Supporting Information

Controllable Synthesis of Spiroaminals with Bimetallic Au/Sc Relay Catalysis: TMS as a disappearing directing group

Shuo Zhang,[a] Zhengliang Xu,[a] Jiong Jia,*[a] Chen-Ho Tung,[ab] and Zhenghu Xu*[a]

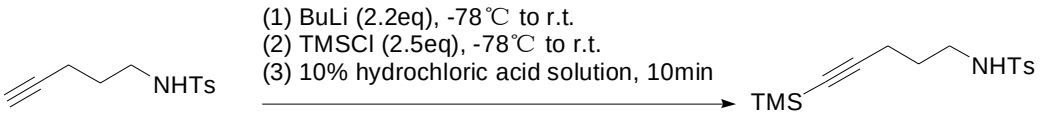
[a] Key Lab for Colloid and Interface Chemistry of Education Ministry, School of chemistry and Chemical Engineering, Shandong University, Jinan 250100, People's Republic of China.

[b] Key Laboratory of Photochemical Conversion and Optoelectronic Materials,Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, PR China

General

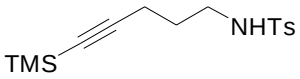
All NMR spectra were recorded on Bruker-400 or 300 MHz spectrometer. HRMS were measured on the Q-TOF6510 instruments . Routine monitoring of the reaction was performed by TLC using precoated silica gel plates. All the reagents and Solvents used in this reaction such as CH_3CN were purchased from Acros or local company and used directly. β,γ-Unsaturated α-keto esters were prepared according to reported procedures[(1)].

Synthesis of the substrates



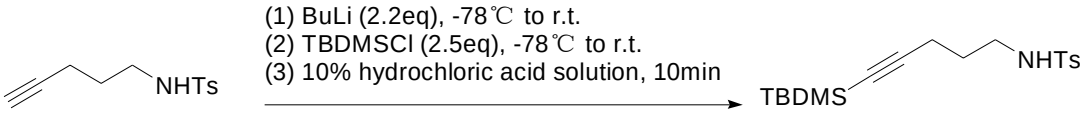
1b

To a solution of alkyne in dry THF was added BuLi (2.2eq) at -78 ℃. The mixture was stirred at -78 ℃ for 0.5h, then it was allowed to warm to room temperature. After 0.5h, TMSCl (2.5eq) were added at -78 ℃, and then the mixture was warmed to room temperature for 1h. Then. the solution was added 10% hydrochloric acid aqueous solution for 10min, then the organic phase was separated and evaporated under reduced pressure. The residue was purified through flash chromatography. The alkyne were prepared according to reported procedures [(2)].



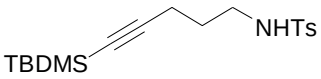
1b

White solid, yield 58% ^{1}HNMR ($CDCl_3$, 400 MHz) δ 0.13 (s, 9H), 1.65-1.70 (dd, J = 6.8 Hz, 13.6Hz, 2H), 2.23-2.26 (t, *J*= 6.8 Hz, 2H), 2.43 (s, 3H), 3.07 (dd, *J*=6.4Hz, 12.8Hz, 2H), 4.66-4.67 (m, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.76 (d, J = 8.1 Hz, 2H).



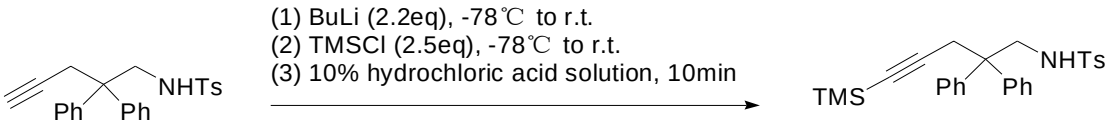
1c

To a solution of alkyne in dry THF was added BuLi (2.2eq) successively at -78 ℃. The mixture was stirred at -78℃ for 0.5h, then it was allowed to warm to room temperature. After 0.5h, TBDMSCl (2.5eq) were added at -78 ℃, and then the mixture was warmed to room temperature for 1h. Then. the solution was added 10% hydrochloric acid aqueous solution for 10min, then the organic phase was separated and evaporated under reduced pressure. The residue was purified through flash chromatography. The alkyne were prepared according to reported procedures [(2).]



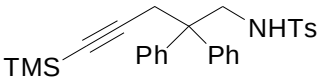
1c

White solid, yield 53%. ^{1}HNMR ($CDCl_3$, 400 MHz) δ 0.06 (s, 6H), 0.89 (s, 9H), 1.68 (t, *J* = 6.8 Hz, 2H), 2.26 (t, *J*=6.8 Hz, 2H), 2.43 (s, 3H), 3.08 (dd, *J*=6.4Hz, 13.2Hz, 2H), 4.58 (t, *J*=6.4H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 2H).



1d

To a solution of alkyne in dry THF was added BuLi (2.2eq) successively at -78 ℃. The mixture was stirred at -78℃ for 0.5h, then it was allowed to warm to room temperature. After 0.5h, TMSCl (2.5eq) were added at -78 ℃, and then the mixture was warmed to room temperature for 1h. Then. the solution was added 10% hydrochloric acid aqueous solution for 10min, then the organic phase was separated and evaporated under reduced pressure. The residue was purified through flash chromatography. The alkyne were prepared according to reported procedures [3].



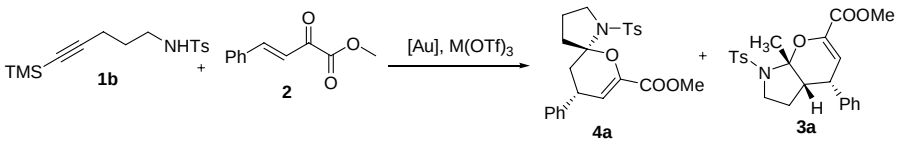
1d

White solid, yield 55%. 1H NMR (CDCl3, 400 MHz) δ 0.01 (s, 9H), 2.43 (s, 3H), 2.97 (s, 2H), 3.70 (d, *J*=9.6 Hz, 2H), 4.08 (t, *J*=6.4, 1H), 7.08-7.30 (m, 12H), 7.65 (d, *J* = 8.0 Hz, 2H).

General procedure of Spiroaminals

To a solution of 2 (1 equiv) and 1 (1.1 equiv) in CH_3CN was added the $Ph_3PAuNTf_2$ (5 mol%) and $Sc(OTf)_3$ (10 mol%). The mixture was kept stirring for 10 min at 65 ℃. After the reaction was completed (monitored by TLC), the solution was filtered on celite and then evaporated under reduced pressure. Purification by flash column chromatography afforded the desired product.

Kinetic-thermodynamic balance



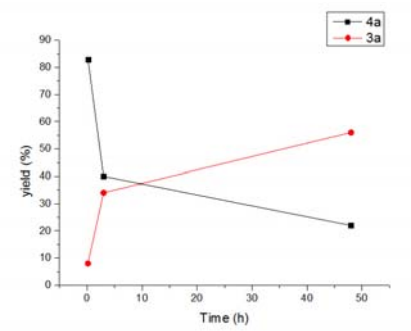
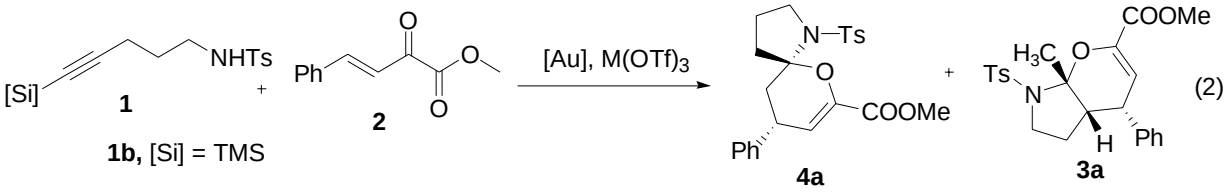


Figure 1. Kinetic-thermodynamic balance

Optimization of reaction conditions



1b, [Si] = TMS

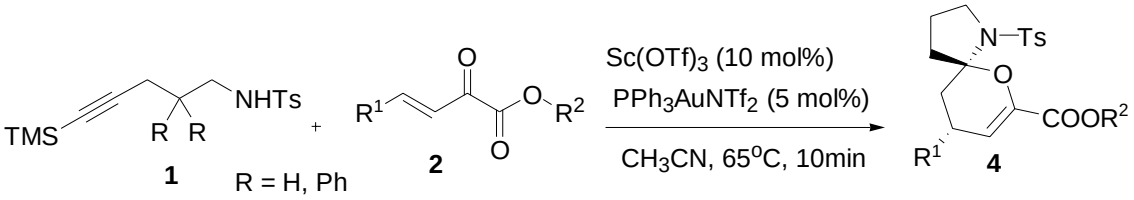
1c, [Si] = TBS

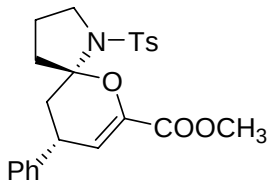
Entry	Substrate	Catalyst A	Catalyst B	Solvent	T	Time	Yeild%(4a)	4a/3a
1	1b	PPh_3AuNTf_2	$Sc(OTf)_3$	CH_3CN	65℃	10min	83	92/08
2	1b	PPh_3AuNTf_2	$Sc(OTf)_3$	CH_3CN	85℃	10min	65	73/27
3	1b	PPh_3AuNTf_2	$Sc(OTf)_3$	CH_3CN	45℃	10min	58	72/28
4	1b	PPh_3AuNTf_2	$Sc(OTf)_3$	CH_3CN	65℃	3hrs	40	55/45
5	1c	PPh_3AuNTf_2	$Sc(OTf)_3$	CH_3CN	65℃	3hrs	0	0
6	1b	$AuCl(CH_3SCH_3)$	$Sc(OTf)_3$	CH_3CN	65℃	10min	45	53/47
7	1b	$PPh_3.AuCl$	$Sc(OTf)_3$	CH_3CN	65℃	10min	75	81/19
8	1b	$AuCl_3$	$Sc(OTf)_3$	CH_3CN	65℃	10min	45	61/39
9	1b	CuOTf.1/2PhH	$Sc(OTf)_3$	CH_3CN	65℃	10min	27	67/23
10	1b	AgOTf	$Sc(OTf)_3$	CH_3CN	65℃	10min	40	59/41
11	1b	AuCl	$Sc(OTf)_3$	CH_3CN	65℃	10min	37	45/55
12	1b	PPh_3AuNTf_2	$La(OTf)_3$	CH_3CN	65℃	10min	37	48/52
13	1b	PPh_3AuNTf_2	$Ga(OTf)_3$	CH_3CN	65℃	10min	28	38/62
14	1b	PPh_3AuNTf_2	$Bi(OTf)_3$	CH_3CN	65℃	10min	43	47/53
15	1b	PPh_3AuNTf_2	$In(OTf)_3$	CH_3CN	65℃	10min	55	64/36
16	1b	PPh_3AuNTf_2	$Sc(OTf)_3$	EtOAc	65℃	10min	32	37/63
17	1b	PPh_3AuNTf_2	$Sc(OTf)_3$	$CHCl_3$	65℃	10min	45	53/47
18	1b	PPh_3AuNTf_2	$Sc(OTf)_3$	Toluene	65℃	10min	66	73/27

References

(1) Xu, Z.; Liu, L.; Wheeler, K.; Wang, H. *Angew. Chem., Int. Ed.* 2011, *50*, 3484.
(2) Wang, X.; Yao, Z.; Dong, S.; Wei, F.; Wang, H, Xu, Z. Org. Lett. 2013, *15*, 2234.
(3) Mo, D.; Ding, C.; Dai, L.; Hou, X. *Chem. Asian. J.* 2011, *6*, 3200

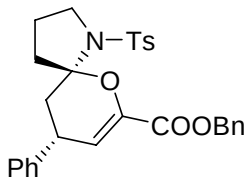
NMR spectra for the products





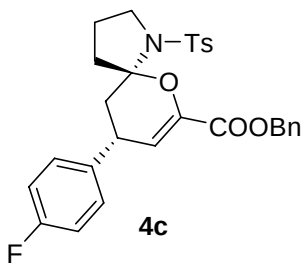
4a

Yield: 83%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.84-1.91 (m, 3H), 2.16-2.21 (m, 1H), 2.22-2.33 (m, 1H), 2.44 (s, 3H), 3.08 (t, *J*= 12.7 Hz, 1H), 3.42-3.44 (m, 1H), 3.45-3.54 (m, 1H), 3.60-3.65 (m, 1H), 3.77 (s, 3H), 6.14 (s, 1H), 7.25-7.28 (m, 3H), 7.30-7.34 (m, 4H), 7.98 (d, *J*= 8Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 21.6, 38.0, 39.2, 39.6, 49.7, 52.1, 97.6, 114.0, 127.1, 127.4, 128.7, 128.8, 129.2, 136.4,142.1, 143.0, 143.3, 162.9; HRMS exact mass calcd for (C23H25NO5S+Na) requires m/z 450.1346, found m/z 450.1335.



4b

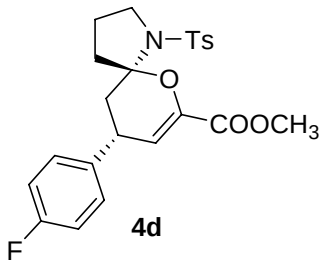
Yield: 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.82-1.90 (m, 3H), 2.18-2.23 (m, 1H), 2.34-2.36 (m, 4H), 3.13 (t, *J*= 12.8 Hz, 1H), 3.39-3.41 (m, 1H), 3.52-3.61 (m, 1H), 3.62-3.65 (m,1H),5.22 (dd, *J*= 12.4, 23, 2H), 6.19 (s, 1H), 7.12 (d, *J*=8.4, 2H), 7.13-7.27 (m, 3H), 7.32-7.37 (m, 7H), 7.95 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 21.5, 38.0, 39.3, 39.7, 49.7, 66.8, 97.7, 114.4, 127.1, 127.5, 128.2, 128.3, 128.58, 128.62,128.8, 129.2, 135.6, 136.3, 142.1, 143.1, 143.2, 162.3; HRMS exact mass calcd for (C29H29NO5S+H) requires m/z 504.1839, found m/z 504.1839.



4c

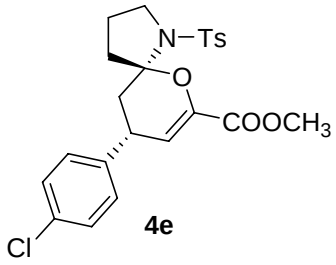
Yield: 69%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.92-2.01 (m, 3H), 2.26-2.31 (m, 1H), 2.44 (m, 4H), 3.18 (t, *J*= 12.8 Hz, 1H), 3.48-3.49 (m, 1H), 3.62-3.64 (m, 1H), 3.728-3.733 (m, 1H),5.35 (dd, *J*= 12.4, 24.4, 2H), 6.25 (s, 1H), 7.10-7.15 (m, , 2H), 7.22 (d, *J*=8.4, 2H), 7.31-7.37 (m, 2H), 7.45-7.48 (m, 5H), 8.05(m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 21.6, 38.0, 38.5, 39.8, 49.7, 52.1, 97.5, 113.7,

115.5, 115.7, 128.7, 128.9, 129.0, 129.2,136.3, 137.82, 137.85, 143.1, 143.3, 160.7, 162.8, 163.1; HRMS exact mass calcd for (C29H28FNO5S+Na) requires m/z 544.1564, found m/z 544.1563.



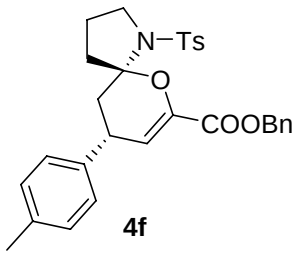
4d

Yield: 65%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.82-1.90 (m, 3H), 2.14-2.19 (m, 1H), 2.31-2.32 (m, 1H), 2.44 (s, 3H), 3.04 (t, *J*= 13.2 Hz, 1H), 3.48-3.49 (m, 1H), 3.52-3.59 (m, 1H), 3.60-3.64 (m, 1H),3.77 (s, 3H), 6.09 (s, 1H), 7.02 (t, *J*=8.4, 2H), 7.22 (dd, *J*=5.2, 8.4, 2H), 7.31 (d, *J*=8.0, 2H), 7.98 (d, *J*=8.4, 2H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 21.6, 38.0, 38.5, 39.8, 49.7, 52.1, 97.5, 113.7, 128.7, 128.9, 129.2, 136.3, 143.1, 143.3, 160.7, 162.8, 163.1; HRMS exact mass calcd for (C23H24FNO5S+K) requires m/z 484.0991, found m/z 484.0993.



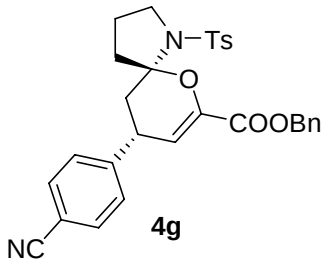
4e

Yield: 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.81-1.90 (m, 3H), 2.03-2.18 (m, 1H), 2.30-2.39 (m, 1H), 2.43 (m, 4H), 3.04 (t, *J*= 12.8 Hz, 1H), 3.42-3.46 (m, 1H), 3.54-3.62 (m, 2H), 3.77 (s, 3H), 6.07 (s, 1H), 7.19 (d, *J*=8.4, 2H), 7.29-7.32 (m, 4H), 7.96 (m, 2H), ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 21.6, 38.0, 38.6, 39.6, 49.7, 52.1, 97.5, 113.2, 128.7, 128.8, 128.9, 129.2, 132.8, 136.3, 140.7, 143.27, 143.31, 162.7; HRMS exact mass calcd for (C23H24ClNO5S+Na) requires m/z 484.0956, found m/z 484.0956.



4f

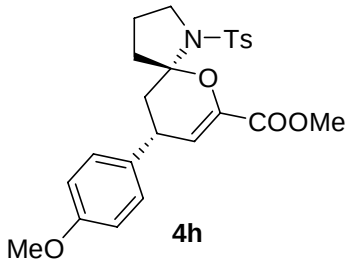
Yield: 79%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.80-1.91 (m, 3H), 2.16-2.21 (m, 1H), 2.35 (m, 7H), 3.11 (t, *J*= 13.2 Hz, 1H), 3.37-3.41 (m, 1H), 3.53-3.54 (m, 2H), 3.59-3.64 (m, 2H), 5.22 (dd, J=12.4, 22.8, 2H), 6.18 (s, 1H), 7.11-7.16 (m, 6H), 7.36-7.38 (m, 5H), 7.98 (d, *J*=8.4, 2H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 21.1, 21.5, 38.0, 39.0, 39.7, 49.7, 97.5, 114.7, 127.4, 128.2, 128.3, 128.6, 129.2, 129.5, 135.7, 136.3, 136.7, 139.1, 142.9, 143.2, 162.3; HRMS exact mass calcd for (C30H31NO5S+Na) requires m/z 540.1815, found m/z 540.1814.



4g

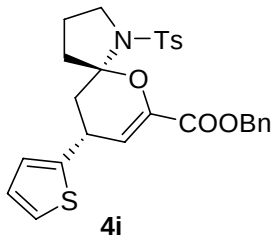
Yield: 75%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.81-1.91 (m, 3H), 2.17-2.19 (m, 1H), 2.34 (m, 4H), 3.08 (t, *J*= 13.2 Hz, 1H), 3.37-3.39 (m, 1H), 3.51-3.53 (m, 2H), 3.67-3.72 (m, 1H), 5.23 (dd, *J*=12.4, 25.2, 2H), 6.11 (s, 1H), 7.10 (d, *J*=8.0, 2H), 7.34-7.39 (m, 7H), 7.63 (d, *J*=8.0, 2H), 7.94 (d, *J*=8.4, 2H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 21.5,

38.0, 39.38, 29.42, 49.7, 67.2, 97.5, 111.1, 112.2, 118.7, 128.30, 128.37, 128.5, 128.7, 129.2, 132.7, 135.4, 136.0, 143.4, 143.9, 147.7, 162.0; HRMS exact mass calcd for (C30H29N2O5S+H) requires m/z 529.1792, found m/z 529.1790.



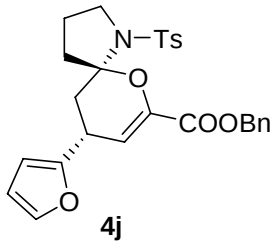
4h

Yield: 75%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.81-1.88 (m, 3H), 2.10-2.32 (m, 2H), 3.05 (t, *J*= 12.4 Hz, 1H), 3.40-3.44 (m, 1H), 3.45-3.60 (m, 1H), 3.78 (s, 3H), 3.81 (s, 3H), 6.10 (s, 1H), 6.86 (d, *J*=8.4, 2H) 7.18 (d, *J*=8.8, 2H), 7.31 (d, *J*=8.0, 2H), 7.98 (d, *J*=8.4, 2H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 21.5, 38.0, 38.4, 39.7, 49.7, 52.0, 55.3, 97.6, 114.2, 114.4, 128.4, 128.6, 128.7, 129.0, 129.1, 136.5, 142.8, 143.2, 162.9; HRMS exact mass calcd for (C24H27NO6S+Na) requires m/z 480.1451, found m/z 480.1454.



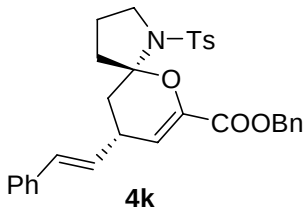
4i

Yield: 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.80-1.89 (m, 3H), 2.29-2.34 (m, 5H), 3.22 (t, *J*= 12.8 Hz, 1H), 3.39-3.42 (m, 1H), 3.53-3.55 (m, 1H), 3.94-3.99 (m, 1H), 5.17-5.26 (dd, *J*=12.4, 20.4, 2H), 6.21 (s, 1H), 6.95-6.97 (m, 2H) 7.10-7.12 (d, *J*=8.0, 2H), 7.187-7.199 (m, 1H), 7.35-7.37 (m, 5H), 7.95 (d, *J*=8.4, 2H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 21.5, 34.4, 37.9, 39.7, 49.7, 66.8, 97.5, 113.7, 123.8, 124.1, 126.9, 128.2, 128.4, 128.57, 128.64, 129.2, 135.6, 136.2, 142.6, 143.3, 145.1, 162.1; HRMS exact mass calcd for (C27H27NO5S2+Na) requires m/z 532.1223, found m/z 532.1220.



4j

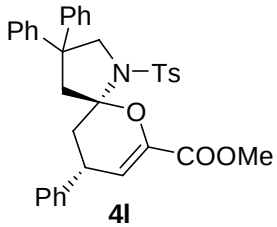
Yield: 78%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.81-1.85 (m, 3H), 2.28-2.32 (m, 5H), 3.18 (t, *J*= 12.4 Hz, 1H), 3.39-3.40 (m, 1H), 3.51-3.57 (m, 1H), 3.73-3.78 (m, 1H), 5.15-5.24 (dd, *J*=12.4 Hz, 23.2, 2H) 6.137-6.144 (d, *J*=11.2 Hz, 1H), 6.20 (s, 1H) 6.30-6.31 (dd, *J*=1.8 Hz, 2.8, 1H) 7.08-7.10 (d, *J*=8.4 Hz, 2H), 7.34-7.35 (m, 6H), 7.92-7.94 (d, *J*=8.4 Hz, 2H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 21.5, 32.8, 35.9, 37.9, 49.7, 66.8, 97.3, 105.1, 110.2, 111.1, 128.3, 128.4, 128.59, 128.63, 129.2, 135.6, 136.2, 141.7, 142.9, 143.3, 154.4, 162.1; HRMS exact mass calcd for (C27H27NO5S2+Na) requires m/z 516.1451, found m/z 516.1451.



4k

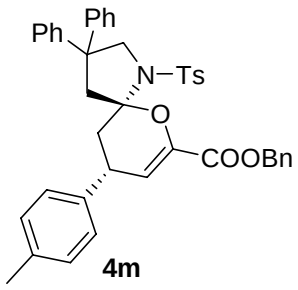
Yield: 89%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.81-1.84 (m, 3H), 2.10-2.14 (m, 1H), 2.26-2.34 (m, 4H), 2.98 (t, *J*= 12.4 Hz, 1H), 3.22 (m, 1H), 3.38 (m, 1H), 3.54-3.56 (m, 1H), 5.21-5.22 (m, 2H), 6.07 (s, 1H), 6.15 (dd, *J*=8Hz, 16Hz, 1H), 6.56 (d, *J*=21.2 Hz, 1H) 7.12 (d, *J*=8.0 Hz, 1H) 7.31 (d,

J=8.0 Hz, 2H) 7.33-7.43 (m, 10H), 7.97 (d, *J*=8.4, 2H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 21.5, 36.7, 37.2, 37.9, 49.7, 66.8, 97.4, 113.4, 126.3, 127.6, 128.2, 128.34, 128.38, 128.58, 128.61, 128.63, 128.67, 128.7, 129.2, 130, 135.6, 136.3, 136.8, 162.2; HRMS exact mass calcd for (C31H31NO5S+Na) requires m/z 552.1815, found m/z 552.1815.



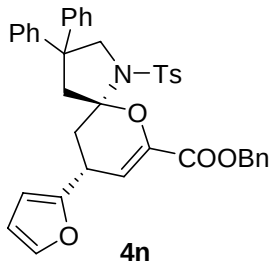
4l

Yield: 82%. ^{1}HNMR (400 MHz, $CDCl_3$) δ 1.28-1.34 (m, 1H), 2.44 (s, 1H), 2.86 (t, *J*=12.8 Hz, 1H), 2.95 (d, *J*= 13.2 Hz, 1H), 3.08 (d, *J*=12.8 Hz, 1H) 3.51-3.55 (m, 1H), 3.73 (s, 3H), 3.78 (d, *J*=6.4 Hz, 1H), 4.48 (d, *J*=10 Hz, 1H) 6.16 (s, 1H), 7.01-7.04 (m, 2H), 7.03-7.36 (m,15H), 7.99 (dd, *J*=8.4Hz, 2H) ; 13C NMR (100 MHz, CDCl3) δ 21.6, 38.8, 39.1, 41.0, 50.2, 51.0, 57.2, 68.2, 97.5, 113.8, 126.38, 126.42, 126.6, 126.8, 127.3, 128.4, 128.8, 128.9, 130.9, 136.1, 141.85, 143.0, 143.3, 144.2, 145.0, 162.7; HRMS exact mass calcd for (C35H33NO5S+Na) requires m/z 602.1972, found m/z 602.1978.



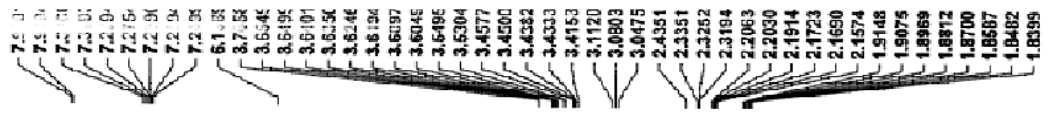
4m

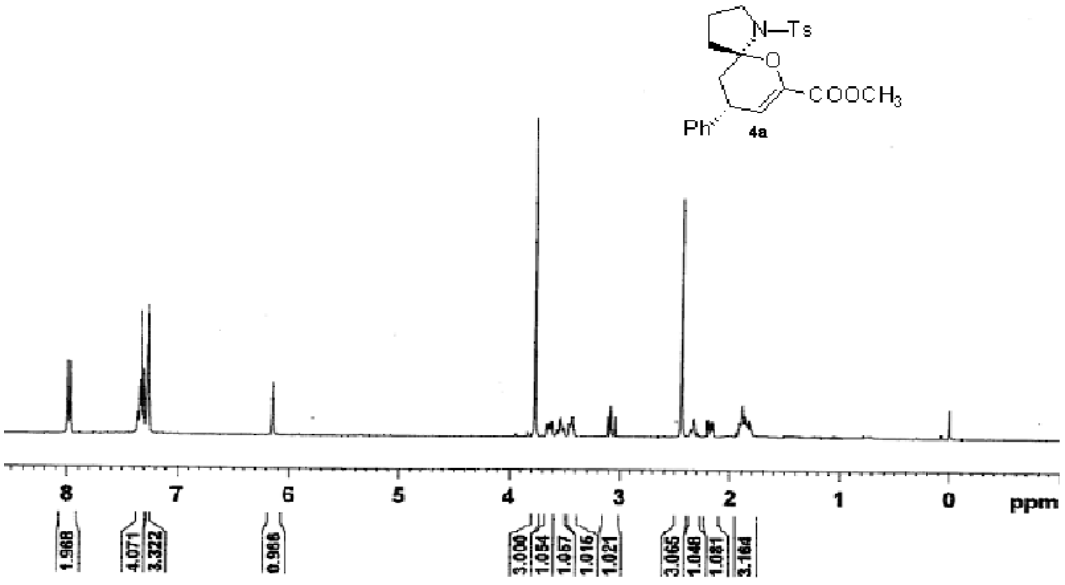
Yield: 85%. ^{1}HNMR (400 MHz, $CDCl_3$) δ 1.28-1.34 (m, 1H), 2.44 (s, 1H), 2.86 (t, *J*=12.8 Hz, 1H), 2.95 (d, *J*= 13.2 Hz, 1H), 3.08 (d, *J*=12.8 Hz, 1H) 3.53 (m, 1H), 3.73 (s, 3H), 3.79 (d, *J*=6.4 Hz, 1H), 4.48 (d, *J*=10 Hz, 1H) 6.16 (s, 1H), 7.01-7.04 (m, 2H), 7.03-7.36 (m,15H), 7.99 (dd, *J*=8.4Hz, 2H) ; 13C NMR (100 MHz, CDCl3) δ 21.6, 38.8, 39.1, 41.0, 50.2, 51.0, 57.2, 68.2, 97.5, 113.8, 126.38, 126.42, 126.6, 126.8, 127.3, 128.4, 128.8, 128.9, 130.9, 136.1, 141.85, 143.0, 143.3, 144.2, 145.0, 162.7; HRMS exact mass calcd for (C35H33NO5S+Na) requires m/z 602.1972, found m/z 602.1978

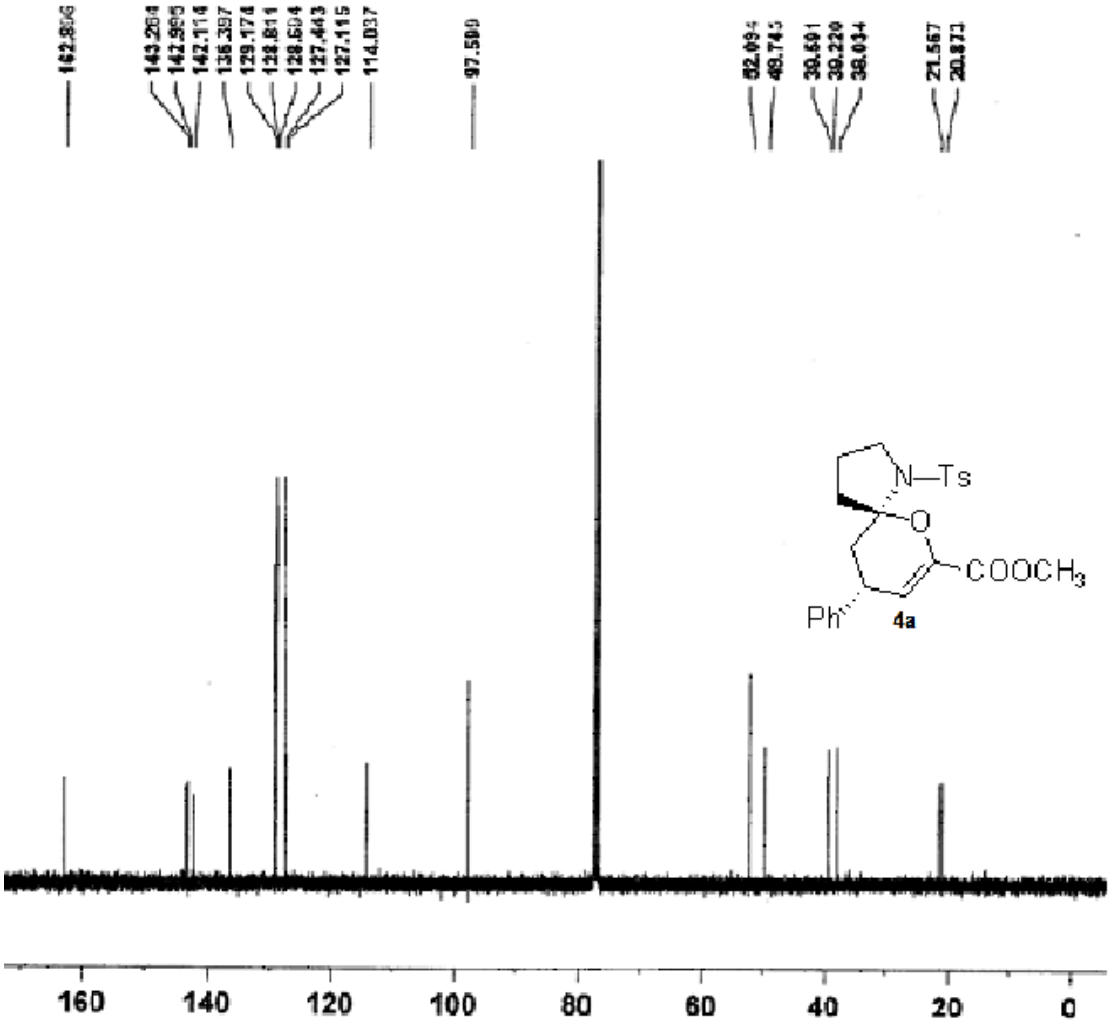


4n

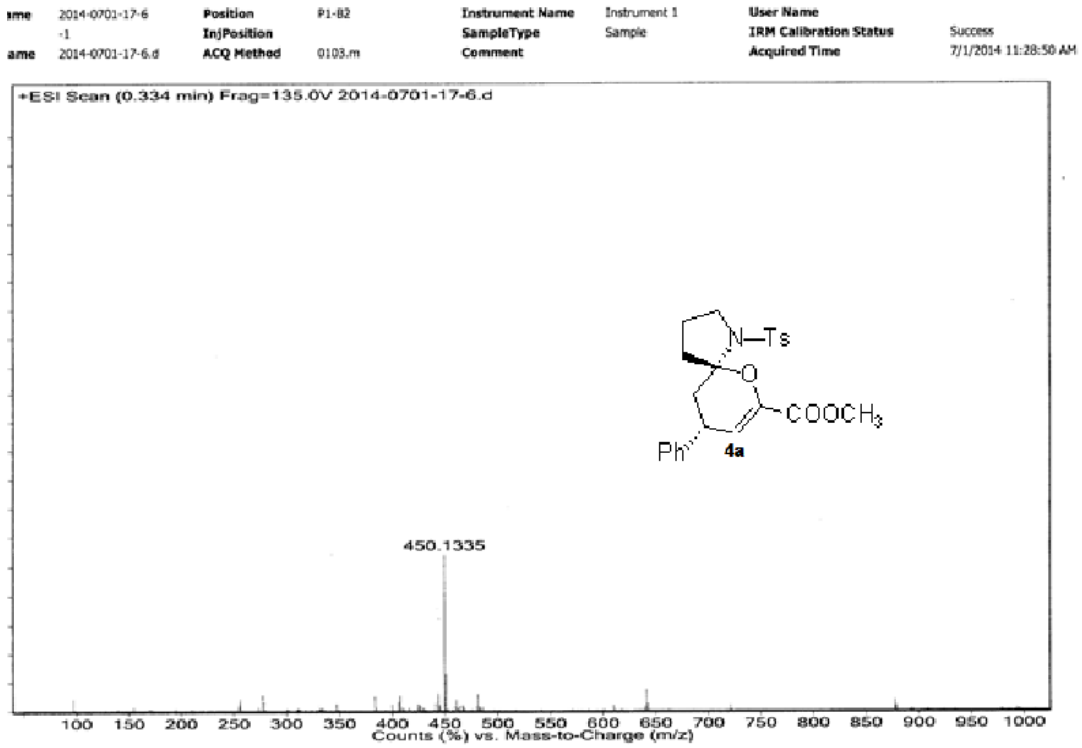
Yield: 89%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.80-1.85 (m, 1H), 2.34 (s, 3H), 2.84 (d, *J*=12.0 Hz, 1H), 3.02 (dd, *J*= 12.4 Hz, 28.4Hz, 2H), 3.65-3.73 (m, 2H) 4.44 (d, *J*=10 Hz, 1H), 5.05 (d, *J*=12.4Hz, 1H), 5.25 (d, *J*=12 Hz, 1H), 6.04 (d, *J*=2.8Hz, 1H), 6.19 (s, 1H), 6.27 (dd, *J*=1.2Hz, 2.8Hz, 1H), 6.96 (d, *J*=2.8, 2H), 7.01-7.4 (m, 16H), 7.9 (m, 2H) ; 13C NMR (100 MHz, CDCl3) δ 21.5, 32.6, 36.0, 50.4, 50.9, 57.4, 66.9, 97.2, 105.1, 110.3, 111.2, 126.3, 126.4, 126.5, 126.8, 128.4, 128.7, 128.78,128.83, 129.3, 135.5, 135.7, 141.7, 142.7, 143.4, 144.1, 145.0, 154.0, 162.1; HRMS exact mass calcd for (C39H35N65S+Na) requires m/z 668.2077, found m/z 668.2076

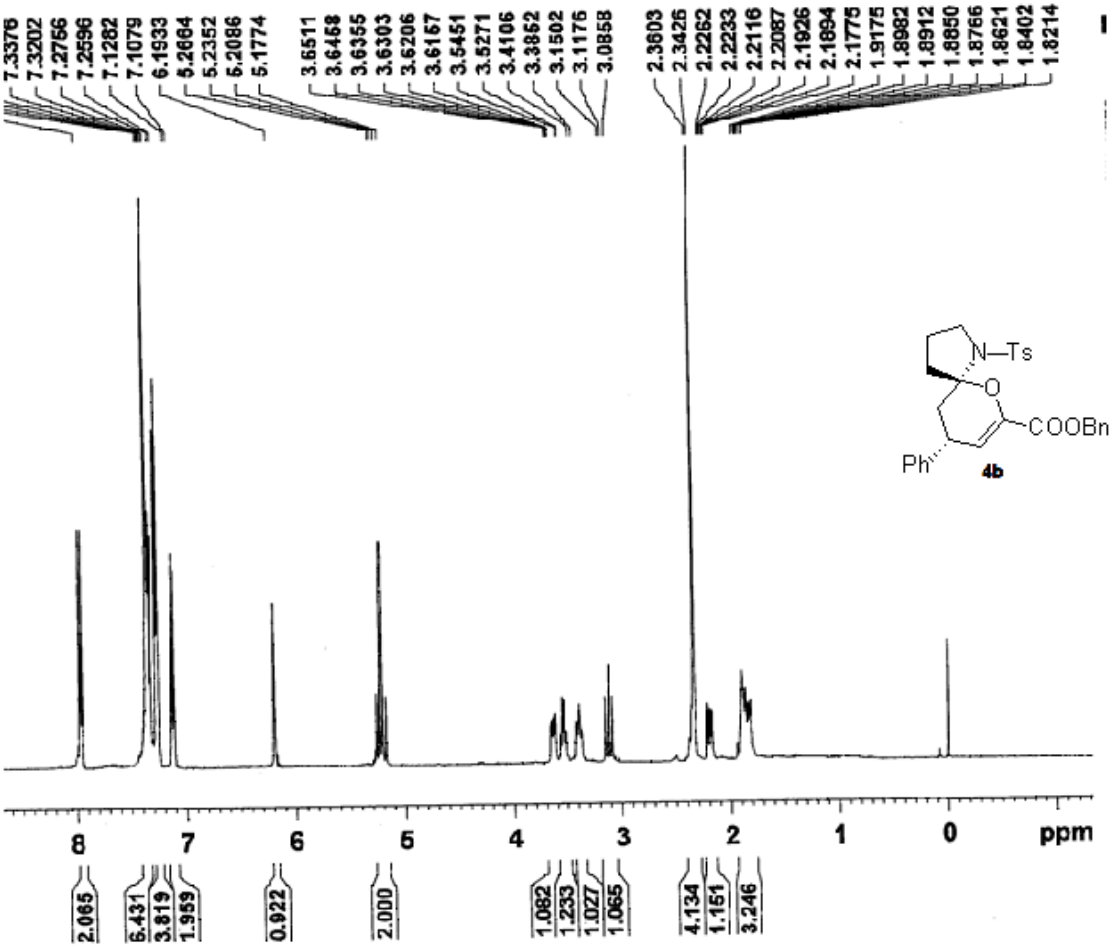


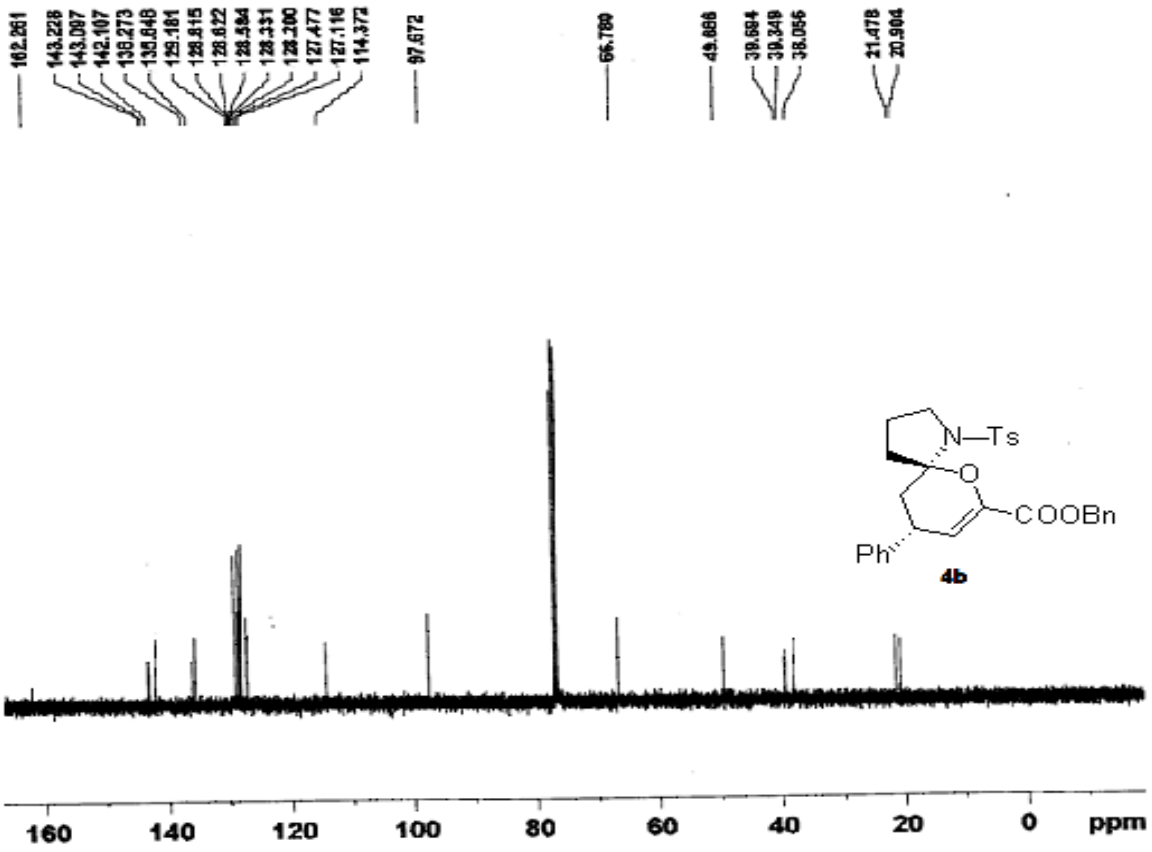

N—Ts
O
COOCH3
Ph
4a
8
7
6
5
4
3
2
1
0
ppm


N—Ts
O
COOCH3
Ph
4a
160
140
120
100
80
60
40
20
0

HRMS exact mass calcd for (C23H25NO5S+Na) requires m/z 450.1346, found m/z 450.1335.

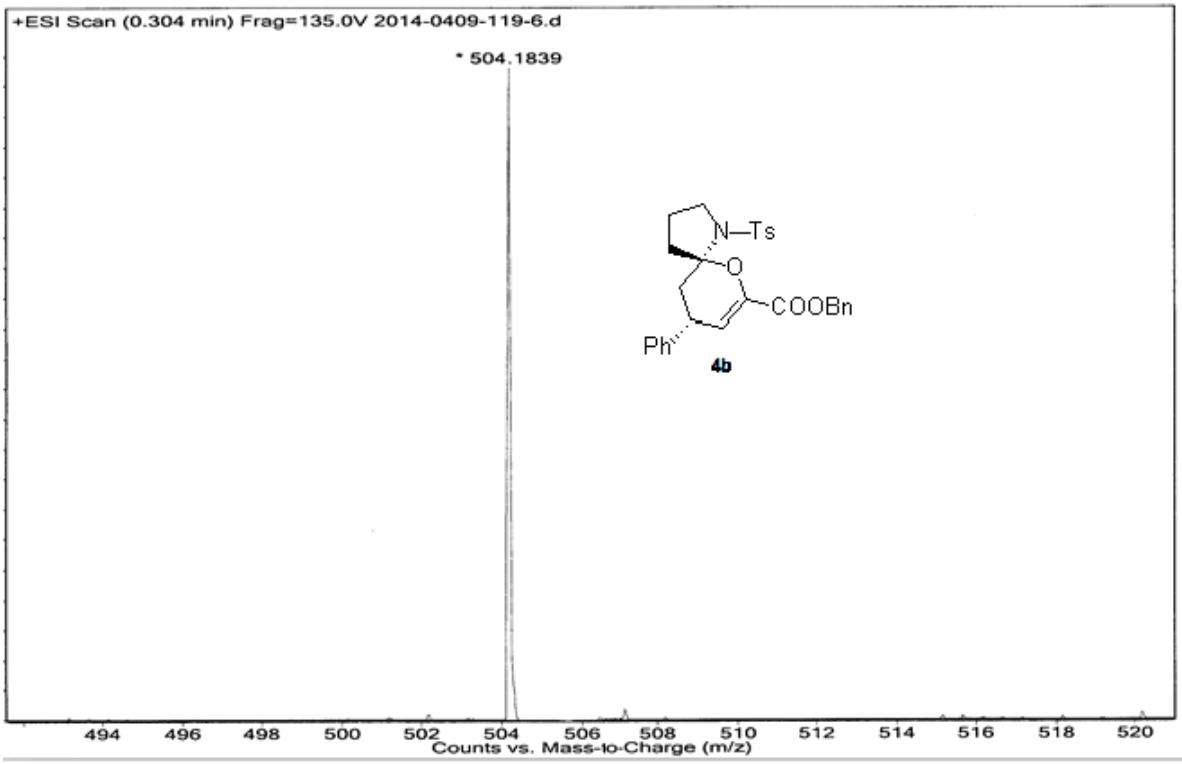


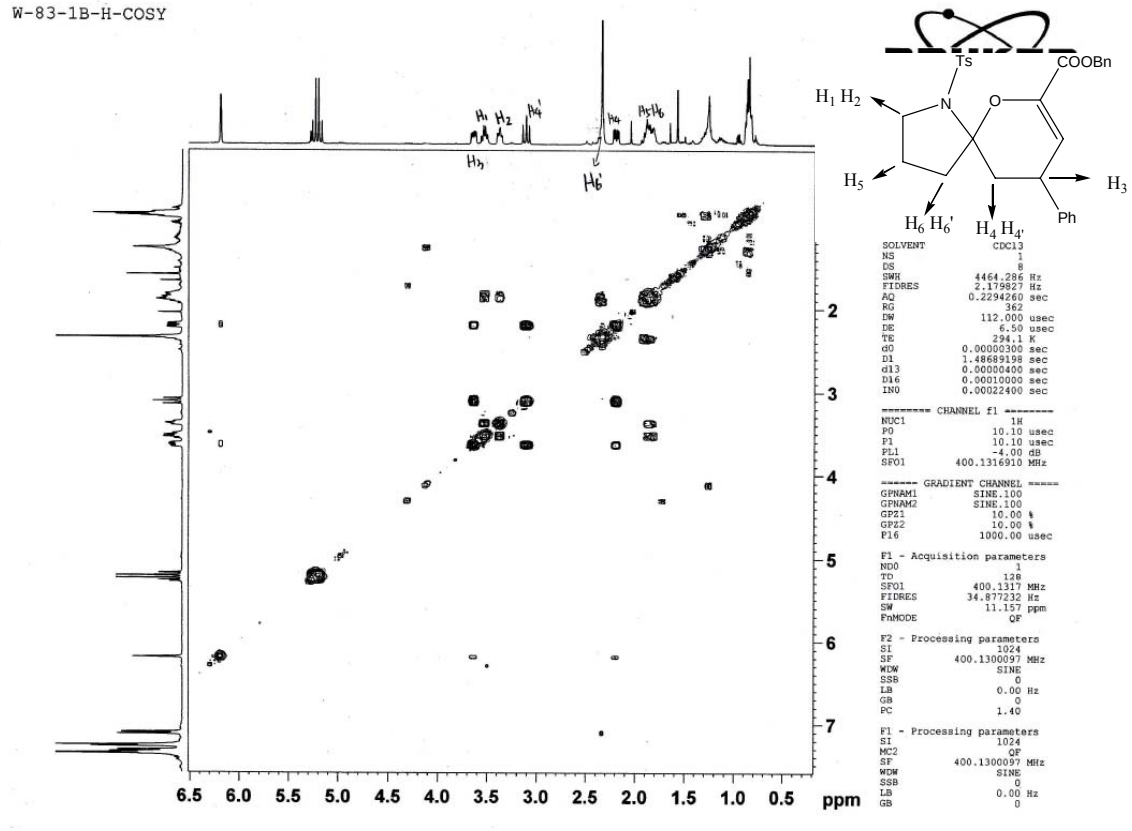


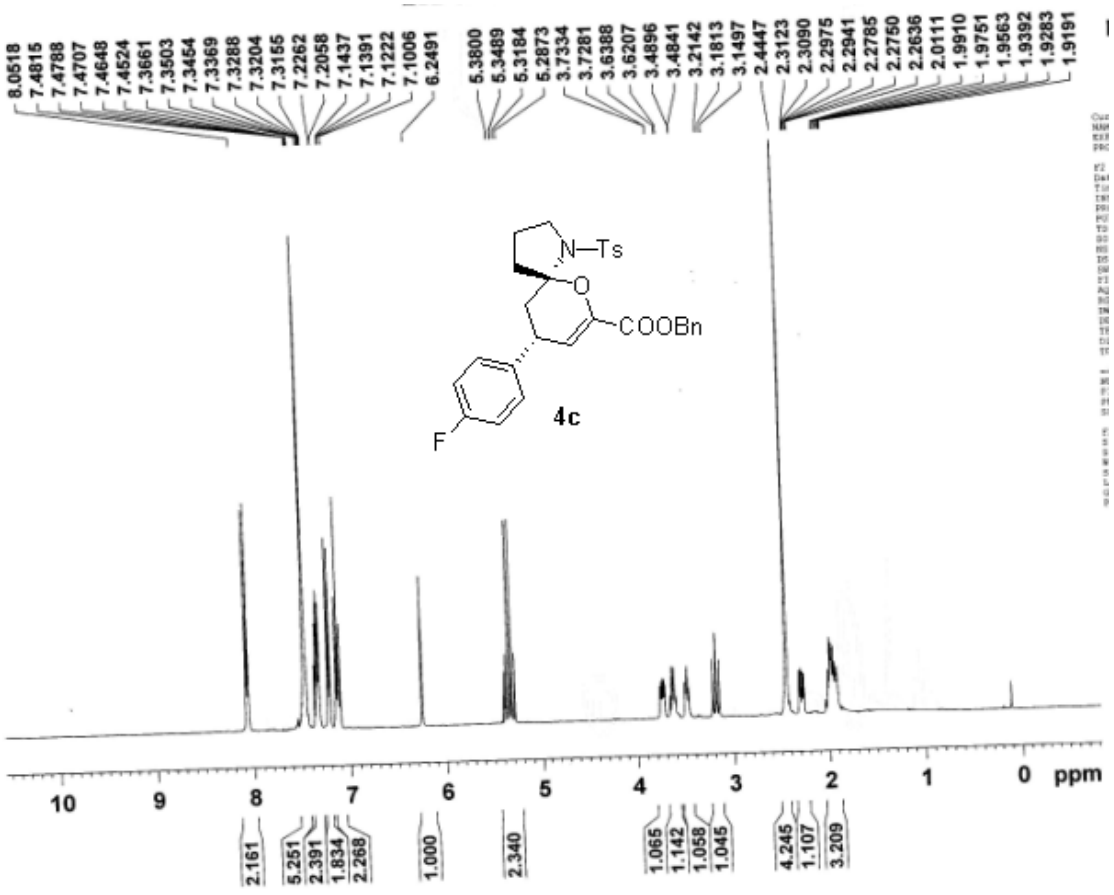


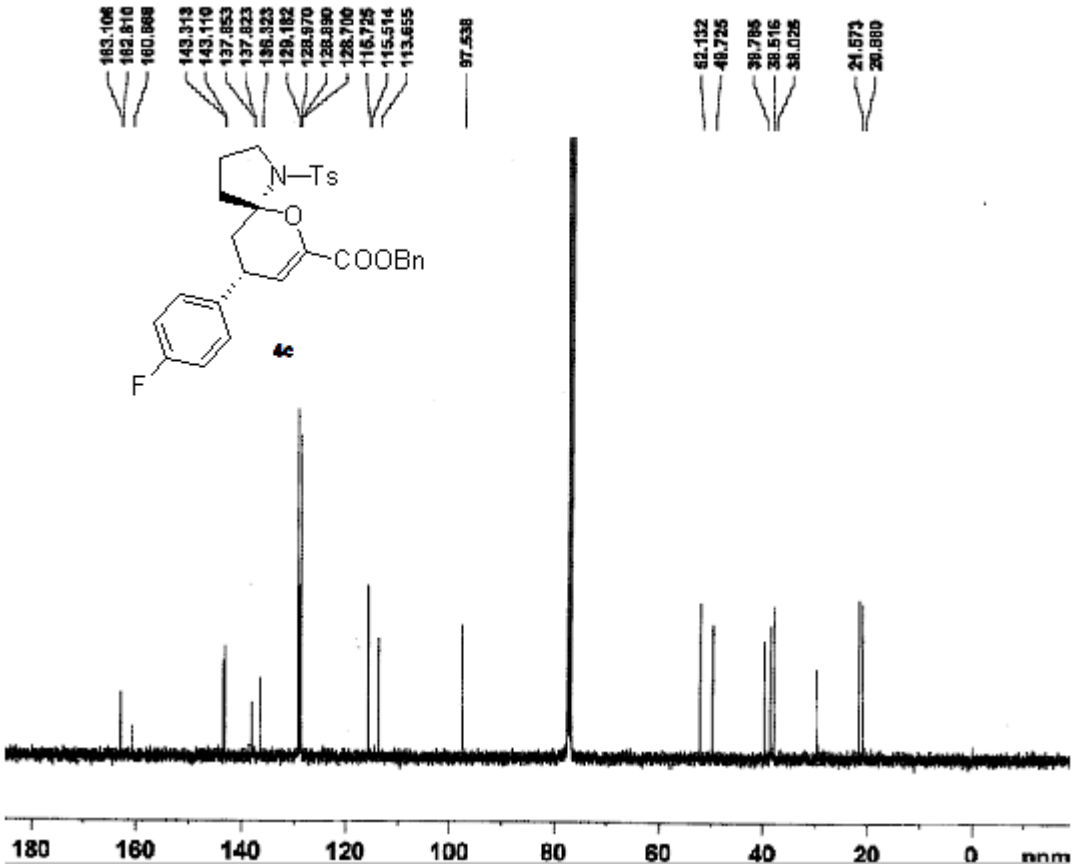
HRMS exact mass calcd for (C29H29NO5S+H) requires m/z 504.1839, found m/z 504.1839.

ıme	2014-0409-119-6	Position	P1-D7	Instrument Name	Instrument 1	User Name	
	-1	InjPosition		SampleType	Sample	IRM Calibration Status	Success
ame	2014-0409-119-6.d	ACQ Method	0103.m	Comment		Acquired Time	4/9/2014 10:02:51 AM

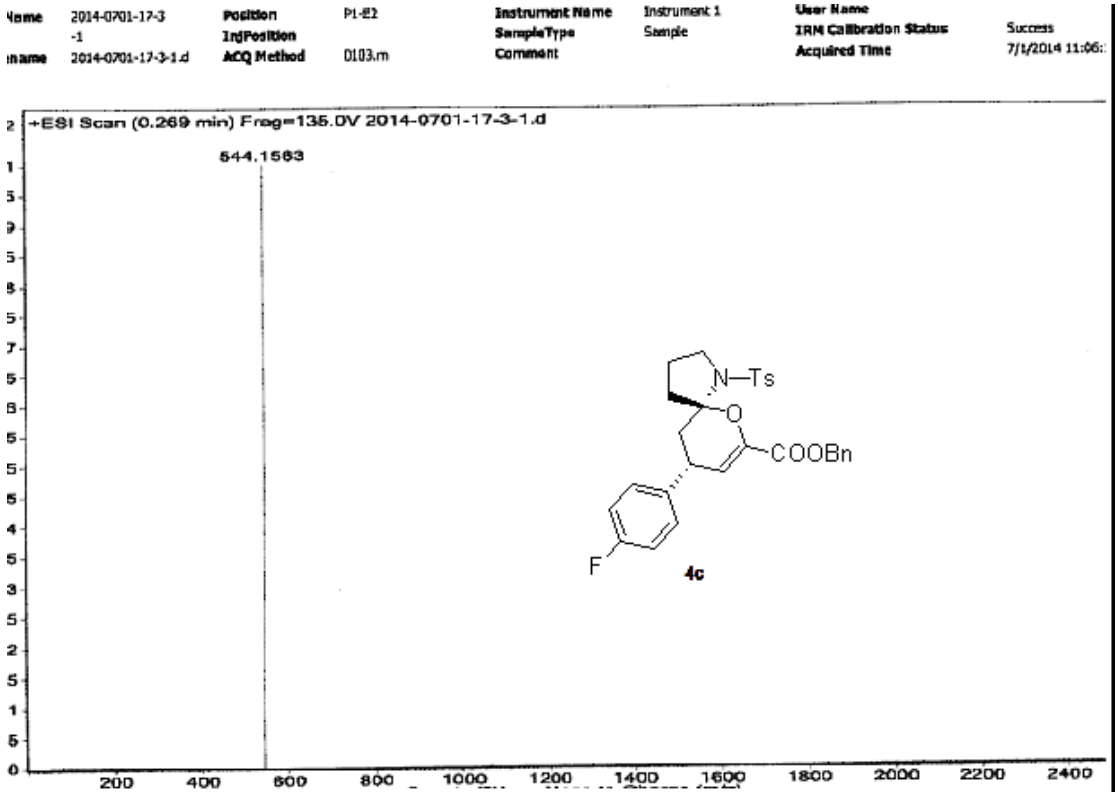


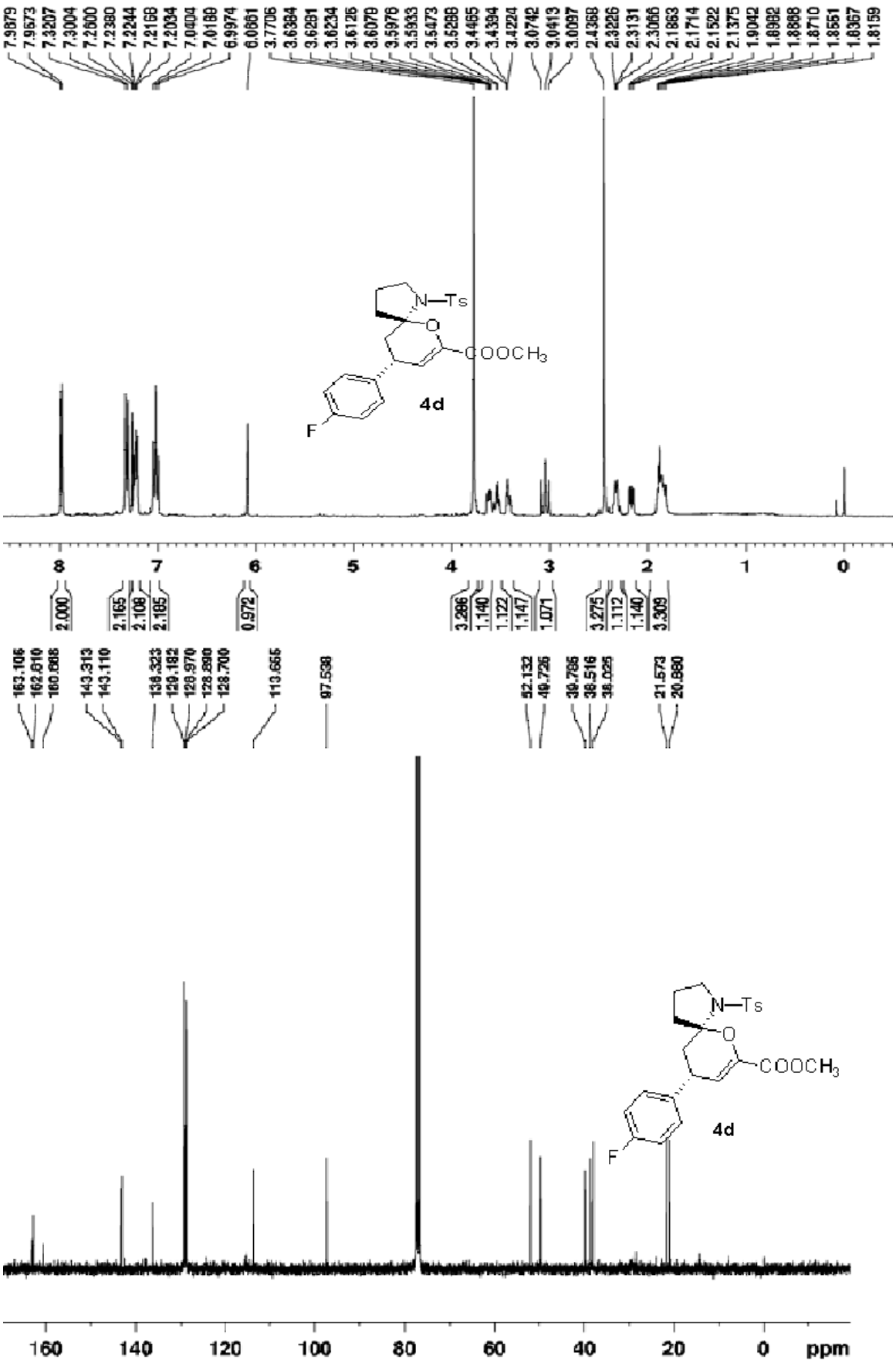

W-83-1B-H-COSY
Ts
COOBn
H1 H2
N
O
H5
H3
H6 H6'
H4 H4'
Ph
SOLVENT CDCl3
NS 1
DS 8
SWH 4464.286 Hz
FIDRES 2.179827 Hz
AQ 0.2294260 sec
RG 362
DW 112.000 usec
DE 6.50 usec
TE 294.1 K
d0 0.00000300 sec
D1 1.48689198 sec
d13 0.00000400 sec
D16 0.00010000 sec
IN0 0.00022400 sec
CHANNEL f1
NUC1 1H
P0 10.10 usec
P1 10.10 usec
PL1 -4.00 dB
SFO1 400.1316910 MHz
GRADIENT CHANNEL
GPNAM1 SINE.100
GPNAM2 SINE.100
GPZ1 10.00 %
GPZ2 10.00 %
P16 1000.00 usec
F1 - Acquisition parameters
ND0 1
TD 128
SFO1 400.1317 MHz
FIDRES 34.877232 Hz
SW 11.157 ppm
FnMODE QF
F2 - Processing parameters
SI 1024
SF 400.1300097 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0
PC 1.40
F1 - Processing parameters
SI 1024
MC2 QF
SF 400.1300097 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0
6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


8.0518 7.4815 7.4788 7.4707 7.4648 7.4524 7.3661 7.3503 7.3454 7.3369 7.3288 7.3204 7.3155 7.2262 7.2058 7.1437 7.1391 7.1222 7.1006 6.2491
5.3800 5.3489 5.3184 5.2873 3.7334 3.7281 3.6388 3.6207 3.4896 3.4841 3.2142 3.1813 3.1497 2.4447 2.3123 2.3090 2.2975 2.2941 2.2785 2.2750 2.2636 2.0111 1.9910 1.9751 1.9563 1.9392 1.9283 1.9191
N—Ts
O
COOBn
F
4c
10 9 8 7 6 5 4 3 2 1 0 ppm
2.161 5.251 2.391 1.834 2.268 1.000 2.340 1.065 1.142 1.058 1.045 4.245 1.107 3.209

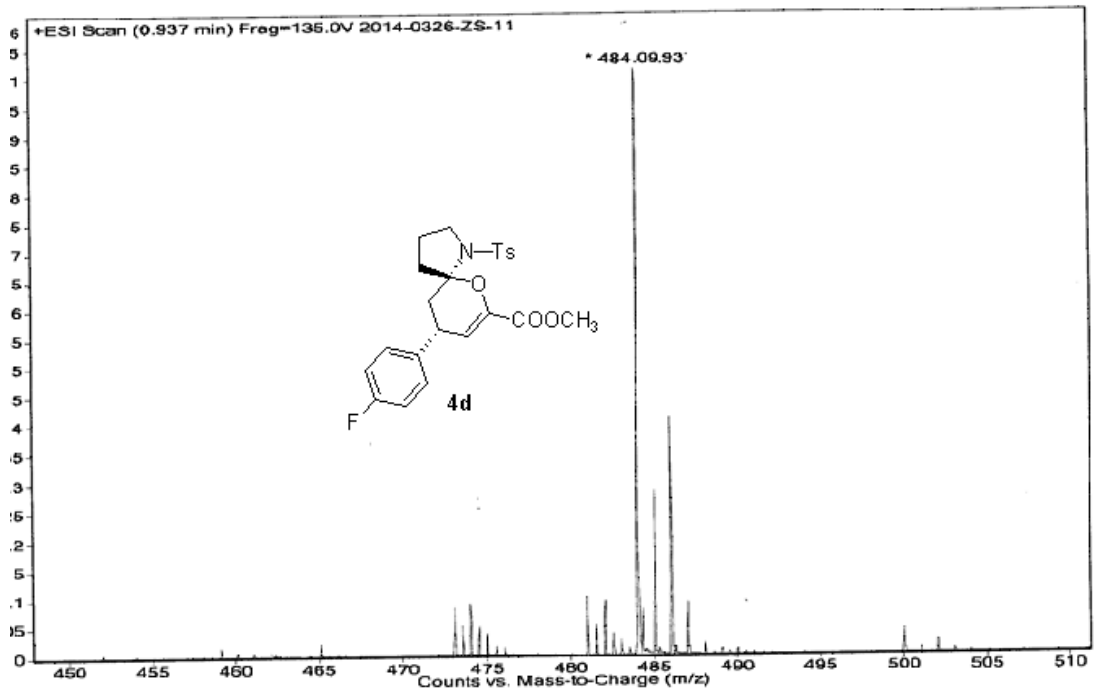


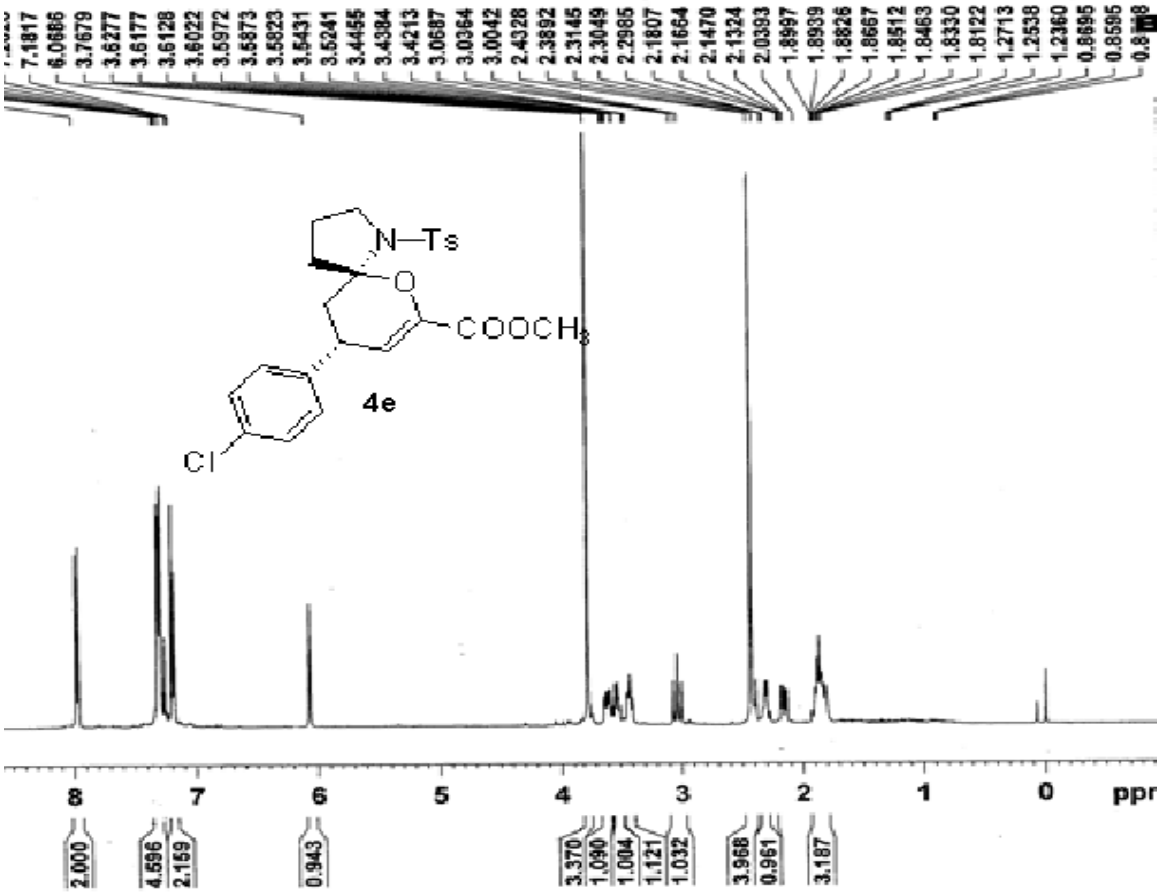
HRMS exact mass calcd for (C29H28FNO5S+Na) requires m/z 544.1564, found m/z 544.1563.

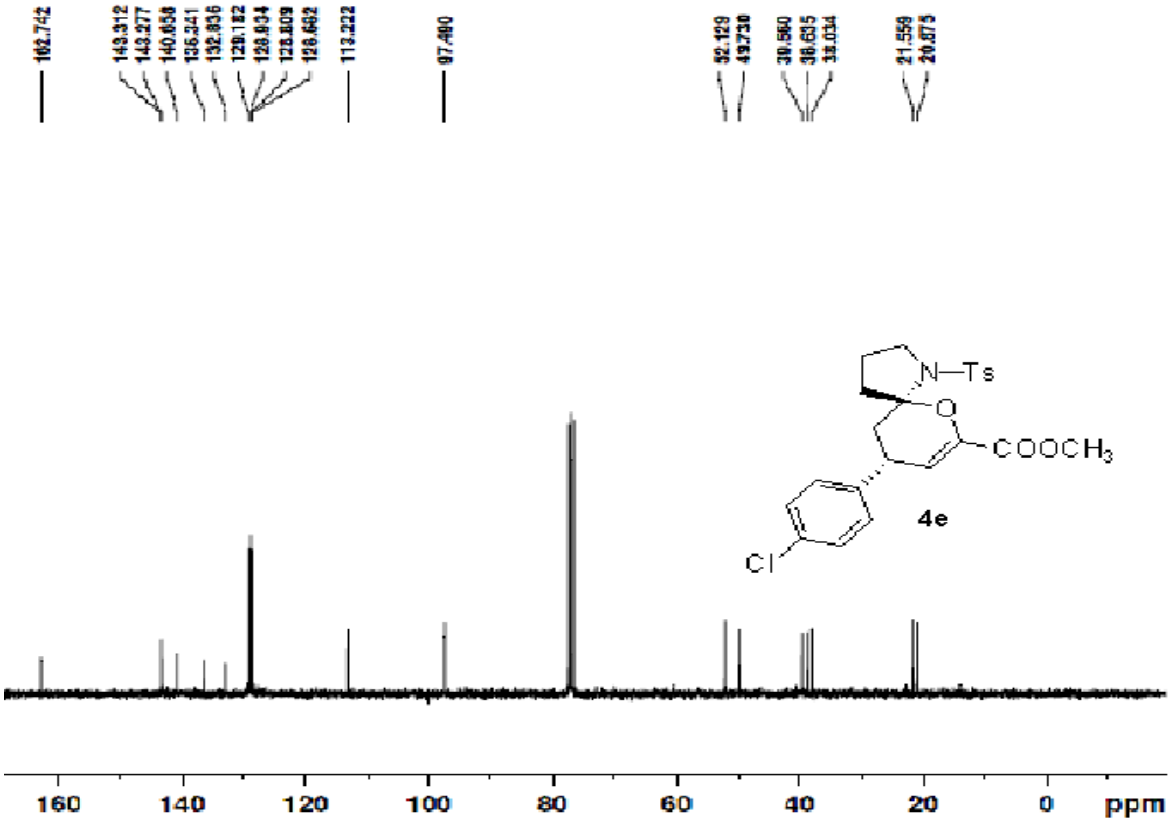



7.9879
7.9573
7.3207
7.3004
7.2600
7.2380
7.2244
7.2168
7.2034
7.0404
7.0188
6.9974
6.0661
3.7706
3.6384
3.6281
3.6234
3.6125
3.6078
3.5976
3.5933
3.5473
3.5288
3.4465
3.4394
3.4224
3.0742
3.0413
3.0097
2.4368
2.3226
2.3131
2.3066
2.1863
2.1714
2.1522
2.1375
1.9042
1.8982
1.8868
1.8710
1.8551
1.8367
1.8159
N—Ts
O
COOCH3
4d
F
8
7
6
5
4
3
2
1
0
2.000
2.165
2.108
2.185
0.972
3.286
1.140
1.122
1.147
1.071
3.275
1.112
1.140
3.309
163.106
162.610
160.668
143.313
143.110
136.323
129.182
128.970
128.890
128.700
113.655
97.538
52.132
49.726
39.785
38.516
38.025
21.573
20.880
N—Ts
O
COOCH3
4d
F
160
140
120
100
80
60
40
20
0
ppm

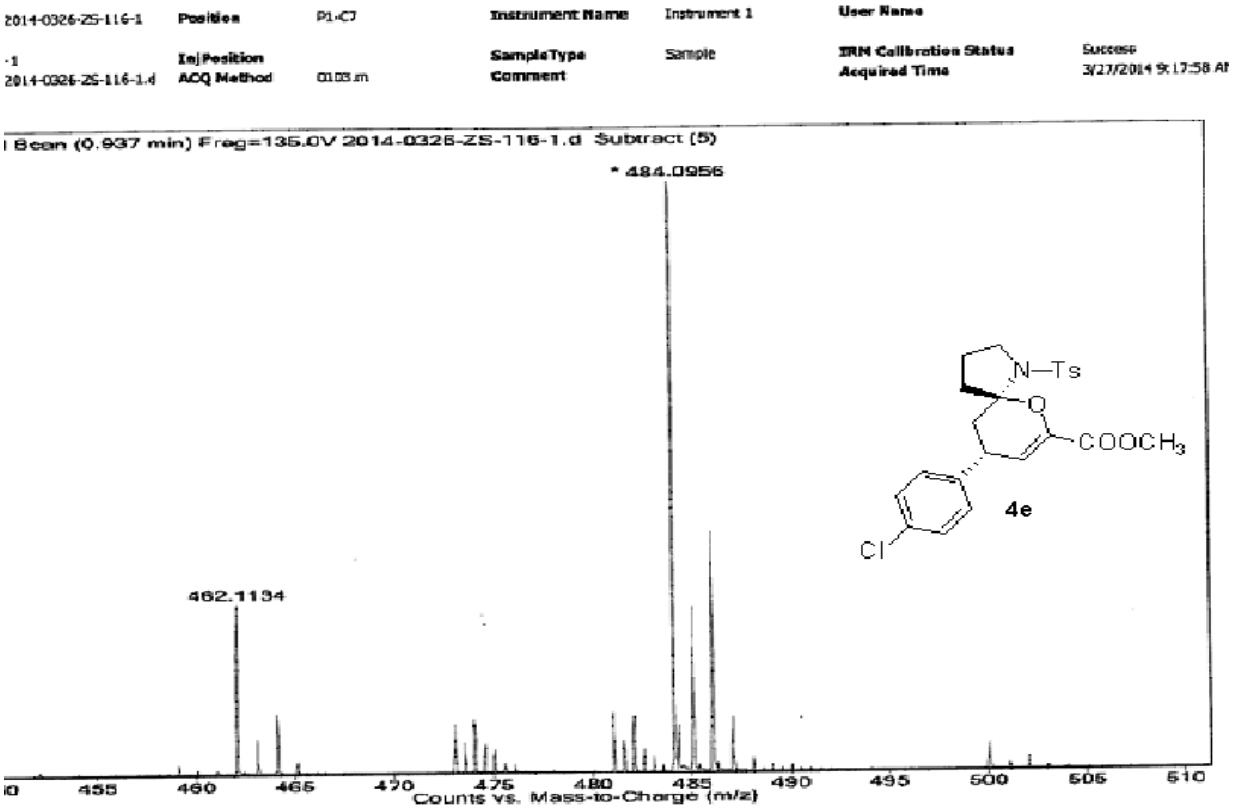
HRMS exact mass calcd for (C23H24FNO5S+K) requires m/z 484.0991, found m/z 484.0993.

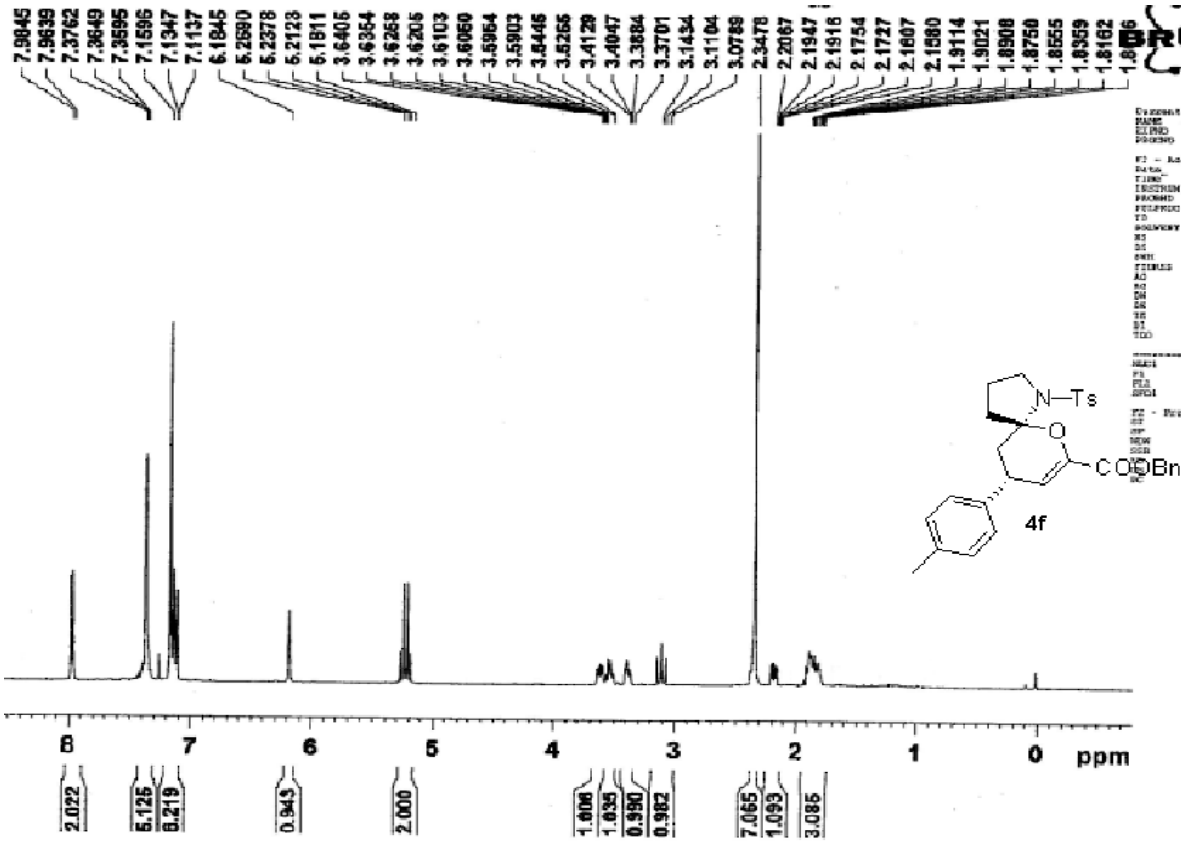




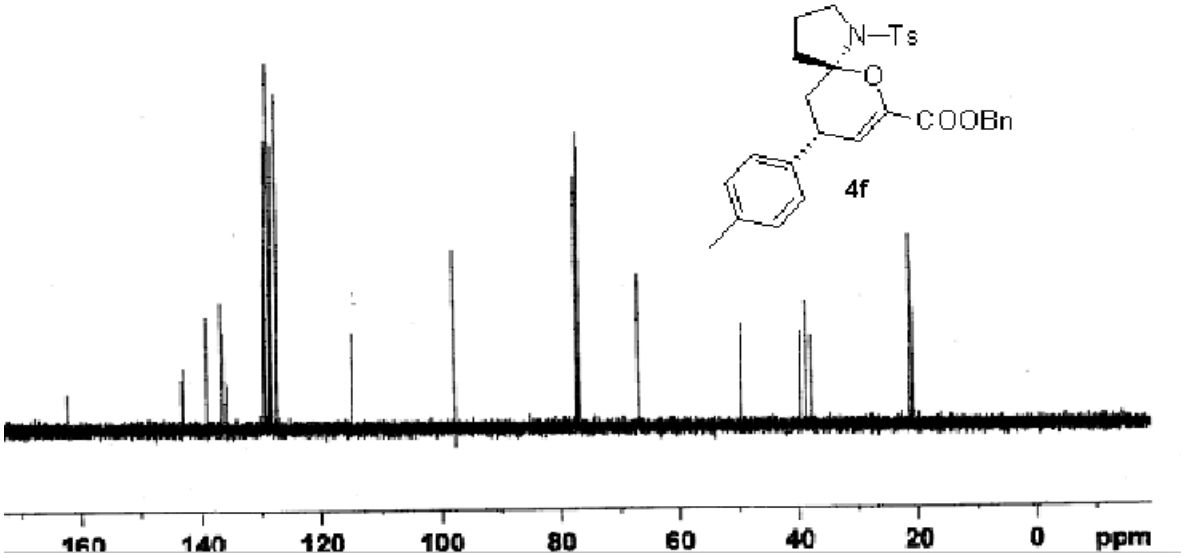


HRMS exact mass calcd for (C23H24ClNO5S+Na) requires m/z 484.0956, found m/z 484.0956.

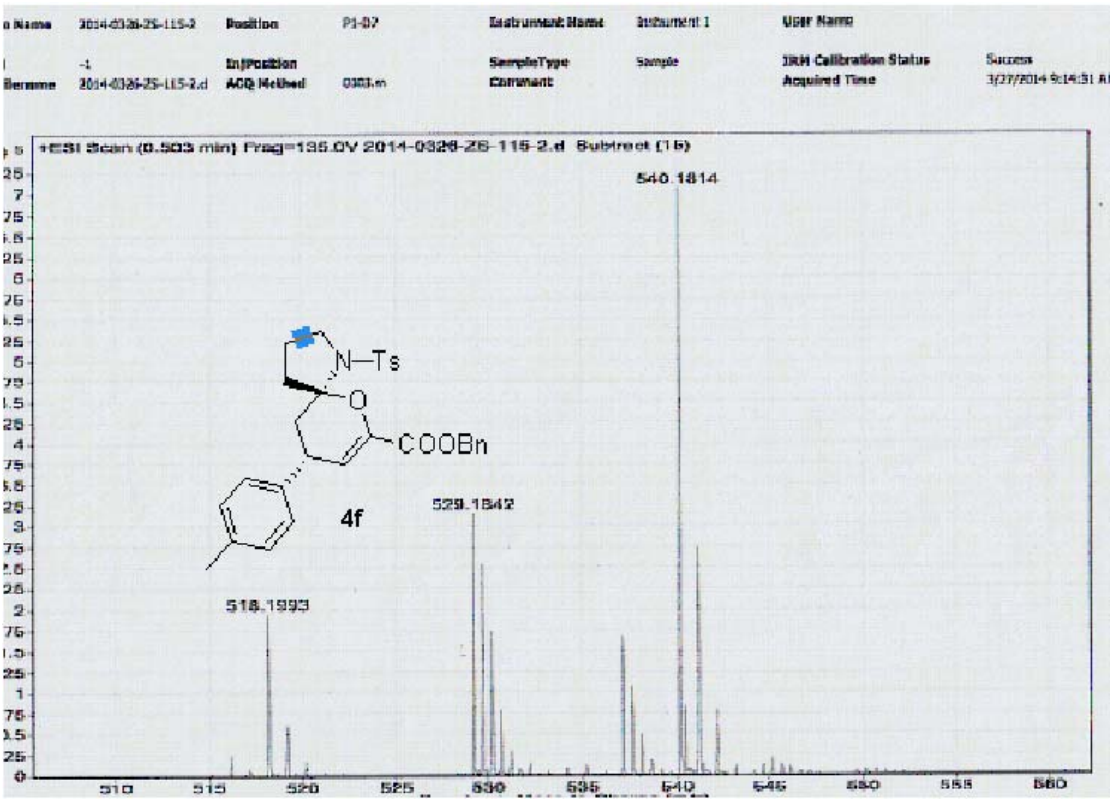


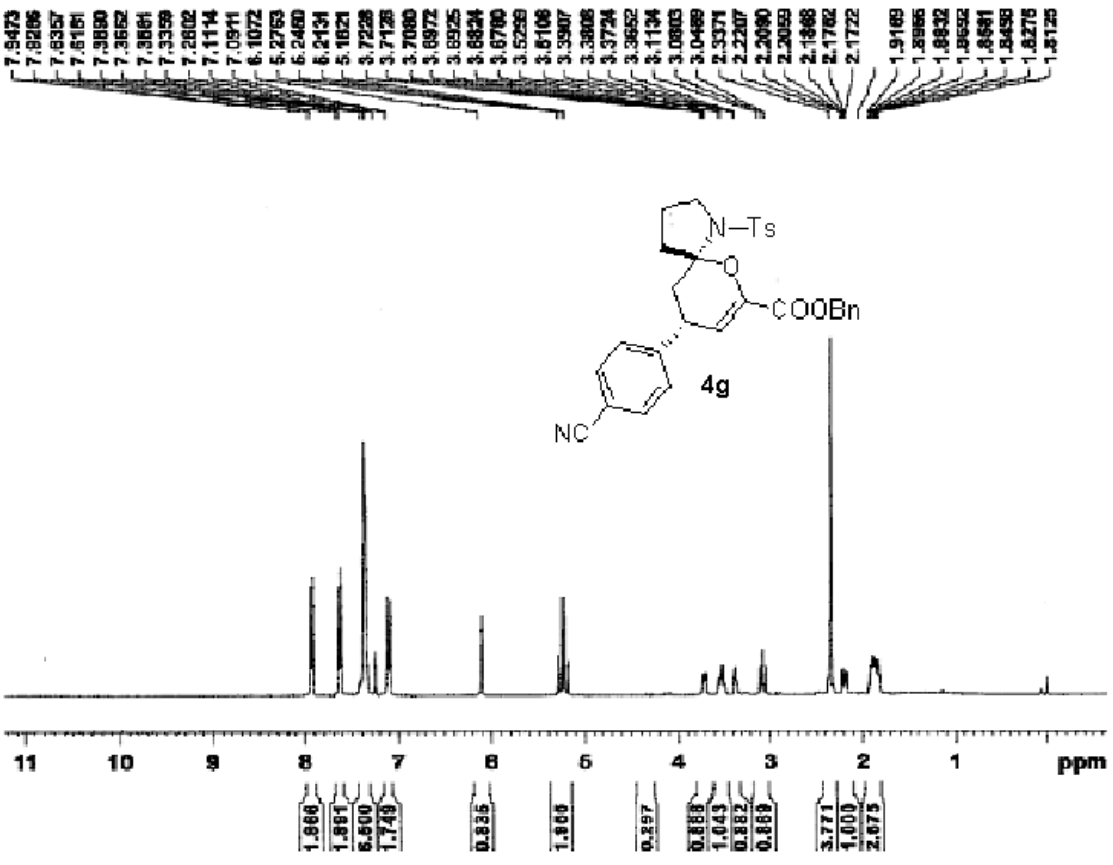

N—Ts
O
COOBn
4f
6
7
6
5
4
3
2
1
0
ppm

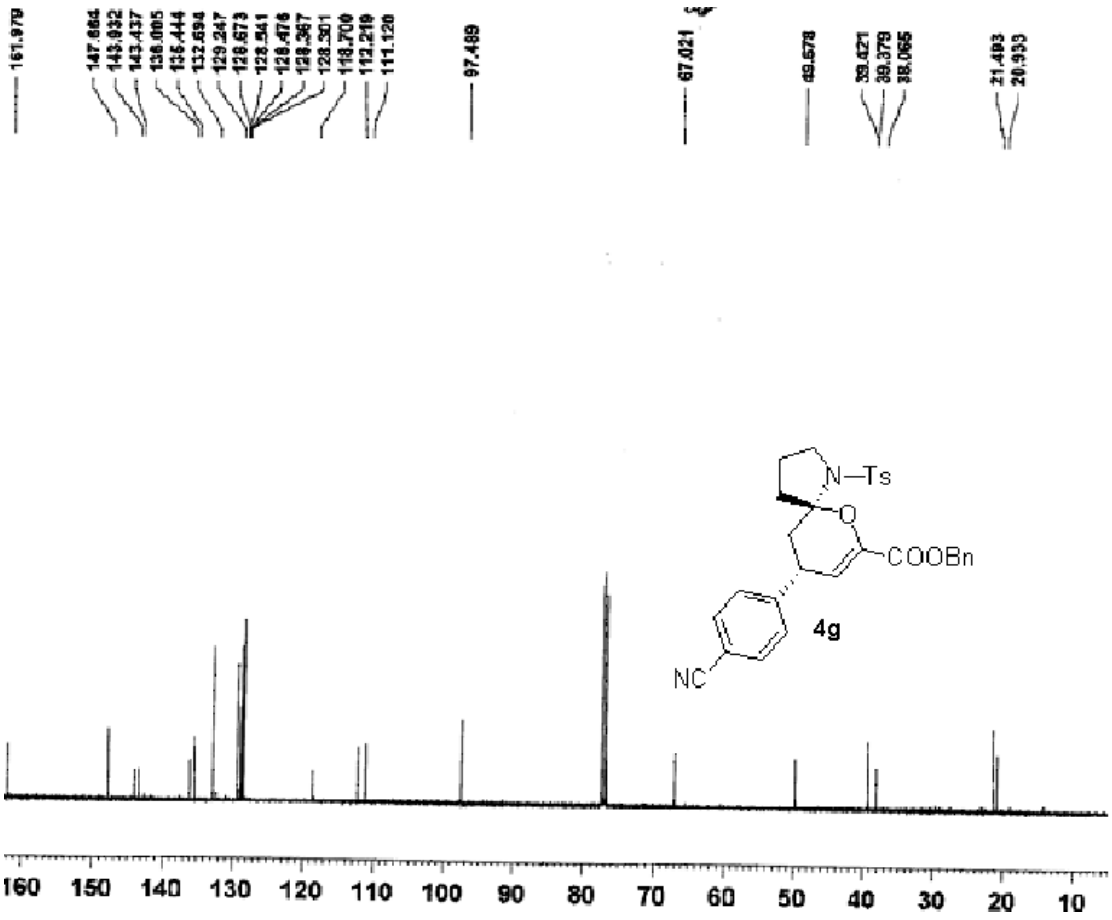
ZSA-116-2-C13


N—Ts
O
COOBn
4f
160
140
120
100
80
60
40
20
0
ppm

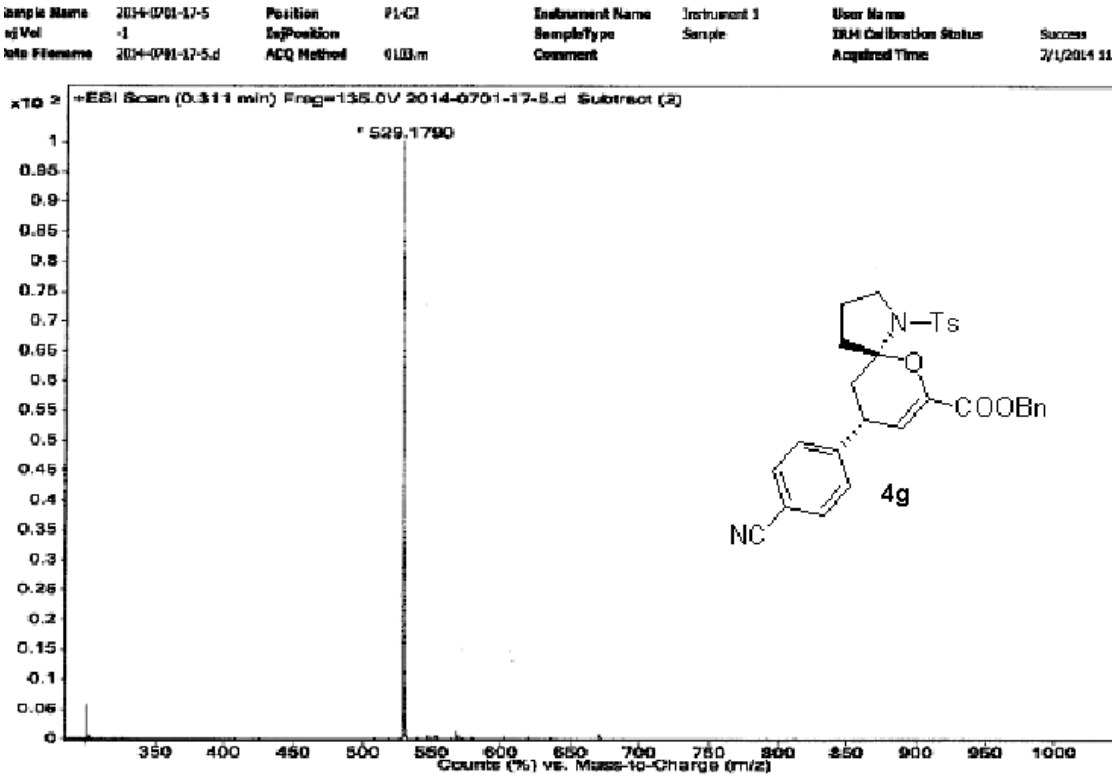
HRMS exact mass calcd for (C30H31NO5S+Na) requires m/z 540.1815, found m/z 540.1814.

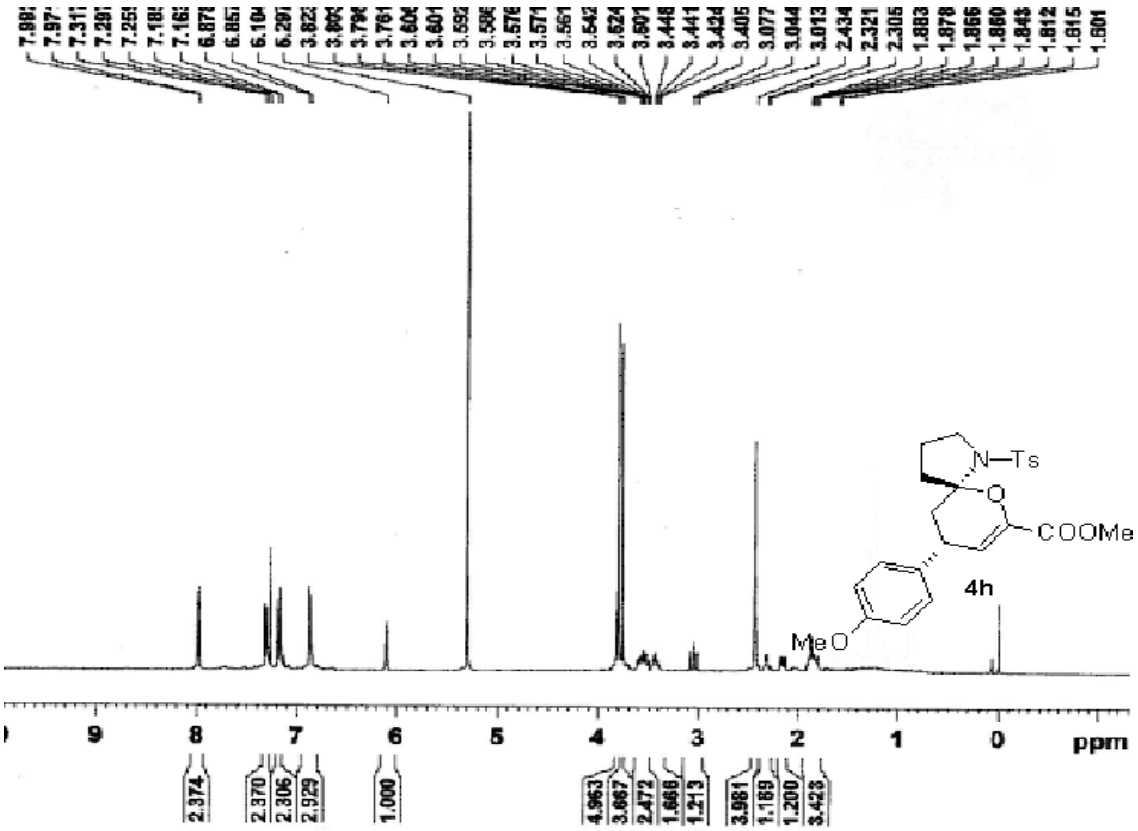


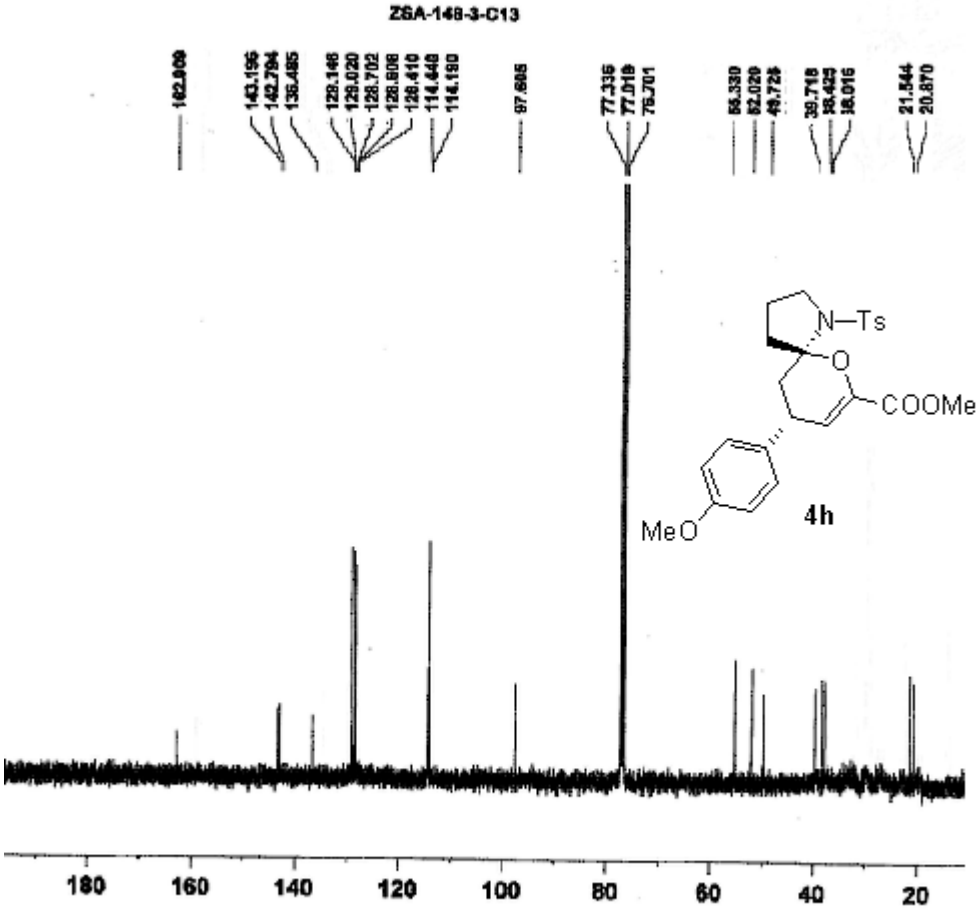




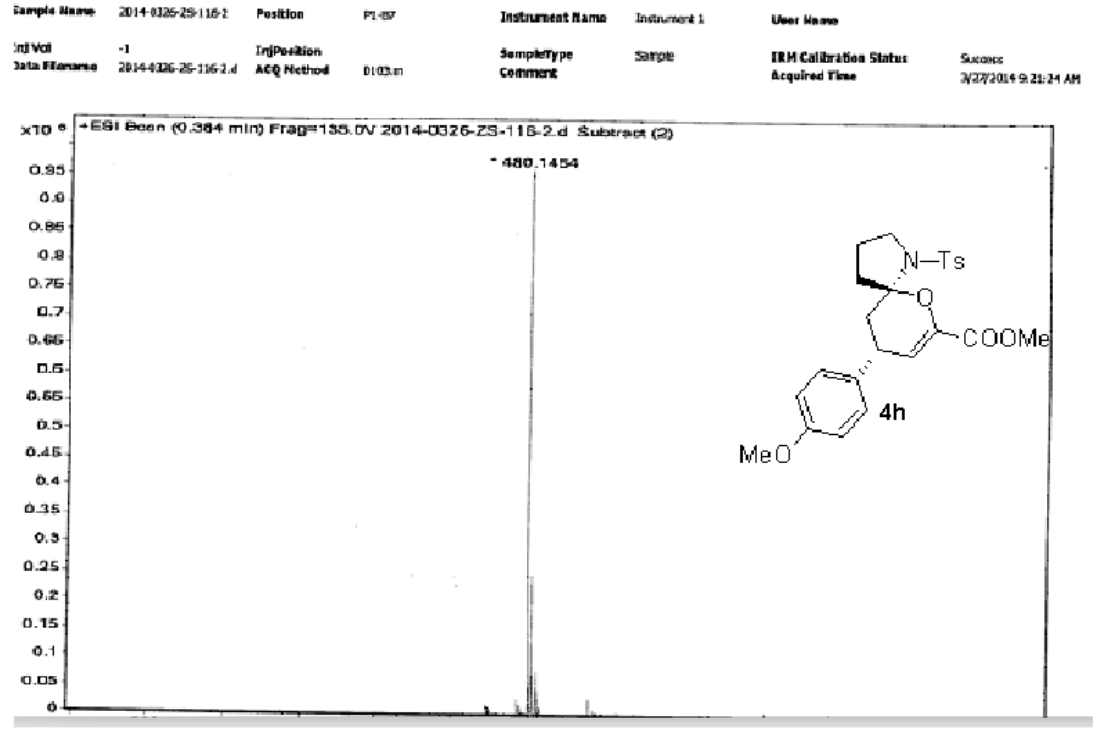
HRMS exact mass calcd for (C30H29N2O5S+H) requires m/z 529.1792, found m/z 529.1790.

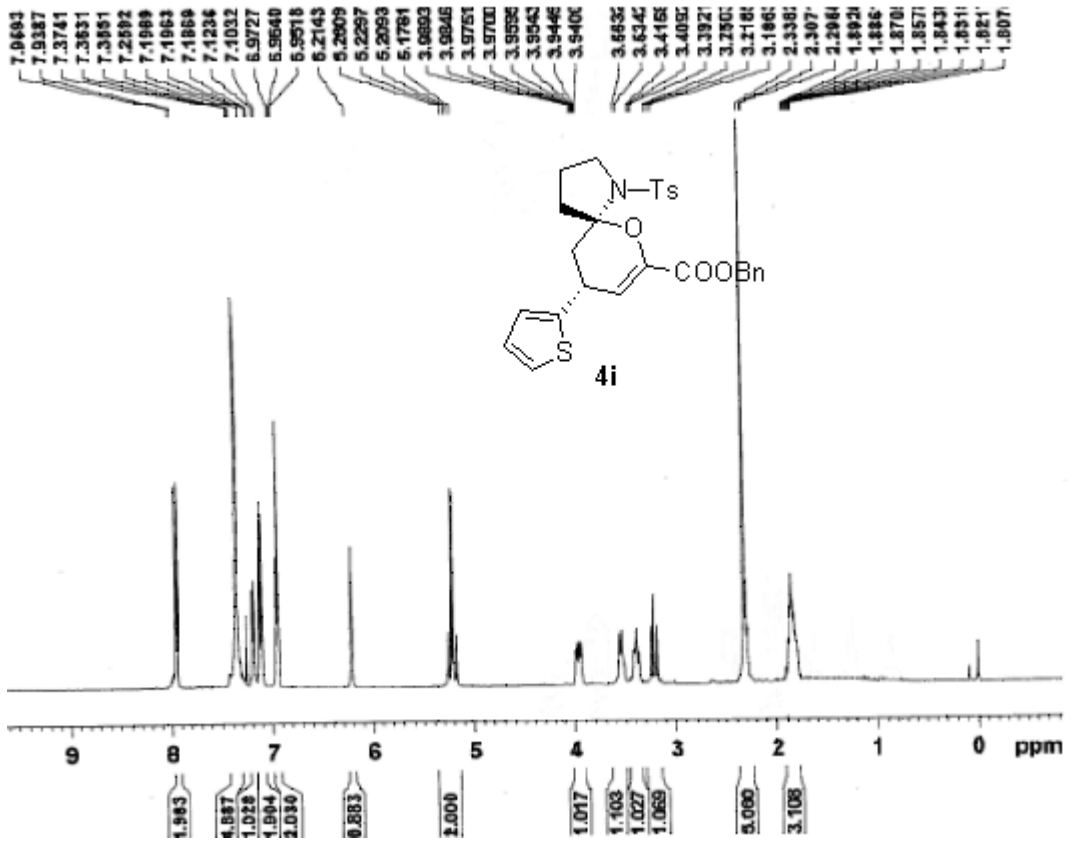


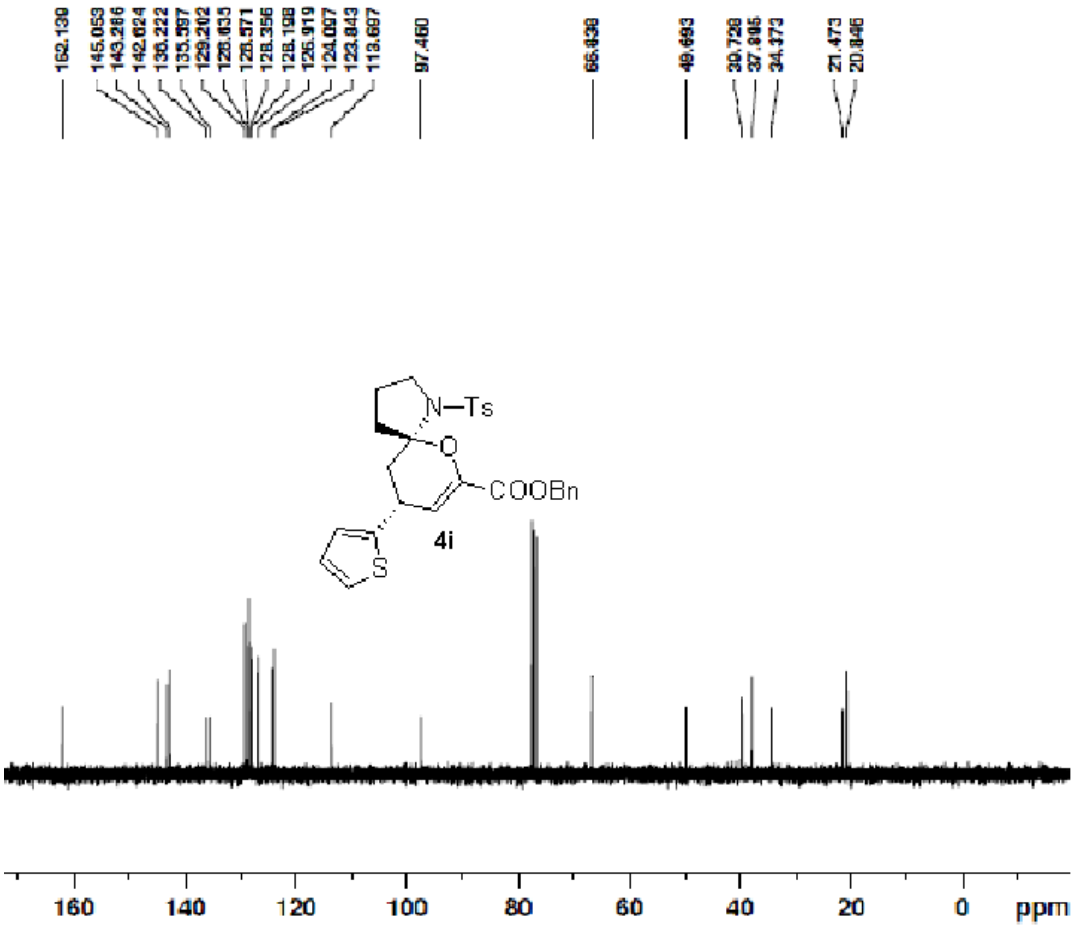

N—Ts
O
COOMe
4h
MeO
9
8
7
6
5
4
3
2
1
0
ppm
2.374
2.370
2.306
2.929
1.000
4.963
3.667
2.472
1.666
1.213
3.961
1.189
1.200
3.423


ZSA-148-3-C13
N—Ts
O
COOMe
4h
MeO
180
160
140
120
100
80
60
40
20

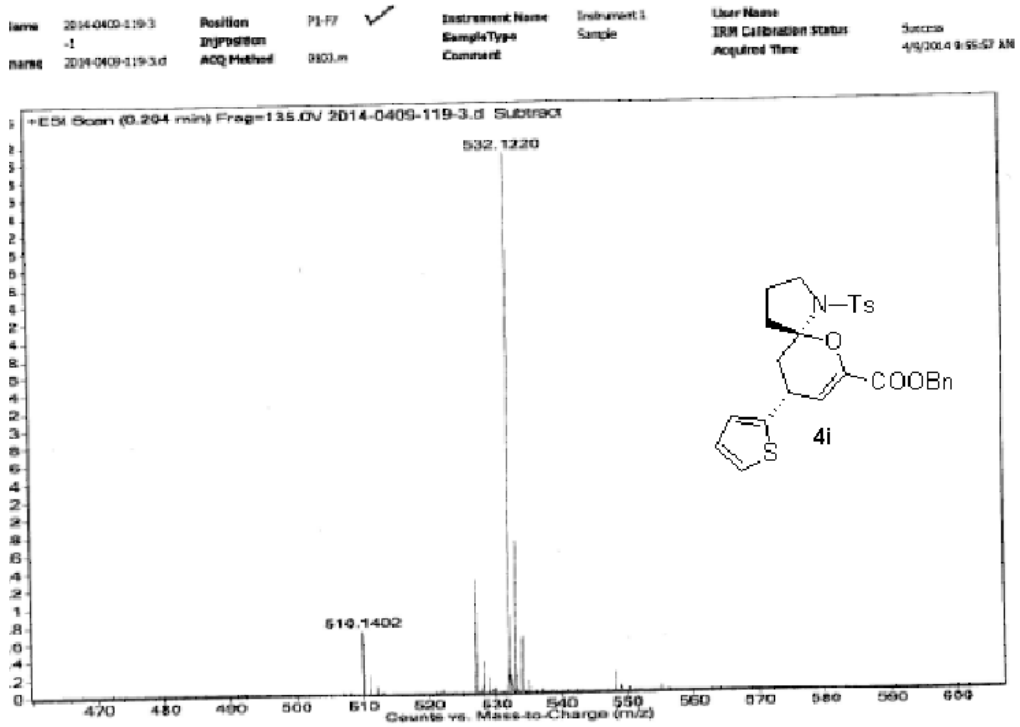
HRMS exact mass calcd for (C24H27NO6S+Na) requires m/z 480.1451, found m/z 480.1454.

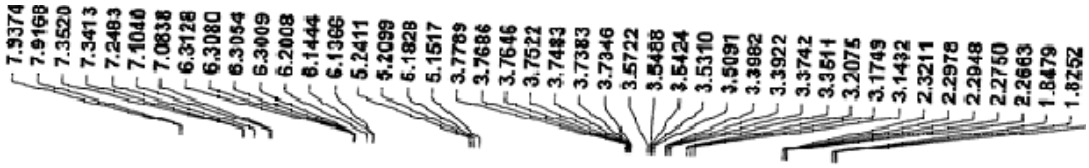


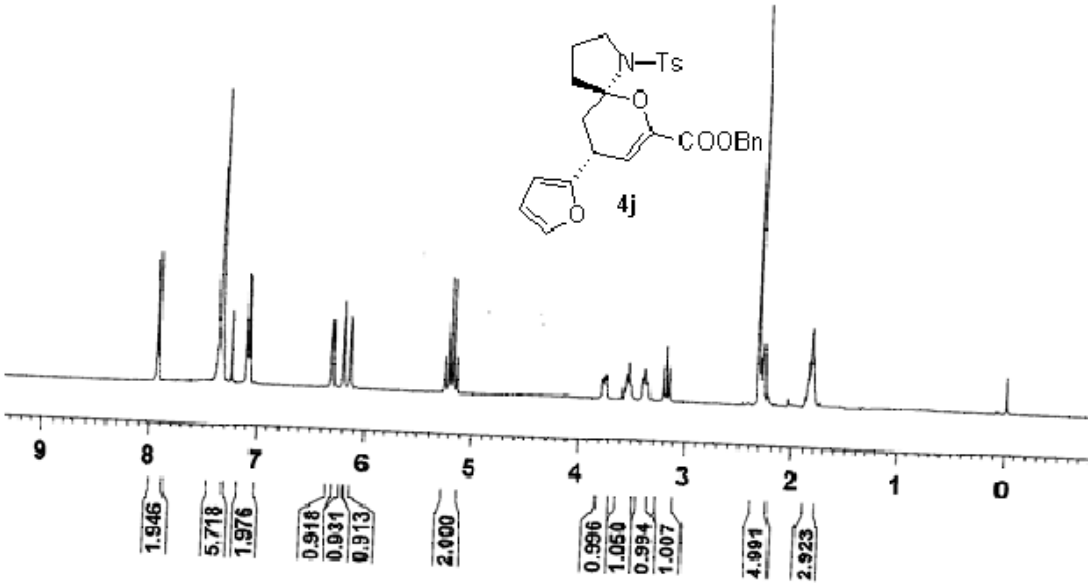


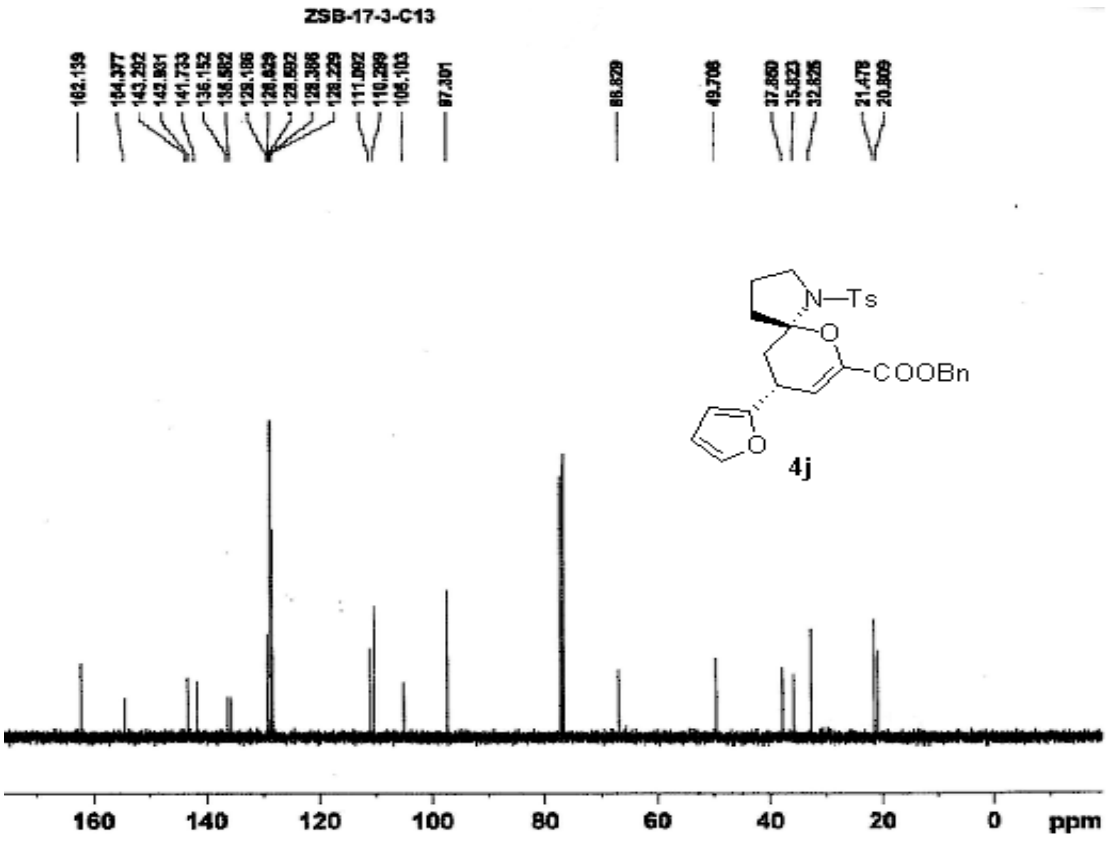


HRMS exact mass calcd for (C27H27NO5S2+Na) requires m/z 532.1223, found m/z 532.1220.

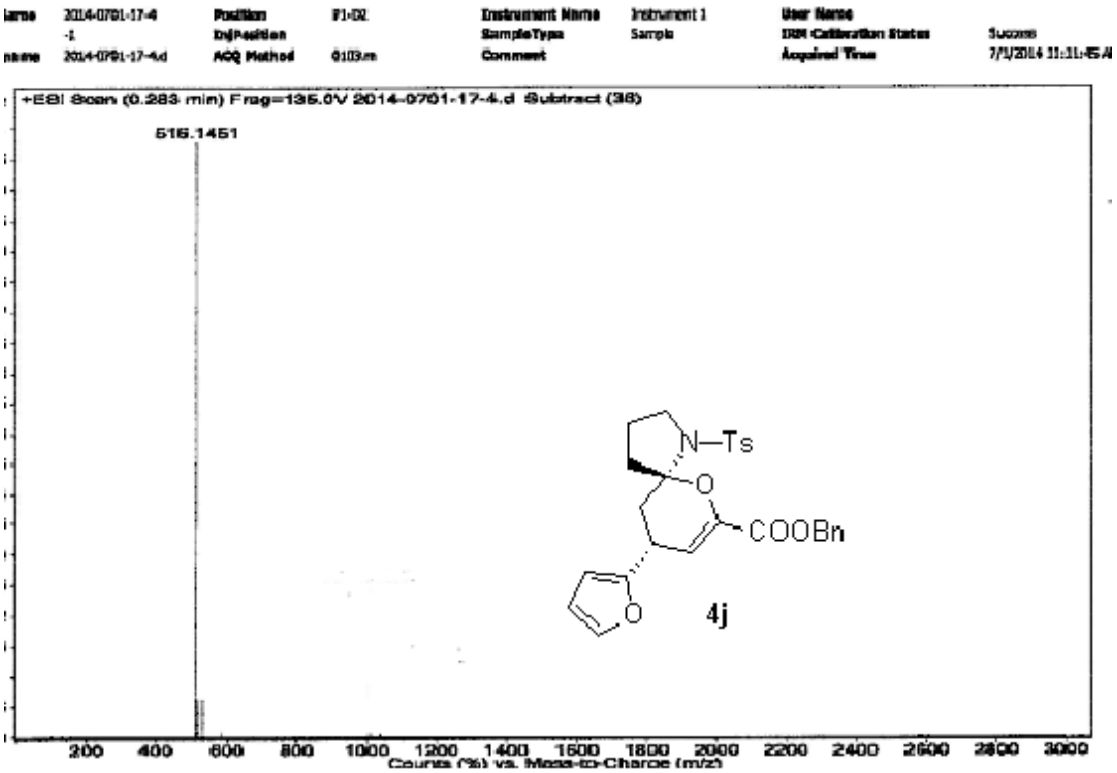


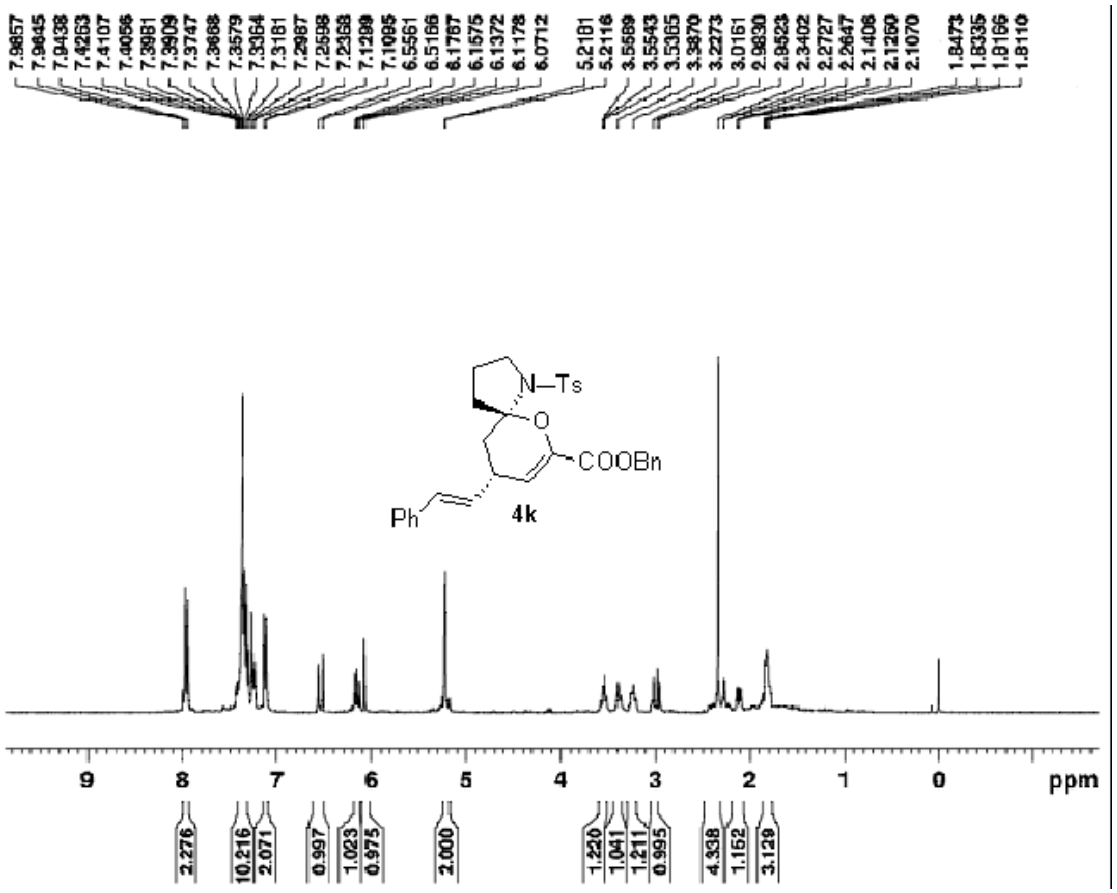

7.9374
7.9168
7.3520
7.3413
7.2483
7.1040
7.0838
6.3128
6.3080
6.3054
6.3009
6.2008
6.1444
6.1366
5.2411
5.2099
5.1828
5.1517
3.7769
3.7686
3.7646
3.7522
3.7483
3.7383
3.7346
3.5722
3.5468
3.5424
3.5310
3.5091
3.3982
3.3922
3.3742
3.3511
3.2075
3.1749
3.1432
2.3211
2.2978
2.2848
2.2750
2.2663
1.8479
1.8252

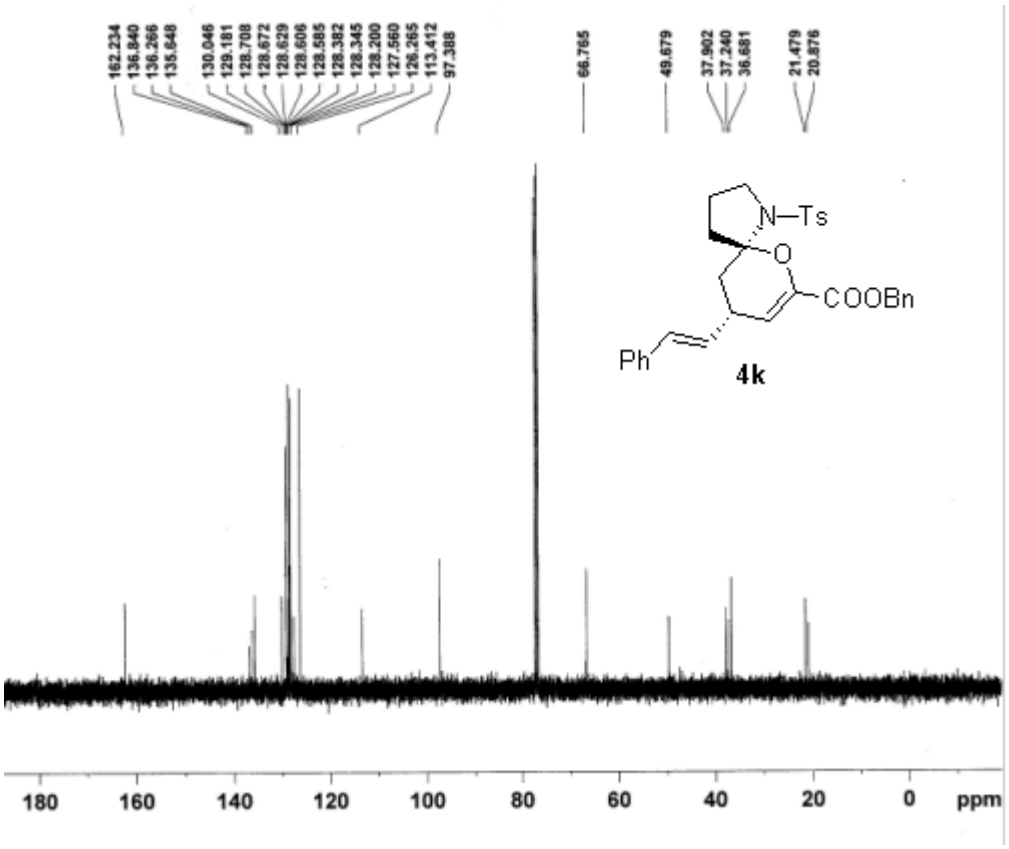

N—Ts
O
COOBn
O
4j
9
8
7
6
5
4
3
2
1
0
1.946
5.718
1.976
0.918
0.931
0.913
2.000
0.996
1.050
0.994
1.007
4.991
2.923


ZSB-17-3-C13
N—Ts
O
COOBn
O
4j
160
140
120
100
80
60
40
20
0
ppm

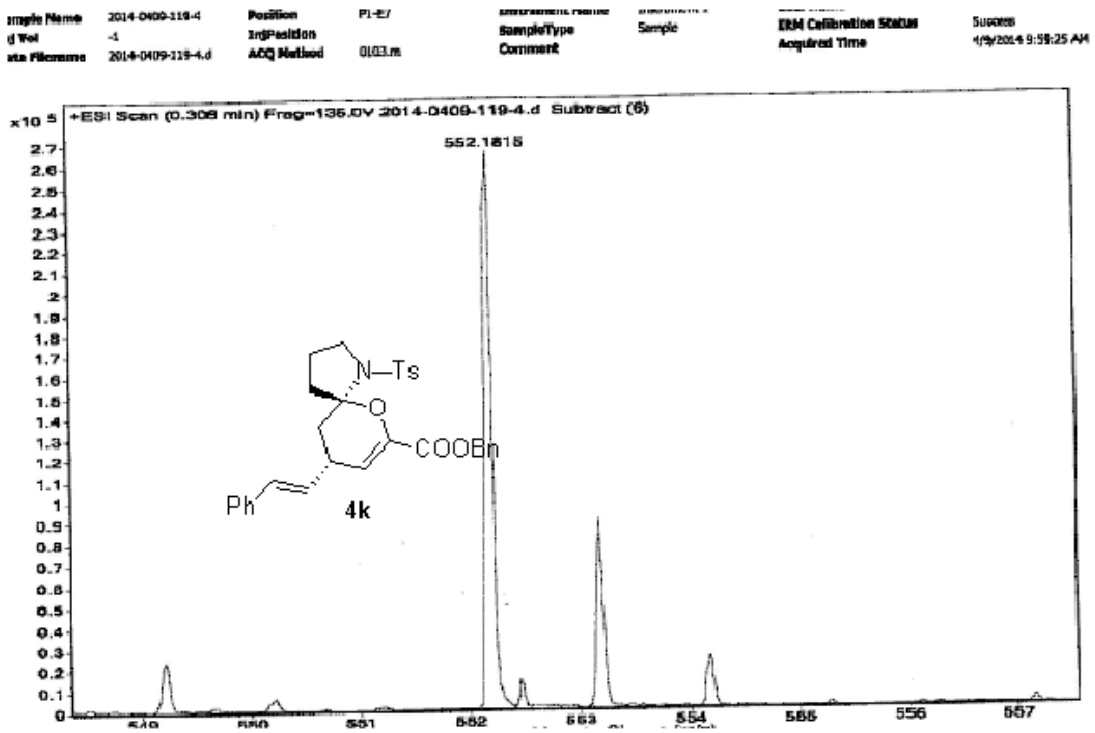
HRMS exact mass calcd for (C27H27NO5S2+Na) requires m/z 516.1451, found m/z 516.1451.

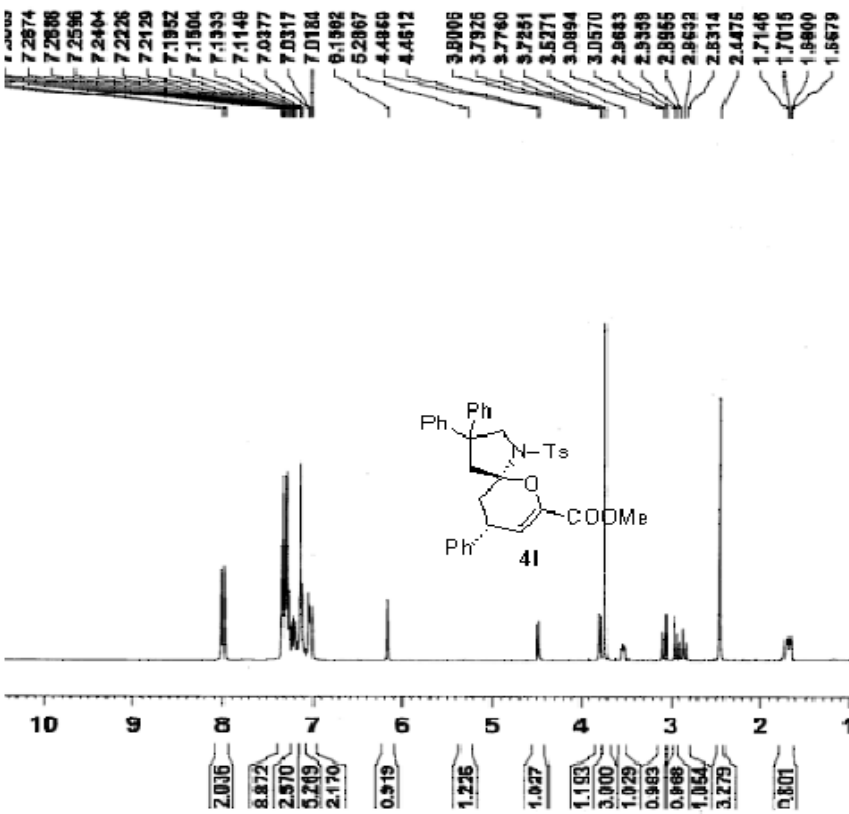


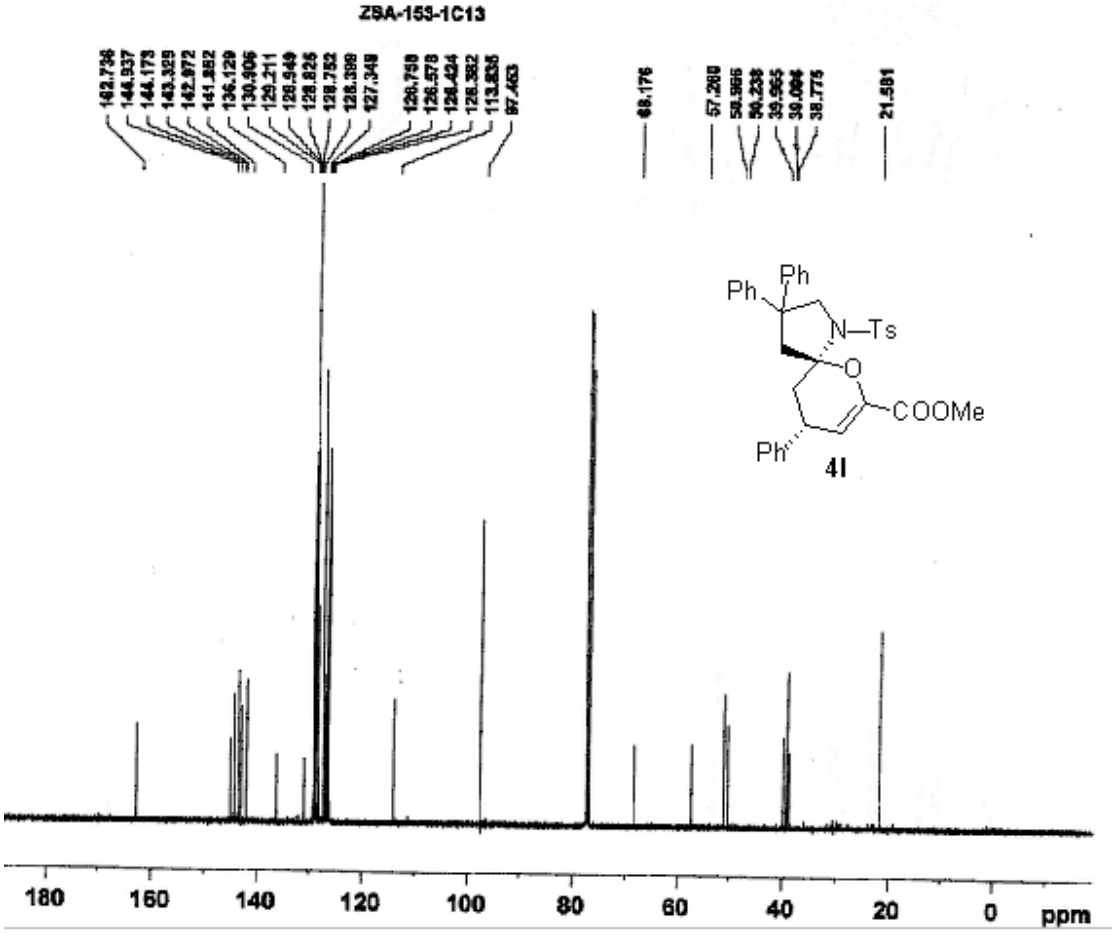




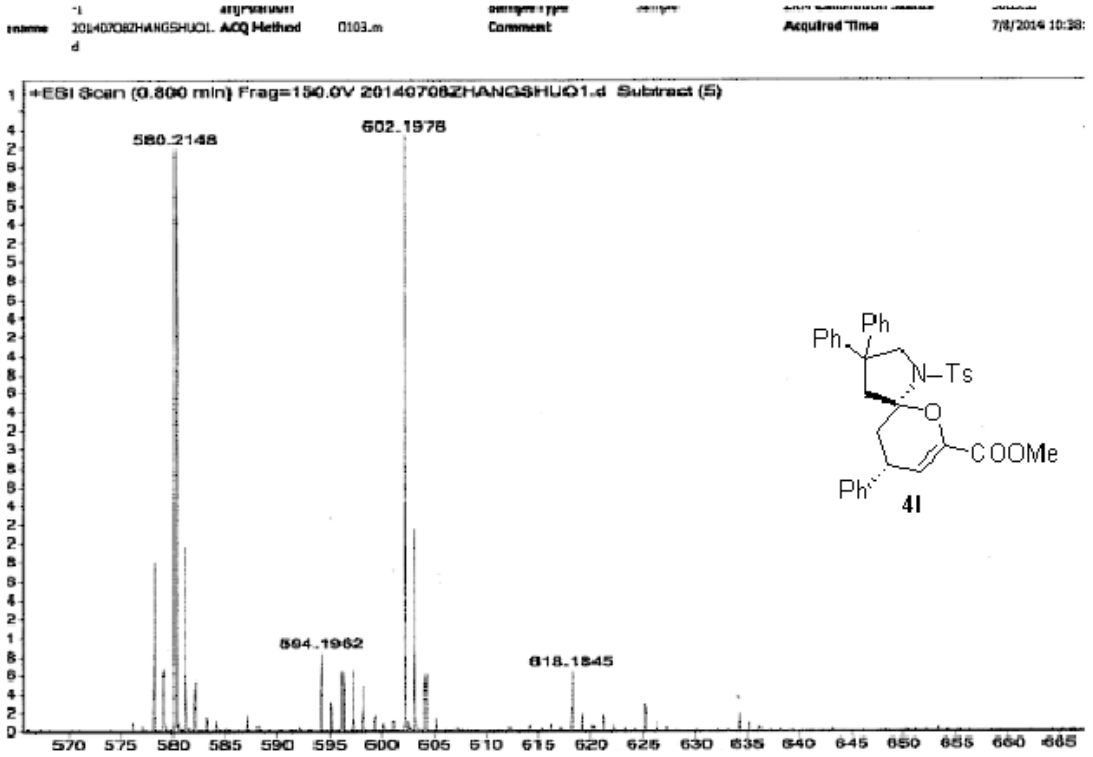
HRMS exact mass calcd for (C31H31NO5S+Na) requires m/z 552.1815, found m/z 552.1815.

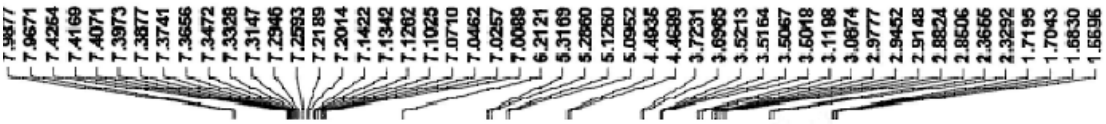


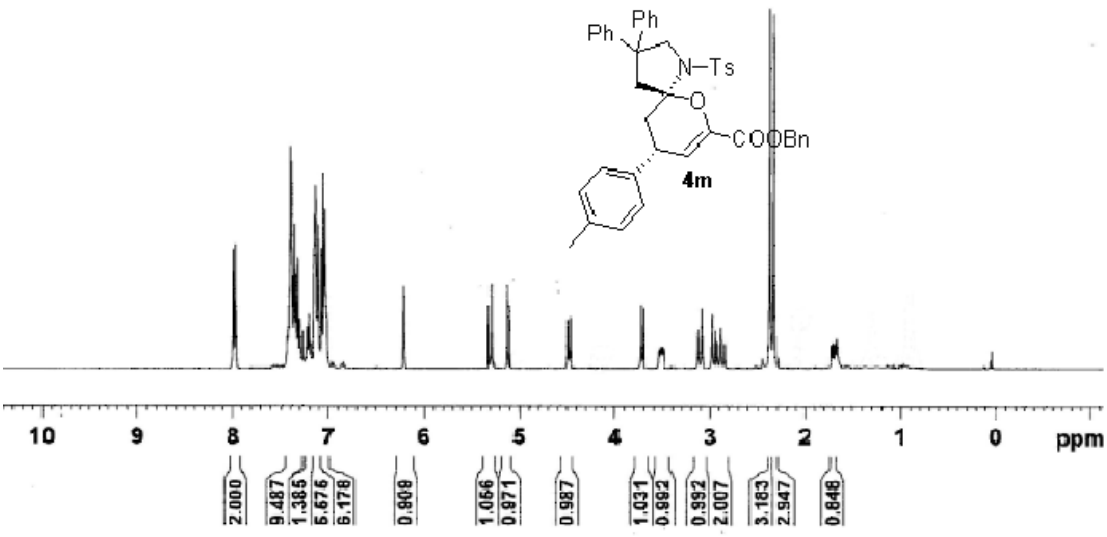

Ph
Ph
N–Ts
O
COOMe
Ph
4l
10
9
8
7
6
5
4
3
2
1
0
ppm

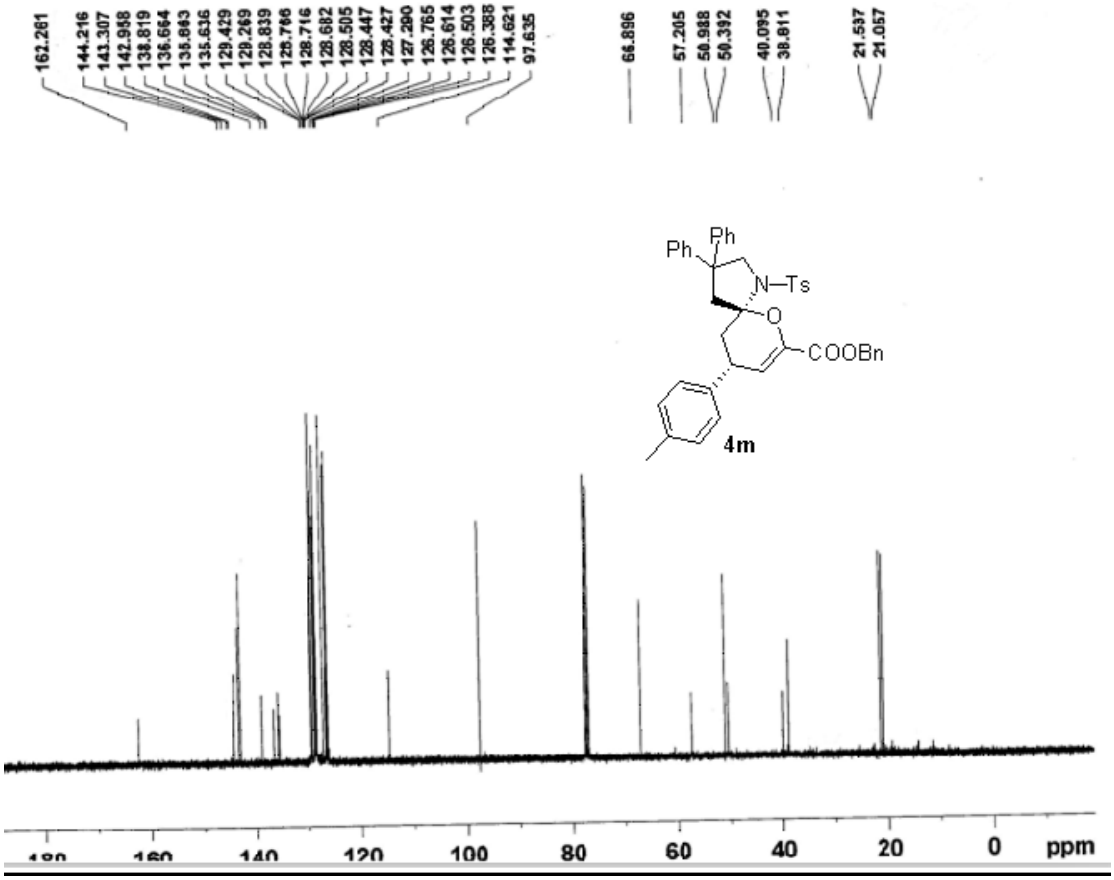

ZSA-153-1C13
Ph
Ph
N–Ts
O
COOMe
Ph
4l
180
160
140
120
100
80
60
40
20
0
ppm

HRMS exact mass calcd for (C35H33NO5S+Na) requires m/z 602.1972, found m/z 602.1978.

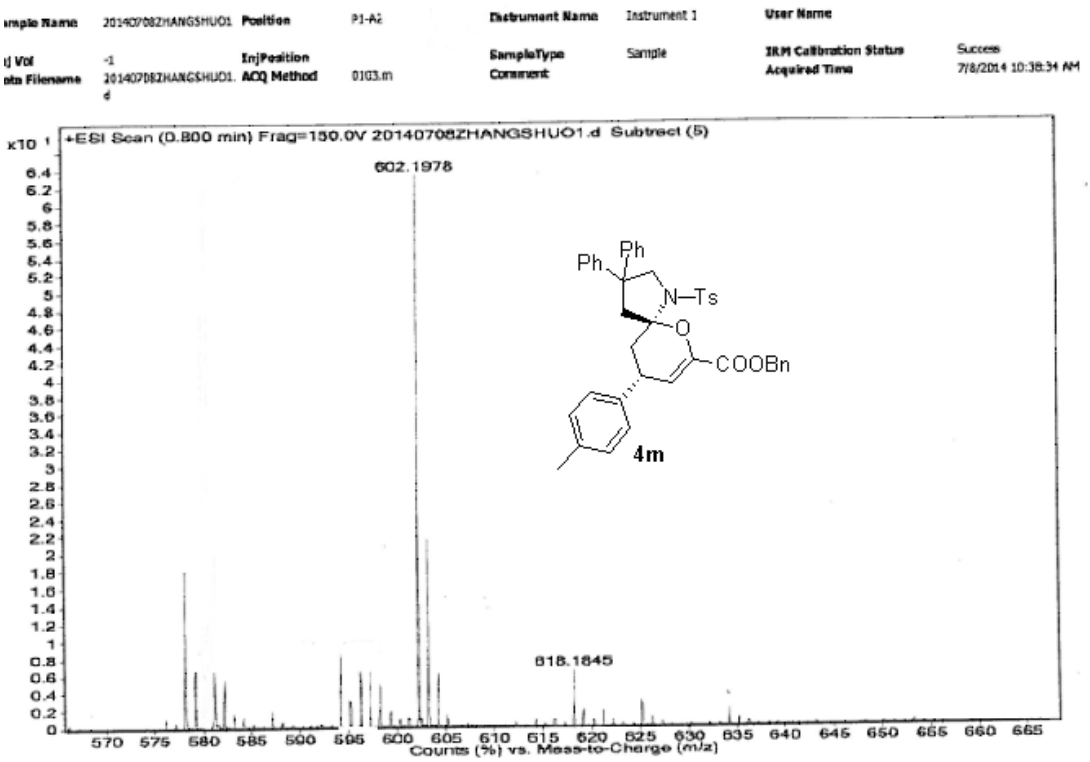


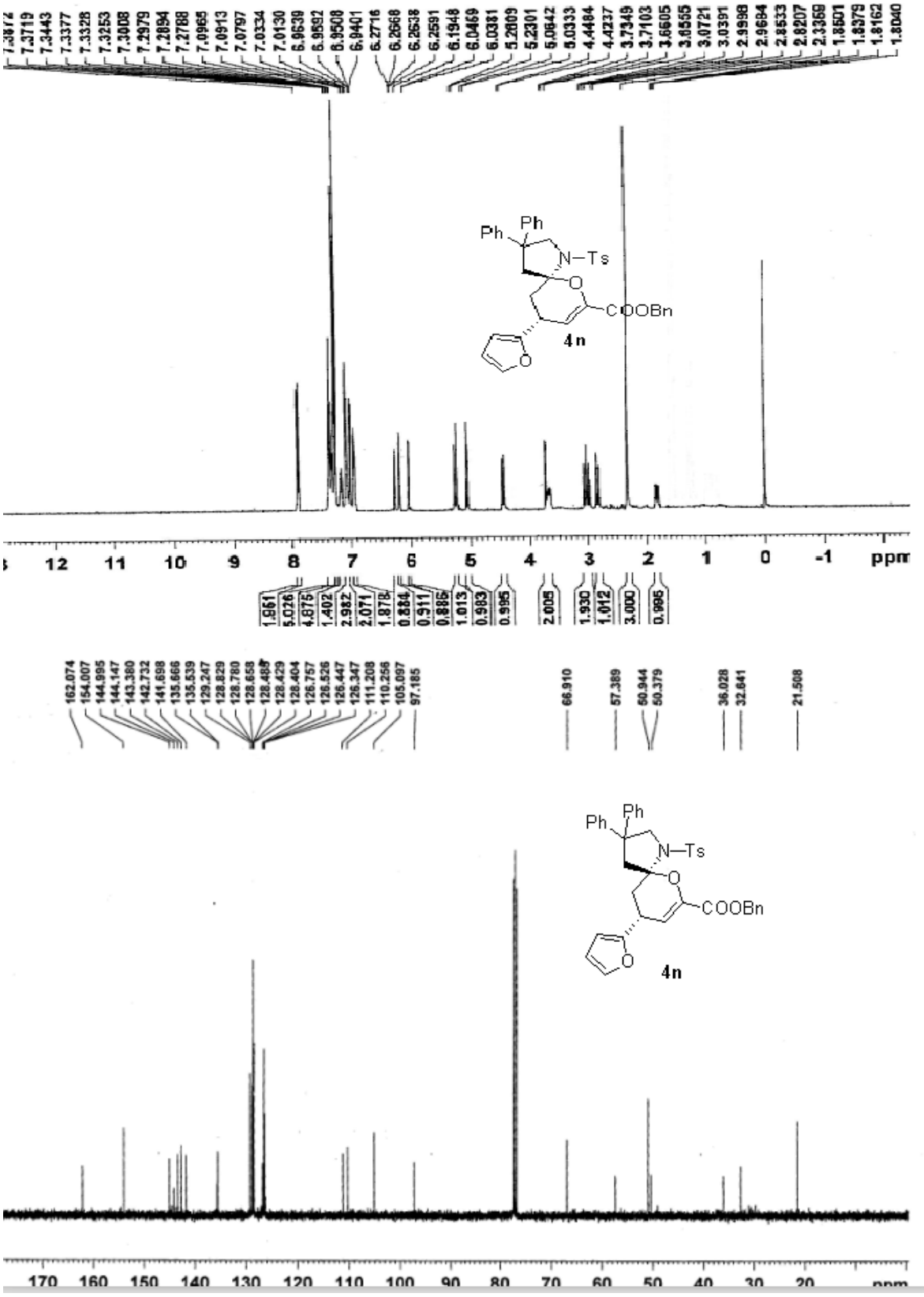






HRMS exact mass calcd for (C35H33NO5S+Na) requires m/z 602.1972, found m/z 602.1978.




Ph
Ph
N—Ts
O
COOBn
4n
ppm
Ph
Ph
N—Ts
O
COOBn
4n
ppm

HRMS exact mass calcd for (C39H35N65S+Na) requires m/z 668.2077, found m/z 668.2076