Asymmetric Allylic Substitution-Isomerization to Axially Chiral Enamides via Hydrogen-Bonding Assisted Central-to-Axial Chirality Transfer

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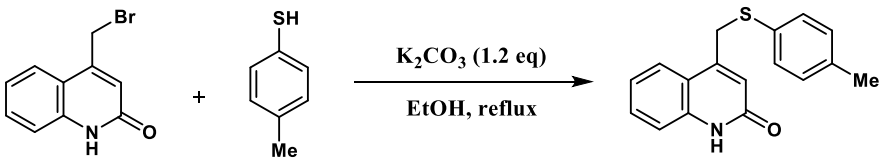
General Information

Unless otherwise noted, all starting materials were purchased from commercial sources and used without any further purification. The reactions were carried out in the glovebox unless otherwise stated. Toluene, 1, 4-dioxane, DCM, and DME were obtained from commercial sources and anhydrous THF is gained from distilling apparatus. Chemicals were used as obtained from the suppliers. The analytical data for the known compounds were found to match with the literature data and stored at -30 °C under an inert atmosphere. Room temperature = 23-25 °C. TLC plates were visualized under UV light (254 nm) or by staining with phosphomolybdic acid or $KMnO_4$ followed by heating. Abbreviations are reported as follows: EA = ethyl acetate, DCM = dichloromethane, DME = dimethoxyethane, THF = tetrahydrofuran, PE = petroleum ether. ^1H NMR, ^{19}F NMR and ^{13}C NMR spectra were recorded on Bruker-AVANCE 500 or Bruker-DMX 400 spectrometer, and chemical shifts are reported in ppm. Multiplicities are reported using the following abbreviations: s = singlet, d =doublet, t = triplet, q = quartet, m = multiplet. The impurities of grease were found in some cases of NMR, however, not affect the yields of the products. High resolution mass spectral data were acquired on Agilent Technologies Accurate-Mass Q-TQF LC/MS 6520 operated by China Pharmaceutical University. Enantiomeric excess was determined on a Thermo Fisher UltiMate 3000 Chiral HPLC using AD, OD and IA column. All cinnamyl carbonates, quinolones and 2-pyridiones are known compounds except **2x**.

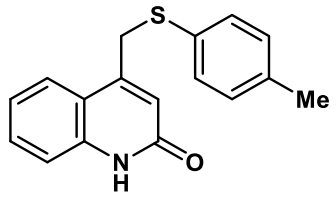
General procedure A: The synthesis of quinolinol analogue



2x

A solution of 4-(bromomethyl)quinolin-2(1*H*)-one (2.36 g, 10.0 mmol), *p*-toluenethiol (1.24 g, 10.0 mmol) and anhydrous potassium carbonate (1.65 g, 12.0 mmol) in 30.0 mL of EtOH was heated at reflux for overnight. When the reaction completed, the resulting solution was diluted with water (20 ml) and filtered, and the yellow solid

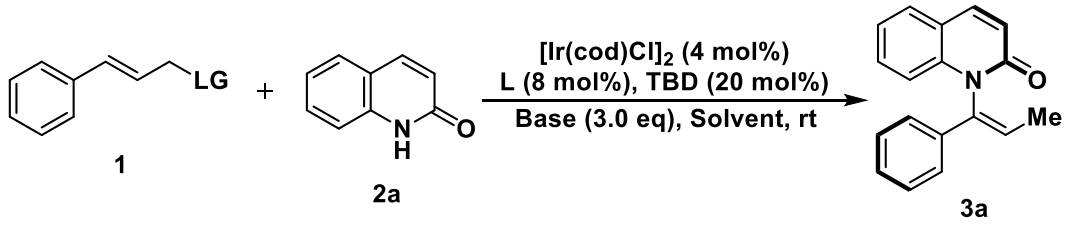
was collected in 91% yield (3.6 g), m.p.158-159 ºC.



2x

^{1}H NMR (500 MHz, DMSO-d_6) δ 11.63 (s, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.46 (t, J = 7.7 Hz, 1H), 7.26 (d, J = 8.2 Hz, 1H), 7.21 (d, J = 7.8 Hz, 2H), 7.16 (t, J = 7.6 Hz, 1H), 7.08 (d, J = 7.8 Hz, 2H), 6.25 (s, 1H), 4.35 (s, 2H), 2.21 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 160.63, 145.99, 138.50, 135.75, 130.42, 129.79, 129.66, 129.15, 124.44, 121.00, 120.59, 117.21, 115.08, 33.74, 20.01. HRMS(ESI) m/z: calculated for $[C_{17}H_{15}NOS + H]^+$ 282.0953, found 282.0948. IR ν 2845.62, 1902.48, 1667.44, 1551.40, 1393.72, 1262.81, 1155.70, 977.19, 864.13, 816.53, 670.74, 581.49, cm^{-1}.

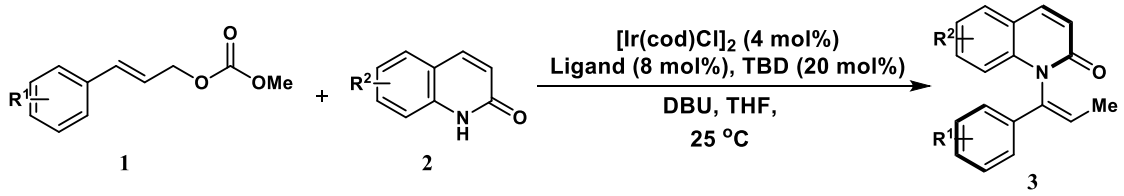
General procedure B: Optimized conditions



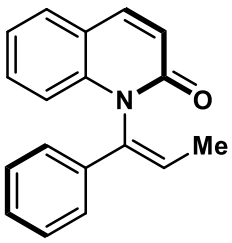
The reactions were proceeded in the glovebox. $[Ir(cod)Cl]_2$ (2.7 mg, 0.004 mmol, 0.04 eq), **L1** (0.008 mmol, 0.08 eq), and TBD (2.8 mg, 0.02 mmol, 0.2 eq) were added to a 2 dram scintillation vial (vial A) equipped with a magnetic stirring bar. The vial was then charged with solvent (0.5 mL) and stirred at 25 ℃ for 30 min, generating an orange solution. To another 2 dram scintillation vial (vial B) was added **1** (0.1 mmol, 1.0 eq), 2-hydroxyquinoline (0.2 mmol, 2.0 eq), base (0.3 mmol, 3.0 eq) and solvent (0.5 mL). The pre-formed catalyst solution (vial A) was then transferred to vial B. The vial B was sealed and stirred at rt with stirring for 48 h. The vial was then removed from the glovebox and uncapped. Saturated NH_4Cl aqueous solution was added and the mixture was extracted with DCM (10 mL x 3), the combined organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo.

The residue was purified by column chromatography over silica gel (PE : EA = 4 : 1) to afford the desired product.

General procedure C: Synthesis of axially chiral enamides



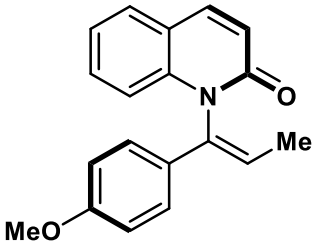
The reactions were proceeded in the glovebox. $[Ir(cod)Cl]_2$ (2.7 mg, 0.004 mmol, 0.04 eq), **L1** (4.3 mg, 0.008 mmol, 0.08 eq), and TBD (2.8 mg, 0.02 mmol, 0.2 eq) were added to a 2 dram scintillation vial (vial A) equipped with a magnetic stirring bar. The vial was then charged with THF (0.5 mL) and stirred at 25 ℃ (Internal temperature of glove box) for 30 min, generating an orange solution. To another 2 dram scintillation vial (vial B) was added propenyl carbonate (0.1 mmol, 1.0 eq), 2-hydroxyquinoline (0.2 mmol, 2.0 eq), DBU (0.3 mmol, 3.0 eq) and THF (0.5 mL). The pre-formed catalyst solution (vial A) was then transferred to vial B. The vial B was sealed and stirred at rt (Internal temperature of glove box) with stirring for 36-48 h. The vial was then removed from the glovebox and uncapped. Saturated NH_4Cl aqueous solution was added and the mixture was extracted with DCM (10 mL x 3), the combined organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography over silica gel (PE : EA = 4 : 1) to afford the desired product. Ps: For series of products **3**, the minor signals in the aromatic part are corresponding to *E*-isomer, as well as in aliphatic part of the methyl signal.



3a

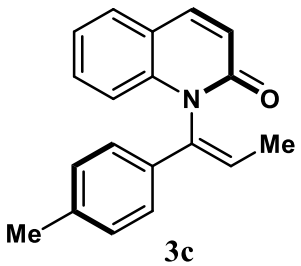
Following the general procedure **C**, **3a** was obtained as yellow solid (23 mg, 88% yield), m.p.142-143 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 9.5 Hz, 1H),

7.61 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.41 – 7.37 (m, 1H), 7.31 – 7.26 (m, 4H), 7.24 – 7.18 (m, 3H), 6.82 (d, *J* = 9.6 Hz, 1H), 6.73 (q, *J* = 7.0 Hz, 1H), 1.60 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 160.20, 139.00, 138.28, 134.76, 134.44, 129.80, 127.78, 127.49, 127.08, 124.44, 123.87, 121.51, 121.22, 119.46, 114.63, 12.41. HRMS(ESI) m/z: calculated for $[C_{18}H_{15}NO + H]^+$ 262.1232, found 262.1226. IR ν 1640.66, 1584.13, 1554.38, 1488.93, 1447.27, 1322.31, 1215.21, 1128.93, 962.31, 825.45, 762.98, 694.55, cm^{-1}. HPLC data (Chiralpak AD column, hexane : isopropanol = 85 : 15, 1.0 mL/min), tr = 23.2 min (major), tr = 13.4 min (minor), ee = 92%.



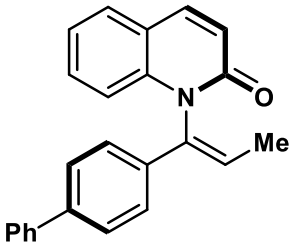
3b

Following the general procedure **C**, **3b** was obtained as white solid (23 mg, 80% yield), m.p.101-102 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 9.5 Hz, 1H), 7.60 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.39 (ddd, *J* = 8.7, 7.1, 1.5 Hz, 1H), 7.23 – 7.18 (m, 4H), 6.82 – 6.78 (m, 3H), 6.58 (q, *J* = 7.0 Hz, 1H), 3.75 (s, 3H), 1.56 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 160.18, 158.52, 138.92, 138.27, 134.36, 129.76, 127.43, 127.13, 125.20, 122.22, 121.46, 121.23, 119.45, 114.69, 113.17, 54.25, 12.24. HRMS(ESI) m/z: calculated for $[C_{19}H_{17}NO_2 + H]^+$ 292.1338, found 292.1339. IR ν 1643.64, 1587.11, 1509.75, 1438.35, 1322.31, 1244.96, 1182.48, 1134.88, 1030.74, 831.40, 751.07, 590.41, cm^{-1}. HPLC data (Chiralpak AD column, hexane : isopropanol = 85 : 15, 1.0 mL/min), tr = 28.3 min (major), tr = 18.9 min (minor), ee = 94%.



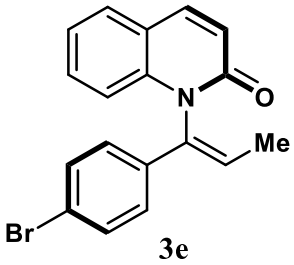
3c

Following the general procedure **C**, **3c** was obtained as white solid (25 mg, 90% yield), m.p.146-147 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 9.5 Hz, 1H), 7.60 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.38 (td, *J* = 7.7, 7.0, 1.5 Hz, 1H), 7.19 (dd, *J* = 8.0, 4.8 Hz, 4H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 9.5 Hz, 1H), 6.67 (q, *J* = 7.0 Hz, 1H), 2.29 (s, 3H), 1.58 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 160.16, 138.88, 138.33, 136.93, 134.75, 131.69, 129.75, 128.46, 127.42, 123.79, 123.28, 121.42, 121.25, 119.44, 114.67, 20.09, 12.29. HRMS(ESI) m/z: calculated for $[C_{19}H_{17}NO + H]^+$ 276.1388, found 276.1385. IR ν 1646.61, 1587.11, 1447.27, 1328.26, 1244.96, 1215.21, 1134.88, 1039.67, 965.29, 810.58, 751.07, 658.84, cm^{-1}. HPLC data (Chiralpak AD column, hexane : isopropanol = 85 : 15, 1.0 mL/min), tr = 19.8 min (major), tr = 13.0 min (minor), ee = 92%.



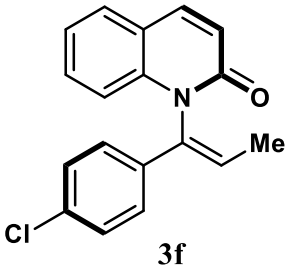
3d

Following the general procedure **C**, **3d** was obtained as white solid (27 mg, 80% yield), m.p.185-186 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 9.6 Hz, 1H), 7.63 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.52 (dd, *J* = 14.5, 8.0 Hz, 4H), 7.42 – 7.36 (m, 5H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.25 – 7.21 (m, 2H), 6.84 (d, *J* = 9.6 Hz, 1H), 6.79 (q, *J* = 6.9 Hz, 1H), 1.63 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 160.22, 139.85, 139.47, 139.05, 138.30, 134.51, 133.39, 129.88, 127.76, 127.54, 126.52, 126.37, 125.94, 124.40, 124.26, 121.57, 121.26, 119.48, 114.62, 12.46. HRMS(ESI) m/z: calculated for $[C_{24}H_{19}NO + H]^+$ 338.1545, found 338.1549. IR ν 1646.61, 1587.11, 1482.98, 1447.27, 1396.69, 1325.29, 1247.93, 1134.88, 959.34, 825.45, 757.02, 688.60, cm^{-1}. HPLC data (Chiralpak AD column, hexane : isopropanol = 85 : 15, 1.0 mL/min), tr = 18.7 min (major), tr = 20.7 min (minor), ee = 97%.



3e

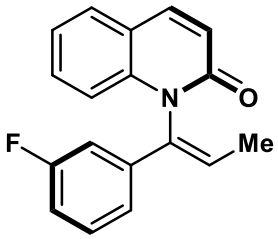
Following the general procedure **C**, **3e** was obtained as white solid (32 mg, 95% yield), m.p.142-143 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 9.5 Hz, 1H), 7.61 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.42 – 7.37 (m, 3H), 7.22 (td, *J* = 7.5, 1.1 Hz, 1H), 7.17 – 7.12 (m, 3H), 6.80 (d, *J* = 9.6 Hz, 1H), 6.72 (q, *J* = 7.0 Hz, 1H), 1.59 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 160.09, 139.13, 138.09, 133.95, 133.59, 130.91, 129.89, 127.61, 125.51, 125.27, 121.67, 121.16, 121.06, 119.47, 114.37, 12.48. HRMS(ESI) m/z: calculated for $[C_{18}H_{14}BrNO + H]^+$ 340.0337, found 340.0338. Isotopic MS, calculated 342.0317, found 342.0319. IR ν 1637.69, 1587.11, 1444.30, 1322.31, 1244.96, 1134.88, 1072.40, 1006.94, 962.31, 804.63, 757.02, 655.87, cm^{-1}. HPLC data (Chiralpak AD column, hexane : isopropanol = 85 : 15, 1.0 mL/min), tr = 22.1 min (major), tr = 18.4 min (minor), ee = 94%.



3f

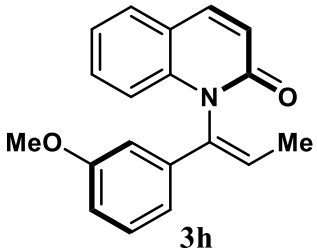
Following the general procedure **C**, **3f** was obtained as white solid (26 mg, 89% yield), m.p.120-121 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 9.5 Hz, 1H), 7.61 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.40 (ddd, *J* = 8.6, 7.3, 1.5 Hz, 1H), 7.24 – 7.20 (m, 5H), 7.14 (d, *J* = 8.5 Hz, 1H), 6.80 (d, *J* = 9.5 Hz, 1H), 6.70 (q, *J* = 6.9 Hz, 1H), 1.59 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 160.11, 139.14, 138.09, 133.88, 133.11, 132.88, 129.90, 127.96, 127.61, 125.21, 125.16, 121.68, 121.15, 119.47, 114.38, 12.46. HRMS(ESI) m/z: calculated for $[C_{18}H_{14}ClNO + H]^+$ 296.0842, found 296.0831. Isotopic MS, calculated 298.0813, found 298.0809. IR ν 1649.59, 1587.11, 1488.93, 1447.27, 1393.72, 1328.26, 1244.96, 1128.93, 1090.25, 1012.89, 813.55,

655.87, cm^{-1}. HPLC data (Chiralpak AD column, hexane : isopropanol = 85 : 15, 1.0 mL/min), tr = 19.9 min (major), tr = 16.0 min (minor), ee = 90%.



3g

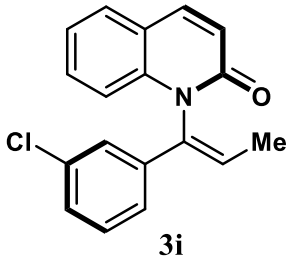
Following the general procedure **C**, **3g** was obtained as white solid (24 mg, 86% yield), m.p.80-81 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 9.6 Hz, 1H), 7.66 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.44 (ddd, *J* = 8.6, 7.2, 1.5 Hz, 1H), 7.31 – 7.26 (m, 2H), 7.19 (d, *J* = 8.5 Hz, 1H), 7.13 – 7.09 (m, 1H), 7.02 (dt, *J* = 10.5, 2.2 Hz, 1H), 6.96 (td, *J* = 8.3, 2.5 Hz, 1H), 6.85 (d, *J* = 9.5 Hz, 1H), 6.79 (q, *J* = 6.9 Hz, 1H), 1.65 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 160.10, 139.16, 138.12, 136.95 (d, *J* = 7.9 Hz), 133.84, 129.89, 129.32 (d, *J* = 8.5 Hz), 127.62, 125.92, 121.67, 121.14, 119.53 (d, *J* = 2.9 Hz), 119.47, 114.37, 114.03, 113.86, 110.90 (d, *J* = 13.1 Hz), 12.46. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -112.77 – -112.85 (m). HRMS(ESI) m/z: calculated for $[C_{18}H_{14}FNO + H]^{+}$ 280.1138, found 280.1128. IR ν 1643.64, 1581.16, 1480.00, 1447.27, 1322.31, 1215.21, 1131.90, 911.74, 828.43, 783.80, 754.05, 667.77, cm^{-1}. HPLC data (Chiralpak AD column, hexane : isopropanol = 85 : 15, 1.0 mL/min), tr = 21.9 min (major), tr = 13.3 min (minor), ee = 90%.



3h

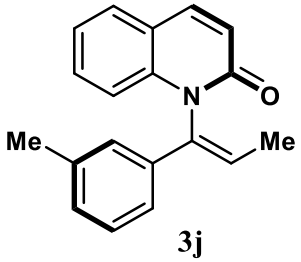
Following the general procedure **C**, **3h** was obtained as white solid (28 mg, 97% yield), m.p.82-83 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 9.5 Hz, 1H), 7.60 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.41 – 7.37 (m, 1H), 7.22 – 7.16 (m, 3H), 6.87 (dd, *J* = 7.7, 1.7 Hz, 1H), 6.84 – 6.77 (m, 3H), 6.72 (q, *J* = 6.9 Hz, 1H), 3.74 (s, 3H), 1.59 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 160.20, 158.90, 139.03, 138.28,

135.99, 134.58, 129.81, 128.80, 127.47, 124.80, 121.52, 121.14, 119.44, 116.45, 114.63, 112.17, 110.00, 54.20, 12.41. HRMS(ESI) m/z: calculated for [$C_{19}H_{17}NO_2$ + H]$^+$ 292.1338, found 292.1338. IR ν 1646.61, 1578.18, 1491.90, 1441.32, 1328.26, 1283.64, 1206.28, 1131.90, 1033.72, 834.38, 754.05, 688.60, cm^{-1}. HPLC data (Chiralpak AD column, hexane : isopropanol = 85 : 15, 1.0 mL/min), tr = 32.0 min (major), tr = 16.2 min (minor), ee = 90%.



3i

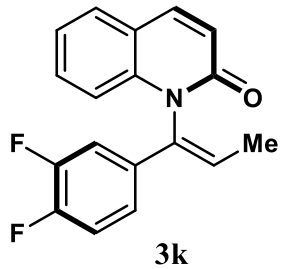
Following the general procedure **C**, **3i** was obtained as white waxy (25 mg, 85% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 9.6 Hz, 1H), 7.62 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.41 (ddd, *J* = 8.7, 7.2, 1.5 Hz, 1H), 7.30 (d, *J* = 2.1 Hz, 1H), 7.25 – 7.17 (m, 3H), 7.15 – 7.12 (m, 2H), 6.81 (d, *J* = 9.5 Hz, 1H), 6.74 (q, *J* = 7.0 Hz, 1H), 1.60 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 160.11, 139.20, 138.09, 136.53, 133.82, 133.72, 129.93, 129.05, 127.64, 127.15, 126.09, 124.02, 122.09, 121.70, 121.14, 119.48, 114.35, 12.49. HRMS(ESI) m/z: calculated for [$C_{18}H_{14}ClNO$ + H]$^+$ 296.0842, found 296.0845. Isotopic MS, calculated 298.0813, found 298.0814. IR ν 1652.56, 1593.06, 1447.27, 1399.67, 1325.29, 1256.86, 1081.32, 1015.87, 870.08, 792.73, 751.07, 691.57, cm^{-1}. HPLC data (Chiralpak AD column, hexane : isopropanol = 85 : 15, 1.0 mL/min), tr = 21.4 min (major), tr = 12.6 min (minor), ee = 91%.



3j

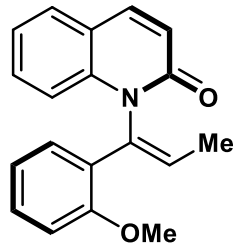
Following the general procedure **C**, **3j** was obtained as white solid (24 mg, 87% yield), m.p.101-102 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 9.5 Hz, 1H), 7.61

(dd, *J* = 8.2, 1.4 Hz, 1H), 7.39 (td, *J* = 8.3, 7.8, 1.5 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 2H), 7.17 – 7.12 (m, 2H), 7.06 (t, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 9.5 Hz, 1H), 6.70 (q, *J* = 6.9 Hz, 1H), 2.27 (s, 3H), 1.58 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 160.20, 138.93, 138.35, 137.33, 134.91, 134.45, 129.77, 127.94, 127.65, 127.44, 124.49, 124.17, 121.44, 121.26, 121.07, 119.45, 114.68, 20.52, 12.36. HRMS(ESI) m/z: calculated for $[C_{19}H_{17}NO + H]^+$ 276.1388, found 276.1382. IR ν 1640.66, 1584.13, 1557.36, 1488.93, 1447.27, 1322.31, 1244.96, 1128.93, 831.40, 754.05, 697.52, 655.87, cm^{-1}. HPLC data (Chiralpak AD column, hexane : isopropanol = 85 : 15, 1.0 mL/min), tr = 20.0 min (major), tr = 11.0 min (minor), ee = 90%.



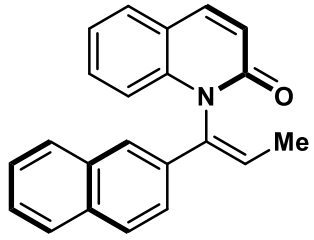
3k

Following the general procedure **C**, **3k** was obtained as white solid (28 mg, 93% yield), m.p.100-101 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 9.5 Hz, 1H), 7.62 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.42 (ddd, *J* = 8.6, 7.3, 1.5 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.14 – 6.99 (m, 4H), 6.80 (d, *J* = 9.5 Hz, 1H), 6.66 (q, *J* = 7.0 Hz, 1H), 1.59 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 160.05, 139.25, 137.98, 133.10, 129.96, 127.71, 125.73, 121.79, 121.11, 120.06 (d, *J* = 3.4 Hz), 120.01 (d, *J* = 3.6 Hz), 119.48, 116.68, 116.54, 114.20, 113.16, 113.01, 12.46. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -137.05 (ddd, *J* = 20.4, 11.7, 7.7 Hz), -138.23 (dtd, *J* = 21.6, 8.3, 7.8, 4.3 Hz). HRMS(ESI) m/z: calculated for $[C_{18}H_{13}F_2NO + H]^+$ 298.1043, found 298.1039. IR ν 1637.69, 1584.13, 1515.70, 1420.50, 1283.64, 1244.96, 1131.90, 938.51, 858.18, 828.43, 762.98, 605.29, cm^{-1}. HPLC data (Chiralpak AD column, hexane : isopropanol = 85 : 15, 1.0 mL/min), tr = 11.1 min (major), tr = 13.1 min (minor), ee = 90%.



3l

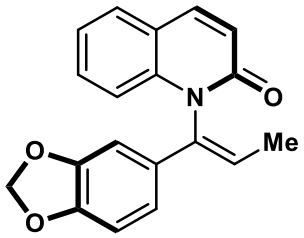
Following the general procedure **C**, **3l** was obtained as white solid (16 mg, 55% yield) (*Z*:*E*=15.3:1), m.p.216-127 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 8.6 Hz, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.18 (td, *J* = 7.5, 3.7 Hz, 2H), 6.99 (d, *J* = 7.6 Hz, 1H), 6.93 (t, *J* = 7.1 Hz, 2H), 6.80 (q, *J* = 7.8, 5.7 Hz, 2H), 3.85 (s, 3H), 1.59 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 156.35, 138.85, 138.46, 130.73, 129.54, 129.45, 127.81, 127.25, 123.63, 121.28, 121.26, 119.78, 119.45, 115.10, 110.44, 54.52, 12.81. IR ν 1646.61, 1584.13, 1488.93, 1444.30, 1325.29, 1247.93, 1120.00, 1021.82, 890.91, 831.40, 760.00, 632.07, cm^{-1}. HRMS(ESI) m/z: calculated for $[C_{19}H_{17}NO_2 + H]^+$ 292.1338, found 292.1328. HPLC data (Chiralpak AD column, hexane : isopropanol = 85 : 15, 1.0 mL/min), tr = 11.7 min (major), tr = 13.2 min (minor), ee = 18%.



3m

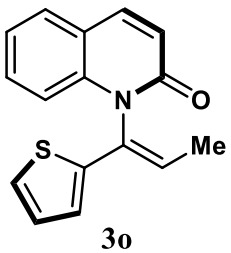
Following the general procedure **C**, **3m** was obtained as white solid (26 mg, 84% yield), m.p.194-195 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 9.6 Hz, 1H), 7.78 (dd, *J* = 15.6, 7.9 Hz, 2H), 7.66 – 7.62 (m, 3H), 7.51 (d, *J* = 1.8 Hz, 1H), 7.42 – 7.35 (m, 3H), 7.23 – 7.19 (m, 2H), 6.90 – 6.85 (m, 2H), 1.66 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 160.27, 139.12, 138.32, 134.91, 132.39, 132.07, 131.76, 129.84, 127.63, 127.52, 127.33, 126.50, 125.25, 125.15, 125.03, 122.84, 121.88, 121.56, 121.26, 119.52, 114.71, 12.54. HRMS(ESI) m/z: calculated for $[C_{22}H_{17}NO + H]^+$ 312.1388, found 312.1376. IR ν 1643.64, 1584.13, 1488.93,

1447.27, 1328.26, 1250.91, 1221.16, 1188.43, 858.18, 819.50, 751.07, 664.79, cm^{-1}. HPLC data (Chiralpak AD column, hexane : isopropanol = 85 : 15, 1.0 mL/min), tr = 34.8 min (major), tr = 21.9 min (minor), ee = 90%.



3n

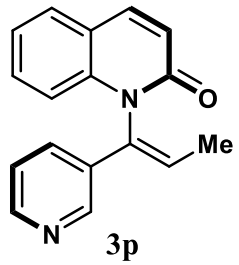
Following the general procedure **C**, **3n** was obtained as white solid (28 mg, 91% yield), m.p.126-127 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 9.6 Hz, 1H), 7.60 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.40 (ddd, *J* = 8.6, 7.2, 1.5 Hz, 1H), 7.22 – 7.17 (m, 2H), 6.83 – 6.79 (m, 2H), 6.73 – 6.67 (m, 2H), 6.55 (q, *J* = 7.0 Hz, 1H), 5.91 – 5.90 (m, 2H), 1.56 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 160.12, 147.18, 146.60, 138.97, 138.24, 134.37, 129.78, 129.01, 127.47, 122.97, 121.51, 121.21, 119.45, 117.86, 114.61, 107.46, 104.51, 100.19, 12.31. HRMS(ESI) m/z: calculated for $[C_{19}H_{15}NO_3 + H]^+$ 306.1130, found 306.1126. IR ν 1640.66, 1587.11, 1497.85, 1399.67, 1322.31, 1221.16, 1161.65, 1033.72, 935.54, 831.40, 760.00, 596.36, cm^{-1}. HPLC data (Chiralpak AD column, hexane : isopropanol = 80 : 20, 1.0 mL/min), tr = 25.7 min (major), tr = 14.2 min (minor), ee = 89%.



3o

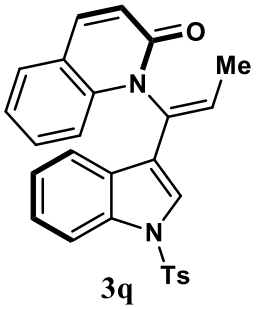
Following the general procedure **C**, **3o** was obtained as yellow solid (25 mg, 95% yield)(*Z*:*E*=4.0:1), m.p.82-83 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 9.6 Hz, 1H), 7.60 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.46 – 7.39 (m, 1H), 7.25 – 7.19 (m, 2H), 7.12 (d, *J* = 5.1 Hz, 1H), 6.84 (dd, *J* = 5.1, 3.7 Hz, 1H), 6.79 (d, *J* = 9.6 Hz, 1H), 6.63 (d, *J* = 3.7 Hz, 1H), 6.58 (q, *J* = 7.0 Hz, 1H), 1.57 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.85, 139.23, 139.09, 138.80, 138.01, 130.03, 129.85,

129.45, 127.47, 127.30, 126.52, 126.15, 125.85, 125.23, 123.81, 123.70, 122.86, 121.62, 121.36, 121.28, 121.12, 119.42, 119.36, 114.94, 114.52, 13.85, 12.00. HRMS(ESI) m/z: calculated for $[C_{16}H_{13}NOS + H]^+$ 268.0796, found 268.0787. IR ν 1646.61, 1590.08, 1488.93, 1438.35, 1319.34, 1250.91, 1221.16 1033.72, 935.54, 831.40, 760.00, 664.79, cm^{-1}. HPLC data (Chiralpak AD column, hexane : isopropanol = 85 : 15, 1.0 mL/min), tr = 12.4 min (*Z*-major), tr = 14.5 min (*Z*-minor), ee = 96%, tr = 10.9 min (*E*-major), tr = 16.3 min (*E*-minor), ee = 91%.



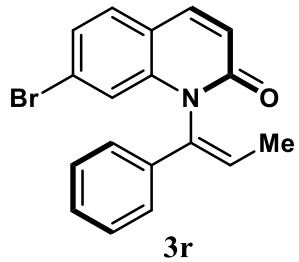
3p

Following the general procedure **C**, **3p** was obtained as white solid (22 mg, 84% yield), m.p.94-95 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.64 (d, *J* = 2.4 Hz, 1H), 8.47 (dd, *J* = 4.9, 1.5 Hz, 1H), 7.83 (d, *J* = 9.6 Hz, 1H), 7.62 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.51 (ddd, *J* = 8.1, 2.5, 1.6 Hz, 1H), 7.41 (ddd, *J* = 8.6, 7.2, 1.5 Hz, 1H), 7.24 – 7.14 (m, 3H), 6.81 – 6.77 (m, 2H), 1.64 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 160.09, 147.99, 145.62, 139.28, 137.93, 132.25, 131.31, 130.48, 130.00, 127.74, 126.79, 122.48, 121.82, 121.07, 119.51, 114.15, 12.47. HRMS(ESI) m/z: calculated for $[C_{17}H_{14}N_2O + H]^+$ 263.1184, found 263.1171. IR ν 1637.69, 1590.08, 1482.98, 1444.30, 1244.96, 1212.23, 1134.88, 962.31, 837.36, 762.98, 706.45, 620.17, cm^{-1}. HPLC data (Chiralpak AD column, hexane : isopropanol = 85 : 15, 1.0 mL/min), tr = 28.8 min (major), tr = 24.8 min (minor), ee = 94%.



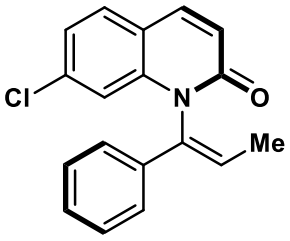
3q

Following the general procedure **C**, **3q** was obtained as white solid (30 mg, 66% yield) (*Z*:*E*=6.1:1), m.p.78-79 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.94 (t, *J* = 8.9 Hz, 1H), 7.84 (dd, *J* = 13.5, 8.6 Hz, 2H), 7.62 (dd, *J* = 10.9, 7.9 Hz, 3H), 7.31 (dt, *J* = 20.4, 7.6 Hz, 3H), 7.25 – 7.19 (m, 2H), 7.14 (t, *J* = 8.2 Hz, 3H), 6.84 (d, *J* = 9.5 Hz, 1H), 6.74 (q, *J* = 6.7 Hz, 1H), 2.31 (s, 3H), 1.63 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.99, 144.07, 139.30, 139.21, 138.77, 137.96, 134.71, 133.64, 129.78, 128.91, 128.64, 127.61, 127.53, 126.94, 125.92, 125.87, 125.81, 124.06, 123.36, 122.83, 122.60, 121.67, 121.33, 121.28, 121.09, 119.93, 119.65, 119.62, 119.51, 119.49, 118.16, 114.78, 114.45, 112.94, 112.62, 20.56, 14.33, 12.13. HRMS(ESI) m/z: calculated for $[C_{27}H_{22}N_2O_3S + H]^+$ 455.1429, found 455.1429. IR ν 1649.59, 1590.08, 1557.36, 1444.30, 1363.97, 1173.55, 1125.95, 980.17, 825.45, 745.12, 667.77, 569.59, cm^{-1}. HPLC data (Chiralpak AD column, hexane : isopropanol = 80 : 20, 1.0 mL/min), tr = 18.2 min (*E*-major), tr = 38.8 min (*E*-minor), ee =70%, tr = 20.7 min (*E*-major), tr = 6.8 min (*E*-minor), ee =70%.



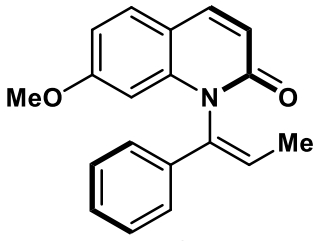
3r

Following the general procedure **C**, **3r** was obtained as yellow waxy (32 mg, 94% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 9.6 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.34 – 7.31 (m, 2H), 7.30 – 7.26 (m, 5H), 6.81 (d, *J* = 9.6 Hz, 1H), 6.73 (q, *J* = 7.0 Hz, 1H), 1.61 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.80, 139.27, 138.38, 134.42, 134.05, 128.69, 127.89, 127.29, 124.88, 124.85, 124.31, 123.81, 121.55, 118.22, 117.29, 12.45. HRMS(ESI) m/z: calculated for $[C_{18}H_{14}BrNO + H]^+$ 340.0337, found 340.0337. Isotopic MS, calculated 342.0317, found 342.0317. IR ν 1646.61, 1581.16, 1545.45, 1414.55, 1241.98, 1134.88, 1078.35, 1000.99, 837.36, 771.90, 691.57, 632.07, cm^{-1}. HPLC data (Chiralpak AD column, hexane : isopropanol = 85 : 15, 1.0 mL/min), tr = 11.8 min (major), tr = 8.9 min (minor), ee = 89%.



3s

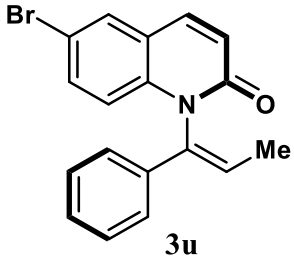
Following the general procedure **C**, **3s** was obtained as white waxy (29 mg, 98% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 9.6 Hz, 1H), 7.53 – 7.51 (m, 1H), 7.29 – 7.24 (m, 5H), 7.17 (d, *J* = 7.4 Hz, 2H), 6.79 (d, *J* = 9.6 Hz, 1H), 6.73 (q, *J* = 7.0 Hz, 1H), 1.61 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.90, 139.18, 138.31, 136.06, 134.45, 134.03, 128.60, 127.89, 127.29, 124.82, 123.81, 122.08, 121.30, 117.90, 114.37, 12.43. HRMS(ESI) m/z: calculated for $[C_{18}H_{14}ClNO + H]^+$ 296.0842, found 296.0841. Isotopic MS, calculated 298.0813, found 298.0814. IR ν 1652.56, 1584.13, 1548.43, 1491.90, 1423.47, 1319.34, 1206.28, 1134.88, 1087.27, 840.33, 751.07, 694.55, cm^{-1}. HPLC data (Chiralpak AD column, hexane : isopropanol = 85 : 15, 1.0 mL/min), tr = 11.3 min (major), tr = 8.4 min (minor), ee = 91%.



3t

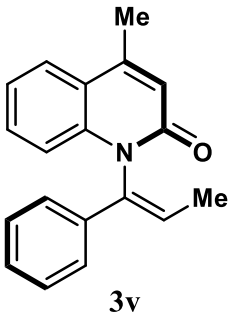
Following the general procedure **C**, **3t** was obtained as yellow solid (21 mg, 74% yield) (*Z*:*E*=16.8:1), m.p.101-102 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 9.5 Hz, 1H), 7.54 (d, *J* = 8.6 Hz, 1H), 7.36 – 7.32 (m, 2H), 7.31 – 7.27 (m, 3H), 6.83 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.75 (q, *J* = 6.9 Hz, 1H), 6.72 – 6.68 (m, 2H), 3.76 (s, 3H), 1.67 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.92, 161.71, 140.96, 139.83, 135.95, 135.49, 129.84, 128.80, 128.09, 125.52, 124.96, 118.93, 114.71, 110.41, 99.69, 55.46, 13.46. HRMS(ESI) m/z: calculated for $[C_{19}H_{17}NO_2 + H]^+$ 292.1338, found 292.1336. IR ν 1637.69, 1584.13, 1548.43, 1405.62, 1360.99, 1221.16, 1146.78, 1018.84, 831.40, 754.05, 691.57, 635.04, cm^{-1}. HPLC data

(Chiralpak AD column, hexane : isopropanol = 85 : 15, 1.0 mL/min), tr = 22.6 min (major), tr = 15.0 min (minor), ee = 87%.



3u

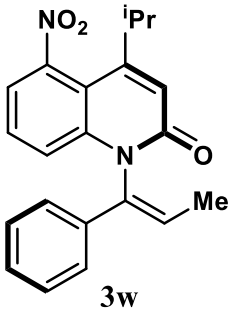
Following the general procedure **C**, **3u** was obtained as yellow waxy (29 mg, 86% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.74 – 7.72 (m, 2H), 7.46 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.30 – 7.22 (m, 5H), 7.06 (d, *J* = 9.0 Hz, 1H), 6.83 (d, *J* = 9.5 Hz, 1H), 6.72 (q, *J* = 7.0 Hz, 1H), 1.60 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.68, 137.72, 137.26, 134.47, 134.08, 132.55, 129.64, 127.87, 127.27, 124.70, 123.77, 122.51, 120.90, 116.42, 114.33, 12.41. HRMS(ESI) m/z: calculated for $[C_{18}H_{14}BrNO + H]^{+}$ 340.0337, found 340.0335. Isotopic MS, calculated 342.0317, found 342.0316. IR ν 1658.51, 1584.13, 1554.38, 1474.05, 1417.52, 1280.66, 1241.98, 1018.84, 893.88, 813.55, 754.05, 691.57, cm^{-1}. HPLC data (Chiralpak AD column, hexane : isopropanol = 85 : 15, 1.0 mL/min), tr = 17.2 min (major), tr = 11.5 min (minor), ee = 92%.



3v

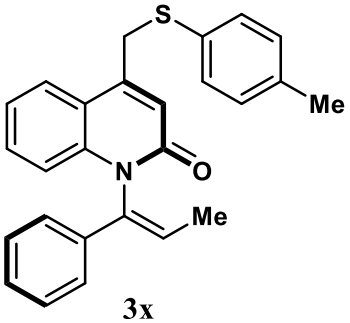
Following the general procedure **C**, **3v** was obtained as white solid (19 mg, 69% yield), m.p.131-132 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.74 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.39 (ddd, *J* = 8.6, 7.2, 1.5 Hz, 1H), 7.30 – 7.24 (m, 4H), 7.24 – 7.20 (m, 3H), 6.74 – 6.70 (m, 2H), 2.55 (d, *J* = 1.2 Hz, 3H), 1.60 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.92, 146.58, 137.96, 134.79, 134.63, 129.61, 127.73, 126.99, 124.45, 124.01, 123.88, 121.30, 120.50, 120.17, 114.90, 18.18, 12.40. HRMS(ESI) m/z: calculated for $[C_{19}H_{17}NO + H]^{+}$ 276.1388, found 276.1382. IR ν

1637.69, 1587.11, 1488.93, 1450.25, 1387.77, 1313.39, 1075.37, 968.26, 864.13, 757.02, 688.60, 563.64, cm^{-1}. HPLC data (Chiralpak AD column, hexane : isopropanol = 85 : 15, 1.0 mL/min), tr = 19.4 min (major), tr = 14.5 min (minor), ee = 92%.



3w

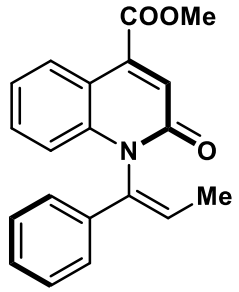
Following the general procedure **C**, **3w** was obtained as white solid (27 mg, 78% yield), m.p.104-105 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.76 (d, *J* = 2.4 Hz, 1H), 8.21 (dd, *J* = 9.3, 2.4 Hz, 1H), 7.33 – 7.25 (m, 6H), 6.86 (s, 1H), 6.76 (q, *J* = 6.9 Hz, 1H), 3.54-3.48 (m, 1H), 1.61 (d, *J* = 7.0 Hz, 3H), 1.44 (dd, *J* = 6.8, 2.0 Hz, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 160.01, 156.01, 142.54, 141.55, 134.36, 133.77, 127.99, 127.51, 125.16, 124.01, 123.71, 119.86, 118.71, 118.47, 115.95, 27.80, 21.33, 12.48. HRMS(ESI) m/z: calculated for $[C_{21}H_{20}N_2O_3 + H]^+$ 349.1552, found 349.1542. IR ν 1670.41, 1593.06, 1518.68, 1429.42, 1337.19, 1271.74, 1099.17, 902.81, 867.11, 828.43, 760.00, 688.60, cm^{-1}. HPLC data (Chiralpak AD column, hexane : isopropanol = 85 : 15, 1.0 mL/min), tr = 18.9 min (major), tr = 25.3 min (minor), ee = 89%.



3x

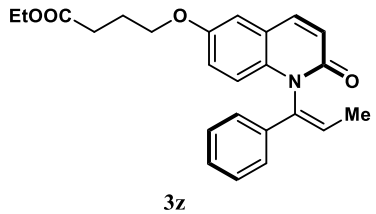
Following the general procedure **C**, **3x** was obtained as white waxy (30 mg, 76% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.1 Hz, 1H), 7.43 (t, *J* = 7.9 Hz, 1H), 7.28 (s, 6H), 7.25 (d, *J* = 10.3 Hz, 3H), 7.12 (d, *J* = 7.7 Hz, 2H), 6.73 (q, *J* =

7.0 Hz, 1H), 6.53 (s, 1H), 4.24 (s, 2H), 2.35 (s, 3H), 1.59 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.46, 146.15, 139.45, 138.21, 135.71, 135.45, 132.76, 130.84, 130.44, 129.96, 128.79, 128.10, 125.49, 125.28, 124.86, 122.43, 121.97, 119.19, 116.22, 37.66, 21.19, 13.39. HRMS(ESI) m/z: calculated for $[C_{26}H_{23}NOS + H]^+$ 398.1579, found 398.1567. IR ν 1646.61, 1593.06, 1563.31, 1488.93, 1444.30, 1387.77, 1304.46, 1069.42, 870.08, 807.60, 751.07, 688.60, cm^{-1}. HPLC data (Chiralpak AD column, hexane : isopropanol = 85 : 15, 1.0 mL/min), tr = 26.9 min (major), tr = 20.1 min (minor), ee = 86%.



3y

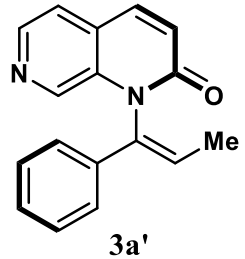
Following the general procedure **C**, **3y** was obtained as white solid (22 mg, 69% yield), m.p.158-159 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.38 (d, *J* = 8.1 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.33 (s, 1H), 7.28 (d, *J* = 7.8 Hz, 7H), 6.76 (q, *J* = 6.9 Hz, 1H), 4.05 (s, 3H), 1.62 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.71, 165.88, 160.11, 139.70, 139.59, 135.57, 135.03, 131.42, 128.87, 128.27, 126.97, 125.65, 124.83, 123.14, 117.25, 116.04, 53.01, 13.45. HRMS(ESI) m/z: calculated for $[C_{20}H_{17}NO_3 + H]^+$ 320.1287, found 320.1281. IR ν 1735.87, 1649.59, 1593.06, 1438.35, 1227.11, 1152.73, 1018.84, 887.93, 786.78, 757.02, 679.67, 584.46, cm^{-1}. HPLC data (Chiralpak AD column, hexane : isopropanol = 85 : 15, 1.0 mL/min), tr = 27.3 min (major), tr = 21.0 min (minor), ee = 75%.



3z

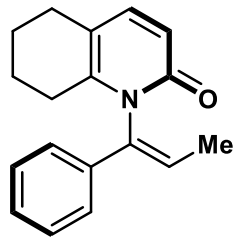
Following the general procedure **C**, **3z** was obtained as white waxy (35 mg, 89% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 9.6 Hz, 1H), 7.32 – 7.20 (m,

5H), 7.10 (d, *J* = 9.2 Hz, 1H), 7.04 (d, *J* = 2.8 Hz, 1H), 6.99 (dd, *J* = 9.2, 2.8 Hz, 1H), 6.81 (d, *J* = 9.6 Hz, 1H), 6.71 (q, *J* = 7.0 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 4.03 (t, *J* = 6.1 Hz, 2H), 2.51 (t, *J* = 7.3 Hz, 2H), 2.11-2.09 (m, 2H), 1.59 (d, *J* = 7.0 Hz, 3H), 1.24 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 172.12, 159.77, 153.23, 138.46, 134.84, 134.46, 132.75, 127.76, 127.05, 124.39, 123.85, 121.77, 120.13, 118.86, 115.98, 109.94, 66.24, 59.48, 29.70, 23.56, 13.22, 12.39. HRMS(ESI) m/z: calculated for $[C_{24}H_{25}NO_4 + H]^+$ 392.1862, found 392.1860. IR ν 1729.92, 1649.59, 1560.33, 1494.88, 1435.37, 1244.96, 1173.55, 1027.77, 971.24, 813.55, 760.00, 688.60, cm^{-1}. HPLC data (Chiralpak AD column, hexane : isopropanol = 70 : 30, 1.0 mL/min), tr = 29.9 min (major), tr = 9.2 min (minor), ee = 90%.



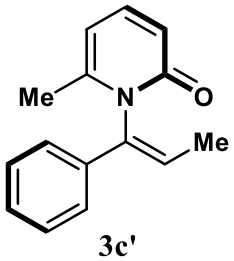
3a'

Following the general procedure **C**, **3a'** was obtained as white waxy (25 mg, 96% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.57 (s, 1H), 8.42 (d, *J* = 5.1 Hz, 1H), 7.79 (d, *J* = 9.6 Hz, 1H), 7.46 (d, *J* = 5.1 Hz, 1H), 7.28 – 7.23 (m, 5H), 7.01 (d, *J* = 9.6 Hz, 1H), 6.75 (q, *J* = 7.0 Hz, 1H), 1.62 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.21, 141.80, 137.57, 137.02, 134.07, 133.66, 133.51, 127.92, 127.43, 126.65, 125.27, 124.05, 123.87, 119.66, 12.52. HRMS(ESI) m/z: calculated for $[C_{17}H_{14}N_2O + H]^+$ 263.1184, found 263.1180. IR ν 1658.51, 1578.18, 1488.93, 1417.52, 1337.19, 1241.98, 1137.85, 956.36, 849.26, 760.00, 688.60, 566.61, cm^{-1}. HPLC data (Chiralpak AD column, hexane : isopropanol = 85 : 15, 1.0 mL/min), tr = 16.8 min (major), tr = 14.9 min (minor), ee = 86%.



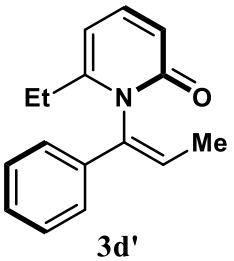
3b'

Following the general procedure **C**, **3b'** was obtained as yellow waxy (19 mg, 72% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.34 – 7.22 (m, 6H), 6.61 – 6.57 (m, 2H), 2.56 (d, *J* = 5.8 Hz, 2H), 2.46 (dt, *J* = 14.8, 6.0 Hz, 1H), 2.26 (dt, *J* = 12.2, 5.2 Hz, 1H), 1.70 (dd, *J* = 11.4, 6.4 Hz, 7H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 161.22, 142.20, 141.46, 135.81, 134.59, 127.77, 126.95, 123.58, 122.92, 117.33, 113.44, 26.11, 25.56, 21.24, 20.90, 12.33. HRMS(ESI) m/z: calculated for $[C_{18}H_{19}NO + H]^+$ 266.1545, found 266.1543. IR ν 1655.54, 1590.08, 1536.53, 1491.90, 1372.89, 1319.34, 1170.58, 962.31, 816.53, 754.05, 724.30, 688.60, cm^{-1}. HPLC data (Chiralpak AD column, hexane : isopropanol = 85 : 15, 1.0 mL/min), tr = 17.0 min (major), tr = 9.8 min (minor), ee = 99%.



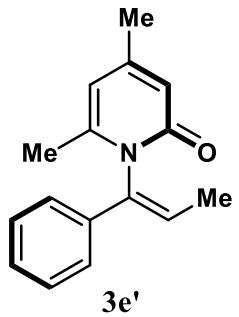
3c'

Following the general procedure **C**, **3c'** was obtained as yellow solid (17 mg, 76% yield), m.p.106-107 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.26 (m, 6H), 6.60 (t, *J* = 7.1 Hz, 2H), 6.15 (d, *J* = 6.8 Hz, 1H), 2.10 (d, *J* = 2.2 Hz, 3H), 1.68 (dd, *J* = 7.1, 2.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.03, 146.51, 139.92, 137.15, 135.32, 128.84, 128.13, 124.58, 123.95, 118.36, 106.39, 20.07, 13.32. HRMS(ESI) m/z: calculated for $[C_{15}H_{15}NO + H]^+$ 226.1232, found 226.1229. IR ν 1649.59, 1578.18, 1539.50, 1491.90, 1390.74, 1250.91, 1134.88, 890.91, 789.75, 762.98, 691.57, 626.12, cm^{-1}. HPLC data (Chiralpak AD column, hexane : isopropanol = 85 : 15, 1.0 mL/min), tr = 16.2 min (major), tr = 9.9 min (minor), ee = 97%.



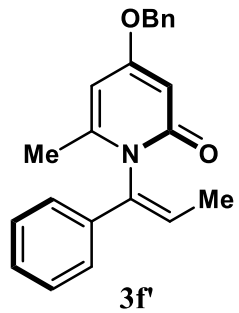
3d'

Following the general procedure **C**, **3d'** was obtained as white solid (19 mg, 79% yield), m.p.108-109 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.40 (dd, *J* = 9.2, 6.9 Hz, 1H), 7.31 – 7.28 (m, 2H), 7.26 – 7.22 (m, 3H), 6.60 – 6.56 (m, 2H), 6.12 (d, *J* = 6.9 Hz, 1H), 2.48 – 2.40 (m, 1H), 2.35 – 2.28 (m, 1H), 1.66 (d, *J* = 7.0 Hz, 3H), 1.08 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 161.82, 150.66, 138.77, 135.65, 134.64, 127.80, 127.03, 123.56, 123.27, 117.28, 102.85, 24.34, 12.49, 10.94. HRMS(ESI) m/z: calculated for $[C_{16}H_{17}NO + H]^+$ 240.1388, found 240.1377. IR ν 1652.56, 1578.18, 1491.90, 1325.29, 1233.06, 1128.93, 1075.37, 965.29, 804.63, 760.00, 697.52, 623.14, cm^{-1}. HPLC data (Chiralpak AD column, hexane : isopropanol = 85 : 15, 1.0 mL/min), tr = 16.3 min (major), tr = 9.3 min (minor), ee = 99%.



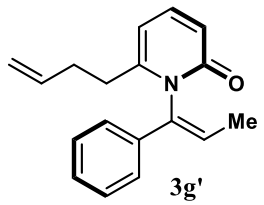
3e'

Following the general procedure **C**, **3e'** was obtained as white solid (18 mg, 76% yield), m.p.76-77 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.31 – 7.23 (m, 5H), 6.56 (q, *J* = 6.9 Hz, 1H), 6.38 (s, 1H), 5.98 (s, 1H), 2.20 – 2.19 (m, 3H), 2.04 (s, 3H), 1.66 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 161.92, 150.32, 144.04, 136.05, 134.58, 127.77, 127.01, 123.58, 122.99, 115.87, 107.89, 20.37, 18.88, 12.32. HRMS(ESI) m/z: calculated for $[C_{16}H_{17}NO + H]^+$ 240.1388, found 240.1383. IR ν 3024.13, 1590.08, 1590.08, 1325.29, 1253.88, 1096.20, 1051.57, 932.56, 864.13, 813.55, 739.17, 646.94, cm^{-1}. HPLC data (Chiralpak AD column, hexane : isopropanol = 85 : 15, 1.0 mL/min), tr = 16.2 min (major), tr = 9.3 min (minor), ee = 98%.



3f'

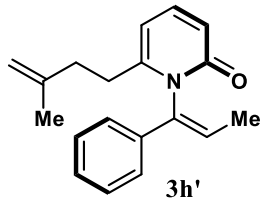
Following the general procedure **C**, **3f'** was obtained as white waxy (14 mg, 40% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.44 – 7.35 (m, 5H), 7.32 – 7.28 (m, 4H), 7.24 (d, *J* = 6.9 Hz, 1H), 6.58 (q, *J* = 6.9 Hz, 1H), 6.04 (d, *J* = 2.6 Hz, 1H), 5.94 (d, *J* = 2.5 Hz, 1H), 5.02 (s, 2H), 2.04 (s, 3H), 1.69 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 166.12, 163.41, 145.26, 135.83, 134.75, 134.40, 127.80, 127.72, 127.47, 127.03, 126.83, 123.56, 123.43, 100.16, 94.98, 69.15, 18.96, 12.35. HRMS(ESI) m/z: calculated for $[C_{22}H_{21}NO_2 + H]^+$ 332.1651, found 332.1640. IR ν 1652.56, 1593.06, 1551.40, 1453.22, 1349.09, 1239.01, 1176.53, 1137.85, 1015.87, 816.53, 757.02, 688.60, cm^{-1}. HPLC data (Chiralpak AD column, hexane : isopropanol = 80 : 20, 1.0 mL/min), tr = 12.9 min (major), tr = 10.9 min (minor), ee = 98%.



3g'

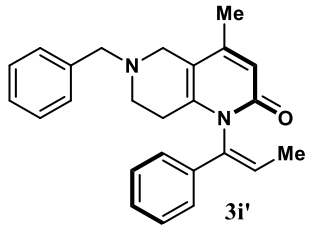
Following the general procedure **C**, **3g'** was obtained as white waxy (20 mg, 75% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.43 (ddd, *J* = 9.2, 7.0, 2.2 Hz, 1H), 7.37 – 7.33 (m, 2H), 7.31 – 7.28 (m, 3H), 6.65 – 6.61 (m, 2H), 6.17 (d, *J* = 6.9 Hz, 1H), 5.72 (ddt, *J* = 16.8, 10.1, 6.5 Hz, 1H), 5.02 – 4.96 (m, 2H), 2.53 (dd, *J* = 9.6, 6.3 Hz, 1H), 2.46 (dd, *J* = 9.2, 6.4 Hz, 1H), 2.30 – 2.26 (m, 1H), 2.22 – 2.19 (m, 1H), 1.72 (dd, *J* = 7.2, 2.2 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 161.84, 148.51, 138.66, 135.67, 135.39, 134.74, 127.83, 127.11, 123.63, 123.54, 117.50, 114.95, 104.11, 30.67, 30.64, 12.62. HRMS(ESI) m/z: calculated for $[C_{18}H_{19}NO + H]^+$ 266.1545, found 266.1550. IR ν 1655.54, 1584.13, 1542.48, 1482.98, 1441.32, 1325.29, 1230.08,

1131.90, 905.79, 798.68, 760.00, 688.60, cm^{-1}. HPLC data (Chiralpak AD column, hexane : isopropanol = 85 : 15, 1.0 mL/min), tr = 11.7 min (major), tr = 7.7 min (minor), ee = 98%.



3h'

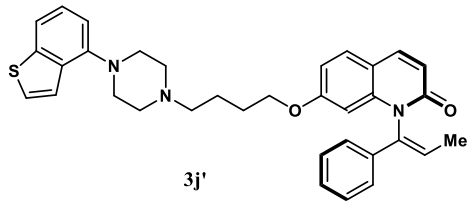
Following the general procedure **C**, **3h'** was obtained as white waxy (15 mg, 54% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.43 (dd, *J* = 9.2, 6.9 Hz, 1H), 7.36–7.33 (m, 2H), 7.31 – 7.30 (m, 3H), 6.66 – 6.61 (m, 2H), 6.17 (d, *J* = 6.9 Hz, 1H), 4.74 (t, *J* = 1.6 Hz, 1H), 4.60 (s, 1H), 2.56 (dd, *J* = 10.1, 5.8 Hz, 1H), 2.51 (dd, *J* = 10.0, 5.9 Hz, 1H), 2.22 (ddd, *J* = 15.5, 10.0, 5.9 Hz, 1H), 2.13 (dd, *J* = 10.0, 5.6 Hz, 1H), 1.73 (d, *J* = 7.0 Hz, 3H), 1.65 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 161.85, 148.91, 142.63, 138.72, 135.70, 134.83, 127.83, 127.11, 123.67, 123.60, 117.41, 110.03, 104.05, 34.89, 29.65, 21.27, 12.66. HRMS(ESI) m/z: calculated for $[C_{19}H_{21}NO + H]^{+}$ 280.1701, found 280.1702. IR ν 1658.51, 1584.13, 1539.50, 1441.32, 1328.26, 1259.83, 884.96, 798.68, 757.02, 688.60, cm^{-1}. HPLC data (Chiralpak AD column, hexane : isopropanol = 85 : 15, 1.0 mL/min), tr = 9.9 min (major), tr = 7.2 min (minor), ee = 98%.



3i'

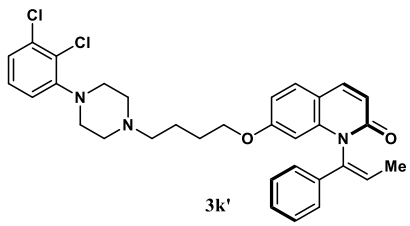
Following the general procedure **C**, **3i'** was obtained as yellow waxy (16 mg, 43% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.37 (d, *J* = 4.4 Hz, 4H), 7.34 (d, *J* = 8.3 Hz, 3H), 7.29 (d, *J* = 7.2 Hz, 3H), 6.60 (q, *J* = 6.9 Hz, 1H), 6.50 (s, 1H), 3.75 (t, *J* = 9.7 Hz, 2H), 3.53 – 3.42 (m, 2H), 2.76 – 2.48 (m, 4H), 2.15 (s, 3H), 1.71 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 160.75, 148.58, 139.67, 135.46,

134.60, 128.06, 127.79, 127.41, 127.01, 126.43, 123.61, 123.44, 116.98, 94.38, 61.25, 50.85, 47.62, 28.69, 26.31, 17.78, 12.45. HRMS(ESI) m/z: calculated for $[C_{25}H_{26}N_2O + H]^+$ 371.2123, found 371.2133. IR ν 1661.49, 1578.18, 1536.53, 1491.90, 1358.02, 1328.26, 1209.26, 1033.72, 962.31, 852.23, 757.02, 697.52, cm^{-1}. HPLC data (Chiralpak AD column, hexane : isopropanol = 70 : 30, 1.0 mL/min), tr = 8.2 min (major), tr = 5.9 min (minor), ee = 99%.



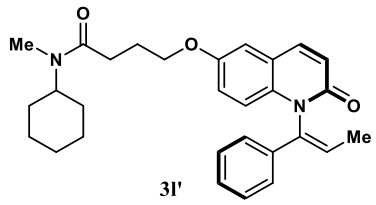
3j'

Following the general procedure **C**, **3j'** was obtained as white solid (41 mg, 75% yield) (*Z*:*E*=10:1), m.p.55-56 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 9.5 Hz, 1H), 7.69 – 7.64 (m, 1H), 7.56 (d, *J* = 8.1 Hz, 1H), 7.52 – 7.47 (m, 1H), 7.40 (s, 2H), 7.33 – 7.27 (m, 3H), 7.26 – 7.21 (m, 2H), 6.88 (d, *J* = 7.7 Hz, 1H), 6.79 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.72 – 6.64 (m, 3H), 3.91 (ddt, *J* = 27.1, 9.2, 6.1 Hz, 2H), 3.20 (t, *J* = 4.9 Hz, 4H), 2.74 (s, 4H), 2.52 (t, *J* = 7.5 Hz, 2H), 1.781-1.72 (m, 2H), 1.71 (dd, *J* = 10.2, 5.3 Hz, 2H), 1.63 (d, *J* = 7.0 Hz, 3H).^{13}C NMR (126 MHz, Chloroform-*d*) δ 160.63, 160.40, 147.42, 140.12, 140.00, 138.78, 134.98, 134.54, 133.05, 128.80, 127.78, 127.04, 125.39, 124.43, 124.01, 123.95, 120.86, 117.85, 116.02, 113.58, 111.15, 109.85, 99.11, 66.95, 57.20, 52.55, 51.08, 26.07, 22.37, 12.47. HRMS(ESI) m/z: calculated for $[C_{34}H_{35}N_3O_2S + H]^+$ 550.2528, found 550.2526. IR ν 1646.61, 1625.79, 1584.13, 1441.32, 1405.62, 1230.08, 1200.33, 1143.80, 968.26, 837.36, 745.12, 694.55, cm^{-1}. HPLC data (Chiralpak AD column, hexane : isopropanol = 85 : 15, 1.0 mL/min), tr = 29.4 min (major), tr = 19.4 min (minor), ee ≈ 92%.



3k'

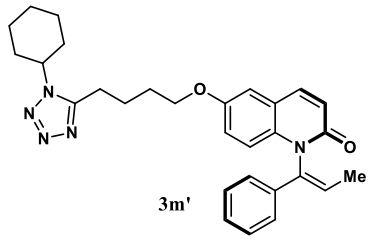
Following the general procedure **C**, **3k'** was obtained as yellow oil (17 mg, 64% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 9.5 Hz, 1H), 7.54 (d, *J* = 8.6 Hz, 1H), 7.37 – 7.33 (m, 2H), 7.30 (d, *J* = 12.3 Hz, 3H), 7.23 – 7.16 (m, 2H), 7.01 – 6.96 (m, 1H), 6.83 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.75 (d, *J* = 6.9 Hz, 1H), 6.69 (dd, *J* = 5.9, 3.6 Hz, 2H), 4.01 – 3.90 (m, 2H), 3.11 (s, 4H), 2.70 (s, 4H), 2.51 (t, *J* = 7.5 Hz, 2H), 1.81 (d, *J* = 7.3 Hz, 2H), 1.73 (d, *J* = 7.6 Hz, 2H), 1.67 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 160.60, 160.36, 150.22, 139.99, 138.74, 134.97, 134.53, 133.01, 128.78, 127.77, 127.04, 126.44, 125.37, 124.41, 123.94, 123.57, 117.87, 117.55, 113.57, 109.80, 99.09, 66.91, 57.09, 52.25, 50.27, 26.03, 22.33, 12.46. HRMS(ESI) m/z: calculated for $[C_{32}H_{33}Cl_2N_3O_2 + H]^+$ 562.2028, found 562.2027. Isotopic MS, calculated 564.1999, found 564.2001. IR ν 1655.54, 1593.06, 1447.27, 1399.67, 1215.21, 1134.88, 1045.62, 965.29, 831.40, 727.27, 688.60, cm^{-1}. HPLC data (Chiralpak AD column, hexane : isopropanol = 70 : 30, 1.0 mL/min), tr = 10.9 min (major), tr = 7.3 min (minor), ee = 94%.



3l'

Following the general procedure **C**, **3l'** was obtained as white waxy (22 mg, 48% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 9.5 Hz, 1H), 7.27 (dd, *J* = 11.0, 3.3 Hz, 5H), 7.13 – 7.02 (m, 3H), 6.84 (d, *J* = 9.5 Hz, 1H), 6.73 (q, *J* = 6.9 Hz, 1H), 4.16 – 4.02 (m, 3H), 2.83 (d, *J* = 6.8 Hz, 3H), 2.53 (dt, *J* = 20.7, 7.0 Hz, 2H), 2.18 – 2.14 (m, 2H), 2.06 (s, 1H), 1.81 (t, *J* = 13.2 Hz, 2H), 1.66 (d, *J* = 13.8 Hz, 2H), 1.61 (d, *J* = 7.0 Hz, 3H), 1.43 – 1.34 (m, 2H), 1.28 (d, *J* = 11.6 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.66, 160.84, 154.39, 154.34, 139.56, 135.82, 135.45, 128.77, 128.07, 125.42, 124.86, 122.72, 122.69, 121.19, 119.91, 117.00, 110.93, 56.54, 52.35, 30.90, 30.24, 29.93, 27.23, 25.78, 25.65, 24.73, 13.41. HRMS(ESI) m/z: calculated for $[C_{29}H_{34}N_2O_3 + H]^+$ 459.2648, found 459.2648. IR ν 1640.66, 1613.88, 1563.31, 1491.90, 1432.40, 1244.96, 1137.85, 1030.74, 974.21, 819.50, 760.00,

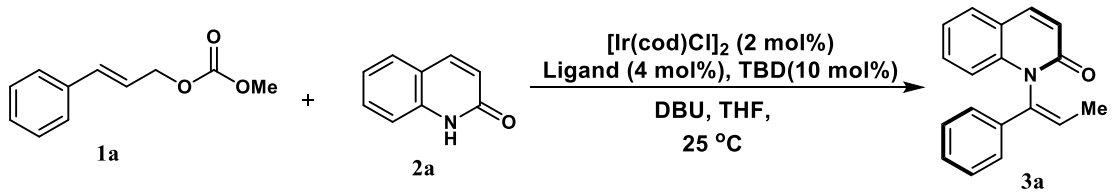
688.60, cm^{-1}. HPLC data (Chiralpak OD column, hexane : isopropanol = 80 : 20, 1.0 mL/min), tr = 27.5 min (major), tr = 24.7 min (minor), ee = 92%.



3m'

Following the general procedure **C**, **3m'** was obtained as brown waxy (17 mg, 35% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 9.5 Hz, 1H), 7.32 (d, *J* = 4.9 Hz, 5H), 7.15 (d, *J* = 9.2 Hz, 1H), 7.09 (d, *J* = 2.8 Hz, 1H), 7.03 (dd, *J* = 9.1, 2.8 Hz, 1H), 6.87 (d, *J* = 9.5 Hz, 1H), 6.76 (q, *J* = 6.9 Hz, 1H), 4.19 – 4.13 (m, 1H), 4.10 (t, *J* = 5.9 Hz, 2H), 2.97 (t, *J* = 7.5 Hz, 2H), 2.11 – 2.08 (m, 3H), 2.07 – 1.97 (m, 9H), 1.81 (d, *J* = 11.9 Hz, 2H), 1.65 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 153.19, 152.43, 144.70, 138.38, 134.84, 134.46, 132.81, 127.76, 127.06, 124.41, 123.85, 121.88, 120.14, 118.75, 116.02, 109.91, 66.62, 56.61, 31.88, 28.69, 27.48, 24.31, 23.77, 22.94, 21.99, 21.69, 12.39. HRMS(ESI) m/z: calculated for $[C_{29}H_{33}N_5O_2 + H]^+$ 484.2713, found 484.2704. IR ν 1646.61, 1563.31, 1491.90, 1438.35, 1331.24, 1247.93, 1140.83, 977.19, 807.60, 762.98, 685.62, cm^{-1}. HPLC data (Chiralpak AD column, hexane : isopropanol = 70 : 30, 1.0 mL/min), tr = 36.8 min (major), tr = 16.5 min (minor), ee = 90%.

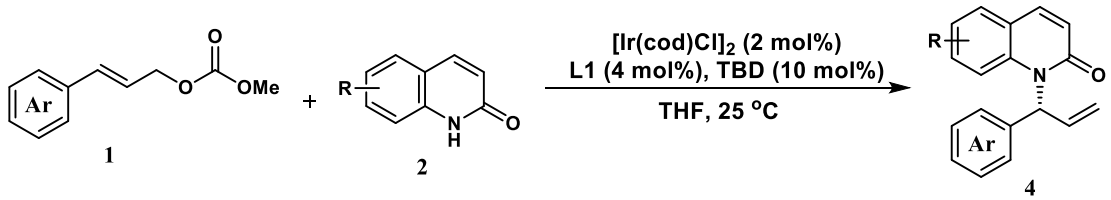
General procedure D: Large scale experiment



The reaction was carried out in the glovebox under argon atmosphere. $[Ir(cod)Cl]_2$ (14 mg, 0.02 mmol), **L1** (25 mg, 0.04 mmol), and TBD (14 mg, 0.1 mmol) were added to a vial equipped with a magnetic stirring bar. The vial was then charged with THF (5.0 mL) and stirred at 25 °C for 30 min. Pressure pipe was added propenyl carbonate (1.0 mmol), 2-Hydroxyquinoline (2.0 mmol), DBU (3.0 mmol) and THF (5.0 mL). The

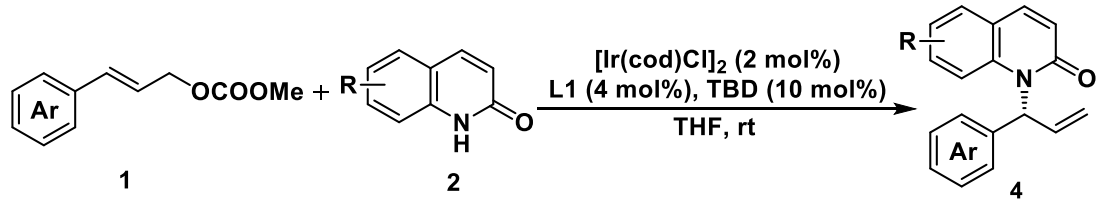
pre-formed catalyst solution was then transferred to pressure pipe. The mixture was stirred at 25 ℃ for 48 h. Upon completion of the reaction, saturated NH_4Cl aqueous solution was added and the mixture was extracted with DCM (10 mL x 3). The combined organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by silica gel flash chromatography (PE : EA = 4 : 1) to afford the desired product **3a** as a yellow solid (190 mg, 73% yield, ee = 91%).

General procedure E: Iridium catalyzed asymmetric allylic amination

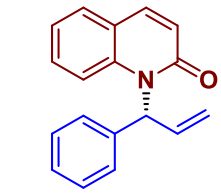


The reactions were proceeded in the glovebox. $[Ir(cod)Cl]_2$ (1.4 mg, 0.002 mmol, 0.02 eq), **L1** (2.5 mg, 0.004 mmol, 0.04 eq), and TBD (1.4 mg, 0.01 mmol, 0.1 eq) were added to a 2 dram scintillation vial (vial A) equipped with a magnetic stirring bar. The vial was then charged with THF (0.5 mL) and stirred at 25 ℃ for 30 min, generating an orange solution. To another 2 dram scintillation vial (vial B) was added **1** (0.1 mmol, 1.0 eq), **2** (0.2 mmol, 2.0 eq) and THF (0.5 mL). The pre-formed catalyst solution (vial A) was then transferred to vial B. The vial B was sealed and stirred at rt with stirring for 48 hour. The vial was removed from the glovebox and uncapped. Saturated NH_4Cl aqueous solution was added and the mixture was extracted with DCM (10 mL x 3), the combined organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography over silica gel (PE : EA = 4 : 1) to afford the desired product. The configuration of the products was assigned according to **4f**.[1]

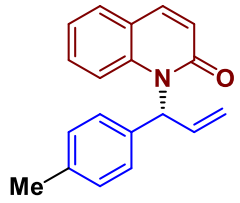
Table S1 Iridium catalyzed asymmetric allylic amination.[a]



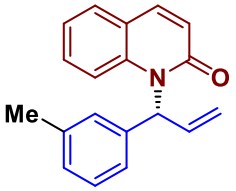
1 2 4



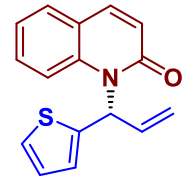
4a, 95% ee, 65% yield



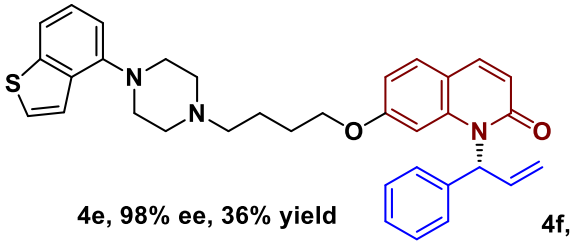
4b, 96% ee, 72% yield



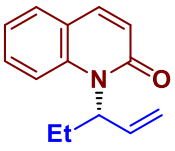
4c, 95% ee, 55% yield



4d, 99% ee, 56% yield

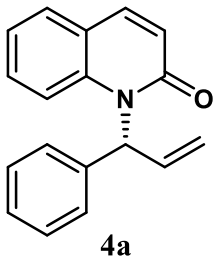


4e, 98% ee, 36% yield



4f, 85% ee, 19% yield

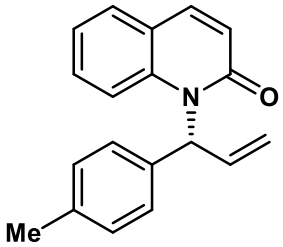
a Reaction conditions: all reactions were run on 0.1 mmol scale with respect to 1. ee determined by chiral HPLC. Isolated yield.



4a

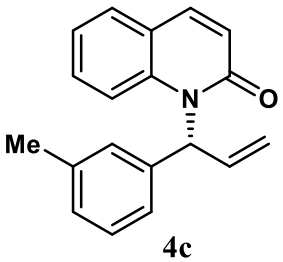
Following the general procedure **E**, **4a** was obtained as yellow oil (17 mg, 65% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 9.5 Hz, 1H), 7.57 – 7.51 (m, 2H), 7.30 (dd, *J* = 8.3, 7.0 Hz, 2H), 7.25 – 7.21 (m, 4H), 7.12 – 7.07 (m, 2H), 6.81 (d, *J* = 9.5 Hz, 1H), 6.64 (ddd, *J* = 17.0, 10.4, 6.6 Hz, 1H), 5.46 (dt, *J* = 10.4, 1.4 Hz, 1H), 5.38 (dt, *J* = 17.1, 1.4 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-d) δ 161.85, 138.67, 137.78, 132.07, 128.37, 127.90, 127.75, 126.03, 125.01, 120.91, 120.64, 120.36, 119.68, 117.05, 117.02, 56.09. HRMS(ESI) m/z: calculated for $[C_{18}H_{15}NO + H]^{+}$ 262.1232, found 262.1225. IR ν 1661.49, 1503.80, 1450.25, 1450.25, 1369.92, 789.75,

765.95, 739.17, 688.60, cm^{-1}. HPLC data (Chiralpak AD column, hexane : isopropanol = 85 : 15, 1.0 mL/min), tr = 8.6 min (major), tr = 9.1 min (minor), ee = 95%.



4b

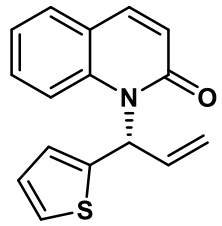
Following the general procedure **E**, **4b** was obtained as yellow oil (20 mg, 72% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 9.4 Hz, 1H), 7.52 (td, *J* = 7.5, 2.9 Hz, 2H), 7.23 (ddd, *J* = 8.6, 7.1, 1.6 Hz, 1H), 7.14 – 7.09 (m, 6H), 6.80 (d, *J* = 9.5 Hz, 1H), 6.63 (ddd, *J* = 16.9, 10.4, 6.5 Hz, 1H), 5.55 – 5.31 (m, 2H), 2.30 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 161.89, 138.64, 137.01, 135.65, 134.72, 132.25, 128.43, 128.34, 127.86, 124.98, 120.88, 120.64, 120.36, 119.34, 117.07, 55.94, 20.00. HRMS(ESI) m/z: calculated for $[C_{19}H_{17}NO + H]^{+}$ 276.1388, found 276.1380. IR ν 1643.64, 1572.23, 1447.27, 1301.49, 1224.13, 1120.00, 929.59, 825.45, 742.15, cm^{-1}. HPLC data (Chiralpak AD column, hexane : isopropanol = 85 : 15, 1.0 mL/min), tr = 9.5 min (major), tr = 10.4 min (minor), ee =96%.



4c

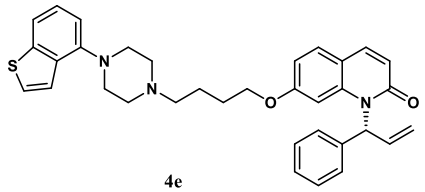
Following the general procedure **E**, **4c** was obtained as yellow oil (15 mg, 55% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 9.4 Hz, 1H), 7.52 (dt, *J* = 7.5, 3.9 Hz, 2H), 7.25 – 7.17 (m, 2H), 7.13 – 7.10 (m, 2H), 7.05 – 7.02 (m, 3H), 6.81 (d, *J* = 9.4 Hz, 1H), 6.64 (ddd, *J* = 17.0, 10.4, 6.6 Hz, 1H), 5.46 – 5.35 (m, 2H), 2.29 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 161.87, 138.65, 137.76, 137.45, 137.02, 132.16, 128.38, 127.87, 127.59, 126.83, 125.68, 122.05, 120.88, 120.63, 120.38, 119.54, 117.02, 56.07, 20.56. HRMS(ESI) m/z: calculated for $[C_{19}H_{17}NO + H]^{+}$

276.1388, found 276.1377. IR ν 1652.56, 1578.18, 1485.95, 1447.27, 1218.18, 1120.00, 926.61, 825.45, 745.12, 691.57, cm^{-1}. HPLC data (Chiralpak AD column, hexane : isopropanol = 90 : 10, 1.0 mL/min), tr = 9.6 min (major), tr = 9.0 min (minor), ee = 95%.



4d

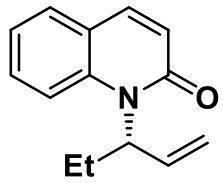
Following the general procedure **E**, **4d** was obtained as yellow oil (15 mg, 56% yield), m.p.51-52 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 9.4 Hz, 2H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.31 (d, *J* = 5.4 Hz, 2H), 7.20 (d, *J* = 5.0 Hz, 1H), 7.14 (ddd, *J* = 8.0, 5.8, 2.3 Hz, 1H), 6.95 – 6.92 (m, 2H), 6.77 (d, *J* = 9.4 Hz, 1H), 6.61 (ddd, *J* = 16.5, 10.4, 5.4 Hz, 1H), 5.42 (dd, *J* = 10.4, 1.8 Hz, 1H), 5.33 (dd, *J* = 17.1, 1.8 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 161.41, 141.81, 138.90, 136.79, 132.52, 128.43, 127.96, 126.05, 123.81, 123.78, 121.11, 120.64, 120.16, 118.58, 116.79, 52.92. HRMS(ESI) m/z: calculated for $[C_{16}H_{13}NOS + H]^+$ 268.0796, found 268.0785. IR ν 1637.69, 1584.13, 1444.30, 1399.67, 1227.11, 1137.85, 926.61, 837.36, 748.10, 697.52, 581.49, cm^{-1}. HPLC data (Chiralpak AD column, hexane : isopropanol = 95 : 5, 1.0 mL/min), tr = 19.8 min (major), tr = 21.0 min (minor), ee > 99%.



4e

Following the general procedure **E**, **4e** was obtained as white solid (20 mg, 36% yield), m.p.178-179 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.63 (t, *J* = 8.5 Hz, 2H), 7.56 (d, *J* = 8.1 Hz, 1H), 7.42 – 7.38 (m, 3H), 7.34 – 7.22 (m, 6H), 6.90 (d, *J* = 7.6 Hz, 1H), 6.70 – 6.60 (m, 3H), 6.52 (d, *J* = 2.3 Hz, 1H), 5.48 (d, *J* = 10.4 Hz, 1H), 5.38 (d, *J* = 17.1 Hz, 1H), 3.78 – 3.76 (m, 1H), 3.54 – 3.52 (m, 1H), 3.21 (s, 4H), 2.72 – 2.71 (m, 4H), 2.47 (t, *J* = 7.2 Hz, 2H), 1.66 (dq, *J* = 12.3, 6.3 Hz, 4H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.25, 158.83, 140.12, 138.55, 138.50, 138.03, 133.02, 131.49,

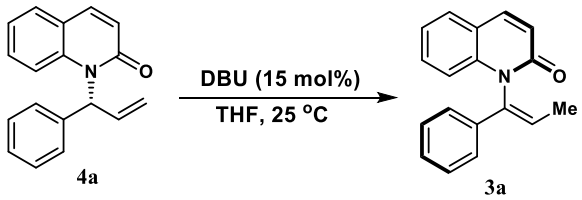
128.94, 127.81, 126.08, 125.13, 124.09, 124.01, 120.72, 119.52, 117.02, 116.18, 114.55, 111.25, 110.39, 101.33, 66.72, 57.09, 52.47, 29.18, 28.71, 25.82, 21.70, 13.14. HRMS(ESI) m/z: calculated for $[C_{34}H_{35}N_3O_2S + H]^+$ 550.2528, found 550.2524. IR ν 1625.79, 1536.53, 1456.20, 1369.92, 1334.21, 1259.83, 1122.98, 1122.98, 974.21, 837.36, 664.79, cm^{-1}. HPLC data (Chiralpak AD column, hexane : isopropanol = 85 : 15, 1.0 mL/min), tr = 24.0 min (major), tr = 22.7 min (minor), ee = 98%.



4f

Following the general procedure **E**, **4f** was obtained as white oil (4 mg, 19% yield). HPLC data (Chiralpak OD column, hexane : isopropanol = 99 : 1, 1.0 mL/min), tr = 25.1 min (major), tr = 29.0 min (minor), ee = 85%.

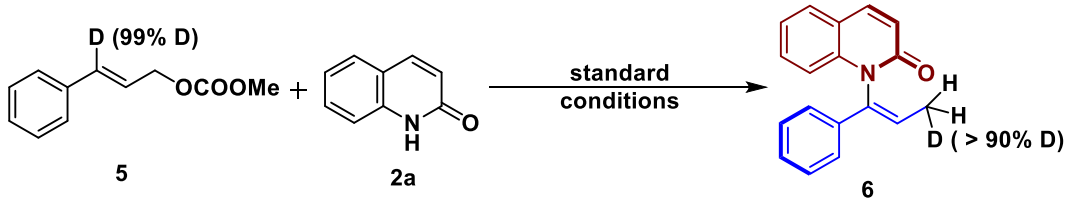
General procedure of isomerization of 4a



4a **3a**

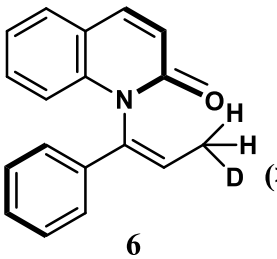
A vail was charged with **4a** (26.1 mg, 0.1 mmol), DBU (15 mol%) and THF (1.0 mL). The reaction mixture was stirred at room temperature for 6 hours. After the reaction complete, the residue was purified by silica gel flash chromatography (PE : EA = 4 : 1) to afford the desired product as a white solid (full conversion, 95% ee). This result indicated the isomerization of the **4a** was attributed to the base of DBU.

Deuterium-labeling experiment



5 **2a** **6**

The substrates **6** was synthesized according to literature [2], the general procedure **C** was used to synthesize **6**.

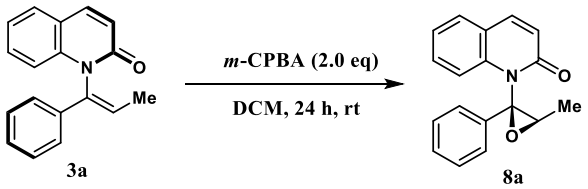


(>90% D)

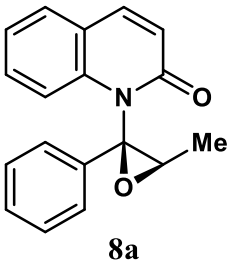
6

Following the general procedure **C**, **6** was obtained as yellow solid (23 mg, 88% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 9.6 Hz, 1H), 7.61 (d, *J* = 7.7 Hz, 1H), 7.40 (q, *J* = 9.0, 7.8 Hz, 1H), 7.29 (dq, *J* = 10.1, 4.9, 3.3 Hz, 4H), 7.24 – 7.18 (m, 3H), 6.82 (d, *J* = 9.5 Hz, 1H), 6.72 (t, *J* = 6.9 Hz, 1H), 1.59 (dt, *J* = 7.3, 2.2 Hz, 2.1H).

General procedure F: Chiral transfer for epoxidation



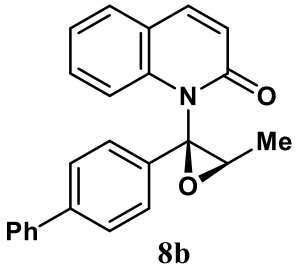
Under an argon atmosphere, a vial was charged with **3a** (26 mg, 0.1 mmol), *m*-CPBA (34 mg, 0.2 mmol) and DCM (1.0 mL). The mixture is stirred for 24 hours at 25 ℃, and then quenched by addition of saturated NH_4Cl aqueous. The layers were separated and the aqueous phase was extracted with DCM (10 mL x 3). The combined organic layers were dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by column chromatography over silica gel (PE: EA = 4 : 1) to afford the desired product.



8a

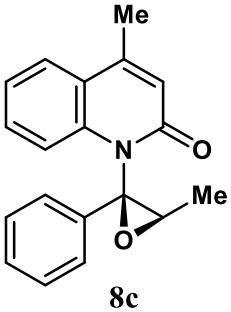
Following the general procedure **F**, **8a** was obtained as pale yellow waxy (19 mg, 69% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 9.5 Hz, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.48 (t, *J* = 7.9 Hz, 1H), 7.34 (q, *J* = 7.0, 5.3 Hz, 4H), 7.30-7.23 (m, 3H), 6.74 (d, *J* = 9.6 Hz, 1H), 3.69 (q, *J* = 5.3 Hz, 1H), 1.20 (d, *J* = 5.2 Hz, 3H). ^{13}C

NMR (101 MHz, Chloroform-*d*) δ 162.32, 139.69, 139.30, 135.93, 130.20, 128.85, 128.82, 128.70, 125.72, 123.42, 122.87, 120.00, 115.31, 70.98, 64.74, 16.05. HRMS(ESI) m/z: calculated for $[C_{18}H_{15}NO_2 + H]^+$ 278.1181, found 278.1168. IR ν 1652.56, 1590.08, 1459.17, 1244.96, 1134.88, 965.29, 822.48, 745.12, 697.52, 632.07, cm^{-1}. HPLC data (Chiralpak AD column, hexane : isopropanol = 85 : 15, 1.0 mL/min), tr = 15.9 min (major), tr = 13.7 min (minor), ee = 90%.



8b

Following the general procedure **F**, **8b** was obtained as white solid (27 mg, 76% yield), m.p.138-139 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 9.6 Hz, 1H), 7.68 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.61 – 7.58 (m, 4H), 7.56 – 7.54 (m, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.44 – 7.39 (m, 2H), 7.36 (dd, *J* = 8.5, 2.0 Hz, 3H), 7.32 (d, *J* = 7.7 Hz, 1H), 6.80 (d, *J* = 9.5 Hz, 1H), 3.77 (q, *J* = 5.2 Hz, 1H), 1.26 (d, *J* = 5.3 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 161.32, 140.83, 139.46, 138.69, 138.28, 133.94, 129.22, 127.79, 127.72, 127.58, 126.65, 126.58, 126.51, 126.11, 125.18, 122.45, 121.88, 119.01, 114.28, 69.91, 63.76, 15.06. HRMS(ESI) m/z: calculated for $[C_{24}H_{19}NO_2 + H]^+$ 354.1494, found 354.1495. IR ν 1664.46, 1584.13, 1485.95, 1444.30, 1128.93, 992.07, 837.36, 754.05, 697.52, 620.17, cm^{-1}. HPLC data (Chiralpak AD column, hexane : isopropanol = 85 : 15, 1.0 mL/min), tr = 30.9 min (major), tr = 25.9 min (minor), ee = 94%.



8c

Following the general procedure **F**, **8c** was obtained as white solid (19 mg, 66% yield), m.p.120-121 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.75 (dd, *J* = 8.1, 1.4 Hz, 1H),

7.46 (ddd, *J* = 8.6, 7.2, 1.5 Hz, 1H), 7.33 – 7.26 (m, 5H), 7.21 (dd, *J* = 6.8, 3.0 Hz, 2H), 6.63 (s, 1H), 3.66 (q, *J* = 5.3 Hz, 1H), 2.50 (d, *J* = 1.1 Hz, 3H), 1.17 (d, *J* = 5.3 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 161.13, 146.32, 137.96, 135.08, 129.00, 127.80, 127.75, 124.74, 124.20, 121.67, 121.54, 119.79, 114.54, 69.84, 63.68, 18.14, 15.03. HRMS(ESI) m/z: calculated for $[C_{19}H_{17}NO_2 + H]^+$ 292.1338, found 292.1329. IR ν 1667.44, 1596.03, 1494.88, 1447.27, 1313.39, 1084.30, 893.88, 795.70, 748.10, 694.55, 649.92, cm^{-1}. HPLC data (Chiralpak AD column, hexane : isopropanol = 85 : 15, 1.0 mL/min), tr = 19.3 min (major), tr = 16.4 min (minor), ee = 92%.

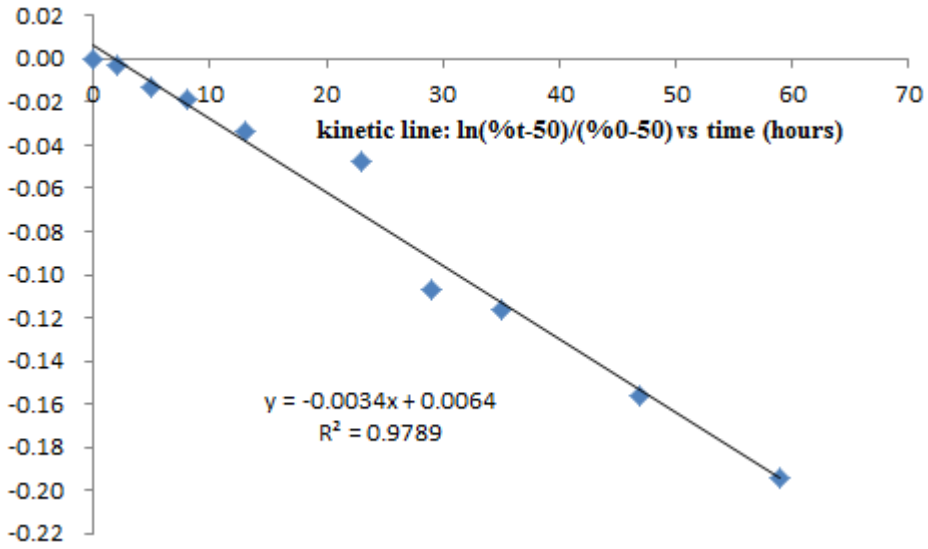
Enantiomerization barrier determination for 3a

The enantiomerisation barrier, corresponding to barrier to rotation for 3a atropisomers, was obtained by kinetic of racemization of an enantiomer. The slope of the first-order kinetic line gives the racemization constant (k racemization =2 * k enantiomersation). Eyring equation gives the enantiomerisation barrier from enantiomerisation constant (k enantiomerisation), R = 8.31451 $J.K^{-1}.mol^{-1}$, h = 6.62608*10 $^{-34}$ J.s and k_B = 1.38066 10 -23 $J.K^{-1}$.

A .solvent: THF

Temperature = 25 °C

Time (hour)	% first eluted enantiomer (%t)	ln((%t-50)/ (%t_0 -50))
0	91.70	0
2	91.58	-0.00288184637488890
5	91.14	-0.01352024457994465
8	90.94	-0.01839354857161229
13	90.32	-0.03365350504164259
23	89.78	-0.04713685537892962
29	87.48	-0.10669367143453433
35	87.12	-0.11634522088675598
47	85.68	-0.15591082109294196
59	84.34	-0.19419027333542629



K racemization = 9.4444386 x 10^{-7} S^{-1}

K enantiomerization =4.7222193 x 10^{-7} S^{-1}

Half-life time $t_{1/2}$ =733921 seconds

=12232.01 mins

= 203.9 hours

=8.5 days

Ps: It is worthy to note that **3a** could be stored as solid at room temperature for at least one month with < 1% ee loss; and in freezer for several months without loss in its enantioselectivity.

DFT results

All density functional theory (DFT) calculations were performed using the Gaussian 16[3] software package on Pitt CRC and XSEDE[4] supercomputers. Geometries were optimized in tetrahydrofuran (THF) with the SMD solvation model[5] using the M06-2X[6] functional and a standard basis set of 6-31G(d). Vibrational frequency calculations were performed for all the stationary points to confirm if each optimized structure is a local minimum or a transition state structure. Single point energies were calculated using M06-2X and 6-311++G(d,p) basis set in THF using the SMD solvation model.

Intrinsic reaction coordinate (IRC) calculations have demonstrated that the transition state connects two corresponding intermediates along the reaction

coordinate. Born–Oppenheimer molecular dynamics (BOMD) simulation on the DBU mediated deprotonation step (**TS-1a** and **TS-1b**) were also performed at the M06-2X/6-31G(d)–SMD(THF) level of theory to gain more insights. BOMD simulation results suggested that the cleavage of benzylic C–H bond and the formation of N–H bond occurred simultaneously along the reaction coordinate. When the **TS-1a** is used as the input structure of BOMD simulation, the interaction of carbonyl oxygen atom with benzylic hydrogen atom is observed during DBU mediated deprotonation. The corresponding O–H distance decreased from 2.48 Å to 1.84 Å in 50 fs. Therefore, the BOMD simulation confirmed that the ion-pair intermediate **7a** is directly generated from the deprotonation transition state **TS-1a**.

The NCIplot 3.0[7] developed by Yang and co-workers was used to visualize the non-covalent interaction in the ion-pair intermediates **7a** and **7b**. As shown in Figure S1, a critical hydrogen bonding interaction could be observed in **7a**. While in **7b**, the corresponding interaction is not observed because the carbonyl oxygen atom is in *trans* position with respect to the N–H bond. Therefore, the chiral ion-pair intermediate **7a** is not only stabilized by the electrostatic attraction but the hydrogen bonding interaction. This hydrogen bonding interaction is also crucial for the stereoretention during central-to-axial chiral transfer because it could fix the relative position of DBU-H cation.

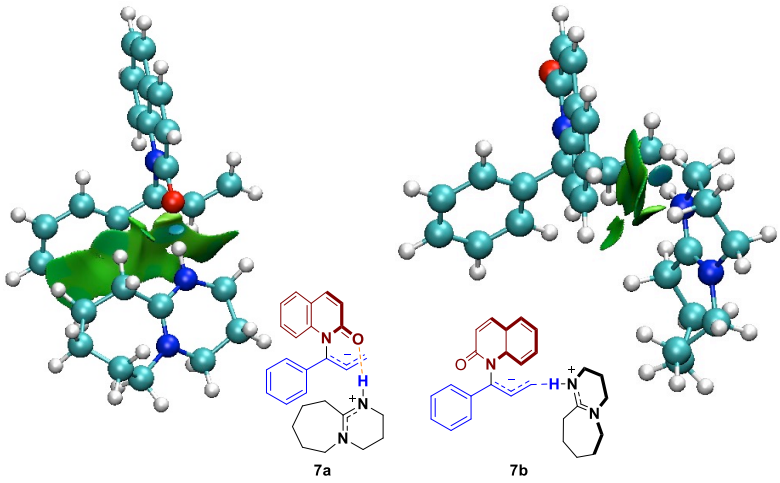


Figure S1. Non-covalent interaction (NCI) plot of chiral ion-pair intermediates **7a** and **7b**.

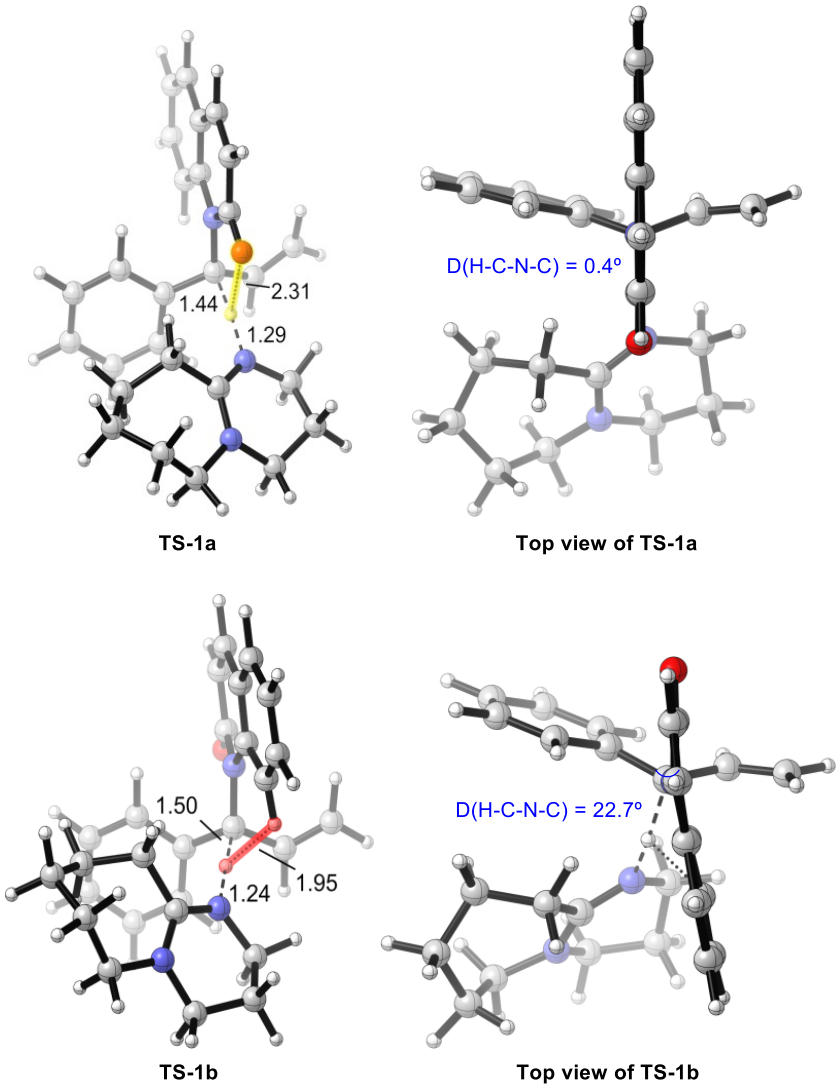


Figure S2. Top view of DBU mediated deprotonation transition states **TS-1a** and **TS-1b**.

Optimized structure of DBU mediated deprotonation transition state **TS-1b** shows that the distance between benzylic hydrogen atom and phenyl hydrogen atom is 1.95 Å (Figure S2), which indicates a remarkable steric repulsion. The steric repulsion is also reflected in the comparison of dihedral angles of H–C–N–C. As shown in the top view of **TS-1a**, the dihedral angle of H–C–N–C is 0.4° while the corresponding value in **TS-1b** is 22.7°. This difference further demonstrates the steric repulsion in transition state **TS-1b**. Therefore, the deprotonation prefers to occur through transition state **TS-1a**.

The dissociation of chiral ion-pair intermediates **7a** and **7b** are shown in Figure S3. Computational results suggest that the dissociation of **7a** is disfavored as it requires an

energy increase of 9.1 kcal/mol, which is in accordance with Paton's study.[8] The dissociation of **7b** is only endergonic by 3.5 kcal/mol because **7b** is less stable than **7a** by 5.3 kcal/mol.[8]

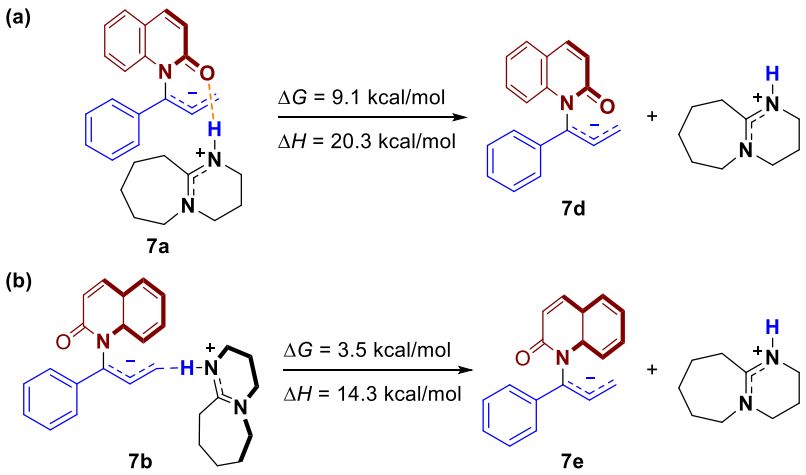


Figure S3. The dissociation of chiral ion-pair intermediates **7a** (a) and **7b** (b).

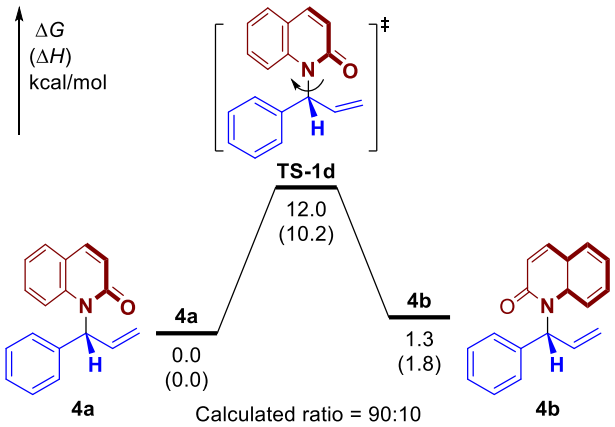


Figure S4. The isomerization between **4a** and **4b**.

The isomerization between **4a** and **4b** could occur through the rotation along the C–N bond. A transition state **TS-1d** was located for this process. As shown in Figure S4, the activation free energy is only 12.0 kcal/mol, which suggests the isomerization is a facile process. Meanwhile, computational results show that **4b** is less stable than **4a** by 1.3 kcal/mol, which corresponds to a ratio of 90:10.

Cartesian coordinates (Å) and energies of optimized structures

(*P*)-3a

M06-2X/6-31G(d) SCF energy in solution: -824.59835943 a.u.

M06-2X/6-31G(d) enthalpy in solution: -824.295431 a.u.

M06-2X/6-31G(d) free energy in solution: -824.356975 a.u.

M06-2X/6-311+G(d,p) SCF energy in solution: -824.82531889 a.u.

M06-2X/6-311+G(d,p) enthalpy in solution: -824.522390 a.u.

M06-2X/6-311+G(d,p) free energy in solution: -824.583934 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	1.471442	-2.515263	1.416745
C	0.756887	-1.352922	1.177423
C	1.241173	-0.410860	0.253412
C	2.463790	-0.656486	-0.406063
C	3.167783	-1.842902	-0.142561
C	2.680347	-2.772362	0.756907
H	1.083097	-3.232995	2.132725
H	-0.170070	-1.168889	1.707663
C	2.959327	0.336021	-1.325033
H	4.107848	-2.010986	-0.661257
H	3.228703	-3.687082	0.955262
C	2.280387	1.477528	-1.545001
C	1.006365	1.763433	-0.886435
H	3.900997	0.142210	-1.832834
H	2.633521	2.242691	-2.226847
O	0.367289	2.787377	-1.081375
N	0.543181	0.769070	-0.011136
C	-0.752974	0.964766	0.584722
C	-0.918366	1.902274	1.523144
H	-1.928185	2.073776	1.888969
C	0.156778	2.782090	2.070566

H	1.154950	2.398693	1.844033
H	0.055551	2.882626	3.155905
C	-1.843156	0.116405	0.042396
C	-2.966513	-0.198251	0.819383
C	-1.765839	-0.387469	-1.261737
C	-3.997465	-0.969949	0.294259
C	-2.797528	-1.162686	-1.784498
H	-0.895955	-0.165847	-1.873908
C	-3.918793	-1.453950	-1.011122
H	-2.723049	-1.539128	-2.800225
H	-4.721154	-2.061702	-1.417831
H	-3.023812	0.146823	1.847743
H	-4.859038	-1.205748	0.911654
H	0.074153	3.786550	1.638855

(*M*)-3a

M06-2X/6-31G(d) SCF energy in solution: -824.59835943 a.u.

M06-2X/6-31G(d) enthalpy in solution: -824.295431 a.u.

M06-2X/6-31G(d) free energy in solution: -824.356975 a.u.

M06-2X/6-311+G(d,p) SCF energy in solution: -824.82531889 a.u.

M06-2X/6-311+G(d,p) enthalpy in solution: -824.522390 a.u.

M06-2X/6-311+G(d,p) free energy in solution: -824.583934 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	1.471442	-2.515263	-1.416745
C	0.756887	-1.352922	-1.177423
C	1.241173	-0.410860	-0.253412
C	2.463790	-0.656486	0.406063
C	3.167783	-1.842902	0.142561
C	2.680347	-2.772362	-0.756907

H	1.083097	-3.232995	-2.132725
H	-0.170070	-1.168889	-1.707663
C	2.959327	0.336021	1.325033
H	4.107848	-2.010986	0.661257
H	3.228703	-3.687082	-0.955262
C	2.280387	1.477528	1.545001
C	1.006365	1.763433	0.886435
H	3.900997	0.142210	1.832834
H	2.633521	2.242691	2.226847
O	0.367289	2.787377	1.081375
N	0.543181	0.769070	0.011136
C	-0.752974	0.964766	-0.584722
C	-0.918366	1.902274	-1.523144
H	-1.928185	2.073776	-1.888969
C	0.156778	2.782090	-2.070566
H	1.154950	2.398693	-1.844033
H	0.055551	2.882626	-3.155905
C	-1.843156	0.116405	-0.042396
C	-2.966513	-0.198251	-0.819383
C	-1.765839	-0.387469	1.261737
C	-3.997465	-0.969949	-0.294259
C	-2.797528	-1.162686	1.784498
H	-0.895955	-0.165847	1.873908
C	-3.918793	-1.453950	1.011122
H	-2.723049	-1.539128	2.800225
H	-4.721154	-2.061702	1.417831
H	-3.023812	0.146823	-1.847743
H	-4.859038	-1.205748	-0.911654
H	0.074153	3.786550	-1.638855

3c

M06-2X/6-31G(d) SCF energy in solution: -824.59463941 a.u.

M06-2X/6-31G(d) enthalpy in solution: -824.291787 a.u.

M06-2X/6-31G(d) free energy in solution: -824.353094 a.u.

M06-2X/6-311+G(d,p) SCF energy in solution: -824.82129409 a.u.

M06-2X/6-311+G(d,p) enthalpy in solution: -824.518442 a.u.

M06-2X/6-311+G(d,p) free energy in solution: -824.579749 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-2.008014	-2.555275	-0.843370
C	-1.107518	-1.502820	-0.843444
C	-1.453506	-0.284769	-0.232783
C	-2.725476	-0.148152	0.363436
C	-3.619735	-1.231166	0.344322
C	-3.270856	-2.429584	-0.249470
H	-1.724088	-3.490223	-1.316619
H	-0.139332	-1.618803	-1.315620
C	-3.067096	1.113319	0.969051
H	-4.594457	-1.103746	0.807477
H	-3.965780	-3.262521	-0.258946
C	-2.192386	2.137047	0.979325
C	-0.856289	2.019298	0.398040
H	-4.051152	1.218308	1.419204
H	-2.421719	3.094757	1.432550
O	-0.021547	2.913888	0.443920
N	-0.569824	0.793676	-0.213139
C	0.742199	0.640231	-0.804534
C	0.926239	1.107038	-2.043203

H	0.055170	1.541101	-2.531327
C	2.209098	1.147335	-2.813689
H	3.081984	0.989346	-2.176589
H	2.309311	2.119692	-3.306575
C	1.749959	-0.030252	0.053804
C	2.624594	-0.987351	-0.475857
C	1.818030	0.264313	1.421825
C	3.561593	-1.618604	0.338351
C	2.754980	-0.366815	2.233571
H	1.146106	1.005359	1.844227
C	3.631034	-1.308364	1.694612
H	2.801995	-0.122140	3.290387
H	4.359337	-1.802272	2.330540
H	2.554652	-1.253911	-1.526908
H	4.229447	-2.361841	-0.086460
H	2.218563	0.387484	-3.604656

4a

M06-2X/6-31G(d) SCF energy in solution: -824.58312417 a.u.

M06-2X/6-31G(d) enthalpy in solution: -824.279625 a.u.

M06-2X/6-31G(d) free energy in solution: -824.340707 a.u.

M06-2X/6-311+G(d,p) SCF energy in solution: -824.81130006 a.u.

M06-2X/6-311+G(d,p) enthalpy in solution: -824.507801 a.u.

M06-2X/6-311+G(d,p) free energy in solution: -824.568883 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	1.221571	-2.531756	1.292594
C	0.574871	-1.347145	0.980830
C	1.231557	-0.354905	0.227044

C	2.554850	-0.603711	-0.203428
C	3.185629	-1.814909	0.125954
C	2.533050	-2.778693	0.869261
H	0.690671	-3.278502	1.874890
H	-0.443098	-1.205249	1.317375
C	3.233300	0.403032	-0.975716
H	4.203597	-1.973424	-0.219687
H	3.026237	-3.711534	1.120673
C	2.625333	1.563943	-1.278537
C	1.265600	1.859064	-0.838867
H	4.249693	0.202695	-1.305276
H	3.108034	2.345137	-1.854200
O	0.712940	2.924632	-1.092720
N	0.616774	0.852971	-0.110505
C	-0.747940	1.183544	0.352549
H	-0.956936	2.138578	-0.134327
C	-0.761719	1.442528	1.840904
H	-0.503949	0.620277	2.505666
C	-1.063906	2.634554	2.347319
H	-1.321914	3.475235	1.706867
H	-1.062663	2.812688	3.418928
C	-1.794338	0.195403	-0.150790
C	-2.963489	-0.029191	0.578719
C	-1.631712	-0.443966	-1.383249
C	-3.950140	-0.884046	0.088782
C	-2.616849	-1.297165	-1.872035
H	-0.726774	-0.276621	-1.961490
C	-3.779699	-1.522639	-1.136417
H	-2.474253	-1.788641	-2.829825
H	-4.546249	-2.190731	-1.516829

H	-3.106560	0.468624	1.533495
H	-4.852594	-1.050034	0.669537

4b

M06-2X/6-31G(d) SCF energy in solution: -824.57982783 a.u.

M06-2X/6-31G(d) enthalpy in solution: -824.276474 a.u.

M06-2X/6-31G(d) free energy in solution: -824.338389 a.u.

M06-2X/6-311+G(d,p) SCF energy in solution: -824.80824139 a.u.

M06-2X/6-311+G(d,p) enthalpy in solution: -824.504888 a.u.

M06-2X/6-311+G(d,p) free energy in solution: -824.566803 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	2.411197	-2.236816	-1.306848
C	1.351784	-1.368199	-1.097199
C	1.508752	-0.247600	-0.259139
C	2.746566	-0.066037	0.400167
C	3.804471	-0.958339	0.162880
C	3.651821	-2.033390	-0.691649
H	2.262111	-3.095386	-1.954260
H	0.399824	-1.591206	-1.562461
C	2.878222	1.018732	1.337937
H	4.745994	-0.786639	0.677774
H	4.472644	-2.720003	-0.868647
C	1.827946	1.808343	1.627004
C	0.530698	1.625639	0.980780
H	3.838823	1.164369	1.825607
H	1.879714	2.610673	2.354054
O	-0.461103	2.279239	1.282242
N	0.479978	0.671387	-0.036384

C	-0.760474	0.596667	-0.834192
H	-0.479335	0.076334	-1.751478
C	-1.253886	1.955719	-1.294437
H	-1.886120	2.509720	-0.610741
C	-0.953849	2.434924	-2.498292
H	-0.321407	1.884588	-3.192254
H	-1.322099	3.401544	-2.830113
C	-1.850247	-0.214877	-0.145587
C	-3.104154	-0.305098	-0.759124
C	-1.631698	-0.899824	1.049526
C	-4.120731	-1.063492	-0.186761
C	-2.650809	-1.658469	1.624566
H	-0.664953	-0.841948	1.540974
C	-3.897075	-1.743048	1.010101
H	-2.466737	-2.182551	2.557672
H	-4.689637	-2.333229	1.459843
H	-3.282415	0.224064	-1.692195
H	-5.088633	-1.122965	-0.675432

4c

M06-2X/6-31G(d) SCF energy in solution: -824.58171393 a.u.

M06-2X/6-31G(d) enthalpy in solution: -824.278425 a.u.

M06-2X/6-31G(d) free energy in solution: -824.338805 a.u.

M06-2X/6-311+G(d,p) SCF energy in solution: -824.80965102 a.u.

M06-2X/6-311+G(d,p) enthalpy in solution: -824.506362 a.u.

M06-2X/6-311+G(d,p) free energy in solution: -824.566742 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	1.818121	-2.632529	0.175130

C	0.957077	-1.562608	0.354625
C	1.395825	-0.249053	0.101026
C	2.710844	-0.056809	-0.379057
C	3.563585	-1.160465	-0.549446
C	3.132791	-2.442216	-0.268460
H	1.454647	-3.635405	0.376966
H	-0.057292	-1.748270	0.678107
C	3.137904	1.276100	-0.713842
H	4.570670	-0.979845	-0.915718
H	3.796143	-3.289934	-0.402674
C	2.296456	2.318600	-0.593374
C	0.936864	2.156957	-0.088427
H	4.151866	1.416219	-1.079883
H	2.579720	3.332799	-0.849957
O	0.165705	3.102874	0.033228
N	0.560320	0.857561	0.279074
C	-0.762479	0.739373	0.922554
H	-1.037077	1.783731	1.103721
C	-0.627138	0.116781	2.299793
H	0.166692	0.571971	2.891510
C	-1.380560	-0.837602	2.836097
H	-2.180916	-1.327889	2.288542
H	-1.209345	-1.165738	3.856963
C	-1.844497	0.178439	0.012558
C	-3.174737	0.243552	0.446895
C	-1.581434	-0.322369	-1.263090
C	-4.211608	-0.210754	-0.361200
C	-2.621077	-0.776000	-2.075616
H	-0.563471	-0.352648	-1.638275
C	-3.936972	-0.728787	-1.626701

H	-2.395750	-1.162669	-3.064952
H	-4.744854	-1.082310	-2.259998
H	-3.396812	0.662339	1.425128
H	-5.235882	-0.151946	-0.005617

TS-1a

M06-2X/6-31G(d) SCF energy in solution: -1286.44831526 a.u.

M06-2X/6-31G(d) enthalpy in solution: -1285.888792 a.u.

M06-2X/6-31G(d) free energy in solution: -1285.975098 a.u.

M06-2X/6-311+G(d,p) SCF energy in solution: -1286.80863424 a.u.

M06-2X/6-311+G(d,p) enthalpy in solution: -1286.249111 a.u.

M06-2X/6-311+G(d,p) free energy in solution: -1286.335417 a.u.

Imaginary frequency: -1355.4818 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	4.972937	0.847966	-1.072762
C	3.646177	0.471098	-0.958544
C	3.203486	-0.249430	0.169086
C	4.147137	-0.571048	1.171107
C	5.489583	-0.178076	1.029041
C	5.910119	0.526911	-0.080864
H	5.285664	1.402992	-1.952104
H	2.947280	0.732121	-1.741808
C	3.699344	-1.301103	2.327189
H	6.188581	-0.442649	1.818255
H	6.947070	0.828523	-0.185087
C	2.409442	-1.661969	2.448092

C	1.411641	-1.338620	1.427433
H	4.426421	-1.550967	3.096201
H	2.035260	-2.212359	3.303937
O	0.237932	-1.675148	1.550457
N	1.864607	-0.630773	0.313380
C	0.900518	-0.330935	-0.745450
H	-0.435138	-0.815565	-0.483798
C	1.163411	-1.100803	-1.974972
H	0.660885	-0.735210	-2.870672
C	1.896843	-2.218361	-2.088388
H	2.428723	-2.647711	-1.242571
H	1.981883	-2.735222	-3.039021
C	0.557021	1.108118	-0.867419
C	0.943619	2.056500	0.099492
C	-0.299337	1.558457	-1.892377
C	0.516637	3.380150	0.032468
C	-0.721006	2.883297	-1.958898
H	-0.657001	0.859954	-2.644020
C	-0.316130	3.810345	-0.999318
H	-1.378219	3.190803	-2.768144
H	-0.646690	4.842942	-1.051945
H	1.585122	1.750663	0.920944
H	0.843537	4.081443	0.795773
C	-5.034615	-0.019264	0.508419
C	-2.606703	-0.568589	0.114005
C	-4.869901	0.482526	1.940690
C	-2.120164	0.391181	1.178125
C	-4.061801	1.777743	2.050477
C	-2.818546	1.755988	1.158635
H	-5.242816	0.823717	-0.167507

H	-2.229596	-0.087133	2.158323
H	-4.420024	-0.315551	2.541133
H	-3.764294	1.922403	3.095597
H	-5.908934	-0.674340	0.472421
H	-5.872978	0.645016	2.348614
H	-1.049334	0.503398	1.019141
H	-4.693946	2.631144	1.779128
H	-2.109220	2.523813	1.483241
H	-3.085284	2.010787	0.125351
C	-4.352901	-1.707535	-1.134254
C	-3.309503	-2.780107	-1.391518
C	-1.972783	-2.106539	-1.646601
H	-1.154410	-2.831555	-1.653415
H	-3.234323	-3.432405	-0.514961
H	-3.607806	-3.391778	-2.246953
H	-4.527638	-1.113186	-2.042374
H	-5.305115	-2.160659	-0.846107
H	-1.974770	-1.610309	-2.626841
N	-1.681329	-1.127403	-0.608785
N	-3.932349	-0.827445	-0.039130

TS-1b

M06-2X/6-31G(d) SCF energy in solution: -1286.44348482 a.u.

M06-2X/6-31G(d) enthalpy in solution: -1285.883721 a.u.

M06-2X/6-31G(d) free energy in solution: -1285.968945 a.u.

M06-2X/6-311+G(d,p) SCF energy in solution: -1286.80565672 a.u.

M06-2X/6-311+G(d,p) enthalpy in solution: -1286.245893 a.u.

M06-2X/6-311+G(d,p) free energy in solution: -1286.331117 a.u.

Imaginary frequency: -1193.0183 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	-1.394995	-3.296568	0.738895
C	-1.359542	-1.917261	0.855243
C	-2.260096	-1.114660	0.126860
C	-3.241266	-1.758164	-0.664132
C	-3.250274	-3.159564	-0.770275
C	-2.329838	-3.932700	-0.089677
H	-0.690792	-3.889996	1.314741
H	-0.654240	-1.455607	1.533036
C	-4.237654	-0.948624	-1.314956
H	-4.009512	-3.622068	-1.395757
H	-2.344246	-5.014121	-0.175487
C	-4.269404	0.381680	-1.115958
C	-3.281761	1.064410	-0.277073
H	-4.976443	-1.440732	-1.943084
H	-5.026877	1.019809	-1.557549
O	-3.340000	2.264930	-0.048999
N	-2.220210	0.276079	0.195405
C	-1.125469	0.975958	0.869604
H	0.164474	0.233468	1.014813
C	-1.420041	1.248826	2.282219
H	-0.748949	1.948278	2.779981
C	-2.360732	0.659149	3.037740
H	-3.073644	-0.050258	2.624333
H	-2.453175	0.890411	4.094261
C	-0.490128	2.026240	0.036352
C	-0.588345	2.013588	-1.370415

C	0.386636	2.978161	0.593113
C	0.131447	2.899938	-2.164296
C	1.106508	3.865226	-0.203396
H	0.515239	3.036467	1.669616
C	0.988699	3.839124	-1.591106
H	1.765886	4.586513	0.272599
H	1.548412	4.532933	-2.210501
H	-1.240398	1.290014	-1.852834
H	0.016639	2.855720	-3.244469
C	4.377622	-1.069209	-0.648872
C	2.093799	-0.565512	0.279290
C	3.892456	-1.985263	-1.768641
C	1.383263	-0.836258	-1.031159
C	3.098657	-1.258093	-2.855592
C	2.091595	-0.268774	-2.266442
H	4.741526	-0.117564	-1.061709
H	1.231013	-1.917611	-1.135128
H	3.304444	-2.797179	-1.326444
H	2.572515	-1.999861	-3.467374
H	5.227485	-1.546006	-0.154996
H	4.775378	-2.453972	-2.215055
H	0.389864	-0.394927	-0.932999
H	3.787050	-0.725997	-3.521850
H	1.338933	-0.009527	-3.017386
H	2.586638	0.672273	-1.996799
C	4.053713	-0.437748	1.708030
C	3.086136	-0.611024	2.866105
C	1.832307	0.192770	2.573926
H	1.034796	-0.027419	3.290176
H	2.832137	-1.670712	2.976068

H	3.556810	-0.275086	3.793365
H	4.417780	0.597033	1.658443
H	4.920121	-1.091308	1.833834
H	2.042096	1.268879	2.634889
N	1.331735	-0.121424	1.243026
N	3.415516	-0.792538	0.432844

TS-1c

M06-2X/6-31G(d) SCF energy in solution: -1286.44646381 a.u.

M06-2X/6-31G(d) enthalpy in solution: -1285.886617 a.u.

M06-2X/6-31G(d) free energy in solution: -1285.971486 a.u.

M06-2X/6-311+G(d,p) SCF energy in solution: -1286.80575722 a.u.

M06-2X/6-311+G(d,p) enthalpy in solution: -1286.245910 a.u.

M06-2X/6-311+G(d,p) free energy in solution: -1286.330779 a.u.

Imaginary frequency: -1289.3499 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	-5.112362	0.596908	1.046147
C	-3.752224	0.378612	0.907514
C	-3.260363	-0.389501	-0.167654
C	-4.185904	-0.900371	-1.106813
C	-5.561739	-0.668016	-0.938243
C	-6.032739	0.069790	0.129986
H	-5.464188	1.193379	1.882561
H	-3.066088	0.803209	1.627911
C	-3.681159	-1.636652	-2.234847
H	-6.246688	-1.079776	-1.675003

H	-7.095885	0.247121	0.253994
C	-2.357071	-1.808373	-2.398360
C	-1.379450	-1.283655	-1.443870
H	-4.392377	-2.037229	-2.953348
H	-1.938607	-2.345490	-3.242101
O	-0.173288	-1.426770	-1.619036
N	-1.891417	-0.629583	-0.322227
C	-0.943500	-0.180543	0.705358
H	0.403279	-0.704375	0.509805
C	-1.227567	-0.839774	1.994678
H	-1.619244	-1.850598	1.856222
C	-1.028353	-0.440360	3.262032
H	-0.675528	0.549197	3.531487
H	-1.252855	-1.115702	4.082273
C	-0.630315	1.267308	0.638327
C	-1.149145	2.105850	-0.366717
C	0.332942	1.830532	1.502209
C	-0.749586	3.434632	-0.484518
C	0.727640	3.160046	1.384019
H	0.807148	1.205358	2.251125
C	0.186118	3.978679	0.393602
H	1.473822	3.555509	2.068346
H	0.493131	5.016081	0.303279
H	-1.871506	1.709973	-1.074322
H	-1.178385	4.049617	-1.271247
C	5.077249	-0.314297	-0.390596
C	2.601476	-0.600143	-0.028359
C	4.991239	0.226789	-1.815604
C	2.237344	0.424809	-1.080176
C	4.329025	1.603334	-1.912542

C	3.082145	1.704187	-1.031227
H	5.359642	0.489751	0.305225
H	2.308022	-0.049253	-2.065794
H	4.468180	-0.508045	-2.436946
H	4.059251	1.794761	-2.957598
H	5.877901	-1.057186	-0.352960
H	6.012534	0.287288	-2.205810
H	1.183147	0.649536	-0.936726
H	5.047198	2.379142	-1.622779
H	2.464244	2.550130	-1.348422
H	3.367776	1.912143	0.007533
C	4.197085	-1.982121	1.179903
C	3.030748	-2.929777	1.394976
C	1.789690	-2.106123	1.686957
H	0.887365	-2.726016	1.674754
H	2.876170	-3.528735	0.491110
H	3.251511	-3.609703	2.221885
H	4.440324	-1.451779	2.111476
H	5.088224	-2.533926	0.869355
H	1.849821	-1.649615	2.683574
N	1.616169	-1.063165	0.685580
N	3.886907	-1.013146	0.123265

7a

M06-2X/6-31G(d) SCF energy in solution: -1286.46437685 a.u.

M06-2X/6-31G(d) enthalpy in solution: -1285.899335 a.u.

M06-2X/6-31G(d) free energy in solution: -1285.986649 a.u.

M06-2X/6-311+G(d,p) SCF energy in solution: -1286.82875833 a.u.

M06-2X/6-311+G(d,p) enthalpy in solution: -1286.263716 a.u.

M06-2X/6-311+G(d,p) free energy in solution: -1286.351030 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	5.357612	0.494960	-1.357934
C	4.011291	0.231886	-1.184390
C	3.517001	-0.096539	0.092008
C	4.414421	-0.153324	1.181124
C	5.779566	0.119387	0.975651
C	6.255137	0.441364	-0.279280
H	5.722023	0.746920	-2.349350
H	3.321641	0.274711	-2.018395
C	3.891376	-0.489727	2.476133
H	6.449992	0.071281	1.829887
H	7.308661	0.650681	-0.432673
C	2.578312	-0.748996	2.639506
C	1.644490	-0.703633	1.521127
H	4.577657	-0.531094	3.318661
H	2.151167	-1.009379	3.601277
O	0.441843	-0.955459	1.676051
N	2.160354	-0.358692	0.284333
C	1.252894	-0.319142	-0.838592
H	-0.805562	-1.135619	0.339646
C	1.178704	-1.507450	-1.610660
H	0.550253	-1.444010	-2.500189
C	1.811333	-2.692841	-1.394920
H	2.464286	-2.851223	-0.540097
H	1.692469	-3.519632	-2.087061
C	0.542330	0.894622	-1.062740

C	-0.468324	1.031379	-2.061099
C	0.785551	2.060997	-0.279256
C	-1.129297	2.231197	-2.276649
C	0.108803	3.252701	-0.503404
H	1.533519	2.020559	0.508116
C	-0.853020	3.368510	-1.509856
H	0.344294	4.112692	0.120229
H	-1.376739	4.303131	-1.682443
H	-0.732888	0.175338	-2.676045
H	-1.883085	2.279185	-3.060142
C	-5.158322	0.032559	0.209324
C	-2.733137	-0.571359	0.314279
C	-5.184501	0.662874	1.599064
C	-2.335238	0.604174	1.179860
C	-4.413844	1.981357	1.678483
C	-3.092695	1.907329	0.915506
H	-5.250841	0.797760	-0.571828
H	-2.439506	0.301129	2.229704
H	-4.792504	-0.065495	2.318120
H	-4.223226	2.223381	2.730248
H	-6.016150	-0.634149	0.108520
H	-6.232000	0.829237	1.869069
H	-1.266744	0.752973	1.007120
H	-5.025108	2.793332	1.268853
H	-2.444801	2.742022	1.198761
H	-3.263112	2.012657	-0.162065
C	-4.239304	-1.937601	-0.999838
C	-3.295401	-3.094186	-0.716005
C	-1.868248	-2.593082	-0.814951
H	-1.145089	-3.310406	-0.421737

H	-3.490179	-3.488054	0.286683
H	-3.467522	-3.894419	-1.439049
H	-4.124586	-1.584441	-2.031833
H	-5.276407	-2.245969	-0.859944
H	-1.599334	-2.385986	-1.856584
N	-1.739361	-1.366270	-0.035387
N	-3.983890	-0.816172	-0.078776

7b

M06-2X/6-31G(d) SCF energy in solution: -1286.45259358 a.u.

M06-2X/6-31G(d) enthalpy in solution: -1285.888823 a.u.

M06-2X/6-31G(d) free energy in solution: -1285.977387 a.u.

M06-2X/6-311+G(d,p) SCF energy in solution: -1286.81782527 a.u.

M06-2X/6-311+G(d,p) enthalpy in solution: -1286.254055 a.u.

M06-2X/6-311+G(d,p) free energy in solution: -1286.342619 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-0.207981	-1.312306	2.115286
C	0.538189	-0.637327	1.164762
C	1.538739	-1.311634	0.436653
C	1.766923	-2.681234	0.705345
C	0.986101	-3.345340	1.667413
C	0.003649	-2.675562	2.372512
H	-0.968674	-0.769938	2.670894
H	0.369730	0.415585	0.972334
C	2.812283	-3.352408	-0.022700
H	1.179930	-4.399267	1.850543

H	-0.589348	-3.192710	3.120026
C	3.560344	-2.682299	-0.918729
C	3.348277	-1.260381	-1.208965
H	2.986733	-4.407510	0.175366
H	4.360629	-3.156670	-1.476119
O	4.038369	-0.651280	-2.014412
N	2.303397	-0.641593	-0.513638
C	1.966306	0.718808	-0.862082
H	-1.068508	-0.431560	-1.477399
C	1.082093	0.862706	-1.935561
H	0.818714	1.889363	-2.194488
C	0.477422	-0.125012	-2.686596
H	0.770507	-1.169008	-2.587911
H	-0.102286	0.138316	-3.566053
C	2.536498	1.770214	-0.065705
C	2.253481	3.146973	-0.277882
C	3.413953	1.480544	1.011492
C	2.804523	4.137832	0.520830
C	3.959275	2.482155	1.805336
H	3.671997	0.445714	1.217547
C	3.665047	3.826504	1.577527
H	4.628253	2.203861	2.616449
H	4.093108	4.607061	2.198215
H	1.592806	3.443531	-1.087058
H	2.557424	5.176505	0.313228
C	-5.005687	0.552646	0.545058
C	-2.811172	0.080711	-0.572016
C	-4.513862	1.860219	1.156711
C	-2.438755	1.529291	-0.800029
C	-4.307881	2.974258	0.130340

C	-3.607137	2.461367	-1.126887
H	-5.767937	0.738716	-0.222330
H	-1.888904	1.885179	0.080854
H	-3.589414	1.660581	1.711126
H	-3.713974	3.774825	0.585115
H	-5.475598	-0.045281	1.328507
H	-5.254428	2.174994	1.898342
H	-1.718727	1.522526	-1.623150
H	-5.275295	3.409002	-0.144259
H	-3.226519	3.303078	-1.712134
H	-4.319560	1.933945	-1.772328
C	-4.273493	-1.757371	-0.055781
C	-3.028651	-2.577750	0.245358
C	-1.957522	-2.239012	-0.774495
H	-0.965597	-2.554447	-0.434263
H	-2.678074	-2.341709	1.254781
H	-3.263229	-3.643801	0.204695
H	-4.674799	-2.006794	-1.045437
H	-5.052241	-1.943983	0.684016
H	-2.161170	-2.722122	-1.735957
N	-1.911465	-0.794389	-0.976466
N	-3.955971	-0.319345	-0.020043

7c

M06-2X/6-31G(d) SCF energy in solution: -1286.45971970 a.u.

M06-2X/6-31G(d) enthalpy in solution: -1285.894541 a.u.

M06-2X/6-31G(d) free energy in solution: -1285.982364 a.u.

M06-2X/6-311+G(d,p) SCF energy in solution: -1286.82280038 a.u.

M06-2X/6-311+G(d,p) enthalpy in solution: -1286.257622 a.u.

M06-2X/6-311+G(d,p) free energy in solution: -1286.345445 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	5.487567	0.193399	-1.311851
C	4.127366	0.016646	-1.134502
C	3.601731	-0.165641	0.160107
C	4.484883	-0.144816	1.263541
C	5.865196	0.029268	1.052184
C	6.371297	0.194442	-0.220994
H	5.872677	0.335088	-2.317217
H	3.456627	0.013307	-1.984413
C	3.931328	-0.285797	2.580885
H	6.522547	0.035800	1.917889
H	7.436299	0.329487	-0.378365
C	2.601230	-0.424910	2.752731
C	1.681158	-0.458714	1.623638
H	4.606364	-0.270603	3.433291
H	2.148374	-0.529443	3.732133
O	0.460930	-0.578863	1.795879
N	2.231754	-0.354344	0.356095
C	1.338294	-0.396056	-0.784605
H	-0.787371	-0.893050	0.504752
C	1.398236	-1.598295	-1.543717
H	1.964305	-2.378343	-1.025387
C	0.930520	-1.957030	-2.775111
H	0.421289	-1.283970	-3.453951
H	1.137077	-2.954931	-3.149071
C	0.621616	0.808924	-1.059220

C	-0.430786	0.878320	-2.016045
C	0.883662	2.015347	-0.347124
C	-1.127251	2.056656	-2.254280
C	0.181967	3.185334	-0.598836
H	1.665240	2.025854	0.407526
C	-0.830101	3.232792	-1.562414
H	0.433323	4.080354	-0.033983
H	-1.372280	4.152019	-1.760683
H	-0.728913	-0.019979	-2.542851
H	-1.924118	2.053177	-2.995410
C	-5.231575	-0.179132	0.182682
C	-2.757874	-0.507351	0.367667
C	-5.324855	0.646925	1.462602
C	-2.479158	0.835728	1.008226
C	-4.699546	2.035902	1.330877
C	-3.379848	1.990184	0.563432
H	-5.405572	0.445230	-0.702587
H	-2.530663	0.704660	2.096969
H	-4.855321	0.081018	2.275299
H	-4.534008	2.452260	2.331055
H	-6.013273	-0.940483	0.196154
H	-6.383604	0.740268	1.723619
H	-1.434734	1.064382	0.775918
H	-5.394877	2.708186	0.815786
H	-2.829578	2.924723	0.704865
H	-3.563823	1.910164	-0.514276
C	-4.087287	-2.204162	-0.719114
C	-3.086951	-3.217016	-0.184528
C	-1.693188	-2.635719	-0.317353
H	-0.958343	-3.192309	0.270507

H	-3.314720	-3.432928	0.864330
H	-3.164270	-4.147272	-0.751553
H	-3.919680	-2.019881	-1.787184
H	-5.108292	-2.565181	-0.590964
H	-1.353357	-2.635544	-1.358627
N	-1.694103	-1.262707	0.177327
N	-3.972018	-0.930453	0.011740

TS-2a

M06-2X/6-31G(d) SCF energy in solution: -1286.45410932 a.u.

M06-2X/6-31G(d) enthalpy in solution: -1285.894536 a.u.

M06-2X/6-31G(d) free energy in solution: -1285.979113 a.u.

M06-2X/6-311+G(d,p) SCF energy in solution: -1286.81282878 a.u.

M06-2X/6-311+G(d,p) enthalpy in solution: -1286.253255 a.u.

M06-2X/6-311+G(d,p) free energy in solution: -1286.337832 a.u.

Imaginary frequency: -1222.4093 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	-4.984158	-0.203876	1.175383
C	-3.664675	0.187226	1.033597
C	-2.852536	-0.411241	0.051756
C	-3.410285	-1.405953	-0.781954
C	-4.753501	-1.786434	-0.612769
C	-5.541101	-1.197495	0.356282
H	-5.594360	0.271561	1.937402
H	-3.246210	0.955233	1.672118
C	-2.579956	-1.989037	-1.801077

H	-5.157816	-2.553723	-1.267835
H	-6.576802	-1.495095	0.481861
C	-1.301164	-1.593581	-1.956252
C	-0.693288	-0.581470	-1.093665
H	-3.012398	-2.747074	-2.449785
H	-0.658507	-2.000886	-2.729023
O	0.474725	-0.221191	-1.224991
N	-1.518250	-0.037324	-0.108588
C	-0.931439	0.958760	0.758703
H	0.625034	-1.301394	1.981460
C	-0.603351	0.581983	2.029228
H	-0.183672	1.367982	2.658280
C	-0.636016	-0.727586	2.591623
H	-1.362042	-1.425386	2.166949
H	-0.594921	-0.773781	3.679845
C	-0.710036	2.280129	0.169835
C	0.161028	3.223266	0.753423
C	-1.356918	2.658067	-1.022168
C	0.350899	4.478847	0.188079
C	-1.158863	3.913149	-1.588554
H	-2.029129	1.956439	-1.508354
C	-0.306870	4.838556	-0.988652
H	-1.678419	4.169105	-2.508058
H	-0.151209	5.816971	-1.432243
H	0.710841	2.965637	1.654353
H	1.031038	5.178865	0.666019
C	4.220118	-0.839508	-0.993149
C	2.421974	-1.123114	0.743240
C	3.849458	0.621385	-1.236263
C	2.538286	0.289469	1.276260

C	4.259618	1.542590	-0.086727
C	3.933959	0.913207	1.266888
H	5.215526	-0.920931	-0.535525
H	1.830917	0.897141	0.697431
H	2.769420	0.672792	-1.414163
H	3.728493	2.496899	-0.184753
H	4.272459	-1.348301	-1.958180
H	4.340388	0.943009	-2.160585
H	2.149403	0.249936	2.296801
H	5.332217	1.761935	-0.144329
H	3.986371	1.672888	2.053130
H	4.680882	0.152139	1.524197
C	3.114741	-3.033587	-0.538397
C	1.641351	-3.407652	-0.600786
C	1.033113	-3.128848	0.762401
H	-0.062915	-3.100109	0.709592
H	1.159527	-2.788331	-1.363231
H	1.521507	-4.460162	-0.870253
H	3.632984	-3.636991	0.218114
H	3.606703	-3.201499	-1.497257
H	1.304934	-3.919080	1.472724
N	1.470585	-1.841818	1.285460
N	3.243325	-1.610826	-0.203226

TS-2b

M06-2X/6-31G(d) SCF energy in solution: -1286.45053353 a.u.

M06-2X/6-31G(d) enthalpy in solution: -1285.891018 a.u.

M06-2X/6-31G(d) free energy in solution: -1285.978065 a.u.

M06-2X/6-311+G(d,p) SCF energy in solution: -1286.81178191 a.u.

M06-2X/6-311+G(d,p) enthalpy in solution: -1286.252266 a.u.

M06-2X/6-311+G(d,p) free energy in solution: -1286.339313 a.u.

Imaginary frequency: -986.3759 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	-0.123133	-1.417348	2.115265
C	0.605008	-0.696219	1.184962
C	1.551818	-1.346774	0.370371
C	1.745962	-2.737911	0.525336
C	0.984342	-3.447390	1.470466
C	0.055039	-2.801317	2.263849
H	-0.845378	-0.896033	2.737480
H	0.453521	0.370851	1.073433
C	2.736081	-3.383451	-0.297402
H	1.149767	-4.517385	1.567721
H	-0.525238	-3.354096	2.995612
C	3.463935	-2.675450	-1.181585
C	3.281112	-1.233370	-1.364487
H	2.885512	-4.454433	-0.181799
H	4.219817	-3.133525	-1.809831
O	3.936623	-0.581075	-2.165772
N	2.300909	-0.638692	-0.564582
C	2.020969	0.762022	-0.778315
H	-1.059359	-0.198549	-1.441282
C	1.014958	1.051889	-1.659549
H	0.785097	2.109930	-1.791813
C	0.173542	0.136697	-2.350235
H	0.569174	-0.871970	-2.498853

H	-0.312689	0.535168	-3.242373
C	2.808010	1.712880	0.001069
C	2.679626	3.110664	-0.152784
C	3.734651	1.262644	0.962952
C	3.424976	3.995179	0.615108
C	4.480702	2.153847	1.728567
H	3.871317	0.195614	1.111462
C	4.333812	3.529296	1.567187
H	5.184255	1.763912	2.459414
H	4.916385	4.224179	2.163815
H	1.994178	3.514207	-0.891609
H	3.297863	5.063927	0.463844
C	-5.251999	0.542415	0.504714
C	-2.955368	0.181259	-0.463651
C	-4.912225	1.897661	1.117889
C	-2.663074	1.658109	-0.642475
C	-4.695104	2.999029	0.079479
C	-3.852281	2.508915	-1.097509
H	-5.951319	0.662053	-0.334431
H	-2.248790	2.047994	0.295640
H	-4.030315	1.780097	1.757834
H	-4.201023	3.851504	0.559350
H	-5.761243	-0.061683	1.258957
H	-5.737484	2.176691	1.780601
H	-1.856422	1.710965	-1.377459
H	-5.663224	3.356764	-0.288772
H	-3.476592	3.363635	-1.667474
H	-4.470392	1.925650	-1.790558
C	-4.353301	-1.722232	0.049632
C	-3.063181	-2.489758	0.292314

C	-2.041057	-2.070074	-0.747734
H	-1.032725	-2.403522	-0.476843
H	-2.691287	-2.260121	1.296193
H	-3.251467	-3.564886	0.236088
H	-4.794209	-1.999255	-0.916756
H	-5.084701	-1.944847	0.828677
H	-2.282973	-2.502711	-1.726084
N	-2.004384	-0.620061	-0.866841
N	-4.103090	-0.273934	0.073622

TS-2c

M06-2X/6-31G(d) SCF energy in solution: -1286.44676720 a.u.

M06-2X/6-31G(d) enthalpy in solution: -1285.886912 a.u.

M06-2X/6-31G(d) free energy in solution: -1285.974916 a.u.

M06-2X/6-311+G(d,p) SCF energy in solution: -1286.80638090 a.u.

M06-2X/6-311+G(d,p) enthalpy in solution: -1286.246526 a.u.

M06-2X/6-311+G(d,p) free energy in solution: -1286.334530 a.u.

Imaginary frequency: -955.7817 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	-5.179571	-1.248375	2.116882
C	-3.973039	-0.903495	1.533093
C	-3.899095	-0.677591	0.145222
C	-5.074937	-0.795514	-0.629559
C	-6.285163	-1.153392	-0.010472
C	-6.346612	-1.382018	1.350451
H	-5.215963	-1.416852	3.188999

H	-3.078447	-0.805785	2.135739
C	-4.991664	-0.532213	-2.041852
H	-7.174055	-1.242268	-0.629730
H	-7.284281	-1.656565	1.822133
C	-3.823321	-0.173765	-2.607843
C	-2.592668	-0.043460	-1.828190
H	-5.895934	-0.625304	-2.638730
H	-3.730756	0.034154	-3.667954
O	-1.525589	0.289299	-2.334534
N	-2.696114	-0.327086	-0.465122
C	-1.487451	-0.204494	0.324890
H	1.546901	-1.269122	0.235347
C	-0.791003	-1.364849	0.553551
H	-1.238293	-2.228602	0.054626
C	0.415145	-1.641807	1.260141
H	0.688022	-0.973429	2.079250
H	0.544813	-2.693968	1.518103
C	-1.152260	1.153330	0.743440
C	0.153746	1.520743	1.130703
C	-2.127958	2.173320	0.743815
C	0.454306	2.823929	1.518602
C	-1.822970	3.471093	1.134652
H	-3.142986	1.940808	0.434629
C	-0.529370	3.810189	1.533270
H	-2.604815	4.225797	1.127836
H	-0.292714	4.824498	1.839317
H	0.950531	0.787453	1.093908
H	1.473974	3.069487	1.804423
C	5.905049	0.109945	-0.708917
C	3.577376	-0.666436	-0.184931

C	6.393903	0.133326	0.737492
C	3.982573	-1.391021	1.084286
C	6.507068	-1.257878	1.364131
C	5.315013	-2.145626	1.006058
H	6.355863	-0.729220	-1.256150
H	4.004081	-0.666327	1.907903
H	5.723702	0.774518	1.320796
H	6.577552	-1.155218	2.452979
H	6.235991	1.024740	-1.204626
H	7.374047	0.620445	0.750581
H	3.170014	-2.086759	1.301938
H	7.432039	-1.740411	1.028752
H	5.273876	-3.002321	1.684976
H	5.438315	-2.559049	-0.001888
C	3.975222	0.775058	-2.104678
C	2.497134	1.113560	-2.010344
C	1.724207	-0.150715	-1.684242
H	0.673656	0.054985	-1.456170
H	2.335881	1.856672	-1.221207
H	2.158761	1.543664	-2.956183
H	4.173601	0.142210	-2.979415
H	4.569745	1.685752	-2.208774
H	1.744678	-0.842599	-2.535665
N	2.321692	-0.804294	-0.525359
N	4.442271	0.086118	-0.890575

TS-3

M06-2X/6-31G(d) SCF energy in solution: -824.55770436 a.u.

M06-2X/6-31G(d) enthalpy in solution: -824.255985 a.u.

M06-2X/6-31G(d) free energy in solution: -824.313644 a.u.

M06-2X/6-311+G(d,p) SCF energy in solution: -1286.77461316 a.u.

M06-2X/6-311+G(d,p) enthalpy in solution: -1286.472894 a.u.

M06-2X/6-311+G(d,p) free energy in solution: -1286.530553 a.u.

Imaginary frequency: -47.6130 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	-0.037052	-2.901175	-1.000597
C	0.046394	-1.516746	-0.979358
C	-0.906826	-0.757572	-0.283206
C	-2.005546	-1.427609	0.298052
C	-2.060991	-2.829600	0.278302
C	-1.075899	-3.571707	-0.347941
H	0.713496	-3.462130	-1.548705
H	0.844818	-1.026574	-1.519512
C	-3.111863	-0.646674	0.805265
H	-2.912763	-3.317648	0.744207
H	-1.127802	-4.655244	-0.363803
C	-3.181028	0.665298	0.526590
C	-2.107061	1.332109	-0.218226
H	-3.912266	-1.157280	1.334125
H	-4.034695	1.283022	0.782301
O	-2.259826	2.394585	-0.787607
N	-0.857771	0.659026	-0.201292
C	0.368005	1.398137	-0.103845
C	0.545057	2.728651	0.049728
H	1.598802	2.968278	0.163017
C	-0.344897	3.929275	0.210689
H	-0.851411	4.201319	-0.718269
H	0.270973	4.772757	0.533798

C	1.623436	0.593792	0.075020
C	2.691500	0.741427	-0.813076
C	1.770916	-0.250731	1.180877
C	3.880284	0.041716	-0.612410
C	2.956914	-0.949656	1.380564
H	0.949054	-0.363159	1.883504
C	4.013897	-0.810323	0.480946
H	3.057972	-1.601621	2.242973
H	4.937702	-1.359234	0.635900
H	2.581706	1.399445	-1.670608
H	4.699552	0.160781	-1.315072
H	-1.123582	3.775757	0.961794

TS-4

M06-2X/6-31G(d) SCF energy in solution: -824.55770436 a.u.

M06-2X/6-31G(d) enthalpy in solution: -824.255985 a.u.

M06-2X/6-31G(d) free energy in solution: -824.313644 a.u.

M06-2X/6-311+G(d,p) SCF energy in solution: -824.78422971 a.u.

M06-2X/6-311+G(d,p) enthalpy in solution: -824.482510 a.u.

M06-2X/6-311+G(d,p) free energy in solution: -824.540169 a.u.

Imaginary frequency: -47.6130 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	-0.037052	-2.901175	-1.000597
C	0.046394	-1.516746	-0.979358
C	-0.906826	-0.757572	-0.283206
C	-2.005546	-1.427609	0.298052
C	-2.060991	-2.829600	0.278302

C	-1.075899	-3.571707	-0.347941
H	0.713496	-3.462130	-1.548705
H	0.844818	-1.026574	-1.519512
C	-3.111863	-0.646674	0.805265
H	-2.912763	-3.317648	0.744207
H	-1.127802	-4.655244	-0.363803
C	-3.181028	0.665298	0.526590
C	-2.107061	1.332109	-0.218226
H	-3.912266	-1.157280	1.334125
H	-4.034695	1.283022	0.782301
O	-2.259826	2.394585	-0.787607
N	-0.857771	0.659026	-0.201292
C	0.368005	1.398137	-0.103845
C	0.545057	2.728651	0.049728
H	1.598802	2.968278	0.163017
C	-0.344897	3.929275	0.210689
H	-0.851411	4.201319	-0.718269
H	0.270973	4.772757	0.533798
C	1.623436	0.593792	0.075020
C	2.691500	0.741427	-0.813076
C	1.770916	-0.250731	1.180877
C	3.880284	0.041716	-0.612410
C	2.956914	-0.949656	1.380564
H	0.949054	-0.363159	1.883504
C	4.013897	-0.810323	0.480946
H	3.057972	-1.601621	2.242973
H	4.937702	-1.359234	0.635900
H	2.581706	1.399445	-1.670608
H	4.699552	0.160781	-1.315072
H	-1.123582	3.775757	0.961794

TS-5

M06-2X/6-31G(d) SCF energy in solution: -1286.43884080 a.u.

M06-2X/6-31G(d) enthalpy in solution: -1285.875372 a.u.

M06-2X/6-31G(d) free energy in solution: -1285.961578 a.u.

M06-2X/6-311+G(d,p) SCF energy in solution: -1286.80172522 a.u.

M06-2X/6-311+G(d,p) enthalpy in solution: -1286.238256 a.u.

M06-2X/6-311+G(d,p) free energy in solution: -1286.324462 a.u.

Imaginary frequency: -153.6640 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	4.805820	0.193524	1.816389
C	3.633930	0.529736	1.164640
C	3.265780	-0.140213	-0.018616
C	4.113926	-1.152640	-0.521207
C	5.300298	-1.475838	0.164660
C	5.649813	-0.815706	1.324540
H	5.072743	0.722582	2.726434
H	2.984969	1.306728	1.548679
C	3.741023	-1.813765	-1.739133
H	5.935931	-2.256753	-0.244725
H	6.564577	-1.069555	1.850007
C	2.599134	-1.479174	-2.374272
C	1.699695	-0.464593	-1.845264
H	4.397445	-2.584497	-2.135643
H	2.281557	-1.958080	-3.293632
O	0.634109	-0.189752	-2.424038
N	2.076110	0.179011	-0.678832
C	1.223801	1.239922	-0.189546

C	1.162940	2.440057	-1.058705
H	0.420085	2.476503	-1.867287
C	1.989293	3.484126	-0.958728
H	2.761890	3.522910	-0.193069
H	1.926903	4.332467	-1.638599
C	0.407047	1.013751	0.919438
C	-0.492478	2.019967	1.421523
C	0.403542	-0.216159	1.665024
C	-1.313227	1.796846	2.513123
C	-0.418022	-0.405901	2.765292
H	1.061640	-1.024028	1.353464
C	-1.307348	0.579345	3.211150
H	-0.368471	-1.360244	3.288108
H	-1.941568	0.420225	4.076811
H	-0.502172	2.993793	0.937650
H	-1.968734	2.602036	2.842784
H	-0.865231	0.441283	-1.656455
C	-4.517702	-1.028375	0.540516
C	-2.479096	-0.278353	-0.697468
C	-4.514328	-2.415864	-0.096601
C	-1.787096	-1.624361	-0.671295
C	-3.370850	-3.304346	0.396079
C	-2.073957	-2.512875	0.538755
H	-4.248611	-1.074927	1.603033
H	-2.034632	-2.145876	-1.605401
H	-4.474899	-2.295253	-1.185544
H	-3.231040	-4.135730	-0.304339
H	-5.526545	-0.616256	0.481622
H	-5.475455	-2.889627	0.125839
H	-0.719152	-1.397093	-0.720686

H	-3.633434	-3.742744	1.365356
H	-1.228080	-3.195108	0.670075
H	-2.104462	-1.889625	1.437831
C	-4.130933	1.361117	-0.079967
C	-3.807329	2.073261	-1.383517
C	-2.306623	2.021764	-1.595246
H	-2.030948	2.292893	-2.617855
H	-4.331083	1.579991	-2.208722
H	-4.143128	3.111416	-1.335090
H	-3.646226	1.861483	0.766957
H	-5.206236	1.341325	0.097871
H	-1.796081	2.704857	-0.908883
N	-1.825400	0.667031	-1.349331
N	-3.660245	-0.032985	-0.133793

7d

M06-2X/6-31G(d) SCF energy in solution: -824.05963841 a.u.

M06-2X/6-31G(d) enthalpy in solution: -823.772718 a.u.

M06-2X/6-31G(d) free energy in solution: -823.831969 a.u.

M06-2X/6-311+G(d,p) SCF energy in solution: -824.30184827 a.u.

M06-2X/6-311+G(d,p) enthalpy in solution: -824.014928 a.u.

M06-2X/6-311+G(d,p) free energy in solution: -824.074179 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	2.243485	-2.506371	0.584194
C	1.250146	-1.548930	0.683464

C	1.407307	-0.295019	0.059966
C	2.598390	-0.040229	-0.658064
C	3.592087	-1.031387	-0.742322
C	3.426105	-2.258084	-0.129762
H	2.099761	-3.466428	1.071372
H	0.338746	-1.745942	1.234058
C	2.750042	1.243686	-1.289675
H	4.495981	-0.808124	-1.303910
H	4.196774	-3.018913	-0.198869
C	1.779694	2.171511	-1.192290
C	0.538119	1.931735	-0.449903
H	3.663661	1.444289	-1.844974
H	1.862754	3.148621	-1.655833
O	-0.339349	2.782276	-0.368692
N	0.410723	0.673710	0.146575
C	-0.783522	0.400377	0.911956
C	-0.677111	0.597113	2.311484
H	-1.574791	0.361702	2.884669
C	0.405676	1.007730	3.026994
H	1.346502	1.272174	2.550783
H	0.355132	1.102213	4.106585
C	-1.925762	-0.060367	0.199864
C	-3.182489	-0.333092	0.821694
C	-1.885112	-0.297195	-1.206432
C	-4.271775	-0.800845	0.104434
C	-2.985637	-0.764683	-1.909844
H	-0.960126	-0.105694	-1.743608
C	-4.201308	-1.029740	-1.274030
H	-2.890353	-0.925950	-2.981974
H	-5.059891	-1.394692	-1.828465

H	-3.301412	-0.165329	1.888000
H	-5.203021	-0.989356	0.635304

7e

M06-2X/6-31G(d) SCF energy in solution: -824.05962049 a.u.

M06-2X/6-31G(d) enthalpy in solution: -823.772723 a.u.

M06-2X/6-31G(d) free energy in solution: -823.832390 a.u.

M06-2X/6-311+G(d,p) SCF energy in solution: -824.30182688 a.u.

M06-2X/6-311+G(d,p) enthalpy in solution: -824.014929 a.u.

M06-2X/6-311+G(d,p) free energy in solution: -824.074596 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-2.241643	-2.506340	0.600288
C	-1.251503	-1.545420	0.698173
C	-1.407502	-0.296089	0.065019
C	-2.596899	-0.048169	-0.658349
C	-3.587594	-1.042604	-0.740609
C	-3.421123	-2.265768	-0.120864
H	-2.097827	-3.462843	1.094519
H	-0.342524	-1.736748	1.254984
C	-2.749154	1.231730	-1.297743
H	-4.489683	-0.825153	-1.307297
H	-4.189197	-3.029359	-0.189004
C	-1.780902	2.162329	-1.202773
C	-0.539233	1.928364	-0.457998
H	-3.661741	1.427004	-1.856783
H	-1.865109	3.136003	-1.673016

O	0.339565	2.778079	-0.383852
N	-0.412185	0.674155	0.147273
C	0.783103	0.405047	0.912896
C	0.683376	0.624963	2.309483
H	1.585664	0.403354	2.880908
C	-0.395365	1.045899	3.025457
H	-1.340590	1.298747	2.551387
H	-0.337341	1.160156	4.102735
C	1.923619	-0.059984	0.200751
C	3.174355	-0.354346	0.824580
C	1.886448	-0.279405	-1.208903
C	4.261446	-0.825908	0.106534
C	2.984405	-0.752665	-1.912300
H	0.966290	-0.072544	-1.748120
C	4.194377	-1.038241	-1.274810
H	2.892163	-0.900658	-2.986612
H	5.051105	-1.406521	-1.829978
H	3.288270	-0.204087	1.894002
H	5.188030	-1.031413	0.639185

DBU

M06-2X/6-31G(d) SCF energy in solution: -461.88371148 a.u.

M06-2X/6-31G(d) enthalpy in solution: -461.623627 a.u.

M06-2X/6-31G(d) free energy in solution: -461.669292 a.u.

M06-2X/6-311+G(d,p) SCF energy in solution: -462.01570567 a.u.

M06-2X/6-311+G(d,p) enthalpy in solution: -461.755621 a.u.

M06-2X/6-311+G(d,p) free energy in solution: -461.801286 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	0.850435	1.456868	-0.270795
C	-0.368885	-0.720510	0.136976
C	2.111182	1.136810	0.531159
C	0.925226	-1.472730	0.402188
C	2.947173	0.002200	-0.066553
C	2.078112	-1.156200	-0.559735
H	1.066995	1.407473	-1.350596
H	1.246919	-1.295789	1.436736
H	1.814358	0.905299	1.560124
H	3.650818	-0.360885	0.691938
H	0.566210	2.492173	-0.061190
H	2.720251	2.045470	0.582989
H	0.647933	-2.525611	0.333558
H	3.549781	0.386691	-0.897887
H	2.697355	-2.049626	-0.688745
H	1.667800	-0.924676	-1.550369
C	-1.582287	1.346715	-0.297695
C	-2.775371	0.615134	0.290051
C	-2.720767	-0.833990	-0.169992
H	-3.479800	-1.431256	0.348051
H	-2.723173	0.659022	1.384031
H	-3.704990	1.099759	-0.023251
H	-1.683339	1.418863	-1.392301
H	-1.524574	2.368212	0.092264
H	-2.961223	-0.892864	-1.241402
N	-1.423760	-1.455262	0.059009
N	-0.339131	0.662686	0.055623

DBU-H

M06-2X/6-31G(d) SCF energy in solution: -462.36299326 a.u.

M06-2X/6-31G(d) enthalpy in solution: -462.087978 a.u.

M06-2X/6-31G(d) free energy in solution: -462.133940 a.u.

M06-2X/6-311+G(d,p) SCF energy in solution: -462.49141710 a.u.

M06-2X/6-311+G(d,p) enthalpy in solution: -462.216402 a.u.

M06-2X/6-311+G(d,p) free energy in solution: -462.262364 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	0.910069	1.498301	-0.231305
C	-0.307007	-0.664827	0.060458
C	2.083288	1.093100	0.654450
C	0.936199	-1.500439	0.262316
C	2.965503	0.006353	0.039283
C	2.133178	-1.100573	-0.606163
H	1.209797	1.554769	-1.285006
H	1.200847	-1.465165	1.325893
H	1.694745	0.782523	1.631049
H	3.605784	-0.419060	0.819817
H	0.572708	2.492894	0.063102
H	2.679760	1.992344	0.835056
H	0.648760	-2.532125	0.048867
H	3.627382	0.447357	-0.713648
H	2.750941	-1.987232	-0.771654
H	1.774983	-0.785328	-1.593007
C	-1.566880	1.339518	-0.427209
C	-2.720109	0.702811	0.329007
C	-2.792354	-0.769041	-0.025674

H	-3.442840	-1.317907	0.657607
H	-2.563792	0.825007	1.405250
H	-3.653328	1.200725	0.058522
H	-1.738806	1.307683	-1.509253
H	-1.444665	2.381752	-0.131180
H	-3.160018	-0.911908	-1.046637
N	-1.450205	-1.339503	0.082467
N	-0.297397	0.645803	-0.131304
H	-1.380373	-2.341650	0.216094

TS-1d

M06-2X/6-31G(d) SCF energy in solution: -824.56465774 a.u.

M06-2X/6-31G(d) enthalpy in solution: -824.262859 a.u.

M06-2X/6-31G(d) free energy in solution: -824.321042 a.u.

M06-2X/6-311+G(d,p) SCF energy in solution: -824.79339958 a.u.

M06-2X/6-311+G(d,p) enthalpy in solution: -824.491601 a.u.

M06-2X/6-311+G(d,p) free energy in solution: -824.549784 a.u.

Imaginary frequency: -32.4851 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	0.703388	-2.983475	-0.350154
C	0.285826	-1.673069	-0.522584
C	1.135805	-0.597063	-0.195927
C	2.463149	-0.907542	0.192984
C	2.857356	-2.244056	0.370290
C	1.982905	-3.285004	0.127340
H	0.019568	-3.784593	-0.613655
H	-0.690371	-1.497514	-0.946591
C	3.428825	0.155660	0.306625
H	3.880494	-2.438220	0.681060
H	2.294324	-4.315129	0.264072

C	3.105699	1.407575	-0.058843
C	1.746208	1.753450	-0.467878
H	4.434676	-0.093176	0.635396
H	3.816370	2.226258	-0.055938
O	1.442998	2.871689	-0.862025
N	0.770034	0.753935	-0.310828
C	-0.612559	1.329810	-0.240535
H	-0.756220	1.900711	-1.160829
C	-0.682152	2.283386	0.936817
H	-0.412373	1.855141	1.901568
C	-1.095247	3.541380	0.844167
H	-1.350626	3.983549	-0.115846
H	-1.188270	4.173765	1.722239
C	-1.760371	0.349945	-0.098962
C	-1.968997	-0.366659	1.085184
C	-2.665310	0.201278	-1.150227
C	-3.043891	-1.241261	1.197947
C	-3.745988	-0.672992	-1.037414
H	-2.514495	0.763940	-2.067859
C	-3.933903	-1.400258	0.134747
H	-4.439092	-0.783613	-1.865843
H	-4.772254	-2.084361	0.223786
H	-1.272195	-0.262659	1.912426
H	-3.188205	-1.801780	2.116560

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X-ray structures of 3f

3f

Table 1 Crystal data and structure refinement for 1941459.

Identification code	1941459
Empirical formula	$C_{18}H_{14}ClNO$
Formula weight	295.75
Temperature/K	173(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	7.1789(9)
b/Å	8.6698(11)
c/Å	24.751(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1540.5(3)
Z	4
ρ_{calc}g/cm^3	1.275
μ/mm^{-1}	1.429
F(000)	616.0
Crystal size/mm^3	0.170 × 0.160 × 0.110
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	6.214 to 105.996
Index ranges	$-8 \le h \le 8$, $-10 \le k \le 10$, $-29 \le l \le 29$
Reflections collected	20404
Independent reflections	2719 [R_{int} = 0.0838, R_{sigma} = 0.0474]
Data/restraints/parameters	2719/0/192
Goodness-of-fit on F^2	1.169
Final R indexes [I>=2σ (I)]	R_1 = 0.0874, wR_2 = 0.1737
Final R indexes [all data]	R_1 = 0.1141, wR_2 = 0.1863
Largest diff. peak/hole / e Å^{-3}	0.20/-0.19
Flack parameter	0.18(2)

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 1941459. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ}tensor.

Atom	*x*	*y*	*z*	U(eq)
C1	4634(15)	5253(13)	2522(3)	101(3)
C2	3405(19)	5126(16)	2090(3)	121(4)
C3	1886(18)	4221(16)	2129(4)	115(4)
C4	1575(16)	3449(13)	2596(4)	107(3)
C5	2749(13)	3561(11)	3028(3)	85(3)
C6	4337(13)	4432(12)	2993(3)	82(2)
C7	5617(12)	4596(10)	3454(3)	74(2)
C8	7485(13)	4687(12)	3409(3)	96(3)
C9	8823(13)	4870(15)	3865(3)	124(4)
C10	4719(13)	3130(13)	4257(3)	86(3)
C11	3768(13)	3159(14)	4769(3)	99(3)
C12	2983(13)	4485(16)	4972(3)	103(3)
C13	3056(12)	5870(13)	4685(3)	82(3)
C14	2318(13)	7238(15)	4889(4)	99(3)
C15	2466(14)	8592(15)	4618(4)	109(3)
C16	3408(12)	8624(12)	4117(4)	92(3)
C17	4123(11)	7307(11)	3900(3)	77(2)
C18	4006(10)	5934(11)	4185(3)	75(2)
Cl1	369(5)	4109(6)	1592.5(12)	186(2)
N1	4744(9)	4545(9)	3980(2)	75.6(18)
O1	5418(11)	1994(8)	4057(2)	108(2)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 1941459. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	108(7)	145(9)	50(4)	11(5)	5(4)	2(7)
C2	144(10)	170(12)	47(4)	9(6)	-18(6)	32(9)
C3	113(8)	156(11)	76(6)	-29(7)	-30(6)	20(8)
C4	119(8)	123(9)	80(6)	-15(6)	-31(6)	12(7)
C5	95(6)	94(6)	65(5)	-3(4)	-10(4)	-1(6)
C6	88(6)	115(7)	44(4)	3(4)	-3(4)	18(6)
C7	87(5)	92(6)	44(3)	0(4)	0(3)	6(5)
C8	83(6)	145(9)	60(4)	1(5)	-6(4)	12(6)
C9	76(6)	211(13)	84(6)	-18(7)	-11(5)	-3(7)

C10	95(6)	117(8)	45(4)	1(4)	-13(4)	-6(6)
C11	104(7)	139(9)	53(5)	18(5)	-1(5)	-3(7)
C12	83(6)	181(11)	45(4)	4(6)	2(4)	-16(7)
C13	75(5)	124(8)	47(4)	-8(5)	-1(4)	-10(5)
C14	79(6)	141(10)	76(6)	-15(6)	-3(5)	0(7)
C15	86(7)	139(10)	101(7)	-35(7)	0(6)	7(7)
C16	79(6)	100(7)	98(6)	-6(6)	-7(5)	1(5)
C17	77(5)	99(7)	56(4)	-11(4)	0(4)	-9(5)
C18	62(4)	118(7)	46(4)	0(4)	-9(3)	-7(5)
Cl1	177(3)	268(5)	112(2)	-44(3)	-90(2)	56(3)
N1	84(4)	98(5)	44(3)	2(3)	-2(3)	0(4)
O1	146(6)	110(5)	67(4)	5(4)	-19(4)	18(5)

Table 4 Bond Lengths for 1941459.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.390(13)	C10	C11	1.439(11)
C1	C6	1.383(11)	C10	N1	1.405(11)
C2	C3	1.347(15)	C11	C12	1.375(14)
C3	C4	1.356(14)	C12	C13	1.395(14)
C3	Cl1	1.720(9)	C13	C14	1.394(13)
C4	C5	1.364(11)	C13	C18	1.415(10)
C5	C6	1.370(12)	C14	C15	1.356(14)
C6	C7	1.471(10)	C15	C16	1.411(13)
C7	C8	1.348(11)	C16	C17	1.363(11)
C7	N1	1.447(9)	C17	C18	1.387(11)
C8	C9	1.490(11)	C18	N1	1.410(10)
C10	O1	1.212(10)			

Table 5 Bond Angles for 1941459.

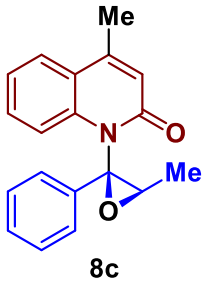
Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	C1	C6	120.7(10)	C11	C10	N1	114.8(9)
C3	C2	C1	120.3(10)	C12	C11	C10	122.0(10)
C2	C3	C4	118.8(9)	C11	C12	C13	121.2(8)
C2	C3	Cl1	119.4(10)	C14	C13	C18	117.8(10)
C4	C3	Cl1	121.8(11)	C14	C13	C12	122.3(8)
C5	C4	C3	122.1(11)	C18	C13	C12	119.8(9)
C4	C5	C6	120.3(9)	C15	C14	C13	121.9(9)

C1	C6	C5	117.7(8)	C14	C15	C16	119.3(11)
C1	C6	C7	120.5(9)	C17	C16	C15	120.7(10)
C5	C6	C7	121.7(7)	C16	C17	C18	119.7(8)
C8	C7	N1	120.4(7)	C17	C18	C13	120.6(9)
C8	C7	C6	124.3(7)	C17	C18	N1	121.8(6)
N1	C7	C6	115.1(7)	C13	C18	N1	117.5(8)
C7	C8	C9	125.9(8)	C7	N1	C10	118.1(7)
O1	C10	C11	124.8(10)	C7	N1	C18	117.4(7)
O1	C10	N1	120.4(8)	C10	N1	C18	124.4(6)

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 1941459.

Atom	*x*	*y*	*z*	U(eq)
H1	5687.64	5910.25	2493.18	121
H2	3638.9	5679.6	1766.06	145
H4	504.61	2808.99	2624.52	129
H5	2464.38	3032.7	3353.66	102
H8	7993.68	4629.39	3055.69	115
H9A	8139.82	5130.24	4195.27	185
H9B	9705.44	5698.04	3780.19	185
H9C	9504.04	3902.64	3918.53	185
H11	3680.37	2233.64	4972.9	118
H12	2380.13	4457.4	5313.33	124
H14	1692.82	7222.39	5227.16	118
H15	1941.72	9508.13	4762.83	130
H16	3545.08	9574.45	3930.14	111
H17	4698.48	7329.78	3554.06	93

X-ray structures of 8c



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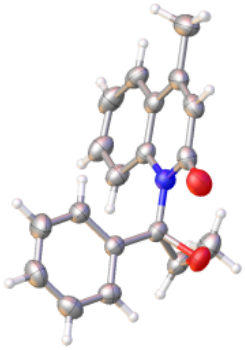


Table 1 Crystal data and structure refinement for 1960857

Identification code	1960857
Empirical formula	$C_{19}H_{17}NO_2$
Formula weight	291.33
Temperature/K	193(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	8.9647(3)
b/Å	9.7465(4)
c/Å	9.2350(3)
α/°	90
β/°	110.2250(10)
γ/°	90
Volume/Å^3	757.15(5)
Z	2
ρ_{calc}g/cm^3	1.278
μ/mm^{-1}	0.420
F(000)	308.0
Crystal size/mm^3	0.120 × 0.110 × 0.090
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	18.17 to 107.918
Index ranges	-10 ≤ h ≤ 10, -11 ≤ k ≤ 11, -11 ≤ l ≤ 11
Reflections collected	12804
Independent reflections	2691 [R_{int} = 0.0306, R_{sigma} = 0.0228]
Data/restraints/parameters	2691/1/201
Goodness-of-fit on F^2	1.068
Final R indexes [I>=2σ (I)]	R_1 = 0.0261, wR_2 = 0.0734
Final R indexes [all data]	R_1 = 0.0263, wR_2 = 0.0737
Largest diff. peak/hole / e Å^{-3}	0.12/-0.11
Flack parameter	0.10(7)

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 20191017ZH_LMF_2KL_0m_a. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C1	5446.9(19)	3251.9(17)	842.6(18)	40.8(4)
C2	6874(2)	3591(2)	658(2)	50.0(4)
C3	7686(2)	4746(2)	1342(2)	54.8(5)
C4	7096(2)	5566(2)	2229(2)	54.0(4)
C5	5684.7(19)	5223.4(17)	2442.1(19)	42.0(4)
C6	4840.4(18)	4065.7(16)	1738.1(16)	33.6(3)
C7	3286.1(18)	3698.1(16)	1909.6(17)	34.5(3)
C8	2835(2)	2258.3(18)	2068.4(19)	42.6(4)
C9	1636(2)	1822(2)	2774(2)	55.0(5)
C10	2893.9(18)	4894.7(16)	4116.3(17)	35.2(3)
C11	3919(2)	3973.9(17)	5148.0(18)	42.4(4)
C12	4134(2)	4060(2)	6705(2)	50.3(4)
C13	3365(3)	5043(2)	7260(2)	54.0(5)
C14	2426(2)	5991(2)	6263(2)	47.7(4)
C15	2183.7(18)	5961.9(17)	4672.6(18)	38.4(3)
C16	1267.4(18)	6997.5(17)	3607(2)	42.4(4)
C17	1099.9(19)	6903.4(19)	2108(2)	44.0(4)
C18	1773.1(17)	5804.2(18)	1477.9(18)	38.8(3)
C19	545(3)	8174(2)	4182(3)	61.1(5)
N1	2577.6(15)	4787.5(13)	2522.6(14)	34.4(3)
O1	2204.9(14)	2988.5(13)	628.7(12)	44.6(3)
O2	1672.5(15)	5726.6(14)	120.5(13)	51.2(3)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 20191017ZH_LMF_2KL_0m_a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	47.4(8)	39.0(8)	35.8(7)	0.4(6)	14.1(6)	3.0(7)
C2	50.8(9)	56.3(11)	48.7(9)	4.0(8)	24.7(8)	10.4(8)
C3	38.7(9)	64.5(12)	64.4(12)	8.2(9)	22.0(8)	1.1(8)
C4	42.8(9)	51.3(10)	66.3(12)	-4.6(8)	16.9(8)	-9.5(7)
C5	40.4(8)	39.4(8)	45.6(8)	-5.8(7)	13.9(7)	-2.7(7)
C6	36.4(7)	33.1(7)	29.0(7)	3.1(5)	8.3(6)	1.2(6)
C7	36.8(7)	35.9(8)	28.1(7)	-1.6(6)	7.7(5)	-2.9(6)
C8	48.3(9)	37.8(9)	38.7(8)	-3.3(6)	11.3(7)	-8.8(7)

C9	60.1(10)	53.6(11)	50.6(10)	-1.9(8)	18.1(8)	-21.8(9)
C10	37.3(7)	36.2(8)	32.4(7)	-2.1(6)	12.5(6)	-7.6(6)
C11	51.8(9)	37.5(9)	34.9(8)	-0.6(6)	11.3(7)	-3.4(7)
C12	65.5(11)	45.6(9)	34.1(8)	0.9(7)	10.0(7)	-8.8(8)
C13	70.5(11)	58.6(11)	32.3(8)	-8.6(8)	17.0(8)	-19.4(9)
C14	52.9(9)	50.3(9)	44.7(9)	-15.1(8)	22.8(7)	-13.4(8)
C15	37.4(7)	38.9(8)	40.5(8)	-5.4(6)	15.4(6)	-9.4(6)
C16	34.4(7)	39.7(8)	55.1(9)	-4.8(7)	18.0(7)	-4.2(6)
C17	35.0(7)	42.7(9)	53.7(9)	9.0(7)	14.5(7)	4.1(7)
C18	33.7(7)	44.4(9)	37.1(8)	7.2(6)	10.4(6)	0.4(6)
C19	54.5(10)	50.6(11)	82.4(14)	-12.4(10)	29.1(10)	3.3(9)
N1	36.5(6)	36.0(7)	30.2(6)	2.3(5)	11.0(5)	1.2(5)
O1	46.1(6)	49.7(7)	33.8(5)	-7.0(5)	8.2(5)	-11.6(5)
O2	53.5(7)	62.3(8)	36.9(6)	12.5(5)	14.4(5)	9.5(6)

Table 4 Bond Lengths for 20191017ZH_LMF_2KL_0m_a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C6	1.385(2)	C10	N1	1.4031(18)
C1	C2	1.388(3)	C10	C15	1.406(2)
C2	C3	1.371(3)	C11	C12	1.386(2)
C3	C4	1.374(3)	C12	C13	1.378(3)
C4	C5	1.387(3)	C13	C14	1.369(3)
C5	C6	1.389(2)	C14	C15	1.408(2)
C6	C7	1.499(2)	C15	C16	1.450(2)
C7	O1	1.4228(18)	C16	C17	1.343(3)
C7	N1	1.449(2)	C16	C19	1.501(2)
C7	C8	1.482(2)	C17	C18	1.447(2)
C8	O1	1.440(2)	C18	O2	1.228(2)
C8	C9	1.498(3)	C18	N1	1.397(2)
C10	C11	1.397(2)			

Table 5 Bond Angles for 20191017ZH_LMF_2KL_0m_a.

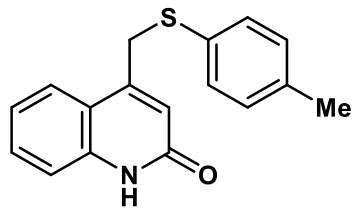
Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C6	C1	C2	120.37(16)	N1	C10	C15	119.04(14)
C3	C2	C1	120.31(17)	C12	C11	C10	119.46(16)
C4	C3	C2	119.95(16)	C13	C12	C11	121.30(18)
C3	C4	C5	120.21(18)	C14	C13	C12	119.28(16)

C4	C5	C6	120.34(16)	C13	C14	C15	121.70(17)
C1	C6	C5	118.81(14)	C14	C15	C10	117.99(16)
C1	C6	C7	119.81(14)	C14	C15	C16	122.73(16)
C5	C6	C7	121.38(14)	C10	C15	C16	119.26(14)
O1	C7	N1	114.60(13)	C17	C16	C15	119.15(15)
O1	C7	C8	59.41(10)	C17	C16	C19	120.56(17)
N1	C7	C8	118.94(13)	C15	C16	C19	120.27(16)
O1	C7	C6	114.79(13)	C16	C17	C18	123.48(16)
N1	C7	C6	114.52(13)	O2	C18	N1	119.98(15)
C8	C7	C6	122.15(14)	O2	C18	C17	124.24(15)
O1	C8	C7	58.26(10)	N1	C18	C17	115.78(14)
O1	C8	C9	115.48(15)	C18	N1	C10	122.71(13)
C7	C8	C9	124.98(16)	C18	N1	C7	116.18(12)
C11	C10	N1	120.95(14)	C10	N1	C7	120.49(12)
C11	C10	C15	120.00(14)	C7	O1	C8	62.33(10)

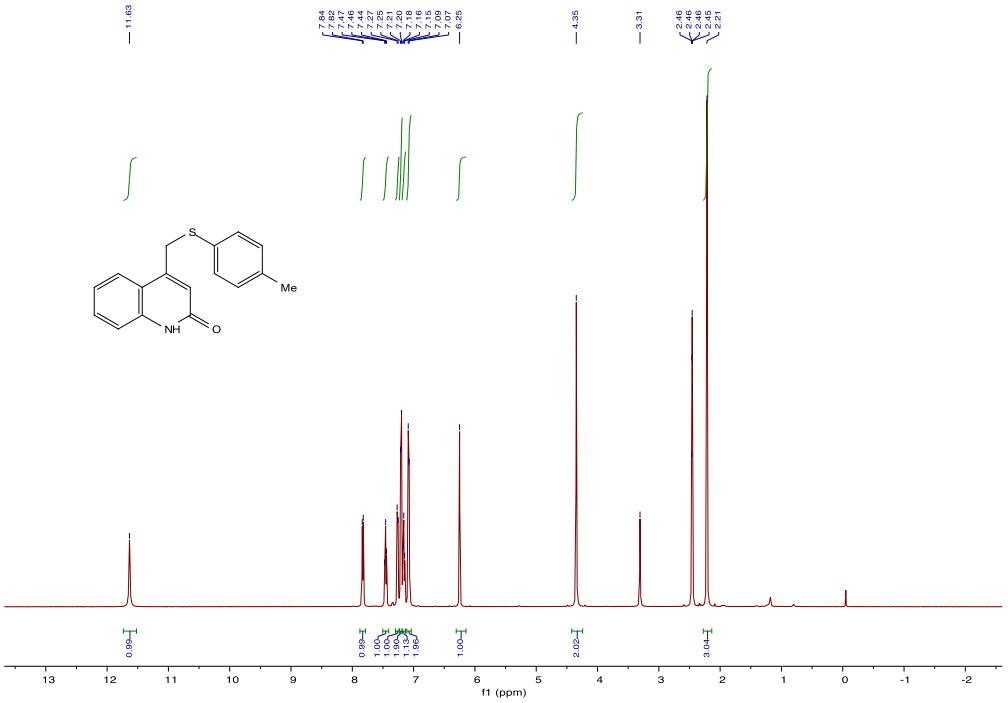
Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 20191017ZH_LMF_2KL_0m_a.

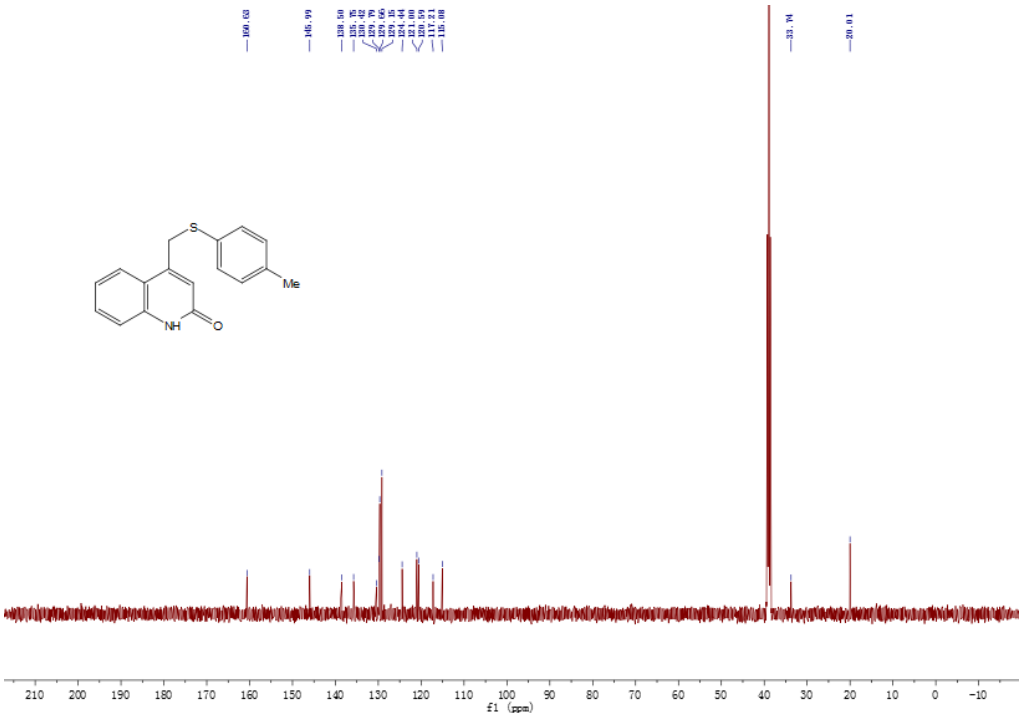
Atom	*x*	*y*	*z*	U(eq)
H1	4882.8	2457.04	352.42	49
H2	7289.21	3020.28	54.46	60
H3	8656.58	4980.4	1202.65	66
H4	7656.96	6368.84	2697.17	65
H5	5293.4	5783.94	3073.23	50
H8	3666.77	1559.24	2114.2	51
H9A	979.81	2610.77	2828.61	83
H9B	2186.7	1467.67	3815.87	83
H9C	957.23	1101.64	2138.54	83
H11	4463.43	3294.59	4784.95	51
H12	4825.09	3428.32	7404.04	60
H13	3485.29	5062.03	8323.03	65
H14	1925.57	6685.67	6653.27	57
H17	507.96	7595.25	1425.32	53
H19A	-25.02	8773.16	3315.23	92
H19B	1387.87	8697.06	4947.06	92
H19C	-197.78	7819.86	4659.37	92

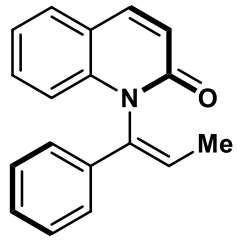
Spectral Data



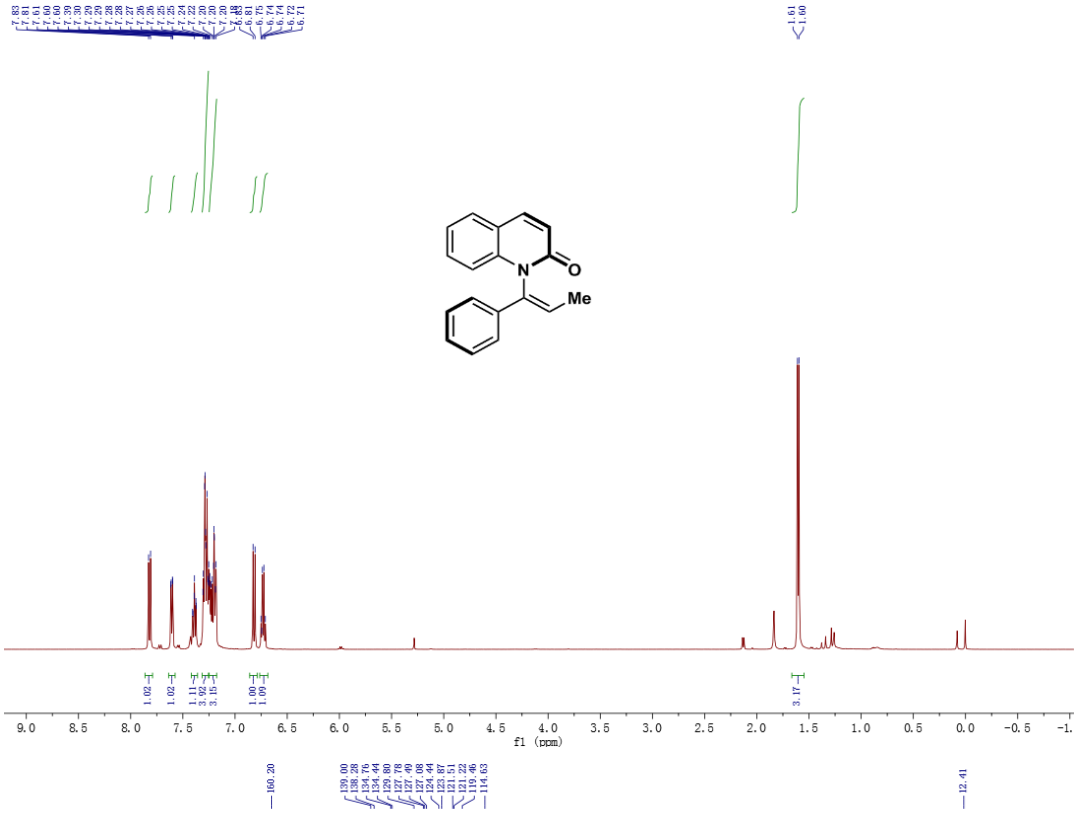
2x






N
O
Me

3a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7.25
7.24
7.22
7.20
7.20
7.20
7.18
6.83
6.81
6.75
6.74
6.74
6.72
6.71
1.61
1.60
N
O
Me
1.02
1.02
1.11
3.92
3.15
1.00
1.00
3.17
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.
f1 (ppm)

160.20
139.00
138.28
134.76
134.44
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127.49
127.08
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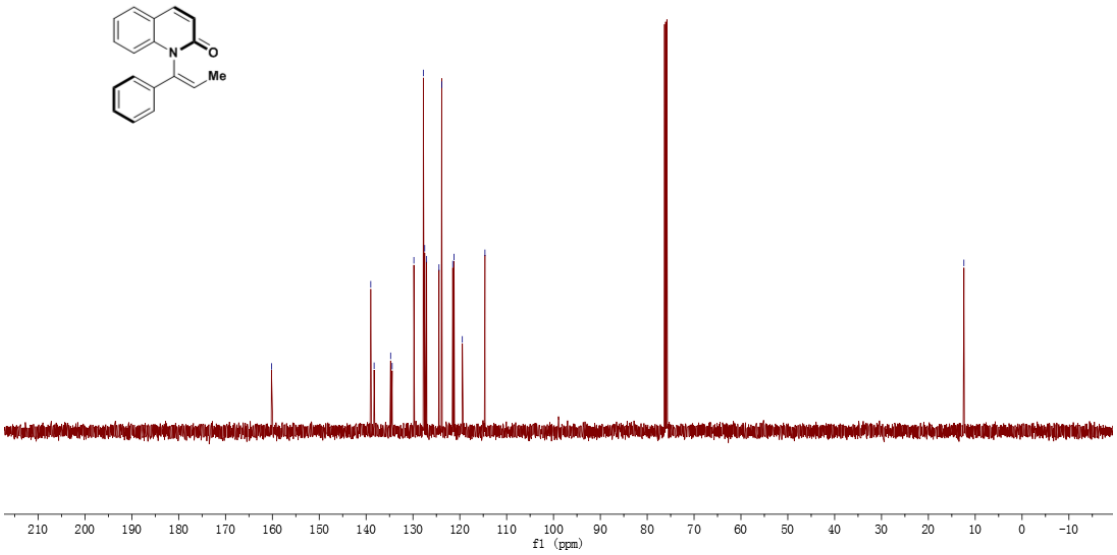
123.87
121.51
121.22
119.46
114.63
12.41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Me
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30
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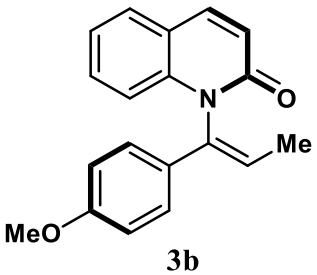
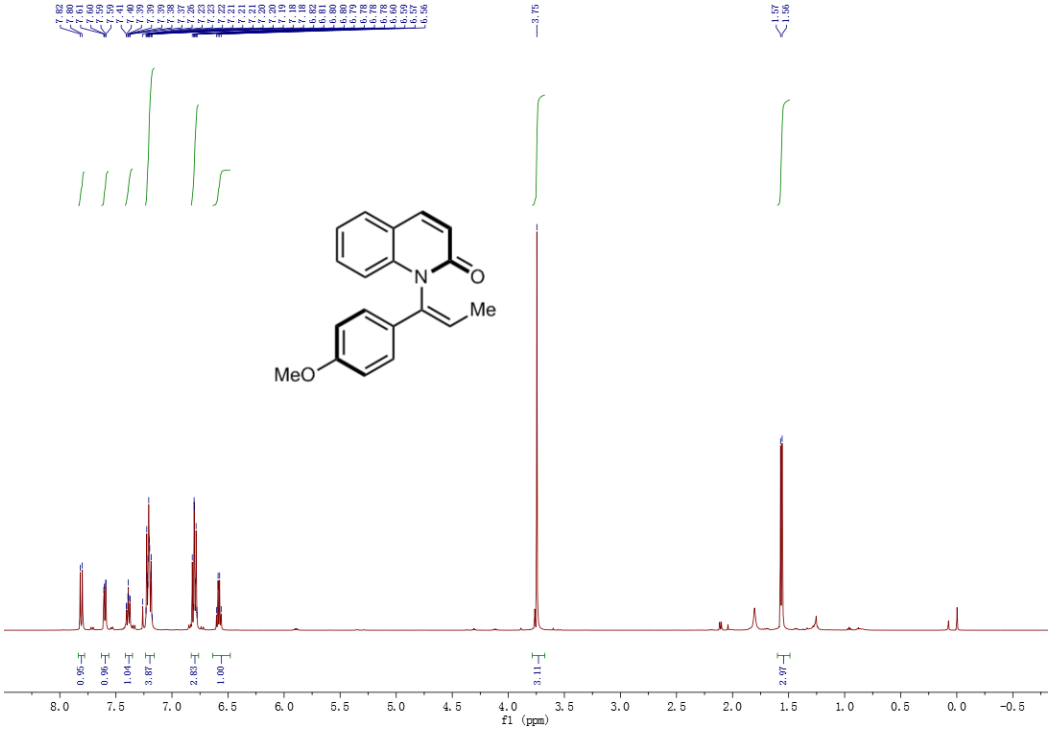
f1 (ppm)


N
O
Me
MeO

3b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7.38
7.37
7.26
7.23
7.22
7.21
7.21
7.20
7.19
7.18
6.82
6.81
6.80
6.79
6.78
6.78
6.60
6.59
6.57
6.56
3.75
1.57
1.56
N
O
Me
MeO
0.95
0.96
1.04
3.87
2.83
1.00
3.11
2.97
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)


160.18
158.52
138.92
138.27
134.36
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125.20
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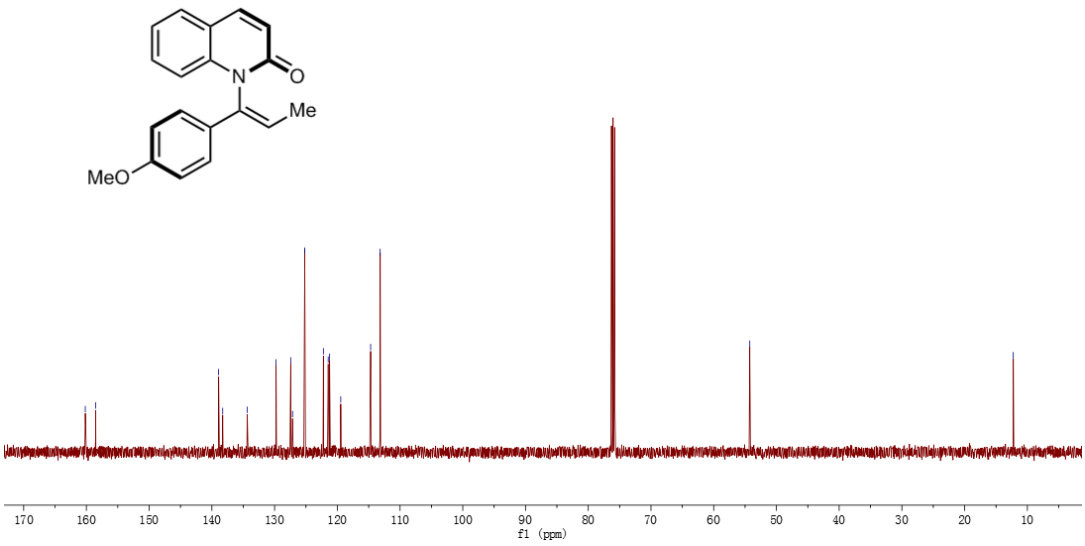
113.17
54.25
12.24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O
Me
MeO
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160
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140
130
120
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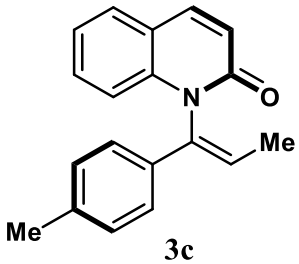
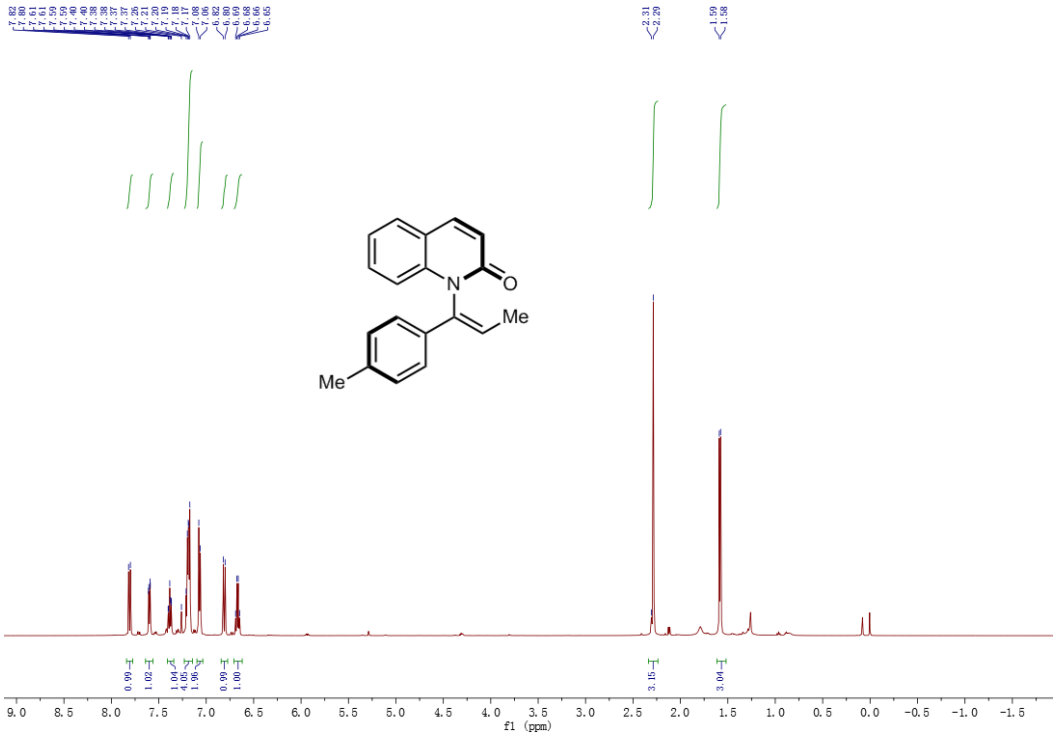
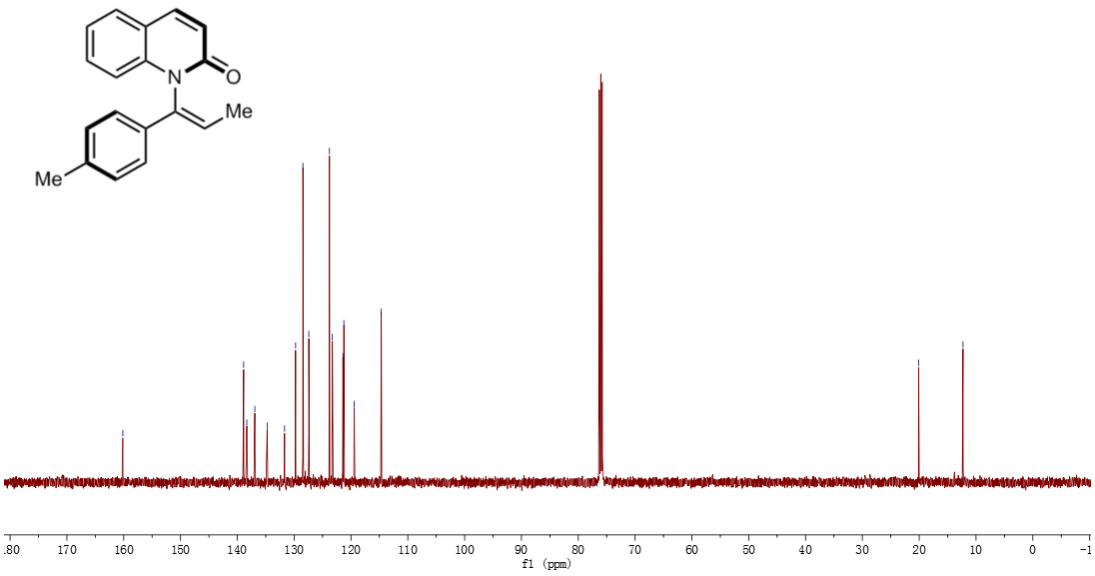
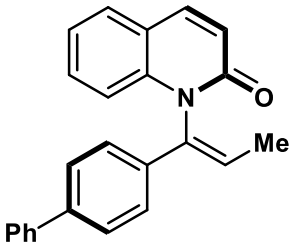
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



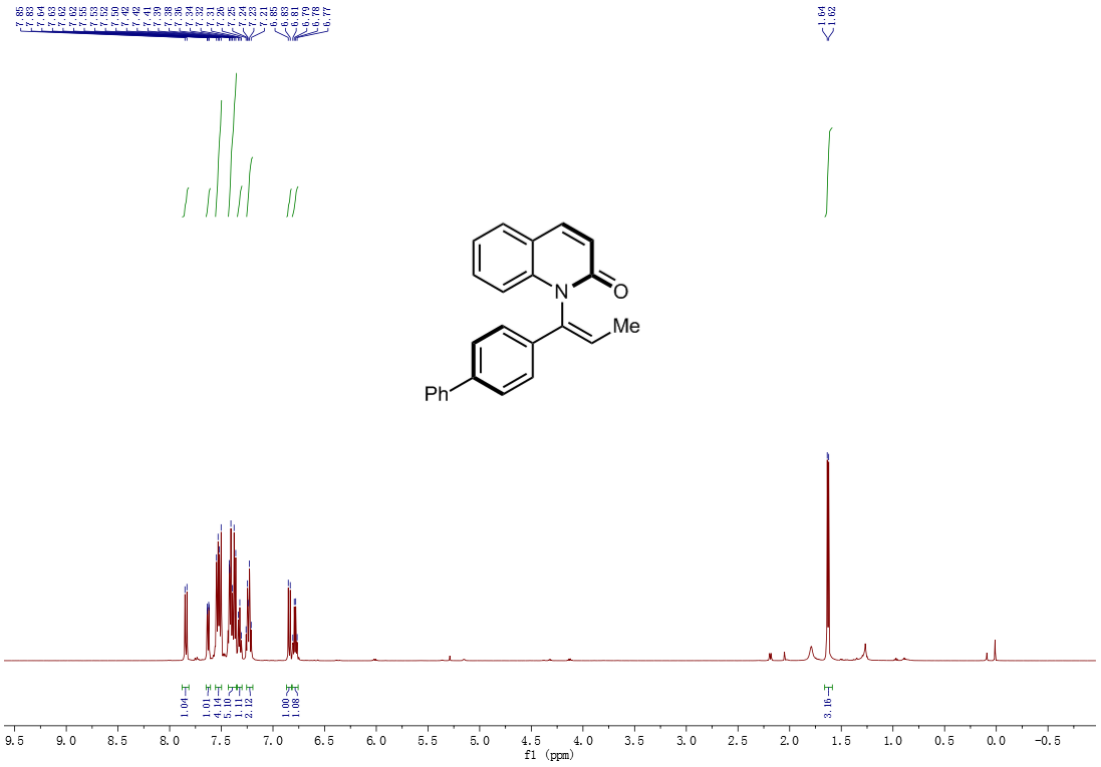
3c






N
O
Me
Ph

3d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N
O
Me
Ph
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1.01
4.14
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1.11
2.12
1.00
1.08
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8.5
8.0
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6.0
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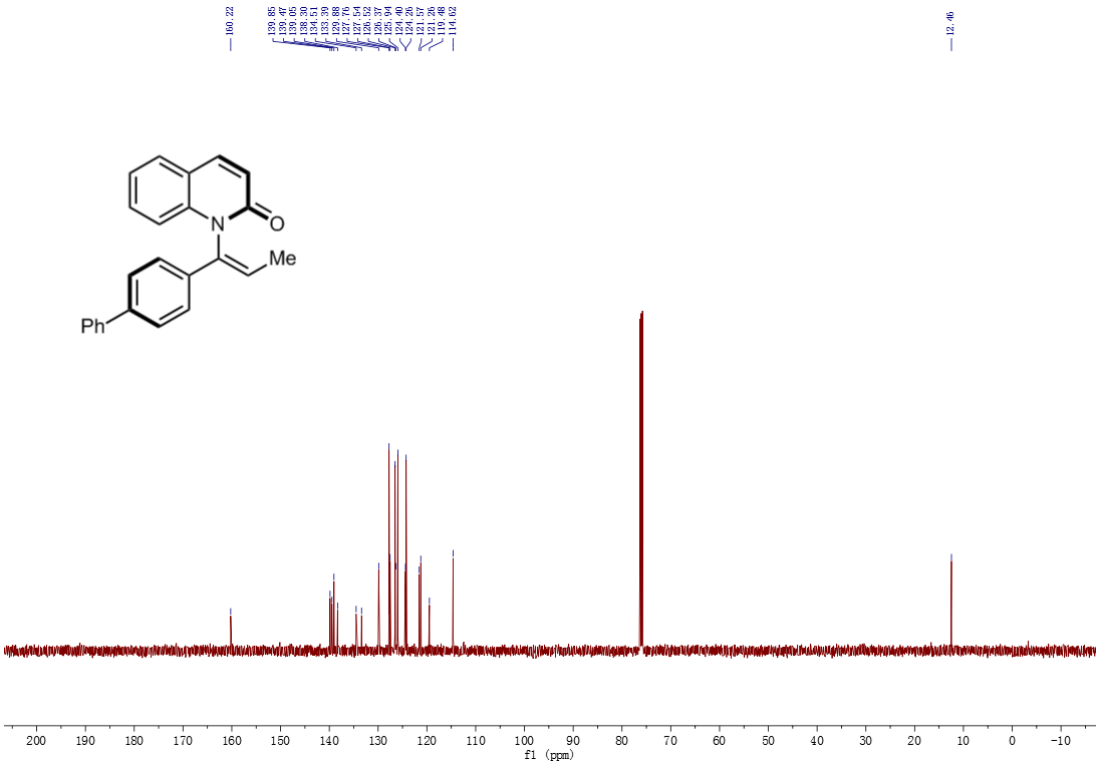
f1 (ppm)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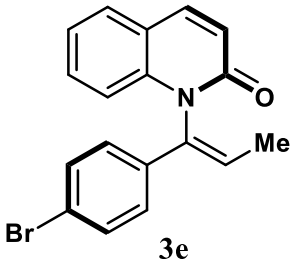
126.37
126.34
124.40
124.26
121.57
121.26
119.48
114.62
12.46
N
O
Me
Ph
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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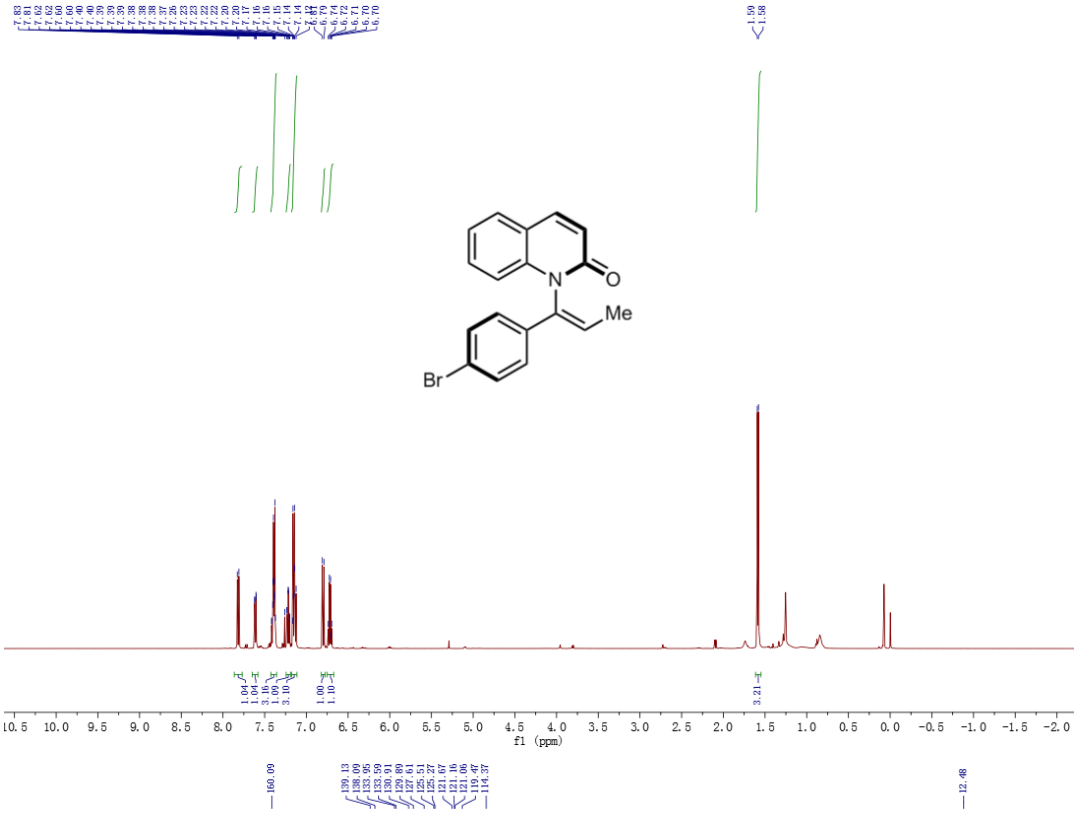
O
Me
Br

3e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7.38
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7.23
7.23
7.22
7.22
7.20
7.20
7.17
7.16
7.16
7.15
7.14
7.14
6.77
6.77
6.74
6.74
6.72
6.71
6.70
6.70
1.59
1.58
N
O
Me
Br
1.04
1.04
1.05
1.00
3.10
1.00
1.10
3.21
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)
160.09
139.13
138.09
133.95
133.59
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127.61
125.51
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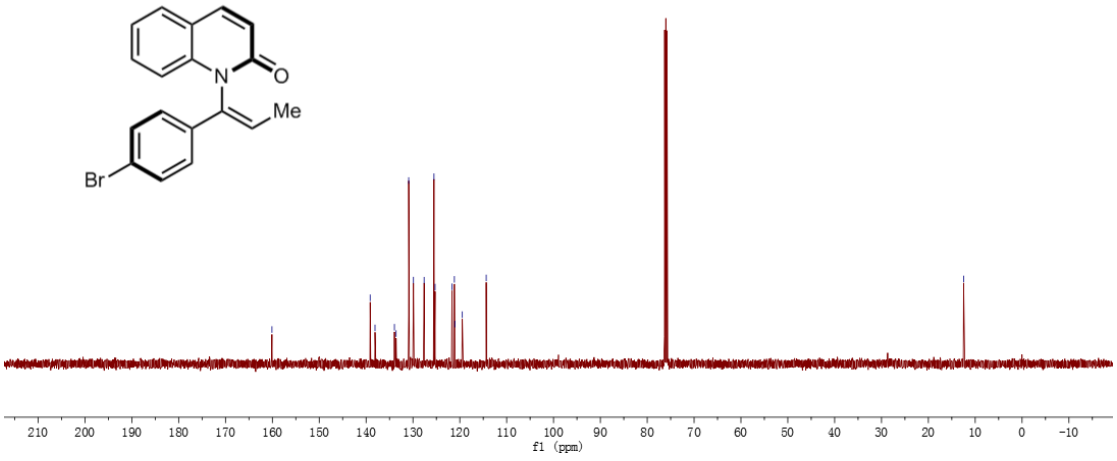
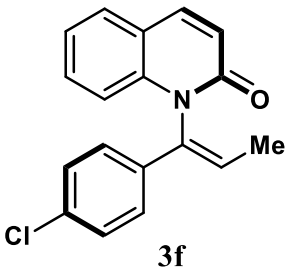
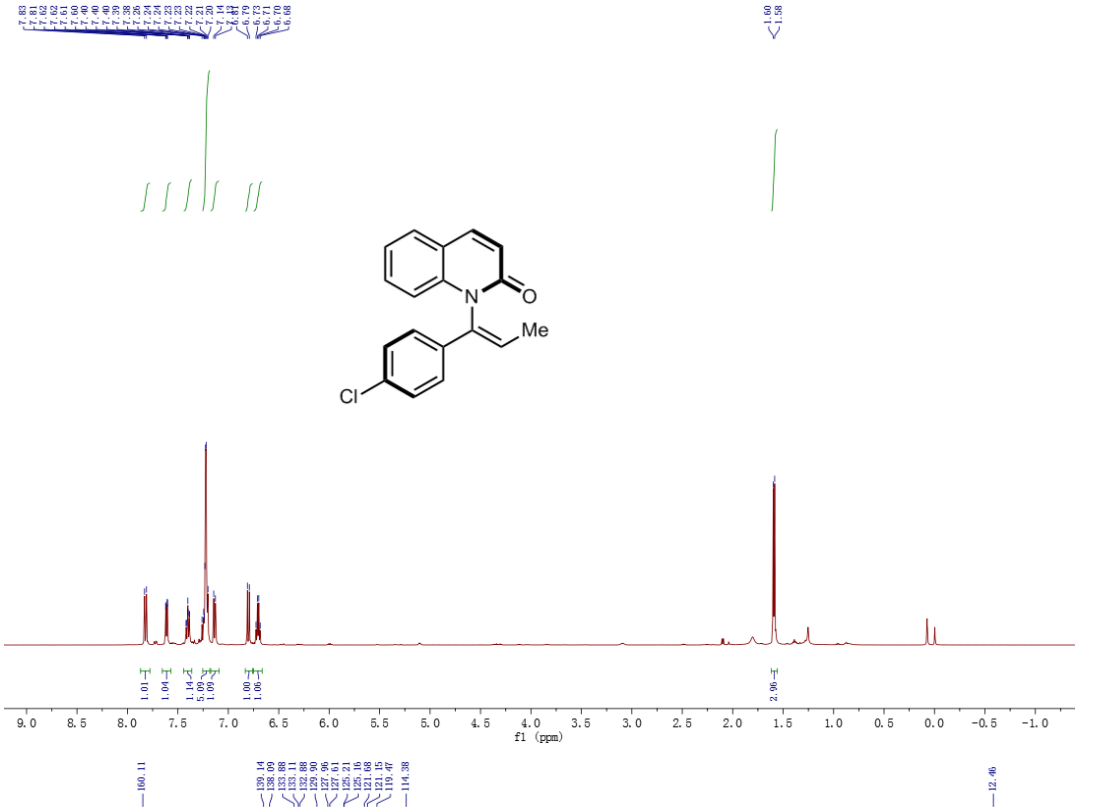
114.37
12.48


N
O
Me
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


N
O
Me
Cl

3f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7.24
7.23
7.22
7.21
7.20
7.14
7.13
6.79
6.73
6.71
6.70
6.68
1.60
1.58
N
O
Me
Cl
1.01
1.04
1.14
5.09
1.09
1.00
1.06
2.96
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

160.11
139.14
138.09
133.88
133.11
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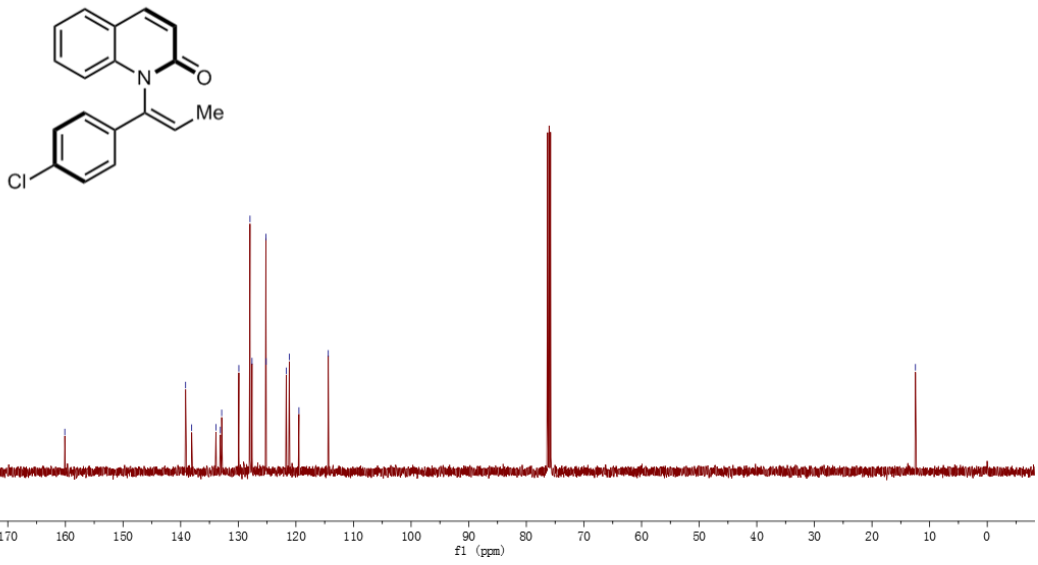
127.96
127.51
125.21
125.16
121.68
121.15
118.47
114.38
12.46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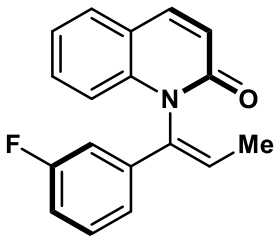
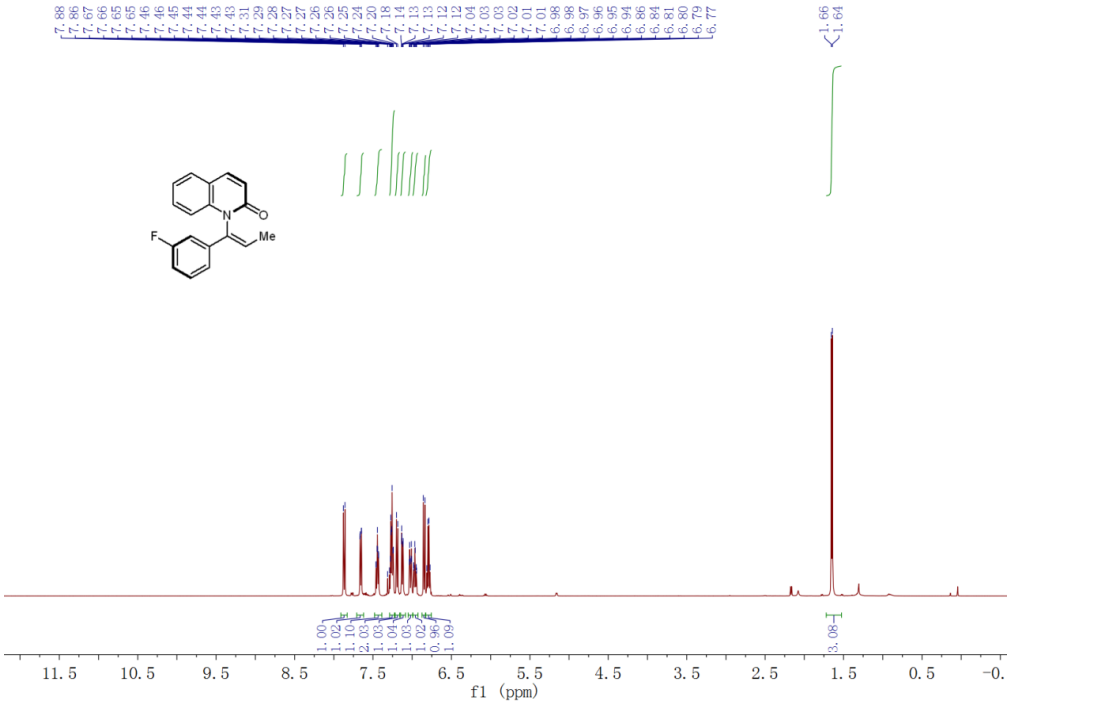
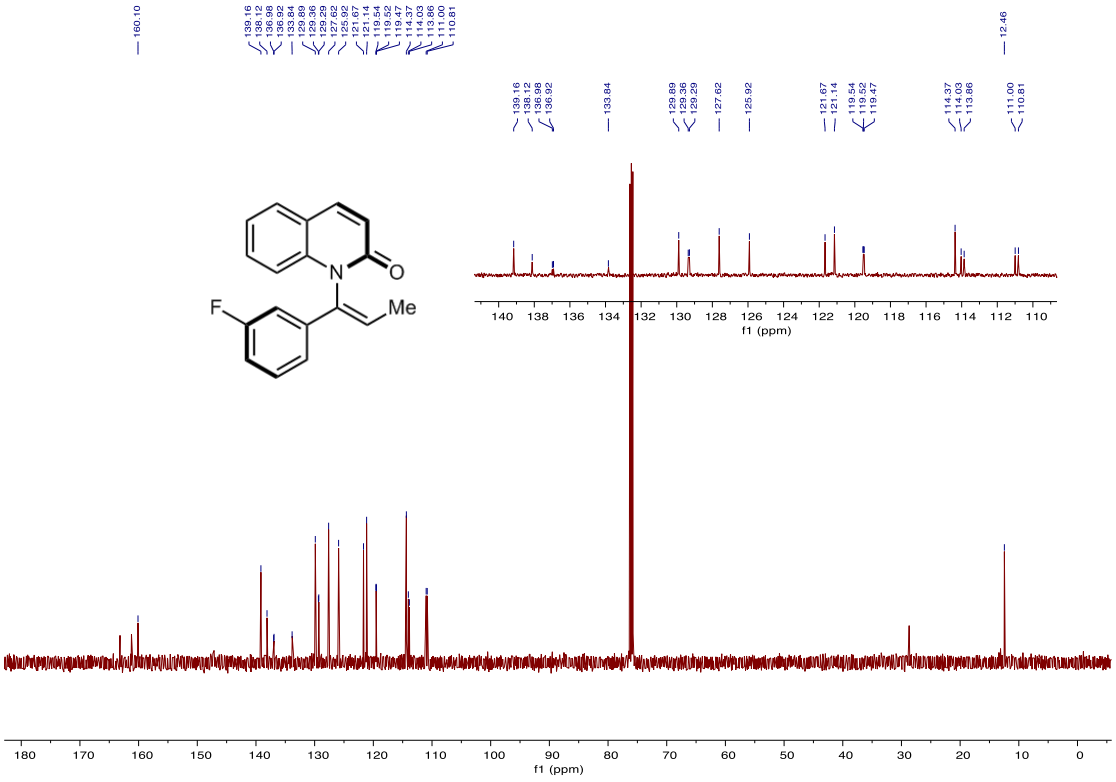
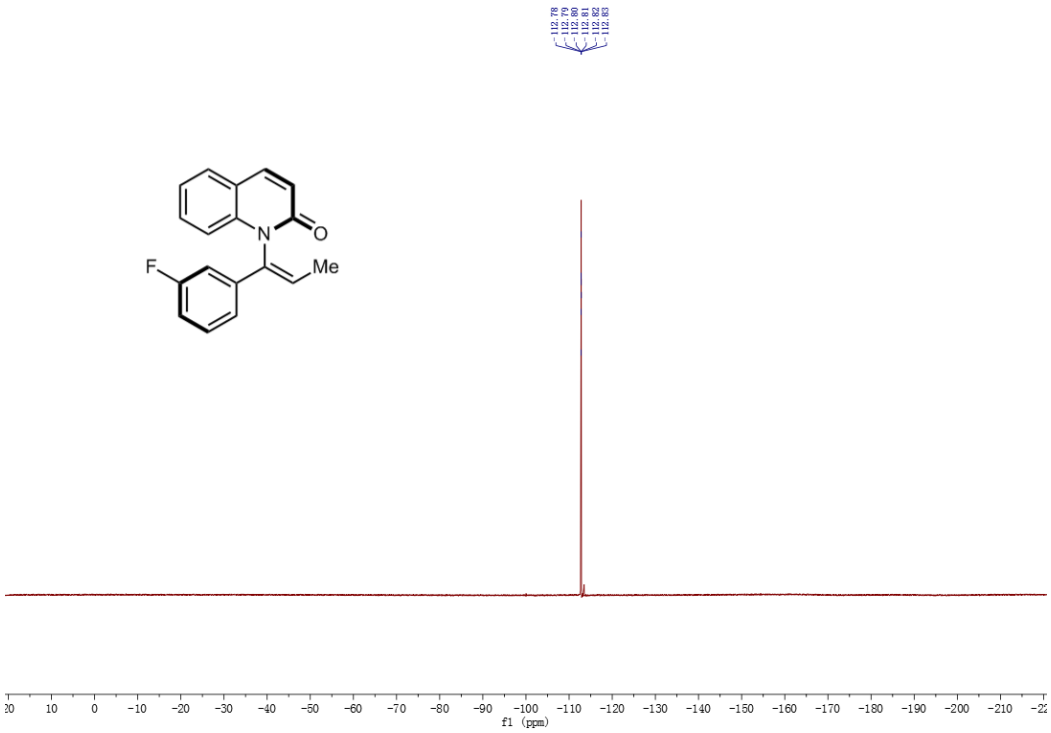
O
Me
Cl
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



3g



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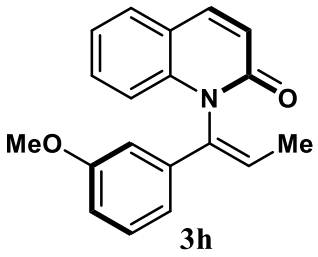
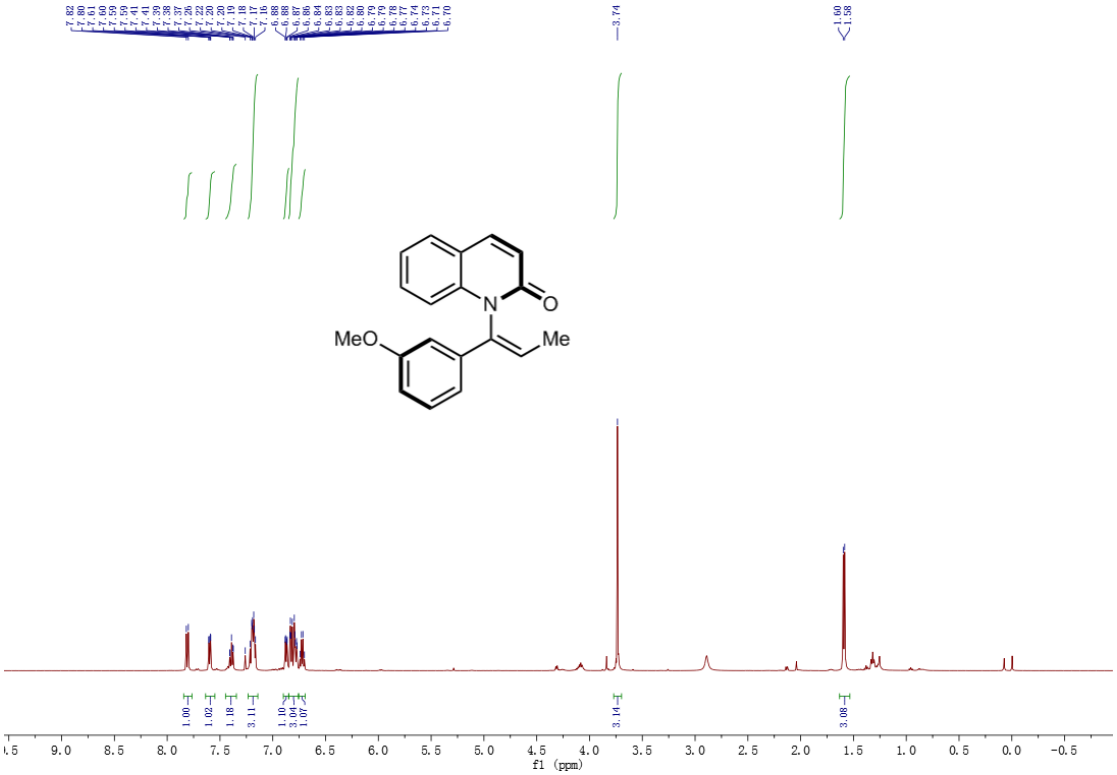
112.83
N
O
F
Me
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −22
f1 (ppm)


N
O
MeO
Me

3h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6.87
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6.83
6.82
6.80
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6.78
6.77
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6.70
3.74
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1.58
N
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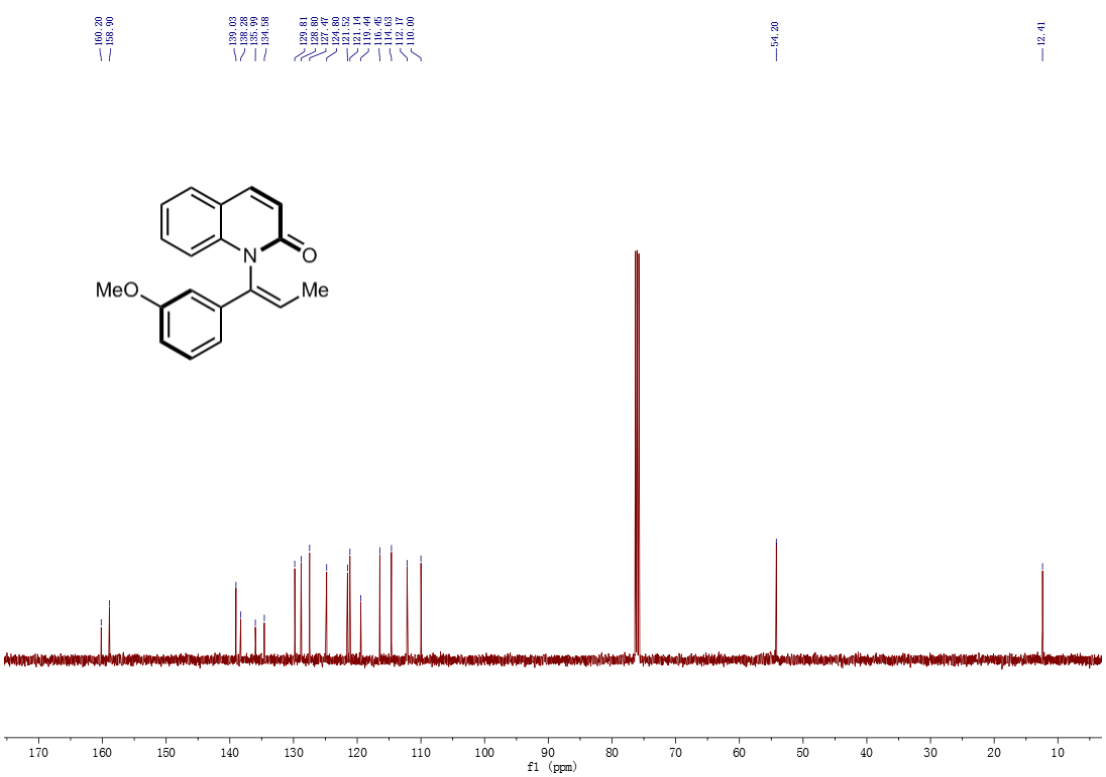
3.08
f1 (ppm)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121.52
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114.03
112.17
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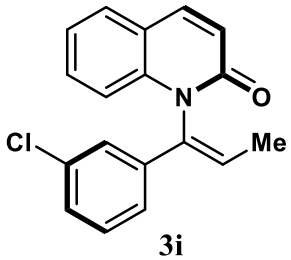
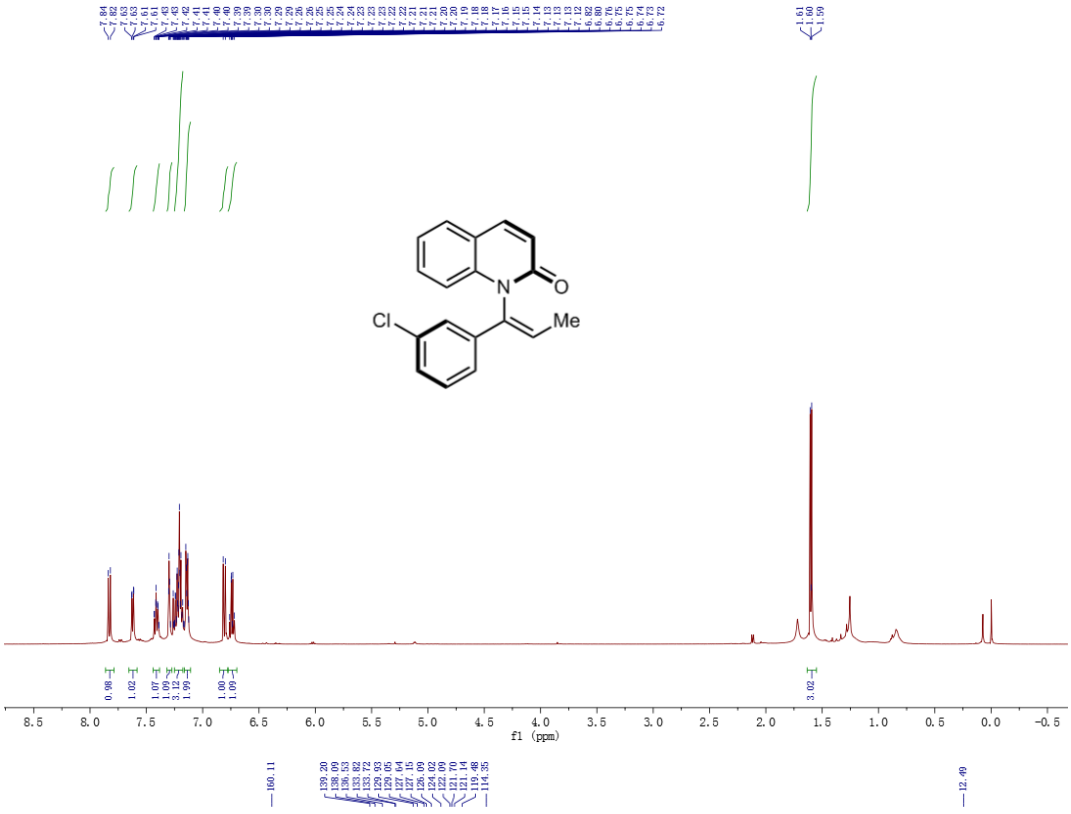
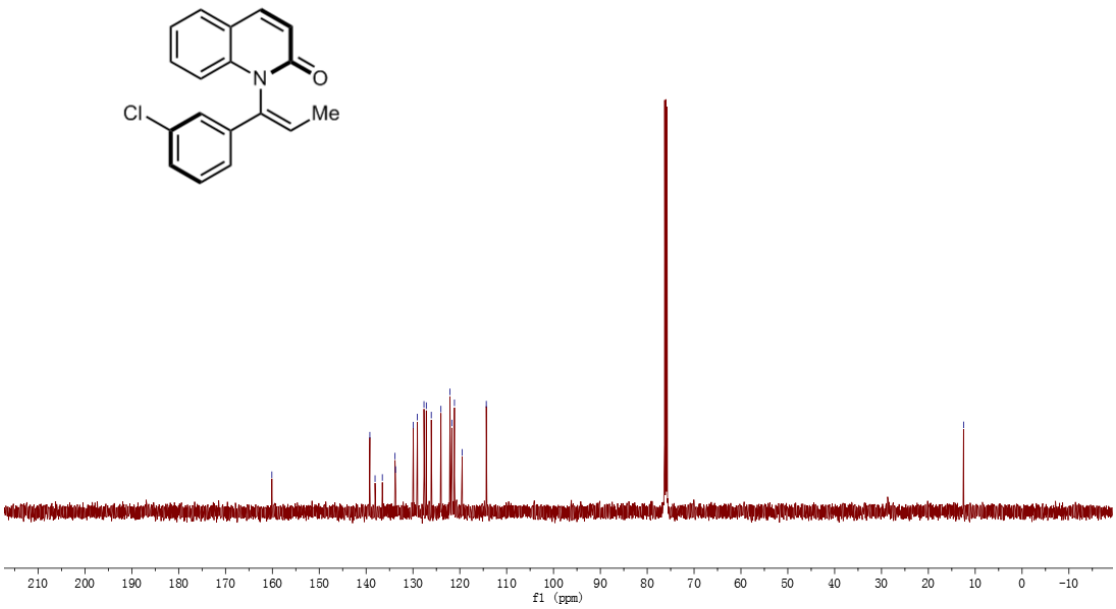
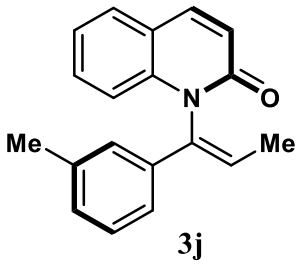
54.20
12.41
N
O
MeO
Me
f1 (ppm)



3i







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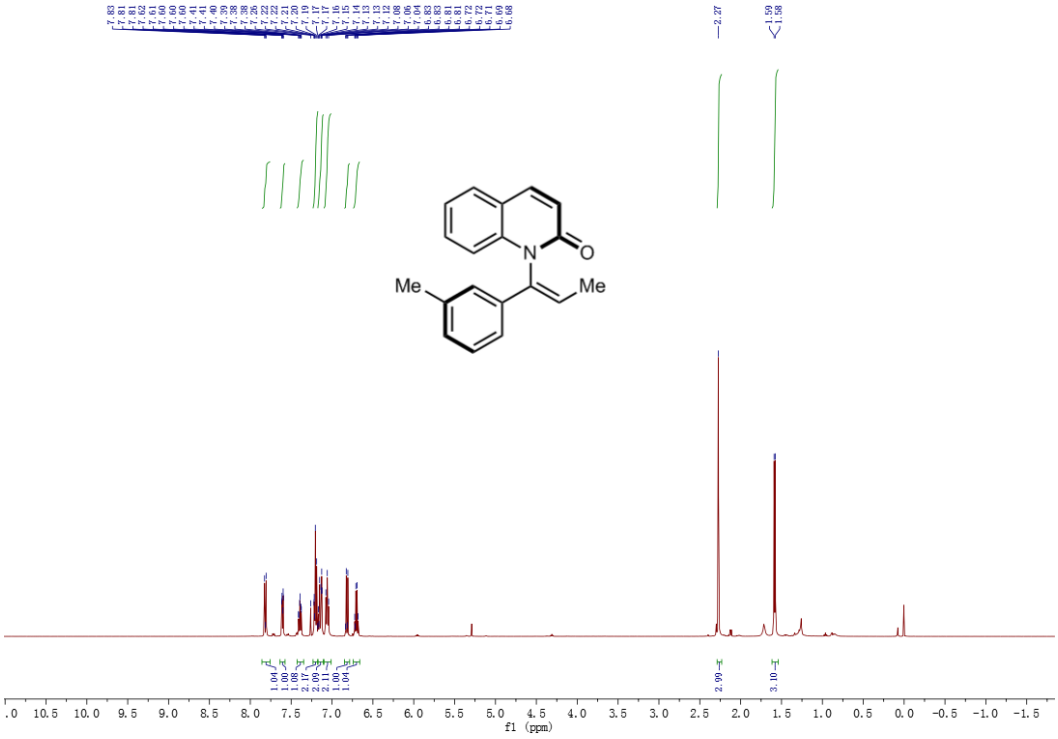

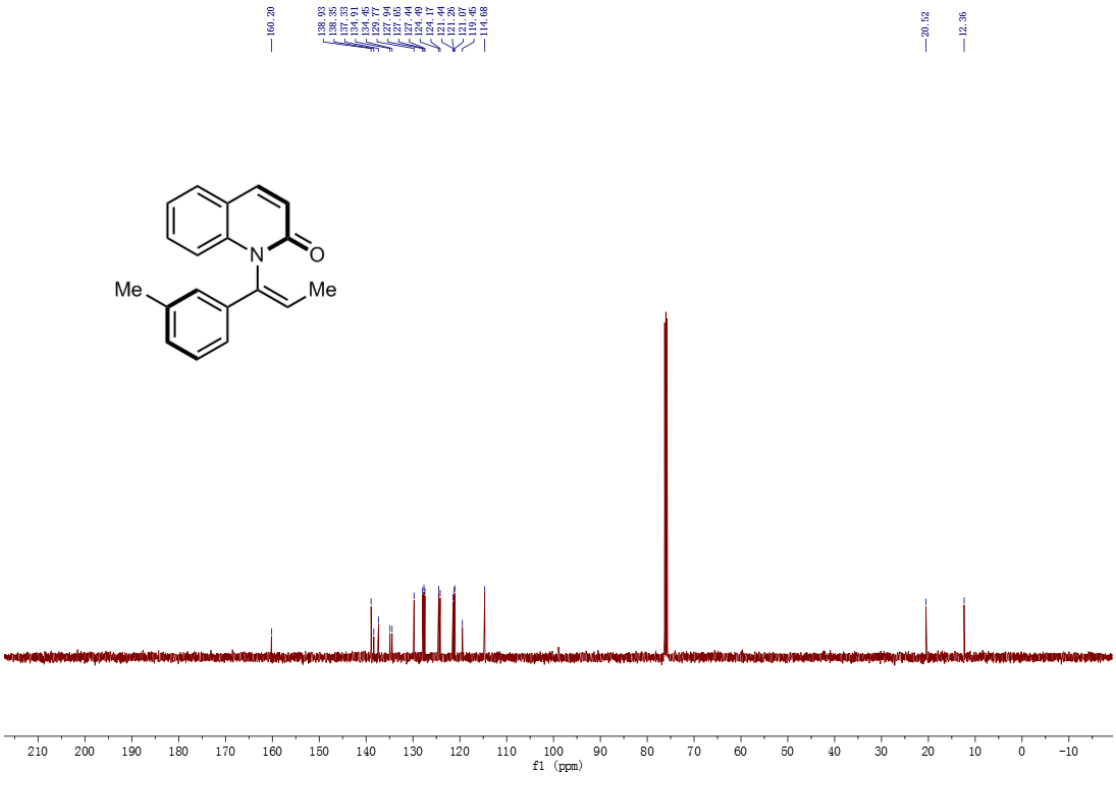

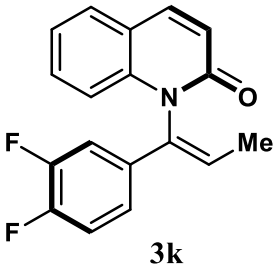

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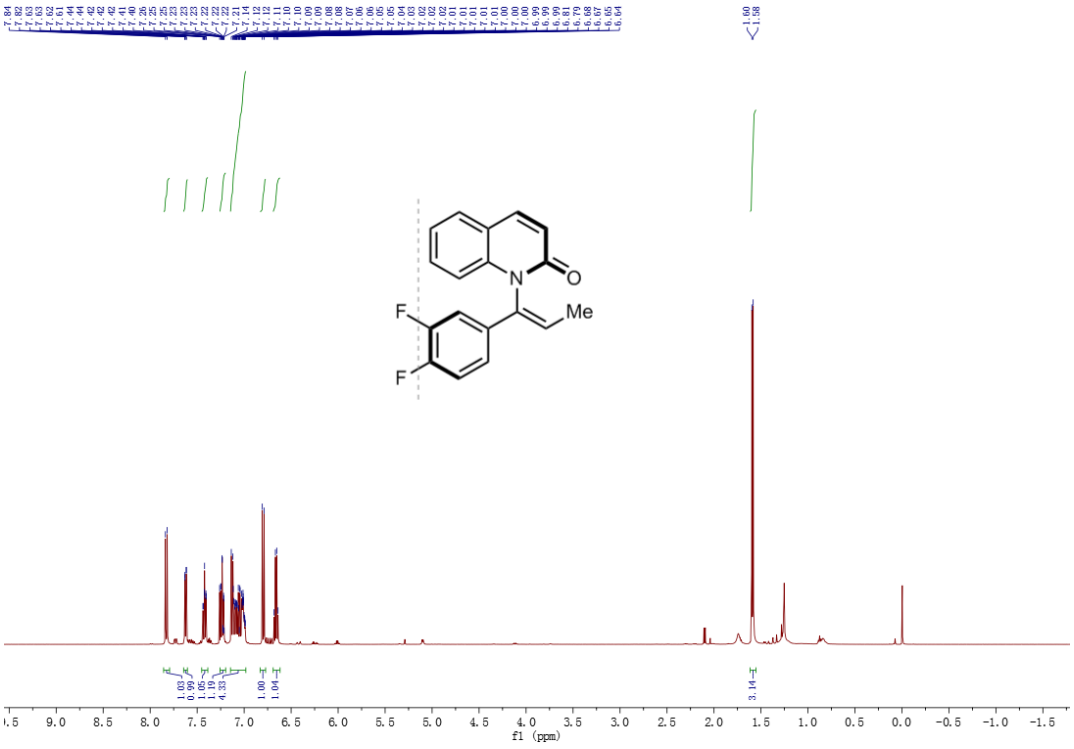

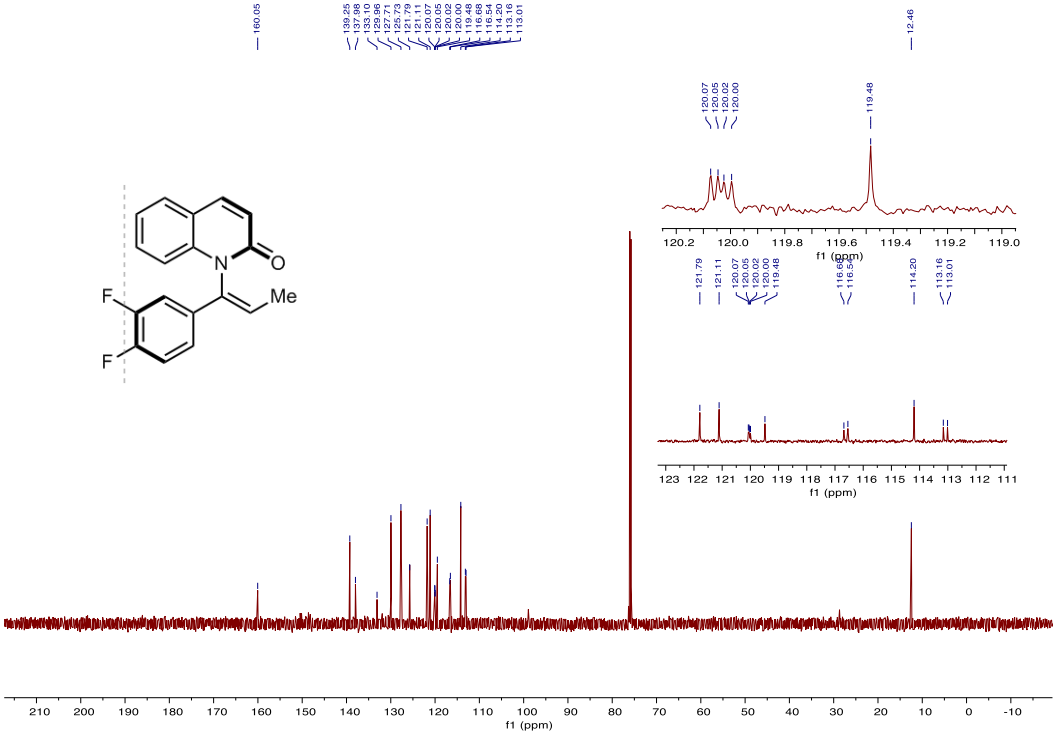

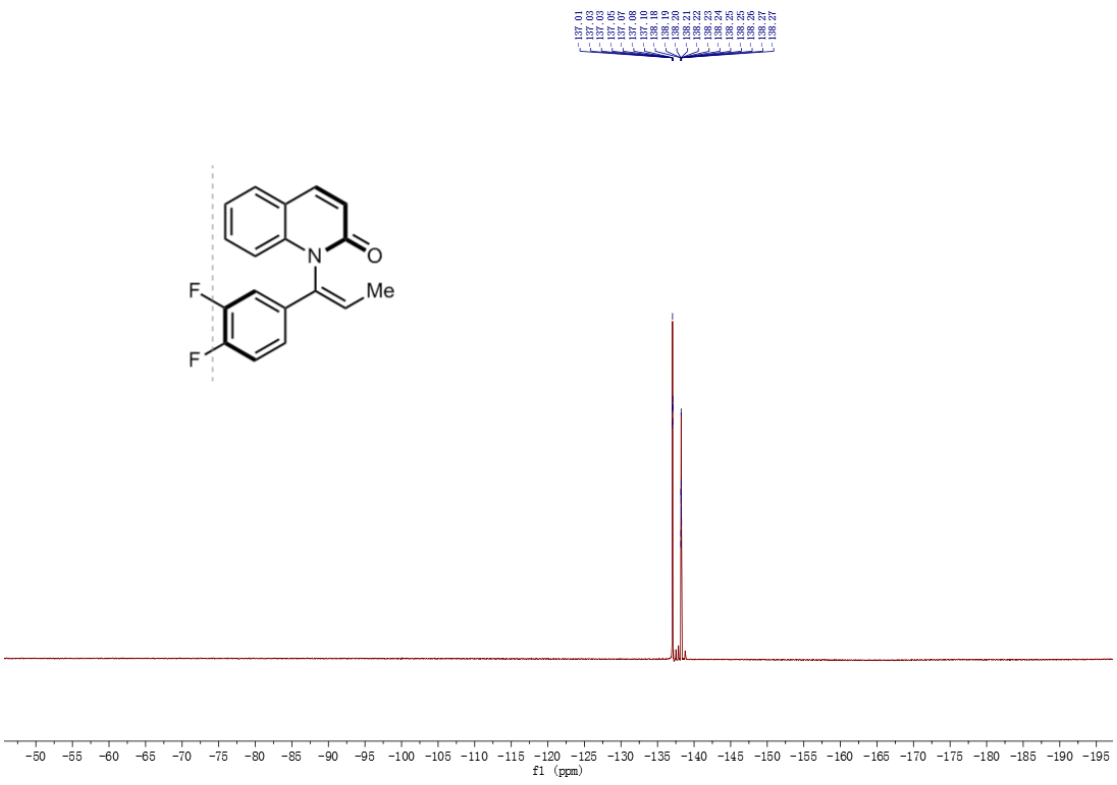
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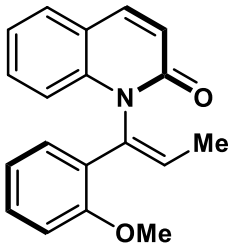
138.23
138.24
138.25
138.25
138.26
138.27
138.27
O
N
Me
F
F
-50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185 -190 -195
f1 (ppm)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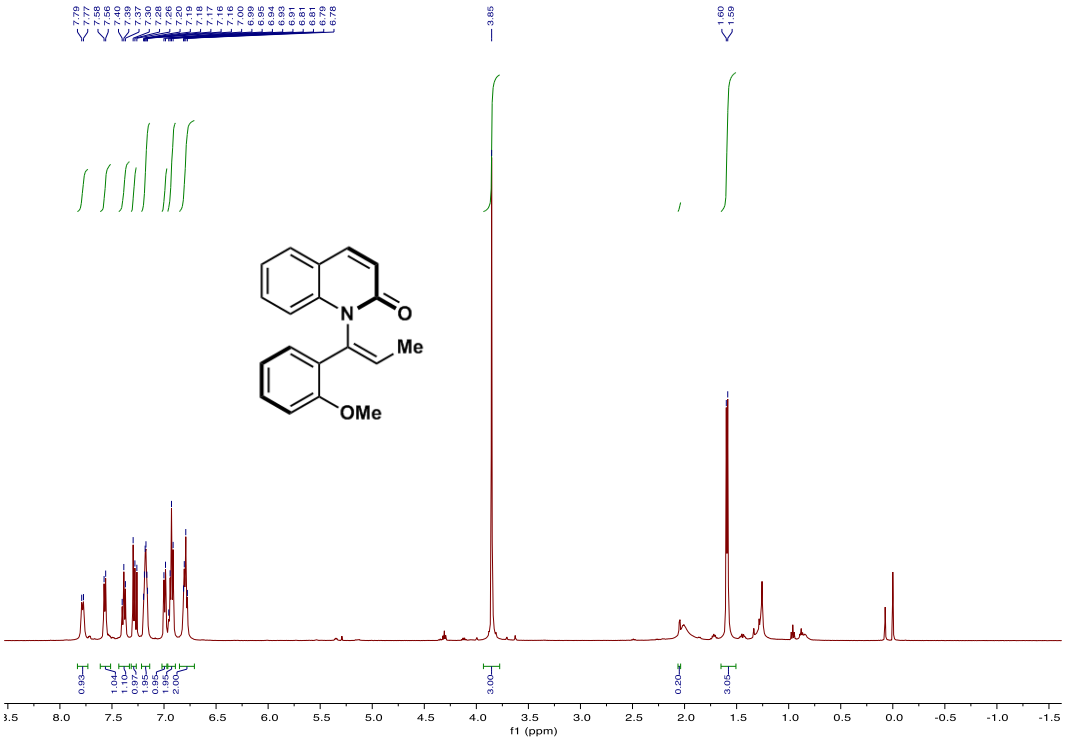
O
Me
OMe

3l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7.37
7.30
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7.26
7.20
7.19
7.18
7.17
7.16
7.16
7.00
6.99
6.95
6.94
6.93
6.91
6.81
6.81
6.79
6.78
3.85
1.60
1.59
N
O
Me
OMe
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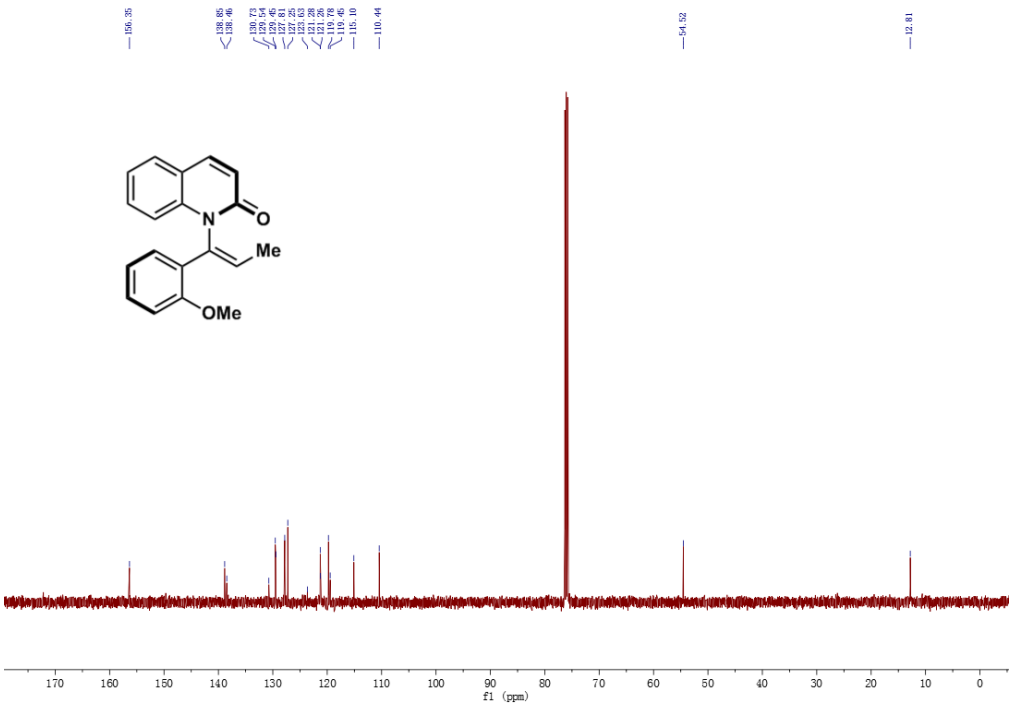
1.04
0.97
1.95
0.95
1.96
2.00
3.00
0.20
3.05
f1 (ppm)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127.25
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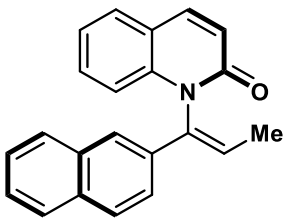
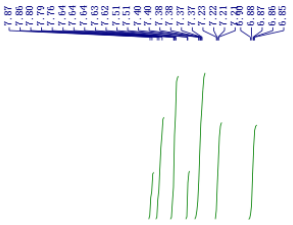
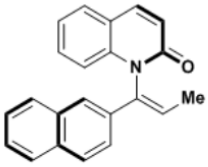
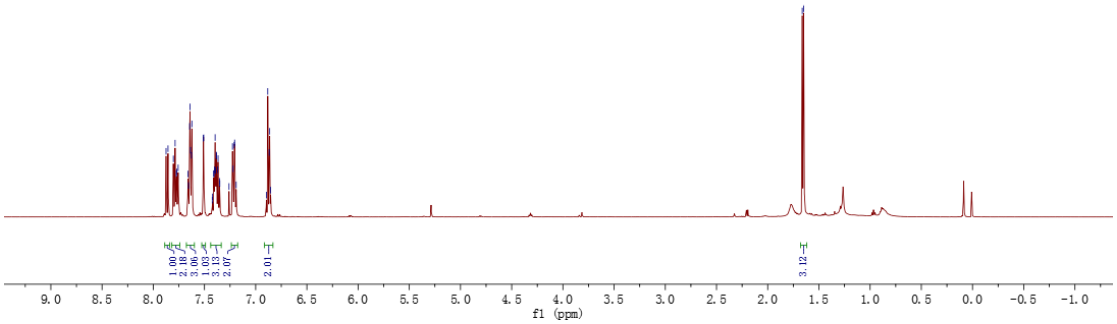
110.44
54.52
12.81
N
O
Me
OMe
f1 (ppm)

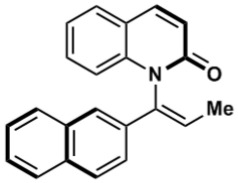


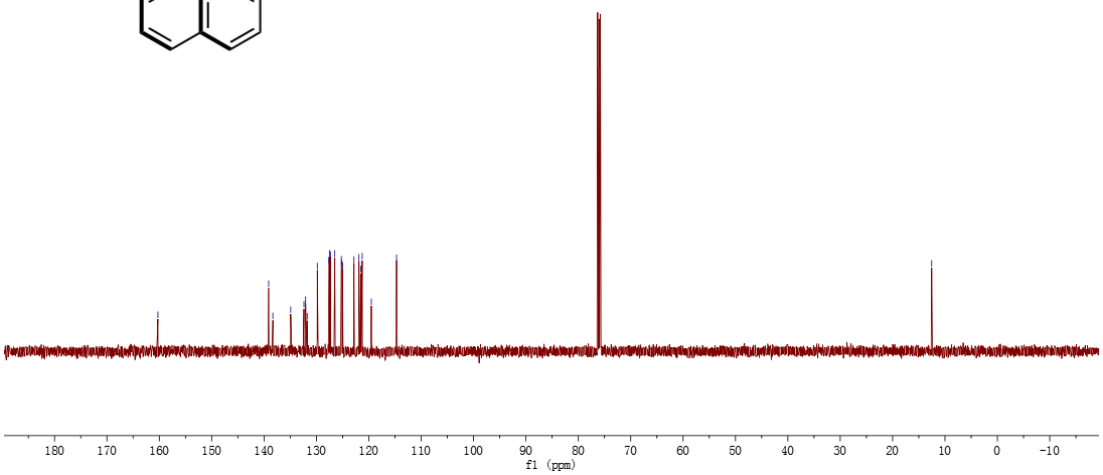
3m

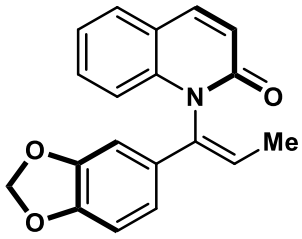












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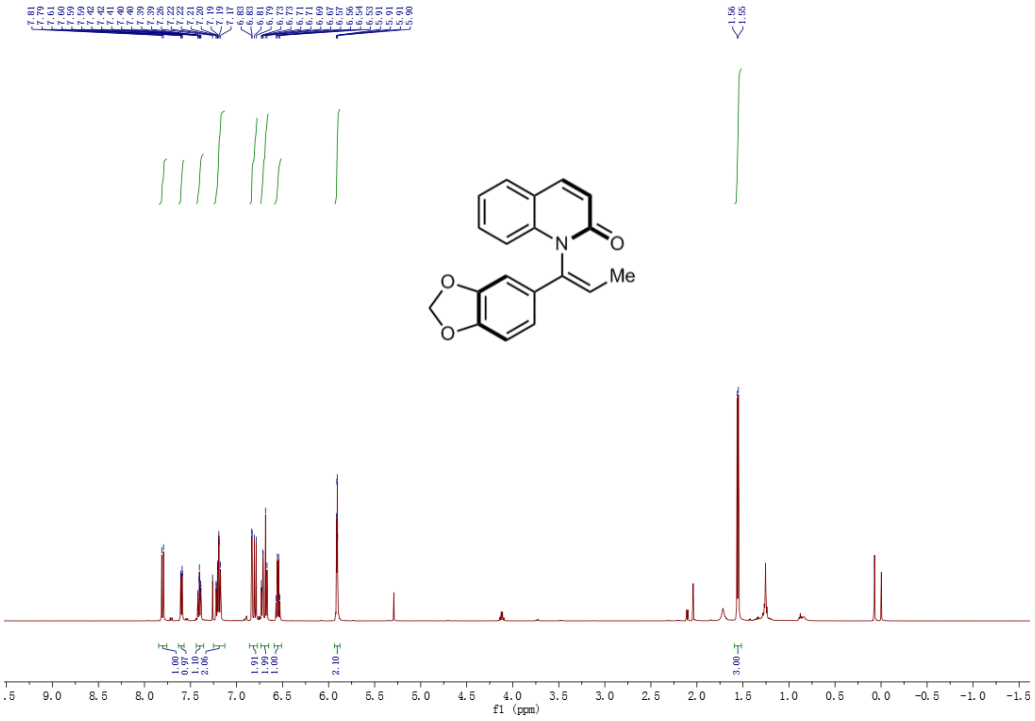

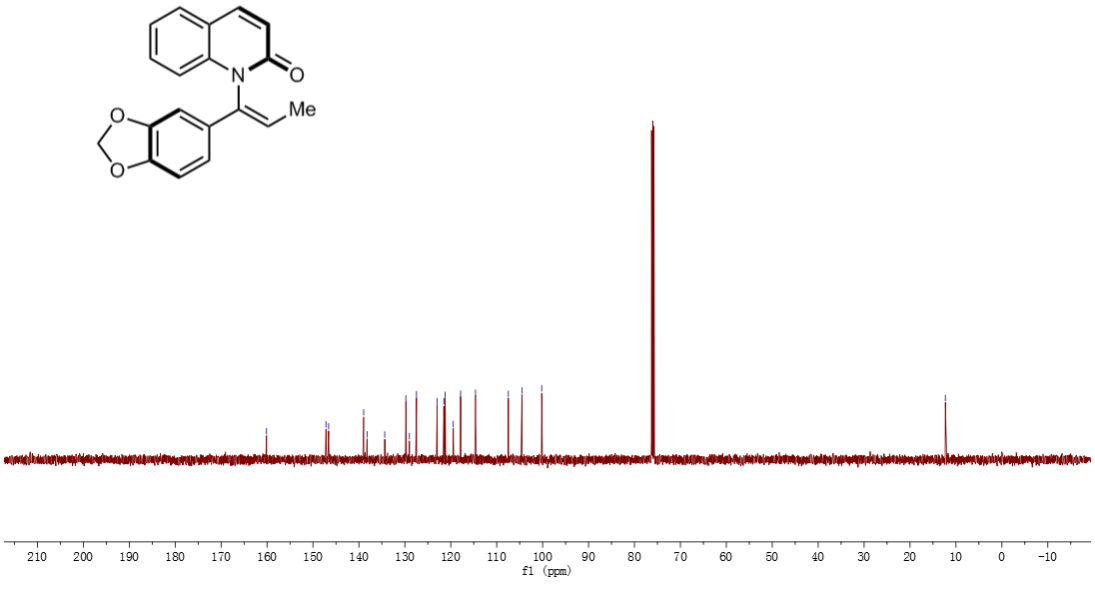

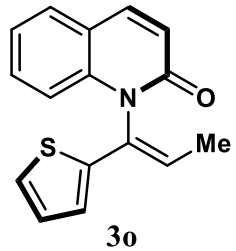

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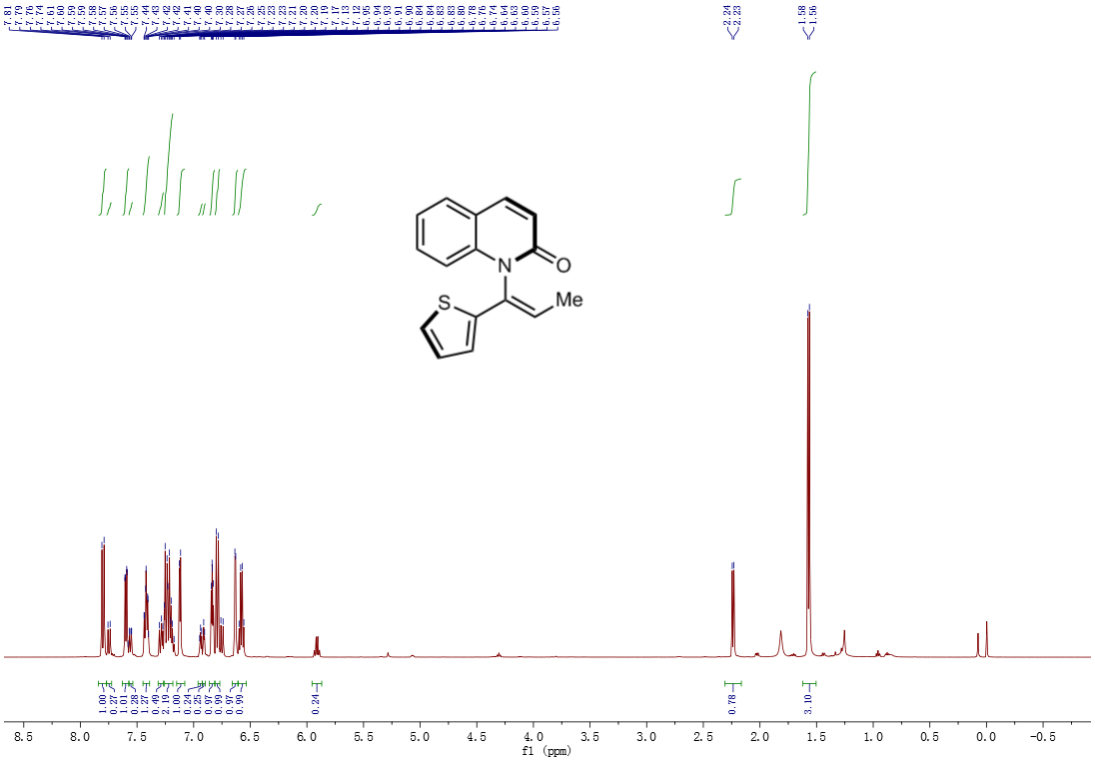
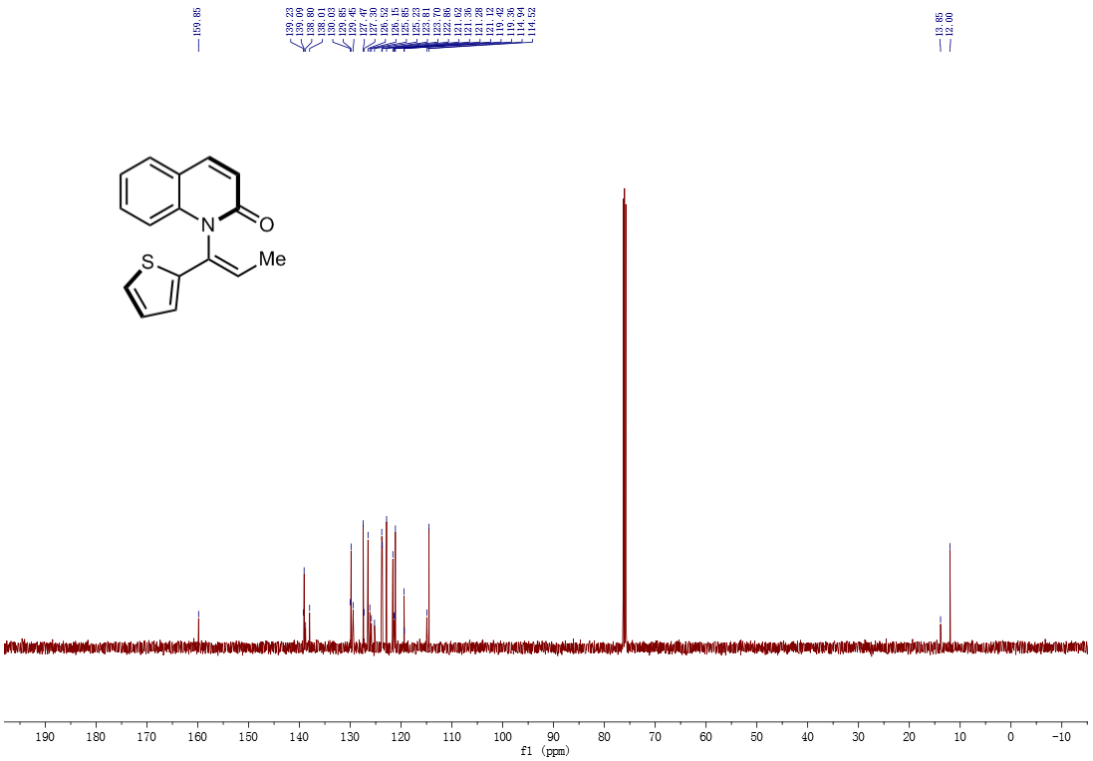
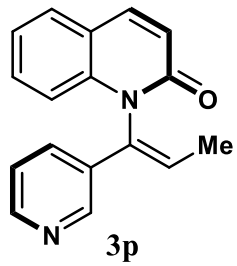
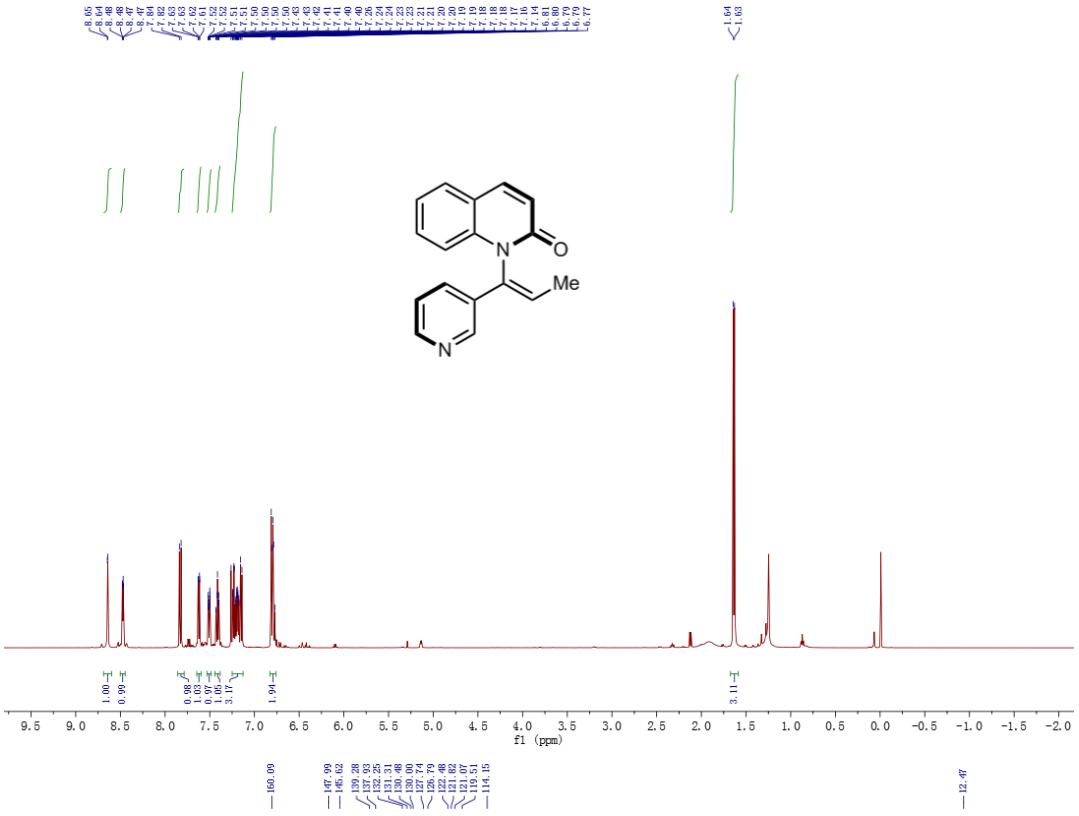





N
O
Me
N

3p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8.48
8.47
7.82
7.63
7.62
7.61
7.52
7.52
7.51
7.51
7.50
7.50
7.50
7.43
7.42
7.41
7.41
7.40
7.40
7.26
7.24
7.24
7.23
7.23
7.21
7.21
7.20
7.20
7.19
7.19
7.18
7.18
7.17
7.17
7.16
7.14
6.81
6.80
6.79
6.77
1.64
1.63
N
O
Me
N
1.00
0.99
0.98
1.03
0.97
1.05
3.17
1.94
3.11
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)

160.09
147.99
145.62
139.28
137.93
132.35
131.31
130.48
130.00
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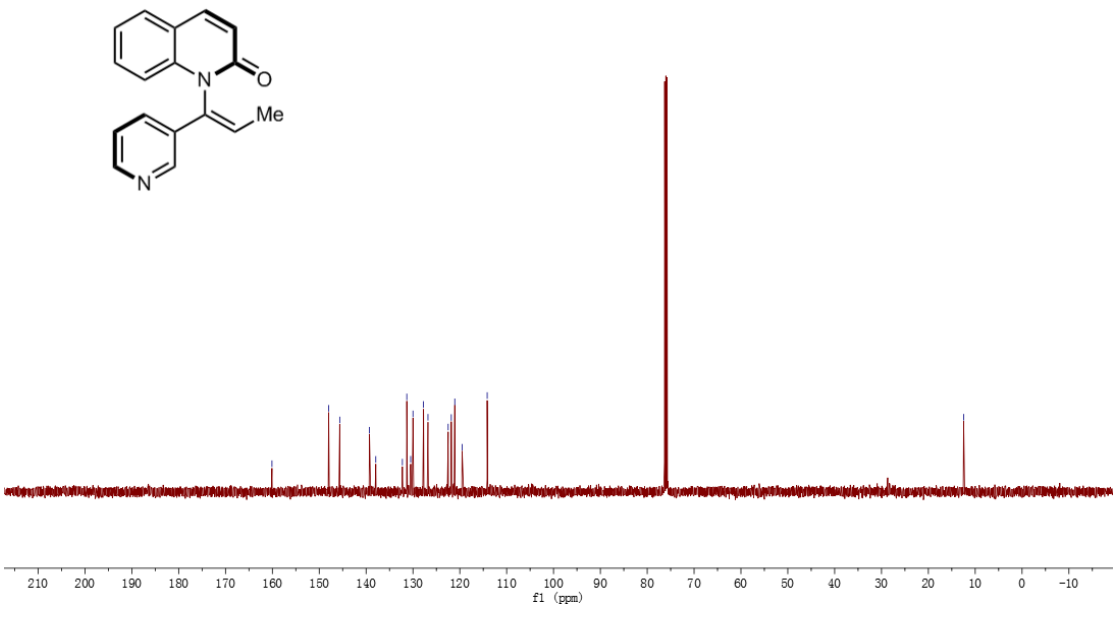
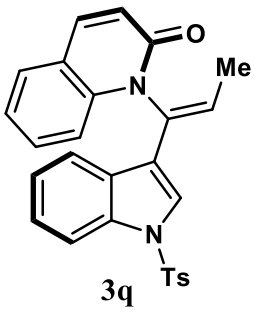
114.15
12.47


N
O
Me
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



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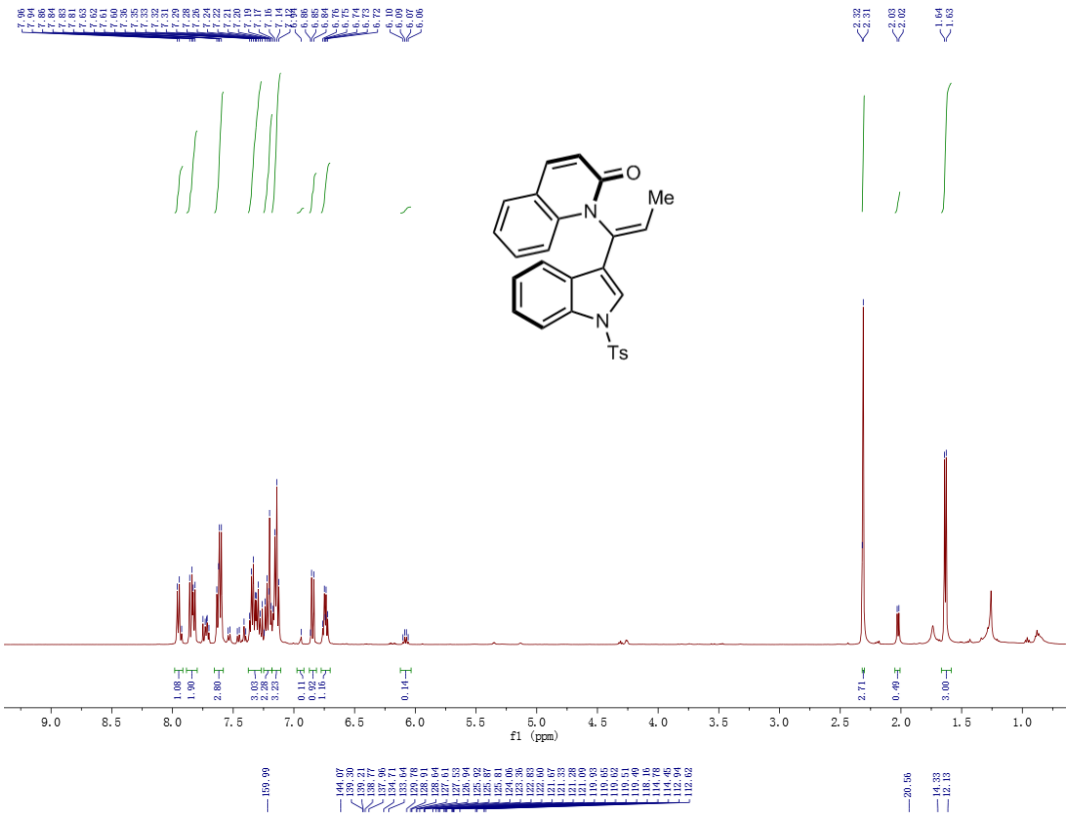
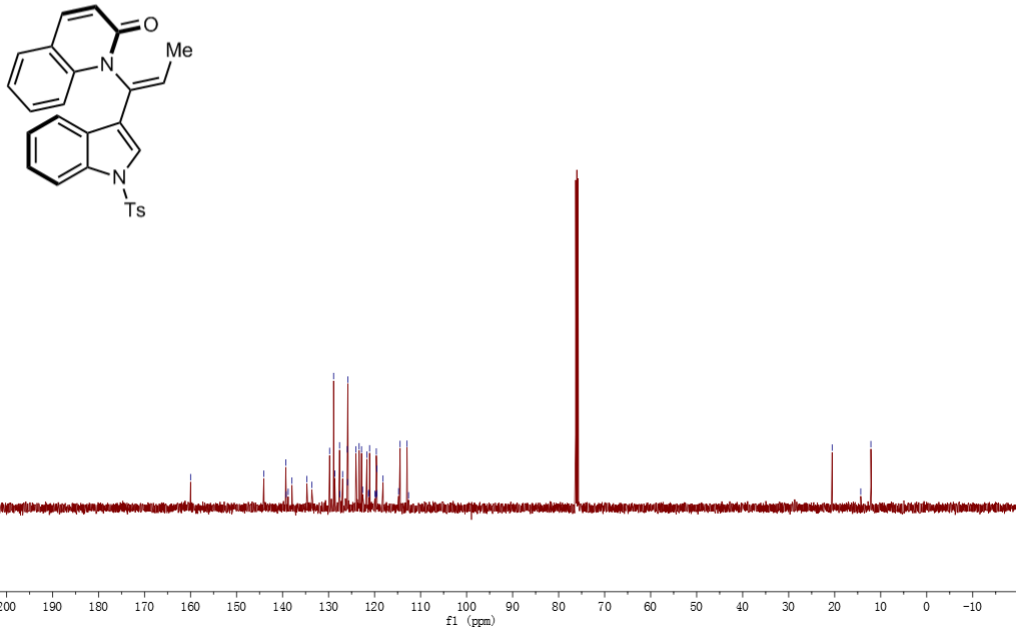
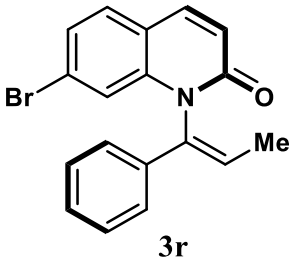
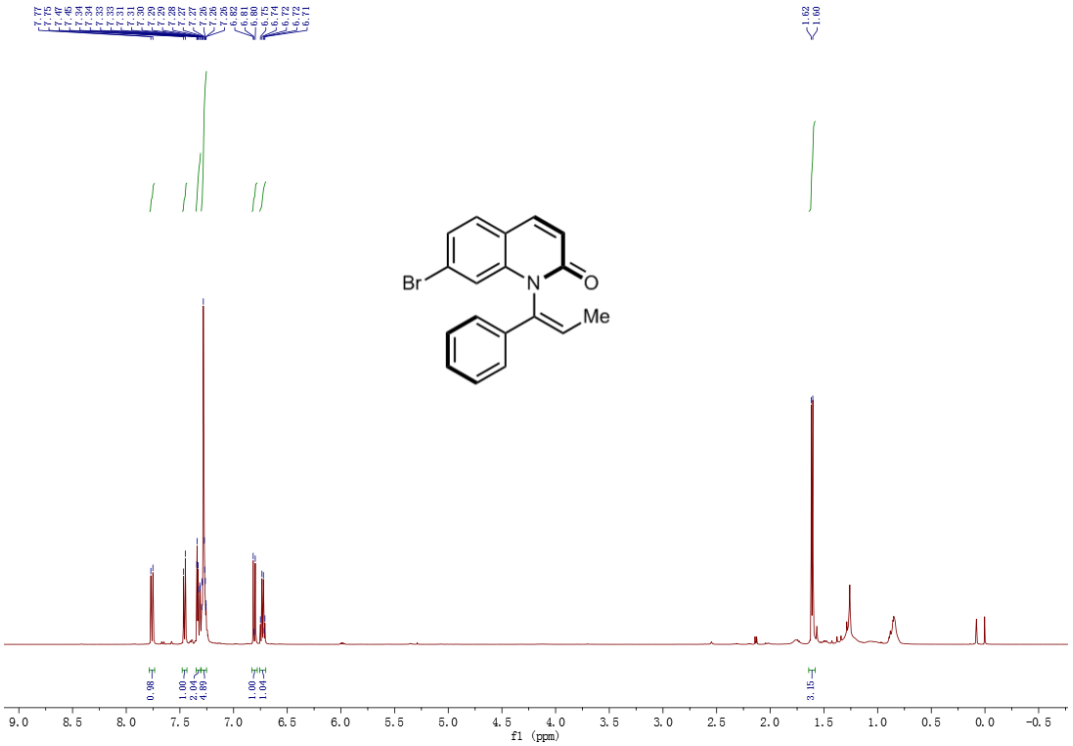
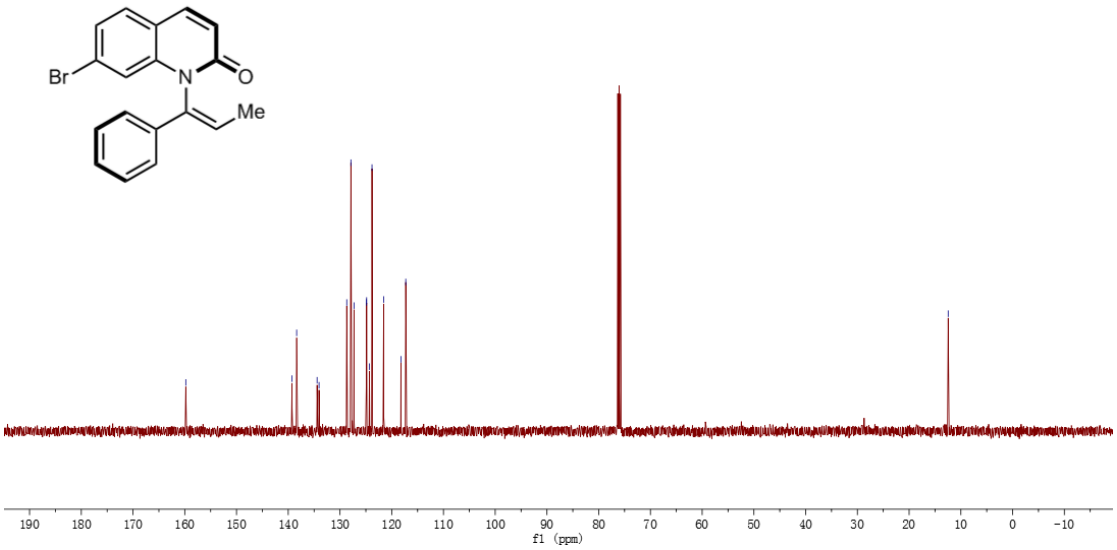


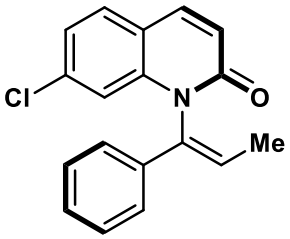




3r







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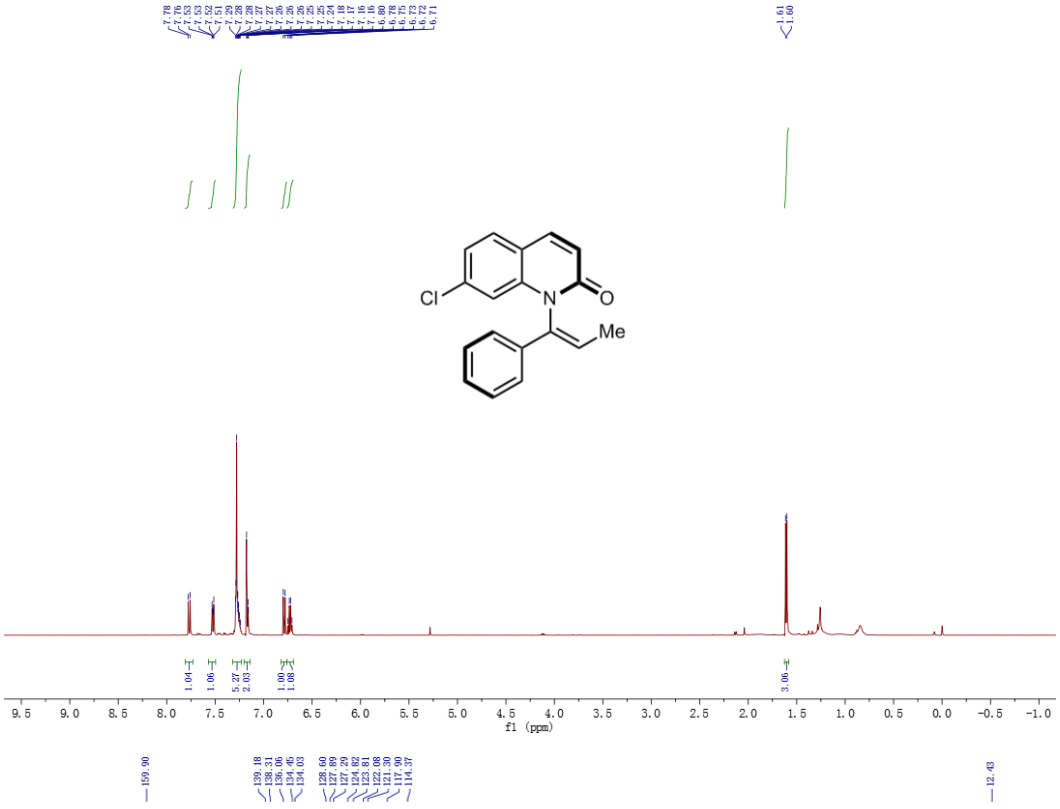
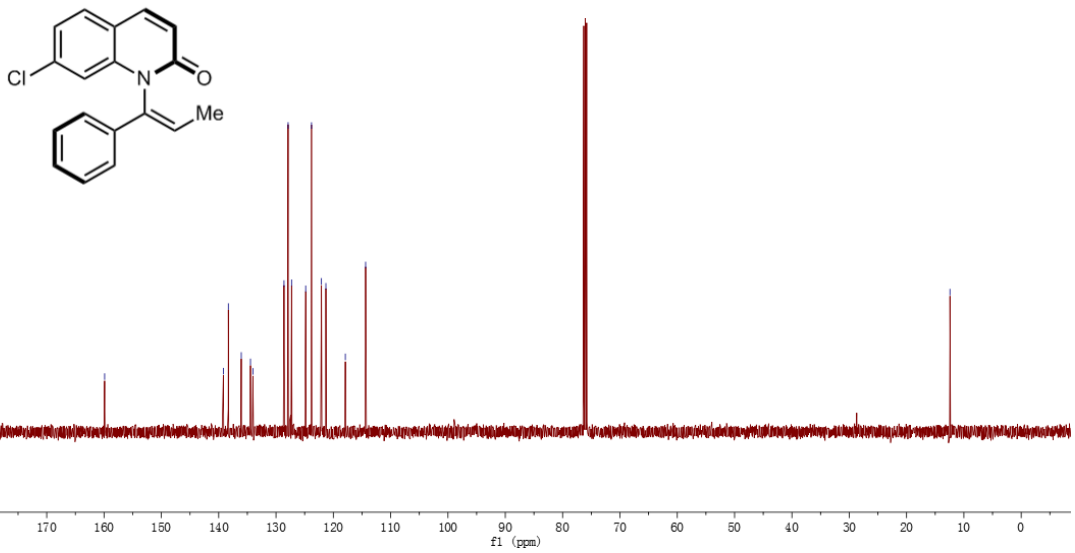
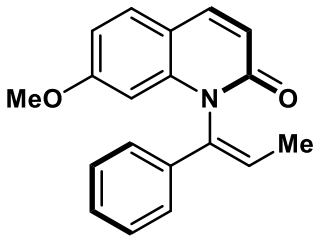
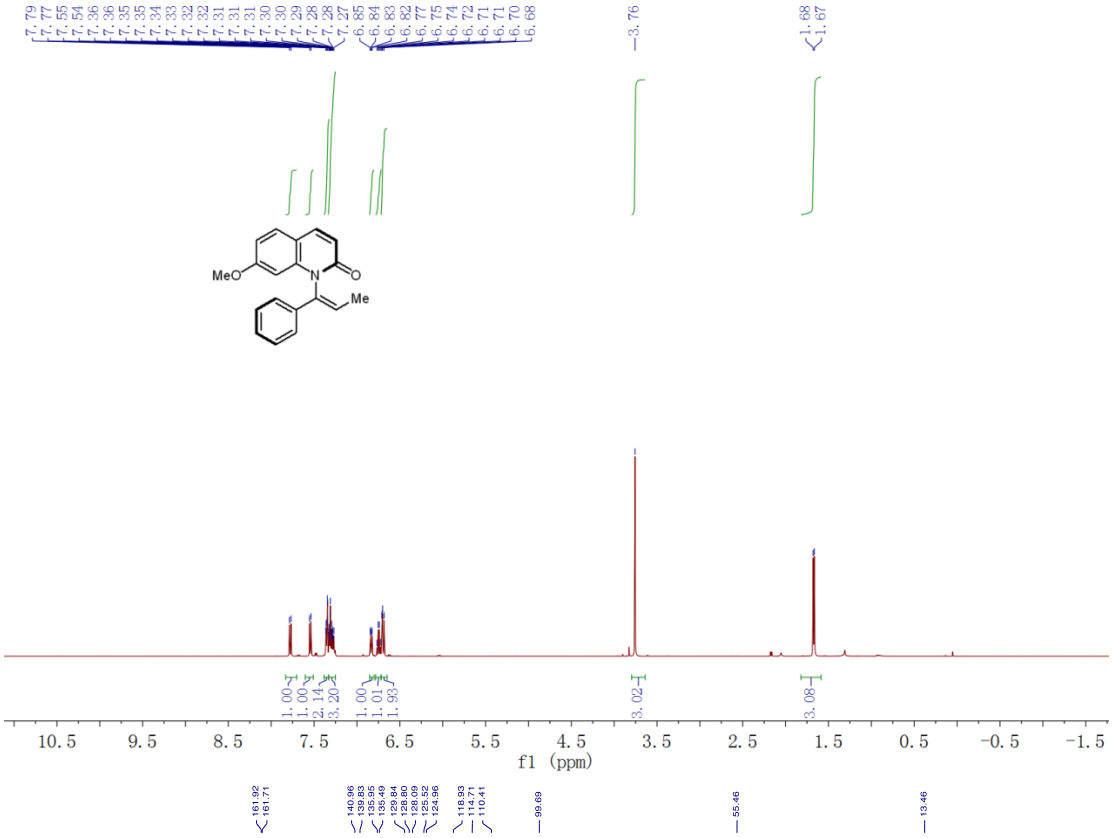





MeO
N
O
Me

3t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7.33
7.32
7.32
7.31
7.31
7.31
7.30
7.30
7.29
7.28
7.28
7.27
6.85
6.84
6.83
6.82
6.77
6.75
6.74
6.72
6.71
6.71
6.70
6.68
3.76
1.68
1.67
MeO
N
O
Me
1.00
1.00
2.14
3.20
1.00
1.01
1.93
3.02
3.08
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5
f1 (ppm)

161.92
161.71
140.96
139.83
135.95
135.49
129.84
128.80
128.09
125.52
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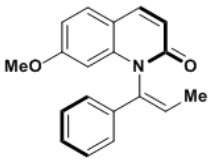
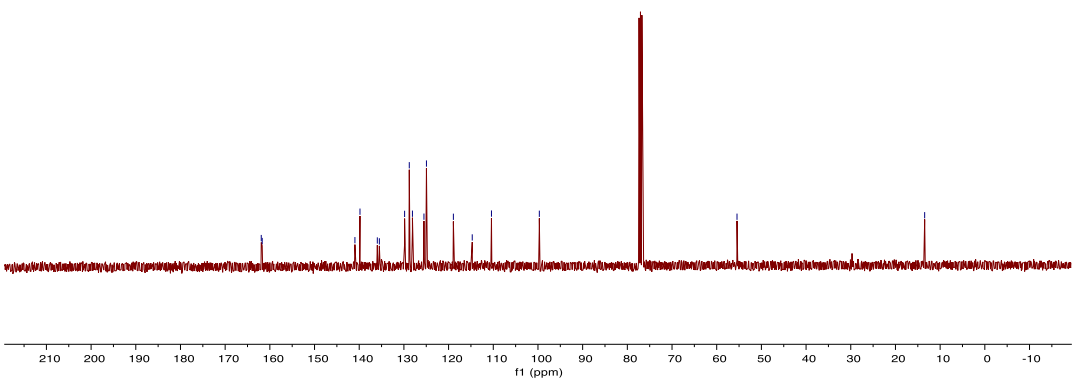
118.93
114.71
110.41
99.69
55.46
13.46


MeO
N
O
Me


210
200
190
180
170
160
150
140
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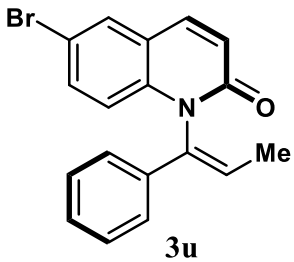
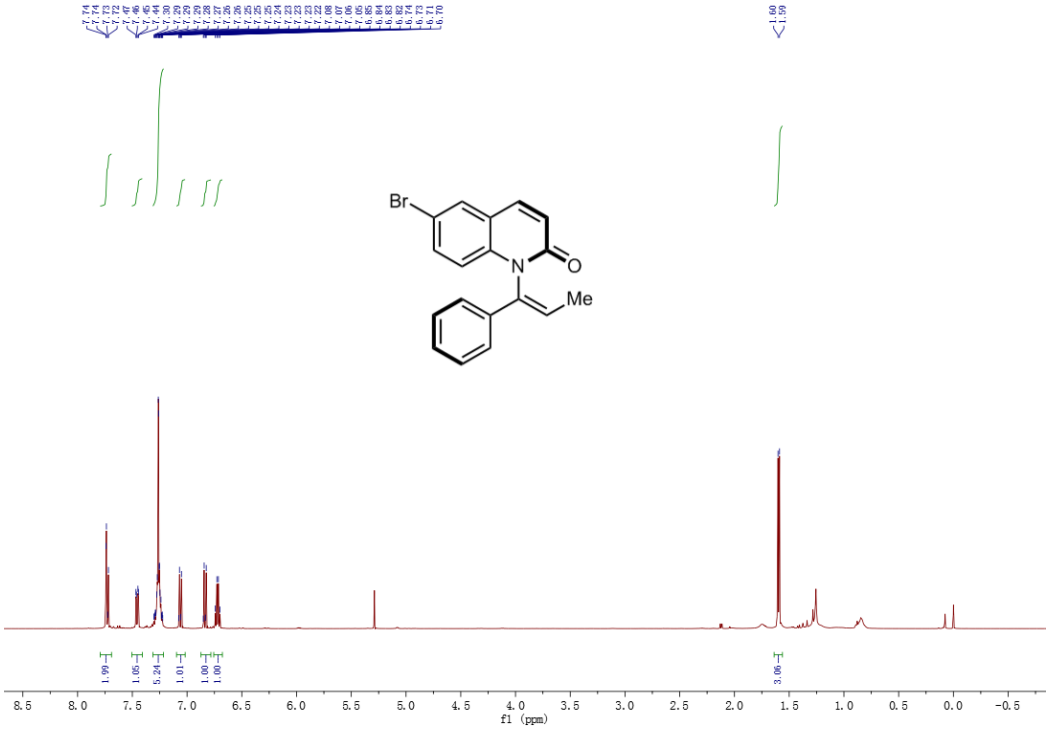
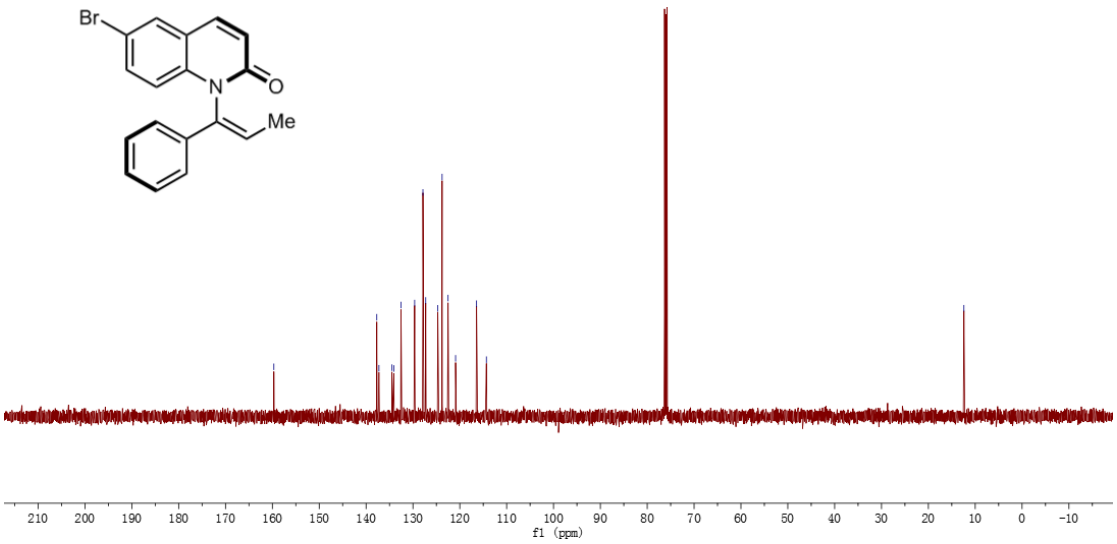
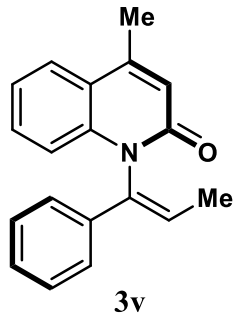
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



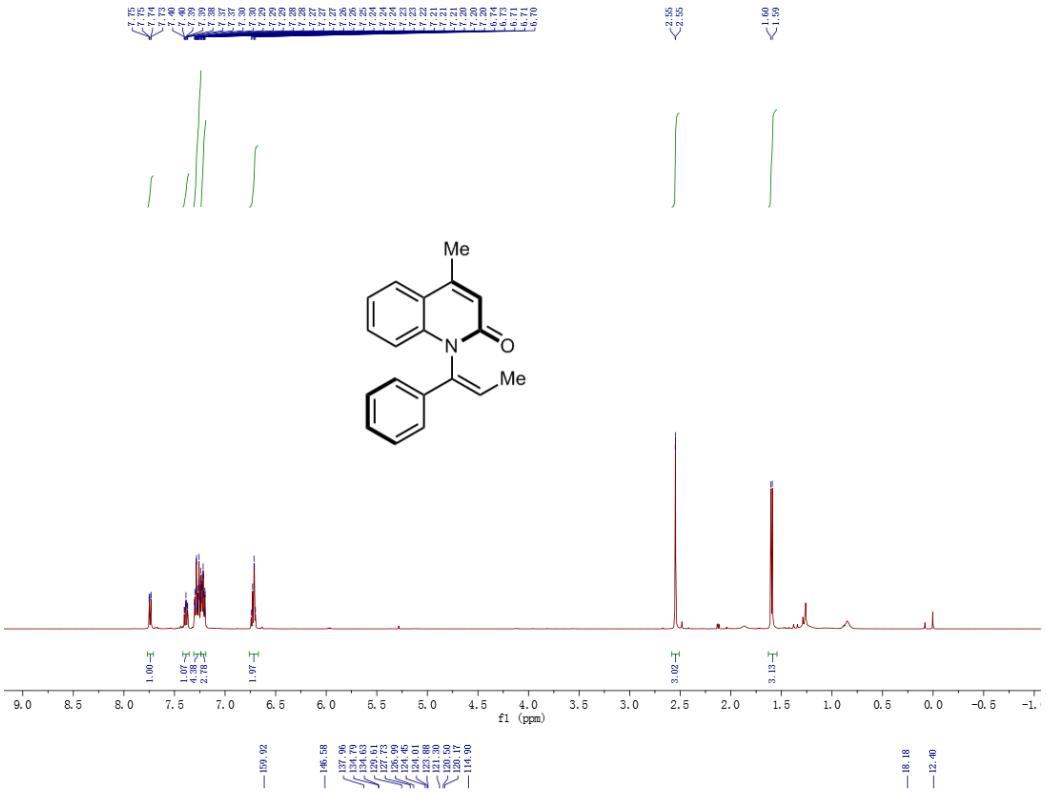
3u

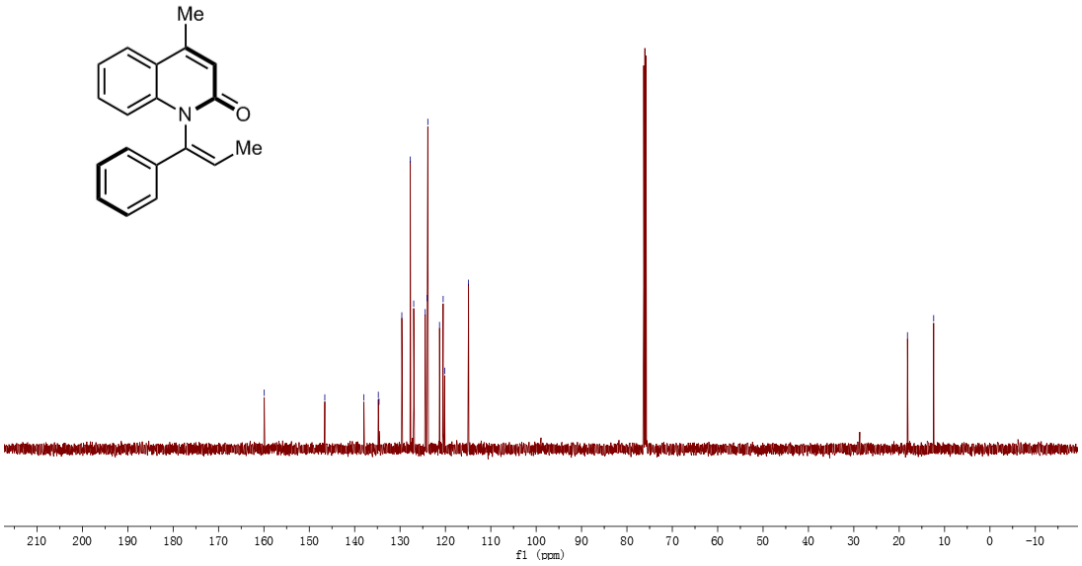


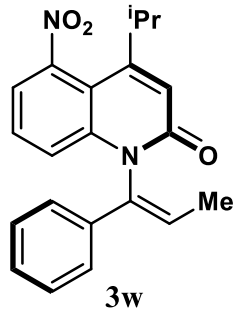




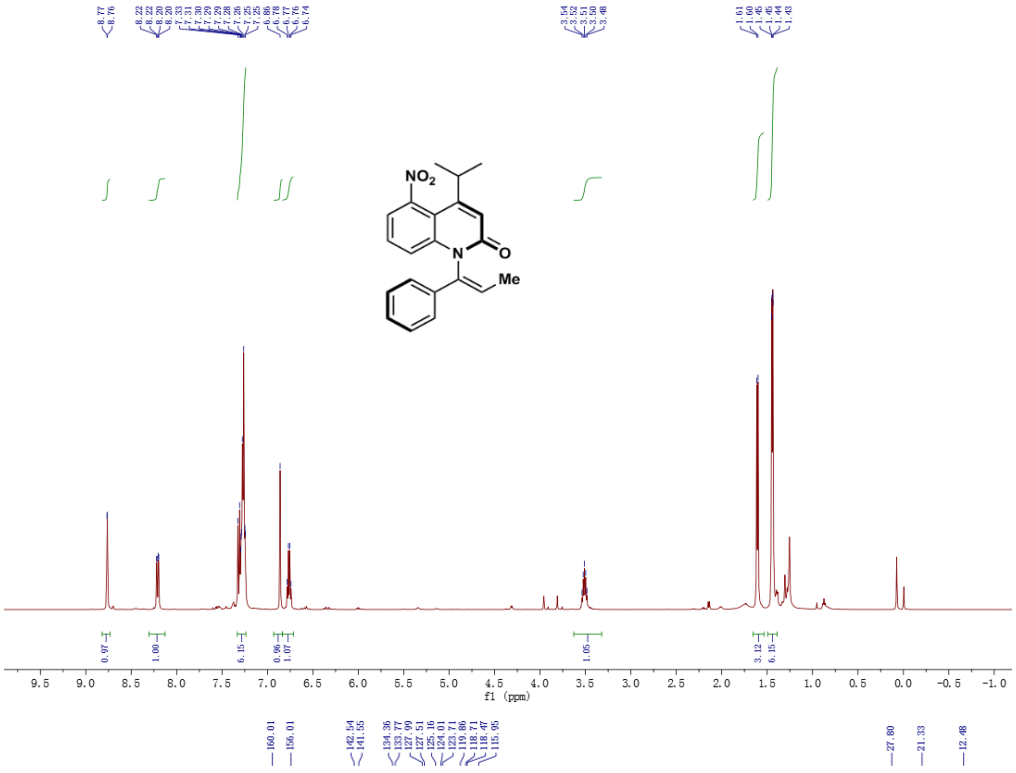
3v

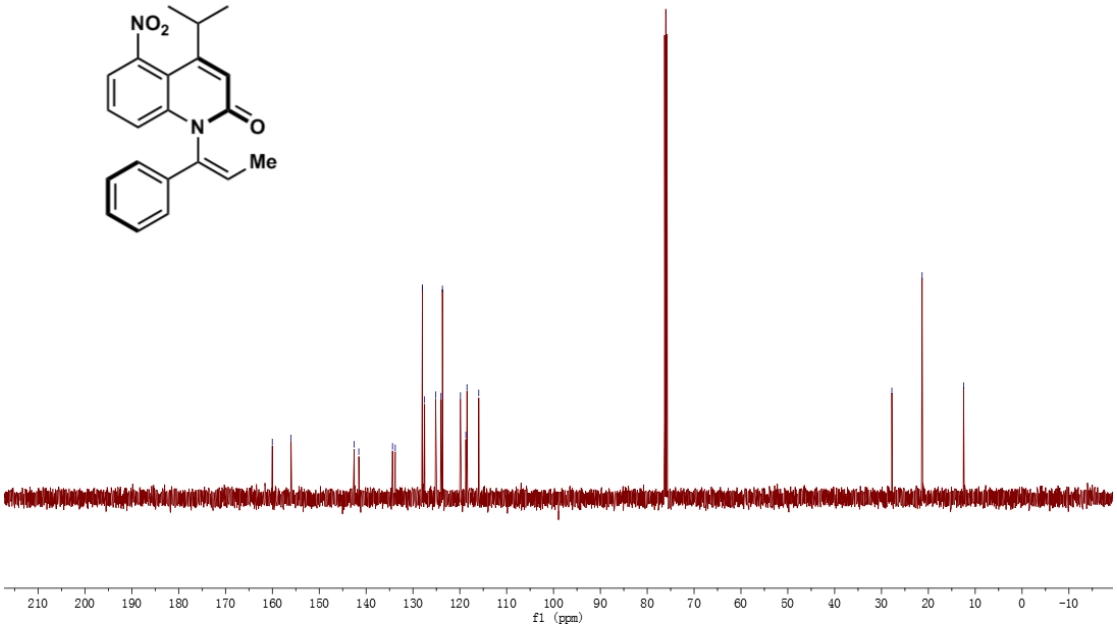


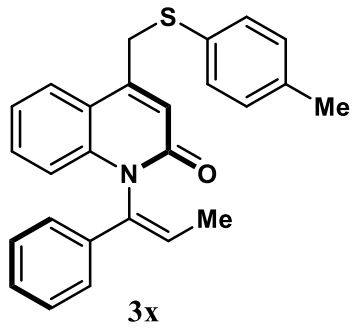




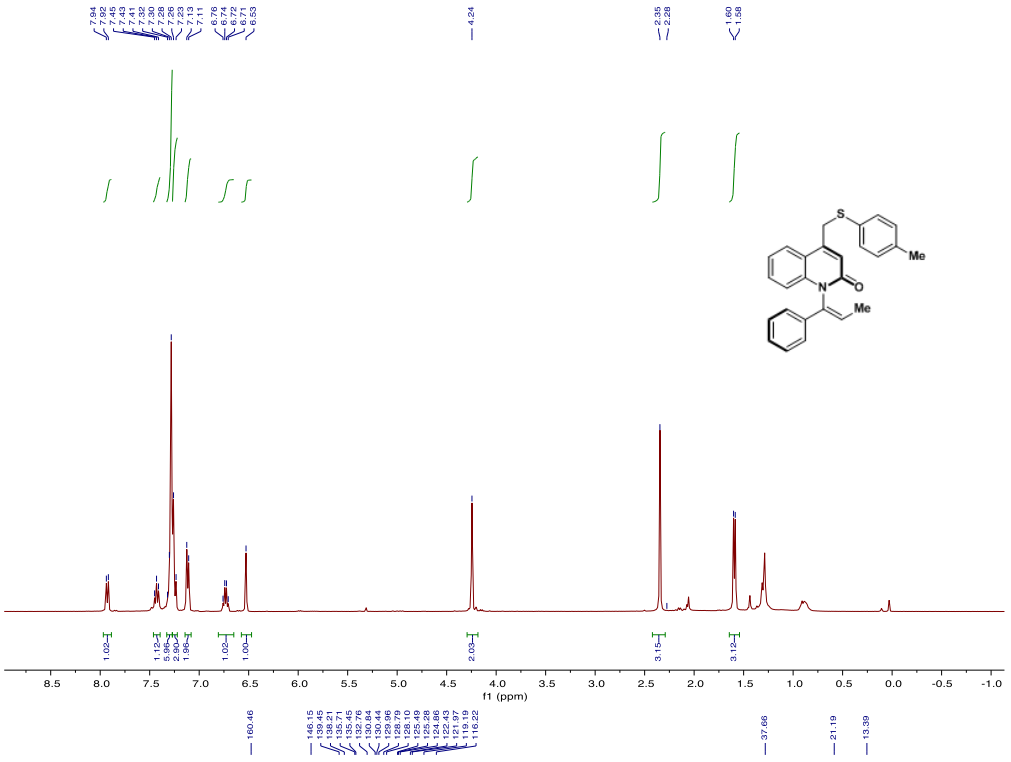
3w






S
Me
N
O
Me

3x


7.94
7.92
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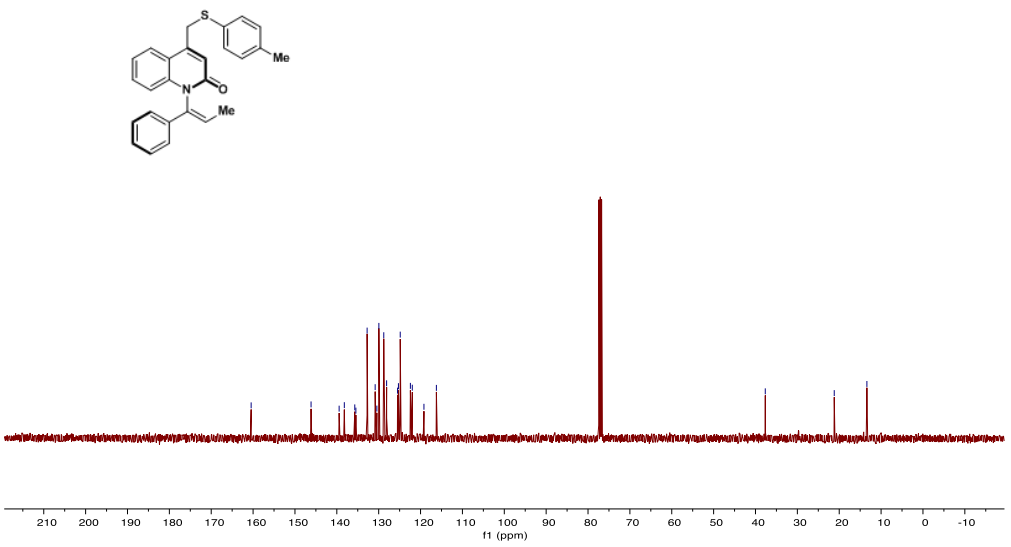
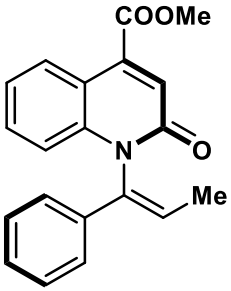
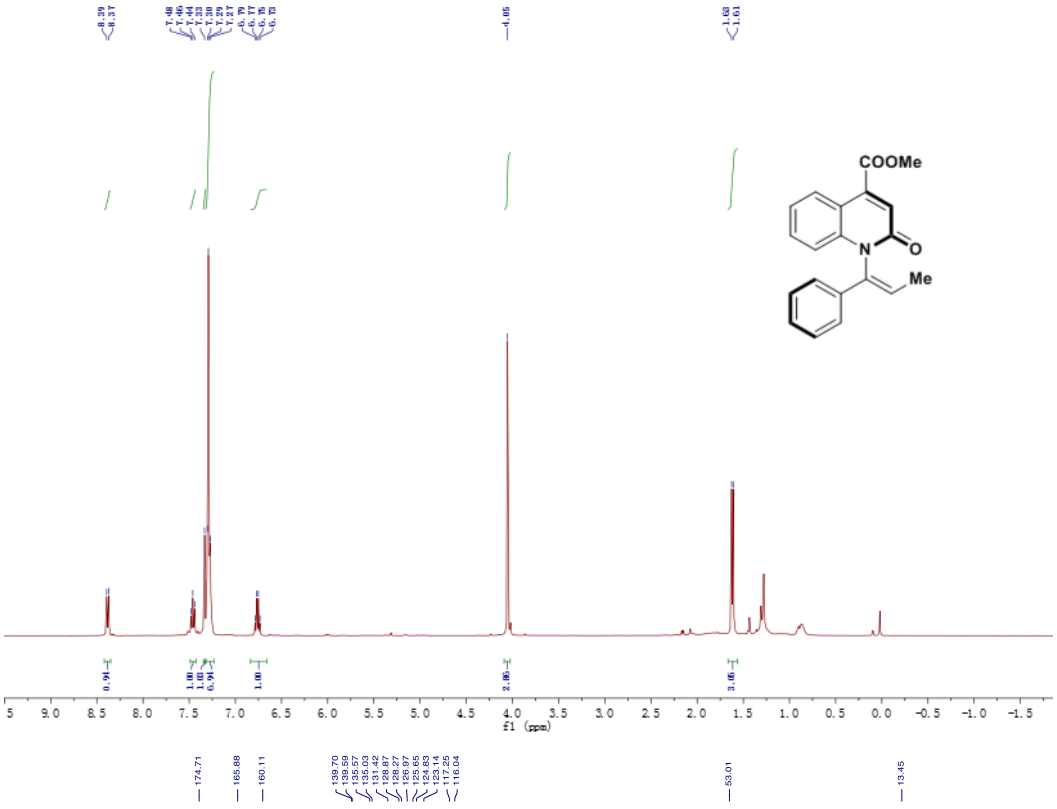
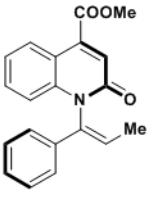
7.41
7.32
7.30
7.28
7.26
7.23
7.13
7.11
6.76
6.74
6.72
6.71
6.53
4.24
2.35
2.28
1.60
1.58
1.02
1.12
0.88
2.90
1.96
1.02
1.00
2.03
3.15
3.12
f1 (ppm)
160.46
146.15
139.45
138.21
135.71
135.45
132.76
130.84
130.44
129.96
128.79
128.10
127.49
125.28
124.86
122.43
121.97
119.19
116.22
37.66
21.19
13.39

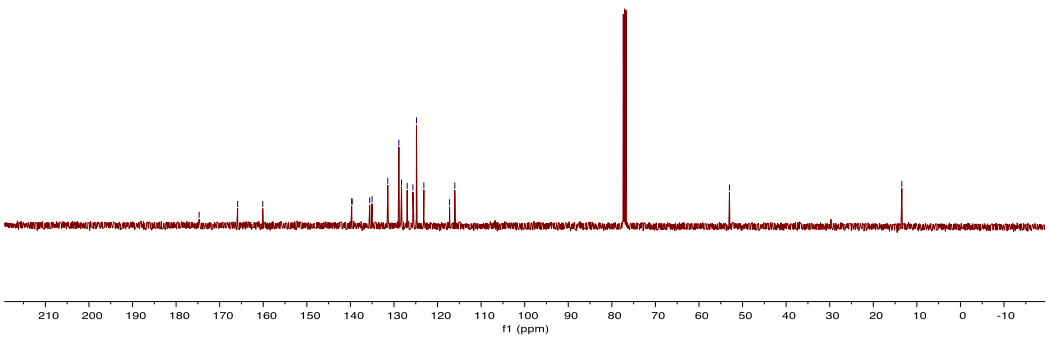

f1 (ppm)

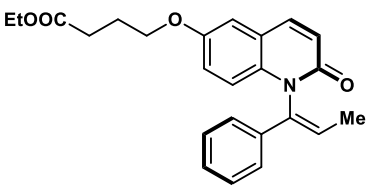


3y









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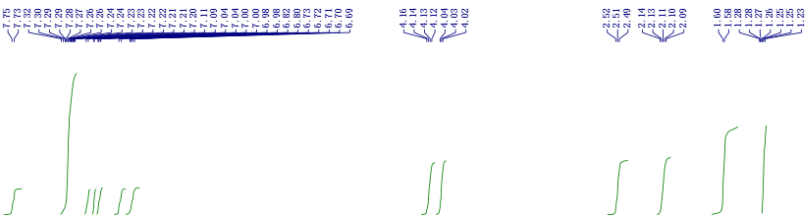
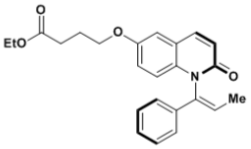
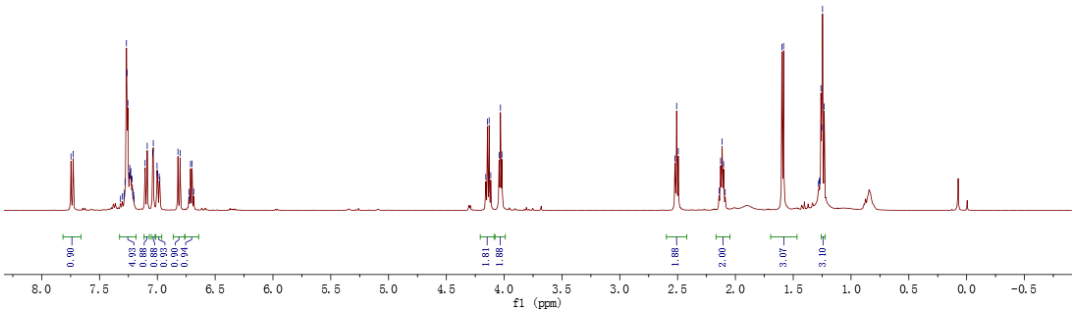
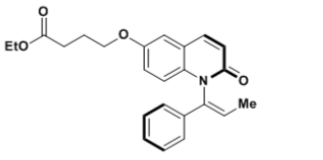
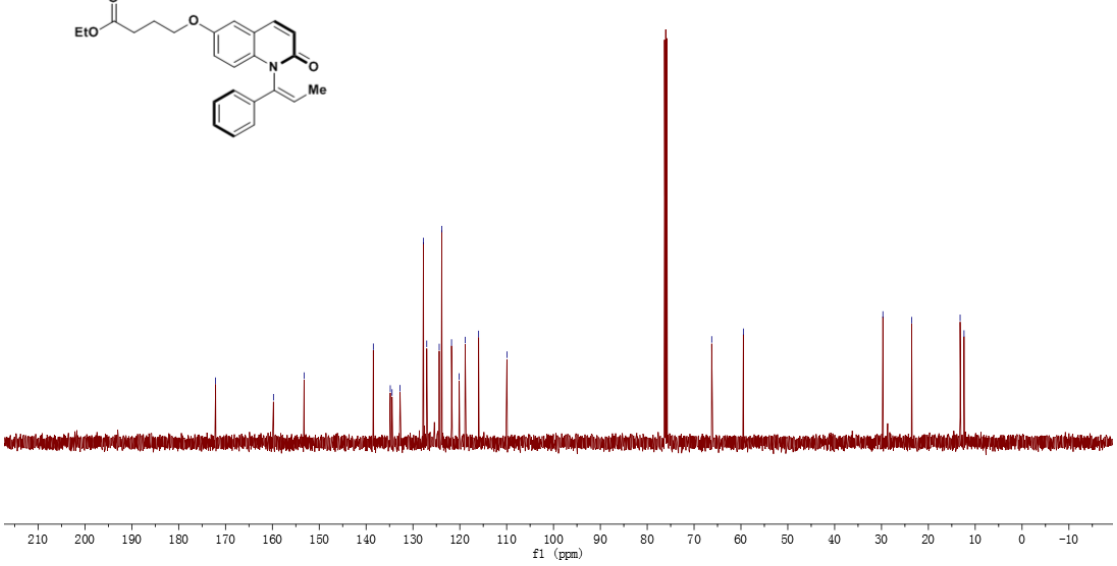
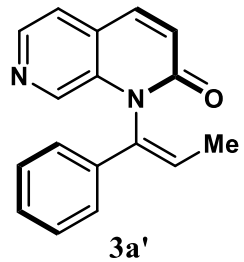




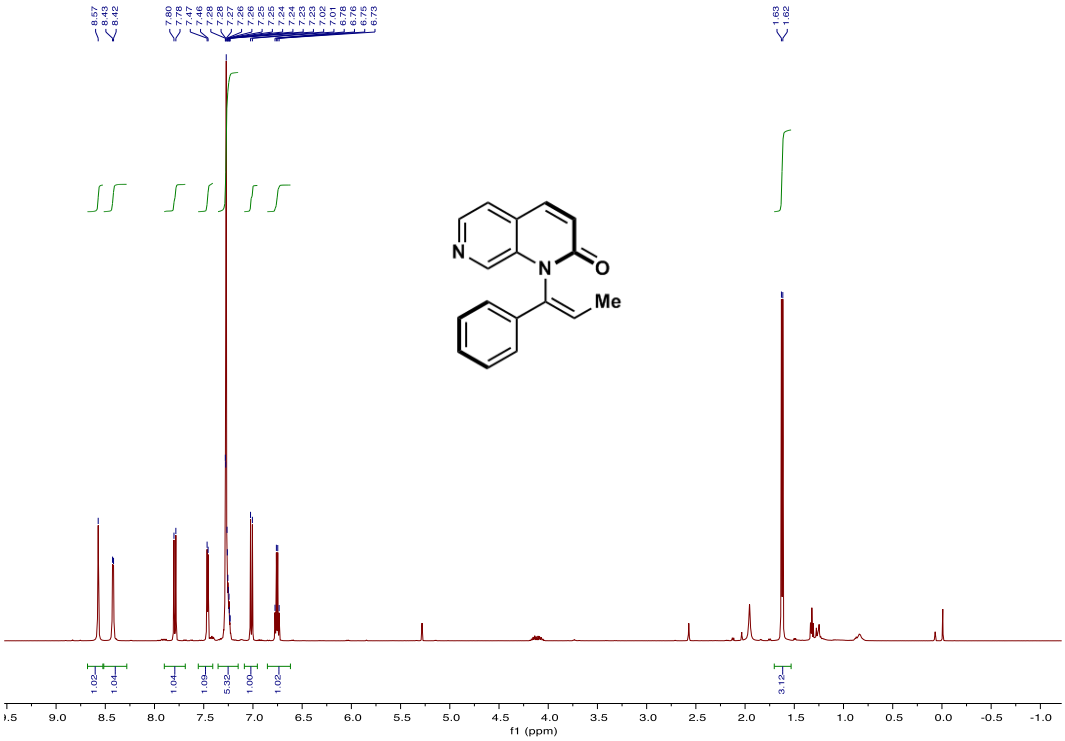







N
N
O
Me

3a'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7.28
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7.25
7.24
7.24
7.23
7.23
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7.01
6.78
6.76
6.75
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1.02
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1.04
1.09
5.32
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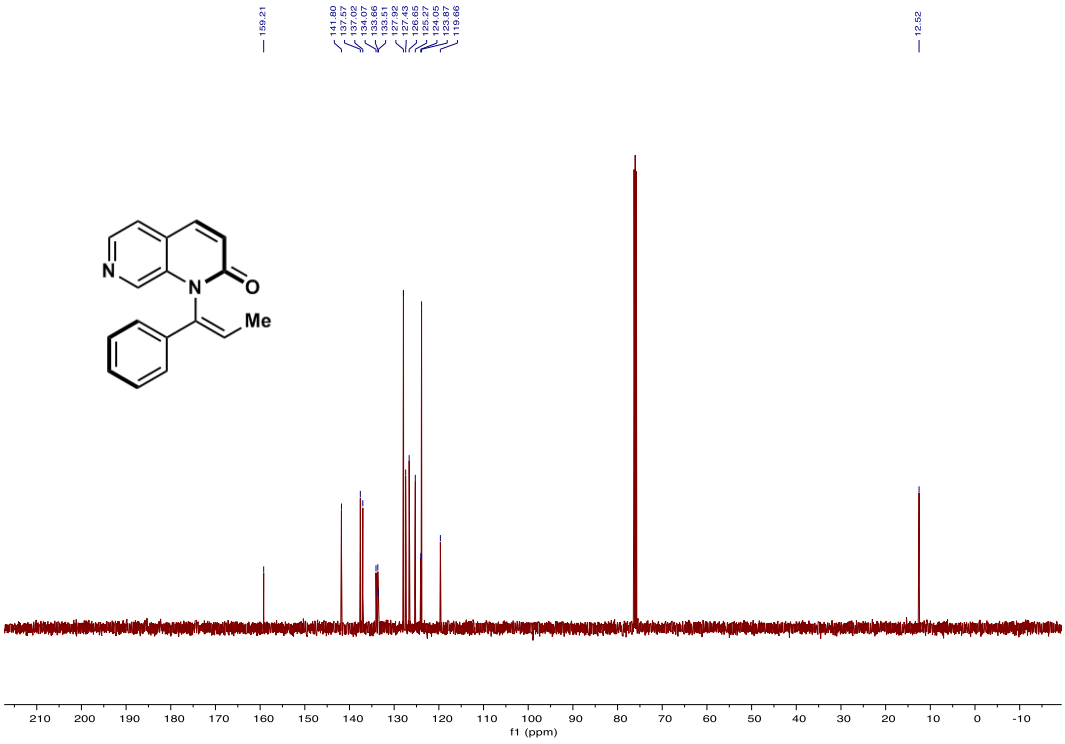
1.02
3.12
f1 (ppm)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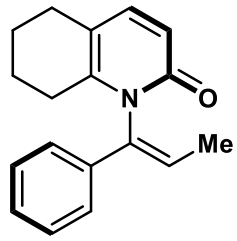
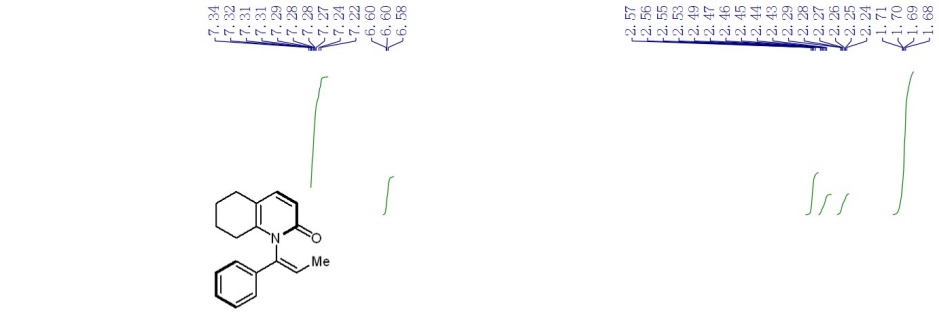
127.46
126.65
126.27
124.05
122.87
119.66
12.52
f1 (ppm)


N
O
Me

3b'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2.46
2.45
2.44
2.43
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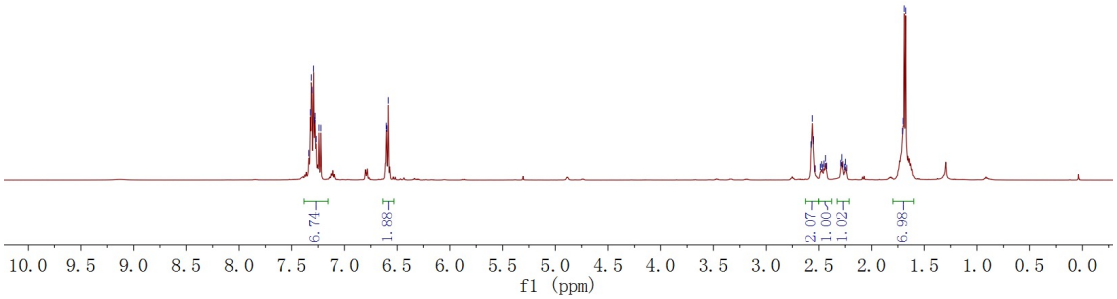
2.27
2.26
2.25
2.24
1.71
1.70
1.69
1.68
N
O
Me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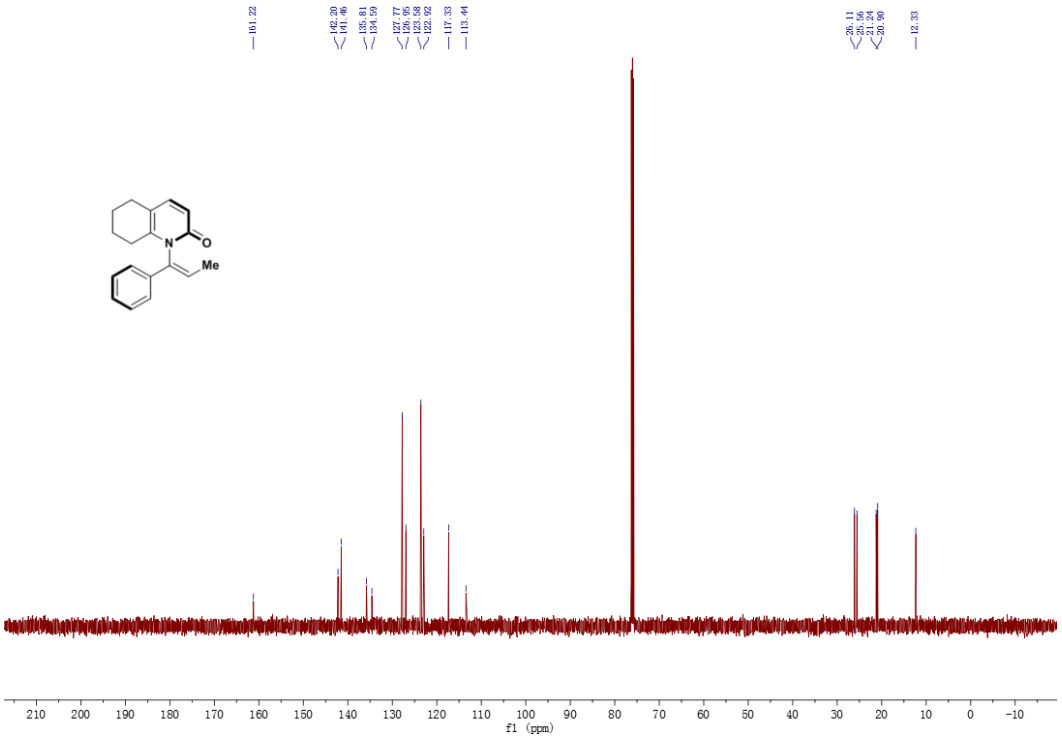
1.88
2.07
1.00
1.02
6.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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141.46
135.81
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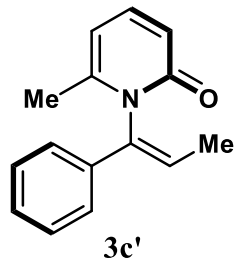
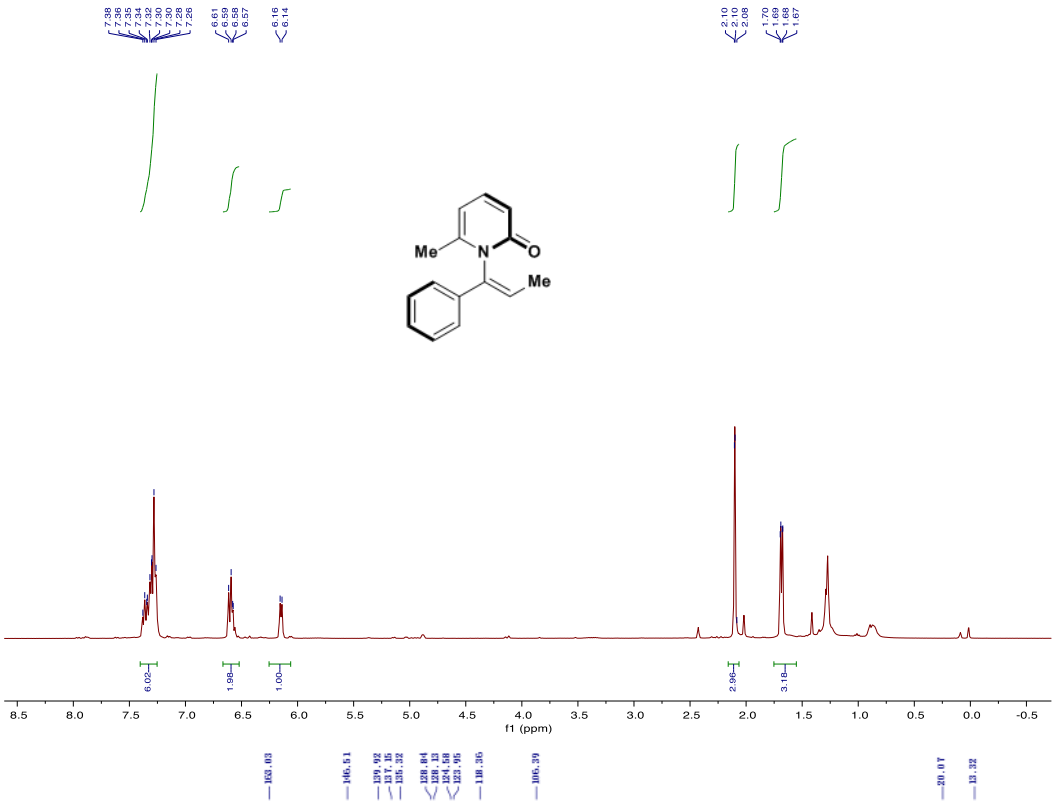
127.77
126.95
125.98
122.92
117.33
113.44
26.11
25.56
21.24
20.80
12.33
N
O
Me
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Me
N
O
Me

3c'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7.34
7.32
7.30
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7.28
7.26
6.61
6.59
6.58
6.57
6.16
6.14
2.10
2.10
2.08
1.70
1.69
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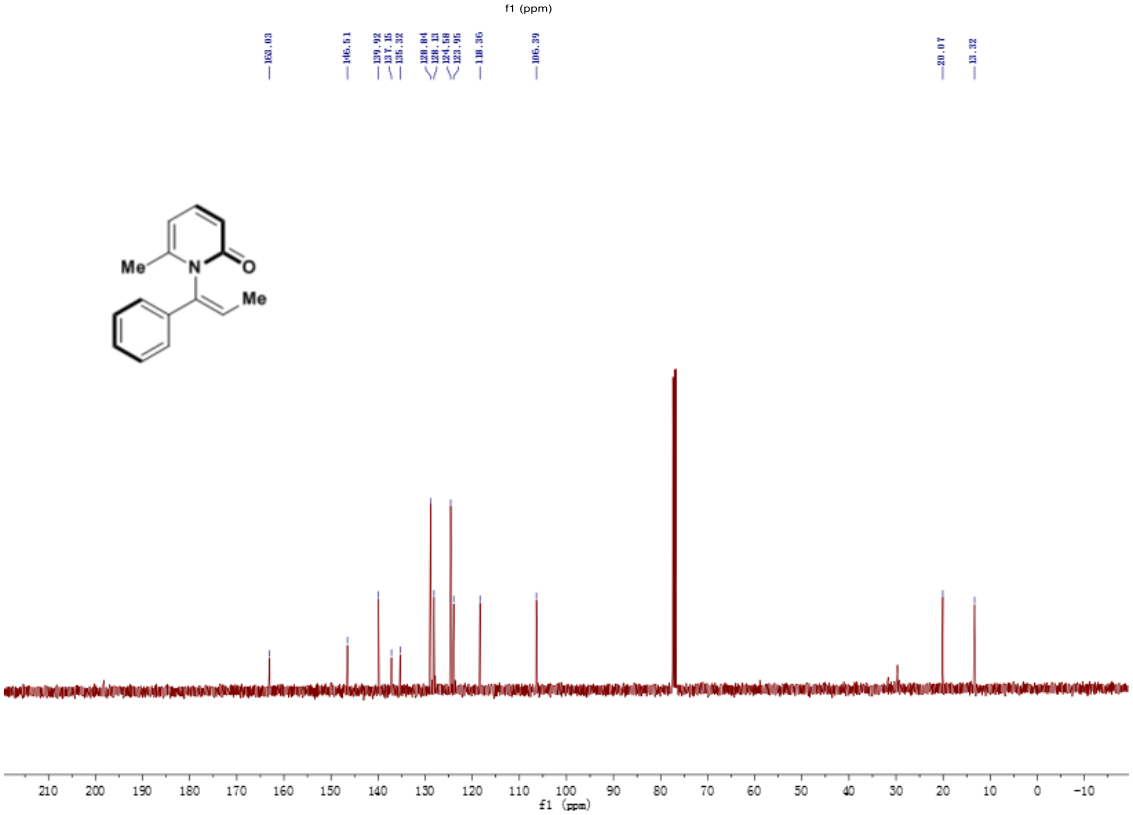
1.67
Me
N
O
Me
6.02
1.98
1.00
2.96
3.18
f1 (ppm)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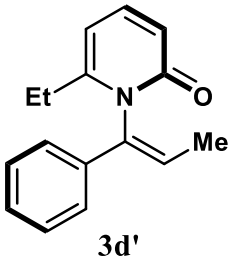
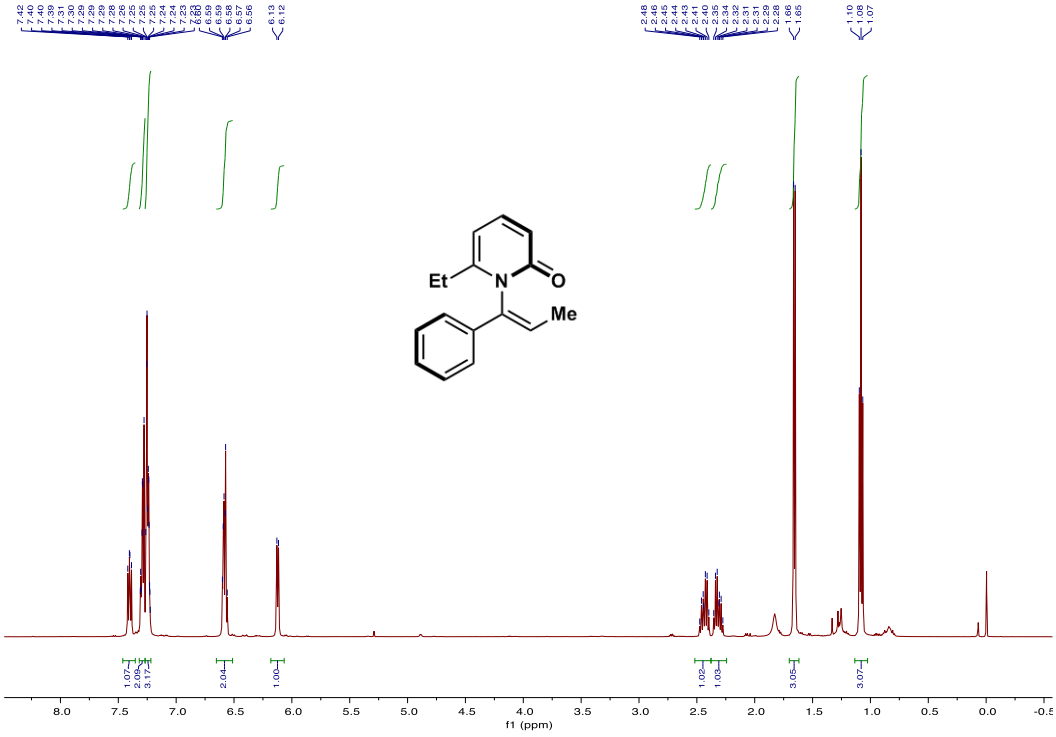
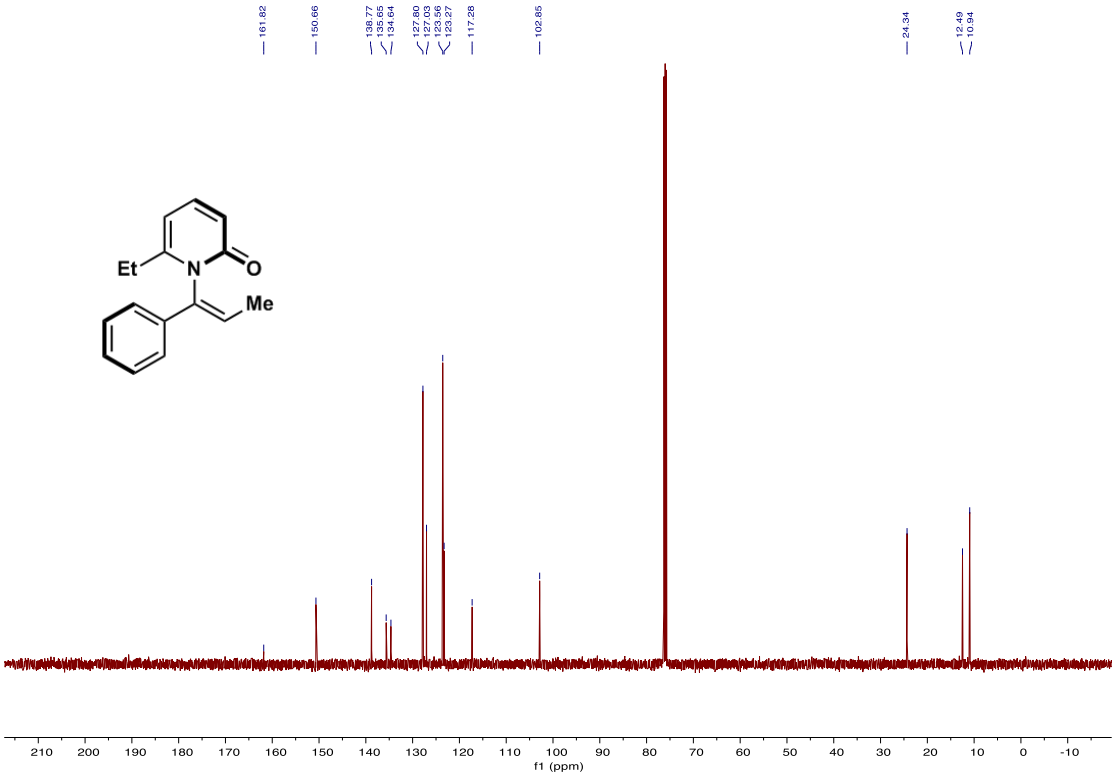
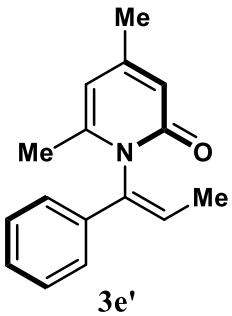
124.56
123.95
118.36
106.39
20.07
13.32
Me
N
O
Me
f1 (ppm)



3d'







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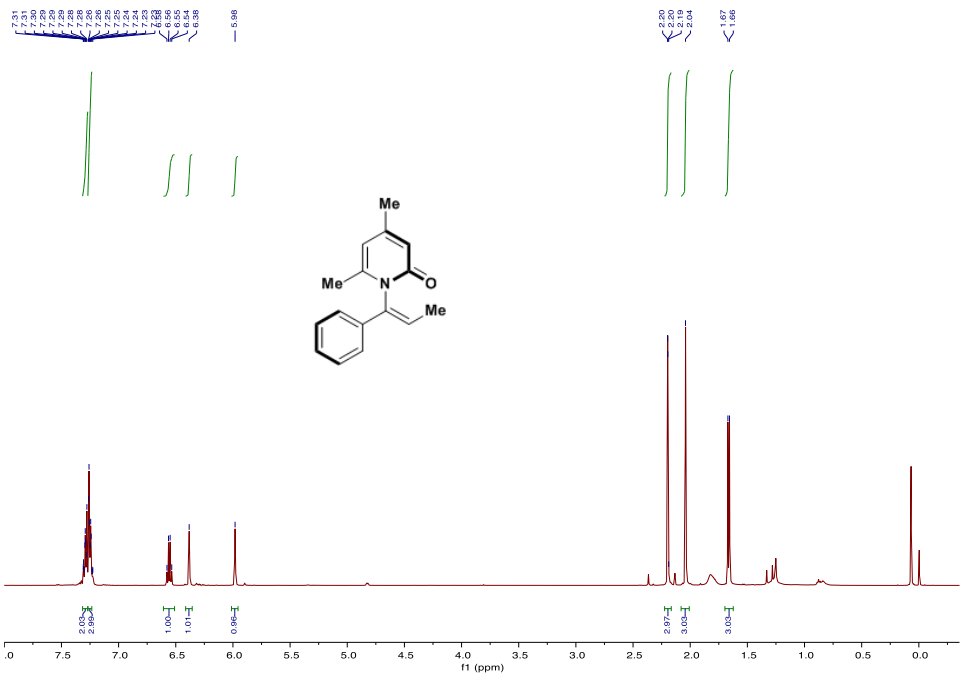
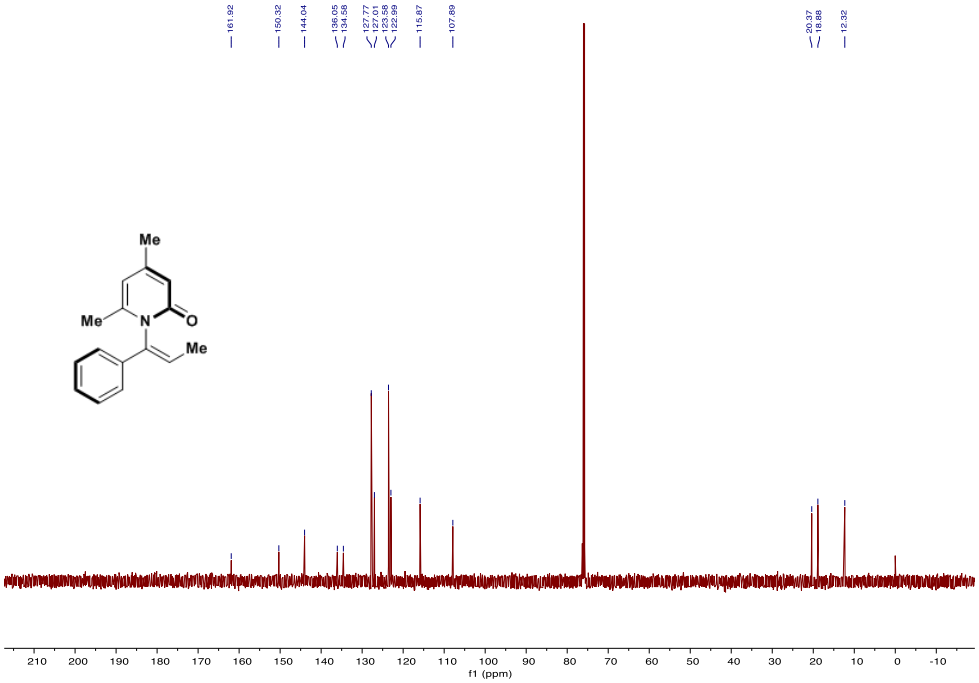
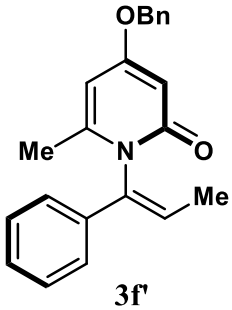
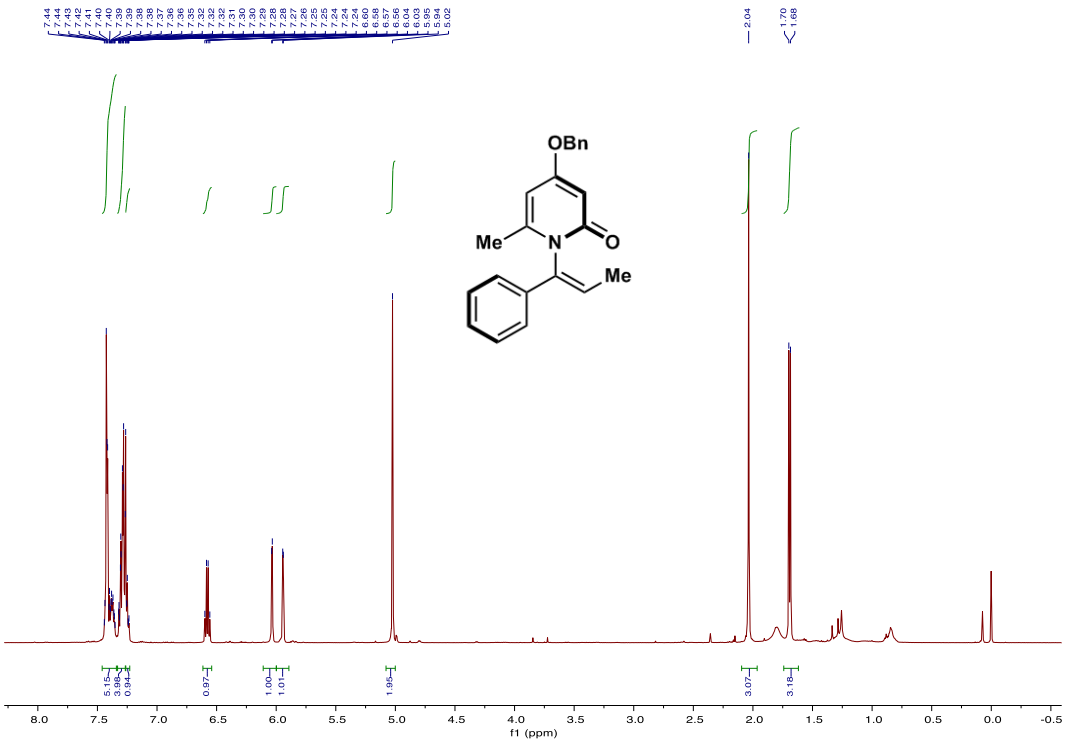
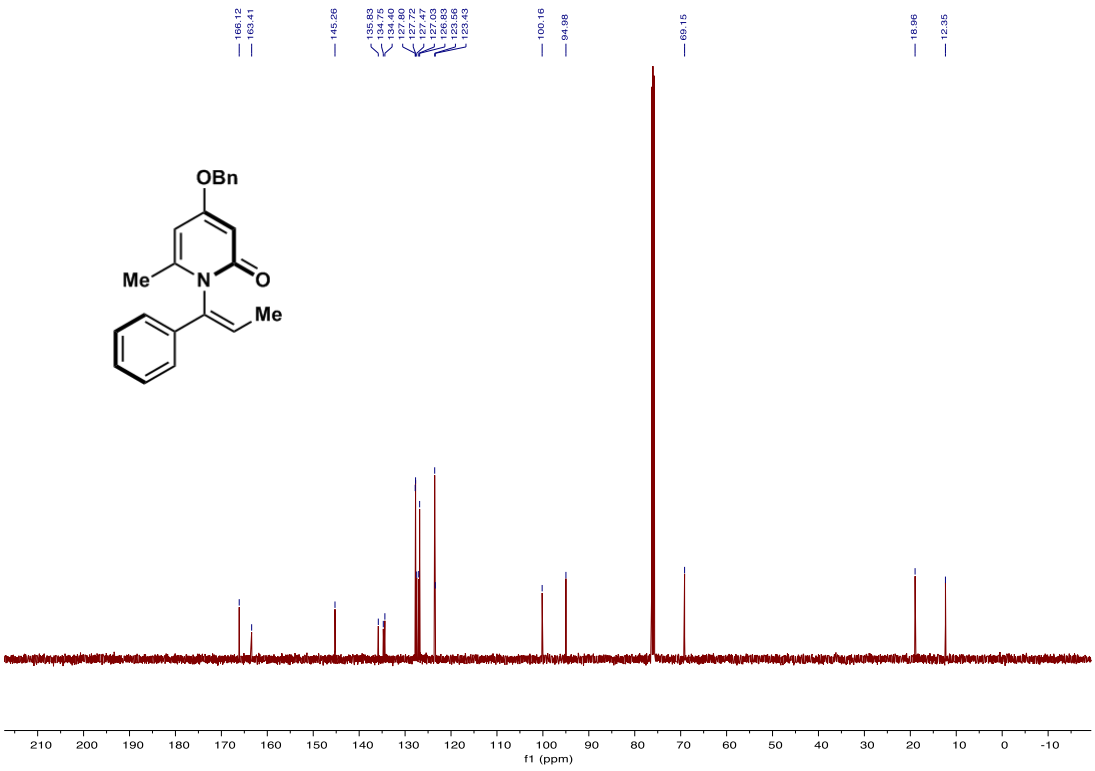


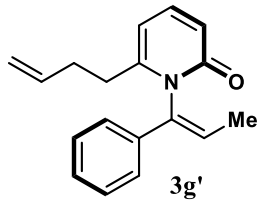




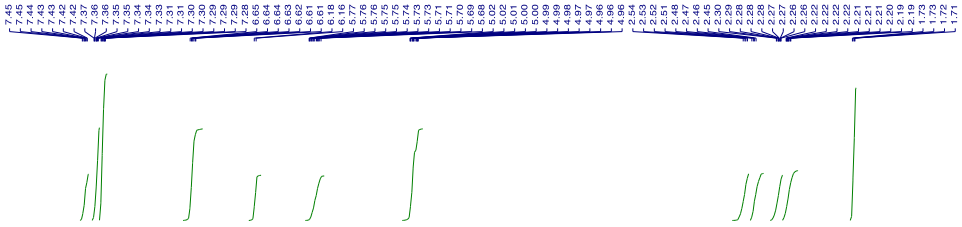
3f'

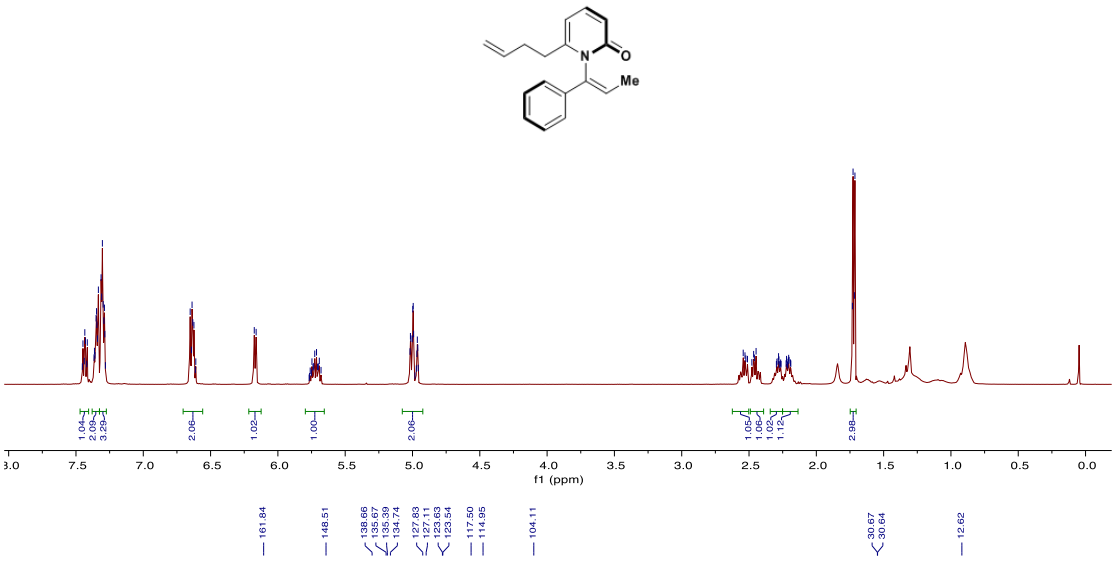


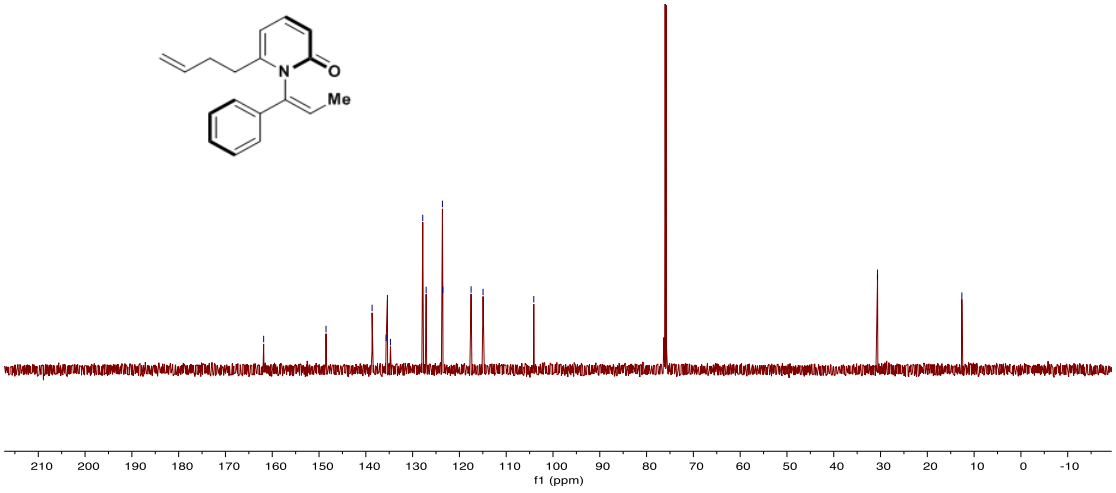


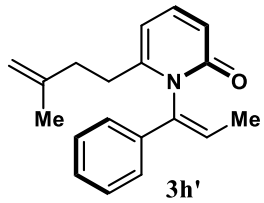


3g'

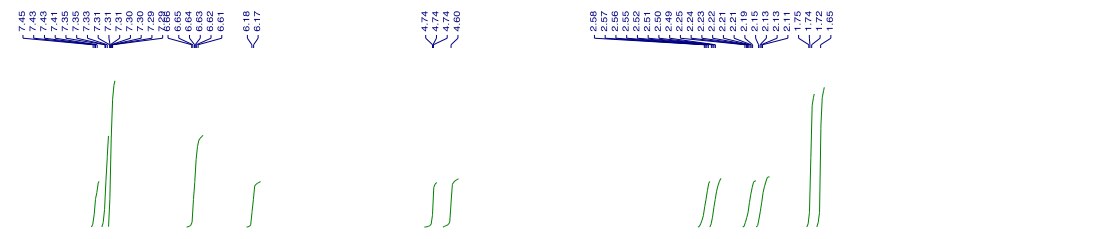


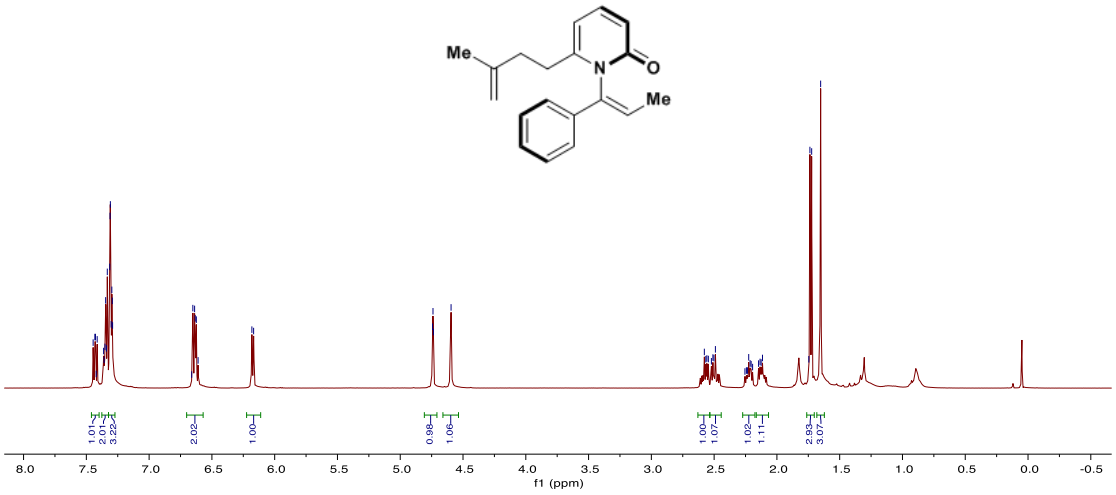


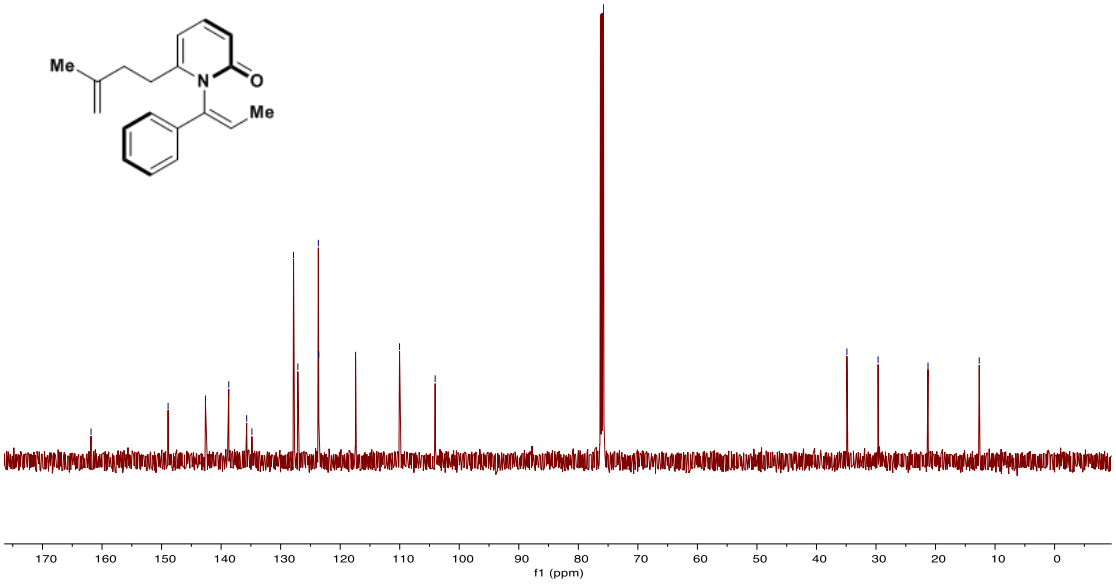


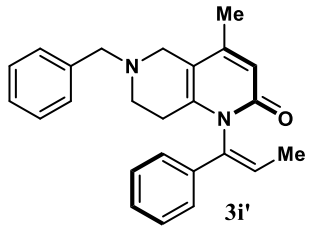


3h'

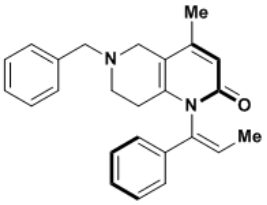


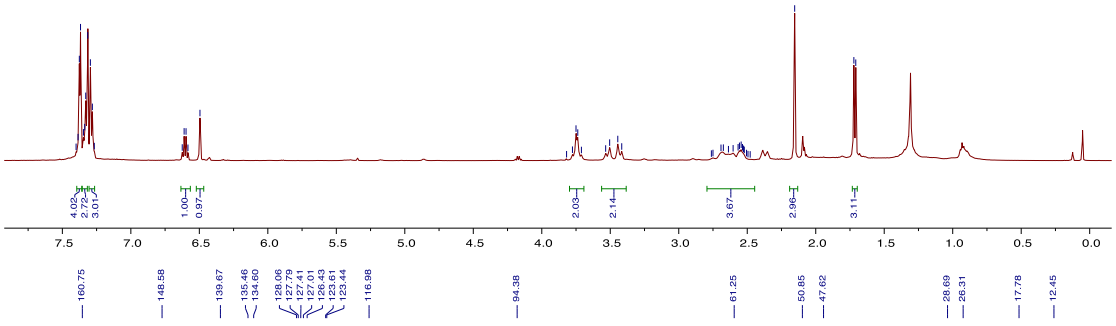


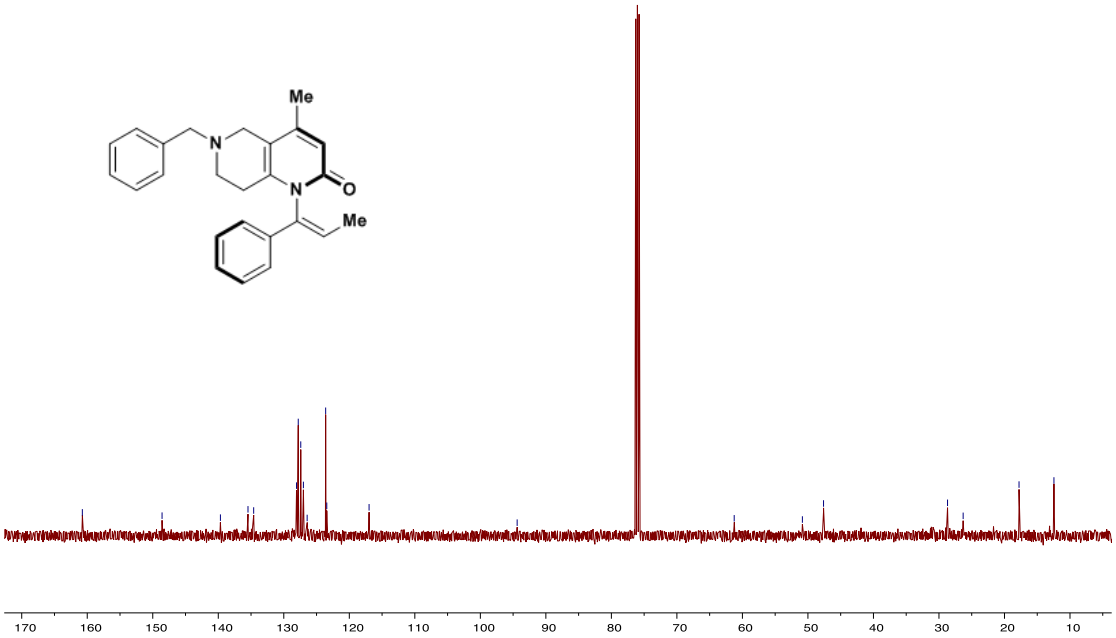


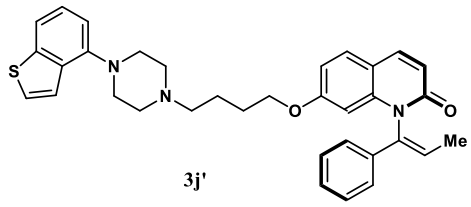


3i'









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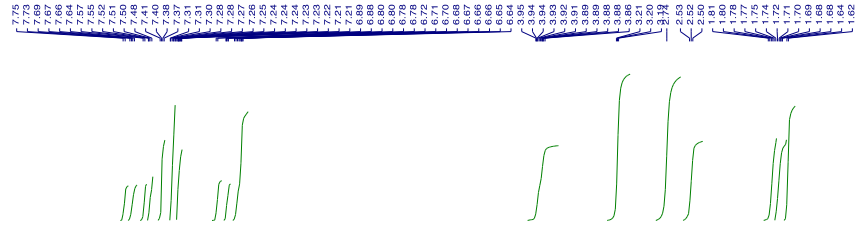
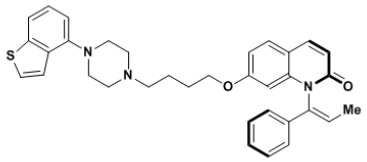
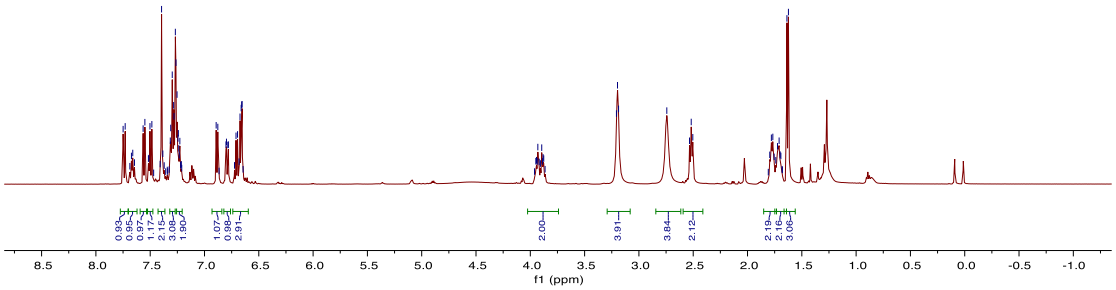
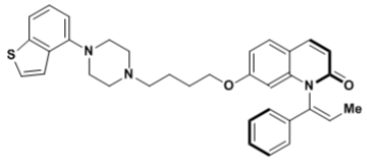
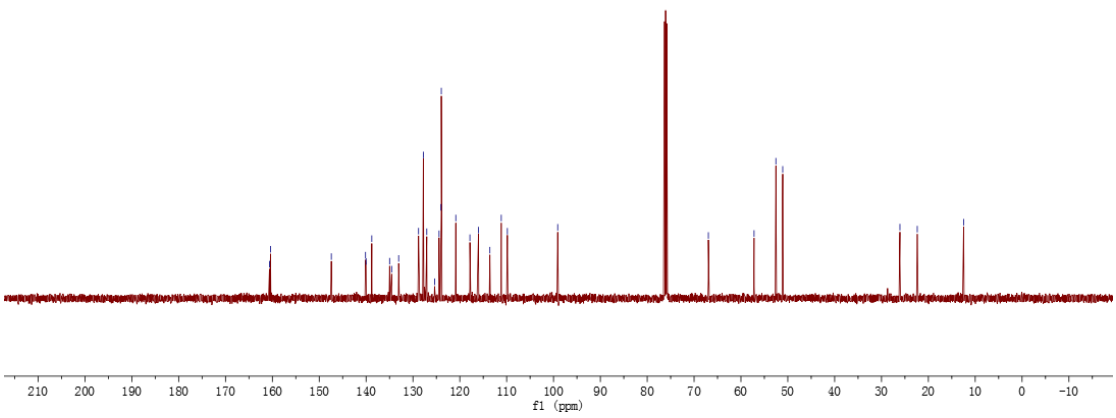
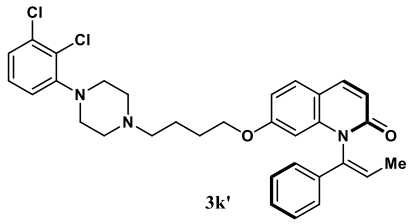




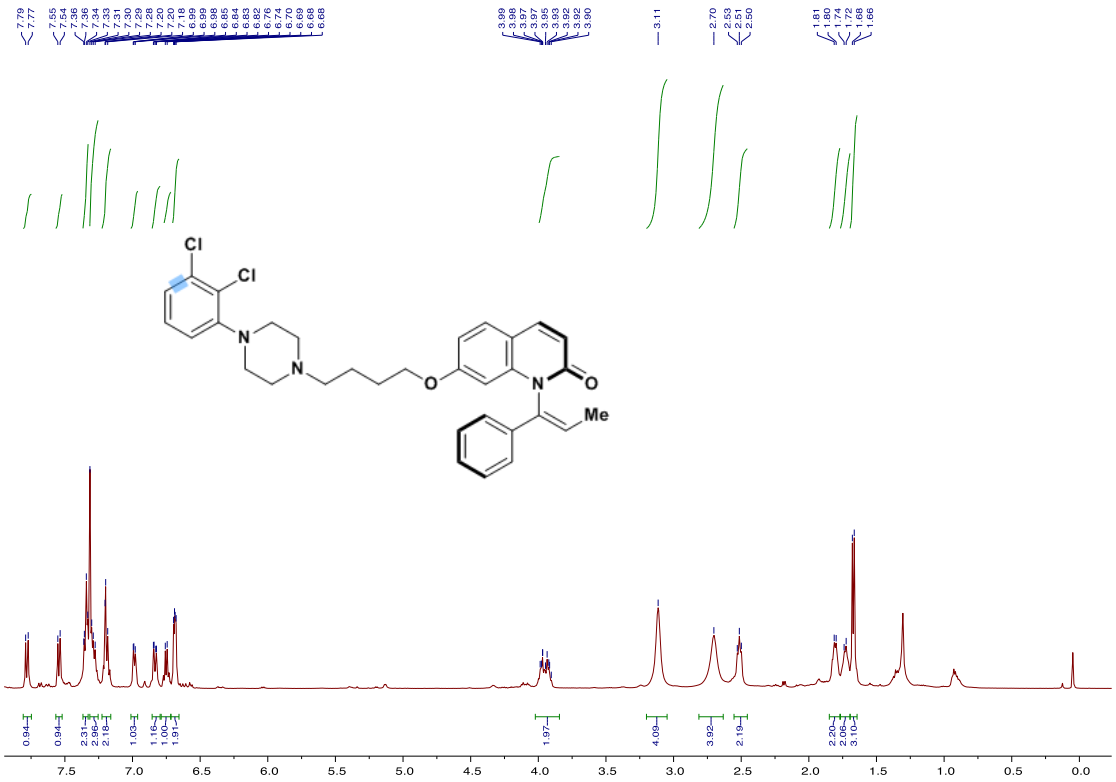







Cl
Cl
N
N
O
N
O
Me

3k'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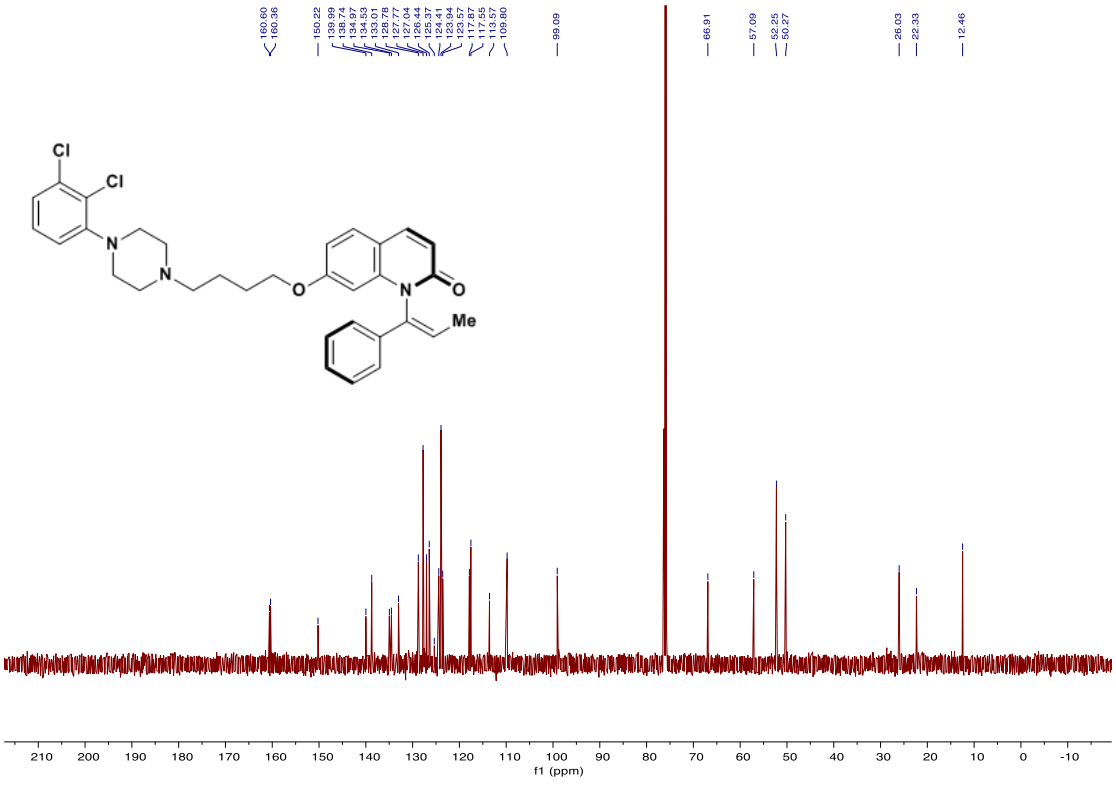
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26.03
22.33
12.46
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Cl
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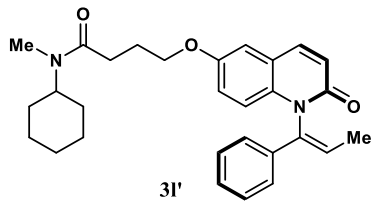
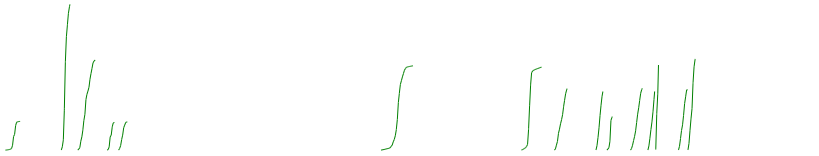
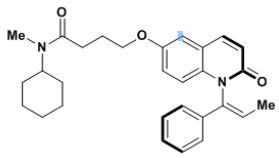
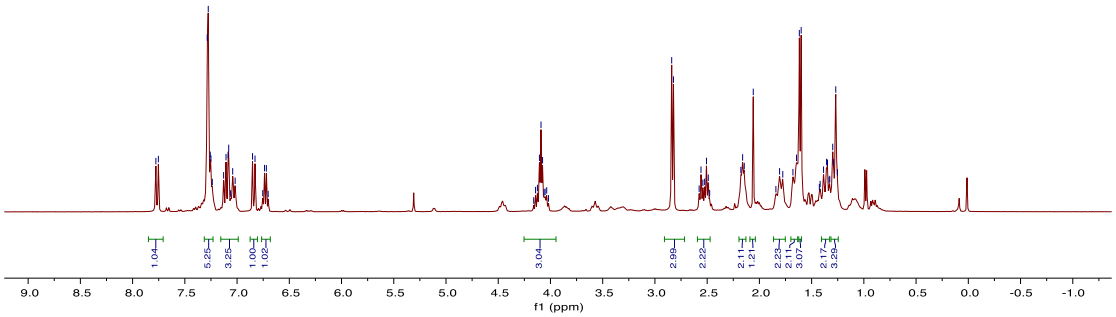
N
O
N
O
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Me
N
O
O
O
N
O
Me

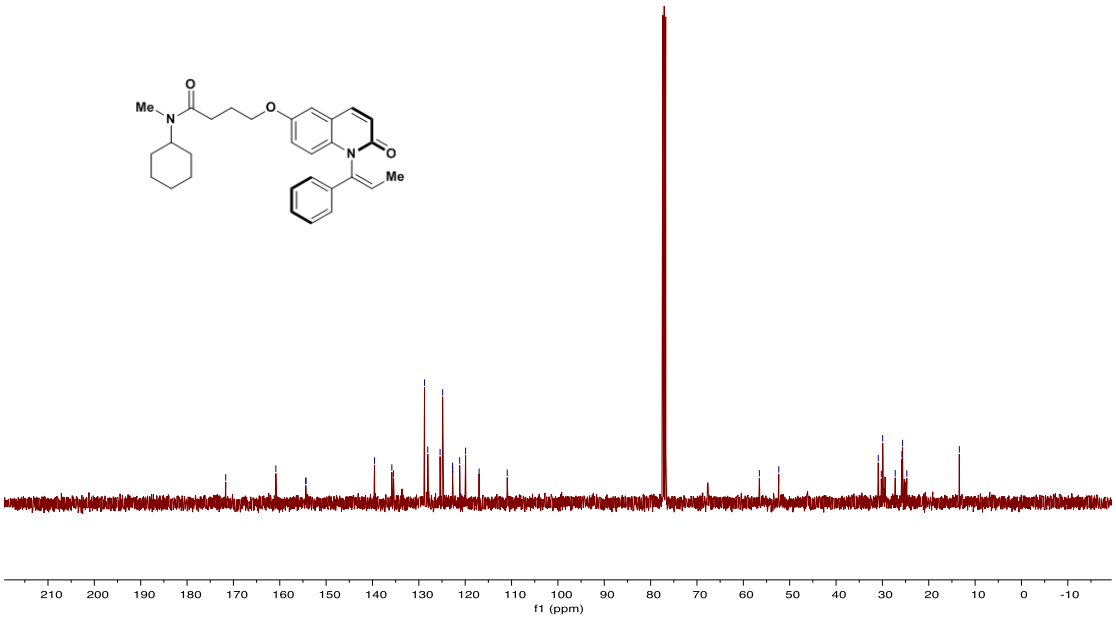
3l'

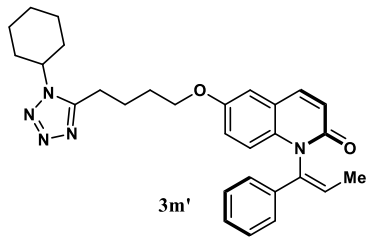



Me
N
O
O
O
N
O
Me

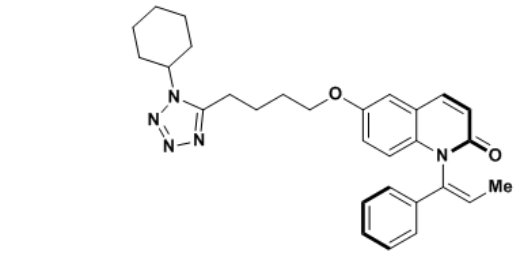

1.04
5.25
3.25
1.00
1.02
3.04
2.99
2.22
2.11
1.21
2.23
2.11
3.07
2.17
3.29
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

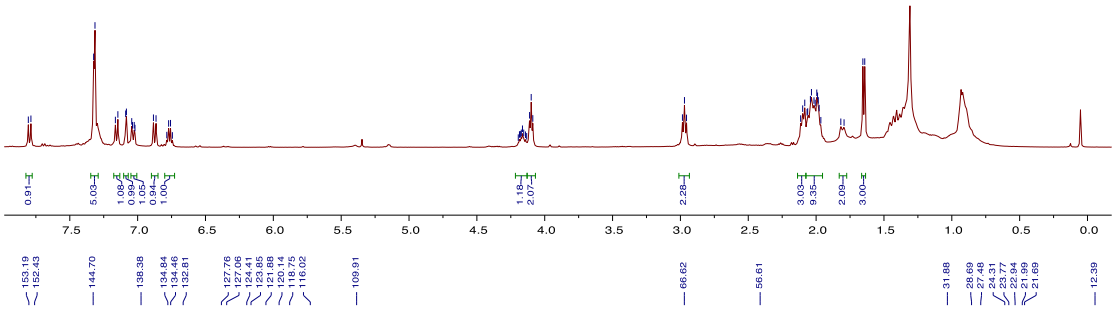
Me
N
O
O
O
N
O
Me

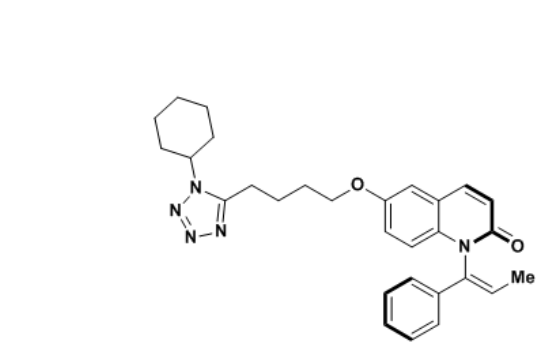

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

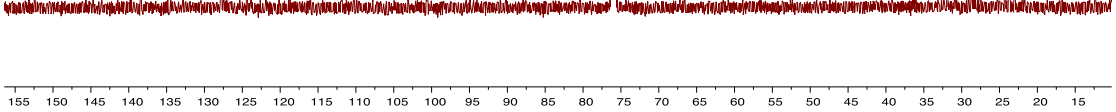


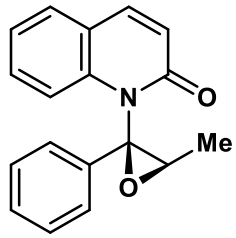
3m'



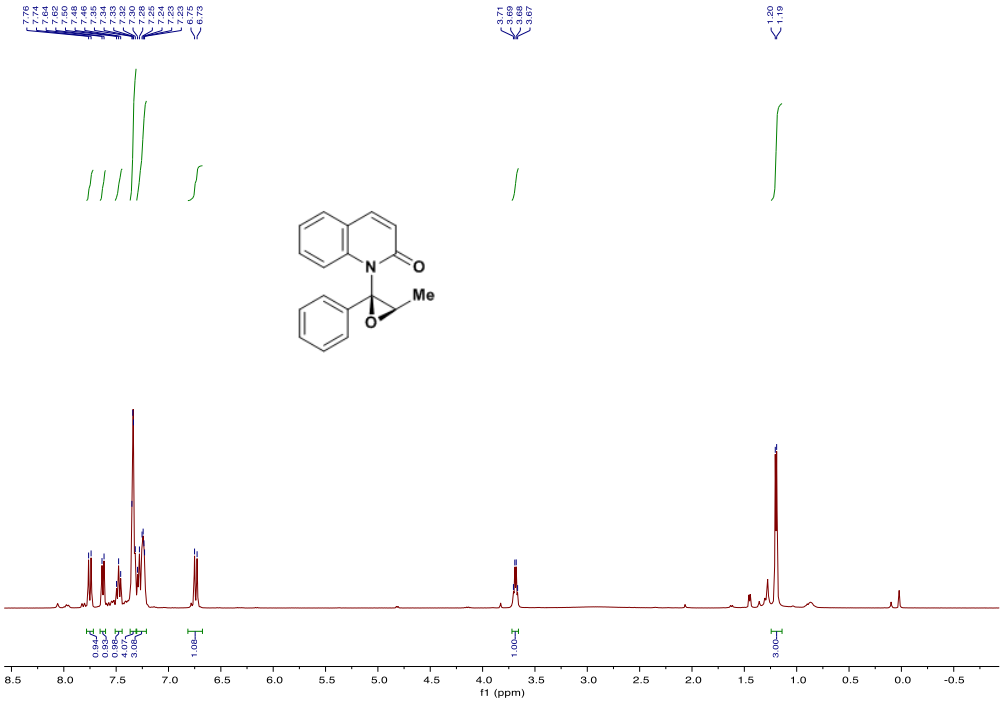


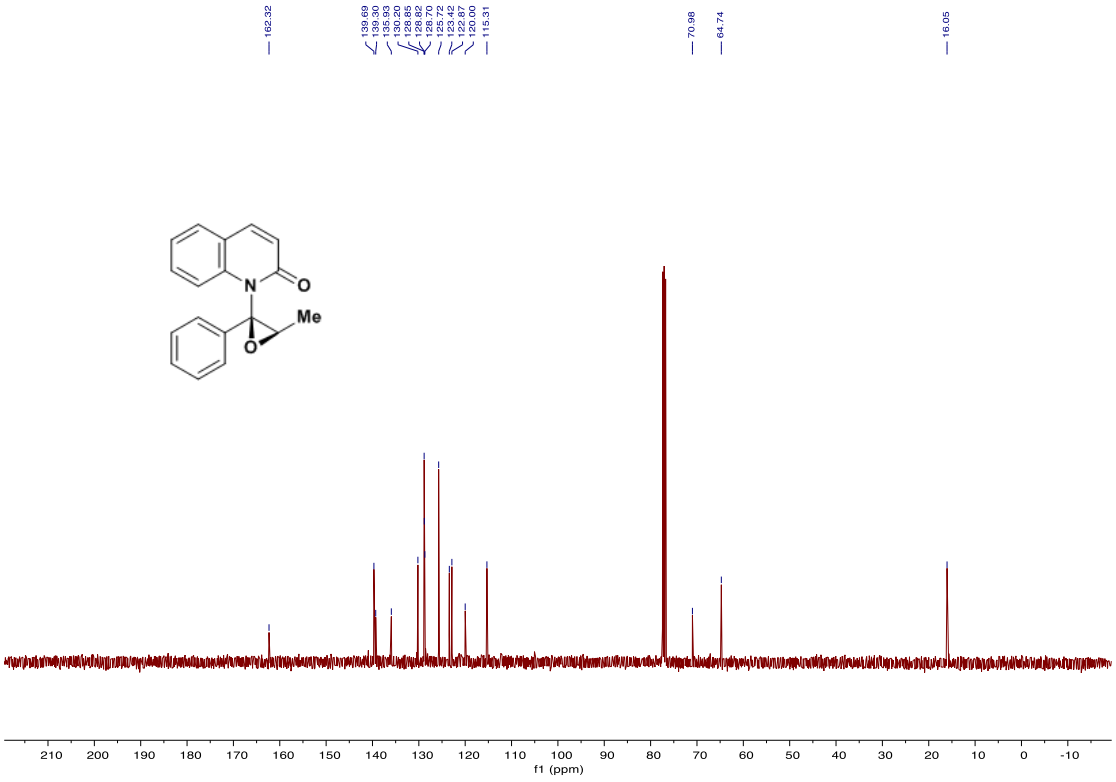


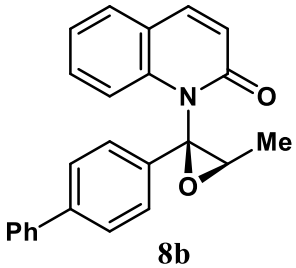



N
O
Me
O

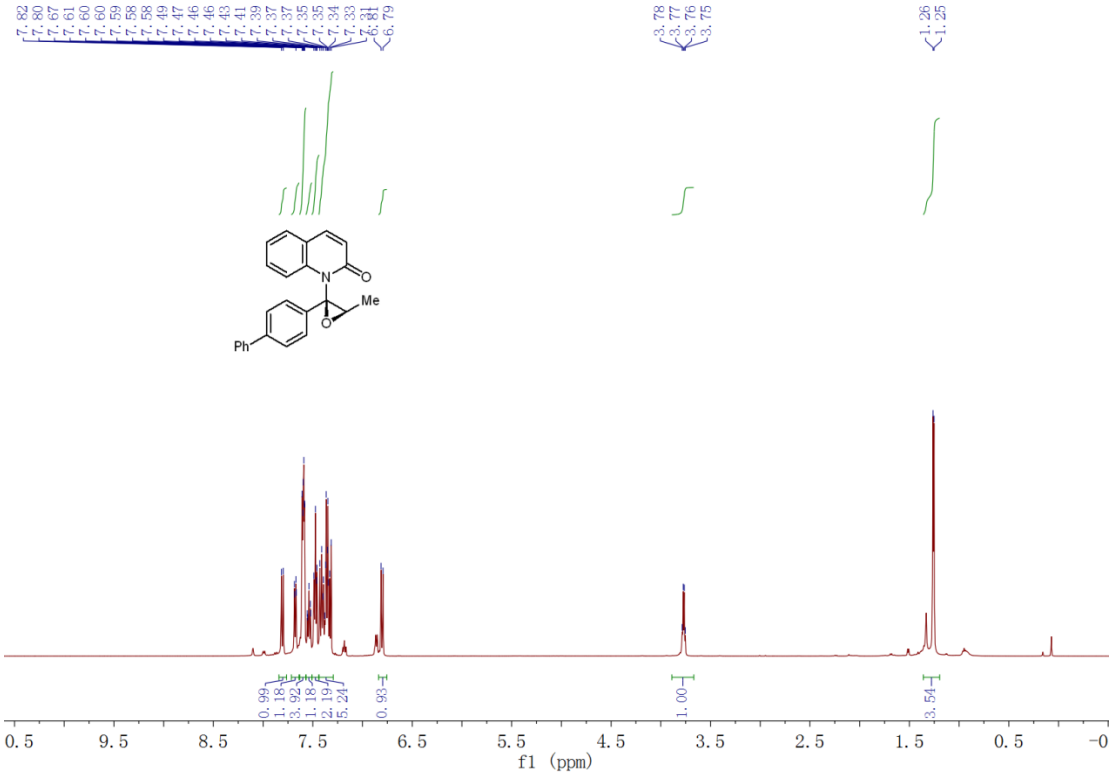
8a

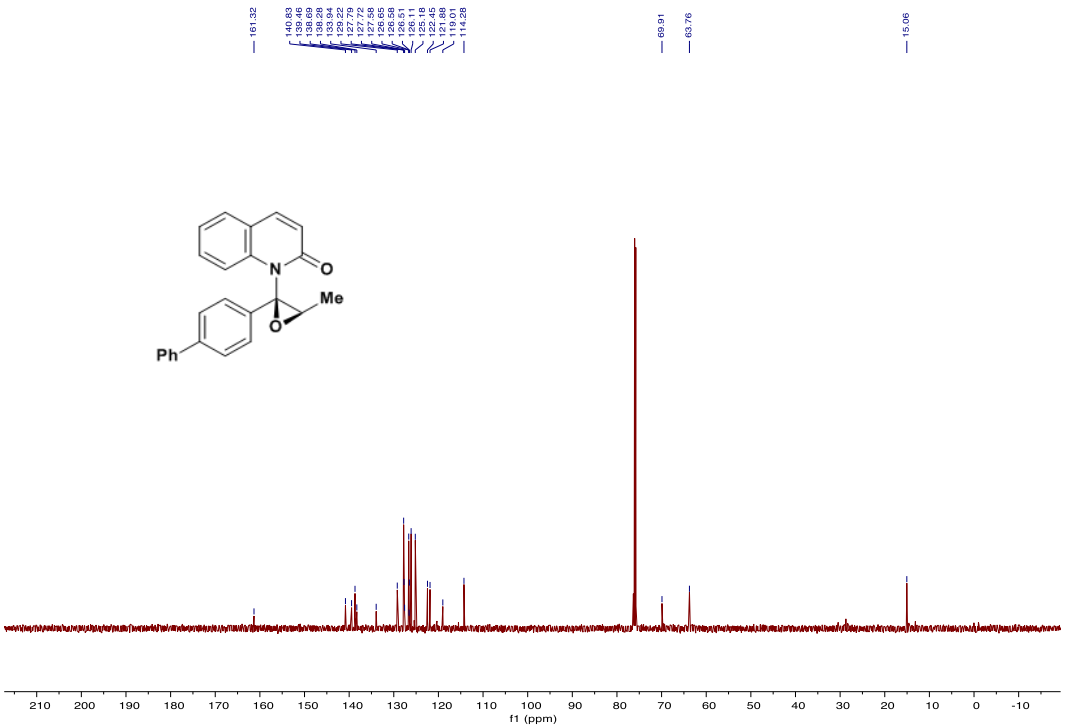

7.76
7.74
7.64
7.62
7.50
7.48
7.46
7.36
7.34
7.33
7.32
7.30
7.28
7.25
7.24
7.23
7.23
6.75
6.73
3.71
3.69
3.68
3.67
1.20
1.19
N
O
Me
O
0.94
0.93
0.98
0.97
3.08
1.08
1.00
3.00
f1 (ppm)

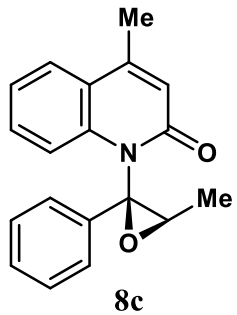

162.32
139.69
139.00
135.93
130.20
128.85
128.82
128.70
125.72
123.42
120.87
120.00
115.31
70.98
64.74
16.05
N
O
Me
O
f1 (ppm)


N
O
Me
O
Ph

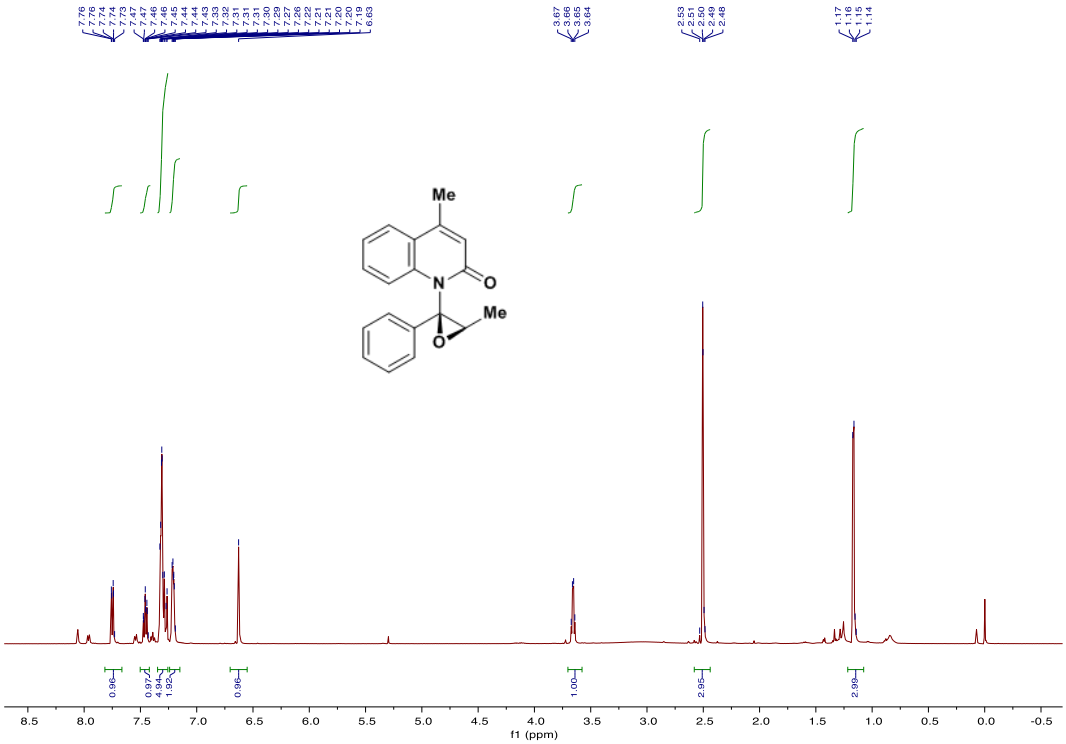
8b


7.82
7.80
7.67
7.61
7.60
7.60
7.59
7.58
7.58
7.49
7.47
7.46
7.46
7.43
7.41
7.39
7.37
7.37
7.35
7.35
7.34
7.33
6.81
6.79
3.78
3.77
3.76
3.75
1.26
1.25
0.99
1.18
3.92
1.18
2.19
5.24
0.93
1.00
3.54
0.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0
f1 (ppm)

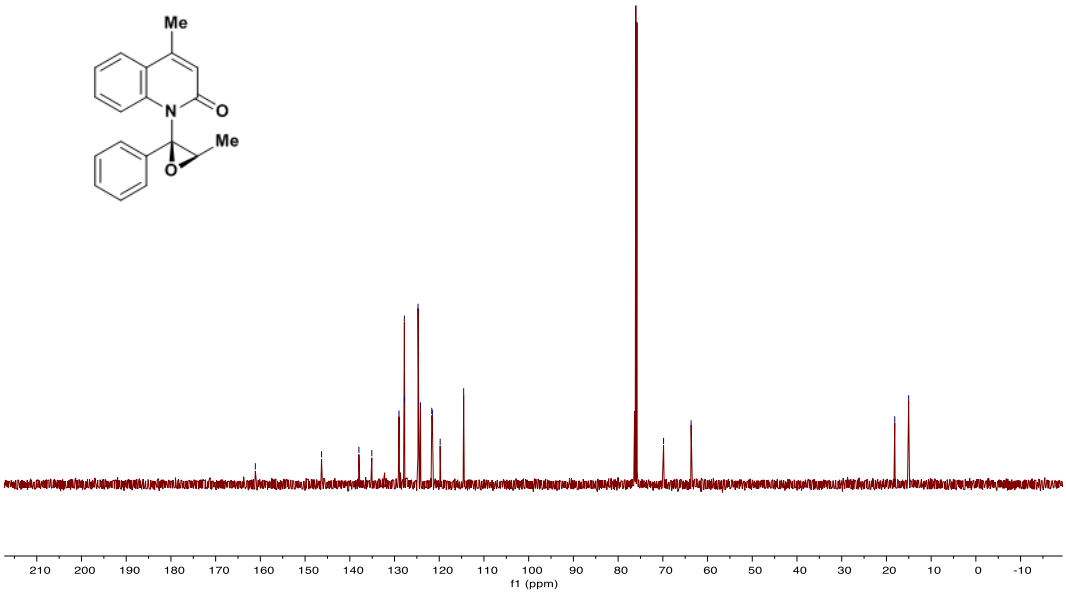

161.32
140.83
139.46
138.69
138.28
133.94
129.22
127.79
127.72
127.58
126.65
126.59
126.51
126.11
125.18
122.45
121.89
119.01
114.28
69.91
63.76
15.06
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

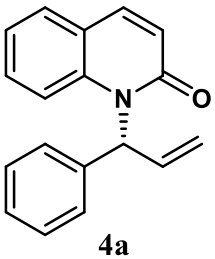

Me
N
O
Me
O

8c

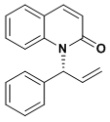

7.76
7.76
7.74
7.74
7.73
7.47
7.47
7.46
7.46
7.45
7.44
7.44
7.43
7.33
7.32
7.31
7.31
7.31
7.30
7.29
7.28
7.27
7.22
7.21
7.21
7.20
7.20
7.19
6.63
3.67
3.66
3.65
3.64
2.53
2.51
2.50
2.49
2.48
1.17
1.16
1.15
1.14
Me
N
O
Me
O
0.96
0.97
4.94
1.92
0.96
1.00
2.95
2.99
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

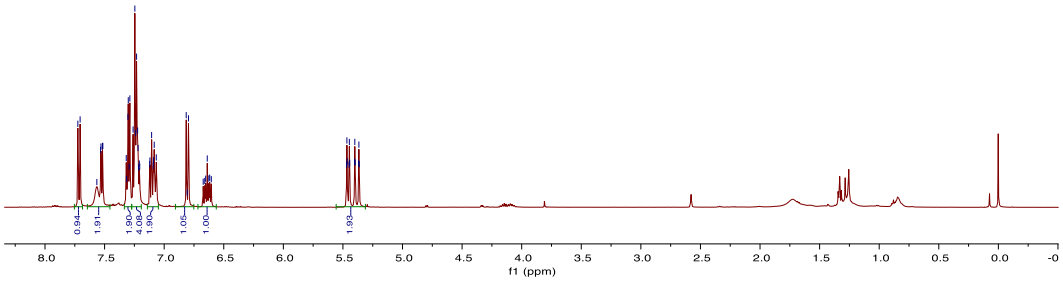

161.13
146.32
137.96
135.08
129.00
127.80
127.75
124.74
124.20
123.67
121.54
119.79
114.54
69.84
63.68
18.14
15.03

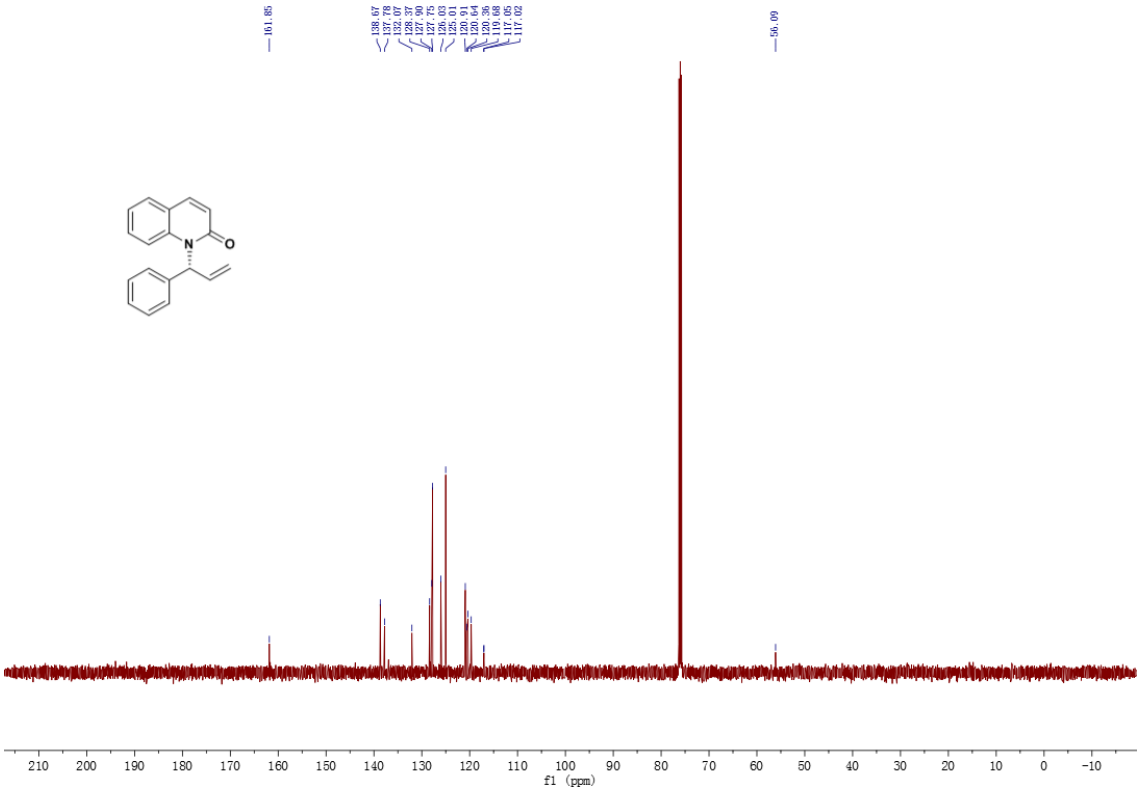

Me
N
O
Me
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

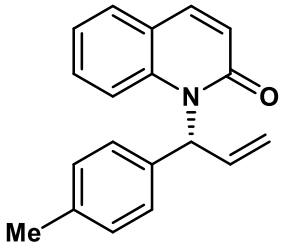


4a

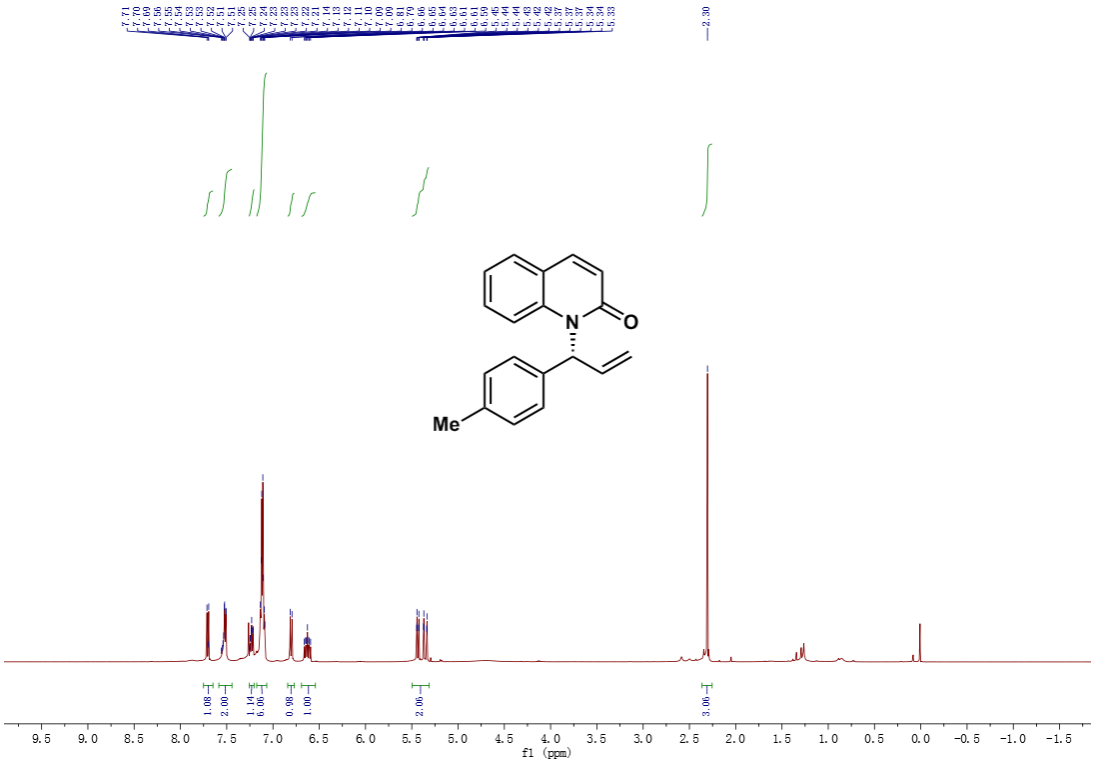



0.94
1.91
1.90
4.68
1.90
1.05
1.00
1.93
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


161.85
138.67
137.78
132.07
128.37
127.90
127.75
126.03
125.01
120.91
120.64
120.36
119.68
117.05
117.02
56.09
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


N
O
Me

4b


7.71
7.70
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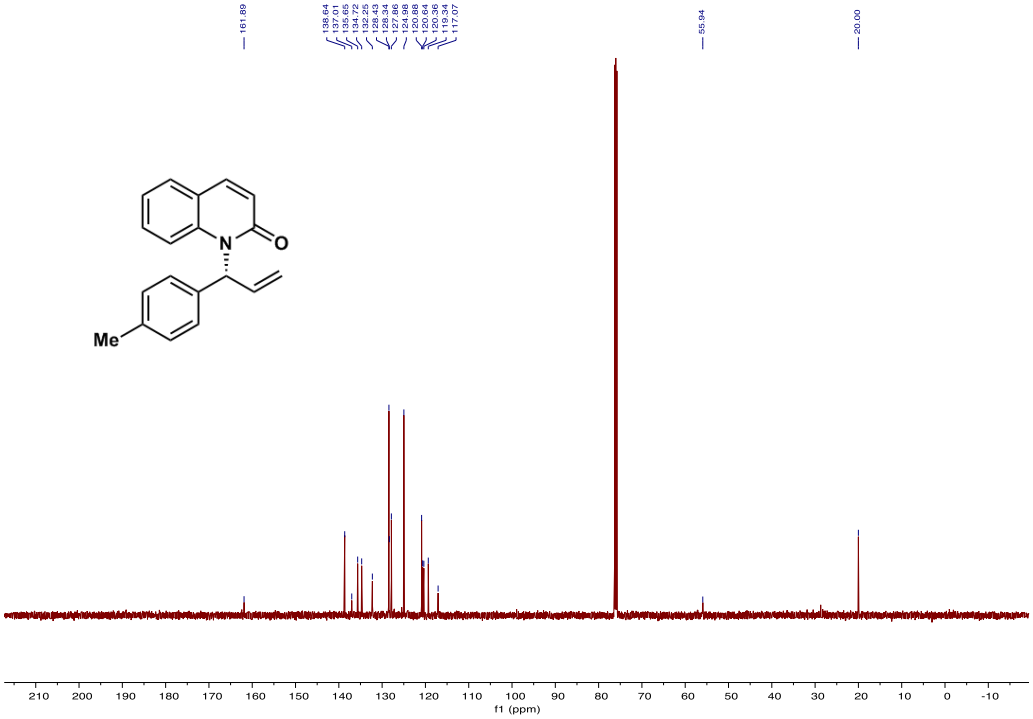
7.56
7.55
7.54
7.53
7.52
7.51
7.25
7.24
7.23
7.23
7.22
7.21
7.14
7.13
7.12
7.11
7.10
7.09
7.09
6.81
6.79
6.66
6.65
6.64
6.63
6.61
6.61
6.59
5.46
5.44
5.44
5.43
5.42
5.37
5.37
5.34
5.34
5.33
2.30
N
O
Me
1.08
2.00
1.14
6.00
0.98
1.00
2.05
3.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)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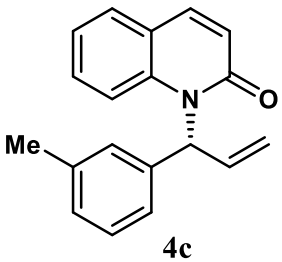
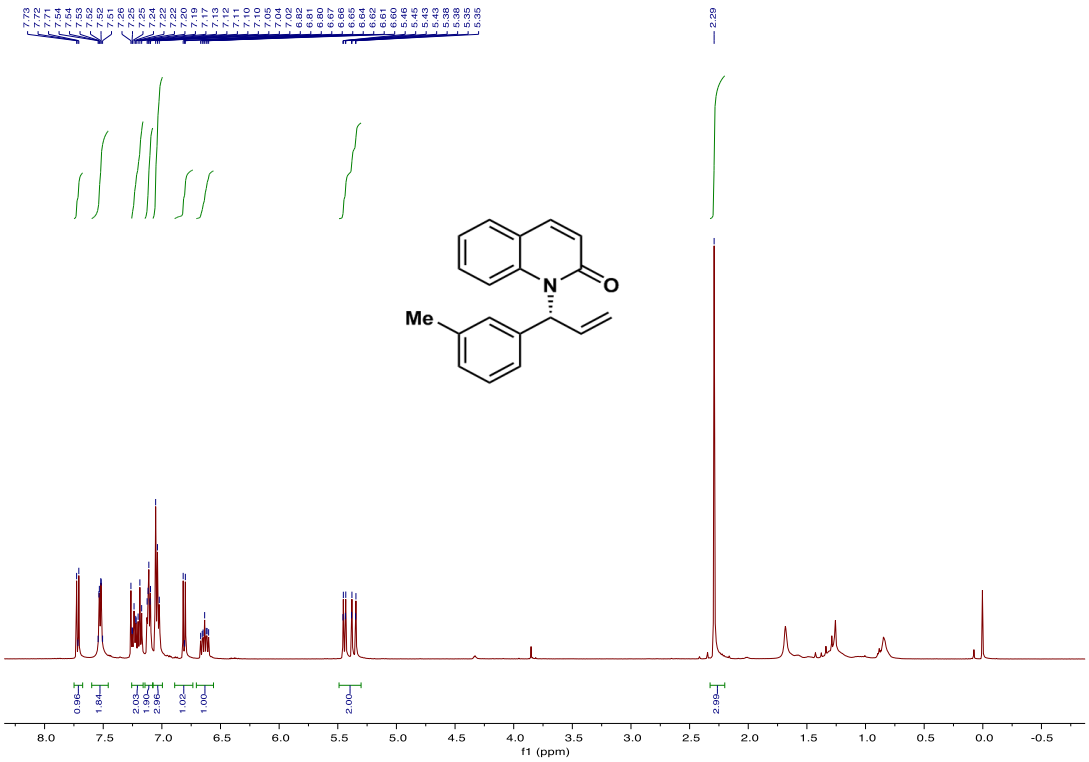
134.72
132.25
129.43
128.34
127.96
125.68
120.88
120.64
120.36
119.34
117.07
55.94
20.00
N
O
Me
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


N
O
Me

4c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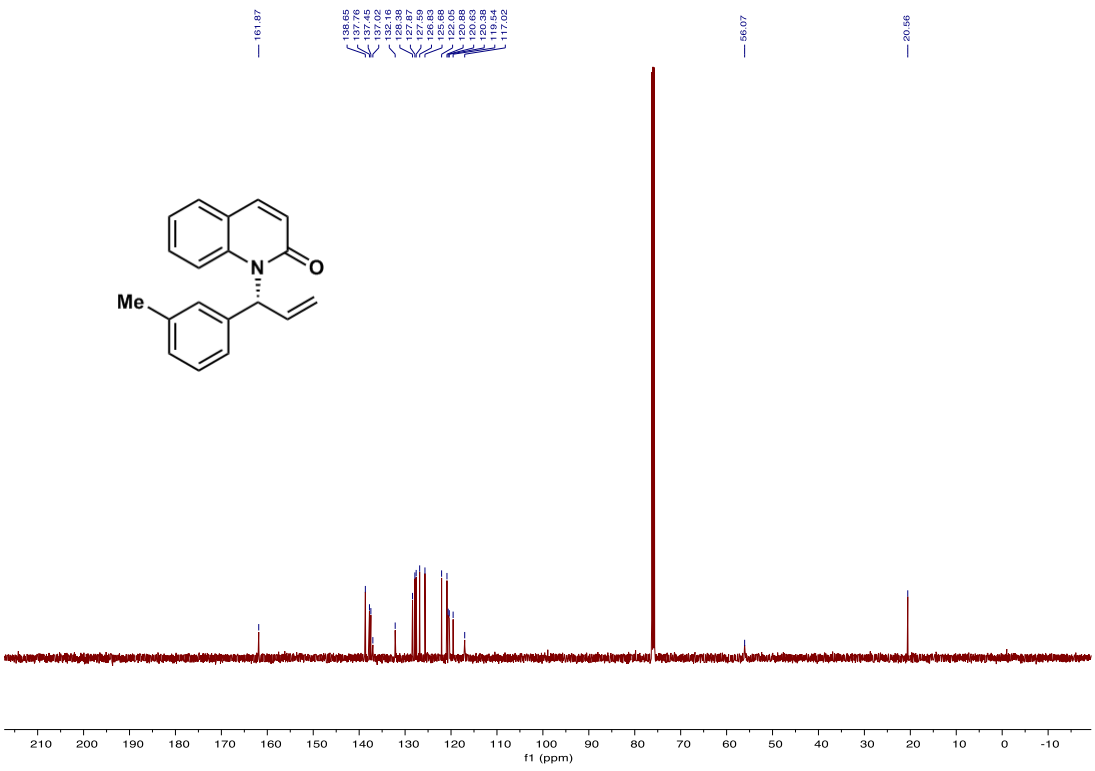
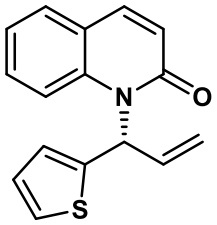
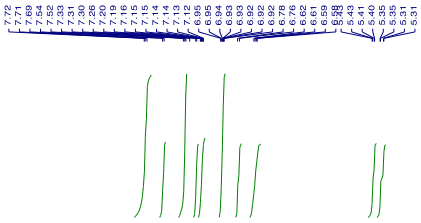
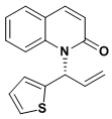
7.72
7.71
7.54
7.54
7.53
7.52
7.51
7.26
7.25
7.25
7.24
7.22
7.22
7.20
7.19
7.17
7.13
7.12
7.11
7.10
7.05
7.04
7.02
6.82
6.81
6.69
6.67
6.66
6.65
6.64
6.62
6.61
6.60
5.46
5.45
5.43
5.43
5.38
5.38
5.35
5.35
2.29
N
O
Me
0.96
1.84
2.03
1.90
2.96
1.02
1.00
2.00
2.99
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

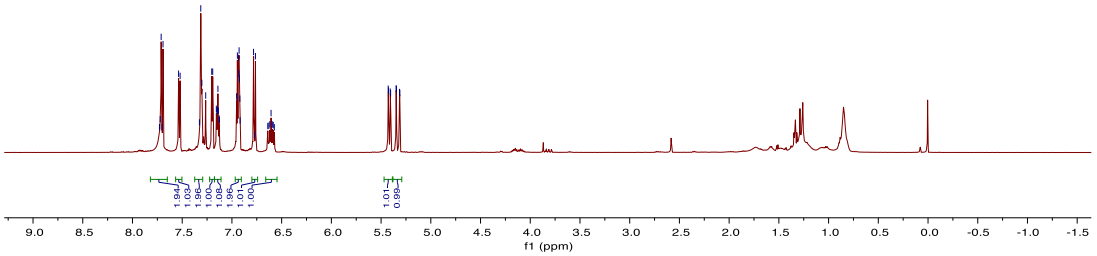

161.87
138.65
137.76
137.45
137.03
132.16
128.38
127.87
127.59
126.83
125.68
122.05
120.88
120.63
120.38
119.54
117.02
56.07
20.56
N
O
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

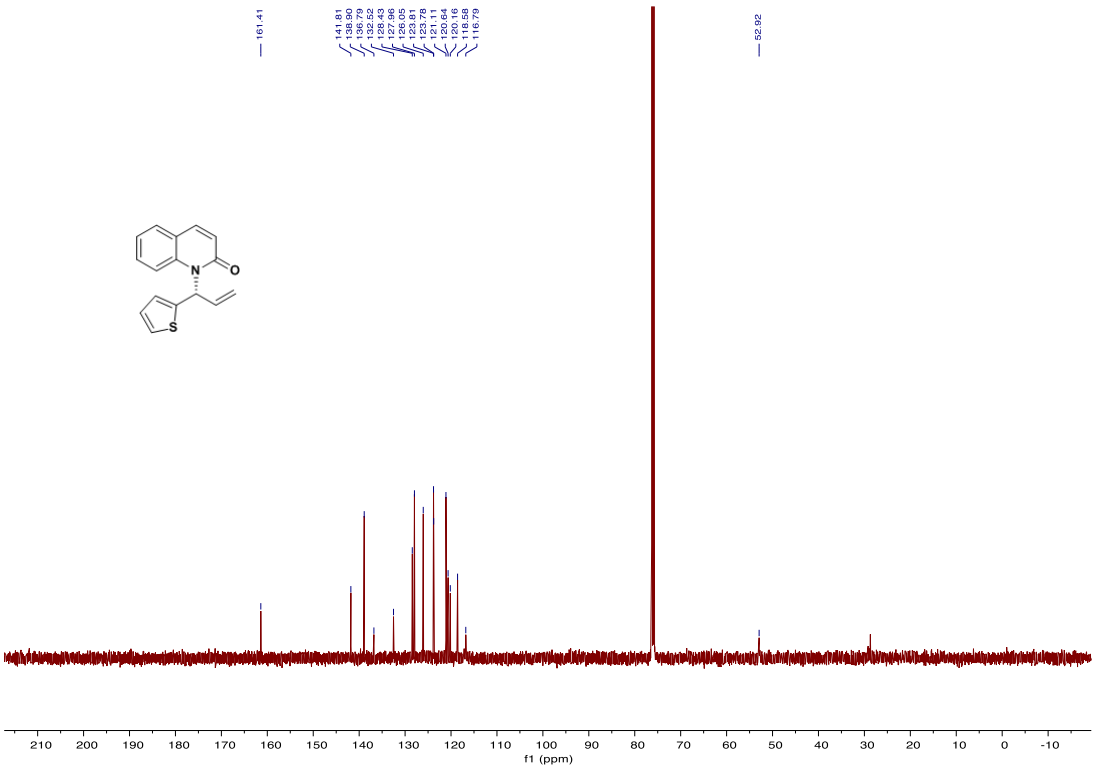


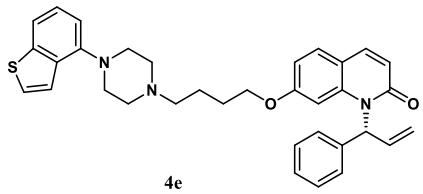
4d



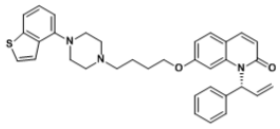


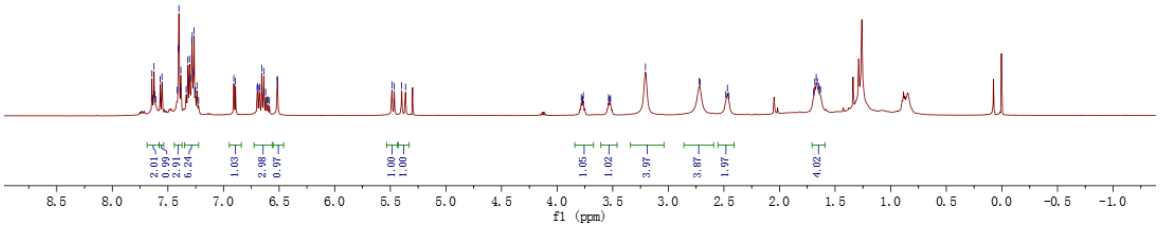


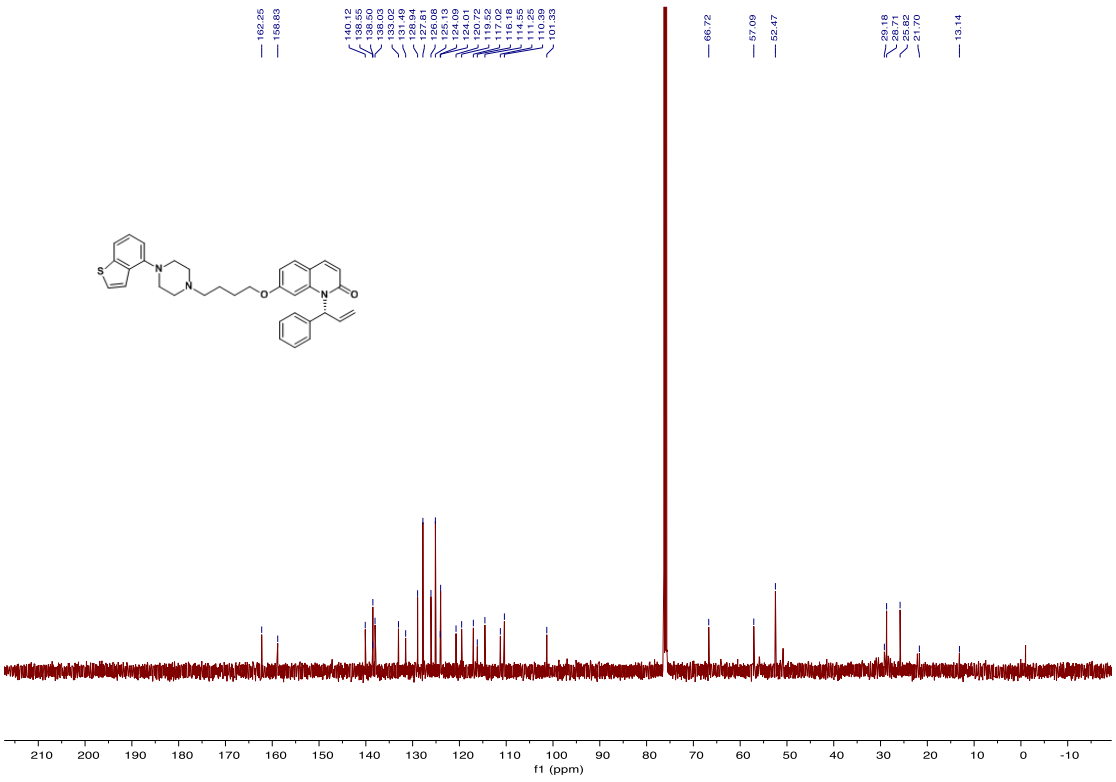


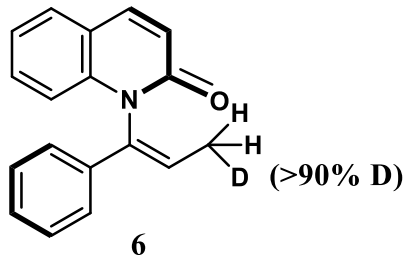


4e





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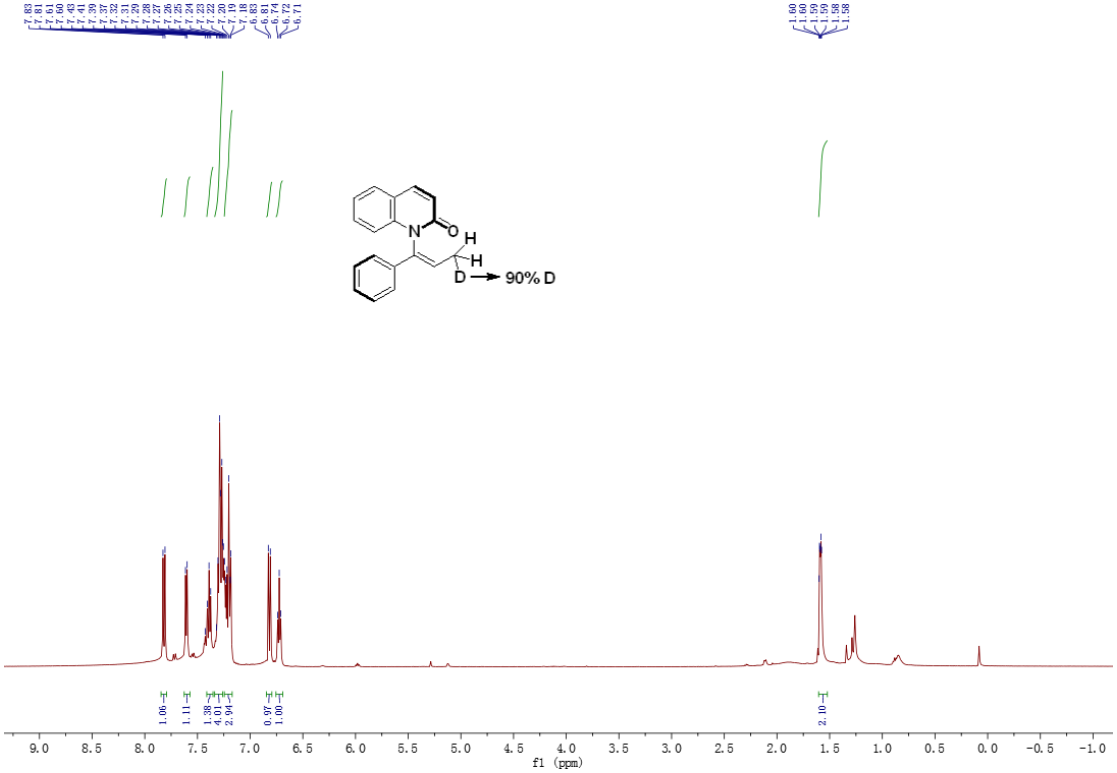
(>90% D)

6


7.83
7.81
7.61
7.60
7.45
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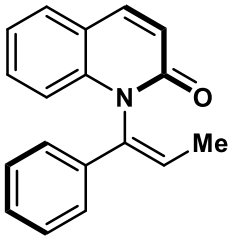
f1 (ppm)

HPLC data

For comparison of Chinese and English of the HPLC data table.

序号	峰名称	保留时间 (min)	峰面积 (mAU*min)	峰高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height (mAU)	Relative peak area (%)	Relative Peak height (%)	Sample volume n.a.



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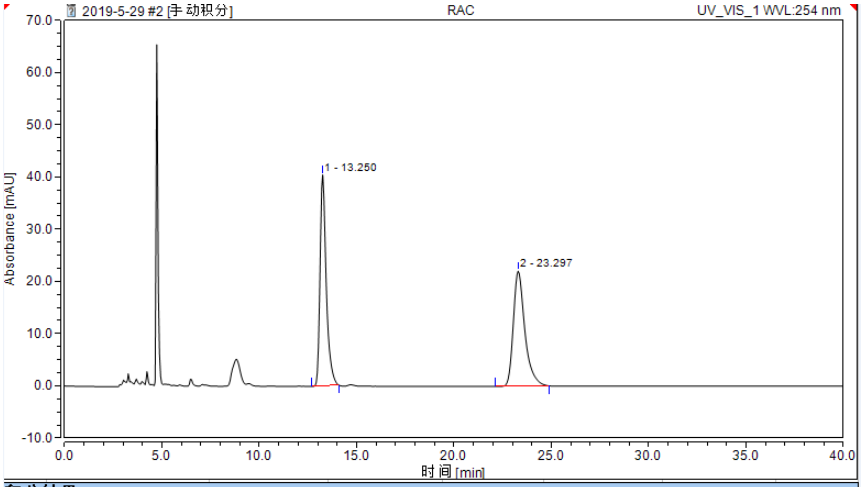
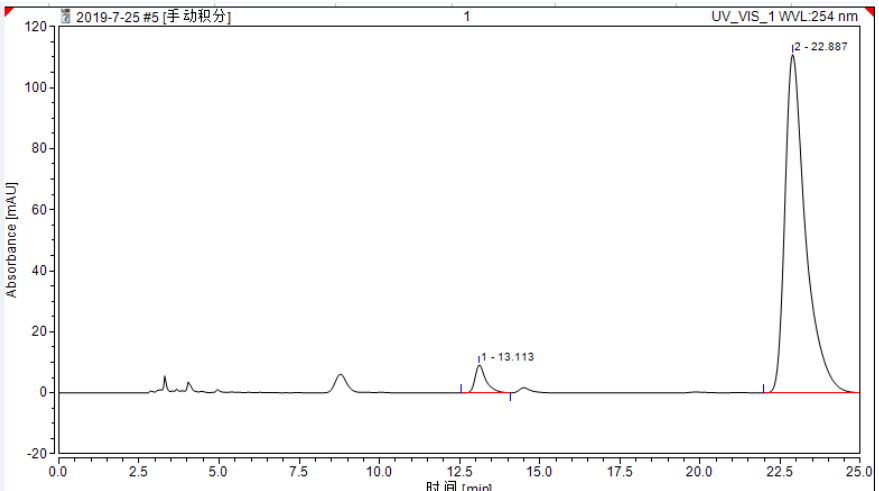


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		13.250	14.874	40.403	49.66	64.70	n.a.
2		23.297	15.078	22.039	50.34	35.30	n.a.

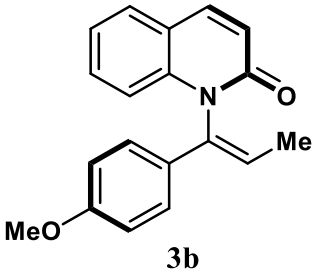


积分结果

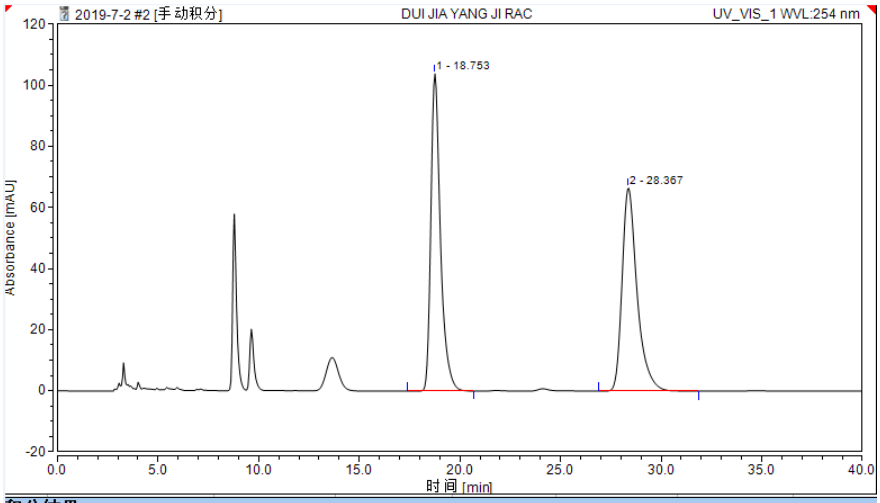
序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		13.113	3.567	9.131	4.15	7.61	n.a.
2		22.887	82.397	110.897	95.85	92.39	n.a.

For comparison of Chinese and English of the HPLC data table.

序号	峰名称	保留时间 (min)	峰面积 (mAU*min)	峰高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height (mAU)	Relative peak area (%)	Relative Peak height (%)	Sample volume n.a.

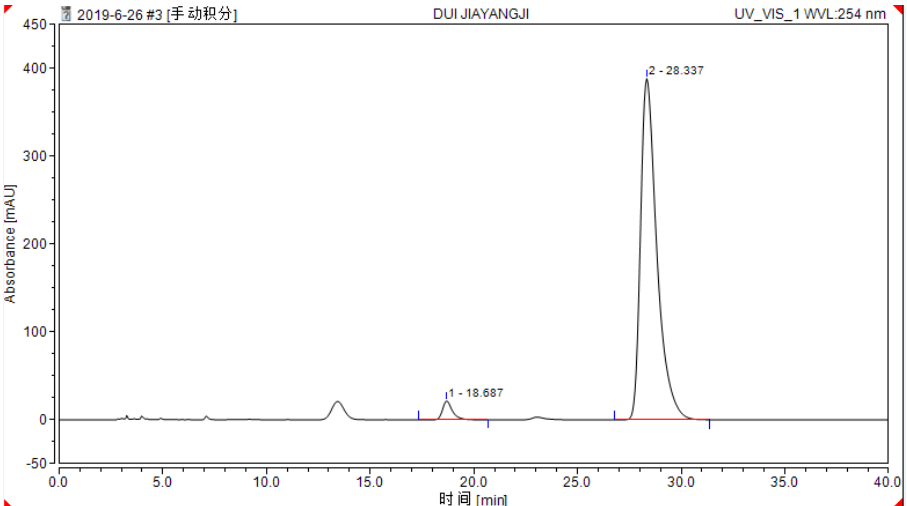


3b



积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		18.753	57.341	103.907	49.98	60.94	n.a.
2		28.367	57.386	66.597	50.02	39.06	n.a.

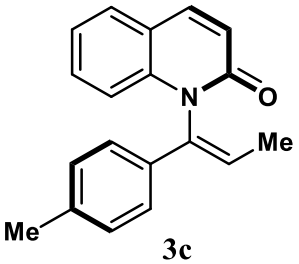


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		18.687	11.772	21.395	3.21	5.22	n.a.
2		28.337	355.032	388.501	96.79	94.78	n.a.

For comparison of Chinese and English of the HPLC data table.

序号	峰 名称	保留时间 (min)	峰 面 积 (mAU*min)	峰 高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height (mAU)	Relative peak area (%)	Relative Peak height (%)	Sample volume n.a.



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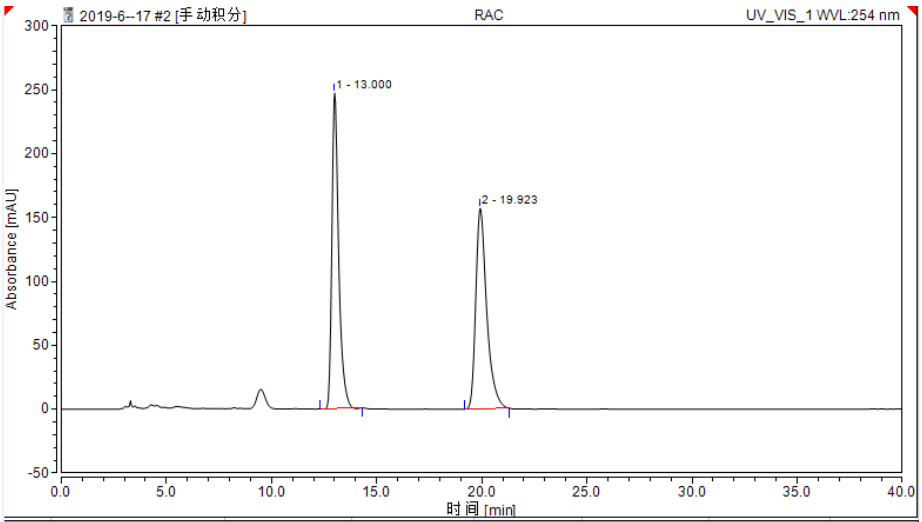
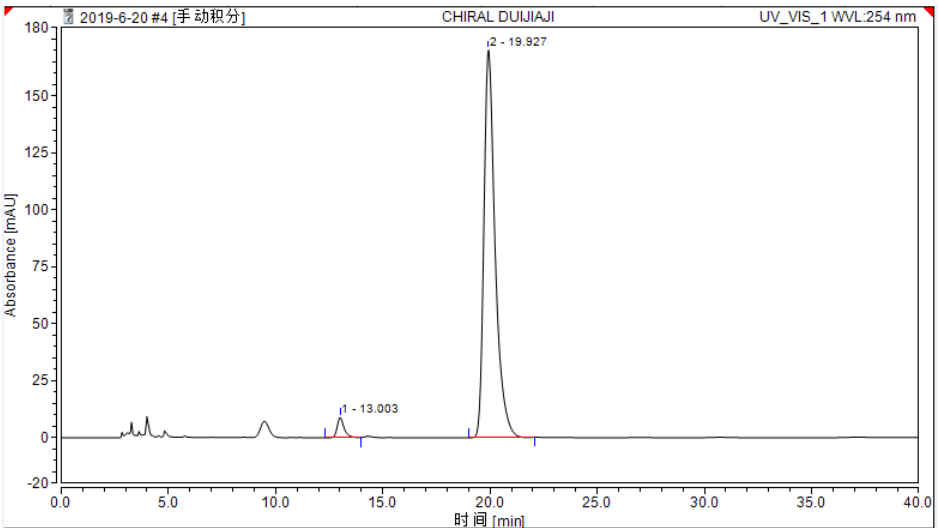


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		13.000	92.054	247.047	49.32	61.14	n.a.
2		19.923	94.583	156.988	50.68	38.86	n.a.

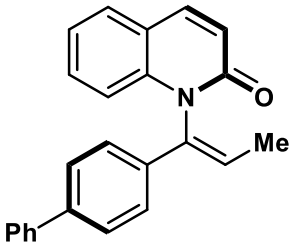


积分结果

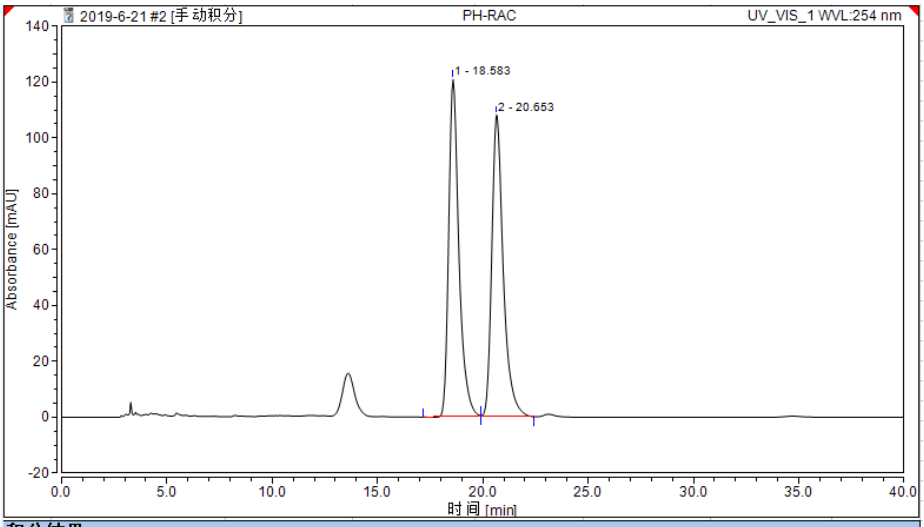
序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		13.003	3.280	8.831	3.08	4.93	n.a.
2		19.927	103.207	170.194	96.92	95.07	n.a.

For comparison of Chinese and English of the HPLC data table.

序号	峰 名称	保留时间 (min)	峰 面 积 (mAU*min)	峰 高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height (mAU)	Relative peak area (%)	Relative Peak height (%)	Sample volume n.a.

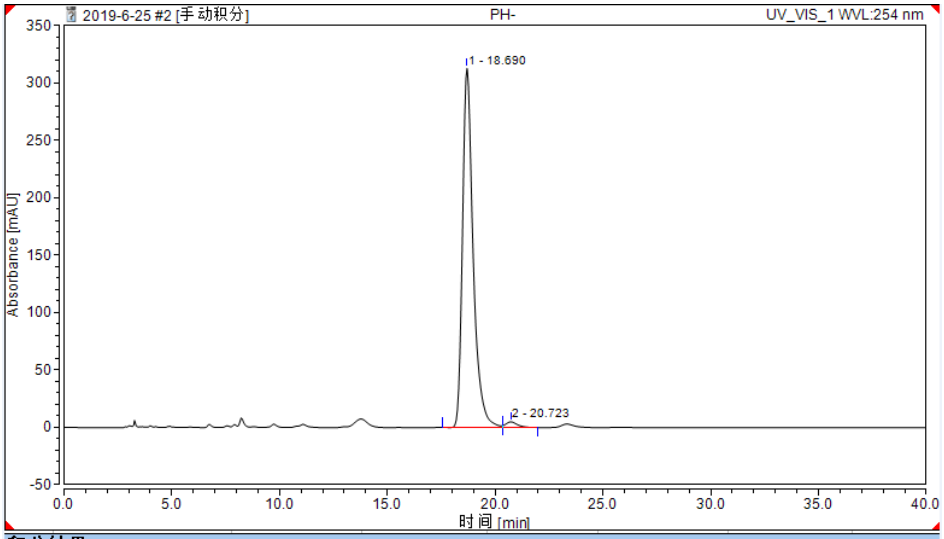


3d



积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		18.583	67.518	120.651	49.89	52.80	n.a.
2		20.653	67.829	107.843	50.11	47.20	n.a.

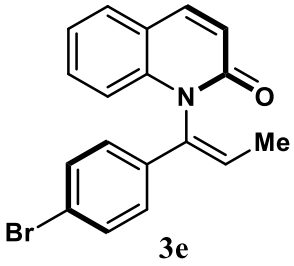


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		18.690	178.910	312.766	98.30	98.43	n.a.
2		20.723	3.088	4.986	1.70	1.57	n.a.

For comparison of Chinese and English of the HPLC data table.

序号	峰名称	保留时间 (min)	峰面积 (mAU*min)	峰高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height (mAU)	Relative peak area (%)	Relative Peak height (%)	Sample volume n.a.



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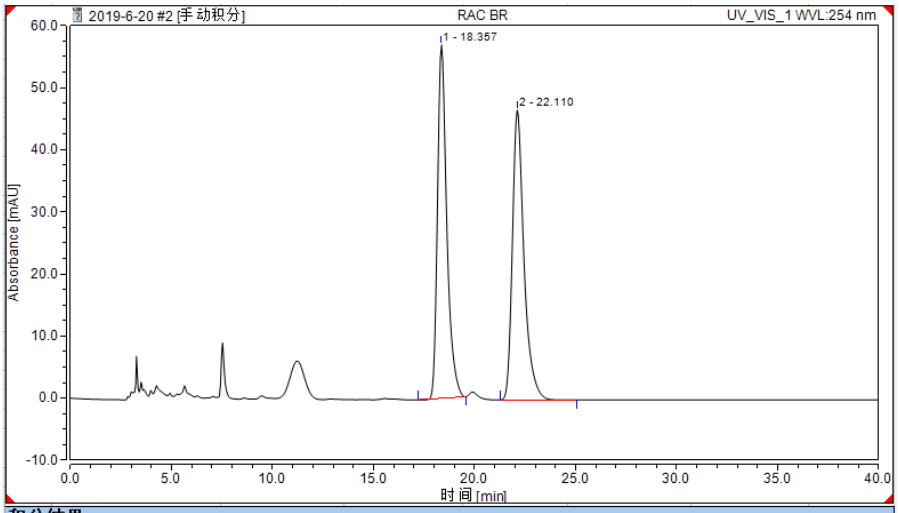
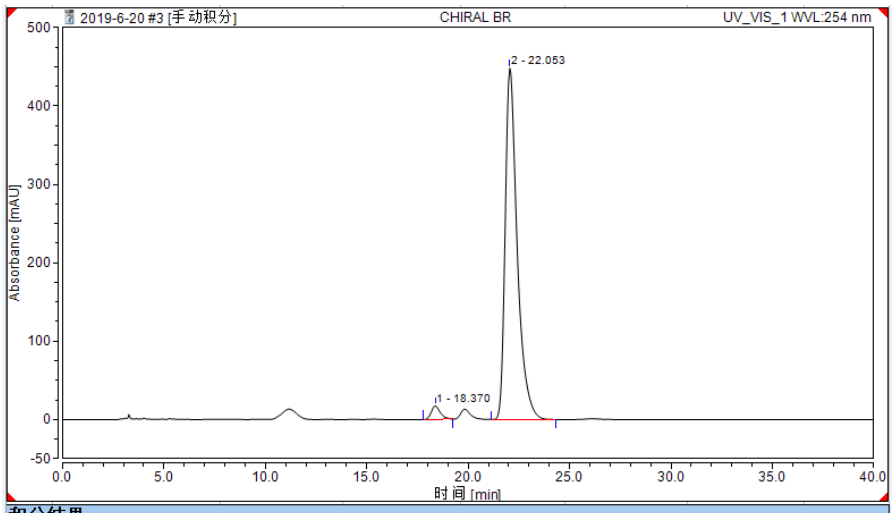


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		18.357	30.299	56.963	49.47	54.98	n.a.
2		22.110	30.946	46.645	50.53	45.02	n.a.

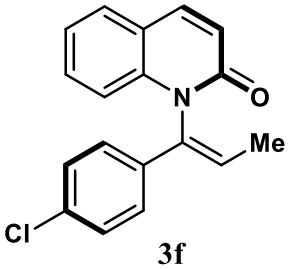


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		18.370	8.838	17.187	2.80	3.69	n.a.
2		22.053	307.134	448.139	97.20	96.31	n.a.

For comparison of Chinese and English of the HPLC data table.

序号	峰名称	保留时间 (min)	峰面积 (mAU*min)	峰高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height (mAU)	Relative peak area (%)	Relative Peak height (%)	Sample volume n.a.



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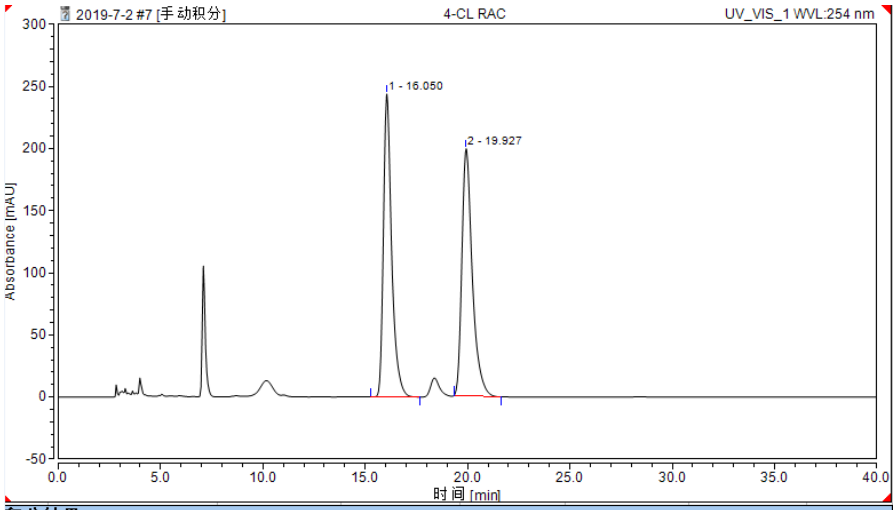
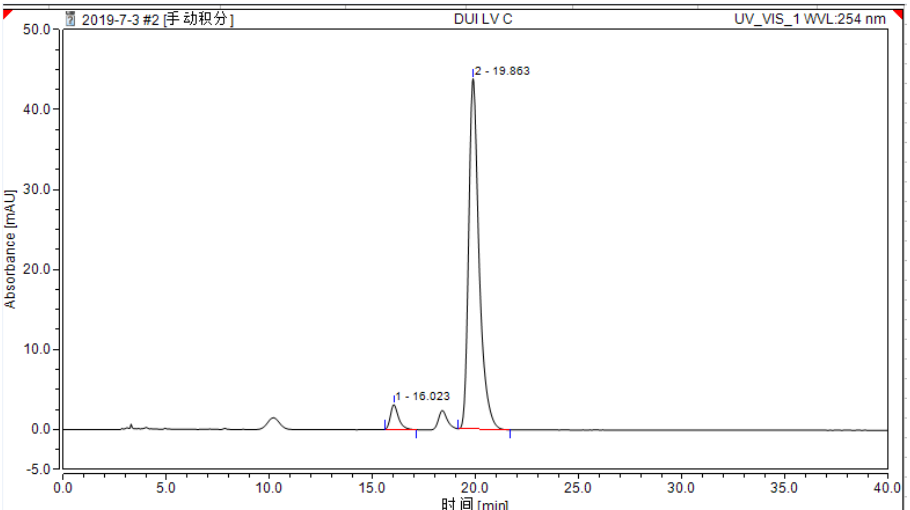


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		16.050	113.361	243.753	49.15	55.06	n.a.
2		19.927	117.290	198.933	50.85	44.94	n.a.

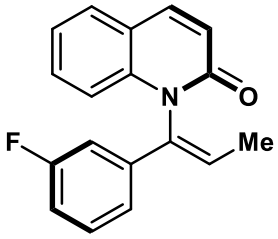


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		16.023	1.412	3.108	5.22	6.63	n.a.
2		19.863	25.630	43.800	94.78	93.37	n.a.

For comparison of Chinese and English of the HPLC data table.

序号	峰 名称	保留时间 (min)	峰 面 积 (mAU*min)	峰 高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height (mAU)	Relative peak area (%)	Relative Peak height (%)	Sample volume n.a.



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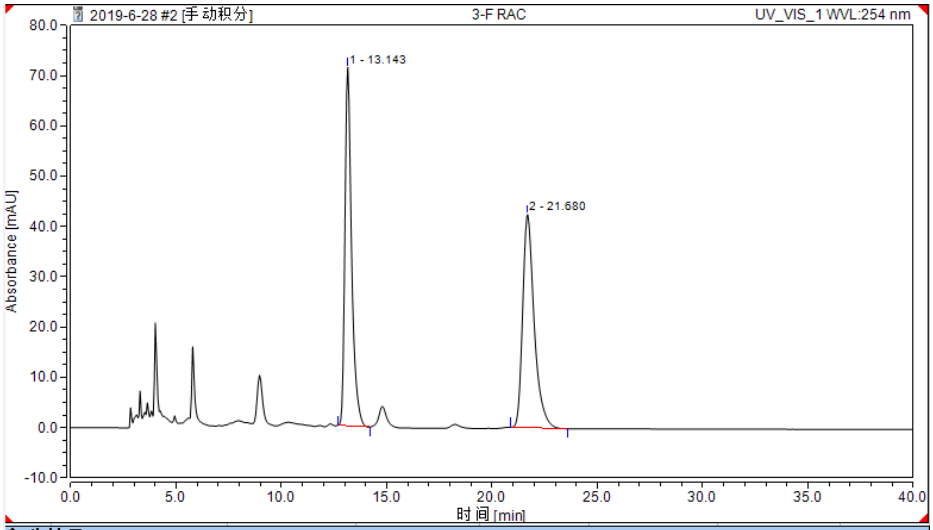
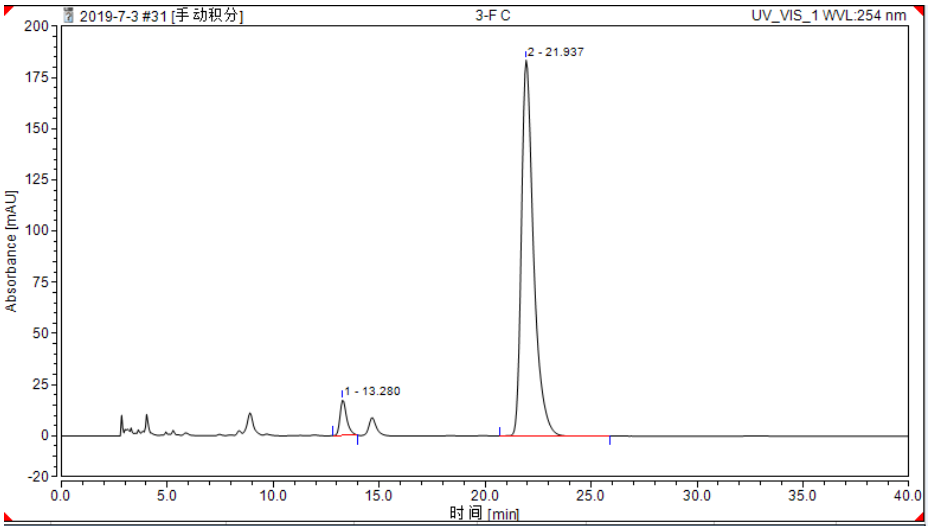


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		13.143	26.179	71.264	49.39	62.71	n.a.
2		21.680	26.831	42.378	50.61	37.29	n.a.

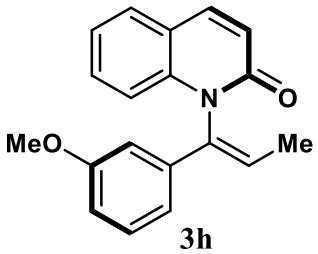


积分结果

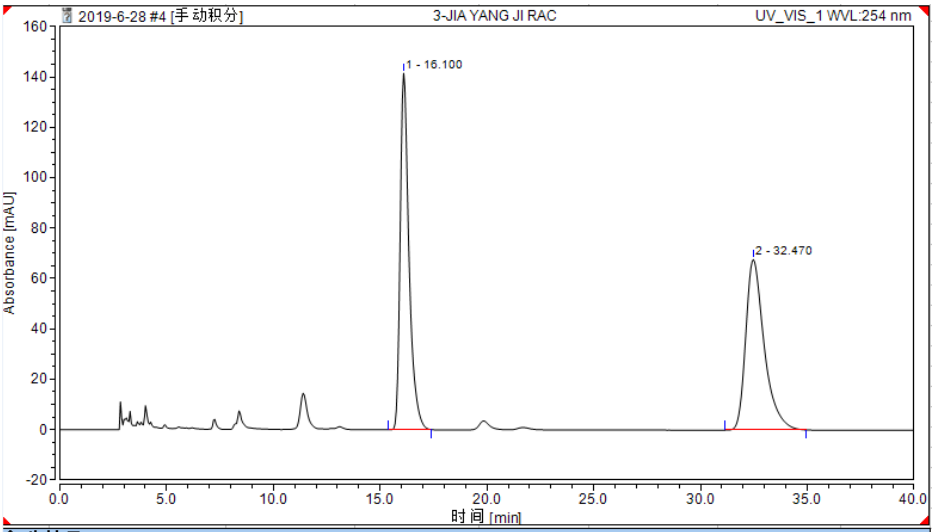
序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		13.280	6.354	17.393	4.95	8.66	n.a.
2		21.937	121.896	183.550	95.05	91.34	n.a.

For comparison of Chinese and English of the HPLC data table.

序号	峰名称	保留时间 (min)	峰面积 (mAU*min)	峰高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height (mAU)	Relative peak area (%)	Relative Peak height (%)	Sample volume n.a.

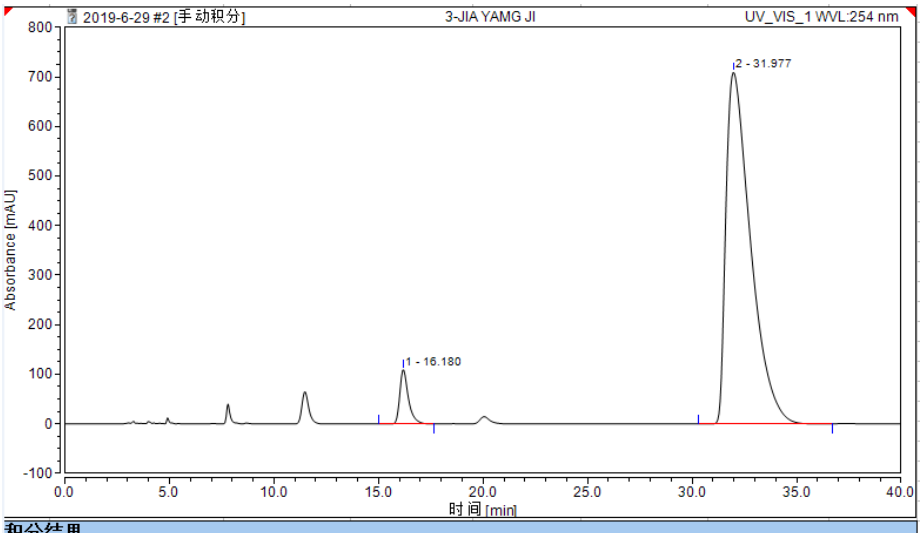


3h



积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		16.100	67.667	141.512	49.86	67.64	n.a.
2		32.470	68.044	67.708	50.14	32.36	n.a.

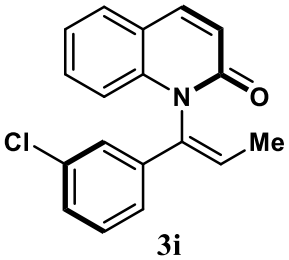


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		16.180	52.423	110.051	5.14	13.43	n.a.
2		31.977	966.547	709.645	94.86	86.57	n.a.

For comparison of Chinese and English of the HPLC data table.

序号	峰名称	保留时间 (min)	峰面积 (mAU*min)	峰高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height (mAU)	Relative peak area (%)	Relative Peak height (%)	Sample volume n.a.



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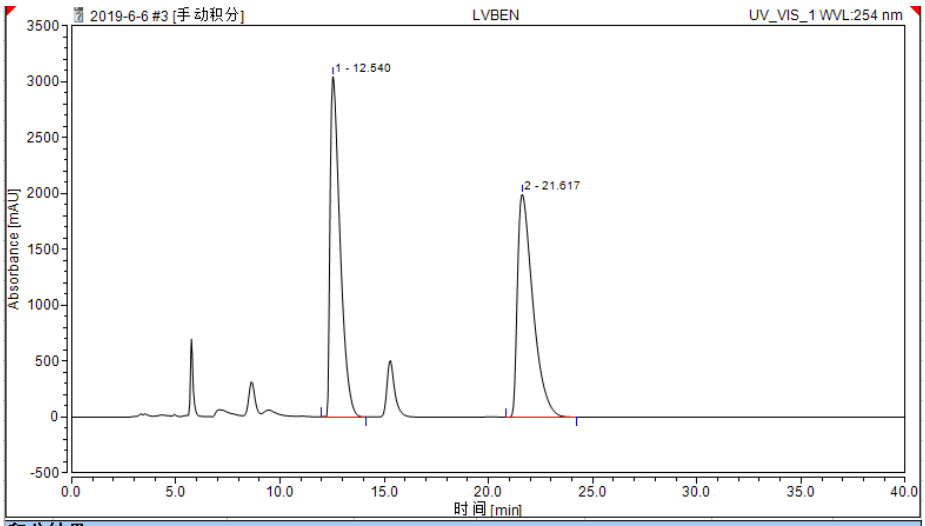
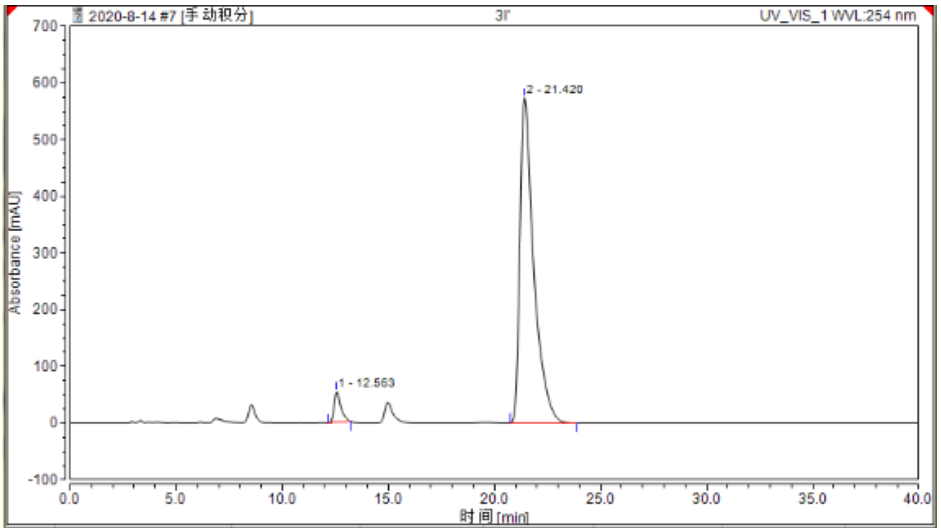


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		12.540	1685.140	3043.222	49.65	60.40	n.a.
2		21.617	1708.968	1995.498	50.35	39.60	n.a.

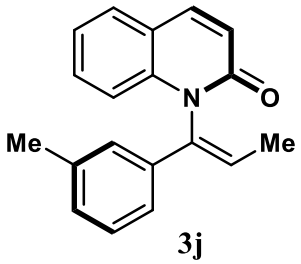


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		12.563	19.989	54.333	4.40	8.65	n.a.
2		21.420	434.003	573.768	95.60	91.35	n.a.

For comparison of Chinese and English of the HPLC data table.

序号	峰名称	保留时间 (min)	峰面积 (mAU*min)	峰高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height (mAU)	Relative peak area (%)	Relative Peak height (%)	Sample volume n.a.



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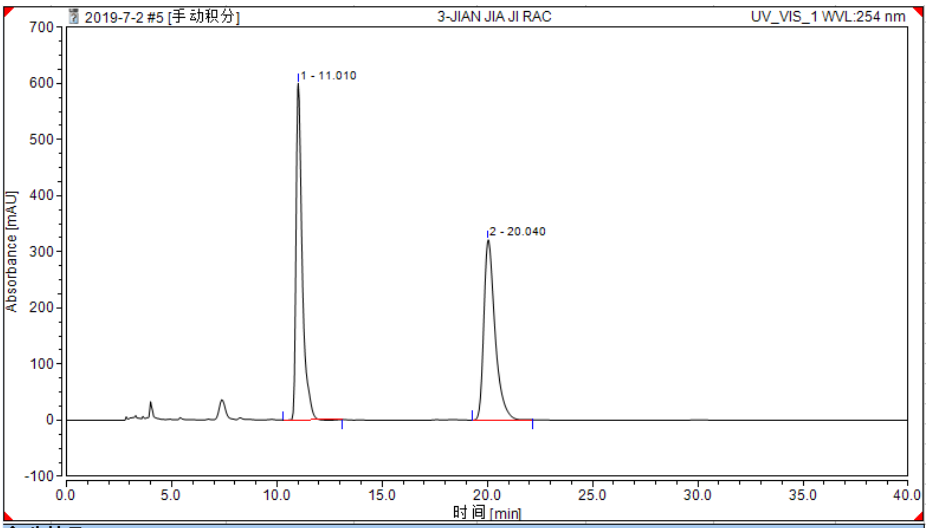
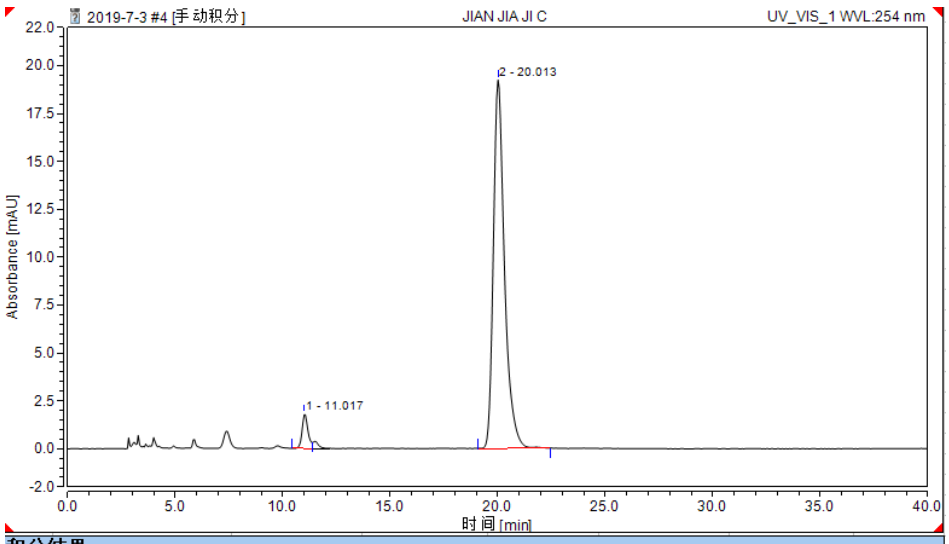


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		11.010	202.647	599.964	50.59	65.12	n.a.
2		20.040	197.960	321.291	49.41	34.88	n.a.

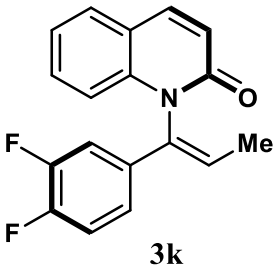


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		11.017	0.565	1.813	4.67	8.61	n.a.
2		20.013	11.547	19.249	95.33	91.39	n.a.

For comparison of Chinese and English of the HPLC data table.

序号	峰名称	保留时间 (min)	峰面积 (mAU*min)	峰高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height (mAU)	Relative peak area (%)	Relative Peak height (%)	Sample volume n.a.



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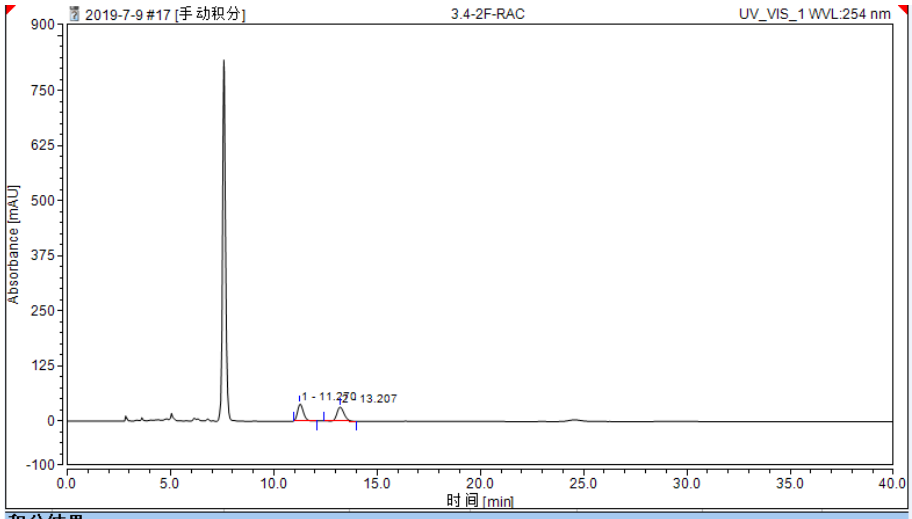
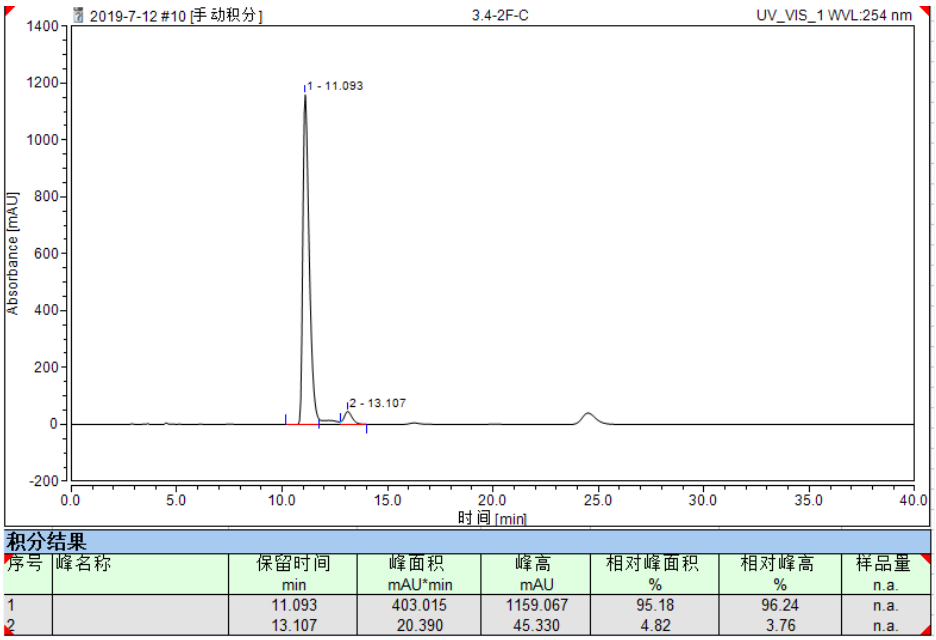


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		11.270	12.507	38.747	49.94	54.76	n.a.
2		13.207	12.535	32.011	50.06	45.24	n.a.

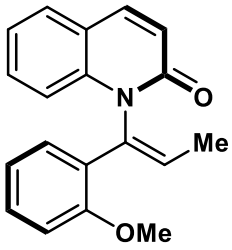


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		11.093	403.015	1159.067	95.18	96.24	n.a.
2		13.107	20.390	45.330	4.82	3.76	n.a.

For comparison of Chinese and English of the HPLC data table.

序号	峰 名称	保留时间 (min)	峰 面 积 (mAU*min)	峰 高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height (mAU)	Relative peak area (%)	Relative Peak height (%)	Sample volume n.a.



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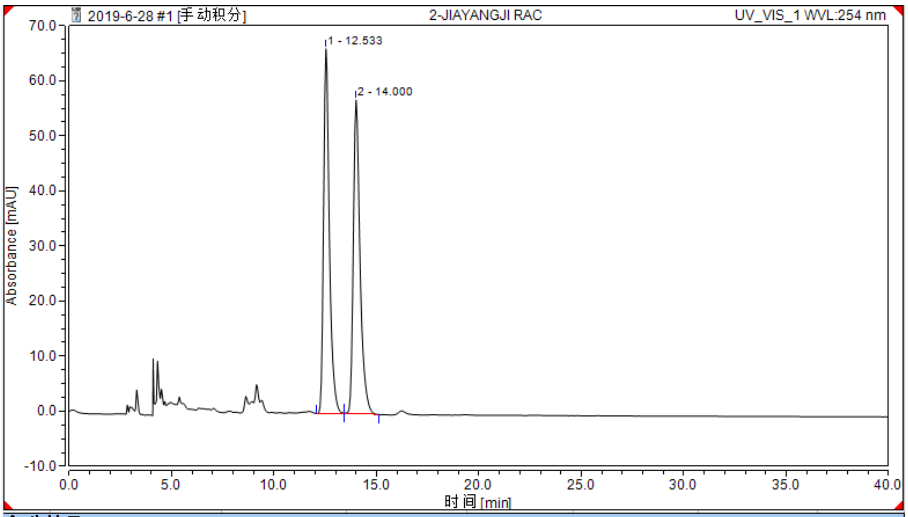
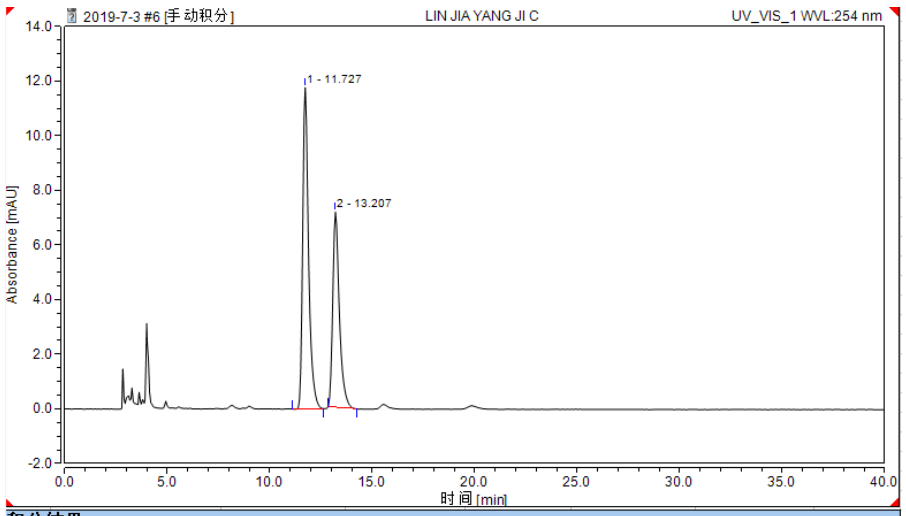


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		12.533	21.562	66.223	49.91	53.76	n.a.
2		14.000	21.636	56.955	50.09	46.24	n.a.

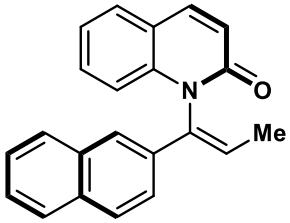


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		11.727	3.880	11.763	59.17	62.16	n.a.
2		13.207	2.677	7.160	40.83	37.84	n.a.

For comparison of Chinese and English of the HPLC data table.

序号	峰 名称	保留时间 (min)	峰 面 积 (mAU*min)	峰 高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height (mAU)	Relative peak area (%)	Relative Peak height (%)	Sample volume n.a.



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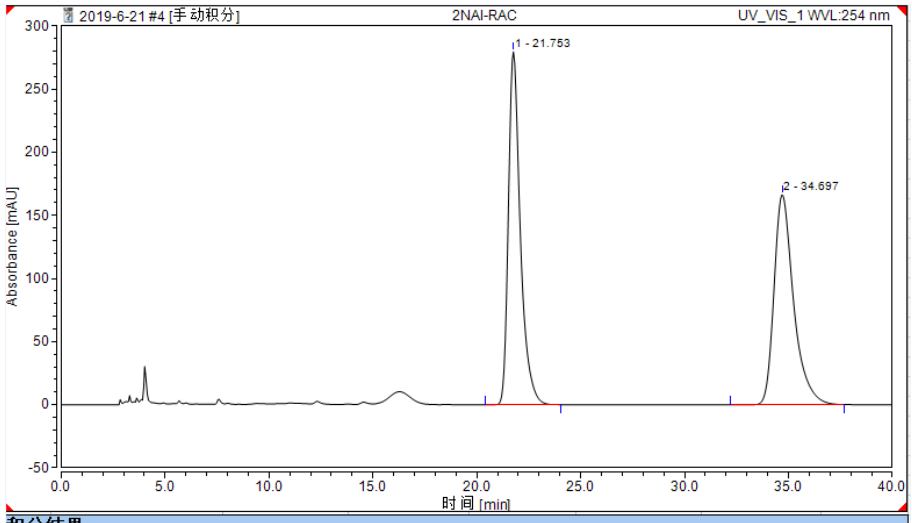
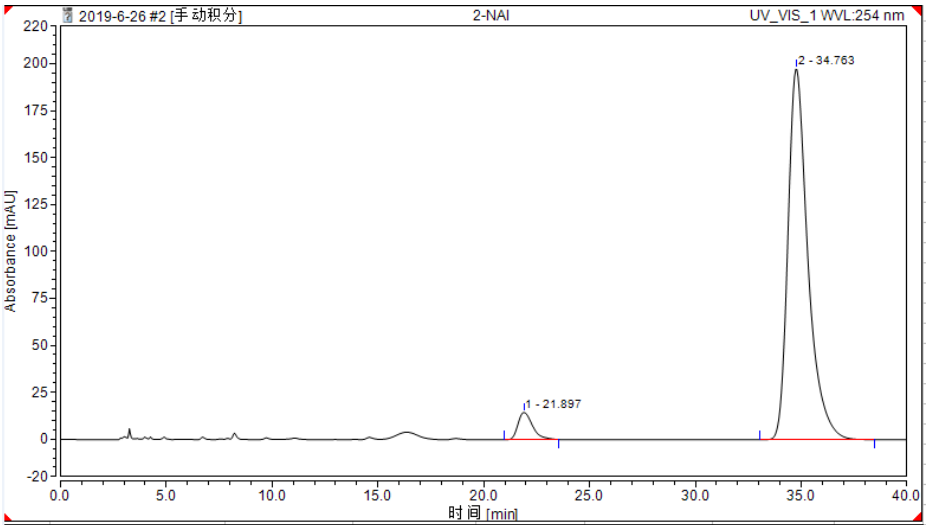


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		21.753	186.072	279.636	50.63	62.71	n.a.
2		34.697	181.471	166.316	49.37	37.29	n.a.

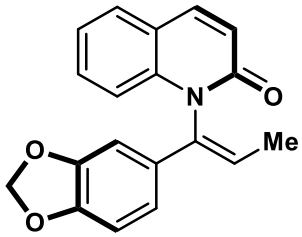


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		21.897	11.553	14.509	5.08	6.84	n.a.
2		34.763	215.914	197.757	94.92	93.16	n.a.

For comparison of Chinese and English of the HPLC data table.

序号	峰 名称	保留时间 (min)	峰 面 积 (mAU*min)	峰 高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height (mAU)	Relative peak area (%)	Relative Peak height (%)	Sample volume n.a.



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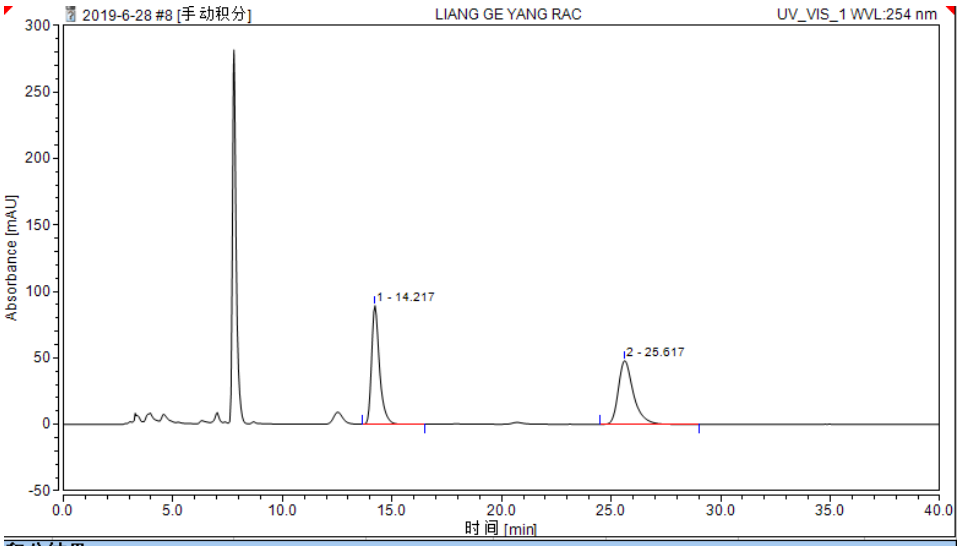
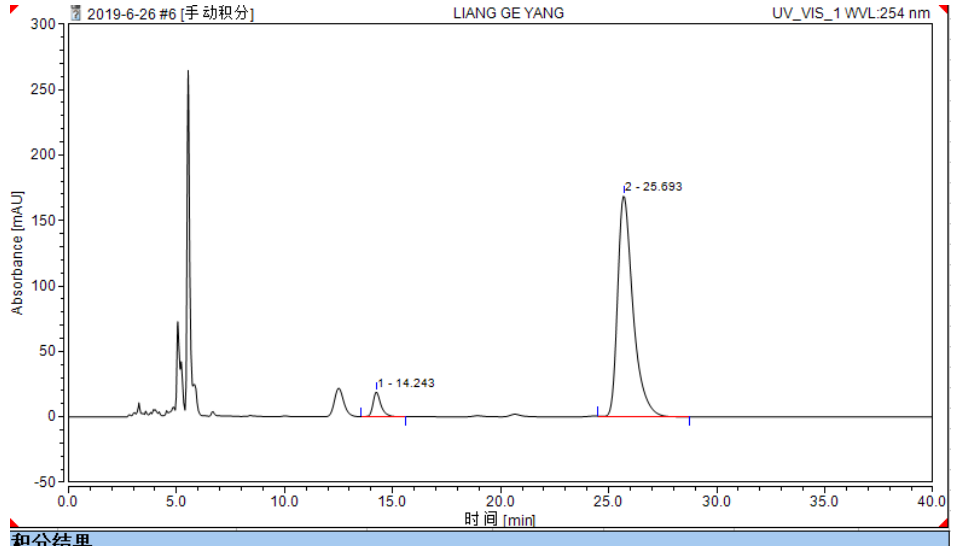


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		14.217	37.384	89.348	49.54	65.10	n.a.
2		25.617	38.073	47.895	50.46	34.90	n.a.

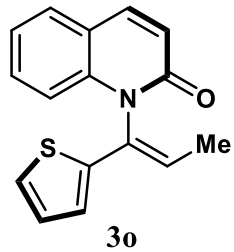


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		14.243	8.006	18.852	5.47	10.06	n.a.
2		25.693	138.386	168.596	94.53	89.94	n.a.

For comparison of Chinese and English of the HPLC data table.

序号	峰 名称	保留时间 (min)	峰 面 积 (mAU*min)	峰 高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height (mAU)	Relative peak area (%)	Relative Peak height (%)	Sample volume n.a.



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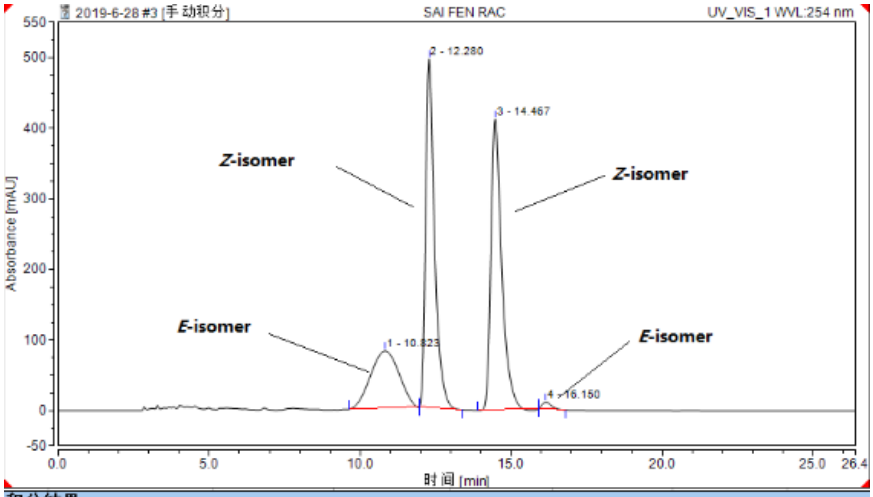
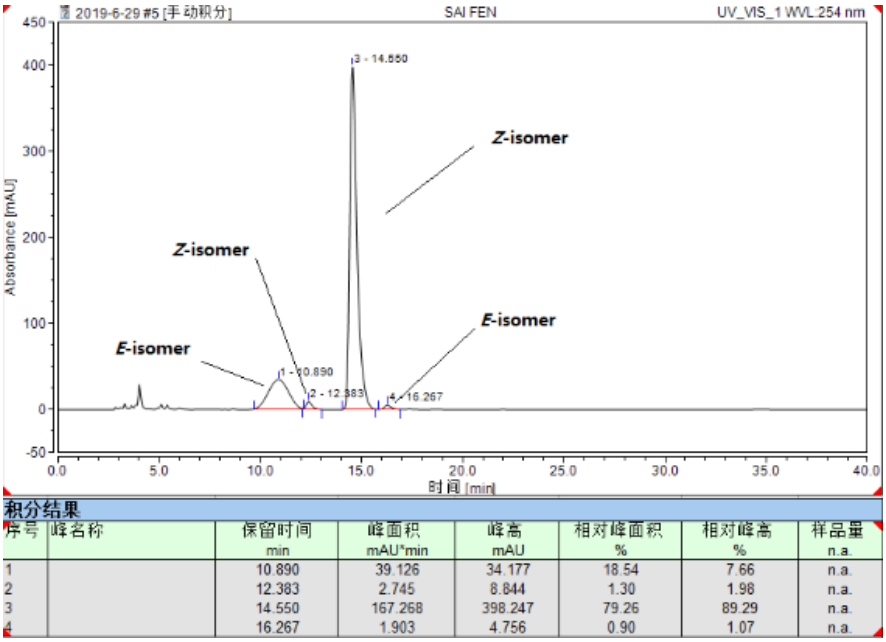


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		10.823	87.884	80.601	20.44	8.10	n.a.
2		12.280	169.397	493.510	39.39	49.58	n.a.
3		14.467	169.555	411.870	39.43	41.38	n.a.
4		16.150	3.172	9.381	0.74	0.94	n.a.

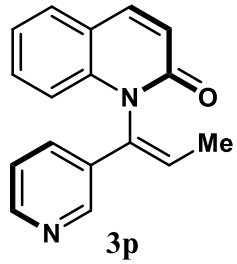


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		10.890	39.126	34.177	18.54	7.66	n.a.
2		12.383	2.745	8.844	1.30	1.98	n.a.
3		14.550	167.268	398.247	79.26	89.29	n.a.
4		16.267	1.903	4.756	0.90	1.07	n.a.

For comparison of Chinese and English of the HPLC data table.

序号	峰名称	保留时间 (min)	峰面积 (mAU*min)	峰高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height (mAU)	Relative peak area (%)	Relative Peak height (%)	Sample volume n.a.



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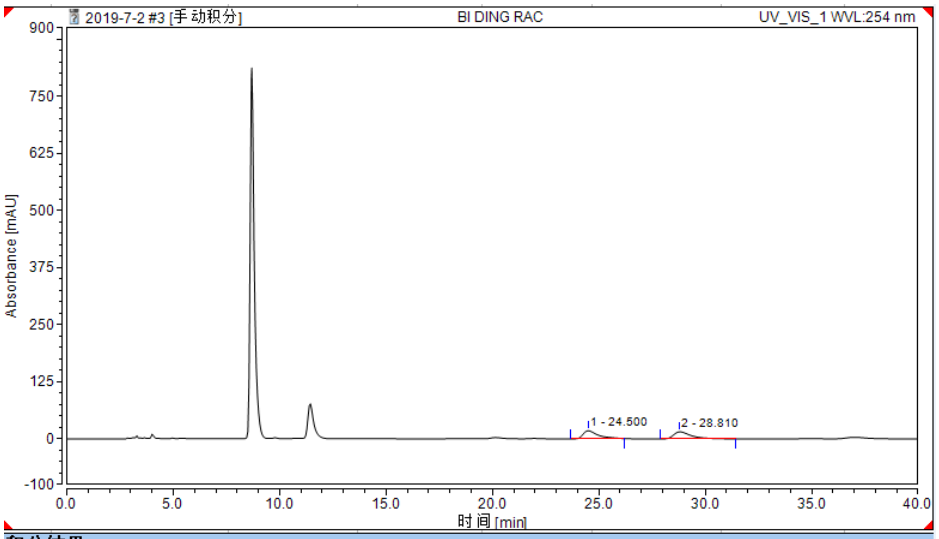
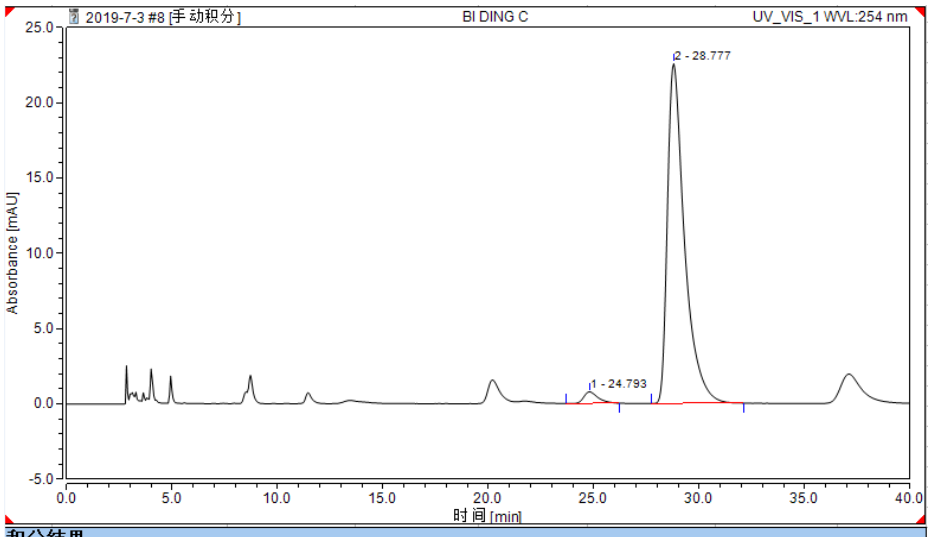


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		24.500	14.436	17.646	49.42	53.19	n.a.
2		28.810	14.776	15.530	50.58	46.81	n.a.

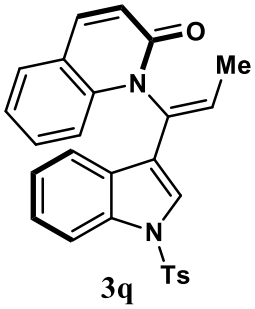


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		24.793	0.606	0.771	2.79	3.30	n.a.
2		28.777	21.151	22.566	97.21	96.70	n.a.

For comparison of Chinese and English of the HPLC data table.

序号	峰名称	保留时间 (min)	峰面积 (mAU*min)	峰高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height (mAU)	Relative peak area (%)	Relative Peak height (%)	Sample volume n.a.



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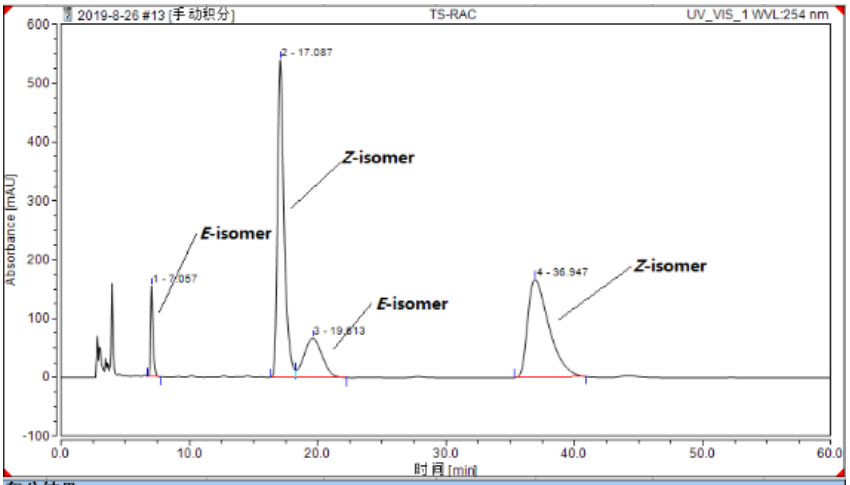
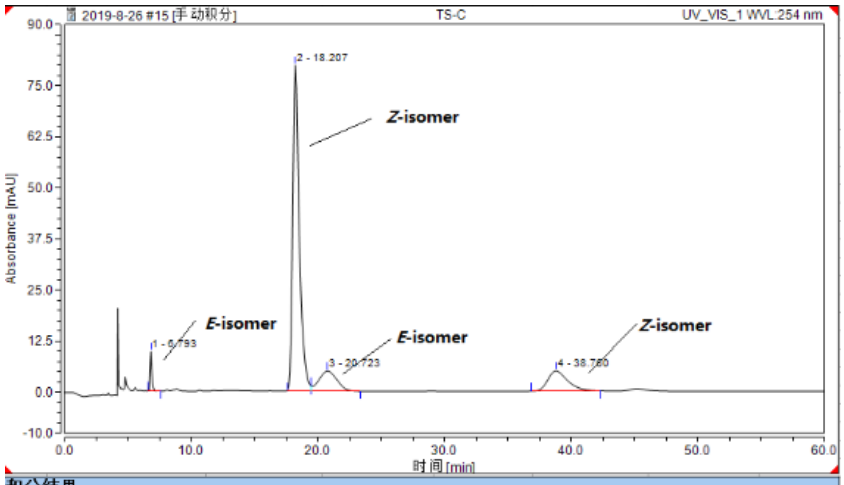


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		7.057	30.289	153.497	3.87	16.58	n.a.
2		17.087	323.882	539.454	41.42	58.27	n.a.
3		19.613	108.117	66.627	13.83	7.20	n.a.
4		36.947	319.574	166.222	40.87	17.95	n.a.

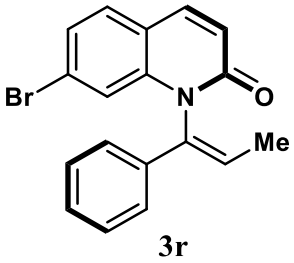


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		6.793	1.311	9.547	1.98	9.64	n.a.
2		18.207	47.982	79.672	72.38	80.47	n.a.
3		20.723	8.018	4.870	12.09	4.92	n.a.
4		38.760	8.984	4.918	13.55	4.97	n.a.

For comparison of Chinese and English of the HPLC data table.

序号	峰 名称	保留时间 (min)	峰 面 积 (mAU*min)	峰 高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height (mAU)	Relative peak area (%)	Relative Peak height (%)	Sample volume n.a.



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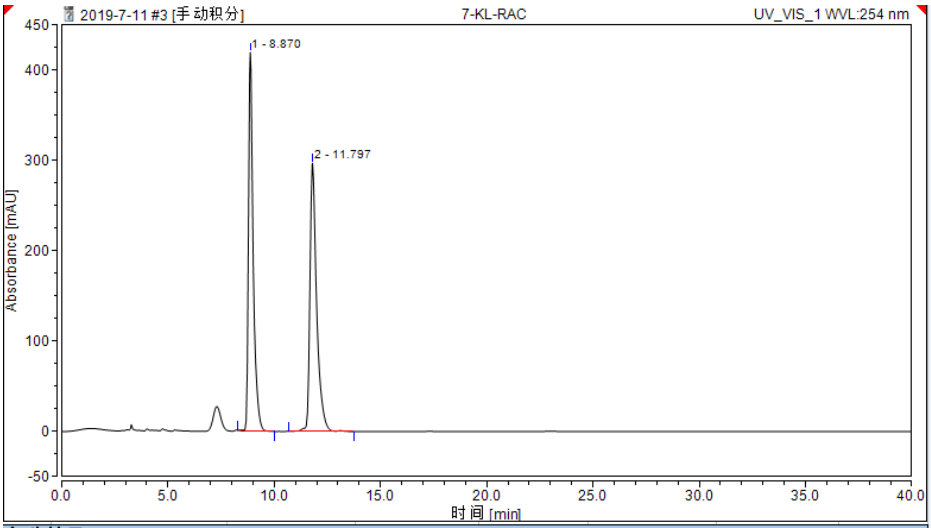
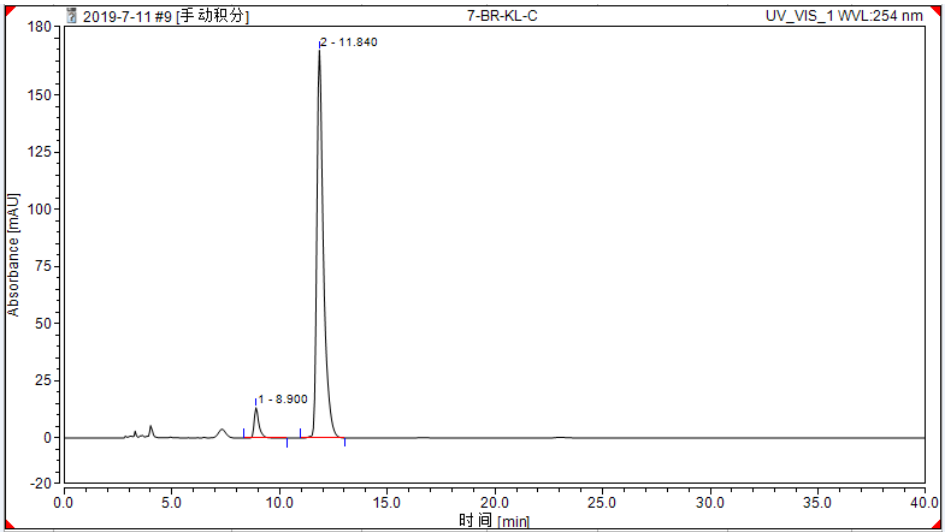


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		8.870	106.274	418.849	49.45	58.51	n.a.
2		11.797	108.631	296.987	50.55	41.49	n.a.

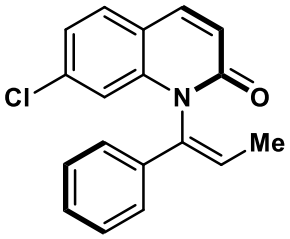


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		8.900	3.392	13.334	5.31	7.28	n.a.
2		11.840	60.479	169.707	94.69	92.72	n.a.

For comparison of Chinese and English of the HPLC data table.

序号	峰 名称	保留时间 (min)	峰 面 积 (mAU*min)	峰 高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height (mAU)	Relative peak area (%)	Relative Peak height (%)	Sample volume n.a.



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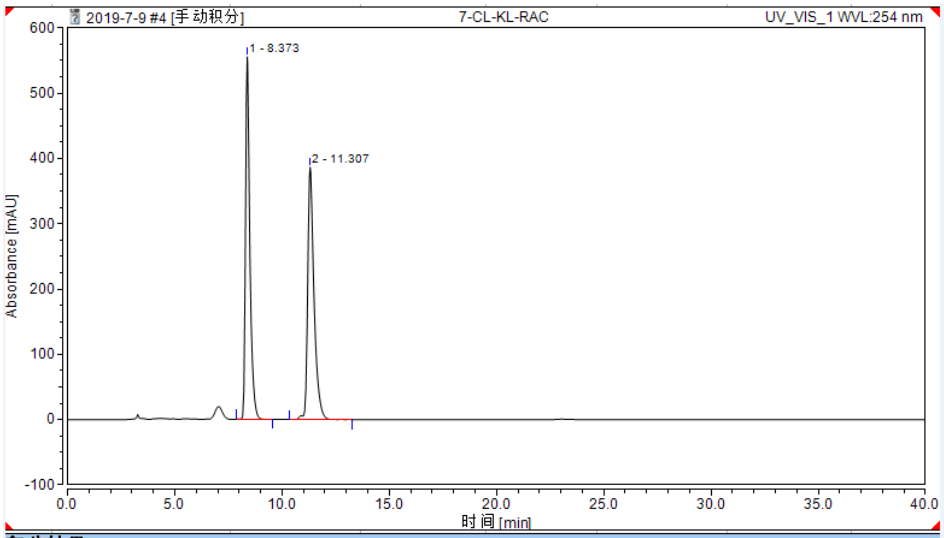
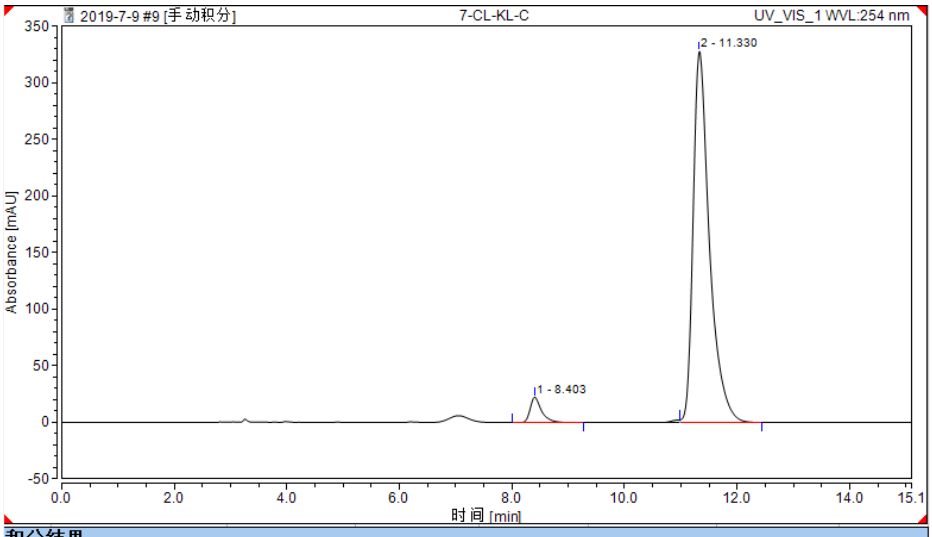


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		8.373	129.534	554.861	49.53	58.93	n.a.
2		11.307	131.967	386.730	50.47	41.07	n.a.

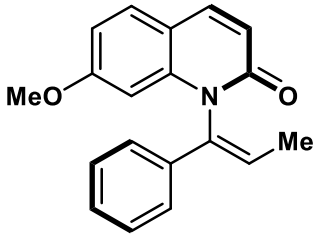


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		8.403	5.162	22.472	4.47	6.41	n.a.
2		11.330	110.288	328.047	95.53	93.59	n.a.

For comparison of Chinese and English of the HPLC data table.

序号	峰名称	保留时间 (min)	峰面积 (mAU*min)	峰高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height (mAU)	Relative peak area (%)	Relative Peak height (%)	Sample volume n.a.



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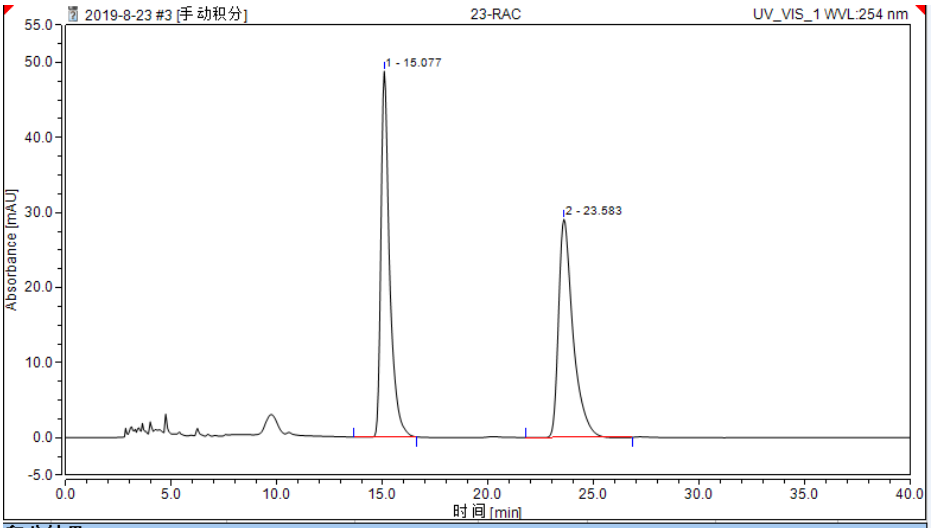
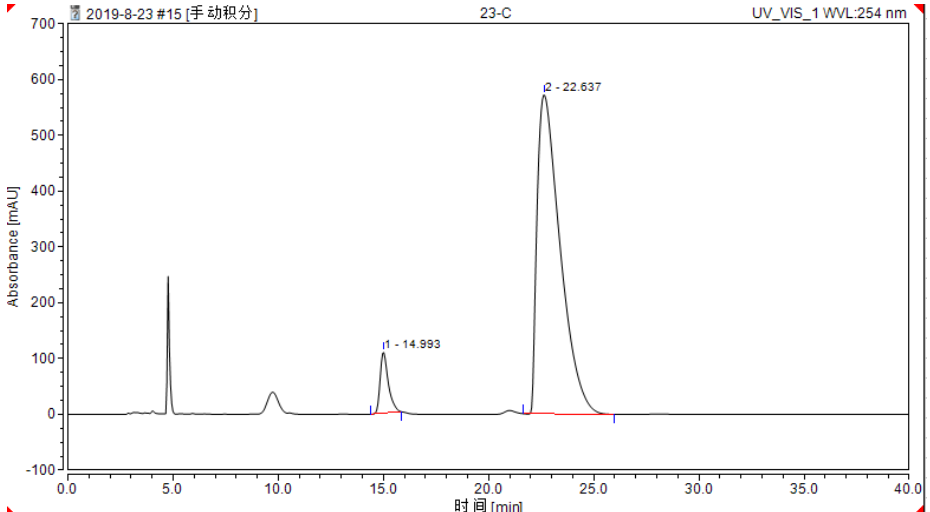


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		15.077	23.195	48.760	50.21	62.62	n.a.
2		23.583	22.997	29.106	49.79	37.38	n.a.

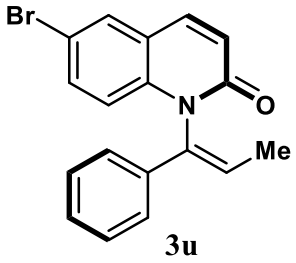


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		14.993	49.152	109.871	6.35	16.11	n.a.
2		22.637	725.133	572.201	93.65	83.89	n.a.

For comparison of Chinese and English of the HPLC data table.

序号	峰名称	保留时间 (min)	峰面积 (mAU*min)	峰高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height (mAU)	Relative peak area (%)	Relative Peak height (%)	Sample volume n.a.



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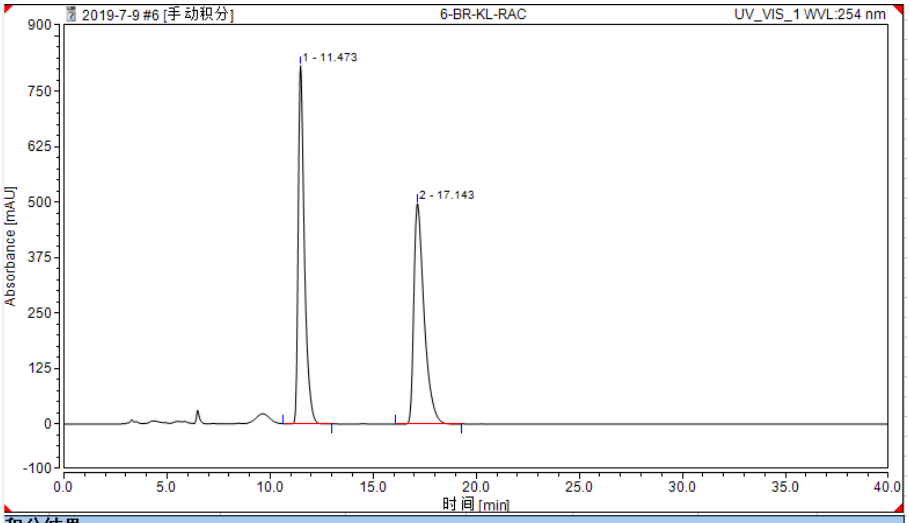
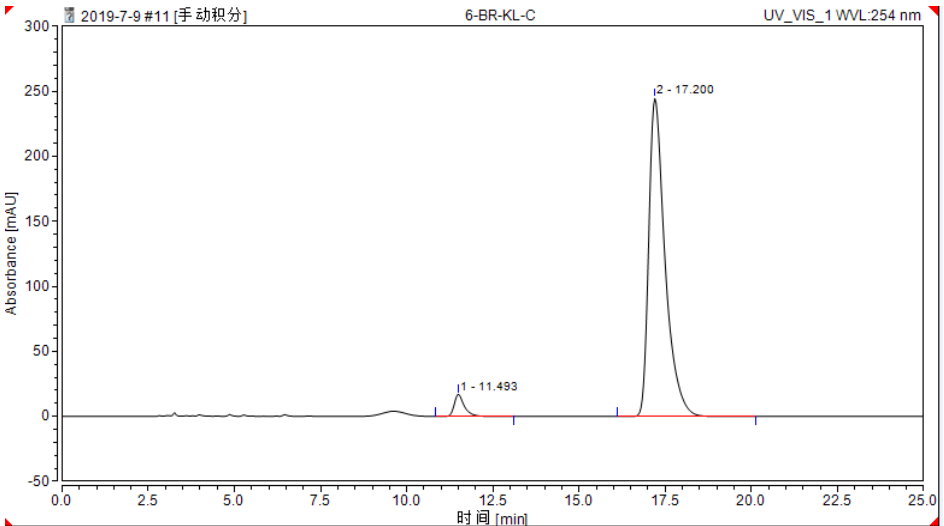


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		11.473	281.062	807.790	49.46	61.91	n.a.
2		17.143	287.236	496.992	50.54	38.09	n.a.

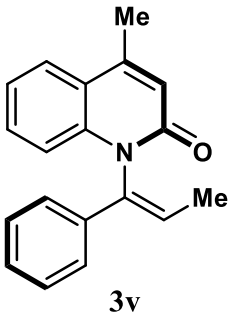


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		11.493	5.698	16.939	4.08	6.48	n.a.
2		17.200	134.130	244.571	95.92	93.52	n.a.

For comparison of Chinese and English of the HPLC data table.

序号	峰名称	保留时间 (min)	峰面积 (mAU*min)	峰高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height (mAU)	Relative peak area (%)	Relative Peak height (%)	Sample volume n.a.



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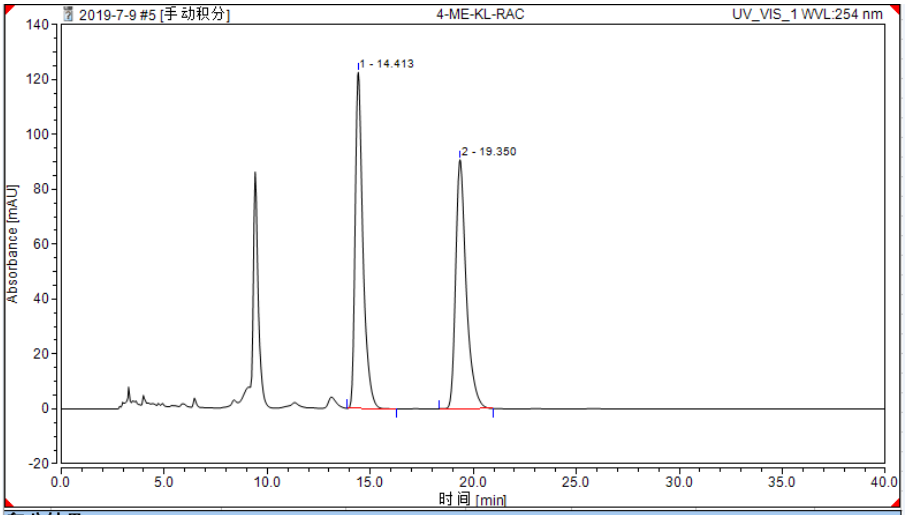
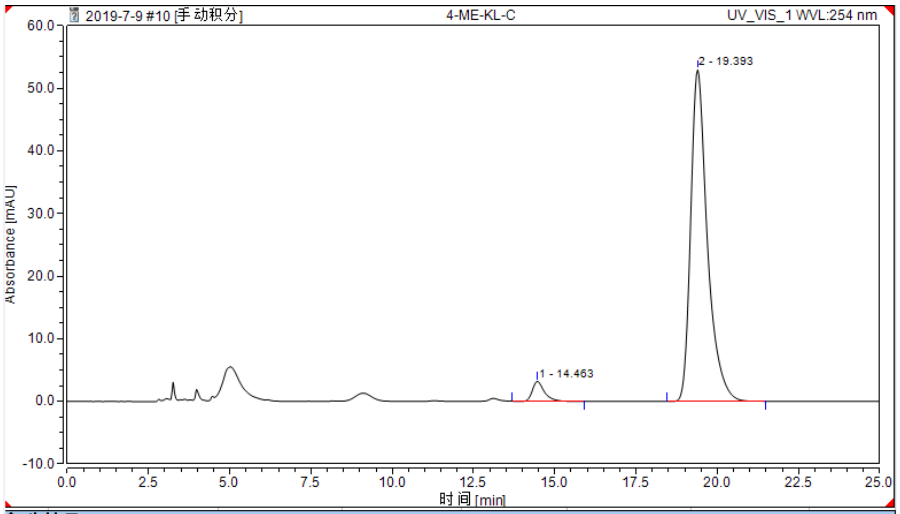


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		14.413	53.714	122.526	49.92	57.45	n.a.
2		19.350	53.876	90.731	50.08	42.55	n.a.

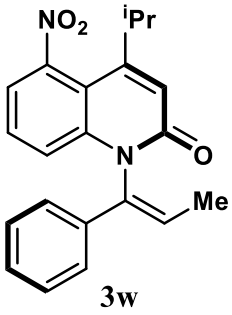


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		14.463	1.345	3.174	4.10	5.65	n.a.
2		19.393	31.504	52.969	95.90	94.35	n.a.

For comparison of Chinese and English of the HPLC data table.

序号	峰名称	保留时间 (min)	峰面积 (mAU*min)	峰高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height (mAU)	Relative peak area (%)	Relative Peak height (%)	Sample volume n.a.



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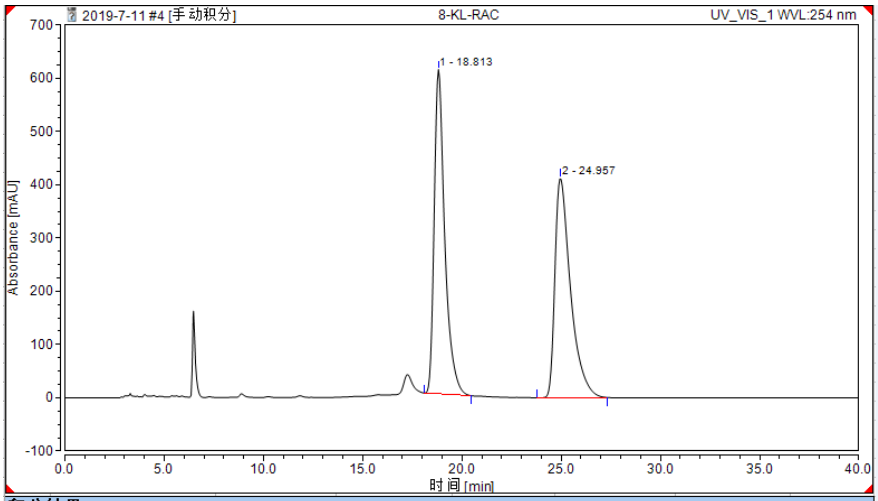
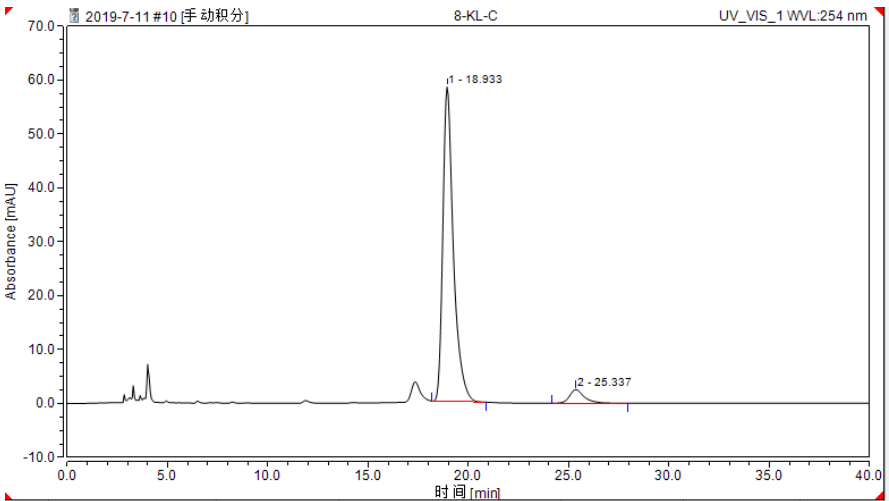


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		18.813	375.763	609.378	50.03	59.66	n.a.
2		24.957	375.297	412.077	49.97	40.34	n.a.

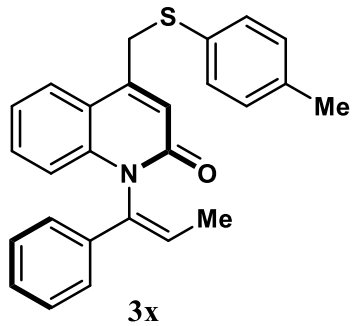


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		18.933	35.666	58.391	94.44	95.89	n.a.
2		25.337	2.102	2.505	5.56	4.11	n.a.

For comparison of Chinese and English of the HPLC data table.

序号	峰 名称	保留时间 (min)	峰 面 积 (mAU*min)	峰 高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height (mAU)	Relative peak area (%)	Relative Peak height (%)	Sample volume n.a.



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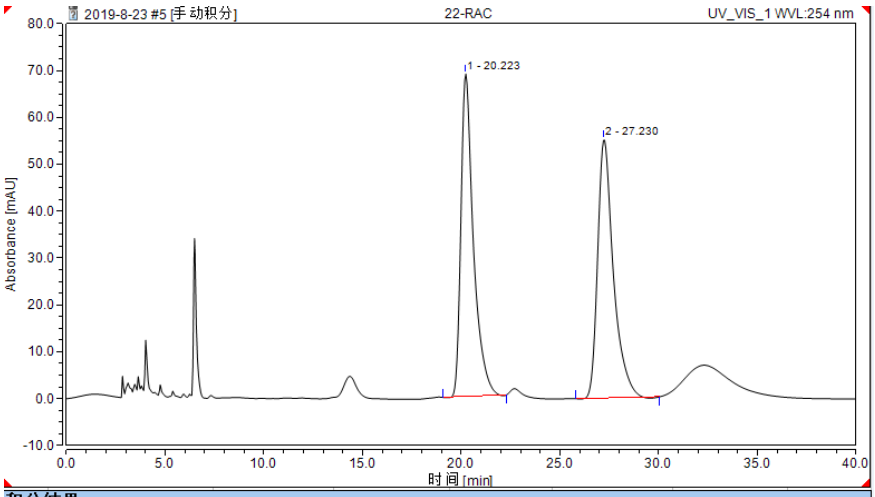
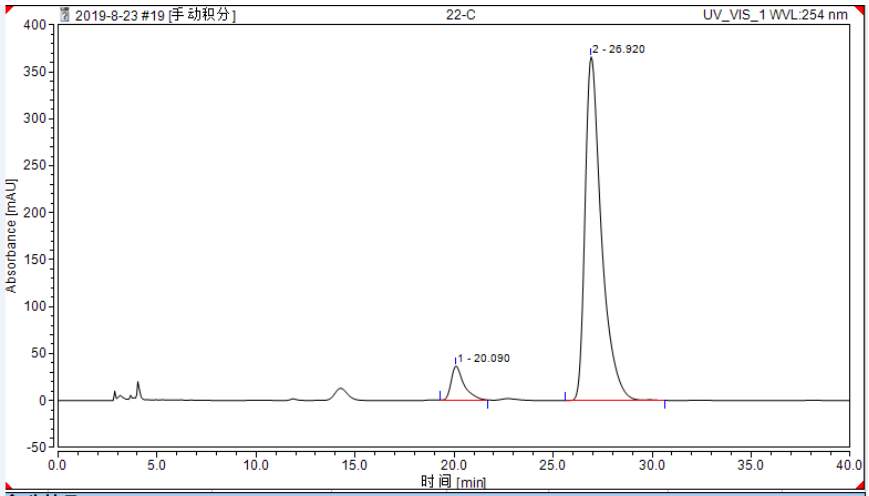


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		20.223	50.319	68.839	49.75	55.50	n.a.
2		27.230	50.824	55.205	50.25	44.50	n.a.

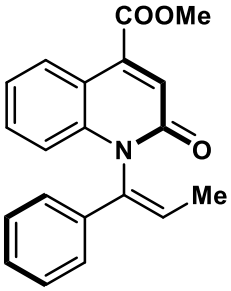


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		20.090	26.777	36.149	7.08	8.99	n.a.
2		26.920	351.613	365.992	92.92	91.01	n.a.

For comparison of Chinese and English of the HPLC data table.

序号	峰 名称	保留时间 (min)	峰 面 积 (mAU*min)	峰 高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height (mAU)	Relative peak area (%)	Relative Peak height (%)	Sample volume n.a.



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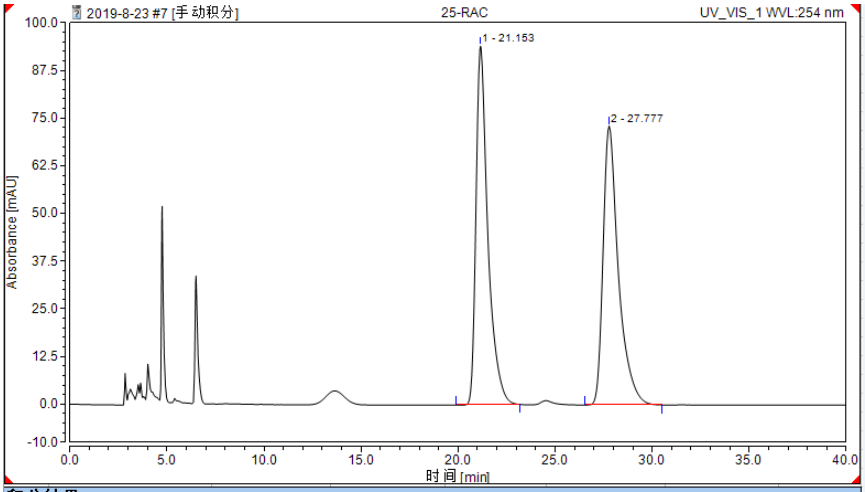
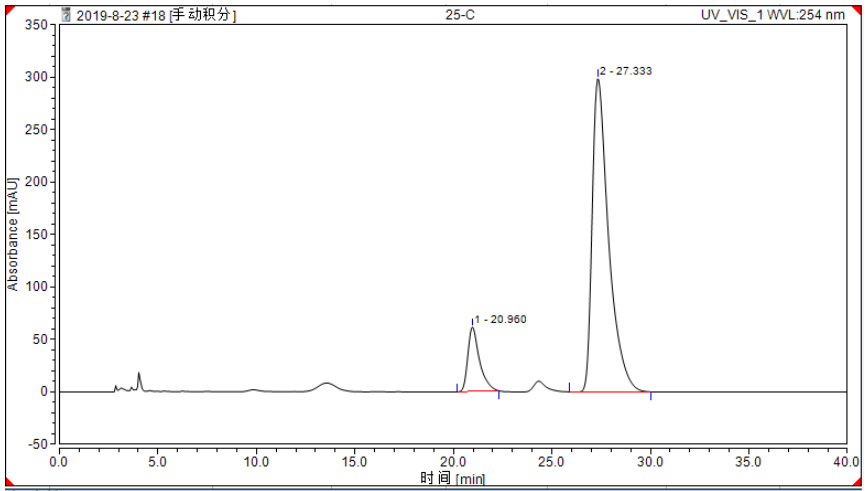


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		21.153	66.566	94.017	49.87	56.24	n.a.
2		27.777	66.911	73.146	50.13	43.76	n.a.

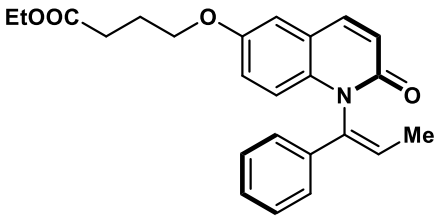


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		20.960	42.111	61.486	12.70	17.05	n.a.
2		27.333	289.473	299.117	87.30	82.95	n.a.

For comparison of Chinese and English of the HPLC data table.

序号	峰名称	保留时间 (min)	峰面积 (mAU*min)	峰高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height (mAU)	Relative peak area (%)	Relative Peak height (%)	Sample volume n.a.



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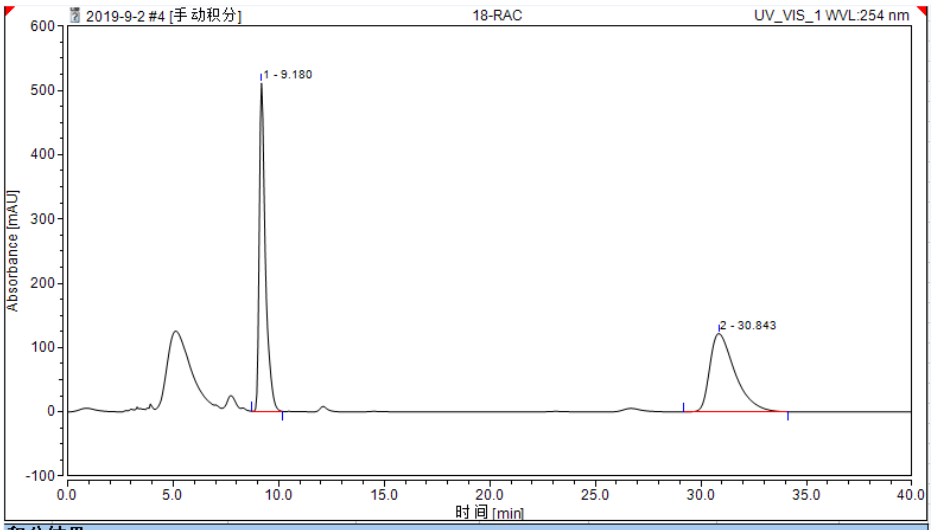
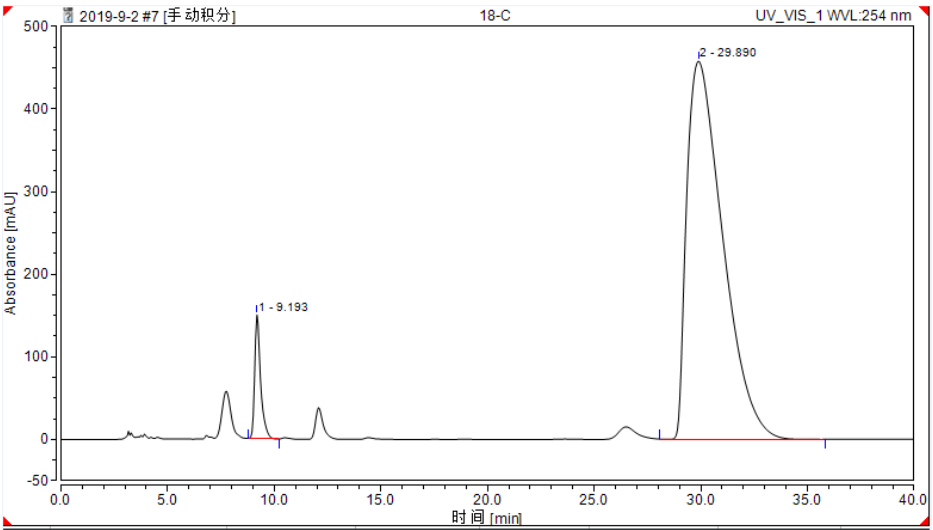


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		9.180	171.306	510.471	50.45	80.74	n.a.
2		30.843	168.260	121.797	49.55	19.26	n.a.

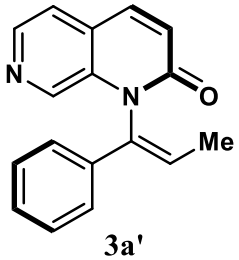


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		9.193	47.972	149.637	5.09	24.65	n.a.
2		29.890	893.997	457.478	94.91	75.35	n.a.

For comparison of Chinese and English of the HPLC data table.

序号	峰名称	保留时间 (min)	峰面积 (mAU*min)	峰高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height (mAU)	Relative peak area (%)	Relative Peak height (%)	Sample volume n.a.



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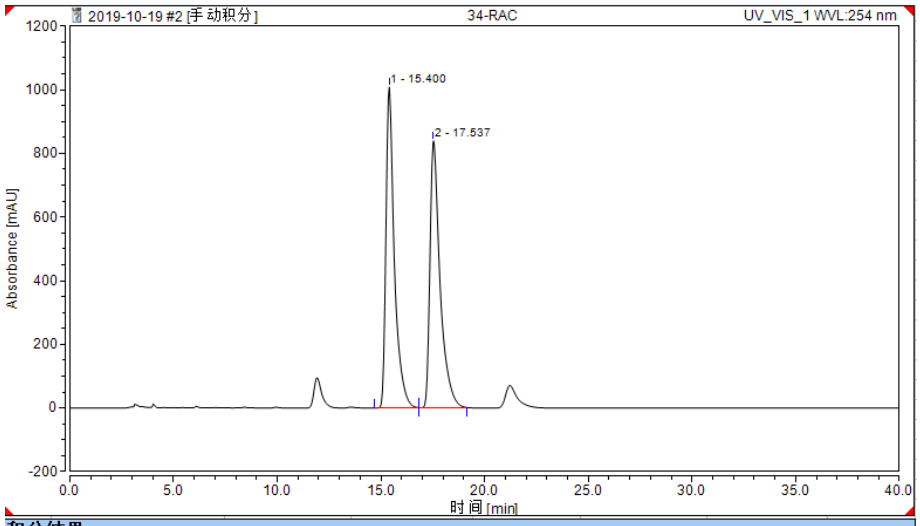
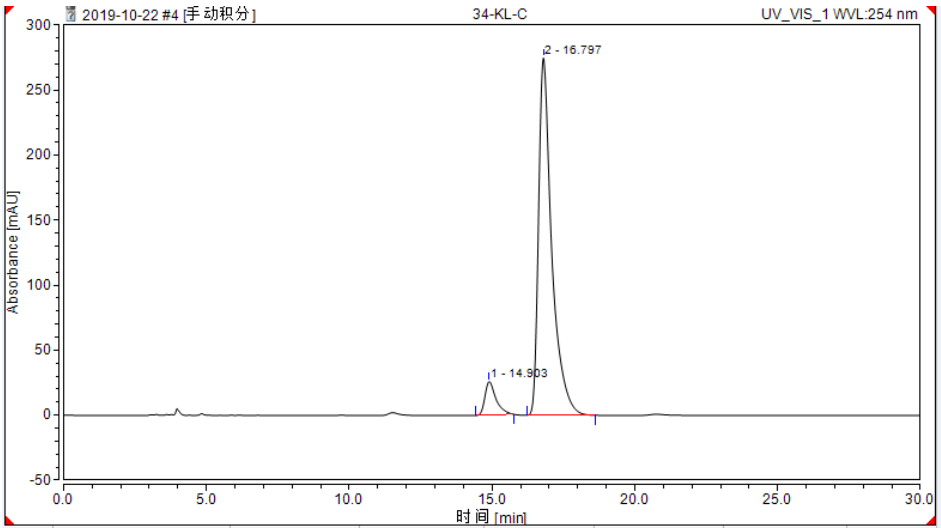


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		15.400	473.087	1008.396	50.01	54.58	n.a.
2		17.537	472.861	839.038	49.99	45.42	n.a.

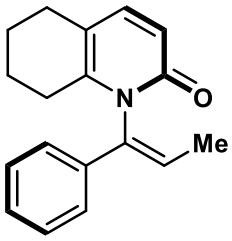


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		14.903	11.488	25.819	7.25	8.59	n.a.
2		16.797	147.058	274.793	92.75	91.41	n.a.

For comparison of Chinese and English of the HPLC data table.

序号	峰 名称	保留时间 (min)	峰 面 积 (mAU*min)	峰 高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height (mAU)	Relative peak area (%)	Relative Peak height (%)	Sample volume n.a.



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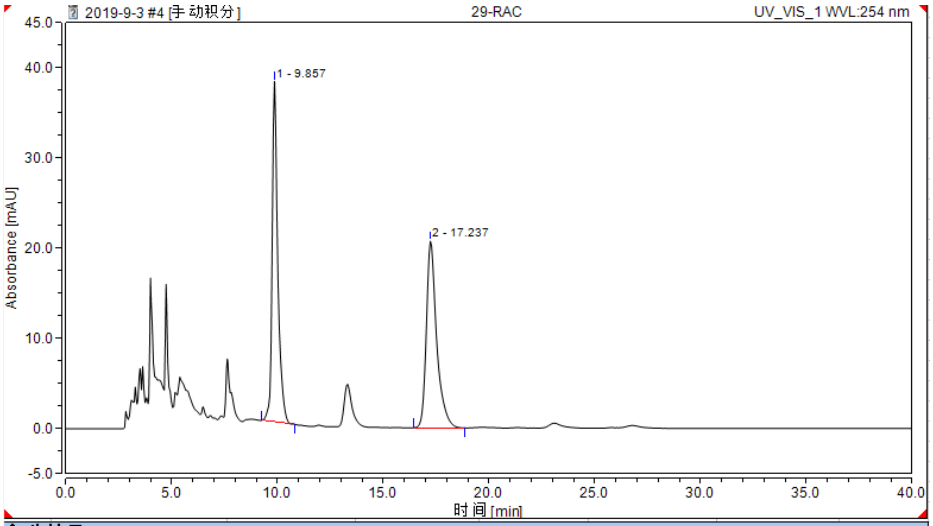
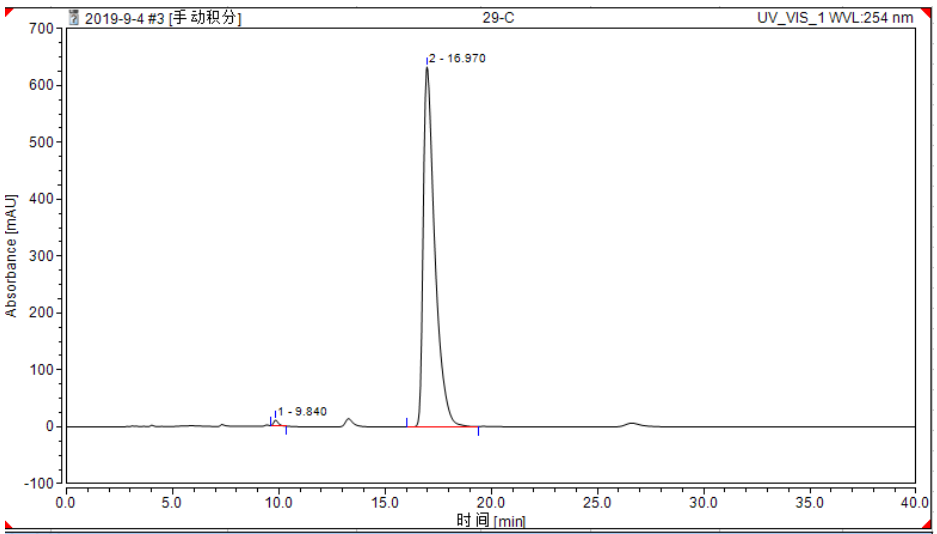


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		9.857	11.521	37.727	49.71	64.56	n.a.
2		17.237	11.656	20.706	50.29	35.44	n.a.

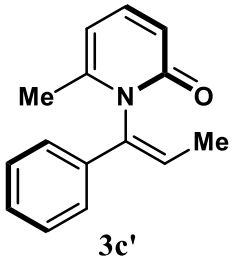


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		9.840	2.502	10.020	0.62	1.56	n.a.
2		16.970	399.375	632.615	99.38	98.44	n.a.

For comparison of Chinese and English of the HPLC data table.

序号	峰 名称	保留时间 (min)	峰 面 积 (mAU*min)	峰 高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height (mAU)	Relative peak area (%)	Relative Peak height (%)	Sample volume n.a.



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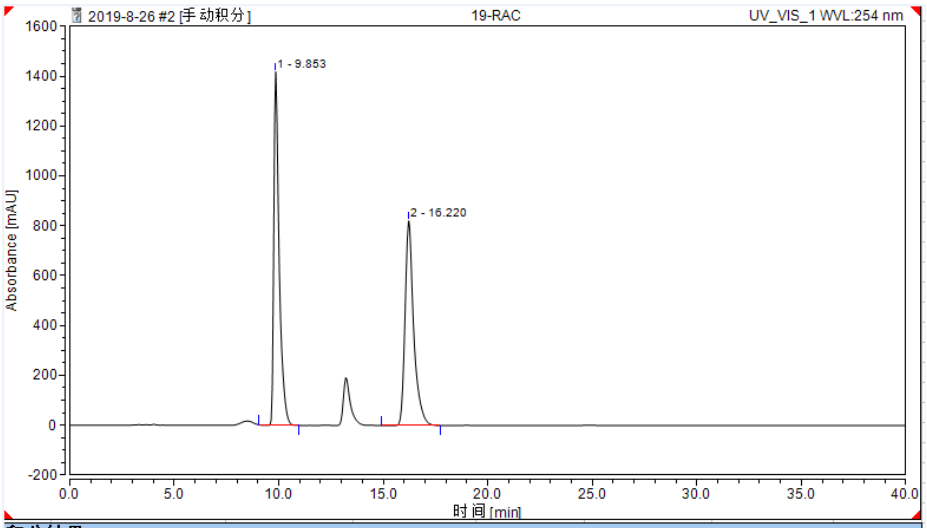
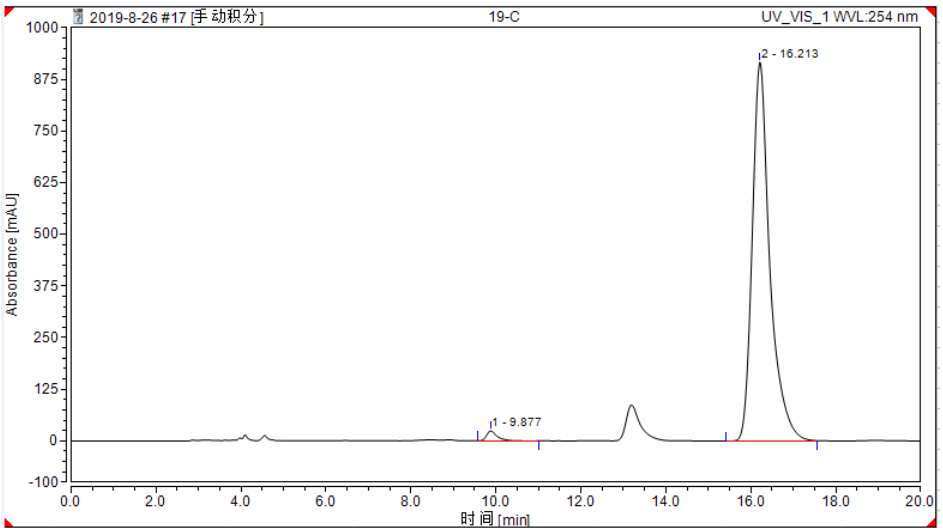


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		9.853	419.746	1416.619	51.67	63.31	n.a.
2		16.220	392.676	821.016	48.33	36.69	n.a.

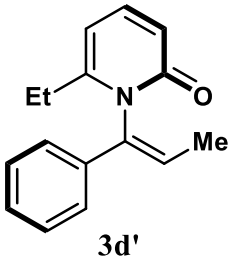


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		9.877	6.676	24.010	1.50	2.55	n.a.
2		16.213	439.252	916.292	98.50	97.45	n.a.

For comparison of Chinese and English of the HPLC data table.

序号	峰 名称	保留时间 (min)	峰 面 积 (mAU*min)	峰 高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height (mAU)	Relative peak area (%)	Relative Peak height (%)	Sample volume n.a.



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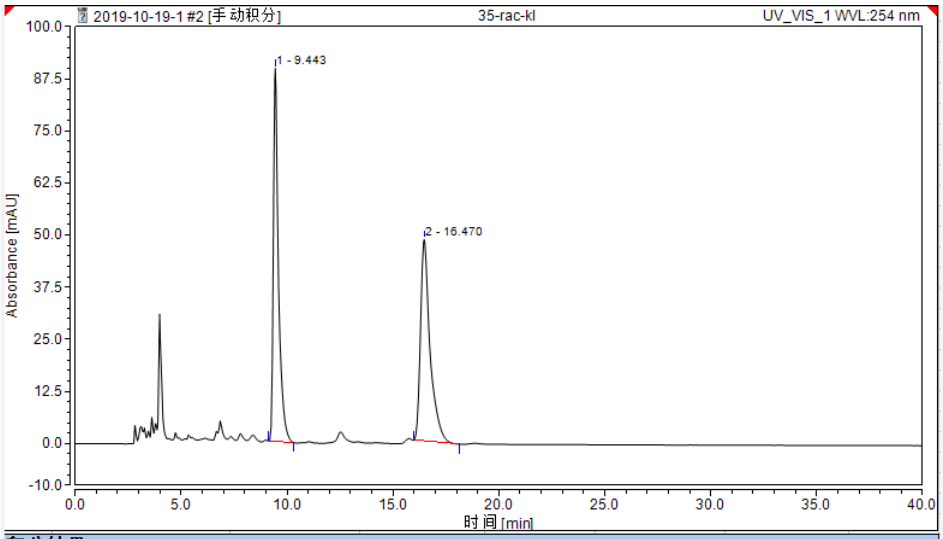
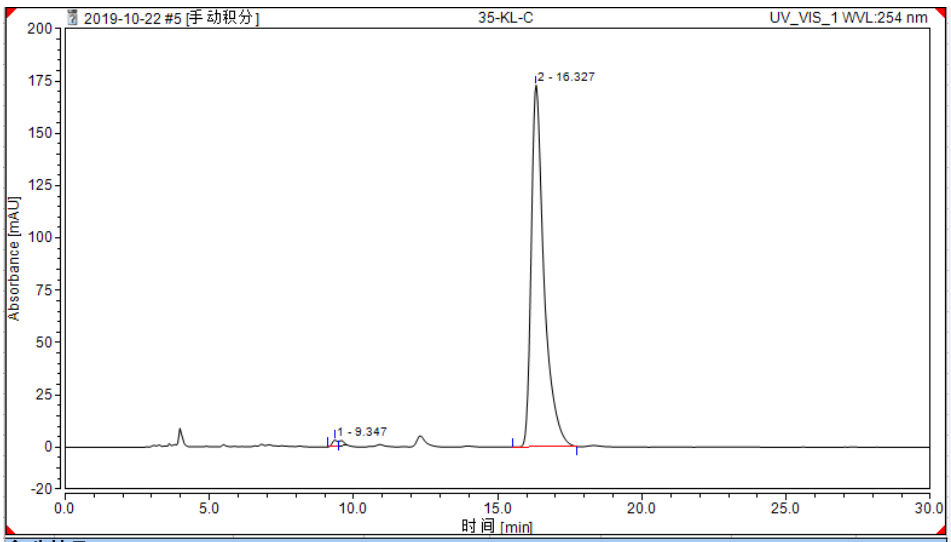


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		9.443	24.982	89.484	49.84	64.95	n.a.
2		16.470	25.144	48.299	50.16	35.05	n.a.

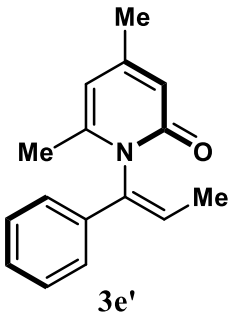


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		9.347	0.611	3.027	0.68	1.72	n.a.
2		16.327	89.053	172.865	99.32	98.28	n.a.

For comparison of Chinese and English of the HPLC data table.

序号	峰名称	保留时间 (min)	峰面积 (mAU*min)	峰高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height (mAU)	Relative peak area (%)	Relative Peak height (%)	Sample volume n.a.



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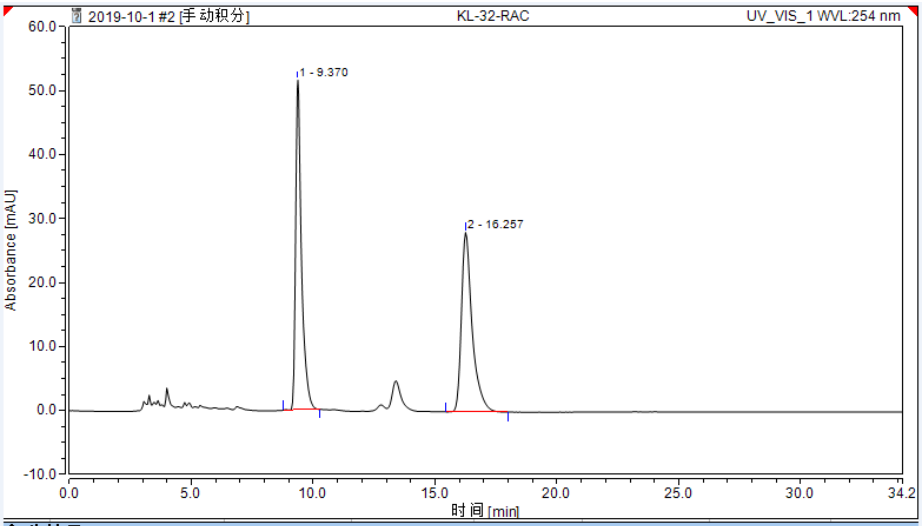
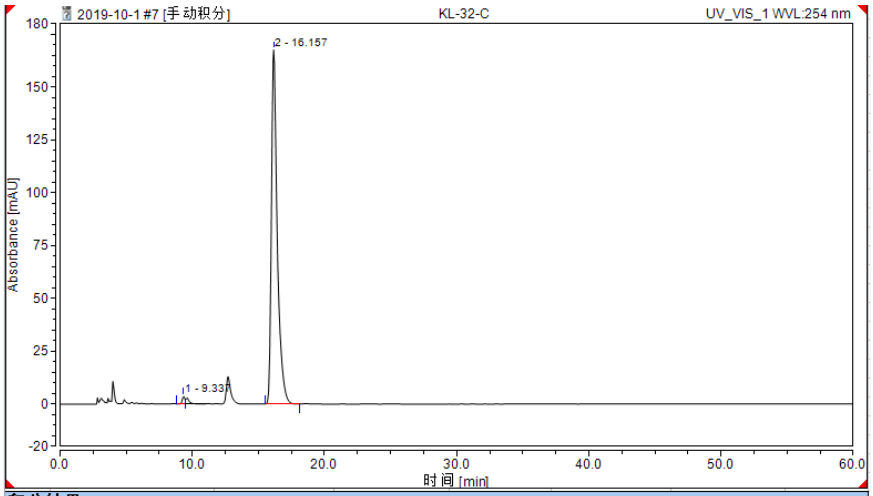


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		9.370	14.339	51.541	49.99	64.73	n.a.
2		16.257	14.344	28.087	50.01	35.27	n.a.

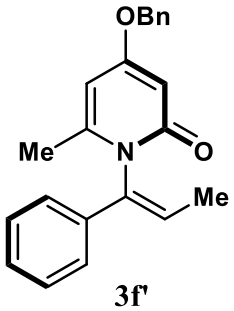


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		9.337	0.792	3.609	0.91	2.11	n.a.
2		16.157	85.923	167.572	99.09	97.89	n.a.

For comparison of Chinese and English of the HPLC data table.

序号	峰名称	保留时间 (min)	峰面积 (mAU*min)	峰高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height (mAU)	Relative peak area (%)	Relative Peak height (%)	Sample volume n.a.



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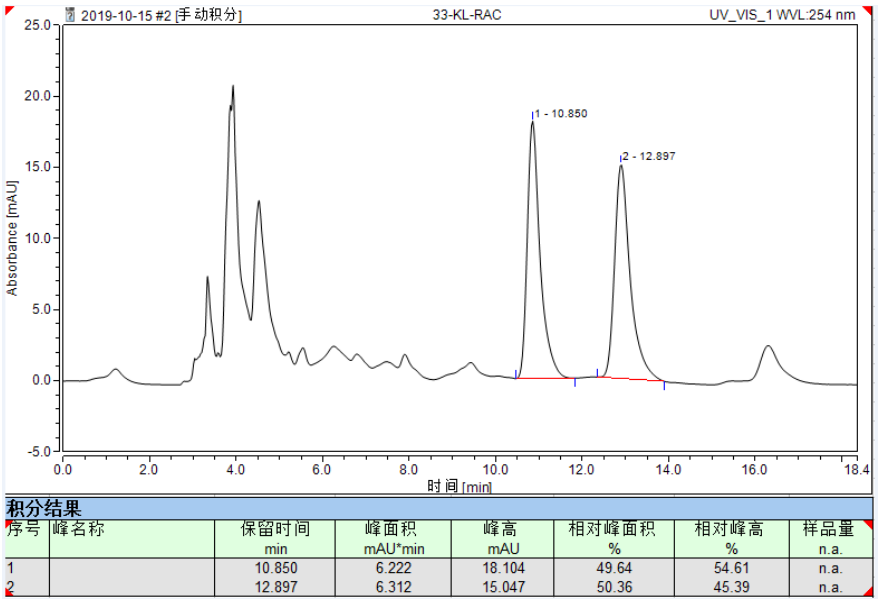
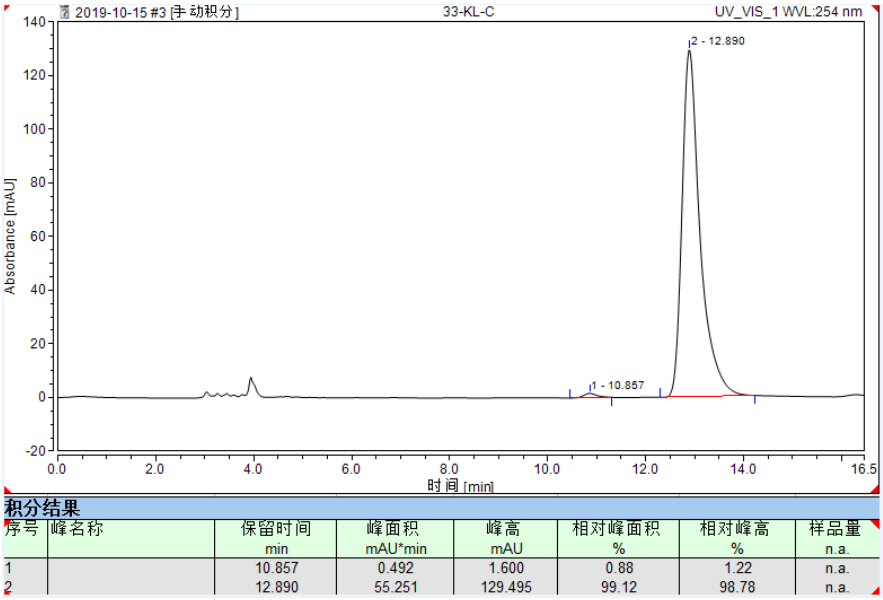


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		10.850	6.222	18.104	49.64	54.61	n.a.
2		12.897	6.312	15.047	50.36	45.39	n.a.

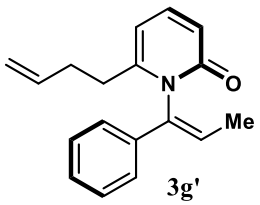


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		10.857	0.492	1.600	0.88	1.22	n.a.
2		12.890	55.251	129.495	99.12	98.78	n.a.

For comparison of Chinese and English of the HPLC data table.

序号	峰名称	保留时间 (min)	峰面积 (mAU*min)	峰高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height (mAU)	Relative peak area (%)	Relative Peak height (%)	Sample volume n.a.



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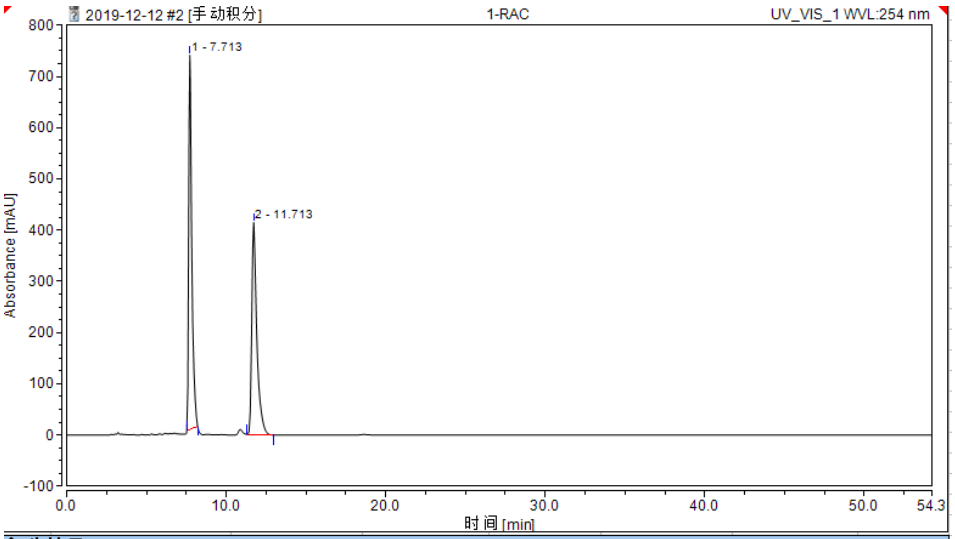
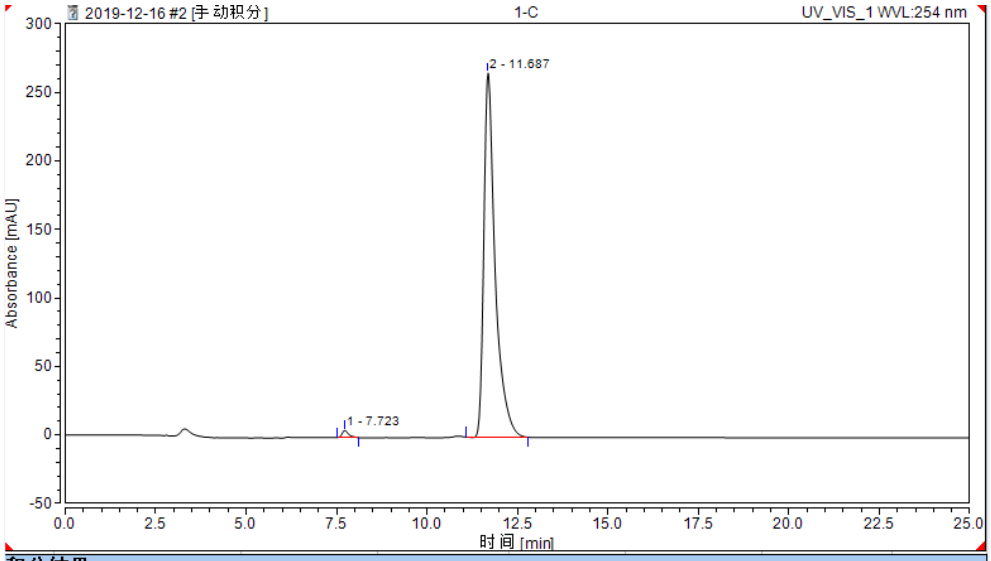


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		7.713	163.125	730.670	51.86	63.84	n.a.
2		11.713	151.421	413.806	48.14	36.16	n.a.

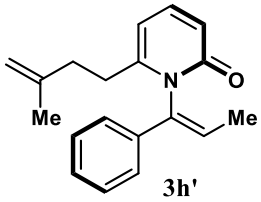


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		7.723	1.068	5.214	1.09	1.92	n.a.
2		11.687	96.540	265.760	98.91	98.08	n.a.

For comparison of Chinese and English of the HPLC data table.

序号	峰名称	保留时间 (min)	峰面积 (mAU*min)	峰高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height (mAU)	Relative peak area (%)	Relative Peak height (%)	Sample volume n.a.



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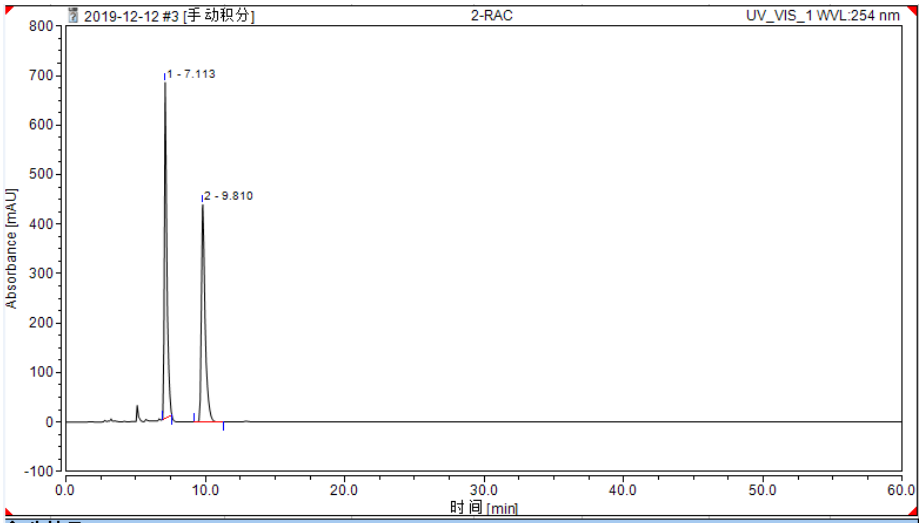
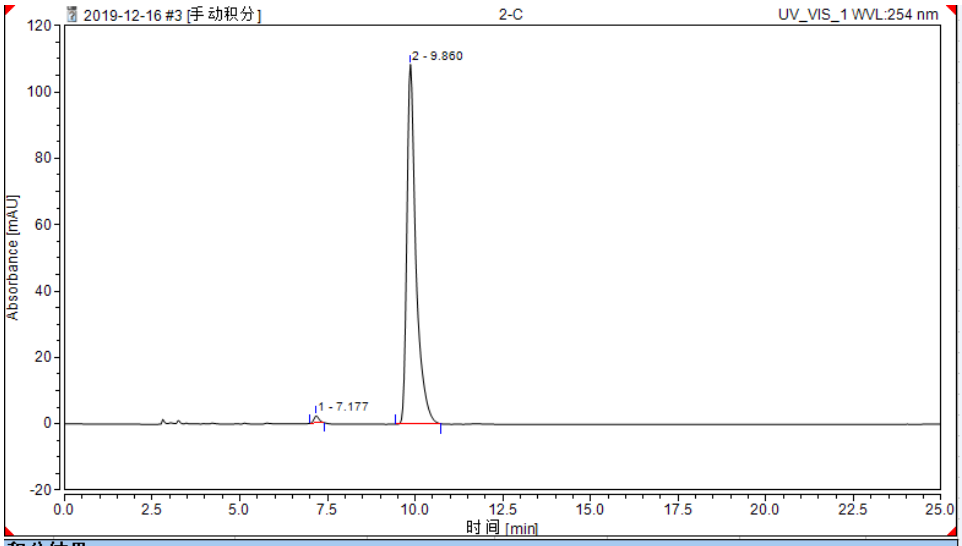


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		7.113	142.858	679.021	51.39	60.75	n.a.
2		9.810	135.112	438.713	48.61	39.25	n.a.

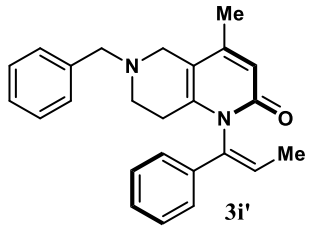


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		7.177	0.350	2.169	1.07	1.96	n.a.
2		9.860	32.534	108.465	98.93	98.04	n.a.

For comparison of Chinese and English of the HPLC data table.

序号	峰名称	保留时间 (min)	峰面积 (mAU*min)	峰高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height (mAU)	Relative peak area (%)	Relative Peak height (%)	Sample volume n.a.



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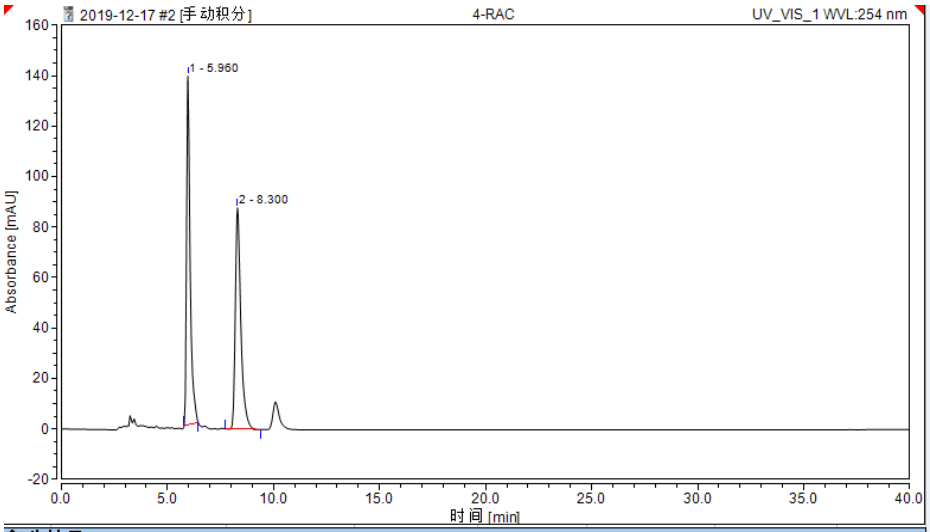
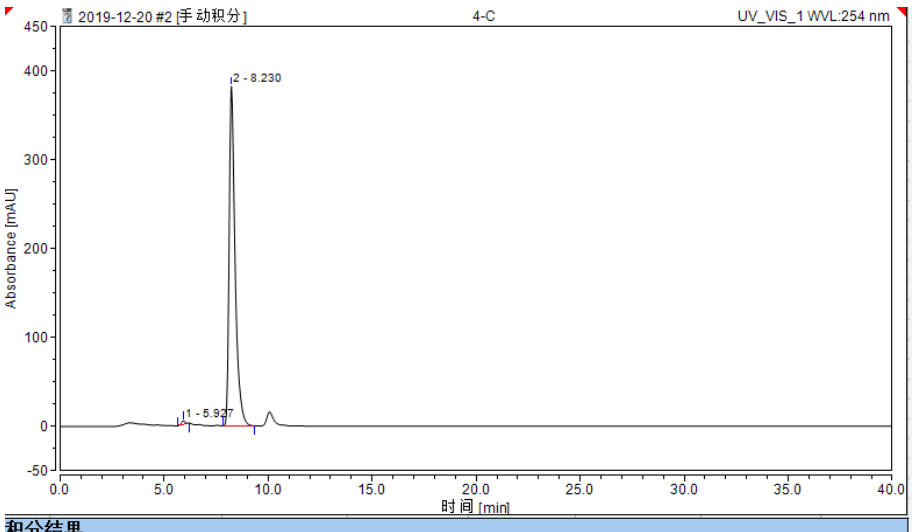


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		5.960	27.075	138.207	50.61	61.17	n.a.
2		8.300	26.425	87.722	49.39	38.83	n.a.

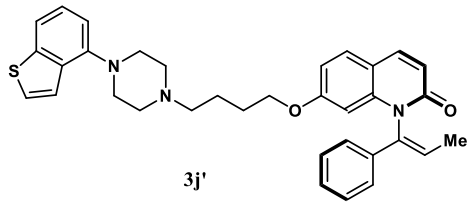


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		5.927	0.832	3.860	0.65	1.00	n.a.
2		8.230	126.630	382.383	99.35	99.00	n.a.

For comparison of Chinese and English of the HPLC data table.

序号	峰名称	保留时间 (min)	峰面积 (mAU*min)	峰高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height (mAU)	Relative peak area (%)	Relative Peak height (%)	Sample volume n.a.



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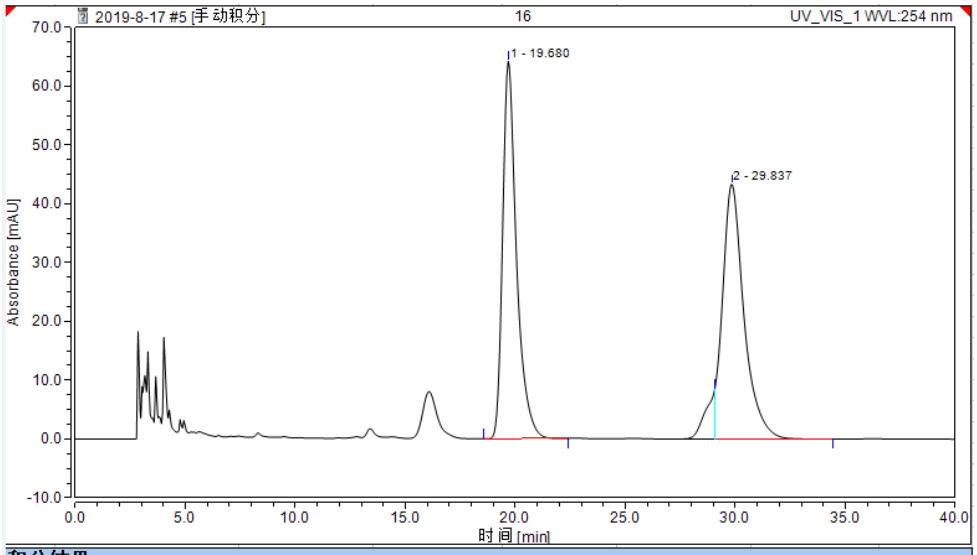
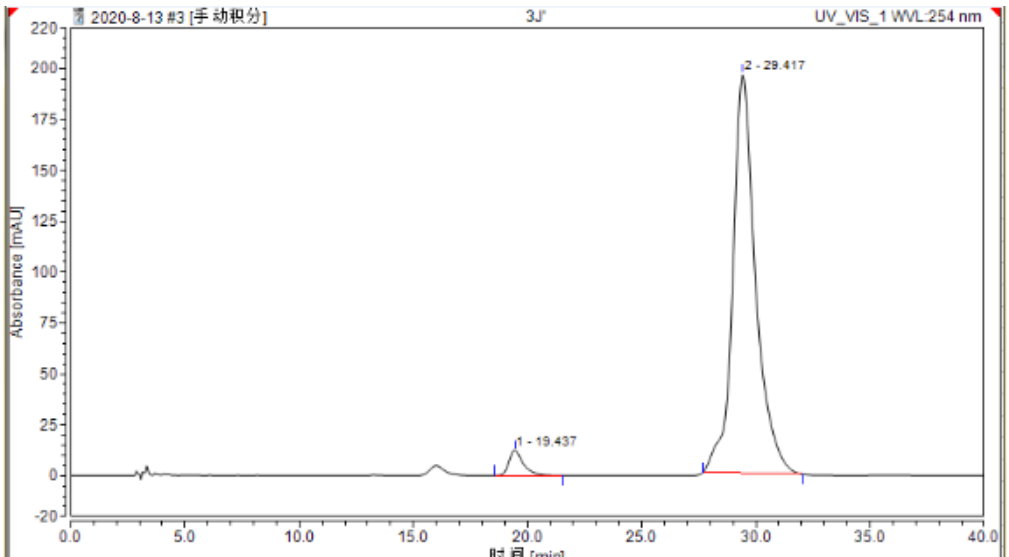


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		19.680	46.845	64.177	48.97	59.68	n.a.
2		29.837	48.813	43.366	51.03	40.32	n.a.

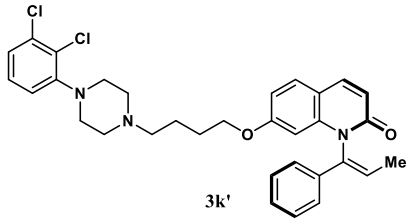


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		19.437	9.090	12.513	3.84	6.01	n.a.
2		29.417	227.717	195.806	96.16	93.99	n.a.

For comparison of Chinese and English of the HPLC data table.

序号	峰名称	保留时间 (min)	峰面积 (mAU*min)	峰高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height (mAU)	Relative peak area (%)	Relative Peak height (%)	Sample volume n.a.



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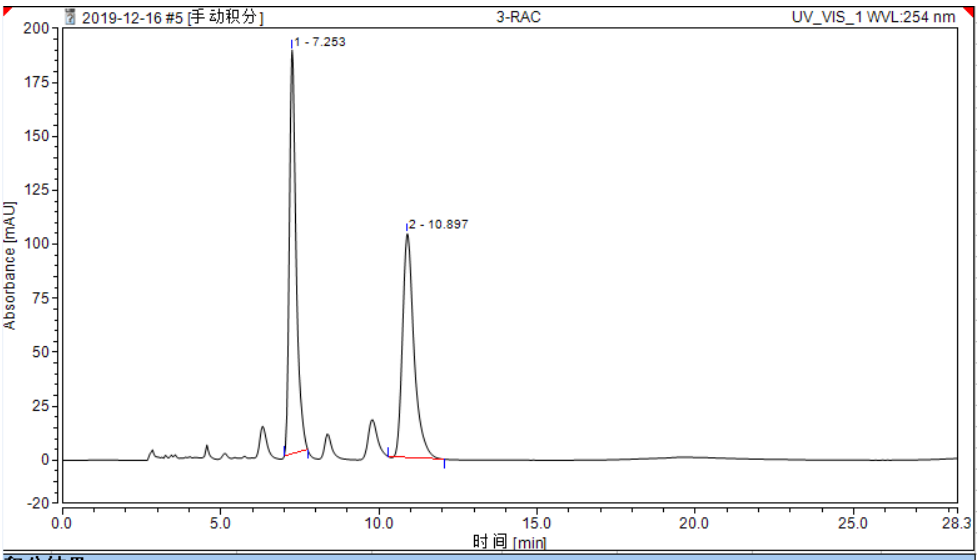
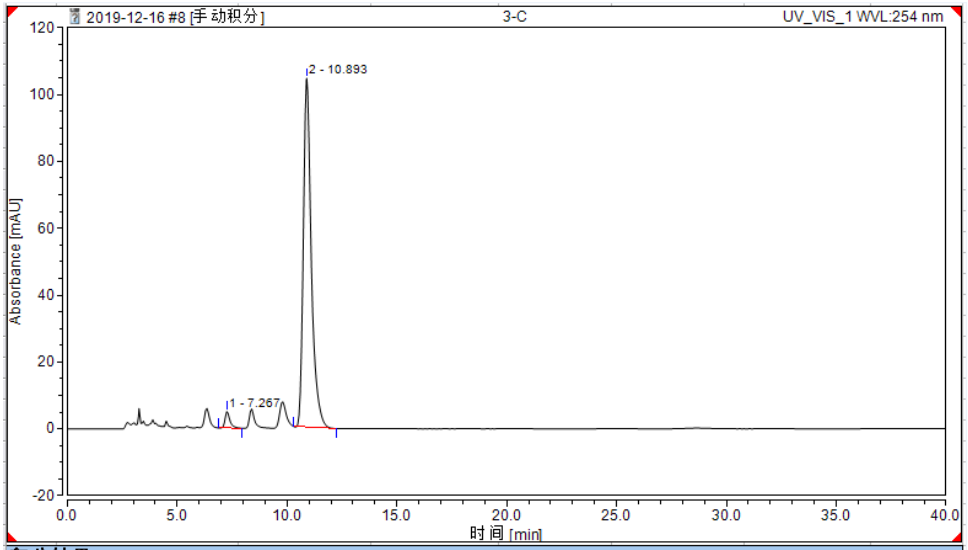


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		7.253	46.501	186.992	51.49	64.33	n.a.
2		10.897	43.810	103.671	48.51	35.67	n.a.

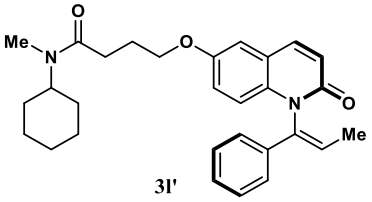


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		7.267	1.285	5.018	2.85	4.59	n.a.
2		10.893	43.782	104.336	97.15	95.41	n.a.

For comparison of Chinese and English of the HPLC data table.

序号	峰名称	保留时间 (min)	峰面积 (mAU*min)	峰高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height (mAU)	Relative peak area (%)	Relative Peak height (%)	Sample volume n.a.



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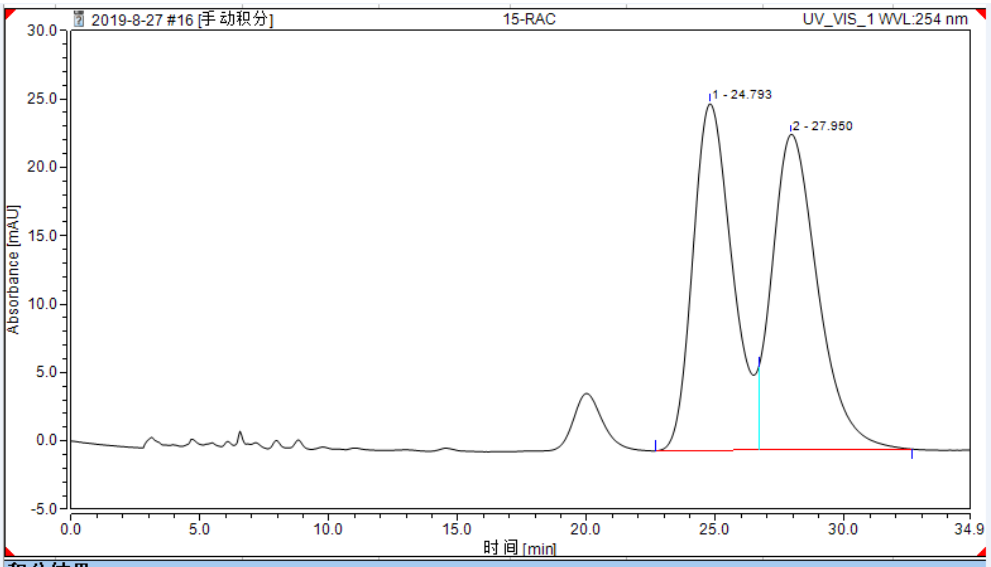
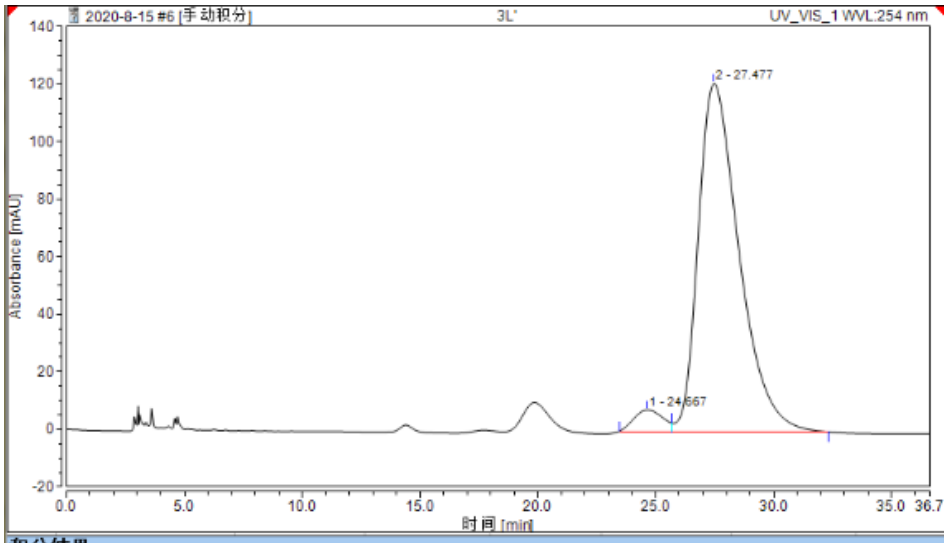


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		24.793	45.214	25.347	48.89	52.34	n.a.
2		27.950	47.276	23.078	51.11	47.66	n.a.

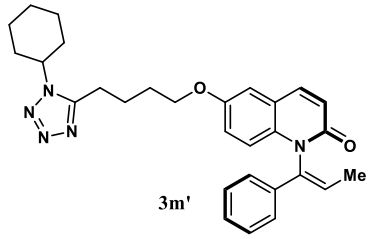


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		24.667	10.516	7.442	4.15	5.79	n.a.
2		27.477	243.105	121.019	95.85	94.21	n.a.

For comparison of Chinese and English of the HPLC data table.

序号	峰 名称	保留时间 (min)	峰 面 积 (mAU*min)	峰 高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height (mAU)	Relative peak area (%)	Relative Peak height (%)	Sample volume n.a.



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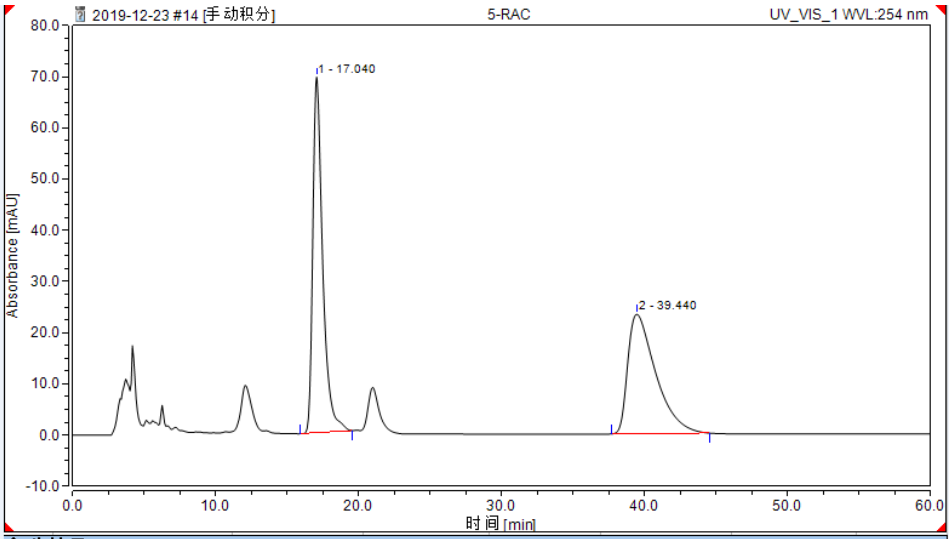
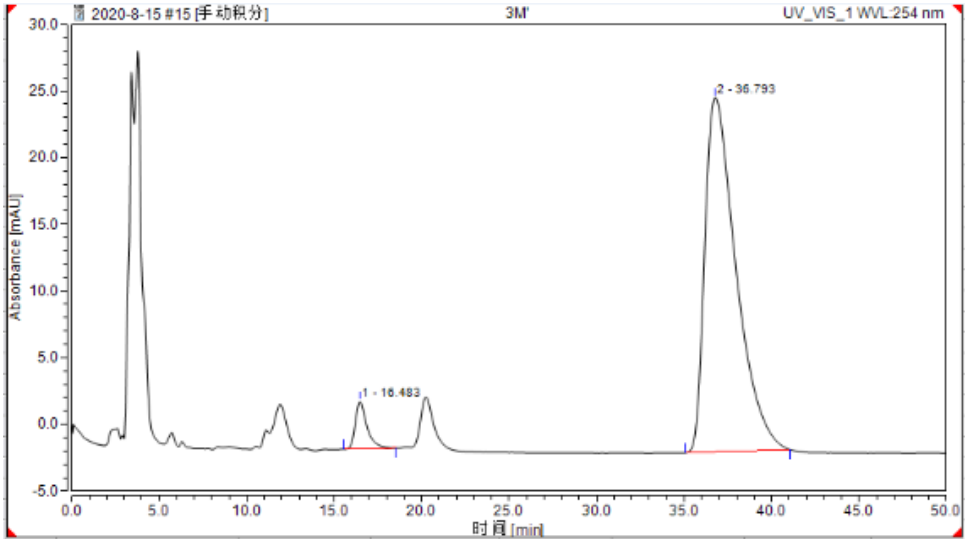


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		17.040	55.732	69.483	51.38	74.86	n.a.
2		39.440	52.731	23.332	48.62	25.14	n.a.

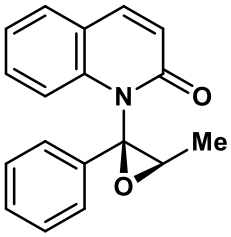


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		16.483	2.748	3.547	4.77	11.77	n.a.
2		36.793	54.855	26.573	95.23	88.23	n.a.

For comparison of Chinese and English of the HPLC data table.

序号	峰名称	保留时间 (min)	峰面积 (mAU*min)	峰高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height (mAU)	Relative peak area (%)	Relative Peak height (%)	Sample volume n.a.



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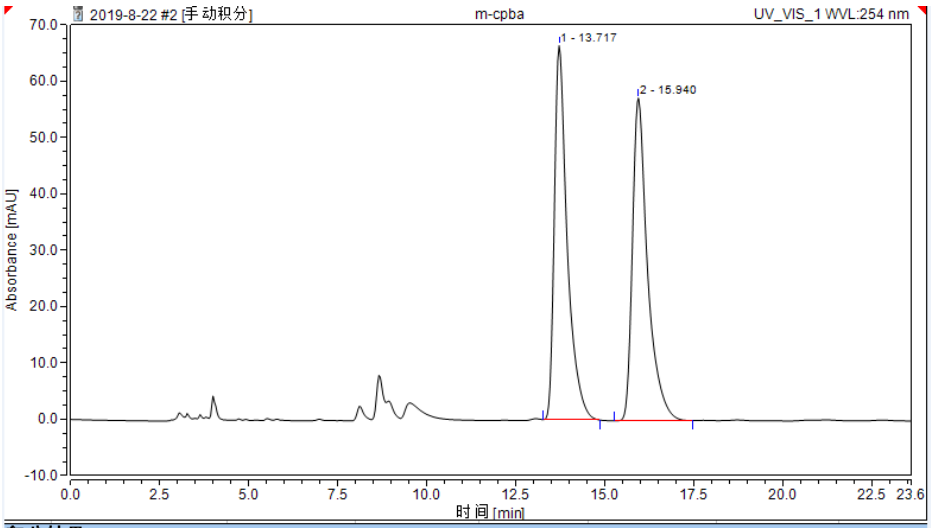
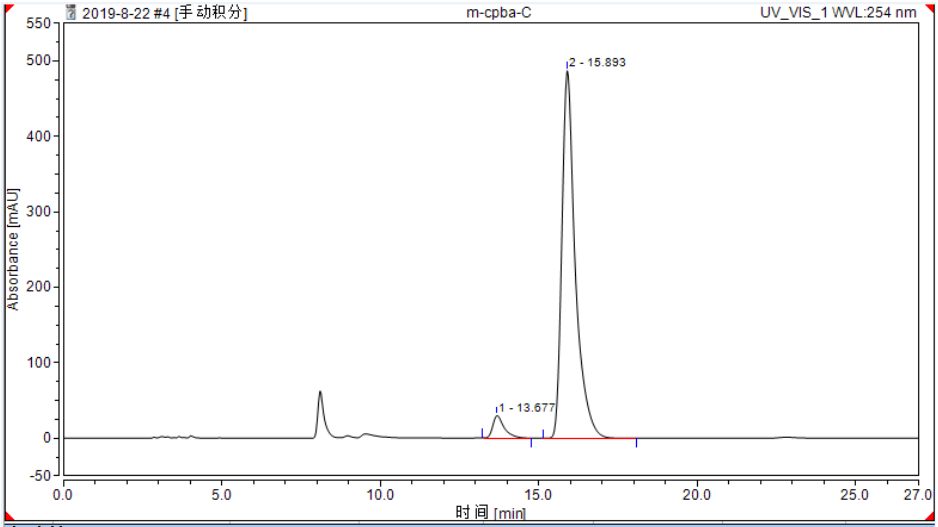


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		13.717	27.923	66.411	49.77	53.70	n.a.
2		15.940	28.182	57.266	50.23	46.30	n.a.

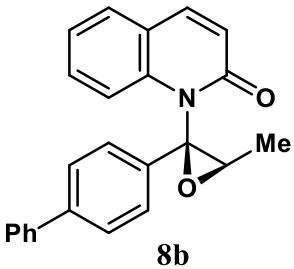


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		13.677	12.313	29.815	4.89	5.77	n.a.
2		15.893	239.325	487.116	95.11	94.23	n.a.

For comparison of Chinese and English of the HPLC data table.

序号	峰名称	保留时间 (min)	峰面积 (mAU*min)	峰高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height (mAU)	Relative peak area (%)	Relative Peak height (%)	Sample volume n.a.



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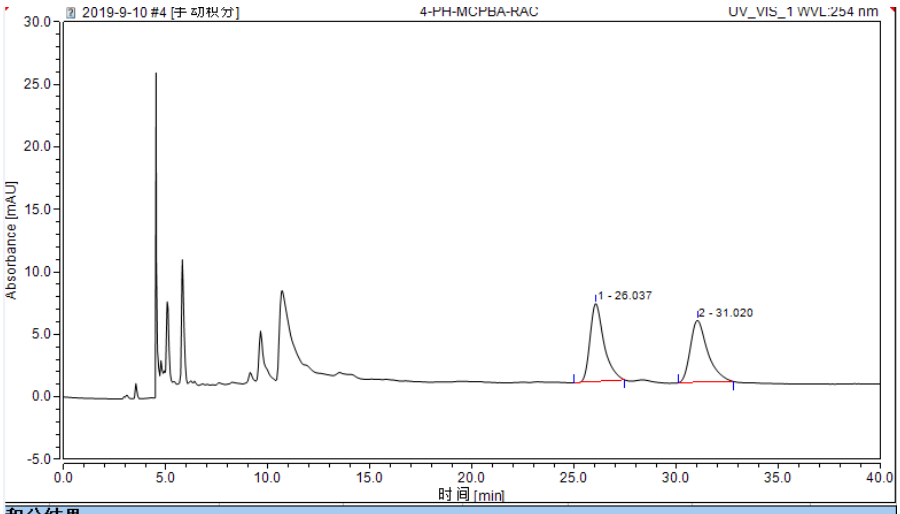
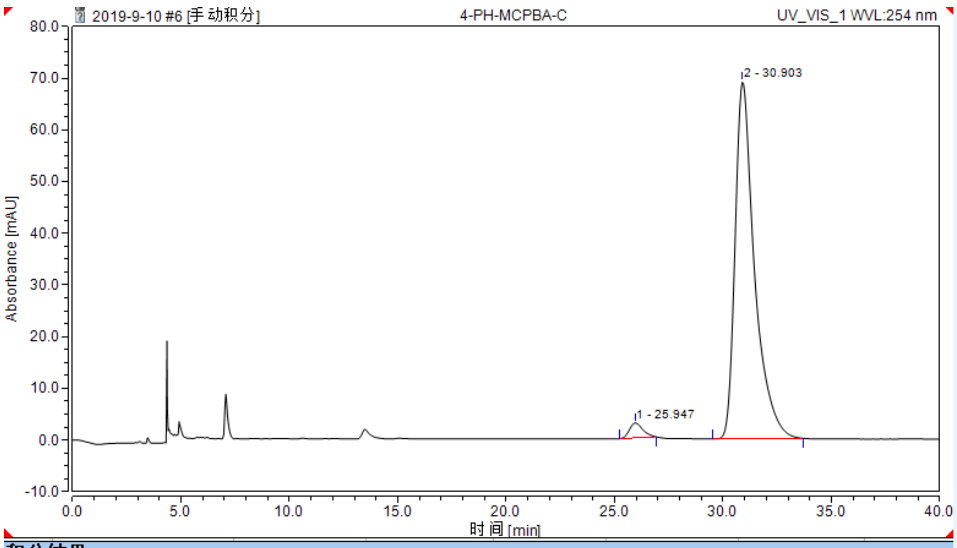


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		26.037	4.941	6.238	50.37	55.73	n.a.
2		31.020	4.868	4.955	49.63	44.27	n.a.

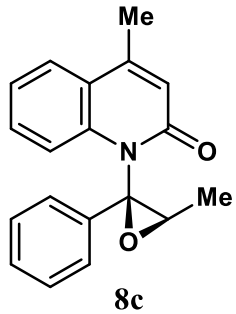


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		25.947	2.058	2.897	2.79	4.03	n.a.
2		30.903	71.616	69.075	97.21	95.97	n.a.

For comparison of Chinese and English of the HPLC data table.

序号	峰名称	保留时间 (min)	峰面积 (mAU*min)	峰高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height (mAU)	Relative peak area (%)	Relative Peak height (%)	Sample volume n.a.



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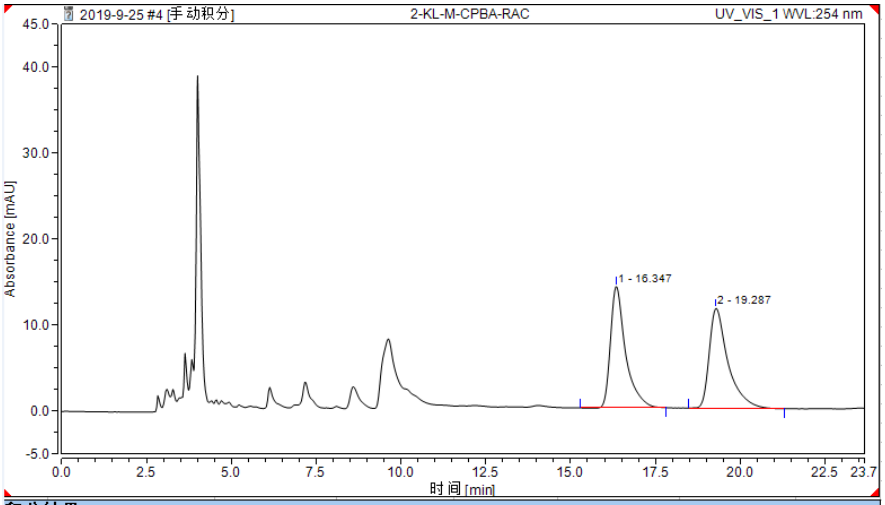
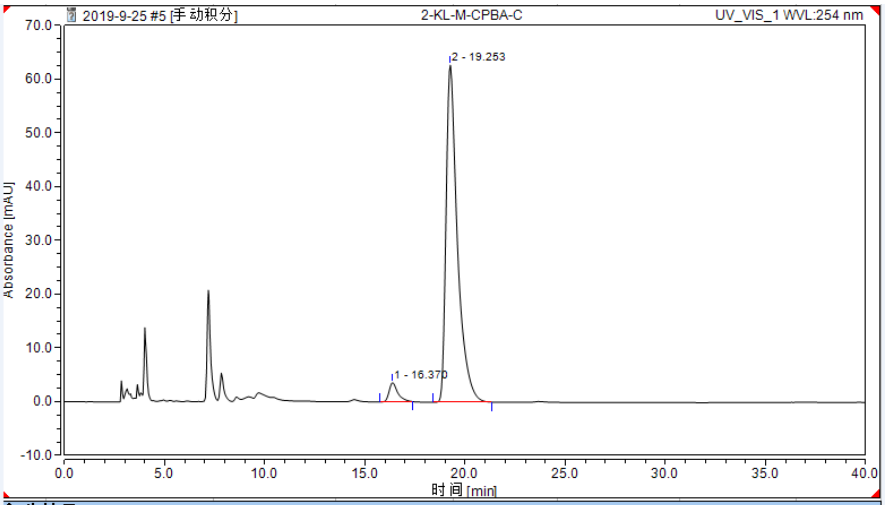


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		16.347	7.268	14.130	49.47	54.88	n.a.
2		19.287	7.423	11.617	50.53	45.12	n.a.

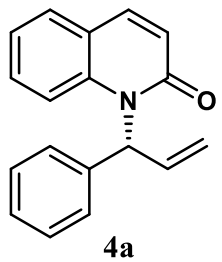


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		16.370	1.815	3.585	4.22	5.41	n.a.
2		19.253	41.167	62.703	95.78	94.59	n.a.

For comparison of Chinese and English of the HPLC data table.

序号	峰名称	保留时间 (min)	峰面积 (mAU*min)	峰高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height (mAU)	Relative peak area (%)	Relative Peak height (%)	Sample volume n.a.



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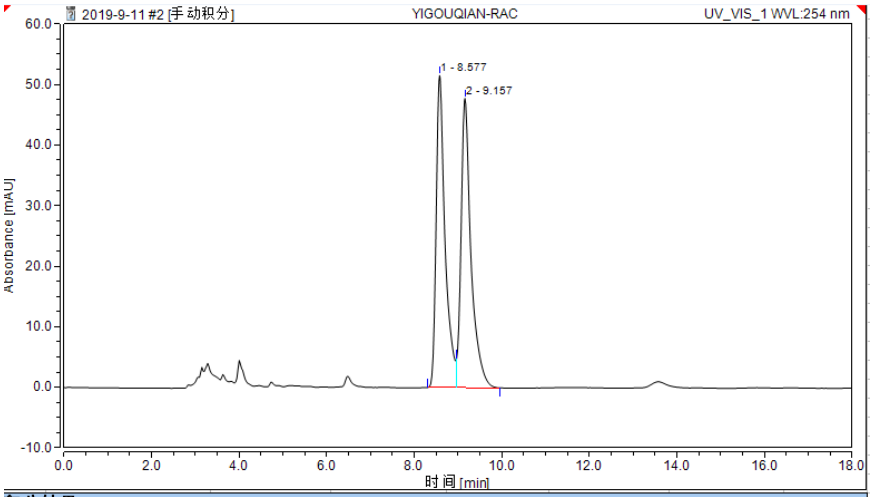
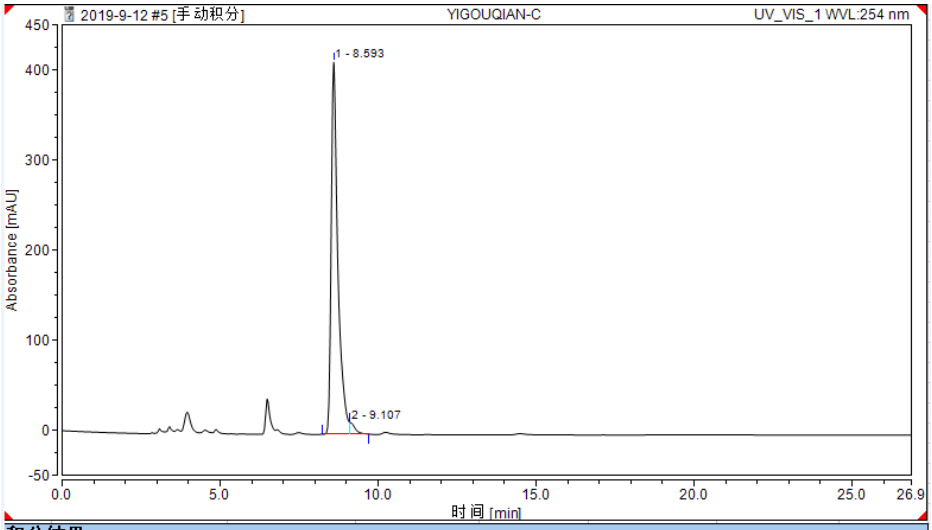


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		8.577	12.196	51.538	49.29	51.89	n.a.
2		9.157	12.546	47.793	50.71	48.11	n.a.

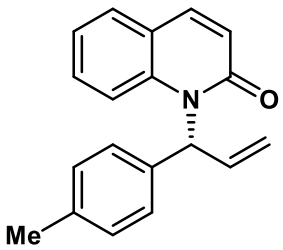


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		8.593	101.324	412.931	97.62	96.99	n.a.
2		9.107	2.468	12.821	2.38	3.01	n.a.

For comparison of Chinese and English of the HPLC data table.

序号	峰名称	保留时间 (min)	峰面积 (mAU*min)	峰高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height (mAU)	Relative peak area (%)	Relative Peak height (%)	Sample volume n.a.



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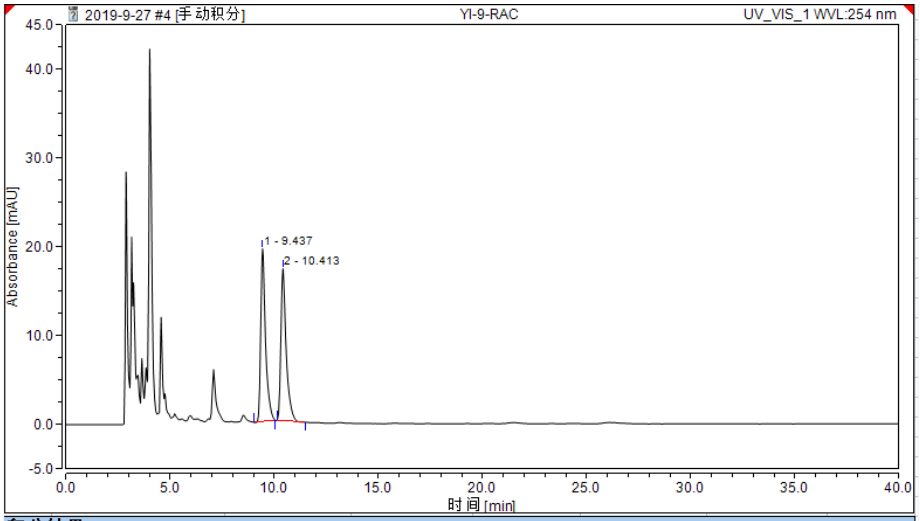
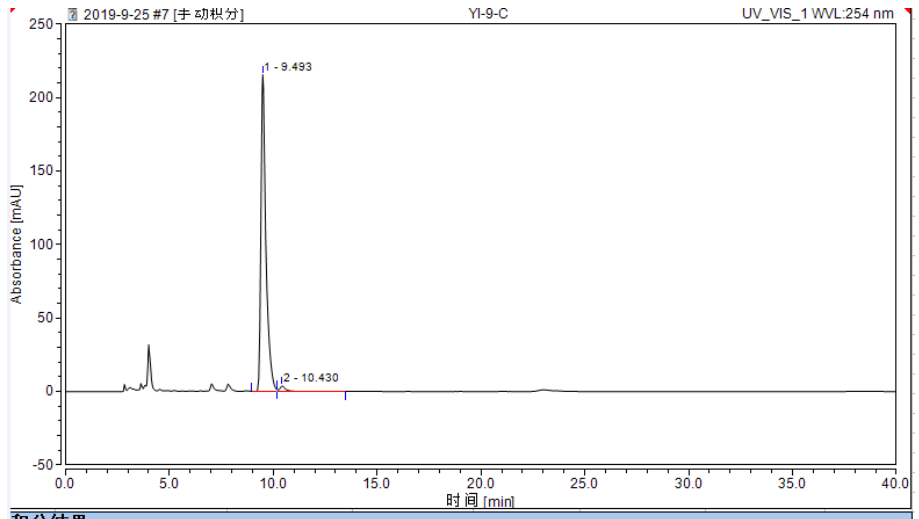


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		9.437	5.128	19.439	50.60	53.22	n.a.
2		10.413	5.006	17.084	49.40	46.78	n.a.

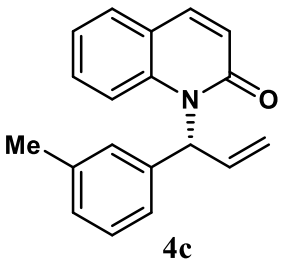


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		9.493	59.700	215.436	98.15	98.31	n.a.
2		10.430	1.127	3.696	1.85	1.69	n.a.

For comparison of Chinese and English of the HPLC data table.

序号	峰名称	保留时间 (min)	峰面积 (mAU*min)	峰高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height (mAU)	Relative peak area (%)	Relative Peak height (%)	Sample volume n.a.



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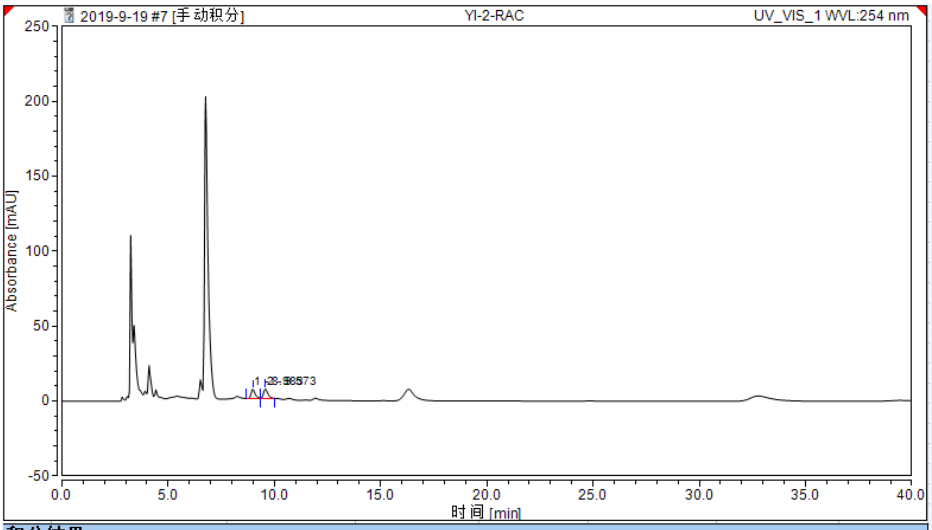
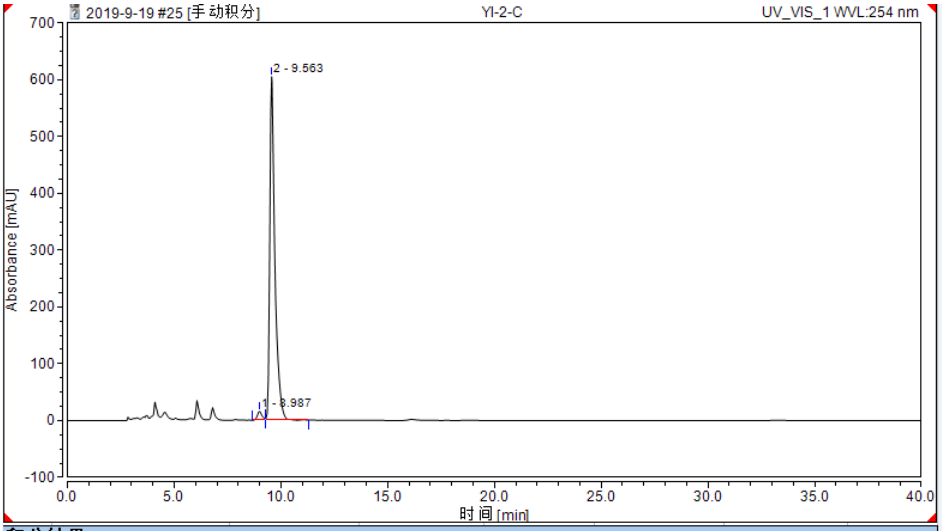


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		8.983	1.380	6.304	47.95	49.45	n.a.
2		9.573	1.498	6.445	52.05	50.55	n.a.

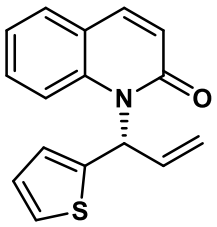


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		8.987	3.998	15.765	2.33	2.54	n.a.
2		9.563	167.332	604.813	97.67	97.46	n.a.

For comparison of Chinese and English of the HPLC data table.

序号	峰名称	保留时间 (min)	峰面积 (mAU*min)	峰高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height (mAU)	Relative peak area (%)	Relative Peak height (%)	Sample volume n.a.



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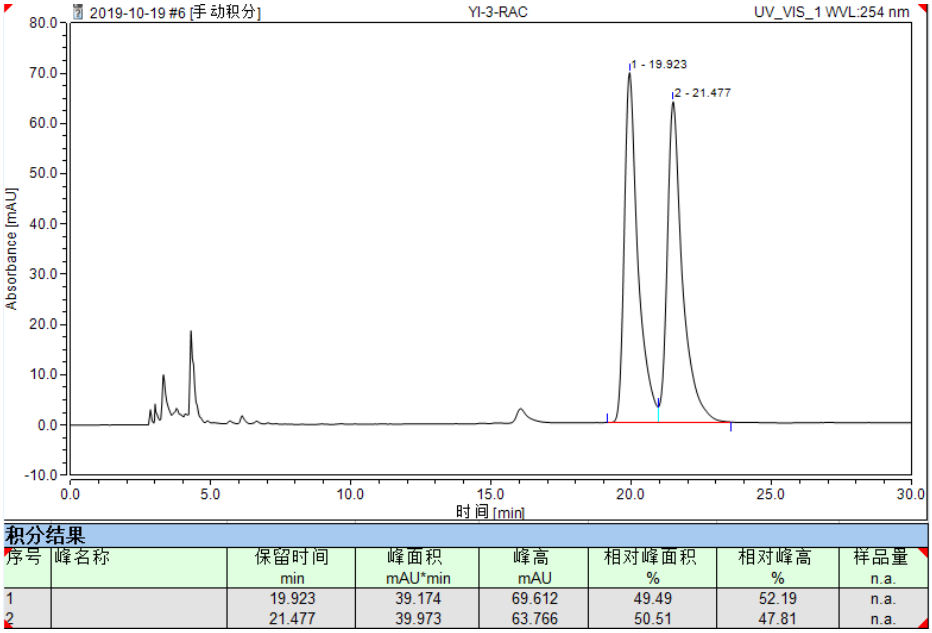
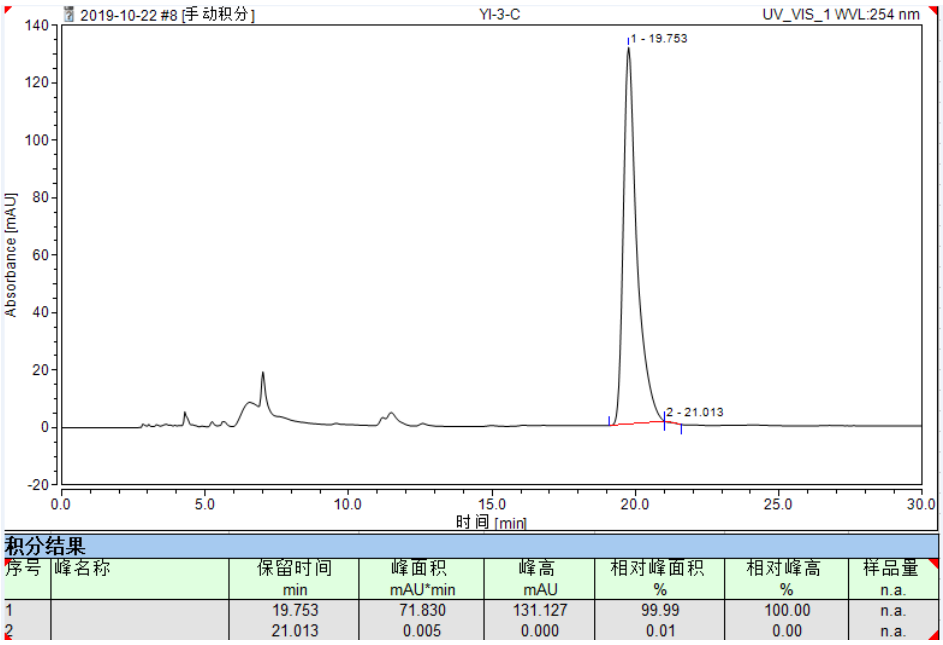


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		19.923	39.174	69.612	49.49	52.19	n.a.
2		21.477	39.973	63.766	50.51	47.81	n.a.



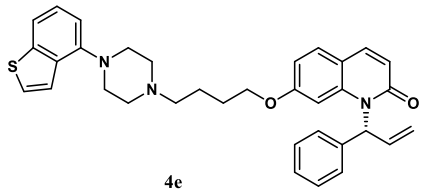
积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		19.753	71.830	131.127	99.99	100.00	n.a.
2		21.013	0.005	0.000	0.01	0.00	n.a.

For comparison of Chinese and English of the HPLC data table.

序号	峰名称	保留时间 (min)	峰面积 (mAU*min)	峰高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height	Relative peak area	Relative Peak height	Sample volume

				(mAU)	(%)	(%)	n.a.



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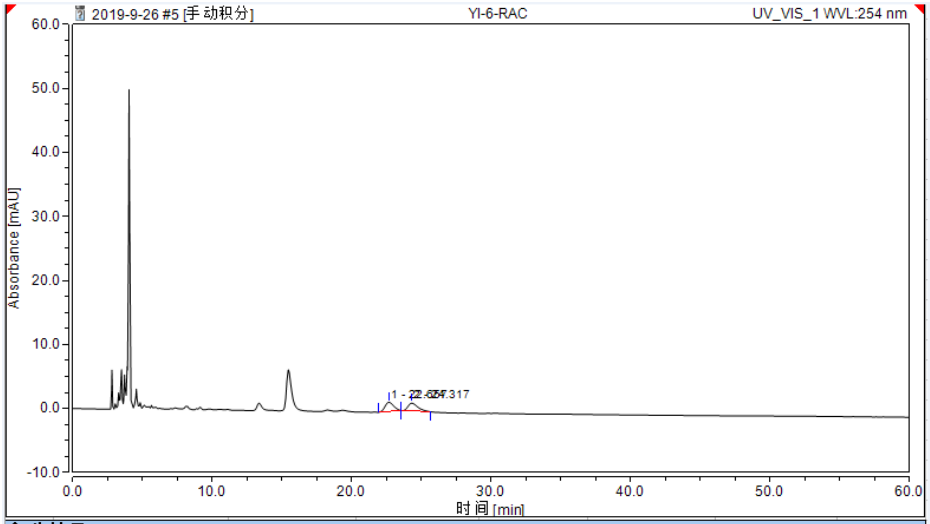
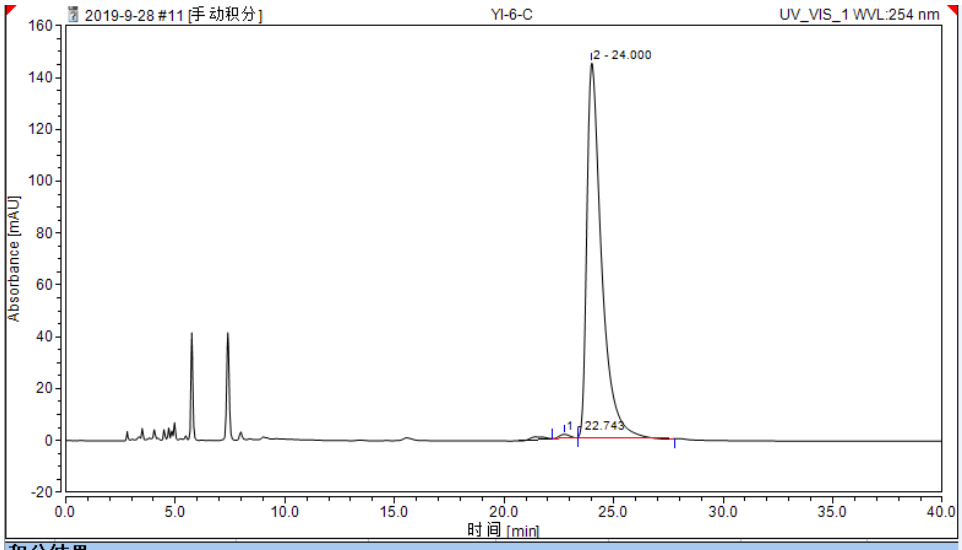


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		22.657	1.039	1.443	50.46	53.81	n.a.
2		24.317	1.020	1.239	49.54	46.19	n.a.

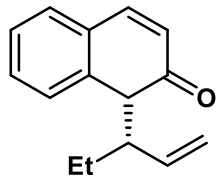


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		22.743	0.773	1.496	0.68	1.02	n.a.
2		24.000	112.348	144.514	99.32	98.98	n.a.

For comparison of Chinese and English of the HPLC data table.

序号	峰名称	保留时间 (min)	峰面积 (mAU*min)	峰高 (mAU)	相对峰面积 (%)	相对峰高 (%)	样品量 n.a.
Entry	Peak name	Retention time (min)	Peak area (mAU*min)	Peak height (mAU)	Relative peak area (%)	Relative Peak height (%)	Sample volume n.a.



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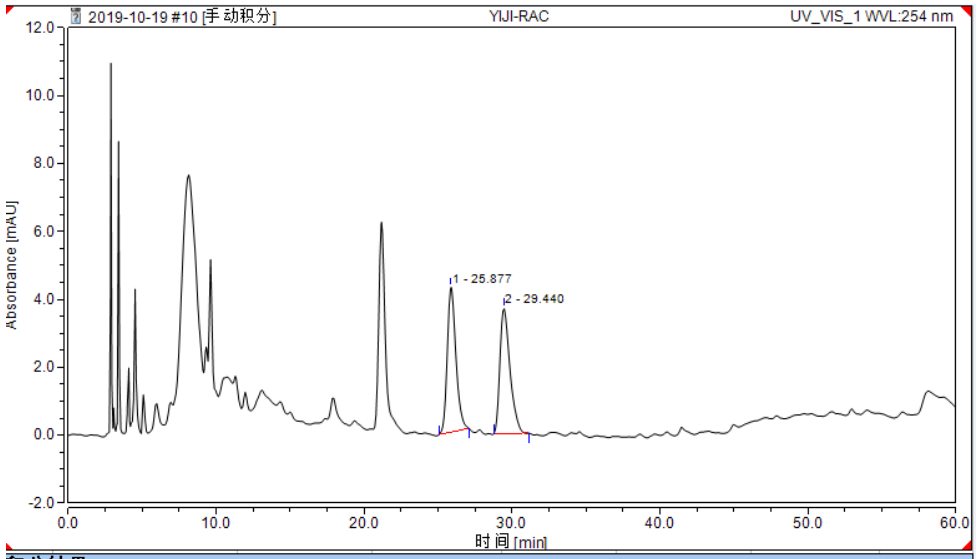
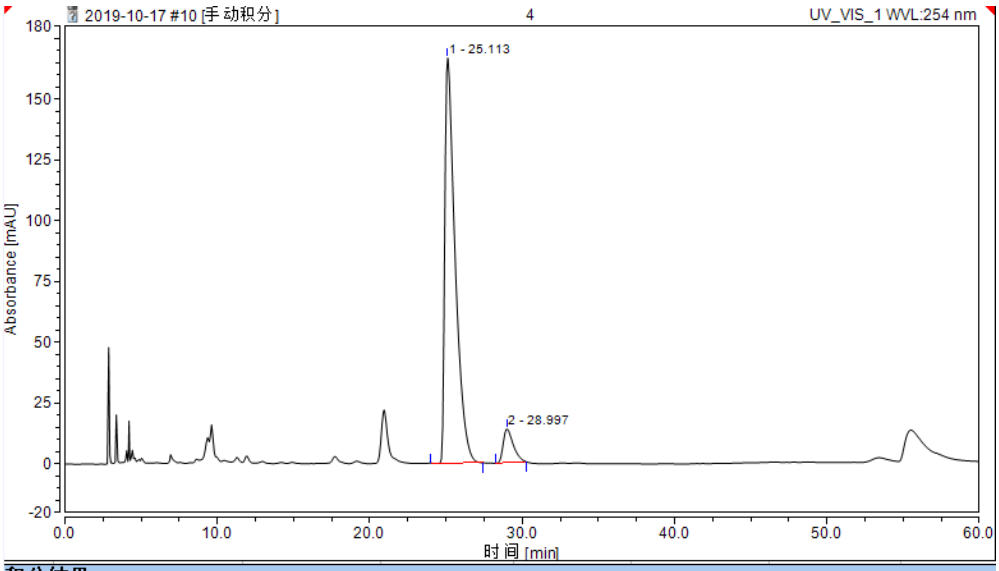


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		25.877	2.901	4.270	49.91	53.61	n.a.
2		29.440	2.912	3.696	50.09	46.39	n.a.



积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		25.113	131.156	166.656	92.50	92.31	n.a.
2		28.997	10.640	13.886	7.50	7.69	n.a.