Supplementary Information for

One step synthesis of benzoxiazepine derivatives via PPh_3 catalyzed aza-MBH domino reaction between salicyl *N*-tosylimines and allenoates

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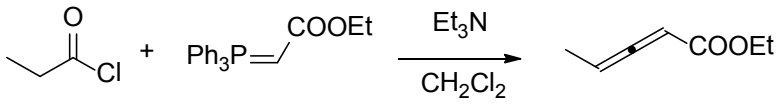
Contents

2. General Information

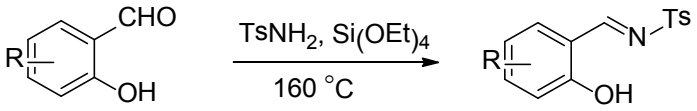
All the solvents were purified according to standard procedures. The ^{1}H NMR and Spectra were recorded at 400MHz, ^{13}C NMR was recorded at 100MHz. ^{1}H and ^{13}C NMR Chemical shifts were calibrated to tetramethylsilane as an external reference. Coupling constants are given in Hz. The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet: t, triplet; q, quartet; m, multiplet; HRMS were recorded on an Agilent Technologies 6520 Accurate-Mass Q-TOF LC/MS. Melting points were measured on a RY-I apparatus and are reported uncorrected.

3. General procedure for the synthesis of 5-Phenyl-penta-2,3-dienoic acid ethyl ester 1.[1]



Allenoate 1 is a known compound and synthesized according to a similar method developed by Hansen.[2] To a solution of (ethoxycarbonylmethylene)-triphenylphosphorane (0.1 mol) in dichloromethane (400 mL) was added 1.1 equivalent of triethylamine (0.11 mmol). After stirred for about 15 minutes, 1.1 equivalent of propanoyl chloride (0.11 mmol) was added dropwise. Then the reaction mixture was allowed to be warmed up to room temperature and stirred overnight. The resulting mixture was carefully evaporated to remove most of the solvent, and the residue was extracted by petroleum ether (b.p. 30-60 ^{o}C, 5 × 100 mL). The combined extracting was concentrated and the residue was subjected to column chromatography (eluant: 5% EtOAc in petroleum ether) to provide the allenoate **2** as yellow oil.

4. General procedure for the synthesis of *N*-Tosylaldimines



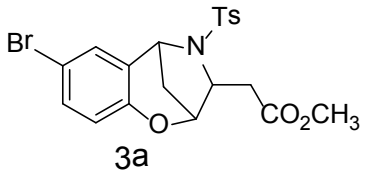
The aldehyde (4.8 mmol), *p*-toluenesufonamide (4.8 mmol), and $Si(OEt)_4$ (5.4 mmol)

were combined in a flask equipped with a still head and heated at 160 °C under nitrogen for 6 hours, during which time EtOH collected in the receiving flask. On cooling, the reaction mixture was suspended in Et_2O (50 ml), filtered, and the precipitate washed with Et_2O, the crude product was then recrystallized (EtOAc/hexanes).[3]

5. General procedure for the synthesis of benzoxiazepine derivatives

Imine ((0.30 mmol, 1.00 equiv) and PPh_3 (0.50 equiv) were dissolved in dry CH_2Cl_2 (3.0 mL), and then, methyl-penta-2,3-dienodate (3.00 equiv) was added to this solution, the reaction mixture was stirred at 40℃. After complete conversion, as indicated by TLC, all volatiles were removed in vacuo and the residue was purified by column chromatography (Petroleum ether(60-90 ^oC)/ethyl acetate = 10:1).

6. Analytical Data for Compounds 3

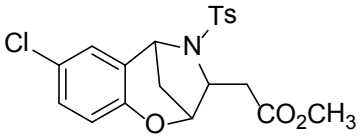


3a

3a methyl 2-(7-bromo-4-tosyl-2,3,4,5-tetrahydro-2,5-methanobenzo[f][1,4]oxazepin-3-yl)acetate

Mp 158-160 ^oC

^1H NMR (400 M, $CDCl_3$, TMS) δ7.34（d, 2H, J=8.4, Ph-H）7.11(d, 1H, J=2.4, Ph-H) 7.06-7.02(m, 3H, Ph-H) 6.29(d, 1H, J=8.8, Ph-H) 4.82(d, 1H, J=4.8, CH) 4.70(s, 1H, CH) 4.16(dd, 1H, J=3.2, 10.8, CH) 3.75(s, 3H, CH_3) 3.27(dd, 1H, J=3.6, 16.8, CH_2) 2.45(dd, 1H, J=10.4, 17.2, CH_2) 2.37(ddd, 1H, J=2.4,4.8，12.4, CH_2) 2.31(s, 3H, CH_3) 2.09(d, 1H, J=12.4, CH_2). ^{13}CNMR (100 M, $CDCl_3$, TMS) δ 171.0, 150.9, 143.4, 134.3, 132.2, 130.7, 129.0, 127.8, 125.0, 117.5, 111.9, 79.6, 64.0, 57.5, 52.0, 38.5, 29.4, 21.5. HRMS(ESI/$[M+H]^+$) Cacld. for: $C_{20}H_{21}BrNO_5S$ 466.0318, found 466.0310.

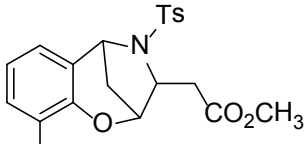


3b

3b methyl 2-(7-chloro-4-tosyl-2,3,4,5-tetrahydro-2,5-methanobenzo[f][1,4]oxazepin-3-yl)acetate

Mp 174-177^{o}C

^{1}H NMR (400 M, $CDCl_3$): δ7.34（d, 2H, J=8.4, Ph-H）7.04(d, 2H, J=8.0, Ph-H) 6.97(d, 1H, J=2.4, Ph-H) 6.90(dd, 1H, J=2.4, 8.4, Ph-H) 6.35(d, 1H, J=8.4, Ph-H) 4.82(d, 1H, J=4.8, CH) 4.70(s, 1H, CH) 4.15(dd, 1H, J=3.6, 10.8, CH) 3.75(s, 3H, CH_3) 3.26(dd, 1H, J=3.6, 16.8, CH_2) 2.45(dd, 1H, J=10.8, 16.8, CH_2) 2.36(ddd, 1H, J=2.8, 5.2, 12.8, CH_2) 2.30(s, 3H, CH_3) 2.10(d, 1H, J=12.4, CH_2). ^{13}C NMR (100 M, $CDCl_3$): δ171.0, 150.3, 143.4, 134.3, 129.3, 128.9, 127.9, 127.7, 124.6, 124.4, 117.0, 79.6, 64.0, 57.5, 52.0, 38.5, 29.4, 21.4. HRMS(ESI/$[M+H]^+$) Cacld. for: $C_{20}H_{21}ClNO_5S$ 422.0823, found 422.0823.

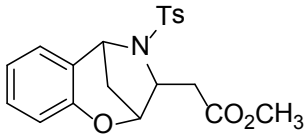


3c

3c methyl 2-(9-chloro-4-tosyl-2,3,4,5-tetrahydro-2,5-methanobenzo[f][1,4]oxazepin-3-yl)acetate

Mp 172-174 ^{o}C

^{1}H NMR (400 M, $CDCl_3$): δ7.16（d, 2H, J=8.0, Ph-H）7.02(dd, 1H, J=1.6, 8.0, Ph-H) 6.96(dd, 1H, J=1.6, 7.6, Ph-H) 6.91(d, 2H, J=8.0, Ph-H) 6.65(t, 1H, J=8.0, 15.6, Ph-H) 4.85(d, 1H, J=5.2, CH) 4.77(s, 1H, CH) 4.07(dd, 1H, J=3.6, 10.4, CH) 3.68(s, 3H, CH_3) 3.09(dd, 1H, J=3.6, 20.0, CH_2) 2.42-2.33(m, 2H, CH_2&CH_2) 2.24(s, 3H, CH_3) 2.04(d, 1H, J=12.8, CH_2). ^{13}C NMR (100 M, $CDCl_3$): δ170.7, 147.9, 143.4, 134.1, 130.3, 128.9, 127.5, 126.3, 125.3, 120.6, 120.4, 80.1, 64.0, 57.7, 52.1, 38.6, 29.6, 21.4. HRMS(ESI/$[M+H]^+$) Cacld. for: $C_{20}H_{21}ClNO_5S$ 422.0823, found 421.0822.

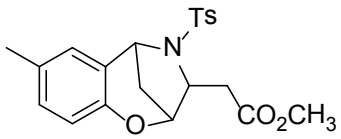


3d

3d methyl 2-(4-tosyl-2,3,4,5-tetrahydro-2,5-methanobenzo[f][1,4]oxazepin-3-yl)acetate

Mp 120-130 ^{o}C

^{1}H NMR (400 M, $CDCl_3$): δ7.22（d, 2H, J=8.0, Ph-H）7.13(dd, 1H, J=1.6, 7.2, Ph-H) 7.03(td, 1H, J=1.6, 7.6, Ph-H) 6.94(d, 2H, J=8.4, Ph-H) 6.77(td, 1H, J=1.2, 7.6, Ph-H) 6.43(d, 1H, J=8.0, Ph-H) 4.92(d, 1H, J=4.8, CH) 4.67(s, 1H, CH) 4.02(dd, 1H, J=3.2, 10.4, CH) 3.74(s, 1H, CH_3) 3.21(dd, 1H, J=3.6, 16.8, CH_2) 2.43(dd, 1H, J=10.8, 16.8, CH_2) 2.37(ddd, 1H, J=2.8, 5.2, 12.4, CH_2) 2.30(s, 3H, CH_3) 2.10(d, 1H, J=12.4, CH_2). ^{13}C NMR (100 M, $CDCl_3$): δ171.0, 152.0, 143.0, 130.2, 130.0, 129.8, 128.9, 127.8, 127.3, 123.7, 119.9, 115.7, 79.4, 63.8, 58.2, 52.0, 38.4, 29.7, 21.4. HRMS(ESI/$[M+H]^+$) Cacld. for: $C_{20}H_{22}NO_5S$ 388.1213, found 388.1215.

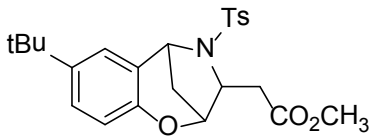


3e

3e methyl 2-(7-methyl-4-tosyl-2,3,4,5-tetrahydro-2,5-methanobenzo[f][1,4]oxazepin-3-yl)acetate

Mp 188-190 °C

^{1}H NMR (400 M, $CDCl_3$): δ7.27-7.25（m, 2H, Ph-H）6.95(d, 2H, J=8.4, Ph-H) 6.85(d, 1H, J=1.6, Ph-H) 6.78(dd, 2H, J=2.0, 8.0, Ph-H) 6.32(d, 1H, J=8.0, Ph-H) 4.84(d, 1H, J=4.8, CH) 4.65(s, 1H, CH) 4.07(dd, 1H, J=3.6, 10.8, CH) 3.74(s, 3H, CH_3) 3.23(dd, 1H, J=3.6, 16.8, CH_2) 2.43(dd, 1H, J=10.8, 16.4, CH_2) 2.34(ddd, 1H, J=2.8, 5.2，12.4, CH_2) 2.27(s, 3H, CH_3) 2.23(s, 3H, CH_3) 2.11(d, 1H, J=12.4, CH_2). ^{13}C NMR (100 M, $CDCl_3$): δ171.0, 149.6, 142.9, 134.5, 130.0, 128.9, 128.7, 128.6, 127.8, 123.0, 115.4, 79.4, 63.9, 58.2, 52.0, 38.5, 29.8, 21.4, 20.2. HRMS(ESI/$[M+H]^+$) Cacld. for: $C_{21}H_{24}NO_5S$ 402.1370, found 402.1375.

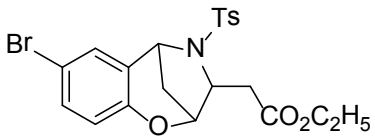


3f

3f methyl 2-(7-(tert-butyl)-4-tosyl-2,3,4,5-tetrahydro-2,5-methanobenzo[f][1,4]oxazepin-3-yl)acetate

^{1}H NMR (400 M, $CDCl_3$): δ7.19（d, 2H, J=8.4, Ph-H）7.16(d, 1H, J=2.4, Ph-H) 7.61(dd, 1H, J=2.8, 8.8, Ph-H) 6.92(d, 2H, J=8.0, Ph-H) 6.35(d, 1H, J=8.4, Ph-H) 4.93(d, 1H, J=4.8, CH) 4.64(s, 1H, CH) 3.99(dd, 1H, J=3.6, 10.8, CH) 3.74(s, 3H, CH_3) 3.22(dd, 1H, J=4.0, 16.8, CH_2) 2.43(dd, 1H, J=10.8, 16.4, CH_2) 2.35(ddd, 1H, J=2.8, 5.2，12.4, CH_2)

2.27(s, 3H, CH_3) 2.12(d, 1H, J=12.4, CH_2) 1.33(s, 9H, CH_3). ^{13}C NMR (100 M, $CDCl_3$): δ171.0, 149.6, 142.8, 142.6, 134.3, 128.8, 127.7, 126.7, 124.9, 123.1, 115.1, 79.4, 63.7, 58.7, 52.0, 38.4, 34.1, 31.6, 29.9, 21.4. HRMS(ESI/$[M+H]^+$) Cacld. for: $C_{24}H_{30}NO_5S$ 444.1839, found 444.1842.

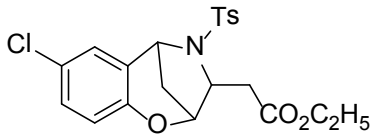


3g

3g ethyl 2-(7-bromo-4-tosyl-2,3,4,5-tetrahydro-2,5-methanobenzo[f][1,4]oxazepin-3-yl)acetate

Mp 122-124 °C

^1H NMR (400 M, $CDCl_3$): δ7.35（d, 2H, J=8.0, Ph-H）7.12(d, 1H, J=2.0, Ph-H) 7.06-7.04(m, 3H, Ph-H) 6.30(d, 1H, J=8.4, Ph-H) 4.82(d, 1H, J=4.8, CH) 4.71(s, 1H, CH) 4.24-4.14(m, 3H, CH_2 &CH) 3.26(dd, 1H, J=3.6, 16.8, CH_2) 2.47-2.36(m, 2H, CH_2&CH_2) 2.31(s, 3H, CH_3) 2.10(d, 1H, J=12.4, CH_2) 1.32(t, 3H, J=7.2, 14.0, CH_3). ^{13}C NMR (100 M, $CDCl_3$): δ170.6, 150.9, 143.3, 134.3, 132.2, 130.7, 128.9, 127.7, 125.0, 117.5, 111.9, 79.6, 64.1, 61.0, 57.5, 38.7, 29.4, 21.4, 14.2. HRMS(ESI/$[M+Na]^+$) Cacld. for: $C_{21}H_{22}BrNO_5SNa$ 502.0294, found 502.0285.

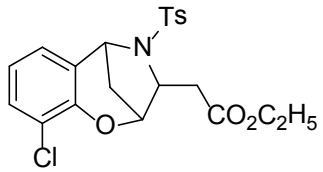


3h

3h ethyl 2-(7-chloro-4-tosyl-2,3,4,5-tetrahydro-2,5-methanobenzo[f][1,4]oxazepin-3-yl)acetate

Mp. 137-139 °C

^1H NMR (400 M, $CDCl_3$): δ7.34（d, 2H, J=8.0, Ph-H）7.03(d, 2H, J=8.0, Ph-H) 6.98(d, 1H, J=2.4, Ph-H) 6.90(dd, 1H, J=2.4, 8.8, Ph-H) 6.35(d, 1H, J=8.8, Ph-h) 4.82(d, 1H, J=5.2, CH) 4.70(s, 1H, CH) 4.23-4.13(m, 3H, CH_2 &CH) 3.25(dd, 1H, J=3.2, 16.8, CH_2) 2.46-2.34(m, 2H, CH_2&CH_2) 2.30(s, 3H, CH_3) 2.10(d, 1H, J=12.4, CH_2) 1.31(t, 3H, J=7.2, 14.4, CH_3). ^{13}C NMR (100 M, $CDCl_3$): δ170.6, 150.4, 143.3, 134.3, 129.2, 128.9, 127.9, 127.7, 124.6, 124.5, 117.0, 79.6, 64.1, 61.0, 57.5, 38.7, 29.4, 21.4, 14.2. HRMS(ESI/$[M+Na]^+$) Cacld. for: $C_{21}H_{22}ClNO_5SNa$ 458.0799, found 458.0797.

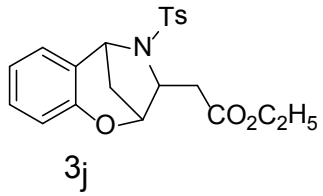


3i

3i ethyl 2-(9-chloro-4-tosyl-2,3,4,5-tetrahydro-2,5-methanobenzo[f][1,4]oxazepin-3-yl)acetate

Mp 154-156 ^{o}C

^{1}H NMR (400 M, $CDCl_3$): δ7.23（d, 2H, J=7.6, Ph-H）7.09(d, 1H, J=8.0, Ph-H) 7.03(d, 1H, J=7.2, Ph-H) 6.98(d, 2H, J=7.6, Ph-H) 6.71(t, 1H, J=7.6, 15.2, Ph-H) 4.92(d, 1H, J=4.8, CH) 4.83(s, 1H, CH) 4.20 (q, 2H, J=6.8, 14.0, CH_2) 4.14(dd, 1H, J=4.0, 11.2, CH) 3.14(dd, 1H, J=3.6, 16.4, CH_2) 2.46-2.40(m, 2H, CH_2&CH_2) 2.31(s, 3H, CH_3) 2.11(d, 1H, J=12.8, CH_2) 1.31(t, 3H, J=7.2, 14.4 CH_3). ^{13}C NMR (100 M, $CDCl_3$): δ170.3, 147.9, 143.4, 134.1, 130.3, 128.9, 127.5, 126.4, 125.3, 120.6, 120.4, 80.1, 64.1, 61.0, 57.7, 38.8, 29.6, 21.4, 14.2. HRMS(ESI/$[M+Na]^+$) Cacld. for: $C_{21}H_{22}ClNO_5SNa$ 458.0799, found 458.798.

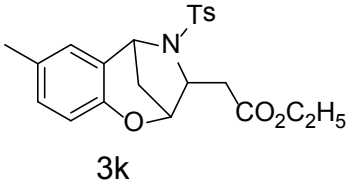


3j

3j ethyl 2-(4-tosyl-2,3,4,5-tetrahydro-2,5-methanobenzo[f][1,4]oxazepin-3-yl)acetate

Mp 121-123 ^{o}C

^{1}H NMR (400 M, $CDCl_3$): δ7.22（d, 2H, J=7.6, Ph-H）7.13(d, 1H, J=7.2, Ph-H) 7.03(t, 1H, J=7.6, 15.6, Ph-H) 6.94(d, 2H, J=7.6, Ph-H) 6.76(t, 1H, J=7.6, 14.8, Ph-H) 6.42(d, 1H, J=8.4, Ph-H) 4.92(d, 1H, J=4.8, CH) 4.67(s, 1H, CH) 4.19(q, 2H, J=6.8, 13.6, CH_2) 4.02(dd, 1H, J=3.2, 14.0, CH) 3.20(dd, 1H, J=3.2, 16.8, CH_2) 2.44-2.35(m, 2H, CH_2&CH_2) 2.28(s, 3H, CH_3) 2.12(d, 1H, J=12.4, CH_2) 1.30(t, 3H, J=7.2, 14.4 CH_3). ^{13}C NMR (100 M, $CDCl_3$): δ170.6, 152.0, 143.0, 134.2, 129.8, 128.9, 128.1, 127.8, 123.7, 119.8, 115.7, 79.4, 63.8, 60.9, 58.2, 38.6, 29.7, 21.4, 14.2. HRMS(ESI/$[M+Na]^+$) Cacld. for: $C_{21}H_{23}NO_5SNa$ 424.1189, found 424.1194.

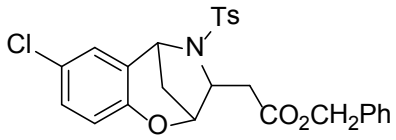


3k

3k ethyl 2-(7-methyl-4-tosyl-2,3,4,5-tetrahydro-2,5-methanobenzo[f][1,4]oxazepin-3-yl)acetate

Mp 102-104 ^{o}C

^{1}H NMR (400 M, $CDCl_3$): δ7.26（d, 2H, J=8.0, Ph-H）6.95(d, 2H, J=8.4, Ph-H) 6.85(d, 1H, J=1.6, Ph-H) 6.78(dd, 1H, J=2.0, 6.8, Ph-H) 6.31(d, 1H, J=8.4, Ph-H) 4.84(d, 1H, J=4.8, CH) 4.65(s, 1H, CH) 4.20(td, 2H, J=2.0, 7.2, CH_2) 4.07(dd, 1H, J=3.2, 10.8, CH) 3.22(dd, 1H, J=3.6, 16.4, CH_2) 2.41(dd, 1H , J=11.2, 16.8, CH_2) 2.34(ddd, 1H, J=2.8, 5.2, 12.4, CH_2) 2.28(s, 3H, CH_3) 2.23(s, 3H, CH_3) 2.10(d, 1H, J=12.4, CH_2) 1.30(t, 3H, J=7.2, 14.4 CH_3). ^{13}C NMR (100 M, $CDCl_3$): δ170.6, 149.6, 142.9, 134.5, 130.0, 128.9, 128.7, 128.6, 127.8, 123.0, 115.4, 79.4, 64.0, 60.9, 58.2, 38.8, 29.8, 21.4, 20.2, 14.2. HRMS(ESI/$[M+H]^+$) Cacld. for: $C_{22}H_{26}NO_5S$ 416.1526, found 416.1531.

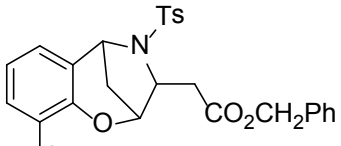


3m

3m benzyl 2-(7-chloro-4-tosyl-2,3,4,5-tetrahydro-2,5-methanobenzo[f][1,4]oxazepin-3-yl)acetate

Mp 222-224 ^{o}C

^{1}H NMR (400 M, $CDCl_3$): δ7.40-7.35(m, 5H, Ph-H) 7.32（d, 2H, J=8.0, Ph-H）7.00(d, 2H, J=8.0, Ph-H) 6.97(d, 1H, J=2.8, Ph-H) 6.90(dd, 1H, J=2.4, 8.8, Ph-H) 6.34(d, 1H, J=8.4, Ph-H) 5.18(s, 2H, CH_2) 4.81(d, 1H, J=4.8, CH) 4.68(s, 1H, CH) 4.16(dd, 1H, J=3.2, 10.8, CH) 3.25(dd, 1H, J=3.6, 16.8, CH_2) 2.48(dd, 1H, J=10.8, 16.4, CH_2) 2.34(ddd, 1H, J=2.8, 5.2, 12.8, CH_2) 2.29(s, 3H, CH_3) 2.08(d, 1H, J=12.4, CH_2). ^{13}C NMR (100 M, $CDCl_3$): δ170.4, 150.4, 143.3, 134.3, 129.3, 128.9, 128.7, 128.5, 128.4, 127.9, 127.7, 124.6, 124.4, 117.0, 79.6, 66.8, 64.0, 57.0, 38.7, 29.4, 21.4. HRMS(ESI/$[M+H]^+$) Cacld. for: $C_{26}H_{25}ClNO_5S$ 498.1136, found 498.1125.



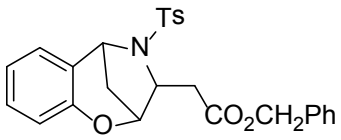
3n

3n benzyl 2-(9-chloro-4-tosyl-2,3,4,5-tetrahydro-2,5-methanobenzo[f][1,4]oxazepin-3-yl)acetate

Mp 192-194 ^{o}C

^{1}H NMR (400 M, $CDCl_3$): δ7.40-7.35(m, 5H, Ph-H) 7.21（d, 2H, J=8.4, Ph-H）7.09(dd,

1H, J=1.6, 8.0, Ph-H) 7.03(dd, 1H, J=1.6, 7.6, Ph-H) 6.93(d, 2H, J=8.0, Ph-H) 6.72(t, 1H, J=7.6, 15.2, Ph-H) 5.19(s, 2H, CH_2) 4.91(d, 1H, J=4.8, CH) 4.82(s, 1H, CH) 4.16(dd, 1H, J=3.6, 10.4, CH) 3.20(dd, 1H, J=3.6, 16.4, CH_2) 2.49(dd, 1H, J=10.8, 16.4, CH_2) 2.39(ddd, 1H, J=2.8, 5.2, 12.8, CH_2) 2.29(s, 3H, CH_3) 2.10(d, 1H, J=12.4, CH_2). ^{13}C NMR (100 M, $CDCl_3$): δ170.1, 147.9, 143.4, 135.5, 133.9, 130.3, 128.9, 128.7, 128.4, 128.3, 127.5, 126.4, 125.2, 120.6, 120.4, 80.1, 66.9, 64.0, 57.8, 38.7, 29.6, 21.4. HRMS(ESI/$[M+H]^+$) Cacld. for: $C_{26}H_{25}ClNO_5S$ 498.1136, found 498.1124.

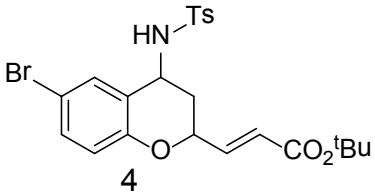


3o

3o benzyl 2-(4-tosyl-2,3,4,5-tetrahydro-2,5-methanobenzo[f][1,4]oxazepin-3-yl)acetate

Mp 169-171 °C

^1H NMR (400 M, $CDCl_3$): δ7.40-7.35(m, 5H, Ph-H) 7.20（d, 2H, J=8.4, Ph-H）7.13(dd, 1H, J=1.6, 7.2, Ph-H) 7.03(td, 1H, J=1.6, 8.0, Ph-H) 6.90(d, 2H, J=8.0, Ph-H) 6.77(td, 1H, J=0.8, 7.6, Ph-H) 6.42(d, 1H, J=8.0, Ph-H) 5.18(d, 1H, J=2.4, CH_2) 4.91(d, 1H, J=4.8, CH) 4.66(s, 1H, CH) 4.04(dd, 1H, J=3.6, 10.8, CH) 3.25(dd, 1H, J=3.6, 16.8, CH_2) 2.48(dd, 1H, J=10.8, 16.8, CH_2) 2.34(ddd, 1H, J=2.4, 4.8, 12.4, CH_2) 2.27(s, 3H, CH_3) 2.12(d, 1H, J=12.4, CH_2). ^{13}C NMR (100 M, $CDCl_3$): δ170.4, 152.0, 143.0, 135.5, 134.1, 129.8, 128.9, 128.7, 128.4, 128.1, 127.8, 123.7, 119.9, 115.7, 79.4, 66.8, 64.0, 58.2, 38.5, 29.7, 21.4. HRMS(ESI/$[M+H]^+$) Cacld. for: $C_{26}H_{26}NO_5S$ 464.1526, found 464.1519.



4

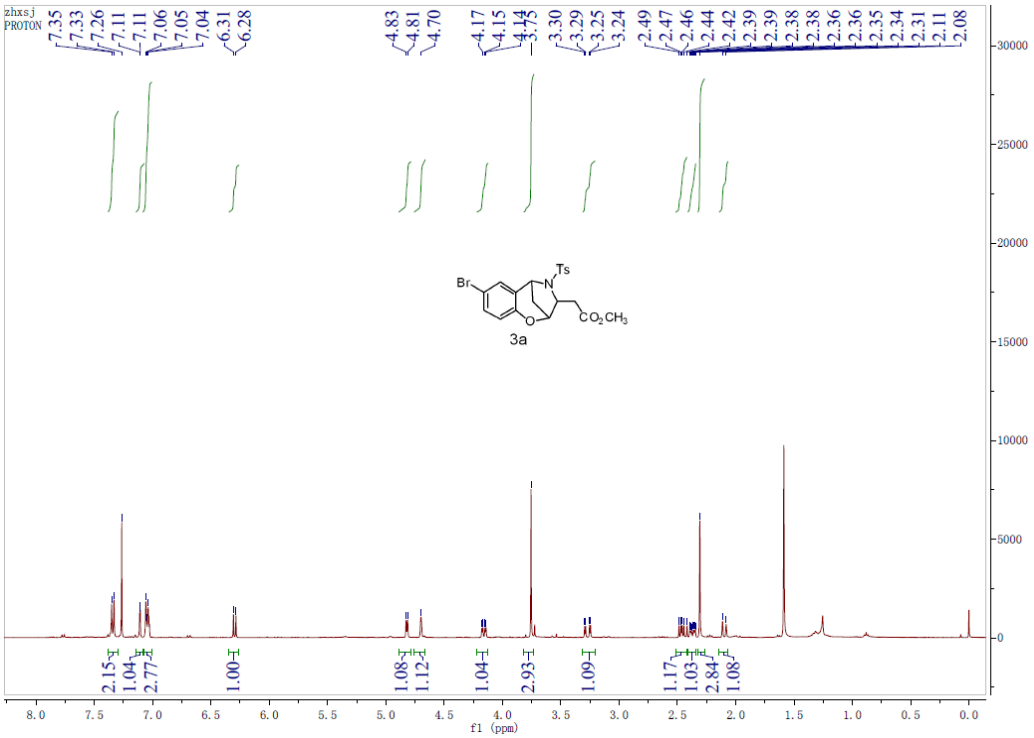
4 (E)-tert-butyl 3-(6-bromo-4-(4-methylphenylsulfonamido)chroman-2-yl)acrylate

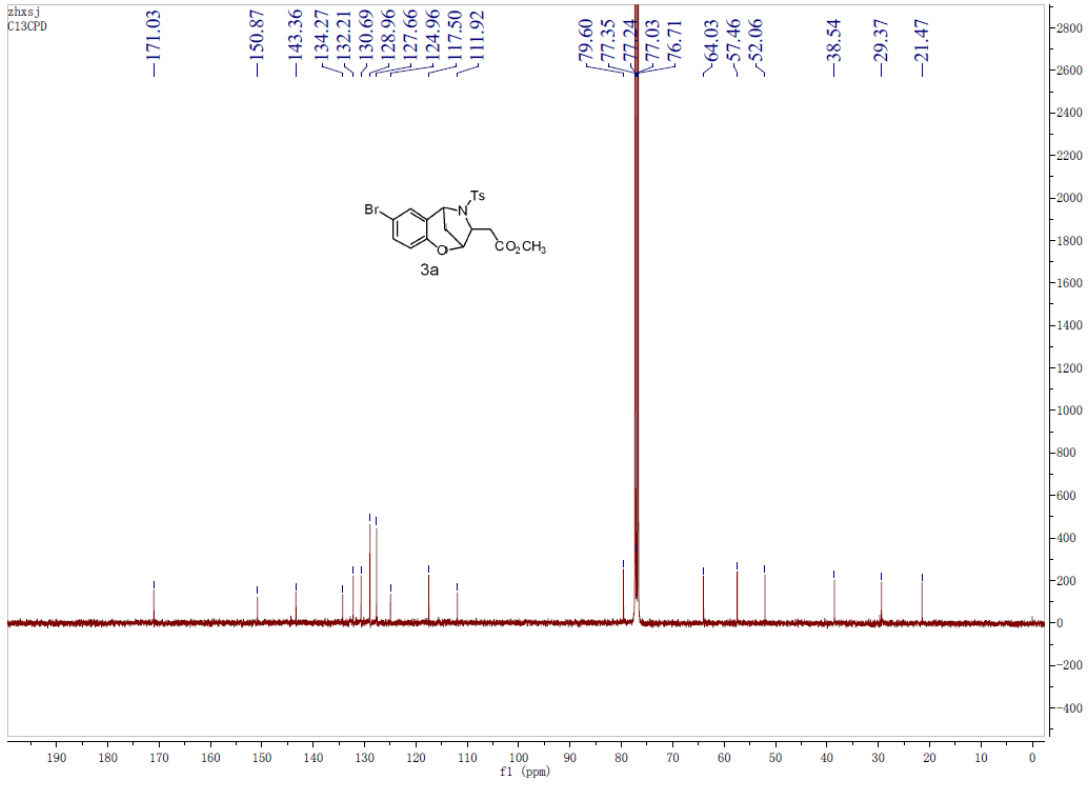
Mp 165-168 °C

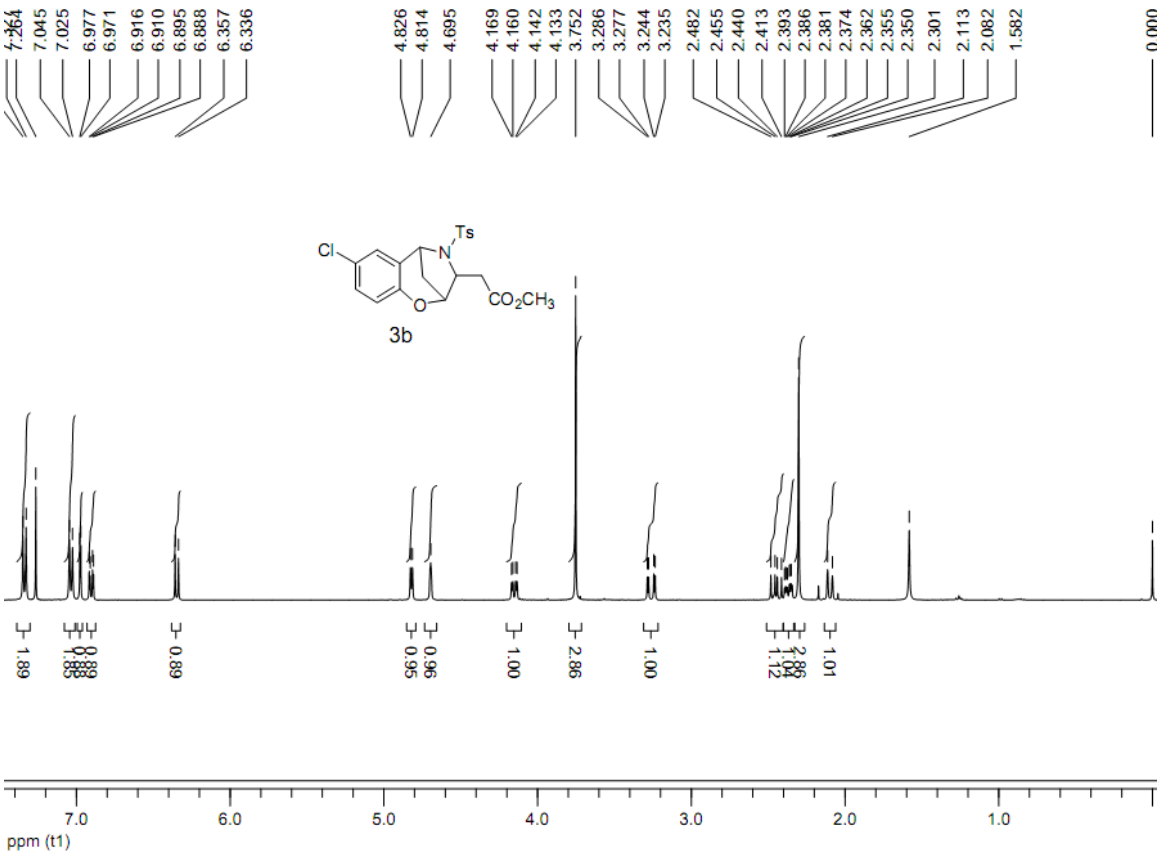
^1H NMR (400 M, $CDCl_3$): δ7.83(d, 2H, J=8.2, Ph-H) 7.38(d, 2H, J=8.1, Ph-H) 7.23(dd, 1H, J=2.3, 8.8, Ph-H) 7.06(d, 1H, J=2.3, Ph-H) 6.87(dd, 1H, J=4.3, 15.6, CH=CH) 6.70(d, 1H, J=8.8, Ph-H) 6.05(dd, 1H, J=1.6, 15.6, CH=CH) 4.72-4.67(m, 3H,

NH&CH&CH) 2.48(s, 3H, CH_3) 2.28-2.23(m, 1H, CH_2) 1.83-1.72(m, 1H, CH_2) 1.49(s, 9H, ^{t}Bu-H). ^{13}C NMR (100 M, $CDCl_3$): δ165.3, 153.3, 144.1, 142.9, 132.4, 130.5, 130.2, 127.2, 126.9, 123.9, 123.8, 118.9, 113.4, 81.0, 48.5, 35.2, 28.1, 21.6. HRMS(ESI/$[M+NH_4]^+$) Cacld. for: $C_{23}H_{27}BrN_2O_5S$ 525.1053, found 525.1029.

7. NMR spectra for all new compounds



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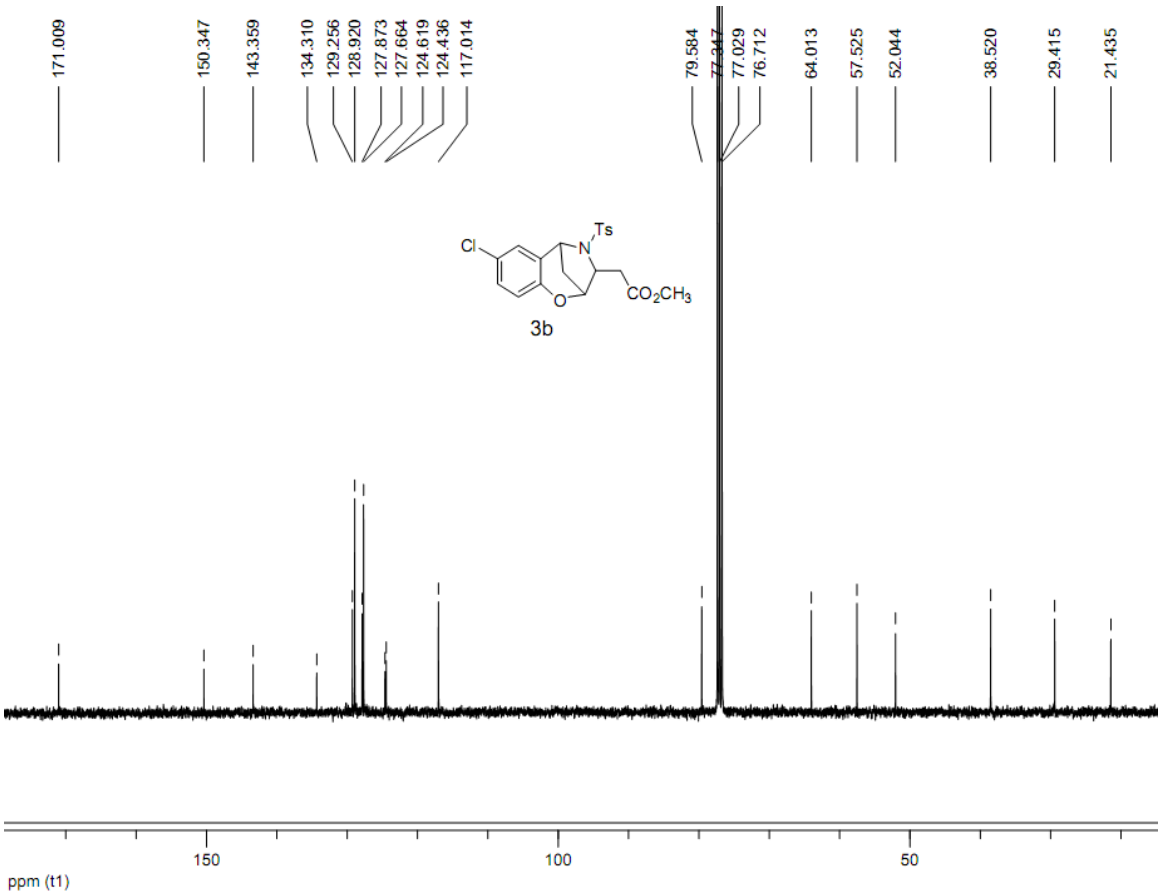
7.025
6.977
6.971
6.916
6.910
6.895
6.888
6.357
6.336
4.826
4.814
4.695
4.169
4.160
4.142
4.133
3.752
3.286
3.277
3.244
3.235
2.482
2.455
2.440
2.413
2.393
2.386
2.381
2.374
2.362
2.355
2.350
2.301
2.113
2.082
1.582
0.000
Cl
Ts
N
O
CO2CH3
3b
1.89
0.89
0.95
0.96
1.00
2.86
1.00
1.01
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)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134.310
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128.920
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127.664
124.619
124.436
117.014
79.584
77.347
77.029
76.712
64.013
57.525
52.044
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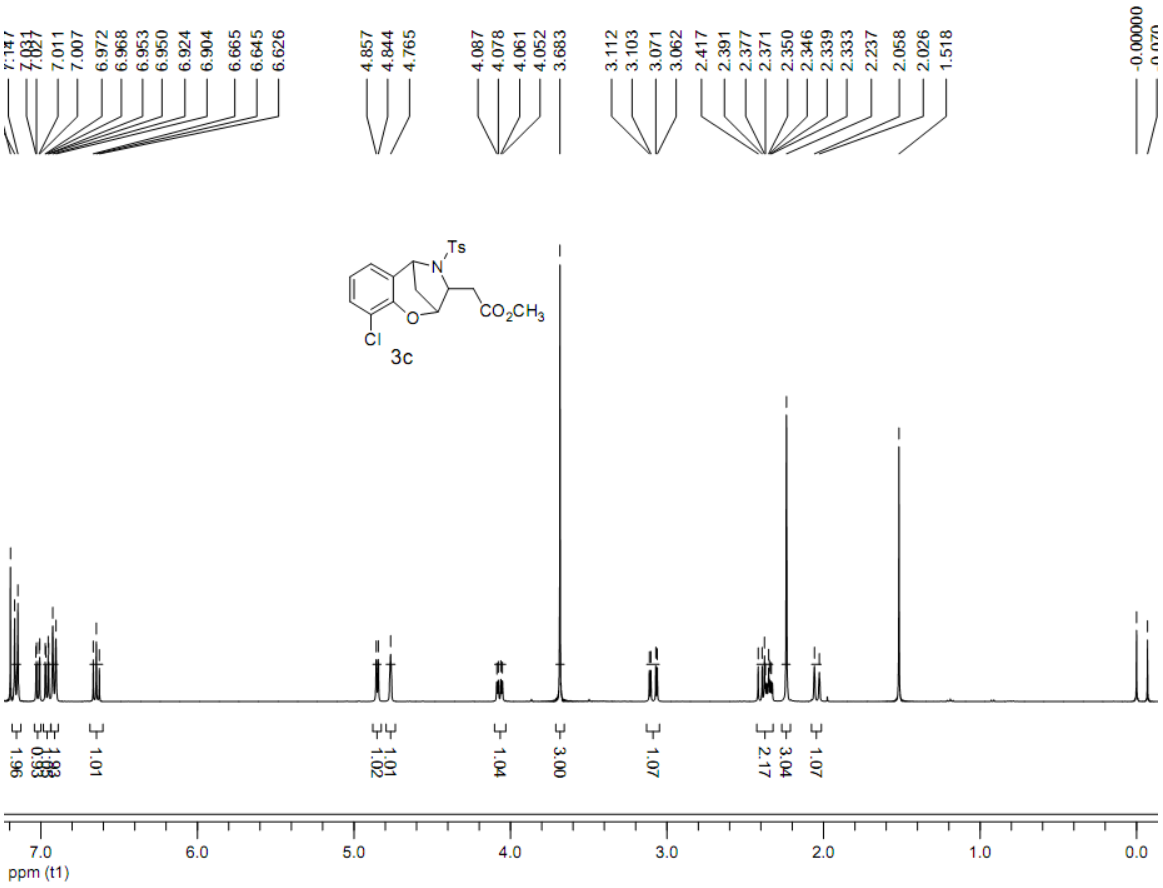
29.415
21.435
Cl
Ts
N
O
CO2CH3
3b
150
100
50
ppm (t1)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6.924
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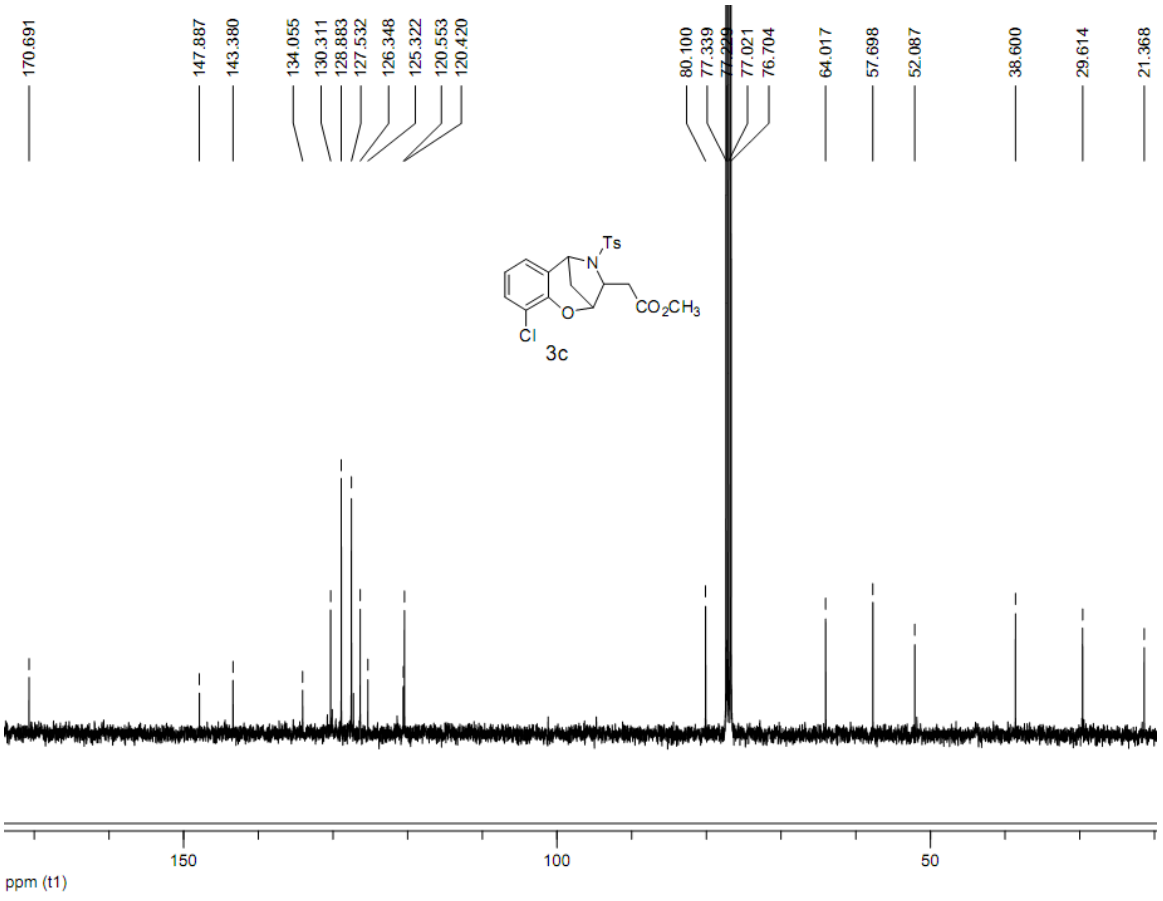
6.665
6.645
6.626
4.857
4.844
4.765
4.087
4.078
4.061
4.052
3.683
3.112
3.103
3.071
3.062
2.417
2.391
2.377
2.371
2.350
2.346
2.339
2.333
2.237
2.058
2.026
1.518
-0.00000
Ts
N
O
CO2CH3
Cl
3c
1.96
1.01
1.02
1.01
1.04
3.00
1.07
2.17
3.04
1.07
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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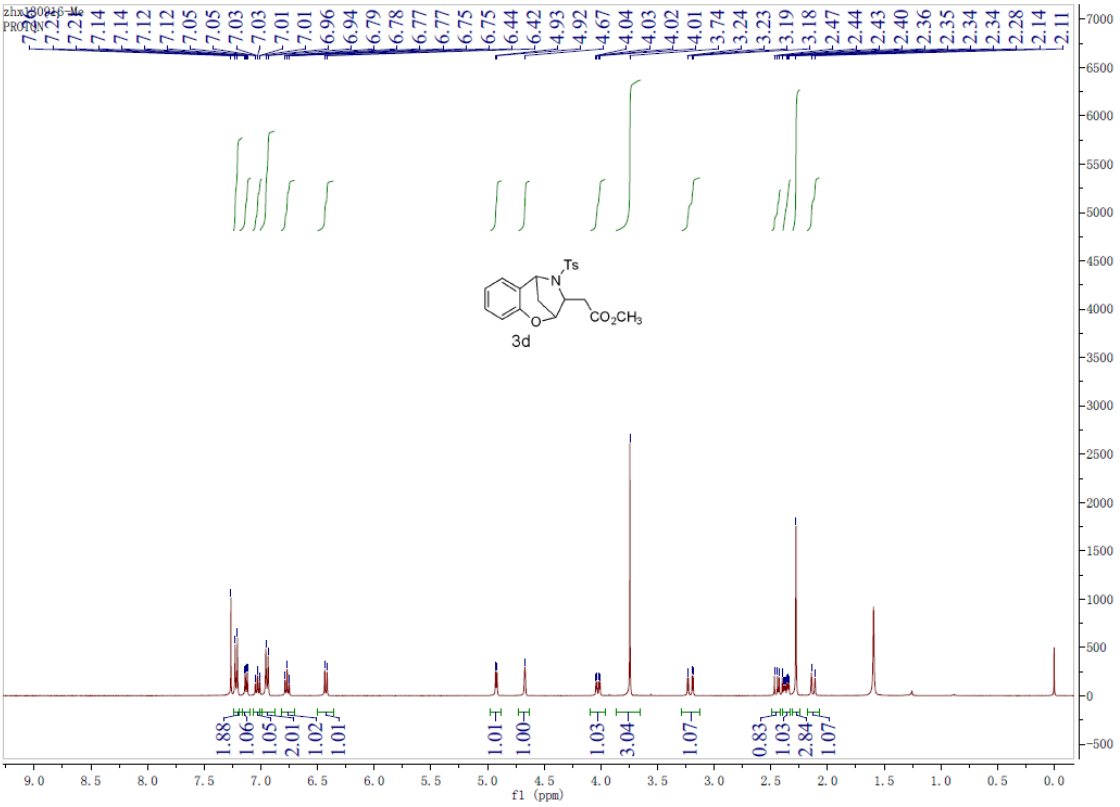
147.887
143.380
134.055
130.311
128.883
127.532
126.348
125.322
120.553
120.420
80.100
77.339
77.021
76.704
64.017
57.698
52.087
38.600
29.614
21.368
Ts
N
O
CO2CH3
Cl
3c
150
100
50
ppm (t1)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7.21
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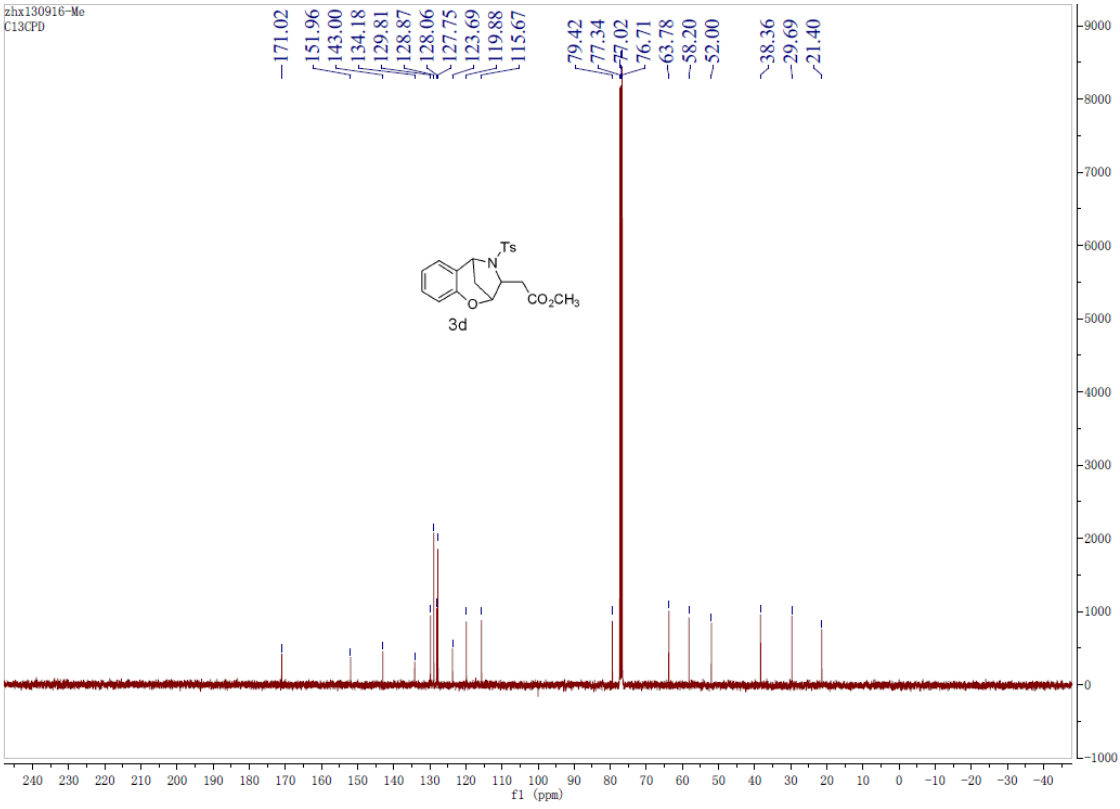
7.12
7.05
7.03
7.01
6.96
6.94
6.79
6.78
6.77
6.75
6.44
6.42
4.93
4.92
4.67
4.04
4.03
4.02
4.01
3.74
3.24
3.23
3.19
3.18
2.47
2.44
2.43
2.40
2.36
2.35
2.34
2.34
2.28
2.14
2.11
Ts
N
O
CO2CH3
3d
1.88
1.06
1.05
2.01
1.02
1.01
1.01
1.00
1.03
3.04
1.07
0.83
1.03
2.84
1.07
f1 (ppm)


zhx130916-Me
C13CPD
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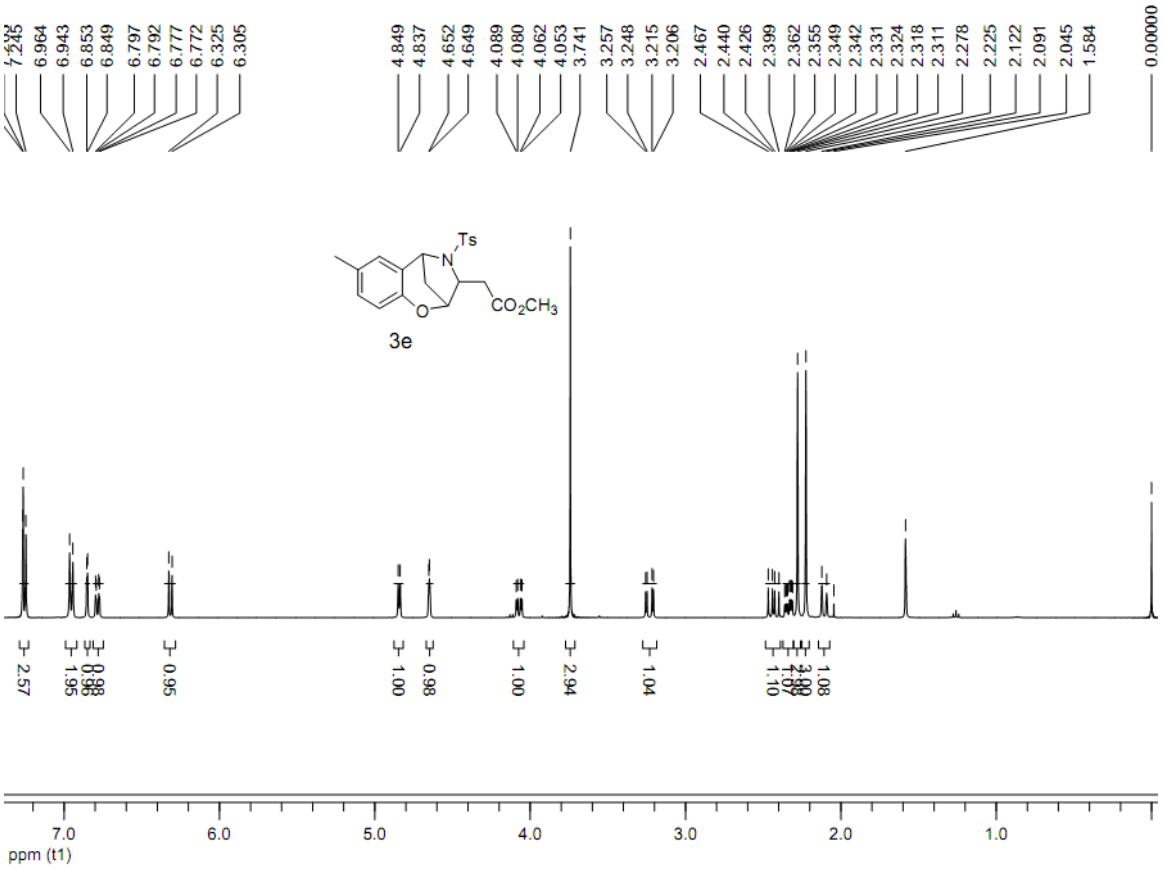
151.96
143.00
134.18
129.81
128.87
128.06
127.75
123.69
119.88
115.67
79.42
77.34
77.02
76.71
63.78
58.20
52.00
38.36
29.69
21.40
Ts
N
O
CO2CH3
3d
f1 (ppm)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6.943
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6.849
6.797
6.792
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6.772
6.325
6.305
4.849
4.837
4.652
4.649
4.089
4.080
4.062
4.053
3.741
3.257
3.248
3.215
3.206
2.467
2.440
2.426
2.399
2.362
2.355
2.349
2.342
2.331
2.324
2.318
2.311
2.278
2.225
2.122
2.091
2.045
1.584
0.00000
Ts
N
O
CO2CH3
3e
2.57
1.95
0.95
1.00
0.98
1.00
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1.04
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1.08
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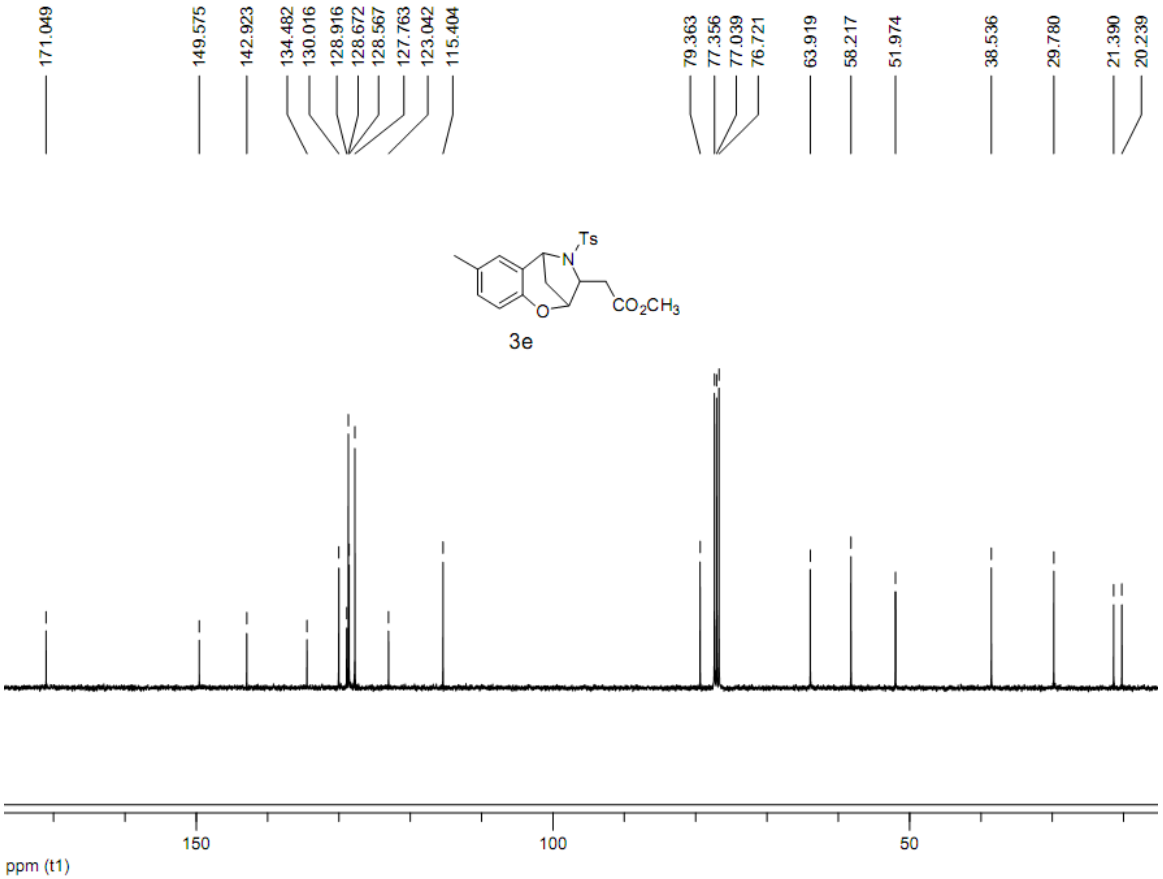
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)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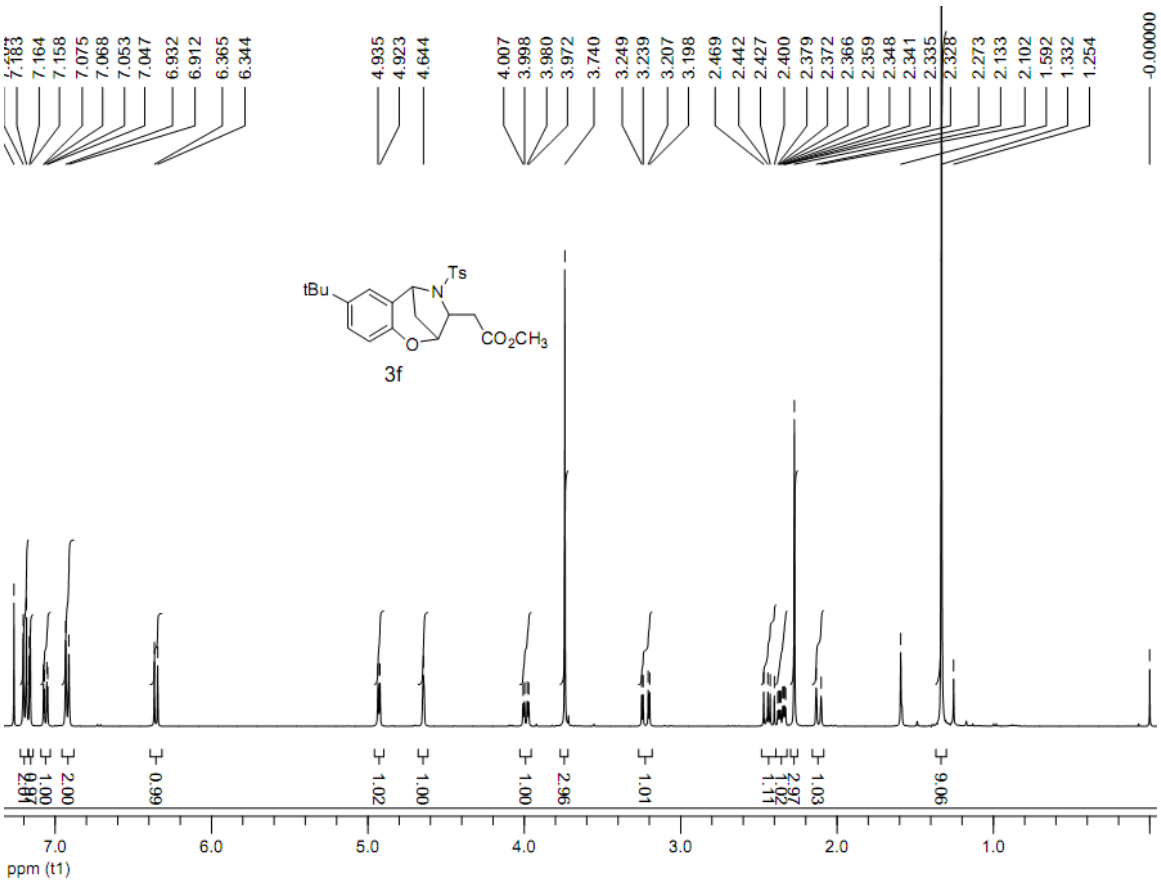
127.763
123.042
115.404
79.363
77.356
77.039
76.721
63.919
58.217
51.974
38.536
29.780
21.390
20.239
Ts
N
O
CO2CH3
3e
150
100
50
ppm (t1)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7.068
7.053
7.047
6.932
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6.365
6.344
4.935
4.923
4.644
4.007
3.998
3.980
3.972
3.740
3.249
3.239
3.207
3.198
2.469
2.442
2.427
2.400
2.379
2.372
2.366
2.359
2.348
2.341
2.335
2.328
2.273
2.133
2.102
1.592
1.332
1.254
-0.00000
tBu
N
Ts
O
CO2CH3
3f
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2.00
0.99
1.02
1.00
1.00
2.96
1.01
1.11
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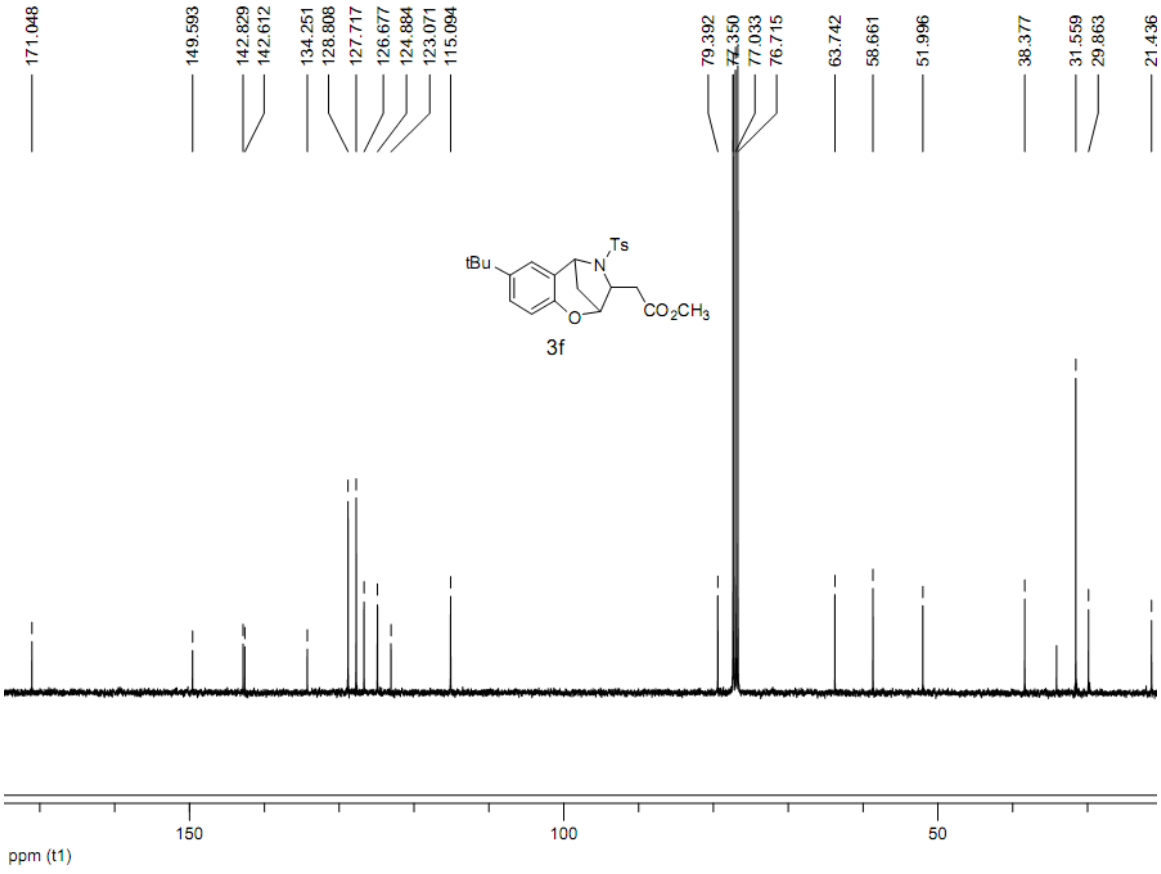
1.02
1.03
9.06
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)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124.884
123.071
115.094
79.392
77.350
77.033
76.715
63.742
58.661
51.996
38.377
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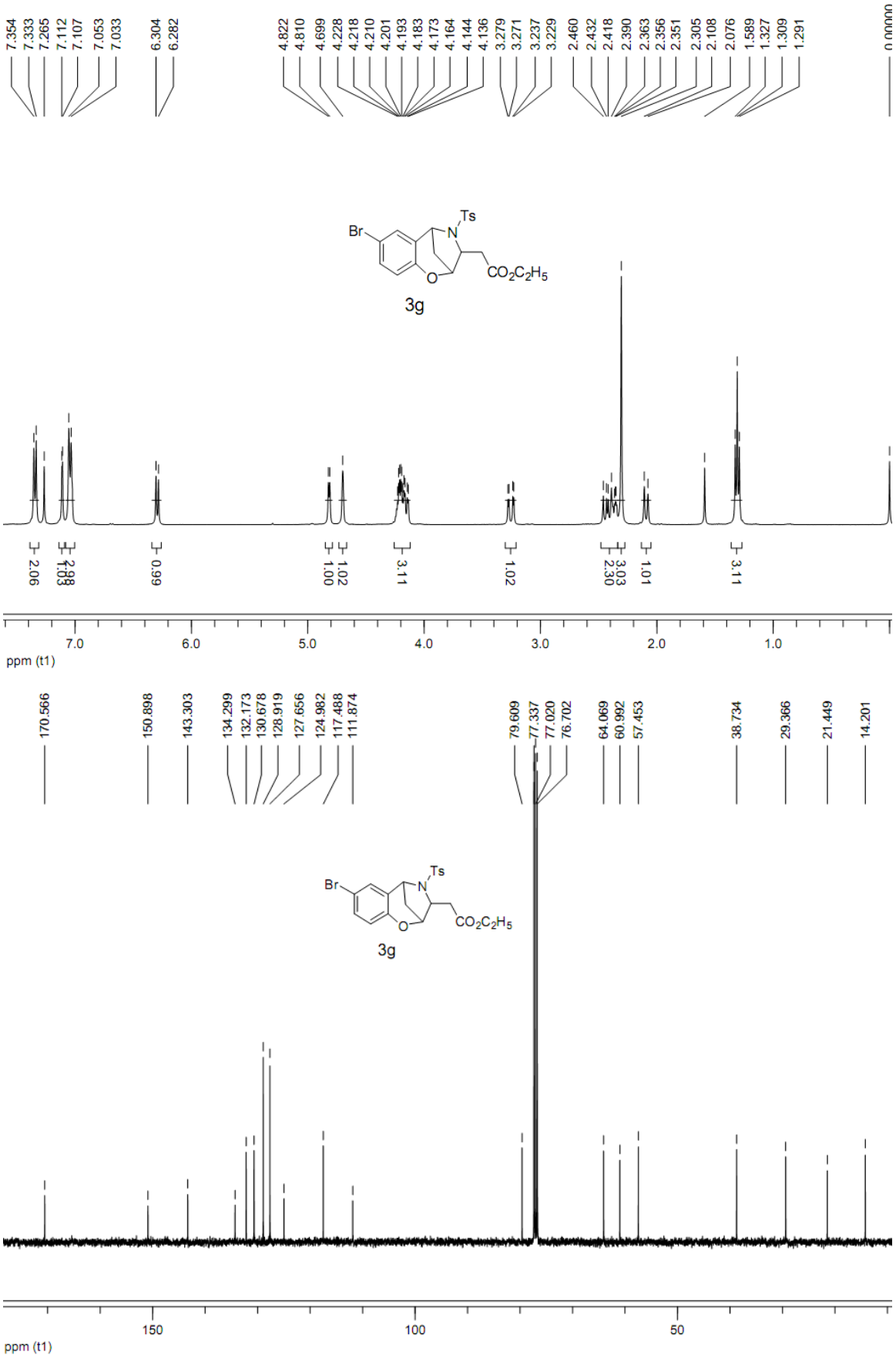
29.863
21.436
tBu
N
Ts
O
CO2CH3
3f
150
100
50
ppm (t1)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7.053
7.033
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6.282
4.822
4.810
4.699
4.228
4.218
4.210
4.201
4.193
4.183
4.173
4.164
4.144
4.136
3.279
3.271
3.237
3.229
2.460
2.432
2.418
2.390
2.363
2.356
2.351
2.305
2.108
2.076
1.589
1.327
1.309
1.291
0.00000
Br
Ts
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O
CO2C2H5
3g
2.06
2.08
0.99
1.00
1.02
3.11
1.02
2.03
1.01
3.11
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
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143.303
134.299
132.173
130.678
128.919
127.656
124.982
117.488
111.874
79.609
77.337
77.020
76.702
64.069
60.992
57.453
38.734
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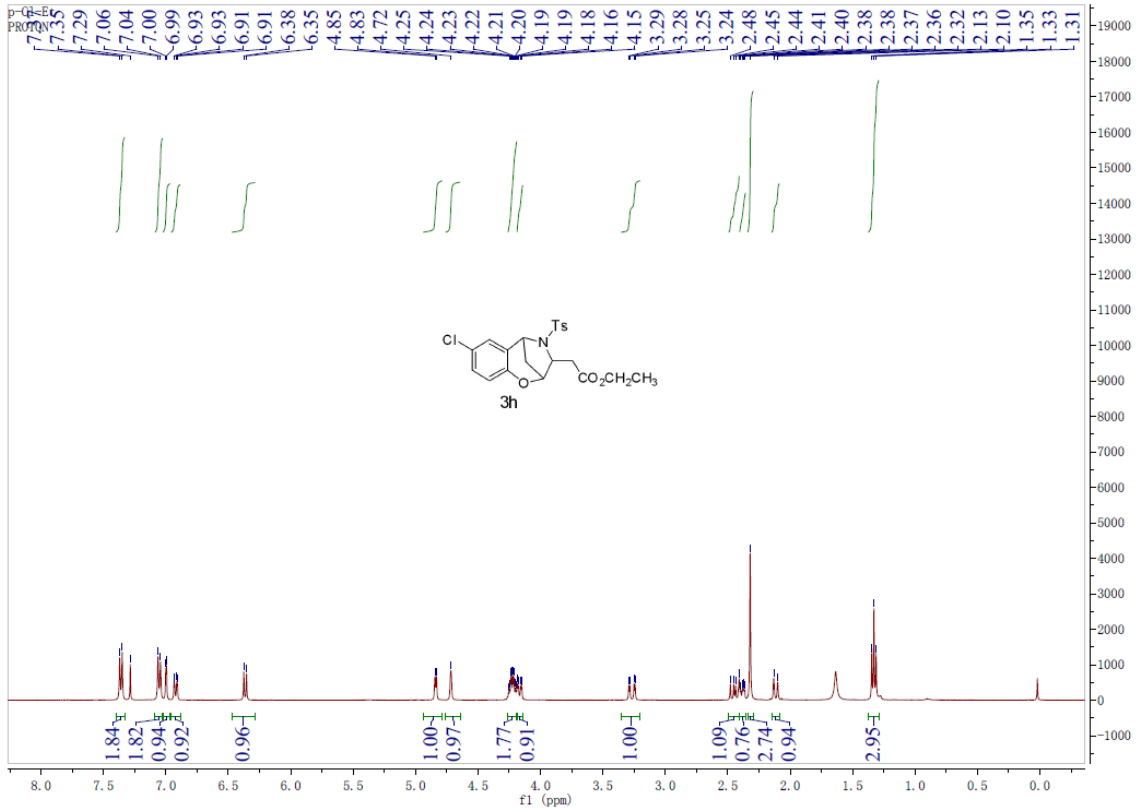
14.201
Br
Ts
N
O
CO2C2H5
3g
150
100
50
ppm (t1)


p-Cl-Et
PROTON
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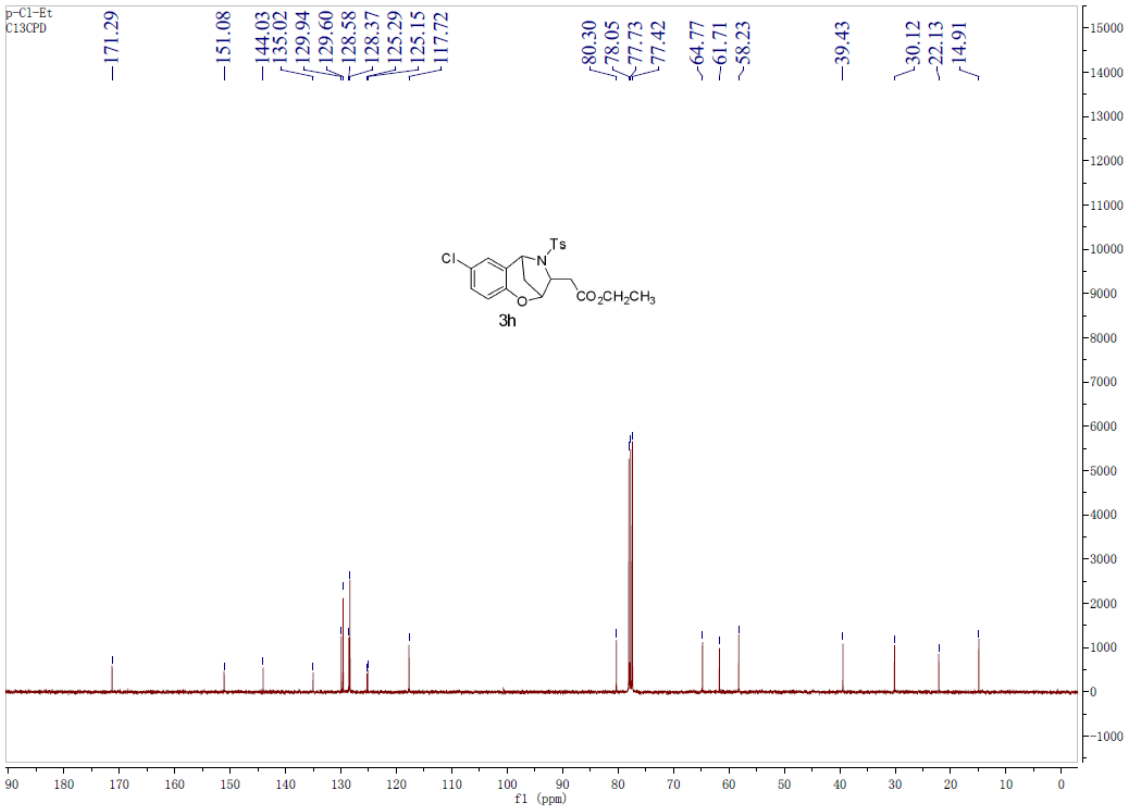
7.29
7.06
7.04
7.00
6.99
6.93
6.93
6.91
6.91
6.38
6.35
4.85
4.83
4.72
4.25
4.24
4.23
4.22
4.21
4.20
4.19
4.19
4.18
4.16
4.15
3.29
3.28
3.25
3.24
2.48
2.45
2.44
2.41
2.40
2.38
2.38
2.37
2.36
2.32
2.13
2.10
1.35
1.33
1.31
Cl
N
Ts
O
CO2CH2CH3
3h
1.84
1.82
0.94
0.92
0.96
1.00
0.97
1.77
0.91
1.00
1.09
0.76
2.74
0.94
2.95
f1 (ppm)


p-Cl-Et
C13CPD
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144.03
135.02
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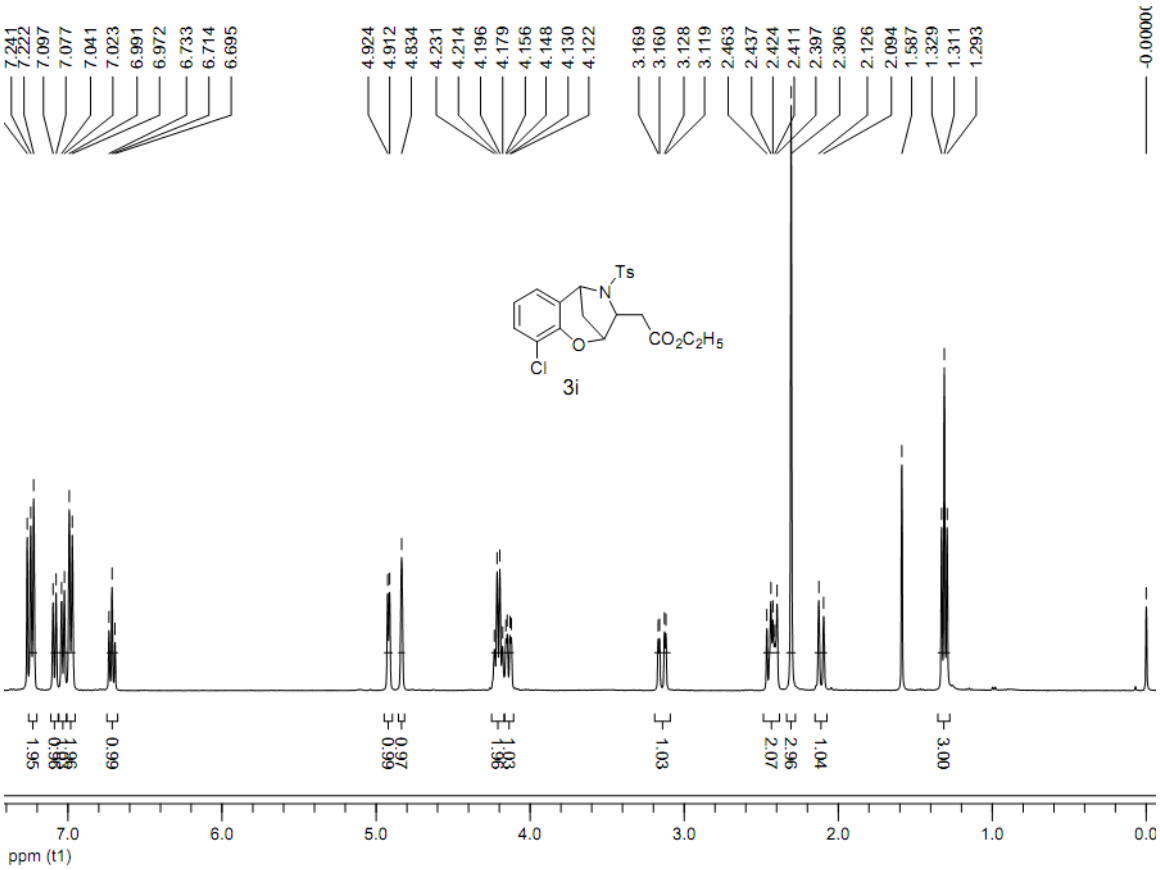
128.58
128.37
125.29
125.15
117.72
80.30
78.05
77.73
77.42
64.77
61.71
58.23
39.43
30.12
22.13
14.91
Cl
N
Ts
O
CO2CH2CH3
3h
f1 (ppm)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4.912
4.834
4.231
4.214
4.196
4.179
4.156
4.148
4.130
4.122
3.169
3.160
3.128
3.119
2.463
2.437
2.424
2.411
2.397
2.306
2.126
2.094
1.587
1.329
1.311
1.293
-0.0000
Ts
N
O
Cl
CO2C2H5
3i
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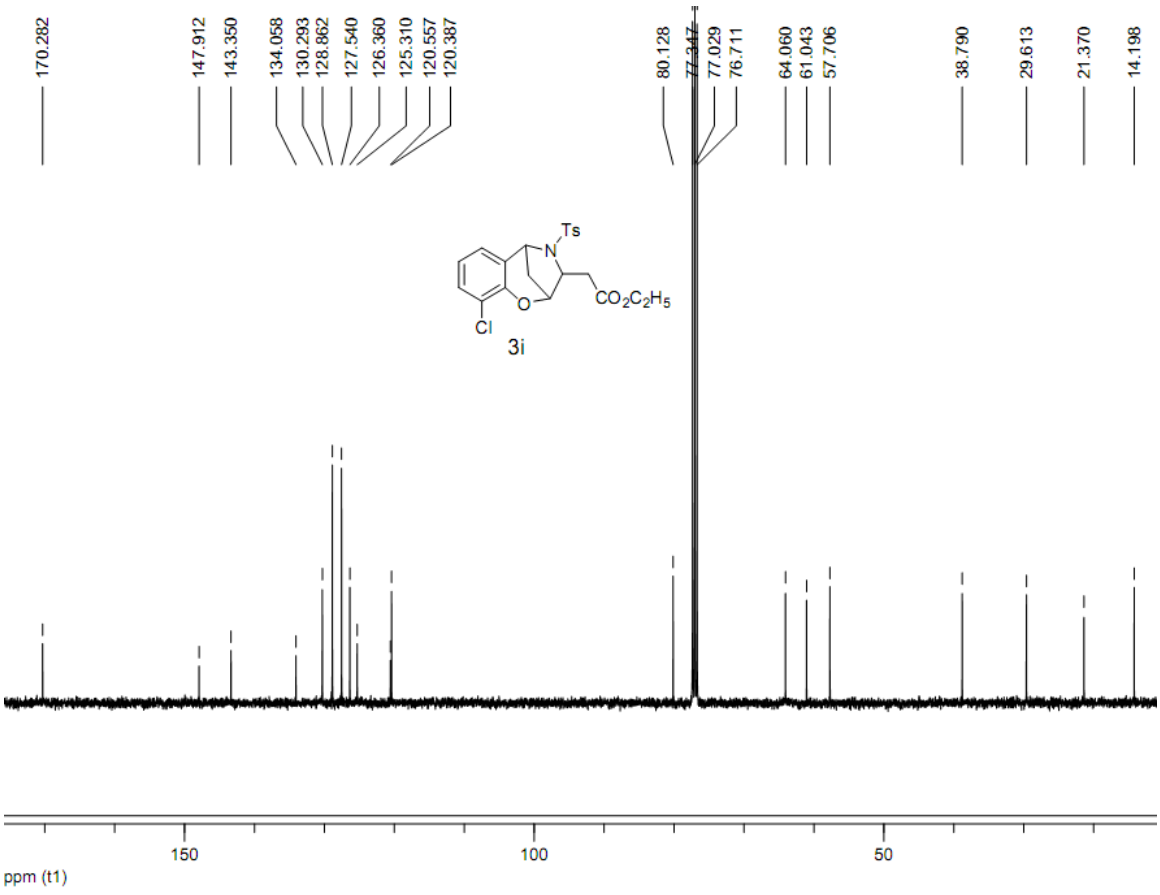
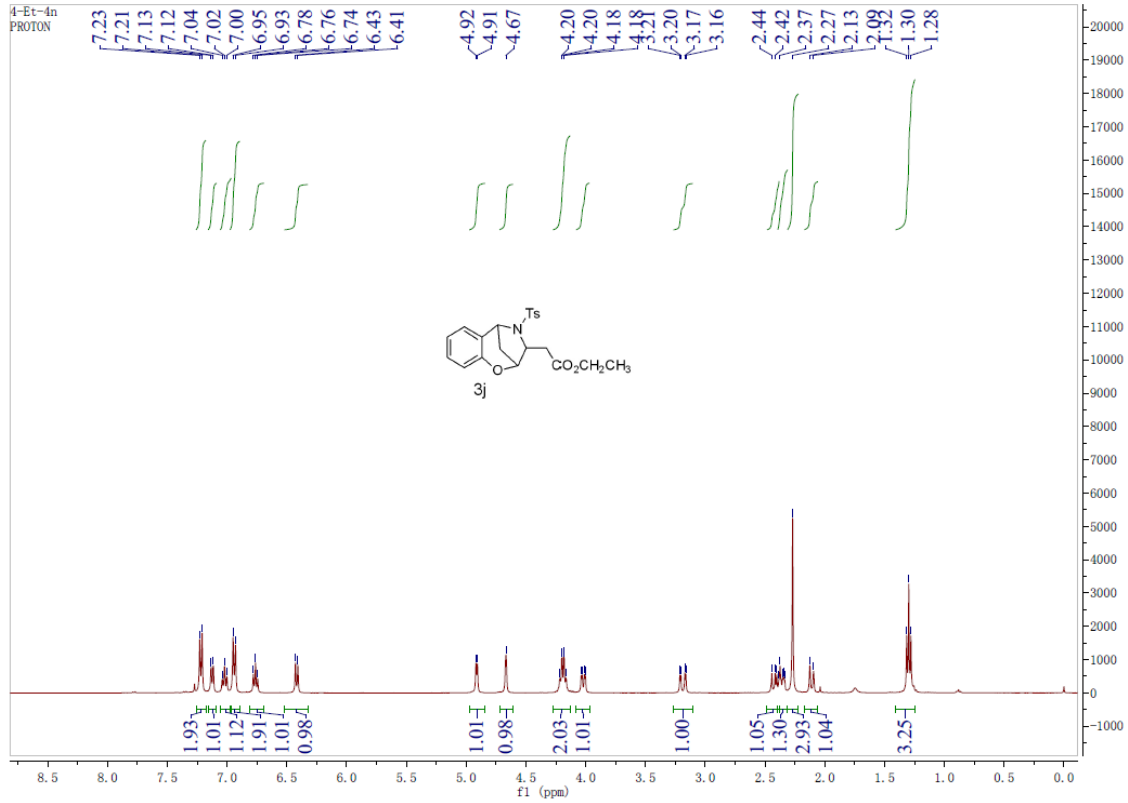
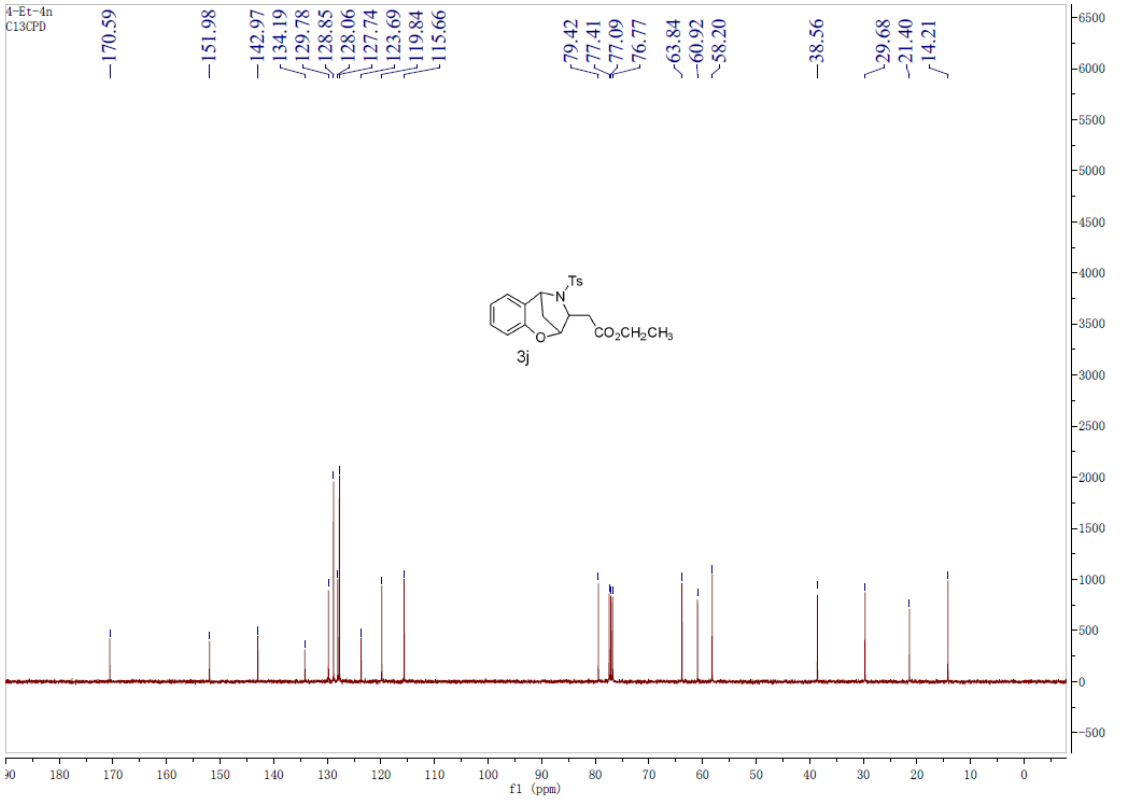
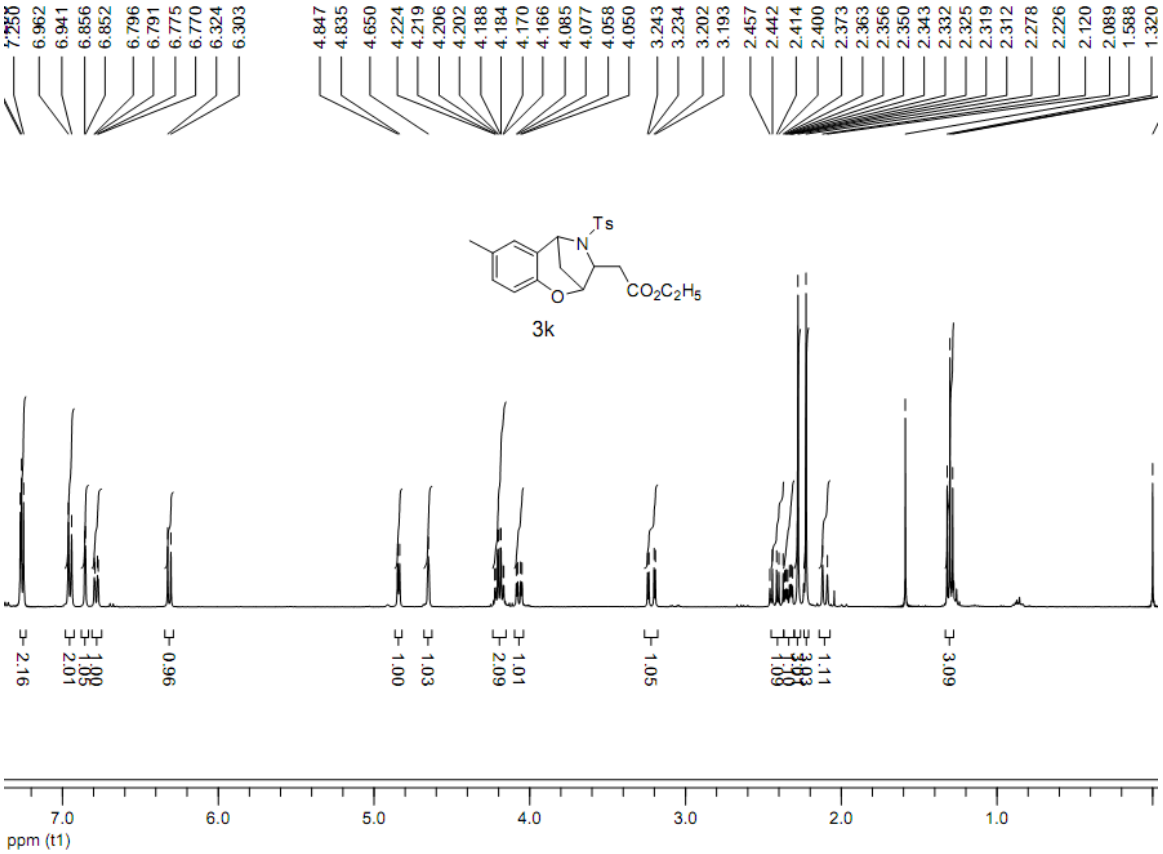
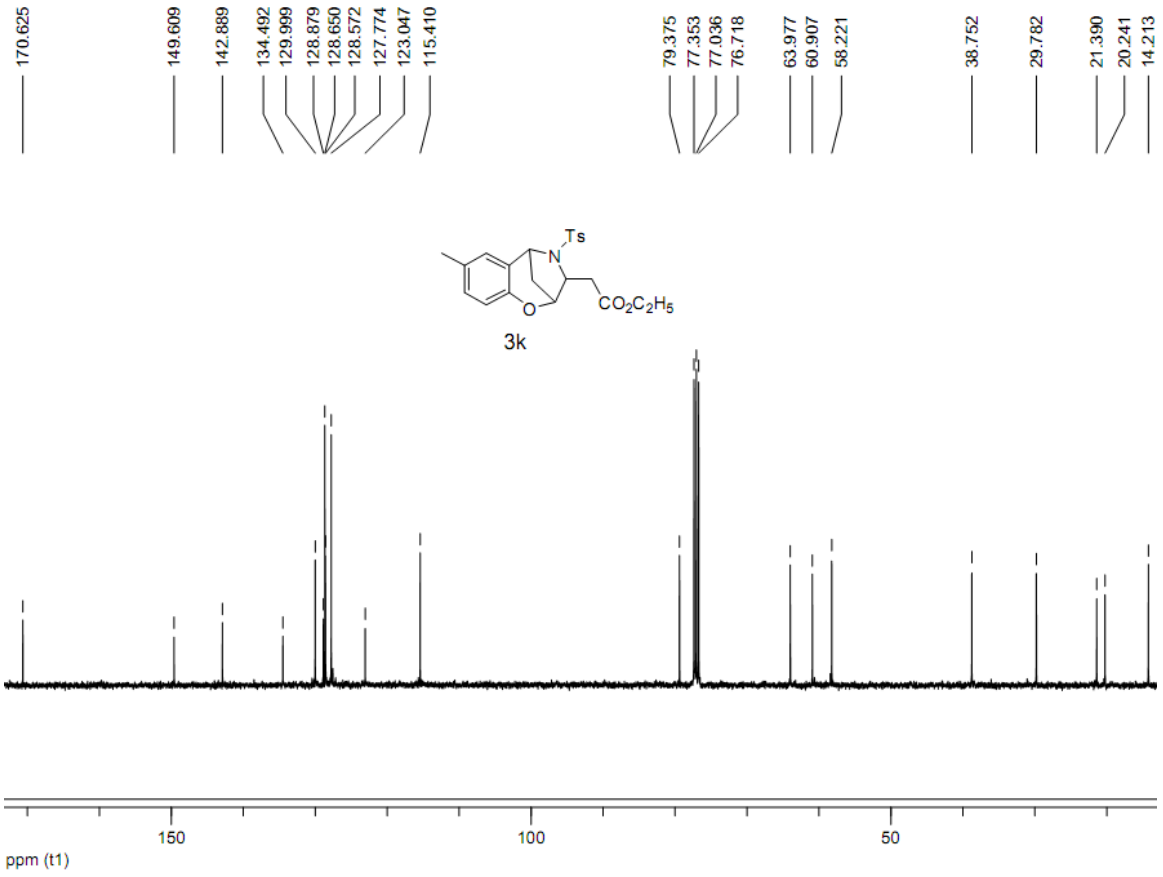
0.99
0.99
0.97
1.03
1.03
2.07
2.96
1.04
3.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

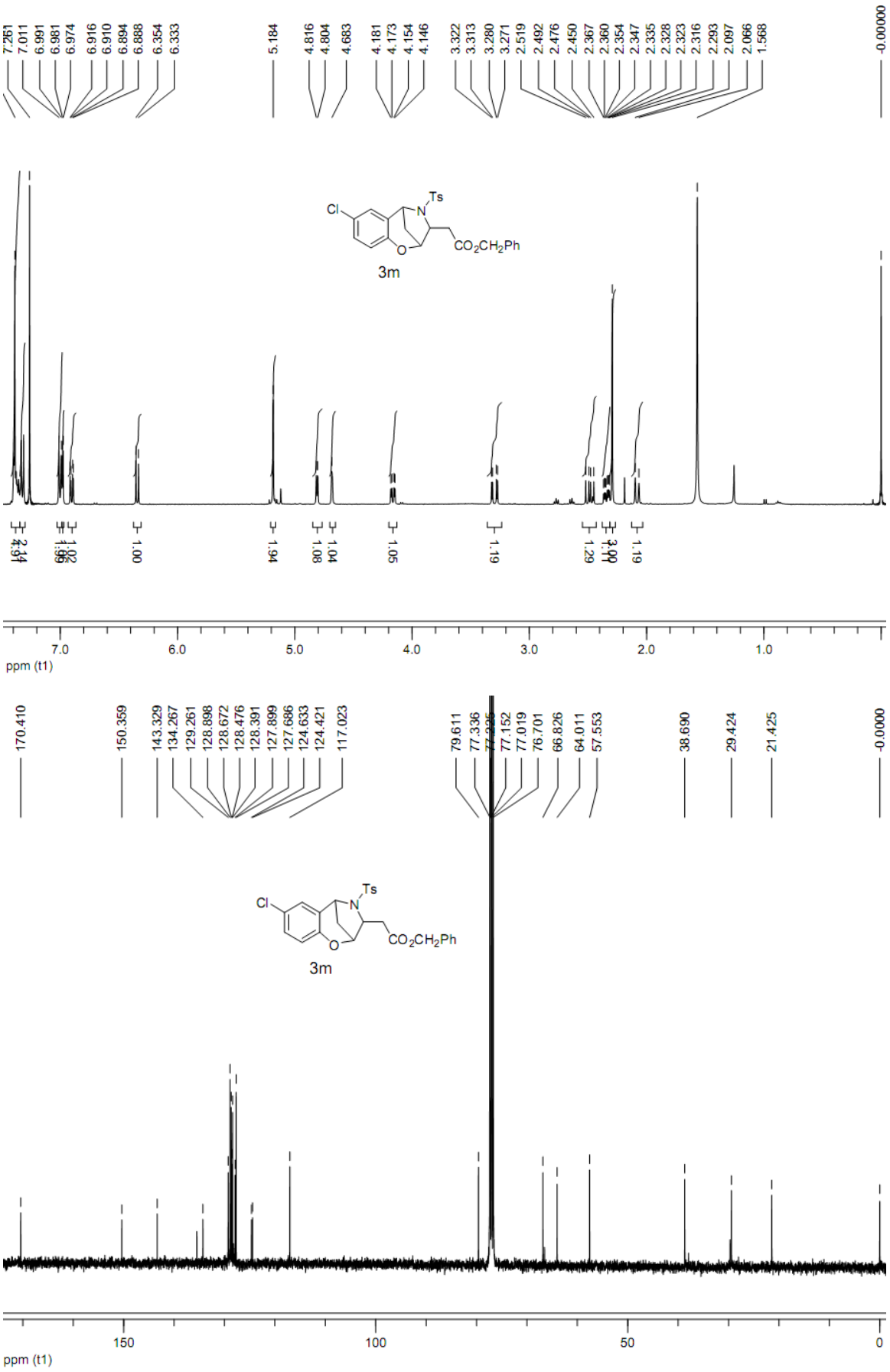

170.282
147.912
143.350
134.058
130.293
128.862
127.540
126.360
125.310
120.557
120.387
80.128
77.347
77.029
76.711
64.060
61.043
57.706
38.790
29.613
21.370
14.198
Ts
N
O
Cl
CO2C2H5
3i
150
100
50
ppm (t1)

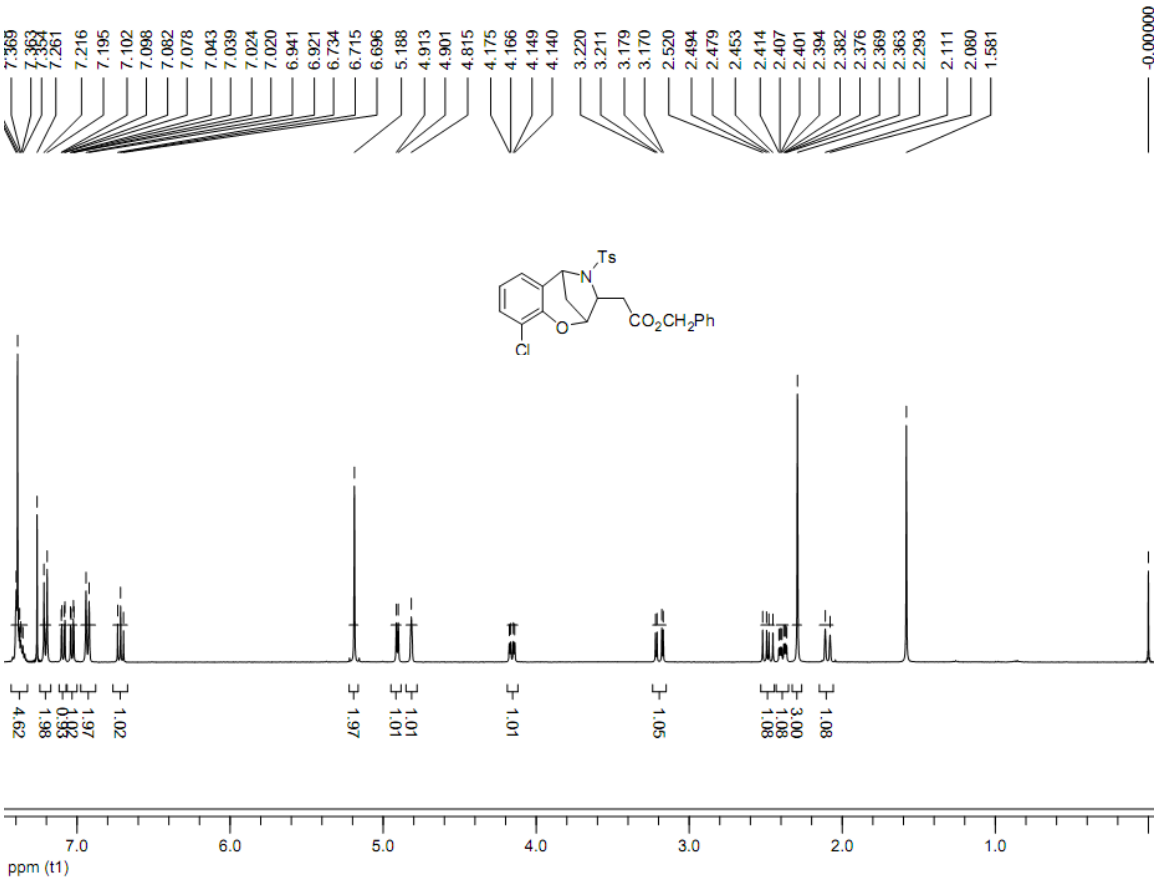

4-Et-4n
PROTON
7.23
7.21
7.13
7.12
7.04
7.02
7.00
6.95
6.93
6.78
6.76
6.74
6.43
6.41
4.92
4.91
4.67
4.20
4.20
4.18
4.18
3.21
3.20
3.17
3.16
2.44
2.42
2.37
2.27
2.13
2.09
1.32
1.30
1.28
Ts
N
O
CO2CH2CH3
3j
1.93
1.01
1.12
1.91
1.01
0.98
1.01
0.98
2.03
1.01
1.00
1.05
1.30
2.93
1.04
3.25
f1 (ppm)

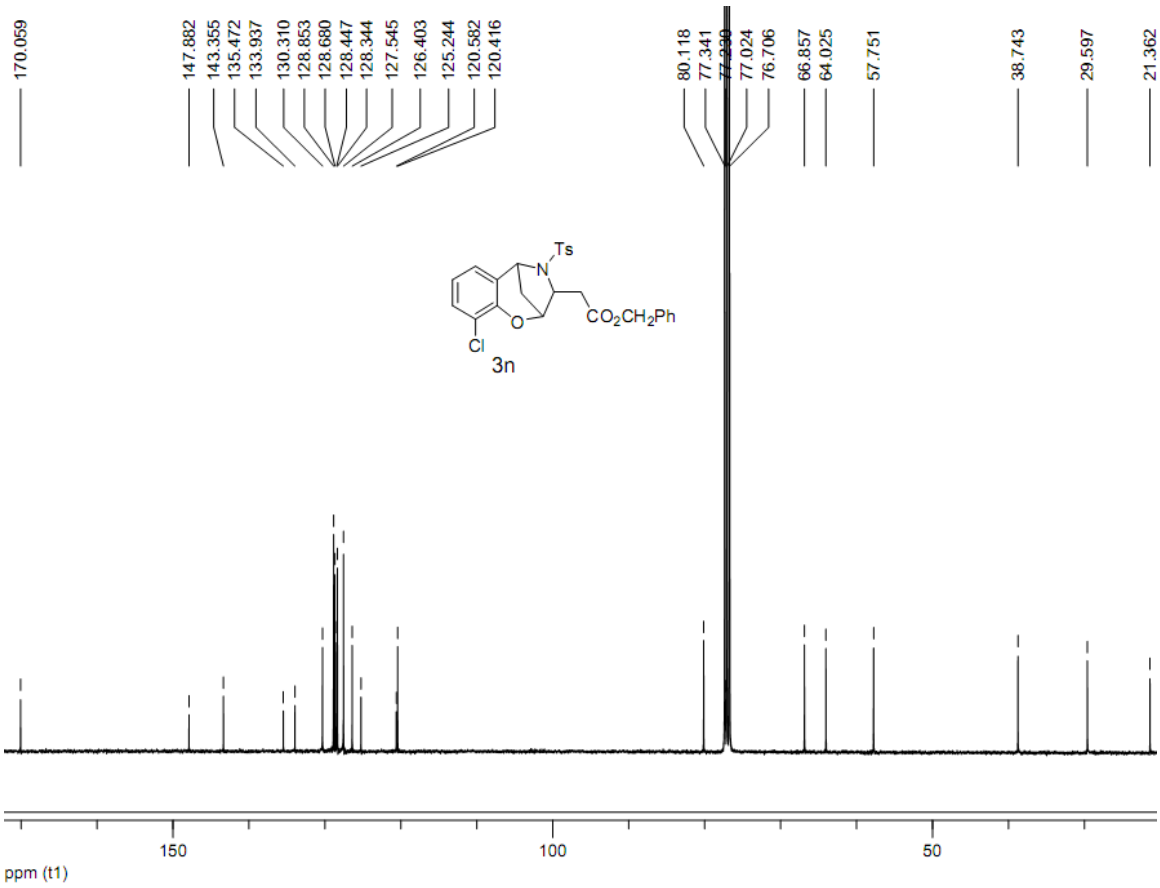

4-Et-4n
C13CPD
170.59
151.98
142.97
134.19
129.78
128.85
128.06
127.74
123.69
119.84
115.66
79.42
77.41
77.09
76.77
63.84
60.92
58.20
38.56
29.68
21.40
14.21
Ts
N
O
CO2CH2CH3
3j
f1 (ppm)

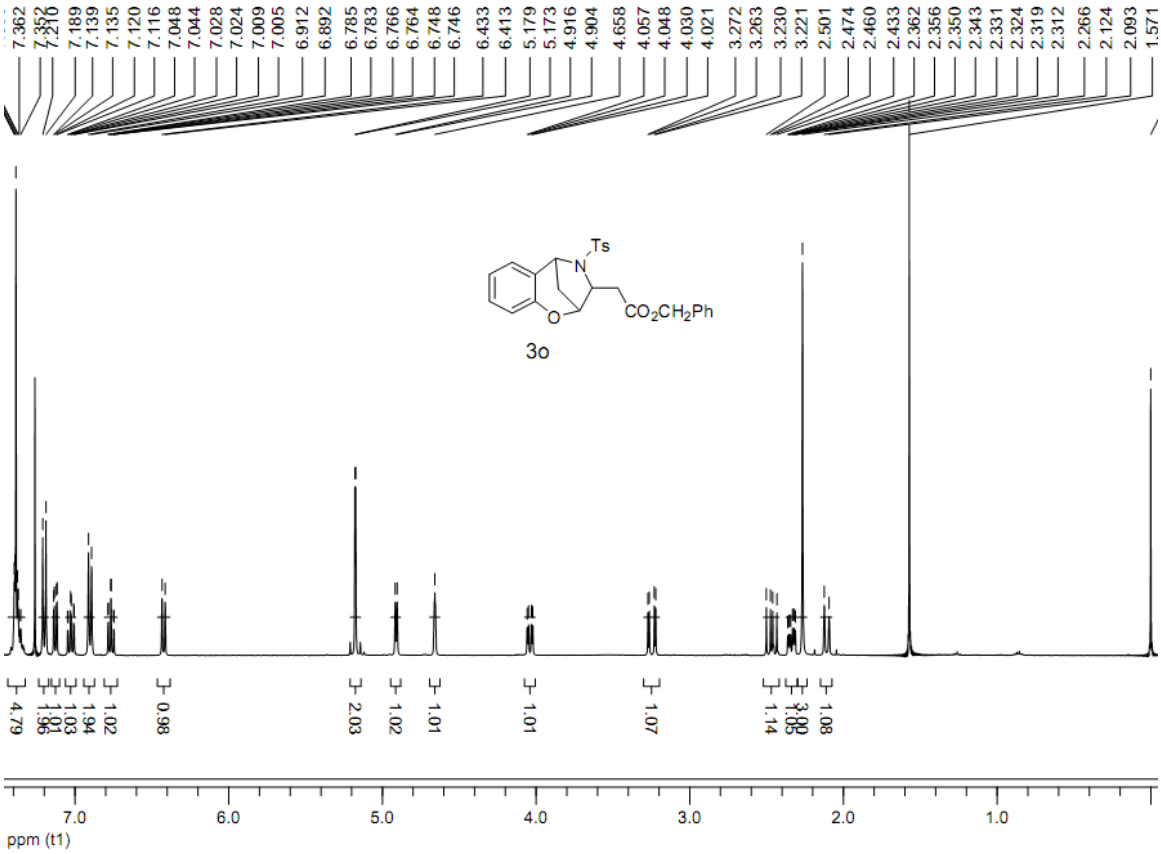

7.250
6.962
6.941
6.856
6.852
6.796
6.791
6.775
6.770
6.324
6.303
4.847
4.835
4.650
4.224
4.219
4.206
4.202
4.188
4.184
4.170
4.166
4.085
4.077
4.058
4.050
3.243
3.234
3.202
3.193
2.457
2.442
2.414
2.400
2.373
2.363
2.356
2.350
2.343
2.332
2.325
2.319
2.312
2.278
2.226
2.120
2.089
1.588
1.320
Ts
N
O
CO2C2H5
3k
2.16
2.01
1.00
0.96
1.00
1.03
2.09
1.01
1.05
1.09
1.11
3.09
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

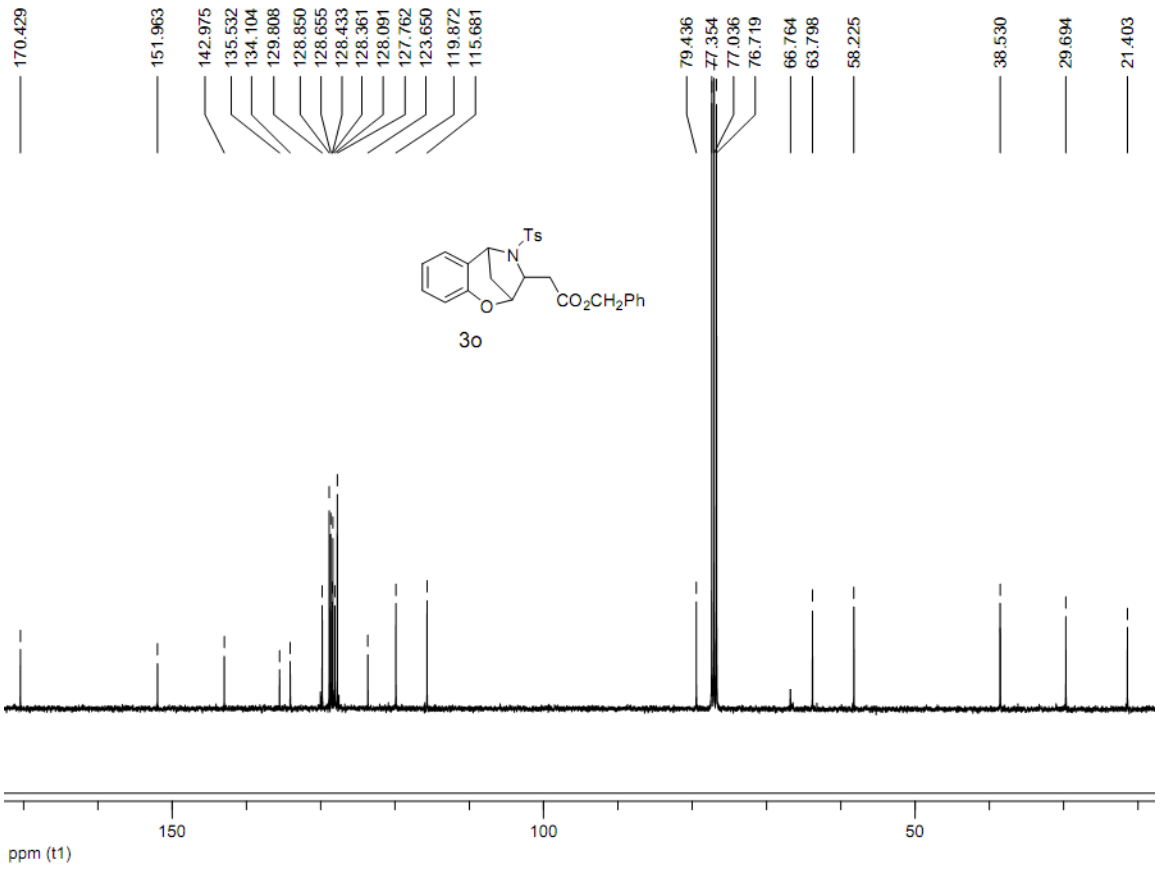

170.625
149.609
142.889
134.492
129.999
128.879
128.650
128.572
127.774
123.047
115.410
79.375
77.353
77.036
76.718
63.977
60.907
58.221
38.752
29.782
21.390
20.241
14.213
Ts
N
O
CO2C2H5
3k
150
100
50
ppm (t1)


7.261
7.011
6.991
6.981
6.974
6.916
6.910
6.894
6.888
6.354
6.333
5.184
4.816
4.804
4.683
4.181
4.173
4.154
4.146
3.322
3.313
3.280
3.271
2.519
2.492
2.476
2.450
2.367
2.360
2.354
2.347
2.335
2.328
2.323
2.316
2.293
2.097
2.066
1.568
-0.00000
Ts
N
Cl
O
CO2CH2Ph
3m
2.14
1.00
1.94
1.08
1.04
1.05
1.19
1.29
3.00
1.19
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
170.410
150.359
143.329
134.267
129.261
128.898
128.672
128.476
128.391
127.899
127.686
124.633
124.421
117.023
79.611
77.336
77.152
77.019
76.701
66.826
64.011
57.553
38.690
29.424
21.425
-0.0000
Ts
N
Cl
O
CO2CH2Ph
3m
150
100
50
0
ppm (t1)


7.369
7.363
7.354
7.261
7.216
7.195
7.102
7.098
7.082
7.078
7.043
7.039
7.024
7.020
6.941
6.921
6.734
6.715
6.696
5.188
4.913
4.901
4.815
4.175
4.166
4.149
4.140
3.220
3.211
3.179
3.170
2.520
2.494
2.479
2.453
2.414
2.407
2.401
2.394
2.382
2.376
2.369
2.363
2.293
2.111
2.080
1.581
-0.00000
Ts
N
O
Cl
CO2CH2Ph
4.62
1.98
1.97
1.02
1.97
1.01
1.01
1.01
1.06
1.08
3.00
1.08
1.08
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


170.059
147.882
143.355
135.472
133.937
130.310
128.853
128.680
128.447
128.344
127.545
126.403
125.244
120.582
120.416
80.118
77.341
77.024
76.706
66.857
64.025
57.751
38.743
29.597
21.362
Ts
N
O
Cl
CO2CH2Ph
3n
150
100
50
ppm (t1)


7.362
7.352
7.210
7.189
7.139
7.135
7.120
7.116
7.048
7.044
7.028
7.024
7.009
7.005
6.912
6.892
6.785
6.783
6.766
6.764
6.748
6.746
6.433
6.413
5.179
5.173
4.916
4.904
4.658
4.057
4.048
4.030
4.021
3.272
3.263
3.230
3.221
2.501
2.474
2.460
2.433
2.362
2.356
2.350
2.343
2.331
2.324
2.319
2.312
2.266
2.124
2.093
1.571
Ts
N
O
CO2CH2Ph
3o
4.79
0.98
2.03
1.02
1.01
1.01
1.07
1.14
1.08
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)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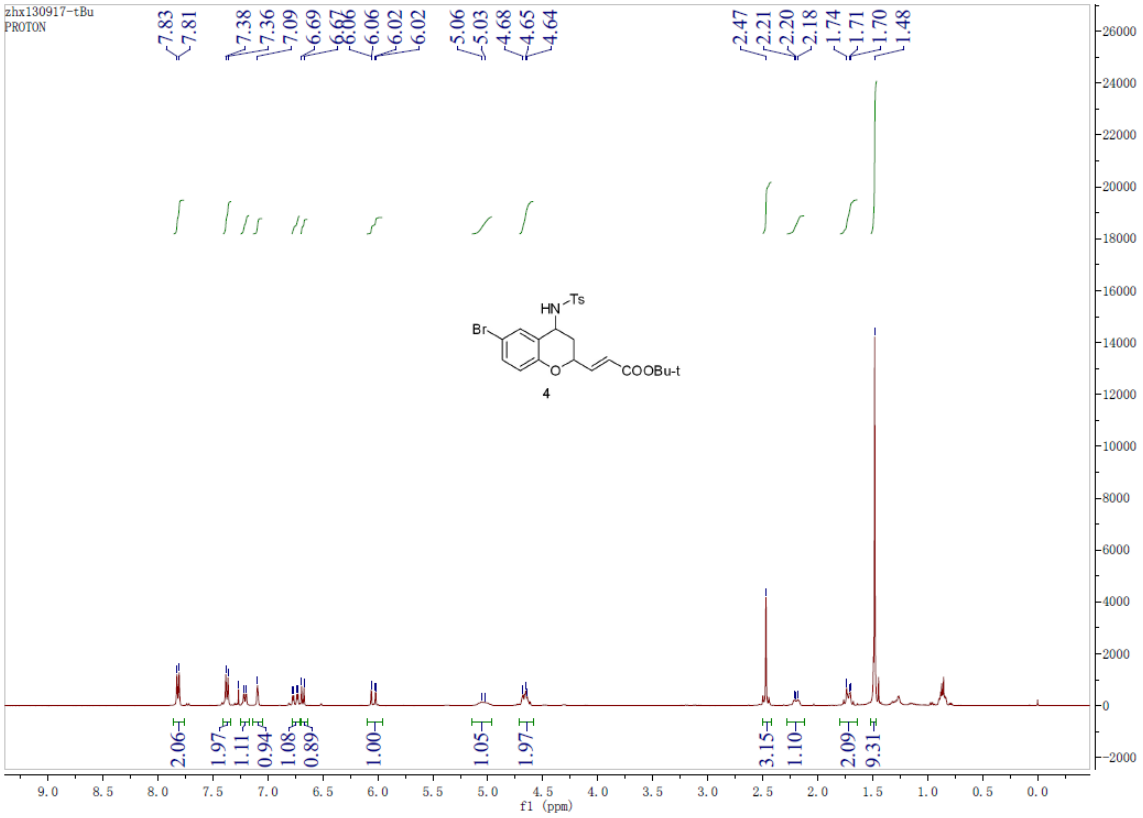
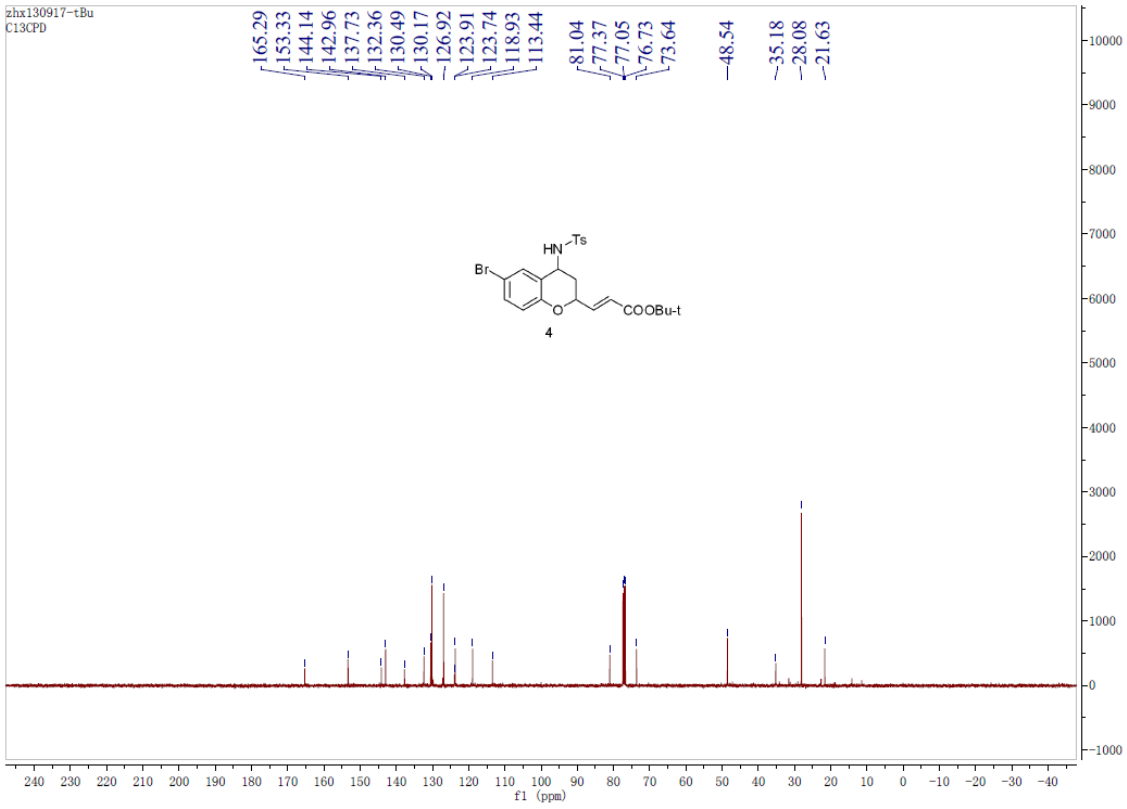
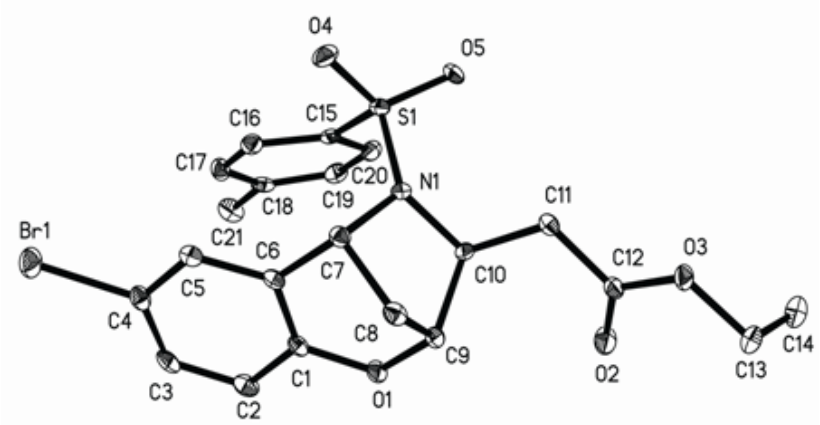
151.963
142.975
135.532
134.104
129.808
128.850
128.655
128.433
128.361
128.091
127.762
123.650
119.872
115.681
79.436
77.354
77.036
76.719
66.764
63.798
58.225
38.530
29.694
21.403
Ts
N
O
CO2CH2Ph
3o
150
100
50
ppm (t1)


zhx130917-tBu
PROTON
7.83
7.81
7.38
7.36
7.09
6.69
6.67
6.06
6.02
6.02
5.06
5.03
4.68
4.65
4.64
2.47
2.21
2.20
2.18
1.74
1.71
1.70
1.48
HN
Ts
Br
O
COOBu-t
4
2.06
1.97
1.11
0.94
1.08
0.89
1.00
1.05
1.97
3.15
1.10
2.09
9.31
f1 (ppm)


zhx130917-tBu
C13CPD
165.29
153.33
144.14
142.96
137.73
132.36
130.49
130.17
126.92
123.91
123.74
118.93
113.44
81.04
77.37
77.05
76.73
73.64
48.54
35.18
28.08
21.63
HN
Ts
Br
O
COOBu-t
4
f1 (ppm)

8. Crystal structure of 3g



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2. R. W. Lang, H.-J. Hansen, *Organic Syntheses.* 1990, **62**, 202.
3. B. E. Love, P. S. Raje, T. C. Williams II, Synlett 1994, 493.