

Supporting Information

Efficiently diastereoselective synthesis of functionalized hydrocarbazoles by base-mediated tandem annulation of 1-(2-aminoaryl)prop-2-en-1-ones and sulfur ylide

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Contents

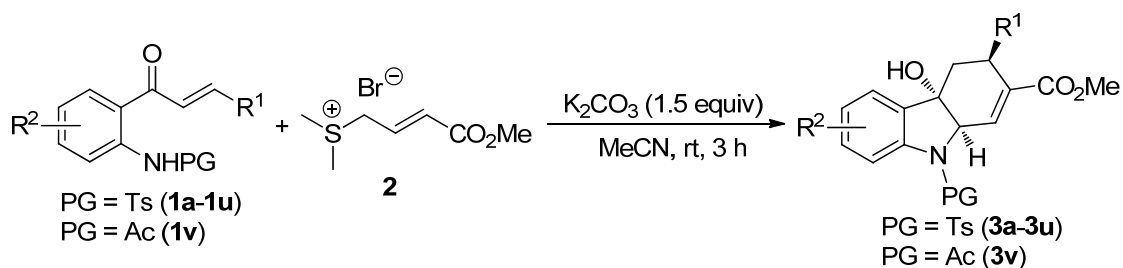
1. General information.....	S2
2. General procedure for base-promoted cascade annulation	S2
3. Synthetic transformations of compounds 3	S13
4. References.....	S16
5. NMR spectra of the compounds 3a–3v , 4 and 5a–5c	S17

1. General information

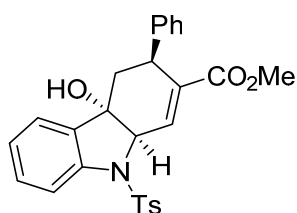
^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE III 400 spectrometer using tetramethylsilane (TMS) as internal reference, and chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. The HRMS analysis was obtained on a Bruker Apex II FT-ICR mass spectrometer with ESI ionization method. Melting points were determined on an XT-4 melting point apparatus and were uncorrected. All syntheses and manipulations were carried out under air. All solvents are commercially available analytically pure. Other chemicals were purchased from commercial suppliers and used directly. Flash column chromatography was carried out utilizing 200–300 mesh silica gel.

Tosyl-protected *o*-amino α,β -unsaturated ketones **1**¹ and (*E*)-(4-methoxy-4-oxobut-2-en-1-yl)dimethylsulfonium bromide (**2**)² were synthesized according to literature methods, respectively.

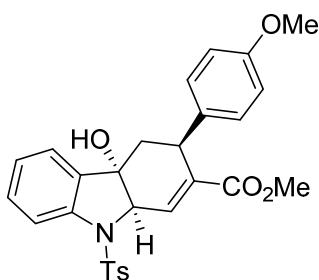
2. General procedure for base-promoted cascade annulation



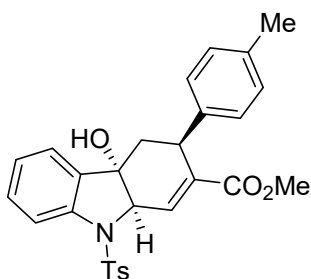
To a mixture of **1** (0.10 mmol) and (*E*)-(4-methoxy-4-oxobut-2-en-1-yl)dimethylsulfonium bromide (**2**) (0.15 mmol, 36 mg) in CH_3CN (1 mL), anhydrous potassium carbonate (0.15 mmol, 21 mg) was added at room temperature. The resulting mixture was stirred at room temperature for 3 h. The reaction mixture was passed through a short silica gel column, and eluted with ethyl acetate. The filtrate was concentrated and the residue was purified by flash column chromatography to afford desired products **3**.



methyl 4a-hydroxy-3-phenyl-9-tosyl-4,4a,9,9a-tetrahydro-3H-carbazole-2-carboxylate (3a). Yield 92%, white solid, mp 133.9–134.5 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.63 – 7.60 (m, 3H), 7.33 (d, *J* = 4.0 Hz, 1H), 7.19 – 7.12 (m, 3H), 6.92 – 6.83 (m, 3H), 6.57 – 6.49 (m, 3H), 6.21 (d, *J* = 7.6 Hz, 1H), 4.66 – 4.65 (m, 1H), 4.18 (t, *J* = 4.0 Hz, 1H), 3.64 (s, 3H), 2.51 – 2.50 (m, 2H), 2.32 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.20, 144.52, 141.95, 140.06, 137.30, 134.02, 133.80, 133.13, 129.94, 129.73, 127.69, 127.27, 126.93, 125.70, 124.78, 123.59, 117.04, 75.36, 69.19, 52.02, 38.82, 38.14, 21.51. HRMS (ESI): Exact Mass Calcd for C₂₇H₂₅NO₅SNa [M+Na]: 498.1346, Found: 498.1342.

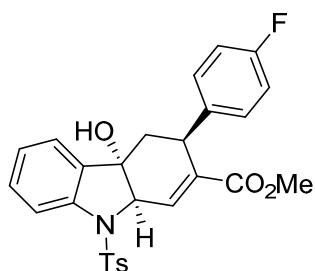


methyl 4a-hydroxy-3-(4-methoxyphenyl)-9-tosyl-4,4a,9,9a-tetrahydro-3H-carbazole-2-carboxylate (3b). Yield 86%, white solid, mp 156.9–157.2 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.64 – 7.60 (m, 3H), 7.31 – 7.30 (m, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.16 – 7.14 (m, 1H), 7.59 (td, *J* = 7.6 Hz, 0.8 Hz, 1H), 6.46 (d, *J* = 8.4 Hz, 2H), 6.38 (d, *J* = 8.8 Hz, 2H), 6.24 (dd, *J* = 8.0 Hz, 0.8 Hz, 1H), 4.65 (dd, *J* = 4.0, 1.2 Hz, 1H), 4.15 – 4.12 (m, 1H), 3.65 (s, 3H), 3.64 (s, 3H), 2.47 – 2.46 (m, 2H), 2.32 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.26, 157.59, 144.59, 139.95, 137.09, 134.09, 133.93, 133.84, 133.28, 129.98, 129.77, 127.83, 127.24, 124.80, 123.70, 117.10, 113.18, 75.34, 69.18, 55.21, 52.11, 38.14, 38.03, 21.58. HRMS (ESI): Exact Mass Calcd for C₂₈H₂₇NO₆SNa [M+Na]: 528.1451, Found: 528.1448.

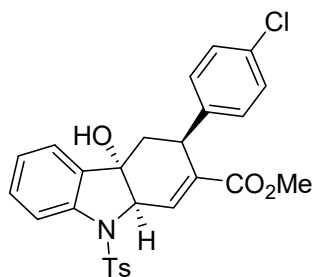


methyl 4a-hydroxy-3-(*p*-tolyl)-9-tosyl-4,4a,9,9a-tetrahydro-3H-carbazole-2-carboxylate (3c). Yield 84%, white solid, mp 139.7–140.0 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.63

– 7.59 (m, 3H), 7.30 (d, $J = 4.0$ Hz, 1H), 7.20 – 7.14 (m, 3H), 6.64 (d, $J = 7.6$ Hz, 2H), 6.52 (t, $J = 7.6$ Hz, 1H), 6.43 (d, $J = 8.0$ Hz, 2H), 6.21 (d, $J = 7.6$ Hz, 1H), 4.64 (d, $J = 3.6$ Hz, 1H), 4.14 (s, 1H), 3.64 (s, 3H), 2.48 – 2.47 (m, 2H), 2.32 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.27, 144.57, 139.99, 138.86, 137.13, 135.15, 133.86, 133.27, 129.88, 129.77, 128.37, 127.25, 126.74, 124.68, 123.69, 117.05, 75.40, 69.18, 52.10, 38.39, 38.18, 21.58, 20.85. HRMS (ESI): Exact Mass Calcd for $\text{C}_{28}\text{H}_{27}\text{NO}_5\text{SNa}$ [$\text{M}+\text{Na}$]: 512.1502, Found: 512.1498.

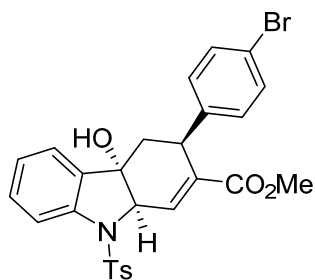


methyl 3-(4-fluorophenyl)-4a-hydroxy-9-tosyl-4,4a,9,9a-tetrahydro-3H-carbazole-2-carboxylate (3d). Yield 89%, white solid, mp 138.5–139.0 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.64 – 7.59 (m, 3H), 7.34 (d, $J = 4.0$ Hz, 1H), 7.20 – 7.16 (m, 3H), 6.60 (td, $J = 7.6, 0.8$ Hz, 1H), 6.57 – 6.49 (m, 4H), 6.23 (dd, $J = 7.6, 0.8$ Hz, 1H), 4.66 (dd, $J = 4.0, 1.2$ Hz, 1H), 4.16 (t, $J = 4.0$ Hz, 1H), 3.65 (s, 3H), 2.49 (d, $J = 4.4$ Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.08, 162.27, 159.85, 144.66, 140.06, 137.69, 133.79, 133.69, 132.85, 130.19, 129.79, 128.34, 128.26, 127.25, 124.87, 123.59, 117.18, 114.57, 114.35, 75.23, 69.13, 52.15, 38.14, 21.57. HRMS (ESI): Exact Mass Calcd for $\text{C}_{27}\text{H}_{24}\text{FNO}_5\text{SNa}$ [$\text{M}+\text{Na}$]: 516.1251, Found: 516.1246.

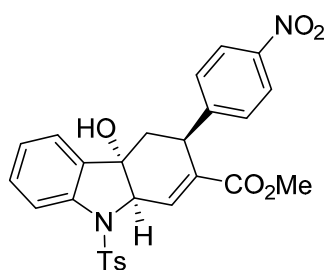


methyl 3-(4-chlorophenyl)-4a-hydroxy-9-tosyl-4,4a,9,9a-tetrahydro-3H-carbazole-2-carboxylate (3e). Yield 80%, white solid, mp 156.7–156.9 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.64 – 7.59 (m, 3H), 7.34 (d, $J = 4.0$ Hz, 1H), 7.22 – 7.18 (m, 3H), 6.81 (d, $J = 8.4$ Hz,

2H), 6.63 – 6.59 (m, 1H), 6.49 (d, $J = 8.0$ Hz, 2H), 6.23 (d, $J = 7.6$ Hz, 1H), 4.66 (dd, $J = 4.0, 0.8$ Hz, 1H), 4.15 – 4.14 (m, 1H), 3.65 (s, 3H), 2.49 – 2.48 (m, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.01, 144.67, 140.59, 140.09, 137.95, 133.77, 133.58, 132.55, 131.62, 130.23, 129.79, 128.21, 127.76, 127.25, 124.90, 123.61, 117.21, 75.23, 69.11, 52.18, 38.29, 38.05, 21.58. HRMS (ESI): Exact Mass Calcd for $\text{C}_{27}\text{H}_{24}\text{ClNO}_5\text{SNa}$ [$\text{M}+\text{Na}$]: 532.0956, Found: 532.0949.

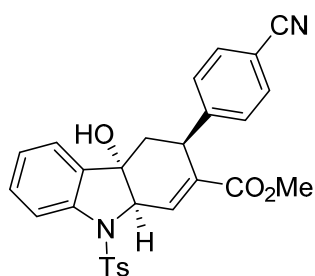


methyl 3-(4-bromophenyl)-4a-hydroxy-9-tosyl-4,4a,9,9a-tetrahydro-3H-carbazole-2-carboxylate (3f). Yield 93%, white solid, mp 180.5–180.9 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.64 – 7.59 (m, 3H), 7.34 (d, $J = 4.0$ Hz, 1H), 7.23 – 7.18 (m, 3H), 6.96 (d, $J = 8.4$ Hz, 2H), 6.61 (t, $J = 7.6$ Hz, 1H), 6.43 (d, $J = 8.4$ Hz, 2H), 6.23 (d, $J = 7.2$ Hz, 1H), 4.66 (dd, $J = 4.0, 0.8$ Hz, 1H), 4.14 – 4.12 (m, 1H), 3.65 (s, 3H), 2.49 – 2.48 (m, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.00, 144.67, 141.13, 140.08, 138.01, 133.76, 133.55, 132.47, 130.69, 130.22, 129.79, 128.60, 127.25, 124.94, 123.60, 119.73, 117.22, 75.22, 69.10, 52.19, 38.36, 38.02, 21.58. HRMS (ESI): Exact Mass Calcd for $\text{C}_{27}\text{H}_{24}\text{BrNO}_5\text{SNa}$ [$\text{M}+\text{Na}$]: 576.0451, Found: 576.0446.

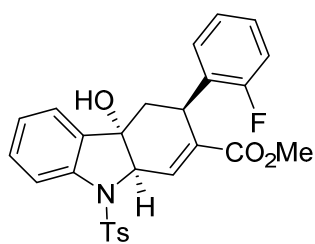


methyl 4a-hydroxy-3-(4-nitrophenyl)-9-tosyl-4,4a,9,9a-tetrahydro-3H-carbazole-2-carboxylate (3g). Yield 82%, white solid, mp 166.1–166.4 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.72 (d, $J = 8.4$ Hz, 2H), 7.65 (d, $J = 8.0$ Hz, 1H), 7.60 (d, $J = 8.0$ Hz, 2H), 7.44 (d, $J = 4.0$ Hz, 1H), 7.21 – 7.18 (m, 3H), 6.75 (d, $J = 8.0$ Hz, 2H), 6.50 (t, $J = 7.6$ Hz, 1H), 6.21 (d,

$J = 7.6$ Hz, 1H), 4.70 (d, $J = 4.0$ Hz, 1H), 4.26 – 4.25 (m, 1H), 3.67 (s, 3H), 2.61 – 2.51 (m, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.76, 150.00, 145.96, 144.84, 140.33, 138.91, 133.59, 133.26, 131.74, 129.85, 127.75, 127.25, 124.77, 123.45, 122.82, 117.42, 75.10, 69.00, 52.32, 38.90, 37.98, 21.59. HRMS (ESI): Exact Mass Calcd for $\text{C}_{27}\text{H}_{24}\text{N}_2\text{O}_7\text{SNa}$ [$\text{M}+\text{Na}$]: 543.1196, Found: 543.1193.

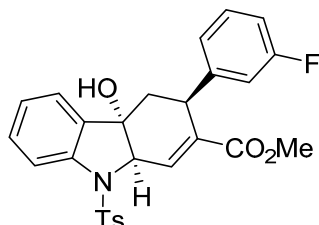


methyl 3-(4-cyanophenyl)-4a-hydroxy-9-tosyl-4,4a,9,9a-tetrahydro-3H-carbazole-2-carboxylate (3h). Yield 81%, white solid, mp 213.5–214.0 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.64 (d, $J = 8.0$ Hz, 1H), 7.60 (d, $J = 8.4$ Hz, 2H), 7.41 (d, $J = 4.0$ Hz, 1H), 7.23 – 7.19 (m, 3H), 7.15 (d, $J = 8.4$ Hz, 2H), 6.69 (d, $J = 8.0$ Hz, 2H), 6.56 (t, $J = 7.6$ Hz, 1H), 6.19 (d, $J = 7.6$ Hz, 1H), 4.69 (d, $J = 4.0$ Hz, 1H), 4.22 – 4.21 (m, 1H), 3.67 (s, 3H), 2.59 – 2.48 (m, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.78, 147.86, 144.79, 140.26, 138.80, 133.67, 133.29, 131.71, 131.45, 130.48, 129.82, 127.70, 127.25, 124.85, 123.43, 118.78, 117.32, 109.57, 75.09, 69.02, 52.26, 39.04, 37.89, 21.57. HRMS (ESI): Exact Mass Calcd for $\text{C}_{28}\text{H}_{24}\text{N}_2\text{O}_5\text{SNa}$ [$\text{M}+\text{Na}$]: 523.1298, Found: 523.1290.

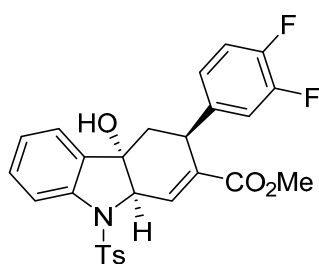


methyl 3-(2-fluorophenyl)-4a-hydroxy-9-tosyl-4,4a,9,9a-tetrahydro-3H-carbazole-2-carboxylate (3i). Yield 90%, white solid, mp 132.5–133.1 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.63 – 7.59 (m, 3H), 7.39 (d, $J = 4.0$ Hz, 1H), 7.19 (d, $J = 8.4$ Hz, 2H), 7.16 – 7.12 (m, 1H), 6.94 – 6.86 (m, 2H), 6.52 (t, $J = 7.6$ Hz, 1H), 6.32 – 6.29 (m, 2H), 5.92 (t, $J = 7.6$ Hz, 1H), 4.68 (d, $J = 4.4$ Hz, 1H), 4.42 (d, $J = 5.6$ Hz, 1H), 3.65 (s, 3H), 2.63 (dd, $J = 14.0, 1.2$ Hz, 1H), 2.42 (dd, $J = 14.0, 2.4$ Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.91,

161.23, 158.79, 144.63, 140.07, 138.48, 133.92, 133.83, 132.29, 130.16, 129.77, 128.81, 128.67, 128.11, 128.07, 127.59, 127.51, 124.90, 123.21, 123.11, 123.08, 117.14, 114.77, 114.55, 75.38, 69.01, 52.15, 35.37, 32.70, 32.68, 21.57. HRMS (ESI): Exact Mass Calcd for C₂₇H₂₄FNO₅SNa [M+Na]: 516.1251, Found: 516.1246.

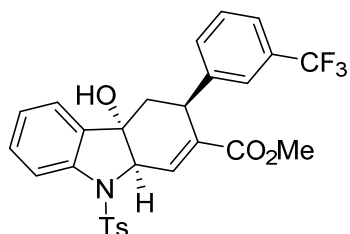


methyl 3-(3-fluorophenyl)-4a-hydroxy-9-tosyl-4,4a,9,9a-tetrahydro-3H-carbazole-2-carboxylate (3j). Yield 96%, white solid, mp 131.7–132.0 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.64 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 4.0 Hz, 1H), 7.20 – 7.15 (m, 3H), 6.85 – 6.80 (m, 1H), 6.64 – 6.56 (m, 2H), 6.38 (d, *J* = 7.6 Hz, 1H), 6.28 – 6.22 (m, 2H), 4.66 (dd, *J* = 4.0, 0.8 Hz, 1H), 4.16 (t, *J* = 4.0 Hz, 1H), 3.65 (s, 3H), 2.50 – 2.49 (m, 2H), 2.32 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.00, 163.64, 161.20, 144.65, 140.07, 137.97, 133.83, 133.66, 132.41, 130.31, 129.78, 129.15, 129.07, 127.26, 124.78, 123.47, 122.72, 122.70, 117.27, 114.14, 113.92, 112.87, 112.66, 75.20, 69.08, 52.17, 38.54, 37.98, 21.56. HRMS (ESI): Exact Mass Calcd for C₂₇H₂₄FNO₅SNa [M+Na]: 516.1251, Found: 516.1246.

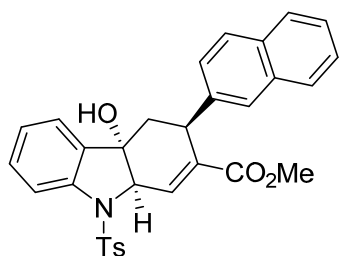


methyl 3-(3,4-difluorophenyl)-4a-hydroxy-9-tosyl-4,4a,9,9a-tetrahydro-3H-carbazole-2-carboxylate (3k). Yield 95%, white solid, mp 134.5–135.2 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 4.4 Hz, 1H), 7.28 – 7.22 (m, 3H), 6.72 – 6.65 (m, 2H), 6.39 – 6.33 (m, 3H), 4.70 (dd, *J* = 4.0, 0.8 Hz, 1H), 4.17 – 4.15 (m, 1H), 3.70 (s, 3H), 2.52 – 2.51 (m, 2H), 2.37 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 165.88, 144.72, 140.15, 138.24, 133.75, 133.65, 132.22, 130.49, 129.80, 127.25, 124.75,

123.46, 117.37, 116.40, 116.23, 116.00, 115.83, 75.10, 69.04, 52.22, 38.13, 38.07, 21.56. HRMS (ESI): Exact Mass Calcd for C₂₇H₂₃F₂NO₅SNa [M+Na]: 534.1157, Found: 534.1152.

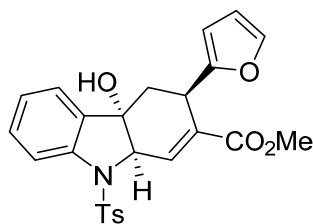


methyl 4a-hydroxy-9-tosyl-3-(3-(trifluoromethyl)phenyl)-4,4a,9,9a-tetrahydro-3H-carbazole-2-carboxylate (3l). Yield 93%, white solid, mp 166.6–167.3 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.64 – 7.59 (m, 3H), 7.40 (d, *J* = 4.0 Hz, 1H), 7.20 – 7.13 (m, 4H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.83 (s, 1H), 6.75 (d, *J* = 7.6 Hz, 1H), 6.51 (t, *J* = 7.6 Hz, 1H), 6.17 (d, *J* = 7.6 Hz, 1H), 4.68 (dd, *J* = 4.0, 1.2 Hz, 1H), 4.23 (t, *J* = 4.0 Hz, 1H), 3.67 (s, 3H), 2.54 (d, *J* = 4.4 Hz, 2H), 2.33 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 165.92, 144.70, 143.12, 140.09, 138.45, 133.77, 133.29, 132.12, 130.47, 130.28, 129.80, 128.20, 127.24, 124.82, 123.38, 117.35, 75.16, 69.06, 52.22, 38.64, 37.95, 21.57. HRMS (ESI): Exact Mass Calcd for C₂₈H₂₄F₃NO₅SNa [M+Na]: 566.1219, Found: 566.1215.

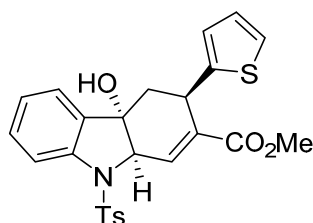


methyl 4a-hydroxy-3-(naphthalen-2-yl)-9-tosyl-4,4a,9,9a-tetrahydro-3H-carbazole-2-carboxylate (3m). Yield 95%, white solid, mp 102.6–103.0 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.65 – 7.59 (m, 4H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.42 (d, *J* = 4.0 Hz, 1H), 7.34 – 7.27 (m, 3H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.98 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.89 – 6.85 (m, 1H), 6.68 (s, 1H), 6.07 – 6.03 (m, 2H), 4.69 (dd, *J* = 4.0, 0.8 Hz, 1H), 4.33 – 4.32 (m, 1H), 3.63 (s, 3H), 2.60 – 2.50 (m, 2H), 2.31 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.17, 144.51, 139.98, 139.05, 137.56, 133.93, 133.85, 132.95, 132.82, 131.77, 130.17, 129.70, 127.79, 127.54, 127.24, 127.03, 125.77, 125.74, 125.44, 125.24, 124.35, 123.35, 116.97, 75.32,

69.23, 52.06, 39.01, 37.36, 21.49. HRMS (ESI): Exact Mass Calcd for C₃₁H₂₇NO₅SNa [M+Na]: 548.1502, Found: 548.1497.

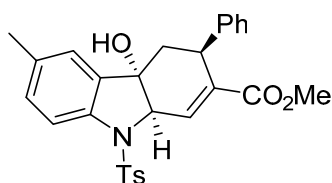


methyl 3-(furan-2-yl)-4a-hydroxy-9-tosyl-4,4a,9,9a-tetrahydro-3H-carbazole-2-carboxylate (3n). Yield 93%, white solid, mp 124.9–125.2 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.62 – 7.59 (m, 3H), 7.24 (dd, *J* = 4.0, 0.4 Hz, 1H), 7.21 – 7.16 (m, 3H), 7.05 (d, *J* = 1.6 Hz, 1H), 6.78 (td, *J* = 7.6, 0.8 Hz, 1H), 6.59 (dd, *J* = 7.6 Hz, *J* = 0.4 Hz, 1H), 5.72 (dd, *J* = 3.2, 2.0 Hz, 1H), 5.00 (dd, *J* = 2.4, 1.2 Hz, 1H), 4.65 (dd, *J* = 4.4, 1.2 Hz, 1H), 4.15 (d, *J* = 4.8 Hz, 1H), 3.71 (s, 3H), 2.78 (dd, *J* = 14.0, 2.4 Hz, 1H), 2.33 (s, 3H), 2.29 (dd, *J* = 14.0, 6.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 165.99, 153.97, 144.61, 140.36, 139.53, 137.76, 134.14, 133.86, 131.20, 130.05, 129.77, 127.23, 125.12, 122.75, 117.28, 110.20, 106.43, 75.36, 68.98, 52.22, 34.49, 33.00, 21.58. HRMS (ESI): Exact Mass Calcd for C₂₅H₂₃NO₆SNa [M+Na]: 488.1138, Found: 488.1133.

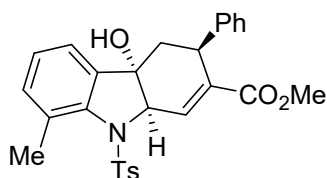


methyl 4a-hydroxy-3-(thiophen-2-yl)-9-tosyl-4,4a,9,9a-tetrahydro-3H-carbazole-2-carboxylate (3o). Yield 94%, white solid, mp 104.8–105.2 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.63 – 7.60 (m, 3H), 7.26 – 7.24 (m, 1H), 7.21 – 7.15 (m, 3H), 6.85 (dd, *J* = 5.2, 0.8 Hz, 1H), 6.67 (t, *J* = 7.6 Hz, 1H), 6.51 (d, *J* = 7.6 Hz, 1H), 6.35 (dd, *J* = 4.8, 3.6 Hz, 1H), 5.85 (d, *J* = 3.6 Hz, 1H), 4.65 (dd, *J* = 4.0, 0.8 Hz, 1H), 4.39 (d, *J* = 5.2 Hz, 1H), 3.68 (s, 3H), 2.61 (dd, *J* = 14.0, 2.0 Hz, 1H), 2.47 (dd, *J* = 14.0, 6.0 Hz, 1H), 2.33 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 165.96, 145.55, 144.59, 139.73, 136.92, 134.01, 133.91, 132.76, 130.05, 129.77, 127.25, 126.14, 124.92, 124.65, 123.49, 123.19, 117.12, 75.27, 68.98, 52.21,

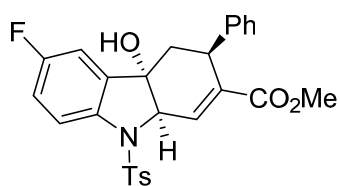
38.36, 34.28, 21.57. HRMS (ESI): Exact Mass Calcd for C₂₅H₂₃NO₅S₂Na [M+Na]: 504.0910, Found: 504.0906.



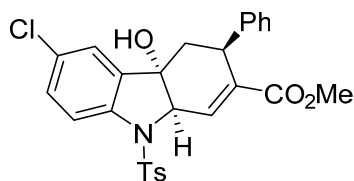
methyl 4a-hydroxy-6-methyl-3-phenyl-9-tosyl-4,4a,9,9a-tetrahydro-3H-carbazole-2-carboxylate (3q). Yield 91%, white solid, mp 68.6–69.3 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.59 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.31 (d, *J* = 4.0 Hz, 1H), 7.17 (d, *J* = 8.4 Hz, 2H), 6.93 – 6.83 (m, 4H), 6.56 (d, *J* = 7.2 Hz, 2H), 5.93 (s, 1H), 4.64 – 4.63 (m, 1H), 4.17 (s, 1H), 3.63 (s, 3H), 2.52 – 2.43 (m, 2H), 2.31 (s, 3H), 1.84 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.15, 144.34, 141.76, 137.71, 137.64, 134.66, 133.87, 133.63, 132.84, 130.77, 129.64, 127.36, 127.21, 126.84, 125.61, 124.28, 116.90, 75.32, 69.36, 51.96, 38.70, 37.99, 21.45, 20.45. HRMS (ESI): Exact Mass Calcd for C₂₈H₂₇NO₅SNa [M+Na]: 512.1502, Found: 512.1498.



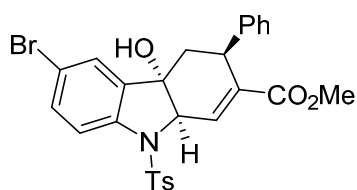
methyl 4a-hydroxy-8-methyl-3-phenyl-9-tosyl-4,4a,9,9a-tetrahydro-3H-carbazole-2-carboxylate (3r). Yield 89%, white solid, mp 132.5–132.7 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.01 – 6.98 (m, 2H), 6.90 – 6.87 (m, 1H), 6.83 – 6.79 (m, 2H), 6.46 (t, *J* = 7.6 Hz, 1H), 6.35 (d, *J* = 7.2 Hz, 2H), 6.09 (d, *J* = 7.2 Hz, 1H), 4.67 (d, *J* = 2.8 Hz, 1H), 4.09 (d, *J* = 6.0 Hz, 1H), 3.58 (s, 3H), 2.57 (s, 3H), 2.54 (s, 1H), 2.48 (dd, *J* = 13.6, 6.4 Hz, 1H), 2.40 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.20, 144.98, 142.06, 138.99, 137.29, 137.13, 133.93, 133.20, 132.33, 131.90, 129.88, 128.14, 127.68, 126.64, 126.50, 125.27, 121.59, 74.89, 69.72, 52.08, 38.47, 38.38, 21.66, 20.02. HRMS (ESI): Exact Mass Calcd for C₂₈H₂₇NO₅SNa [M+Na]: 512.1502, Found: 512.1498.



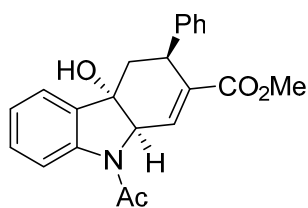
methyl 6-fluoro-4a-hydroxy-3-phenyl-9-tosyl-4,4a,9,9a-tetrahydro-3H-carbazole-2-carboxylate (3s). Yield 86%, white solid, mp 148.8–149.3 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.59 – 7.55 (m, 3H), 7.30 (d, J = 4.0 Hz, 1H), 7.21 (d, J = 8.4 Hz, 2H), 6.99 – 6.95 (m, 1H), 6.93 – 6.89 (m, 2H), 6.84 (td, J = 8.8, 2.8 Hz, 1H), 6.59 (d, J = 7.2 Hz, 2H), 5.84 (dd, J = 8.0, 2.8 Hz, 1H), 4.65 (dd, J = 4.0, 0.8 Hz, 1H), 4.19 (m, 1H), 3.65 (s, 3H), 2.51 – 2.43 (m, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.09, 161.33, 158.89, 144.80, 141.67, 137.21, 136.05, 136.03, 135.95, 135.87, 133.56, 133.09, 129.85, 127.76, 127.31, 126.78, 126.12, 118.64, 118.55, 117.30, 117.06, 110.77, 110.53, 75.31, 75.30, 69.57, 52.15, 38.57, 38.27, 21.57. HRMS (ESI): Exact Mass Calcd for $\text{C}_{27}\text{H}_{24}\text{FNO}_5\text{SNa}$ [$\text{M}+\text{Na}$]: 516.1251, Found: 516.1246.



methyl 6-chloro-4a-hydroxy-3-phenyl-9-tosyl-4,4a,9,9a-tetrahydro-3H-carbazole-2-carboxylate (3t). Yield 90%, white solid, mp 59.6–60.0 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.59 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.4 Hz, 1H), 7.30 (d, J = 4.0 Hz, 1H), 7.20 (d, J = 8.0 Hz, 2H), 7.07 (dd, J = 8.4, 2.4 Hz, 1H), 7.00 – 6.97 (m, 1H), 6.93 – 6.89 (m, 2H), 6.58 (d, J = 7.6 Hz, 2H), 6.09 (d, J = 2.0 Hz, 1H), 4.65 (d, J = 4.0, 1H), 4.18 (t, J = 4.0 Hz, 1H), 3.64 (s, 3H), 2.45 (d, J = 4.4 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.03, 144.73, 141.37, 138.61, 137.07, 135.44, 133.66, 133.15, 130.07, 129.79, 127.62, 127.19, 126.64, 126.34, 124.15, 118.01, 75.15, 69.39, 52.06, 38.51, 38.23, 21.48. HRMS (ESI): Exact Mass Calcd for $\text{C}_{27}\text{H}_{24}\text{ClNO}_5\text{SNa}$ [$\text{M}+\text{Na}$]: 532.0956, Found: 532.0949.



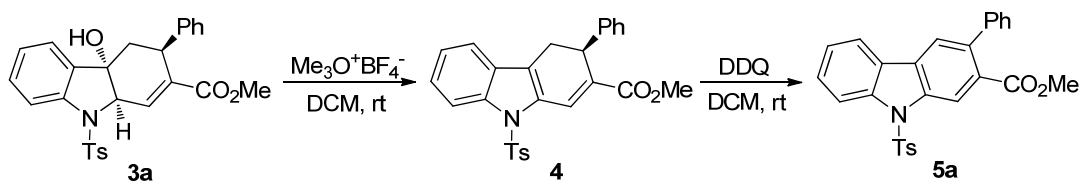
methyl 6-bromo-4a-hydroxy-3-phenyl-9-tosyl-4,4a,9,9a-tetrahydro-3H-carbazole-2-carboxylate (3u). Yield 80%, white solid, mp 155.9–156.1 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.60 (d, $J = 8.4$ Hz, 2H), 7.48 (d, $J = 8.8$ Hz, 1H), 7.30 (d, $J = 4.0$ Hz, 1H), 7.24 – 7.21 (m, 3H), 7.03 – 6.99 (m, 1H), 6.94 – 6.90 (m, 2H), 6.59 (d, $J = 7.2$ Hz, 2H), 6.24 (d, $J = 2.0$ Hz, 1H), 4.64 (d, $J = 3.6$ Hz, 1H), 4.20 (t, $J = 4.0$ Hz, 1H), 3.66 (s, 3H), 2.46 (d, $J = 4.4$ Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.07, 144.82, 141.35, 139.19, 137.10, 135.76, 133.75, 133.24, 133.02, 129.88, 127.71, 127.24, 126.68, 126.58, 118.49, 117.69, 75.21, 69.43, 52.13, 38.58, 38.24, 21.56. HRMS (ESI): Exact Mass Calcd for $\text{C}_{27}\text{H}_{24}\text{BrNO}_5\text{SNa}$ [$\text{M}+\text{Na}$]: 576.0451, Found: 576.0446.



methyl 9-acetyl-4a-hydroxy-3-phenyl-4,4a,9,9a-tetrahydro-3H-carbazole-2-carboxylate (3v). Yield 42%, white solid, mp 130.1–132.3 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.34 – 7.30 (m, 1H), 7.26 – 7.23 (m, 3H), 7.19 – 7.15 (m, 3H), 7.12 (t, $J = 2.4$ Hz, 1H), 7.08 – 7.06 (m, 2H), 4.79 (t, $J = 2.8$ Hz, 1H), 3.77 – 3.72 (m, 1H), 3.58 (s, 3H), 2.66 (dd, $J = 13.6, 6.0$ Hz, 1H), 1.99 – 1.94 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.65, 159.84, 143.15, 139.64, 139.28, 134.85, 129.40, 128.51, 127.20, 126.51, 126.31, 124.77, 124.35, 123.16, 82.03, 70.77, 51.88, 41.02, 40.82, 21.32. HRMS (ESI): Exact Mass Calcd for $\text{C}_{22}\text{H}_{21}\text{NO}_4\text{Na}$ [$\text{M}+\text{Na}$]: 386.1363, Found: 386.1357.

3. Synthetic transformations of compounds 3

Method A:



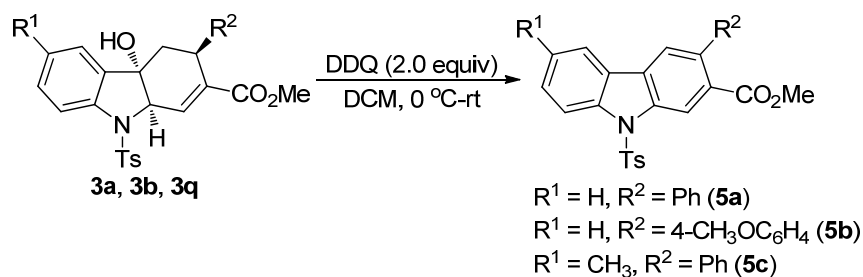
To a solution of compound **3a** (0.2 mmol, 95 mg) in DCM (2 mL), $\text{Me}_3\text{O}^+\text{BF}_4^-$ (0.22 mmol, 33 mg) was added. The reaction system was stirred for 5 h at room temperature (monitored by TLC). After the reaction was complete, the mixture was quenched with saturated sodium carbonate and the aqueous layer was extracted with DCM (10 mL \times 3). Then the organic phase was combined and dried over anhydrous MgSO_4 . The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 6:1) to give product **4** as a white solid.

methyl 3-phenyl-9-tosyl-4,9-dihydro-3H-carbazole-2-carboxylate (4). Yield 90%, mp 188.4–189.6 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.44 (s, 1H), 8.21 (d, J = 8.0 Hz, 1H), 7.65 (d, J = 8.4 Hz, 2H), 7.36 – 7.31 (m, 2H), 7.24 – 7.19 (m, 1H), 7.15 (d, J = 8.0 Hz, 2H), 7.12 – 7.08 (m, 1H), 7.03 – 6.96 (m, 4H), 4.32 (d, J = 9.2 Hz, 1H), 3.78 (s, 3H), 3.31 (dd, J = 17.6, 9.6 Hz, 1H), 3.12 (dd, J = 17.6, 1.2 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.03, 145.00, 142.43, 138.29, 135.24, 132.67, 130.57, 129.91, 129.01, 127.30, 126.93, 126.76, 126.65, 126.30, 124.20, 121.90, 119.72, 115.18, 52.09, 37.27, 28.08, 21.65. HRMS (ESI): Exact Mass Calcd for $\text{C}_{27}\text{H}_{24}\text{NO}_4\text{S}$ [M+H]: 458.1421, Found: 458.1417.

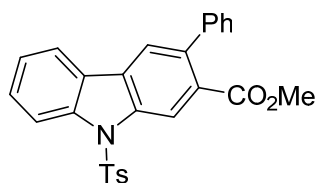
To a solution of compound **4** (0.1 mmol, 46 mg) in DCM (1 mL), DDQ (0.15 mmol, 34 mg) was added at 0 °C. The reaction mixture was warmed to room temperature and stirred for 2 h (monitored by TLC). After the reaction was complete, the mixture was quenched with saturated $\text{Na}_2\text{S}_2\text{O}_3$ and the aqueous layer was extracted with DCM (10 mL \times 3). Then the organic phase was combined and dried over anhydrous MgSO_4 . The solvent was removed under reduced pressure and the residue was purified by a silica gel column chromatography (petroleum ether/EtOAc = 6:1) to give product **5a** as a white solid.

methyl 3-phenyl-9-tosyl-9*H*-carbazole-2-carboxylate (5a). Yield 91%, mp 187.0–188.7 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.72 (s, 1H), 8.25 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.77 (s, 1H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.46 – 7.42 (m, 1H), 7.35 – 7.25 (m, 6H), 7.04 (d, *J* = 8.4 Hz, 2H), 3.64 (s, 3H), 2.17 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 167.74, 144.14 140.25, 138.48, 137.51, 135.86, 133.74, 128.84, 128.78, 127.50, 127.04, 126.19, 125.53, 124.36, 123.14, 120.95, 119.59, 115.49, 114.13, 51.19, 20.46. HRMS (ESI): Exact Mass Calcd for C₂₇H₂₂NO₄S [M+H]: 456.1264, Found: 456.1258.

Method B:

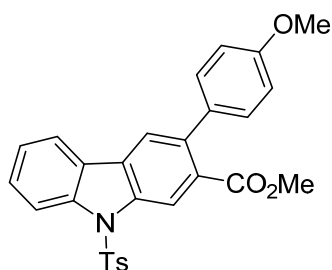


To a solution of compound **3** (0.1 mmol) in DCM (1 mL), DDQ (0.2 mmol, 45 mg) was added at 0 °C. The reaction mixture was warmed to room temperature and stirred for 36 h (monitored by TLC). After the reaction was complete, the mixture was quenched with saturated Na₂S₂O₃ and the aqueous layer was extracted with DCM (10 mL × 3). The organic phase was combined and dried over anhydrous MgSO₄. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 6:1) to give product **5** as a white solid.

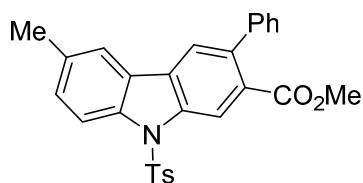


methyl 3-phenyl-9-tosyl-9*H*-carbazole-2-carboxylate (5a). Yield 75%, mp 187.0–188.7 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.81 (s, 1H), 8.35 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.87 (s, 1H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.57 – 7.53 (m, 1H), 7.45 – 7.36 (m, 6H), 7.15 (d, *J* = 8.0 Hz, 2H), 3.74 (s, 3H), 2.29 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 167.74, 144.14

140.25, 138.48, 137.51, 135.86, 133.74, 128.84, 128.78, 127.50, 127.04, 126.19, 125.53, 124.36, 123.14, 120.95, 119.59, 115.49, 114.13, 51.19, 20.46. HRMS (ESI): Exact Mass Calcd for C₂₇H₂₂NO₄S [M+H]: 456.1264, Found: 456.1258.



methyl 3-(4-methoxyphenyl)-9-tosyl-9H-carbazole-2-carboxylate (5b). Yield 67%, mp 196.0–196.8 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.77 (s, 1H), 8.34 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 7.6 Hz, 1H), 7.85 (s, 1H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.56 – 7.52 (m, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 8.8 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 3.85 (s, 3H), 3.77 (s, 3H), 2.28 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.98, 158.94, 145.14, 139.49, 138.11, 136.67, 134.74, 133.55, 129.87, 129.80, 129.60, 128.53, 128.46, 126.55, 125.45, 124.14, 121.95, 120.59, 116.44, 115.17, 113.57, 55.23, 52.29, 21.51. HRMS (ESI): Exact Mass Calcd for C₂₈H₂₄NO₅S [M+H]: 486.1370, Found: 486.1371.



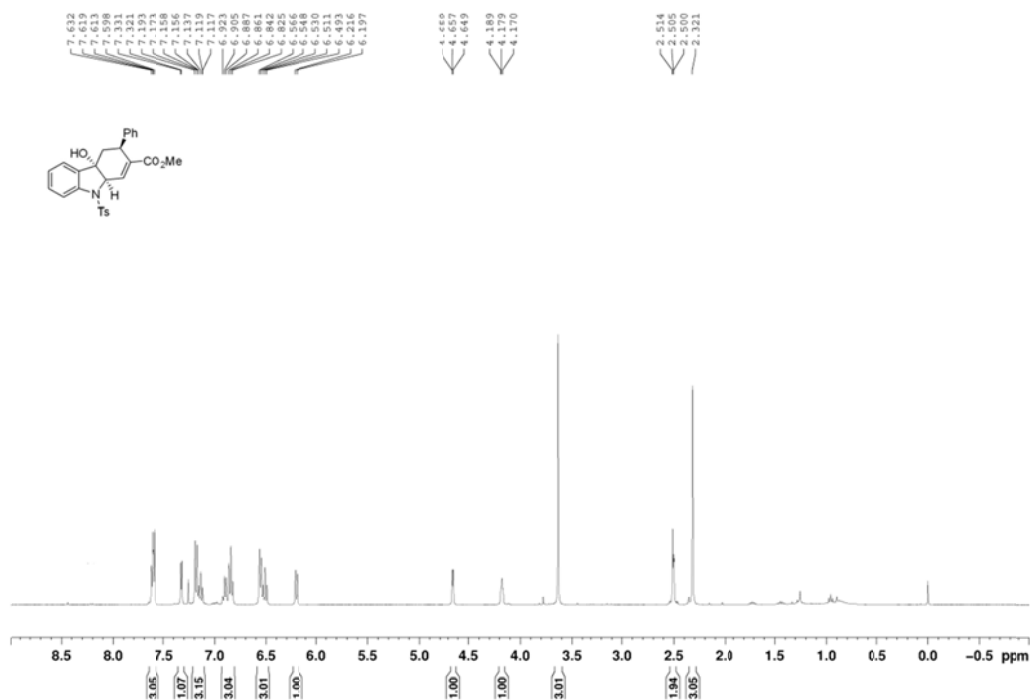
methyl 6-methyl-3-phenyl-9-tosyl-9H-carbazole-2-carboxylate (5c). Yield 56%, mp 104.2–105.1 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.78 (s, 1H), 8.21 (d, *J* = 8.4 Hz, 1H), 7.83 (s, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.70 (s, 1H), 7.44 – 7.35 (m, 6H), 7.14 (d, *J* = 8.4 Hz, 2H), 3.73 (s, 3H), 2.47 (s, 3H), 2.29 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.81, 145.03, 141.32, 138.45, 137.66, 137.11, 134.72, 133.98, 129.76, 129.65, 128.61, 128.49, 128.05, 127.17, 126.54, 125.56, 121.89, 120.63, 116.56, 114.89, 52.21, 21.49, 21.22. HRMS (ESI): Exact Mass Calcd for C₂₈H₂₄NO₄S [M+H]: 470.1421, Found: 470.1423.

4. References

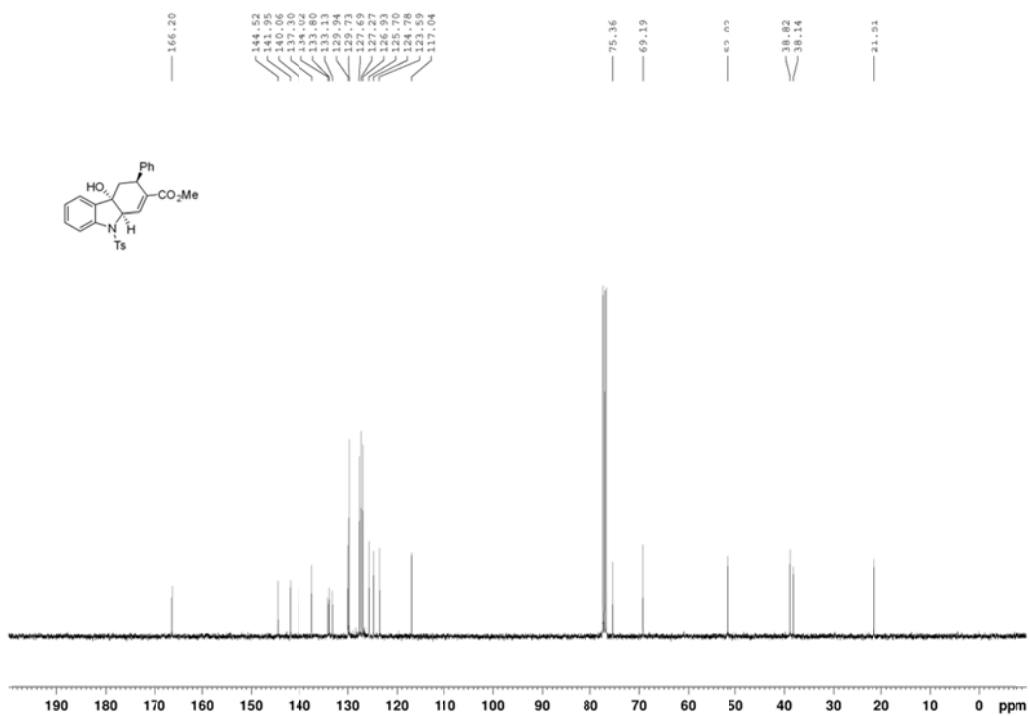
- [1] Z. Wang, X. Xu, Z. Gu, W. Feng, H. Qian, Z. Li, X. Sun, O. Kwon, *Chem. Commun.* **2016**, 52, 2811–2814.
- [2] Q.-G. Wang, X.-M. Deng, B.-H. Zhu, L.-W. Ye, X.-L. Sun, C.-Y. Li, C.-Y. Zhu, Q. Shen, Y. Tang, *J. Am. Chem. Soc.* **2008**, 130, 5408–5409.

5. NMR spectra of the compounds 3a–3v, 4 and 5a–5c

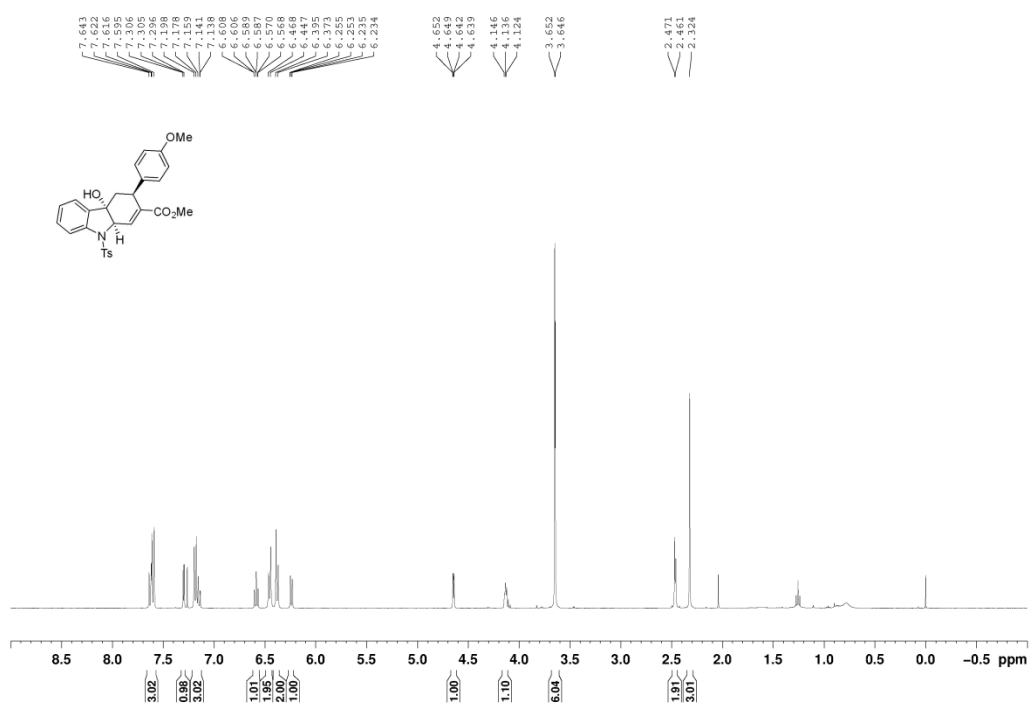
^1H NMR spectrum of compound **3a** (CDCl_3 , 400 MHz)



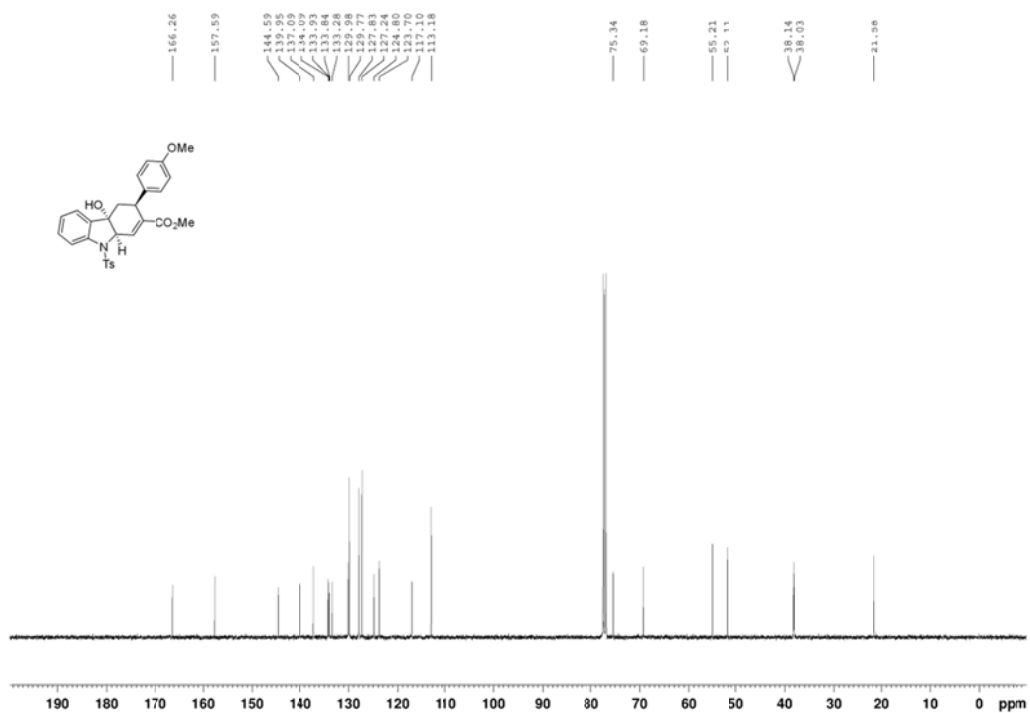
^{13}C NMR spectrum of compound **3a** (CDCl_3 , 100 MHz)



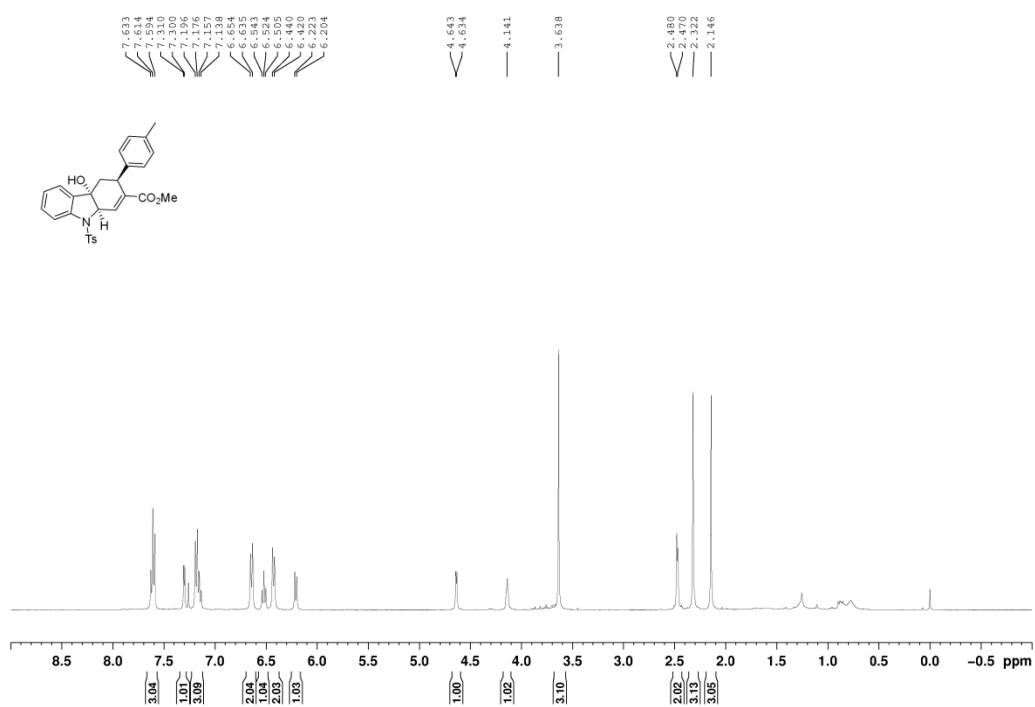
¹H NMR spectrum of compound **3b** (CDCl₃, 400 MHz)



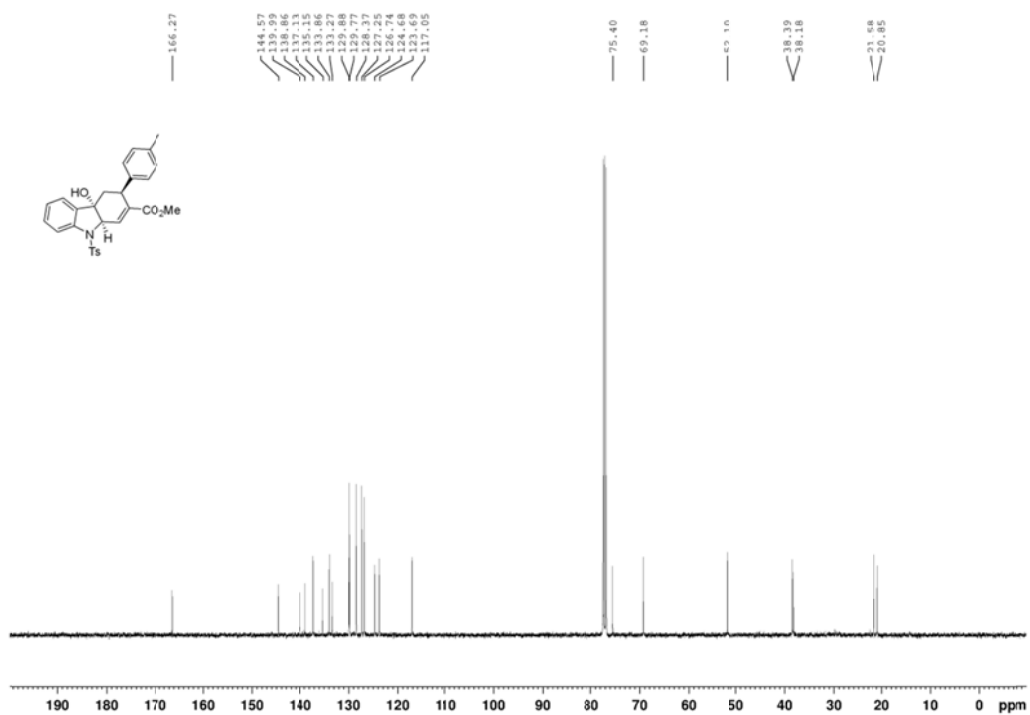
¹³C NMR spectrum of compound **3b** (CDCl₃, 100 MHz)



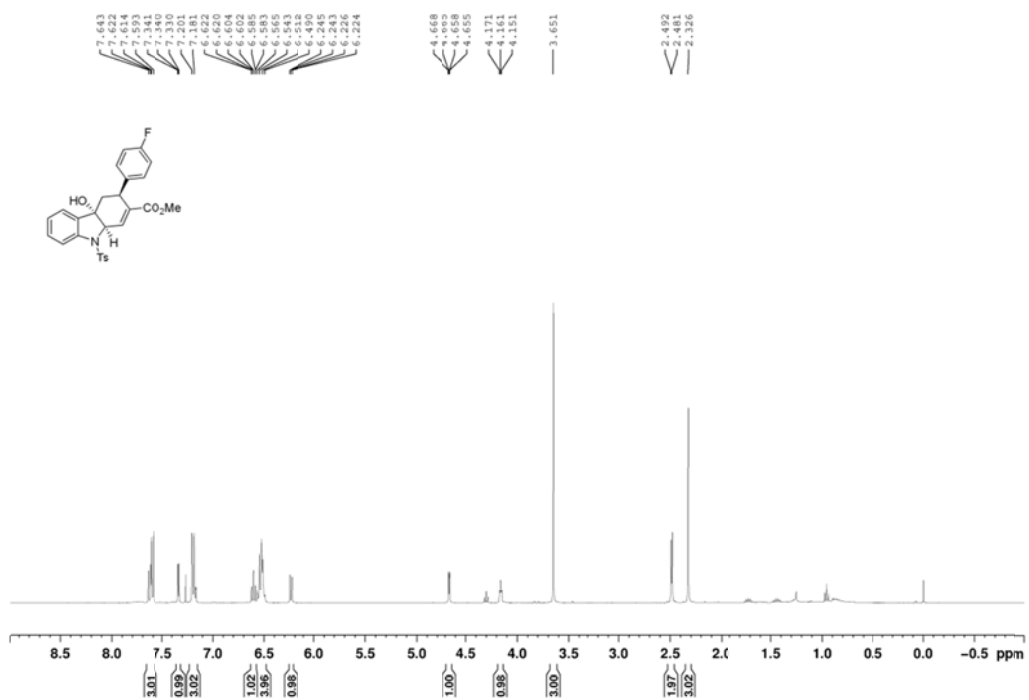
¹H NMR spectrum of compound **3c** (CDCl₃, 400 MHz)



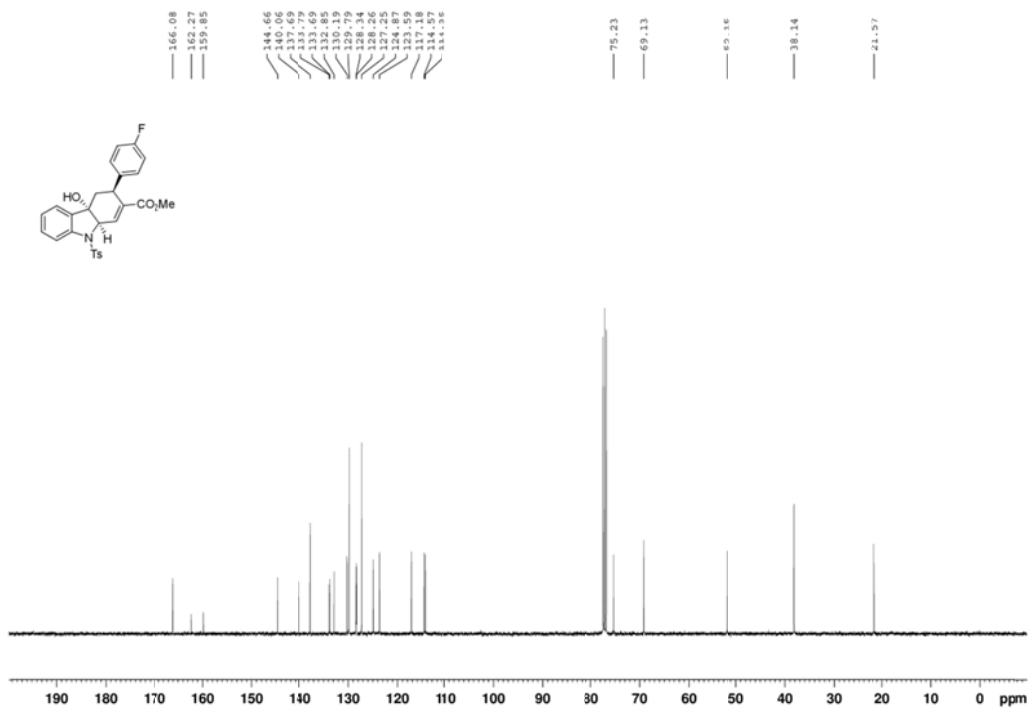
¹³C NMR spectrum of compound **3c** (CDCl₃, 100 MHz)



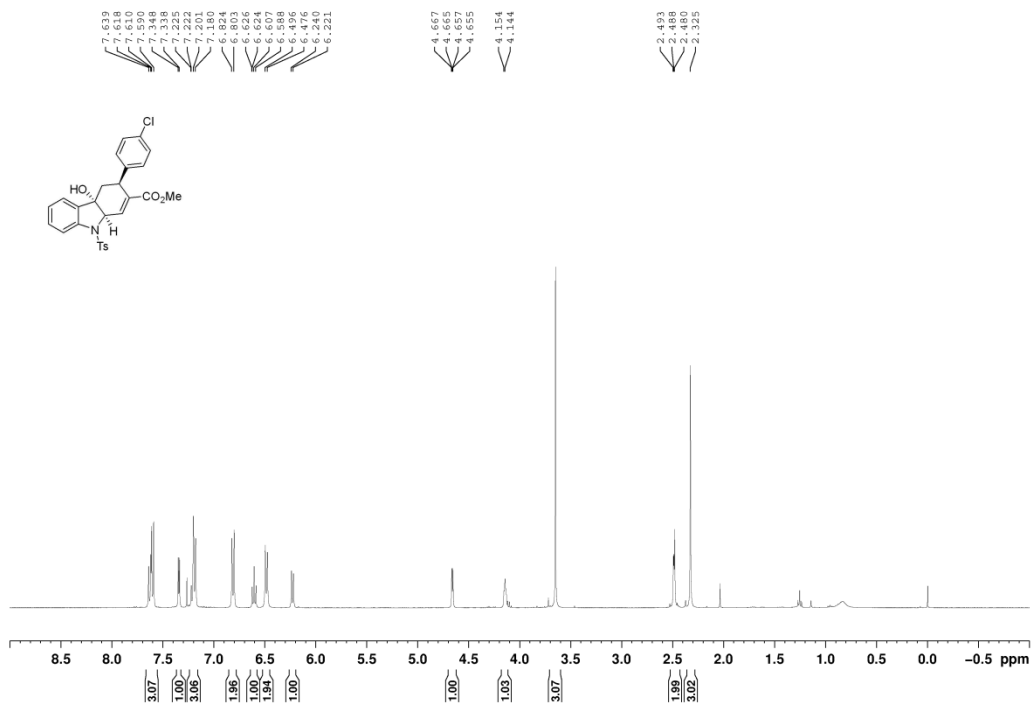
¹H NMR spectrum of compound **3d** (CDCl₃, 400 MHz)



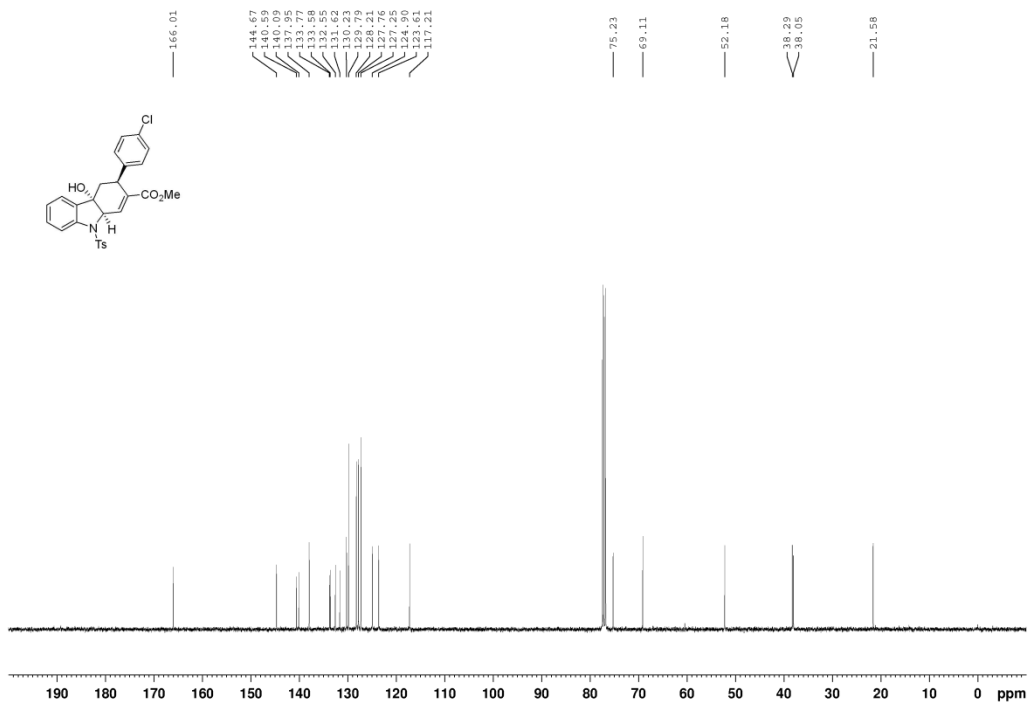
¹³C NMR spectrum of compound **3d** (CDCl₃, 100 MHz)



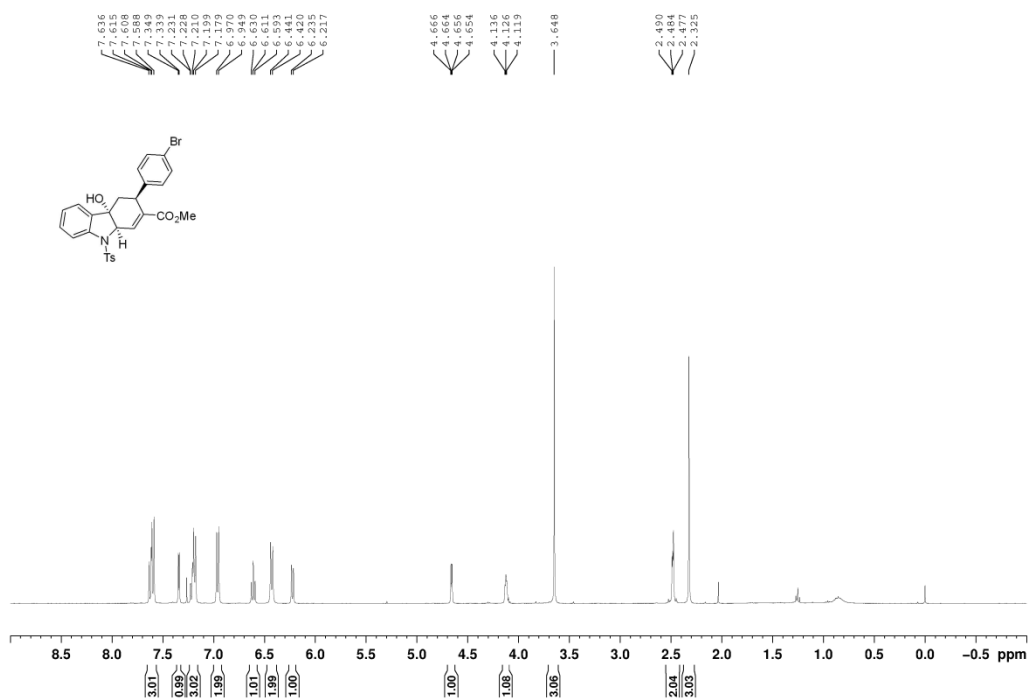
¹H NMR spectrum of compound **3e** (CDCl₃, 400 MHz)



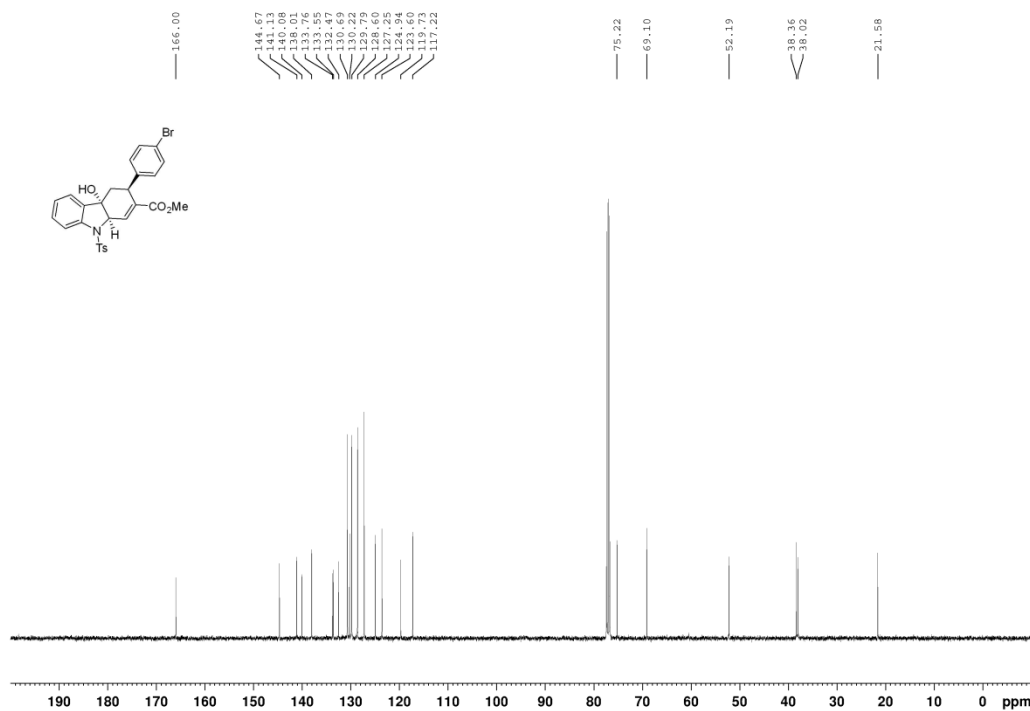
¹³C NMR spectrum of compound **3e** (CDCl₃, 100 MHz)



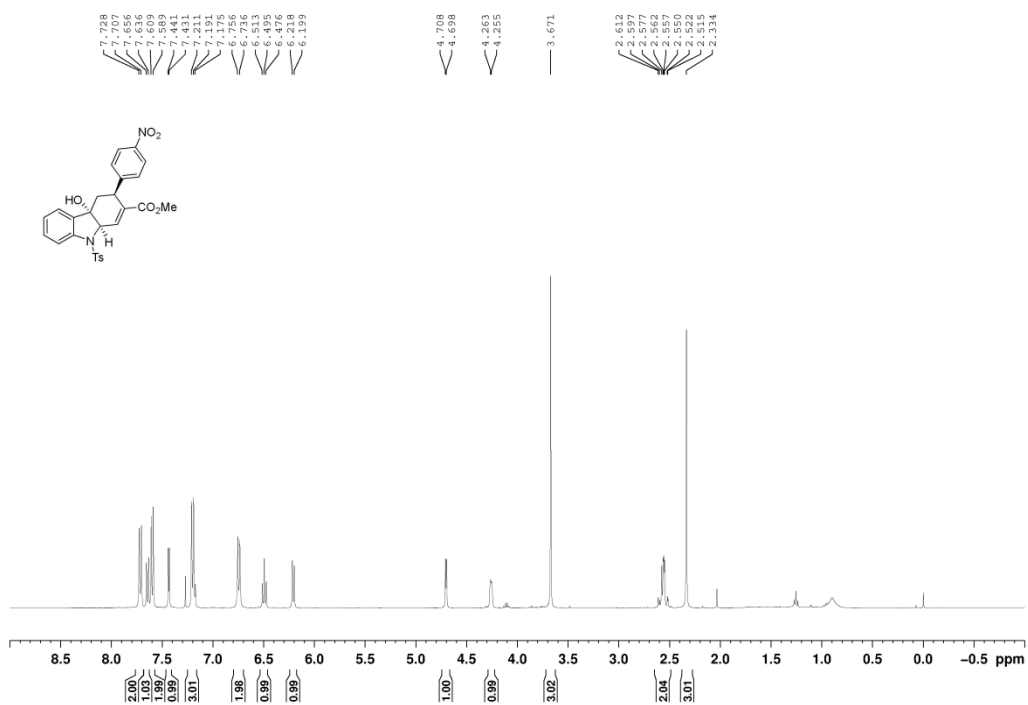
¹H NMR spectrum of compound **3f** (CDCl₃, 400 MHz)



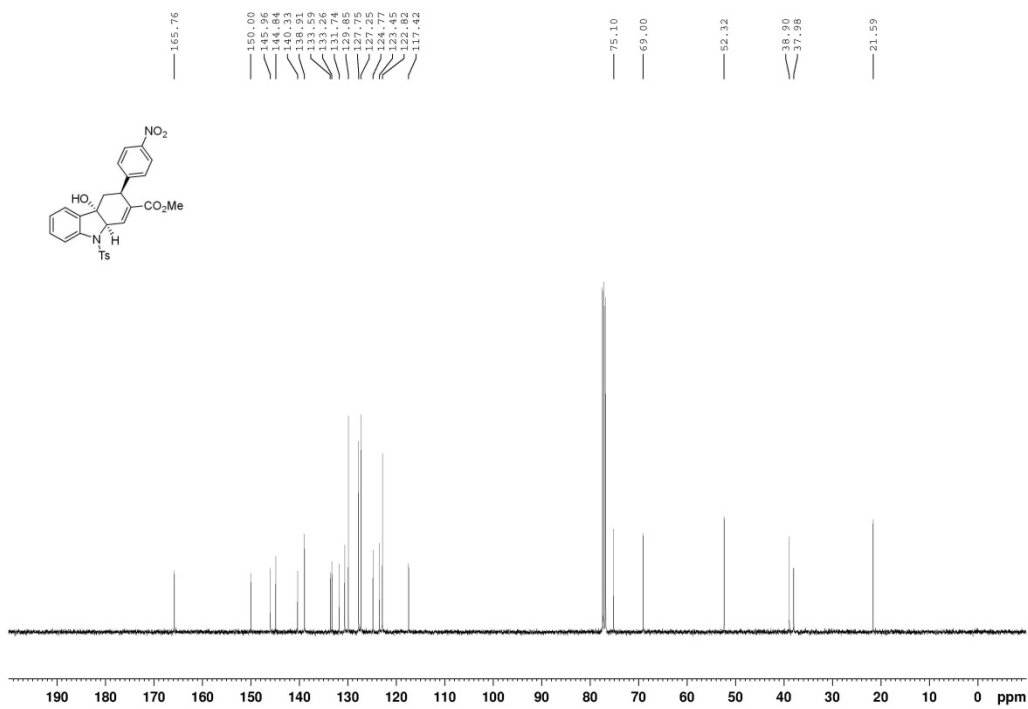
¹³C NMR spectrum of compound **3f** (CDCl₃, 100 MHz)



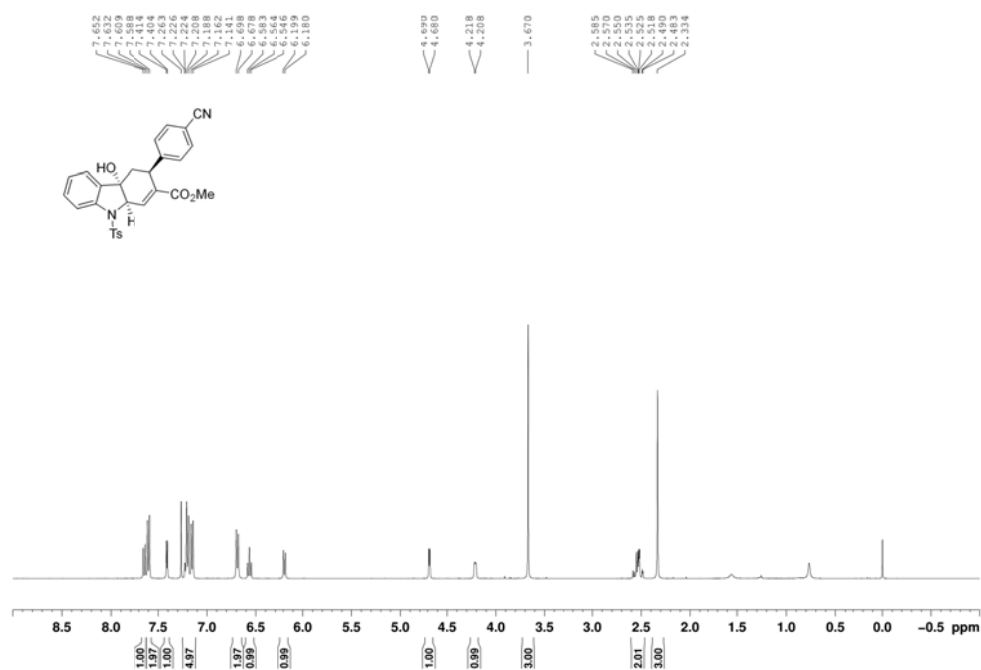
¹H NMR spectrum of compound **3g** (CDCl₃, 400 MHz)



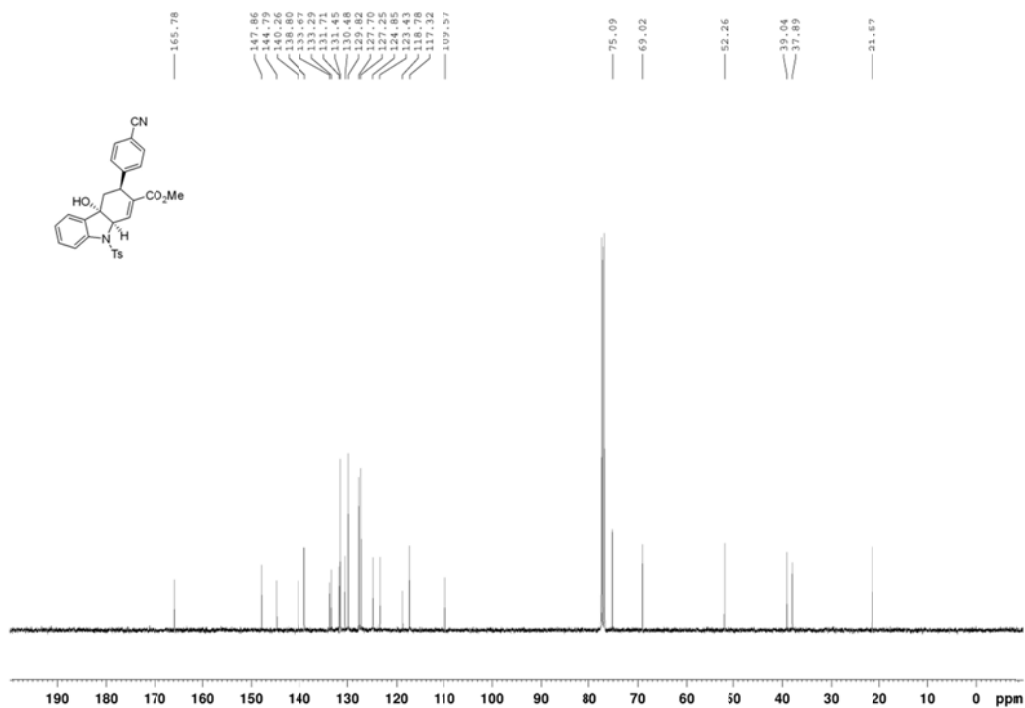
¹³C NMR spectrum of compound **3g** (CDCl₃, 100 MHz)



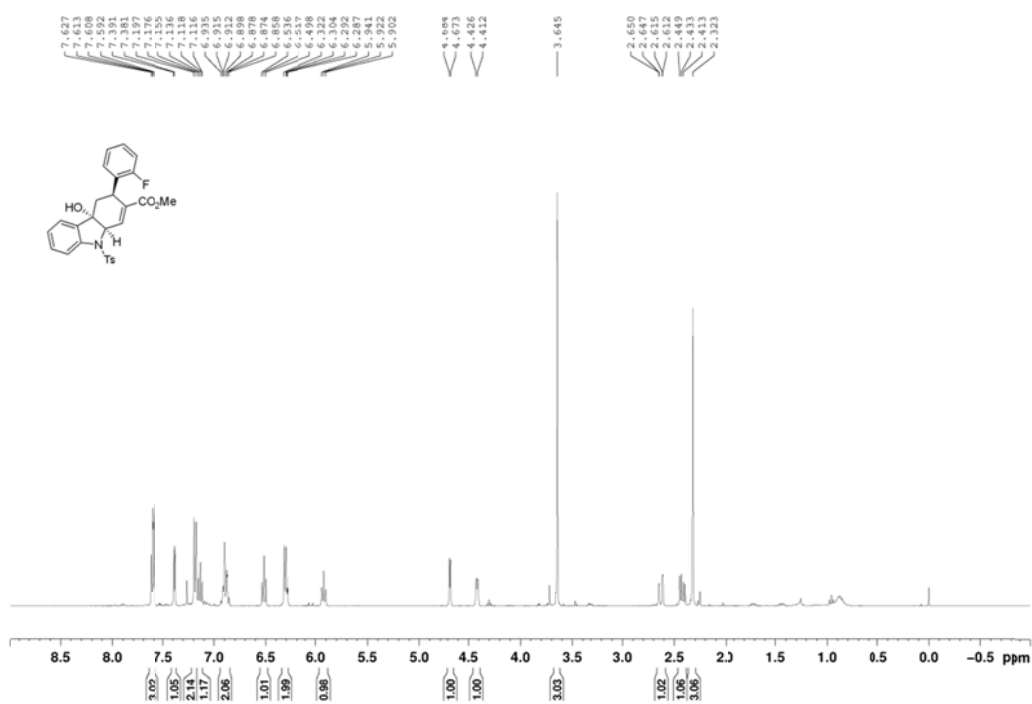
^1H NMR spectrum of compound **3h** (CDCl_3 , 400 MHz)



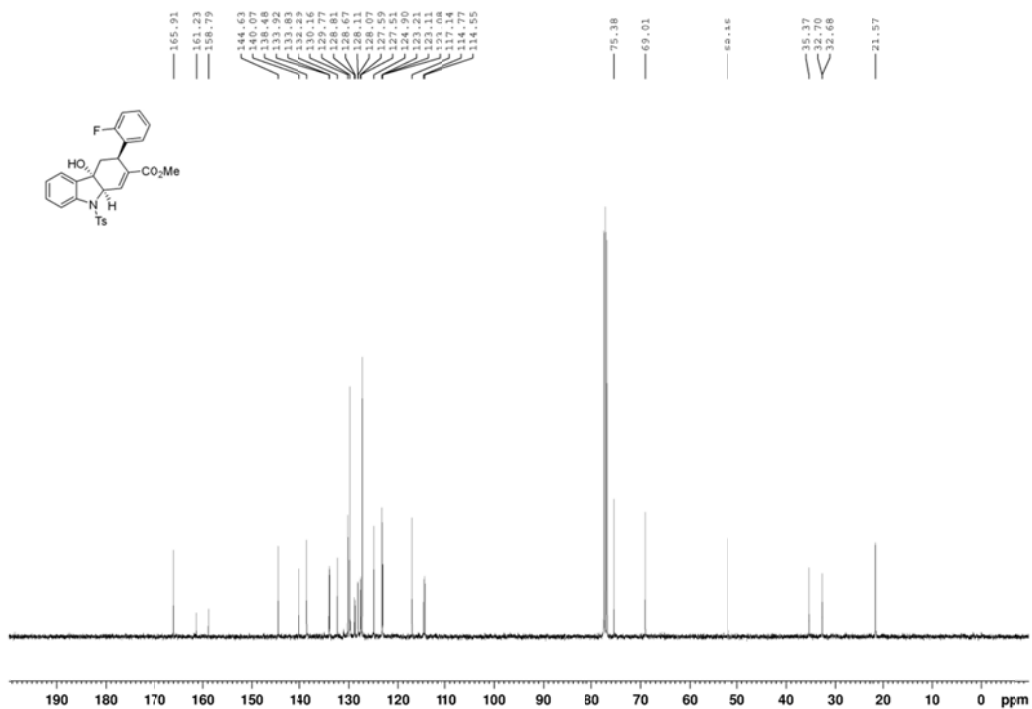
^{13}C NMR spectrum of compound **3h** (CDCl_3 , 100 MHz)



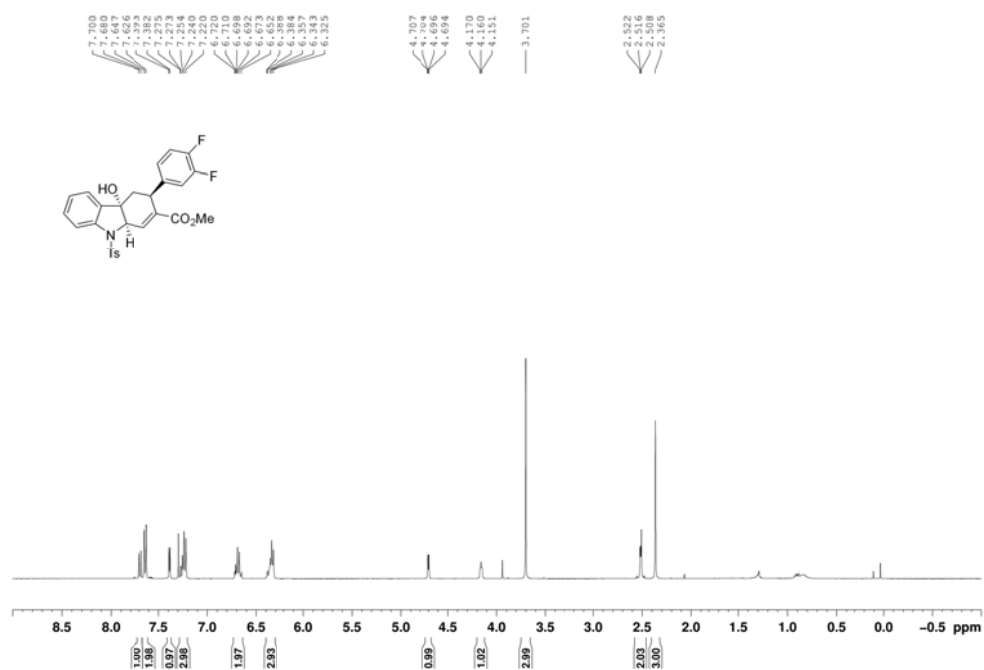
¹H NMR spectrum of compound **3i** (CDCl₃, 400 MHz)



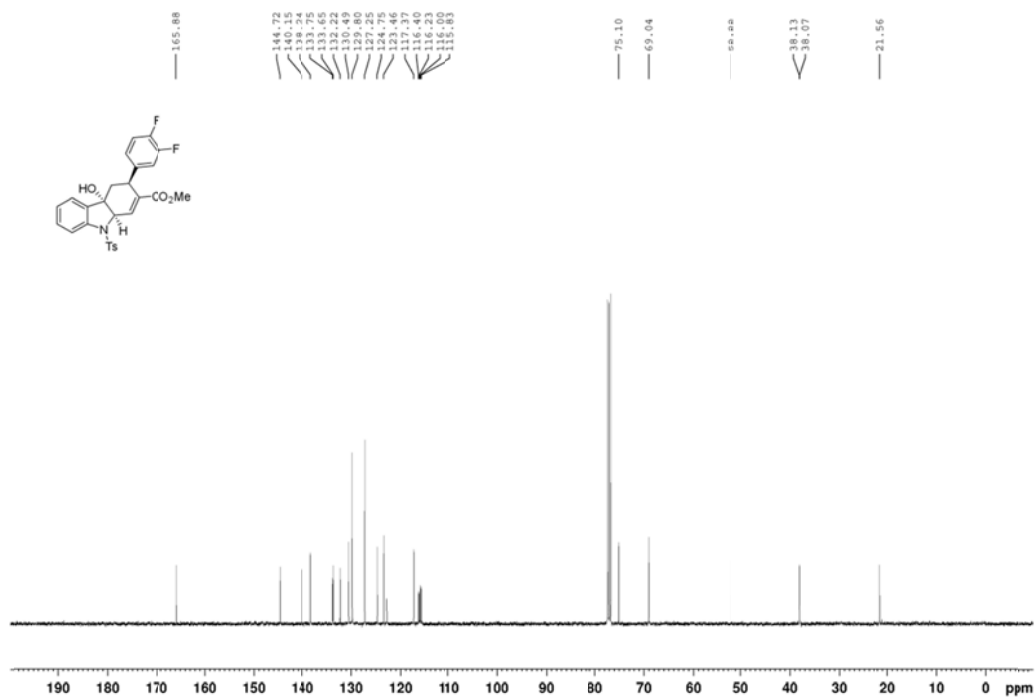
¹³C NMR spectrum of compound **3i** (CDCl₃, 100 MHz)



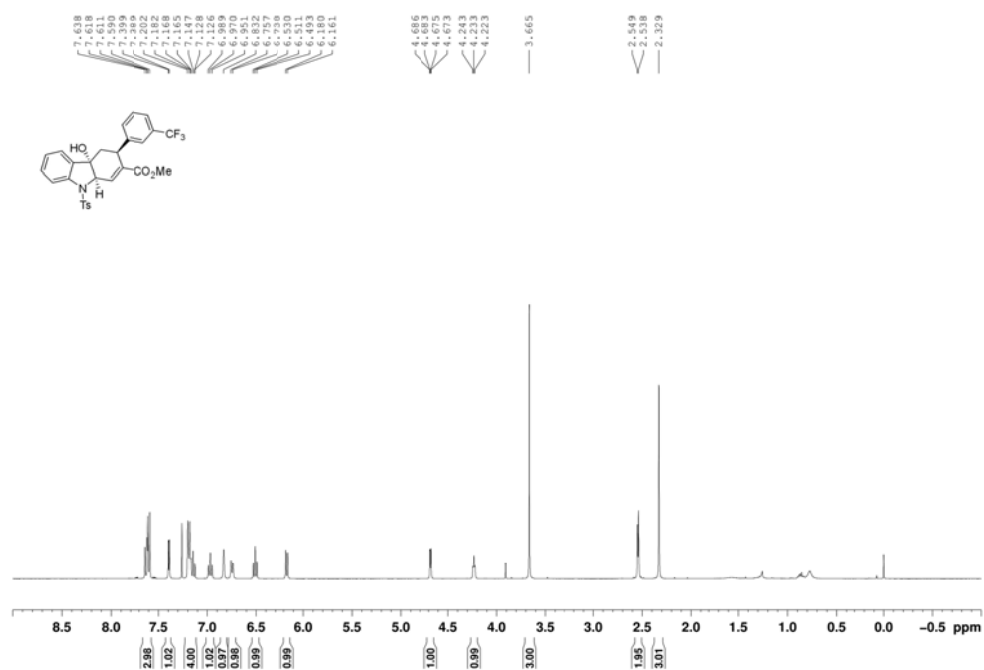
^1H NMR spectrum of compound **3k** (CDCl_3 , 400 MHz)



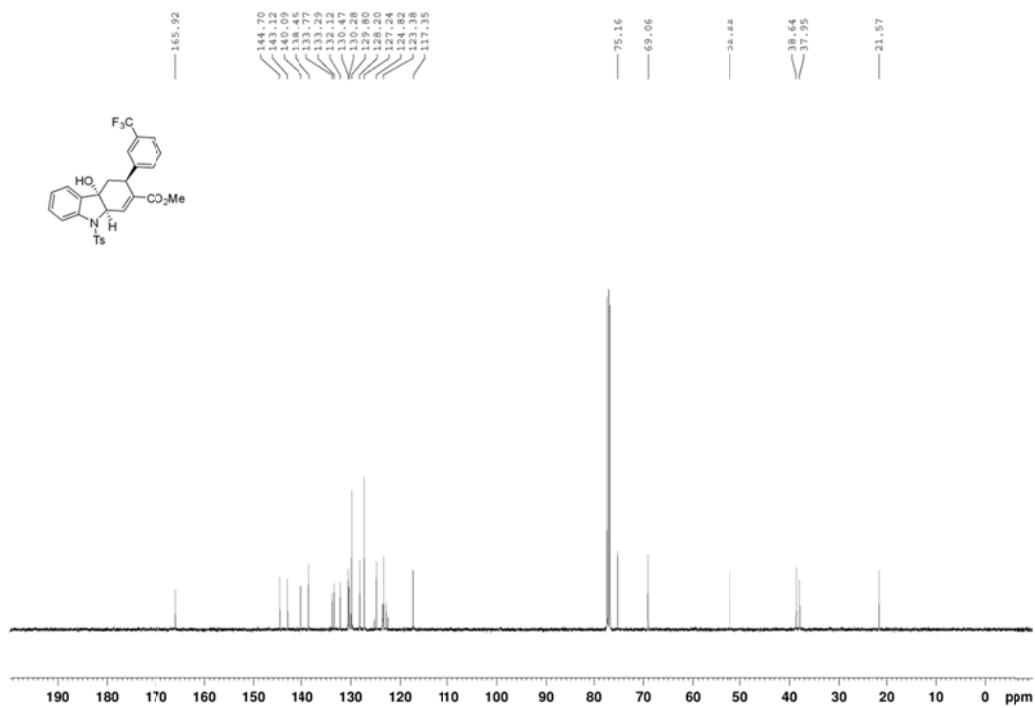
^{13}C NMR spectrum of compound **3k** (CDCl_3 , 100 MHz)



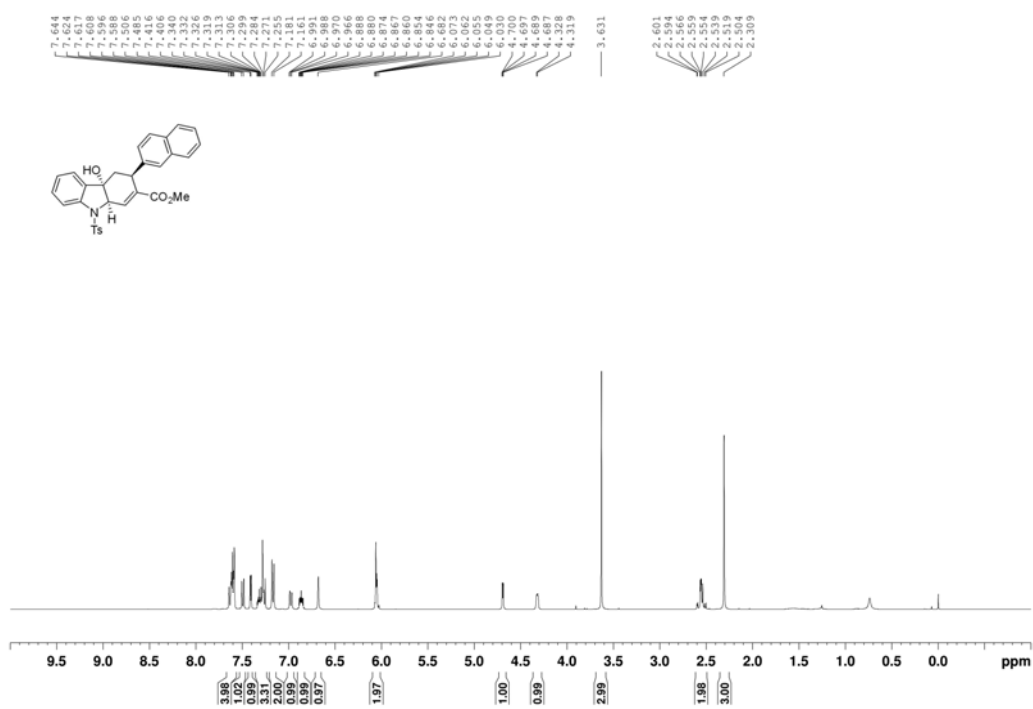
¹H NMR spectrum of compound **31** (CDCl₃, 400 MHz)



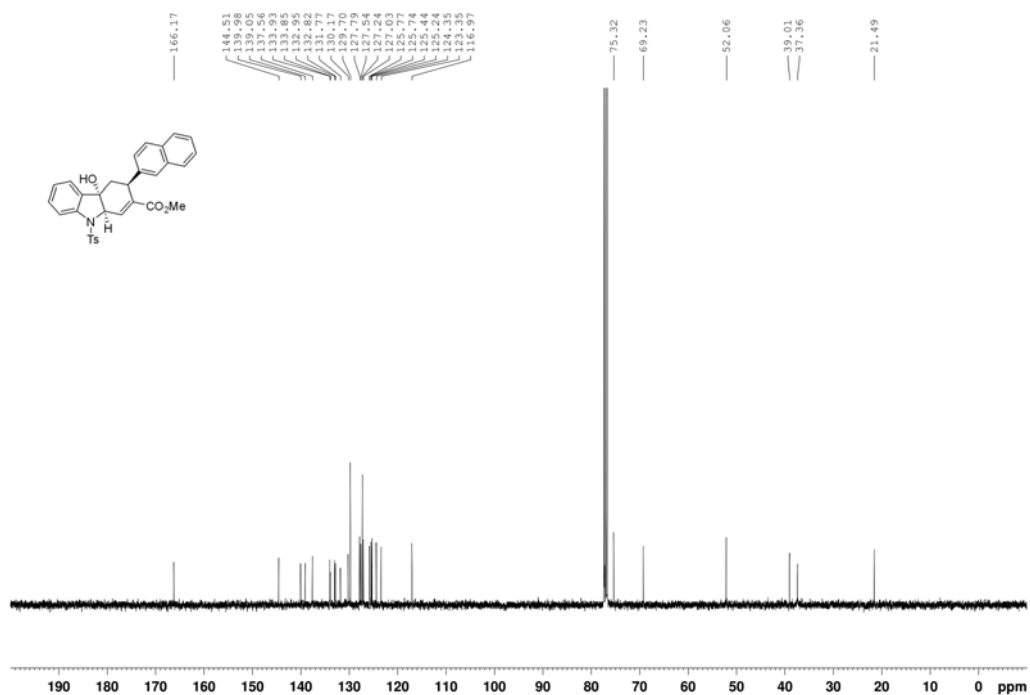
¹³C NMR spectrum of compound **31** (CDCl₃, 100 MHz)



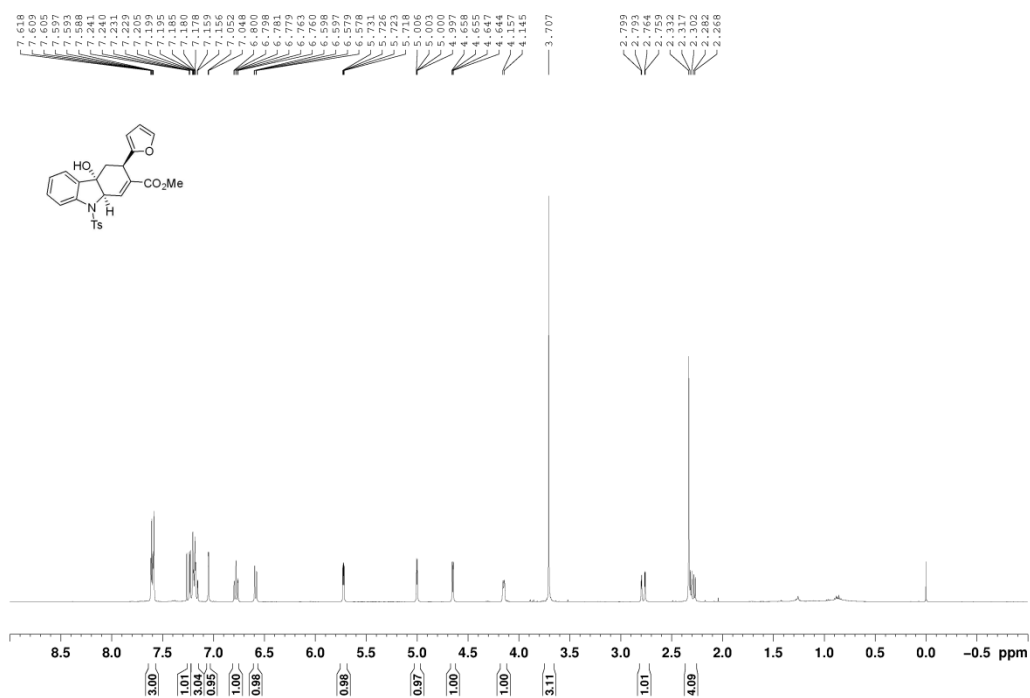
¹H NMR spectrum of compound **3m** (CDCl₃, 400 MHz)



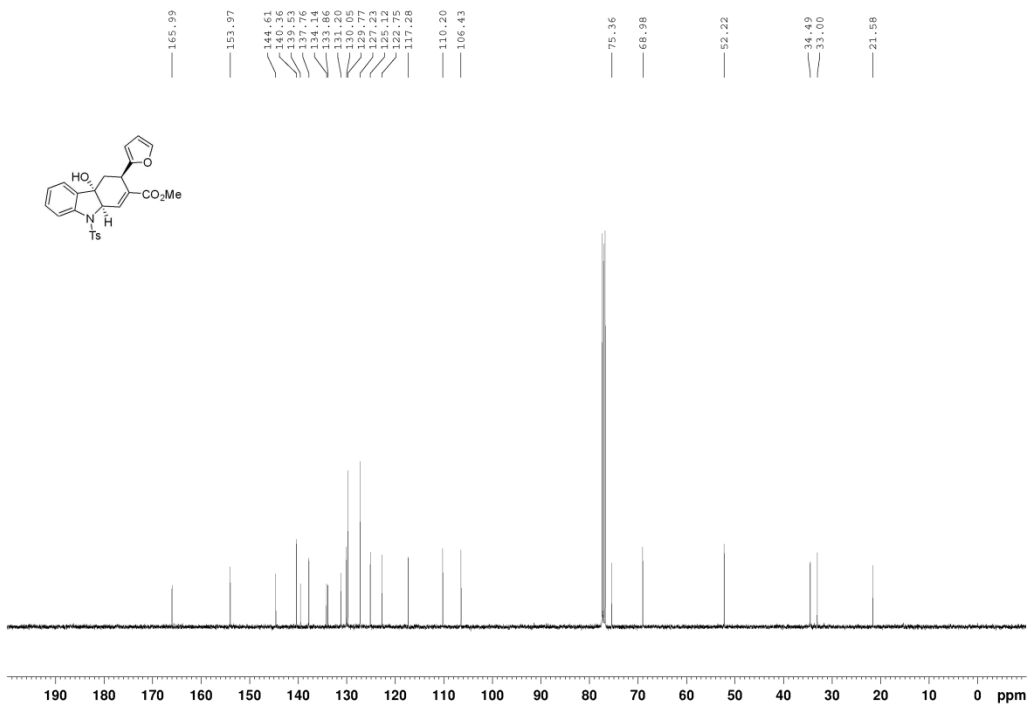
¹³C NMR spectrum of compound **3m** (CDCl₃, 100 MHz)



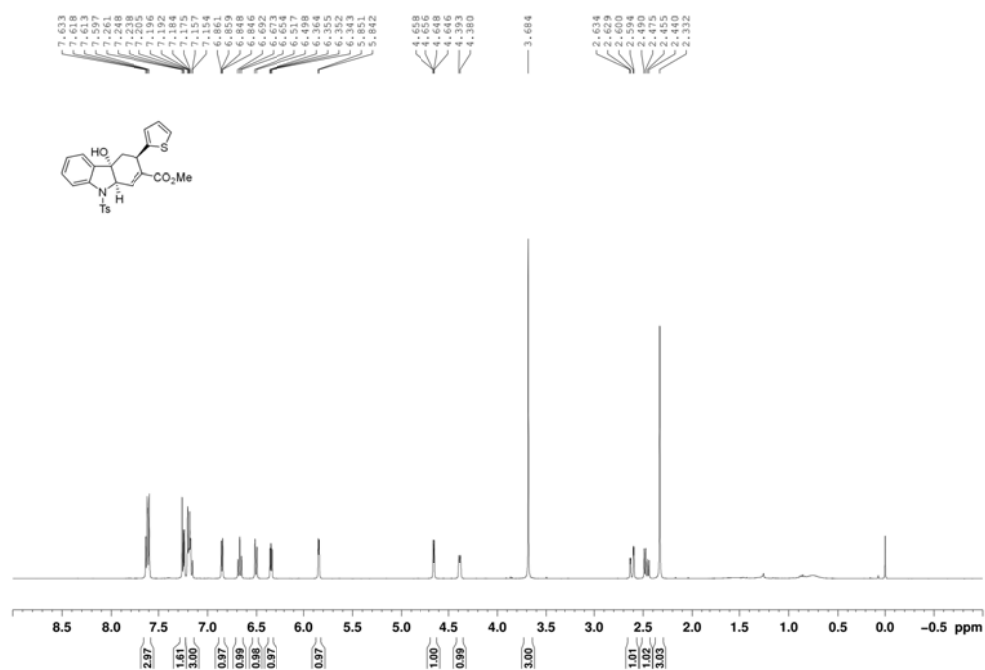
^1H NMR spectrum of compound **3n** (CDCl_3 , 400 MHz)



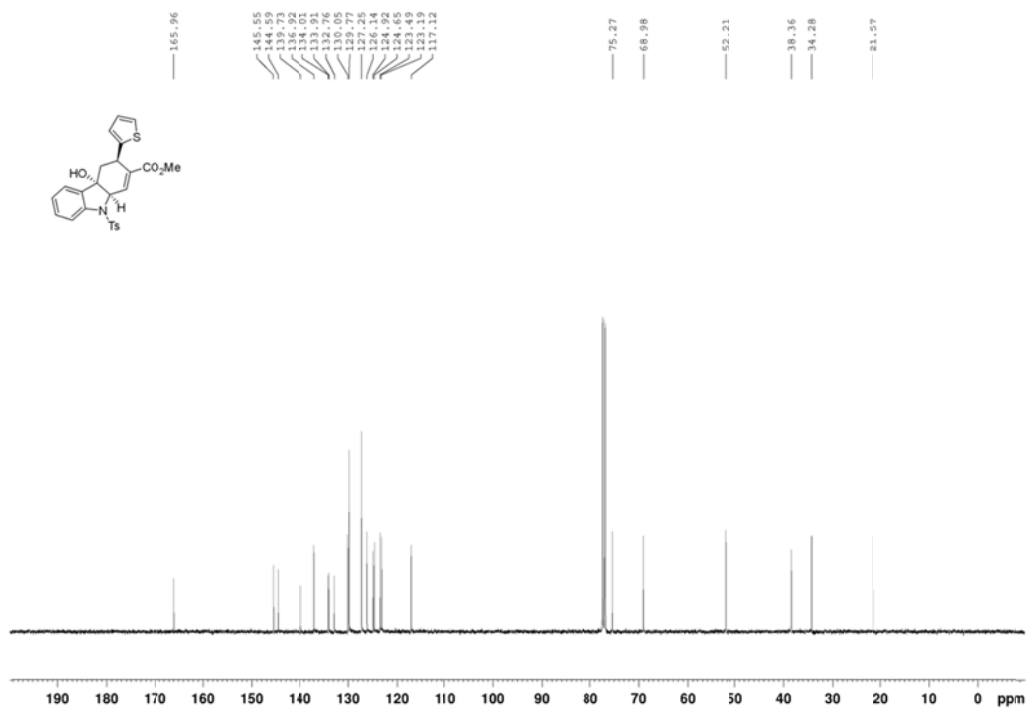
^{13}C NMR spectrum of compound **3n** (CDCl_3 , 100 MHz)



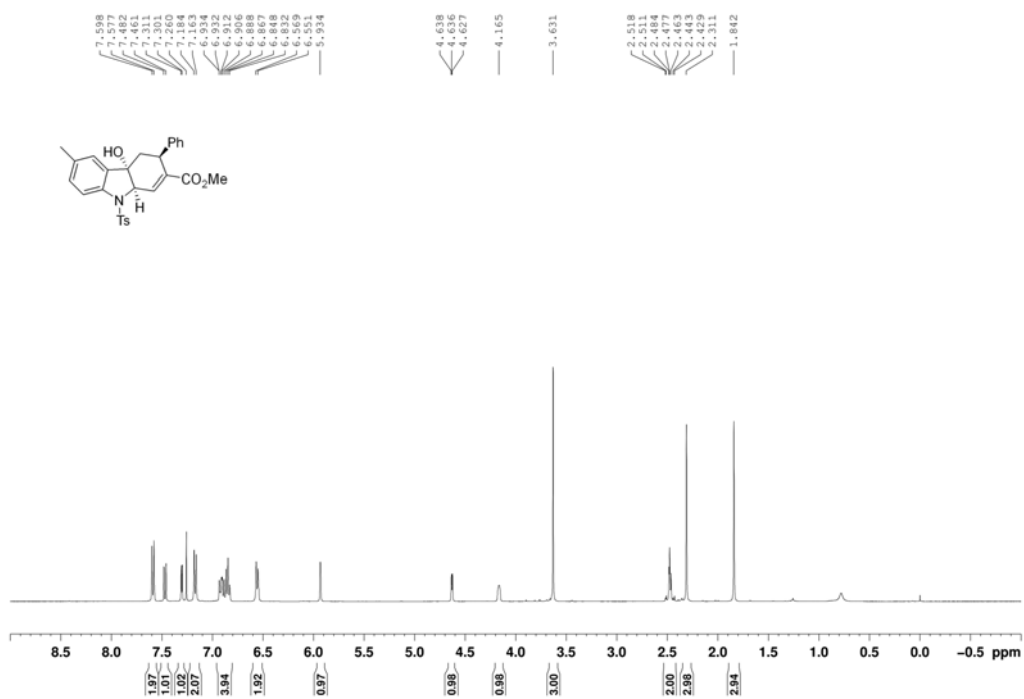
^1H NMR spectrum of compound **3o** (CDCl_3 , 400 MHz)



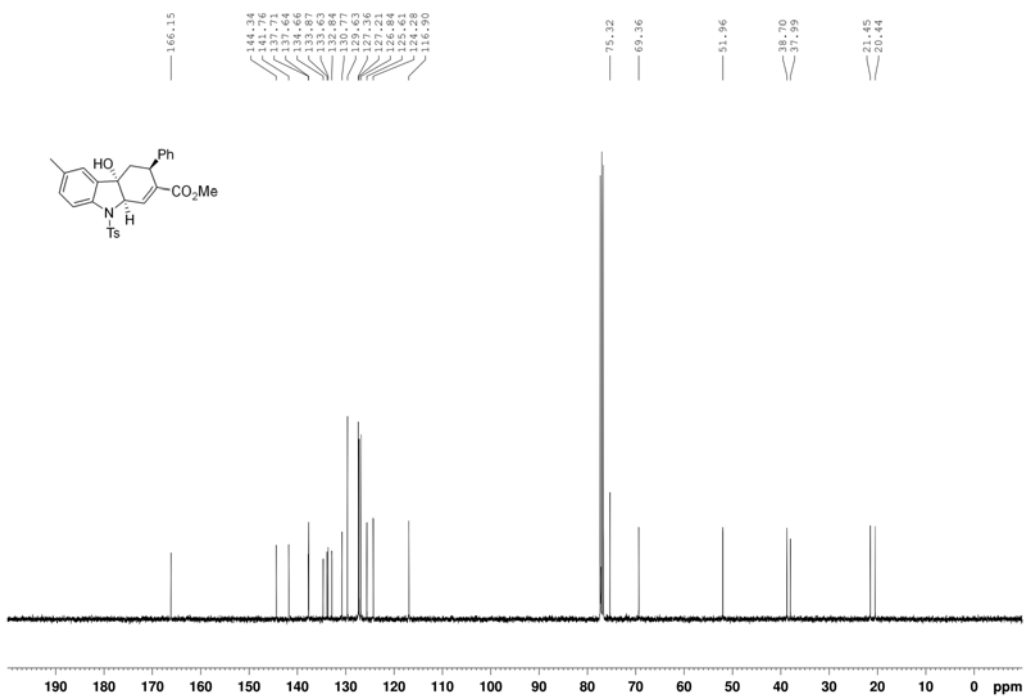
^{13}C NMR spectrum of compound **3o** (CDCl_3 , 100 MHz)



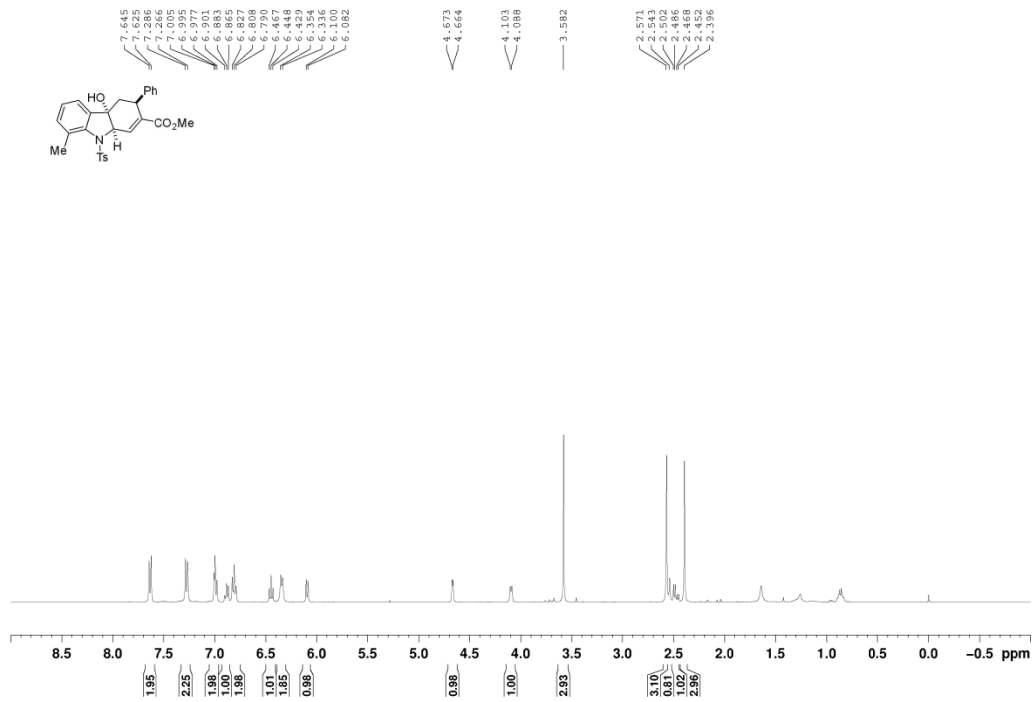
^1H NMR spectrum of compound **3q** (CDCl_3 , 400 MHz)



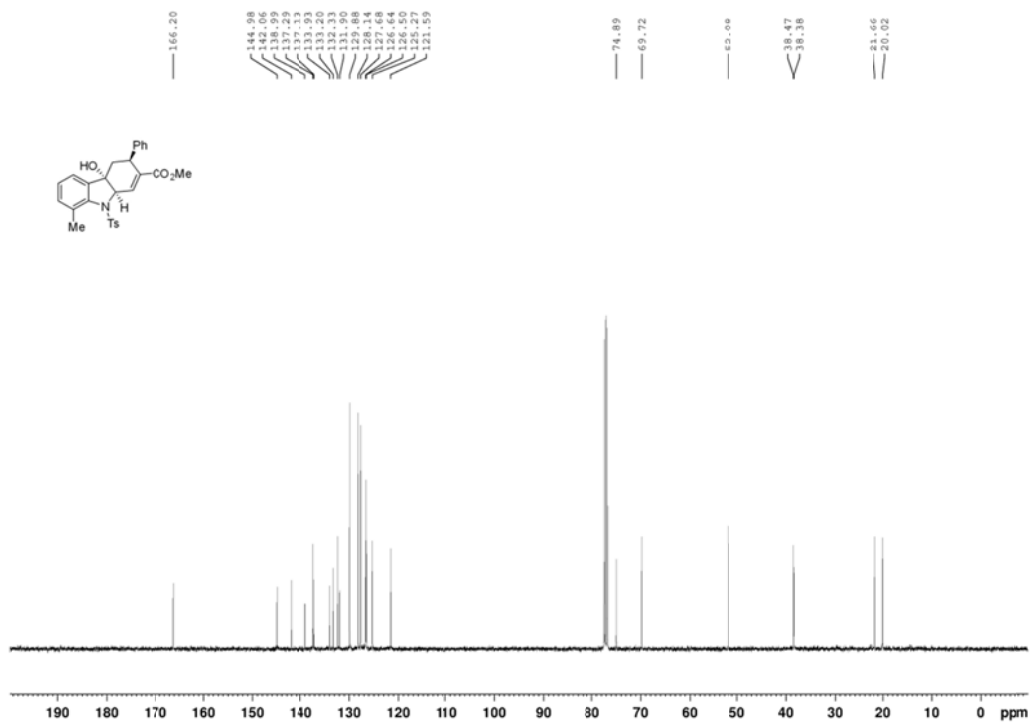
^{13}C NMR spectrum of compound **3q** (CDCl_3 , 100 MHz)



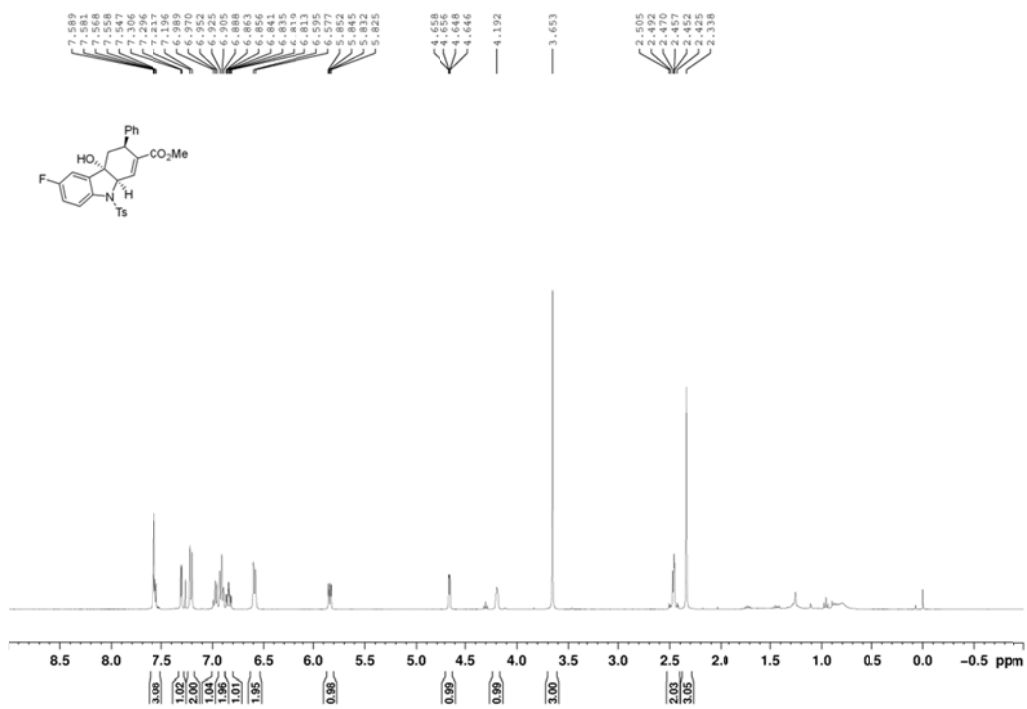
^1H NMR spectrum of compound **3r** (CDCl_3 , 400 MHz)



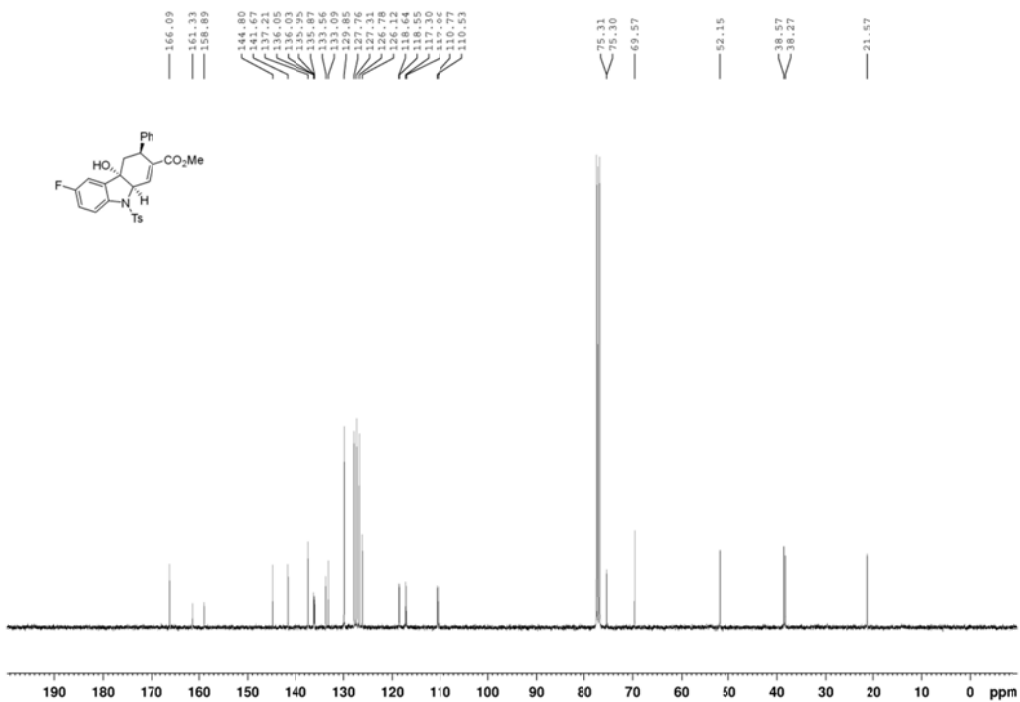
^{13}C NMR spectrum of compound **3r** (CDCl_3 , 100 MHz)



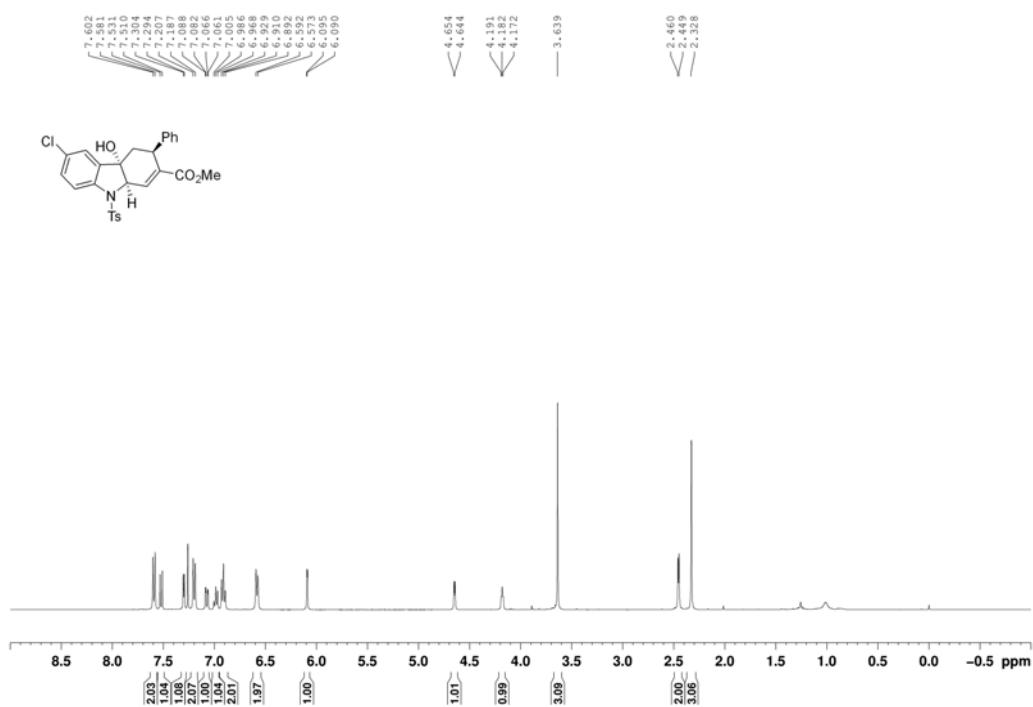
¹H NMR spectrum of compound **3s** (CDCl₃, 400 MHz)



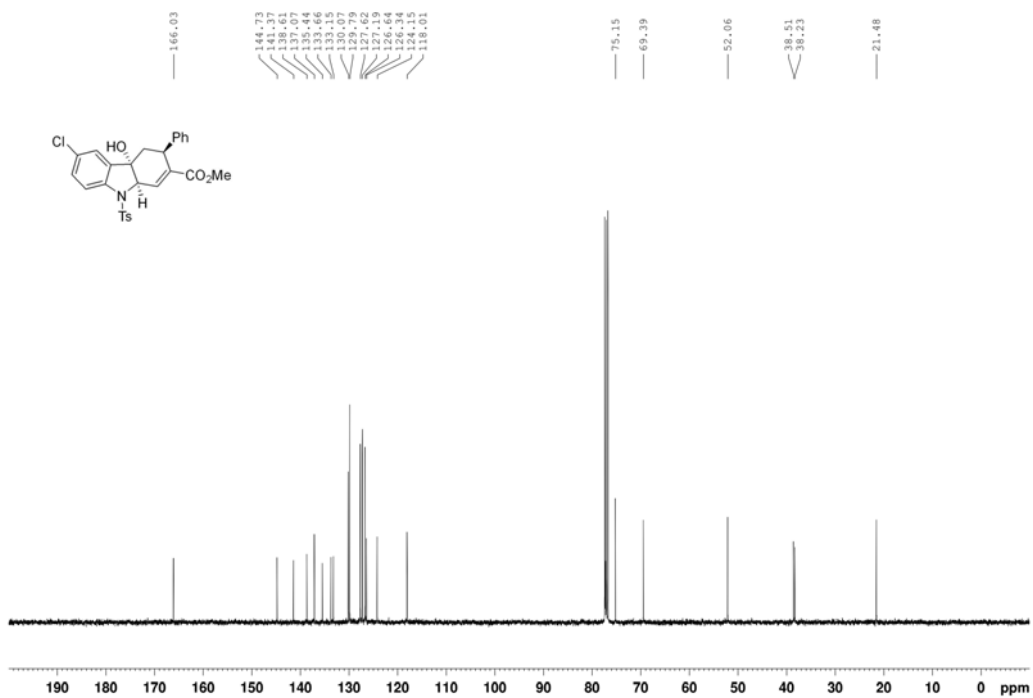
¹³C NMR spectrum of compound **3s** (CDCl₃, 100 MHz)



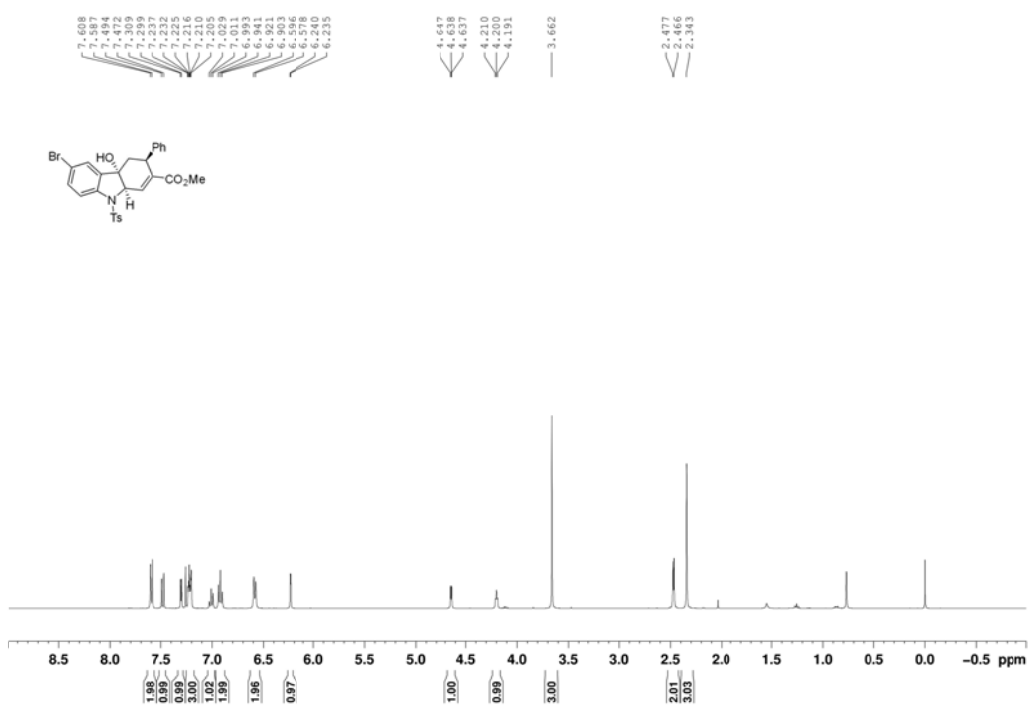
¹H NMR spectrum of compound **3t** (CDCl₃, 400 MHz)



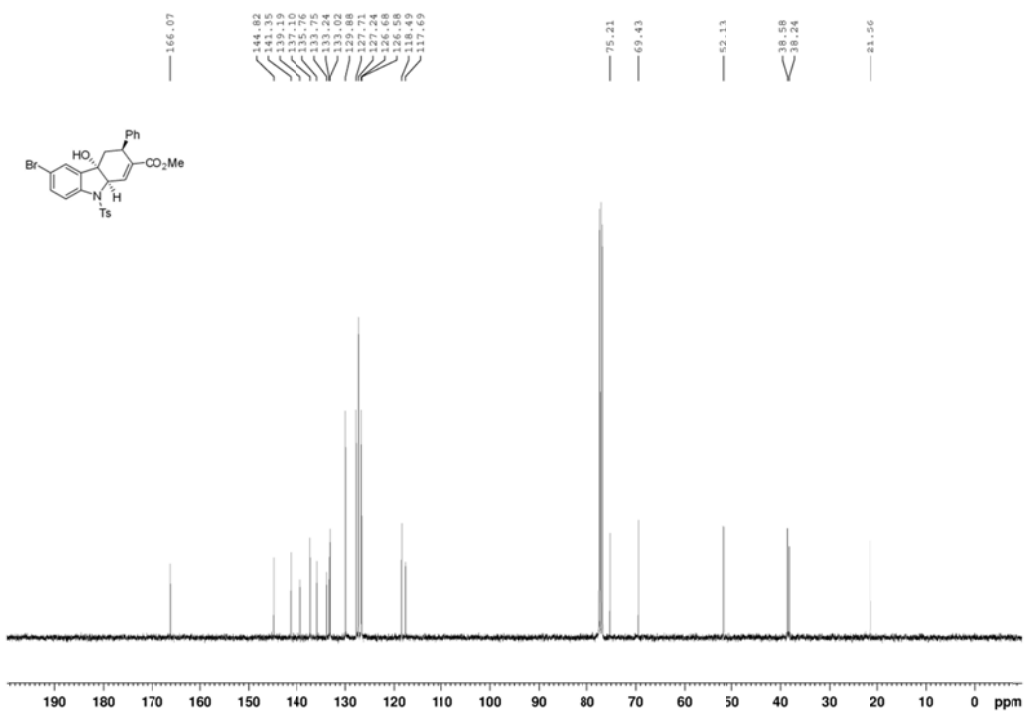
¹³C NMR spectrum of compound **3t** (CDCl₃, 100 MHz)



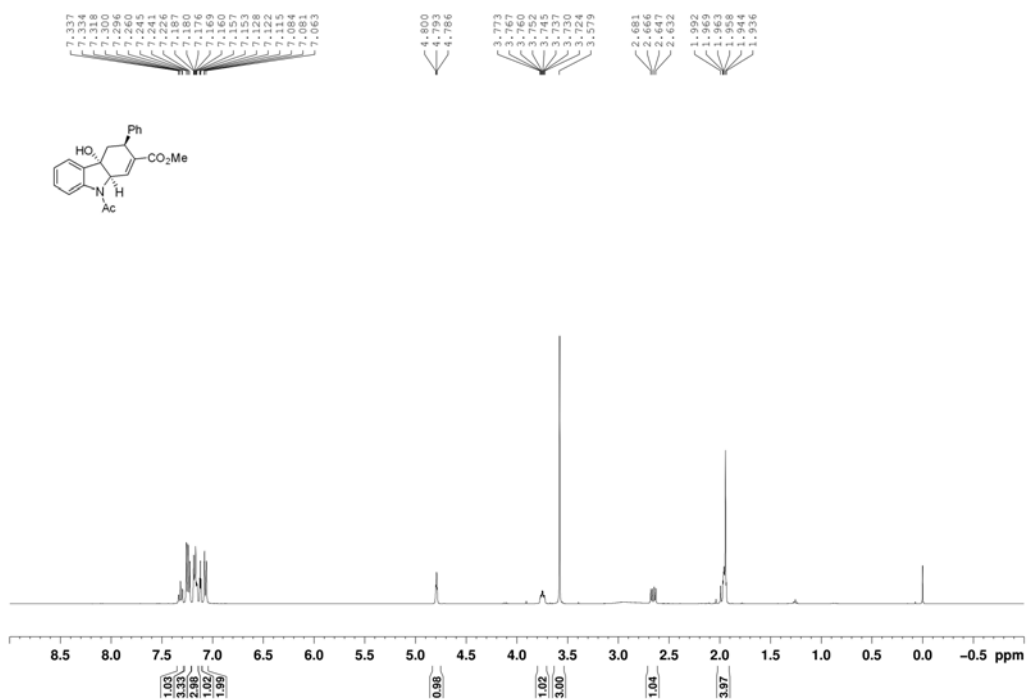
^1H NMR spectrum of compound **3u** (CDCl_3 , 400 MHz)



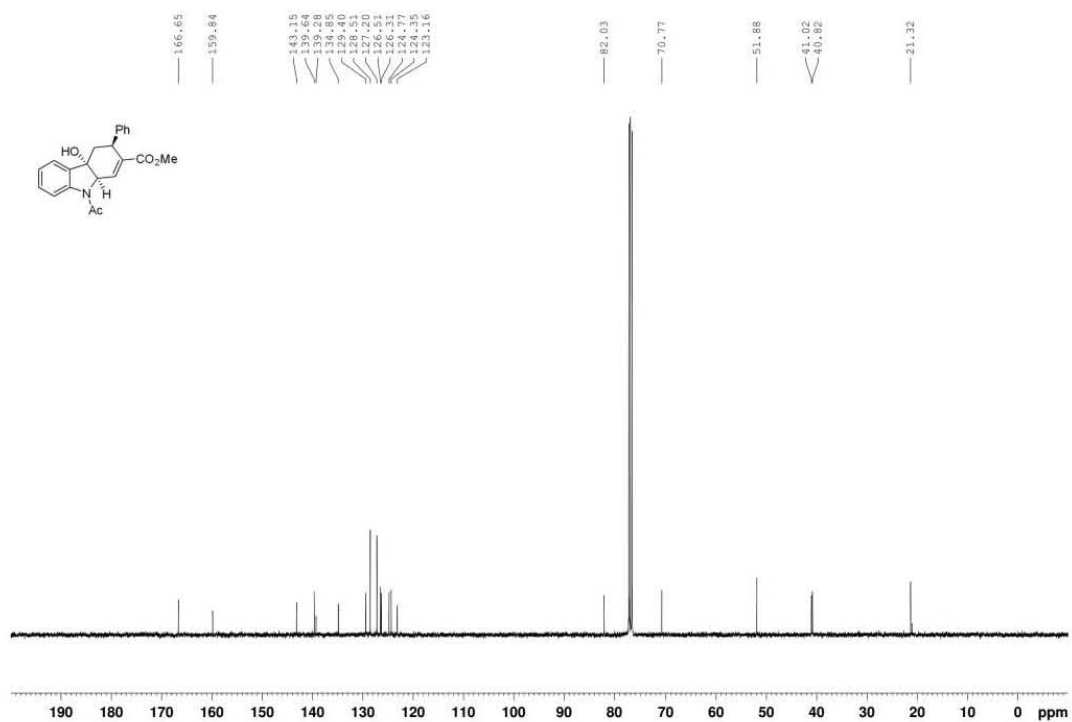
^{13}C NMR spectrum of compound **3u** (CDCl_3 , 100 MHz)



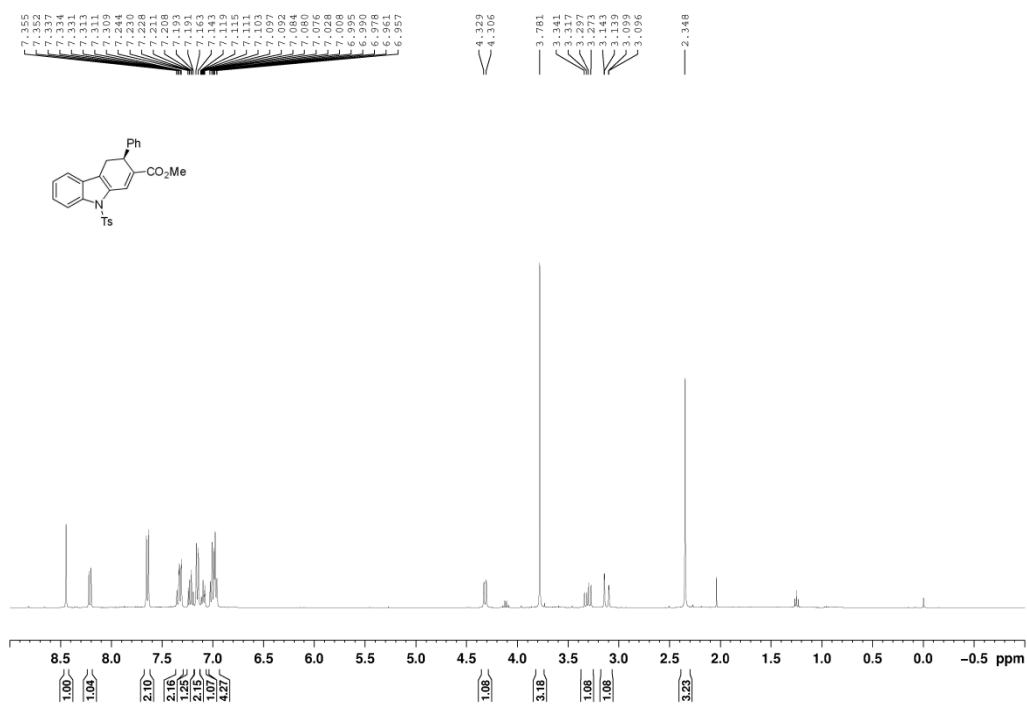
¹H NMR spectrum of compound **3v** (CDCl₃, 400 MHz)



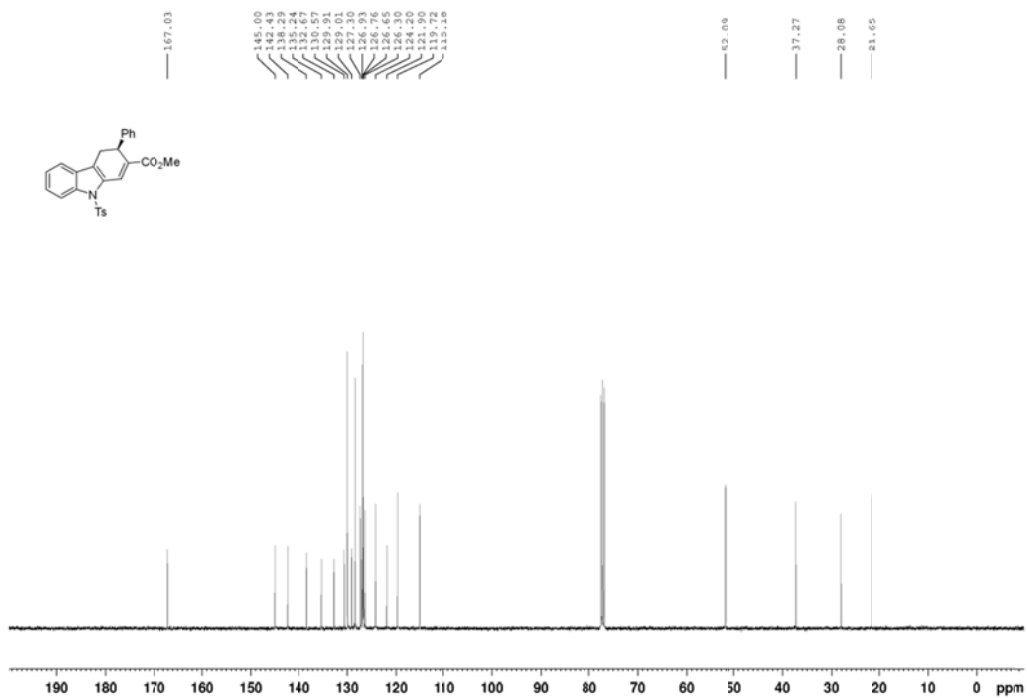
¹³C NMR spectrum of compound **3v** (CDCl₃, 100 MHz)



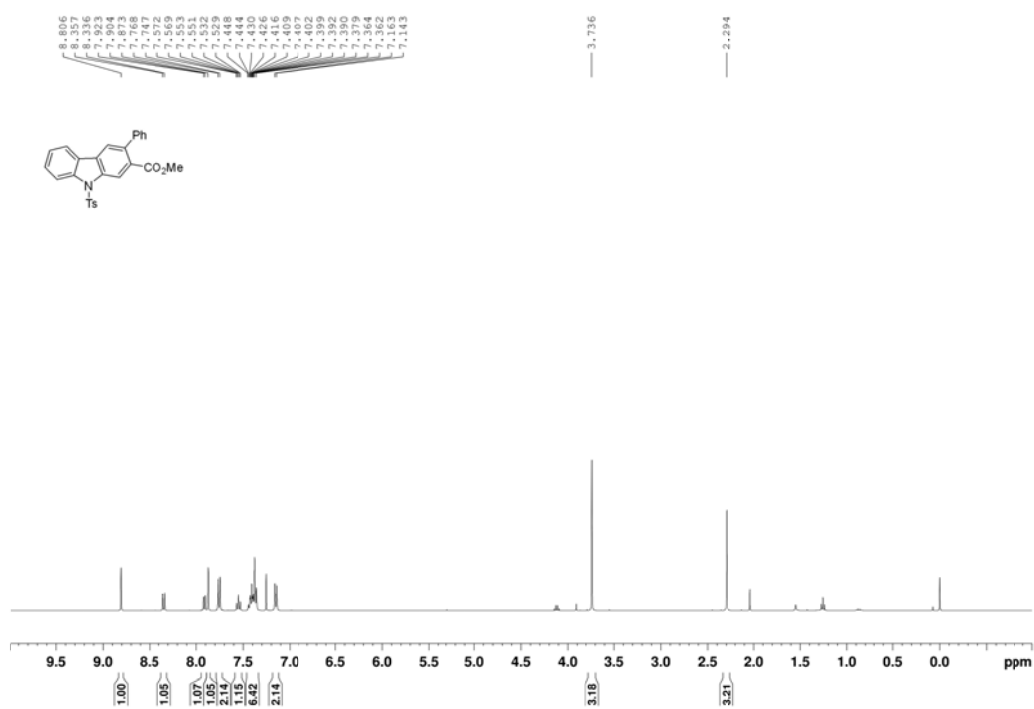
^1H NMR spectrum of compound **4** (CDCl_3 , 400 MHz)



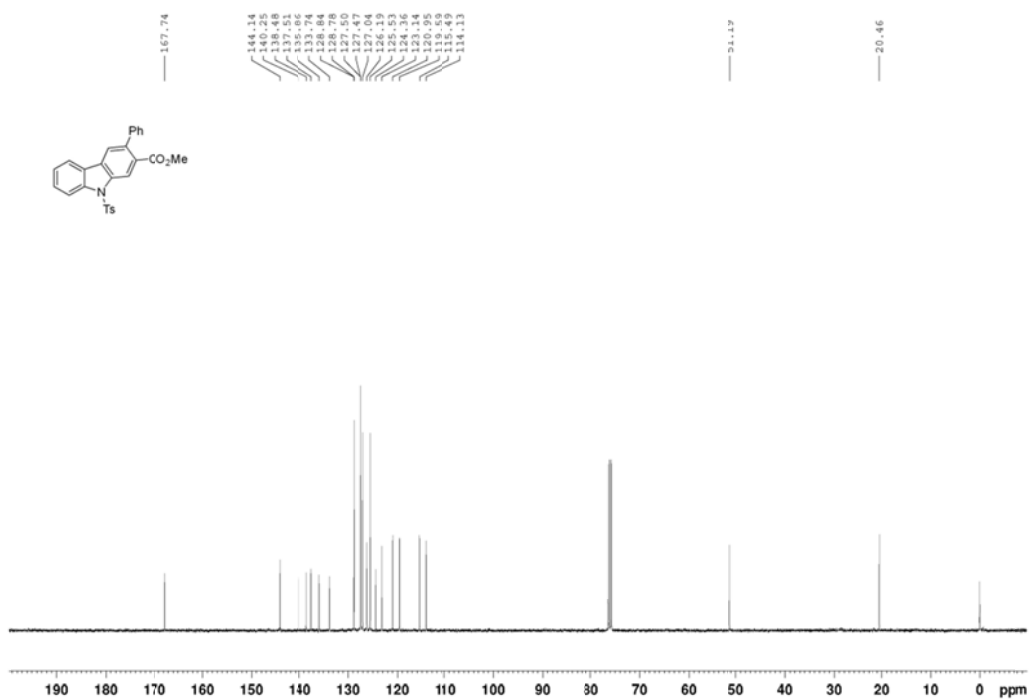
^{13}C NMR spectrum of compound **4** (CDCl_3 , 100 MHz)



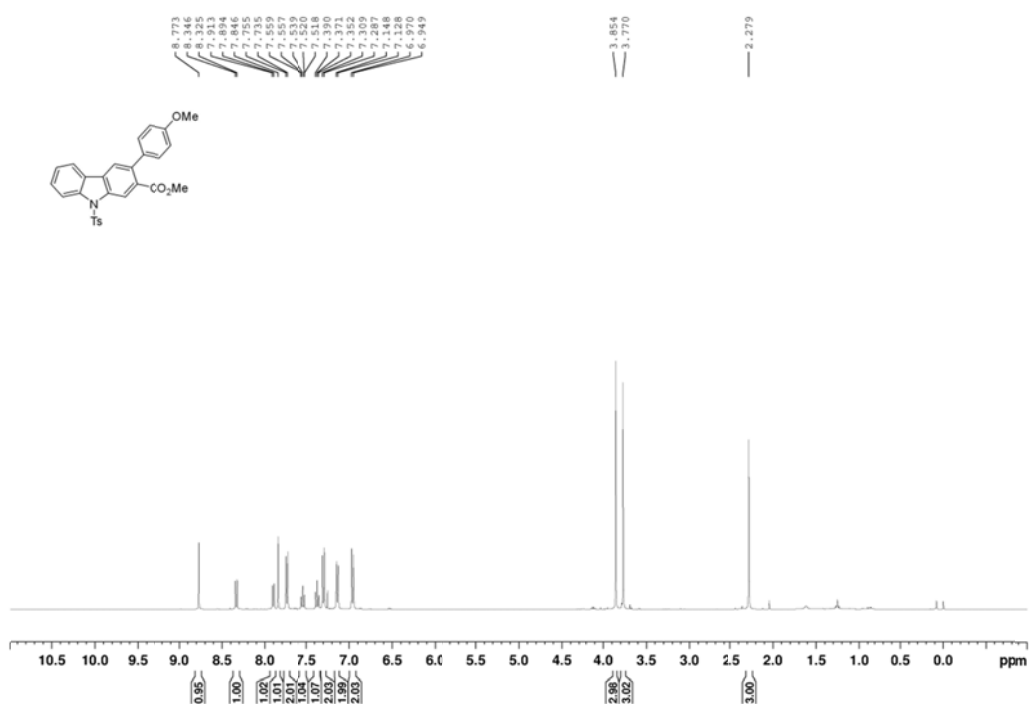
¹H NMR spectrum of compound **5a** (CDCl₃, 400 MHz)



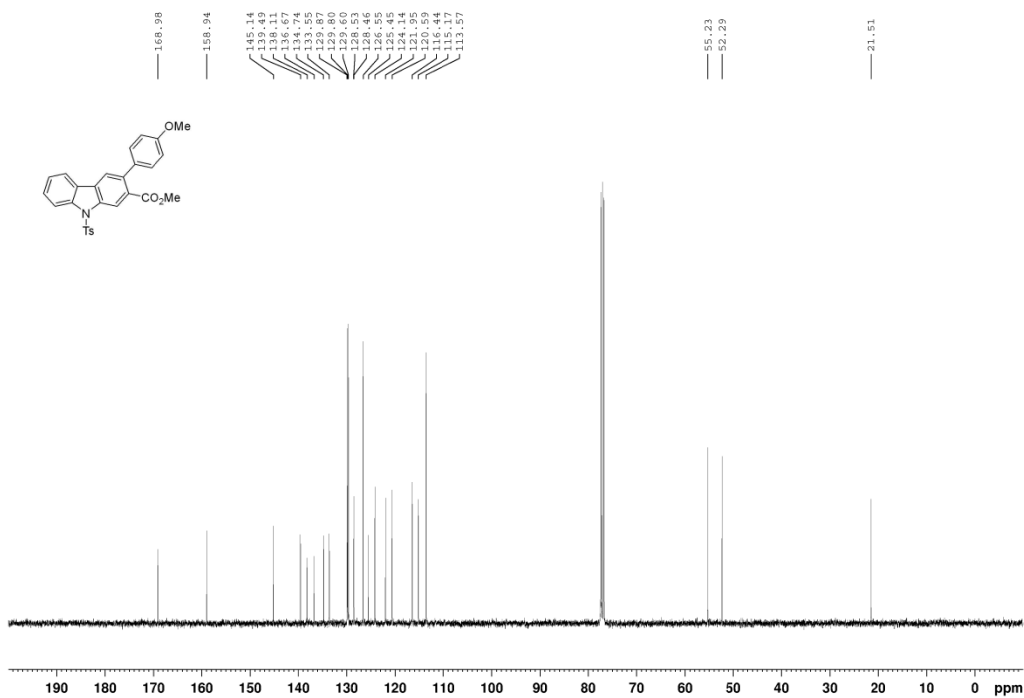
¹³C NMR spectrum of compound **5a** (CDCl₃, 100 MHz)



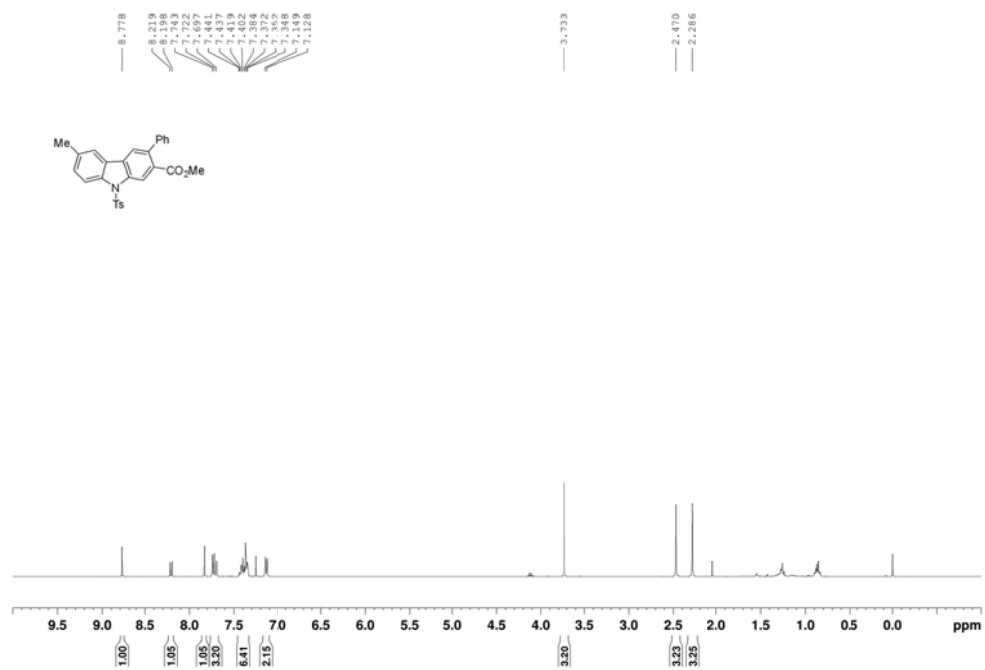
^1H NMR spectrum of compound **5b** (CDCl_3 , 400 MHz)



^{13}C NMR spectrum of compound **5b** (CDCl_3 , 100 MHz)



^1H NMR spectrum of compound **5c** (CDCl_3 , 400 MHz)



^{13}C NMR spectrum of compound **5c** (CDCl_3 , 100 MHz)

