Supporting Information

Rhodium(III)-Catalyzed Oxidative Bicyclization of 4-Arylbut-3-yn-1-amines with Internal Alkynes Through C-H Functionalization

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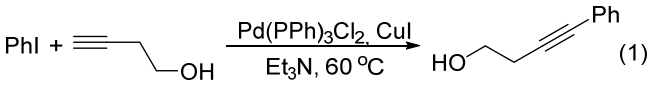
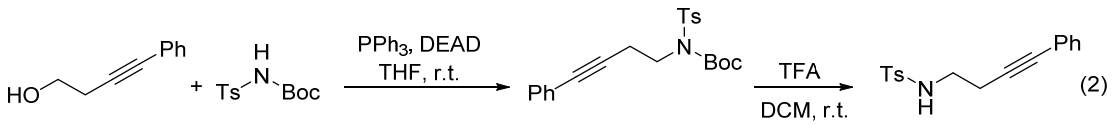
(A) Typical experimental procedure

(a) Typical Experimental Procedure for the synthesis of 1a:[1,2]



(1)

Bis(triphenylphosphine)palladiu (II) dichloride (2 mol%), copper (I) iodide (1 mol%), aryl halide (1.0 mmol) and 3-butyn-1-ol (1.2 mmol) were dissolved in dry triethylamide (6 mL) and subsequently heated to reflux. After 2.5 h, the reaction mixture was quenched with an ethyl acetate/water mixture (1/1, 25 mL) and the aqueous and organic phases were separated. The organic layer was washed with water and then brine, dried over anhydrous sodium sulfate, filtered, concentrated in vacuo, and purified by flash column chromatography on silica gel to afford a as clear, orange oils.



(2)

N-Boc *p*-toluenesulfonamide (1.5 mmol) was dissolved in dry THF (3 mL) and triphenylphosphine (3.0 equiv) was added. The solution was stirred under nitrogen atmosphere and the 4-phenylbut-3-yn-1-ol (1.0 equiv) was added followed by diethylazodicarboxylate (2.5 equiv). The mixture was stirred at room temperature for 3 h, concentrated under reduced pressure and the product was purified by flash chromatography to give *tert*-butyl (4-phenylbut-3-yn-1-yl)(tosyl)carbamate.

To a solution of the *tert*-butyl (4-phenylbut-3-yn-1-yl)(tosyl)carbamate (1.0 mmol) in CH_2Cl_2 (5 mL) was then added trifluoroacetic acid (20 equiv) at 0 °C, and the mixture was stirred at room temperature for 3 h. The mixture was diluted with EtOAc,

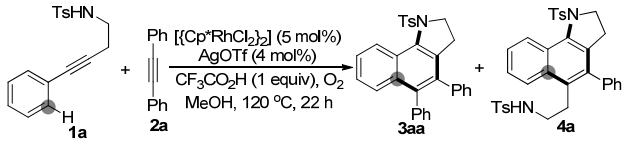
and the organic layer was washed with saturated $NaHCO_3$ solution and saturated NaCl solution, dried and concentrated to afford the products **1a** as white solid.

(b) Typical Experimental Procedure for Rh(III)-Catalyzed Bicyclization of 4-Arylbut-3-yn-1-amines (1) with Internal Alkynes (2):

To a Schlenk tube was added 4-Arylbut-3-yn-1-amines **1** (0.2 mmol), alkynes **2** (1.5 equiv), [{Cp*$RhCl_2$}$_2$] (5 mol%), AgOTf (4 mol%), TFA(1 equiv) and CH_3OH (2 mL). Then the tube was charged with O_2 (1 atm), and was stirred at 120 ^oC (oil bath temperature) for the indicated time (about 22 h) until complete consumption of starting material as monitored by TLC. After the reaction was finished, the reaction mixture was cooled to room temperature, and the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate) to afford the desired products **3** and/or **4**.

(c) Table S1. Screening of the optimal reaction conditions

Table S1. Screening of the optimal reaction conditions[a]



1a 2a 3aa 4a

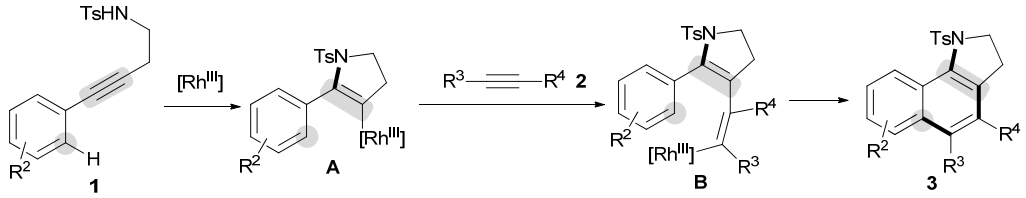
Entry	Variation from the Standard Conditions	Isolated yield [%]	
		3aa	**4aa**
1[b]	none	66	8
2	at 130 °C	65	10
3	at 100 °C	28	trace
4[c]	[{Cp*$RhCl_2$}$_2$] (10 mol%)	21	15
5	without [{Cp*$RhCl_2$}$_2$]	0	0
6	without AgOTf	0	0
7	$AgSbF_6$ instead of AgOTf	35	5
8	AgOAc instead of AgOTf	19	trace
9	$AgCO_2CF_3$ instead of AgOTf	18	trace
10	$Cu(OTf)_2$ instead of AgOTf	40	10
11	$Sc(OTf)_3$ instead of AgOTf	trace	trace
12	without CF_3CO_2H	46	9

13	TfOH instead of CF_3CO_2H	10	trace
14	AcOH instead of CF_3CO_2H	15	trace
15	PivOH instead of CF_3CO_2H	20	trace
16	*tert*-amyl alcohol instead of MeOH	27	5
17	toluene instead of MeOH	16	trace
18	N_2 (1 atm) instead of O_2	27	trace
19	$Cu(OAc)_2$ (1 equiv) instead of O_2	21	trace

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (1.5 equiv), [{Cp*$RhCl_2$}$_2$] (5 mol%), AgOTf (5 mol%), CF_3CO_2H (1 equiv), O_2 (1 atm), MeOH (anhydrous, 2 mL), 120 °C, 22 h. [b] Other side-products, including 4-methyl-*N*-(4-oxo-4-phenylbutyl)benzenesulfonamide (**5a**; 15%), were observed. [c] Side-product **5a** in 36% yield.

(d) Scheme S1. Another Possible Mechanism

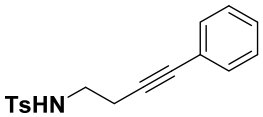
We can not rule out the other possible mechanism initiated by the first nucleophilic cyclization.



Scheme S1

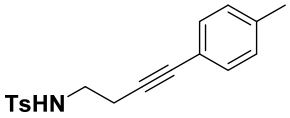
(B) Analytical data

4-Methyl-*N*-(4-phenylbut-3-yn-1-yl)benzenesulfonamide (1a):



White solid, mp 101.1-103.2 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (d, *J* = 4.0 Hz, 2H), 7.23-7.21 (m, 2H), 7.14 (d, *J* = 4.0 Hz, 5H), 5.35 (t, *J* = 8.0 Hz, 1H), 3.08-3.03 (m, 2H), 2.45 (t, *J* = 8.0 Hz, 2H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.3, 136.7, 131.4, 129.5, 128.0, 127.8, 126.8, 122.8, 85.7, 82.3, 41.8, 21.3, 20.5.

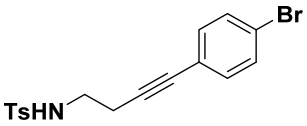
4-Methyl-*N*-(4-(*p*-tolyl)but-3-yn-1-yl)benzenesulfonamide (1b):



White solid, mp 97.8-100.3 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77 (d, *J* = 4.0 Hz, 2H), 7.29 (d, *J* = 4.0 Hz, 2H), 7.23 (d, *J* = 4.0 Hz, 2H), 7.08 (d, *J* = 4.0 Hz, 2H), 4.99 (t, *J* = 8.0 Hz, 1H),

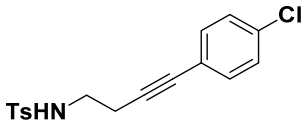
3.19-3.15 (m, 2H), 2.55 (t, *J* = 4.0 Hz, 2H), 2.41 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.5, 138.2, 136.9, 131.5, 129.8, 129.0, 127.1, 119.8, 84.8, 82.9, 41.9, 21.5, 21.4, 20.7.

***N*-(4-(4-Bromophenyl)but-3-yn-1-yl)-4-methylbenzenesulfonamide (1c):**



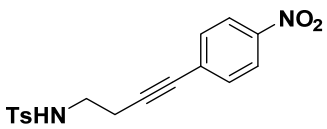
White solid, mp 108.4-110.6 ºC (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77 (d, *J* = 4.0 Hz, 2H), 7.37 (d, *J* = 4.0 Hz, 2H), 7.27 (d, *J* = 4.0 Hz, 2H), 7.18 (d, *J* = 4.0 Hz, 2H), 5.33 (t, *J* = 8.0 Hz, 1H), 3.19-3.14 (m, 2H), 2.55 (t, *J* = 8.0 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.5, 136.8, 133.0, 131.3, 129.7, 126.9, 122.1, 121.9, 86.9, 81.5, 41.7, 21.4, 20.7.

***N*-(4-(4-Chlorophenyl)but-3-yn-1-yl)-4-methylbenzenesulfonamide (1d):**



White solid, mp 101.6-103.4 ºC (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77 (d, *J* = 4.0 Hz, 2H), 7.28 (d, *J* = 4.0 Hz, 3H), 7.25 (d, *J* = 4.0 Hz, 3H), 5.19 (t, *J* = 8.0 Hz, 1H), 3.19-3.15 (m, 2H), 2.56 (t, *J* = 8.0 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.6, 136.9, 134.1, 132.9, 129.8, 128.6, 127.1, 121.5, 86.8, 81.6, 41.8, 21.5, 20.8.

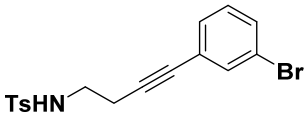
4-Methyl-*N*-(4-(4-nitrophenyl)but-3-yn-1-yl)benzenesulfonamide (1e):



Yellow solid, mp 104.5-107.1 ºC (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.12 (d, *J* = 4.0 Hz, 2H), 7.78 (d, *J* = 4.0 Hz, 2H), 7.48 (d, *J* = 4.0 Hz, 2H), 7.30 (d, *J* = 4.0 Hz, 2H), 5.24 (t, *J* = 4.0 Hz, 1H), 3.24-3.19 (m, 2H), 2.64 (t, *J* = 4.0 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.9, 143.7, 136.9, 132.4, 130.0, 129.8, 127.1, 123.5, 91.7, 81.1,

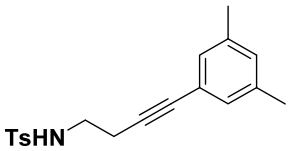
41.6, 21.5, 21.1.

***N*-(4-(3-Bromophenyl)but-3-yn-1-yl)-4-methylbenzenesulfonamide (1f):**



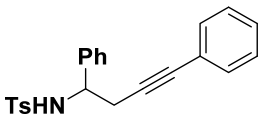
White solid, mp 106.4-109.2 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77 (d, *J* = 4.0 Hz, 2H), 7.46 (s, 1H), 7.41 (d, *J* = 4.0 Hz, 1H), 7.27 (t, *J* = 8.0 Hz, 3H), 7.13 (t, *J* = 8.0 Hz, 1H), 5.17 (t, *J* = 8.0 Hz, 1H), 3.20-3.15 (m, 2H), 2.57 (t, *J* = 8.0 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.5, 136.8, 134.3, 131.2, 130.1, 129.7, 129.6, 126.9, 124.9, 121.9, 87.2, 81.1, 41.7, 21.5, 20.7.

***N*-(4-(3,5-Dimethylphenyl)but-3-yn-1-yl)-4-methylbenzenesulfonamide (1g):**



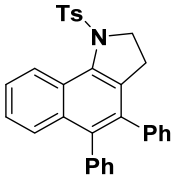
White solid, mp 97.8-99.2 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69 (d, *J* = 4.0 Hz, 2H), 7.18 (d, *J* = 4.0 Hz, 2H), 6.89 (s, 2H), 6.83 (s, 1H), 5.08 (t, *J* = 8.0 Hz, 1H), 3.09-3.05 (m, 2H), 2.45 (t, *J* = 8.0 Hz, 2H), 2.31 (s, 3H), 2.17 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.4, 137.7, 136.8, 129.9, 129.6, 129.2, 126.9, 122.4, 84.7, 82.9, 41.9, 21.4, 20.9, 20.6.

***N*-(1,4-diphenylbut-3-yn-1-yl)-4-methylbenzenesulfonamide (1h):**



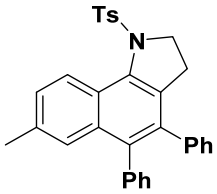
White solid, mp 89.3-92.2 °C (uncorrected);^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62 (d, *J* = 4.0 Hz, 2H), 7.25 (s, 5H), 7.20 (s, 5H), 7.08 (d, *J* = 4.0 Hz, 2H), 5.58 (d, *J* = 4.0 Hz, 1H), 4.58-4.53 (m, 1H), 2.81 (d, *J* = 4.0 Hz, 2H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.1, 139.5, 137.1, 131.5, 129.4, 128.3, 128.1, 128.0, 127.7, 127.0, 126.5, 122.8, 84.6, 83.8, 56.2, 28.4, 21.3.

4,5-Diphenyl-1-tosyl-2,3-dihydro-1*H*-benzo[*g*]indole (3aa):



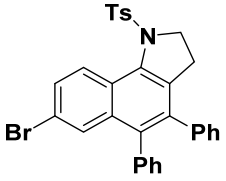
White solid, mp 213.1-215.2 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.65 (d, *J* = 8.4 Hz, 1H), 7.60-7.56 (m, 2H), 7.42-7.38 (m, 1H), 7.35-7.33 (m, 2H), 7.25-7.18 (m, 5H), 7.11-7.10 (m, 2H), 7.08-7.06 (m, 3H), 6.72-6.70 (m, 2H), 4.11 (t, *J* = 7.6 Hz, 2H), 2.44 (s, 3H), 2.00 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ:144.2, 139.2, 138.6, 138.0, 137.9, 135.6, 134.1, 133.7, 133.1, 131.3, 129.3, 129.2, 128.0, 127.6, 127.5, 126.8, 126.7, 126.6, 126.5, 126.1, 125.9, 125.8, 53.1, 29.8, 21.5; HRMS *m/z* (ESI) calcd for $C_{31}H_{26}NO_2S$ $[M+H]^+$ 476.1679, found 476.1687.

7-Methyl-4,5-diphenyl-1-tosyl-2,3-dihydro-1*H*-benzo[*g*]indole (3ba):



White solid, mp 145.8-147.3 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.47 (d, *J* = 4.4 Hz, 1H), 7.36 (d, *J* = 4.4 Hz, 1H), 7.25 (d, *J* = 4.0 Hz, 3H), 7.19-7.7.10 (m, 5H), 7.00 (d, *J* = 1.2 Hz, 2H), 6.99-6.98 (m, 3H), 6.63-6.60 (m, 2H), 4.02 (t, *J* = 7.2 Hz, 2H), 2.36 (s, 3H), 2.33 (s, 3H), 1.89 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.9, 139.2, 138.6, 137.8, 137.2, 135.7, 135.5, 133.5, 133.2, 132.9, 131.2, 129.2, 129.0, 127.9, 127.8, 127.5, 127.4, 126.5, 126.2, 125.6, 125.5, 124.8, 52.9, 29.5, 21.8, 21.4; HRMS *m/z* (ESI) calcd for $C_{32}H_{28}NO_2S$ $[M+H]^+$ 490.1835, found 490.1843.

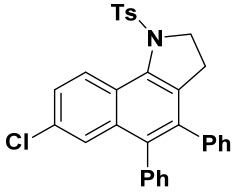
7-Bromo-4,5-diphenyl-1-tosyl-2,3-dihydro-1*H*-benzo[*g*]indole (3ca):



White solid, mp 222.6-225.3 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.45 (d, *J* = 4.4 Hz, 1H), 7.66 (d, *J* = 0.8 Hz, 1H), 7.59-7.57 (m, 1H), 7.24 (s, 1H), 7.19-7.17 (m, 3H), 7.14-7.10 (m, 3H), 7.01-6.99 (m, 5H), 6.62-6.59 (m, 2H), 4.03 (t, *J* = 7.2 Hz, 2H), 2.37 (s, 3H), 1.91

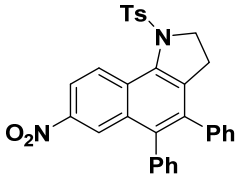
(t, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.45, 138.8, 138.2, 137.8, 137.3, 136.9, 134.7, 134.4, 133.5, 131.2, 130.0, 129.8, 129.3, 129.2, 128.9, 128.0, 127.9, 127.7, 127.1, 126.7, 125.2, 120.8, 53.1, 29.8, 21.6; HRMS *m/z* (ESI) calcd for $C_{31}H_{25}{}^{79}BrNO_2S$ $[M+H]^+$ 554.0784, found 554.0792.

7-Chloro-4,5-diphenyl-1-tosyl-2,3-dihydro-1*H*-benzo[*g*]indole (3da):



White solid, mp 213.8-215.3 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.52 (d, *J* = 4.4 Hz, 1H), 7.48 (d, *J* = 0.8 Hz, 1H), 7.45-7.42 (m, 1H), 7.25 (d, *J* = 4.0 Hz, 2H), 7.19-7.12 (m, 5H), 7.01-6.99 (m, 5H), 6.62-6.59 (m, 2H), 4.02 (t, *J* = 7.2 Hz, 2H), 2.37 (s, 3H), 1.92(t, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.4, 138.8, 138.1, 137.9, 137.4, 136.9, 134.6, 133.9, 133.5, 132.3, 131.2, 129.3, 129.2, 128.0, 127.9, 127.8, 127.7, 127.1, 126.8, 126.7, 125.6, 124.9, 53.2, 29.8, 21.6; HRMS *m/z* (ESI) calcd for $C_{31}H_{25}{}^{35}ClNO_2S$ $[M+H]^+$ 510.1289, found 510.1296.

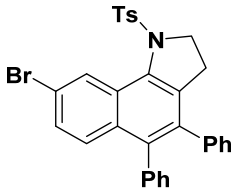
7-Nitro-4,5-diphenyl-1-tosyl-2,3-dihydro-1*H*-benzo[*g*]indole (3ea):



Yellow solid, mp 216.2-218.6 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.69 (d, *J* = 4.8 Hz, 1H), 8.49 (d, *J* = 1.2 Hz, 1H), 8.25-8.22 (m, 1H), 7.27 (s, 1H), 7.22 (d, *J* = 2.0 Hz, 3H), 7.19-7.15(m, 3H), 7.04-7.02 (m, 5H), 6.64-6.62 (m, 2H), 4.06 (t, *J* = 7.2 Hz, 2H), 2.39 (s, 3H), 2.01 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.7, 144.7, 140.3, 138.7, 138.4, 138.1, 137.9, 136.9, 133.4, 132.2, 131.1, 129.5, 129.1, 128.9, 128.1,

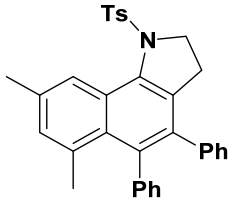
128.0, 127.9, 127.7, 127.6, 127.1, 123.8, 119.2, 53.1, 30.2, 21.6; HRMS *m/z* (ESI) calcd for $C_{31}H_{25}N_2O_4S$ $[M+H]^+$ 521.1529, found 521.1537.

6-Bromo-4,5-diphenyl-1-tosyl-2,3-dihydro-1*H*-benzo[*g*]indole (3fa):



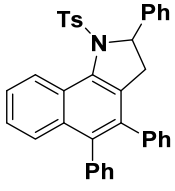
White solid, mp 226.8-229.3 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.79 (s, 1H), 7.44 (s, 2H), 7.35 (d, *J* = 4.0 Hz, 2H), 7.25-7.7.20 (m, 5H), 7.08-7.07 (m, 5H), 6.70-6.68 (m, 2H), 4.08 (t, *J* = 7.2 Hz, 2H), 2.45 (s, 3H), 2.00 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.7, 139.0, 138.5, 138.3, 137.5, 136.4, 135.8, 133.8, 131.9, 131.4, 129.8, 129.6, 129.5, 128.9, 128.4, 128.3, 128.1, 128.0, 127.9, 127.3, 126.9, 120.8, 53.4, 30.2, 21.9; HRMS *m/z* (ESI) calcd for $C_{31}H_{25}{}^{79}BrNO_2S$ $[M+H]^+$ 554.0784, found 554.0780.

6,8-Dimethyl-4,5-diphenyl-1-tosyl-2,3-dihydro-1*H*-benzo[*g*]indole (3ga):



White solid, mp 192.3-194.7 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.26 (s, 1H), 7.24 (d, *J* = 4.0 Hz, 2H), 7.10 (d, *J* = 3.2 Hz, 2H), 7.05-7.03 (m, 4H), 6.96-6.93 (m, 5H), 6.55-6.53 (m, 2H), 3.99 (t, *J* = 7.2 Hz, 2H), 2.45 (s, 3H), 2.34 (s, 3H), 1.79 (s, 3H), 1.77 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.1, 142.0, 139.7, 138.1, 137.9, 136.2, 135.3, 135.1, 133.7, 133.5, 133.1, 131.3, 130.2, 129.4, 129.2, 128.4, 128.1, 127.3, 126.9, 126.4, 126.1, 123.9, 53.1, 29.9, 25.2, 21.6, 21.5; HRMS *m/z* (ESI) calcd for $C_{33}H_{30}NO_2S$ $[M+H]^+$ 504.1992, found 504.1999.

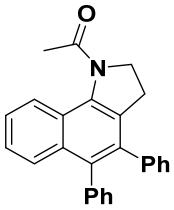
2,4,5-Triphenyl-1-tosyl-2,3-dihydro-1*H*-benzo[*g*]indole (3ha):



White solid, mp 198.4-200.2 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.76 (d, *J* = 4.0 Hz, 1H), 7.60 (d, *J* = 4.8 Hz, 2H), 7.41 (d, *J*

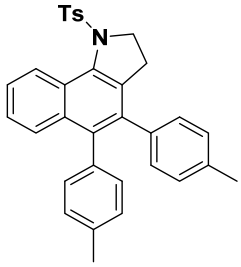
= 4.0 Hz, 1H), 7.38 (d, *J* = 4.0 Hz, 2H), 7.32 (d, *J* = 4.0 Hz, 2H), 7.24-7.16 (m, 9H), 7.05-7.00 (m, 4H), 6.67 (s, 2H), 5.50 (d, *J* = 4.0 Hz, 1H), 2.53-2.47 (m, 1H), 2.45 (s, 3H), 2.35 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.3, 141.5, 139.0, 138.5, 138.3, 137.2, 135.7, 133.7, 133.3, 132.5, 131.4, 131.2, 129.3, 128.6, 128.0, 127.8, 127.7, 127.5, 127.4, 126.9, 126.7, 126.5, 126.2, 125.9, 125.8, 66.1, 37.7, 21.6; HRMS *m/z* (ESI) calcd for $C_{37}H_{30}NO_2S$ $[M+H]^+$ 504.1992, found 504.1997.

1-(4,5-Diphenyl-2,3-dihydro-1*H*-benzo[*g*]indol-1-yl)ethan-1-one (3ia):



Brown solid, mp 205.4-209.2 °C (uncorrected); ^{1}H NMR (400 MHz, CD_3COCD_3) δ: 7.81 (d, *J* = 4.0 Hz, 1H), 7.34-7.27 (m, 2H), 7.19 (t, *J* = 8.0 Hz, 1H), 7.14-7.02 (m, 10H), 4.17 (t, *J* = 8.0 Hz, 2H), 2.82 (t, *J* = 8.0 Hz, 2H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ: 169.2, 139.6, 139.3, 138.7, 136.1, 136.0, 132.8, 131.4, 131.1, 129.8, 127.6, 127.5, 126.6, 126.5, 126.4, 126.3, 125.1, 124.3, 124.2, 51.6, 30.3, 23.4; HRMS *m/z* (ESI) calcd for $C_{26}H_{22}NO$ $[M+H]^+$ 364.1696, found 364.1691.

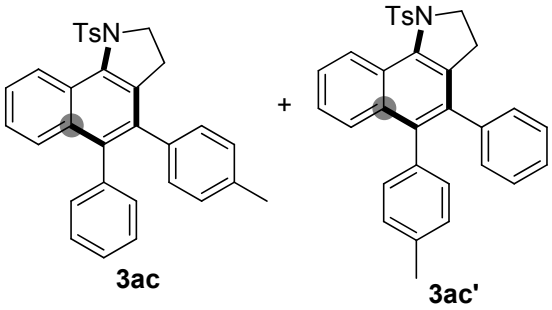
4,5-Di-*p*-tolyl-1-tosyl-2,3-dihydro-1*H*-benzo[*g*]indole (3ab):



White solid, mp 143.1-145.3 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.56 (d, *J* = 8.4 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 2H), 7.33-7.30 (m, 1H), 7.26-7.24 (m, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 7.6 Hz, 2H), 6.81 (d, *J* = 8.0 Hz, 2H), 6.52 (d, *J* = 8.0 Hz, 2H), 4.01 (t, *J* = 7.6 Hz, 2H), 2.37 (s, 3H), 2.26 (s, 3H), 2.15 (s, 3H), 1.90 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.1, 138.1, 137.8, 136.3, 136.2, 135.9, 135.6, 134.4, 133.7, 133.4, 131.1, 129.2, 128.4, 128.3,

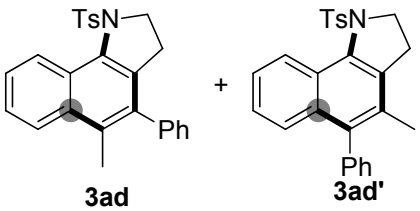
128.1, 126.9, 126.6, 126.0, 125.8, 125.7, 53.1, 29.2, 21.6, 21.3, 21.1; HRMS *m/z* (ESI) calcd for $C_{33}H_{30}NO_2S$ $[M+H]^+$ 504.1992, found 504.1999.

5-Phenyl-4-(*p*-tolyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*g*]indole (3ac) and 4-Phenyl-5-(*p*-tolyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*g*]indole (3ac'):



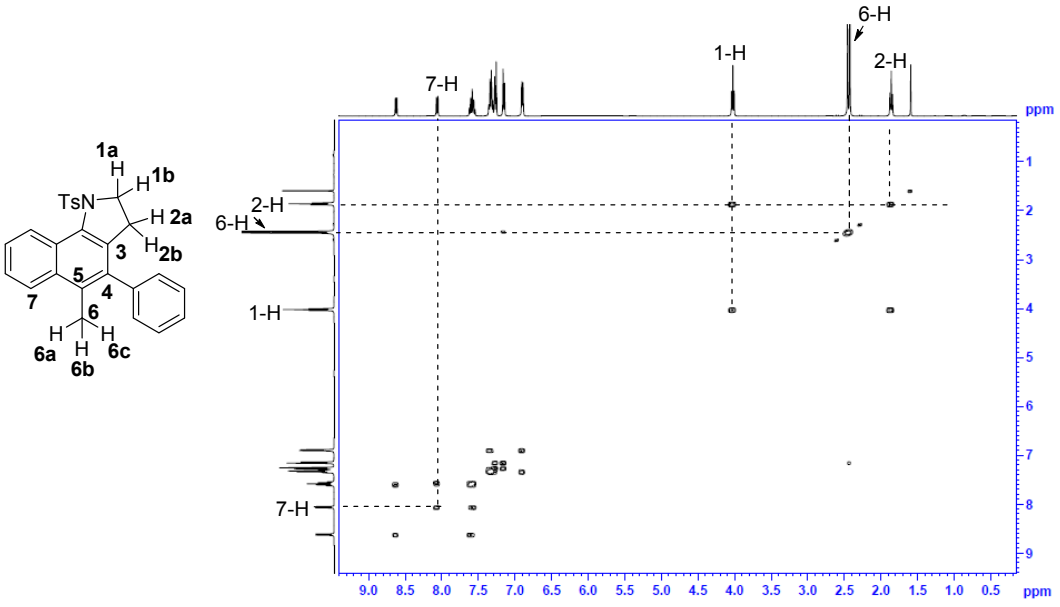
3ac:3ac'=1.5:1, White solid, mp 216.0-218.4 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.64 (d, *J* = 4.0 Hz, 1H), 7.57 (t, *J* = 8.0 Hz, 2H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 4.0 Hz, 2H), 7.24 (d, *J* = 4.0 Hz, 1H), 7.18 (d, *J* = 4.0 Hz, 2H), 7.11-7.04 (m, 4H), 6.98 (d, *J* = 4.0 Hz, 1H), 6.87 (d, *J* = 4.0 Hz, 1H), 6.72-6.69 (m, 1H), 6.58 (d, *J* = 4.0 Hz, 1H), 4.09 (t, *J* = 8.0 Hz, 2H), 2.44 (s, 3H), 2.31 (s, 1.8H), 2.20 (s, 1.2H), 2.00-1.96 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.1, 139.3, 138.7, 138.0, 137.7, 136.2, 136.0, 135.9, 135.6, 135.4, 134.3, 134.1, 133.6, 133.2, 133.1, 131.2, 131.0, 129.3, 129.2, 128.3, 128.2, 128.0, 127.6, 127.5, 126.8, 126.7, 126.6, 126.4, 125.9, 125.8, 125.7, 53.1, 29.8, 21.5, 21.2, 21.0; HRMS *m/z* (ESI) calcd for $C_{32}H_{28}NO_2S$ $[M+H]^+$ 490.1835, found 490.1848.

5-Methyl-4-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[*g*]indole (3ad) and 4-methyl-5-phenyl-1-tosyl-2,3-dihydro-1H-benzo[g]indole (3ad'):

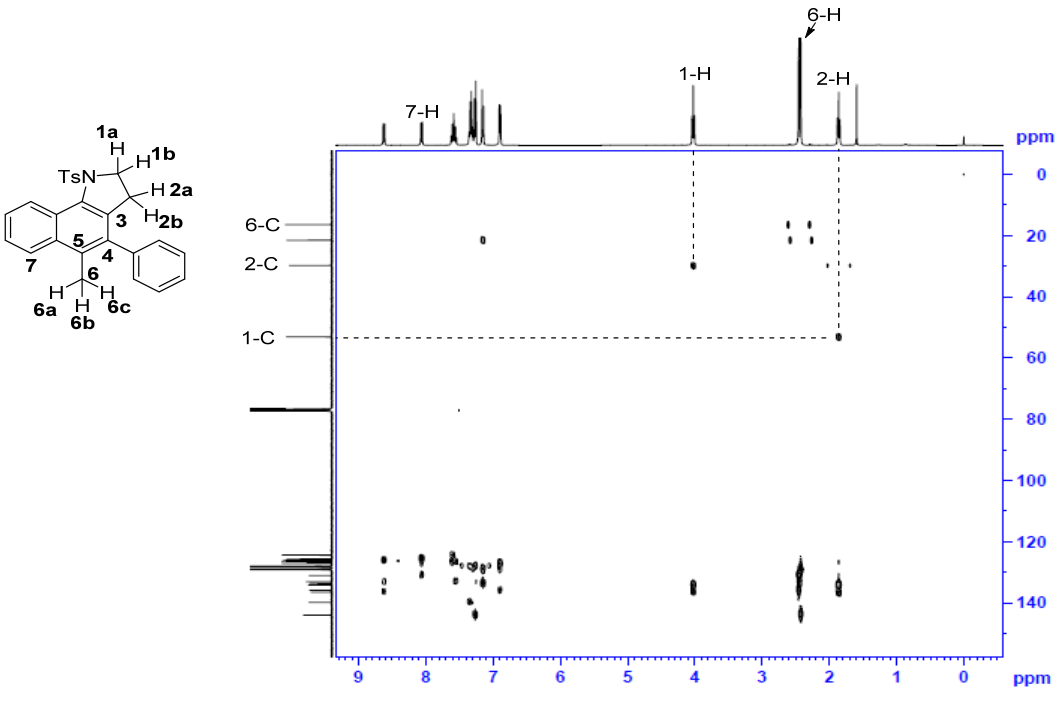


3ad:3ad'>20:1; White solid, mp 195.8-197.9 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.64-8.61 (m, 1H), 8.06 (d, *J* = 4.0 Hz, 1H), 7.61-7.57 (m, 2H), 7.36-7.30 (m, 3H), 7.28-7.26 (m, 2H), 7.15 (d, *J* = 4.0 Hz, 2H),

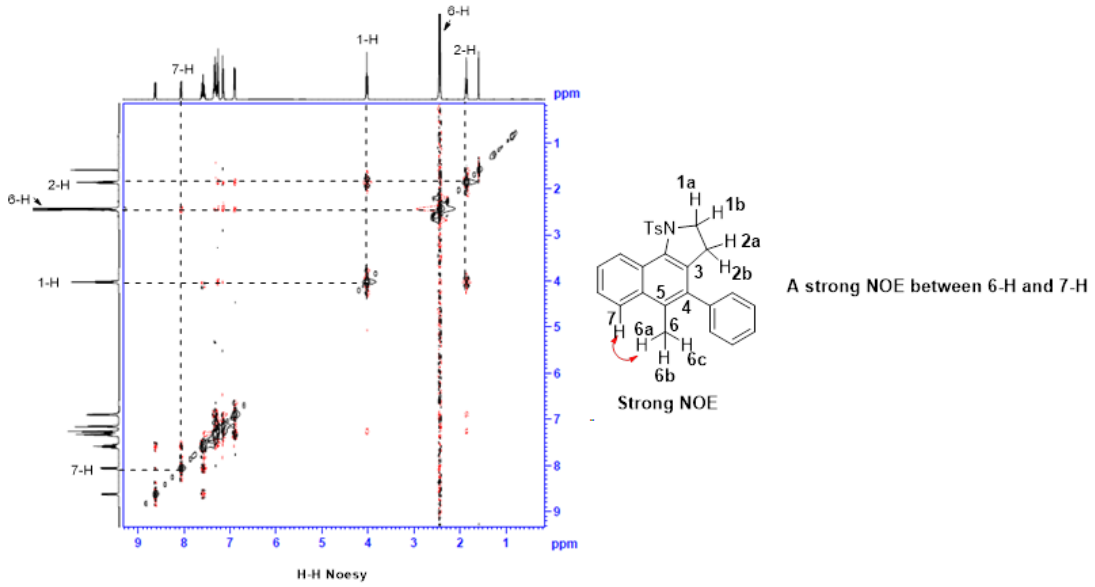
6.91-6.89 (m, 2H), 4.03 (t, J = 7.2 Hz, 2H), 2.46 (s, 3H), 2.43 (s, 3H), 1.86 (t, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.0, 139.9, 136.6, 135.9, 134.2, 133.6, 133.1, 131.1, 129.2, 128.9, 128.3, 128.0, 127.1, 126.7, 126.5, 126.2, 125.8, 124.4, 53.1, 29.8, 21.6, 16.5; HRMS m/z (ESI) calcd for $C_{26}H_{24}NO_2S$ $[M+H]^+$: 414.1552, found 414.1559.



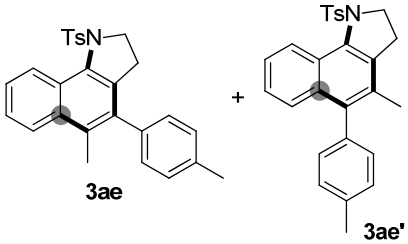
H-H cosy



HMBC

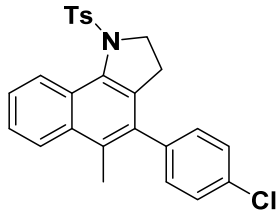


5-Methyl-4-(*p*-tolyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*g*]indole (3ae) and 4-Methyl-5-(*p*-tolyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*g*]indole (3ae'):



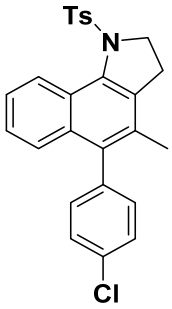
3ae:3ae' = 1.5:1; White solid, mp 196.1-198.4 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.54 (d, *J* = 4.4 Hz, 1H), 8.48 (d, *J* = 4.4 Hz, 0.6H), 7.97 (d, *J* = 4.0 Hz, 1H), 7.53-7.47 (m, 2.1H), 7.42-7.38 (m, 0.8H), 7.30 (t, *J* = 7.2 Hz, 0.9H), 6.53 (d, *J* = 7.2 Hz, 1H), 4.37 (t, *J* = 7.6 Hz, 1H), 4.21 (t, *J* = 5.6 Hz, 1H), 7.24-7.17 (m, 6.3H), 7.08-7.04 (m, 6.1H), 6.69 (d, *J* = 4.0 Hz, 2H), 4.07 (d, *J* = 7.2 Hz, 1.1H), 3.93 (d, *J* = 7.2 Hz, 2H), 2.39 (s, 1.7H), 2.38 (s, 3H), 2.34 (s, 3H), 2.30 (s, 1.7H), 2.29 (s, 3H), 2.16 (t, *J* = 7.2 Hz, 1.1H), 1.81 (s, 1.7H), 1.77 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.1, 144.0, 138.2, 137.4, 136.8, 136.5, 135.9, 134.6, 134.5, 133.9, 133.6, 133.1, 131.3, 130.2, 129.2, 129.1, 128.9, 128.8, 128.0, 127.9, 126.7, 126.4, 126.3, 126.1, 125.8, 125.7, 124.9, 124.5, 53.1, 53.0, 29.9, 29.1, 21.7, 21.6, 21.4, 21.2, 17.5, 16.5; HRMS *m/z* (ESI) calcd for $C_{27}H_{26}NO_2S$ $[M+H]^+$ 428.1679, found 428.1685.

4-(4-Chlorophenyl)-5-methyl-1-tosyl-2,3-dihydro-1*H*-benzo[*g*]indole (3af):



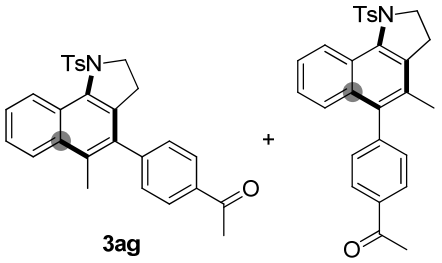
3af, 35.5% yield; White solid, mp 217.2-219.4 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.50 (d, *J* = 4.0Hz, 1H), 7.42 (d, *J* = 4.0 Hz, 3H), 7.25 (d, *J* = 4.0 Hz, 4H), 7.11-7.06 (m, 4H), 4.09 (t, *J* = 7.2 Hz, 2H), 2.33 (s, 3H), 2.19 (d, *J* = 7.2 Hz, 2H), 1.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.2, 138.0, 137.9, 136.7, 134.5, 133.9, 133.3, 133.2, 131.8, 129.6, 129.2, 128.8, 127.9, 126.0, 125.9, 125.8, 125.1, 53.1, 29.1, 21.6, 17.4; HRMS *m/z* (ESI) calcd for $C_{26}H_{23}{}^{35}ClNO_2S$ $[M+H]^+$ 448.1133, found 448.1140.

5-(4-Chlorophenyl)-4-methyl-1-tosyl-2,3-dihydro-1*H*-benzo[*g*]indole (3af'):



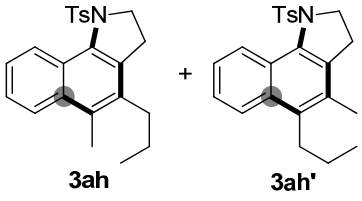
3af', 35.5% yield; White solid, mp 211.4-214.5 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.53 (d, *J* = 4.0 Hz, 1H), 7.9f8 (d, *J* = 4.0 Hz, 1H), 7.56-7.49 (m, 2H), 7.29 (d, *J* = 2.4 Hz, 2H), 7.19 (d, *J* = 4.0 Hz, 2H), 7.08 (d, *J* = 4.0 Hz, 2H), 6.76 (d, *J* = 4.0 Hz, 2H), 3.95 (t, *J* = 7.6 Hz, 2H), 2.37 (s, 3H), 2.35 (s, 3H), 1.77 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.1, 138.3, 136.8, 134.6, 133.9, 133.6, 133.2, 133.1, 131.2, 130.3, 129.2, 128.6, 128.1, 126.8, 126.5, 126.3, 125.9, 124.4, 53.1, 29.8, 21.6, 16.5; HRMS *m/z* (ESI) calcd for $C_{26}H_{23}{}^{35}ClNO_2S$ $[M+H]^+$ 448.1133, found 448.1142.

1-(4-(5-Methyl-1-tosyl-2,3-dihydro-1*H*-benzo[*g*]indol-4-yl)phenyl)ethan -1-one (3ag) and 1-(4-(4-Methyl-1-tosyl-2,3-dihydro-1*H*-benzo[*g*]indol-5-yl)phenyl)ethan-1-one (3ag')



3ai:3ai' = 2.7:1; White solid, mp 215.8-217.9 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.62 (d, *J* = 4.0 Hz, 1H), 8.58 (d, *J* = 4.0 Hz, 0.4H), 8.11 (d, *J* = 4.0 Hz, 0.8H), 8.07 (d, *J* = 4.0 Hz, 1H), 7.95 (d, *J* = 4.0 Hz, 2H), 7.65-7.57 (m, 2.1H), 7.50 (t, *J* = 7.2 Hz, 0.4H), 7.36 (d, *J* = 4.0 Hz, 0.9H), 7.35-7.34 (m, 1.2H), 7.29-7.28 (m, 1.4H), 7.17 (d, *J* = 4.0 Hz, 2.4H), 7.14 (s, 0.4H), 7.01 (d, *J* = 4.0 Hz, 2H), 4.17 (t, *J* = 7.2 Hz, 0.8H), 4.04 (t, *J* = 7.2 Hz, 2H), 2.71 (s, 1.1H), 2.64 (s, 3H), 2.46 (s, 3H), 2.45 (s, 3H), 2.40 (s, 1H), 2.28 (t, *J* = 7.2 Hz, 0.8H), 1.89 (s, 1.1H), 1.84 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 197.9, 197.7, 144.9, 144.2, 138.1, 136.9, 136.8, 136.1, 135.9, 134.7, 134.6, 133.9, 133.6, 133.5, 133.4, 133.1, 132.9, 131.0, 130.7, 129.4, 129.3, 129.2, 128.6, 128.4, 128.0, 127.9, 126.8, 126.5, 126.4, 126.1, 125.9, 125.8, 125.7, 125.2, 124.4, 53.1, 53.0, 29.6, 29.0, 26.7, 26.6, 21.6, 17.4, 16.5; HRMS *m/z* (ESI) calcd for $C_{28}H_{26}NO_3S$ $[M+H]^+$ 456.1628, found 456.1620.

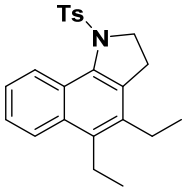
5-Methyl-4-propyl-1-tosyl-2,3-dihydro-1*H*-benzo[*g*]indole (3ah) and 4-Methyl-5-propyl-1-tosyl-2,3-dihydro-1*H*-benzo[*g*]indole (3ah'):



3ah:3ah' = 2.1:1; White solid, mp 139.7-141.4 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.48-8.44 (m, 1.4H), 7.94-7.91 (m, 1.5H), 7.44-7.39 (m, 3H), 7.13-7.09 (m, 2.9H), 6.97 (d, *J* = 4.0 Hz, 3H), 4.01 (t, *J* = 7.2 Hz, 2H), 3.99 (t, *J* = 7.2 Hz, 0.9H), 2.95 (t, *J* = 8.0 Hz, 0.9H), 2.52 (s, 3H), 2.43 (t, *J* = 7.2 Hz, 2H), 2.27 (s, 1.4H), 2.26 (s, 3H), 2.11 (t, *J* = 7.2 Hz, 2H), 2.05 (s, 1.4H), 1.59-1.53 (m, 0.9H),

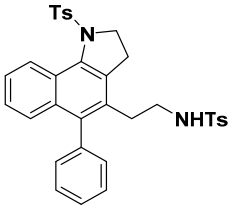
1.19-1.14 (m, 2H), 0.98 (t, J = 7.2 Hz, 1H), 0.78 (t, J = 7.2 Hz, 1.4H), 0.74 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.0, 143.9, 136.5, 136.3, 135.8, 134.8, 134.6, 134.2, 133.7, 133.3, 132.4, 130.7, 129.3, 129.2, 129.1, 127.9, 127.8, 126.5, 126.4, 126.2, 126.0, 125.8, 124.8, 124.7, 123.9, 123.7, 52.8, 32.8, 30.6, 29.2, 28.8, 23.5, 22.9, 21.4, 16.3, 14.6, 14.3, 14.0; HRMS *m/z* (ESI) calcd for $C_{23}H_{26}NO_2S$ $[M+H]^+$ 380.1679, found 380.1687.

4,5-Diethyl-1-tosyl-2,3-dihydro-1*H*-benzo[*g*]indole (3ai):



White solid, mp 140.0-142.4 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.57-8.55 (m, 1H), 8.04-8.02 (m, 1H), 7.53-7.48 (m, 2H), 7.18 (d, J = 4.0 Hz, 2H), 7.05 (d, J = 4.0 Hz, 2H), 4.11 (t, J = 7.2 Hz, 2H), 3.12-3.06 (m, 2H), 2.57-2.51 (m, 2H), 2.35 (s, 3H), 2.19 (t, J = 7.2 Hz, 2H), 1.29 (t, J = 7.2 Hz, 3H), 0.89 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.9, 136.8, 136.7, 135.1, 134.3, 133.6, 132.3, 129.2, 127.9, 126.6, 126.4, 125.8, 124.8, 123.7, 52.8, 28.5, 23.6, 21.5, 21.3, 15.8, 14.4; HRMS *m/z* (ESI) calcd for $C_{23}H_{26}NO_2S$ $[M+H]^+$: 380.1679, found 380.1688.

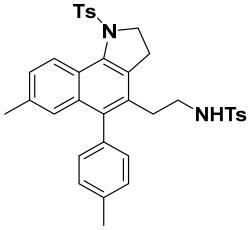
4-Methyl-*N*-(2-(5-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[*g*]indol-4-yl)ethyl)benzen esulfonamide (4a):



White solid, mp 172.4-174.6 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.48 (d, J = 4.0 Hz, 1H), 7.41 (d, J = 4.0 Hz, 3H), 7.37 (t, J = 4.0 Hz, 3H), 7.24-7.17 (m, 4H), 7.12 (d, J = 4.0 Hz, 2H), 7.07-7.04 (m, 4H), 4.27 (t, J = 8.0 Hz, 1H), 4.10 (t, J = 8.0 Hz, 2H), 2.57-2.52 (m, 2H), 2.37 (d, J = 4.0 Hz, 2H), 2.34 (s, 3H), 2.30 (s, 3H), 2.16 (t, J = 8.0 Hz, 2H);

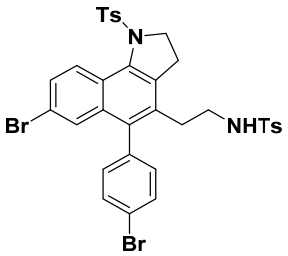
^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.7, 143.4, 138.9, 138.7, 138.6, 136.9, 133.9, 133.7, 133.5, 130.2, 129.6, 129.4, 129.3, 128.6, 127.8, 127.6, 126.9, 126.4, 126.3, 126.1, 125.9, 125.7, 53.0, 42.4, 31.8, 28.7, 21.6, 21.5; HRMS *m/z* (ESI) calcd for $C_{34}H_{33}N_2O_4S_2$ $[M+H]^+$ 597.1876, found 597.1869.

4-Methyl-*N*-(2-(7-methyl-5-(*p*-tolyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*g*]indol-4-yl)ethyl)benzenesulfonamide (4b):



White solid, mp 183.4-186.2 ºC (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.45 (d, *J* = 4.0 Hz, 1H), 7.48 (d, *J* = 4.0 Hz, 2H), 7.35 (d, *J* = 4.0 Hz, 1H), 7.25 (t, *J* = 8.0 Hz, 4H), 7.20 (d, *J* = 4.0 Hz, 2H), 7.13 (d, *J* = 4.0 Hz, 2H), 7.00 (t, *J* = 8.0 Hz, 3H), 4.11 (t, *J* = 4.0 Hz, 2H), 2.60 (t, *J* = 8.0 Hz, 2H), 2.47 (s, 3H), 2.42-2.39 (m, 5H), 2.38 (s, 3H), 2.34 (s, 3H), 2.18 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.6, 143.4, 138.4, 138.3, 137.1, 137.0, 135.7, 135.6, 133.9, 133.7, 132.9, 130.0, 129.6, 129.4, 129.3, 127.9, 127.8, 126.9, 125.7, 125.4, 124.5, 126.2, 53.0, 42.4, 31.7, 28.5, 21.9, 21.6, 21.5, 21.4; HRMS *m/z* (ESI) calcd for $C_{36}H_{37}N_2O_4S_2$ $[M+H]^+$ 625.2189, found 625.2183.

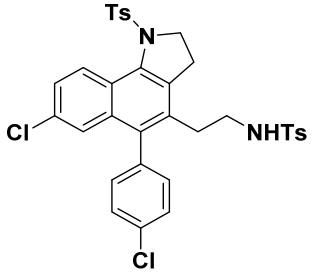
***N*-(7-Bromo-5-(4-bromophenyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*g*]indol-4-yl)-4-methylbenzenesulfonamide (4c):**



White solid, mp 208.4-210.2 ºC (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.44 (d, *J* = 4.0 Hz, 1H), 7.60-7.56 (m, 3H), 7.51 (d, *J* = 4.0 Hz, 2H), 7.34 (d, *J* = 4.0 Hz, 1H), 7.28 (d, *J* = 4.0 Hz, 2H), 7.25 (d, *J* = 4.0 Hz, 2H), 7.16 (d, *J* = 4.0 Hz, 2H), 6.98 (d, *J* = 4.0 Hz, 2H), 4.19 (t, *J* = 8.0 Hz, 1H) 4.14 (t, *J* = 8.0 Hz, 2H), 2.63-2.58

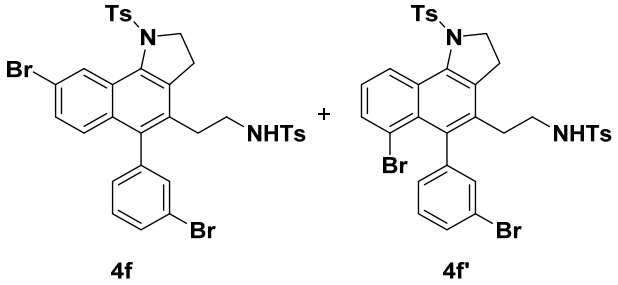
(m, 2H), 2.45 (s, 3H), 2.42 (d, *J* = 4.0 Hz, 2H) , 2.39 (s, 3H), 2.26 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.9, 143.6, 139.2, 136.8, 136.6, 136.5, 134.6, 134.4, 133.6, 132.0, 131.8, 130.8, 129.7, 129.5, 129.3, 128.1, 127.9, 127.7, 126.8, 124.7, 122.2, 121.1, 53.0, 42.2, 31.9, 28.7, 21.7, 21.6; HRMS *m/z* (ESI) calcd for $C_{34}H_{31}{}^{79}BrN_2O_4S_2$ $[M+H]^+$ 753.0087, found 753.0083.

_N_-(2-(7-Chloro-5-(4-chlorophenyl)-1-tosyl-2,3-dihydro-1_H_-benzo[_g_]indol-4-yl)eth yl)-4-methylbenzenesulfonamide (4d):



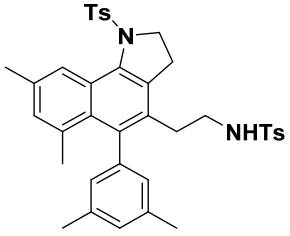
White solid, mp 209.4-211.2 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.51 (d, *J* = 4.0 Hz, 1H), 7.50 (d, *J* = 4.0 Hz, 2H), 7.46-7.41 (m, 3H), 7.28 (d, *J* = 4.0 Hz, 2H), 7.24 (d, *J* = 4.0 Hz, 2H), 7.17-7.16 (m, 3H), 7.04 (d, *J* = 4.0 Hz, 2H), 4.14 (t, *J* = 8.0 Hz, 2H), 2.63-2.58 (m, 2H), 2.44-2.39 (m, 8H), 2.27 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.9, 143.6, 139.1, 136.8, 136.6, 136.2, 134.4, 134.1, 134.0, 133.6, 132.5, 131.5, 130.9, 129.7, 129.5, 129.1, 127.9, 127.7, 126.8, 126.7, 124.8, 124.5, 53.0, 42.2, 32.0, 28.7, 21.6, 21.5; HRMS *m/z* (ESI) calcd for $C_{34}H_{31}{}^{35}ClN_2O_4S_2$ $[M+H]^+$ 665.1697, found 665.1694.

_N_-(2-(8-Bromo-5-(3-bromophenyl)-1-tosyl-2,3-dihydro-1_H_-benzo[_g_]indol-4-yl)eth yl)-4-methylbenzenesulfonamide (4f) and _N_-(2-(6-bromo-5-(3-bromophenyl)-1-tosyl-2,3-dihydro-1_H_-benzo[_g_]indol-4-yl)eth yl)-4-methylbenzenesulfonamide (4f'):



4f:4f' = 2.5:1; White solid, mp 206.4-208.9 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.63 (d, *J* = 4.0 Hz, 1H), 7.76 (s, 0.4H), 7.64 (d, *J* = 4.0 Hz, 1H), 7.53 (d, *J* = 4.0 Hz, 1.2H), 7.48 (d, *J* = 4.0 Hz, 0.8H), 7.44 (d, *J* = 4.0 Hz, 2H), 7.39 (s, 0.5H), 7.33-7.31 (m, 1.1H), 7.29 (s, 0.5H), 7.25 (t, *J* = 8.0 Hz, 3H), 7.21-7.18 (m, 2H), 7.17-7.13 (m, 2.9H), 7.10 (d, *J* = 4.0 Hz, 2H), 7.00-6.98 (m, 2H), 6.89 (d, *J* = 4.0 Hz, 0.4H), 5.01 (t, *J* = 8.0 Hz, 0.4H), 4.28 (t, *J* = 8.0 Hz, 1H), 4.06 (t, *J* = 8.0 Hz, 2H), 3.18 (t, *J* = 8.0 Hz, 0.8H), 2.95 (t, *J* = 8.0 Hz, 0.8H), 2.55 (t, *J* = 8.0 Hz, 2H), 2.38 (d, *J* = 4.0 Hz, 2H), 2.34 (s, 3H), 2.32 (s, 1.2H), 2.31 (s, 3H), 2.22 (t, *J* = 8.0 Hz, 2H), 1.97 (s, 1.2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.8, 143.5, 143.4, 140.7, 140.1, 138.7, 138.2, 137.2, 136.9, 135.3, 133.6, 132.8, 131.7, 131.1, 130.3, 130.0, 129.7, 129.6, 129.5, 128.8, 128.2, 127.8, 127.7, 127.2, 127.0, 126.8, 126.7, 122.8, 120.6, 60.4, 52.9, 43.8, 42.2, 33.5, 32.0, 31.0, 29.6, 28.7, 21.6, 21.5, 21.0, 14.2; HRMS *m/z* (ESI) calcd for $C_{34}H_{31}{}^{79}BrN_2O_4S_2$ $[M+H]^+$ 753.0087, found 753.0092.

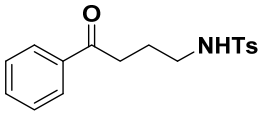
_N_-(2-(5-(3,5-Dimethylphenyl)-6,8-dimethyl-1-tosyl-2,3-dihydro-1_H_-benzo[_g_]indol-4-yl)ethyl)-4-methylbenzenesulfonamide (4g):



White solid, mp 186.3-188.7 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.23 (s, 1H), 7.80 (d, *J* = 4.0 Hz, 1H), 7.50 (d, *J* = 4.0 Hz, 2H), 7.28 (d, *J* = 4.0 Hz, 2H), 7.21 (d, *J* = 4.0 Hz, 2H), 7.15 (d, *J* = 4.0 Hz, 2H), 7.02 (s, 2H), 6.74 (s, 1H), 4.16 (t, *J* = 8.0 Hz, 1H),

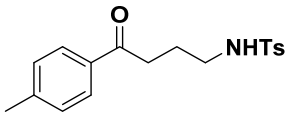
4.10 (t, *J* = 8.0 Hz, 2H), 2.62-2.52 (m, 2H), 2.46 (s, 3H), 2.43 (s, 3H), 2.41 (s, 3H), 2.39 (s, 3H), 2.34-2.27 (m, 8H), 2.14 (t, *J* = 4.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.6, 143.3, 141.8, 138.9, 138.7, 137.3, 137.2, 134.9, 134.7, 133.7, 133.2, 133.0, 129.7, 129.5, 129.3, 129.2, 128.8, 128.2, 127.8, 126.8, 126.4, 123.9, 52.9, 42.6, 31.8, 28.7, 24.9, 21.6, 21.5, 21.4, 21.4, 21.3; HRMS *m/z* (ESI) calcd for $C_{38}H_{41}lN_2O_4S_2$ $[M+H]^+$ 653.2502, found 653.2506.

4-Methyl-*N*-(4-oxo-4-phenylbutyl)benzenesulfonamide (5a):



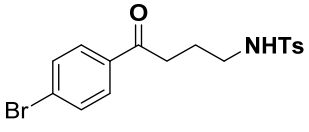
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.82 (d, *J* = 4.0 Hz, 2H), 7.65 (d, *J* = 4.0 Hz, 2H), 7.48 (t, *J* = 8.0 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 4.0 Hz, 2H), 4.96 (t, *J* = 8.0 Hz, 1H), 2.99-2.92 (m, 4H), 2.31 (s, 3H), 1.84 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 199.6, 143.4, 136.8, 136.6, 133.3, 129.7, 128.6, 128.0, 127.1, 42.7, 35.4, 23.6, 21.5; LRMS (EI, 70 eV) *m/z* (%): 317 (M^+, 19), 162 (100), 105 (51).

4-Methyl-*N*-(4-oxo-4-(p-tolyl)butyl)benzenesulfonamide (5b):



White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.72 (d, *J* = 4.0 Hz, 2H), 7.65 (d, *J* = 4.0 Hz, 2H), 7.17 (t, *J* = 8.0 Hz, 4H), 4.91 (t, *J* = 4.0 Hz, 1H), 2.97-2.89 (m, 4H), 2.33 (s, 3H), 2.31 (s, 3H), 1.83 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 199.3, 144.1, 143.3, 136.9, 134.1, 129.7, 129.3, 128.2, 127.1, 42.8, 35.3, 23.7, 21.6, 21.5; LRMS (EI, 70 eV) *m/z* (%): 331 (M^+, 27), 176 (100), 119 (67).

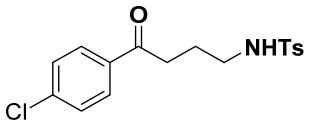
***N*-(4-(4-Bromophenyl)-4-oxobutyl)-4-methylbenzenesulfonamide(5c):**



White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69-7.64 (m,

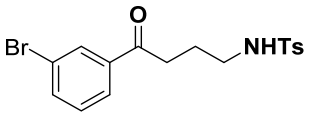
4H), 7.49 (d, *J* = 4.0 Hz, 2H), 7.18 (d, *J* = 4.0 Hz, 2H), 4.94 (t, *J* = 8.0 Hz, 1H), 2.98-2.90 (m, 4H), 2.32 (s, 3H), 1.86-1.81 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 198.6, 143.5, 136.8, 135.3, 131.9, 129.7, 129.5, 127.0, 126.4, 42.6, 35.3, 23.6, 21.5; LRMS (EI, 70 eV) *m/z* (%): 397 (M^++2, 1), 395 (M^+, 1), 91 (100), 155 (73).

***N*-(4-(4-Chlorophenyl)-4-oxobutyl)-4-methylbenzenesulfonamide(5d):**



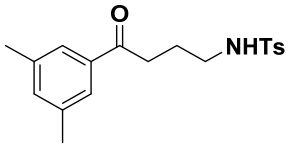
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.83 (d, *J* = 4.0 Hz, 2H), 7.32 (d, *J* = 4.0 Hz, 2H), 7.40 (d, *J* = 4.0 Hz, 2H), 7.26 (d, *J* = 4.0 Hz, 2H), 4.99 (t, *J* = 8.0 Hz, 1H), 3.07-2.98 (m, 4H), 2.39 (s, 3H), 1.94-1.87 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 198.3, 143.5, 139.7, 136.8, 134.9, 129.7, 129.5, 128.9, 127.0, 42.6, 35.3, 23.6, 21.5; LRMS (EI, 70 eV) *m/z* (%):353 (M^++2, 1), 351 (M^+, 3), 195 (100) 155 (54).

***N*-(4-(3-Bromophenyl)-4-oxobutyl)-4-methylbenzenesulfonamide(5f):**



White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.99 (s, 1H), 7.81 (d, *J* = 4.0 Hz, 1H), 7.72 (d, *J* = 4.0 Hz, 2H), 7.66 (d, *J* = 4.0 Hz, 1H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 4.0 Hz, 2H), 5.12 (t, *J* = 8.0 Hz, 1H), 3.06-2.97 (m, 4H), 2.38 (s, 3H), 1.94-1.87 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 198.1, 143.5, 138.3, 136.8, 136.0, 131.0, 130.2, 129.7, 127.0, 126.6, 122.9, 42.6, 35.4, 23.5, 21.5; LRMS (EI, 70 eV) *m/z* (%): 397 (M^++2, 2), 395 (M^+, 2), 91 (100), 133 (42).

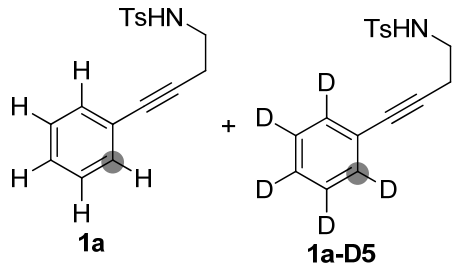
***N*-(4-(3,5-dimethylphenyl)-4-oxobutyl)-4-methylbenzenesulfonamide(5g):**



White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.72 (d, *J* = 4.0 Hz, 2H), 7.51 (s, 2H), 7.24 (d, *J* = 4.0 Hz, 2H), 7.19 (d, *J* = 4.0 Hz, 1H), 5.06 (t, *J* = 4.0 Hz, 1H), 3.06-2.97 (m, 4H), 2.38 (s, 3H), 2.35 (s, 6H), 1.93-1.86 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 200.0, 143.3, 138.2, 136.9, 136.7, 134.9, 129.7, 127.1, 125.8, 42.8, 35.5, 23.7, 21.5, 21.2; LRMS (EI, 70 eV) *m/z* (%): 345 (1), 190 (100), 133 (64).

(C) Mechanistic Studies: Kinetic Isotopic Effect (KIE) Experiments:

(a) Experimental detail for determination of the intermolecular KIE



21% yield (1 h), k_H/k_D = 3.0

To a Schlenk tube was added 4-methyl-*N*-(4-phenylbut-3-yn-1-yl)-benzenesulfonamide **1a** (0.1 mmol), 4-methyl-*N*-(4-(phenyl-d5)but-3-yn-1-yl)-benzenesulfonamide **1a-D5** (0.1 mmol), alkynes **2a** (1.5equiv), $[Cp^*RhCl_2]_2$ (5 mol%), AgOTf (4 mol%), TFA (1 equiv) and CH_3OH (2 mL). Then the tube was charged with O_2 (1 atm), and was stirred at 120 ^oC (oil bath temperature) for about 1 h. After the reaction mixture was cooled to room temperature, and the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate) to afford **3aa** and **3aa-D5**.

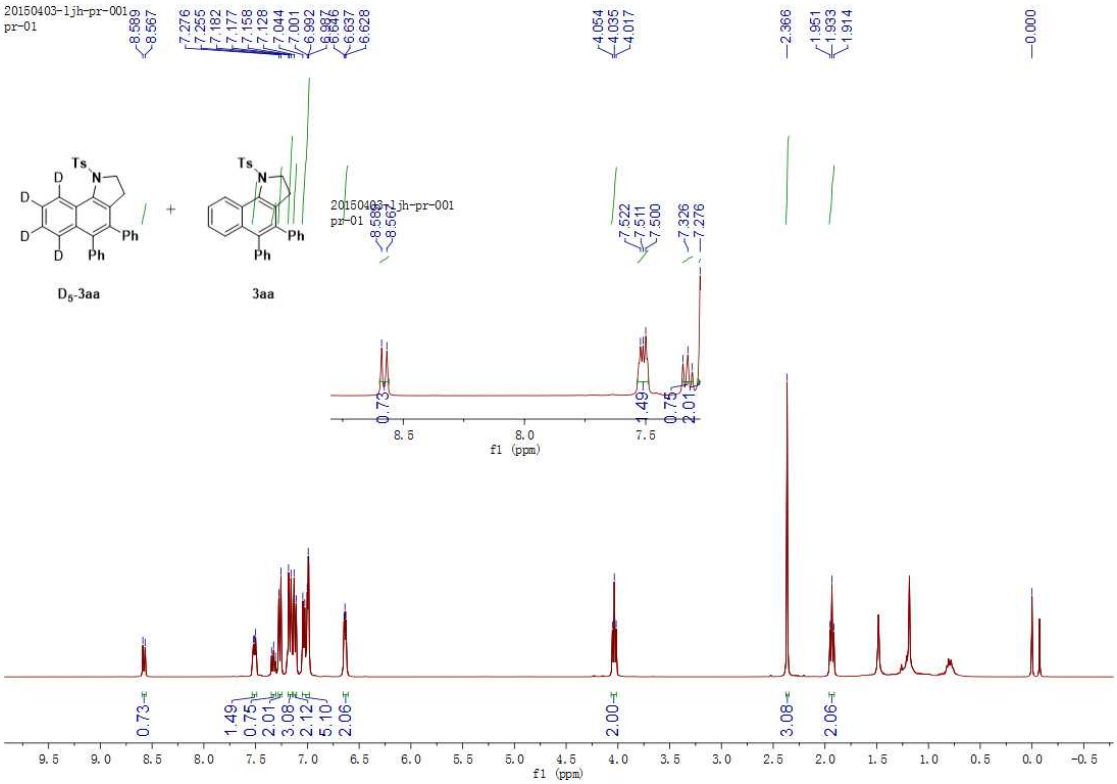
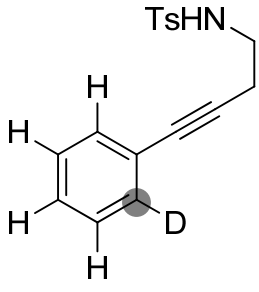


Figure S1. [1]HNMR of the products **3aa-D5 and 3aa**

(b) Intramolecular KIE Experiment:



1a-D1

65% yield (22 h), k_H/k_D = 2.3

To a Schlenk tube was added 4-methyl-*N*-(4-(phenyl-2-d)but-3-yn-1-yl)-benzensulfonamide **1a-D1** (0.2 mmol), alkynes **2a** (1.5equiv), $[Cp^*RhCl_2]_2$ (5 mol%), AgOTf (4 mol%),TFA (1 equiv) and CH_3OH (2 mL). Then the tube was charged with O_2 (1 atm), and was stirred at 120 ºC (oil bath temperature) for about 22 h. After the

reaction mixture was cooled to room temperature, and the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate) to afford **3aa** and **3aa-D1**.

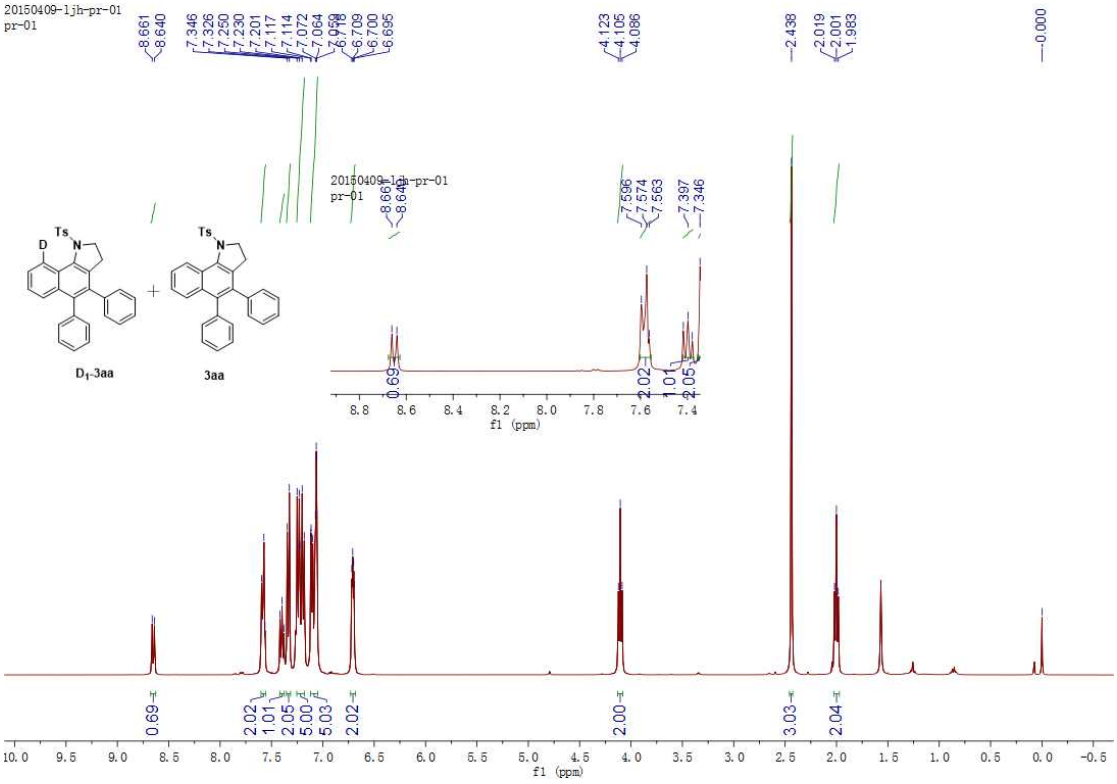


Figure S2. ^{1}HNMR of the products **3aa-D1 and 3aa**

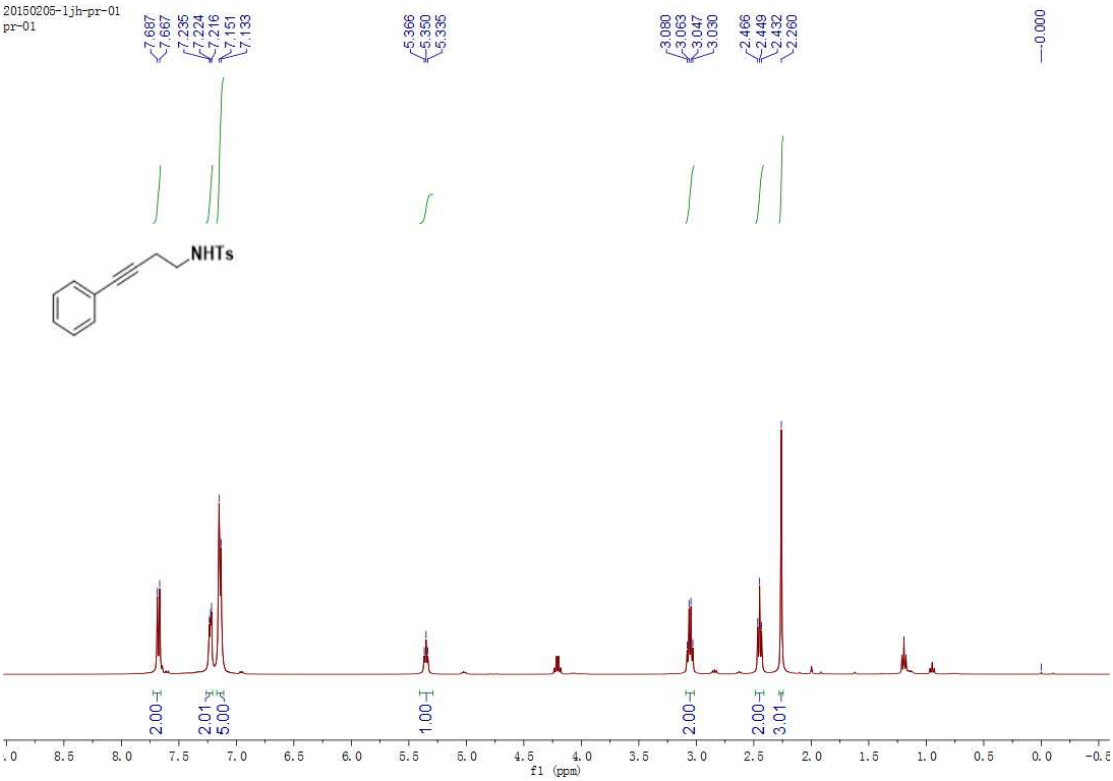
(D) References

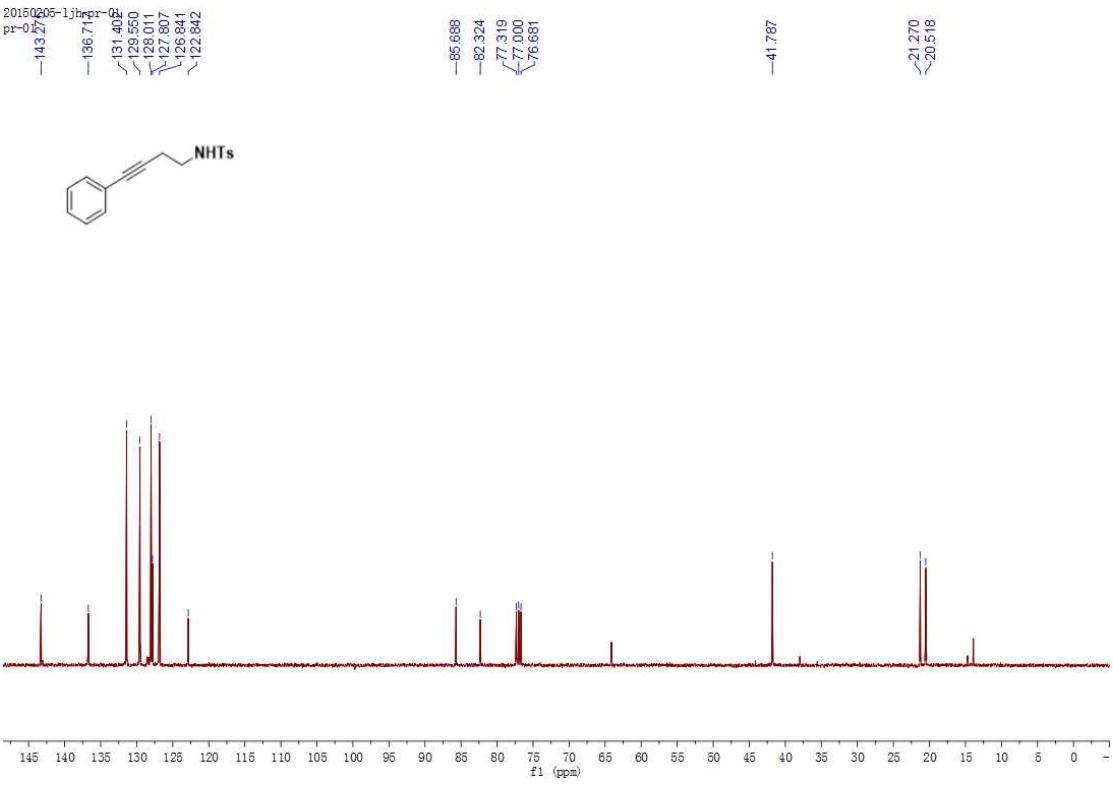
[1] N. O. Rourke, K. Davies, J. Wulff, *J. Org. Chem.*, **2012**, *77*, 8634.

[2] M.-B. Zhou, R.-J. Song, C.-Y. Wang, J.-H. Li, *Angew. Chem. Int. Ed.*, **2013**, *52*, 10805.

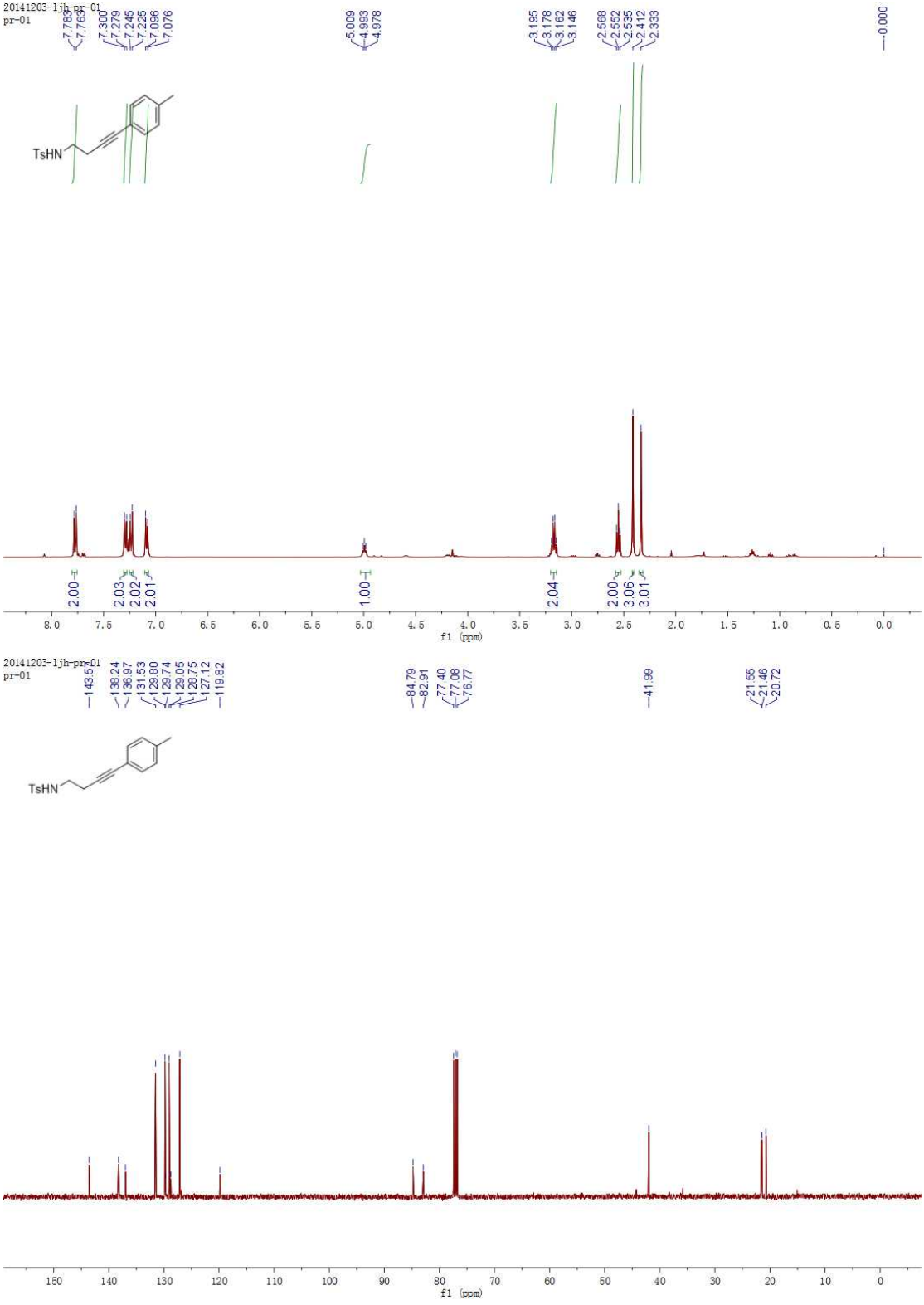
(E) Spectra

N-(1,4-diphenylbut-3-yn-1-yl)-4-methylbenzenesulfonamide (1a)

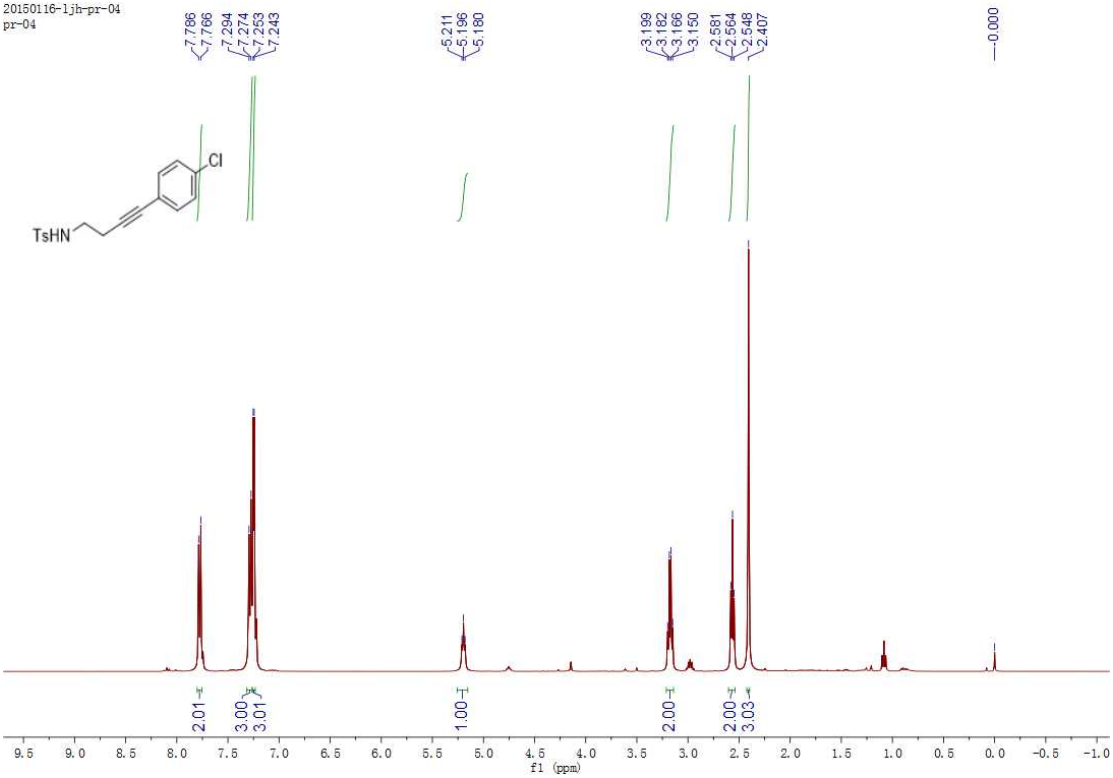


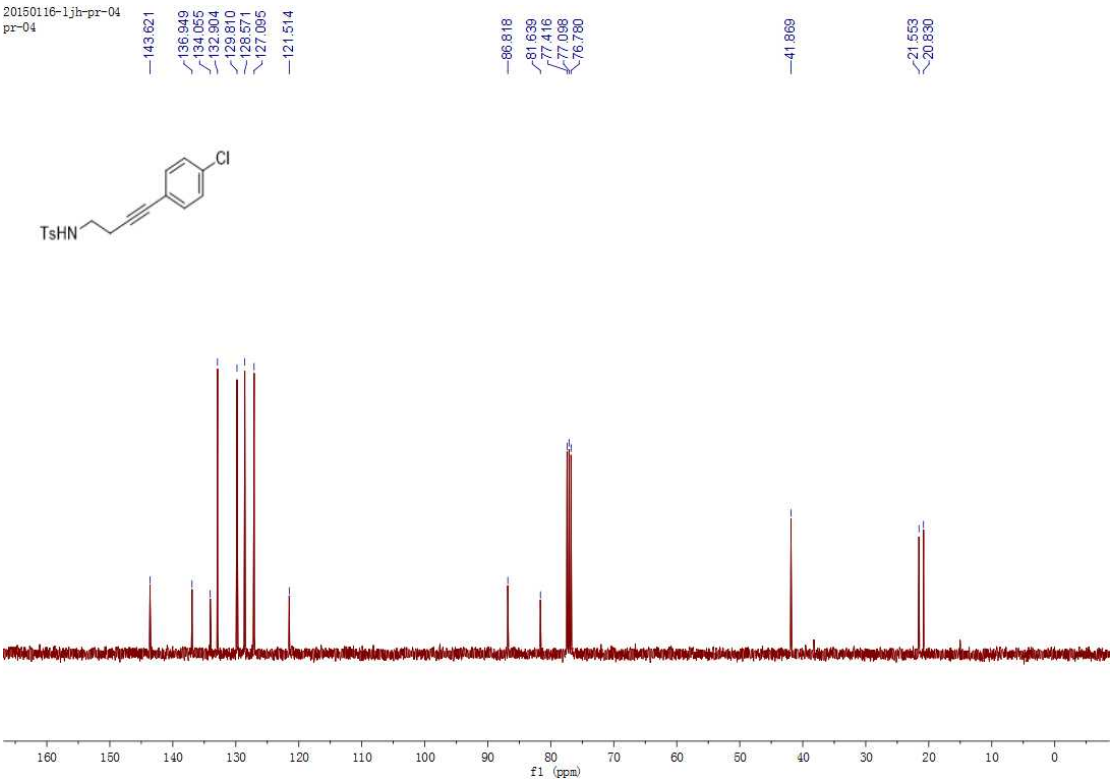


4-Methyl-*N*-(4-(*p*-tolyl)but-3-yn-1-yl)benzenesulfonamide (1b)

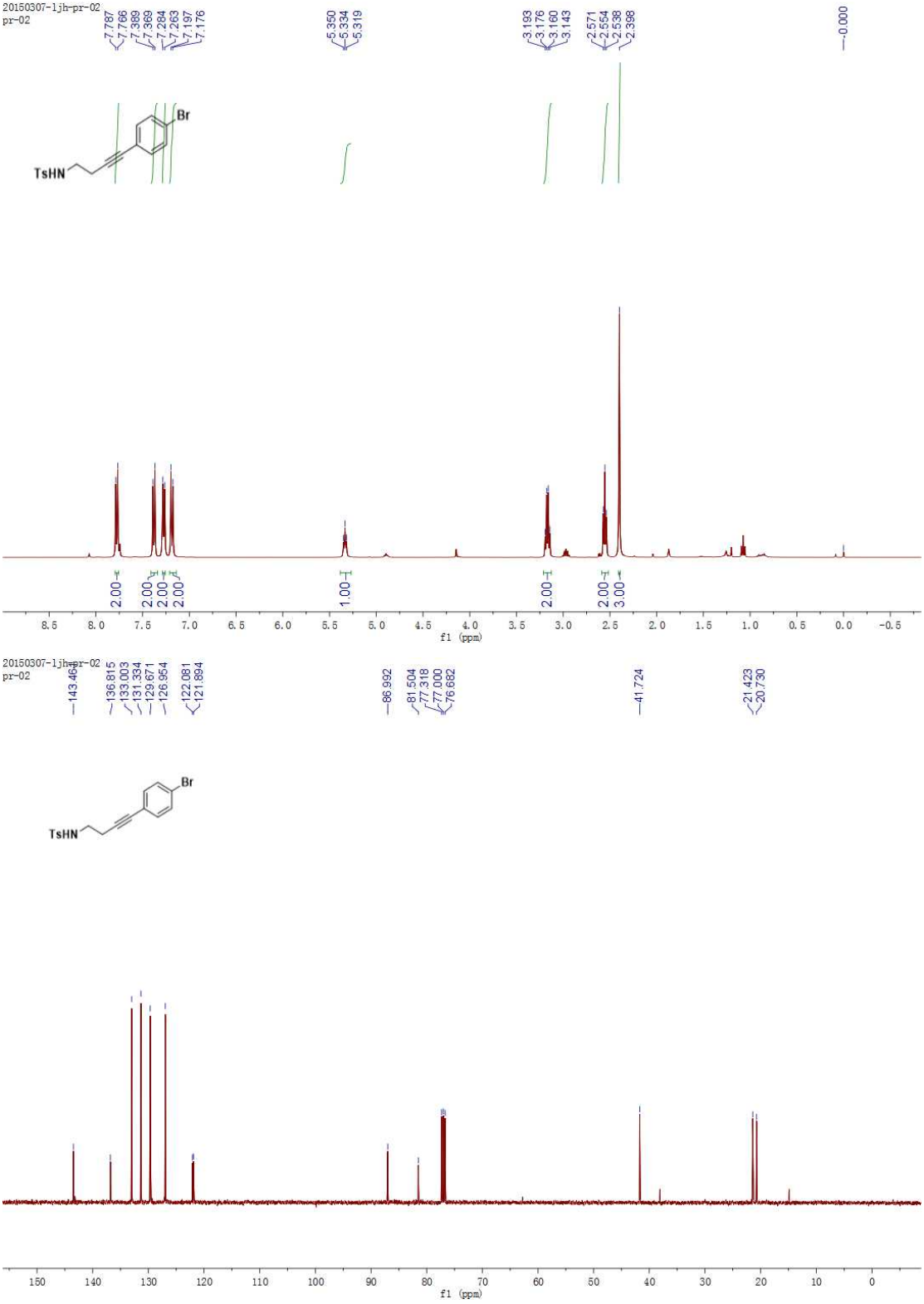


N-(4-(4-Chlorophenyl)but-3-yn-1-yl)-4-methylbenzenesulfonamide (1c)

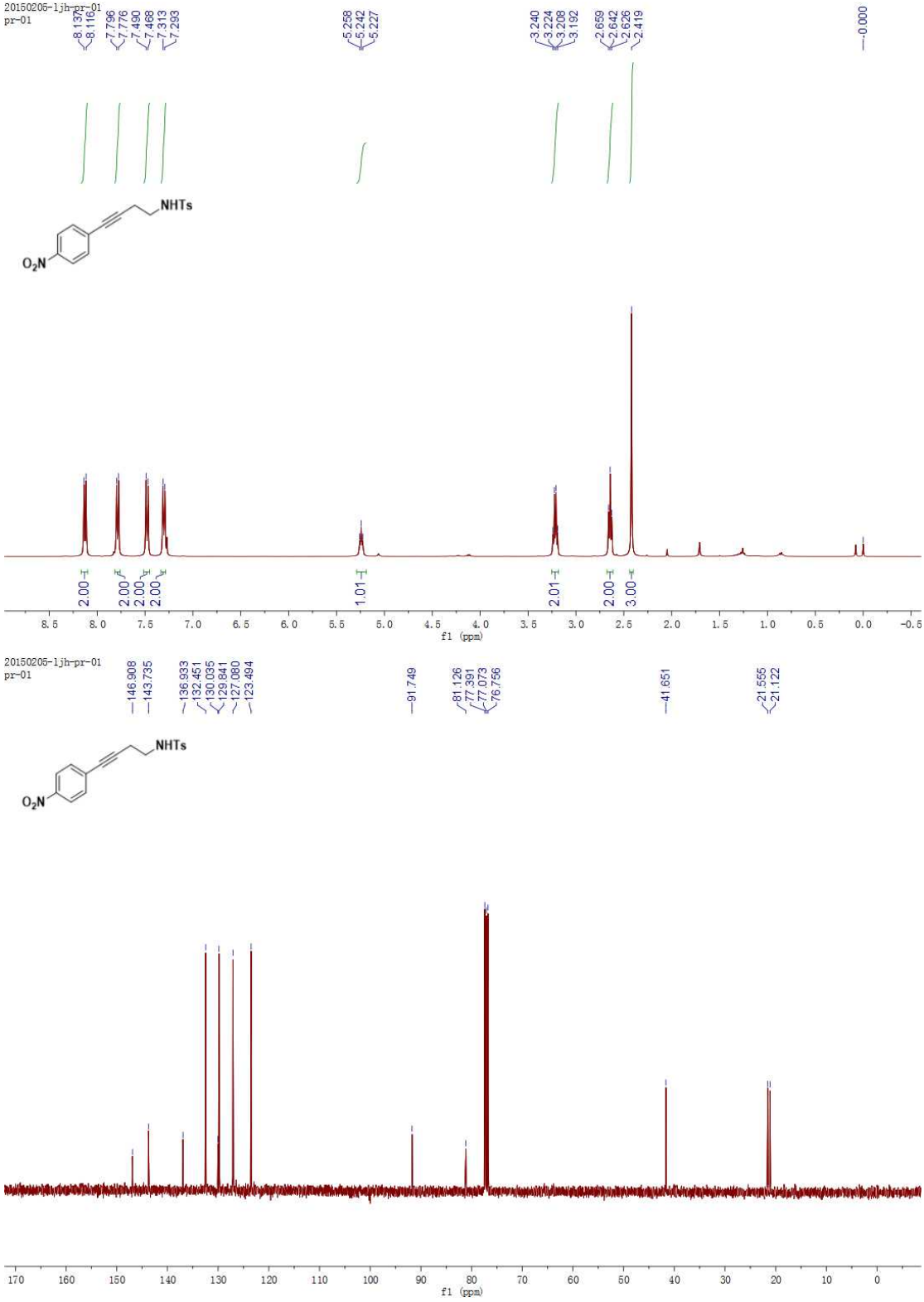




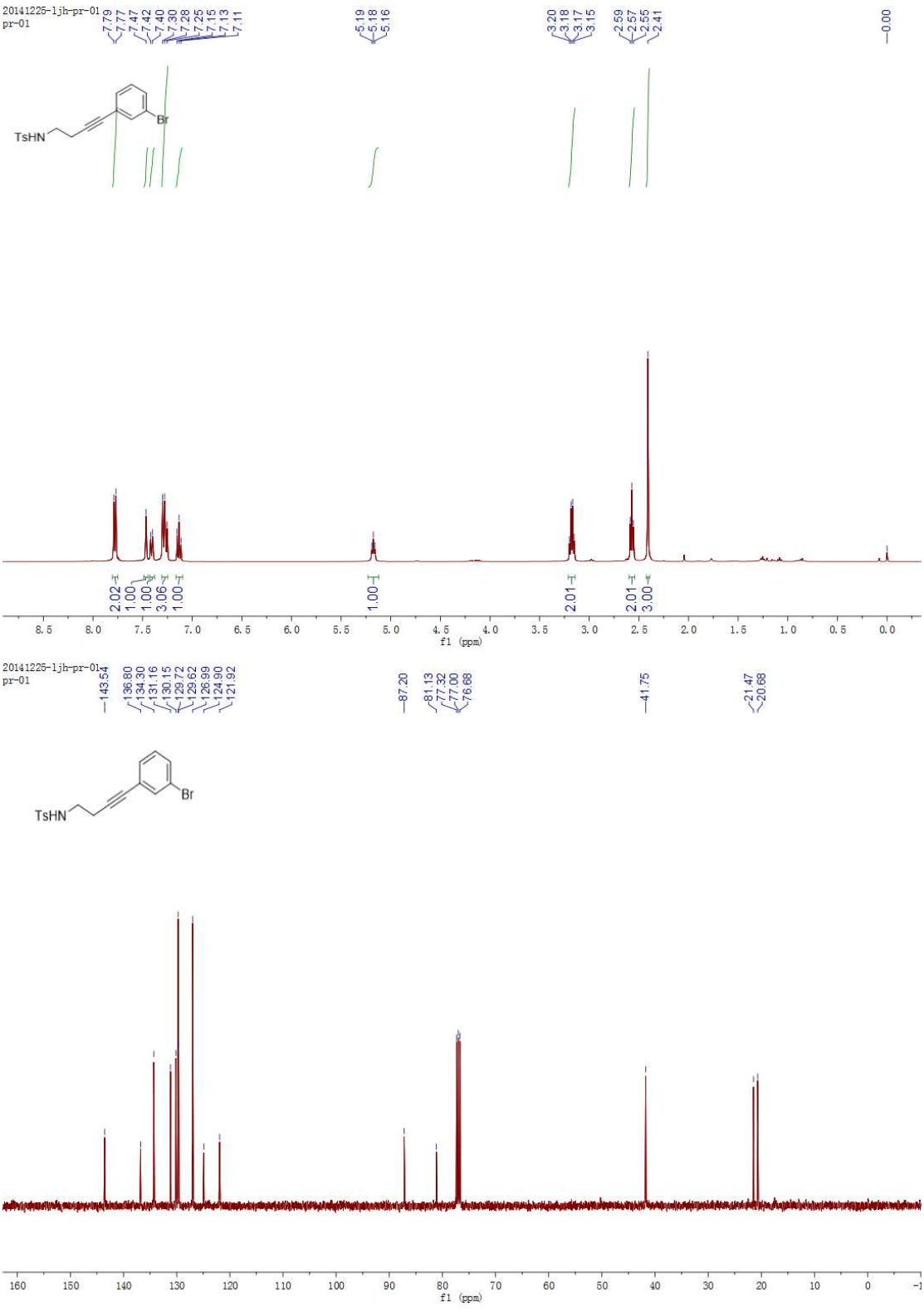
N-(4-(4-bromophenyl)but-3-yn-1-yl)-4-methylbenzenesulfonamide (1d)



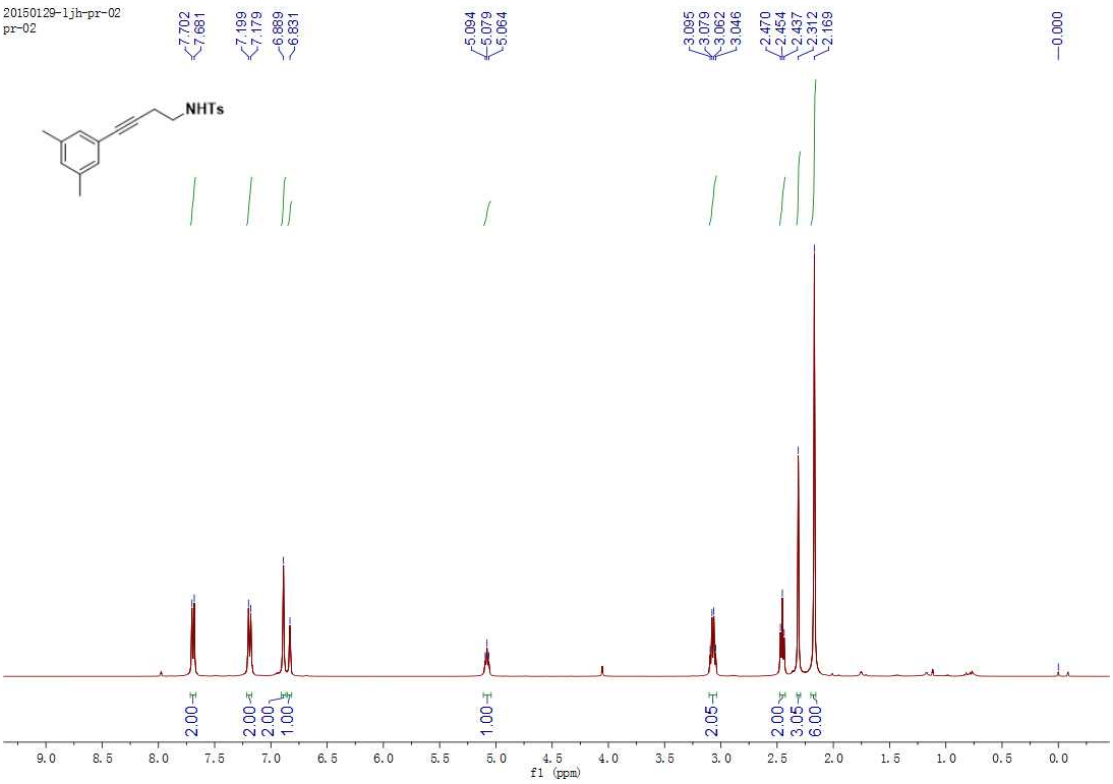
4-Methyl-*N*-(4-(4-nitrophenyl)but-3-yn-1-yl)benzenesulfonamide (1e)

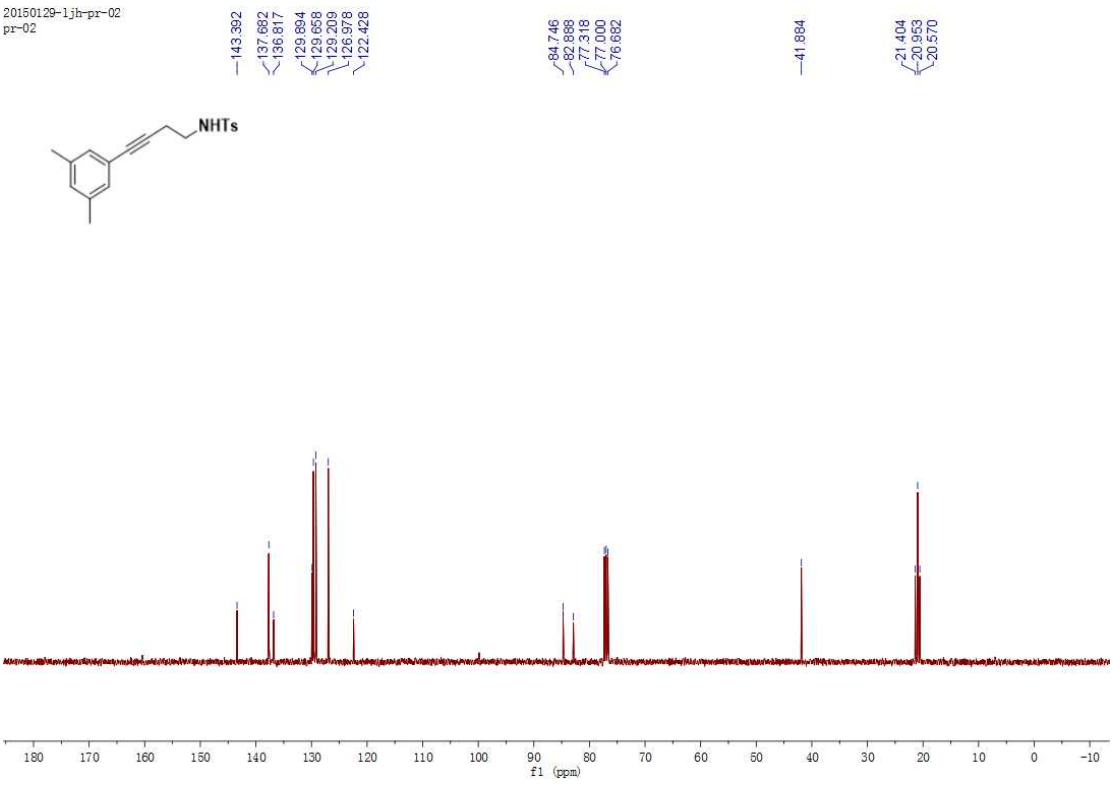


_N_-(4-(3-bromophenyl)but-3-yn-1-yl)-4-methylbenzenesulfonamide (1f)

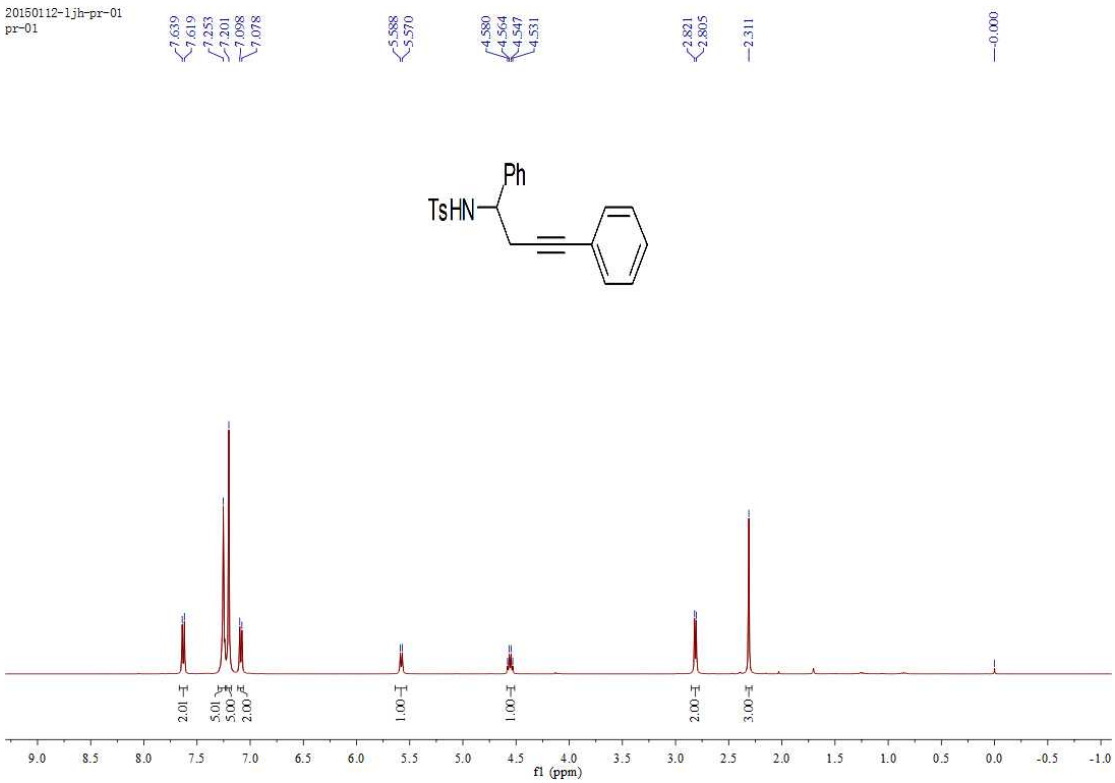


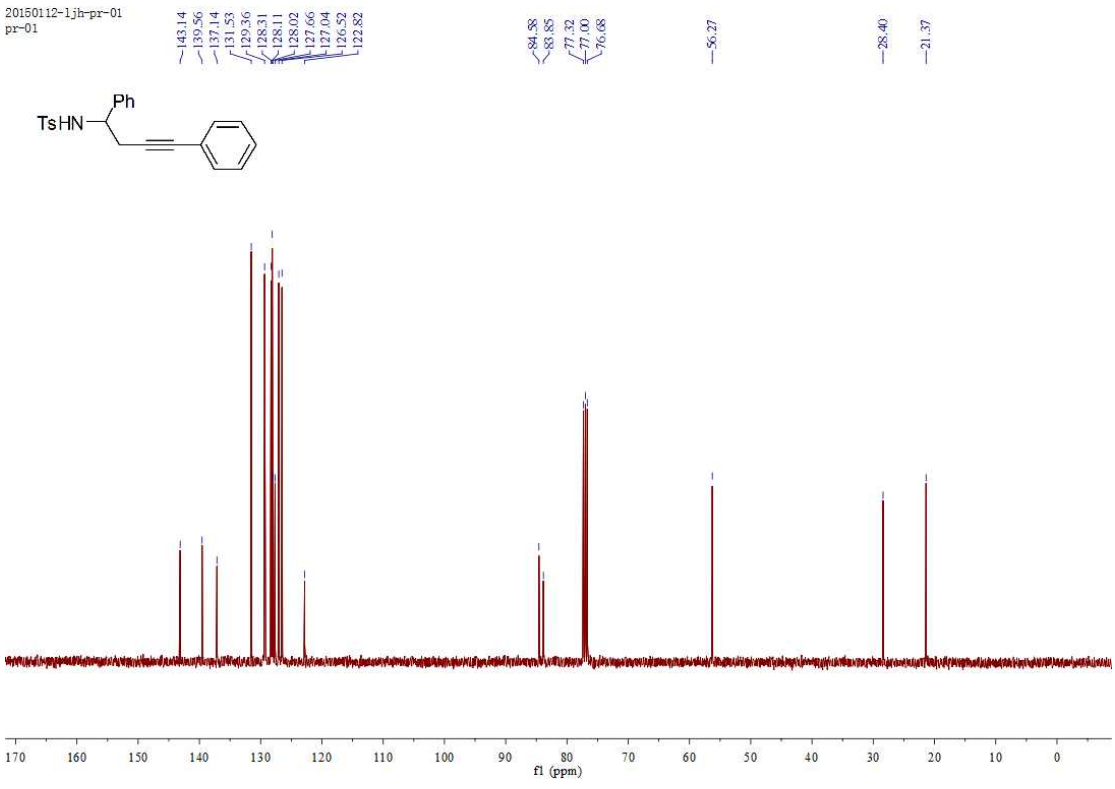
N-(4-(3,5-dimethylphenyl)but-3-yn-1-yl)-4-methylbenzenesulfonamide (1g)



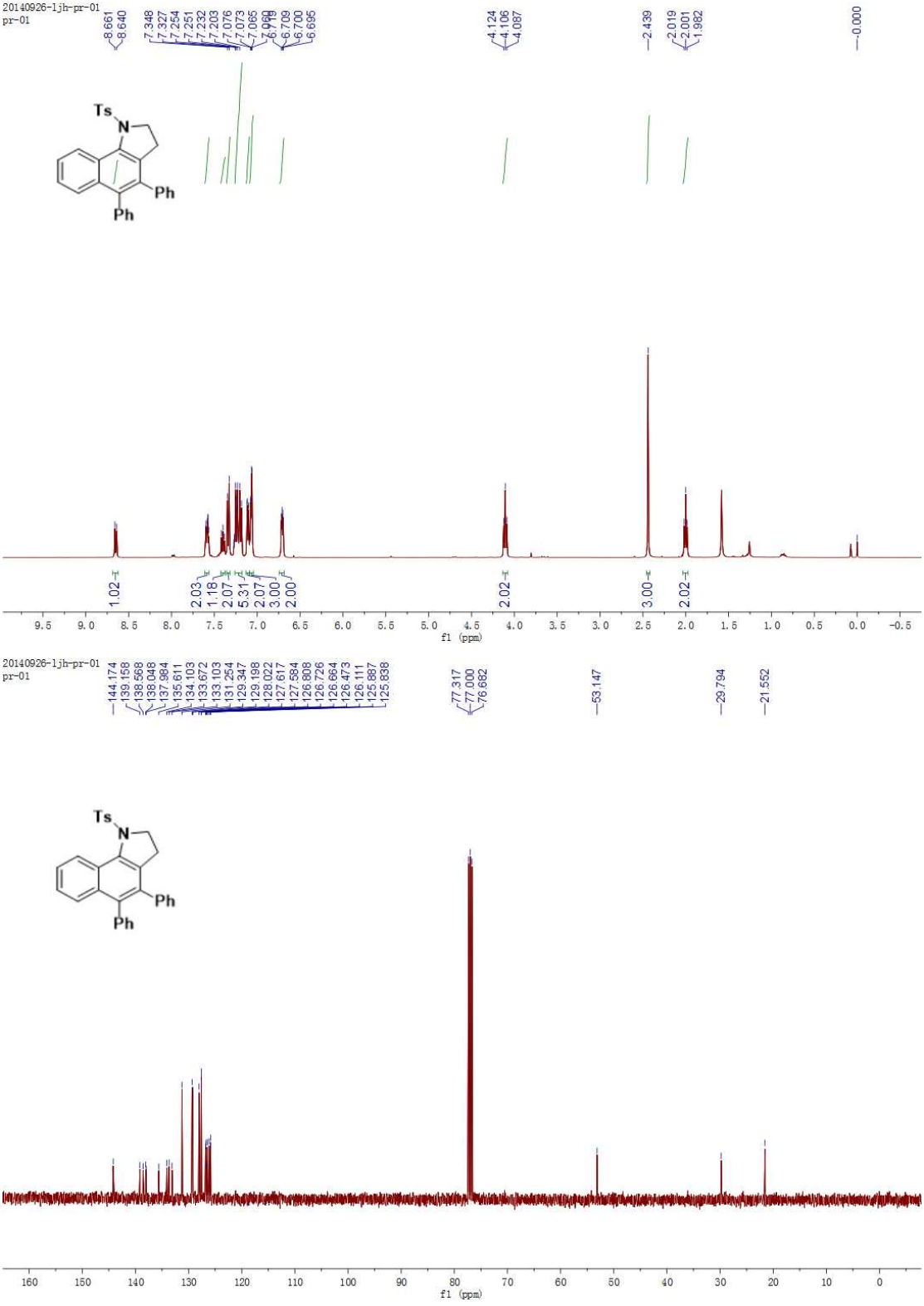


N-(1,4-diphenylbut-3-yn-1-yl)-4-methylbenzenesulfonamide (1h)

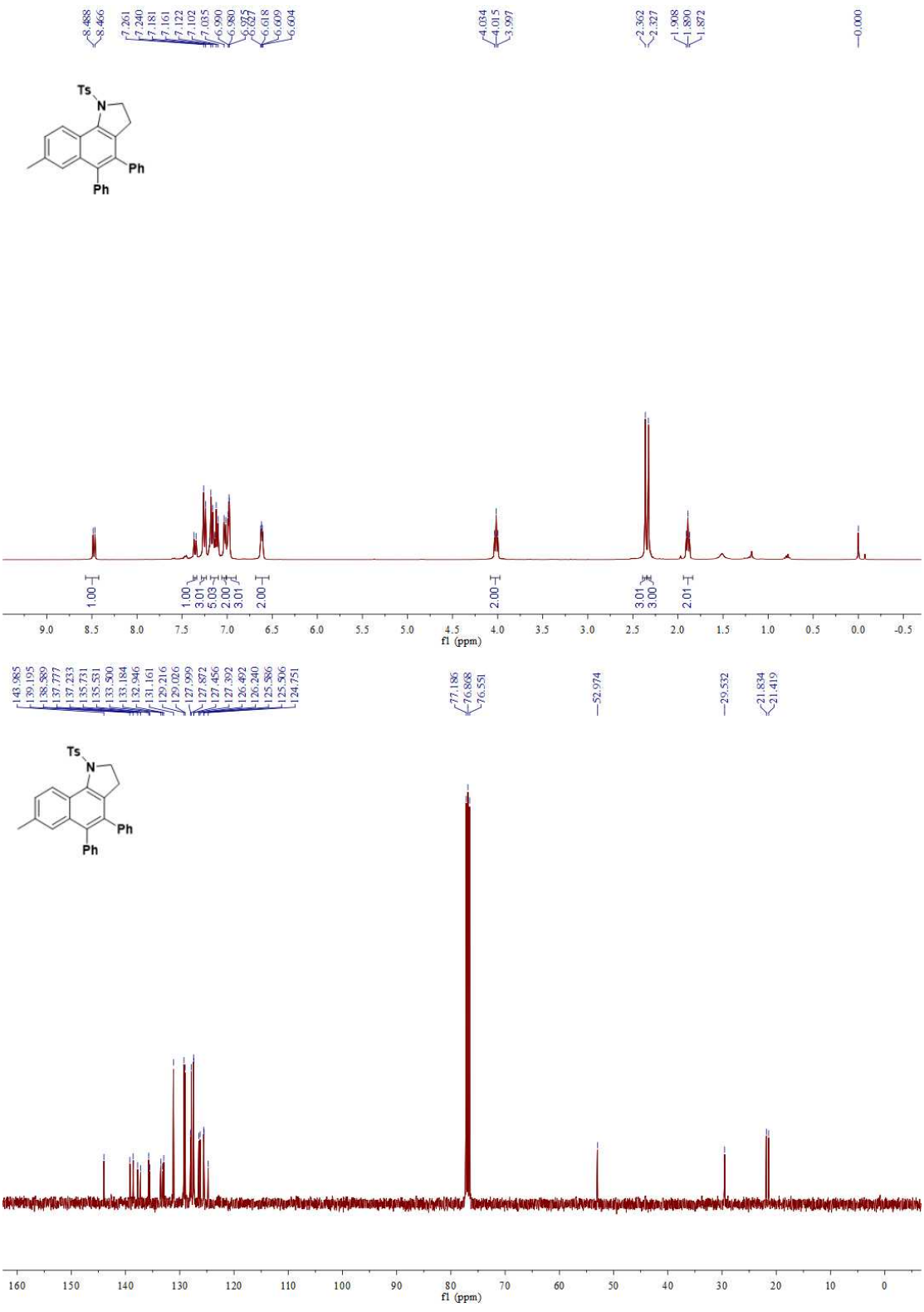




4,5-Diphenyl-1-tosyl-2,3-dihydro-1H-benzo[g]indole (3aa)

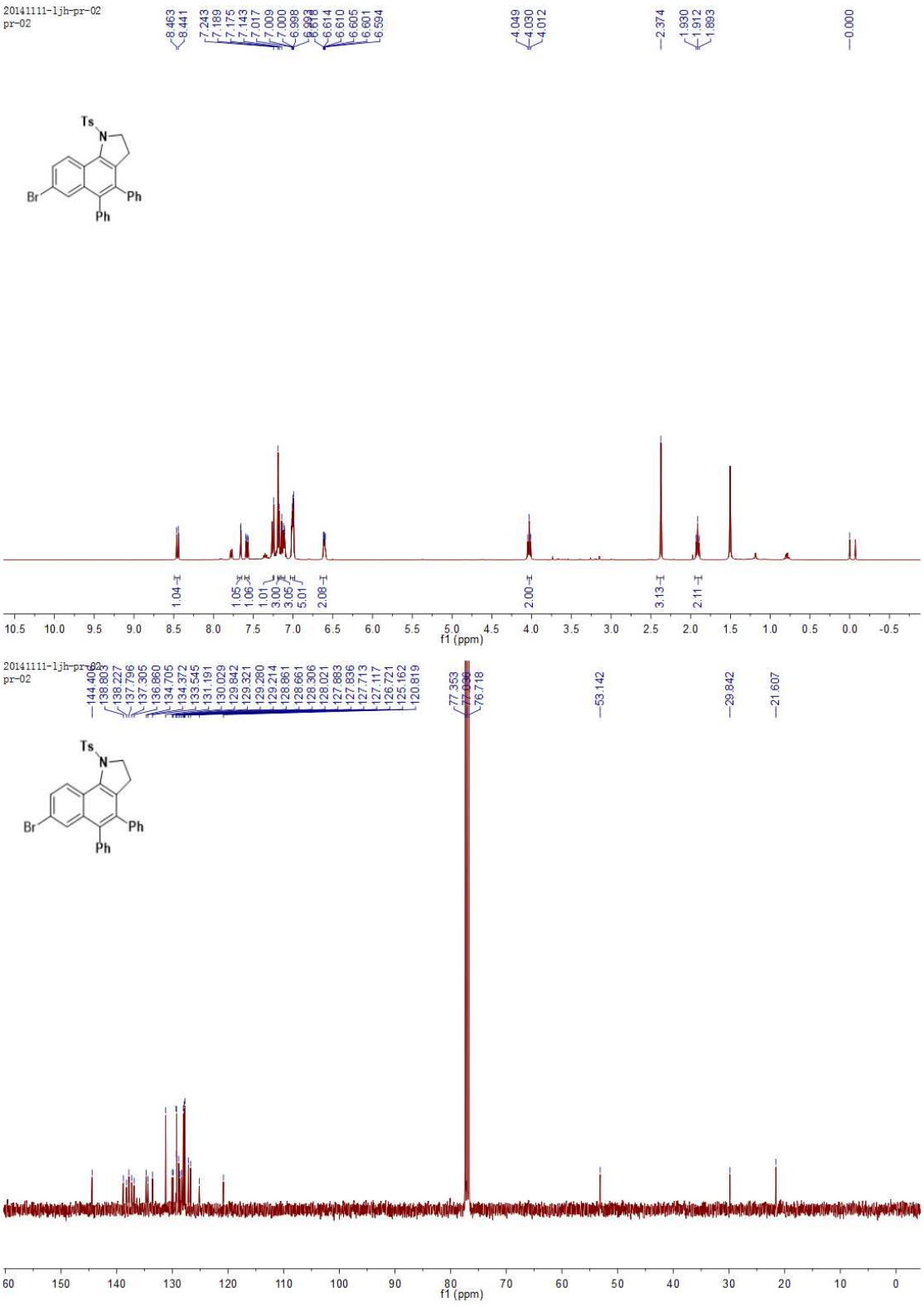


3-Octyl-2,4'-diphenyl-1'-tosylspiro[indene-1,2'-pyrrolidine] (3ba)

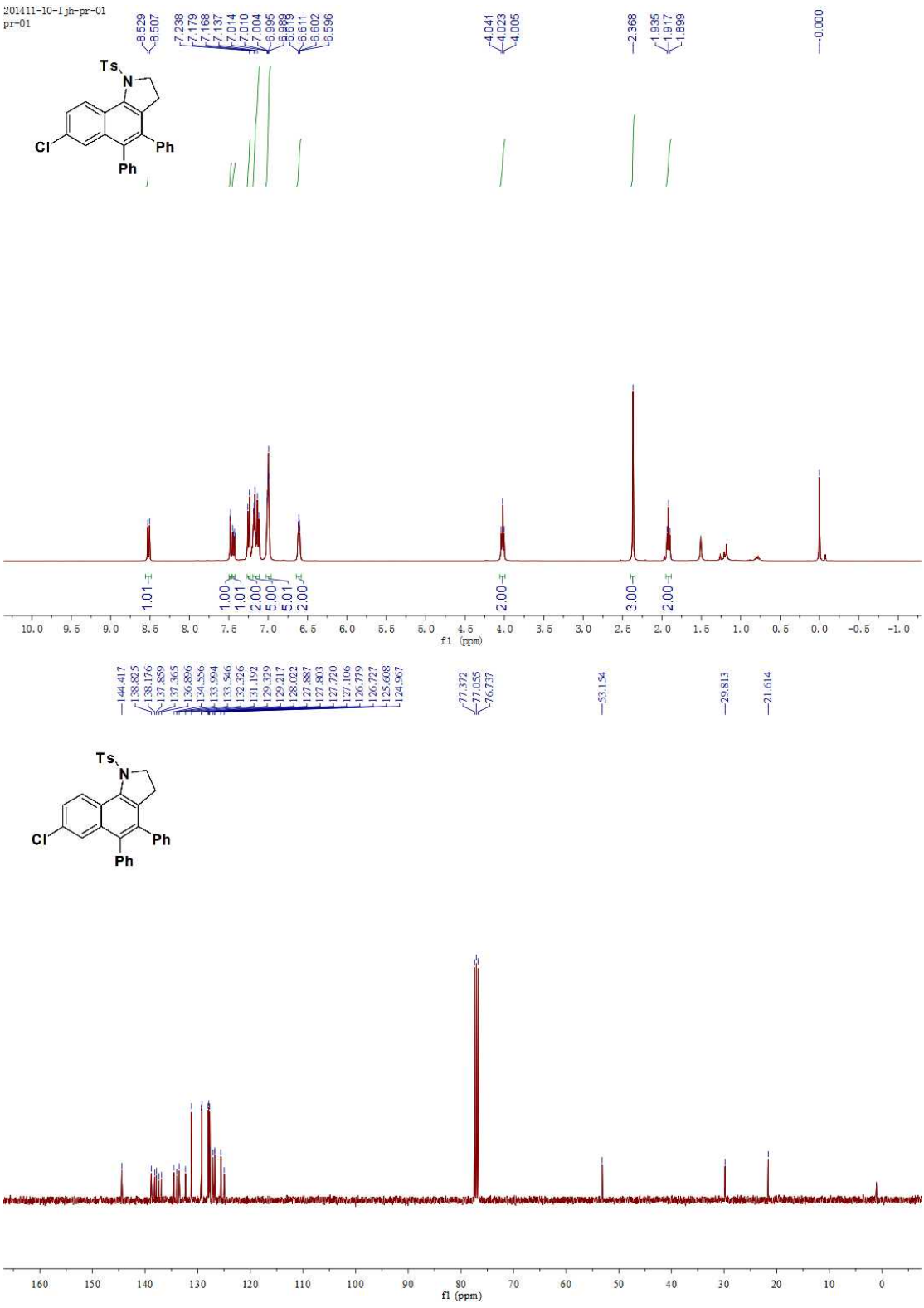


2-(4-Methoxyphenyl)-3-octyl-4'-phenyl-1'-tosylspiro[indene-1,2'-pyrrolidine]

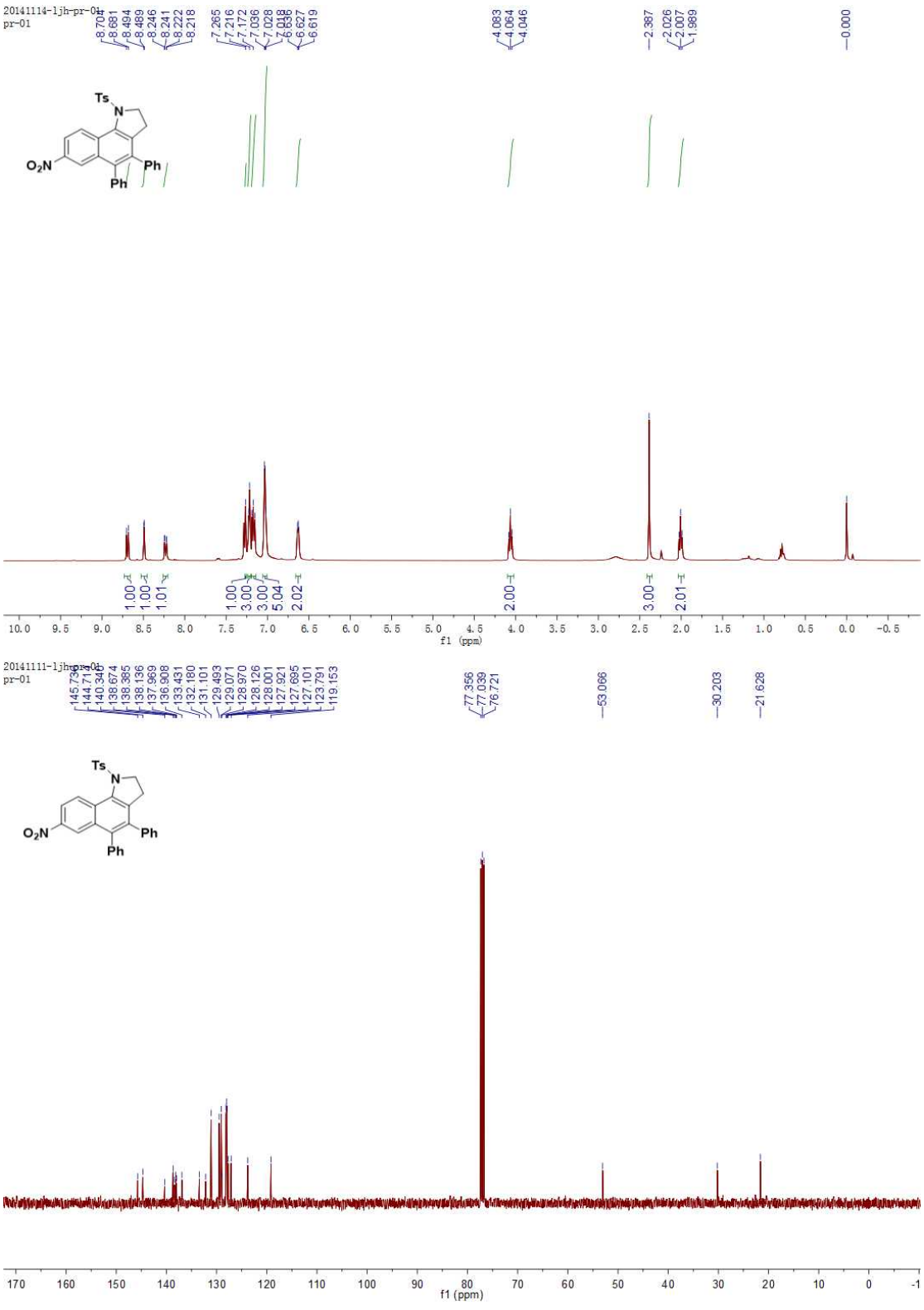
(3ca)



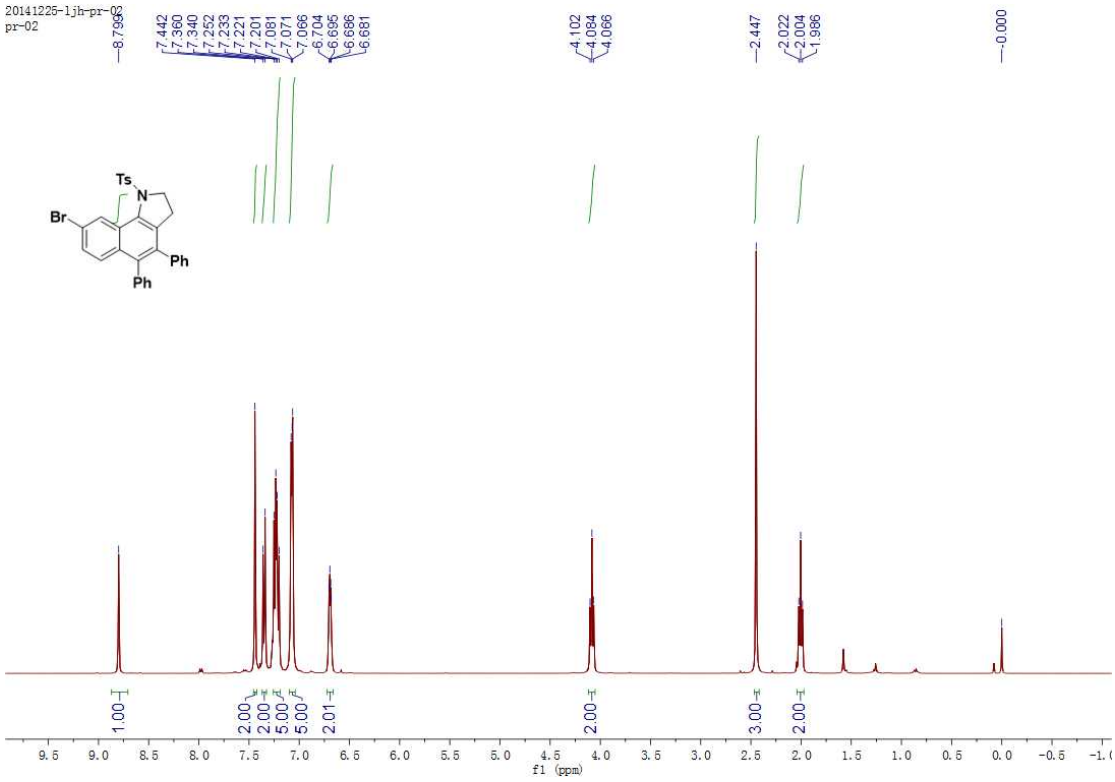
3-(4-Methoxybutyl)-2,4'-diphenyl-1'-tosylspiro[indene-1,2'-pyrrolidine] (3da)

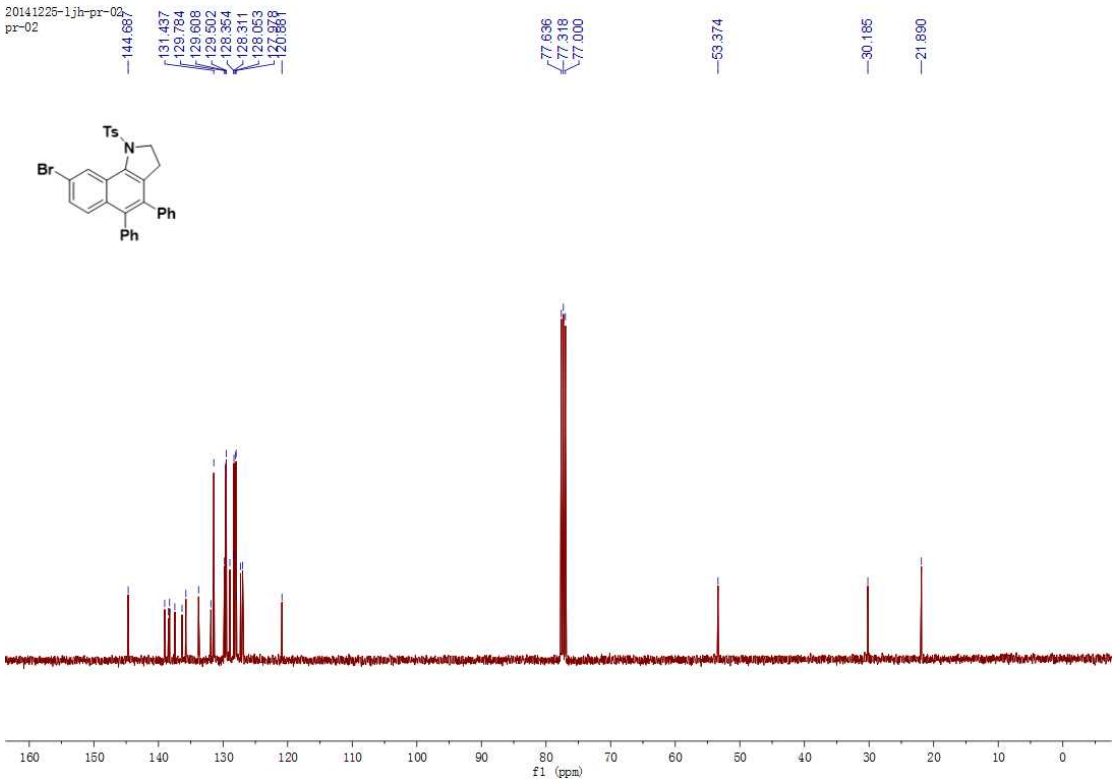


4-(2,4'-Diphenyl-1'-tosylspiro[indene-1,2'-pyrrolidin]-3-yl)butyl acetate (3ea)

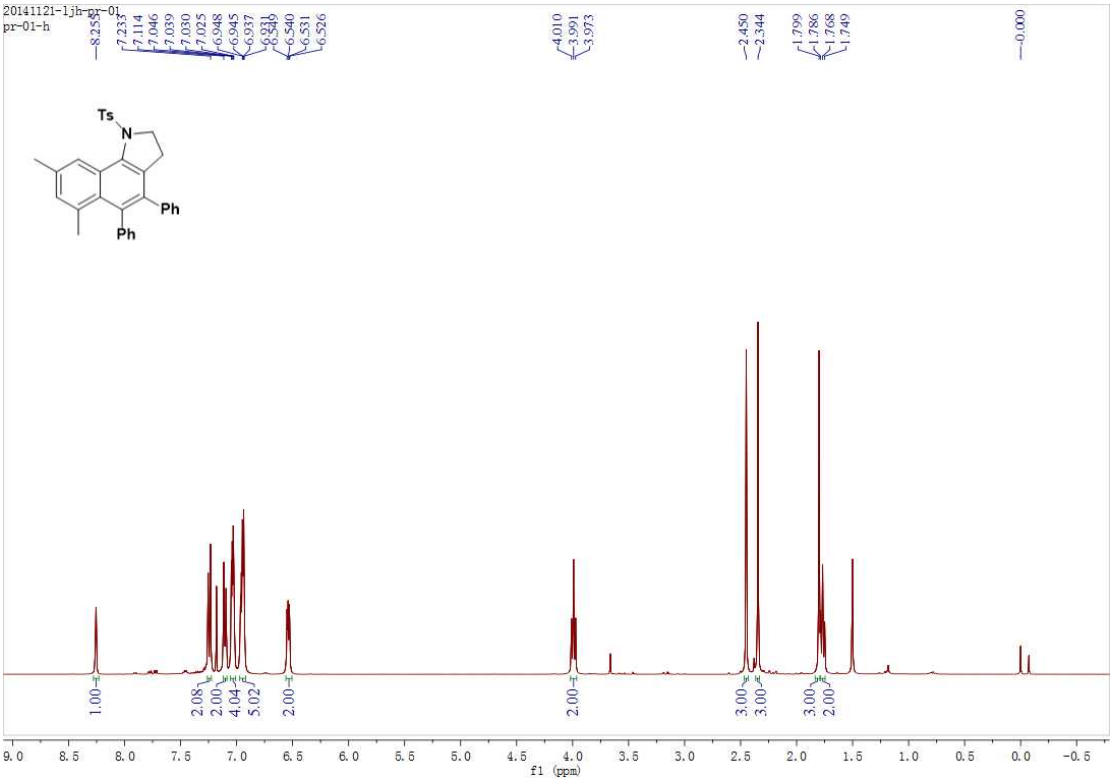


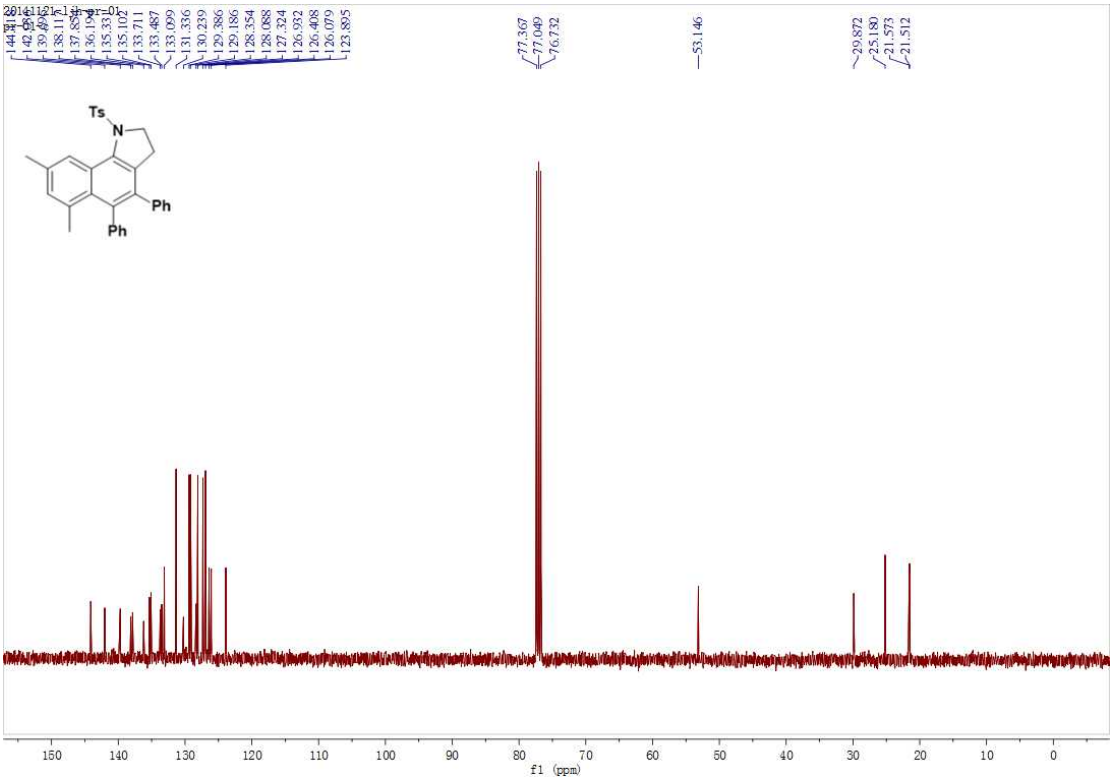
6-Bromo-4,5-diphenyl-1-tosyl-2,3-dihydro-1H-benzo[g]indole (3fa)



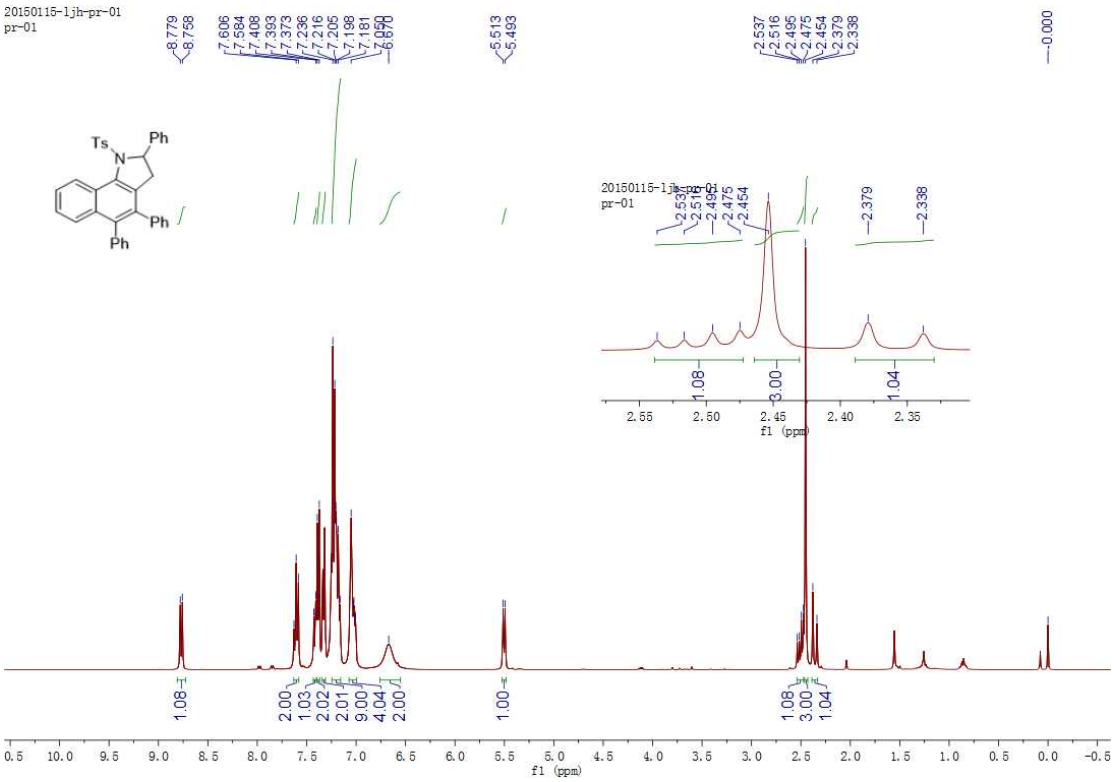


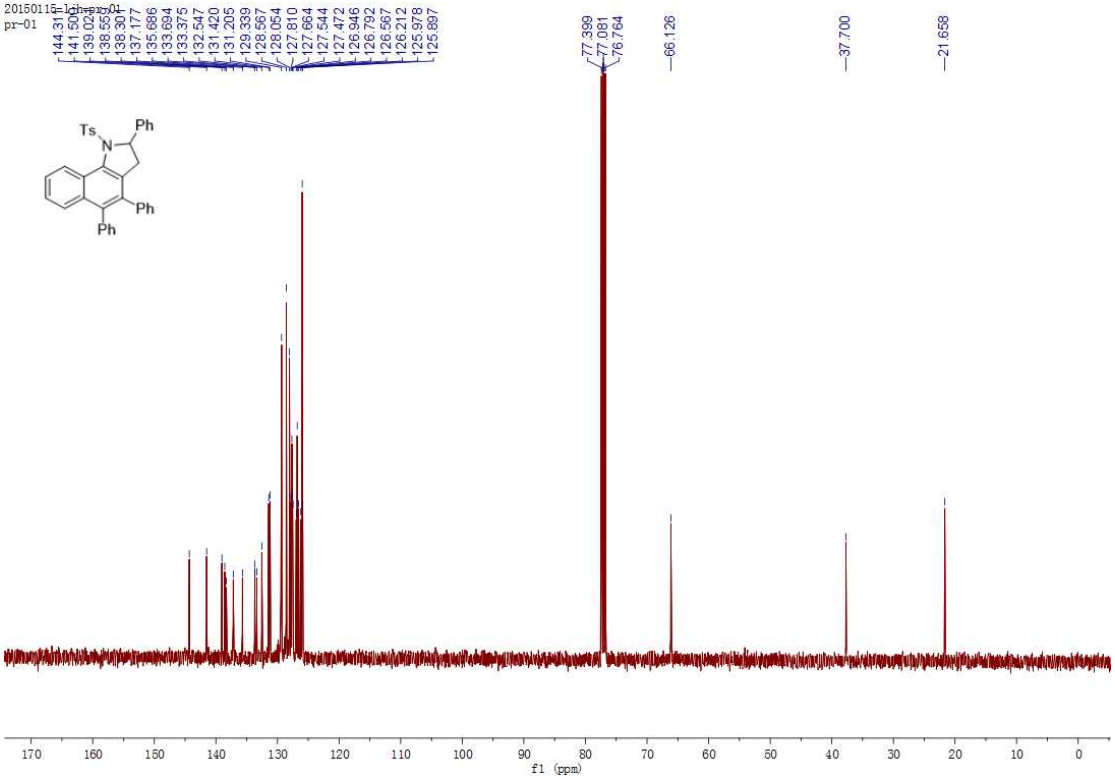
6,8-Dimethyl-4,5-diphenyl-1-tosyl-2,3-dihydro-1H-benzo[g]indole (3ga)



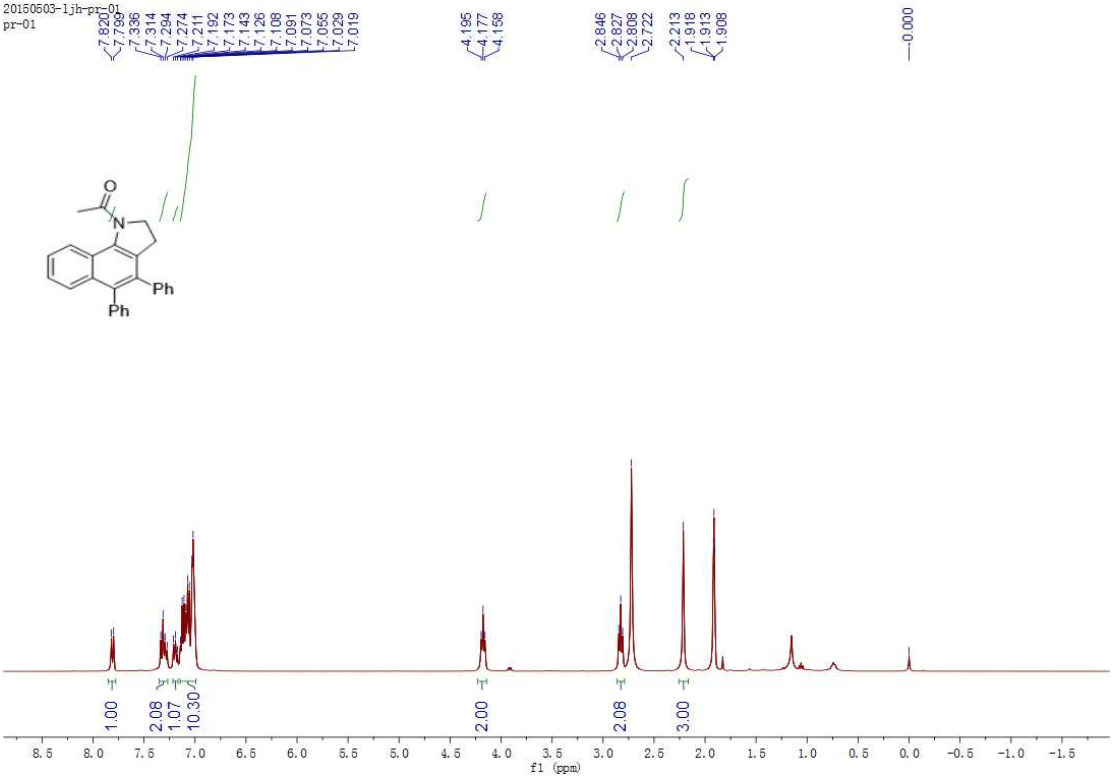


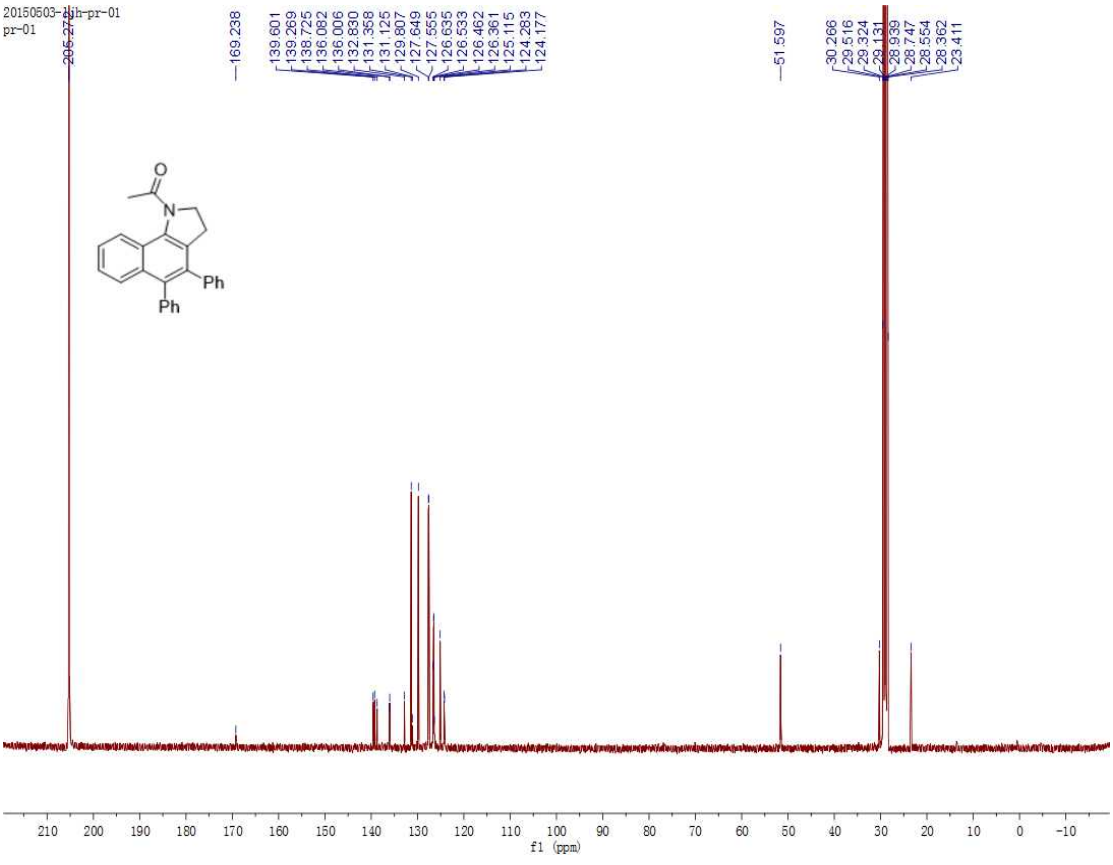
2,4,5-Triphenyl-1-tosyl-2,3-dihydro-1*H*-benzo[g]indole (3ha)



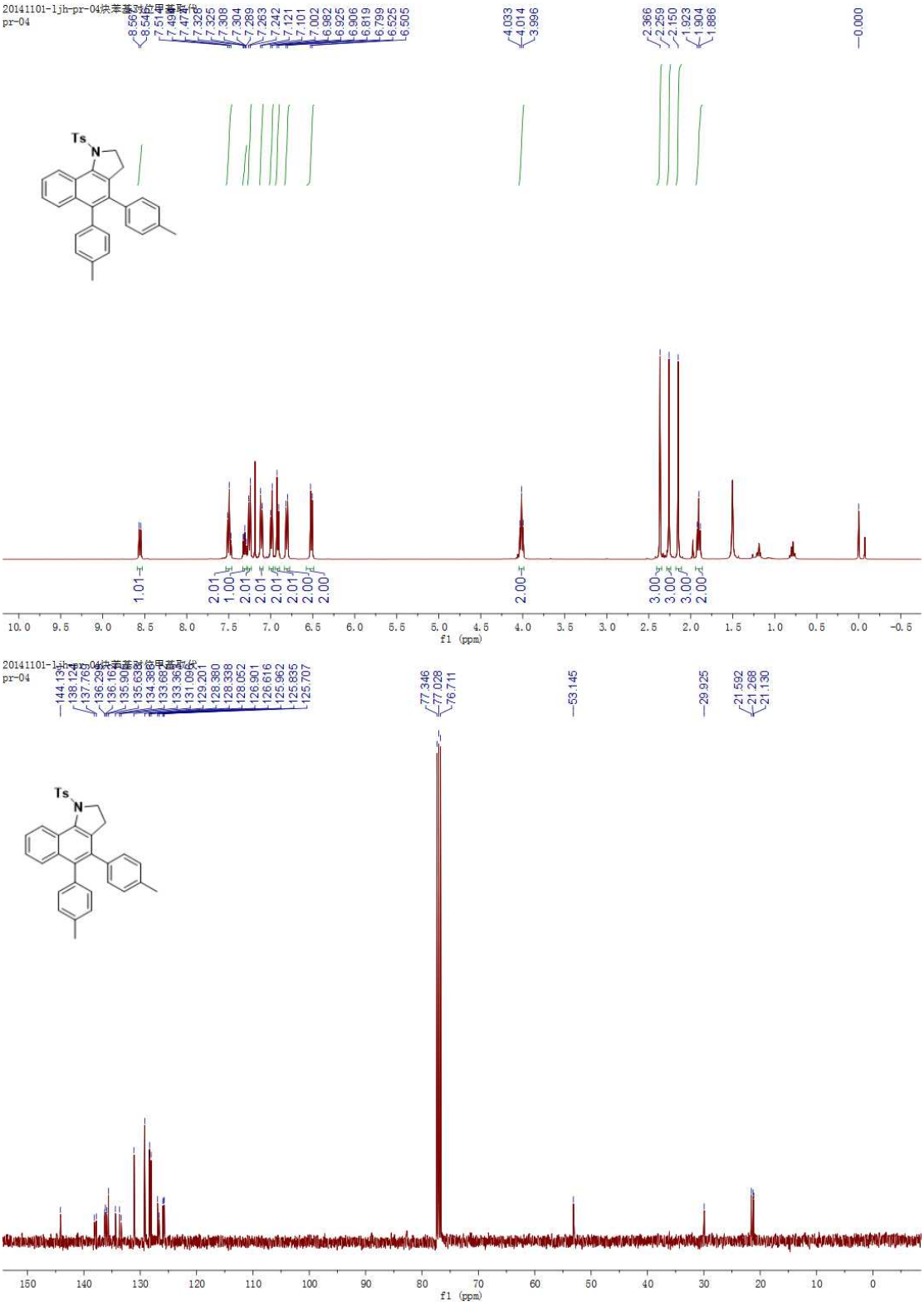


1-(4,5-Diphenyl-2,3-dihydro-1*H*-benzo[*g*]indol-1-yl)ethan-1-one (3ia)

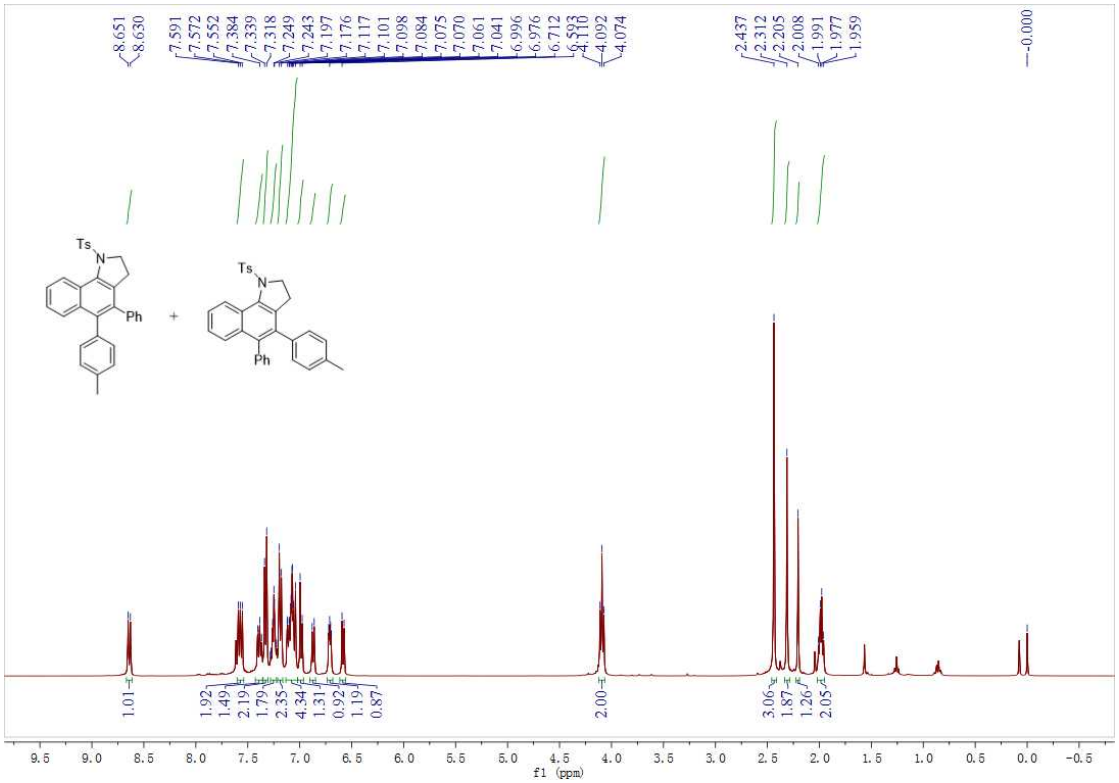


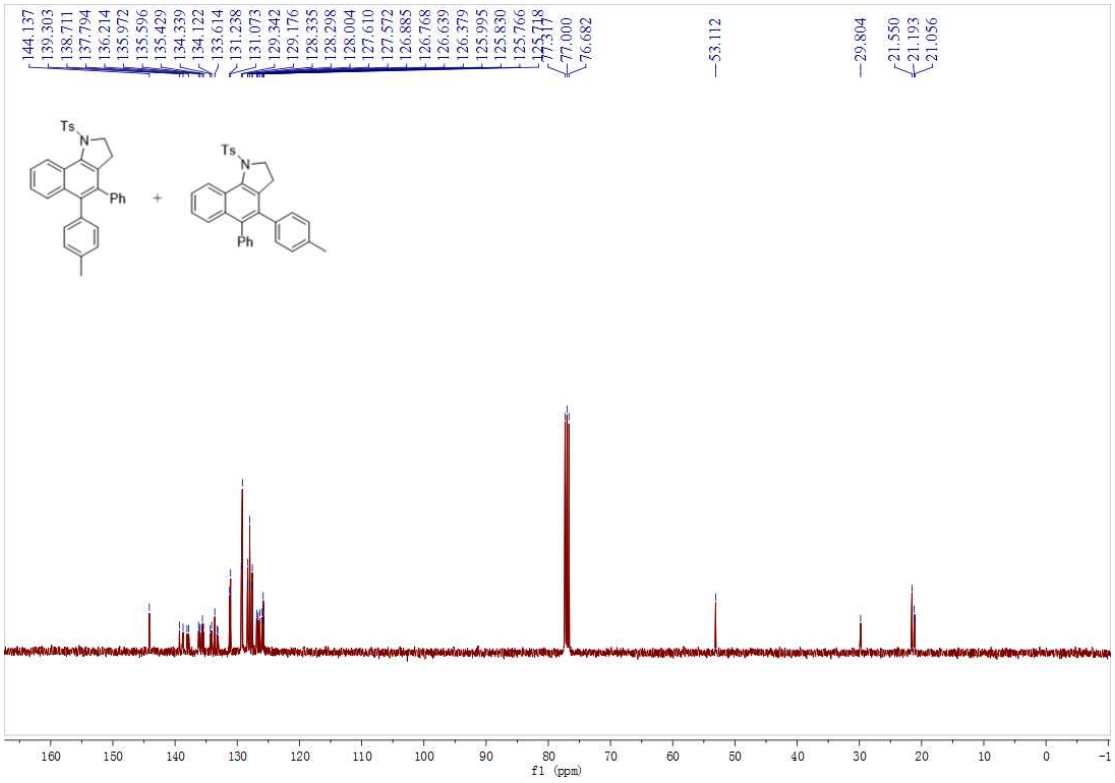


4,5-Di-p-tolyl-1-tosyl-2,3-dihydro-1H-benzo[g]indole (3ab)

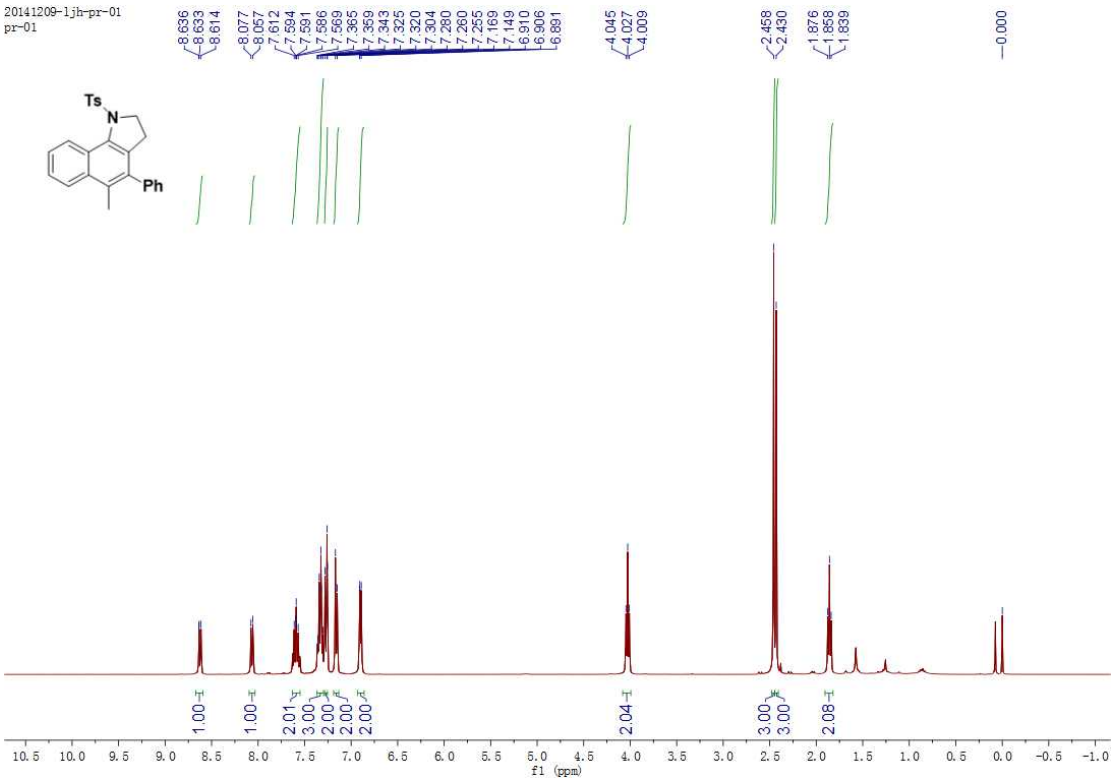


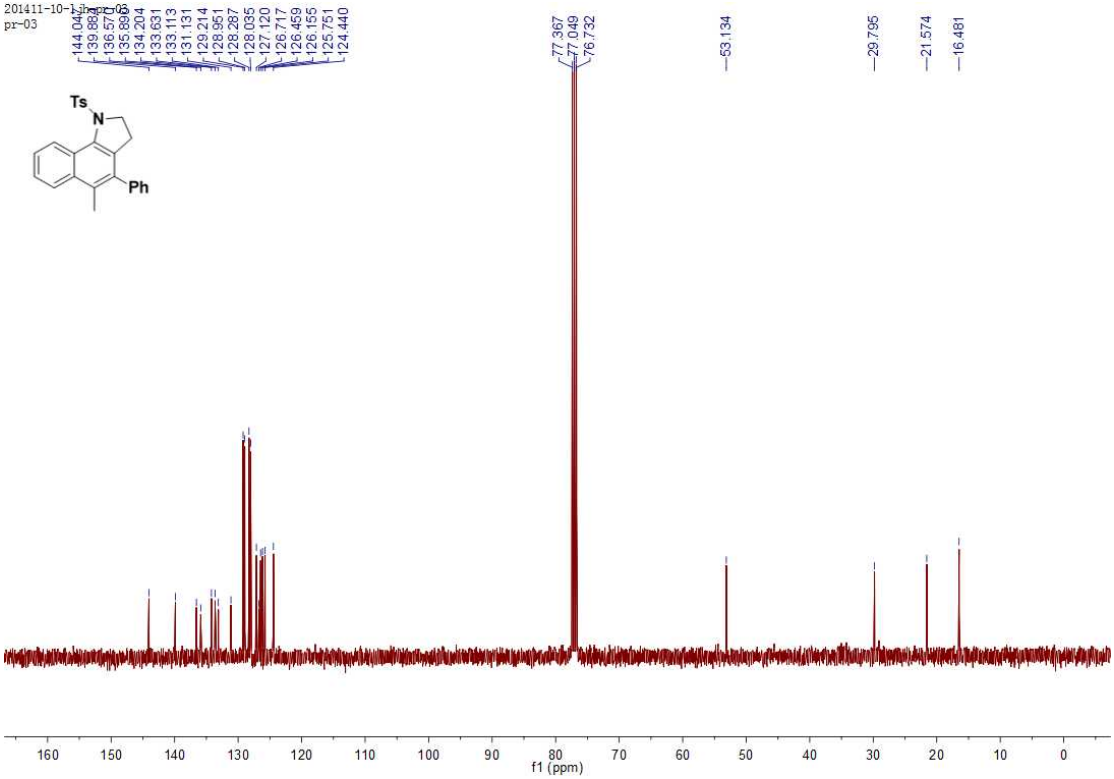
5-Phenyl-4-(p-tolyl)-1-tosyl-2,3-dihydro-1H-benzo[g]indole (3ac)



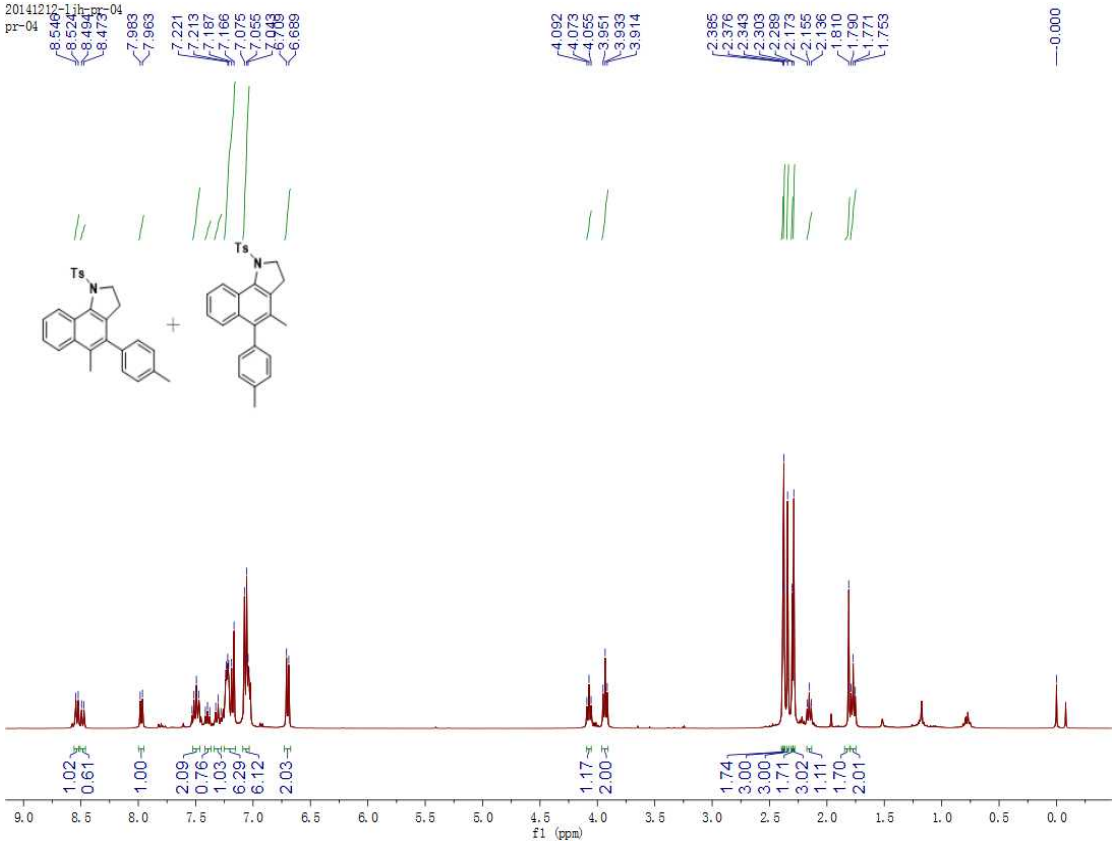


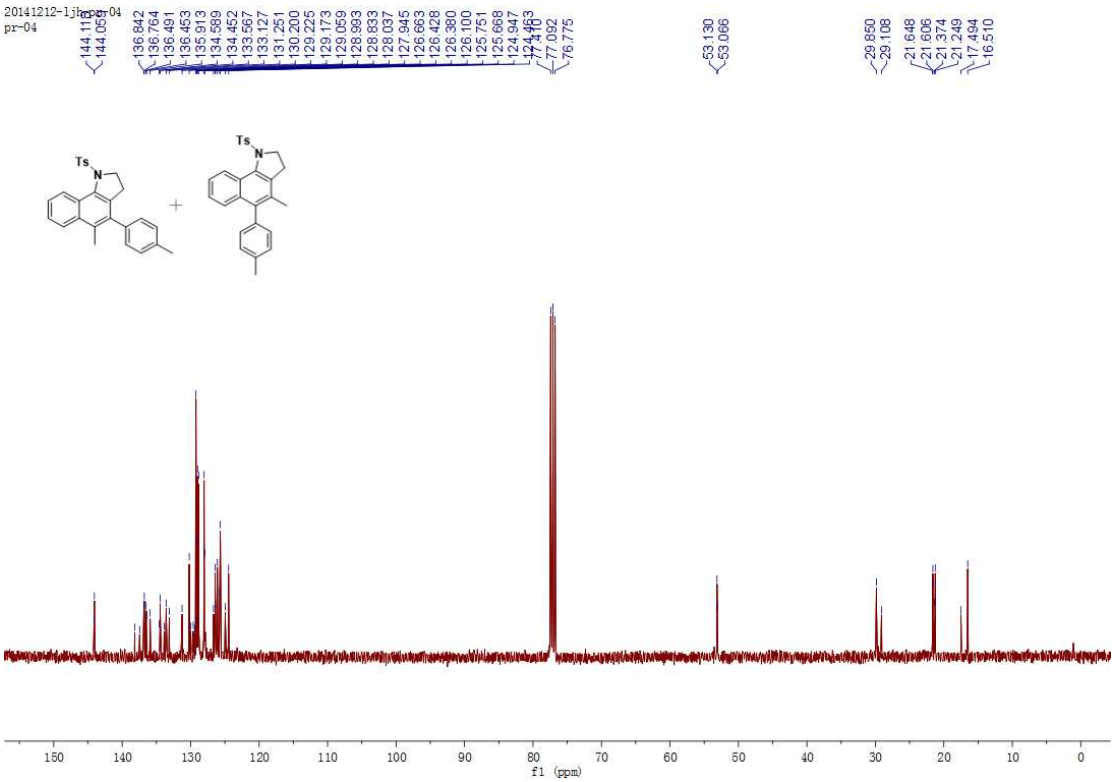
3-(3-Chloropropyl)-2,4'-diphenyl-1'-tosylspiro[indene-1,2'-pyrrolidine] (3ad)



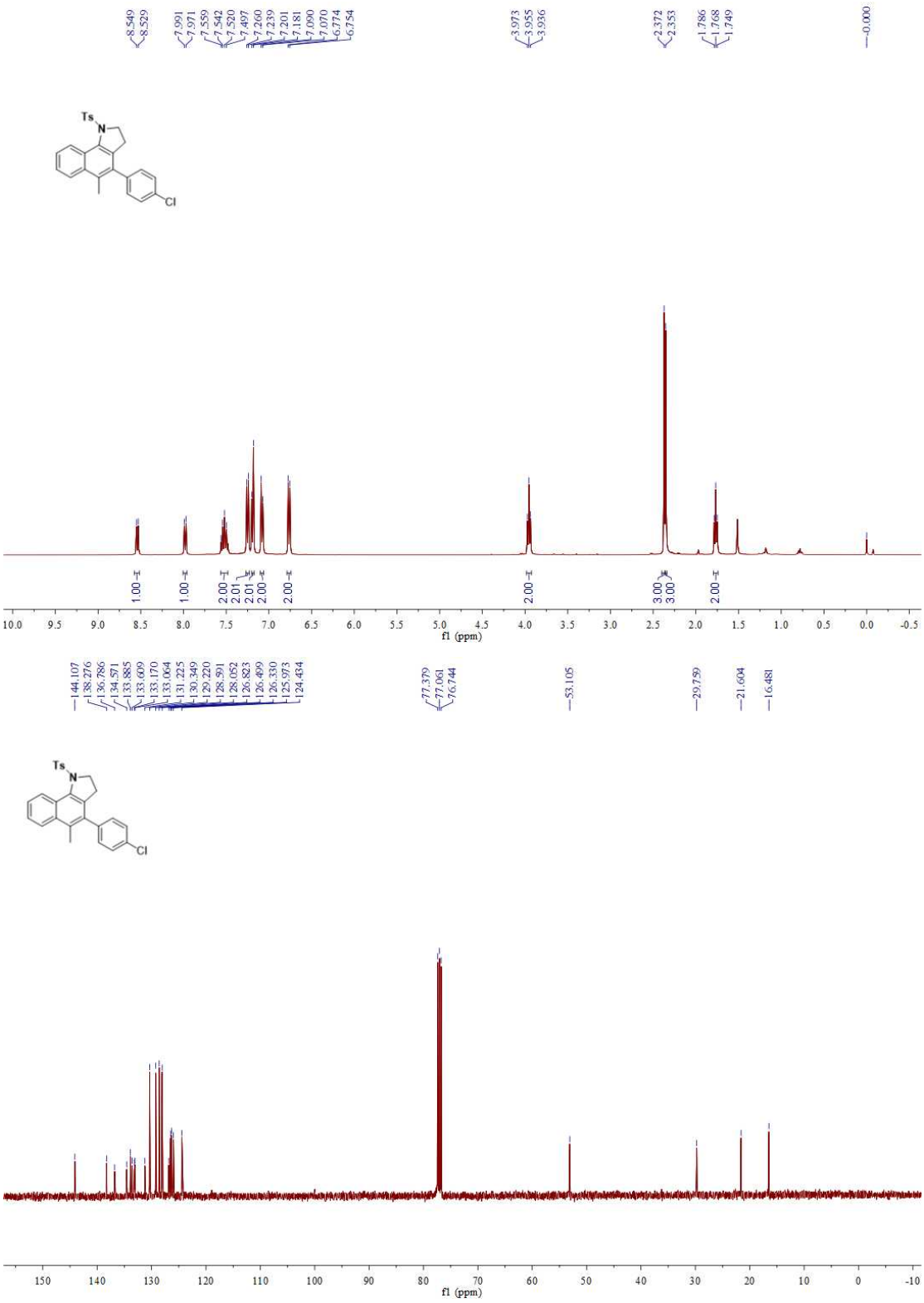


4-Methyl-5-(*p*-tolyl)-1-tosyl-2,3-dihydro-1*H*-benzo[g]indole (3ae)

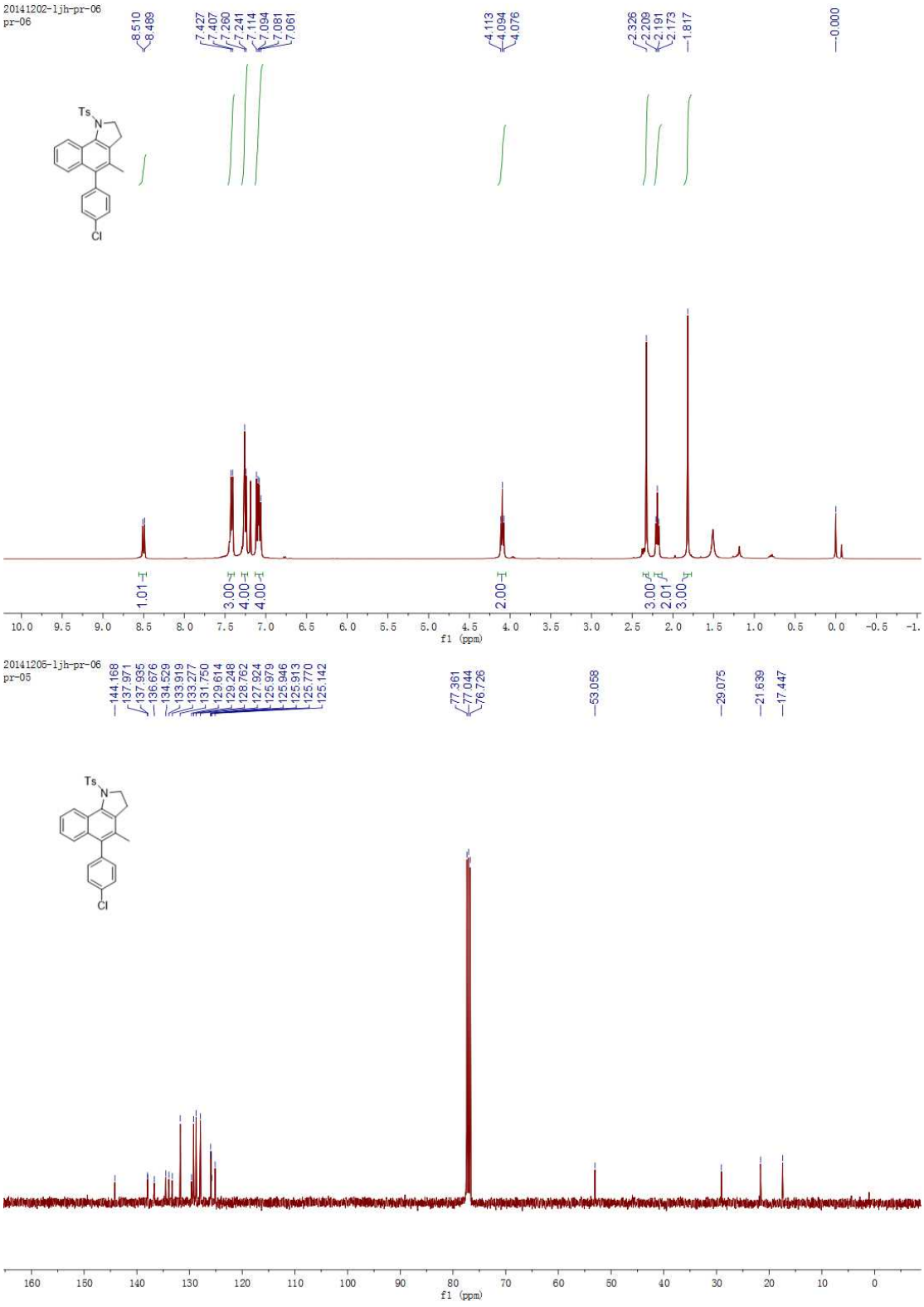




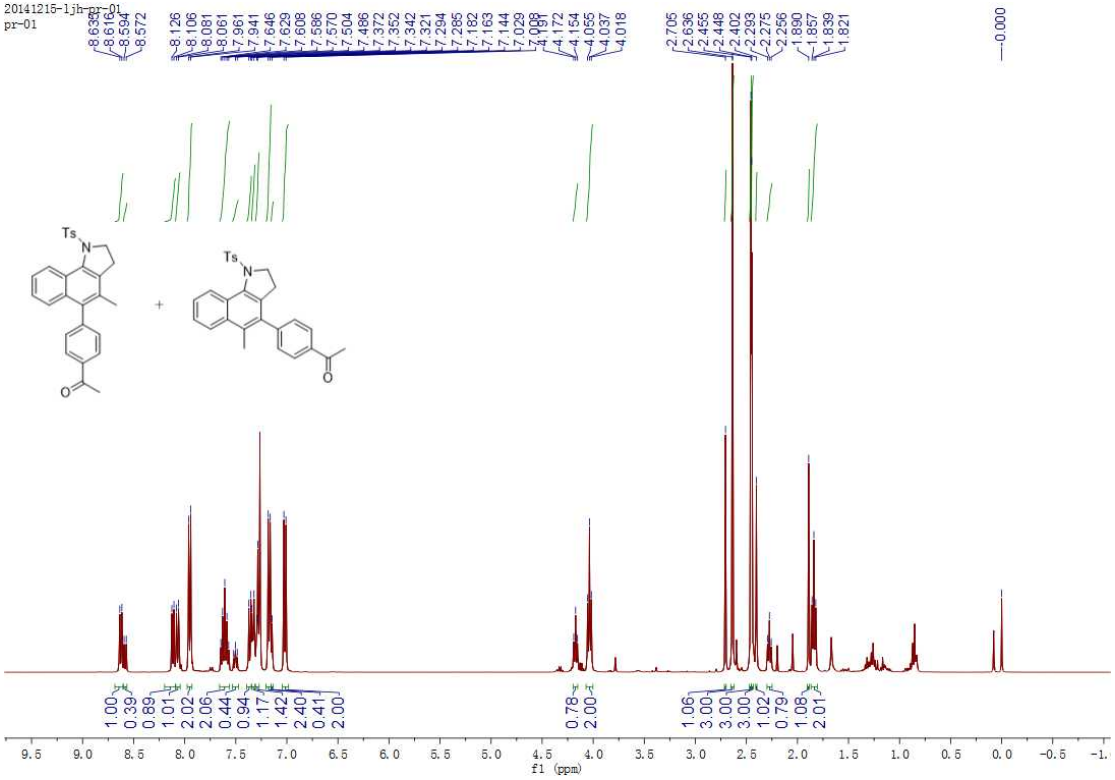
5-(4-Chlorophenyl)-4-methyl-1-tosyl-2,3-dihydro-1*H*-benzo[g]indole (3af)

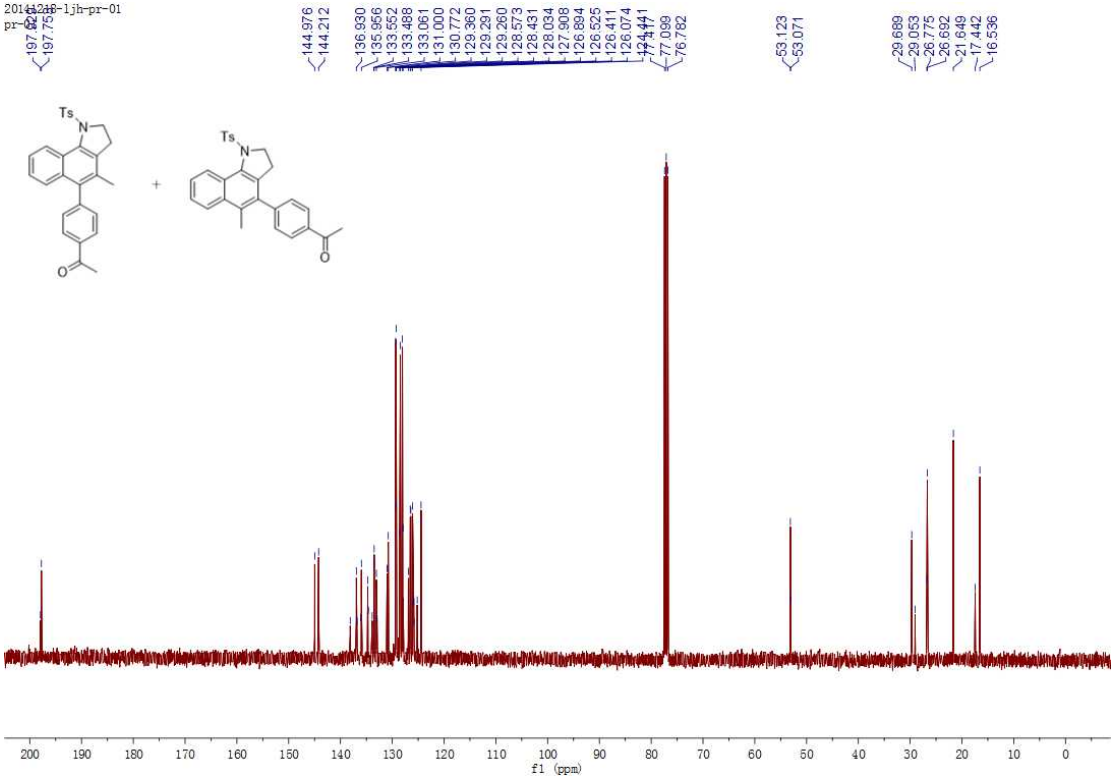


4-(4-Chlorophenyl)-5-methyl-1-tosyl-2,3-dihydro-1*H*-benzo[g]indole (3af')

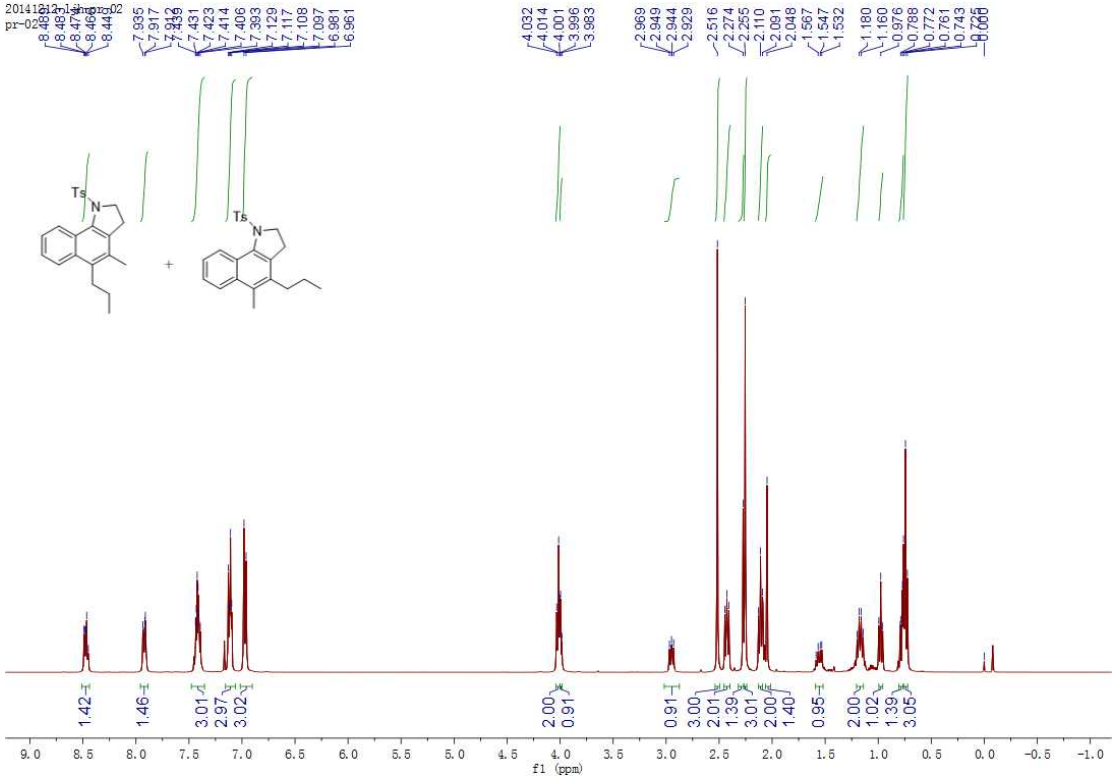


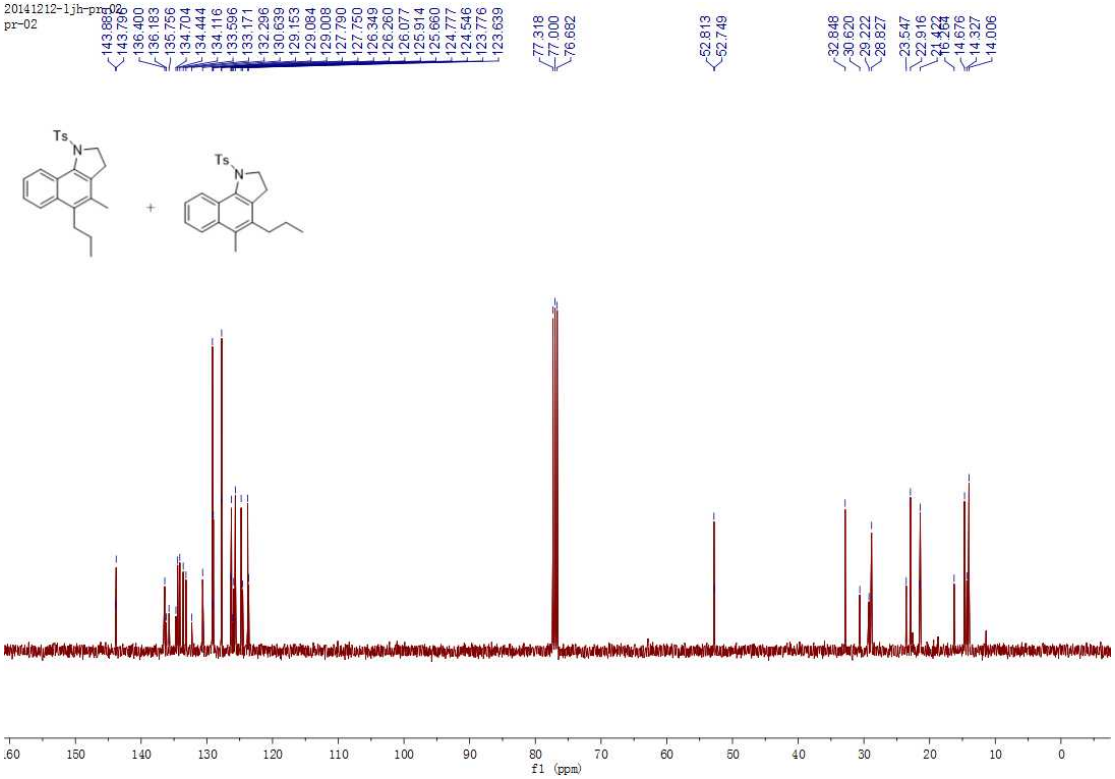
1-(4-(4-Methyl-1-tosyl-2,3-dihydro-1*H*-benzo[g]indol-5-yl)phenyl)ethan-1-one (3ag)



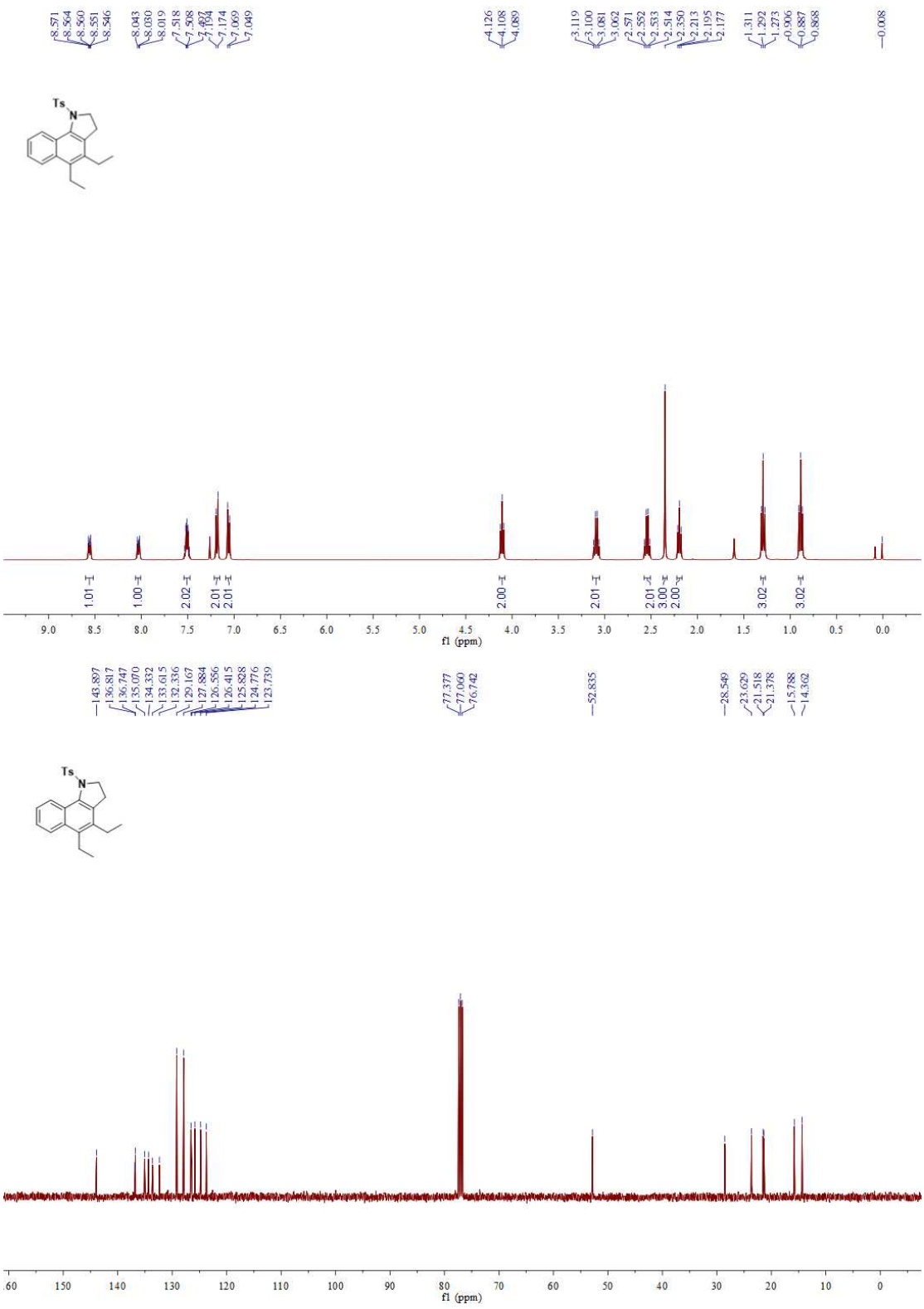


4-Methyl-5-propyl-1-tosyl-2,3-dihydro-1*H*-benzo[g]indole (3ah)



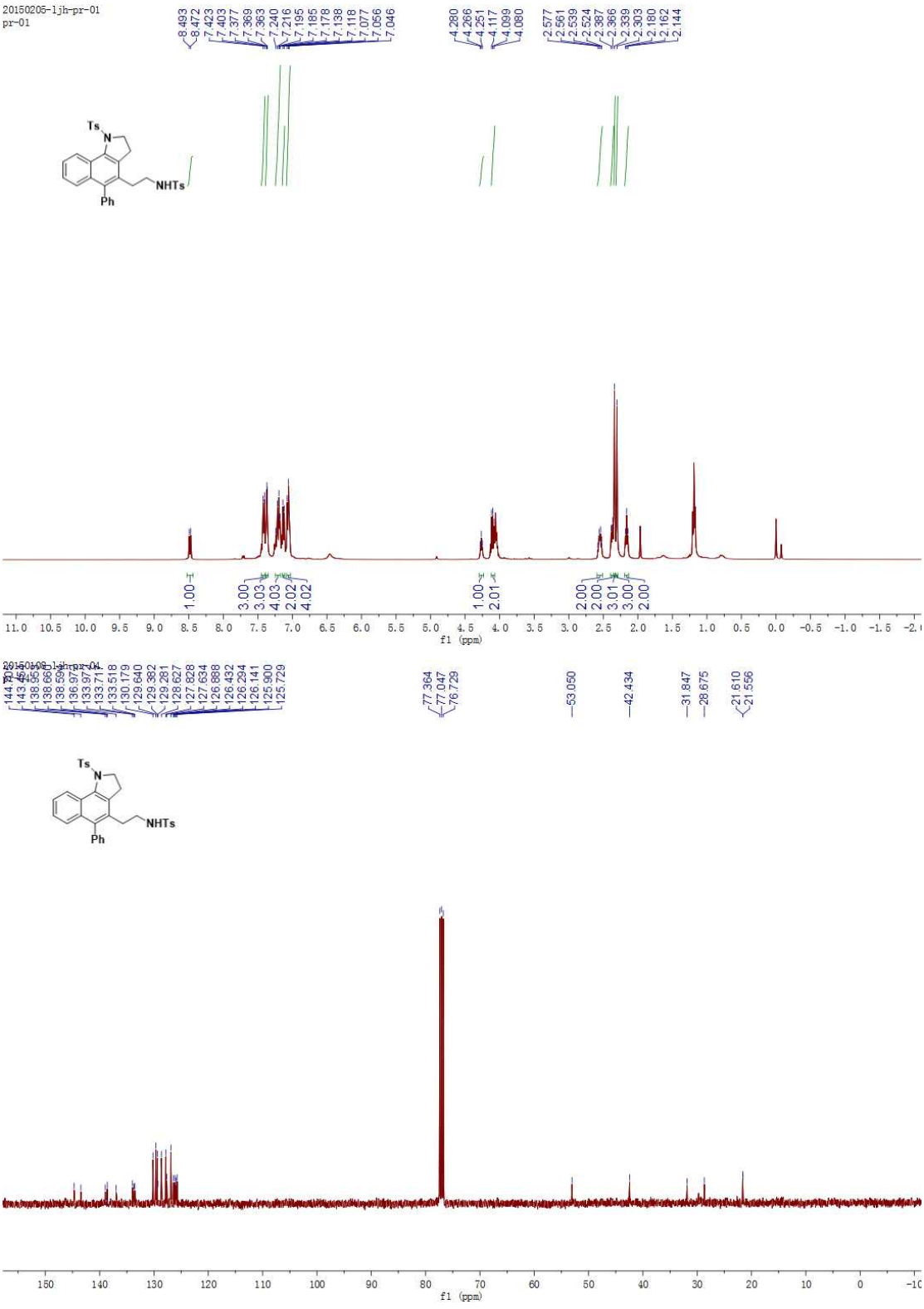


4,5-Diethyl-1-tosyl-2,3-dihydro-1*H*-benzo[g]indole (3ai)



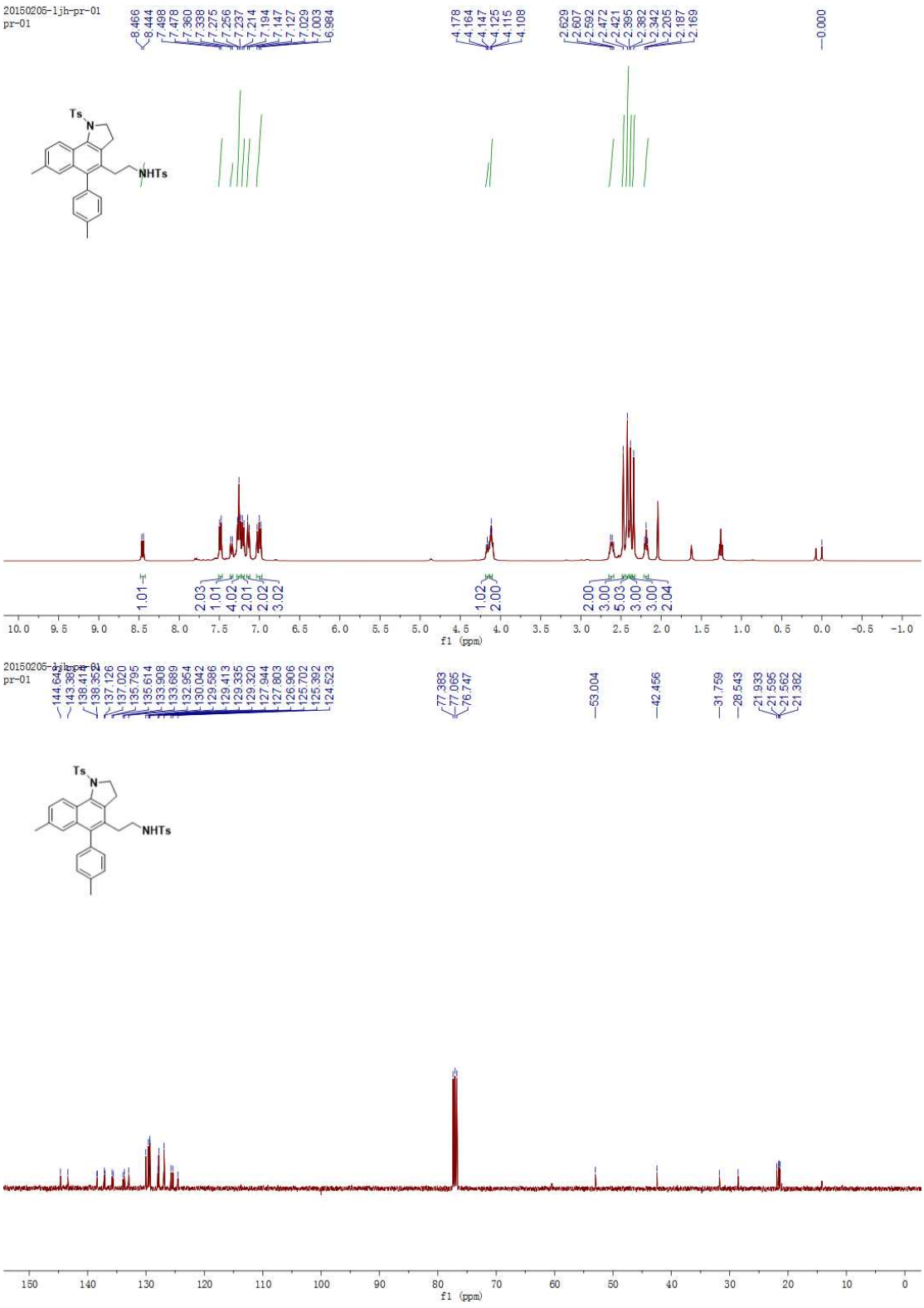
4-Methyl-*N*-(2-(5-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[g]indol-4-yl)ethyl)benzen

esulfonamide (4a)

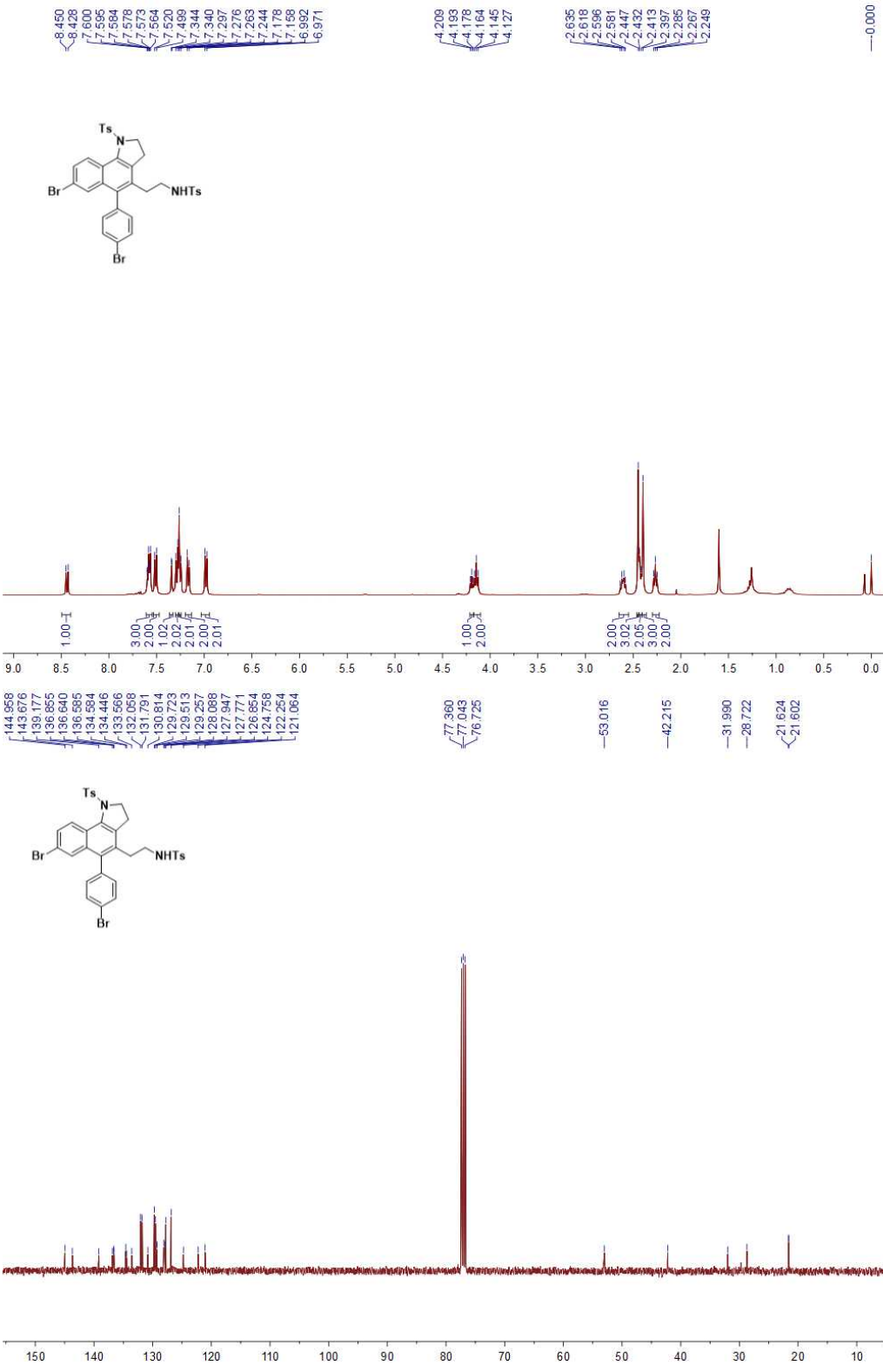


4-Methyl-*N*-(2-(7-methyl-5-(p-tolyl)-1-tosyl-2,3-dihydro-1*H*-benzo[g]indol-4-yl)et

hyl)benzenesulfonamide (4b)

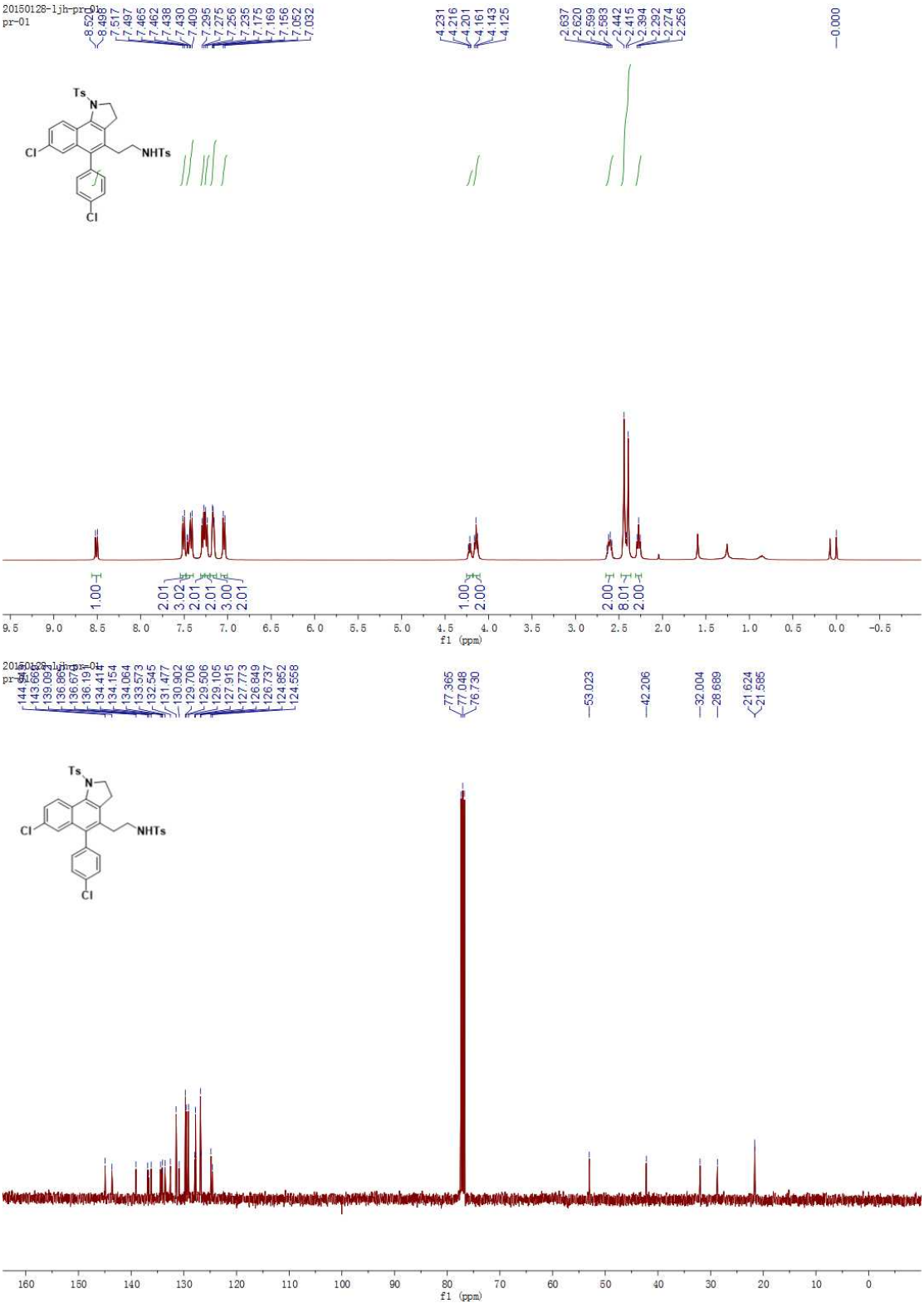


_N_-(7-Bromo-5-(4-bromophenyl)-1-tosyl-2,3-dihydro-1H-benzo[g]indol-4-yl)-4-methylbenzenesulfonamide (4c)

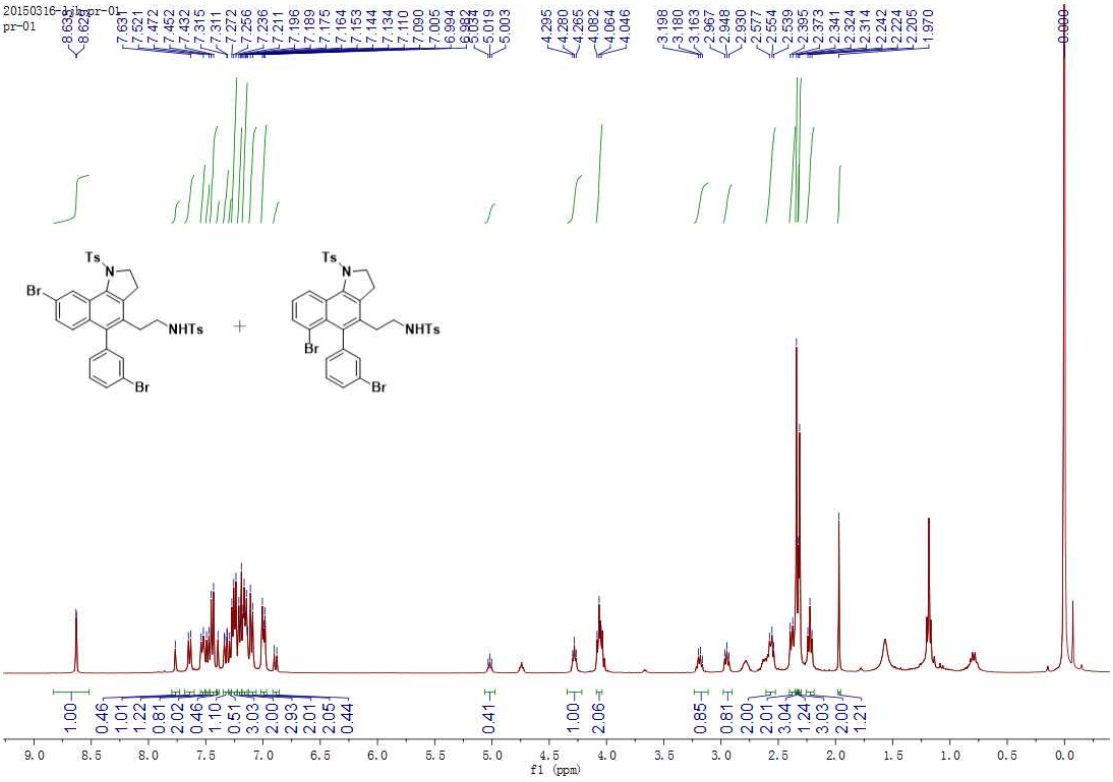


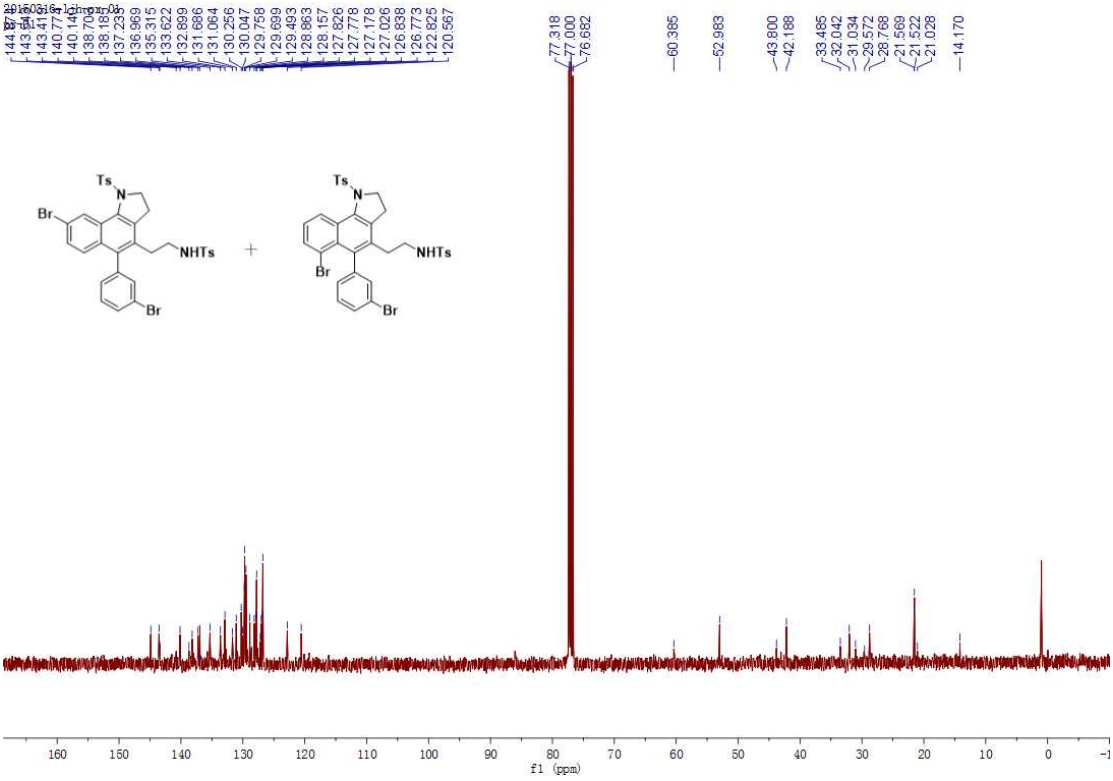
_N_-(2-(7-Chloro-5-(4-chlorophenyl)-1-tosyl-2,3-dihydro-1_H_-benzo[g]indol-4-yl)eth

yl)-4-methylbenzenesulfonamide (4d)

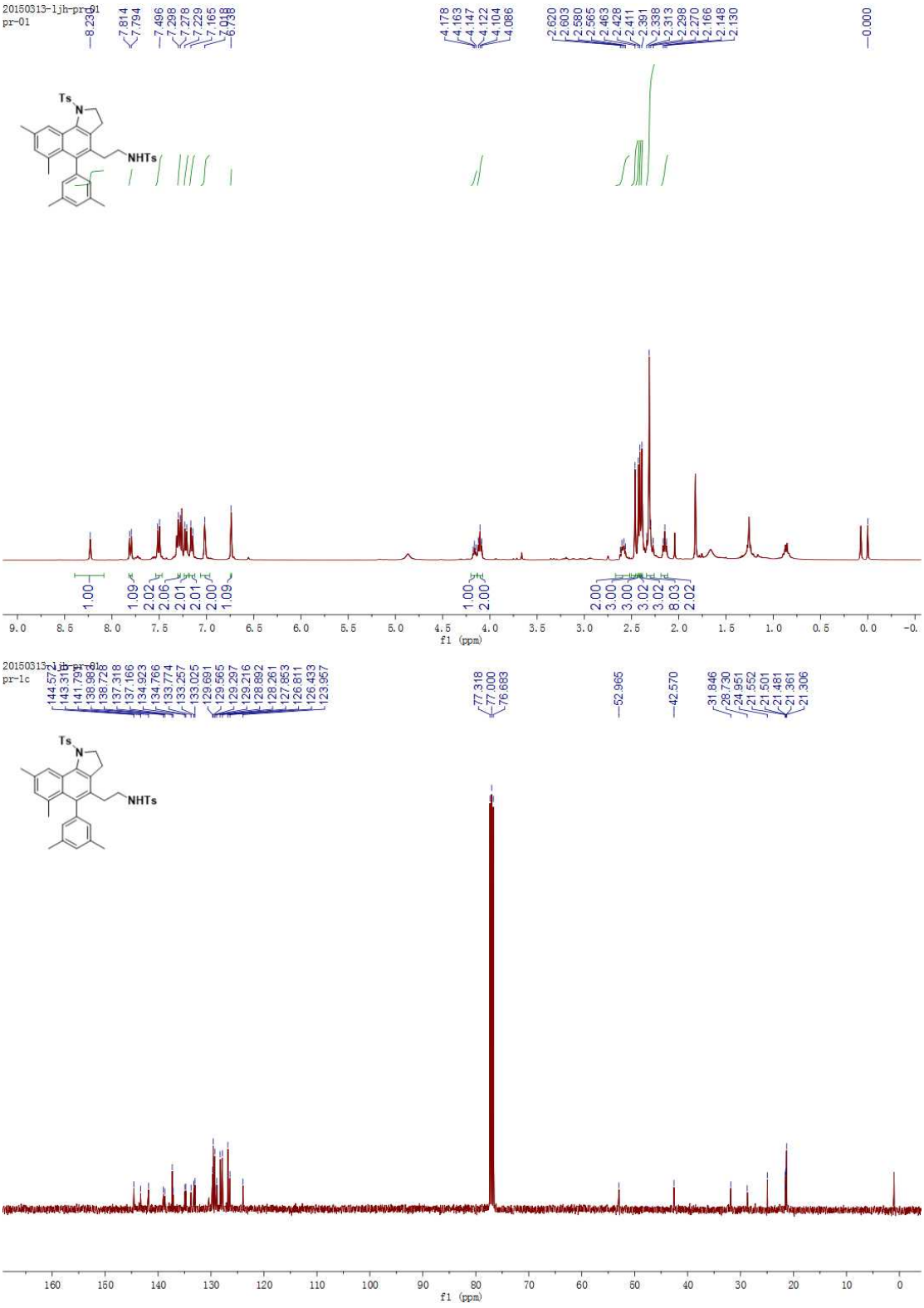


_N_-(2-(8-Bromo-5-(3-bromophenyl)-1-tosyl-2,3-dihydro-1H-benzo[g]indol-4-yl)eth yl)-4-methylbenzenesulfonamide (4f)

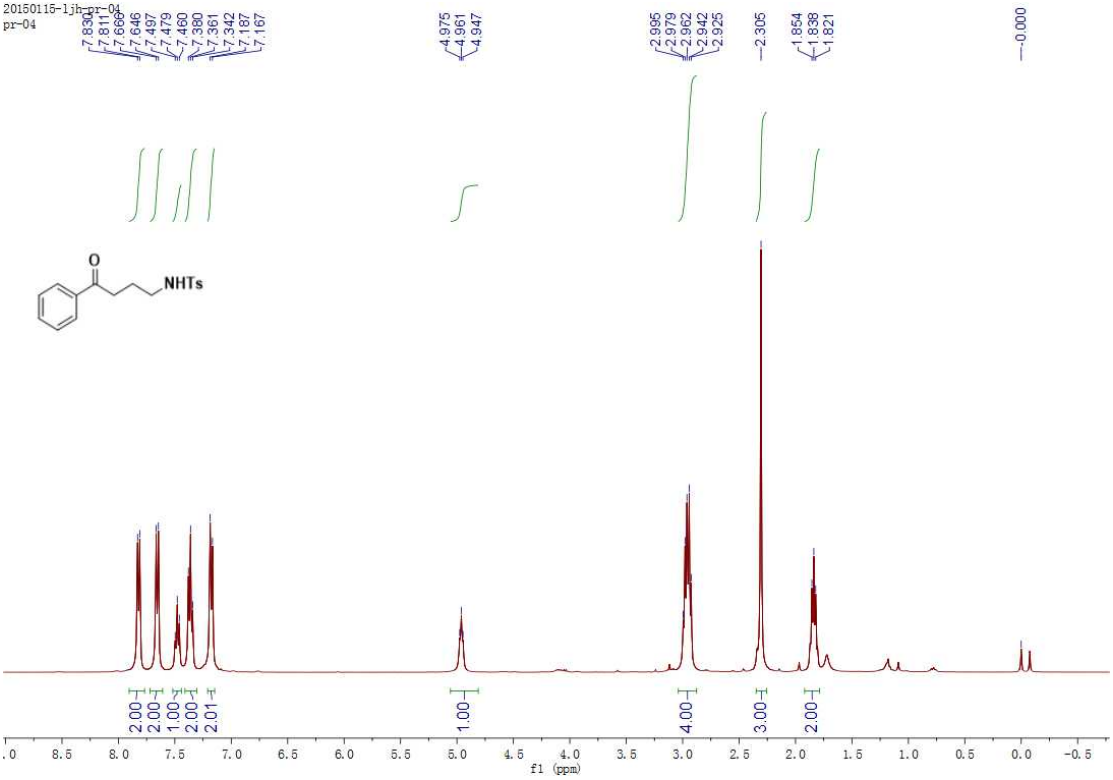


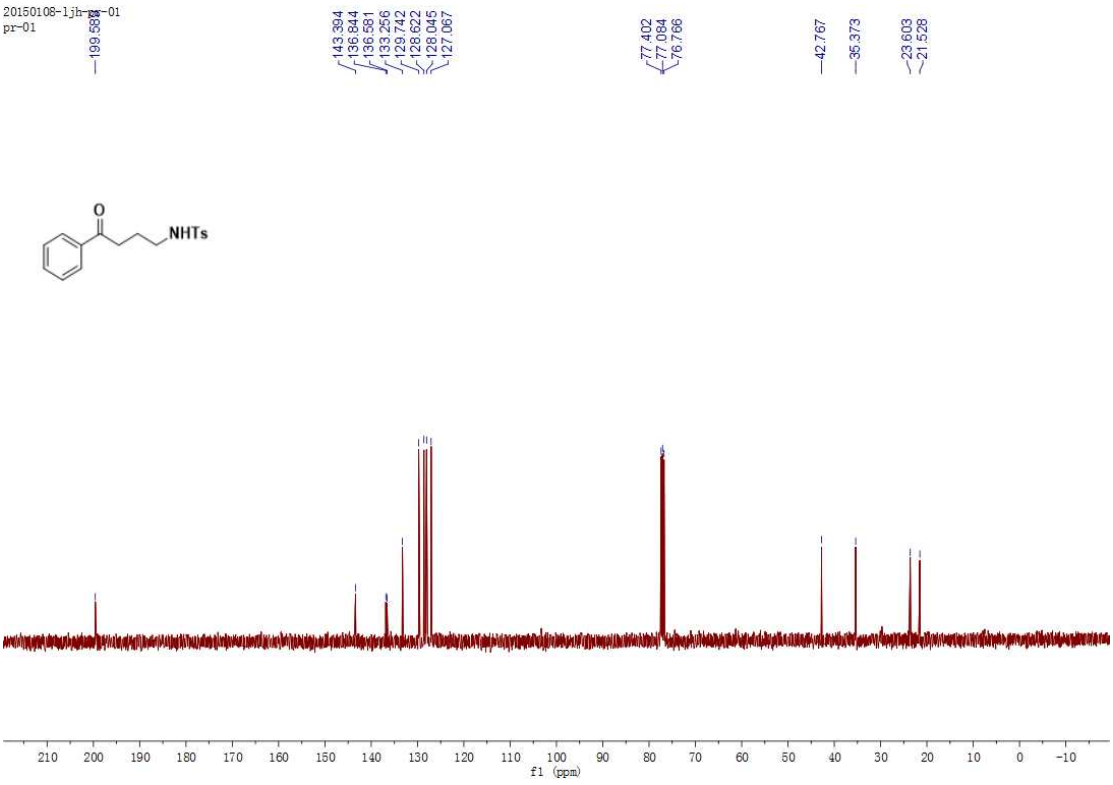


_N_-(2-(5-(3,5-Dimethylphenyl)-6,8-dimethyl-1-tosyl-2,3-dihydro-1H-benzo[g]indol-4-yl)ethyl)-4-methylbenzenesulfonamide (4g)

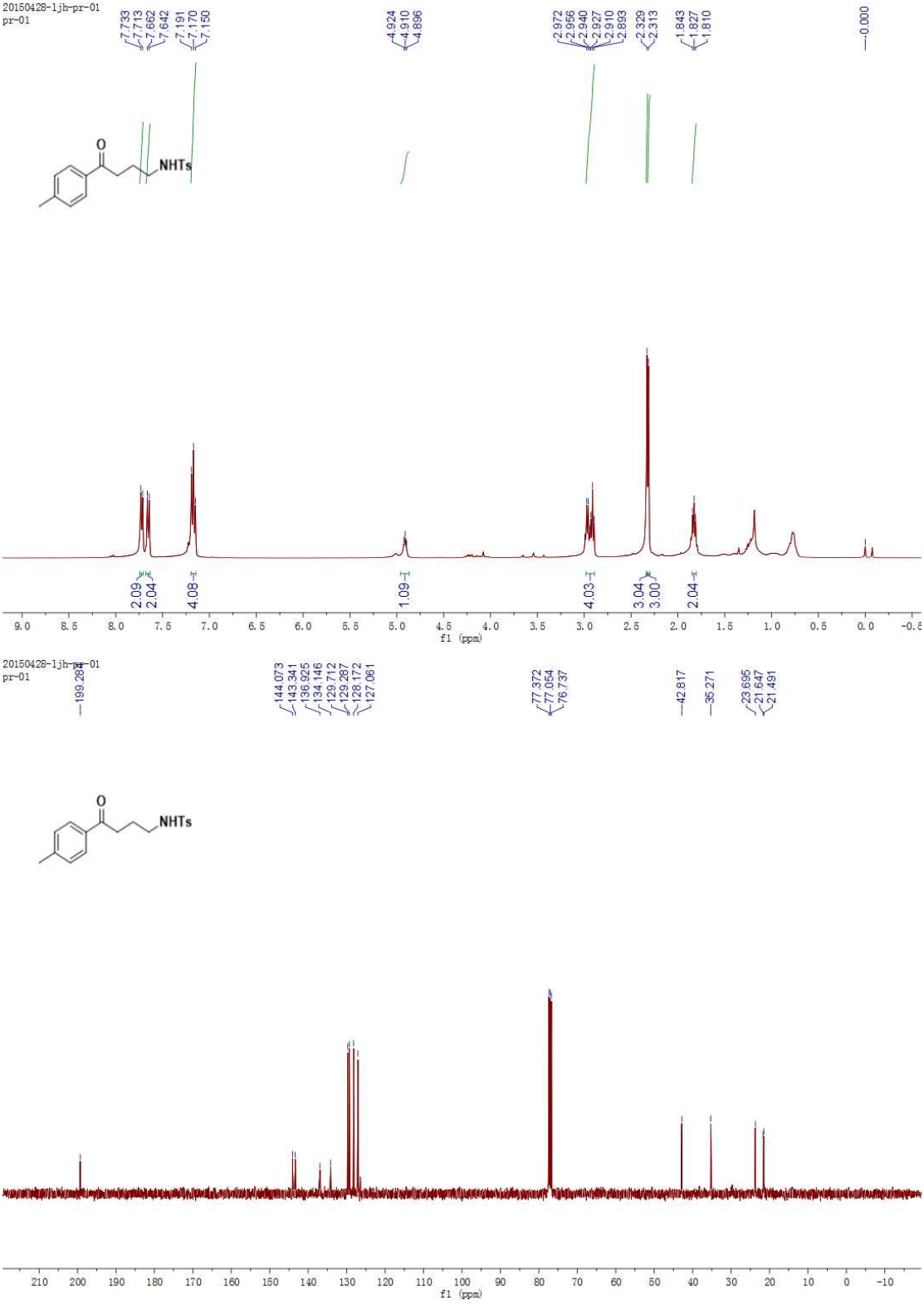


4-Methyl-*N*-(4-oxo-4-phenylbutyl)benzenesulfonamide (5a)

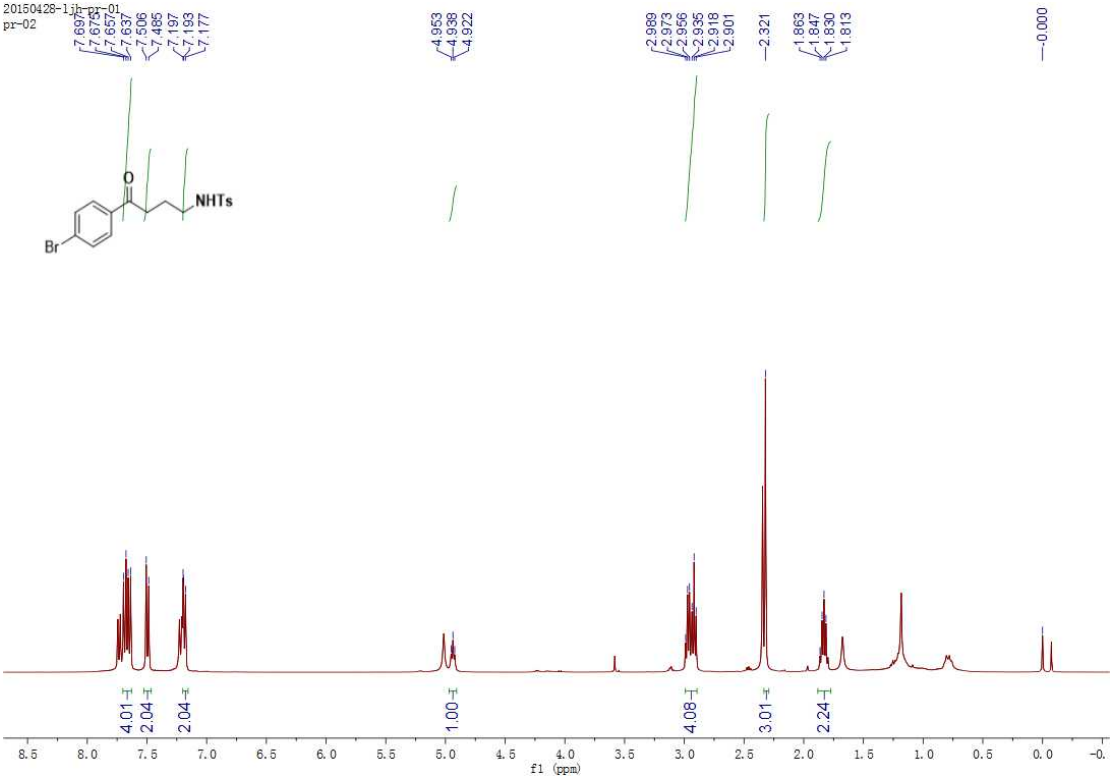


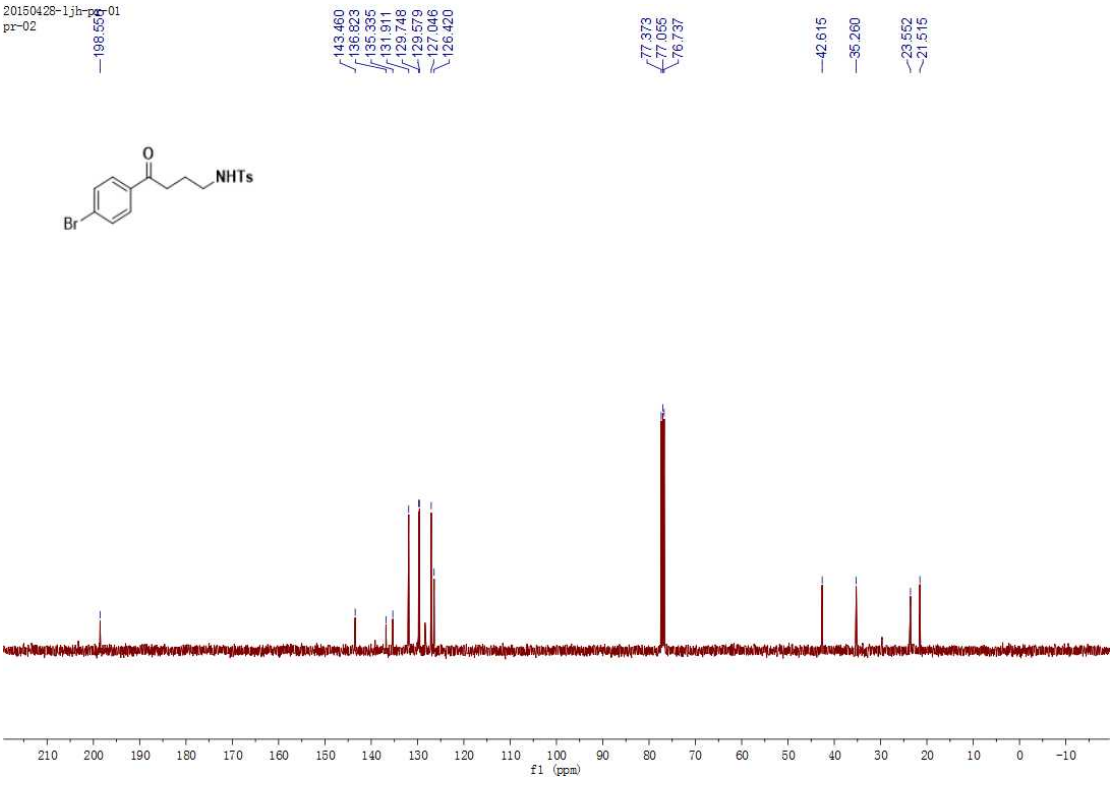


4-Methyl-*N*-(4-oxo-4-(p-tolyl)butyl)benzenesulfonamide(5b)

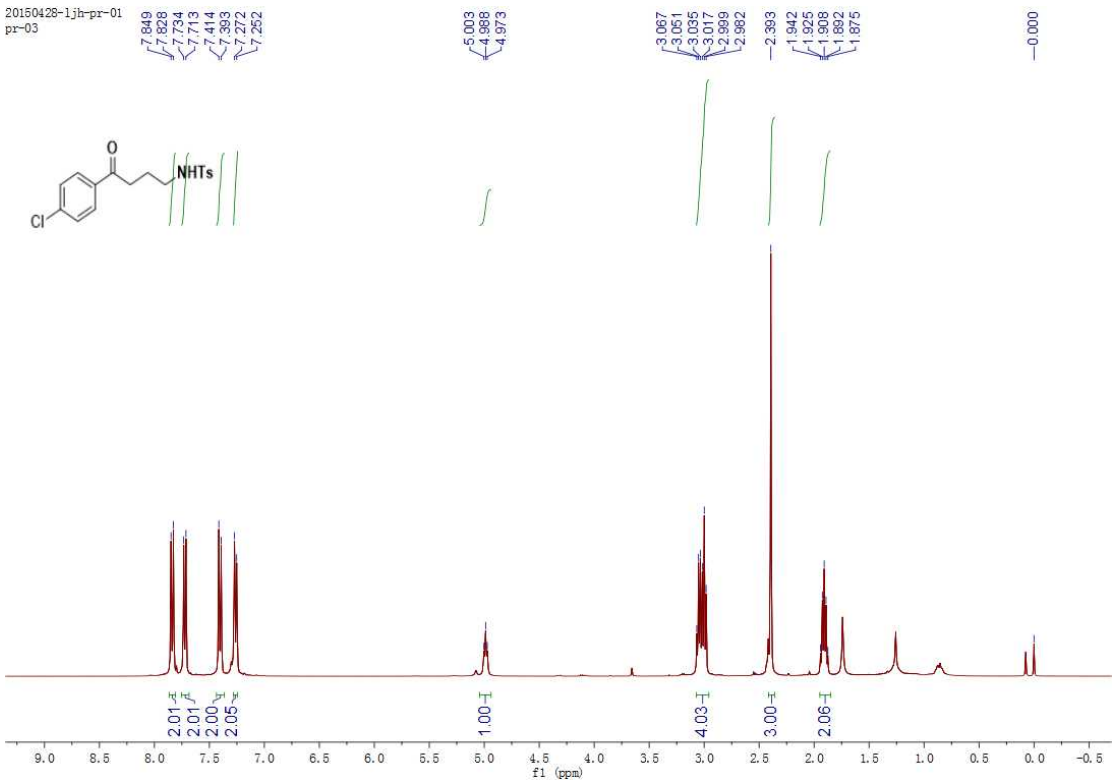


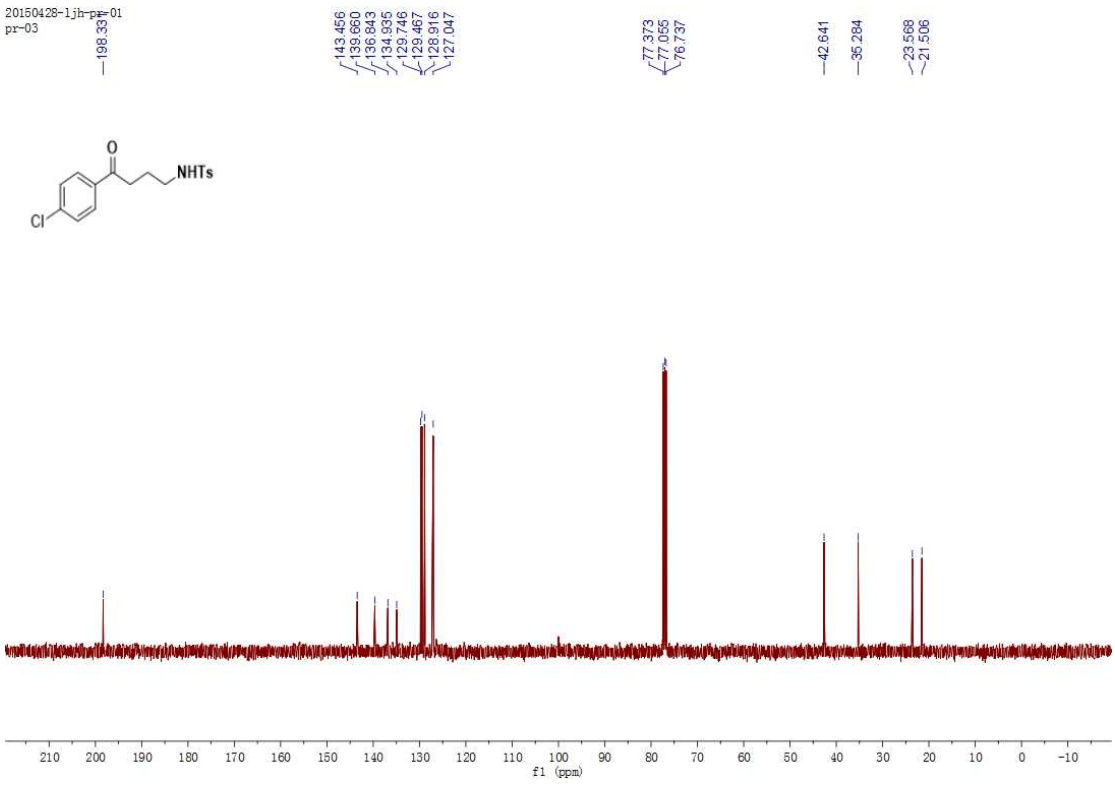
N-(4-(4-Bromophenyl)-4-oxobutyl)-4-methylbenzenesulfonamide(5c)



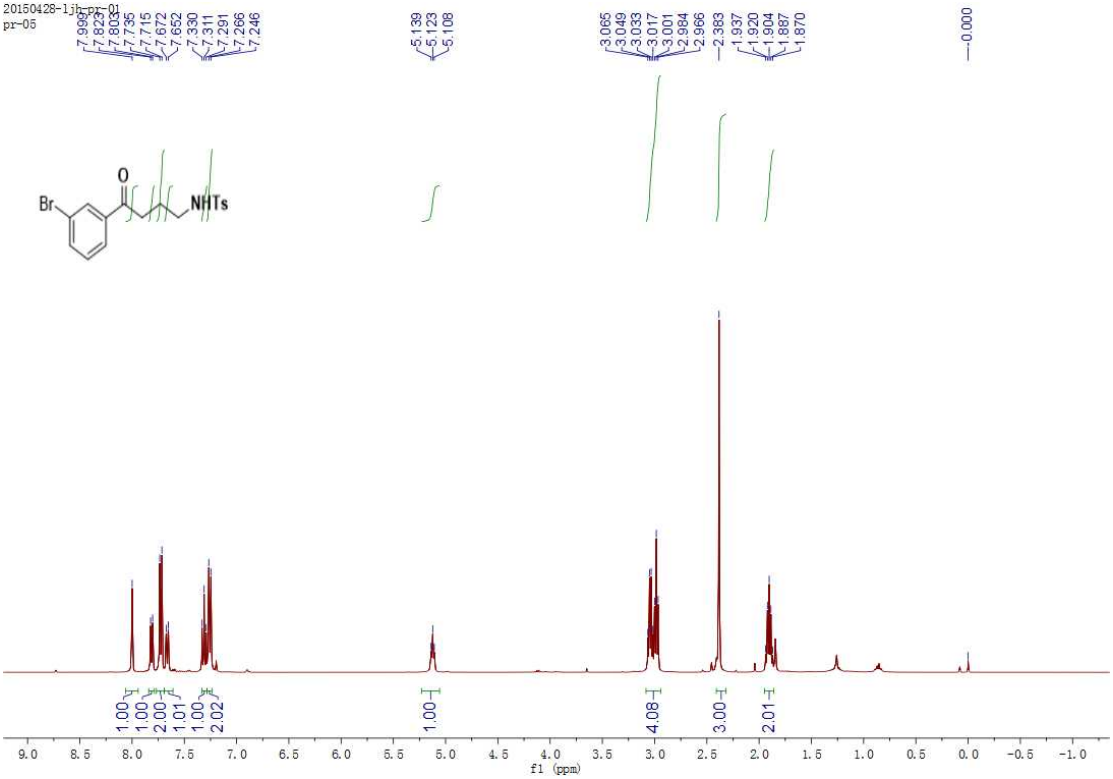


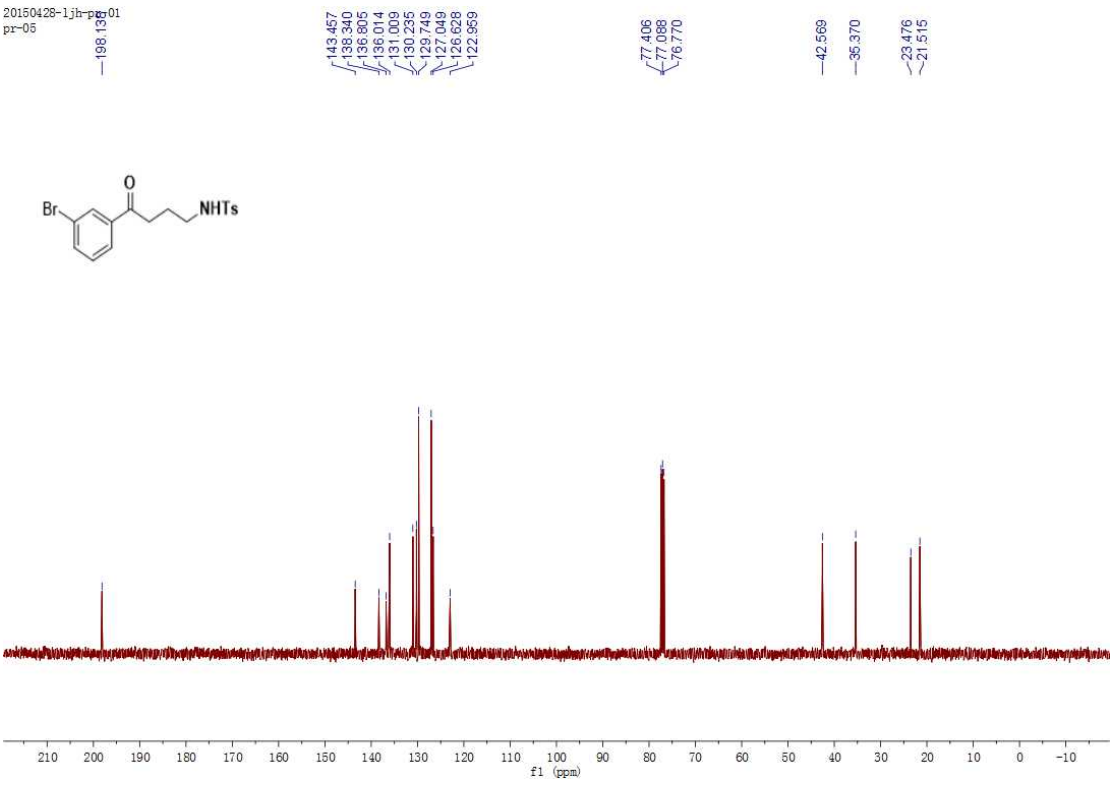
N-(4-(4-Chlorophenyl)-4-oxobutyl)-4-methylbenzenesulfonamide(5d)



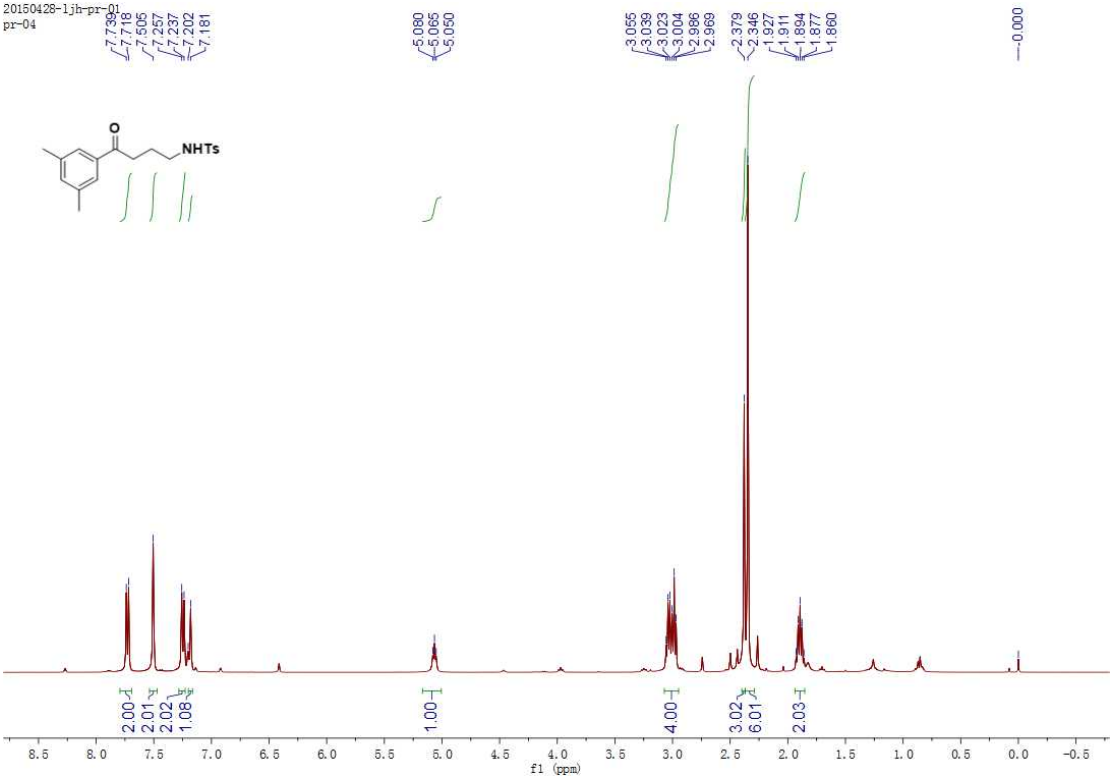


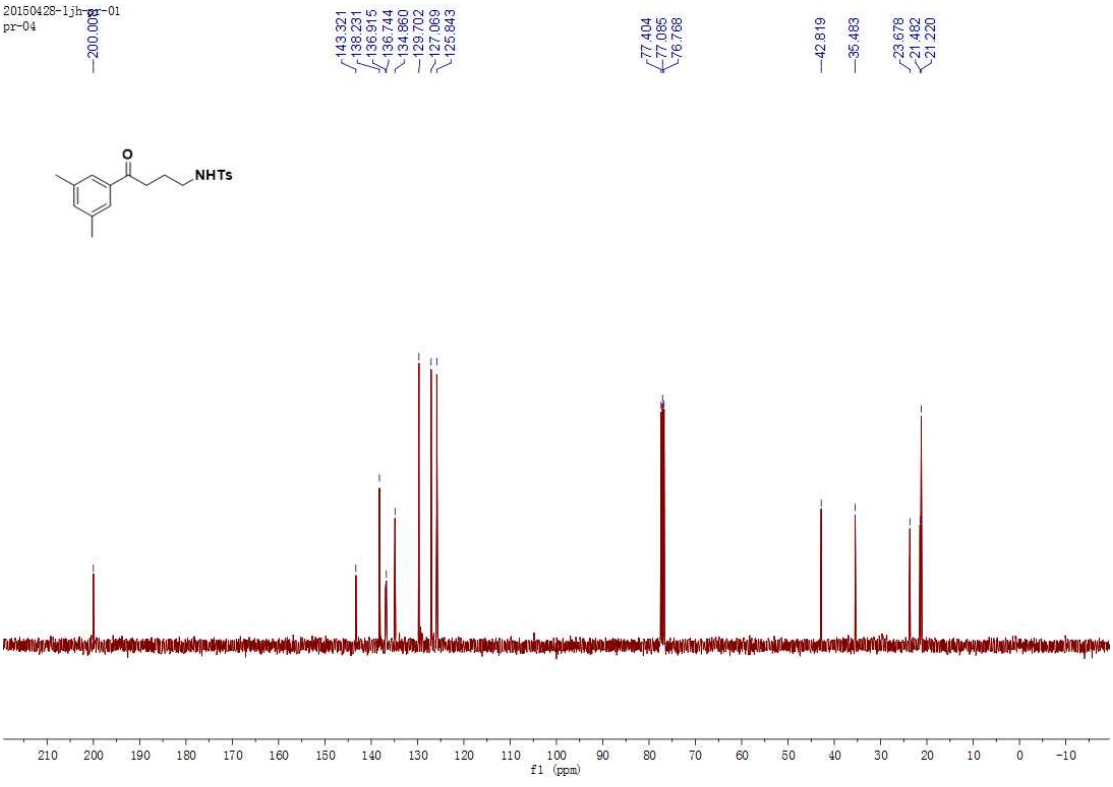
N-(4-(3-Bromophenyl)-4-oxobutyl)-4-methylbenzenesulfonamide(5f)



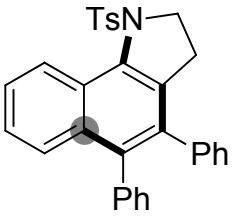


N-(4-(3,5-dimethylphenyl)-4-oxobutyl)-4-methylbenzenesulfonamide(5g)

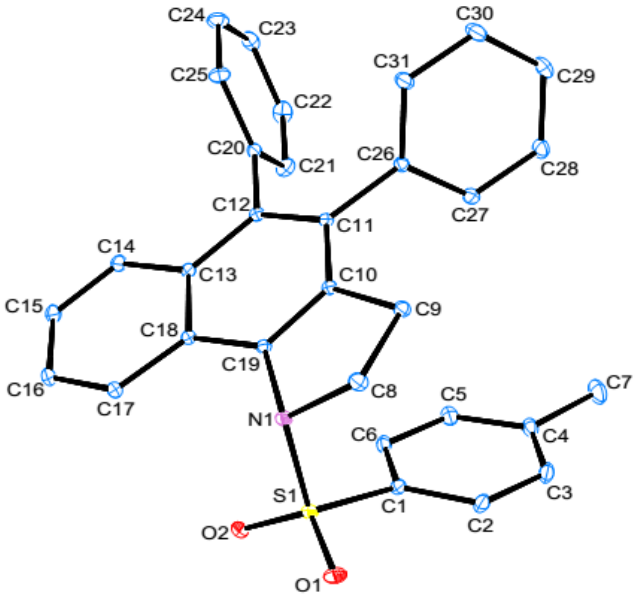


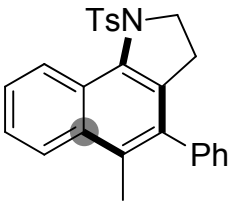


(F) The X-ray single-crystal diffraction analysis of 3aa, 3ad and 4c

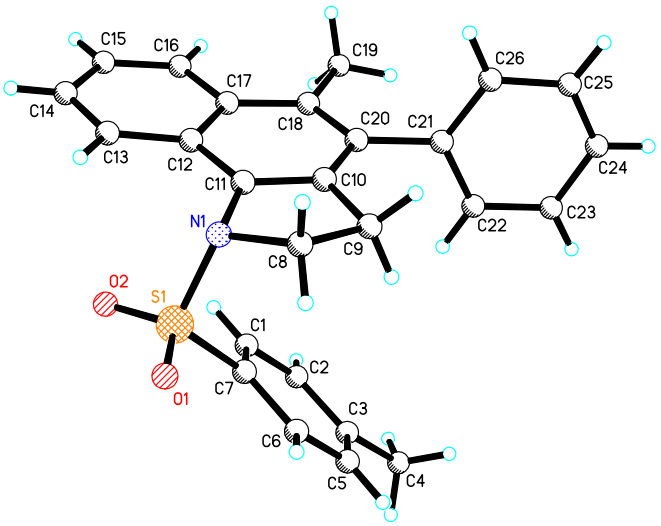


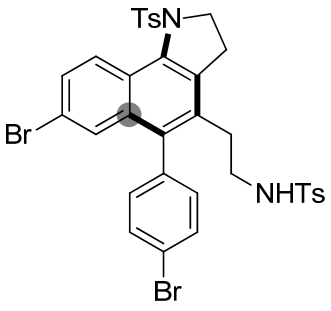
3aa



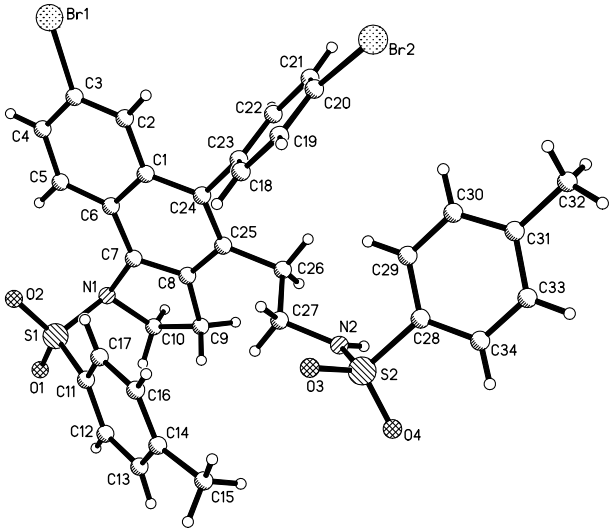


3ad




TsN
Br
NHTs
Br

4c


Br1
Br2
C1
C2
C3
C4
C5
C6
C7
C8
C9
C10
C11
C12
C13
C14
C15
C16
C17
C18
C19
C20
C21
C22
C23
C24
C25
C26
C27
C28
C29
C30
C31
C32
C33
C34
N1
N2
O1
O2
O3
O4
S1
S2