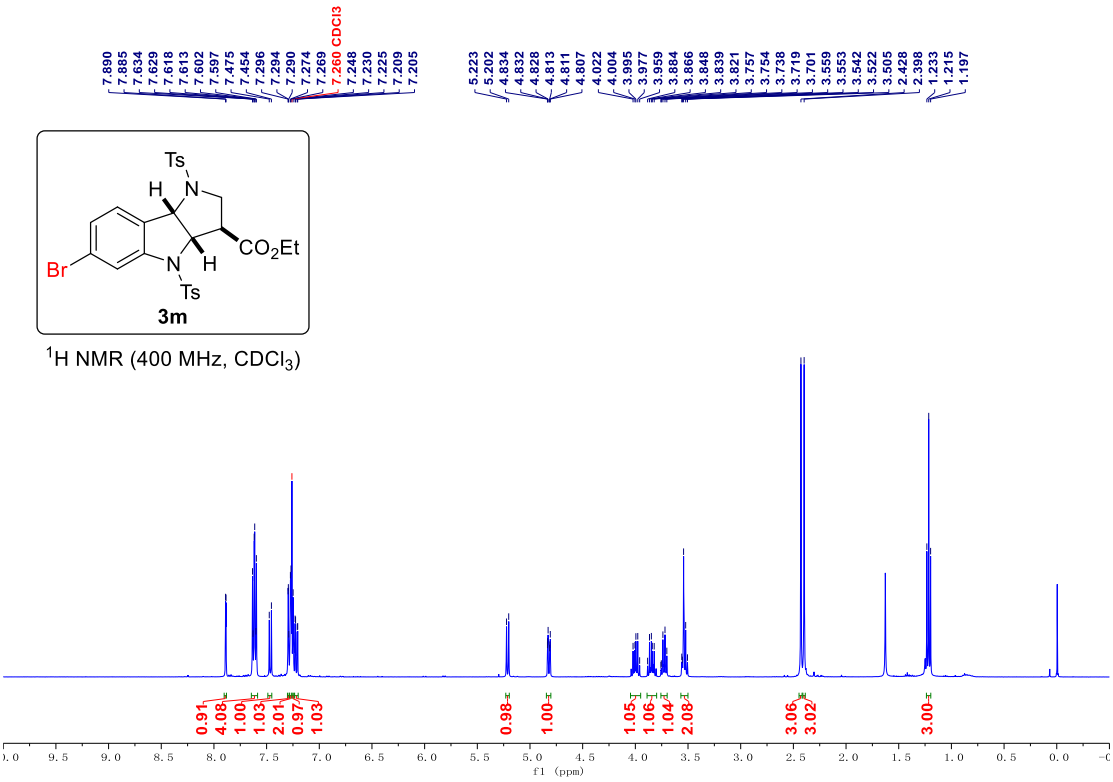
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

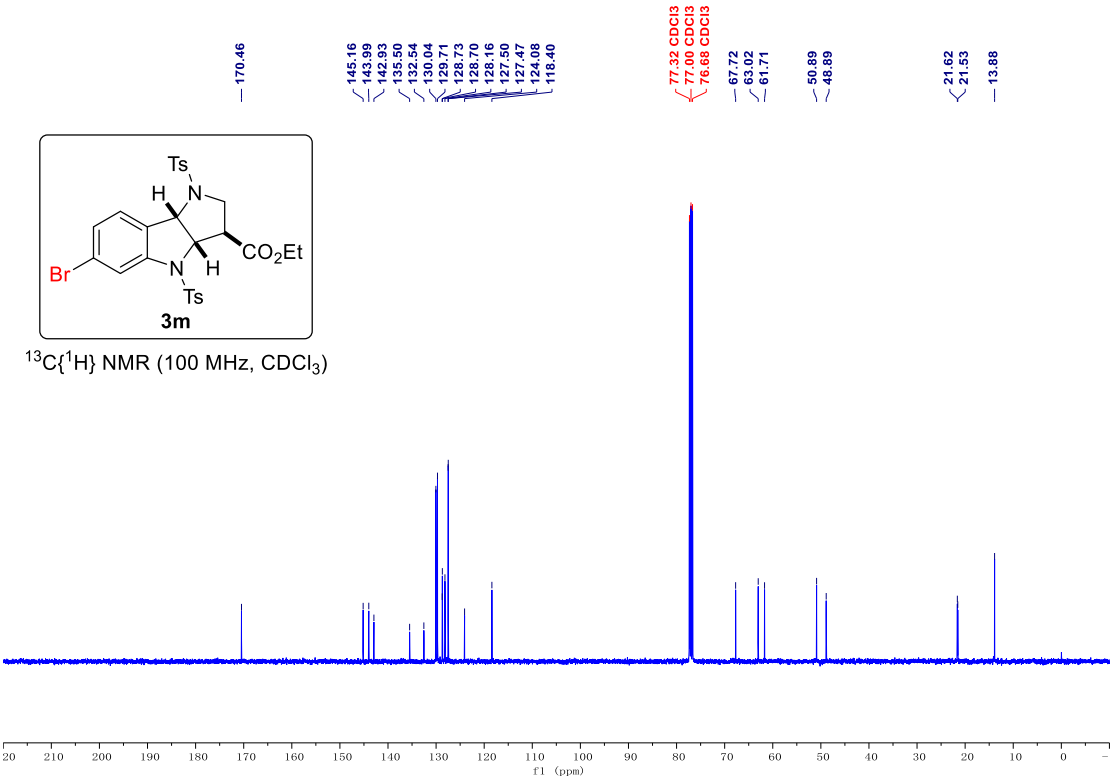


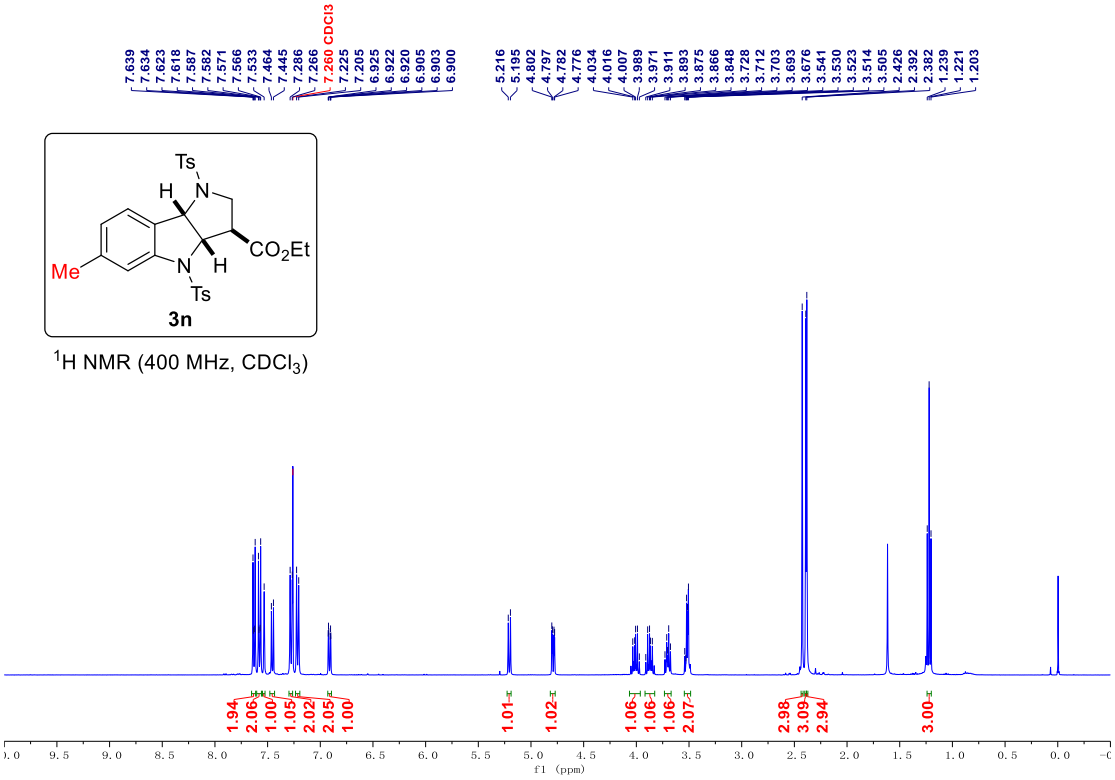
^{1}H NMR (400 MHz, $CDCl_3$)



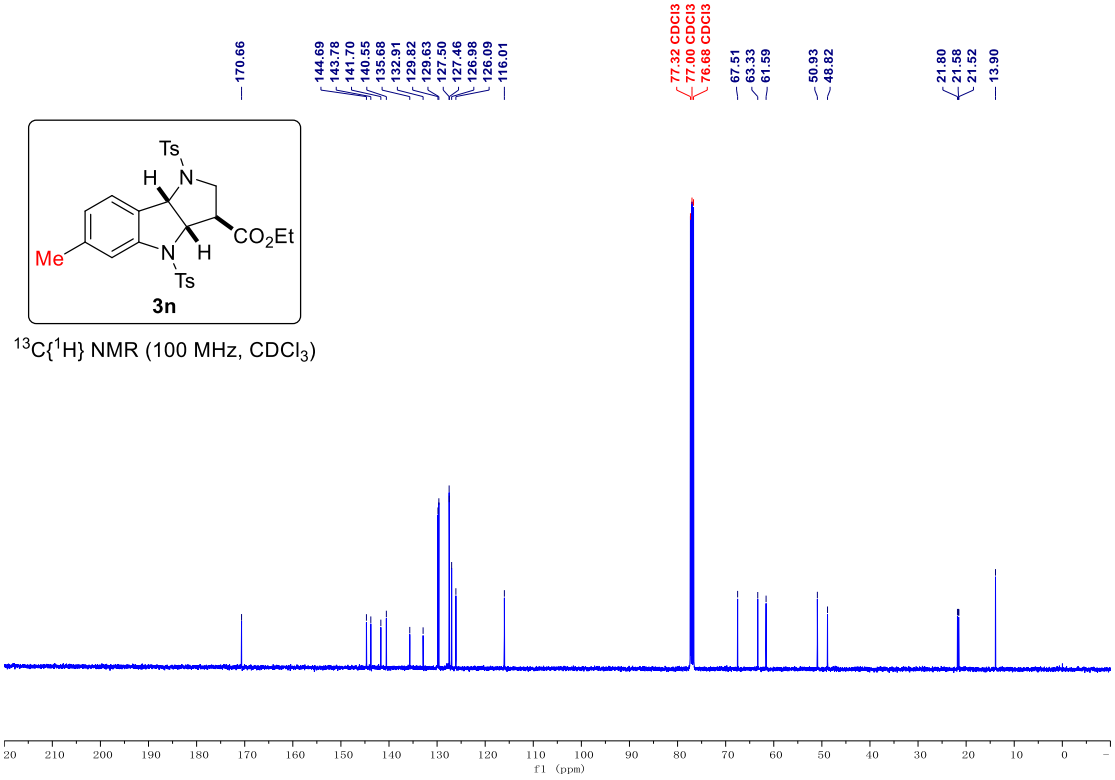
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)


7.890
7.885
7.634
7.629
7.618
7.613
7.602
7.597
7.475
7.454
7.296
7.294
7.290
7.274
7.269
7.260 CDCl3
7.248
7.230
7.225
7.209
7.205
5.223
5.202
4.834
4.832
4.828
4.813
4.811
4.807
4.022
4.004
3.995
3.977
3.959
3.884
3.866
3.848
3.839
3.821
3.757
3.754
3.738
3.719
3.701
3.559
3.553
3.542
3.522
3.505
2.428
2.398
1.233
1.215
1.197
Ts
H
N
CO2Et
Br
N
H
Ts
3m
1H NMR (400 MHz, CDCl3)
0.91
4.08
1.00
1.03
2.01
0.97
1.03
0.98
1.00
1.05
1.06
1.04
2.08
3.06
3.02
3.00
f1 (ppm)

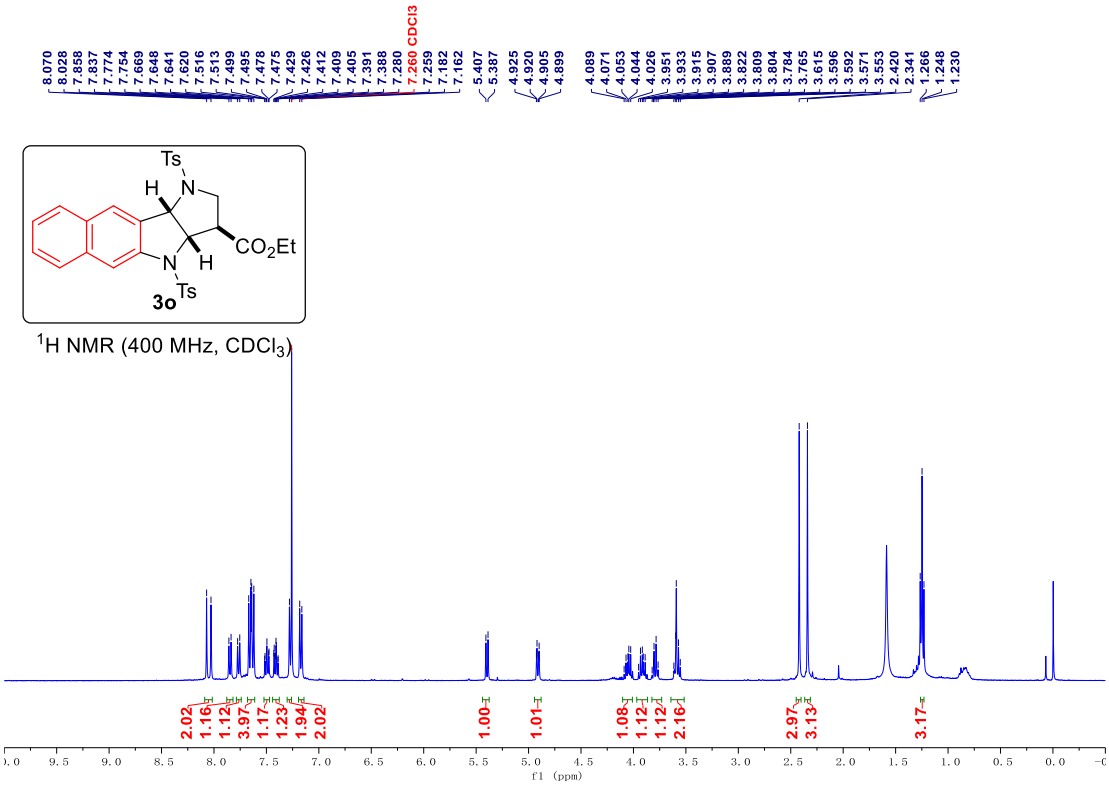

170.46
145.16
143.99
142.93
135.50
132.54
130.04
129.71
128.73
128.70
128.16
127.50
127.47
124.08
118.40
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
67.72
63.02
61.71
50.89
48.89
21.62
21.53
13.88
Ts
H
N
CO2Et
Br
N
H
Ts
3m
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)

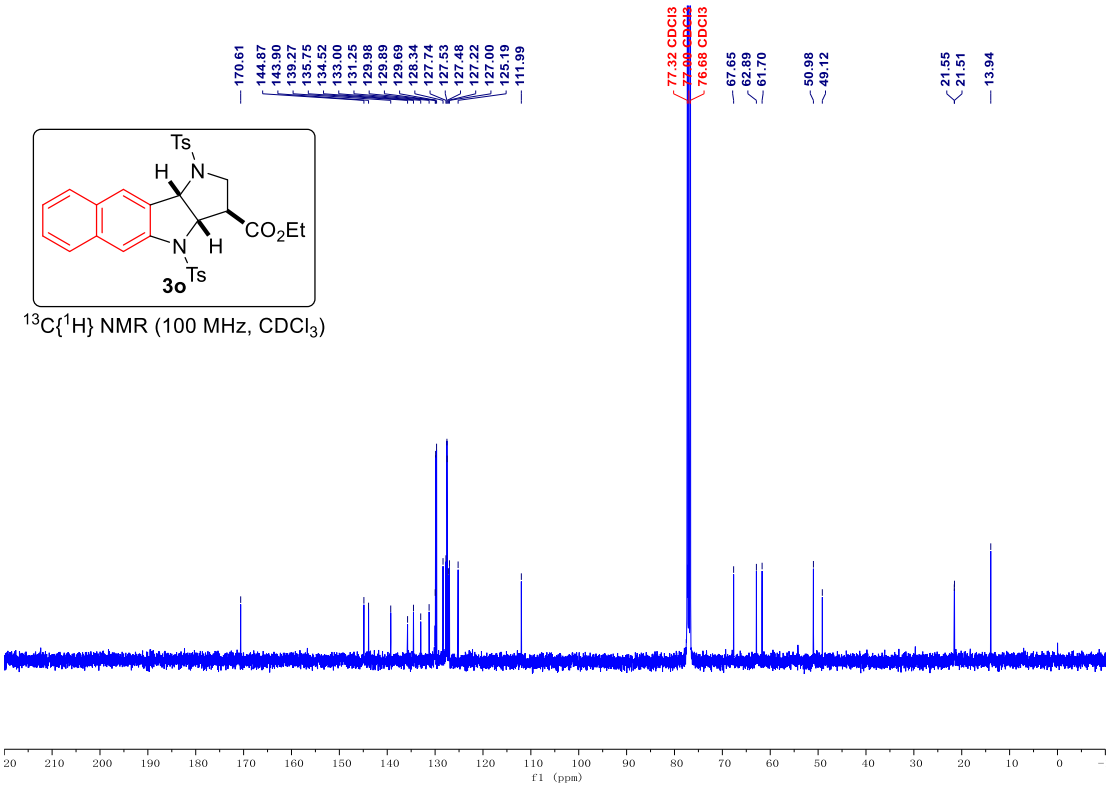


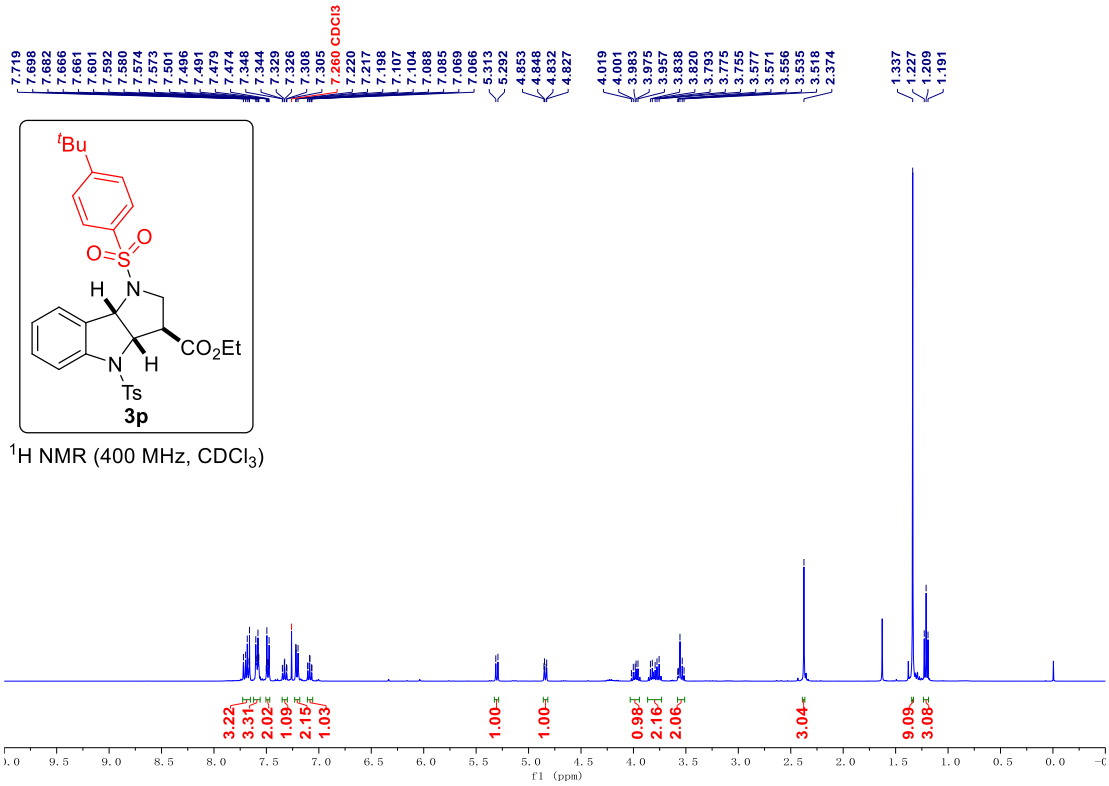
^{1}H NMR (400 MHz, $CDCl_3$)



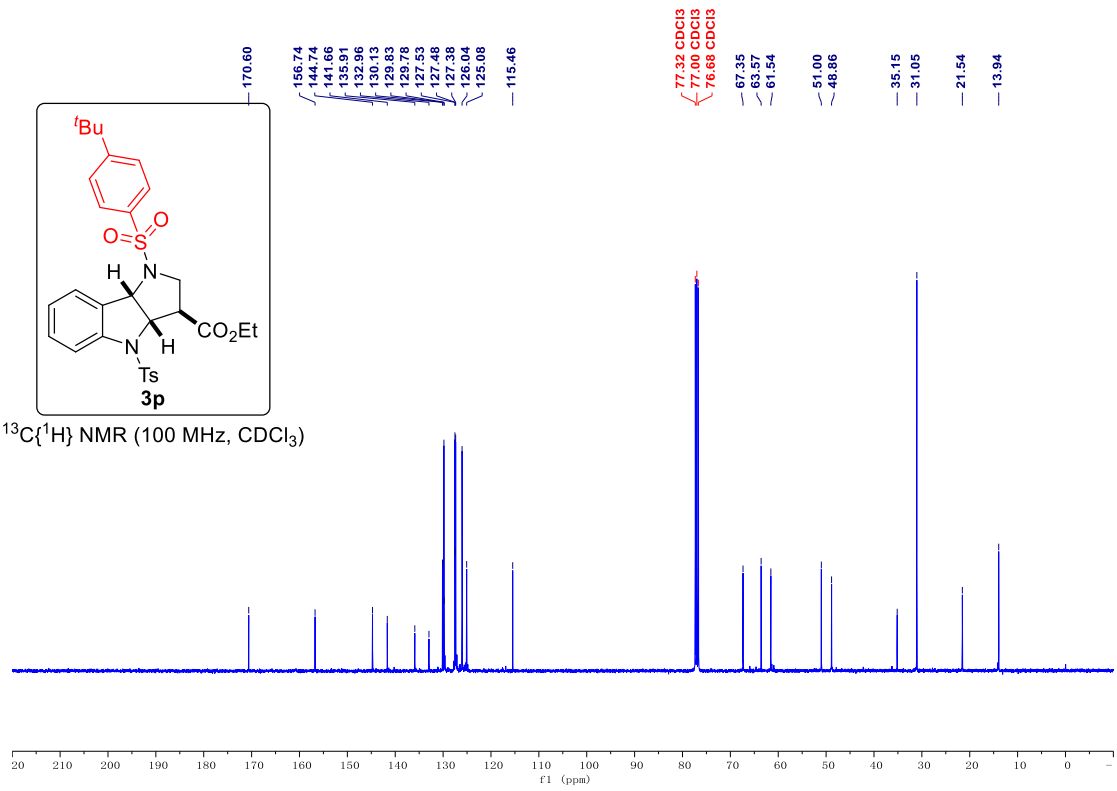
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)


8.070
8.028
7.858
7.837
7.774
7.754
7.669
7.648
7.641
7.620
7.516
7.513
7.499
7.495
7.478
7.475
7.429
7.426
7.412
7.409
7.405
7.391
7.388
7.280
7.260 CDCl3
7.259
7.182
7.162
5.407
5.387
4.925
4.920
4.905
4.899
4.089
4.071
4.053
4.044
4.026
3.951
3.933
3.915
3.907
3.889
3.822
3.809
3.804
3.784
3.765
3.615
3.596
3.592
3.571
3.553
2.420
2.341
1.266
1.248
1.230
Ts
H
N
CO2Et
N
H
Ts
3o
1H NMR (400 MHz, CDCl3)
2.02
1.16
1.12
3.97
1.17
1.23
1.94
2.02
1.00
1.01
1.08
1.12
1.12
2.16
2.97
3.13
3.17
f1 (ppm)

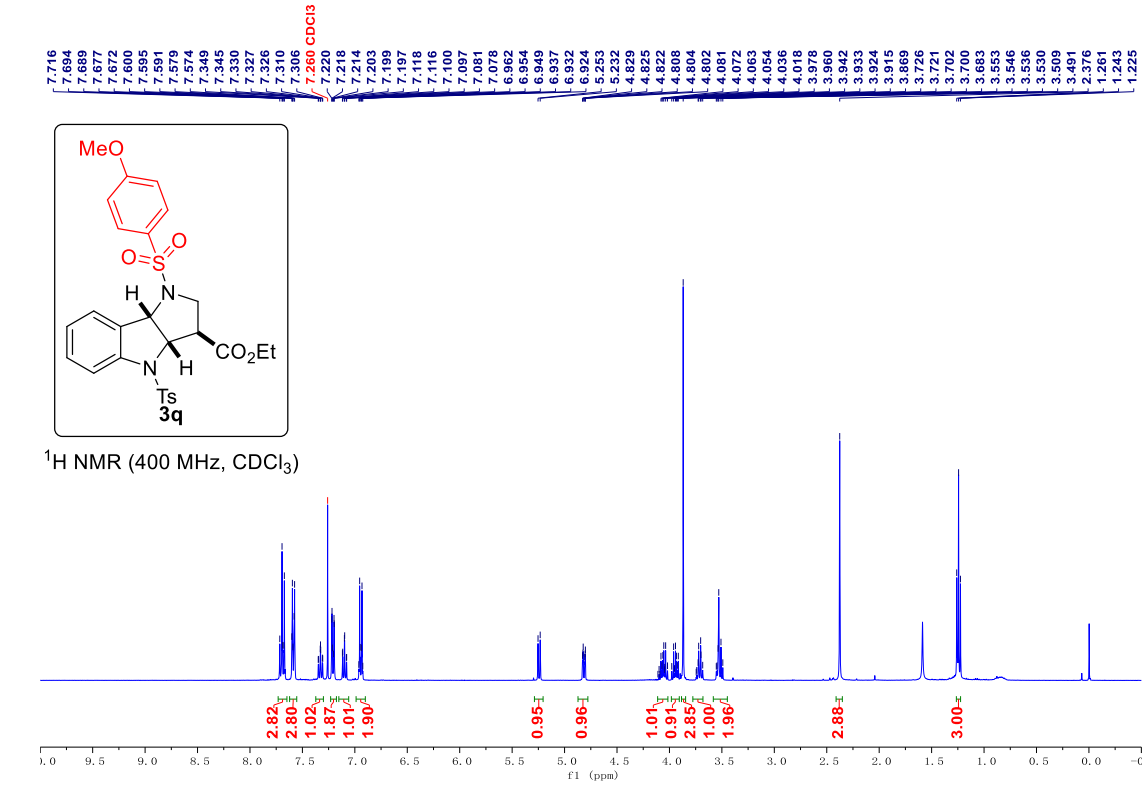

170.61
144.87
143.90
139.27
135.75
134.52
133.00
131.25
129.98
129.89
129.69
128.34
127.74
127.53
127.48
127.22
127.00
125.19
111.99
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
67.65
62.89
61.70
50.98
49.12
21.55
21.51
13.94
Ts
H
N
CO2Et
N
H
Ts
3o
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)



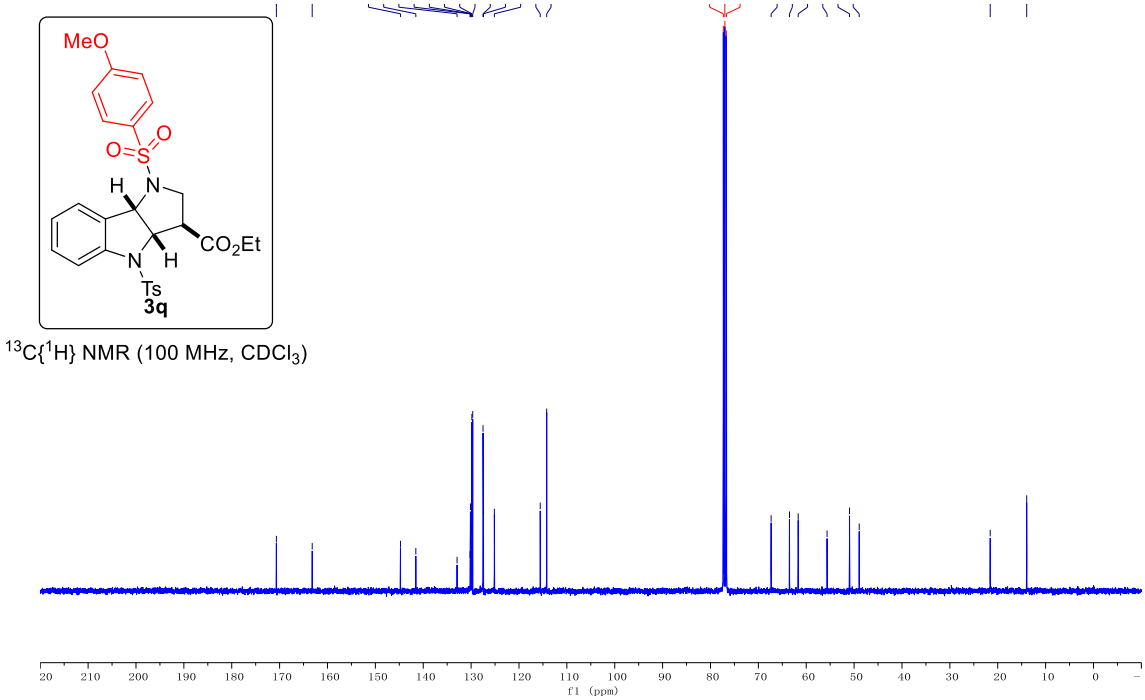
^{1}H NMR (400 MHz, $CDCl_3$)



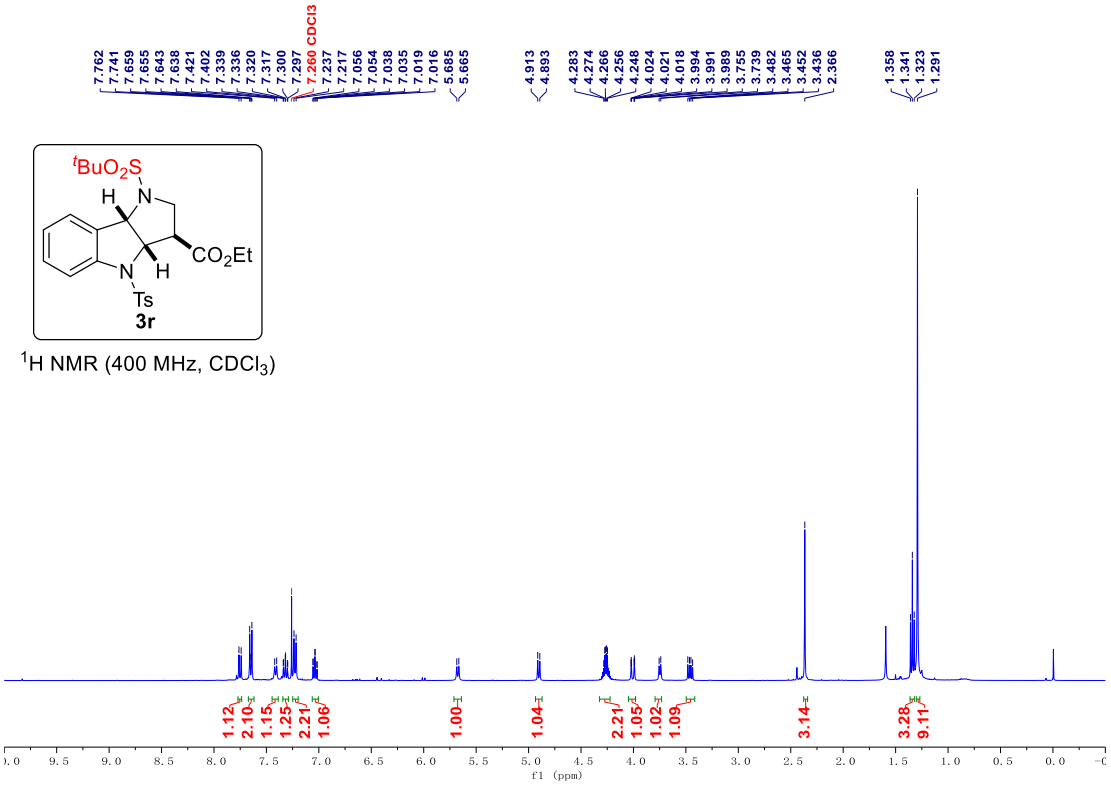
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)



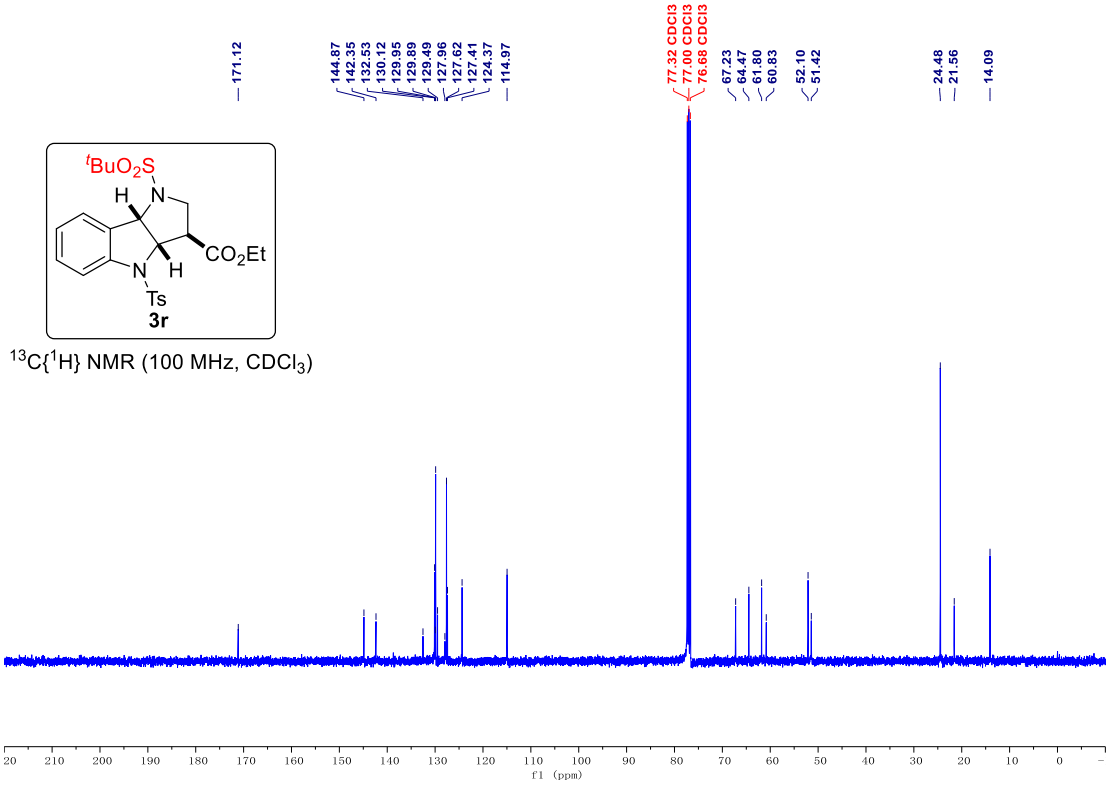
^{1}H NMR (400 MHz, $CDCl_3$)



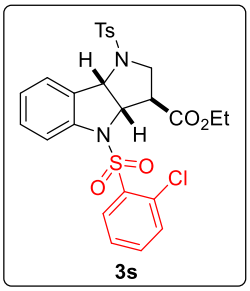
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)

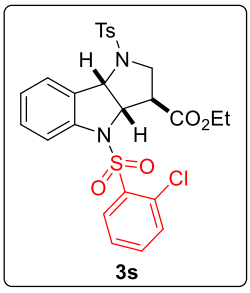


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



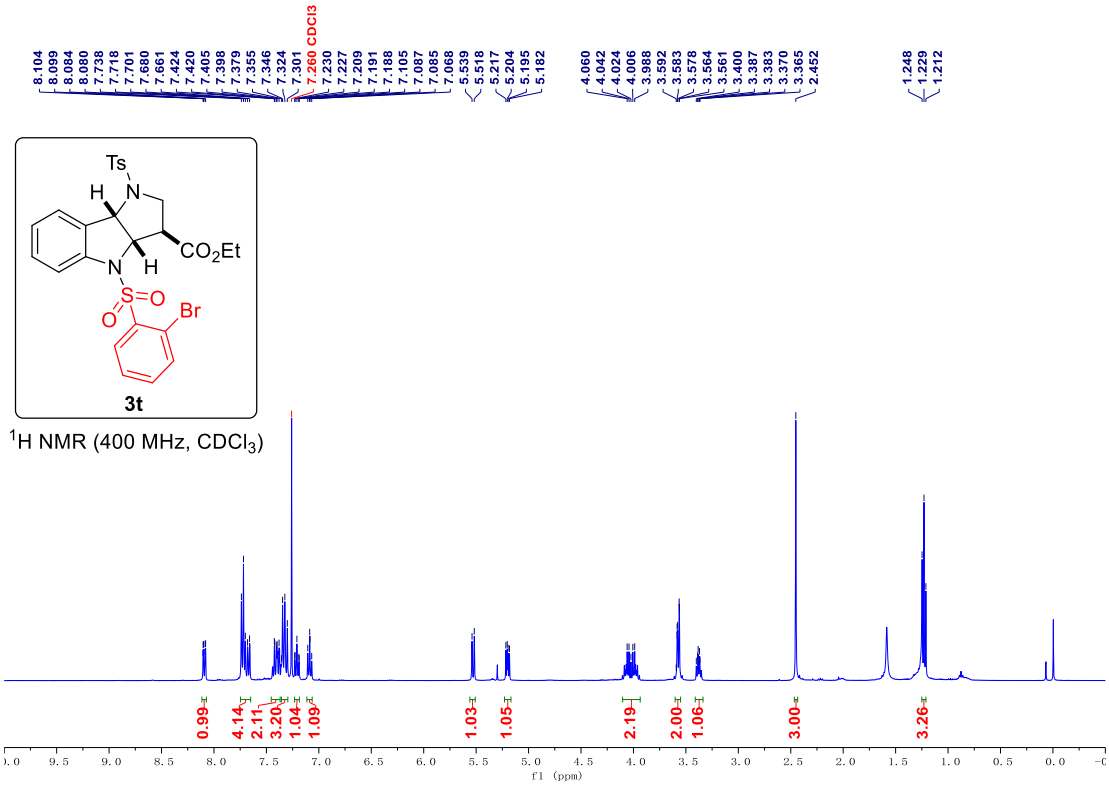
3s

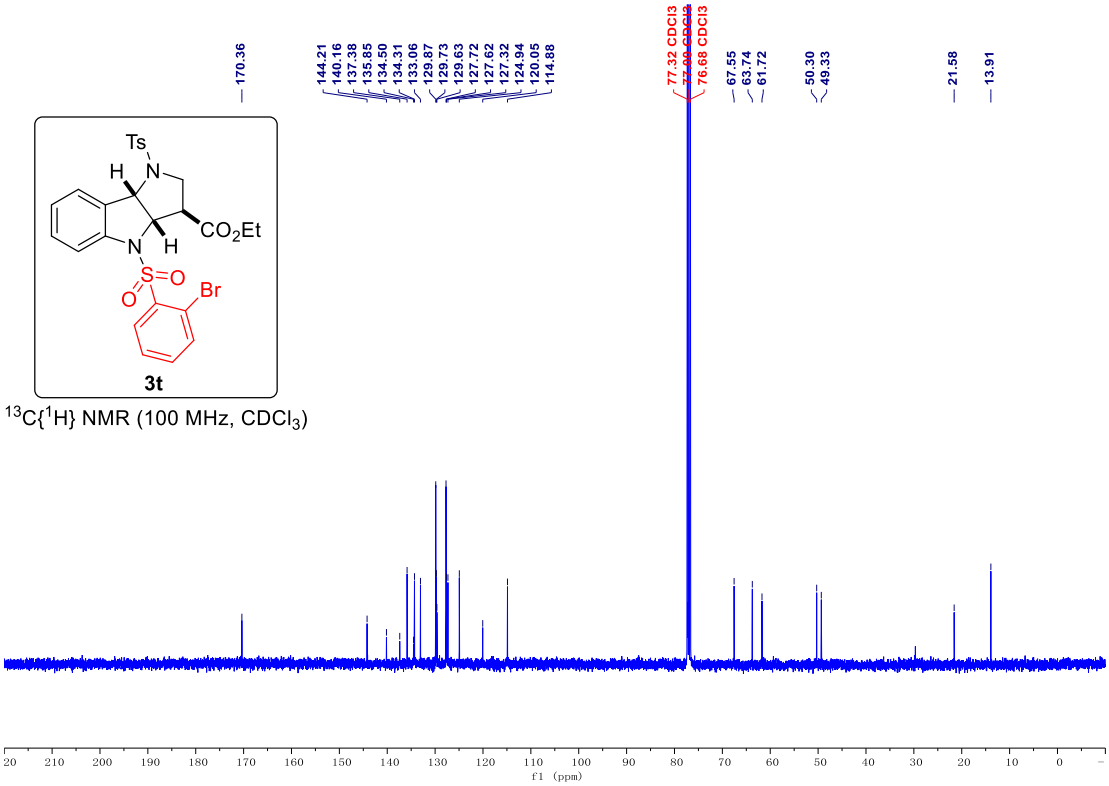
^{1}H NMR (400 MHz, $CDCl_3$)

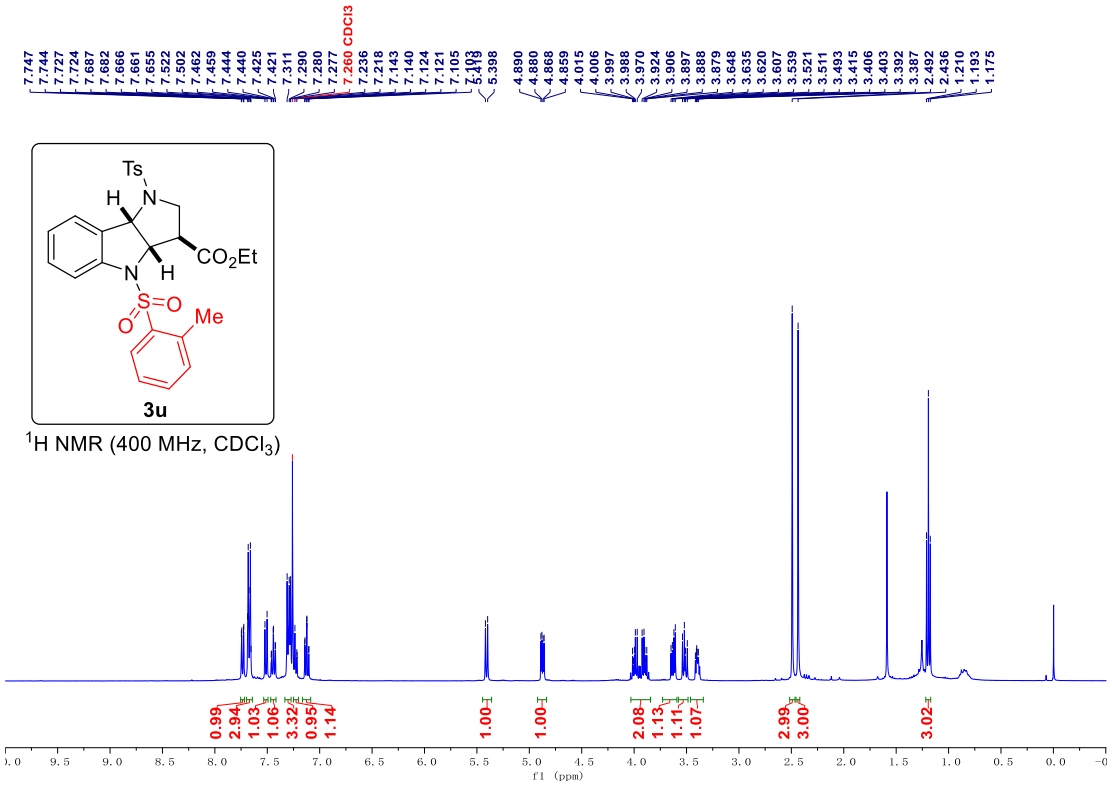


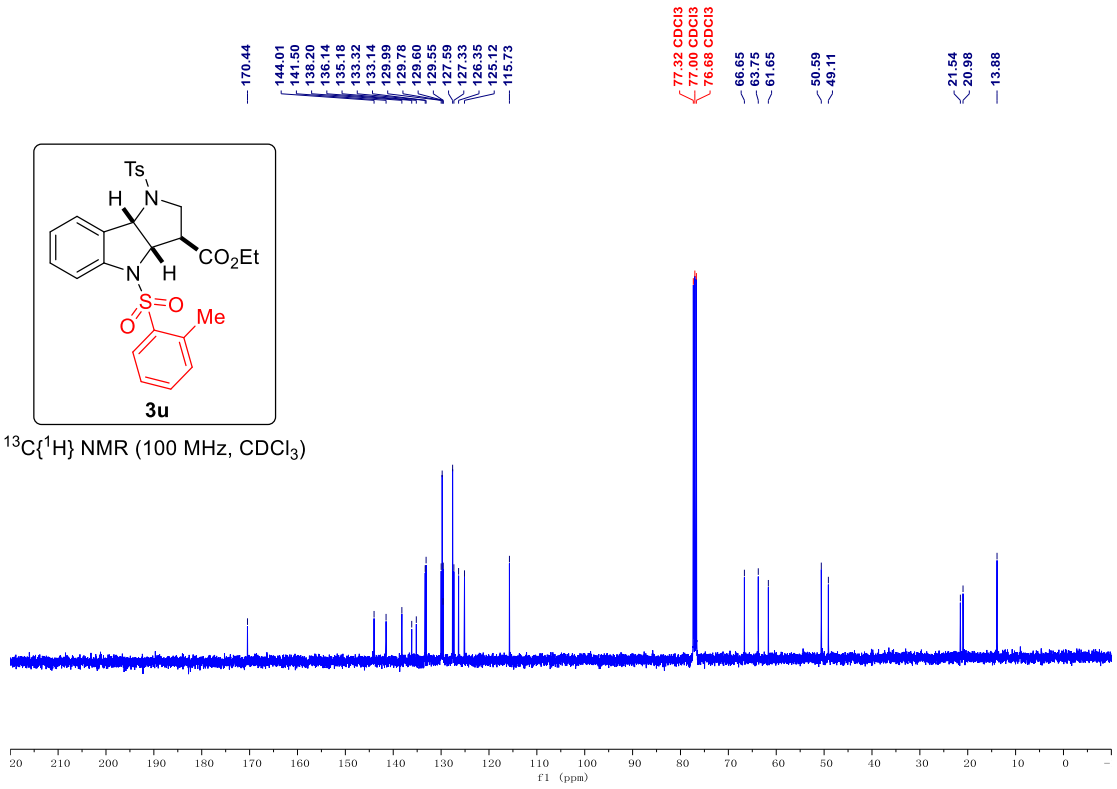
3s

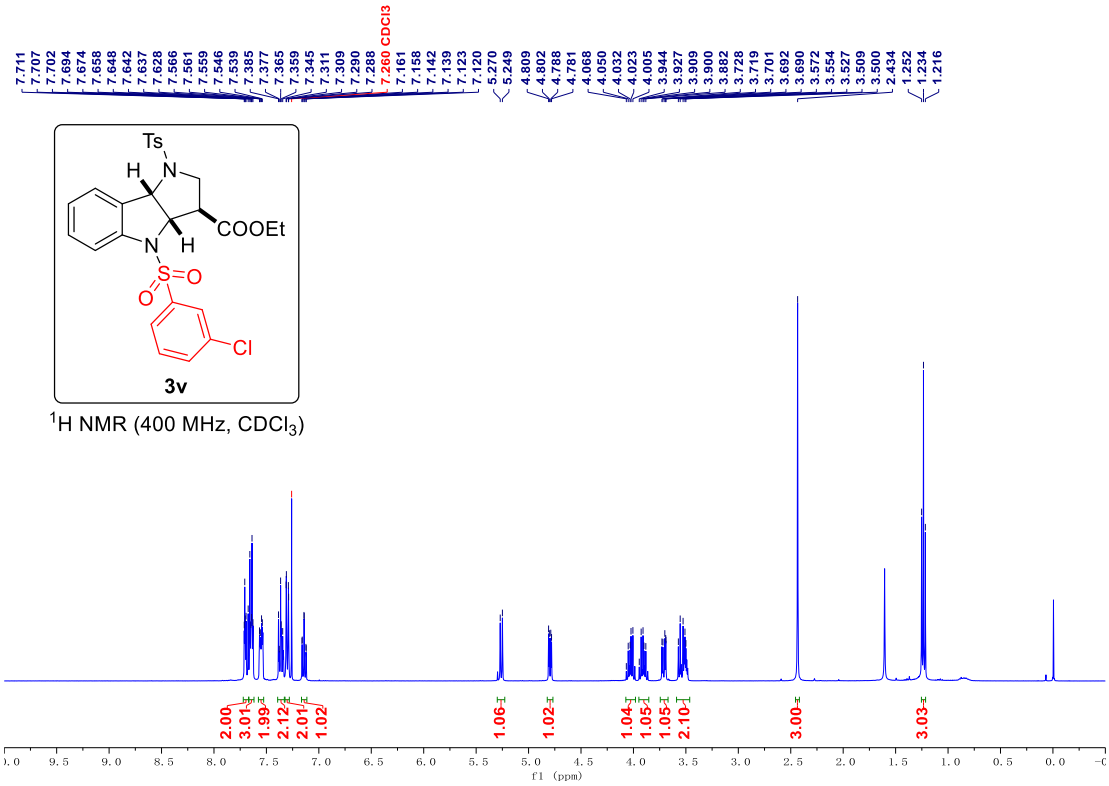
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)


8.104
8.099
8.084
8.080
7.738
7.718
7.701
7.680
7.661
7.424
7.420
7.405
7.398
7.379
7.355
7.346
7.324
7.301
7.260 CDCl3
7.230
7.227
7.209
7.191
7.188
7.105
7.087
7.085
7.068
5.539
5.518
5.217
5.204
5.195
5.182
4.060
4.042
4.024
4.006
3.988
3.592
3.583
3.578
3.564
3.561
3.400
3.387
3.383
3.370
3.365
2.452
1.248
1.229
1.212
Ts
H
N
CO2Et
N
H
S=O
O
Br
3t
1H NMR (400 MHz, CDCl3)
0.99
4.14
2.11
3.20
1.04
1.09
1.03
1.05
2.19
2.00
1.06
3.00
3.26
f1 (ppm)

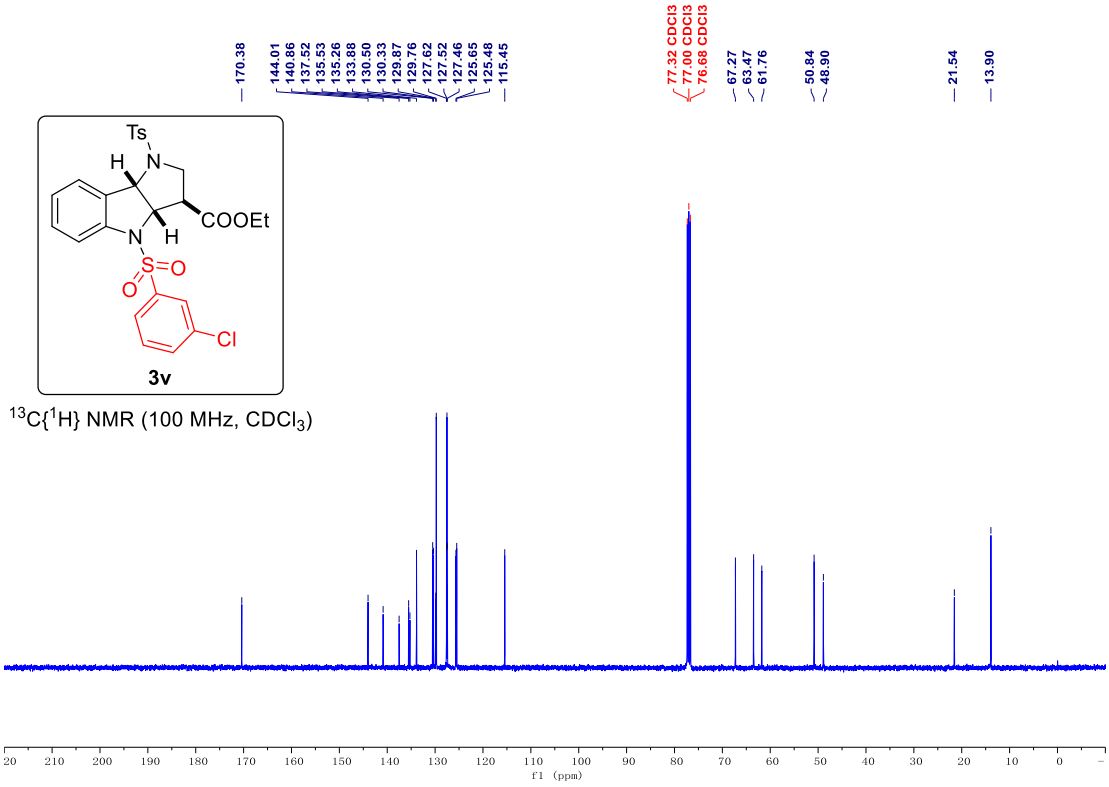

170.36
144.21
140.16
137.38
135.85
134.50
134.31
133.06
129.87
129.73
129.63
127.72
127.62
127.32
124.94
120.05
114.88
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
67.55
63.74
61.72
50.30
49.33
21.58
13.91
Ts
H
N
CO2Et
N
H
S=O
O
Br
3t
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)


7.747
7.744
7.727
7.724
7.687
7.682
7.666
7.661
7.655
7.522
7.502
7.462
7.459
7.444
7.440
7.425
7.421
7.311
7.290
7.280
7.277
7.260 CDCl3
7.236
7.218
7.143
7.140
7.124
7.121
7.105
5.398
4.890
4.880
4.868
4.859
4.015
4.006
3.997
3.988
3.970
3.924
3.906
3.897
3.888
3.879
3.648
3.635
3.620
3.607
3.539
3.521
3.511
3.493
3.415
3.406
3.403
3.392
3.387
2.492
2.436
1.210
1.193
1.175
Ts
H
N
CO2Et
N
H
S
O
O
Me
3u
1H NMR (400 MHz, CDCl3)
0.99
2.94
1.03
1.06
3.32
0.95
1.14
1.00
1.00
2.08
1.13
1.11
1.07
2.99
3.00
3.02
f1 (ppm)

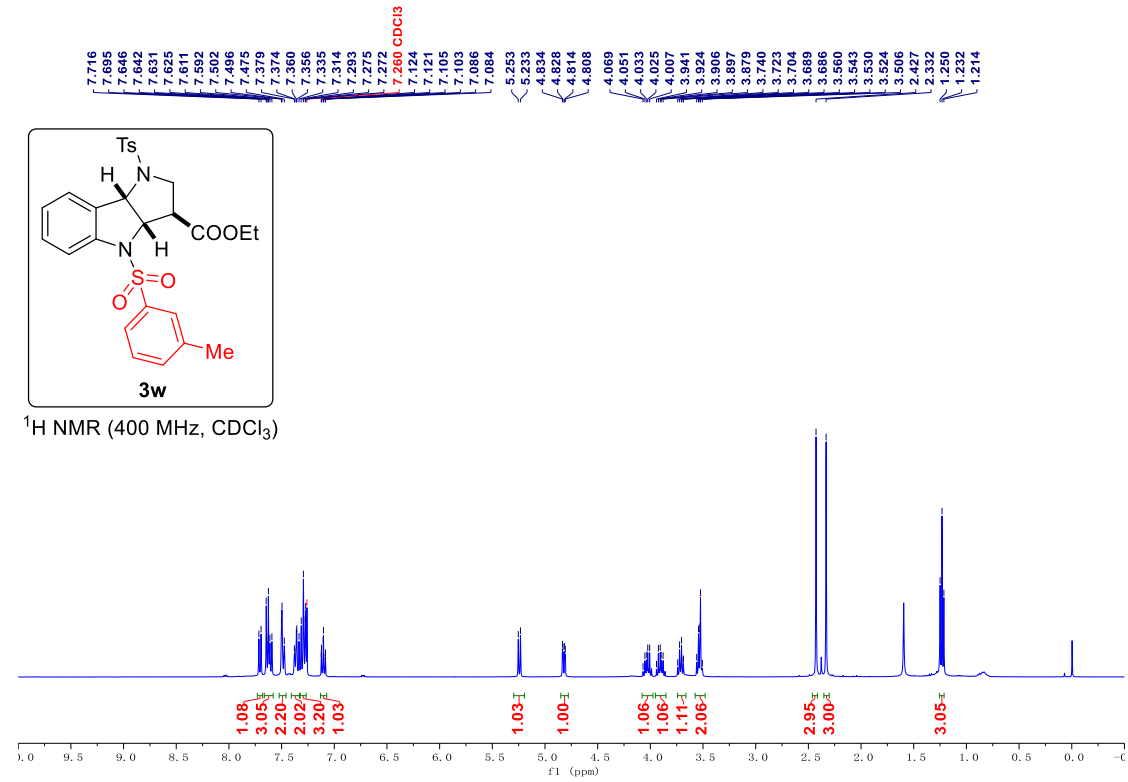

170.44
144.01
141.50
138.20
136.14
135.18
133.32
133.14
129.99
129.78
129.60
129.55
127.59
127.33
126.35
125.12
115.73
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
66.65
63.75
61.65
50.59
49.11
21.54
20.98
13.88
Ts
H
N
CO2Et
N
H
S
O
O
Me
3u
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)



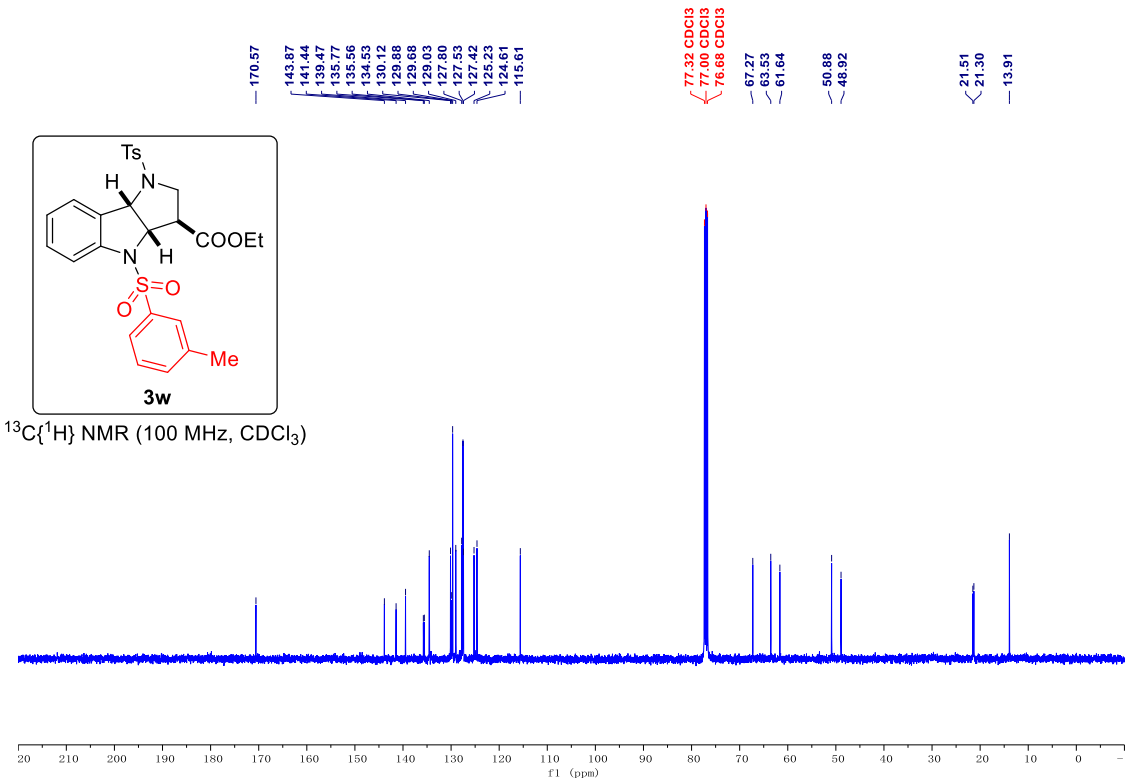
^{1}H NMR (400 MHz, $CDCl_3$)



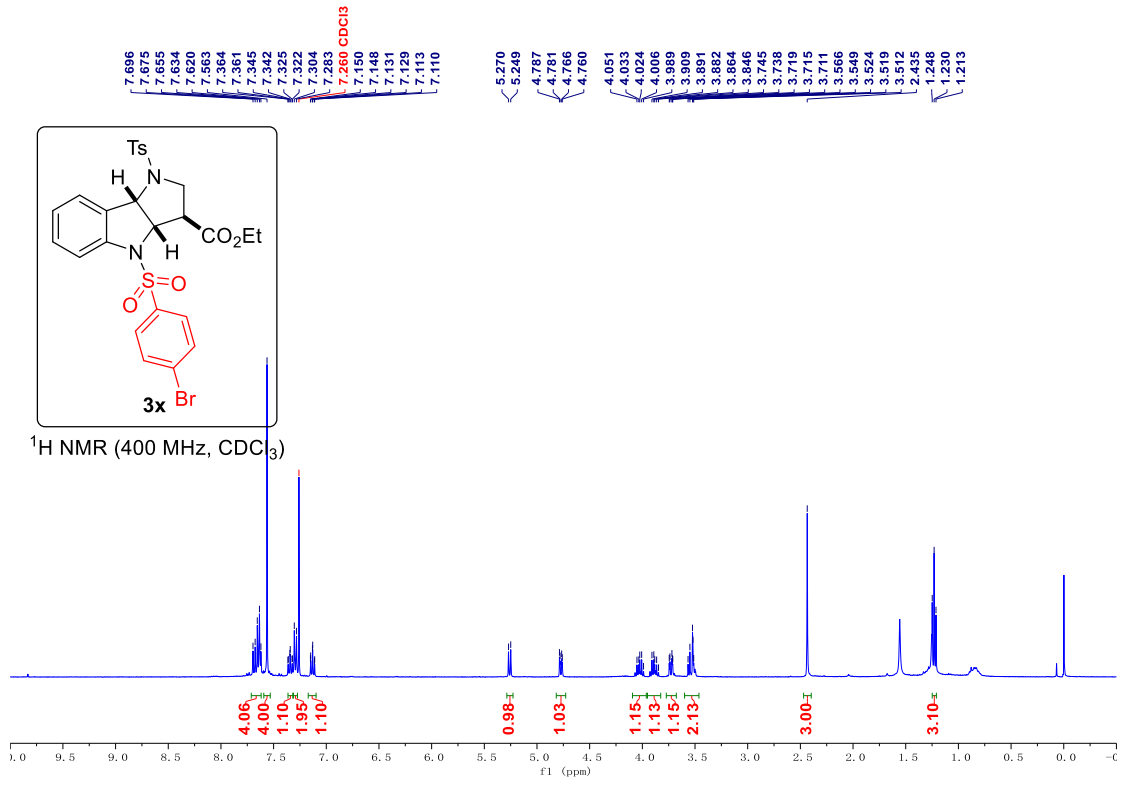
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



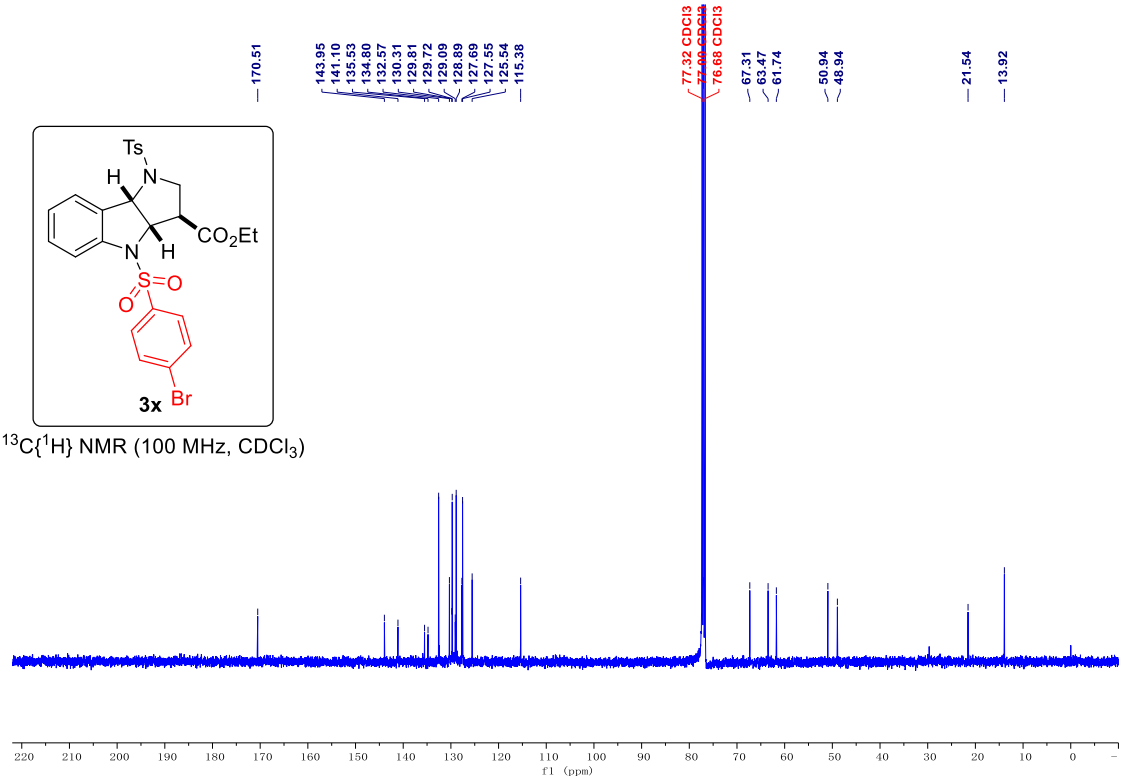
^{1}H NMR (400 MHz, $CDCl_3$)



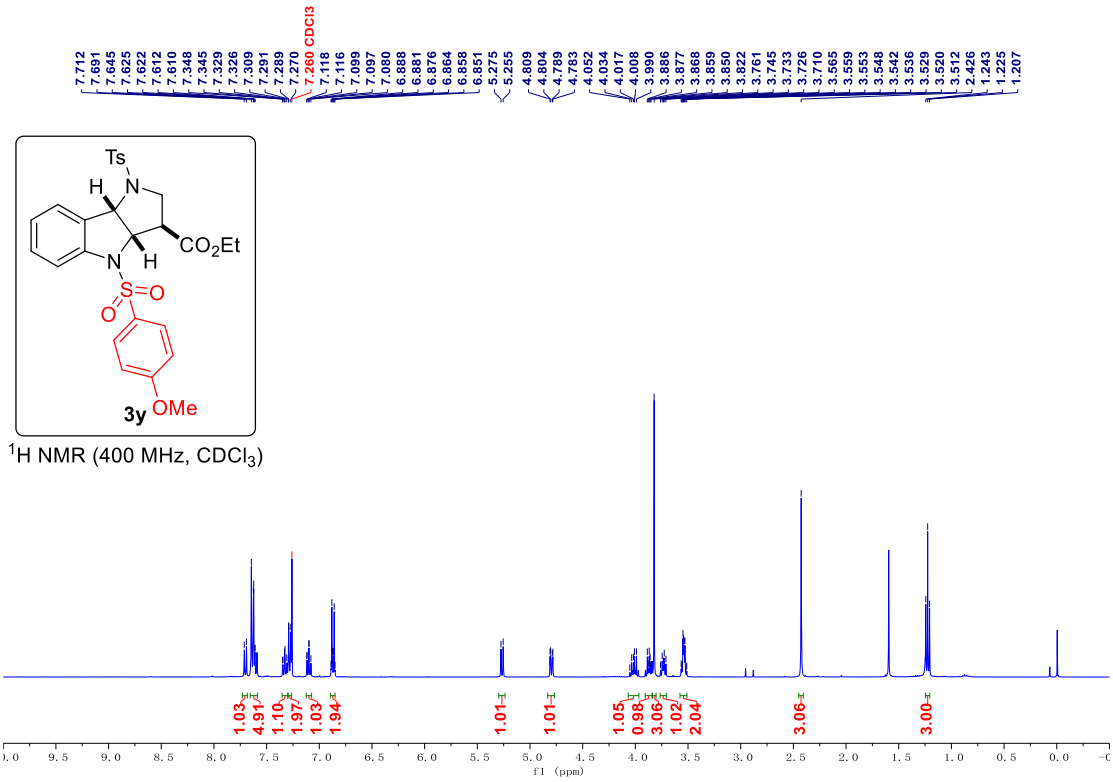
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

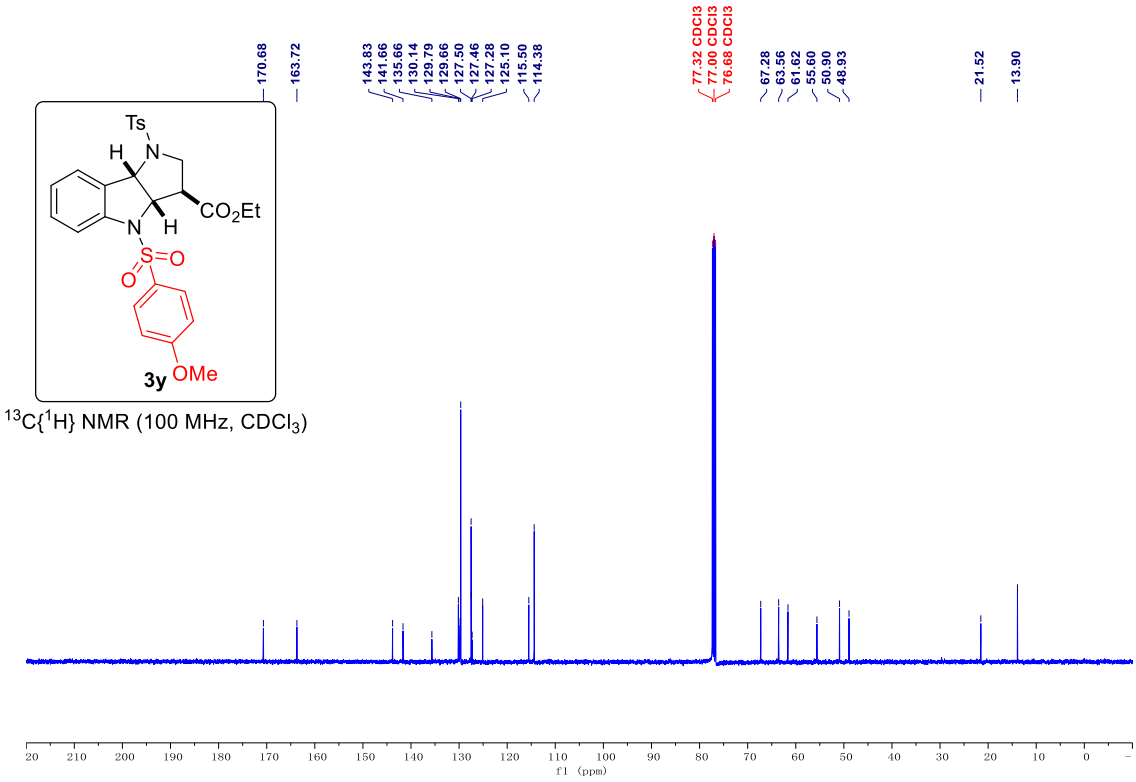


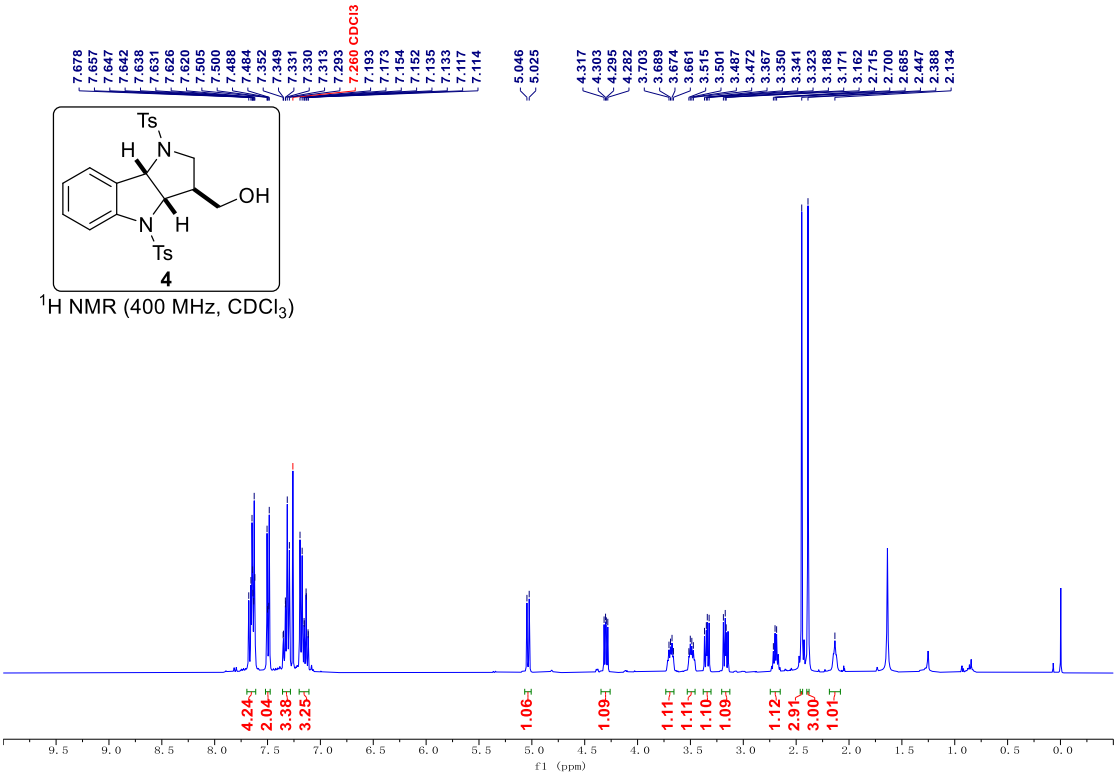
^{1}H NMR (400 MHz, $CDCl_3$)



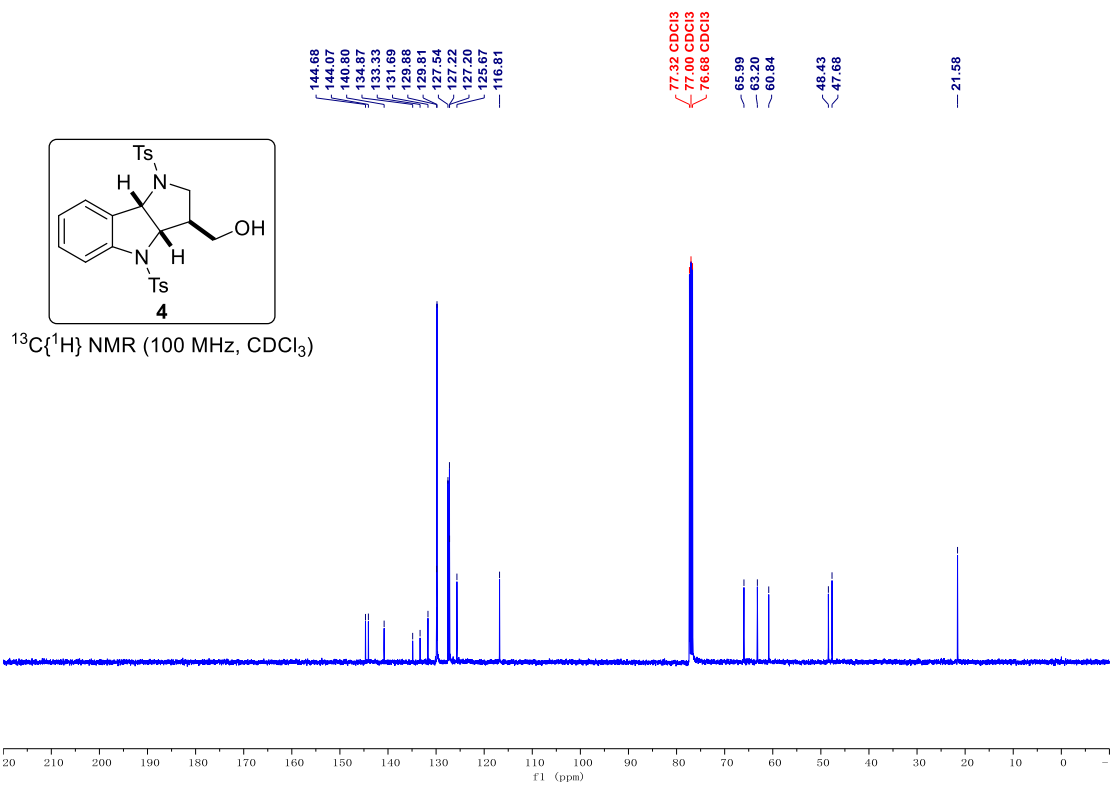
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)


7.712
7.691
7.645
7.625
7.622
7.612
7.610
7.348
7.345
7.329
7.326
7.309
7.291
7.289
7.270
7.260 CDCl3
7.118
7.116
7.099
7.097
7.080
6.888
6.881
6.876
6.864
6.858
6.851
5.275
5.255
4.809
4.804
4.789
4.783
4.052
4.034
4.017
4.008
3.990
3.886
3.877
3.868
3.859
3.850
3.822
3.761
3.745
3.733
3.726
3.710
3.565
3.559
3.553
3.548
3.542
3.536
3.529
3.520
3.512
2.426
1.243
1.225
1.207
Ts
H
N
CO2Et
N
H
S=O
O
3y OMe
1H NMR (400 MHz, CDCl3)
1.03
4.91
1.10
1.97
1.03
1.94
1.01
1.01
1.05
0.98
3.06
1.02
2.04
3.06
3.00
f1 (ppm)

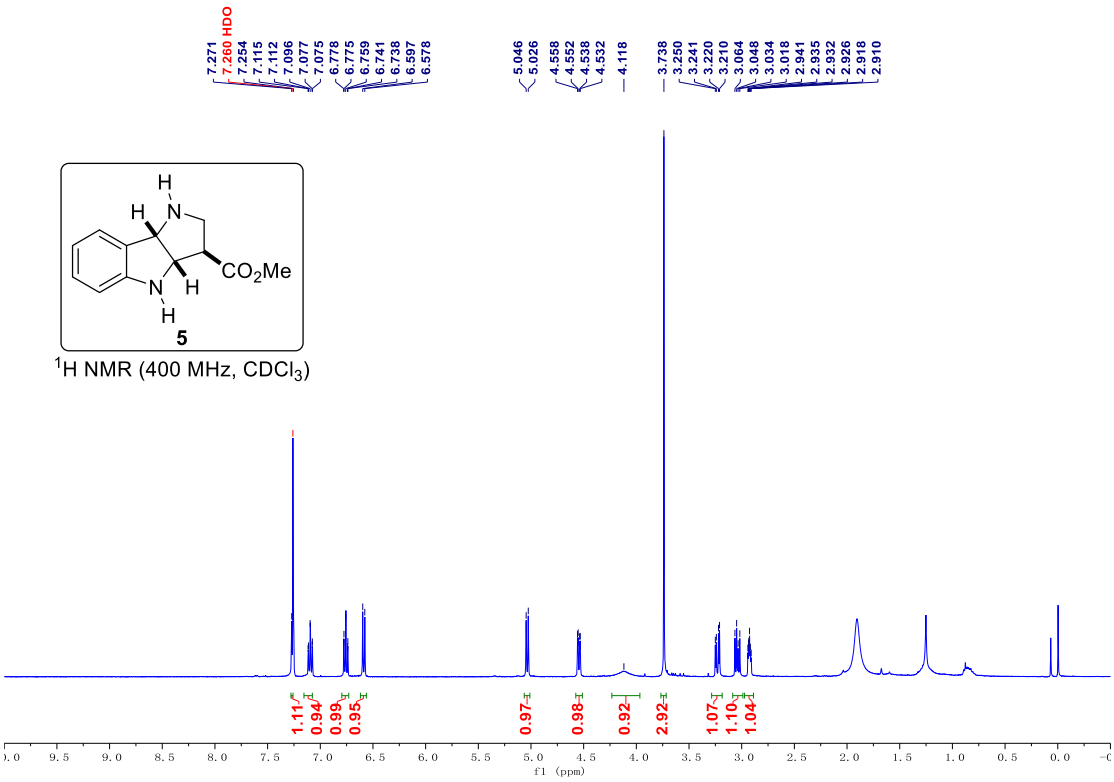

170.68
163.72
143.83
141.66
135.66
130.14
129.79
129.66
127.50
127.46
127.28
125.10
115.50
114.38
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
67.28
63.56
61.62
55.60
50.90
48.93
21.52
13.90
Ts
H
N
CO2Et
N
H
S=O
O
3y OMe
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)



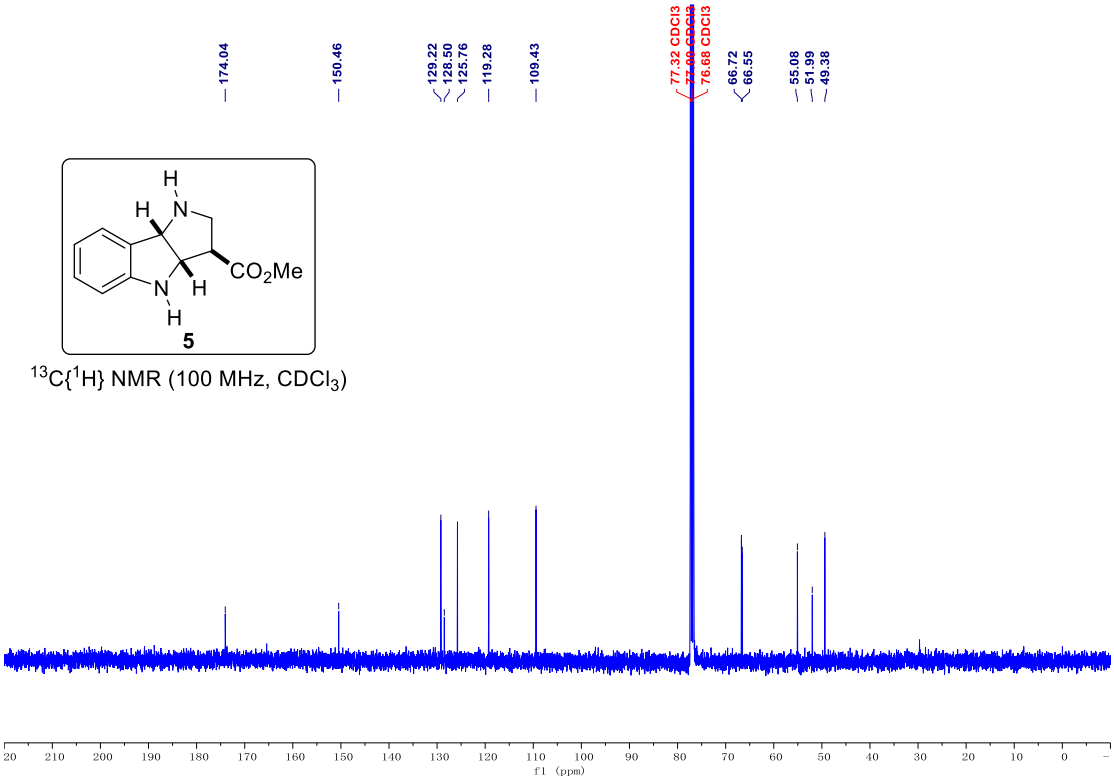
^{1}H NMR (400 MHz, $CDCl_3$)



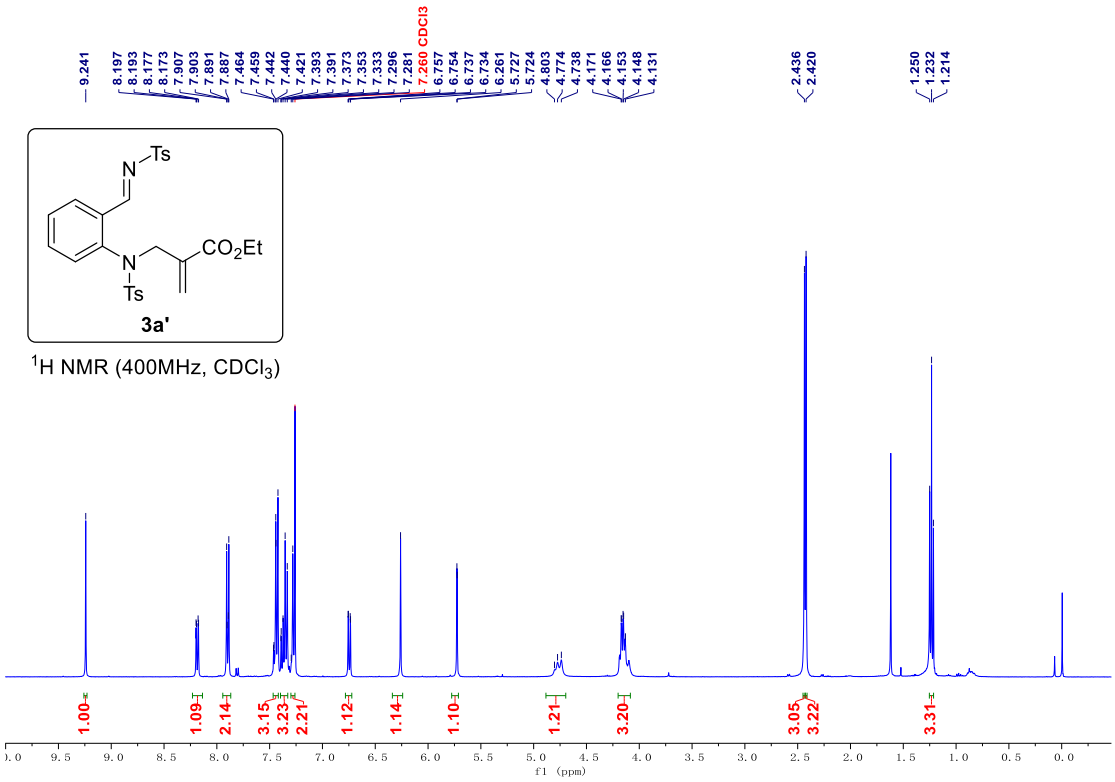
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

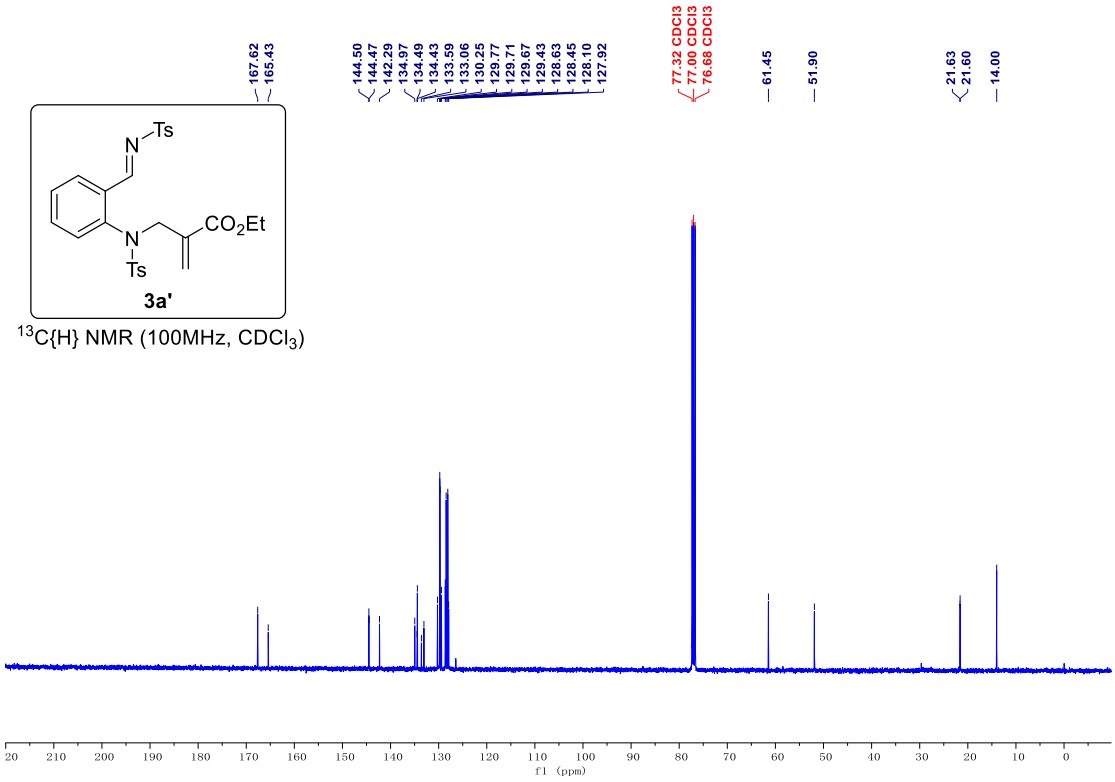


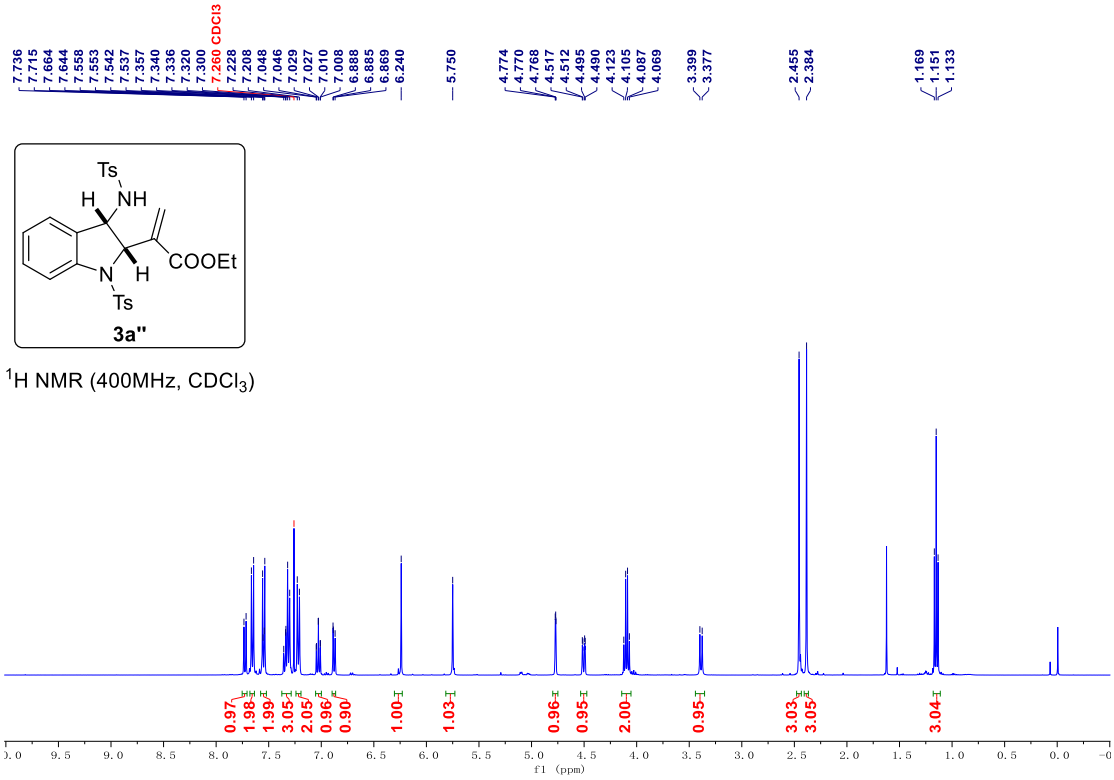
^{1}H NMR (400 MHz, $CDCl_3$)



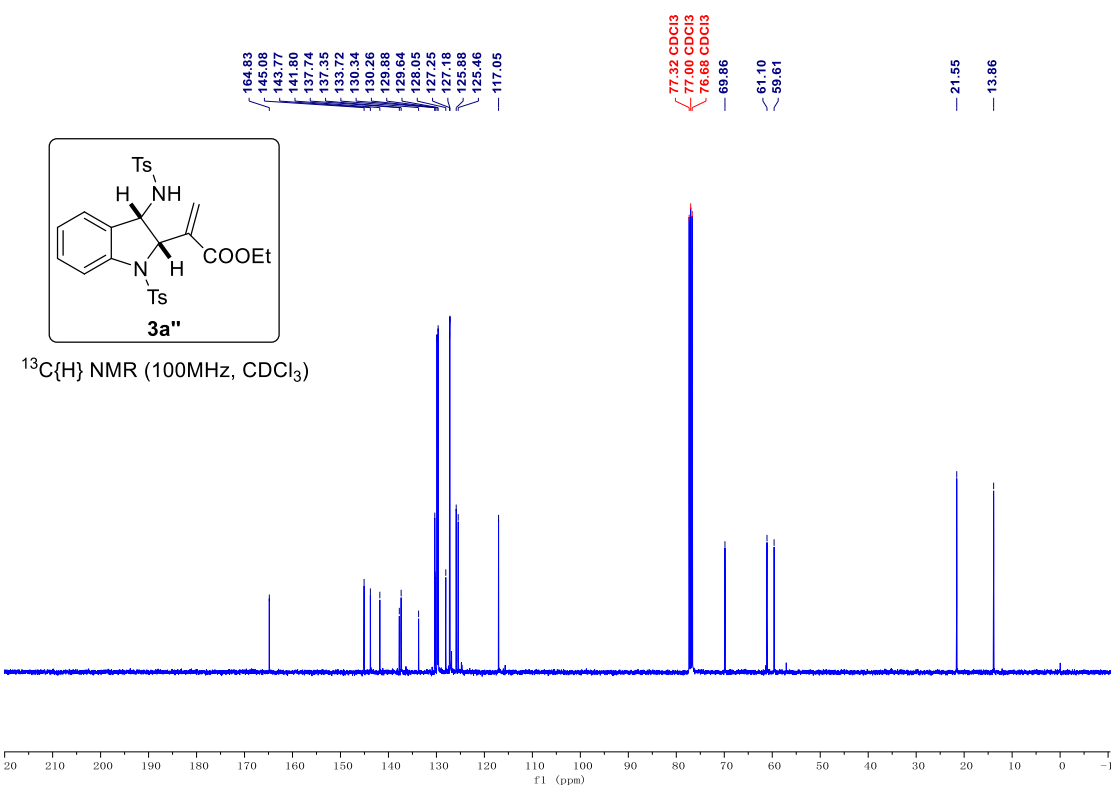
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)


9.241
8.197
8.193
8.177
8.173
7.907
7.903
7.891
7.887
7.464
7.459
7.442
7.440
7.421
7.393
7.391
7.373
7.353
7.333
7.296
7.281
7.260 CDCl3
6.757
6.754
6.737
6.734
6.261
5.727
5.724
4.803
4.774
4.738
4.171
4.166
4.153
4.148
4.131
2.436
2.420
1.250
1.232
1.214
Ts
N
CO2Et
N
Ts
3a'
1H NMR (400MHz, CDCl3)
1.00
1.09
2.14
3.15
3.23
2.21
1.12
1.14
1.10
1.21
3.20
3.05
3.22
3.31
f1 (ppm)

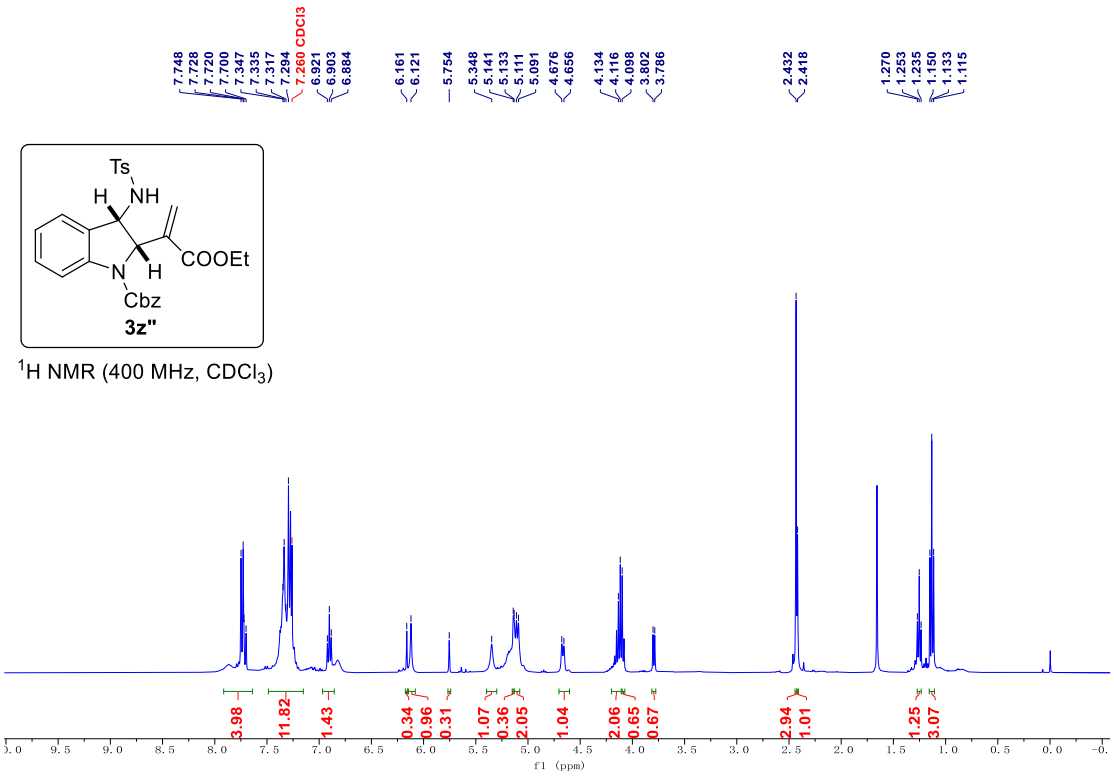

167.62
165.43
144.50
144.47
142.29
134.97
134.49
134.43
133.59
133.06
130.25
129.77
129.71
129.67
129.43
128.63
128.45
128.10
127.92
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
61.45
51.90
21.63
21.60
14.00
Ts
N
CO2Et
N
Ts
3a'
13C{H} NMR (100MHz, CDCl3)
f1 (ppm)



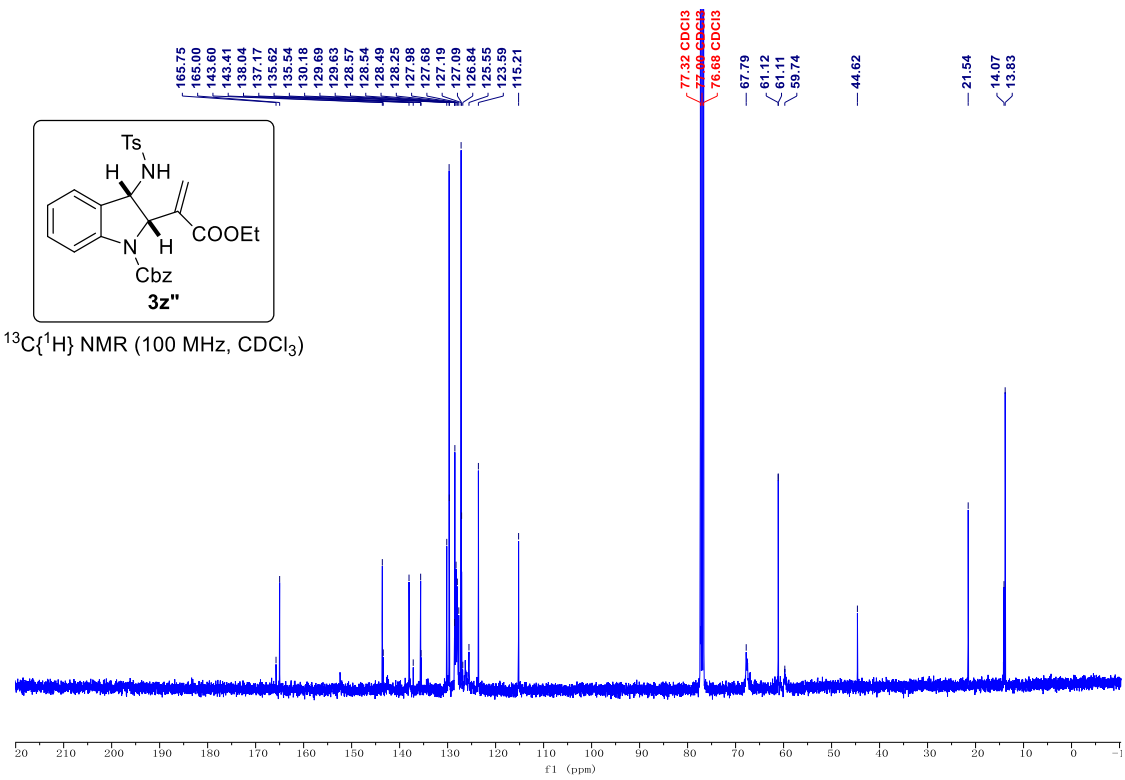
^{1}H NMR (400MHz, $CDCl_3$)



^{13}C{H} NMR (100MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)