Supporting Information

Cascade Photoredox/Gold Catalysis: Access to Multisubstituted Indoles via Aminoarylation of Alkynes

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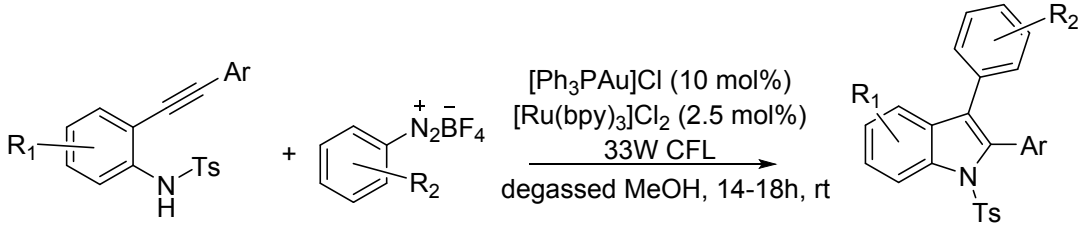
General Information

^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra were measured on 400 MHz spectrometer, using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. Chemical shifts (δ) are given in ppm relative to TMS, the coupling constants *J* are given in Hz. HRMS were obtained in the ESI mode. All reactions were carried out under Ar atmosphere unless otherwise noted. All solvents were obtained from commercial suppliers. Aryldiazonium salts were prepared according the procedure of Hanson.[1] *N*-Ts-2-alkynyl anilines (**1a-1r**) were prepared according the procedure of Helaja.[2] Reactions were monitored by TLC on silica gelplates (GF254), and the analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gel plates.The 33W CFL were directly got from the supermarket.

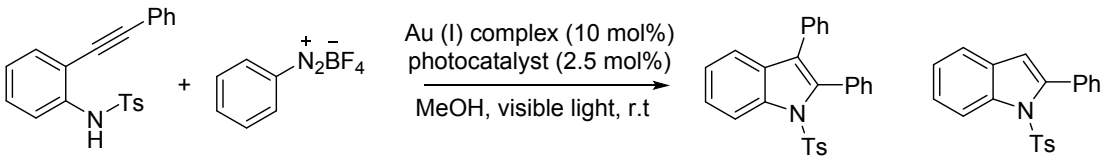
Experimental procedure for the aminoarylation of 2-ethynylaniline derivatives



1 **2** **3**

$[Ru(bpy)_3]Cl_2$ (2.1 mg, 2.5 μmol, 2.5 mol%), Ph_3PAuCl (4.9 mg, 10.0 μmol, 10 mol%), the aryldiazonium salt **2** (0.4 mmol, 4.0 eq.) and the 2-ethynylaniline derivatives 1 (0.10 mmol, 1.0 eq.) were added to a flame-dried Schlenk flask containing a stirring bar and purged by evacuating the flask and backfilling with argon three times. In the absence of light, anhydrous MeOH (1.0 ml, 0.10 M) was added and the flask was sealed. The mixture was then stirred under irradiation from 33 W CFL. After 14-16 h, the crude products were purified by column chromatography over silica gel.

Optimization of the Reaction Conditions Of Radical Annulation 1[a]



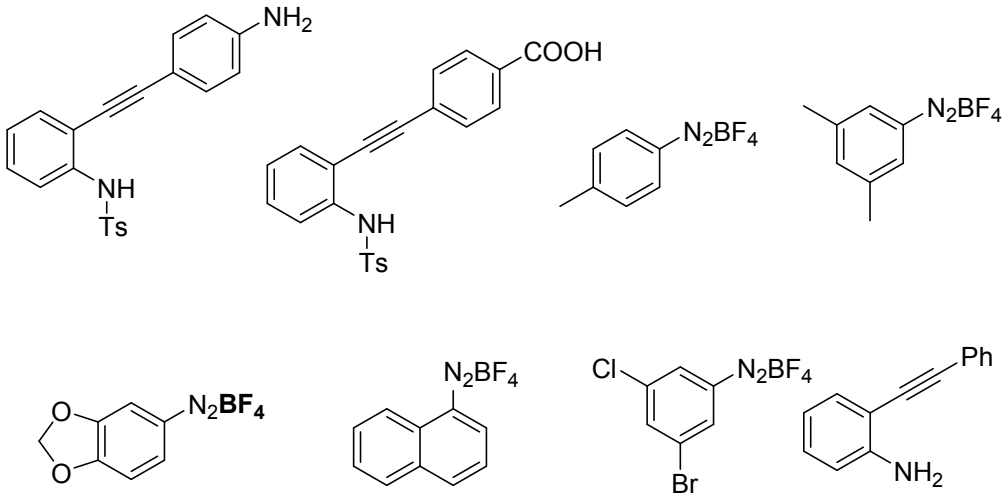
1a **2a** **3aa** 4

Entry	Photocatalyst	Au (I) Complex	Solvent	Additive	T(°C)	Yield[%][b] (**3aa**/**4**)
1	$Ru(Phen)_3Cl$	$[Ph_3PAu]NTf$	MeOH	/	r.t	0/98
2	$[Ru(bpy)_3]PF_6$	$[Ph_3PAu]NTf$	MeOH	/	r.t	42/56
3	$Ru(bpy)_3Cl_2$	$[Ph_3PAu]NTf$	MeOH	/	r.t	57/41
4	$Ru(bpy)_3Cl_2$	$[Ph_3PAu]NTf$	MeOH	K_2CO_3	r.t	22/42

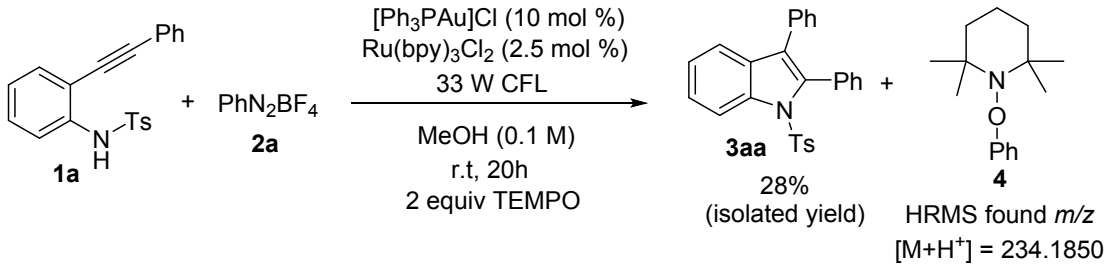
5[c]	$Ru(bpy)_3Cl_2$	$[Ph_3PAu]NTf$	MeOH	/	40	35/45
6	$Ru(bpy)_3Cl_2$	$[Ph_3PAu]NTf$	DMSO	/	r.t	N.R
7	$Ru(bpy)_3Cl_2$	$[Ph_3PAu]NTf$	DMF	/	r.t	-
8	$Ru(bpy)_3Cl_2$	$[Ph_3PAu]NTf$	DCE	/	r.t	-
9	$Ru(bpy)_3Cl_2$	$[Ph_3PAu]NTf$	toluene	/	r.t	-
10	$Ru(bpy)_3Cl_2$	$AuCl(SMe_2)$	MeOH	/	r.t	50/48
11	$Ru(bpy)_3Cl_2$	AuI	MeOH	/	r.t	trace
12	$Ru(bpy)_3Cl_2$	$[Ph_3PAu]Cl$	MeOH	/	r.t	98/0
13	$Ru(bpy)_3Cl_2$	/	MeOH	/	r.t	/
14	/	$[Ph_3PAu]Cl$	MeOH	/	r.t	0/95
15	$Ru(bpy)_3Cl_2$	$[Ph_3PAu]Cl$	MeOH	/	r.t	0/90

[a]Reaction were performed on a 0.1 mmol scale using 4 equiv of **2a**, Solvent (1mL) and a 33 W CFL bulb to illuminate the reaction vessel, r.t, 14h. [b]Yield determined by ^1H NMR using 1,1,2,2 tetrachloroethane as an internal standard. [c]The mixture was stirred under irradiation from 5W blue LEDs. [d]Reaction in the dark. DCE = dichloroethane, DMSO = dimethyl sulfoxide, DMF = N,N-Dimethylformamide.

Unsuccessful Substrates:

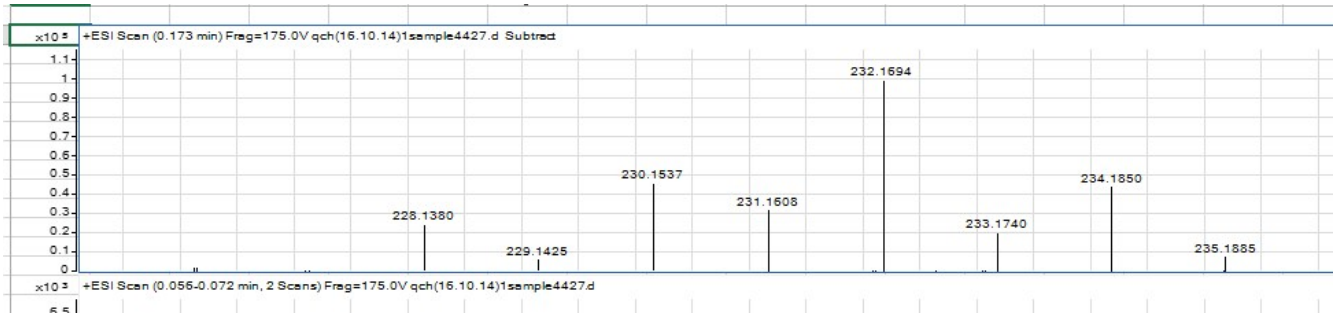


Control experiments in the presence of radical scavengers



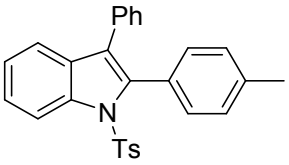
Procedure: To a flame-dried Schlenk tubes equipped with a magnetic stir bar were added **1a** (35 mg, 0.1 mmol), **2a** (80 mg, 0.4 mmol), $[Ph_3PAu]Cl$ (5 mg, 0.01 mmol), $Ru(bpy)_3Cl_2$ (2.1 mg, 2.5 μmol, 2.5 mol%) and 2,2,6,6-Tetramethylpiperidine 1-oxyl (TEMPO, 62 mg, 0.2

mmol). The tube was evacuated and backfilled with Ar for three times, and then solvent (MeOH, 1.0 mL) was added via syringe. The mixture was then stirred under irradiation from 33 W CFL. After 20 h, the crude products were purified by column chromatography over silica gel to give the product **3aa** (12 mg, 28% yield) and unclean TEMPO trapping product **4** (15 mg).



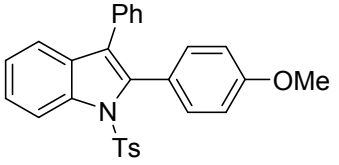
Characterization data of compounds

3-phenyl-2-(*p*-tolyl)-1-tosyl-1*H*-indole (3ba)



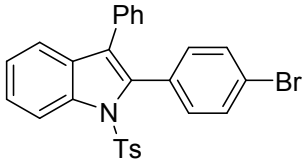
16h, 99% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$):δ= 8.39 (d, J = 8.4 Hz, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.38 (t, J = 8.0 Hz, 1H), 7.34 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 7.6 Hz, 1H), 7.24-7.18 (m, 3H), 7.14 (d, J = 8.0 Hz, 2H), 7.29-7.04 (m, 6H), 2.36 (s, 3H), 2.29 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.5, 138.3, 137.2, 137.1, 135.3, 132.8, 131.9, 130.6, 129.9, 129.3, 128.2, 128.1, 127.9, 127.0, 126.9, 125.0, 124.2, 119.9, 116.3, 21.6, 21.5 ppm; HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{28}H_{23}NO_2SNa^+$) requires *m/z* 460.1342, found *m/z* 460.1344.

2-(4-methoxyphenyl)-3-phenyl-1-tosyl-1*H*-indole (3ca)



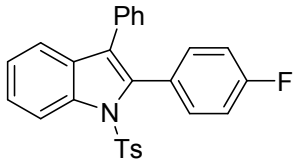
16h, 89% yield;^{1}H NMR (400 MHz, $CDCl_3$):δ= 8.40 (d, J = 8.4 Hz, 1H), 7.47 (d, J = 7.6 Hz, 1H), 7.41-7.37 (m, 1H), 7.32 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 7.6 Hz, 1H), 7.25-7.18 (m, 3H), 7.15 (d, J = 8.4 Hz, 2H), 7.08 (dd, J = 6.8 Hz, J = 12.0 Hz, 4H), 6.80 (d, J = 8.4 Hz, 2H) 3.82 (s, 3H), 2.30 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.7, 144.5, 137.2, 136.8, 135.4, 133.4, 132.9, 130.5, 129.9, 129.3, 128.2, 126.9, 126.9, 125.0, 124.1, 123.0, 119.8, 116.3, 112.8, 55.2, 21.6 ppm; HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{28}H_{23}NO_3SNa^+$) requires *m/z* 476.1291, found *m/z* 476.1294.

2-(4-bromophenyl)-3-phenyl-1-tosyl-1*H*-indole (3da)



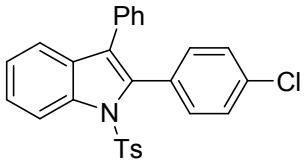
16h, 99% yield; ^{1}H N MR (400 MHz, $CDCl_3$):δ=8.31 (d, J = 8.4 Hz, 1H), 7.38-7.31 (m, 4H), 7.25-7.14 (m, 6H), 7.04-6.97 (m, 6H), 2.22 (s, 3H) ppm;^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.8, 137.4, 135.5, 135.1, 133.6, 132.3, 130.6, 130.5, 129.9, 129.8, 129.4, 127.2, 126.8, 125.5, 125.4, 124.4, 123.0, 120.1, 116.3, 21.6 ppm; HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{27}H_{20}BrNO_2SNa^+$) requires *m/z* 524.0290, found *m/z* 524.0287.

2-(4-fluorophenyl)-3-phenyl-1-tosyl-1*H*-indole (3d)



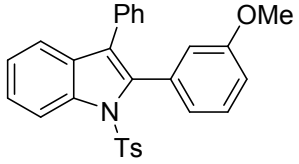
16h, 99% yield, ^{1}HNMR (400 MHz, $CDCl_3$): δ= 8.40 (d, J = 8.4 Hz, 1H), 7.47 (d, J = 7.6 Hz, 1H), 7.44-7.40 (m, 1H), 7.32-7.19 (m, 8H), 7.09-7.07 (m, 4H), 6.96 (t, J = 8.8 Hz, 2H), 2.31 (s, 3H) ppm;^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.8 (d, J = 247.3 Hz), 144.7, 137.3, 135.7, 135.2, 133.9 (d, J = 8.6 Hz),132.4,130.3, 129.8, 129.4, 128.3,127.1, 126.8, 125.3, 125.0, 124.3, 120.0, 116.2, 114.5 (d, J = 21.2), 21.5 ppm; ^{19}F NMR(376 MHz, $CDCl_3$): δ = -112.4 ppm; HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{27}H_{20}FNO_2SNa^+$) requires *m/z* 464.1091, found *m/z* 464.1095.

2-(4-chlorophenyl)-3-phenyl-1-tosyl-1H-indole (3fa)



16h, 98% yield, ^{1}HNMR (400 MHz, $CDCl_3$): δ= 8.39 (d, J = 8.4 Hz, 1H), 7.46-7.39 (m, 2H), 7.32 (d, J = 8.4 Hz, 2H), 7.28-7.21 (m, 6H), 7.09-7.05 (m, 4H), 2.31 (s, 3H) ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.8, 137.4， 135.5， 135.1， 134.6， 133.3， 132.3， 130.5, 129.8, 129.4, 129.4, 128.4, 127.7, 127.2, 126.9, 125.5, 125.4, 124.4, 120.1, 116.3, 21.6 ppm; HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{27}H_{20}ClNO_2SNa^+$) requires *m/z* 480.0795, found *m/z* 480.0800.

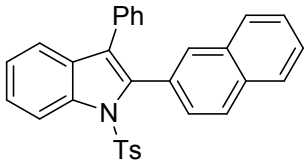
2-(3-methoxyphenyl)-3-phenyl-1-tosyl-1*H*-indole （3ga)



16h, 99% yield, ^{1}HNMR (400 MHz, $CDCl_3$): δ= 8.40 (d, J = 8.4 Hz, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.42-7.35 (m, 3H), 7.28 (d, J = 7.2 Hz, 1H), 7.23-7.18 (m, 3H), 7.15 (d, J = 7.6 Hz, 1H), 7.11-7.05 (m, 4 H), 6.88 (dd, J = 2.4 Hz, J = 7.6 Hz, 1H), 6.83-6.79 (m, 2H), 3.69 (s, 3H),

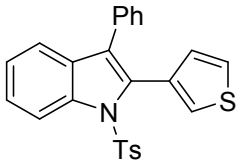
2.29 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.5, 144.6, 137.3, 136.6, 135.3, 132.7, 132.1, 129.8, 129.3, 128.3, 128.2, 127.0, 125.2, 124.7, 124.2, 120.1, 117.5, 116.3, 114.6, 55.2, 21.6 ppm; HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{28}H_{23}NO_3SNa^+$) requires *m/z* 476.1291, found *m/z* 476.1295.

2-(naphthalen-2-yl)-3-phenyl-1-tosyl-1H-indole (3ha)



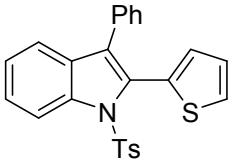
16h, 99% yield, ^{1}HNMR (400 MHz, $CDCl_3$): δ= 8.44 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* =8.0 Hz, 1H), 7.60 (s, 1H), 7.52-7.41 (m, 6H), 7.30 (t, *J* = 8.0 Hz, 2H), 7.17-7.09 (m, 5H), 7.03 (d, *J* = 8.0 Hz, 2H), 2.30 (s, 3H) ppm;^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.6, 137.4, 136.7, 135.3, 133.0, 132.6, 132.5, 131.4, 130.6, 129.9, 129.7, 129.3, 128.5, 128.3, 128.2, 127.8, 127.0, 126.7, 126.6, 126.1, 125.3, 125.2, 124.3, 120.1, 116.3, 21.6 ppm; HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{31}H_{23}NO_2SNa^+$) requires *m/z* 496.1342, found *m/z* 496.1345.

3-phenyl-2-(thiophen-3-yl)-1-tosyl-1H-indole (3ia)



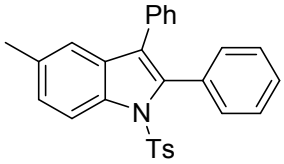
16h, 73% yield, ^{1}HNMR (400 MHz, $CDCl_3$): δ= 8.41 (d, *J* = 8.4 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.42-7.38 (m, 1H), 7.35-7.33 (m, 2H), 7.29-7.21 (m, 5H), 7.13-7.10 (m, 2H), 7.08-7.06 (m, 3H), 6.99 (dd, *J* = 1.2 Hz, *J* = 3.2 Hz, 1H) 2.30 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.6, 137.3, 135.5, 132.8, 131.7, 131.3, 130.6, 130.1, 129.7, 129.4, 128.3, 127.9, 127.1, 126.9, 125.3, 125.1, 124.1, 123.9, 112.0, 116.1, 21.6 ppm; HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{25}H_{19}NO_2S_2Na^+$) requires *m/z* 452.0749, found *m/z* 452.0753.

3-phenyl-2-(thiophen-2-yl)-1-tosyl-1H-indole (3ja)



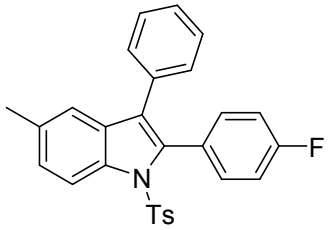
16h, 91% yield, ^{1}HNMR (400 MHz, $CDCl_3$): δ= 8.40 (d, *J* = 8.8 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.44-7.42 (m, 3H), 7.36 (dd, *J* = 1.6 Hz, *J* = 4.2 Hz, 1H), 7.28-7.25 (m, 4H), 7.20-7.18 (m, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.05 (dd, *J* = 0.8 Hz, *J* = 3.2 Hz, 1H), 4.29 (s, 2H), 6.99 (dd, *J* = 3.6 Hz, *J* = 5.2 Hz, 1H), 2.32 (s, 3H) ppm; ^{13}C NMR (100 MHz,$CDCl_3$): δ = 144.7, 137.4, 135.5, 132.5, 132.2, 131.0, 129.8, 129.7, 129.4, 128.9, 128.3, 128.2, 127.3, 127.0, 126.3, 125.6, 124.1, 120.2, 116.0, 21.6 ppm; HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{25}H_{19}NO_2S_2Na^+$) requires *m/z* 452.0749, found *m/z* 452.0750.

5-methyl-2,3-diphenyl-1-tosyl-1*H*-indole (3ka)



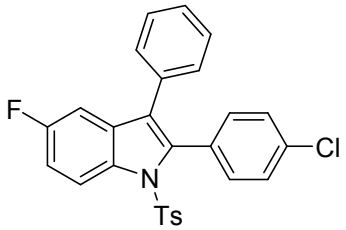
16h, 91% yield, ^{1}HNMR (400 MHz, $CDCl_3$): δ = 8.27 (d, J = 8.4 Hz, 1H), 7.32 (d, J = 8.0 Hz, 3H), 7.28-7.18 (m, 9H), 7.08-7.05 (m, 4H), 2.39 (s, 3H), 2.30 (s, 3H) ppm; ^{13}C NMR (100 MHz,$CDCl_3$): δ = 144.5, 137.0, 135.5, 135.3, 133.9, 132.8, 132.1, 131.0, 130.8, 129.9, 129.3, 128.4, 128.2, 127.3, 126.9, 126.6, 119.8, 116.0, 21.6, 21.3 ppm; HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{28}H_{23}NO_2SNa^+$) requires *m/z* 460.1342, found *m/z* 460.1346.

2-(4-fluorophenyl)-5-methyl-3-phenyl-1-tosyl-1H-indole (3la)



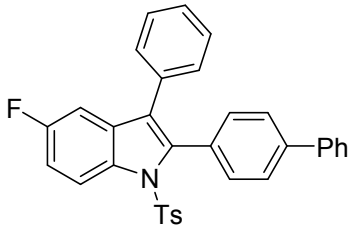
16h, 53% yield, ^{1}HNMR (400 MHz, $CDCl_3$): δ= 8.26 (d, J = 8.8 Hz, 1H), 7.30 (d, J = 8.0 Hz, 2H), 7.26-7.18 (m, 7H), 7.08-7.05 (m, 4H), 6.96 (t, J = 8.4 Hz, 2H), 2.40 (s, 3H), 2.31 (s, 3H) ppm; ^{13}C NMR (100 MHz,$CDCl_3$): δ = 162.8 (d, J = 247.4 Hz), 144.6, 135.8, 135.5, 135.3, 134.0, 133.8 (d, J = 8.5 Hz), 132.6, 130.6, 129.8, 129.3, 128.3, 127.0, 126.8 (t, J = 10.8 Hz), 125.0, 119.8, 116.0, 114.5 (d, J = 21.2 Hz), 21.6, 21.3 ppm; ^{19}F NMR(376 MHz, $CDCl_3$): δ = -112.5 ppm; HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{28}H_{22}FNO_2SNa^+$) requires *m/z* 478.1247, found *m/z* 478.1249.

2-(4-chlorophenyl)-5-fluoro-3-phenyl-1-tosyl-1H-indole (3ma)



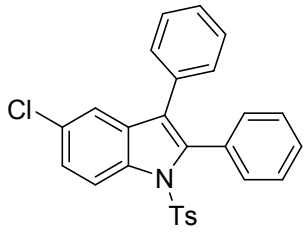
16h, 97% yield, ^{1}HNMR (400 MHz, $CDCl_3$): δ= 8.34 (dd, J = 4.8 Hz, J = 9.2 Hz, 1H), 7.30-7.23 (m, 7H), 7.18-7.08 (m, 6H), 7.04-7.01 (m, 2H), 2.32 (s, 3H) ppm; ^{13}C NMR (100 MHz,$CDCl_3$): δ = 160.4 (d, J = 240.1 Hz), 146.0, 137.2, 134.8 (d, J = 5.8 Hz), 133.6, 133.2, 131.8, 131.7 (d, J = 9.5 Hz), 129.6, 129.5, 129.1, 128.5, 127.7, 127.4, 126.8, 125.2 (d, J = 3.6 Hz), 117.7 (d, J = 9.1 Hz), 113.3 (d, J = 25.3 Hz), 106.7 (d, J = 24.4 Hz), 21.6 ppm; ^{19}F NMR(376 MHz, $CDCl_3$): δ = -118.1 ppm; HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{27}H_{20}ClFNO_2S^+$) requires *m/z* 476.0882, found *m/z* 476.0876.

2-([1,1'-biphenyl]-4-yl)-5-fluoro-3-phenyl-1-tosyl-1*H*-indole (3na)



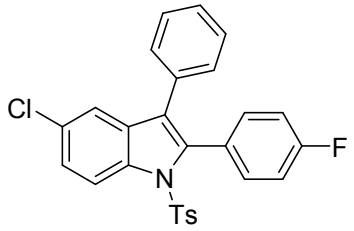
16h, 99% yield, ^{1}HNMR (400 MHz, $CDCl_3$): δ= 8.36 (dd, J = 4.8 Hz, J = 10.0 Hz, 1H), 7.65-7.63 (m, 2H), 7.54-7.51 (m, 2H), 7.44 (t, J = 7.6 Hz, 2H), 7.37-7.30 (m, 5H), 7.24-7.20 (m, 3H), 7.15-7.07 (m, 6H), 2.32 (s, 3H) ppm; ^{13}C NMR (100 MHz,$CDCl_3$): δ = 160.4 (d, J = 240.1 Hz), 144.8, 141.1, 140.3, 138.4, 134.9, 132.4, 132.2, 131.9 (d, J = 9.9 Hz), 129.7, 129.5, 129.4, 128.8, 128.4, 127.6, 127.3, 127.1, 127.0, 125.9, 124.9 (d, J = 4.1 Hz), 117.7 (d, J = 9.1 Hz), 105.6 (d, J = 24.3 Hz),21.6ppm; ^{19}F NMR(376 MHz, $CDCl_3$): δ =-103.9 (d, J = 277.5 Hz), -109.3 (d, J = 277.5 Hz) ppm; HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{33}H_{24}FNO_2SNa^+$) requires *m/z* 540.1404, found *m/z* 540.1408.

5-chloro-2,3-diphenyl-1-tosyl-1*H*-indole (3oa)



16h, 99% yield, ^{1}HNMR (400 MHz, $CDCl_3$): δ= 8.33 (d, J = 8.8 Hz, 1H), 7.44 (s, 1H), 7.37-7.33 (m, 2H), 7.29 (m, 4H), 7.21-7.20 (m,4H), 7.07 (dd, J = 8.4 Hz, J = 14 Hz, 4H), 2.32 (s, 3H) ppm; ^{13}C NMR (100 MHz,$CDCl_3$): δ = 144.9, 138.2, 135.6, 135.1, 132.0, 132.0, 131.7, 130.4, 130.1, 129.7, 129.4, 128.8, 128.4, 127.4, 127.2, 126.9, 125.3, 124.1, 119.6, 117.4, 21.6 ppm ^{19}F NMR(376 MHz, $CDCl_3$): δ = -101.4 (d, J = 283.1 Hz), -107.3 (d, J = 283.1 Hz) ppm; HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{27}H_{20}ClNO_2SNa^+$) requires *m/z* 480.0795, found *m/z* 480.0796.

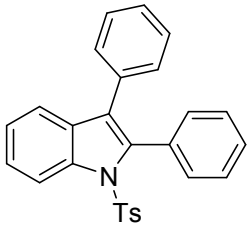
5-chloro-2-(4-fluorophenyl)-3-phenyl-1-tosyl-1*H*-indole (3pa)



16h, 80% yield, ^{1}HNMR (400 MHz, $CDCl_3$): δ = 8.33 (d, J = 8.8 Hz, 1H), 7.43 (d, J =2.0 Hz, 1H), 7.37 (dd, J = 2.0 Hz, J = 8.8 Hz, 1H), 7.29-7.17 (m, 7H), 7.10 (d, J = 8.0 Hz, 2H), 7.05-7.03 (m, 2H), 6.97 (t, J = 8.8 Hz, 2H), 2.33 (s, 3H) ppm; ^{13}C NMR (100 MHz,$CDCl_3$): δ =

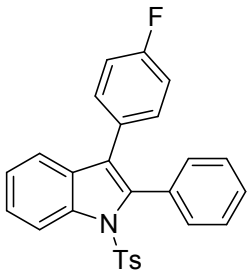
163.0 (d, *J* = 247.8 Hz), 145.1, 137.0, 135.3 (d, *J* = 52.4 Hz), 133.9 (d, *J* = 8.2 Hz), 131.7 (d, *J* = 19.9 Hz), 130.2, 129.7, 129.5, 128.5, 127.4, 126.9, 126.4, 125.5, 119.7, 117.4, 114.6 (d, J = 21.7 Hz), 21.6 ppm; ^{19}F NMR(376 MHz, $CDCl_3$): δ = -118 (s) ppm; HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{27}H_{19}ClFNO_2SNa^+$) requires *m/z* 498.0701, found *m/z* 498.0705.

2,3-diphenyl-1-tosyl-1*H*-indole (3aa)



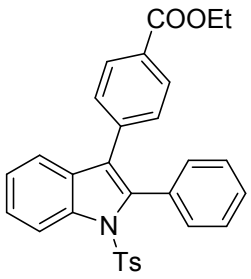
16h, 99% yield, ^{1}HNMR (400 MHz, $CDCl_3$): δ= 8.41 (d, *J* = 8.4 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.42-7.38 (m, 1H), 7.35-7.18 (m, 8H), 7.09-7.05 (m, 4H), 2.30 (s, 3H) ppm; ^{13}C NMR (100 MHz,$CDCl_3$): δ = 144.6, 137.3, 136.9, 135.3, 132.7, 132.1, 130.9, 130.5, 129.9, 129.3, 128.5, 128.2, 127.3, 127.0, 125.2, 124.2, 120.0, 116.3, 21.6 ppm; HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{27}H_{21}NO_2SNa^+$) requires *m/z* 446.1185, found *m/z* 446.1187.

3-(4-fluorophenyl)-2-phenyl-1-tosyl-1*H*-indole (3ab)



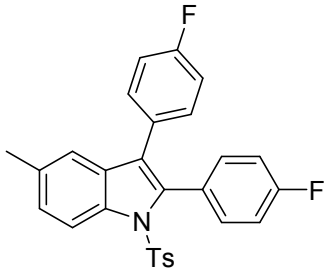
16h, 74% yield, ^{1}HNMR (400 MHz, $CDCl_3$): δ= 8.41 (dd, *J* = 4.0 Hz, *J* = 8.4 Hz, 1H), 7.45-7.40 (m, 2H), 7.37-7.32 (m, 3H), 7.31-7.27 (m, 3H), 7.24-7.21 (m, 1H), 2.31 (s, 3H), ppm; ^{13}C NMR (100 MHz,$CDCl_3$): δ = 161.8 (d, *J* = 245.1 Hz), 144.7 (d, J = 2.7 Hz), 137.2, 136.9, 135.4, 132.1, 131.5 (d, *J* = 8.1 Hz), 130.8, 130.3, 129.4, 128.6, 127.4, 127.0, 125.3, 124.3, 123.7, 119.8, 116.2, 115.3 (d, J = 21.2 Hz), 21.6 ppm; ^{19}F NMR(376 MHz, $CDCl_3$): δ = -114.8 (s) ppm; HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{27}H_{20}FNO_2SNa^+$) requires *m/z* 464.1091, found *m/z* 464.1098.

ethyl 4-(2-phenyl-1-tosyl-1H-indol-3-yl)benzoate (3ac)



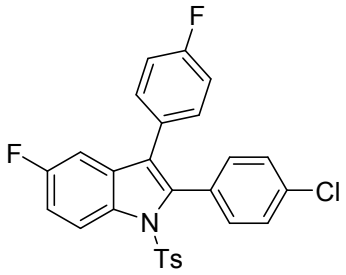
16h, 77% yield, ^{1}HNMR (400 MHz, $CDCl_3$): δ= 8.42 (dd, J = 8.4 Hz, 1H), 7.90 (d, J = 8.0 Hz, J = 18.4 Hz, 2H), 7.49-7.39 (m, 2H), 7.39-7.25 (m, 6H), 7.17-7.07 (m, 5H), 4.36 (q, J = 7.2Hz, 2H), 2.32 (s, 3H), 1.39 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz,$CDCl_3$): δ = 166.4, 144.8, 137.7, 137.4, 137.2, 135.4, 132.1, 131.6, 130.5, 129.8, 129.6, 129.5, 129.1, 128.9, 128.8, 128.6, 127.5, 127.3, 127.0, 125.4, 124.6, 124.4, 123.6, 120.4, 119.7, 116.2, 61.0, 21.6, 14.3 ppm; HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{30}H_{25}NO_4SNa^+$) requires *m/z* 518.1397, found *m/z* 518.1400.

2,3-bis(4-fluorophenyl)-5-methyl-1-tosyl-1*H*-indole (3ad)



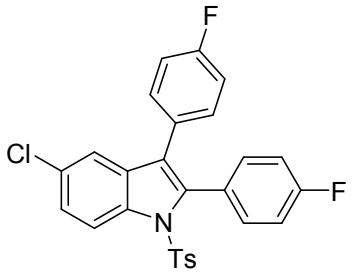
16h, 90% yield, ^{1}HNMR (400 MHz, $CDCl_3$): δ= 8.19 (d, J = 8.4 Hz, 1H), 7.23 (d, J = 8.4 Hz, 2H), 7.17-7.15 (m, 1H), 7.12-7.09 (m, 3H), 7.01 (d, J = 8.4 Hz, 2H), 6.97-6.84 (m, 6H), 2.33 (s, 3H), 2.24 (s, 3H) ppm; ^{13}C NMR (100 MHz,$CDCl_3$): δ = 162.3 (dd, J = 104.3 Hz, J = 247.4 Hz), 144.7, 135.9, 135.3 (d, J = 11.3 Hz), 134.1, 133.8 (d, J = 8.1 Hz), 131.4 (d, J = 8.1 Hz), 130.4, 129.4, 128.5 (d, J = 3.2 Hz), 126.8, 126.8, 123.9, 119.6, 116.0, 115.0 (dd, J = 21.2 Hz, J = 81.2 Hz), 21.6, 21.3 ppm; ^{19}F NMR(376 MHz, $CDCl_3$): δ = -112.2 (s), -114.6 (s) ppm; HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{28}H_{21}F_2NO_2SNa^+$) requires *m/z* 496.1153, found *m/z* 496.1153.

2-(4-chlorophenyl)-5-fluoro-3-(4-fluorophenyl)-1-tosyl-1*H*-indole (3ae)



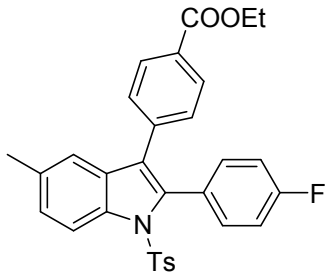
16h, 93% yield, ^{1}HNMR (400 MHz, $CDCl_3$): δ= 8.26 (dd, J = 4.4 Hz, J = 9.2 Hz, 1H), 7.33 (d, J = 4.8 Hz, 1H), 7.22-7.13 (m, 3H), 7.08-7.06 (m, 3H), 7.03-6.96 (m, 4H), 6.94-6.84 (m, 3H), 2.25 (s, 3H) ppm; ^{13}C NMR (100 MHz,$CDCl_3$): δ = 161.2 (dd, J = 162.9 Hz, J = 246.0 Hz), 145.1, 137.3, 134.9 (d, J = 20.3 Hz), 133.5, 133.2, 131.5, 131.3 (d, J = 8.1 Hz), 129.5, 129.4, 128.9, 127.9, 127.8, 126.8, 126.7, 124.1 (d, J = 3.7 Hz), 117.7 (d, J = 9.1 Hz), 115.7 (d, J = 21.2 Hz), 113.4 (d, J = 24.6 Hz), 105.5 (d, J = 24.4 Hz), 21.6 ppm; ^{19}F NMR(376 MHz, $CDCl_3$): δ = -113.9 (s), -118.0 (s) ppm; HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{27}H_{18}ClF_2NO_2SNa^+$) requires *m/z* 516.0607, found *m/z* 516.0610.

5-chloro-2,3-bis(4-fluorophenyl)-1-tosyl-1*H*-indole (3af)



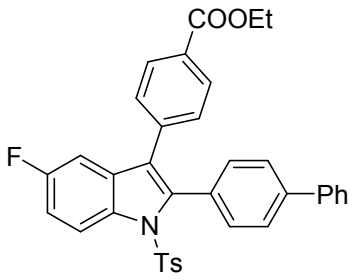
16h, 99% yield, ^{1}HNMR (400 MHz, $CDCl_3$): δ= 8.25 (dd, J = 0.8 Hz, J = 8.4 Hz, 1H), 7.31-7.28 (m, 2H), 7.21-7.17 (m, 2H), 7.11-7.08 (m, 2H), 7.03 (d, J = 8.0 Hz, 2H), 6.95-6.84 (m, 6H), 2.26 (s, 3H) ppm; ^{13}C NMR (100 MHz,$CDCl_3$): δ = 162.5 (dd, J = 105.6 Hz, J = 248.3 Hz), 145.2, 137.1, 135.5, 135.1, 133.9 (d, J = 8.6 Hz), 131.4 (d, J = 8.2 Hz), 130.2, 129.5, 127.7 (d, J = 3.2 Hz), 126.9, 126.2 (d, J = 3.6 Hz), 125.6, 123.3, 21.6 ppm; HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{27}H_{18}ClF_2NO_2SNa^+$) requires *m/z* 516.0607, found *m/z* 516.0608.

ethyl 4-(2-(4-fluorophenyl)-5-methyl-1-tosyl-1*H*-indol-3-yl)benzoate (3ag)



16h, 72% yield, ^{1}HNMR (400 MHz, $CDCl_3$): δ= 8.28 (d, J = 8.4 Hz, 1H), 7.93-7.90 (m, 2H), 7.30 (d, J = 8.4 Hz, 2H), 7.26-7.23 (m, 2H), 7.20-7.13 (m, 4H), 7.09 (d, J = 8.0 Hz, 2H), 6.97 (t, J = 8.4 Hz, 2H), 4.35 (q, J = 7.2 Hz, 2H), 2.41 (s, 3H), 2.32 (s, 3H), 1.37 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz,$CDCl_3$): δ = 166.4, 164.8 (dd, J = 47.4 Hz, J = 264.0 Hz), 137.7, 137.6, 136.3, 136.3, 135.4 (d, J = 18.5 Hz), 134.2, 133.9 (d, J = 7.9 Hz), 129.9, 129.9, 129.8, 129.8, 129.6, 129.5, 129.4, 129.0, 128.6, 126.9, 126.8, 126.6 (d, J = 3.6 Hz), 123.9, 119.6, 116.0, 114.7 (d, J = 21.7 Hz), 61.0, 21.6, 21.4, 14.3 ppm; ^{19}F NMR(376 MHz, $CDCl_3$): δ = -111.9 (s) ppm; HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{31}H_{26}FNO_4SNa^+$) requires *m/z* 550.1459, found *m/z* 550.1461.

ethyl 4-(2-([1,1'-biphenyl]-4-yl)-5-fluoro-1-tosyl-1H-indol-3-yl)benzoate (3ah)



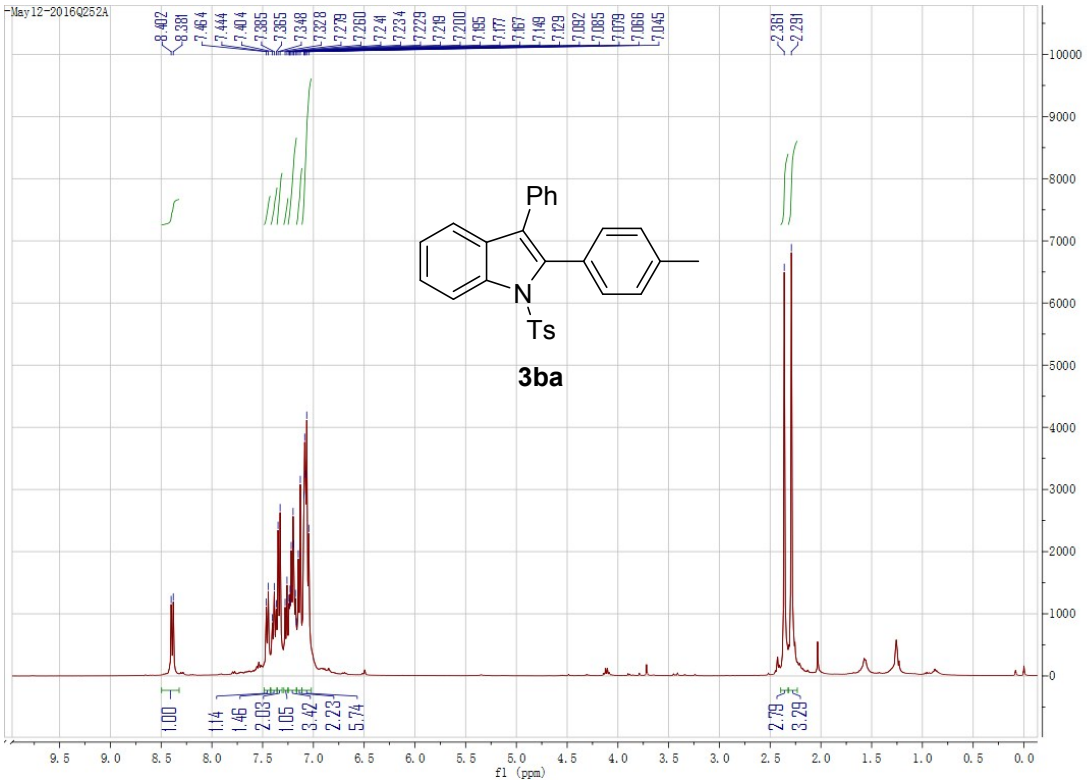
16h, 75% yield, ^{1}HNMR (400 MHz, $CDCl_3$): δ= 8.38 (dd, J = 4.4 Hz, J = 9.2 Hz, 1H), 7.92 dd, J = 3.6 Hz, J = 8.4 Hz, 1H), 7.66-7.62 (m, 3H), 7.54 (d, J = 8.4 Hz, 2H), 7.46 (t, J = 7.2 Hz, 2H), 7.37 (d, J = 7.2 Hz, 1H), 7.33 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.18-7.09 (m, 6H), 4.34 (q, J = 7.2 Hz, 2H), 2.33 (s, 3H), 1.35 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz,$CDCl_3$): δ = 166.3, 163.5 (dd, J = 47.4, J = 520.2 Hz), 145.0, 141.5, 140.2, 138.9, 137.2, 134.9, 133.6, 132.4, 132.1, 131.1 (d, J = 9.5 Hz), 129.7, 129.6, 129.5, 129.2, 129.0, 129.0, 128.9, 127.7, 127.3 (d, J = 2.8 Hz), 127.1, 127.0, 126.1, 123.7 (d, J = 3.6 Hz), 117.7 (d, J = 9.1 Hz), 113.3 (d, J = 24.9 Hz), 105.4 (d, J = 24.4 Hz), 61.0, 21.6, 14.3 ppm; ^{19}F NMR(376 MHz, $CDCl_3$): δ = -116.7 (s) ppm; HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{36}H_{28}FNO_4SNa^+$) requires *m/z* 612.1615, found *m/z* 612.1618.

References:

1．P. Hanson, J. Jones, A. Taylor, P. H. Walton and A. W. Timms, *J. Chem. Soc., Perkin Trans 2*, 2002, 1135.

2. J. Helaja et. al, *Angew. Chem. Int. Ed*. 2013, **52**, 11835.

Copies ^{1}H NMR, ^{13}C NMR, ^{19}F NMR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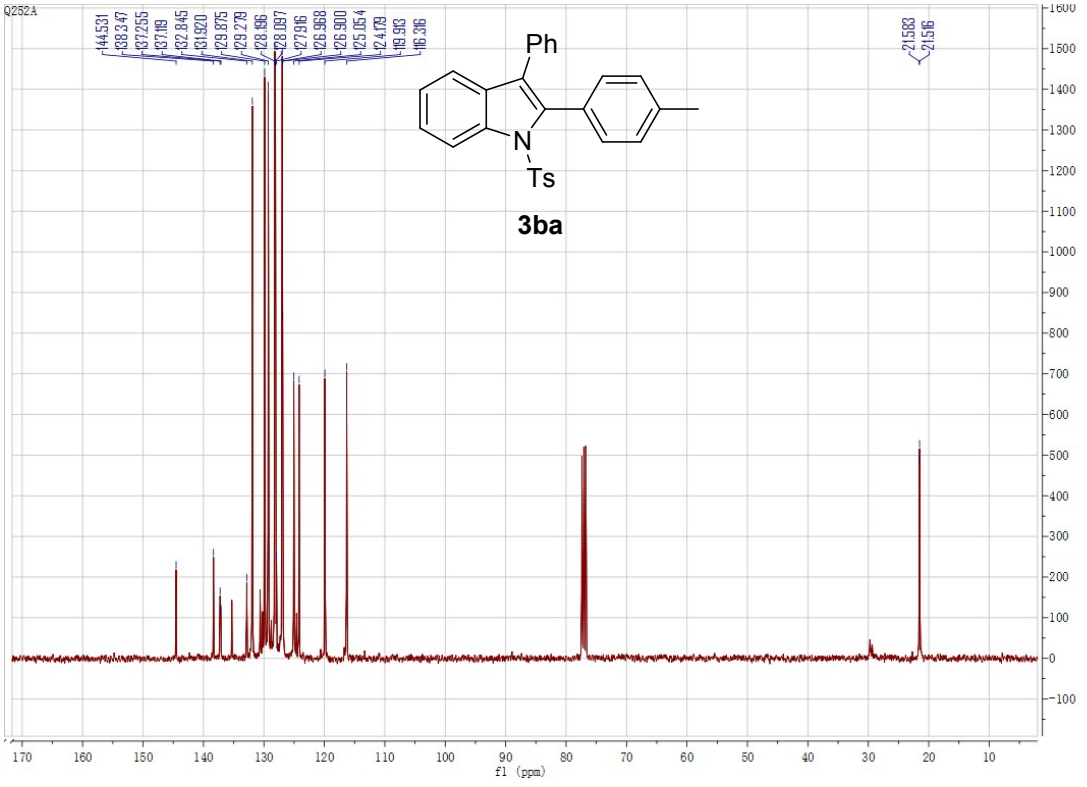
N
Ts
3ba
f1 (ppm)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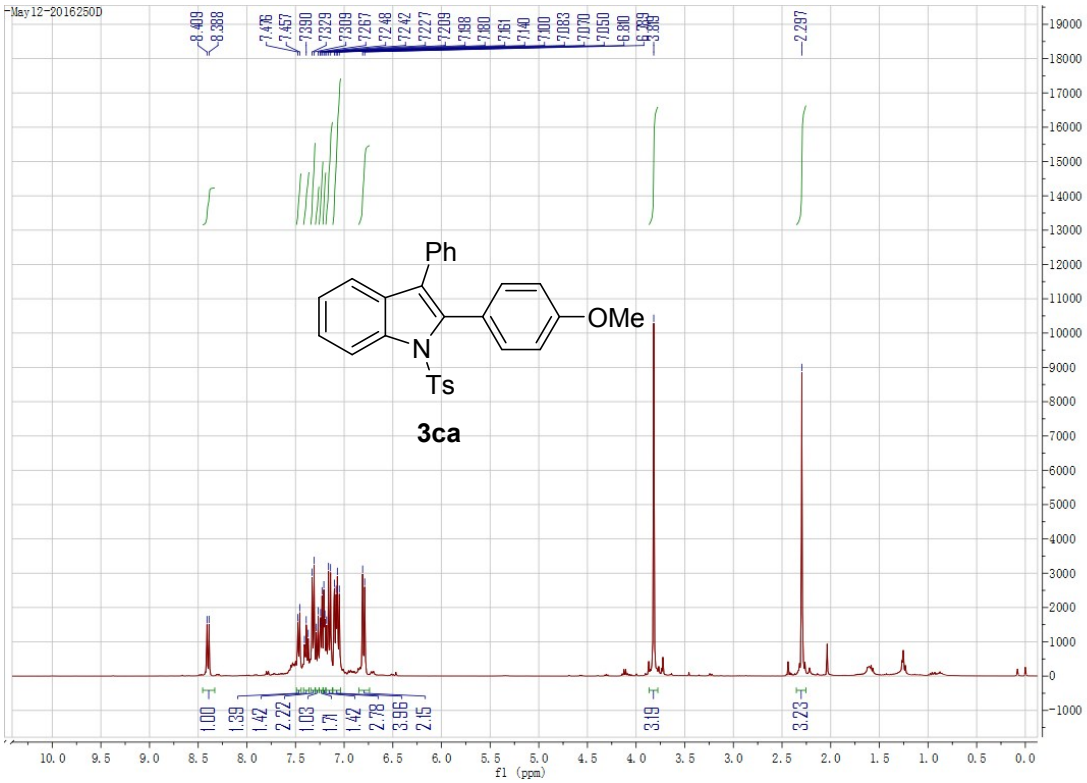
N
Ts
3ba
f1 (ppm)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Ts
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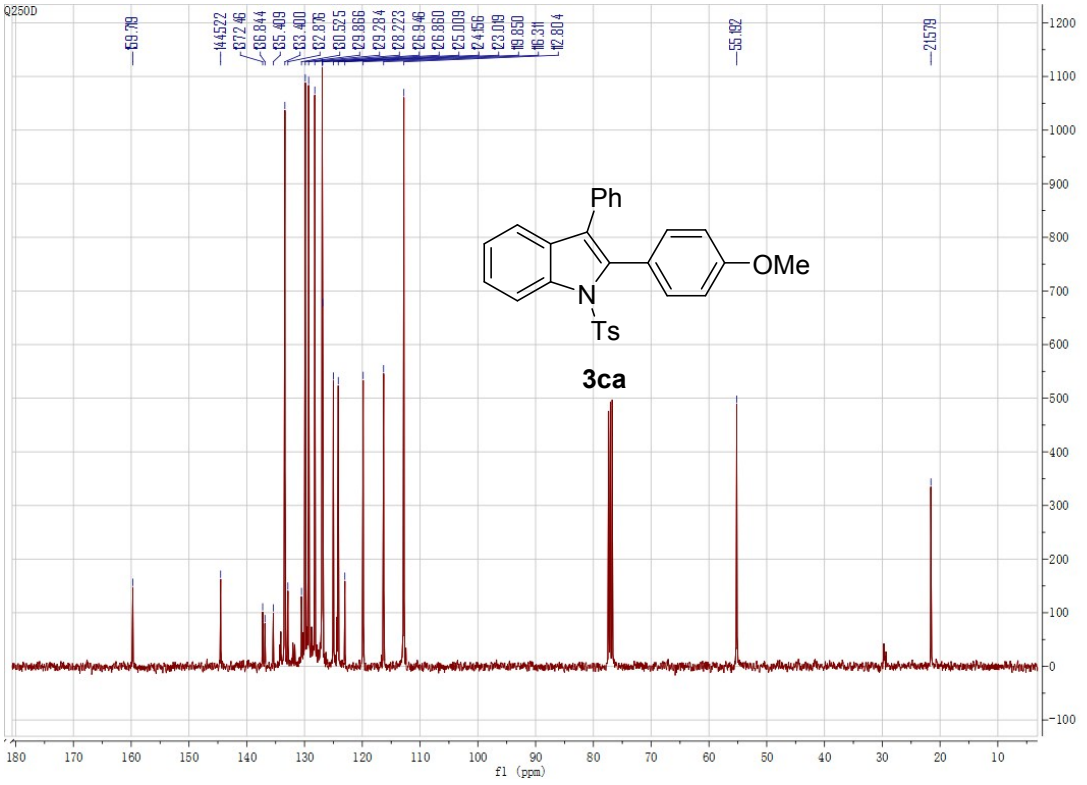
f1 (ppm)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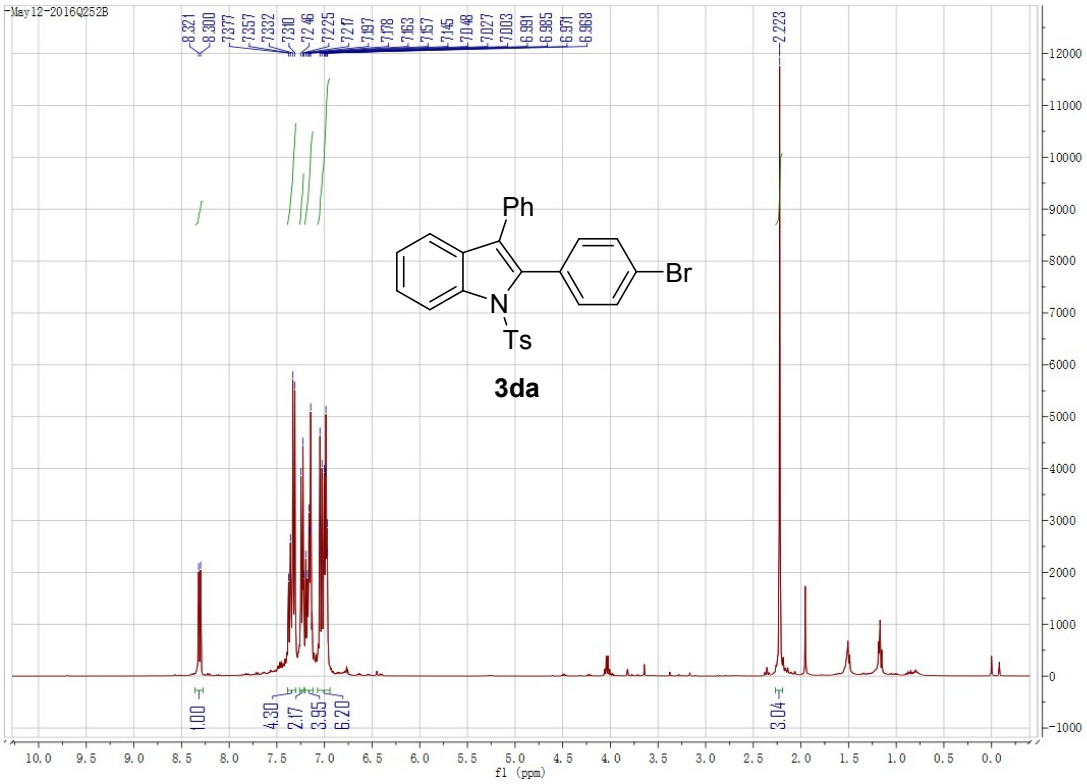
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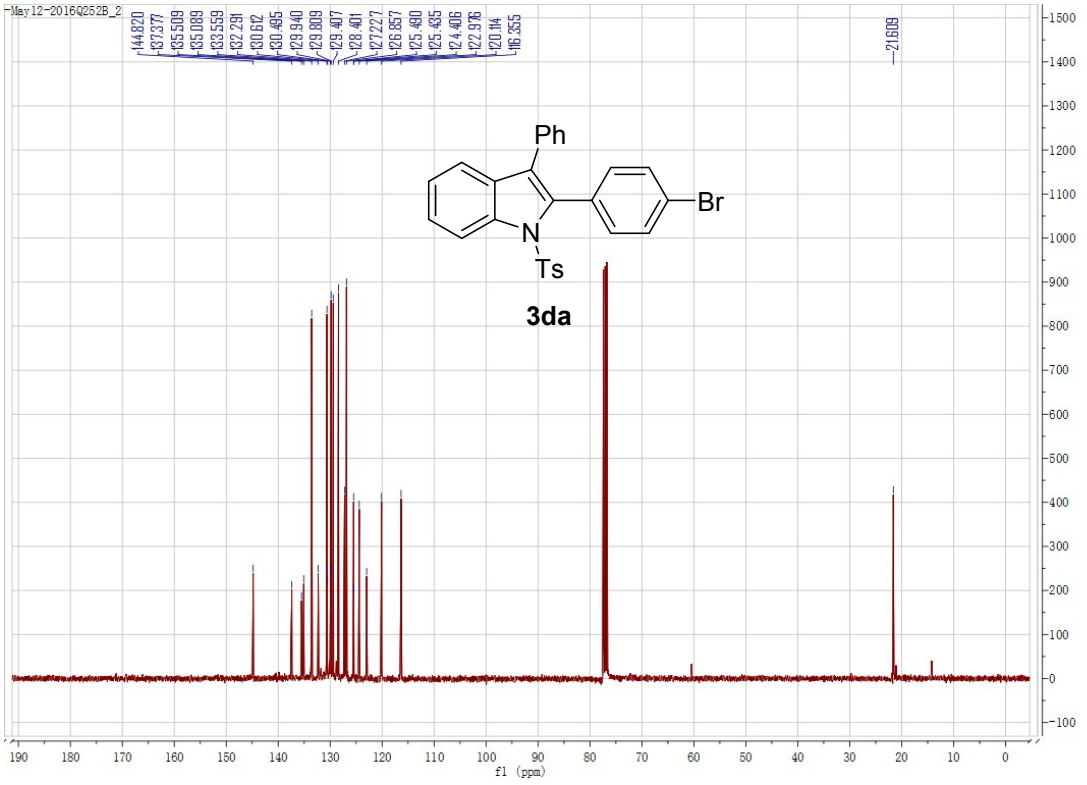
Ph
Br
N
Ts
3da
fl (ppm)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Br
N
Ts
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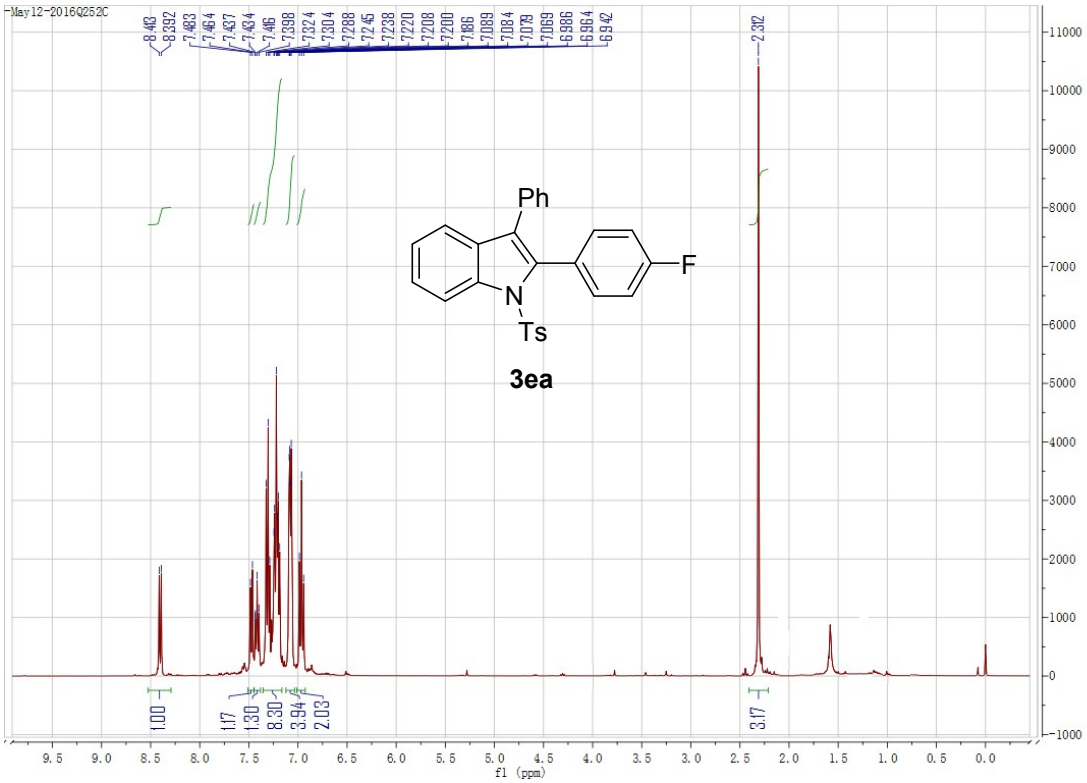
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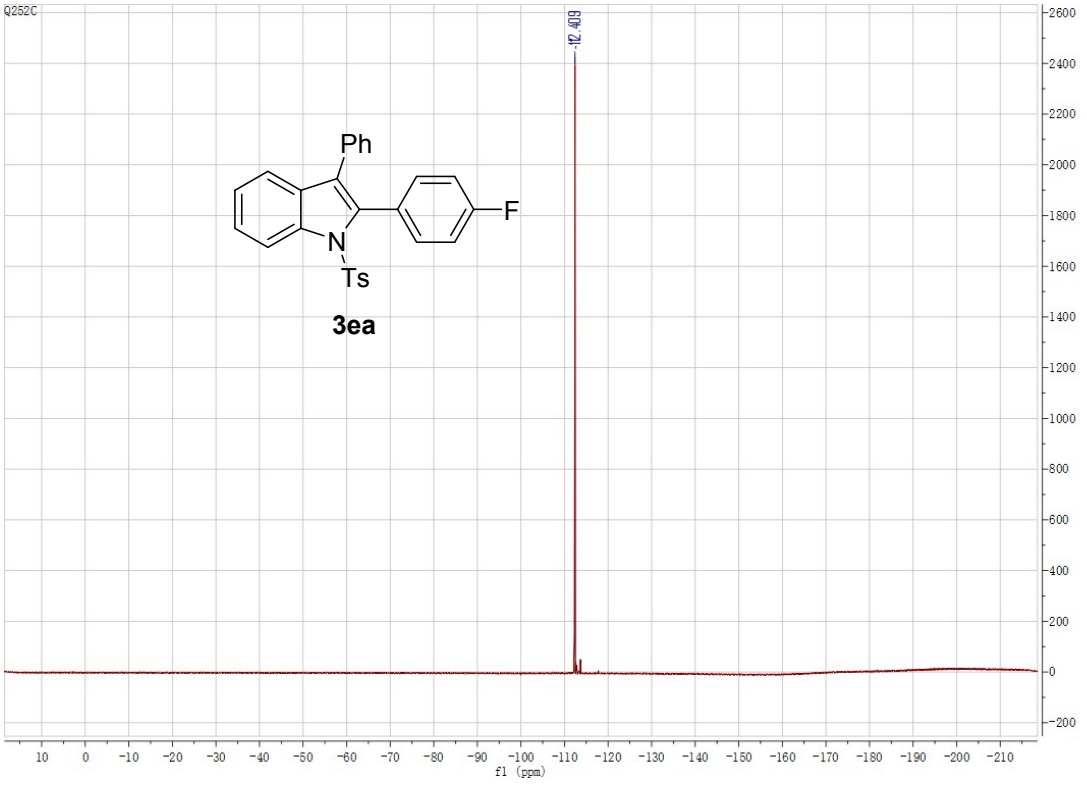
Ph
F
N
Ts
3ea
f1 (ppm)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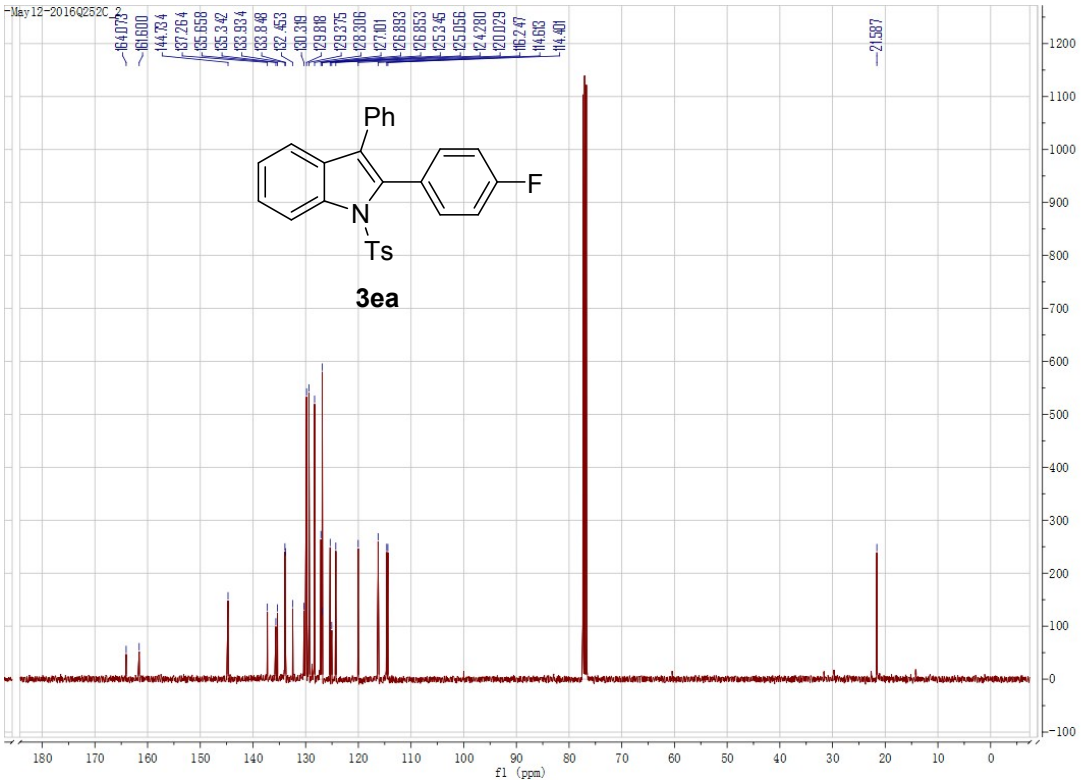
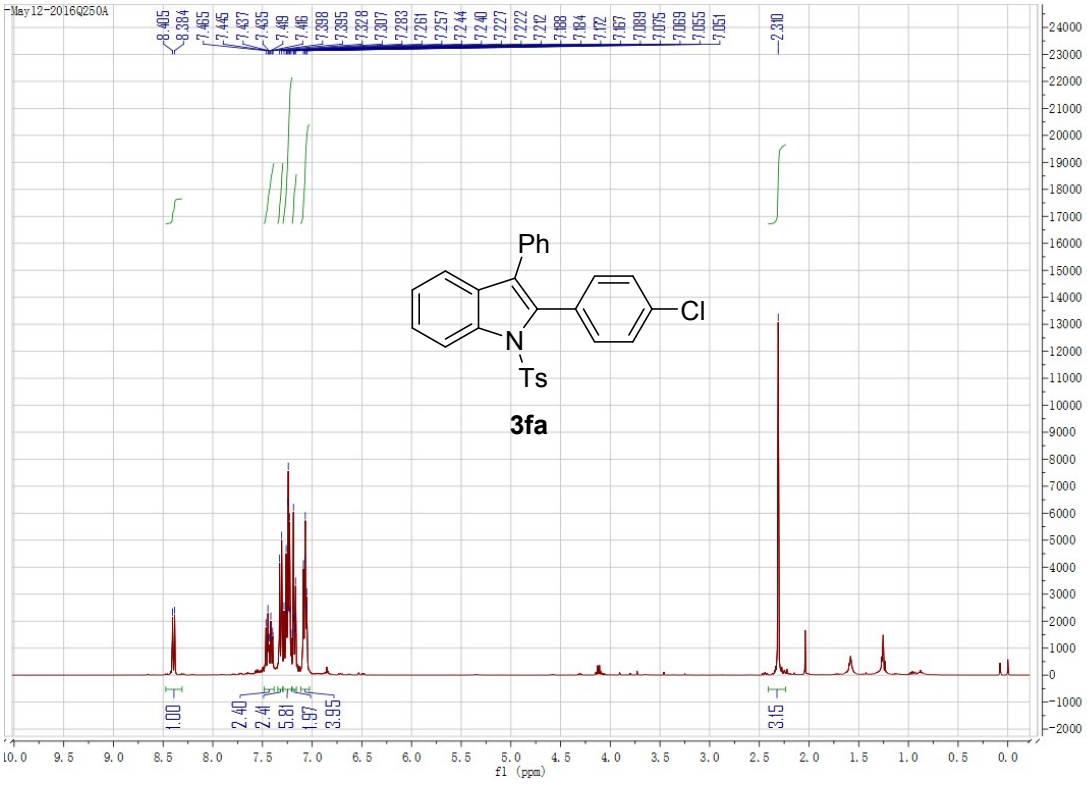
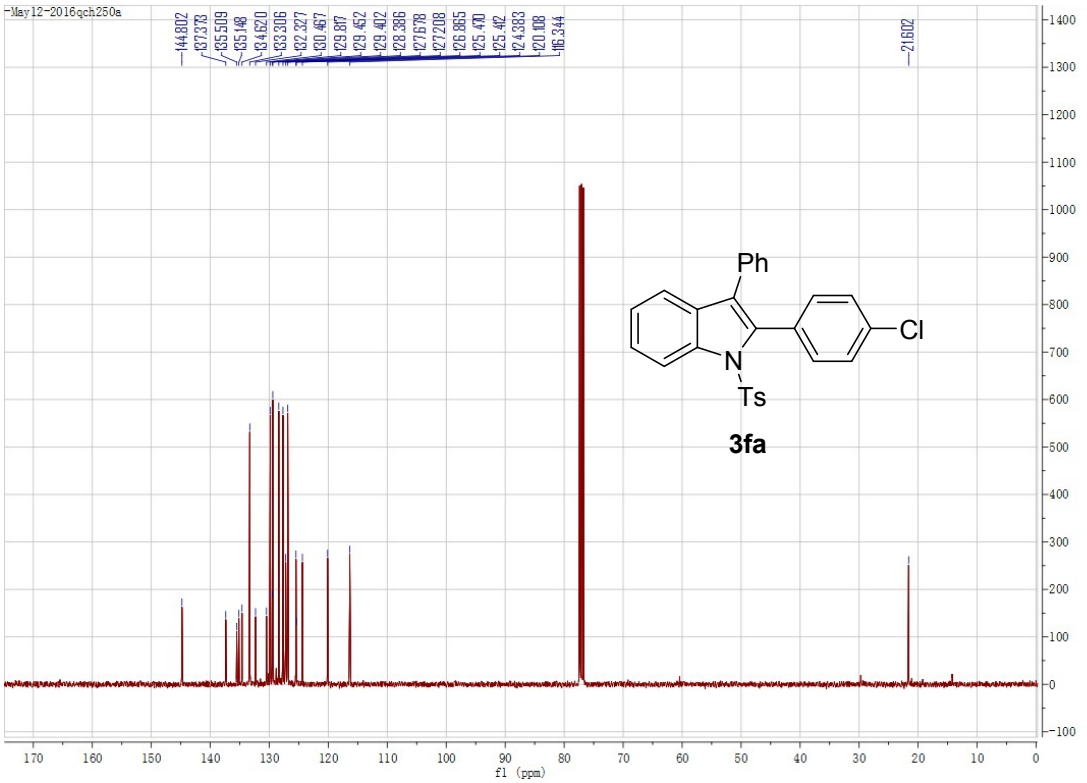
Ph
F
N
Ts
3ea
f1 (ppm)

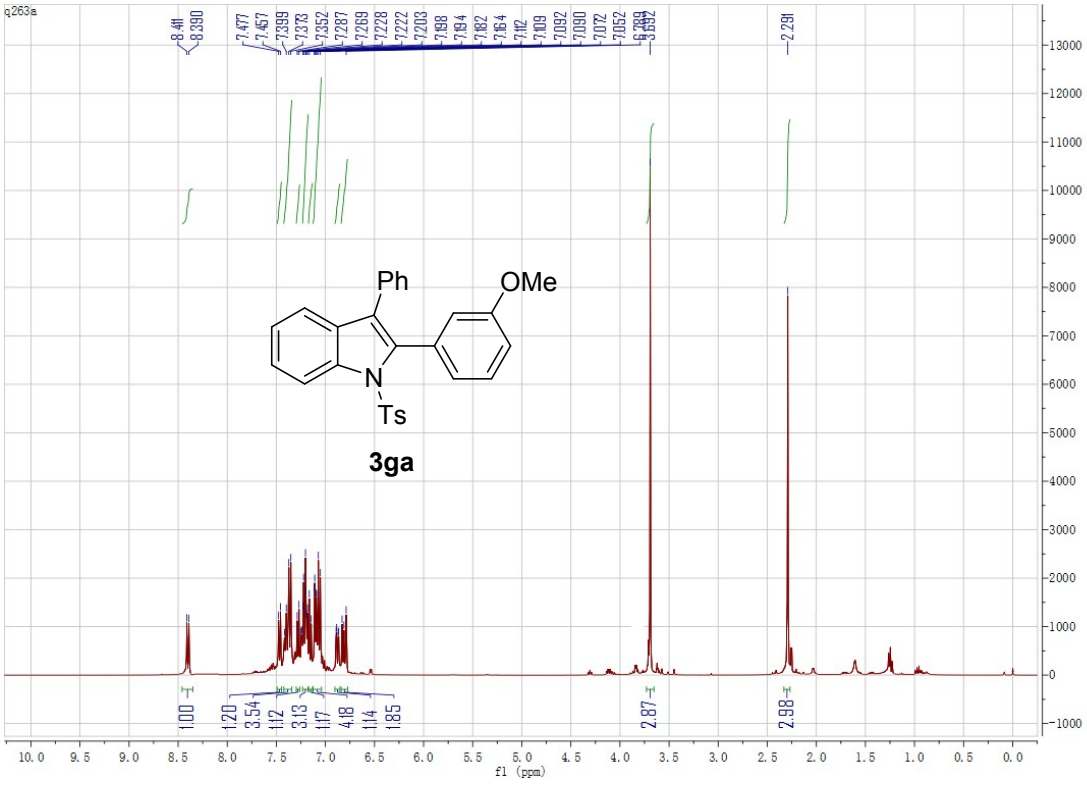


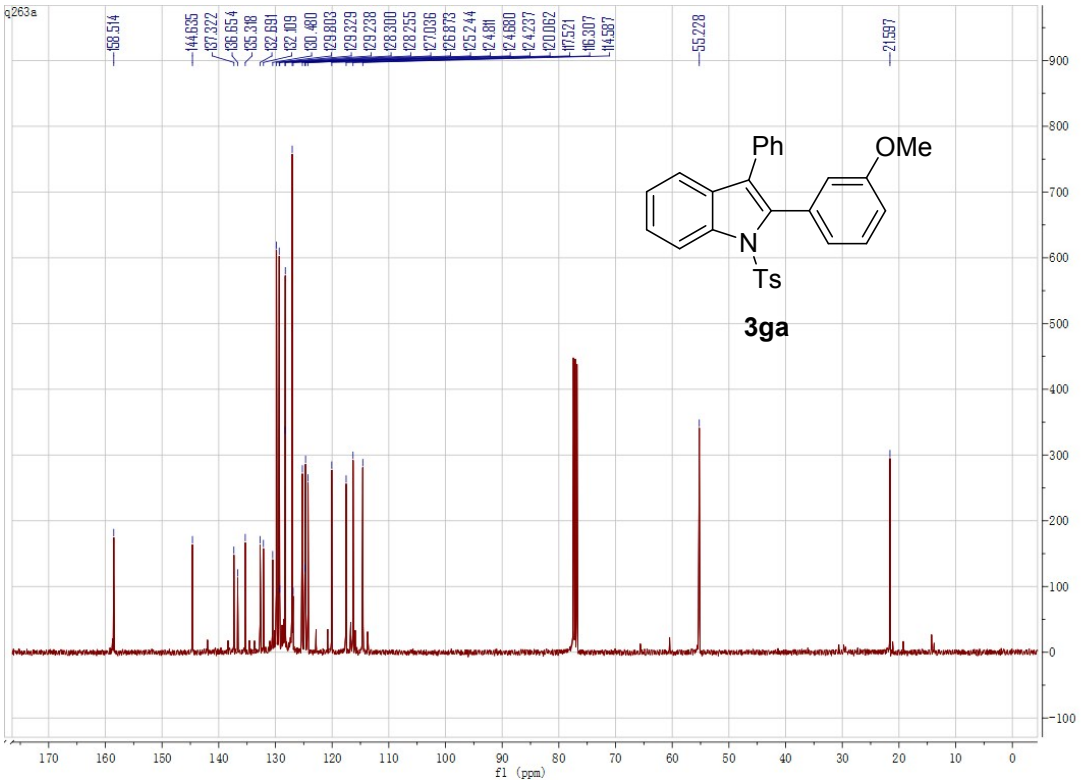
3ea

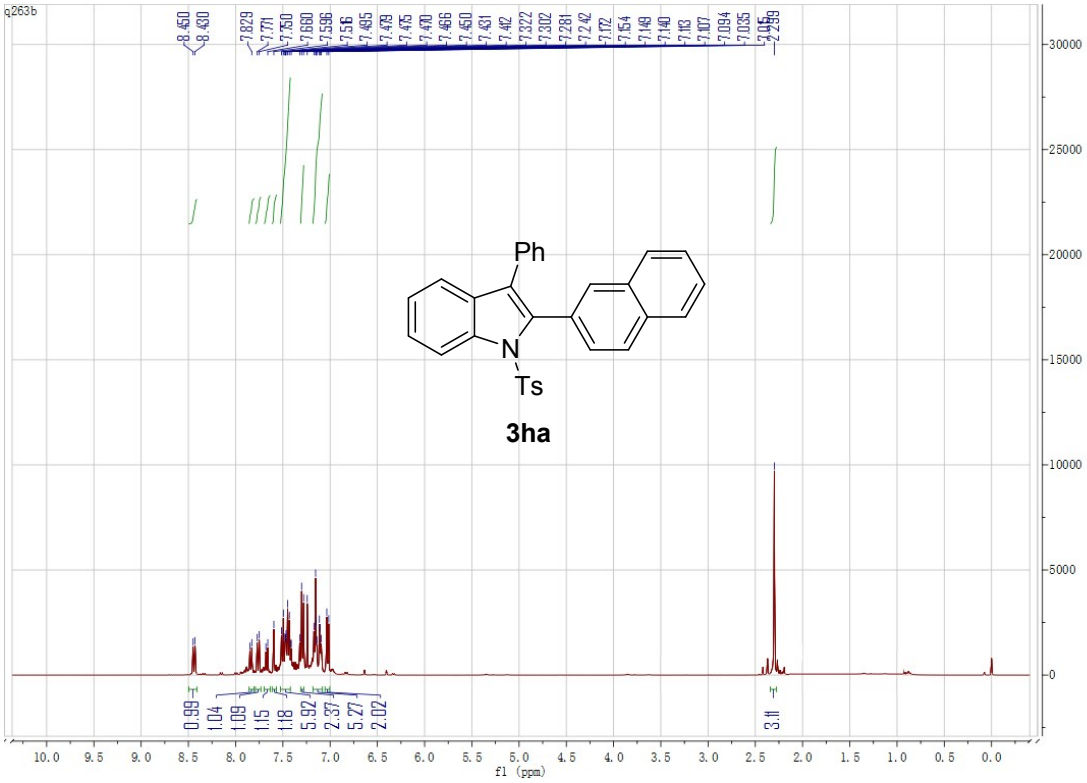


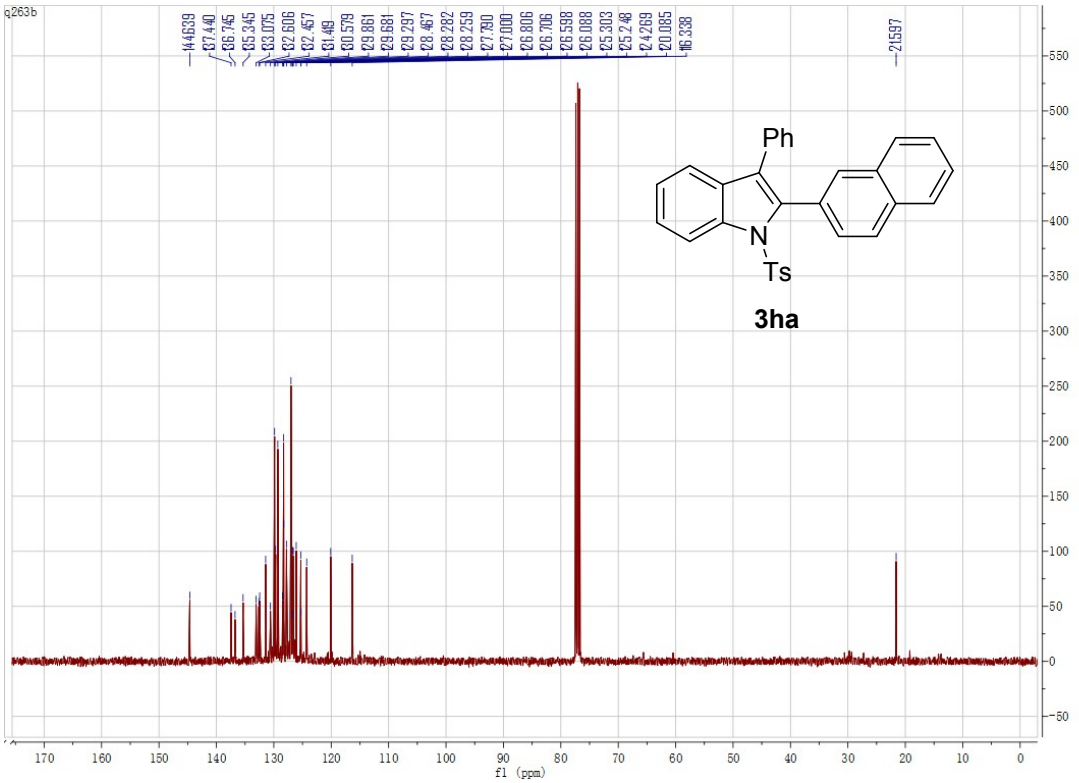
3fa


May12-2016qch250a
Ph
Cl
N
Ts
3fa
f1 (ppm)

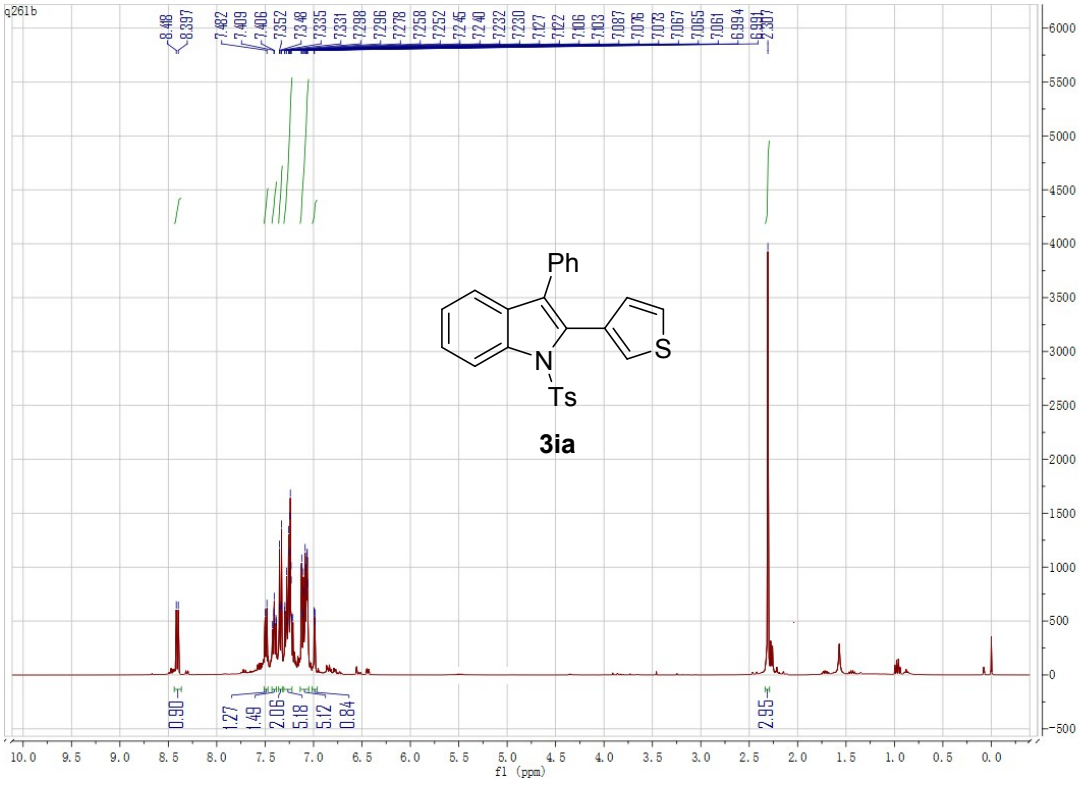

q263a
Ph
OMe
N
Ts
3ga
f1 (ppm)


q263a
158.514
144.635
137.322
136.654
135.398
132.691
132.109
130.480
129.803
129.329
129.238
128.300
128.255
127.036
126.873
125.244
124.811
124.680
124.237
120.062
117.521
116.307
114.587
55.228
21.597
Ph
OMe
N
Ts
3ga
f1 (ppm)

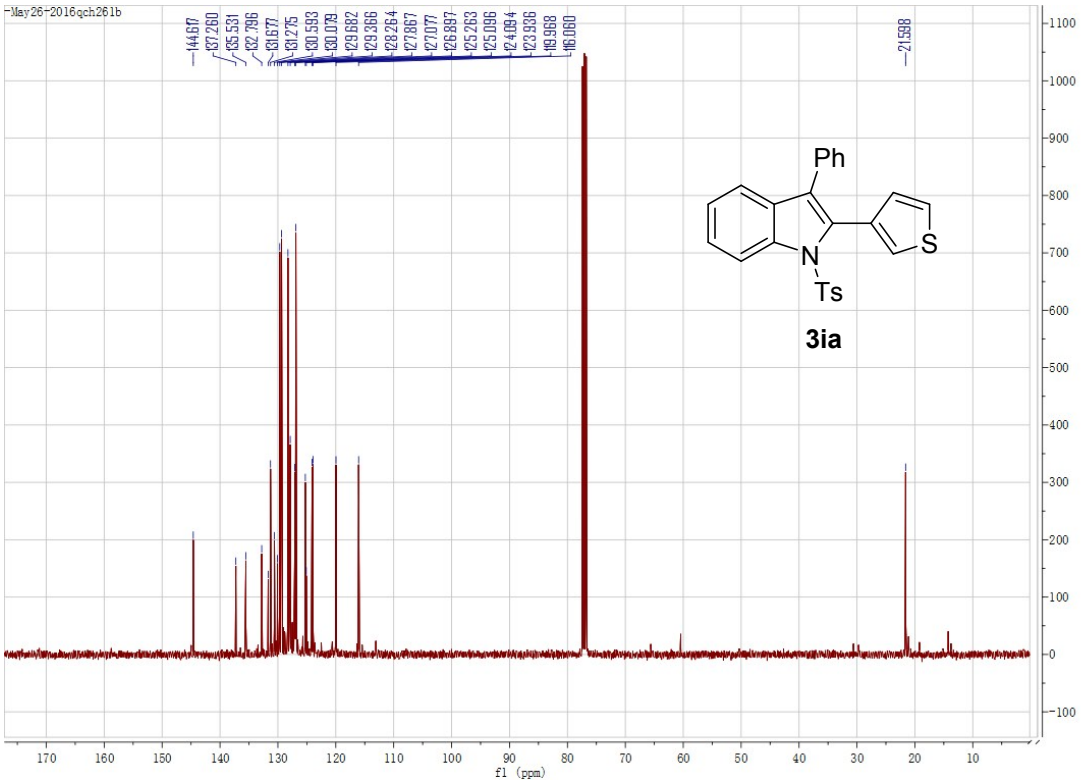

q263b
8.450
8.400
7.829
7.771
7.750
7.680
7.596
7.516
7.495
7.478
7.475
7.470
7.466
7.450
7.431
7.412
7.322
7.302
7.281
7.242
7.172
7.154
7.149
7.140
7.113
7.107
7.094
7.035
2.596
0.99
1.04
1.09
1.15
1.18
5.92
2.37
5.27
2.02
3.11
Ph
N
Ts
3ha
f1 (ppm)

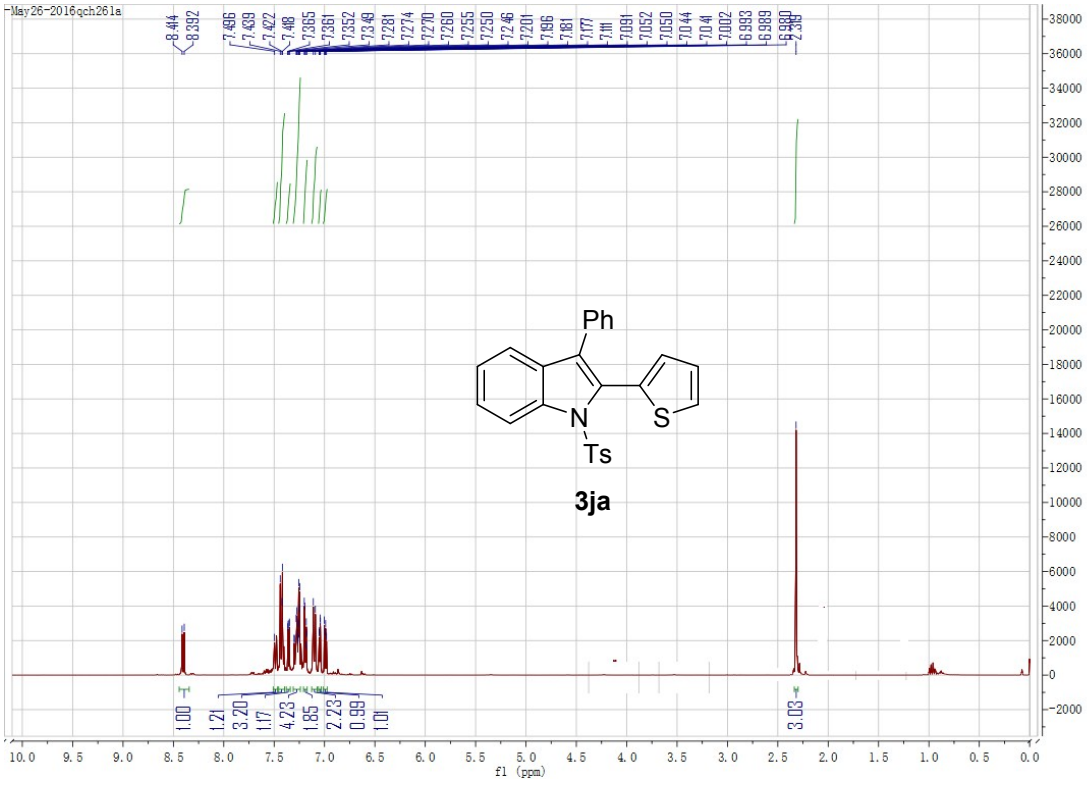


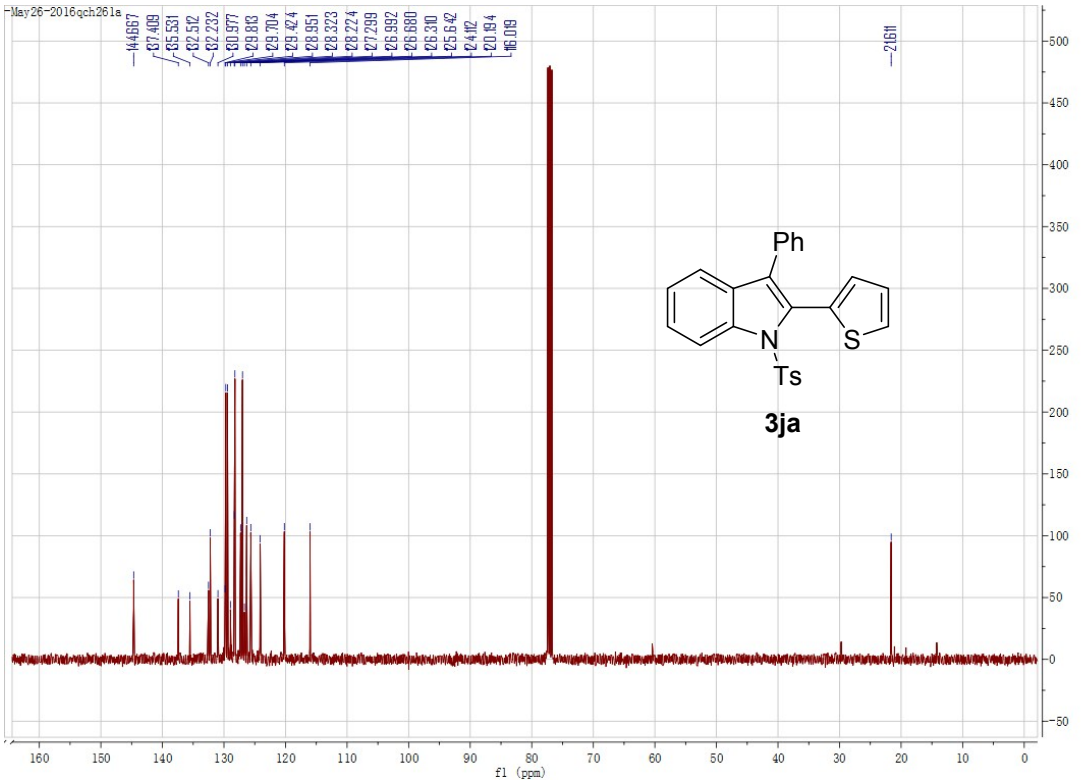
3ha

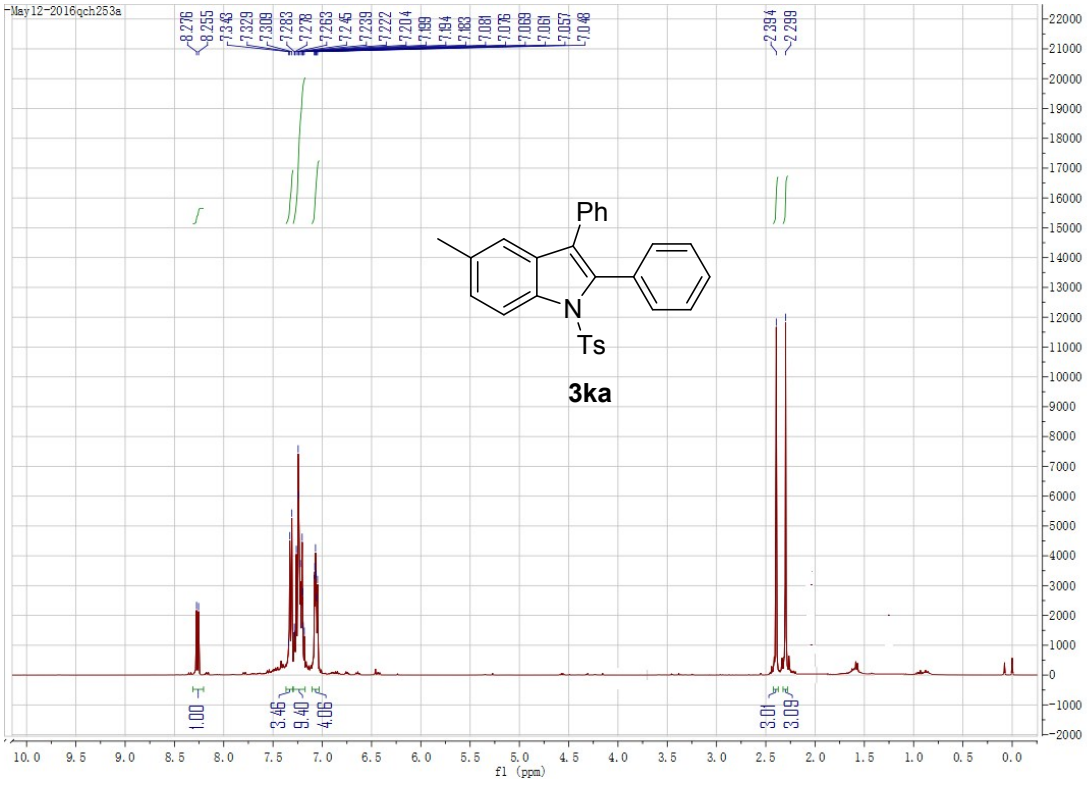


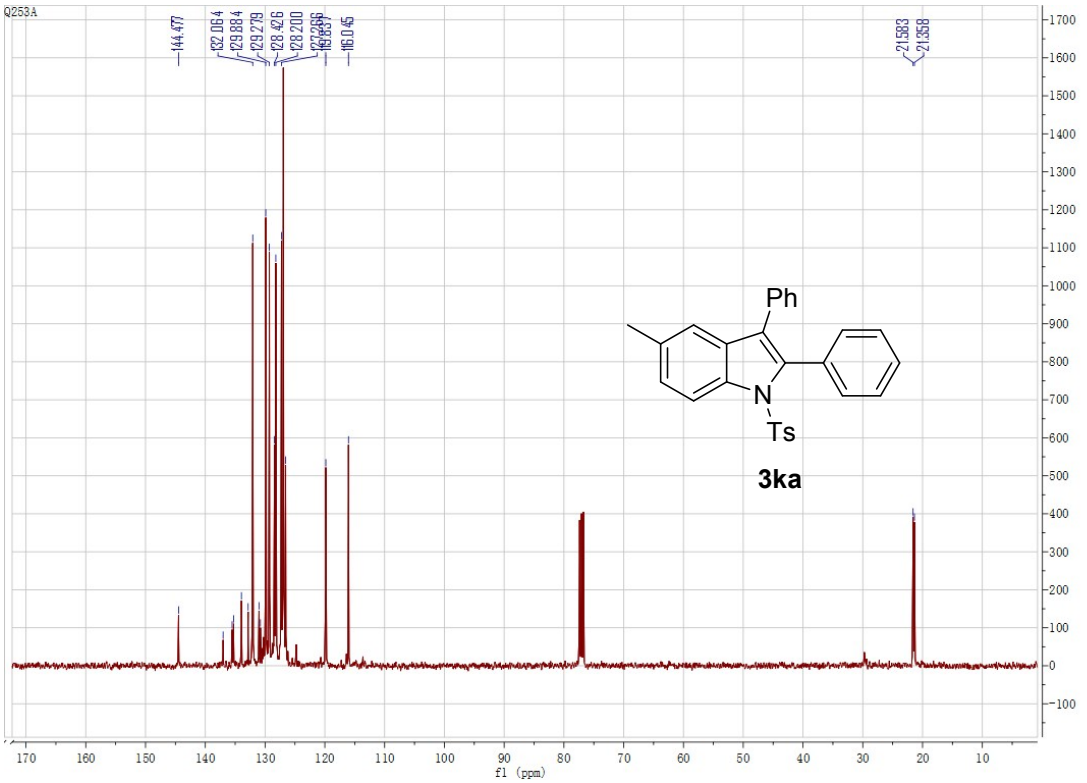
3ia

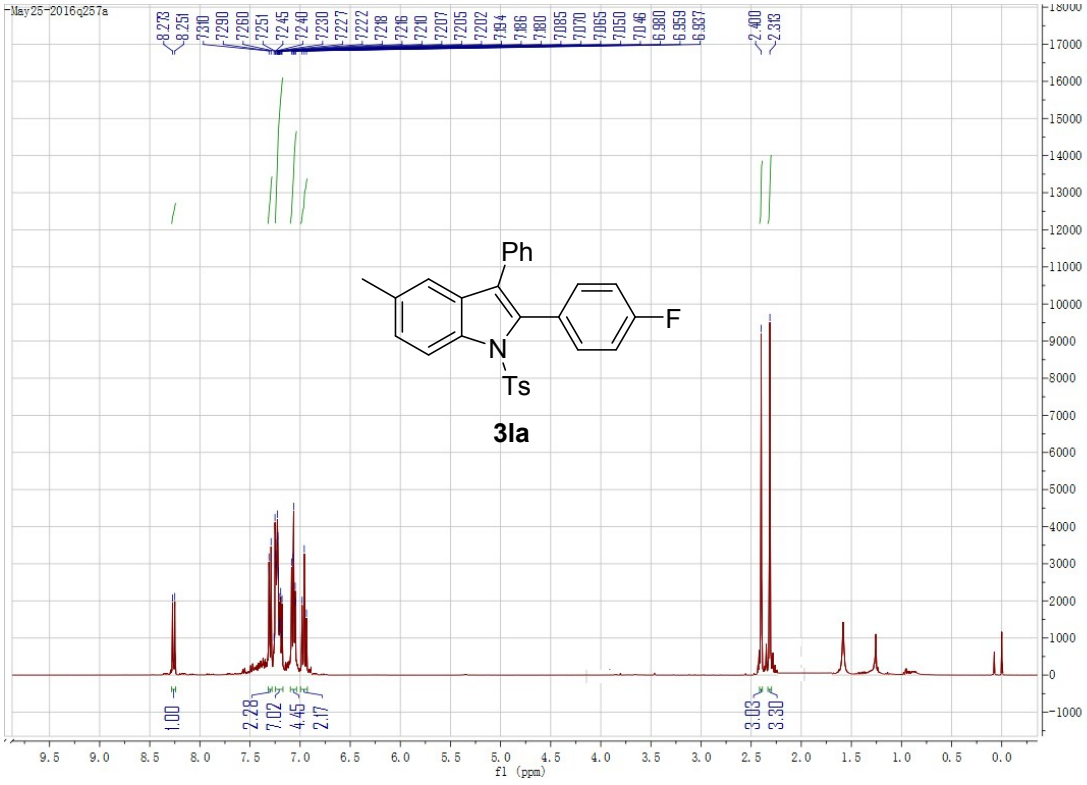

May26-2016qch261b
Ph
N
Ts
S
3ia
f1 (ppm)

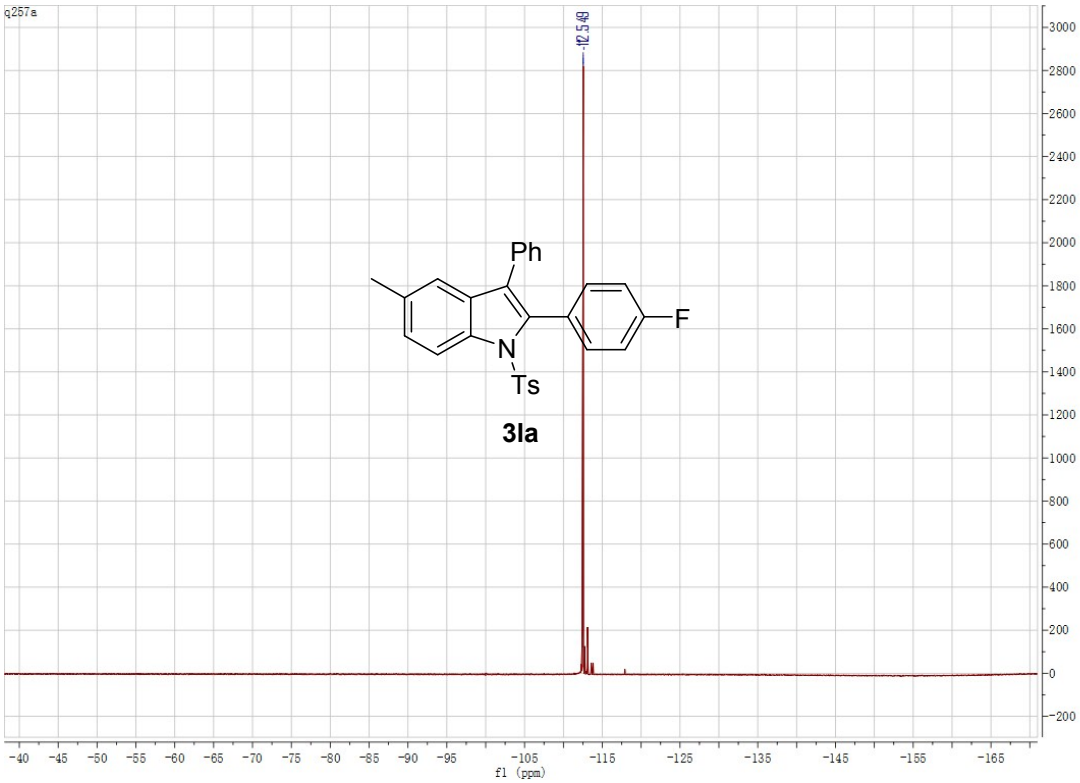

May26-2016qch261a
Ph
N
Ts
S
3ja
f1 (ppm)

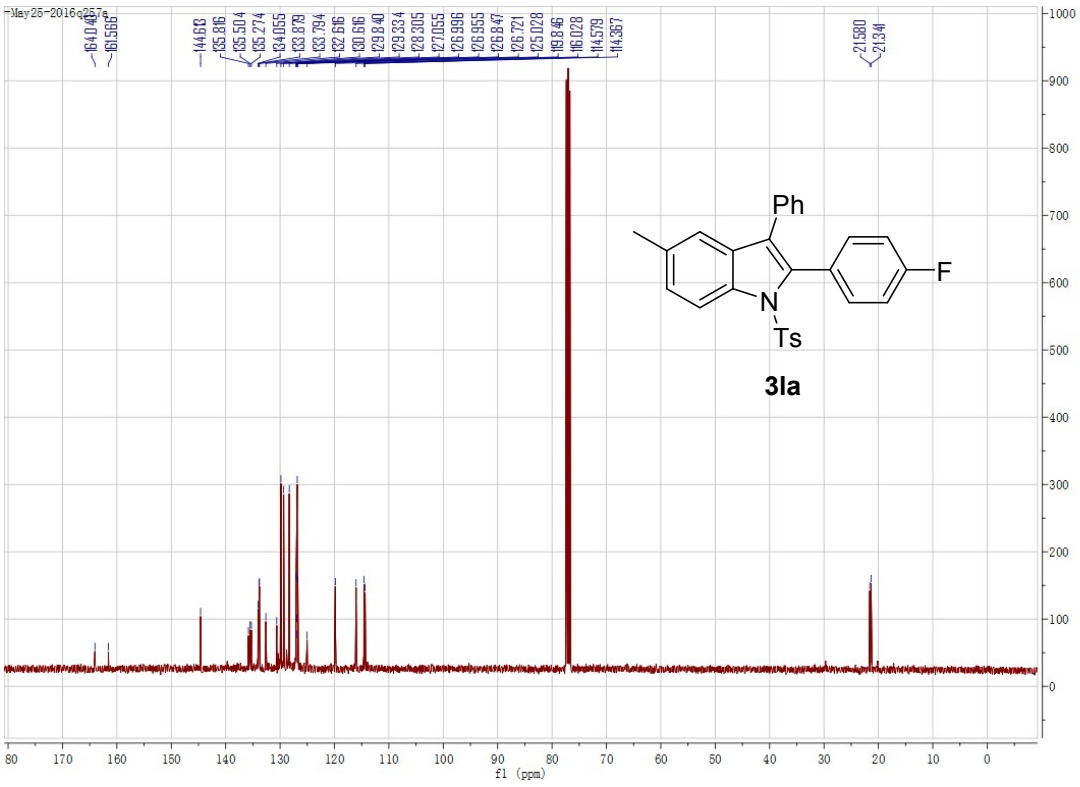

May26-2016qch261a
Ph
N
S
Ts
3ja
f1 (ppm)

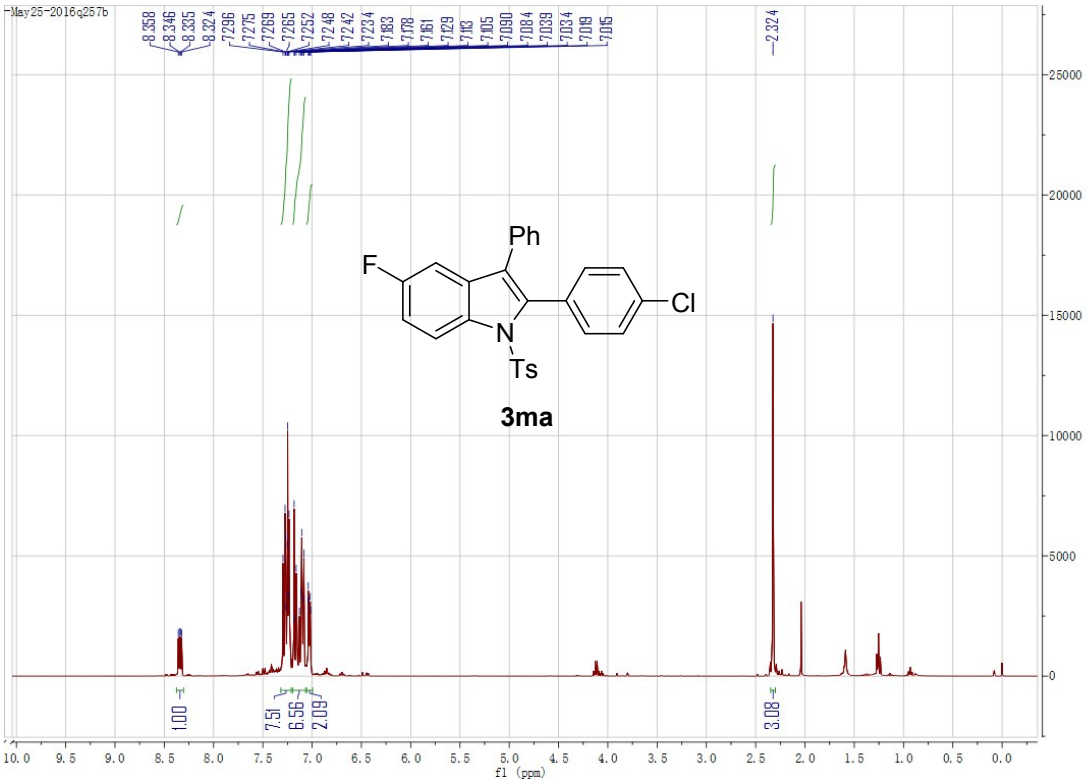

May12-2016qch253a
Ph
N
Ts
3ka
f1 (ppm)

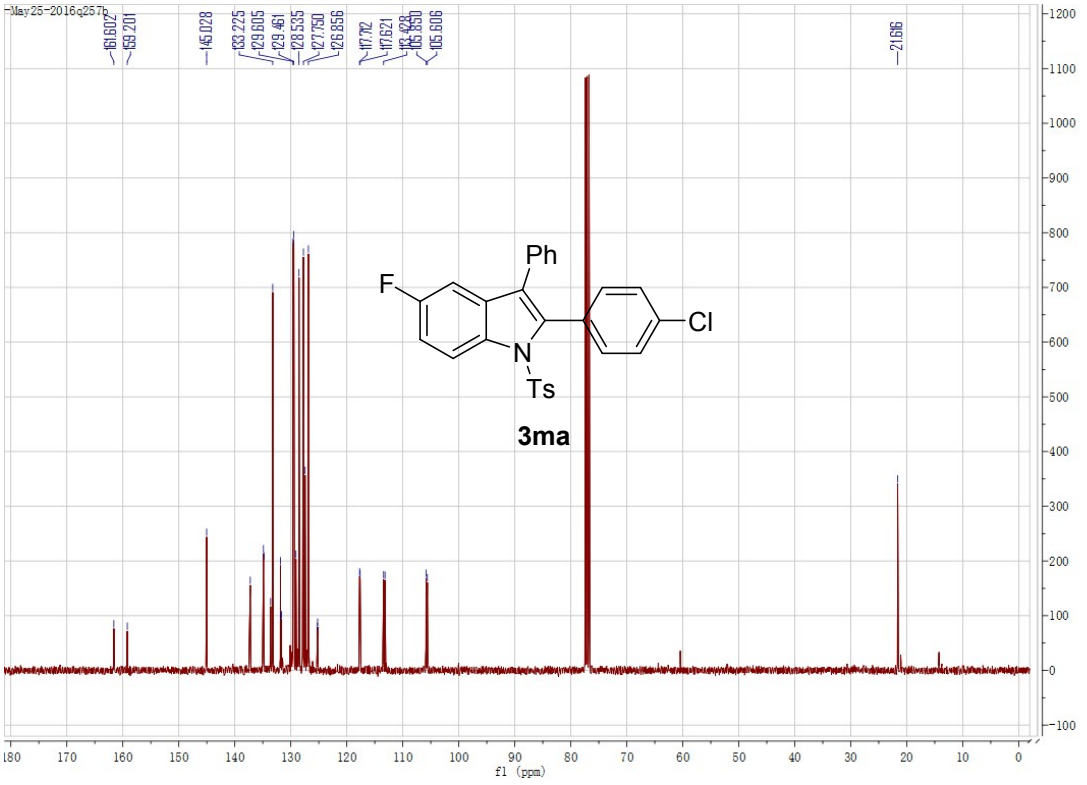

Q253A
Ph
N
Ts
3ka
f1 (ppm)

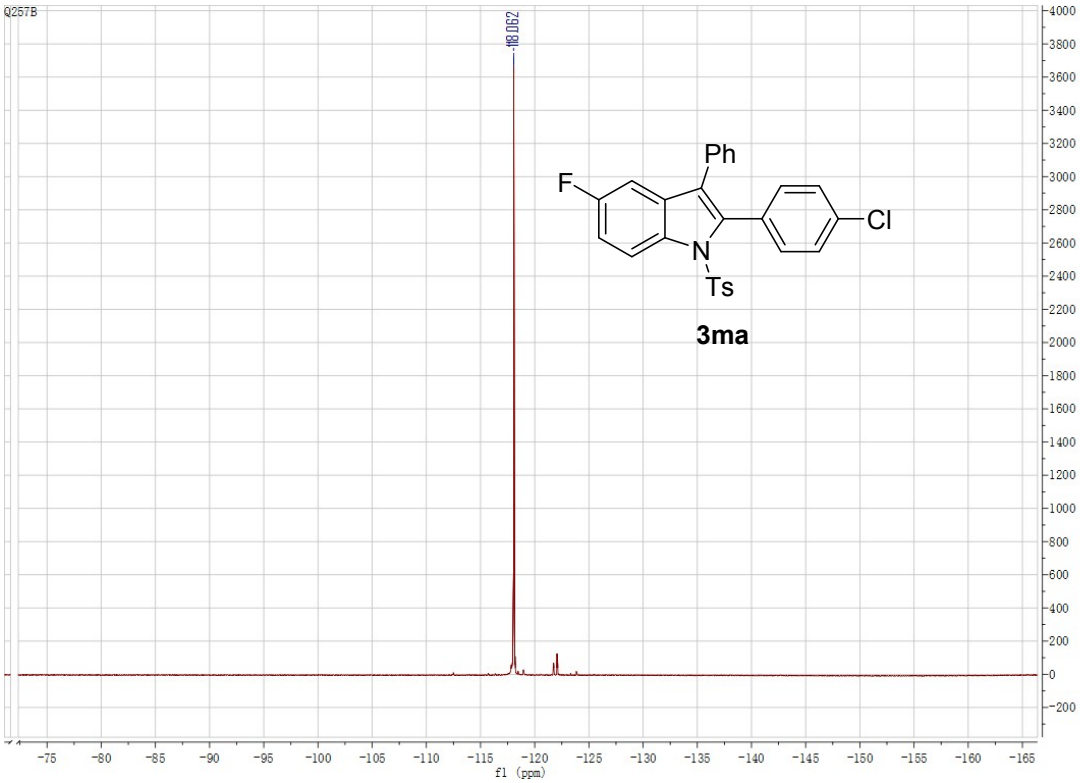

May26-2016q257a
Ph
F
N
Ts
3la
f1 (ppm)

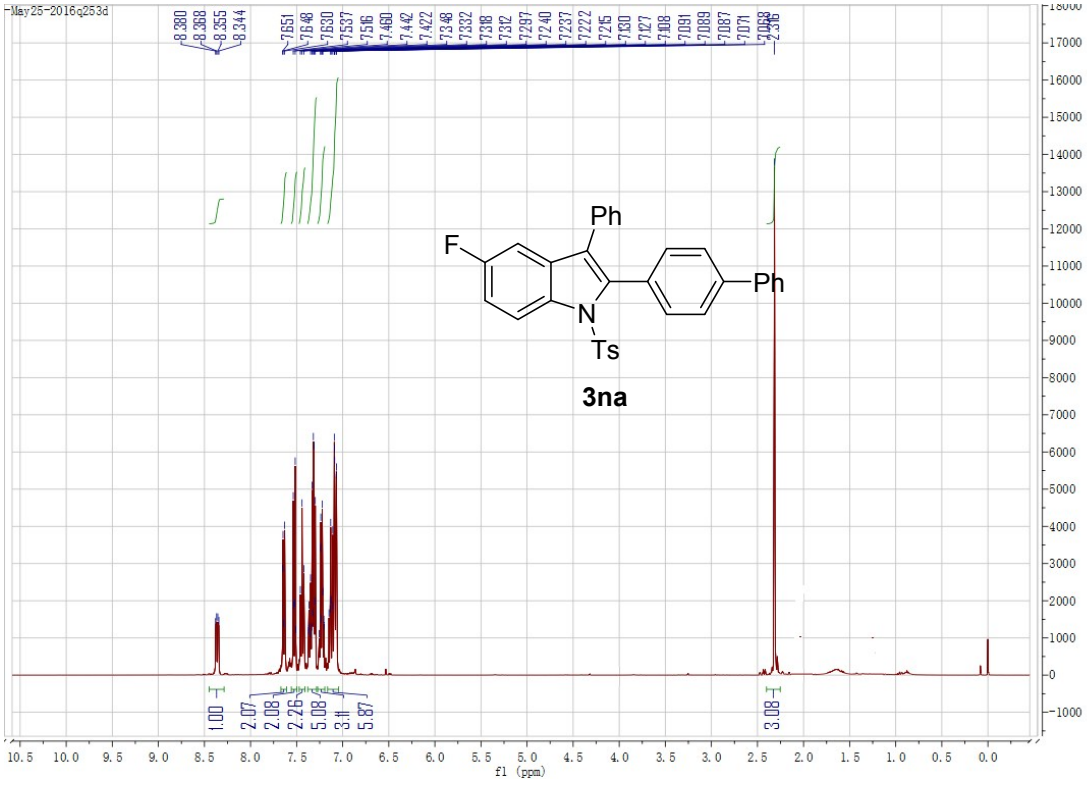

q257a
-112.548
Ph
F
N
Ts
3la
f1 (ppm)

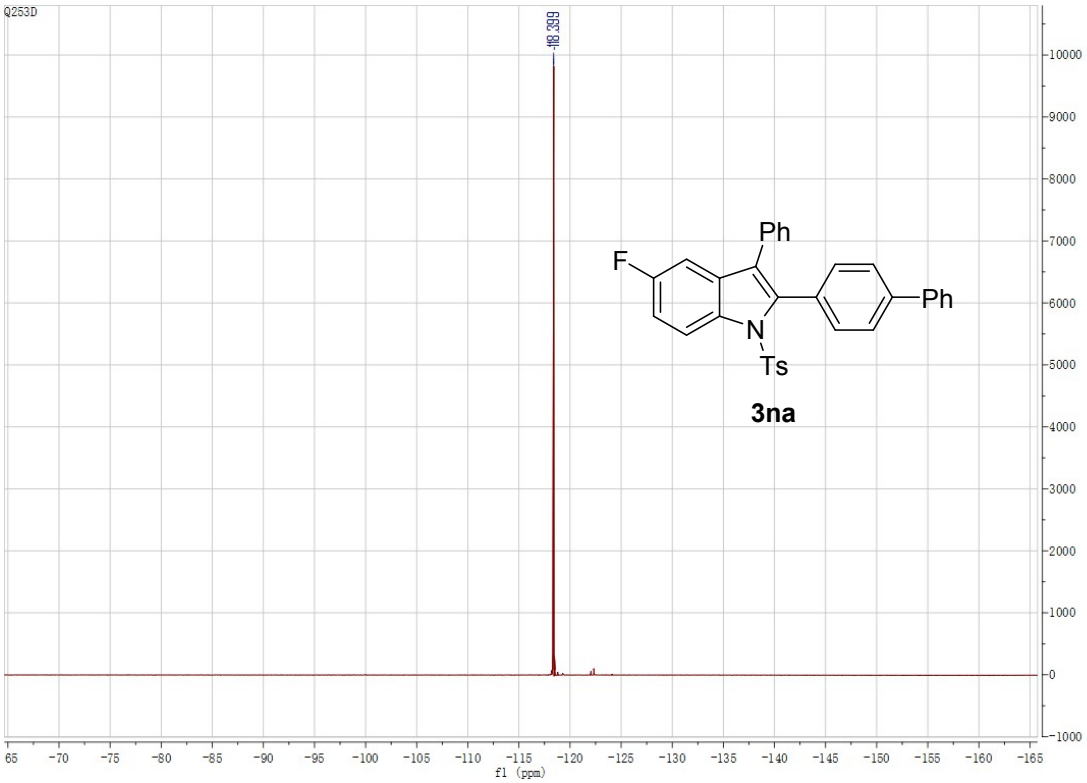

May26-2016q257a
164.048
161.568
144.613
135.816
135.504
135.274
134.055
133.878
133.794
132.616
130.616
129.840
129.334
128.305
127.055
126.996
126.955
126.847
126.721
125.028
119.846
116.028
114.579
114.387
21.580
21.344
Ph
F
N
Ts
3la
f1 (ppm)

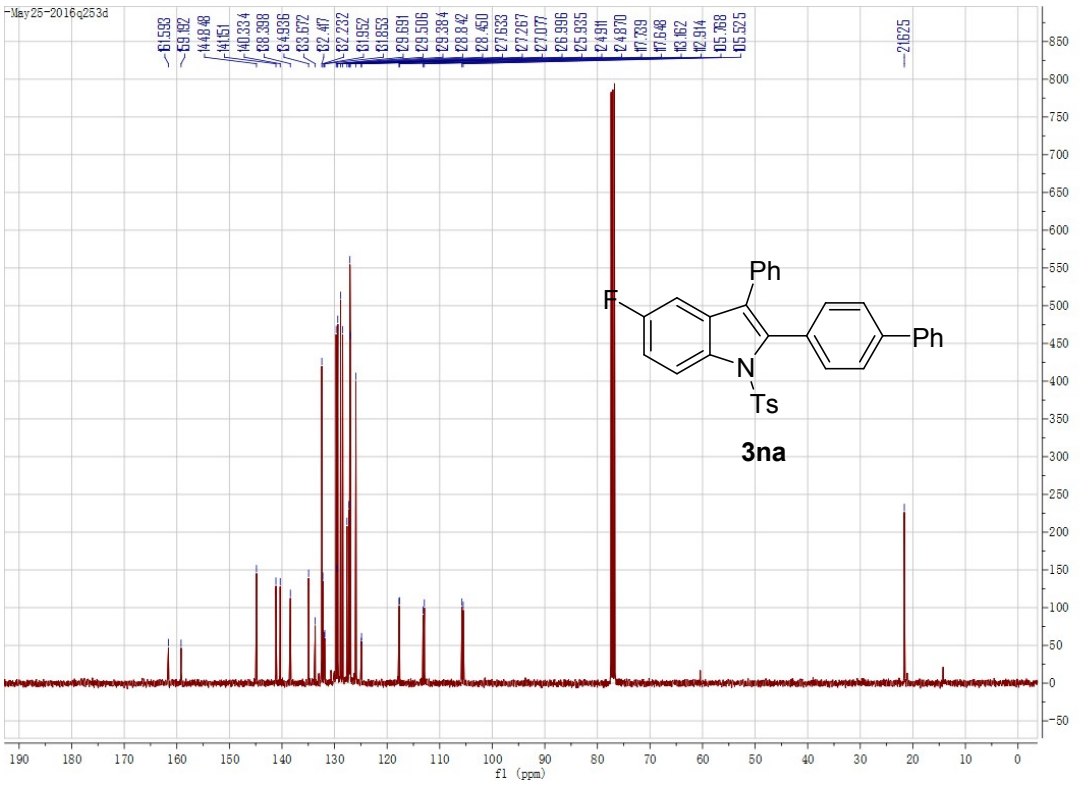

May25-2016q257b
8.358
8.346
8.335
8.324
7.296
7.275
7.269
7.265
7.252
7.248
7.242
7.234
7.183
7.178
7.161
7.129
7.113
7.105
7.090
7.084
7.039
7.034
7.019
7.015
2.324
Ph
F
Cl
N
Ts
3ma
1.00
7.51
6.56
2.09
3.08
fl (ppm)


May25-2016q257b
161.607
159.201
145.028
133.225
129.605
129.461
128.535
127.750
126.856
117.702
117.621
105.850
105.606
21.666
Ph
F
Cl
N
Ts
3ma
fl (ppm)


Q257B
-118.062
Ph
F
Cl
N
Ts
3ma
f1 (ppm)


May25-2016q253d
8.380
8.368
8.355
8.344
7.651
7.648
7.630
7.537
7.516
7.480
7.442
7.422
7.348
7.332
7.318
7.312
7.297
7.240
7.237
7.222
7.215
7.130
7.127
7.108
7.091
7.089
7.087
7.071
2.316
Ph
F
Ph
N
Ts
3na
1.00
2.07
2.08
2.26
5.08
3.11
5.87
3.08
f1 (ppm)


Q253D
-118.399
F
Ph
Ph
N
Ts
3na
f1 (ppm)


May26-2016q253d
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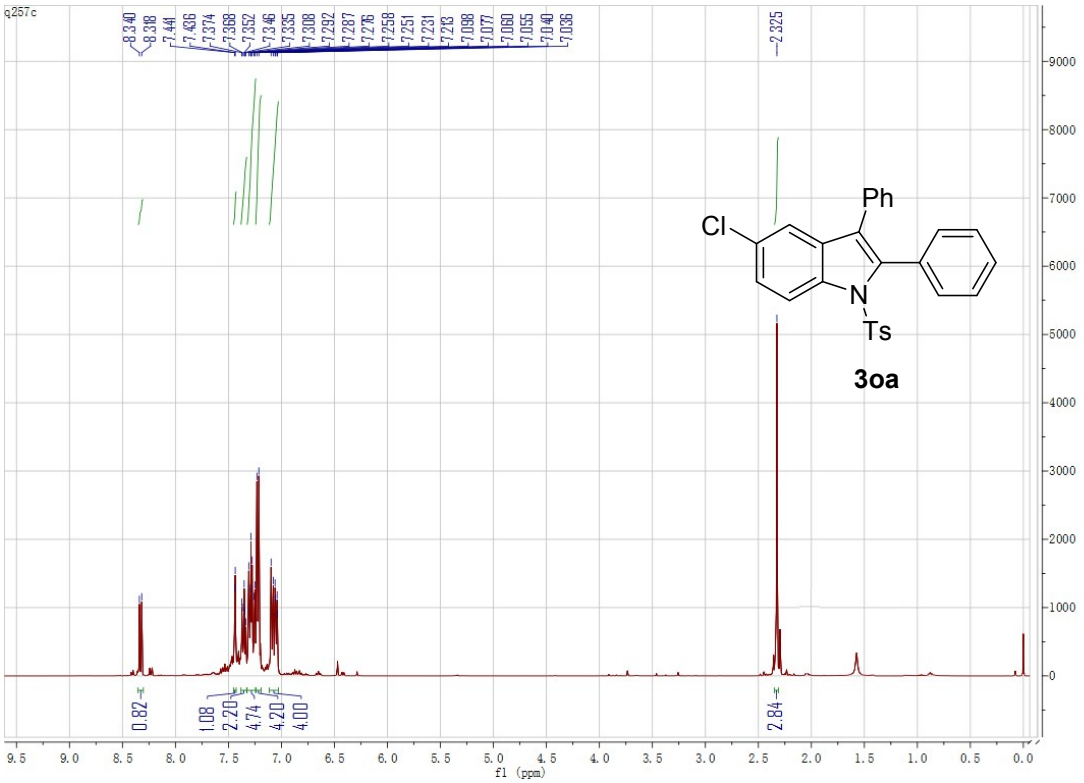
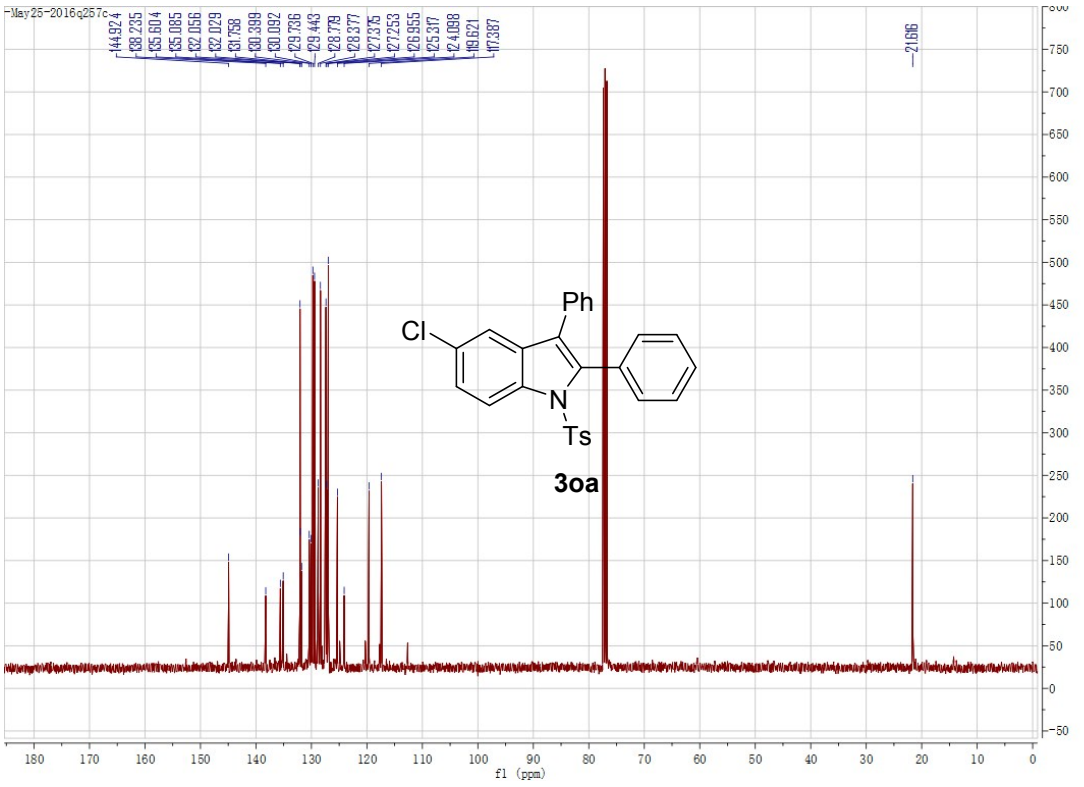
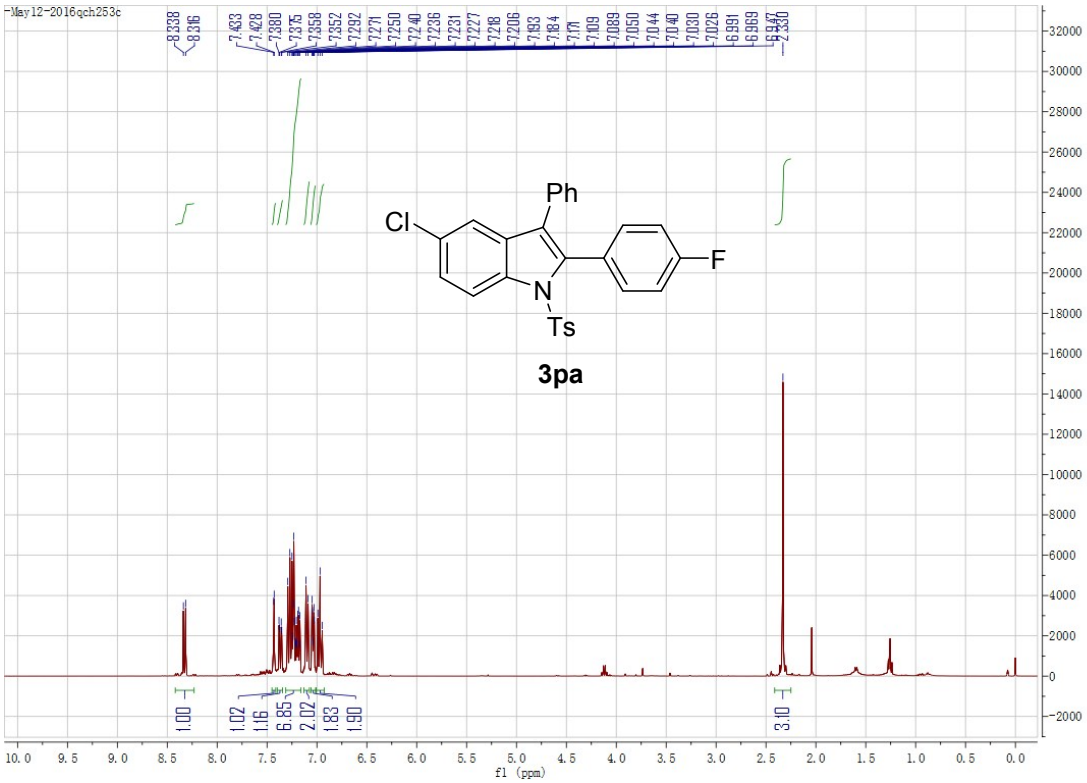
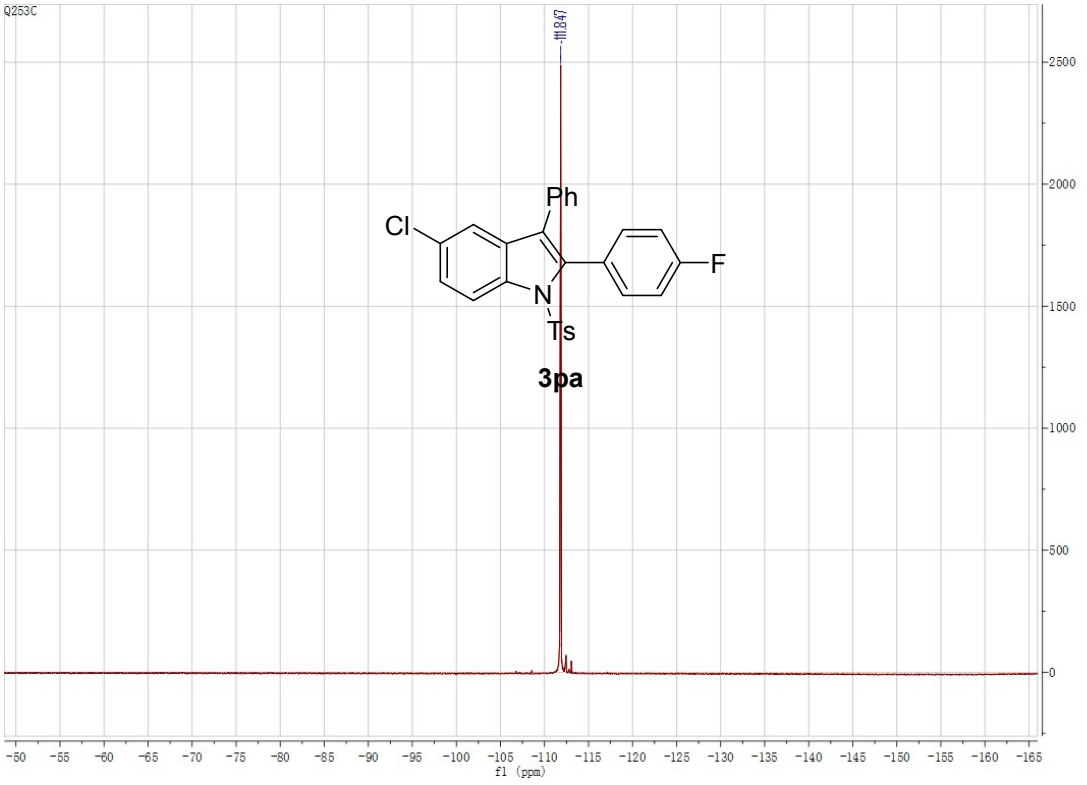
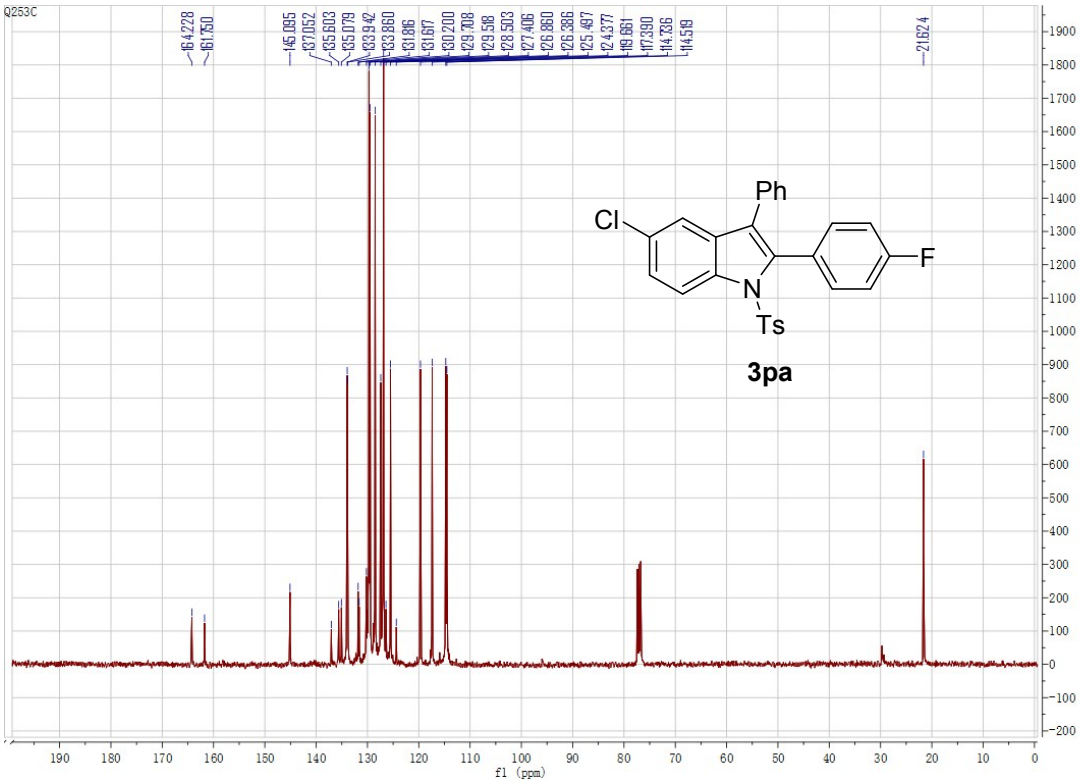
59.892
144.848
141.451
140.334
138.398
64.936
63.672
62.417
62.232
61.952
61.853
129.691
129.506
129.384
128.842
128.450
127.633
127.267
127.077
126.996
125.935
124.911
124.870
117.739
117.648
143.162
142.914
105.768
105.525
21.625
F
Ph
Ph
N
Ts
3na
f1 (ppm)

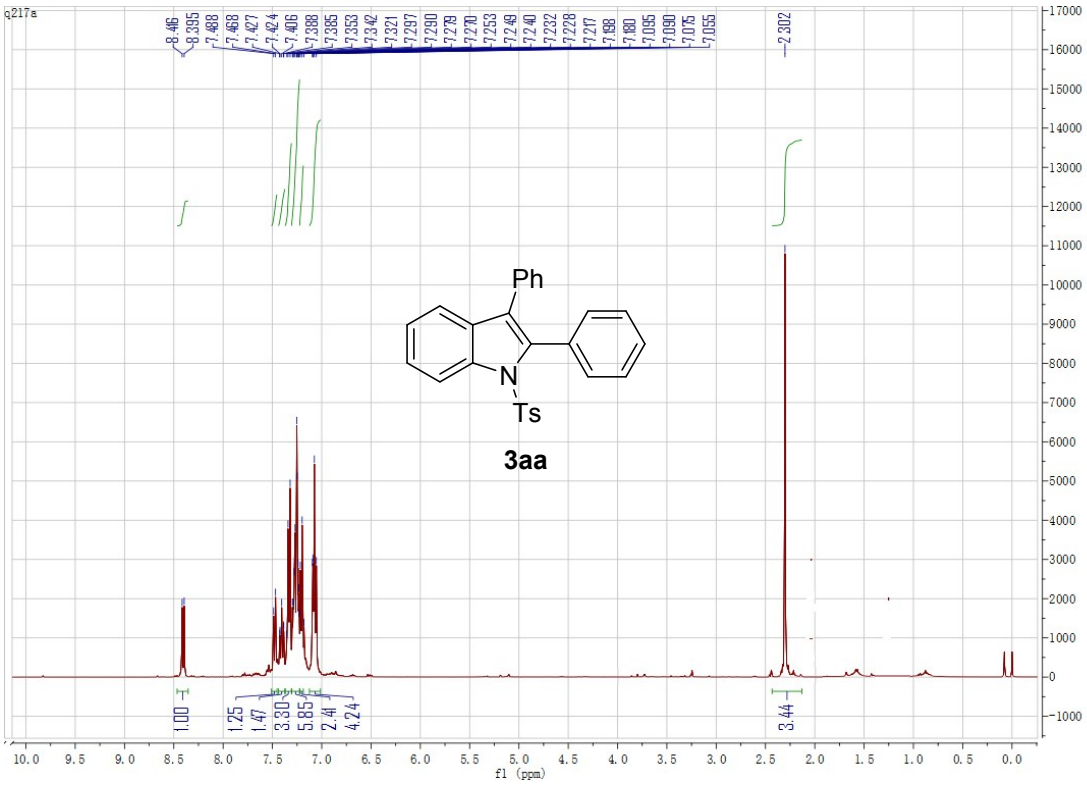

q257c
Ph
Cl
N
Ts
3oa
f1 (ppm)

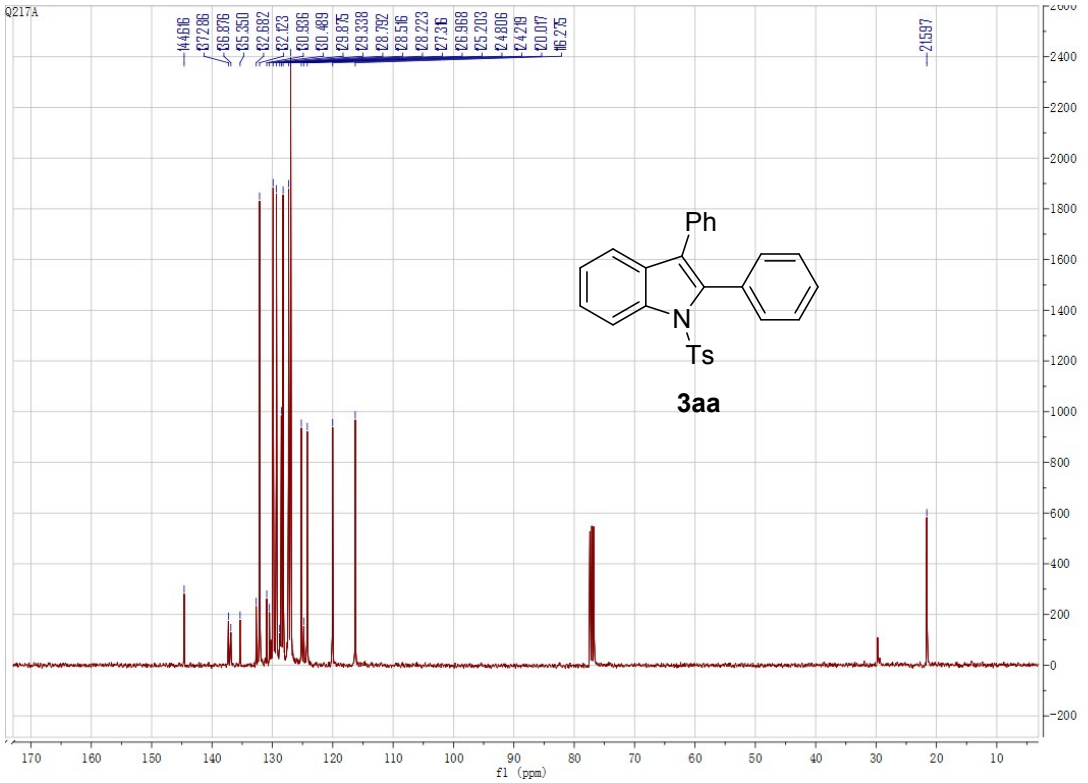

May26-2016q257c
Ph
Cl
N
Ts
3oa
f1 (ppm)

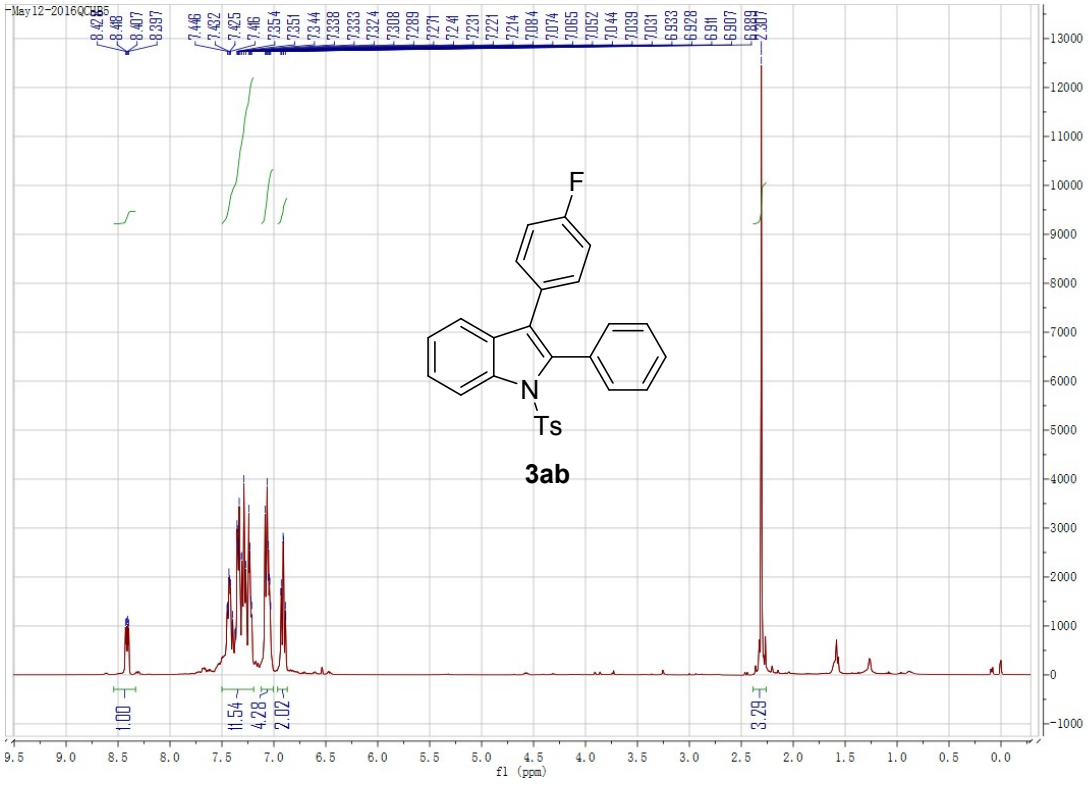

May12-2016qch253c
Ph
Cl
F
N
Ts
3pa
fl (ppm)

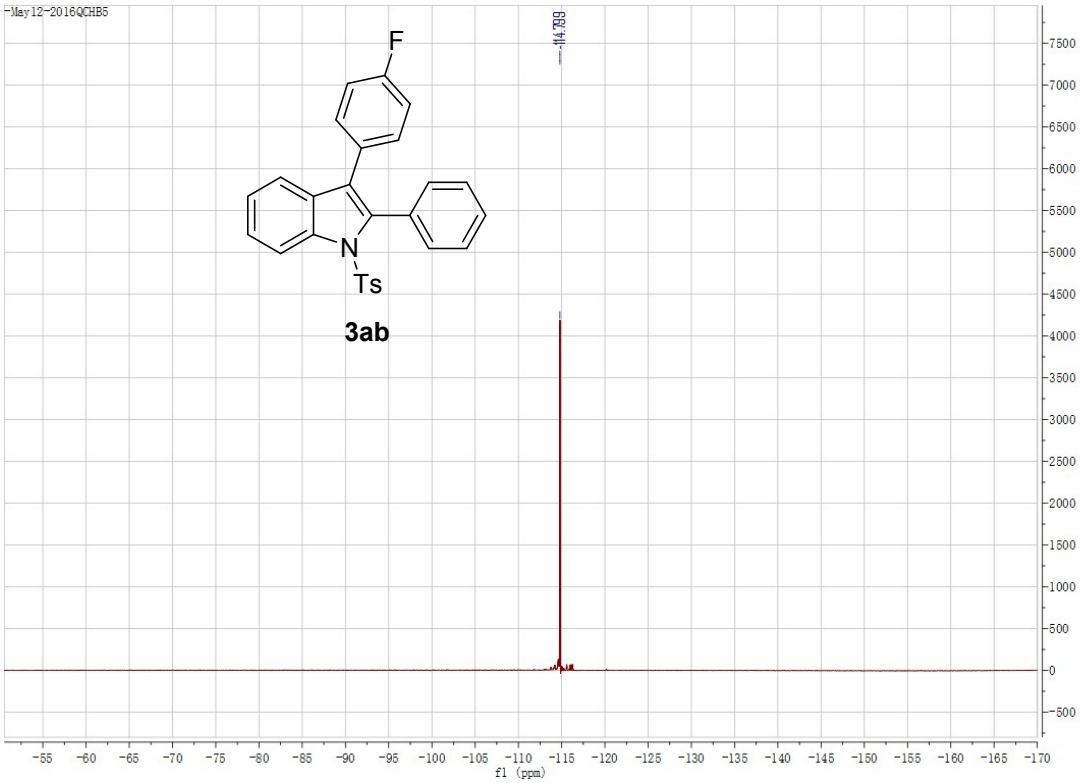

Q253C
Ph
Cl
F
N
Ts
3pa
fl (ppm)

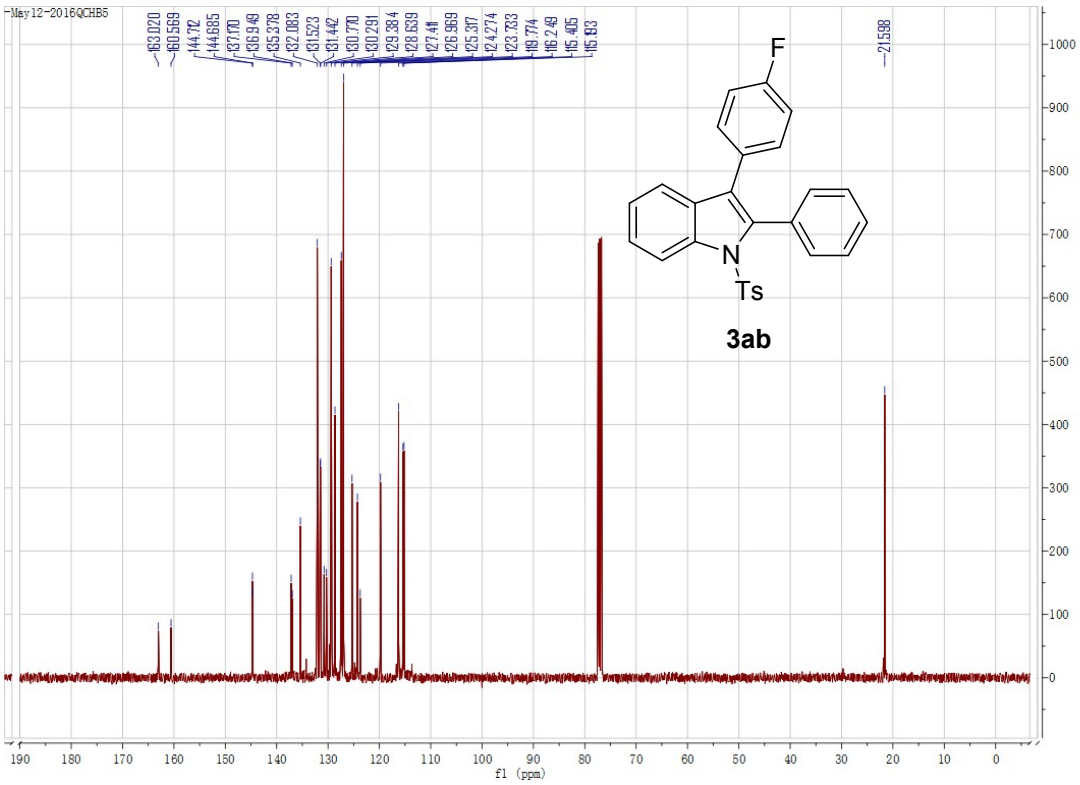

Q253C
Ph
Cl
F
N
Ts
3pa
f1 (ppm)

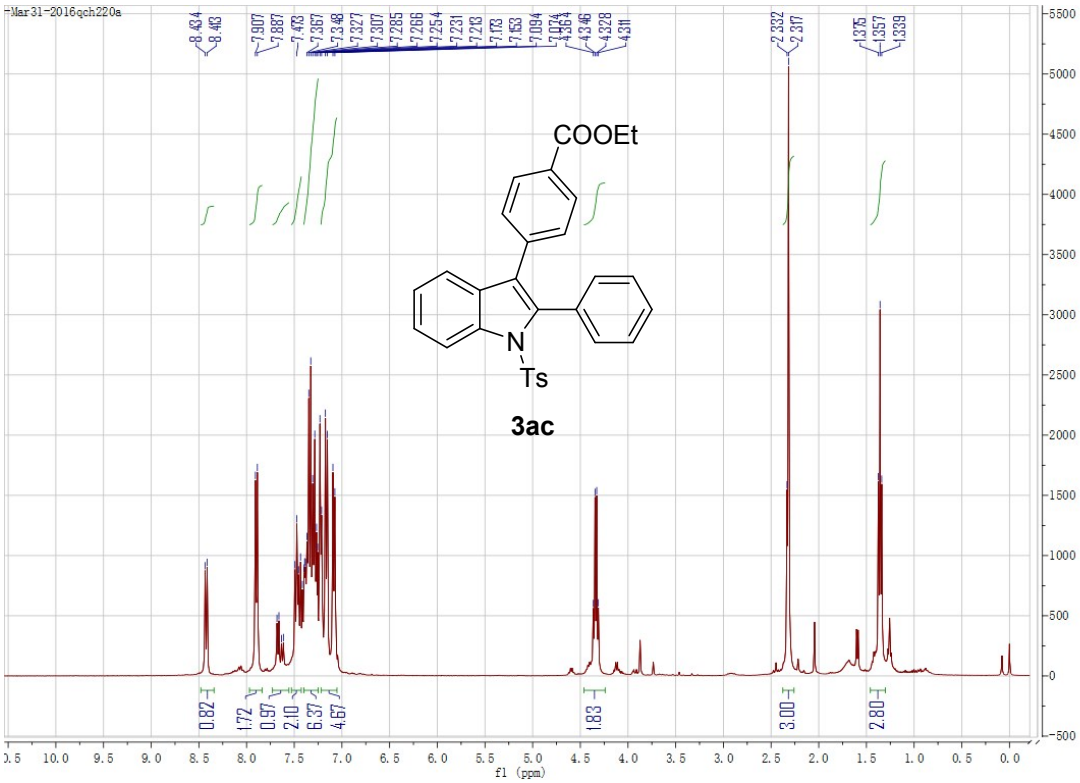

q217a
Ph
N
Ts
3aa
f1 (ppm)

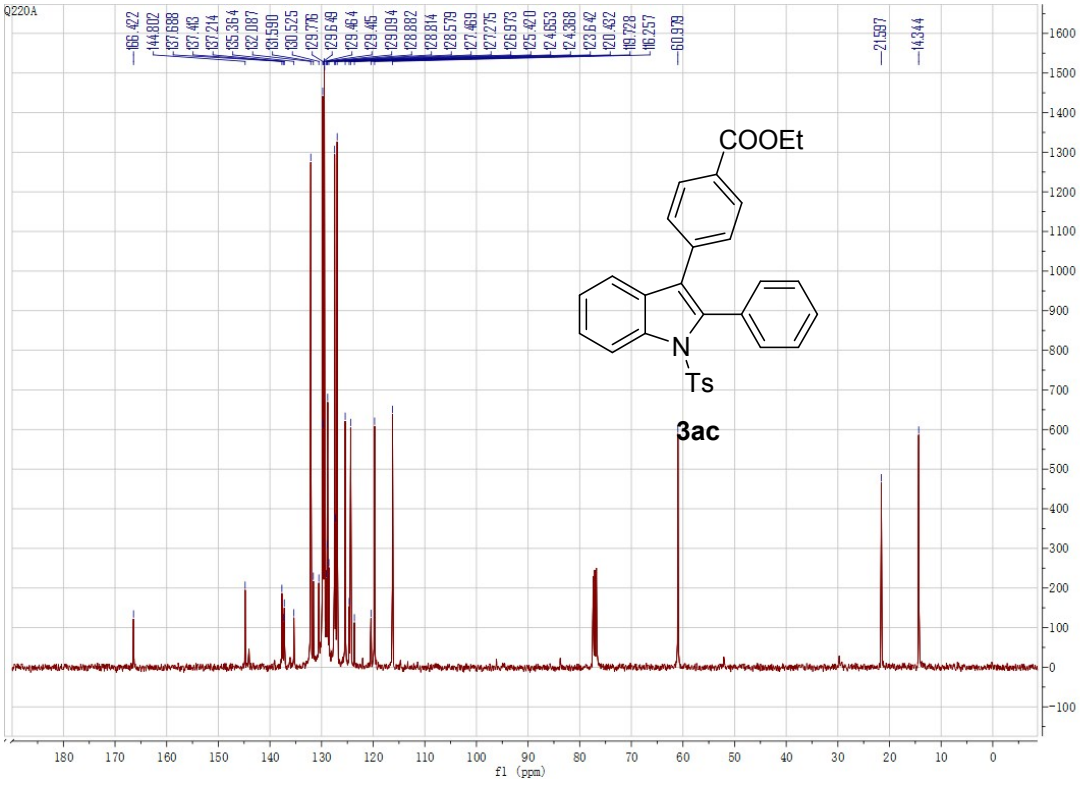

Q217A
Ph
N
Ts
3aa
f1 (ppm)

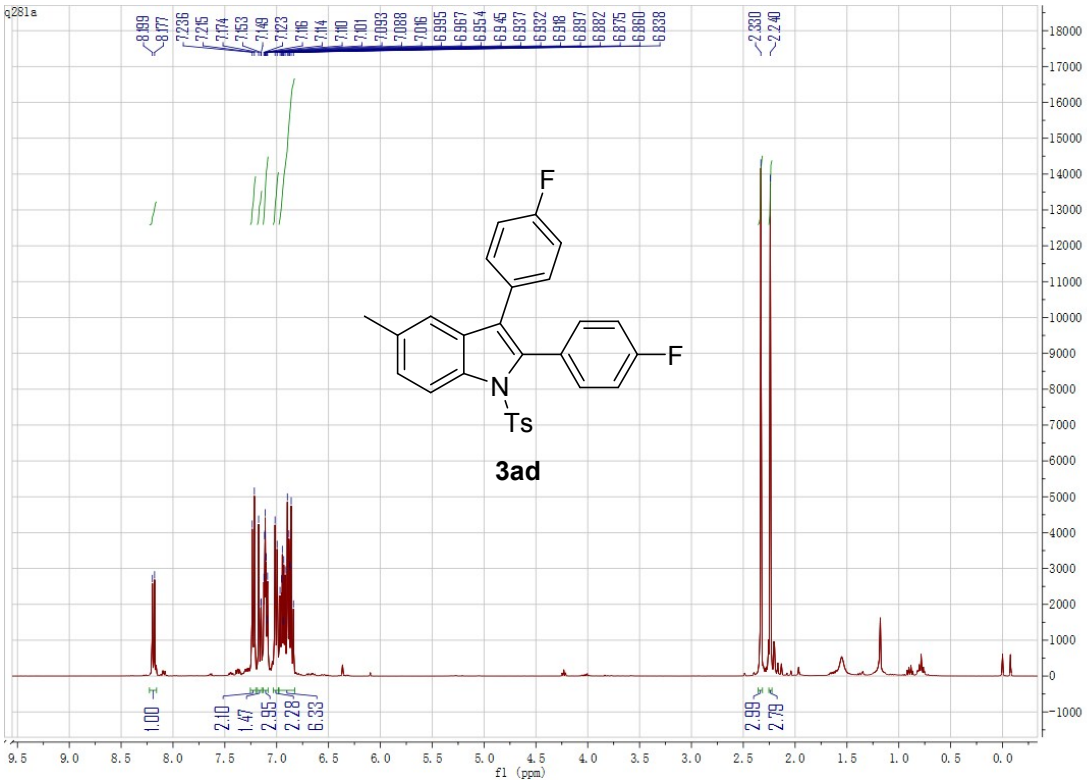

F
N
Ts
3ab
1.00
11.54
4.28
2.02
3.29
f1 (ppm)


May12-2016QCHB5
-114.799
F
N
Ts
3ab
f1 (ppm)

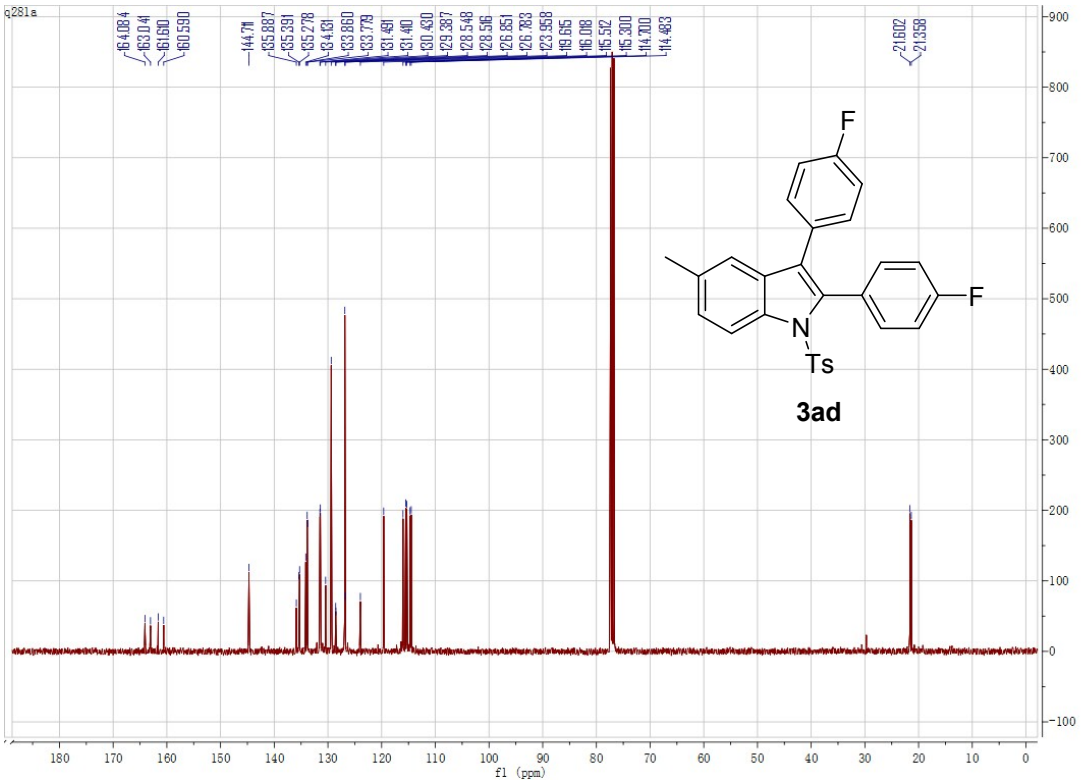

May12-2016QCHB5
163.020
160.569
144.712
144.685
137.170
136.949
135.378
132.083
131.523
131.442
130.770
130.291
129.384
128.639
127.441
126.969
125.317
124.274
123.733
119.774
116.249
115.405
115.193
21.598
F
N
Ts
3ab
f1 (ppm)


COOEt
N
Ts
3ac


COOEt
N
Ts
3ac


F
F
N
Ts
3ad


F
F
N
Ts
3ad


q281a
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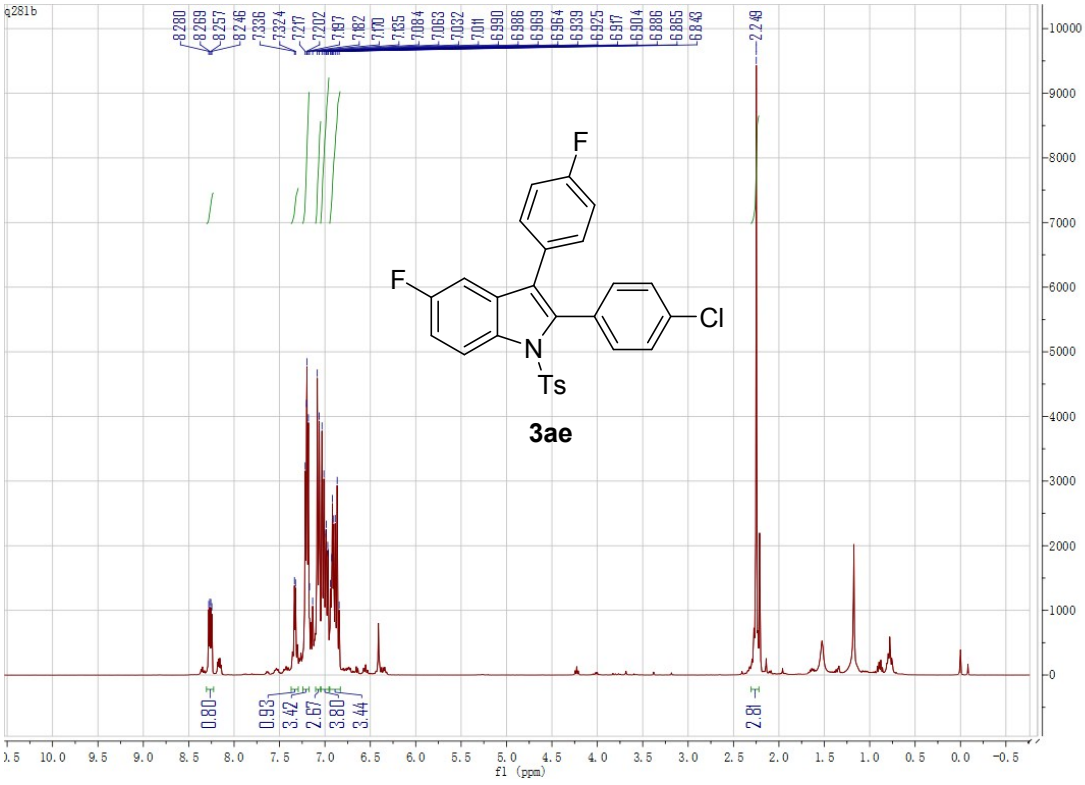
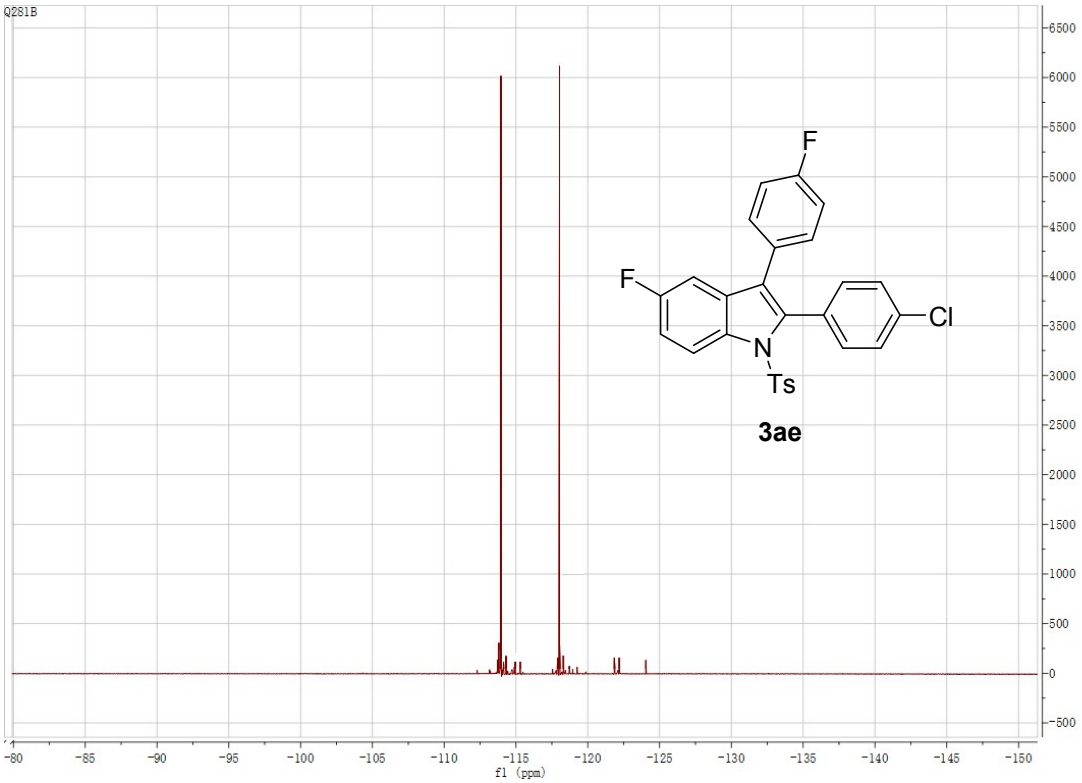
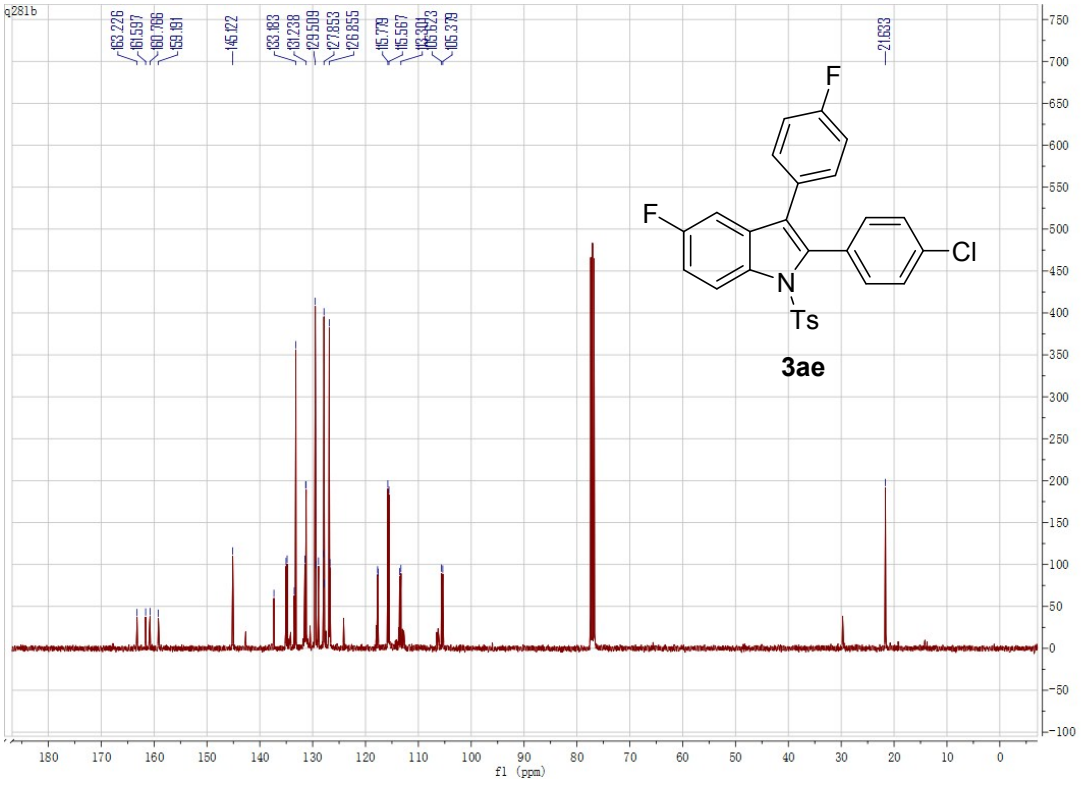
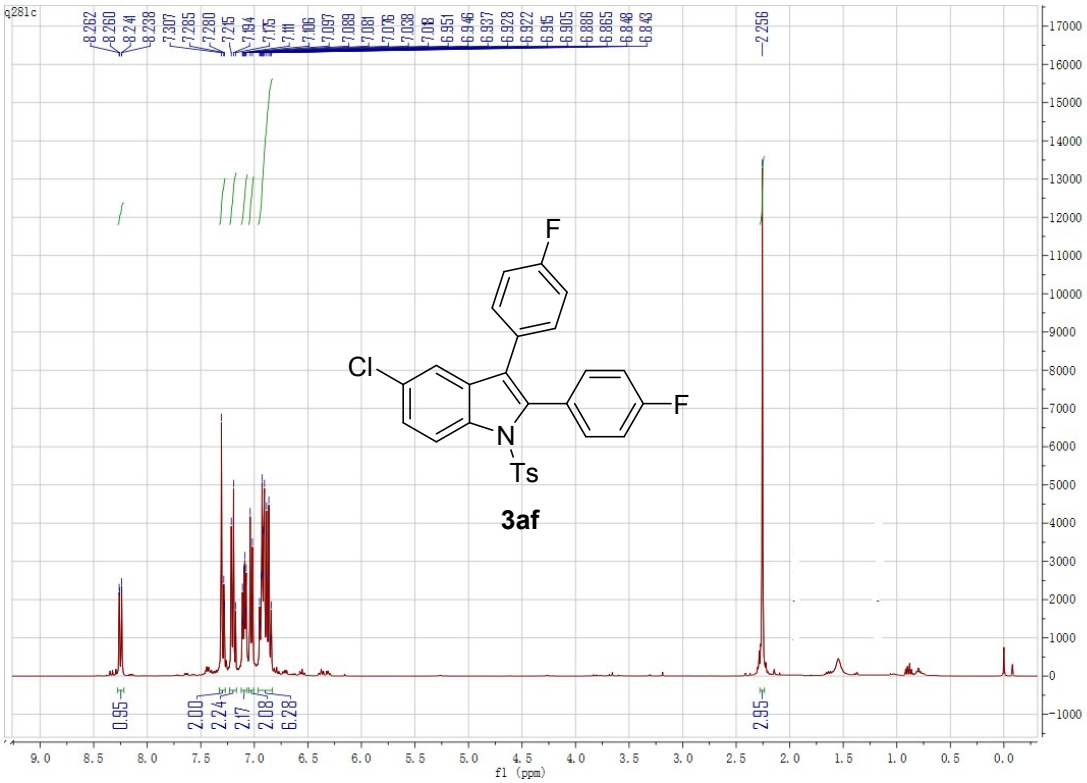
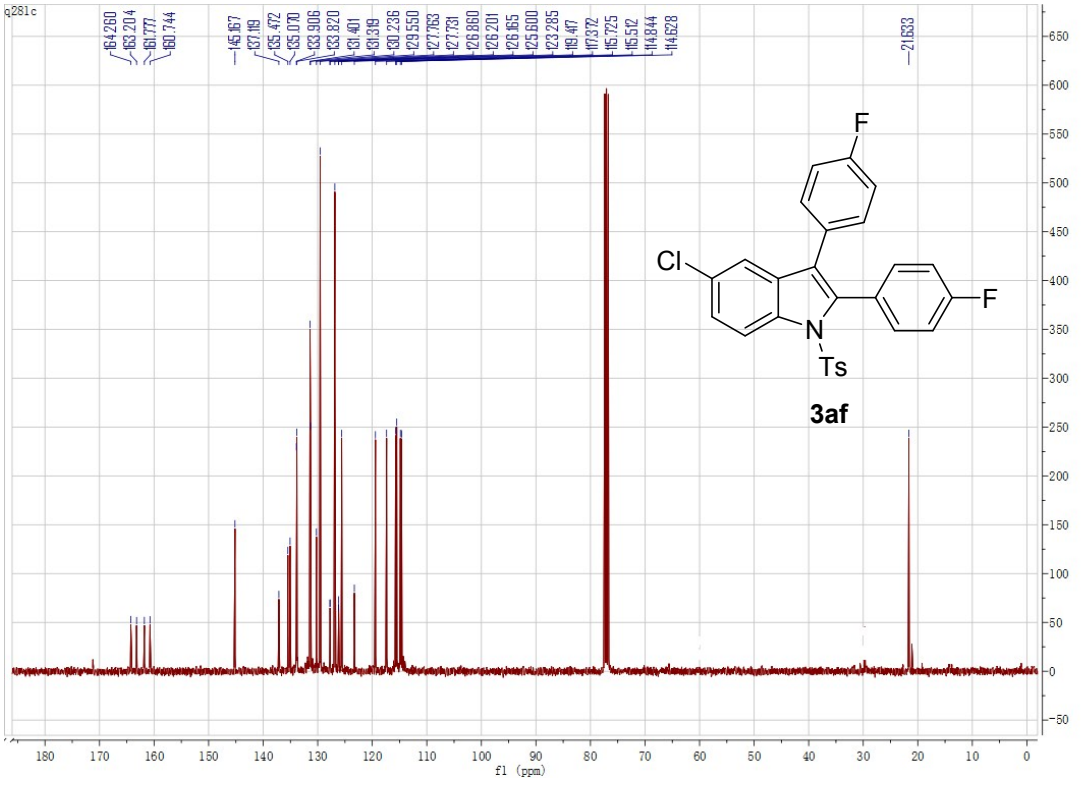
F
N
Ts
3ad
f1 (ppm)

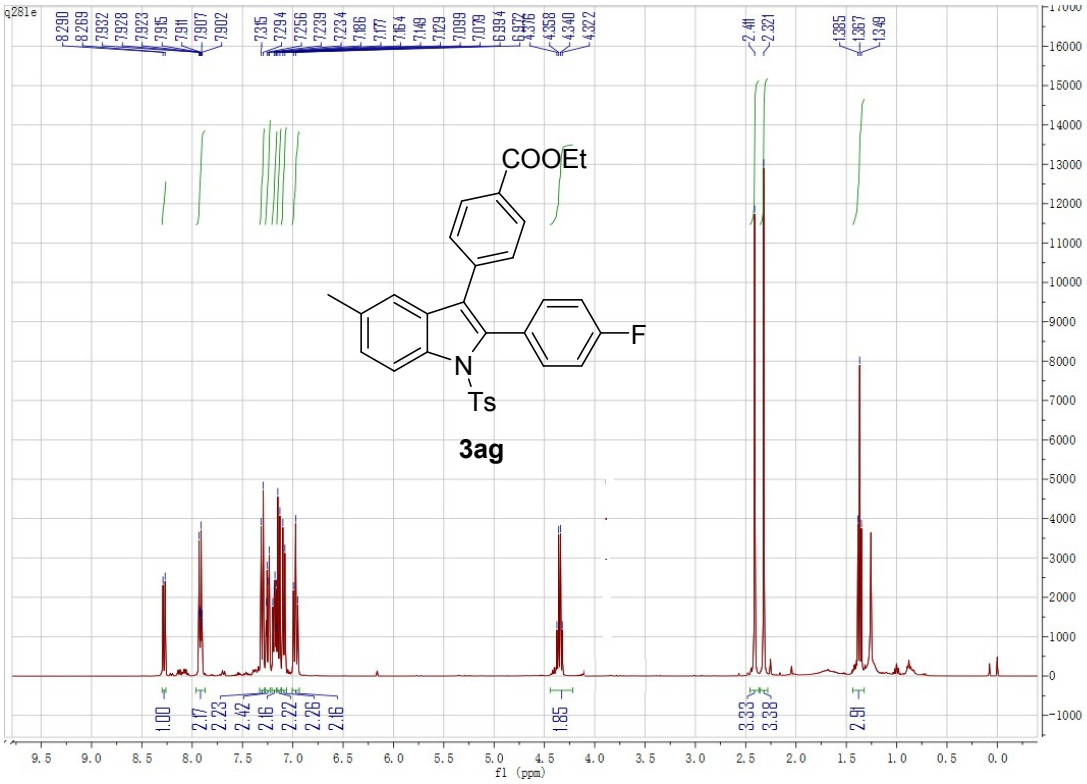

q281b
F
F
Cl
N
Ts
3ae
f1 (ppm)

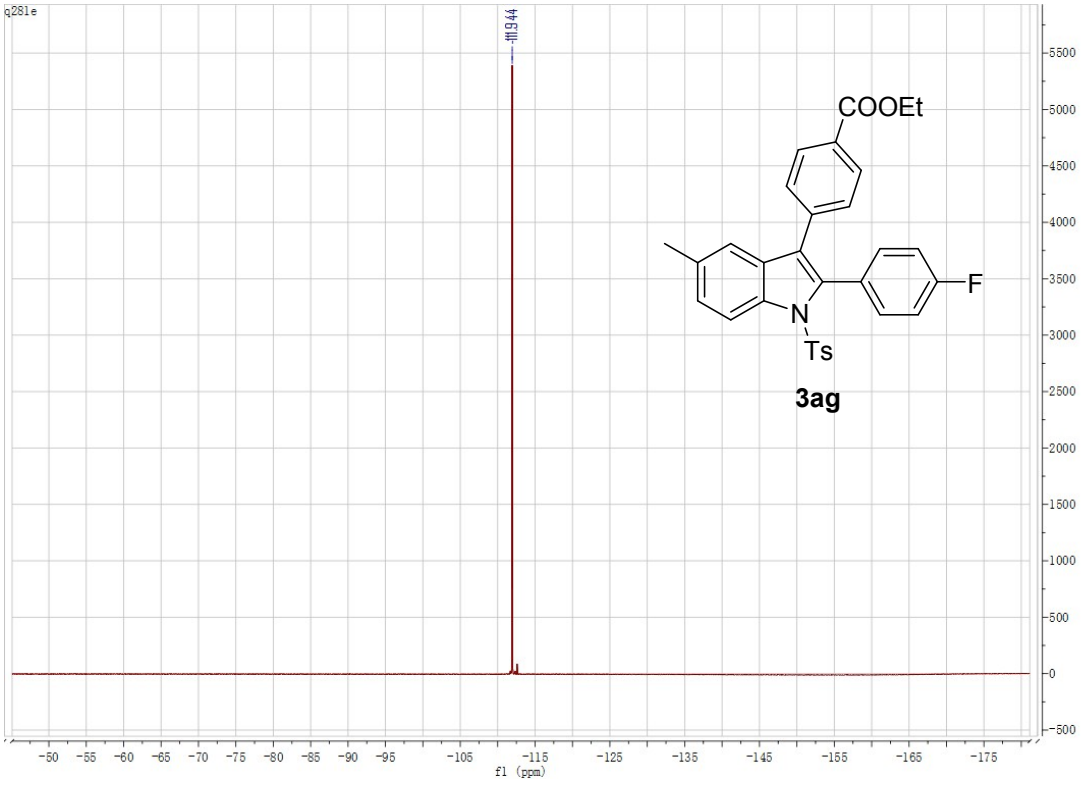

Q281B
F
F
Cl
N
Ts
3ae
f1 (ppm)

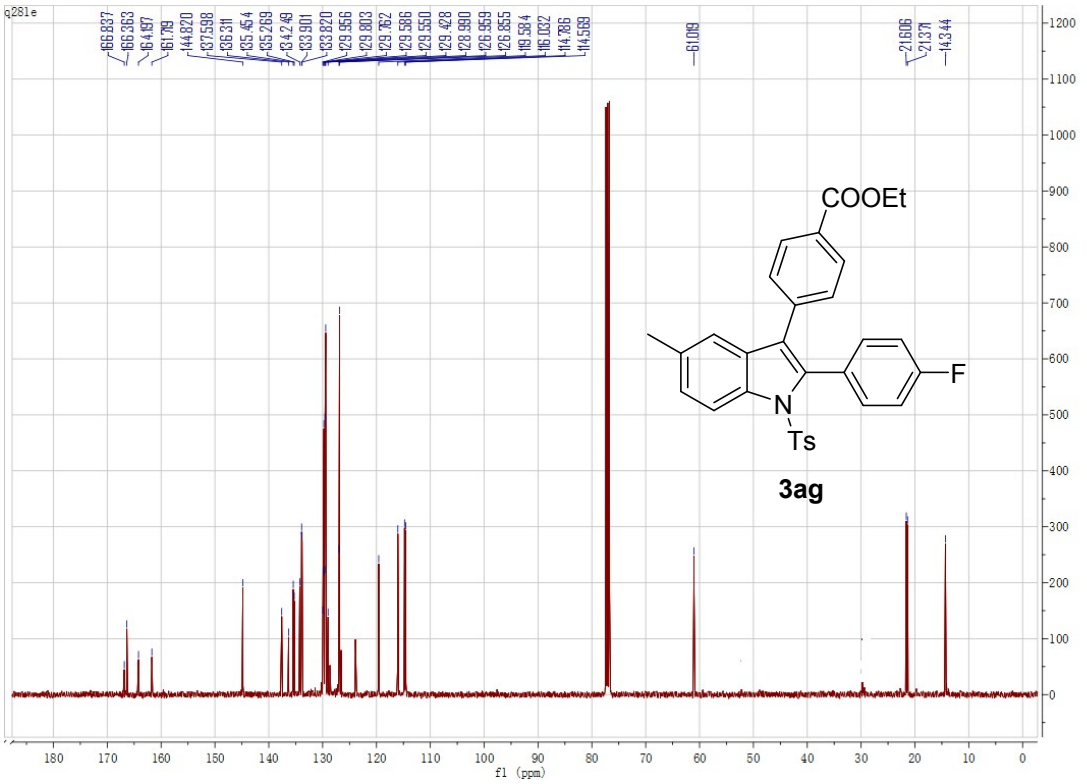

q281b
163.226
161.597
160.706
159.191
145.122
133.183
131.238
129.509
127.853
126.855
115.779
115.567
112.304
105.379
21.633
F
F
Cl
N
Ts
3ae
f1 (ppm)

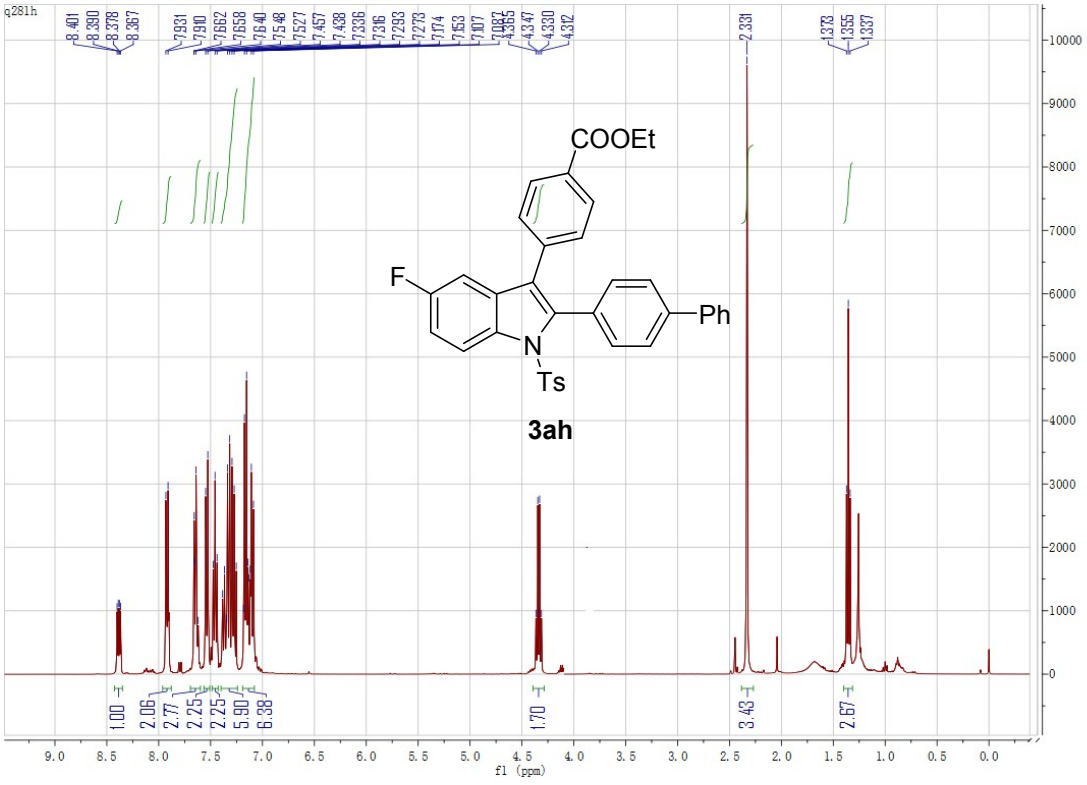

F
Cl
F
N
Ts
3af

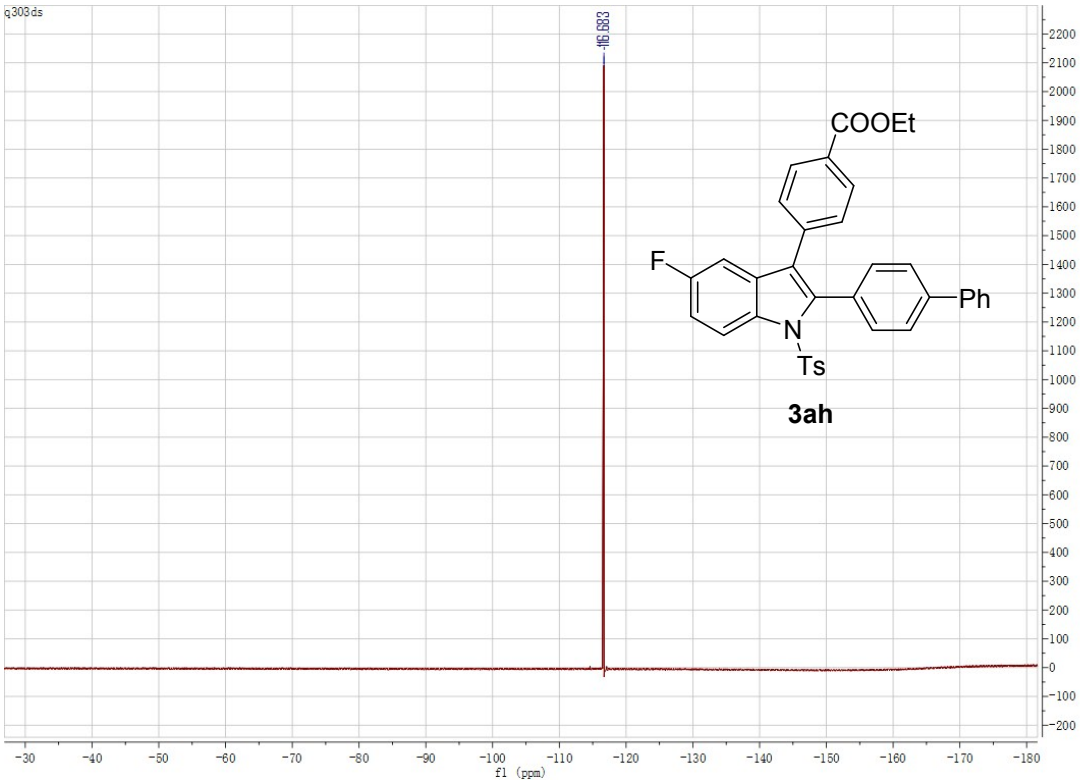

F
Cl
F
N
Ts
3af

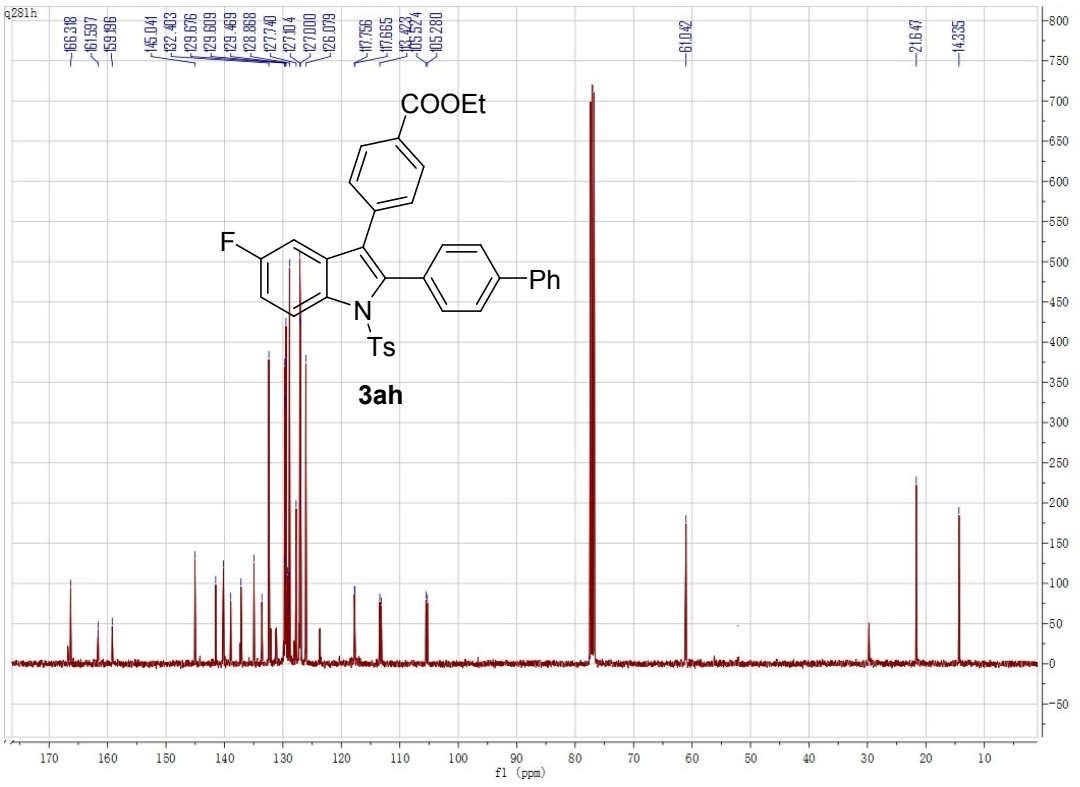

COOEt
F
N
Ts
3ag
f1 (ppm)


COOEt
F
N
Ts
3ag
f1 (ppm)


COOEt
F
N
Ts
3ag
f1 (ppm)


COOEt
F
Ph
N
Ts
3ah
f1 (ppm)


q303ds
-116.6983
COOEt
F
Ph
N
Ts
3ah
f1 (ppm)


q281h
166.318
161.597
159.196
145.041
132.403
129.676
129.609
129.469
128.868
127.740
127.104
127.000
126.079
117.756
117.665
113.423
105.524
105.280
61.042
21.647
14.335
COOEt
F
Ph
N
Ts
3ah
f1 (ppm)