Supporting Information for

N-Heterocyclic Carbene-Catalyzed Enantioselective Intramolecular *N*-Tethered Aldehyde-Ketone Benzoin Reactions

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General methods. Unless stated otherwise, all reactions were carried out in flame-dried glassware under a dry argon atmosphere. All solvents were purified and dried according to standard methods prior to use.

^{1}H and ^{13}C NMR spectra were recorded on Varian instruments (300 MHz and 75 MHz or 400 MHz and 100 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protio solvent signals. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet or unresolved, coupling constant(s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm).

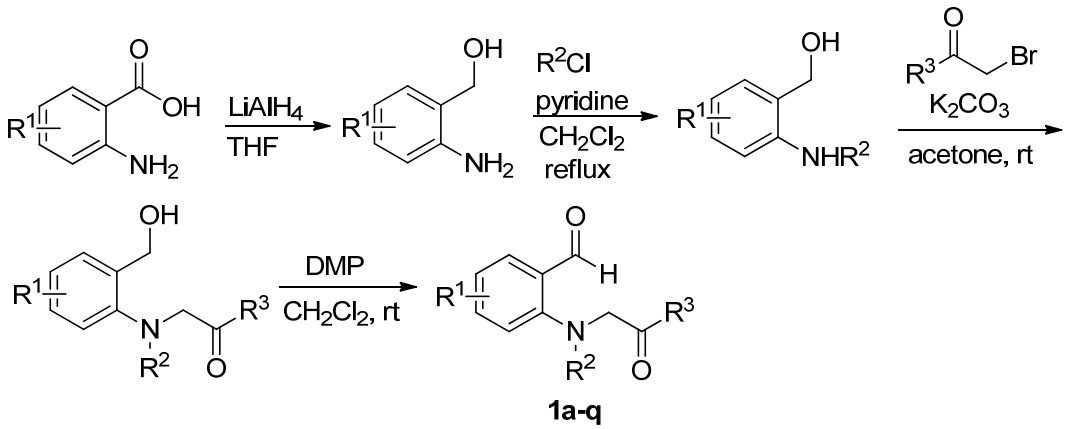
The D-camphor-derived triazolium salts[1] were prepared according to the reported procedures.

(1) Li, Y.; Feng, Z.; You, S-L. *Chem. Commun.,* **2008**, 2263.

(2) (a) Khan, H. A.; Kou, K. G. M.; Dong, V. M. *Chem. Sci.* **2011**, *2*, 407. (b) Jiang, F.; Wu, Z.; Zhang, W. *Tetrahedron* **2011**, *67*, 1501.

Substrate synthesis

General procedure for the synthesis of substrates[2]

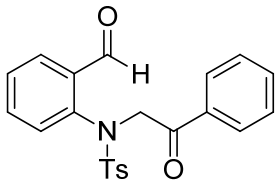


To a solution of substituted 2-amino-benzoic acid (30 mmol) in dry THF (40 mL) was added dropwise a solution of $LiAlH_4$ in THF (1M, 60 mL) while the temperature was maintained at 0 °C. The resulting mixture was allowed to warm to room temperature and was stirred for 2 h. The mixture was then hydrolyzed by addition of water (2.5 mL) and 5% NaOH (7.5 mL). The resulting suspension was filtered, and the precipitate was washed with ethyl acetate. Then the combined organic collection was evaporated. The residue was recrystallized from ethyl acetate and petroleum ether, affording the corresponding alcohols quantitatively as a white or pale yellow solid.

To a round-bottom flask was added the above obtained substituted 2-aminobenzyl alcohol (20 mmol) and CH_2Cl_2 (12 mL). To the resulting solution were added sulfonyl chloride (MsCl or TsCl, 1.1 equiv.) and pyridine (2.0 mL, 26 mmol) dropwise at 0 ^{o}C. The reaction mixture was refluxed for 12 h (for MsCl, rt for 12h) and then transferred to a separatory funnel with 30 mL of water. The aqueous phase was extracted with CH_2Cl_2 (3×15 mL), and the combined organic phases washed with dilute acid (1×20 mL 1M HCl), water (1×20 mL), and brine (1×20 mL) respectively. The organic phase was separated, dried with Na_2SO_4 and then concentrated. After the removal of the solvent, the residue was crystallized from CH_2Cl_2/petroleum ether to afford the *N*-protected 2-aminobenzyl alcohol.

The *N*-protected 2-aminobenzyl alcohol (20 mmol) was dissolved in acetone (50 mL) and to this mixture were added K_2CO_3 (3.32 g, 24 mmol, 1.2 equiv.) and substituted 2-bromoacetophenone (21.0 mmol, 1.05 equiv.). The resulting suspension was stirred at rt. Upon completion (about 24 h, monitored by TLC), 50 mL of water was added to the reaction mixture. Then the acetone in the reaction mixture was evaporated. The reasulting aqueous phase was extracted with EtOAc (3×25 mL) and the combined organic phases were washed with brine (20 mL). The organic phase was dried (Na_2SO_4) and concentrated. The residue was purified by column chromatography on silica gel to afford the product (eluent: ethyl acetate/petroleum ether = 1/3).

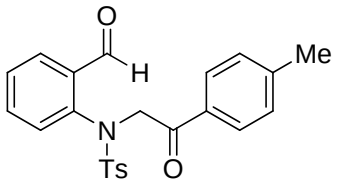
The keto-alcohol (3 mmol) was dissolved in CH_2Cl_2 (30 mL). To this mixture was added DMP (2.54 g, 6 mmol, 2 equiv.) at 0 ^oC and the resulting suspension was stirred at rt for about 3 h. After the oxidation was complete (monitored by TLC), 20 mL of saturated Na_2SO_3 (aq) was added to the reaction mixture at 0 ^oC. The reaction mixture was extracted with CH_2Cl_2 (3×15 mL). The solvent was removed under reduced pressure, and the crude keto-aldehyde was recrystallized from CH_2Cl_2/petroleum ether to give the product as white solid (30-61% total yield).



1a

***N*-(2-Formylphenyl)-4-methyl-*N*-(2-oxo-2-phenylethyl)benzenesulfonamide**[2a]

White solid, 54% yield. ^1H NMR (300 MHz, $CDCl_3$) δ 10.46 (s, 1H), 7.98 (t, *J* = 4.8 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.56-7.39 (m, 6H), 7.31 (d, *J* = 8.1 Hz, 2H), 6.97-6.84 (m, 1H), 5.30 (brs, 1H), 4.92 (brs, 1H), 2.47 (s, 3H).

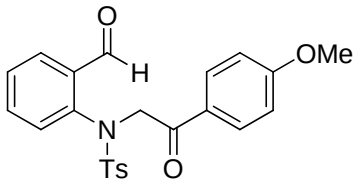


1b

***N*-(2-Formylphenyl)-4-methyl-*N*-(2-oxo-2-(p-tolyl)ethyl)benzenesulfonamide**

White solid, 61% yield. M.p. 192-194 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 10.50 (s,

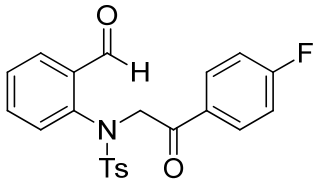
1H), 7.99-7.92 (m, 1H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.45-7.39 (m, 2H), 7.29 (d, *J* = 8.4 Hz, 2H) 7.24 (d, *J* = 8.0 Hz, 2H), 6.91-6.84 (m, 1H), 5.30 (brs, 1H), 4.85 (brs, 1H), 2.45 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 190.5, 145.0, 144.4, 141.3, 135.8, 134.2, 133.9, 132.1, 129.7, 129.5, 128.81, 128.76, 128.1, 128.0, 127.9, 57.1, 21.7, 21.6; IR (thin film): ν_{max} (cm^{-1}) = 2974, 2925, 1694, 1684, 1605, 1596, 1342, 1270, 1157, 978, 874, 811, 724, 661; MS (ESI-TOF) 408 ($[M+H]^+$); HRMS (ESI-TOF) calcd for $C_{23}H_{22}NO_4S$ ($[M+H]^+$): 408.1264. Found: 408.1257.



1c

***N*-(2-Formylphenyl)-*N*-(2-(4-methoxyphenyl)-2-oxoethyl)-4-methylbenzenesulfonamide**

White solid, 30% yield. M.p. 193-195 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.46 (s, 1H), 8.00-7.94 (m, 1H), 7.91-7.84 (m, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.46-7.40 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.97-6.86 (m, 3H), 5.30 (brs, 1H), 4.82 (brs, 1H), 3.87 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.0, 190.5, 164.1, 144.4, 141.3, 135.8, 134.2, 133.9, 130.5, 129.7, 128.8, 128.8, 128.0, 127.9, 127.5, 114.0, 56.9, 55.5, 21.6; IR (thin film): ν_{max} (cm^{-1}) = 1682, 1598, 1340, 1218, 1187, 981, 874, 833, 728, 661; MS (ESI-TOF) 424 ($[M+H]^+$); HRMS (ESI-TOF) calcd for $C_{23}H_{22}NO_5S$ ($[M+H]^+$): 424.1213. Found: 424.1211.

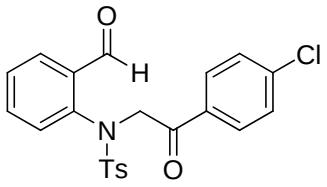


1d

***N*-(2-(4-Fluorophenyl)-2-oxoethyl)-*N*-(2-formylphenyl)-4-methylbenzenesulfonamide**

White solid, 58% yield. M.p. 209-210 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.46 (s, 1H), 8.02-7.86 (m, 3H), 7.49 (d, *J* = 8.4 Hz, 2H),7.46-7.40 (m, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.13 (t, *J* = 8.4 Hz, 2H), 6.94-6.87 (m, 1H), 5.30 (brs, 1H), 4.85 (brs, 1H),

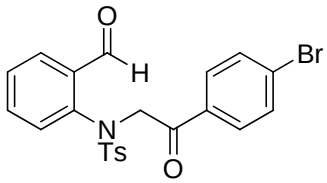
2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 190.4, 166.1 (d, *J* = 255.2 Hz), 144.6, 141.1, 135.7, 134.1, 134.0, 131.0 (d, *J* = 3.0 Hz), 130.4 (d, *J* = 9.4 Hz), 129.7, 128.9, 128.05, 127.99, 116.1 (d, *J* = 21.9 Hz), 57.1, 21.6; IR (thin film): ν_{max} (cm^{-1}) = 1687, 1594, 1341, 1220, 1156, 1087, 830, 727, 661; MS (ESI-TOF) 412 ($[M+H]^+$); HRMS (ESI-TOF) calcd for $C_{22}H_{19}FNO_4S$ ($[M+H]^+$): 412.1013. Found: 412.1013.



1e

***N*-(2-(4-Chlorophenyl)-2-oxoethyl)-*N*-(2-formylphenyl)-4-methylbenzenesulfonamide**

White solid, 40% yield. M.p. 196-198 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.47 (s, 1H), 8.04-7.93 (m, 1H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.46-7.40 (m, 4H), 7.30 (d, *J* = 8.4 Hz, 2H), 6.97-6.90 (m, 1H), 5.30 (brs, 1H), 4.85 (brs, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 190.4, 144.6, 141.1, 140.5, 135.7, 134.1, 134.0, 132.9, 129.7, 129.4, 129.2, 129.0, 128.1, 128.0, 57.2, 21.6; IR (thin film): ν_{max} (cm^{-1}) = 1686, 1593, 1399, 1342, 1217, 1158, 984, 876, 818, 729, 662; MS (ESI-TOF) 428 ($[M+H]^+$); HRMS (ESI-TOF) calcd for $C_{22}H_{19}ClNO_4S$ ($[M+H]^+$): 428.0718. Found: 428.0709.

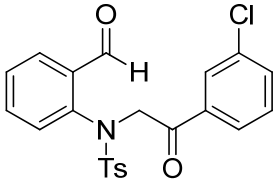


1f

***N*-(2-(4-Bromophenyl)-2-oxoethyl)-*N*-(2-formylphenyl)-4-methylbenzenesulfonamide**

White solid, 52% yield. M.p. 211-213 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.47 (s, 1H), 8.02-7.92 (m, 1H), 7.75 (d, *J* = 8.8 Hz, 2H), 7.60 (d, *J* = 8.8 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H),7.46-7.41 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.95-6.87 (m, 1H), 5.30 (brs, 1H), 4.89 (brs, 1H), 2.46 (s, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.8, 190.3, 144.6, 141.1, 135.7, 134.1, 134.0, 133.3, 132.2, 129.7, 129.5, 129.3, 129.00, 128.98, 128.1, 128.0, 57.2, 21.6; IR (thin film): ν_{max} (cm^{-1}) = 3060, 2949, 1682, 1581, 1396, 1213, 1155, 812, 724, 659; MS (ESI-TOF) 472 ($[M+H]^+$); HRMS (ESI-TOF) calcd for

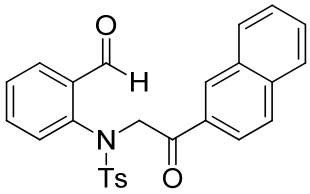
$C_{22}H_{19}BrNO_4S$ ([M+H]$^+$): 472.0213. Found: 472.0200.



1g

***N*-(2-(3-Chlorophenyl)-2-oxoethyl)-*N*-(2-formylphenyl)-4-methylbenzenesulfonamide**

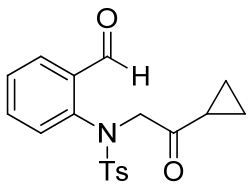
White solid, 51% yield. M.p. 171-173 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 10.50 (s, 1H), 8.02-7.95 (m, 1H), 7.80-7.82 (m, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.47-7.42 (m, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 6.95-6.85 (m, 1H), 5.30 (brs, 1H), 4.91 (brs, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 190.4, 144.6, 141.1, 136.0, 135.7, 135.2, 134.1, 134.0, 133.9, 130.2, 129.7, 129.0, 128.11, 128.05, 127.97, 126.1, 57.3, 21.6; IR (thin film): ν_{max} (cm^{-1}) = 1702, 1676, 1339, 1213, 1157, 870, 818, 721, 659; MS (ESI-TOF) 445 ([M+H]$^+$); HRMS (ESI-TOF) calcd for $C_{22}H_{22}ClN_2O_4S$ ([M+H]$^+$): 445.0983. Found: 445.0971.



1h

***N*-(2-Formylphenyl)-4-methyl-*N*-(2-(naphthalen-2-yl)-2-oxoethyl)benzenesulfonamide**

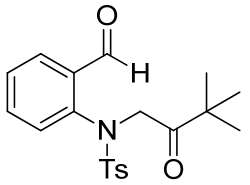
White solid, 44% yield. M.p. 210-211 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 10.52 (s, 1H), 8.43 (s, 1H), 8.03-7.85 (m, 5H), 7.68-7.56 (m, 2H), 7.56-7.50 (d, *J* = 8.0 Hz, 2H), 7.50-7.41 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.05-6.93 (m, 1H), 5.30 (brs, 1H), 5.08 (brs, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.6, 190.5, 144.5, 141.3, 135.8, 135.8, 134.3, 134.0, 132.3, 131.9, 129.9, 129.7, 129.6, 129.00, 128.95, 128.92, 128.86, 128.3, 128.1, 127.9, 127.1, 123.4, 57.4, 21.7; IR (thin film): ν_{max} (cm^{-1}) = 1683, 1343, 1158, 862, 818, 753, 723, 692, 660; MS (ESI-TOF) 444 ([M+H]$^+$); HRMS (ESI-TOF) calcd for $C_{26}H_{22}NO_4S$ ([M+H]$^+$): 444.1264. Found: 444.1264.



1i

***N*-(2-Cyclopropyl-2-oxoethyl)-*N*-(2-formylphenyl)-4-methylbenzenesulfonamide**

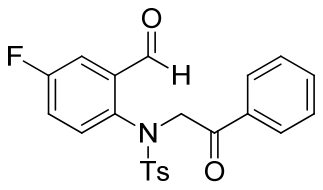
White solid, 50% yield. M.p. 133-135 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.56 (d, *J* = 0.4 Hz, 1H), 8.03-7.95 (m, 1H), 7.49-7.40 (m, 4H), 7.30-7.26 (m, 2H), 6.85-6.76 (m, 1H), 4.80 (brs, 1H), 4.45 (brs, 1H), 2.45 (s, 3H), 2.05-1.95 (m, 1H), 1.06-0.84 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.5, 190.4, 144.5, 141.5, 135.6, 133.9, 129.6, 128.8, 128.7, 127.9, 127.6, 60.4, 21.6, 18.3, 11.6; IR (thin film): ν_{max} (cm^{-1}) = 1706, 1681, 1594, 1345, 1160, 894, 814, 721, 663; MS (ESI-TOF) 358 ($[M+H]^+$); HRMS (ESI-TOF) calcd for $C_{19}H_{20}NO_4S$ ($[M+H]^+$): 358.1108. Found: 358.1111.



1j

***N*-(3,3-Dimethyl-2-oxobutyl)-*N*-(2-formylphenyl)-4-methylbenzenesulfonamide**

White solid, 58% yield. M.p. 122-124 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.56 (s, 1H), 8.02-7.96 (m, 1H), 7.54-7.38 (m, 4H), 7.27 (d, *J* = 7.6 Hz, 2H), 6.94-6.86 (m, 1H), 4.67 (brs, 2H), 2.44 (s, 3H), 1.11 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.9, 190.9, 144.3, 141.5, 135.8, 134.4, 133.8, 129.6, 128.6, 128.5, 127.7, 127.5, 55.1, 43.2, 25.9, 21.5. IR (thin film): ν_{max} (cm^{-1}) = 2964, 1718, 1684, 1596, 1343, 1158, 873, 824, 725, 660; MS (ESI-TOF) 391 ($[M+NH_4]^+$); HRMS (ESI-TOF) calcd for $C_{20}H_{27}N_2O_4S$ ($[M+NH_4]^+$): 391.1686. Found: 391.1693.

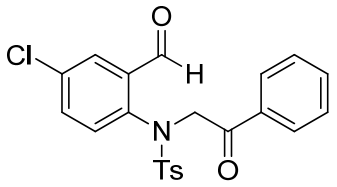


1k

***N*-(4-Fluoro-2-formylphenyl)-4-methyl-*N*-(2-oxo-2-phenylethyl)benzenesulfonamide**

White solid, 38% yield. M.p. 192-194 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.46 (d, *J* = 2.8 Hz, 1H), 7.86 (d, *J* = 7.2 Hz, 2H), 7.63 (dd, *J* = 8.8, 3.2 Hz, 1H), 7.59 (d, *J* = 7.2

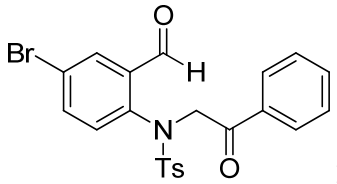
Hz, 1H), 7.54-7.41 (m, 4H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.15-7.05 (m, 1H), 6.86 (dd, *J* = 8.8, 4.4 Hz, 1H), 5.38 (d, *J* = 15.6 Hz, 1H), 4.83 (d, *J* = 15.6 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.6, 189.3, 162.1 (d, *J* = 250.6 Hz), 144.7, 137.9 (d, *J* = 6.8 Hz), 137.1 (d, *J* = 3.3 Hz), 134.4, 134.1, 134.0, 130.0 (d, *J* = 9.1 Hz), 129.80, 128.89, 127.95, 127.93, 120.8 (d, *J* = 23.2 Hz), 115.1 (d, *J* = 23.4 Hz), 57.2, 21.6; IR (thin film): ν_{max} (cm^{-1}) = 1698, 1683, 1594, 1492, 1343, 1158, 983, 875, 813, 756, 693, 667; MS (ESI-TOF) 429 ($[M+NH_4]^+$); HRMS (ESI-TOF) calcd for $C_{22}H_{22}FN_2O_4S$ ($[M+NH_4]^+$): 429.1279. Found: 429.1289.



1l

***N*-(4-Chloro-2-formylphenyl)-4-methyl-*N*-(2-oxo-2-phenylethyl)benzenesulfonamide**

White solid, 46% yield. M.p. 152-154 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.45 (s, 1H), 7.93 (d, *J* = 2.4 Hz, 1H), 7.86 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.53-7.43 (m, 4H), 7.37 (dd, *J* = 8.4, 2.8 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 1H), 5.35 (brs, 1H), 4.82 (brs, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.5, 189.1, 144.8, 139.6, 137.1, 135.3, 134.4, 134.1, 133.9, 133.7, 129.8, 129.2, 128.9, 128.7, 128.0, 127.9, 57.0, 21.7; IR (thin film): ν_{max} (cm^{-1}) = 1698, 1681, 1597, 1344, 1219, 1159, 870, 814, 750, 727, 687, 666; MS (ESI-TOF) 428 ($[M+H]^+$); HRMS (ESI-TOF) calcd for $C_{22}H_{19}ClNO_4S$ ($[M+H]^+$): 428.0718. Found: 428.0713.

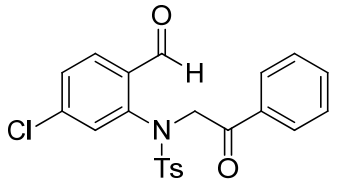


1m

***N*-(4-Bromo-2-formylphenyl)-4-methyl-*N*-(2-oxo-2-phenylethyl)benzenesulfonamide**

White solid, 40% yield. M.p. 178-180 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.45 (s, 1H), 8.09 (d, *J* = 2.4 Hz, 1H), 7.86 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.55-7.39 (m, 5H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.72 (d, *J* = 8.4 Hz, 1H), 5.35 (brs, 1H),

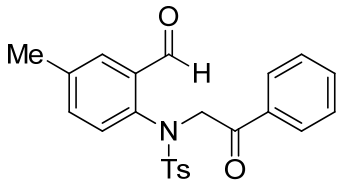
4.82 (brs, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.4, 189.1, 144.8, 140.1, 137.2, 136.6, 134.4, 134.1, 133.9, 131.8, 129.9, 129.3, 128.9, 128.0, 127.9, 123.2, 56.9, 21.7; IR (thin film): ν_{max} (cm^{-1}) = 1697, 1682, 1596, 1343, 1219, 1158, 865, 814, 751, 725, 691, 664; MS (ESI-TOF) 472 ($[M+H]^+$); HRMS (ESI-TOF) calcd for $C_{22}H_{19}BrNO_4S$ ($[M+H]^+$): 472.0213. Found: 472.0206.



1n

***N*-(5-Chloro-2-formylphenyl)-4-methyl-*N*-(2-oxo-2-phenylethyl)benzenesulfonamide**

White solid, 41% yield. M.p. 189-190 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.47 (s, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 7.2 Hz, 2H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.54-7.43 (m, 4H), 7.41 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 2.0 Hz, 1H), 5.30 (brs, 1H), 4.87 (brs, 1H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 189.4, 144.9, 142.4, 139.6, 134.40, 134.36, 134.1, 133.8, 129.9, 129.8, 129.3, 128.9, 128.2, 127.95, 127.92, 57.0, 21.6; IR (thin film): ν_{max} (cm^{-1}) = 1685, 1586, 1353, 1214, 1159, 982, 889, 836, 809, 754, 725, 670; MS (ESI-TOF) 445 ($[M+NH_4]^+$); HRMS (ESI-TOF) calcd for $C_{22}H_{22}ClN_2O_4S$ ($[M+NH_4]^+$): 445.0983. Found: 445.0978.

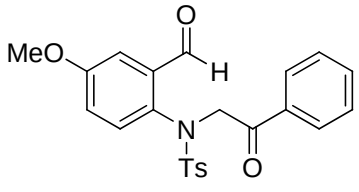


1o

***N*-(2-Formyl-4-methylphenyl)-4-methyl-*N*-(2-oxo-2-phenylethyl)benzenesulfonamide**

White solid, 50% yield. M.p. 198-200 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.44 (s, 1H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.76 (d, *J* = 1.6 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.50 (d, *J* = 7.6 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.23 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 5.32 (brs, 1H), 4.83 (brs, 1H), 2.46 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.8, 190.8, 144.4, 139.1, 138.7, 135.3,

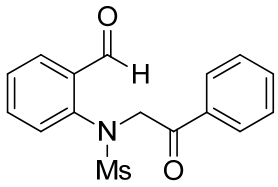
134.64, 134.59, 134.2, 133.9, 129.6, 129.1, 128.8, 128.00, 127.97, 127.7, 57.2, 21.6, 21.0; IR (thin film): ν_{max} (cm^{-1}) = 1695, 1677, 1598, 1343, 1215, 1159, 983, 874, 815, 752, 691, 667; MS (ESI-TOF) 408 ($[M+H]^+$); HRMS (ESI-TOF) calcd for $C_{23}H_{22}NO_4S$ ($[M+H]^+$): 408.1264. Found: 408.1265.



1p

***N*-(2-Formyl-4-methoxyphenyl)-4-methyl-*N*-(2-oxo-2-phenylethyl)benzenesulfonamide**

White solid, 48% yield. M.p. 202-204 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 10.42 (s, 1H), 7.88 (d, *J* = 7.2 Hz, 2H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.47-7.40 (m, 3H), 7.30 (d, *J* = 8.4 Hz, 2H), 6.94 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.78 (d, *J* = 8.8 Hz, 1H), 5.35 (d, *J* = 17.2 Hz, 1H), 4.79 (d, *J* = 16.8 Hz, 1H), 3.83 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.9, 190.4, 159.5, 144.4, 136.7, 134.6, 134.2, 133.94, 133.93, 129.7, 129.3, 128.8, 128.0, 121.1, 111.2, 57.3, 55.7, 21.6; IR (thin film): ν_{max} (cm^{-1}) = 1688, 1675, 1599, 1495, 1340, 1214, 1157, 981, 875, 813, 753, 693, 666; MS (ESI-TOF) 441 ($[M+NH_4]^+$); HRMS (ESI-TOF) calcd for $C_{23}H_{25}N_2O_5S$ ($[M+NH_4]^+$): 441.1479. Found: 441.1484.

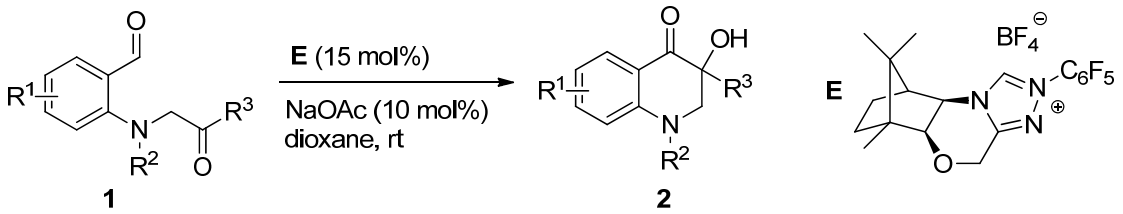


1q

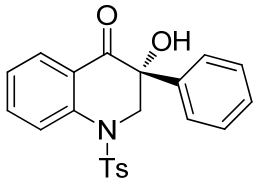
N-(2-Formylphenyl)-N-(2-oxo-2-phenylethyl)methanesulfonamide[2a]

White solid, 43% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 10.49 (s, 1H), 7.99 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.95-7.85 (m, 2H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.70-7.55 (m, 2H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.50-7.42 (m, 2H), 5.26 (brs, 2H), 3.21 (s, 3H).

General procedure for *N*-heterocyclic carbene-catalyzed enantioselective intramolecular *N*-tethered aldehyde-ketone benzoin reactions



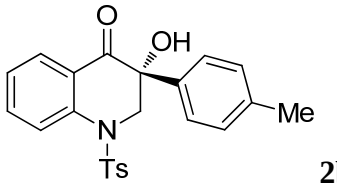
A flame-dried Schlenk tube was cooled to room temperature and filled with argon. To this flask were added triazolium salt **E** (14.6 mg, 0.03 mmol, 15 mol%), dioxane (4.0 mL), NaOAc (1.6 mg, 0.02 mmol, 10 mol%). The reaction mixture was stirred at room temperature for 60 min. The substrate **1** (0.2 mmol) was then added. After the reaction was complete (monitored by TLC), the reaction mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford the product (eluent: ethyl acetate/petrol ether = 1/4).



2a

(*R*)-3-Hydroxy-3-phenyl-1-tosyl-2,3-dihydroquinolin-4(1H)-one

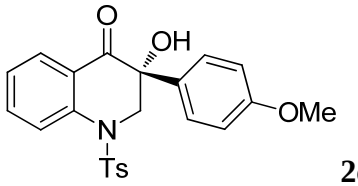
White solid, 76% yield, 92% ee [Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 80/20, v = 1.0 mL·min^{-1}, λ = 254 nm, t (minor) = 19.4 min, t (major) = 28.2 min]; $[\alpha]_D^{20}$ = +166 (c = 0.2, $CHCl_3$). M.p. 106-108 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.11 (dd, J = 8.0, 1.6 Hz, 1H), 7.68 (d, J = 8.4 Hz, 1H), 7.50-7.41 (m, 1H), 7.40-7.27 (m, 7H), 7.20-7.06 (m, 3H), 5.11 (d, J = 13.2 Hz, 1H), 4.06 (s, 1H), 3.94 (d, J = 13.2 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8, 144.4, 142.8, 138.8, 135.6, 135.3, 129.7, 128.72, 128.69, 127.4, 126.5, 123.4, 121.5, 118.6, 75.3, 55.1, 21.4; IR (thin film): ν_{max} (cm^{-1}) = 3481, 2921, 2851, 1683, 1596, 1492, 1448, 1153, 1055, 1035, 905, 749, 697; MS (ESI-TOF) 411 ($[M+NH_4]^+$); HRMS (ESI-TOF) calcd for $C_{22}H_{23}N_2O_4S$ ($[M+NH_4]^+$): 411.1373. Found: 411.1367.



2b

(*R*)-3-Hydroxy-3-(p-tolyl)-1-tosyl-2,3-dihydroquinolin-4(1H)-one

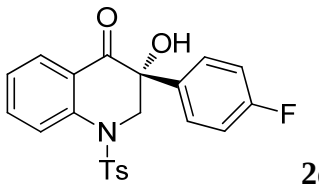
White solid, 71% yield, 90% ee [Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 60/40, v = 0.7 mL·min^{-1}, λ = 254 nm, t (minor) = 14.7 min, t (major) = 20.5 min]; $[\alpha]_D^{20}$ = +158 (c = 0.2, $CHCl_3$). M.p. 88-90 ^oC. ^1H NMR (300 MHz, $CDCl_3$) δ 8.09 (dd, J = 7.8, 1.5 Hz, 1H), 7.69 (d, J = 8.6 Hz, 1H), 7.44 (dt, J = 7.2, 1.5 Hz, 1H), 7.34 (d, J = 8.1 Hz, 2H), 7.27-7.18 (d, J = 8.1 Hz, 2H), 7.16-7.05 (m, 5H), 5.10 (d, J = 13.2 Hz, 1H), 3.90 (d, J = 13.2 Hz, 1H), 3.76 (s, 1H), 2.34 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.9, 144.4, 142.8, 138.6, 135.6, 135.5, 135.3, 129.6, 129.4, 128.7, 127.4, 126.4, 123.4, 121.4, 118.6, 75.1, 55.0, 21.5, 21.1; IR (thin film): ν_{max} (cm^{-1}) = 1696, 1596, 1477, 1456, 1340, 1158, 911, 816, 775, 750, 697; MS (ESI-TOF) 425 ([M+NH_4]$^+$); HRMS (ESI-TOF) calcd for $C_{23}H_{25}N_2O_4S$ (M+NH_4]$^+$): 425.1530. Found: 425.1537.



2c

(*R*)-3-Hydroxy-3-(4-methoxyphenyl)-1-tosyl-2,3-dihydroquinolin-4(1H)-one

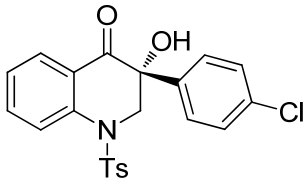
Pale yellow solid, 54% yield, 88% ee [Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 60/40, v = 0.7 mL·min^{-1}, λ = 254 nm, t (minor) = 21.7 min, t (major) = 30.1 min]; $[\alpha]_D^{20}$ = +148 (c = 0.1, $CHCl_3$). M.p. 56-58 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, J = 8.0, 1.6 Hz, 1H), 7.71 (d, J = 8.8 Hz, 1H), 7.48-7.42 (m, 1H), 7.38 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.8 Hz, 2H), 7.18-7.09 (m, 3H), 6.82 (d, J = 8.8 Hz, 2H), 5.09 (d, J = 12.8 Hz, 1H), 3.89 (d, J = 12.8 Hz, 1H), 3.78 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.9, 159.9, 144.4, 142.8, 135.6, 135.4, 130.5, 129.7, 128.8, 127.9, 127.4, 123.4, 121.4, 118.6, 114.1, 74.9, 55.2, 55.0, 21.5; IR (thin film): ν_{max} (cm^{-1}) = 3481, 2958, 2922, 2853, 1688, 1598, 1353, 1161, 911, 810, 752, 699; MS (ESI-TOF) 441 ([M+NH_4]$^+$); HRMS (ESI-TOF) calcd for $C_{23}H_{25}N_2O_5S$ ([M+NH_4]$^+$): 441.1479. Found: 441.1492.



2d

(*R*)-3-(4-Fluorophenyl)-3-hydroxy-1-tosyl-2,3-dihydroquinolin-4(1H)-one

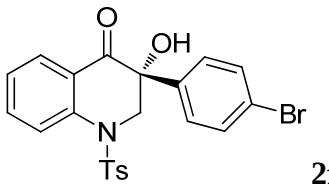
White solid, 65% yield, 91% ee [Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 60/40, v = 0.7 mL·min^{-1}, λ = 254 nm, t (minor) = 11.9 min, t (major) = 15.1 min]; $[\alpha]_D^{20}$ = +156 (c = 0.2, $CHCl_3$). M.p. 93-94 ^oC. ^1H NMR (300 MHz, $CDCl_3$) δ 8.09 (d, J = 7.8 Hz, 1H), 7.73 (d, J = 8.7 Hz, 1H), 7.49 (d, J = 7.5 Hz, 1H), 7.43 (d, J = 8.1 Hz, 2H), 7.38-7.25 (m, 2H), 7.22-7.08 (m, 3H), 6.96 (t, J = 8.7 Hz, 2H), 5.02 (d, J = 12.9 Hz, 1H), 4.16 (s, 1H), 3.91 (d, J = 12.9 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.5, 162.8 (d, J = 246.8 Hz), 144.6, 142.9, 135.8, 135.5, 134.5 (d, J = 3.2 Hz), 129.8, 128.8, 128.4 (d, J = 8.3 Hz), 127.2, 123.6, 121.3, 118.7, 115.6 (d, J = 21.3 Hz), 74.7, 55.3, 21.5; IR (thin film): ν_{max} (cm^{-1}) = 1691, 1597, 1508, 1459, 1345, 1159, 912, 836, 778, 750, 724; MS (ESI-TOF) 429 ($[M+H]^+$); HRMS (ESI-TOF) calcd for $C_{22}H_{22}FN_2O_4S$ ($[M+NH_4]^+$): 429.1279. Found: 429.1279.



2e

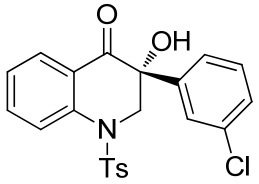
(*R*)-3-(4-Chlorophenyl)-3-hydroxy-1-tosyl-2,3-dihydroquinolin-4(1H)-one

Pale yellow oil, 71% yield, 91% ee [Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 60/40, v = 0.7 mL·min^{-1}, λ = 254 nm, t (minor) = 12.7 min, t (major) = 17.9 min]; $[\alpha]_D^{20}$ = +97 (c = 0.2, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 8.09 (d, J = 7.8 Hz, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.50 (t, J = 8.1 Hz, 1H), 7.39 (d, J = 8.1 Hz, 2H), 7.24 (s, 4H), 7.20-7.10 (m, 3H), 5.01 (d, J = 13.2 Hz, 1H), 3.92 (d, J = 13.2 Hz, 1H), 3.90 (s, 1H), 2.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.3, 144.6, 143.0, 137.3, 135.9, 135.4, 134.8, 129.8, 128.9, 128.8, 127.9, 127.1, 123.6, 121.3, 118.8, 74.7, 55.4, 21.5; IR (thin film): ν_{max} (cm^{-1}) = 1689, 1597, 1477, 1458, 1352, 1161, 911, 812, 751, 701; MS (ESI-TOF) 445 ($[M+NH_4]^+$); HRMS (ESI-TOF) calcd for $C_{22}H_{22}ClN_2O_4S$ ($[M+NH_4]^+$): 445.0983. Found: 445.0986.



2f

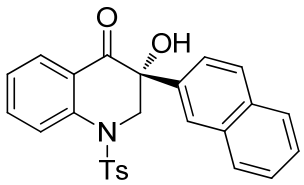
(*R*)-3-(4-Bromophenyl)-3-hydroxy-1-tosyl-2,3-dihydroquinolin-4(1H)-oneWhite solid, 65% yield, 91% ee [Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 60/40, *v* = 0.7 mL·min^{-1}, λ = 254 nm, t (minor) = 13.6 min, t (major) = 20.9 min]; $[\alpha]_D^{20}$ = +121 (c = 0.2, $CHCl_3$). M.p. 62-64 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.2 Hz, 1H), 7.79 (d, *J* = 8.8 Hz, 1H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.45-7.32 (m, 3H), 7.17 (d, *J* = 7.6 Hz, 4H), 5.01 (d, *J* = 13.2 Hz, 1H), 4.10 (s, 1H), 3.92 (d, *J* = 13.2 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 144.7, 143.0, 137.9, 135.9, 135.4, 131.8, 129.8, 128.9, 128.2, 127.2, 123.6, 123.1, 121.3, 118.8, 74.8, 55.3, 21.6; IR (thin film): ν_{max} (cm^{-1}) = 1685, 1596, 1476, 1458, 1344, 1159, 910, 812, 750, 721; MS (ESI-TOF) 489 ($[M+NH_4]^+$); HRMS (ESI-TOF) calcd for $C_{22}H_{22}BrN_2O_4S$ $[M+NH_4]^+$): 489.0478. Found: 489.0478.



2g

(*R*)-3-(3-Chlorophenyl)-3-hydroxy-1-tosyl-2,3-dihydroquinolin-4(1H)-one

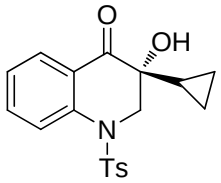
White solid, 55% yield, 92% ee [Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 60/40, *v* = 0.7 mL·min^{-1}, λ = 254 nm, t (minor) = 13.1 min, t (major) = 17.4 min]; $[\alpha]_D^{20}$ = +87 (c = 0.2, $CHCl_3$). M.p. 53-54 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.55-7.46 (m, 1H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.34-7.09 (m, 7H), 4.97 (d, *J* = 13.2 Hz, 1H), 4.08 (s, 1H), 3.95 (d, *J* = 13.2 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.0, 144.7, 143.1, 140.9, 136.0, 135.5, 134.6, 130.0, 129.8, 129.0, 128.9, 127.2, 126.7, 124.7, 123.7, 121.4, 119.0, 74.9, 55.5, 21.5; IR (thin film): ν_{max} (cm^{-1}) = 1687, 1597, 1475, 1458, 1348, 1161, 913, 812, 751, 702; MS (ESI-TOF) 445 ($[M+NH_4]^+$); HRMS (ESI-TOF) calcd for $C_{22}H_{22}ClN_2O_4S$ ($[M+NH_4]^+$): 445.0983. Found: 445.0998.



2h

(*R*)-3-Hydroxy-3-(naphthalen-2-yl)-1-tosyl-2,3-dihydroquinolin-4(1H)-one

White solid, 61% yield, 90% ee [Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 60/40, v = 0.7 mL·min^{-1}, λ = 254 nm, t (minor) = 19.9 min, t (major) = 37.7 min]; $[\alpha]_D^{20}$ = +128 (c = 0.2, $CHCl_3$). M.p. 93-95 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.17 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.79 (dt, *J* = 8.4, 0.4 Hz, 1H), 7.66 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.53-7.44 (m, 2H), 7.44-7.38 (m, 2H), 7.17 (t, *J* = 8.0 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.63 (d, *J* = 8.0 Hz, 2H), 5.23 (d, *J* = 13.6 Hz, 1H), 4.17 (s, 1H), 4.02 (d, *J* = 13.6 Hz, 1H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.0, 144.2, 143.0, 136.4, 135.8, 135.1, 133.2, 132.7, 129.3, 128.9, 128.8, 128.4, 127.5, 127.2, 126.7, 126.2, 125.8, 124.1, 123.5, 121.7, 118.9, 75.4, 55.4, 21.3; IR (thin film): ν_{max} (cm^{-1}) = 1687, 1596, 1475, 1457, 1345, 1160, 910, 810, 749; MS (ESI-TOF) 461 ($[M+NH_4]^+$); HRMS (ESI-TOF) calcd for $C_{26}H_{25}N_2O_4S$ ($[M+NH_4]^+$): 461.1530. Found: 461.1538.

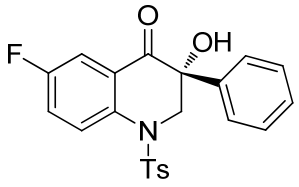


2i

(*R*)-3-Cyclopropyl-3-hydroxy-1-tosyl-2,3-dihydroquinolin-4(1H)-one

Pale yellow oil, 96% yield, 68% ee [Daicel Chiralpak IC, *n*-hexane/2-propanol = 60/40, v = 0.4 mL·min^{-1}, λ = 254 nm, t (minor) = 16.2 min, t (major) = 17.2 min]; $[\alpha]_D^{20}$ = +7.9 (c = 0.5, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 8.8 Hz, 1H), 7.56-7.44 (m, 1H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.14 (t, *J* = 7.6 Hz, 1H), 4.72 (d, *J* = 12.4 Hz, 1H), 3.65 (d, *J* = 12.4 Hz, 1H), 3.24 (s, 1H), 2.42 (s, 3H), 1.34-1.16 (m, 1H), 0.74-0.60 (m, 1H), 0.56-0.40 (m, 2H), 0.40-0.26 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 144.6, 142.7, 136.4, 135.4, 130.0, 128.9, 127.0, 123.4, 120.1, 118.8, 71.5, 54.9, 21.5, 14.3, 0.3, 0.2; IR (thin film): ν_{max} (cm^{-1}) = 1690, 1599, 1476, 1459, 1351, 1163, 899, 813, 750, 703;

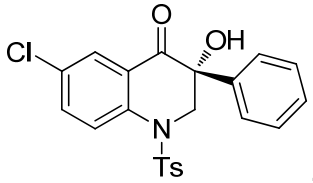
MS (ESI-TOF) 375 ($[M+NH_4]^+$); HRMS (ESI-TOF) calcd for $C_{19}H_{23}N_2O_4S$ ($[M+NH_4]^+$): 375.1373. Found: 375.1390.



2k

(*R*)-6-Fluoro-3-hydroxy-3-phenyl-1-tosyl-2,3-dihydroquinolin-4(1H)-one

White solid, 76% yield, 88% ee [Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 60/40, v = 0.7 mL·min^{-1}, λ = 254 nm, t (minor) = 13.1 min, t (major) = 20.2 min]; $[\alpha]_D^{20}$ = +151 (c = 0.2, $CHCl_3$). M.p. 125-127 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.80-7.65 (m, 2H), 7.40-7.27 (m, 7H), 7.20-7.14 (m, 1H), 7.12 (d, J = 8.4 Hz, 2H), 5.02 (d, J = 13.2 Hz, 1H), 4.06 (s, 1H), 3.95 (d, J = 13.2 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.0, 158.4 (d, J = 243.7 Hz), 144.6, 139.1 (d, J = 2.4 Hz), 138.45, 135.0, 129.8, 128.9, 128.8, 127.4, 126.4, 122.9 (d, J = 23.3 Hz), 122.9 (d, J = 6.2 Hz), 120.8 (d, J = 7.1 Hz), 114.1 (d, J = 23.2 Hz), 75.5, 55.3, 21.5; IR (thin film): ν_{max} (cm^{-1}) = 1688, 1483, 1330, 1148, 1043, 826, 754, 697; MS (ESI-TOF) 429 ($[M+NH_4]^+$); HRMS (ESI-TOF) calcd for $C_{22}H_{22}FN_2O_4S$ ($[M+NH_4]^+$): 429.1279. Found: 429.1287.

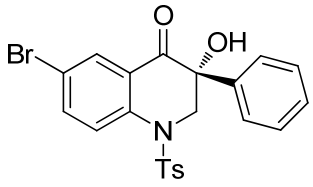


2l

(*R*)-6-Chloro-3-hydroxy-3-phenyl-1-tosyl-2,3-dihydroquinolin-4(1H)-one

White solid, 82% yield, 92% ee [Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 60/40, v = 0.7 mL·min^{-1}, λ = 254 nm, t (minor) = 13.9 min, t (major) = 22.8 min]; $[\alpha]_D^{20}$ = +173 (c = 0.2, $CHCl_3$). M.p. 159-161 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 2.6 Hz, 1H), 7.67 (d, J = 9.1 Hz, 1H), 7.44-7.26 (m, 7H), 7.12 (d, J = 8.2 Hz, 2H), 5.07 (d, J = 13.2 Hz, 1H), 4.06 (s, 1H), 3.92 (d, J = 13.2 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.9, 144.7, 141.3, 138.4, 135.3, 134.9, 129.8, 129.3, 129.0, 128.8, 128.1, 127.4, 126.5, 122.5, 120.2, 75.3, 55.0, 21.5; IR (thin film): ν_{max} (cm^{-1}) = 2920, 2851, 1694, 1473, 1335, 1159, 1051, 910, 827, 754, 697; MS

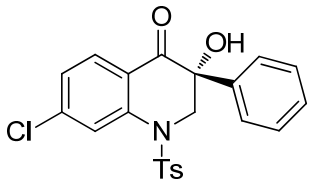
(ESI-TOF) 445 ([M+NH_4]$^+$); HRMS (ESI-TOF) calcd for $C_{22}H_{22}ClN_2O_4S$ ([M+NH_4]$^+$): 445.0983. Found: 445.0996.



2m

(*R*)-6-Bromo-3-hydroxy-3-phenyl-1-tosyl-2,3-dihydroquinolin-4(1H)-one

White solid, 82% yield, 87% ee [Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 60/40, v = 0.7 mL·min^{-1}, λ = 254 nm, t (minor) = 14.5 min, t (major) = 23.4 min]; $[\alpha]_D^{20}$ = +218 (c = 0.2, $CHCl_3$). M.p. 172-174 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 2.4 Hz, 1H), 7.60 (d, J = 9.2 Hz, 1H), 7.51 (dd, J = 8.8, 2.4 Hz, 1H), 7.44-7.22 (m, 7H), 7.12 (d, J = 8.0 Hz, 2H), 5.08 (d, J = 13.2 Hz, 1H), 4.05 (s, 1H), 3.91 (d, J = 13.2 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.7, 144.8, 141.7, 138.3, 138.1, 134.8, 131.1, 129.8, 129.0, 128.8, 127.4, 126.4, 122.8, 120.4, 116.7, 75.3, 54.9, 21.5; IR (thin film): ν_{max} (cm^{-1}) = 1693, 1593, 1471, 1337, 1158, 1052, 910, 823, 752, 697; MS (ESI-TOF) 489 ([M+NH_4]$^+$); HRMS (ESI-TOF) calcd for $C_{22}H_{22}BrN_2O_4S$ ([M+NH_4]$^+$): 489.0478. Found: 489.0466.

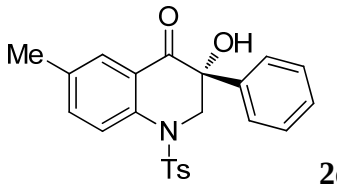


2n

(*R*)-7-Chloro-3-hydroxy-3-phenyl-1-tosyl-2,3-dihydroquinolin-4(1H)-one

White solid, 80% yield, 92% ee [Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 60/40, v = 0.7 mL·min^{-1}, λ = 254 nm, t (major) = 13.5 min, t (minor) = 17.4 min]; $[\alpha]_D^{20}$ = +155 (c = 0.2, $CHCl_3$). M.p. 153-155 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.4 Hz, 1H), 7.75 (d, J = 1.6 Hz, 1H), 7.40-7.28 (m, 7H), 7.14 (d, J = 8.4 Hz, 2H), 7.09 (dd, J = 8.4, 1.6 Hz, 1H), 5.08 (d, J = 13.2 Hz, 1H), 4.11 (s, 1H), 3.91 (d, J = 13.2 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8, 144.9, 143.5, 142.2, 138.5, 134.6, 129.9, 129.8, 128.9, 128.8, 127.5, 126.4, 123.9, 119.8, 118.7, 75.1, 55.0, 21.5; IR (thin film): ν_{max} (cm^{-1}) = 1694, 1593, 1474, 1355, 1163, 1060, 813, 755, 697; MS (ESI-TOF) 445 ([M+NH_4]$^+$); HRMS (ESI-TOF) calcd for

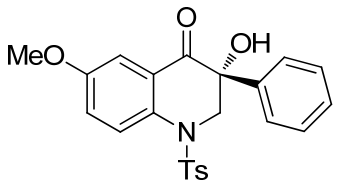
$C_{22}H_{22}ClN_2O_4S$ ([M+NH_4]$^+$): 445.0983. Found: 445.0986.



2o

(*R*)-3-hydroxy-6-methyl-3-phenyl-1-tosyl-2,3-dihydroquinolin-4(1H)-one

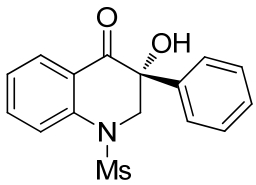
White solid, 66% yield, 82% ee [Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 60/40, v = 0.7 mL·min^{-1}, λ = 254 nm, t (minor) = 15.9 min, t (major) = 26.5 min]; $[\alpha]_D^{20}$ = +179 (c = 0.2, $CHCl_3$). M.p. 122-124 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 1.2 Hz, 1H), 7.59 (d, J = 8.4 Hz, 1H), 7.42-7.21 (m, 8H), 7.10 (d, J = 8.0 Hz, 2H), 5.07 (d, J = 12.8 Hz, 1H), 4.11 (s, 1H), 3.91 (d, J = 12.8 Hz, 1H), 2.33 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.0, 144.3, 140.6, 139.0, 136.6, 135.4, 133.2, 129.7, 128.7, 128.5, 127.4, 126.5, 121.3, 118.6, 104.9, 75.3, 55.2, 21.4, 20.3; IR (thin film): ν_{max} (cm^{-1}) = 1686, 1489, 1336, 1157, 1050, 840, 810, 757, 697; MS (ESI-TOF) 425 ([M+NH_4]$^+$); HRMS (ESI-TOF) calcd for $C_{23}H_{25}N_2O_4S$ ([M+NH_4]$^+$): 425.1530. Found: 425.1539.



2p

(*R*)-3-Hydroxy-6-methoxy-3-phenyl-1-tosyl-2,3-dihydroquinolin-4(1H)-one

Pale yellow solid, 51% yield, 84% ee [Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 60/40, v = 0.7 mL·min^{-1}, λ = 254 nm, t (minor) = 21.9 min, t (major) = 32.7 min]; $[\alpha]_D^{20}$ = +206 (c = 0.2, $CHCl_3$). M.p. 64-66 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 9.6 Hz, 1H), 7.53 (d, J = 3.2 Hz, 1H), 7.40-7.27 (m, 7H), 7.11 (d, J = 8.0 Hz, 2H), 7.06 (dd, J = 9.2, 3.2 Hz, 1H), 5.01 (d, J = 13.2 Hz, 1H), 4.00 (s, 1H), 3.94 (d, J = 13.2 Hz, 1H), 3.81 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.9, 155.6, 144.3, 139.0, 136.8, 135.4, 129.7, 128.75, 128.71, 127.4, 126.5, 124.0, 122.5, 120.6, 109.9, 75.6, 55.6, 55.5, 21.5; IR (thin film): ν_{max} (cm^{-1}) = 1691, 1490, 1427, 1158, 1054, 843, 772, 695; MS (ESI-TOF) 441 ([M+NH_4]$^+$); HRMS (ESI-TOF) calcd for $C_{23}H_{25}N_2O_5S$ ([M+NH_4]$^+$): 441.1479. Found: 441.1487.

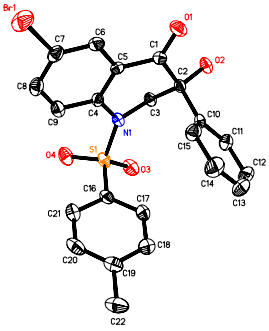


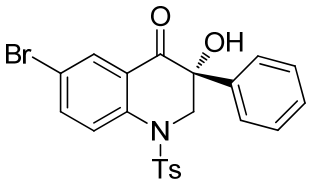
2q

(*R*)-3-Hydroxy-1-(methylsulfonyl)-3-phenyl-2,3-dihydroquinolin-4(1H)-one

White solid, 85% yield, 85% ee [Daicel Chiralcel OD-H, *n*-hexane/2-propanol = 90/10, v = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 21.4 min, t (minor) = 27.0 min]; $[\alpha]_D^{20}$ = +193 (c = 0.2, $CHCl_3$). M.p. 163-164 ^oC. ^1H NMR (300 MHz, $CDCl_3$) δ 8.23 (d, J = 7.8 Hz, 1H), 7.91 (d, J = 8.7 Hz, 1H), 7.61 (t, J = 7.2 Hz, 1H), 7.40-7.22 (m, 6H), 4.93 (d, J = 13.8 Hz, 1H), 4.04 (s, 1H), 4.01 (d, J = 14.1 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.0, 142.8, 139.2, 136.3, 129.0, 128.7, 126.8, 124.3, 122.2, 119.3, 106.7, 75.4, 55.4, 38.6; IR (thin film): ν_{max} (cm^{-1}) = 3481, 2852, 1688, 1596, 1475, 1458, 1339, 1148, 757, 705; MS (ESI-TOF) 335 ($[M+NH_4]^+$); HRMS (ESI-TOF) calcd for $C_{16}H_{19}N_2O_4S$ ($[M+NH_4]^+$): 335.1060. Found: 335.1072.

X-ray of enantiopure (*R*)-**2m** (cd212725)



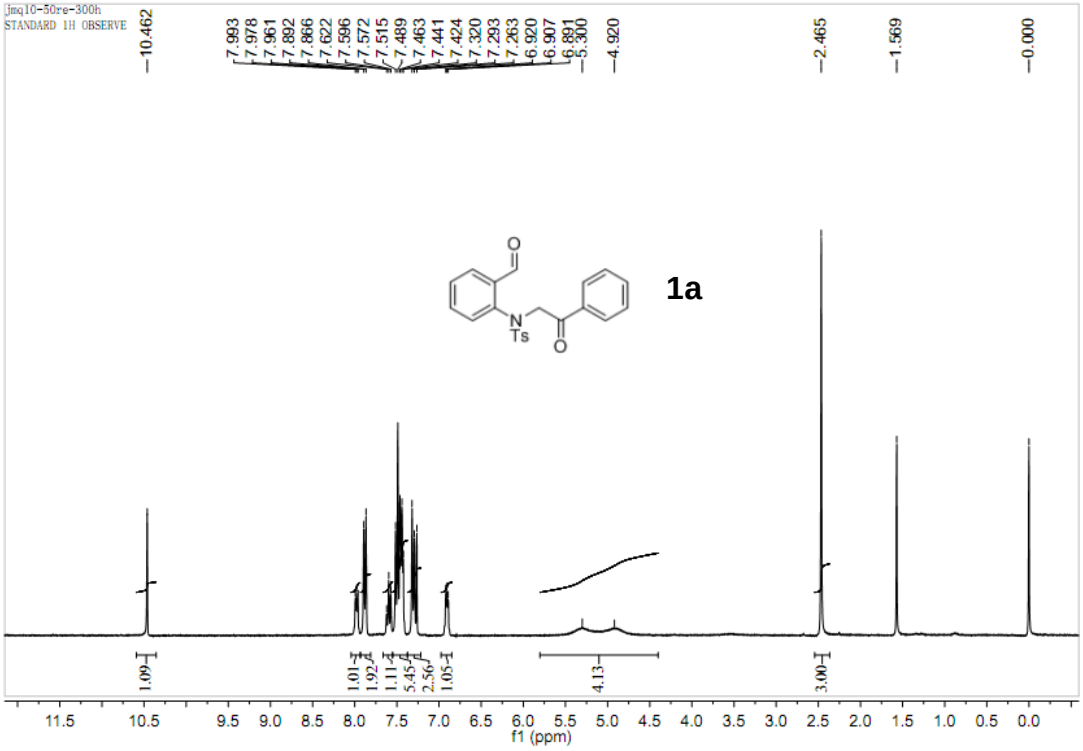


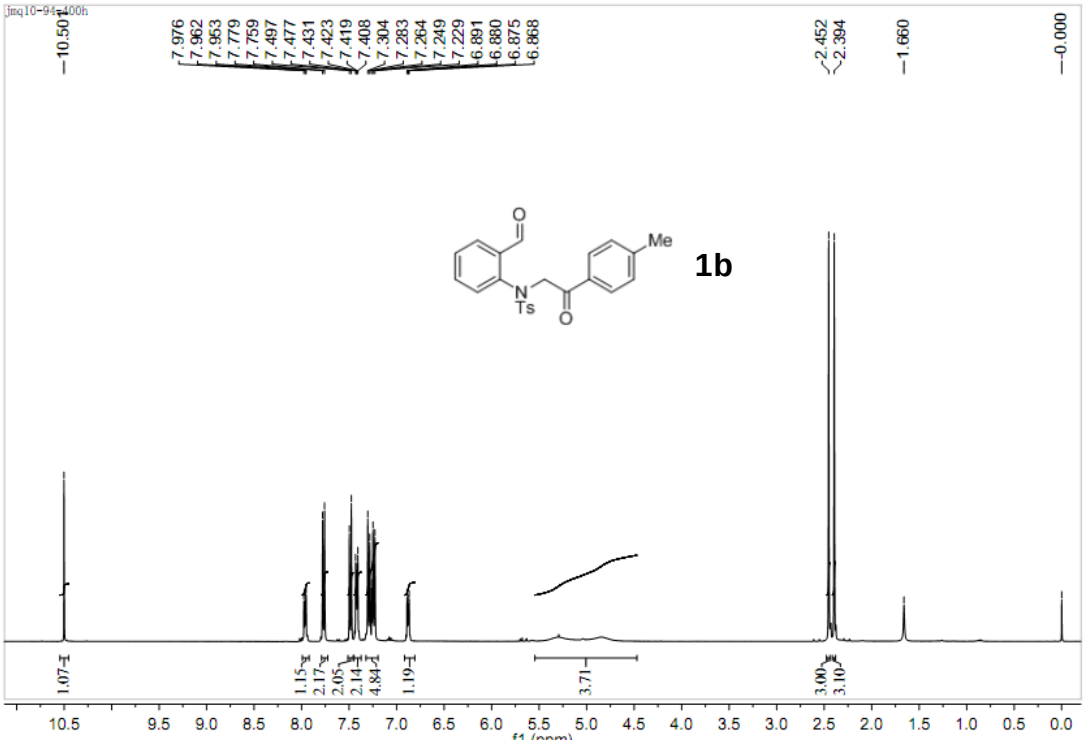
2m

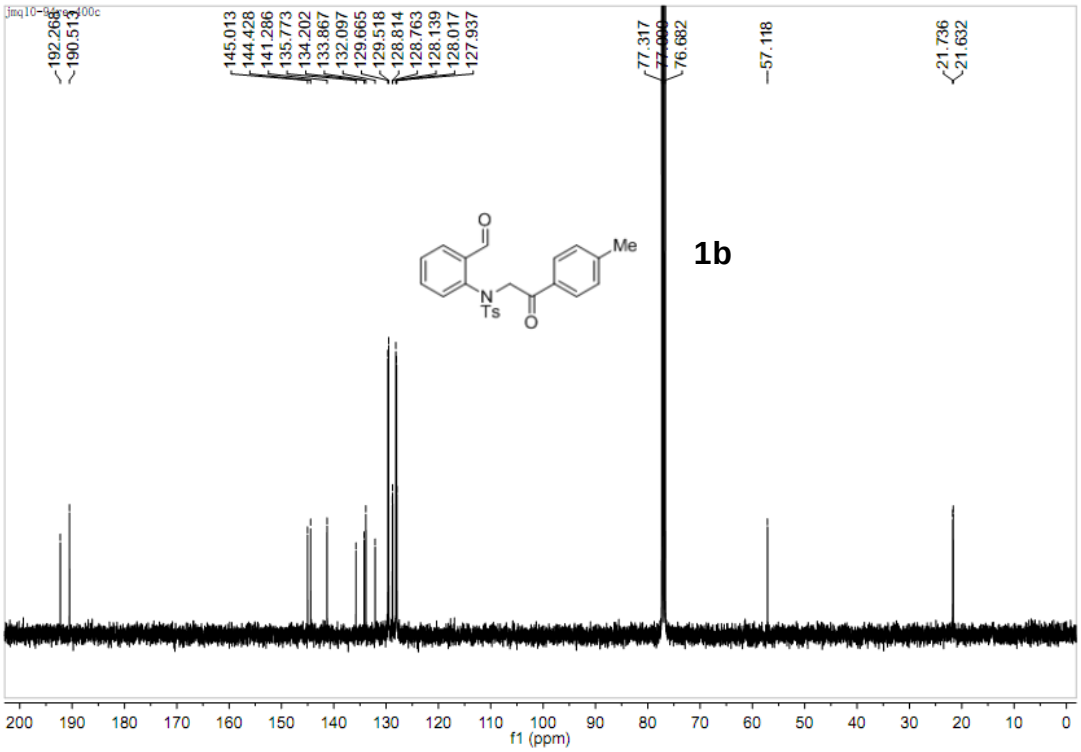
Table 1. Crystal data and structure refinement for cd212725.

Identification code	cd212725
Empirical formula	C22 H18 Br N O4 S
Formula weight	472.34
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 8.6638(10) A alpha = 90 deg.
	b = 10.6945(12) A beta = 90 deg.
	c = 21.769(2) A gamma = 90 deg.
Volume	2017.0(4) A^3
Z, Calculated density	4, 1.555 Mg/m^3
Absorption coefficient	2.171 mm^-1
F(000)	960
Crystal size	0.254 x 0.211 x 0.143 mm
Theta range for data collection	1.87 to 25.97 deg.
Limiting indices	-10<=h<=10, -10<=k<=13, -26<=l<=20
Reflections collected / unique	12030 / 3948 [R(int) = 0.0648]
Completeness to theta = 25.97	100.0 %
Absorption correction	Empirical
Max. and min. transmission	1.00000 and 0.16324
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3948 / 0 / 265
Goodness-of-fit on F^2	0.978
Final R indices [I>2sigma(I)]	R1 = 0.0463, wR2 = 0.1026
R indices (all data)	R1 = 0.0633, wR2 = 0.1108
Absolute structure parameter	0.006(10)
Extinction coefficient	0.0027(6)
Largest diff. peak and hole	0.699 and -0.380 e.A^-3

NMR and HPLC Spectra



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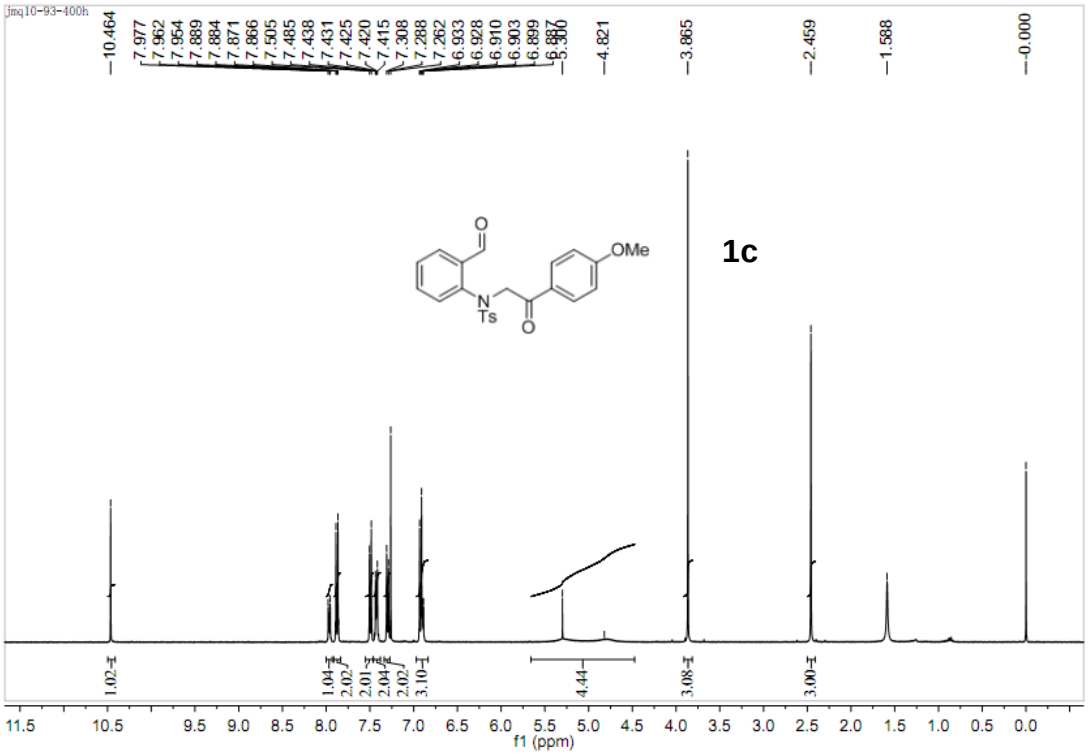
1b
Me
Ts
f1 (ppm)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6.933
6.928
6.910
6.903
6.899
4.821
3.865
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1.588
0.000
1c
OMe
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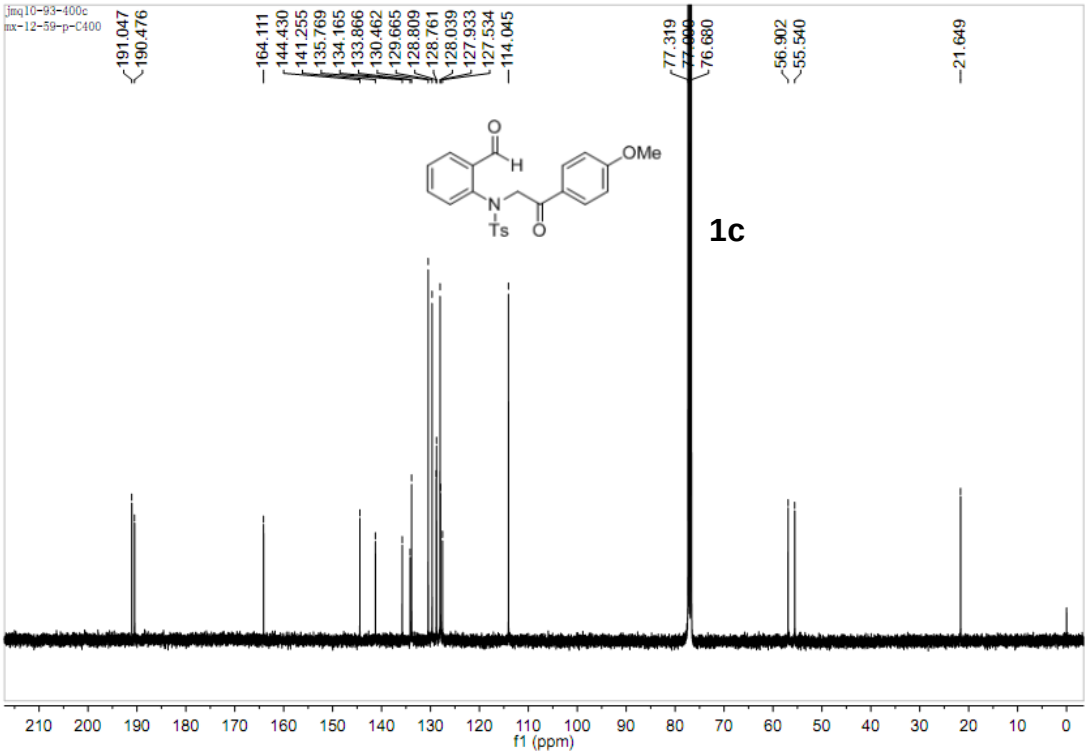
3.00
f1 (ppm)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56.902
55.540
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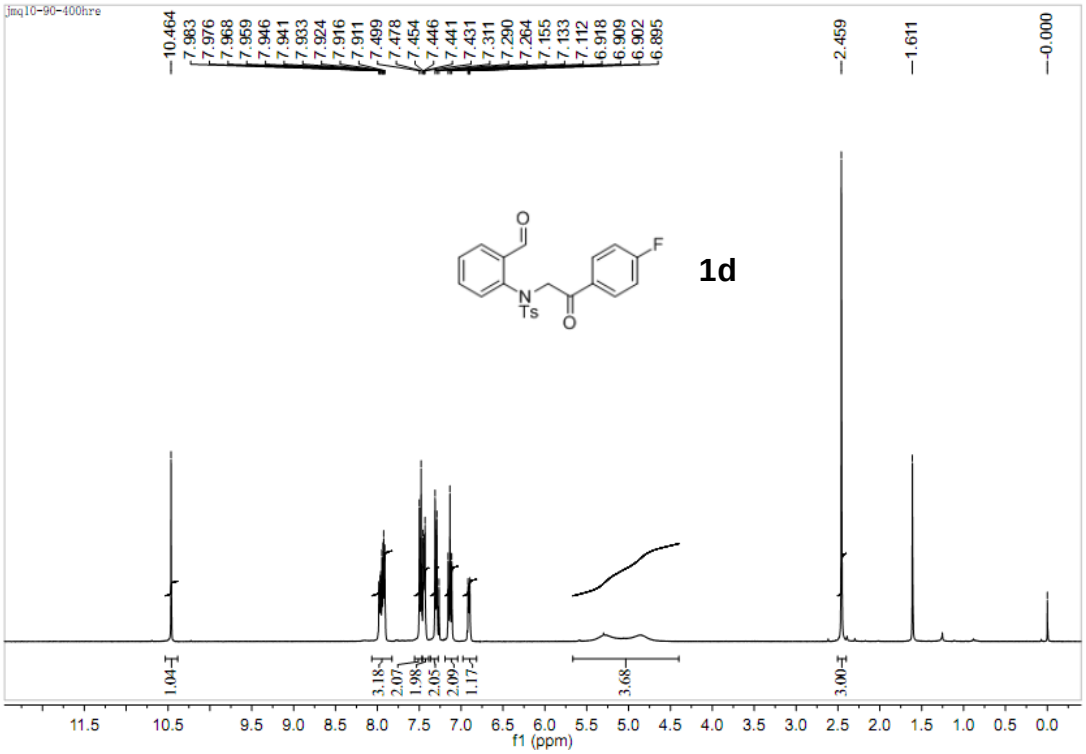
OMe
N
Ts
O
1c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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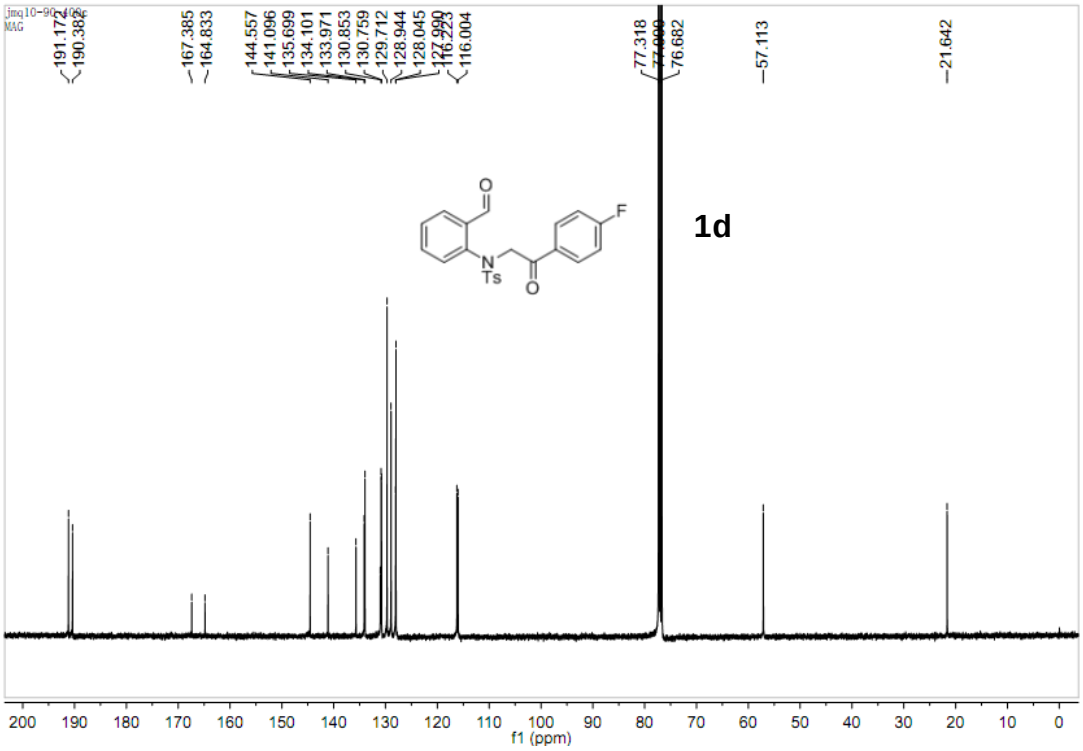
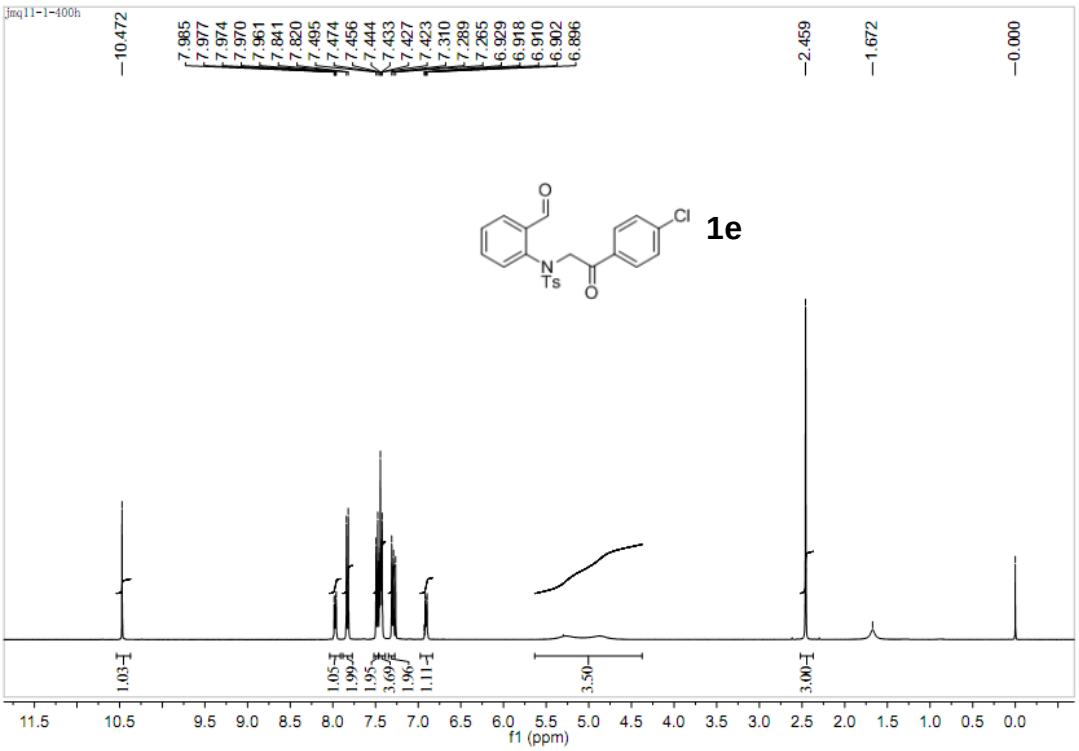
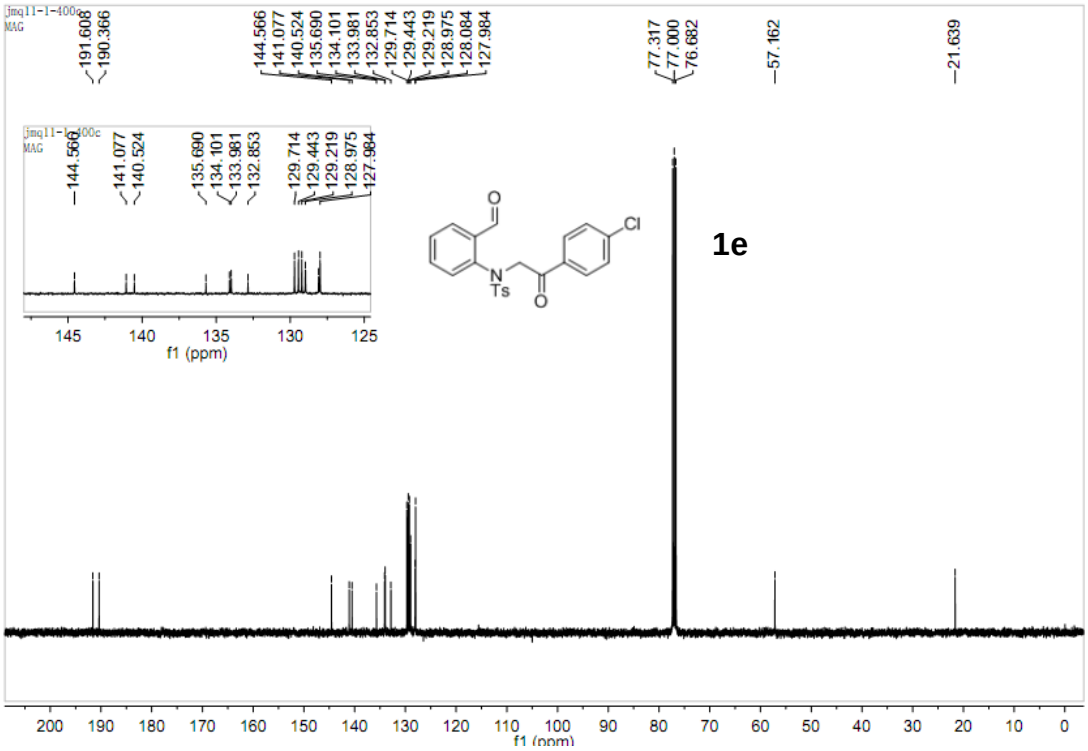
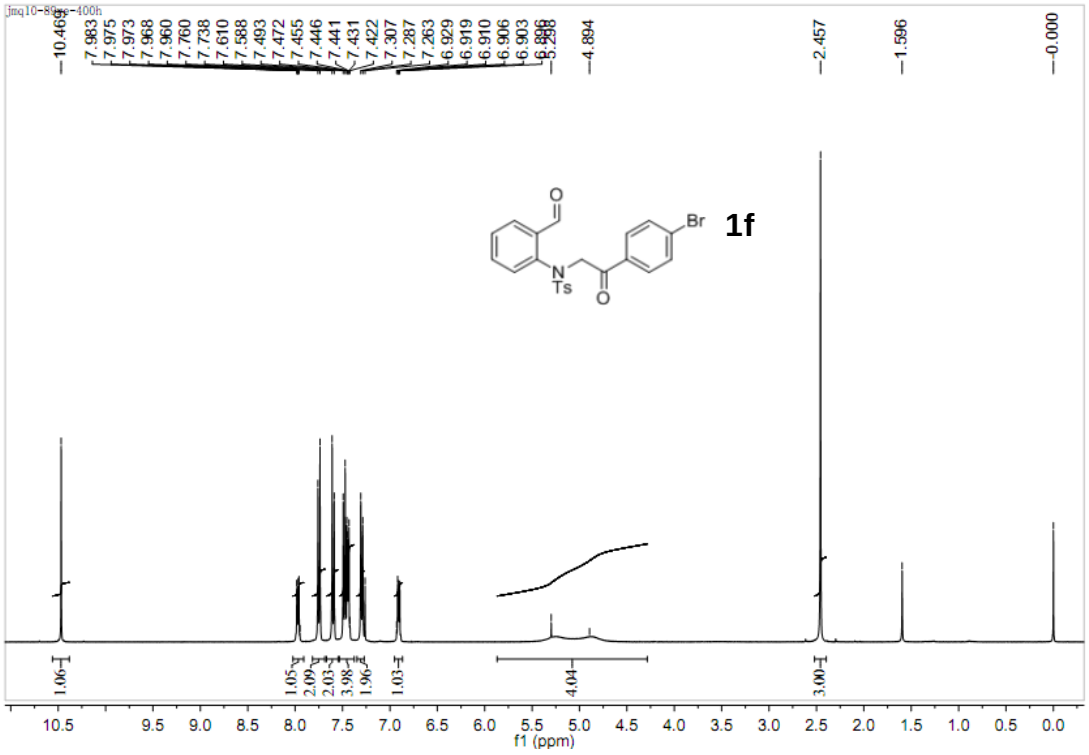
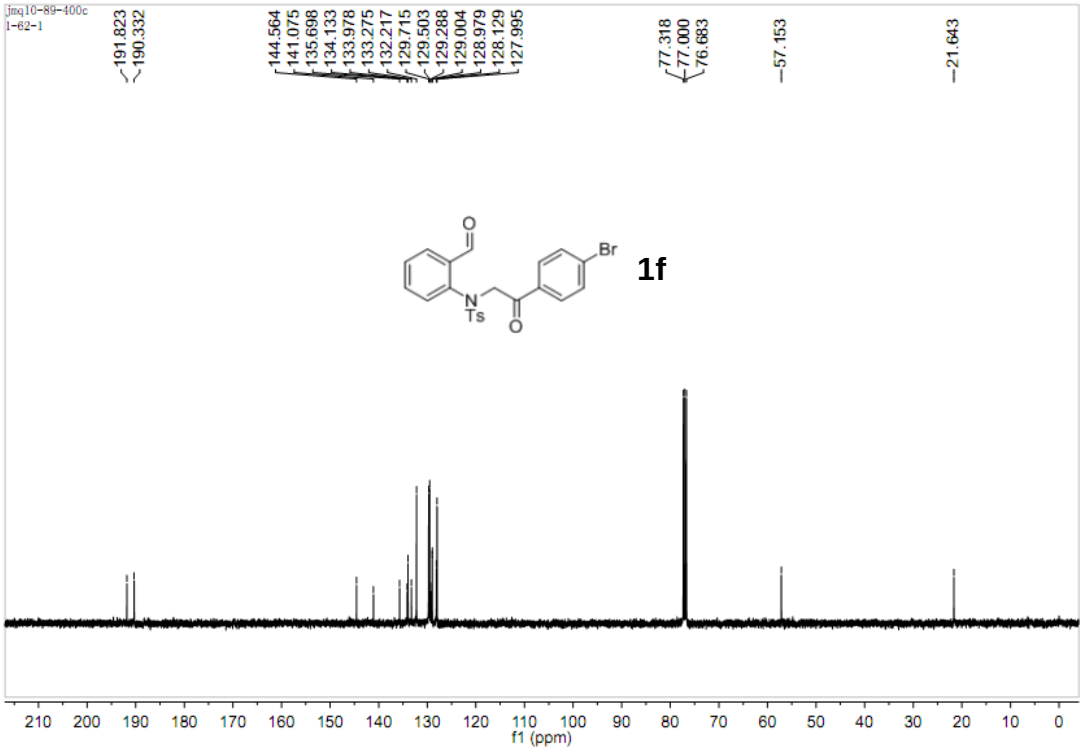
1d
1.04
3.18
2.07
1.98
2.05
2.09
1.17
3.68
3.00
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

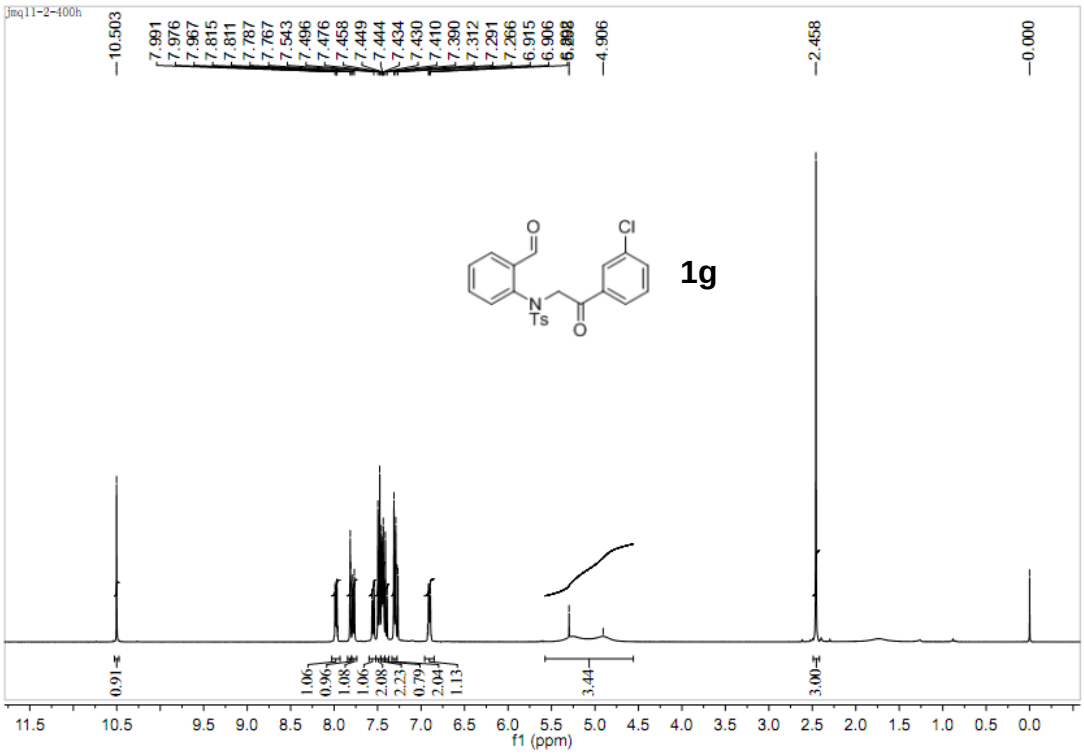

191.174
190.382
167.385
164.833
144.557
141.096
135.699
134.101
133.971
130.853
130.759
129.712
128.944
128.045
116.004
77.318
76.682
57.113
21.642
1d
f1 (ppm)

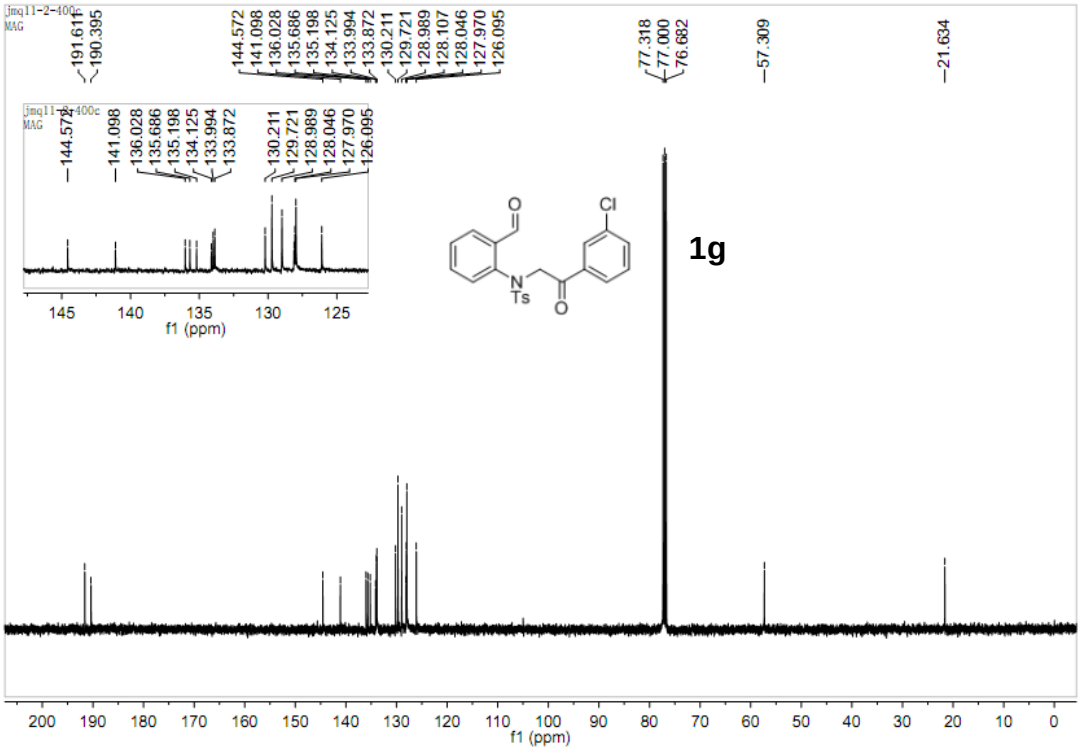

10.472
7.985
7.977
7.974
7.970
7.961
7.841
7.820
7.495
7.474
7.456
7.444
7.433
7.427
7.423
7.310
7.289
7.265
6.929
6.918
6.910
6.902
6.896
2.459
1.672
0.000
1e
1.03
1.05
1.99
1.95
3.69
1.96
1.11
3.50
3.00
f1 (ppm)

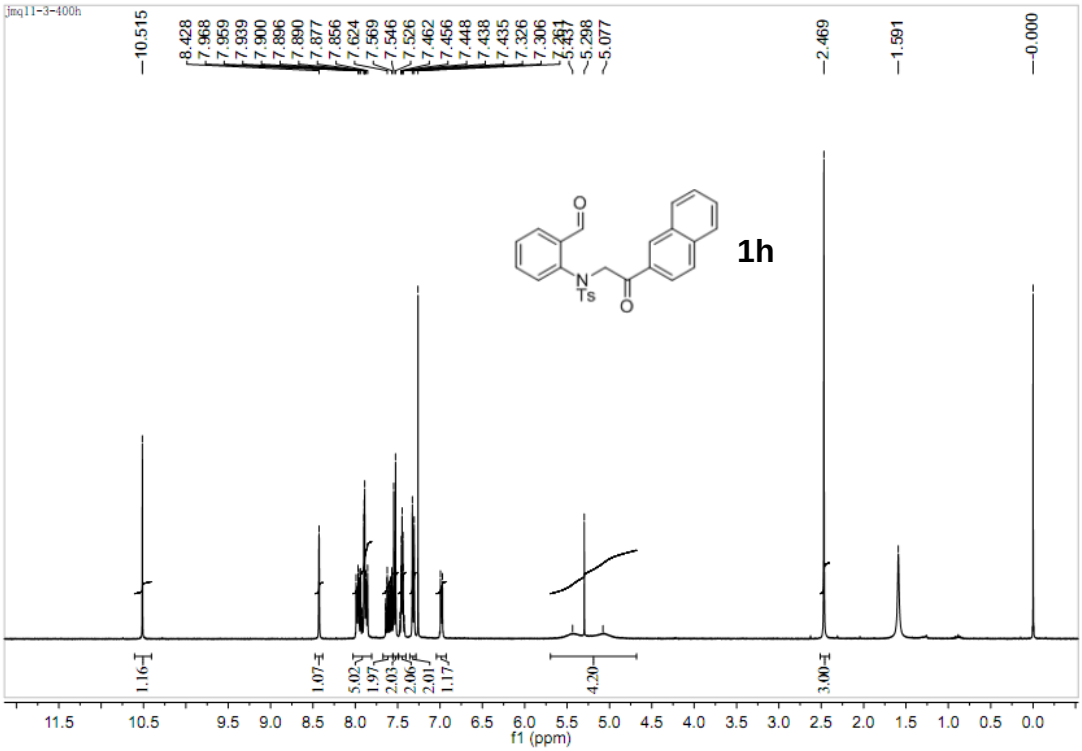

191.608
190.366
144.566
141.077
140.524
135.690
134.101
133.981
132.853
129.714
129.443
129.219
128.975
128.084
127.984
77.317
77.000
76.682
57.162
21.639
1e
f1 (ppm)

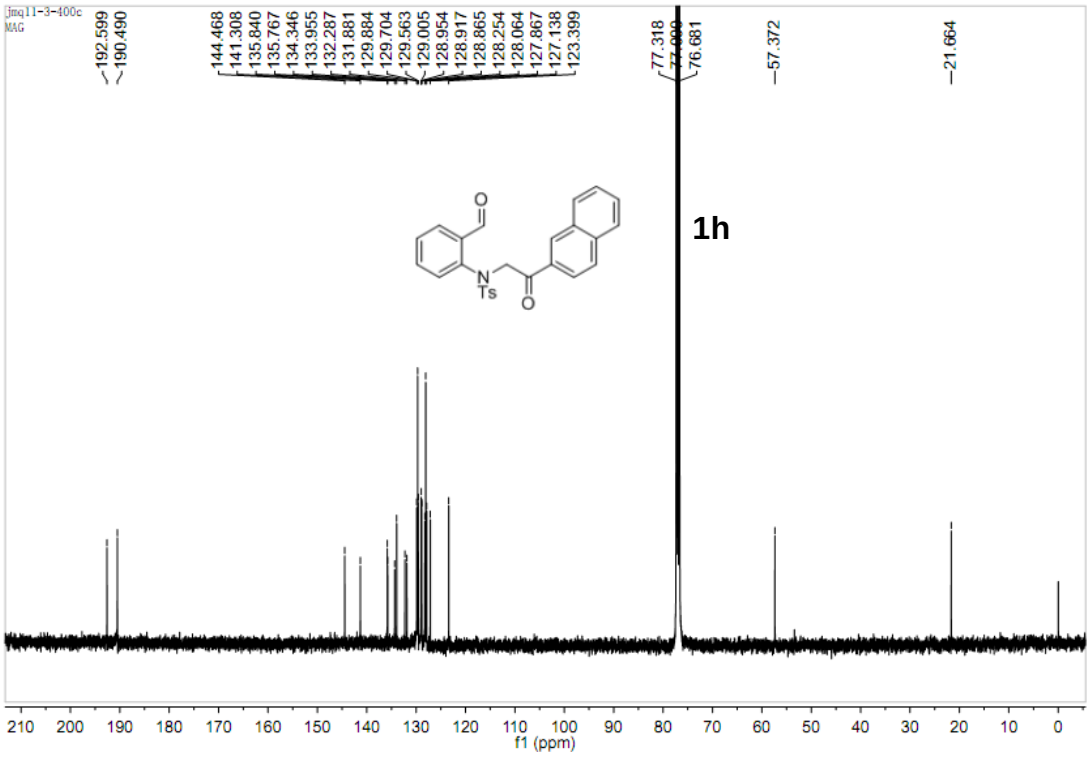

10.469
7.983
7.975
7.973
7.968
7.960
7.760
7.738
7.610
7.588
7.493
7.472
7.455
7.446
7.441
7.431
7.422
7.307
7.287
7.263
6.929
6.919
6.910
6.906
6.903
4.894
2.457
1.596
0.000
1f
f1 (ppm)

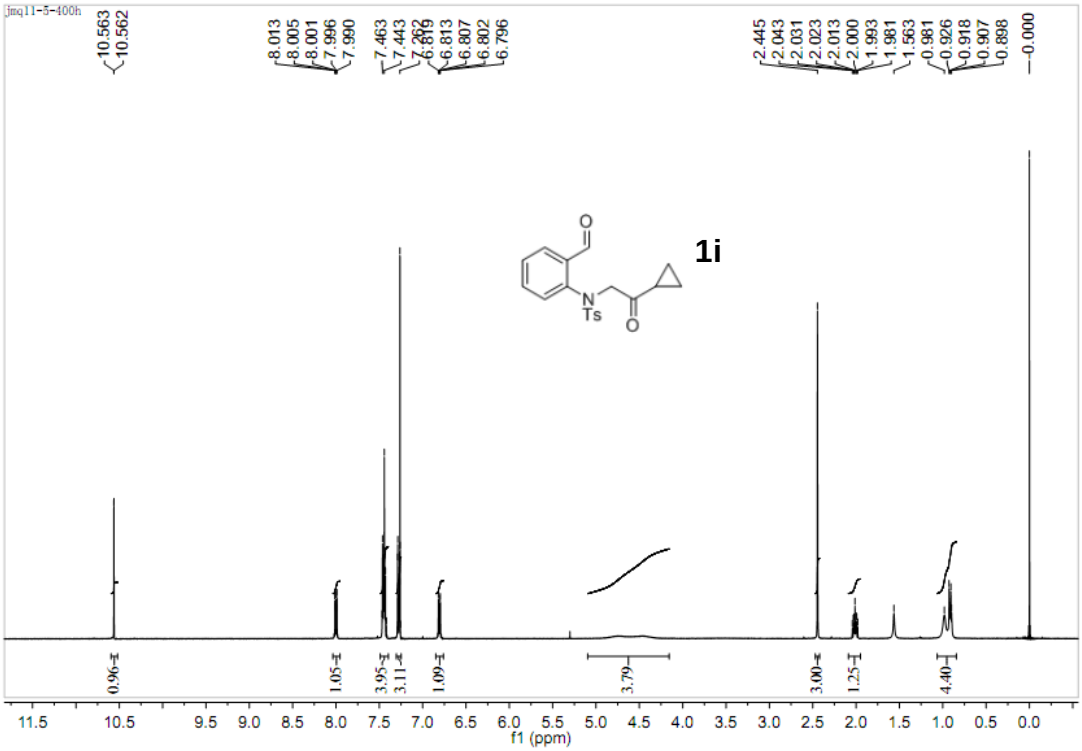

jmq10-89-400c
1-62-1
191.823
190.332
144.564
141.075
135.698
134.133
133.978
133.275
132.217
129.715
129.503
129.288
129.004
128.979
128.129
127.995
77.318
77.000
76.683
57.153
21.643
O
Br
N
Ts
O
1f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

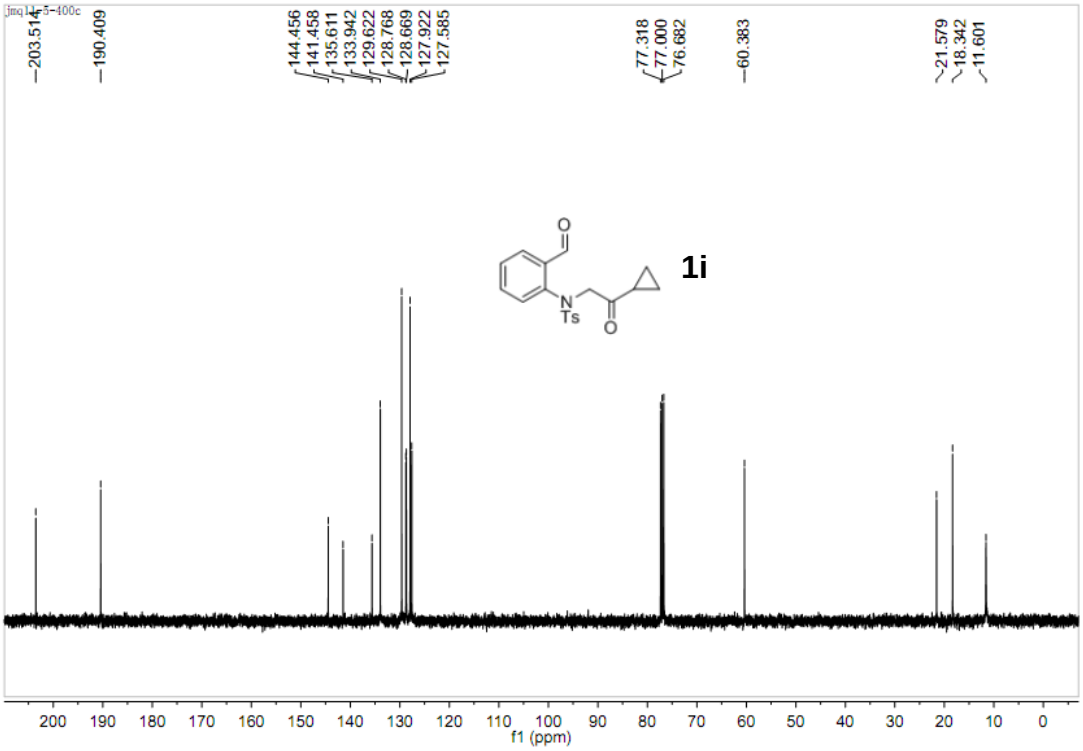

jmq11-2-400h
10.503
7.991
7.976
7.967
7.815
7.811
7.787
7.767
7.543
7.496
7.476
7.458
7.449
7.444
7.434
7.430
7.410
7.390
7.312
7.291
7.266
6.915
6.906
4.906
2.458
0.000
O
Cl
N
Ts
O
1g
0.91
1.06
0.96
1.08
1.06
2.08
2.23
0.79
2.04
1.13
3.44
3.00
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

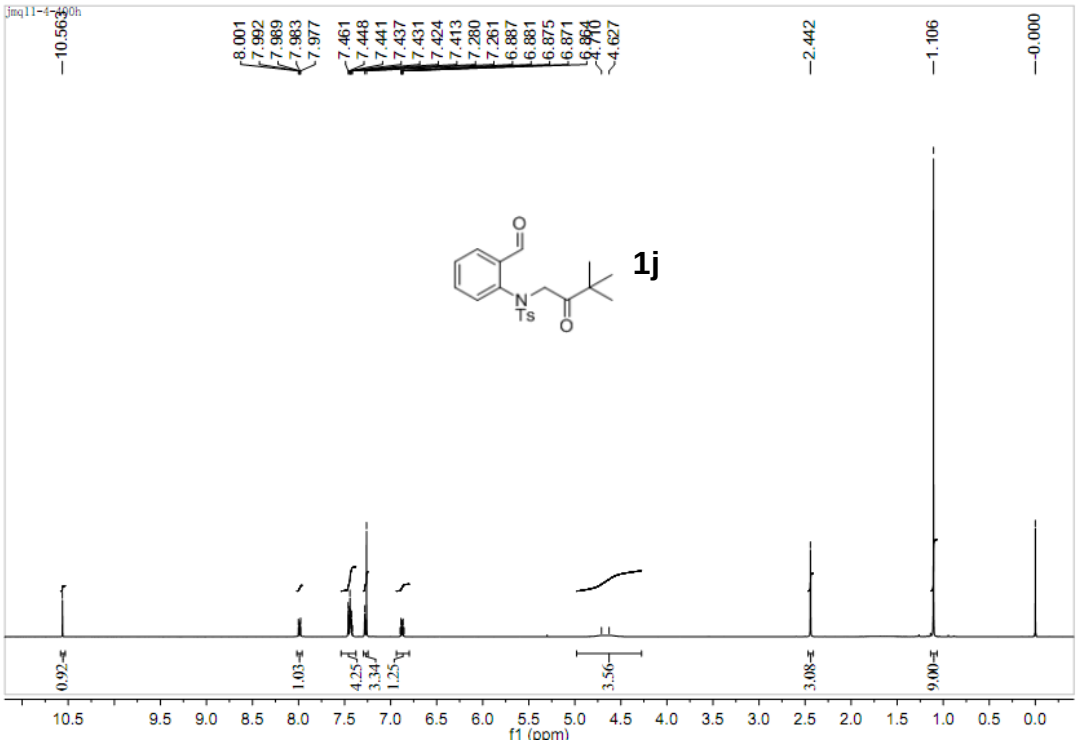

1g
f1 (ppm)

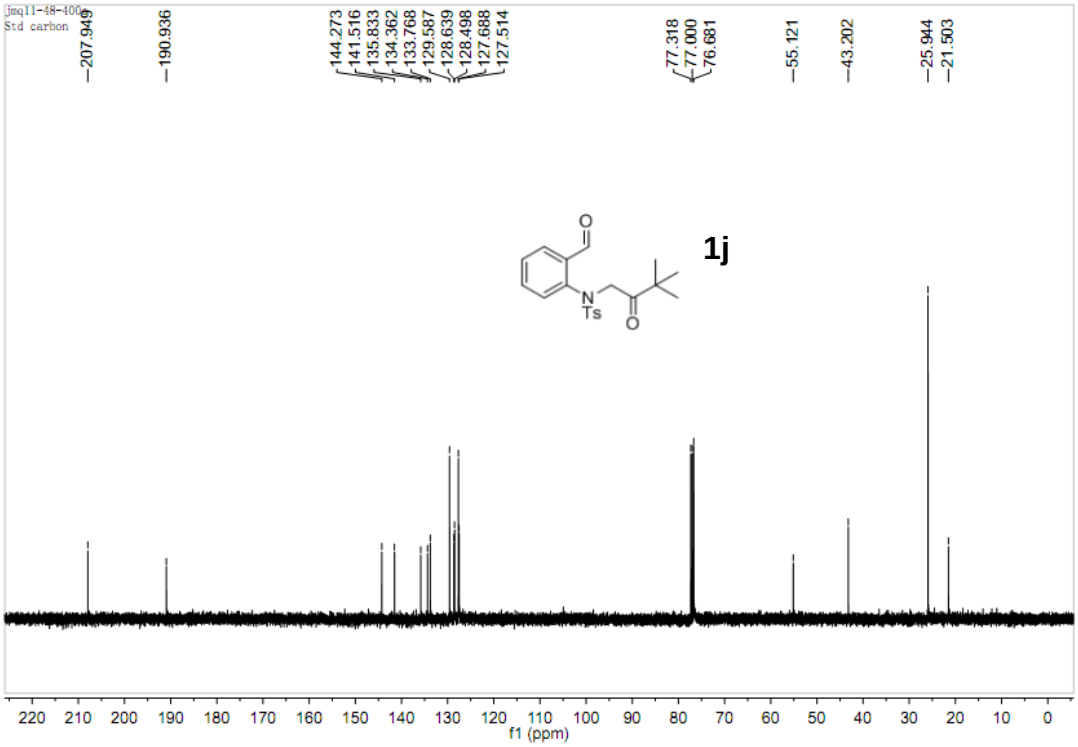

1h
f1 (ppm)

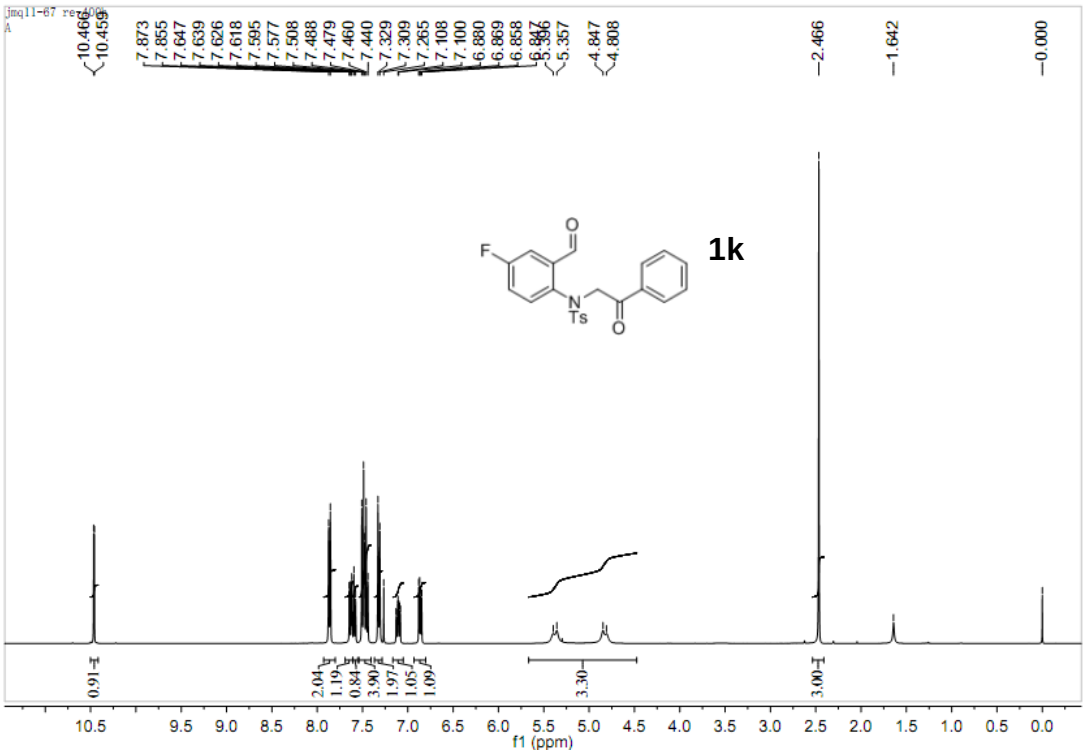

jmq11-3-400c
MAG
192.599
190.490
144.468
141.308
135.840
135.767
134.346
133.955
132.287
131.881
129.884
129.704
129.563
129.005
128.954
128.917
128.865
128.254
128.064
127.867
127.138
123.399
77.318
77.000
76.681
57.372
21.664
1h
f1 (ppm)

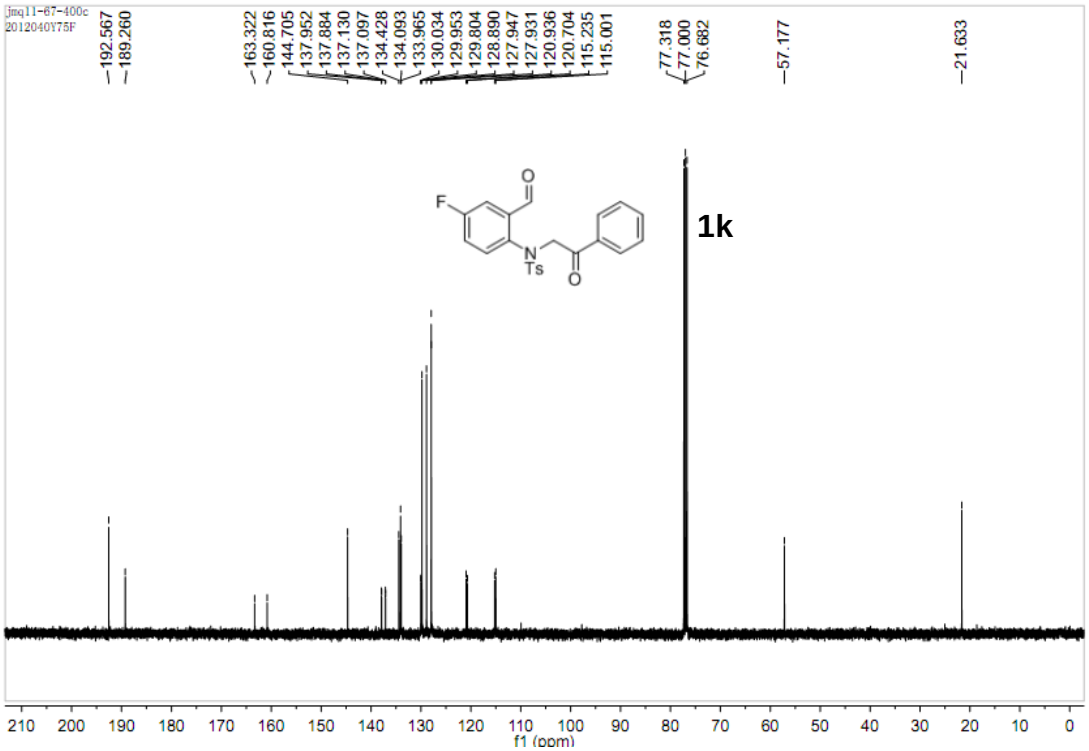

jmq11-5-400h
10.563
10.562
8.013
8.005
8.001
7.996
7.990
7.463
7.443
7.262
6.819
6.813
6.807
6.802
6.796
2.445
2.043
2.031
2.023
2.013
2.000
1.993
1.981
1.563
0.981
0.926
0.918
0.907
0.898
0.000
1i
0.96
1.05
3.95
3.11
1.09
3.79
3.00
1.25
4.40
f1 (ppm)

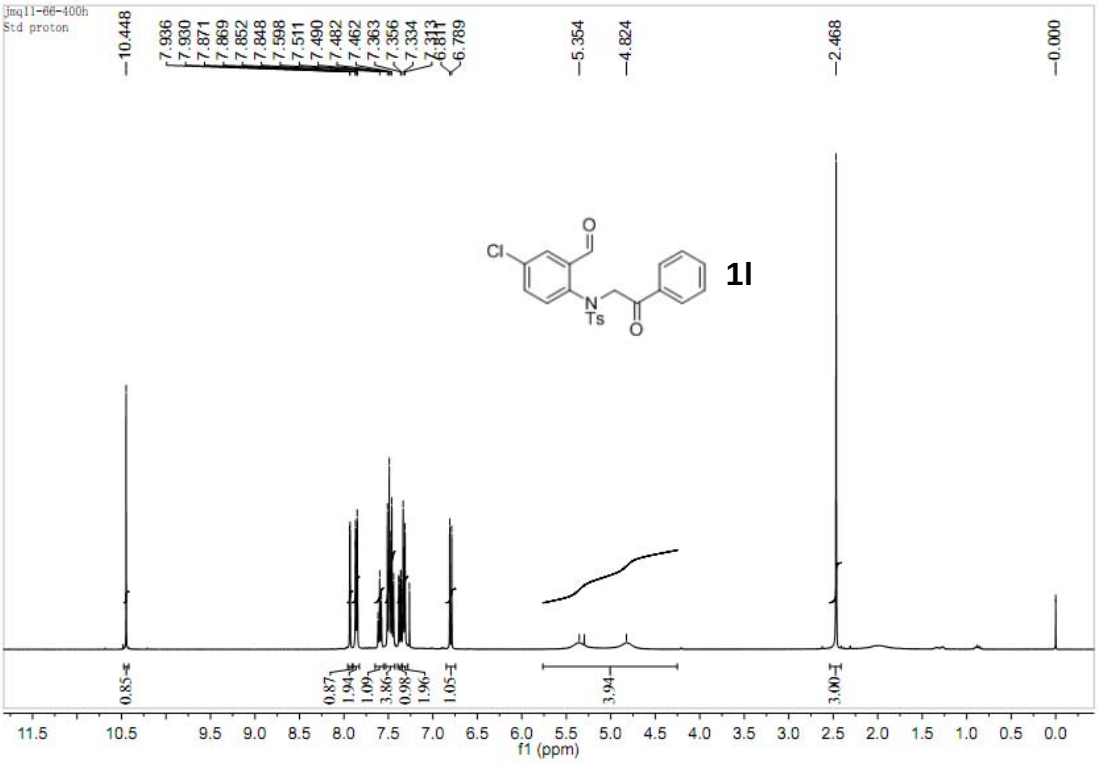

203.514
190.409
144.456
141.458
135.611
133.942
129.622
128.768
128.669
127.922
127.585
77.318
77.000
76.682
60.383
21.579
18.342
11.601
1i
f1 (ppm)

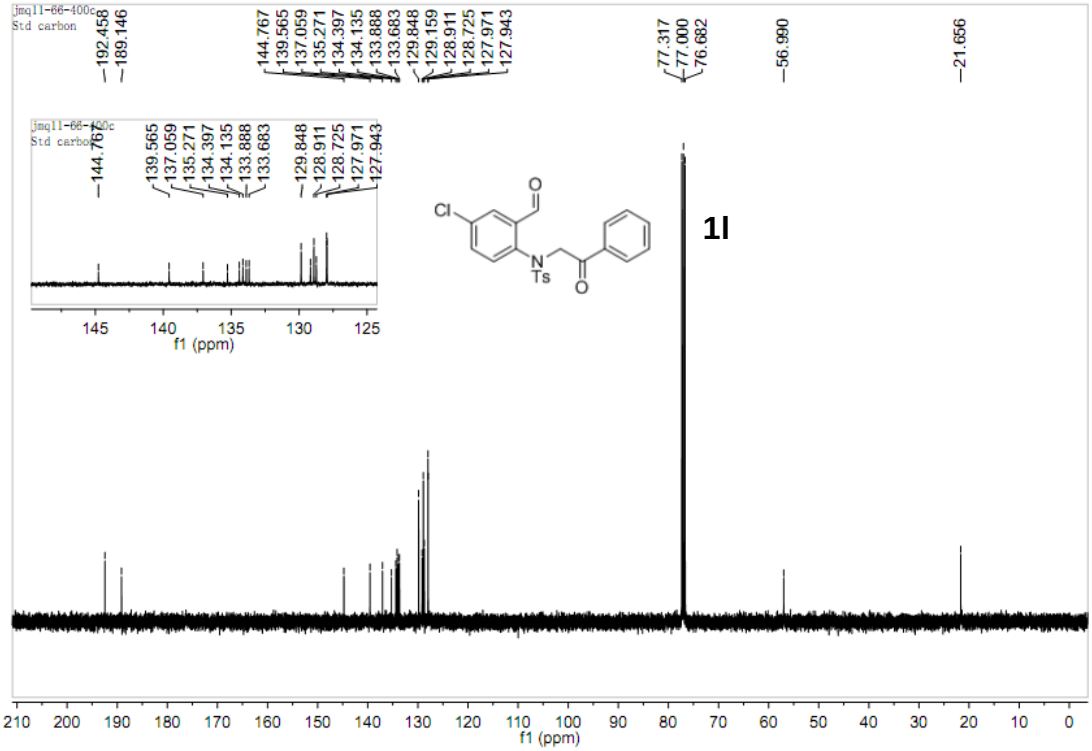

10.563
8.001
7.992
7.989
7.983
7.977
7.461
7.448
7.441
7.437
7.431
7.424
7.413
7.280
7.261
6.887
6.881
6.875
6.871
4.627
2.442
1.106
0.000
1j
0.92
1.03
4.25
3.34
1.25
3.56
3.08
9.00
f1 (ppm)

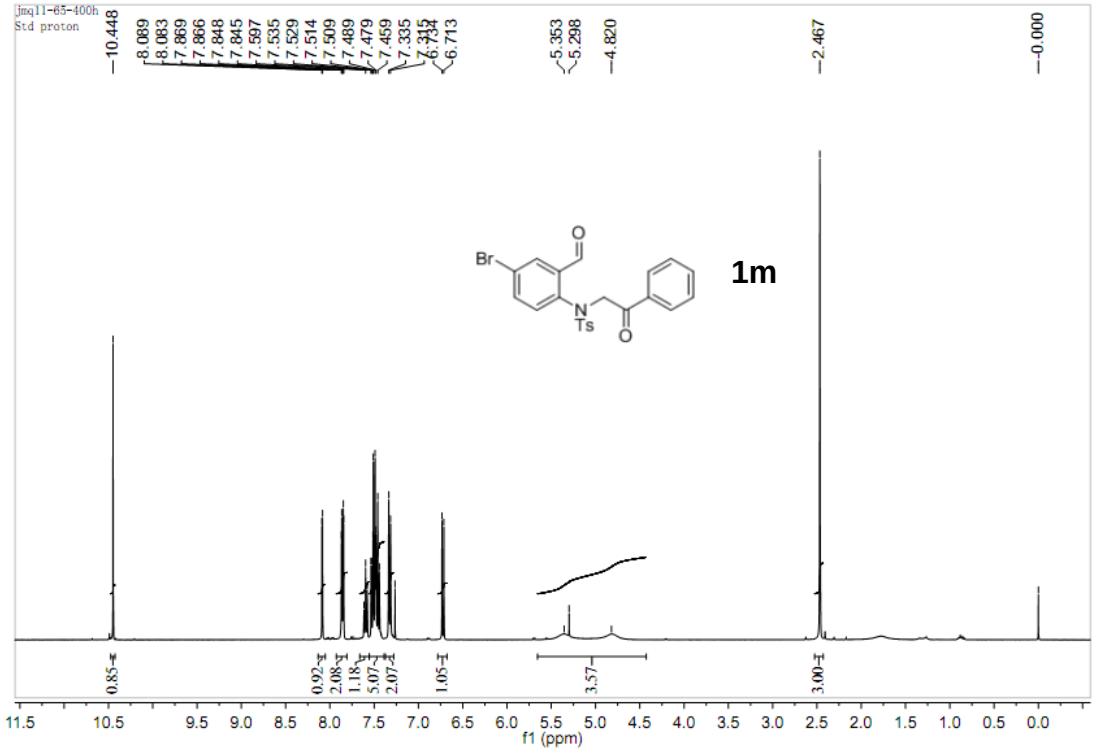

jmq11-48-400
Std carbon
207.949
190.936
144.273
141.516
135.833
134.362
133.768
129.587
128.639
128.498
127.688
127.514
77.318
77.000
76.681
55.121
43.202
25.944
21.503
1j
f1 (ppm)

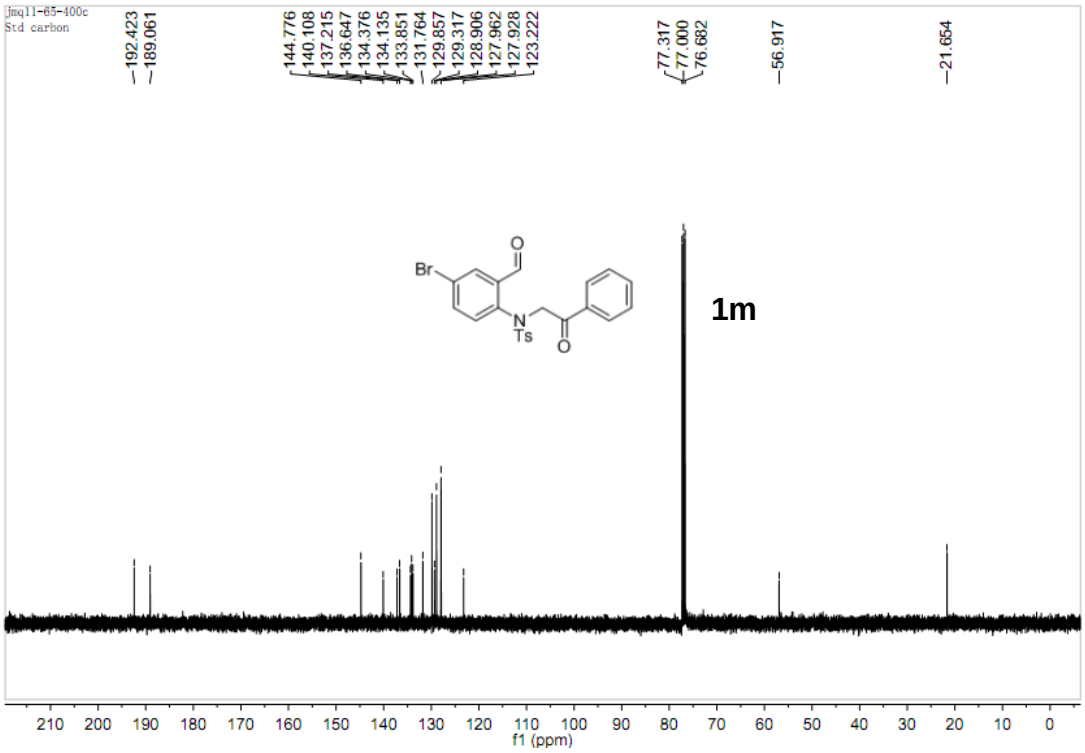

10.466
10.459
7.873
7.855
7.647
7.639
7.626
7.618
7.595
7.577
7.508
7.488
7.479
7.460
7.440
7.329
7.309
7.265
7.108
7.100
6.880
6.869
6.858
5.357
4.847
4.808
2.466
1.642
0.000
1k
0.91
2.04
1.19
0.84
3.90
1.97
1.05
1.09
3.30
3.00
f1 (ppm)

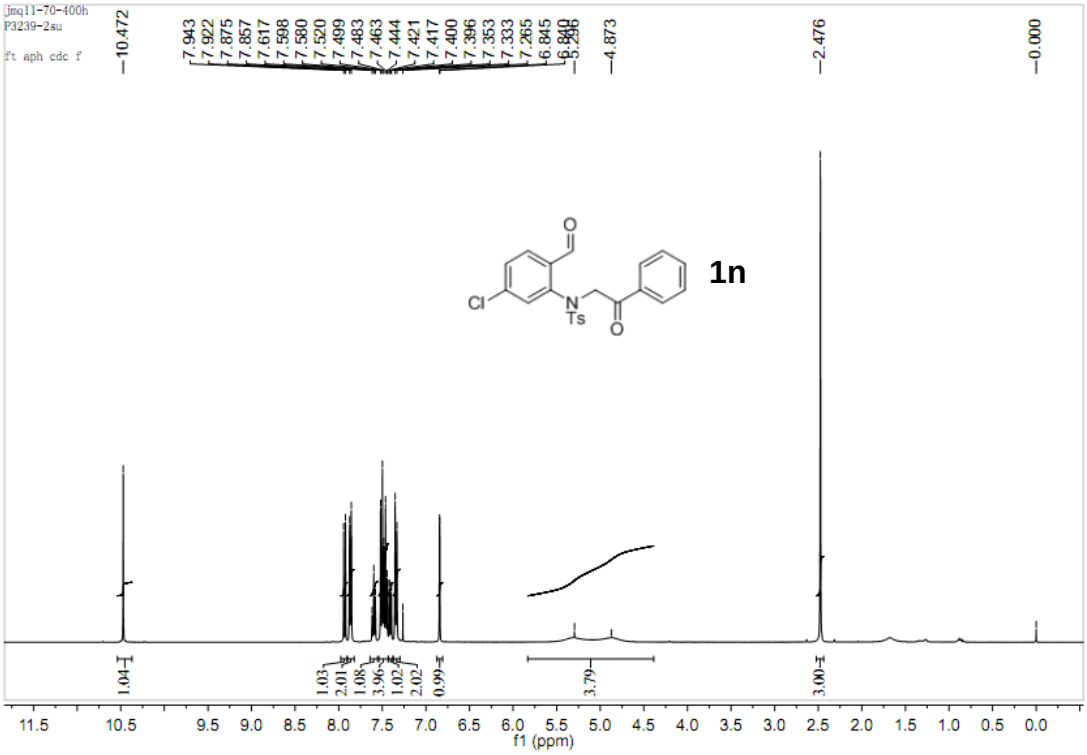

jmq11-67-400c
2012040Y75F
192.567
189.260
163.322
160.816
144.705
137.952
137.884
137.130
137.097
134.428
134.093
133.965
130.034
129.953
129.804
128.890
127.947
127.931
120.936
120.704
115.235
115.001
77.318
77.000
76.682
57.177
21.633
1k
f1 (ppm)

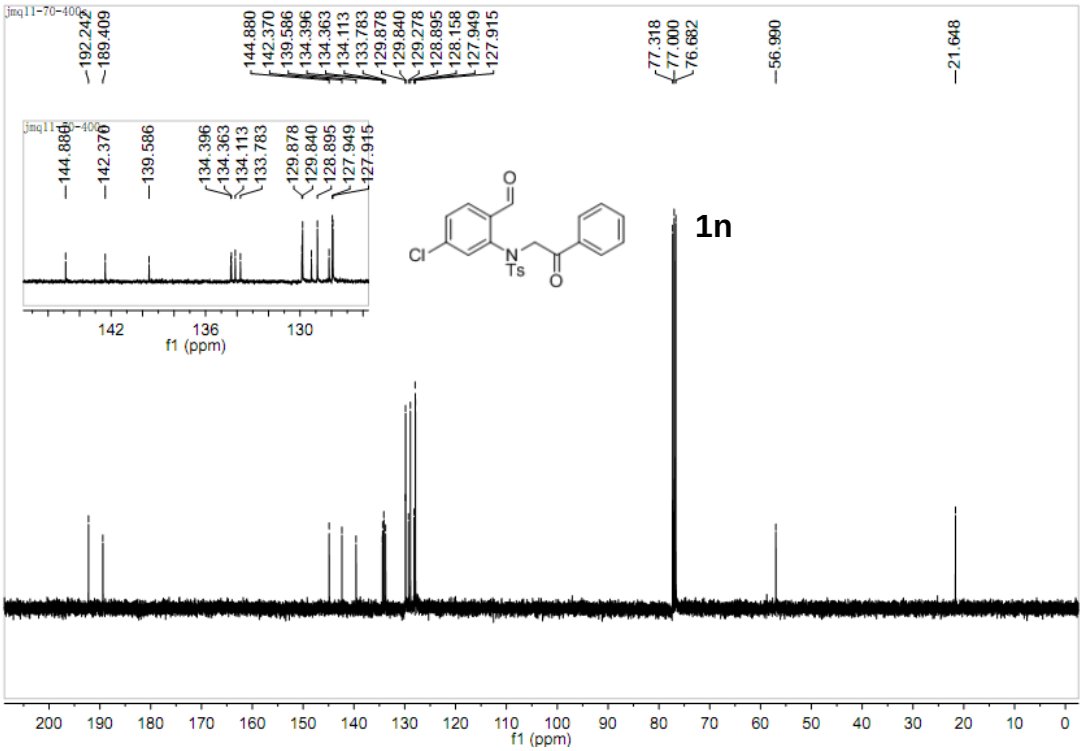

jmq11-66-400h
Std proton
10.448
7.936
7.930
7.871
7.869
7.852
7.848
7.598
7.511
7.490
7.482
7.462
7.363
7.356
7.334
6.789
5.354
4.824
2.468
0.000
1l
f1 (ppm)

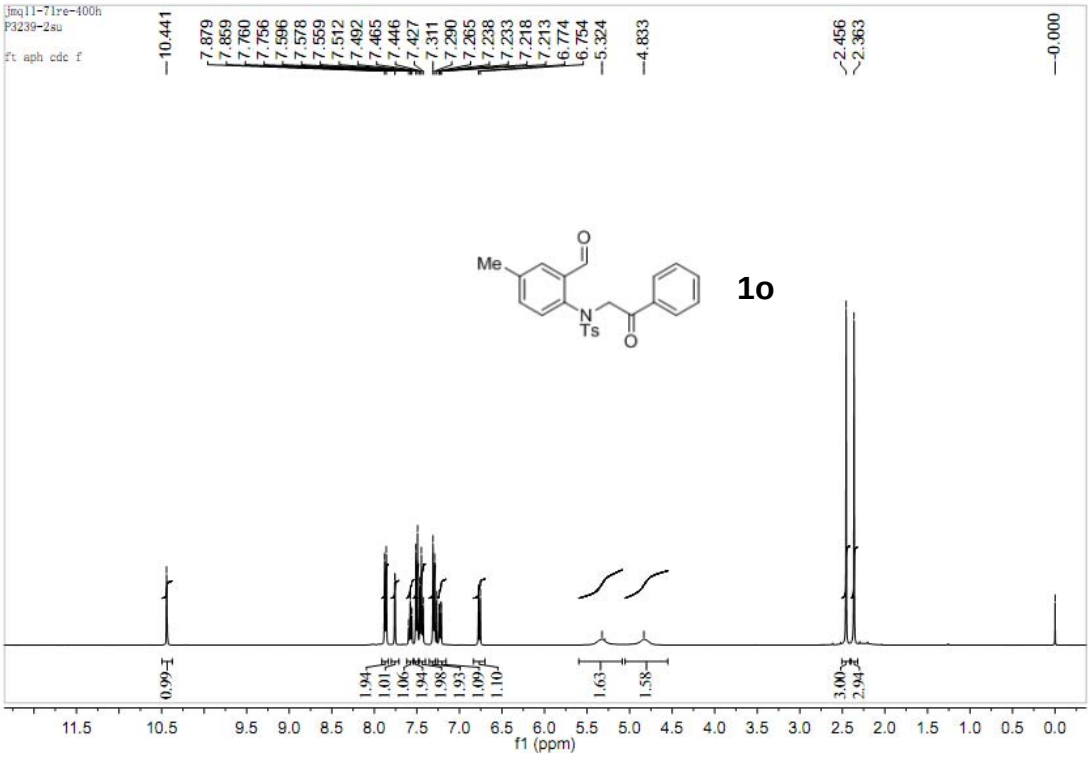

jmq11-66-400c
Std carbon
192.458
189.146
144.767
139.565
137.059
135.271
134.397
134.135
133.888
133.683
129.848
129.159
128.911
128.725
127.971
127.943
77.317
77.000
76.682
56.990
21.656
Cl
O
N
Ts
O
1l
f1 (ppm)

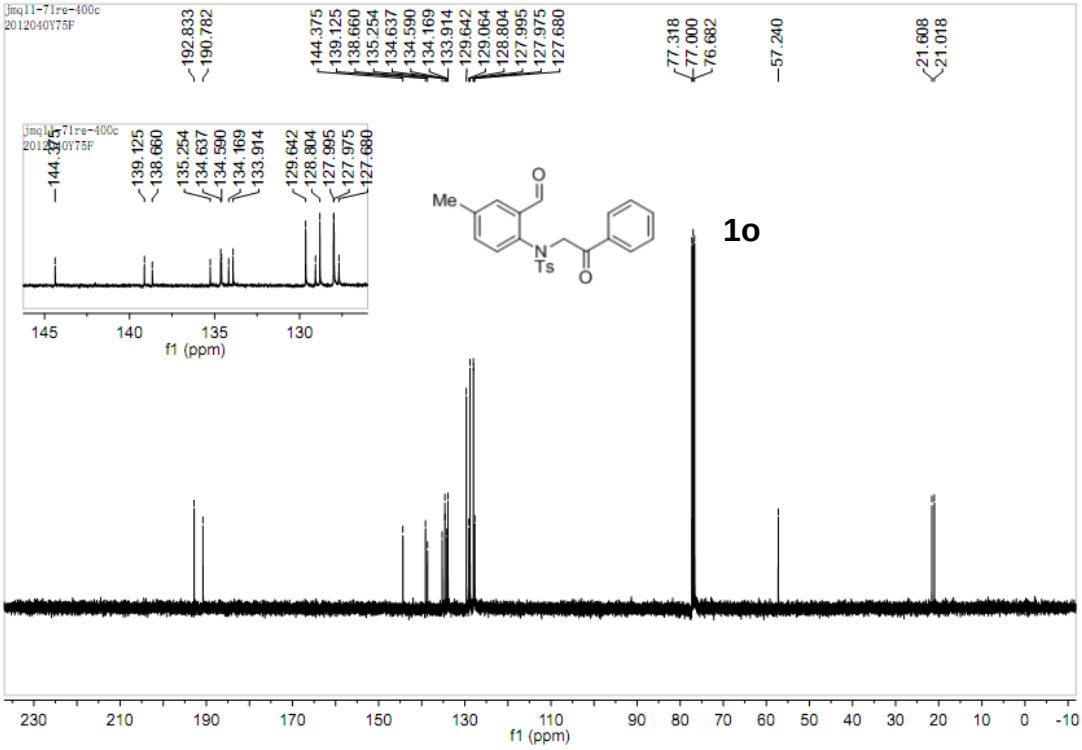

jmq11-65-400h
Std proton
10.448
8.089
8.083
7.869
7.866
7.848
7.845
7.597
7.535
7.529
7.514
7.509
7.489
7.479
7.459
7.335
6.734
6.713
5.353
5.298
4.820
2.467
0.000
Br
O
N
Ts
O
1m
0.85
0.92
2.08
1.18
5.07
2.07
1.05
3.57
3.00
f1 (ppm)

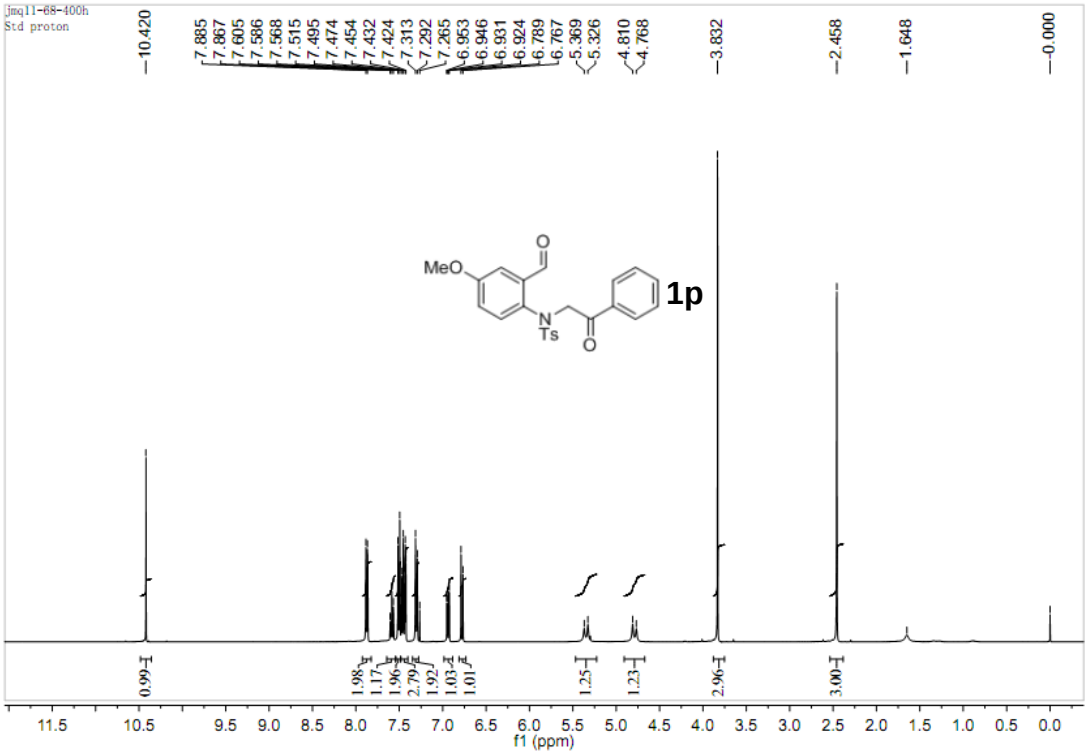

jmq11-65-400c
Std carbon
192.423
189.061
144.776
140.108
137.215
136.647
134.376
134.135
133.851
131.764
129.857
129.317
128.906
127.962
127.928
123.222
77.317
77.000
76.682
56.917
21.654
Br
O
N
Ts
O
1m
f1 (ppm)

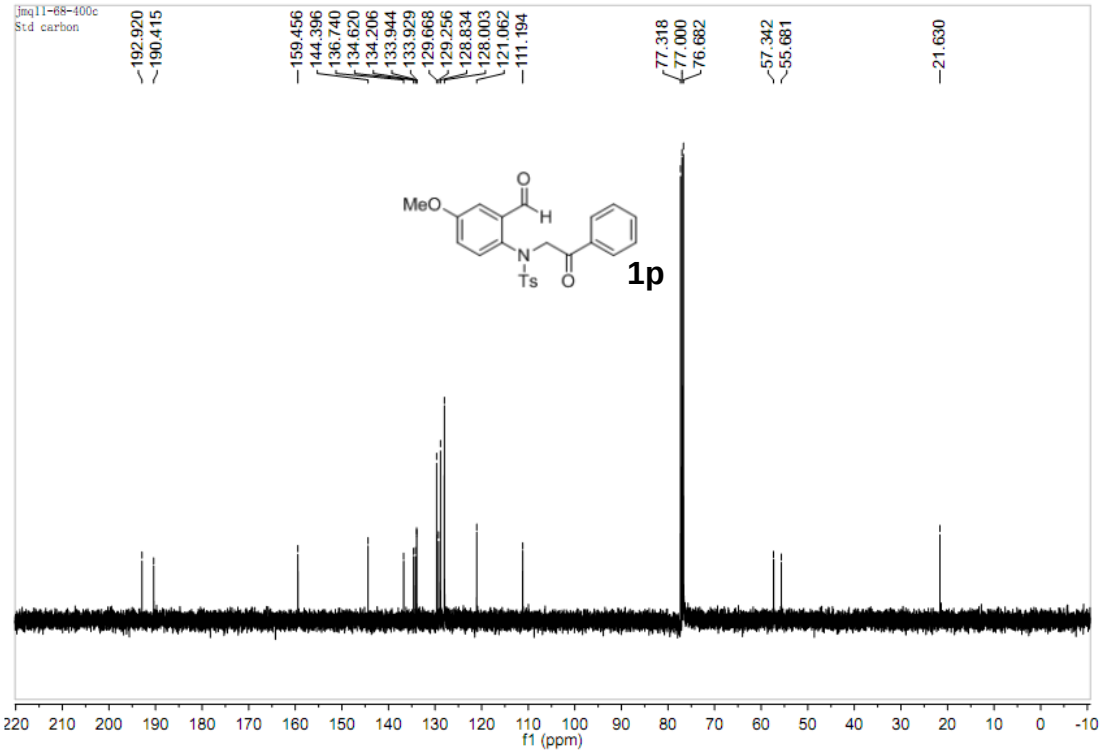

jmq11-70-400h
P3239-2su
ft aph cdc f
10.472
7.943
7.922
7.875
7.857
7.617
7.598
7.580
7.520
7.499
7.483
7.463
7.444
7.421
7.417
7.400
7.396
7.353
7.333
7.265
6.845
4.873
2.476
0.000
Cl
O
N
Ts
O
1n
1.04
1.03
2.01
1.08
3.96
1.02
2.02
0.99
3.79
3.00
f1 (ppm)

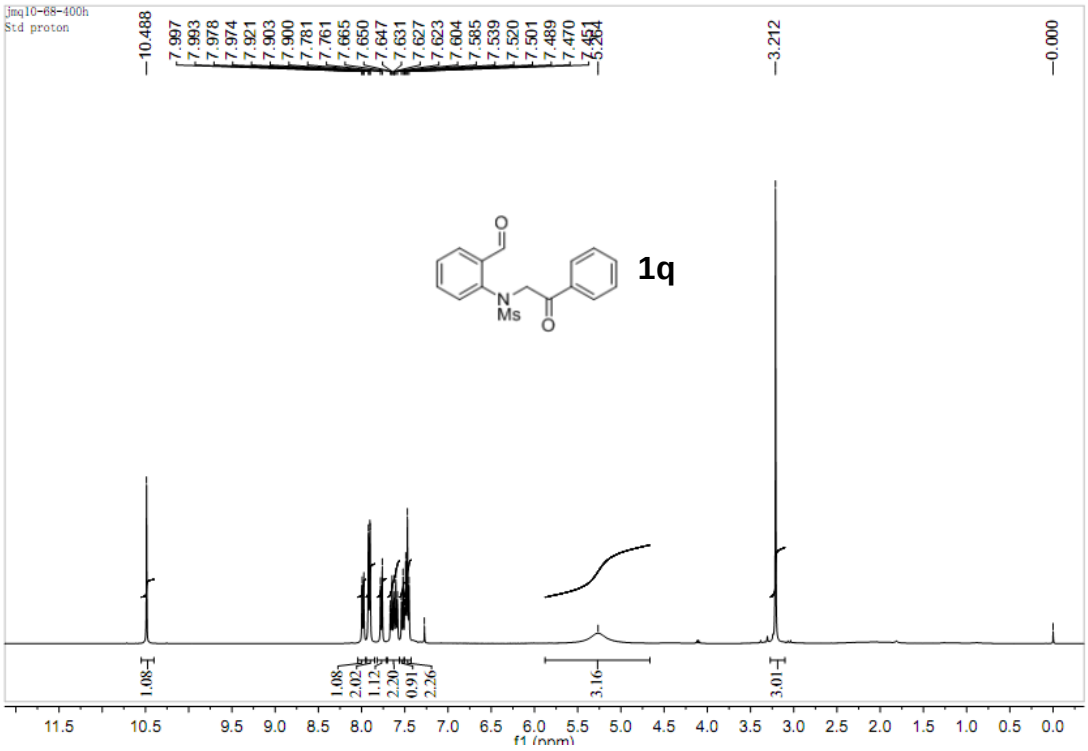

192.242
189.409
144.880
142.370
139.586
134.396
134.363
134.113
133.783
129.878
129.840
129.278
128.895
128.158
127.949
127.915
77.318
77.000
76.682
56.990
21.648
1n
Cl
N
Ts
O
f1 (ppm)

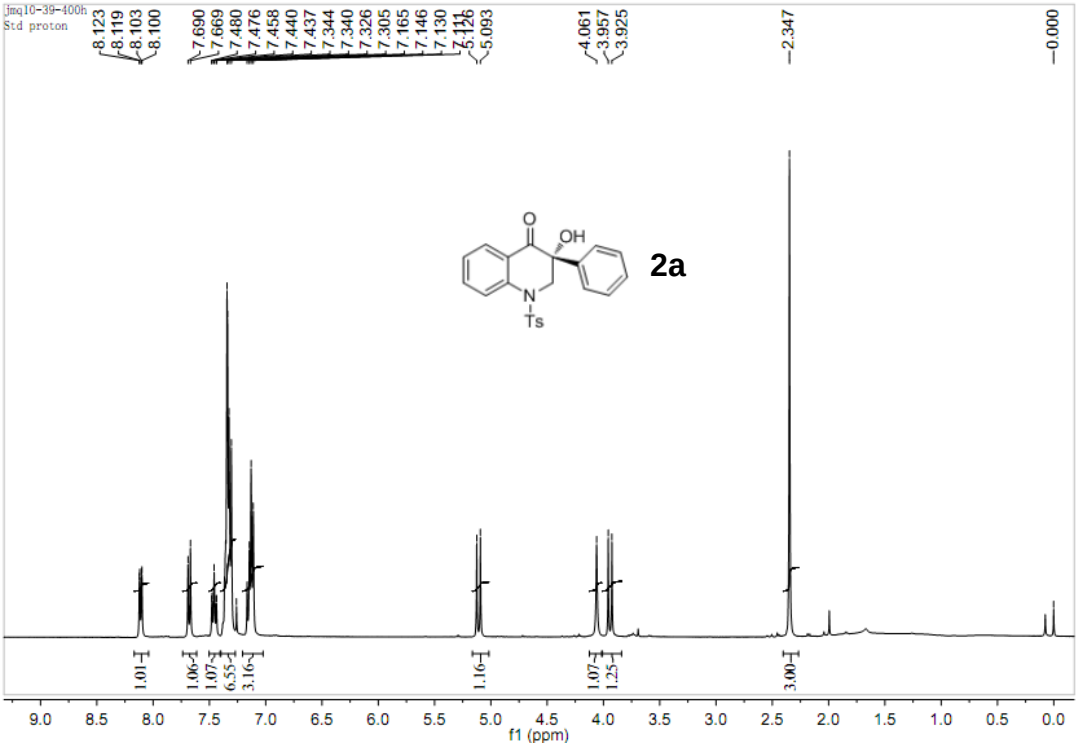

10.441
7.879
7.859
7.760
7.756
7.596
7.578
7.559
7.512
7.492
7.465
7.446
7.427
7.311
7.290
7.265
7.238
7.233
7.218
7.213
6.774
6.754
5.324
4.833
2.456
2.363
0.000
1o
Me
N
Ts
O
0.99
1.94
1.01
1.06
1.94
1.98
1.93
1.09
1.10
1.63
1.58
3.00
2.94
f1 (ppm)

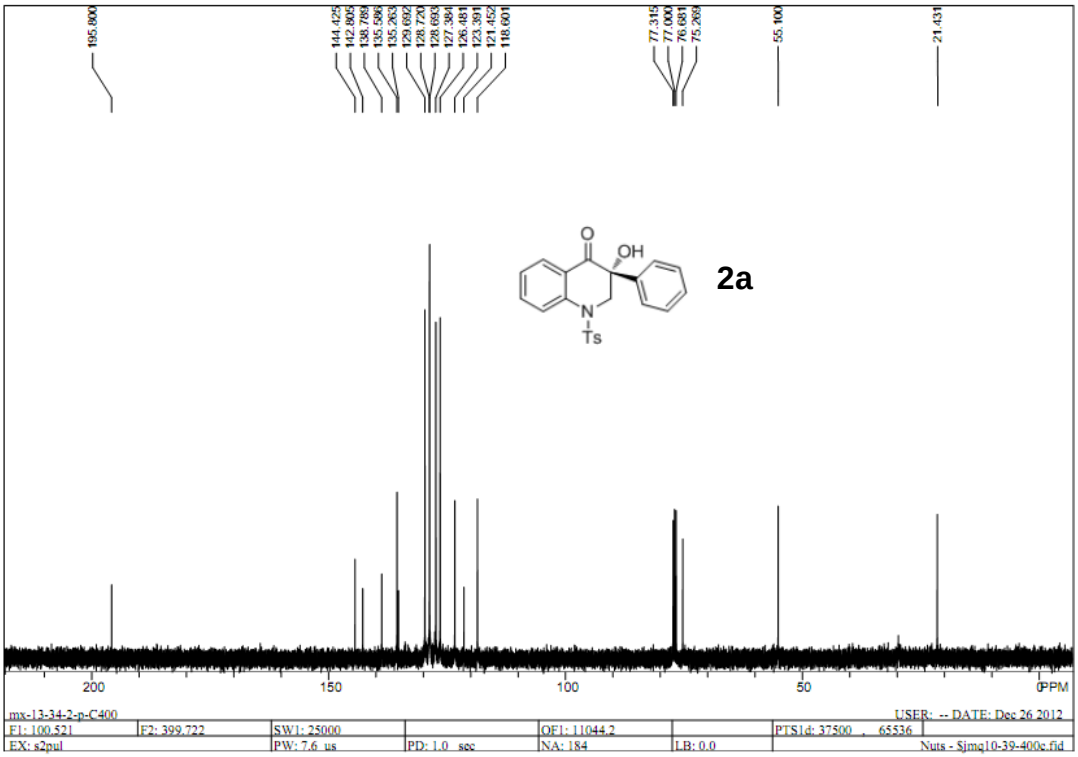

jmq11-71re-400c
2012040Y75F
192.833
190.782
144.375
139.125
138.660
135.254
134.637
134.590
134.169
133.914
129.642
129.064
128.804
127.995
127.975
127.680
77.318
77.000
76.682
57.240
21.608
21.018
Me
O
N
Ts
O
1o
f1 (ppm)

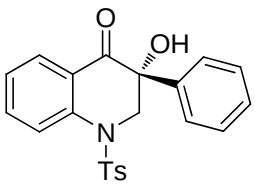

jmq11-68-400h
Std proton
10.420
7.885
7.867
7.605
7.586
7.568
7.515
7.495
7.474
7.454
7.432
7.424
7.313
7.292
7.265
6.953
6.946
6.931
6.924
6.789
6.767
5.369
5.326
4.810
4.768
3.832
2.458
1.648
0.000
MeO
O
N
Ts
O
1p
0.99
1.98
1.17
1.96
2.79
1.92
1.03
1.01
1.25
1.23
2.96
3.00
f1 (ppm)


jmq11-68-400c
Std carbon
192.920
190.415
159.456
144.396
136.740
134.620
134.206
133.944
133.929
129.668
129.256
128.834
128.003
121.062
111.194
77.318
77.000
76.682
57.342
55.681
21.630
MeO
O
H
N
Ts
O
1p
f1 (ppm)

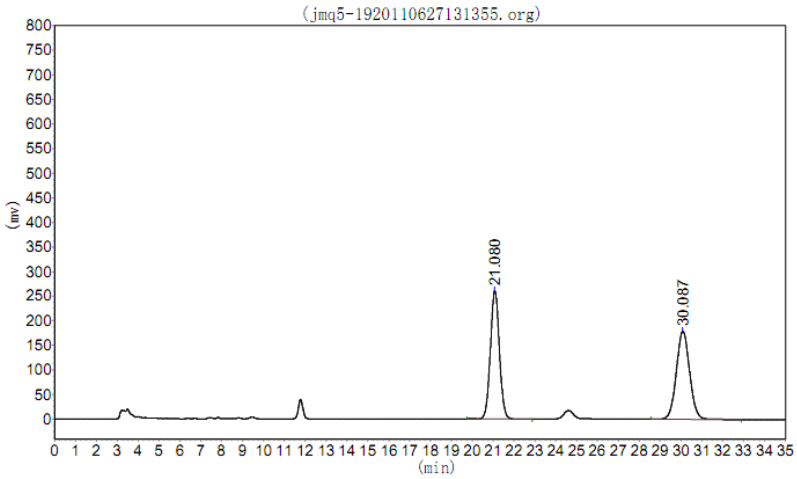

jmq10-68-400h
Std proton
10.488
7.997
7.993
7.978
7.974
7.921
7.903
7.900
7.781
7.761
7.665
7.650
7.647
7.631
7.627
7.623
7.604
7.585
7.539
7.520
7.501
7.489
7.470
7.451
5.264
3.212
0.000
O
N
Ms
O
1q
1.08
1.08
2.02
1.12
2.20
0.91
2.26
3.16
3.01
f1 (ppm)


jmq10-39-400h
Std proton
8.123
8.119
8.103
8.100
7.690
7.669
7.480
7.476
7.458
7.440
7.437
7.344
7.340
7.326
7.305
7.165
7.146
7.130
7.111
5.126
5.093
4.061
3.957
3.925
2.347
0.000
1.01
1.06
1.07
6.55
3.16
1.16
1.07
1.25
3.00
O
OH
N
Ts
2a
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

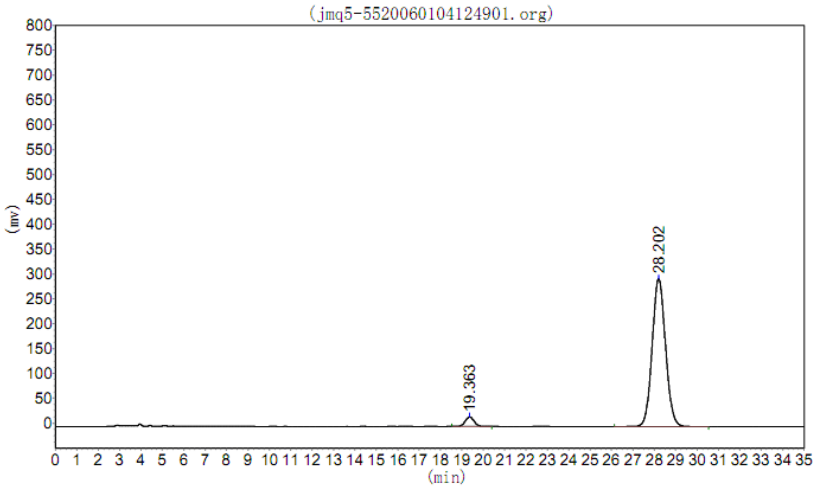

195.800
144.425
142.805
138.789
135.586
135.263
129.692
128.720
128.693
127.384
126.481
123.391
121.452
118.601
77.315
77.000
76.681
75.269
55.100
21.431
O
OH
N
Ts
2a
200
150
100
50
0
PPM
mx-13-34-2-p-C400
USER: -- DATE: Dec 26 2012
F1: 100.521
F2: 399.722
SW1: 25000
OF1: 11044.2
PTS1d: 37500 , 65536
EX: s2pul
PW: 7.6 us
PD: 1.0 sec
NA: 184
LB: 0.0
Nuts - Sjmq10-39-400c.fid



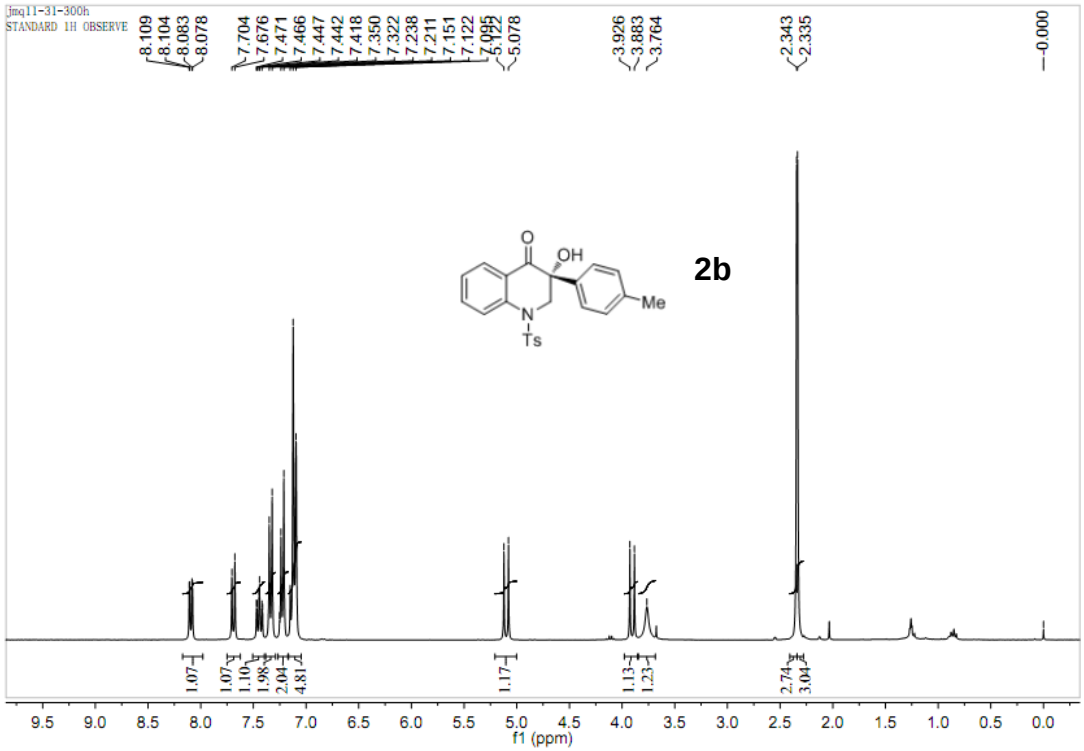
2a

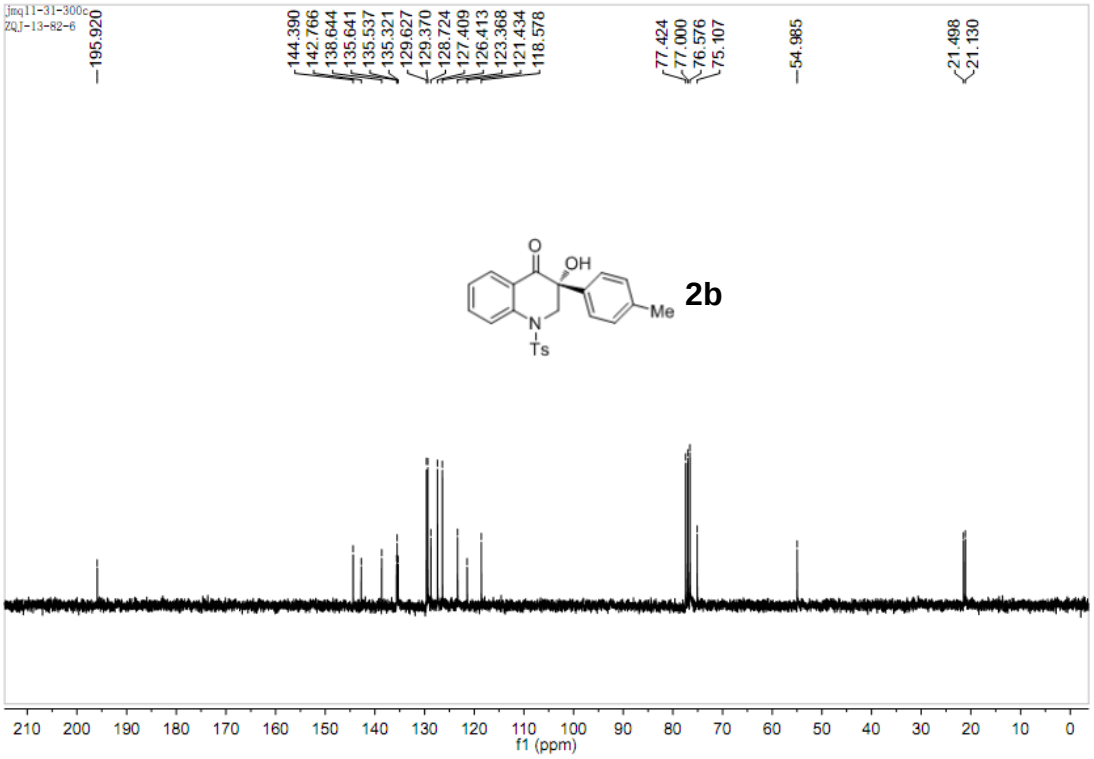


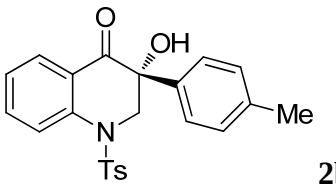
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	21.080	261277.297	7838713.500	49.7824
2	30.087	179244.422	7907245.500	50.2176
Total		440521.719	15745959.000	100.0000



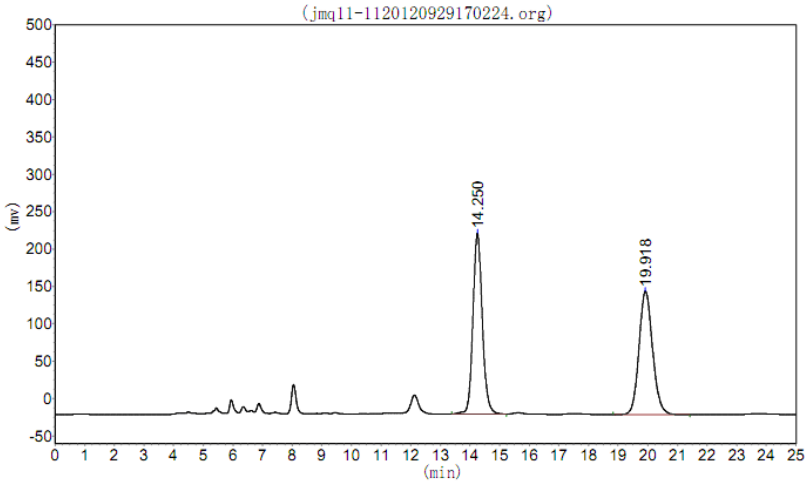
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	19.363	19304.674	544967.000	4.0440
2	28.202	297205.594	12931070.000	95.9560
Total		316510.268	13476037.000	100.0000


jmq11-31-300h
STANDARD 1H OBSERVE
8.109
8.104
8.083
8.078
7.704
7.676
7.471
7.466
7.447
7.442
7.418
7.350
7.322
7.238
7.211
7.151
7.122
7.095
5.122
5.078
3.926
3.883
3.764
2.343
2.335
0.000
1.07
1.07
1.10
1.98
2.04
4.81
1.17
1.13
1.23
2.74
3.04
O
OH
Me
N
Ts
2b
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

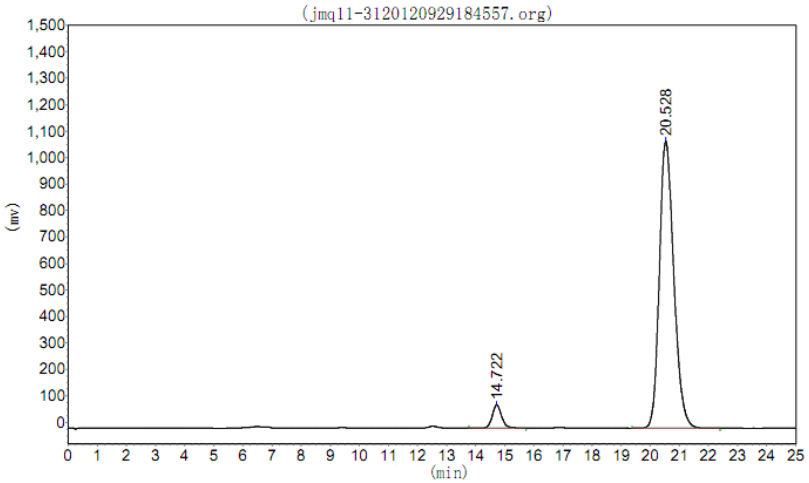

jmq11-31-300c
ZQJ-13-82-6
195.920
144.390
142.766
138.644
135.641
135.537
135.321
129.627
129.370
128.724
127.409
126.413
123.368
121.434
118.578
77.424
77.000
76.576
75.107
54.985
21.498
21.130
O
OH
Me
N
Ts
2b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



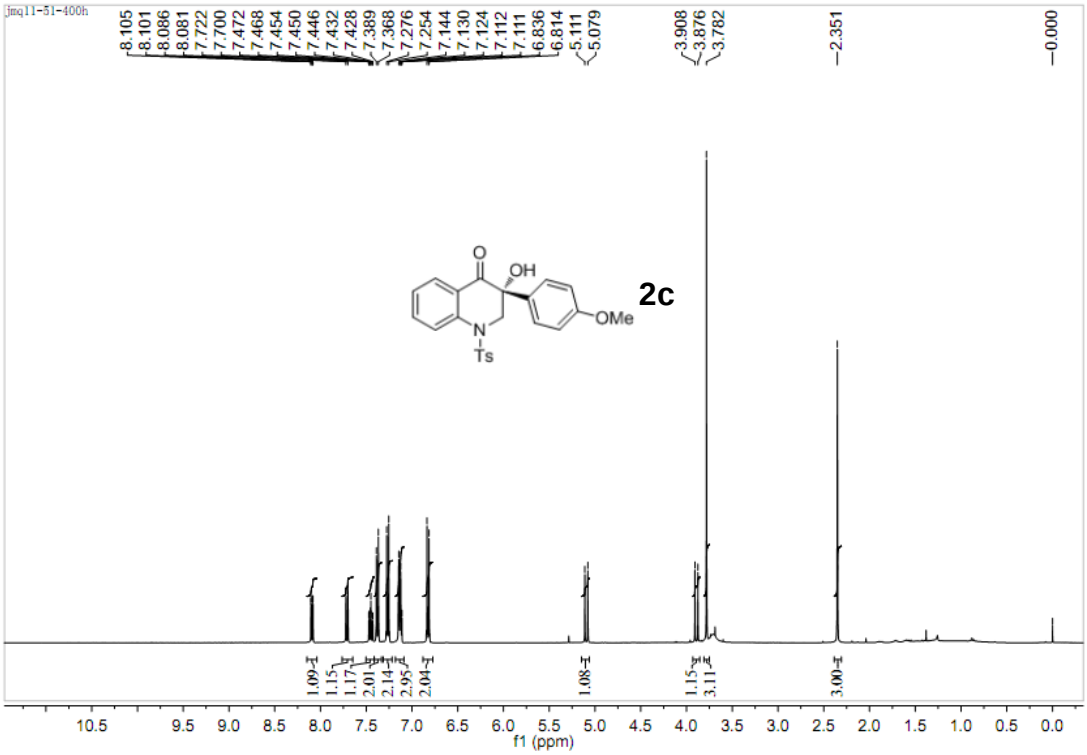
2b

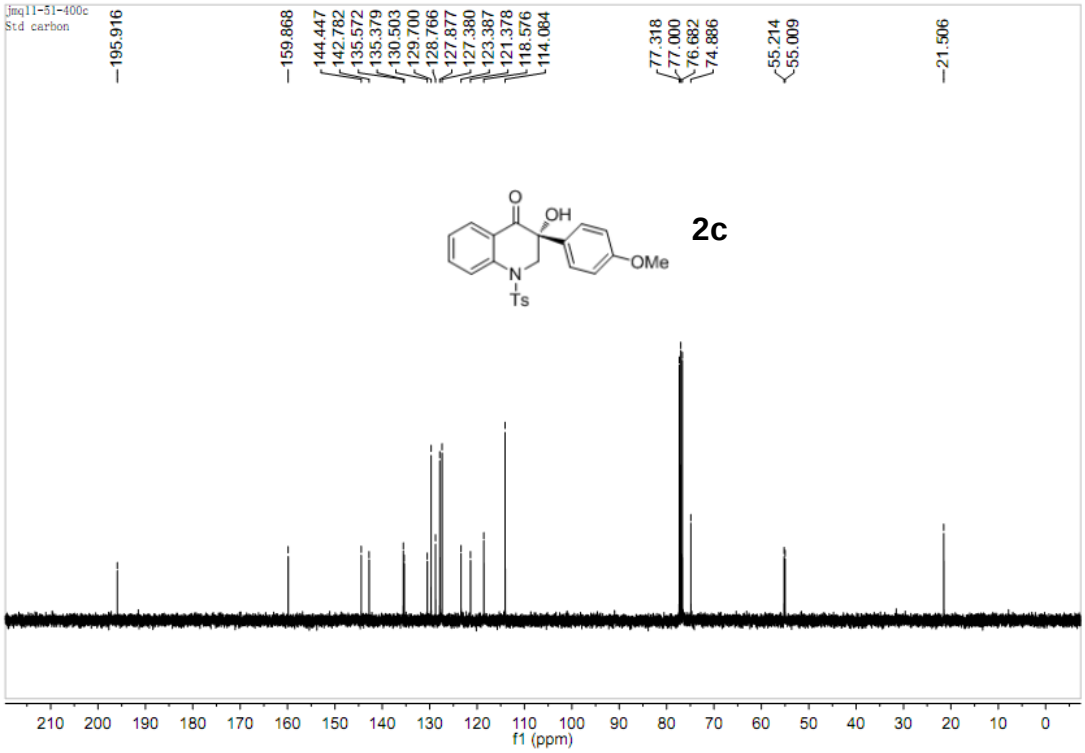


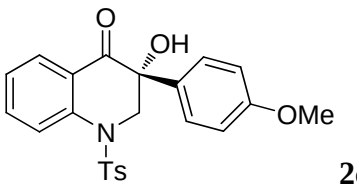
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	14.250	242021.234	5330919.000	50.2875
2	19.918	165086.719	5269962.000	49.7125
Total		407107.953	10600881.000	100.0000



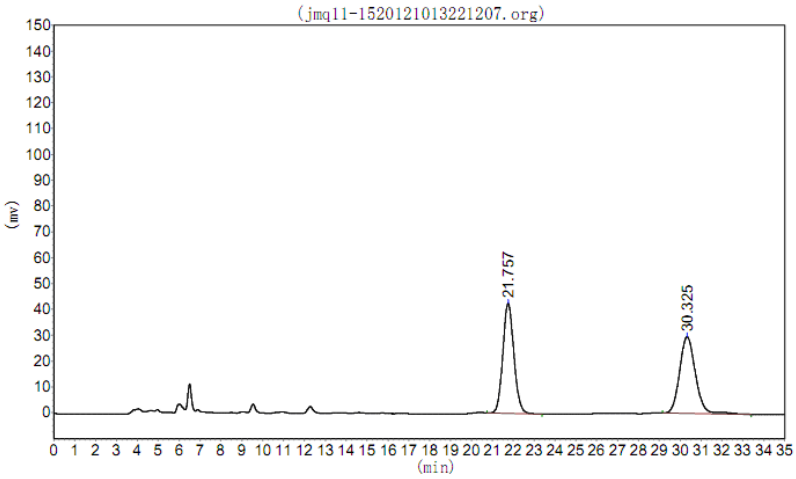
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	14.722	86894.836	1980978.250	5.0375
2	20.528	1083605.000	37343484.000	94.9625
Total		1170499.836	39324462.250	100.0000


jmq11-51-400h
8.105
8.101
8.086
8.081
7.722
7.700
7.472
7.468
7.454
7.450
7.446
7.432
7.428
7.389
7.368
7.276
7.254
7.144
7.130
7.124
7.112
7.111
6.836
6.814
5.111
5.079
3.908
3.876
3.782
2.351
0.000
2c
OH
OMe
N
Ts
1.09
1.15
1.17
2.01
2.14
2.95
2.04
1.08
1.15
3.11
3.00
f1 (ppm)

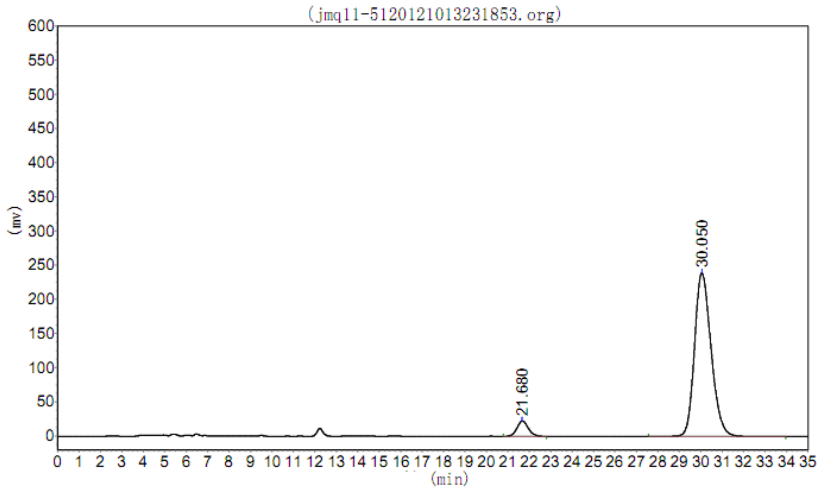

jmq11-51-400c
Std carbon
195.916
159.868
144.447
142.782
135.572
135.379
130.503
129.700
128.766
127.877
127.380
123.387
121.378
118.576
114.084
77.318
77.000
76.682
74.886
55.214
55.009
21.506
2c
OH
OMe
N
Ts
f1 (ppm)



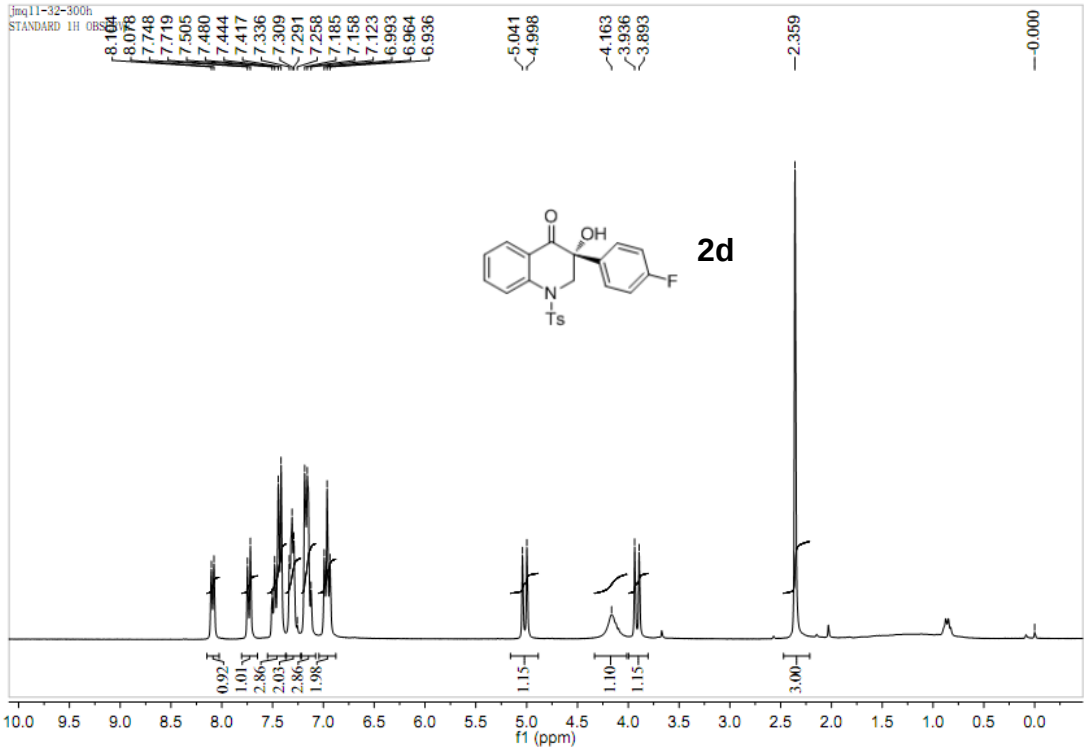
2c

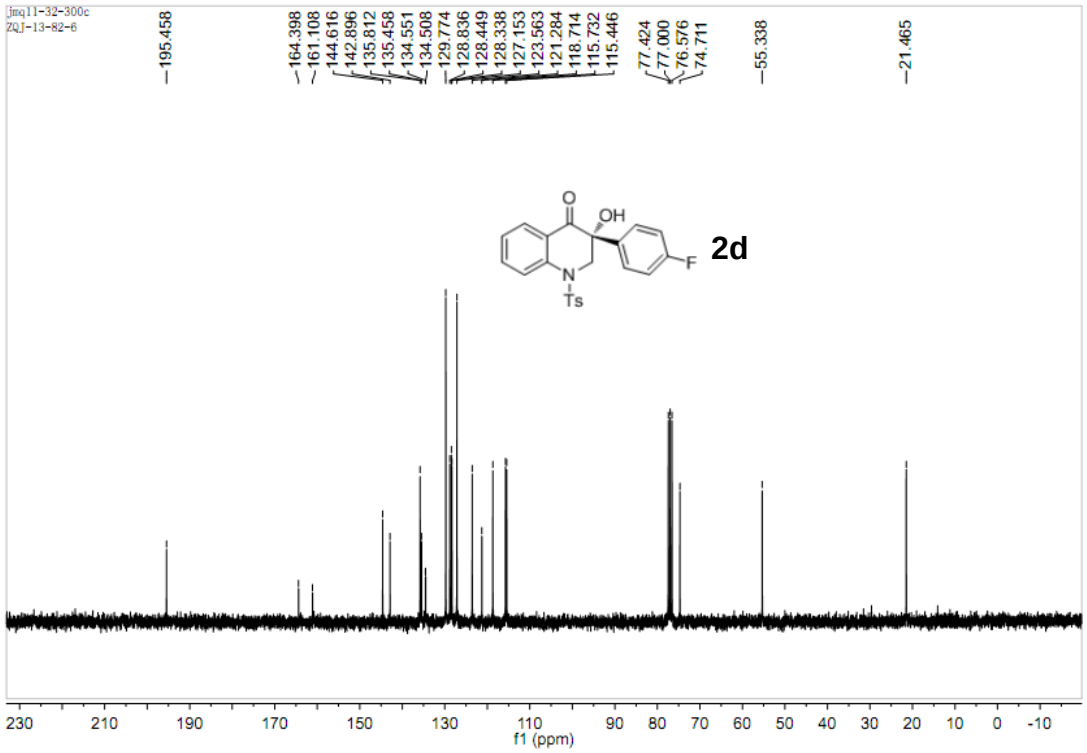


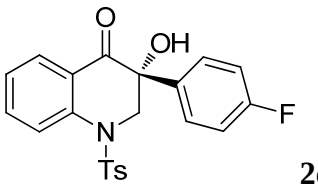
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	21.757	42560.270	1568704.875	50.0215
2	30.325	29693.314	1567357.625	49.9785
Total		72253.584	3136062.500	100.0000



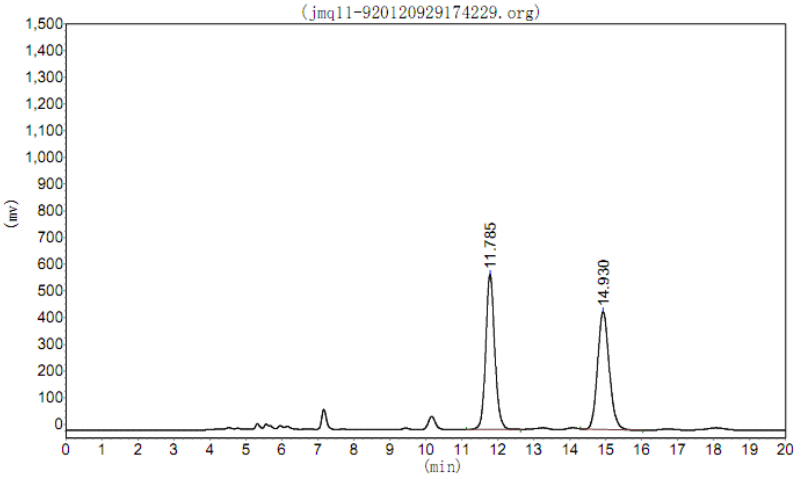
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	21.680	22159.053	810614.250	5.9232
2	30.050	239345.313	12874726.000	94.0768
Total		261504.365	13685340.250	100.0000


jmq11-32-300h
STANDARD 1H OBSERVE
8.104
8.078
7.748
7.719
7.505
7.480
7.444
7.417
7.336
7.309
7.291
7.258
7.185
7.158
7.123
6.993
6.964
6.936
5.041
4.998
4.163
3.936
3.893
2.359
-0.000
0.92
1.01
2.86
2.03
2.86
1.98
1.15
1.10
1.15
3.00
2d
f1 (ppm)

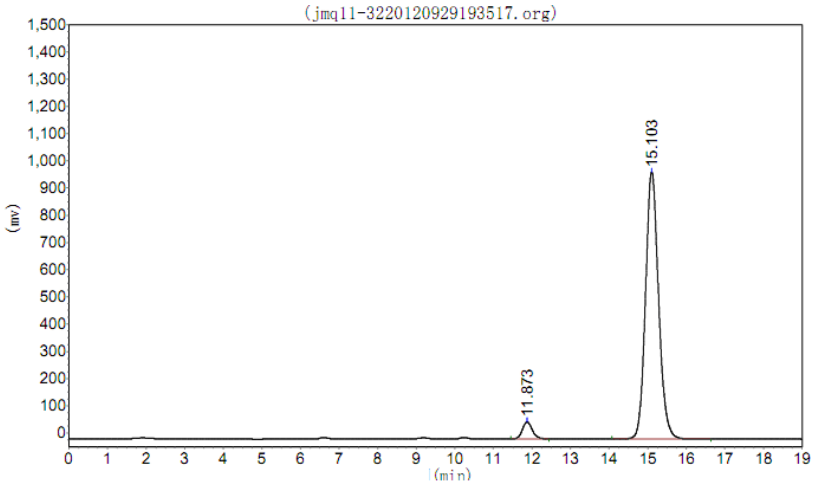

jmq11-32-300c
ZQJ-13-82-6
195.458
164.398
161.108
144.616
142.896
135.812
135.458
134.551
134.508
129.774
128.836
128.449
128.338
127.153
123.563
121.284
118.714
115.732
115.446
77.424
77.000
76.576
74.711
55.338
21.465
2d
f1 (ppm)



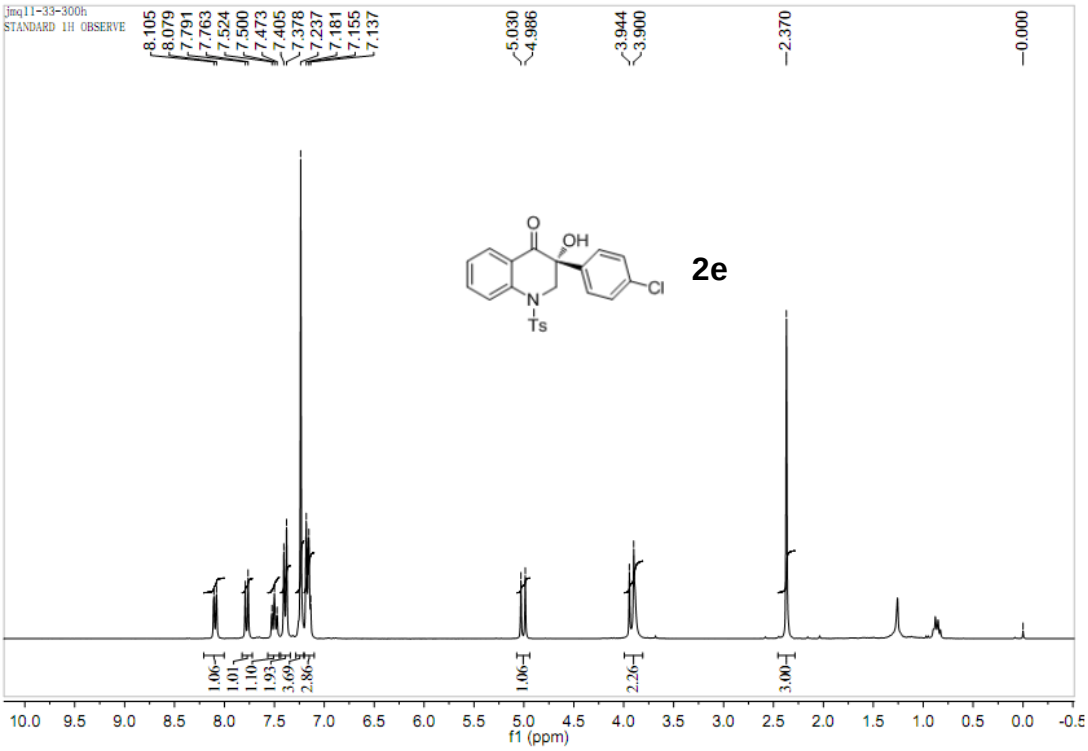
2d

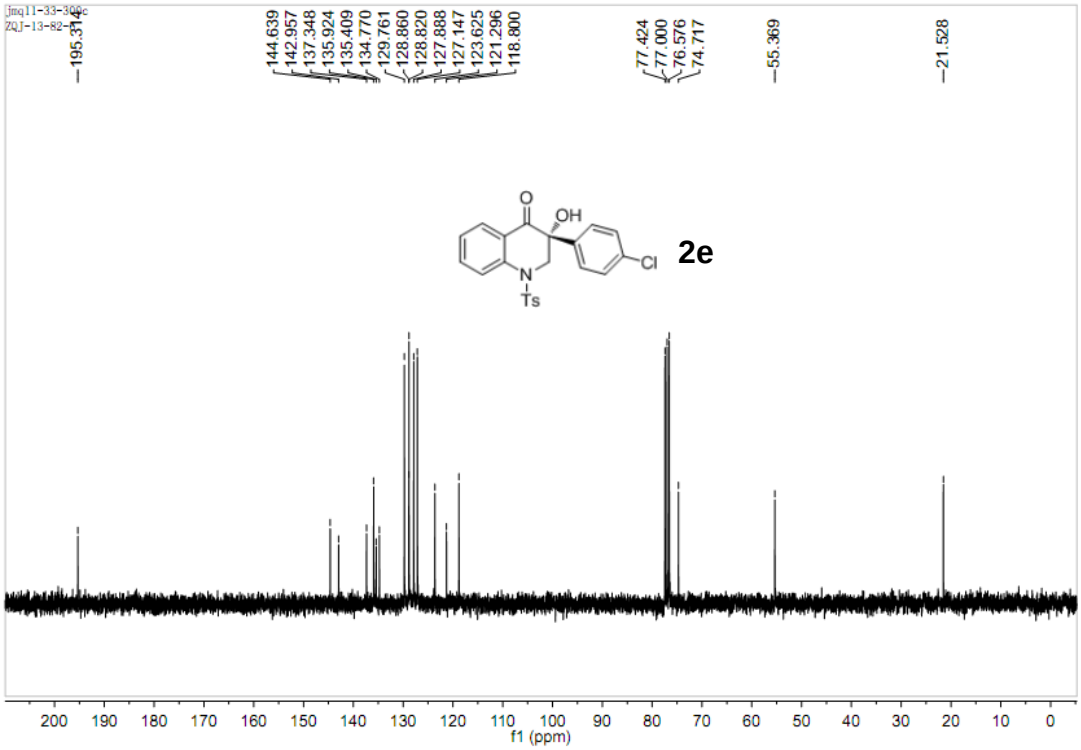


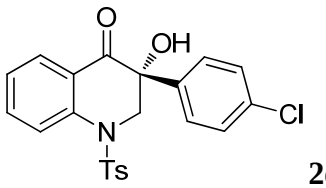
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	11.785	580507.000	10143598.000	50.6267
2	14.930	440513.219	9892453.000	49.3733
Total		1021020.219	20036051.000	100.0000



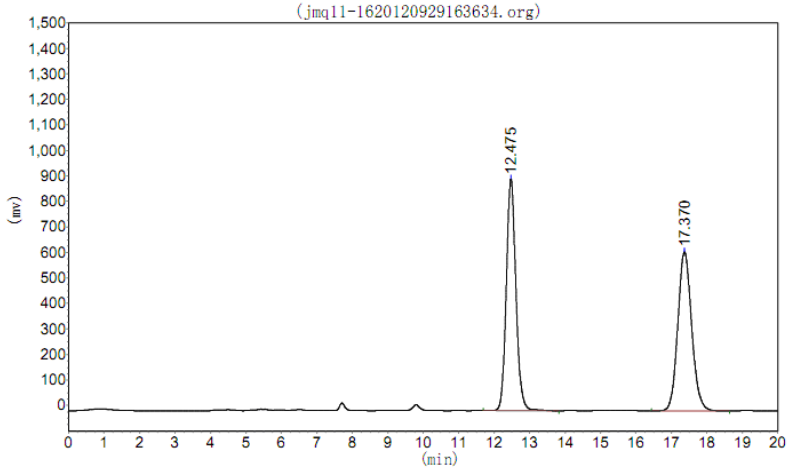
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	11.873	63156.418	1115322.250	4.6126
2	15.103	980914.625	23064448.000	95.3874
Total		1044071.043	24179770.250	100.0000


jmq11-33-300h
STANDARD 1H OBSERVE
8.105
8.079
7.791
7.763
7.524
7.500
7.473
7.405
7.378
7.237
7.181
7.155
7.137
5.030
4.986
3.944
3.900
2.370
0.000
O
OH
N
Ts
Cl
2e
1.06
1.01
1.10
1.93
3.69
2.86
1.06
2.26
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

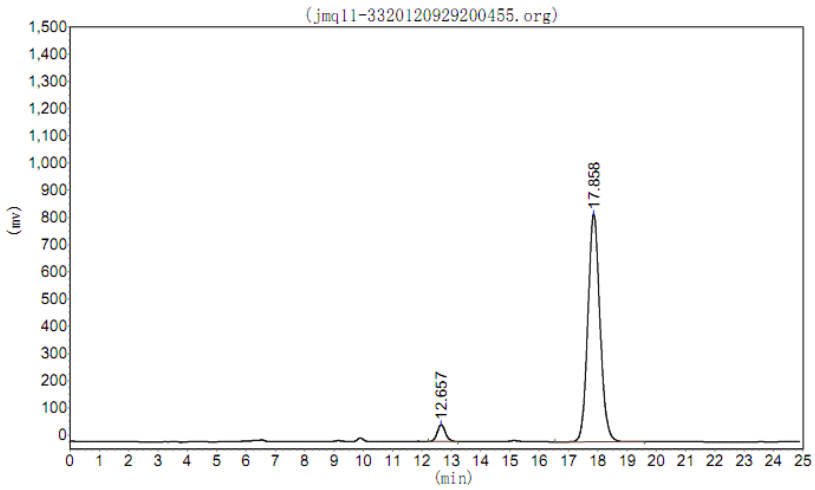

jmq11-33-300c
ZQJ-13-82-
195.314
144.639
142.957
137.348
135.924
135.409
134.770
129.761
128.860
128.820
127.888
127.147
123.625
121.296
118.800
77.424
77.000
76.576
74.717
55.369
21.528
O
OH
N
Ts
Cl
2e
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



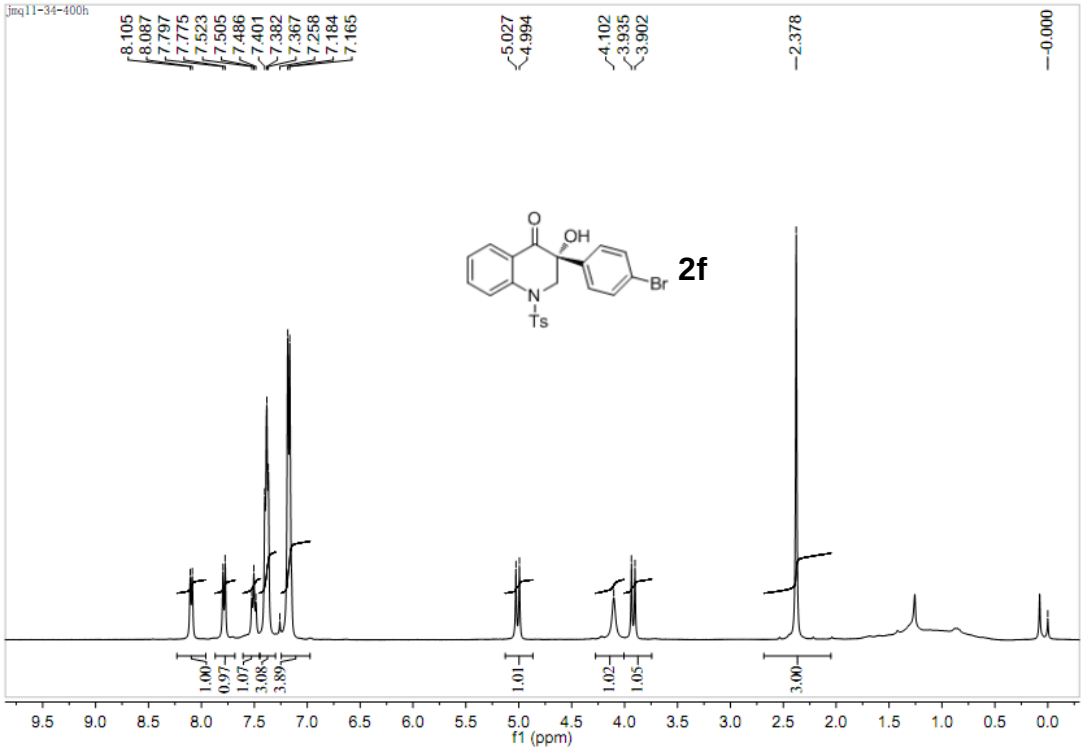
2e

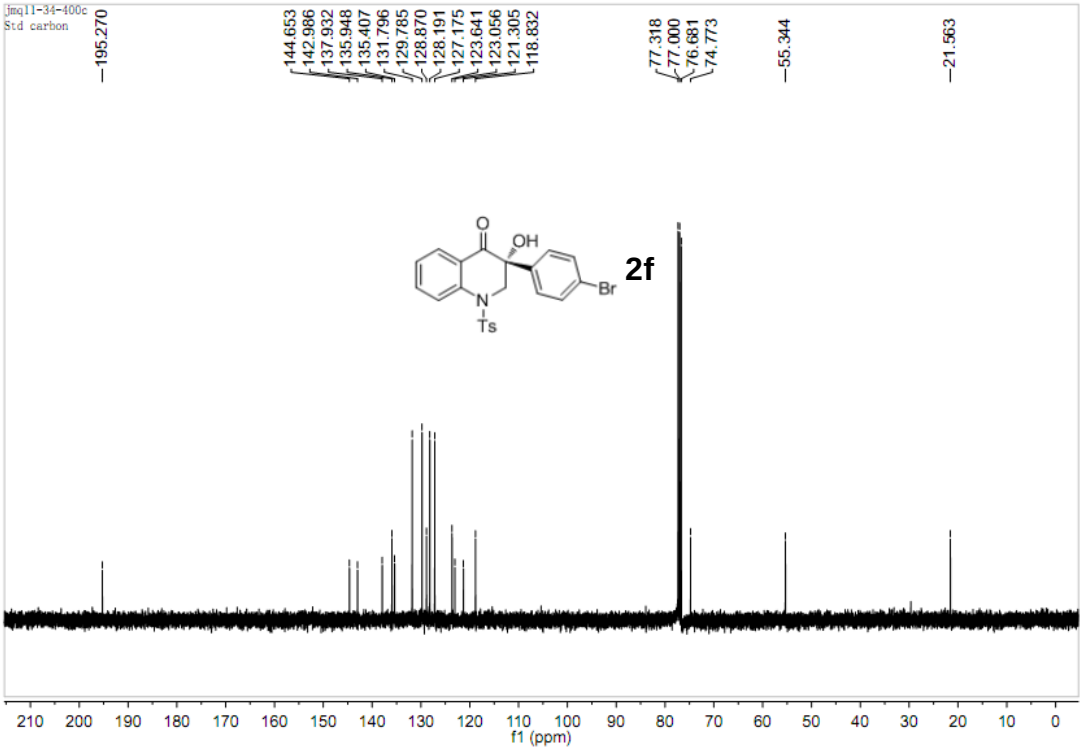


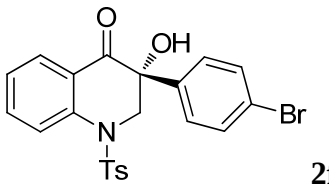
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	12.475	909147.000	17003092.000	50.0682
2	17.370	623172.875	16956800.000	49.9318
Total		1532319.875	33959892.000	100.0000



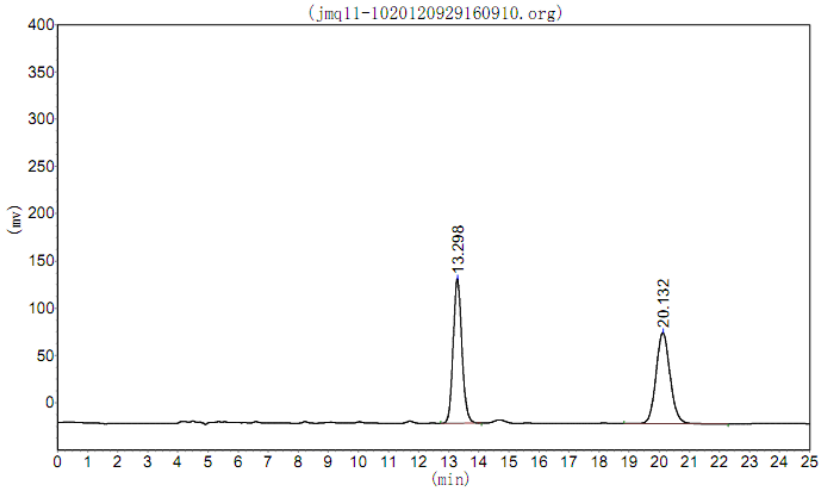
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	12.657	62089.188	1189652.000	4.7529
2	17.858	835431.313	23840152.000	95.2471
Total		897520.500	25029804.000	100.0000


jmq11-34-400h
8.105
8.087
7.797
7.775
7.523
7.505
7.486
7.401
7.382
7.367
7.258
7.184
7.165
5.027
4.994
4.102
3.935
3.902
2.378
-0.000
O
OH
N
Ts
Br
2f
1.00
0.97
1.07
3.08
3.89
1.01
1.02
1.05
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

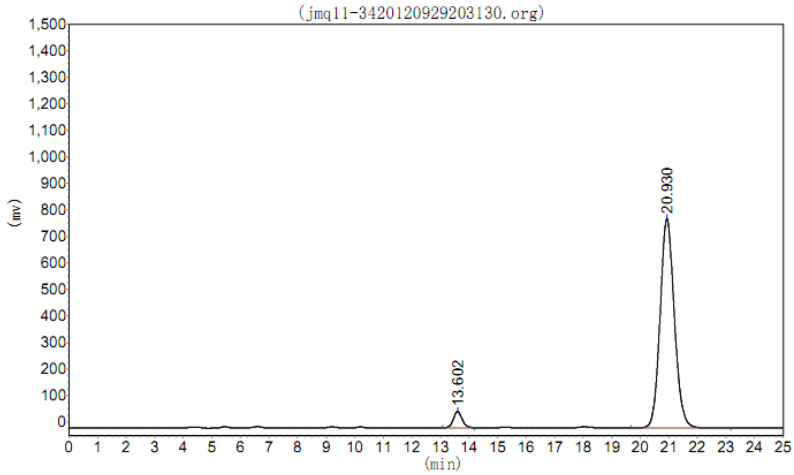

jmq11-34-400c
Std carbon
195.270
144.653
142.986
137.932
135.948
135.407
131.796
129.785
128.870
128.191
127.175
123.641
123.056
121.305
118.832
77.318
77.000
76.681
74.773
55.344
21.563
O
OH
N
Ts
Br
2f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



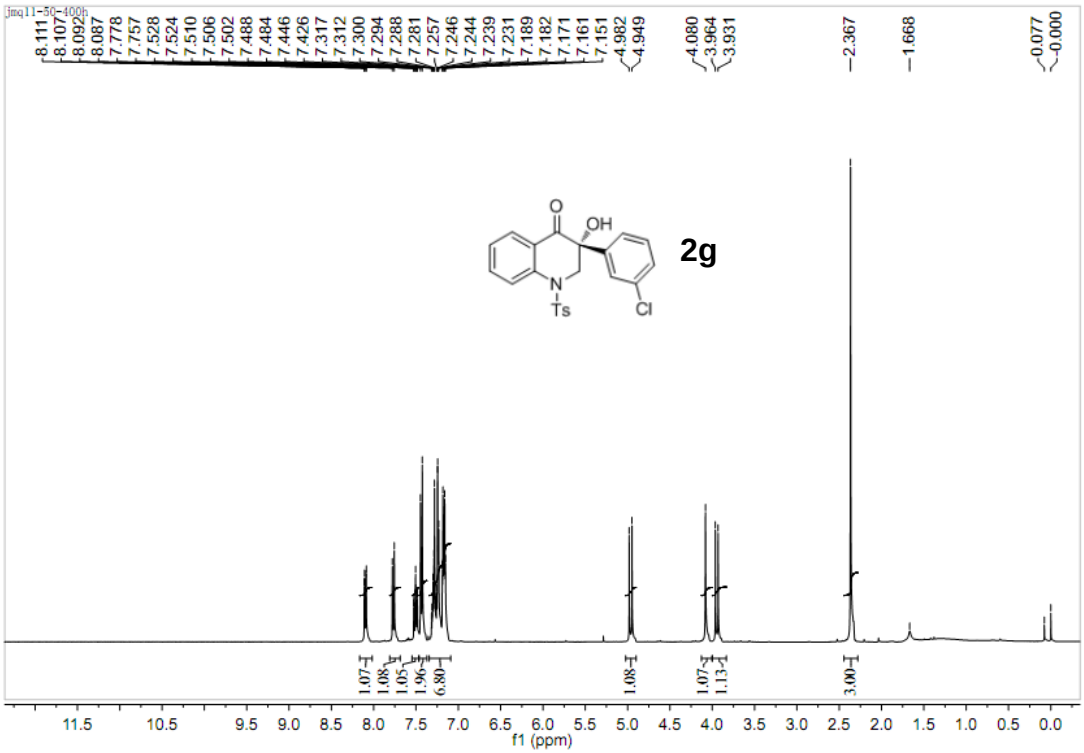
2f

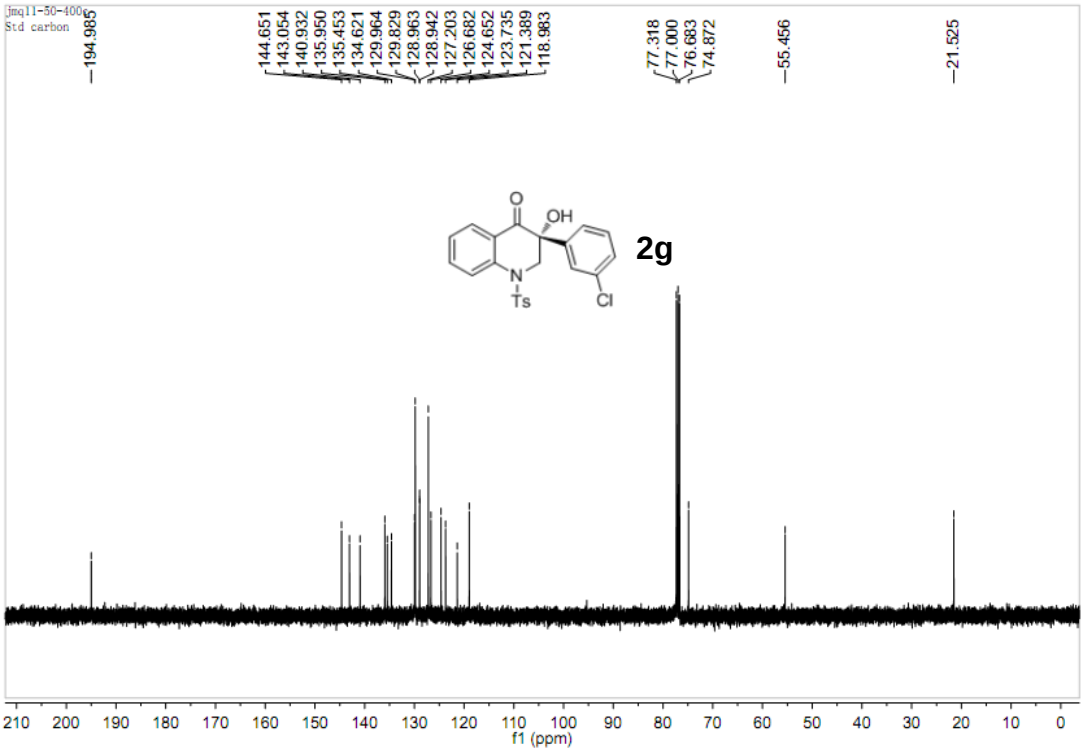


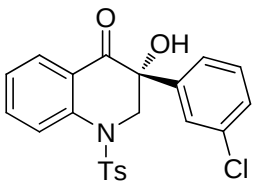
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	13.298	152761.734	3117914.750	49.9023
2	20.132	96360.250	3130124.750	50.0977
Total		249121.984	6248039.500	100.0000



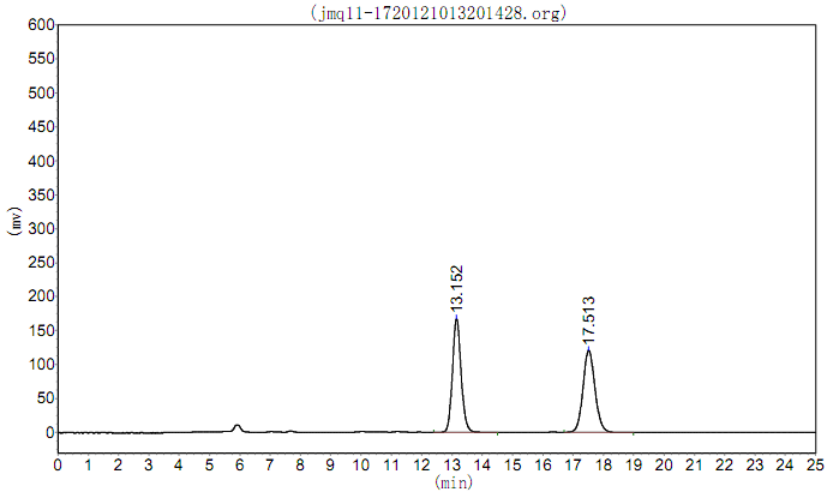
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	13.602	61149.379	1286109.000	4.4968
2	20.930	790220.000	27314618.000	95.5032
Total		851369.379	28600727.000	100.0000


jmq11-50-400h
8.111
8.107
8.092
8.087
7.778
7.757
7.528
7.524
7.510
7.506
7.502
7.488
7.484
7.446
7.426
7.317
7.312
7.300
7.294
7.288
7.281
7.257
7.246
7.244
7.239
7.231
7.189
7.182
7.171
7.161
7.151
4.982
4.949
4.080
3.964
3.931
2.367
1.668
0.077
0.000
O
OH
N
Ts
Cl
2g
1.07
1.08
1.05
1.96
6.80
1.08
1.07
1.13
3.00
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

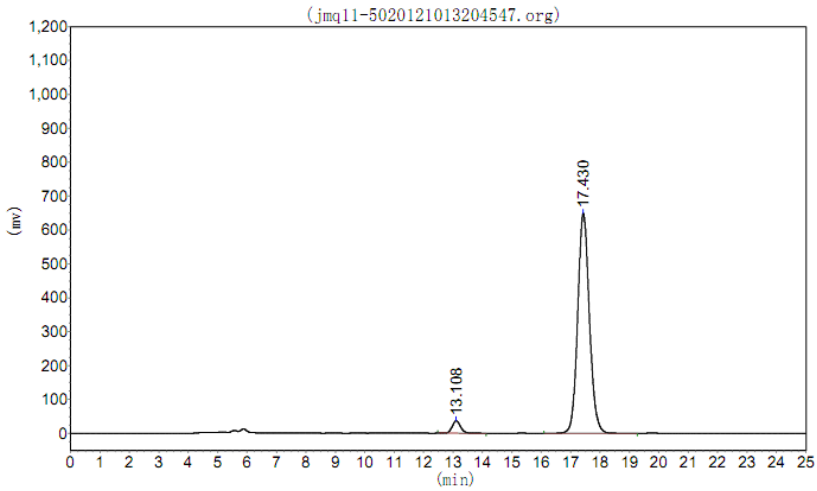

jmq11-50-400c
Std carbon
194.985
144.651
143.054
140.932
135.950
135.453
134.621
129.964
129.829
128.963
128.942
127.203
126.682
124.652
123.735
121.389
118.983
77.318
77.000
76.683
74.872
55.456
21.525
O
OH
N
Ts
Cl
2g
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



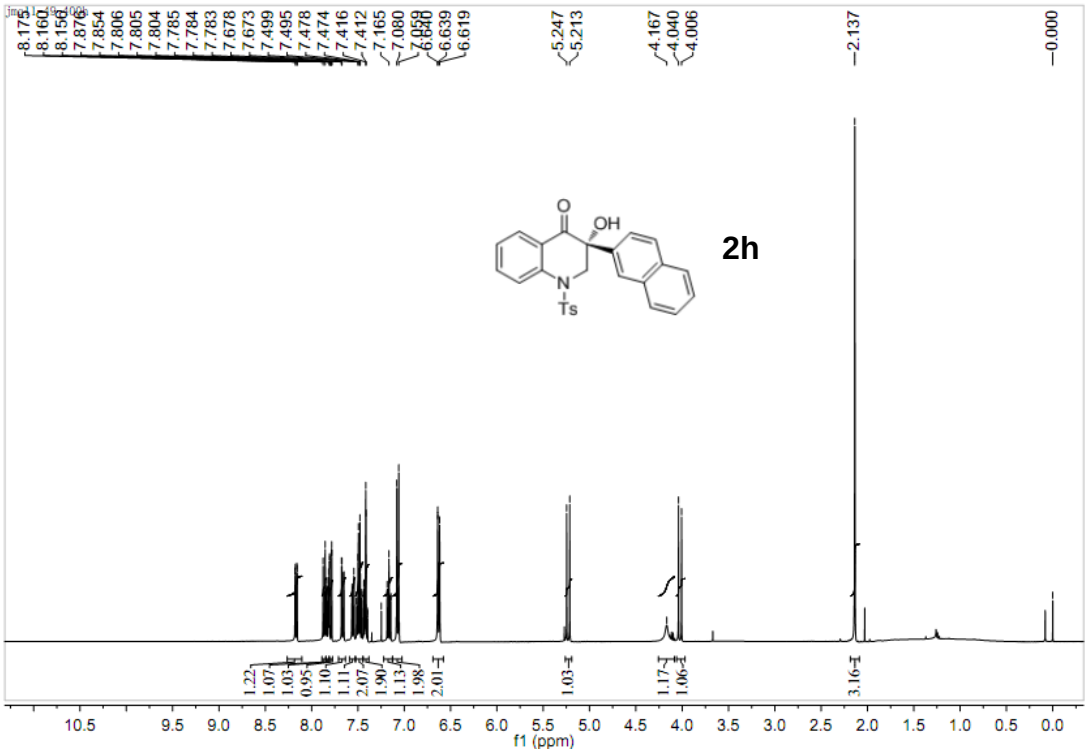
2g

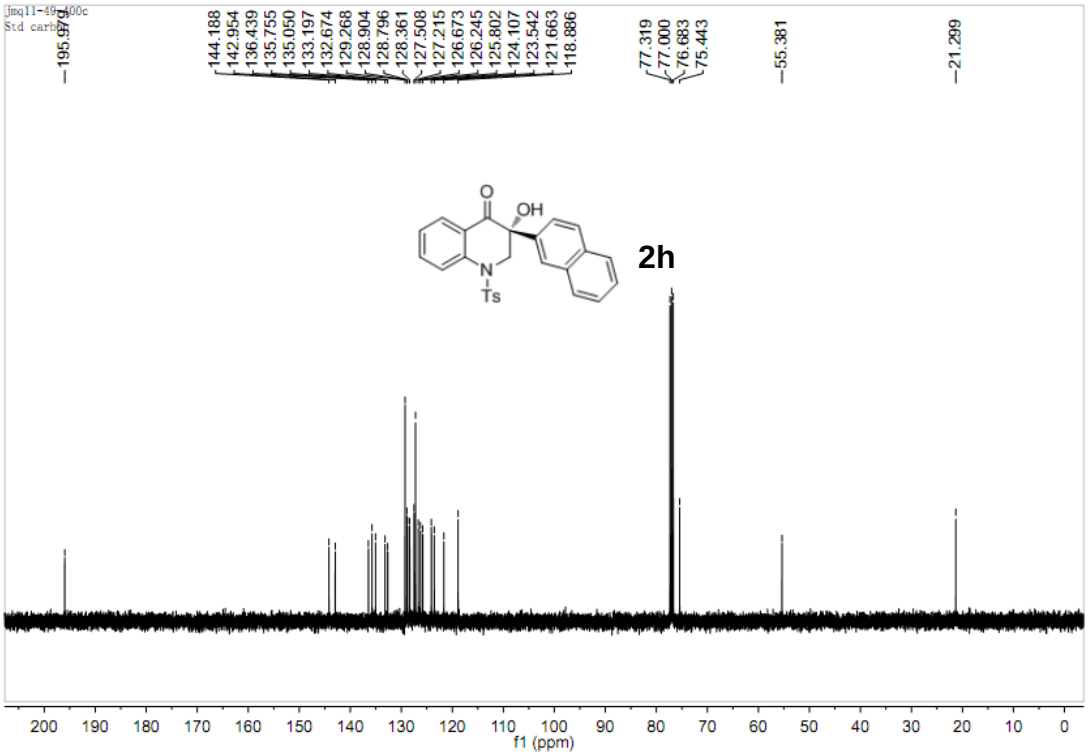


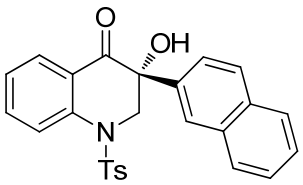
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	13.152	167000.813	3353985.250	50.0103
2	17.513	121145.336	3352598.000	49.9897
Total		288146.148	6706583.250	100.0000



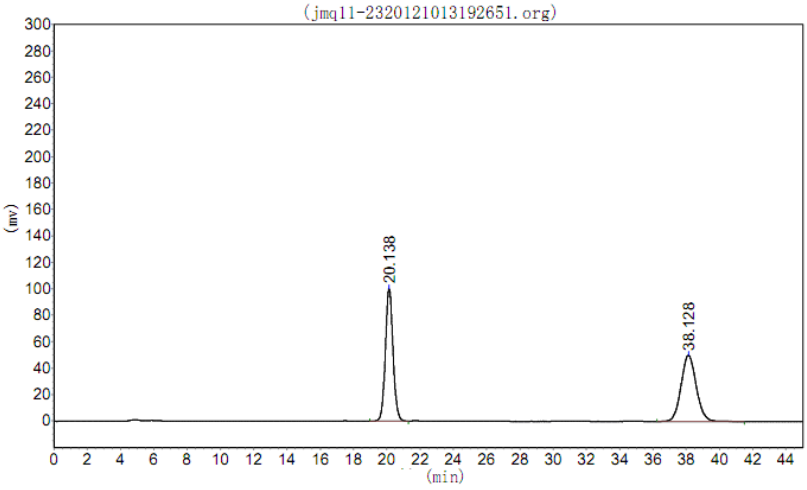
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	13.108	36724.473	725537.625	3.8854
2	17.430	649376.250	17947860.000	96.1146
Total		686100.723	18673397.625	100.0000


2h
f1 (ppm)

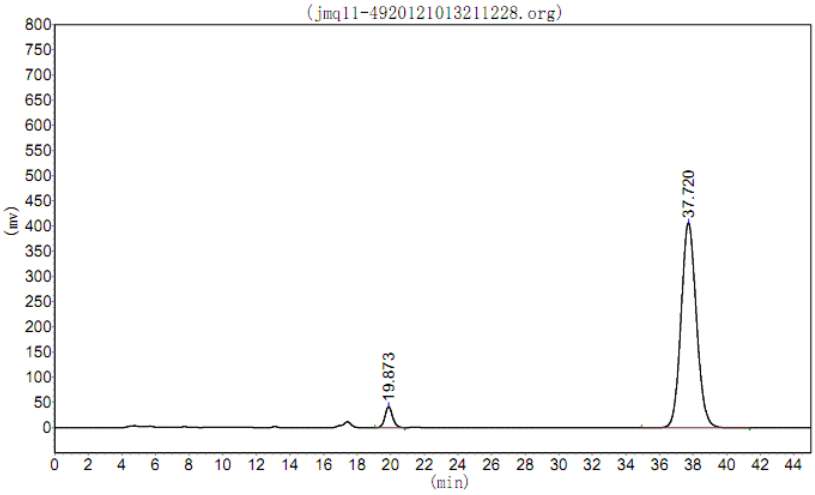

2h
f1 (ppm)



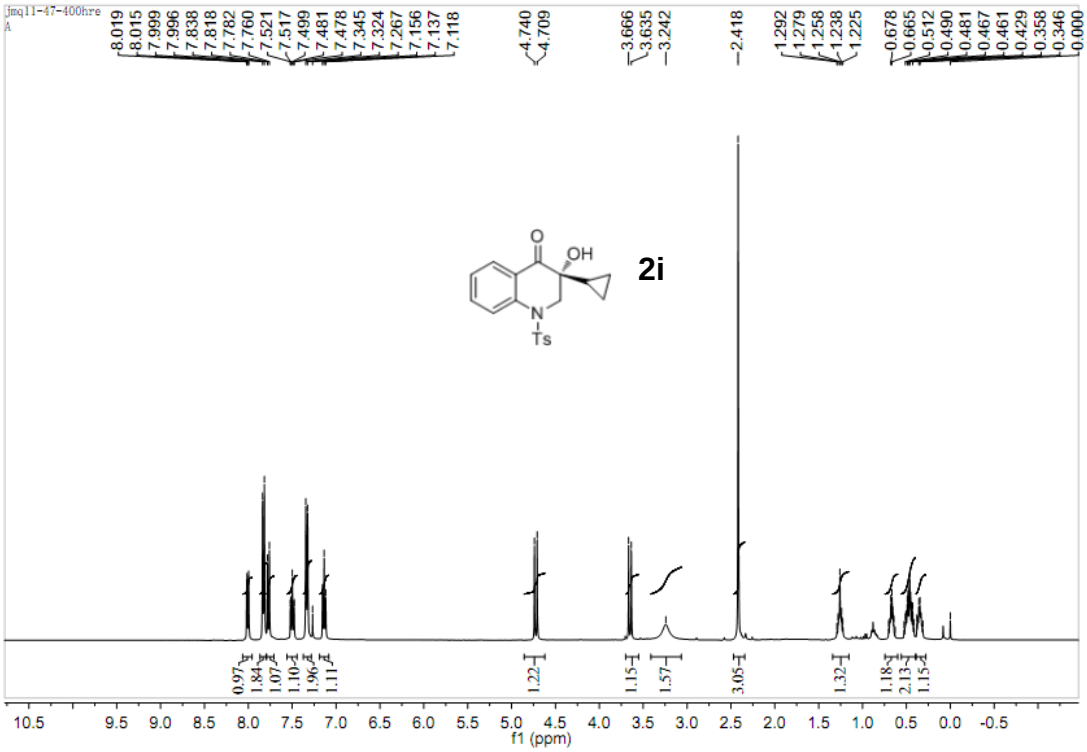
2h

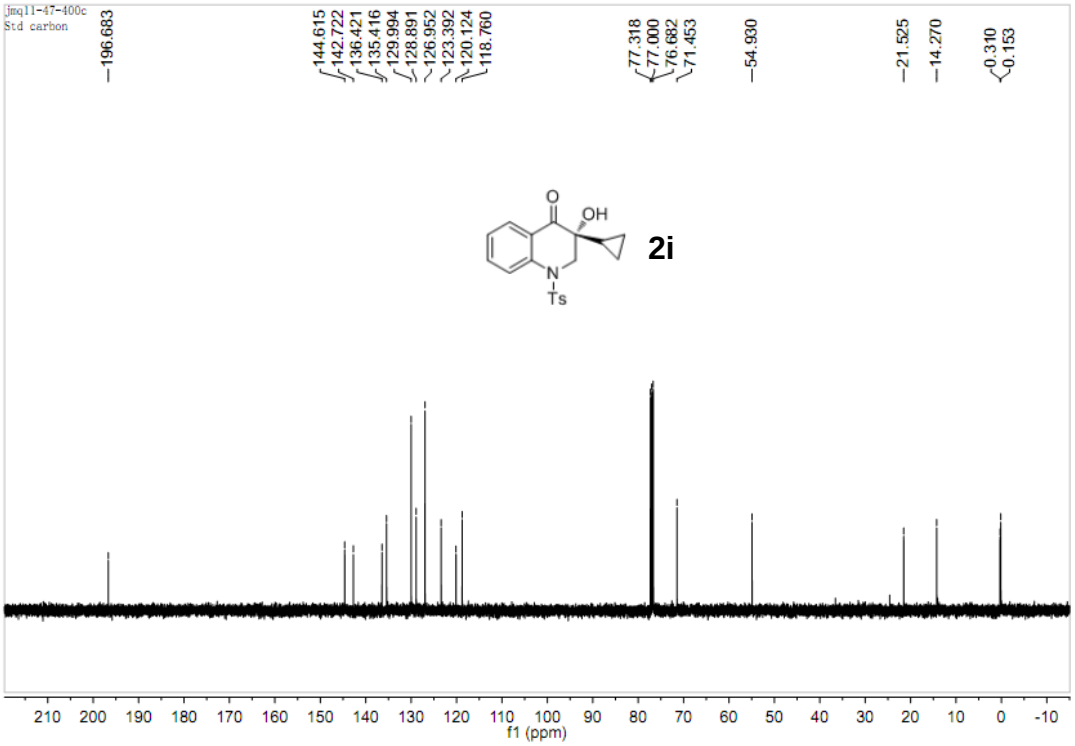


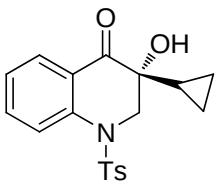
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	20.138	100354.742	3208019.750	50.2724
2	38.128	50103.602	3173256.750	49.7276
Total		150458.344	6381276.500	100.0000



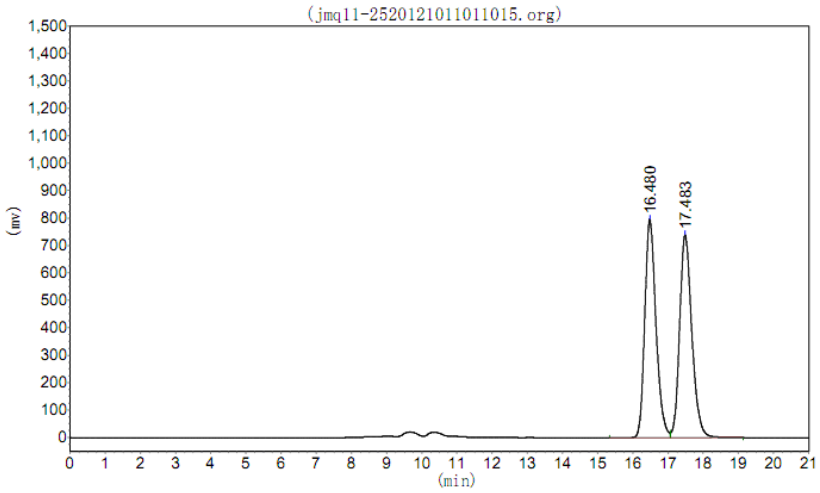
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	19.873	41117.906	1296735.500	4.7969
2	37.720	405991.844	25735848.000	95.2031
Total		447109.750	27032583.500	100.0000


jmq11-47-400hre
A
8.019
8.015
7.999
7.996
7.838
7.818
7.782
7.760
7.521
7.517
7.499
7.481
7.478
7.345
7.324
7.267
7.156
7.137
7.118
4.740
4.709
3.666
3.635
3.242
2.418
1.292
1.279
1.258
1.238
1.225
0.678
0.665
0.512
0.490
0.481
0.467
0.461
0.429
0.358
0.346
0.000
O
OH
N
Ts
2i
0.97
1.84
1.07
1.10
1.96
1.11
1.22
1.15
1.57
3.05
1.32
1.18
2.13
1.15
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

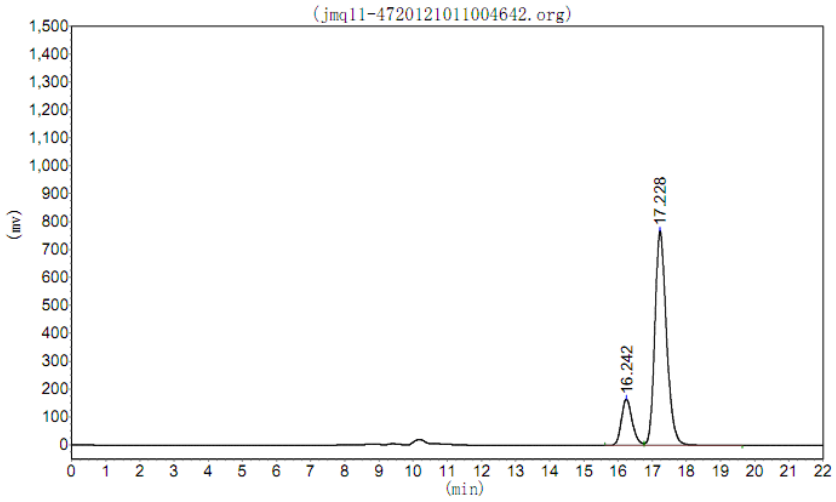

jmq11-47-400c
Std carbon
196.683
144.615
142.722
136.421
135.416
129.994
128.891
126.952
123.392
120.124
118.760
77.318
77.000
76.682
71.453
54.930
21.525
14.270
0.310
0.153
O
OH
N
Ts
2i
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



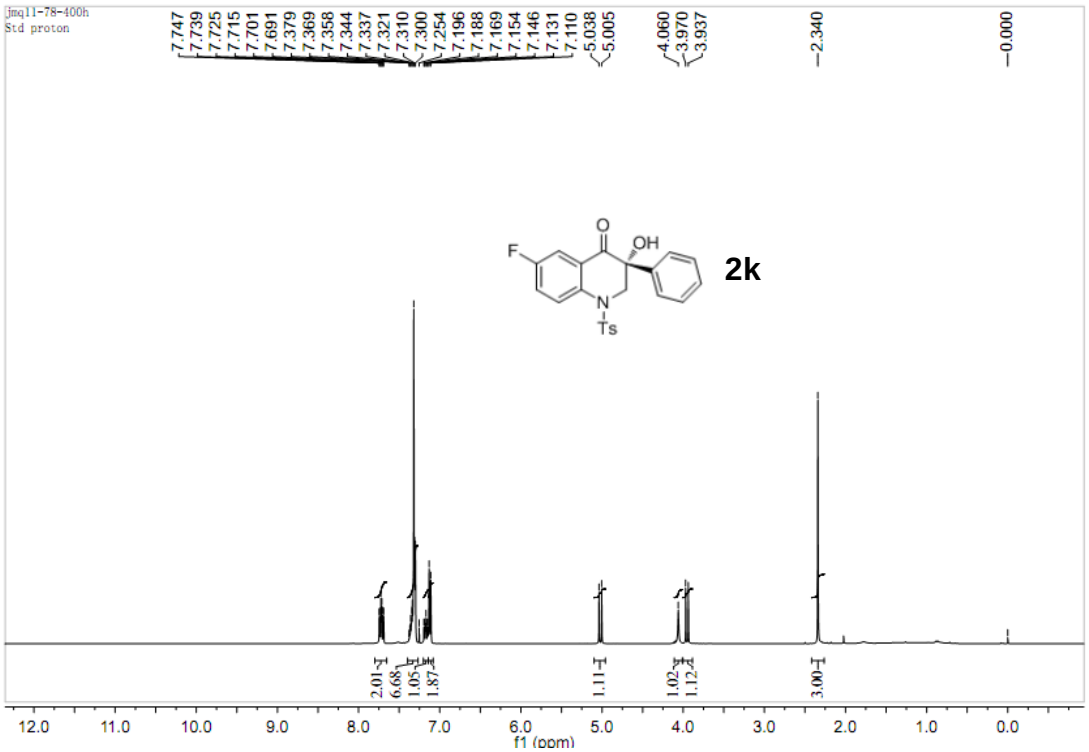
2i

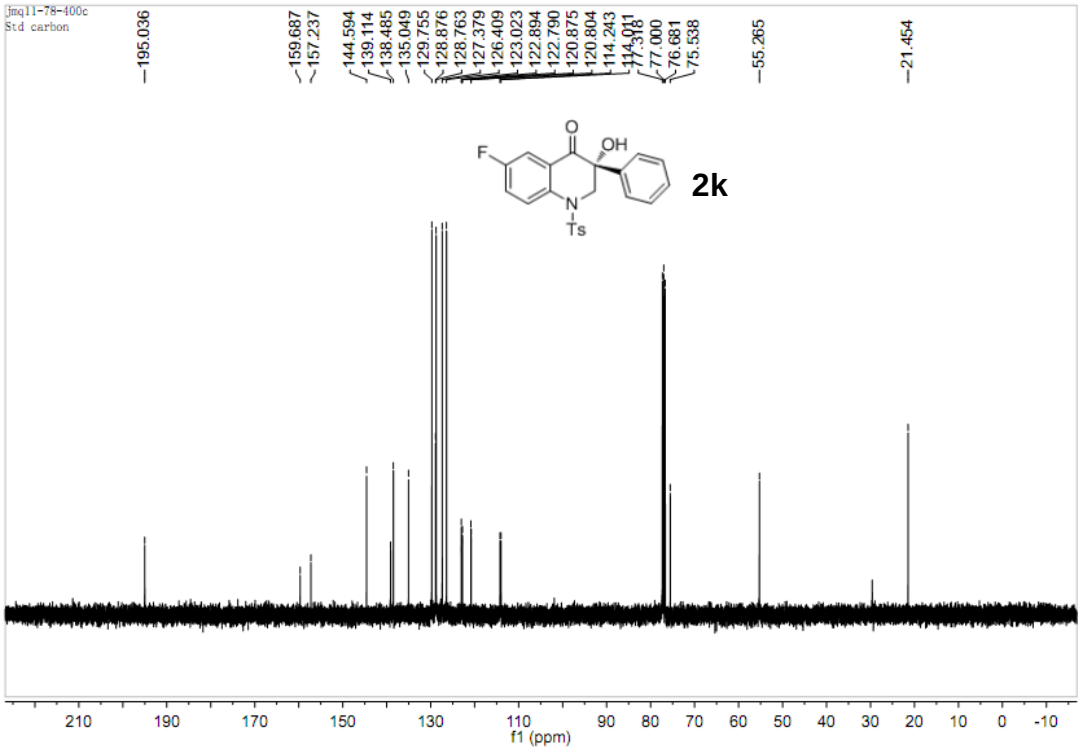


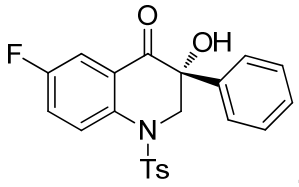
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	16.480	795747.375	17576864.000	49.6448
2	17.483	739377.438	17828382.000	50.3552
Total		1535124.813	35405246.000	100.0000



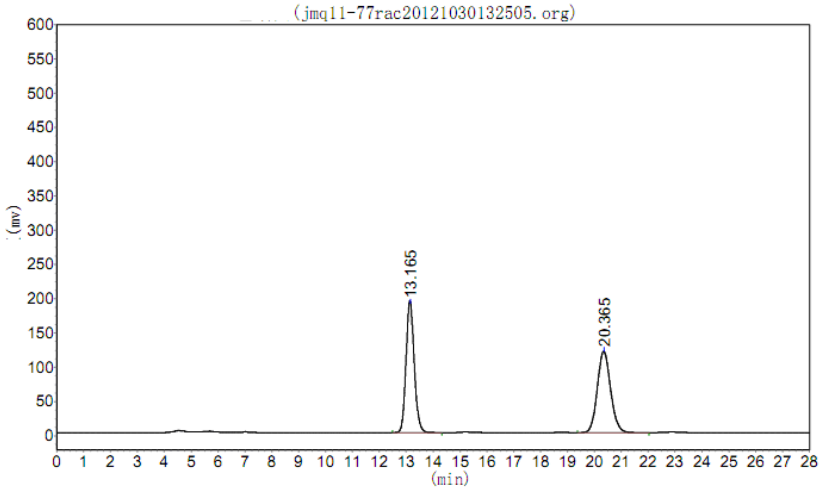
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	16.242	165597.063	3648914.000	16.6998
2	17.228	769016.063	18201080.000	83.3002
Total		934613.125	21849994.000	100.0000


jmq11-78-400h
Std proton
7.747
7.739
7.725
7.715
7.701
7.691
7.379
7.369
7.358
7.344
7.337
7.321
7.310
7.300
7.254
7.196
7.188
7.169
7.154
7.146
7.131
7.110
5.038
5.005
4.060
3.970
3.937
2.340
0.000
2.01
6.68
1.05
1.87
1.11
1.02
1.12
3.00
F
O
OH
N
Ts
2k
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

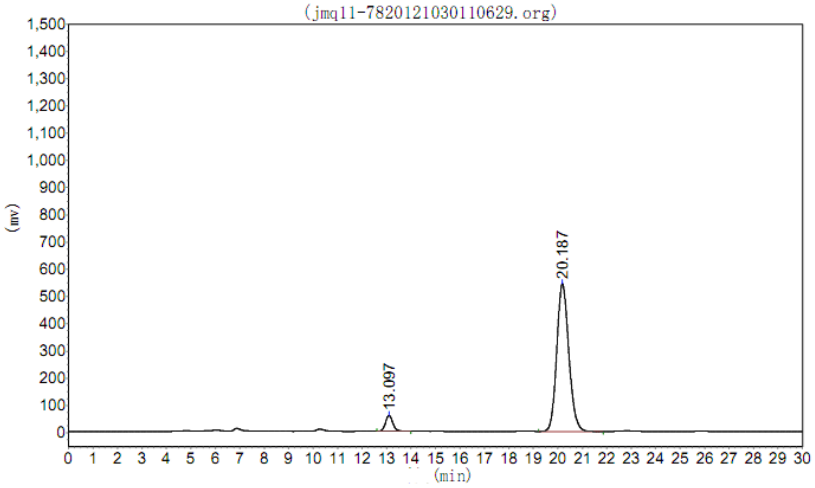

jmq11-78-400c
Std carbon
195.036
159.687
157.237
144.594
139.114
138.485
135.049
129.755
128.876
128.763
127.379
126.409
123.023
122.894
122.790
120.875
120.804
114.243
114.011
77.318
77.000
76.681
75.538
55.265
21.454
F
O
OH
N
Ts
2k
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



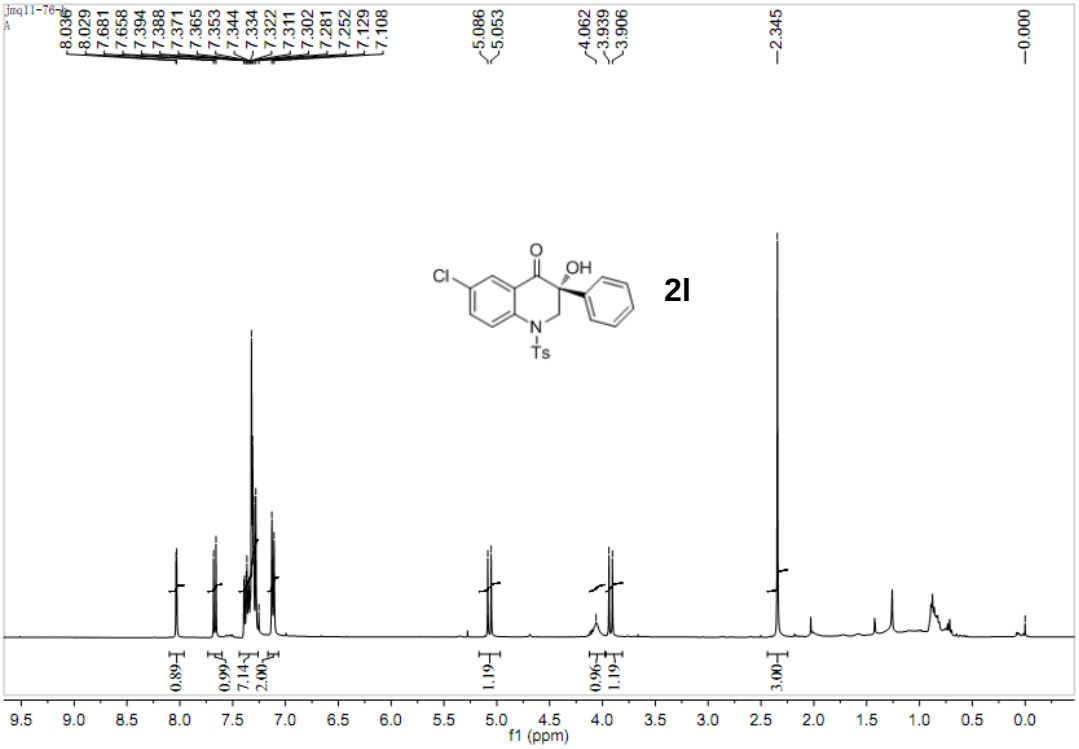
2k

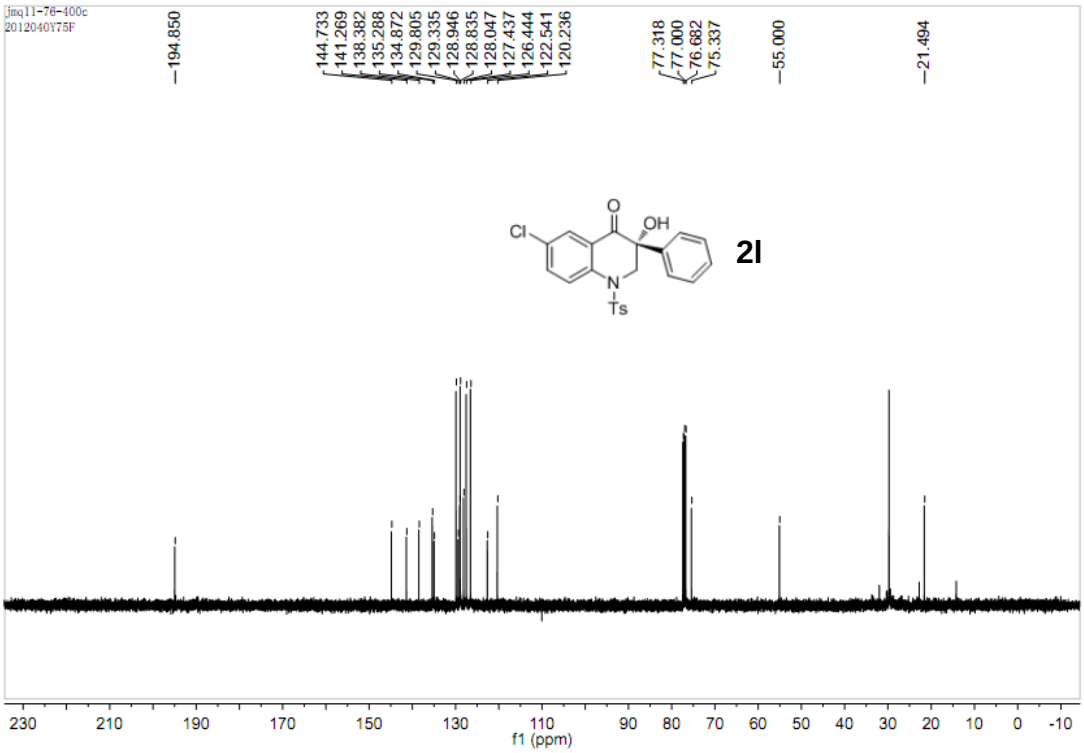


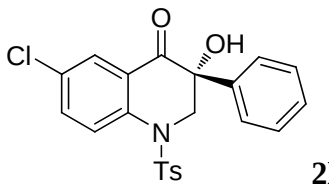
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	13.165	191403.297	4082283.000	49.9676
2	20.365	118783.820	4087581.500	50.0324
Total		310187.117	8169864.500	100.0000



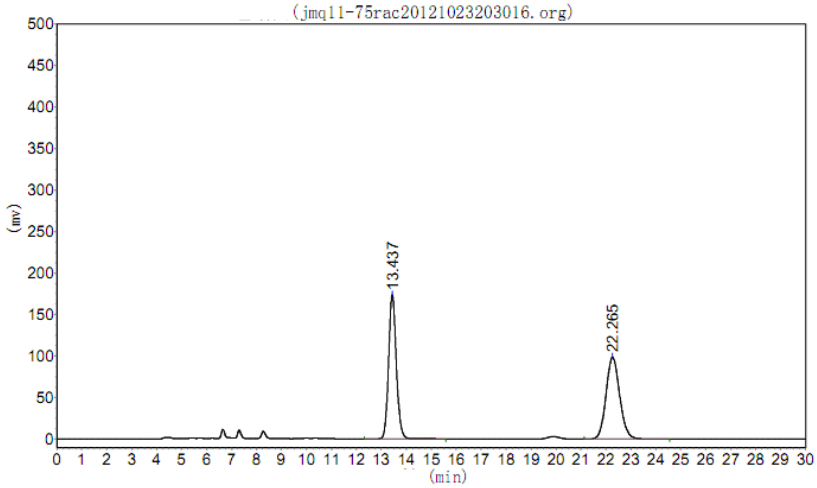
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	13.097	58901.234	1238938.000	6.2370
2	20.187	543105.000	18625438.000	93.7630
Total		602006.234	19864376.000	100.0000


jmq11-76-1
A
8.036
8.029
7.681
7.658
7.394
7.388
7.371
7.365
7.353
7.344
7.334
7.322
7.311
7.302
7.281
7.252
7.129
7.108
5.086
5.053
4.062
3.939
3.906
2.345
0.000
Cl
O
OH
N
Ts
2l
0.89
0.99
7.14
2.00
1.19
0.96
1.19
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

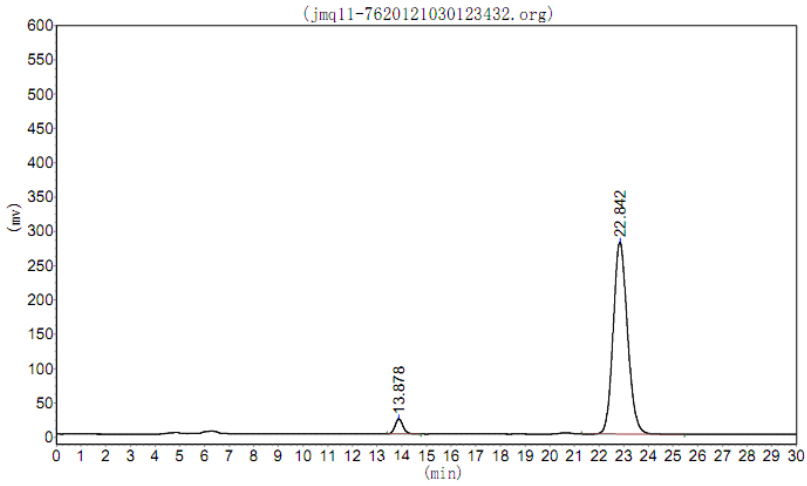

jmq11-76-400c
2012040Y75F
194.850
144.733
141.269
138.382
135.288
134.872
129.805
129.335
128.946
128.835
128.047
127.437
126.444
122.541
120.236
77.318
77.000
76.682
75.337
55.000
21.494
Cl
O
OH
N
Ts
2l
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



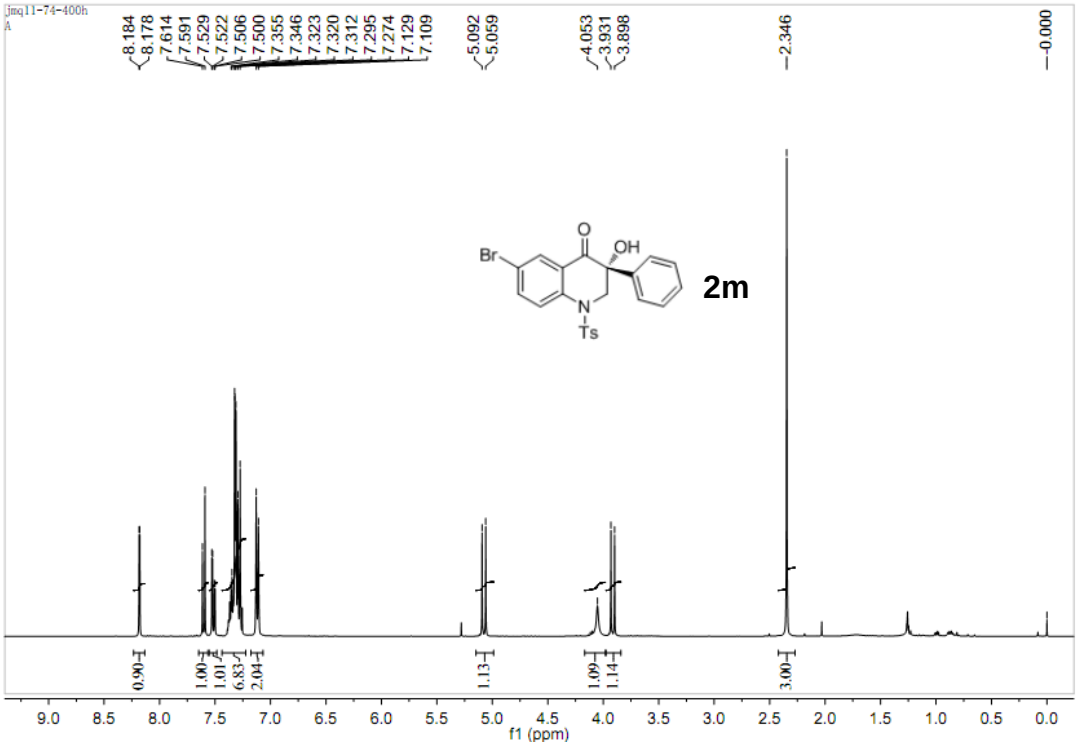
2l

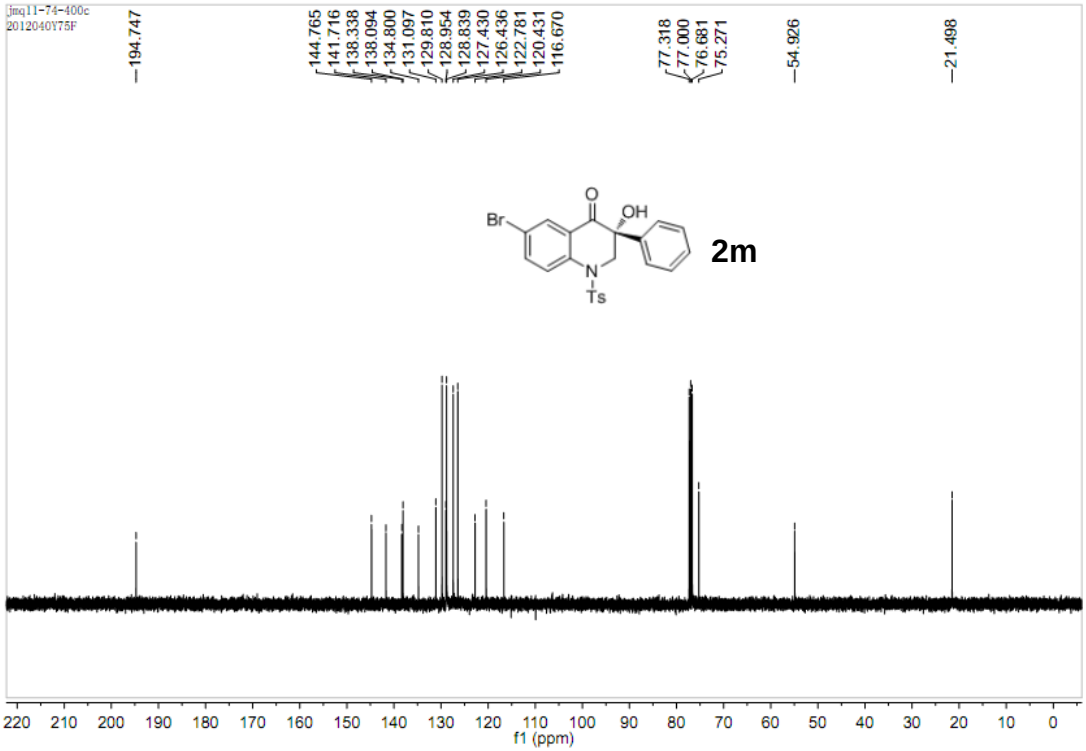


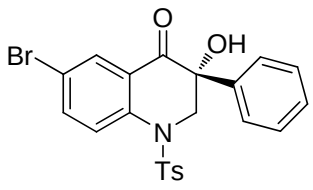
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	13.437	173323.078	3765261.250	49.9706
2	22.265	98811.344	3769696.750	50.0294
Total		272134.422	7534958.000	100.0000



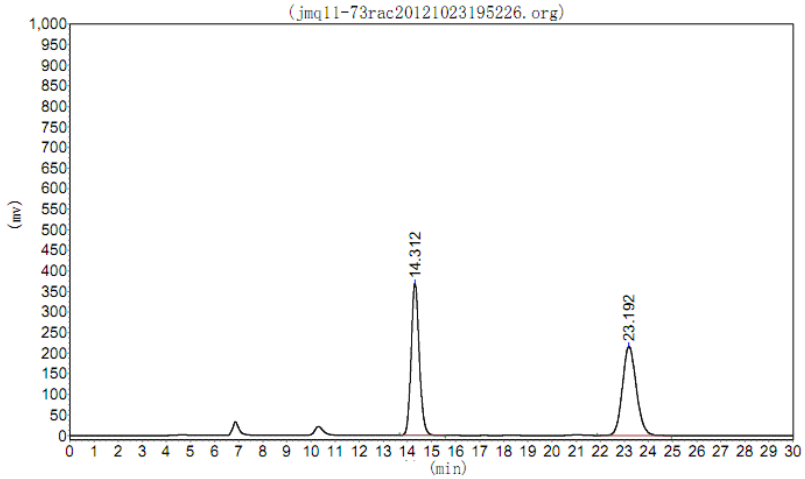
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	13.878	22044.283	500589.188	4.2459
2	22.842	279875.281	11289302.000	95.7541
Total		301919.564	11789891.188	100.0000


jmq11-74-400h
A
8.184
8.178
7.614
7.591
7.529
7.522
7.506
7.500
7.355
7.346
7.323
7.320
7.312
7.295
7.274
7.129
7.109
5.092
5.059
4.053
3.931
3.898
2.346
0.000
0.90
1.00
1.01
6.83
2.04
1.13
1.09
1.14
3.00
Br
O
OH
N
Ts
2m
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

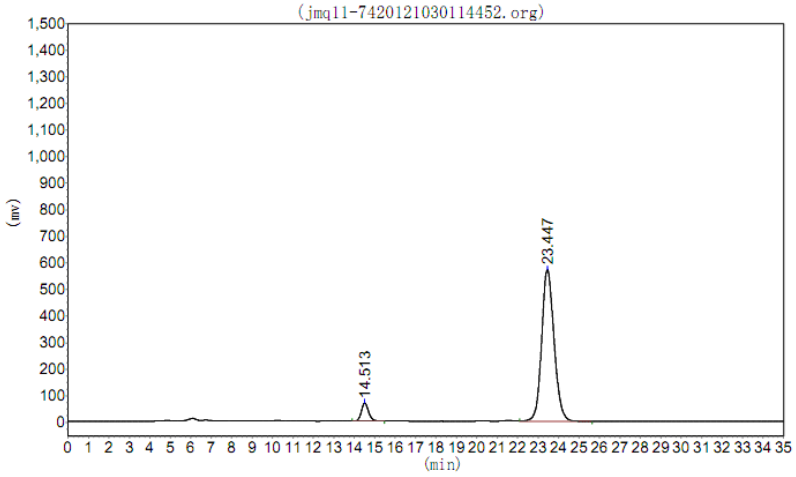

jmq11-74-400c
2012040Y75F
194.747
144.765
141.716
138.338
138.094
134.800
131.097
129.810
128.954
128.839
127.430
126.436
122.781
120.431
116.670
77.318
77.000
76.681
75.271
54.926
21.498
Br
O
OH
N
Ts
2m
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



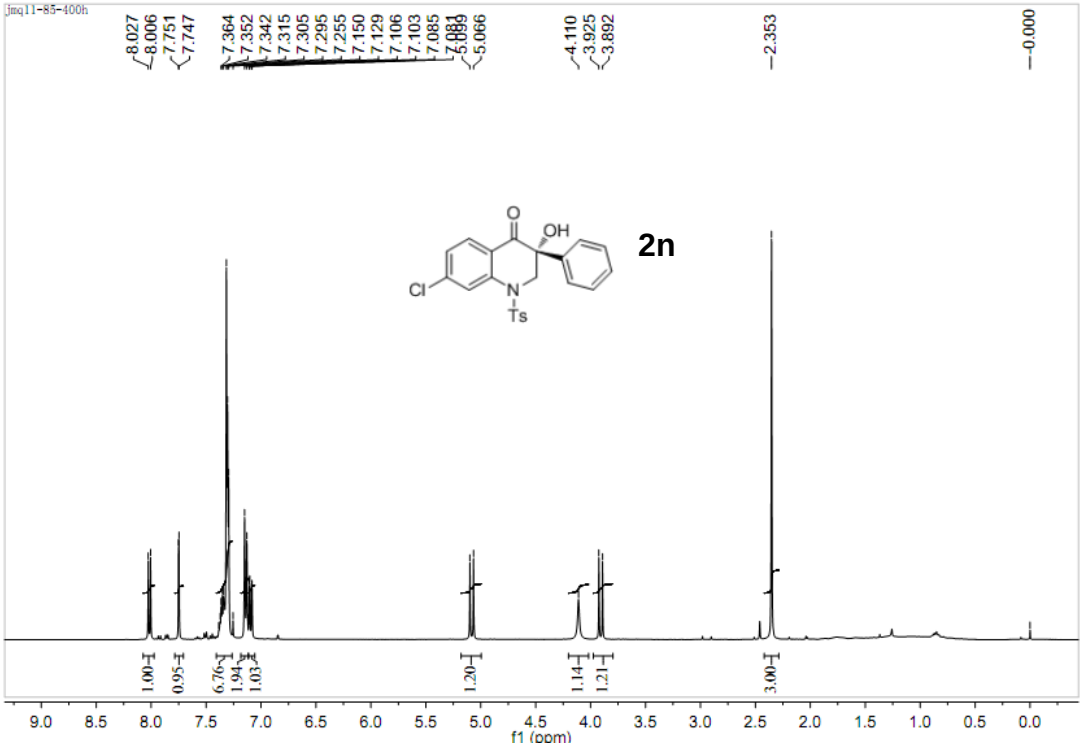
2m

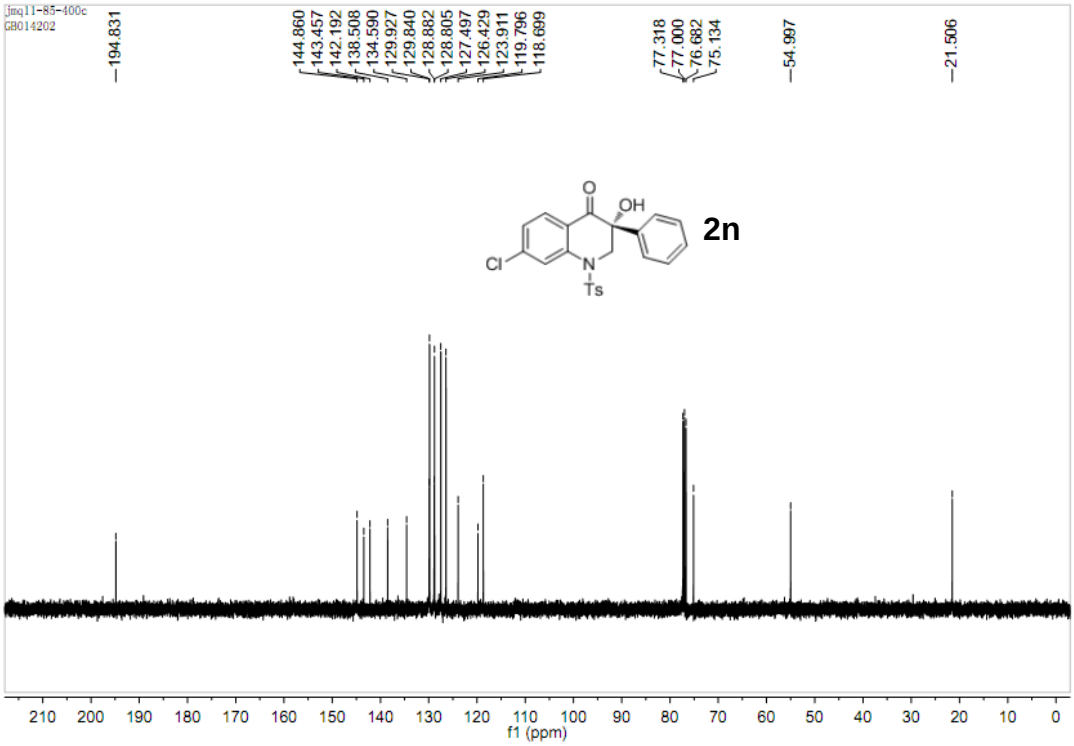


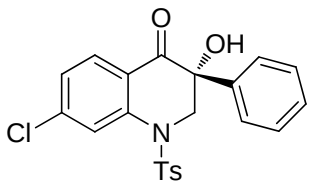
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	14.312	368645.781	8669413.000	49.9167
2	23.192	216862.031	8698363.000	50.0833
Total		585507.813	17367776.000	100.0000



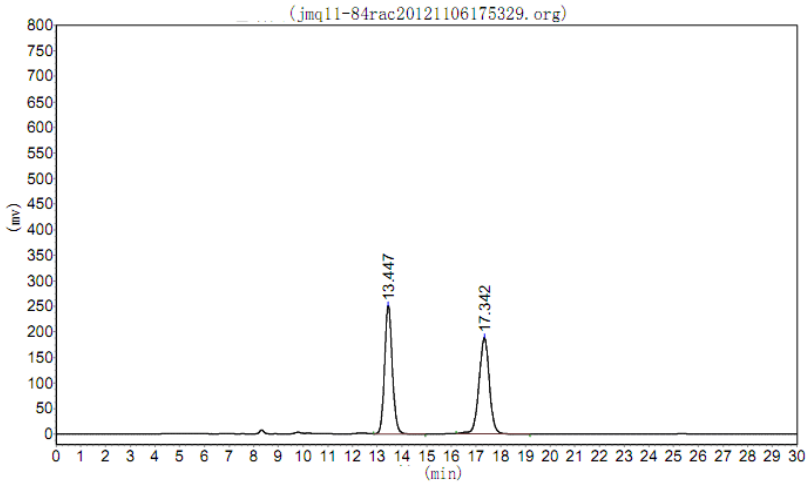
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	14.513	67570.469	1669176.875	6.4703
2	23.447	570392.375	24128388.000	93.5297
Total		637962.844	25797564.875	100.0000


jmq11-85-400h
8.027
8.006
7.751
7.747
7.364
7.352
7.342
7.315
7.305
7.295
7.255
7.150
7.129
7.106
7.103
7.085
5.066
4.110
3.925
3.892
2.353
0.000
2n
O
OH
Cl
N
Ts
1.00
0.95
6.76
1.94
1.03
1.20
1.14
1.21
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

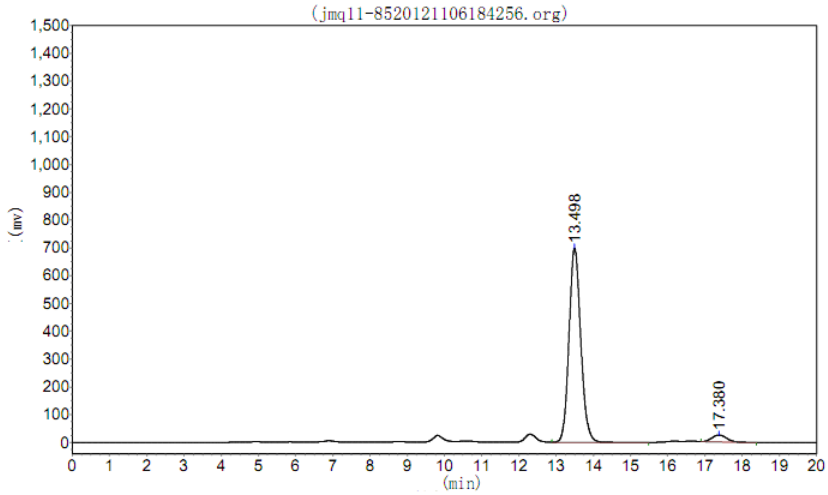

jmq11-85-400c
GB014202
194.831
144.860
143.457
142.192
138.508
134.590
129.927
129.840
128.882
128.805
127.497
126.429
123.911
119.796
118.699
77.318
77.000
76.682
75.134
54.997
21.506
2n
O
OH
Cl
N
Ts
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



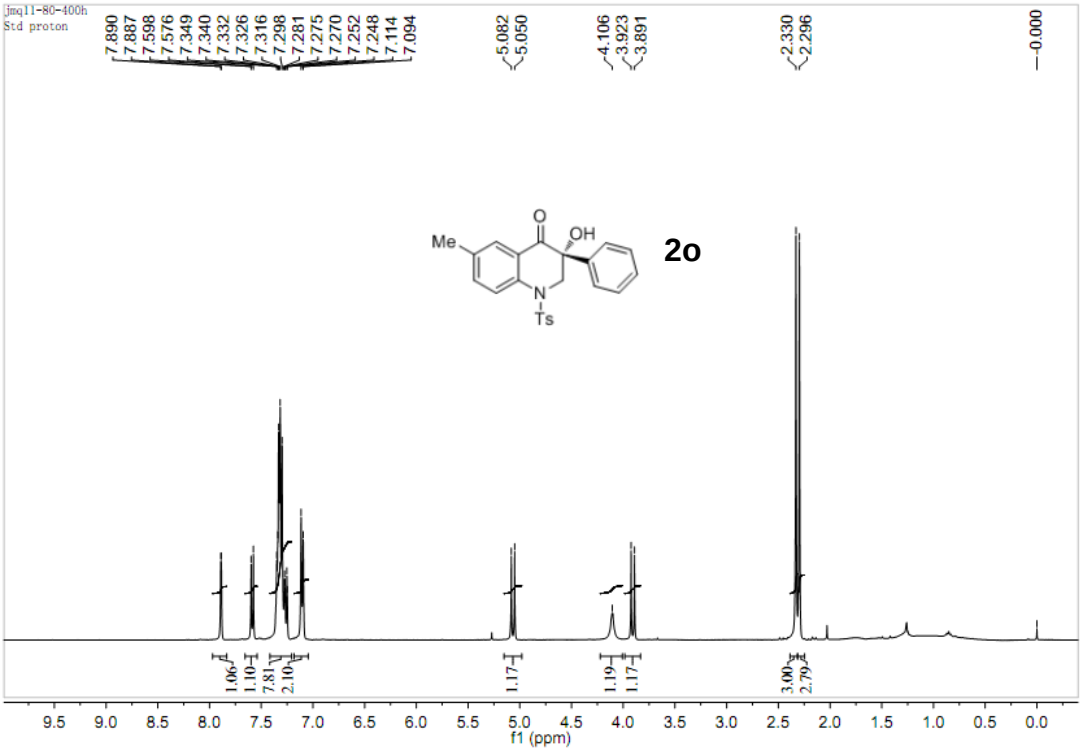
2n

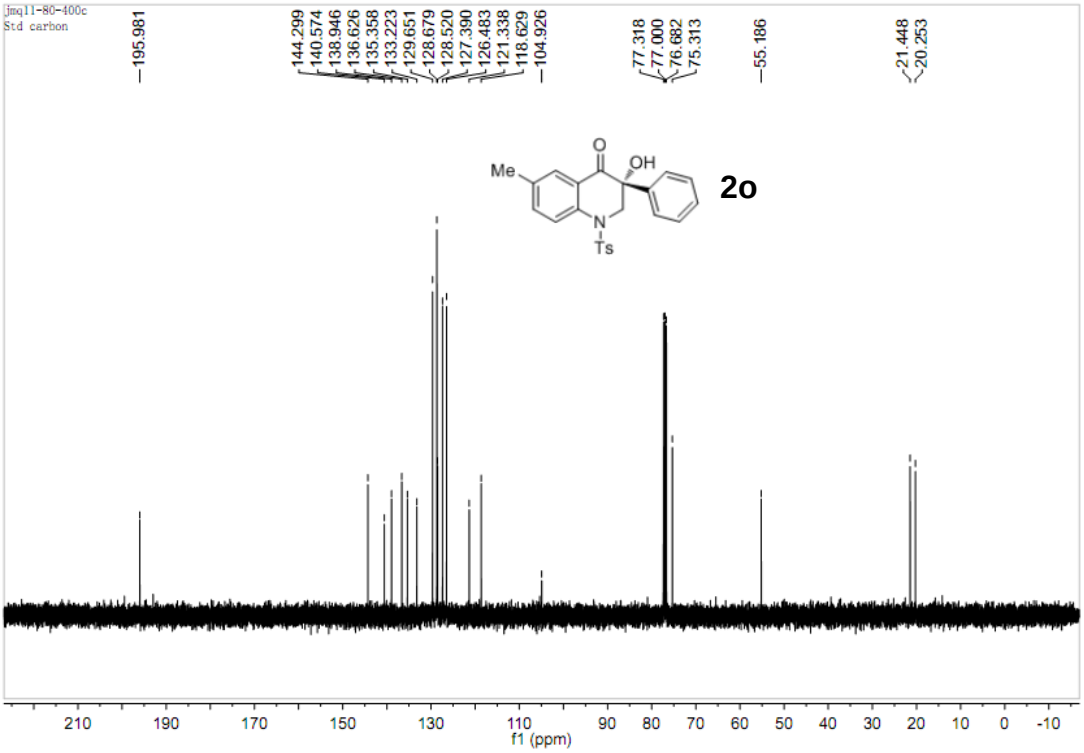


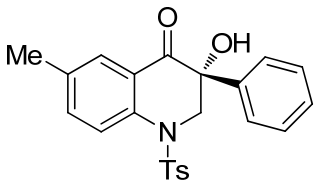
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	13.447	250577.859	5433581.500	49.9952
2	17.342	187626.828	5434626.500	50.0048
Total		438204.688	10868208.000	100.0000



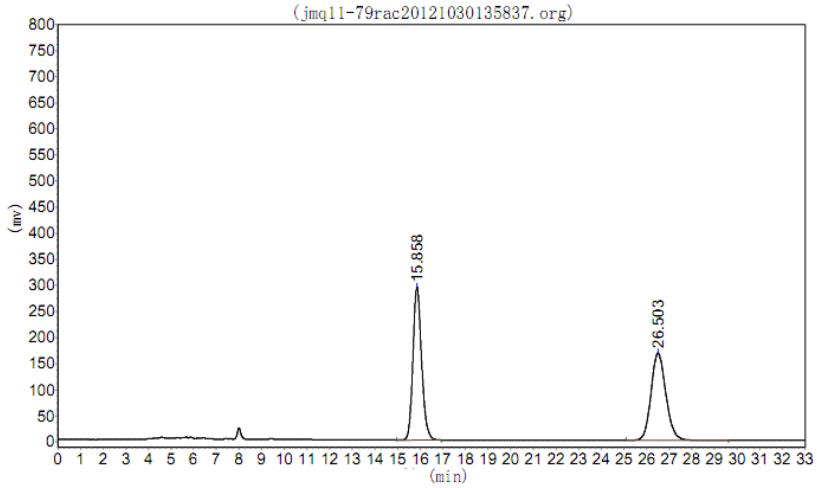
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	13.498	699549.250	15359561.000	95.8726
2	17.380	24984.908	661238.750	4.1274
Total		724534.158	16020799.750	100.0000


jmq11-80-400h
Std proton
7.890
7.887
7.598
7.576
7.349
7.340
7.332
7.326
7.316
7.298
7.281
7.275
7.270
7.252
7.248
7.114
7.094
5.082
5.050
4.106
3.923
3.891
2.330
2.296
0.000
Me
O
OH
N
Ts
2o
1.06
1.10
7.81
2.10
1.17
1.19
1.17
3.00
2.79
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

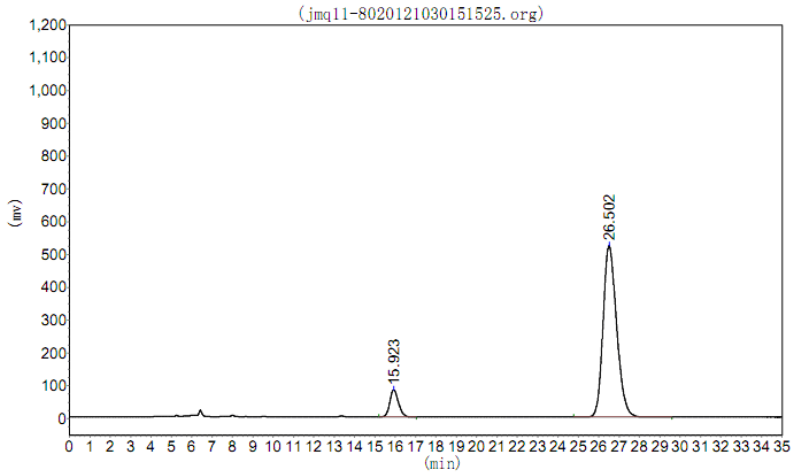

jmq11-80-400c
Std carbon
195.981
144.299
140.574
138.946
136.626
135.358
133.223
129.651
128.679
128.520
127.390
126.483
121.338
118.629
104.926
77.318
77.000
76.682
75.313
55.186
21.448
20.253
Me
O
OH
N
Ts
2o
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



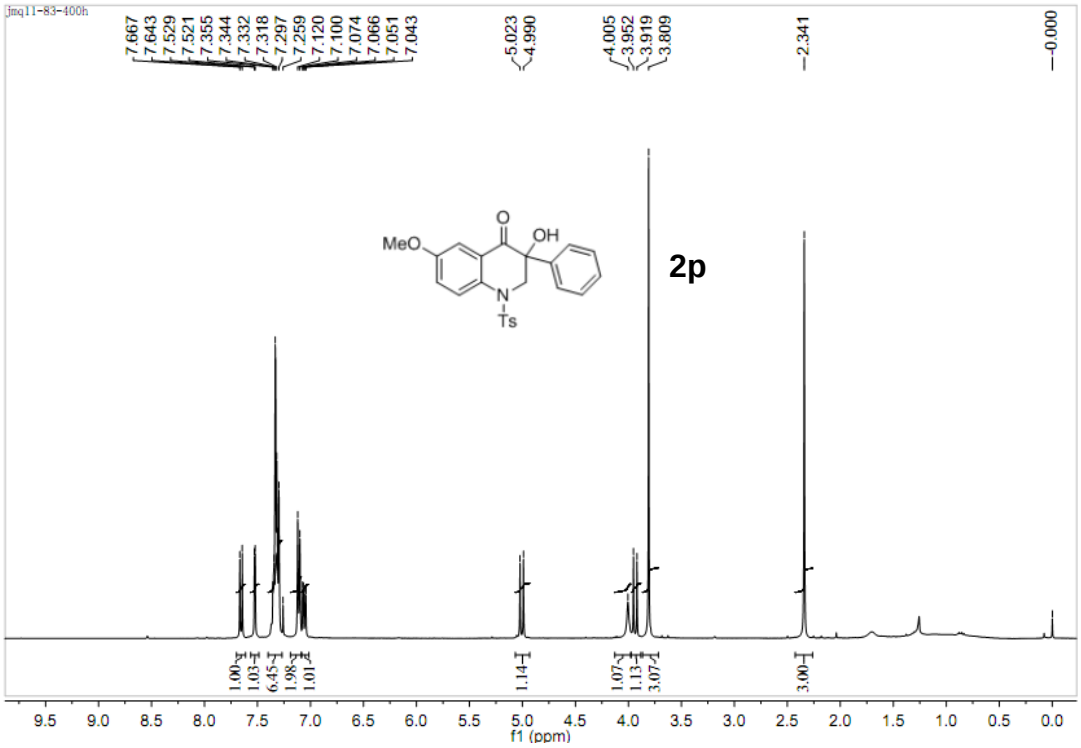
2o

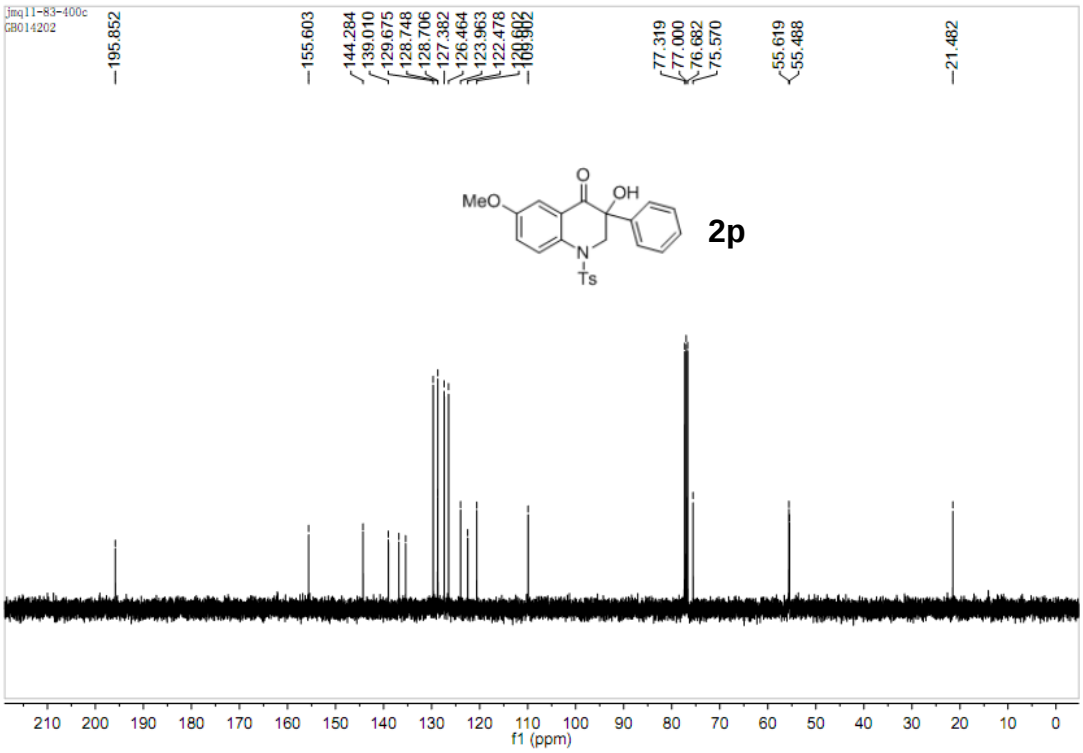


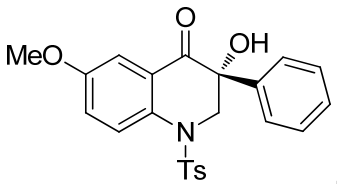
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	15.858	292948.031	7769294.500	50.6822
2	26.503	166899.109	7560126.000	49.3178
Total		459847.141	15329420.500	100.0000



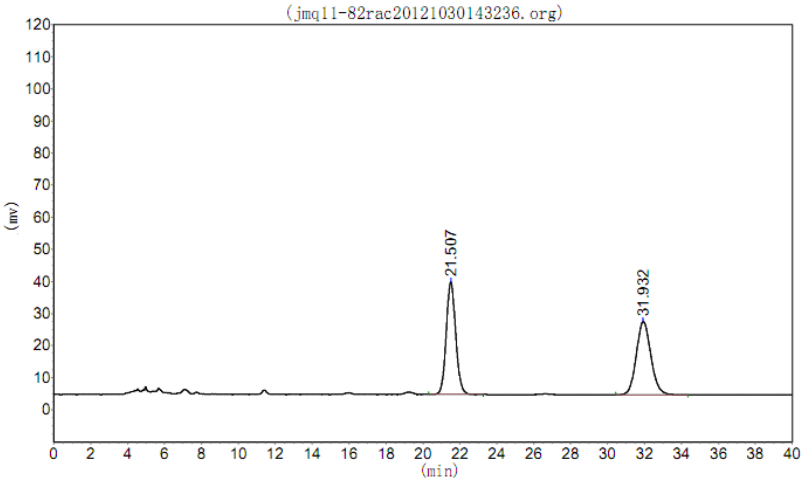
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	15.923	82491.375	2444420.750	9.1817
2	26.502	521391.625	24178464.000	90.8183
Total		603883.000	26622884.750	100.0000


jmq11-83-400h
7.667
7.643
7.529
7.521
7.355
7.344
7.332
7.318
7.297
7.259
7.120
7.100
7.074
7.066
7.051
7.043
5.023
4.990
4.005
3.952
3.919
3.809
2.341
0.000
MeO
O
OH
N
Ts
2p
1.00
1.03
6.45
1.98
1.01
1.14
1.07
1.13
3.07
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

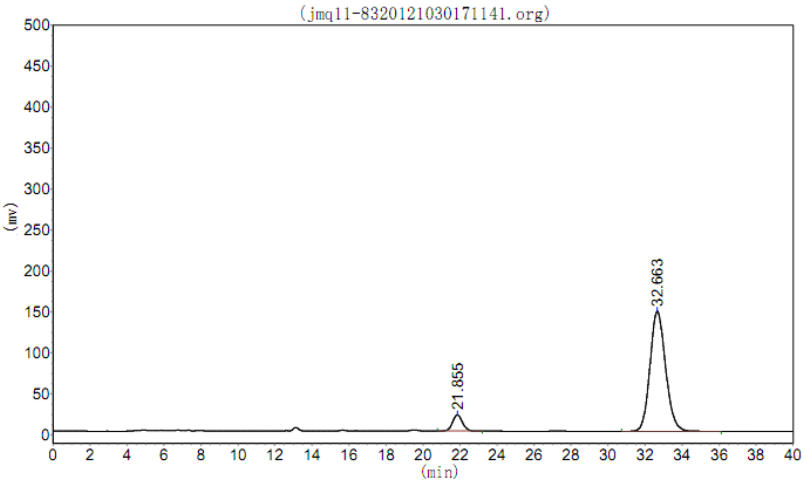

jmq11-83-400c
CB014202
195.852
155.603
144.284
139.010
129.675
128.748
128.706
127.382
126.464
123.963
122.478
77.319
77.000
76.682
75.570
55.619
55.488
21.482
MeO
O
OH
N
Ts
2p
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



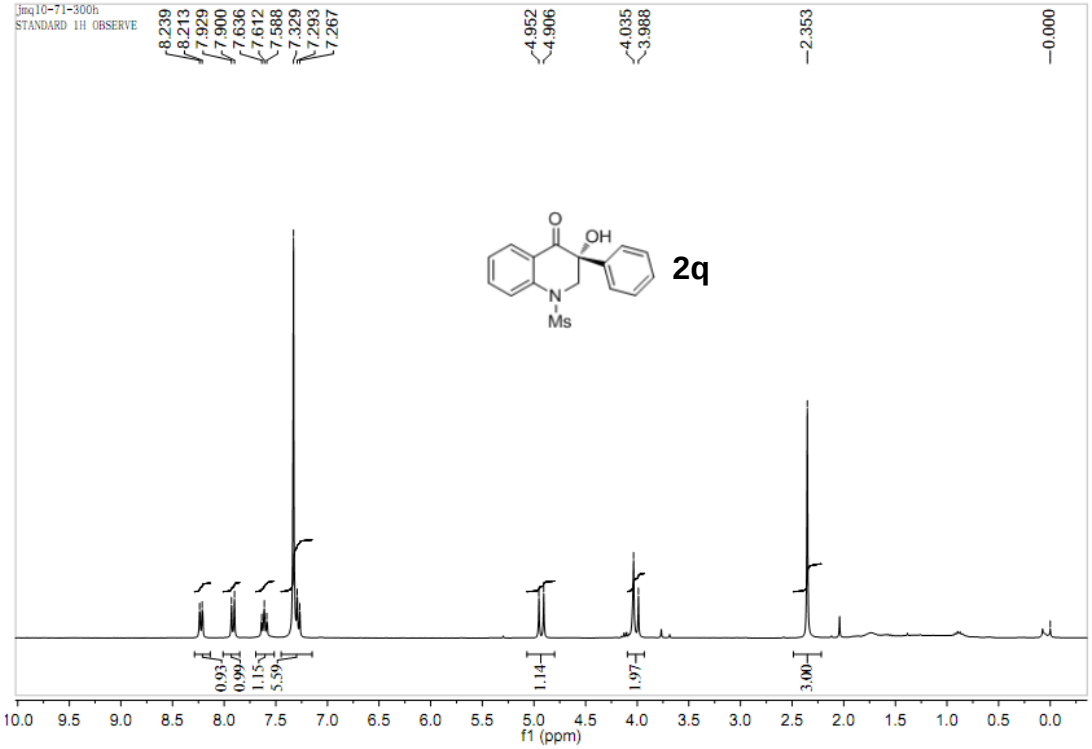
2p

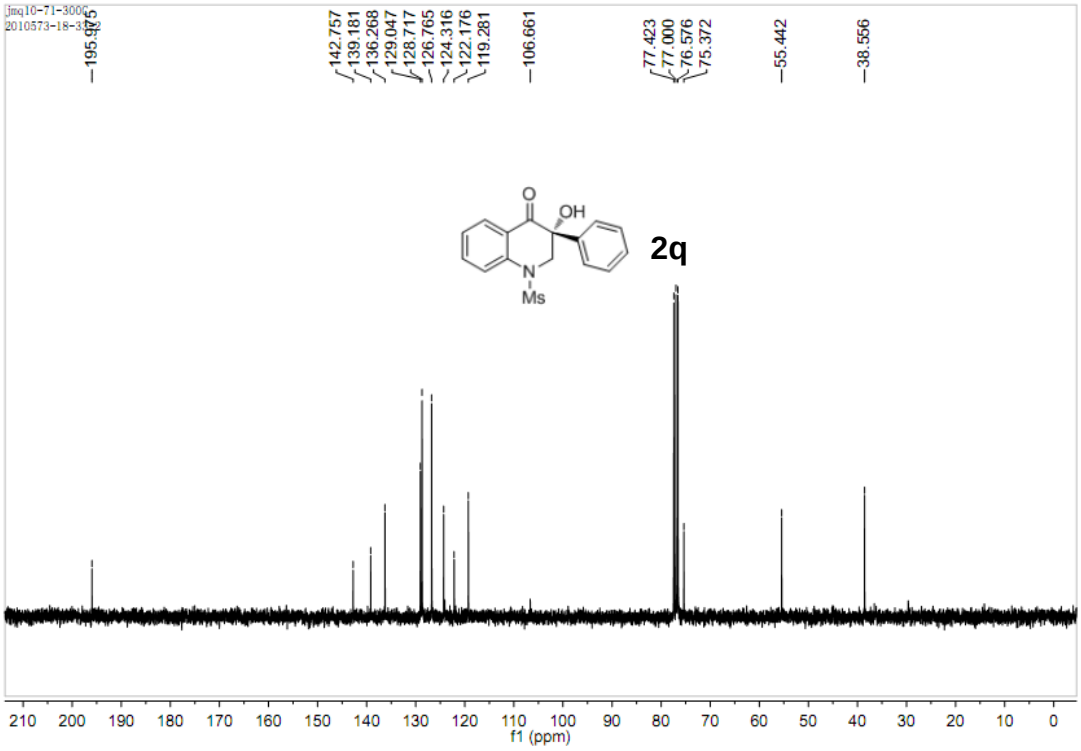


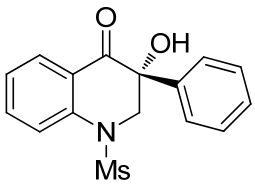
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	21.507	34987.582	1245221.250	49.9742
2	31.932	22751.240	1246507.375	50.0258
Total		57738.822	2491728.625	100.0000



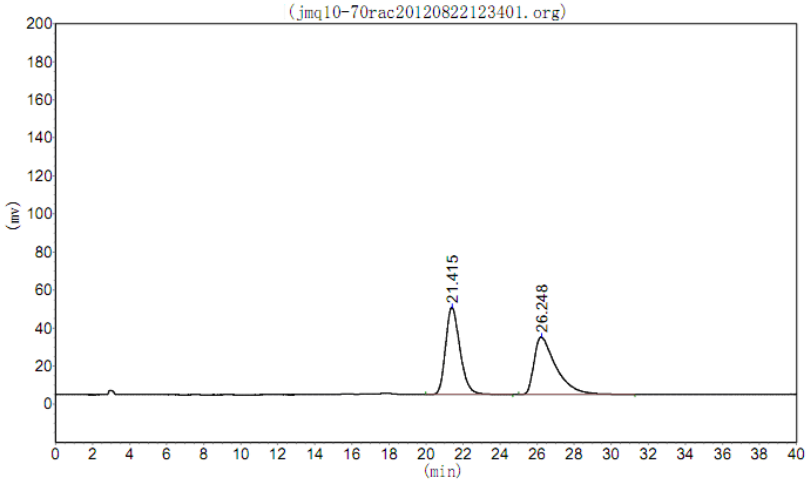
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	21.855	19792.014	744794.188	7.9787
2	32.663	146244.500	8590038.000	92.0213
Total		166036.514	9334832.188	100.0000


jmq10-71-300h
STANDARD 1H OBSERVE
8.239
8.213
7.929
7.900
7.636
7.612
7.588
7.329
7.293
7.267
4.952
4.906
4.035
3.988
2.353
0.000
O
OH
N
Ms
2q
0.93
0.99
1.15
5.59
1.14
1.97
3.00
f1 (ppm)

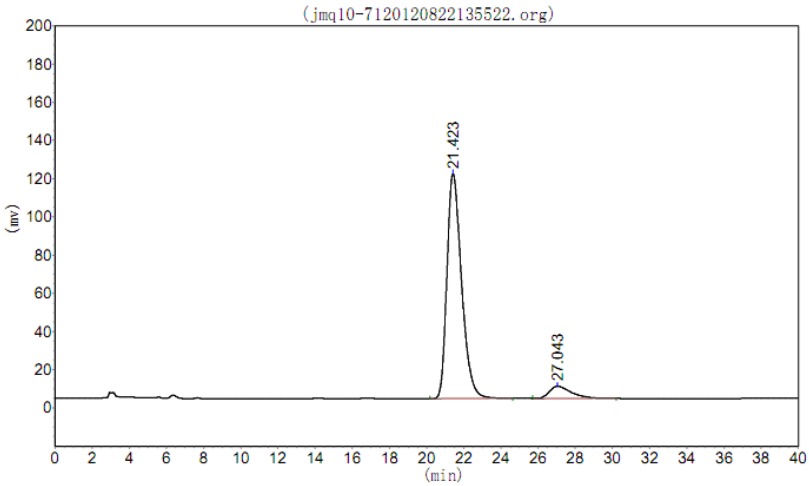

jmq10-71-300h
2010573-18-3
195.975
142.757
139.181
136.268
129.047
128.717
126.765
124.316
122.176
119.281
106.661
77.423
77.000
76.576
75.372
55.442
38.556
O
OH
N
Ms
2q
f1 (ppm)



2q



Peak No.	R. Time	Peak Height	Peak Area	Percent
1	21.415	45691.738	2464644.250	49.9831
2	26.248	30177.953	2466311.750	50.0169
Total		75869.691	4930956.000	100.0000



Peak No.	R. Time	Peak Height	Peak Area	Percent
1	21.423	117737.063	6411694.500	92.4096
2	27.043	6454.137	526651.063	7.5904
Total		124191.200	6938345.563	100.0000