Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Cascade cyclization reactions of alkylidenecyclopropanes for the construction of polycyclic lactams and lactones by visible light photoredox catalysis

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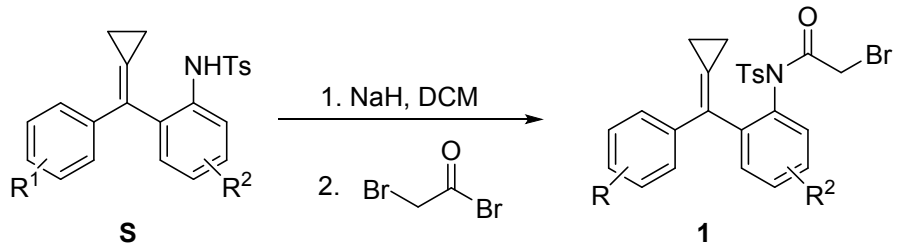
Contents

General Remarks

^{1}H NMR spectra were recorded on a Varian Mercury-300 and 400 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard; coupling constants *J* are given in Hz. ^{13}C NMR spectra were recorded on a Varian Mercury-300 and 400 spectrophotometers (75 or 100 MHz) with complete proton decoupling spectrophotometers ($CDCl_3$: 77.0 ppm). Mass and HRMS spectra were recorded by EI method. Organic solvents used were dried by standard methods when necessary. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. Commercially obtained reagents were used without further purification. All these reactions were monitored by TLC with silica gel coated plates or ^{19}F NMR. Flash column chromatography was carried out using silica gel at increased pressure. All the MCPs involved are known compounds prepared according to a general procedure in literature.[1]

General Procedure for the Preparation of 1

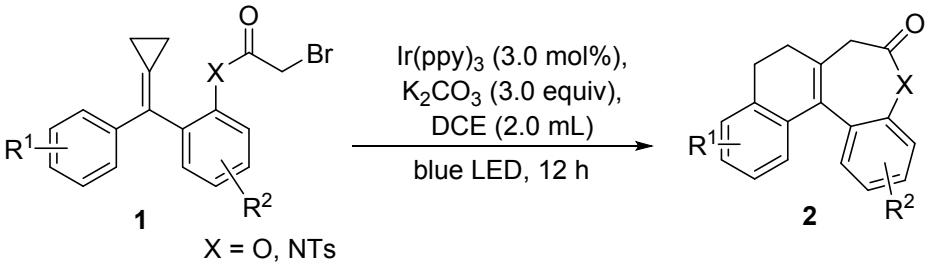


Compound **S** was prepared according to the previous literature.[1]

Compound **S** (2.0 mmol) was dissolved in 5 mL DCM and NaH (80 mg, 2.0 mmol) was added portionwise. When bubbling ceased, the reaction mixture was continued to stir for another 20 min. Afterwards, bromoacetyl bromide (0.17 mL, 2.0 mmol) dissolved in 2 mL DCM was added and the mixture was continued to stir for another 30 min. Then, the solvent was removed under reduced pressure and the residue was purified by a flash silica gel chromatography (PE:EA = 20:1).

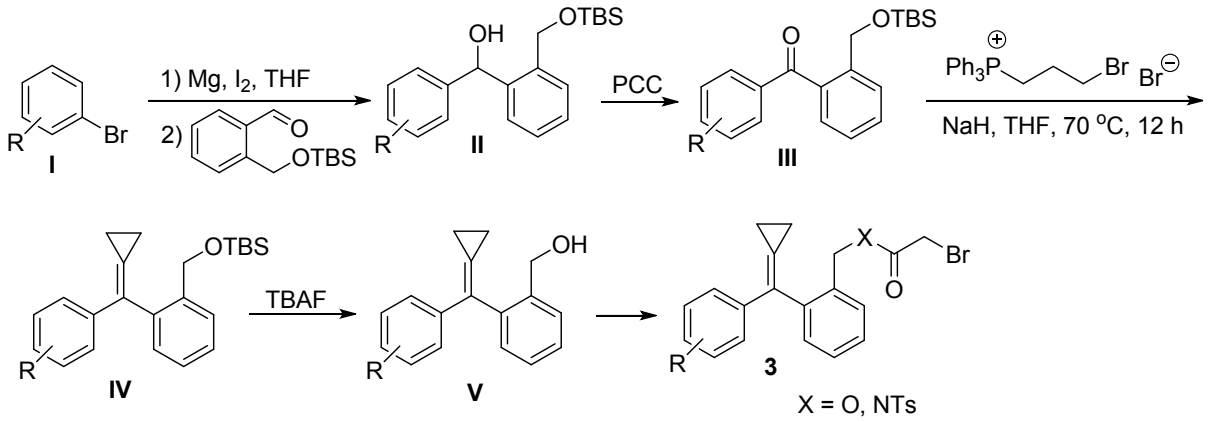
Substrate **1n** was synthesized simply by the esterification of **S** with bromoacetyl bromide in the presence of pyridine.

General Procedure for the Synthesis of 2

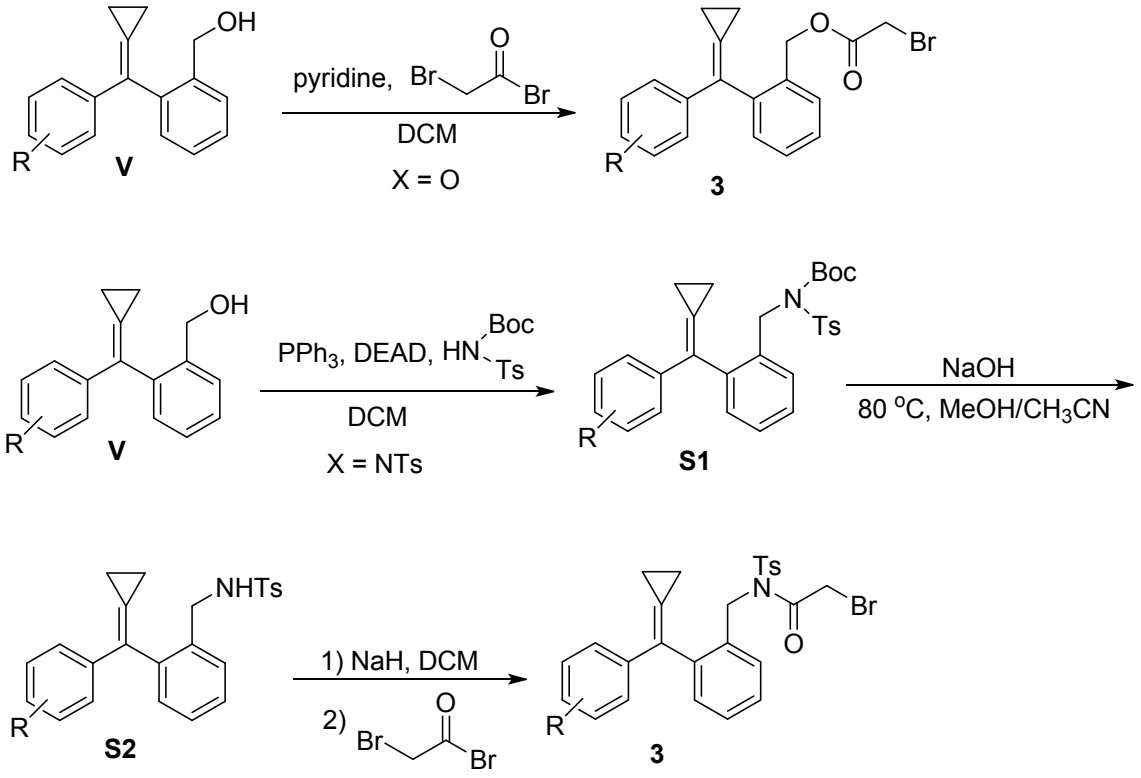


Compound **1** (0.2 mmol), $Ir(ppy)_3$ (3.9 mg, 0.006 mmol) and K_2CO_3 (82.8 mg, 0.6 mmol) were weighed into a Schlenk tube and Ar was charged. Then 2 mL DCE was injected and the mixture was stirred upon exposing to blue LED at ambient temperature for about 12 h. When it finished, the solvent was removed in vacuum and the residue was purified by a flash silica gel chromatography (PE:EA = 10:1). If necessary, the obtained product was further purified by a GPC operation (gel permeation chromatography).

General Procedure for the Preparation of 3



The preparation of **3** needs several steps. Firstly, the key intermediate **V** should be synthesized. Grignard reagent was prepared from **I** followed by a nucleophilic attack to the TBS-protected aldehyde to form compound **II**. Then, compiund **II** was oxidized by PCC to afford the corresponding aldehyde **III**, which could be easily transformed to alkylidenecyclopropane **IV** according to our previous procedure.[2] Then, TBS was removed with TBAF and the key intermediate **V** could be prepared in gram scale.

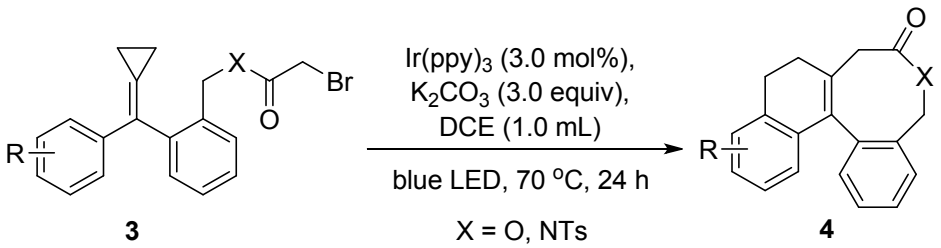


When X = O, compound **V** (2.0 mmol) was dissolved in 10 mL DCM and pyridine (0.5 mL, 5.0 mmol) was injected. Then bromoacetyl bromide (0.17 mL, 2.0 mmol) dissolved in 2 mL DCM was injected slowly and the mixture was continued to stir for about 30 min. When it finished, the solvent was removed in vacuum and the residue was purified by a flash silica gel chromatography to afford

the pure product **3** (PE:EA = 20 :1).

When X = NTs, the –OH group in compound **V** was first substituted with HN(Boc)Ts through a Mitsunobu reaction. Compound **V** (2.0 mmol), PPh_3 (3.0 mmol) and BocNHTs (3.0 mmol) were dissolved in 10 mL DCM and DEAD (3.0 mmol) was added dropwise at 0 °C. The mixture was stirred overnight to afford **S1**. Then –Boc group in **S1** was removed by NaOH (400 mg, 10.0 mmol) dissolved in 20 mL (MeOH/CH_3CN = 1:1) at 80 °C for about 6 h to afford **S2**. Compound **3** was synthesized in the same way as that of **1** from **S2**.

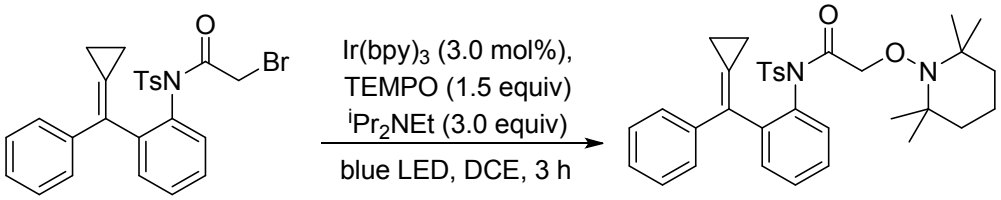
General Procedure for the Synthesis of 4



3 **4**

Compound **3** (0.2 mmol), $Ir(ppy)_3$ (3.9 mg, 0.006 mmol) and K_2CO_3 (82.8 mg, 0.6 mmol) were weighed into a Schlenk tube and Ar was charged. Then 1.0 mL DCE was injected and the mixture was stirred upon exposing to blue LED at 70 °C for about 24 h. When it finished, the solvent was removed in vacuum and the residue was purified by a flash silica gel chromatography (PE:EA = 10:1). If necessary, the obtained product was further purifies by a GPC operation (gel permeation chromatography).

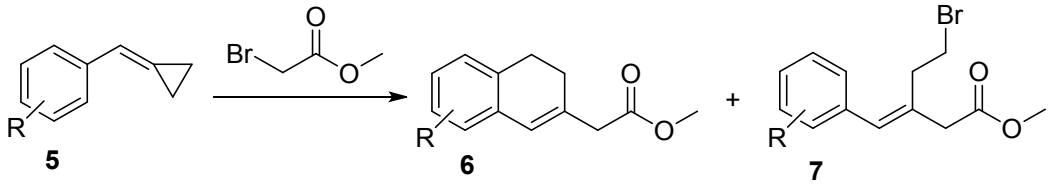
Experiment for the capture of radical intermediate with TEMPO



1a **1a-TMP** (60%)

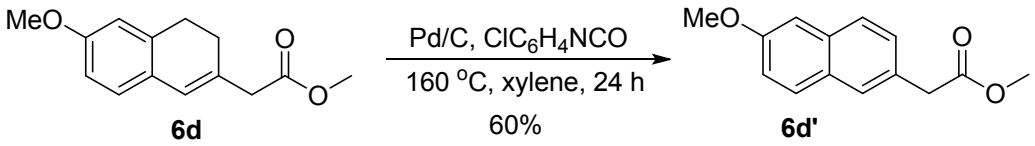
Substrate **1a** (99.2 mg, 0.2 mmol) and $Ir(ppy)_3$ (3.9 mg, 0.006 mmol) were weighed into a Schlenk tube and Ar was charged. Then $^iPr_2NEt$ (77.5 mg, 0.6 mmol) and 2 mL DCE were injected, and the mixture was stirred upon exposing to blue LED at ambient temperature for 3 h. When it finished, the solvent was removed in vacuum and the residue was purified by a flash silica gel chromatography (PE:EA = 10:1) to afford **1a-TMP** as a White solid (68.7 mg, 60%).

Procedure for the intermolecular reaction



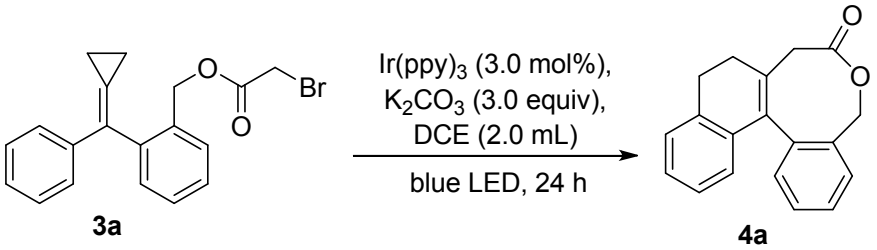
Substrate **5** (0.2 mmol), $Ir(ppy)_3$ (3.9 mg, 0.006 mmol) and K_2CO_3 (82.8 mg, 0.6 mmol) were weighed into a Schlenk tube and Ar was charged. Afterwards, 0.5 mL DCE was injected. Then exposing to blue LED, methyl bromoacetate (MBA) (30.5 mg, 0.2 mmol) dissolved in 4 mL DCE was added dropwise through a syringe pump within 4 h. The reaction finished when MBA was all added. Then 1,3,5-trimethoxybenzene (33.6 mg, 0.2 mmol) was added and the solvent was removed in vacuum. 0.5 mL $CDCl_3$ was added and the yield and ratio of **6** and **7** were determined by ^1H NMR spectroscopic data. Afterwards, product **6** was purified by a flash silica gel chromatography (PE:EA = 10:1) and was further purified by a GPC operation (gel permeation chromatography).

Procedure for the dehydrogenation of 6d



Product **6d** (23.2 mg, 0.1 mmol), Pd/C (30.0 mg, 0.03 mmol) and *para*-ClC_6H_4NCO (46.0 mg, 0.3 mmol) were placed in a pressure tube and 2 mL xylene was injected. The mixture was stirred at 160 ^oC for 24 h. When it finished, the mixture was cooled to room temperature and filtered. The filtrate was concentrated under reduce pressure and the residue was purified by a flash silica gel chromatography (PE:EA = 20:1) to afford **6d'** as a colorless oil in a yield of 60%.

Condition optimization of 4



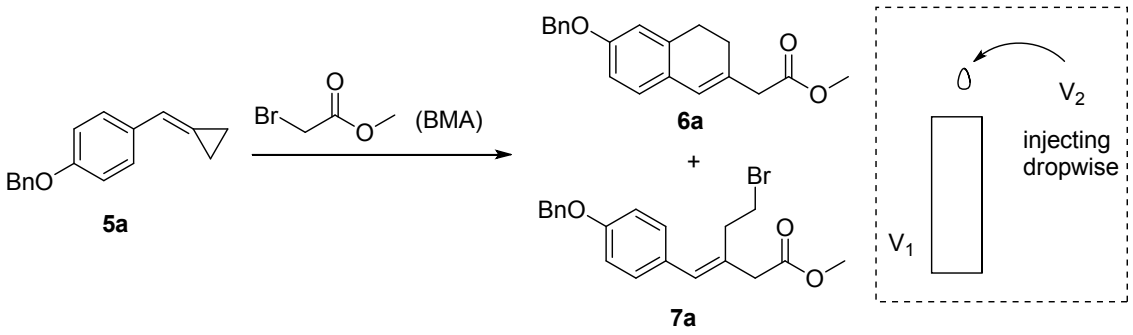
3a **4a**

entry[a]	T/°C	t/h	yield/%[b]	SMR/%[c]
1	40	24	5	38
2	60	24	18	24
3	70	24	25	14
4	80	24	18	7
5[d]	70	24	30	-
6[e]	70	24	35	-
7[f]	70	24	18	15

[a]Reaction conditions:**3a** (0.2 mmol), $Ir(ppy)_3$ (3 mol%) and K_2CO_3 (3.0 equiv) were weighed in a reaction tube and Ar was charged. Then the mixture was stirred at T (°C) upon exposing to blue LED for 24 h. [b]Isolated yield. [c]SMR = starting material recovery. [d]0.5 mL DCE. [e]1.0 mL DCE. [f]4.0 mL DCE.

Raising the temperature promoted the transformation of **3a** to **4a** and 70 °C was identified as the best one (entries 1-4). The volume of DCE also imposed influence on the yield of **4a** and 1.0 mL DCE was the best (entries 5-7). Thus, the highest yield of **4a** could be achieved when the reaction was conducted in 1.0 mL DCE at 70 °C.

Condition optimization for the production of 6

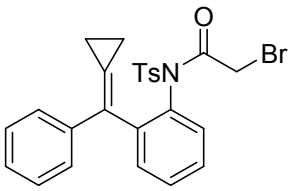


entry[a]	V_1/V_2 (mL)	injection time/h	yield/%[b] **6a**:**7a**	yield/%[b] **6a+7a**
1	0.5/2.0	4	50:17	67
2	2.0/0.5	4	50:15	65
3	**0.5/4.0**	**4**	**54(45)[c]:10**	**64**
4	0.5/4.0	8	50:10	60

[a]**5a** (0.2 mmol), $Ir(ppy)_3$ (3.9 mg, 0.006 mmol) and K_2CO_3 (82.8 mg, 0.6 mmol) were weighed into a Schlenk tube and Ar was charged. Afterwards, V_1 mL DCE was injected. Then exposing to blue LED, methyl bromoacetate (0.2 mmol) dissolved in V_2 mL DCE was added dropwise through a syringe pump within 4 h. [b]The yields were determined by ^1H NMR spectroscopy with 1,3,5-trimethoxybenzene as an internal standard. [c]Isolated yield.

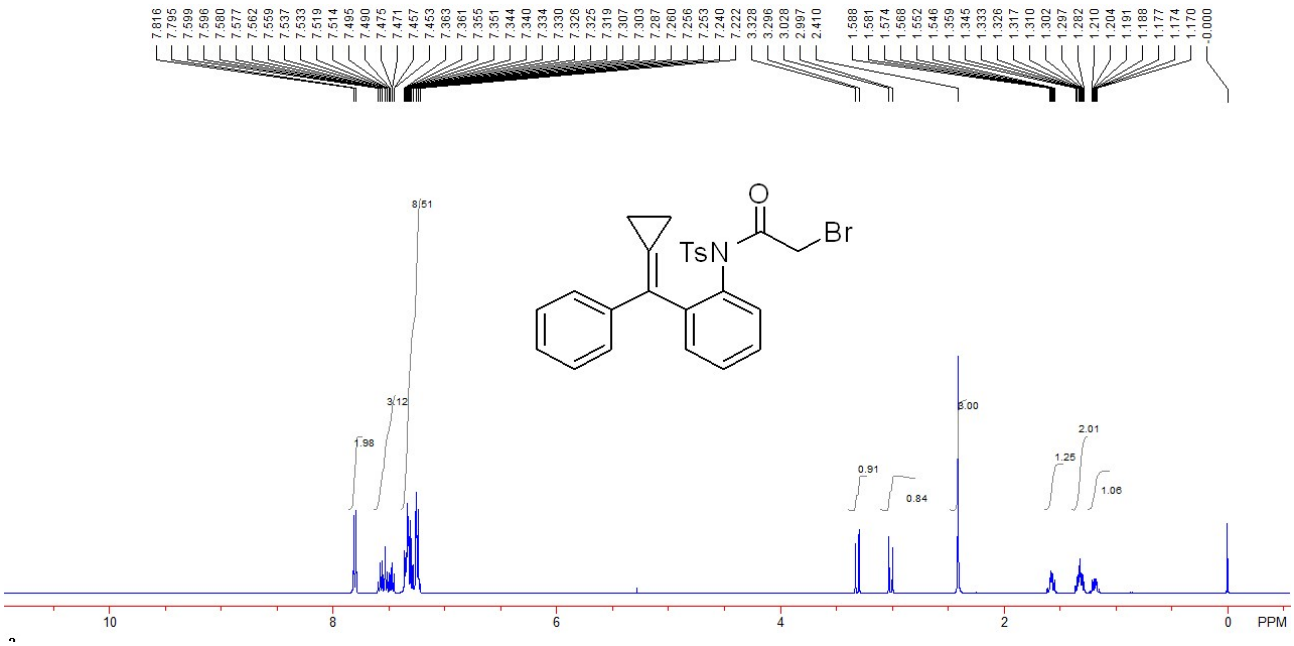
The ratio of V_1/V_2 seemed not to affect the ratio of **6a**:**7a** and the yield of **6a** + **7a** (entries 1 and 2), while the increase of V_1+V_2 could enhance the yield of **6a** from 50% to 54% and decrease the yield of **7a** from 15% to 10% (entries 2 and 3). Prolonged the reaction time could not enhance the yield of **6a** either (entries 3 and 4). Thus, the condition shown in entry 3 was the best one and **6a** could be afforded in an isolated yield of 45%.

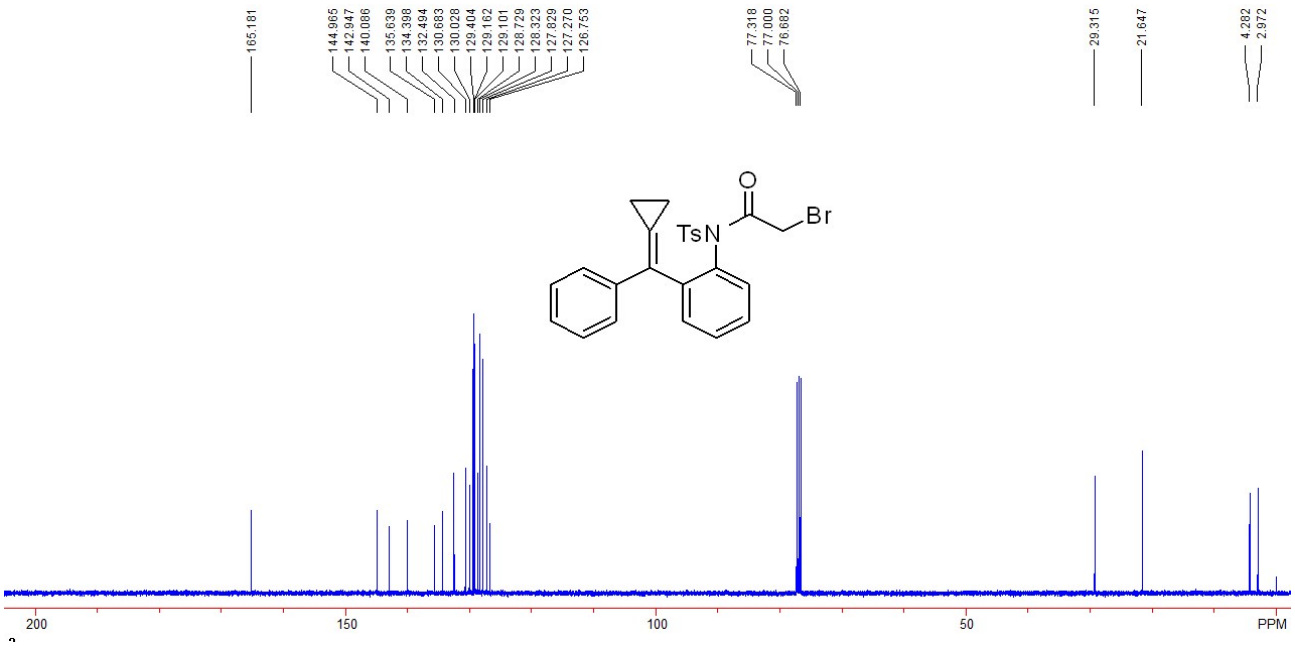
Spectroscopic Data of 1, 2, 3, 4, 6, 6d', 7a and 7i

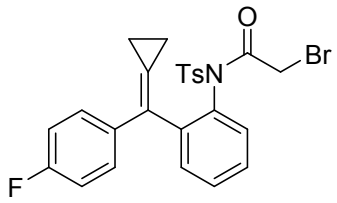


2-bromo-N-(2-(cyclopropylidene(phenyl)methyl)phenyl)-N-tosylacetamide (1a).

A white solid, 496.4 mg, 50% yield. M.p.: 172-174 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.17-1.21 (m, 1H, CH_2), 1.28-1.36 (m, 2H, CH_2), 1.55-1.59 (m, 1H, CH_2), 2.41 (s, 3H, CH_3), 3.01 (d, J = 12.4 Hz, 1H, CH_2), 3.31 (d, J = 12.4 Hz, 1H, CH_2), 7.22-7.36 (m, 8H, ArH), 7.45-7.60 (m, 3H, ArH), 7.80 (d, J = 8.4 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 3.0, 4.3, 21.6, 29.3, 126.8, 127.3, 127.8, 128.3, 128.7, 129.1, 129.2, 129.4, 130.0, 130.7, 132.5, 134.4, 135.6, 140.1, 142.9, 145.0, 165.2. IR (CH_2Cl_2) ν 2959, 2919, 2849, 1707, 1260, 1170, 1118, 1087, 1024, 800, 700 cm^{-1}. HRMS (M+H^{+}) calcd. for $C_{25}H_{23}O_3NBrS$: 496.0577, Found: 496.0573.

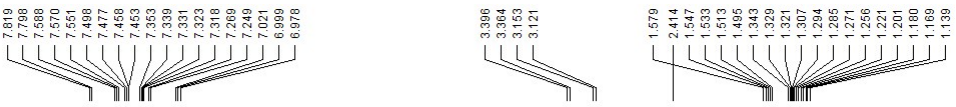






(Z)-4-(2-(benzyloxy)phenyl)-3-((trifluoromethyl)thio)but-3-en-1-yl formate (1b).

A white solid, 483.5 mg, 47% yield. M.p.: 139-141 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.14-1.22 (m, 1H, CH_2), 1.26-1.34 (m, 2H, CH_2), 1.50-1.58 (m, 1H, ArH), 2.41 (s, 3H, CH_3), 3.14 (d, J = 12.8 Hz, 1H, CH_2), 3.38 (d, J = 12.8 Hz, 1H, CH_2), 7.00 (t, J = 8.4 Hz, 2H, ArH), 7.26 (d, J = 8.0 Hz, 2H, ArH), 7.32-7.35 (m, 3H, ArH), 7.45-7.50 (m, 2H, ArH), 7.57 (t, J = 7.2 Hz, 1H, ArH), 7.81 (d, J = 8.4 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 3.1, 4.2, 21.6, 29.5, 115.1, 115.3, 125.8, 128.8, 128.9 (d, J = 1.2 Hz), 129.3 (d, J = 18.0 Hz), 129.5 (d, J = 8.1 Hz), 130.1, 130.7, 132.4, 134.4, 135.6, 136.3 (d, J = 3.5 Hz), 142.6, 145.1, 161.9 (d, J = 245.5 Hz), 165.1. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -114.64. IR (CH_2Cl_2) ν 2972, 2920, 1707, 1600, 1507, 1364, 1171, 1087, 1045, 807 cm^{-1}. HRMS ($M+H^+$) calcd. for $C_{25}H_{22}O_3NBrFS$: 514.0482, Found: 514.0479.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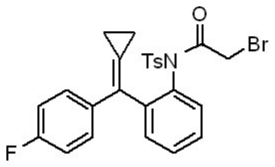
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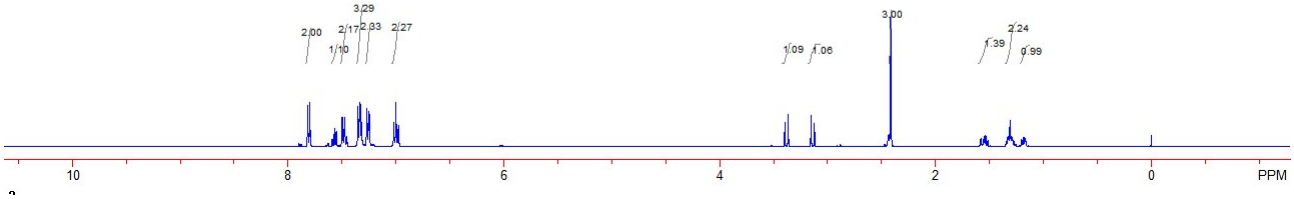
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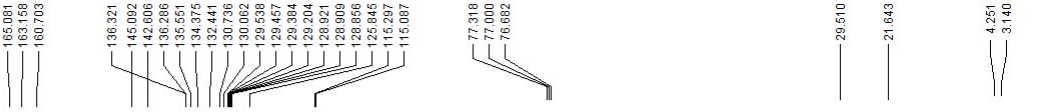
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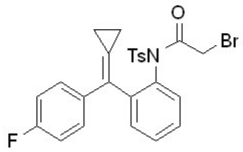
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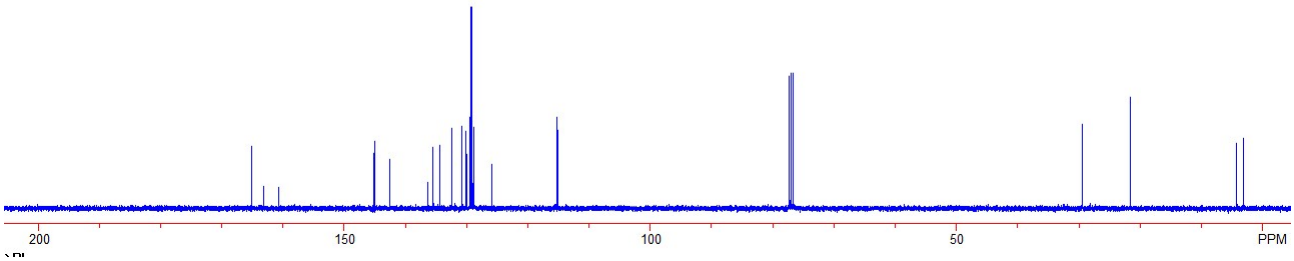
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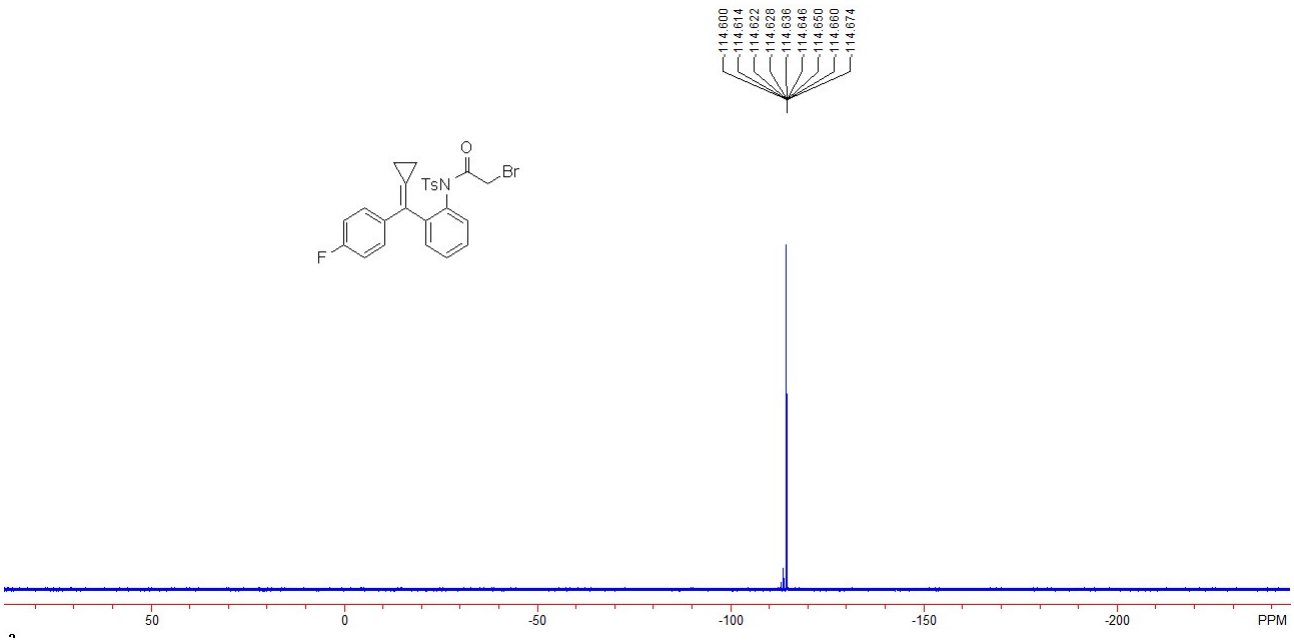
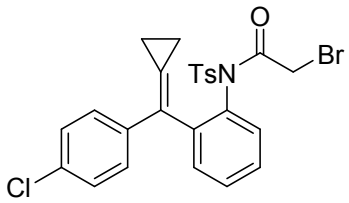
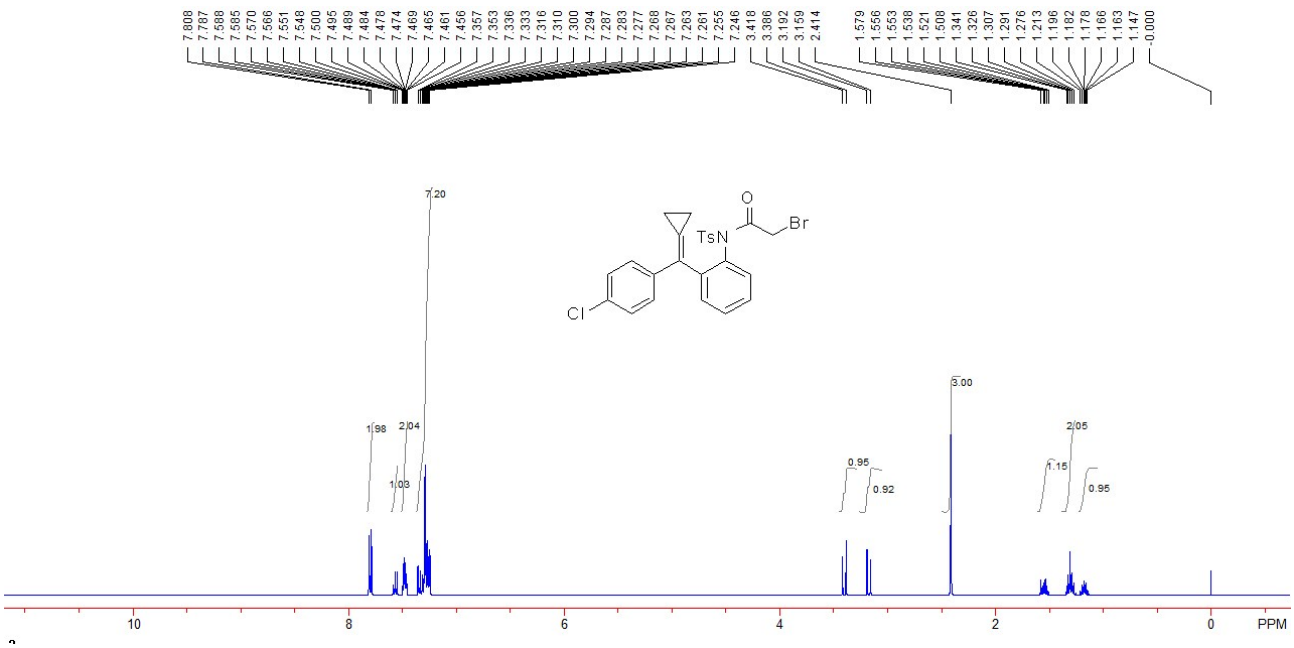
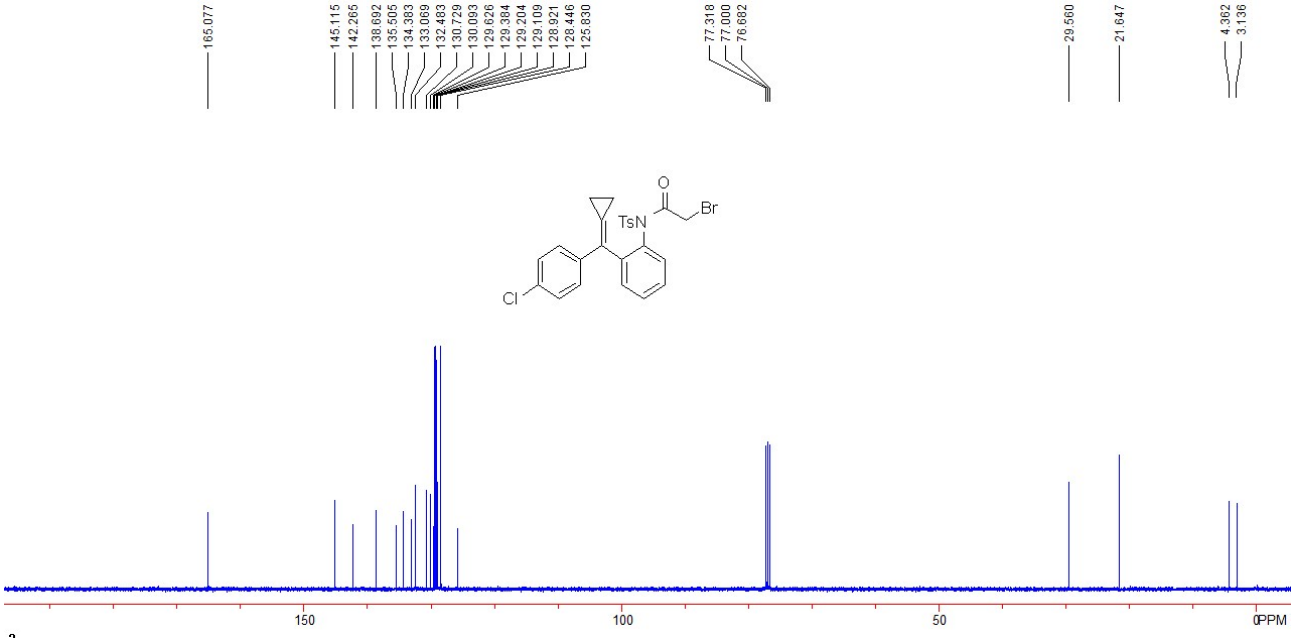


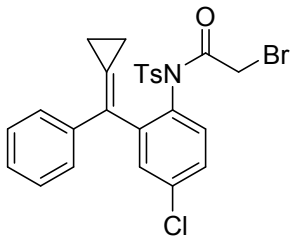


2-bromo-N-(2-((4-chlorophenyl)(cyclopropylidene)methyl)phenyl)-N-tosylacetamide (1c).

A white solid, 488.4 mg, 46% yield. M.p.: 154-156 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.15-1.21 (m, 1H, CH_2), 1.28-1.34 (m, 2H, CH_2), 1.51-1.58 (m, 1H, CH_2), 2.41 (s, 3H, CH_3), 3.18 (d, J = 12.8 Hz, 1H, CH_2), 3.40 (d, J = 12.8 Hz, 1H, CH_2), 7.25-7.36 (m, 7H, ArH), 7.46-7.50 (m, 2H, ArH), 7.57 (dt, J = 1.2 Hz, 7.6 Hz, 1H, ArH), 7.79 (d, J = 8.4 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 3.1, 4.4, 21.6, 29.6, 125.8, 128.4, 128.9, 129.1, 129.2, 129.4, 129.6, 130.1, 130.7, 132.5, 133.1, 134.4, 135.5, 138.7, 142.3, 145.1, 165.1. IR (CH_2Cl_2) ν 2959, 2917, 2855, 1701, 1485, 1362, 1258, 1170, 1088, 1043, 1019, 801, 658 cm^{-1}. HRMS ($M+H^+$) calcd. for $C_{25}H_{22}O_3NBrClS$: 530.0187, Found: 530.0185.



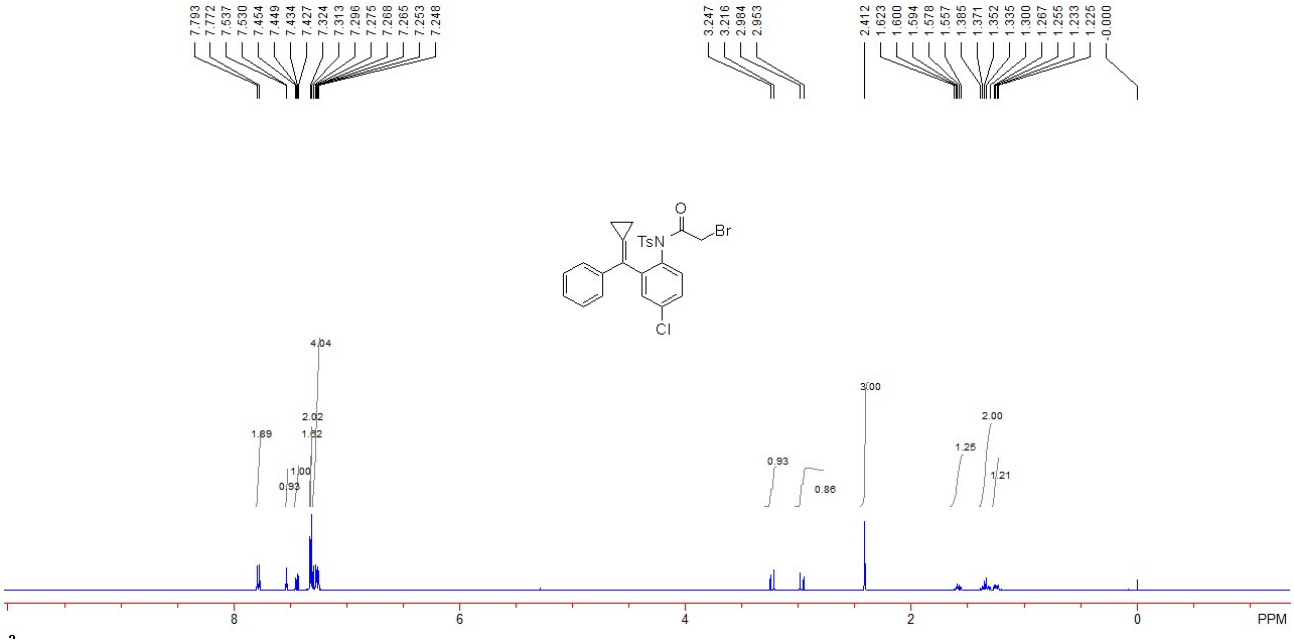


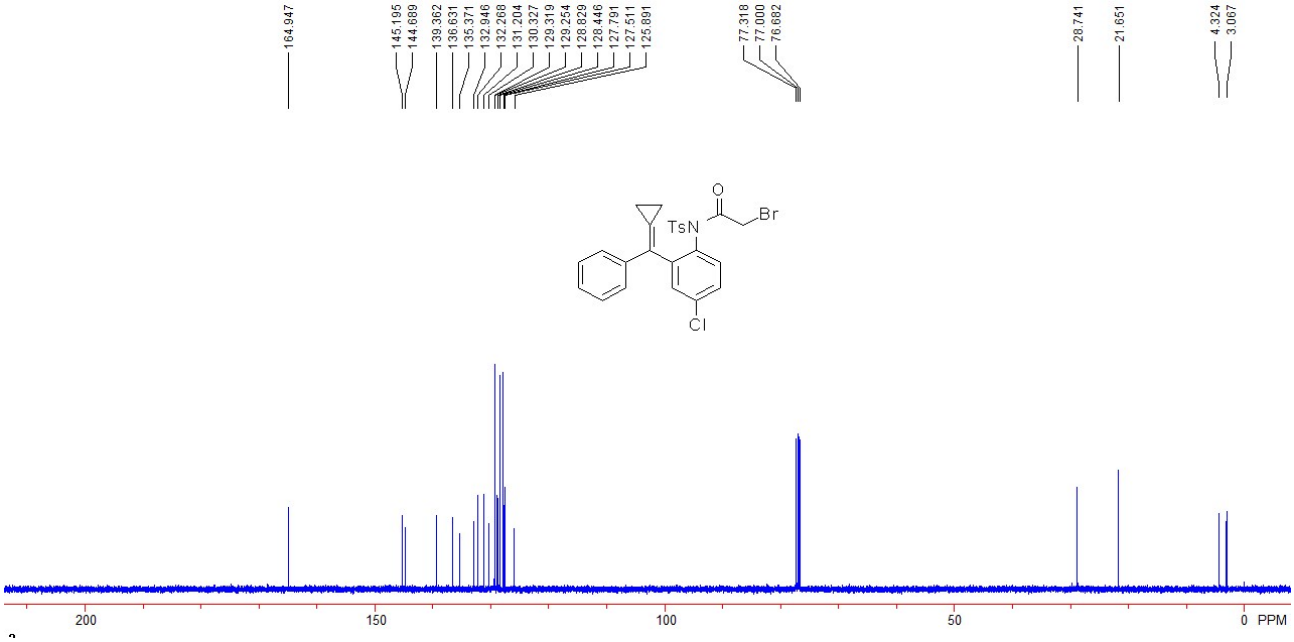


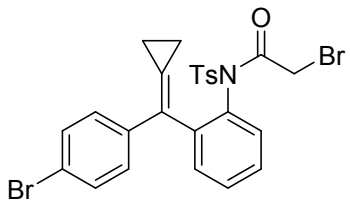
2-bromo-N-(4-chloro-2-(cyclopropylidene(phenyl)methyl)phenyl)-N-tosylacetamide (1d).

A white solid, 552.1 mg, 52% yield. M.p.: 199-201 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.23-1.27 (m, 1H, CH_2), 1.30-1.38 (m, 2H, CH_2), 1.56-1.62 (m, 1H, CH_2), 2.41 (s, 3H, CH_3), 2.97 (d, J = 12.4 Hz, 1H, CH_2), 3.23 (d, J = 12.4 Hz, 1H, CH_2), 7.25-7.30 (m, 4H, ArH), 7.31 (s, 2H, ArH), 7.32

(s, 2H, ArH), 7.44 (dd, J = 2.0 Hz, 8.0 Hz, 1H, ArH), 7.53 (d, J = 2.8 Hz, 1H, ArH), 7.78 (d, J = 8.4 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 3.1, 4.3, 21.6, 28.7, 125.9, 127.5, 127.8, 128.4, 128.8, 129.2, 129.3, 130.3, 131.2, 132.3, 132.9, 135.4, 136.6, 139.4, 144.7, 145.2, 164.9. IR (CH_2Cl_2) ν 2962, 2925, 2852, 1714, 1365, 1266, 1170, 1088, 1024, 801 cm^{-1}. HRMS ($M+H^+$) calcd. for $C_{25}H_{22}O_3NBrClS$: 530.0187, Found: 530.0183.

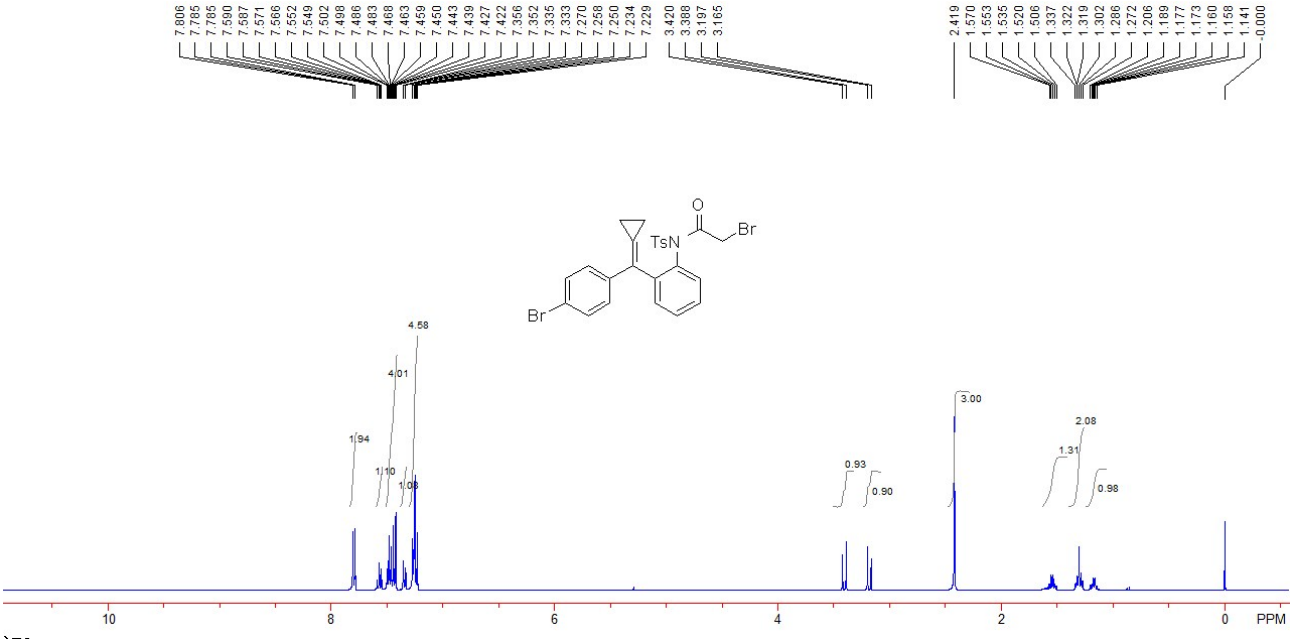


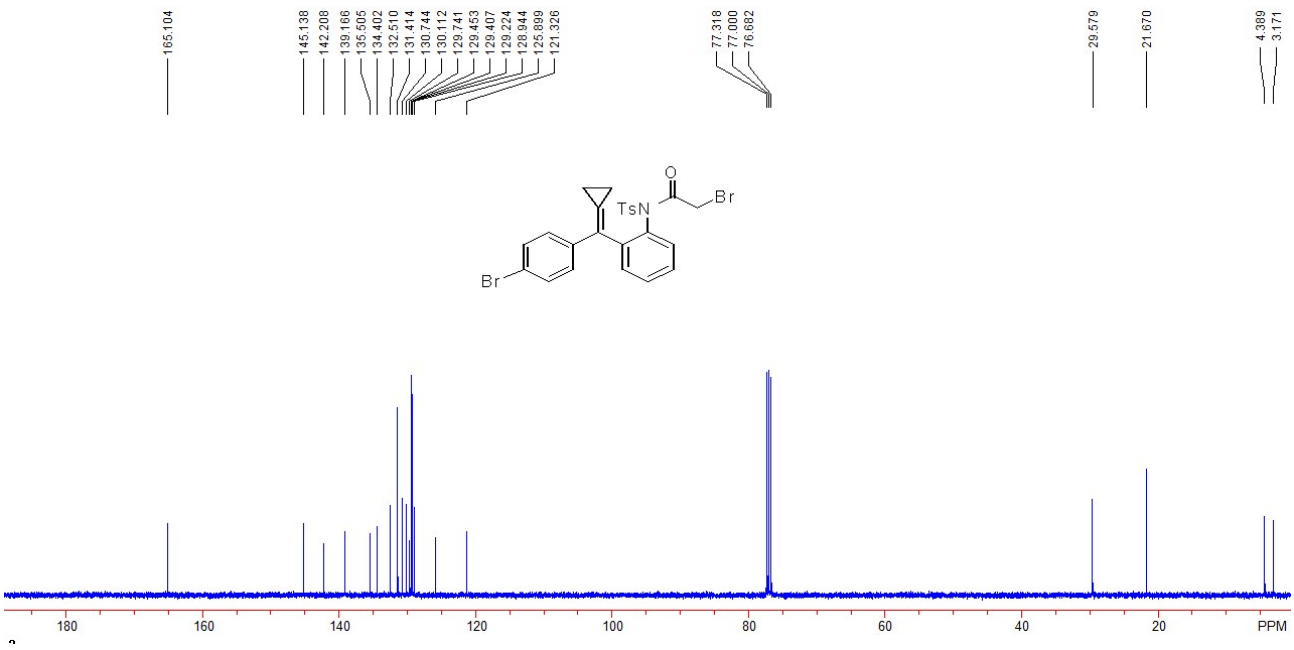


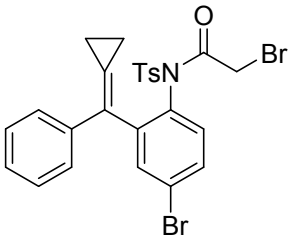


2-bromo-N-(2-((4-bromophenyl)(cyclopropylidene)methyl)phenyl)-N-tosylacetamide (1e).

A white solid, 563.8 mg, 49% yield. M.p.: 155-157 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.14-1.19 (m, 1H, CH_2), 1.27-1.34 (m, 2H, CH_2), 1.52-1.57 (m, 1H, CH_2), 2.42 (s, 3H, CH_3), 3.18 (d, J = 12.8 Hz, 1H, CH_2), 3.40 (d, J = 12.8 Hz, 1H, CH_2), 7.23-7.27 (m, 4H, ArH), 7.33-7.36 (m, 1H, ArH), 7.42-7.50 (m, 4H, ArH), 7.55-7.59 (m, 1H, ArH), 7.79 (d, J = 8.4 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 3.2, 4.4, 21.7, 29.6, 121.3, 125.9, 128.9, 129.2, 129.4, 129.7, 130.1, 130.7, 131.4, 132.5, 134.4, 135.5, 139.2, 142.2, 145.1, 165.1. IR (CH_2Cl_2) ν 2956, 1707, 1488, 1428, 1360, 1260, 1086, 1022, 800 cm^{-1}. HRMS ($M+H^+$) calcd. for $C_{25}H_{22}O_3NBr_2S$: 573.9682, Found: 573.9685.

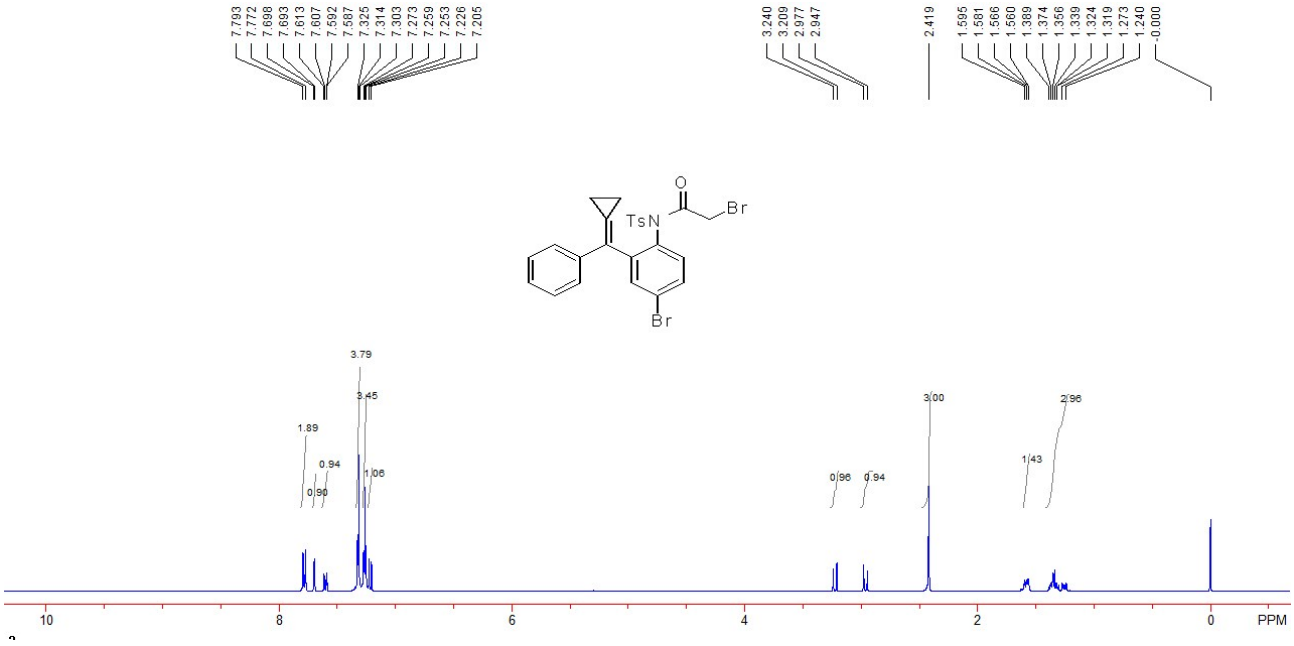


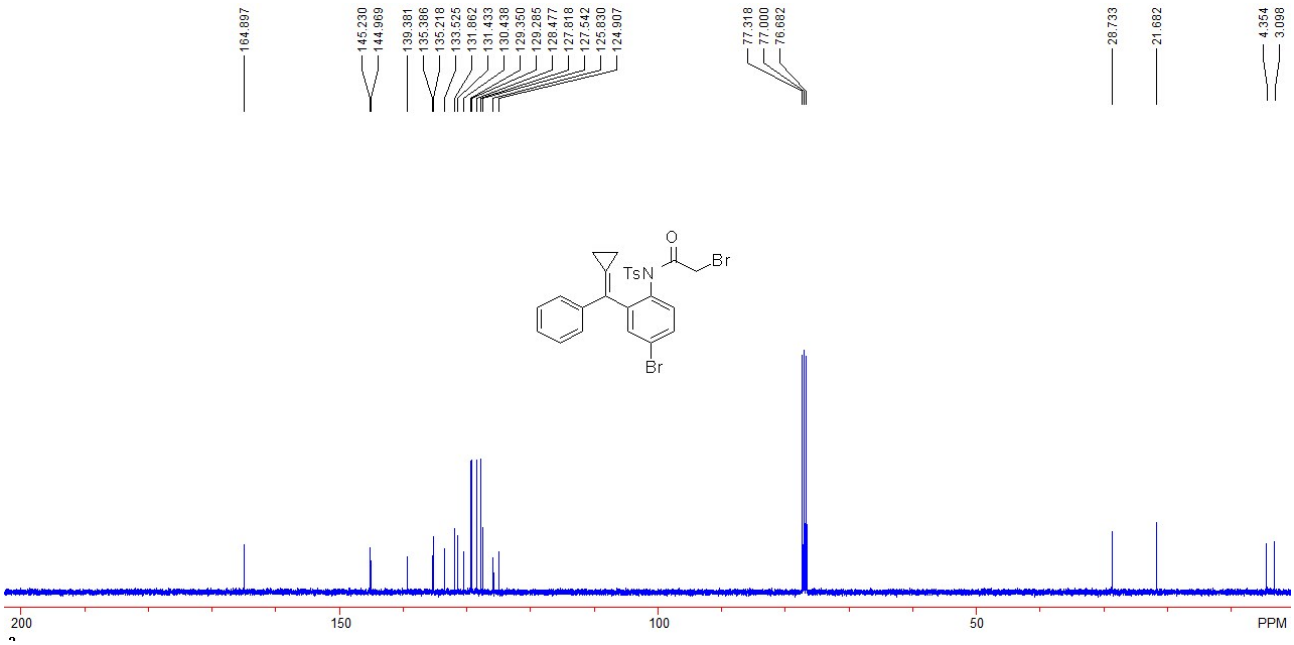


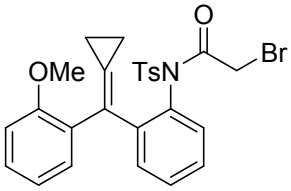


2-bromo-N-(4-bromo-2-(cyclopropylidene(phenyl)methyl)phenyl)-N-tosylacetamide (1f).

A white solid, 586.8 mg, 51% yield. M.p.: 214-216 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.24-1.39 (m, 3H, CH_2), 1.57-1.60 (m, 1H, CH_2), 2.42 (s, 3H, CH_3), 2.96 (d, J = 12.0 Hz, 1H, CH_2), 3.22 (d, J = 12.0 Hz, 1H, CH_2), 7.21 (d, J = 8.4 Hz, 1H, ArH), 7.25-7.27 (m, 3H, ArH), 7.30-7.32 (m, 4H, ArH), 7.60 (dd, J = 2.4 Hz, 8.4 Hz, 1H, ArH), 7.70 (d, J = 2.0 Hz, 1H, ArH), 7.78 (d, J = 8.4 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 3.1, 4.4, 21.7, 28.7, 124.9, 125.8, 127.5, 127.8, 128.5, 129.3, 129.4, 130.4, 131.4, 131.9, 133.5, 135.2, 135.4, 139.4, 145.0, 145.2, 164.9. IR (CH_2Cl_2) ν 2969, 1639, 1258, 1085, 1044, 874, 799, 700 cm^{-1}. HRMS ($M+H^+$) calcd. for $C_{25}H_{22}O_3NBr_2S$: 573.9682, Found: 573.9682.



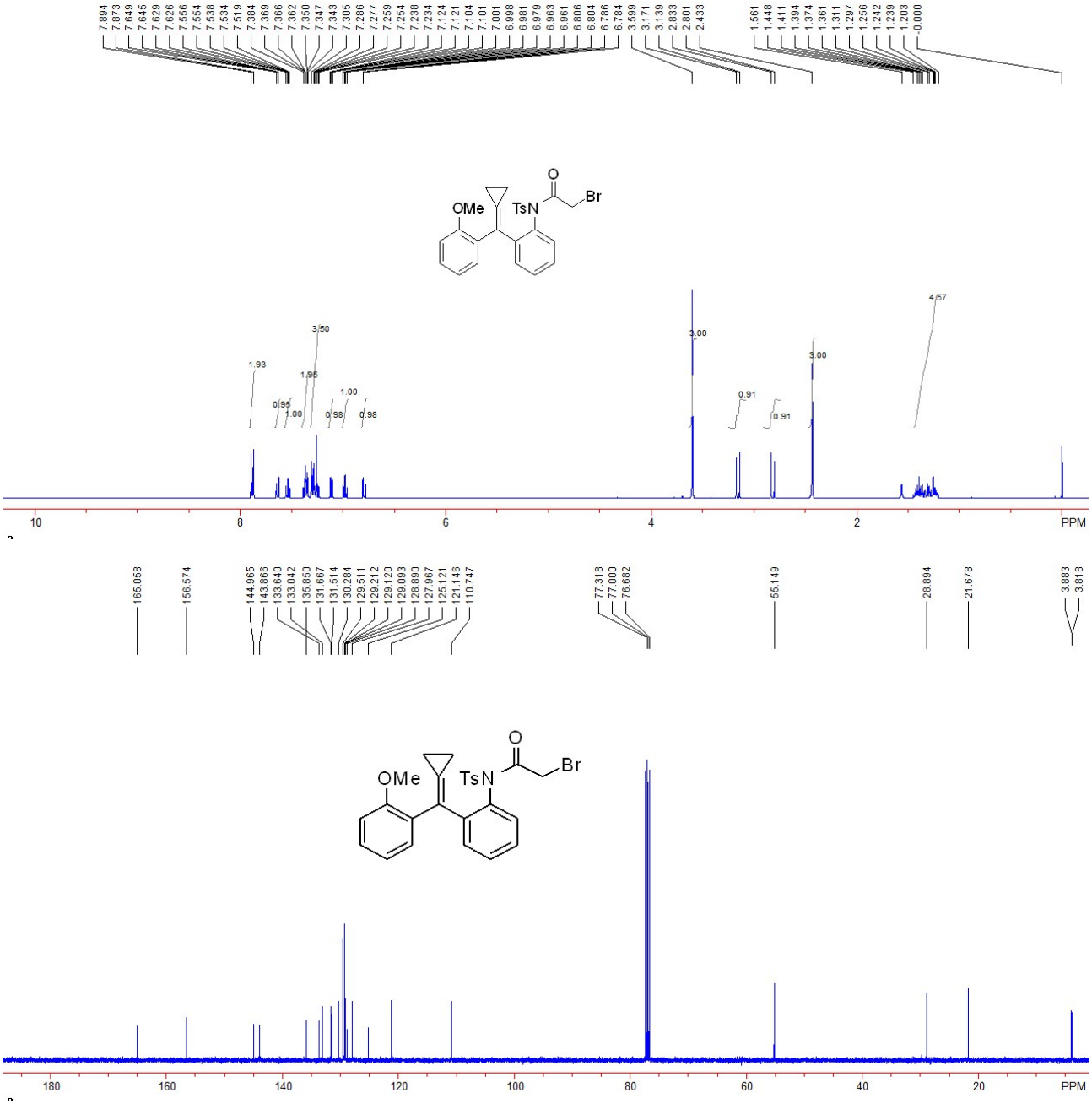


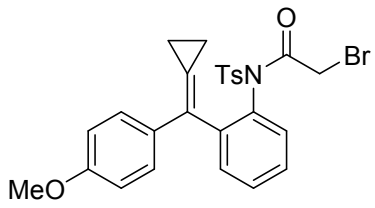


2-bromo-N-(2-(cyclopropylidene(2-methoxyphenyl)methyl)phenyl)-N-tosylacetamide (1g).

A white solid, 442.2 mg, 42% yield. M.p.: 129-131 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.20-1.45 (m, 4H, CH_2), 2.43 (s, 3H, CH_3), 2.82 (d, J = 12.8 Hz, 1H, CH_2), 3.15 (d, J = 12.8 Hz, 1H, CH_2), 3.60 (s, 3H, CH_3), 6.80 (dd, J = 0.8 Hz, 8.0 Hz, 1H, ArH), 6.98 (dt, J = 0.8 Hz, 8.0 Hz, 1H, ArH), 7.11 (dd, J = 1.2 Hz, 8.0 Hz, 1H, ArH), 7.23-7.30 (m, 3H, ArH), 7.34-7.38 (m, 2H, ArH),

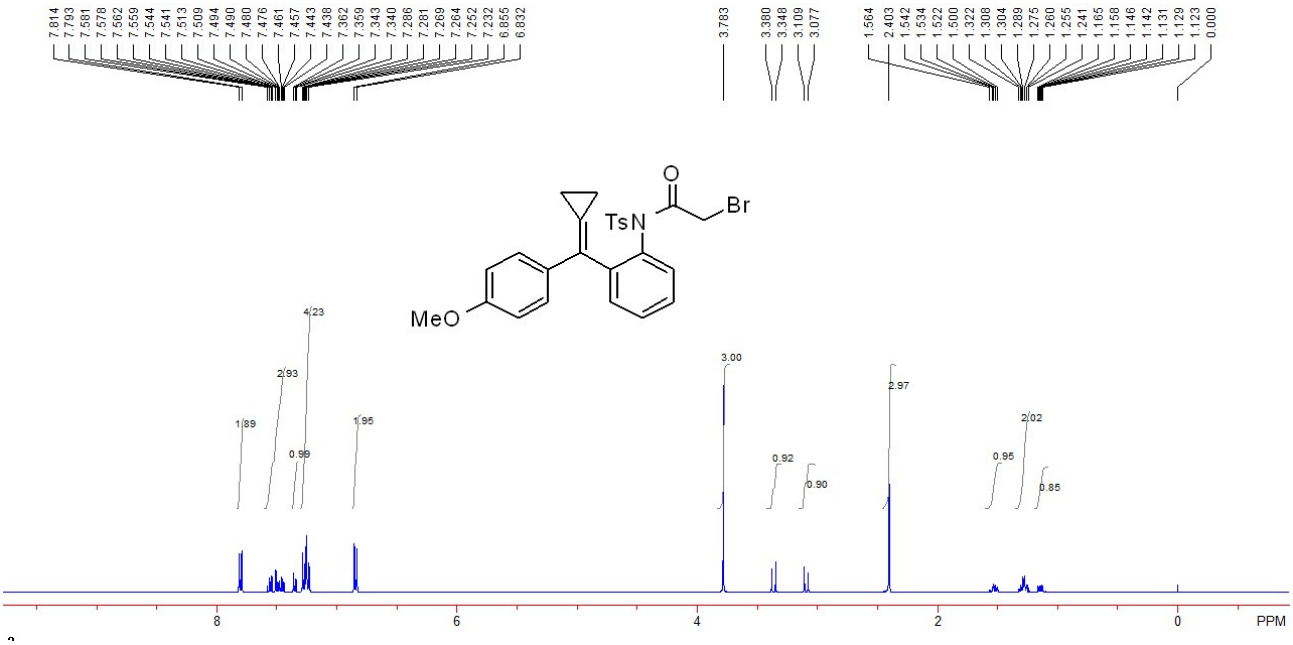
7.54 (dt, J = 1.6 Hz, 7.6 Hz, 1H, ArH), 7.63 (dd, J = 1.6 Hz, 8.0 Hz, 1H, ArH), 7.88 (d, J = 8.4 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 3.8, 3.9, 21.7, 28.9, 55.1, 110.7, 121.1, 125.1, 128.0, 128,9, 129.1, 129,12, 129.2, 129.5, 130.3, 131.5, 131,7, 133.0, 133.6, 135.8, 143.9, 145.0, 156.6, 165.0. IR (CH_2Cl_2) ν 2973, 2922, 1707, 1367, 1172, 1087, 1046, 880, 755, 665 cm^{-1}. HRMS ($M+H^+$) calcd. for $C_{26}H_{25}O_4NBrS$: 526.0682, Found: 526.0680.

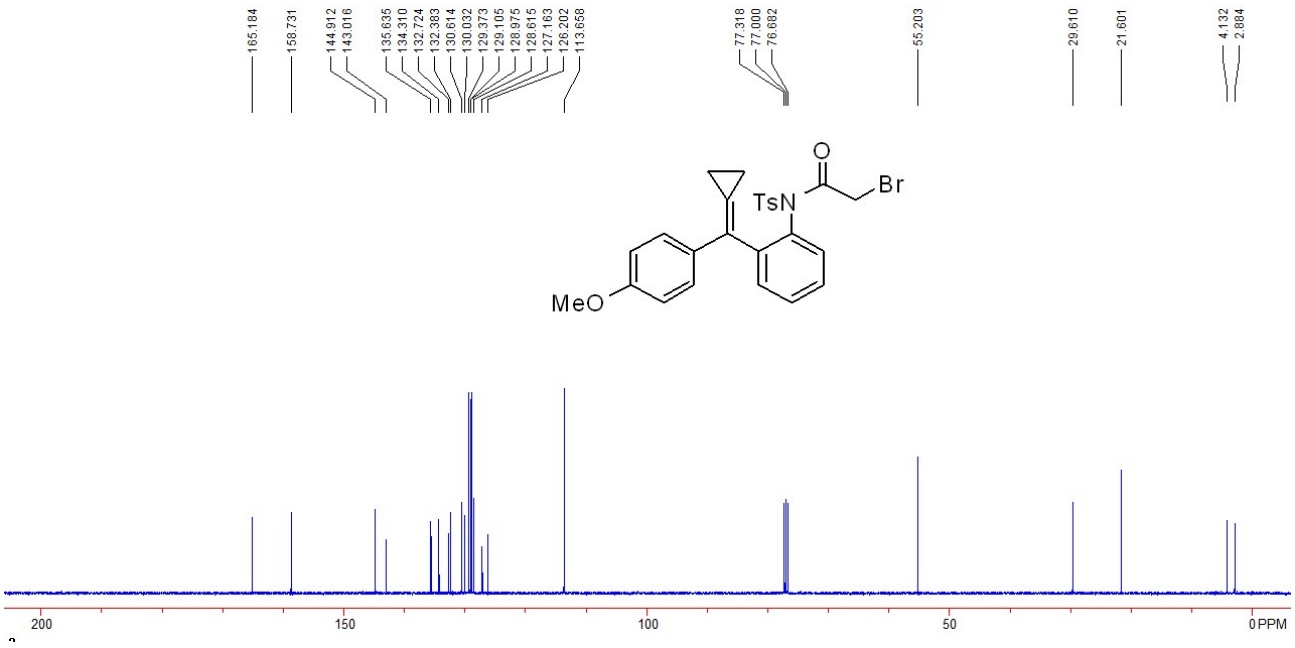


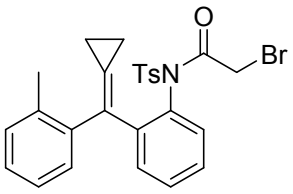


2-bromo-N-(2-(cyclopropylidene(4-methoxyphenyl)methyl)phenyl)-N-tosylacetamide (1h).

A white solid, 505.3 mg, 48% yield. M.p.: 84-86 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.12-1.16 (m, 1H, CH_2), 1.24-1.32 (m, 2H, CH_2), 1.50-1.56 (m, 1H, CH_2), 2.40 (s, 3H, CH_3), 3.09 (d, *J* = 12.8 Hz, 1H, CH_2), 3.36 (d, *J* = 12.8 Hz, 1H, CH_2), 3.78 (s, 3H, CH_3), 6.84 (d, *J* = 9.2 Hz, 2H, ArH), 7.23-7.29 (m, 4H, ArH), 7.35 (dd, *J* = 1.2 Hz, 7.6 Hz, 1H, ArH), 7.44-7.58 (m, 3H, ArH), 7.80 (d, *J* = 8.4 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 2.9, 4.1, 21.6, 29.6, 55.2, 113.6, 126.2, 127.2, 128.6, 129.0, 129.1, 129.4, 130.0, 130.6, 132.4, 132.7, 134.3, 135.6, 143.0, 144.9, 158.7, 165.2. IR (CH_2Cl_2) ν 2974, 2886, 1641, 1375, 1087, 1045, 879 cm^{-1}. HRMS (M+H^{+}) calcd. for $C_{26}H_{25}O_4NBrS$: 526.0682, Found: 526.0680.

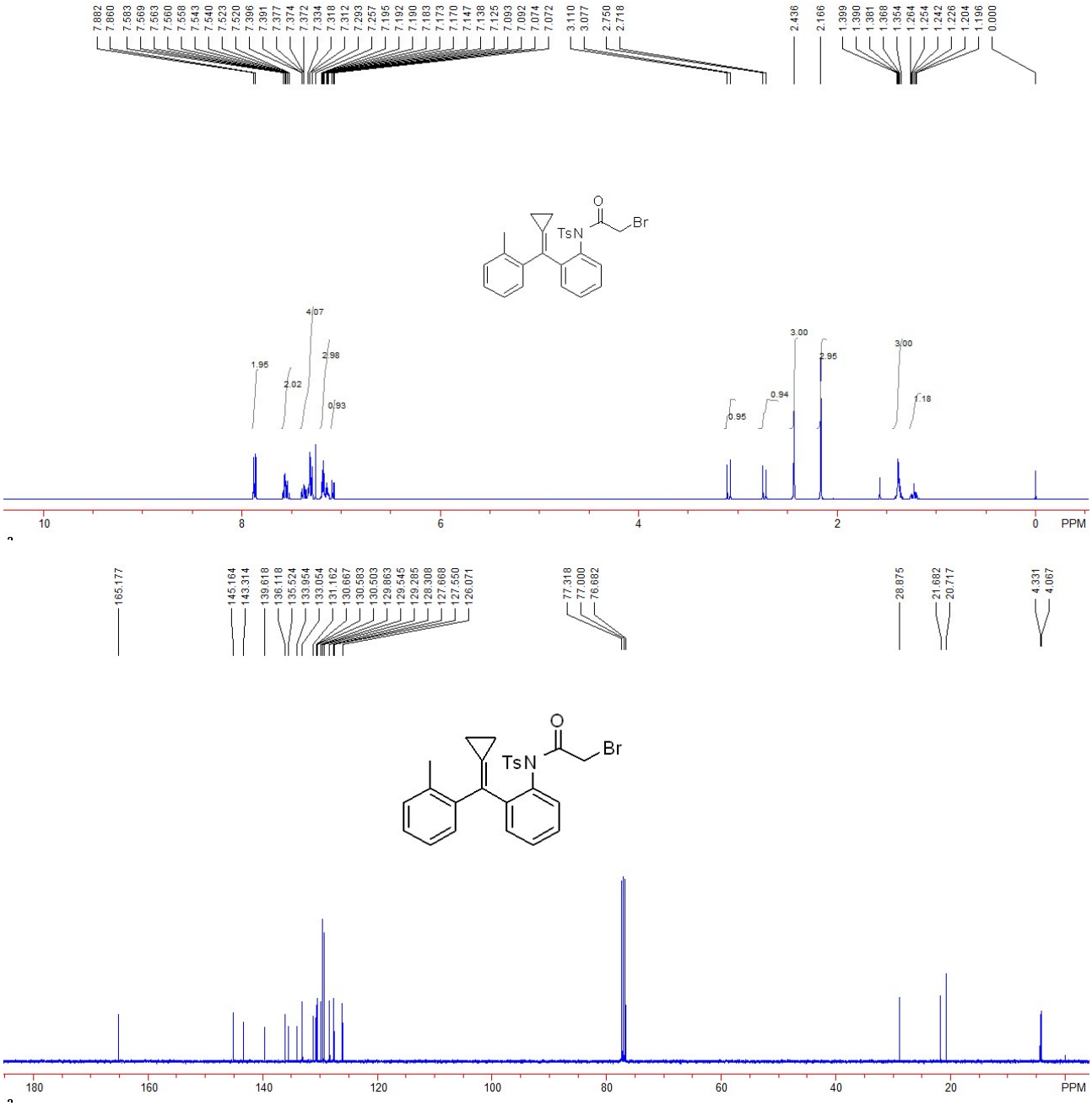






2-bromo-N-(2-(cyclopropylidene(o-tolyl)methyl)phenyl)-N-tosylacetamide (1i).

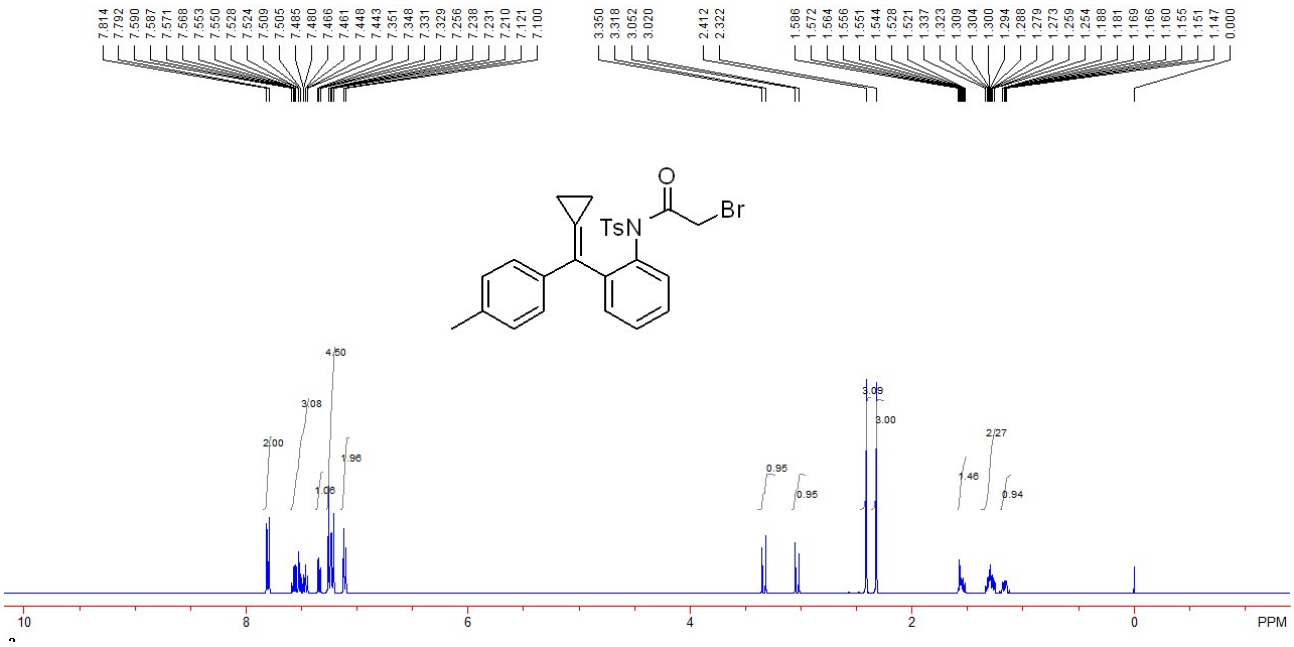
A white solid, 469.6 mg, 46% yield. M.p.: 162-164 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.20-1.26 (m, 1H, CH_2), 1.35-1.40 (m, 3H, CH_2), 2.17 (s, 3H, CH_3), 2.44 (s, 3H, CH_3), 2.73 (d, J = 12.8 Hz, 1H, CH_2), 3.09 (d, J = 12.8 Hz, 1H, CH_2), 7.08 (dd, J = 0.4 Hz, 7.6 Hz, 1H, ArH), 7.12-7.20 (m, 3H, ArH), 7.29-7.40 (m, 4H, ArH), 7.52-7.58 (m, 2H, ArH), 7.87 (d, J = 8.8 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 4.1, 4.3, 20.7, 21.7, 28.9, 126.1, 127.6, 127.7, 128.3, 129.3, 129.5, 129.9, 130.5, 130.6, 130.7, 131.2, 133.0, 134.0, 135.5, 136.1, 139.6, 143.3, 145.2, 165.2. IR (CH_2Cl_2) ν 2975, 2930, 1709, 1360, 1172, 1087, 1046, 877 cm^{-1}. HRMS (M+H^{+}) calcd. for $C_{26}H_{25}O_3NBrS$: 510.0733, Found: 510.0732.

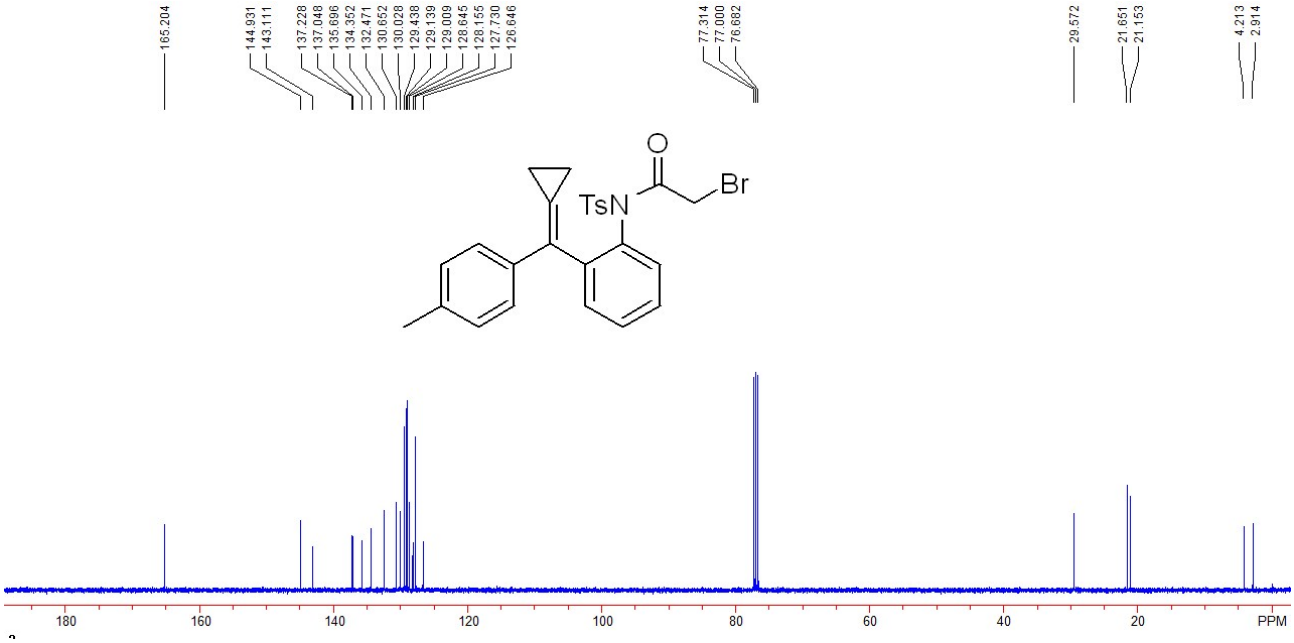


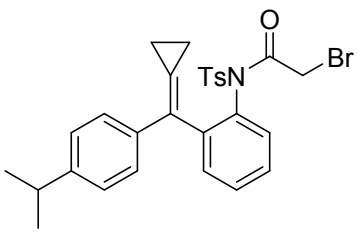
2-bromo-N-(2-(cyclopropylidene(p-tolyl)methyl)phenyl)-N-tosylacetamide (1j).

A white solid, 479.8 mg, 47% yield. M.p.: 146-148 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.15-1.19 (m, 1H, CH_2), 1.25-1.34 (m, 2H, CH_2), 1.52-1.59 (m, 1H, CH_2), 2.32 (s, 3H, CH_3), 2.41 (s, 3H, CH_3), 3.04 (d, J = 12.8 Hz, 1H, CH_2), 3.33 (d, J = 12.8 Hz, 1H, CH_2), 7.11 (d, J = 8.4 Hz, 2H, ArH), 7.21-7.26 (m, 4H, ArH), 7.34 (dd, J = 0.8 Hz, 8.0 Hz, 1H, ArH), 7.44-7.60 (m, 3H, ArH), 7.80 (d, J

= 8.8 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 2.9, 4.2, 21.2, 21.6, 29.6, 126.6, 127.7, 128.2, 128.6, 129.0, 129.1, 129.4, 130.0, 130.6, 132.5, 134.4, 135.7, 137.0, 137.2, 143.1, 144.9, 165.2. IR (CH_2Cl_2) ν 2959, 2920, 2844, 1705, 1363, 1171, 1087, 1020, 813, 660 cm^{-1}. HRMS ($M+H^+$) calcd. for $C_{26}H_{25}O_3NBrS$: 510.0733, Found: 510.0731.

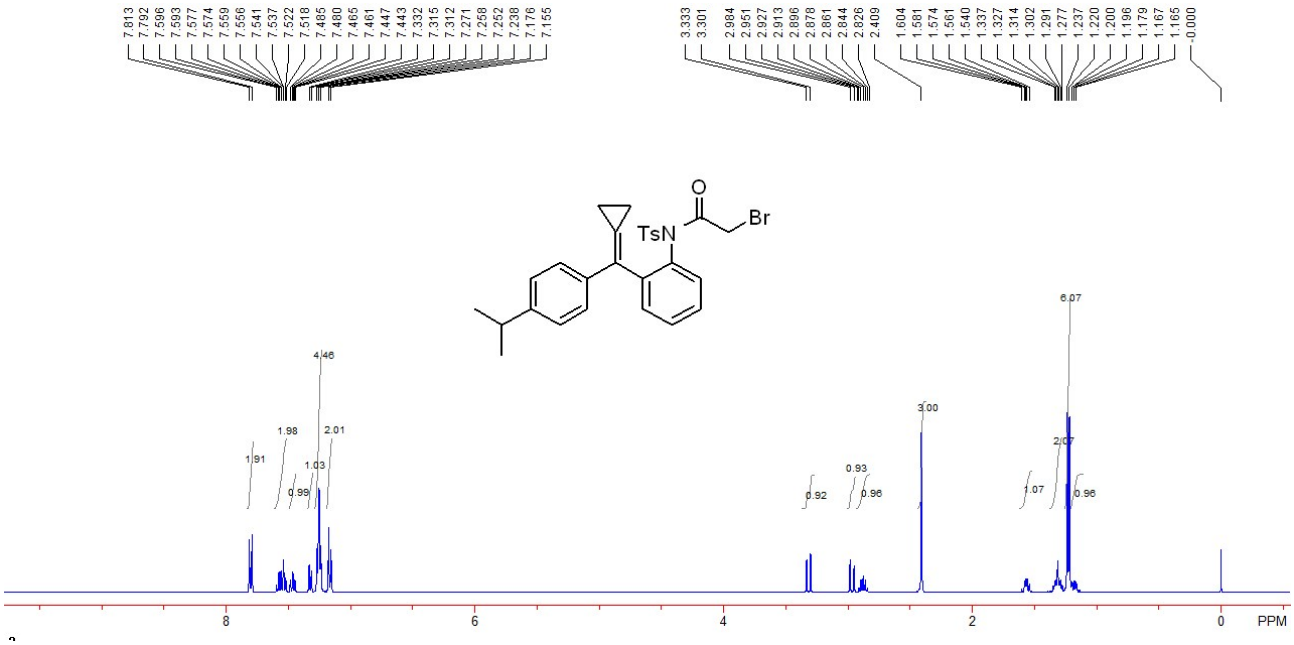


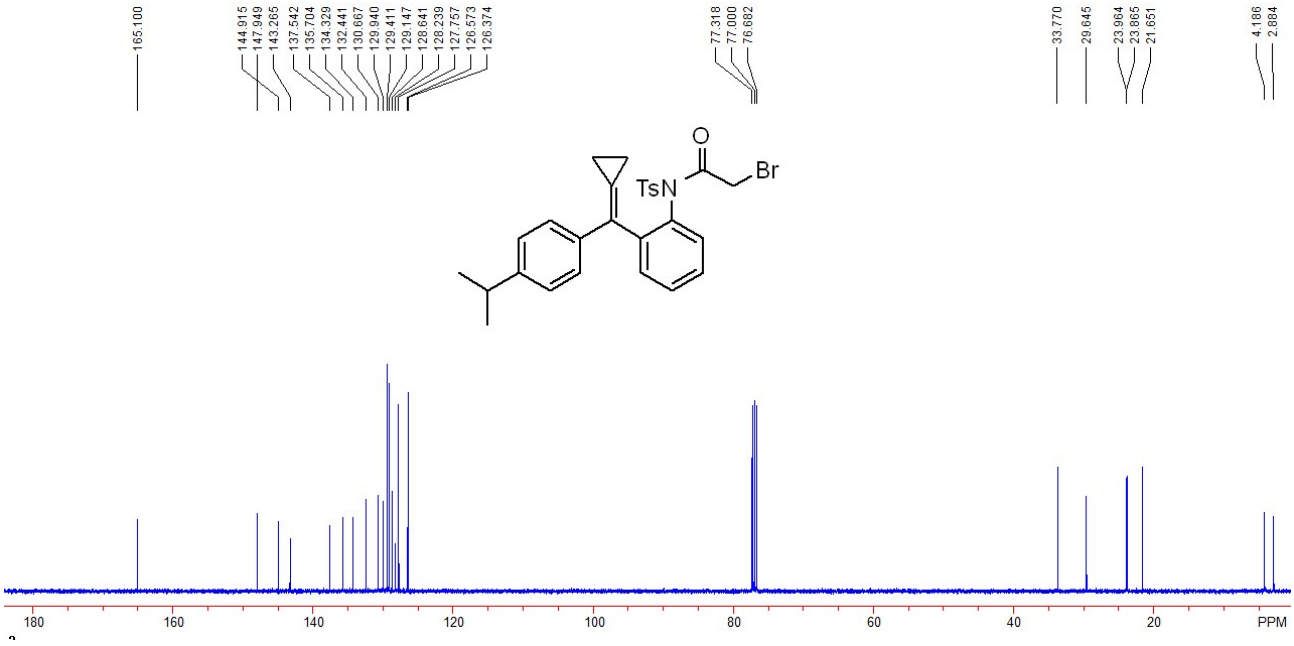


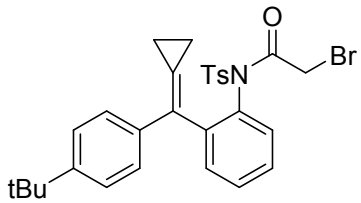


2-bromo-N-(2-(cyclopropylidene(4-isopropylphenyl)methyl)phenyl)-N-tosylacetamide (1k).

A white solid, 452.3 mg, 42% yield. M.p.: 139-141 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.16-1.20 (m, 1H, CH_2), 1.23 (d, *J* = 6.8 Hz, 6H, CH_3), 1.28-1.34 (m, 2H, CH_2), 1.54-1.60 (m, 1H, CH_2), 2.41 (s, 3H, CH_3), 2.88 (sept, *J* = 6.8 Hz, 1H, CH), 2.97 (d, *J* = 12.8 Hz, 1H, CH_2), 3.32 (d, *J* = 12.8 Hz, 1H, CH_2), 7.17 (d, *J* = 8.4 Hz, 2H, ArH), 7.24-7.27 (m, 4H, ArH), 7.32 (d, *J* = 6.8 Hz, 1H, ArH), 7.46 (dt, *J* = 1.6 Hz, 7.2 Hz, 1H, ArH), 7.52-7.60 (m, 2H, ArH), 7.80 (d, *J* = 8.4 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 2.9, 4.2, 21.6, 23.9, 24.0, 29.6, 33.8, 126.4, 126.6, 127.7, 128.2, 128.6, 129.1, 129.4, 129.9, 130.7, 132.4, 134.3, 135.7, 137.5, 143.3, 144.9, 147.9, 165.1. IR (CH_2Cl_2) ν 2956, 1707, 1365, 1255, 1171, 1086, 1044, 804 cm^{-1}. HRMS ($M+H^+$) calcd. for $C_{28}H_{29}O_3NBrS$: 538.1046, Found: 538.1044.

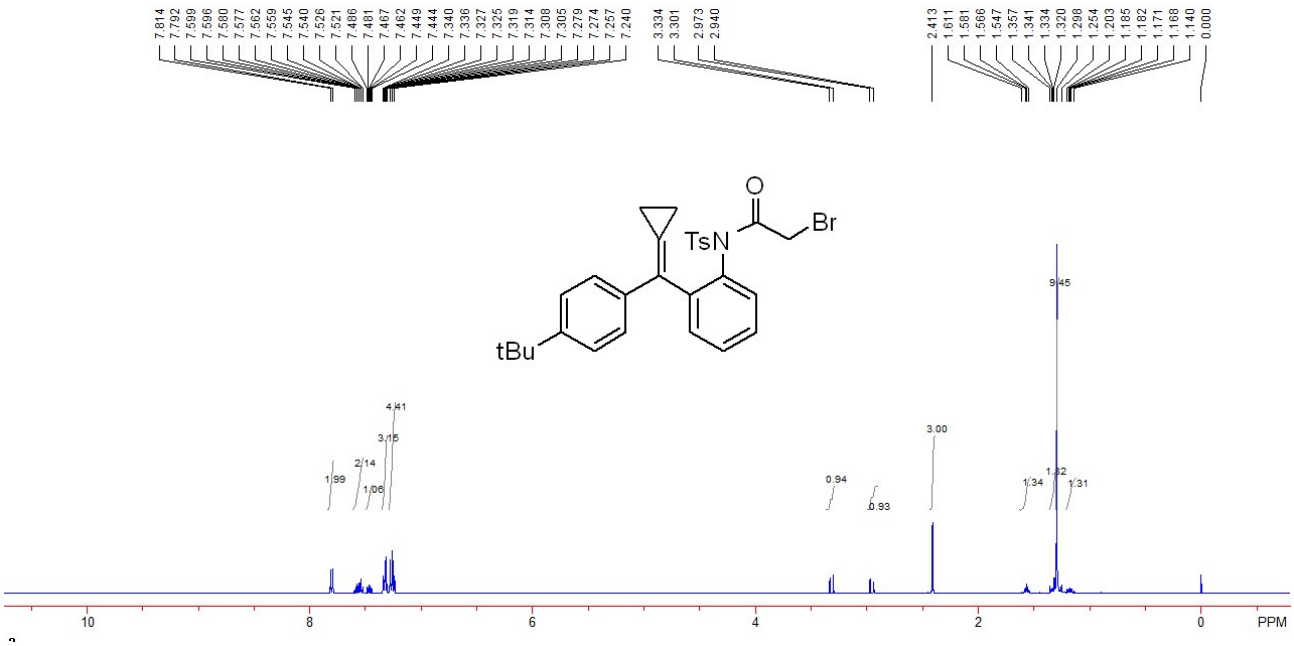


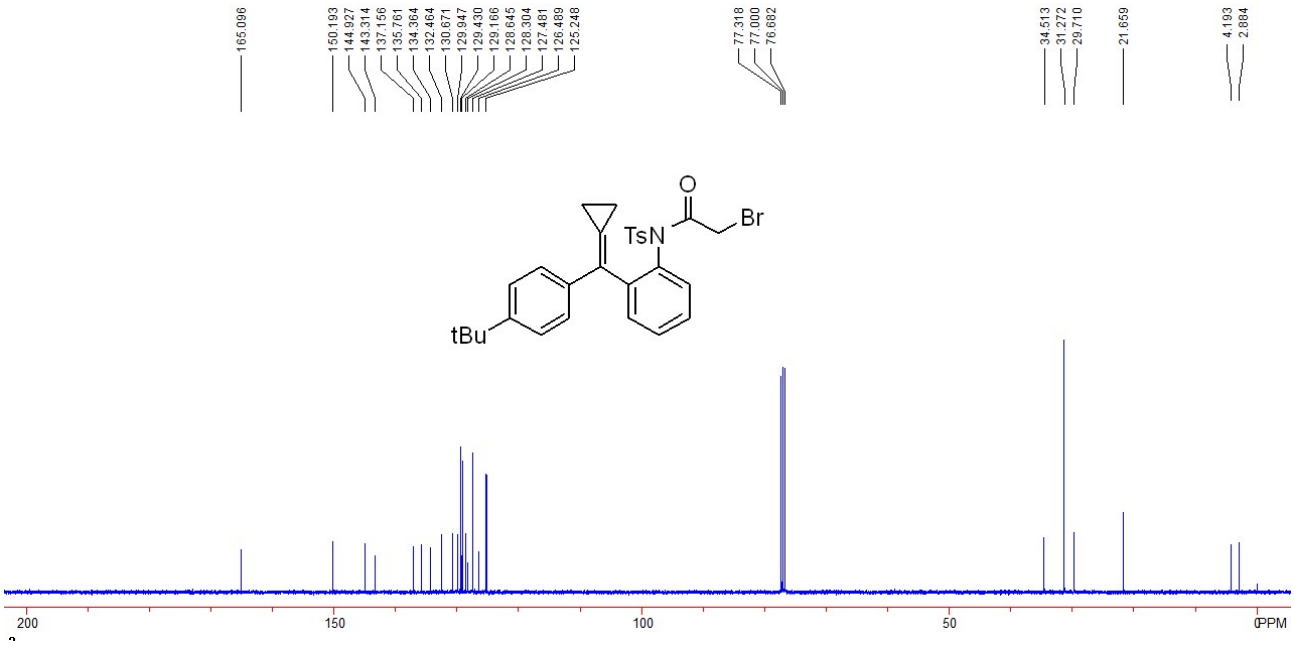


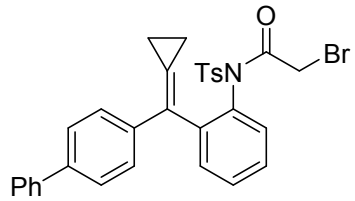


2-bromo-N-(2-((4-(tert-butyl)phenyl)(cyclopropylidene)methyl)phenyl)-N-tosylacetamide (1l).

A white solid, 475.2 mg, 43% yield. M.p.: 104-106 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.14-1.18 (m, 1H, CH_2), 1.30 (s, 9H, CH_3), 1.32-1.36 (m, 2H, CH_2), 1.55-1.61 (m, 1H, CH_2), 2.41 (s, 3H, CH_3), 2.96 (d, J = 13.2 Hz, 1H, CH_2), 3.32 (d, J = 13.2 Hz, 1H, CH_2), 7.24-7.28 (m, 4H, ArH), 7.30-7.34 (m, 3H, ArH), 7.46 (dt, J = 2.0 Hz, 7.6 Hz, 1H, ArH), 7.52-7.56 (m, 2H, ArH), 7.80 (d, J = 8.8 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 2.9, 4.2, 21.6, 29.7, 31.3, 34.5, 125.2, 126.5, 127.5, 128.3, 128.6, 129.2, 129.4, 129.9, 130.7, 132.5, 134.4, 135.8, 137.2, 143.3, 144.9, 150.2, 165.1. IR (CH_2Cl_2) ν 2964, 1712, 1600, 1482, 1364, 1258, 1172, 1087, 1018, 817 cm^{-1}. HRMS (M+H^{+}) calcd. for $C_{29}H_{31}O_3NBrS$: 552.1203, Found: 552.1200.



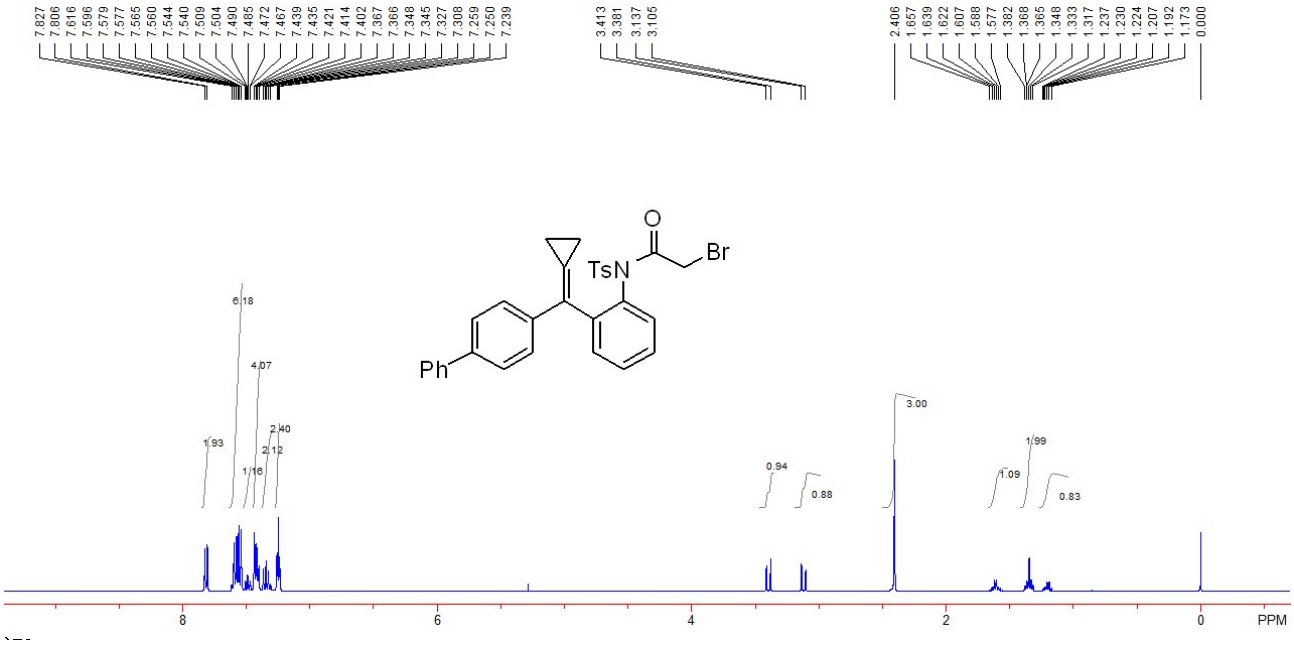


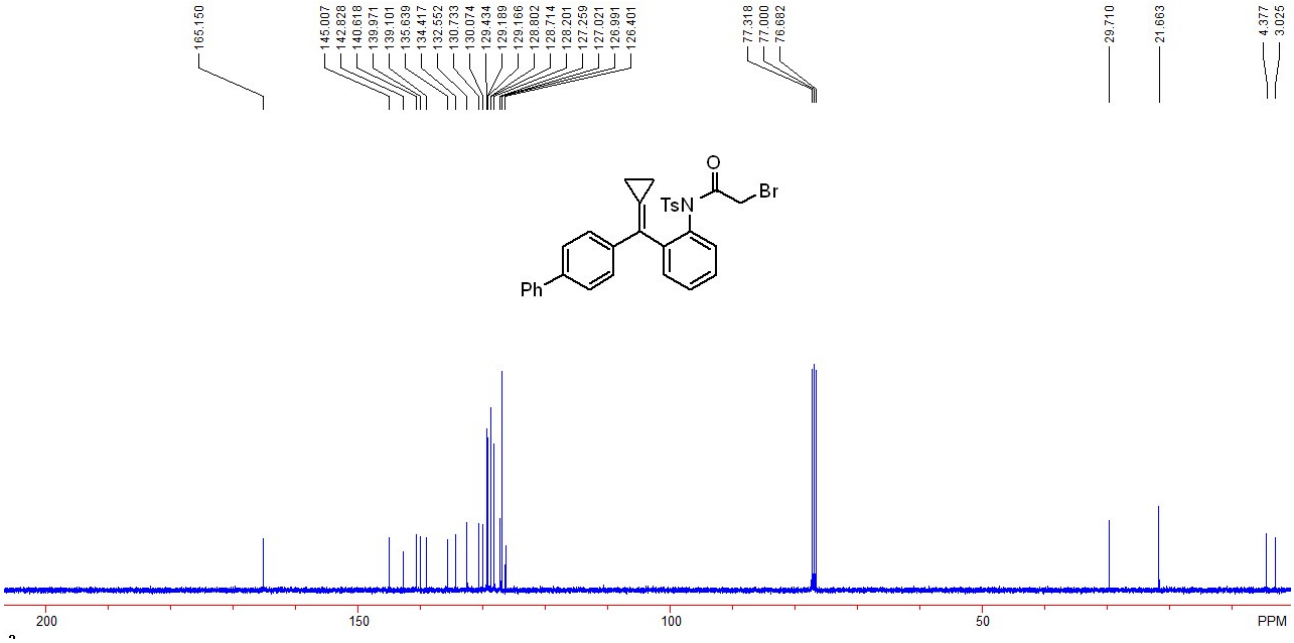


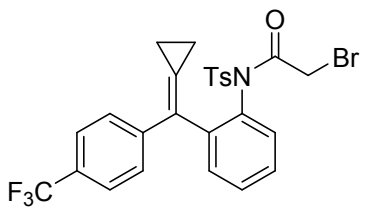
N-(2-([1,1'-biphenyl]-4-yl(cyclopropylidene)methyl)phenyl)-2-bromo-N-tosylacetamide (1m).

A white solid, 515.2 mg, 45% yield. M.p.: 99-101 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.17-1.24 (m, 1H, CH_2), 1.32-1.38 (m, 2H, CH_2), 1.58-1.66 (m, 1H, CH_2), 2.41 (s, 3H, CH_3), 3.12 (d, J = 12.8 Hz, 1H, CH_2), 3.40 (d, J = 12.8 Hz, 1H, CH_2), 7.25 (d, J = 8.0 Hz, 2H, ArH), 7.31-7.34 (m, 2H, ArH), 7.40-7.44 (m, 4H, ArH), 7.49 (dt, J = 2.0 Hz, 7.6 Hz, 1H, ArH), 7.54-7.62 (m, 6H, ArH),

7.82 (d, J = 8.4 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 3.0, 4.4, 21.7, 29.7, 126.4, 126.99, 127.02, 127.2, 128.2, 128.7, 128.8, 129.16, 129.18, 129.4, 130.1, 130.7, 132.6, 134.4, 135.6, 139.1, 140.0, 140.6, 142.8, 145.0, 165.2. IR (CH_2Cl_2) ν 2969, 2899, 1649, 1380, 1169, 1087, 1045, 880, 799 cm^{-1}. HRMS ($M+H^+$) calcd. for $C_{31}H_{27}O_3NBrS$: 572.0890, Found: 572.0886.

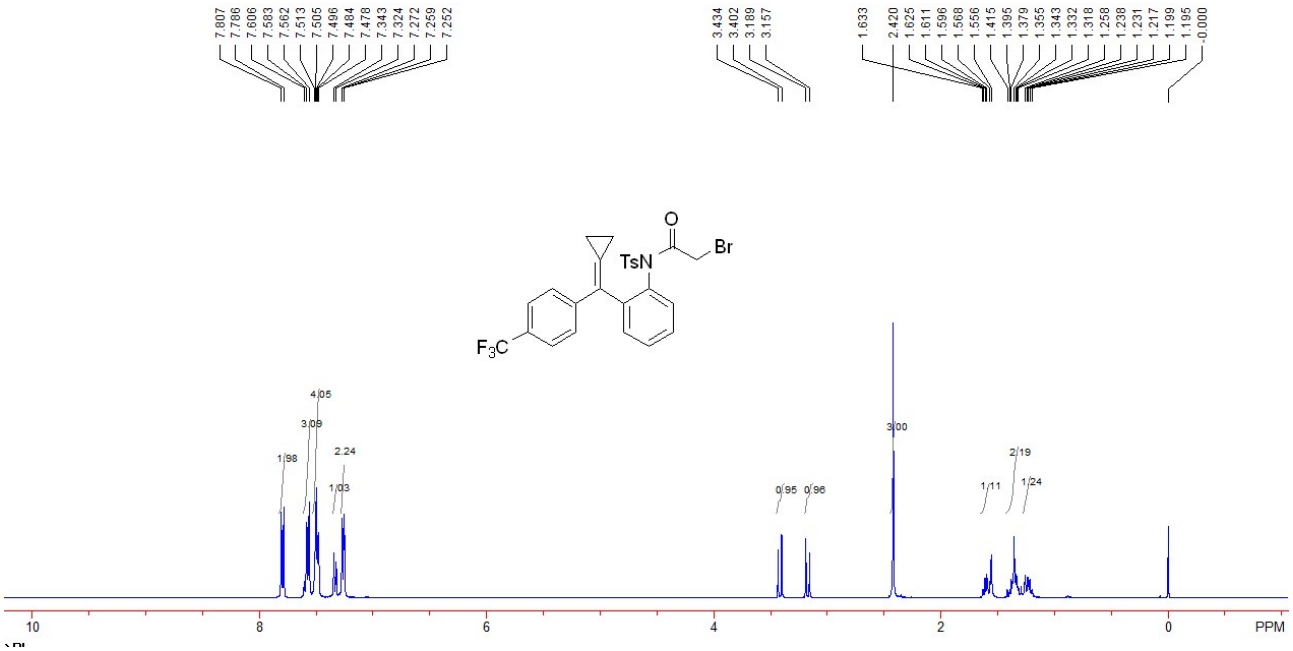


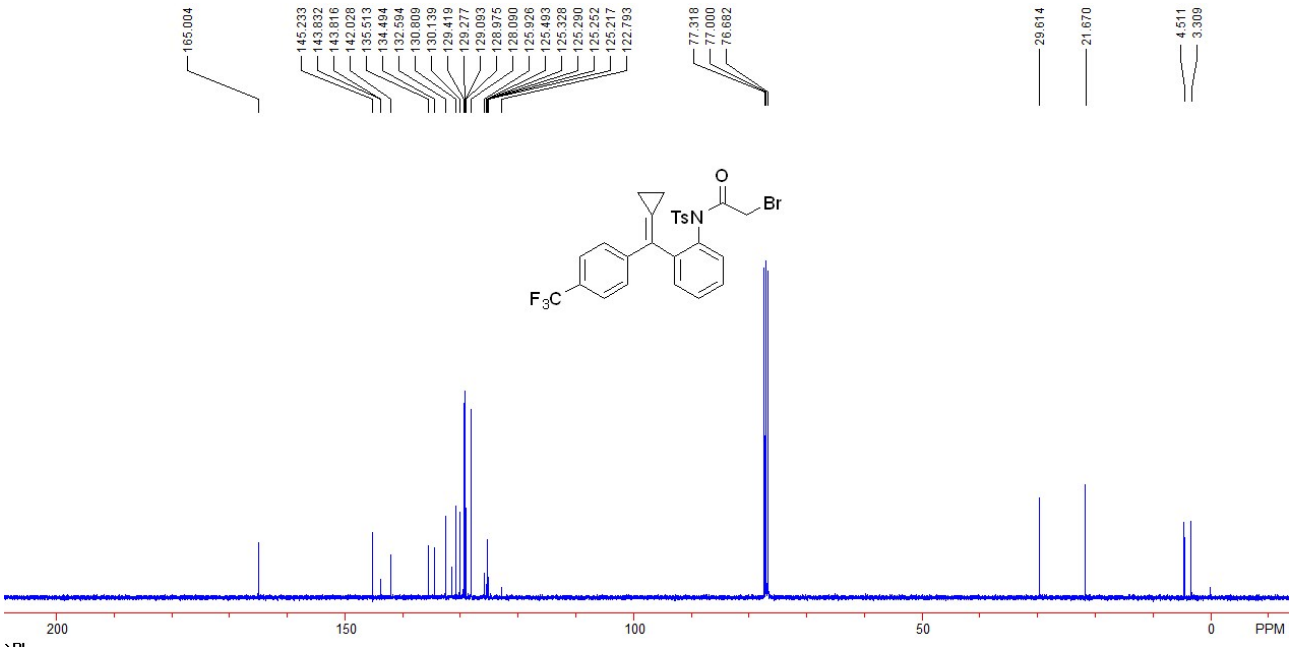


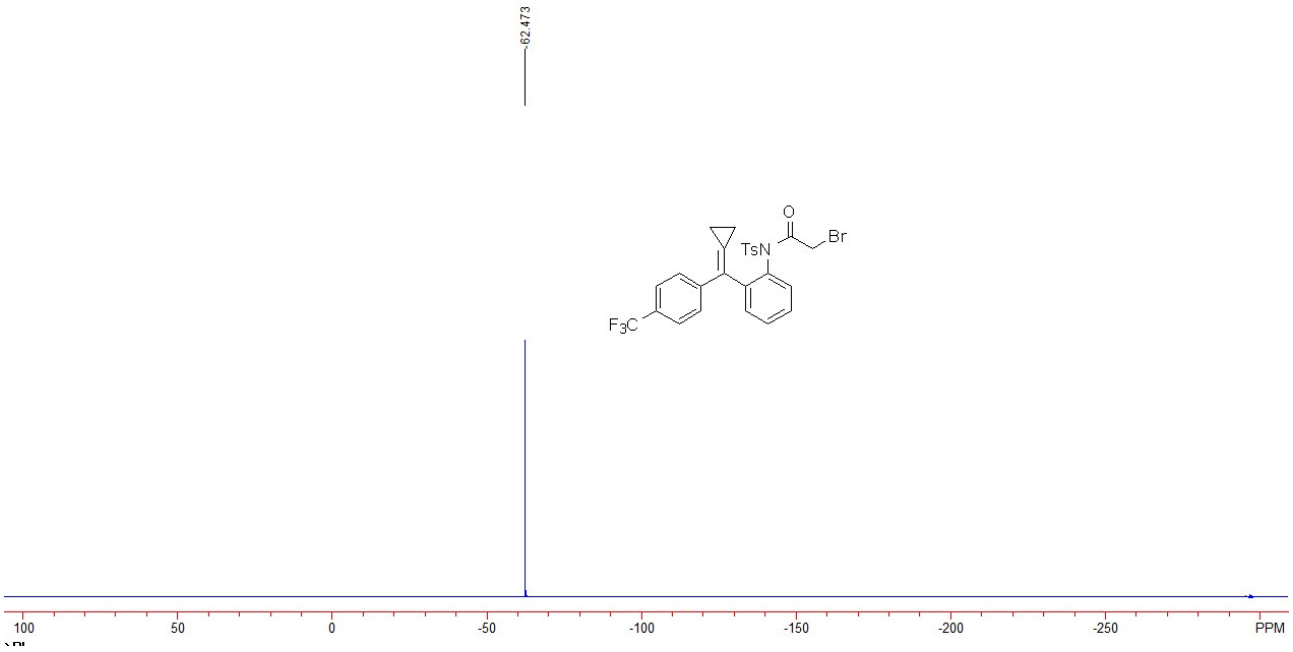


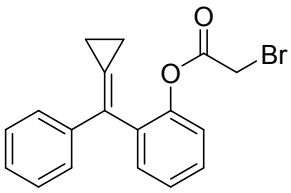
2-bromo-N-(2-(cyclopropylidene(4-(trifluoromethyl)phenyl)methyl)phenyl)-N-tosylacetamide (1n).

A white solid, 337.8 mg, 30% yield. M.p.: 78-80 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.20-1.26 (m, 1H, CH_2), 1.32-1.42 (m, 2H, CH_2), 1.57-1.63 (m, 1H, ArH), 2.42 (s, 3H, CH_3), 3.17 (d, J = 12.8 Hz, 1H, CH_2), 3.42 (d, J = 12.8 Hz, 1H, CH_2), 7.26 (d, J = 8.0 Hz, 2H, ArH), 7.33 (d, J = 7.6 Hz, 1H, ArH), 7.48-7.51 (m, 4H, ArH), 7.56-7.61 (m, 3H, ArH), 7.80 (d, J = 8.4 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 3.3, 4.5, 21.7, 29.6, 124.1 (q, J = 270.0 Hz), 125.3 (q, J = 3.8 Hz), 125.9, 128.1, 129.0, 129.1, 129.3, 139.4, 130.1, 130.8, 132.6, 134.5, 135.5, 142.0, 143.8 (q, J = 1.6 Hz), 145.2, 165.0. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -62.47. IR (CH_2Cl_2) ν 2972, 2880, 1710, 1364, 1325, 1168, 1087, 1046, 875 cm^{-1}. HRMS ($M+Na^+$) calcd. for $C_{26}H_{21}O_3NBrF_3NaS$: 586.0270, Found: 586.0264.





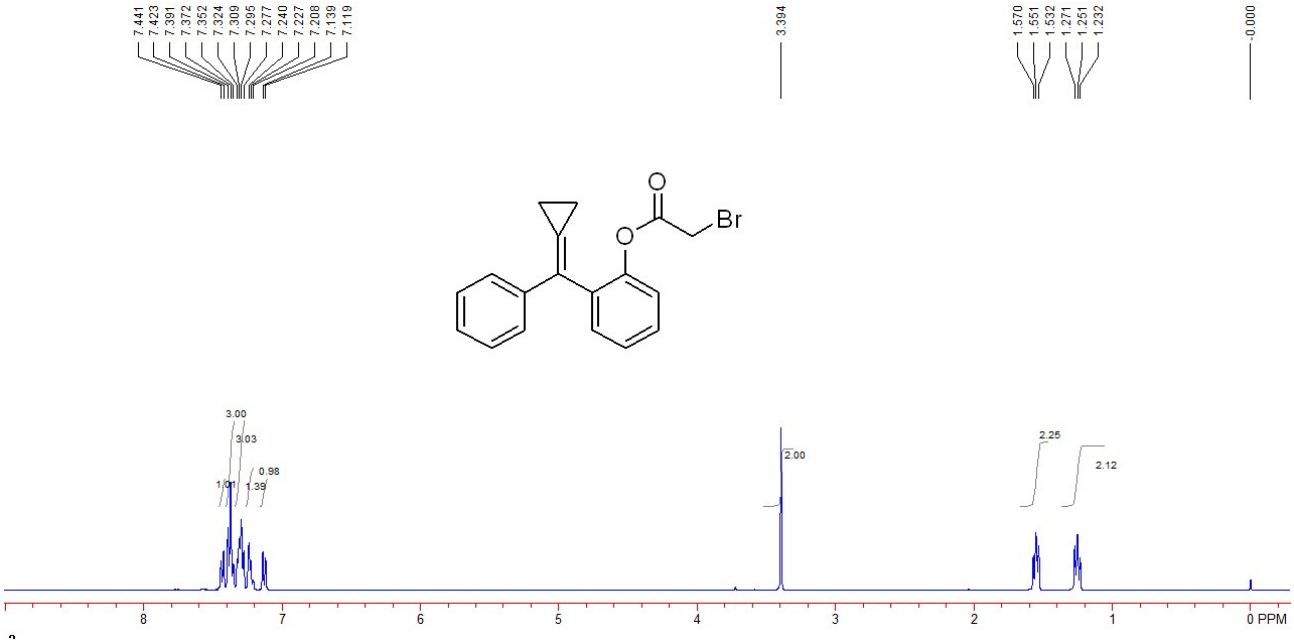


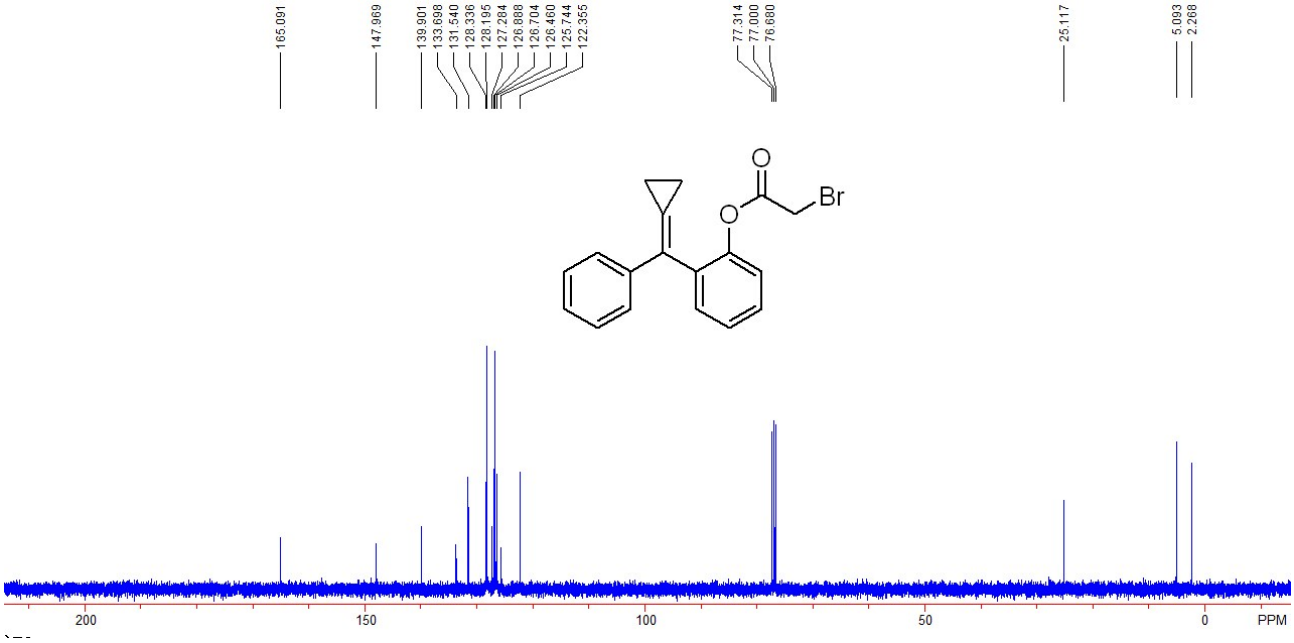


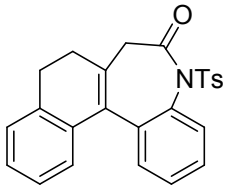
2-(cyclopropylidene(phenyl)methyl)phenyl 2-bromoacetate (1o).

A colorless oil, 617.8 mg, 90% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.25 (t, *J* = 7.6 Hz, 2H, CH_2), 1.55 (t, *J* =7.6 Hz, 2H, CH_2), 3.39 (s, 2H, CH_2), 7.13 (d, *J* = 8.0 Hz, 1H, ArH), 7.21-7.24 (m, 1H, ArH), 7.28-7.32 (m, 3H, ArH), 7.35-7.39 (m, 3H, ArH), 7.43 (d, *J* = 7.2 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 2.3, 5.1, 25.1, 122.4, 125.7, 126.5, 126.7, 126.9, 127.3, 128.2,

128.3, 131.5, 133.7, 139.9, 148.0, 165.1. IR (CH_2Cl_2) ν 3082, 3056, 2975, 1758, 1488, 1440, 1254, 1182, 1120, 765, 696 cm^{-1}. HRMS ($M+H^+$) calcd. for $C_{18}H_{16}O_2Br$: 343.0328, Found: 343.0328.



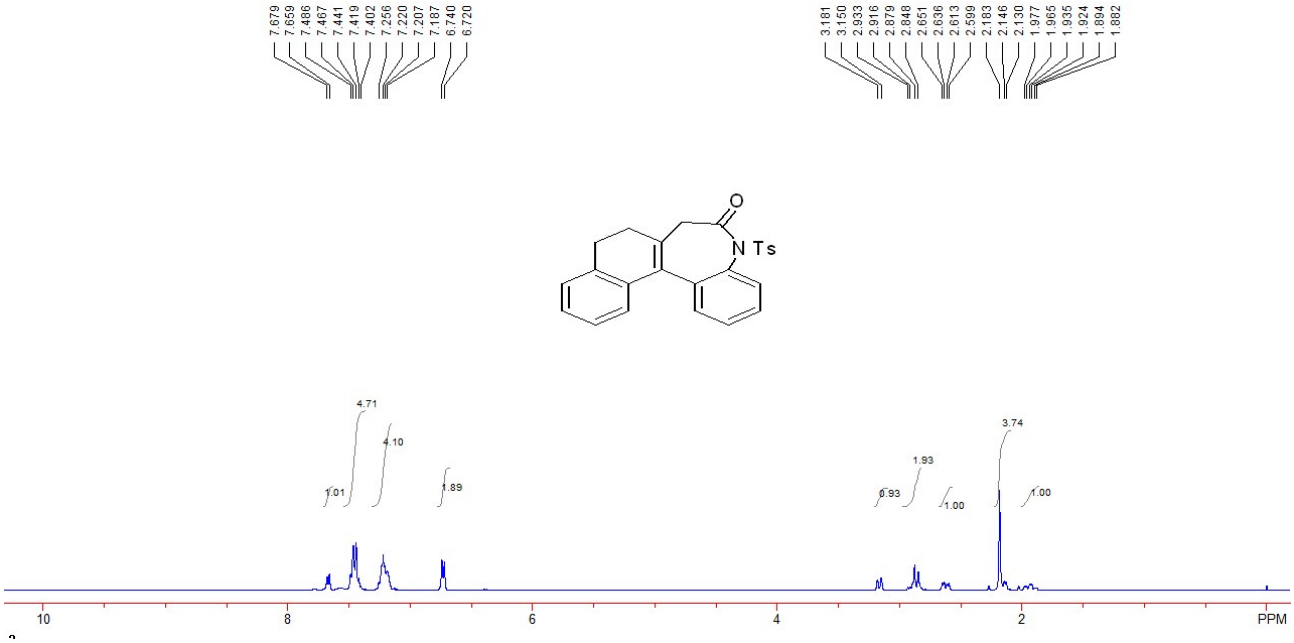


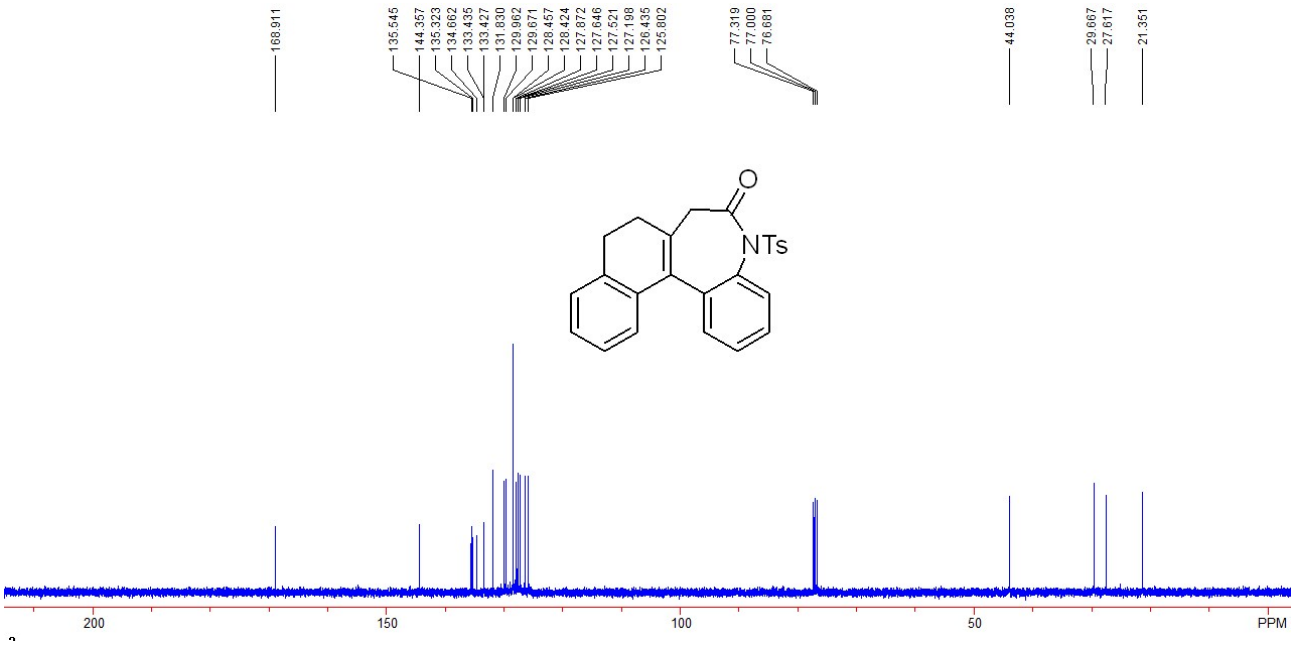


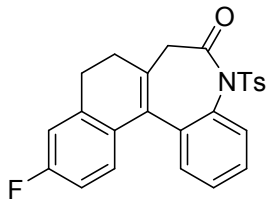
5-tosyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (2a).

A white solid, 45.7 mg, 55% yield. M.p.: 194-196 °C. ^1H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.88-1.98 (m, 1H, CH_2), 2.13-2.18 (m, 1H, CH_2), 2.18 (s, 3H, CH_3), 2.62 (dd, J = 6.0 Hz, 14.8 Hz, 1H,

CH_2), 2.85-2.93 (m, 2H, CH_2), 3.16 (d, J = 12.4 Hz, 1H, CH_2), 6.73 (d, J = 8.0 Hz, 2H, ArH), 7.19-7.26 (m, 4H, ArH), 7.40-7.49 (m, 5H, ArH), 7.67 (d, J =8.0 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.4, 27.6, 29.7, 44.0, 125.8, 126.4, 127.2, 127.5, 127.6, 127.9, 128.4, 128.5, 129.7, 130.0, 131.8, 133.43, 133.44, 134.7, 135.3, 135.5, 144.4, 168.9. IR (CH_2Cl_2) ν 2956, 2922, 2849, 1713, 1362, 1170, 1087, 1018, 802, 672 cm^{-1}. HRMS ($M+H^+$) calcd. for $C_{25}H_{22}O_3NS$: 416.1315, Found: 416.1310.

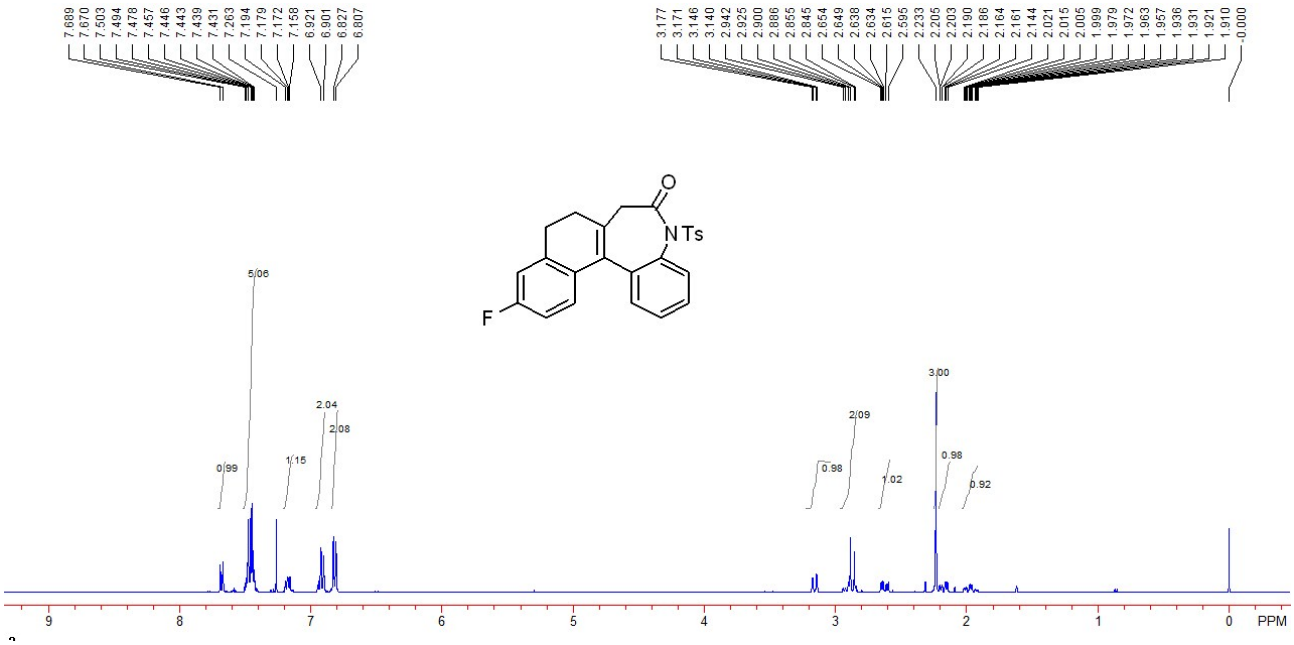


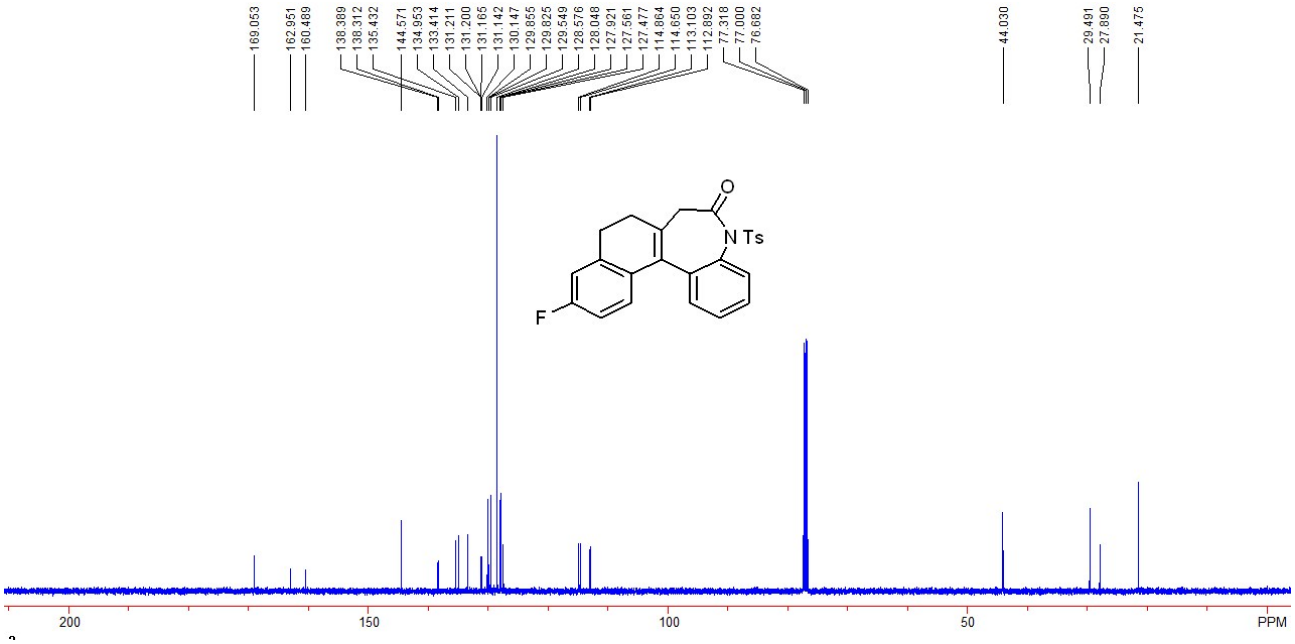


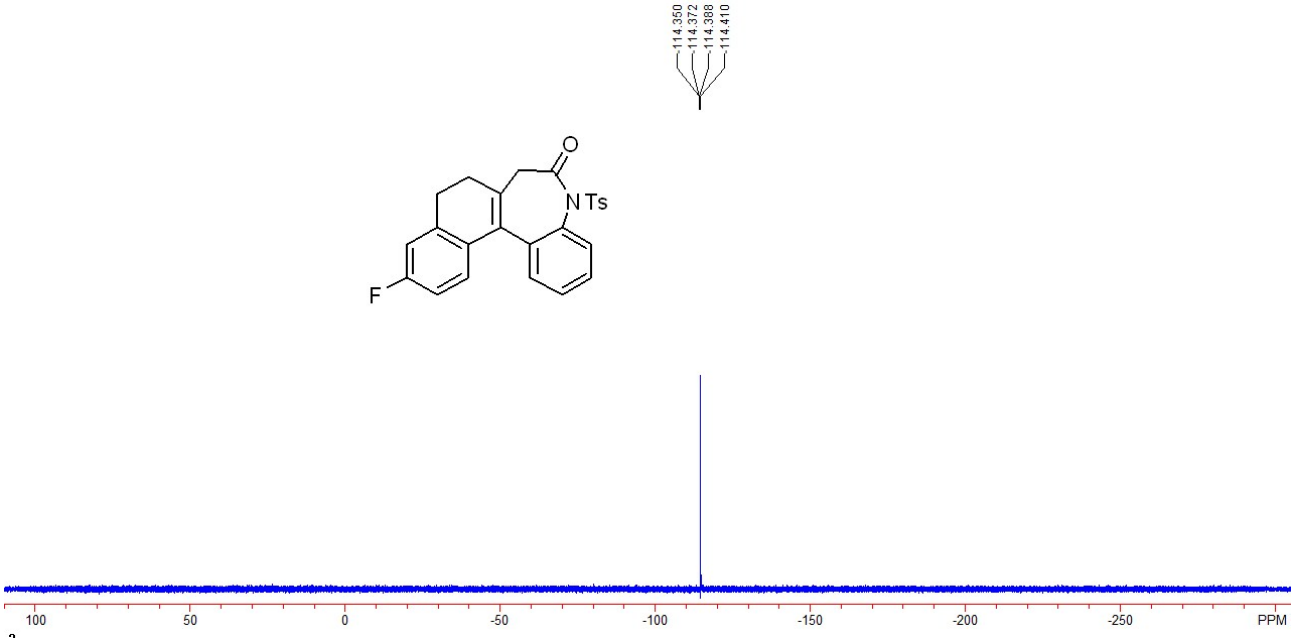


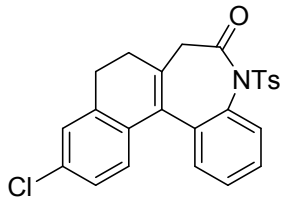
11-fluoro-5-tosyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (2b).

A white solid, 46.0 mg, 53% yield. M.p.: 210-212 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.91-2.02 (m, 1H, CH_2), 2.14-2.20 (m, 1H, CH_2), 2.23 (s, 3H, CH_3), 2.60-2.65 (m, 1H, CH_2), 2.84-2.94 (m, 2H, CH_2), 3.16 (dd, *J* = 2.4 Hz, 12.4 Hz, 1H, CH_2), 6.82 (d, *J* = 8.0 Hz, 2H, ArH), 6.91 (d, *J* = 8.0 Hz, 2H, ArH), 7.16-7.19 (m, 2H, ArH), 7.43-7.50 (m, 5H, ArH), 7.68 (d, *J* =7.6 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.5, 27.9, 29.5, 44.0, 112.9, 113.0 (d, *J* = 21.1 Hz), 114.8 (d, *J* = 21.4 Hz), 127.5, 127.6, 127.9, 128.0, 128.6, 129.5, 129.8 (d, *J* = 3.0 Hz), 130.1, 131.1 (d, *J* = 2.3 Hz), 131.2 (d, *J* = 1.1 Hz), 133.4, 135.0, 135.4, 138.3 (d, *J* = 7.7 Hz), 144.6, 161.7 (d, *J* = 246.2 Hz), 169.0. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -114.38. IR (CH_2Cl_2) ν 2959, 2920, 1714, 1495, 1365, 1266, 1171, 1089, 1015, 806 cm^{-1}. HRMS ($M+H^+$) calcd. for $C_{25}H_{21}O_3NFS$: 434.1221, Found: 434.1219.





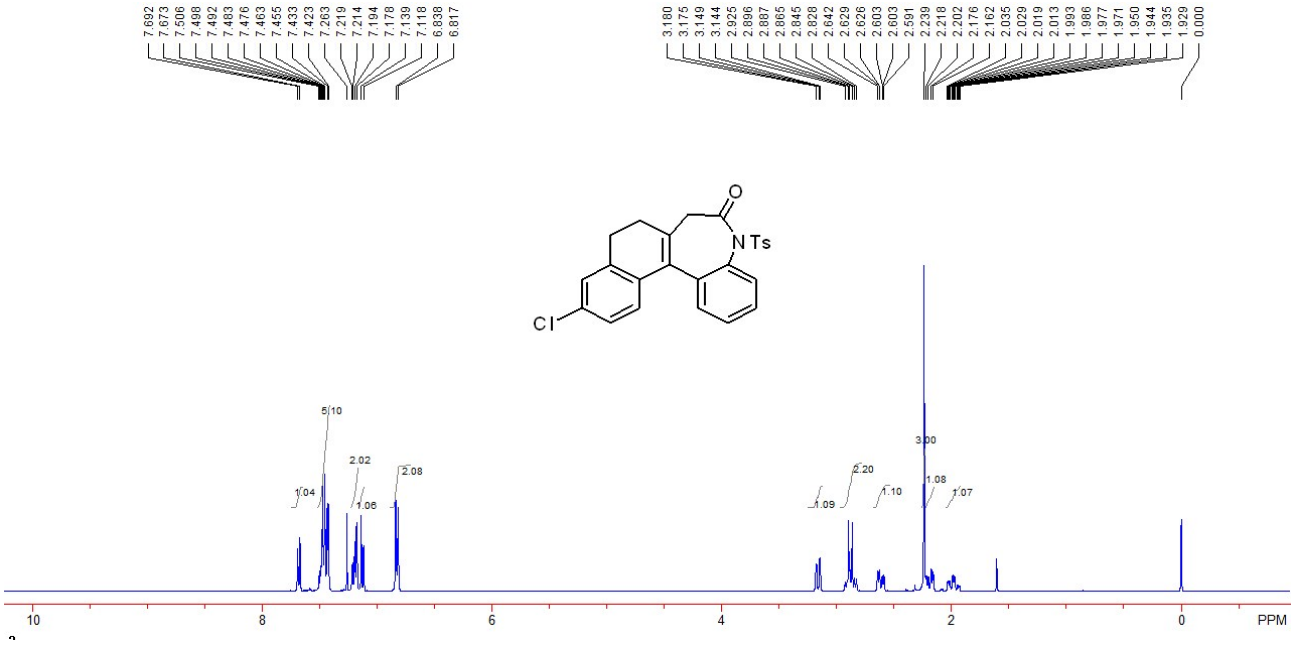


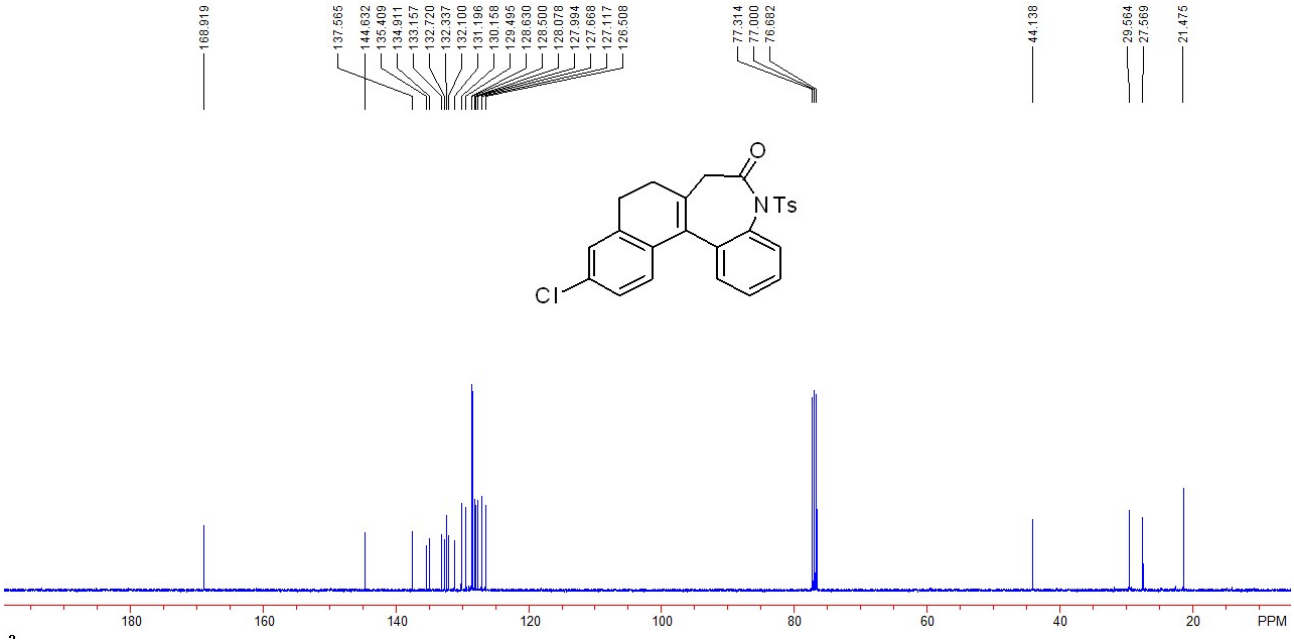


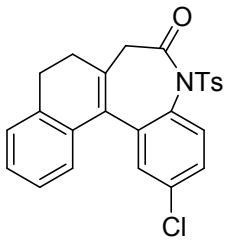
11-chloro-5-tosyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (2c).

A white solid, 45.9 mg, 51% yield. M.p.: 216-218 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.93-2.04 (m, 1H, CH_2), 2.16-2.22 (m, 1H, CH_2), 2.24 (s, 3H, CH_3), 2.59-2.64 (m, 1H, CH_2), 2.83-2.92 (m, 2H, CH_2), 3.16 (dd, J = 2.0 Hz, 12.4 Hz, 1H, CH_2), 6.83 (d, J = 8.4 Hz, 2H, ArH), 7.13 (d, J = 6.4 Hz, 1H, ArH), 7.18-7.22 (m, 2H, ArH), 7.42-7.51 (m, 5H, ArH), 7.68 (d, J =7.6 Hz, 1H, ArH).

^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.5, 27.6, 29.6, 44.1, 121.9, 126.5, 127.1, 127.7, 128.0, 128.1, 128.5, 128.6, 129.5, 130.2, 131.2, 132.1, 132.3, 132.7, 133.2, 134.9, 135.4, 137.6, 144.6, 168.9. IR (CH_2Cl_2) ν 2956, 2920, 2847, 1714, 1493, 1263, 1166, 1090, 1022, 811 cm^{-1}. HRMS ($M+H^+$) calcd. for $C_{25}H_{21}O_3NClS$: 450.0925, Found: 450.0920.

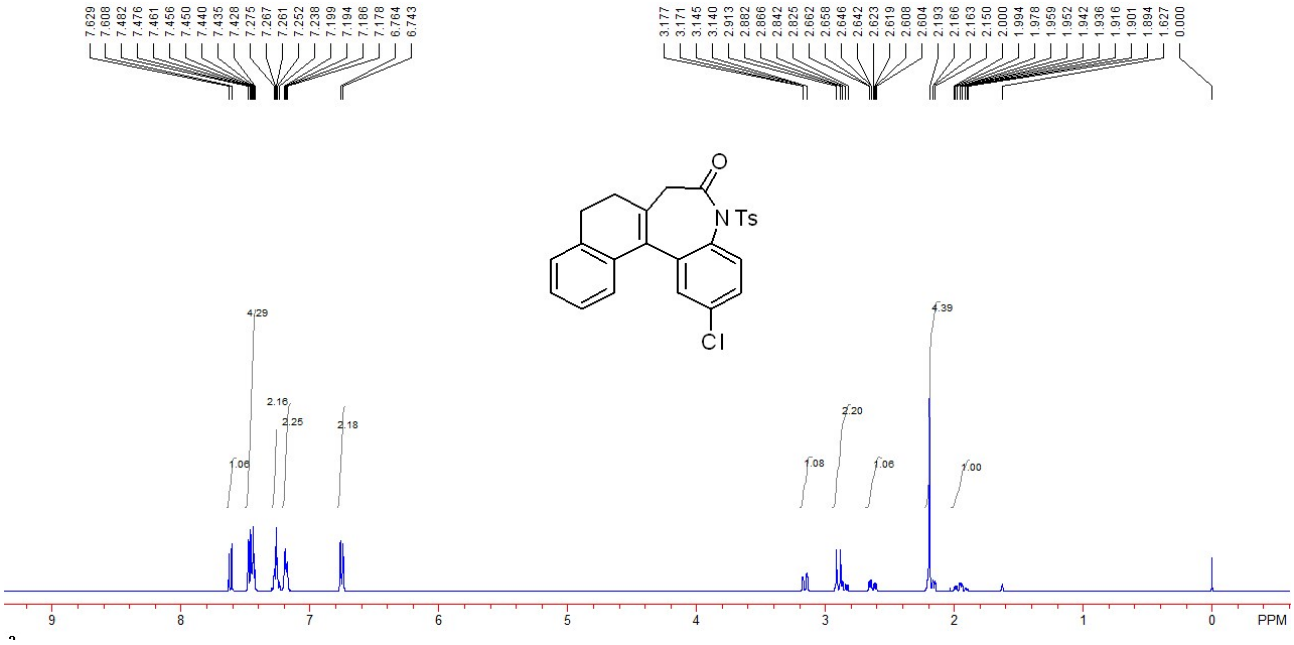


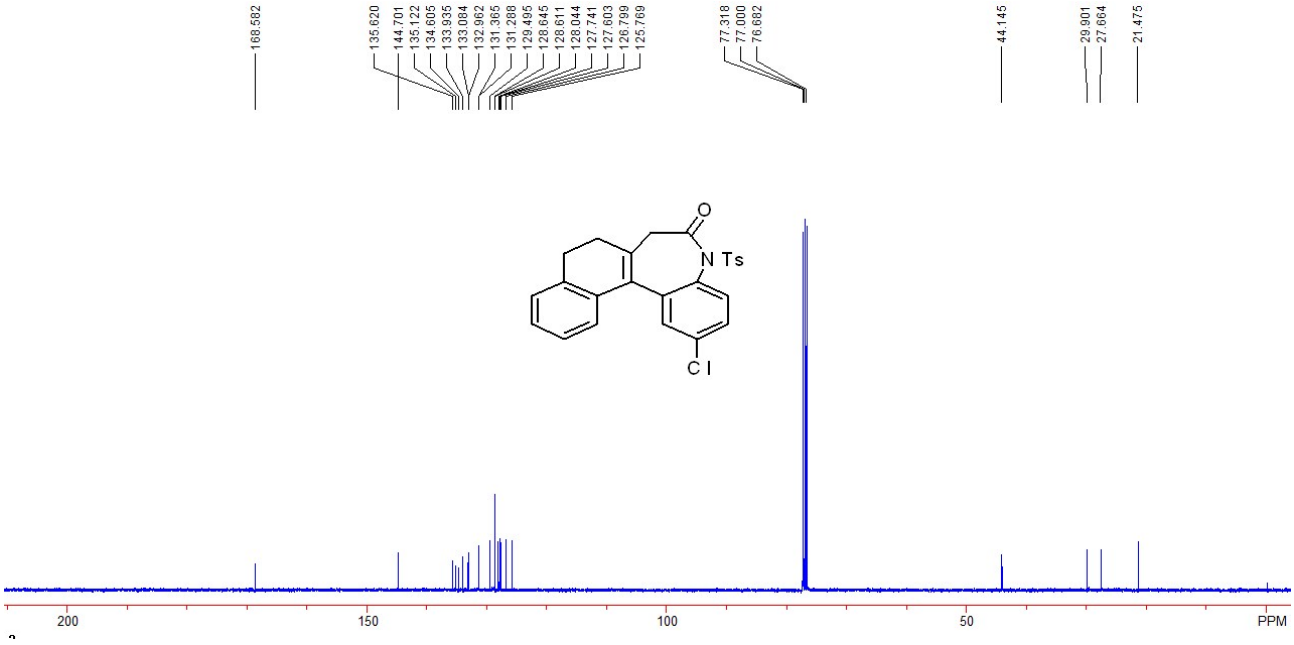


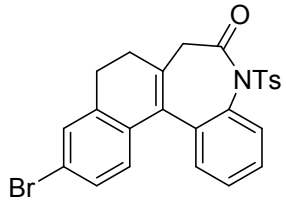


2-chloro-5-tosyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (2d).

A white solid, 45.0 mg, 50% yield. M.p.: 236-238 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.90-2.00 (m, 1H, CH_2), 2.15-2.19 (m, 1H, CH_2), 2.19 (s, 3H, CH3), 2.60-2.66 (m, 1H, CH_2), 2.82-2.91 (m, 2H, CH_2), 3.16 (dd, *J* = 2.4 Hz, 12.8 Hz, 1H, CH_2), 6.76 (d, *J* = 8.0 Hz, 2H, ArH), 7.18-7.20 (m, 2H, ArH), 7.24-7.28 (m, 2H, ArH), 7.43-7.48 (m, 4H, ArH), 7.61 (d, *J* = 8.4 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.5, 27.7, 29.9, 44.1, 125.8, 126.8, 127.6, 127.7, 128.61, 128.64, 129.5, 131.3, 131.4, 133.0, 133.1, 134.6, 135.1, 135.6, 144.7, 168.6. IR (CH_2Cl_2) ν 2962, 2925, 1260, 1118, 1089, 1023, 801, 700 cm^{-1}. HRMS ($M+H^+$) calcd. for $C_{25}H_{21}O_3NClS$: 450.0925, Found: 450.0925.

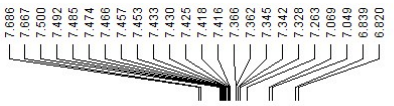


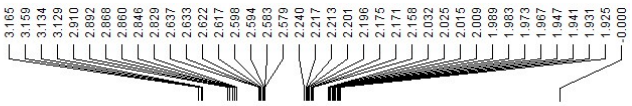


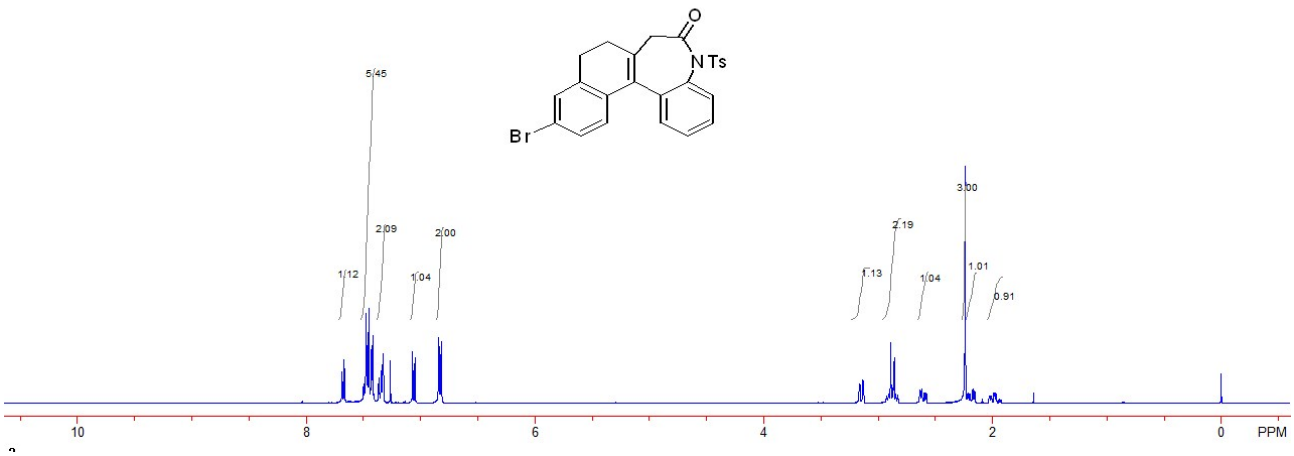


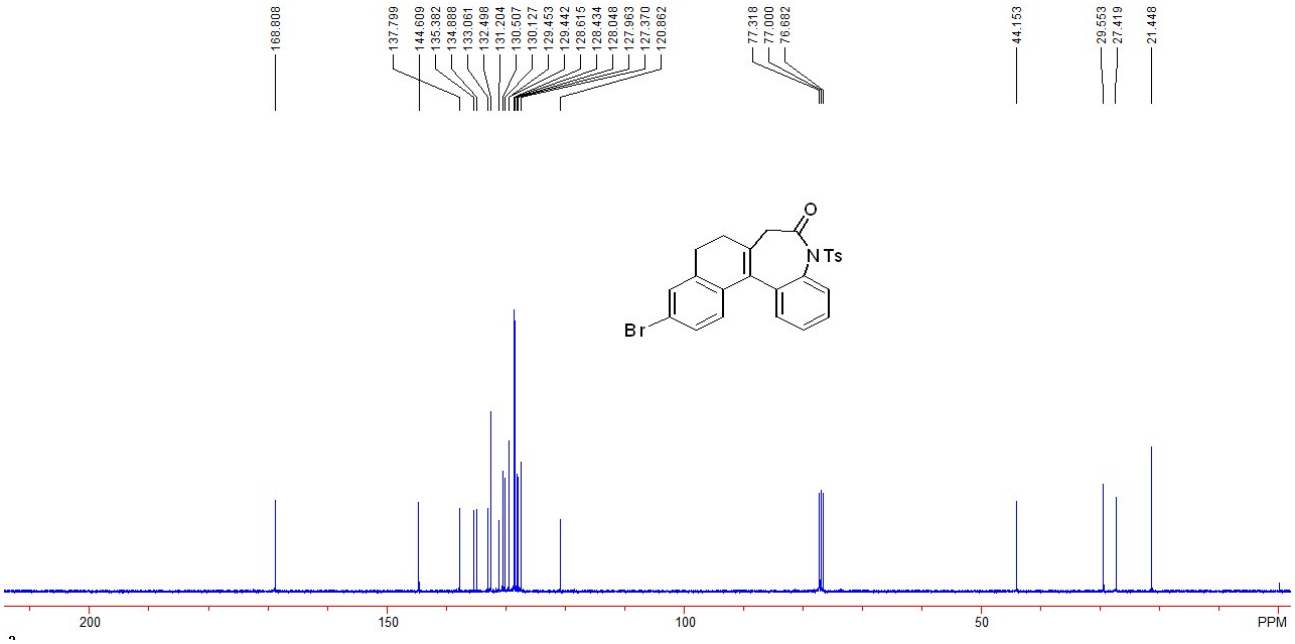
11-bromo-5-tosyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (2e).

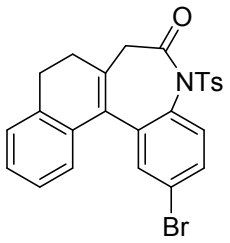
A white solid, 44.5 mg, 45% yield. M.p.: 211-213 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.92-2.03 (m, 1H, CH_2), 2.16-2.22 (m, 1H, CH_2), 2.24 (s, 3H, CH_3), 2.60-2.64 (m, 1H, CH_2), 2.83-2.91 (m, 2H, CH_2), 3.15 (dd, J = 2.4 Hz, 12.4 Hz, 1H, CH_2), 6.83 (d, J = 7.6 Hz, 2H, ArH), 7.05 (d, J = 8.0 Hz, 1H, ArH), 7.33-7.37 (m, 2H, ArH), 7.42-7.50 (m, 5H, ArH), 7.68 (d, J = 7.6 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.4, 27.4, 29.6, 44.2, 120.9, 127.4, 127.96, 128.05, 128.4, 128.6, 129.4, 129.5, 130.1, 130.5, 131.2, 132.5, 133.1, 134.9, 135.4, 137.8, 144.6, 168.8. IR (CH_2Cl_2) ν 2961, 2922, 1713, 1367, 1168, 1088, 1020, 817, 669 cm^{-1}. MS (%) m/e 235 (5.74), 163 (5.79), 147 (8.71), 145 (5.88), 91 (M^+, 100.00), 131 (14.48), 92 (9.25), 65 (7.93). HRMS (EI) HRMS ($M+H^+$) calcd. for $C_{25}H_{21}O_3NBrS$: 494.0420, Found: 494.0419.





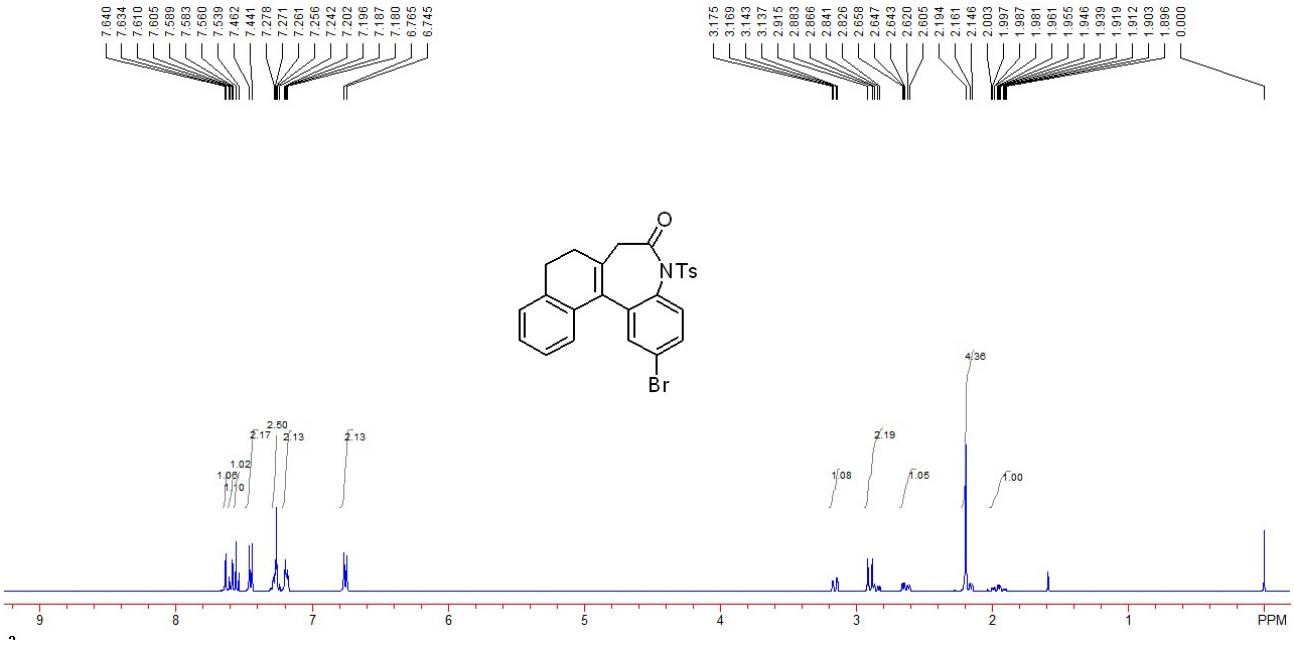


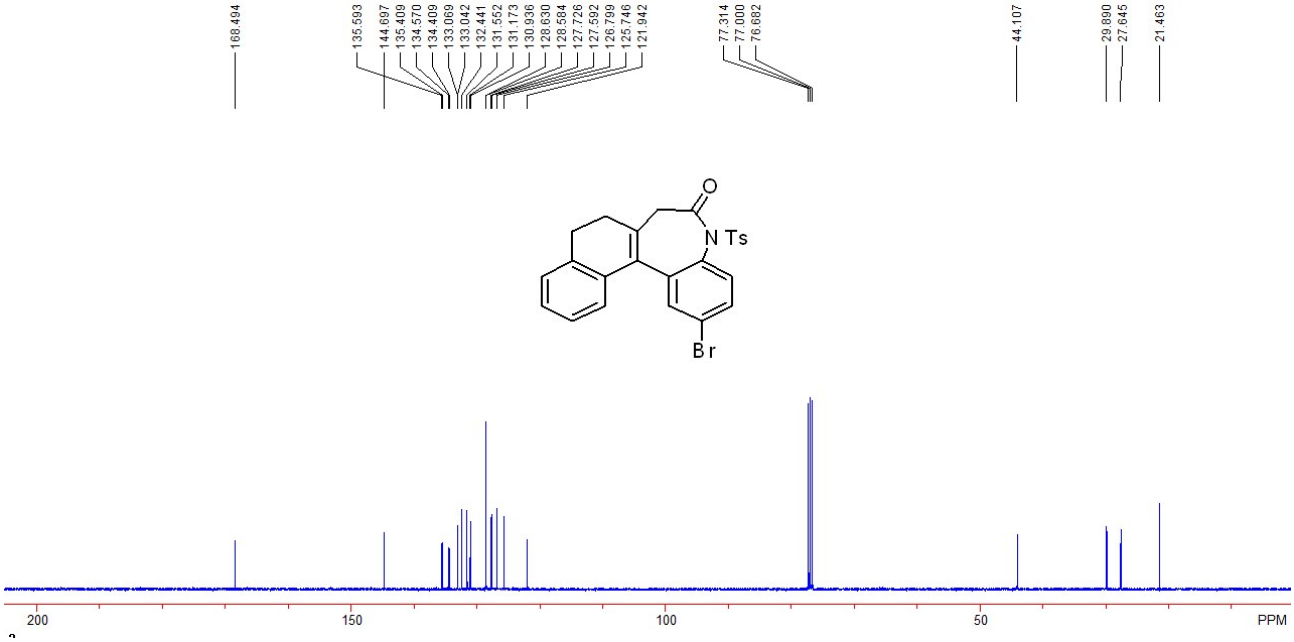


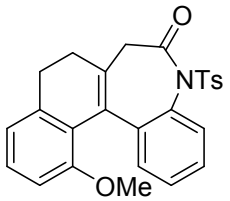


2-bromo-5-tosyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (2f).

A white solid, 48.4 mg, 49% yield. M.p.: 232-234 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.90-2.00 (m, 1H, CH_2), 2.15-2.19 (m, 1H, CH_2), 2.19 (s, 3H, CH_3), 2.60-2.66 (m, 1H, CH_2), 2.83-2.92 (m, 2H, CH_2), 3.16 (dd, *J* = 2.4 Hz, 12.8 Hz, 1H, CH_2), 6.76 (d, *J* = 8.0 Hz, 2H, ArH), 7.18-7.20 (m, 2H, ArH), 7.24-7.28 (m, 2H, ArH), 7.45 (d, *J* = 8.4 Hz, 2H, ArH), 7.55 (d, *J* = 8.4 Hz, 1H, ArH), 7.59 (dd, *J* = 2.4 Hz, 8.4 Hz, 1H, ArH), 7.64 (d, *J* = 2.4 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.5, 27.6, 29.9, 44.1, 121.9, 125.7, 126.8, 127.6, 127.7, 128.58, 128.63, 130.9, 131.2, 131.6, 132.4, 133.0, 133.1, 134.4, 134.6, 135.4, 135.6, 144.7, 168.5. IR (CH_2Cl_2) ν 2963, 2922, 2846, 1717, 1260, 1171, 1088, 1024, 800 cm^{-1}. HRMS ($M+H^+$) calcd. for $C_{25}H_{21}O_3NBrS$: 494.0420, Found: 494.0419.



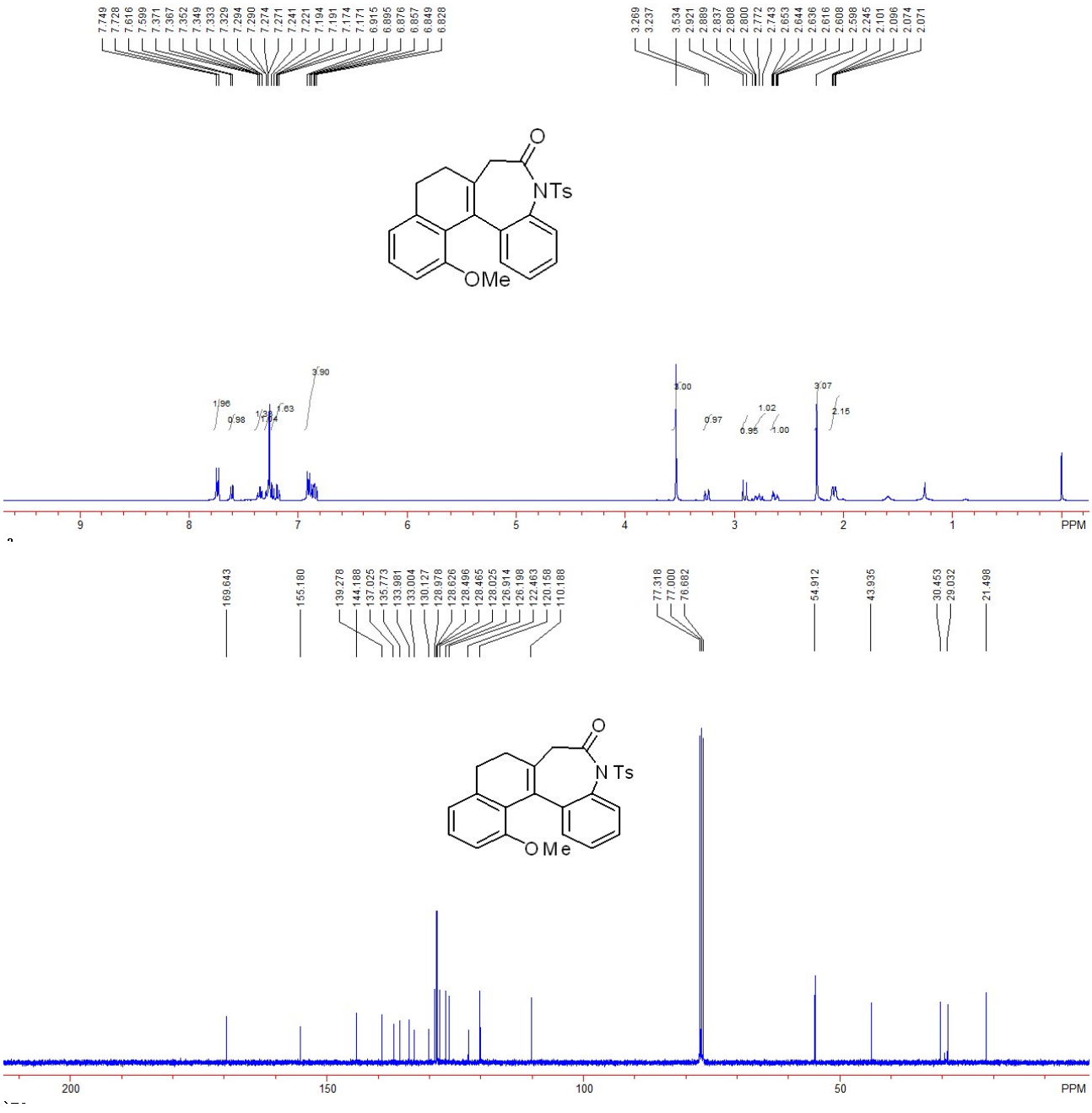


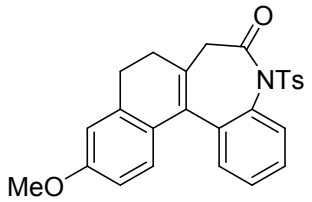


13-methoxy-5-tosyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (2g).

A white solid, 47.2 mg, 53% yield. M.p.: 237-239 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.07-2.10 (m, 2H, CH_2), 2.24 (s, 3H, CH_3), 2.63 (dt, J = 3.2 Hz, 14.4 Hz, 1H, CH_2), 2.74-2.84 (m, 1H, CH_2), 2.90 (d, J = 12.8 Hz, 1H, CH_2), 3.25 (d, J = 12.8 Hz, 1H, CH_2), 3.53 (s, 3H, CH_3), 6.83-6.92 (m, 4H, ArH), 7.17-7.29 (m, 3H, ArH), 7.35 (dt, J = 1.6 Hz, 7.6 Hz, 1H, ArH), 7.61 (d, J = 6.0 Hz,

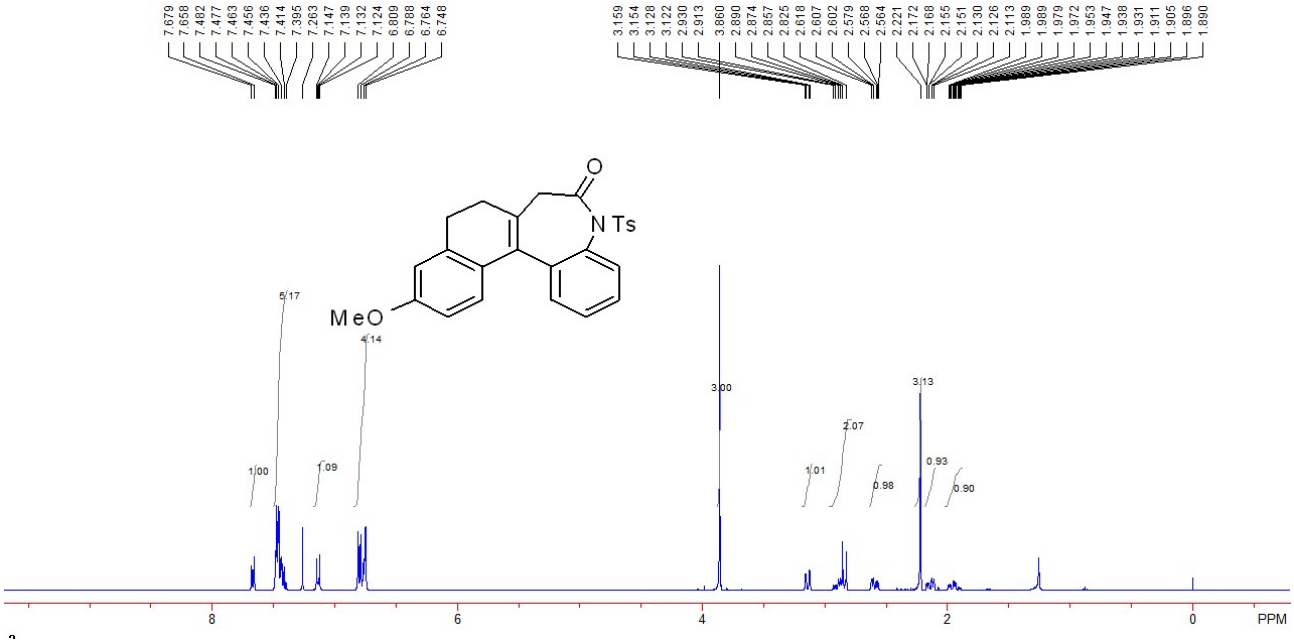
1H, ArH), 7.74 (d, J = 8.4 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.5, 29.0, 30.4, 43.9, 54.9, 110.2, 120.2, 122.5, 126.2, 126.9, 128.0, 128.46, 128.49, 128.6, 129.0, 130.1, 133.0, 134.0, 135.8, 137.0, 139.3, 144.2, 155.2, 169.6. IR (CH_2Cl_2) ν 2963, 2924, 2846, 1713, 1470, 1362, 1262, 1170, 1085, 1024, 802 cm^{-1}. HRMS ($M+H^+$) calcd. for $C_{26}H_{24}O_4NS$: 446.1421, Found: 446.1422.

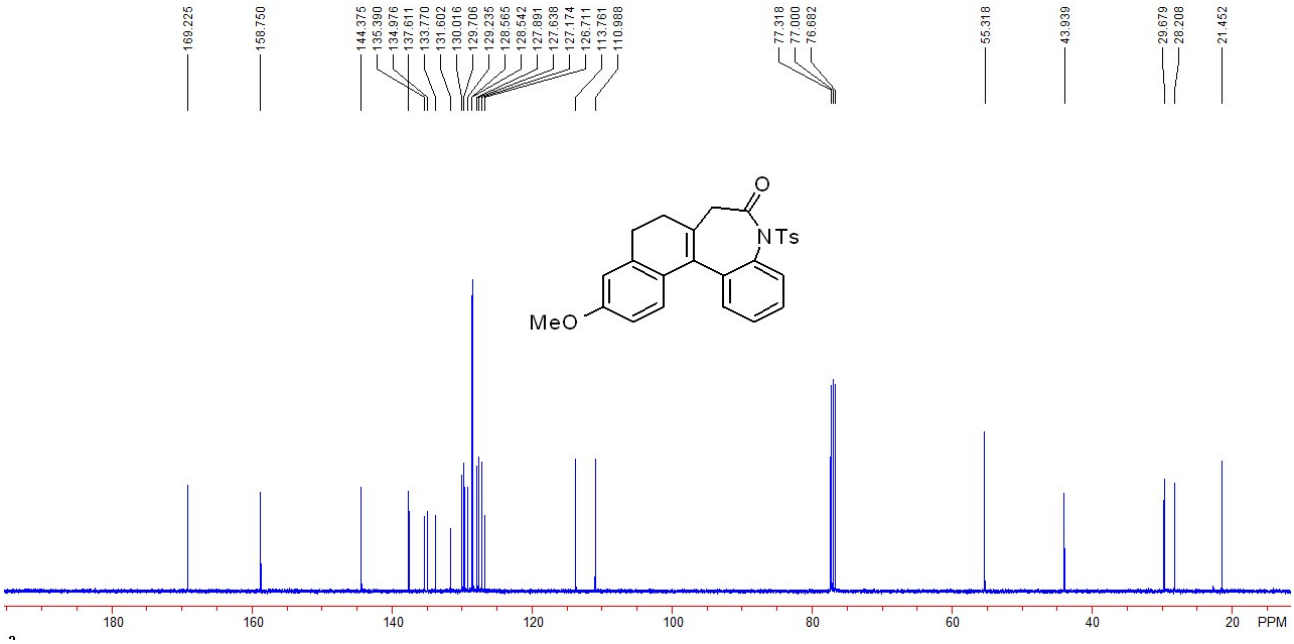


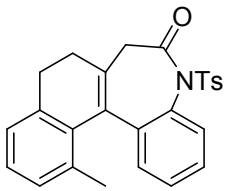


11-methoxy-5-tosyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (2h).

A A white solid, 45.4 mg, 51% yield. M.p.:159-161 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.89-1.99 (m, 1H, CH_2), 2.11-2.17 (m, 1H, CH_2), 2.22 (s, 3H, CH_3), 2.56-2.62 (m, 1H, CH_2), 2.82-2.93 (m, 2H, CH_2), 3.14 (dd, J = 2.0 Hz, 12.4 Hz, 1H, CH_2), 3.86 (s, 3H, CH_3), 6.75-6.81 (m, 4H, ArH), 7.12-7.15 (m, 1H, ArH), 7.40-7.48 (m, 5H, ArH), 7.67 (d, J =7.6 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.4, 28.2, 29.7, 43.9, 55.3, 111.0, 113.8, 126.7, 127.2, 127.6, 127.9, 128.5, 128.6, 129.2, 129.7, 130.0, 131.6, 133.8, 135.0, 135.4, 137.6, 144.4, 158.8, 169.2. IR (CH_2Cl_2) ν 2975, 2922, 2852, 1712, 1600, 1365, 1254, 1169, 1087, 1040, 806, 673 cm^{-1}. HRMS ($M+H^+$) calcd. for $C_{26}H_{24}O_4NS$: 446.1421, Found: 446.1421.

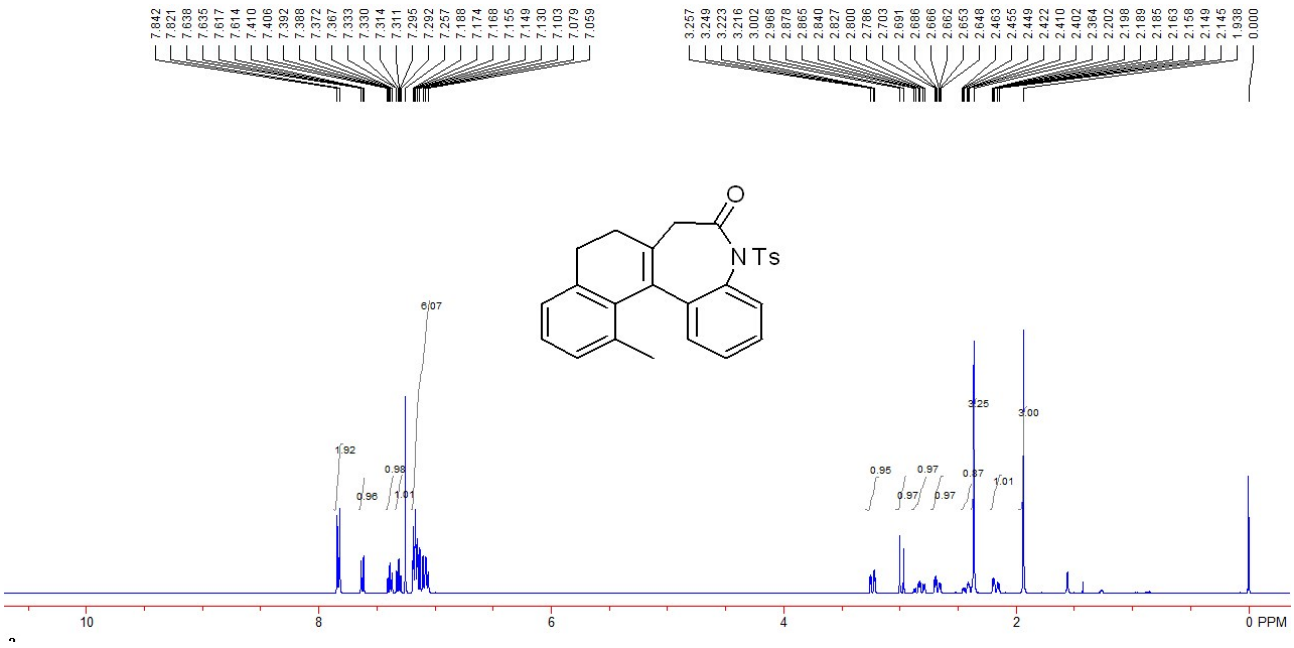


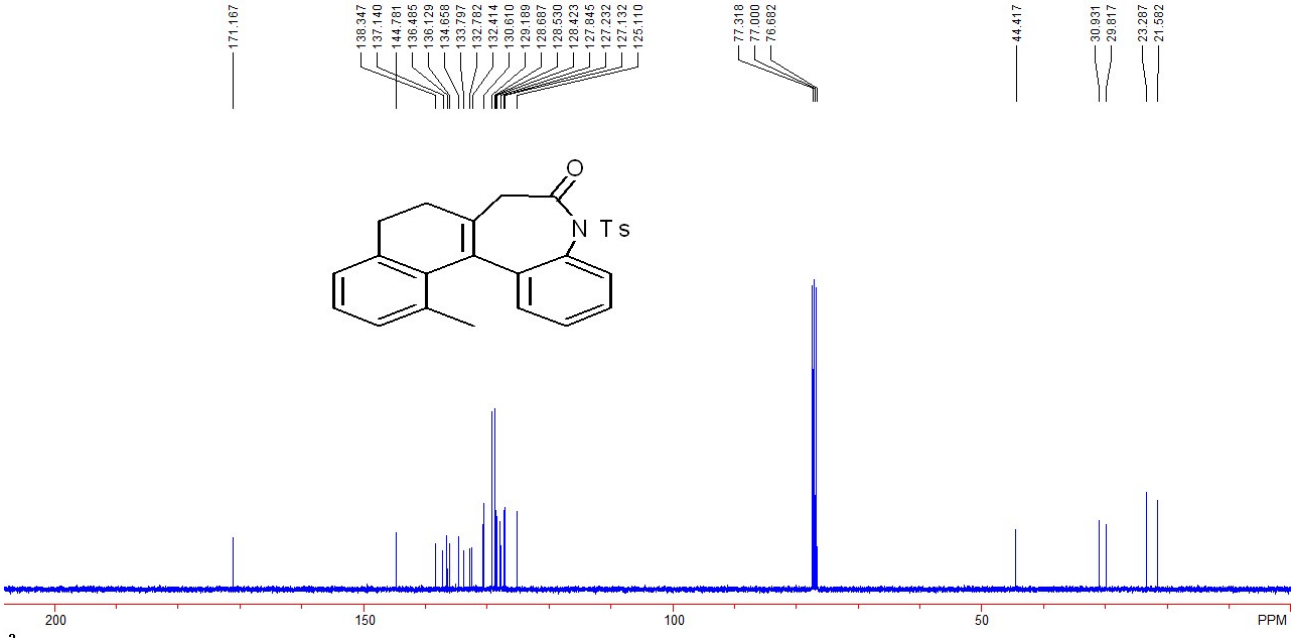


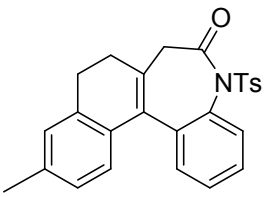


13-methyl-5-tosyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (2i).

A white solid, 30.1 mg, 35% yield. M.p.: 210-212 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.94 (s, 3H, CH_3), 2.14-2.20 (m, 1H, CH_2), 2.36 (s, 3H, CH_3), 2.40-2.46 (m, 1H, CH_2), 2.65-2.70 (m, 1H, CH_2), 2.79-2.88 (m, 1H, CH_2), 2.98 (d, J = 13.6 Hz, 1H, CH_2), 3.24 (dd, J = 2.8 Hz, 13.2 Hz, 1H, CH_2), 7.06-7.19 (m, 6H, ArH), 7.31 (dt, J = 1.2 Hz, 7.6 Hz, 1H, ArH), 7.39 (dt, J = 1.6 Hz, 7.2 Hz, 1H, ArH), 7.63 (dd, J = 1.2 Hz, 8.4 Hz, 1H, ArH), 7.83 (d, J = 8.4 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.6, 23.3, 29.8, 30.9, 44.4, 125.1, 127.1, 127.2, 127.8, 128.4, 128.5, 128.7, 129.2, 130.6, 132.4, 132.8, 133.8, 134.6, 136.1, 136.5, 137.1, 138.3, 144.8, 171.2. IR (CH_2Cl_2) ν 2953, 2923, 2854, 1716, 1260, 1172, 1085, 1044, 1012, 799, 782, 697 cm^{-1}. HRMS (M+H^{+}) calcd. for $C_{26}H_{24}O_3NS$: 430.1471, Found: 430.1465.



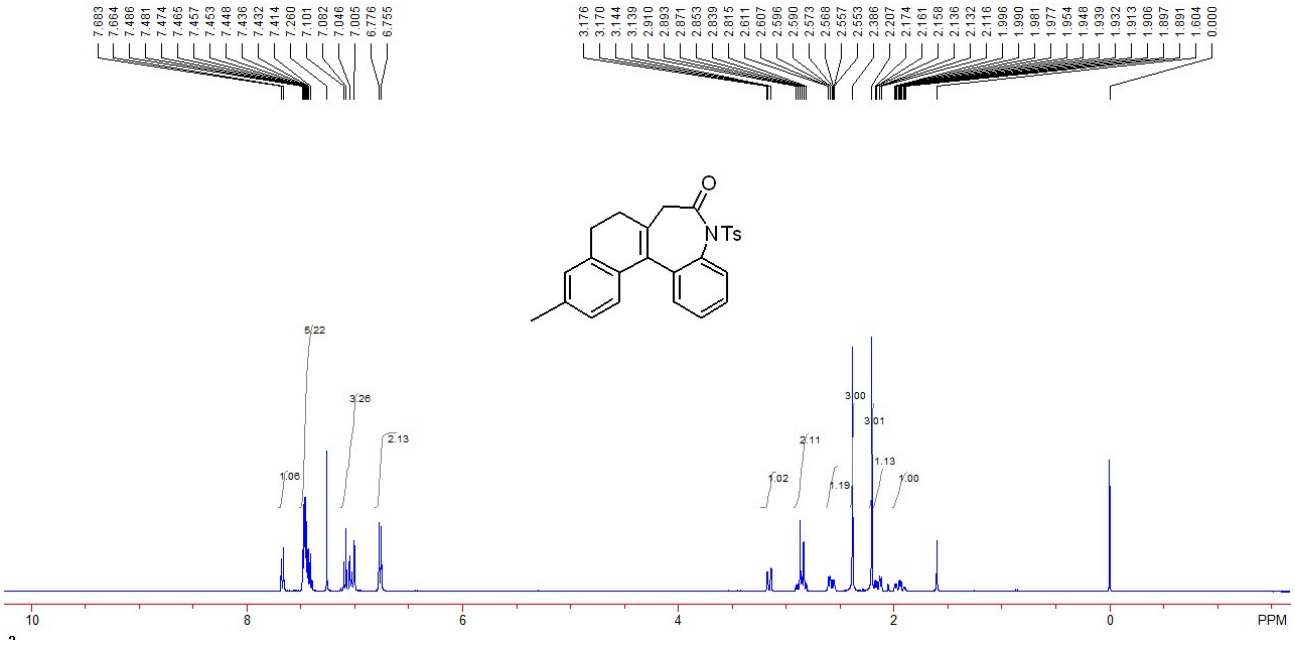


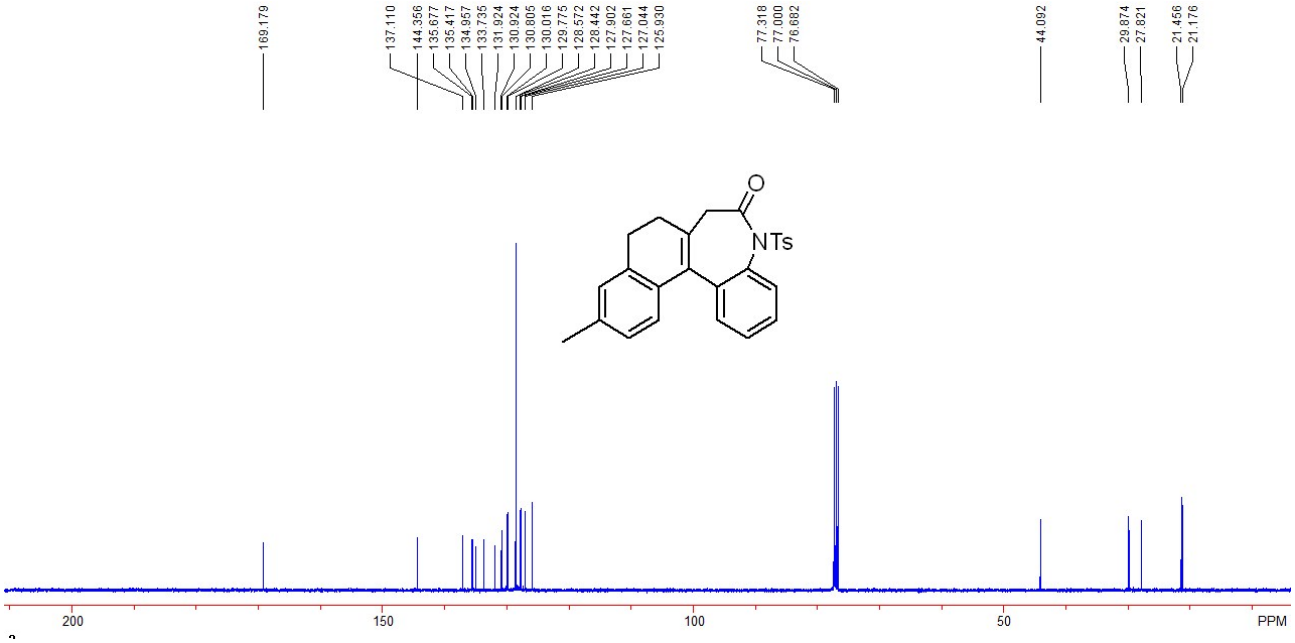


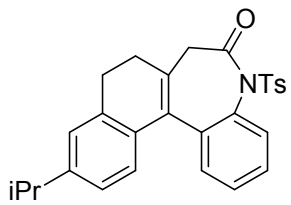
11-methyl-5-tosyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (2j).

A white solid, 38.6 mg, 45% yield. M.p.: 209-211 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.89-2.00 (m, 1H, CH_2), 2.12-2.17 (m, 1H, CH_2), 2.21 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 2.55-2.61 (m, 1H, CH_2), 2.82-2.91 (m, 2H, CH_2), 3.16 (dd, *J* = 2.0 Hz, 12.4 Hz, 1H, CH_2), 6.77 (d, *J* = 8.4 Hz, 2H, ArH), 7.00-7.10 (m, 3H, ArH), 7.41-7.49 (m, 5H, ArH), 7.67 (d, *J* =7.6 Hz, 1H, ArH). ^{13}C NMR

($CDCl_3$, TMS, 100 MHz) δ 21.2, 21.4, 27.8, 29.9, 44.1, 125.9, 127.0, 127.7, 127.9, 128.4, 128.6, 129.8, 130.0, 130.8, 130.9, 131.9, 133.7, 135.0, 135.4, 135.7, 137.1, 144.4, 169.2. IR (CH_2Cl_2) ν 2963, 2929, 2854, 1713, 1440, 1260, 1170, 1113, 1088, 1023, 800 cm^{-1}. HRMS ($M+H^+$) calcd. for $C_{26}H_{24}O_3NS$: 430.1471, Found: 430.1470.

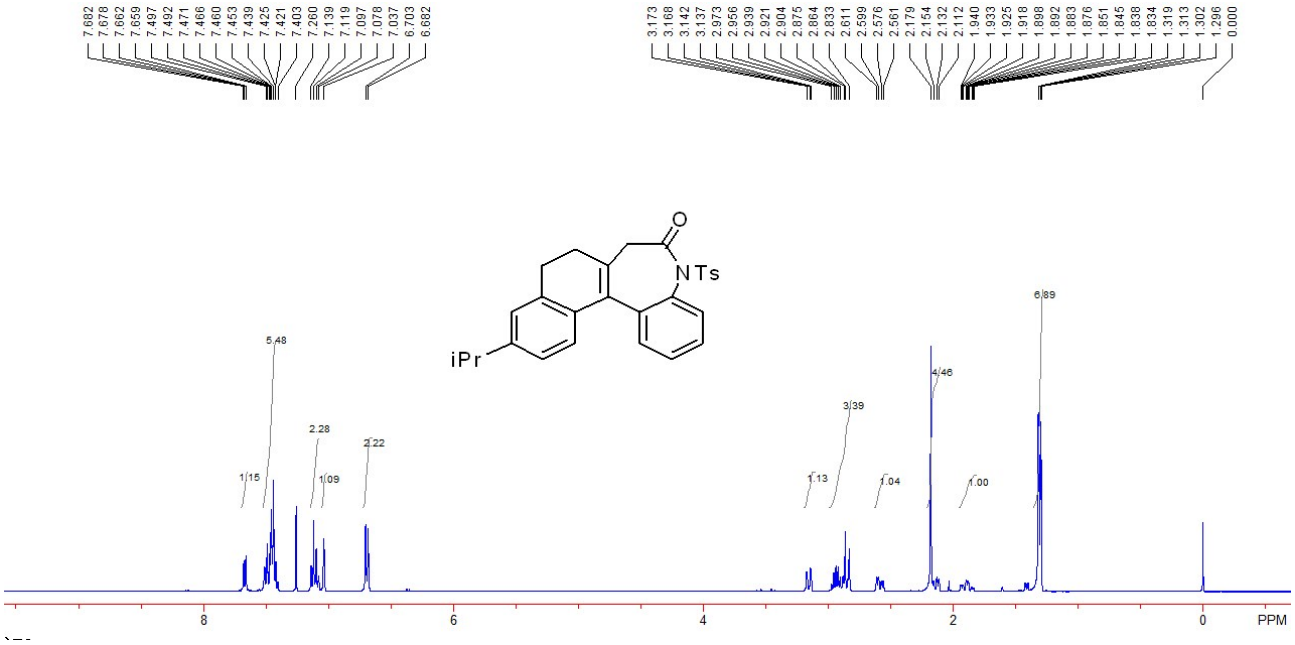


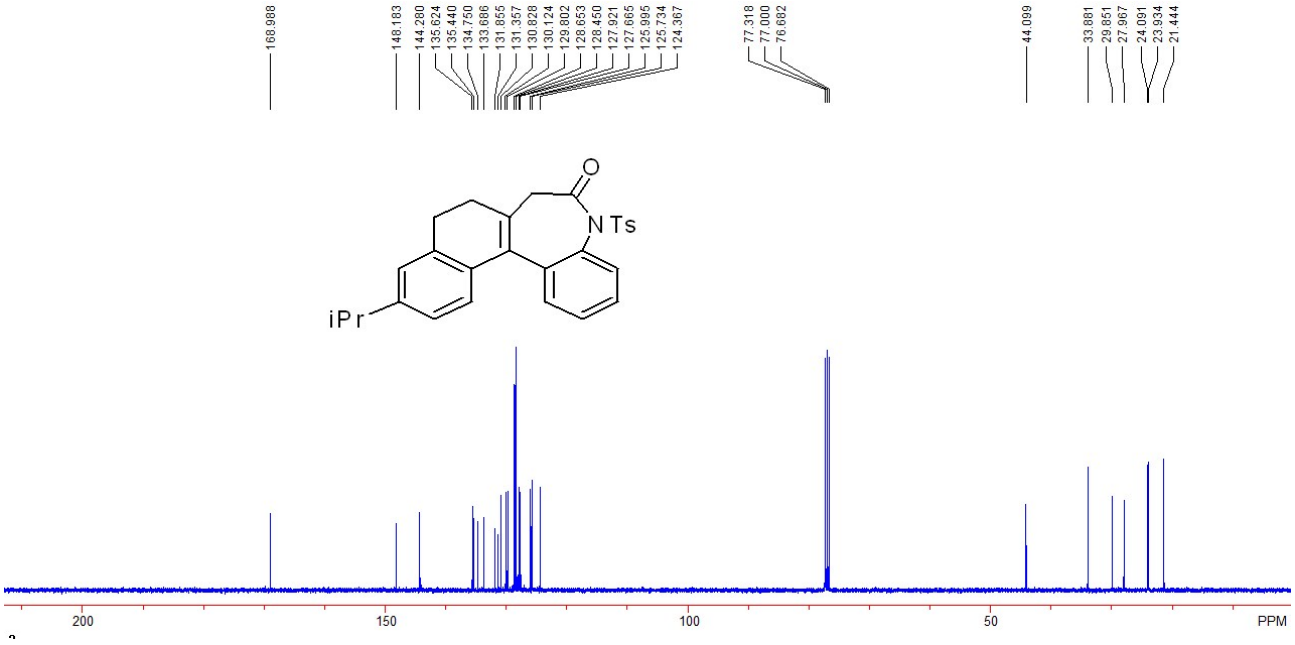


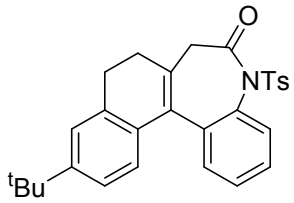


11-isopropyl-5-tosyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (2k).

A white solid, 41.2 mg, 45% yield. M.p.: 213-215 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.30 (d, J = 2.4 Hz, 3H, CH_3), 1.32 (d, J = 2.4 Hz, 3H, CH_3), 1.83-1.94 (m, 1H, CH_2), 2.11-2.18 (m, 1H, CH_2), 2.18 (s, 3H, CH_3), 2.56-2.61 (m, 1H, CH_2), 2.83-2.97 (m, 3H, CH&CH_2), 3.16 (dd, J = 2.0 Hz, 12.4 Hz, 1H, CH_2), 6.69 (d, J = 8.4 Hz, 2H, ArH), 7.04 (s, 1H, ArH), 7.08-7.14 (m, 2H, ArH), 7.40-7.50 (m, 5H, ArH), 7.67 (dd, J = 1.2 Hz, 8.0 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.4, 23.9, 24.1, 28.0, 29.8, 33.9, 44.1, 124.4, 125.7, 126.0, 127.7, 127.9, 128.4, 128.6, 129.8, 130.1, 130.8, 131.4, 131.8, 133.7, 134.8, 135.4, 135.6, 144.3, 148.2, 169.0. IR (CH_2Cl_2) ν 2960, 2924, 1714, 1362, 1260, 1170, 1089, 1020, 803, 672 cm^{-1}. HRMS ($M+H^+$) calcd. for $C_{28}H_{28}O_3NS$: 458.1784, Found: 458.1782.

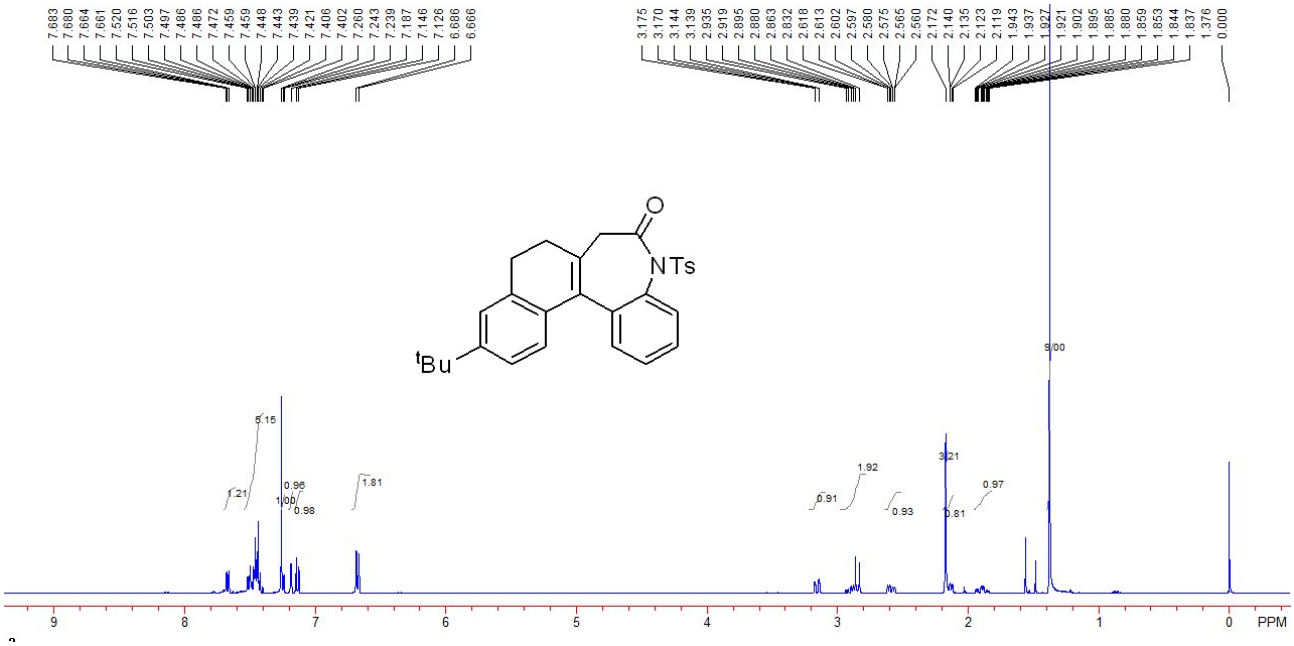


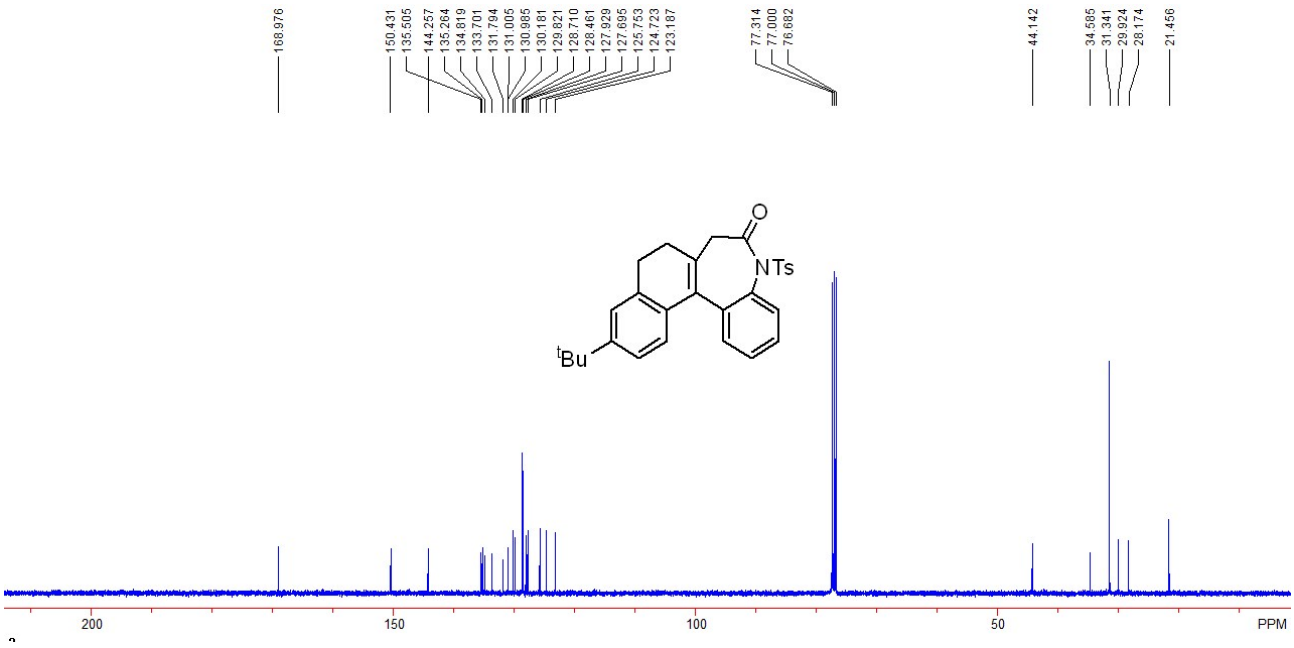


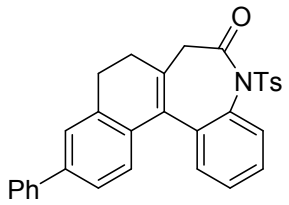


11-(tert-butyl)-5-tosyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (2l).

A white solid, 50.9 mg, 54% yield. M.p.: 244-246 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.38 (s, 9H, CH_3), 1.84-1.94 (m, 1H, CH_2), 2.12-2.14 (m, 1H, CH_2), 2.17 (s, 3H, CH_3), 2.56-2.62 (m, 1H, CH_2), 2.83-2.94 (m, 2H, CH_2), 3.16 (dd, *J* = 2.0 Hz, 12.4 Hz, 1H, CH_2), 6.68 (d, *J* = 8.0 Hz, 2H, ArH), 7.14 (d, *J* = 8.0 Hz, 1H, ArH), 7.19 (s, 1H, ArH), 7.24-7.26 (m, 1H, ArH), 7.40-7.52 (m, 5H, ArH), 7.67 (dd, *J* = 1.2 H, 7.6 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.4, 28.2, 29.9, 31.3, 34.6, 44.1, 123.2, 124.7, 125.8, 127.7, 127.9, 128.5, 128.7, 129.8, 130.2, 130.98, 131.0, 131.8, 133.7, 134.8, 135.3, 135.5, 144.2, 150.4, 169.0. IR (CH_2Cl_2) ν 2963, 2908, 1704, 1364, 1260, 1174, 1118, 1088, 1022, 800 cm^{-1}. HRMS (M+H^{+}) calcd. for $C_{29}H_{30}O_3NS$: 472.1941, Found: 472.1942.

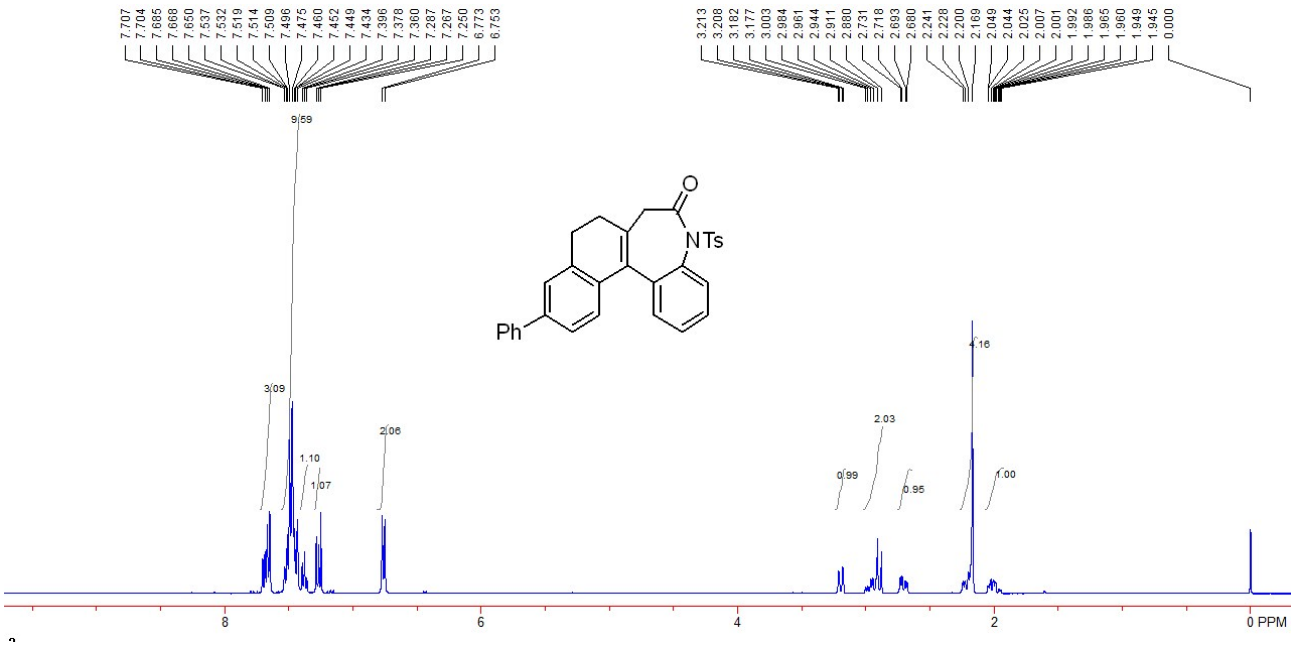


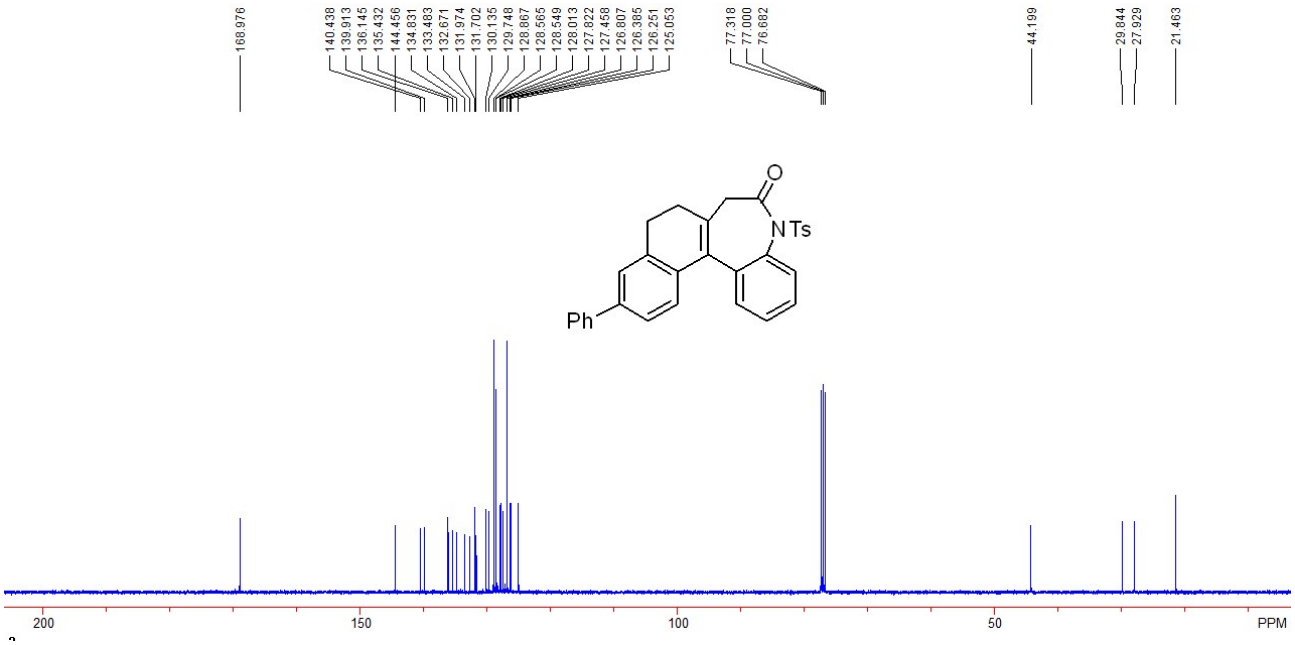


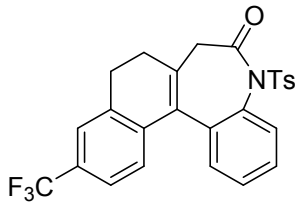


11-phenyl-5-tosyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (2m).

A white solid, 45.2 mg, 46% yield. M.p.: 231-233 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.94-2.05 (m, 1H, CH_2), 2.17-2.24 (m, 1H, CH_2), 2.17 (s, 3H, CH_3), 2.68-2.73 (m, 1H, CH_2), 2.88-3.00 (m, 2H, CH_2), 3.19 (dd, *J* = 2.0 Hz, 12.4 Hz, 1H, CH_2), 6.76 (d, *J* = 8.0 Hz, 2H, ArH), 7.27 (d, *J* = 8.0 Hz, 1H, ArH), 7.38 (t, *J* = 7.2 Hz, 1H, ArH), 7.43-7.54 (m, 9H, ArH), 7.65-7.71 (m, 3H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.5, 27.9, 29.8, 44.2, 125.0, 126.2, 126.4, 126.8, 127.4, 127.8, 128.0, 128.5, 128.6, 128.9, 129.7, 130.1, 131.7, 132.0, 132.7, 133.5, 134.8, 135.4, 136.1, 139.9, 140.4, 144.4, 169.0. IR (CH_2Cl_2) ν 2955, 2922, 2841, 1261, 1164, 1089, 1022, 800, 699 cm^{-1}. HRMS ($M+H^+$) calcd. for $C_{31}H_{26}O_3NS$: 492.1628, Found: 492.1629.



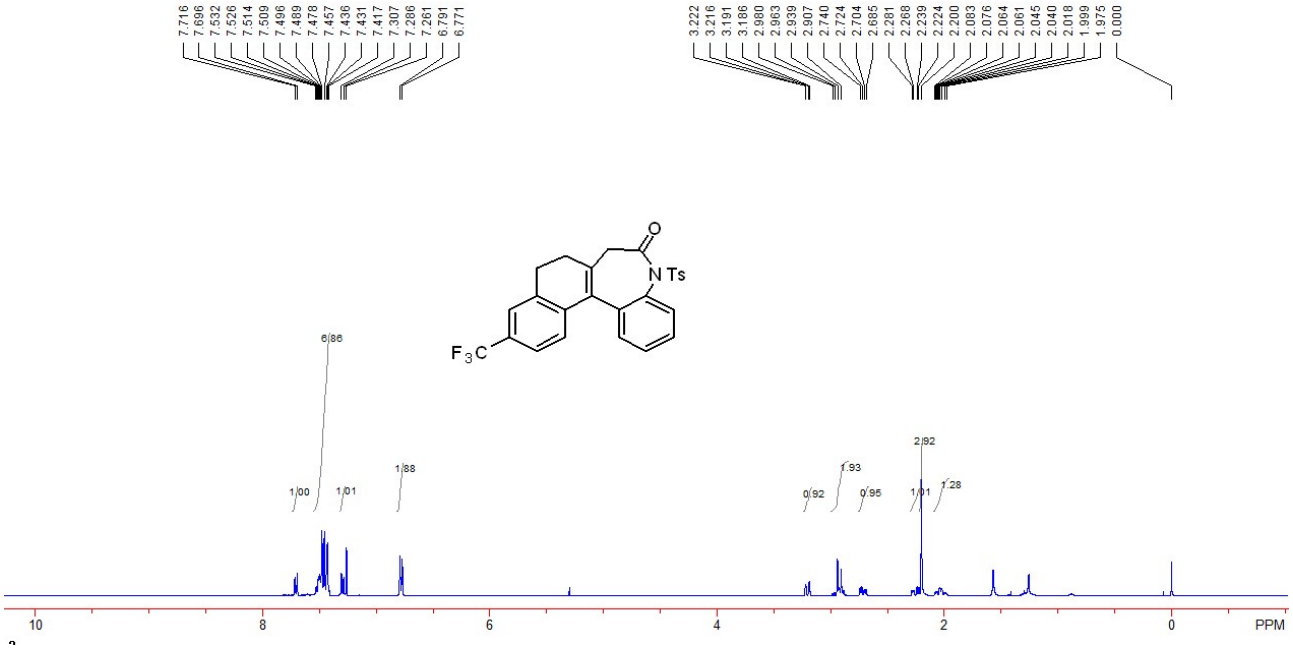


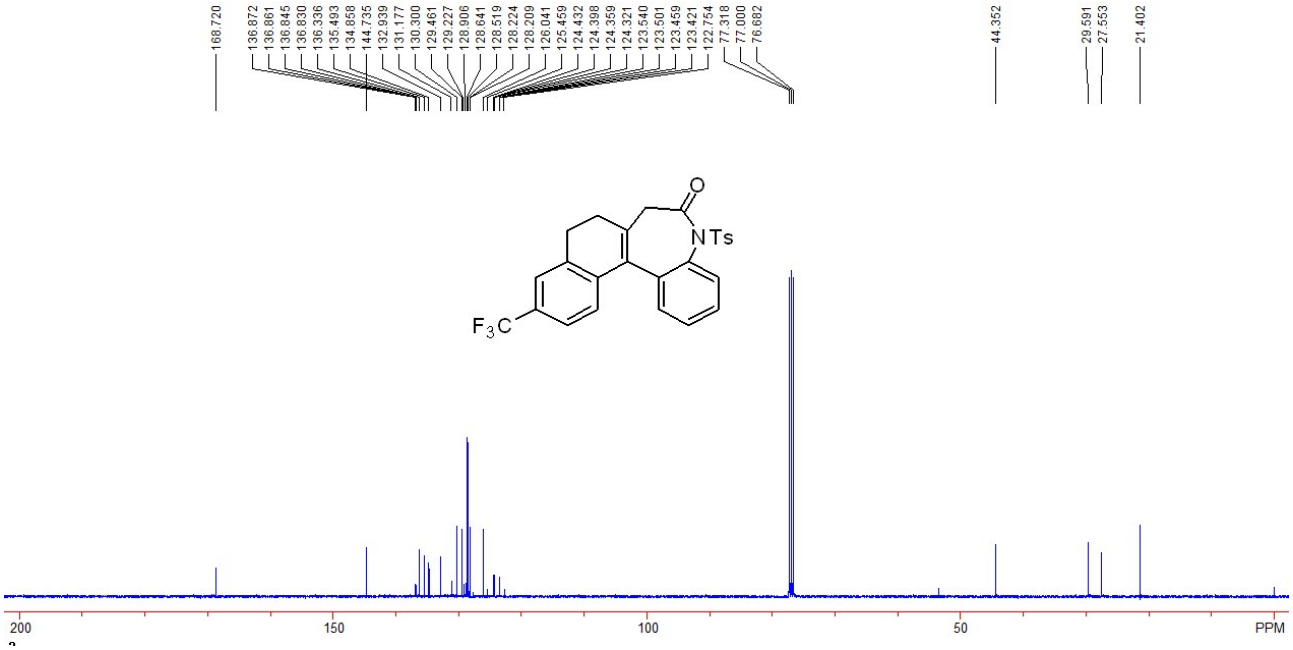


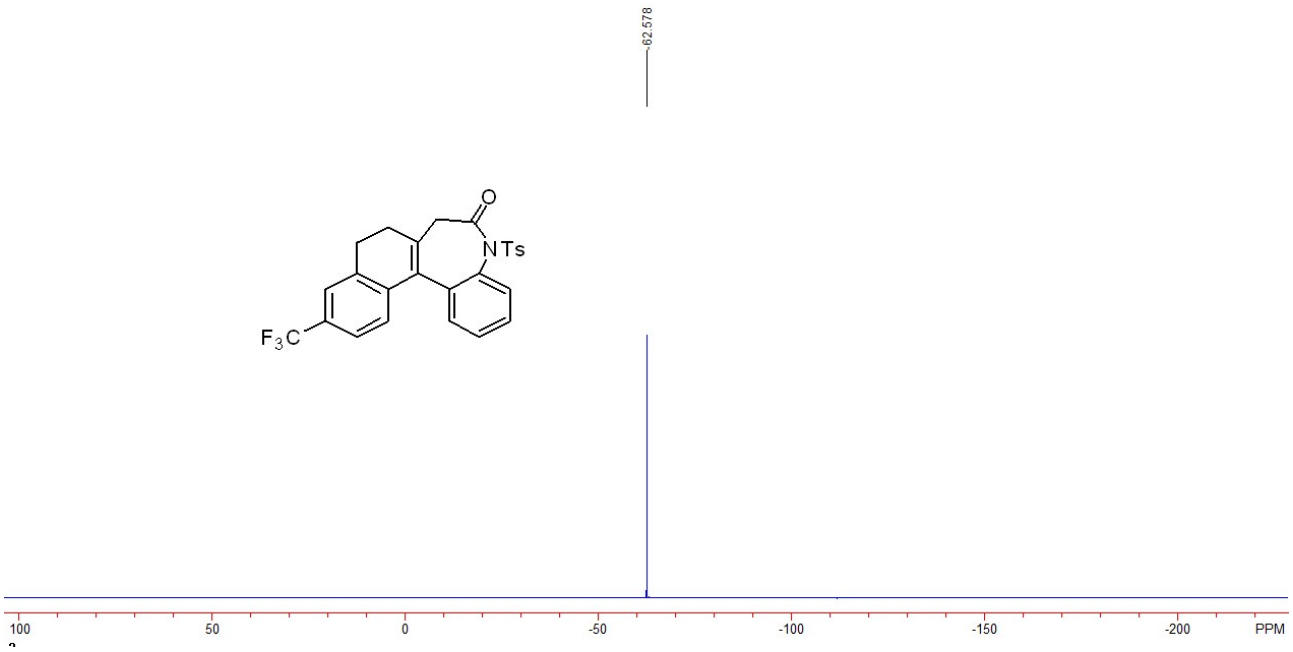
5-tosyl-11-(trifluoromethyl)-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (2n).

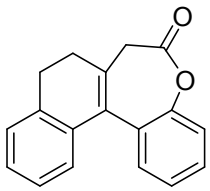
A light yellow solid, 40.6 mg, 42% yield. M.p.: 228-230 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.98-2.08 (m, 1H, CH_2), 2.20 (s, 3H, CH_3), 2.22-2.28 (m, 1H, CH_2), 2.68-2.74 (m, 1H, CH_2), 2.91-2.98 (m, 2H, CH_2), 3.19-3.22 (m, 1H, CH_2), 6.78 (d, J = 8.0 Hz, 2H, ArH), 7.30 (d, J = 8.4 Hz, 1H,

ArH), 7.42-7.53 (m, 7H, ArH), 7.71 (d, J =8.0 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.4, 27.6, 29.6, 44.4, 123.5 (q, J = 4.2 Hz), 124.1 (q, J = 270.5 Hz), 124.4 (q, J = 3.9 Hz), 126.0, 128.21, 128.22, 128.5, 128.6, 129.1 (q, J = 32.1 Hz), 129.5, 130.3, 131.2, 132.9, 134.8, 135.5, 136.3, 136.9 (q, J = 1.6 Hz), 144.7, 168.7. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -62.58. IR (CH_2Cl_2) ν 2969, 2924, 1705, 1320, 1087, 1046, 880, 671 cm^{-1}. HRMS ($M+H^+$) calcd. for $C_{26}H_{21}O_3NF_3S$: 484.1189, Found: 484.1183.



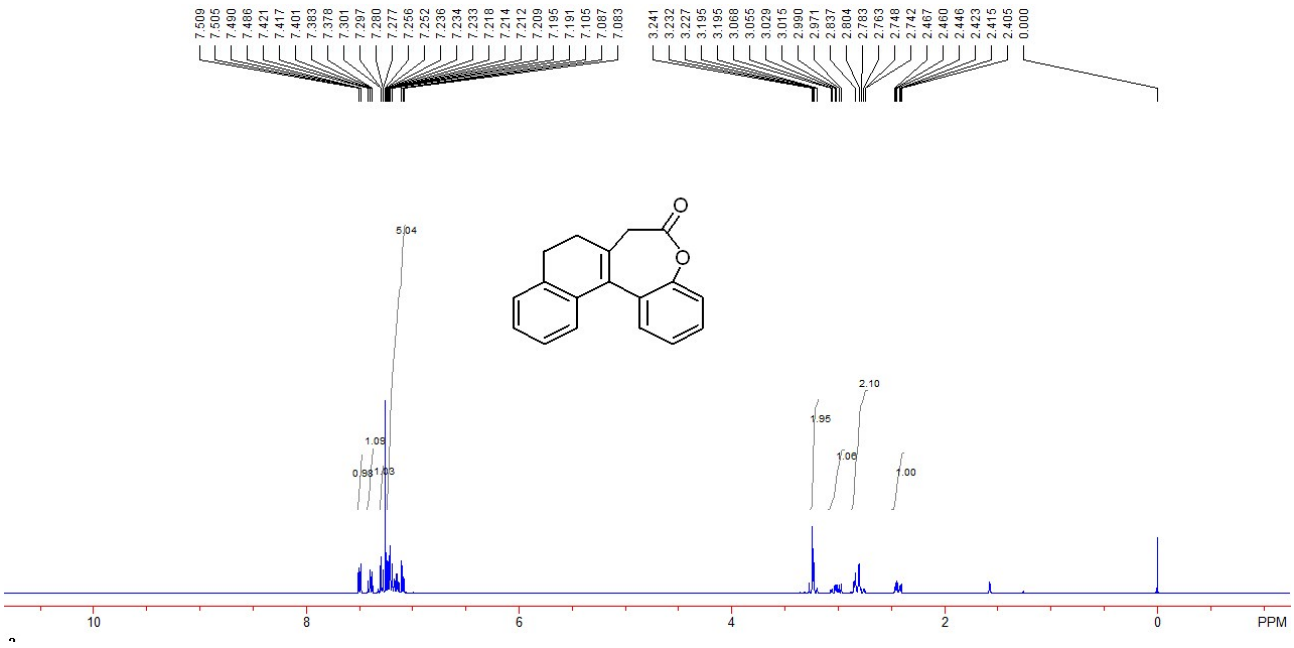


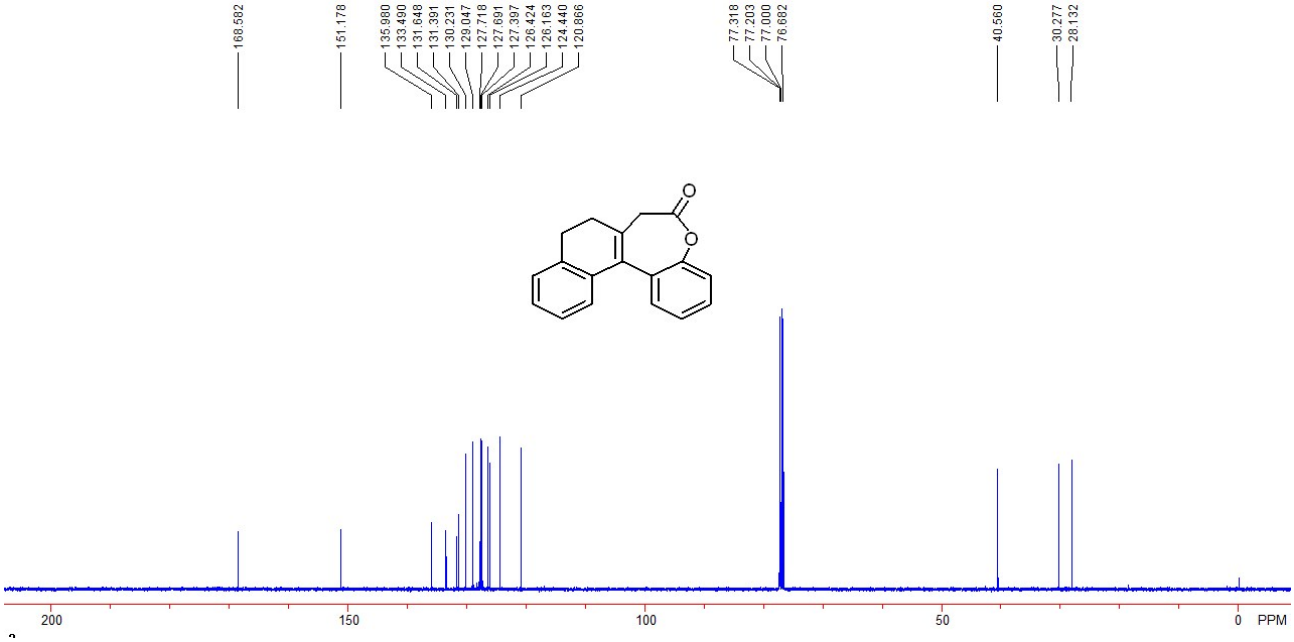


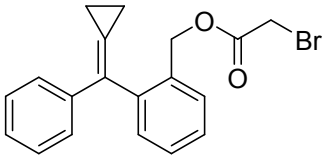


8,9-dihydrobenzo[b]naphtho[1,2-d]oxepin-6(7H)-one (2o).

A colorless oil, 25.2 mg, 45% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.40-2.47 (m, 1H, CH_2), 2.74-2.84 (m, 2H, CH_2), 2.97-3.07 (m, 1H, CH_2), 3.20-3.24 (m, 2H, CH_2), 7.08-7.24 (m, 5H, ArH), 7.29 (dd, *J* = 1.6 Hz, 8.4 Hz, 1H, ArH), 7.38-7.42 (m, 1H, ArH), 7.50 (dd, *J* = 1.6 Hz, 7.6 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 28.1, 30.3, 40.6, 120.9, 124.4, 126.2, 126.4, 127.4, 127.69, 127.72, 129.0, 130.2, 131.4, 131.6, 133.5, 136.0, 151.2, 168.6. IR (CH_2Cl_2) ν 3060, 2974, 2922, 1731, 1485, 1448, 1260, 1205, 1094, 1033, 758 cm^{-1}. HRMS ($M+H^+$) calcd. for $C_{18}H_{15}O_2$: 263.1067, Found: 263.1067.



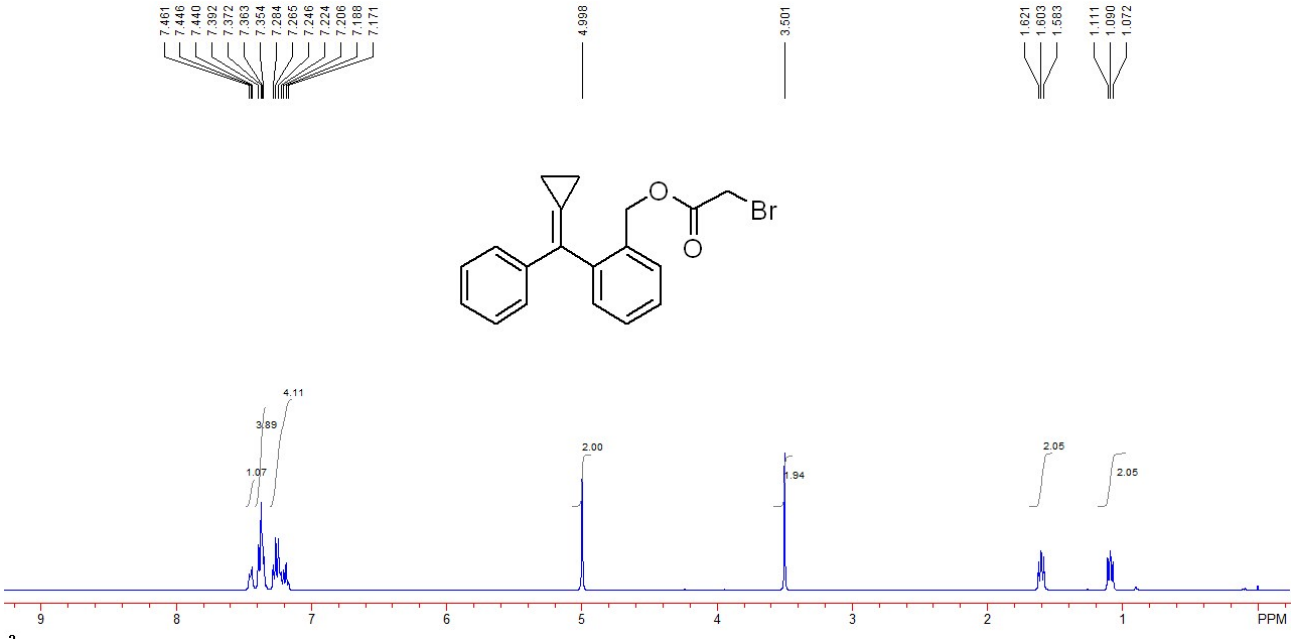


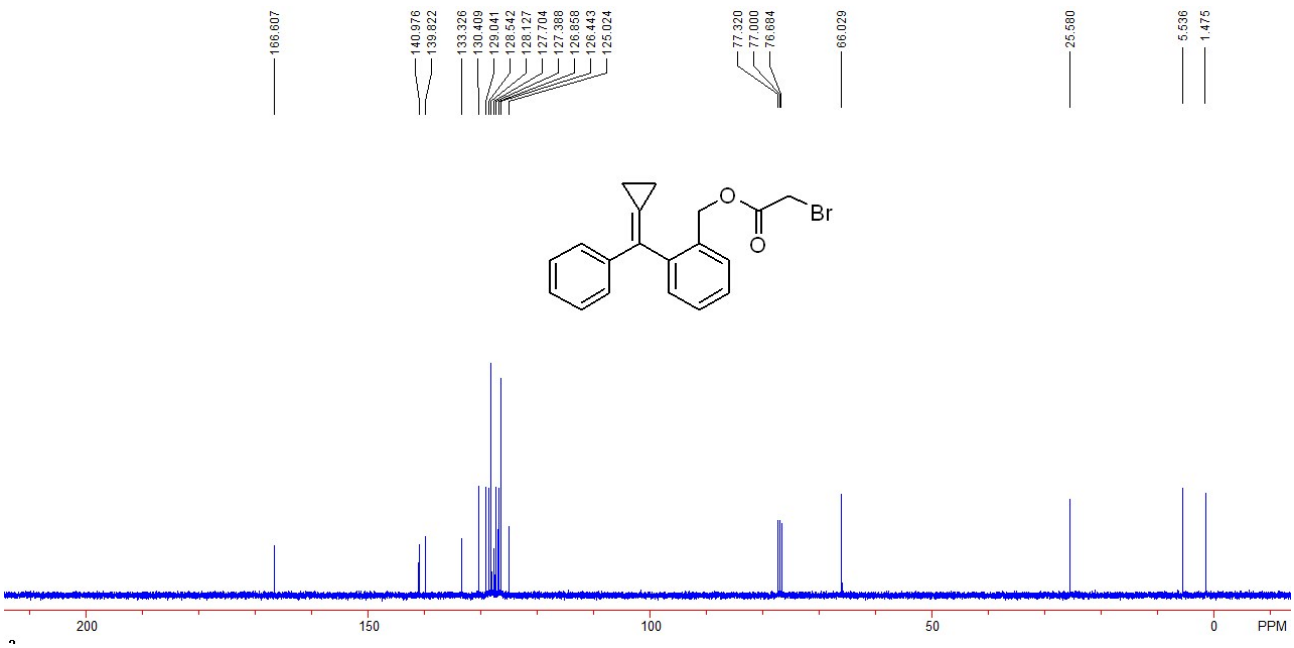


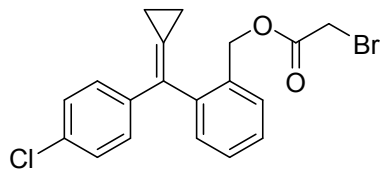
2-(cyclopropylidene(phenyl)methyl)benzyl 2-bromoacetate (3a).

A colorless oil, 643.0 mg, 90% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.09 (t, J = 7.2 Hz, 2H, CH_2), 1.60 (t, J = 7.2 Hz, 2H, CH_2), 3.50 (s, 2H, CH_2), 5.00 (s, 2H, CH_2), 7.17-7.28 (m, 4H, ArH), 7.35-7.39 (m, 4H, ArH), 7.44-7.46 (m, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 1.5, 5.5, 25.6, 66.0, 125.0, 126.4, 126.9, 127.4, 127.7, 128.1, 128.5, 129.0, 130.4, 133.3, 139.8, 141.0, 166.6.

IR (CH_2Cl_2) ν 3056, 2967, 1735, 1274, 1157, 1109, 972, 756, 696 cm^{-1}. HRMS ($M+H^+$) calcd. for $C_{19}H_{18}O_2Br$: 357.0485, Found: 357.0481.



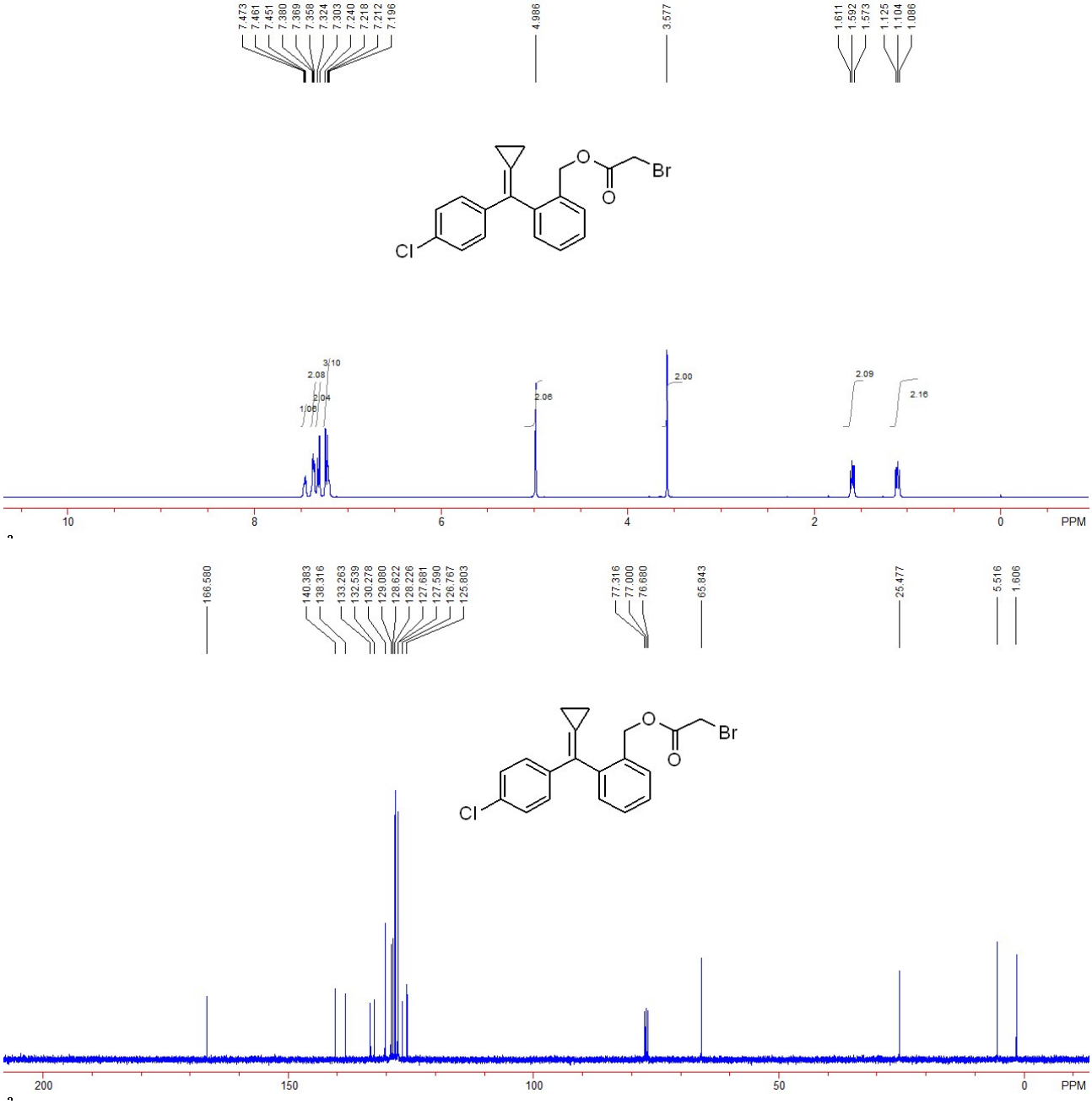


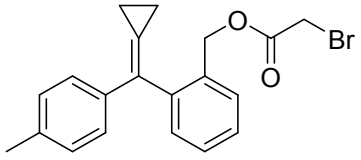


2-((4-chlorophenyl)(cyclopropylidene)methyl)benzyl 2-bromoacetate (3b).

A colorless oil, 658.0 mg, 84% yield. ^1H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.10 (t, J = 7.6 Hz, 2H, CH_2), 1.59 (t, J = 7.6 Hz, 2H, CH_2), 3.58 (s, 2H, CH_2), 4.99 (s, 2H, CH_2), 7.20-7.24 (m, 3H, ArH),

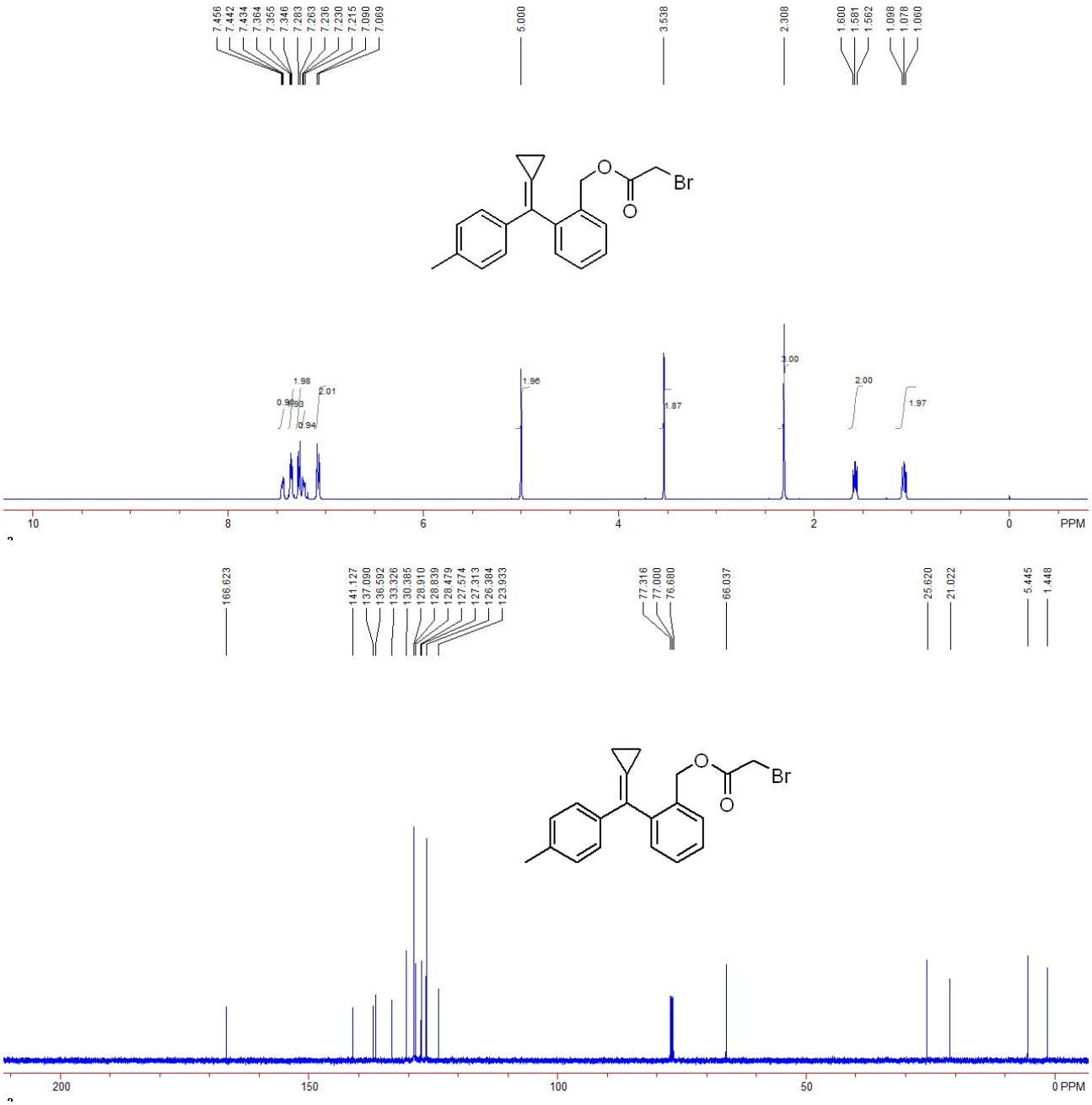
7.31 (d, J = 8.4 Hz, 2H, ArH), 7.36-7.38 (m, 2H, ArH), 7.45-7.47 (m, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 1.6, 5.5, 25.5, 65.8, 125.8, 126.8, 127.6, 127.7, 128.2, 128.6, 129.1, 130.3, 132.5, 133.3, 138.3, 140.4, 166.6. IR (CH_2Cl_2) ν 3058, 2966, 1737, 1489, 1275, 1093, 830, 760 cm^{-1}. HRMS ($M+Na^+$) calcd. for $C_{19}H_{16}O_2BrClNa$: 412.9914, Found: 412.9916.

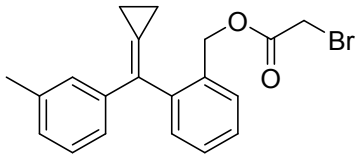




2-(cyclopropylidene(p-tolyl)methyl)benzyl 2-bromoacetate (3c).

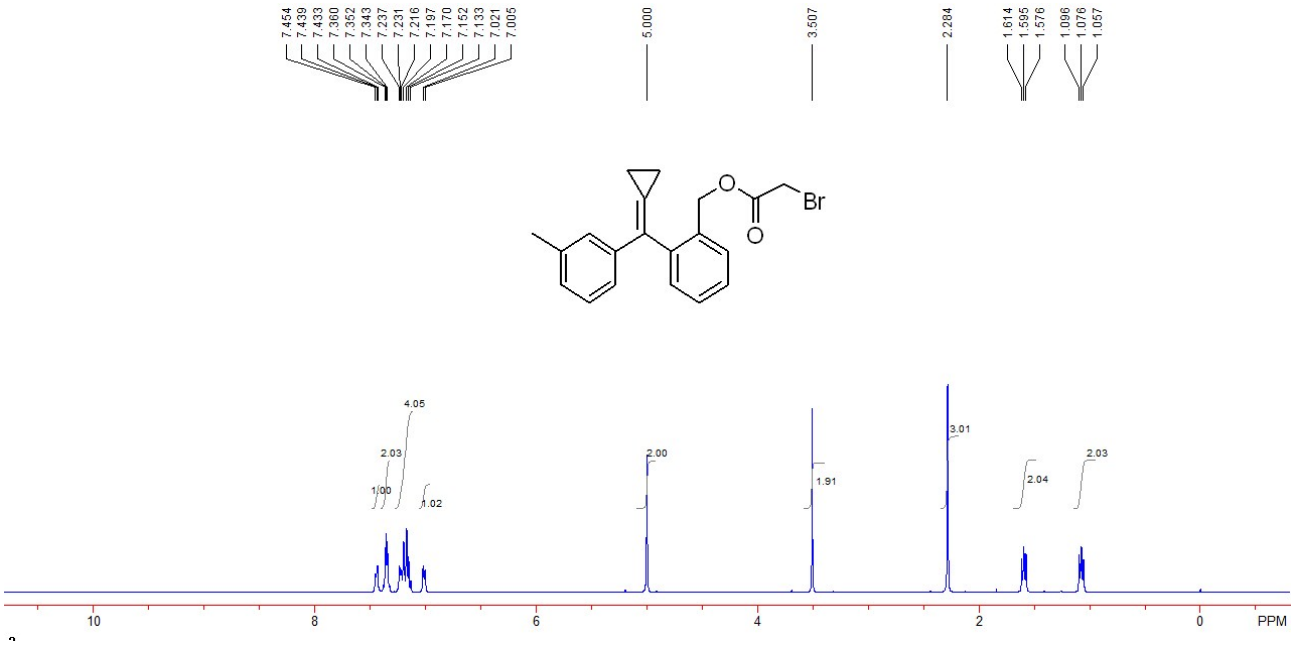
A colorless oil, 660.9 mg, 89% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.08 (t, J = 7.6 Hz, 2H, CH_2), 1.58 (t, J = 7.6 Hz, 2H, CH_2), 2.31 (s, 3H, CH_3), 3.54 (s, 2H, CH_2), 5.00 (s, 2H, CH_2), 7.08 (d, J = 8.4 Hz, 2H, ArH), 7.22-7.24 (m, 1H, ArH), 7.27 (d, J = 8.0 Hz, 2H, ArH), 7.36 (t, J = 3.6 Hz, 2H, ArH), 7.43-7.46 (m, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 1.4, 5.4, 21.0, 25.6, 66.0, 123.9, 126.4, 127.3, 127.6, 128.5, 128.8, 128.9, 130.4, 133.3, 136.6, 137.1, 141.1, 166.6. IR (CH_2Cl_2) ν 3024, 2966, 1736, 1511, 1274, 1156, 1103, 820, 755 cm^{-1}. HRMS ($M+H^+$) calcd. for $C_{20}H_{20}O_2Br$: 371.0641, Found: 371.0637.

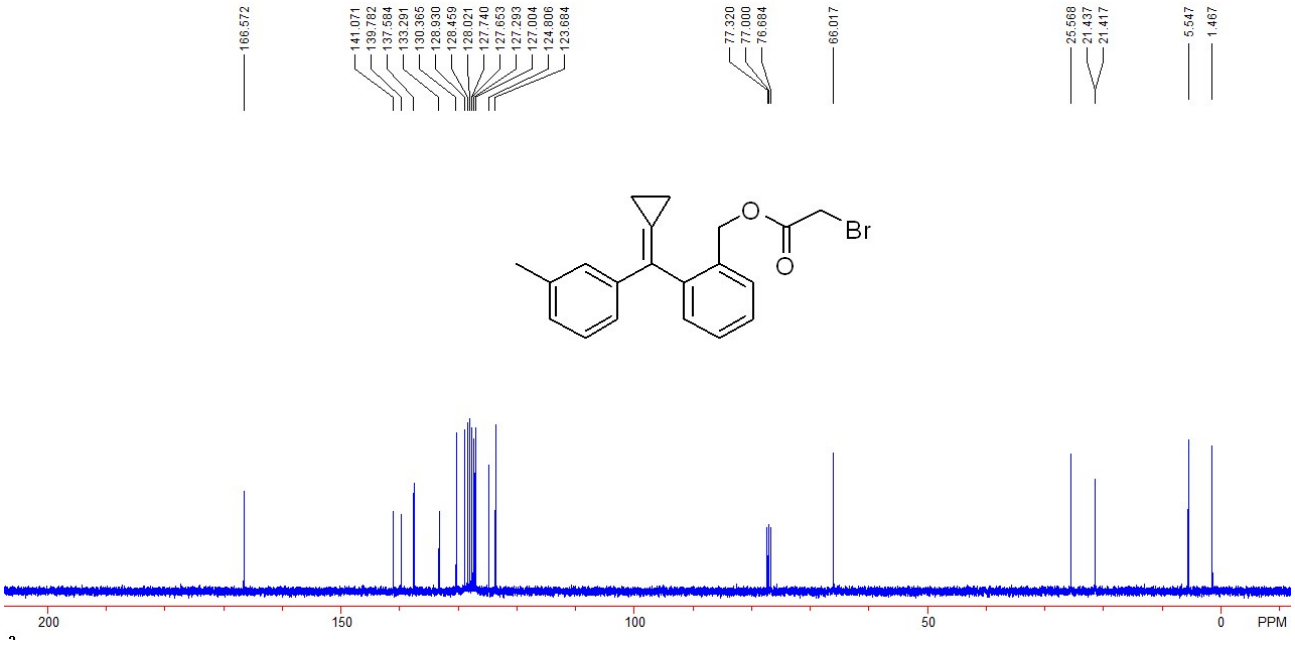


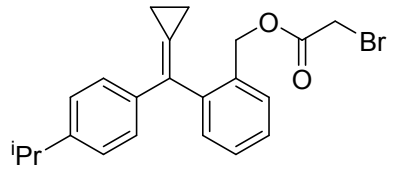


2-(cyclopropylidene(m-tolyl)methyl)benzyl 2-bromoacetate (3d).

A colorless oil, 653.5 mg, 88% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.08 (t, *J* = 7.6 Hz, 2H, CH_2), 1.60 (t, *J* = 7.6 Hz, 2H, CH_2), 2.28 (s, 3H, CH_2), 3.51 (s, 2H, CH_2), 5.00 (s, 2H, CH_2), 7.01 (d, *J* = 6.4 Hz, 1H, ArH), 7.13-7.24 (m, 4H, ArH), 7.34-7.36 (m, 2H, ArH), 7.43-7.45 (m, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 1.5, 5.5, 21.42, 21.44, 25.6, 66.0, 123.7, 124.8, 127.0, 127.3, 127.6, 127.7, 128.0, 128.9, 130.4, 133.3, 137.6, 139.8, 141.1, 166.6. IR (CH_2Cl_2) ν 3016, 2974, 2916, 1736, 1275, 1158, 972, 756, 701 cm^{-1}. HRMS ($M+H^+$) calcd. for $C_{20}H_{20}O_2Br$: 371.0641, Found: 371.0636.

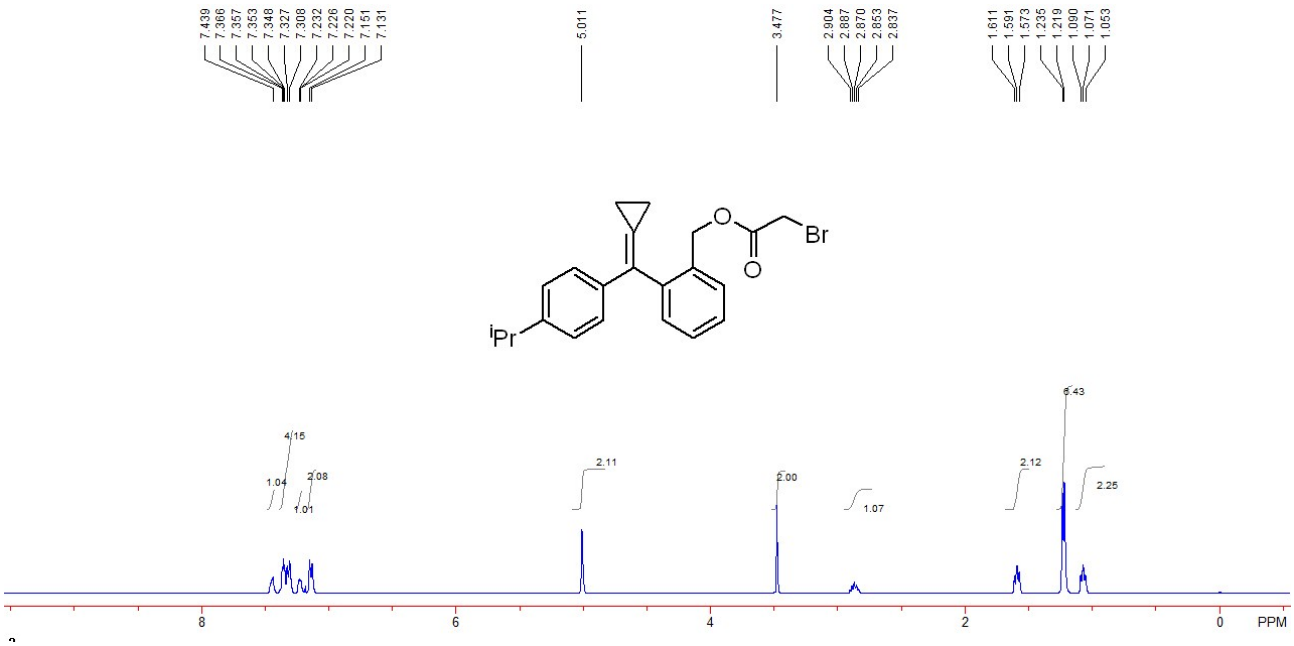


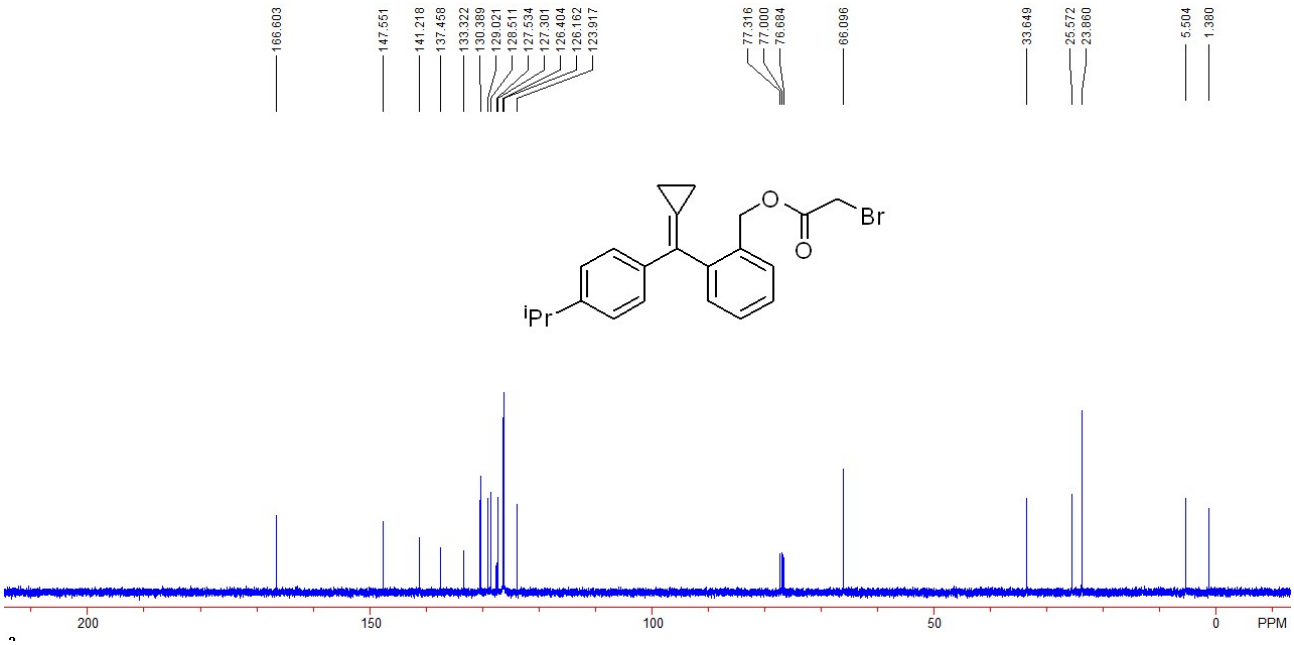


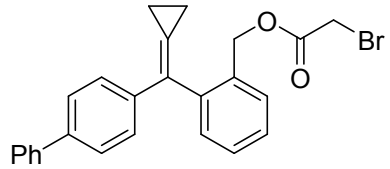


2-(cyclopropylidene(4-isopropylphenyl)methyl)benzyl 2-bromoacetate (3e).

A colorless oil, 734.7 mg, 92% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.07 (t, J = 7.6 Hz, 3H, CH_2), 1.22 (s, 3H, CH_3), 1.24 (s, 3H, CH_3), 1.59 (t, J = 7.6 Hz, 2H, CH_2), 2.87 (sept, J = 6.8 Hz, 1H, CH), 3.48 (s, 2H, CH_2), 5.01 (s, 2H, CH_2), 7.14 (d, J = 8.0 Hz, 2H, ArH), 7.22-7.23 (m, 1H, ArH), 7.31-7.37 (m, 4H, ArH), 7.44 (br, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 1.4, 5.5, 23.9, 25.6, 33.6, 66.1, 123.9, 126.2, 126.4, 127.3, 127.5, 128.5, 129.0, 130.4, 133.3, 137.4, 141.2, 147.6, 166.6. IR (CH_2Cl_2) ν 2959, 2867, 1736, 1511, 1275, 1156, 1105, 833 cm^{-1}. HRMS ($M+H^+$) calcd. for $C_{22}H_{24}O_2Br$: 399.0954, Found: 399.0948.



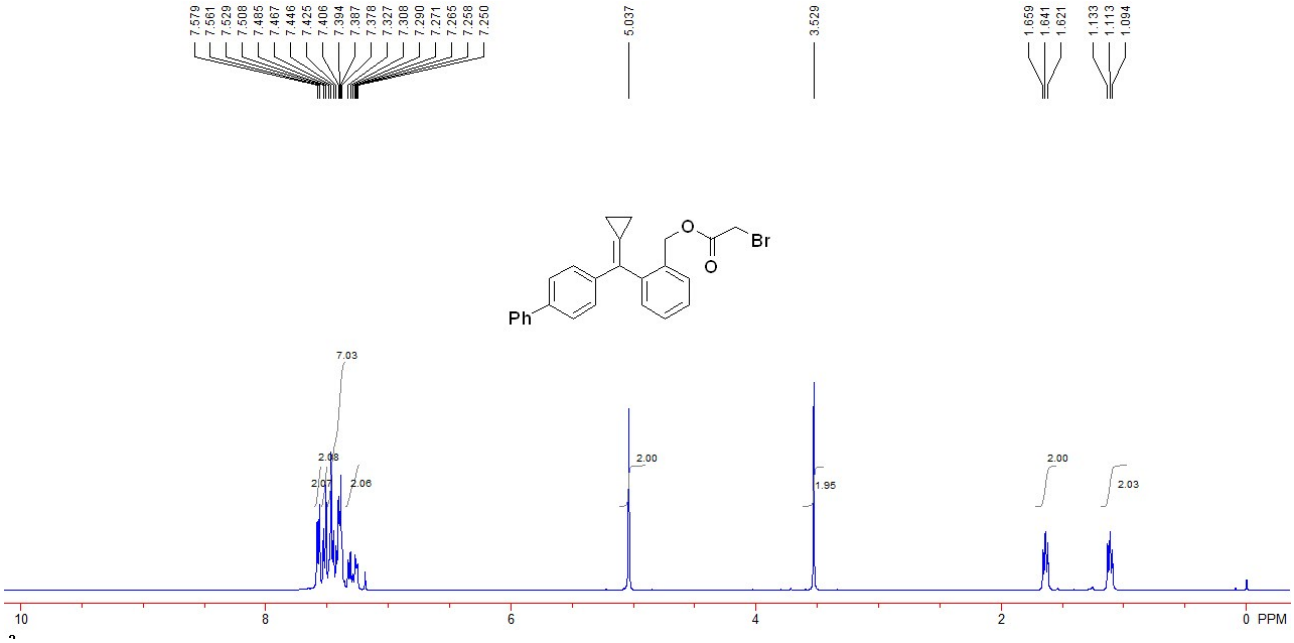


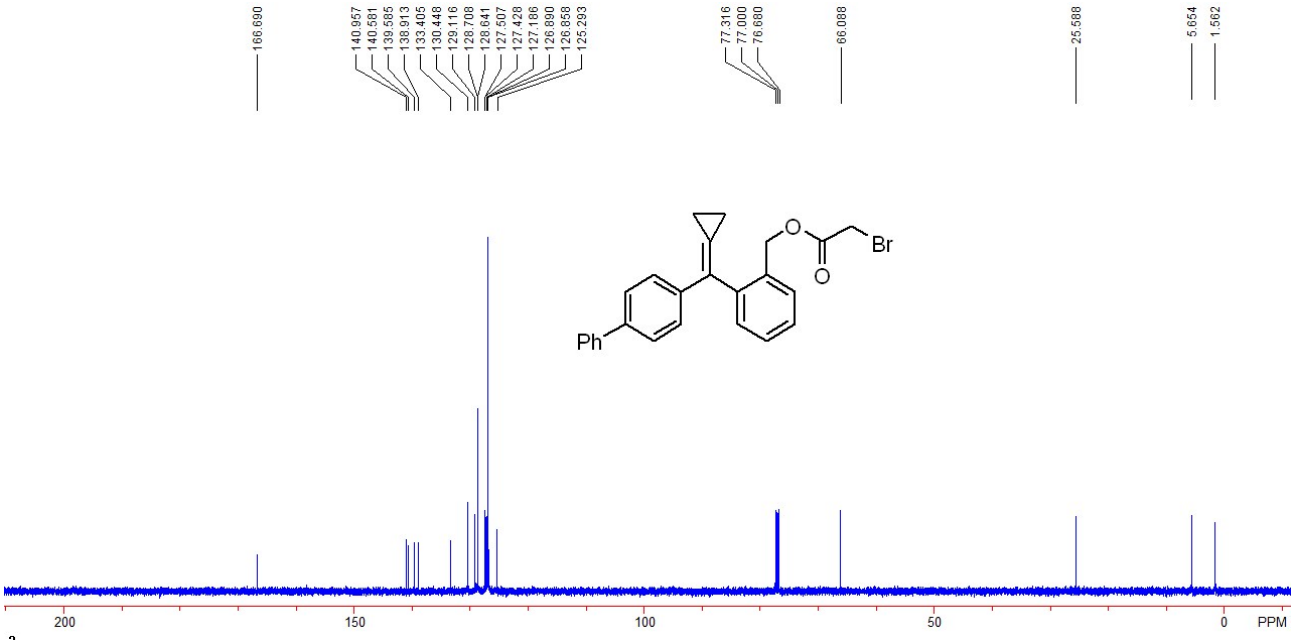


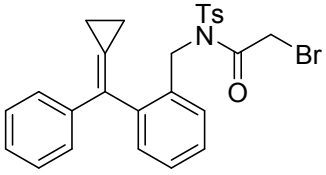
2-([1,1'-biphenyl]-4-yl(cyclopropylidene)methyl)benzyl 2-bromoacetate (3f).

A colorless oil, 736.6 mg, 85% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.11 (t, J = 8.0 Hz, 2H, CH_2), 1.64 (t, J = 8.0 Hz, 2H, CH_2), 3.53 (s, 2H, CH_2), 5.04 (s, 2H, CH_2), 7.25-7.33 (m, 2H, ArH), 7.38-7.48 (m, 7H, ArH), 7.52 (d, J = 8.4 Hz, 2H, ArH), 7.57 (d, J = 7.2 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 1.6, 5.6, 25.6, 66.1, 125.3, 126.8, 126.9, 127.2, 127.4, 127.5, 128.6,

128.7, 129.1, 130.4, 133.4, 138.9, 139.6, 140.6, 141.0, 166.7. IR (CH_2Cl_2) ν 3024, 2916, 1738, 1487, 1276, 1155, 766, 698 cm^{-1}. HRMS ($M+H^+$) calcd. for $C_{25}H_{22}O_2Br$: 433.0798, Found: 433.0796.



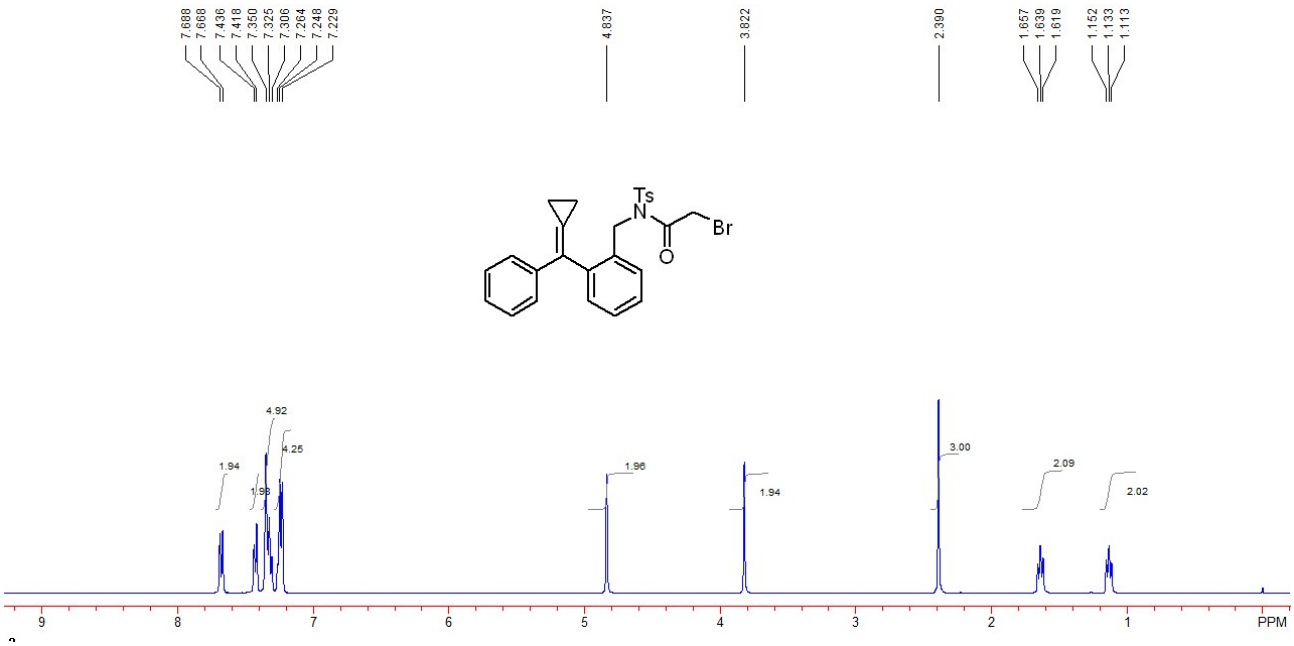


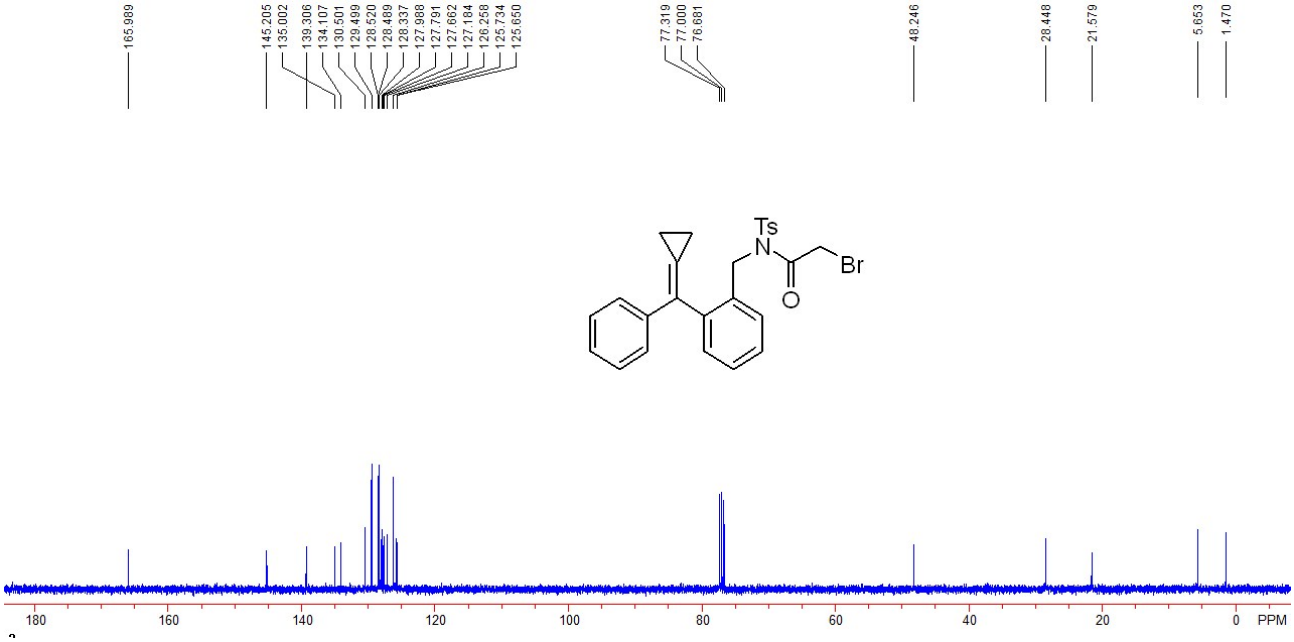


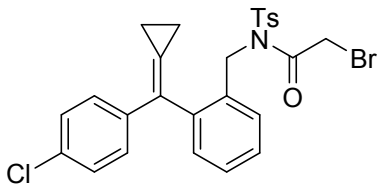
2-bromo-N-(2-(cyclopropylidene(phenyl)methyl)benzyl)-N-tosylacetamide (3g).

A white solid, 510.4 mg, 50% yield. M.p.: 74-76 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.13 (t, *J* = 8.0 Hz, 2H, CH_2), 1.64 (t, *J* = 8.0 Hz, 2H, CH_2), 2.39 (s, 3H, CH_3), 3.82 (s, 2H, CH_2), 4.84 (s, 2H,

CH_2), 7.23-7.26 (m, 4H, ArH), 7.31-7.35 (m, 5H, ArH), 7.43 (d, J = 7.2 Hz, 2H, ArH), 7.68 (d, J = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 1.5, 5.6, 21.6, 28.4, 48.2, 125.6, 125.7, 126.2, 127.2, 127.7, 127.8, 128.0, 128.3, 128.49, 128.52, 129.5, 130.5, 134.1, 135.0, 139.3, 145.2, 166.0. IR (CH_2Cl_2) ν 2954, 2917, 2849, 1704, 1361, 1168, 1088, 760, 660 cm^{-1}. HRMS ($M+H^+$) calcd. for $C_{26}H_{25}O_3NBrS$: 510.0733, Found: 510.0741.

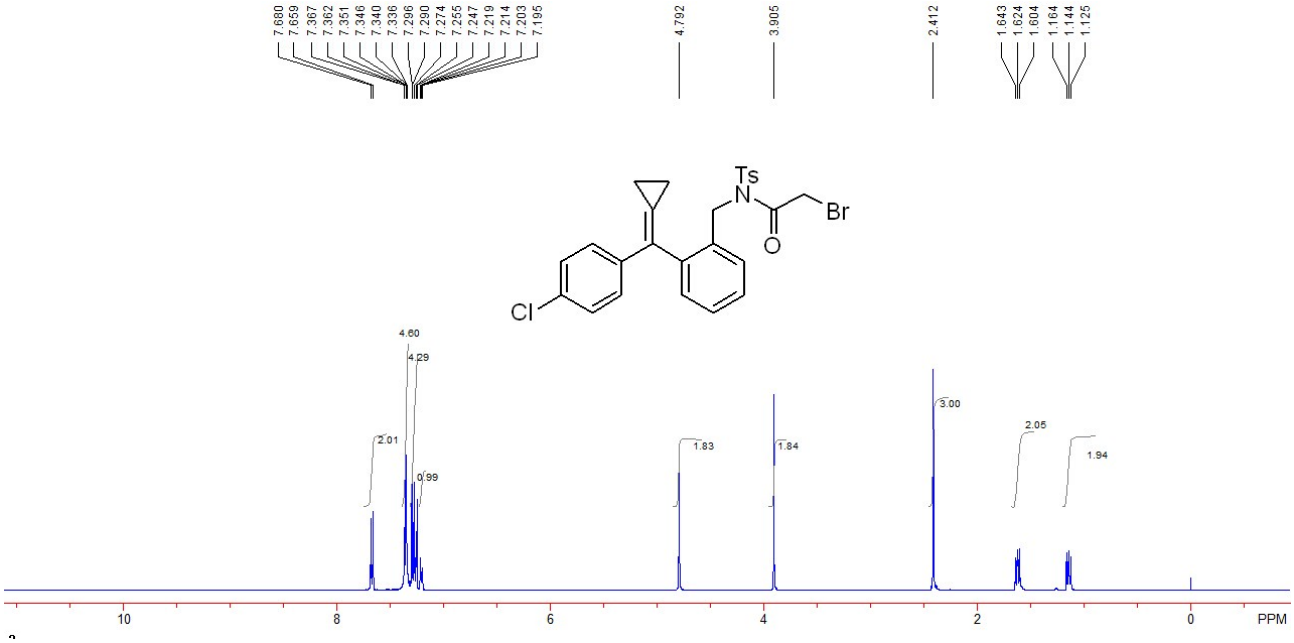


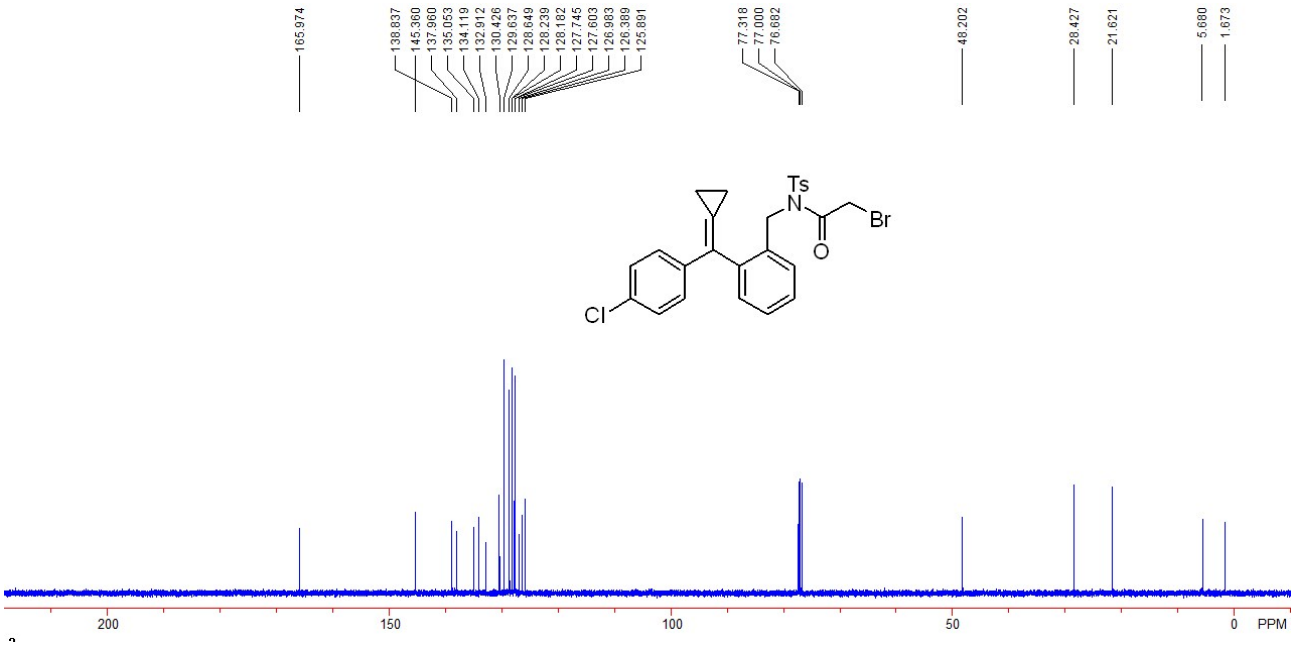


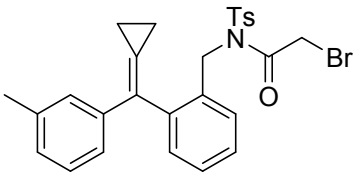


2-bromo-N-(2-((4-chlorophenyl)(cyclopropylidene)methyl)benzyl)-N-tosylacetamide (3h).

A white solid, 555.8 mg, 51% yield. M.p.: 79-81 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.14 (t, *J* = 8.0 Hz, 2H, CH_2), 1.62 (t, *J* = 8.0 Hz, 2H, CH_2), 2.41 (s, 3H, CH_3), 3.90 (s, 2H, CH_2), 4.79 (s, 2H, CH_2), 7.20-7.22 (m, 1H, ArH), 7.25-7.30 (m, 4H, ArH), 7.34-7.37 (m, 5H, ArH), 7.67 (d, *J* = 8.4 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 1.7, 5.7, 21.6, 28.4, 48.2, 125.9, 126.4, 127.0, 127.6, 127.7, 128.18, 128.24, 128.6, 129.6, 130.4, 132.9, 134.1, 135.0, 138.0, 138.8, 145.4, 166.0. IR (CH_2Cl_2) ν 2972, 1700, 1487, 1359, 1167, 1088, 1049, 760, 661 cm^{-1}. HRMS ($M+H^+$) calcd. for $C_{26}H_{24}O_3NBrClS$: 544.0343, Found: 544.0350.

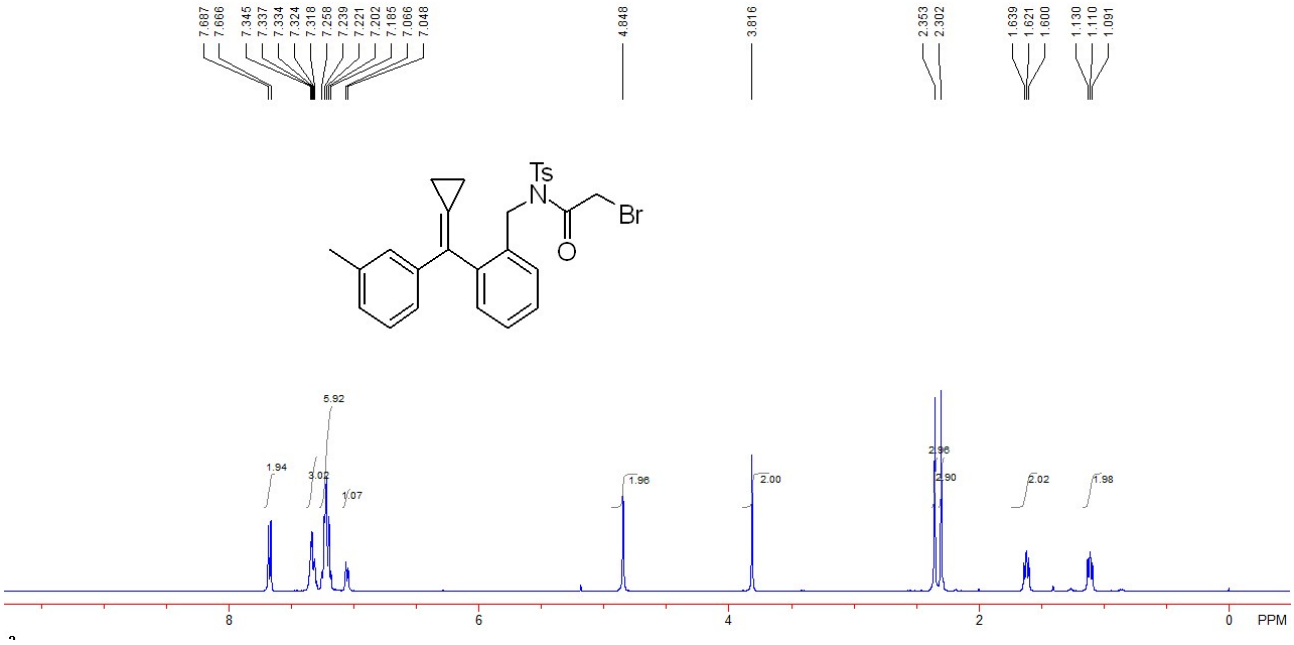


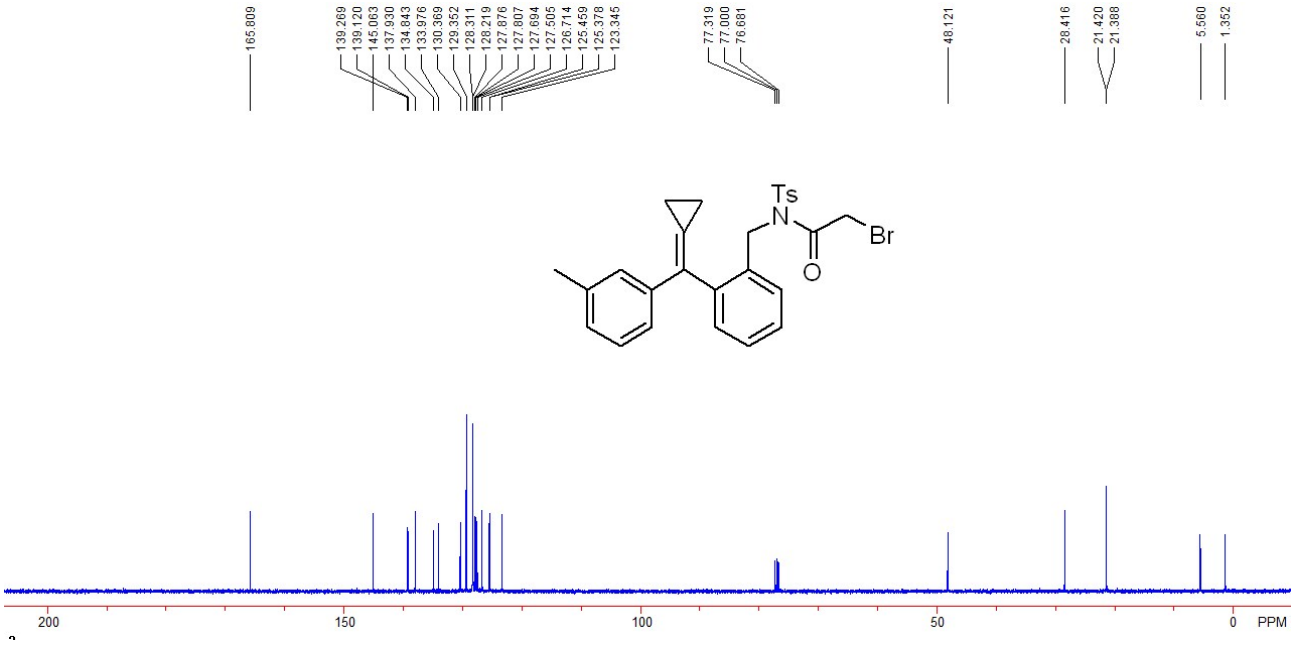


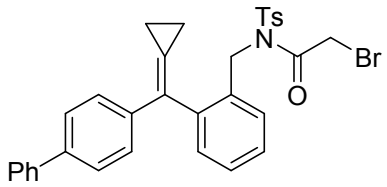


2-bromo-N-(2-(cyclopropylidene(m-tolyl)methyl)benzyl)-N-tosylacetamide (3i).

A white solid, 493.0 mg, 47% yield. M.p.: 69-71 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.11 (t, *J* = 8.0 Hz, 2H, CH_2), 1.62 (t, *J* = 8.0 Hz, 2H, CH_2), 2.30 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 3.82 (s, 2H, CH_2), 4.85 (s, 2H, CH_2), 7.06 (d, *J* = 7.2 Hz, 1H, ArH), 7.18-7.26 (m, 6H, ArH), 7.32-7.34 (m, 3H, ArH), 7.68 (d, *J* = 8.4 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 1.4, 5.6, 21.38, 21.42, 28.4, 48.1, 123.3, 125.4, 125.5, 126.7, 127.5, 127.7, 127.8, 127.9, 128.2, 128.3, 129.4, 130.4, 134.0, 134.8, 137.9, 139.1, 139.3, 145.1, 165.8. IR (CH_2Cl_2) ν 3040, 2958, 1702, 1592, 1485, 1360, 1168, 1087, 663 cm^{-1}. HRMS ($M+H^+$) calcd. for $C_{27}H_{27}O_3NBrS$: 524.0890, Found: 524.0899.

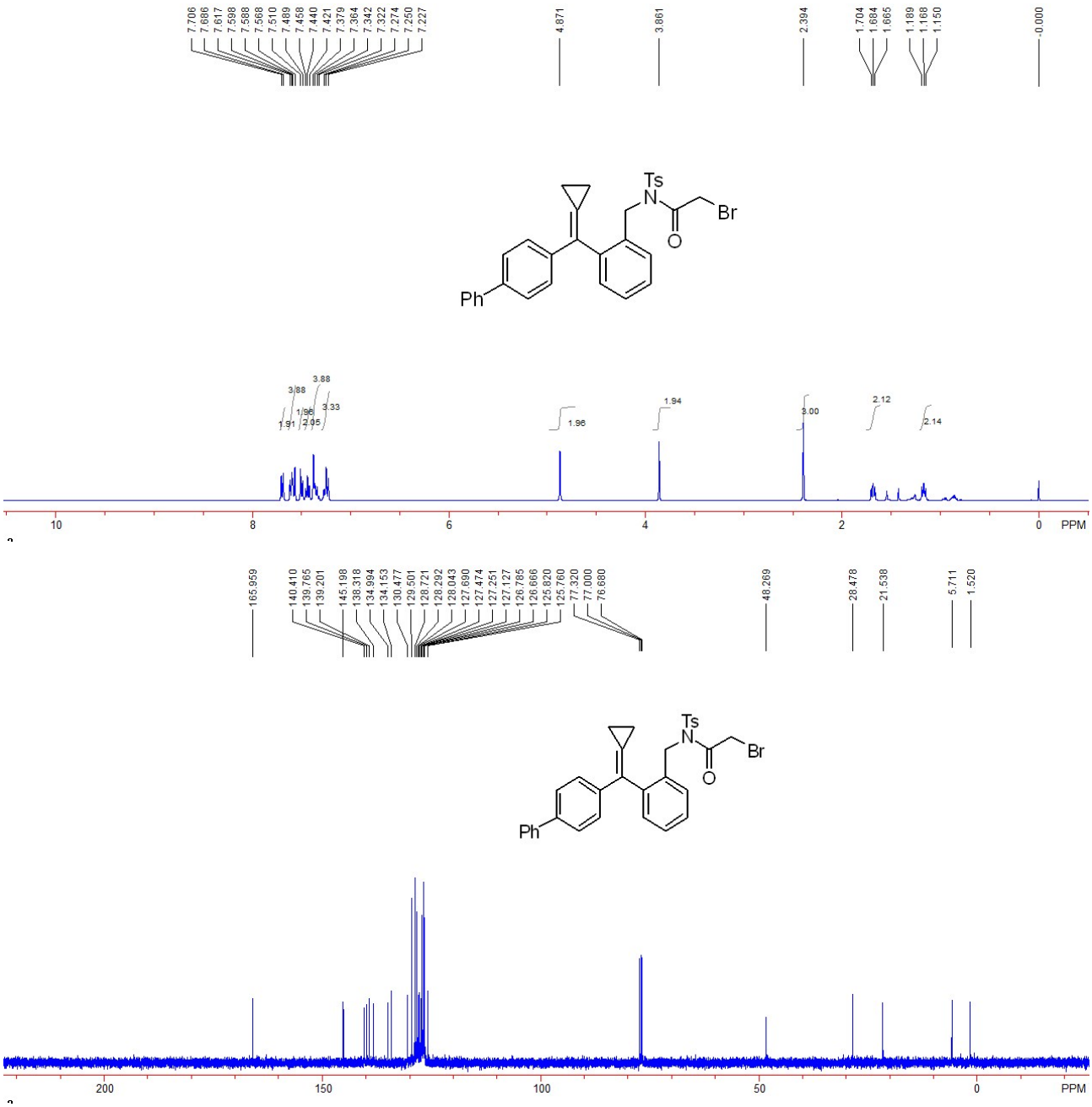






N-(2-([1,1'-biphenyl]-4-yl(cyclopropylidene)methyl)benzyl)-2-bromo-N-tosylacetamide (3j).

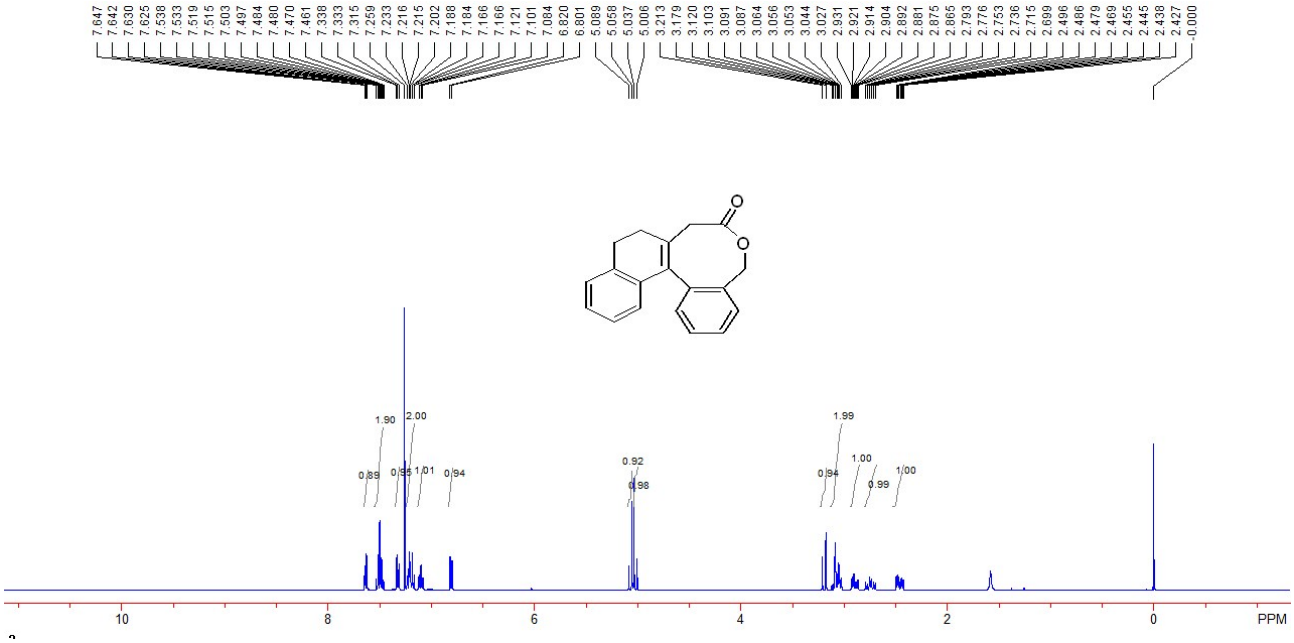
A white solid, 527.8 mg, 45% yield. M.p.: 89-91 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.17 (t, *J* = 8.0 Hz, 2H, CH_2), 1.68 (t, *J* = 8.0 Hz, 2H, CH_2), 2.39 (s, 3H, CH_3), 3.86 (s, 2H, CH_2), 4.87 (s, 2H, CH_2), 7.23-7.27 (m, 3H, ArH), 7.32-7.38 (m, 4H, ArH), 7.44 (t, *J* = 7.2 Hz, 2H, ArH), 7.50 (d, *J* = 8.4 Hz, 2H, ArH), 7.57-7.62 (m, 4H, ArH), 7.70 (d, *J* = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 1.5, 5.7, 21.5, 28.5, 48.3, 125.76, 125.82, 126.7, 126.8, 127.1, 127.2, 127.5, 127.6, 128.0, 128.3, 128.7, 129.5, 130.5, 134.2, 135.0, 138.3, 139.2, 139.8, 140.4, 145.2, 166.0. IR (CH_2Cl_2) ν 3029, 2914, 2848, 2040, 1703, 1487, 1360, 1169, 1087, 840, 767, 659 cm^{-1}. HRMS ($M+Na^+$) calcd. for $C_{32}H_{28}O_3NBrNaS$: 608.0865, Found: 608.0870.

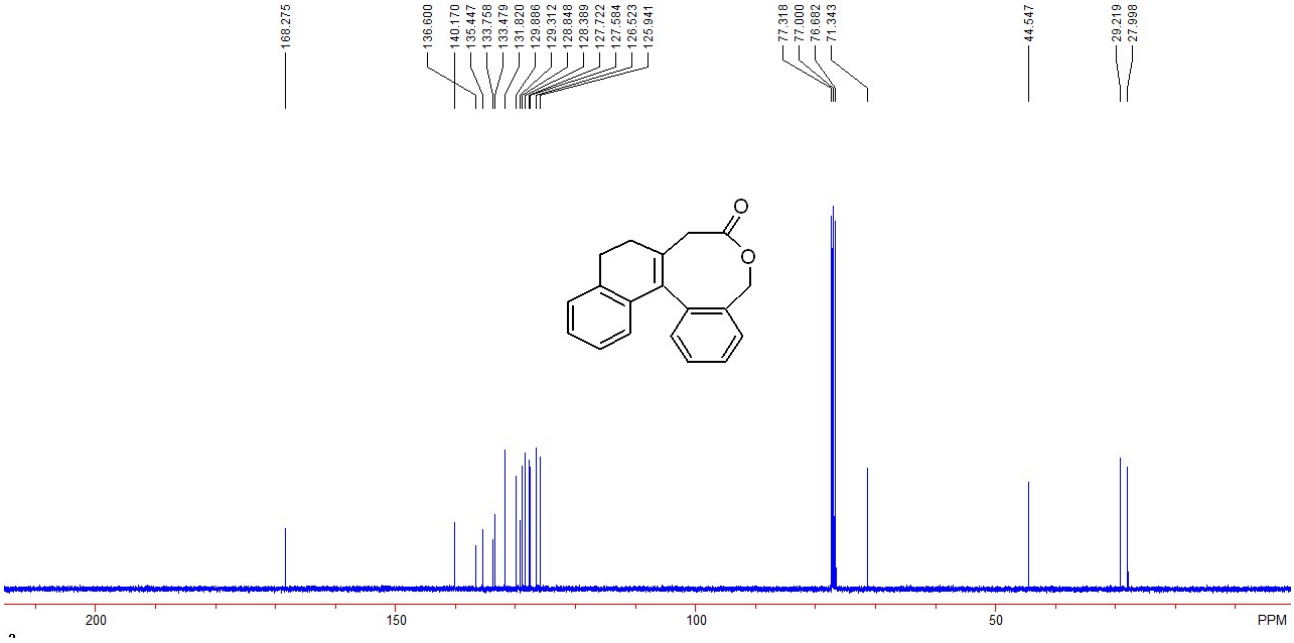


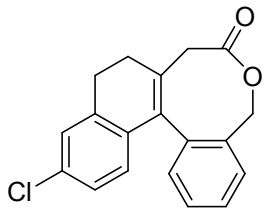
5,8,9,10-tetrahydro-7H-benzo[c]naphtho[1,2-e]oxocin-7-one (4a).

A colorless oil, 19.3 mg, 35% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.43-2.50 (m, 1H, CH_2), 2.70-2.79 (m, 1H, CH_2), 2.86-2.93 (m, 1H, CH_2), 3.03-3.12 (m, 2H, CH_2), 3.20 (d, J = 14.4 Hz, 1H, CH_2), 5.02 (d, J = 12.4 Hz, 1H, CH_2), 5.07 (d, J = 12.4 Hz, 1H, CH_2), 6.81 (d, J = 7.6 Hz, 1H, ArH),

7.08-7.12 (m, 1H, ArH), 7.17-7.23 (m, 2H, ArH), 7.32-7.34 (m, 1H, ArH), 7.46-7.54 (m, 2H, ArH), 7.64 (dd, J = 2.0 Hz, 6.8 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 28.0, 29.2, 44.5, 71.3, 125.9, 126.5, 127.6, 128.4, 128.8, 129.3, 129.9, 131.8, 133.5, 133.8, 135.4, 136.6, 140.2, 168.3. IR (CH_2Cl_2) ν 3066, 2924, 2828, 1730, 1487, 1448, 1188, 1019, 770 cm^{-1}. HRMS ($M+H^+$) calcd. for $C_{19}H_{17}O_2$: 277.1223, Found: 277.1220.

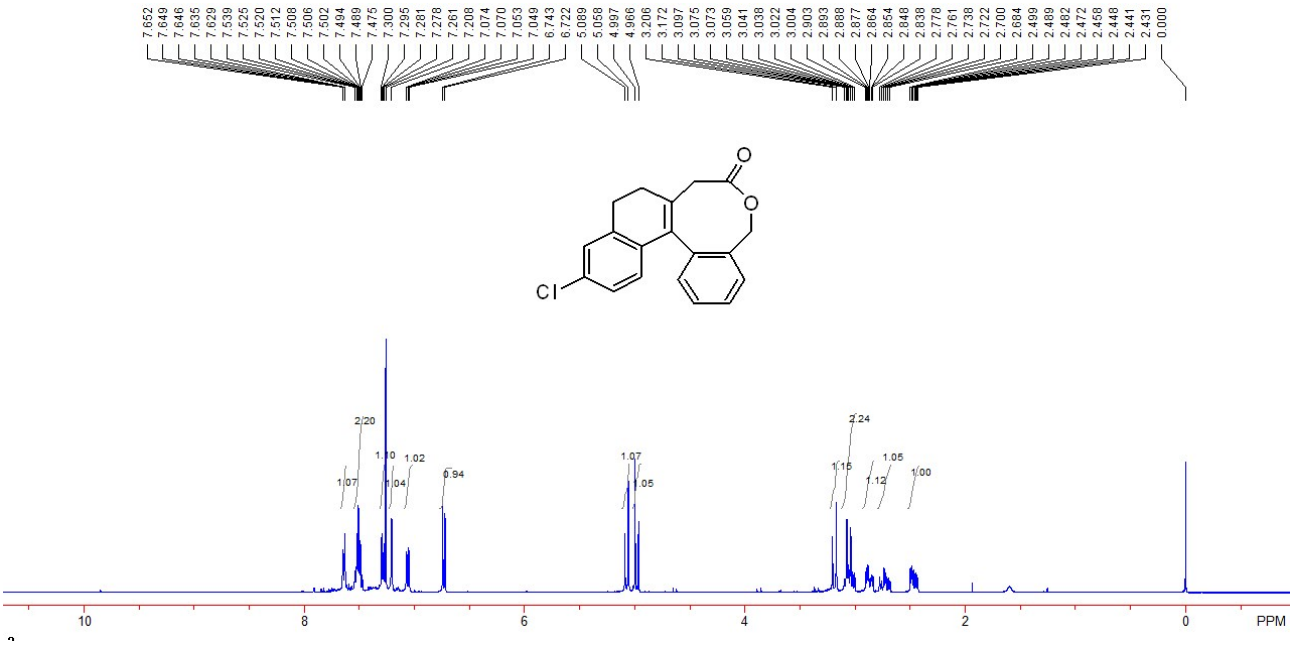


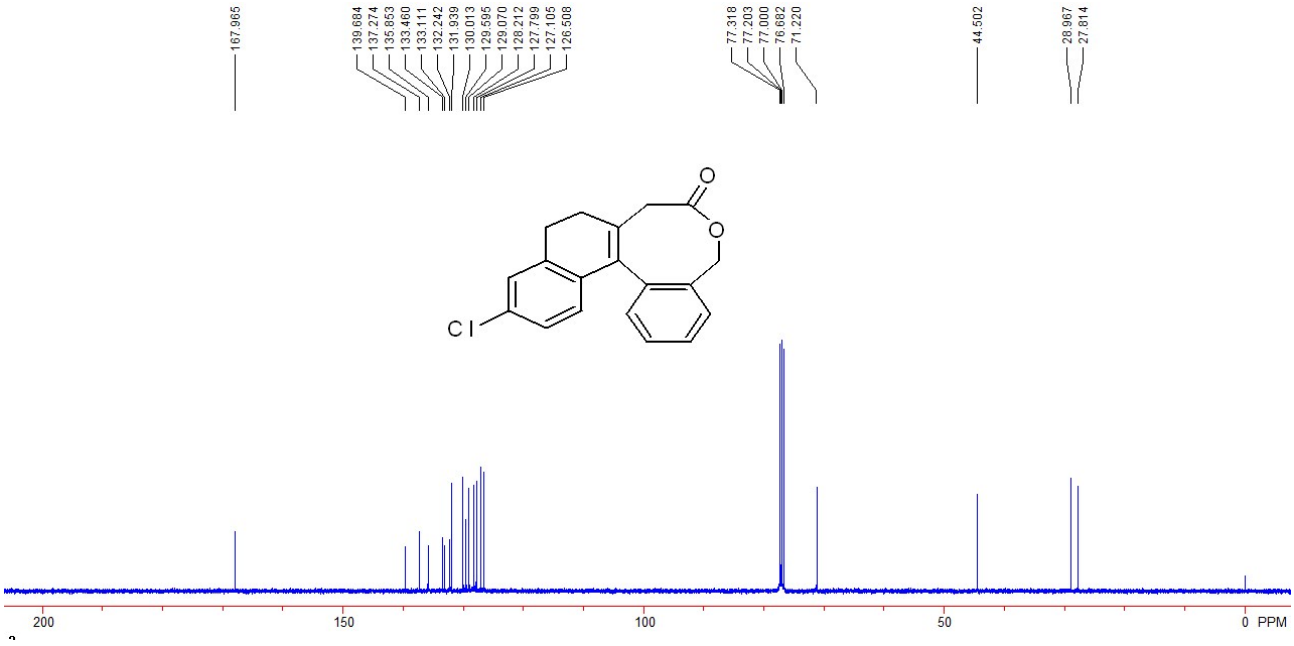


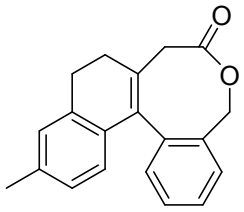


12-chloro-5,8,9,10-tetrahydro-7H-benzo[c]naphtho[1,2-e]oxocin-7-one (4b).

A colorless oil, 17.4 mg, 28% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.43-2.50 (m, 1H, CH_2), 2.68-2.78 (m, 1H, CH_2), 2.84-2.90 (m, 1H, CH_2), 3.00-3.10 (m, 2H, CH_2), 3.19 (d, *J* = 15.6 Hz, 1H, CH_2), 4.98 (d, *J* = 12.4 Hz, 1H, CH_2), 5.07 (d, *J* = 12.4 Hz, 1H, CH_2), 6.73 (d, *J* = 8.4 Hz, 1H, ArH), 7.06 (dd, *J* = 1.6 Hz, 8.4 Hz, 1H, ArH), 7.21 (s, 1H, ArH), 7.26-7.30 (m, 1H, ArH), 7.48-7.54 (m, 2H, ArH), 7.63-7.65 (m, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 27.8, 29.0, 44.5, 71.2, 126.5, 127.1, 127.8, 128.2, 129.1, 129.6, 130.0, 131.9, 132.2, 133.1, 133.5, 135.8, 137.3, 139.7, 168.0. IR (CH_2Cl_2) ν 3060, 2927, 1732, 1490, 1182, 1011, 823, 760 cm^{-1}. HRMS ($M+H^+$) calcd. for $C_{19}H_{16}O_2Cl$: 311.0833, Found: 311.0831.

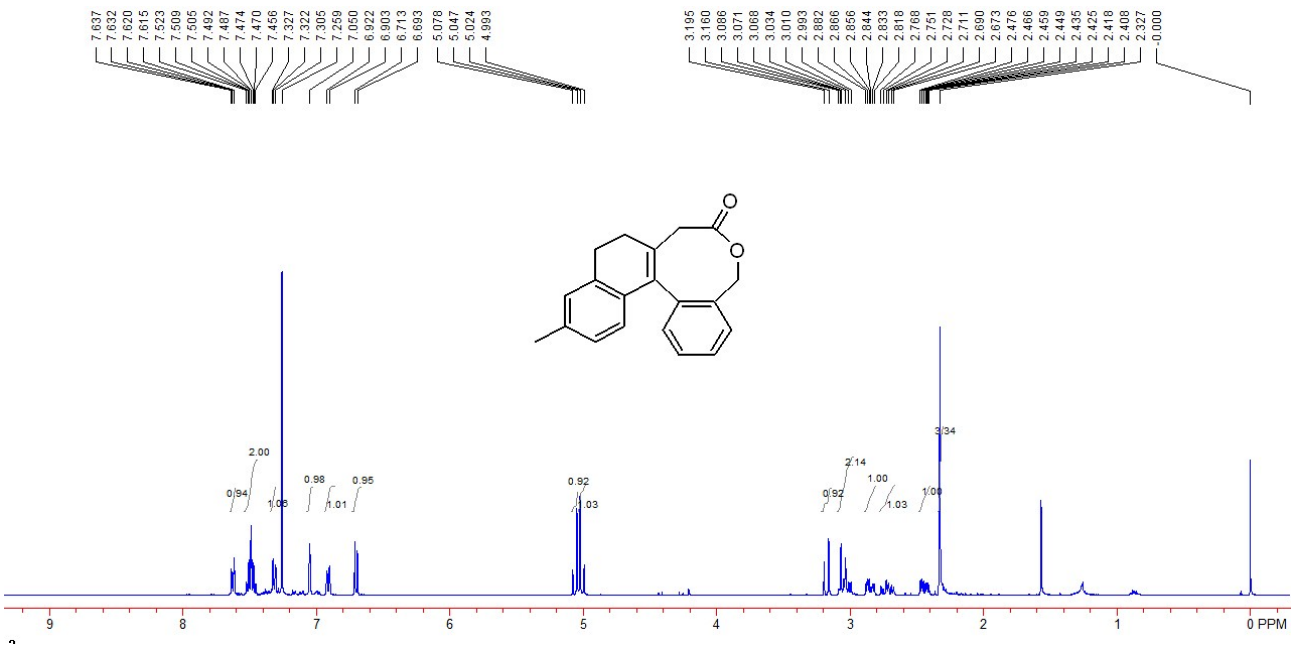


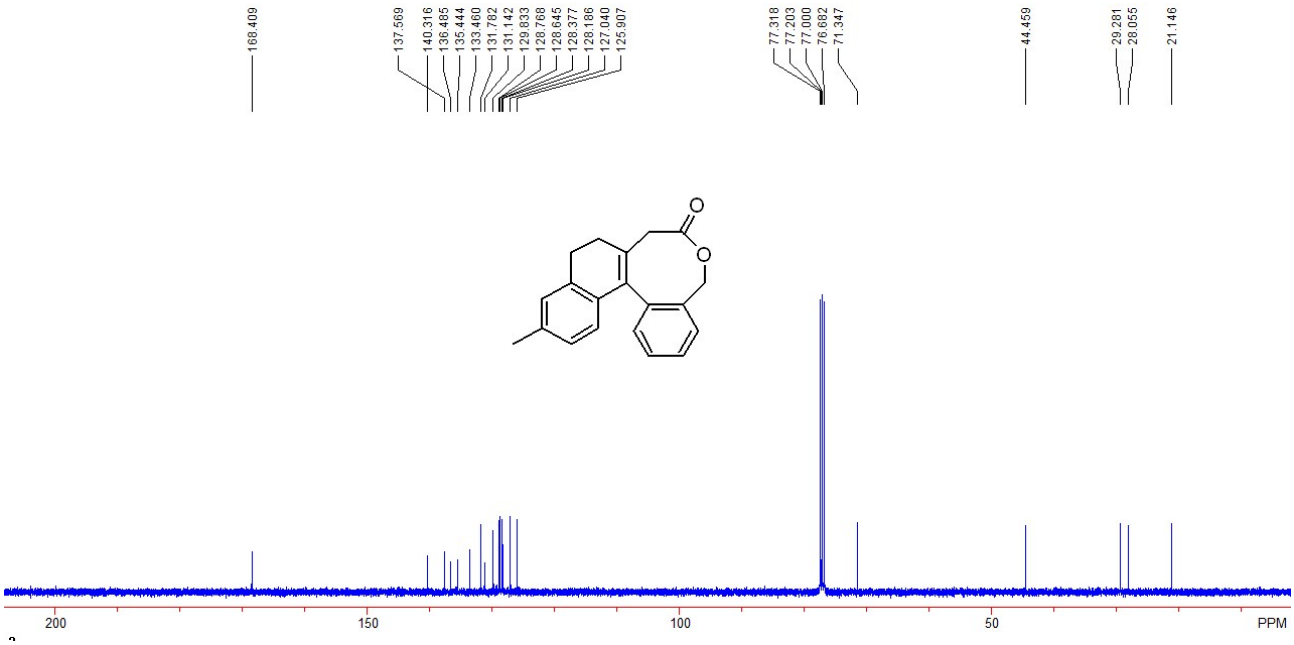


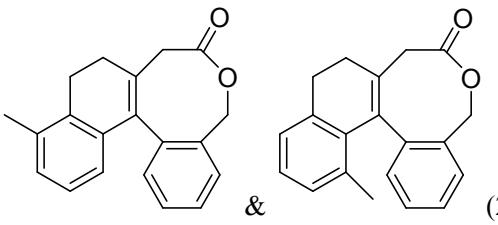


12-methyl-5,8,9,10-tetrahydro-7H-benzo[c]naphtho[1,2-e]oxocin-7-one (4c).

A colorless oil, 8.7 mg, 15% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.33 (s, 3H, CH_3), 2.41-2.48 (m, 1H, CH_2), 2.67-2.77 (m, 1H, CH_2), 2.82-2.88 (m, 1H, ArH), 2.99-3.09 (m, 2H, CH2), 3.18 (d, *J* = 14.0 Hz, 1H, CH_2), 5.01 (d, *J* = 12.4 Hz, 1H, CH_2), 5.06 (d, *J* = 12.4 Hz, 1H, CH_2), 6.70 (d, *J* = 8.0 Hz, 1H, ArH), 6.91 (d, *J* = 7.6 Hz, 1H, ArH), 7.05 (s, 1H, ArH), 7.30-7.33 (m, 1H, ArH), 7.46-7.52 (m, 2H, ArH), 7.63 (dd, *J* = 2.0 Hz, 7.2 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.1, 28.0, 29.3, 44.4, 71.3, 125.9, 127.0, 128.2, 128.4, 128.6, 128.8, 129.8, 131.1, 131.8, 133.5, 135.4, 136.5, 137.6, 140.3, 168.4. IR (CH_2Cl_2) ν 2922, 1728, 1707, 1493, 1443, 1193, 822, 759 cm^{-1}. HRMS ($M+H^+$) calcd. for $C_{20}H_{19}O_2$: 291.1380, Found: 291.1377.







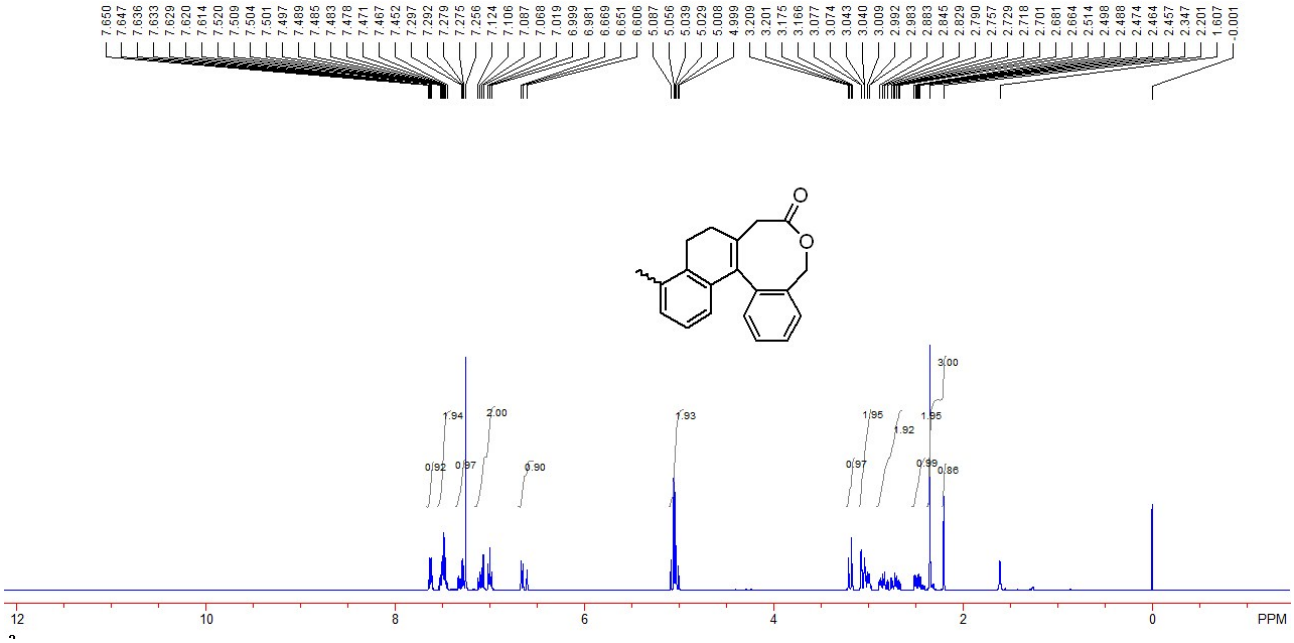
& (2.3:1)

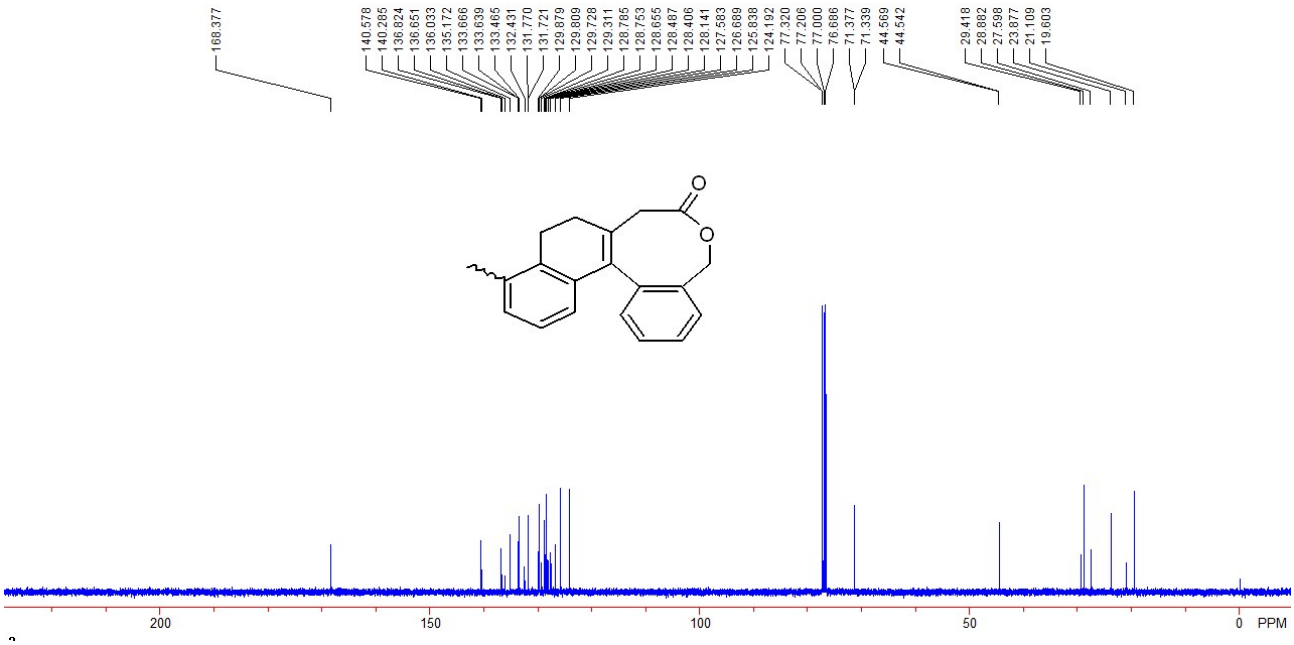
11-methyl-5,8,9,10-tetrahydro-7H-benzo[c]naphtho[1,2-e]oxocin-7-one. &

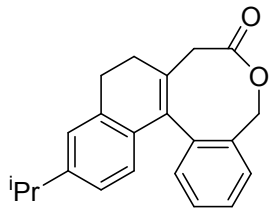
14-methyl-5,8,9,10-tetrahydro-7H-benzo[c]naphtho[1,2-e]oxocin-7-one (4d)

A colorless oil, 11.6 mg, 20% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.20 & 2.35 (s, 3H, CH_3), 2.46-2.51 (m, 1H, CH_2), 2.66-2.88 (m, 2H, CH_2), 2.98-3.08 (m, 2H, CH_2), 3.17-3.21 (m, 1H, CH_2),

5.00-5.09 (m, 2H, CH_2), 6.61-6.67 (m, 1H, ArH), 6.98-7.12 (m, 2H, ArH), 7.26-7.30 (m, 1H, ArH), 7.45-7.52 (m, 2H, ArH), 7.61-7.65 (m, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 19.6, 21.1, 23.9, 27.6, 28.9, 29.4, 44.5, 44.6, 71.3, 71.4, 124.2, 125.8, 126.7, 127.6, 128.1, 128.4, 128.5, 128.6, 128.7, 128.8, 129.3, 129.7, 129.8, 129.9, 131.7, 131.8, 132.4, 133.5, 133.6, 133.7, 135.2, 136.0, 136.6, 136.8, 140.3, 140.6, 168.4. IR (CH_2Cl_2) ν 2950, 2830, 1732, 1461, 1190, 1144, 791, 758 cm^{-1}. HRMS ($M+H^+$) calcd. for $C_{20}H_{19}O_2$: 291.1380, Found: 291.1377.

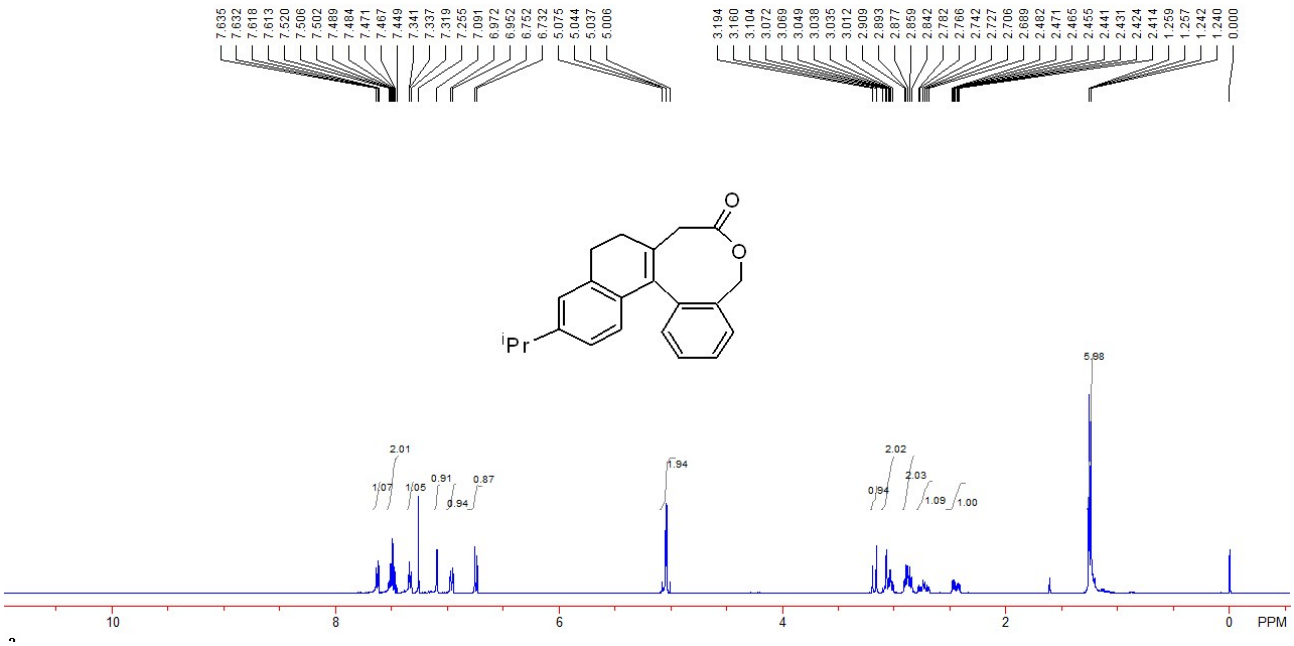


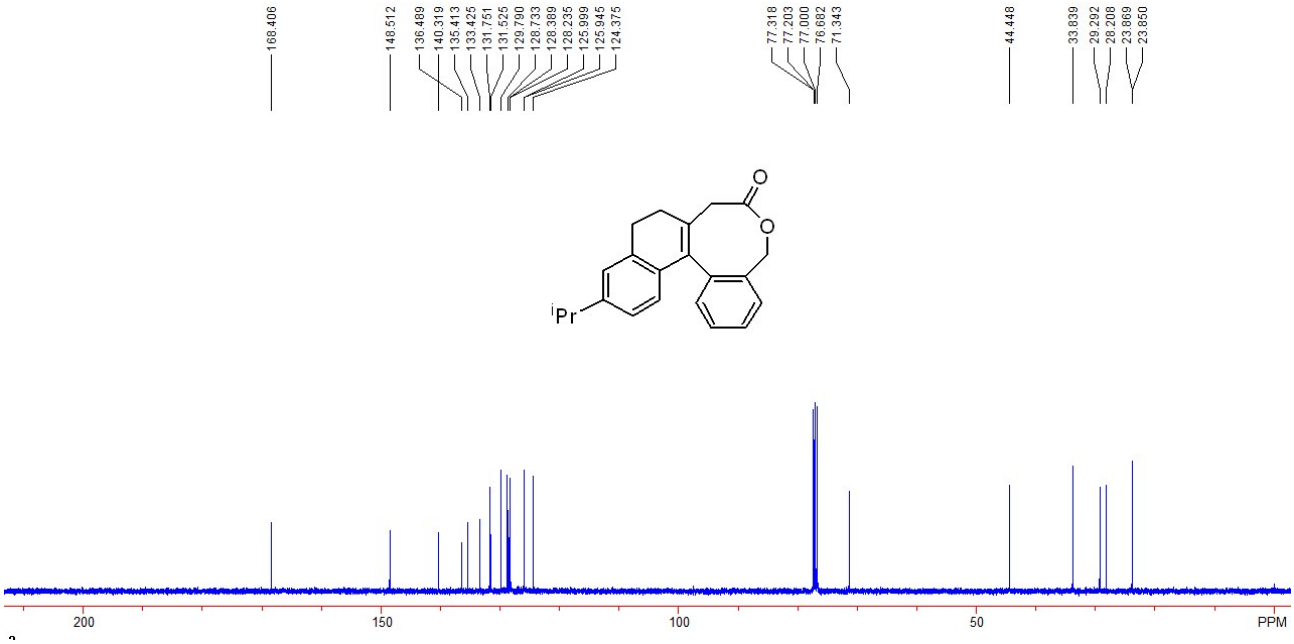


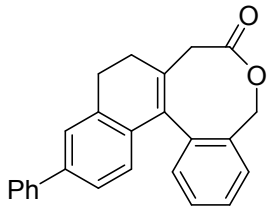


12-isopropyl-5,8,9,10-tetrahydro-7H-benzo[c]naphtho[1,2-e]oxocin-7-one (4e).

A colorless oil, 6.4 mg, 10% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.24 (d, J = 0.8 Hz, 3H, CH_3), 1.26 (d, J = 0.8 Hz, 3H, CH_3), 2.41-2.48 (m, 1H, CH_2), 2.69-2.78 (m, 1H, CH_2), 2.84-2.91 (m, 2H, CH_2), 3.01-3.10 (m, 2H, CH_2), 3.18 (d, J = 13.6 Hz, 1H, CH_2), 5.02 (d, J = 12.4 Hz, 1H, CH_2), 5.06 (d, J = 12.4 Hz, 1H, CH_2), 6.74 (d, J = 8.0 Hz, 1H, ArH), 6.96 (d, J = 8.0 Hz, 1H, ArH), 7.09 (s, 1H, ArH), 7.32-7.34 (m, 1H, ArH), 7.45-7.52 (m, 2H, ArH), 7.61-7.64 (m, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 23.8, 23.9, 28.2, 29.3, 33.8, 44.4, 71.3, 124.4, 125.9, 126.0, 128.2, 128.4, 128.7, 129.8, 131.5, 131.8, 133.4, 135.4, 136.5, 140.3, 148.5, 168.4. IR (CH_2Cl_2) ν 2959, 2919, 1728, 1178, 1144, 1045, 880, 831, 759 cm^{-1}. HRMS ($M+H^+$) calcd. for $C_{22}H_{23}O_2$: 319.1693, Found: 319.1689.

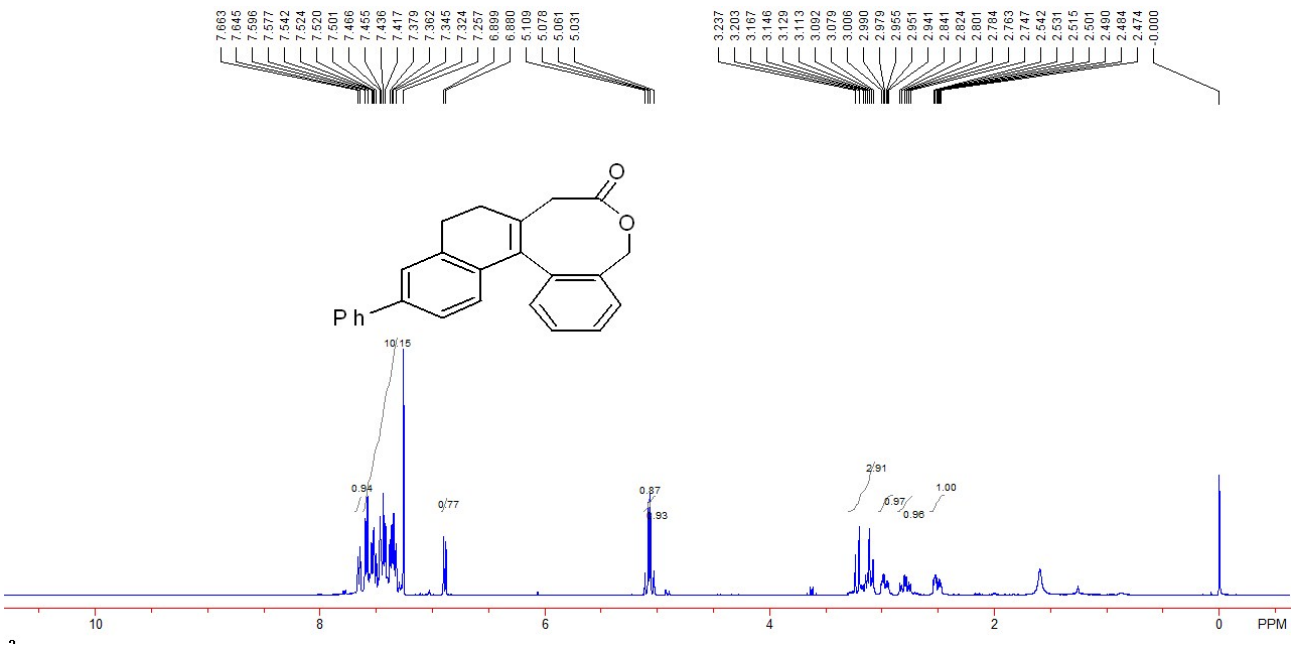


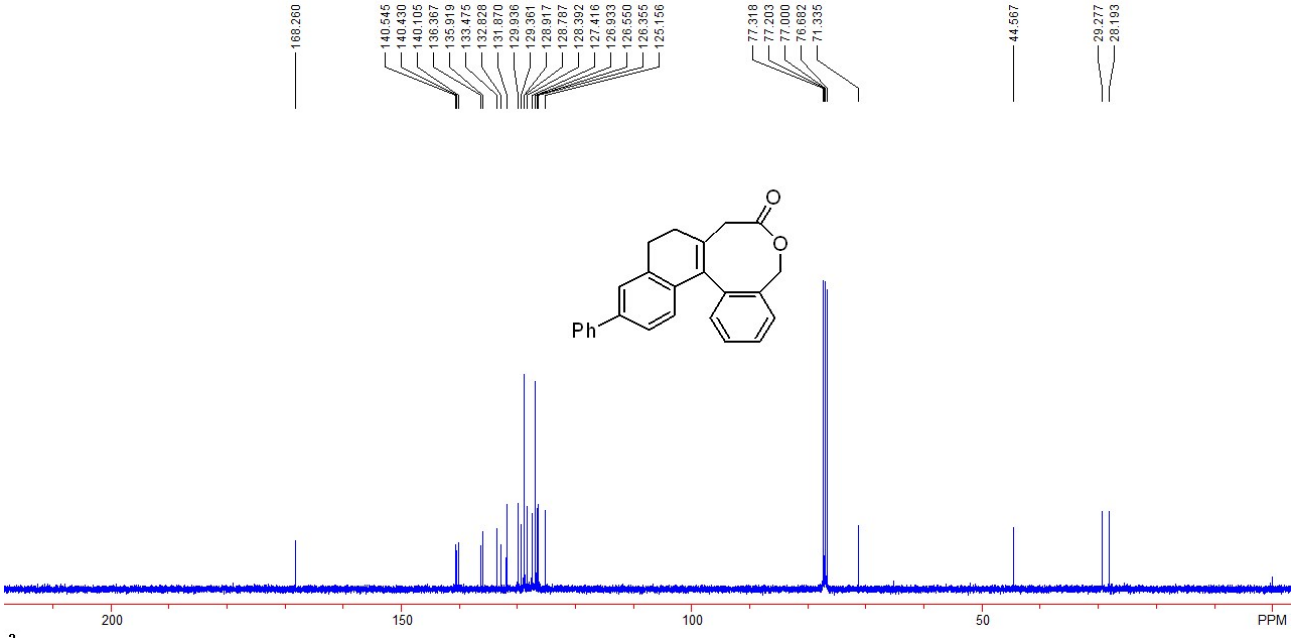


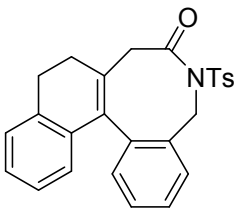


12-phenyl-5,8,9,10-tetrahydro-7H-benzo[c]naphtho[1,2-e]oxocin-7-one (4f).

A colorless oil, 17.6 mg, 25% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.47-2.54 (m, 1H, CH_2), 2.75-2.84 (m, 1H, CH_2), 2.94-3.01 (m, 1H, CH), 3.08-3.24 (m, 3H, CH2), 5.05 (d, *J* = 12.4 Hz, 1H, CH_2), 5.09 (d, *J* = 12.4 Hz, 1H, CH_2), 6.89 (d, *J* = 7.6 Hz, 1H, ArH), 7.32-7.60 (m, 10H, ArH), 7.65 (d, *J* = 7.2 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 28.2, 29.3, 44.6, 71.3, 125.2, 126.4, 126.6, 126.9, 127.4, 128.4, 128.8, 128.9, 129.4, 129.9, 131.9, 132.8, 133.5, 135.9, 136.4, 140.1, 140.4, 140.5, 168.3. IR (CH_2Cl_2) ν 2927, 2822, 1726, 1482, 1185, 1024, 766, 698 cm^{-1}. HRMS ($M+H^+$) calcd. for $C_{25}H_{21}O_2$: 353.1536, Found: 353.1531.



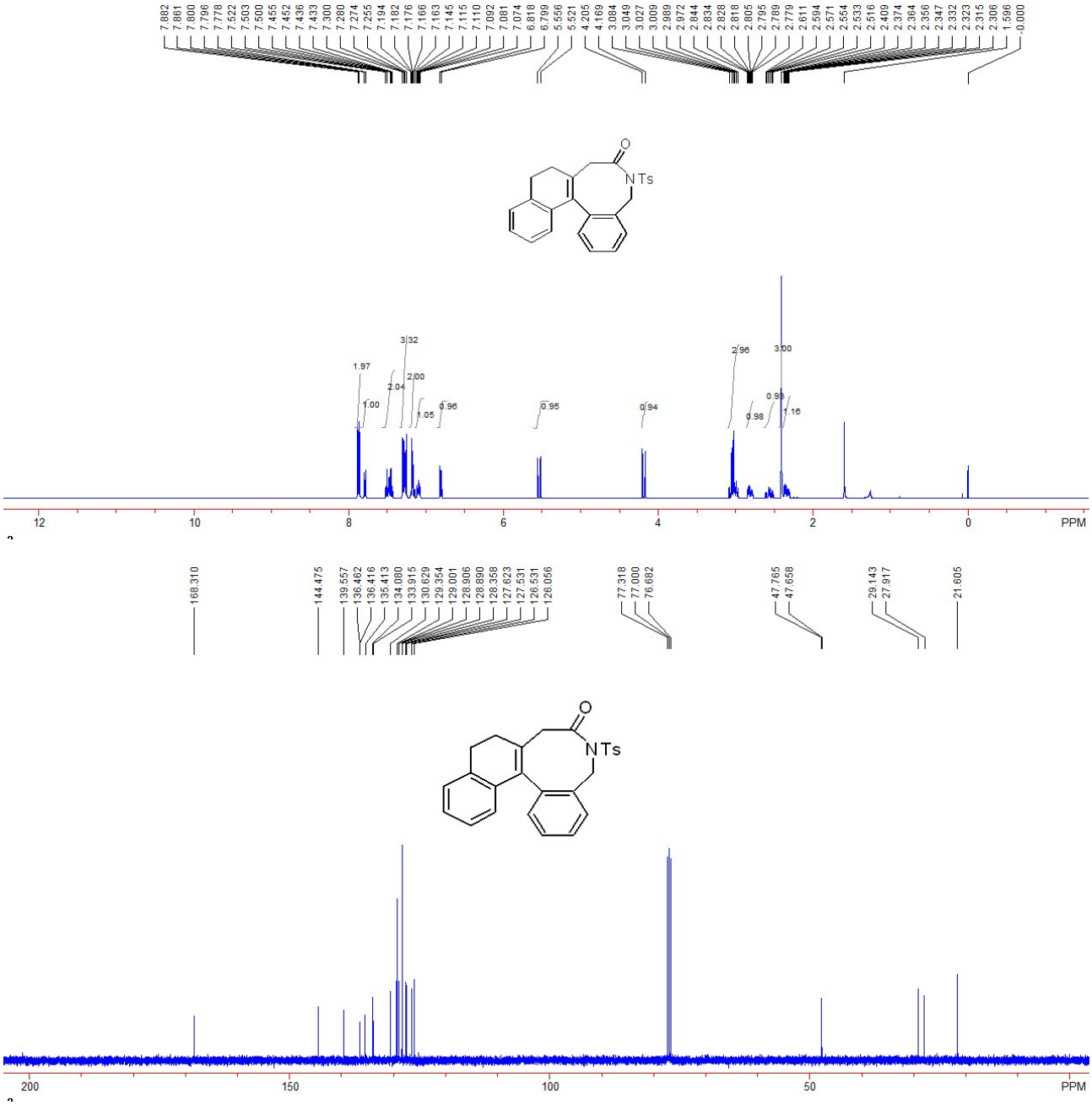


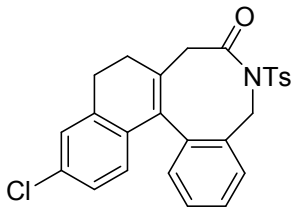


6-tosyl-5,8,9,10-tetrahydrobenzo[c]naphtho[1,2-e]azocin-7(6H)-one (4g).

A white solid, 25.8 mg, 30% yield. M.p.: 194-196 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.31-2.37 (m, 1H, CH_2), 2.41 (s, 3H, CH_3), 2.52-2.61 (m, 1H, CH_2), 2.78-2.84 (m, 1H, CH_2), 2.97-3.08 (m, 3H, CH_2), 4.19 (d, J = 14.4 Hz, 1H, CH_2), 5.54 (d, J = 14.4 Hz, 1H, CH_2), 6.81 (d, J = 7.6 Hz,

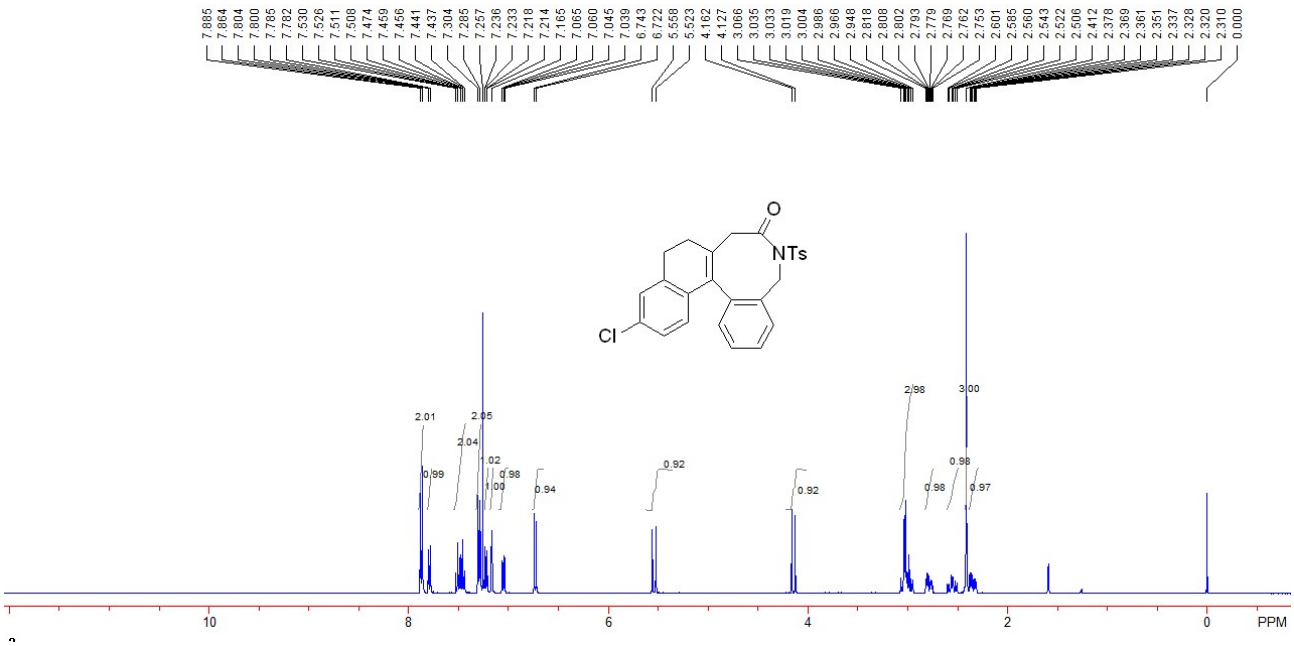
1H, CH_2), 7.07-7.12 (m, 1H, ArH), 7.14-7.19 (m, 2H, ArH), 7.26-7.30 (m, 3H, ArH), 7.43-7.52 (m, 2H, ArH), 7.79 (dd, *J* = 1.6 Hz, 7.2 Hz, 1H, ArH), 7.87 (d, *J* = 8.4 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.6, 27.9, 29.1, 47.6, 47.8, 126.0, 126.5, 127.5, 127.6, 128.4, 128.89, 128.91, 129.0, 129.4, 130.6, 133.9, 134.1, 135.4, 136.4, 136.5, 139.6, 144.5, 168.3. IR (CH_2Cl_2) ν 2922, 2851, 1639, 1453, 1354, 1168, 1076, 1014. HRMS ($M+Na^+$) calcd. for $C_{26}H_{23}O_3NNaS$: 452.1291, Found: 452.1291.

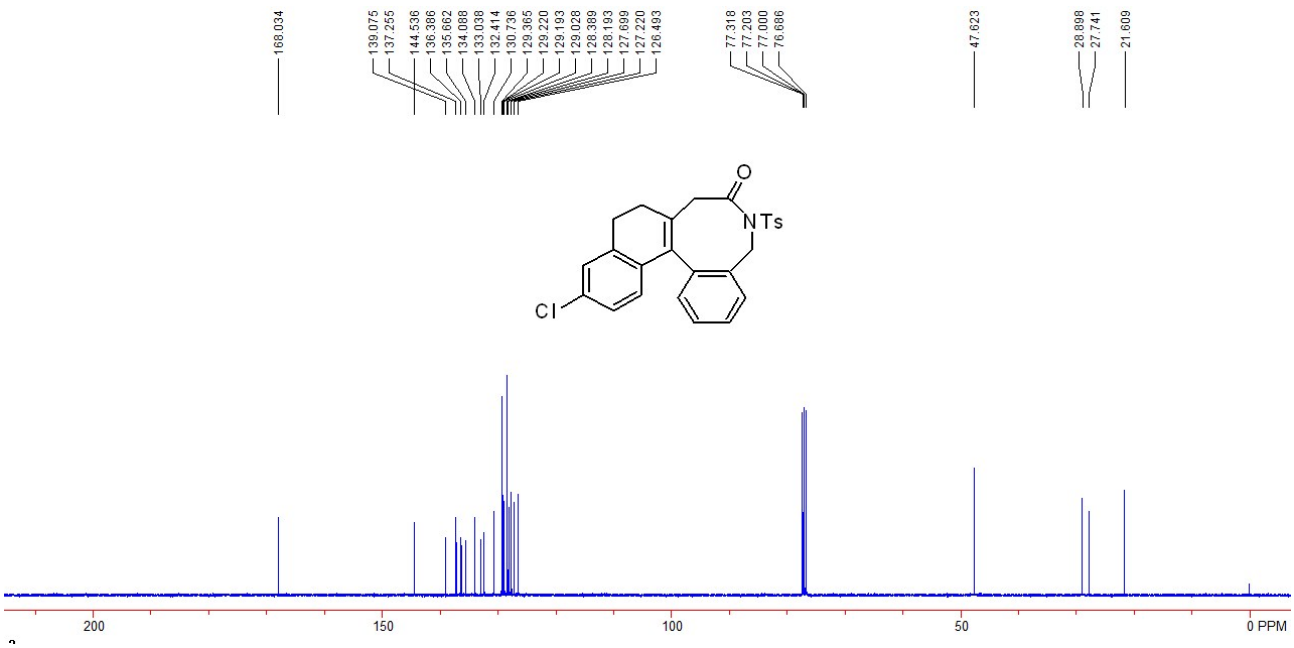


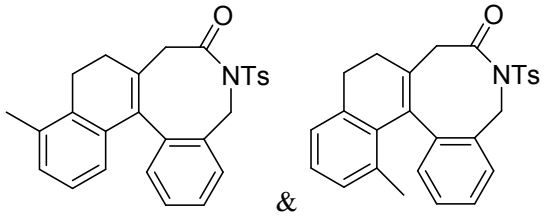


12-chloro-6-tosyl-5,8,9,10-tetrahydrobenzo[c]naphtho[1,2-e]azocin-7(6H)-one (4h).

A white solid, 23.2 mg, 25% yield. M.p.: 189-191 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.31-2.38 (m, 1H, CH_2), 2.41 (s, 3H, CH_3), 2.51-2.60 (m, 1H, CH_2), 2.75-2.82 (m, 1H, ArH), 2.95-3.07 (m, 3H, CH_2), 4.14 (d, *J* = 14.0 Hz, 1H, CH_2), 5.54 (d, *J* = 14.0 Hz, 1H, CH_2), 6.73 (d, *J* = 8.4 Hz, 1H, ArH), 7.05 (dd, *J* = 2.0 Hz, 8.0 Hz, 1H, ArH), 7.16 (s, 1H, ArH), 7.22 (dd, *J* = 1.2 Hz, 7.2 Hz, 1H, ArH), 7.29 (d, *J* = 7.6 Hz, 2H, ArH), 7.44-7.53 (m, 2H, ArH), 7.79 (dd, *J* = 1.6 Hz, 7.6 Hz, 1H, ArH), 7.87 (d, *J* = 8.4 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.6, 27.7, 28.9, 47.6, 126.5, 127.2, 127.7, 128.2, 128.4, 129.19, 129.22, 129.4, 130.7, 132.4, 133.0, 134.1, 135.7, 136.4, 137.2, 139.1, 144.5, 168.0. IR (CH_2Cl_2) ν 2969, 2919, 1692, 1341, 1171, 1086, 1046, 880 cm^{-1}. HRMS ($M+H^+$) calcd. for $C_{26}H_{23}O_3NClS$: 464.1082, Found: 464.1090.





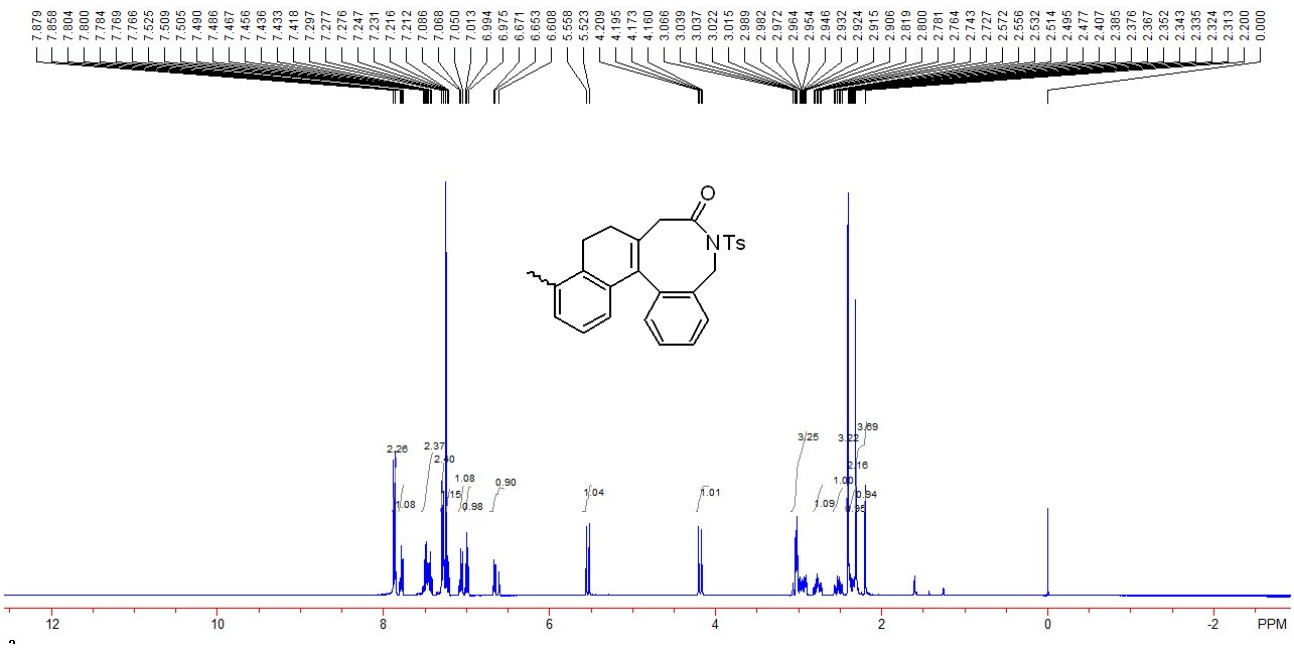


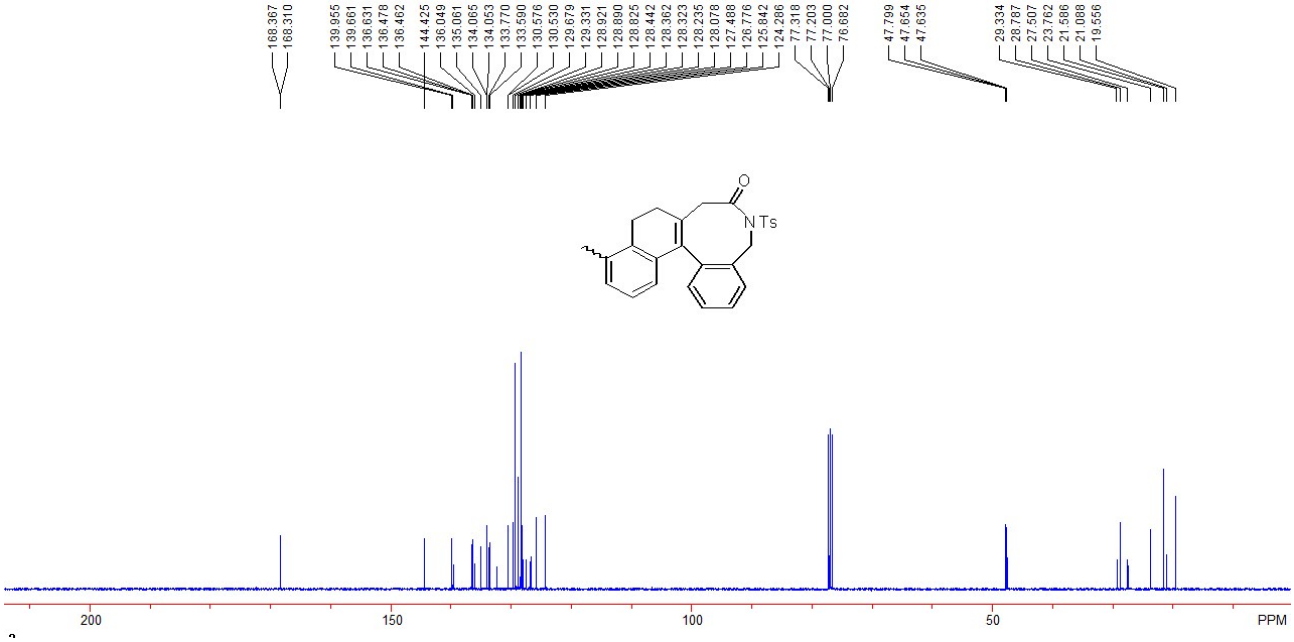
& (2:1)

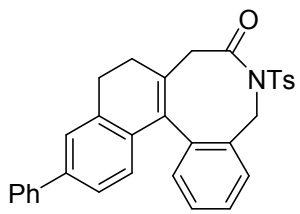
11-methyl-6-tosyl-5,8,9,10-tetrahydrobenzo[c]naphtho[1,2-e]azocin-7(6H)-one &

14-methyl-6-tosyl-5,8,9,10-tetrahydrobenzo[c]naphtho[1,2-e]azocin-7(6H)-one (4i).

A white solid, 17.7 mg, 20% yield. M.p.: 118-120 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.20 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 2.32-2.38 (m, 1H, CH_2), 2.41 (s, 3H, CH_3), 2.48-2.57 (m, 1H, CH_2), 2.73-2.82 (m, 1H, CH_2), 2.91-3.07 (m, 3H, CH_2), 4.18 (d, J = 14.0 Hz, 1H, CH_2), 4.19 (d, J = 14.0 Hz, 1H, CH_2), 5.54 (d, J = 14.4 Hz, 1H, CH_2), 6.61-6.67 (m, 1H, ArH), 6.99 (t, J = 7.6 Hz, 1H, ArH), 7.07 (t, J = 7.2 Hz, 1H, ArH), 7.22-7.23 (m, 1H, ArH), 7.28-7.30 (m, 2H, ArH), 7.42-7.52 (m, 2H, ArH), 7.77-7.80 (m, 1H, ArH), 7.87 (d, J = 8.4 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 19.6, 21.1, 21.6, 23.8, 27.5, 28.8, 29.3, 47.64, 47.65, 47.8, 124.3, 125.8, 126.8, 127.5, 128.1, 128.2, 128.3, 128.36, 128.44, 128.82, 128.89, 128.92, 129.3, 129.7, 130.5, 130.6, 133.6, 133.8, 134.0, 134.1, 135.1, 136.0, 136.46, 136.47, 136.6, 139.7, 140.0, 144.4, 168.3, 168.4. IR (CH_2Cl_2) ν 2972, 1694, 1356, 1167, 1084, 1046, 878, 707, 660 cm^{-1}. HRMS ($M+H^+$) calcd. for $C_{27}H_{26}O_3NS$: 444.1628, Found: 444.1634.



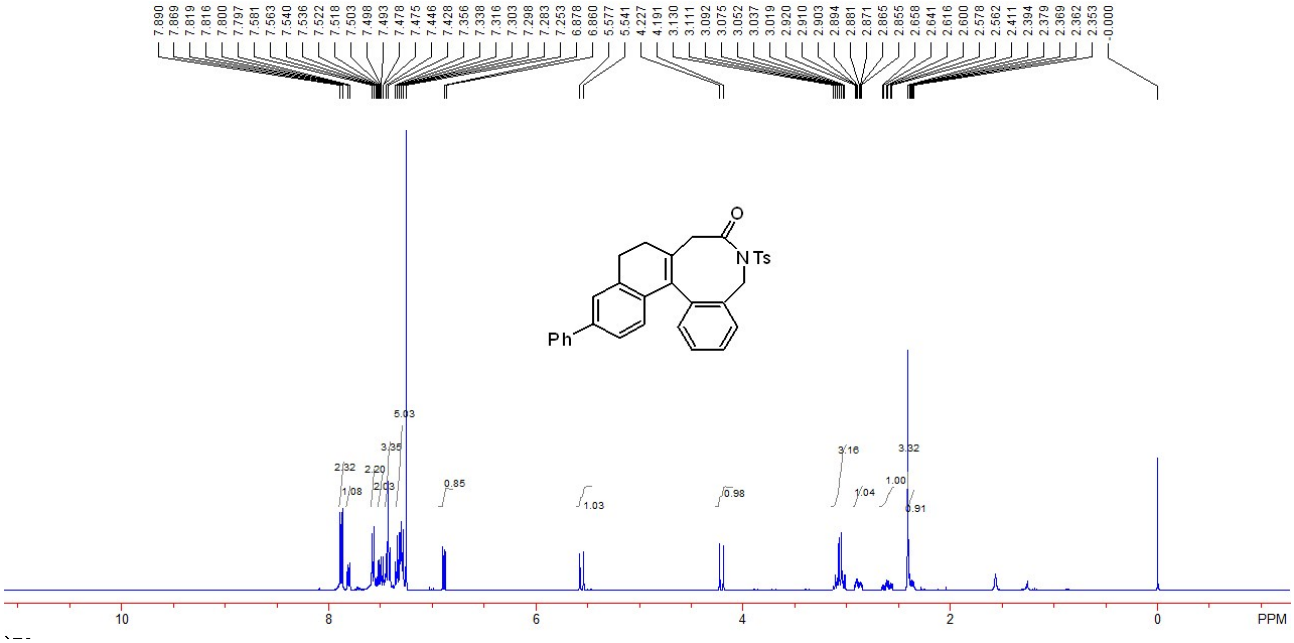


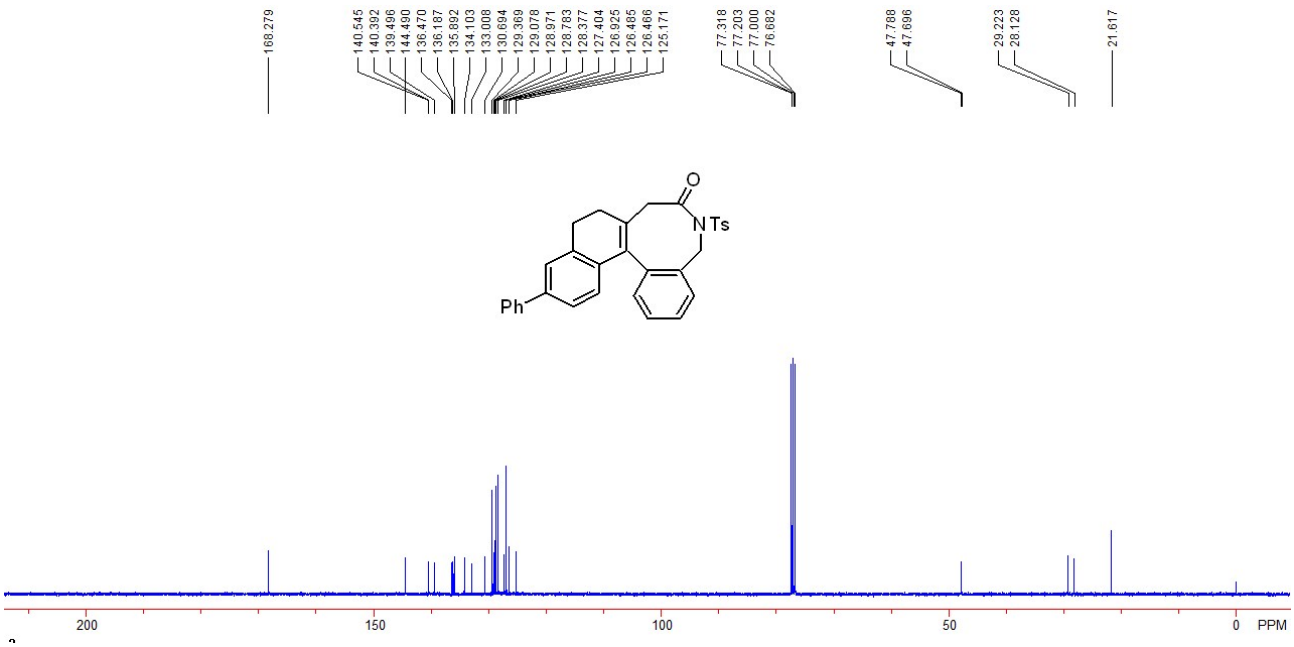


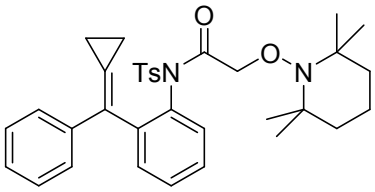
12-phenyl-6-tosyl-5,8,9,10-tetrahydrobenzo[c]naphtho[1,2-e]azocin-7(6H)-one (4j).

A white solid, 22.2 mg, 22% yield. M.p.: 129-131 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.35-2.39 (m, 1H, CH_2), 2.41 (s, 3H, CH_3), 2.56-2.66 (m, 1H, CH_2), 2.86-2.92 (m, 1H, CH_2), 3.02-3.13 (m, 3H, CH_2), 4.21 (d, J = 14.4 Hz, 1H, CH_2), 5.56 (d, J = 14.4 Hz, 1H, CH_2), 6.87 (d, J = 7.2 Hz,

1H, ArH), 7.28-7.36 (m, 5H, ArH), 7.43-7.45 (m, 3H, ArH), 7.48-7.52 (m, 2H, ArH), 7.56-7.58 (m, 2H, ArH), 7.81 (dd, J = 1.2 Hz, 7.6 Hz, 1H, ArH), 7.88 (d, J = 8.4 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.6, 28.1, 29.2, 47.7, 47.8, 125.2, 126.46, 126.48, 126.9, 127.4, 128.4, 128.8, 129.0, 129.1, 129.4, 130.7, 133.0, 134.1, 135.9, 136.2, 136.5, 139.5, 140.4, 140.5, 144.5, 168.3. IR (CH_2Cl_2) ν 2969, 2869, 1660, 1380, 1166, 1086, 1045, 875 cm^{-1}. HRMS ($M+H^+$) calcd. for $C_{32}H_{28}O_3NS$: 506.1784, Found: 506.1793.

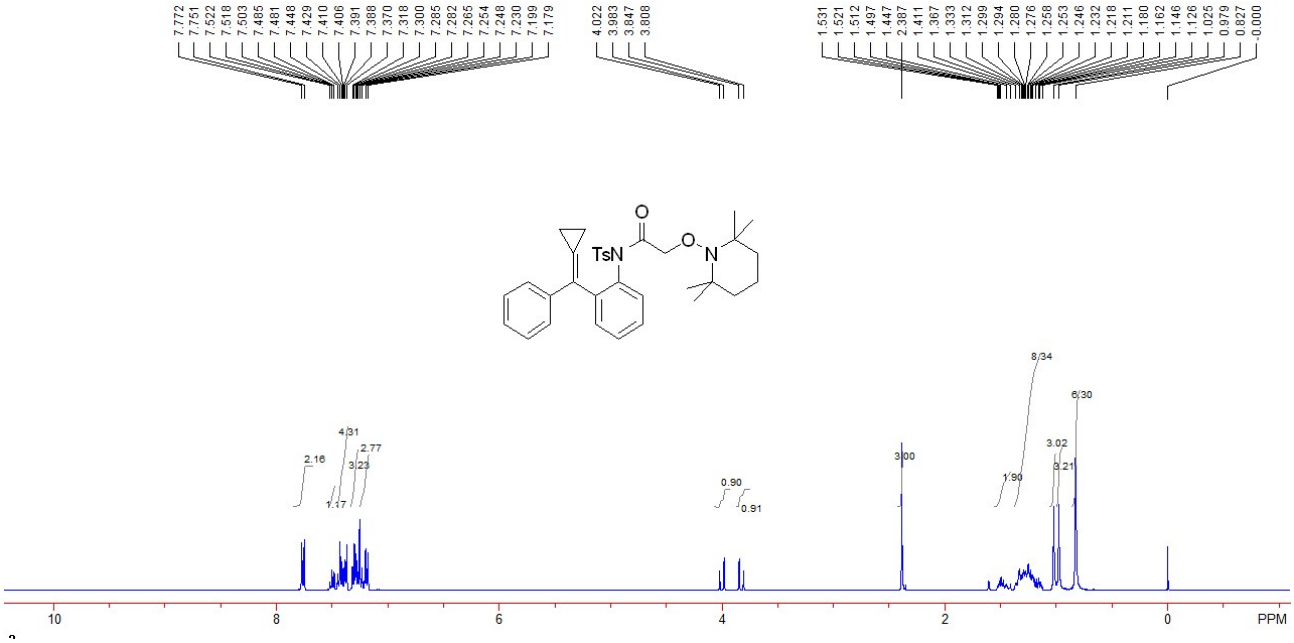


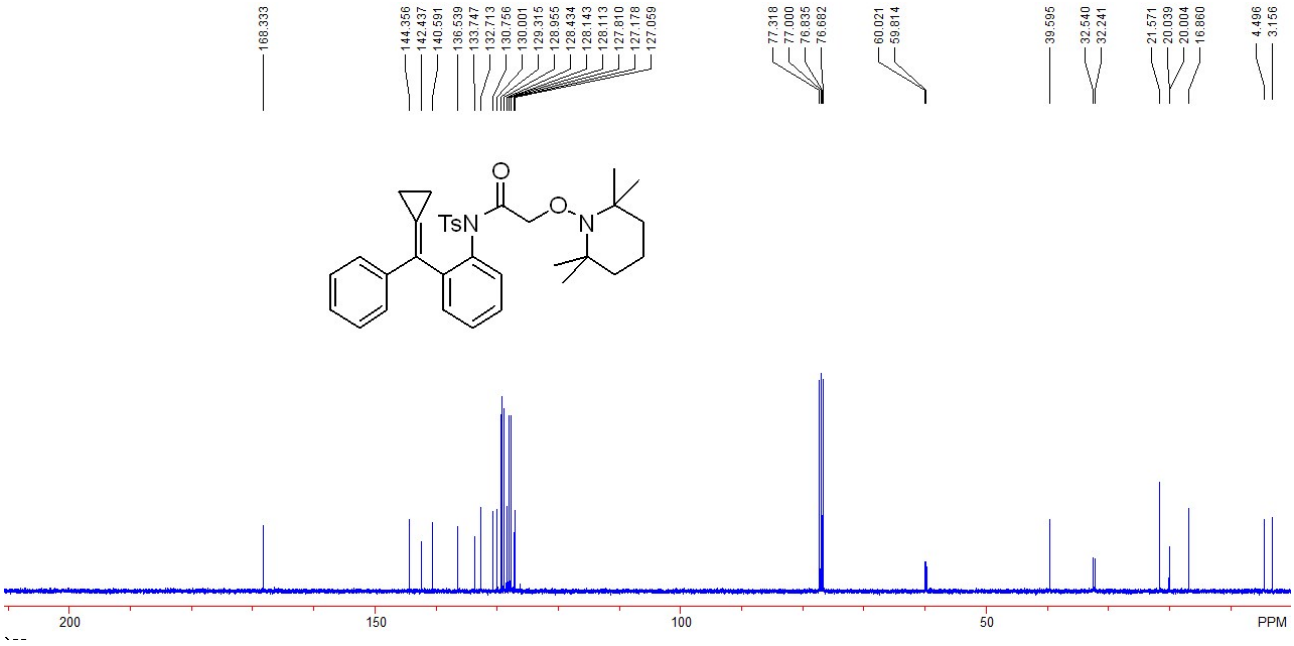


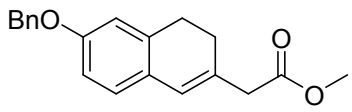


N-(2-(cyclopropylidene(phenyl)methyl)phenyl)-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-N-tosylacetamide (1a-TMP).

A white solid, 68.7 mg, 60% yield. M.p.: 82-84 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.83 (s, 6H, CH_3), 0.98 (s, 3H, CH_3), 1.02 (s, 3H, CH_3), 1.13-1.33 (m, 8H, CH_2), 1.41-1.53 (m, 2H, CH_2), 2.39 (s, 3H, CH_3), 3.83 (d, J = 14.7 Hz, 1H, CH_2), 4.00 (d, J = 14.7 Hz, 1H, CH_2), 7.18-7.23 (m, 3H, ArH), 7.25-7.32 (m, 3H, ArH), 7.37-7.45 (m, 4H, ArH), 7.49 (dt, J = 1.6 Hz, 7.6 Hz, 1H, ArH), 7.76 (d, J = 8.4 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 3.2, 4.5, 16.9, 20.00, 20.04, 21.6, 32.2, 32.5, 39.6, 59.8, 60.2, 127.0, 127.2, 127.8, 128.11, 128.14, 128.4, 129.0, 129.3, 130.0, 130.8, 132.7, 133.7, 136.5, 140.6, 142.4, 144.4, 168.3. IR (CH_2Cl_2) ν 2969, 2928, 1714, 1492, 1445, 1363, 1169, 1085, 666 cm^{-1}. HRMS ($M+H^+$) calcd. for $C_{34}H_{41}O_4N_2S$: 573.2782, Found: 573.2789.

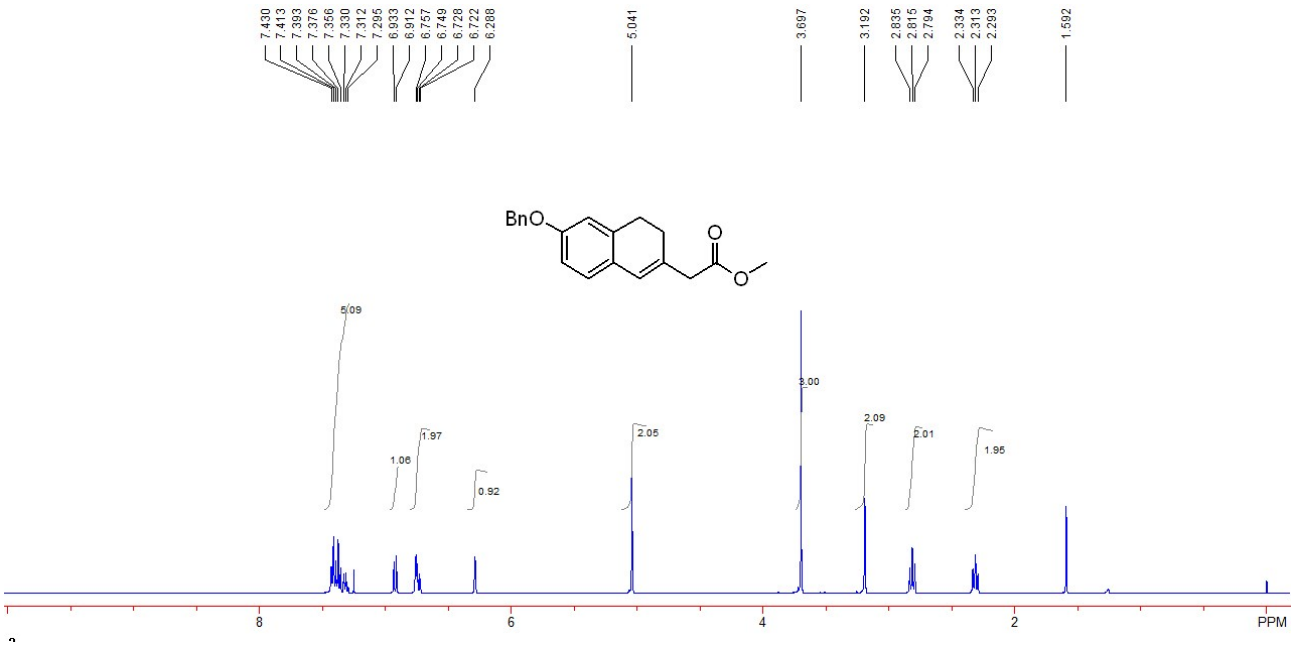


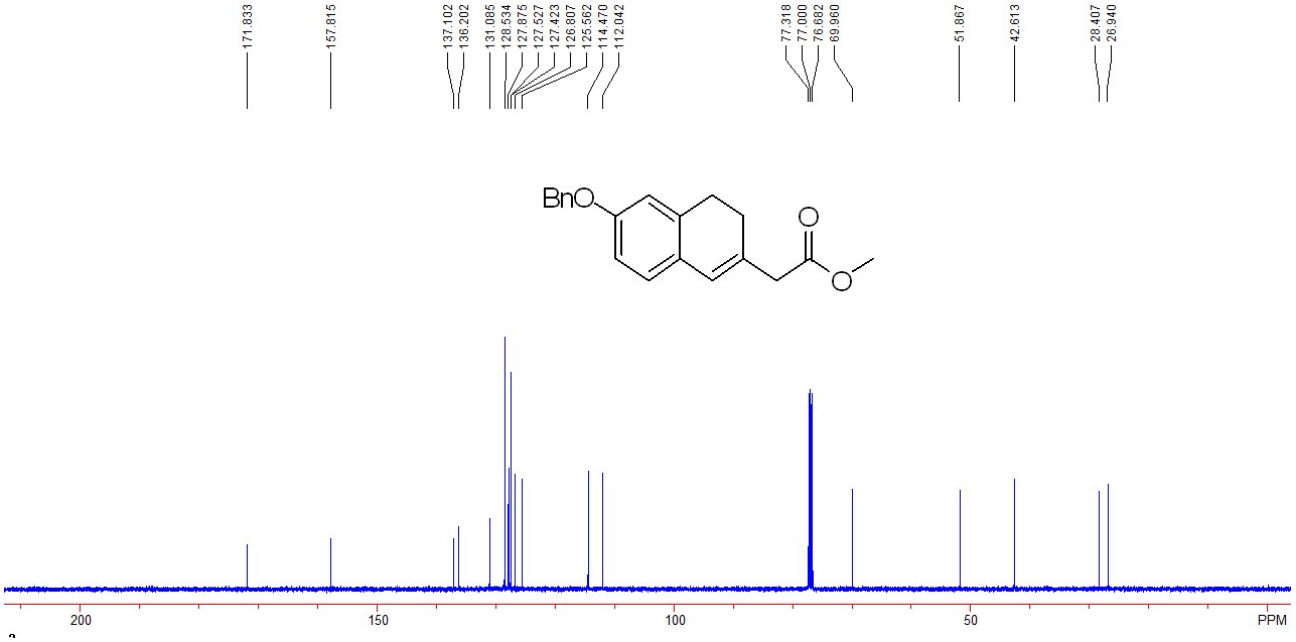


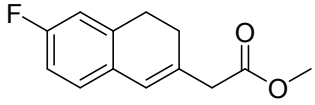


methyl 2-(6-(benzyloxy)-3,4-dihydronaphthalen-2-yl)acetate (6a).

A colorless oil, 27.7 mg, 45% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.31 (t, J = 8.0 Hz, 2H, CH_2), 2.82 (t, J = 8.0 Hz, 2H, CH_2), 3.19 (s, 2H, CH_2), 3.70 (s, 3H, CH_3), 5.04 (s, 2H, CH_2), 6.29 (s, 1H, CH), 6.72-6.76 (m, 2H, ArH), 6.92 (d, J = 8.4 Hz, 1H, ArH), 7.30-7.43 (m, 5H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 26.9, 28.4, 42.6, 51.9, 70.0, 112.0, 114.5, 125.6, 126.8, 127.4, 127.5, 127.9, 128.5, 131.1, 136.2, 137.1, 157.8, 171.8. IR (CH_2Cl_2) ν 3037, 2948, 2830, 1735, 1605, 1498, 1430, 1270, 1248, 1160, 1025, 734, 697 cm^{-1}. MS (%) m/e 308 (38.25), 218 (14.35), 205 (11.65), 157 (21.15), 129 (14.77), 128 (12.07), 115 (15.41), 91 (M^+, 100.00). HRMS (EI) calcd. for $C_{20}H_{20}O_3$: 308.1412, Found: 308.1417.



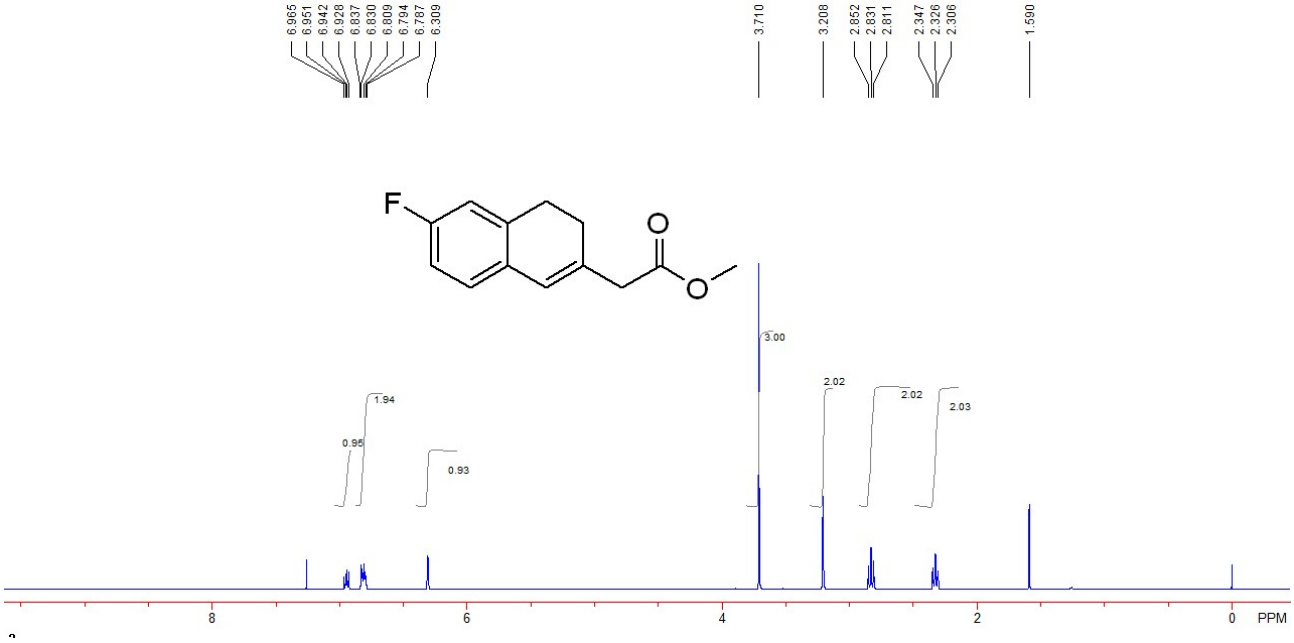


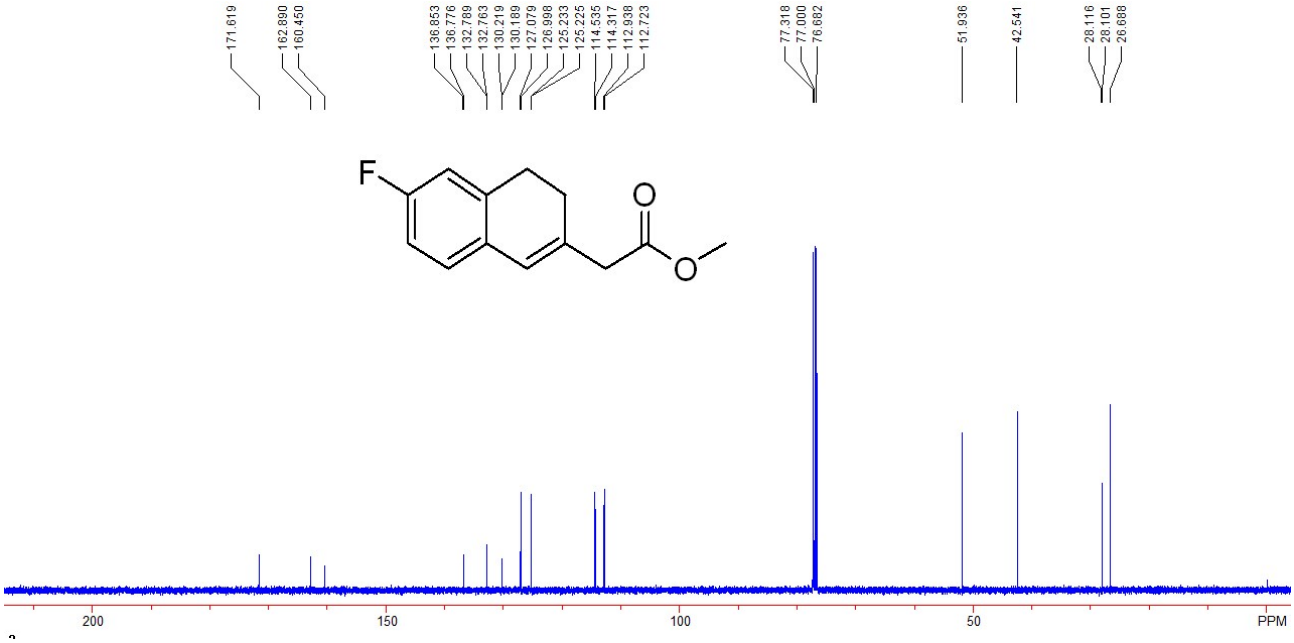


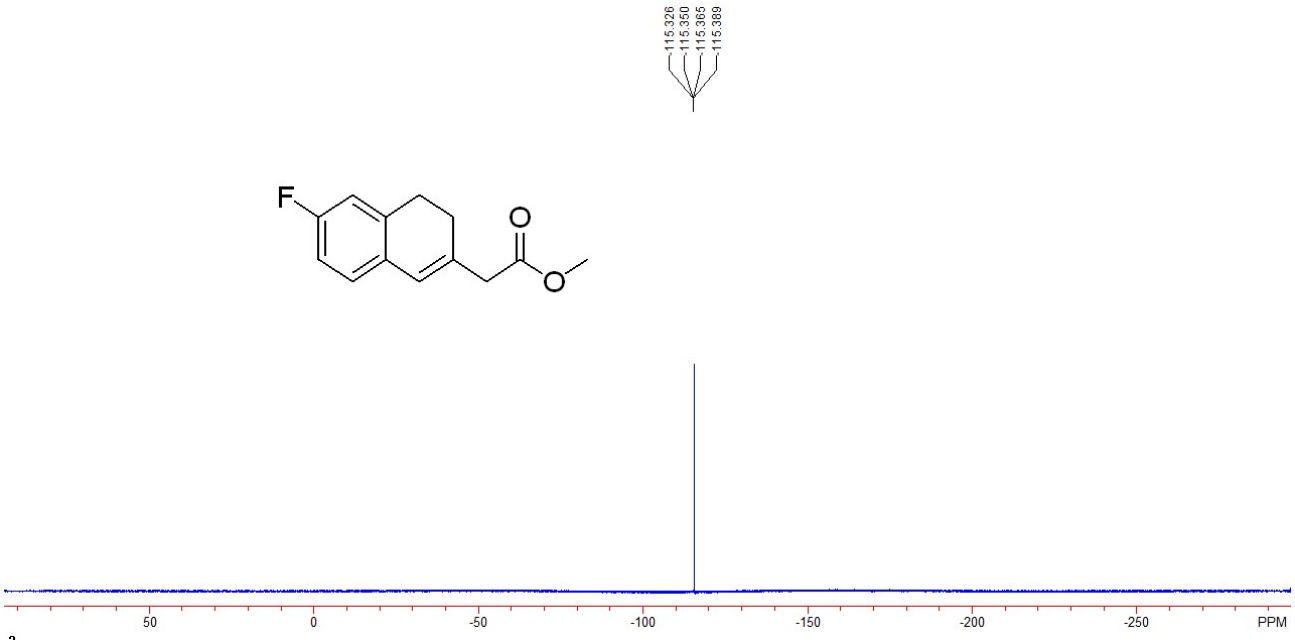
methyl 2-(6-fluoro-3,4-dihydronaphthalen-2-yl)acetate (6b).

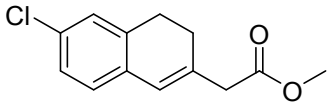
A colorless oil, 18.5 mg, 42% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.33 (t, J = 8.0 Hz, 2H, CH_2), 2.83 (t, J = 8.0 Hz, 2H, CH_2), 3.21 (s, 2H, CH_2), 3.71 (s, 3H, CH_3), 6.31 (s, 1H, CH), 6.79-6.84 (m, 2H, ArH), 6.93-6.96 (m, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 26.7, 28.1 (d, J = 1.5 Hz), 42.5, 51.9, 112.8 (d, J = 21.5 Hz), 114.4 (d, J = 21.8 Hz), 125.2 (d, J = 0.8 Hz), 127.0 (d, J = 8.1 Hz), 130.2 (d, J = 3.0 Hz), 132.8 (d, J = 2.6 Hz), 136.8 (d, J = 7.7 Hz), 161.7 (d, J = 244.0

Hz), 171.6. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ −115.36. IR (CH_2Cl_2) ν 2932, 2830, 1736, 1493, 1435, 1267, 1233, 1160, 1139, 864, 810 cm^{-1}. MS (%) m/e 220 (53.37), 162 (9.62), 161 (79.07), 160 (79.38), 159 (53.26), 147 (22.31), 146 (M^+, 100.00), 133 (29.22). HRMS (EI) calcd. for $C_{13}H_{13}O_2F$: 220.0900, Found: 220.0895.



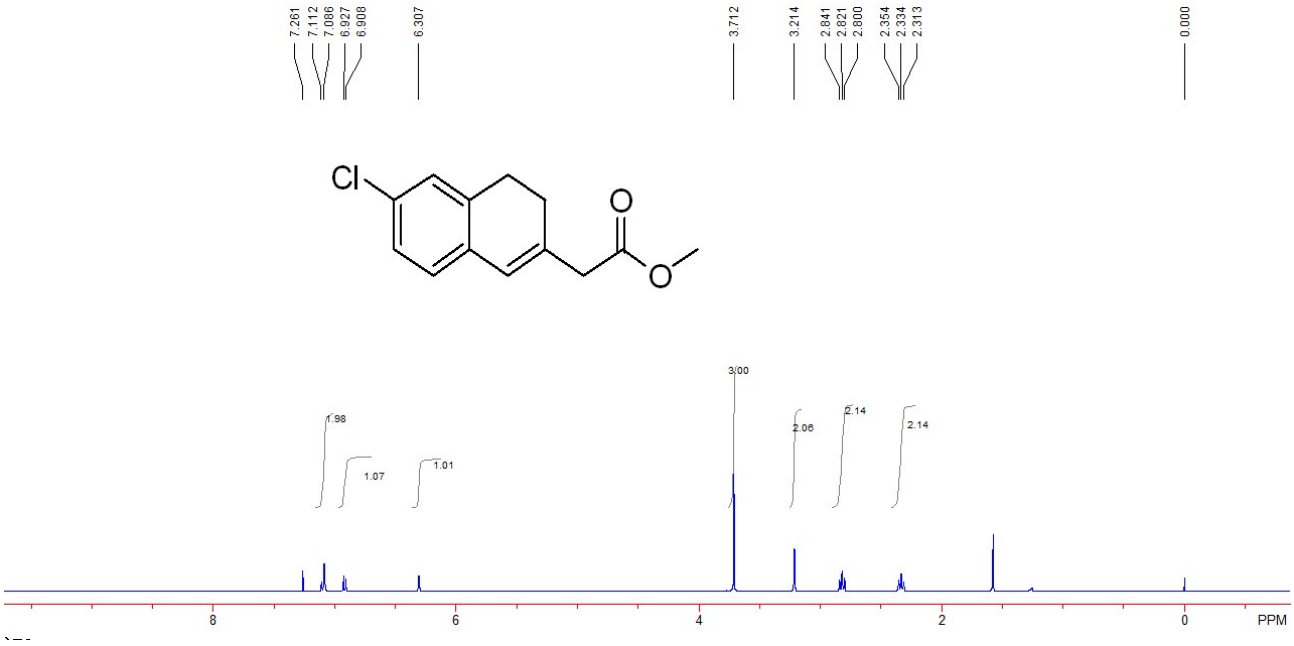


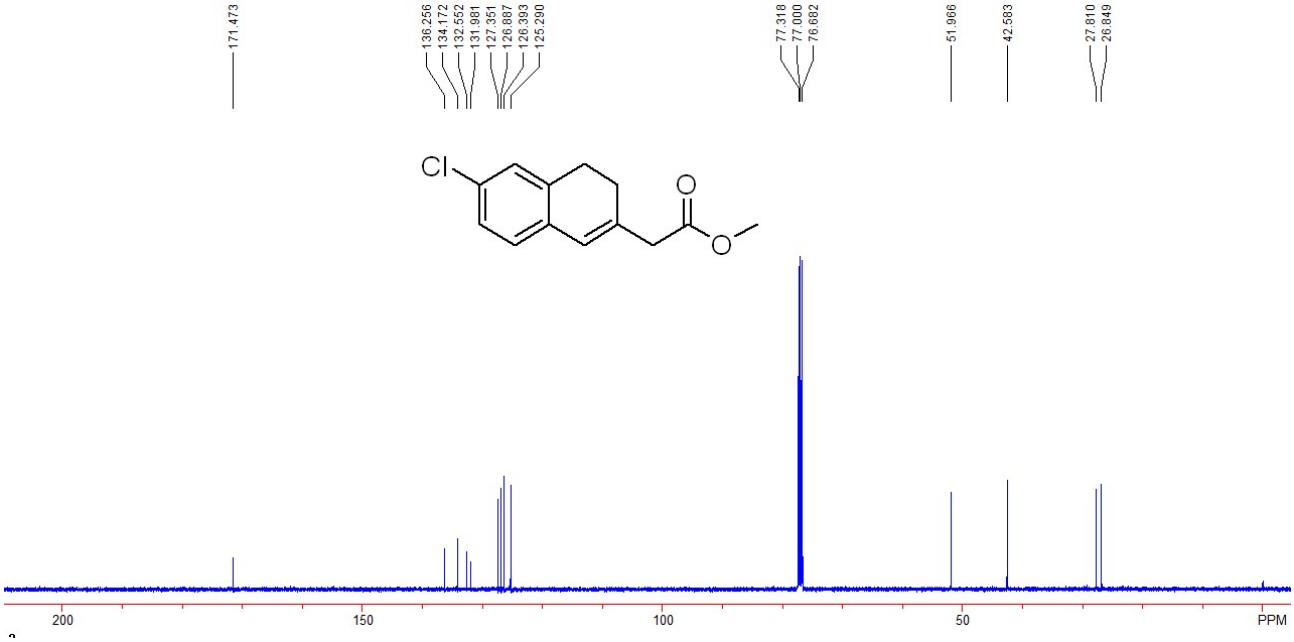


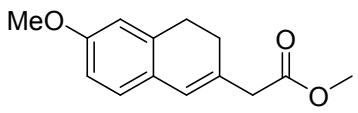


methyl 2-(6-chloro-3,4-dihydronaphthalen-2-yl)acetate (6c).

A colorless oil, 16.6 mg, 35% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.33 (t, J = 8.0 Hz, 2H, CH_2), 2.82 (t, J = 8.0 Hz, 2H, CH_2), 3.21 (s, 2H, CH_2), 3.71 (s, 3H, CH_3), 6.31 (s, 1H, CH_2), 6.92 (d, J = 7.6 Hz, 1H, CH), 7.10 (d, J = 10.4 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 26.8, 27.8, 42.6, 52.0, 125.3, 126.4, 126.9, 127.4, 132.0, 132.6, 134.2, 136.2, 171.5. IR (CH_2Cl_2) ν 2948, 2922, 2833, 1736, 1482, 1438, 1247, 1195, 1155, 862, 820 cm^{-1}. MS (%) m/e 236 (55.28), 177 (67.04), 176 (36.62), 162 (57.41), 146 (26.20), 142 (56.86), 141 (M^+, 100.00), 115 (28.81). HRMS (EI) calcd. for $C_{13}H_{13}O_2Cl$: 236.0604, Found: 236.0611.



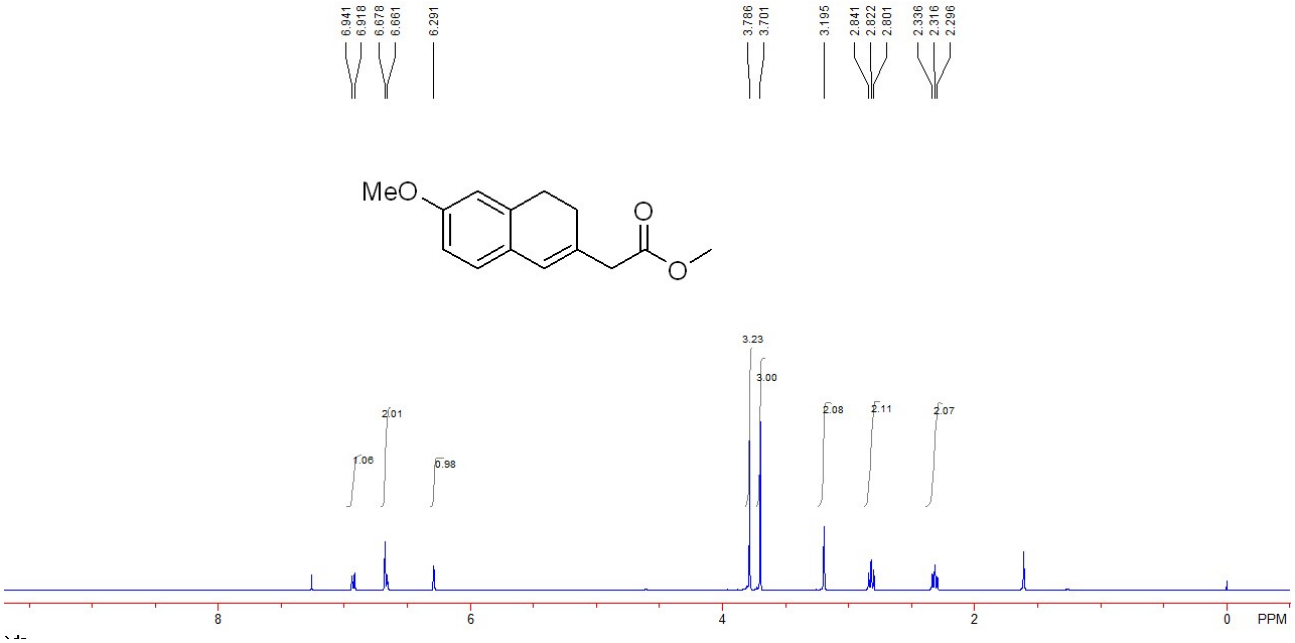


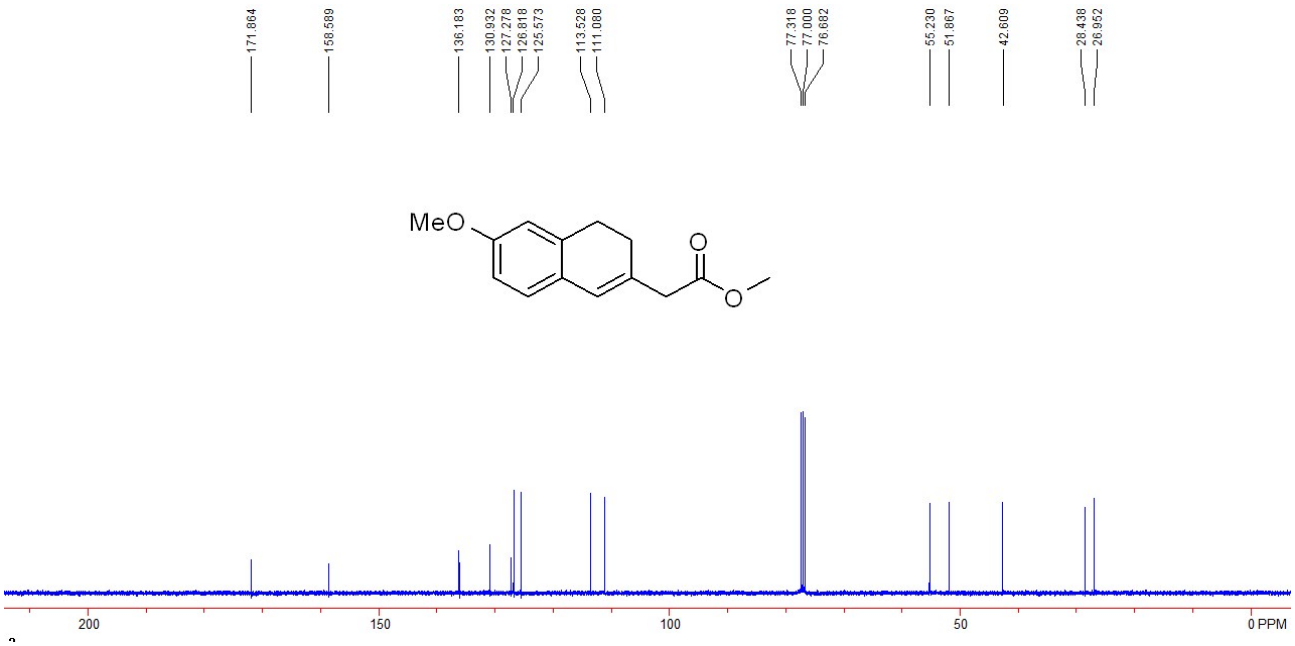


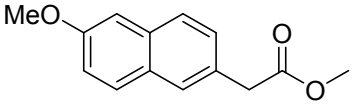
methyl 2-(6-methoxy-3,4-dihydronaphthalen-2-yl)acetate (6d).

A colorless oil, 21.8 mg, 47% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.32 (t, J = 8.0 Hz, 2H, CH_2), 2.82 (t, J = 8.0 Hz, 2H, CH_2), 3.20 (s, 2H, CH_2), 3.70 (s, 3H, CH_3), 3.79 (s, 3H, CH_3), 6.29 (s, 1H, CH), 6.66-6.68 (m, 2H, ArH), 6.92-6.94 (m, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 27.0, 28.4, 42.6, 51.9, 55.2, 111.1, 113.5, 125.6, 126.8, 127.3, 130.9, 136.2, 158.6, 171.9. IR (CH_2Cl_2) ν 2995, 2956, 2828, 1736, 1610, 1499, 1430, 1270, 1250, 1161, 1037, 864 cm^{-1}. MS (%)

m/e 232 (55.88), 173 (M^+, 100.00), 172 (19.64), 158 (32.12), 128 (21.60), 115 (17.73), 86 (39.61), 84 (58.49). HRMS (EI) calcd. for $C_{14}H_{16}O_3$: 232.1099, Found: 232.1103.

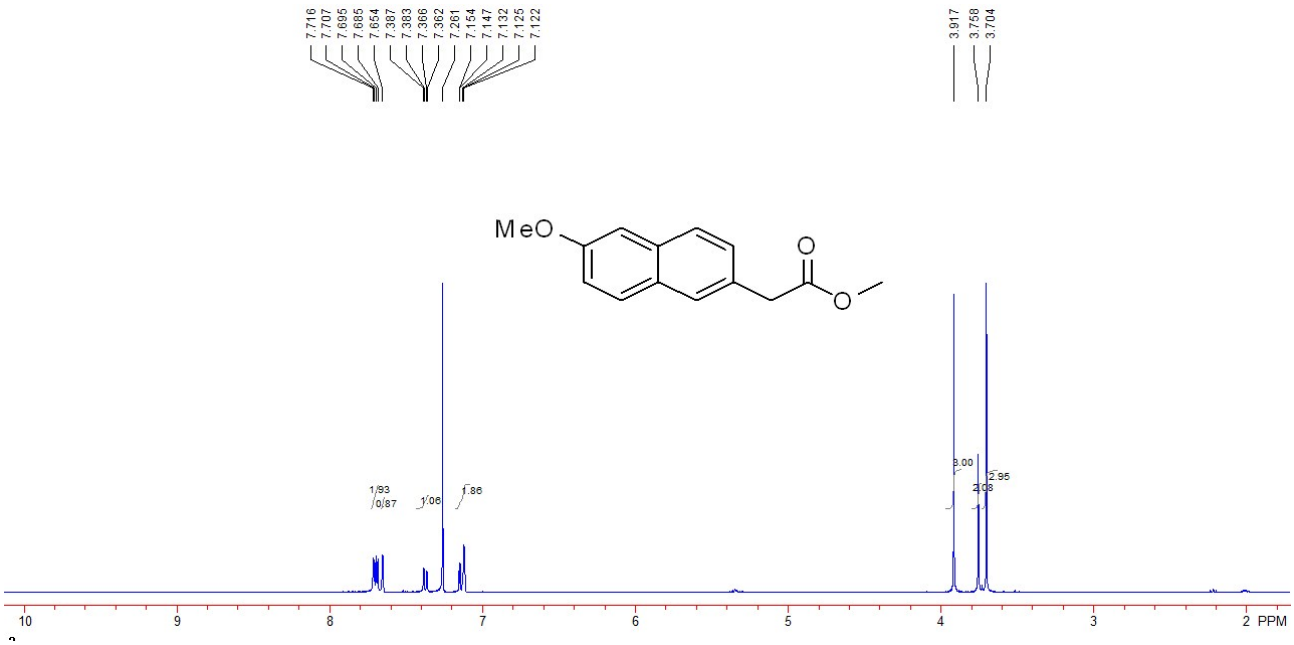


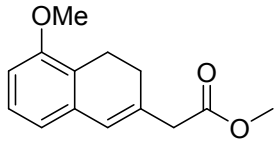




methyl 2-(6-methoxynaphthalen-2-yl)acetate (6d').

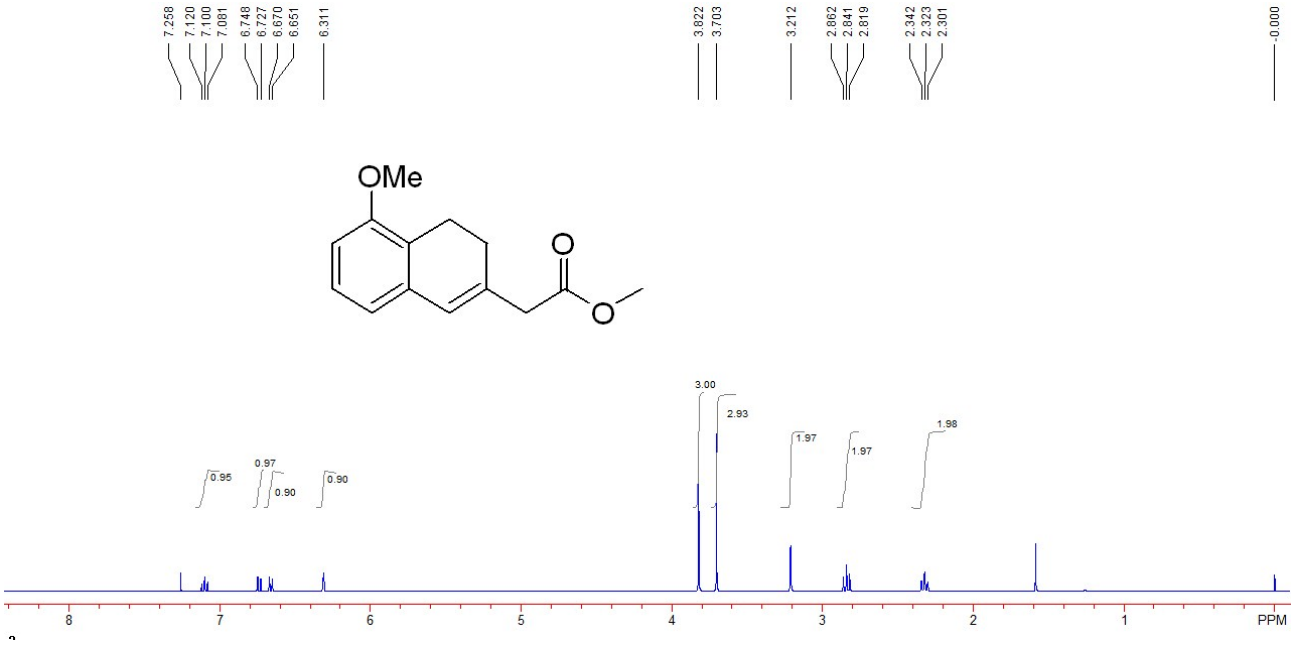
A known compound, colorless oil, 13.8 mg, 60% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 3.70 (s, 3H, CH_3), 3.76 (s, 2H, CH_2), 3.92 (s, 3H, CH_3), 7.12-7.15 (m, 2H, ArH), 7.37 (dd, *J* = 1.6 Hz, 8.4 Hz, 1H, ArH), 7.65 (s, 1H, ArH), 7.68-7.72 (m, 2H, ArH).

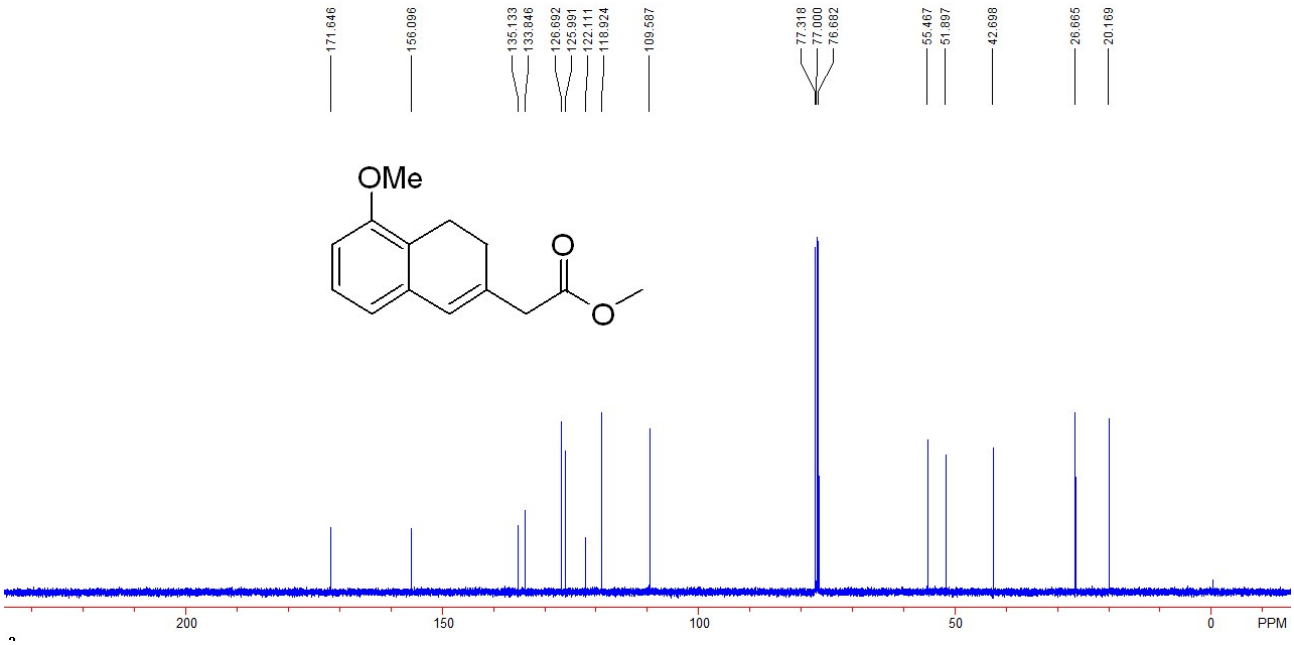


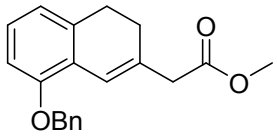


methyl 2-(5-methoxy-3,4-dihydronaphthalen-2-yl)acetate (6e).

A colorless oil, 20.9 mg, 45% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.32 (t, *J* = 8.4 Hz, 2H, CH_2), 2.84 (t, *J* = 8.4 Hz, 2H, CH_2), 3.21 (s, 2H, CH_2), 3.70 (s, 3H, CH_3), 3.82 (s, 3H, CH_3), 6.31 (s, 1H, CH), 6.66 (d, *J* = 7.6 Hz, 1H, ArH), 6.73 (d, *J* = 8.4 Hz, 1H, ArH), 7.10 (t, *J* = 8.0 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 20.2, 26.7, 42.7, 51.9, 55.5, 109.6, 118.9, 122.1, 126.0, 126.7, 133.8, 135.1, 156.1, 171.6. IR (CH_2Cl_2) ν 3006, 2948, 2830, 1735, 1576, 1470, 1437, 1344, 1263, 1151, 1090, 773, 715 cm^{-1}. MS (%) m/e 232 (44.96), 173 (29.38), 172 (26.42), 159 (36.06), 158 (M^+, 100.00), 141 (14.88), 128 (21.49), 115 (19.06). HRMS (EI) calcd. for $C_{14}H_{16}O_3$: 232.1099, Found: 232.1110.



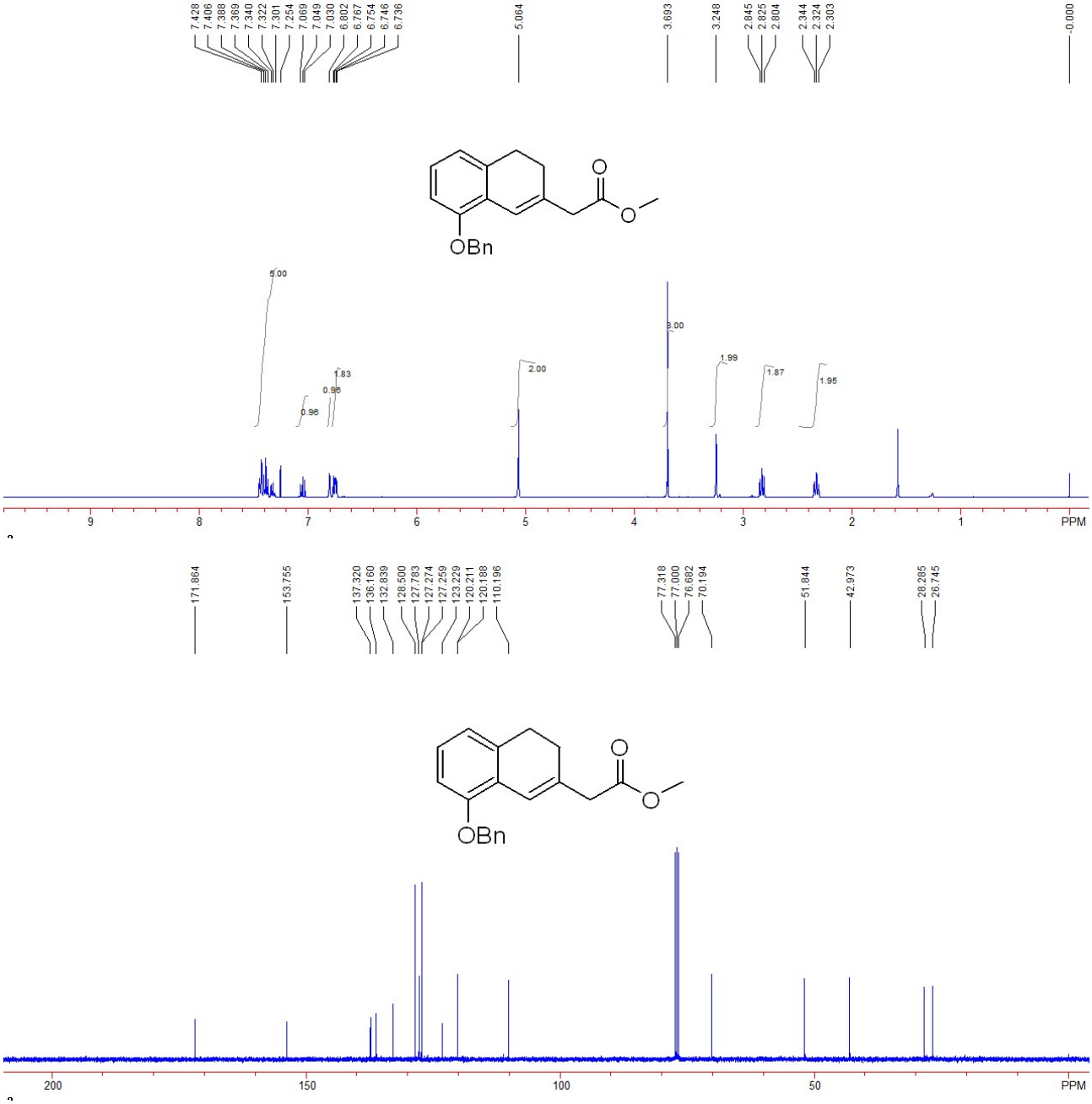


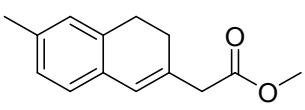


methyl 2-(8-(benzyloxy)-3,4-dihydronaphthalen-2-yl)acetate (6f).

A colorless oil, 26.5 mg, 43% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.32 (t, J = 8.0 Hz, 2H, CH_2), 2.82 (t, J = 8.0 Hz, 2H, CH_2), 3.25 (s, 2H, CH_2), 3.70 (s, 3H, CH_3), 5.06 (s, 2H, CH_2), 6.74-6.77 (m, 2H, ArH), 6.80 (s, 1H, CH), 7.05 (d, J = 8.0 Hz, 1H, ArH), 7.25-7.43 (m, 5H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 26.7, 28.3, 43.0, 51.8, 70.2, 110.2, 120.19, 120.21, 123.2, 127.26,

127.27, 127.8, 128.5, 132.8, 136.2, 137.3, 153.8, 171.9. IR (CH_2Cl_2) ν 3032, 2922, 2835, 1735, 1574, 1460, 1260, 1171, 1061, 736, 696 cm^{-1}. MS (%) m/e 308 (19.37), 157 (36.95), 91 (78.99), 88 (10.89), 86 (64.08), 84 (M^+, 100.00), 49 (16.49), 47 (19.04). HRMS (EI) calcd. for $C_{20}H_{20}O_3$: 308.1412, Found: 308.1424.

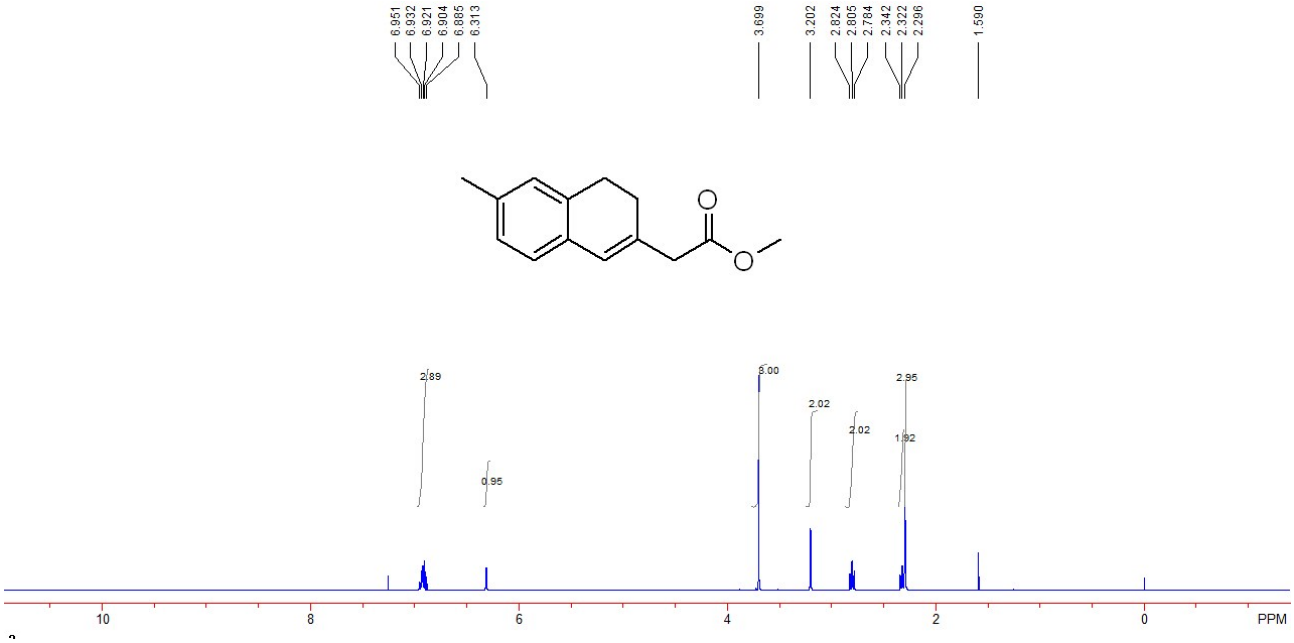


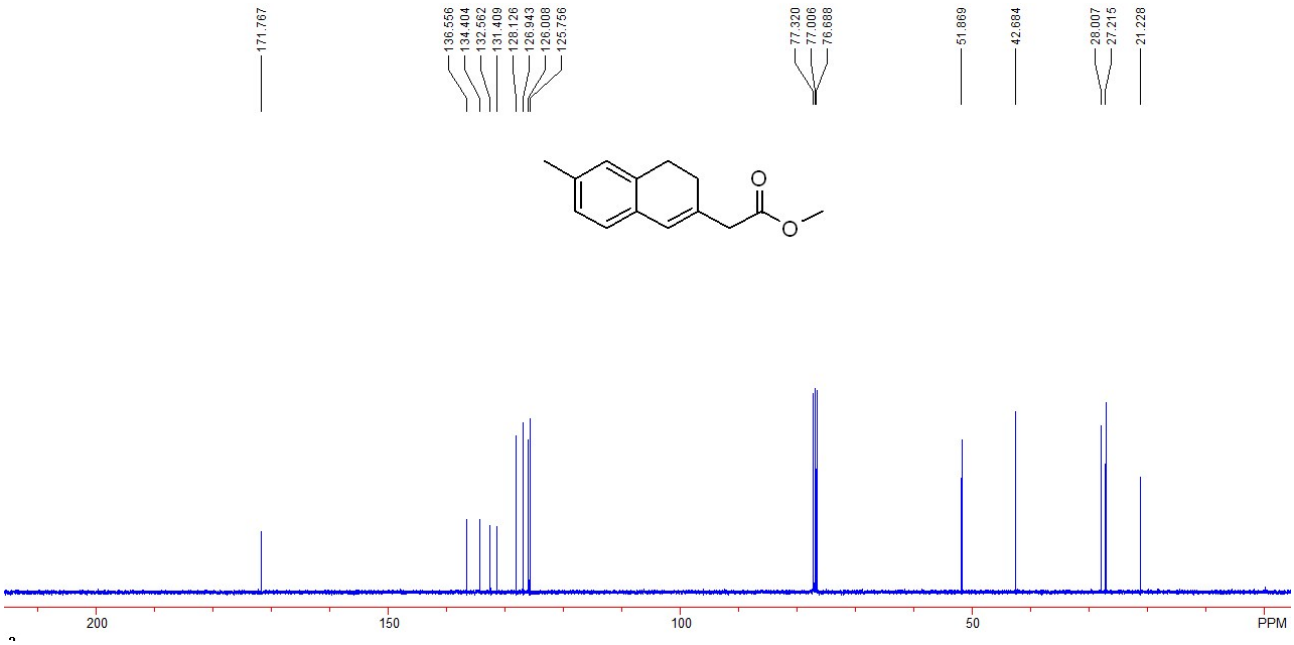


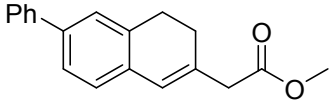
methyl 2-(6-methyl-3,4-dihydronaphthalen-2-yl)acetate (6g).

A colorless oil, 17.3 mg, 40% yield. ^1H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.30 (s, 3H, CH_3), 2.32 (t,

J = 8.0 Hz, 2H, CH_2), 2.80 (t, J = 8.0 Hz, 2H, CH_2), 3.20 (s, 2H, CH_2), 3.70 (s, 3H, CH_3), 6.31 (s, 1H, CH), 6.88-6.95 (m, 3H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.2, 27.2, 28.0, 42.7, 51.9, 125.8, 126.0, 126.9, 128.1, 131.4, 132.6, 134.4, 136.6, 171.8. IR (CH_2Cl_2) ν 3005, 2932, 2828, 1735, 1493, 1432, 1346, 1254, 1147, 1011, 810 cm^{-1}. MS (%) m/e 216 (58.25), 157 (72.40), 156 (49.82), 155 (23.65), 143 (27.46), 142 (M^+, 100.00), 141 (47.09), 128 (17.42). HRMS (EI) calcd. for $C_{14}H_{16}O_2$: 216.1150, Found: 216.1159.

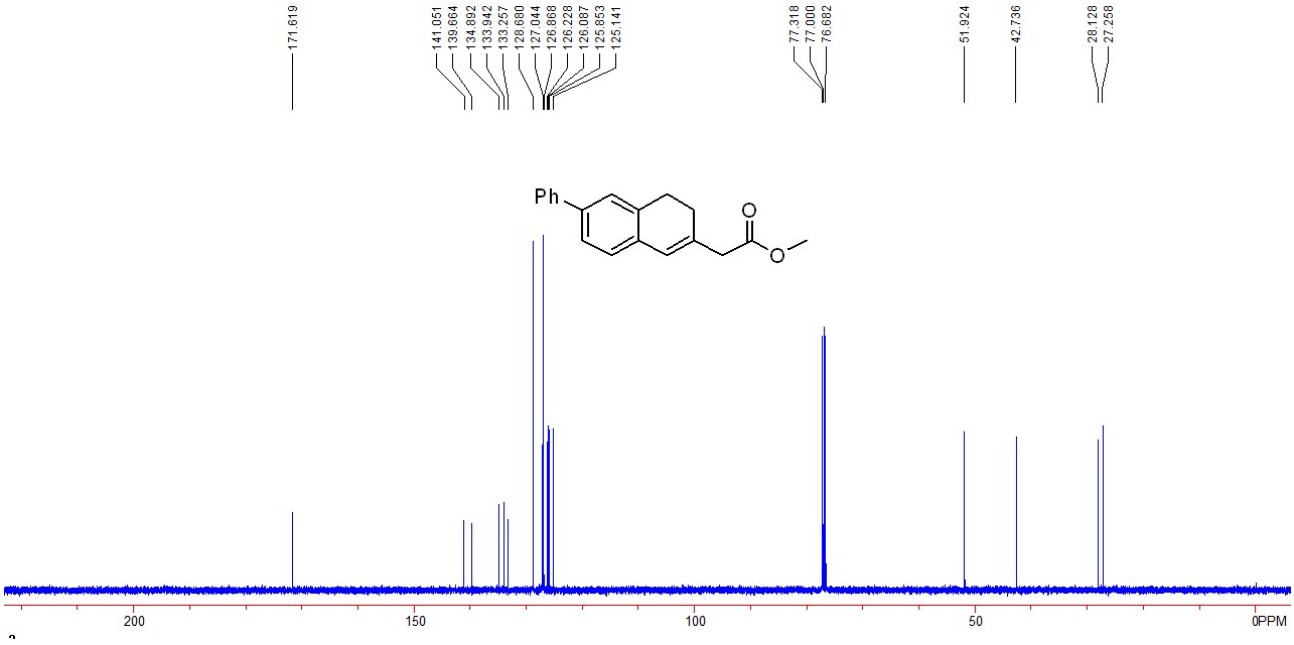


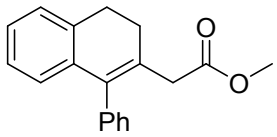




methyl 2-(6-phenyl-3,4-dihydronaphthalen-2-yl)acetate (6h).

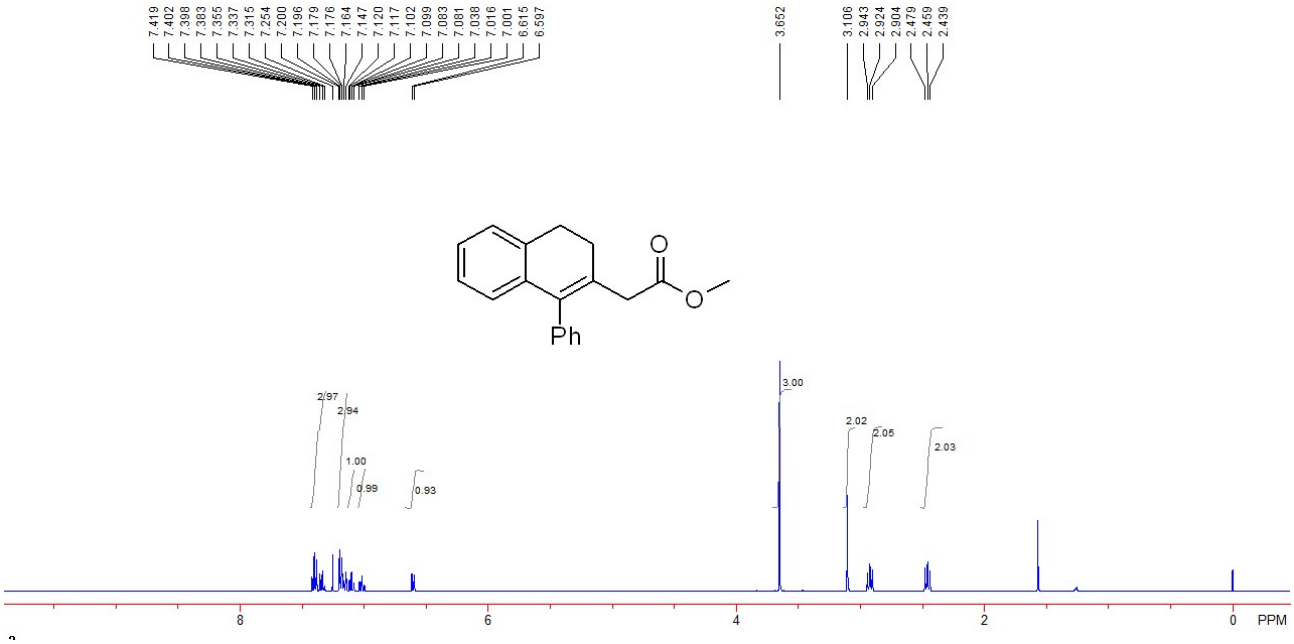
A colorless oil, 22.3 mg, 40% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.39 (t, J = 8.0 Hz, 2H, CH_2), 2.91 (t, J = 8.0 Hz, 2H, CH_2), 3.24 (s, 2H, CH_2), 3.71 (s, 3H, CH_3), 6.39 (s, 1H, CH), 7.07 (d, J = 8.0 Hz, 1H, ArH), 7.29-7.43 (m, 5H, ArH), 7.58 (d, J = 7.2 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 27.2, 28.1, 42.7, 51.9, 125.1, 125.8, 126.1, 126.2, 126.9, 127.0, 128.7, 133.2, 133.9, 134.9, 139.7, 141.0, 171.6. IR (CH_2Cl_2) ν 3032, 2948, 2825, 1734, 1483, 1430, 1257, 1150, 1008, 760, 696 cm^{-1}. MS (%) m/e 278 (M^+, 100.00), (219 (89.58), 218 (57.43), 217 (30.44), 205 (33.70), 204 (95.20), 203 (36.44), 202 (34.59). HRMS (EI) calcd. for $C_{19}H_{18}O_2$: 278.1307, Found: 278.1310.

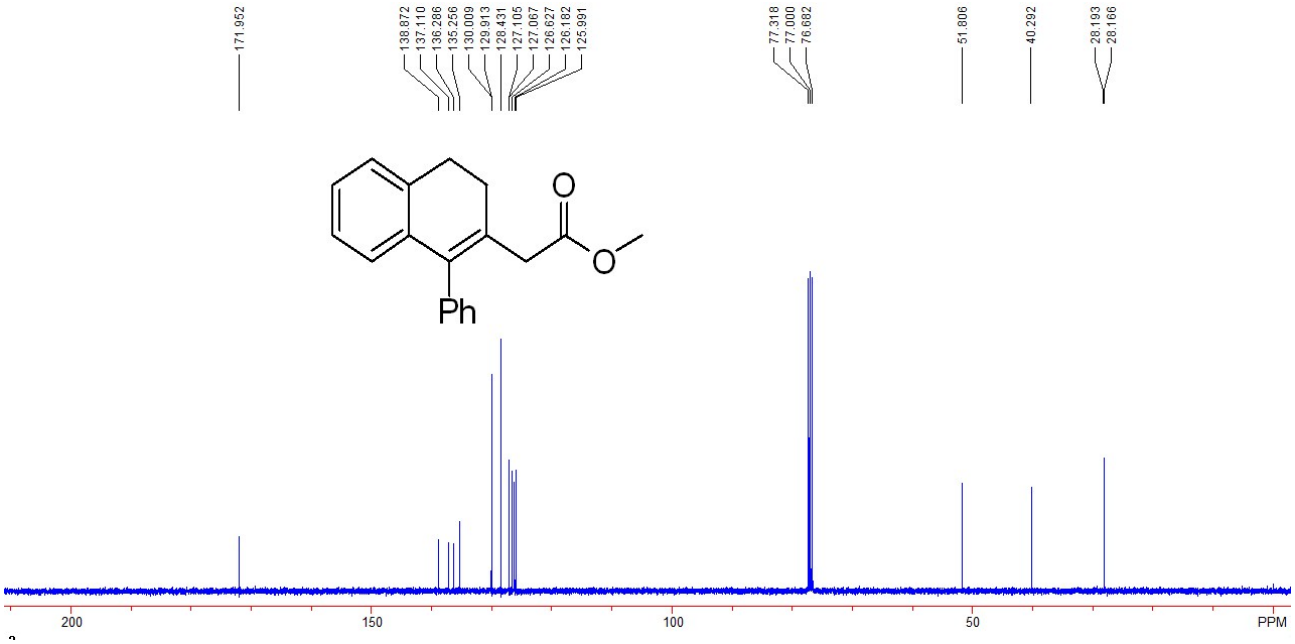


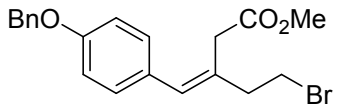


methyl 2-(1-phenyl-3,4-dihydronaphthalen-2-yl)acetate (6i).

A colorless oil, 8.3 mg, 15% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.46 (t, J = 8.0 Hz, 2H, CH_2), 2.92 (t, J = 8.0 Hz, 2H, CH_2), 3.11 (s, 2H, CH_2), 3.65 (s, 3H, CH_3), 6.61 (d, J = 7.2 Hz, 1H, ArH), 7.00-7.04 (m, 1H, ArH), 7.10 (dt, J = 1.2 Hz, 7.2 Hz, 1H, ArH), 7.15-7.20 (m, 3H, ArH), 7.32-7.42 (m, 3H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 28.16, 28.2, 40.3, 51.8, 126.0, 126.2, 126.6, 127.07, 127.10, 128.4, 129.9, 130.0, 135.2, 136.3, 137.1, 138.9, 172.0. IR (CH_2Cl_2) ν 3019, 2927, 2828, 1735, 1427, 1328, 1195, 1016, 768, 703 cm^{-1}. MS (%) m/e 278 (5.43), 218 (4.08), 204 (7.44), 88 (11.10), 86 (65.56), 84 (M^+, 100.00), 49 (16.70), 47 (19.04). HRMS (EI) calcd. for $C_{19}H_{18}O_2$: 278.1307, Found: 278.1309.

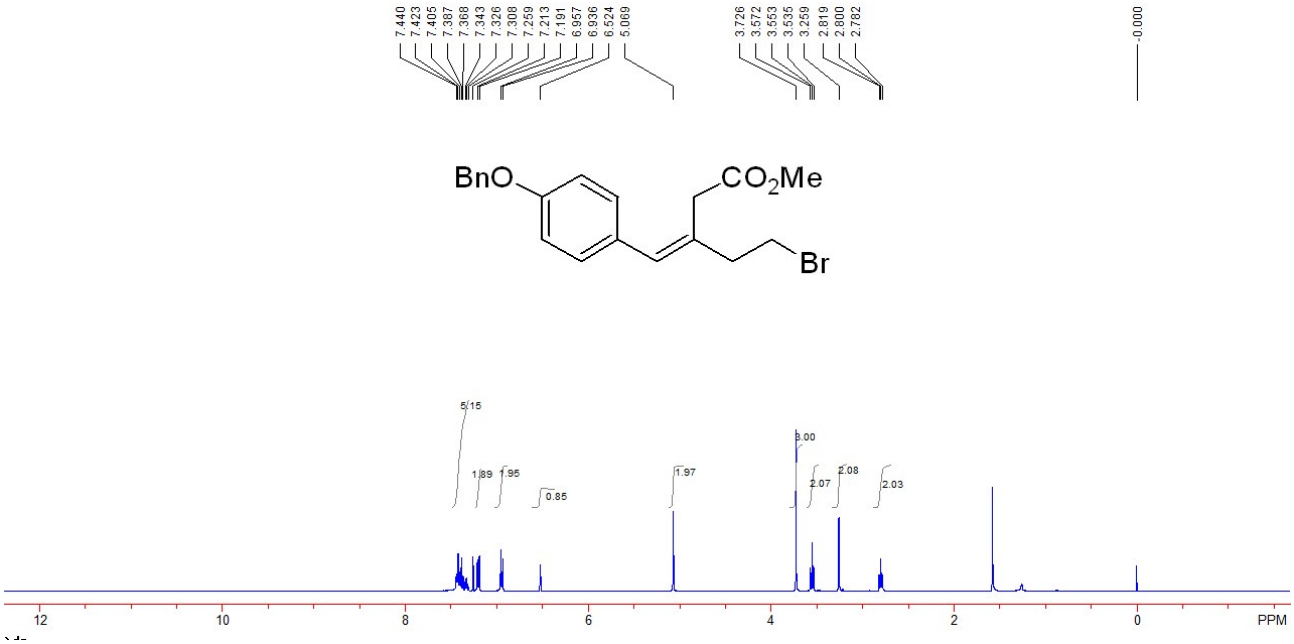


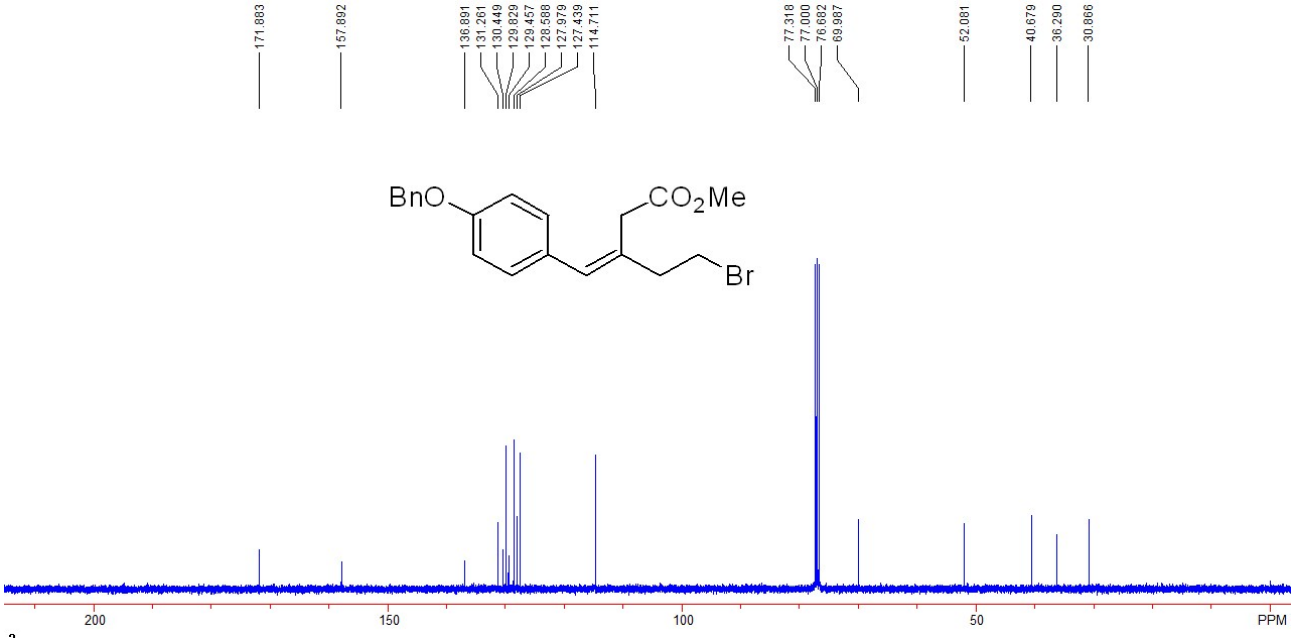


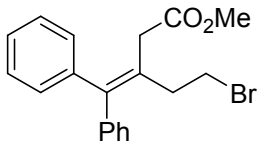


methyl (E)-3-(4-(benzyloxy)benzylidene)-5-bromopentanoate (7a).

A colorless oil, 3.9 mg, 5% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.80 (t, *J* = 7.6 Hz, 2H, CH_2), 3.26 (s, 2H, CH_2), 3.55 (t, *J* = 7.6 Hz, 2H, CH_2), 3.73 (s, 3H, CH_3), 5.07 (s, 2H, CH_2), 6.52 (s, 1H, CH), 6.95 (d, *J* = 8.4 Hz, 2H, ArH), 7.20 (d, *J* = 8.8 Hz, 1H, ArH), 7.31-7.44 (m, 5H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 30.9, 36.3, 40.7, 52.1, 70.0, 114.7, 127.4, 128.0, 128.6, 129.4, 129.8, 130.4, 131.3, 136.9, 157.9, 171.9. IR (CH_2Cl_2) ν 3037, 2945, 2922, 2846, 1732, 1606, 1508, 1243, 1175, 1013, 735, 696 cm^{-1}. MS (%) m/e 308 (4.77), 218 (5.17), 157 (13.40), 129 (5.02), 115 (6.46), 92 (9.79), 91 (M^+, 100.00), 65 (7.03). HRMS (EI) calcd. for $C_{20}H_{21}O_3Br$: 388.0674, Found: 388.0677.



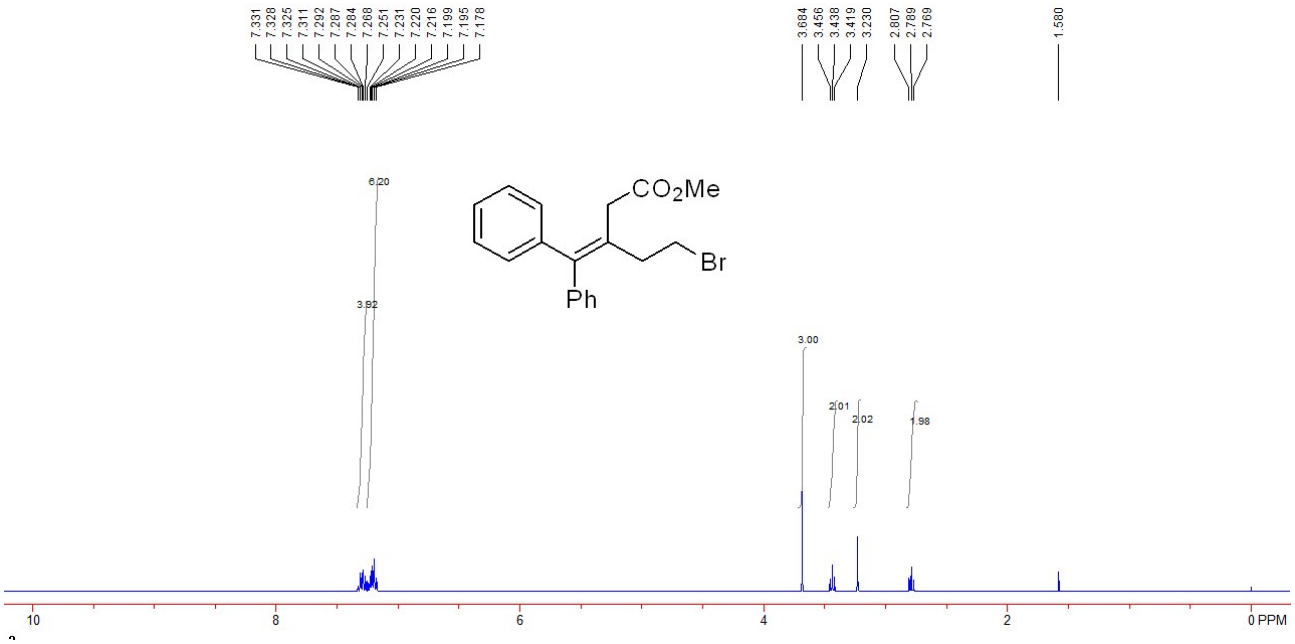


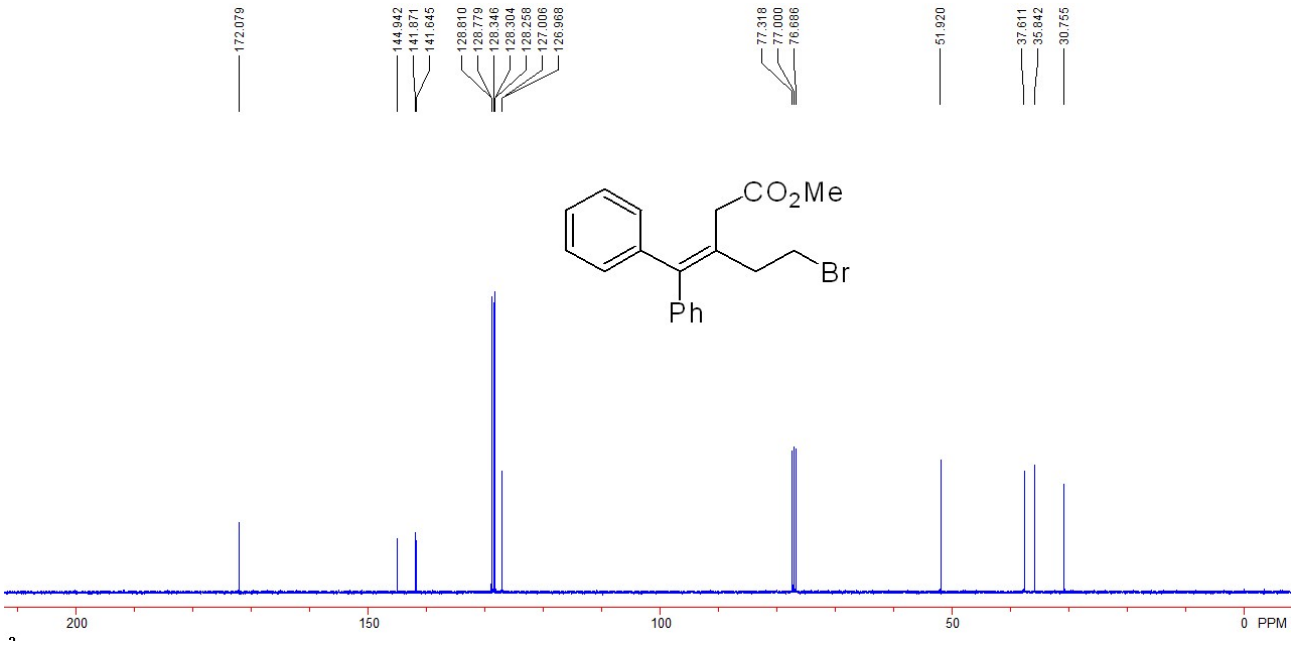


methyl 5-bromo-3-(diphenylmethylene)pentanoate (7i).

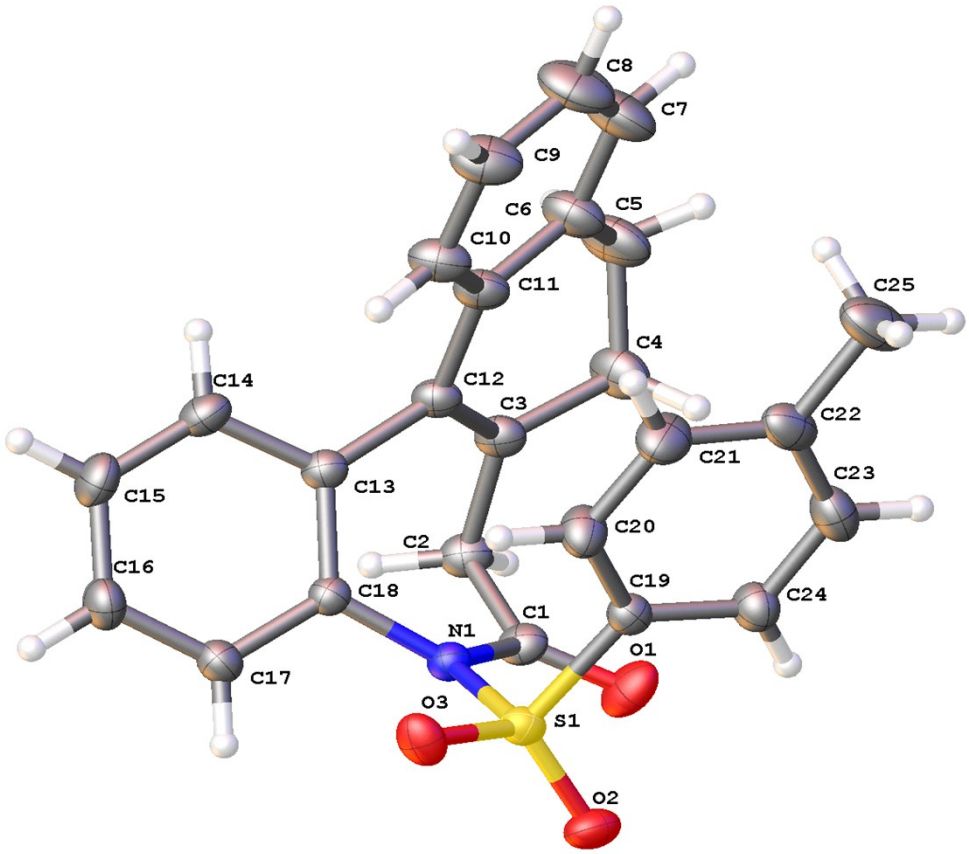
A colorless oil, 21.5 mg, 30% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.79 (t, J = 8.0 Hz, 2H, CH_2), 3.23 (s, 2H, CH_2), 3.44 (t, J = 8.0 Hz, 2H, CH_2), 3.68 (s, 3H, CH_3), 7.18-7.25 (m, 6H, ArH), 7.27-7.33 (m, 4H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 30.8, 35.8, 37.6, 51.9, 126.97, 127.00, 128.2, 128.30, 128.35, 128.78, 128.81, 141.6, 141.9, 144.9, 172.1. IR (CH_2Cl_2) ν 3055,

3021, 2943, 1733, 1435, 1336, 1270, 1168, 1014, 765 cm^{-1}. MS (%) m/e 278 (34.37), 219 (68.64), 218 (M^+, 100.00), 205 (87.30), 204 (75.27), 203 (38.88), 191 (35.35), 141 (31.64). HRMS (EI) calcd. for $C_{19}H_{19}O_2Br$: 358.0568, Found: 358.0570.





The Crystal Data of 2a



The crystal data of **2a** have been deposited in CCDC with number 1842217. Empirical formula: $C_{25}H_{21}NO_3S$, Formula weight: 415.49, Crystal system: Triclinic, Space group: P-1, Unit cell dimensions: a = 9.23890(10) Å, α = 70.3440(10)°; b = 9.9067(2) Å, β = 77.1870(10)°; c = 12.3018(2) Å, γ = 80.7730(10)°. Volume: 1029.42(3) $Å^3$, Z = 2, Density (calculated): 1.340 Mg/m^3, $F_{(000)}$ = 436, Crystal size: 0.08 x 0.06 x 0.03 mm^3, Final R indices [I>2sigma(I)]: R1 = 0.0399, wR2 = 0.1046.

References

1. K. Chen, R. Sun, Q. Xu, Y. Wei and M. Shi, *Org. Biomol. Chem.* 2013, **11**, 3949.

2. M.-T. Chen, X.-Y. Tang and M. Shi, *Org. Chem. Front.*, 2017, **4**, 86.