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Supporting Information

Photoinduced carbene transfer for copper-catalyzed asymmetric [4+1] cycloadditions: an entry to chiral indolines bearing quaternary stereocenters

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1. General Information

NMR spectra: ^{1}H NMR spectra were recorded on a 400/600 MHz spectrometer. Chemical shifts are reported in parts per million (ppm) and the spectra are calibrated to the resonance resulting from incomplete deuteration of the solvent ($CDCl_3$: 7.26 ppm). ^{13}C NMR spectra were recorded on the same spectrometer with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($^{13}CDCl_3$: 77.0 ppm,). Data are reported as follows: chemical shift δ/ppm, integration (^{1}H only), multiplicity (s = singlet, d = doublet, t = triplet of doublets, m = multiplet or combinations thereof; ^{13}C signals are singlets unless otherwise stated), coupling constants *J* in Hz, assignment. ^{19}F NMR spectra were recorded on the same Spectrometer.

High Resolution Mass Spectrometry (HRMS): All were recorded on Bruker micrOTOF II ESI-TOF by ESI or APCI. Measured values are reported to 4 decimal places of the calculated value. The calculated values are based on the most abundant isotope.

Chromatography: Analytical thin layer chromatography was performed using Qingdao Puke Parting Materials Co. silica gel plates (Silicagel 60 F254). Visualisation was by ultraviolet fluorescence (λ = 254 nm) and/or staining with Phosphomolybdic acid or potassium permanganate ($KMnO_4$). Flash column chromatography was performed using 200-300 mesh silica gel. Optical rotations were measured with a polarimeter. [α]. D values are reported at a given temperature (ºC) in degrees $cm^2\ g^{-1}$ with concentration in mg mL^{-1}.

Chiral HPLC: Enantiomeric excesses (ee) values were determined by chiral HPLC with chiral AS-H, AD-H, AZ-H columns with hexane and *i*-PrOH as solvents.

UV/Vis: Measurements were made on a Shimadzu RF-6000 Spectro Fluorophotometer.

Materials: All the solvents were treated according to standard methods or through solvent purification systems before use. Substrates **1**,[1] **2a**[2] and **4**[3] were prepared according to previous methods and sulfides, copper salts and chiral ligands are commercially available.

Reference

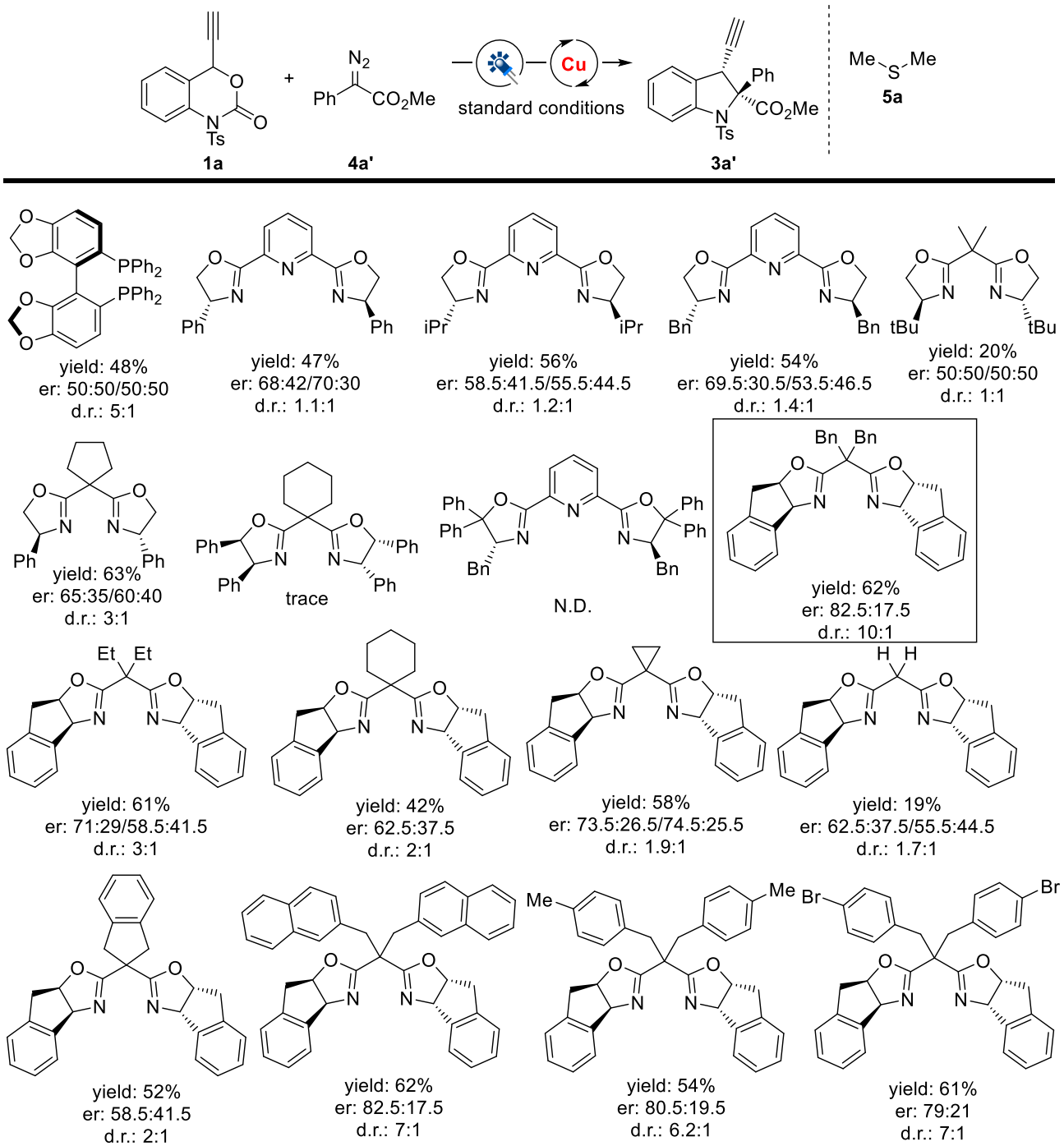
1 (a) Q. Wang, T.-R. Li, L.-Q. Lu, M.-M. Li, K. Zhang and W.-J. Xiao, *J. Am. Chem. Soc.*, 2016, **138**, 8360-8363; (b) T.-R. Li, B.-Y. Cheng, Y.-N. Wang, M.-M. Zhang, L.-Q. Lu and W.-J. Xiao, *Angew. Chem. Int. Ed.*, 2016, **55**, 12422-12426.

2 M. Ma, L. Peng, C. Li, X. Zhang, J. Wang, *J. Am. Chem. Soc.*, 2005, **127**, 15016-15017.

3. (a) R. Hommelsheim, Y. Guo, Z. Yang, C. Empel and R. M. Koenigs, *Angew. Chem. Int. Ed.*, 2019, **58**, 1203-1207; (b) S. Jana, Z. Yang, C. Pei, X. Xu and R. M. Koenigs, *Chem. Sci.*, 2019, **10**, 10129-10134; (c) X. Gao,; B. Wu, W.-X. Huang, M.-W. Chen, Y.-G. Zhou, *Angew. Chem. Int. Ed*., 2015, **54**, 11956-11960.

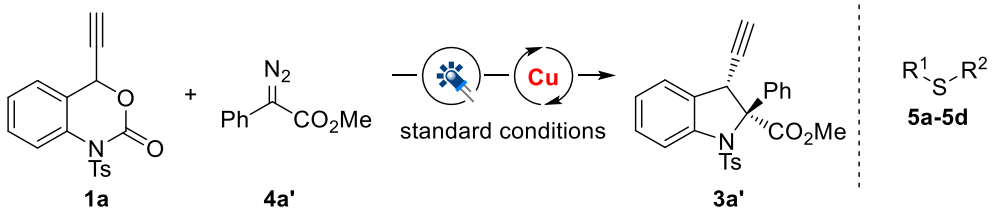
2. Details for Condition Optimizations

Table S1 The effect of ligand[a]



[a]Reaction conditions: **5a** (0.4 mmol), **4a'** (0.2 mmol) in 1 mL anhydrous toluene at r.t. under 6 W blue LEDs for 6 h; then the resulting solution of **4a'** together with **1a** (0.1 mmol) were added to the pre-prepared soultion of $Cu(OTf)_2$ (10 mol%), ligand (15 mol%) and $^iPr_2NEt$ (0.12 mmol) in 1 mL anhydrous THF at 0 °C. [b]Yield of isolated product. [c]The diastereomeric ratios were determined by ^1H NMR spectroscopic analysis. [d]The er values were determined by HPLC.

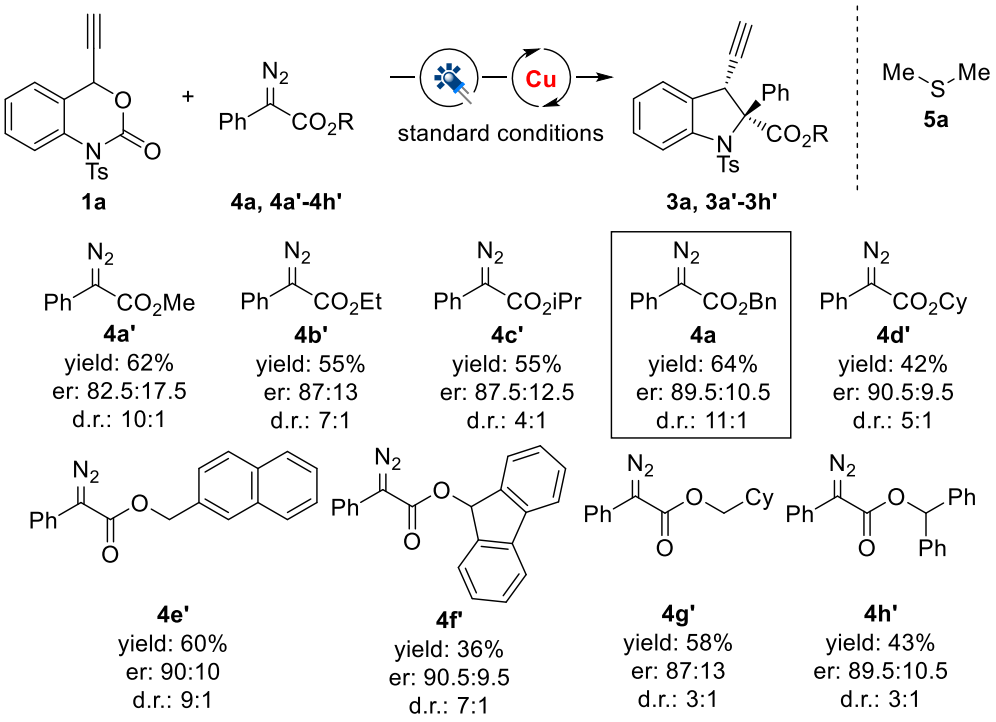
Table S2 The effect of sulfur ether[a]



Entry	R^1	R^2	Yield (%)[b]	d.r.[c]	e.r.[d]
1	Me	Me	62	10:1	82.5:17.5
2	Me	Et	59	8:1	70:30
3	Et	Et	44	5:1	77:23
4	Me	Ph	trace	-	-

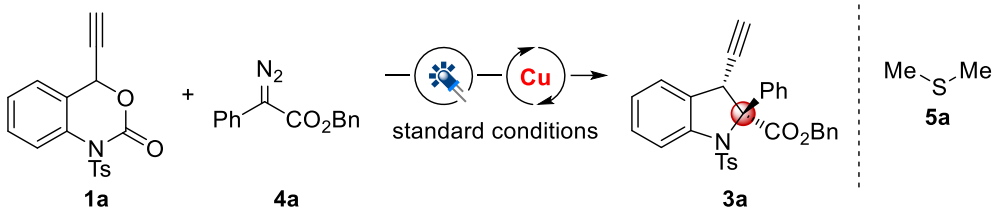
[a]Reaction conditions: **5a-5d** (0.4 mmol), **4a'** (0.2 mmol) in 1 mL anhydrous toluene at r.t. under 6 W blue LEDs for 6 h; then the resulting solution of **5a-5d** together with **1a** (0.1 mmol) were added to the pre-prepared soultion of $Cu(OTf)_2$ (10 mol%), ligand (15 mol%) and $^iPr_2NEt$ (0.12 mmol) in 1 mL anhydrous THF at 0 °C. [b]Yield of isolated product. [c]The diastereomeric ratios were determined by ^1H NMR spectroscopic analysis. [d]The er values were determined by HPLC.

Table S3 The effect of ester group[a]



[a]Reaction conditions: **5a** (0.4 mmol), **4a**, **4a'-4h'** (0.2 mmol) in 1 mL anhydrous toluene at r.t. under 6 W blue LEDs for 6 h; then the resulting solution of **4a, 4a'-4h'** together with **1a** (0.1 mmol) were added to the pre-prepared soultion of $Cu(OTf)_2$ (10 mol%), ligand (15 mol%) and $^{i}Pr_2NEt$ (0.12 mmol) in 1 mL anhydrous THF at 0 °C. [b]Yield of isolated product. [c]The diastereomeric ratios were determined by ^1H NMR spectroscopic analysis. [d]The er values were determined by HPLC.

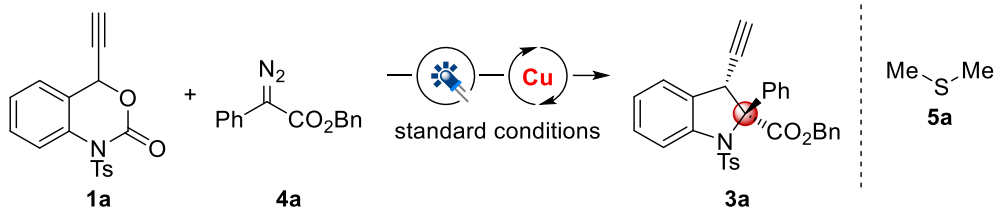
Table S4 The effect of copper salts[a]



Entry	Copper salts	Yield (%)[b]	d.r.[c]	e.r.[d]
1	$Cu(OTf)_2$	64	11:1	89.5:10.5
2	CuI	58	9:1	87.5:12.5
3	$Cu(MeCN)_4BF_4$	58	9:1	89.5:10.5
4	$Cu(MeCN)_4PF_6$	59	10:1	91:9
5	CuOTf·Tol1/2	55	15:1	89.5:10.5

[a]Reaction conditions: **5a** (0.4 mmol), **4a** (0.2 mmol) in 1 mL anhydrous toluene at r.t. under 6 W blue LEDs for 6 h; then the resulting solution of **4a** together with **1a** (0.1 mmol) were added to the pre-prepared soultion of copper salts (10 mol%), ligand (15 mol%) and $^{i}Pr_2NEt$ (0.12 mmol) in 1 mL anhydrous THF at 0 ℃. [b]Yield of isolated product. [c]The diastereomeric ratios were determined by ^1H NMR spectroscopic analysis. [d]The er values were determined by HPLC.

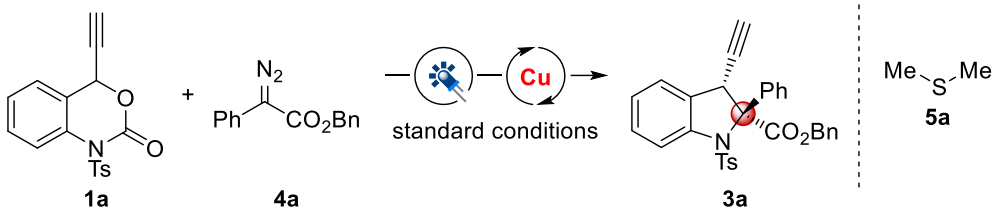
Table S5 The effect of solvent[a]



Entry	Solvent	Yield (%)[b]	d.r.[c]	e.r.[d]
1	THF	59	10:1	91:9
2	Et_2O	57	4:1	87:13
3	DCM	62	10:1	90:10
4	1,4-Dioxane	78	9:1	88.5:11.5
5	Acetone	52	10:1	91.5:8.5
6[e]	4-methyl-2-pentanone	56	13:1	93:7

[a]Reaction conditions: **5a** (0.4 mmol), **4a** (0.2 mmol) in 1 mL anhydrous toluene at r.t. under 6 W blue LEDs for 6 h; then the resulting solution of **4a** together with **1a** (0.1 mmol) were added to the pre-prepared soultion of $Cu(MeCN)_4PF_6$ (10 mol%), ligand (15 mol%) and $^{i}Pr_2NEt$ (0.12 mmol) in 1 mL anhydrous solvent at 0 ℃. [b]Yield of isolated product. [c]The diastereomeric ratios were determined by ^1H NMR spectroscopic analysis. [d]The ee values were determined by HPLC. [e]**5a** (0.4 mmol), **4a** (0.2 mmol) in 1 mL anhydrous 4-methyl-2-pentanone at r.t. under 6 W blue LEDs for 6 h; then the resulting solution of **4a** together with **1a** (0.1 mmol) were added to the pre-prepared soultion of $Cu(MeCN)_4PF_6$ (10 mol%), ligand (15 mol%) and $^{i}Pr_2NEt$ (0.12 mmol) in 1 mL anhydrous 4-methyl-2-pentanone at 0 ℃.

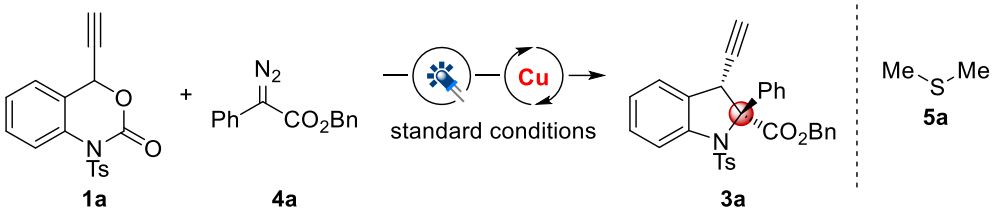
Table S6 The effect of temperature[a]



Entry	Temperature (°C)	Time	Yield (%)[b]	d.r.[c]	e.r.[d]
1	0	12 h	56	13:1	93:7
2	-10	16 h	64	13:1	94:6
3	-20	60 h	83	16:1	94:6

[a]Reaction conditions: [a]**4a** (0.4 mmol), **2a** (0.2 mmol) in 1 mL anhydrous 4-methyl-2-pentanone at r.t. under 6 W blue LEDs for 6 h; then the resulting solution of **4a** together with **1a** (0.1 mmol) were added to the pre-prepared soultion of $Cu(MeCN)_4PF_6$ (10 mol%), ligand (15 mol%) and $^{i}Pr_2NEt$ (0.12 mmol) in 1 mL anhydrous 4-methyl-2-pentanone at indicated temperature. [b]Yield of isolated product. [c]The diastereomeric ratios were determined by ^1H NMR spectroscopic analysis. [d]The er values were determined by HPLC.

Table S7 The effect of concentration[a]



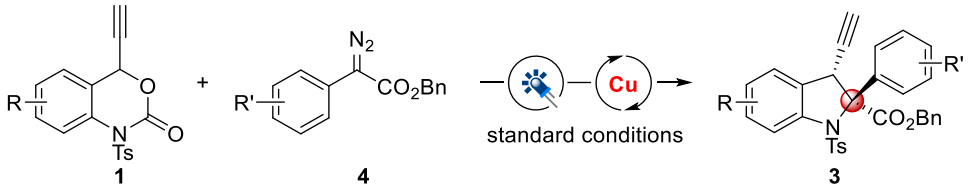
1a 4a 3a

Entry	Concentration	Yield (%)[b]	d.r.[c]	e.r.[d]
1	1 mL	57	13:1	91.5:8.5
2	2 mL	83	16:1	94:6
3	3 mL	82	19:1	95:5
4	4 mL	75	19:1	94.5:5.5

[a]Reaction conditions: [a]**4a** (0.4 mmol), **2a** (0.2 mmol) in 1 mL anhydrous 4-methyl-2-pentanone at r.t. under 6 W blue LEDs for 6 h; then the resulting solution of **4a** together with **1a** (0.1 mmol) were added to the pre-prepared soultion of $Cu(MeCN)_4PF_6$ (10 mol%), ligand (15 mol%) and $^{i}Pr_2NEt$ (0.12 mmol) in X mL anhydrous 4-methyl-2-pentanone at indicated temperature. [b]Yield of isolated product. [c]The diastereomeric ratios were determined by ^1H NMR spectroscopic analysis. [d]The er values were determined by HPLC.

3. General Procedures and Characterization Data of Products

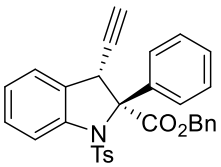
3.1 General Procedures



General procedure (one-pot procedure with product **3a** as an example)**:** Under argon atmosphere, a flame-dried 10 mL Schlenk tube was charged with dimethyl sulfide (0.4 mmol, 4.0 equiv), α-diazoketesters (0.2 mmol, 2.0 equiv) and anhydrous 4-Methyl-2-pentanone (1 mL). The resulting solution was stirred for 6 h at room temperature. To another flame-dried 10 mL Schlenk tube, $Cu(MeCN)_4PF_6$ (0.01 mmol, 10 mol%), L (0.015 mmol, 15 mol%) and anhydrous 4-Methyl-2-pentanone (1 mL) were added and the resulting solution was stirred for 30 min at room temperature. Then, the reaction mixture was cooled to -20 ℃, after that, the reaction solution in the first Schlenk were moved to the second one and ethynyl benzoxazinanones (0.1 mmol), i-Pr_2NEt (0.12 mmol, 1.2 eq.) and anhydrous 4-Methyl-2-pentanone (1 mL) were added sequentially. The resulting solution was stirred until complete conversion of ethynyl benzoxazinanones (monitored by TLC). 4-Methyl-2-pentanone was removed under the reduced pressure and the residue was purified by flash column chromatography on silica gel (petrol ether/ethyl acetate = 20/1 to 10/1) to afford the product.

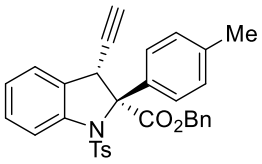
3.2 Characterization Data of Products

Benzyl (2S,3S)-3-ethynyl-2-phenyl-1-tosylindoline-2-carboxylate (**3a**)



82% isolated yield, colorless oil, $[\alpha]_D^{25}$ = 3.60 (c = 0.75 in $CHCl_3$); 95:5 er, 19:1 d.r., determined by HPLC analysis (Chiralpak AD-H column, hexane/*i*-PrOH, 80:20 v/v, flow rate 0.5 mL/min, λ = 254 nm, 25 ºC), tR (major) = 48.32 min, tR (minor) = 50.86 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.75 – 7.65 (m, 2H), 7.51 – 7.43 (m, 1H), 7.32 – 7.27 (m, 4H), 7.26 – 7.21 (m, 8H), 7.08 – 7.02 (m, 1H), 6.99 (d, *J* = 8.1 Hz, 2H), 5.32 (d, *J* = 12.7 Hz, 1H), 5.22 (d, *J* = 12.6 Hz, 1H), 4.82 – 4.75 (m, 1H), 2.29 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.8, 143.6, 141.5, 139.6, 137.0, 135.1, 129.2, 129.1, 128.2, 128.2, 128.2, 128.0, 128.0, 127.8, 127.2, 127.0, 124.7, 123.1, 113.0, 79.6, 79.4, 75.0, 67.5, 50.1, 21.4. **HRMS** (ESI) for $C_{31}H_{25}NO_4S$ $[M+Na]^+$: calcd 530.1397, found 530.1390.

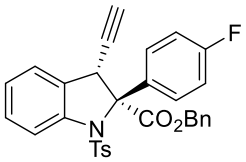
Benzyl (2S,3S)-3-ethynyl-2-(p-tolyl)-1-tosylindoline-2-carboxylate (**3b**)



60% isolated yield, colorless oil, $[\alpha]_D^{25}$ = 26.10 (c = 0.99 in $CHCl_3$); 91.5:8.5 er, 7:1 d.r., determined by HPLC analysis (Chiralpak AD-H column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 ºC), tR (major) = 23.40 min, tR (minor) = 44.10 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.44 (m, 2H), 7.41 – 7.35 (m, 1H), 7.23 – 7.18 (m, 4H), 7.18 – 7.13 (m, 5H), 7.00 – 6.93 (m, 3H), 6.93 – 6.87 (m, 2H), 5.24 (d, *J* = 12.6 Hz, 1H), 5.13 (d, *J* = 12.7 Hz, 1H), 4.72 – 4.66 (m, 1H), 2.26 (s, 3H), 2.23 – 2.18 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.9, 143.5, 141.6, 138.1, 137.1, 136.6, 135.1, 129.2, 129.0, 128.5, 128.1, 128.1, 128.0, 127.8, 127.2, 127.1,

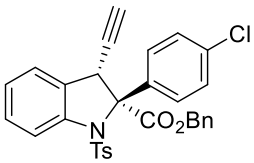
124.7, 123.1, 113.1, 79.6, 79.5, 74.9, 67.5, 50.0, 21.4, 21.0. **HRMS** (ESI) for $C_{12}H_{27}NO_4S$ $[M+Na]^+$: calcd 544.1553, found 544.1550.

Benzyl (2S,3S)-3-ethynyl-2-(4-fluorophenyl)-1-tosylindoline-2-carboxylate (**3c**)



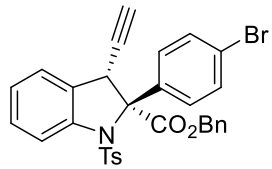
78% isolated yield, colorless oil, $[\alpha]_D^{25}$ = -3.33 (c = 0.91 in $CHCl_3$); 94.5:5.5 er, 19:1 d.r., determined by HPLC analysis (Chiralpak AD-H column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 ºC), tR (major) = 19.19 min, tR (minor) = 24.35 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 8.7, 5.2 Hz, 2H), 7.53 – 7.45 (m, 1H), 7.34 – 7.28 (m, 3H), 7.28 – 7.22 (m, 4H), 7.22 – 7.16 (m, 2H), 7.10 – 6.98 (m, 3H), 6.93 (t, *J* = 8.5 Hz, 2H), 5.30 (d, *J* = 12.7 Hz, 1H), 5.18 (d, *J* = 12.7 Hz, 1H), 4.71 (d, *J* = 2.5 Hz, 1H), 2.30 – 2.27 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.0, 162.3 (d, *J* = 248.5 Hz), 144.2, 141.8, 137.3, 135.8, (d, *J* = 3.4 Hz) 135.2, 130.5 (d, *J* = 8.1 Hz), 129.6, 129.5, 128.5, 128.3, 128.2, 127.4, 127.1, 125.1, 123.6, 115.0 (d, *J* = 21.4 Hz), 113.4, 79.4, 75.5, 67.9, 50.6, 21.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -113.64. **HRMS** (ESI) for $C_{31}H_{24}FNO_4S$ $[M+Na]^+$: calcd 548.1302, found 548.1309.

Benzyl (2S,3S)-2-(4-chlorophenyl)-3-ethynyl-1-tosylindoline-2-carboxylate (**3d**)



84% isolated yield, white semi-solid, $[\alpha]_D^{25}$ = 32.93 (c = 1.0 in $CHCl_3$); 95:5 er, 17:1 d.r., determined by HPLC analysis (Chiralpak AD-H column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 ºC), tR (major) = 18.02 min, tR (minor) = 33.51 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 – 7.61 (m, 2H), 7.54 – 7.49 (m, 1H), 7.25 – 7.21 (m, 3H), 7.21 – 7.17 (m, 3H), 7.09 – 6.98 (m, 3H), 6.97 – 6.87 (m, 1H), 7.04 (dd, *J* = 22.0, 7.8 Hz, 3H), 6.97 – 6.86 (m, 1H), 5.28 (d, *J* = 12.7 Hz, 1H), 5.16 (d, *J* = 12.4 Hz, 1H), 4.69 – 4.65 (m, *J* = 2.5 Hz, 1H), 2.30 (s, 1H), 2.29 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.5, 143.9, 141.5, 138.0, 136.9, 134.9, 134.3, 129.6, 129.3, 129.2, 128.2, 128.0, 127.9, 127.9, 127.0, 126.7, 124.7, 123.3, 113.1, 79.0, 78.9, 75.2, 67.6, 50.1, 21.5. **HRMS** (ESI) for $C_{31}H_{24}ClNO_4S$ $[M+Na]^+$: calcd 564.1007, found 564.1011.

Benzyl (2S,3S)-2-(4-bromophenyl)-3-ethynyl-1-tosylindoline-2-carboxylate (**3e**)

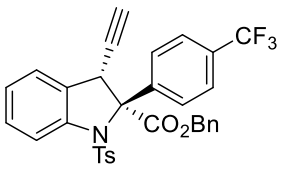


77% isolated yield, white solid, $[\alpha]_D^{25}$ = 22.43 (c = 0.86 in $CHCl_3$); 94.5:5.5 er, 18:1 d.r., determined by HPLC analysis (Chiralpak AD-H column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 ºC), tR (major) = 18.68 min, tR (minor) = 39.75 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 – 7.49 (m, 3H), 7.38 – 7.27 (m, 6H), 7.26 – 7.21 (m, 3H), 7.21 – 7.14 (m, 2H), 7.12 – 6.99 (m, 3H), 5.29 (d, *J* = 12.7 Hz, 1H), 5.16 (d, *J* = 12.7 Hz, 1H), 4.70 – 4.64 (m, 1H), 2.31 (s, 3H), 2.29 (d, *J* = 2.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.5, 143.9, 141.6, 138.5, 137.0, 134.9, 130.9, 129.9, 129.4, 129.2, 128.2, 127.9, 127.9, 127.0, 126.7, 124.7, 123.3, 122.5, 113.1, 79.0, 78.9, 75.2, 67.6, 50.1, 21.5. **HRMS** (ESI) for $C_{31}H_{24}BrNO_4S$ $[M+Na]^+$: calcd 608.0502, found 608.0503.

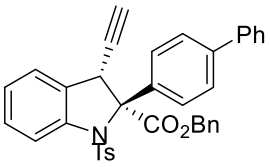
Benzyl (2S,3S)-3-ethynyl-1-tosyl-2-(4-(trifluoromethyl)phenyl)indoline-2-carboxylate (**3f**)

63% isolated yield, colorless oil, $[\alpha]_D^{25}$ = 2.97 (c = 0.97 in $CHCl_3$); 90:10 er, 19:1 d.r., determined by HPLC analysis (Chiralpak AD-H column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min, λ = 210

nm, 25 °C), tR (major) = 12.64 min, tR (minor) = 31.82 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 – 7.82 (m, 2H), 7.56 – 7.55 (m, 1H), 7.50 – 7.45 (m, 2H), 7.33 – 7.26 (m, 4H), 7.26 – 7.21 (m, 3H), 7.20 – 7.13 (m, 2H), 7.12 – 7.05 (m, 1H), 7.02 – 6.95 (m, 2H), 5.29 (d, *J* = 12.6 Hz, 1H), 5.16 (d, *J* = 12.7 Hz, 1H), 4.71 – 4.65 (m, 1H), 2.31 (d, *J* = 2.6 Hz, 1H), 2.29 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.3, 144.0, 143.3, 141.6, 136.8, 134.8, 130.4, 130.1, 129.5, 129.4, 129.2, 128.6, 128.6, 128.2, 127.9, 126.9, 126.7, 124.8 (q, *J* = 3.7 Hz), 123.5, 113.2, 78.9, 78.7, 75.3, 67.7, 50.2, 21.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -62.77. **HRMS** (ESI) for $C_{32}H_{21}F_3NO_2S$ $[M+Na]^+$: calcd 598.1270, found 598.1259.

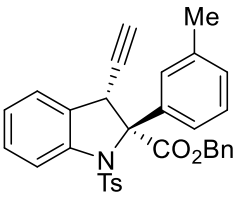


Benzyl (2S,3S)-2-([1,1'-biphenyl]-4-yl)-3-ethynyl-1-tosylindoline-2-carboxylate (3g)



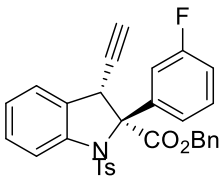
59% isolated yield, white solid, $[\alpha]_D^{25}$ = 6.60 (c = 0.31 in $CHCl_3$); 91:9 er, 13:1 d.r., determined by HPLC analysis (Chiralpak IC-H column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C), tR (major) = 75.95 min, tR (minor) = 32.13 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 – 7.71 (m, 2H), 7.60 – 7.48 (m, 3H), 7.49-7.42 (m, 4H), 7.40 – 7.34 (m, 1H), 7.33 – 7.23 (m, 9H), 7.12 – 7.04 (m, 1H), 6.99 – 6.92 (m, 2H), 5.34 (d, *J* = 12.6 Hz, 1H), 5.25 (d, *J* = 12.6 Hz, 1H), 4.87 – 4.80 (m, 1H), 2.31 (d, *J* = 2.6 Hz, 1H), 2.27 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.9, 143.6, 141.0, 140.3, 138.4, 137.1, 135.1, 129.3, 129.1, 128.8, 128.7, 128.2, 128.0, 127.8, 127.6, 127.1, 127.0, 126.5, 124.8, 123.2, 113.1, 79.3, 79.3, 75.0, 67.6, 50.1, 21.4. **HRMS** (ESI) for $C_{37}H_{29}NO_4S$ $[M+Na]^+$: calcd 606.1710, found 606.1700.

Benzyl (2S,3S)-3-ethynyl-2-(m-tolyl)-1-tosylindoline-2-carboxylate (3h)



74% isolated yield, colorless oil, $[\alpha]_D^{25}$ = -5.90 (c = 1.02 in $CHCl_3$); 91.5:8.5 er, 12:1 d.r., determined by HPLC analysis (Chiralpak AD-H column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C), tR (major) = 14.85 min, tR (minor) = 18.98 min; **^{1}H NMR** δ 7.62 – 7.57 (m, 1H), 7.55 – 7.50 (m, 1H), 7.34 (s, 1H), 7.32 – 7.26 (m, 2H), 7.25 – 7.20 (m, 7H), 7.19 – 7.12 (m, 1H), 7.11 – 7.03 (m, 2H), 7.01 – 6.95 (m, 2H), 5.33 (d, *J* = 12.7 Hz, 1H), 5.22 (d, *J* = 12.7 Hz, 1H), 4.80 – 4.74 (m, 1H), 2.31 – 2.27 (m, 4H), 2.18 (s, 3H); **^{13}C NMR** δ 168.2, 143.8, 142.0, 139.5, 137.8, 137.4, 135.5, 129.5, 129.3, 129.2, 129.1, 128.5, 128.2, 128.2, 128.1, 127.4, 127.4, 125.8, 125.0, 123.4, 113.3, 79.8, 79.6, 75.3, 67.7, 50.6, 21.7, 21.7. **HRMS** (ESI) for $C_{32}H_{27}NO_4S$ $[M+Na]^+$: calcd 544.1553, found 544.1558.

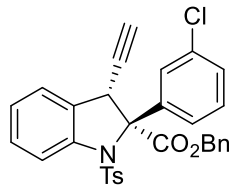
Benzyl (2S,3S)-3-ethynyl-2-(3-fluorophenyl)-1-tosylindoline-2-carboxylate (3i)



83% isolated yield, colorless oil, $[\alpha]_D^{25}$ = 1.18 (c = 0.91 in $CHCl_3$); 92:8 er, 12:1 d.r., determined by HPLC analysis (Chiralpak AD-H column, hexane/*i*-PrOH, 80:20 v/v, flow rate 0.5 mL/min, λ = 220 nm, 25 °C), tR (major) = 39.77 min, tR (minor) = 37.77 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 – 7.46 (m, 3H), 7.39 – 7.33 (m, 2H), 7.33 – 7.26 (m, 2H), 7.25 – 7.15 (m, 6H), 7.10 – 6.96 (m, 4H), 5.29 (d, *J* = 12.7 Hz, 1H), 5.16 (d, *J* = 12.7 Hz, 1H), 4.70 – 4.65 (m, 1H), 2.32 – 2.27 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.4, 162.21 (d, *J* = 1.9 Hz), 143.9, 142.0 (d, *J* = 7.4 Hz), 141.6, 136.9, 134.9, 129.4 (d, *J* = 8.2 Hz), 129.2, 128.2, 127.9, 127.8, 127.1, 126.8, 124.7, 123.7, 123.7 (d, *J* = 2.9 Hz),

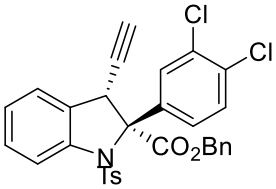
123.3, 115.7 (d, *J* = 24.3 Hz), 115.1 (d, *J* = 21.0 Hz), 113.1, 79.0 (d, *J* = 1.9 Hz), 78.8, 75.22 , 67.6, 50.3, 21.5; **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -112.40. **HRMS** (ESI) for $C_{31}H_{24}FNO_4S$ $[M+Na]^+$: calcd 548.1302, found 548.1308.

Benzyl (2S,3S)-2-(3-chlorophenyl)-3-ethynyl-1-tosylindoline-2-carboxylate (3j)



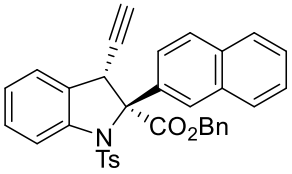
62% isolated yield, white solid, $[\alpha]_D^{25}$ = -49.90 (c = 1.0 in $CHCl_3$); 91.5:8.5 er, 14:1 d.r., determined by HPLC analysis (Chiralpak AD-H column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 ºC), tR (major) = 15.96 min, tR (minor) = 17.34 min; **^{1}H NMR** (400 MHz, $CDCl_3$) 1H NMR (400 MHz, Chloroform-d) δ 7.72 – 7.67 (m, 1H), 7.51 – 7.46 (m, 2H), 7.28 – 7.23 (m, 3H), 7.20 – 7.14 (m, 6H), 7.13 – 7.08 (m, 2H), 7.02 – 6.95 (m, 3H), 5.23 (d, *J* = 12.7 Hz, 1H), 5.10 (d, *J* = 12.7 Hz, 1H), 4.61 – 4.55 (m, 1H), 2.24 (s, 3H), 2.23 (d, *J* = 2.6 Hz, 1H).; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.4, 144.0, 141.3, 136.9, 134.9, 133.9, 129.3, 129.3, 129.3, 129.2, 128.3, 128.2, 127.9, 127.8, 126.9, 126.7, 126.5, 124.7, 123.3, 113.1, 78.9, 78.7, 75.3, 67.6, 50.4, 21.5. **HRMS** (ESI) for $C_{31}H_{24}ClNO_4S$ $[M+Na]^+$: calcd 564.1007, found 564.1011.

Benzyl (2S,3S)-2-(3,4-dichlorophenyl)-3-ethynyl-1-tosylindoline-2-carboxylate (3k)



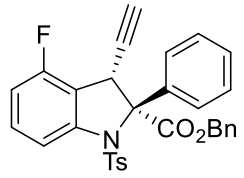
72% isolated yield, colorless oil, $[\alpha]_D^{25}$ = -7.30 (c = 0.92 in $CHCl_3$); 91.5:8.5 er, 19:1 d.r., determined by HPLC analysis (Chiralpak AD-H column, hexane/*i*-PrOH, 80:20 v/v, flow rate 0.5 mL/min, λ = 254 nm, 25 ºC), tR (major) = 25.68 min, tR (minor) = 41.50 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.67 – 7.64 (m, 1H), 7.62 – 7.57 (m, 1H), 7.40 – 7.34 (m, 2H), 7.34 – 7.21 (m, 6H), 7.18 – 7.12 (m, 2H), 7.11 – 7.01 (m, 3H), 5.28 (d, *J* = 12.6 Hz, 1H), 5.14 (d, *J* = 12.6 Hz, 1H), 4.63 – 4.59 (m, 1H), 2.33 (s, 3H), 2.30 (d, *J* = 2.5 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.2, 144.2, 141.7, 139.4, 137.0, 134.8, 132.5, 132.1, 130.2, 129.7, 129.5, 129.3, 128.2, 127.9, 127.9, 127.7, 126.7, 126.5, 124.8, 123.5, 113.2, 78.4, 75.5, 67.7, 50.3, 21.5. **HRMS** (ESI) for $C_{31}H_{23}Cl_2NO_4S$ $[M+Na]^+$: calcd 598.0617, found 598.0624.

Benzyl (2S,3S)-3-ethynyl-2-(naphthalen-2-yl)-1-tosylindoline-2-carboxylate (3l)



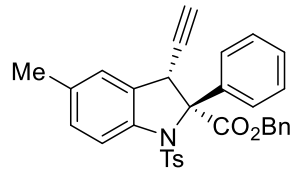
54% isolated yield, white solid, $[\alpha]_D^{25}$ = 26.60 (c = 0.94 in $CHCl_3$); 90:10 er, 9:1 d.r., determined by HPLC analysis (Chiralpak AD-H column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 ºC), tR (major) = 25.77 min, tR (minor) = 45.25 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 1.9 Hz, 1H), 7.80 – 7.75 (m, 1H), 7.74 – 7.70 (m, 1H), 7.65 – 7.56 (m, 3H), 7.53 – 7.43 (m, 2H), 7.36 – 7.29 (m, 2H), 7.25 (s, 5H), 7.18 (d, *J* = 8.2 Hz, 2H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.78 (d, *J* = 8.1 Hz, 2H), 5.37 (d, *J* = 12.6 Hz, 1H), 5.25 (d, *J* = 12.7 Hz, 1H), 4.87 (d, *J* = 2.6 Hz, 1H), 2.30 (d, *J* = 2.6 Hz, 1H), 2.20 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.9, 143.5, 141.9, 137.1, 136.2, 135.2, 132.8, 132.5, 129.3, 129.0, 128.9, 128.2, 128.0, 127.8, 127.6, 127.1, 127.1, 126.9, 126.7, 126.1, 125.4, 124.8, 123.2, 113.2, 79.6, 79.2, 75.0, 67.5, 50.2, 21.3. **HRMS** (ESI) for $C_{35}H_{27}NO_4S$ $[M+Na]^+$: calcd 580.1553, found 580.1551.

Benzyl (2S,3S)-3-ethynyl-4-fluoro-2-phenyl-1-tosylindoline-2-carboxylate (3m)



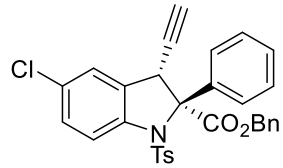
82% isolated yield, colorless oil, $[\alpha]_D^{25}$ = 29.13 (c = 0.98 in $CHCl_3$); 95:5 er, 10:1 d.r., determined by HPLC analysis (Chiralpak AZ-H column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C), tR (major) = 24.16 min, tR (minor) = 36.40 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 – 7.63 (m, 2H), 7.37 – 7.31 (m, 3H), 7.31 – 7.26 (m, 6H), 7.24 – 7.15 (m, 2H), 7.02 – 6.95 (m, 2H), 6.78 – 6.69 (m, 1H), 5.35 (d, *J* = 12.5 Hz, 1H), 5.29 (d, *J* = 12.5 Hz, 1H), 4.86 – 4.81 (m, 1H), 2.32 (d, *J* = 2.6 Hz, 1H), 2.29 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.6, 158.8 (d, *J* = 250.0 Hz), 143.8, 143.7 (d, *J* = 6.9 Hz), 139.4, 136.6, 135.0, 131.3 (d, *J* = 8.6 Hz), 129.2, 128.5, 128.4, 128.3, 128.1, 128.0, 128.0, 127.4, 113.4 (d, *J* = 19.9 Hz), 110.2 (d, *J* = 19.5 Hz), 108.9 (d, *J* = 3.3 Hz), 80.6, 78.0, 75.1, 67.9, 46.5, 21.5; **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -117.26. **HRMS** (ESI) for $C_{31}H_{24}FNO_4S$ $[M+Na]^+$: calcd 548.1302, found 548.1302.

Benzyl (2S,3S)-3-ethynyl-5-methyl-2-phenyl-1-tosylindoline-2-carboxylate (3n)



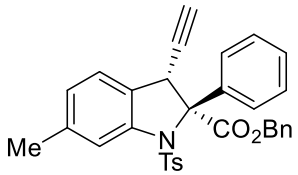
61% isolated yield, colorless oil, $[\alpha]_D^{25}$ = 0.57 (c = 1.05 in $CHCl_3$); 93.5:6.5 er, 9:1 d.r., determined by HPLC analysis (Chiralpak AD-H column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C), tR (major) = 75.26 min, tR (minor) = 80.24 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 – 7.65 (m, 2H), 7.37 – 7.32 (m, 1H), 7.30 – 7.21 (m, 10H), 7.10 – 7.04 (m, 2H), 7.00 – 6.94 (m, 2H), 5.31 (d, *J* = 12.7 Hz, 1H), 5.21 (d, *J* = 12.7 Hz, 1H), 4.76 – 4.71 (m, 1H), 2.31 (s, 3H), 2.29 (d, *J* = 2.6 Hz, 1H), 2.28 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 167.9, 143.5, 139.6, 139.3, 137.1, 135.1, 132.9, 129.7, 129.0, 128.3, 128.2, 128.1, 128.0, 127.9, 127.9, 127.2, 127.0, 125.2, 112.8, 79.8, 79.6, 74.9, 67.5, 50.1, 21.4, 20.7. **HRMS** (ESI) for $C_{32}H_{27}NO_4S$ $[M+Na]^+$: calcd 544.1553, found 544.1553.

Benzyl (2S,3S)-5-chloro-3-ethynyl-2-phenyl-1-tosylindoline-2-carboxylate (3o)



63% isolated yield, colorless oil, $[\alpha]_D^{25}$ = -11.07 (c = 0.89 in $CHCl_3$); 91.5:8.5 er, 10:1 d.r., determined by HPLC analysis (Chiralpak AD-H column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C), tR (major) = 14.48 min, tR (minor) = 20.85 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 – 7.63 (m, 2H), 7.44 – 7.38 (m, 1H), 7.34 – 7.26 (m, 6H), 7.25 – 7.17 (m, 6H), 7.04 – 6.97 (m, 2H), 5.32 (d, *J* = 12.6 Hz, 1H), 5.20 (d, *J* = 12.6 Hz, 1H), 4.78 – 4.71 (m, 1H), 2.33 – 2.27 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 167.5, 143.9, 140.3, 139.0, 136.6, 134.9, 129.2, 128.8, 128.4, 128.2, 128.1, 128.1, 128.0, 127.1, 124.9, 113.9, 80.0, 78.4, 75.6, 67.7, 49.7, 21.5. HRMS (ESI) for $C_{31}H_{24}ClNO_4S$ $[M+Na]^+$: calcd 564.1007, found 564.1003.

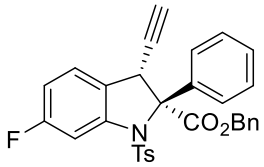
Benzyl (2S,3S)-3-ethynyl-6-methyl-2-phenyl-1-tosylindoline-2-carboxylate (3p)



61% isolated yield, colorless oil, $[\alpha]_D^{25}$ = 3.67 (c = 0.88 in $CHCl_3$); 92.5:7.5 er, 6:1 d.r., determined by HPLC analysis (Chiralpak AD-H column, hexane/*i*-PrOH, 80:20 v/v, flow rate 0.5 mL/min, λ = 254 nm, 25 °C), tR (major) = 31.58 min, tR (minor) = 45.35 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 – 7.65 (m, 2H), 7.30 – 7.24 (m, 7H), 7.24 – 7.20 (m, 4H), 7.18 – 7.13 (m, 1H), 7.00 – 6.95 (m, 2H), 6.88 – 6.83 (m, 1H), 5.32 (d, *J* = 12.6 Hz, 1H), 5.23 (d, *J* =

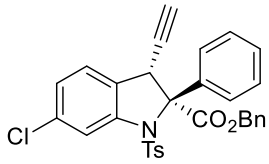
12.6 Hz, 1H), 4.77 – 4.72 (m, 1H), 2.36 (s, 3H), 2.29 (s, 3H), 2.27 (d, *J* = 2.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.9, 143.5, 141.6, 139.7, 139.5, 137.1, 135.1, 129.1, 128.2, 128.2, 128.1, 127.9, 127.8, 127.2, 124.4, 124.2, 124.0, 113.7, 79.9, 79.7, 74.8, 67.6, 49.8, 21.9, 21.4. **HRMS** (ESI) for $C_{32}H_{27}NO_4S$ $[M+Na]^+$: calcd 544.1553, found 544.1555.

Benzyl (2S,3S)-3-ethynyl-6-fluoro-2-phenyl-1-tosylindoline-2-carboxylate (3q)



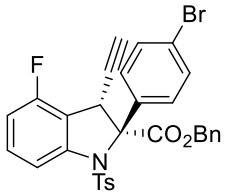
73% isolated yield, colorless oil, $[\alpha]_D^{25}$ = 2.20 (c = 0.74 in $CHCl_3$); 94:6 er, 11:1 d.r., determined by HPLC analysis (Chiralpak AD-H column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C), tR (major) = 14.89 min, tR (minor) = 21.56 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 – 7.64 (m, 2H), 7.34 – 7.15 (m, 12H), 7.01 (d, J = 8.1 Hz, 2H), 6.74 (td, *J* = 8.5, 2.3 Hz, 1H), 5.33 (d, *J* = 12.6 Hz, 1H), 5.24 (d, *J* = 12.6 Hz, 1H), 4.78 – 4.72 (m, 1H), 2.31 (s, 3H), 2.29 (d, J = 2.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.6, 163.6 (d, *J* = 245.1 Hz), 143.9, 142.9 (d, *J* = 12.0 Hz), 139.0, 136.6, 135.0, 129.2, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.2, 125.5 (d, *J* = 10.1 Hz), 122.5 (d, *J* = 2.5 Hz), 109.7 (d, *J* = 23.1 Hz), 101.5 (d, *J* = 29.5 Hz), 80.4, 79.0, 75.2, 67.7, 49.5, 21.5; **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -111.36. **HRMS** (ESI) for $C_{31}H_{24}FNO_4S$ $[M+Na]^+$: calcd 548.1302, found 548.1304.

Benzyl (2S,3S)-6-chloro-3-ethynyl-2-phenyl-1-tosylindoline-2-carboxylate (3r)



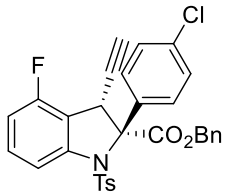
70% isolated yield, colorless oil, $[\alpha]_D^{25}$ = 12.33 (c = 1.33 in $CHCl_3$); 91:9 er, 11:1 d.r., determined by HPLC analysis (Chiralpak AD-H column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min, λ = 220 nm, 25 °C), tR (major) = 14.20 min, tR (minor) = 20.74 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 – 7.62 (m, 2H), 7.52 – 7.47 (m, 1H), 7.33 – 7.26 (m, 6H), 7.26 – 7.22 (m, 2H), 7.21 – 7.15 (m, 3H), 7.05 – 6.99 (m, 3H), 5.32 (d, *J* = 12.6 Hz, 1H), 5.24 (d, *J* = 12.6 Hz, 1H), 7.76 – 7.71 (m, 1H), 2.31 (s, 3H), 2.28 (d, *J* = 2.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.5, 144.0, 142.7, 139.0, 136.6, 135.1, 135.0, 129.3, 128.4, 128.3, 128.2, 128.1, 128.1, 127.9, 127.2, 125.7, 125.5, 123.2, 113.4, 80.1, 78.7, 75.4, 67.7, 49.6, 21.5. HRMS (ESI) for $C_{31}H_{24}ClNO_4S$ $[M+Na]^+$: calcd 564.1007, found 564.1057.

Benzyl (2S,3S)-2-(4-bromophenyl)-3-ethynyl-4-fluoro-1-tosylindoline-2-carboxylate (3s)



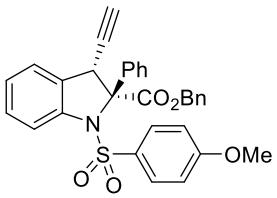
78% isolated yield, colorless oil, $[\alpha]_D^{25}$ = 170.43 (c = 1.0 in $CHCl_3$); 96:4 er, 15:1 d.r., determined by HPLC analysis (Chiralpak AZ-H column, hexane/*i*-PrOH, 75:25 v/v, flow rate 1.0 mL/min, λ = 220 nm, 25 °C), tR (major) = 25.79 min, tR (minor) = 56.75 min; **^{1}H NMR** (400 MHz, $CDCl_3$) 1H NMR (400 MHz, Chloroform-d) δ 7.56 – 7.51 (m, 2H), 7.38 – 7.32 (m, 4H), 7.32 – 7.28 (m, 5H), 7.24 – 7.22 (m, 2H), 7.03 (d, *J* = 8.1 Hz, 2H), 6.78 – 6.72 (m, 1H), 5.33 (d, *J* = 12.3 Hz, 1H), 5.25 (d, *J* = 12.5 Hz, 1H), 4.73 (d, *J* = 2.5 Hz, 1H), 2.33 – 2.32 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.3, 158.8 (d, *J* = 250.2 Hz), 144.1, 143.7 (d, *J* = 6.8 Hz), 138.3, 136.6, 134.8, 131.5 (d, J = 8.5 Hz), 131.1, 129.4, 129.3, 128.3, 128.3, 128.1, 127.1, 122.9, 113.1 (d, J = 19.8 Hz), 110.4 (d, J = 19.5 Hz), 108.9 (d, J = 3.4 Hz), 79.9, 77.6, 75.3, 68.0, 46.5, 21.5; **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -117.01. HRMS (ESI) for $C_{31}H_{23}BrFNO_4S$ $[M+Na]^+$: calcd 626.0407, found 626.0401.

Benzyl (2S,3S)-2-(4-chlorophenyl)-3-ethynyl-4-fluoro-1-tosylindoline-2-carboxylate (3t)



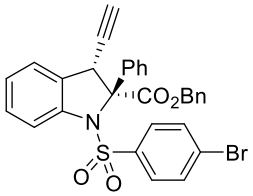
81% isolated yield, colorless oil, $[\alpha]_D^{25}$ = 76.1 (c = 1.0 in $CHCl_3$); 95.5:4.5 er, 16:1 d.r., determined by HPLC analysis (Chiralpak AZ-H column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min, λ = 220 nm, 25 °C), tR (major) = 27.63 min, tR (minor) = 60.14 min; **^{1}H NMR** (400 MHz, $CDCl_3$) 1H NMR (400 MHz, Chloroform-d) δ 7.63 – 7.58 (m, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.32 – 7.27 (m, 5H), 7.25 – 7.19 (m, 4H), 7.03 (d, *J* = 8.1 Hz, 2H), 6.78 – 6.71 (m, 1H), 5.33 (d, *J* = 12.4 Hz, 1H), 5.25 (d, *J* = 12.5 Hz, 1H), 4.73 (d, *J* = 2.5 Hz, 1H), 2.34 – 2.30 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.3, 158.8 (d, *J* = 250.1 Hz), 144.1, 143.7, 137.8, 136.7 (d, *J* = 11.4 Hz), 131.5 (d, *J* = 8.5 Hz), 129.4, 129.3, 128.4, 128.3, 128.1, 128.1, 127.1, 126.6, 122.9, 113.2 (d, *J* = 19.6 Hz), 110.4 (d, *J* = 19.3 Hz), 108.9 (d, *J* = 3.5 Hz), 79.9, 77.6, 75.3, 68.1, 46.5, 21.5; **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -117.07. HRMS (ESI) for $C_{31}H_{23}ClFNO_4S$ $[M+Na]^+$: calcd 582.0913, found 582.0915.

Benzyl (2S,3S)-3-ethynyl-1-((4-methoxyphenyl)sulfonyl)-2-phenylindoline-2-carboxylate (3u)



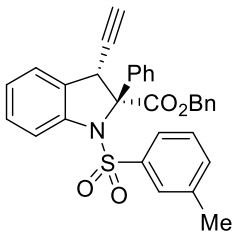
80% isolated yield, white solid, $[\alpha]_D^{25}$ = 20.53 (c = 1.20 in $CHCl_3$); 94.5:5.5 er, 15:1 d.r., determined by HPLC analysis (Chiralpak AD-H column, hexane/*i*-PrOH, 90:10 v/v, flow rate 0.5 mL/min, λ = 254 nm, 25 °C), tR (major) = 69.58 min, tR (minor) = 66.05 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 – 7.67 (m, 2H), 7.46 – 7.40 (m, 1H), 7.33 – 7.23 (m, 12H), 7.07 – 7.00 (m, 1H), 6.67 – 6.61 (m, 2H), 5.32 (d, *J* = 12.7 Hz, 1H), 5.23 (d, *J* = 12.6 Hz, 1H), 4.81 – 4.76 (m, 1H), 3.74 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.9, 162.9, 141.5, 139.7, 135.1, 131.4, 129.5, 129.2, 128.2, 128.2, 128.1, 128.0, 128.0, 127.8, 127.0, 124.7, 123.1, 113.6, 112.9, 79.6, 79.4, 74.9, 67.5, 55.5, 50.1. **HRMS** (ESI) for $C_{31}H_{25}NO_4S$ $[M+Na]^+$: calcd 546.1346, found 546.1340.

Benzyl (2S,3S)-1-((4-bromophenyl)sulfonyl)-3-ethynyl-2-phenylindoline-2-carboxylate (3v)



76% isolated yield, colorless oil, $[\alpha]_D^{25}$ = 22.10 (c = 1.20 in $CHCl_3$); 92.5:7.5 er, 15:1 d.r., determined by HPLC analysis (Chiralpak AD-H column, hexane/*i*-PrOH, 90:10 v/v, flow rate 0.5 mL/min, λ = 210 nm, 25 °C), tR (major) = 32.31 min, tR (minor) = 27.64 min; **^{1}H NMR** (400 MHz, $CDCl_3$) 1H NMR (400 MHz, Chloroform-d) δ 7.68 – 7.64 (m, 2H), 7.48 – 7.43 (m, 1H), 7.33 – 7.28 (m, 5H), 7.27 – 7.24 (m, 7H), 7.20 – 7.15 (m, 2H), 7.08 (t, J = 7.5 Hz, 1H), 5.32 (d, J = 12.5 Hz, 1H), 5.24 (d, J = 12.6 Hz, 1H), 4.82 (d, J = 2.5 Hz, 1H), 2.32 (d, J = 2.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.7, 141.1, 139.2, 138.8, 134.9, 131.7, 129.4, 128.5, 128.4, 128.2, 128.1, 128.1, 128.0, 127.8, 127.0, 125.0, 123.6, 113.6, 112.9, 79.6, 79.3, 75.1, 67.7; **HRMS** (ESI) for $C_{30}H_{22}BrNO_4S$ $[M+Na]^+$: calcd 594.0345, found 594.0349.

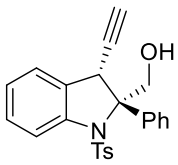
Benzyl (2S,3S)-3-ethynyl-2-phenyl-1-(m-tolylsulfonyl)indoline-2-carboxylate (3w)



75% isolated yield, colorless oil, $[\alpha]_D^{25}$ = -2.90 (c = 0.87 in $CHCl_3$); 94:6 er, 12:1 d.r., determined by HPLC analysis (Chiralpak AD-H column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C), tR (major) = 13.53 min, tR (minor) = 18.46 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 – 7.64 (m, 2H), 7.55 – 7.49 (m, 1H), 7.35 – 7.27 (m, 4H), 7.26 – 7.17 (m, 8H), 7.16 – 7.03 (m, 2H), 6.85 (s, 1H), 5.34 (d, *J* = 12.7 Hz, 1H), 5.23 (d, *J* = 12.7 Hz, 1H),

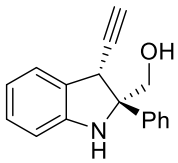
4.85 – 4.80 (m, 1H), 2.28 (d, *J* = 2.6 Hz, 1H), 2.16 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.8, 141.6, 139.8, 139.3, 138.7, 135.1, 133.5, 129.3, 128.5, 128.3, 128.2, 128.2, 128.0, 127.8, 127.8, 127.4, 127.0, 124.7, 124.1, 123.1, 113.0, 79.3, 79.2, 75.0, 67.5, 50.2, 21.2. **HRMS** (ESI) for $C_{24}H_{21}ClO_2$ $[M+Na]^+$: calcd 530.1397, found 530.1403.

((2S,3S)-3-ethynyl-2-phenyl-1-tosylindolin-2-yl)methanol (6)



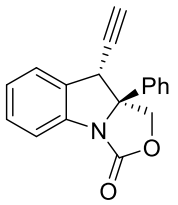
87% isolated yield, colorless oil, $[\alpha]_D^{25}$ = -1.80 (c = 1.00 in $CHCl_3$); 94.5:5.5 er, 19:1 d.r., determined by HPLC analysis (Chiralpak AD-H column, hexane/*i*-PrOH, 90:10 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C), tR (major) = 41.52 min, tR (minor) = 44.32 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 – 7.62 (m, 2H), 7.59 – 7.53 (m, 1H), 7.47 – 7.40 (m, 2H), 7.32 – 7.26 (m, 3H), 7.25 – 7.20 (m, 2H), 7.19 – 7.15 (m, 2H), 7.06 – 6.98 (m, 1H), 4.86 (dd, *J* = 12.8, 5.9 Hz, 1H), 4.75 (dd, *J* = 12.8, 8.3 Hz, 1H), 4.47 (d, *J* = 2.5 Hz, 1H), 2.78 – 2.67 (m, 1H), 2.38 (d, *J* = 2.7 Hz, 1H), 2.36 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.9, 142.1, 141.7, 137.4, 129.4, 128.9, 128.5, 128.5, 128.3, 127.9, 127.3, 126.2, 124.4, 123.7, 114.0, 79.7, 79.3, 74.9, 65.1, 47.8, 21.5. **HRMS** (ESI) for $C_{24}H_{21}NO_3S$ $[M+Na]^+$: calcd 426.1134, found 426.1126.

((2S,3S)-3-ethynyl-2-phenylindolin-2-yl)methanol (7)



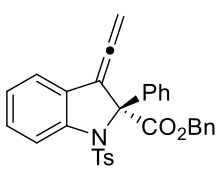
85% isolated yield, colorless oil, $[\alpha]_D^{25}$ = -12.10 (c = 1.00 in $CHCl_3$); 94.5:5.5 er, 19:1 d.r., determined by HPLC analysis (Chiralpak AD-H column, hexane/*i*-PrOH, 90:10 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C), tR (major) = 14.59 min, tR (minor) = 18.12 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (d, J = 7.7 Hz, 2H), 7.31 (t, J = 7.6 Hz, 2H), 7.27 – 7.18 (m, 2H), 7.14 (d, J = 7.9 Hz, 1H), 7.04 (t, J = 7.7 Hz, 1H), 6.83 – 6.60(m, 2H), 4.15 (d, J = 2.6 Hz, 1H), 4.07 (d, J = 11.4 Hz, 1H), 3.80 (d, J = 11.5 Hz, 1H), 2.35 (d, J = 2.3 Hz, 1H).; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.4, 143.1, 128.7, 128.6, 127.8, 127.6, 126.0, 124.1, 119.5, 110.5, 80.3, 73.3, 72.2, 66.5, 44.1. **HRMS** (ESI) for $C_{17}H_{15}NO$ $[M+Na]^+$: calcd 272.10, found 272.11

(9S,9S)-9-ethynyl-9-phenyl-9,9-dihydro-1H,3H-oxazolo[3,4-a]indol-3-one (8)



90% isolated yield, colorless oil, $[\alpha]_D^{25}$ = 6.77 (c = 1.00 in $CHCl_3$); 94.5:5.5 er, 19:1 d.r., determined by HPLC analysis (Chiralpak AD-H column, hexane/*i*-PrOH, 95:5 v/v, flow rate 1.0 mL/min, λ = 220 nm, 25 °C), tR (major) = 15.77 min, tR (minor) = 19.9 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (d, J = 7.9 Hz, 1H), 7.42 – 7.24 (m, 7H), 7.17 (t, J = 7.5 Hz, 1H), 5.32 (d, J = 8.9 Hz, 1H), 4.60 (d, J = 8.9 Hz, 1H), 4.23 (d, J = 2.6 Hz, 1H).; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.5, 144.2, 139.9, 131.8, 129.5, 128.2, 125.9, 125.5, 124.2, 116.3, 79.5, 74.5, 73.3, 46.3, 22.5. **HRMS** (ESI) for $C_{18}H_{13}NO_2$ $[M+Na]^+$: calcd 298.08, found 298.09.

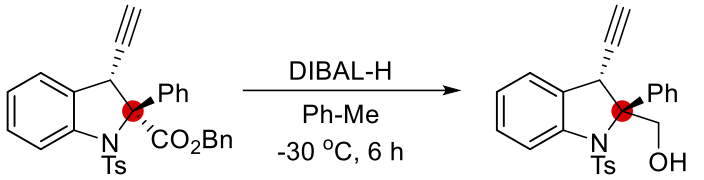
Benzyl (R)-2-phenyl-1-tosyl-3-vinylideneindoline-2-carboxylate (9)



83% isolated yield, colorless oil, [α]D^{25} = 55.57 (c = 0.85 in CHCl3); 93:7 er, determined by HPLC analysis (Chiralpak AZ-H column, hexane/i-PrOH, 80:20 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 oC), tR (major) = 13.53 min, tR (minor) = 20.70 min; **^{1}H NMR** (400 MHz, CDCl3) δ 7.58 – 7.53 (m, 2H), 7.43 –

7.34 (m, 3H), 7.34 – 7.27 (m, 4H), 7.26 – 7.17 (m, 5H), 7.04 – 6.98 (m, 1H), 6.95 (s, 4H), 5.37 (s, 2H), 5.20 (d, *J* = 13.4 Hz, 1H), 5.04 (d, *J* = 13.4 Hz, 1H), 2.27 (s, 3H); **^{13}C NMR** (100 MHz, CDCl3) δ 202.5, 168.4, 143.4, 138.0, 137.2, 135.5, 130.3, 129.6, 129.1, 128.3, 128.3, 128.1, 127.7, 126.9, 123.2, 122.6, 112.9, 85.8, 67.9, 21.4. **HRMS** (ESI) for C31H25NO4S [M+Na]+: calcd 530.1397, found 530.1395.

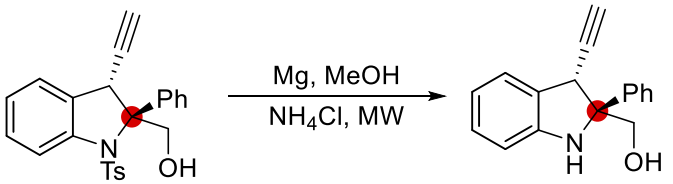
3.3 Synthetic transformation



3a: 0.2 mmol
95:5 er, dr: 19:1

6: 87% yield,
94.5:5.5 er, dr: 19:1

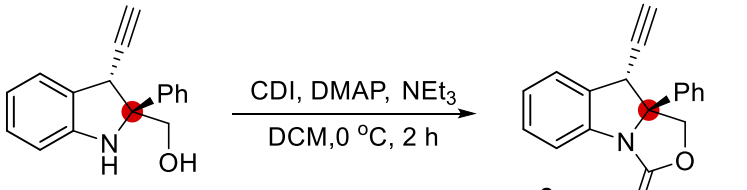
Procedure I: Under argon atmosphere, a flame-dried 10 mL Schlenk tube was charged with compound **3aa** (101.4 mg, 0.20 mmol) and anhydrous Ph-Me (2.0 mL) and cooled to -30 °C. To this solution, DIBAL-H (5.0 equiv., 1.5 M in Ph-Me) was added dropwise, and the reaction mixture was maintained at -30 °C for 6 hours. The reaction was quenched with saturated NH_4Cl aqueous solution and extracted with ethyl acetate. The combined organic layer was dried with Na_2SO_4, and evaporated under reduced pressure. The residue was purified by column chromatography afford the desired product **5aa** in 87% yield and 94.5:5.5 er.



6: 0.2 mmol,
94.5:5.5 er, dr: 19:1

7: 85% yield
94.5:5.5 er, dr: 19:1

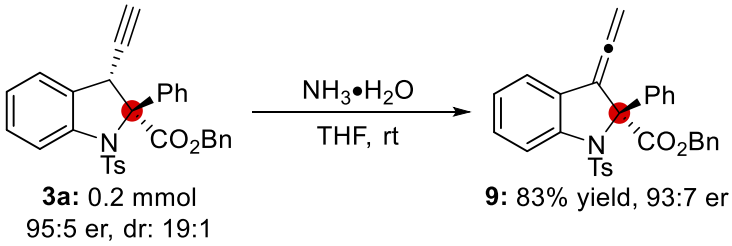
Procedure II: Under argon atmosphere, a flame-dried 10 mL Schlenk tube was charged with compound **6** (80.6 mg, 0.20 mmol) and Mg (240 mg, 10 mmol, 200-300 mesh) and NH_4Cl (642mg 12 mmol) and anhydrous MeOH (4.0 mL. The resulting solution was in MW for 4 h. Then NH4Cl (3 mL) was added to the reaction mixture to quench excess magnesium powder. The aqueous phase was extracted with ethyl acetate (4×5 mL). The combined organic layers were dried over Na2SO4, filtered and concentrated in vacuo. TThe residue was purified by column chromatography afford the desired product **7** in 85% yield and 94.5:5.5 er.



7: 0.2 mmol
94.5:5.5 er, dr: 19:1

8:
90% yield, 94.5:5.5 er, dr: 19:1

Procedure III: Under argon atmosphere, a flame-dried 10 mL Schlenk tube was charged with compound **7** (50 mg, 0.20 mmol) and anhydrous DCM (2.0 mL) and cooled to 0 °C. To this solution, DMAP (2.4 mg, 0.02 mmol), Et_3N (61 μL, 4.4 mmol), and 1,1'-carbonyldiimidazole (42.2mg, 0.26 mmol). The mixture was stirred at 0 °C for 2 h. Remove the solvent under vacuum. The residue was purified by column chromatography afford the desired product **8** in 90% yield and 94.5:5.5 er.

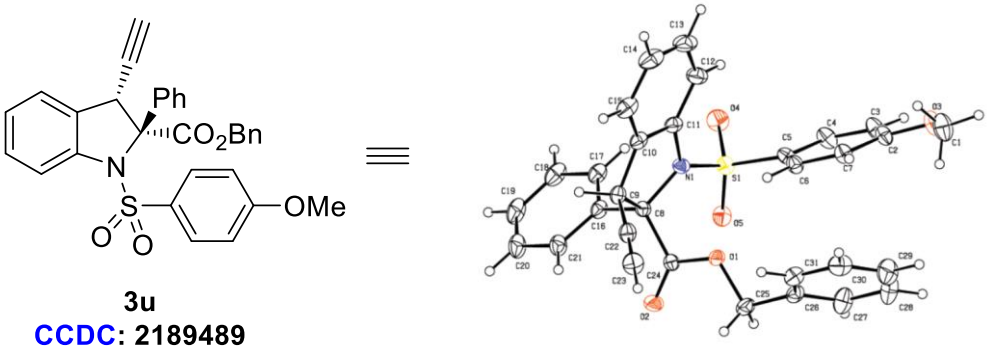


3a: 0.2 mmol
95:5 er, dr: 19:1

9: 83% yield, 93:7 er

Procedure IV: In a flame-dried 10 ml Schlenk tube **3a** (101.43. mg, 0.20 mmol) were dissolved in THF (2.0 mL). To the resulting solution, $NH_3 \cdot H_2O$ (3.0 mL) was added sequentially. After stirred for 3 h, the solvent was removed under vacuum. The reaction mixture was directly purified by flash column chromatography on silica gel to afford the desired product **9** in 83% yield and 93:7 ee.

4. X-Ray Structures of Product 3u

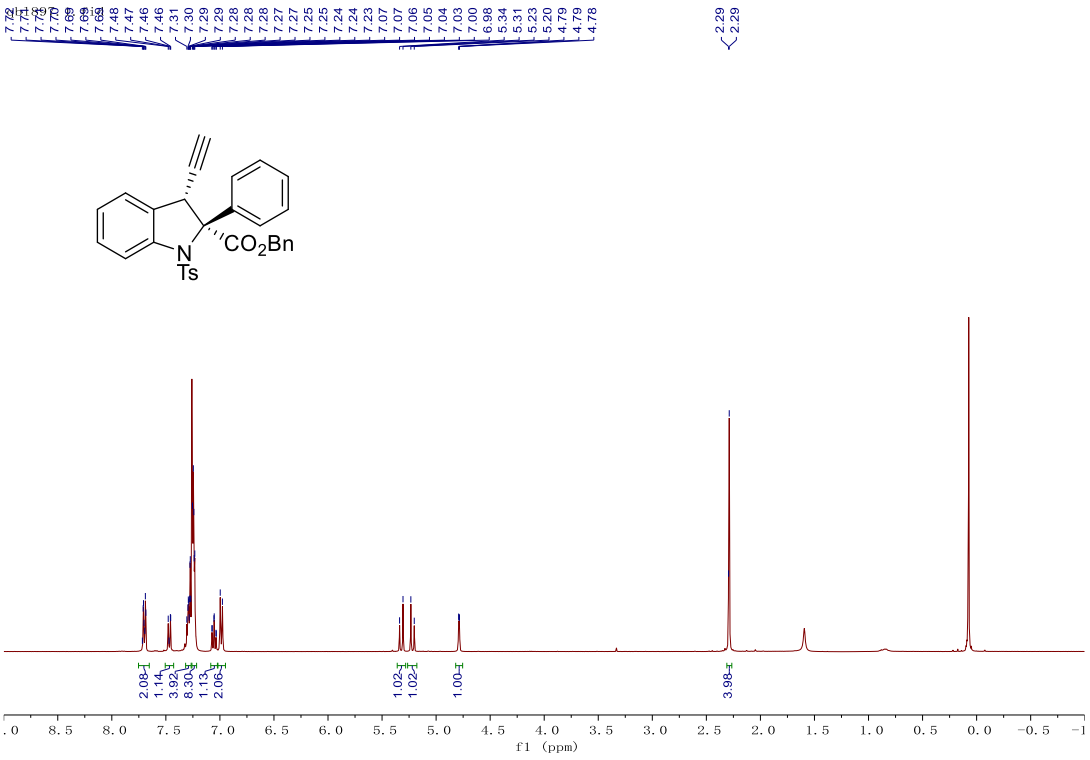


3u
CCDC: 2189489

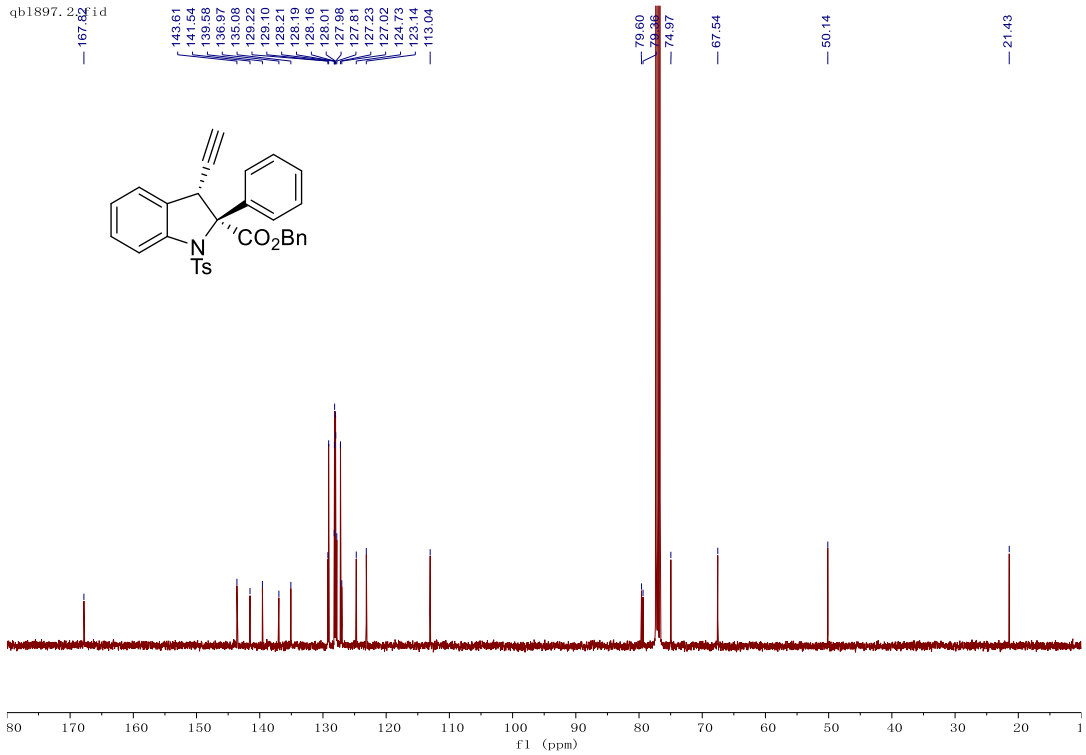
Figure S1. X-ray crystallography of **3u**

5. Copies of NMR Spectra

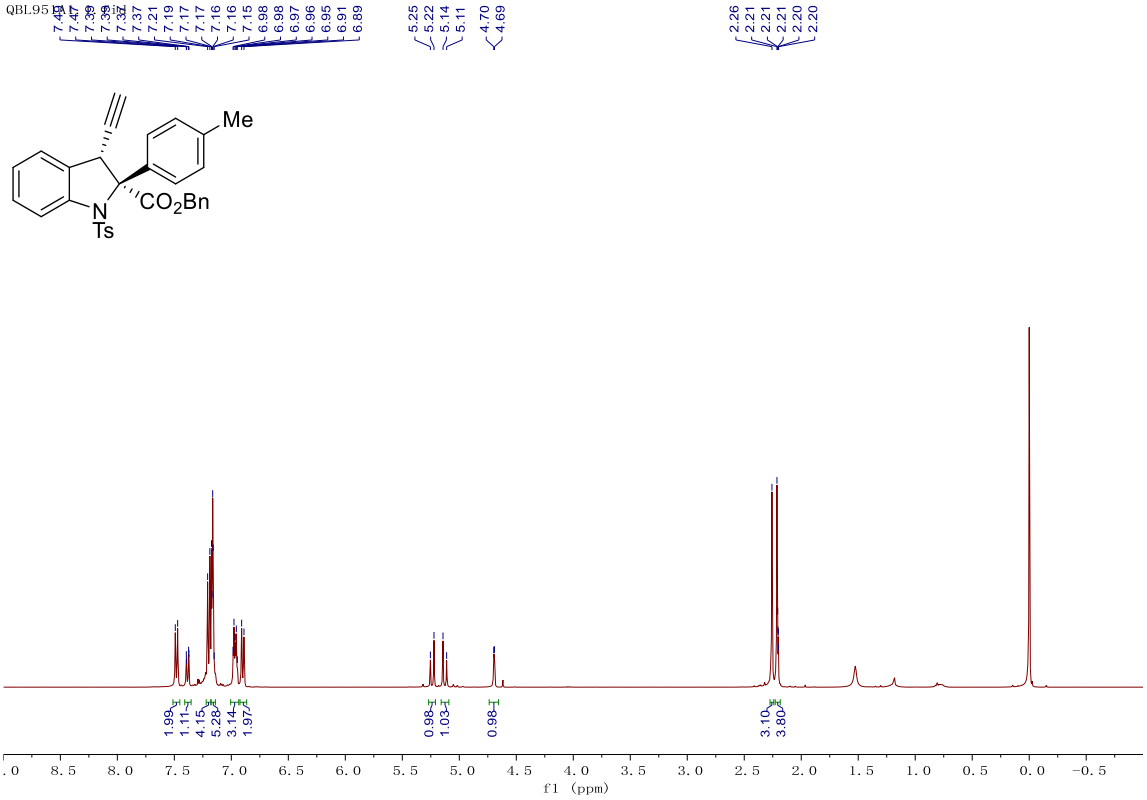
^{1}H NMR spectrum of compound 3a (400 MHz, $CDCl_3$)



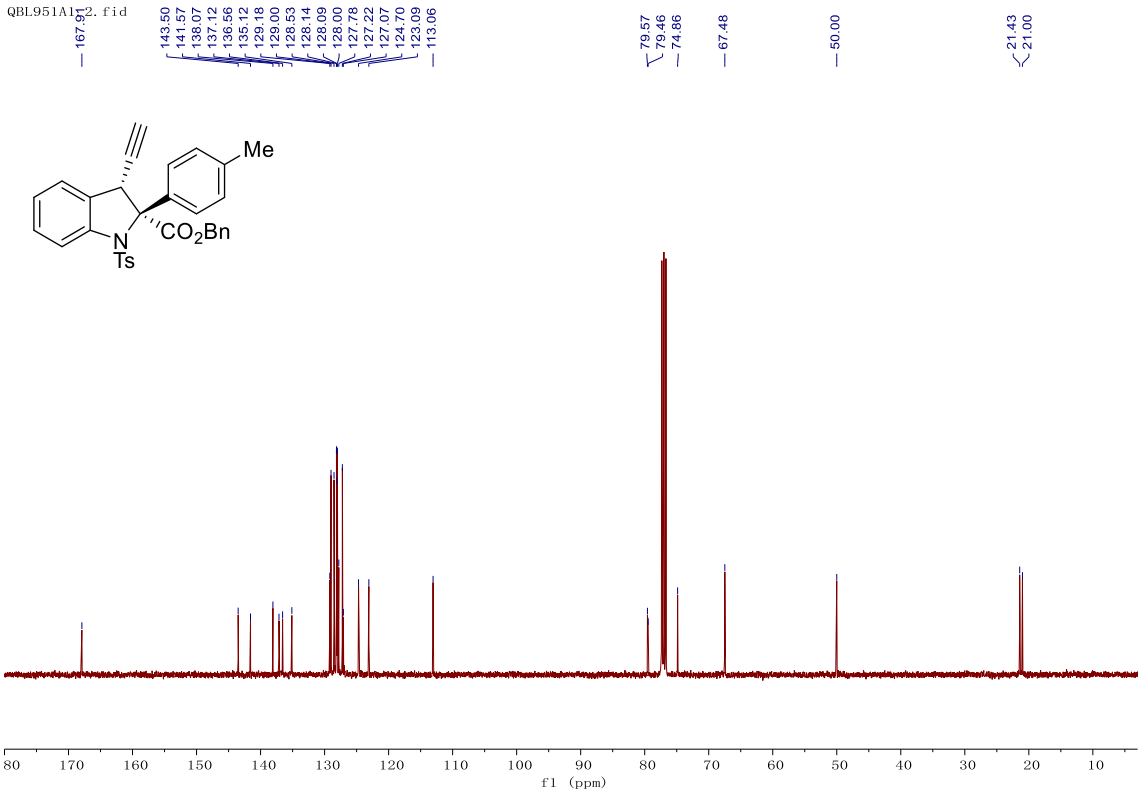
^{13}C NMR spectrum of compound 3a (100 MHz, $CDCl_3$)



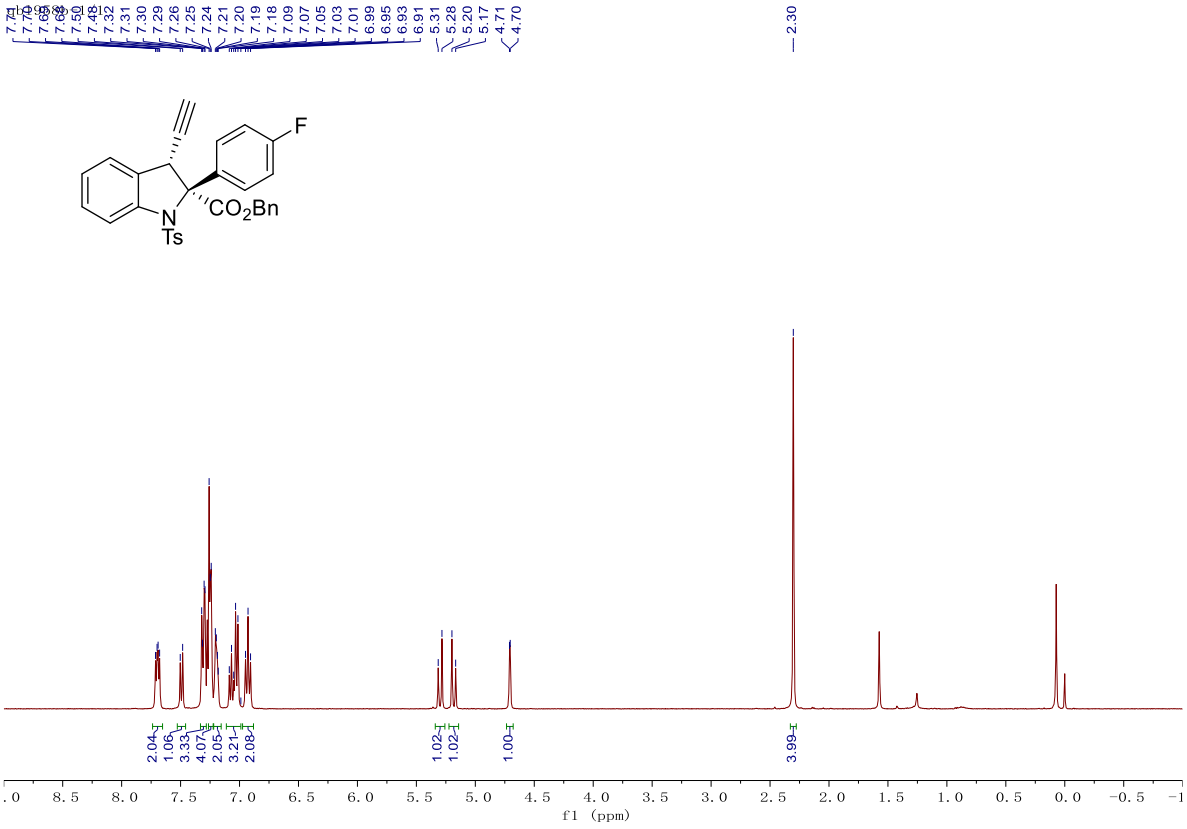
^{1}H NMR spectrum of compound 3b (400 MHz, $CDCl_3$)



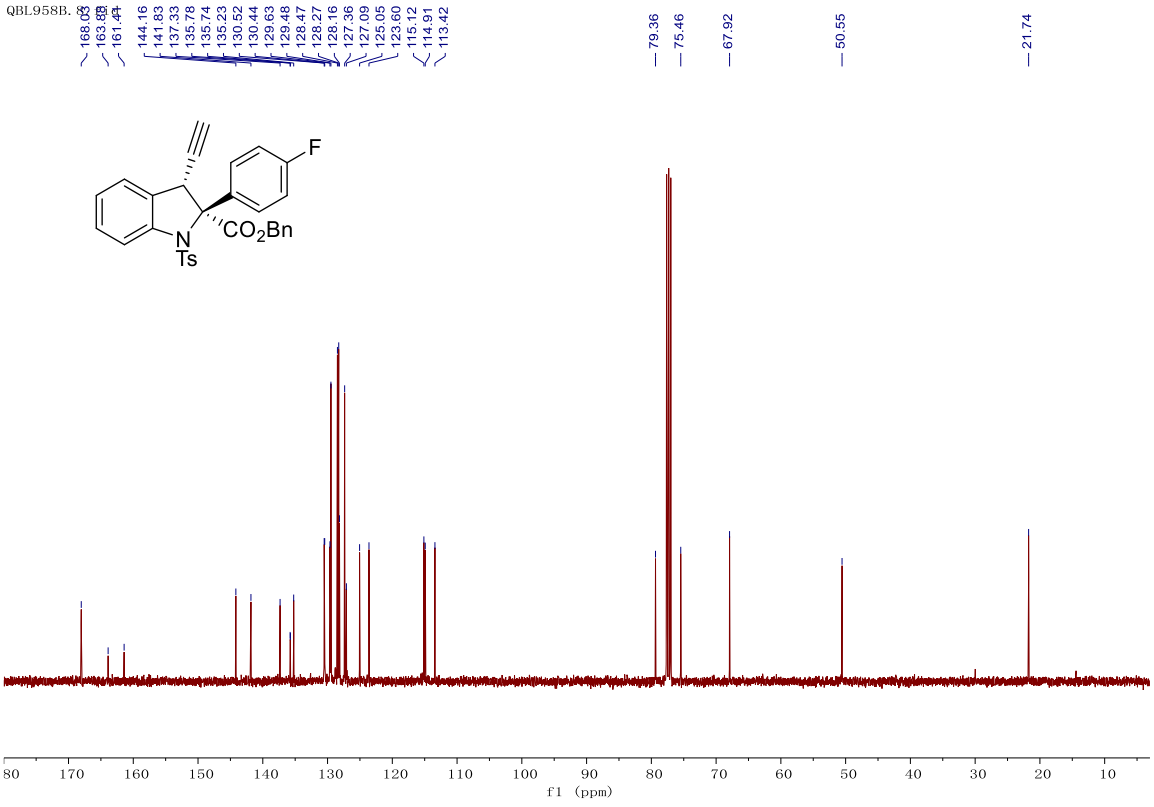
^{13}C NMR spectrum of compound 3b (100 MHz, $CDCl_3$)



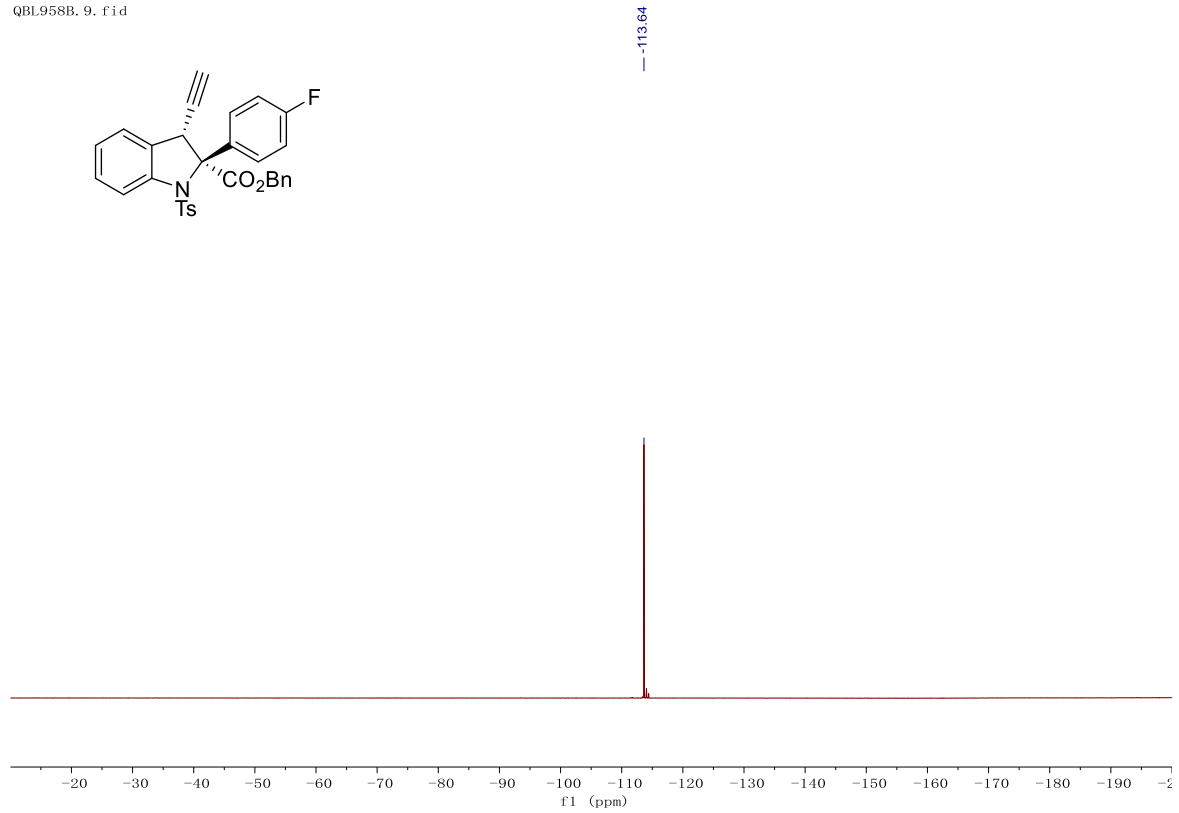
^{1}H NMR spectrum of compound 3c (400 MHz, $CDCl_3$)



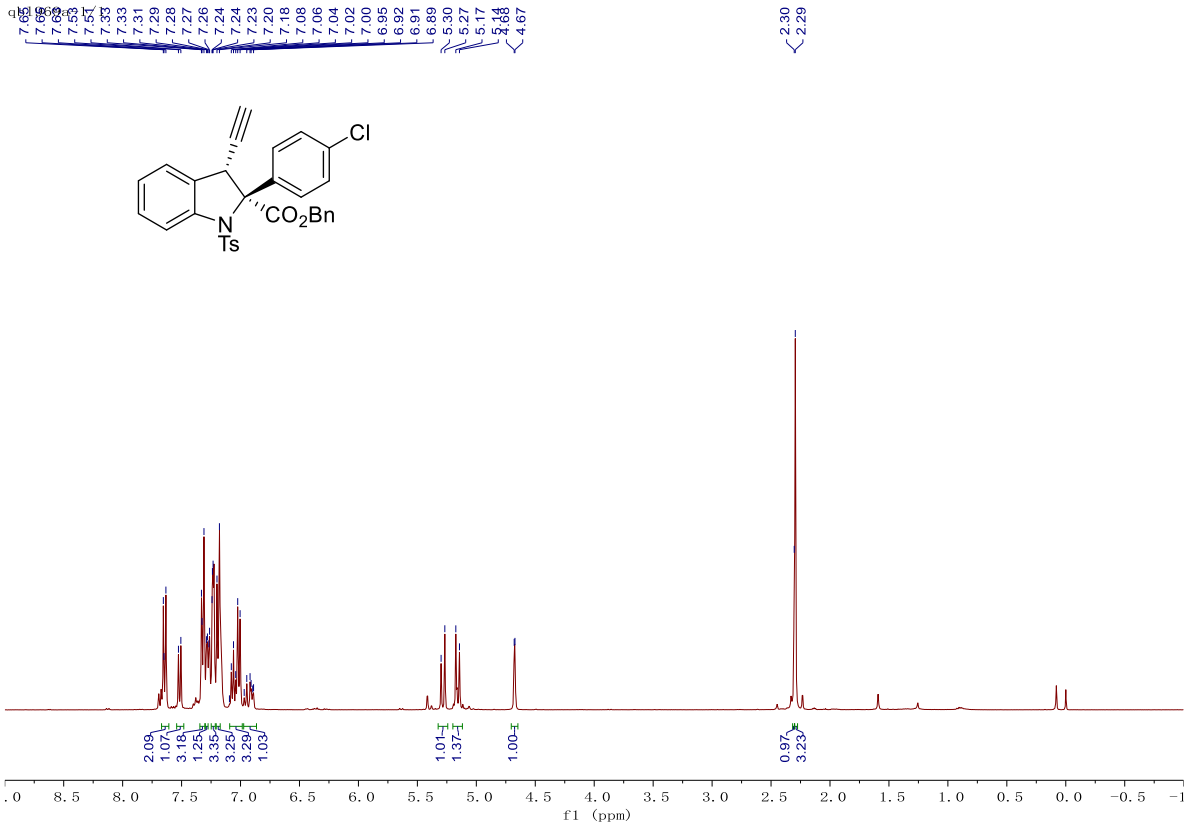
^{13}C NMR spectrum of compound 3c (100 MHz, $CDCl_3$)



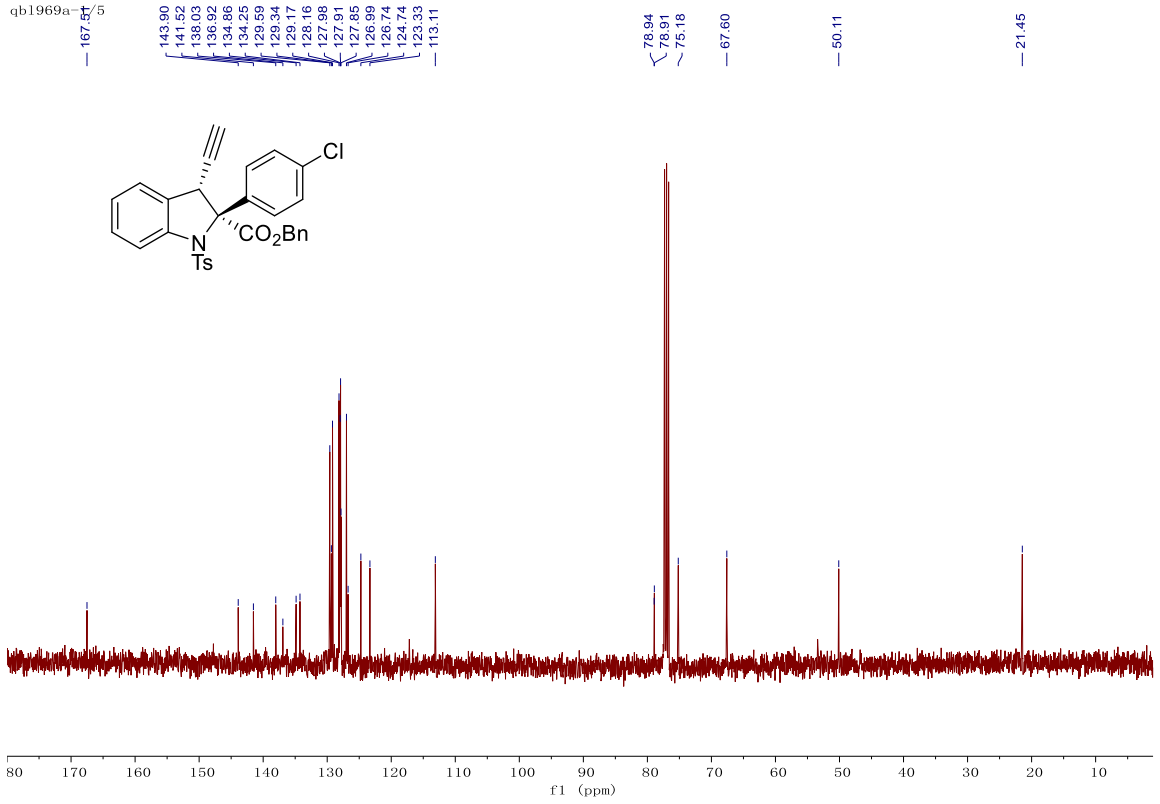
^{19}F NMR spectrum of compound 3c (376 MHz, $CDCl_3$)



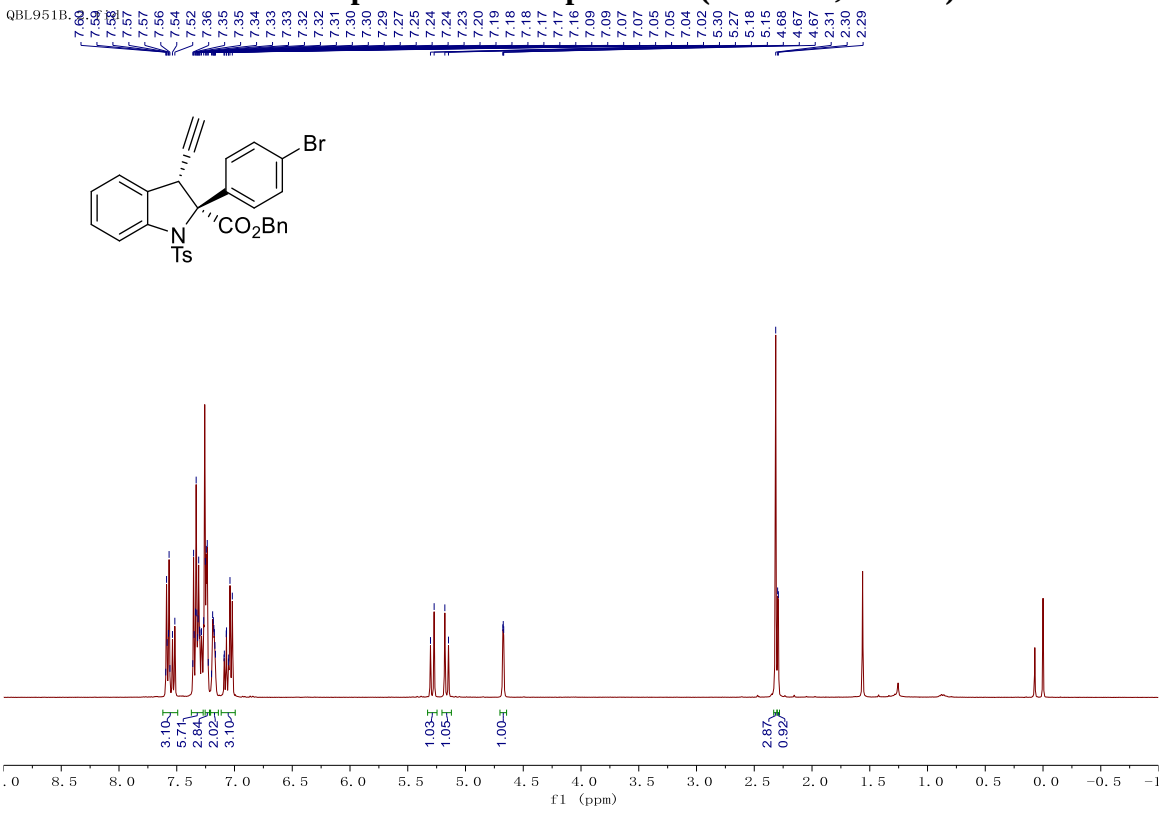
^{1}H NMR spectrum of compound 3d (400 MHz, $CDCl_3$)



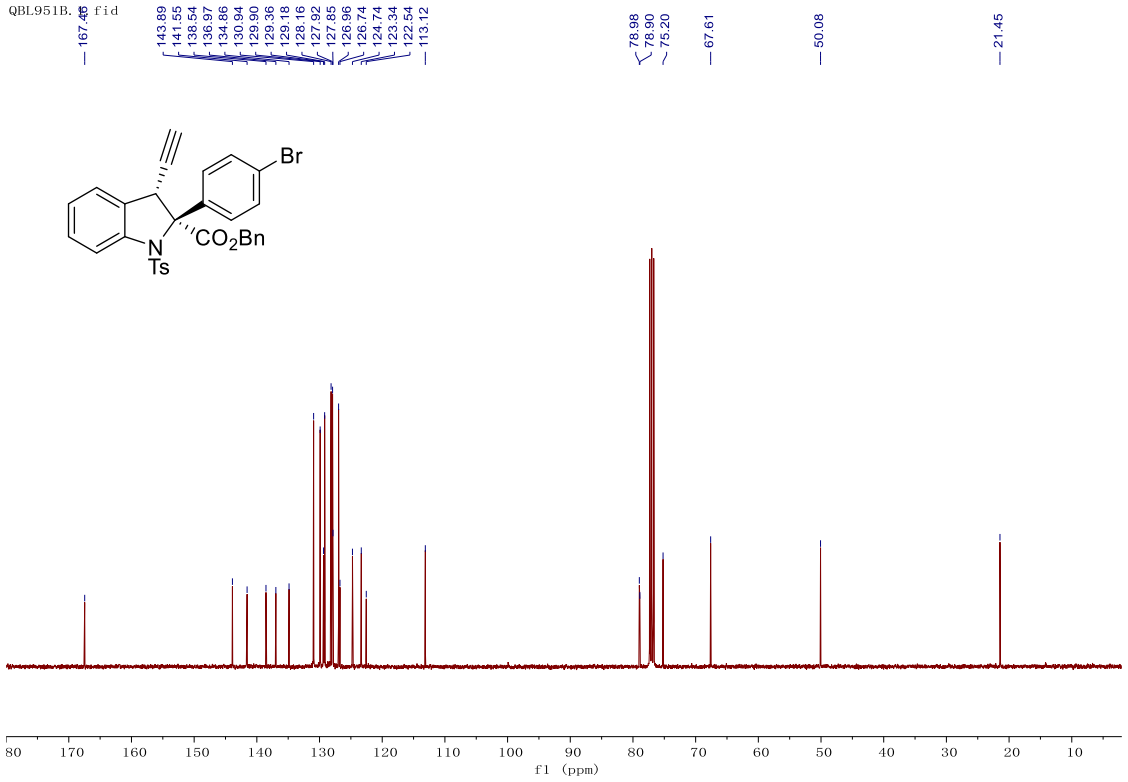
^{13}C NMR spectrum of compound 3d (100 MHz, $CDCl_3$)



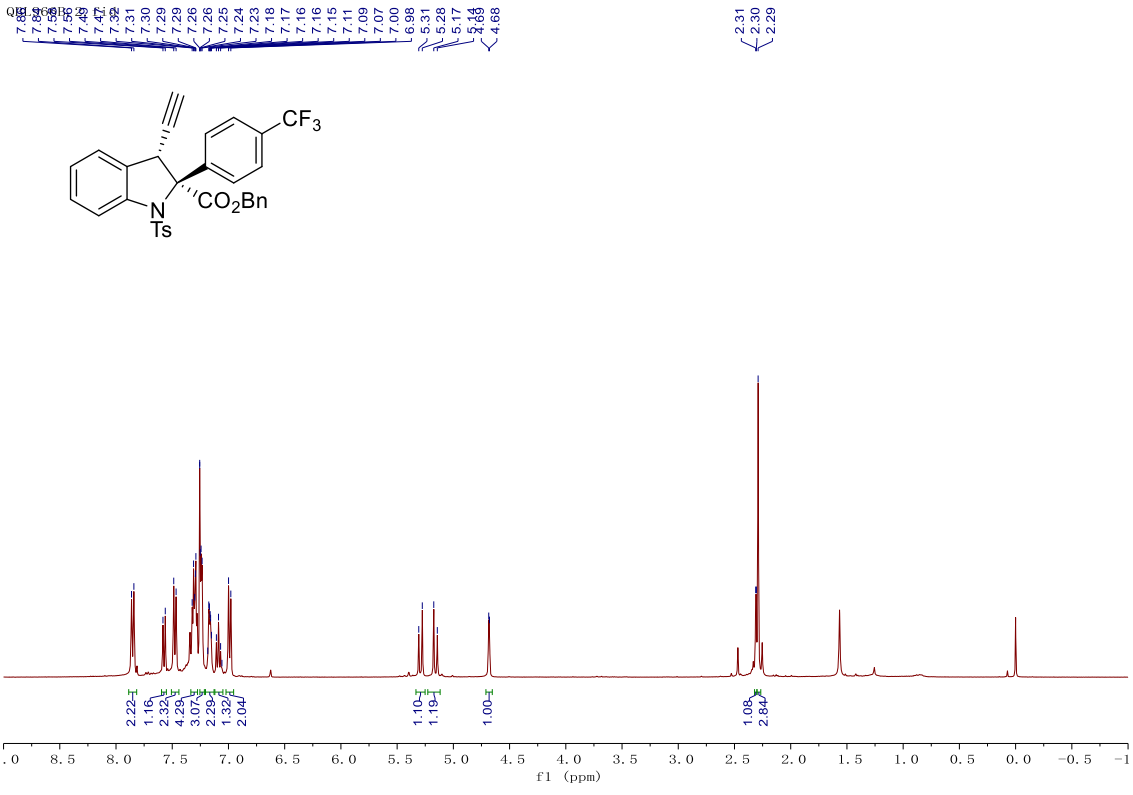
1H NMR spectrum of compound 3e (400 MHz, CDCl3)



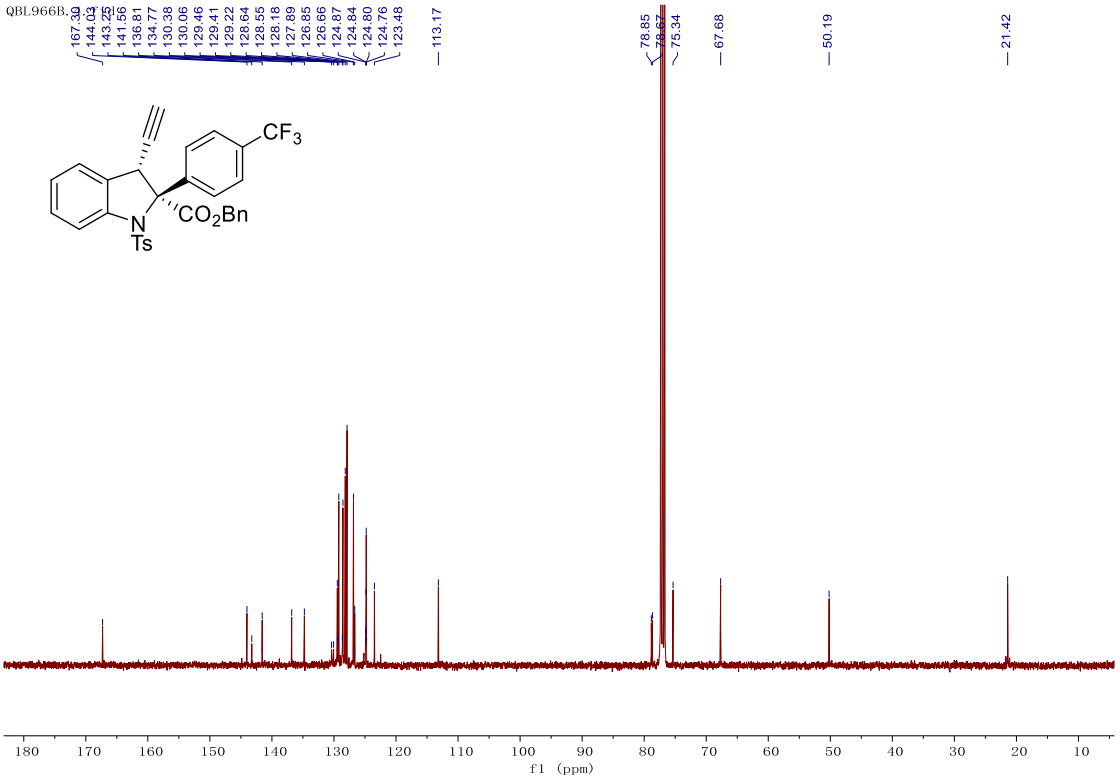
^{13}C NMR spectrum of compound 3e (100 MHz, $CDCl_3$)



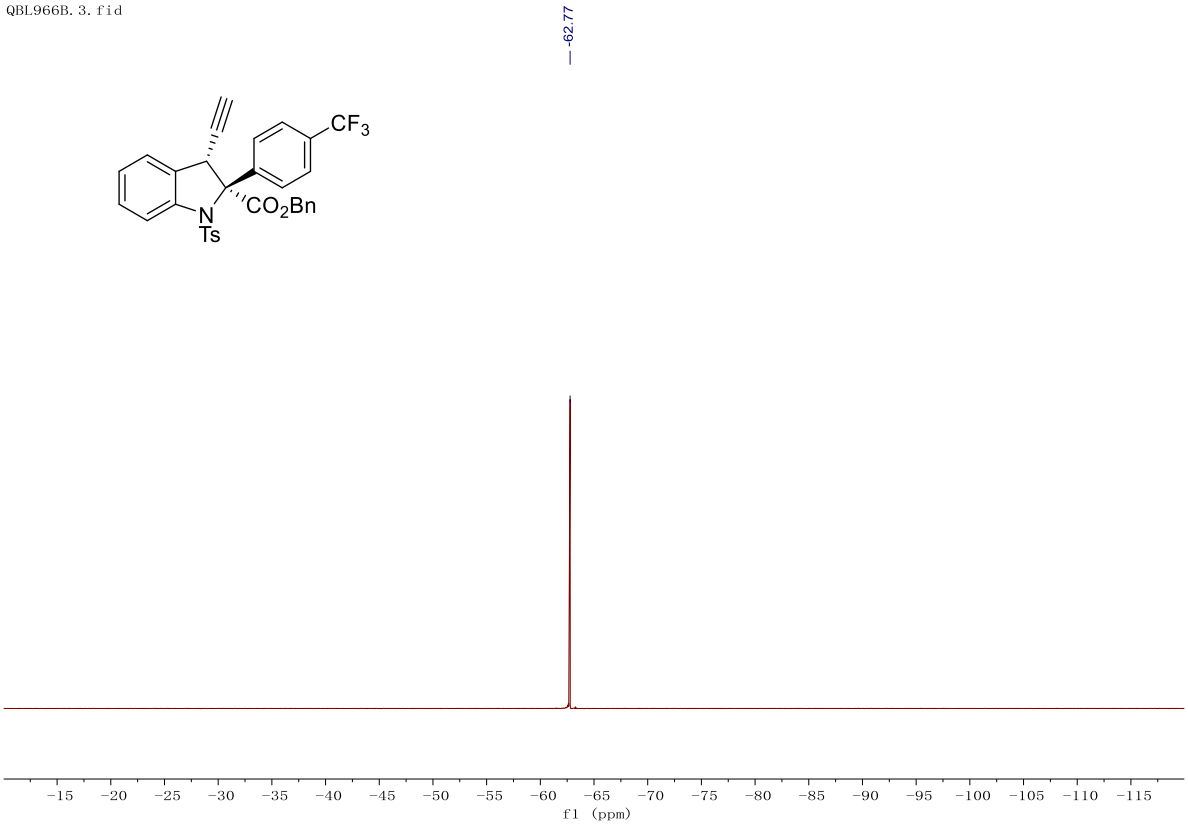
^{1}H NMR spectrum of compound 3f (400 MHz, $CDCl_3$)



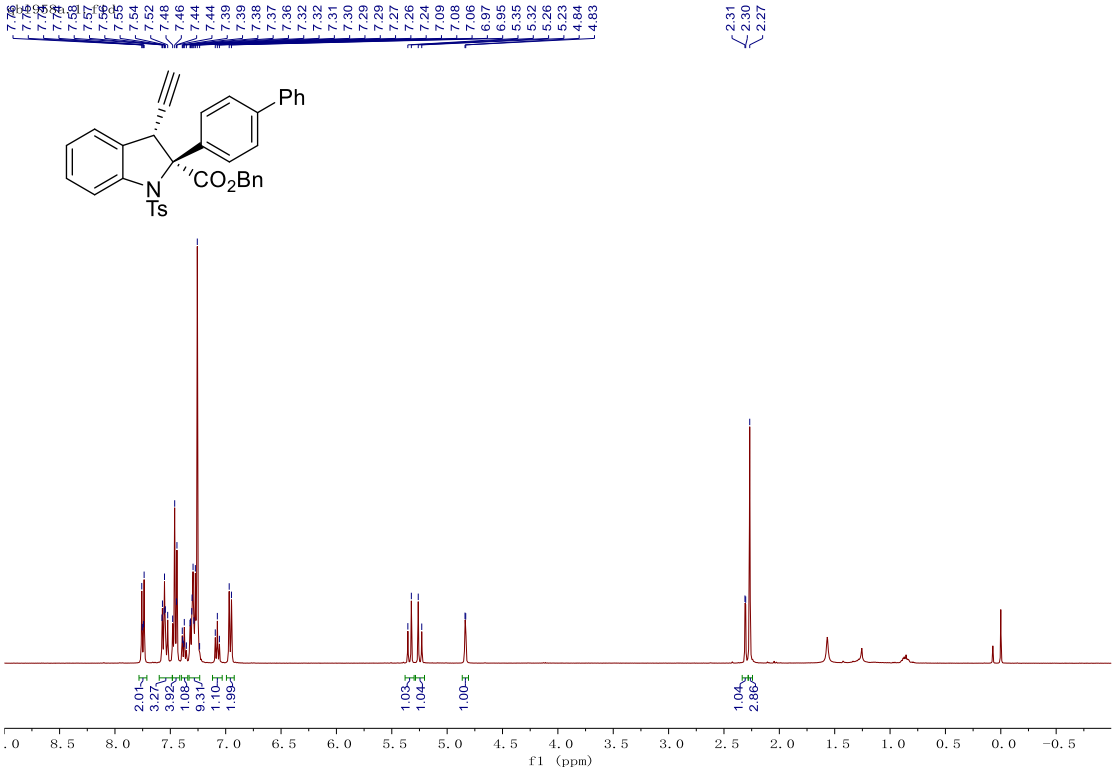
^{13}C NMR spectrum of compound 3f (100 MHz, $CDCl_3$)



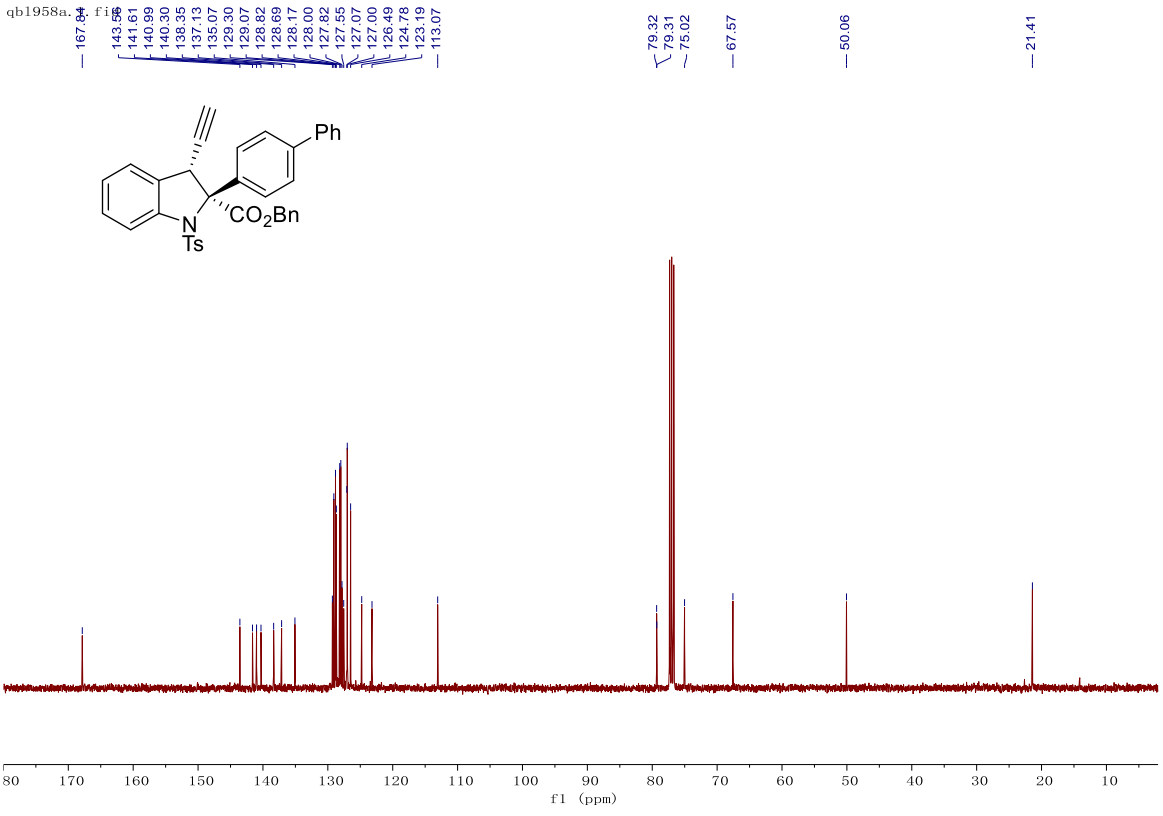
^{19}F NMR spectrum of compound 3f (376 MHz, $CDCl_3$)



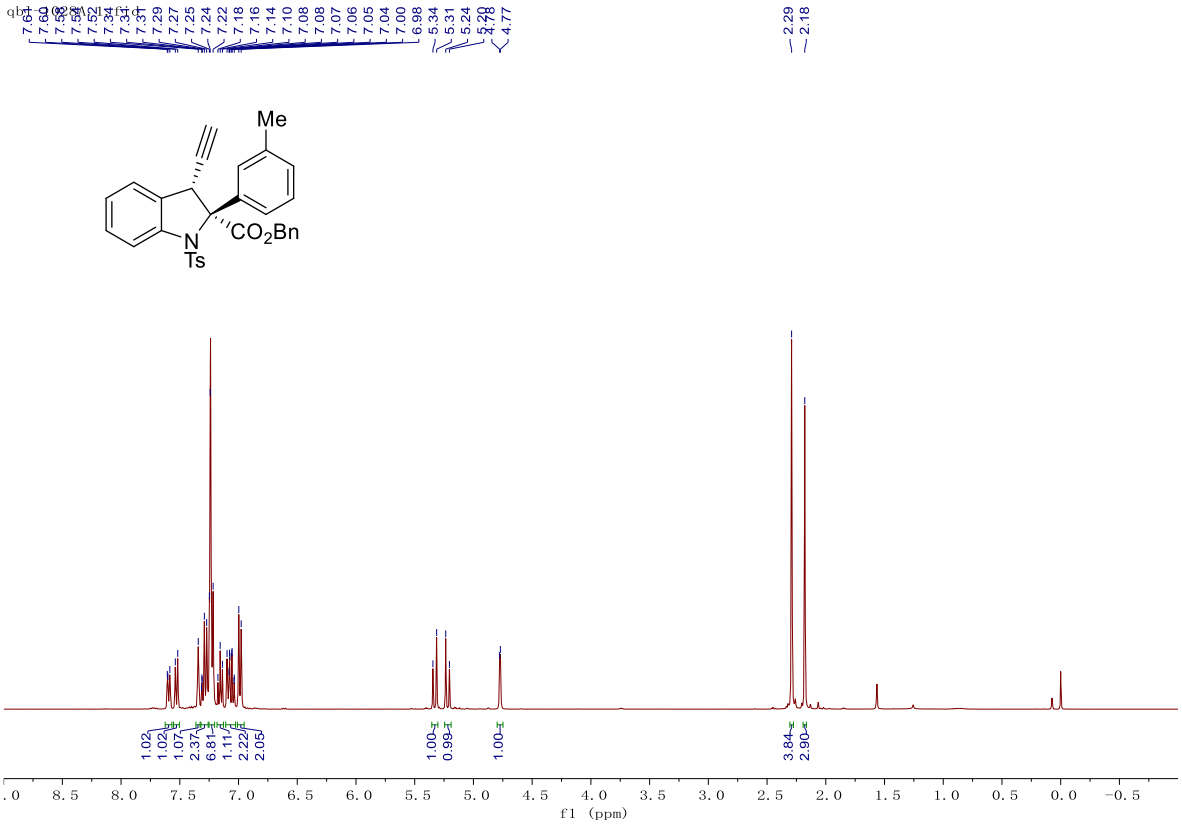
^{1}H NMR spectrum of compound 3g (400 MHz, $CDCl_3$)



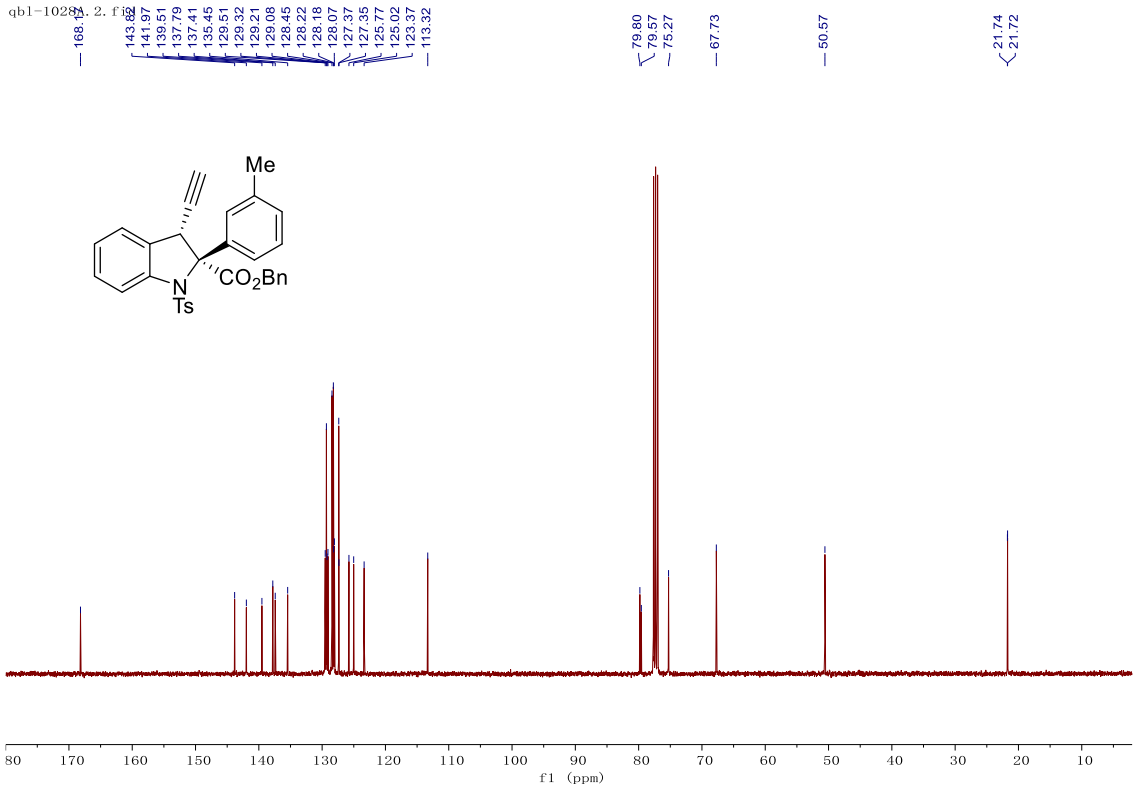
^{13}C NMR spectrum of compound 3g (100 MHz, $CDCl_3$)



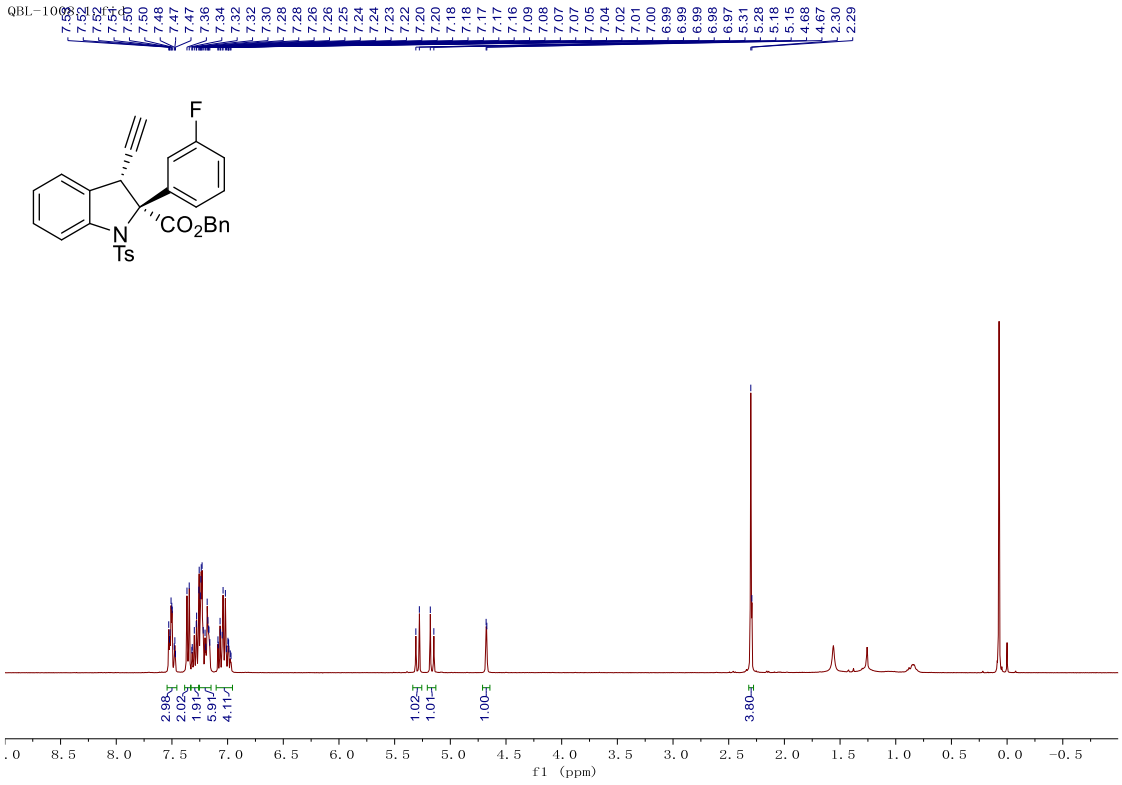
^{1}H NMR spectrum of compound 3h (400 MHz, $CDCl_3$)



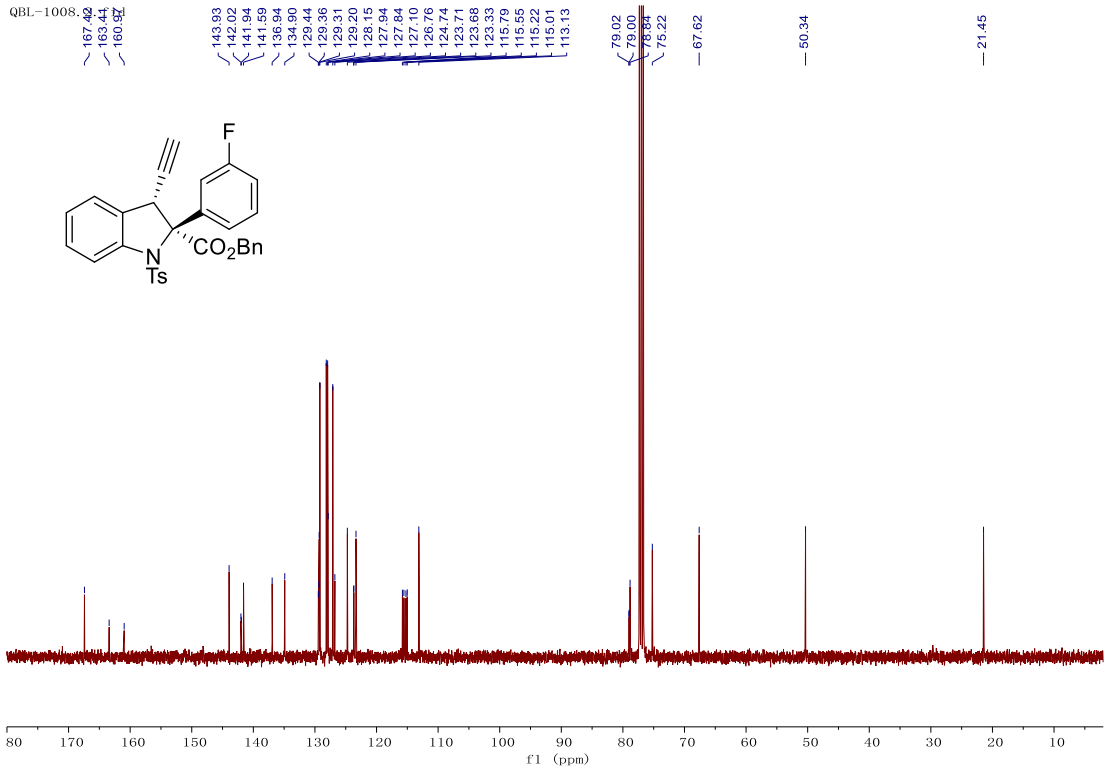
^{13}C NMR spectrum of compound 3h (100 MHz, $CDCl_3$)



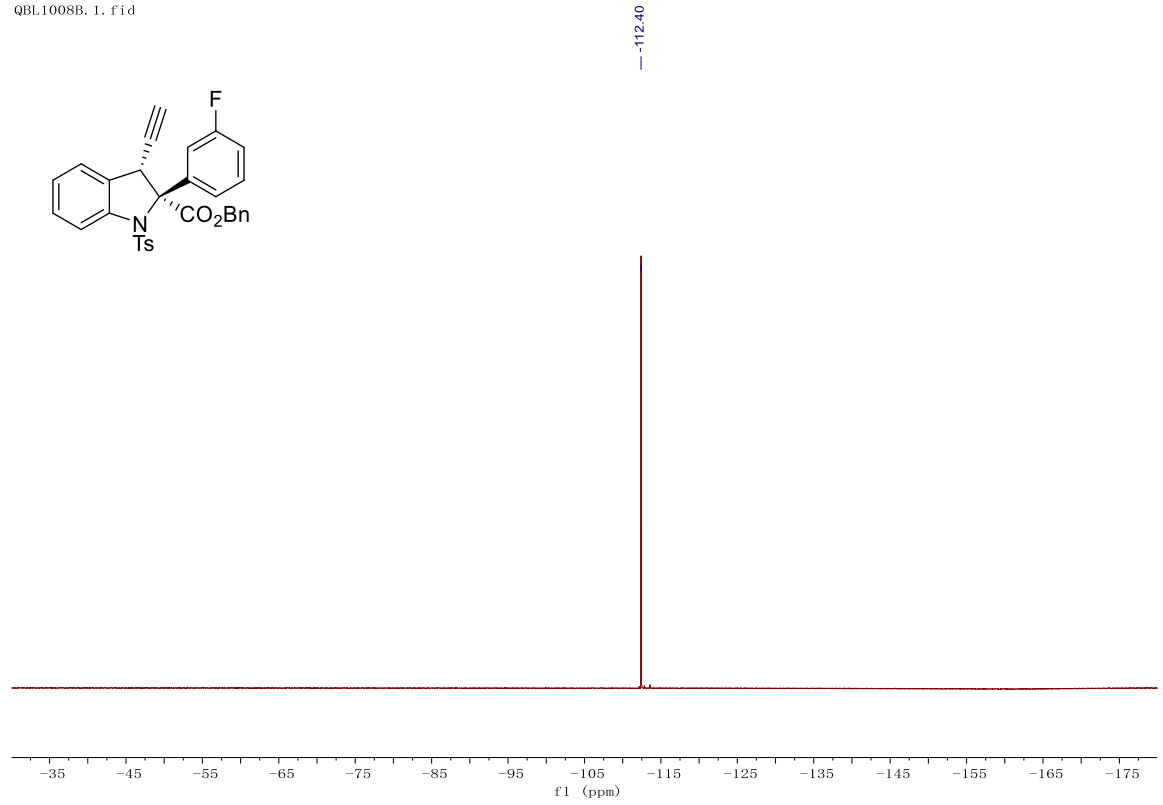
^{1}H NMR spectrum of compound 3i (400 MHz, $CDCl_3$)



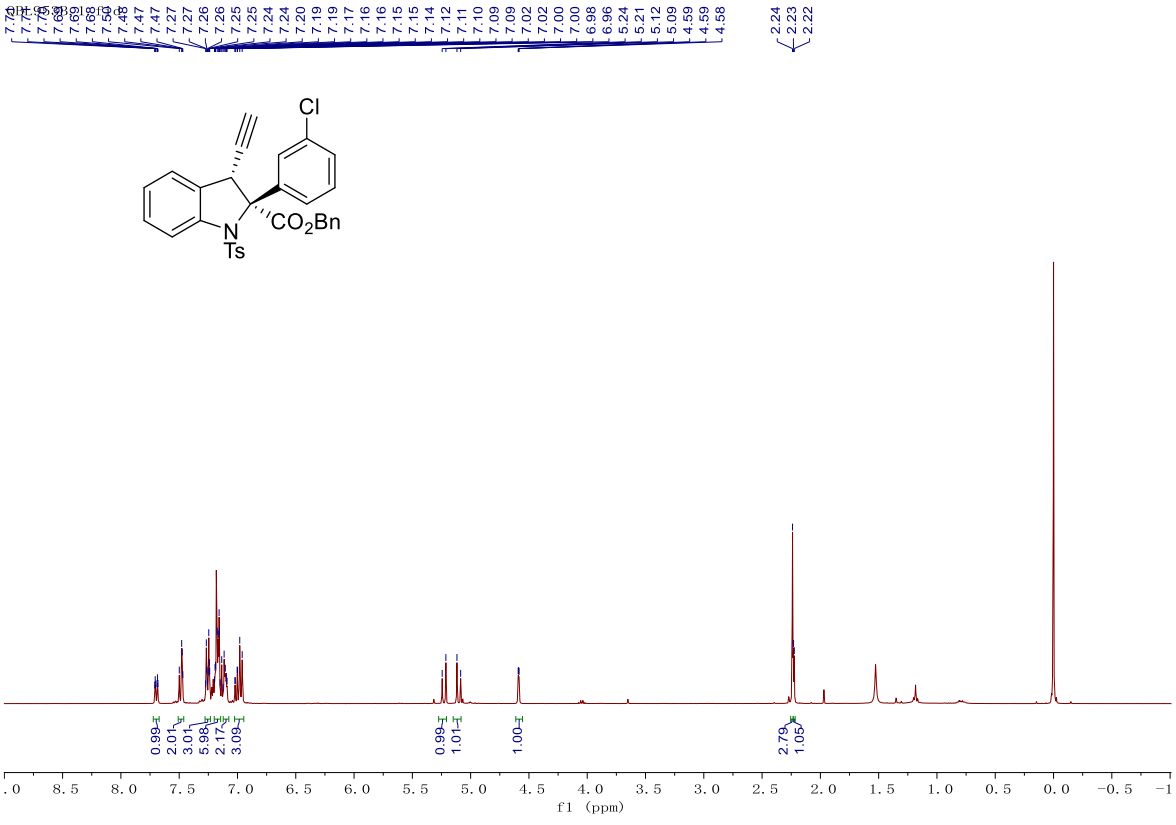
^{13}C NMR spectrum of compound 3i (100 MHz, $CDCl_3$)



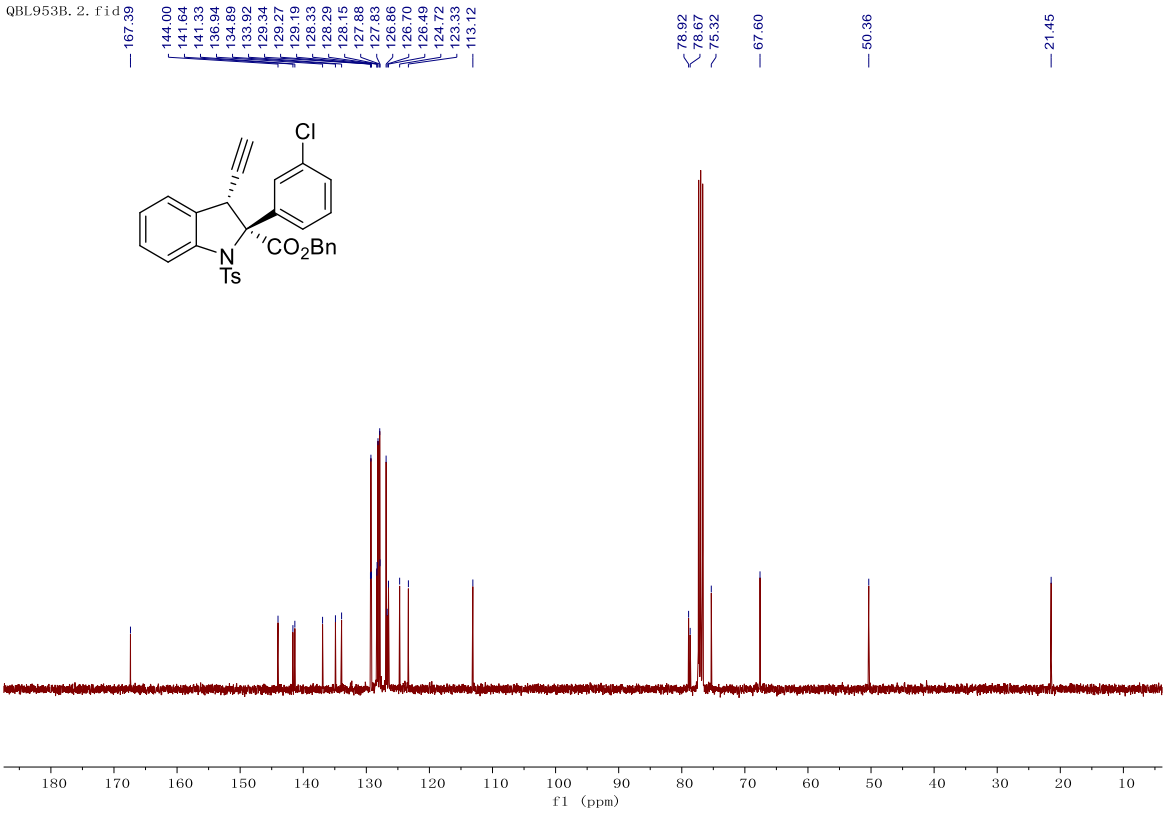
^{19}F NMR spectrum of compound 3i (376 MHz, $CDCl_3$)



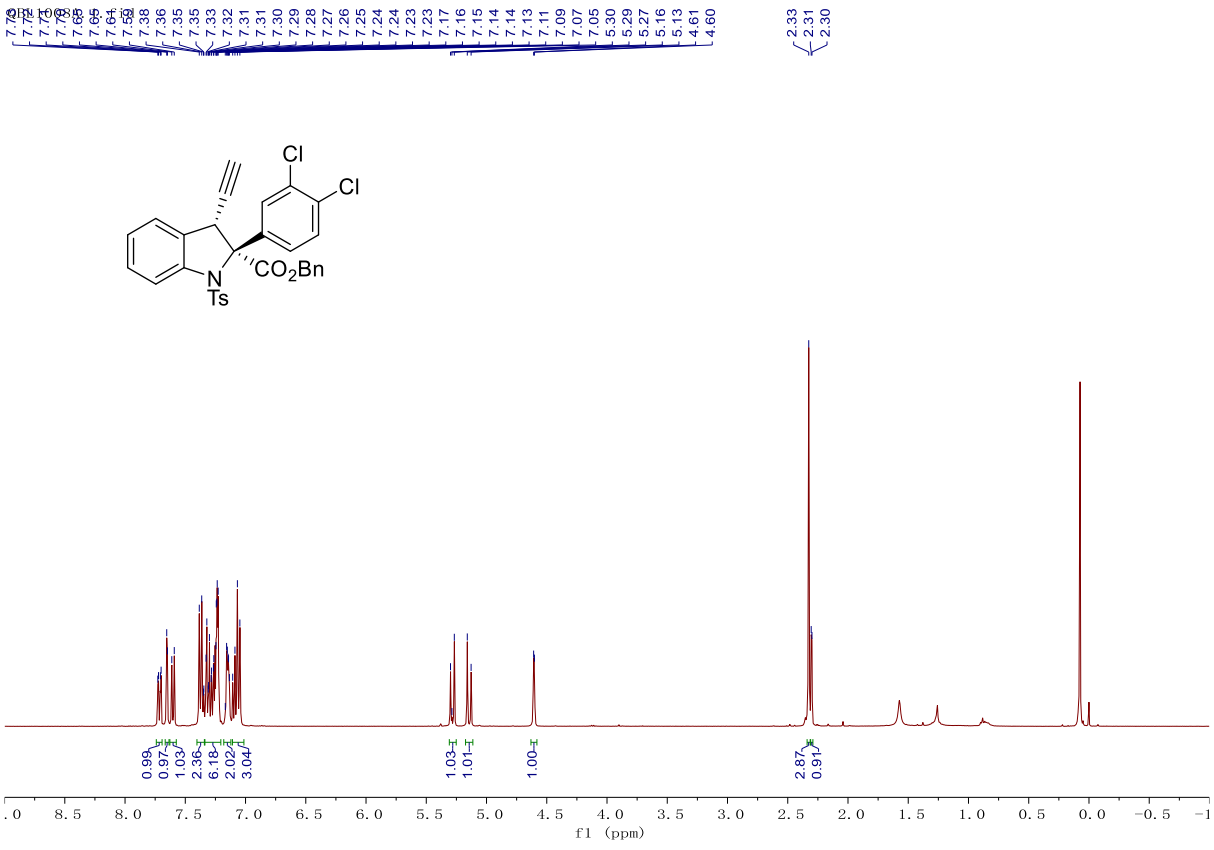
^{1}H NMR spectrum of compound 3j (400 MHz, $CDCl_3$)



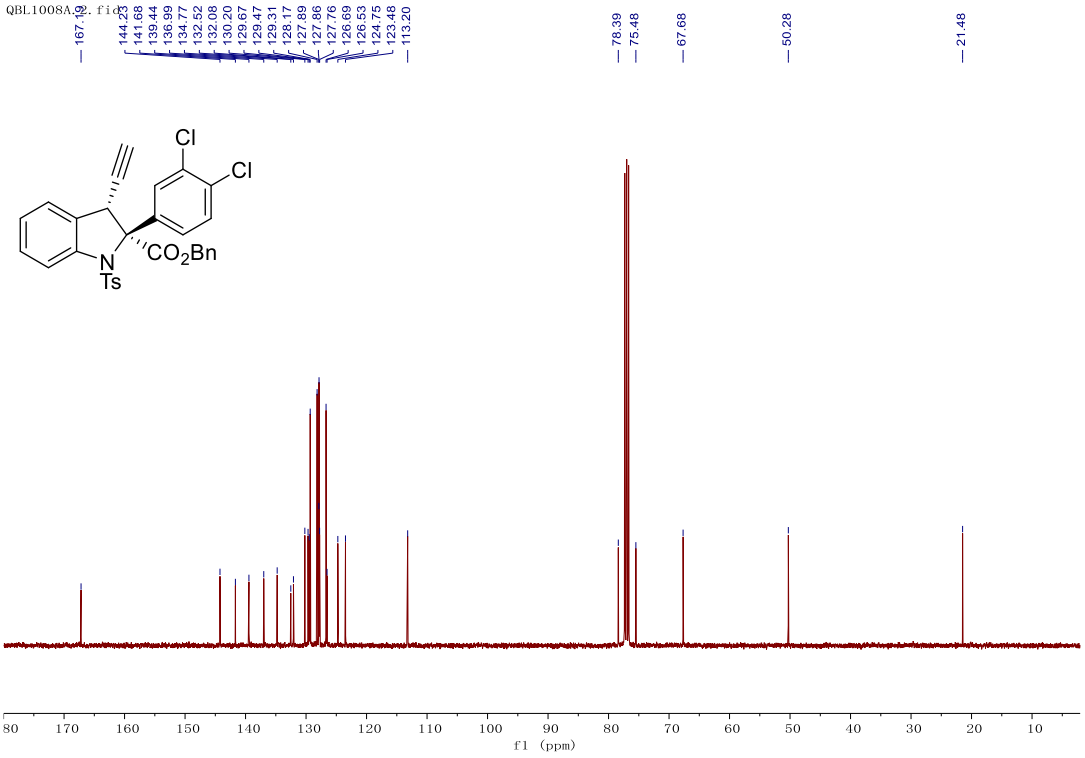
13C NMR spectrum of compound 3j (100 MHz, CDCl3)



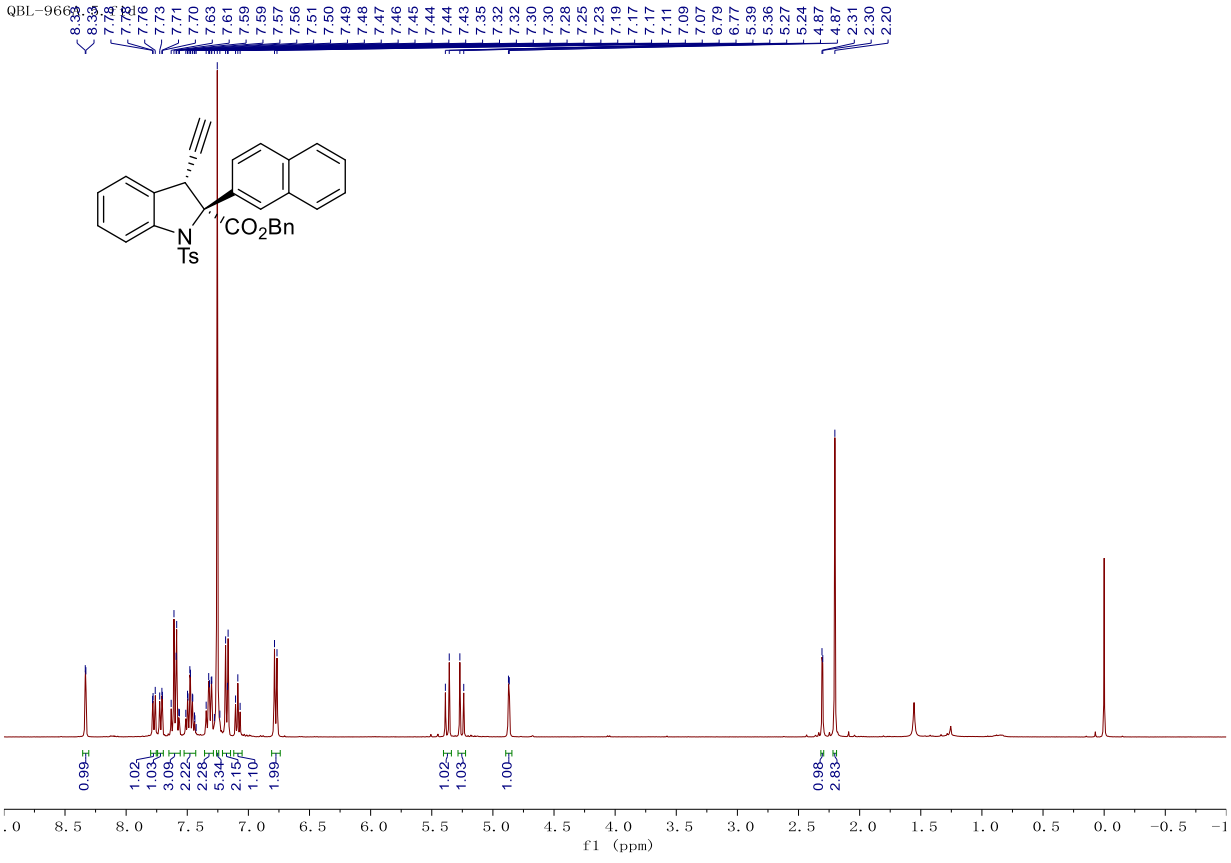
^{1}H NMR spectrum of compound 3k (400 MHz, $CDCl_3$)



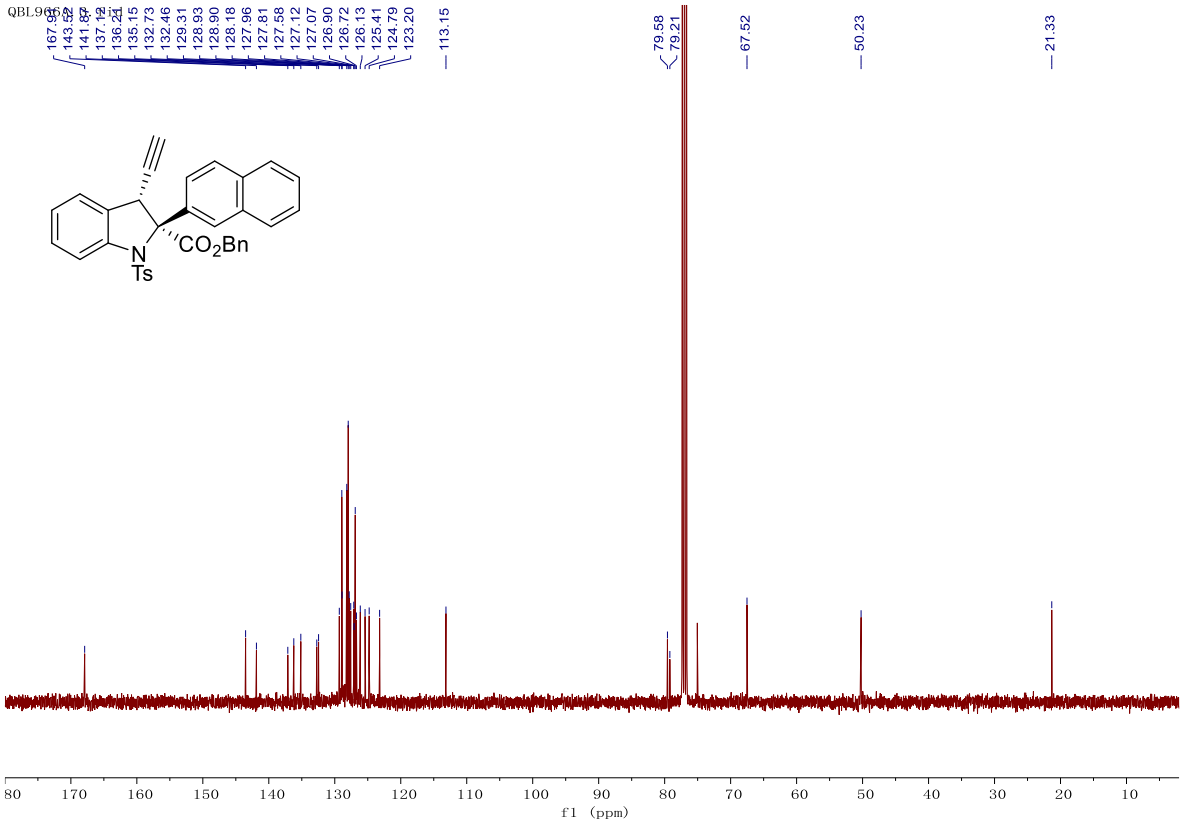
^{13}C NMR spectrum of compound 3k (100 MHz, $CDCl_3$)



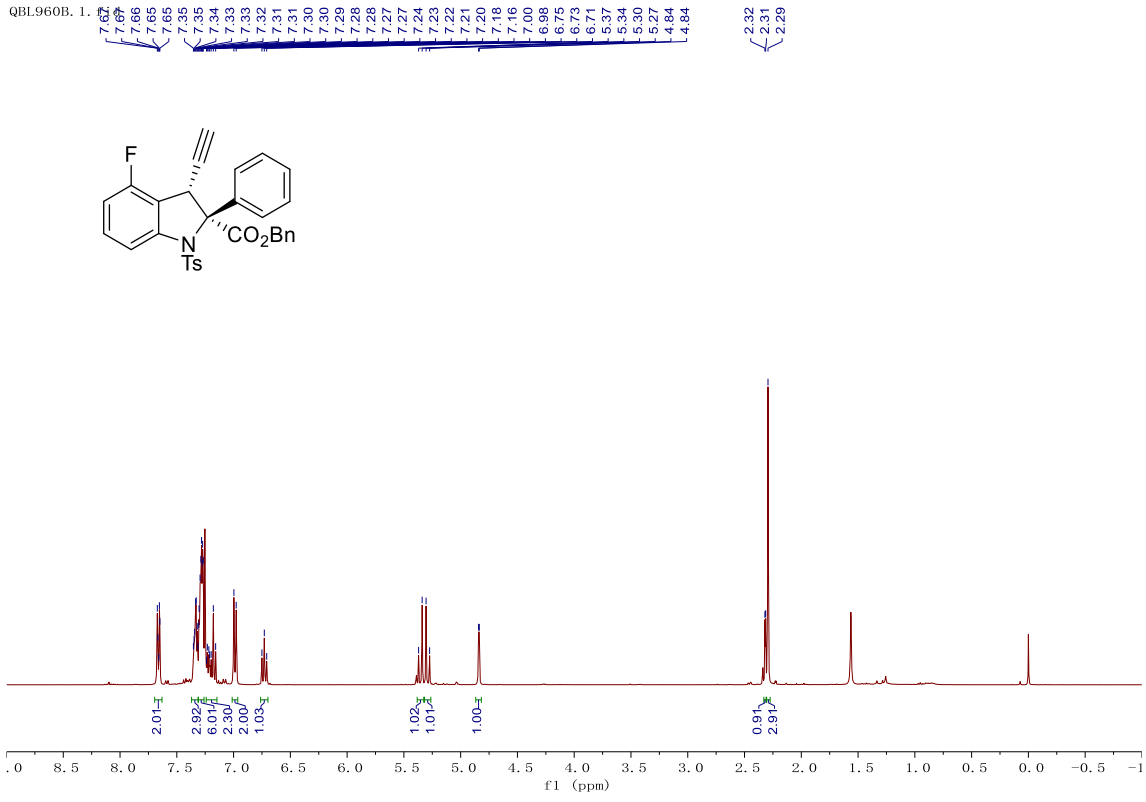
^{1}H NMR spectrum of compound 3l (400 MHz, $CDCl_3$)



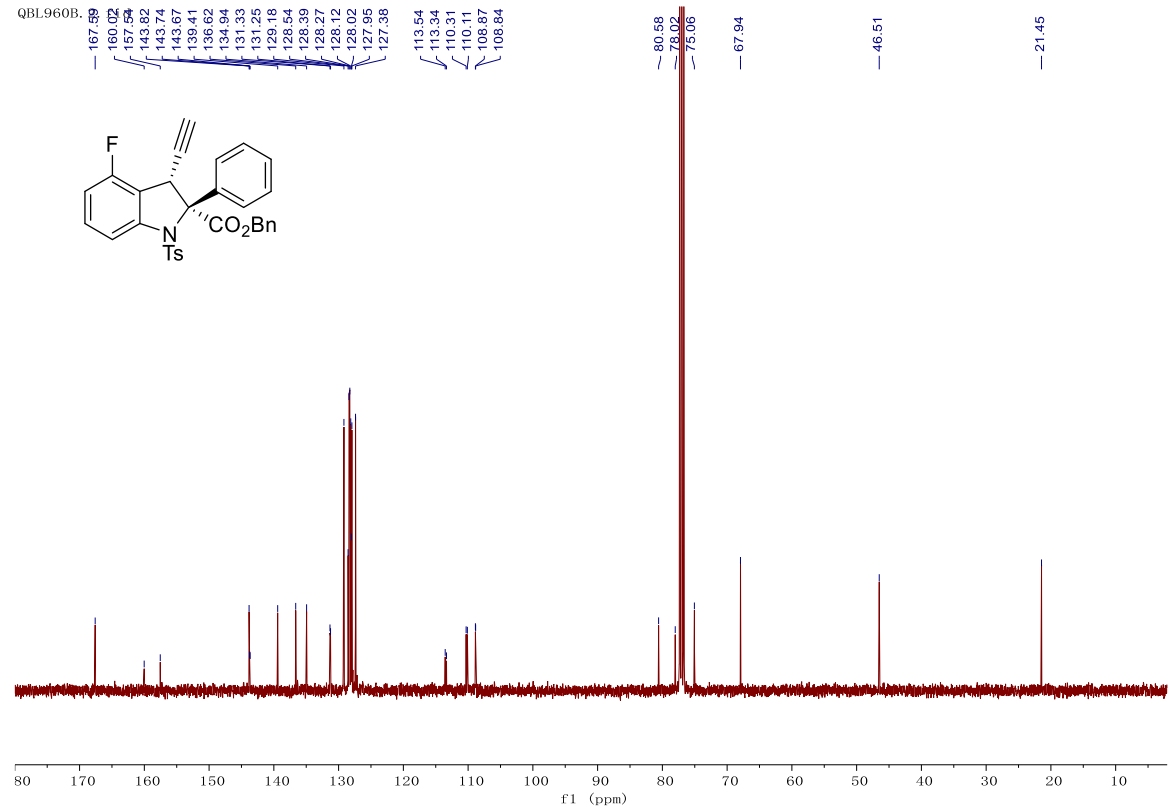
^{13}C NMR spectrum of compound 4l (100 MHz, $CDCl_3$)



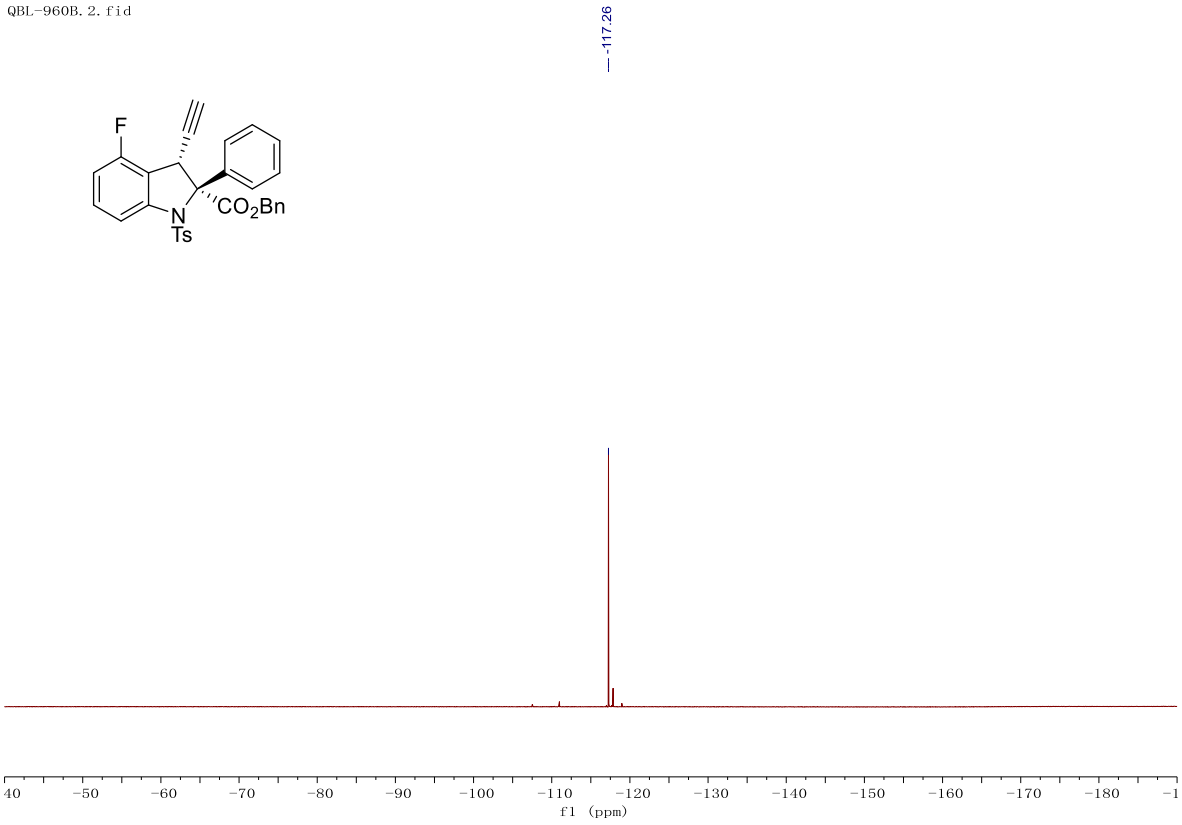
^{1}H NMR spectrum of compound 3m (400 MHz, $CDCl_3$)



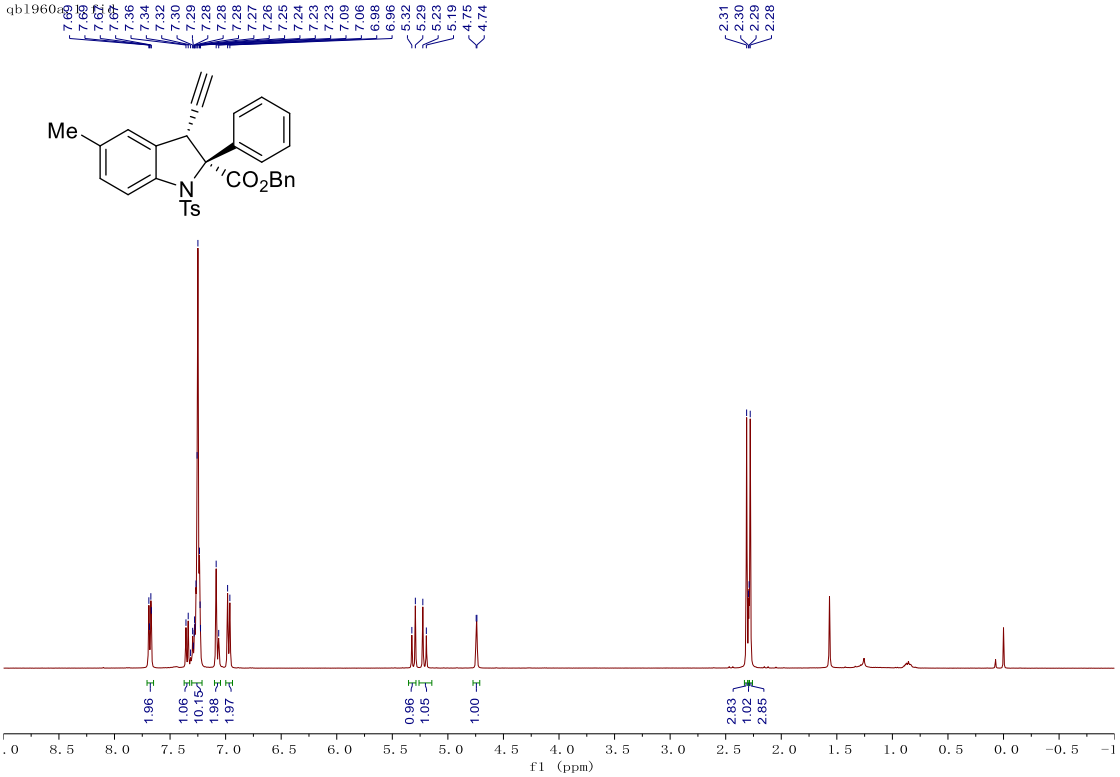
^{13}C NMR spectrum of compound 3m (100 MHz, $CDCl_3$)



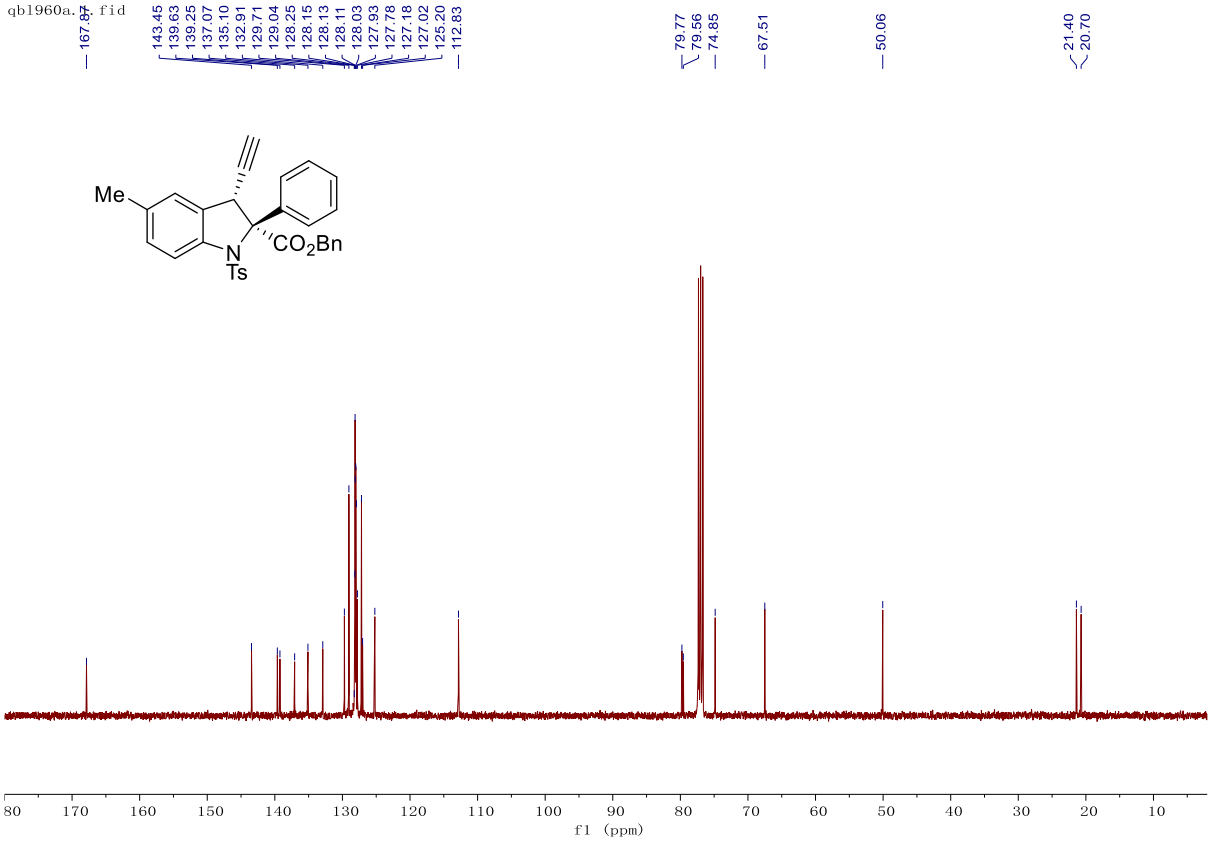
^{19}F NMR spectrum of compound 3m (376 MHz, $CDCl_3$)



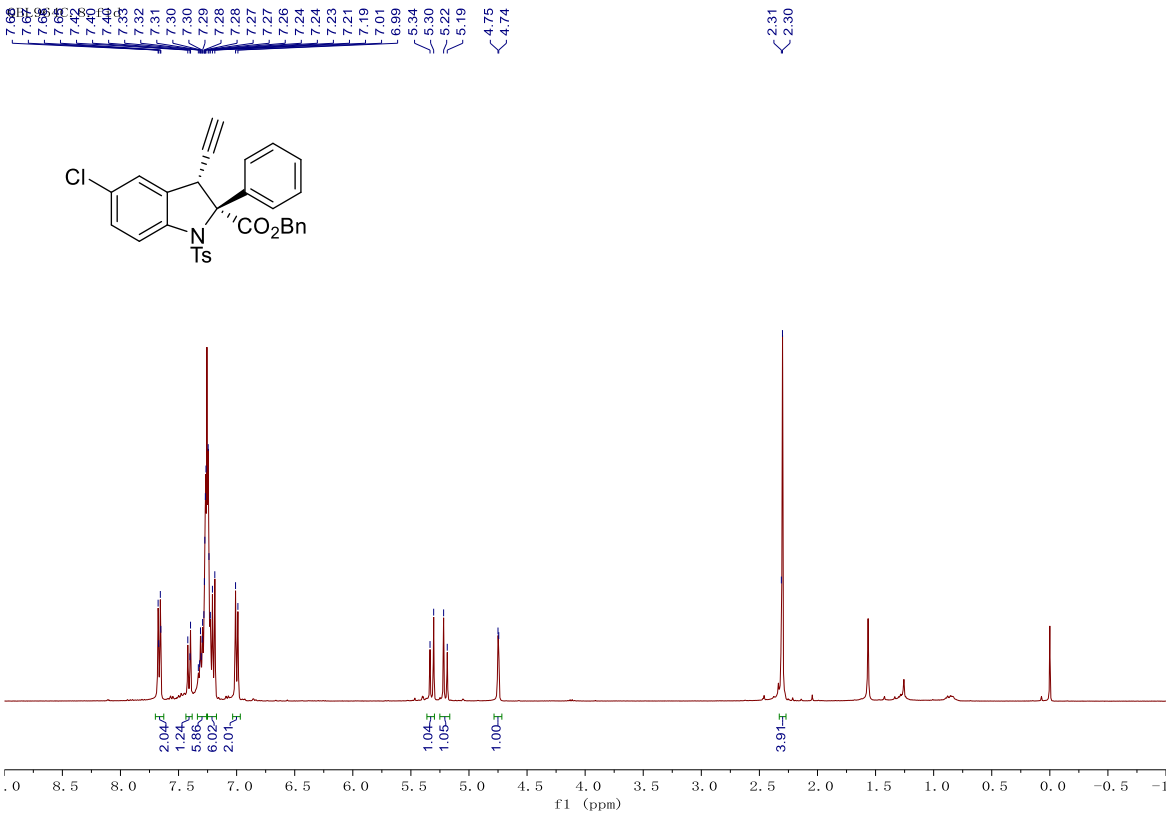
^{1}H NMR spectrum of compound 3n (400 MHz, $CDCl_3$)



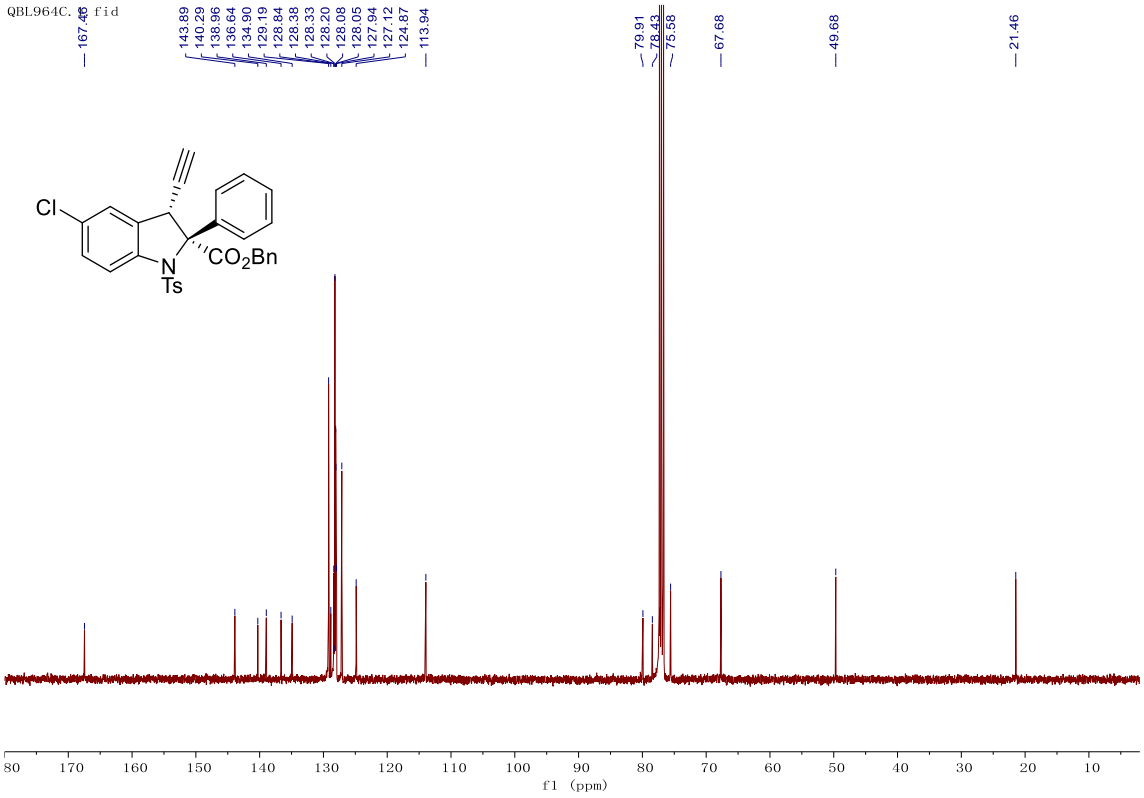
^{13}C NMR spectrum of compound 3n (100 MHz, $CDCl_3$)



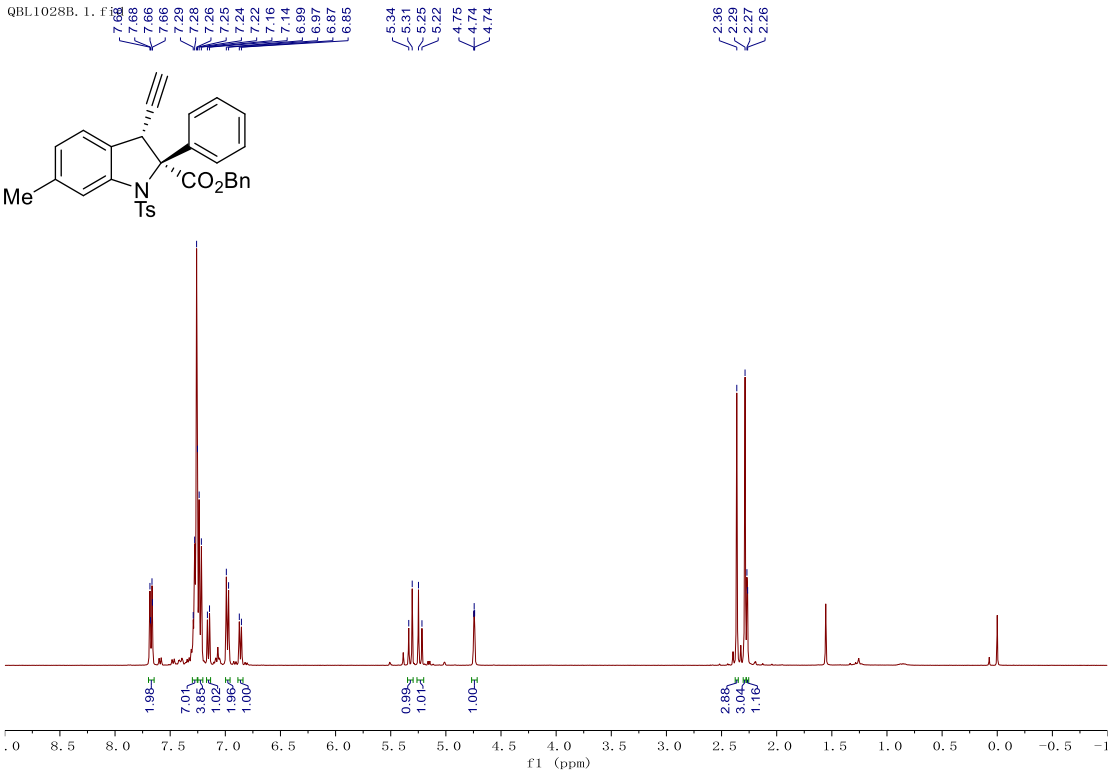
^{1}H NMR spectrum of compound 3o (400 MHz, $CDCl_3$)



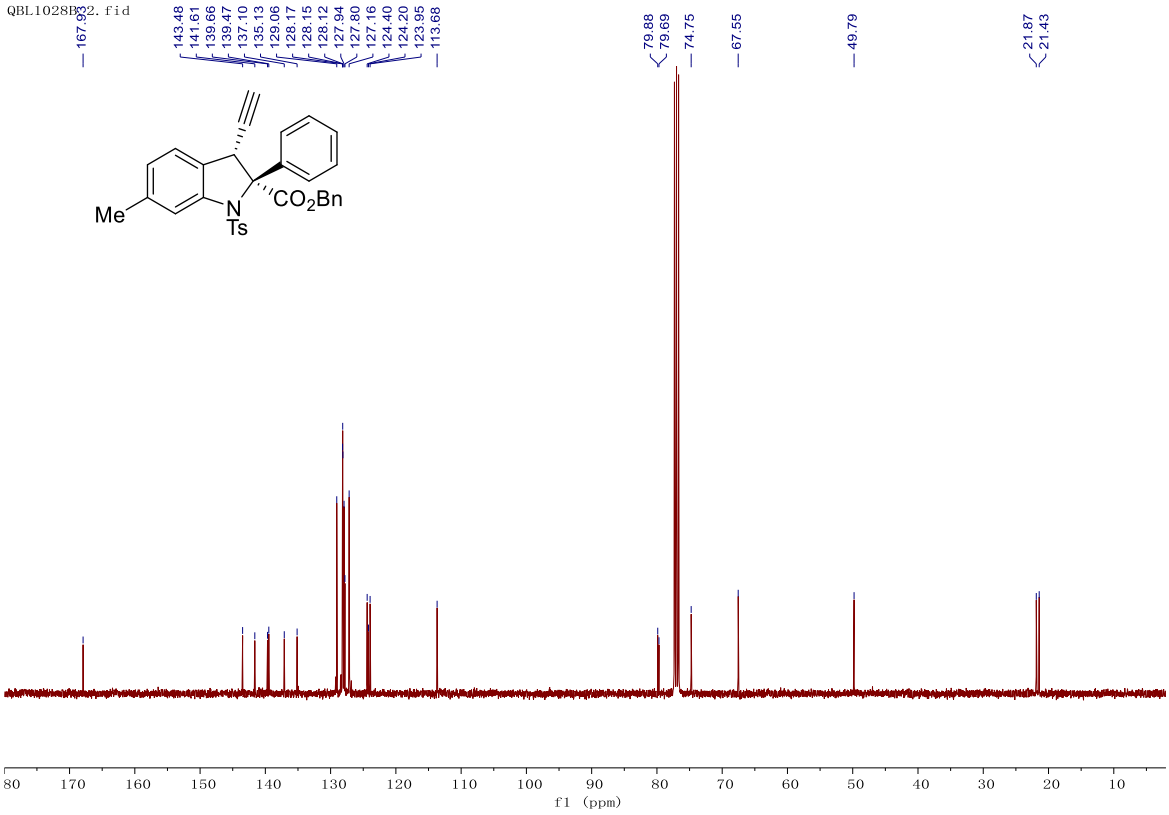
^{13}C NMR spectrum of compound 3o (100 MHz, $CDCl_3$)



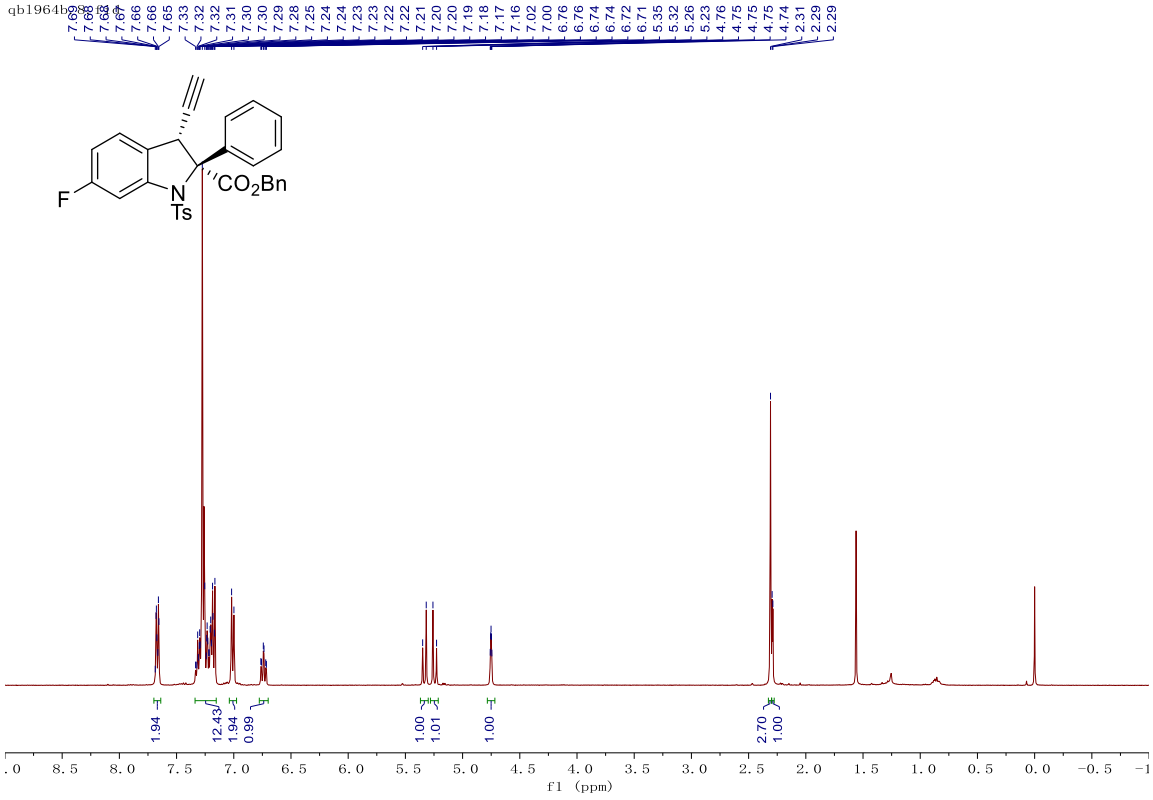
^{1}H NMR spectrum of compound 3p (400 MHz, $CDCl_3$)



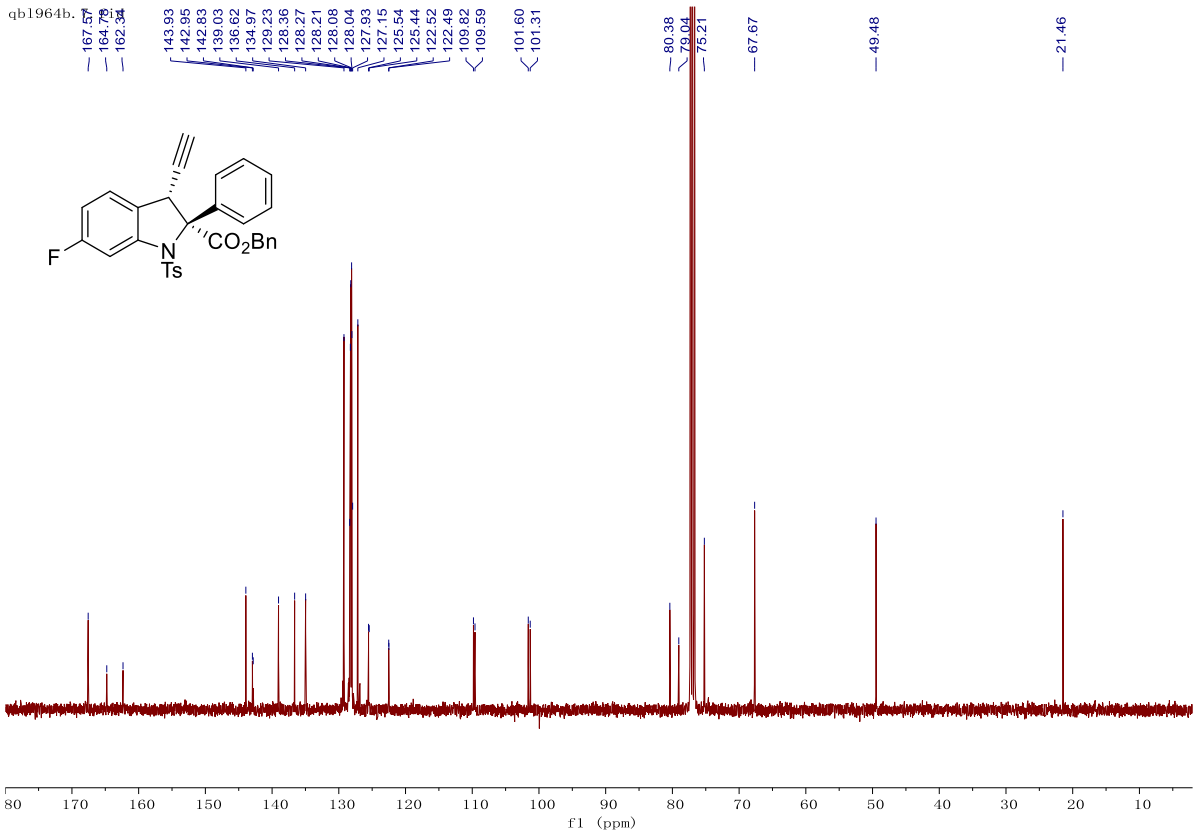
^{13}C NMR spectrum of compound 3p (100 MHz, $CDCl_3$)



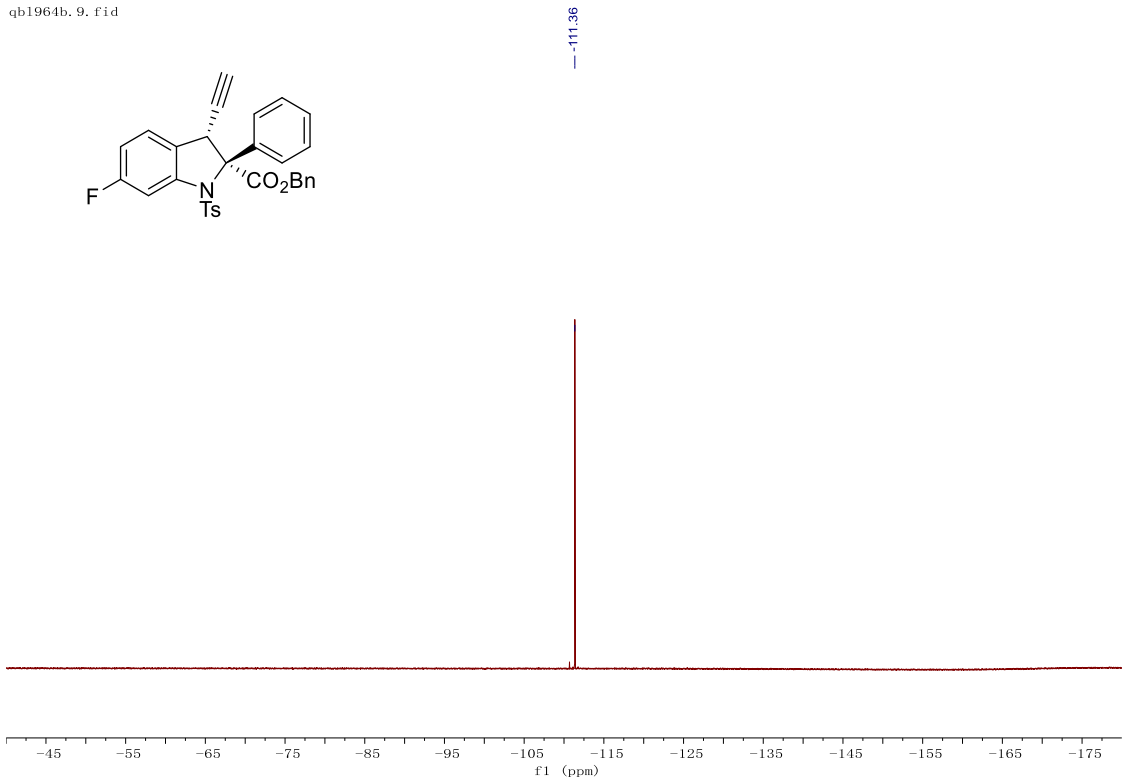
^{1}H NMR spectrum of compound 3q (400 MHz, $CDCl_3$)



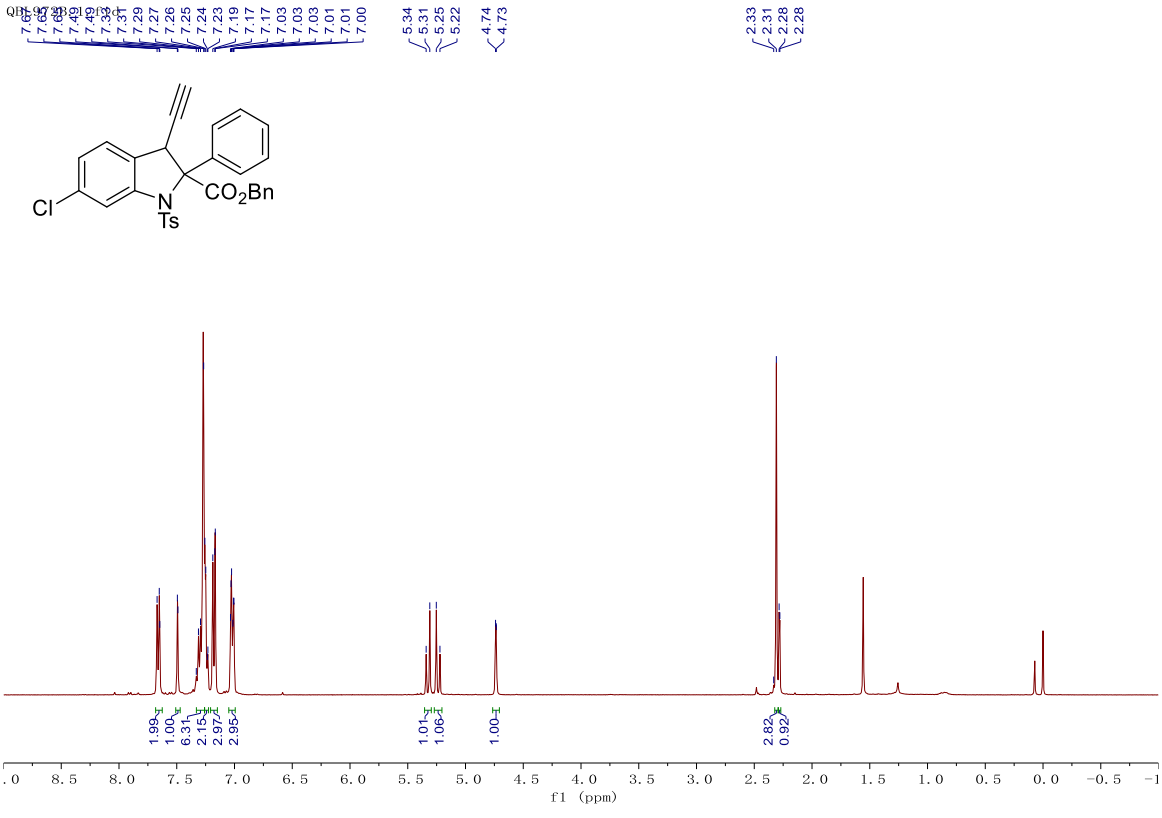
^{1}H NMR spectrum of compound 3q (400 MHz, $CDCl_3$)



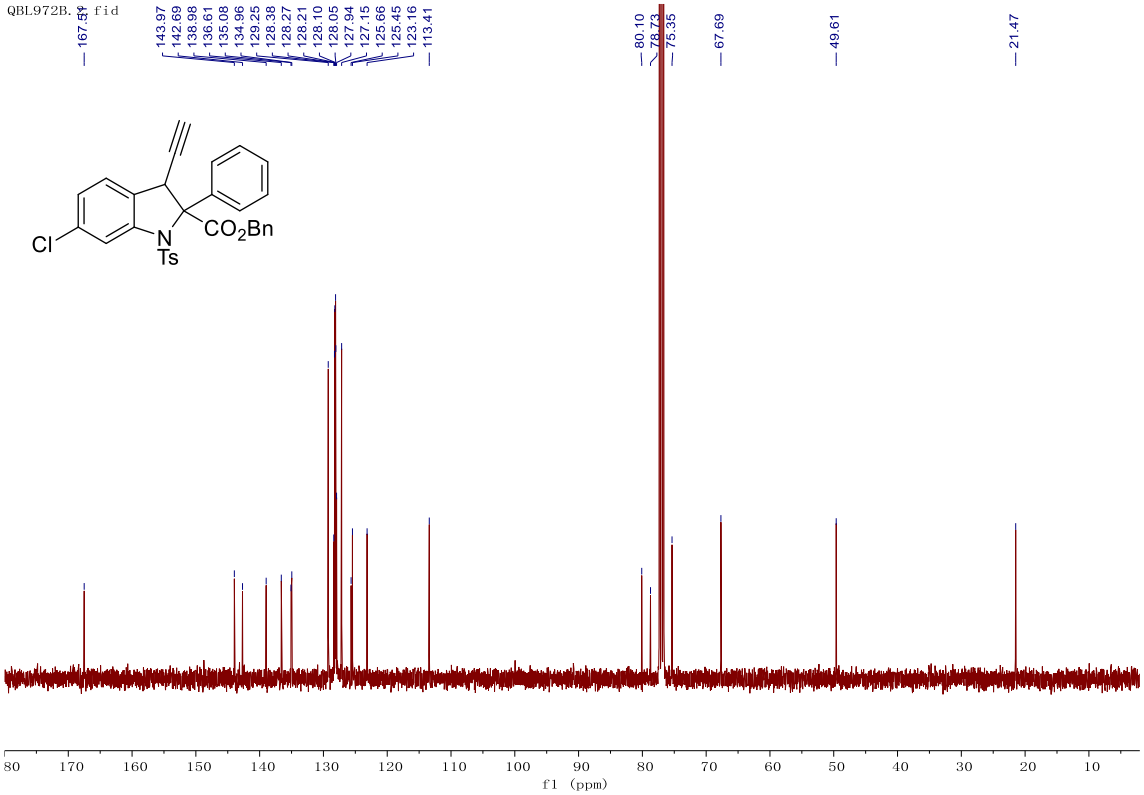
^{19}F NMR spectrum of compound 3q (376 MHz, $CDCl_3$)



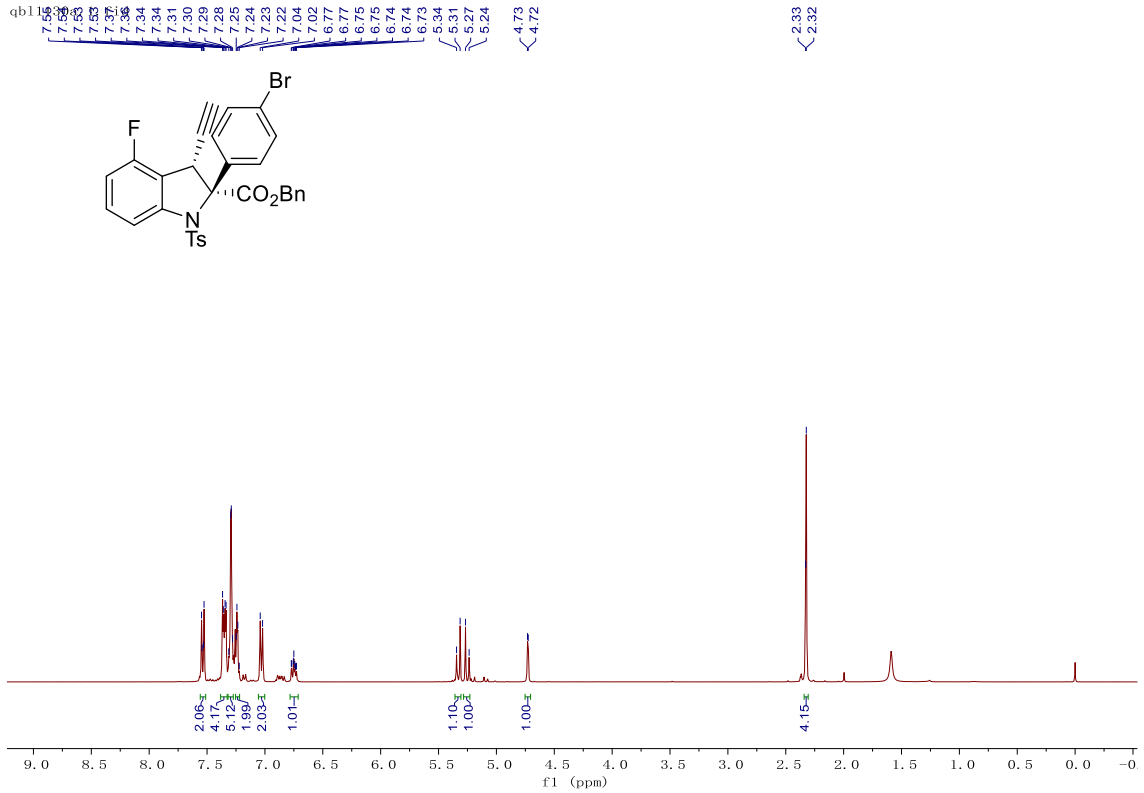
^{1}H NMR spectrum of compound 3r (400 MHz, $CDCl_3$)



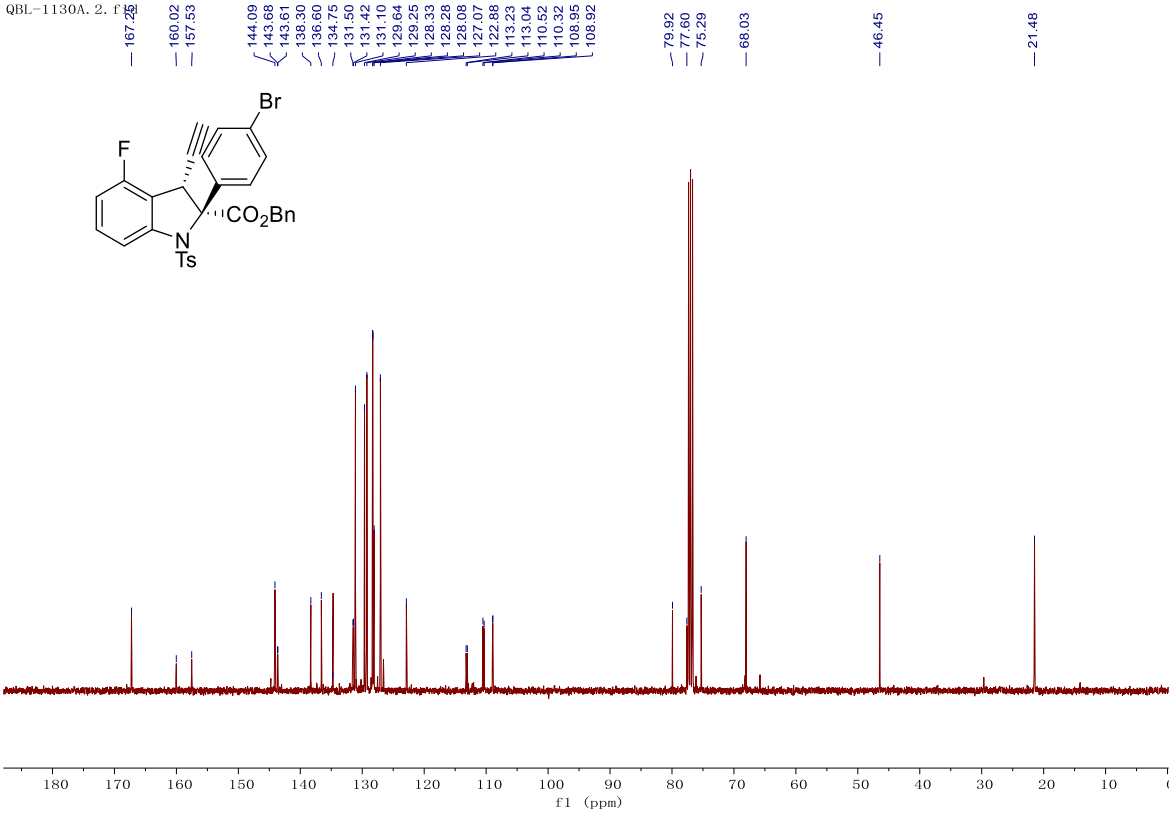
^{13}C NMR spectrum of compound 3r (100 MHz, $CDCl_3$)



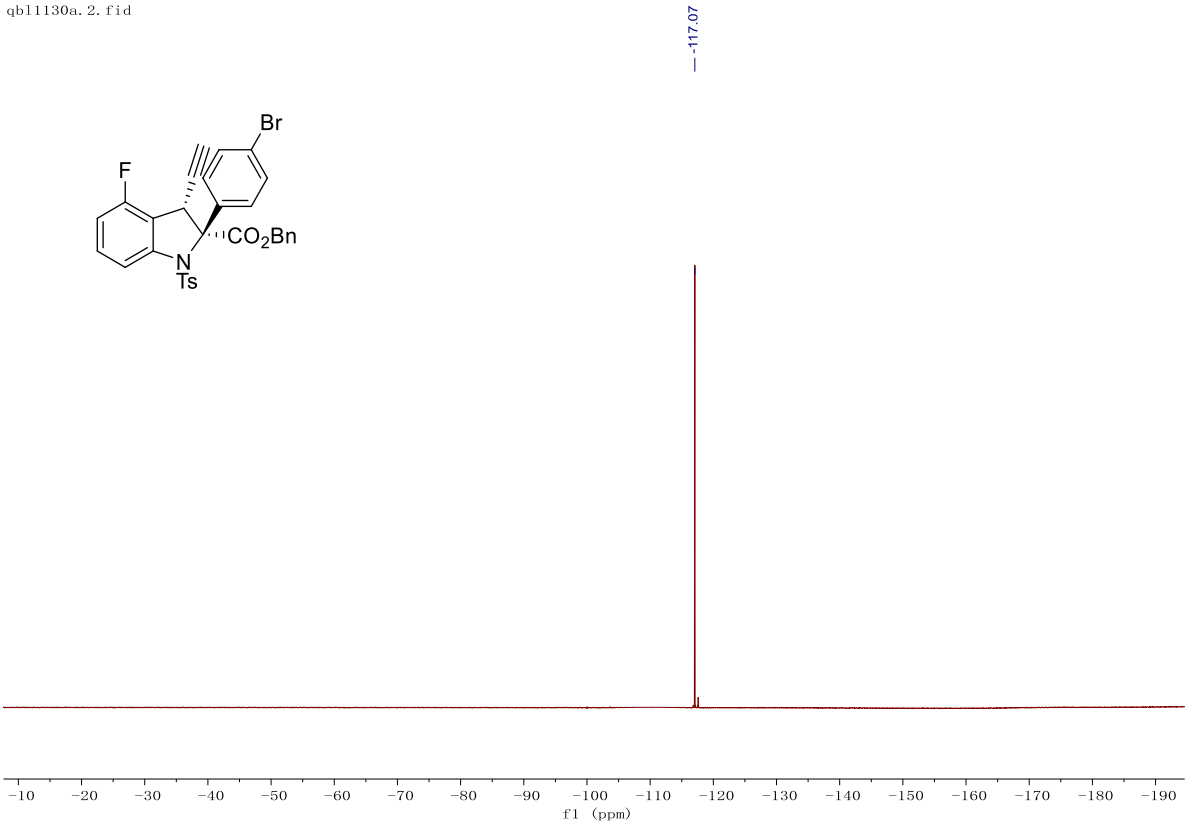
^{1}H NMR spectrum of compound 3s (400 MHz, $CDCl_3$)



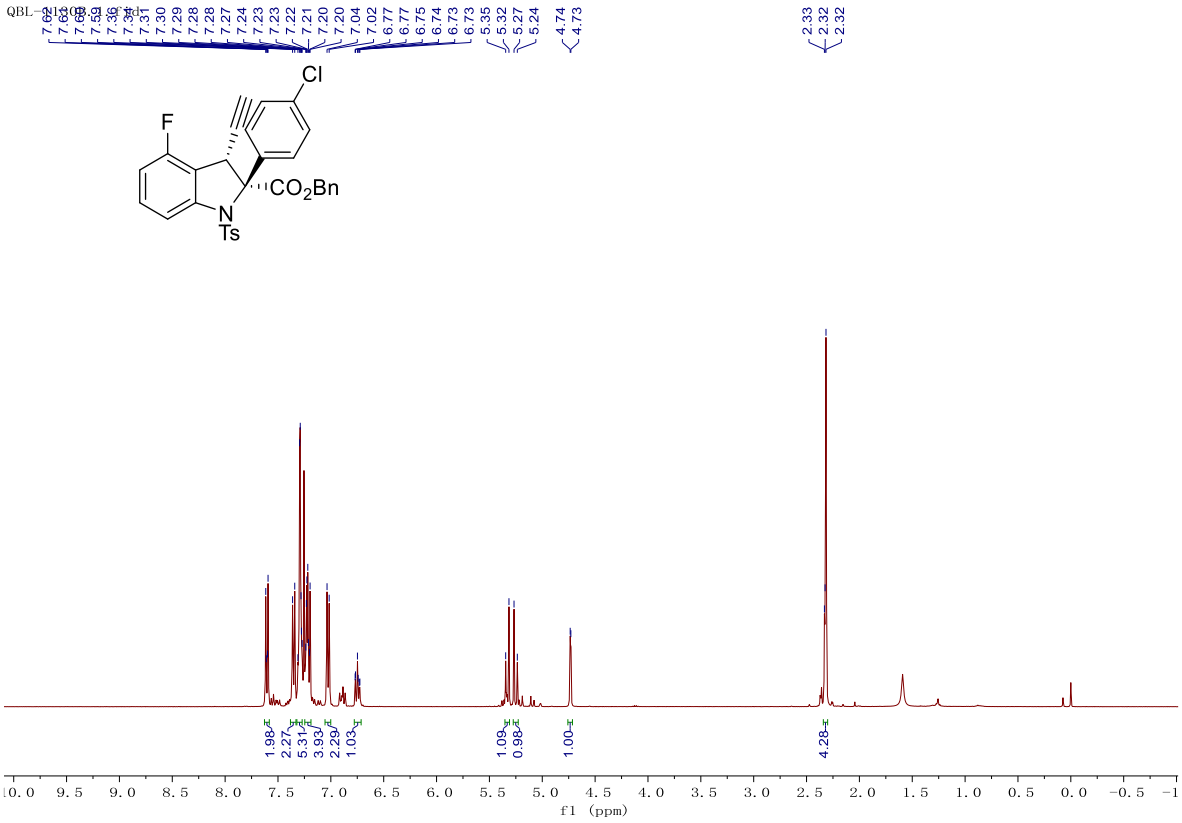
^{13}C NMR spectrum of compound 3s (100 MHz, $CDCl_3$)



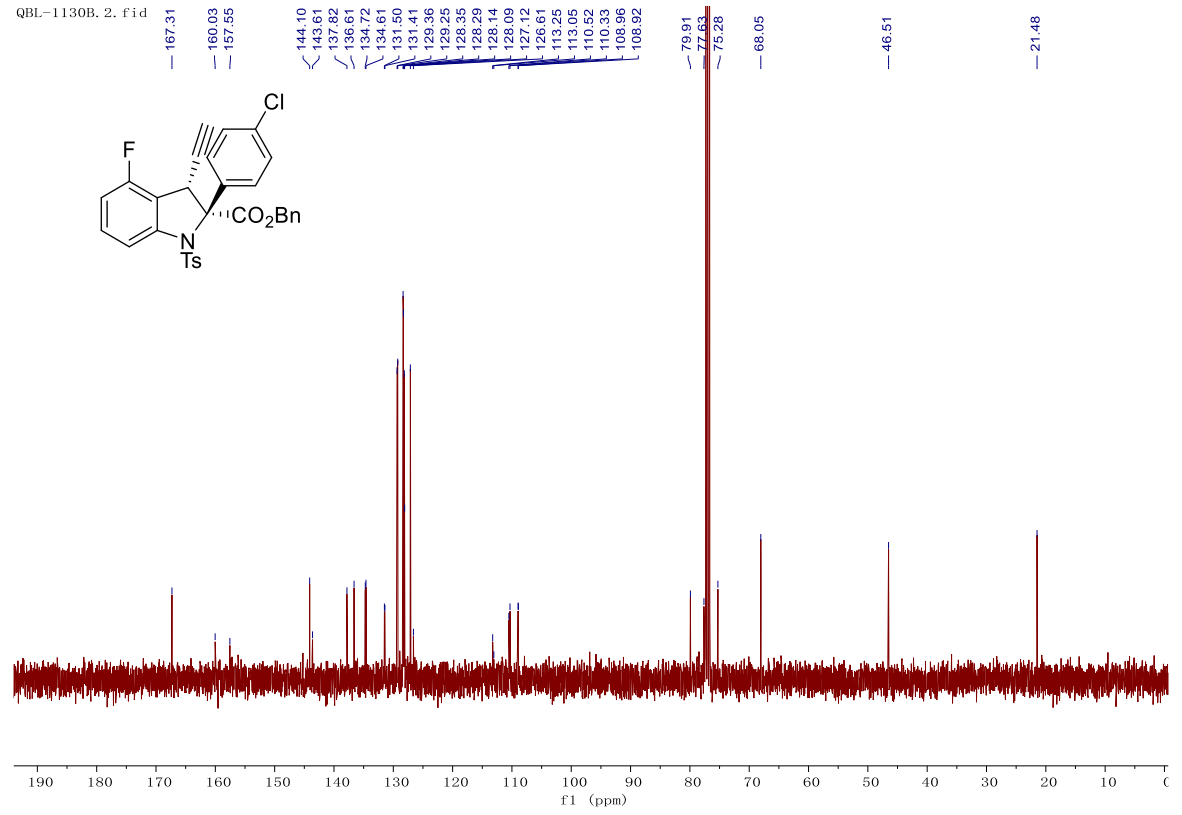
^{19}F NMR spectrum of compound 3s (376 MHz, $CDCl_3$)



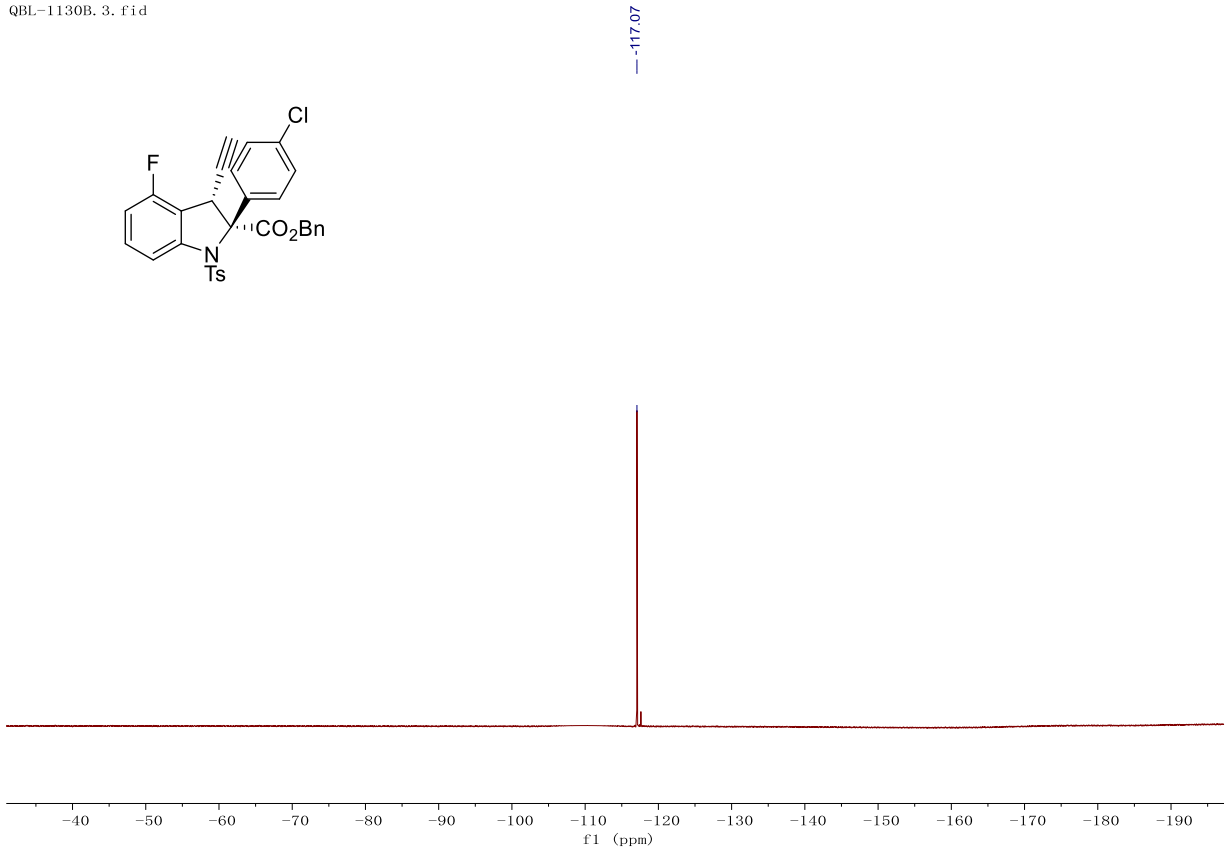
^{1}H NMR spectrum of compound 3t (400 MHz, $CDCl_3$)



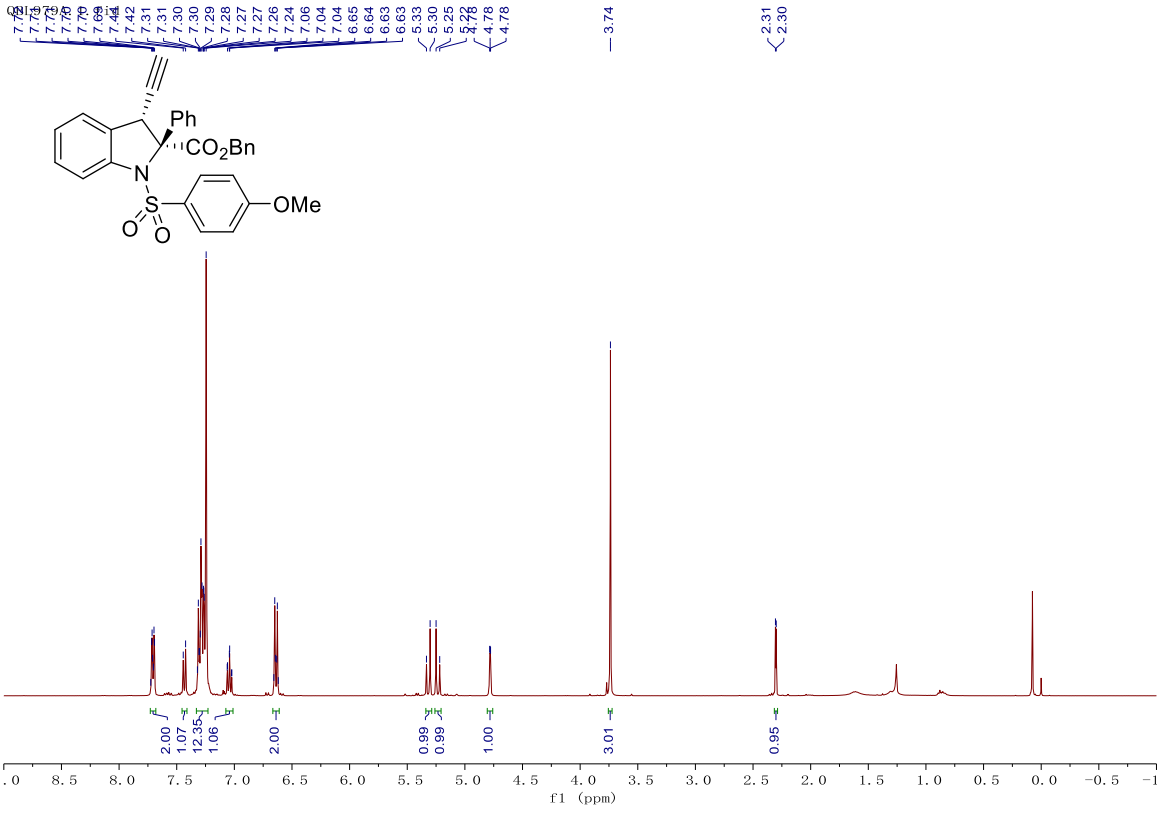
^{13}C NMR spectrum of compound 3t (100 MHz, $CDCl_3$)



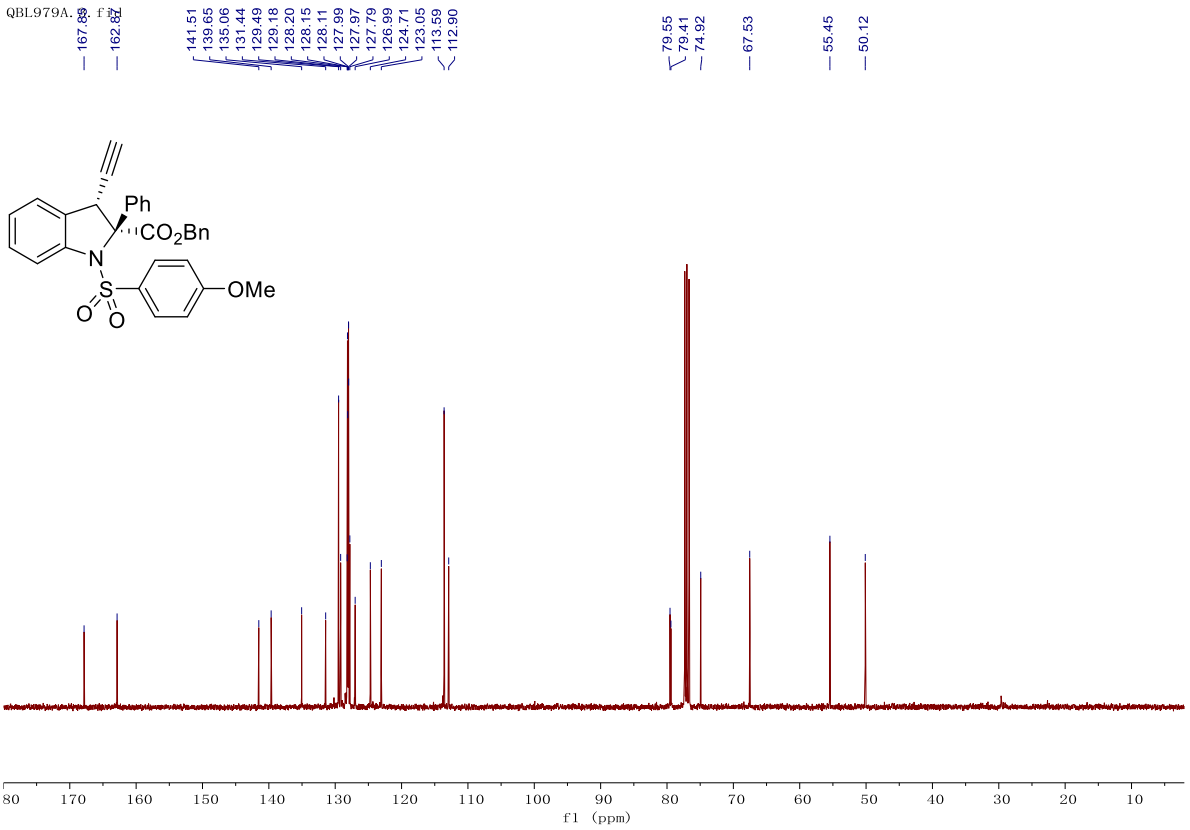
^{19}F NMR spectrum of compound 3t (376 MHz, $CDCl_3$)



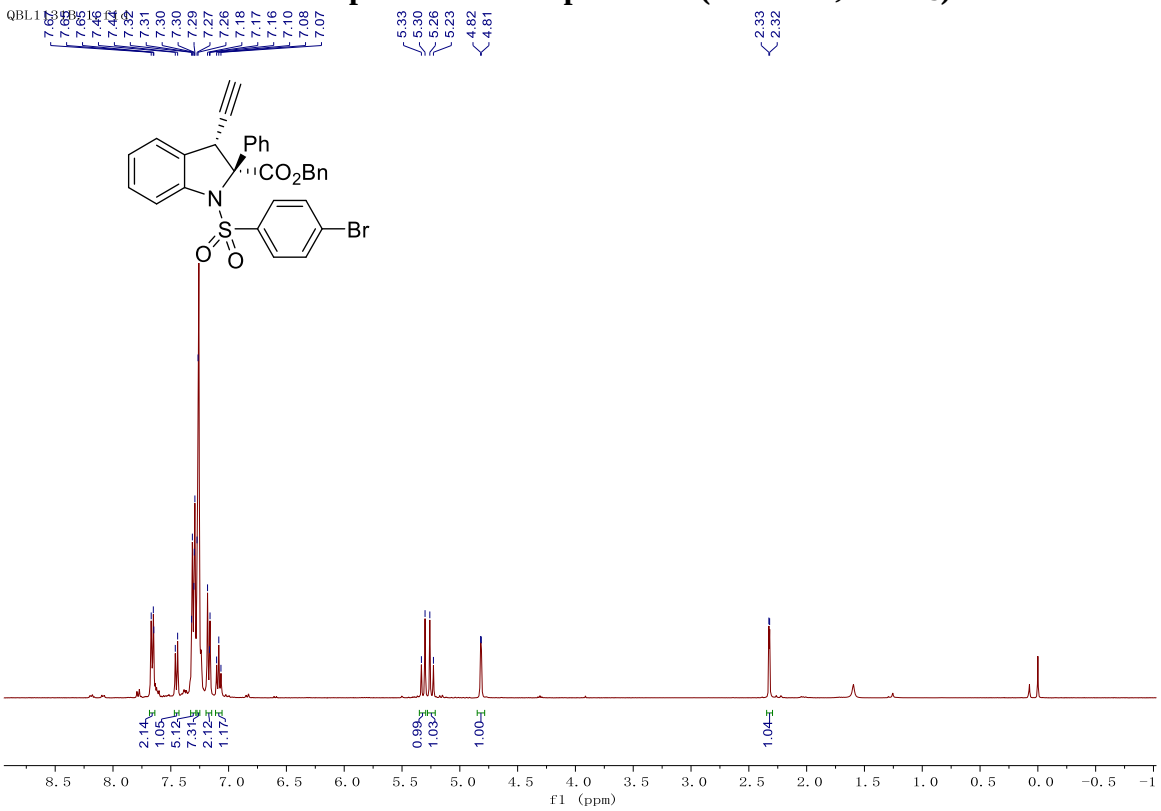
^{1}H NMR spectrum of compound 3u (400 MHz, $CDCl_3$)



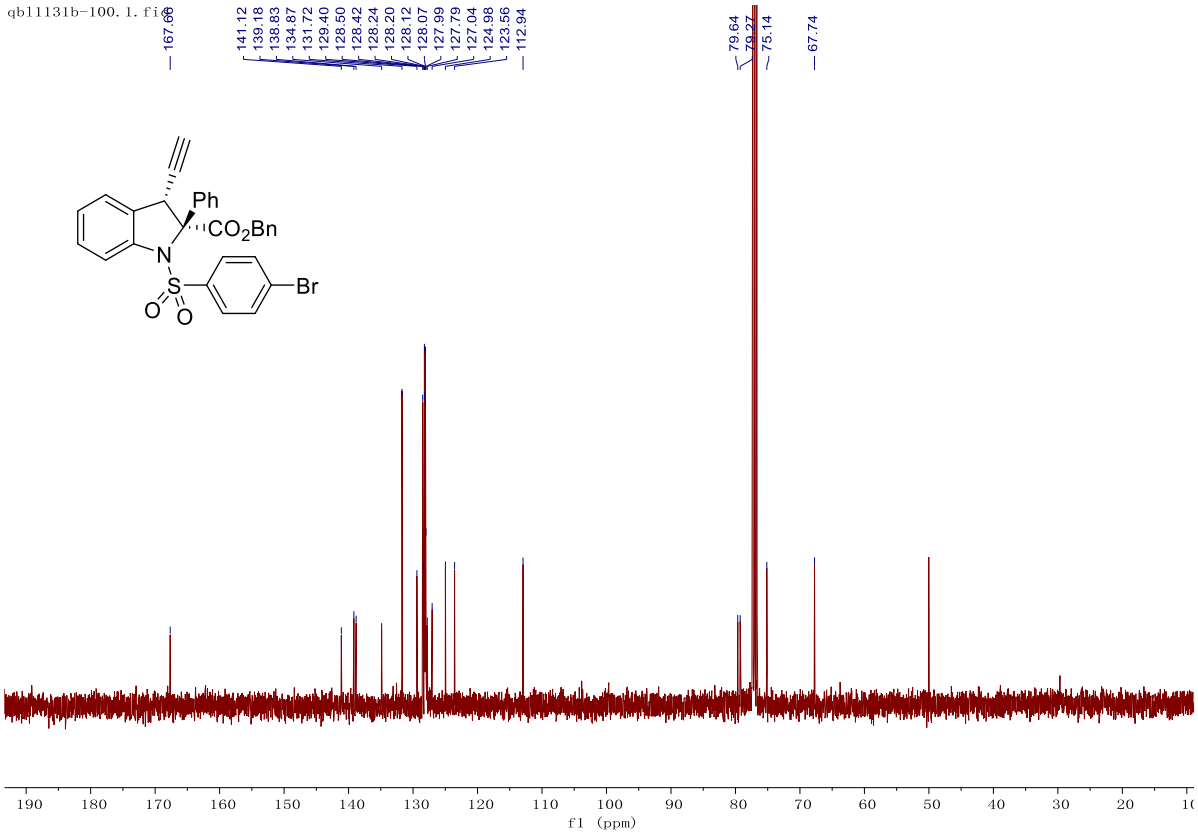
^{13}C NMR spectrum of compound 3u (100 MHz, $CDCl_3$)



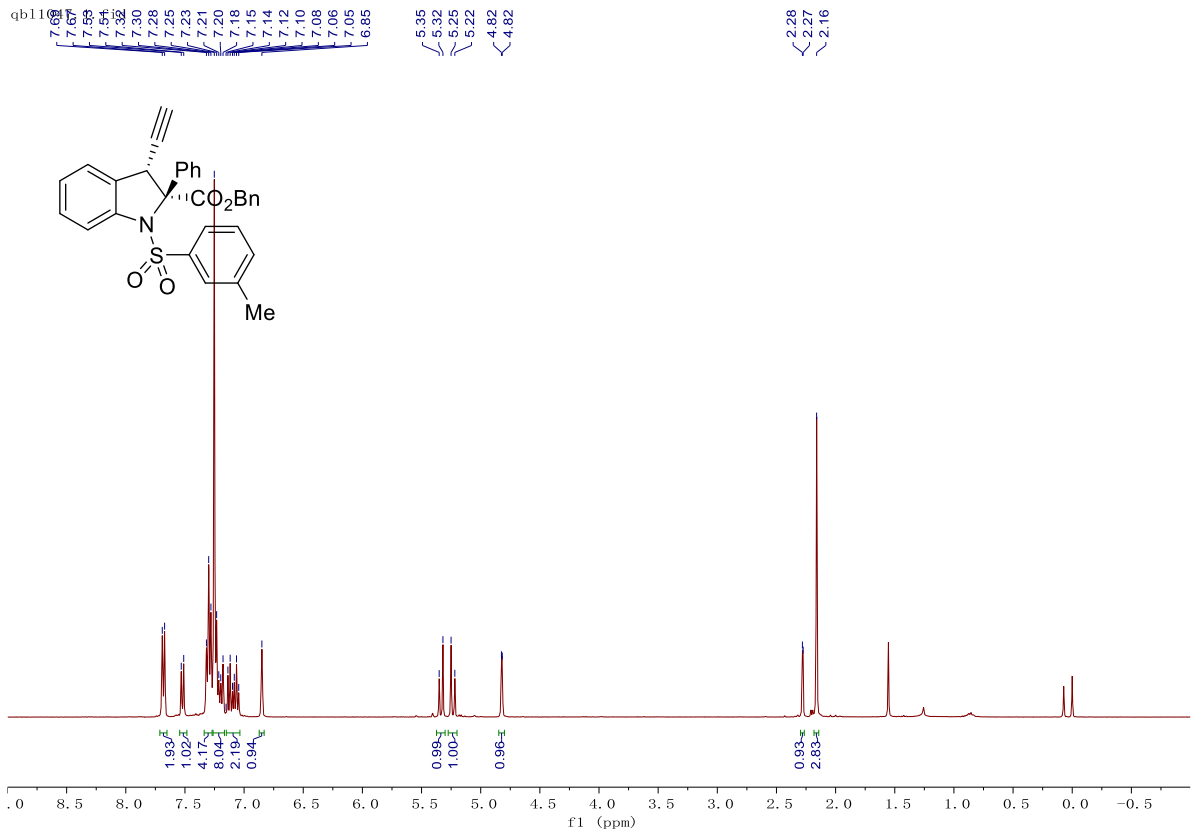
^{1}H NMR spectrum of compound 3v (400 MHz, $CDCl_3$)



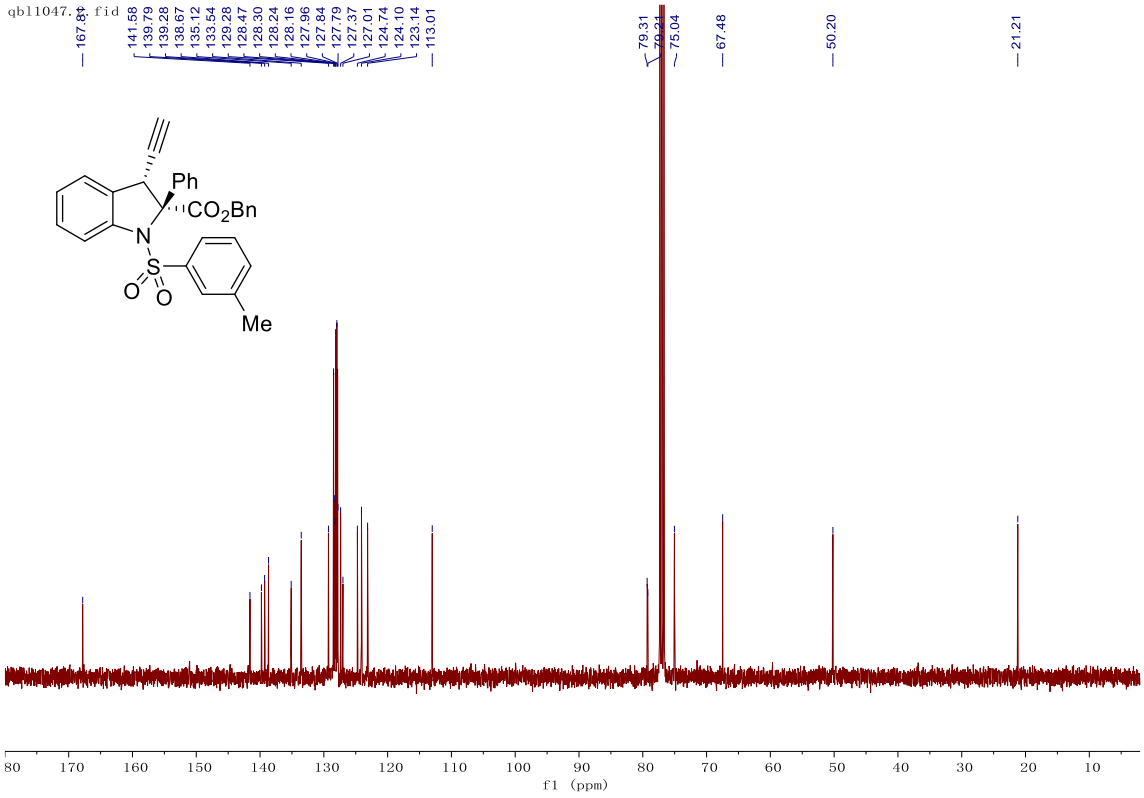
^{13}C NMR spectrum of compound 3v (100 MHz, $CDCl_3$)



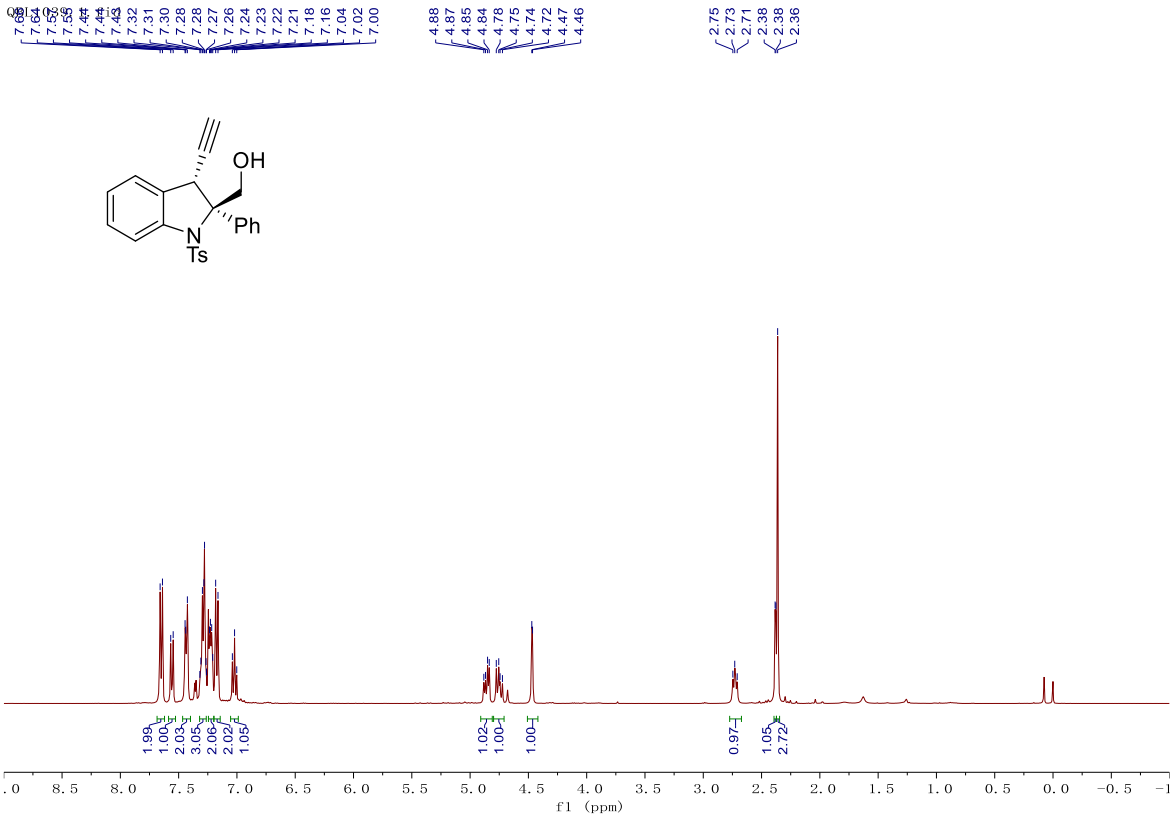
^{1}H NMR spectrum of compound 3w (400 MHz, $CDCl_3$)



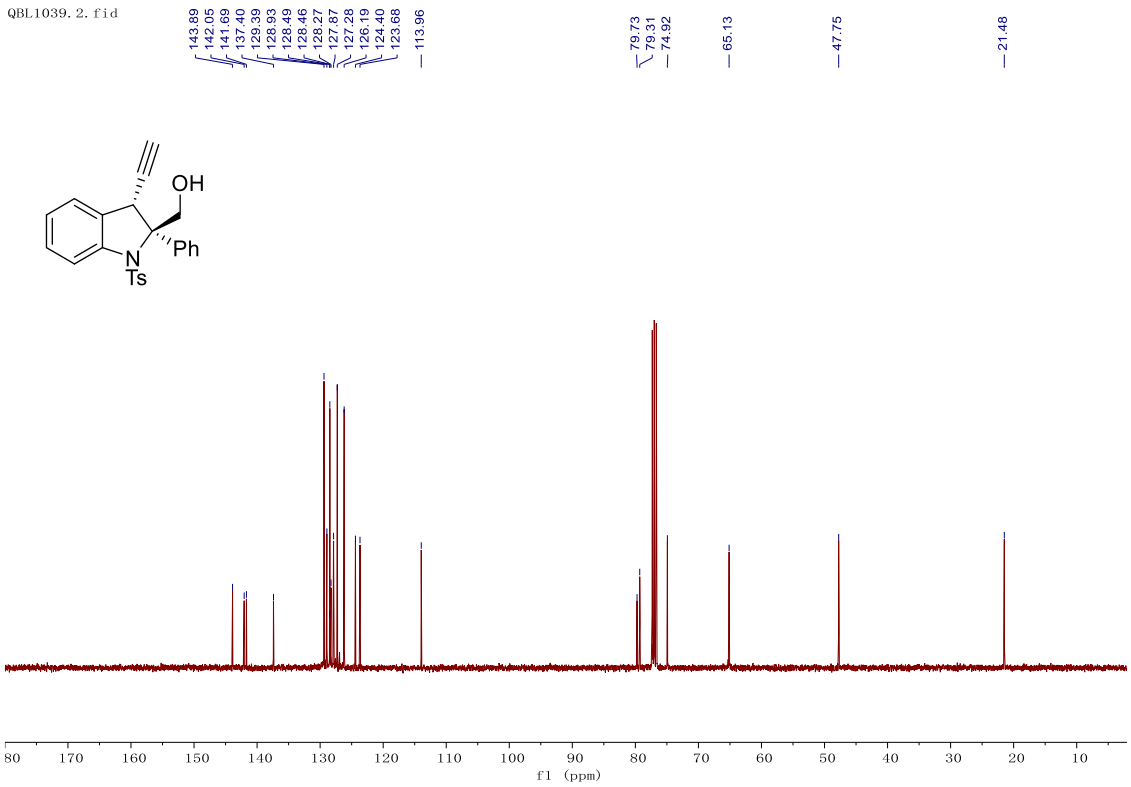
^{13}C NMR spectrum of compound 3w (100 MHz, $CDCl_3$)



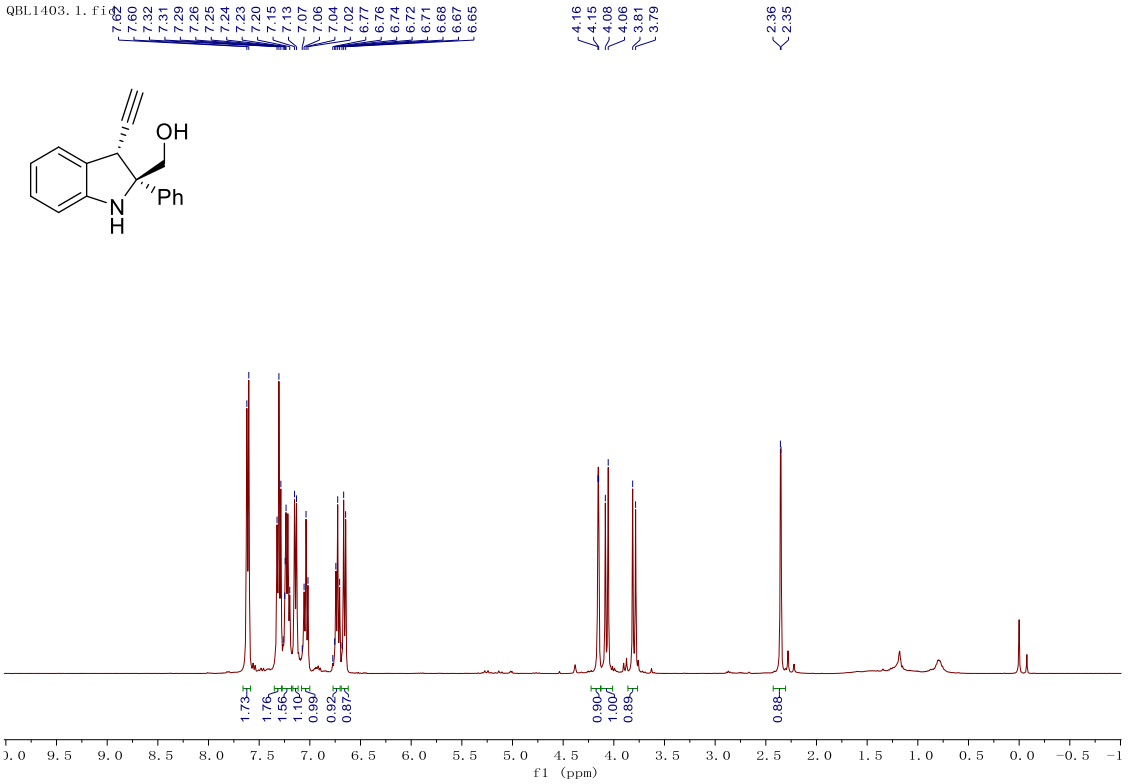
^{1}H NMR spectrum of compound 6 (400 MHz, $CDCl_3$)



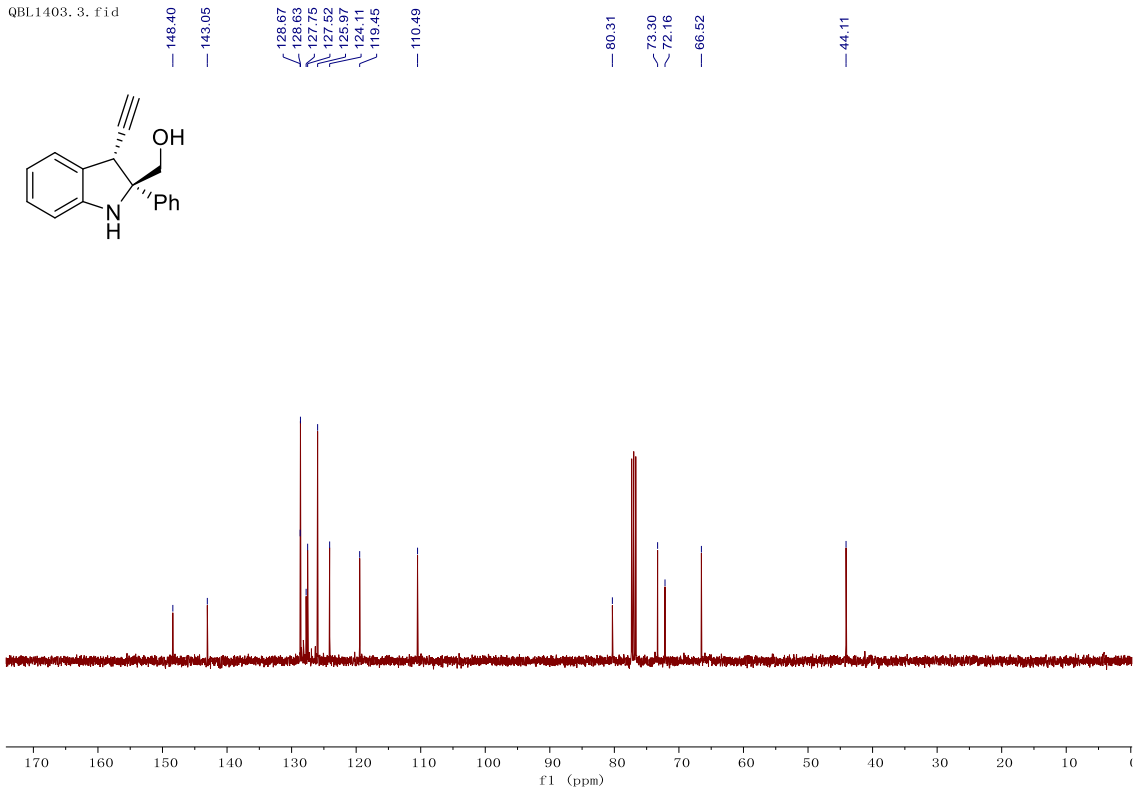
^{13}C NMR spectrum of compound 6 (100 MHz, $CDCl_3$)



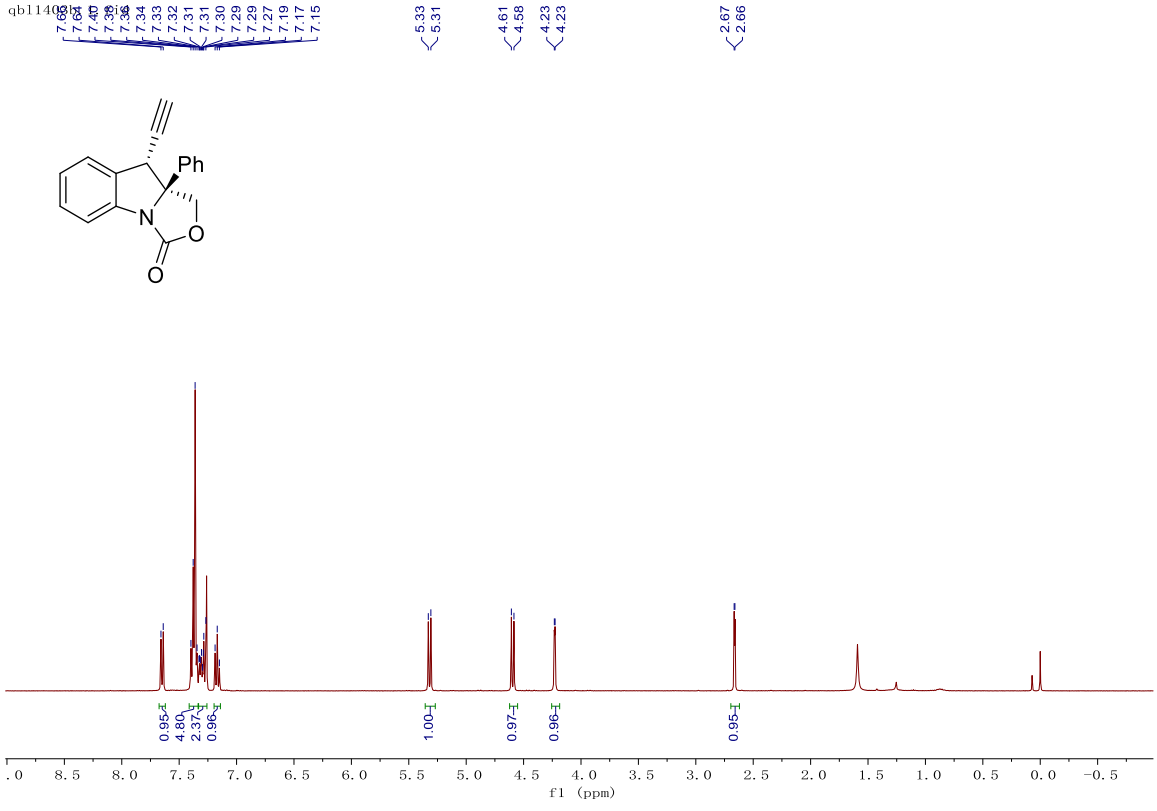
^{1}H NMR spectrum of compound 7 (400 MHz, $CDCl_3$)



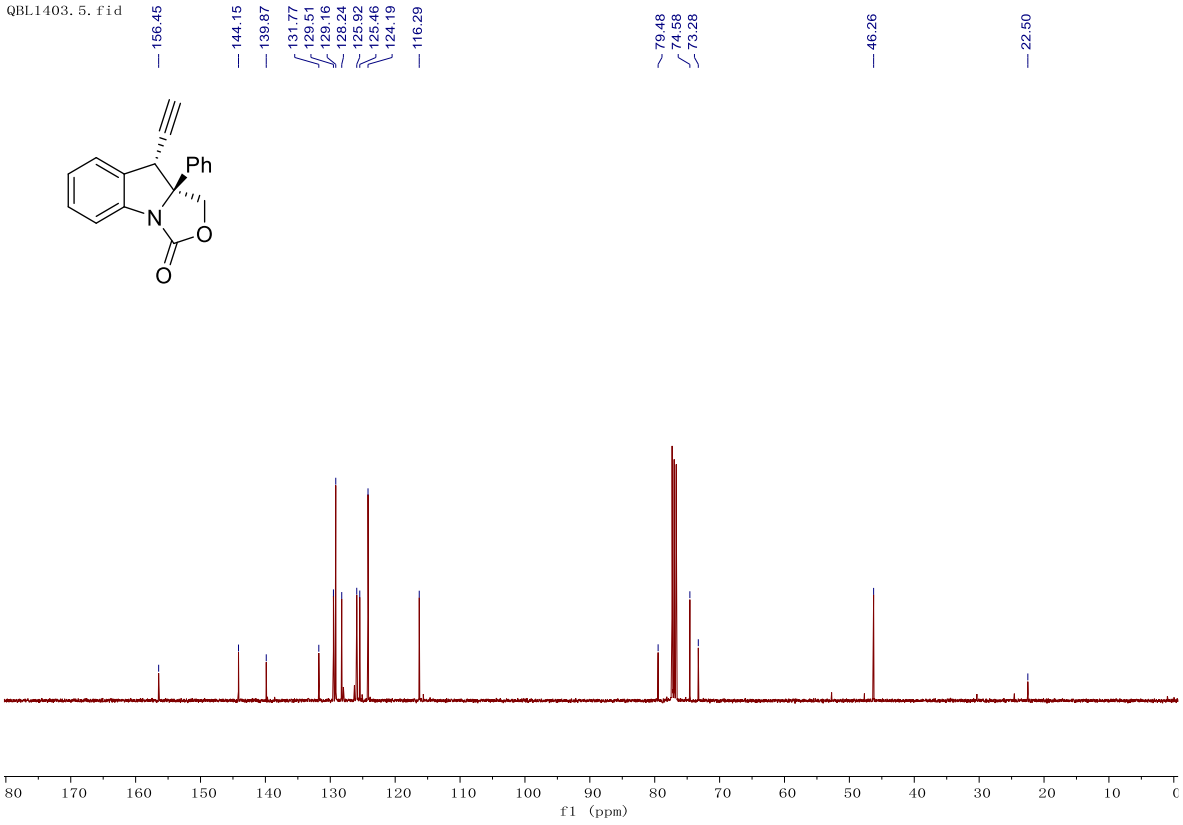
^{13}C NMR spectrum of compound 7 (100 MHz, $CDCl_3$)



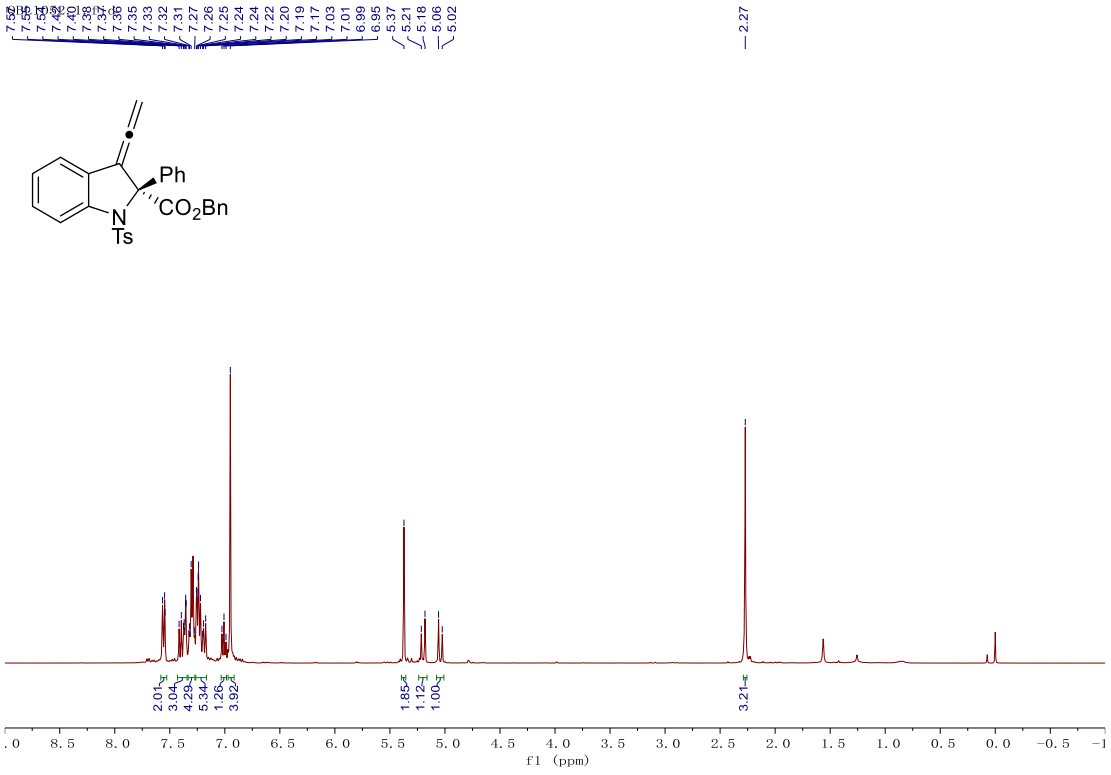
^{1}H NMR spectrum of compound 8 (400 MHz, $CDCl_3$)



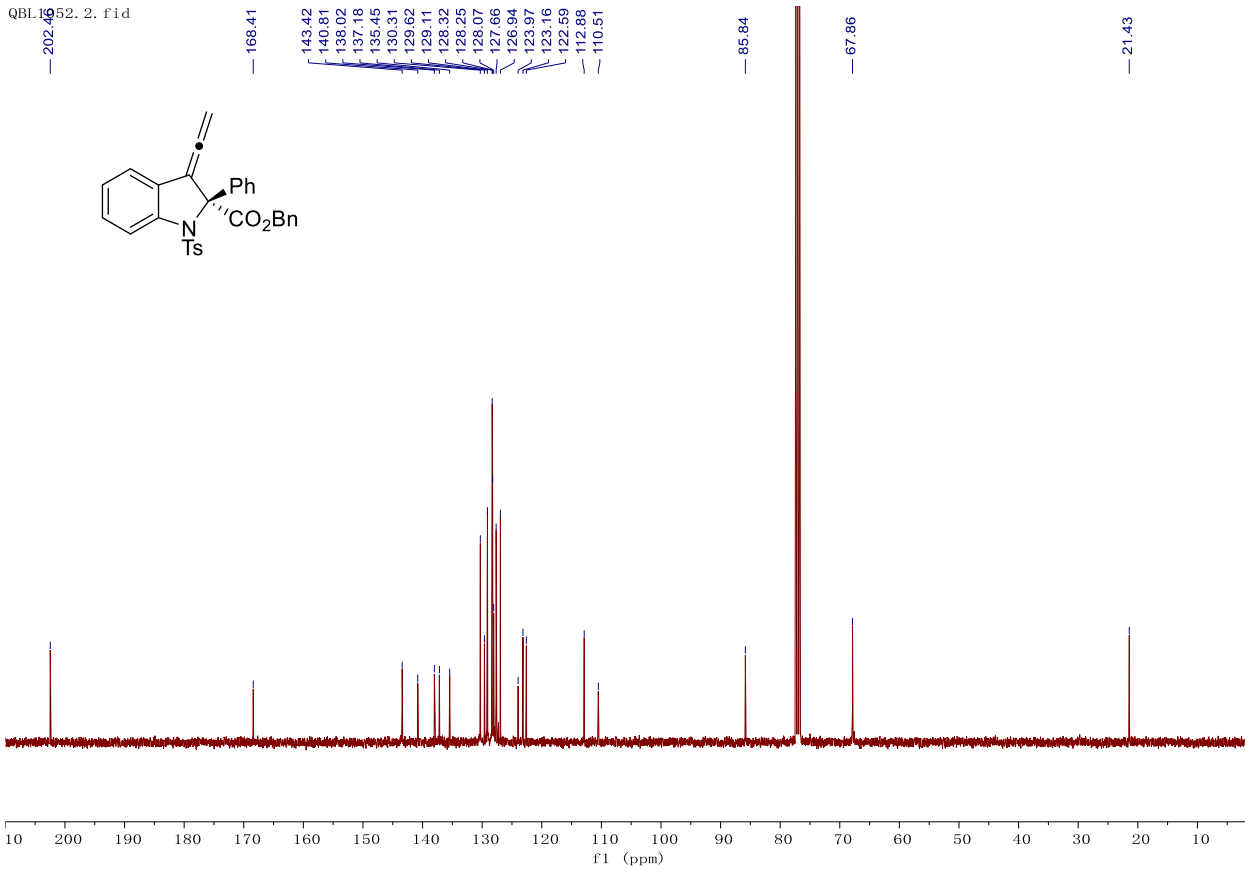
^{13}C NMR spectrum of compound 8 (100 MHz, $CDCl_3$)



^{1}H NMR spectrum of compound 9 (400 MHz, $CDCl_3$)

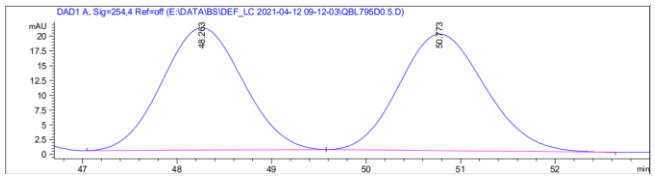


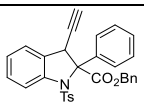
^{13}C NMR spectrum of compound 9 (100 MHz, $CDCl_3$)



6. Copies of HPLC Spectra

HPLC spectrum of racemic 3a

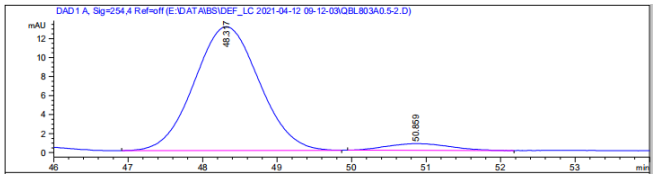


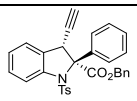


***rac*-3a**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	48.263	BB	0.8538	1230.16296	20.68695	49.7153
2	50.773	BB	0.8802	1244.25159	19.71780	50.2847

HPLC spectrum of 3a

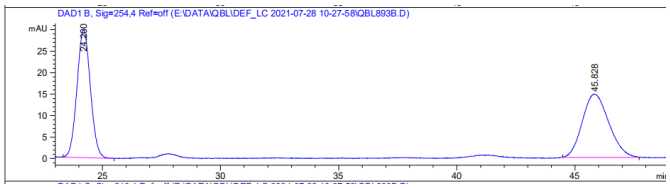


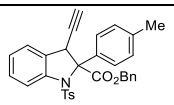


3a

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	48.317	BB	0.9152	789.37970	13.02188	94.9196
2	50.859	BB	0.7323	42.25006	7.16163e-1	5.0804

HPLC spectrum of racemic 3b

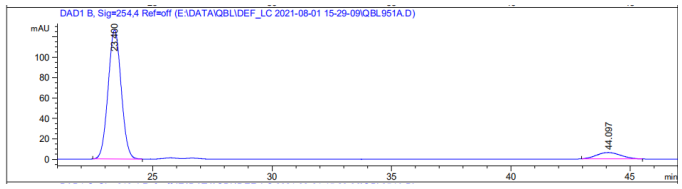


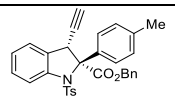


***rac*-3b**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	24.200	BB	0.5881	1172.66956	29.73348	50.6311
2	45.828	BB	0.9191	1143.43713	14.73920	49.3689

HPLC spectrum of 3b

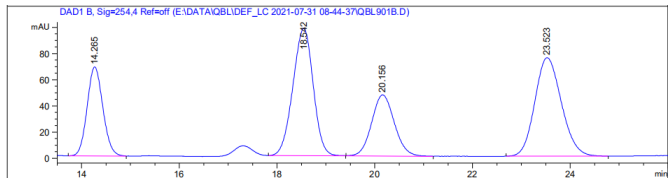


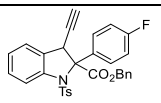


3b

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	23.400	BB	0.5859	4810.12988	126.41457	91.5915
2	44.097	BB	0.8312	441.59152	6.25859	8.4085

HPLC spectrum of racemic 3c

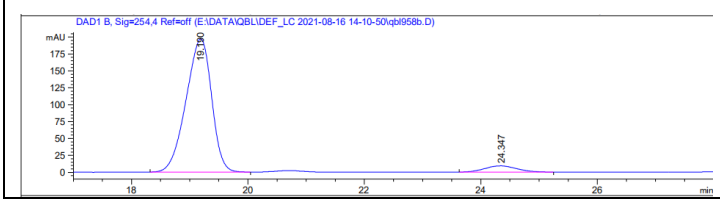


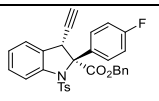


***rac*-3c**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.265	BB	0.3428	1520.18762	68.00169	17.5412
2	18.542	BB	0.4588	2805.01660	97.16734	32.3666
3	20.156	BB	0.4956	1501.18030	46.62340	17.3218
4	23.523	BB	0.5828	2840.01978	75.17506	32.7705

HPLC spectrum of 3c

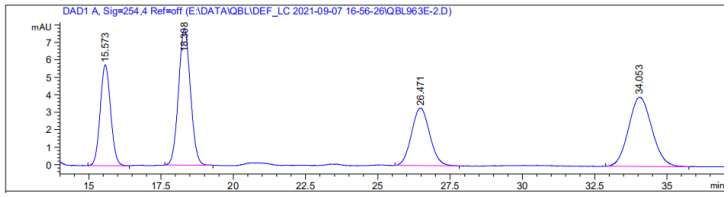


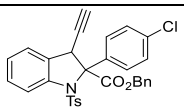


3c

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.190	BB	0.4692	6001.36572	197.09412	94.4744
2	24.347	BB	0.4675	351.00403	9.23379	5.5256

HPLC spectrum of racemic 3d

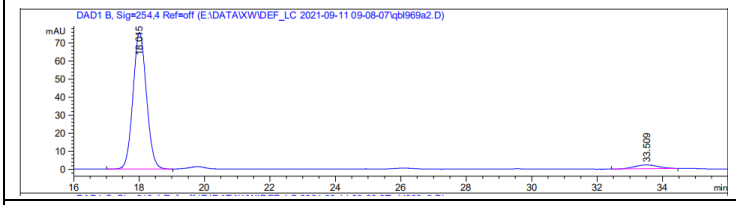


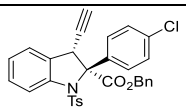


***rac*-3d**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.573	BB	0.3867	144.65961	5.76501	19.6349
2	18.308	BB	0.4459	224.48845	7.79617	30.4701
3	26.471	BB	0.5888	144.75035	3.30618	19.6472
4	34.053	BB	0.6989	222.85080	3.95803	30.2479

HPLC spectrum of 3d

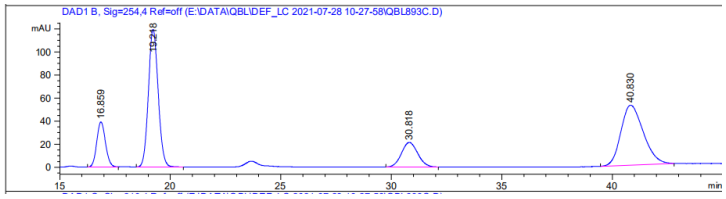


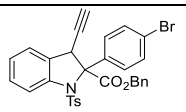


3d

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.015	BV	0.4434	2159.11987	75.54601	95.3480
2	33.509	BB	0.6772	105.34396	2.10015	4.6520

HPLC spectrum of racemic 3e

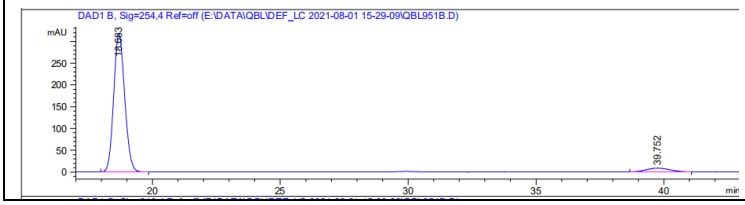


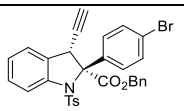


***rac*-3e**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.859	BB	0.4173	1070.11279	39.09487	11.2702
2	19.218	BB	0.4767	3668.60303	119.33127	38.6370
3	30.818	BB	0.6357	1096.15271	21.32385	11.5445
4	40.830	BB	0.9640	3660.17871	51.94664	38.5483

HPLC spectrum of 3e

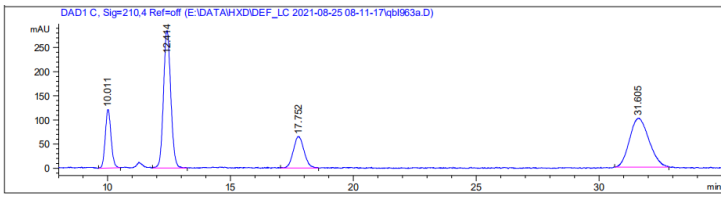


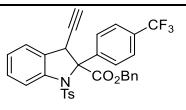


3e

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.683	BB	0.4639	9476.20313	317.79935	94.5164
2	39.752	BB	0.7484	549.79016	8.70979	5.4836

HPLC spectrum of racemic 3f

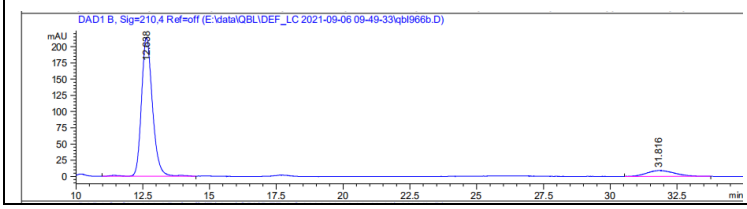


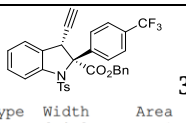


***rac*-3f**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.011	BV R	0.2390	1986.57324	121.33531	12.9173
2	12.414	VV R	0.3137	5856.90039	284.72473	38.0834
3	17.752	VV R	0.3815	1974.17603	65.15001	12.8367
4	31.605	VV R	0.6459	5561.49414	101.39738	36.1626

HPLC spectrum of 3f

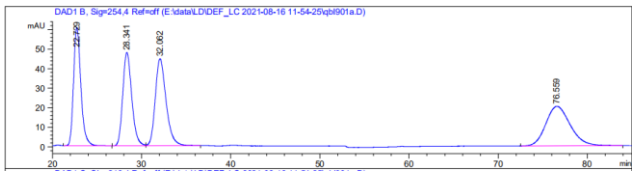


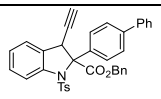


3f

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.638	VV R	0.4340	6125.74414	214.01921	90.1235
2	31.816	BB	0.8732	671.31421	9.09411	9.8765

HPLC spectrum of racemic 3g

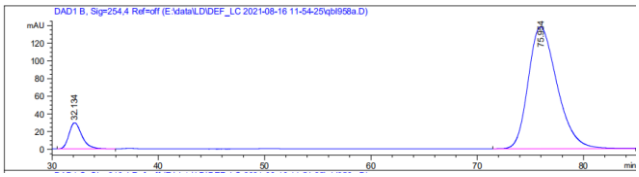


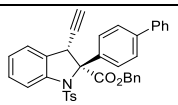


***rac*-3g**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	22.729	BB	0.8803	3470.05444	60.58092	24.0558
2	28.341	BV	1.0919	3358.05103	47.78162	23.2794
3	32.062	VB	1.2896	3760.28833	44.51208	26.0678
4	76.559	BB	2.4673	3836.61475	20.20539	26.5970

HPLC spectrum of 3g

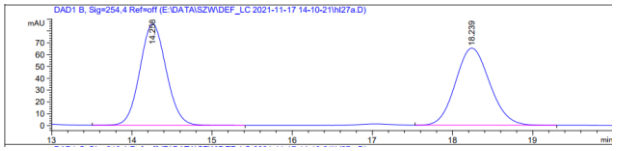


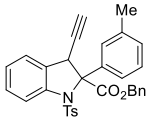


3g

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	32.134	VB	1.2870	2492.78467	29.58451	8.7729
2	75.954	BBA	2.8678	2.59217e4	137.72528	91.2271

HPLC spectrum of racemic 3l

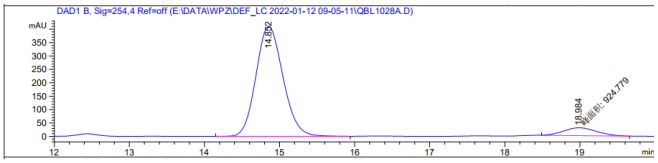


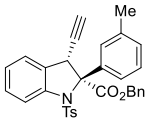


***rac*-3l**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.258	BB	0.3557	1950.95837	85.66096	50.1834
2	18.239	BB	0.4648	1936.69897	65.15800	49.8166

HPLC spectrum of 3l

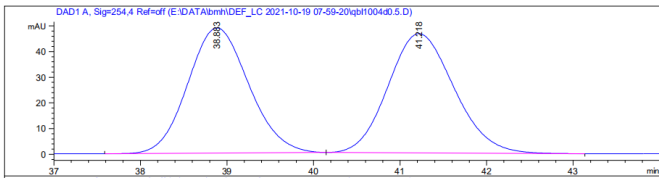


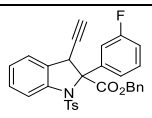


3l

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.852	BB	0.3889	1.02269e4	410.20135	91.7072
2	18.984	MM	0.5215	924.77881	29.55631	8.2928

HPLC spectrum of racemic 3i

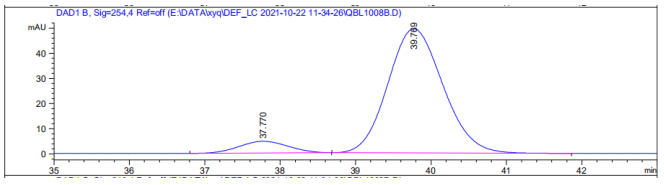


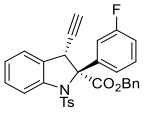


***rac*-3i**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	38.883	BB	0.7574	2388.17090	48.76152	49.2134
2	41.218	BB	0.8210	2464.51660	46.45378	50.7866

HPLC spectrum of 3i

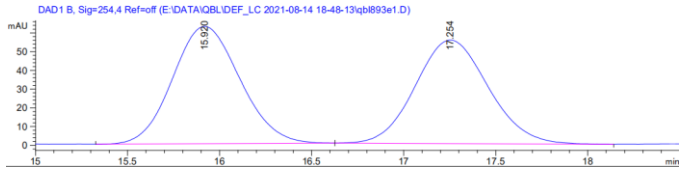


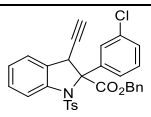


3i

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	37.770	BB	0.6045	212.53212	4.67388	7.8199
2	39.769	BB	0.7784	2505.31055	49.33963	92.1801

HPLC spectrum of racemic 3j

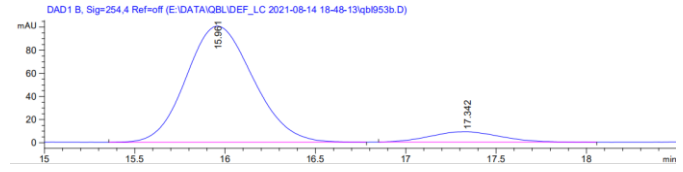


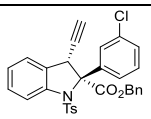


***rac*-3j**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.920	BB	0.3887	1593.95044	62.67661	51.0591
2	17.254	BB	0.4262	1527.82214	55.32069	48.9409

HPLC spectrum of 3j

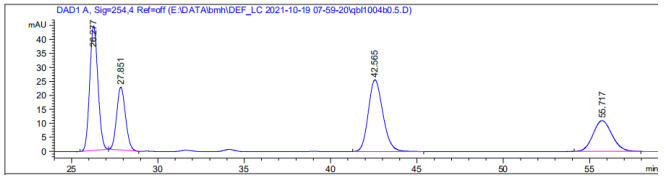


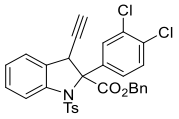


3j

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.961	BB	0.4010	2592.86133	100.49010	91.4422
2	17.342	BB	0.3387	242.65880	8.99517	8.5578

HPLC spectrum of racemic 3k

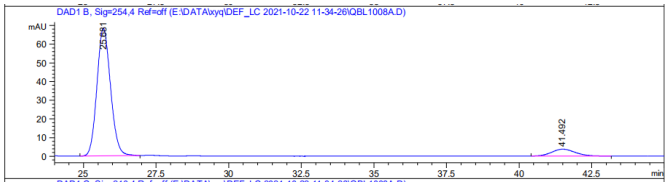


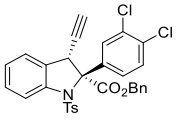


***rac*-3k**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	26.277	BB	0.5107	1466.99023	44.48631	31.8503
2	27.851	BB	0.5444	799.54608	22.51241	17.3592
3	42.565	BB	0.8847	1504.15833	25.62928	32.6573
4	55.717	BB	0.9636	835.19720	11.00307	18.1332

HPLC spectrum of 3k

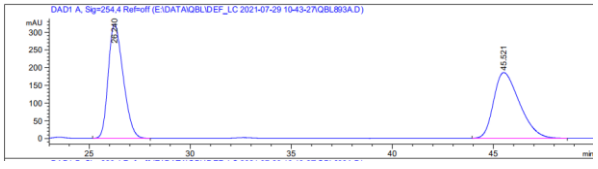


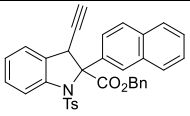


3k

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	25.681	BB	0.5043	2223.32471	68.20927	91.4676
2	41.492	BB	0.6697	207.39995	3.69016	8.5324

HPLC spectrum of racemic 3l

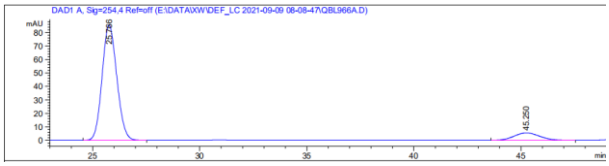


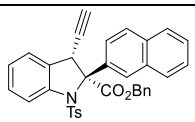


***rac*-3l**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	26.240	BB	0.7980	1.65535e4	321.89844	50.1104
2	45.521	BB	1.2914	1.64805e4	185.33432	49.8896

HPLC spectrum of 3l

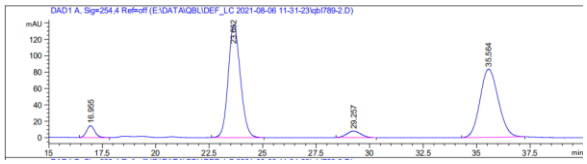


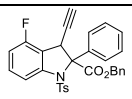


3l

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	25.766	BB	0.7468	4082.99438	85.55220	89.9145
2	45.250	BB	0.9884	457.97958	5.50593	10.0855

HPLC spectrum of racemic 3m

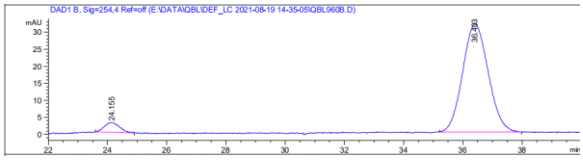


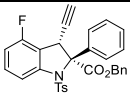


***rac*-3m**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.955	BB	0.3956	382.09906	14.40061	3.4431
2	23.652	BB	0.6153	5431.51611	136.76633	48.9438
3	29.257	BB	0.5465	357.81537	7.83938	3.2243
4	35.564	BB	0.8514	4926.01904	83.12062	44.3887

HPLC spectrum of 3m

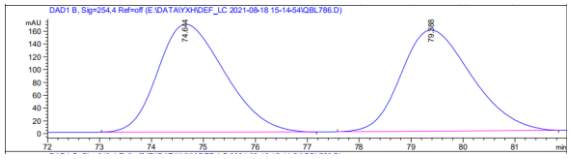


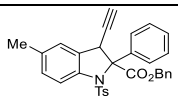


3m

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	24.155	BB	0.4261	102.19530	2.86545	5.1080
2	36.403	BB	0.7123	1898.49890	31.62892	94.8920

HPLC spectrum of racemic 3n

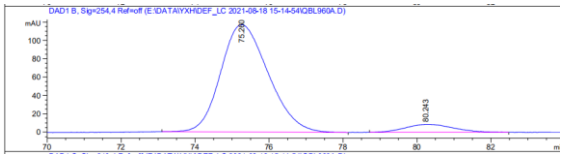


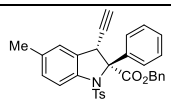


***rac*-3n**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	74.644	BB	1.0628	1.50982e4	168.27826	50.3553
2	79.388	BB	1.1313	1.48851e4	157.68823	49.6447

HPLC spectrum of 3n

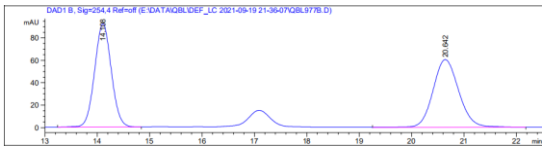


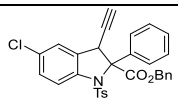


3n

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	75.260	BB	1.2268	1.04714e4	116.92561	92.9332
2	80.243	BB	1.0707	796.26788	8.77491	7.0668

HPLC spectrum of racemic 3o

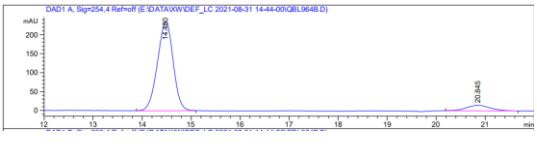


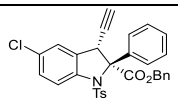


***rac*-3o**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.108	BB	0.3425	2042.79443	92.21248	49.8163
2	20.642	BB	0.5292	2057.85645	60.44816	50.1837

HPLC spectrum of 3o

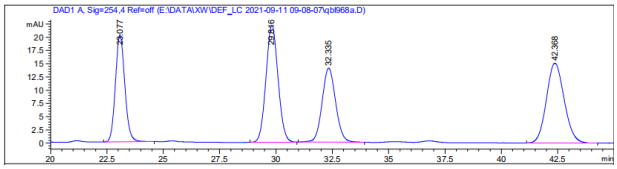


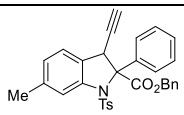


3o

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.480	BB	0.3454	5216.94629	234.64496	91.6161
2	20.845	BB	0.4056	477.40897	14.51964	8.3839

HPLC spectrum of racemic 3p

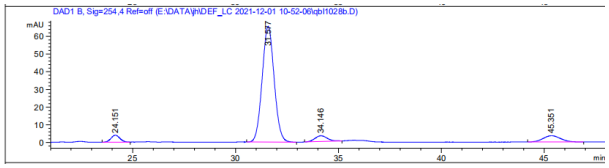


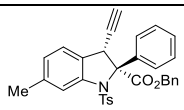


***rac*-3p**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	23.077	BB	0.4461	586.91199	20.25302	20.7972
2	29.816	BB	0.5778	824.33246	22.06944	29.2102
3	32.335	BB	0.6297	585.24792	14.00049	20.7383
4	42.368	BB	0.8219	825.57355	15.09859	29.2542

HPLC spectrum of 3p

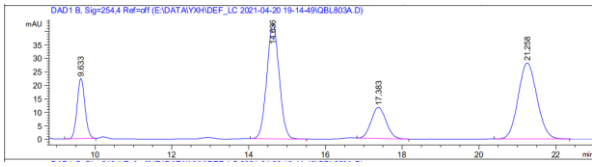


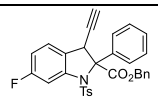


3p

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	24.151	BB	0.4380	118.01991	3.93421	3.7900
2	31.577	BB	0.6351	2650.67114	65.35944	85.1213
3	34.146	BB	0.5004	135.25203	3.25741	4.3434
4	45.351	BB	0.7070	210.04935	3.55680	6.7453

HPLC spectrum of racemic 3q

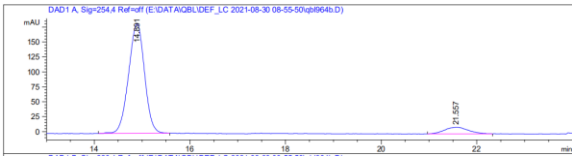


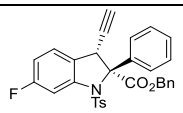


***rac*-3q**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.633	BB	0.2209	317.45682	22.18800	12.5080
2	14.636	BB	0.3527	953.65851	42.03705	37.5748
3	17.383	BB	0.4264	310.27069	11.51234	12.2249
4	21.258	BB	0.5267	956.64240	28.13139	37.6923

HPLC spectrum of 3q

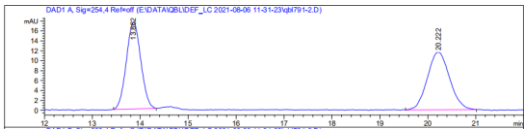


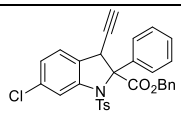


3q

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.494	BB	0.2444	40.43941	2.50355	1.1030
2	16.134	BB	0.3812	3625.72119	147.27196	98.8970

HPLC spectrum of racemic 3r

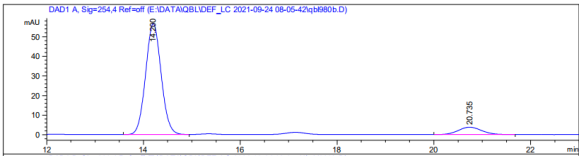


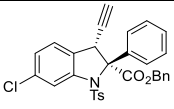


***rac*-3r**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.862	BB	0.3222	366.24289	17.49954	49.4509
2	20.222	BB	0.4308	374.37640	11.59261	50.5491

HPLC spectrum of 3r

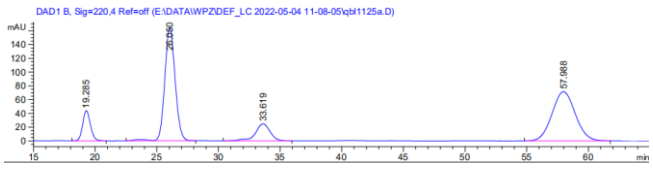


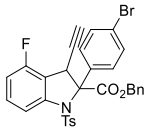


3r

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.200	BB	0.3457	1258.08191	56.51557	90.8785
2	20.735	BB	0.5075	126.27468	3.76342	9.1215

HPLC spectrum of racemic 3s

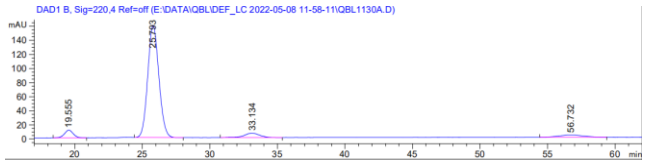


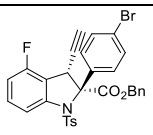


***rac*-3s**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.285	BB	0.6738	1910.61768	43.72711	8.3337
2	26.050	VB R	0.8975	9620.02148	164.35527	41.9606
3	33.619	BB	1.2492	2029.53735	24.73686	8.8524
4	57.988	BB	1.9618	9366.14355	71.42918	40.8532

HPLC spectrum of 3s

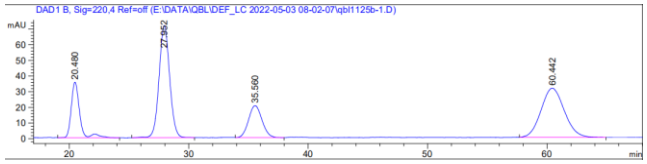


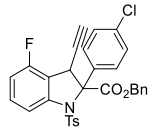


3s

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.555	BB	0.6822	498.76178	10.97449	4.7538
2	25.793	BB	0.8871	9095.28125	159.05850	86.6884
3	33.134	BB	0.9768	503.76654	6.24716	4.8015
4	56.732	BB	1.5017	394.11707	3.10313	3.7564

HPLC spectrum of racemic 3t

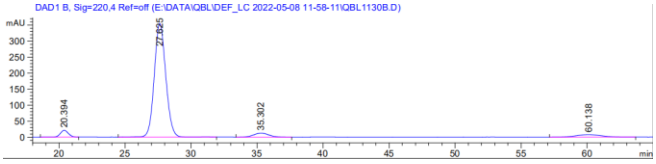


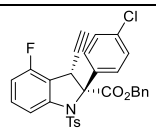


***rac*-3t**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.480	BV R	0.7069	1736.57898	35.51460	14.4776
2	27.952	VB R	0.9595	4432.57959	71.57798	36.9536
3	35.560	BB	1.2075	1593.15320	20.39088	13.2818
4	60.442	BB	2.0624	4232.66406	31.44425	35.2870

HPLC spectrum of 3t

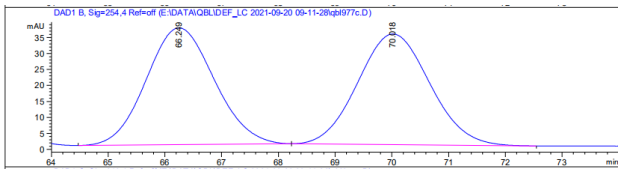


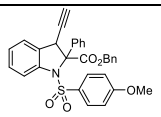


3t

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.394	BB	0.6530	888.50214	21.02602	3.6455
2	27.625	BV R	0.9359	2.14335e4	354.83679	87.9410
3	35.302	BB	1.2250	1017.46429	12.77807	4.1746
4	60.138	BB	1.8336	1033.12646	7.64041	4.2389

HPLC spectrum of racemic 3u

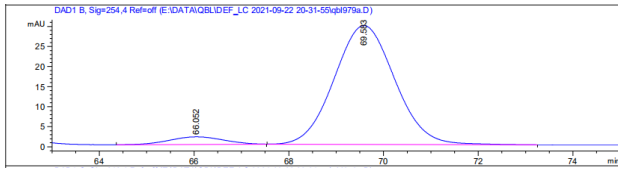


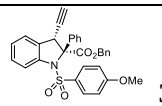


***rac*-3u**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	66.249	BB	1.2543	3046.27612	36.55230	49.8834
2	70.018	BB	1.3107	3060.51855	34.64305	50.1166

HPLC spectrum of 3u

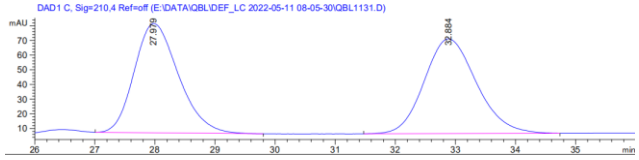


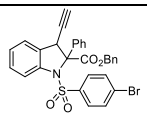


3u

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	66.052	BB	1.0940	148.50117	1.88718	5.3258
2	69.583	BB	1.4032	2639.81030	29.63686	94.6742

HPLC spectrum of racemic 3v

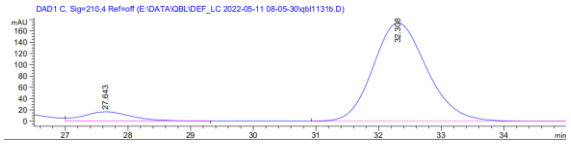


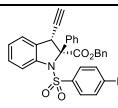


***rac*-3v**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	27.979	BB	0.7761	3803.92896	74.45191	49.3428
2	32.884	BB	0.8857	3905.26416	64.56218	50.6572

HPLC spectrum of 3v

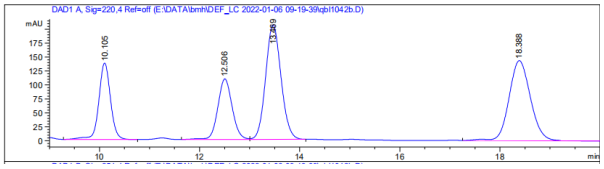


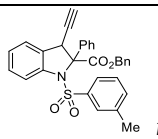


3v

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	27.643	VB	0.8101	857.70111	16.18911	7.6660
2	32.308	BB	0.9171	1.03306e4	173.88759	92.3340

HPLC spectrum of racemic 3w

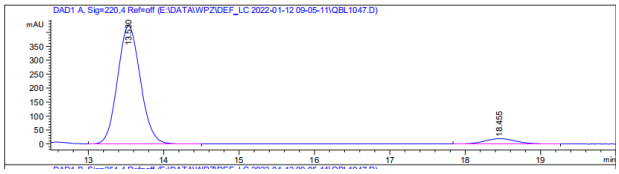


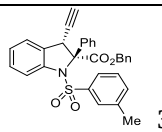


***rac*-3w**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.105	BB	0.2486	2214.48975	136.96439	17.0449
2	12.506	BV	0.3048	2145.79272	108.46814	16.5162
3	13.469	VB	0.3306	4376.29736	205.33977	33.6843
4	18.388	BB	0.4600	4255.50146	143.50348	32.7546

HPLC spectrum of 3w

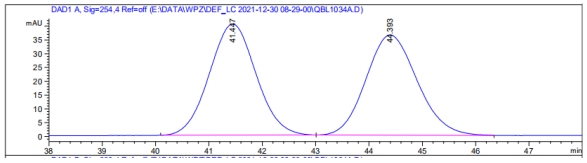


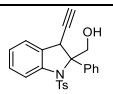


3w

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.530	VB	0.3265	8888.71680	424.15143	94.2296
2	18.455	BB	0.4410	544.31964	18.95827	5.7704

HPLC spectrum of racemic 6

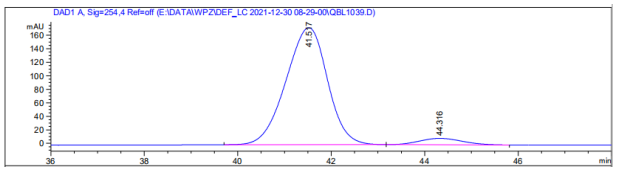


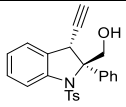


***rac*-6**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	41.447	BB	0.9003	2453.08789	40.29300	50.2570
2	44.393	BB	0.9849	2427.99902	36.36797	49.7430

HPLC spectrum of 6

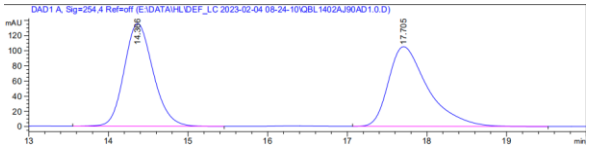


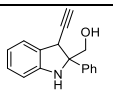


6

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	41.517	BB	0.9572	1.07047e4	173.16896	94.6357
2	44.316	BB	0.7599	606.78784	9.51659	5.3643

HPLC spectrum of racemic 7

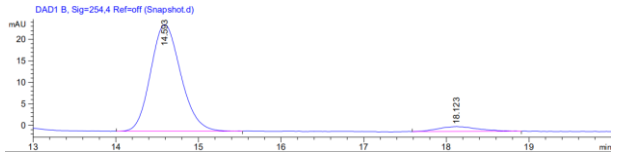


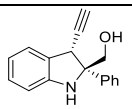


***rac*-7**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.366	BB	0.3913	3429.71265	135.48079	48.6496
2	17.705	BB	0.5173	3620.10815	105.24466	51.3504

HPLC spectrum of 7

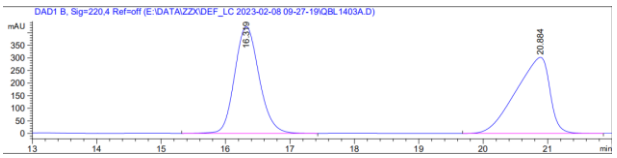


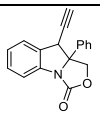


7

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.593	BB	0.3922	629.42072	24.79563	94.3376
2	18.123	BB	0.4078	37.77952	1.13073	5.6624

HPLC spectrum of racemic 8

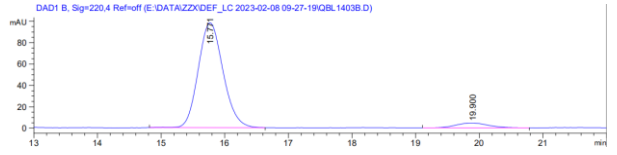


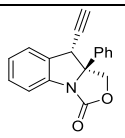


***rac*-8**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.319	BB	0.4096	1.11770e4	423.96460	50.2427
2	20.884	BB	0.5414	1.10690e4	302.15015	49.7573

HPLC spectrum of 8

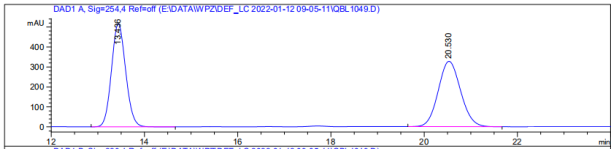


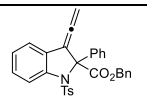


8

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.771	VB R	0.4214	2649.33252	97.99590	94.3778
2	19.900	BB	0.4173	157.82471	4.56594	5.6222

HPLC spectrum of racemic 9

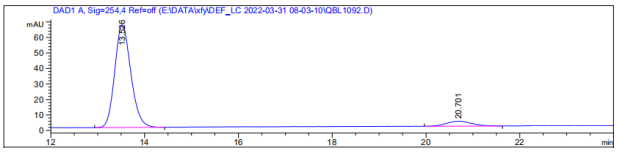


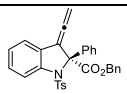


***rac*-9**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.436	BB	0.3289	1.09236e4	516.22754	50.0129
2	20.530	BB	0.5195	1.09180e4	327.02280	49.9871

HPLC spectrum of9





9

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.526	BB	0.3684	1580.36035	66.22723	93.0323
2	20.701	BB	0.4695	118.36166	3.17081	6.9677