Supporting Information

Palladium-Catalyzed Oxidative *6-exo*-trig Cyclization of 1,6-Enynes: Facile Synthesis of Bicyclo[4.1.0]heptan-5-ones

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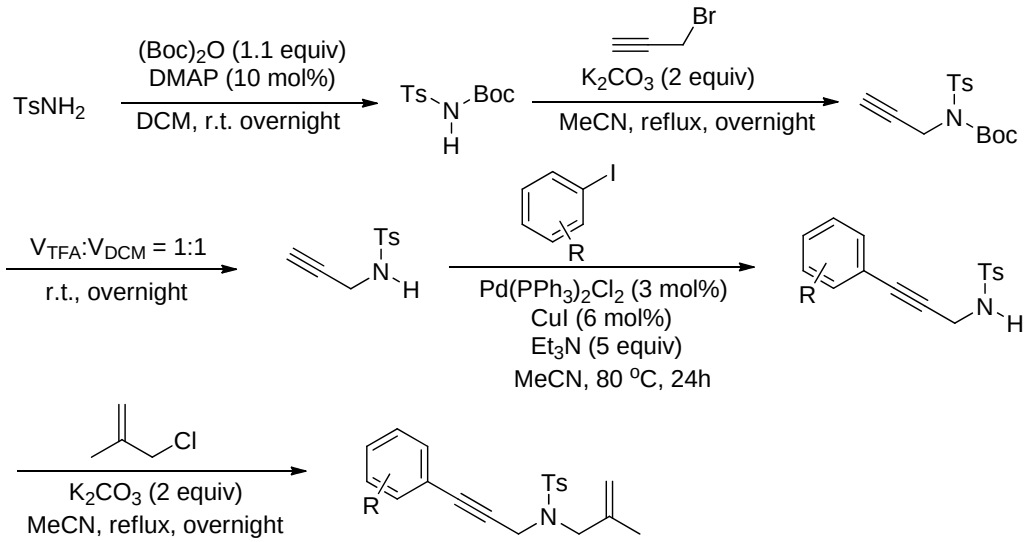
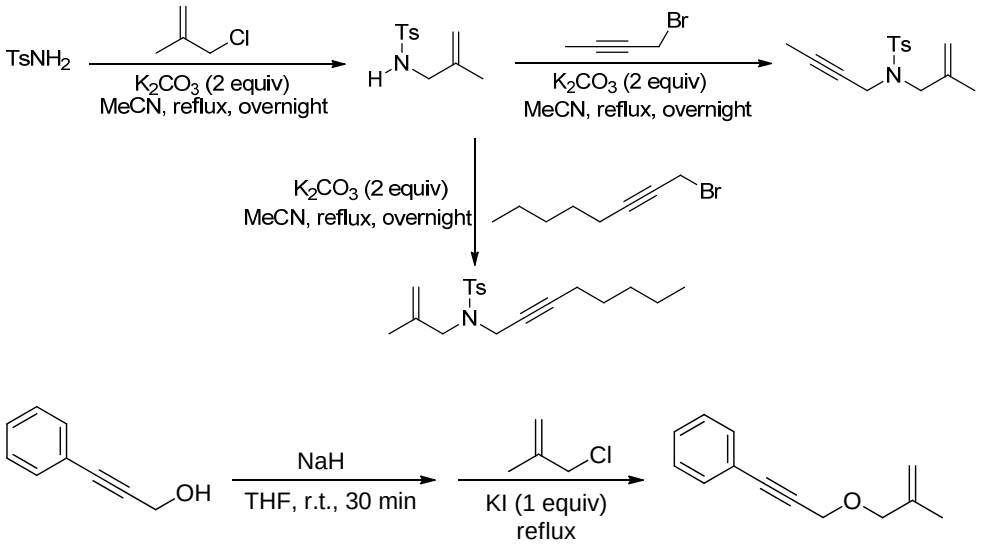
(1) General Procedures

(a) General Procedures for the Pd-Catalyzed Oxidative *6-exo-trig* Cyclization of 1,6-Enynes:

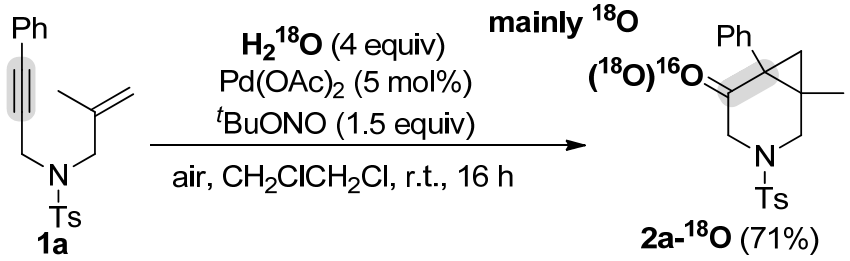
To a solution of 1,6-enyne **1** (0.2 mmol) in anhydrous 1,2-dichloroethane (1 mL) were added H_2O (4 equiv), $Pd(OAc)_2$ (5 mol%) and *tert*-butyl nitrite (1.5 equiv). The mixture was stirred at room temperature for 16 or 24 h under air condition until complete consumption of starting material as monitored by TLC analysis. After the reaction was finished, the reaction mixture was washed with brine. The aqueous phase was re-extracted with EtOAc. The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by silica gel flash column chromatography (hexane/ethyl acetate) to afford the desired products **2**.

(b) Preparation of ,16-Enyne Substrates

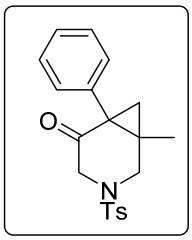




(c) The ^{18}O-labeled Experiment

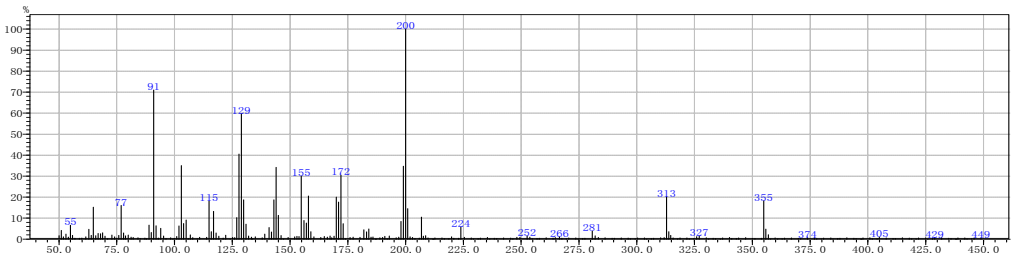


1-Methyl-6-phenyl-3-tosyl-3-azabicyclo[4.1.0]heptan-5-one (2a)



Chemical Formula: $C_{20}H_{21}NO_3S$

Molecular Weight: 355



[MS Spectrum]

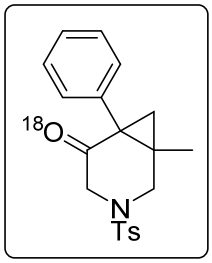
# of Peaks 266

Raw Spectrum 22.570 (scan : 3815) Base Peak m/z 200.00 (Inten : 167,814)

Background No Background Spectrum

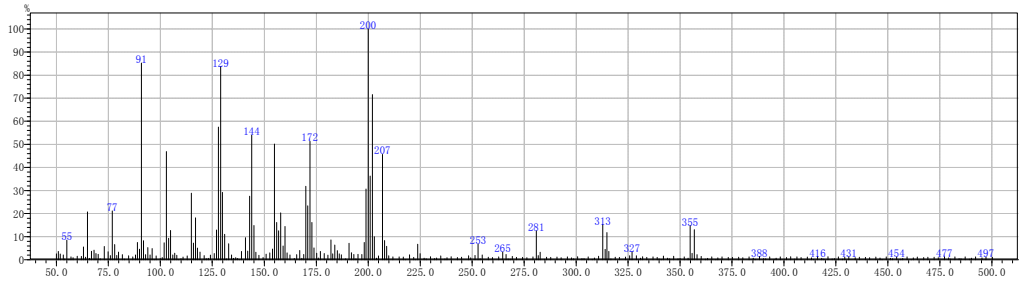
m/z	Absolute Intensity		m/z	Absolute Intensity		m/z	Absolute Intensity	
51.00	6940	4.14	118.00	4983	2.97	200.00	167814	100.00
53.00	4057	2.42	126.95	17135	10.21	200.95	24382	14.53
55.00	11081	6.60	127.95	67909	40.47	206.90	17654	10.52
62.95	7955	4.74	128.95	100141	59.67	223.90	9580	5.71
64.95	25529	15.21	129.95	31391	18.71	280.75	6475	3.86
76.95	26951	16.06	143.00	31481	18.76	281.95	2668	1.59
78.00	5042	3.00	143.95	57352	34.18	312.90	33833	20.16
88.95	11253	6.71	144.95	18945	11.29	313.90	5918	3.53
90.00	5366	3.20	154.90	50297	29.97	**354.90**	**30641**	**18.26**
91.00	119097	70.97	156.00	15028	8.96	355.85	8088	4.82
92.00	10690	6.37	157.00	12914	7.70	**356.95**	**3570**	**2.13**
94.00	8609	5.13	157.95	34473	20.54	357.90	121	0.07
101.95	10596	6.31	159.00	5975	3.56	359.90	924	0.55
102.95	58783	35.03	170.00	33556	20.00			
103.95	12556	7.48	171.00	29601	17.64			
105.00	15318	9.13	172.00	51199	30.51			
114.95	30530	18.19	173.00	12482	7.44			
115.95	5981	3.56	198.00	14103	8.40			
116.95	22108	13.17	199.00	58356	34.77			

1-Methyl-6-phenyl-3-tosyl-3-azabicyclo[4.1.0]heptan-5-one (2a-^{18}O)



Chemical Formula: $C_{20}H_{21}NO_2{}^{18}OS$

Molecular Weight: 357



[MS Spectrum]

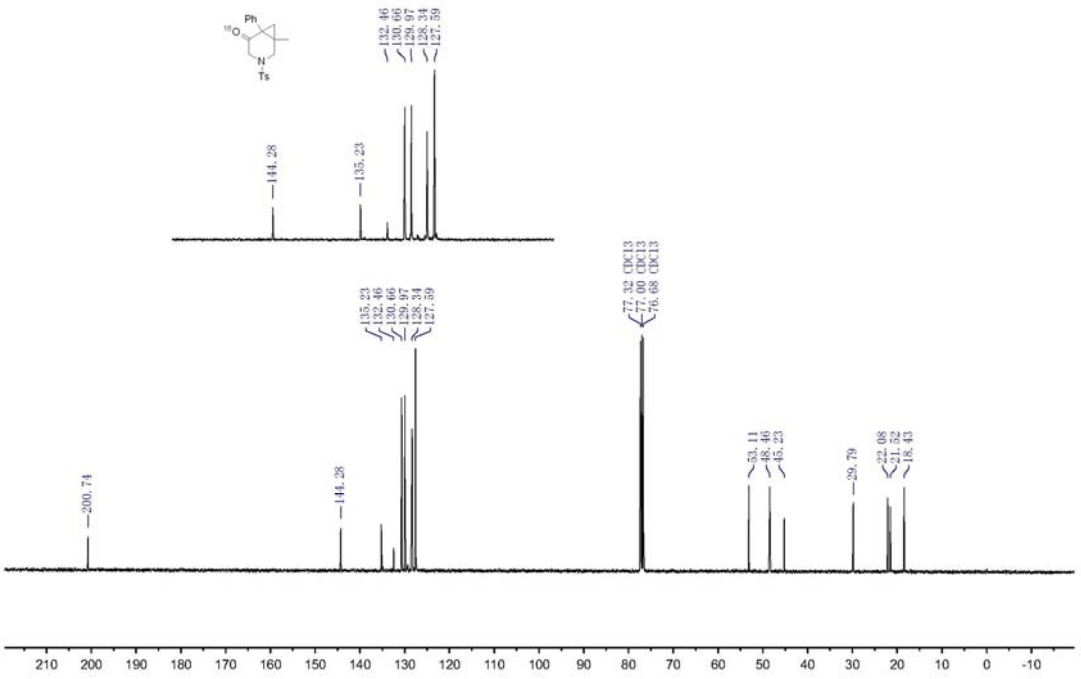
# of Peaks 307

Raw Spectrum 22.445 (scan : 3790) Base Peak m/z 199.95 (Inten : 98,709)

Background No Background Spectrum

m/z	Absolute Intensity		m/z	Absolute Intensity		m/z	Absolute Intensity	
50.90	4721	4.78	67.95	3044	3.08	80.10	2625	2.66
52.10	1994	2.02	68.95	4907	4.97	81.95	3073	3.11
55.05	6997	7.09	73.00	2644	2.68	88.90	8748	8.86
62.95	4317	4.37	75.05	2227	2.26	90.05	4562	4.62
63.95	2402	2.43	76.95	21404	21.68	90.95	86321	87.45
65.00	18570	18.81	78.00	3980	4.03	91.95	9594	9.72
67.00	4234	4.29	78.95	3051	3.09	93.90	5638	5.71

95.05	2383	2.41	154.90	49143	49.79	202.95	9468	9.59
101.90	9385	9.51	155.95	15574	15.78	206.85	31054	31.46
102.95	46098	46.70	156.95	11300	11.45	207.85	5833	5.91
103.90	9617	9.74	157.95	22921	23.22	208.85	5534	5.61
104.95	10898	11.04	159.00	5410	5.48	223.85	8764	8.88
106.85	3879	3.93	159.95	14827	15.02	248.70	2569	2.60
114.95	28339	28.71	161.00	3532	3.58	252.90	3385	3.43
115.95	5666	5.74	162.80	2202	2.23	264.90	2652	2.69
116.95	19522	19.78	169.95	31494	31.91	266.75	2724	2.76
118.05	4381	4.44	170.95	24633	24.96	280.85	6880	6.97
126.95	14100	14.28	172.00	49314	49.96	281.85	2393	2.42
127.95	57883	58.64	172.90	17106	17.33	282.95	2124	2.15
128.95	84826	85.94	174.05	4786	4.85	312.85	16549	16.77
129.95	29147	29.53	175.05	2177	2.21	313.85	2914	2.95
131.00	9079	9.20	182.00	6998	7.09	314.85	13024	13.19
132.95	5434	5.51	182.95	3762	3.81	315.95	3480	3.53
134.80	2564	2.60	183.95	6016	6.09	325.95	1944	1.97
138.95	2345	2.38	184.90	2519	2.55	326.95	1458	1.48
141.00	7924	8.03	185.90	4538	4.60	330.90	2028	2.05
141.95	3369	3.41	190.85	5881	5.96	345.90	1409	1.43
143.00	29014	29.39	192.70	2782	2.82	**354.90**	**13996**	**14.18**
144.00	49103	49.75	197.95	7895	8.00	355.85	4073	4.13
144.95	16786	17.01	199.00	32799	33.23	**356.90**	**11098**	**11.24**
146.10	2582	2.62	199.95	98709	100.00	357.85	2384	2.42
152.90	3908	3.96	200.95	38283	38.78	**358.90**	**1737**	**1.76**
153.95	3032	3.07	202.00	70673	71.60			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N
Ts
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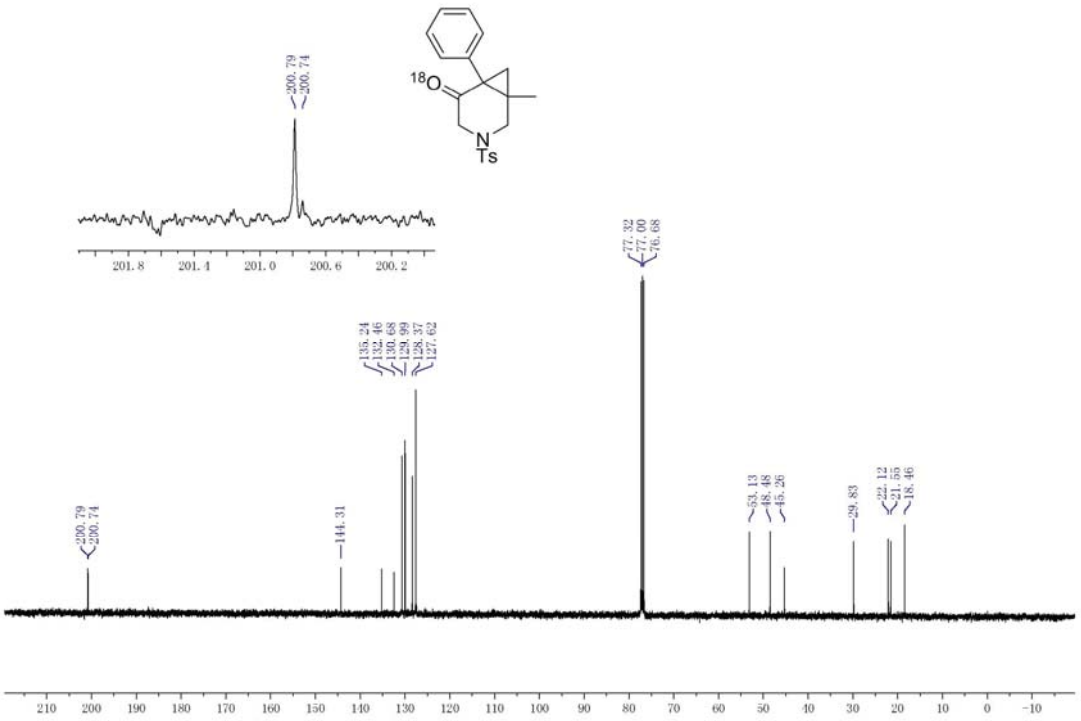
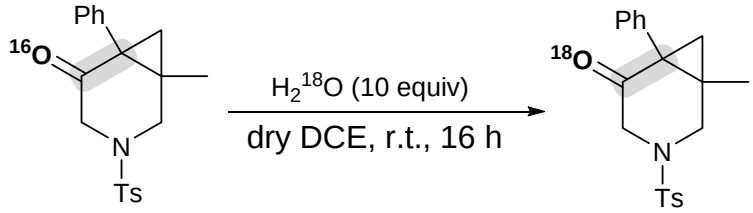
130.66
129.97
128.34
127.59
144.28
135.23
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
53.11
48.46
45.23
29.79
22.08
21.52
18.43
200.74
144.28
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


200.79
200.74
18O
N
Ts
201.8 201.4 201.0 200.6 200.2
77.32
77.00
76.68
135.24
132.46
130.68
129.99
128.37
127.62
53.13
48.48
46.26
29.83
22.12
21.55
18.46
200.79
200.74
144.31
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10



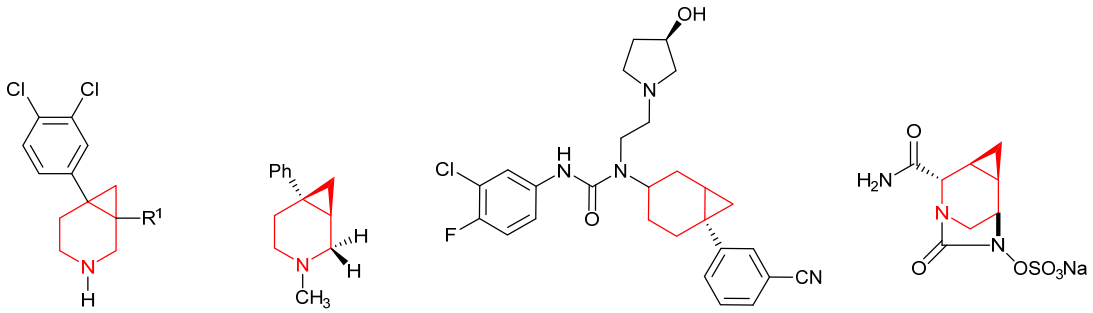
2a-^{16}O

354.85	**399008**	**20.52**
355.90	99050	5.09
356.90	**32882**	**1.69**
357.85	5732	0.29

2a-^{18}O

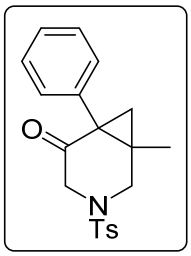
354.90	**462970**	**21.01**
355.90	119351	5.42
356.85	**38390**	**1.74**
357.85	8068	0.3

(d) The examples of natural products and pharmaceticals



(2) Analytical data

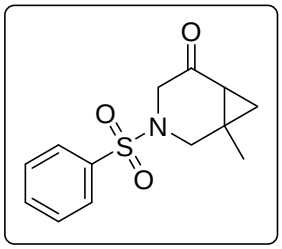
1-Methyl-6-phenyl-3-tosyl-3-azabicyclo[4.1.0]heptan-5-one (2a)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.33 - 7.27 (m, 3H), 7.04 (d, *J* = 6.8 Hz, 2H), 4.26 (d, *J* = 18.0 Hz, 1H), 4.08 (d, *J* = 12.0 Hz, 1H), 3.06 (d, *J* = 18.0 Hz, 1H), 2.79 (d, *J* = 12.0 Hz, 1H), 2.46 (m, 4H), 1.57 (d, *J* = 5.2 Hz, 1H), 0.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.7, 144.3, 135.2, 132.5, 130.7, 130.0, 128.3, 127.6, 53.1, 48.5, 45.2, 29.8, 22.1, 21.5, 18.4; LRMS (EI, 70 eV) *m/z*

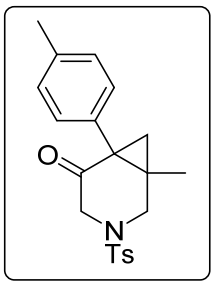
(%): 355 (M^+, 18), 313 (20), 200 (100), 91 (71); HRMS (ESI): calculated for [$C_{20}H_{22}NO_3S^+$] 356.1315, found 356.1325.

1-Methyl-3-(phenylsulfonyl)-3-azabicyclo[4.1.0]heptan-5-one (2d)



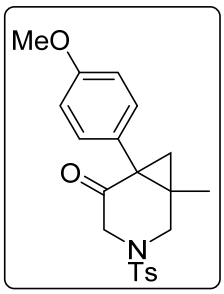
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.8 Hz, 2H),, 7.66 - 7.62 (m, 1H), 7.59 - 7.55 (m, 2H), 4.13 (d, *J* = 18.0 Hz, 1H), 4.01 (d, *J* = 12.0 Hz, 1H), 2.89 (d, *J* = 18.0 Hz, 1H), 2.62 (d, *J* = 12.0 Hz, 1H), 1.98 (t, *J* = 4.8 Hz, 1H), 1.71 (dd, *J* = 10.0 Hz, 5.2 Hz, 1H), 1.25 (s, 3H), 1.13 (dd, *J* = 10.0 Hz, 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.0, 135.5, 133.3, 129.3, 127.5, 127.4, 52.4, 47.5, 33.4, 24.3, 20.4, 18.2; LRMS (EI, 70 eV) *m/z* (%): 265 (M^+, 2), 141 (6), 124 (100), 95 (21); HRMS (ESI): calculated for [$C_{13}H_{16}NO_3S^+$] 266.0845, found 266.0857.

1-Methyl-6-(*p*-tolyl)-3-tosyl-3-azabicyclo[4.1.0]heptan-5-one (2e)



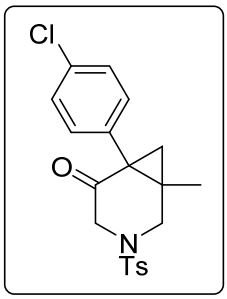
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 7.6 Hz, 2H), 6.93 (d, *J* = 7.6 Hz, 2H), 4.25 (d, *J* = 18.0 Hz, 1H), 4.08 (d, *J* = 12.0 Hz, 1H), 3.05 (d, *J* = 18.0 Hz, 1H), 2.77 (d, *J* = 12.0 Hz, 1H), 2.46 - 2.45 (m, 4H), 2.31 (s, 3H), 1.55 (d, *J* = 5.2 Hz, 1H), 0.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.1, 144.3, 137.3, 132.3, 132.1, 130.5, 130.0, 129.1, 127.6, 53.1, 48.5, 44.9, 29.8, 22.2, 21.5, 21.1, 18.4; LRMS (EI, 70 eV) *m/z* (%): 306 (M^+, 100), 274 (30), 247 (99), 219 (62); HRMS (ESI): calculated for [$C_{21}H_{24}NO_3S^+$] 370.1471, found 370.1485.

6-(4-Methoxyphenyl)-1-methyl-3-tosyl-3-azabicyclo[4.1.0]heptan-5-one (2f)



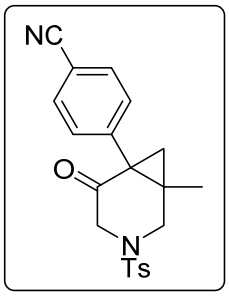
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.2 Hz, 2H), 7.37 (d, *J* = 7.6 Hz, 2H), 6.96 (d, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 8.0 Hz, 2H), 4.24 (d, *J* = 18.0 Hz, 1H), 4.07 (d, *J* = 12.0 Hz, 1H), 3.77 (s, 3H), 3.05 (d, *J* = 18.0 Hz, 1H), 2.77 (d, *J* = 11.9 Hz, 1H), 2.48 - 2.46 (m, 4H), 1.53 (d, *J* = 4.8 Hz, 1H), 0.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.2, 158.9, 144.3, 132.3, 131.7, 130.0, 127.6, 127.2, 113.8, 55.1, 53.1, 48.4, 44.6, 29.9, 22.4, 21.5, 18.4; LRMS (EI, 70 eV) *m/z* (%): 385 (M^+, 35), 343 (8), 230 (56), 174 (100); HRMS (ESI): calculated for [$C_{21}H_{24}NO_4S^+$] 386.1421, found 386.1430.

6-(4-Chlorophenyl)-1-methyl-3-tosyl-3-azabicyclo[4.1.0]heptan-5-one (2g)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.2 Hz, 2H), 7.38 (d, *J* = 7.2 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 2H), 6.99 (d, *J* = 7.2 Hz, 2H), 4.25 (d, *J* = 18.0 Hz, 1H), 4.08 (d, *J* = 12.0 Hz, 1H), 3.06 (d, *J* = 18.0 Hz, 1H), 2.78 (d, *J* = 12.0 Hz, 1H), 2.48 - 2.46 (m, 4H), 1.54 (s, 1H), 0.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.5, 144.4, 133.8, 133.6, 132.2, 132.0, 130.0, 128.6, 127.6, 53.1, 48.3, 44.6, 30.0, 22.3, 21.5, 18.4; LRMS (EI, 70 eV) *m/z* (%): 391 (M^++2, 10), 389 (M^+, 25), 347 (28), 234 (100), 143 (69); HRMS (ESI): calculated for [$C_{20}H_{21}{}^{35}ClNO_3S^+$] 390.0925, found 390.0933.

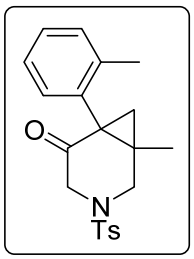
4-(1-Methyl-5-oxo-3-tosyl-3-azabicyclo[4.1.0]heptan-6-yl)benzonitrile (2h)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.61

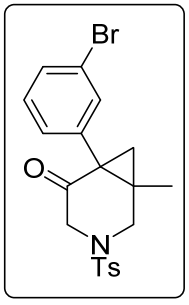
(d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 4.27 (d, J = 18.0 Hz, 1H), 4.10 (d, J = 12.0 Hz, 1H), 3.08 (d, J = 18.0 Hz, 1H), 2.80 (d, J = 12.0 Hz, 1H), 2.55 (d, J = 5.6 Hz, 1H), 2.47 (s, 3H), 1.58 (d, J = 5.6 Hz, 1H), 0.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.9, 144.5, 140.9, 132.4, 132.2, 131.6, 130.1, 127.6, 118.5, 111.7, 53.1, 48.3, 45.1, 30.4, 22.2, 21.6, 18.4; HRMS (ESI): calculated for [$C_{21}H_{21}N_2O_3S^+$] 381.1267, found 381.1280.

1-Methyl-6-(*o*-tolyl)-3-tosyl-3-azabicyclo[4.1.0]heptan-5-one (2i)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 7.2 Hz, 2H), 7.38 (d, J = 7.6 Hz, 2H), 7.19 - 7.13 (m, 4H), 4.27 (d, J = 17.6 Hz, 1H), 4.12 (d, J = 12.0 Hz, 1H), 3.05 (d, J = 18.0 Hz, 1H), 2.81 (d, J = 12.0 Hz, 1H), 2.47 (s, 3H), 2.39 (d, J = 4.8 Hz, 1H), 1.96 (s, 3H), 1.59 (d, J = 4.8 Hz, 1H), 0.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.9, 144.3, 137.8, 134.2, 132.5, 130.9, 130.0, 127.8, 127.5, 126.2, 52.7, 48.1, 44.3, 29.3, 21.6, 21.1, 19.7, 16.6; LRMS (EI, 70 eV) *m/z* (%): 369 (M^+, 10), 327 (3), 214 (100), 186 (26); HRMS (ESI): calculated for [$C_{21}H_{24}NO_3S^+$] 370.1471, found 370.1479.

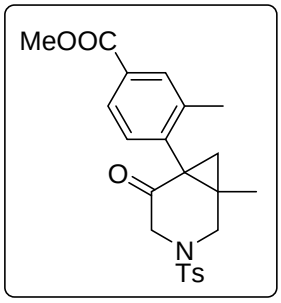
6-(3-Bromophenyl)-1-methyl-3-tosyl-3-azabicyclo[4.1.0]heptan-5-one (2j)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8.0 Hz, 2H), 7.42 - 7.37 (m, 3H), 7.20 - 7.16 (m, 2H), 6.98 (d, J = 7.8 Hz, 1H), 4.25 (d, J = 18.0 Hz, 1H), 4.08 (d, J = 12.0 Hz, 1H), 3.05 (d, J = 18.0 Hz, 1H), 2.77 (d, J = 12.0 Hz, 1H), 2.48 - 2.46 (m, 4H), 1.55 (d, J = 5.6 Hz,

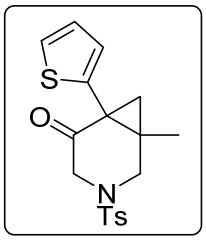
1H), 0.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.3, 144.4, 137.6, 133.7, 132.2, 130.8, 130.0, 129.9, 129.4, 127.6, 122.4, 53.1, 48.3, 44.8, 30.0, 22.1, 21.6, 18.4; LRMS (EI, 70 eV) *m/z* (%): 435 (M^++2, 15), 433 (16), 393 (17), 278 (64), 135 (100); HRMS (ESI): calculated for [$C_{20}H_{21}{}^{79}BrNO_3S^+$] 434.0420, found 434.0435.

Methyl 3-methyl-4-(1-methyl-5-oxo-3-tosyl-3-azabicyclo[4.1.0]heptan-6-yl)-benzoate (2k)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 - 7.83 (m, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 1H), 4.28 (d, *J* = 18.0 Hz, 1H), 4.13 (d, *J* = 12.0 Hz, 1H), 3.89 (s, 3H), 3.05 (d, *J* = 18.0 Hz, 1H), 2.81 (d, *J* = 12.0 Hz, 1H), 2.47 (s, 3H), 2.44 (d, *J* = 5.6 Hz, 1H), 2.01 (s, 3H), 1.61 (d, *J* = 5.6 Hz, 1H), 0.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3, 166.8, 144.4, 139.7, 138.3, 132.5, 131.2, 131.1, 130.1 129.6, 127.5, 127.4, 52.7, 52.1, 48.0, 44.2, 29.6, 21.6, 21.3, 19.7, 16.6; LRMS (EI, 70 eV) *m/z* (%): 427 (M^+, 11), 396 (5), 272 (100), 244 (21); HRMS (ESI): calculated for [$C_{23}H_{26}NO_5S^+$] 428.1526, found 428.1536.

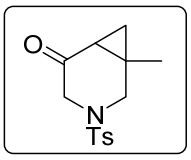
1-Methyl-6-(thiophen-2-yl)-3-tosyl-3-azabicyclo[4.1.0]heptan-5-one (2l)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.2 Hz, 2H), 7.38 (d, *J* = 6.8 Hz, 2H), 7.25 (d, *J* = 6.8 Hz, 1H), 6.97 - 6.96 (m, 1H), 6.79 (m, 1H), 4.26 (d, *J* = 18.0 Hz, 1H), 4.08 (d, *J* = 12.0 Hz, 1H), 3.08 (d, *J* = 18.0 Hz, 1H), 2.78 (d, *J* = 12.0 Hz, 1H), 2.60 (d, *J* = 4.4 Hz, 1H), 2.46 (s, 3H),

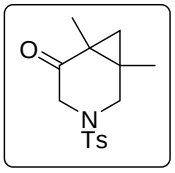
1.70 (d, J = 4.4 Hz, 1H), 1.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.6, 144.4, 137.9, 132.3, 130.0, 128.7, 127.6, 126.6, 126.0, 53.1, 48.2, 39.9, 31.6, 24.7, 21.6, 17.9; LRMS (EI, 70 eV) *m/z* (%): 361 (M^+, 24), 319 (18), 206 (65), 150 (100); HRMS (ESI): calculated for [$C_{18}H_{20}NO_3S_2^+$] 362.0879, found 362.0890.

1-Methyl-3-tosyl-3-azabicyclo[4.1.0]heptan-5-one (2m)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 4.11 (d, J = 18.0 Hz, 1H), 3.98 (d, J = 12.0 Hz, 1H), 2.87 (d, J = 18.0 Hz, 1H), 2.58 (d, J = 12.0 Hz, 1H), 2.44 (s, 3H), 1.99 (t, J = 4.8 Hz, 1H), 1.70 (dd, J = 10.0 Hz, 4.8 Hz, 1H), 1.24 (s, 3H), 1.12 (dd, J = 10.0 Hz, 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.2, 144.2, 132.5, 129.9, 127.5, 52.5, 47.6, 33.4, 24.3, 21.5, 20.4, 18.2; LRMS (EI, 70 eV) *m/z* (%): 279 (M^+, 3), 155 (7), 124 (100), 91 (25); HRMS (ESI): calculated for [$C_{14}H_{18}NO_3S^+$] 280.1002, found 280.1022.

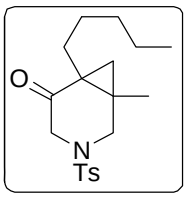
1,6-Dimethyl-3-tosyl-3-azabicyclo[4.1.0]heptan-5-one (2n)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 7.2 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 4.11 (d, J = 18.0 Hz, 1H), 3.93 (d, J = 11.6 Hz, 1H), 2.94 (d, J = 18.0 Hz, 1H), 2.59 (d, J = 11.6 Hz, 1H), 2.44 (s, 3H), 2.19 (d, J = 4.8 Hz, 1H), 1.26 (s, 3H), 1.22 (s, 3H), 0.85 (d, J = 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.7, 144.2, 132.3, 129.9, 127.6, 52.6, 48.2, 34.8, 28.3, 24.3, 21.5, 16.6, 13.6; LRMS (EI, 70 eV) *m/z* (%): 293 (M^+, 5), 252 (4), 155 (12), 138

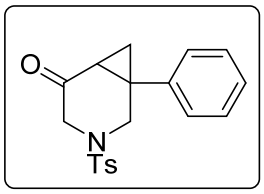
(100); HRMS (ESI): calculated for [$C_{15}H_{20}NO_3S^+$] 294.1158, found 294.1170.

1-Methyl-6-pentyl-3-tosyl-3-azabicyclo[4.1.0]heptan-5-one (2o)



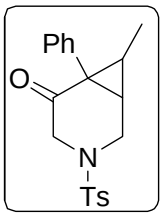
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.2 Hz, 2H), 7.35 (d, *J* = 7.6 Hz, 2H), 4.10 (d, *J* = 18.0 Hz, 1H), 3.91 (d, *J* = 11.6 Hz, 1H), 2.87 (d, *J* = 18.0 Hz, 1H), 2.58 (d, *J* = 12.0 Hz, 1H), 2.44 (s, 3H), 2.07 (d, *J* = 4.8 Hz, 1H), 1.29 - 1.23 (m, 11H), 0.85 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.8, 144.2, 132.4, 130.0, 127.6, 53.1, 48.7, 39.4, 32.2, 29.1, 28.5, 27.1, 23.2, 22.5, 21.6, 16.9, 14.0; LRMS (EI, 70 eV) *m/z* (%): 349 (M^+, 2), 308 (2), 194 (100), 166 (8), 91 (18); HRMS (ESI): calculated for [$C_{19}H_{28}NO_3S^+$] 350.1784, found 350.1794.

1-Phenyl-3-tosyl-3-azabicyclo[4.1.0]heptan-5-one (2q)

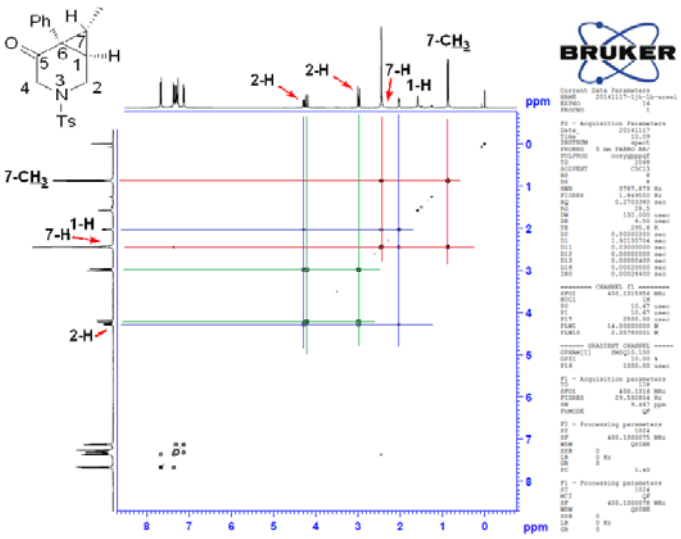


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.0 Hz, 2H), 7.36 - 7.28 (m, 7H), 4.27 - 4.21 (m, 2H), 2.99 (d, *J* = 18.0 Hz, 1H), 2.81 (d, *J* = 12.0 Hz, 1H), 2.43 (s, 3H), 2.38 (t, *J* = 4.8 Hz, 1H), 2.16 (dd, *J* = 10.0 Hz, 4.8 Hz, 1H), 1.57 (dd, *J* = 10.0 Hz, 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.5, 144.3, 138.8, 132.5, 130.0, 128.9, 128.7, 128.2, 127.5, 52.8, 48.5, 33.1, 32.8, 21.5, 17.2; LRMS (EI, 70 eV) *m/z* (%): 341 (M^+, 14), 313 (3), 186 (48), 130 (100); HRMS (ESI): calculated for [$C_{19}H_{20}NO_3S^+$] 342.1158, found 342.1170.

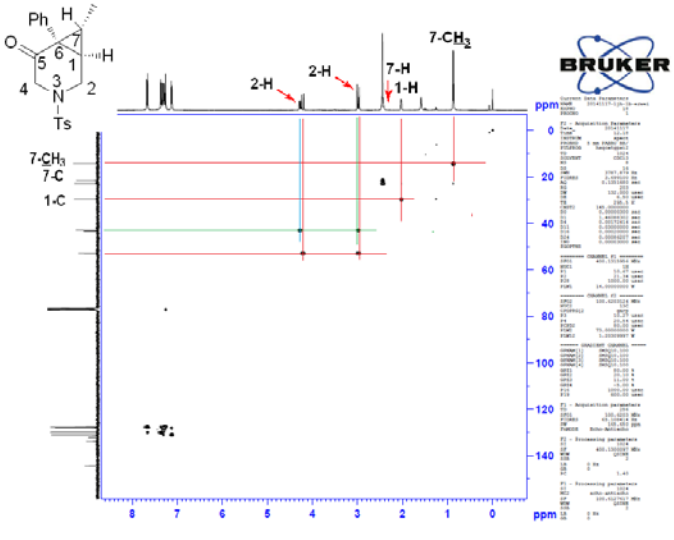
7-Methyl-6-phenyl-3-tosyl-3-azabicyclo[4.1.0]heptan-5-one (2s)



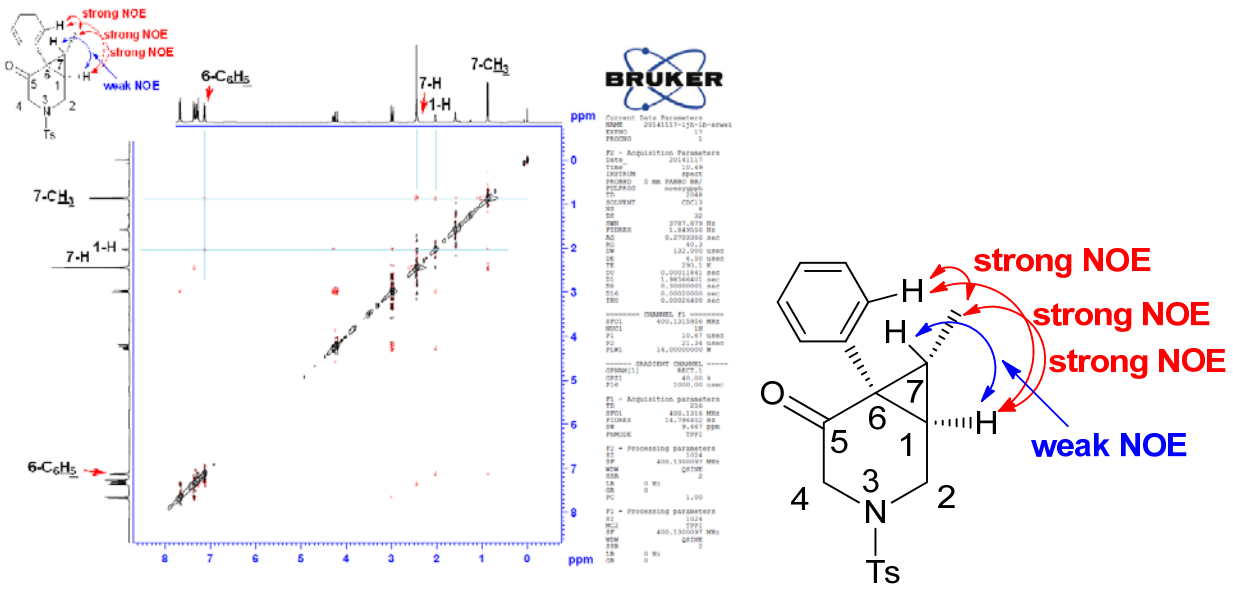
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.34 - 7.28 (m, 3H), 7.14 - 7.11 (m, 2H), 4.28 (dd, *J* = 12.0, 1.6 Hz, 1H), 4.21 (d, *J* = 17.6 Hz, 1H), 3.01 - 2.97 (m, 2H), 2.47 - 2.41 (m, 4H), 2.04 - 2.02 (m, 1H), 0.87 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.9, 144.3, 133.8, 132.3, 131.0, 130.0, 128.1, 127.6, 127.5, 53.0, 43.4, 43.0, 29.8, 23.0, 21.5, 14.3; LRMS (EI, 70 eV) *m/z* (%): 355 (M^+, 14), 341 (27), 281 (58), 253 (34), 207 (100); HRMS (ESI): calculated for [$C_{20}H_{22}NO_3S^+$] 356.1315, found 356.1324.



H-H COSY

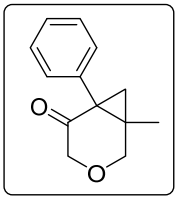


C-H HSQC



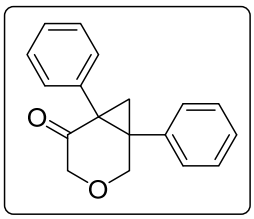
H-H Noesy

1-Methyl-6-phenyl-3-oxabicyclo[4.1.0]heptan-5-one (2t)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 - 7.25 (m, 3H), 7.15 (d, *J* = 7.2 Hz, 2H), 4.29 (d, *J* = 18.0 Hz, 1H), 4.01 (d, *J* = 11.6 Hz, 1H), 3.95 (d, *J* = 18.4 Hz, 1H), 3.79 (d, *J* = 11.6 Hz, 1H), 2.39 (d, *J* = 4.4 Hz, 1H), 1.56 (d, *J* = 4.4 Hz, 1H), 0.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.7, 135.4, 130.7, 128.3, 127.4, 72.8, 68.4, 45.8, 29.4, 21.2, 16.3; LRMS (EI, 70 eV) *m/z* (%): 202 (M^+, 81), 160 (41), 129 (100), 103 (52); HRMS (ESI): calculated for [$C_{13}H_{15}O_2^+$] 203.1067, found 203.1078.

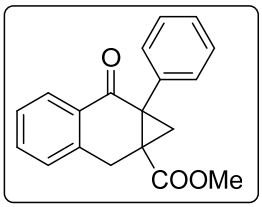
1,6-Diphenyl-3-oxabicyclo[4.1.0]heptan-5-one (2u)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 - 7.00 (m, 10H), 4.41

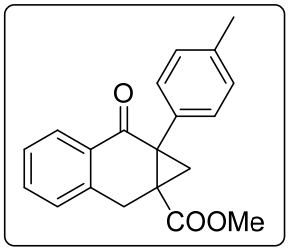
(d, *J* = 18.0 Hz, 1H), 4.28 (d, *J* = 12.0 Hz, 1H), 4.16 - 4.10 (m, 2H), 2.74 (d, *J* = 5.6 Hz, 1H), 2.37 (d, *J* = 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.8, 134.8, 134.1, 130.7, 128.9, 128.2, 127.8, 127.5, 127.1, 73.1, 68.6, 47.2, 39.2, 17.9; LRMS (EI, 70 eV) *m/z* (%): 264 (M^+, 34), 206 (100), 160 (31), 91 (74); HRMS (ESI): calculated for [$C_{18}H_{17}O_2^+$] 265.1223, found 265.1236.

Methyl 7-oxo-7a-phenyl-1,2,7,7a-tetrahydro-1aH-cyclopropa[b]naphthalene-1a-carboxylate (2v)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.6, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.37 - 7.22 (m, 7H), 4.08 (d, *J* = 17.6 Hz, 1H), 3.36 (d, *J* = 17.6 Hz, 1H), 3.30 (s, 3H), 2.59 (d, *J* = 5.6 Hz, 1H), 1.61 (d, *J* = 5.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.1, 170.2, 137.9, 135.5, 133.4, 130.6, 130.2, 128.6, 128.2, 127.8, 127.6, 127.4, 52.1, 45.8, 33.3, 29.6, 21.6; LRMS (EI, 70 eV) *m/z* (%): 292 (M^+, 45), 260 (39), 233 (100), 205 (66); HRMS (ESI): calculated for [$C_{19}H_{17}O_3^+$] 293.1172, found 293.1179.

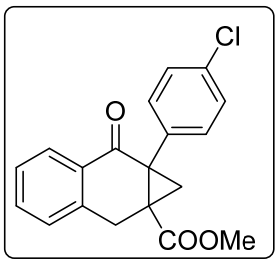
Methyl 7-oxo-7a-(*p*-tolyl)-1,2,7,7a-tetrahydro-1aH-cyclopropa[*b*]naphthalene-1a-carboxylate (2w)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 6.8 Hz, 1H), 7.15 - 7.10 (m, 4H), 4.06 (d, *J* = 17.6 Hz, 1H), 3.38 - 3.33 (m, 4H), 2.56 (d, *J* = 5.2 Hz, 1H), 2.33 (s, 3H),

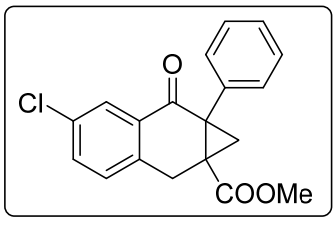
1.58 (d, J = 5.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.2, 170.2, 137.9, 137.2, 133.3, 132.3, 130.6, 130.0, 129.0, 128.5, 127.8, 127.4, 52.1, 45.5, 33.3, 29.6, 21.6, 21.2; LRMS (EI, 70 eV) *m/z* (%): 306 (M^+, 100), 274 (30), 247 (99), 219 (62); HRMS (ESI): calculated for [$C_{20}H_{19}O_3^+$] 307.1329, found 307.1325.

Methyl 7a-(4-chlorophenyl)-7-oxo-1,2,7,7a-tetrahydro-1aH-cyclopropa[b]-naphthalene-1a-carboxylate (2x)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.0 Hz, 1H), 7.53 (t, J = 7.6 Hz, 1H), 7.36 - 7.28 (m, 4H), 7.17 (d, J = 8.4 Hz, 2H), 4.06 (d, J = 17.6 Hz, 1H), 3.39 - 3.35 (m, 4H), 2.55 (d, J = 5.2 Hz, 1H), 1.62 (d, J = 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.6, 169.9, 137.8, 134.1, 133.5, 131.6, 130.3, 128.6, 128.4, 127.8, 127.5, 52.2, 45.1, 33.3, 29.4, 21.6; LRMS (EI, 70 eV) *m/z* (%): 391 (M^++2, 10), 389 (M^+, 25), 347 (28), 234 (100), 143 (69); HRMS (ESI): calculated for [$C_{19}H_{16}{}^{35}ClO_3^+$] 327.0782, found 327.0796.

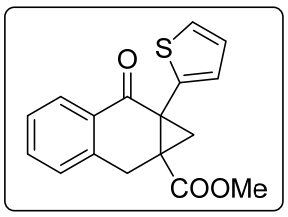
Methyl 5-chloro-7-oxo-7a-phenyl-1,2,7,7a-tetrahydro-1aH-cyclopropa[b]-naphthalene-1a-carboxylate (2y)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 7.6 Hz, 1H), 7.47 (d, J = 7.6 Hz, 1H), 7.36 - 7.29 (m, 3H), 7.23 - 7.20 (m, 3H), 4.03 (d, J = 17.6 Hz, 1H), 3.34 (d, J = 17.6 Hz, 1H), 3.30 (s, 3H), 2.61 (d, J = 5.2 Hz, 1H), 1.59 (d, J = 5.6 Hz, 1H); ^{13}C NMR

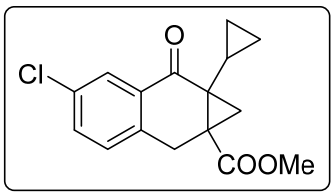
(100 MHz, $CDCl_3$) δ 193.8, 169.8, 136.2, 135.0, 133.4, 133.3, 131.8, 130.2, 130.1, 128.2, 127.7, 127.5, 52.1, 45.6, 33.3, 29.0, 21.4; LRMS (EI, 70 eV) *m/z* (%): 328 (M^++2, 15), 326 (M^+, 44), 294 (34), 267 (100), 203 (74); HRMS (ESI): calculated for [$C_{19}H_{16}{}^{35}ClO_3^+$] 327.0782, found 327.0793.

Methyl 7-oxo-7a-(thiophen-2-yl)-1,2,7,7a-tetrahydro-1aH-cyclopropa[*b*]-naphthalene-1a-carboxylate (2z)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.6 Hz, 1H), 7.52 (td, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.29 - 7.25 (m, 2H), 7.16 (dd, *J* = 2.8 Hz, 1.2 Hz, 1H), 6.96 (dd, *J* = 4.8, 1.2 Hz, 1H), 4.05 (d, *J* = 17.6 Hz, 1H), 3.40 (s, 3H), 3.34 (d, *J* = 17.6 Hz, 1H), 2.57 (d, *J* = 5.2 Hz, 1H), 1.61 (d, *J* = 5.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.5, 169.9, 137.8, 135.4, 133.4, 130.5, 129.0, 128.6, 127.8, 127.4, 125.1, 124.9, 52.2, 40.6, 33.6, 29.5, 22.0; LRMS (EI, 70 eV) *m/z* (%): 298 (M^+, 100), 270 (20), 239 (92), 211 (68), 178 (60); HRMS (ESI): calculated for [$C_{17}H_{15}O_3S^+$] 299.0736, found 299.0753.

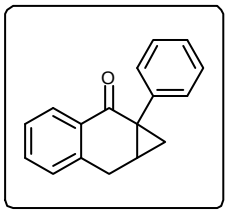
Methyl 5-chloro-7a-cyclopropyl-7-oxo-1,2,7,7a-tetrahydro-1aH-cyclopropa[*b*]-naphthalene-1a-carboxylate (2aa)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 2.0 Hz, 1H), 7.42 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 1H), 3.79 (s, 3H), 3.73 (d, *J* = 17.2 Hz, 1H), 3.23 (d, *J* = 17.2 Hz, 1H), 1.62 (d, *J* = 5.6 Hz, 1H), 1.23 - 1.16 (m, 1H), 1.00 (d, *J* = 6.0 Hz, 1H),

0.96 - 0.85 (m, 1H), 0.46 - 0.35 (m, 1H), 0.31 - 0.24 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.4, 170.2, 135.7, 133.4, 132.9, 132.8, 129.8, 127.2, 52.4, 40.0, 33.2, 29.9, 17.5, 8.0, 4.1, 2.3; LRMS (EI, 70 eV) *m/z* (%): 290 (M^+, 3), 262 (15), 231 (100), 195 (51); HRMS (ESI): calculated for [$C_{16}H_{16}{}^{35}ClO_3^+$] 291.0782, found 291.0798.

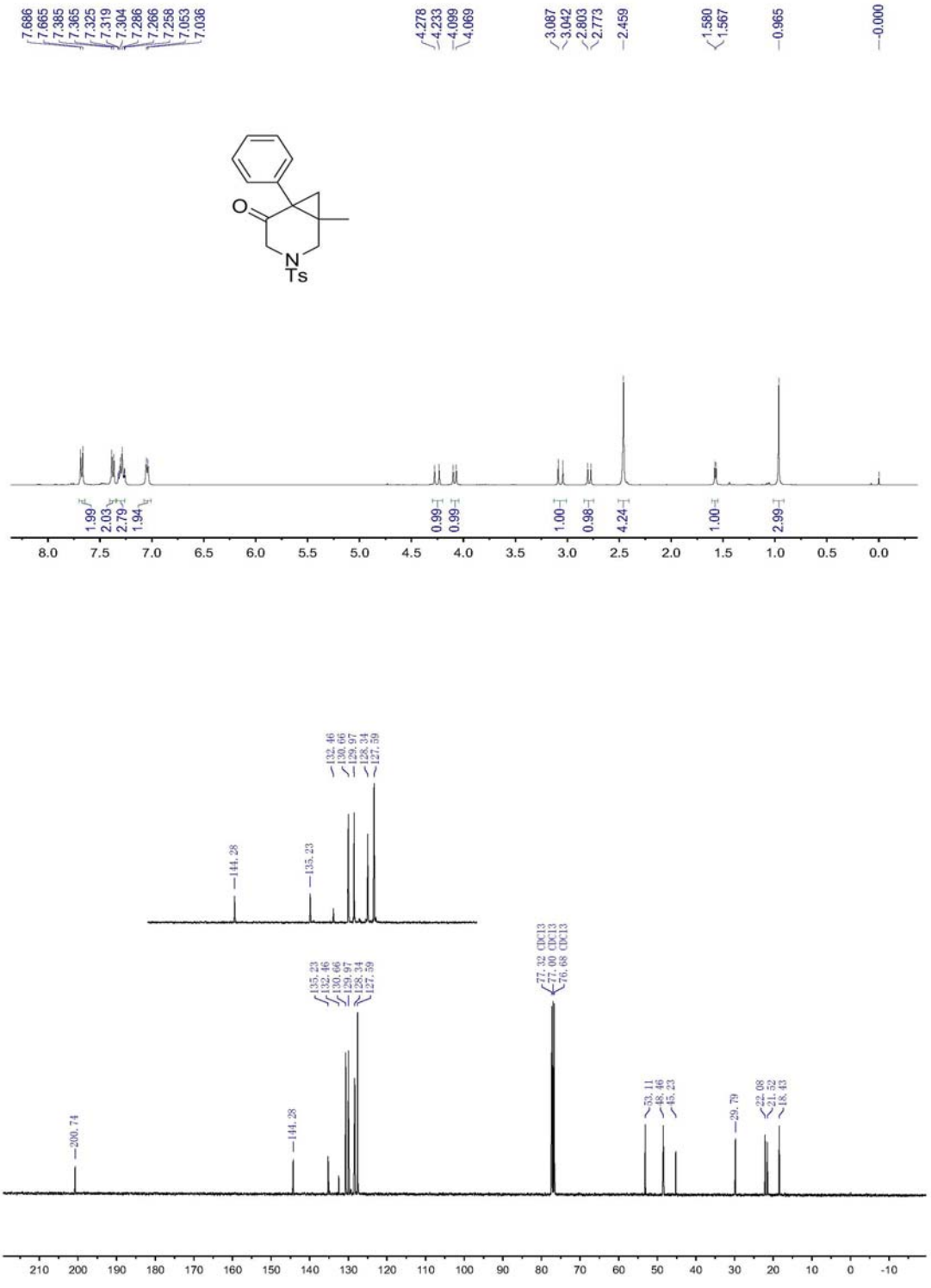
1*a*-Phenyl-1,1a,7,7a-tetrahydro-2*H*-cyclopropa[*b*]naphthalen-2-one (2ab)



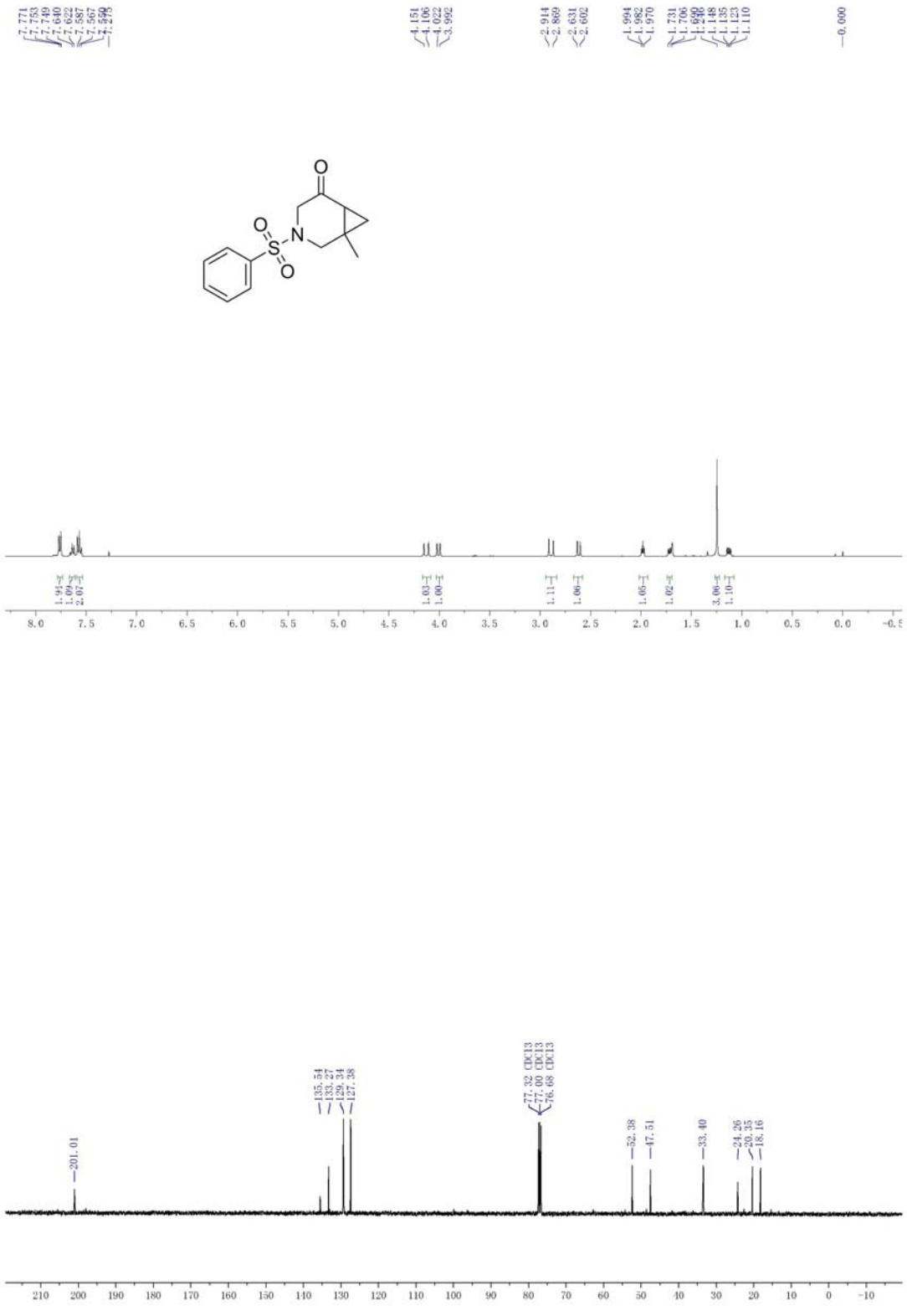
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.37 - 7.27 (m, 6H), 7.21 (d, *J* = 7.6 Hz, 1H), 3.56 (dd, *J* = 17.6, 4.4 Hz, 1H), 3.31 (d, *J* = 17.6 Hz, 1H), 2.28-2.23 (m, 1H), 1.69 (dd, *J* = 8.0, 4.8 Hz, 1H), 1.37 (t, *J* = 5.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 139.5, 138.2, 133.0, 131.5, 130.4, 128.7, 128.3, 127.6, 127.3, 127.1, 39.3, 28.1, 22.1, 19.5; LRMS (EI, 70 eV) *m/z* (%): 234 (M^+, 100), 206 (84), 191 (30); HRMS (ESI): calculated for [$C_{17}H_{15}O^+$] 235.1117, found 235.1125.

(C) Spectra

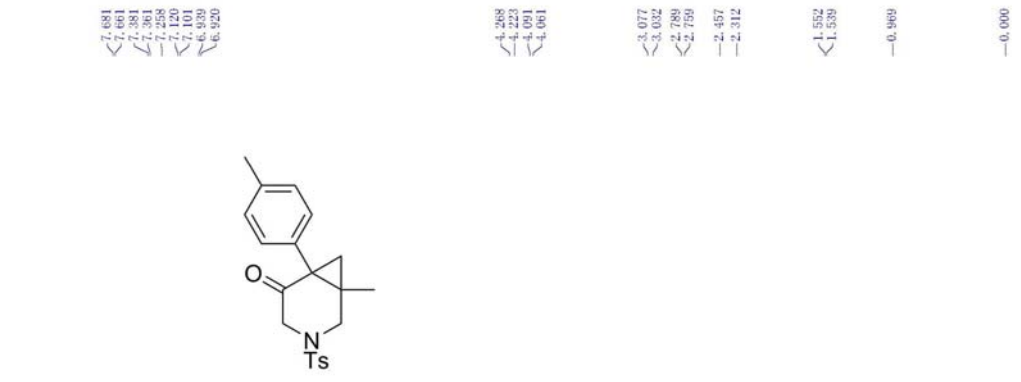
1-Methyl-6-phenyl-3-tosyl-3-azabicyclo[4.1.0]heptan-5-one (2a)

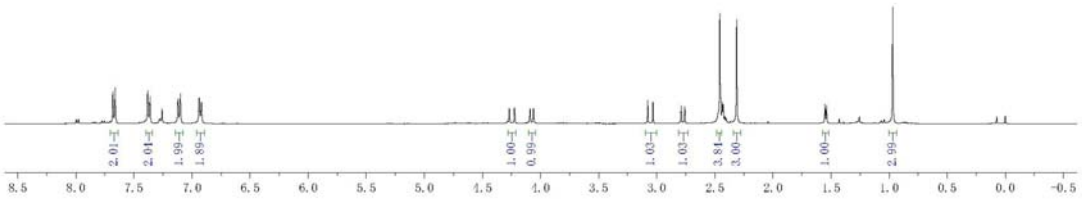


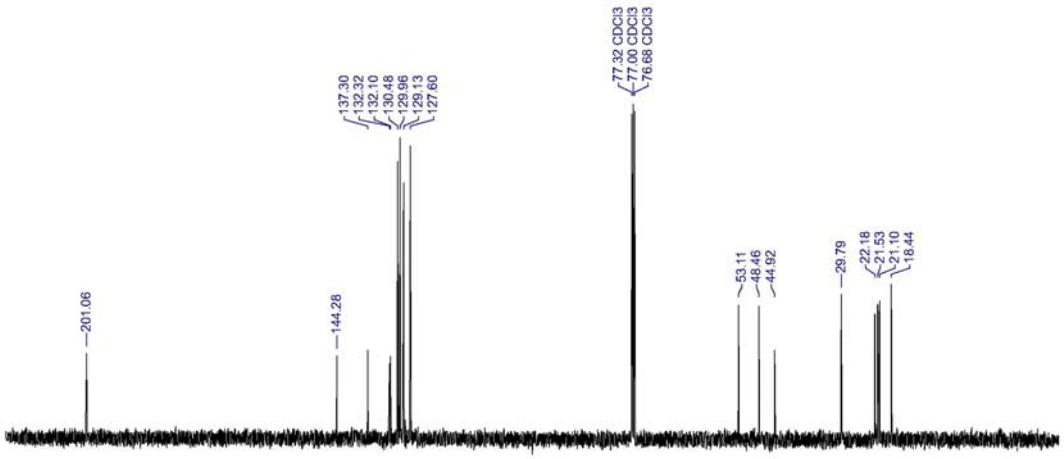
1-Methyl-3-(phenylsulfonyl)-3-azabicyclo[4.1.0]heptan-5-one (2d)



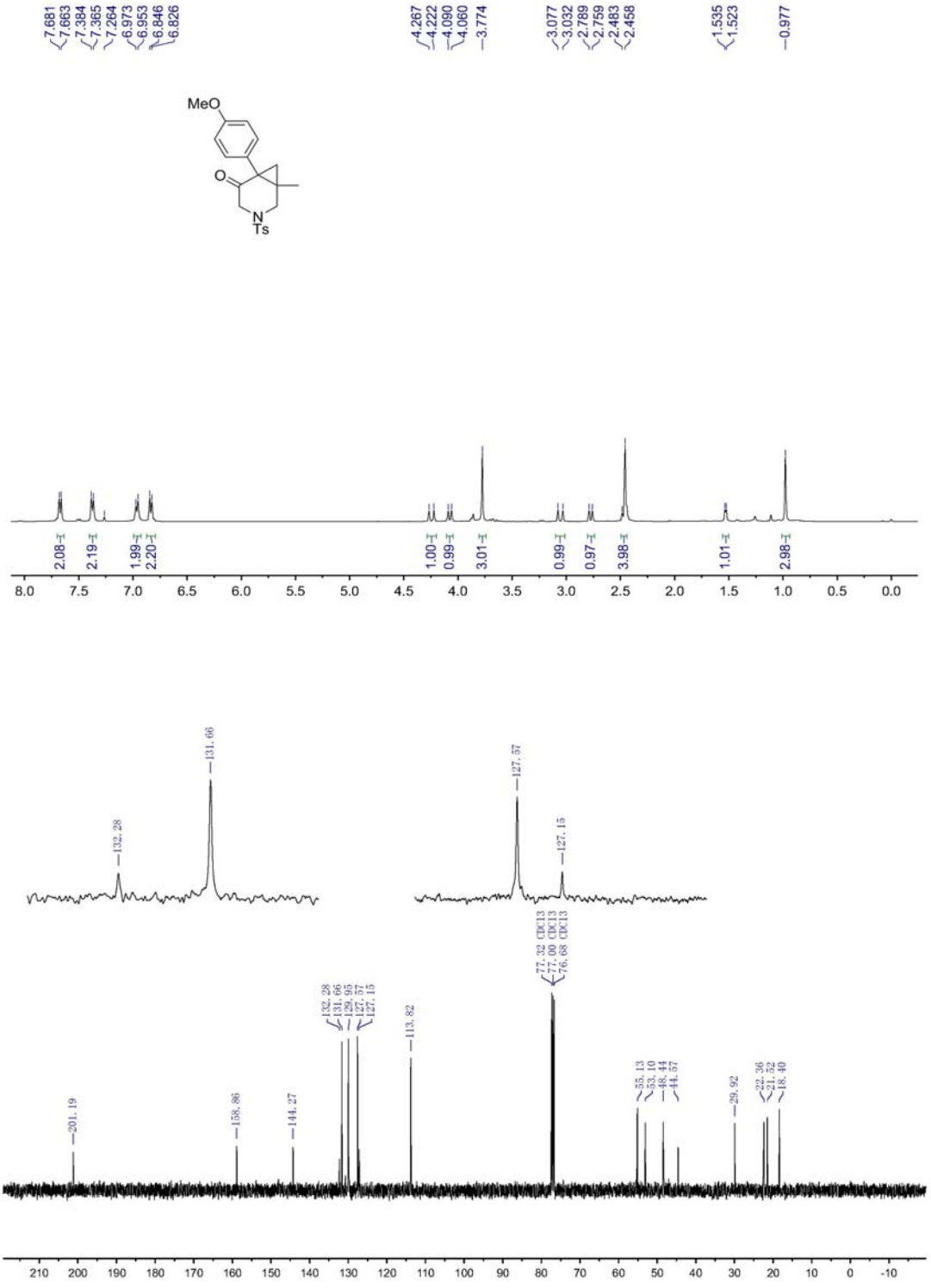
1-Methyl-6-(*p*-tolyl)-3-tosyl-3-azabicyclo[4.1.0]heptan-5-one (2e)



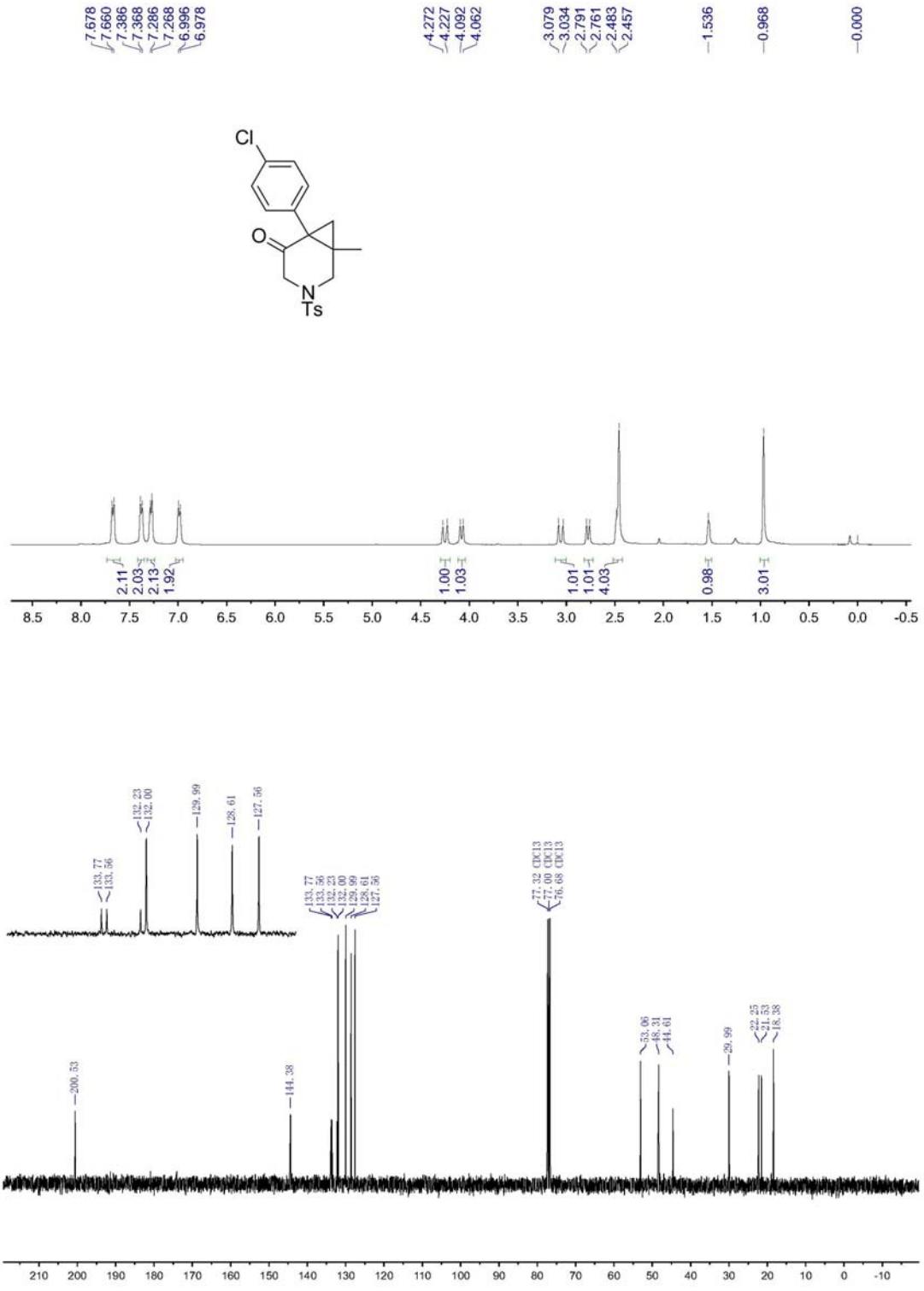




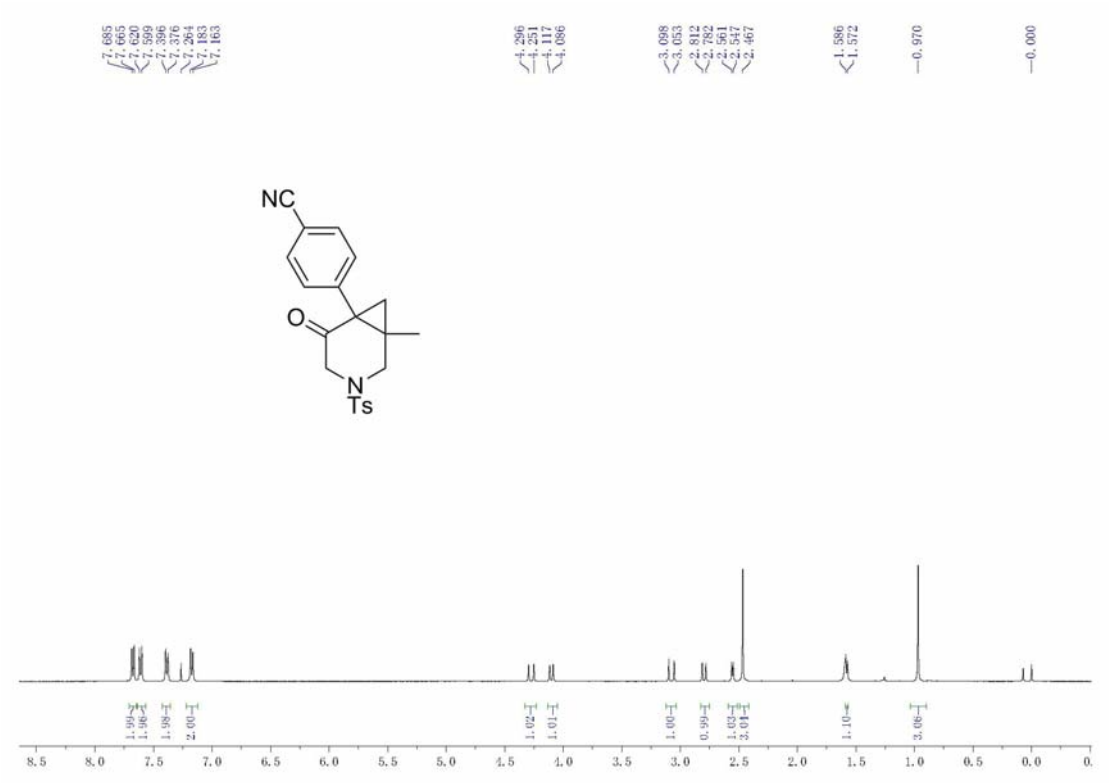
6-(4-Methoxyphenyl)-1-methyl-3-tosyl-3-azabicyclo[4.1.0]heptan-5-one (2f)

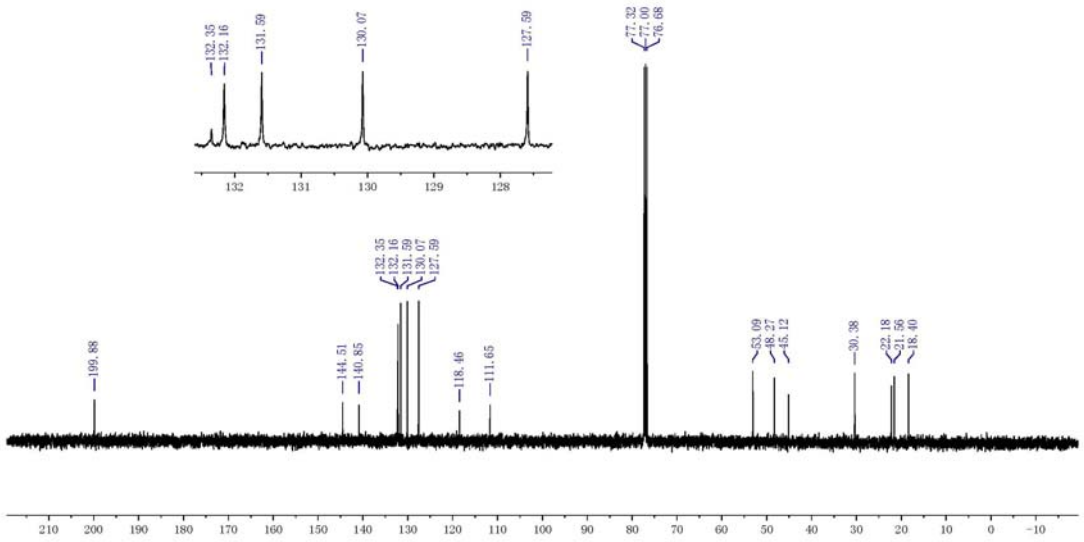


6-(4-Chlorophenyl)-1-methyl-3-tosyl-3-azabicyclo[4.1.0]heptan-5-one (2g)

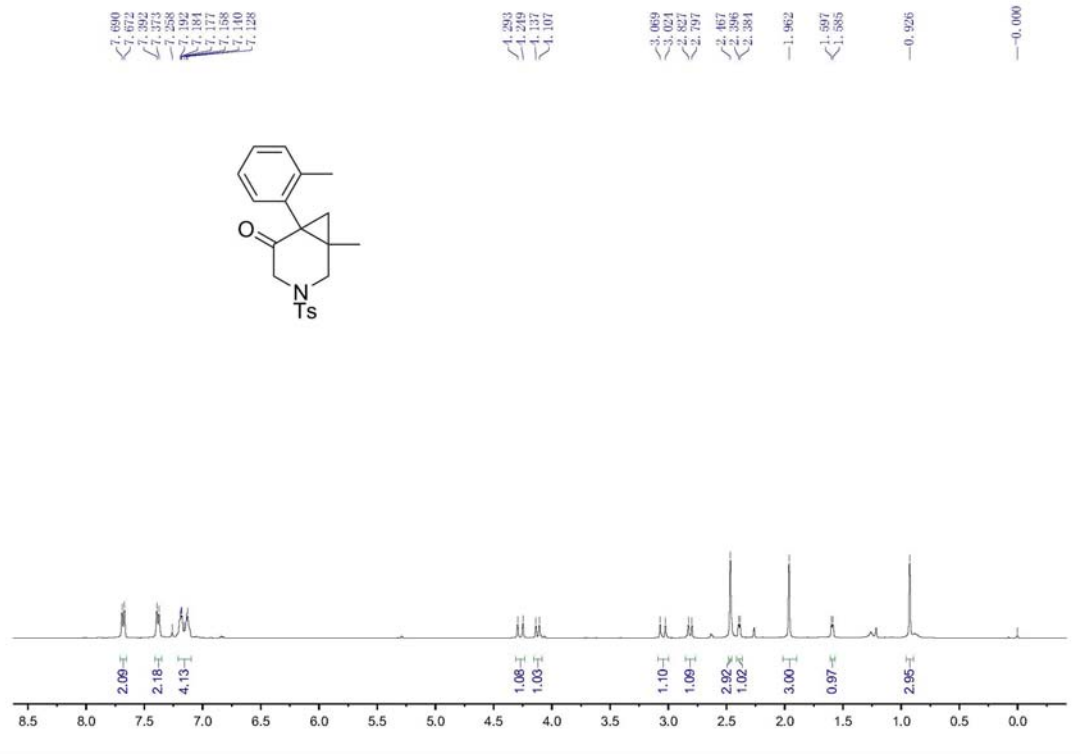


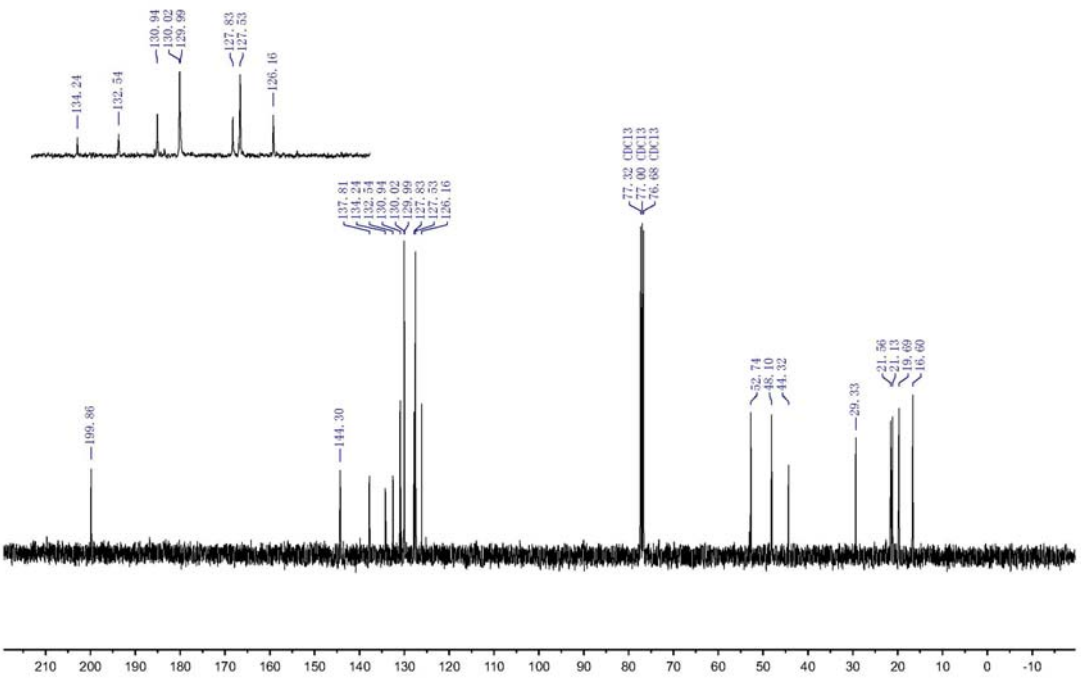
4-(1-Methyl-5-oxo-3-tosyl-3-azabicyclo[4.1.0]heptan-6-yl)benzonitrile (2h)



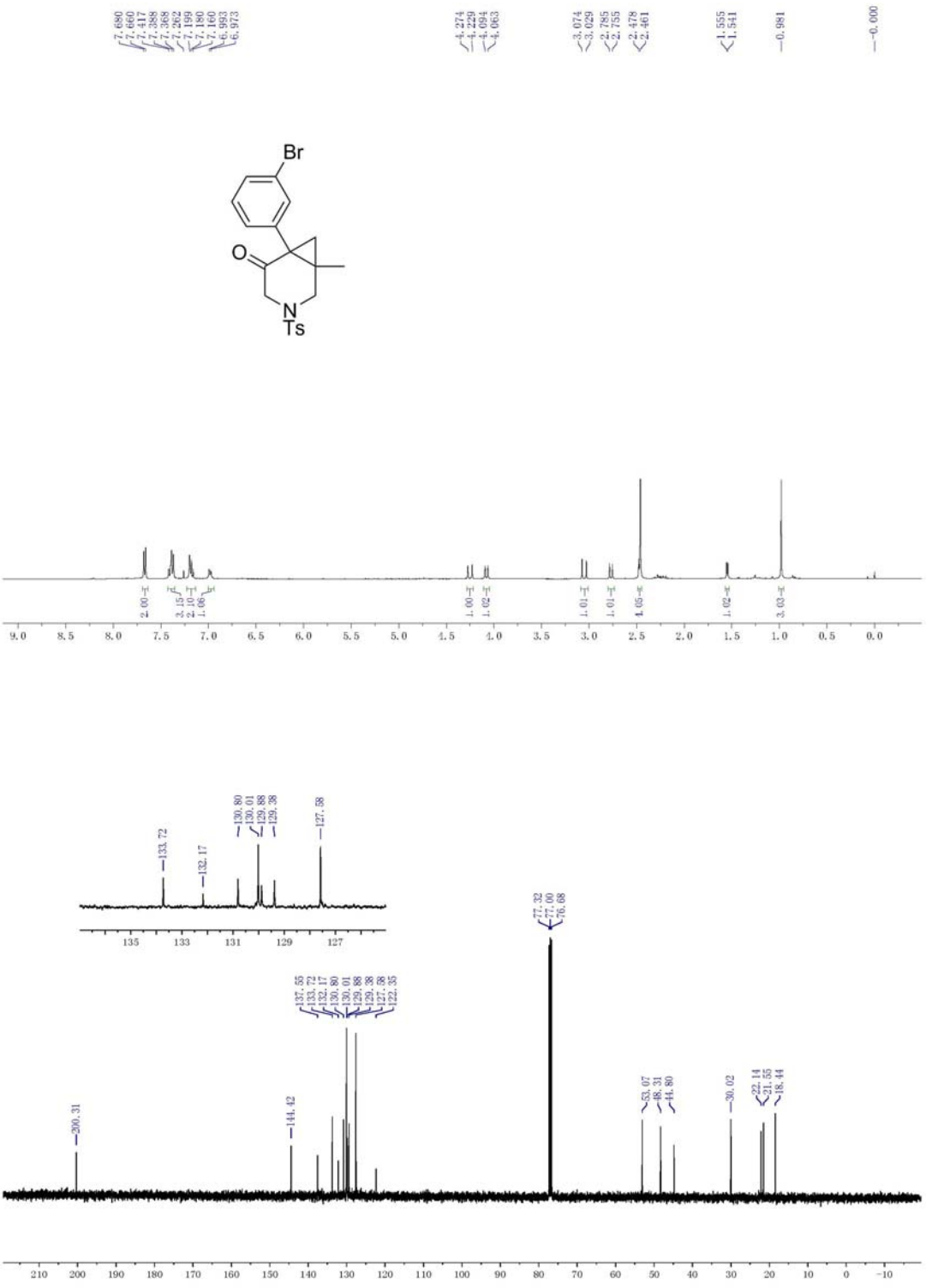


1-Methyl-6-(*o*-tolyl)-3-tosyl-3-azabicyclo[4.1.0]heptan-5-one (2i)

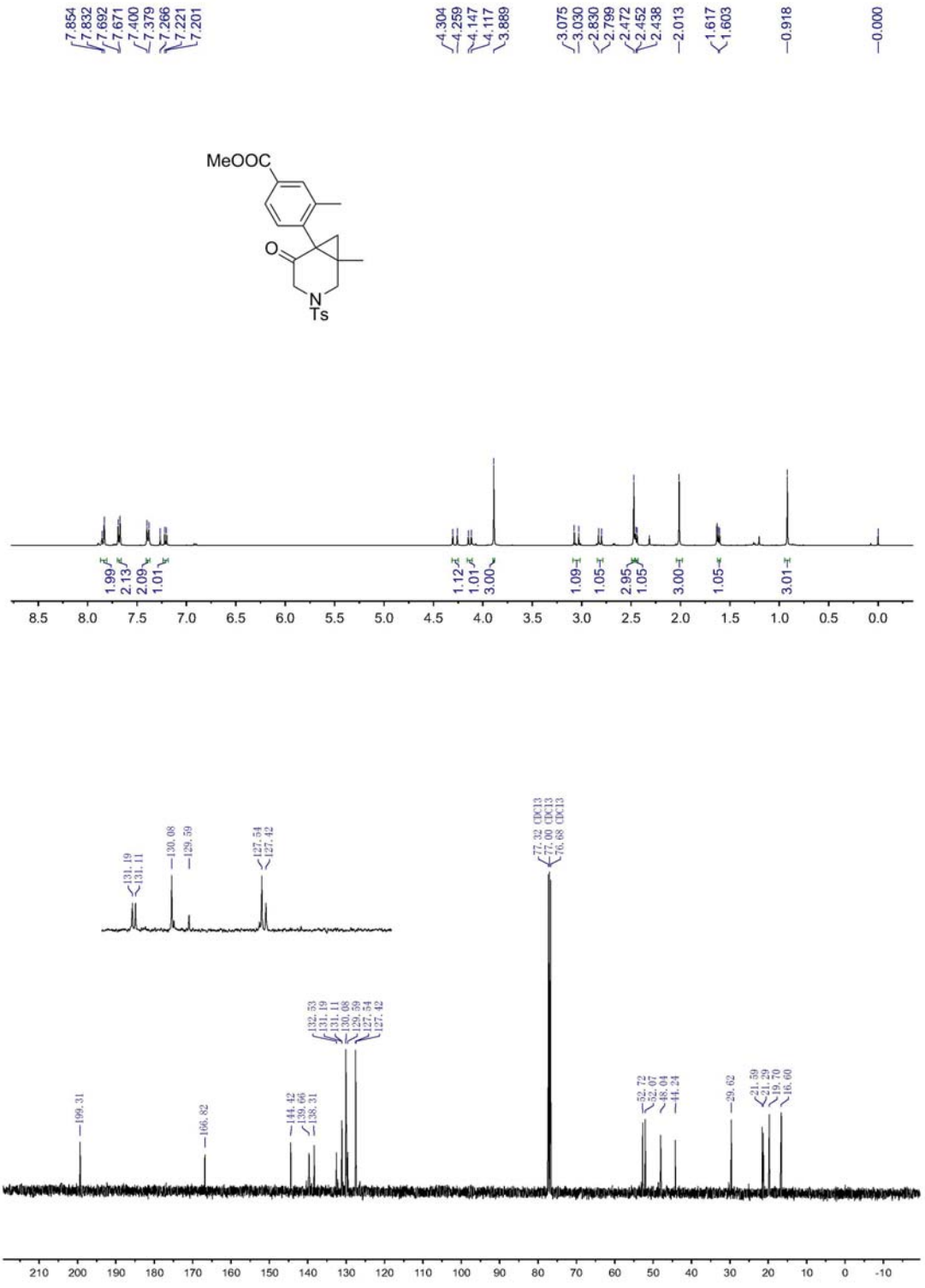




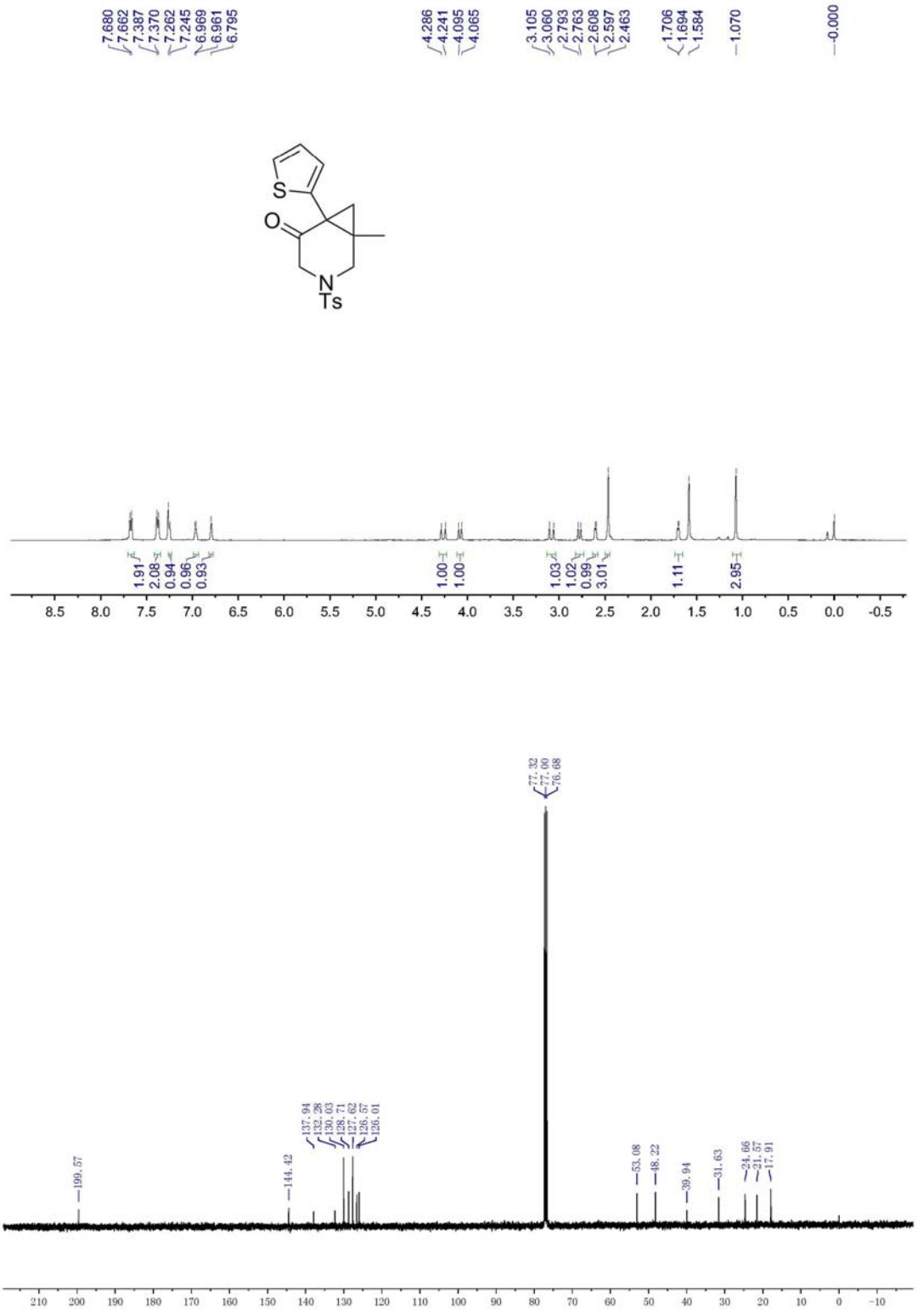
6-(3-Bromophenyl)-1-methyl-3-tosyl-3-azabicyclo[4.1.0]heptan-5-one (2j)



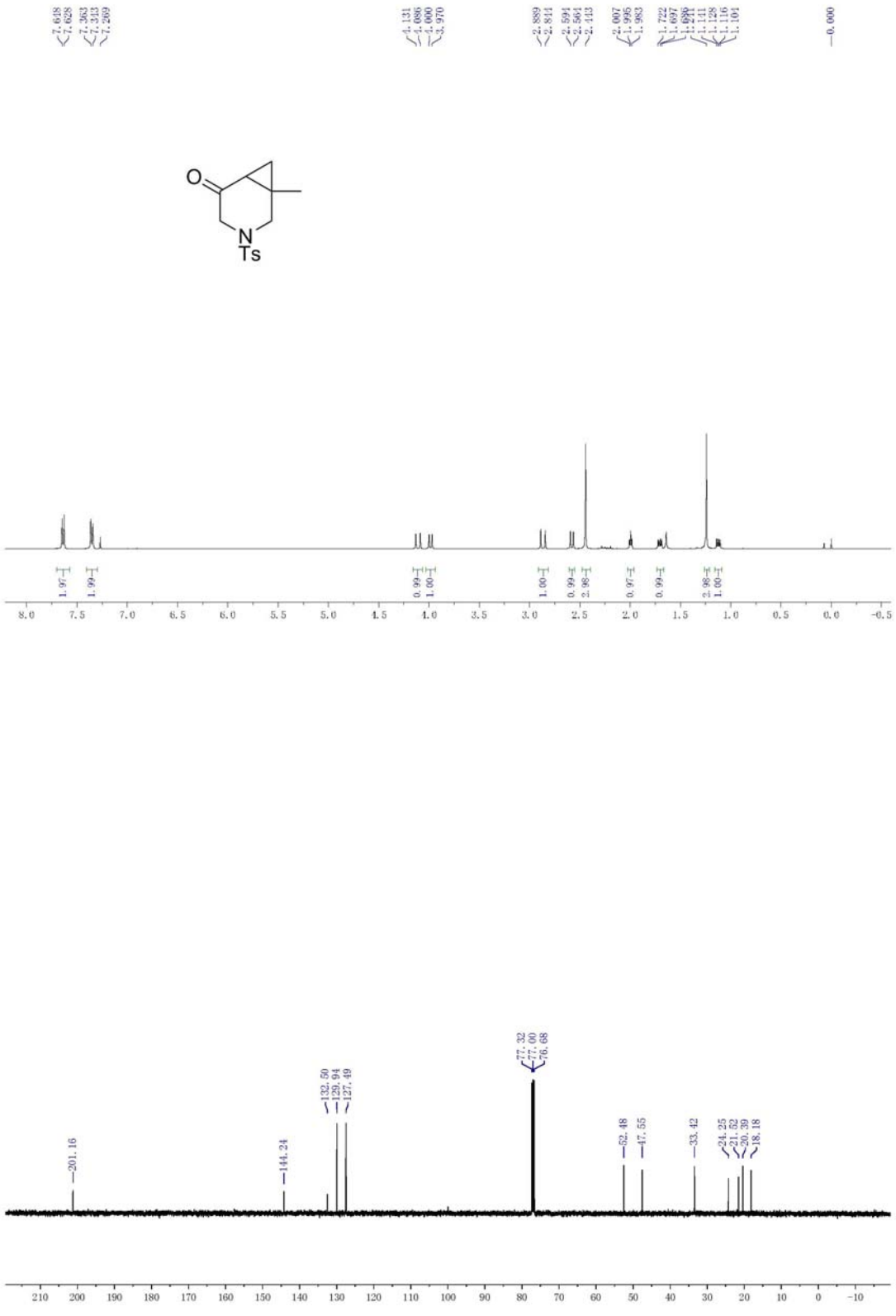
Methyl 3-methyl-4-(1-methyl-5-oxo-3-tosyl-3-azabicyclo[4.1.0]heptan-6-yl)benzoate (2k)



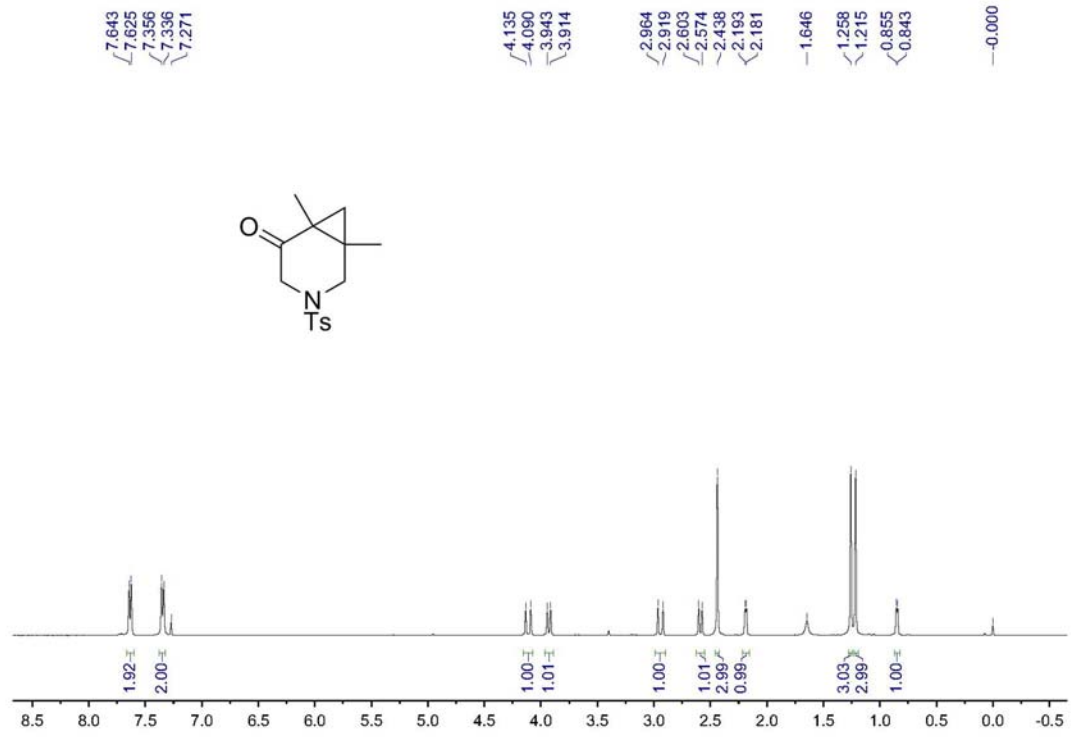
1-Methyl-6-(thiophen-2-yl)-3-tosyl-3-azabicyclo[4.1.0]heptan-5-one (2l)

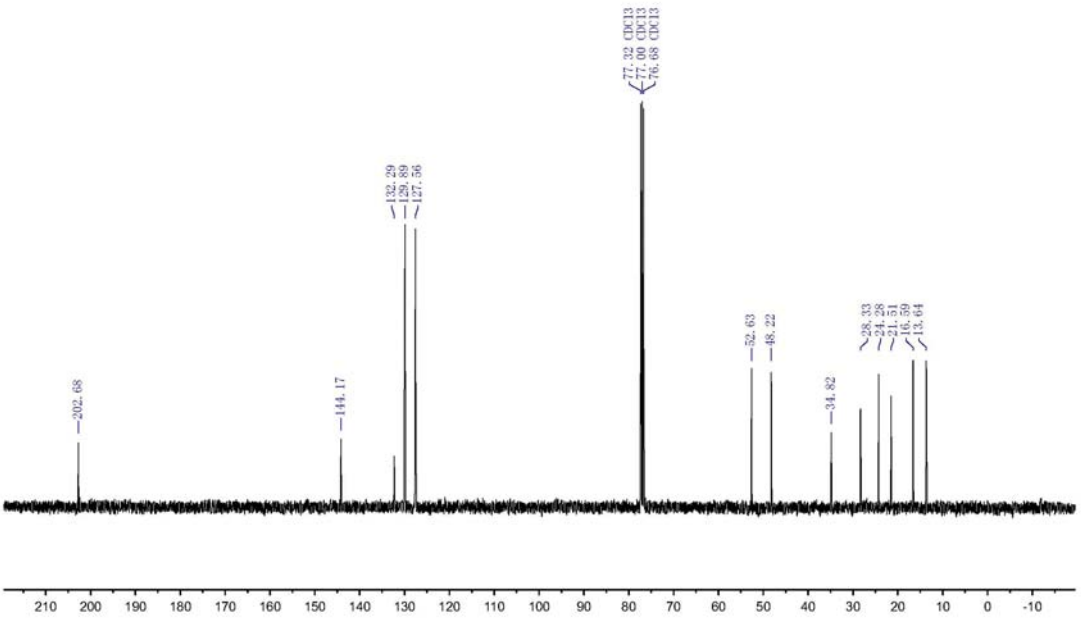


1-Methyl-3-tosyl-3-azabicyclo[4.1.0]heptan-5-one (2m)

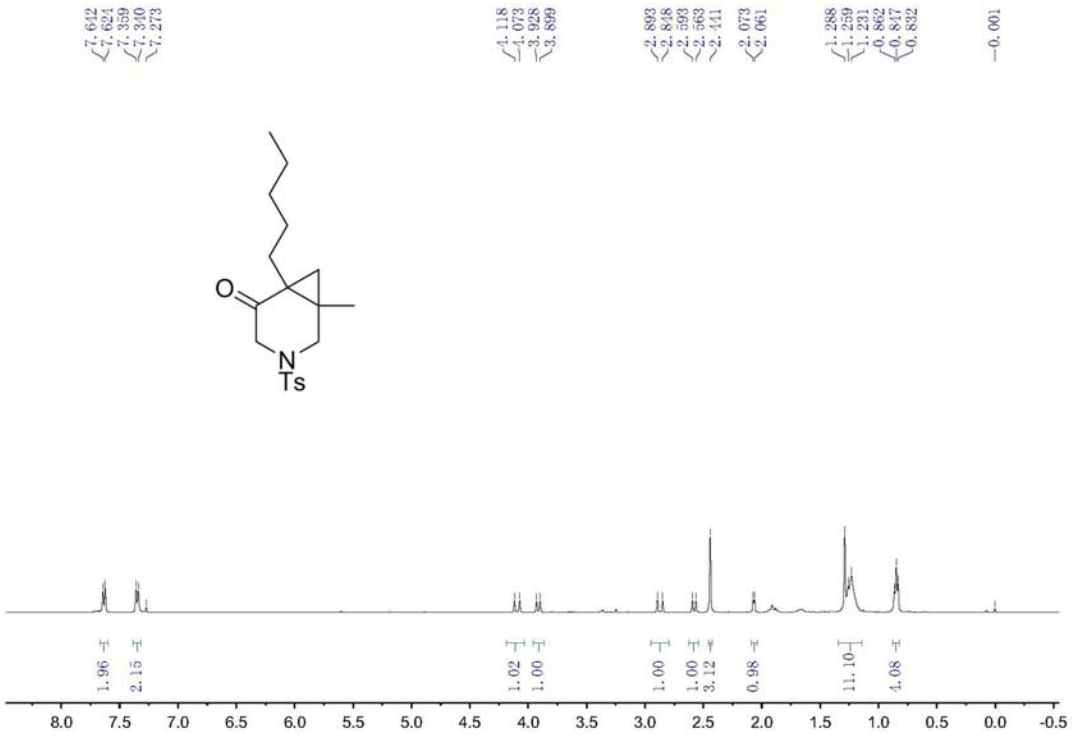


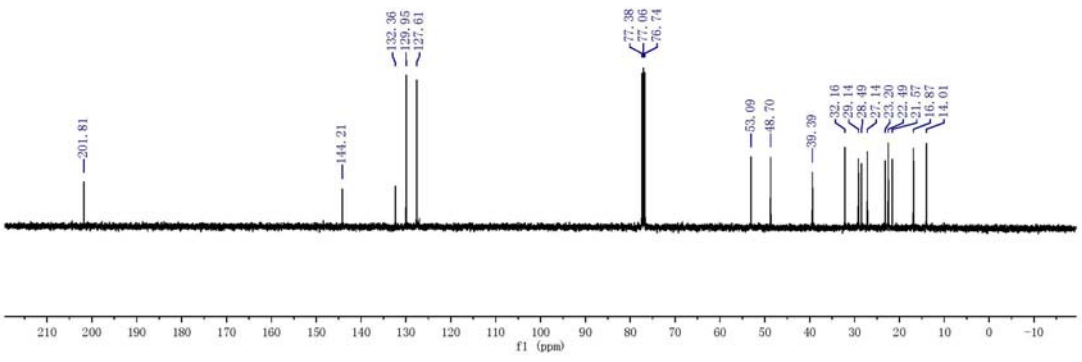
1,6-Dimethyl-3-tosyl-3-azabicyclo[4.1.0]heptan-5-one (2n)



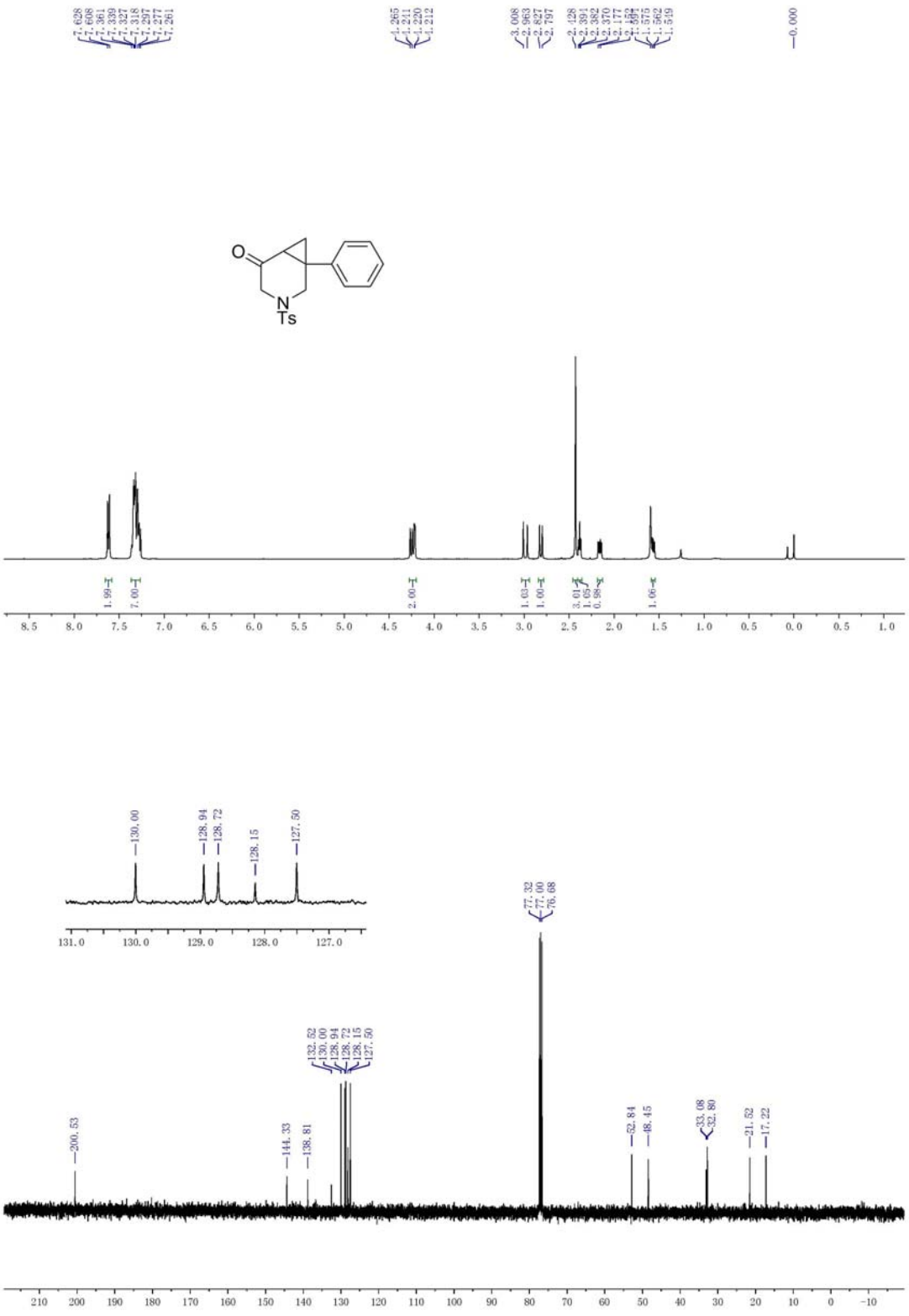


1-Methyl-6-pentyl-3-tosyl-3-azabicyclo[4.1.0]heptan-5-one (2o)

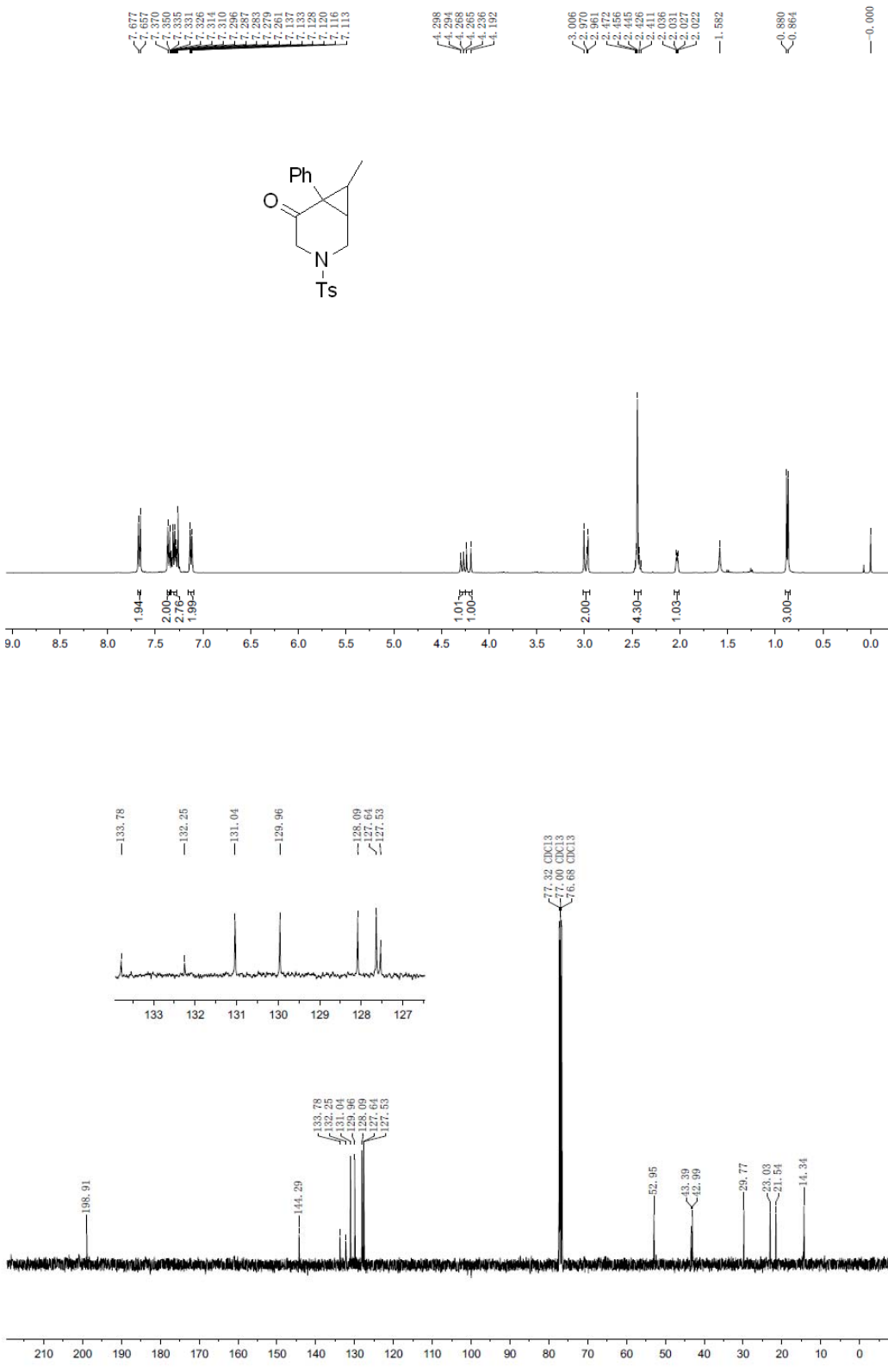




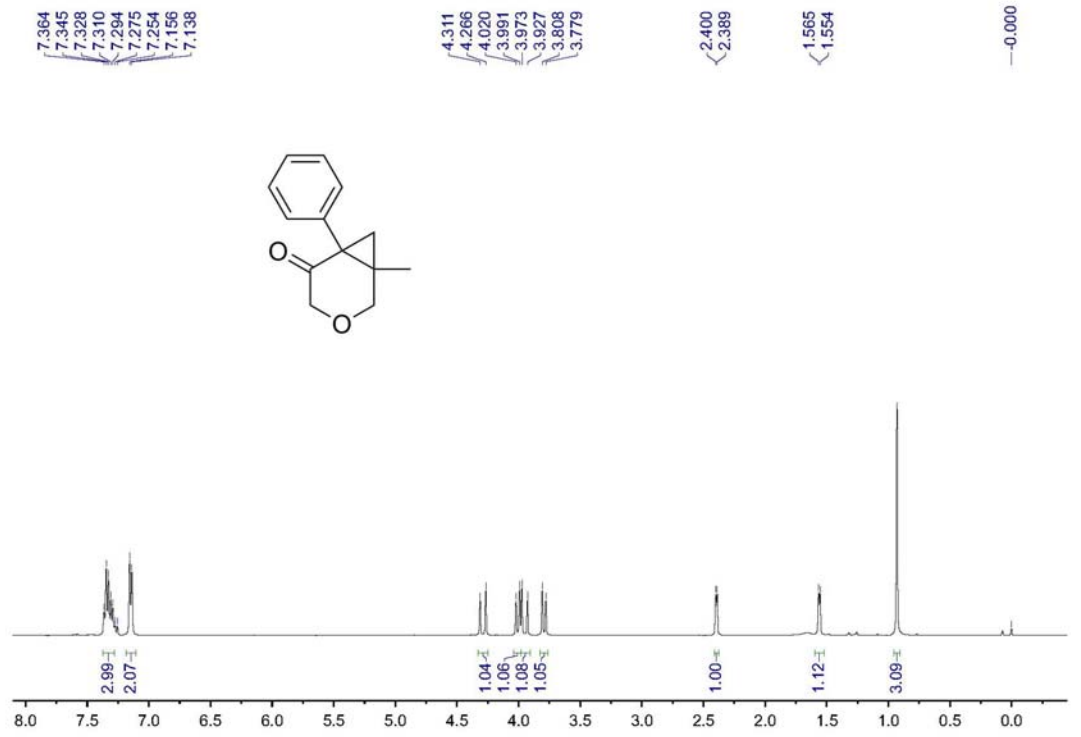
1-Phenyl-3-tosyl-3-azabicyclo[4.1.0]heptan-5-one (2q)

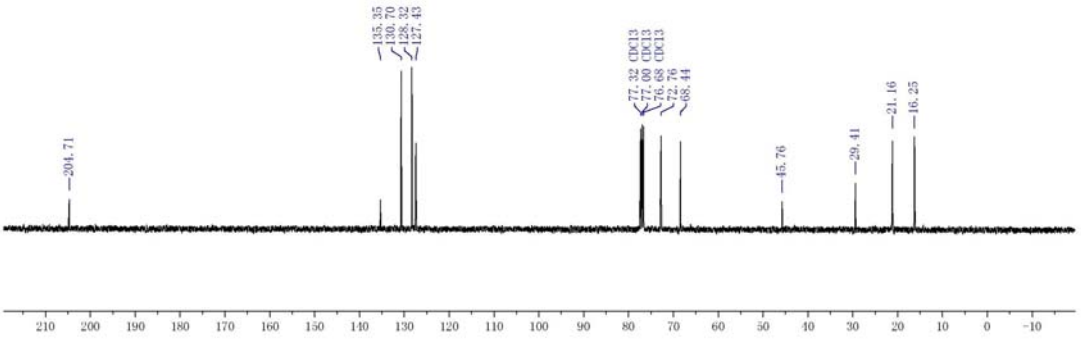


7-Methyl-6-phenyl-3-tosyl-3-azabicyclo[4.1.0]heptan-5-one (2s)

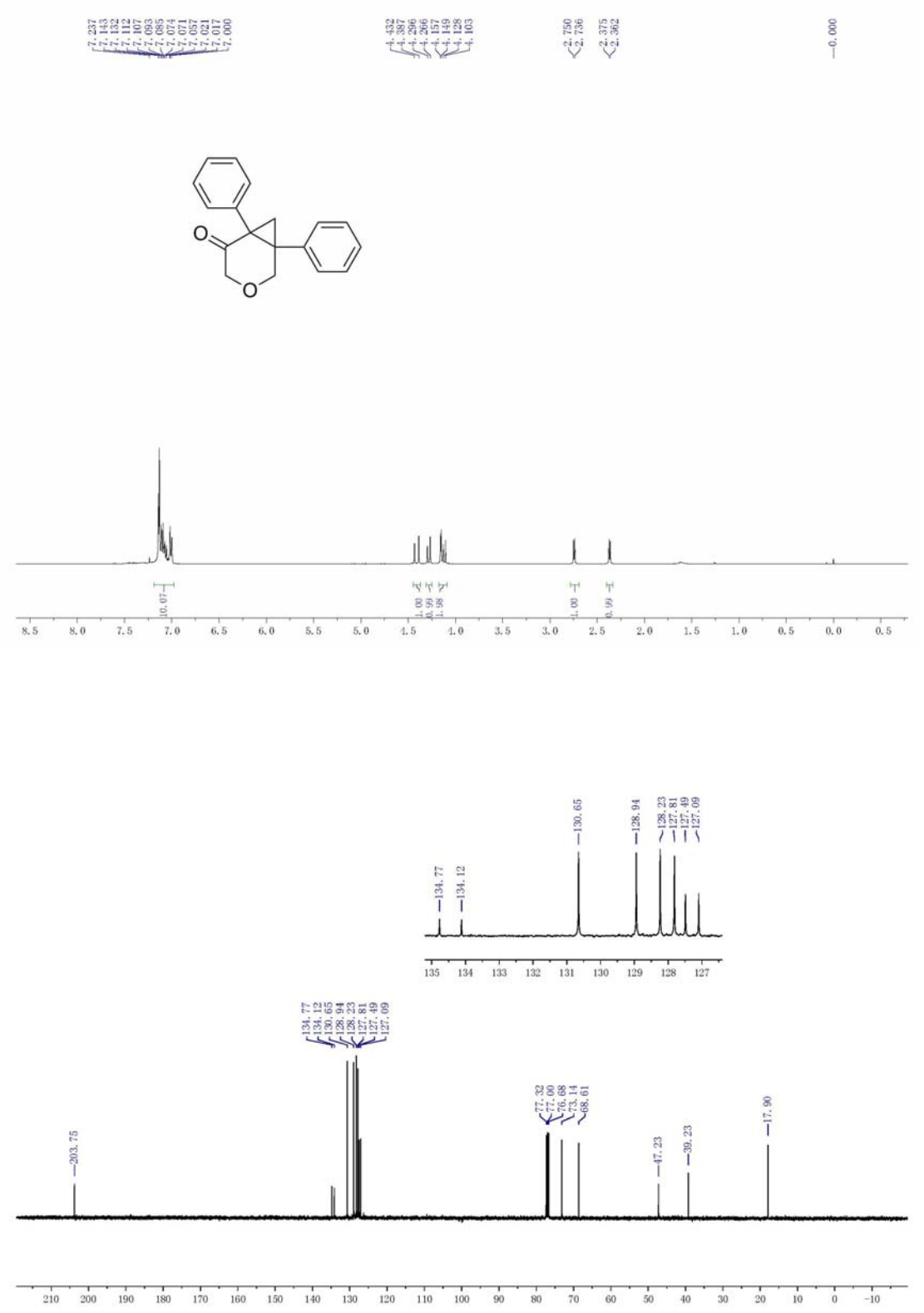


1-Methyl-6-phenyl-3-oxabicyclo[4.1.0]heptan-5-one (2t)

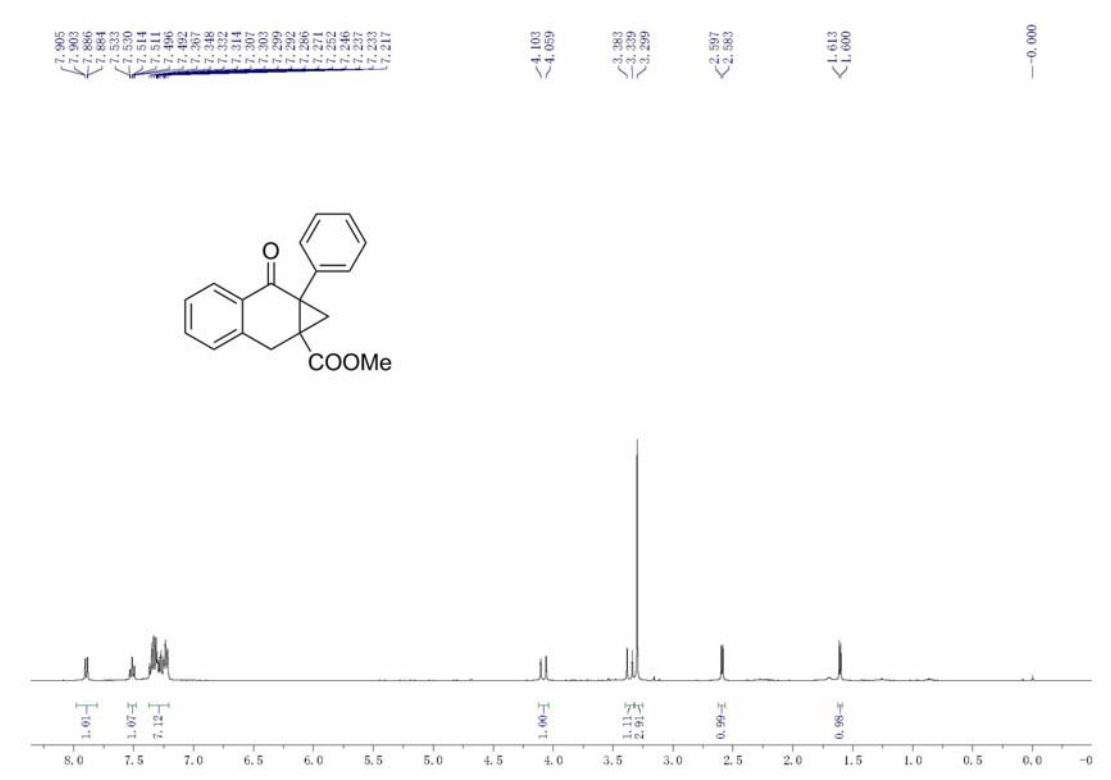


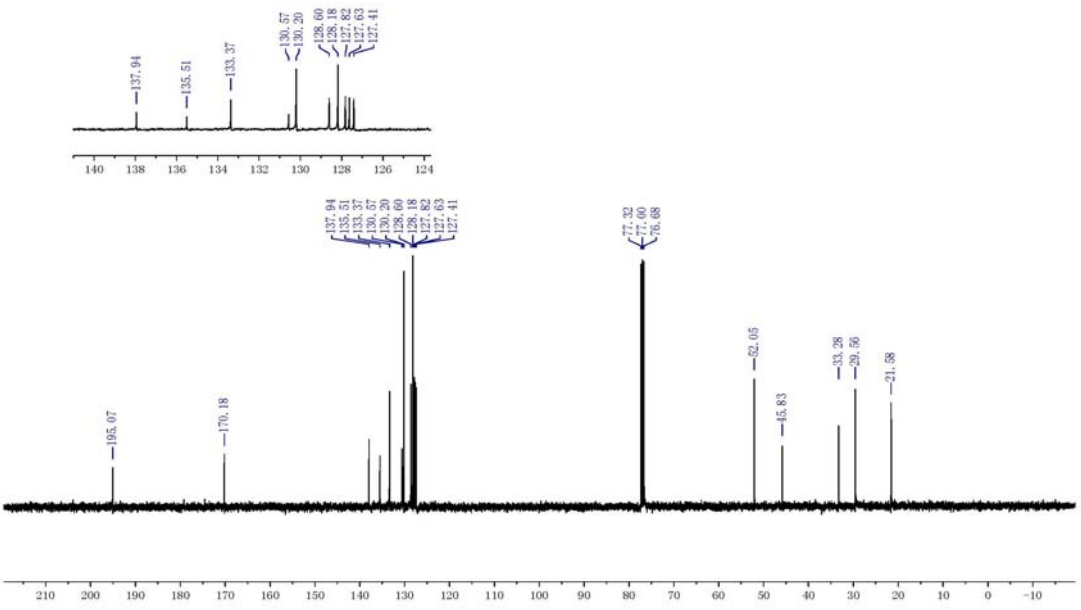


1,6-Diphenyl-3-oxabicyclo[4.1.0]heptan-5-one (2u)

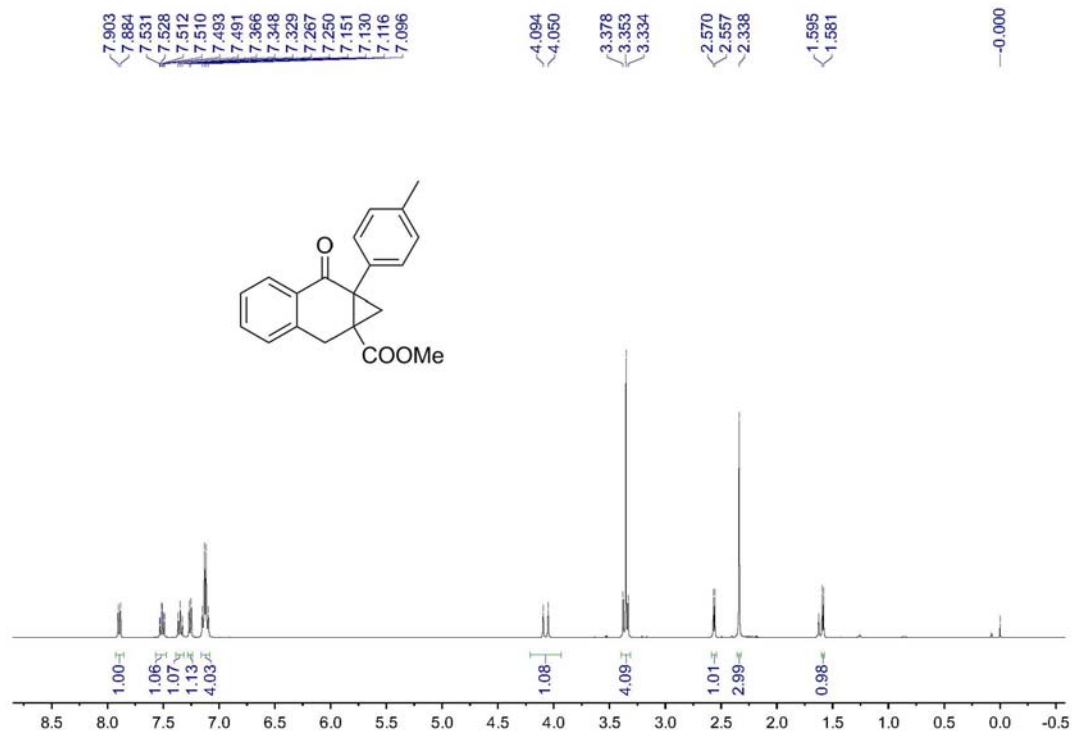


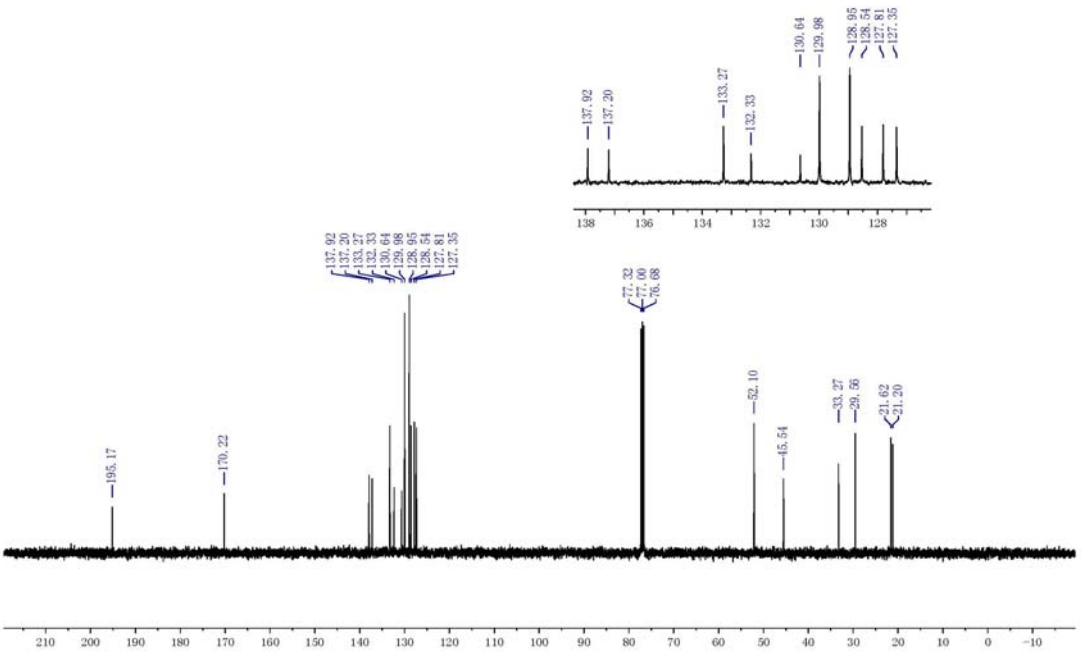
Methyl 7-oxo-7a-phenyl-1,2,7,7a-tetrahydro-1aH-cyclopropa[b]naphthalene-1a-carboxylate (2v)



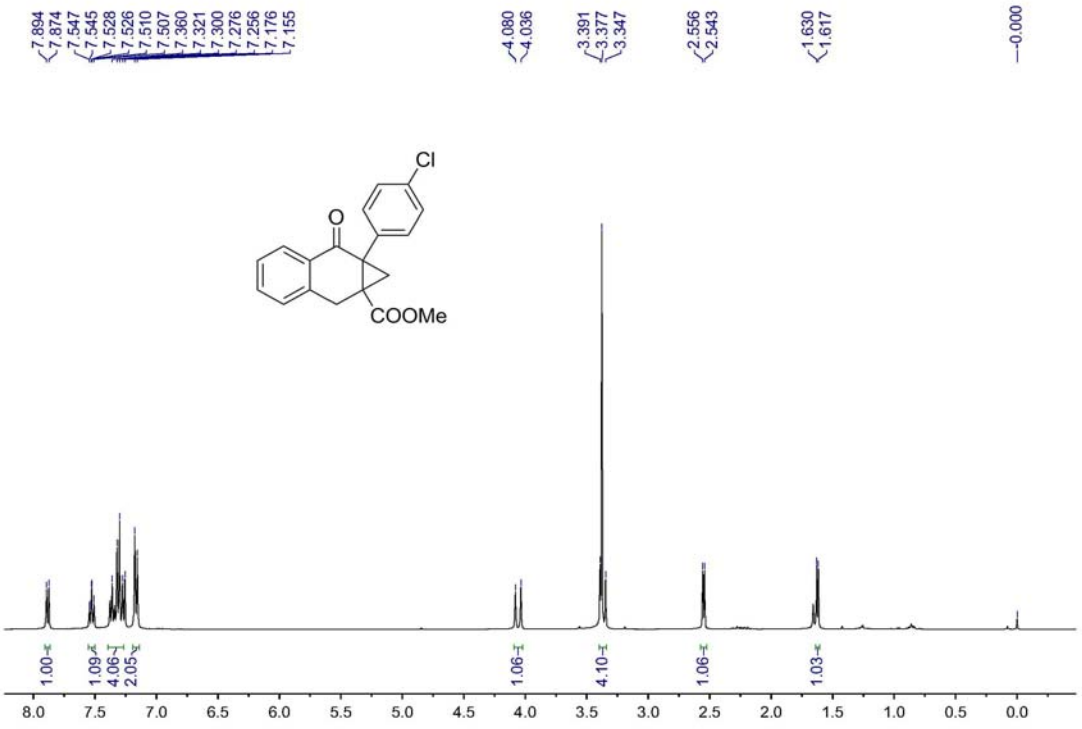


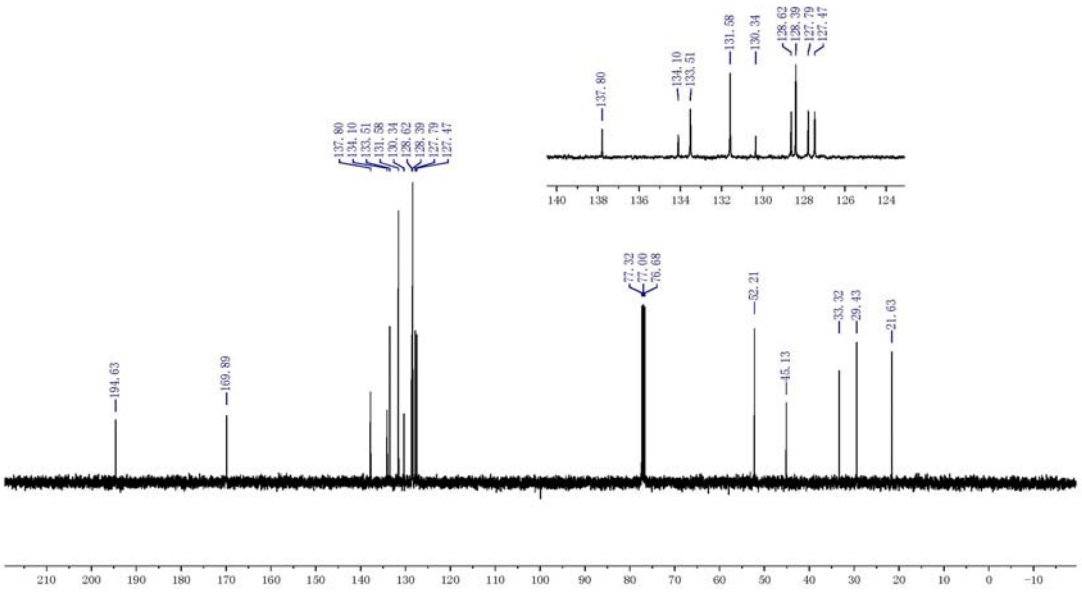
Methyl 7-oxo-7a-(*p*-tolyl)-1,2,7,7a-tetrahydro-1aH-cyclopropa[*b*]naphthalene-1a-carboxylate (2w)



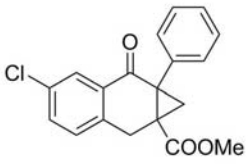


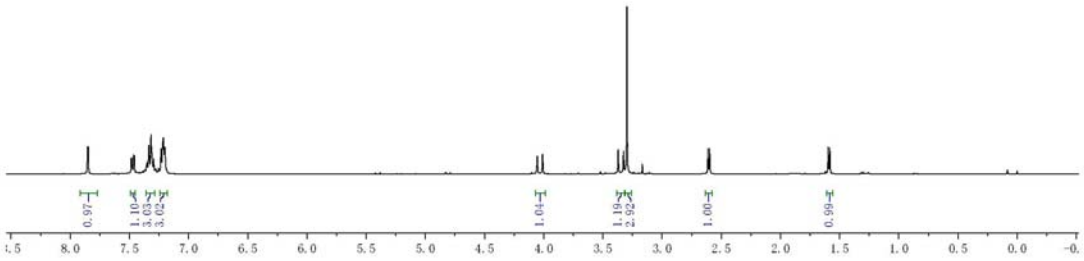
Methyl 7a-(4-chlorophenyl)-7-oxo-1,2,7,7a-tetrahydro-1aH-cyclopropa[b]naphthalene-1a-carboxylate (2x)

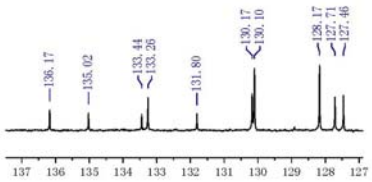


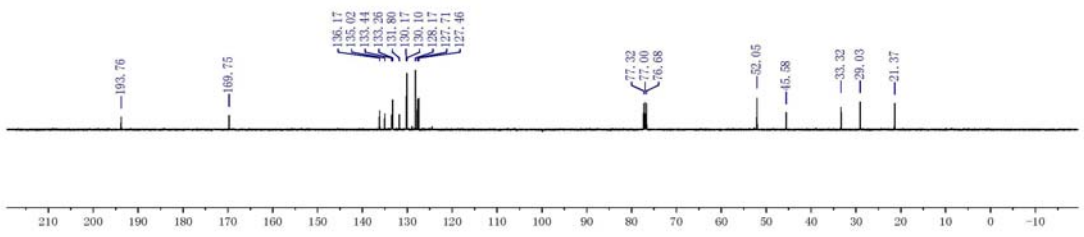


Methyl 5-chloro-7-oxo-7a-phenyl-1,2,7,7a-tetrahydro-1aH-cyclopropa[b]naphthalene-1a-carboxylate (2y)

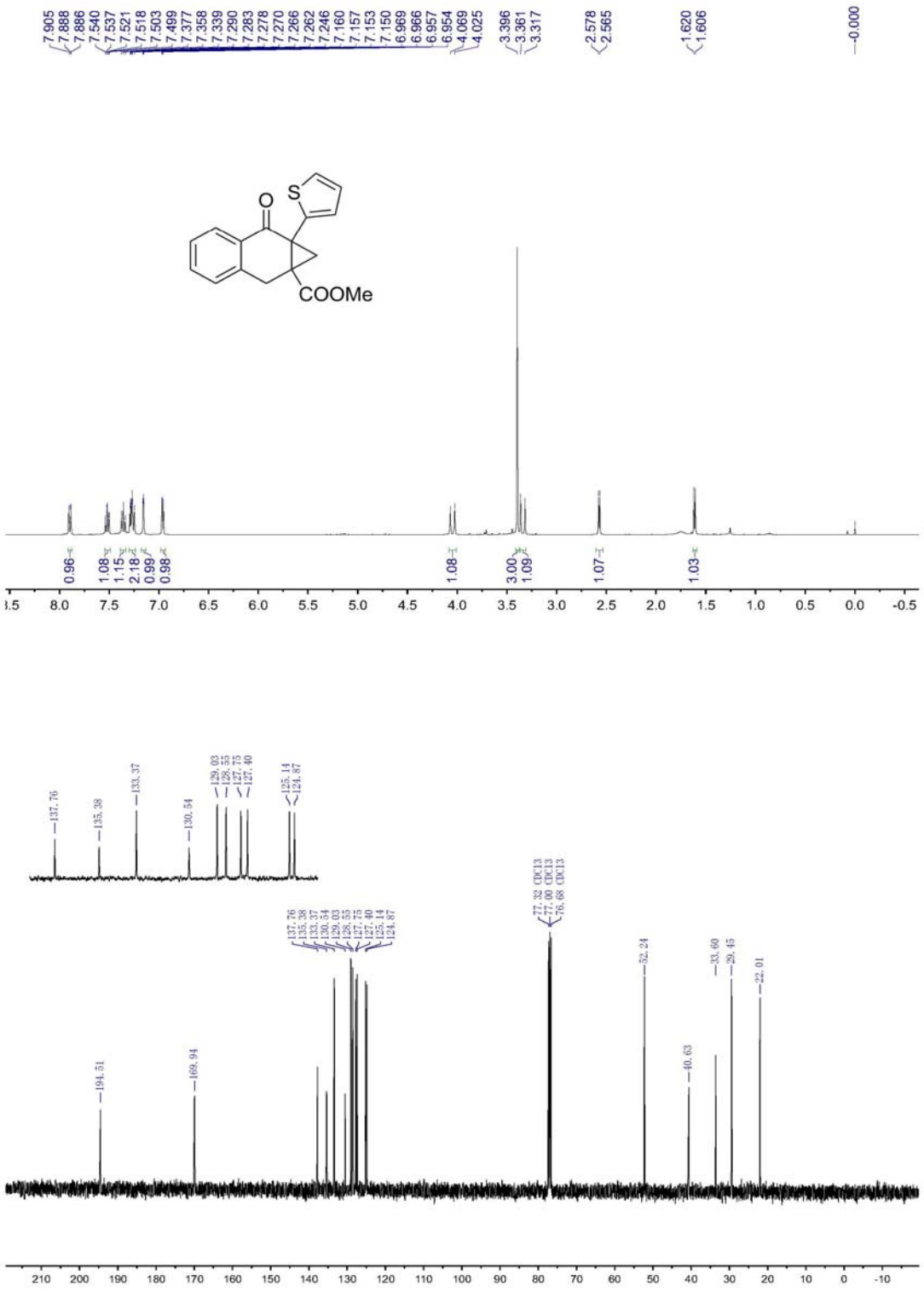




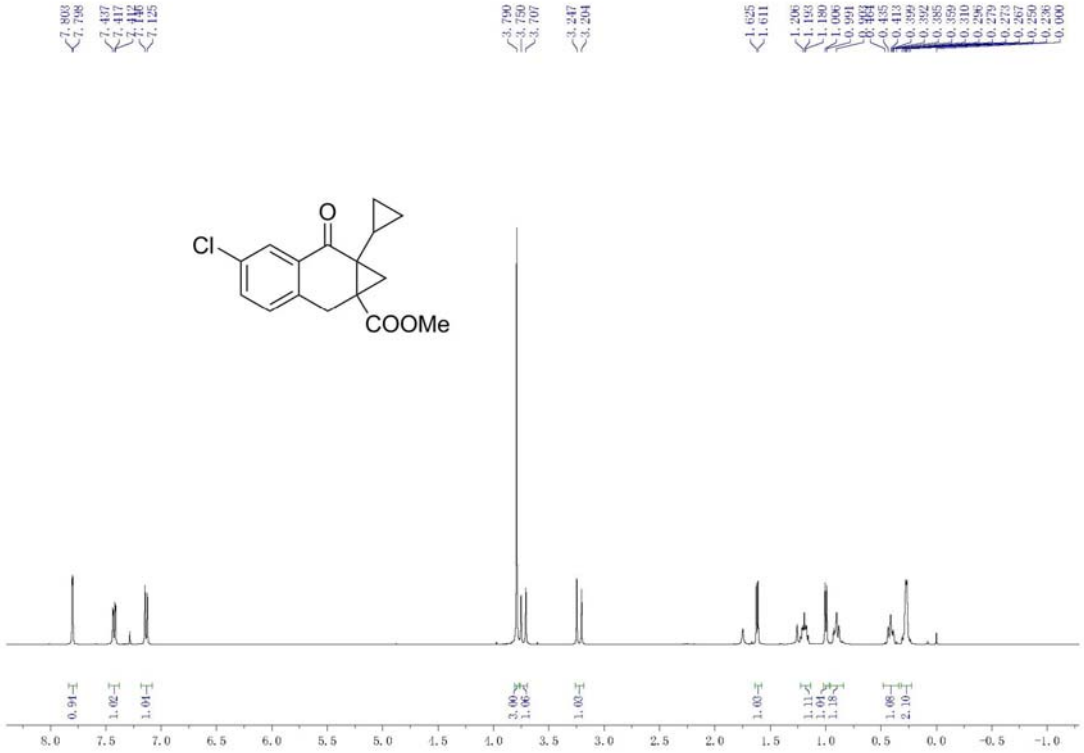


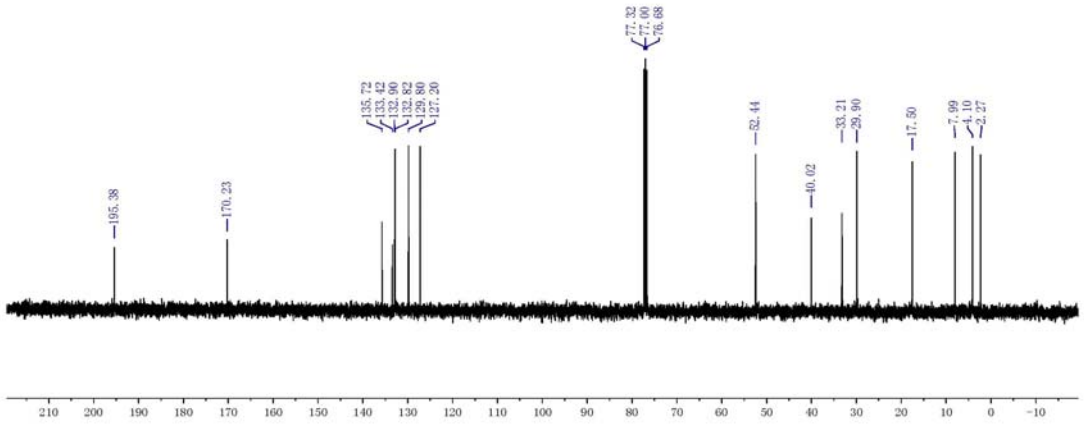


Methyl 7-oxo-7a-(thiophen-2-yl)-1,2,7,7a-tetrahydro-1aH-cyclopropa[*b*]naphthalene-1a-carboxylate (2z)

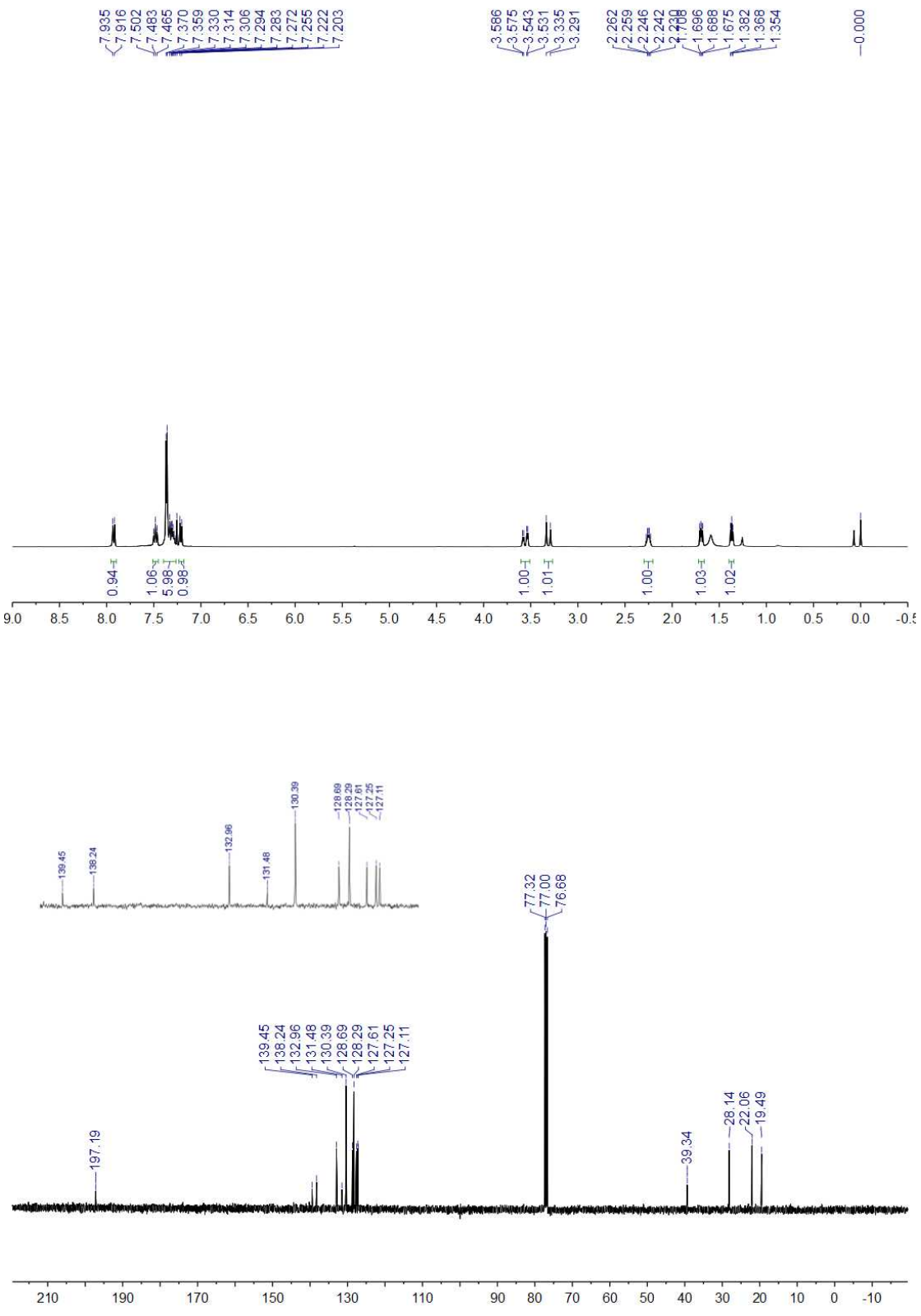


Methyl 5-chloro-7a-cyclopropyl-7-oxo-1,2,7,7a-tetrahydro-1aH-cyclopropa[*b*]naphthalene-1a-carboxylate (2aa)





1*a*-Phenyl-1,1a,7,7a-tetrahydro-2*H*-cyclopropa[*b*]naphthalen-2-one (2ab)



(D) The X-ray Single-crystal Diffraction Analysis of Product 2a

CCDC 1029834

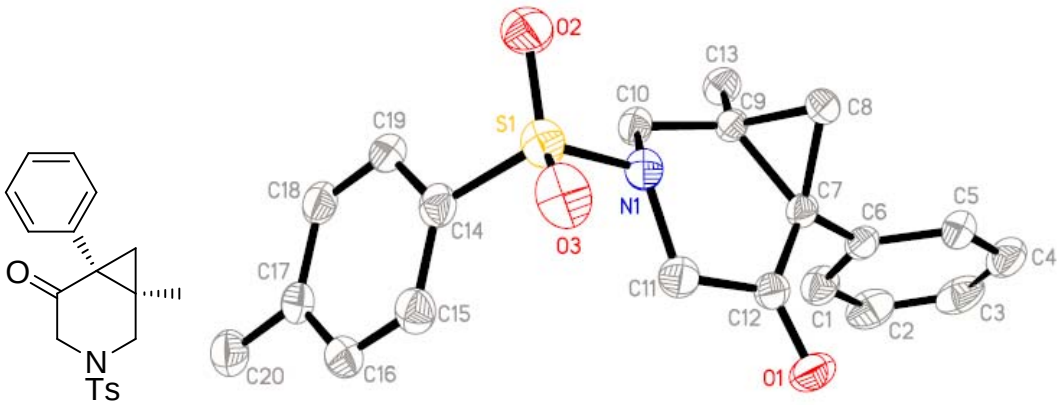


Table 1. Crystal data and structure refinement for mo_20140503D_0m.

Identification code	mo_20140503d_0m
Empirical formula	C20 H21 N O3 S
Formula weight	355.44
Temperature	298(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21/c
Unit cell dimensions	a = 10.7830(9) A alpha = 90 deg.
	b = 12.0241(10) A beta = 93.965(2) deg.
	c = 14.0523(12) A gamma = 90 deg.
Volume	1817.6(3) A^3
Z, Calculated density	4, 1.299 Mg/m^3
Absorption coefficient	0.196 mm^-1
F(000)	752
Crystal size	0.24 x 0.20 x 0.15 mm

Theta range for data collection	2.23 to 26.00 deg.
Limiting indices	-13<=h<=13, -12<=k<=14, -15<=l<=17
Reflections collected / unique	14373 / 3550 [R(int) = 0.0209]
Completeness to theta = 26.00	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9711 and 0.9544
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3550 / 0 / 228
Goodness-of-fit on F^2	1.085
Final R indices [I>2sigma(I)]	R1 = 0.0387, wR2 = 0.1157
R indices (all data)	R1 = 0.0483, wR2 = 0.1225
Largest diff. peak and hole	0.206 and -0.264 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mo_20140503D_0m. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
S(1)	1447(1)	1171(1)	1405(1)	55(1)
N(1)	2617(1)	1433(1)	738(1)	45(1)
O(1)	3331(1)	1249(1)	-1713(1)	62(1)
O(2)	1943(1)	1206(1)	2367(1)	72(1)
O(3)	865(1)	178(1)	1033(1)	75(1)
C(1)	5341(2)	3400(2)	-1499(1)	58(1)
C(2)	6172(2)	3835(2)	-2103(1)	72(1)

C(3)	7185(2)	3222(2)	-2330(1)	75(1)
C(4)	7364(2)	2174(2)	-1966(1)	67(1)
C(5)	6547(2)	1747(2)	-1352(1)	53(1)
C(6)	5534(2)	2353(1)	-1100(1)	43(1)
C(7)	4641(1)	1901(1)	-418(1)	39(1)
C(8)	5191(2)	1314(1)	487(1)	44(1)
C(9)	4590(1)	2412(1)	585(1)	38(1)
C(10)	3348(1)	2429(1)	1011(1)	43(1)
C(11)	2331(2)	1338(2)	-295(1)	51(1)
C(12)	3462(2)	1463(1)	-875(1)	42(1)
C(13)	5359(2)	3427(1)	848(1)	51(1)
C(14)	421(2)	2294(1)	1208(1)	49(1)
C(15)	-469(2)	2262(2)	447(1)	54(1)
C(16)	-1179(2)	3195(2)	240(1)	56(1)
C(17)	-1025(2)	4166(2)	772(1)	50(1)
C(18)	-143(2)	4169(2)	1538(1)	55(1)
C(19)	584(2)	3255(2)	1760(1)	54(1)
C(20)	-1786(2)	5177(2)	511(2)	66(1)

Table 3. Bond lengths [A] and angles [deg] for mo_20140503D_0m.

S(1)-O(2)	1.4203(15)
S(1)-O(3)	1.4306(15)
S(1)-N(1)	1.6534(13)
S(1)-C(14)	1.7554(17)
N(1)-C(11)	1.467(2)
N(1)-C(10)	1.471(2)

O(1)-C(12)	1.2051(19)
C(1)-C(2)	1.380(3)
C(1)-C(6)	1.388(2)
C(1)-H(1)	0.9300
C(2)-C(3)	1.373(3)
C(2)-H(2)	0.9300
C(3)-C(4)	1.369(3)
C(3)-H(3)	0.9300
C(4)-C(5)	1.375(3)
C(4)-H(4)	0.9300
C(5)-C(6)	1.380(2)
C(5)-H(5)	0.9300
C(6)-C(7)	1.506(2)
C(7)-C(12)	1.480(2)
C(7)-C(8)	1.537(2)
C(7)-C(9)	1.542(2)
C(8)-C(9)	1.481(2)
C(8)-H(8A)	0.9700
C(8)-H(8B)	0.9700
C(9)-C(10)	1.505(2)
C(9)-C(13)	1.507(2)
C(10)-H(10A)	0.9700
C(10)-H(10B)	0.9700
C(11)-C(12)	1.520(2)
C(11)-H(11A)	0.9700
C(11)-H(11B)	0.9700
C(13)-H(13A)	0.9600

C(13)-H(13B)	0.9600
C(13)-H(13C)	0.9600
C(14)-C(15)	1.386(2)
C(14)-C(19)	1.396(2)
C(15)-C(16)	1.379(3)
C(15)-H(15)	0.9300
C(16)-C(17)	1.389(3)
C(16)-H(16)	0.9300
C(17)-C(18)	1.386(2)
C(17)-C(20)	1.498(3)
C(18)-C(19)	1.374(3)
C(18)-H(18)	0.9300
C(19)-H(19)	0.9300
C(20)-H(20A)	0.9600
C(20)-H(20B)	0.9600
C(20)-H(20C)	0.9600
O(2)-S(1)-O(3)	119.96(9)
O(2)-S(1)-N(1)	106.40(8)
O(3)-S(1)-N(1)	106.50(8)
O(2)-S(1)-C(14)	108.63(9)
O(3)-S(1)-C(14)	109.16(9)
N(1)-S(1)-C(14)	105.17(7)
C(11)-N(1)-C(10)	113.16(13)
C(11)-N(1)-S(1)	115.46(11)
C(10)-N(1)-S(1)	115.05(10)
C(2)-C(1)-C(6)	120.46(19)
C(2)-C(1)-H(1)	119.8

C(6)-C(1)-H(1)	119.8
C(3)-C(2)-C(1)	120.0(2)
C(3)-C(2)-H(2)	120.0
C(1)-C(2)-H(2)	120.0
C(4)-C(3)-C(2)	120.10(18)
C(4)-C(3)-H(3)	119.9
C(2)-C(3)-H(3)	119.9
C(3)-C(4)-C(5)	119.88(19)
C(3)-C(4)-H(4)	120.1
C(5)-C(4)-H(4)	120.1
C(4)-C(5)-C(6)	121.16(19)
C(4)-C(5)-H(5)	119.4
C(6)-C(5)-H(5)	119.4
C(5)-C(6)-C(1)	118.34(16)
C(5)-C(6)-C(7)	121.68(15)
C(1)-C(6)-C(7)	119.98(14)
C(12)-C(7)-C(6)	114.87(13)
C(12)-C(7)-C(8)	117.78(13)
C(6)-C(7)-C(8)	117.71(12)
C(12)-C(7)-C(9)	117.00(12)
C(6)-C(7)-C(9)	120.11(13)
C(8)-C(7)-C(9)	57.52(9)
C(9)-C(8)-C(7)	61.40(10)
C(9)-C(8)-H(8A)	117.6
C(7)-C(8)-H(8A)	117.6
C(9)-C(8)-H(8B)	117.6
C(7)-C(8)-H(8B)	117.6

H(8A)-C(8)-H(8B)	114.7
C(8)-C(9)-C(10)	117.10(13)
C(8)-C(9)-C(13)	120.51(13)
C(10)-C(9)-C(13)	112.40(12)
C(8)-C(9)-C(7)	61.08(9)
C(10)-C(9)-C(7)	117.26(12)
C(13)-C(9)-C(7)	119.61(13)
N(1)-C(10)-C(9)	111.17(12)
N(1)-C(10)-H(10A)	109.4
C(9)-C(10)-H(10A)	109.4
N(1)-C(10)-H(10B)	109.4
C(9)-C(10)-H(10B)	109.4
H(10A)-C(10)-H(10B)	108.0
N(1)-C(11)-C(12)	113.64(13)
N(1)-C(11)-H(11A)	108.8
C(12)-C(11)-H(11A)	108.8
N(1)-C(11)-H(11B)	108.8
C(12)-C(11)-H(11B)	108.8
H(11A)-C(11)-H(11B)	107.7
O(1)-C(12)-C(7)	122.62(15)
O(1)-C(12)-C(11)	117.29(15)
C(7)-C(12)-C(11)	119.98(13)
C(9)-C(13)-H(13A)	109.5
C(9)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(9)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5

H(13B)-C(13)-H(13C)	109.5
C(15)-C(14)-C(19)	120.37(16)
C(15)-C(14)-S(1)	119.68(14)
C(19)-C(14)-S(1)	119.65(13)
C(16)-C(15)-C(14)	119.01(16)
C(16)-C(15)-H(15)	120.5
C(14)-C(15)-H(15)	120.5
C(15)-C(16)-C(17)	121.73(17)
C(15)-C(16)-H(16)	119.1
C(17)-C(16)-H(16)	119.1
C(18)-C(17)-C(16)	118.05(17)
C(18)-C(17)-C(20)	121.47(17)
C(16)-C(17)-C(20)	120.48(17)
C(19)-C(18)-C(17)	121.61(17)
C(19)-C(18)-H(18)	119.2
C(17)-C(18)-H(18)	119.2
C(18)-C(19)-C(14)	119.20(16)
C(18)-C(19)-H(19)	120.4
C(14)-C(19)-H(19)	120.4
C(17)-C(20)-H(20A)	109.5
C(17)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(17)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for mo_20140503D_0m.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
S(1)	53(1)	53(1)	61(1)	16(1)	14(1)	0(1)
N(1)	46(1)	43(1)	48(1)	3(1)	8(1)	2(1)
O(1)	67(1)	76(1)	43(1)	-14(1)	0(1)	-5(1)
O(2)	70(1)	89(1)	59(1)	30(1)	12(1)	4(1)
O(3)	71(1)	48(1)	106(1)	13(1)	17(1)	-12(1)
C(1)	74(1)	53(1)	47(1)	6(1)	12(1)	5(1)
C(2)	100(2)	68(1)	48(1)	11(1)	11(1)	-14(1)
C(3)	75(1)	111(2)	41(1)	-3(1)	17(1)	-28(1)
C(4)	57(1)	97(2)	49(1)	-12(1)	14(1)	-3(1)
C(5)	52(1)	60(1)	47(1)	-7(1)	8(1)	5(1)
C(6)	49(1)	46(1)	35(1)	-4(1)	5(1)	1(1)
C(7)	46(1)	36(1)	36(1)	-1(1)	4(1)	7(1)
C(8)	48(1)	42(1)	41(1)	3(1)	2(1)	10(1)
C(9)	44(1)	37(1)	33(1)	0(1)	4(1)	5(1)
C(10)	47(1)	39(1)	42(1)	-1(1)	8(1)	5(1)
C(11)	47(1)	55(1)	51(1)	-6(1)	2(1)	-1(1)
C(12)	51(1)	34(1)	41(1)	-2(1)	1(1)	7(1)
C(13)	54(1)	49(1)	49(1)	-6(1)	4(1)	-3(1)
C(14)	43(1)	55(1)	50(1)	3(1)	14(1)	-2(1)

C(15)	44(1)	57(1)	62(1)	-10(1)	7(1)	-7(1)
C(16)	41(1)	70(1)	55(1)	-9(1)	3(1)	0(1)
C(17)	42(1)	62(1)	48(1)	-1(1)	14(1)	3(1)
C(18)	52(1)	64(1)	52(1)	-15(1)	12(1)	4(1)
C(19)	47(1)	75(1)	41(1)	-7(1)	6(1)	3(1)
C(20)	60(1)	70(1)	68(1)	-1(1)	13(1)	14(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for mo_20140503D_0m.

	x	y	z	U(eq)
H(1)	4646	3810	-1358	69
H(2)	6047	4544	-2356	86
H(3)	7750	3519	-2732	90
H(4)	8038	1751	-2134	81
H(5)	6680	1038	-1101	63
H(8A)	4757	666	706	52
H(8B)	6089	1279	587	52
H(10A)	3474	2465	1701	51
H(10B)	2892	3087	795	51
H(11A)	1728	1904	-495	62
H(11B)	1953	619	-433	62
H(13A)	5474	3484	1530	76
H(13B)	4940	4079	598	76
H(13C)	6155	3365	585	76
H(15)	-585	1620	83	65
H(16)	-1777	3175	-269	67

H(18)	-40	4806	1910	66
H(19)	1178	3275	2272	65
H(20A)	-2394	5285	971	98
H(20B)	-2199	5078	-110	98
H(20C)	-1253	5816	507	98

Table 6. Torsion angles [deg] for mo_20140503D_0m.

O(2)-S(1)-N(1)-C(11)	174.72(12)
O(3)-S(1)-N(1)-C(11)	45.66(14)
C(14)-S(1)-N(1)-C(11)	-70.13(13)
O(2)-S(1)-N(1)-C(10)	-50.58(13)
O(3)-S(1)-N(1)-C(10)	-179.65(11)
C(14)-S(1)-N(1)-C(10)	64.56(13)
C(6)-C(1)-C(2)-C(3)	1.5(3)
C(1)-C(2)-C(3)-C(4)	0.7(3)
C(2)-C(3)-C(4)-C(5)	-1.8(3)
C(3)-C(4)-C(5)-C(6)	0.7(3)
C(4)-C(5)-C(6)-C(1)	1.4(3)
C(4)-C(5)-C(6)-C(7)	-179.25(16)
C(2)-C(1)-C(6)-C(5)	-2.5(3)
C(2)-C(1)-C(6)-C(7)	178.15(17)
C(5)-C(6)-C(7)-C(12)	-101.36(17)
C(1)-C(6)-C(7)-C(12)	77.99(19)
C(5)-C(6)-C(7)-C(8)	44.1(2)
C(1)-C(6)-C(7)-C(8)	-136.56(16)
C(5)-C(6)-C(7)-C(9)	110.72(17)

C(1)-C(6)-C(7)-C(9)	-69.9(2)
C(12)-C(7)-C(8)-C(9)	-105.84(14)
C(6)-C(7)-C(8)-C(9)	109.72(15)
C(7)-C(8)-C(9)-C(10)	107.77(15)
C(7)-C(8)-C(9)-C(13)	-109.24(15)
C(12)-C(7)-C(9)-C(8)	107.20(15)
C(6)-C(7)-C(9)-C(8)	-105.54(15)
C(12)-C(7)-C(9)-C(10)	-0.31(19)
C(6)-C(7)-C(9)-C(10)	146.95(14)
C(8)-C(7)-C(9)-C(10)	-107.51(14)
C(12)-C(7)-C(9)-C(13)	-142.12(14)
C(6)-C(7)-C(9)-C(13)	5.1(2)
C(8)-C(7)-C(9)-C(13)	110.69(16)
C(11)-N(1)-C(10)-C(9)	-61.80(16)
S(1)-N(1)-C(10)-C(9)	162.48(10)
C(8)-C(9)-C(10)-N(1)	-34.40(18)
C(13)-C(9)-C(10)-N(1)	179.72(13)
C(7)-C(9)-C(10)-N(1)	35.28(17)
C(10)-N(1)-C(11)-C(12)	50.66(18)
S(1)-N(1)-C(11)-C(12)	-173.81(11)
C(6)-C(7)-C(12)-O(1)	16.1(2)
C(8)-C(7)-C(12)-O(1)	-129.35(16)
C(9)-C(7)-C(12)-O(1)	165.04(14)
C(6)-C(7)-C(12)-C(11)	-159.96(14)
C(8)-C(7)-C(12)-C(11)	54.62(19)
C(9)-C(7)-C(12)-C(11)	-11.0(2)
N(1)-C(11)-C(12)-O(1)	170.34(14)

N(1)-C(11)-C(12)-C(7)	-13.4(2)
O(2)-S(1)-C(14)-C(15)	-159.61(13)
O(3)-S(1)-C(14)-C(15)	-27.14(16)
N(1)-S(1)-C(14)-C(15)	86.80(14)
O(2)-S(1)-C(14)-C(19)	26.58(15)
O(3)-S(1)-C(14)-C(19)	159.04(13)
N(1)-S(1)-C(14)-C(19)	-87.01(14)
C(19)-C(14)-C(15)-C(16)	0.6(2)
S(1)-C(14)-C(15)-C(16)	-173.13(13)
C(14)-C(15)-C(16)-C(17)	0.1(3)
C(15)-C(16)-C(17)-C(18)	-1.1(3)
C(15)-C(16)-C(17)-C(20)	178.24(16)
C(16)-C(17)-C(18)-C(19)	1.4(3)
C(20)-C(17)-C(18)-C(19)	-177.91(16)
C(17)-C(18)-C(19)-C(14)	-0.7(3)
C(15)-C(14)-C(19)-C(18)	-0.3(2)
S(1)-C(14)-C(19)-C(18)	173.44(13)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for mo_20140503D_0m [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)