Supporting Information

Cooperative Catalysis of Carbenes and Lewis Acids for the Highly Enantioselective Synthesis of Dihydroquinolones via In Situ Generation of Aza-*Ortho*-Quinone Methides and Enolates Intermediates

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I. General information:

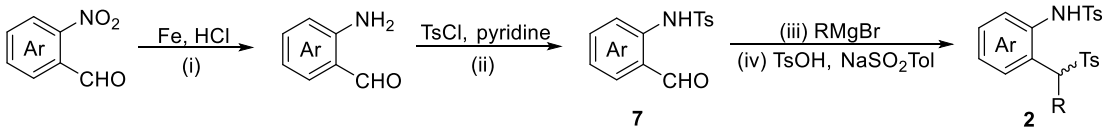
Commercially available materials purchased from regent company were used as received, except aldehydes that were purified *via* distillation or column chromatography prior to use. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker (300 MHz) spectrometer. Chemical shifts were recorded in parts per million (ppm, δ) relative to chloroform (δ = 7.26, singlet). ^{1}H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), dd (doublet of doublets), m (multiplets), and etc. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br). Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker (300 MHz) (75 MHz) spectrometer. High resolution mass spectrometry (HRMS) analysis was performed

using electrospray ionization (ESI) with a quadrupole-time of flight (QTOF) mass analyzer. The determination of *ee* was performed *via* chiral HPLC analysis using Agilent G7129A HPLC workstation. *X*-ray crystallography analysis was performed on XtaLAB PRO *X*-ray diffraction meter. Optical rotations were measured using a 10 mL cell with a 10 cm path length on a Shanghai Shenguang WZZ-2A polarimeter and are reported as follows: $[\alpha]^{rt}_D$ (*c* in g per 100 mL solvent). Analytical thin-layer chromatography (TLC) was carried out on GF254 pre-coated silica gel plate (0.2 mm thickness). Visualization was performed using a UV lamp.

II. Preparation of substrates

2-(Tosylmethyl)anilines **1** and *α*-Chloro aldehyde **2** were prepared according to the reported procedure. A typical procedure for the synthesis of starting material is shown below.

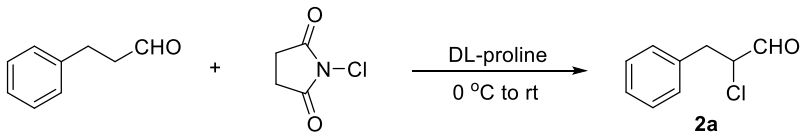
A typical method for synthesis of substrates 2-(Tosylmethyl)anilines **1**[1]**:**



(iii) Under N_2 condition, a solution of Grignard reagent (2.5 equiv.) was slowly added to aldehyde **7** (9.0 mmol) in dry THF (10 mL). After being stirred at room temperature for 3 h, the reaction mixture was quenched by saturated NH_4Cl (20 mL) and extracted with DCM. The combined extracts were washed with brine, then dried over Na_2SO_4, filtered and concentrated. The resulting crude solid was used in next step without purification.

(iv) $TolSO_2Na$ (1.25 equiv.) and TsOH (1.75 equiv.) were placed in a dried Schlenk tube, and dry DCM (20 mL) was added. The resulting mixture was stirred at room temperature for 5 min. Then, the solution (15 mL) of the crude product diaryl methanols in DCM was added and stirred for 1.5 h. The reaction mixture was quenched and adjusted to pH = 8 by a saturated $NaHCO_3$. After extracted with DCM, the combined extracts were washed with 1 M HCl and brine, then dried over Na_2SO4, filtered and concentrated. The resulting crude solid was purified on silica gel column chromatography (eluent: 3/1 (v/v) ethyl acetate/petroleum ether) to afford the desired product as a white or brown solid (67%-84% yield).

Typical method for synthesis of α-Chloro aldehyde **2a**[2]**:**

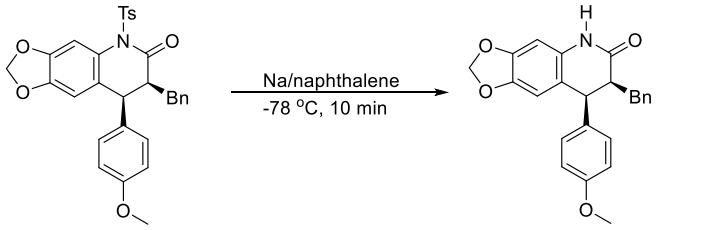


To a stirred solution of 3-Phenylpropionaldehyde (1.34 g, 10 mmol) in CH_2Cl_2 (40 mL) was added DL-proline (230 mg, 2 mmol) and NCS (1.33 g, 10 mmol) at 0 ℃. The reaction mixture was stirred at 0 ℃ for 1 h, and then allowed to reach rt and stirred for additional 1.5 h. The reaction mixture was quenched by addition of pentane (50 mL), filtered through a short plug of celite, the organic phase was concentrated under reduced pressure and the residue was subjected to column chromatography directly using hexane/ether (4:1) as eluent to afford the desired product **2a** as a colorless oil (1.09 g, 65% yield).

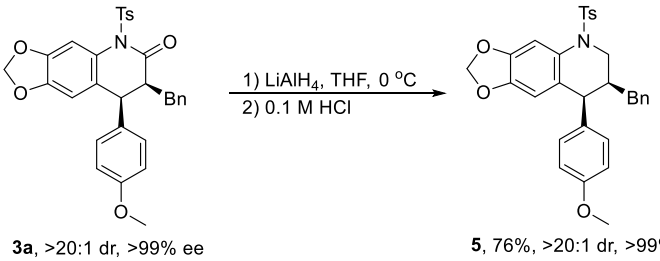
III. General procedure for the catalytic synthesis of products 3

To a dry schlenk reaction tube equipped with a magnetic stir bar, was added N-(6-((4-methoxyphenyl)(tosyl)methyl)benzo[d][1,3]dioxol-5-yl)-4-methylbenzenesulfonamide **1a** (56.5 mg, 0.1 mmol), α-Chloro aldehyde **2a** (33.6 mg, 0.2 mmol), NHC Cat. **A** (8.4 mg, 0.02 mmol), Cs_2CO_3 (97.5 mg, 0.3 mmol) and LiF (1.3 mg, 0.05 mmol). The schlenk tube was then evacuated and refilled with dry N_2. Anhydrous DCM (1 mL) was added. The mixture was stirred at rt for 24 h. Solvent was removed under reduced pressure, and the residue was purified via column chromatography on silica gel with hexane/EtOAc (typically 10:1) as eluent to afford the products **3a** (47 mg, 84% yield).

IV: Procedure for the synthetic transformations of the product 3a

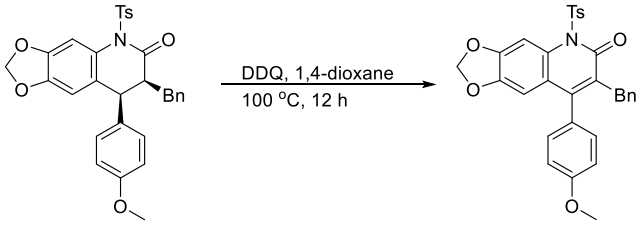


To a solution **3a** (108.2 mg, 0.20 mmol, 1.0 equiv) in 2 mL of THF was added 0.4 mL Na/naphthalene THF solution (the Na/naphthalene solution was prepared with 5 mmol Na, 5 mmol naphthalene in 3 mL THF), and the reaction was stirred at -78 °C for 10 minutes. Then H_2O (2 mL) was added to quench the reaction and the resulting mixture was extracted with CH_2Cl_2 (1 mL X 2). The combined organic layer was dried over Na_2SO_4, filtered and concentrated to dryness under reduced pressure at 40 °C. The residue was purified through column chromatography on silica gel (petroleum ether/ethyl acetate = 8:1 to 3:1) to afford the desired product **4** as a white solid in 91% yield (70.4 mg).



To a stirred solution of **3a** (108.2 mg, 0.20 mmol, 1.0 equiv) in THF (1.0 mL) at 0 °C, under N_2 atmosphere, was dropwise added $LiAlH_4$ (22.8 mg, 0.6 mmol, 3.0 equiv) in dry THF (1 mL). The reaction was stirred at 0 °C for 2 h. Then the solution was quenched with an 0.1 M HCl solution. The aqueous phase was extracted three times with EtOAc. The combined organic phases were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was

purified through column chromatography on silica gel (petroleum ether/ethyl acetate = 6:1) to afford **5** (80.1 mg, 76%).



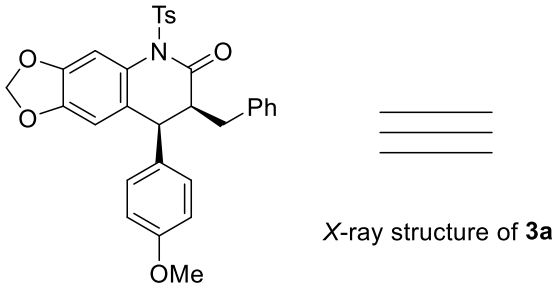
3a, >20:1 dr, >99% ee

6, 87% yield

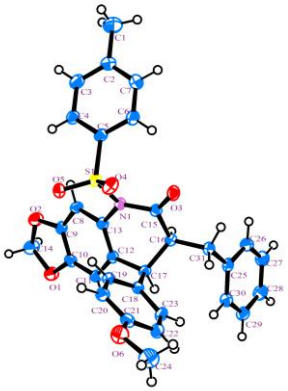
To a solution of **3a** (54.1 mg, 0.10 mmol, 1.0 equiv) in 1 mL of 1,4-dioxane was added DDQ (45.4 mg, 0.20 mmol, 2.0 equiv), and the reaction mixture was stirred at 100 °C for 12 h. Then H_2O (2 mL) was added and the resulting mixture was extracted with ethyl acetate (2 mL x 2). The combined organic layer was dried over Na_2SO_4, filtered and concentrated to dryness under reduced pressure at 40 °C. The residue was purified through column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1 to 5:1) to afford the desired product **6** as a white solid in 87% yield (46.8 mg).

V: Stereochemistry determination via *X*-ray crystallographic analysis:

Good quality crystal of **3a** (colorless needle crystal) was obtained by vaporization of a hexane/ethyl acetate solution of compound **3a**. CCDC 2291789 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



X-ray structure of **3a**

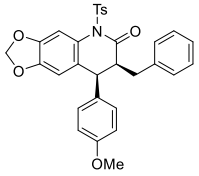


References cited in the SI:

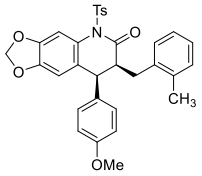
[1] X. Liu, K. Wang, W. Guo, Y. Liu and C. Li, An organic-base catalyzed asymmetric 1,4-addition of tritylthiol to in situ generated aza-o-quinone methides at the H_2O/DCM interface, *Chem. Commun.*, 2019, **55**, 2668-2671.

[2] (a) T. Borg, J. Danielsson, M. Mohiti, P. Restorp and P. Somfai, Diastereoselective Nucleophilic Addition to Aldehydes with Polar α- and α,β-Substituents, *Adv. Synth. Catal.*, 2011, **353**, 2022-2036; (b) Y. Jing, C. G. Daniliuc and A. Studer, Direct Conversion of Alcohols to α-Chloro Aldehydes and α-Chloro Ketones, *Org. Lett.*, 2014, **16**, 4932-4935.

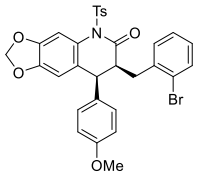
VI. Characterization of Products:



(7R,8S)-7-benzyl-8-(4-methoxyphenyl)-5-tosyl-7,8-dihydro-[1,3]dioxolo[4,5-g]quinolin-6(5H)-one (3a): Yield: 46 mg (87%), white solid, mp: 114-116 °C; ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.42 (s, 1H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 6.6 Hz, 1H), 7.26 – 7.16 (m, 2H), 7.04 (d, *J* = 6.3 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.69 (d, *J* = 8.7 Hz, 2H), 6.59 (s, 1H), 5.95 (d, *J* = 4.7 Hz, 2H), 3.77 (s, 3H), 3.73 (d, *J* = 5.7 Hz, 1H), 3.35 (dd, *J* = 14.7, 4.2 Hz, 1H), 3.24 – 2.99 (m, 1H), 2.49 (s, 4H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 171.88, 158.72, 146.58, 145.49, 145.11, 138.80, 136.36, 129.45, 129.42, 129.35, 129.07, 128.93, 128.63, 128.54, 127.36, 126.50, 114.15, 107.81, 105.05, 101.74, 55.20, 49.44, 44.34, 32.35, 21.77; HRMS (ESI, m/z): calcd. for $C_{31}H_{27}NO_6S[M+H]^+$ 542.1632, found 542.1631; $[\alpha]^{25}_D$ = +117.7 (*c* = 1.3, CH_2Cl_2); HPLC analysis: 99% ee (Chiralcel IB N-5, 20:80 ^{i}PrOH/Hexane, 0.5 mL/min), R_t (minor) = 28.4 min, R_t (major) = 26.6 min.

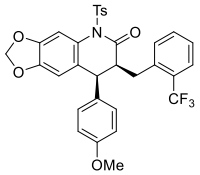


(7R,8S)-8-(4-methoxyphenyl)-7-(2-methylbenzyl)-5-tosyl-7,8-dihydro-[1,3]dioxolo[4,5-g]quinolin-6(5H)-one (3b): Yield: 49 mg (89%), white solid, mp: 124-126 °C; ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 8.1 Hz, 2H), 7.43 – 7.33 (m, 3H), 7.17 – 7.04 (m, 3H), 6.89 (dd, *J* = 16.6, 7.6 Hz, 3H), 6.69 (d, *J* = 8.5 Hz, 2H), 6.64 (s, 1H), 5.95 (d, *J* = 6.9 Hz, 2H), 3.78 (s, 4H), 3.33 (dd, *J* = 14.9, 4.1 Hz, 1H), 3.13 (dt, *J* = 10.0, 5.0 Hz, 1H), 2.61 (dd, *J* = 15.0, 10.0 Hz, 1H), 2.50 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (75 MHz, Chloroform-d) δ 172.09, 158.68, 146.56, 145.52, 145.12, 136.81, 136.55, 136.32, 130.65, 129.50, 129.44, 129.31, 129.18, 129.05, 128.38, 127.40, 126.58, 125.99, 114.24, 107.74, 105.14, 101.77, 55.22, 47.64, 44.36, 29.42, 21.79, 19.50; HRMS (ESI, m/z): calcd. for $C_{32}H_{29}NO_6S[M+H]^+$ 556.1789, found 556.1786; $[\alpha]^{25}_D$ = +225.3 (*c* = 0.3, CH_2Cl_2); HPLC analysis: 99% ee (Chiralcel IB N-5, 20:80 ^{i}PrOH/Hexane, 0.5 mL/min), R_t (minor) = 23.9 min, R_t (major) = 21.0 min.

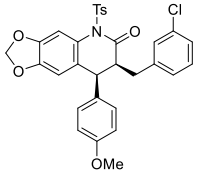


(7S,8S)-7-(2-bromobenzyl)-8-(4-methoxyphenyl)-5-tosyl-7,8-dihydro-[1,3]dioxolo[4,5-g]quinolin-6(5H)-one (3c): Yield: 53 mg (86%), white solid, mp: 117-119 °C; ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.48 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.41 – 7.31 (m, 3H), 7.19 – 7.11 (m, 1H), 7.05 (ddd, *J* = 10.2, 8.2, 2.0 Hz, 2H), 6.98 – 6.85 (m, 2H), 6.75 – 6.61 (m, 3H), 6.02 – 5.89 (m, 2H), 3.80 (d, *J* = 5.6 Hz, 1H), 3.77 (s, 3H), 3.35 (dd, *J* = 13.8, 5.8 Hz, 1H), 3.26 (dt, *J* = 7.4, 5.7 Hz, 1H), 2.76 (dd, *J* = 13.9, 7.3 Hz, 1H), 2.48 (s, 3H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 171.64, 158.71,

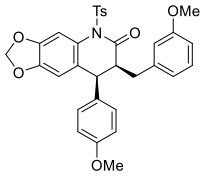
146.56, 145.53, 145.03, 138.35, 136.29, 132.90, 132.05, 129.45, 129.40, 129.29, 129.15, 128.40, 128.30, 127.32, 124.61, 114.24, 107.67, 105.24, 101.75, 55.21, 47.38, 45.46, 33.77, 21.76; HRMS (ESI, m/z): calcd. for $C_{31}H_{26}BrNO_6S[M+Na]^+$ 642.0557, found 642.0542; $[\alpha]^{25}_D$ = +187.3 (*c* = 0.4, CH_2Cl_2); HPLC analysis: 99% ee (Chiralcel IB N-5, 20:80 ^{i}PrOH/Hexane, 0.5 mL/min), R_t (minor) = 25.3 min, R_t (major) = 23.1 min.



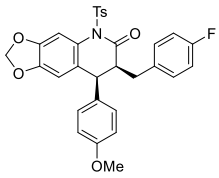
(7S,8S)-8-(4-methoxyphenyl)-5-tosyl-7-(2-(trifluoromethyl)benzyl)-7,8-dihydro-[1,3]dioxolo[4,5-g] quinolin-6(5H)-one (3d): Yield: 55 mg (91%), white solid, mp: 121-123 °C; ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.1 Hz, 2H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.54 – 7.21 (m, 6H), 6.91 (d, *J* = 8.4 Hz, 2H), 6.67 (d, *J* = 6.6 Hz, 3H), 5.94 (d, *J* = 3.8 Hz, 2H), 3.89 (d, *J* = 5.5 Hz, 1H), 3.76 (s, 3H), 3.47 (dd, *J* = 14.8, 5.9 Hz, 1H), 3.09 (q, *J* = 6.1 Hz, 1H), 2.87 (dd, *J* = 14.8, 6.8 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (75 MHz, Chloroform-d) δ 171.61, 158.73, 146.62, 145.62, 145.08, 137.85, 136.20, 132.16, 131.84, 129.46, 129.40, 129.12, 129.03, 128.42, 127.38, 126.74, 126.37, 114.26, 107.59, 105.35, 101.80, 55.19, 49.02, 45.58, 29.98, 21.74; HRMS (ESI, m/z): calcd. for $C_{35}H_{29}F_3NO_6S[M+H]^+$, found 556.1786; $[\alpha]^{25}_D$ = +211.5 (*c* = 0.4, CH_2Cl_2); HPLC analysis: 99% ee (Chiralcel IB N-5, 20:80 ^{i}PrOH/Hexane, 0.5 mL/min), R_t (minor) = 20.5 min, R_t (major) = 18.1 min.



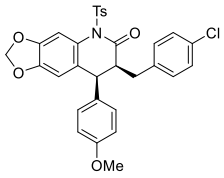
(7S,8S)-7-(3-chlorobenzyl)-8-(4-methoxyphenyl)-5-tosyl-7,8-dihydro-[1,3]dioxolo[4,5-g]quinolin-6 (5H)-one (3e): Yield: 50 mg (88%), white solid, mp: 132-134 °C; ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 8.1 Hz, 2H), 7.43 (s, 1H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 4.7 Hz, 2H), 7.03 (s, 1H), 6.96 – 6.85 (m, 3H), 6.71 (d, 2H), 6.60 (s, 1H), 5.93 (d, *J* = 5.9, 1.4 Hz, 2H), 3.76 (s, 3H), 3.73 (d, *J* = 5.7 Hz, 1H), 3.30 (dd, *J* = 14.6, 4.6 Hz, 1H), 3.18 – 3.05 (m, 1H), 2.48 (s, 4H); ^{13}C NMR (75 MHz, Chloroform-d) δ 171.53, 158.84, 146.67, 145.58, 145.23, 141.04, 136.28, 134.31, 129.91, 129.47, 129.42, 129.29, 129.01, 128.91, 128.46, 127.24, 127.09, 126.76, 114.26, 107.84, 105.06, 101.83, 55.22, 49.28, 44.74, 32.38, 21.77; HRMS (ESI, m/z): calcd. for $C_{31}H_{26}ClNO_6S[M+Na]^+$ 598.1062, found 598.1068; $[\alpha]^{25}_D$ = +174.5 (*c* = 0.4, CH_2Cl_2); HPLC analysis: 99% ee (Chiralcel IB N-5, 20:80 ^{i}PrOH/Hexane, 0.5 mL/min), R_t (minor) = 29.7 min, R_t (major) = 26.4 min.



(7R,8S)-7-(3-methoxybenzyl)-8-(4-methoxyphenyl)-5-tosyl-7,8-dihydro-[1,3]dioxolo[4,5-g]quinolin-6(5H)-one (3f): Yield: 53 mg (93%), white solid, mp: 138-140 °C; ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 3H), 7.28 (s, 1H), 6.95 (d, *J* = 8.5 Hz, 2H), 6.76 – 6.63 (m, 3H), 6.54 (s, 1H), 5.97 (d, *J* = 6.7 Hz, 2H), 3.77 (s, 4H), 3.70 (s, 3H), 3.33 – 3.18 (m, 2H), 2.73 (dt, *J* = 12.1, 5.7 Hz, 1H), 2.49 (s, 3H); ^{13}C NMR (75 MHz, Chloroform-d) δ 171.72, 158.86, 153.38, 146.66, 145.62, 145.14, 136.36, 136.13, 130.28, 129.43, 129.31, 129.25, 129.14, 128.25, 127.05, 125.15, 121.30, 115.48, 114.30, 107.66, 105.12, 101.79, 56.22, 55.25, 46.97, 45.76, 31.95, 21.75; HRMS (ESI, m/z): calcd. for $C_{32}H_{29}NO_7S[M+H]^+$, found 556.1786; $[\alpha]^{25}_D$ = +154.5 (*c* = 0.4, CH_2Cl_2); HPLC analysis: 99% ee (Chiralcel IB N-5, 20:80 ^{i}PrOH/Hexane, 0.5 mL/min), R_t (minor) = 39.6 min, R_t (major) = 29.4 min.

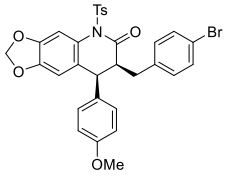


(7S,8S)-7-(4-fluorobenzyl)-8-(4-methoxyphenyl)-5-tosyl-7,8-dihydro-[1,3]dioxolo[4,5-g]quinolin-6(5H)-one (3g): Yield: 49 mg (88%), white solid, mp: 148-150 °C; ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.4 Hz, 2H), 7.41 (s, 1H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.00 – 6.90 (m, 4H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.72 – 6.64 (m, 2H), 6.60 (s, 1H), 6.00 – 5.91 (m, 2H), 3.77 (s, 3H), 3.70 (d, *J* = 5.8 Hz, 1H), 3.28 (dd, *J* = 14.6, 4.6 Hz, 1H), 3.14 – 3.01 (m, 1H), 2.49 (s, 4H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.72, 161.55 (d, *J* = 242.9 Hz), 158.76, 146.62, 145.54, 145.16, 136.30, 134.35 (d, *J* = 3.3 Hz), 130.34 (d, *J* = 7.8 Hz), 129.43, 129.25, 129.07, 128.96, 128.47, 127.19, 115.41 (d, *J* = 21.0 Hz), 114.20, 107.77, 105.06, 101.77, 55.21, 49.52, 44.52, 31.75, 21.77; HRMS (ESI, m/z): calcd. for $C_{31}H_{26}FNO_6S[M+Na]^+$ 582.1358, found 582.1348; $[\alpha]^{25}_D$ = +203.1 (*c* = 0.4, CH_2Cl_2); HPLC analysis: 99% ee (Chiralcel IB N-5, 20:80 ^{i}PrOH/Hexane, 0.5 mL/min), R_t (minor) = 32.9 min, R_t (major) = 26.5 min.

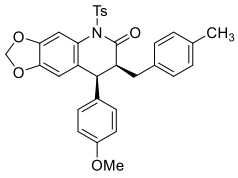


(7S,8S)-7-(4-chlorobenzyl)-8-(4-methoxyphenyl)-5-tosyl-7,8-dihydro-[1,3]dioxolo[4,5-g]quinolin-6(5H)-one (3h): Yield: 52 mg (90%), white solid, mp: 143-145 °C; ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.4 Hz, 2H), 7.44 – 7.31 (m, 3H), 7.25 – 7.18 (m, 2H), 6.95 (d, *J* = 8.4 Hz, 2H), 6.89 – 6.81 (m, 2H), 6.73 – 6.63 (m, 2H), 6.60 (s, 1H), 5.96 (dd, *J* = 6.2, 1.4 Hz, 2H), 3.77 (s, 3H), 3.69 (d, *J* = 5.8 Hz, 1H), 3.27 (dd, *J* = 14.6, 4.6 Hz, 1H), 3.14 – 3.02 (m, 1H), 2.49 (s, 4H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 171.60, 158.79, 146.64, 145.16, 137.28, 136.30, 132.26, 130.28, 129.42, 129.25,

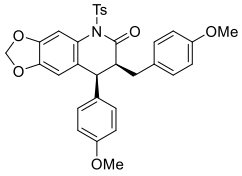
128.88, 128.72, 128.45, 127.11, 114.21, 107.77, 105.05, 101.78, 55.21, 49.34, 44.57, 31.96, 21.77; HRMS (ESI, m/z): calcd. for $C_{31}H_{26}ClNO_6S[M+Na]^+$ 598.1062, found 598.1048; $[\alpha]^{25}_D$ = +190.6 (*c* = 0.4, CH_2Cl_2); HPLC analysis: 99% ee (Chiralcel IB N-5, 20:80 ^{i}PrOH/Hexane, 0.5 mL/min), R_t (minor) = 41.8 min, R_t (major) = 33.7 min.



(7S,8S)-7-(4-bromobenzyl)-8-(4-methoxyphenyl)-5-tosyl-7,8-dihydro-[1,3]dioxolo[4,5-g]quinolin-6(5H)-one (3i): Yield: 49 mg (79%), white solid, mp: 152-154 ^{o}C; ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.4 Hz, 2H), 7.44 – 7.31 (m, 5H), 6.94 – 6.81 (m, 4H), 6.75 – 6.64 (m, 2H), 6.60 (s, 1H), 6.00 – 5.91 (m, 2H), 3.76 (s, 3H), 3.70 (d, *J* = 5.7 Hz, 1H), 3.25 (dd, *J* = 14.6, 4.6 Hz, 1H), 3.14 – 3.02 (m, 1H), 2.48 (s, 4H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 171.59, 158.80, 146.65, 145.57, 145.20, 137.85, 136.28, 131.68, 130.71, 129.45, 129.42, 129.27, 128.88, 128.46, 127.11, 120.31, 114.22, 107.80, 105.05, 101.80, 55.21, 49.27, 44.61, 32.08, 21.78; HRMS (ESI, m/z): calcd. for $C_{31}H_{26}BrNO_6S[M+Na]^+$ 642.0557, found 642.0541; $[\alpha]^{25}_D$ = +156.7 (*c* = 0.4, CH_2Cl_2); HPLC analysis: 99% ee (Chiralcel IB N-5, 20:80 ^{i}PrOH/Hexane, 0.5 mL/min), R_t (minor) = 45.8 min, R_t (major) = 34.2 min.

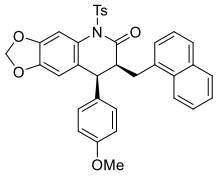


(7R,8S)-8-(4-methoxyphenyl)-7-(4-methylbenzyl)-5-tosyl-7,8-dihydro-[1,3]dioxolo[4,5-g]quinolin-6(5H)-one (3j): Yield: 46 mg (85%), white solid, mp: 134-136 ^{o}C; ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.42 (s, 1H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.07 (d, *J* = 7.8 Hz, 2H), 6.97 – 6.83 (m, 4H), 6.69 (d, *J* = 8.7 Hz, 2H), 6.59 (s, 1H), 5.99 – 5.91 (m, 2H), 3.77 (s, 4H), 3.31 (dd, *J* = 14.7, 4.2 Hz, 1H), 3.17 – 3.05 (m, 1H), 2.54 – 2.39 (m, 4H), 2.32 (s, 3H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 171.95, 158.70, 146.55, 145.47, 145.08, 136.40, 136.02, 135.61, 129.44, 129.40, 129.37, 129.31, 129.12, 128.79, 128.57, 127.44, 114.12, 107.82, 105.04, 101.73, 55.20, 49.51, 44.22, 31.85, 21.76, 21.05; HRMS (ESI, m/z): calcd. for $C_{32}H_{29}NO_6S[M+Na]^+$ 578.1608, found 578.1594; $[\alpha]^{25}_D$ = +211.7 (*c* = 0.3, CH_2Cl_2); HPLC analysis: 99% ee (Chiralcel IB N-5, 20:80 ^{i}PrOH/Hexane, 0.5 mL/min), R_t (minor) = 26.8 min, R_t (major) = 25.1 min.

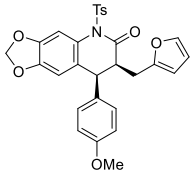


(7S,8S)-7-(4-methoxybenzyl)-8-(4-methoxyphenyl)-5-tosyl-7,8-dihydro-[1,3]dioxolo[4,5-g]quinolin-6(5H)-one (3k): Yield: 50 mg (89%), white solid, mp: 165-167 ^{o}C; ^{1}H NMR (300 MHz, Chloroform-*d*)

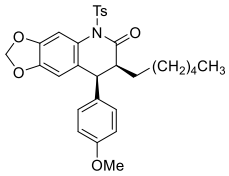
δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.42 (s, 1H), 7.36 (d, *J* = 8.2 Hz, 2H), 6.97 – 6.85 (m, 4H), 6.80 (d, *J* = 8.6 Hz, 2H), 6.68 (d, *J* = 8.7 Hz, 2H), 6.59 (s, 1H), 5.95 (d, *J* = 4.9 Hz, 2H), 3.77 (d, *J* = 4.0 Hz, 6H), 3.73 (d, *J* = 5.7 Hz, 1H), 3.28 (dd, *J* = 14.6, 4.3 Hz, 1H), 3.14 – 3.01 (m, 1H), 2.48 (s, 3H), 2.47 – 2.35 (m, 1H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 171.97, 158.70, 158.20, 146.55, 145.48, 145.09, 136.38, 130.62, 129.88, 129.43, 129.41, 129.34, 129.14, 128.54, 127.43, 114.13, 114.01, 107.81, 105.04, 101.74, 55.27, 55.20, 49.62, 44.26, 31.46, 21.77; HRMS (ESI, m/z): calcd. for $C_{37}H_{29}NO_7S[M+Na]^+$ 594.1557, found 594.1546; $[\alpha]^{25}_D$ = +126.3 (*c* = 0.4, CH_2Cl_2); HPLC analysis: 99% ee (Chiralcel IA, 30:70 ^{i}PrOH/Hexane, 0.5 mL/min), R_t (minor) = 55.4 min, R_t (major) = 31.7 min.



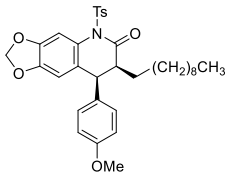
(7S,8S)-8-(4-methoxyphenyl)-7-(naphthalen-1-ylmethyl)-5-tosyl-7,8-dihydro-[1,3]dioxolo[4,5-g]quinolin-6(5H)-one (3l): Yield: 54 mg (92%), white solid, mp: 108-110 °C; ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.30 (d, *J* = 8.4 Hz, 1H), 8.04 (d, *J* = 8.1 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.67 – 7.30 (m, 7H), 6.93 (dd, *J* = 15.5, 8.0 Hz, 3H), 6.71 (d, *J* = 8.2 Hz, 2H), 6.54 (s, 1H), 5.90 (s, 2H), 3.89 (dd, *J* = 14.7, 3.7 Hz, 1H), 3.80 (s, 3H), 3.68 (d, *J* = 5.8 Hz, 1H), 3.28 – 3.16 (m, 1H), 2.92 (dd, *J* = 14.8, 9.8 Hz, 1H), 2.52 (s, 3H); ^{13}C NMR (75 MHz, Chloroform-d) δ 171.83, 158.77, 146.54, 145.48, 145.24, 136.21, 134.07, 132.66, 131.14, 131.07, 129.58, 129.47, 129.22, 129.17, 128.14, 127.26, 127.02, 126.83, 125.59, 125.44, 123.88, 114.37, 107.68, 105.05, 101.74, 55.25, 48.06, 44.67, 29.34, 21.81; HRMS (ESI, m/z): calcd. for $C_{35}H_{29}NO_6S[M+H]^+$ 592.1789, found 592.1799; $[\alpha]^{25}_D$ = +142.8 (*c* = 0.4, CH_2Cl_2); HPLC analysis: 99% ee (Chiralcel IB N-5, 20:80 ^{i}PrOH/Hexane, 0.5 mL/min), R_t (minor) = 35.2 min, R_t (major) = 29.5 min.



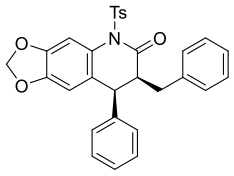
(7S,8S)-7-(furan-2-ylmethyl)-8-(4-methoxyphenyl)-5-tosyl-7,8-dihydro-[1,3]dioxolo[4,5-g]quinolin-6(5H)-one (3m): Yield: 38 mg (71%), white solid, mp: 237-239 °C; ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.44 (s, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 1.9 Hz, 1H), 7.00 – 6.89 (m, 2H), 6.75 – 6.66 (m, 2H), 6.64 (s, 1H), 6.29 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.05 – 5.92 (m, 3H), 3.87 (d, *J* = 5.3 Hz, 1H), 3.75 (s, 3H), 3.30 – 3.14 (m, 2H), 2.64 – 2.52 (m, 1H), 2.47 (s, 3H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 171.14, 158.83, 152.71, 146.70, 145.57, 145.11, 141.52, 136.45, 129.61, 129.42, 129.31, 128.85, 128.56, 127.07, 114.08, 110.33, 107.98, 107.07, 105.01, 101.77, 55.18, 47.45, 44.62, 25.15, 21.73; HRMS (ESI, m/z): calcd. for $C_{29}H_{25}NO_7S[M+Na]^+$ 554.1244, found 554.1249; $[\alpha]^{25}_D$ = +214.2 (*c* = 0.2, CH_2Cl_2); HPLC analysis: 99% ee (Chiralcel IB N-5, 20:80 ^{i}PrOH/Hexane, 0.5 mL/min), R_t (minor) = 27.2 min, R_t (major) = 24.3 min.



(7S,8S)-7-hexyl-8-(4-methoxyphenyl)-5-tosyl-7,8-dihydro-[1,3]dioxolo[4,5-g]quinolin-6(5H)-one (3n): Yield: 34 mg (63%), white solid, mp: 159-161 °C; ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.43 (s, 1H), 7.31 (d, *J* = 7.9 Hz, 2H), 6.97 – 6.83 (m, 2H), 6.70 (s, 1H), 6.69 – 6.60 (m, 2H), 6.04 – 5.83 (m, 2H), 3.93 (d, *J* = 5.5 Hz, 1H), 3.74 (s, 3H), 2.77 – 2.60 (m, 1H), 2.45 (s, 3H), 1.89 – 1.74 (m, 1H), 1.41 – 1.30 (m, 3H), 1.24 (m, 6H), 0.89 – 0.79 (m, 3H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 172.22, 158.66, 146.55, 145.50, 144.88, 136.52, 129.32, 129.29, 129.08, 128.89, 127.42, 114.00, 107.73, 105.21, 101.74, 55.17, 48.42, 45.21, 31.59, 29.18, 27.41, 26.67, 22.57, 21.71, 14.04; HRMS (ESI, m/z): calcd. for $C_{30}H_{33}NO_6S[M+Na]^+$, found 578.1594; $[\alpha]^{25}_D$ = +189.5 (*c* = 0.2, CH_2Cl_2); HPLC analysis: 99% ee (Chiralcel IB N-5, 20:80 ^{i}PrOH/Hexane, 0.5 mL/min), R_t (minor) = 26.0 min, R_t (major) = 18.0 min.

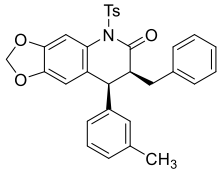


(7S,8S)-7-decyl-8-(4-methoxyphenyl)-5-tosyl-7,8-dihydro-[1,3]dioxolo[4,5-g]quinolin-6(5H)-one (3o): Yield: 40 mg (68%), colorless oil; ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.43 (s, 1H), 7.31 (d, *J* = 8.2 Hz, 2H), 6.95 – 6.81 (m, 2H), 6.74 – 6.60 (m, 3H), 6.02 – 5.93 (m, 2H), 3.93 (d, *J* = 5.6 Hz, 1H), 3.74 (s, 3H), 2.69 (q, *J* = 6.6, 5.9 Hz, 1H), 2.45 (s, 3H), 1.86 – 1.74 (m, 1H), 1.31 – 1.18 (m, 17H), 0.88 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 172.22, 158.65, 146.55, 145.50, 144.87, 136.52, 129.32, 129.28, 129.07, 128.88, 127.42, 114.00, 107.73, 105.22, 101.73, 55.16, 48.42, 45.18, 31.90, 29.56, 29.50, 29.39, 29.31, 27.43, 26.64, 22.68, 21.71, 14.12; HRMS (ESI, m/z): calcd. for $C_{34}H_{41}NO_6S[M+Na]^+$ 614.2547, found 614.2533; $[\alpha]^{25}_D$ = +199.3 (*c* = 0.3, CH_2Cl_2); HPLC analysis: 99% ee (Chiralcel IB N-5, 20:80 ^{i}PrOH/Hexane, 0.5 mL/min), R_t (minor) = 23.7 min, R_t (major) = 16.1 min.

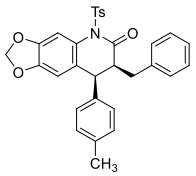


(7S,8S)-7-benzyl-8-phenyl-5-tosyl-7,8-dihydro-[1,3]dioxolo[4,5-g]quinolin-6(5H)-one (3p): Yield: 43 mg (85%), white solid, mp: 137-139 °C; ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.4 Hz, 2H), 7.43 (s, 1H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 2.2 Hz, 1H), 7.24 – 7.11 (m, 5H), 7.05 – 6.98 (m, 2H), 6.98 – 6.89 (m, 2H), 6.61 (s, 1H), 6.00 – 5.91 (m, 2H), 3.77 (d, *J* = 5.8 Hz, 1H), 3.36 (dd, *J* = 14.7, 4.2 Hz, 1H), 3.20 – 3.11 (m, 1H), 2.49 (s, 4H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 171.75, 146.66, 145.49, 145.14, 138.75, 137.12, 136.28, 129.52, 129.39, 129.07, 128.92, 128.79, 128.64, 128.23, 127.33, 126.94, 126.52, 107.88, 105.05, 101.76, 49.25, 45.05, 32.35, 21.77; HRMS (ESI, m/z):

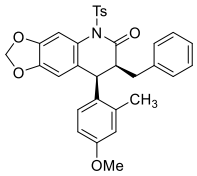
calcd. for $C_{30}H_{25}NO_5S[M+Na]^+$ 534.1346, found 534.1334; $[\alpha]^{25}_D$ = +242.3 (*c* = 0.3, CH_2Cl_2); HPLC analysis: 99% ee (Chiralcel IB N-5, 20:80 ^{i}PrOH/Hexane, 0.5 mL/min), R_t (minor) = 24.0 min, R_t (major) = 22.2 min.



(7S,8S)-7-benzyl-8-(m-tolyl)-5-tosyl-7,8-dihydro-[1,3]dioxolo[4,5-g]quinolin-6(5H)-one (3q): Yield: 39 mg (76%), white solid, mp: 121-123 ºC; ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 6.6 Hz, 1H), 7.25 – 7.18 (m, 2H), 7.08 – 7.00 (m, 4H), 6.97 (s, 1H), 6.76 – 6.69 (m, 1H), 6.62 (s, 1H), 6.00 – 5.91 (m, 2H), 3.76 (d, *J* = 5.8 Hz, 1H), 3.37 (dd, *J* = 14.7, 4.2 Hz, 1H), 3.20 – 3.07 (m, 1H), 2.53 (dd, *J* = 14.7, 10.1 Hz, 1H), 2.48 (s, 3H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 171.91, 146.62, 145.46, 145.05, 138.87, 138.59, 136.93, 136.62, 129.47, 129.27, 129.18, 128.95, 128.61, 128.18, 127.19, 126.49, 125.10, 107.91, 104.94, 101.74, 49.41, 44.97, 32.40, 21.76, 21.41; HRMS (ESI, m/z): calcd. for $C_{31}H_{27}NO_5S[M+Na]^+$ 548.1503, found 548.1493; $[\alpha]^{25}_D$ = +200.3 (*c* = 0.3, CH_2Cl_2); HPLC analysis: 99% ee (Chiralcel IB N-5, 20:80 ^{i}PrOH/Hexane, 0.5 mL/min), R_t (minor) = 17.2 min, R_t (major) = 14.8 min.

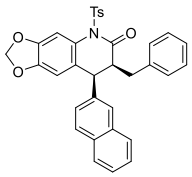


(7S,8S)-7-benzyl-8-(p-tolyl)-5-tosyl-7,8-dihydro-[1,3]dioxolo[4,5-g]quinolin-6(5H)-one (3r): Yield: 41 mg (78%), white solid, mp: 122-124 ºC; ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.4 Hz, 2H), 7.42 (s, 1H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.28 (t, *J* = 2.0 Hz, 1H), 7.26 – 7.19 (m, 2H), 7.07 – 6.99 (m, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 8.2 Hz, 2H), 6.60 (s, 1H), 6.02 – 5.80 (m, 2H), 3.74 (d, *J* = 5.7 Hz, 1H), 3.35 (dd, *J* = 14.6, 4.2 Hz, 1H), 3.20 – 3.07 (m, 1H), 2.60 – 2.40 (m, 4H), 2.29 (s, 3H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 171.84, 146.58, 145.47, 145.05, 138.86, 136.94, 136.37, 134.00, 129.46, 129.38, 128.94, 128.61, 128.09, 127.25, 126.48, 107.83, 105.04, 101.72, 49.37, 44.71, 32.35, 21.75, 21.04; HRMS (ESI, m/z): calcd. for $C_{31}H_{27}NO_5S[M+Na]^+$ 548.1503, found 548.1494; $[\alpha]^{25}_D$ = +197.3 (*c* = 0.3, CH_2Cl_2); HPLC analysis: 99% ee (Chiralcel IB N-5, 20:80 ^{i}PrOH/Hexane, 0.5 mL/min), R_t (minor) = 22.5 min, R_t (major) = 20.7 min.

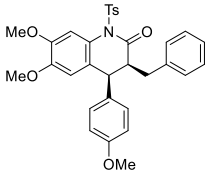


(7S,8S)-7-benzyl-8-(4-methoxy-2-methylphenyl)-5-tosyl-7,8-dihydro-[1,3]dioxolo[4,5-g]quinolin-6(5H)-one (3s): Yield: 29 mg (52%), white solid, mp: 113-115 ºC; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 8.5 Hz, 2H), 7.46 – 7.36 (m, 3H), 7.20 (d, *J* = 7.6 Hz, 3H), 6.90 – 6.81 (m, 2H), 6.72 (d, *J*

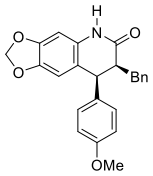
= 8.6 Hz, 1H), 6.67 (d, *J* = 2.8 Hz, 1H), 6.60 (s, 1H), 6.41 (dd, *J* = 8.7, 2.9 Hz, 1H), 5.94 (dd, *J* = 13.3, 1.4 Hz, 2H), 3.96 (d, *J* = 6.3 Hz, 1H), 3.76 (s, 3H), 3.28 (dd, *J* = 14.4, 4.7 Hz, 1H), 3.21 – 3.14 (m, 1H), 2.51 (s, 3H), 2.43 – 2.35 (m, 1H), 2.03 (s, 3H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 172.51, 158.18, 146.36, 145.39, 145.20, 138.49, 137.78, 136.34, 129.54, 129.46, 128.79, 128.58, 128.24, 127.95, 126.92, 126.49, 116.89, 111.71, 107.70, 105.08, 101.70, 55.08, 49.21, 39.10, 32.46, 21.78, 20.68; HRMS (ESI, m/z): calcd. for $C_{32}H_{29}NO_6S[M+Na]^+$ 578.1608, found 578.1600; $[\alpha]^{25}_D$ = +262.5 (*c* = 0.2, CH_2Cl_2); HPLC analysis: 99% ee (Chiralcel IB N-5, 20:80 ^{i}PrOH/Hexane, 0.5 mL/min), R_t (minor) = 24.8 min, R_t (major) = 22.8 min.



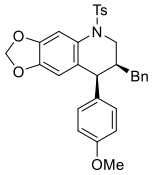
(7S,8S)-7-benzyl-8-(naphthalen-2-yl)-5-tosyl-7,8-dihydro-[1,3]dioxolo[4,5-g]quinolin-6(5H)-one (3t): Yield: 48 mg (86%), white solid, mp: 123-125 °C; ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 8.4 Hz, 2H), 7.83 – 7.73 (m, 1H), 7.65 (t, *J* = 7.8 Hz, 2H), 7.56 – 7.38 (m, 4H), 7.28 (d, *J* = 6.4 Hz, 1H), 7.25 – 7.22 (m, 2H), 7.20 (s, 1H), 7.15 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.08 – 7.00 (m, 2H), 6.71 (s, 1H), 5.97 (dd, *J* = 8.0, 1.4 Hz, 2H), 3.96 (d, *J* = 5.6 Hz, 1H), 3.45 (dd, *J* = 14.6, 4.3 Hz, 1H), 3.31 – 3.14 (m, 1H), 2.65 (dd, *J* = 14.7, 10.1 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 171.92, 146.74, 145.55, 145.00, 138.82, 136.45, 134.55, 133.33, 132.48, 129.40, 129.17, 128.93, 128.67, 128.50, 128.23, 127.44, 127.09, 126.93, 126.57, 126.38, 126.12, 126.08, 107.94, 105.24, 101.79, 49.50, 44.92, 32.62, 21.74; HRMS (ESI, m/z): calcd. for $C_{34}H_{27}NO_5S[M+Na]^+$ 584.1503, found 584.1496; $[\alpha]^{25}_D$ = +215.8 (*c* = 0.4, CH_2Cl_2); HPLC analysis: 99% ee (Chiralcel IB N-5, 20:80 ^{i}PrOH/Hexane, 0.5 mL/min), R_t (minor) = 26.5 min, R_t (major) = 22.5 min.



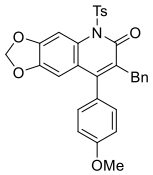
(3S,4S)-3-benzyl-6,7-dimethoxy-4-(4-methoxyphenyl)-1-tosyl-3,4-dihydroquinolin-2(1H)-one (3u): Yield: 48 mg (83%), white solid, mp: 108-110 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.4 Hz, 2H), 7.56 (s, 1H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 6.9 Hz, 1H), 7.26 – 7.17 (m, 2H), 7.05 (d, *J* = 6.8 Hz, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 6.62 (d, *J* = 8.7 Hz, 2H), 6.58 (s, 1H), 3.95 (s, 3H), 3.80 (s, 3H), 3.77 – 3.73 (m, 4H), 3.33 (dd, *J* = 14.7, 4.2 Hz, 1H), 3.23 – 3.14 (m, 1H), 2.49 (s, 3H), 2.45 – 2.37 (m, 1H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 171.78, 158.66, 147.54, 146.98, 145.07, 138.89, 136.29, 129.57, 129.42, 129.36, 129.31, 129.01, 128.62, 128.14, 126.45, 125.65, 114.07, 110.69, 107.76, 56.35, 56.05, 55.17, 49.57, 44.32, 32.31, 21.76; HRMS (ESI, m/z): calcd. for $C_{32}H_{31}NO_6S[M+Na]^+$ 580.1756, found 580.1765; $[\alpha]^{25}_D$ = +163.5 (*c* = 0.3, CH_2Cl_2); HPLC analysis: 99% ee (Chiralcel IH, 20:80 ^{i}PrOH/Hexane, 0.5 mL/min), R_t (minor) = 31.9 min, R_t (major) = 42.1 min.



(7S,8S)-7-benzyl-8-(4-methoxyphenyl)-7,8-dihydro-[1,3]dioxolo[4,5-g]quinolin-6(5H)-one (4): Yield: 49 mg (91%), white solid, mp: 116-118 ºC; ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.48 (s, 1H), 7.31 (t, *J* = 7.2 Hz, 2H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.17 – 7.08 (m, 2H), 7.05 – 6.99 (m, 2H), 6.85 – 6.71 (m, 2H), 6.51 (s, 1H), 6.39 (s, 1H), 5.85 (dd, *J* = 14.9, 1.4 Hz, 2H), 3.76 (s, 4H), 3.47 (dd, *J* = 14.5, 4.5 Hz, 1H), 3.29 (ddd, *J* = 10.6, 6.5, 4.3 Hz, 1H), 2.44 (dd, *J* = 14.6, 10.3 Hz, 1H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 172.06, 158.76, 147.07, 143.50, 139.74, 132.02, 130.16, 129.06, 128.46, 126.25, 121.22, 114.21, 108.42, 101.22, 97.80, 55.20, 46.14, 44.73, 31.75; HRMS (ESI, m/z): calcd. for $C_{24}H_{21}NO_4S[M+H]^+$ 388.1544, found 388.1558; $[\alpha]^{25}_D$ = +226.4 (*c* = 0.3, CH_2Cl_2); HPLC analysis: 99% ee (Chiralcel IB N-5, 20:80 ^{i}PrOH/Hexane, 0.5 mL/min), R_t (minor) = 23.9 min, R_t (major) = 18.0 min.

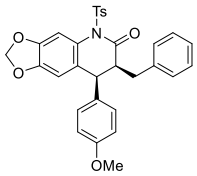


(7S,8S)-7-benzyl-8-(4-methoxyphenyl)-5-tosyl-5,6,7,8-tetrahydro-[1,3]dioxolo[4,5-g]quinoline (5): Yield: 41 mg (76%), white solid, mp: 115-117 ºC; ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 7.4 Hz, 1H), 7.24 (s, 1H), 7.22 – 7.12 (m, 3H), 6.83 (s, 1H), 6.71 (q, *J* = 8.8 Hz, 4H), 6.57 (s, 1H), 5.85 (dd, *J* = 10.3, 1.4 Hz, 2H), 4.05 (d, *J* = 11.7 Hz, 1H), 3.77 (s, 3H), 3.49 (d, *J* = 10.9 Hz, 1H), 3.15 (d, *J* = 12.0 Hz, 1H), 2.75 – 2.60 (m, 2H), 2.49 (s, 3H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 158.03, 146.64, 145.93, 143.51, 140.77, 137.97, 134.46, 133.12, 129.93, 129.39, 128.95, 128.50, 127.47, 127.43, 126.07, 113.94, 107.71, 101.42, 60.23, 55.23, 46.03, 45.27, 34.77, 21.63; HRMS (ESI, m/z): calcd. for $C_{31}H_{29}NO_5S[M+H]^+$ 528.1840, found 528.1824; $[\alpha]^{25}_D$ = +175.7 (*c* = 0.3, CH_2Cl_2); HPLC analysis: 99% ee (Chiralcel IB N-5, 20:80 ^{i}PrOH/Hexane, 0.5 mL/min), R_t (minor) = 26.4 min, R_t (major) = 24.2 min.

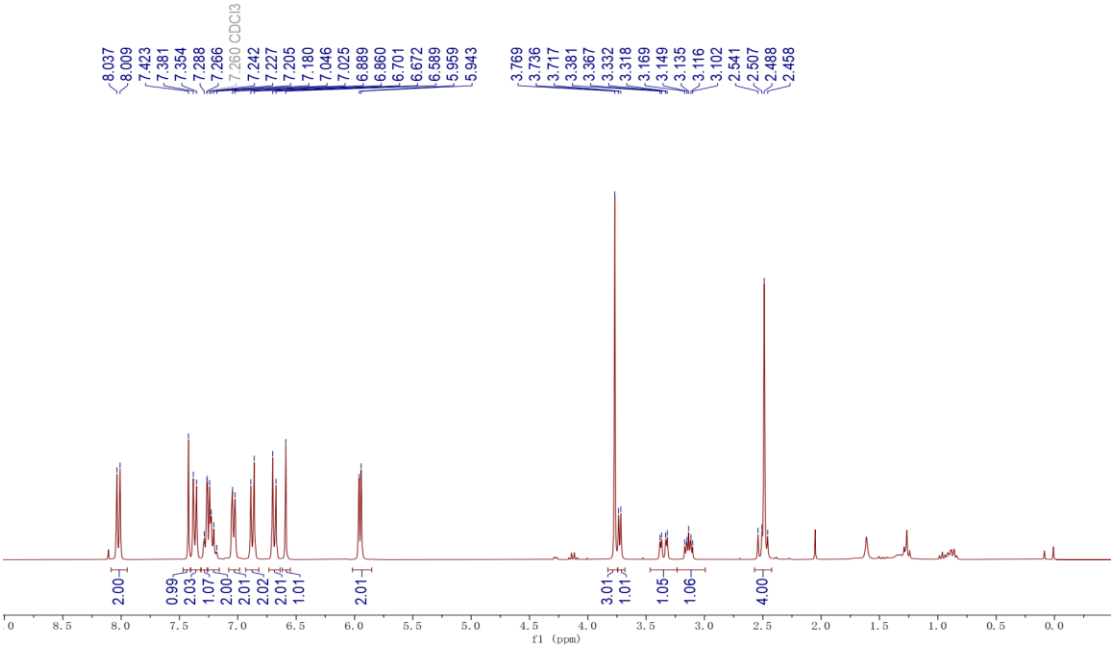


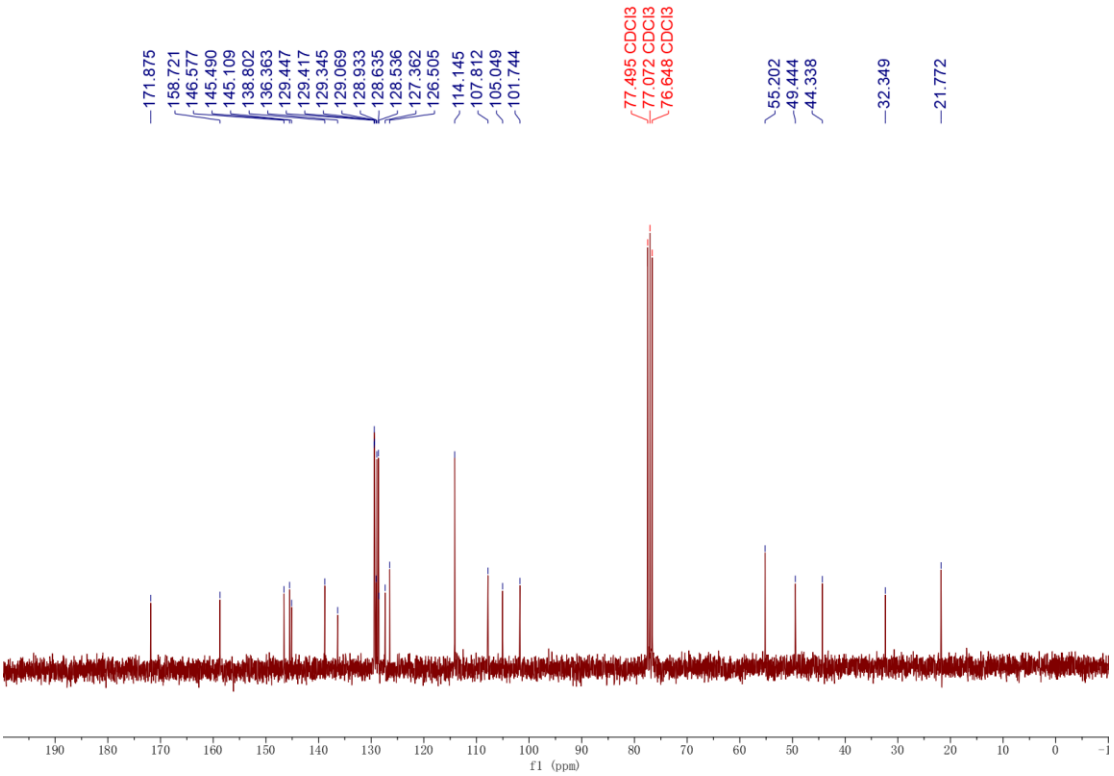
7-benzyl-8-(4-methoxyphenyl)-5-tosyl-[1,3]dioxolo[4,5-g]quinolin-6(5H)-one (6): Yield: 47 mg (87%), white solid, mp: 118-120 ºC; ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.18 – 7.09 (m, 4H), 7.07 – 7.01 (m, 2H), 7.00 – 6.93 (m, 2H), 6.90 (dd, *J* = 7.4, 2.1 Hz, 2H), 6.62 (s, 1H), 6.02 (s, 2H), 3.93 (s, 2H), 3.86 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 159.52, 154.16, 150.72, 150.46, 147.73, 144.80, 142.57, 139.71, 134.81, 130.43, 129.29, 129.07, 128.44, 128.15, 125.90, 124.41, 121.52, 114.06, 105.01, 102.28, 101.81, 55.36, 33.34, 21.73; HRMS (ESI, m/z): calcd. for $C_{31}H_{25}NO_6S[M+H]^+$ 540.1476, found 540.1491;

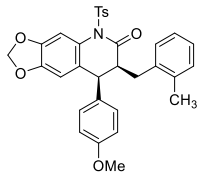
VII: ^{1}H, ^{13}C and HPLC spectra:



3a






Ts
N
O
O
O
CH3
OMe

3b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7.134
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7.088
7.072
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6.909
6.878
6.850
6.704
6.676
6.635
5.961
5.938
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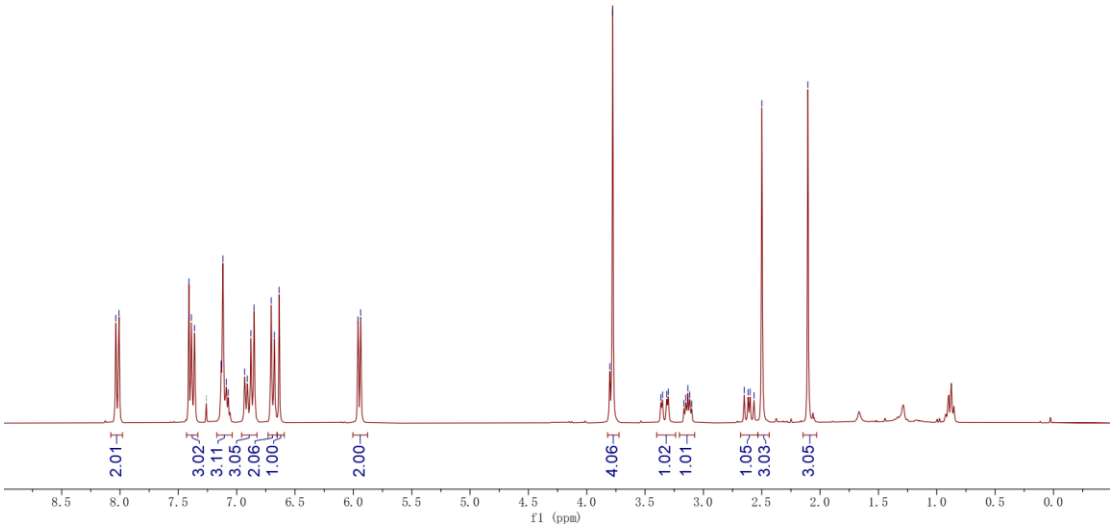
2.499
2.105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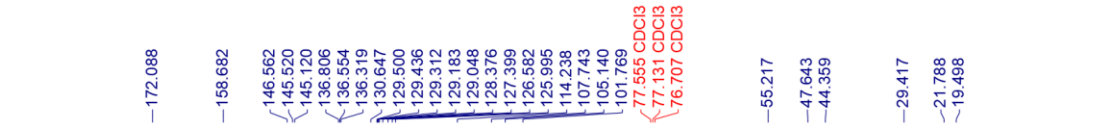
4.06
1.02
1.01
1.05
3.03
3.05
f1 (ppm)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129.048
128.376
127.399
126.582
125.995
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107.743
105.140
101.769
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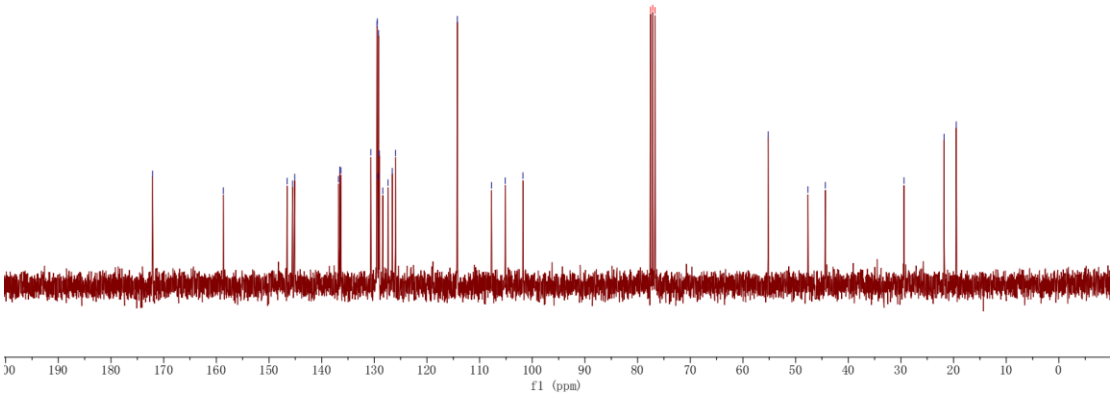
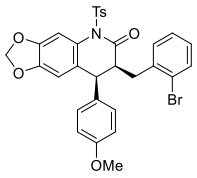
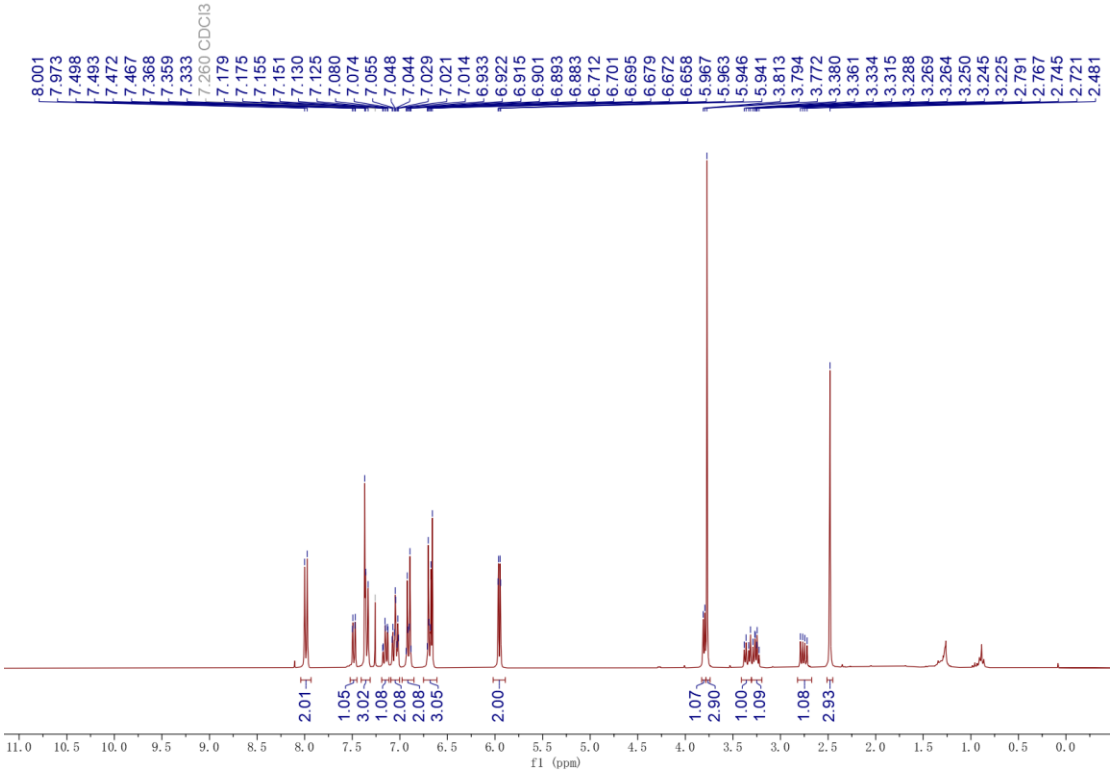
44.359
29.417
21.788
19.498


f1 (ppm)


Ts
N
O
O
O
Br
OMe

3c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7.029
7.021
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6.883
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6.658
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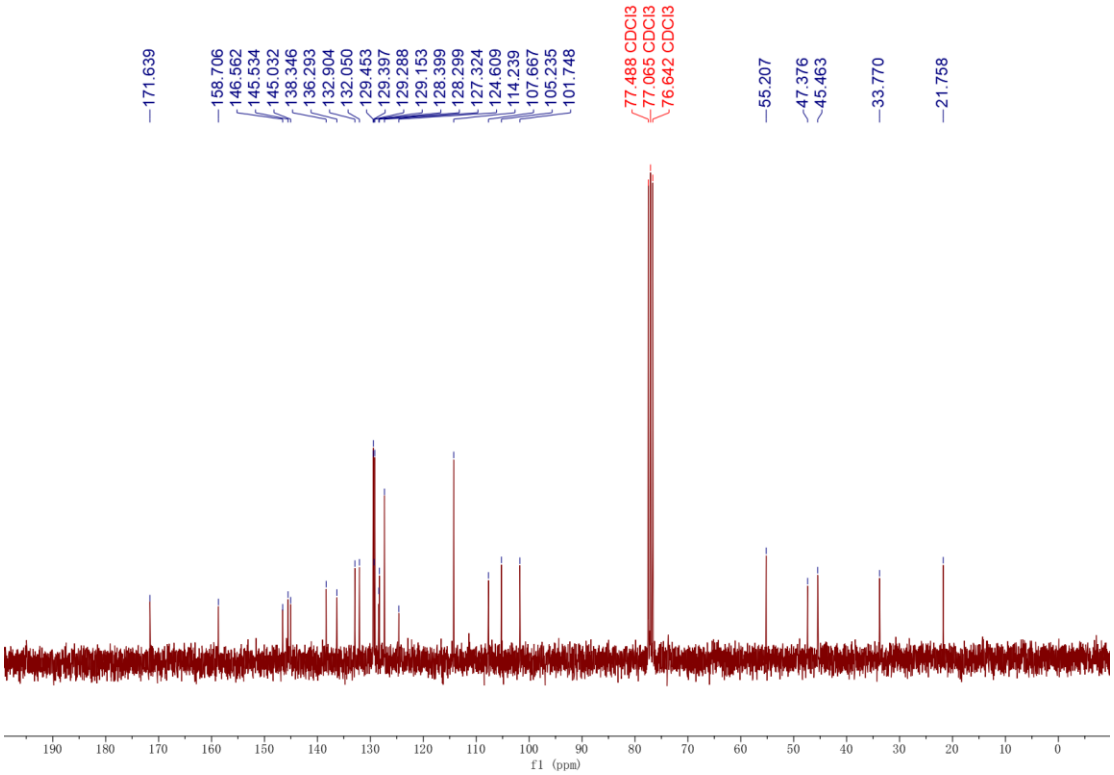
1.00
1.09
1.08
2.93
f1 (ppm)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127.324
124.609
114.239
107.667
105.235
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45.463
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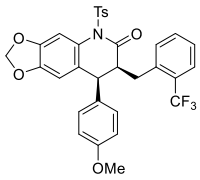
21.758
f1 (ppm)


Ts
N
O
O
O
CF3
OMe

3d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7.277
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7.235
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6.892
6.682
6.660
5.948
5.935
3.902
3.884
3.762
3.503
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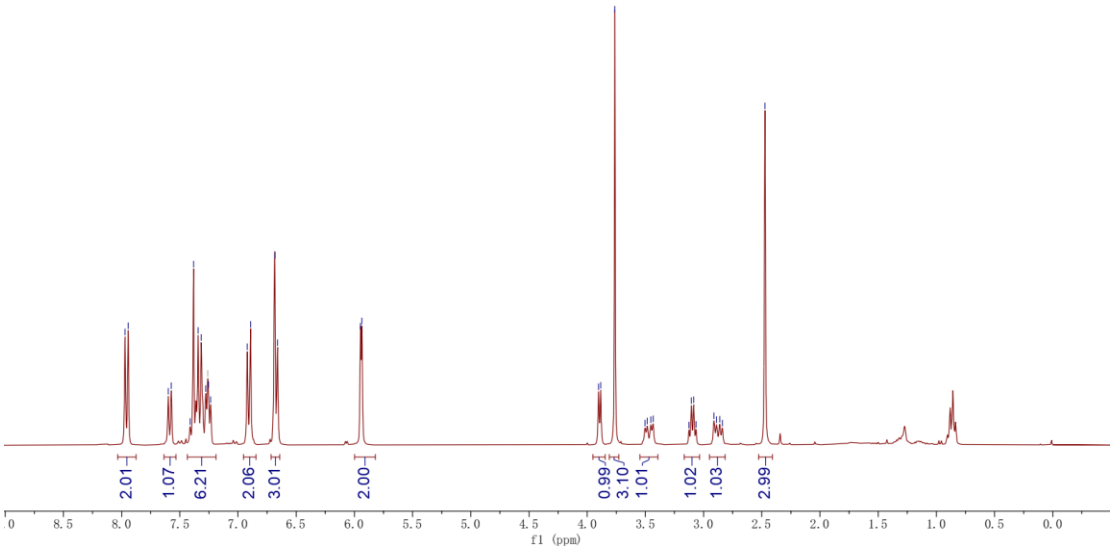
2.839
2.473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1.03
2.99
f1 (ppm)


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145.618
145.079
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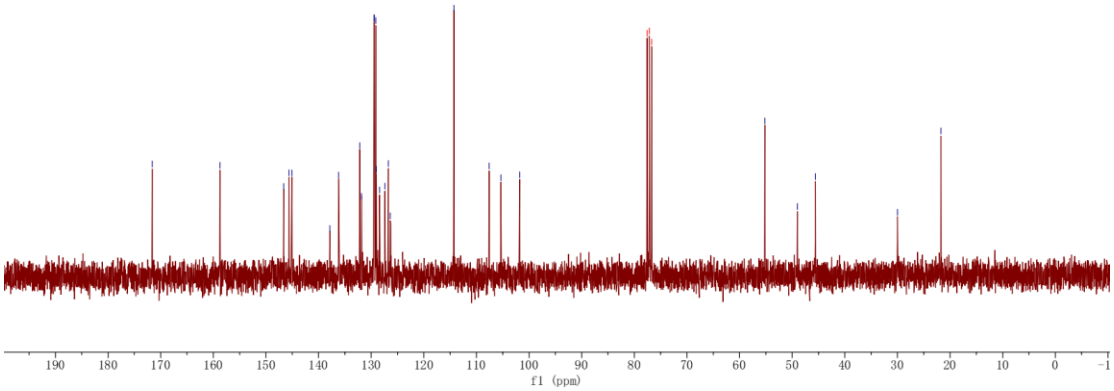
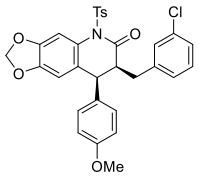
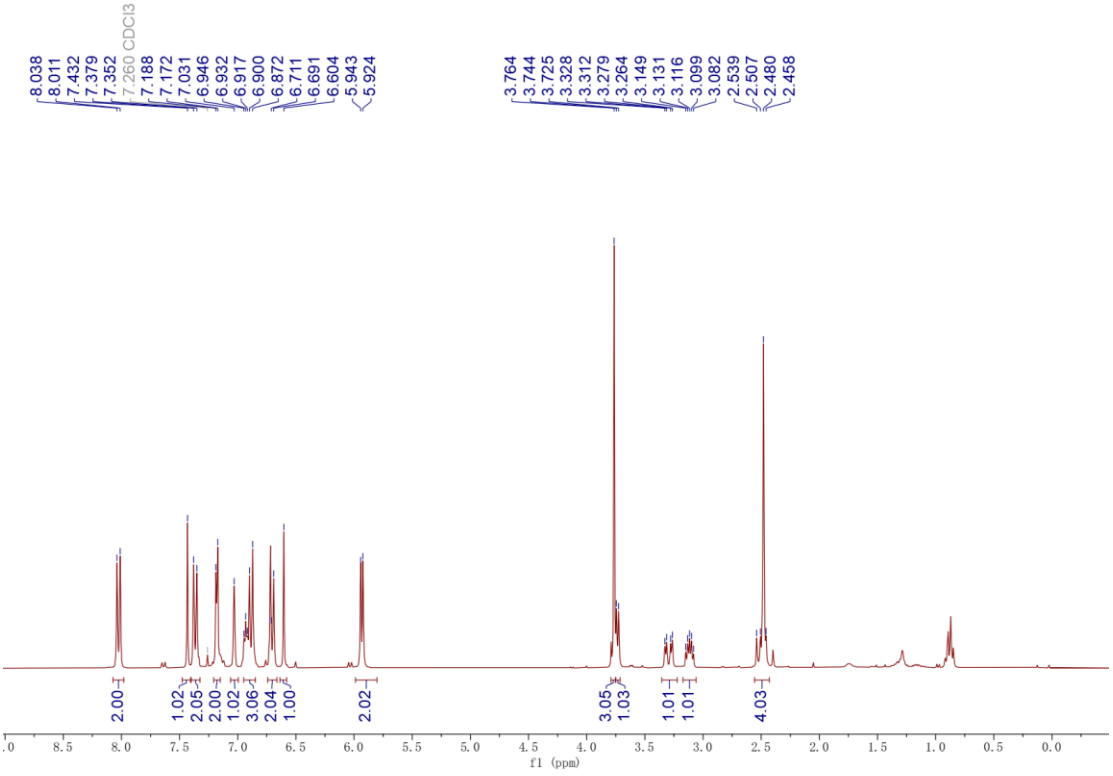

f1 (ppm)


Ts
N
O
O
O
Cl
OMe

3e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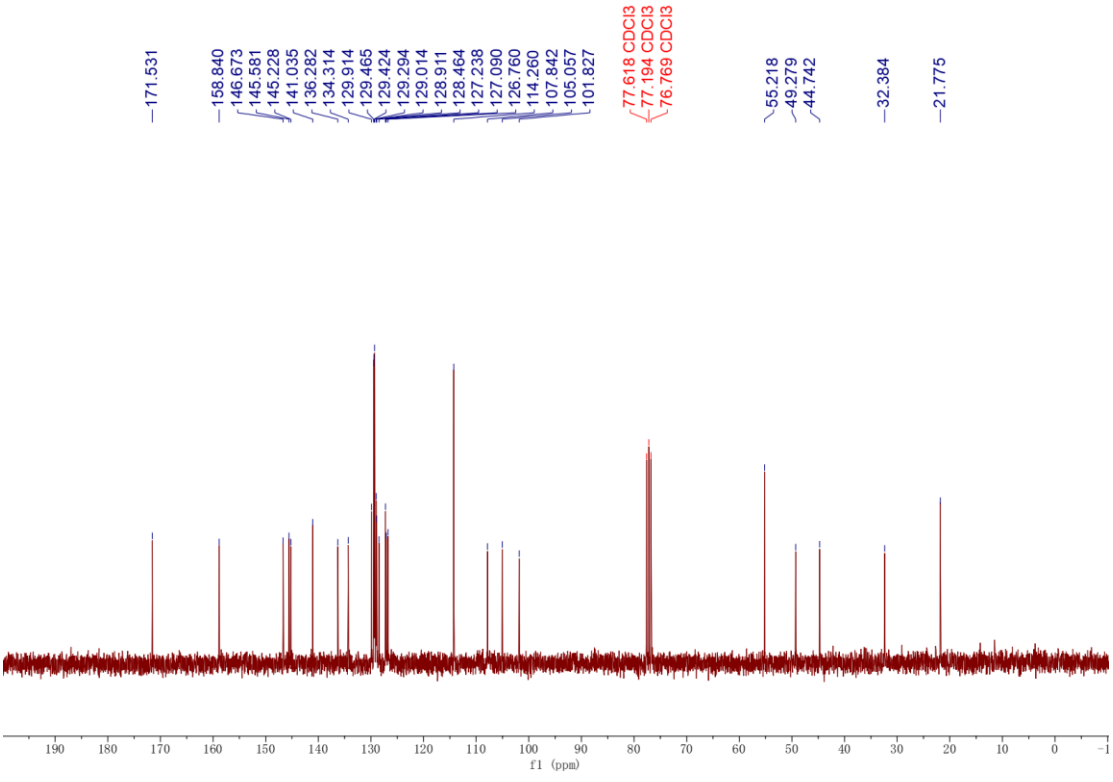
6.917
6.900
6.872
6.711
6.691
6.604
5.943
5.924
3.764
3.744
3.725
3.328
3.312
3.279
3.264
3.149
3.131
3.116
3.099
3.082
2.539
2.507
2.480
2.458
2.00
1.02
2.05
2.00
1.02
3.06
2.04
1.00
2.02
3.05
1.03
1.01
1.01
4.03
f1 (ppm)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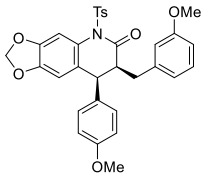
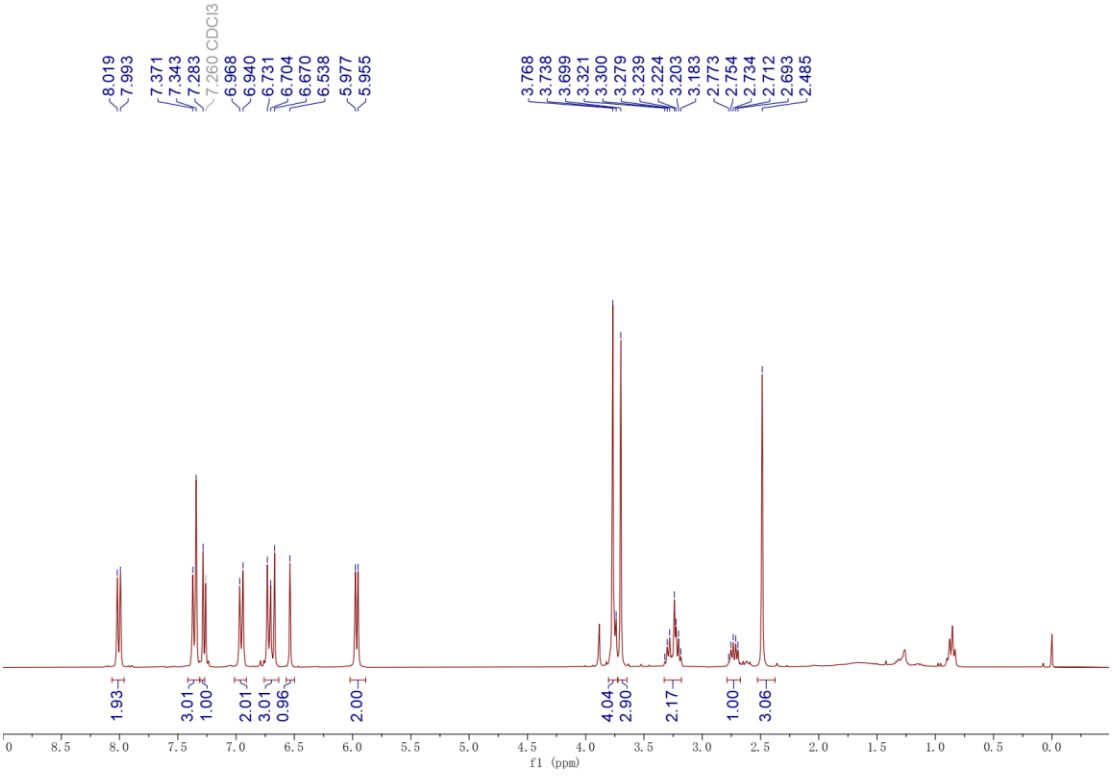
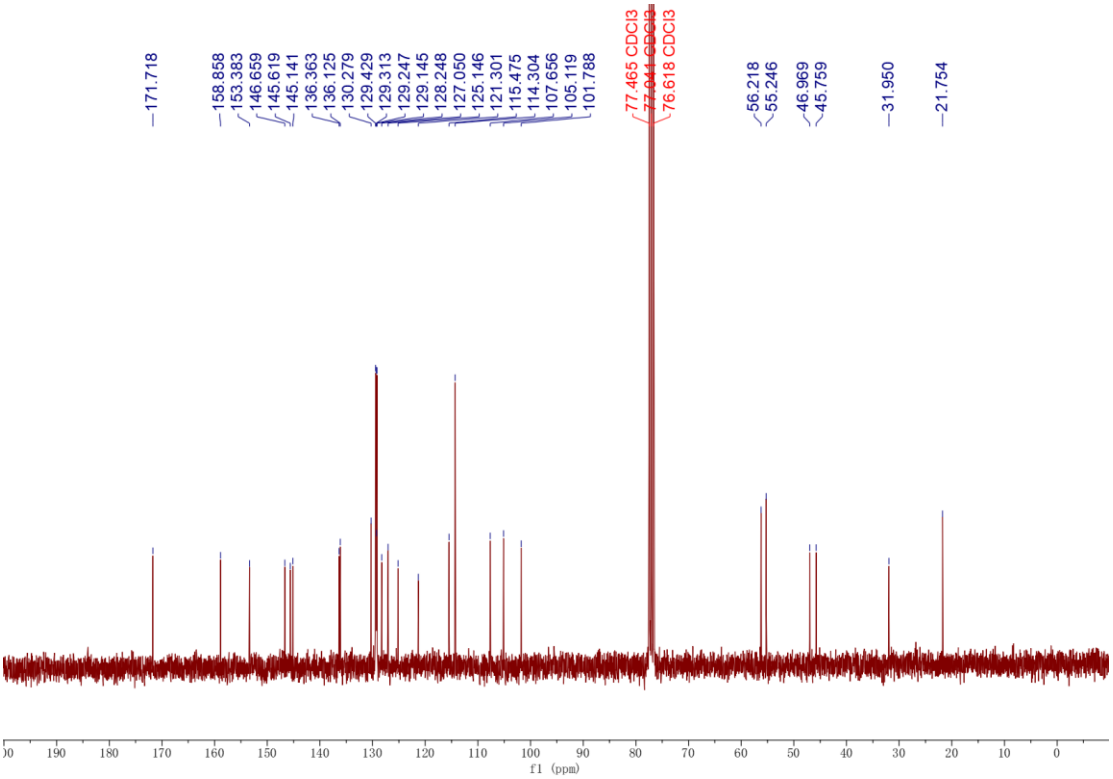
158.840
146.673
145.581
145.228
141.035
136.282
134.314
129.914
129.465
129.424
129.294
129.014
128.911
128.464
127.238
127.090
126.760
114.260
107.842
105.057
101.827
77.618 CDCl3
77.194 CDCl3
76.769 CDCl3
55.218
49.279
44.742
32.384
21.775
f1 (ppm)


Ts
OMe
O
O
N
O
OMe

3f


8.019
7.993
7.371
7.343
7.283
7.260 CDCl3
6.968
6.940
6.731
6.704
6.670
6.538
5.977
5.955
3.768
3.738
3.699
3.321
3.300
3.279
3.239
3.224
3.203
3.183
2.773
2.754
2.734
2.712
2.693
2.485
1.93
3.01
1.00
2.01
3.01
0.96
2.00
4.04
2.90
2.17
1.00
3.06
f1 (ppm)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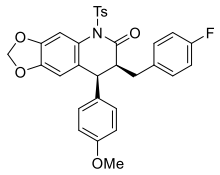
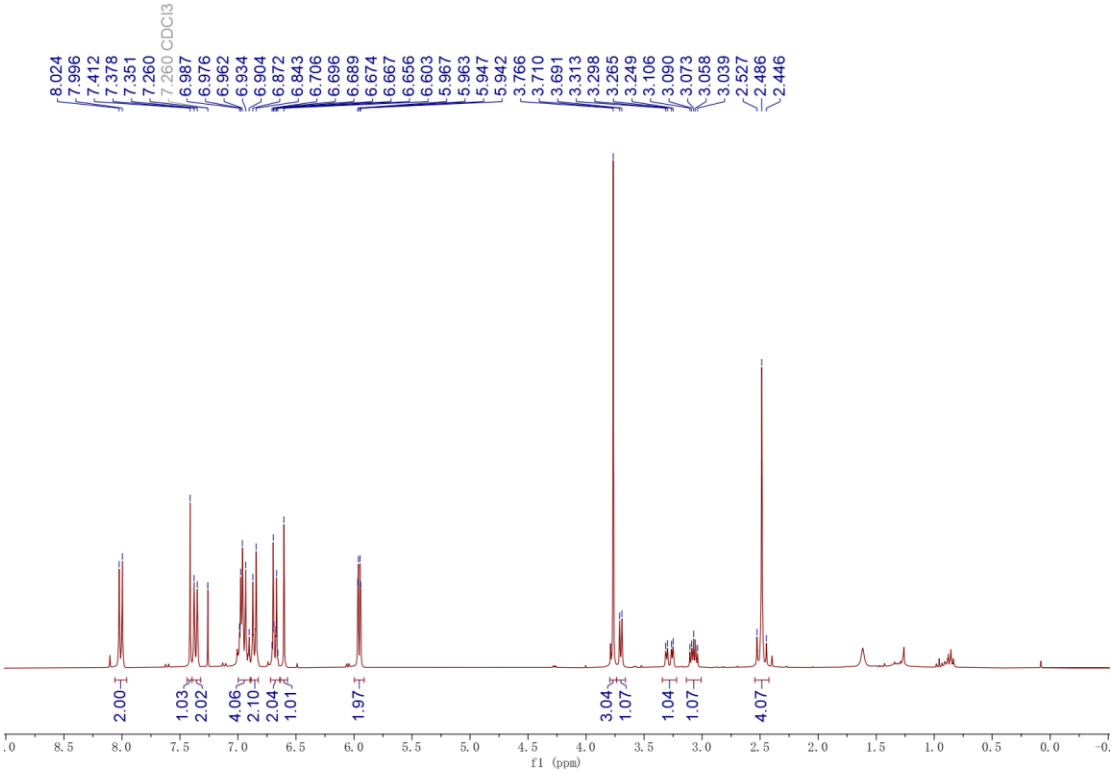
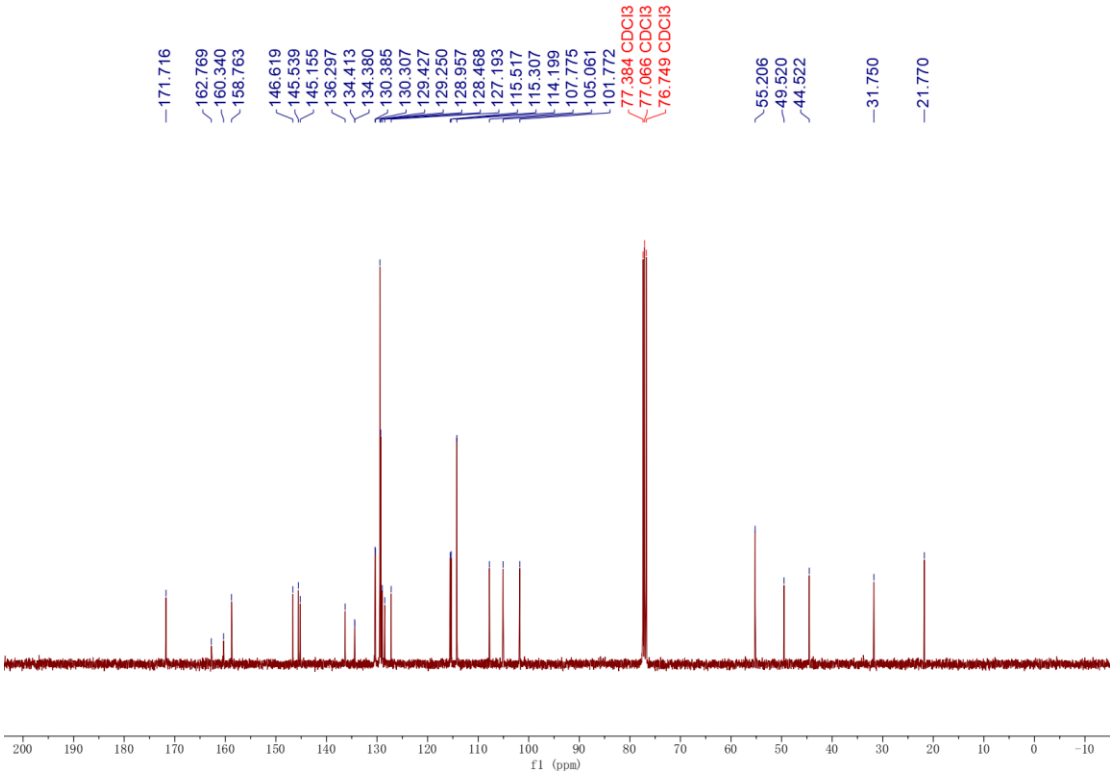
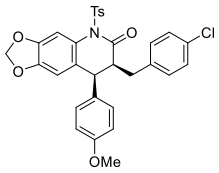
153.383
146.659
145.619
145.141
136.363
136.125
130.279
129.429
129.313
129.247
129.145
128.248
127.050
125.146
121.301
115.475
114.304
107.656
105.119
101.788
77.465 CDCl3
77.041 CDCl3
76.618 CDCl3
56.218
55.246
46.969
45.759
31.950
21.754
f1 (ppm)


Ts
N
O
O
O
F
OMe

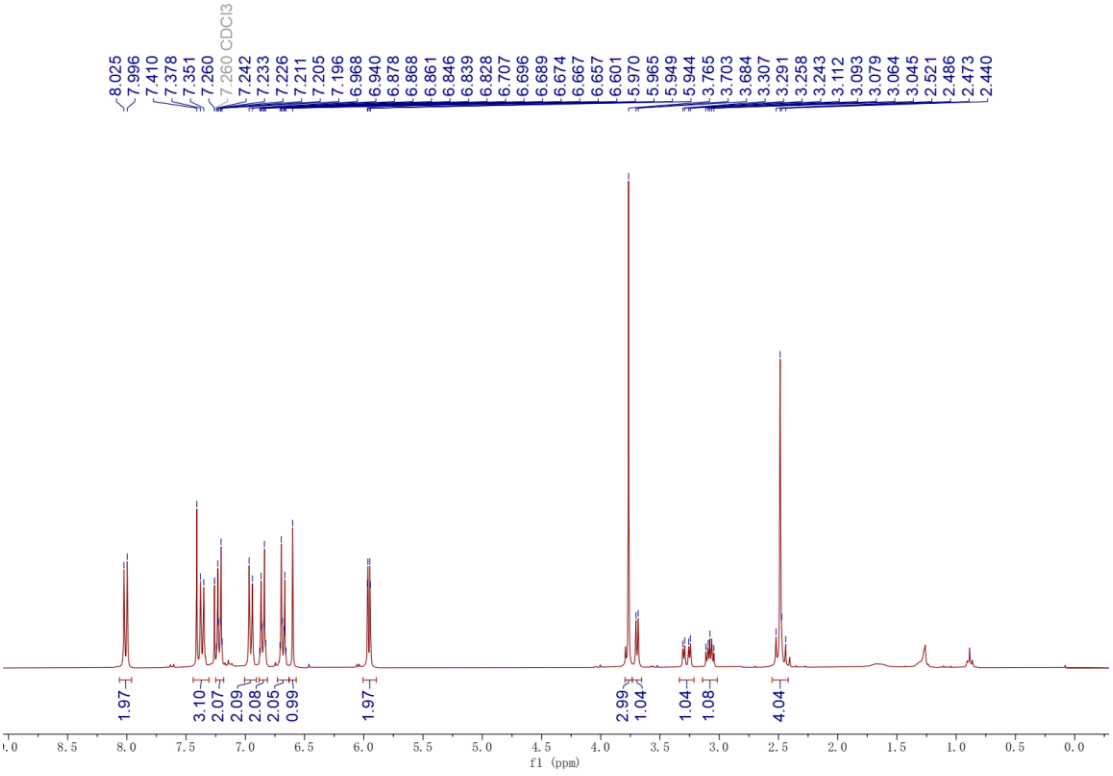
3g

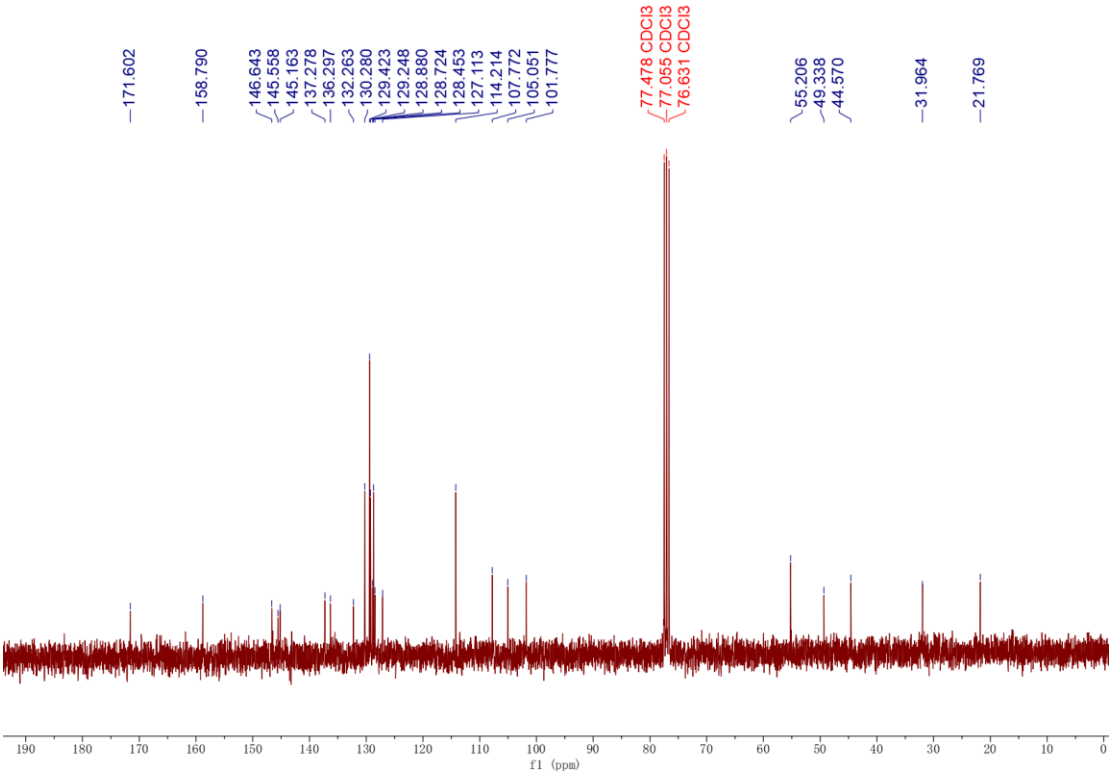

8.024
7.996
7.412
7.378
7.351
7.260
7.260 CDCl3
6.987
6.976
6.962
6.934
6.904
6.872
6.843
6.706
6.696
6.689
6.674
6.667
6.656
6.603
5.967
5.963
5.947
5.942
3.766
3.710
3.691
3.313
3.298
3.265
3.249
3.106
3.090
3.073
3.058
3.039
2.527
2.486
2.446
2.00
1.03
2.02
4.06
2.10
2.04
1.01
1.97
3.04
1.07
1.04
1.07
4.07
f1 (ppm)


171.716
162.769
160.340
158.763
146.619
145.539
145.155
136.297
134.413
134.380
130.385
130.307
129.427
129.250
128.957
128.468
127.193
115.517
115.307
114.199
107.775
105.061
101.772
77.384 CDCl3
77.066 CDCl3
76.749 CDCl3
55.206
49.520
44.522
31.750
21.770
f1 (ppm)


Ts
N
O
O
O
Cl
OMe

3h


8.025
7.996
7.410
7.378
7.351
7.260
7.260 CDCl3
7.242
7.233
7.226
7.211
7.205
7.196
6.968
6.940
6.878
6.868
6.861
6.846
6.839
6.828
6.707
6.696
6.689
6.674
6.667
6.657
6.601
5.970
5.965
5.949
5.944
3.765
3.703
3.684
3.307
3.291
3.258
3.243
3.112
3.093
3.079
3.064
3.045
2.521
2.486
2.473
2.440
1.97
3.10
2.07
2.09
2.08
2.05
0.99
1.97
2.99
1.04
1.04
1.08
4.04
f1 (ppm)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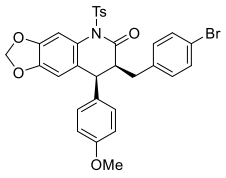
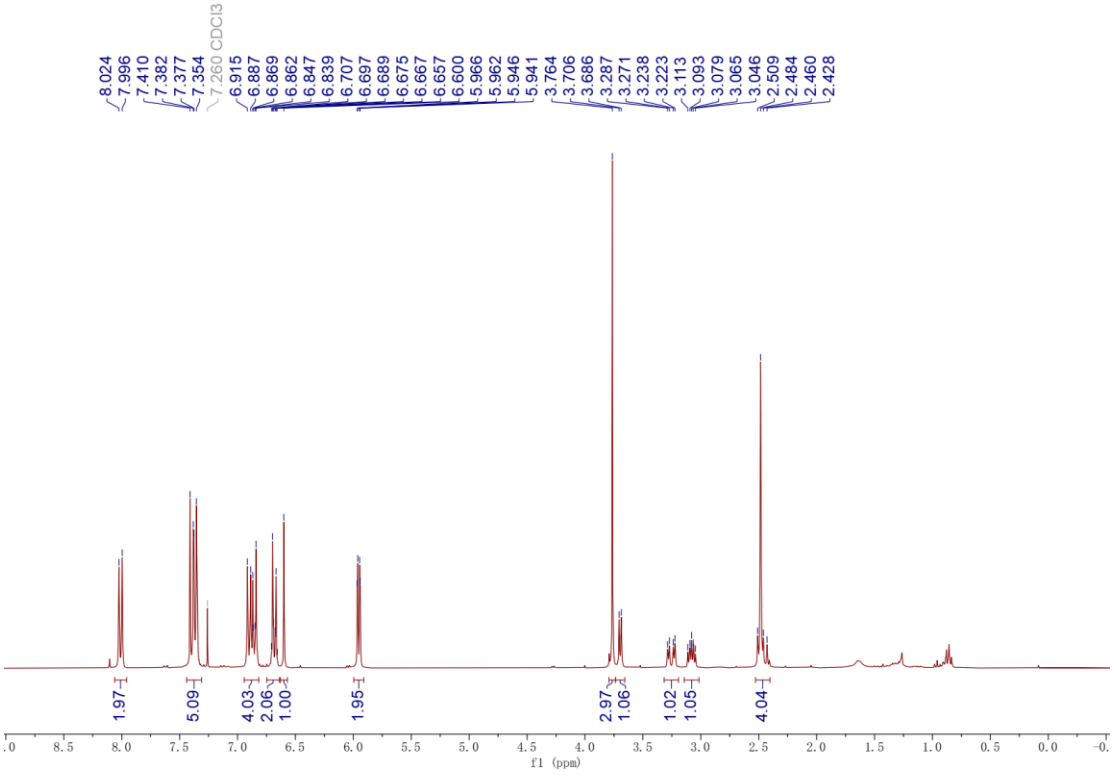
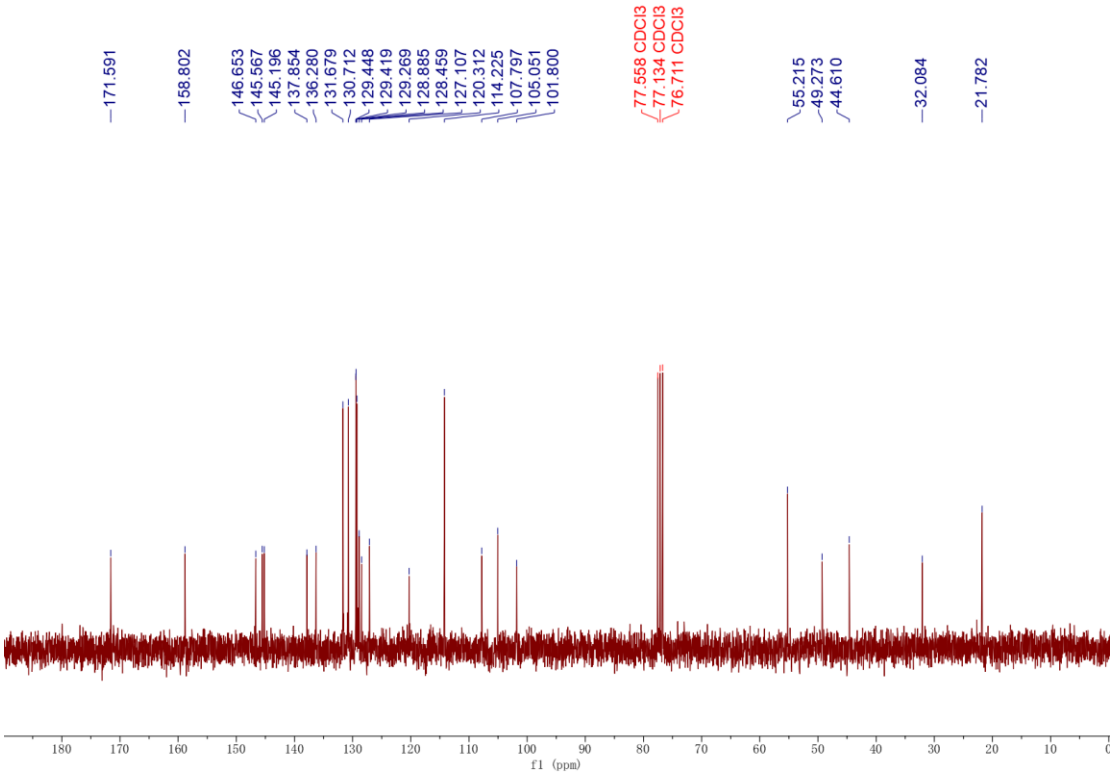
158.790
146.643
145.558
145.163
137.278
136.297
132.263
130.280
129.423
129.248
128.880
128.724
128.453
127.113
114.214
107.772
105.051
101.777
77.478 CDCl3
77.055 CDCl3
76.631 CDCl3
55.206
49.338
44.570
31.964
21.769
f1 (ppm)


Ts
N
O
O
O
Br
OMe

3i


8.024
7.996
7.410
7.382
7.377
7.354
7.260 CDCl3
6.915
6.887
6.869
6.862
6.847
6.839
6.707
6.697
6.689
6.675
6.667
6.657
6.600
5.966
5.962
5.946
5.941
3.764
3.706
3.686
3.287
3.271
3.238
3.223
3.113
3.093
3.079
3.065
3.046
2.509
2.484
2.460
2.428
1.97
5.09
4.03
2.06
1.00
1.95
2.97
1.06
1.02
1.05
4.04
f1 (ppm)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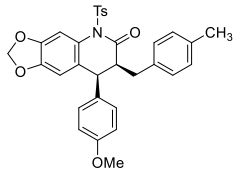
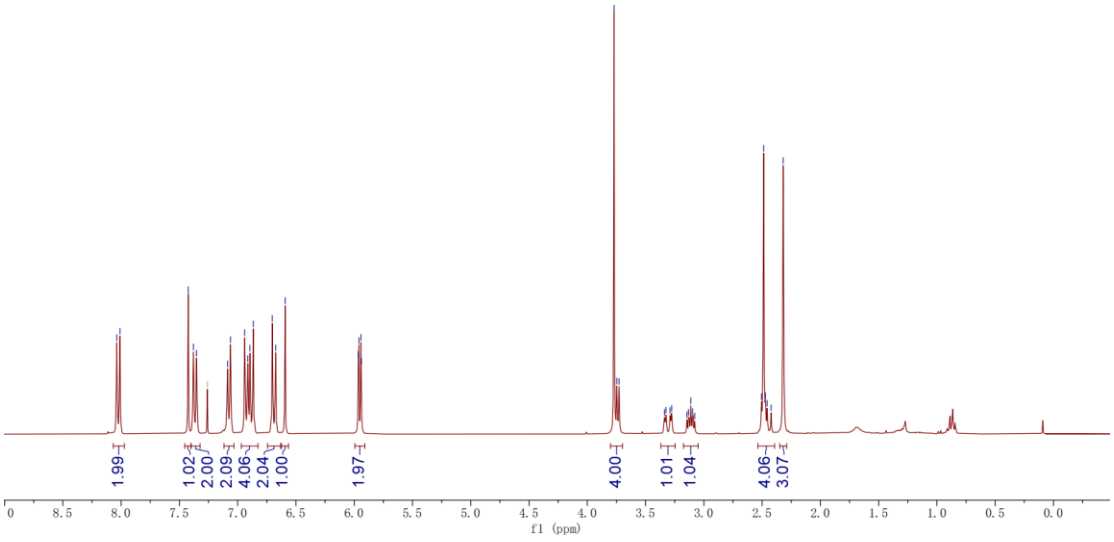
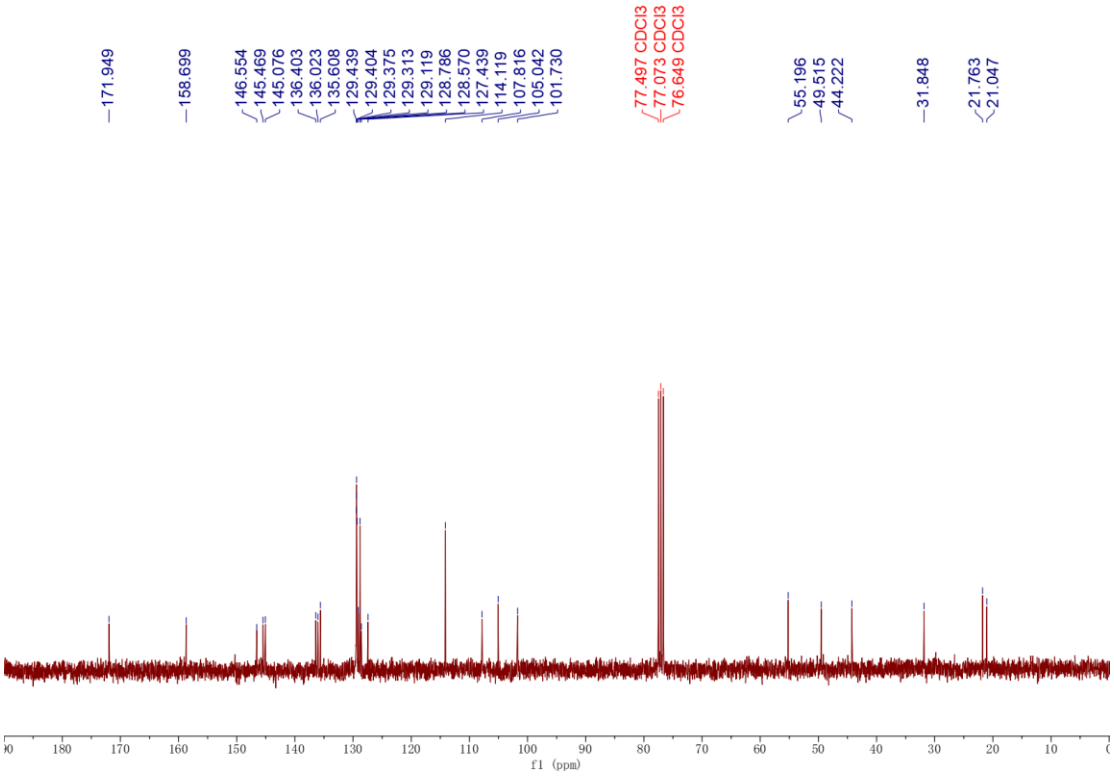
158.802
146.653
145.567
145.196
137.854
136.280
131.679
130.712
129.448
129.419
129.269
128.885
128.459
127.107
120.312
114.225
107.797
105.051
101.800
77.558 CDCl3
77.134 CDCl3
76.711 CDCl3
55.215
49.273
44.610
32.084
21.782
f1 (ppm)


Ts
N
O
O
O
CH3
OMe

3j


8.038
8.010
7.425
7.380
7.353
7.260 CDCl3
7.088
7.062
6.939
6.913
6.895
6.866
6.703
6.674
6.593
5.964
5.960
5.943
5.939
3.770
3.746
3.727
3.338
3.324
3.289
3.276
3.145
3.131
3.111
3.097
3.078
2.506
2.487
2.471
2.457
2.423
2.319


1.99
1.02
2.00
2.09
4.06
2.04
1.00
1.97
4.00
1.01
1.04
4.06
3.07
f1 (ppm)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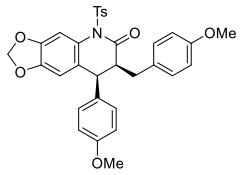
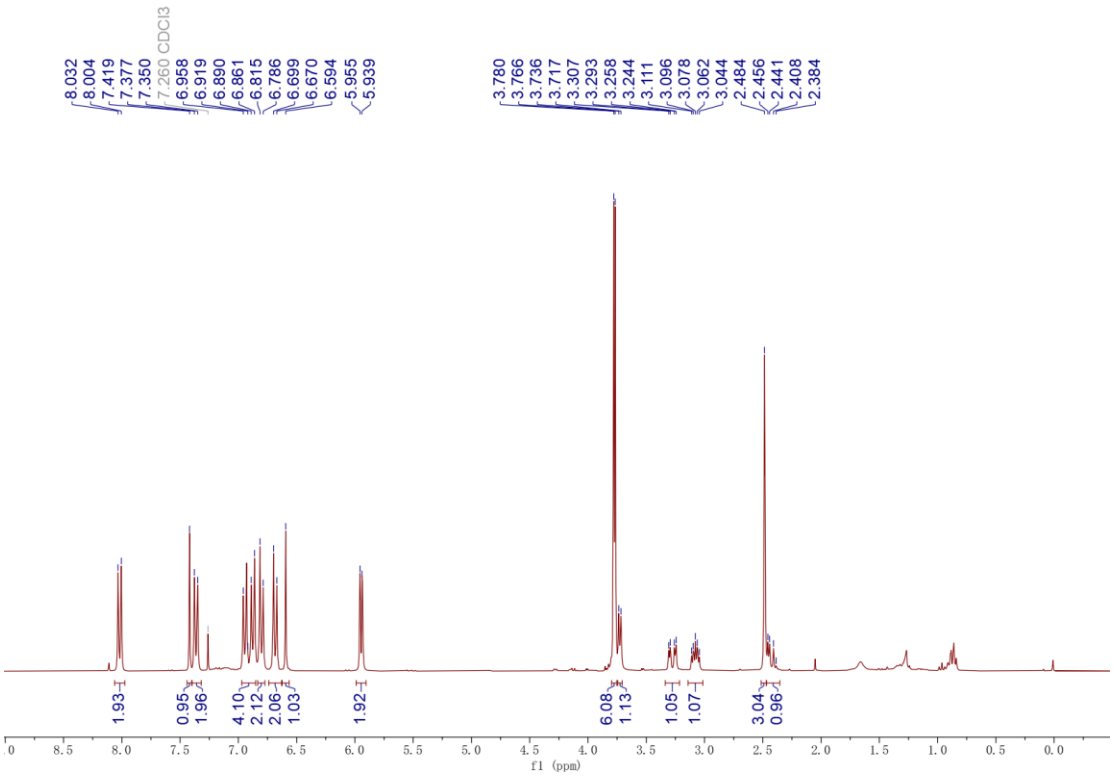
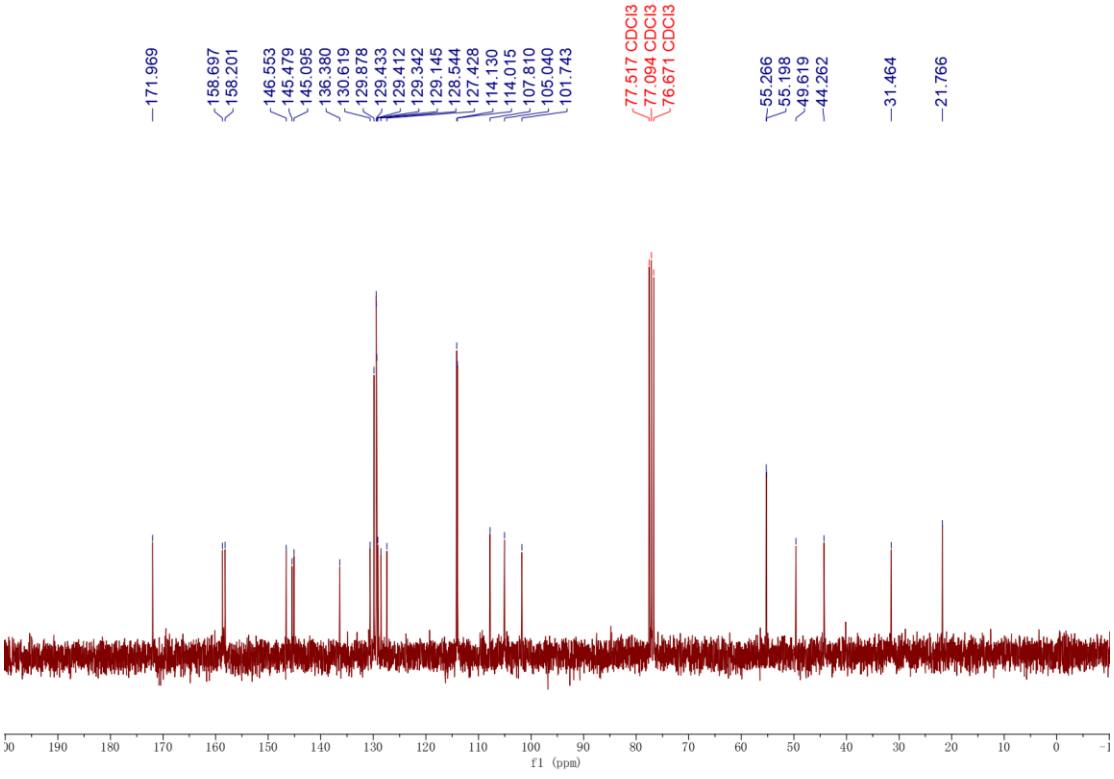
158.699
146.554
145.469
145.076
136.403
136.023
135.608
129.439
129.404
129.375
129.313
129.119
128.786
128.570
127.439
114.119
107.816
105.042
101.730
77.497 CDCl3
77.073 CDCl3
76.649 CDCl3
55.196
49.515
44.222
31.848
21.763
21.047
f1 (ppm)


Ts
N
O
O
O
O
OMe
OMe

3k


8.032
8.004
7.419
7.377
7.350
7.260 CDCl3
6.958
6.919
6.890
6.861
6.815
6.786
6.699
6.670
6.594
5.955
5.939
3.780
3.766
3.736
3.717
3.307
3.293
3.258
3.244
3.111
3.096
3.078
3.062
3.044
2.484
2.456
2.441
2.408
2.384
1.93
0.95
1.96
4.10
2.12
2.06
1.03
1.92
6.08
1.13
1.05
1.07
3.04
0.96
f1 (ppm)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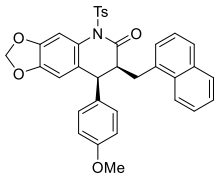
145.095
136.380
130.619
129.878
129.433
129.412
129.342
129.145
128.544
127.428
114.130
114.015
107.810
105.040
101.743
77.517 CDCl3
77.094 CDCl3
76.671 CDCl3
55.266
55.198
49.619
44.262
31.464
21.766
f1 (ppm)


Ts
N
O
O
O
OMe

3l


8.311
8.283
8.052
8.025
7.835
7.807
7.592
7.564
7.541
7.510
7.482
7.457
7.435
7.409
7.382
7.358
7.260 CDCl3
6.967
6.942
6.917
6.889
6.727
6.699
6.544
5.904
3.920
3.908
3.871
3.859
3.796
3.692
3.673
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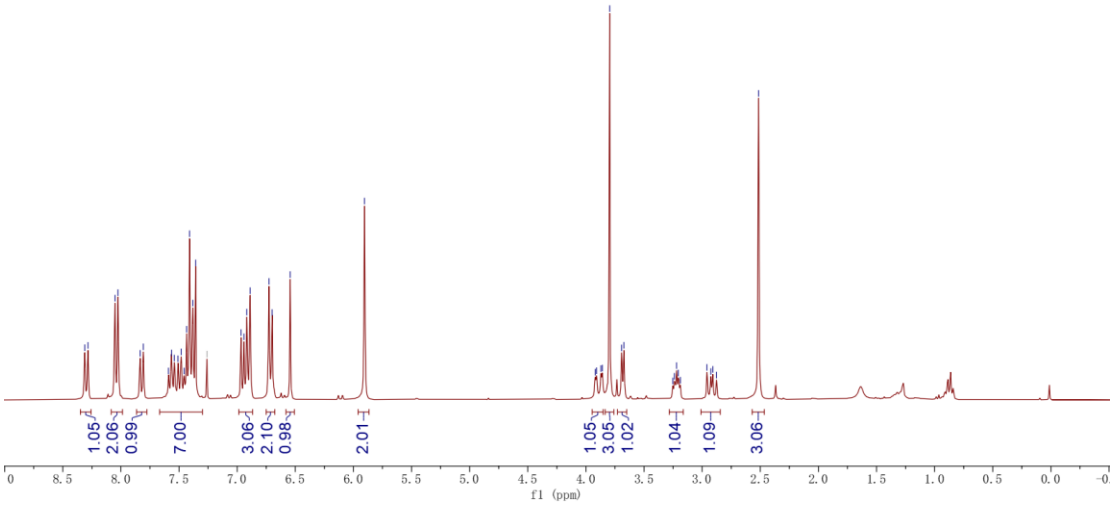
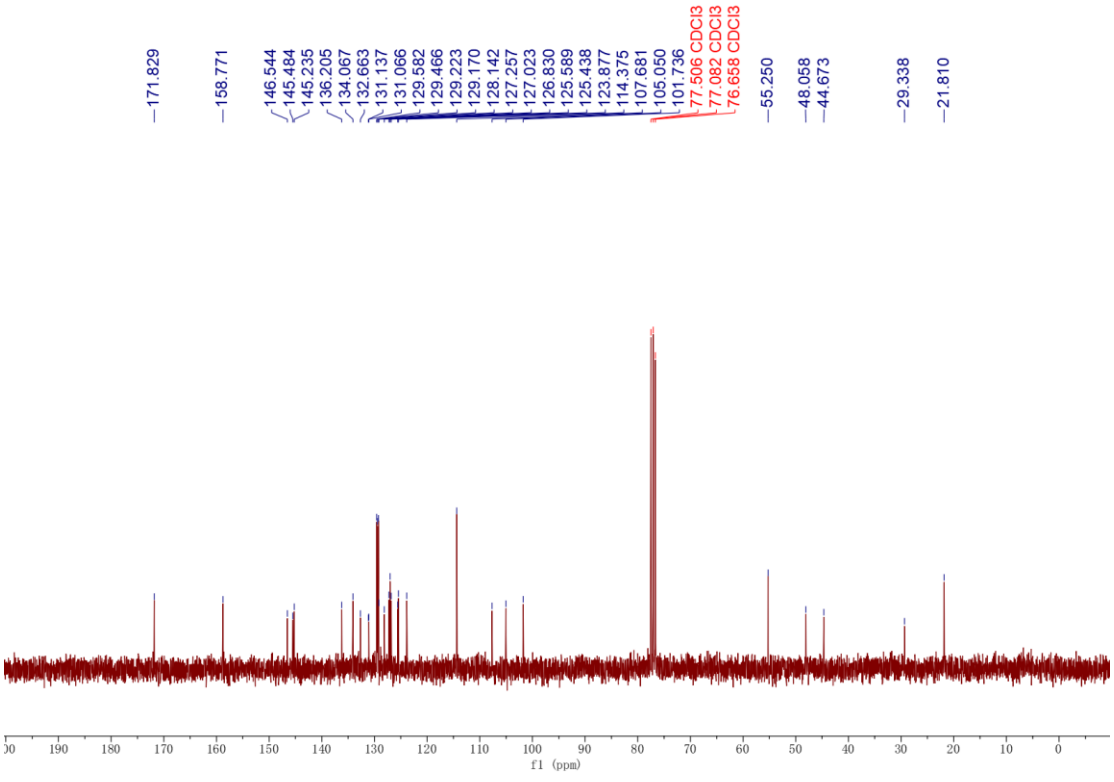
3.187
2.958
2.925
2.909
2.876
2.515


1.05
2.06
0.99
7.00
3.06
2.10
0.98
2.01
1.05
3.05
1.02
1.04
1.09
3.06
f1 (ppm)


171.829
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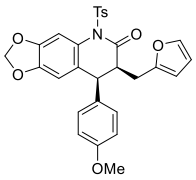
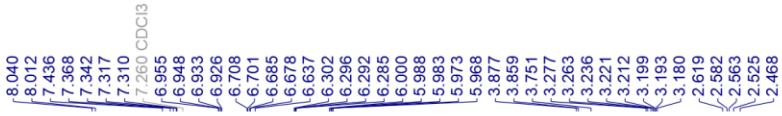
145.484
145.235
136.205
134.067
132.663
131.137
131.066
129.582
129.466
129.223
129.170
128.142
127.257
127.023
126.830
125.589
125.438
123.877
114.375
107.681
105.050
101.736
77.506 CDCl3
77.082 CDCl3
76.658 CDCl3
55.250
48.058
44.673
29.338
21.810
f1 (ppm)


Ts
N
O
O
O
O
OMe

3m


8.040
8.012
7.436
7.368
7.342
7.317
7.310
7.260 CDCl3
6.955
6.948
6.933
6.926
6.708
6.701
6.685
6.678
6.637
6.302
6.296
6.292
6.285
6.000
5.988
5.983
5.973
5.968
3.877
3.859
3.751
3.277
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3.236
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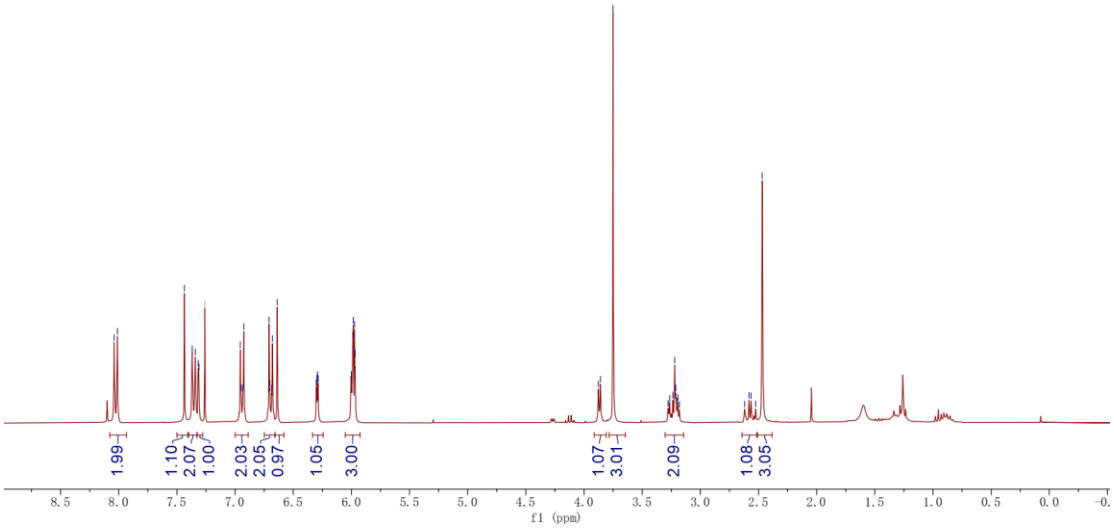
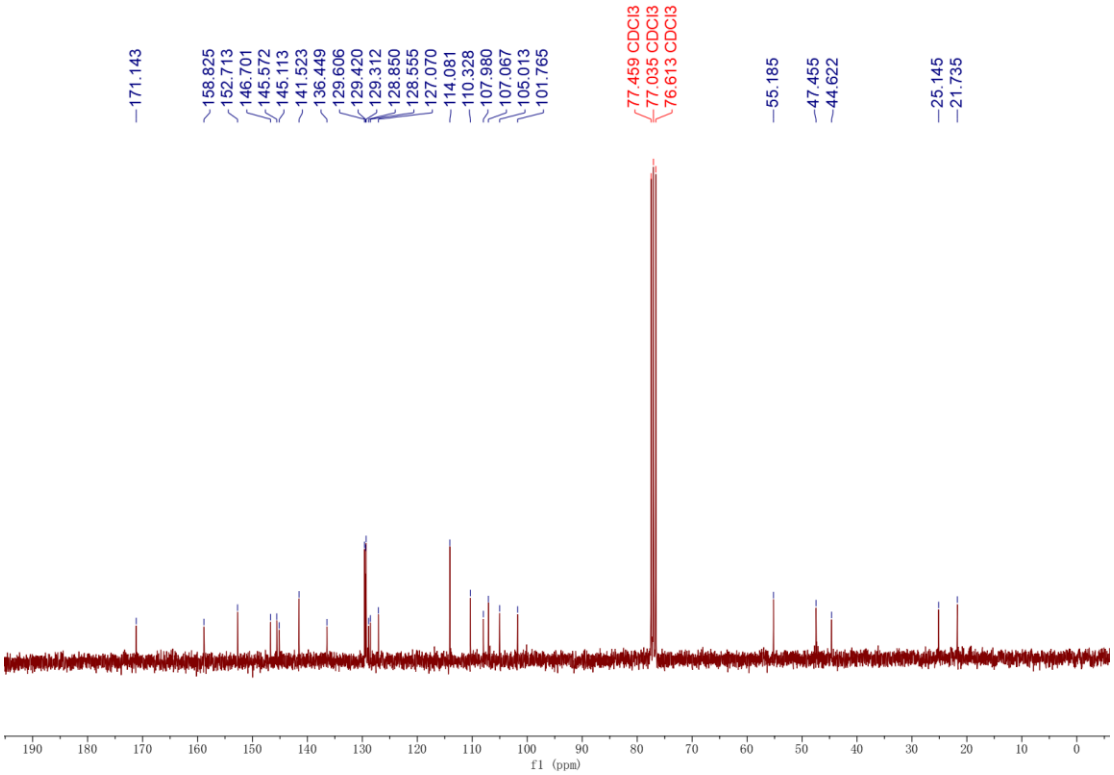
3.212
3.199
3.193
3.180
2.619
2.582
2.563
2.525
2.468


1.99
1.10
2.07
1.00
2.03
2.05
0.97
1.05
3.00
1.07
3.01
2.09
1.08
3.05
f1 (ppm)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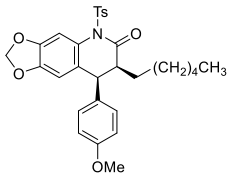
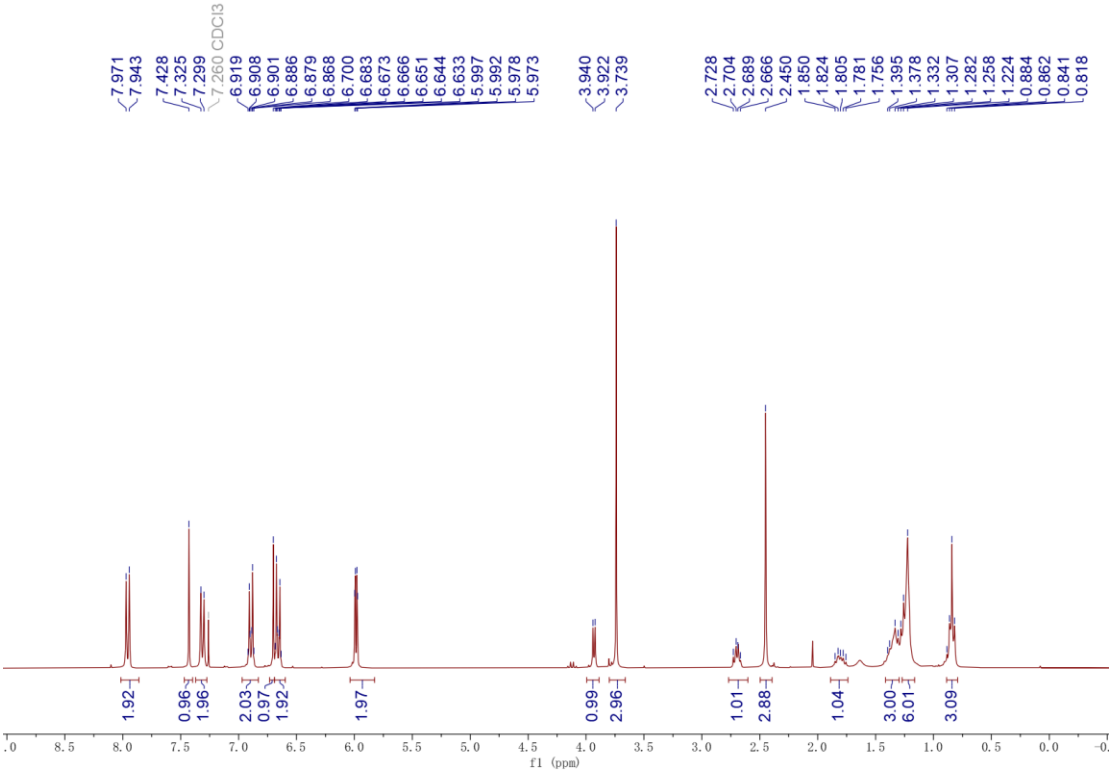
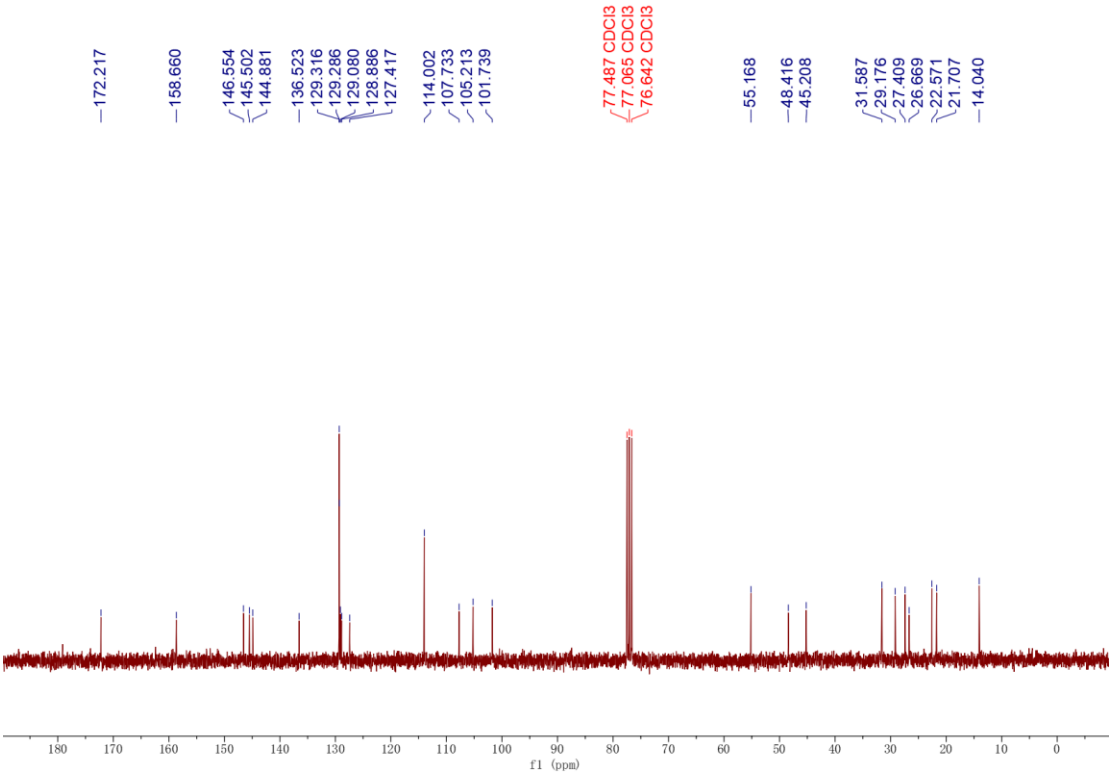
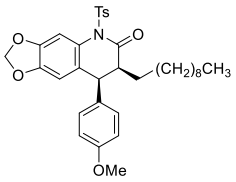
145.113
141.523
136.449
129.606
129.420
129.312
128.850
128.555
127.070
114.081
110.328
107.980
107.067
105.013
101.765
77.459 CDCl3
77.035 CDCl3
76.613 CDCl3
55.185
47.455
44.622
25.145
21.735
f1 (ppm)


Ts
N
O
O
O
(CH2)4CH3
OMe

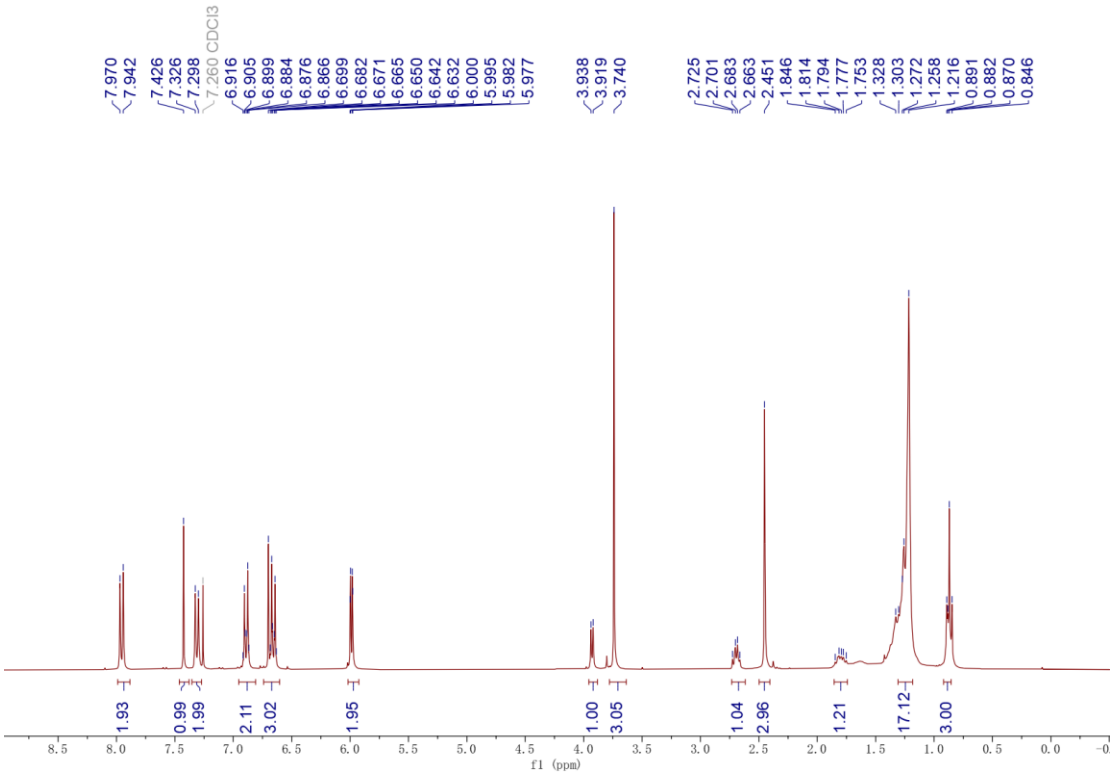
3n

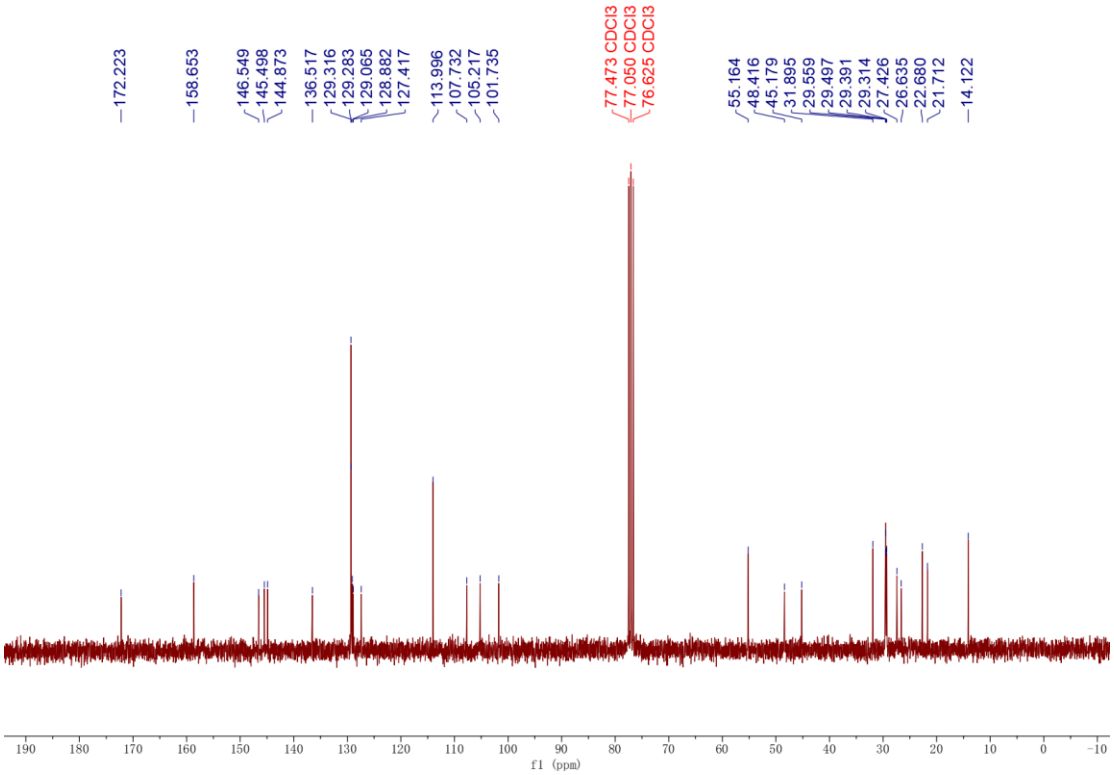

7.971
7.943
7.428
7.325
7.299
7.260 CDCl3
6.919
6.908
6.901
6.886
6.879
6.868
6.700
6.683
6.673
6.666
6.651
6.644
6.633
5.997
5.992
5.978
5.973
3.940
3.922
3.739
2.728
2.704
2.689
2.666
2.450
1.850
1.824
1.805
1.781
1.756
1.395
1.378
1.332
1.307
1.282
1.258
1.224
0.884
0.862
0.841
0.818
1.92
0.96
1.96
2.03
0.97
1.92
1.97
0.99
2.96
1.01
2.88
1.04
3.00
6.01
3.09
f1 (ppm)


172.217
158.660
146.554
145.502
144.881
136.523
129.316
129.286
129.080
128.886
127.417
114.002
107.733
105.213
101.739
77.487 CDCl3
77.065 CDCl3
76.642 CDCl3
55.168
48.416
45.208
31.587
29.176
27.409
26.669
22.571
21.707
14.040
f1 (ppm)


Ts
N
O
O
O
(CH2)8CH3
OMe

3o


7.970
7.942
7.426
7.326
7.298
7.260 CDCl3
6.916
6.905
6.899
6.884
6.876
6.866
6.699
6.682
6.671
6.665
6.650
6.642
6.632
6.000
5.995
5.982
5.977
3.938
3.919
3.740
2.725
2.701
2.683
2.663
2.451
1.846
1.814
1.794
1.777
1.753
1.328
1.303
1.272
1.258
1.216
0.891
0.882
0.870
0.846
1.93
0.99
1.99
2.11
3.02
1.95
1.00
3.05
1.04
2.96
1.21
17.12
3.00
f1 (ppm)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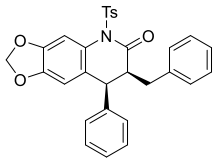
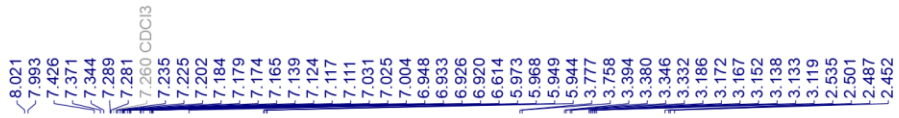
158.653
146.549
145.498
144.873
136.517
129.316
129.283
129.065
128.882
127.417
113.996
107.732
105.217
101.735
77.473 CDCl3
77.050 CDCl3
76.625 CDCl3
55.164
48.416
45.179
31.895
29.559
29.497
29.391
29.314
27.426
26.635
22.680
21.712
14.122
f1 (ppm)


Ts
N
O
O
O

3p


8.021
7.993
7.426
7.371
7.344
7.289
7.281
7.260 CDCl3
7.235
7.225
7.202
7.184
7.179
7.174
7.165
7.139
7.124
7.117
7.111
7.031
7.025
7.004
6.948
6.933
6.926
6.920
6.614
5.973
5.968
5.949
5.944
3.777
3.758
3.394
3.380
3.346
3.332
3.186
3.172
3.167
3.152
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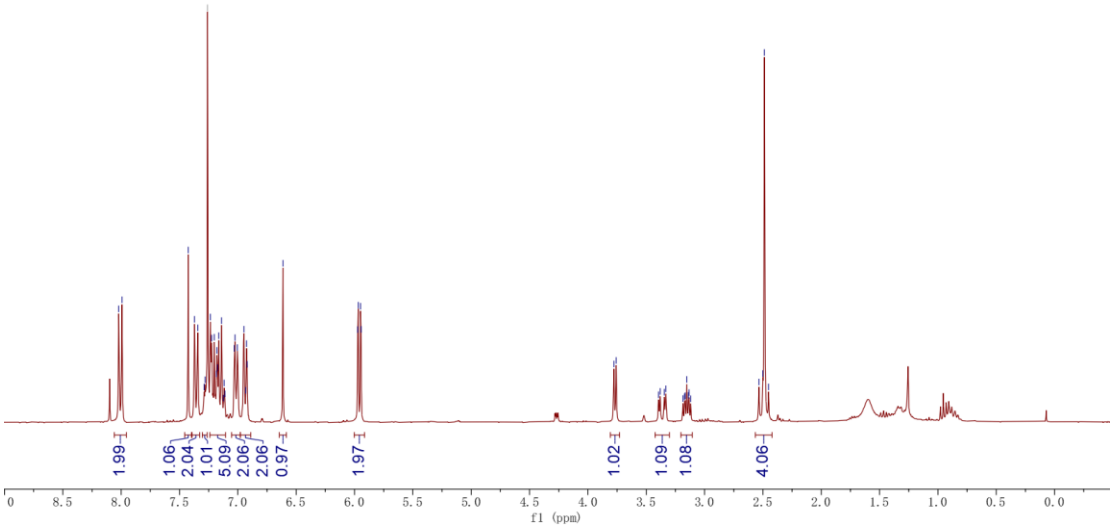
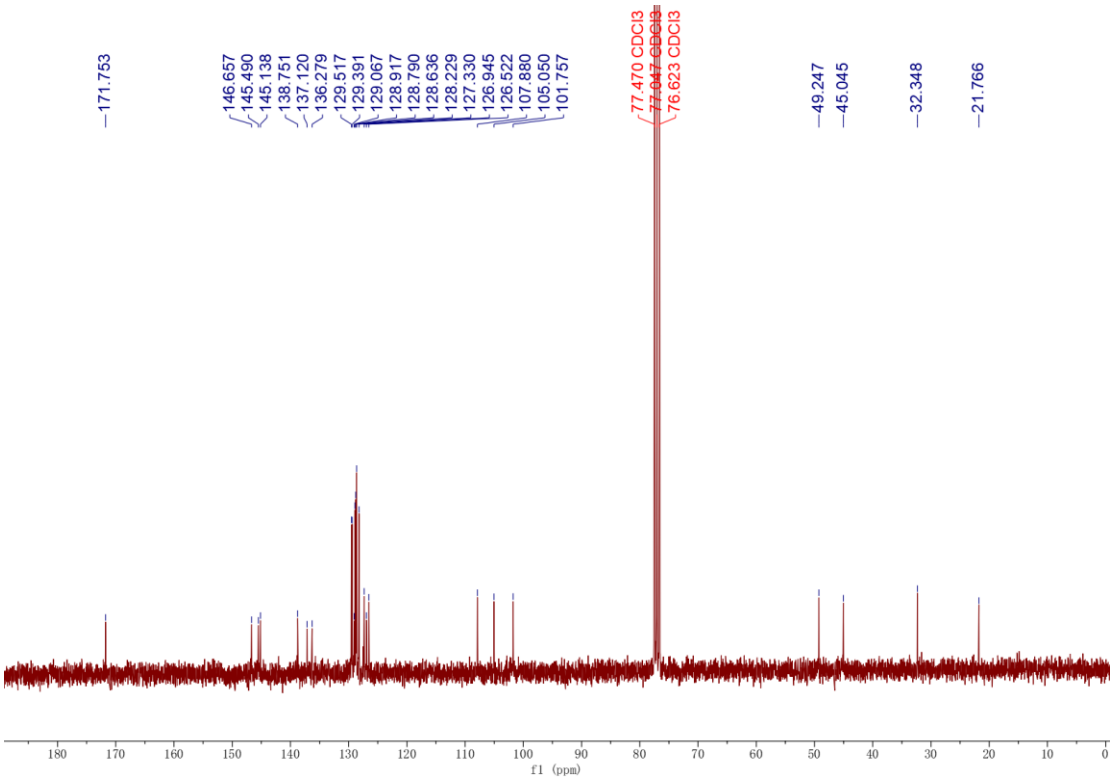
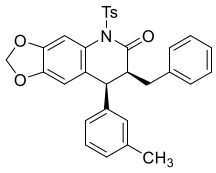
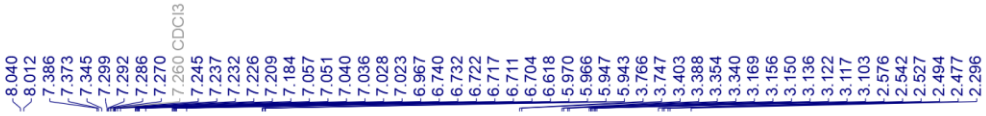
3.133
3.119
2.535
2.501
2.487
2.452

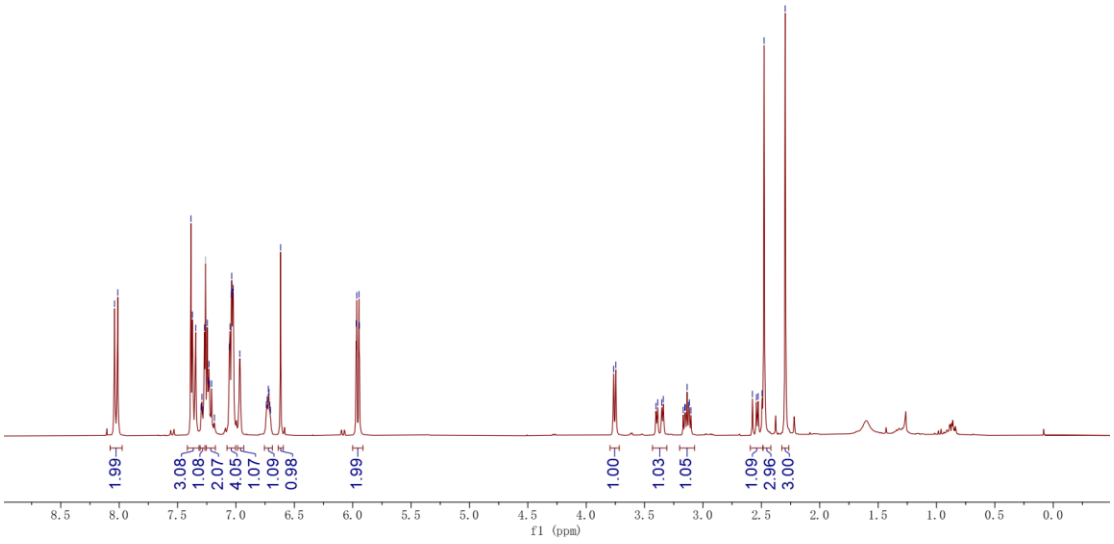

1.99
1.06
2.04
1.01
5.09
2.06
2.06
0.97
1.97
1.02
1.09
1.08
4.06
f1 (ppm)

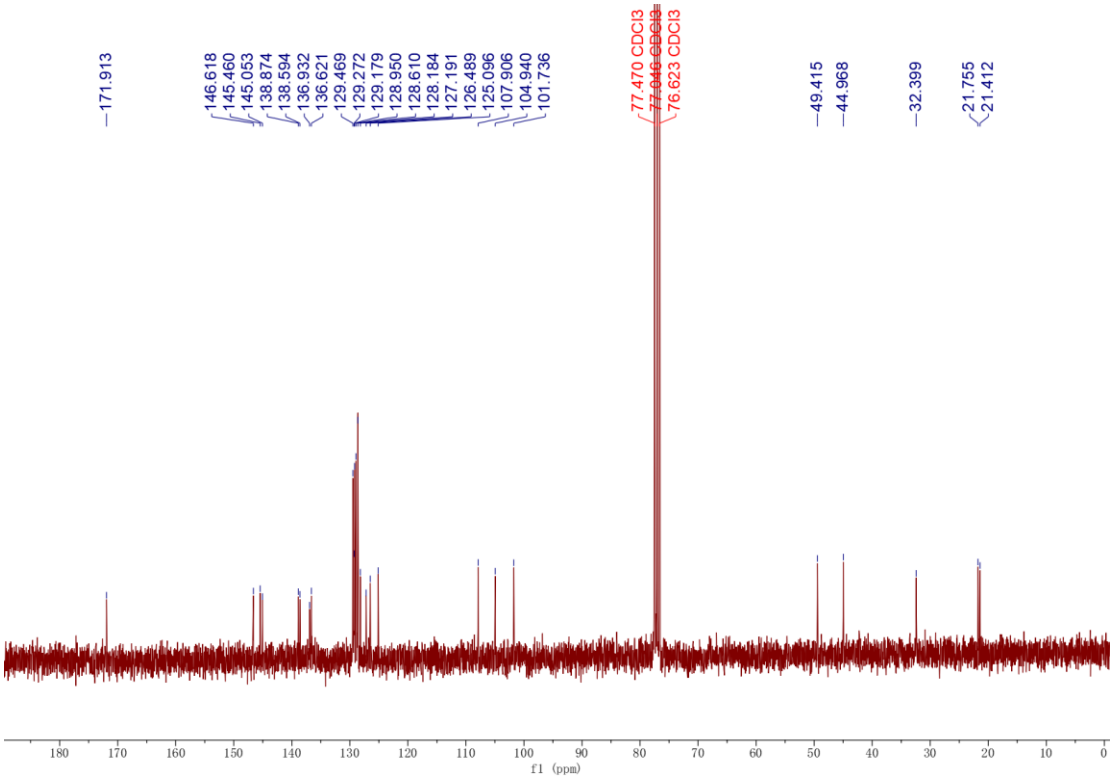

171.753
146.657
145.490
145.138
138.751
137.120
136.279
129.517
129.391
129.067
128.917
128.790
128.636
128.229
127.330
126.945
126.522
107.880
105.050
101.757
77.470 CDCl3
77.047 CDCl3
76.623 CDCl3
49.247
45.045
32.348
21.766
f1 (ppm)

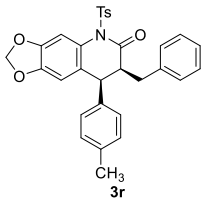

Ts
N
O
O
O
CH3

3q

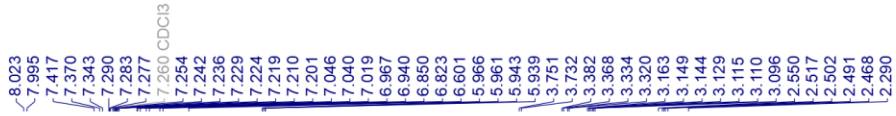

8.040
8.012
7.386
7.373
7.345
7.299
7.292
7.286
7.270
7.260 CDCl3
7.245
7.237
7.232
7.226
7.209
7.184
7.057
7.051
7.040
7.036
7.028
7.023
6.967
6.740
6.732
6.722
6.717
6.711
6.704
6.618
5.970
5.966
5.947
5.943
3.766
3.747
3.403
3.388
3.354
3.340
3.169
3.156
3.150
3.136
3.122
3.117
3.103
2.576
2.542
2.527
2.494
2.477
2.296

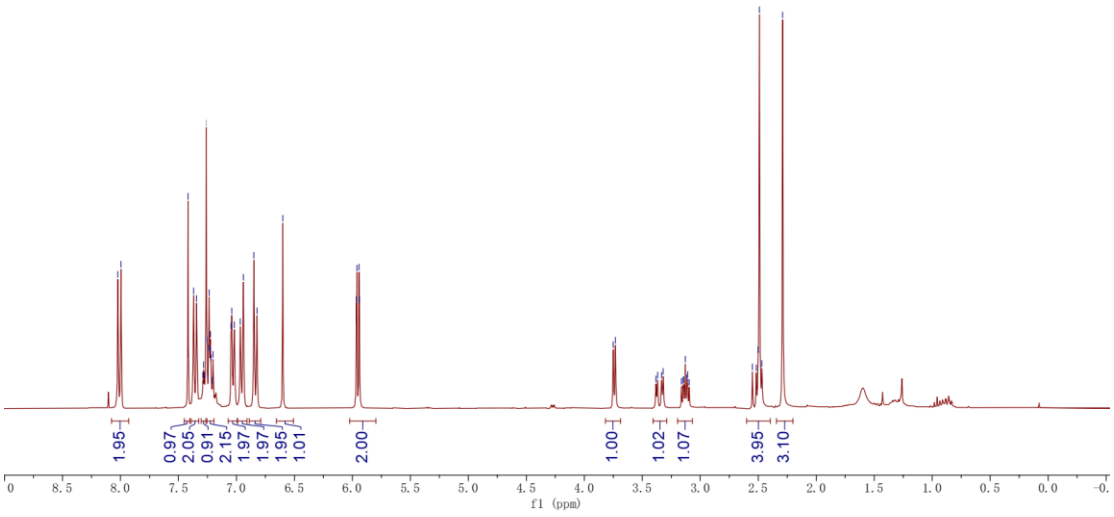

1.99
3.08
1.08
2.07
4.05
1.07
1.09
0.98
1.99
1.00
1.03
1.05
1.09
2.96
3.00
f1 (ppm)

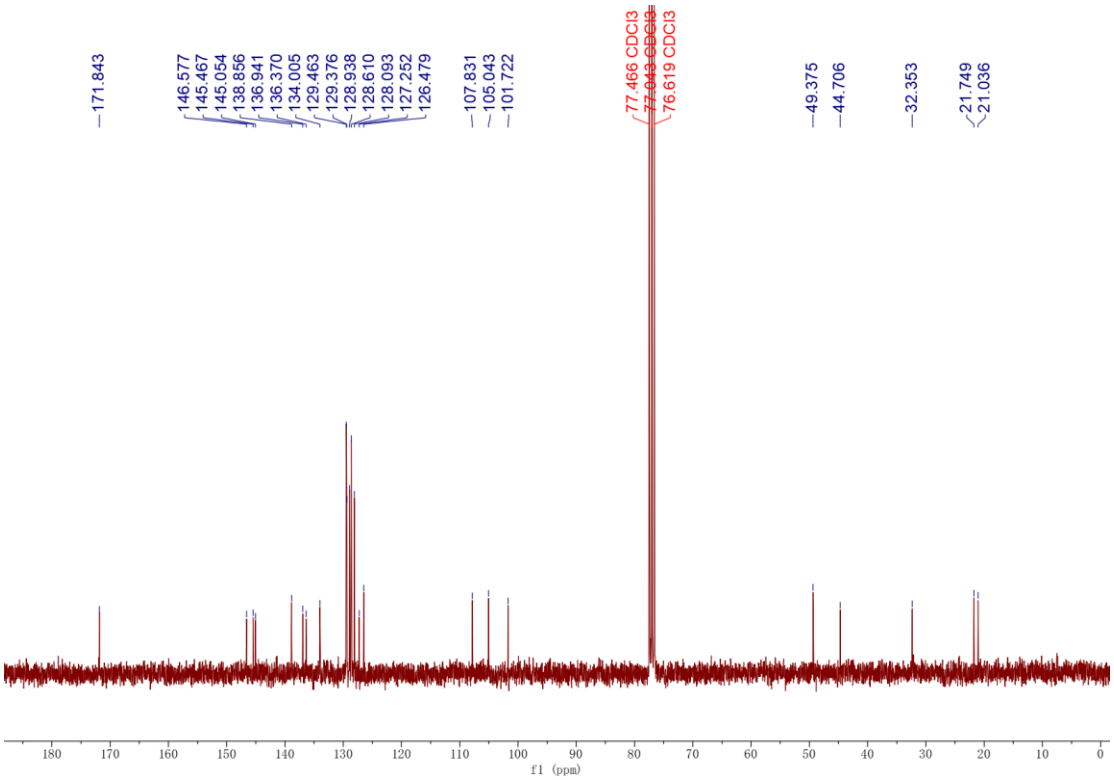

171.913
146.618
145.460
145.053
138.874
138.594
136.932
136.621
129.469
129.272
129.179
128.950
128.610
128.184
127.191
126.489
125.096
107.906
104.940
101.736
77.470 CDCl3
77.046 CDCl3
76.623 CDCl3
49.415
44.968
32.399
21.755
21.412
f1 (ppm)

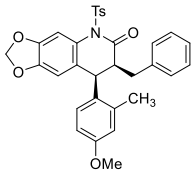

Ts
N
O
O
O
O
CH3

3r

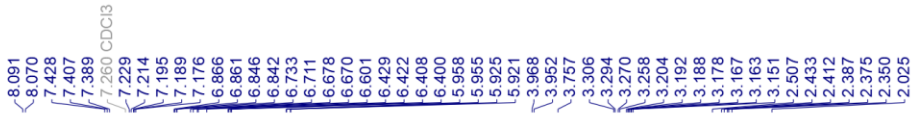

8.023
7.995
7.417
7.370
7.343
7.290
7.283
7.277
7.260 CDCl3
7.254
7.242
7.236
7.229
7.224
7.219
7.210
7.201
7.046
7.040
7.019
6.967
6.940
6.850
6.823
6.601
5.966
5.961
5.943
5.939
3.751
3.732
3.382
3.368
3.334
3.320
3.163
3.149
3.144
3.129
3.115
3.110
3.096
2.550
2.517
2.502
2.491
2.468
2.290

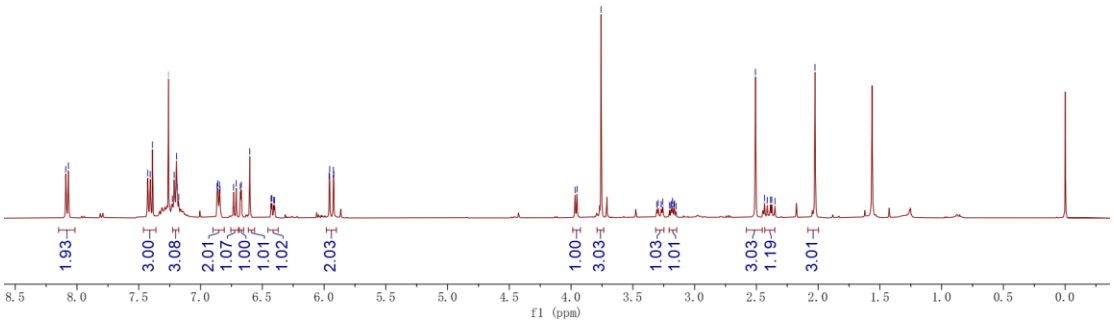

1.95
0.97
2.05
0.91
2.15
1.97
1.97
1.95
1.01
2.00
1.00
1.02
1.07
3.95
3.10
f1 (ppm)

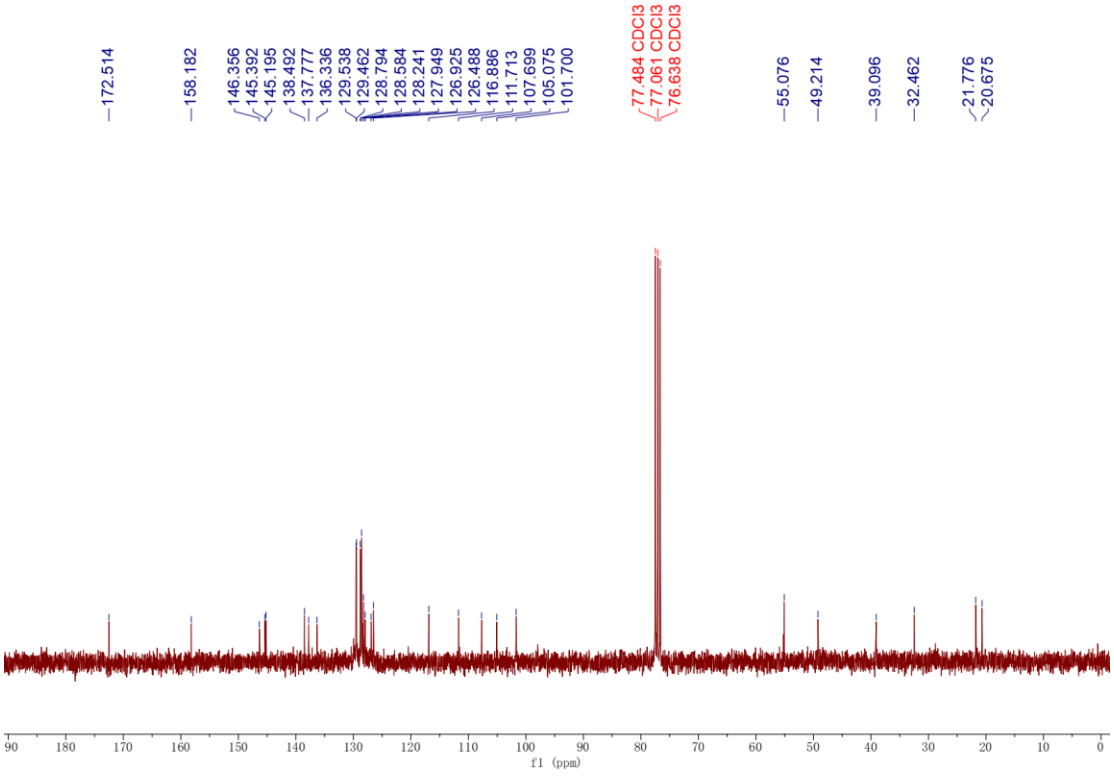

171.843
146.577
145.467
145.054
138.856
136.941
136.370
134.005
129.463
129.376
128.938
128.610
128.093
127.252
126.479
107.831
105.043
101.722
77.466 CDCl3
77.043 CDCl3
76.619 CDCl3
49.375
44.706
32.353
21.749
21.036
f1 (ppm)

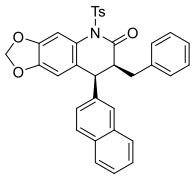

Ts
N
O
O
O
O
CH3
OMe

3s

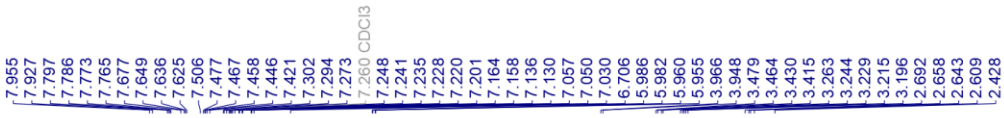

8.091
8.070
7.428
7.407
7.389
7.260 CDCl3
7.229
7.214
7.195
7.189
7.176
6.866
6.861
6.846
6.842
6.733
6.711
6.678
6.670
6.601
6.429
6.422
6.408
6.400
5.958
5.955
5.925
5.921
3.968
3.952
3.757
3.306
3.294
3.270
3.258
3.204
3.192
3.188
3.178
3.167
3.163
3.151
2.507
2.433
2.412
2.387
2.375
2.350
2.025

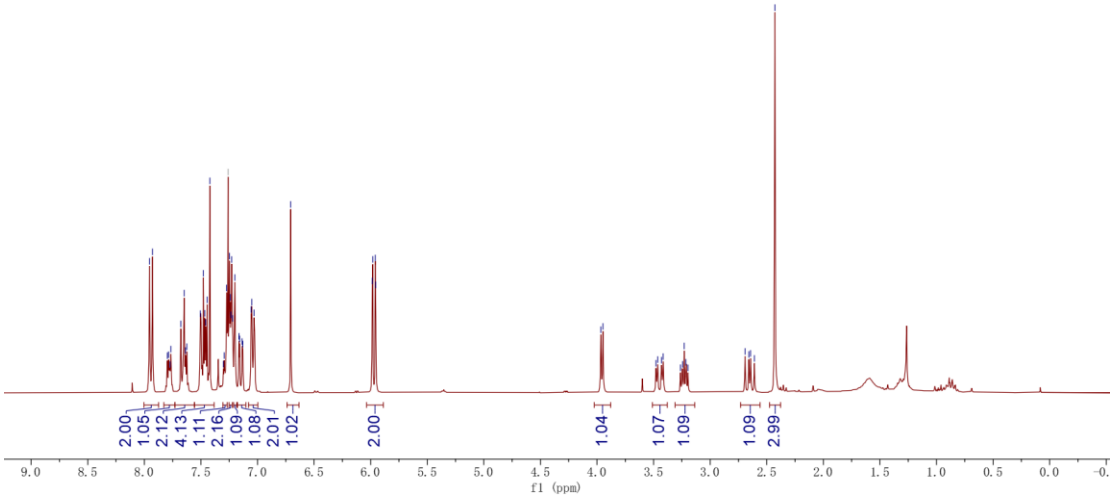

1.93
3.00
3.08
2.01
1.07
1.00
1.01
1.02
2.03
1.00
3.03
1.03
1.01
3.03
1.19
3.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


172.514
158.182
146.356
145.392
145.195
138.492
137.777
136.336
129.538
129.462
128.794
128.584
128.241
127.949
126.925
126.488
116.886
111.713
107.699
105.075
101.700
77.484 CDCl3
77.061 CDCl3
76.638 CDCl3
55.076
49.214
39.096
32.462
21.776
20.675
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

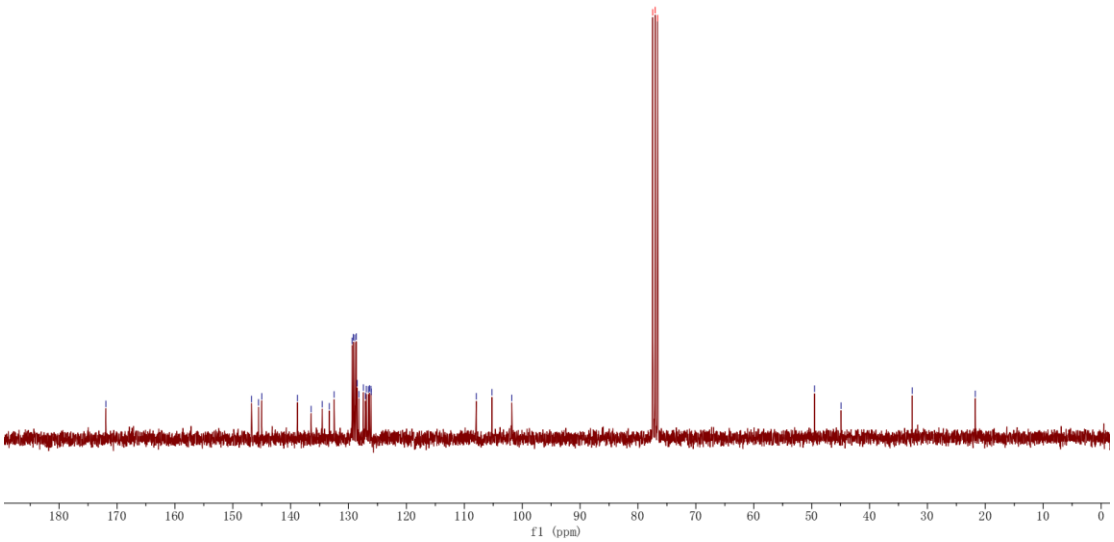

Ts
N
O
O
O

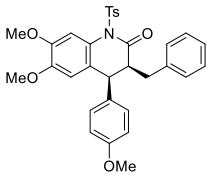
3t


7.955
7.927
7.797
7.786
7.773
7.765
7.677
7.649
7.636
7.625
7.506
7.477
7.467
7.458
7.446
7.421
7.302
7.294
7.273
7.260 CDCl3
7.248
7.241
7.235
7.228
7.220
7.201
7.164
7.158
7.136
7.130
7.057
7.050
7.030
6.706
5.986
5.982
5.960
5.955
5.966
3.948
3.479
3.464
3.430
3.415
3.263
3.244
3.229
3.215
3.196
2.692
2.658
2.643
2.609
2.428


2.00
1.05
2.12
4.13
1.11
2.16
1.09
1.08
2.01
1.02
2.00
1.04
1.07
1.09
1.09
2.99
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)

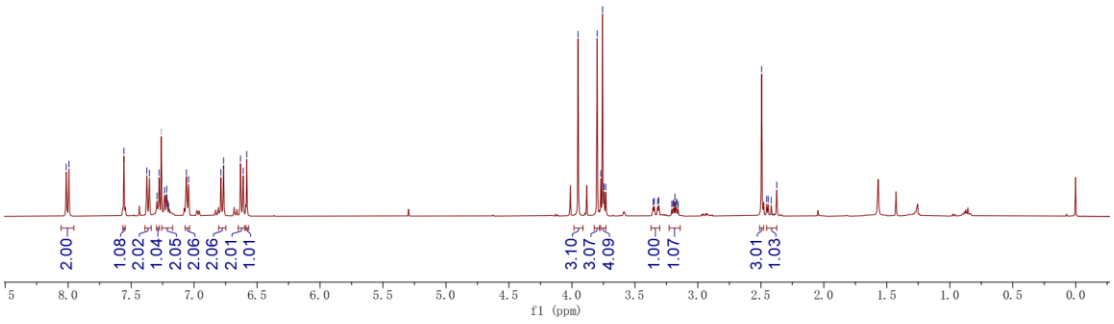

171.921
146.742
145.549
144.995
138.816
136.447
134.553
133.328
132.484
129.400
129.174
128.932
128.671
128.499
128.228
127.437
127.089
126.932
126.571
126.377
126.122
126.079
107.940
105.235
101.786
77.462 CDCl3
77.039 CDCl3
76.616 CDCl3
49.502
44.921
32.621
21.736

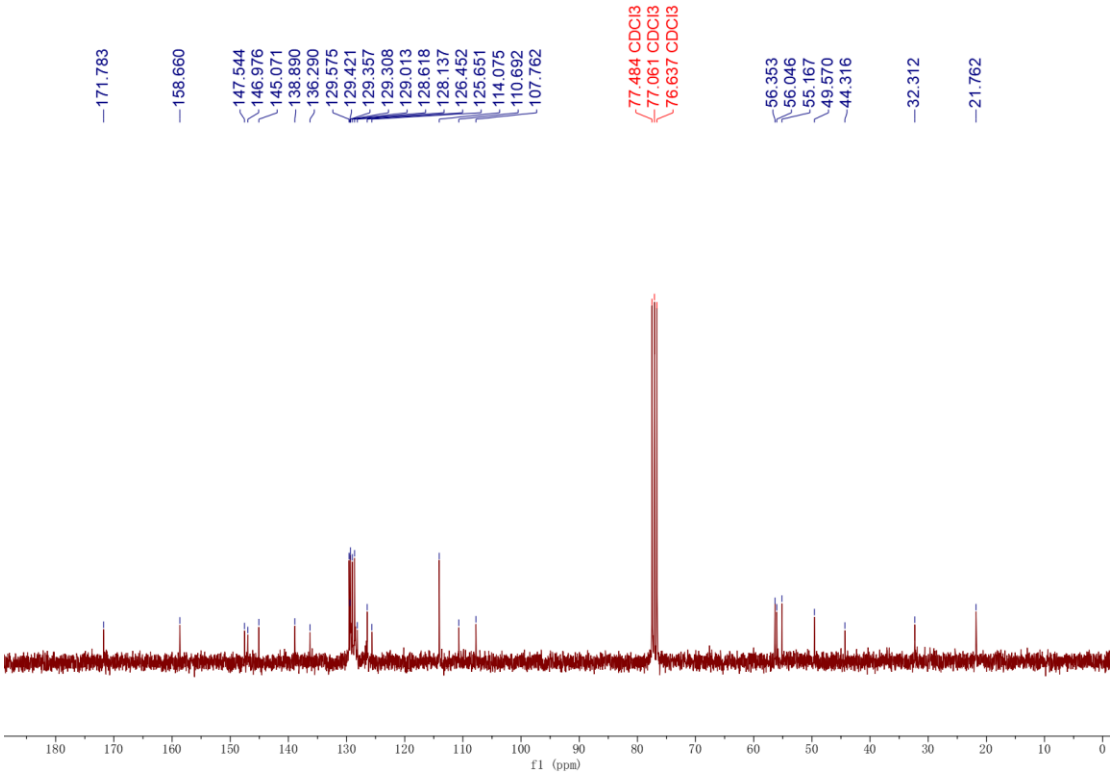

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

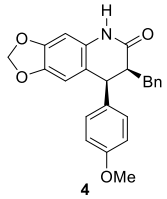

Ts
N
O
MeO
MeO
OMe

3u

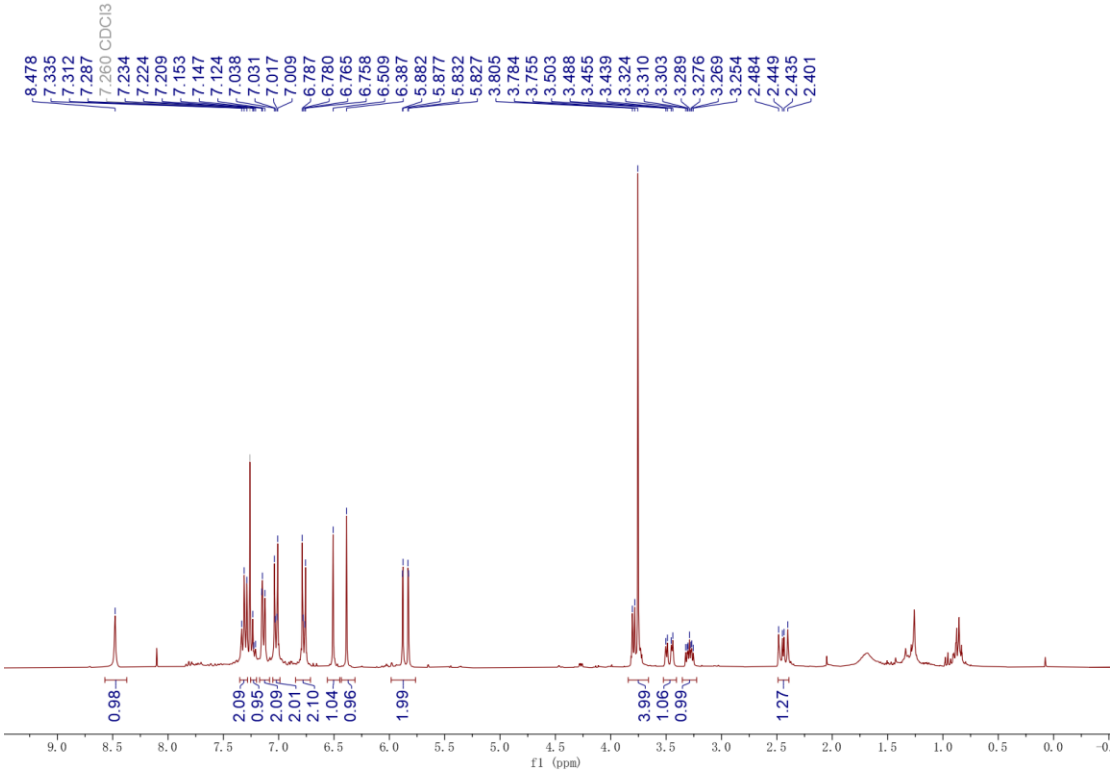

8.016
7.995
7.557
7.376
7.355
7.295
7.278
7.260 CDCl3
7.235
7.222
7.217
7.209
7.202
7.061
7.044
6.788
6.766
6.631
6.610
6.581
3.951
3.800
3.771
3.757
3.745
3.731
3.356
3.346
3.320
3.309
3.207
3.197
3.193
3.182
3.172
3.167
3.157
2.494
2.453
2.442
2.416
2.374

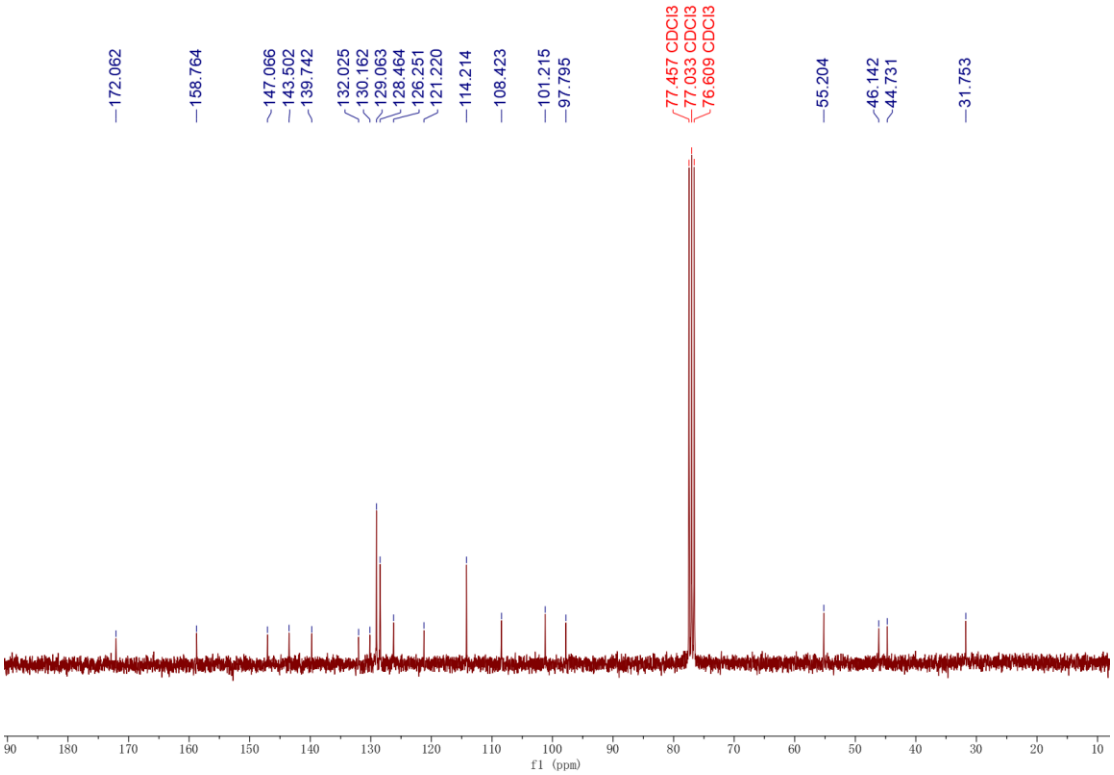

2.00
1.08
2.02
1.04
2.05
2.06
2.06
2.01
1.01
3.10
3.07
4.09
1.00
1.07
3.01
1.03
f1 (ppm)

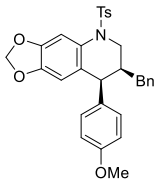

171.783
158.660
147.544
146.976
145.071
138.890
136.290
129.575
129.421
129.357
129.308
129.013
128.618
128.137
126.452
125.651
114.075
110.692
107.762
77.484 CDCl3
77.061 CDCl3
76.637 CDCl3
56.353
56.046
55.167
49.570
44.316
32.312
21.762
f1 (ppm)


H
N
O
O
O
Bn
OMe

4

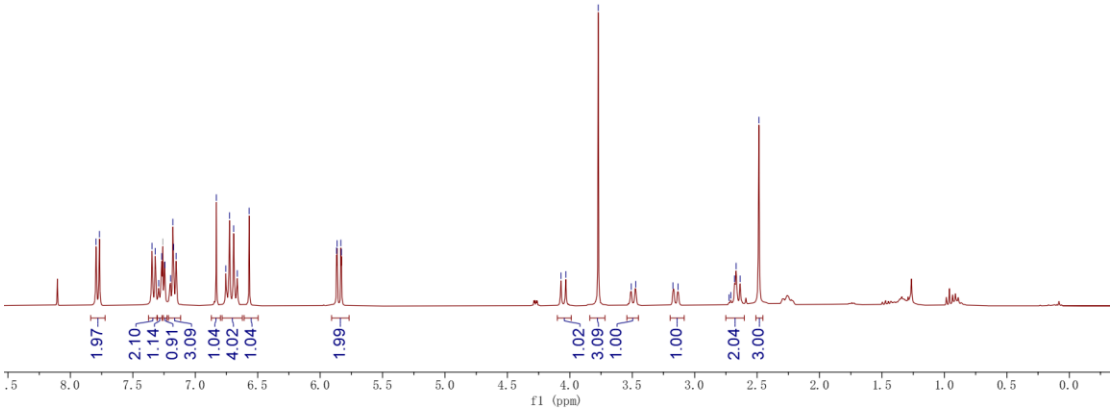

8.478
7.335
7.312
7.287
7.260 CDCl3
7.234
7.224
7.209
7.153
7.147
7.124
7.038
7.031
7.017
7.009
6.787
6.780
6.765
6.758
6.509
6.387
5.882
5.877
5.832
5.827
3.805
3.784
3.755
3.503
3.488
3.455
3.439
3.324
3.310
3.303
3.289
3.276
3.269
3.254
2.484
2.449
2.435
2.401
0.98
2.09
0.95
2.09
2.01
2.10
1.04
0.96
1.99
3.99
1.06
0.99
1.27
f1 (ppm)


172.062
158.764
147.066
143.502
139.742
132.025
130.162
129.063
128.464
126.251
121.220
114.214
108.423
101.215
97.795
77.457 CDCl3
77.033 CDCl3
76.609 CDCl3
55.204
46.142
44.731
31.753
f1 (ppm)

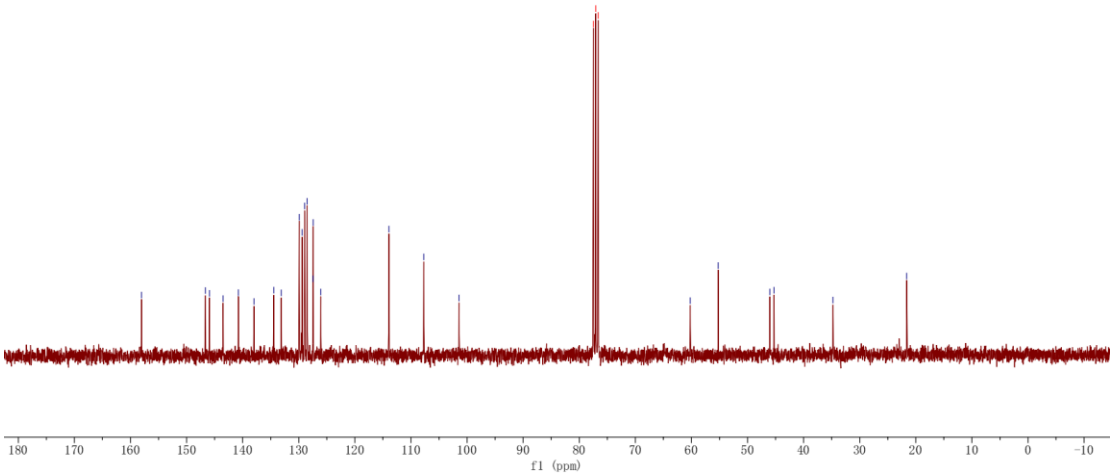

Ts
N
O
O
Bn
OMe

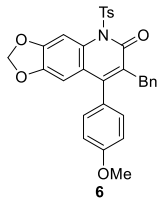
5


7.795
7.767
7.347
7.320
7.293
7.268
7.260 CDCl3
7.243
7.198
7.180
7.173
7.153
6.831
6.756
6.726
6.692
6.663
6.568
5.868
5.864
5.834
5.829
4.072
4.033
3.773
3.508
3.471
3.174
3.134
2.726
2.711
2.680
2.668
2.636
2.486

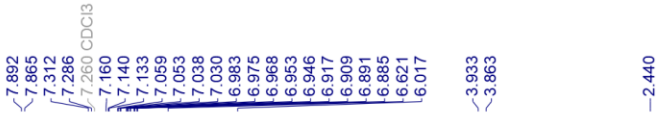

1.97
2.10
1.14
0.91
3.09
1.04
4.02
1.04
1.99
1.02
3.09
1.00
1.00
2.04
3.00
f1 (ppm)

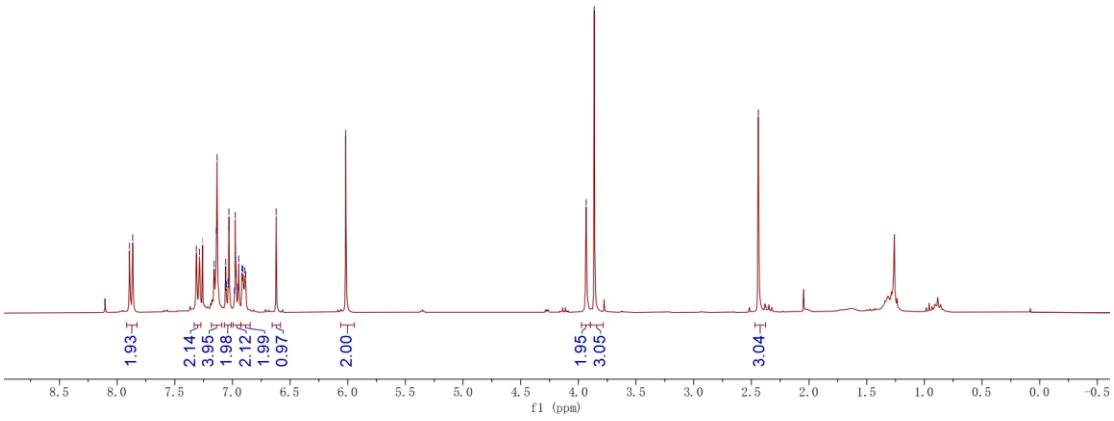

158.032
146.635
145.928
143.505
140.765
137.970
134.463
133.118
129.928
129.394
128.952
128.496
127.472
127.425
126.069
113.936
107.711
101.424
77.488 CDCl3
77.065 CDCl3
76.642 CDCl3
60.226
55.229
46.026
45.269
34.765
21.631

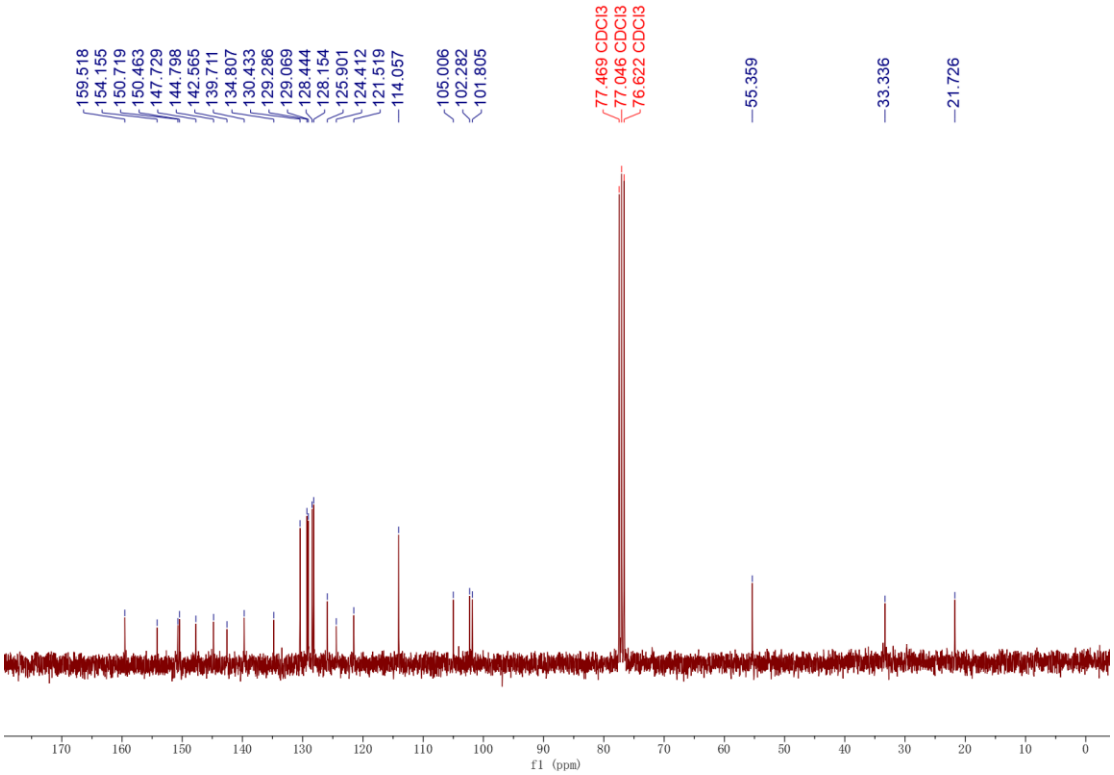

f1 (ppm)


Ts
N
O
O
O
Bn
OMe

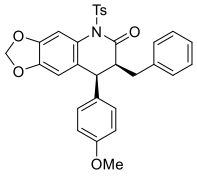
6


7.892
7.865
7.312
7.286
7.260 CDCl3
7.160
7.140
7.133
7.059
7.053
7.038
7.030
6.983
6.975
6.968
6.953
6.946
6.917
6.909
6.891
6.885
6.621
6.017
3.933
3.863
2.440

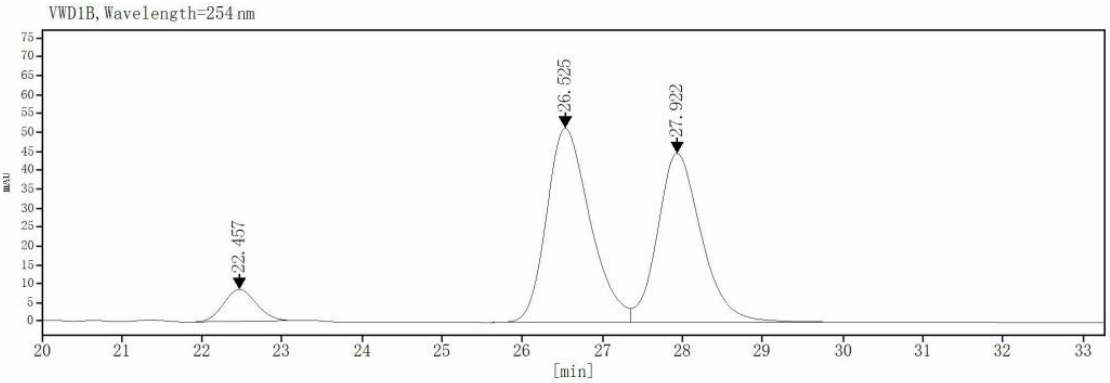

1.93
2.14
3.95
1.98
2.12
1.99
0.97
2.00
1.95
3.05
3.04
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


159.518
154.155
150.719
150.463
147.729
144.798
142.565
139.711
134.807
130.433
129.286
129.069
128.444
128.154
125.901
124.412
121.519
114.057
105.006
102.282
101.805
77.469 CDCl3
77.046 CDCl3
76.622 CDCl3
55.359
33.336
21.726
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

HPLC spectra of products.

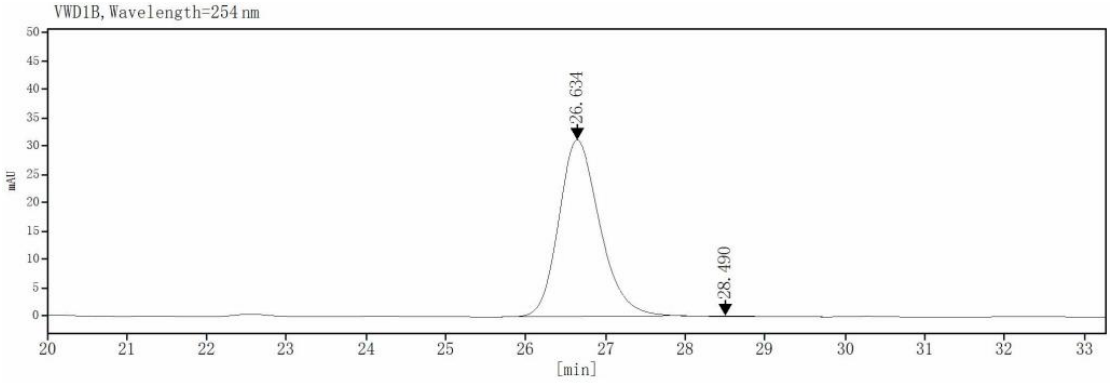


3a



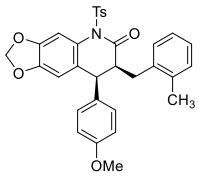
VWD1B,Wavelength=254 nm

Ret.Time	Area	Height	Area%
22.457	239.91	8.46	6.17
26.525	1937.15	51.32	49.86
27.922	1708.21	44.67	43.97
Total	3885.27	104.45	100.00

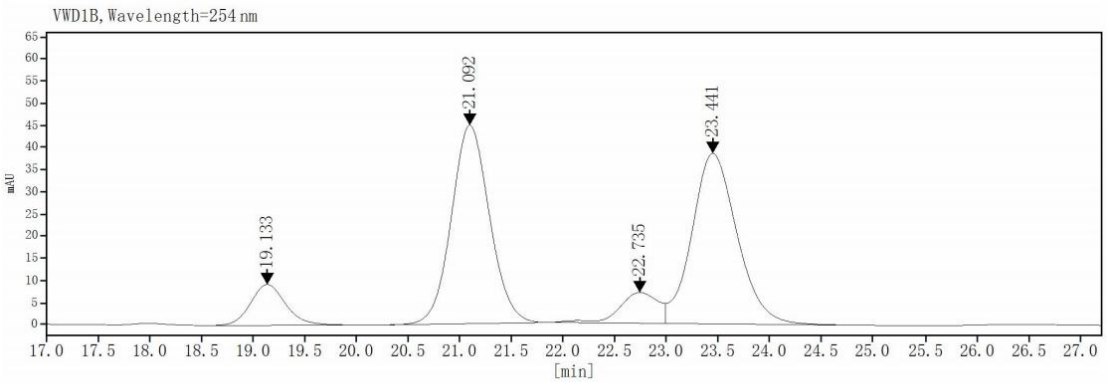


VWD1B,Wavelength=254 nm

Ret.Time	Area	Height	Area%
26.634	1111.79	31.15	99.70
28.490	3.32	0.08	0.30
Total	1115.11	31.23	100.00

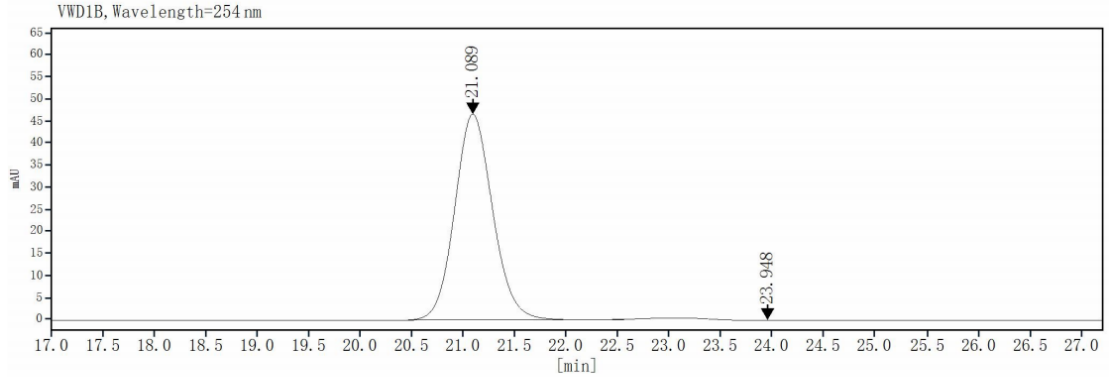


3b



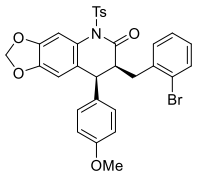
VWD1B,Wavelength=254 nm

Ret.Time	Area	Height	Area%
19.133	218.87	9.22	8.06
21.092	1147.68	44.77	42.26
22.735	179.95	6.93	6.63
23.441	1169.45	38.46	43.06
Total	2715.94	99.37	100.00

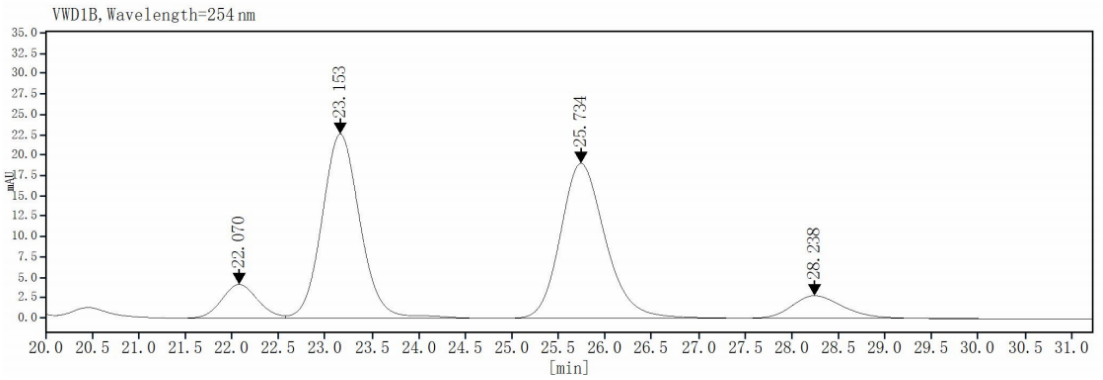


VWD1B,Wavelength=254 nm

Ret.Time	Area	Height	Area%
21.089	1187.07	46.60	99.87
23.948	1.49	0.05	0.13
Total	1188.56	46.66	100.00

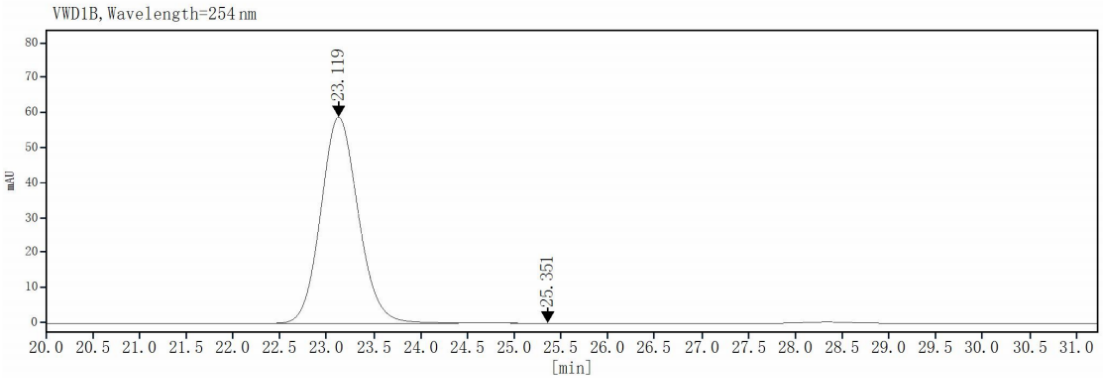


3c



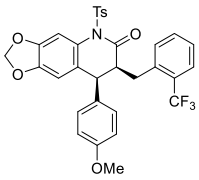
VWD1B,Wavelength=254 nm

Ret.Time	Area	Height	Area%
22.070	111.21	4.15	7.45
23.153	641.45	22.62	42.97
25.734	633.62	19.01	42.44
28.238	106.61	2.78	7.14
Total	1492.88	48.56	100.00

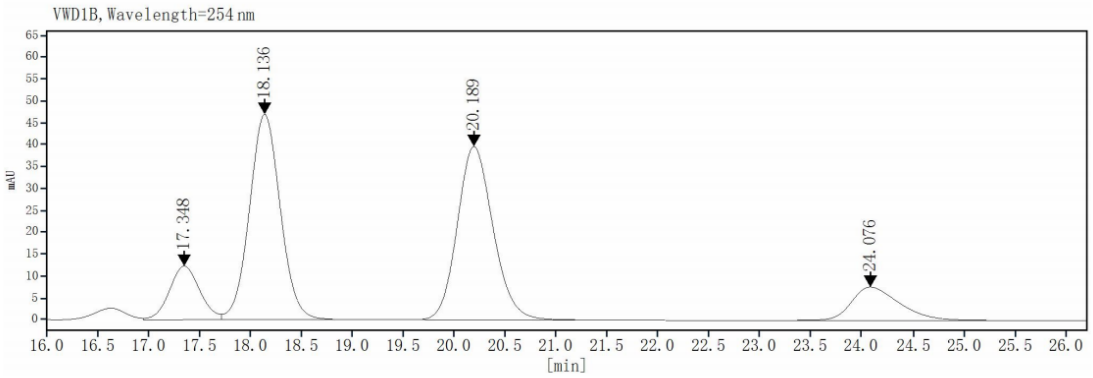


VWD1B,Wavelength=254 nm

Ret.Time	Area	Height	Area%
23.119	1636.29	58.91	99.94
25.351	1.06	0.02	0.06
Total	1637.35	58.93	100.00

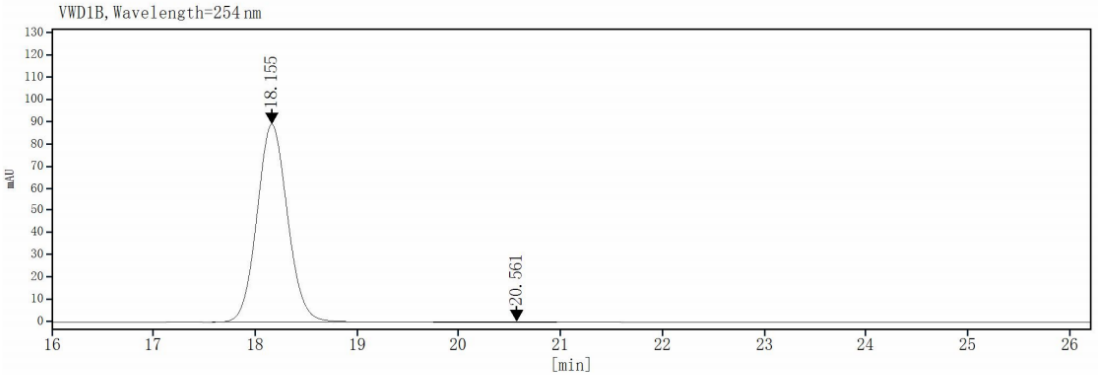


3d



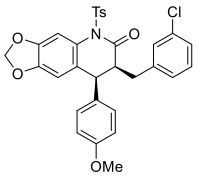
VWD1B,Wavelength=254 nm

Ret.Time	Area	Height	Area%
17.348	253.61	12.27	10.32
18.136	988.45	46.90	40.24
20.189	966.80	39.61	39.36
24.076	247.42	7.60	10.07
Total	2456.28	106.39	100.00

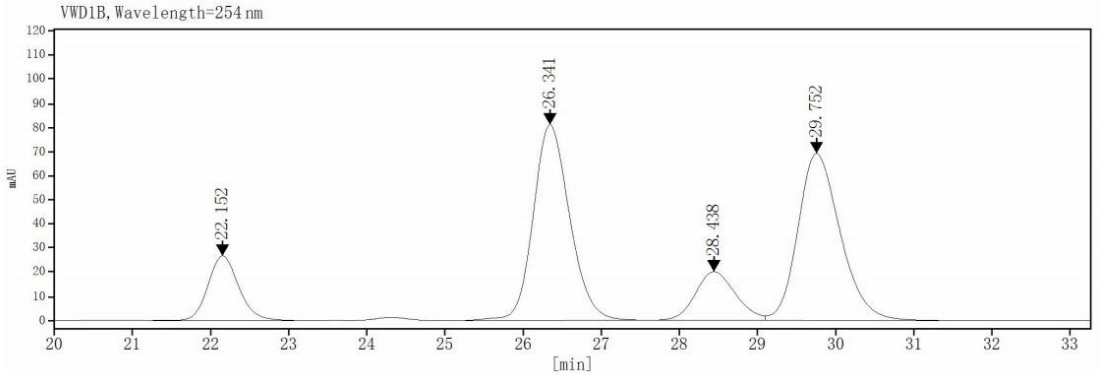


VWD1B,Wavelength=254 nm

Ret.Time	Area	Height	Area%
18.155	1851.27	89.24	99.58
20.561	7.74	0.13	0.42
Total	1859.01	89.37	100.00

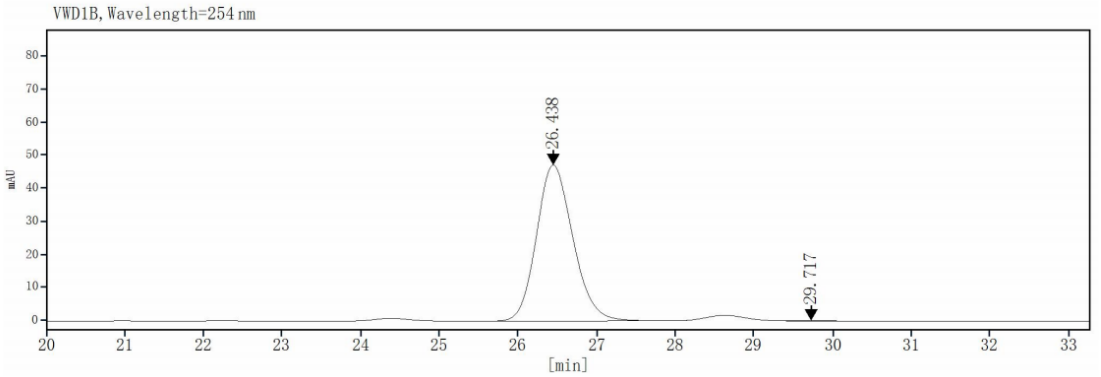


3e



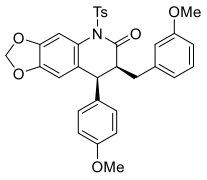
VWD1B,Wavelength=254 nm

Ret.Time	Area	Height	Area%
22.152	733.70	26.85	10.94
26.341	2636.78	81.24	39.32
28.438	719.08	20.17	10.72
29.752	2616.77	69.32	39.02
Total	6706.32	197.59	100.00

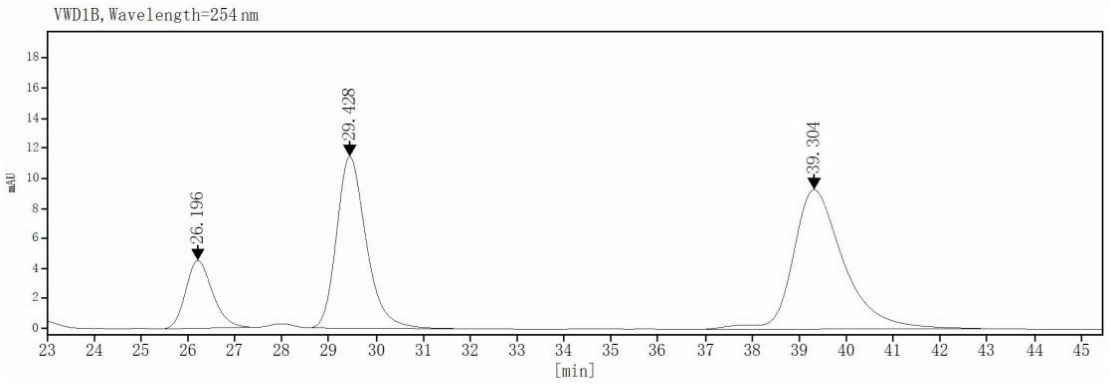


VWD1B,Wavelength=254 nm

Ret.Time	Area	Height	Area%
26.438	1521.57	47.20	99.60
29.717	6.04	0.08	0.40
Total	1527.61	47.28	100.00

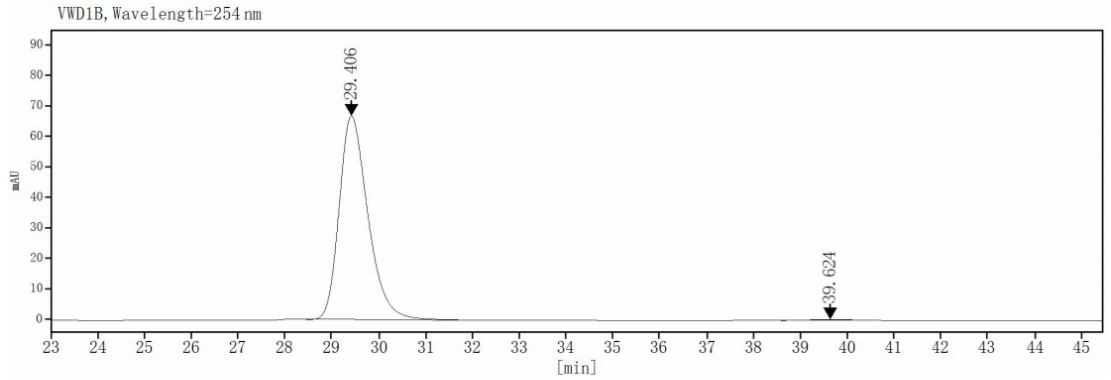


3f



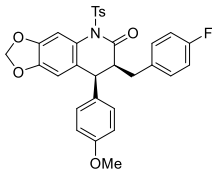
VWD1B,Wavelength=254 nm

Ret.Time	Area	Height	Area%
26.196	178.20	4.51	12.99
29.428	500.24	11.41	36.46
39.304	693.51	9.27	50.55
Total	1371.95	25.18	100.00

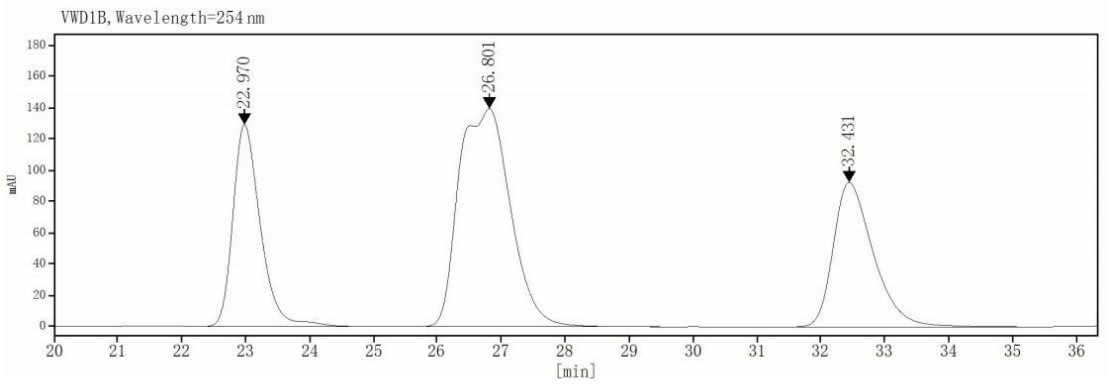


VWD1B,Wavelength=254 nm

Ret.Time	Area	Height	Area%
29.406	2826.86	66.46	99.70
39.624	8.64	0.22	0.30
Total	2835.50	66.68	100.00

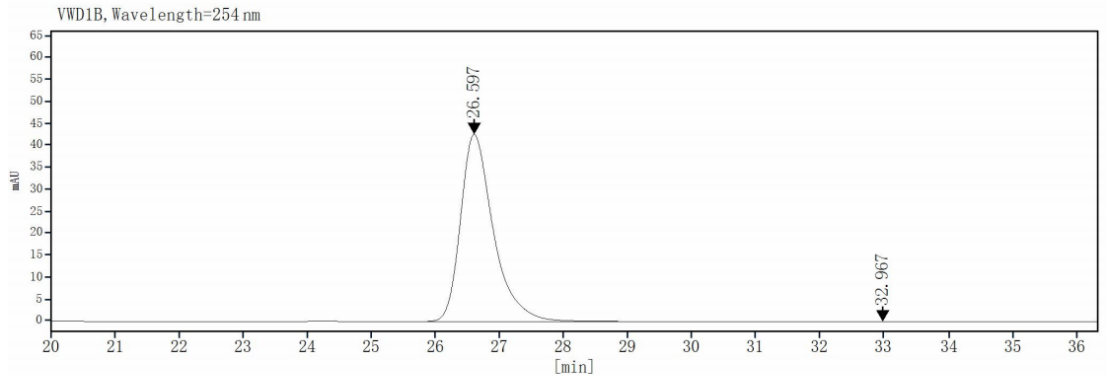


3g



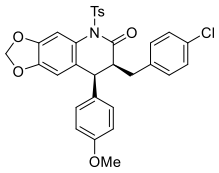
VWD1B,Wavelength=254 nm

Ret.Time	Area	Height	Area%
22.970	3852.78	128.96	24.59
26.801	7786.16	139.19	49.70
32.431	4027.86	92.34	25.71
Total	15666.81	360.48	100.00

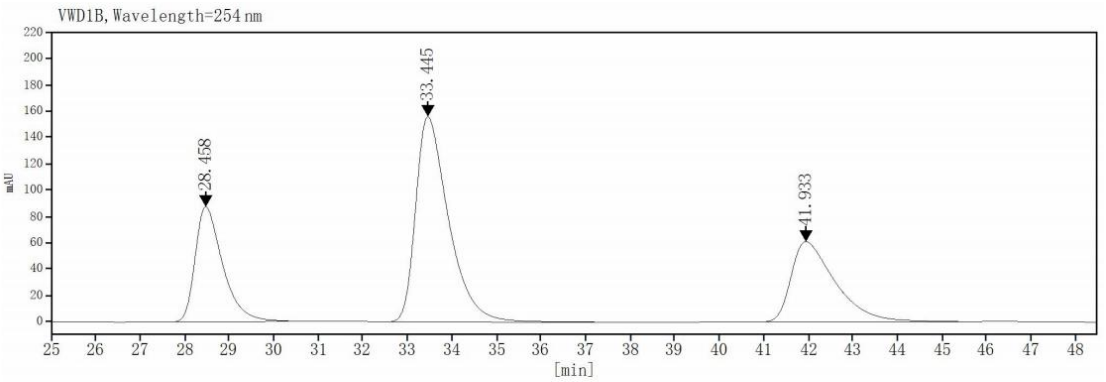


VWD1B,Wavelength=254 nm

Ret.Time	Area	Height	Area%
26.597	1517.25	42.61	99.98
32.967	0.25	0.01	0.02
Total	1517.50	42.62	100.00

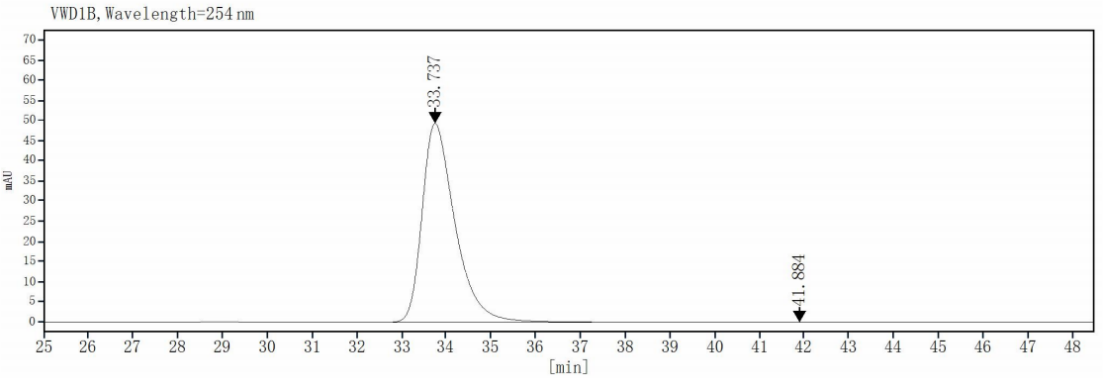


3h



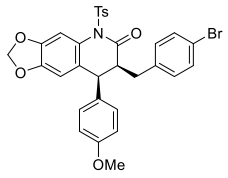
VWD1B,Wavelength=254 nm

Ret.Time	Area	Height	Area%
28.458	3763.78	87.51	23.57
33.445	8020.53	156.20	50.24
41.933	4181.08	60.92	26.19
Total	15965.39	304.64	100.00

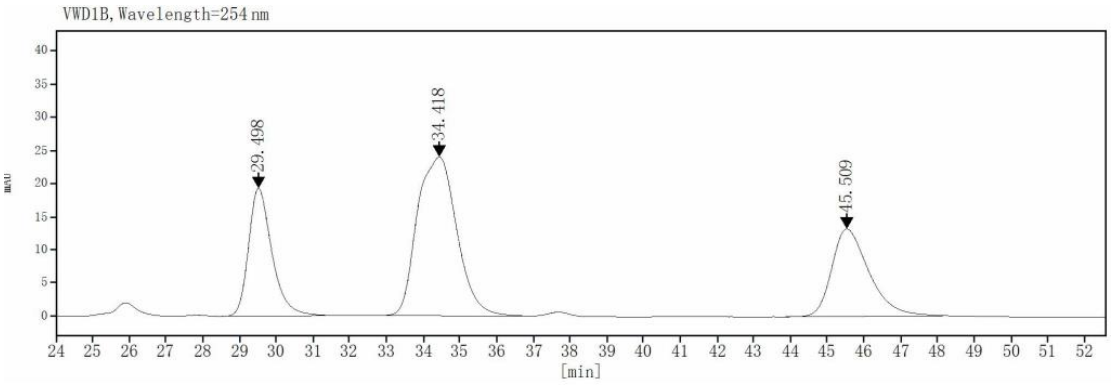


VWD1B,Wavelength=254 nm

Ret.Time	Area	Height	Area%
33.737	2542.97	49.56	99.91
41.884	2.19	0.02	0.09
Total	2545.16	49.57	100.00

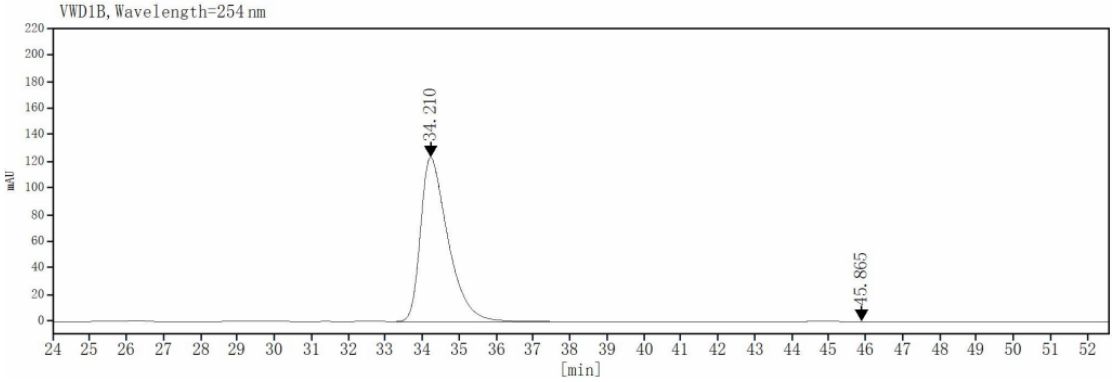


3i



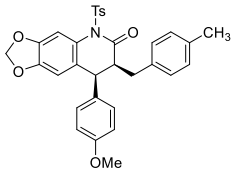
VWD1B,Wavelength=254 nm

Ret.Time	Area	Height	Area%
29.498	852.45	19.25	23.87
34.418	1790.43	23.93	50.14
45.509	928.31	13.19	25.99
Total	3571.19	56.37	100.00

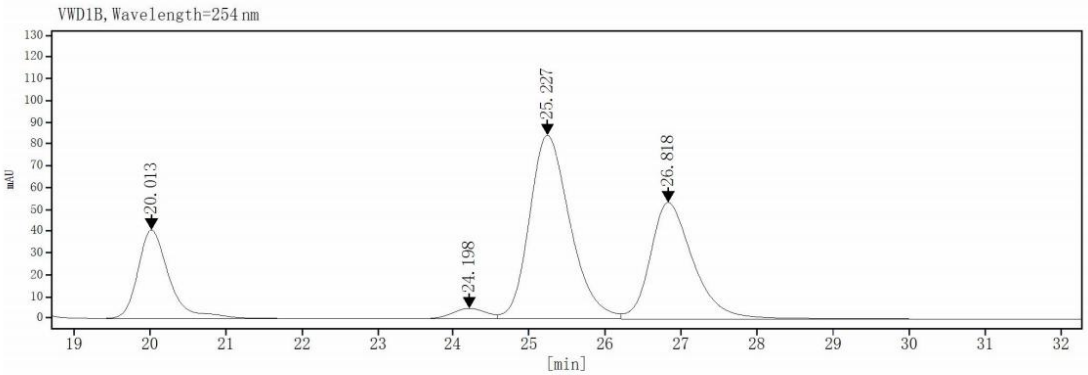


VWD1B,Wavelength=254 nm

Ret.Time	Area	Height	Area%
34.210	6363.78	123.44	99.91
45.865	5.46	0.09	0.09
Total	6369.25	123.52	100.00

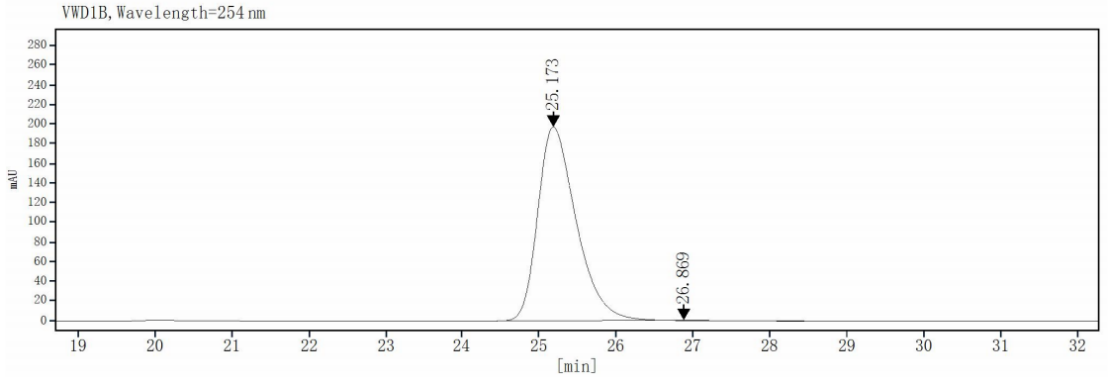


3j



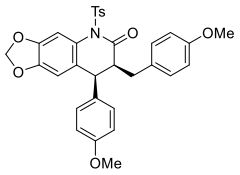
VWD1B,Wavelength=254 nm

Ret.Time	Area	Height	Area%
20.013	1166.14	40.62	17.83
24.198	147.65	4.78	2.26
25.227	3131.64	84.25	47.89
26.818	2093.31	53.37	32.01
Total	6538.74	183.03	100.00

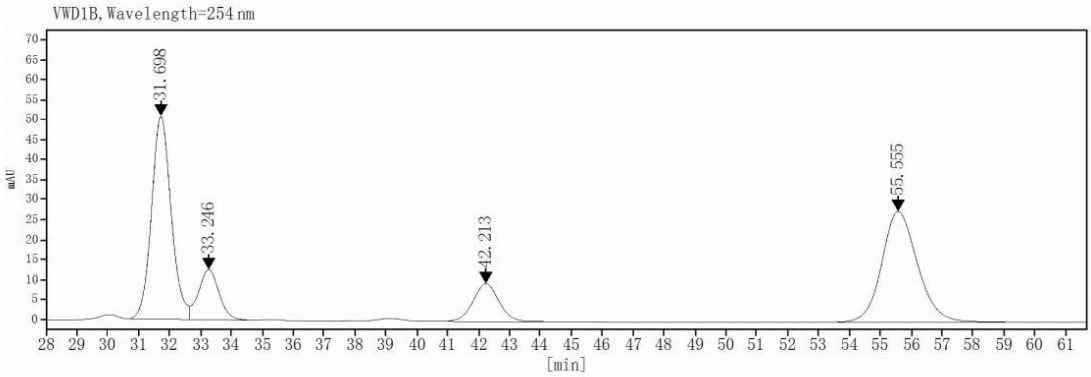


VWD1B,Wavelength=254 nm

Ret.Time	Area	Height	Area%
25.173	6840.25	197.49	99.78
26.869	14.94	0.26	0.22
Total	6855.19	197.75	100.00

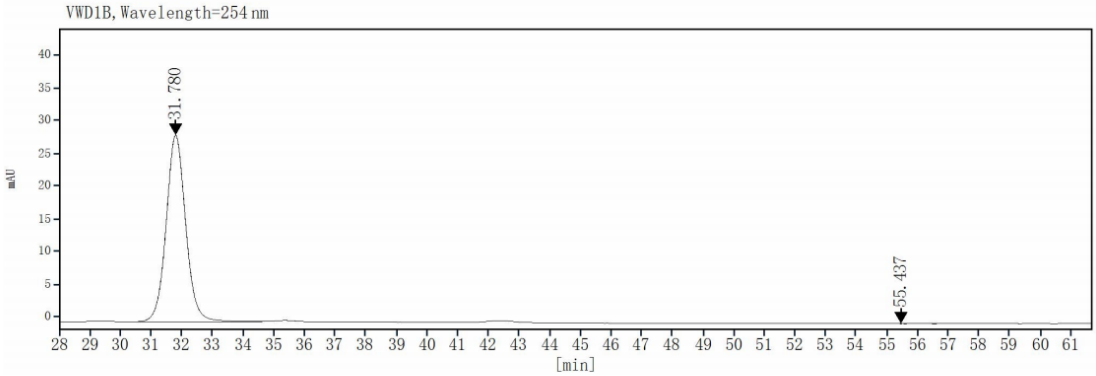


3k



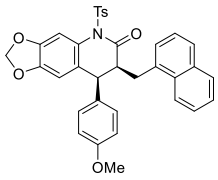
VWD1B,Wavelength=254 nm

Ret.Time	Area	Height	Area%
31.698	2249.86	50.93	39.89
33.246	580.05	12.59	10.28
42.213	563.48	9.54	9.99
55.555	2247.01	27.83	39.84
Total	5640.40	100.89	100.00

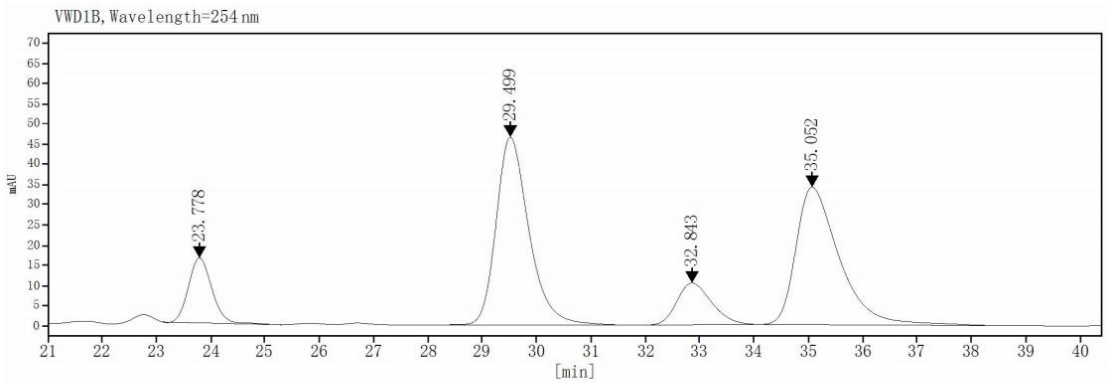


VWD1B,Wavelength=254 nm

Ret.Time	Area	Height	Area%
31.780	1260.75	28.53	99.93
55.437	0.90	0.01	0.07
Total	1261.65	28.54	100.00

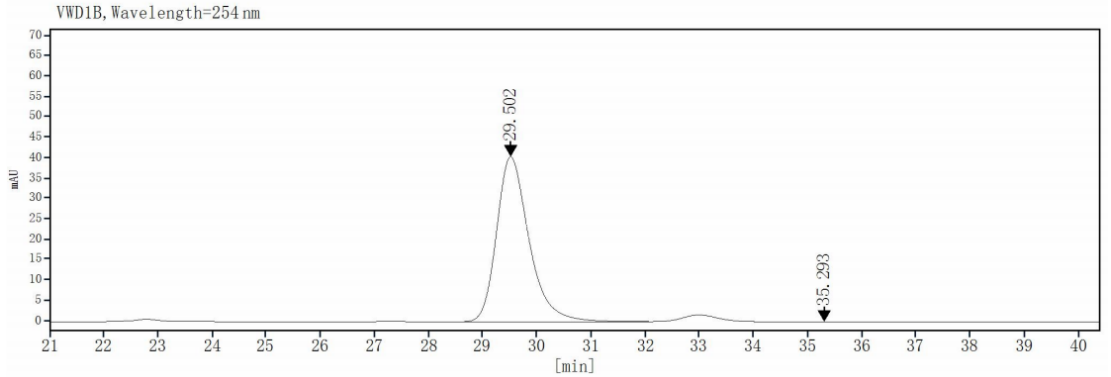


3l



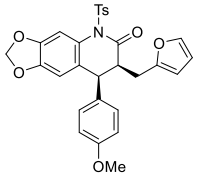
VWD1B,Wavelength=254 nm

Ret.Time	Area	Height	Area%
23.778	482.75	16.12	10.05
29.499	1963.05	46.63	40.88
32.843	459.69	10.38	9.57
35.052	1896.14	34.13	39.49
Total	4801.62	107.25	100.00

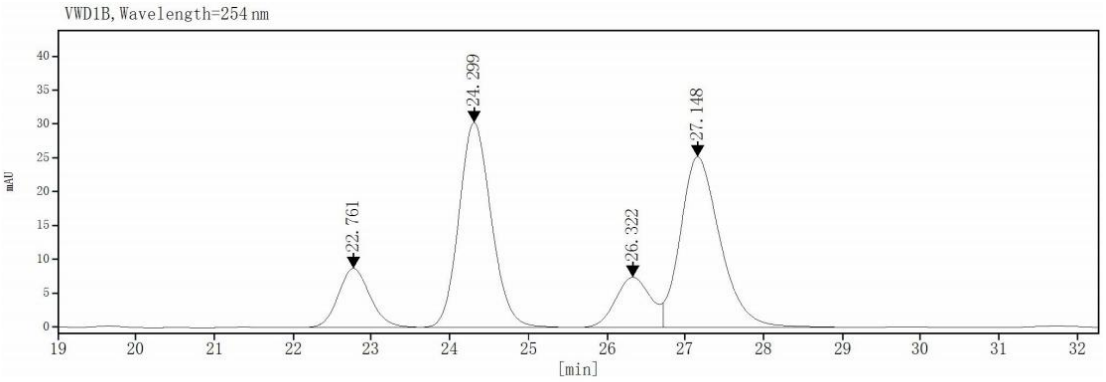


VWD1B,Wavelength=254 nm

Ret.Time	Area	Height	Area%
29.502	1684.30	40.48	99.90
35.293	1.64	0.02	0.10
Total	1685.94	40.51	100.00

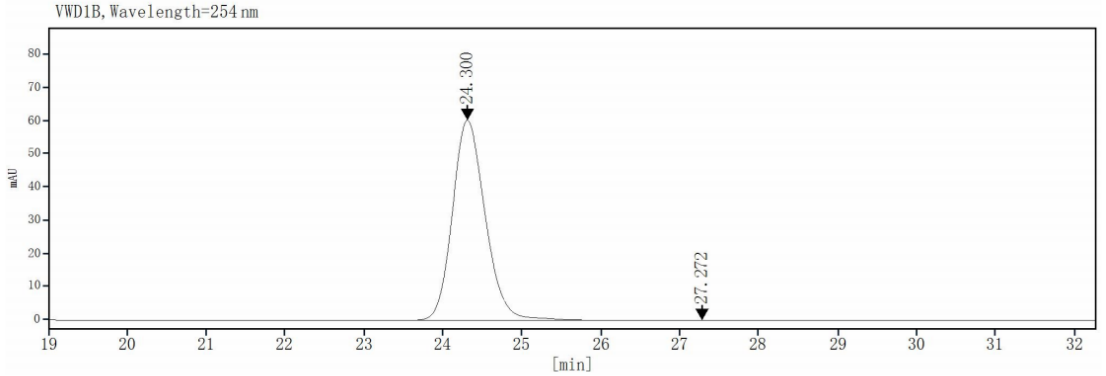


3m



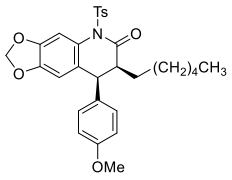
VWD1B,Wavelength=254 nm

Ret.Time	Area	Height	Area%
22.761	243.19	8.71	10.92
24.299	866.75	30.28	38.93
26.322	232.95	7.40	10.46
27.148	883.46	25.18	39.68
Total	2226.35	71.57	100.00

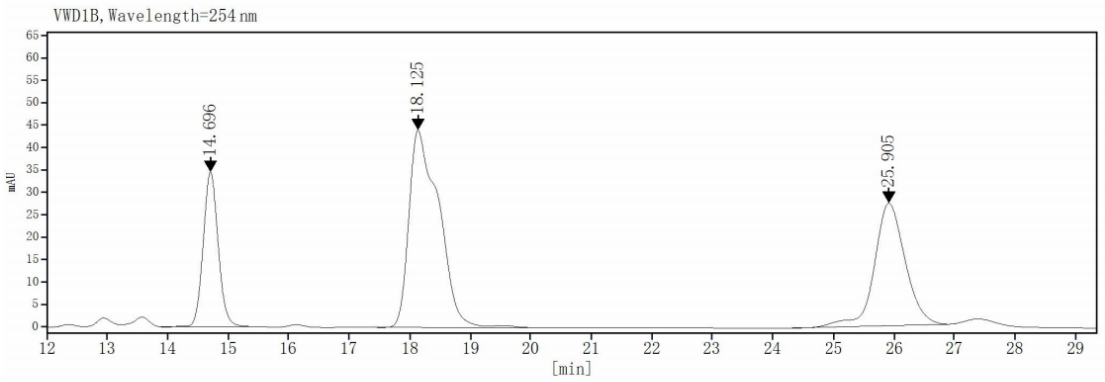


VWD1B,Wavelength=254 nm

Ret.Time	Area	Height	Area%
24.300	1741.05	60.37	99.96
27.272	0.76	0.03	0.04
Total	1741.81	60.40	100.00

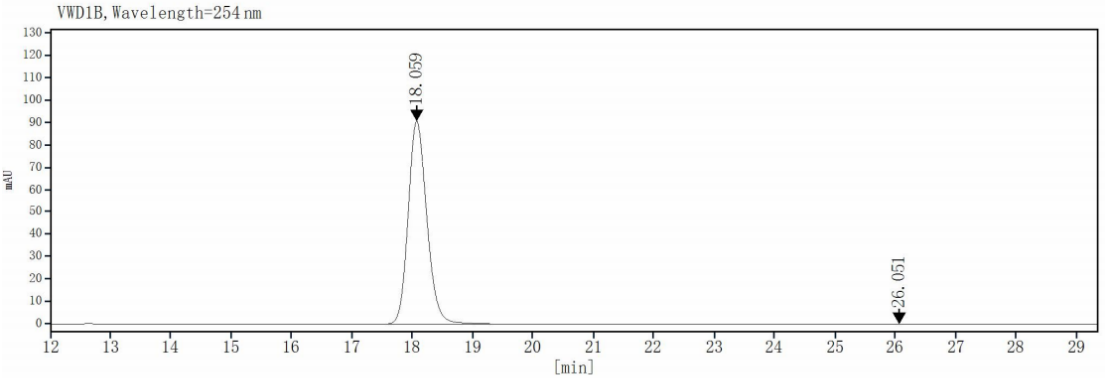


3n



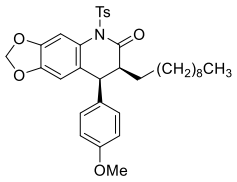
VWD1B,Wavelength=254 nm

Ret.Time	Area	Height	Area%
14.696	593.02	34.50	19.25
18.125	1516.61	44.05	49.23
25.905	971.00	27.37	31.52
Total	3080.63	105.91	100.00

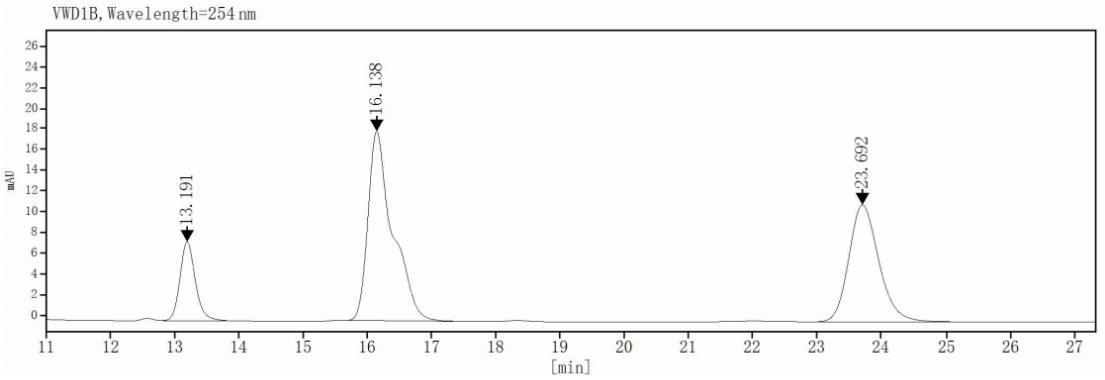


VWD1B,Wavelength=254 nm

Ret.Time	Area	Height	Area%
18.059	1957.27	90.97	99.99
26.051	0.12	0.01	0.01
Total	1957.39	90.99	100.00

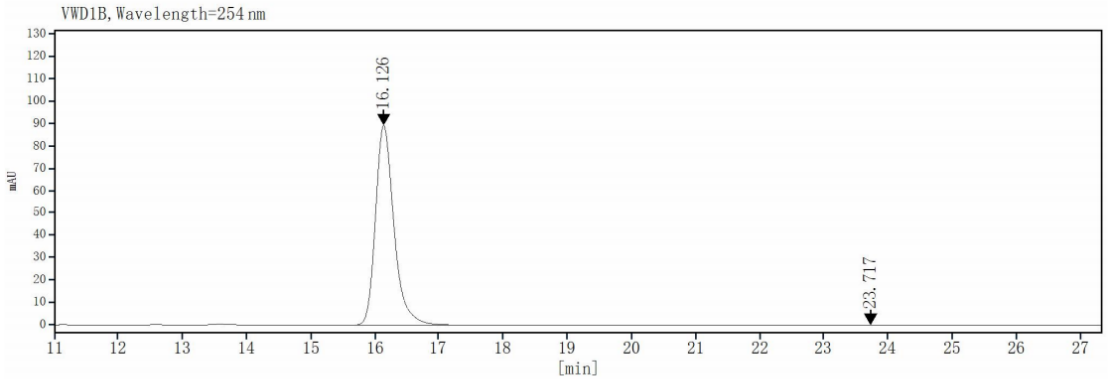


3o



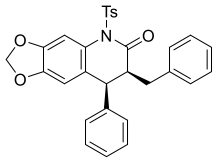
VWD1B,Wavelength=254 nm

Ret.Time	Area	Height	Area%
13.191	127.49	7.65	12.97
16.138	487.69	18.29	49.62
23.692	367.60	11.31	37.40
Total	982.78	37.24	100.00

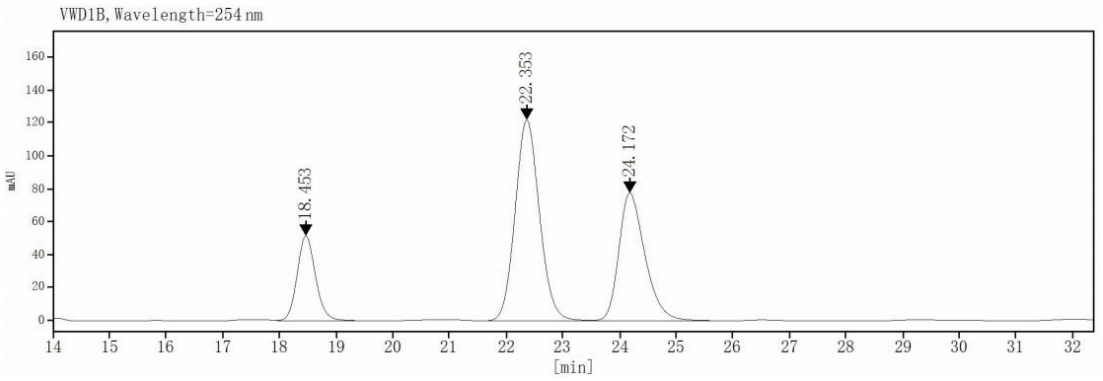


VWD1B,Wavelength=254 nm

Ret.Time	Area	Height	Area%
16.126	1792.50	89.54	99.94
23.717	1.11	0.03	0.06
Total	1793.61	89.57	100.00

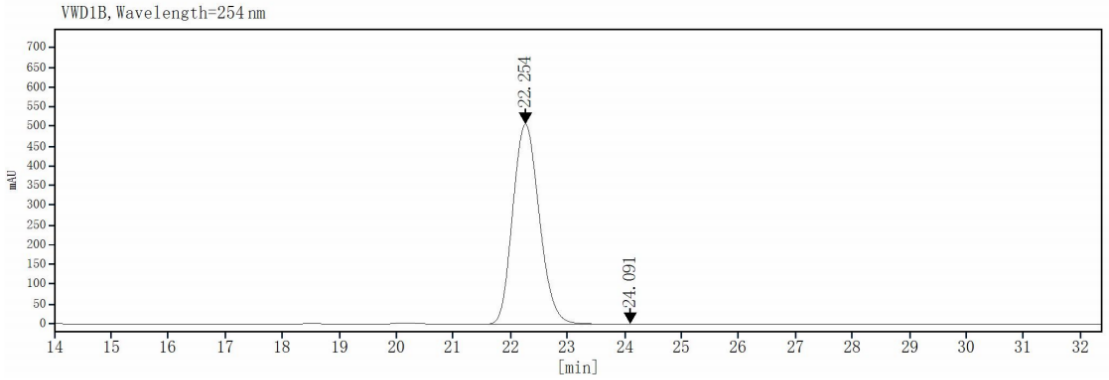


3p



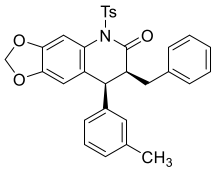
VWD1B,Wavelength=254 nm

Ret.Time	Area	Height	Area%
18.453	1171.16	51.67	16.03
22.353	3653.48	122.04	49.99
24.172	2483.09	77.58	33.98
Total	7307.73	251.29	100.00

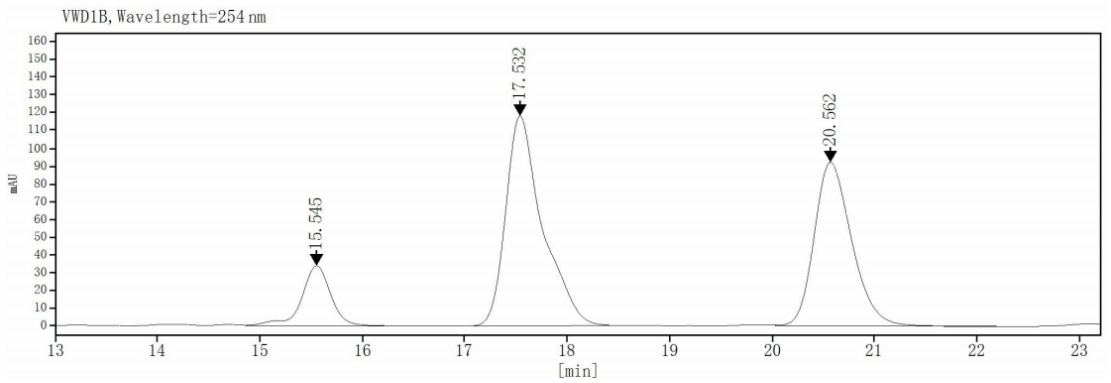


VWD1B,Wavelength=254 nm

Ret.Time	Area	Height	Area%
22.254	16361.27	507.48	99.85
24.091	24.79	0.30	0.15
Total	16386.07	507.78	100.00

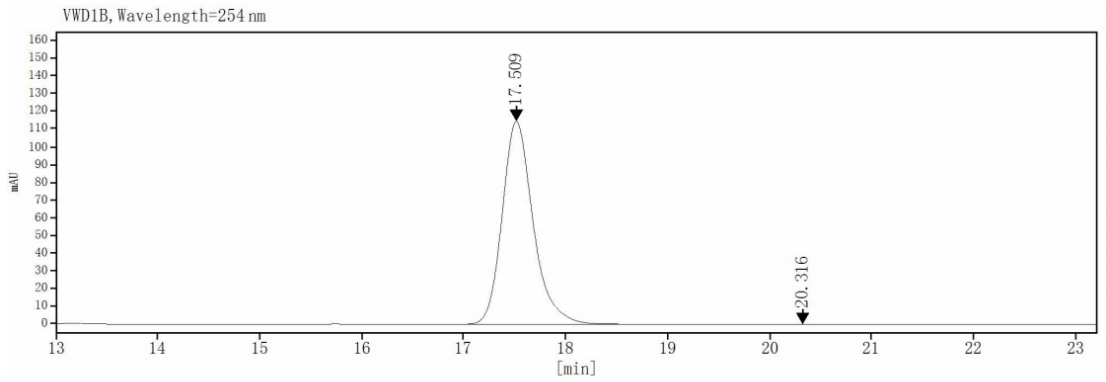


3q



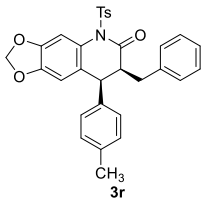
VWD1B,Wavelength=254 nm

Ret.Time	Area	Height	Area%
15.545	681.94	33.98	11.36
17.532	2960.98	118.43	49.34
20.562	2358.03	92.38	39.29
Total	6000.96	244.79	100.00

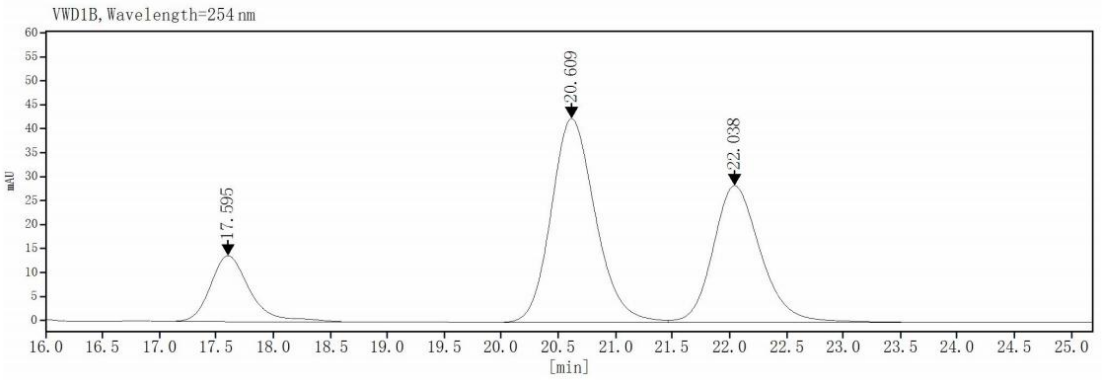


VWD1B,Wavelength=254 nm

Ret.Time	Area	Height	Area%
17.509	2426.51	114.87	99.99
20.316	0.26	0.01	0.01
Total	2426.77	114.89	100.00

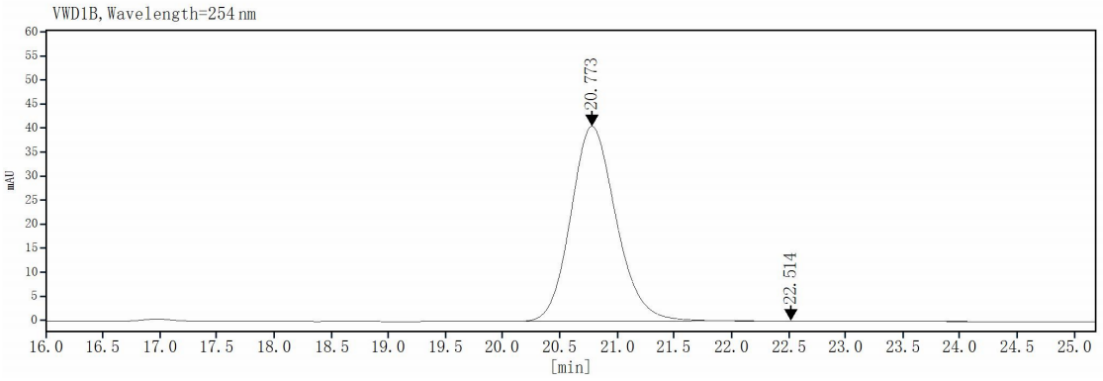


3r



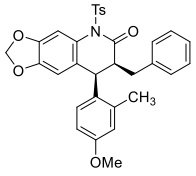
VWD1B,Wavelength=254 nm

Ret.Time	Area	Height	Area%
17.595	331.13	13.77	14.34
20.609	1148.57	42.59	49.73
22.038	829.82	28.57	35.93
Total	2309.52	84.93	100.00

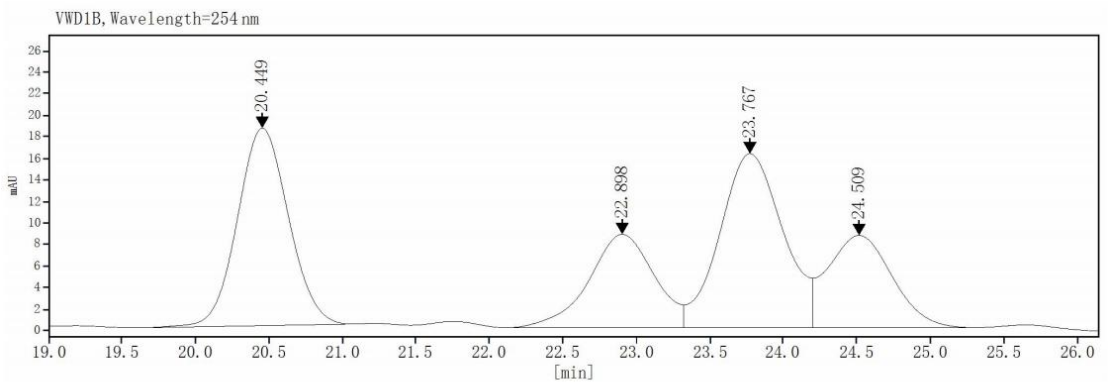


VWD1B,Wavelength=254 nm

Ret.Time	Area	Height	Area%
20.773	1118.45	40.59	99.62
22.514	4.32	0.07	0.38
Total	1122.77	40.66	100.00

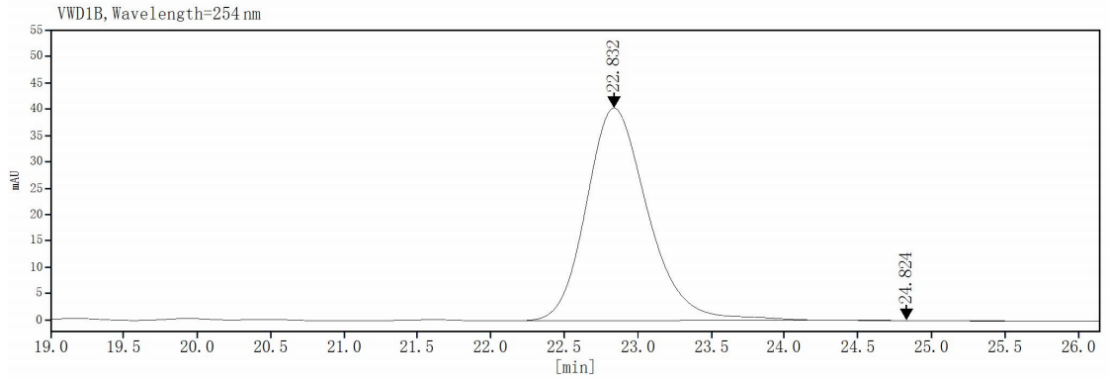


3s



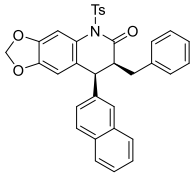
VWD1B,Wavelength=254 nm

Ret.Time	Area	Height	Area%
20.449	442.31	18.34	30.43
22.898	267.79	8.67	18.42
23.767	482.47	16.16	33.19
24.509	260.90	8.57	17.95
Total	1453.46	51.74	100.00

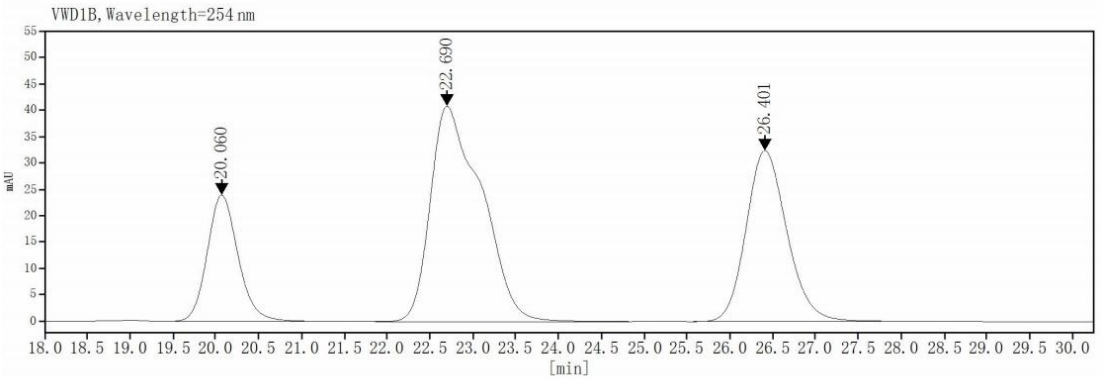


VWD1B,Wavelength=254 nm

Ret.Time	Area	Height	Area%
22.832	1170.68	40.29	99.76
24.824	2.86	0.05	0.24
Total	1173.54	40.35	100.00

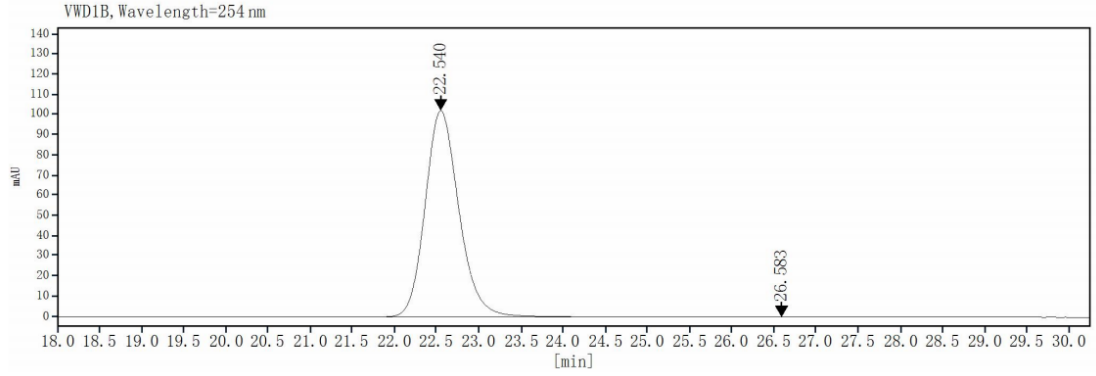


3t



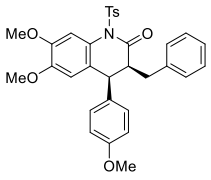
VWD1B,Wavelength=254 nm

Ret.Time	Area	Height	Area%
20.060	601.84	23.98	17.85
22.690	1694.13	40.85	50.24
26.401	1076.38	32.42	31.92
Total	3372.35	97.25	100.00

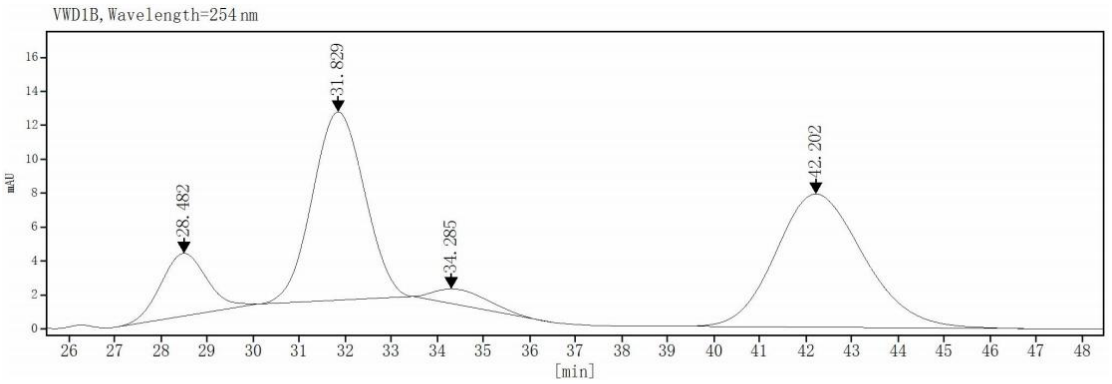


VWD1B,Wavelength=254 nm

Ret.Time	Area	Height	Area%
22.540	2861.55	102.37	99.97
26.583	0.92	0.02	0.03
Total	2862.47	102.39	100.00

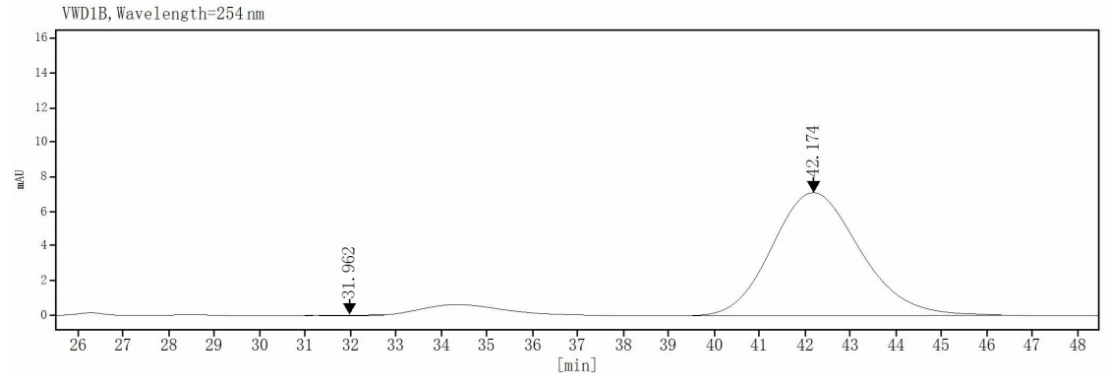


3u



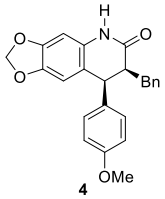
VWD1B,Wavelength=254 nm

Ret.Time	Area	Height	Area%
28.482	256.27	3.69	11.40
31.829	873.20	11.10	38.85
34.285	73.83	0.86	3.28
42.202	1044.57	7.85	46.47
Total	2247.88	23.50	100.00

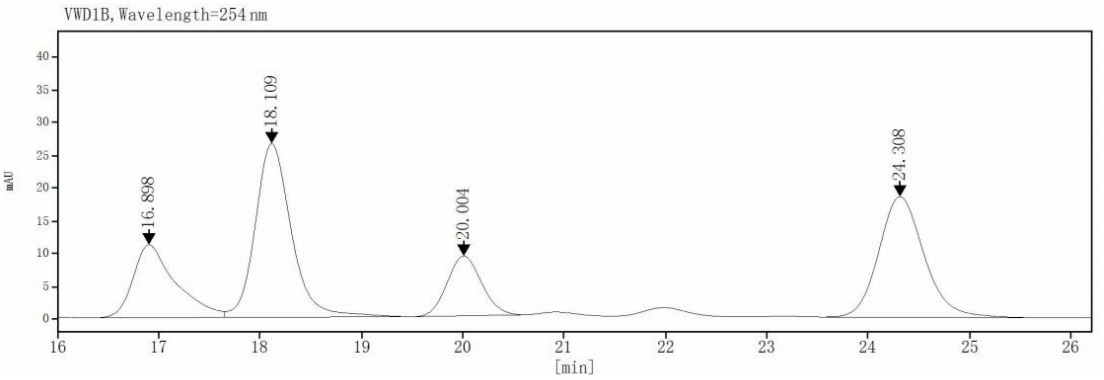


VWD1B,Wavelength=254 nm

Ret.Time	Area	Height	Area%
31.962	2.26	0.03	0.23
42.174	962.76	7.12	99.77
Total	965.03	7.16	100.00

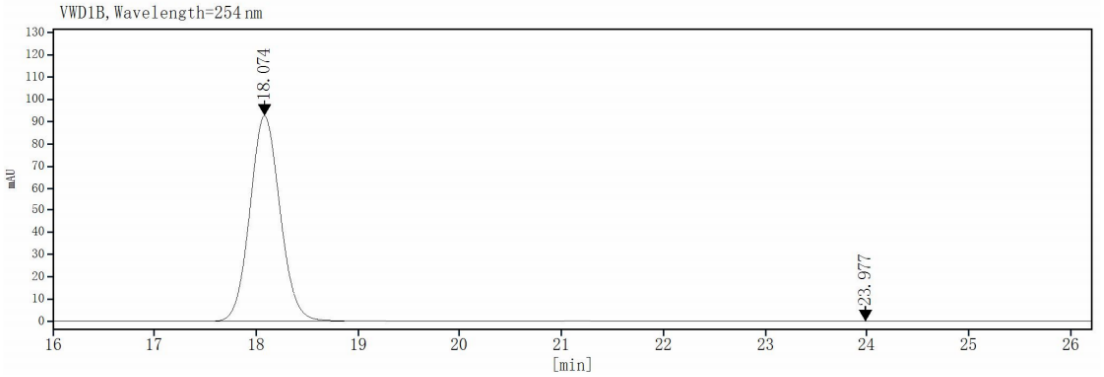


4



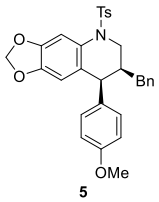
VWD1B,Wavelength=254 nm

Ret.Time	Area	Height	Area%
16.898	326.16	11.16	18.41
18.109	656.76	26.54	37.08
20.004	215.46	9.13	12.17
24.308	572.79	18.42	32.34
Total	1771.16	65.24	100.00

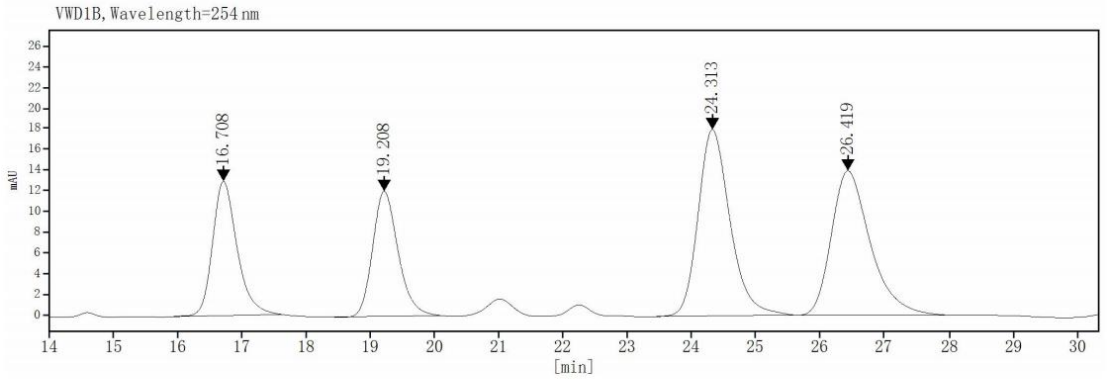


VWD1B,Wavelength=254 nm

Ret.Time	Area	Height	Area%
18.074	1904.69	92.69	99.99
23.977	0.11	0.00	0.01
Total	1904.80	92.70	100.00

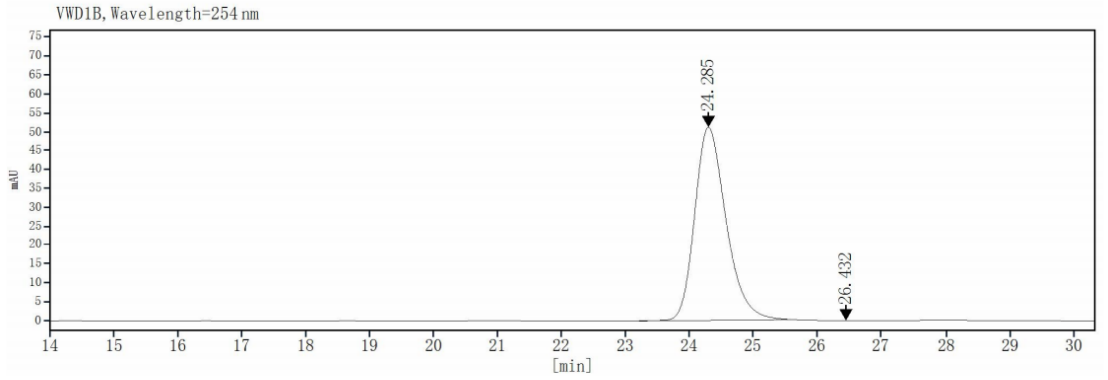


5



VWD1B,Wavelength=254 nm

Ret.Time	Area	Height	Area%
16.708	344.58	13.00	18.28
19.208	331.82	12.10	17.61
24.313	621.51	18.03	32.98
26.419	586.68	13.96	31.13
Total	1884.59	57.08	100.00



VWD1B,Wavelength=254 nm

Ret.Time	Area	Height	Area%
24.285	1743.29	51.17	99.98
26.432	0.43	0.02	0.02
Total	1743.72	51.19	100.00