Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Radical Rearrangement of *N*-Sulfonyl-*N*-Aryl Propynamides: Proceeding with Homolytic N-SO_2 Bond Cleavage and 6-*endo*-*dig* Cyclization toward 3-Sulfonyl-2(1*H*)-Quinolinones

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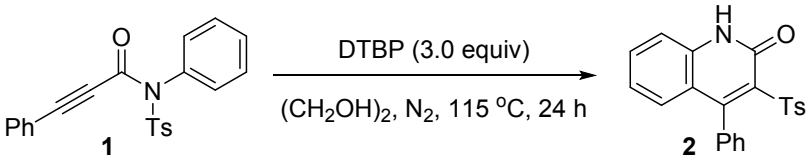
1. General experimental details

All of the manipulations were performed under N_2 atmosphere, using standard Schlenk techniques. Chemicals were used as received without special purification unless stated otherwise. *N*-Sulfonyl-*N*-aryl propynamides **1a-1t** were prepared according to the published procedure.[1,2] ^1H and ^{13}C NMR were recorded at ambient temperature on a 400 or 300 MHz NMR spectrometer (100 or 75 MHz for ^{13}C NMR). NMR experiments are reported in δ units, parts per million (ppm), and were referenced to $CDCl_3$ (7.26 or 77.16 ppm) or DMSO-d_6 (2.54 or 40.03 ppm) as the internal standard. NMR analysis was carried out at 298 K unless noted otherwise. HRMS was obtained on an ESI-APCI-LC-MS/MS spectrometer.

General procedure:

N-Sulfonyl-*N*-aryl propynamides (0.1 mmol), DTBP (0.3 mmol, 44 mg) and $(CH_2OH)_2$ (2.0 mL) was added into a 20 mL of Schlenk tube equipped with a Teflon cap. The reaction vessel was evacuated to about -0.1 MPa (last 30 seconds per time) and backfilled with N_2 (1 atm.) in three times. The sealed Schlenk tube was stirred at 115 °C for the desired time. After the reaction mixture was cooled to room temperature, saturated brine water (3.0 mL) was added to terminate the reaction. The reaction mixture was diluted with EtOAc and washed with saturated brine water. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuum. The residue was purified by flash column chromatography on silica gel with ethyl acetate-dichloromethane as eluent to give the desired product.

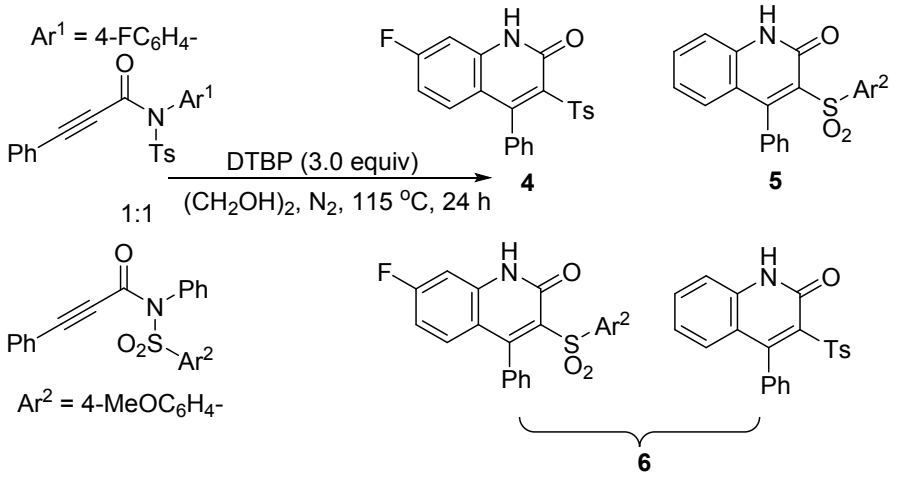
2. The reaction of *N*-sulfonyl-*N*-aryl propynamides and DTBP



N-Sulfonyl-*N*-aryl propynamides (0.1 mmol), DTBP (0.3 mmol, 44 mg) and $(CH_2OH)_2$ (2.0 mL) was added into a 20 mL Schlenk tube equipped with a Teflon cap. The reaction vessel was evacuated to about -0.1 MPa (last 30 seconds per time) and backfilled with N_2 (1 atm.) in three times. The sealed Schlenk tube was stirred at 115 °C for the desired time. After the reaction mixture was cooled to room temperature, saturated brine water (3.0 mL) was added to terminate the reaction. The reaction mixture was diluted with EtOAc and washed with saturated brine water. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuum. The residue was purified by flash column chromatography on silica gel with ethyl acetate-dichloromethane (1:3) as eluent to give the desired product **2a** in 83% yield.

3. Mechanistic studies

3.1 The cross experiment



N-Sulfonyl-*N*-aryl propynamides **1i** (0.1 mmol, 39 mg) and **1k** (0.1 mmol, 39 mg), DTBP (0.6 mmol, 88 mg) and $(CH_2OH)_2$ (2.0 mL) was added into a 20 mL Schlenk tube equipped with a Teflon cap. The reaction vessel was evacuated to about -0.1 MPa (last 30 seconds per time) and backfilled with N_2 (1 atm) in three times. The sealed Schlenk tube was stirred at 115 °C for the desired time. After the reaction mixture was cooled to room temperature, saturated brine water (3.0 mL) was added to terminate the reaction. The reaction mixture was diluted with EtOAc and washed with saturated brine water. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuum. The residue was purified by flash column chromatography on silica gel with ethyl acetate-dichloromethane (1:3) as eluent to give the desired product. Product **4** (14.3 mg) and **5** (15.6 mg) was isolated, along with product **6** (25.8 mg) as one mixture. The ^{1}HNMR and LC-MS was tested as follows.

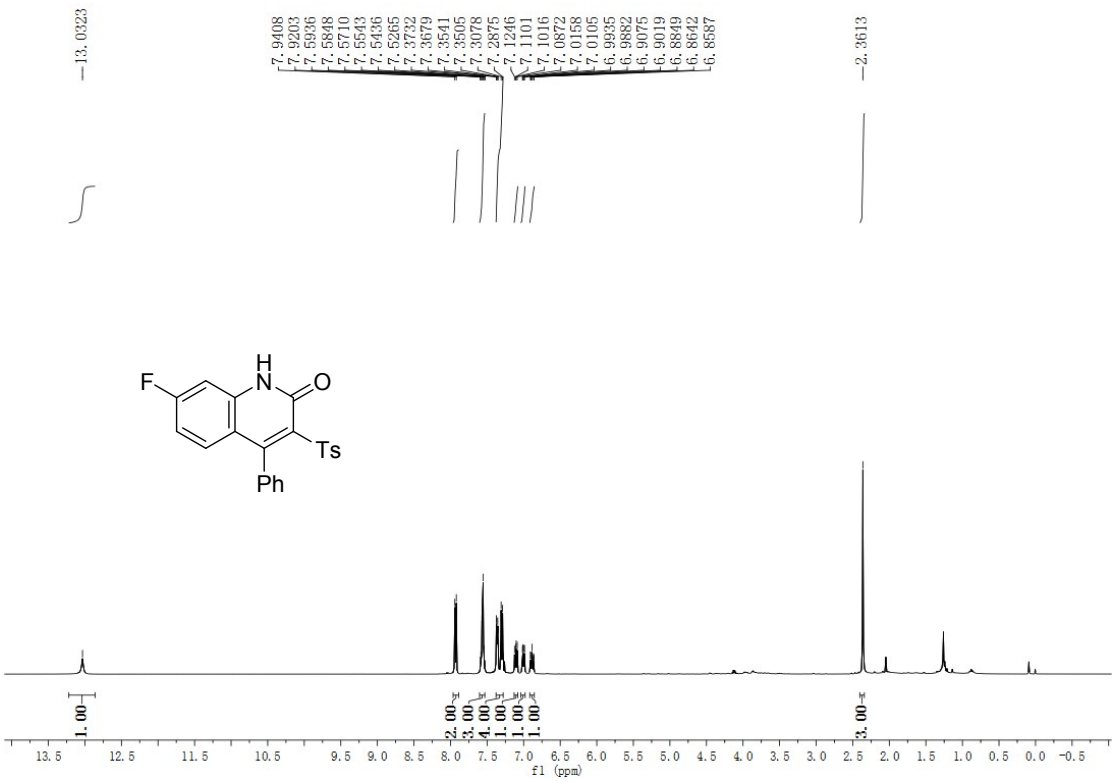


Figure 1. The ^{1}H NMR spectrum of product **4** after the cross reaction of **1i** and **1k**.

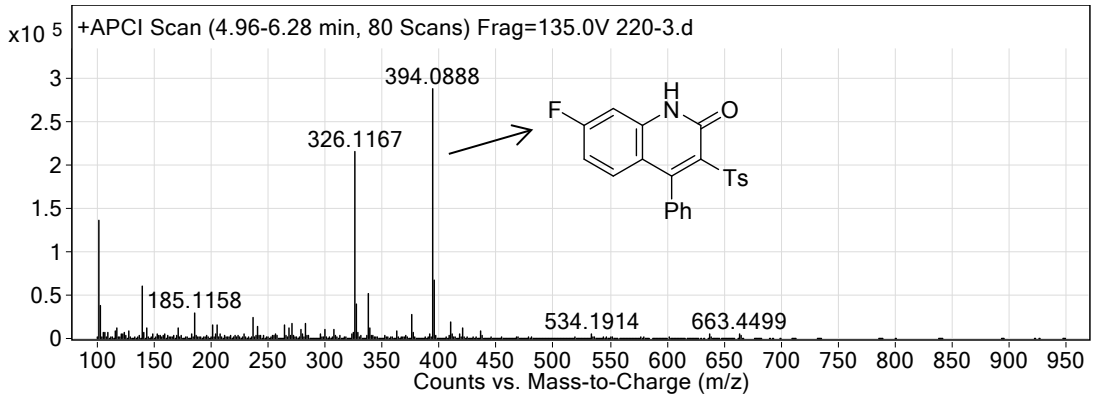


Figure 2. The LC-MS spectrum of product **4** after the cross reaction of **1i** and **1k**.

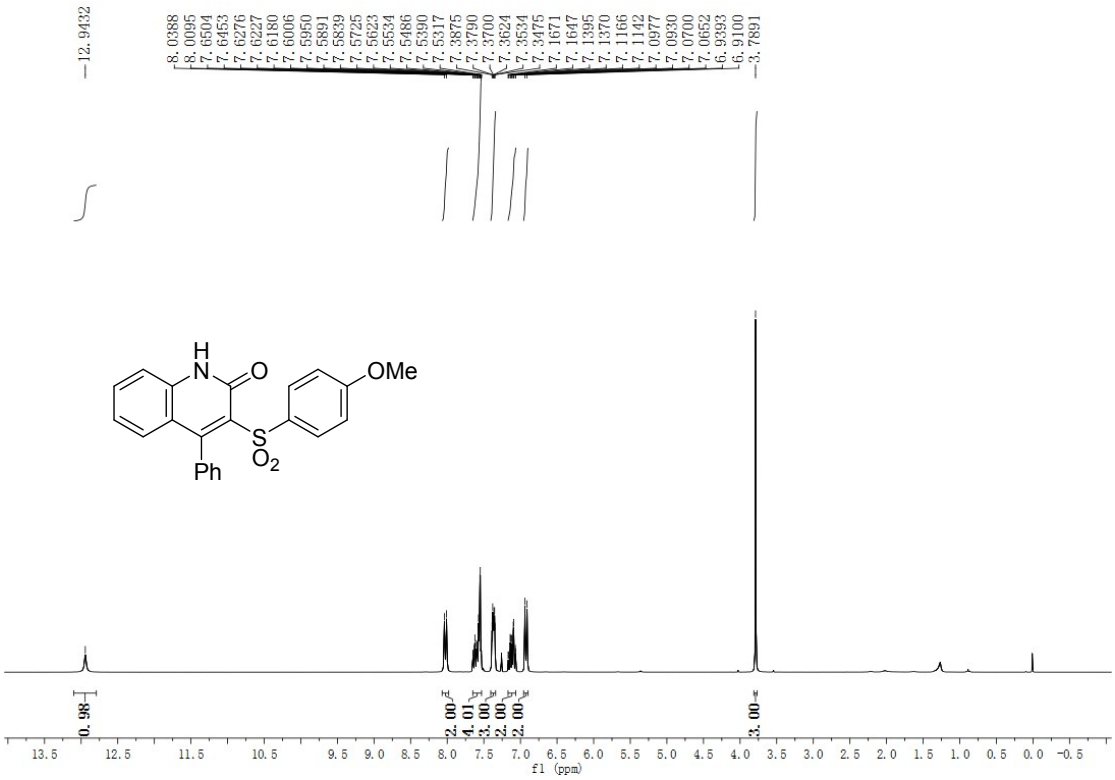


Figure 3. The [1] H NMR spectrum of product **5** after the cross reaction of **1i** and **1k**.

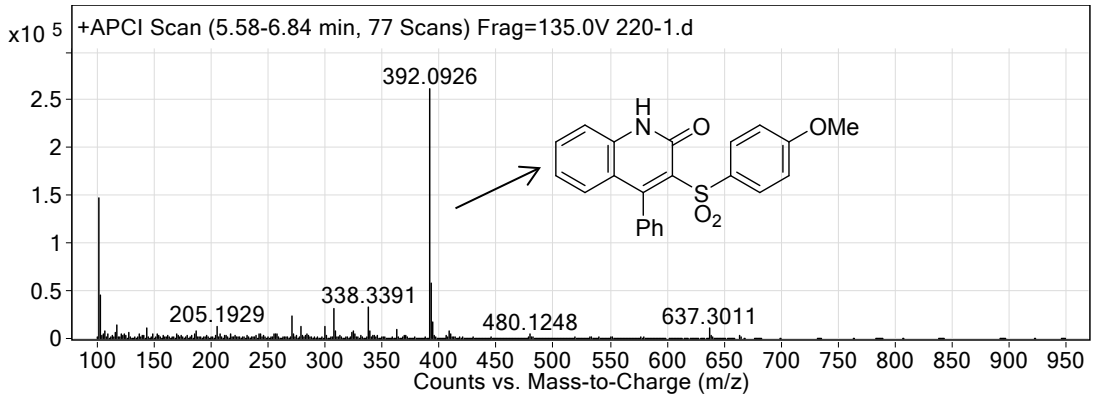


Figure 4. The LC-MS spectrum of product **5** after the cross reaction of **1i** and **1k**.

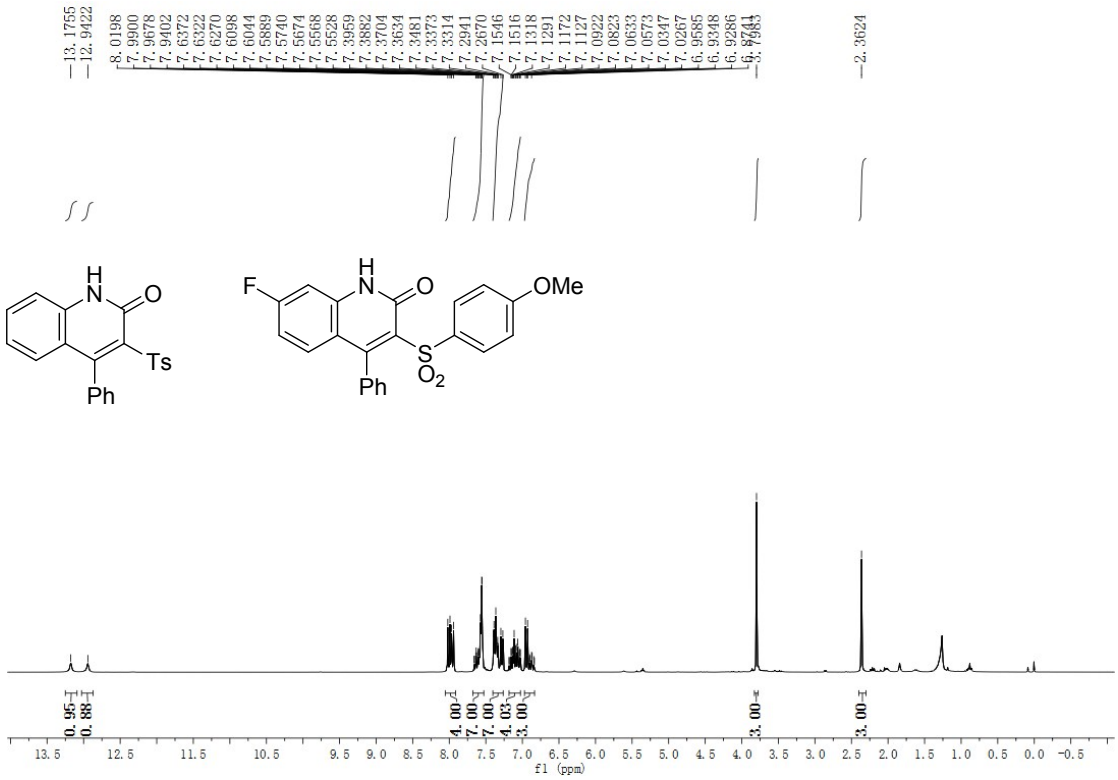


Figure 5. The [1] H NMR spectrum of product **6** after the cross reaction of **1i** and **1k**.

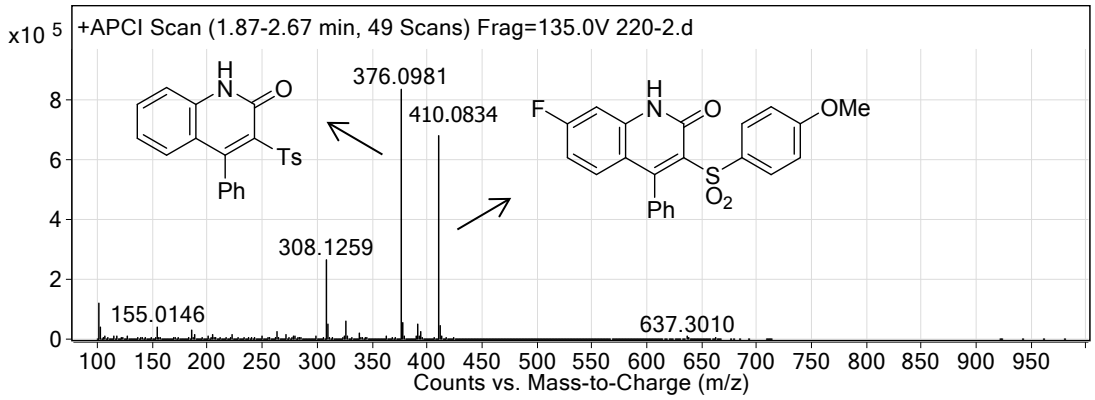
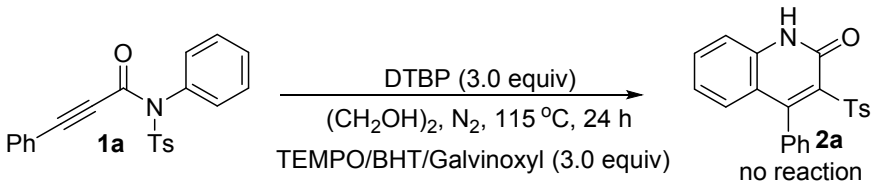
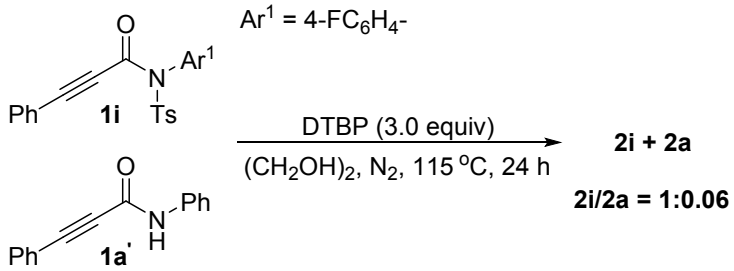


Figure 6. The LC-MS spectrum of product **6** after the cross reaction of **1i** and **1k**.

3.2 The control experimentals



N-Sulfonyl-*N*-aryl propynamides (0.1 mmol), DTBP (0.3 mmol, 44 mg), TEMPO (0.3 mmol, 47 mg) or BHT (0.3 mmol, 66 mg) or galvinoxyl (0.3 mmol, 126 mg) and $(CH_2OH)_2$ (2.0 mL) was added into a 20 mL Schlenk tube equipped with a Teflon cap. The reaction vessel was evacuated to about -0.1 MPa (last 30 seconds per time) and backfilled with N_2 (1 atm.) in three times. The sealed Schlenk tube was stirred at 115 °C for the desired time. No product was observed.



N-Sulfonyl-*N*-aryl propynamides **1i** (0.1 mmol, 39 mg) and **1a**' (0.05 mmol, 11 mg), DTBP (0.3 mmol, 44 mg) and $(CH_2OH)_2$ (2.0 mL) was added into a 20 mL Schlenk tube equipped with a Teflon cap. The reaction vessel was evacuated to about -0.1 MPa (last 30 seconds per time) and backfilled with N_2 (1 atm) in three times. The sealed Schlenk tube was stirred at 115 °C for the desired time. After the reaction mixture was cooled to room temperature, saturated brine water (3.0 mL) was added to terminate the reaction. The reaction mixture was diluted with EtOAc and washed with saturated brine water. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuum. The residue was purified by flash column chromatography on silica gel with ethyl acetate-dichloromethane (1:3) as eluent to give the desired product. Product **2i** and **2a** (30.0 mg) as one mixture. The ^{1}HNMR was tested as follows.

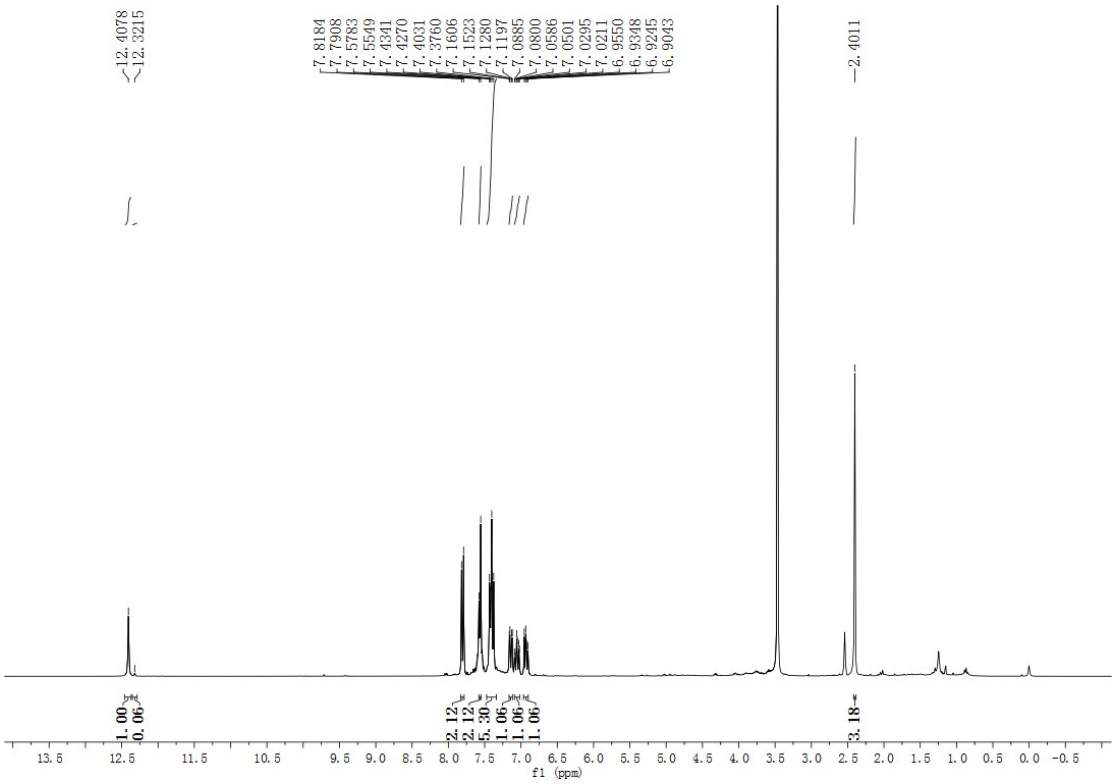
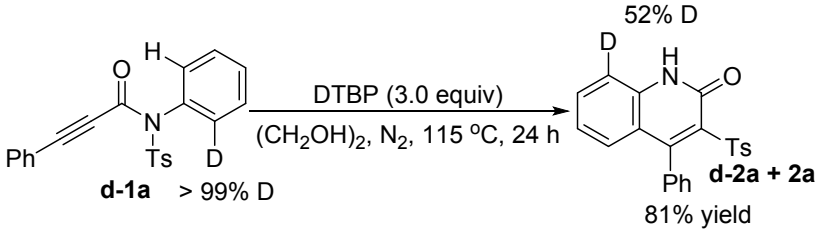


Figure 7. The [1] H NMR spectrum of product **2i** and **2a** after the reaction of **1i** and **1a'**.

3.3 Intramolecular KIE studies

a) Intramolecular KIE experiment: d-1a were synthesized by deuterated substrates according the literature procedure.[1-3]

In a sealed tube, the mixture of **d-1a** (0.1 mmol) was treated by standard procedures and heated for 24 h. The mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with ethyl acetate-dichloromethane (1:3) as eluent to give product **d-2a**. The mixture was analyzed using ^{1}H NMR spectrometer. As shown in Figure 8, the KIE is nearly **1.08:1**.



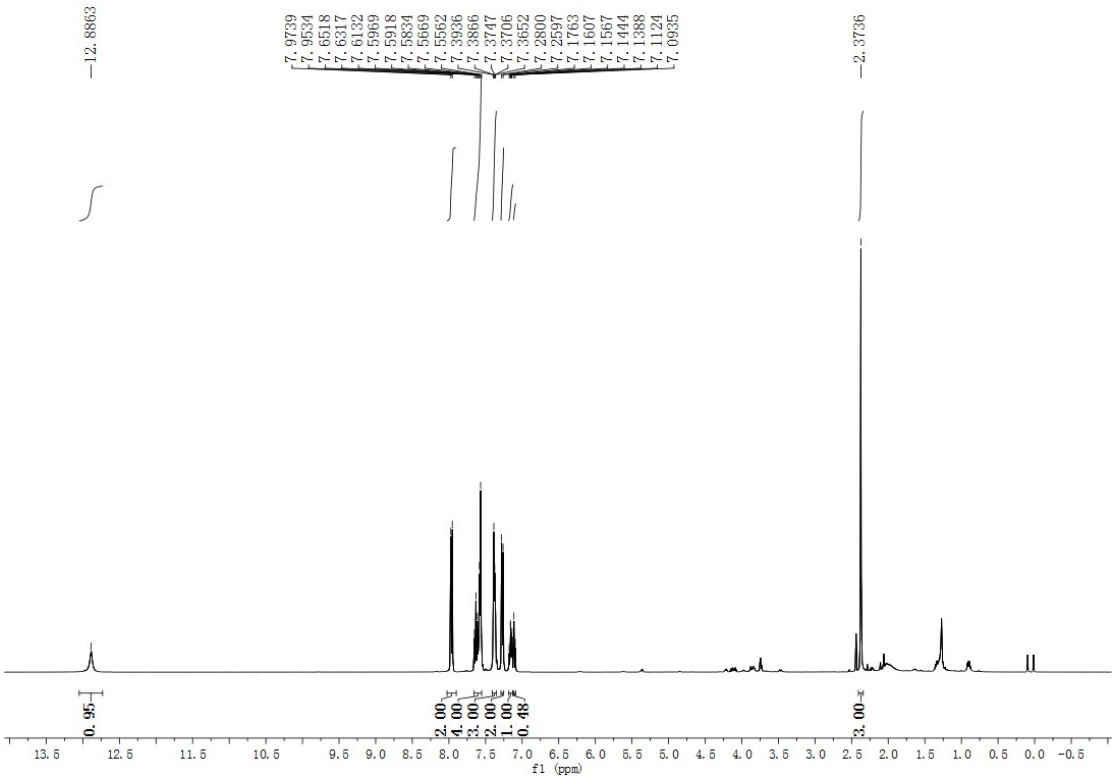
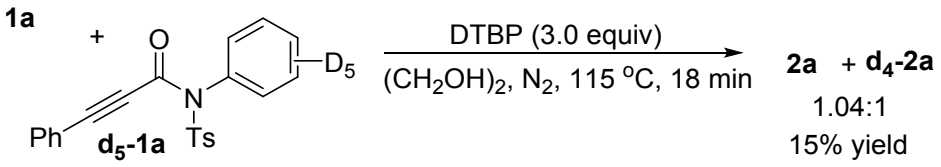


Figure 8. The ^{1}H-NMR spectrum of intramolecular KIE study.

b): Intermolecular KIE experiment: d_5-1a was synthesized according the literature procedure.[1,2,4]

In a sealed tube, the mixture of **1a** (0.05 mmol) and **d_5-1a** (0.05 mmol) was treated by standard procedures and heated for 18 min. The mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with ethyl acetate-dichloromethane (1:3) as eluent to give product **2a** and **d_4-2a**. The mixture was analyzed using ^{1}H NMR spectrometer. As shown in Figure 9, the ratio of **2a** and **d_4-2a** is nearly 1.04:1.



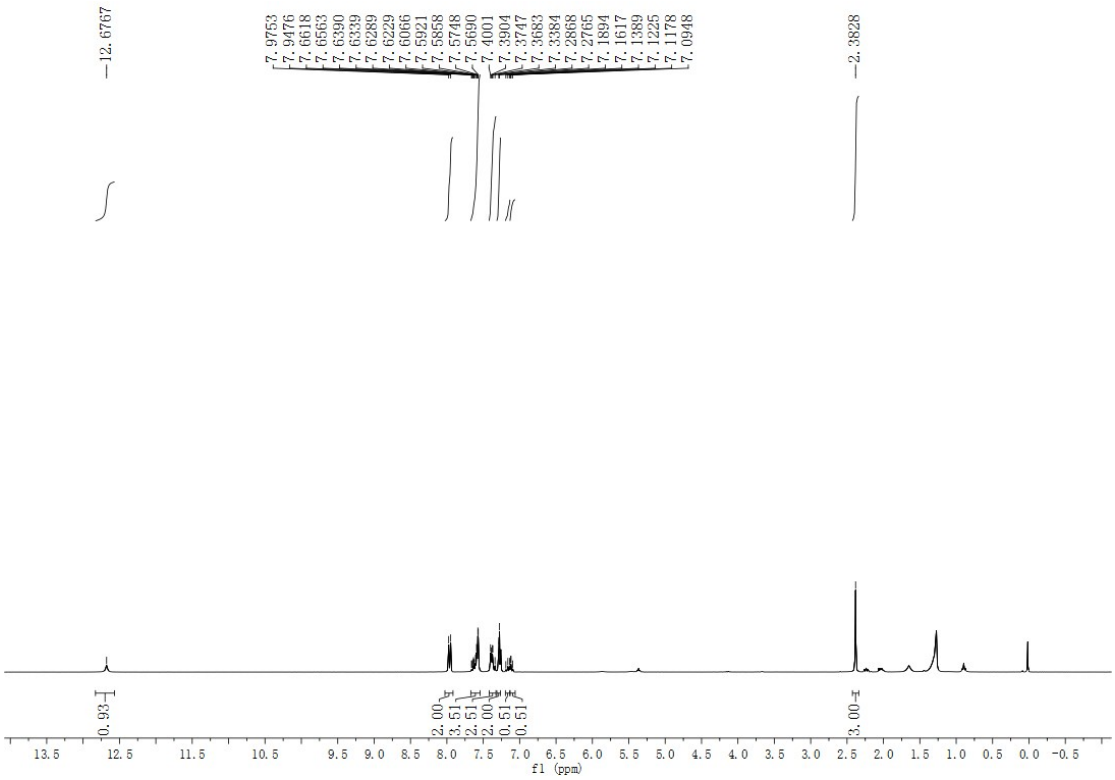
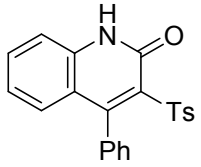


Figure 9. The ^{1}H-NMR spectrum of intermolecular KIE study.

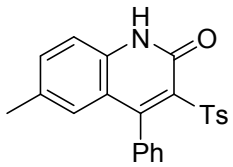
4. Characterization data for the products

4-phenyl-3-tosylquinolin-2(1*H*)-one (2a)



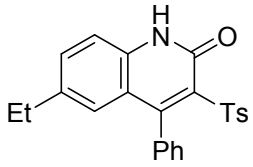
Flash column chromatography on a silica gel (ethyl acetate-dichloromethane 1:3, R_f = 0.31) give the product (31.2 mg, 83% yield) as a white solid. m.p. > 250 °C. The compound is unknown. ^{1}H NMR (DMSO-d_6 300 MHz): δ 12.34 (s, 1H), 7.82 (d, J = 8.2 Hz, 2H), 7.53-7.66 (m, 4H), 7.37-7.43 (m, 5H), 7.14 (t, J = 7.5 Hz, 1H), 6.89 (d, J = 7.7 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR ($CDCl_3$ 100 MHz): δ 159.7, 156.9, 144.0, 139.5, 138.7, 134.4, 133.4, 129.5, 129.2, 129.0, 128.9, 128.6, 128.0, 127.9, 123.3, 120.6, 116.3, 21.7. MS (EI): 375 (M^+); HRMS (ESI-TOF) m/z [M + H]$^+$calcd. for $[C_{22}H_{18}NO_3S]^+$ 376.1002, found 376.0996.

6-methyl-4-phenyl-3-tosylquinolin-2(1*H*)-one (2b)



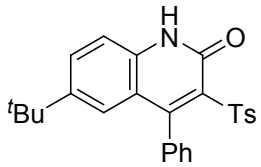
Flash column chromatography on a silica gel (ethyl acetate-dichloromethane, 1:3, R_f = 0.41) give the product (38.9 mg, 64% yield) as a white solid. m.p. > 250 °C. The compound is unknown. ^{1}H NMR (DMSO-d_6 300 MHz): δ 12.23 (s, 1H), 7.79 (d, J = 8.2 Hz, 2H), 7.36-7.56 (m, 7H), 7.18 (s, 1H), 6.98 (d, J = 8.5 Hz, 1H), 6.76 (d, J = 8.4 Hz, 1H), 2.39 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (DMSO-d_6 75 MHz): δ 157.6, 156.1, 145.0, 144.1, 140.6, 139.4, 135.3, 129.6, 129.3, 128.7, 128.7, 128.4, 128.3, 124.8, 118.0, 115.6, 22.0, 21.7. MS (EI): 389 (M^+); HRMS (ESI-TOF) m/z [M + H]$^+$calcd. for $[C_{23}H_{20}NO_3S]^+$ 390.1158, found 390.1146.

6-ethyl-4-phenyl-3-tosylquinolin-2(1*H*)-one (2c)



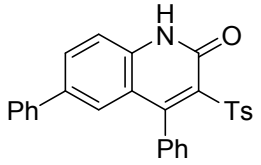
Flash column chromatography on a silica gel (ethyl acetate-dichloromethane, 1:3, R_f = 0.63) give the product (30.9 mg, 76% yield) as a white solid. m.p. > 250 °C. The compound is unknown. ^{1}H NMR (DMSO-d_6 400 MHz): δ 12.21 (s, 1H), 7.78 (d, J = 8.2 Hz, 2H), 7.51-7.58 (m, 3H), 7.37 (d, J = 8.4 Hz, 4H), 7.20 (s, 1H), 7.01-7.03 (m, 1H), 6.79 (d, J = 8.5 Hz, 1H), 2.63-2.69 (m, 2H), 2.38 (s, 3H), 1.17 (t, J = 7.6 Hz, 3H). ^{13}C NMR (DMSO-d_6 100 MHz): δ 157.7, 156.3, 151.2, 144.3, 140.8, 139.5, 135.4, 129.7, 129.5, 128.8, 128.5, 123.9, 118.3, 114.6, 29.0, 21.8, 15.6. MS (EI): 403 (M^+); HRMS (ESI-TOF) m/z [M + H]$^+$calcd. for $[C_{24}H_{22}NO_3S]^+$ 404.1315, found 404.1322.

6-(*tert*-butyl)-4-phenyl-3-tosylquinolin-2(1*H*)-one (2d)



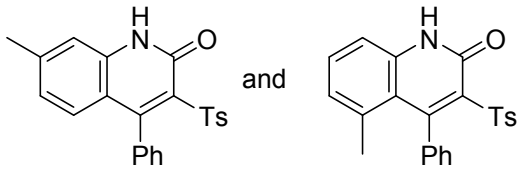
Flash column chromatography on a silica gel (ethyl acetate-dichloromethane, 1:3, R_f = 0.51) give the product (35.4 mg, 82% yield) as a white solid. m.p. > 250 °C. The compound is unknown. ^{1}H NMR (DMSO-d_6 400 MHz): δ 12.16 (s, 1H), 7.79 (d, J = 8.2 Hz, 2H), 7.52-7.58 (m, 3H), 7.36-7.38 (m, 5H), 7.23-7.26 (m, 1H), 6.82 (d, J = 8.8 Hz, 1H), 2.39 (s, 3H), 1.27 (s, 9H). ^{13}C NMR (DMSO-d_6 100 MHz): δ 157.6, 157.5, 156.0, 144.0, 140.5, 139.4, 135.3, 129.5, 129.1, 128.7, 128.6, 128.4, 128.3, 121.5, 117.9, 112.1, 35.6, 31.1, 21.7. MS (EI): 431 (M^+); HRMS (ESI-TOF) m/z [M + H]$^+$calcd. for $[C_{26}H_{26}NO_3S]^+$ 432.1628, found 432.1594.

4,6-diphenyl-3-tosylquinolin-2(1*H*)-one (2e)



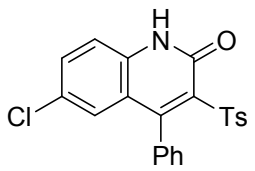
Flash column chromatography on a silica gel (ethyl acetate-petroleum ether, 1:1, R_f = 0.39) give the product (25.9 mg, 57% yield) as a white solid. m.p. > 250 °C. The compound is unknown. ^{1}H NMR (DMSO-d_6 300 MHz): δ 12.36 (s, 1H), 7.84 (d, J = 8.1 Hz, 2H), 7.38-7.68 (m, 14H), 6.96 (d, J = 8.6 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (DMSO-d_6 75 MHz): δ 157.5, 155.9, 145.4, 144.1, 140.9, 139.3, 139.0, 135.2, 130.1, 129.8, 129.6, 129.5, 129.2, 128.7, 128.4, 128.4, 127.6, 122.0, 119.3, 113.4, 21.7. MS (EI): 451 (M^+); HRMS (ESI-TOF) m/z [M + H]$^+$calcd. for $[C_{28}H_{22}NO_3S]^+$ 452.1315, found 452.1287.

7-methyl-4-phenyl-3-tosylquinolin-2(1*H*)-one (2f)



Flash column chromatography on a silica gel (ethyl acetate-dichloromethane, 1:3, R_f = 0.36) give the product (17.6 mg, 45% yield (5:2)) as a white solid. m.p. > 250 °C. The compound is unknown. ^{1}H NMR (DMSO-d_6 400 MHz): δ 12.49 (s, 0.41H), 12.26 (s, 1H), 7.81-7.84 (m, 4H), 7.53-7.59 (m, 6H), 7.31-7.46 (m, 12H), 6.78 (d, J = 2.2 Hz, 0.41H), 6.66 (s, 1H), 2.38 (s, 6H), 2.16 (s, 4H). ^{13}C NMR (DMSO-d_6 100 MHz): δ 157.3, 157.2, 155.9, 155.0, 144.4, 144.1, 139.4, 139.2, 139.0, 138.6, 135.4, 135.2, 134.5, 133.8, 132.1, 130.7, 129.6, 129.5, 129.5, 129.0, 128.9, 128.8, 128.7, 128.6, 128.4, 128.3, 127.9, 127.0, 121.4, 120.0, 118.2, 116.1, 21.7, 21.2. MS (EI): 389 (M^+); HRMS (ESI-TOF) m/z [M + H]$^+$calcd. for $[C_{23}H_{20}NO_3S]^+$ 390.1158, found 390.1133.

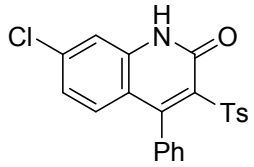
6-chloro-4-phenyl-3-tosylquinolin-2(1*H*)-one (2g)



Flash column chromatography on a silica gel (ethyl acetate-dichloromethane, 1:3, R_f = 0.54) give the product (32.5 mg, 79% yield) as a white solid. m.p. > 250 °C. The

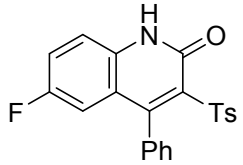
compound is unknown. ^{1}H NMR (DMSO-d_6 300 MHz): δ 12.40 (s, 1H), 7.81 (d, J = 8.3 Hz, 2H), 7.54-7.60 (m, 3H), 7.38-7.44 (m, 5H), 7.20-7.23 (m, 1H), 6.89 (d, J = 8.9 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (DMSO-d_6 75 MHz): δ 157.4, 155.8, 144.3, 141.1, 139.0, 138.6, 134.8, 131.4, 129.7, 129.7, 128.9, 128.8, 128.5, 128.4, 123.5, 119.1, 115.3, 21.7. MS (EI): 409 (M^+); HRMS (ESI-TOF) m/z [M + H]$^+$calcd. for $[C_{22}H_{17}ClNO_3S]^+$ 410.0612, found 410.0587.

7-chloro-4-phenyl-3-tosylquinolin-2(1*H*)-one (2h)



Flash column chromatography on a silica gel (ethyl acetate-dichloromethane, 1:3, R_f = 0.43) give the product (20.9 mg, 51% yield) as a white solid. m.p. > 250 ^{o}C. The compound is unknown. ^{1}H NMR (DMSO-d_6 400 MHz): δ 12.47 (s, 1H), 7.80 (d, J = 8.1 Hz, 2H), 7.65-7.68 (m, 1H), 7.57 (t, J = 6.7 Hz, 3H), 7.37-7.43 (m, 5H), 6.76 (t, J = 2.0 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (DMSO-d_6 100 MHz): δ 157.3, 155.1, 144.5, 139.2, 139.0, 134.5, 133.9, 130.7, 129.7, 129.1, 128.9, 128.6, 128.5, 127.9, 127.1, 121.4, 118.3, 21.8. MS (EI): 409 (M^+); HRMS (ESI-TOF) m/z [M + H]$^+$calcd. for $[C_{22}H_{17}ClNO_3S]^+$ 410.0612, found 410.0593.

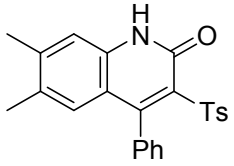
6-fluoro-4-phenyl-3-tosylquinolin-2(1*H*)-one (2i)



Flash column chromatography on a silica gel (ethyl acetate-dichloromethane, 1:3, R_f = 0.57) give the product (30.0 mg, 76% yield) as a white solid. m.p. > 250 ^{o}C. The compound is unknown. ^{1}H NMR (DMSO-d_6 300 MHz): δ 12.43 (s, 1H), 7.83 (d, J = 8.2 Hz, 2H), 7.37-7.60 (m, 7H), 6.90-7.16 (m, 3H), 2.39 (s, 3H). ^{13}C NMR ($CDCl_3$ 75 MHz): δ 167.2, 163.8, 160.2, 156.6, 144.3, 141.1 (d, J = 12.8 Hz), 138.6, 134.1, 132.4

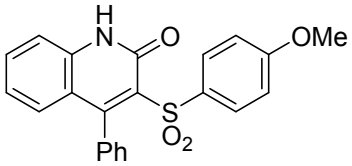
(d, J = 10.5 Hz), 129.1, 128.9, 128.3 (d, J = 3.0 Hz), 128.2, 127.8, 117.6 (d, J = 1.5 Hz), 112.4 (d, J = 23.3 Hz), 102.3 (d, J = 25.5 Hz), 21.6. MS (EI): 393 (M^+); HRMS (ESI-TOF) m/z $[M + H]^+$calcd. for $[C_{22}H_{17}FNO_3S]^+$ 394.0908, found 394.0884.

6,7-dimethyl-4-phenyl-3-tosylquinolin-2(1*H*)-one (2j)



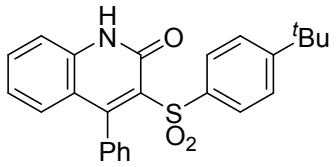
Flash column chromatography on a silica gel (ethyl acetate-dichloromethane, 1:3, R_f = 0.33) give the product (23.9 mg, 59% yield) as a white solid. m.p. > 250 °C. The compound is unknown. ^{1}H NMR (DMSO-d_6 300 MHz): δ 11.16 (s, 1H), 7.79 (d, J = 8.2 Hz, 2H), 7.55 (d, J = 6.5 Hz, 3H), 7.36 (d, J = 7.8 Hz, 4H), 7.17 (s, 1H), 6.60 (s, 1H), 2.38 (s, 3H), 2.29 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (DMSO-d_6 75 MHz): δ 157.4, 155.9, 144.6, 144.1, 139.5, 139.0, 135.4, 131.9, 129.5, 128.8, 128.7, 128.6, 128.4, 128.3, 118.2, 116.3, 21.7, 20.6, 19.8. MS (EI): 403 (M^+); HRMS (ESI-TOF) m/z $[M + H]^+$calcd. for $[C_{24}H_{22}NO_3S]^+$ 404.1315, found 404.1296.

3-((4-methoxyphenyl)sulfonyl)-4-phenylquinolin-2(1*H*)-one (2k)



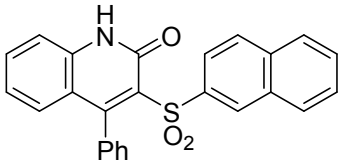
Flash column chromatography on a silica gel (ethyl acetate-dichloromethane, 1:3, R_f = 0.26) give the product (22.2 mg, 56% yield) as a yellow solid. m.p. > 250 °C. The compound is unknown. ^{1}H NMR ($CDCl_3$ 300 MHz): δ 12.94 (s, 1H), 8.02 (d, J = 8.8 Hz, 2H), 7.55-7.65 (m, 4H), 7.35-7.39 (m, 3H), 7.07-7.16 (m, 2H), 6.92 (d, J = 8.8 Hz, 2H), 3.78 (s, 3H). ^{13}C NMR ($CDCl_3$ 75 MHz): δ 163.4, 156.5, 139.4, 134.5, 133.3, 133.0, 131.4, 129.5, 128.6, 128.0, 127.9, 123.3, 120.7, 116.2, 113.5, 55.6. MS (EI): 391 (M^+); HRMS (ESI-TOF) m/z $[M + H]^+$calcd. for $[C_{22}H_{18}NO_4S]^+$ 392.0951, found 392.0931.

3-((4-(*tert*-butyl)phenyl)sulfonyl)-4-phenylquinolin-2(1*H*)-one (2l)



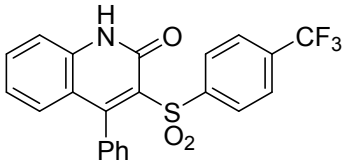
Flash column chromatography on a silica gel (ethyl acetate-dichloromethane, 1:3, R_f = 0.58) give the product (32.7mg, 78% yield) as a white solid. m.p. > 250 °C. The compound is unknown. ^{1}H NMR ($CDCl_3$ 300 MHz): δ 13.07 (s, 1H), 8.03 (d, J = 8.6 Hz, 2H), 7.37-7.69 (m, 9H), 7.08-7.18 (m, 2H), 1.27 (s, 9H). ^{13}C NMR ($CDCl_3$ 75 MHz): δ 159.8, 156.9, 156.8, 139.4, 138.4, 134.4, 133.4, 129.5, 129.2, 128.9, 128.6, 128.0, 127.9, 125.3, 123.2, 120.6, 116.3, 35.2, 31.1. MS (EI): 417 (M^+); HRMS (ESI-TOF) m/z [M + H]$^+$calcd. for $[C_{25}H_{24}NO_3S]^+$ 418.1471, found 418.1448.

3-(naphthalen-2-ylsulfonyl)-4-phenylquinolin-2(1*H*)-one (2m)



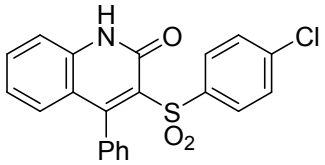
Flash column chromatography on a silica gel (ethyl acetate-dichloromethane, 1:3, R_f = 0.44) give the product (24.4 mg, 59% yield) as a white solid. m.p. > 250 °C. The compound is unknown. ^{1}H NMR (DMSO-d_6 300 MHz): δ 12.32 (s, 1H), 8.59 (s, 1H), 8.21 (d, J = 7.6 Hz, 1H), 8.04-8.11 (m, 2H), 7.89-7.92 (m, 1H), 7.50-7.75 (m, 8H), 7.40 (d, J = 8.1 Hz, 1H), 7.18 (t, J = 7.8 Hz, 1H), 6.94 (d, J = 8.0 Hz, 1H). ^{13}C NMR (DMSO-d_6 75 MHz): δ 157.4, 156.7, 140.5, 139.4, 135.1, 135.0, 134.1, 132.1, 130.0, 129.6, 129.4, 129.1, 129.0, 128.8, 128.6, 128.4, 128.0, 123.6, 123.2, 120.1, 116.2. MS (EI): 411 (M^+); HRMS (ESI-TOF) m/z [M + H]$^+$calcd. for $[C_{25}H_{18}NO_3S]^+$ 412.1002, found 412.0981.

4-phenyl-3-((4-(trifluoromethyl)phenyl)sulfonyl)quinolin-2(1*H*)-one (2o)



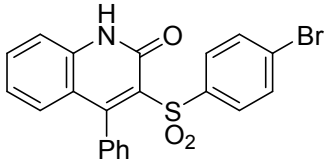
Flash column chromatography on a silica gel (ethyl acetate-dichloromethane, 1:3, R_f = 0.70) give the product (34.1 mg, 79% yield) as a white solid. m.p. > 250 °C. The compound is unknown. ^{1}H NMR (DMSO-d_6 400 MHz): δ 12.43 (s, 1H), 8.15 (d, J = 8.2 Hz, 2H), 7.96 (d, J = 8.2 Hz, 2H), 7.67 (t, J = 7.5 Hz, 1H), 7.42-7.59 (m, 6H), 7.17 (t, J = 7.7 Hz, 1H), 6.95 (d, J = 8.2 Hz, 1H). ^{13}C NMR (DMSO-d_6 100 MHz): δ 157.5, 157.4, 146.2, 140.6, 134.7, 134.4, 133.2 (q, J = 31.9 Hz), 129.5, 129.3, 129.0, 128.6, 128.5, 128.4, 126.4 (q, J = 3.5 Hz), 124.1 (q, J = 271.2 Hz), 123.4, 120.1, 116.3. MS (EI): 429 (M^+); HRMS (ESI-TOF) m/z [M + H]$^+$calcd. for $[C_{22}H_{15}F_3NO_3S]^+$ 430.0719, found 430.0701.

3-((4-chlorophenyl)sulfonyl)-4-phenylquinolin-2(1*H*)-one (2p)



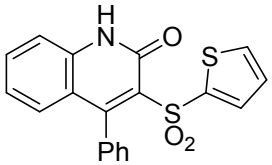
Flash column chromatography on a silica gel (ethyl acetate-dichloromethane, 1:3, R_f = 0.51) give the product (33.8 mg, 85% yield) as a white solid. m.p. > 250 °C. The compound is unknown. ^{1}H NMR (DMSO-d_6 300 MHz): δ 12.41 (s, 1H), 7.95 (d, J = 8.6 Hz, 2H), 7.63-7.68 (m, 3H), 7.53-7.60 (m, 3H), 7.41-7.46 (m, 3H), 7.13-7.18 (m, 1H), 6.93 (t, J = 4.1 Hz, 1H). ^{13}C NMR (DMSO-d_6 75 MHz): δ 157.3, 156.8, 141.0, 140.5, 138.6, 134.8, 134.2, 130.5, 129.4, 129.2, 128.8, 128.7, 128.4, 128.3, 123.2, 120.0, 116.1. MS (EI): 395 (M^+); HRMS (ESI-TOF) m/z [M + H]$^+$calcd. for $[C_{21}H_{15}ClNO_3S]^+$ 396.0456, found 396.0431.

3-((4-bromophenyl)sulfonyl)-4-phenylquinolin-2(1*H*)-one (2q)



Flash column chromatography on a silica gel (ethyl acetate-dichloromethane, 1:3, R_f = 0.51) give the product (32.5 mg, 74% yield) as a white solid. m.p. > 250 °C. The compound is unknown. ^{1}H NMR (DMSO-d_6 400 MHz): δ 12.40 (s, 1H), 7.78-7.87 (m, 4H), 7.66 (t, J = 7.4 Hz, 1H), 7.53-7.59 (m, 3H), 7.41-7.44 (m, 3H), 7.16 (t, J = 7.6 Hz, 1H), 6.92 (d, J = 8.2 Hz, 1H). ^{13}C NMR (DMSO-d_6 100 MHz): δ 157.4, 156.9, 141.5, 140.5, 134.8, 134.3, 132.2, 130.62, 129.5, 128.8, 128.8, 128.4, 128.4, 127.7, 123.3, 120.1, 116.2. MS (EI): 438 (M^+); HRMS (ESI-TOF) m/z [M + H]$^+$calcd. for $[C_{21}H_{15}BrNO_3S]^+$ 439.9951, found 439.9928.

4-phenyl-3-(thiophen-2-ylsulfonyl)quinolin-2(1*H*)-one (2t)



Flash column chromatography on a silica gel (ethyl acetate-dichloromethane, 1:3, R_f = 0.33) give the product (22.2 mg, 60% yield) as a yellow solid. m.p. > 250 °C. The compound is unknown. ^{1}H NMR ($CDCl_3$ 300 MHz): δ 13.18 (s, 1H), 7.91-7.93 (m, 1H), 7.55-7.69 (m, 6H), 7.32-7.35 (m, 2H), 7.04-7.18 (m, 3H). ^{13}C NMR (DMSO-d_6 75 MHz): δ 157.5, 155.9, 142.9, 140.4, 135.9, 135.6, 135.0, 134.2, 129.7, 129.5, 128.8, 128.4, 128.3, 127.9, 123.2, 120.0, 116.1. MS (EI): 367 (M^+); HRMS (ESI-TOF) m/z [M + H]$^+$calcd. for $[C_{19}H_{14}NO_3S_2]^+$ 368.0410, found 368.0392.

References

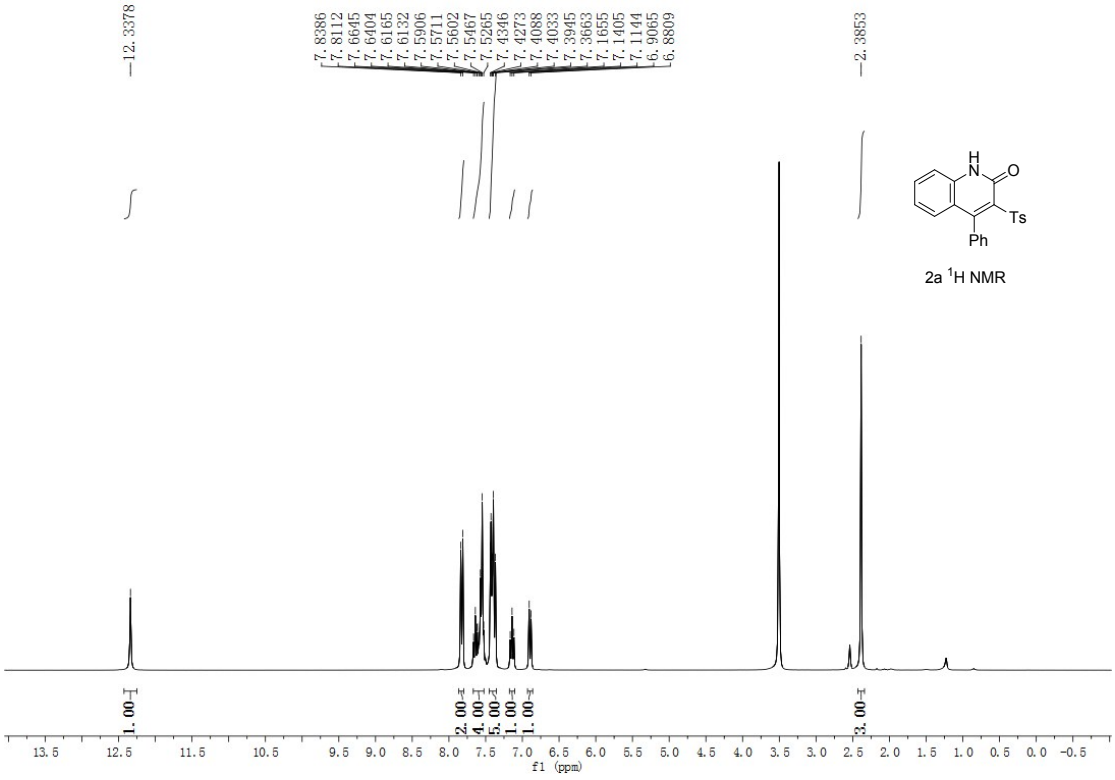
[1] Li, X.; Zou, G. *Chem. Commun*. **2015**, *51*, 5089.

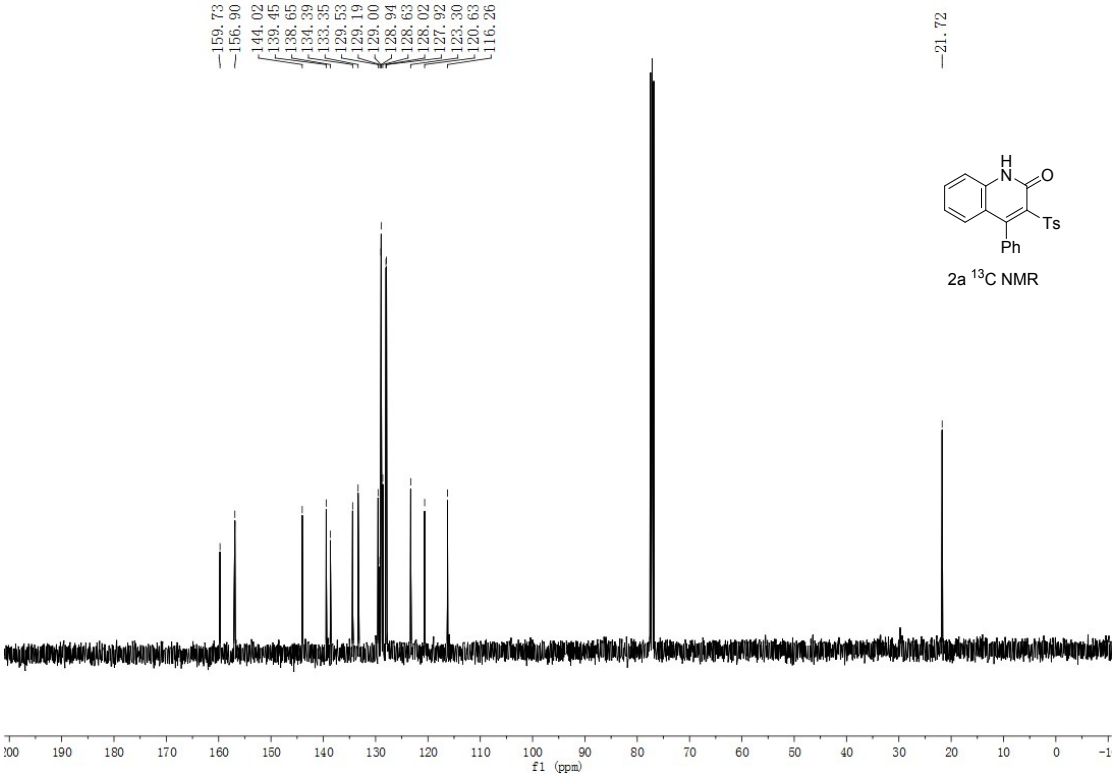
[2] Chen, M.; Yang, C.; Wang, Y.; Li, D.; Xia, W. *Org. Lett.* **2016**, *18*, 2280.

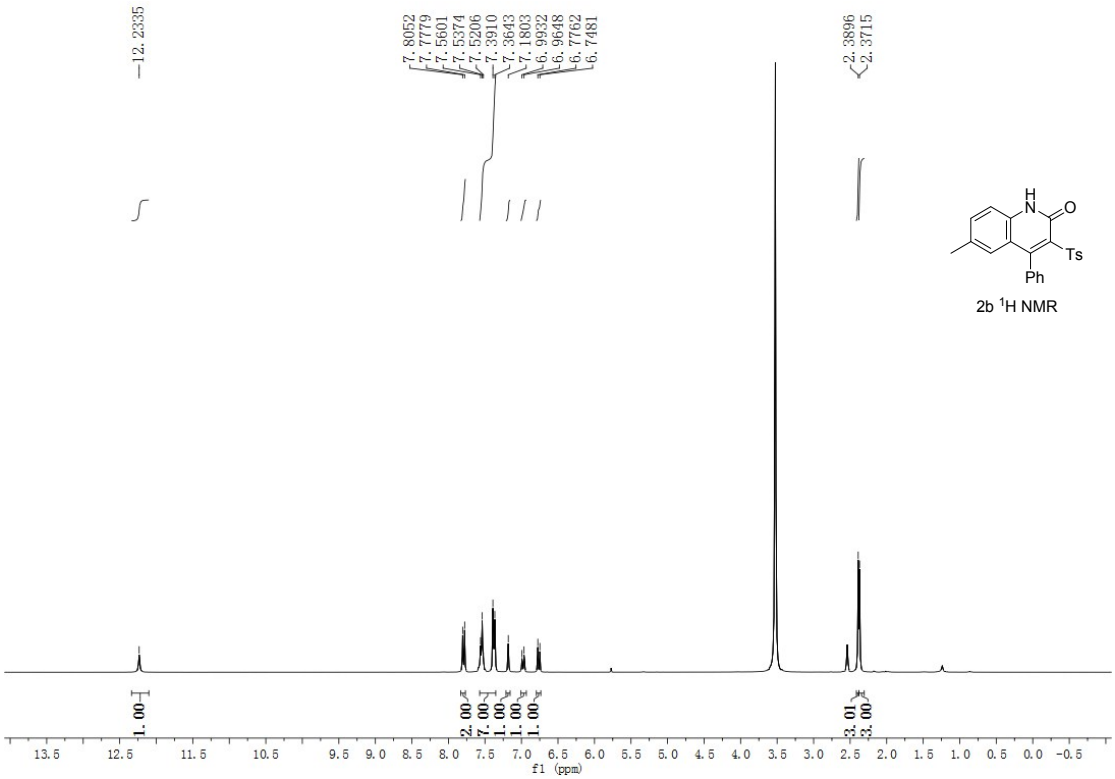
[3] Chi, Y.; Zhang, W.; Xi, Z. *Org. Lett.* **2014**, *16*, 6274.

[4] Keenan, C. S.; Murphree, S. S. *Synth. Commun.* **2017**, *47*, 1085.

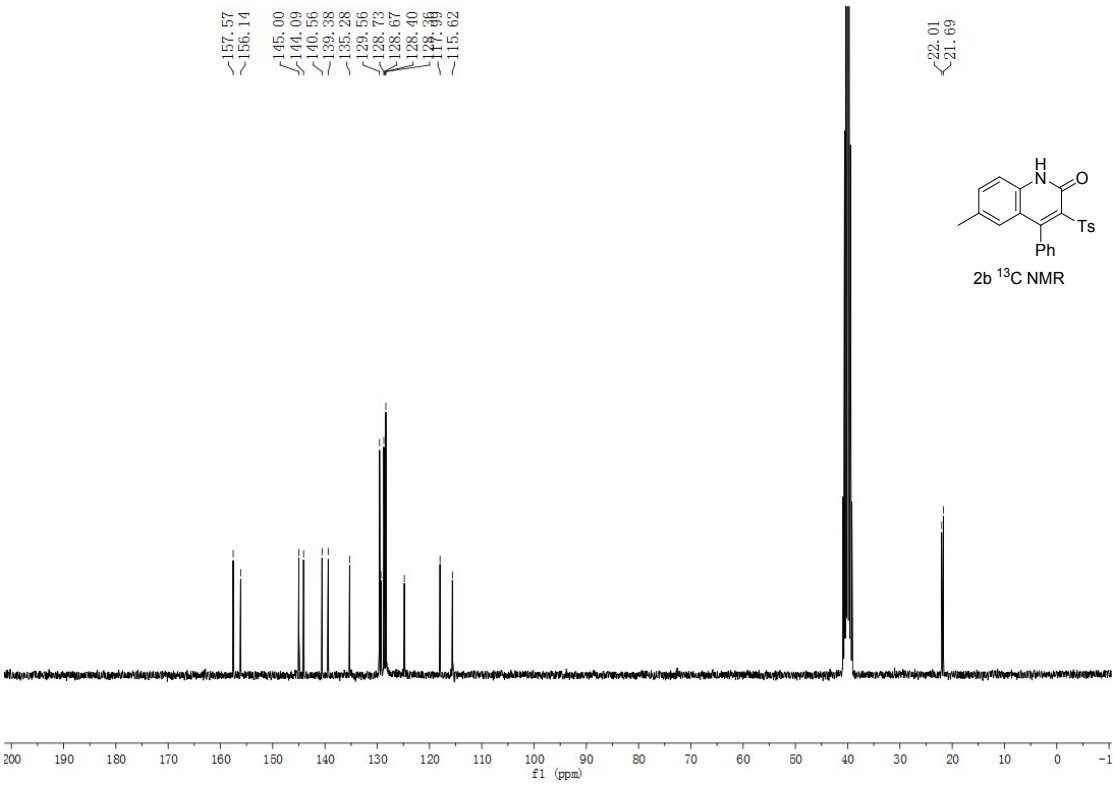
5. Copies of ^{1}H NMR and ^{13}C NMR spectra of 2a-2t



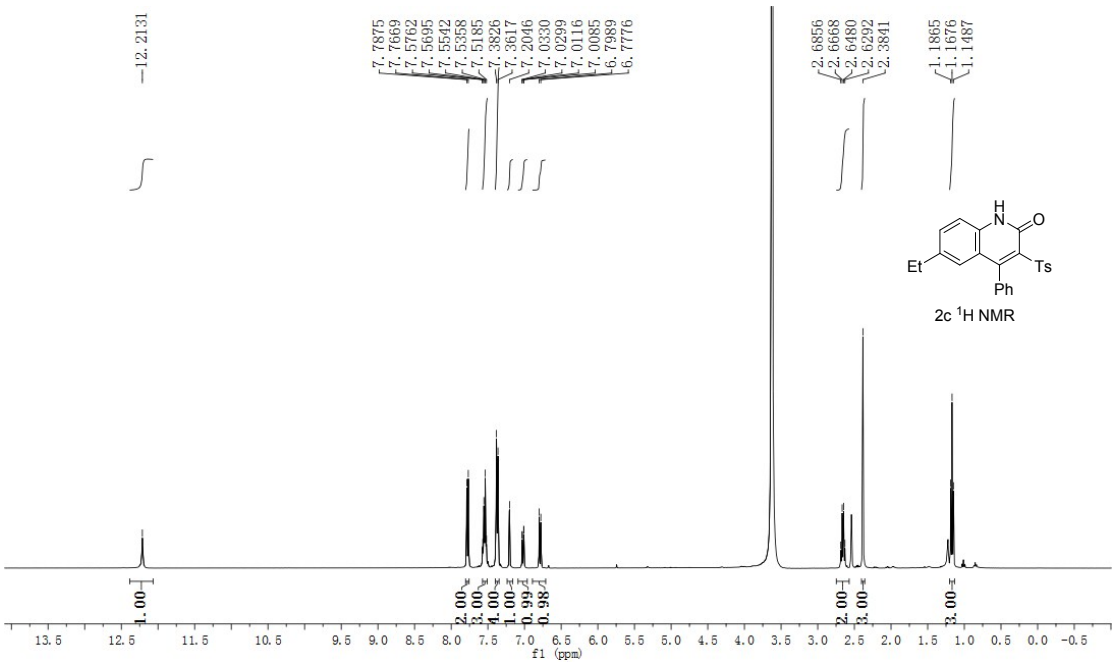




2b ^{1}H NMR



2b ^{13}C NMR



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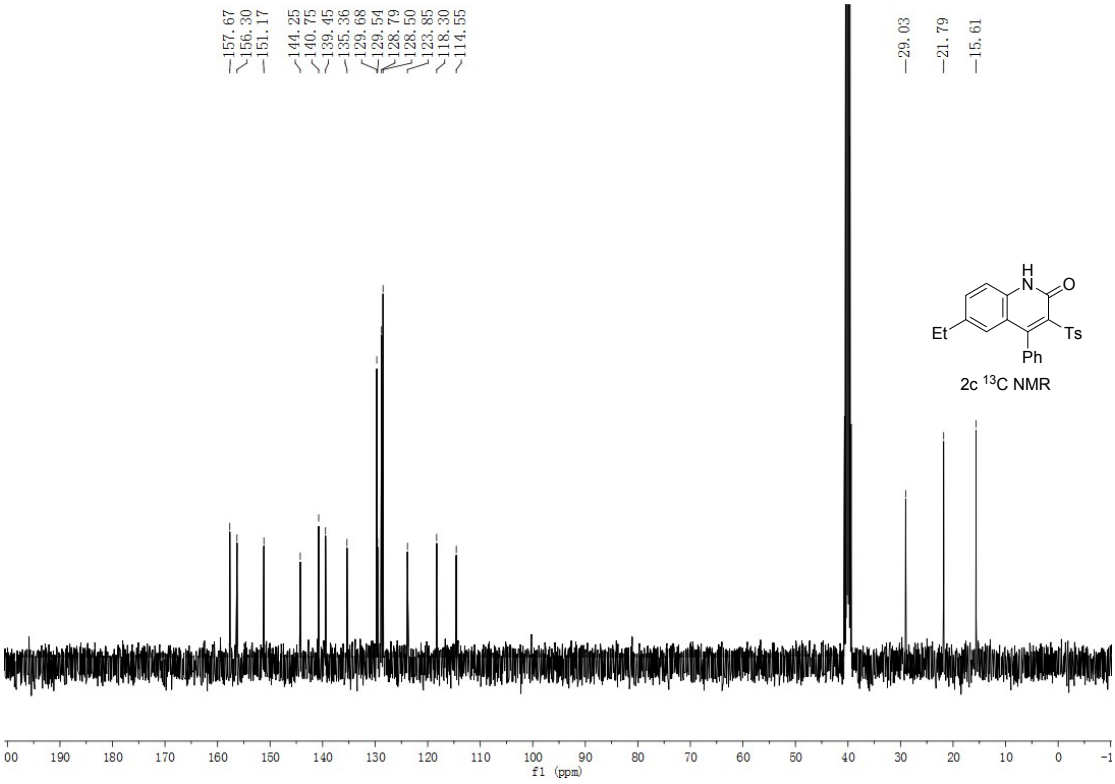

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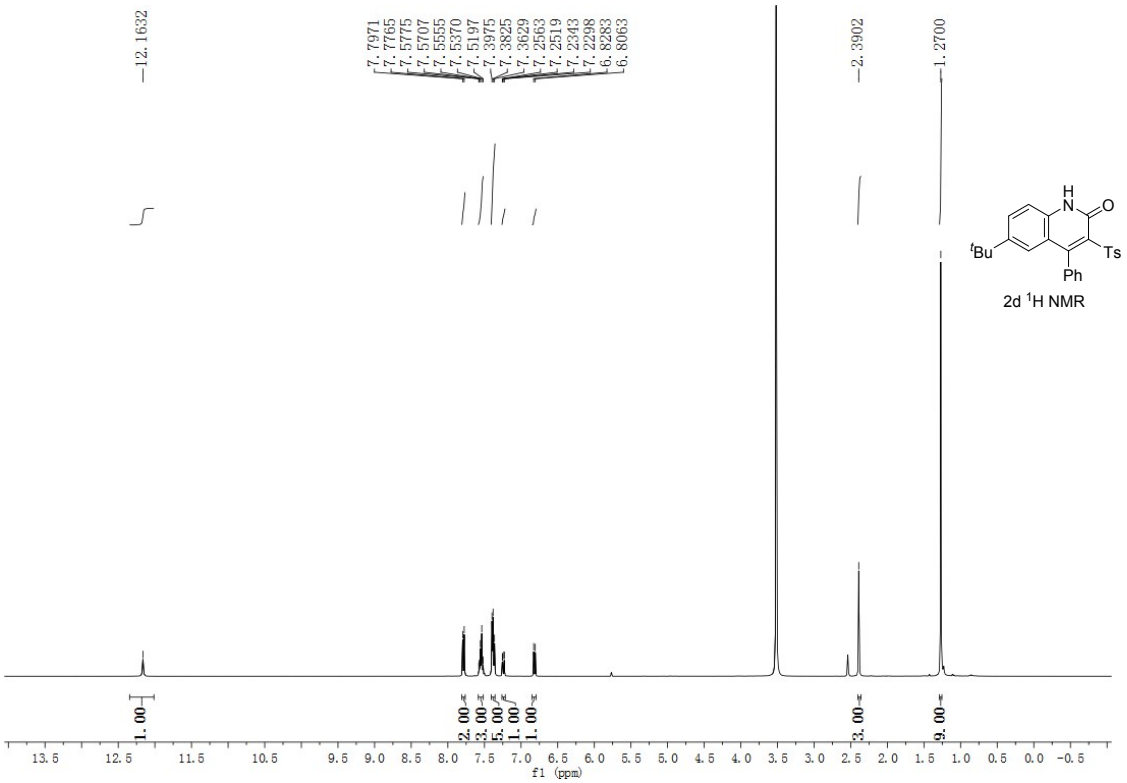

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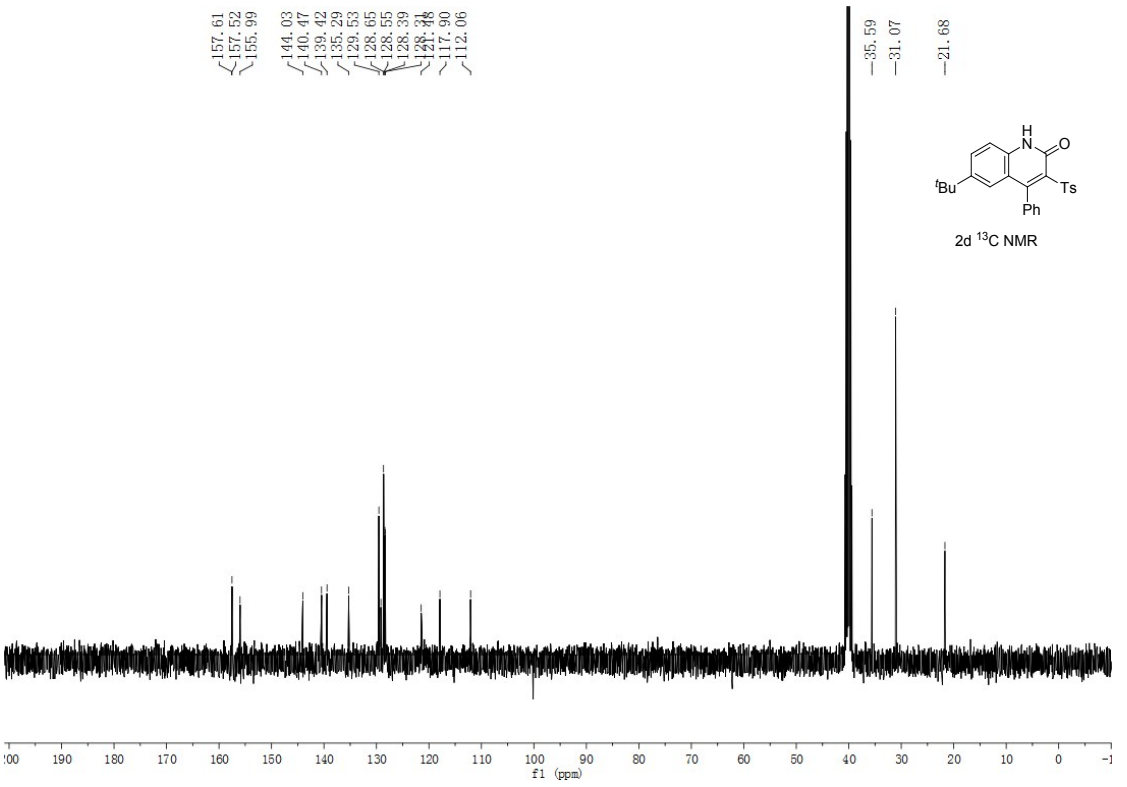
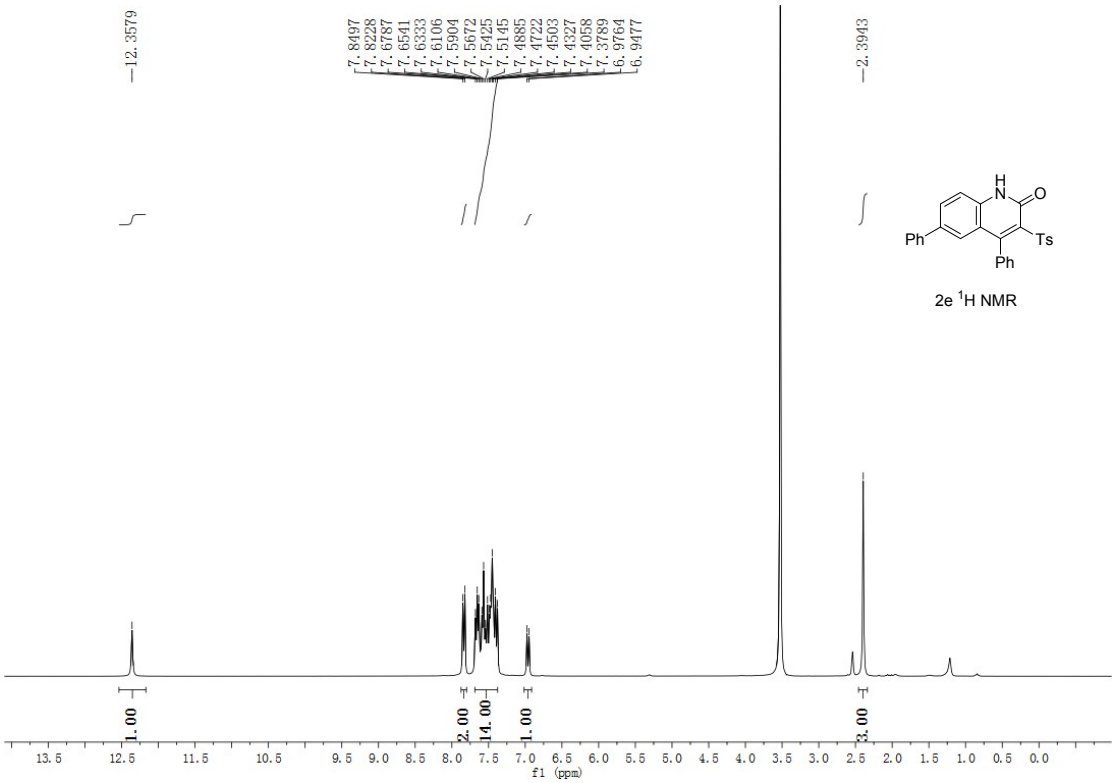


2d ^{13}C NMR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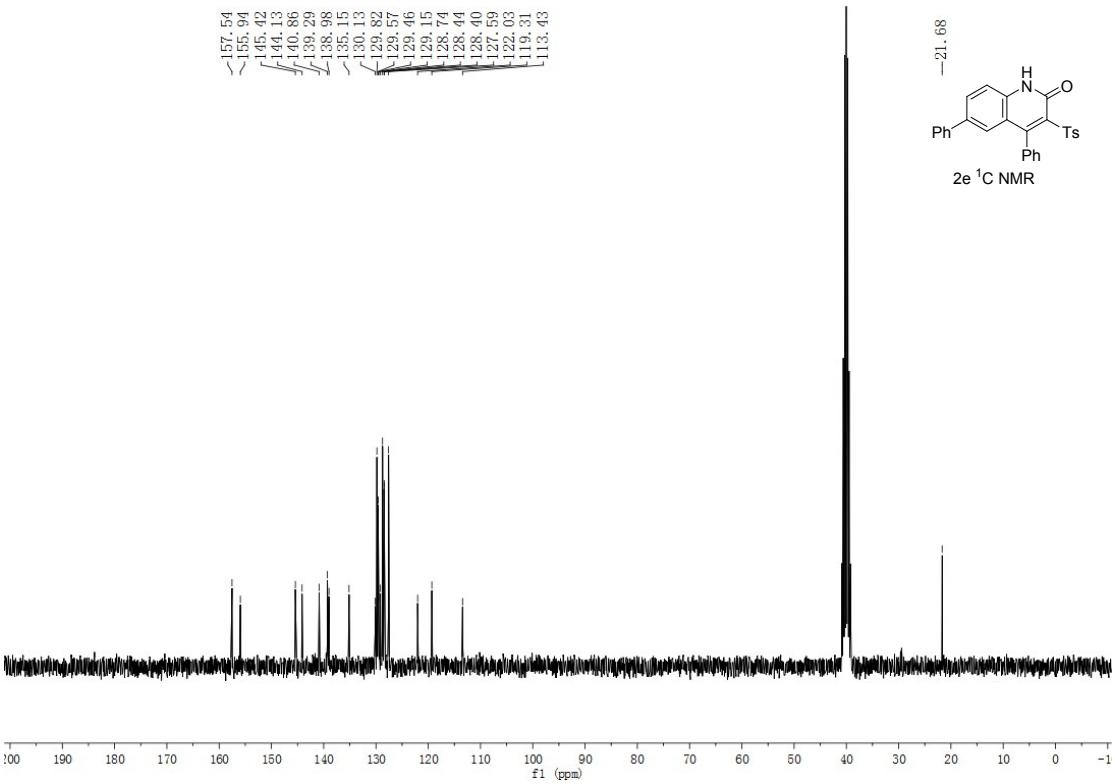
7.8497
7.8228
7.6787
7.6541
7.6333
7.6106
7.5904
7.5672
7.5425
7.5145
7.4885
7.4722
7.4503
7.4327
7.4058
7.3789
6.9764
6.9477
2.3943
1.00
2.00
14.00
1.00
3.00
f1 (ppm)
Ph
Ts
Ph
2e 1H NMR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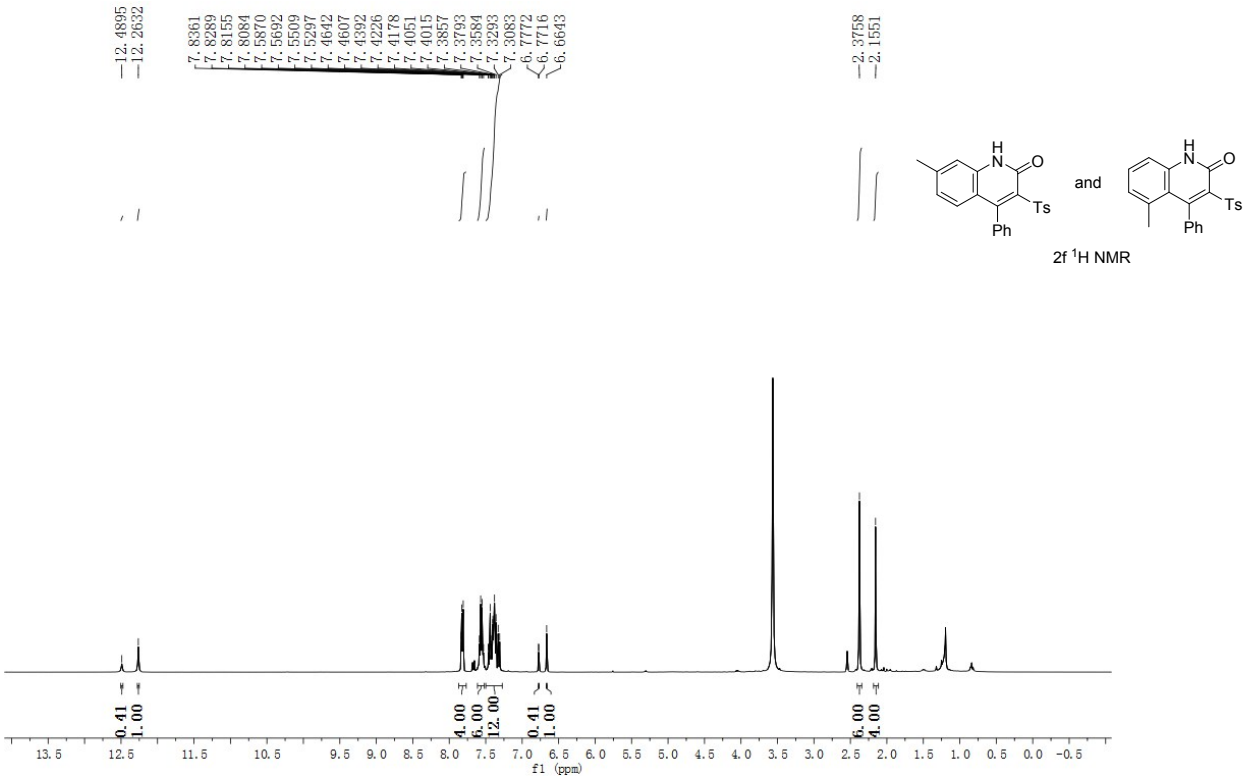
155.94
145.42
144.13
140.86
139.29
138.98
135.15
130.13
129.82
129.57
129.46
129.15
128.74
128.44
128.40
127.59
122.03
119.31
113.43
21.68
f1 (ppm)
Ph
Ts
Ph
2e 1C NMR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7.5692
7.5509
7.5297
7.4642
7.4607
7.4392
7.4226
7.4178
7.4051
7.4015
7.3857
7.3793
7.3584
7.3293
7.3083
6.7772
6.7716
6.6643
2.3758
2.1551
and
Ts
Ph
2f ^{1}H NMR
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1.00
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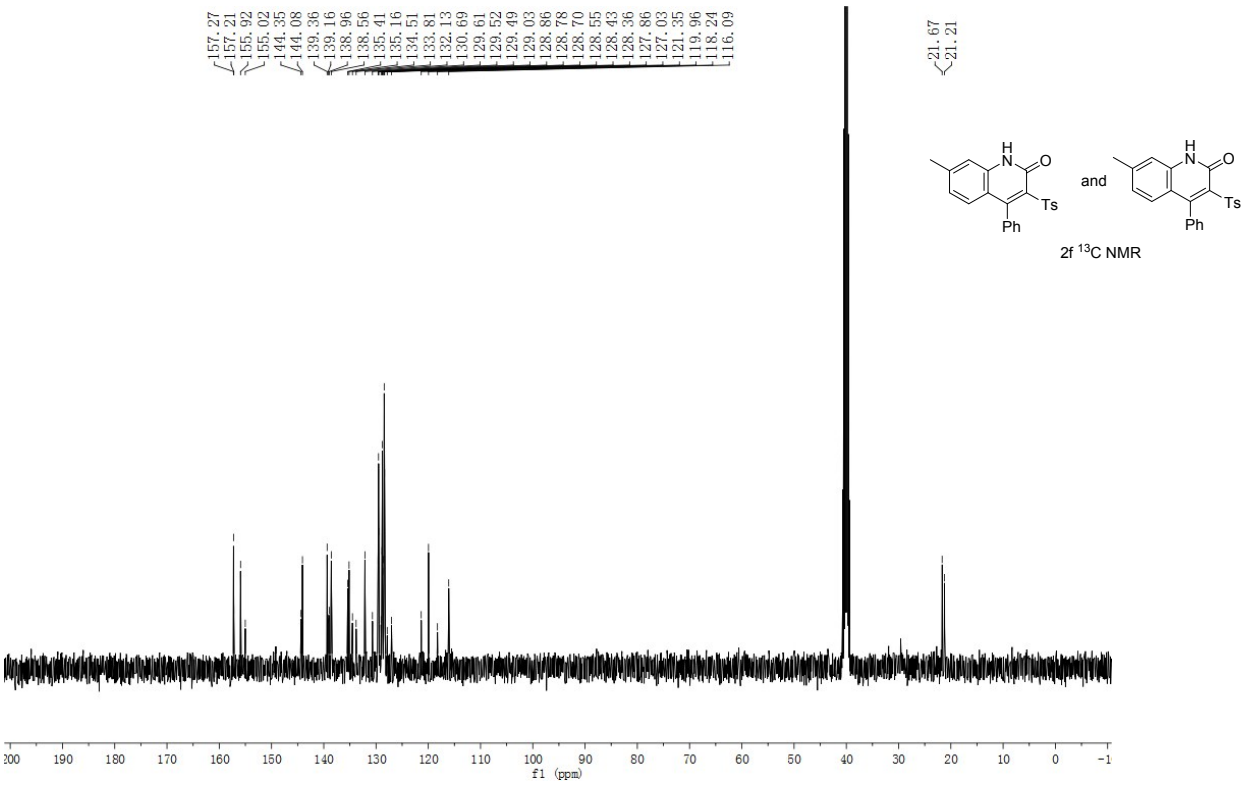
6.00
12.00
0.41
1.00
6.00
4.00
f1 (ppm)


157.27
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155.02
144.35
144.08
139.36
139.16
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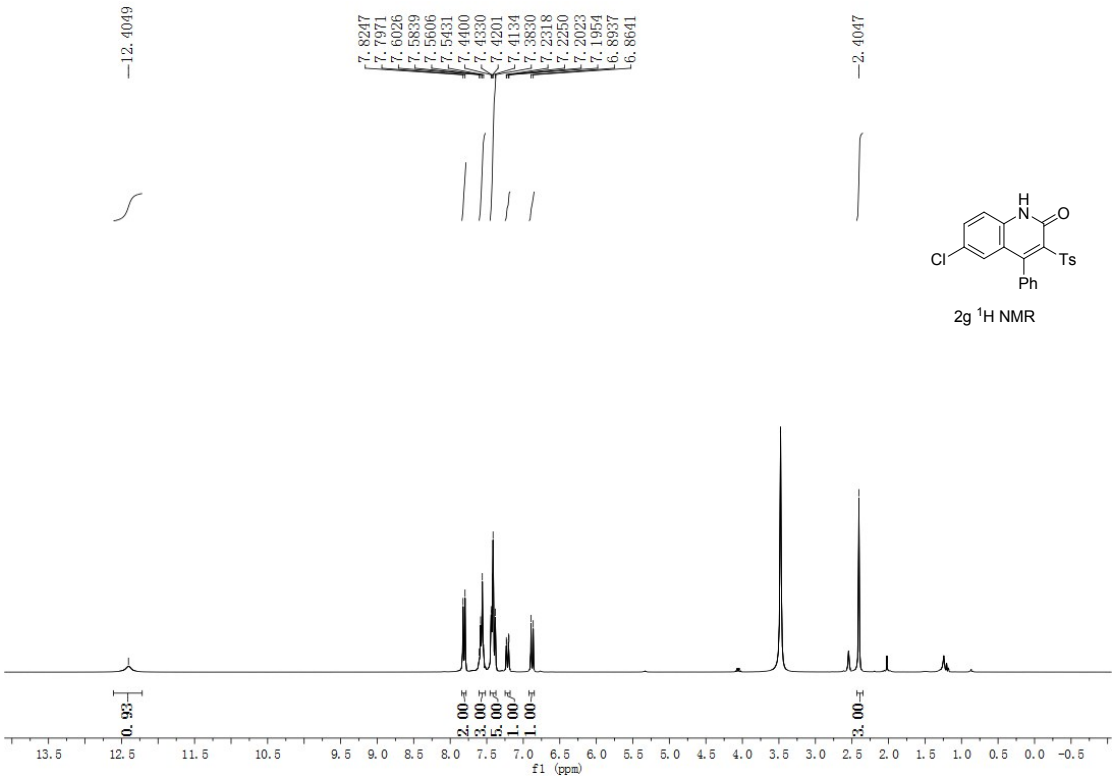
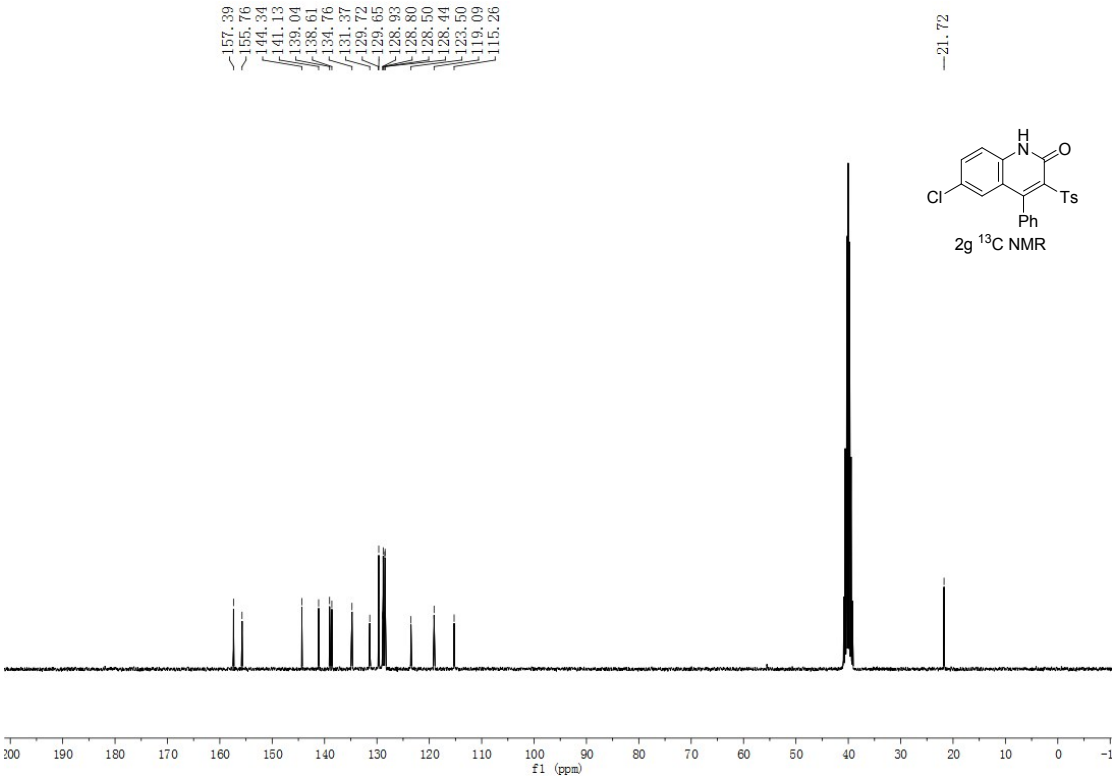
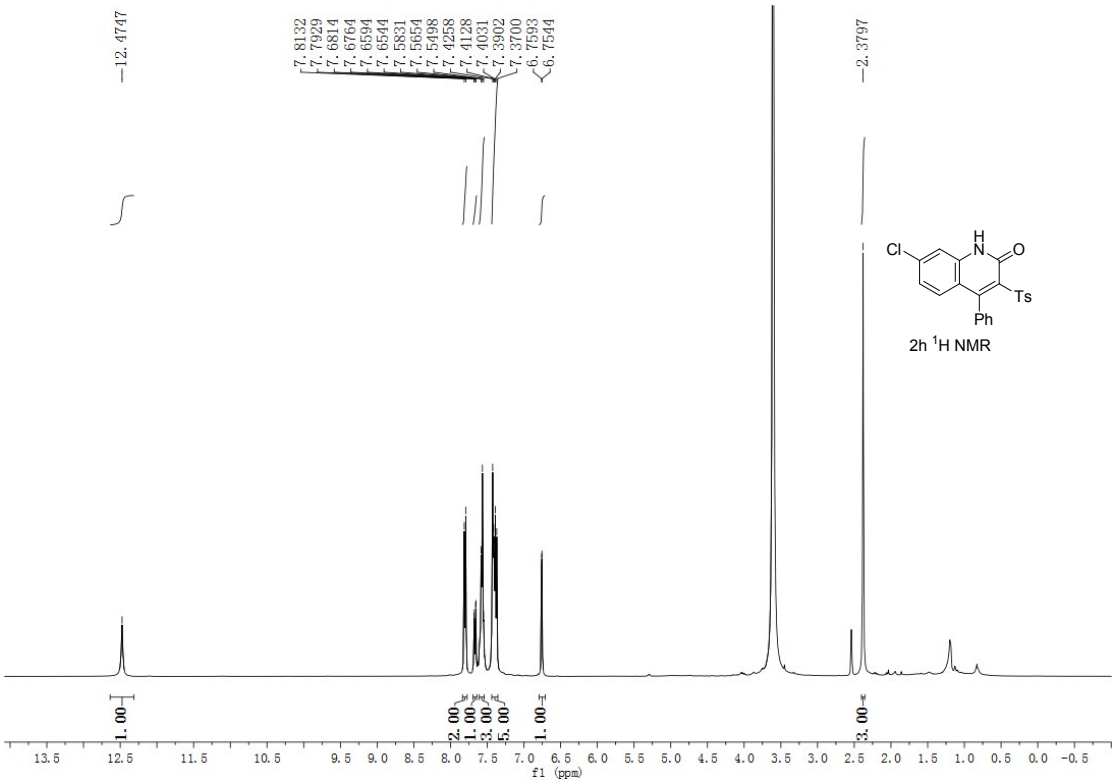
138.56
135.41
135.16
134.51
133.81
132.13
130.69
129.61
129.52
129.49
129.03
128.86
128.78
128.70
128.55
128.43
128.36
127.86
127.03
121.35
119.96
118.24
116.09
21.67
21.21
and
Ts
Ph
2f ^{13}C NMR
f1 (ppm)



2g ^{1}H NMR



2g ^{13}C NMR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7.4031
7.3902
7.3700
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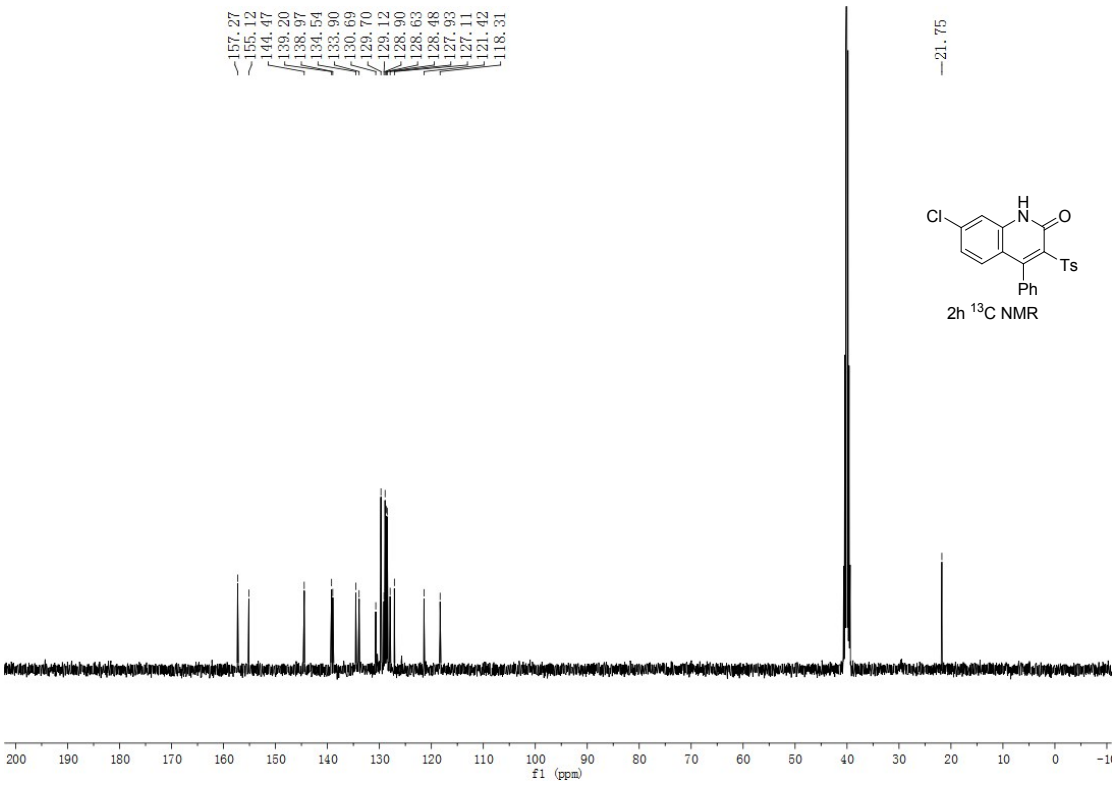
Cl
H
N
O
Ts
Ph
2h ^{1}H NMR


157.27
155.12
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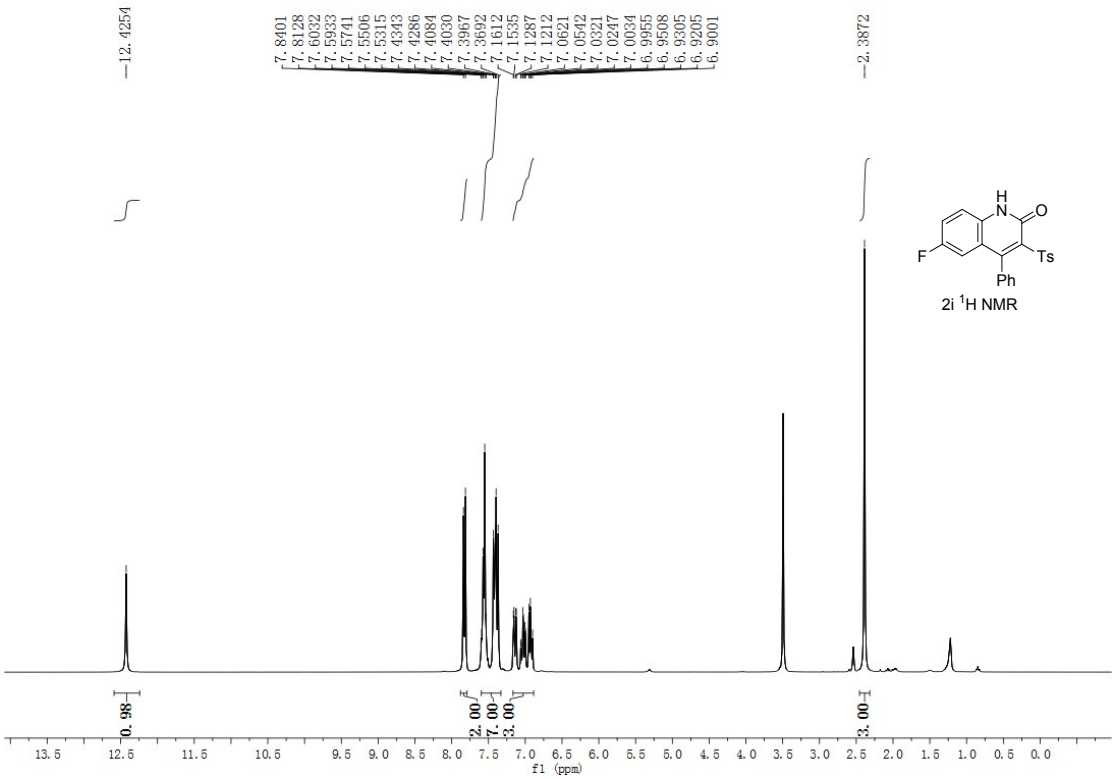
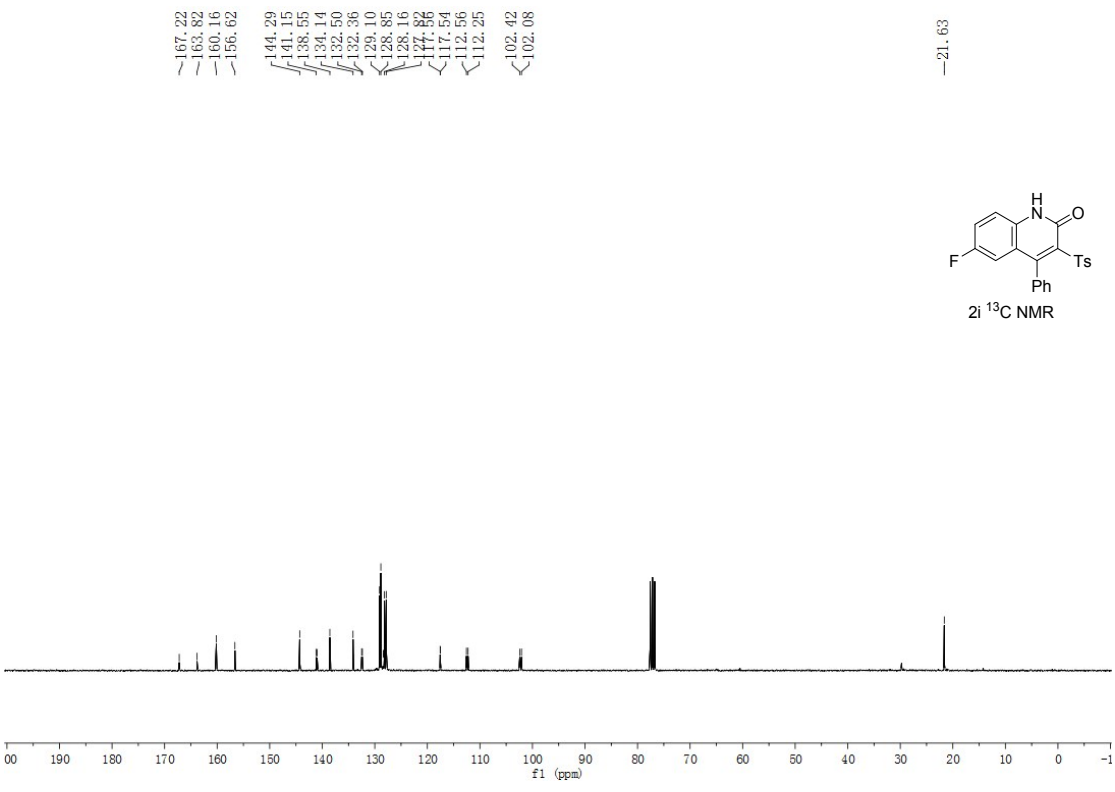
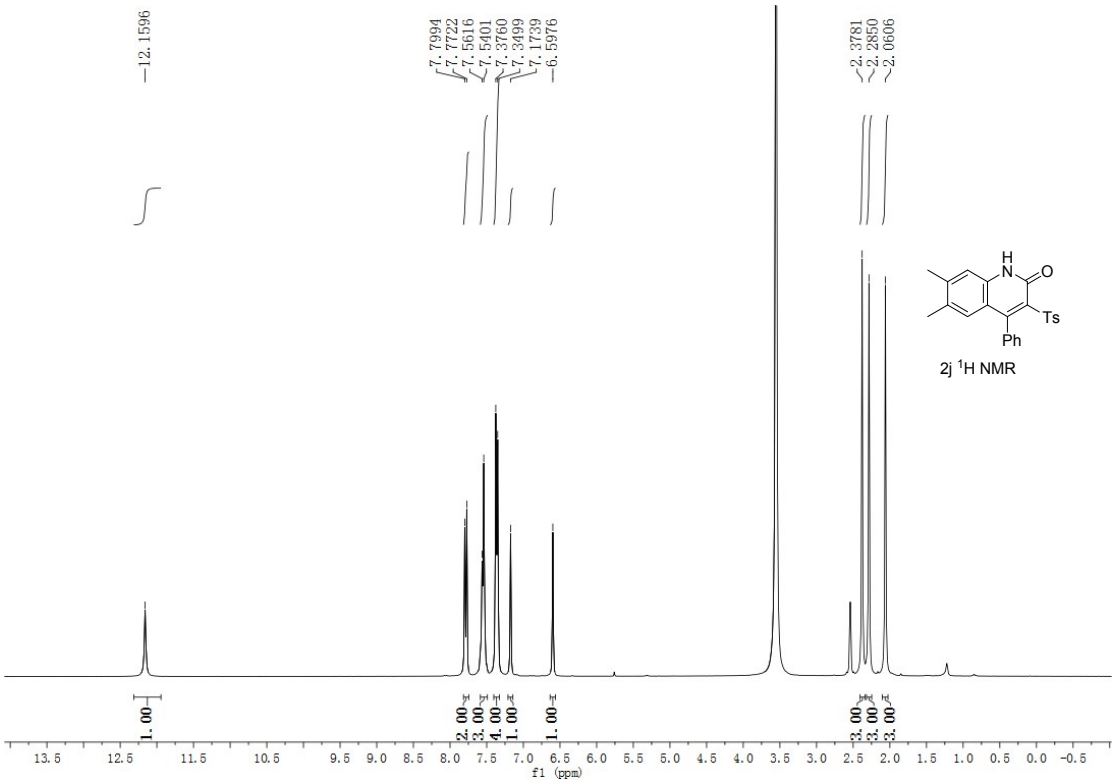
133.90
130.69
129.70
129.12
128.90
128.63
128.48
127.93
127.11
121.42
118.31
21.75
f1 (ppm)
Cl
H
N
O
Ts
Ph
2h ^{13}C NMR



2i ^{1}H NMR



2i ^{13}C NMR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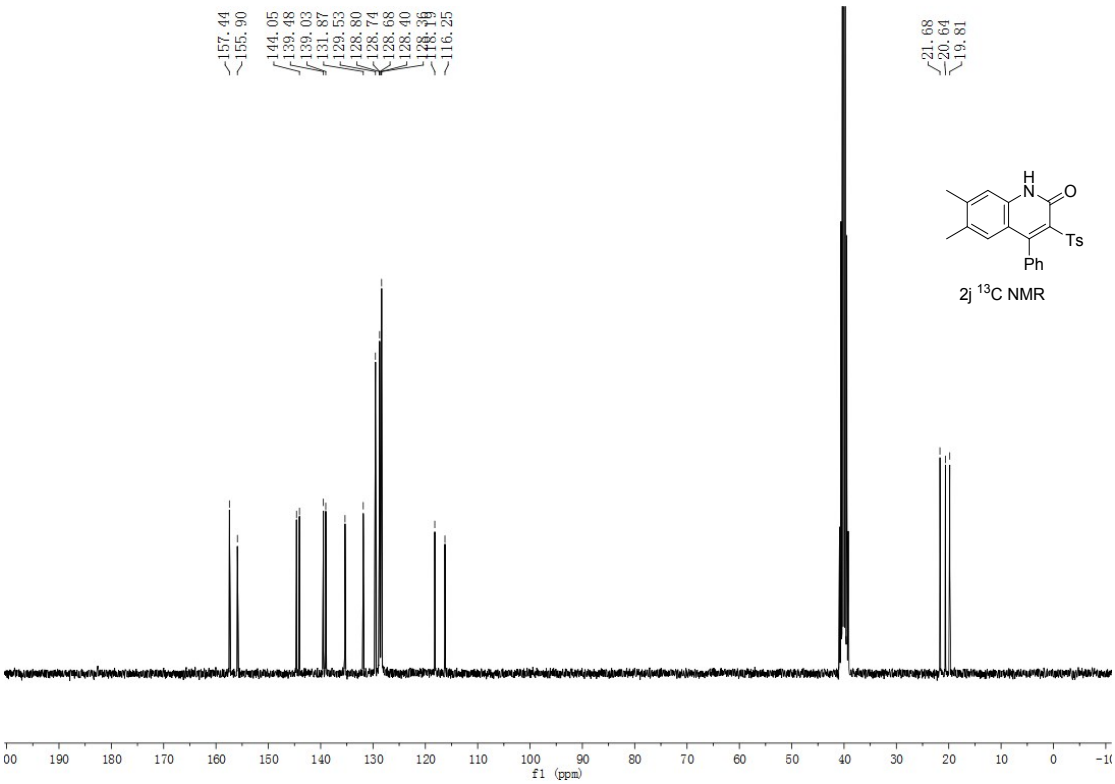
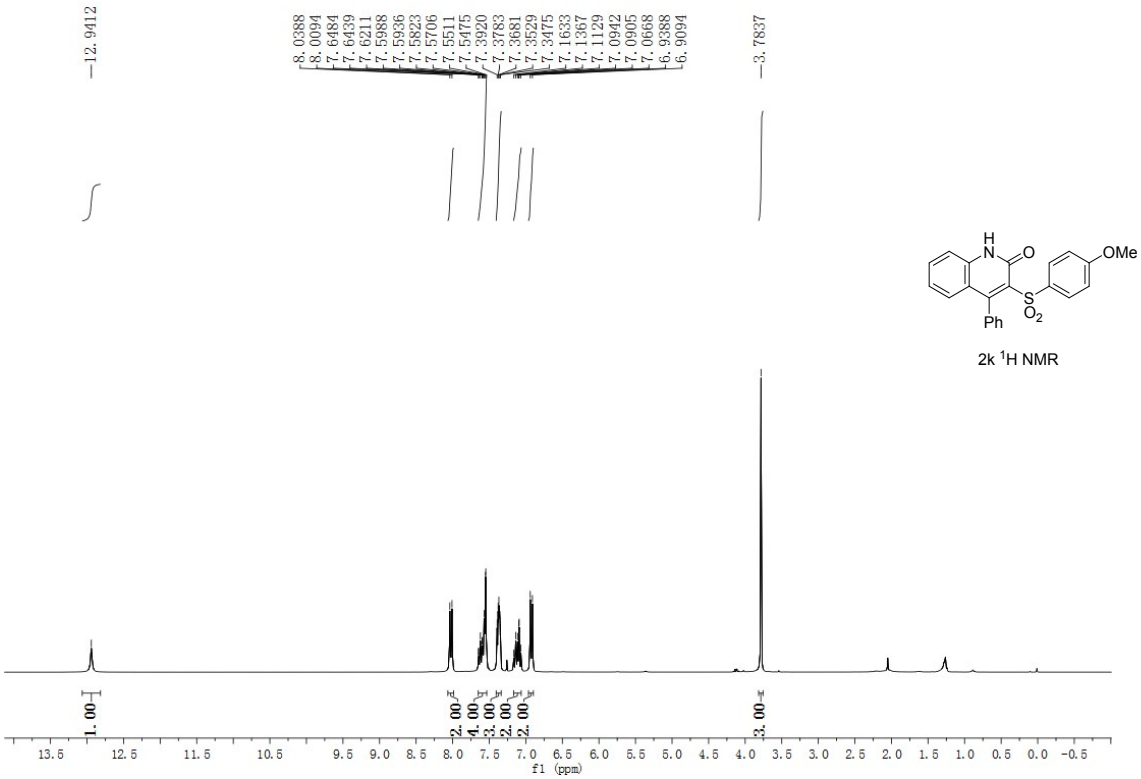
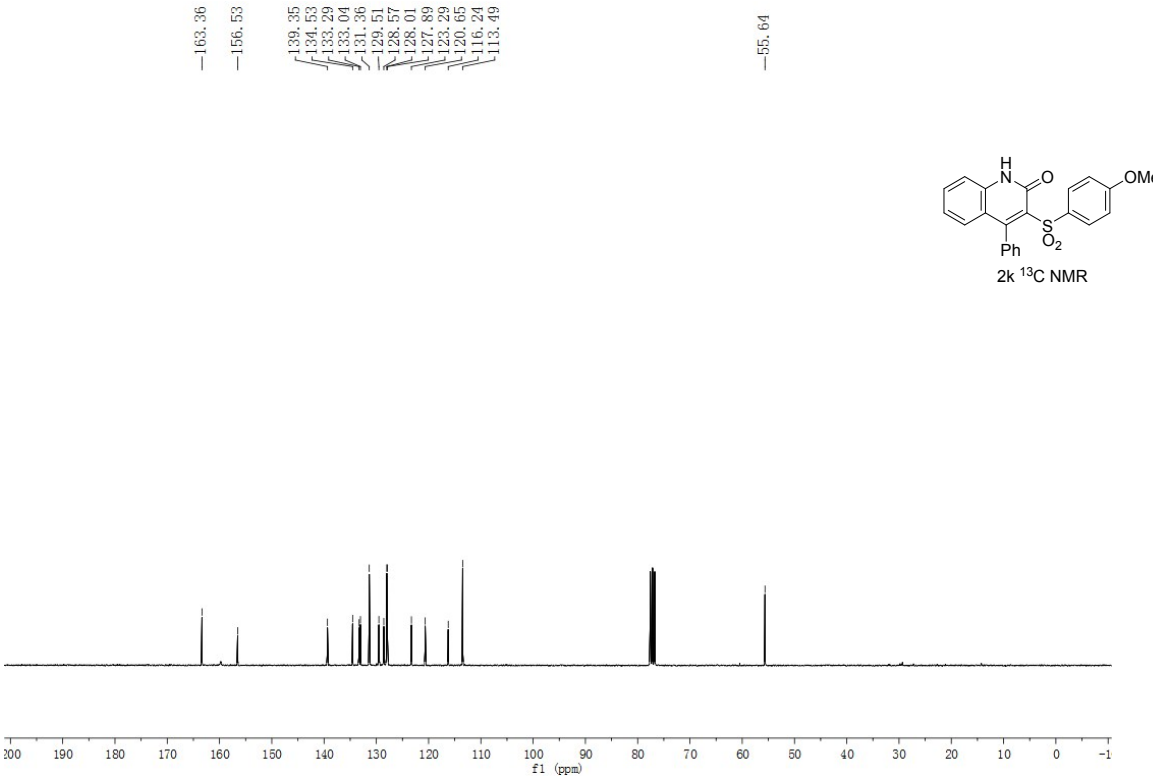
7.5616
7.5401
7.3760
7.3499
7.1739
6.5976
2.3781
2.2850
2.0606
1.00
2.00
3.00
4.00
1.00
1.00
3.00
3.00
3.00
f1 (ppm)
Ts
Ph
2j ^{1}H NMR

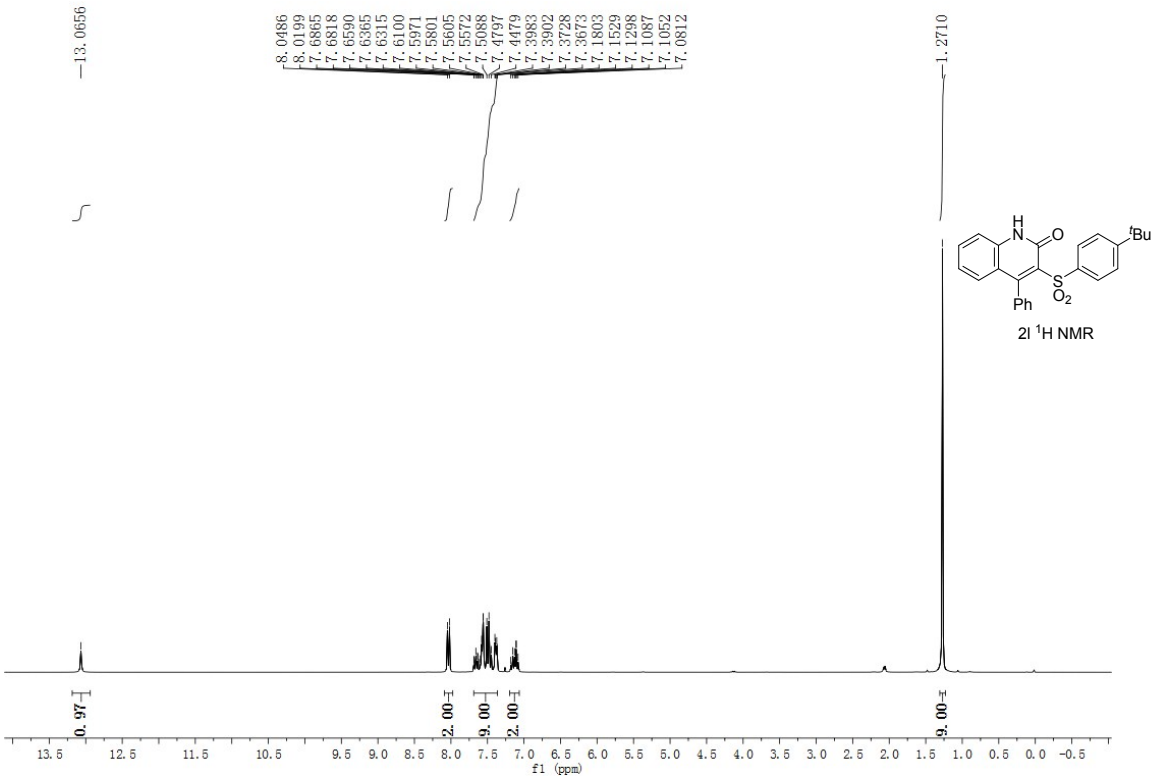

157.44
155.90
144.05
139.48
139.03
131.87
129.53
128.80
128.74
128.68
128.40
116.25
21.68
20.64
19.81
f1 (ppm)
Ts
Ph
2j ^{13}C NMR



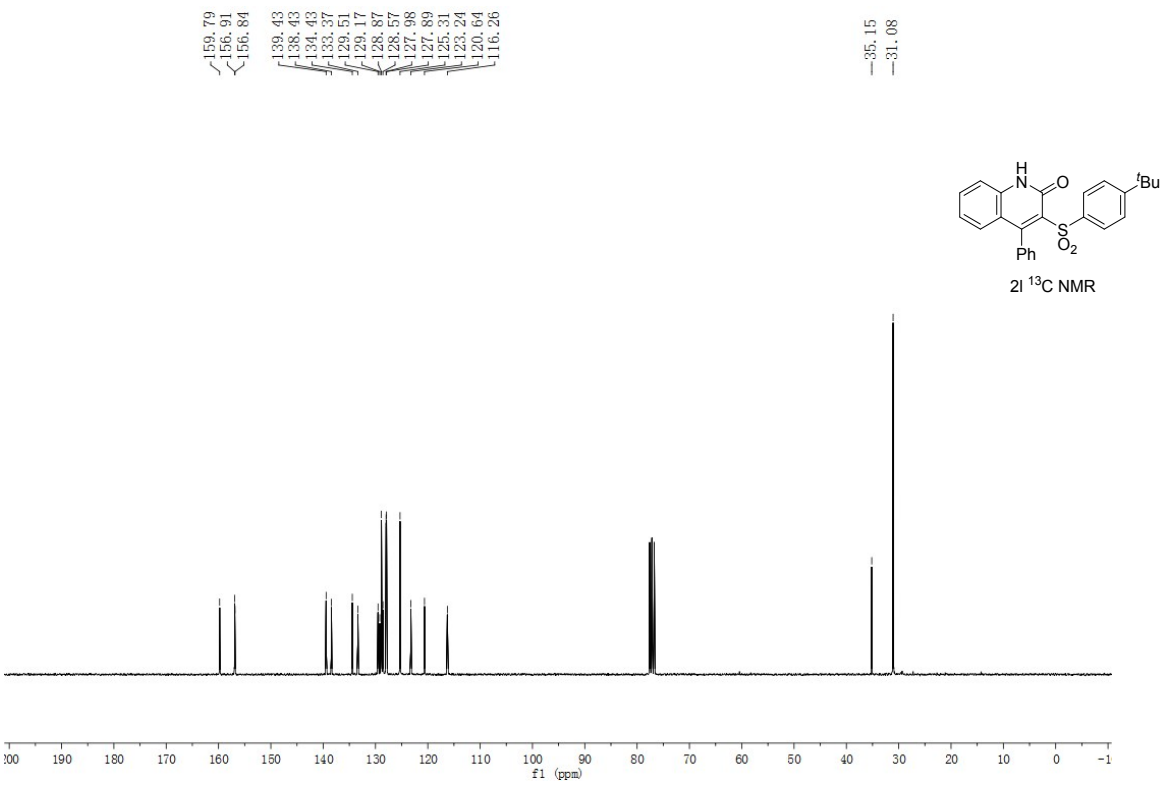
2k ^{1}H NMR



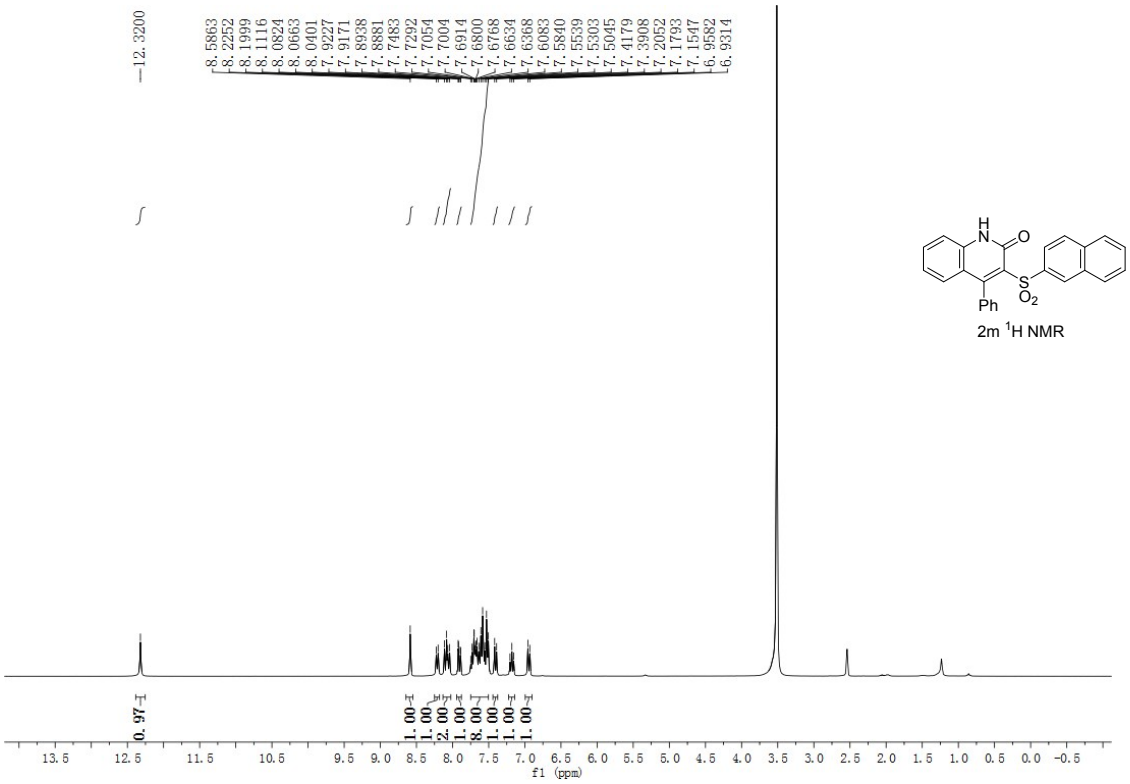
2k ^{13}C NMR



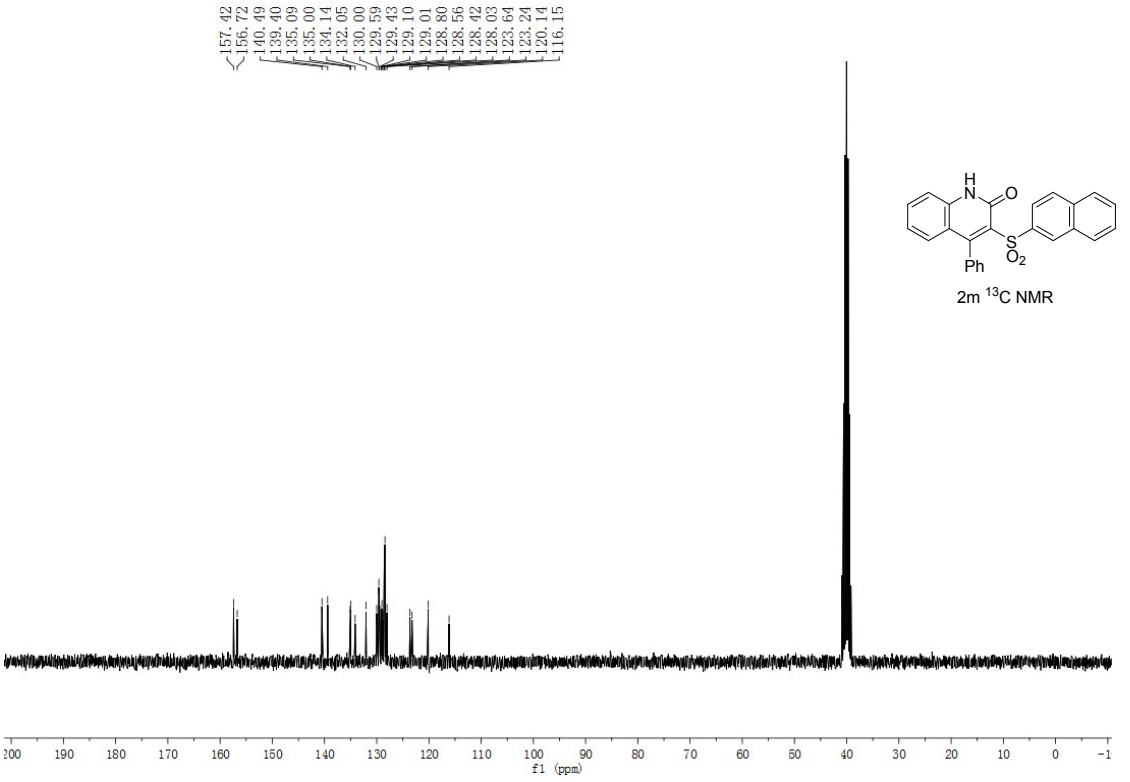
2l ^{1}H NMR



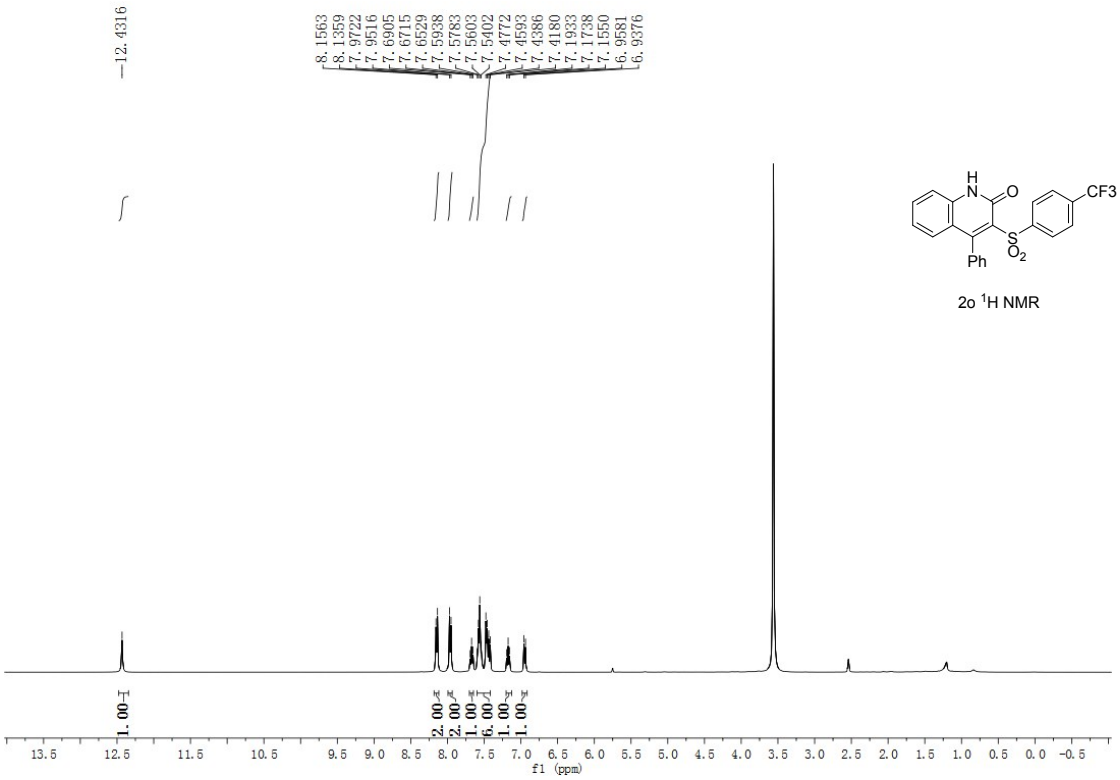
2l ^{13}C NMR



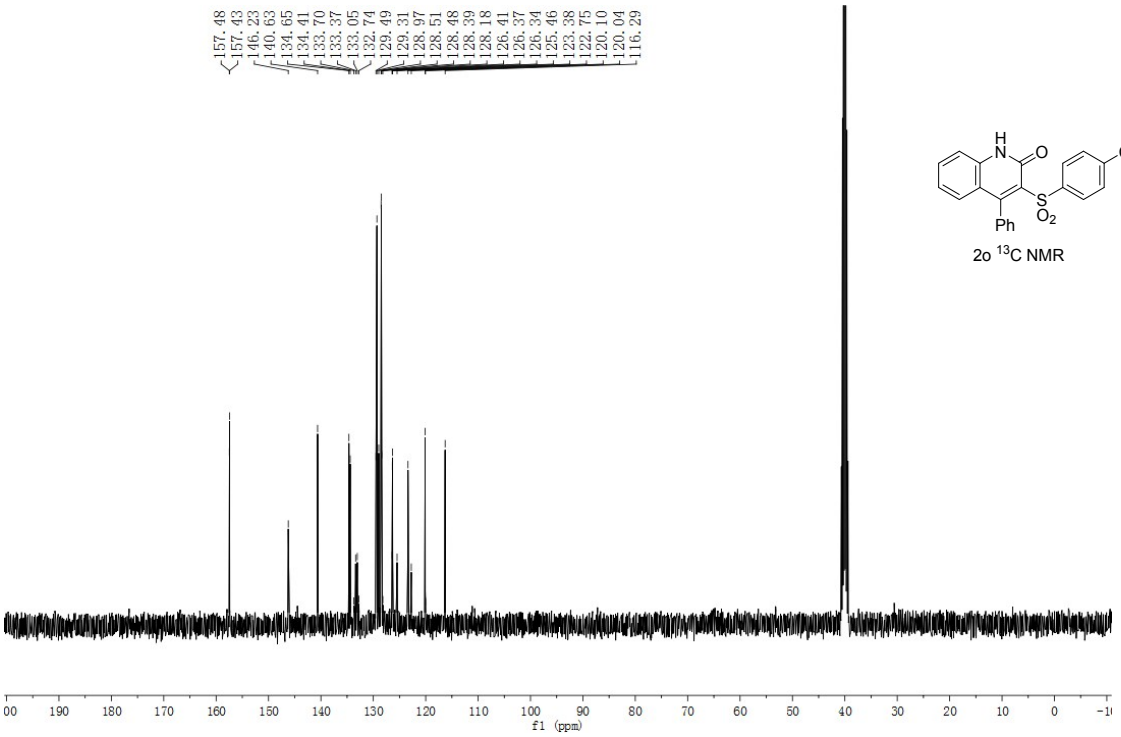
2m ^{1}H NMR



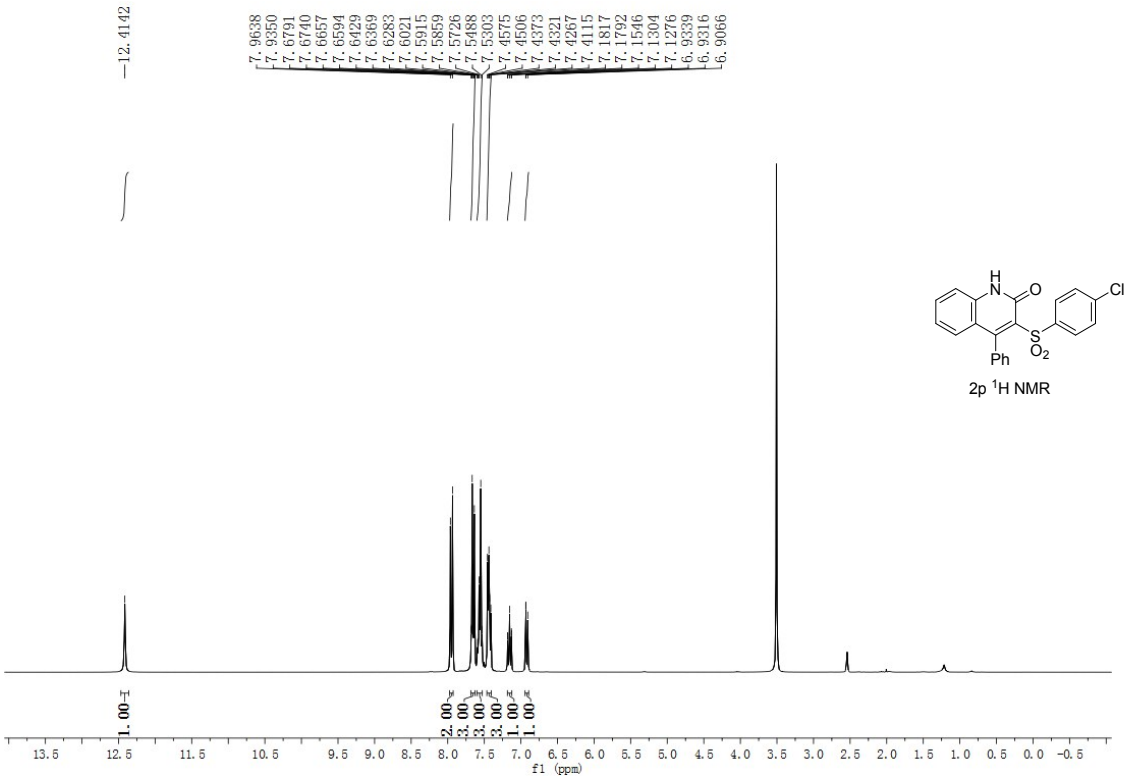
2m ^{13}C NMR



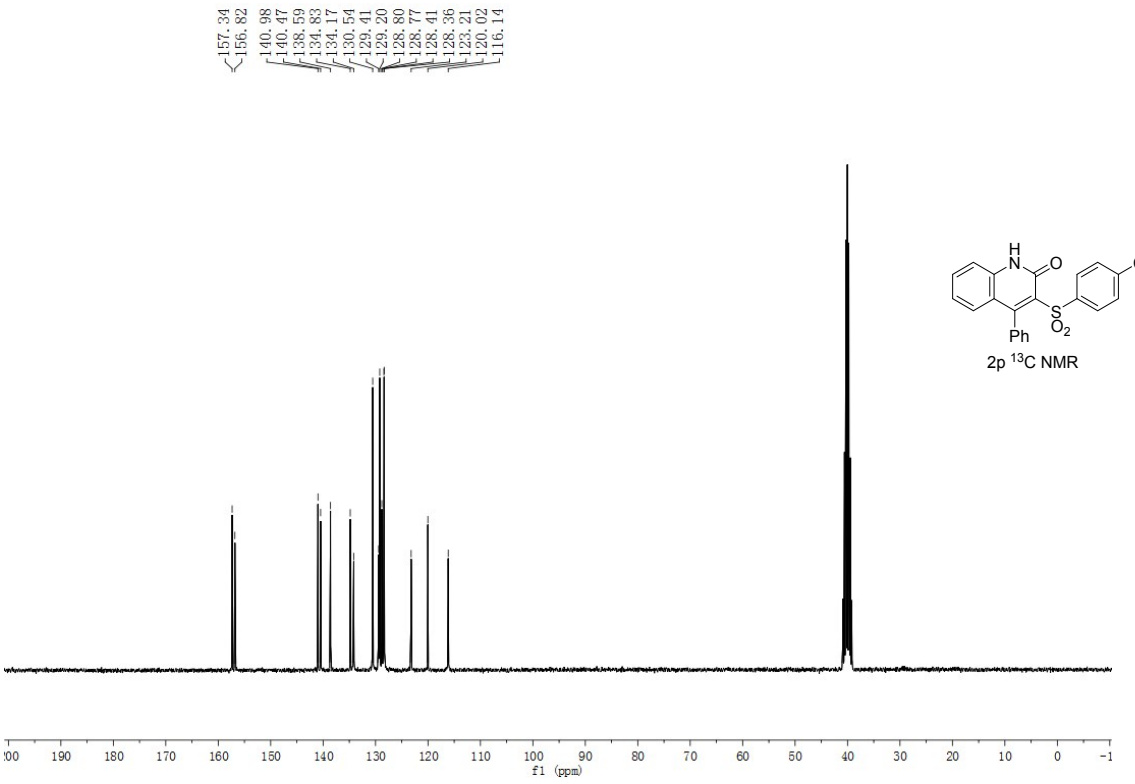
2o ^{1}H NMR



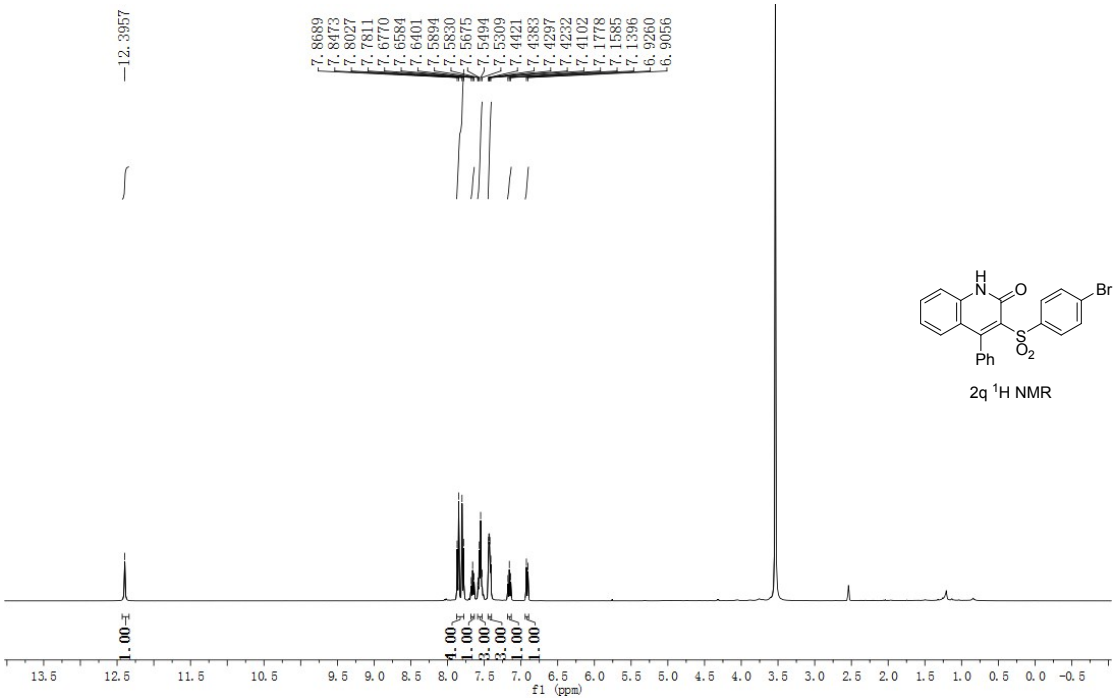
2o ^{13}C NMR



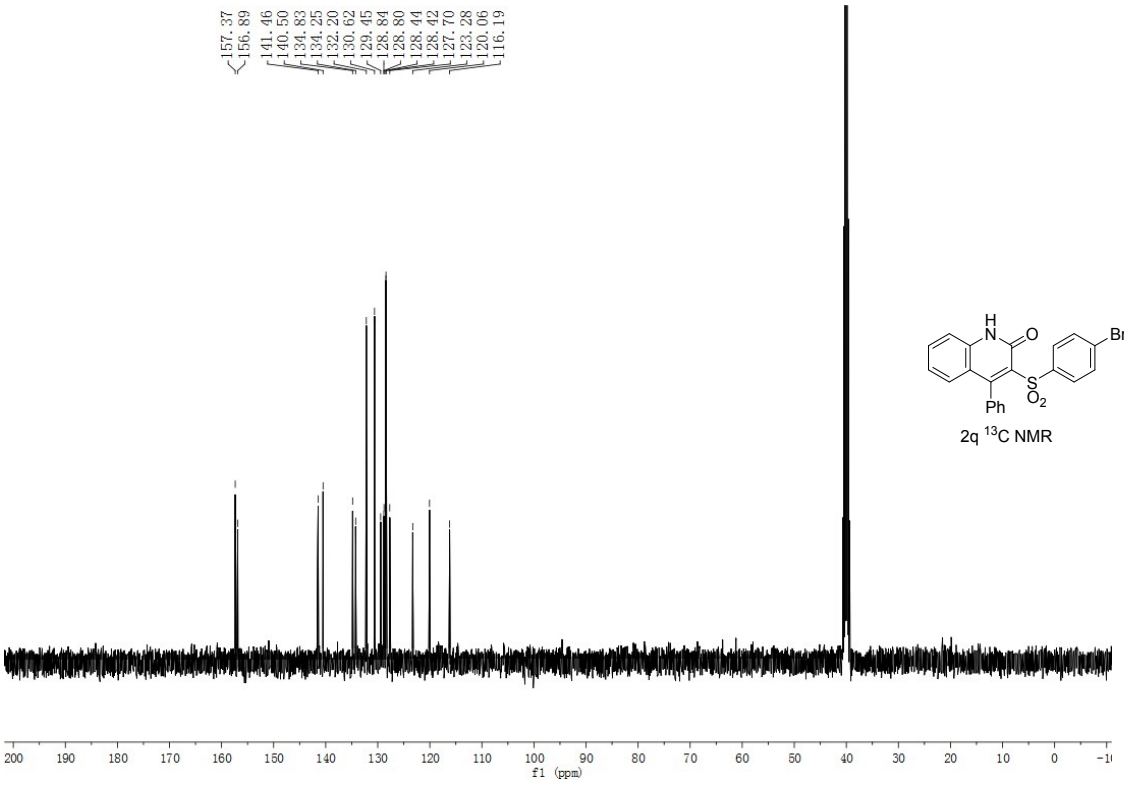
2p ^{1}H NMR



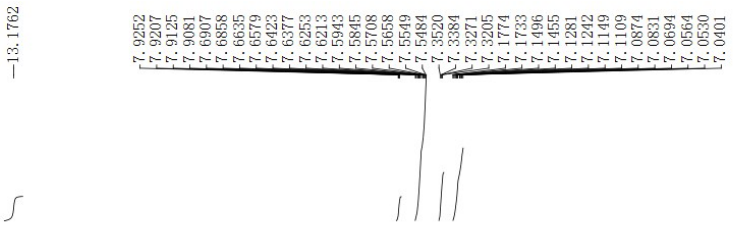
2p ^{13}C NMR

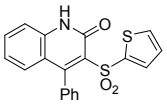


2q ^{1}H NMR

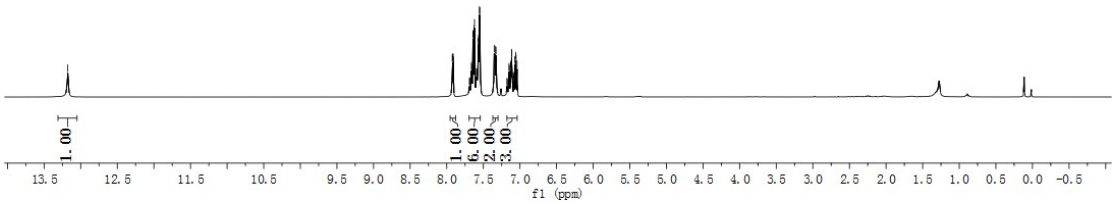


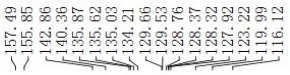
2q ^{13}C NMR

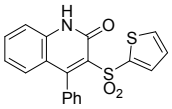




2t ^{1}H NMR







2t ^{13}C NMR