Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Ring expansion and ring opening of 3-halooxindoles with *N*-alkoxycarbonyl-*O*-tosylhydroxylamines for divergent access to 4-aminoquinolin-2-ones and *N*-Cbz-*N*′-arylureas

Wei-Cheng Yuan,[a]* Jian Zuo,[b] Shu-Pei Yuan,[b] Jian-Qiang Zhao,[a]* Zhen-Hua Wang,[a] and Yong You[a]

[a]Institute for Advanced Study, Chengdu University, Chengdu 610106, China.
[b]National Engineering Research Center of Chiral Drugs, Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu, 610041, China.

E-mail: yuanwc@cioc.ac.cn
zhaojianqiang@cdu.edu.cn

Supporting Information

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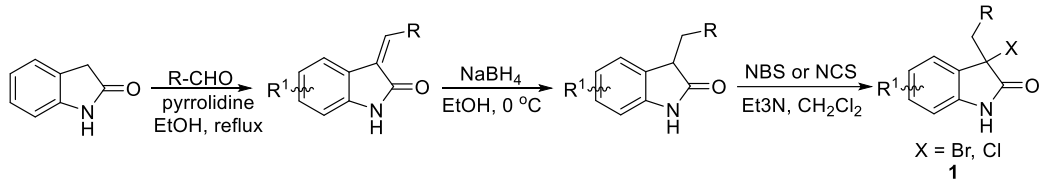
1. General experimental information

Reagents were purchased from commercial sources and were used as received unless mentioned otherwise. Reactions were monitored by Thin-Layer Chromatography (TLC). ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded in DMSO-d_6. ^{1}H NMR chemical shifts are reported in ppm relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard (DMSO-d_6 at 2.50 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard (DMSO-d_6 at 39.51 ppm). Melting points were recorded on a Büchi Melting Point B-545 unit. HRMS was recorded on Bruker Q-TOF.

2. General experimental procedure for synthesis of compounds 1[1,2].



A mixture of indolin-2-one (10 mmol), aldehyde (10 mmol) and pyrrolidine (0.1 mL) in ethanol (30 mL) was heated to reflux for 2 h. Then, the mixture was cooled to 0 °C, and sodium hydroborate (50 mmol) was added in batches at 0 °C. The resulting mixture was stirred at rt for 2 h, quenched by water and extracted three times by ethyl acetate. The organic phase was dried over anhydrous Na_2SO_4 and evaporated in vacuo. The residue was dissolved in dichloromethane (40 mL) and triethylamine (0.3 mL) was added. Next, the reaction mixture was cooled to 0 °C, and *N*-bromosuccinimide (NBS) or *N*-chlorosuccinimide (NCS) (10 mmol) was added over 30 minutes by portion. Then, the mixture was warmed to room temperature and stirred for 1 h. After being concentrated in vacuo, the residue was subjected to flash chromatograph (PE/EtOAc 10:1) on silica gel (or recrystallization from the mixed solvent of PE and EtOAc) to afford 3-halooxindoles **1** as a light yellow solid.

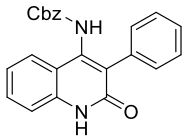
Reference

(1) Y.-H. Liao, Z.-J. Wu, W.-Y. Han, X.-M. Zhang and W.-C. Yuan. Organocatalytic Enantioselective Stereoablative Hydroxylation of 3-Halooxindoles: An Effective Method for the Construction of Enantioenriched 3-Substituted 3-Hydroxy-2-Oxindoles. *Chem. Eur. J.*, 2012, **18**, 8916.

(2) X. Xie, L. Jing, D. Qin, W. He, S Wu, L. Jin and G. Luo. Regioselective asymmetric stereoablative *O*-alkylation of *α*-nitrophosphonates via *o*-azaxylylene intermediates generated in situ from 3-bromooxindoles. *RSC Adv.*, 2014, **4**, 11605.

3. General experimental procedure for synthesis of compounds 3.

To a reaction tube were added 3-halooxindoles **1** (0.1 mmol), *N*-alkoxycarbonyl-*O*-tosylhydroxylamines **2** (0.15 mmol) and Cs_2CO_3 (0.7 mmol, 7.0 equiv), followed by addition CH_3CN (2.0 mL). Then the mixture was stirred for 72 h at room temperature. After completion, the resulting mixture was concentrated and the residue was purified by flash chromatography (petroleum ether/ethyl acetate = 2:1 ~ 1:1) to give the corresponding product **3**.



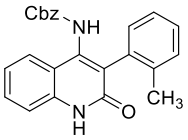
benzyl (2-oxo-3-phenyl-1,2-dihydroquinolin-4-yl)carbamate (3a)

White solid, 34.8 mg, 94% yield; mp 203.4-205.1 ºC;

^{1}H NMR (DMSO-d_6, 300 MHz), δ 12.04 (s, 1H), 9.38 (s, 1H), 7.62 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.59 – 7.49 (m, 1H), 7.44 – 7.26 (m, 9H), 7.26 – 7.11 (m, 3H), 4.97 (s, 2H);

^{13}C NMR (DMSO-d_6, 75 MHz), δ 161.6, 154.0, 140.8, 138.0, 136.7, 134.0, 130.6, 130.2, 130.0, 128.3, 127.8, 127.4, 127.5, 127.3, 124.4, 121.9, 118.4, 115.1, 65.7;

HRMS (ESI-TOF) calcd for $C_{23}H_{19}N_2NaO_3$ $[M + H]^+$: 371.1390; found: 371.1394.



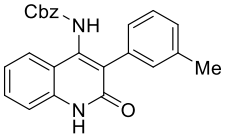
benzyl (2-oxo-3-(*o*-tolyl)-1,2-dihydroquinolin-4-yl)carbamate (3b)

White solid, 33.1 mg, 86% yield; mp 176.5-178.1 ºC;

^{1}H NMR (DMSO-d_6, 300 MHz),δ 12.01 (s, 1H), 9.30 (s, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.59 – 7.51 (m, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.37 – 7.14 (m, 7H), 7.14 – 7.07 (m, 2H), 7.02 (d, *J* = 7.5 Hz, 1H), 4.97 (s, 2H), 2.10 (s, 3H);

^{13}C NMR (DMSO-d_6, 75 MHz), δ 161.1, 153.9, 141.5, 138.1, 137.5, 136.7, 134.1, 130.9, 130.6, 129.5, 129.4, 128.3, 127.8, 127.5, 127.4, 125.0, 124.4, 121.8, 118.2, 115.2, 65.6, 19.5;

HRMS (ESI-TOF) calcd for $C_{24}H_{21}N_2O_3$ $[M + H]^+$: 385.1547; found: 385.1548.



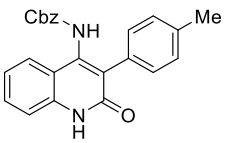
benzyl (2-oxo-3-(*m*-tolyl)-1,2-dihydroquinolin-4-yl)carbamate (3c)

White solid, 36.5 mg, 95% yield; mp 150.1-161.7 ºC;

^{1}H NMR (DMSO-d_6, 300 MHz), δ 12.02 (s, 1H), 9.35 (s, 1H), 7.61 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.58 – 7.49 (m, 1H), 7.42 – 7.29 (m, 4H), 7.29 – 7.20 (m, 2H), 7.16 (dd, *J* = 7.0, 2.4 Hz, 3H), 7.13 – 7.03 (m, 2H), 4.98 (s, 2H), 2.28 (s, 3H);

^{13}C NMR (DMSO-d_6, 75 MHz), δ 161.6, 154.0, 140.8, 137.9, 136.7, 136.3, 133.9, 130.6, 130.5, 130.3, 128.3, 128.0, 127.8, 127.5, 127.4, 127.1, 124.4, 121.8, 118.4, 115.1, 65.7, 21.1;

HRMS (ESI-TOF) calcd for $C_{24}H_{21}N_2O_3$ $[M + H]^+$: 385.1547; found: 385.1549.



benzyl (2-oxo-3-(*p*-tolyl)-1,2-dihydroquinolin-4-yl)carbamate (3d)

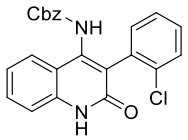
White solid, 33.4 mg, 87% yield; mp 255.1-256.8 ºC (decomposition);

^{1}H NMR (DMSO-d_6, 300 MHz), δ 11.99 (s, 1H), 9.31 (s, 1H), 7.59 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.57 – 7.49 (m, 1H), 7.40 – 7.29 (m, 4H), 7.24 – 7.14 (m, 7H), 4.98 (s, 2H), 2.35 (s, 3H);

^{13}C NMR (DMSO-d_6, 75 MHz), δ 161.6, 154.0, 140.6, 137.8, 136.7, 136.5, 130.9, 130.5, 130.3,

129.8, 128.3, 128.0, 127.8, 127.5, 124.3, 121.8, 118.4, 115.1, 65.6, 20.9;

HRMS (ESI-TOF) calcd for $C_{24}H_{21}N_2O_3$ $[M + H]^+$: 385.1547; found: 385.1548.



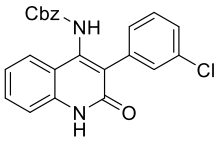
benzyl (3-(2-chlorophenyl)-2-oxo-1,2-dihydroquinolin-4-yl)carbamate (3e)

White solid, 37.2 mg, 92% yield; mp 120.7-122.3 ºC;

^{1}H NMR (DMSO-d_6, 300 MHz), δ 12.05 (s, 1H), 9.49 (s, 1H), 7.69 – 7.62 (m, 1H), 7.62 – 7.53 (m, 1H), 7.50 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.43-7.37 (m, 2H), 7.36 – 7.27 (m, 4H), 7.27 – 7.19 (m, 2H), 7.18 – 7.10 (m, 2H), 5.07 – 4.90 (m, 2H);

^{13}C NMR (DMSO-d_6, 75 MHz), δ 160.7, 153.7, 142.2, 138.3, 136.7, 133.6, 133.4, 131.9, 130.9, 129.3, 128.9, 128.3, 127.8, 127.4, 126.4, 124.6, 121.8, 117.8, 115.3, 65.7;

HRMS (ESI-TOF) calcd for $C_{23}H_{18}ClN_2O_3$ $[M + H]^+$: 405.1000; found: 405.1011.



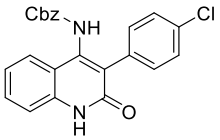
benzyl (3-(3-chlorophenyl)-2-oxo-1,2-dihydroquinolin-4-yl)carbamate (3f)

White solid, 36.8 mg, 91% yield; mp 194.6-196.2 ºC.

^{1}H NMR (DMSO-d_6, 300 MHz), δ 12.13 (s, 1H), 9.57 (s, 1H), 7.66 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.61 – 7.52 (m, 1H), 7.45 – 7.29 (m, 7H), 7.27 – 7.19 (m, 2H), 7.18 – 7.11 (m, 2H), 4.96 (s, 2H);

^{13}C NMR (DMSO-d_6, 75 MHz), δ 161.2, 153.7, 141.3, 138.1, 136.6, 136.2, 132.1, 131.0, 129.8, 129.4, 128.6, 128.3, 127.9, 127.5, 127.3, 124.5, 122.0, 118.1, 115.2, 65.8.

HRMS (ESI-TOF) calcd for $C_{23}H_{18}ClN_2O_3$ $[M + H]^+$: 405.1000; found: 405.1011.



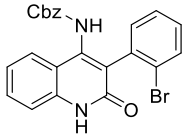
benzyl (3-(4-chlorophenyl)-2-oxo-1,2-dihydroquinolin-4-yl)carbamate (3g)

White solid, 36.8 mg, 91% yield; mp 204.1-205.9 ºC;

^{1}H NMR (DMSO-d_6, 300 MHz), δ 12.09 (s, 1H), 9.49 (s, 1H), 7.65 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.60 – 7.51 (m, 1H), 7.45 – 7.27 (m, 8H), 7.26 – 7.19 (m, 1H), 7.19 – 7.11 (m, 2H), 4.98 (s, 2H);

^{13}C NMR (DMSO-d_6, 75 MHz), δ 161.3, 153.7, 141.1, 138.0, 136.7, 132.9, 132.1, 131.9, 130.9, 128.8, 128.3, 127.9, 127.6, 124.4, 122.0, 118.2, 115.2, 65.8;

HRMS (ESI-TOF) calcd for $C_{23}H_{18}ClN_2O_3$ $[M + H]^+$: 405.1000; found: 405.1022.

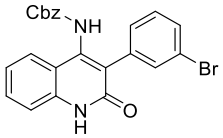


benzyl (3-(2-bromophenyl)-2-oxo-1,2-dihydroquinolin-4-yl)carbamate (3h)

White solid, 40.4 mg, 90% yield; mp 114.2-115.7 ºC;

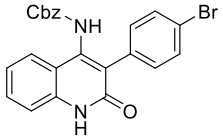
^{1}H NMR (DMSO-d_6, 300 MHz), δ 12.05 (s, 1H), 9.48 (s, 1H), 7.71 – 7.62 (m, 2H), 7.61 – 7.53 (m, 1H), 7.43 – 7.27 (m, 6H), 7.27 – 7.19 (m, 2H), 7.18 – 7.11 (m, 2H), 5.08 – 4.88 (m, 2H);

^{13}C NMR (DMSO-d_6, 75 MHz), δ 160.7, 153.8, 142.0, 138.4, 136.7, 135.4, 131.9, 132.0, 130.9, 130.0, 129.4, 128.3, 127.8, 127.4, 127.0, 124.6, 124.1, 121.9, 117.9, 115.3, 65.7;
HRMS (ESI-TOF) calcd for $C_{23}H_{18}BrN_2O_3$ $[M + H]^+$: 449.0495; found: 449.0502.



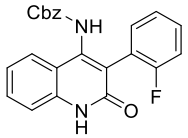
benzyl (3-(3-bromophenyl)-2-oxo-1,2-dihydroquinolin-4-yl)carbamate (3i)

White solid, 41.3 mg, 92% yield; mp 211.3-213.1 ºC;
^{1}H NMR (DMSO-d_6, 300 MHz), δ 12.11 (s, 1H), 9.54 (s, 1H), 7.66 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.61 – 7.52 (m, 2H), 7.51 – 7.47 (m, 1H), 7.42 – 7.27 (m, 6H), 7.26 – 7.20 (m, 1H), 7.20 – 7.12 (m, 2H), 4.97 (s, 2H);
^{13}C NMR (DMSO-d_6, 75 MHz), δ 161.2, 153.7, 141.3, 138.1, 136.6, 136.4, 132.6, 131.0, 130.2, 129.6, 129.0, 128.4, 127.9, 127.5, 124.5, 122.0, 120.7, 118.1, 115.2, 65.9;
HRMS (ESI-TOF) calcd for $C_{23}H_{18}BrN_2O_3$ $[M + H]^+$: 449.0495; found: 449.0501.



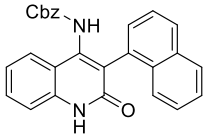
benzyl (3-(4-bromophenyl)-2-oxo-1,2-dihydroquinolin-4-yl)carbamate (3j)

White solid, 36.4 mg, 81% yield; mp 245.6-247.4 ºC (decomposition);
^{1}H NMR (DMSO-d_6, 300 MHz), δ 12.08 (s, 1H), 9.48 (s, 1H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.60 – 7.51 (m, 3H), 7.41 – 7.31 (m, 4H), 7.27 – 7.19 (m, 3H), 7.19 – 7.12 (m, 2H), 4.98 (s, 2H);
^{13}C NMR (DMSO-d_6, 75 MHz), δ 161.2, 153.7, 141.0, 138.0, 136.6, 133.3, 132.1, 130.8, 130.4, 128.8, 128.3, 127.8, 127.5, 124.4, 121.9, 120.7, 118.1, 115.2, 65.7;
HRMS (ESI-TOF) calcd for $C_{23}H_{18}BrN_2O_3$ $[M + H]^+$: 449.0495; found: 449.0501.



benzyl (3-(2-fluorophenyl)-2-oxo-1,2-dihydroquinolin-4-yl)carbamate (3k)

White solid, 31.8 mg, 82% yield; mp 212.8-214.6 ºC;
^{1}H NMR (DMSO-d_6, 300 MHz), δ 12.09 (s, 1H), 9.57 (s, 1H), 7.66 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.62 – 7.52 (m, 1H), 7.49 – 7.28 (m, 5H), 7.27 – 7.17 (m, 4H), 7.17 – 7.08 (m, 2H), 4.95 (s, 2H);
^{13}C NMR (DMSO-d_6, 75 MHz), *δ* (ppm): 160.0 (d, *J* = 245.1 Hz, 1C), 157.2 (d, *J* = 537.8 Hz, 1C), 142.5, 138.3, 136.6, 131.7 (d, *J* = 3.6 Hz, 1C), 131.0, 129.8 (d, *J* = 8.1 Hz, 1C), 128.3, 127.8, 127.5, 125.0, 124.5, 123.6, 122.1, 121.9, 117.7, 115.3 (d, *J* = 21.7 Hz, 1C), 115.2, 65.7;
HRMS (ESI-TOF) calcd for $C_{23}H_{18}FN_2O_3$ $[M + H]^+$: 389.1296; found: 389.1307.



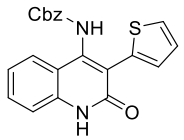
benzyl (3-(naphthalen-1-yl)-2-oxo-1,2-dihydroquinolin-4-yl)carbamate (3l)

White solid, 32.8 mg, 78% yield; mp 248.8-251.4 ºC;

^{1}H NMR (DMSO-d_6, 300 MHz), δ 12.11 (s, 1H), 9.29 (s, 1H), 8.03 – 7.90 (m, 2H), 7.69 – 7.42 (m, 6H), 7.42 – 7.35 (m, 1H), 7.34 – 7.19 (m, 5H), 7.08 – 6.92 (m, 2H), 4.87 (s, 2H);

^{13}C NMR (DMSO-d_6, 75 MHz), δ 161.7, 154.0, 142.6, 138.4, 136.6, 133.1, 132.1, 131.6, 130.7, 129.5, 128.2, 128.0, 127.9, 127.7, 127.6, 127.3, 125.8, 125.7, 125.6, 125.3, 124.7, 121.9, 118.2, 115.3, 65.5;

HRMS (ESI-TOF) calcd for $C_{27}H_{21}N_2O_3$ $[M + H]^+$: 421.1547; found: 421.1562.



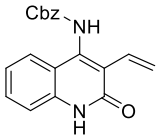
benzyl (2-oxo-3-(thiophen-2-yl)-1,2-dihydroquinolin-4-yl)carbamate (3m)

White solid, 20.7 mg, 55% yield; mp 237.4-239.2 ºC (decomposition);

^{1}H NMR (DMSO-d_6, 300 MHz), δ 12.21 (s, 1H), 9.71 (s, 1H), 7.75 – 7.60 (m, 3H), 7.60 – 7.49 (m, 1H), 7.49 – 7.14 (m, 7H), 7.11 (dd, *J* = 5.1, 3.7 Hz, 1H), 5.07 (s, 2H);

^{13}C NMR (DMSO-d_6, 75 MHz), δ 160.8, 153.9, 139.5, 137.1, 136.7, 133.8, 130.7, 129.2, 128.4, 128.0, 127.8, 127.7, 126.0, 124.5, 122.7, 122.2, 118.5, 115.1, 66.1;

HRMS (ESI-TOF) calcd for $C_{21}H_{17}N_2O_3S$ $[M + H]^+$: 377.0979; found: 377.0975.



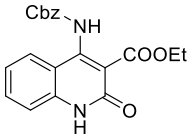
benzyl (2-oxo-3-vinyl-1,2-dihydroquinolin-4-yl)carbamate (3n)

White solid, 9.6 mg, 30% yield; mp 242.3-243.9 ºC (decomposition);

^{1}H NMR (DMSO-d_6, 300 MHz), δ 11.95 (s, 1H), 9.67 (s, 1H), 7.59 (d, *J* = 8.1 Hz, 1H), 7.53 - 7.31 (m, 7H), 7.21 - 7.16 (m, 1H), 6.74 - 6.64 (m, 1H), 6.59 - 6.53 (m, 1H), 5.51 - 5.46 (m, 1H), 5.14 (s, 2H);

^{13}C NMR (DMSO-d_6, 75 MHz), *δ* 161.4, 154.0, 140.7, 137.3, 136.6, 130.5, 128.9, 128.4, 128.0, 127.8, 124.3, 123.8, 121.8, 121.2, 117.9, 115.0, 66.2;

HRMS (ESI-TOF) calcd for $C_{19}H_{16}N_2NaO_3$ $[M + Na]^+$: 343.1053; found: 343.1057.



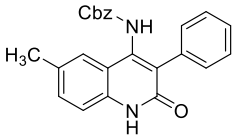
ethyl 4-(((benzyloxy)carbonyl)amino)-2-oxo-1,2-dihydroquinoline-3-carboxylate (3o)

White solid, 27.5 mg, 75% yield; mp 225.2-226.7 ºC (decomposition);

^{1}H NMR (DMSO-d_6, 300 MHz), δ 12.18 (s, 1H), 10.08 (s, 1H), 7.91 (d, *J* = 2.0 Hz, 1H), 7.76 - 7.73 (m, 1H), 7.58 - 7.27 (m, 6H), 7.23 (d, *J* = 7.4 Hz, 1H), 5.15 (s, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 1.19 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (DMSO-d_6, 75 MHz), δ 164.0, 159.5, 153.9, 142.5, 138.1, 136.6, 135.1, 128.9, 128.6, 128.5, 128.4, 127.4, 118.2, 117.8, 114.4, 67.1, 61.2, 14.3;

HRMS (ESI-TOF) calcd for $C_{20}H_{19}N_2O_5$ $[M + H]^+$: 367.1288; found: 367.1280.



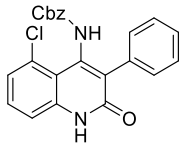
benzyl (6-methyl-2-oxo-3-phenyl-1,2-dihydroquinolin-4-yl)carbamate (3q)

White solid, 33.1 mg, 86% yield; mp 237.4-239.2 ºC (decomposition);

^{1}H NMR (DMSO-d_6, 300 MHz), δ 11.99 (s, 1H), 9.34 (s, 1H), 7.41 – 7.30 (m, 8H), 7.30 – 7.23 (m, 3H), 7.21 – 7.12 (m, 2H), 4.98 (s, 2H), 2.33 (s, 3H);

^{13}C NMR (DMSO-d_6, 75 MHz),δ 161.4, 154.0, 140.6, 136.8, 136.0, 134.1, 131.8, 130.8, 130.3, 130.0, 128.3, 127.8, 127.5, 127.4, 127.3, 123.8, 118.3, 115.1, 65.6, 20.7;

HRMS (ESI-TOF) calcd for $C_{24}H_{21}N_2O_3$ $[M + H]^+$: 385.1547; found: 385.1553.



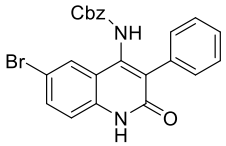
benzyl (5-chloro-2-oxo-3-phenyl-1,2-dihydroquinolin-4-yl)carbamate (3r)

White solid, 29.1 mg, 72% yield; mp 222.1-223.8 ºC (decomposition);

^{1}H NMR (DMSO-d_6, 300 MHz), δ 12.30 (s, 1H), 9.38 – 8.75 (m, 1H), 7.54 – 7.44 (m, 1H), 7.42 – 7.21 (m, 10H), 7.14 (d, *J* = 6.6 Hz, 2H), 5.00 (s, 2H);

^{13}C NMR (DMSO-d_6, 75 MHz), δ 160.8, 154.0, 140.4, 139.6, 137.0, 136.8, 133.7, 130.5, 130.1, 129.8, 128.2, 127.7, 127.5, 127.4, 125.6, 115.4, 115.2, 65.5;

HRMS (ESI-TOF) calcd for $C_{23}H_{18}ClN_2O_3$ $[M + H]^+$: 405.1000; found: 405.1019.



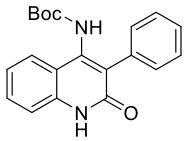
benzyl (6-bromo-2-oxo-3-phenyl-1,2-dihydroquinolin-4-yl)carbamate (3s)

White solid, 35.9 mg, 80% yield; mp 239.2-240.9 ºC (decomposition);

^{1}H NMR (DMSO-d_6, 300 MHz), δ 12.19 (s, 1H), 9.44 (s, 1H), 7.81 – 7.63 (m, 2H), 7.49 – 7.24 (m, 9H), 7.24 – 7.07 (m, 2H), 4.98 (s, 2H);

^{13}C NMR (DMSO-d_6, 75 MHz), δ 161.3, 153.9, 139.7, 137.0, 136.7, 133.6, 133.2, 131.3, 129.9, 128.4, 127.9, 127.6, 127.5, 127.5, 126.4, 120.1, 117.4, 113.8, 65.8;

HRMS (ESI-TOF) calcd for $C_{23}H_{18}BrN_2O_3$ $[M + H]^+$: 449.0495; found: 449.0501.



***tert*-butyl (2-oxo-3-phenyl-1,2-dihydroquinolin-4-yl)carbamate (3t)**

White solid, 20.9 mg, 62% yield; mp 275.4-277.2 ºC (decomposition);

^{1}H NMR (DMSO-d_6, 300 MHz), δ 12.00 (s, 1H), 8.95 (s, 1H), 7.63 (d, *J* = 8.1 Hz, 1H), 7.57 – 7.49 (m, 1H), 7.42 – 7.28 (m, 6H), 7.26 – 7.18 (m, 1H), 1.23 (s, 9H);

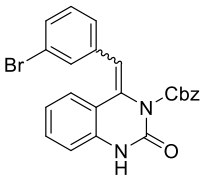
^{13}C NMR (DMSO-d$_6$, 75 MHz), δ 161.6, 152.9, 141.2, 137.9, 134.3, 130.4, 130.0, 127.3, 127.1, 124.4, 121.7, 118.5, 115.0, 78.9, 27.8;

HRMS (ESI-TOF) calcd for $C_{20}H_{21}N_2O_3$ $[M + H]^+$: 337.1547; found: 337.1553.

4. General experimental procedure for synthesis of compounds 4.

To a reaction tube were added 3-bromooxindole **1** (0.1 mmol), *N*-benzylcarbonyl-*O*-tosylhydroxylamine **2a** (0.15 mmol) and K_2CO_3 (0.2 mmol, 2.0 equiv), followed by addition CH_3CN (2.0 mL). Then the mixture was stirred for 16 h at room temperature. After completion, the

resulting mixture was concentrated and the residue was purified by flash chromatography (petroleum ether/ethyl acetate = 4:1 ~ 1:1) to give the corresponding product **4**.



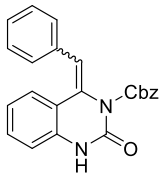
benzyl 4-(3-bromobenzylidene)-2-oxo-1,4-dihydroquinazoline-3(2*H*)-carboxylate (4a)

White solid, 44.0 mg, 98% yield; mp 200.7-202.4 ºC;

^{1}H NMR (DMSO-d_6, 300 MHz), δ 10.75 (s, 1H), 7.77 – 7.62 (m, 2H), 7.57 – 7.41 (m, 2H), 7.39 – 7.18 (m, 5H), 7.21 – 7.05 (m, 3H), 7.00 (d, *J* = 7.8 Hz, 1H), 6.89 (s, 1H), 4.87 (s, 2H);

^{13}C NMR (DMSO-d_6, 75 MHz), δ 149.8, 148.5, 137.5, 135.2, 135.1, 130.7, 130.5, 130.4, 130.1, 129.7, 128.2, 128.0, 127.6, 126.4, 123.6, 123.2, 122.6, 121.8, 121.4, 115.1, 67.8;

HRMS (ESI-TOF) calcd for $C_{23}H_{17}BrN_2NaO_3$ $[M + Na]^+$: 471.0315; found: 471.0318.



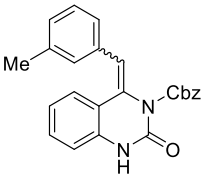
benzyl 4-benzylidene-2-oxo-1,4-dihydroquinazoline-3(2*H*)-carboxylate (4b)

White solid, 36.7 mg, 99% yield; mp 190.2-191.7 ºC;

^{1}H NMR (DMSO-d_6, 300 MHz), δ 10.71 (s, 1H), 7.70 (d, *J* = 7.7 Hz, 1H), 7.50 (d, *J* = 7.5 Hz, 2H), 7.39 – 7.24 (m, 7H), 7.15 – 7.03 (m, 3H), 6.99 (d, *J* = 7.9 Hz, 1H), 6.88 (s, 1H), 4.84 (s, 2H);

^{13}C NMR (DMSO-d_6, 75 MHz), δ 149.9, 148.8, 135.3, 135.1, 135.0, 129.4, 128.8, 128.7, 128.5, 128.2, 128.0, 127.9, 127.7, 127.5, 123.5, 123.3, 123.2, 115.0, 67.6;

HRMS (ESI-TOF) calcd for $C_{23}H_{18}N_2NaO_3$ $[M + Na]^+$: 393.1210; found: 393.1209.



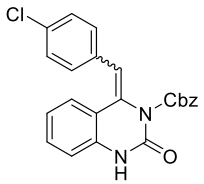
benzyl 4-(3-methylbenzylidene)-2-oxo-1,4-dihydroquinazoline-3(2*H*)-carboxylate (4c)

White solid, 38.0 mg, 99% yield; mp 173.1-174.8 ºC;

^{1}H NMR (DMSO-d_6, 300 MHz), δ 10.68 (s, 1H), 7.68 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.37 – 7.19 (m, 7H), 7.15 – 7.03 (m, 4H), 6.99 (dd, *J* = 8.0, 1.1 Hz, 1H), 6.82 (s, 1H), 4.83 (s, 2H), 2.26 (s, 3H);

^{13}C NMR (DMSO-d_6, 75 MHz), δ 149.9, 148.8, 137.5, 135.3, 135.1, 134.9, 129.3, 128.9, 128.7, 128.6, 128.3, 128.2, 127.9, 127.5, 124.9, 123.4, 123.2, 123.1, 115.0, 67.6, 21.0.;

HRMS (ESI-TOF) calcd for $C_{24}H_{20}N_2NaO_3$ $[M + Na]^+$: 407.1366; found: 407.1367.



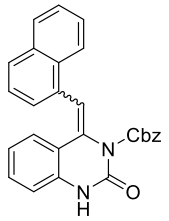
benzyl 4-(4-chlorobenzylidene)-2-oxo-1,4-dihydroquinazoline-3(2*H*)-carboxylate (4d)

White solid, 39.3 mg, 97% yield; mp 197.6-199.3 ºC;

^{1}H NMR (DMSO-d_6, 300 MHz), δ 10.74 (s, 1H), 7.70 (d, *J* = 7.7 Hz, 1H), 7.47 (d, *J* = 8.3 Hz, 2H), 7.41 – 7.31 (m, 3H), 7.31 – 7.24 (m, 3H), 7.17 – 7.04 (m, 3H), 6.99 (d, *J* = 7.9 Hz, 1H), 6.89 (s, 1H), 4.90 (s, 2H);

^{13}C NMR (DMSO-d_6, 75 MHz), δ 149.8, 148.7, 135.3, 135.1, 134.0, 132.2, 129.6, 129.4, 128.5, 128.2, 128.0, 127.9, 127.6, 123.5, 123.2, 122.9, 122.1, 115.1, 67.7;

HRMS (ESI-TOF) calcd for $C_{23}H_{17}ClN_2NaO_3$ $[M + Na]^+$: 427.0820; found: 427.0823.



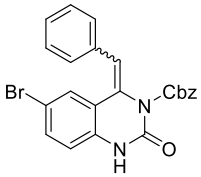
benzyl 4-(naphthalen-1-ylmethylene)-2-oxo-1,4-dihydroquinazoline-3(2*H*)-carboxylate (4e)

White solid, 38.7 mg, 92% yield; mp 180.8-182.6 ºC (decomposition);

^{1}H NMR (DMSO-d_6, 300 MHz), δ 10.66 (s, 1H), 8.29 – 8.12 (m, 1H), 8.06 – 7.93 (m, 2H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.68 – 7.42 (m, 4H), 7.43 – 7.27 (m, 2H), 7.25 – 7.08 (m, 4H), 7.04 (d, *J* = 7.9 Hz, 1H), 6.85 – 6.65 (m, 2H), 4.28 (s, 2H);

^{13}C NMR (DMSO-d_6, 75 MHz), δ 149.9, 148.7, 135.2, 134.7, 133.3, 131.7, 131.5, 131.1, 129.7, 128.4, 128.0, 127.9, 127.8, 127.4, 126.2, 126.1, 125.3, 125.0, 124.8, 124.0, 123.1, 121.7, 117.9, 114.8, 67.4;

HRMS (ESI-TOF) calcd for $C_{27}H_{20}N_2NaO_3$ $[M + Na]^+$: 443.1366; found: 443.1376.



benzyl 4-benzylidene-6-bromo-2-oxo-1,4-dihydroquinazoline-3(2*H*)-carboxylate (4f)

White solid, 43.6 mg, 97% yield; mp 220.1-221.9 ºC;

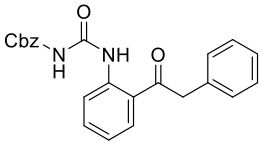
^{1}H NMR (DMSO-d_6, 300 MHz), δ 10.81 (s, 1H), 7.94 (s, 1H), 7.50 (d, *J* = 6.7 Hz, 3H), 7.44 – 7.16 (m, 6H), 7.18 – 6.98 (m, 3H), 6.93 (d, *J* = 8.5 Hz, 1H), 4.84 (s, 2H);

^{13}C NMR (DMSO-d_6, 75 MHz), δ 149.8, 148.6, 135.2, 134.8, 134.5, 131.9, 128.5, 128.2, 128.1, 128.1, 127.9, 127.5, 127.3, 125.9, 125.2, 124.7, 117.0, 114.9, 67.7;

HRMS (ESI-TOF) calcd for $C_{23}H_{17}BrN_2NaO_3$ $[M + Na]^+$: 471.0315; found: 471.0314.

5. General experimental procedure for synthesis of compounds 5.

To a reaction tube were added 3-bromooxindole **1** (0.1 mmol), *N*-benzylcarbonyl-*O*-tosylhydroxylamine **2a** (0.15 mmol) and K_2CO_3 (0.2 mmol, 2.0 equiv), followed by addition CH_3CN (2.0 mL). Then the mixture was stirred for 16 h at room temperature. And then, TsOH (2.5 equiv) was added into the reaction the mixture and it was stirred at room temperature for another 8 h. The resulting mixture was concentrated and the residue was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1 ~ 4:1) to give the corresponding product **5**.



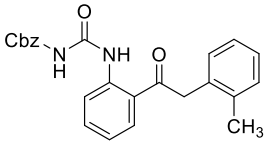
1-benzyloxycarbonyl-3-(2-(2-phenylacetyl)phenyl)urea (5a)

White solid, 35.7 mg, 92% yield; mp 153.1-154.6 ºC;

^{1}H NMR (DMSO-d_6, 300 MHz), δ 11.88 (s, 1H), 10.53 (s, 1H), 8.35 (dd, *J* = 8.5, 1.2 Hz, 1H), 8.19 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.64 – 7.52 (m, 1H), 7.43 – 7.19 (m, 11H), 5.20 (s, 2H), 4.42 (s, 2H);

^{13}C NMR (DMSO-d_6, 75 MHz), δ 200.6, 153.4, 150.9, 138.6, 135.7, 135.1, 133.7, 131.1, 129.8, 128.5, 128.3, 128.2, 128.0, 126.6, 124.4, 122.8, 121.8, 66.7, 46.2;

HRMS (ESI-TOF) calcd for $C_{23}H_{20}N_2NaO_4$ $[M + Na]^+$: 411.1315; found: 411.1325.



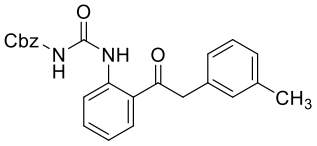
1-benzyloxycarbonyl-3-(2-(2-(o-tolyl)acetyl)phenyl)urea (5b)

White solid, 38.6 mg, 96% yield; mp 176.6-178.2 ºC;

^{1}H NMR (DMSO-d_6, 300 MHz), δ 11.81 (s, 1H), 10.54 (s, 1H), 8.44 – 8.32 (m, 1H), 8.22 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.71 – 7.54 (m, 1H), 7.43 – 7.31 (m, 5H), 7.28 – 7.20 (m, 1H), 7.20 – 7.11 (m, 4H), 5.17 (s, 2H), 4.47 (s, 2H), 2.15 (s, 3H);

^{13}C NMR (DMSO-d_6, 75 MHz), δ 200.5, 153.5, 150.9, 138.3, 137.0, 135.7, 134.1, 133.6, 130.8, 130.8, 129.9, 128.5, 128.2, 128.1, 126.9, 125.8, 124.9, 122.8, 121.9, 66.7, 44.7, 19.2;

HRMS (ESI-TOF) calcd for $C_{24}H_{22}N_2NaO_4$ $[M + Na]^+$: 425.1472; found: 425.1484.



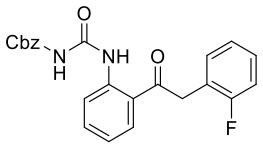
1-benzyloxycarbonyl-3-(2-(2-(*m*-tolyl)acetyl)phenyl)urea (5c)

White solid, 39.8 mg, 99% yield; mp 152.7-154.1 ºC.

^{1}H NMR (DMSO-d_6, 300 MHz), δ 11.88 (s, 1H), 10.54 (s, 1H), 8.35 (dd, *J* = 8.5, 1.2 Hz, 1H), 8.17 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.67 – 7.49 (m, 1H), 7.47 – 7.31 (m, 5H), 7.27 – 7.14 (m, 2H), 7.05 (d, *J* = 7.9 Hz, 3H), 5.20 (s, 2H), 4.37 (s, 2H), 2.27 (s, 3H);

^{13}C NMR (DMSO-d_6, 75 MHz), δ 200.6, 153.5, 150.9, 138.6, 137.4, 135.7, 135.0, 133.7, 131.1, 130.3, 128.5, 128.3, 128.2, 128.0, 127.2, 126.9, 124.4, 122.8, 121.8, 66.7, 46.2, 21.0;

HRMS (ESI-TOF) calcd for $C_{24}H_{22}N_2NaO_4$ $[M + Na]^+$: 425.1472; found: 425.1489.

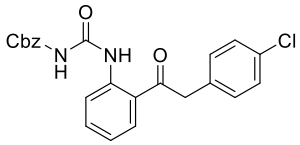


1-benzyloxycarbonyl-3-(2-(2-(2-fluorophenyl)acetyl)phenyl)urea (5d)

White solid, 39.4 mg, 97% yield; mp 167.6-179.2 ºC;

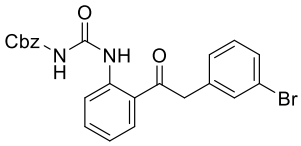
^{1}H NMR (DMSO-d_6, 300 MHz), δ 11.84 (s, 1H), 10.53 (s, 1H), 8.38 (dd, *J* = 8.6, 1.2 Hz, 1H), 8.23 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.68 – 7.55 (m, 1H), 7.49 – 7.28 (m, 7H), 7.30 – 7.09 (m, 3H), 5.18 (s, 2H), 4.52 (s, 2H);

^{13}C NMR (DMSO-d_6, 75 MHz), δ 199.0, 160.9 (d, *J* = 242.7 Hz, 1C), 152.1 (d, *J* = 191.3 Hz, 1C), 138.5, 135.7, 133.9, 132.5 (d, *J* = 4.6 Hz, 1C), 131.0, 129.0 (d, *J* = 8.0 Hz, 1C), 128.5, 128.2, 128.0, 124.3 (d, *J* = 3.3 Hz, 1C), 124.0, 122.8, 122.6, 122.4, 121.8, 115.0 (d, *J* = 21.3 Hz, 1C), 66.7, 40.3;
HRMS (ESI-TOF) calcd for $C_{23}H_{19}FN_2NaO_4$ $[M + Na]^+$: 429.1221; found: 429.1234.



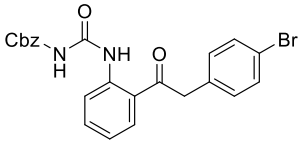
1-benzyloxycarbonyl-3-(2-(2-(4-chlorophenyl)acetyl)phenyl)urea (5e)

White solid, 39.7 mg, 94% yield; mp 178.2-179.8 ºC;
^{1}H NMR (DMSO-d_6, 300 MHz), δ 11.84 (s, 1H), 10.51 (s, 1H), 8.34 (dd, *J* = 8.5, 1.2 Hz, 1H), 8.18 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.66 – 7.53 (m, 1H), 7.45 – 7.33 (m, 7H), 7.32 – 7.26 (m, 2H), 7.26 – 7.18 (m, 1H), 5.19 (s, 2H), 4.46 (s, 2H);
^{13}C NMR (DMSO-d_6, 75 MHz), δ 200.1, 153.4, 150.9, 138.5, 135.7, 134.2, 133.8, 131.9, 131.3, 131.0, 128.5, 128.3, 128.2, 128.0, 124.3, 122.8, 121.8, 66.7, 45.4;
HRMS (ESI-TOF) calcd for $C_{23}H_{20}ClN_2O_4$ $[M + H]^+$: 423.1106; found: 423.1119.



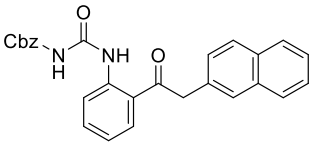
1-benzyloxycarbonyl-3-(2-(2-(3-bromophenyl)acetyl)phenyl)urea (5f)

White solid, 44.4 mg, 95% yield; mp 168.2-169.9 ºC;
^{1}H NMR (DMSO-d_6, 300 MHz), δ 11.84 (s, 1H), 10.54 (s, 1H), 8.36 (d, *J* = 8.4 Hz, 1H), 8.18 (d, *J* = 7.9 Hz, 1H), 7.67 – 7.55 (m, 1H), 7.54 – 7.44 (m, 2H), 7.44 – 7.33 (m, 5H), 7.31 – 7.19 (m, 3H), 5.19 (s, 2H), 4.48 (s, 2H);
^{13}C NMR (DMSO-d_6, 75 MHz), δ 199.9, 153.4, 150.8, 138.5, 137.9, 135.7, 133.8, 132.8, 131.0, 130.3, 129.4, 129.2, 128.5, 128.2, 128.0, 124.4, 122.8, 121.8, 121.4, 66.7, 45.5;
HRMS (ESI-TOF) calcd for $C_{23}H_{20}BrN_2O_4$ $[M + H]^+$: 467.0601; found: 467.0624.



1-benzyloxycarbonyl-3-(2-(2-(4-bromophenyl)acetyl)phenyl)urea (5g)

White solid, 45.3 mg, 97% yield; mp 181.3-183.2 ºC;
^{1}H NMR (DMSO-d_6, 300 MHz), δ 11.84 (s, 1H), 10.51 (s, 1H), 8.35 (dd, *J* = 8.5, 1.2 Hz, 1H), 8.17 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.64 – 7.56 (m, 1H), 7.56 – 7.47 (m, 2H), 7.43 – 7.34 (m, 5H), 7.29 – 7.18 (m, 3H), 5.19 (s, 2H), 4.44 (s, 2H);
^{13}C NMR (DMSO-d_6, 75 MHz), δ 200.0, 153.4, 150.8, 138.5, 135.7, 134.6, 133.7, 132.3, 131.1, 131.0, 128.5, 128.2, 128.0, 124.3, 122.8, 121.8, 119.8, 66.7, 45.4;
HRMS (ESI-TOF) calcd for $C_{23}H_{20}BrN_2O_4$ $[M + H]^+$: 467.0601; found: 467.0613.



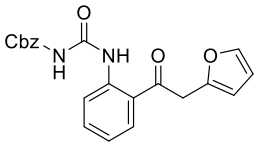
1-benzyloxycarbonyl-3-(2-(2-(naphthalen-2-yl)acetyl)phenyl)urea (5h)

White solid, 41.2 mg, 94% yield; mp 182.9-184.4 ºC;

^{1}H NMR (DMSO-d_6, 300 MHz), δ 11.80 (s, 1H), 10.50 (s, 1H), 8.44 – 8.32 (m, 2H), 7.94 (dd, *J* = 7.7, 1.9 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 2H), 7.67 – 7.58 (m, 1H), 7.56 – 7.41 (m, 4H), 7.35 (d, *J* = 2.8 Hz, 5H), 7.30 – 7.22 (m, 1H), 5.10 (s, 2H), 4.95 (s, 2H);

^{13}C NMR (DMSO-d_6, 75 MHz), δ 200.7, 153.4, 150.8, 138.5, 135.7, 133.7, 133.4, 132.3, 132.1, 131.1, 128.5, 128.4, 128.2, 128.0, 127.4, 126.1, 125.7, 125.6, 124.6, 124.4, 122.8, 121.9, 66.7, 44.1;

HRMS (ESI-TOF) calcd for $C_{27}H_{23}N_2O_4$ $[M + H]^+$: 439.1652; found: 439.1671.



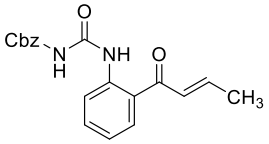
1-benzyloxycarbonyl-3-(2-(2-(furan-2-yl)acetyl)phenyl)urea (5i)

White solid, 21.6 mg, 57% yield; mp 151.7-153.6 ºC;

^{1}H NMR (DMSO-d_6, 300 MHz), δ 11.89 (s, 1H), 10.56 (s, 1H), 8.37 (dd, *J* = 8.5, 1.2 Hz, 1H), 8.15 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.69 – 7.52 (m, 2H), 7.52 – 7.31 (m, 5H), 7.29 – 7.15 (m, 1H), 6.42 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.35 – 6.20 (m, 1H), 5.22 (s, 2H), 4.50 (s, 2H);

^{13}C NMR (DMSO-d_6, 75 MHz), δ 198.2, 153.5, 150.9, 148.9, 142.4, 138.7, 135.7, 134.0, 131.3, 128.5, 128.2, 128.1, 123.8, 122.7, 121.8, 110.7, 108.5, 66.7, 39.5;

HRMS (ESI-TOF) calcd for $C_{21}H_{19}N_2O_5$ $[M + H]^+$: 379.1288; found: 379.1293.



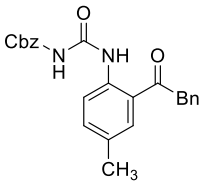
1-benzyloxycarbonyl-3-(2-(but-2-enoyl)phenyl)urea (5j)

White solid, 12.5 mg, 37% yield; mp 158.2-159.5 ºC;

^{1}H NMR (DMSO-d_6, 300 MHz), δ 11.56 (s, 1H), 10.54 (s, 1H), 8.27 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.86 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.61 – 7.52 (m, 1H), 7.48 – 7.32 (m, 5H), 7.25 – 7.16 (m, 1H), 7.01 – 6.84 (m, 2H), 5.22 (s, 2H), 2.08 – 1.85 (m, 3H);

^{13}C NMR (DMSO-d_6, 75 MHz), δ 192.1, 153.6, 150.8, 146.2, 138.0, 135.7, 132.9, 130.2, 129.1, 128.5, 128.2, 128.0, 126.4, 122.9, 122.1, 66.7, 18.3;

HRMS (ESI-TOF) calcd for $C_{19}H_{19}N_2O_4$ $[M + H]^+$: 339.1339; found: 339.1343.



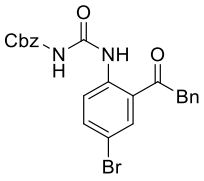
1-benzyloxycarbonyl-3-(4-methyl-2-(2-phenylacetyl)phenyl)urea (5k)

White solid, 39.0 mg, 97% yield; mp 168.4-171.0 ºC;

^{1}H NMR (DMSO-d_6, 300 MHz), δ 11.76 (s, 1H), 10.48 (s, 1H), 8.23 (d, *J* = 8.5 Hz, 1H), 8.01 (d, *J* = 2.1 Hz, 1H), 7.44 – 7.21 (m, 11H), 5.19 (s, 2H), 4.42 (s, 2H), 2.35 (s, 3H);

^{13}C NMR (DMSO-d_6, 75 MHz), δ 200.5, 153.4, 150.8, 136.0, 135.7, 135.1, 134.2, 131.9, 131.1, 129.8, 128.4, 128.3, 128.2, 128.0, 126.5, 124.5, 121.8, 66.6, 46.1, 20.2;

HRMS (ESI-TOF) calcd for $C_{24}H_{23}N_2O_4$ $[M + H]^+$: 403.1652; found: 403.1659.



1-benzyloxycarbonyl-3-(4-bromo-2-(2-phenylacetyl)phenyl)urea (5l)

White solid, 44.9 mg, 96% yield; mp 173.1-174.6 ºC;

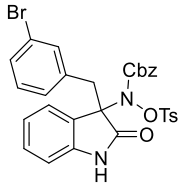
^{1}H NMR (DMSO-d_6, 300 MHz), δ 11.80 (s, 1H), 10.61 (s, 1H), 8.36 – 8.24 (m, 2H), 7.76 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.45 – 7.28 (m, 7H), 7.29 – 7.17 (m, 3H), 5.19 (s, 2H), 4.47 (s, 2H);

^{13}C NMR (DMSO-d_6, 75 MHz), δ 199.6, 153.5, 150.8, 137.6, 136.1, 135.6, 134.8, 133.0, 129.9, 128.5, 128.3, 128.2, 128.0, 126.6, 126.4, 123.9, 114.5, 66.8, 46.3;

HRMS (ESI-TOF) calcd for $C_{23}H_{20}BrN_2O_4$ $[M + H]^+$: 467.0601; found: 467.0620.

6. General experimental procedures for synthesis of compounds 6.

To a reaction tube were added 3-bromooxindole **1i** (0.1 mmol), *N*-benzylcarbonyl-*O*-tosylhydroxylamine **2a** (0.15 mmol) and K_2CO_3 (0.1 mmol, 1.0 equiv), followed by addition CH_2Cl_2 (2.0 mL). Then the mixture was stirred for 12 h at room temperature. The resulting mixture was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1) to give the corresponding product **6**.



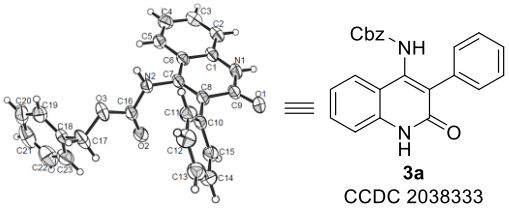
benzyl (3-(3-bromobenzyl)-2-oxoindolin-3-yl)(tosyloxy)carbamate (6)

^{1}H NMR (DMSO-d_6, 300 MHz), δ 10.25 (s, 1H), 7.97 – 7.81 (m, 2H), 7.43 (d, *J* = 8.0 Hz, 3H), 7.34 – 7.23 (m, 4H), 7.23 – 7.11 (m, 1H), 7.11 – 6.91 (m, 4H), 6.82 – 6.74 (m, 1H), 6.71 – 6.60 (m, 1H), 6.47 (d, *J* = 7.8 Hz, 1H), 4.83 - 4.76 (s, 2H), 3.40 (s, 1H), 3.15 (s, 1H), 2.40 (s, 3H).

^{13}C NMR (DMSO-d_6, 75 MHz), δ 172.9, 155.6, 146.7, 135.2, 134.3, 132.8, 130.1, 129.9, 129.5, 129.3, 129.2, 128.2, 128.1, 127.5, 123.6, 121.9, 120.6, 109.6, 72.5, 68.5, 59.7, 21.3.

HRMS (ESI-TOF) calcd for $C_{30}H_{26}BrN_2O_6S$ $[M + H]^+$: 621.0689; found: 621.0712.

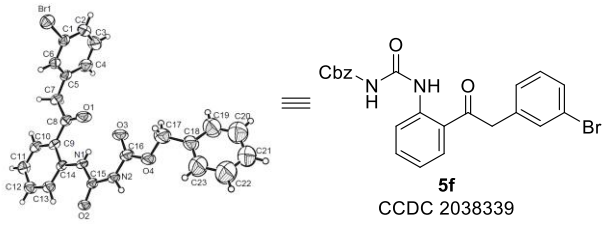
7. X-ray crystal structure of compounds 3a and 5f



Crystal data and structure refinement for 3a

Identification code	**3a**
Empirical formula	$C_{23}H_{18}N_2O_3$
Formula weight	370.39
Temperature/K	290(2)

Crystal system	monoclinic
Space group	C2/c
a/Å	22.8325(5)
b/Å	9.9872(3)
c/Å	16.8182(4)
α/°	90.00
β/°	100.658(2)
γ/°	90.00
Volume/Å^3	3768.94(17)
Z	8
ρ_{calc}mg/mm^3	1.306
m/mm^{-1}	0.708
F(000)	1552.0
Crystal size/mm^3	0.35 × 0.32 × 0.24
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection	7.88 to 130.16 °
Index ranges	-26 ≤ h ≤ 26, -7 ≤ k ≤ 11, -12 ≤ l ≤ 19
Reflections collected	7695
Independent reflections	3190[R(int) = 0.0199]
Data/restraints/parameters	3190/3/254
Goodness-of-fit on F^2	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0473, wR_2 = 0.1365
Final R indexes [all data]	R_1 = 0.0567, wR_2 = 0.1478
Largest diff. peak/hole / e Å^{-3}	0.52/-0.26



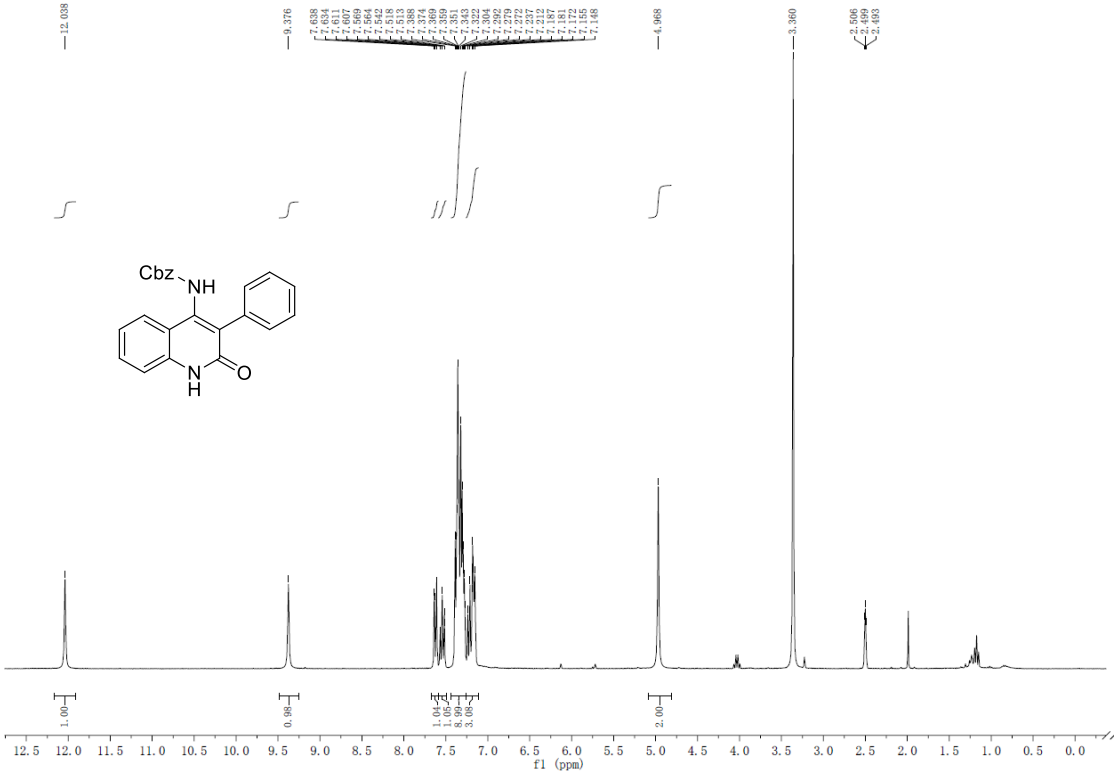
Crystal data and structure refinement for 5f

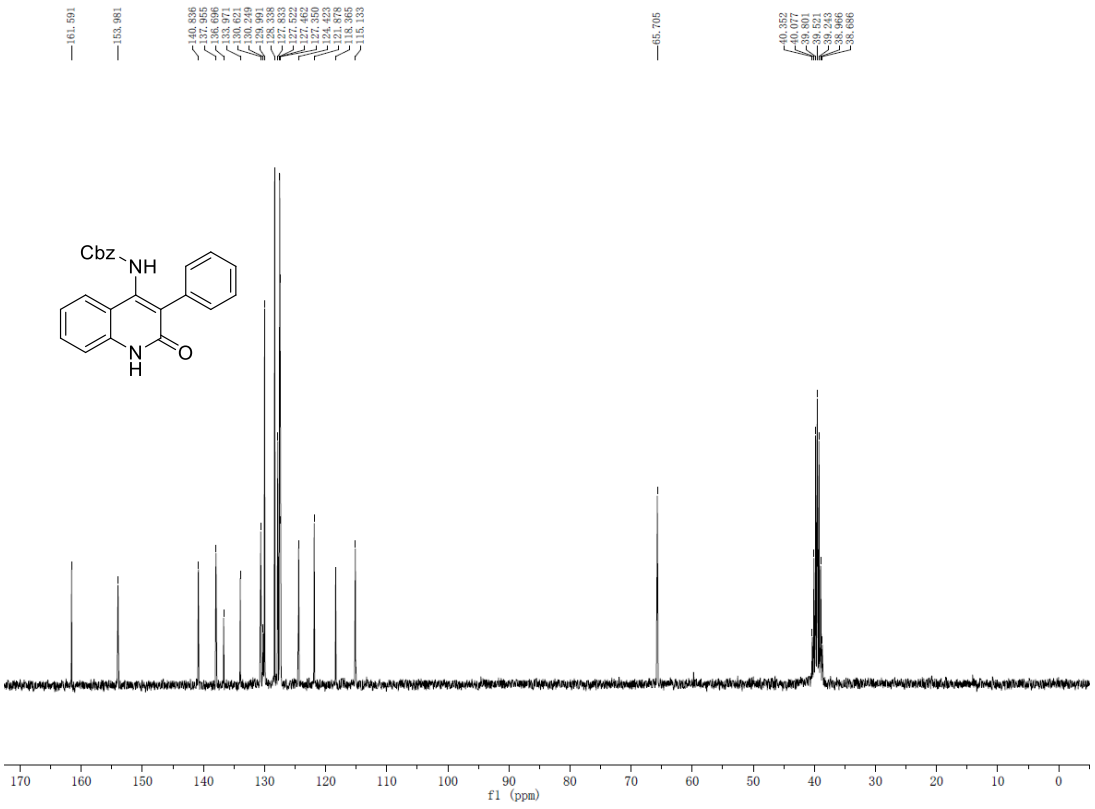
Identification code	**5f**
Empirical formula	$C_{23}H_{19}BrN_2O_4$
Formula weight	467.31
Temperature/K	289(2)
Crystal system	triclinic
Space group	P-1
a/Å	5.1989(2)
b/Å	14.7652(12)
c/Å	16.2473(10)
α/°	111.325(7)

β/°	91.273(4)
γ/°	91.541(4)
Volume/Å^3	1160.69(14)
Z	2
ρ_{calc}g/cm^3	1.337
μ/mm^{-1}	1.800
F(000)	476.0
Crystal size/mm^3	0.35 × 0.31 × 0.28
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.032 to 58.322
Index ranges	-6 ≤ h ≤ 7, -18 ≤ k ≤ 18, -21 ≤ l ≤ 20
Reflections collected	10518
Independent reflections	5265 [R_{int} = 0.0290, R_{sigma} = 0.0554]
Data/restraints/parameters	5265/52/279
Goodness-of-fit on F^2	1.073
Final R indexes [I>=2σ (I)]	R_1 = 0.0762, wR_2 = 0.1940
Final R indexes [all data]	R_1 = 0.1208, wR_2 = 0.2120
Largest diff. peak/hole / e Å^{-3}	0.72/-0.46

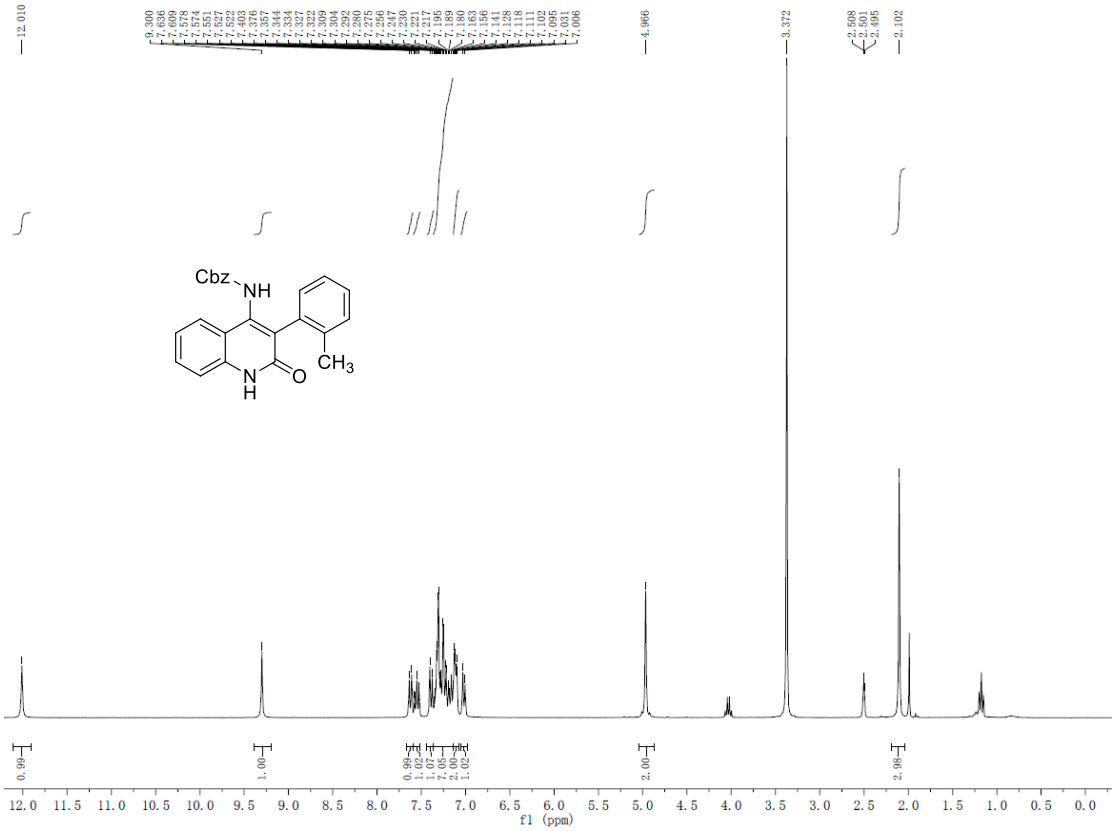
8. ^{1}H NMR, ^{13}C NMR and HPLC spectra of compounds 3,4,5,6

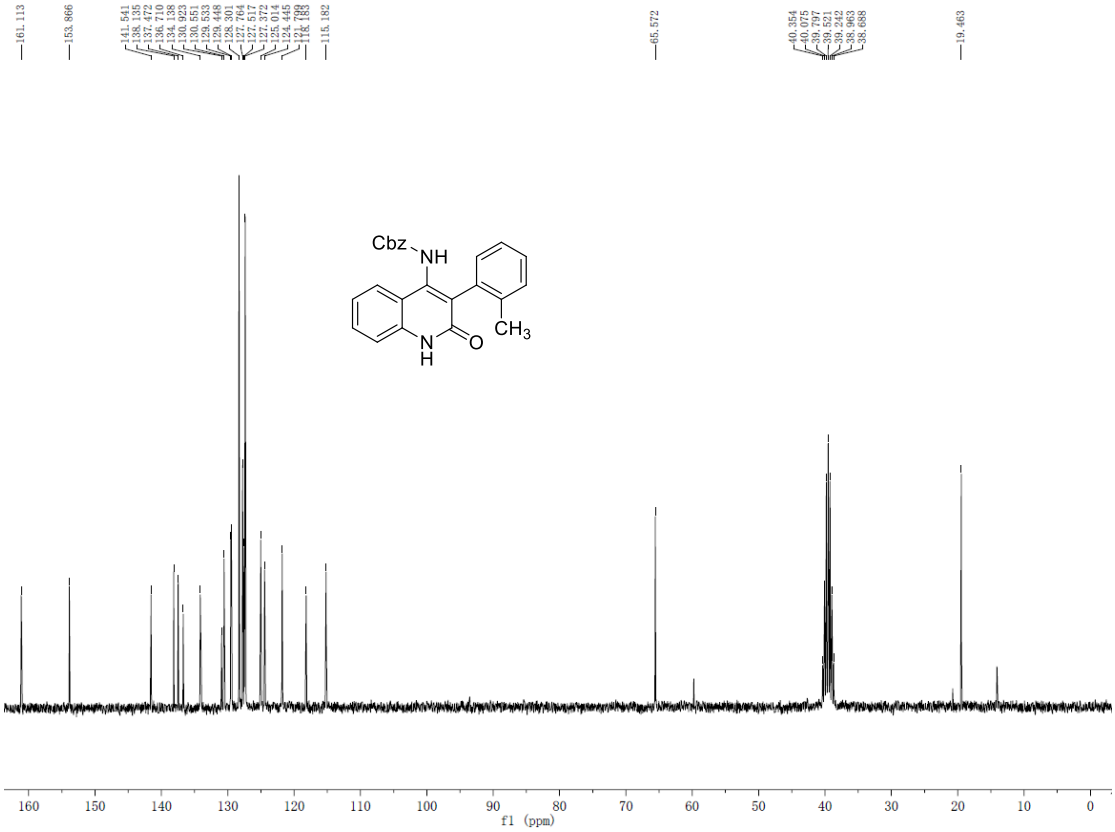
^{1}H NMR and ^{13}C NMR of **3a**



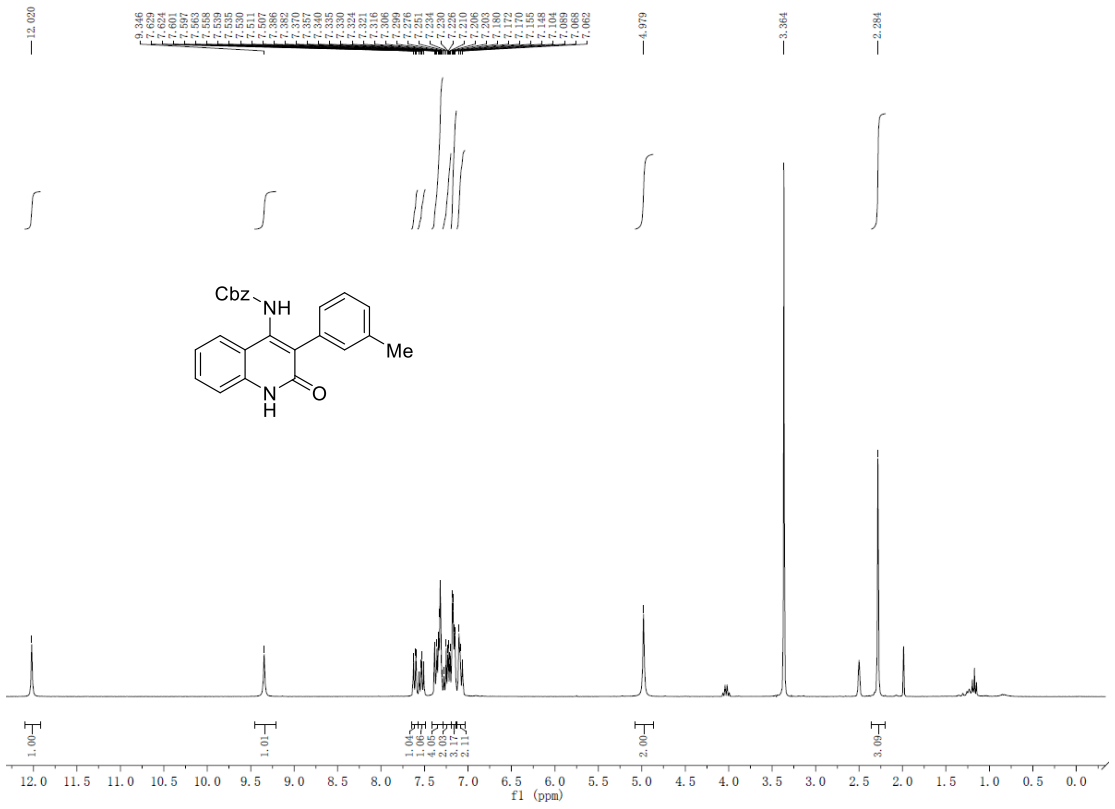


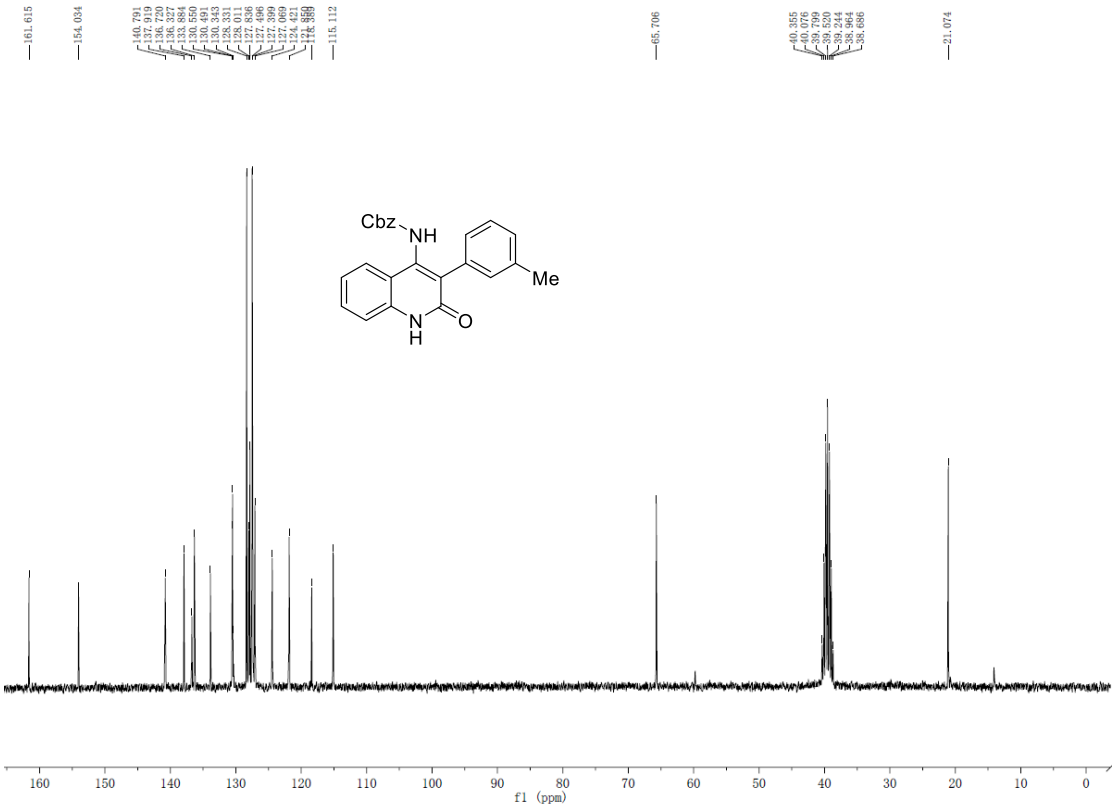
^{1}H NMR and ^{13}C NMR of **3b**



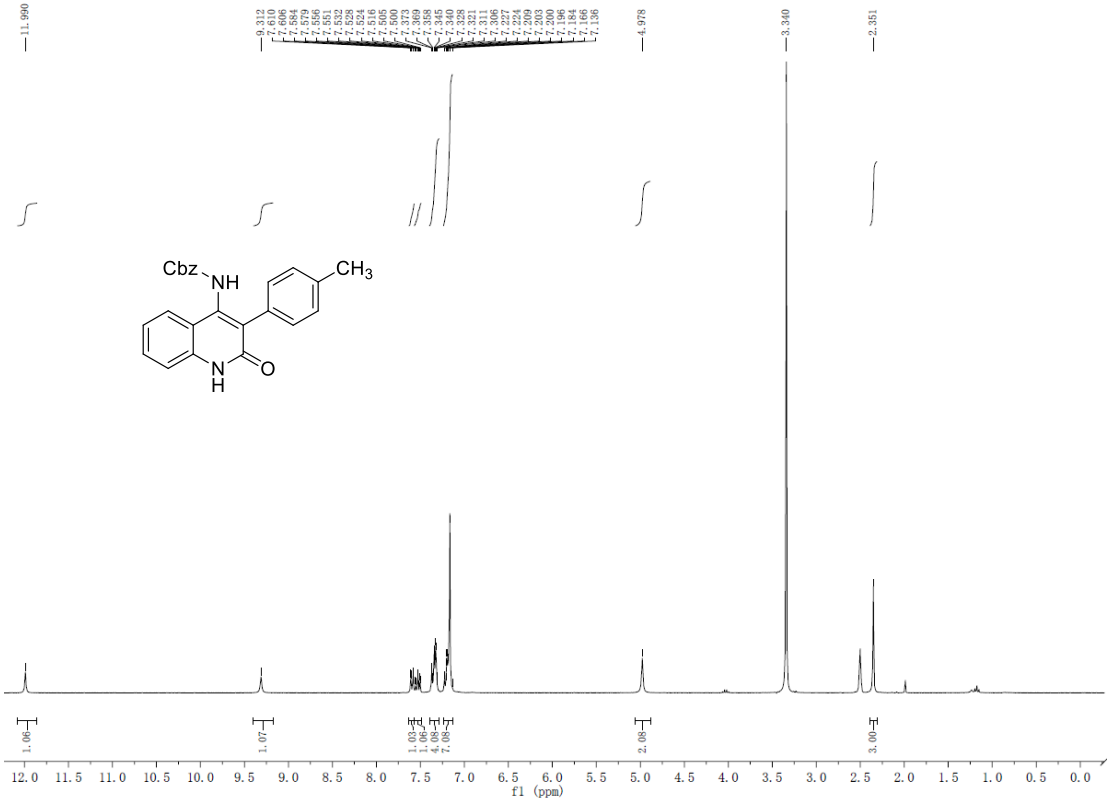


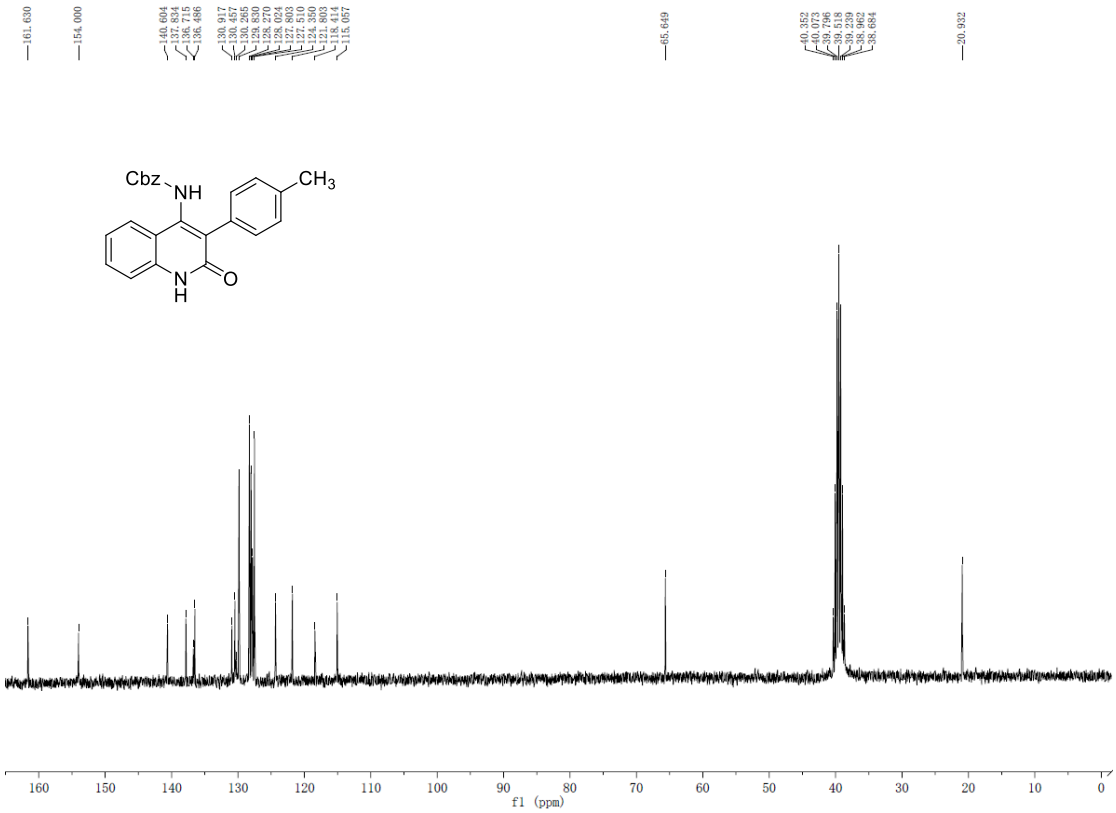
^{1}H NMR and ^{13}C NMR of **3c**



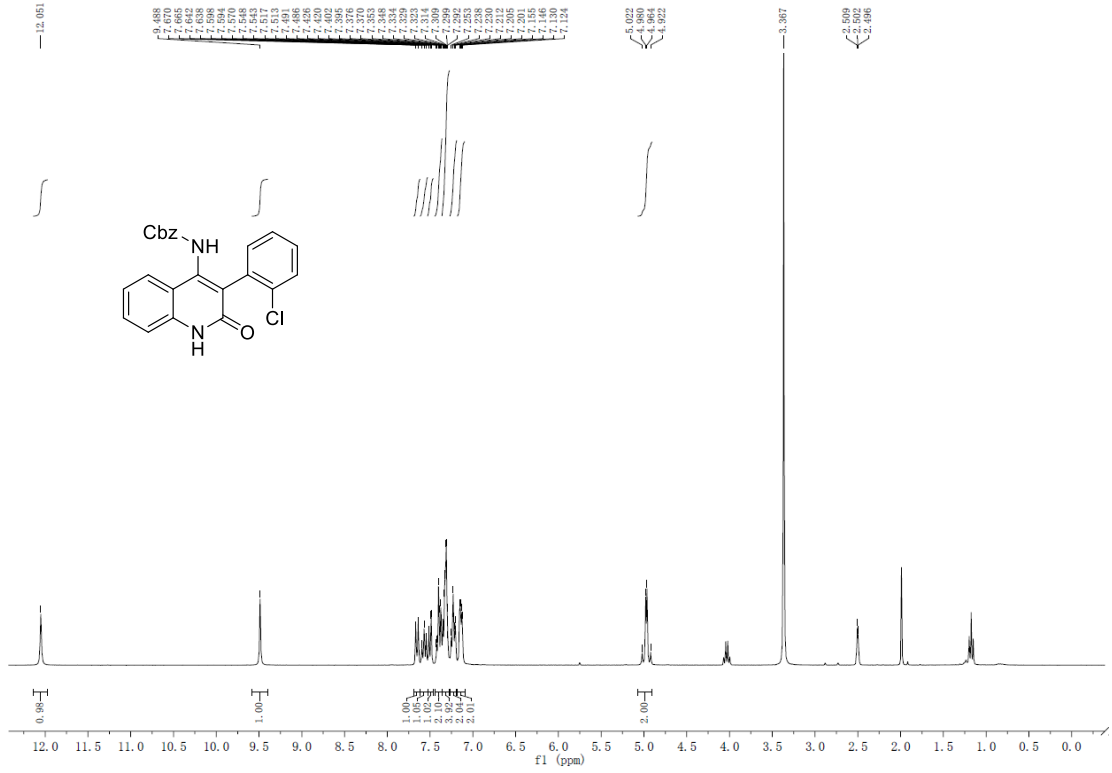


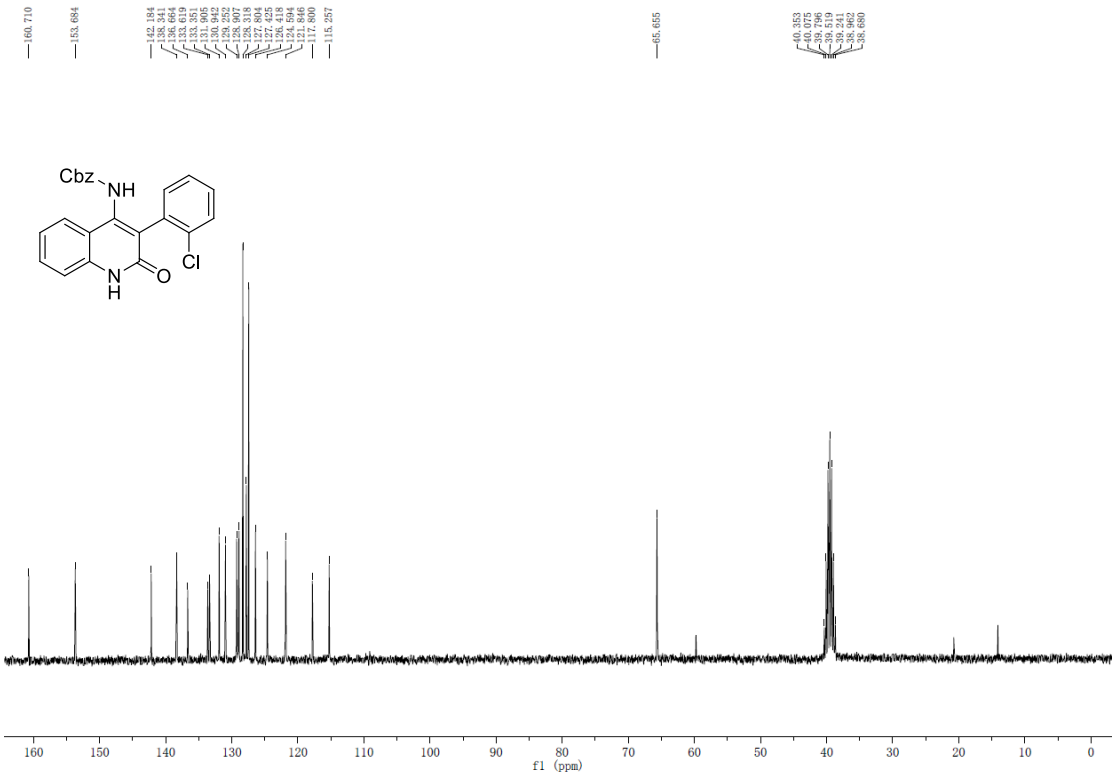
^{1}H NMR and ^{13}C NMR of **3d**



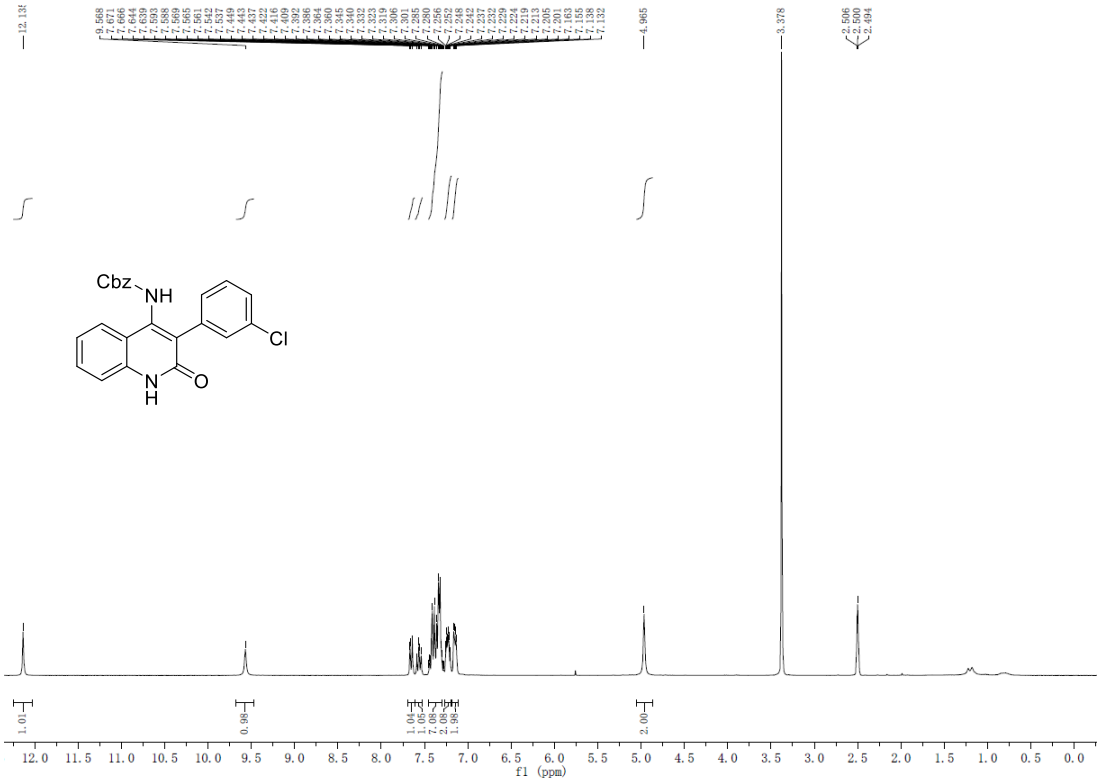


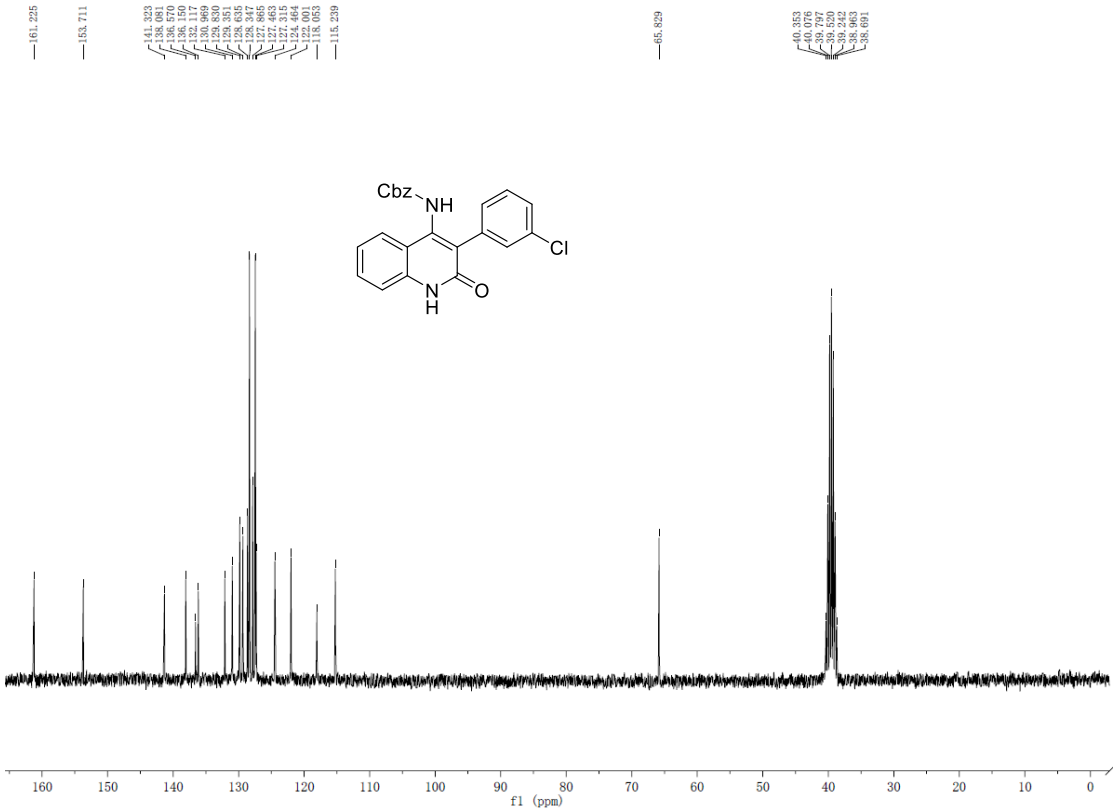
^{1}H NMR and ^{13}C NMR of **3e**



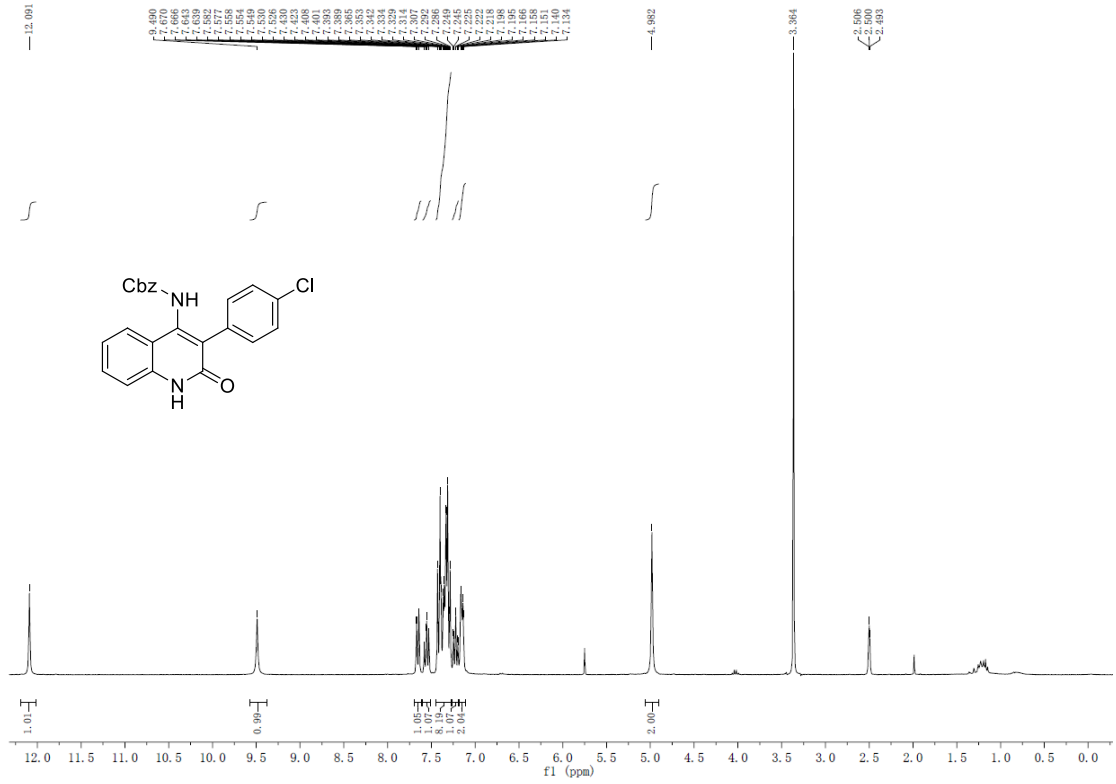


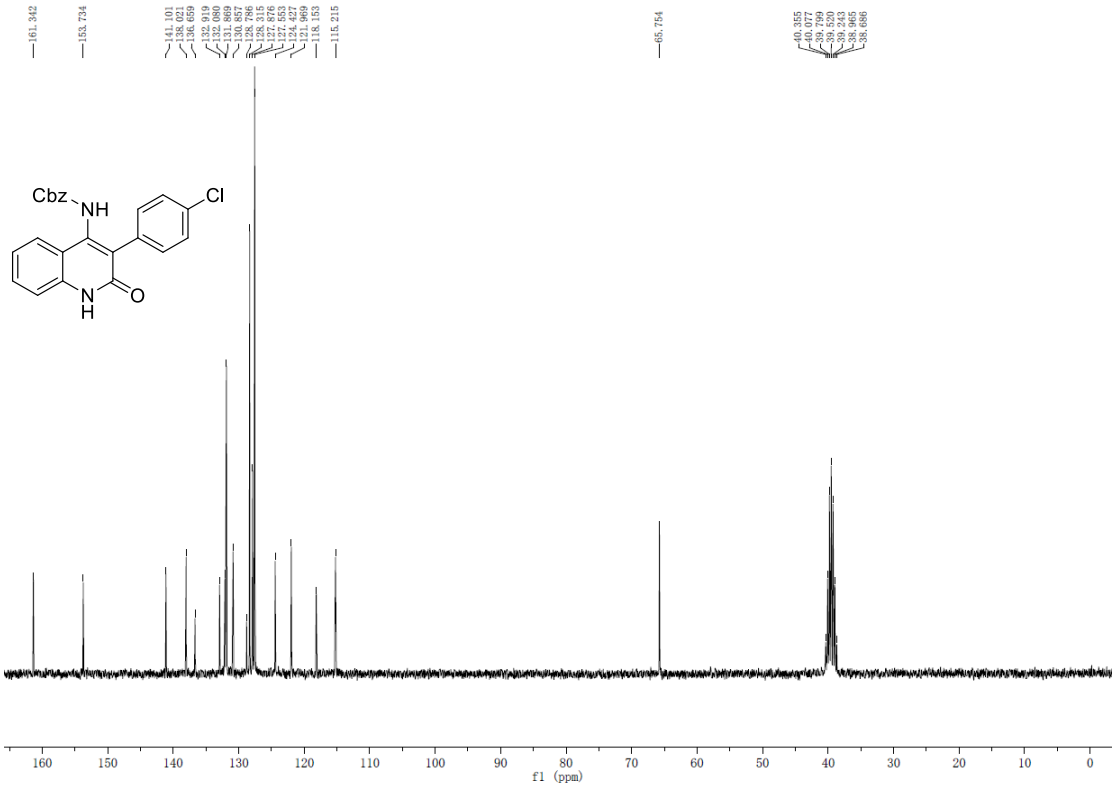
^{1}H NMR and ^{13}C NMR of **3f**



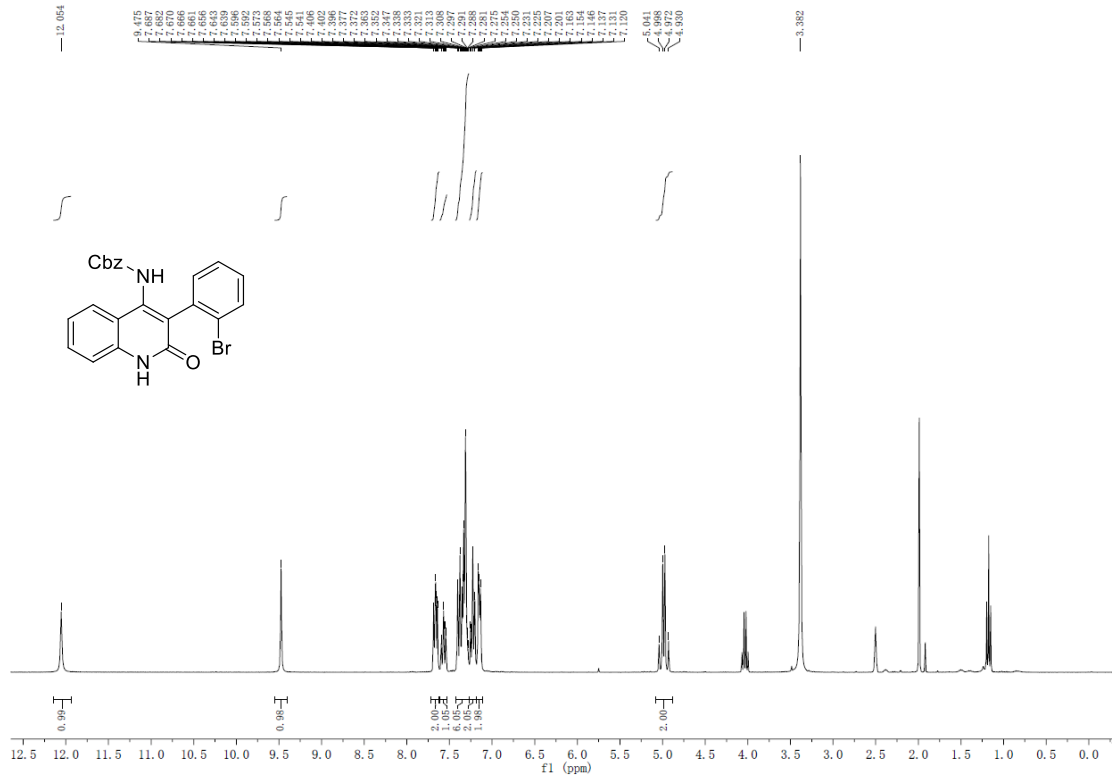


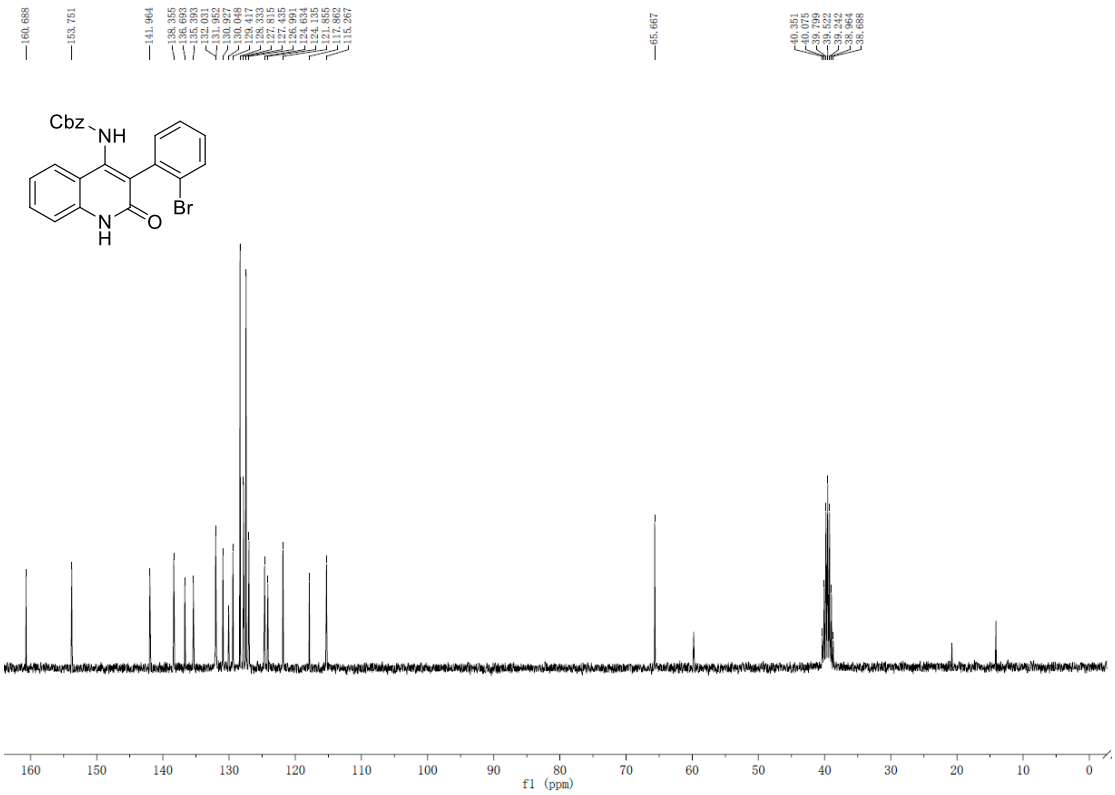
^{1}H NMR and ^{13}C NMR of **3g**



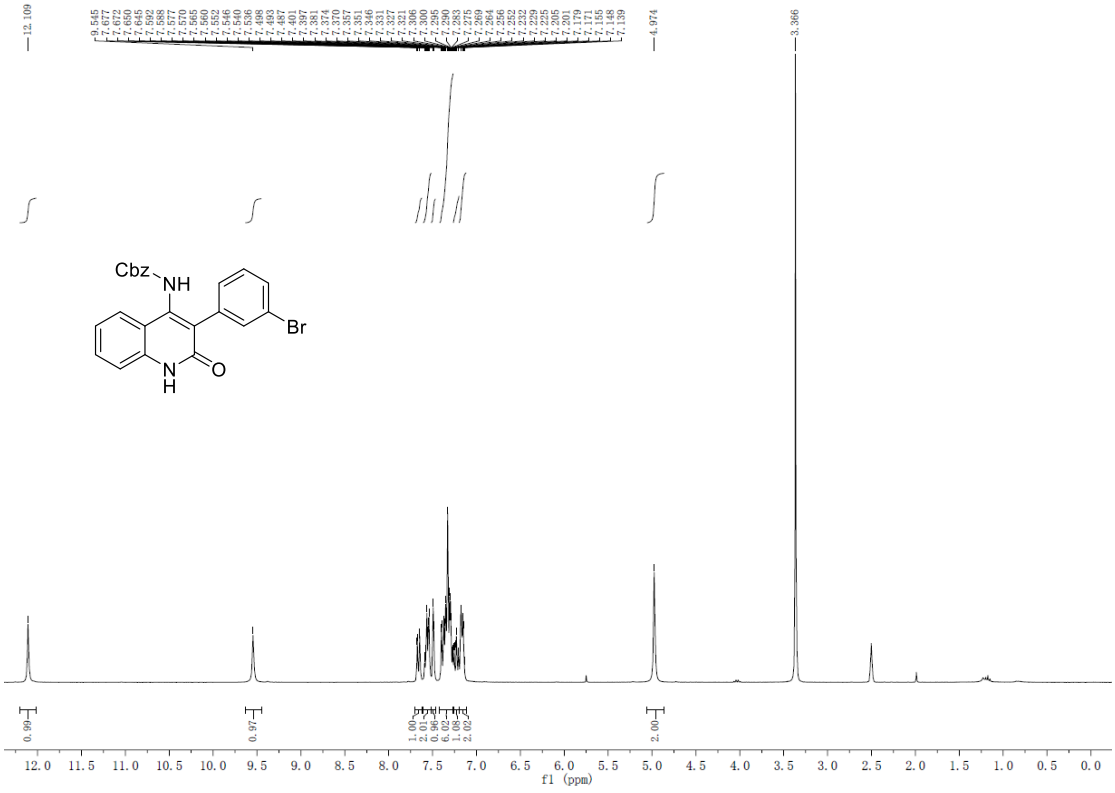


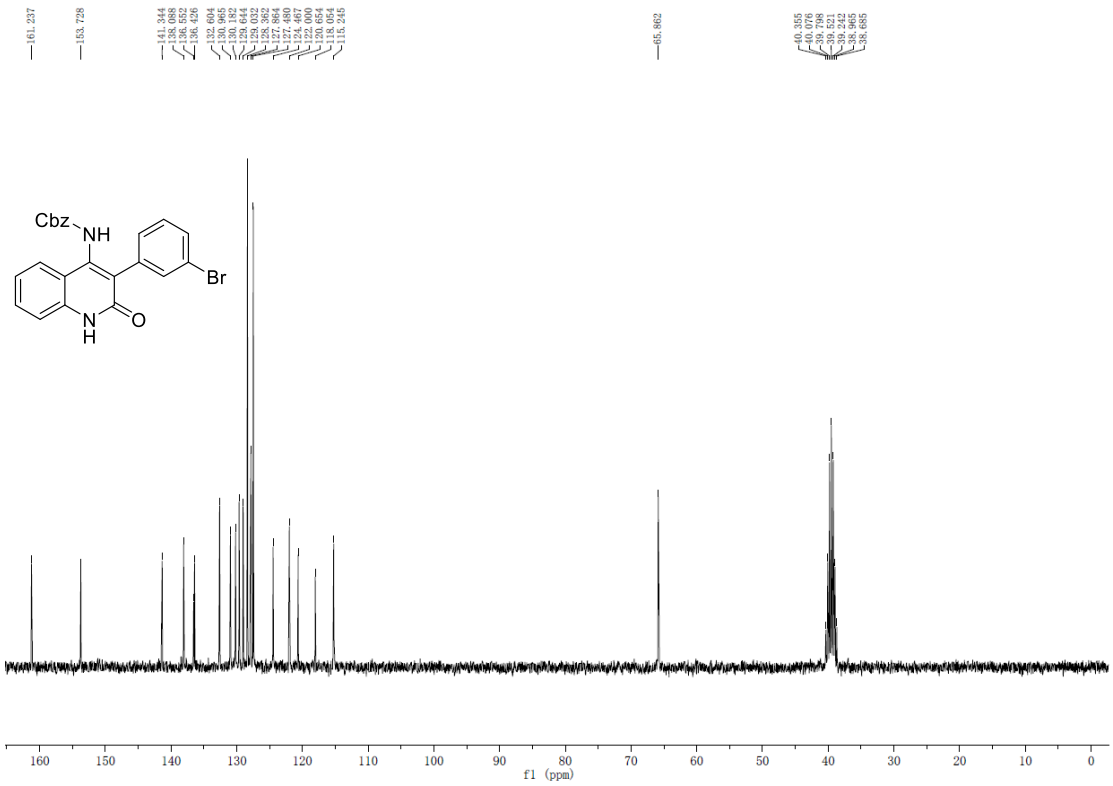
^{1}H NMR and ^{13}C NMR of **3h**



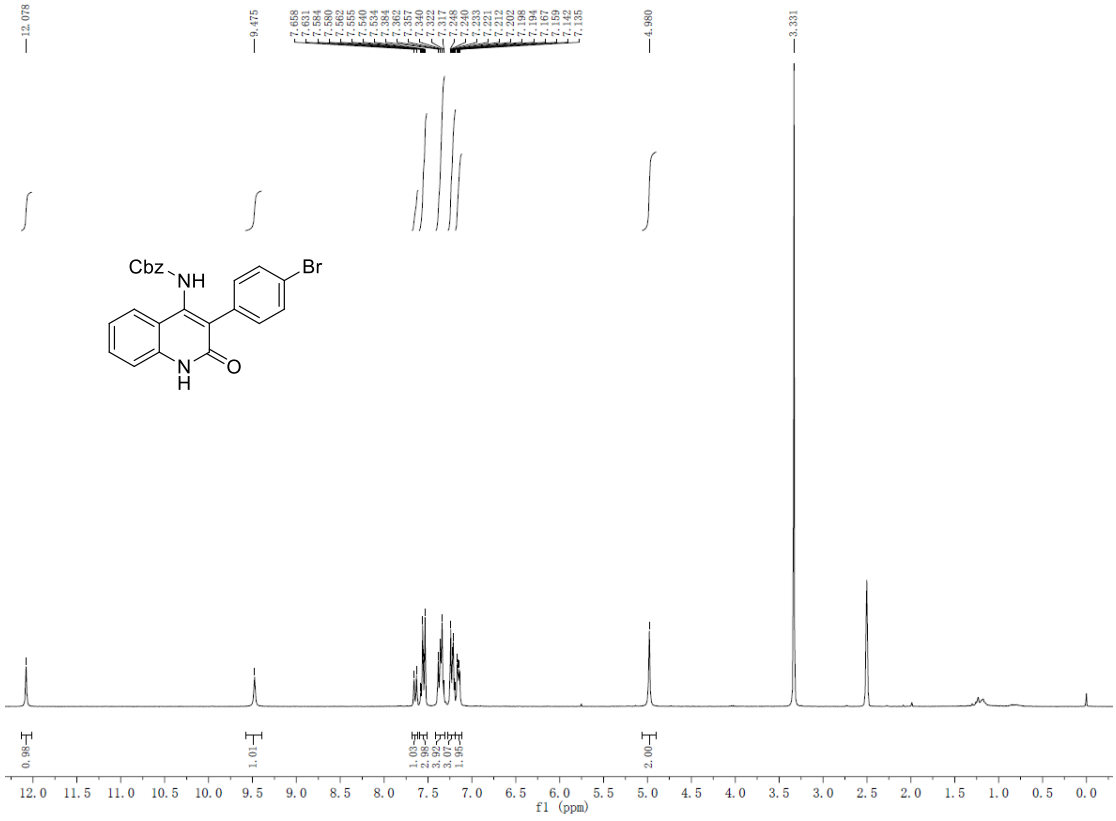


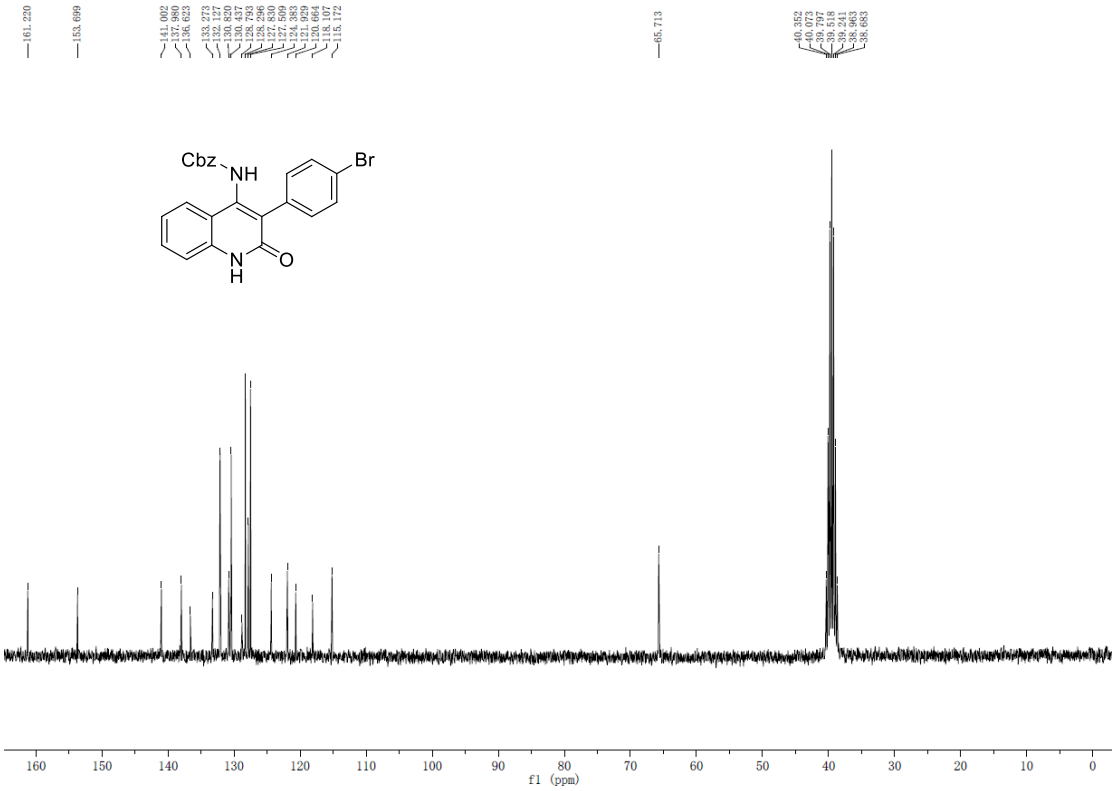
^{1}H NMR and ^{13}C NMR of **3i**



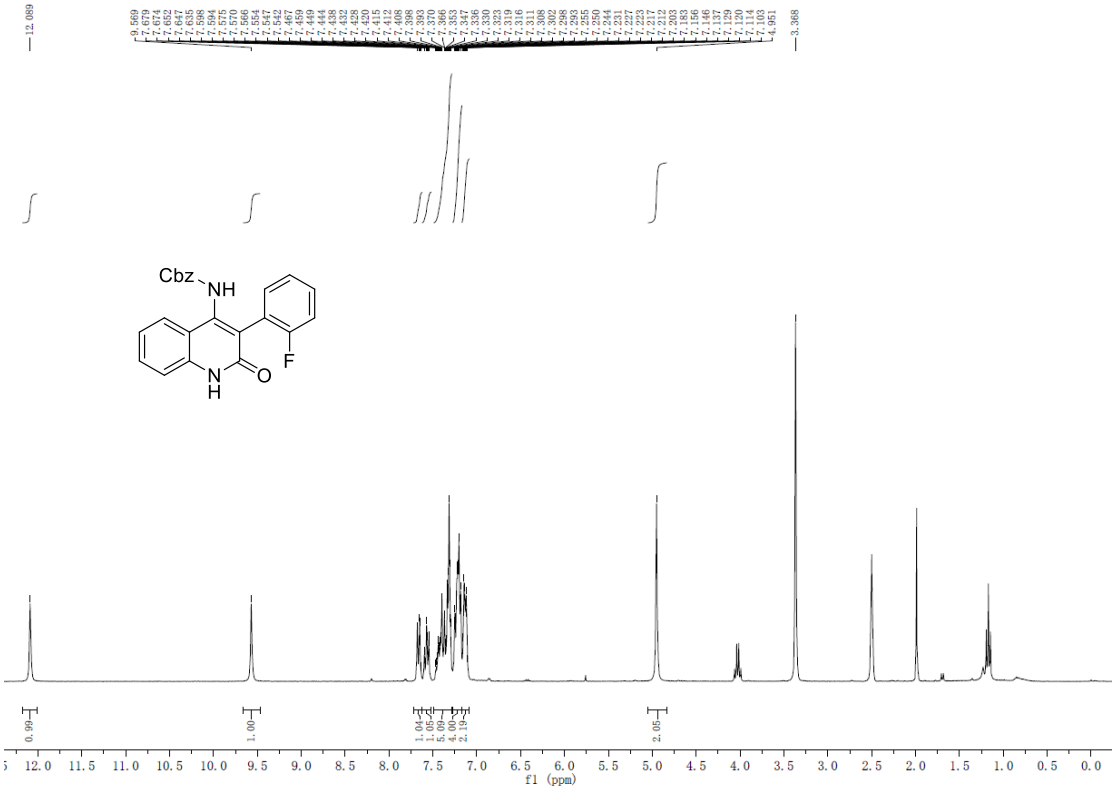


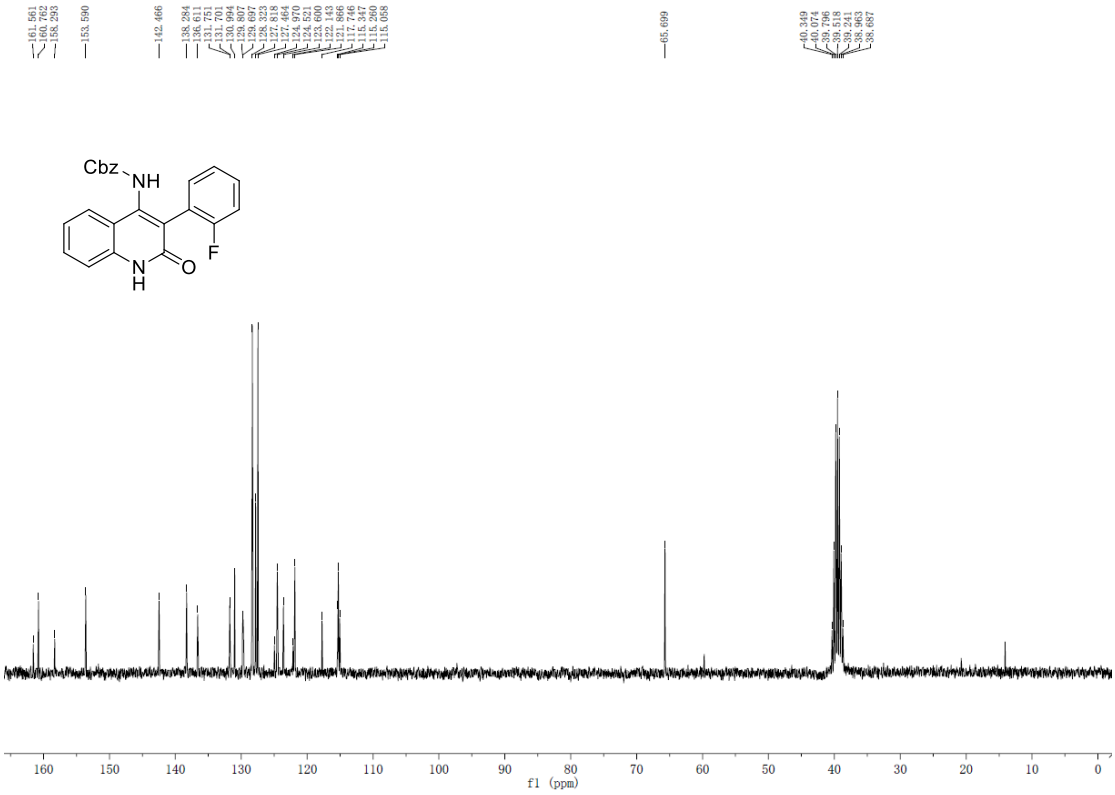
^{1}H NMR and ^{13}C NMR of **3j**



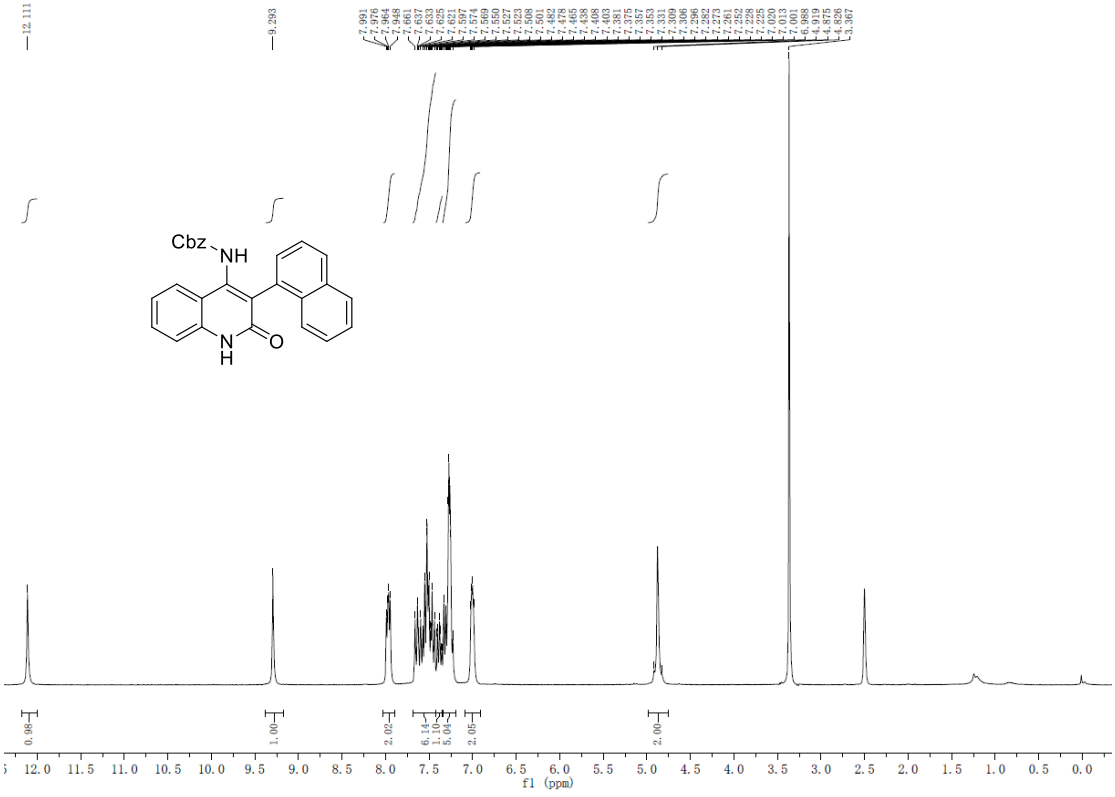


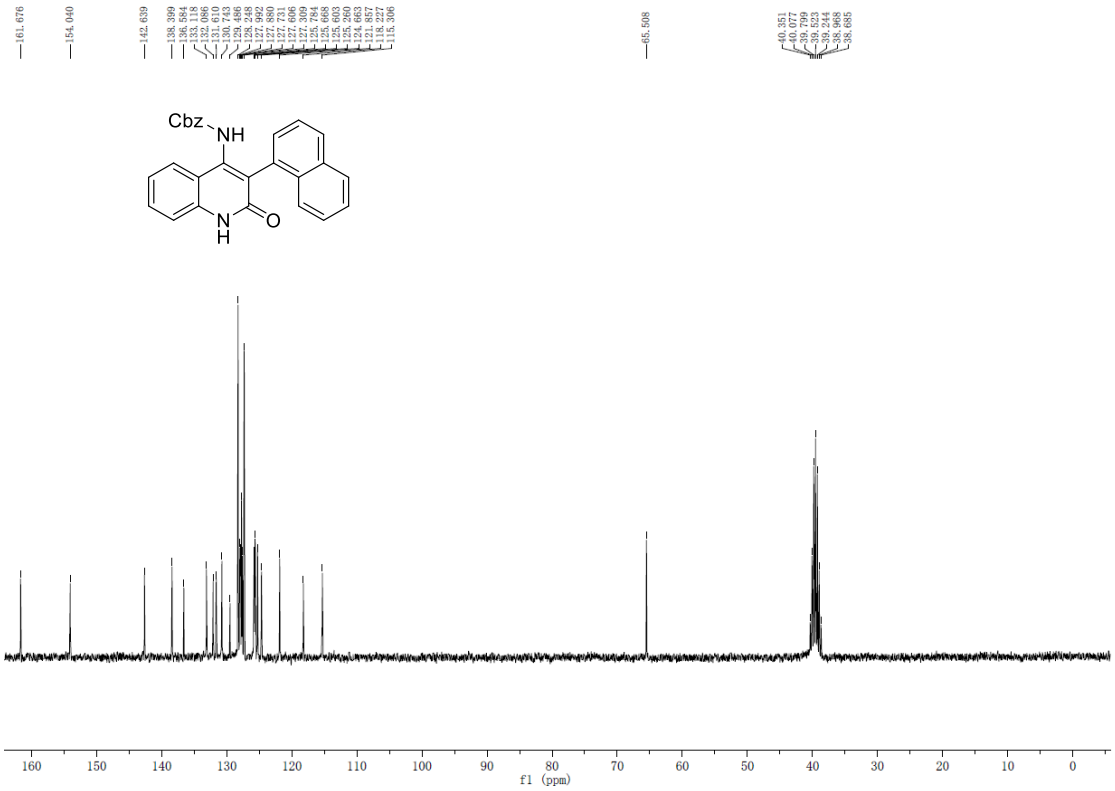
^{1}H NMR and ^{13}C NMR of **3k**



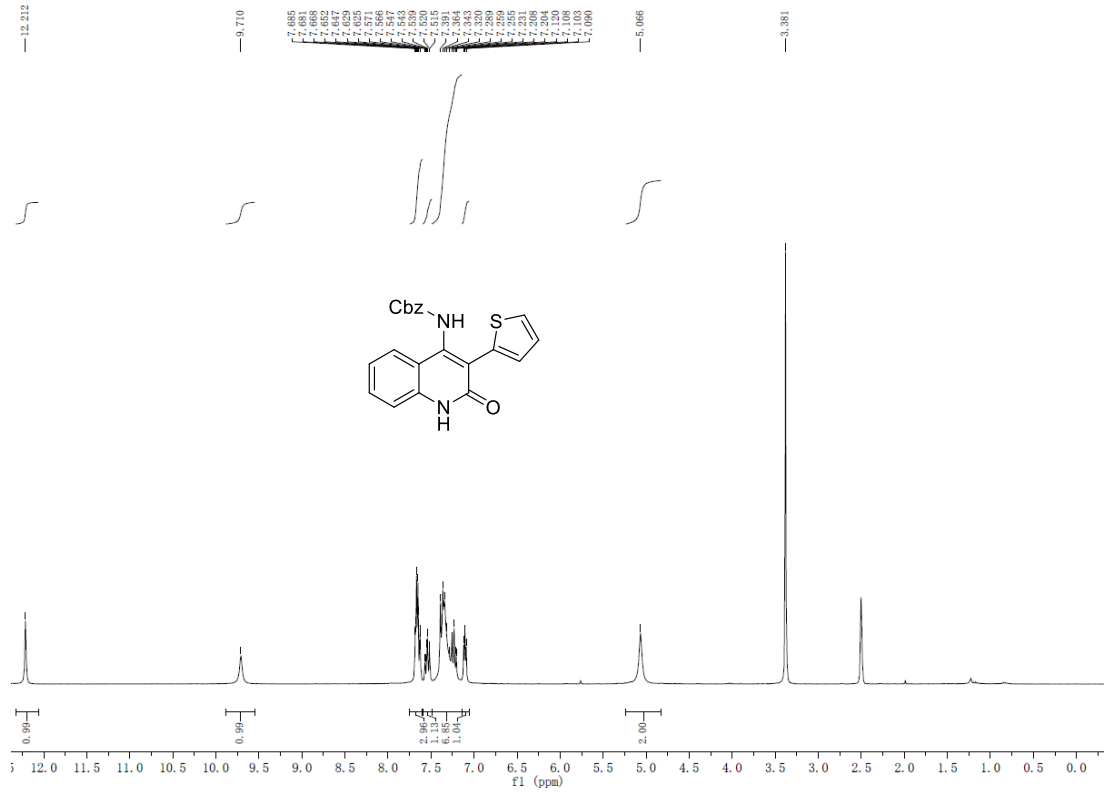


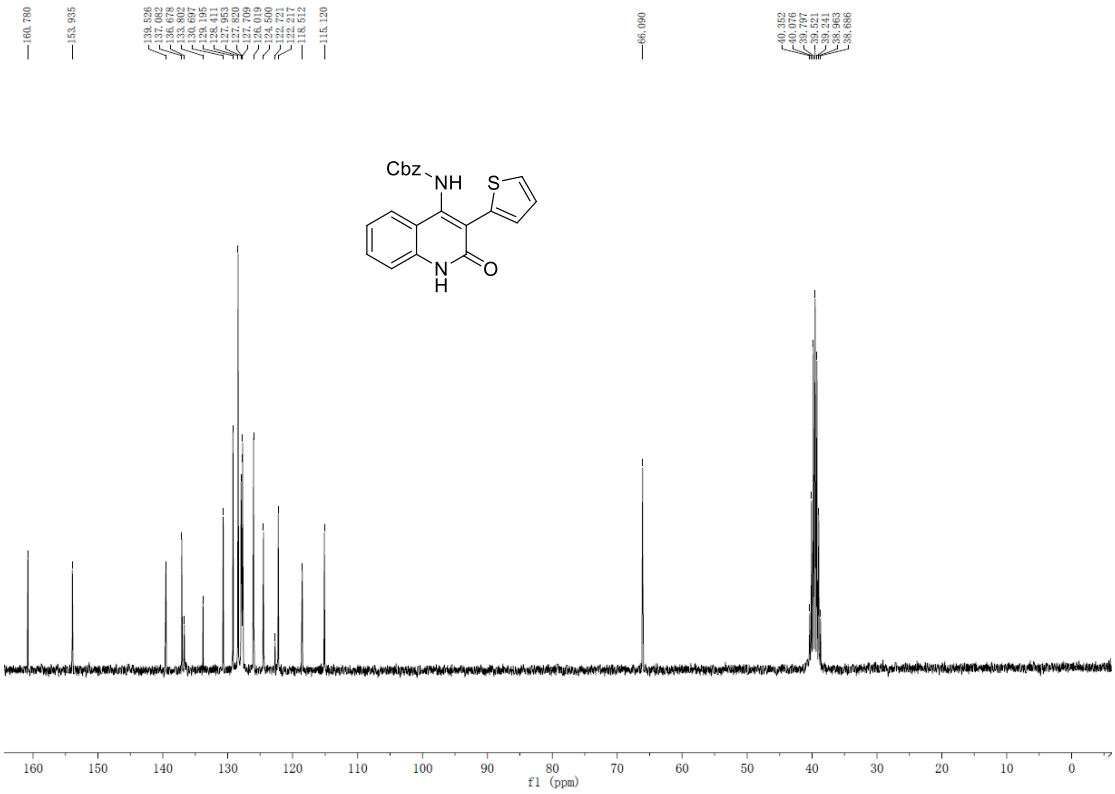
^{1}H NMR and ^{13}C NMR of **3l**



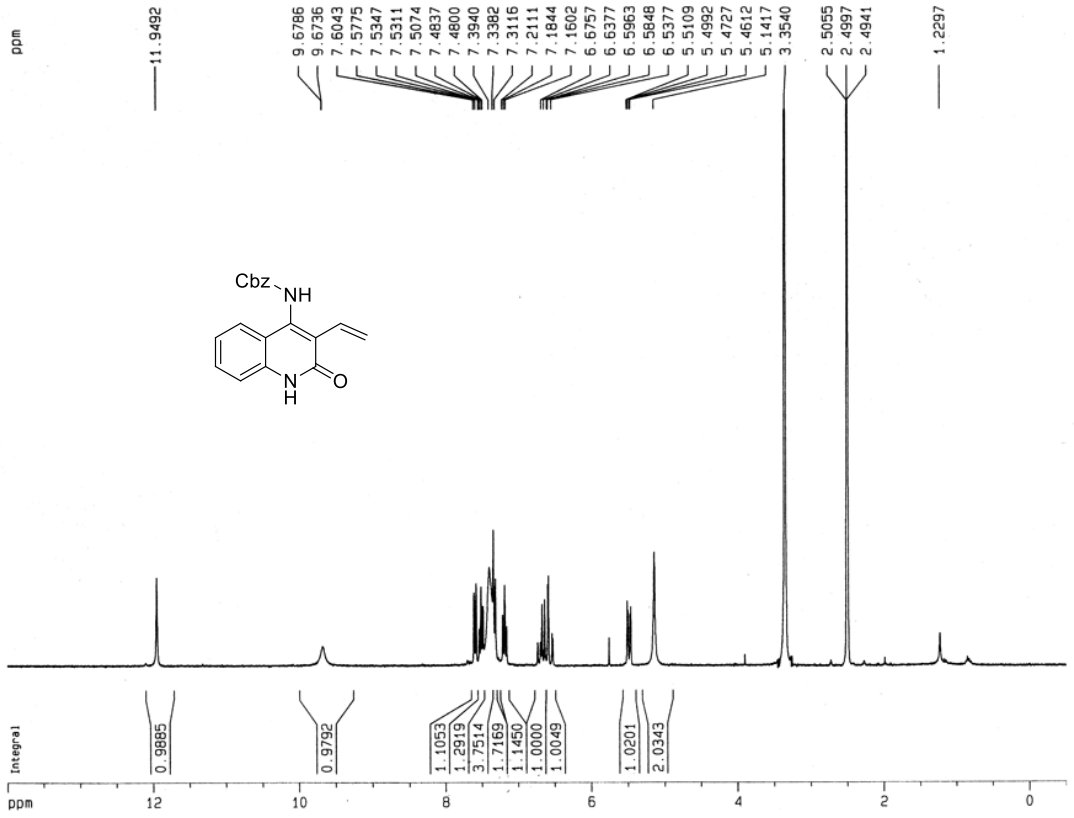


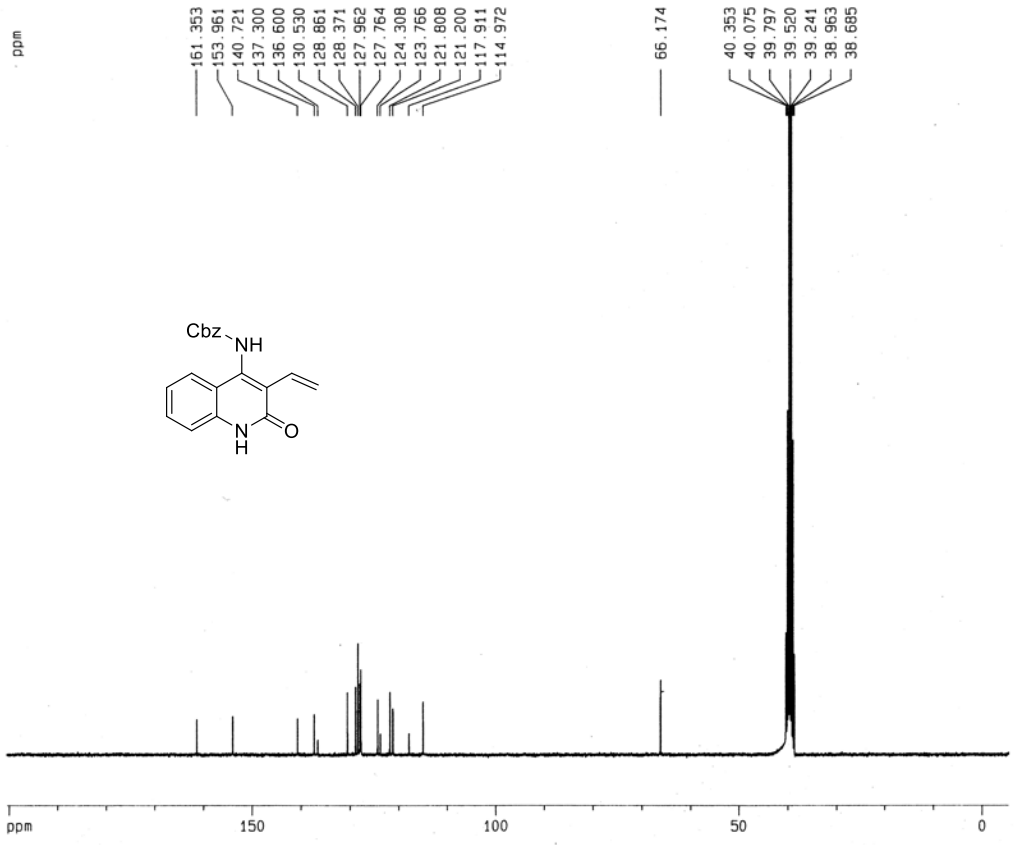
^{1}H NMR and ^{13}C NMR of **3m**



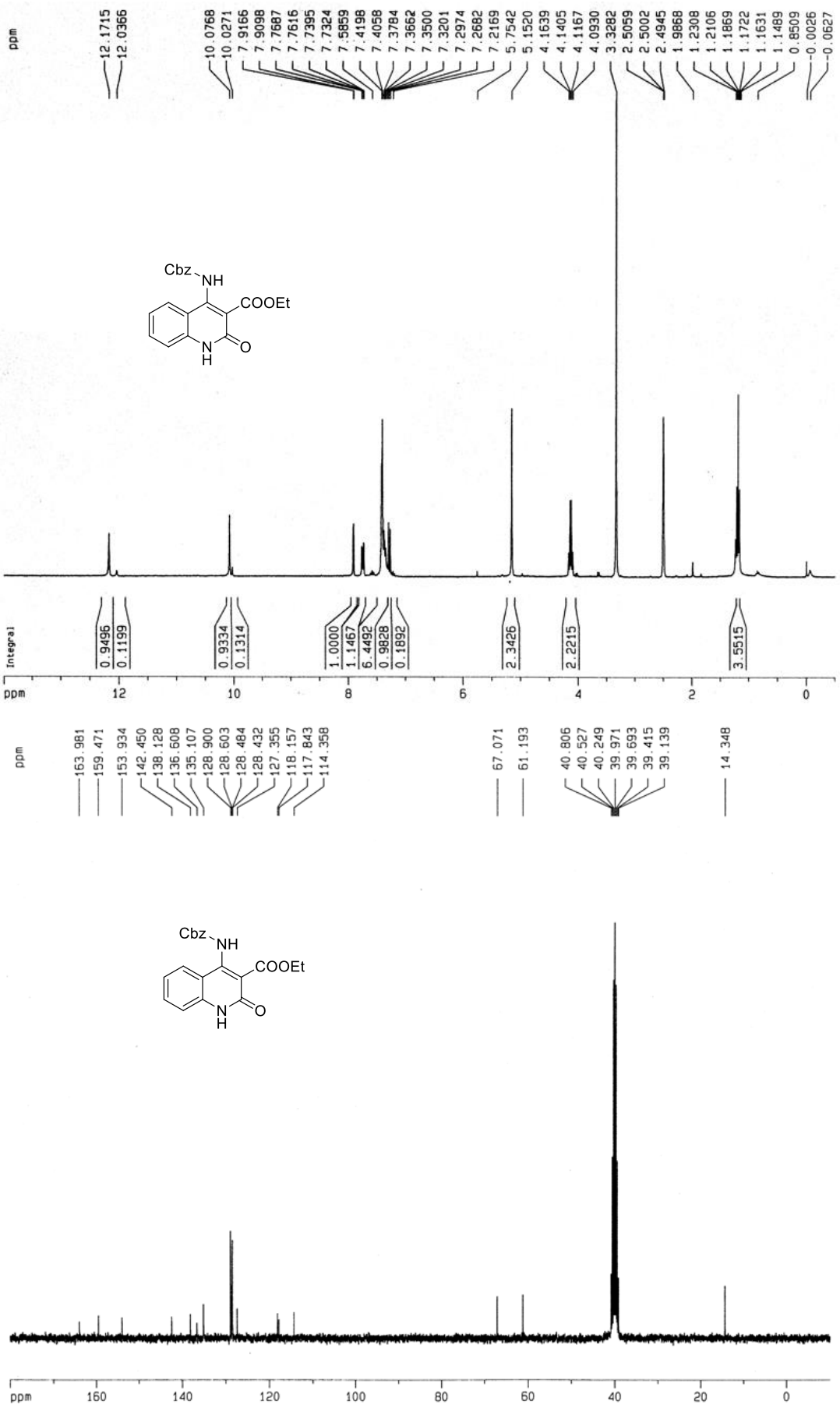


^{1}H NMR and ^{13}C NMR of **3n**





^{1}H NMR and ^{13}C NMR of **3o**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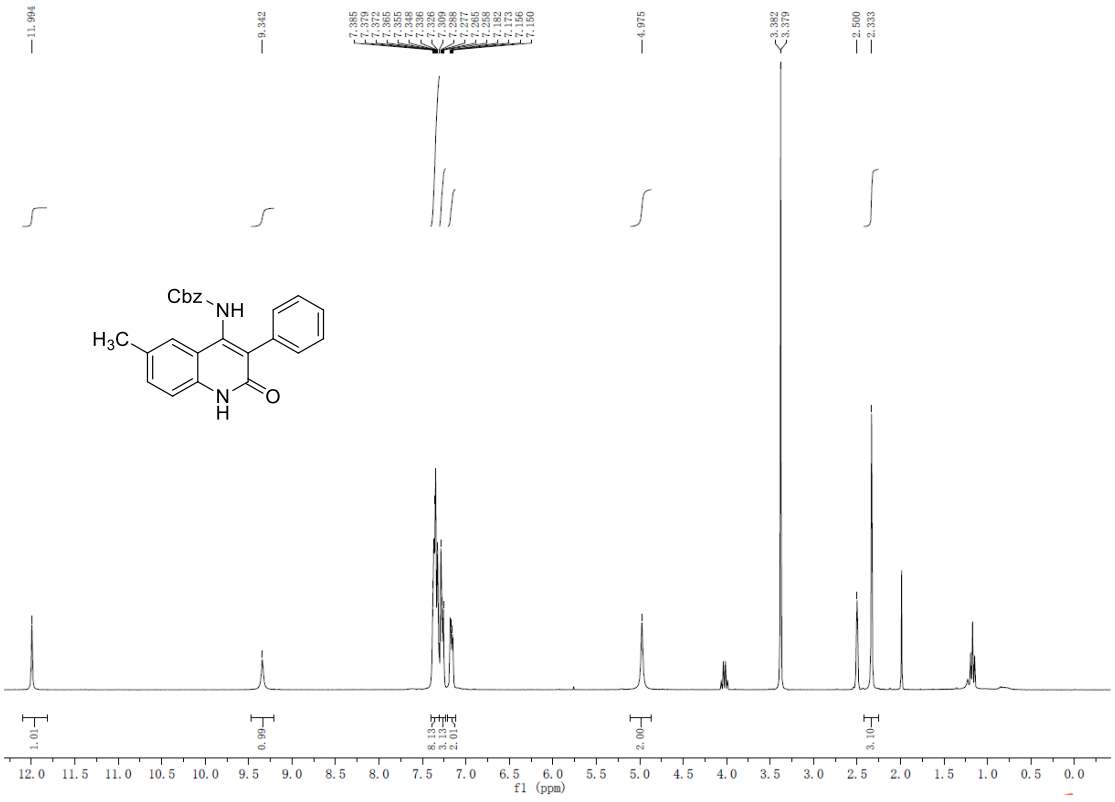
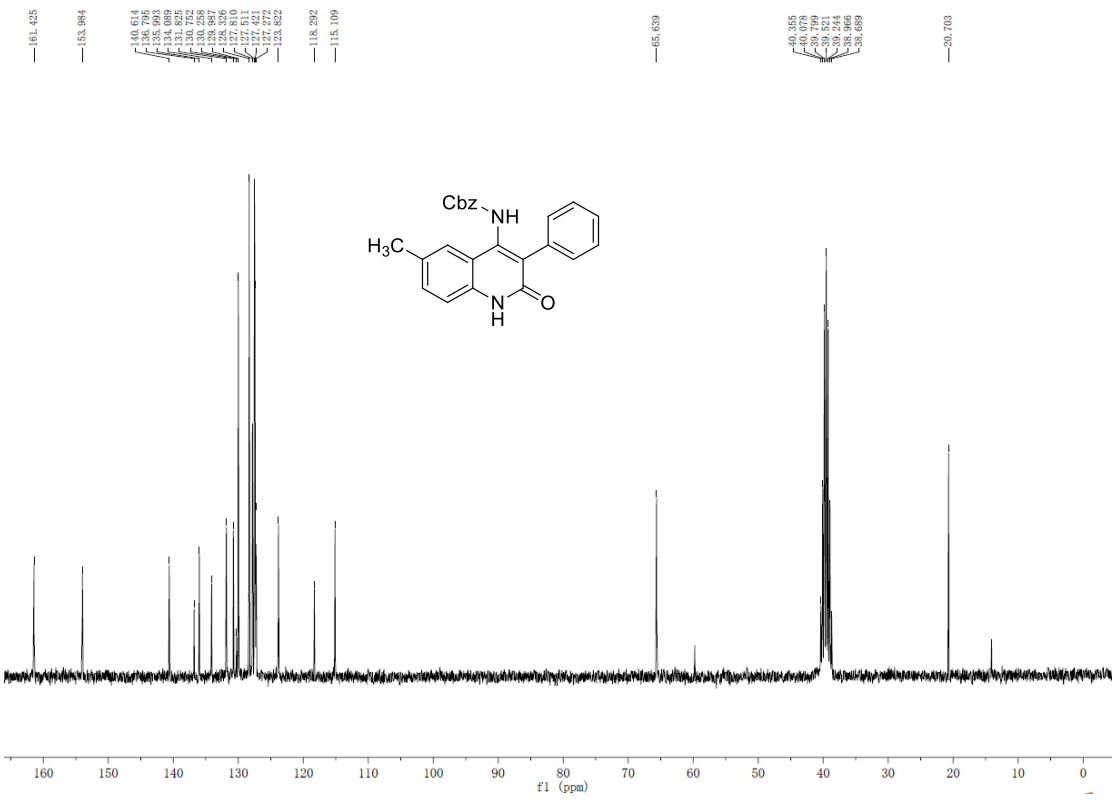
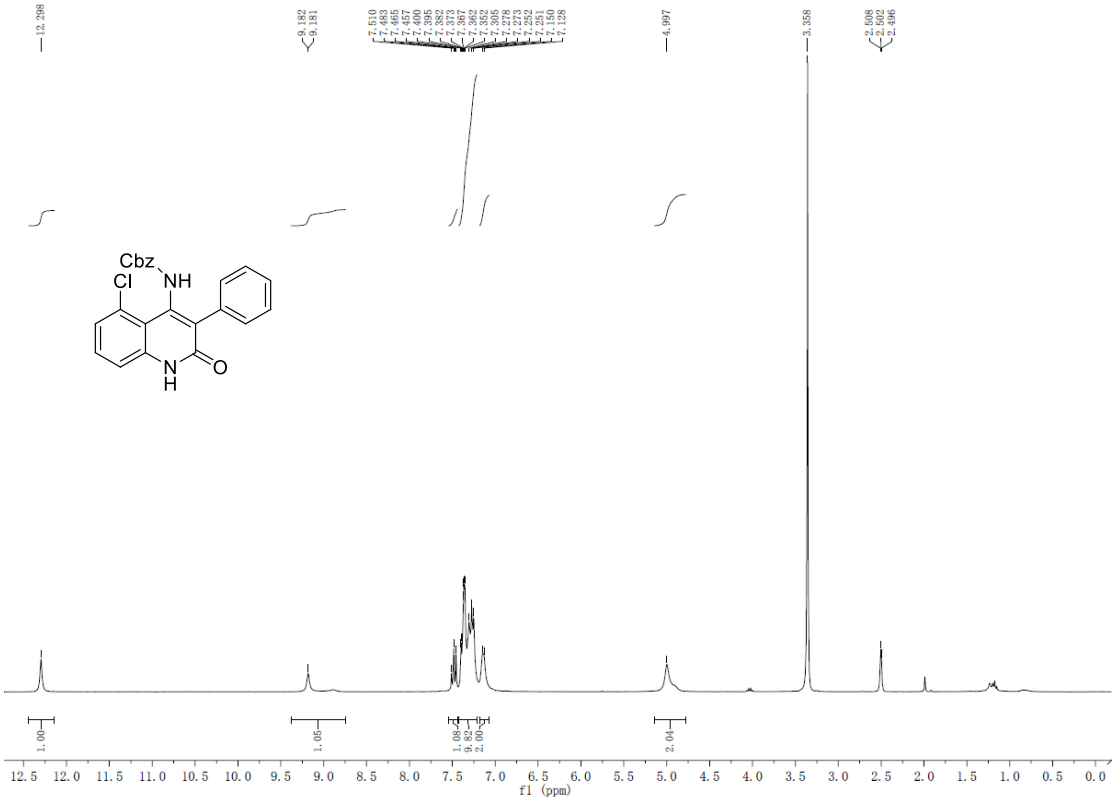
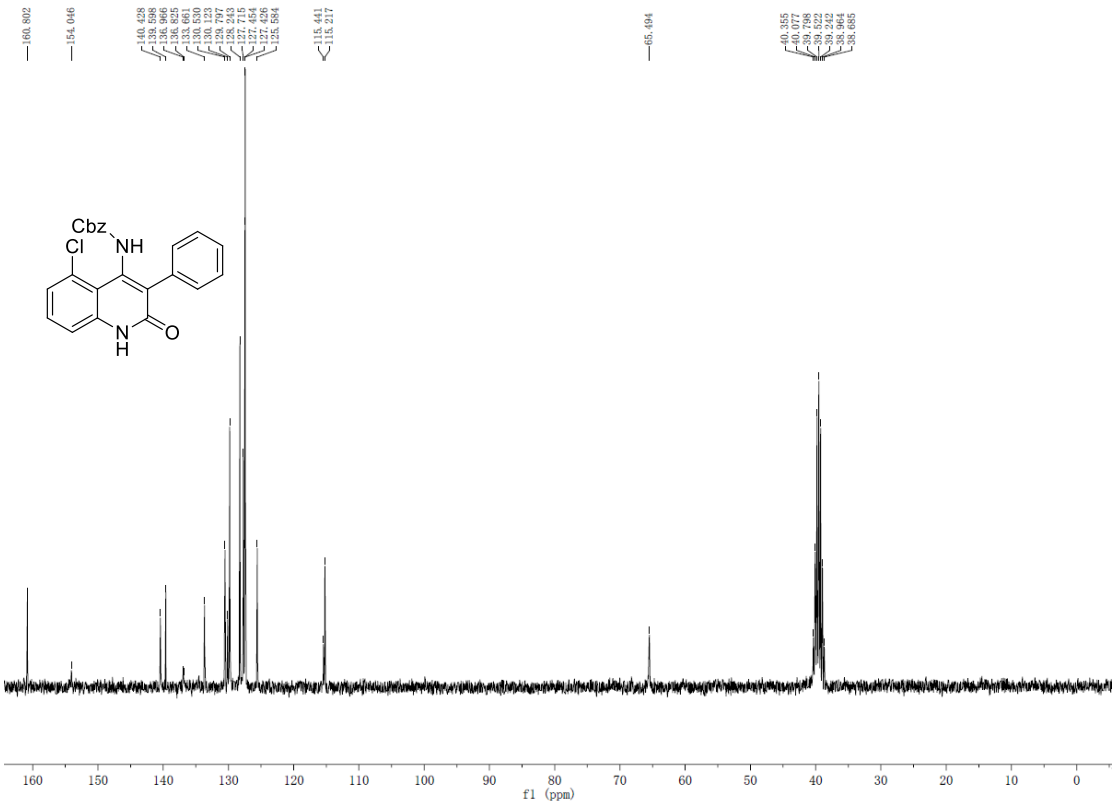
^{1}H NMR and ^{13}C NMR of **3q**



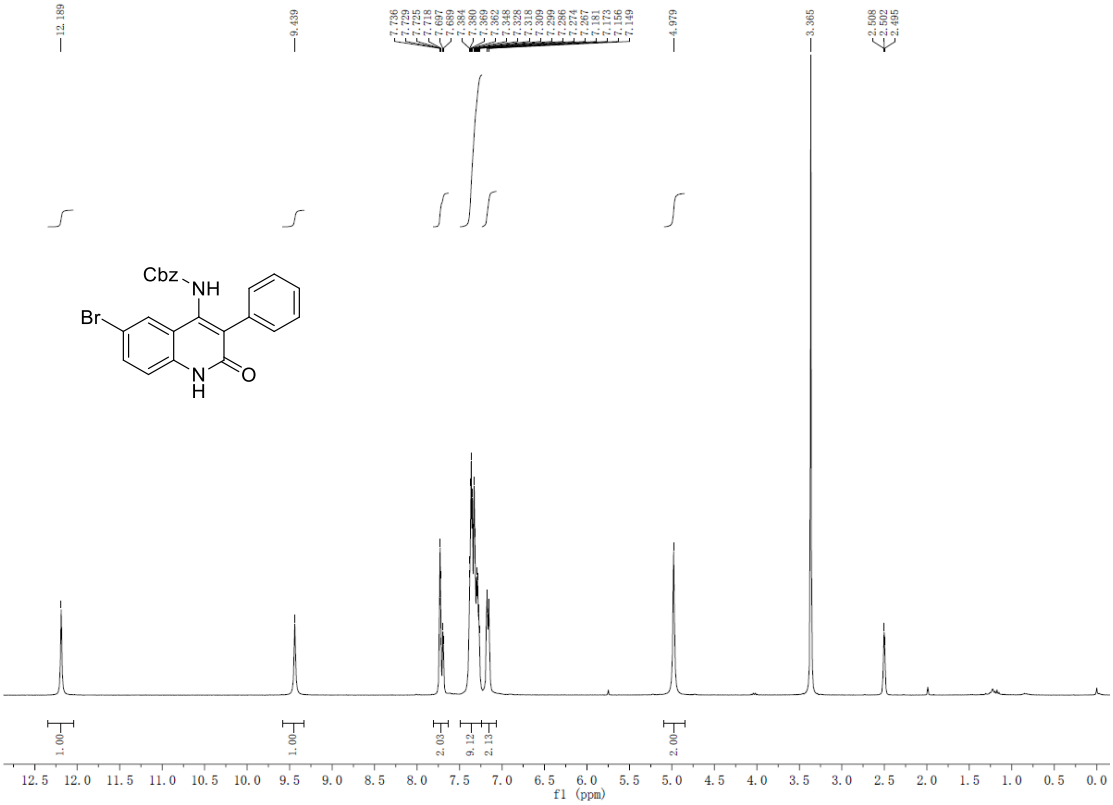


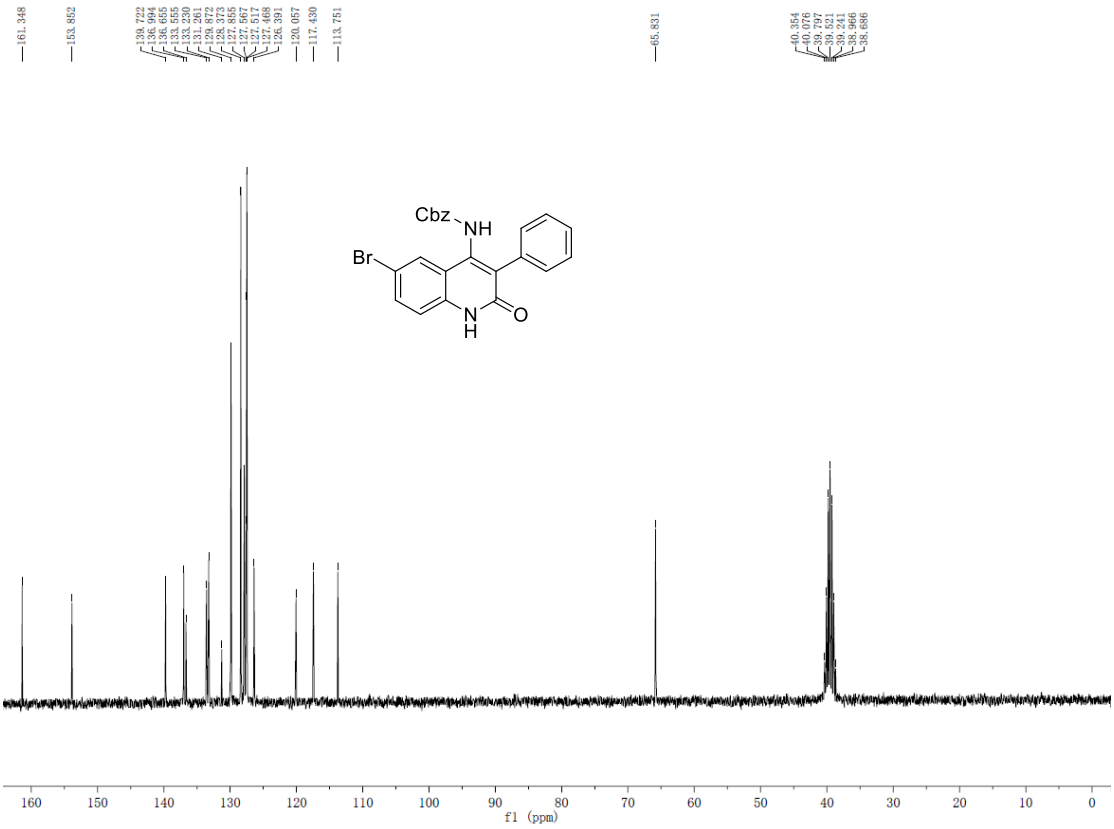
^{1}H NMR and ^{13}C NMR of **3r**



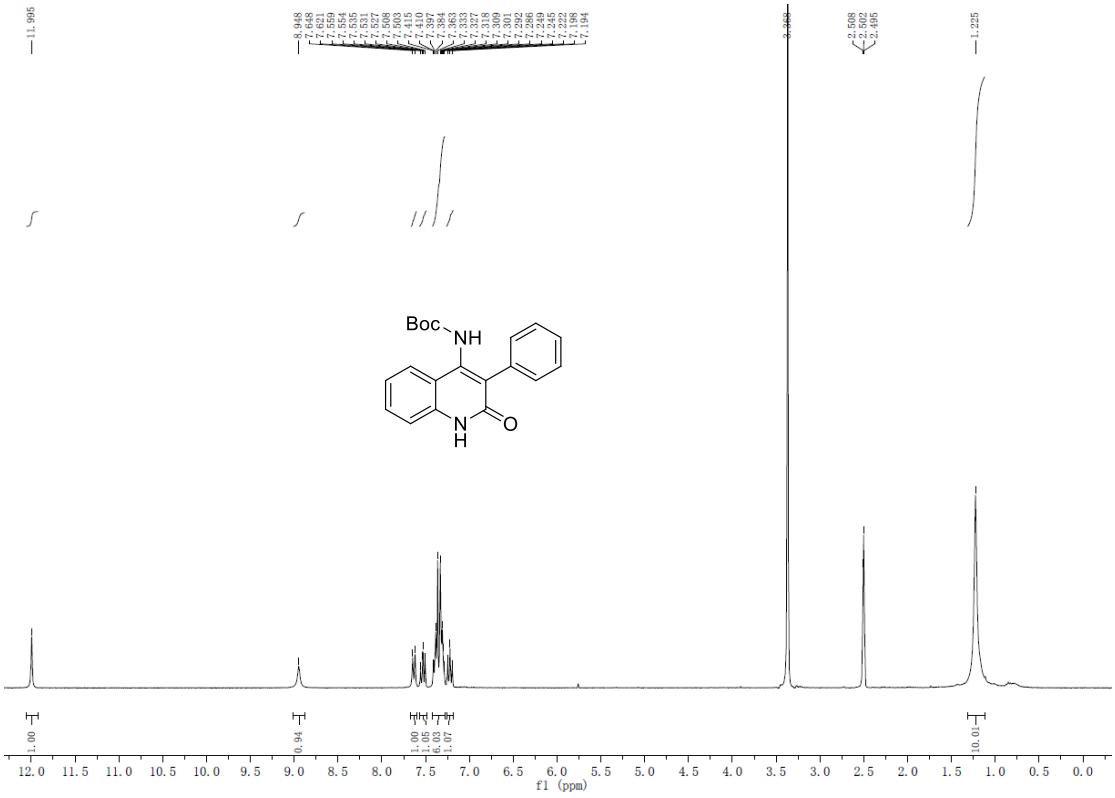


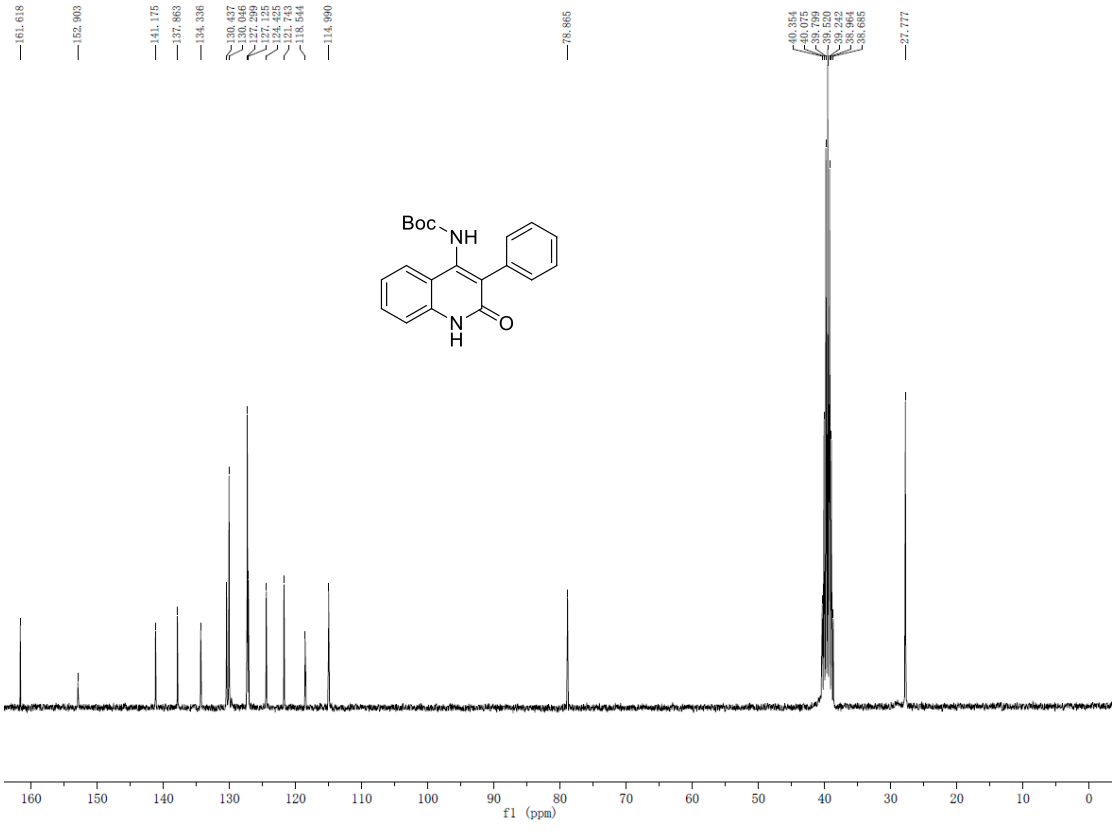
^{1}H NMR and ^{13}C NMR of **3s**



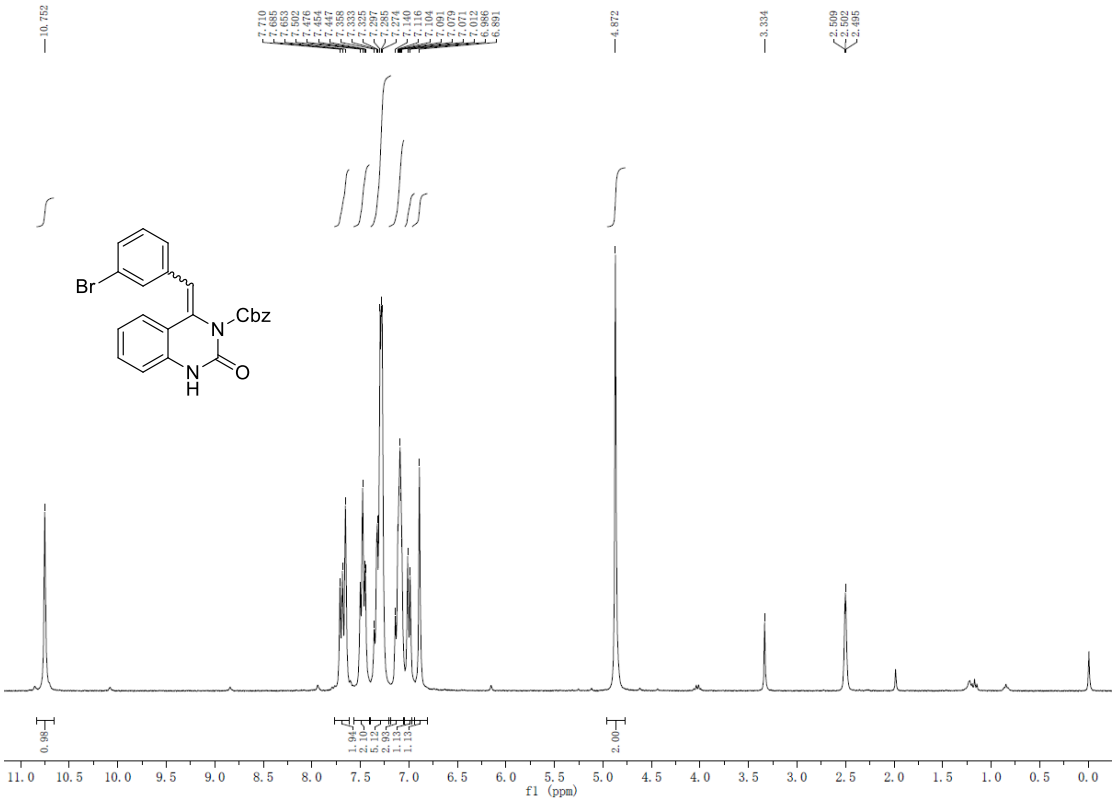


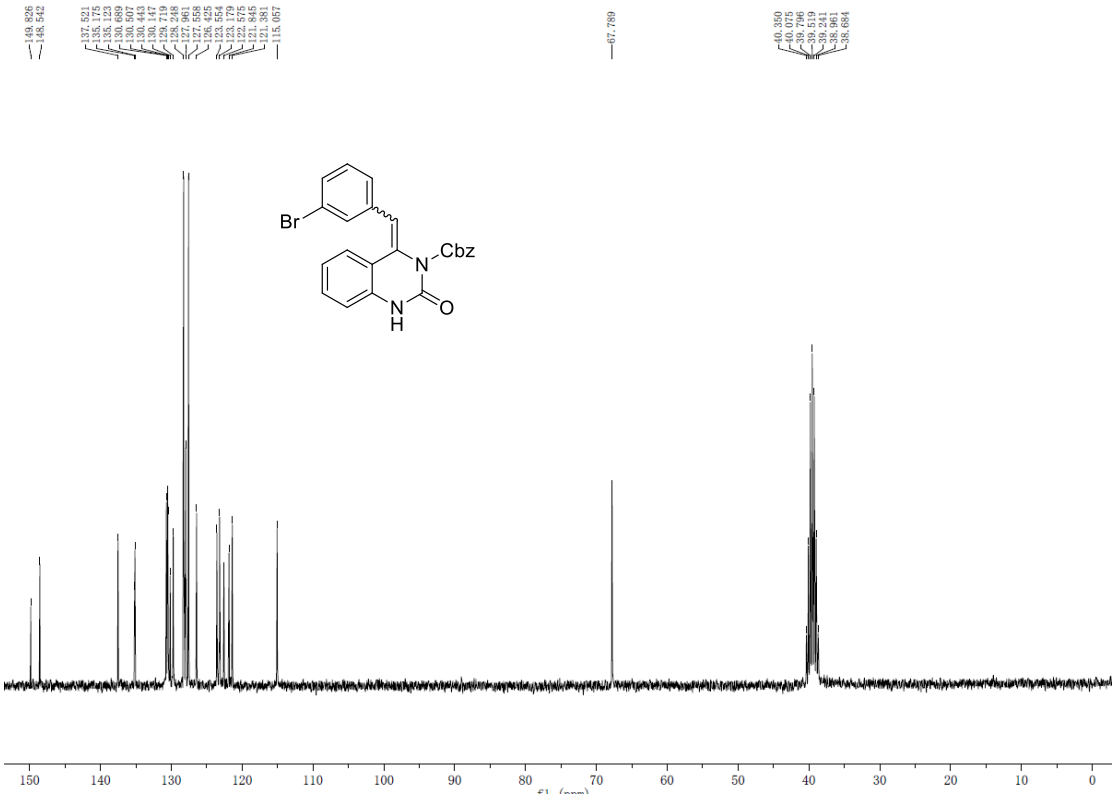
^{1}H NMR and ^{13}C NMR of **3t**



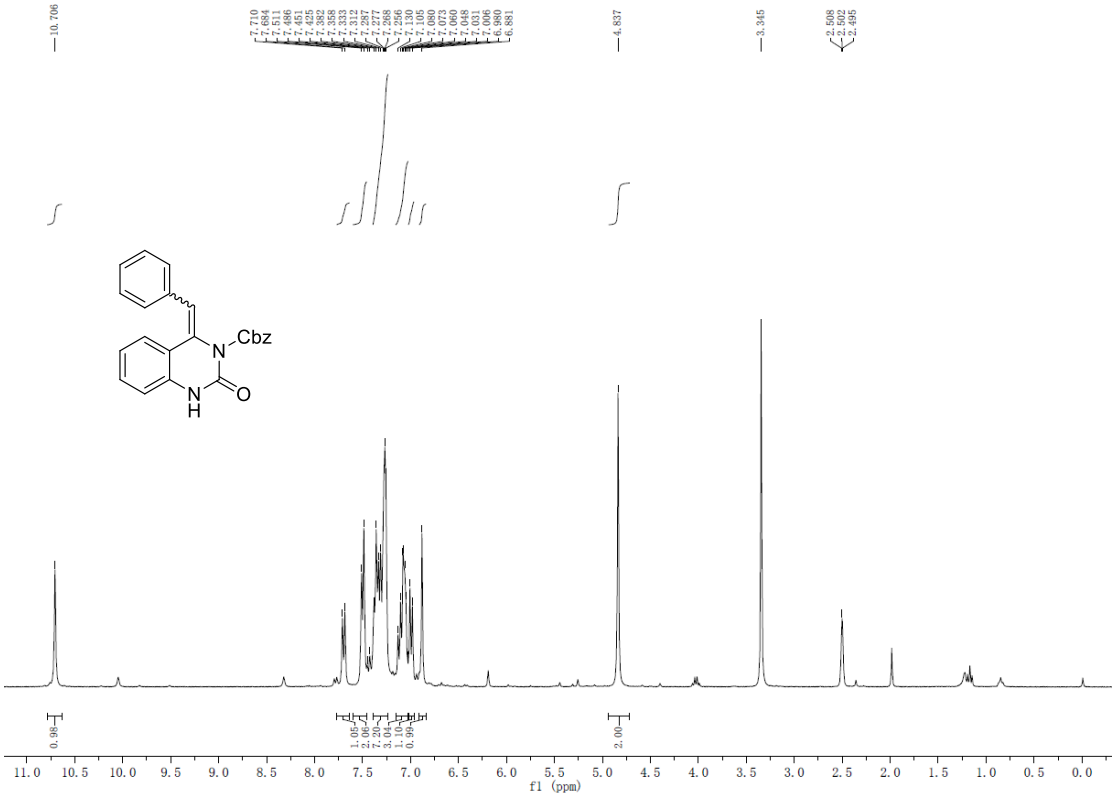


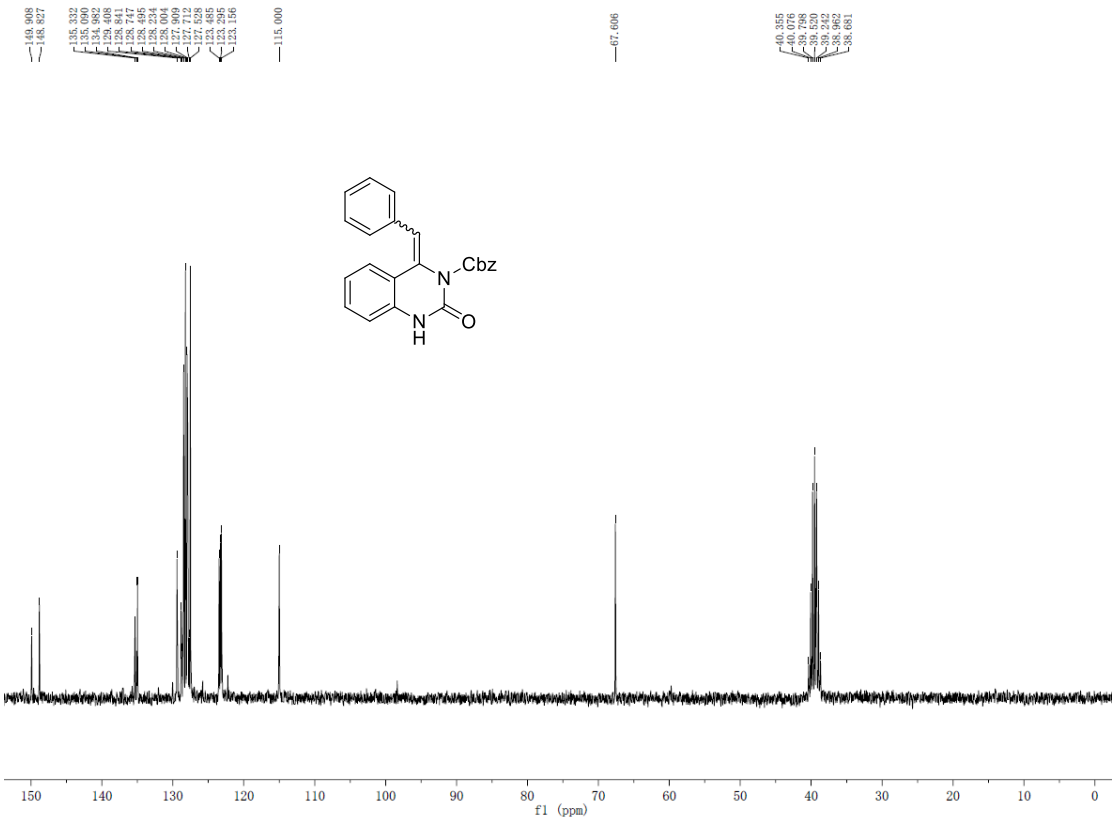
^{1}H NMR and ^{13}C NMR of **4a**



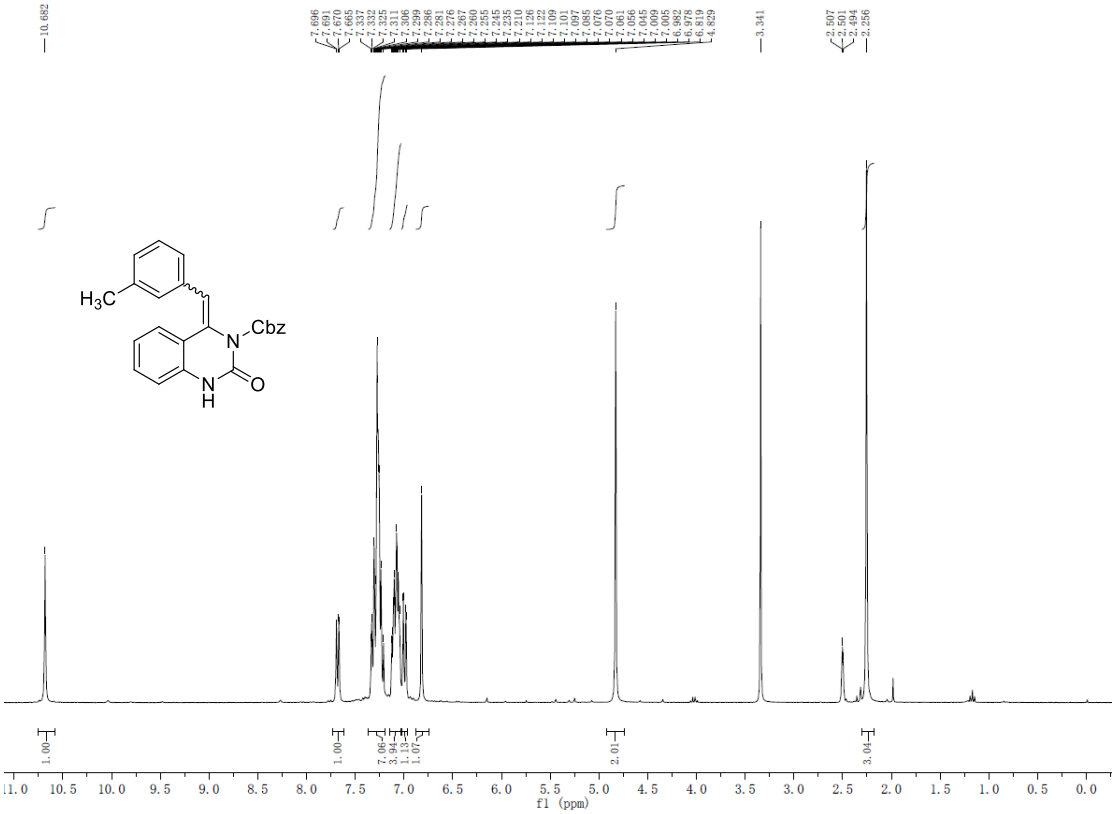


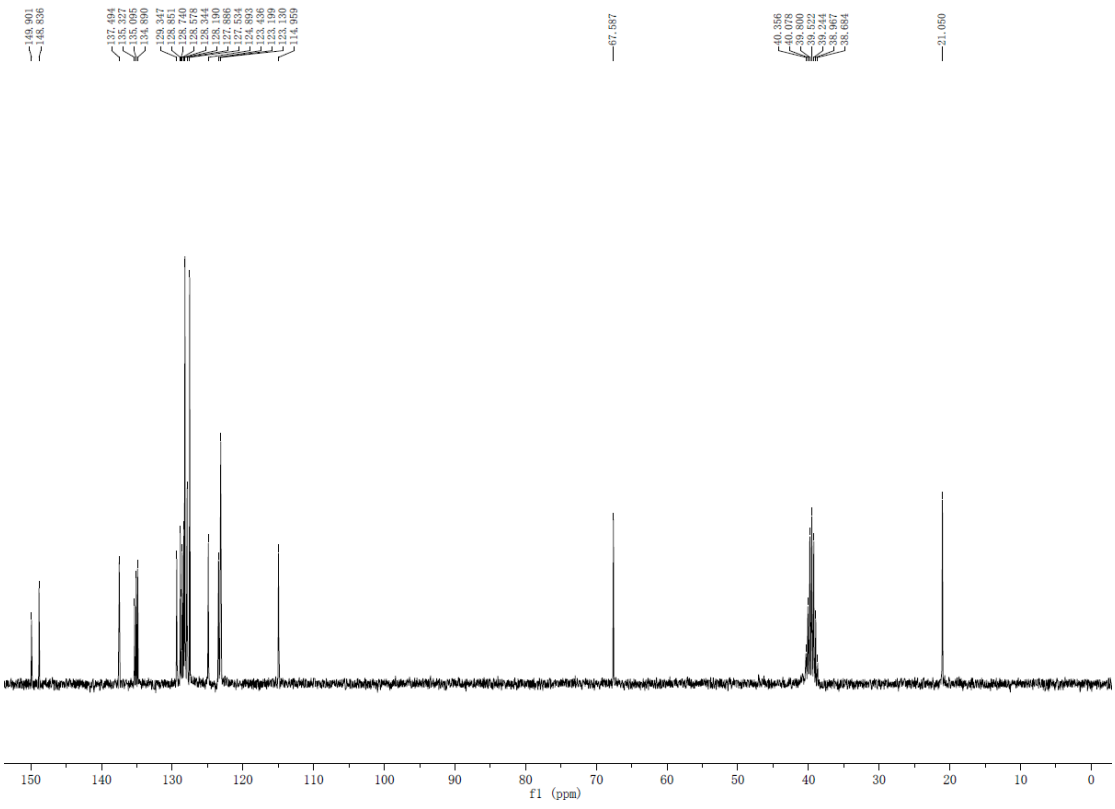
^{1}H NMR and ^{13}C NMR of **4b**



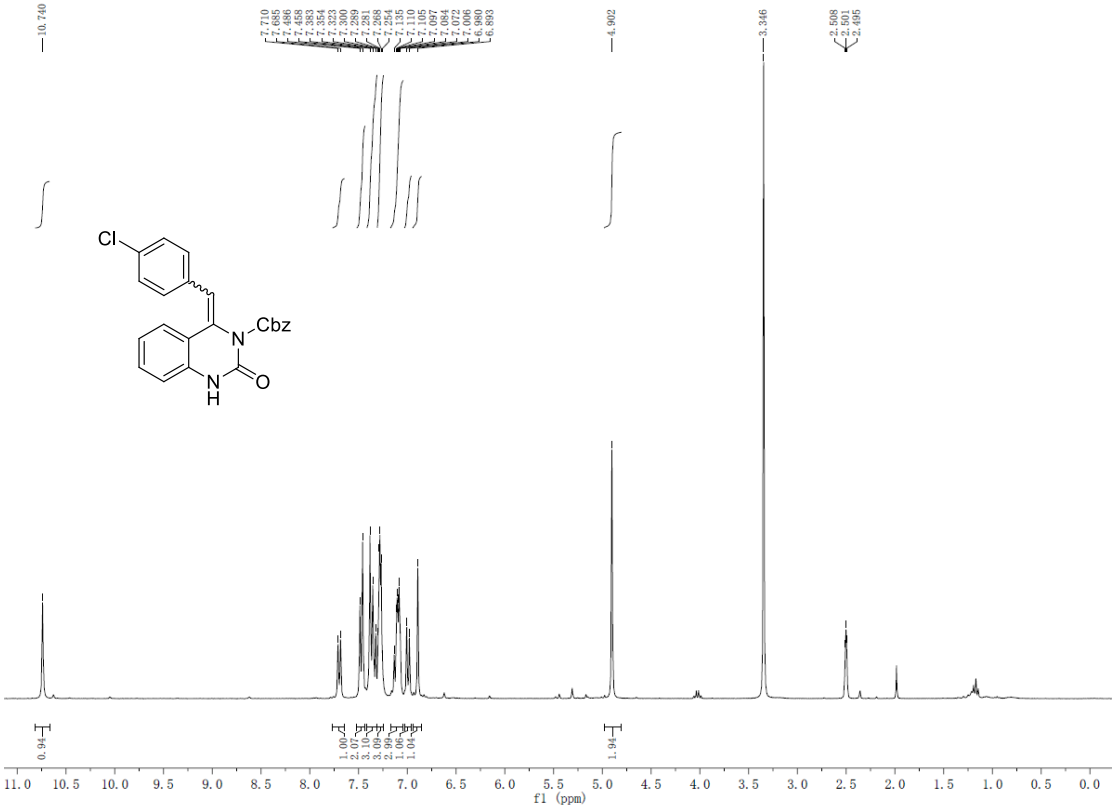


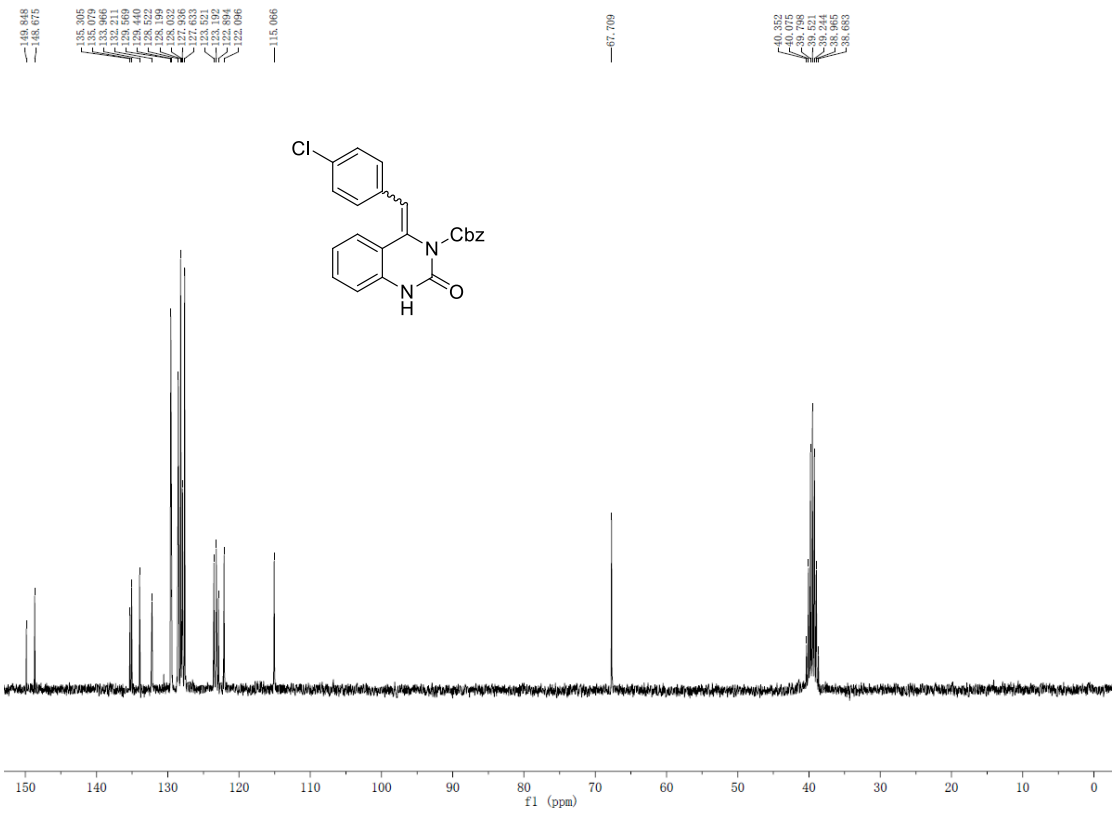
^{1}H NMR and ^{13}C NMR of **4c**



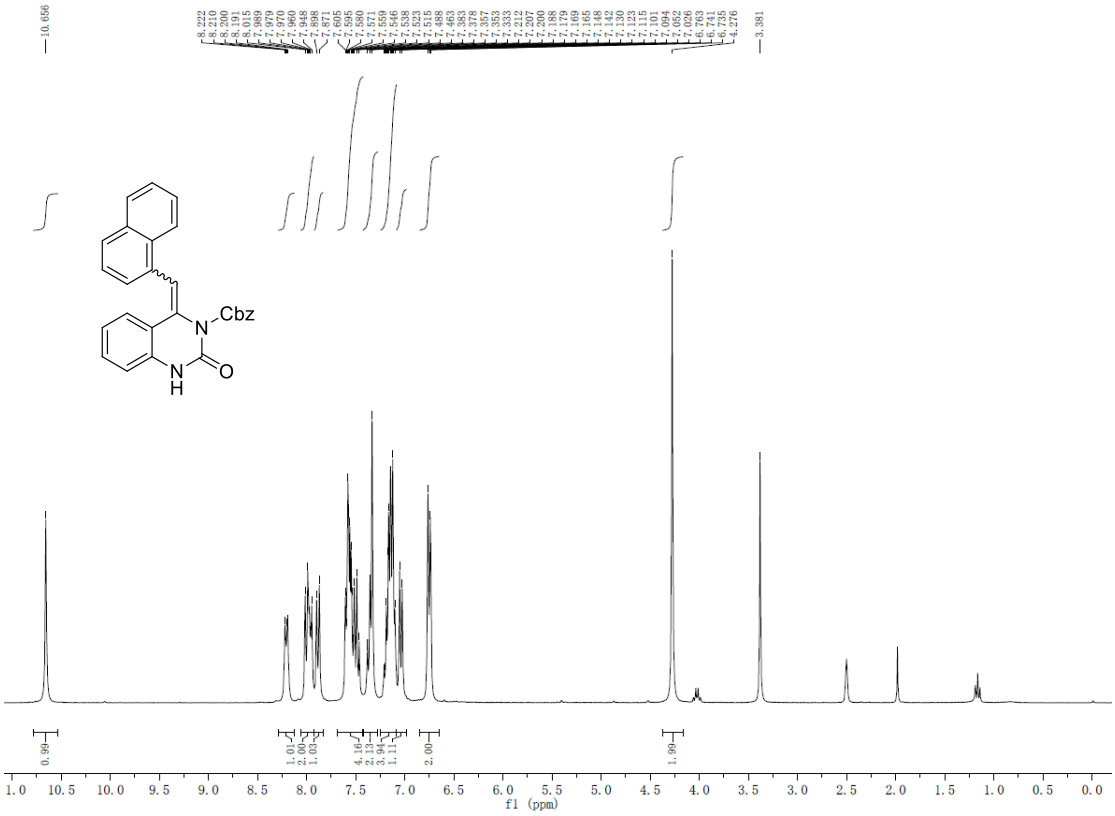


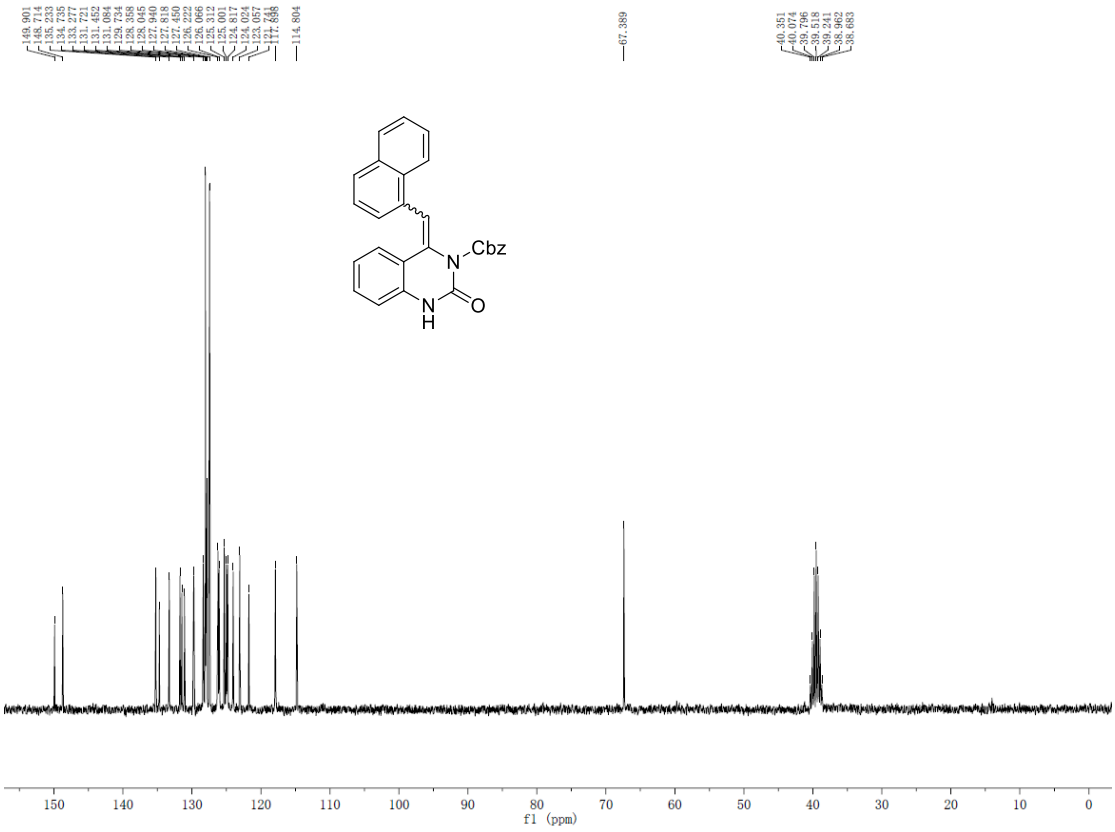
^{1}H NMR and ^{13}C NMR of **4d**



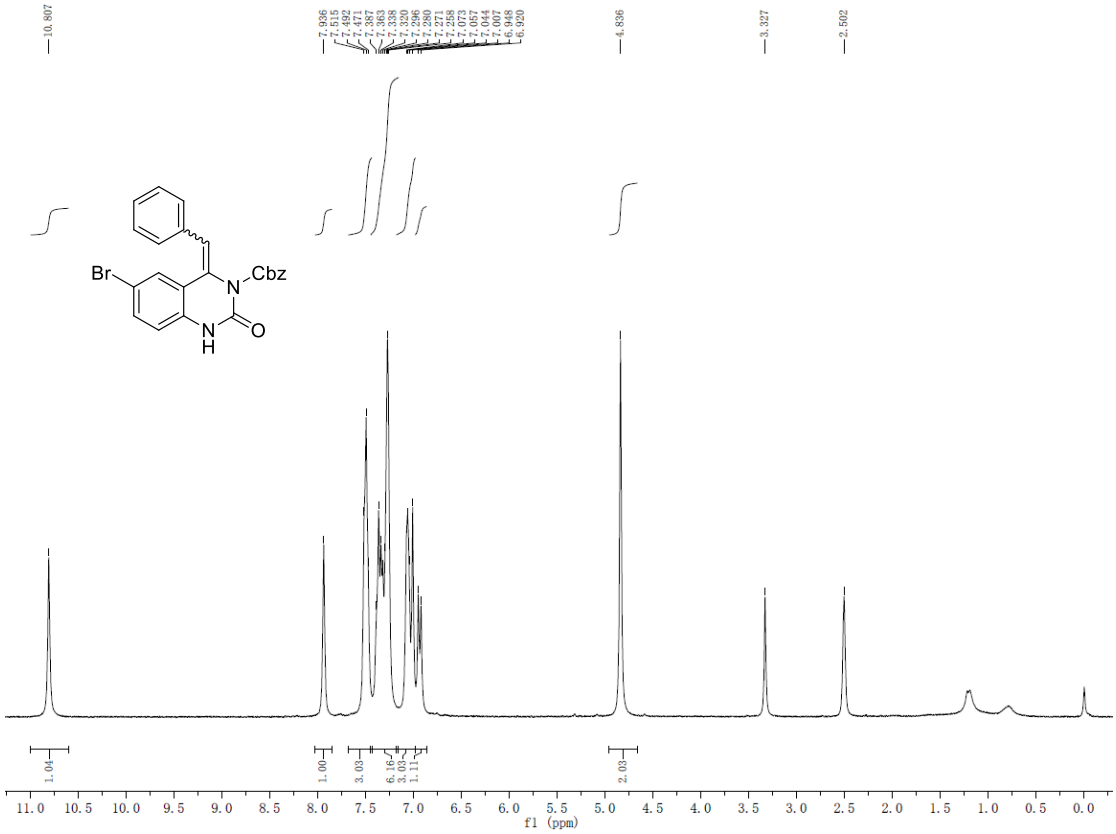


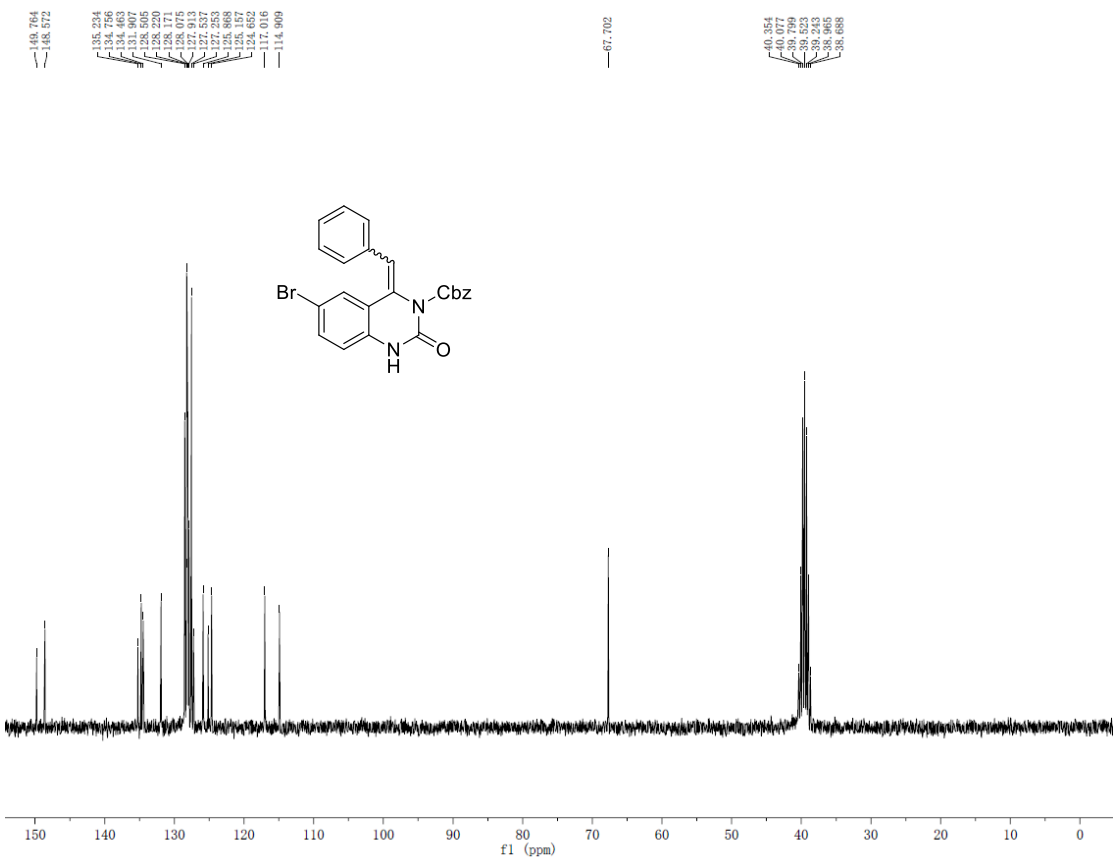
^{1}H NMR and ^{13}C NMR of **4e**



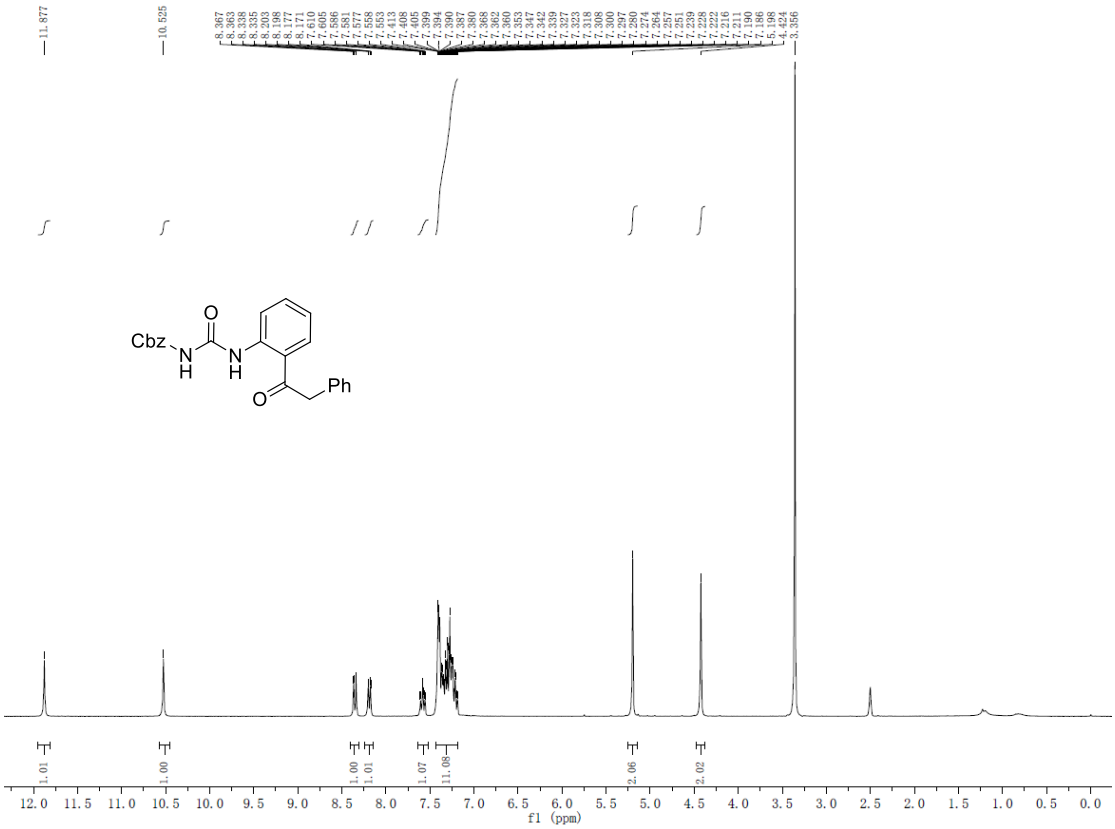


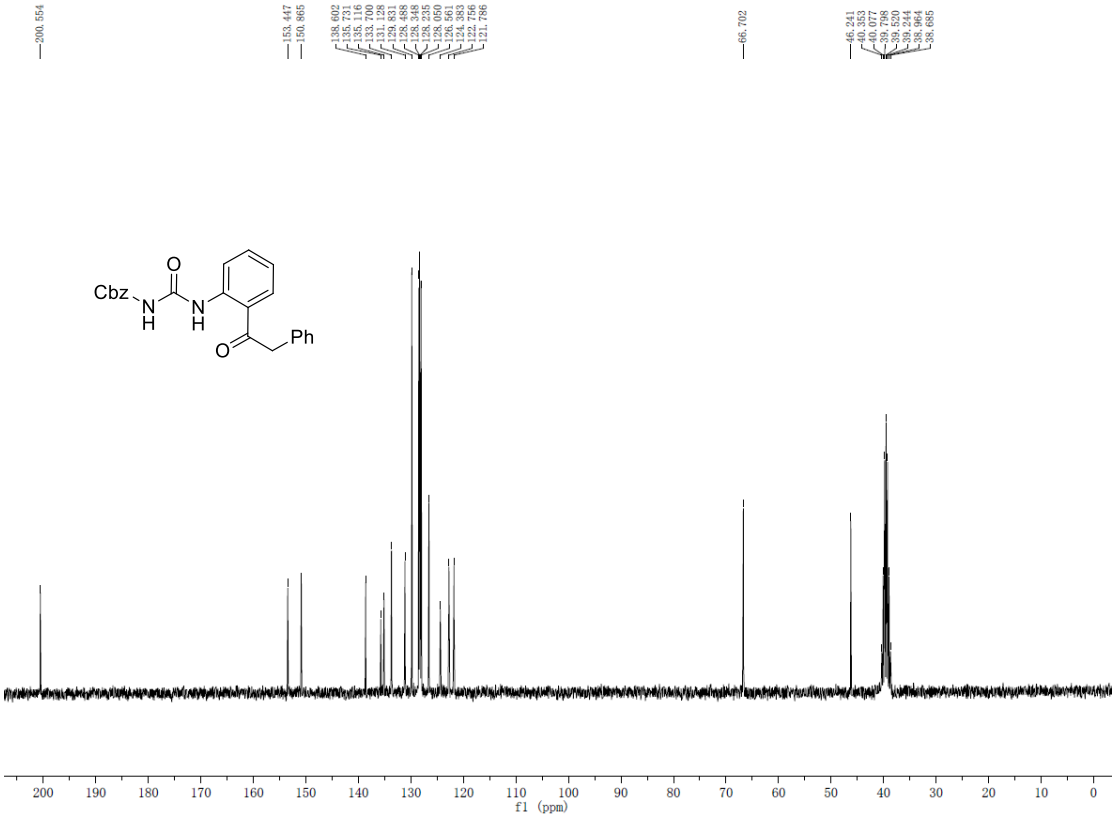
^{1}H NMR and ^{13}C NMR of **4f**



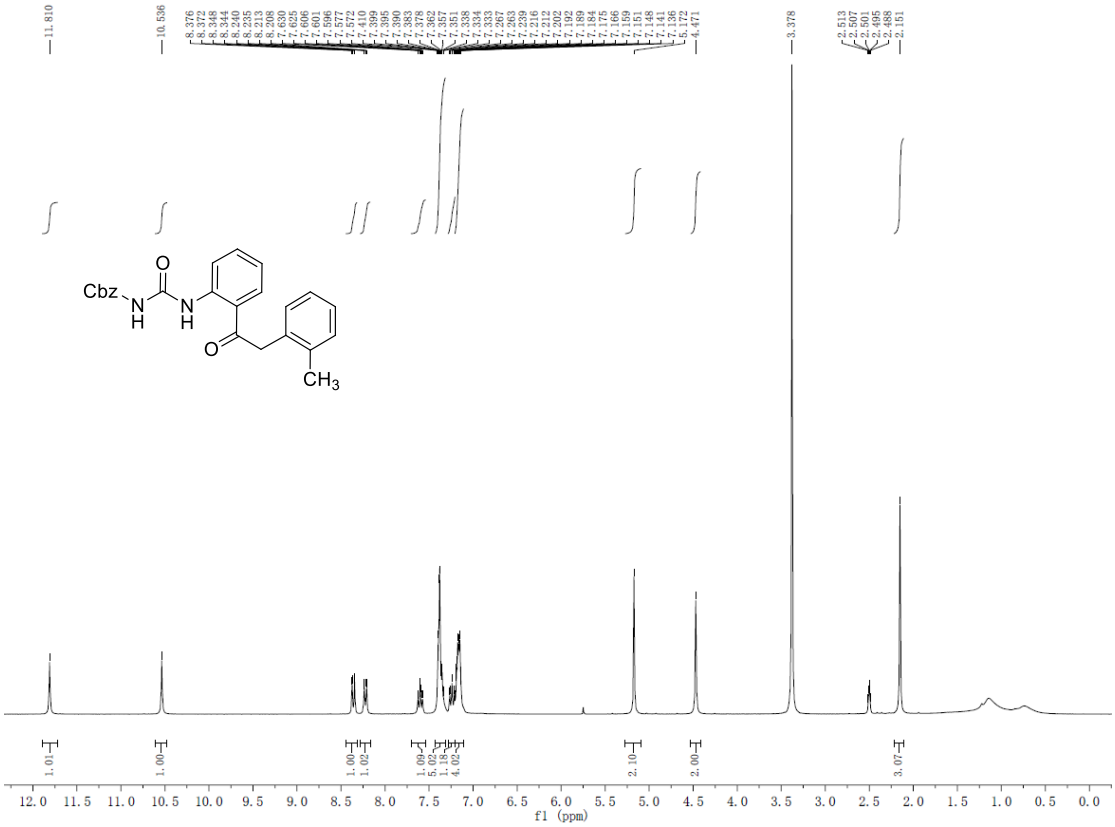


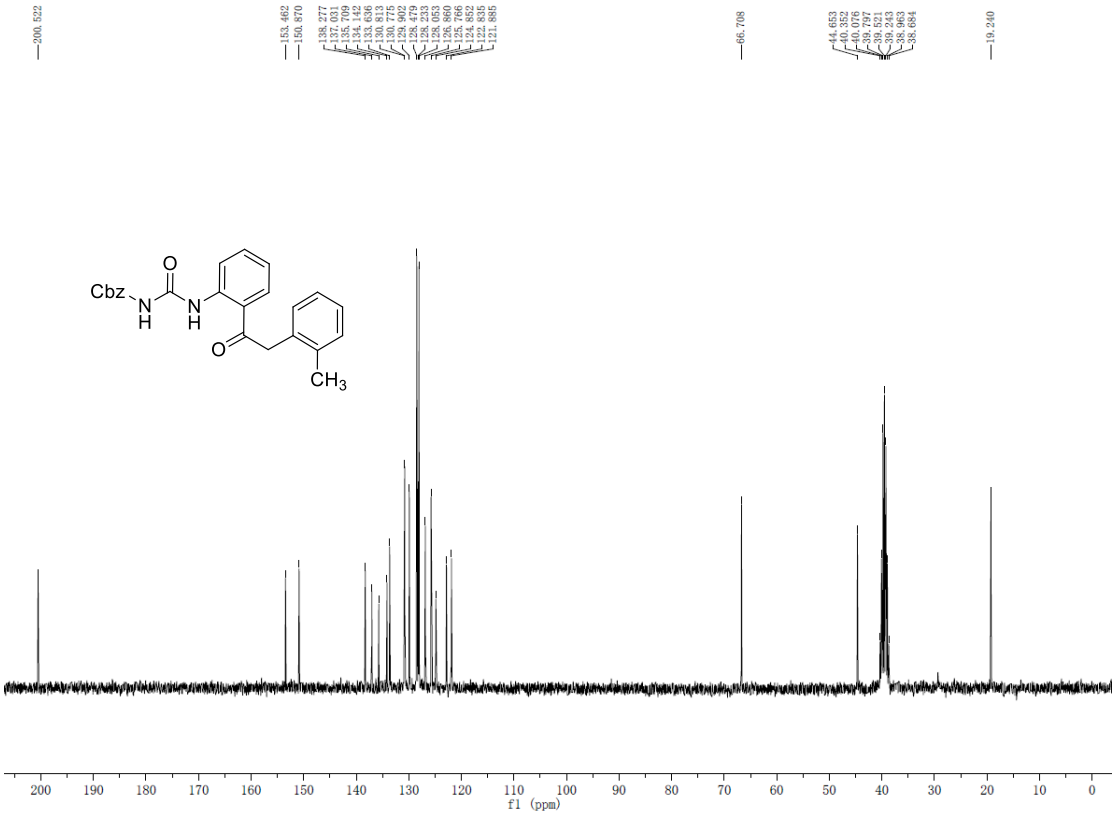
^{1}H NMR and ^{13}C NMR of **5a**



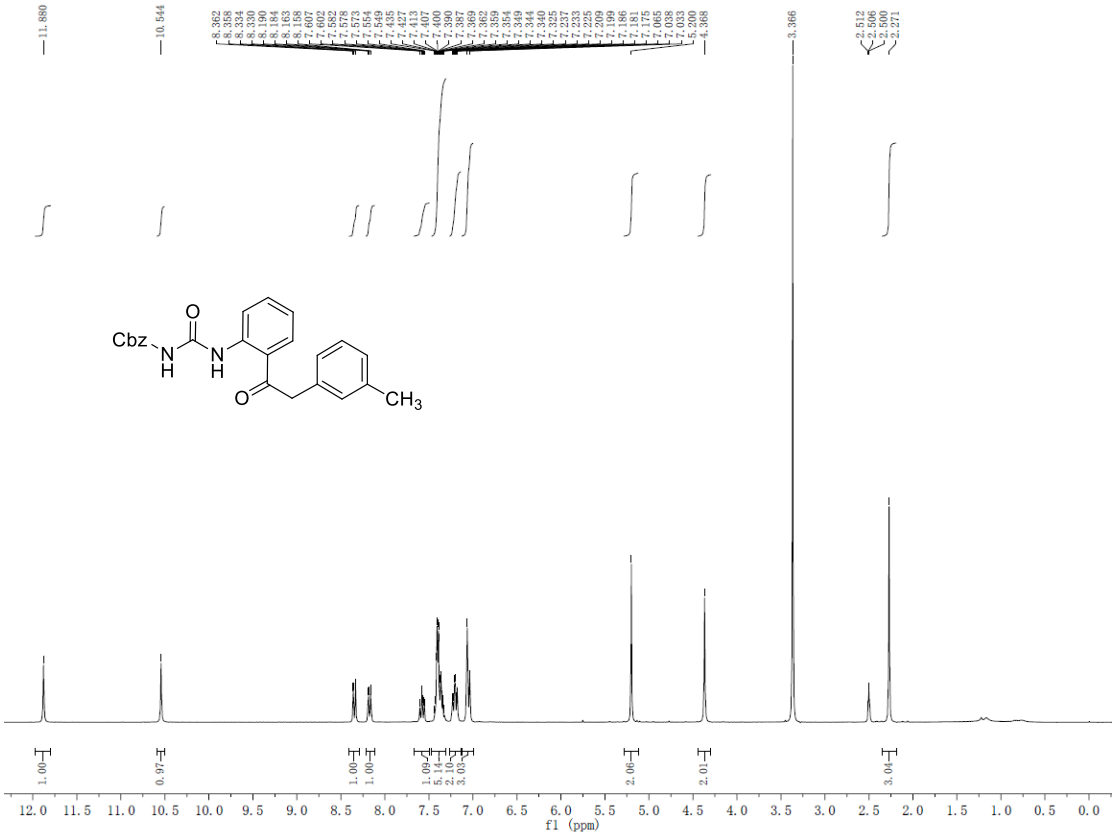


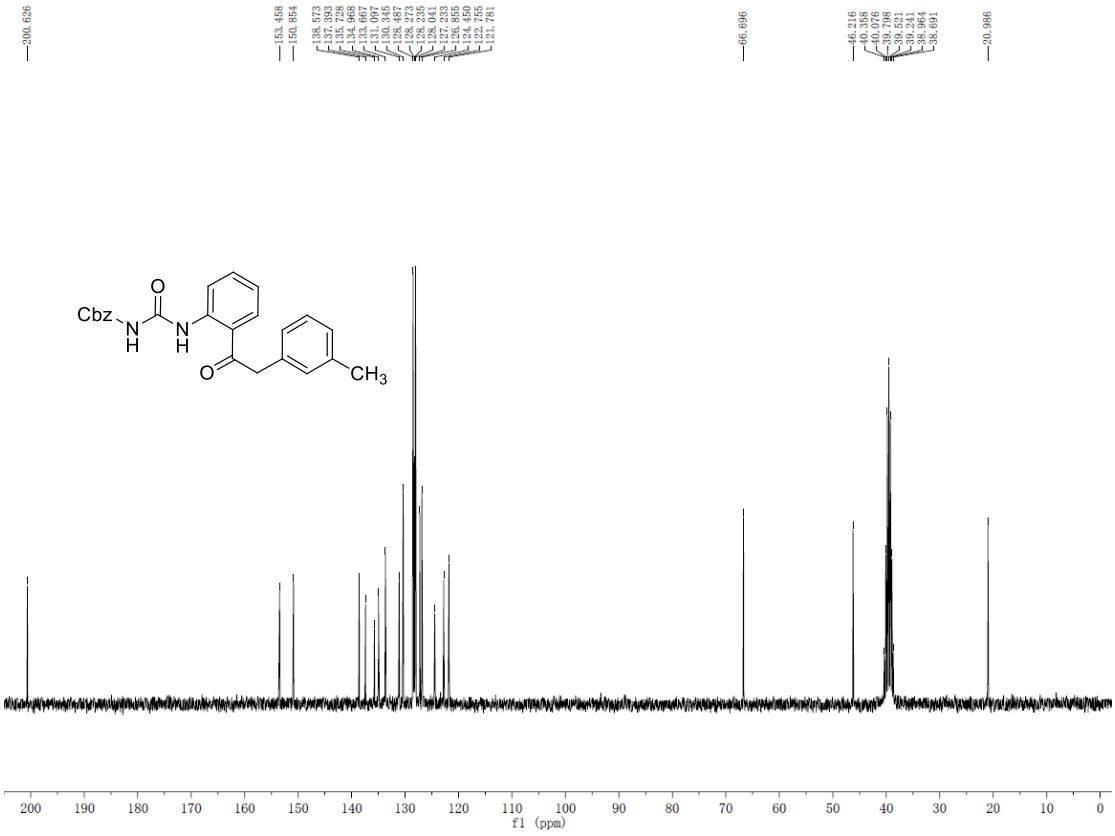
^{1}H NMR and ^{13}C NMR of **5b**



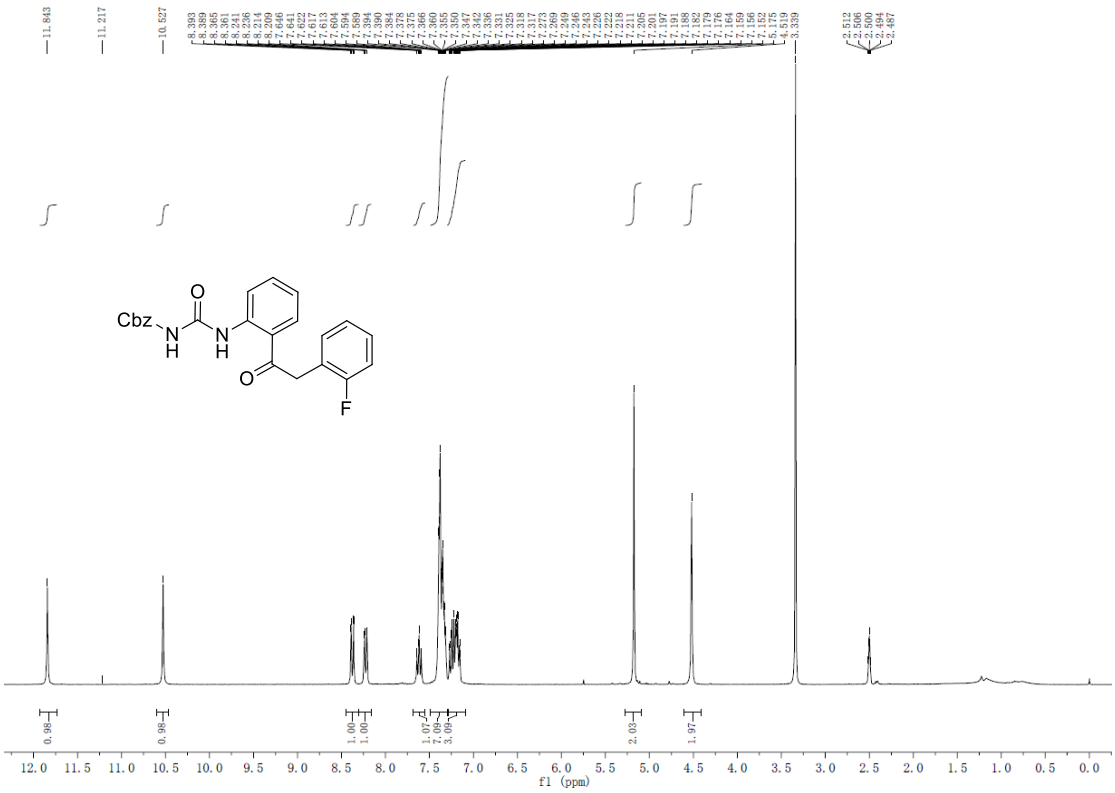


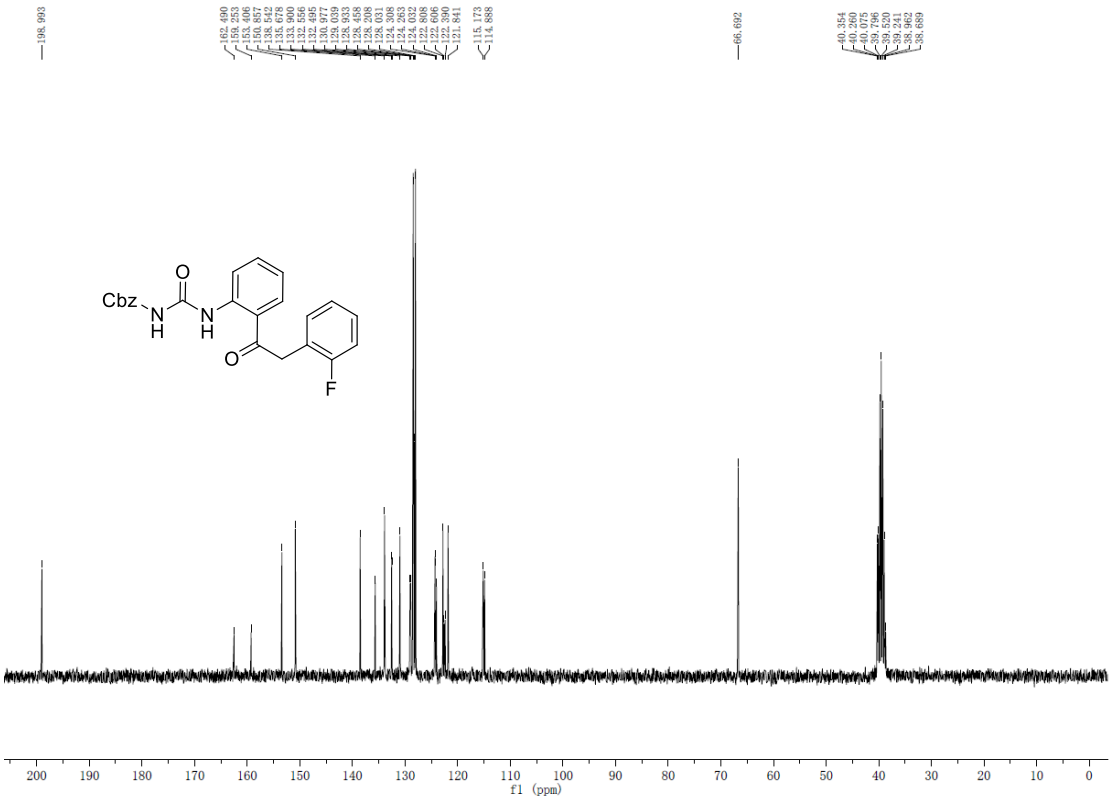
^{1}H NMR and ^{13}C NMR of **5c**



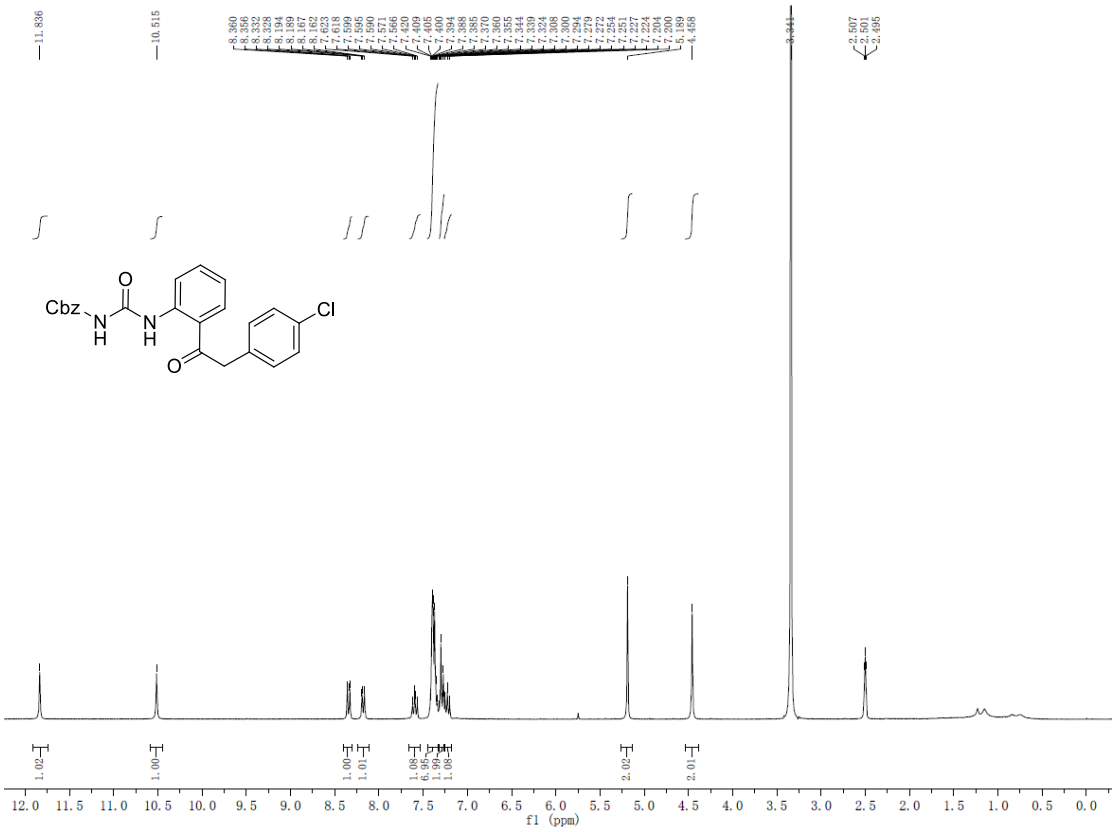


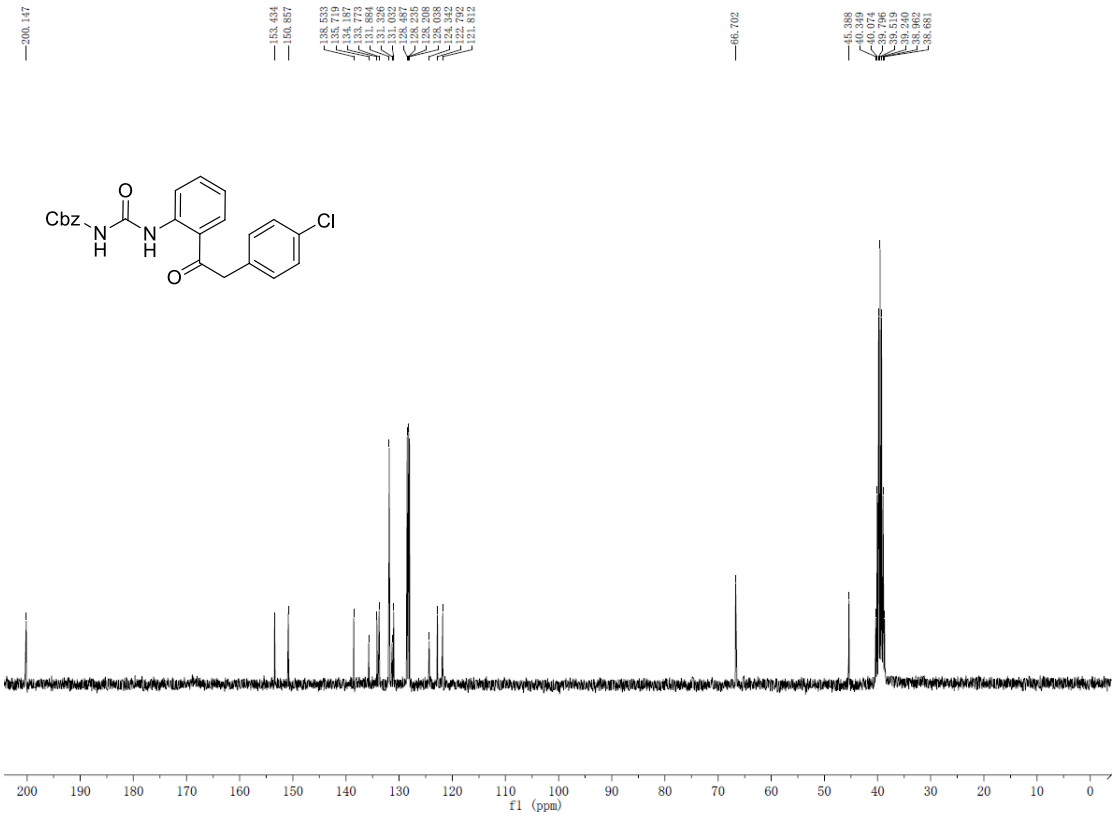
^{1}H NMR and ^{13}C NMR of **5d**



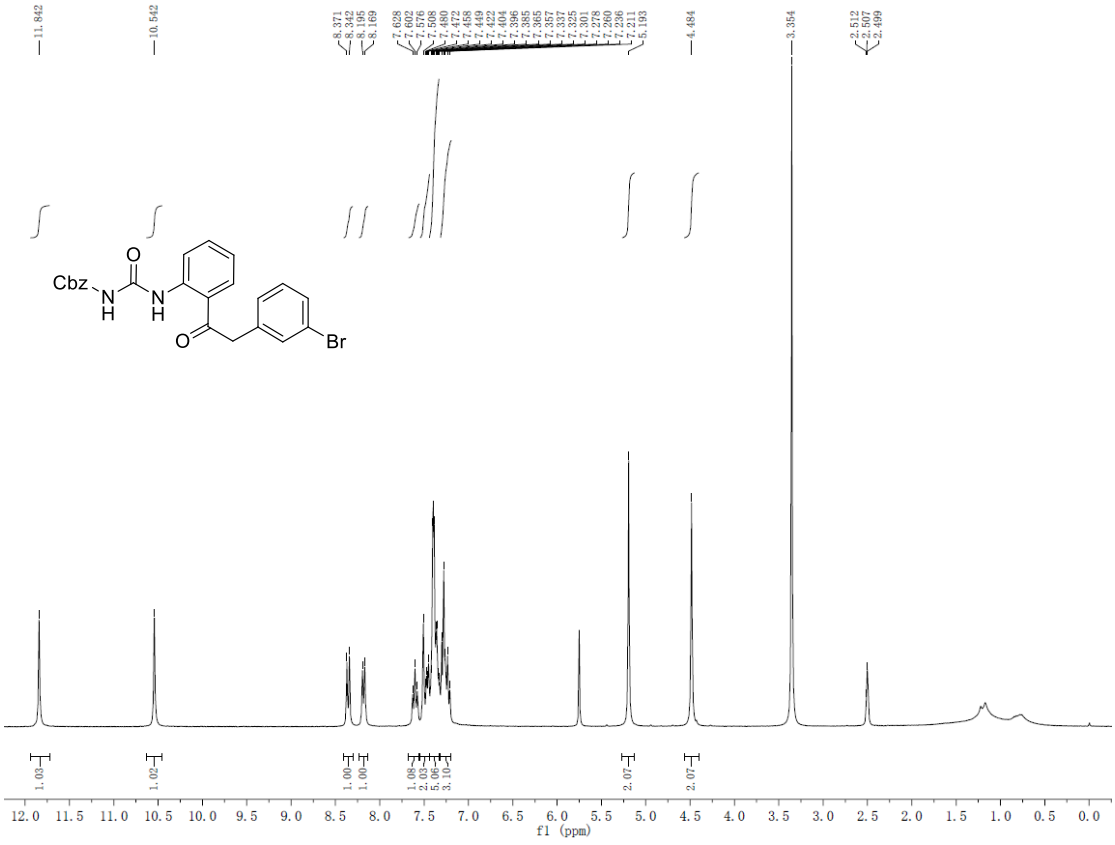


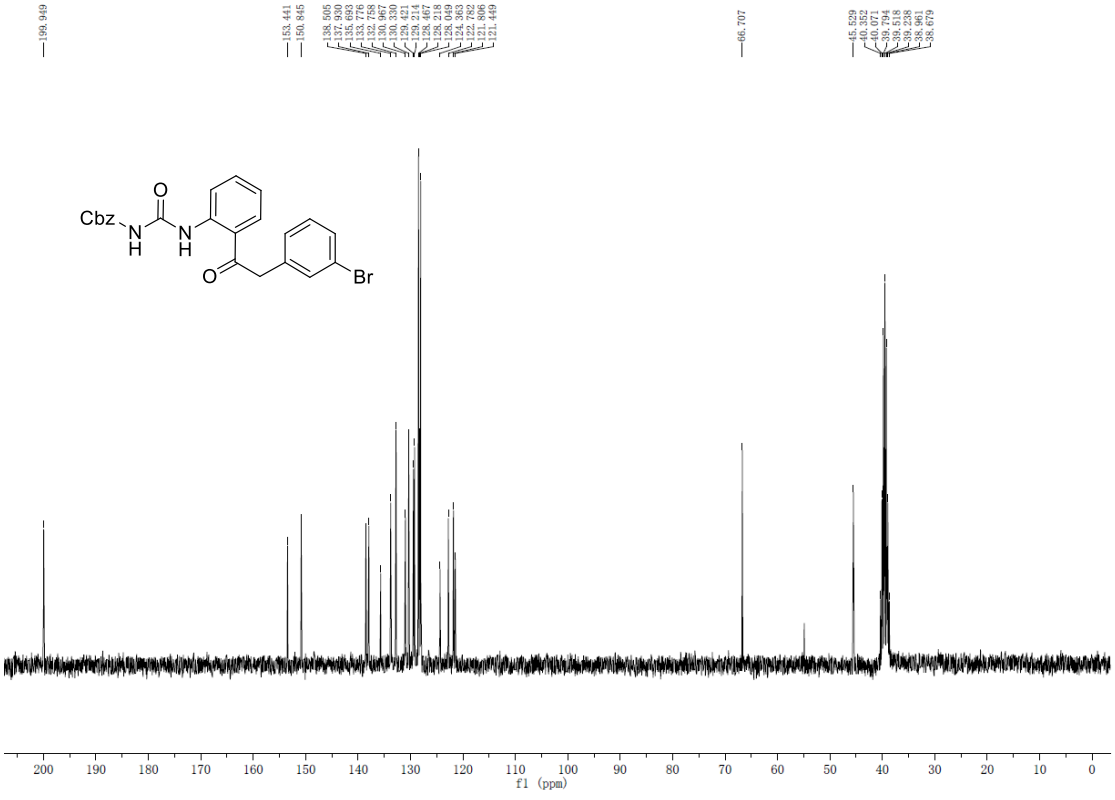
^{1}H NMR and ^{13}C NMR of **5e**



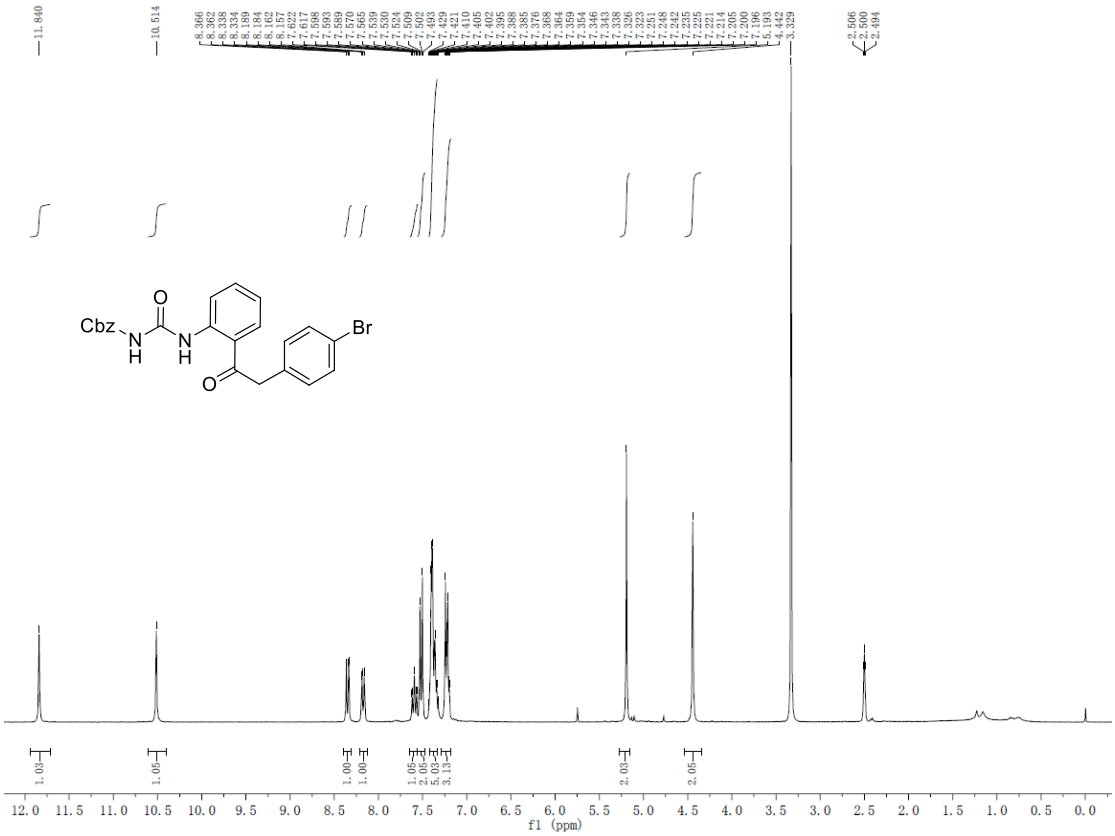


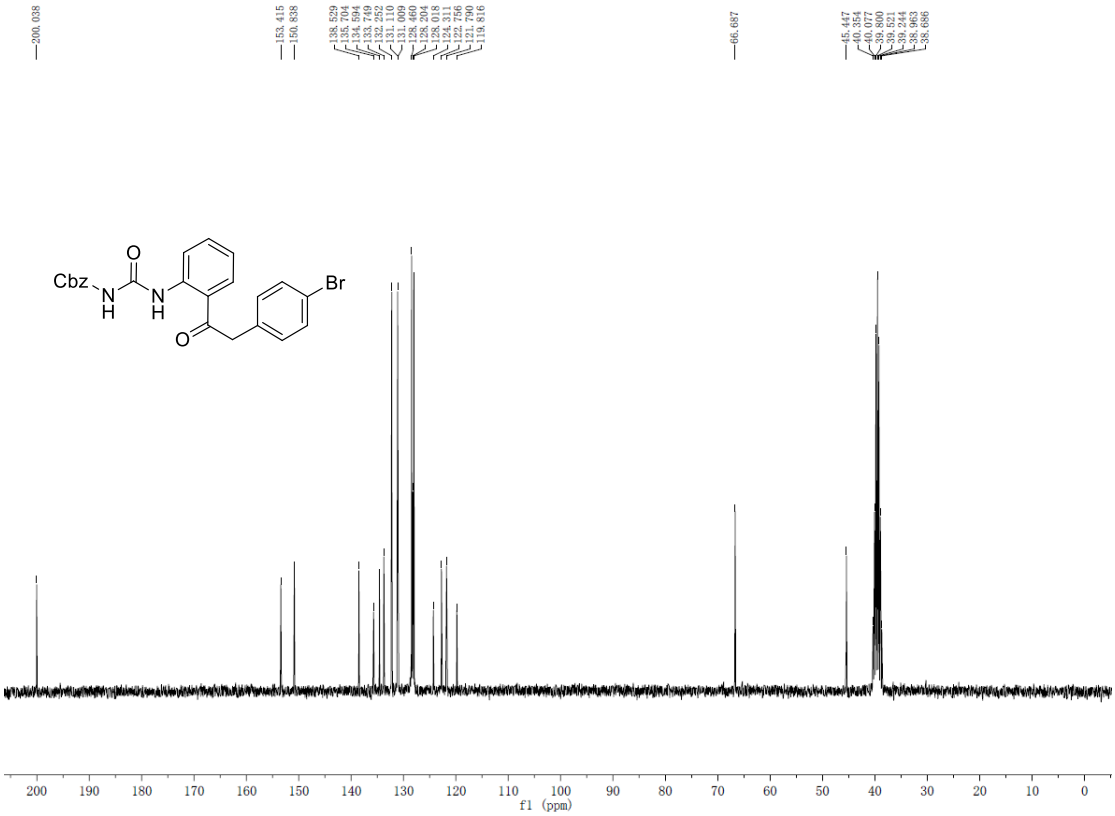
^{1}H NMR and ^{13}C NMR of **5f**



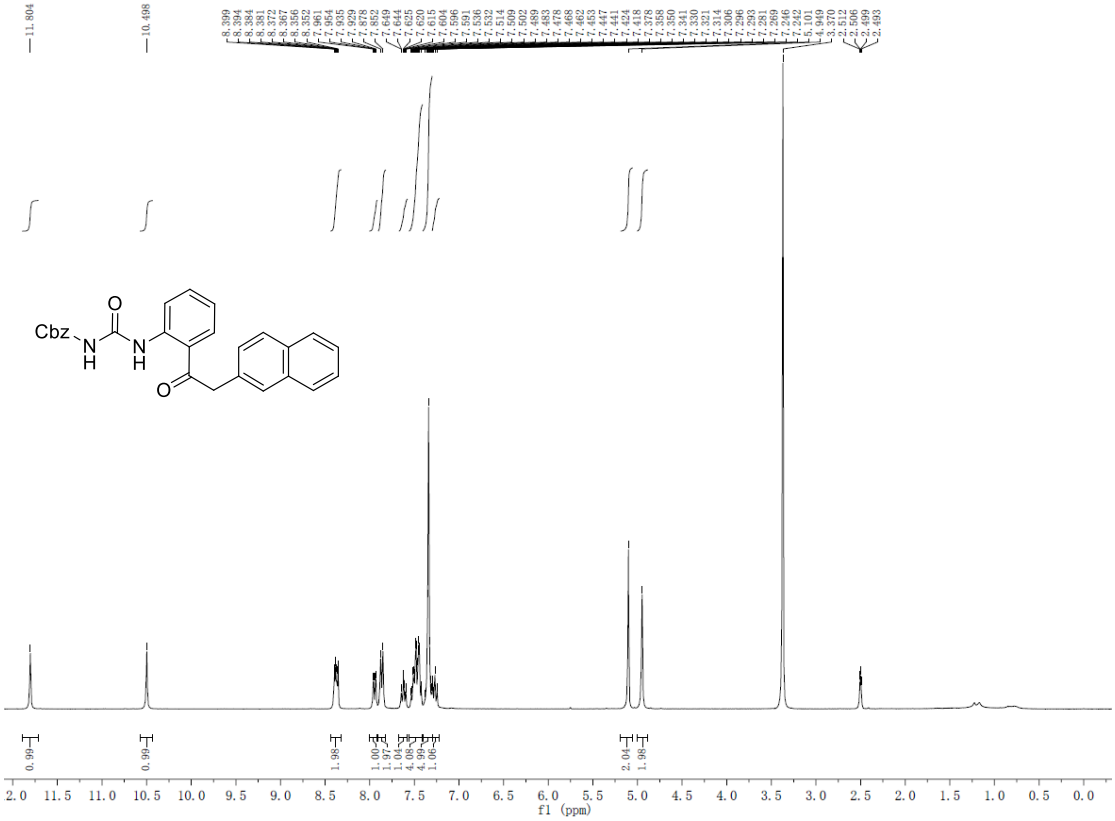


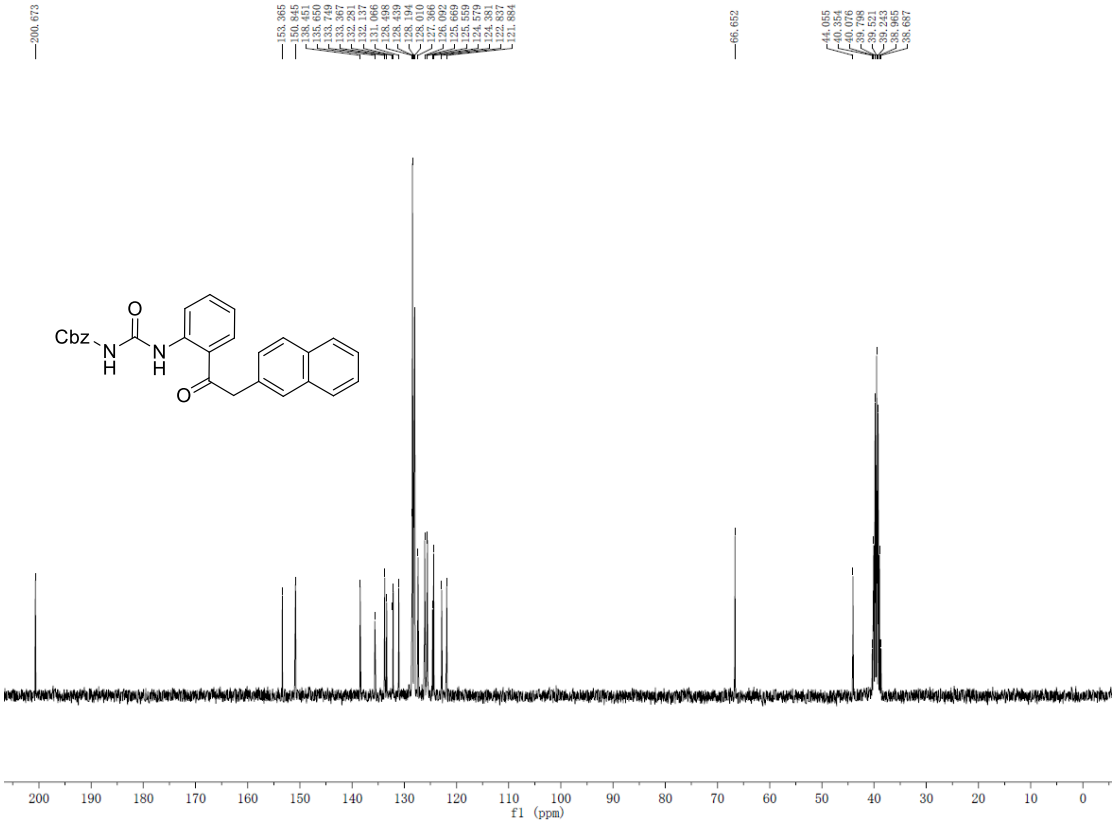
^{1}H NMR and ^{13}C NMR of **5g**



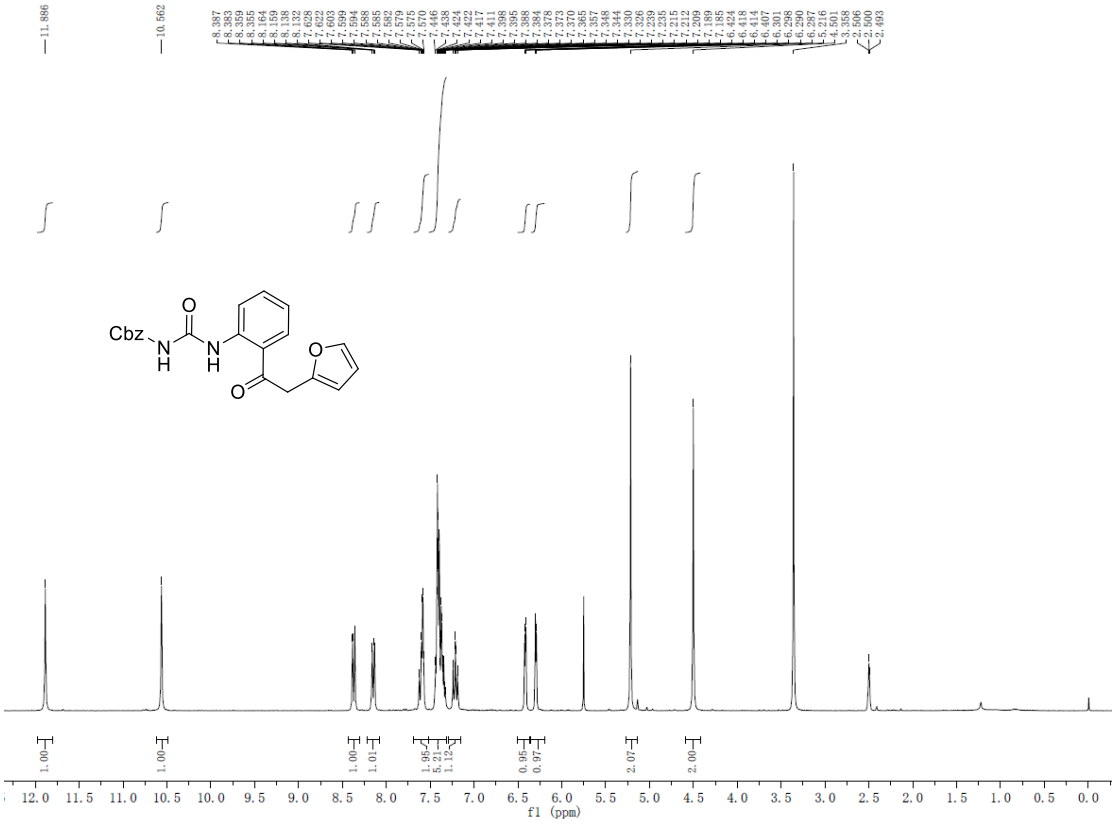


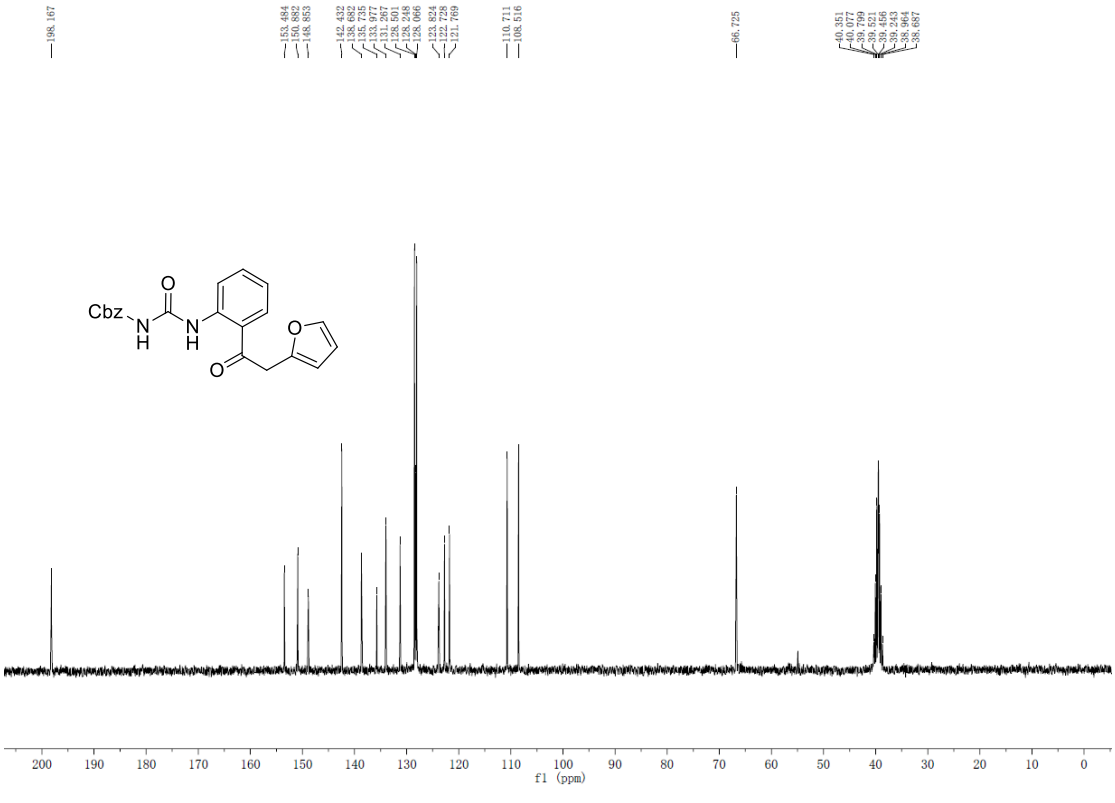
^{1}H NMR and ^{13}C NMR of **5h**



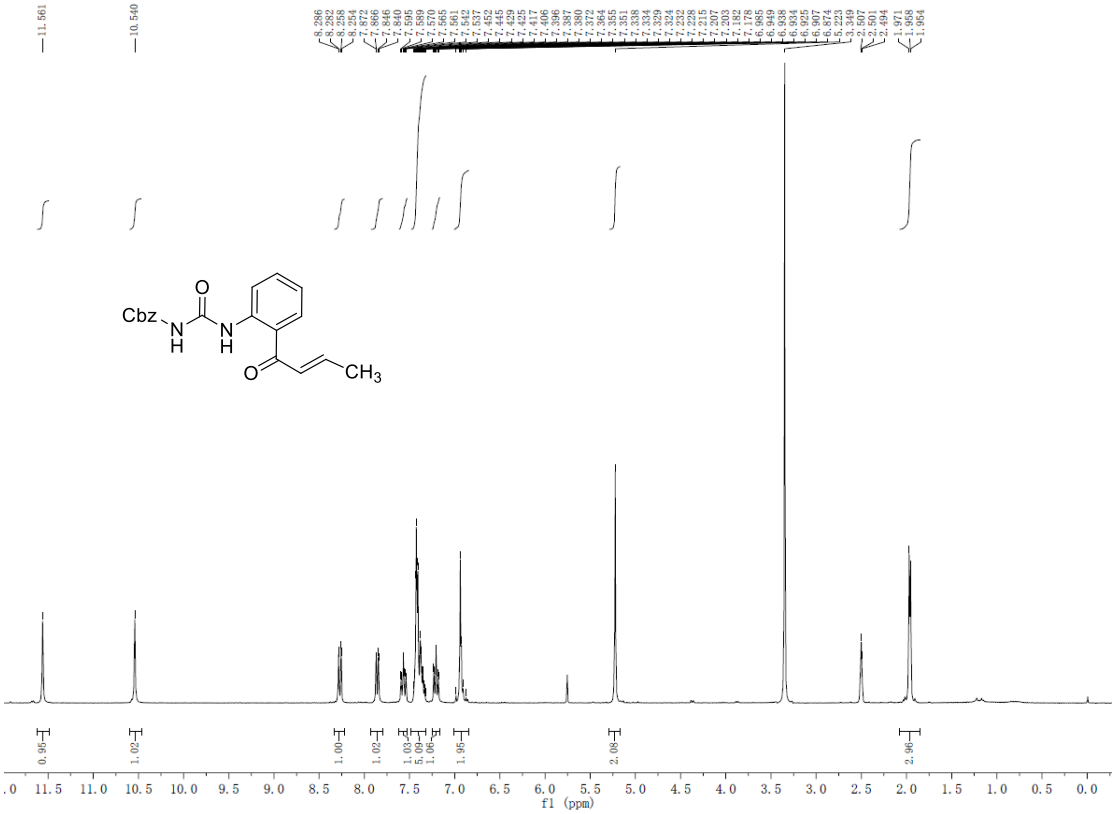


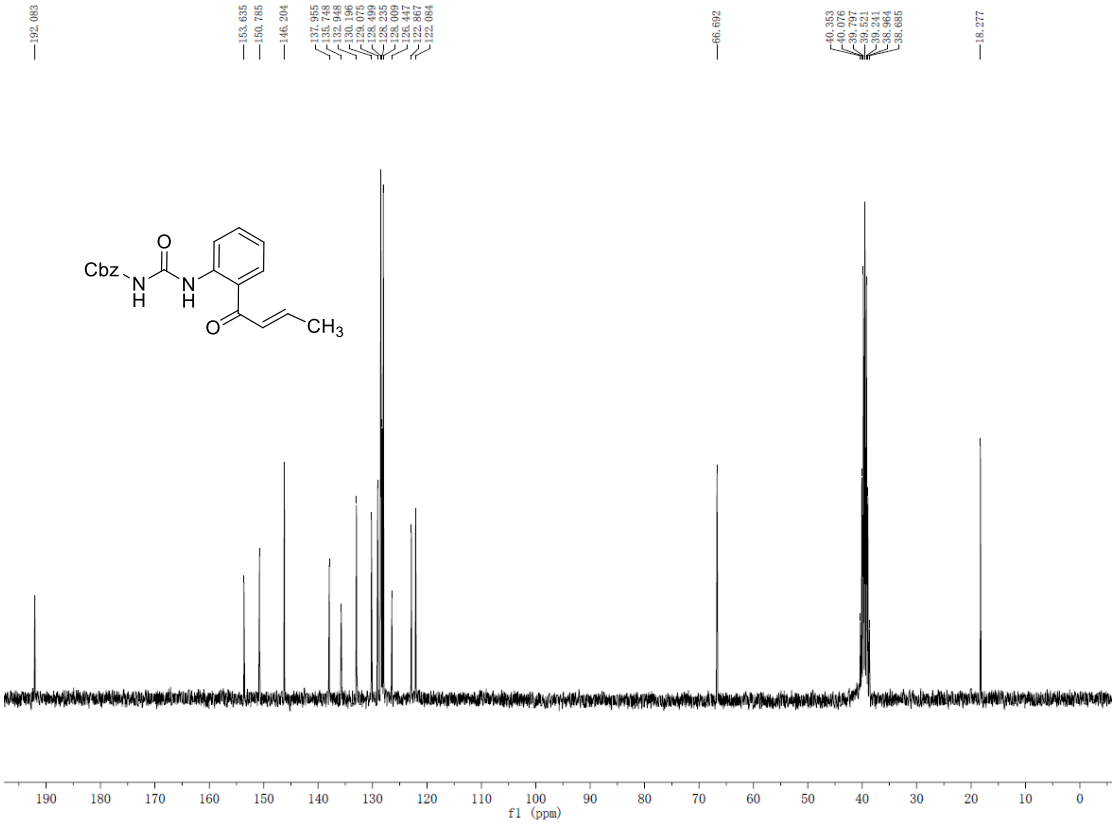
^{1}H NMR and ^{13}C NMR of **5i**



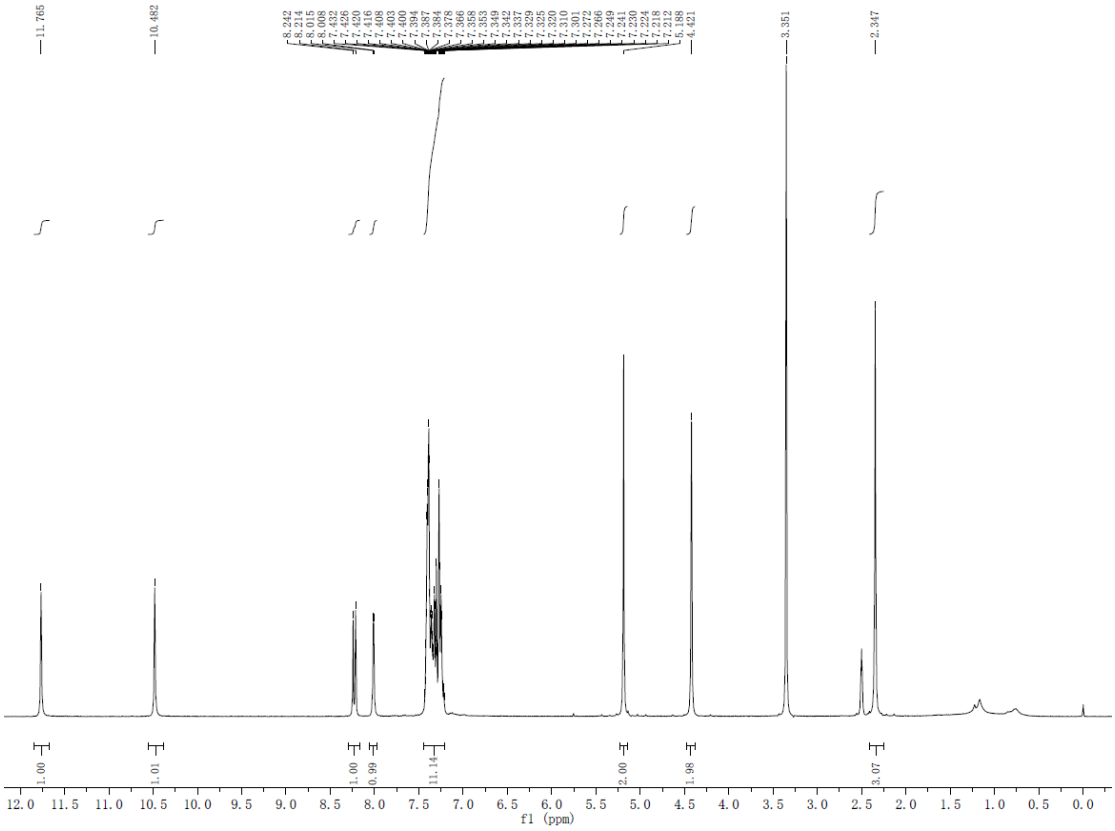


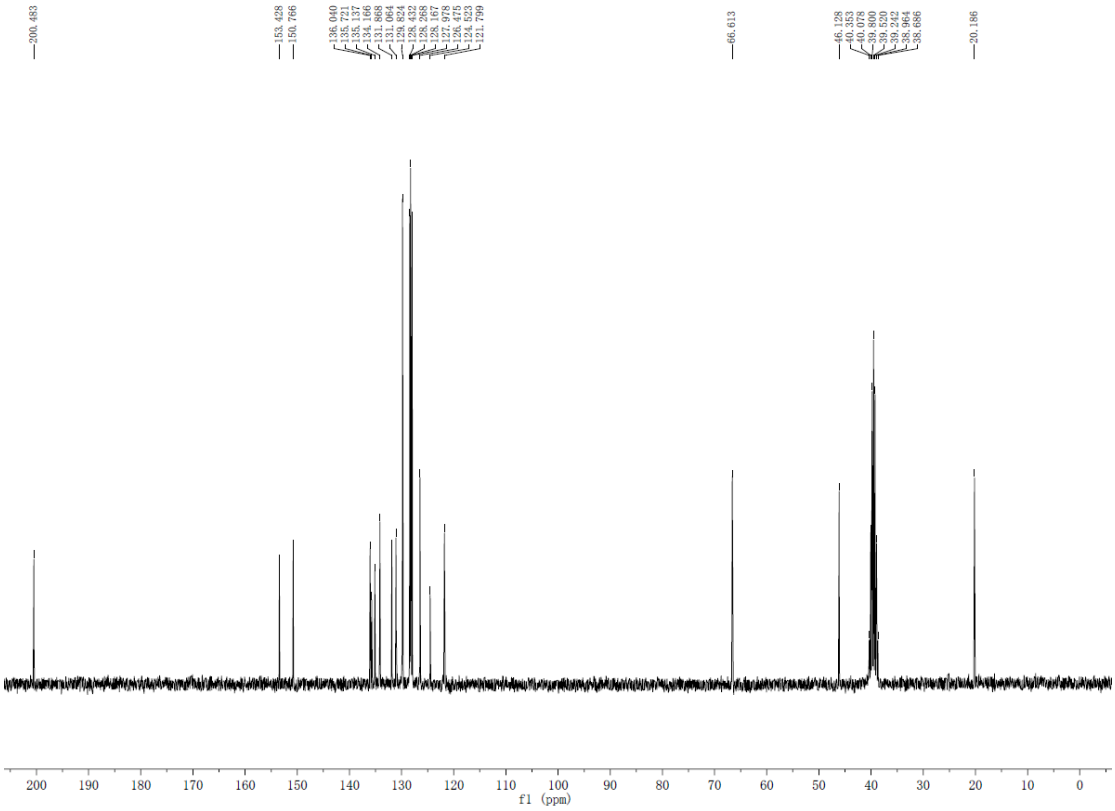
^{1}H NMR and ^{13}C NMR of **5j**



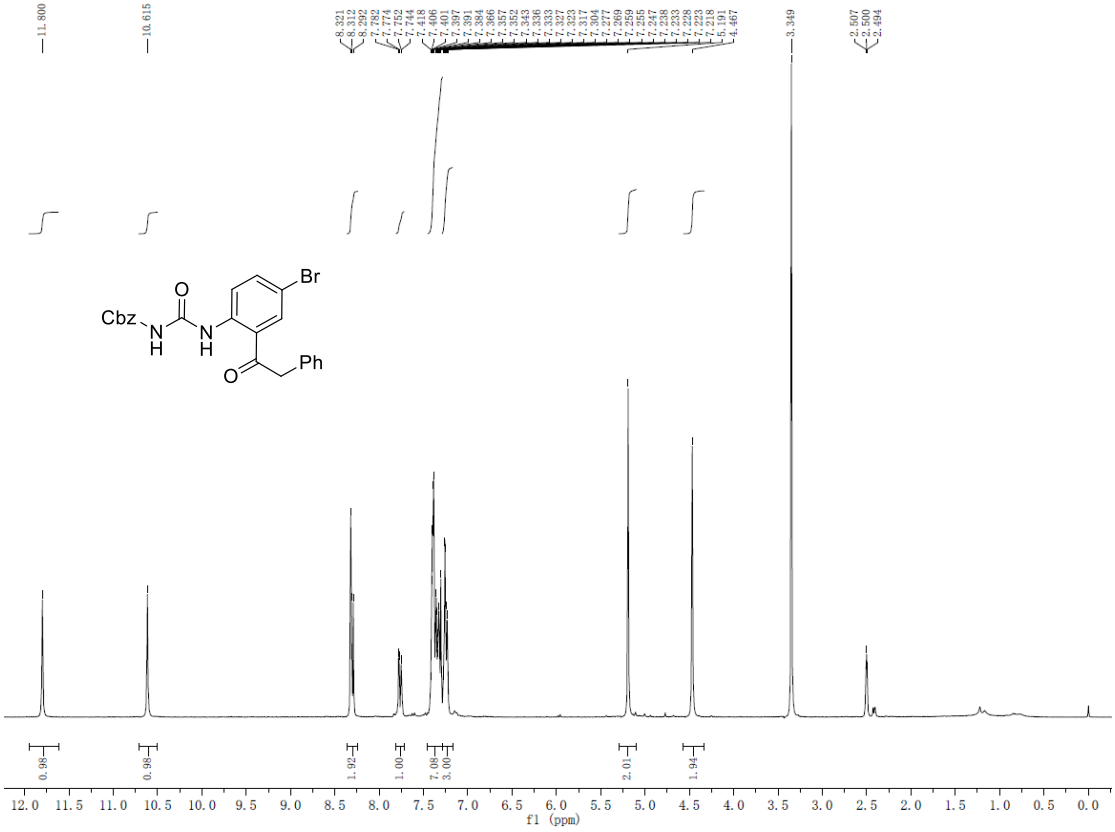


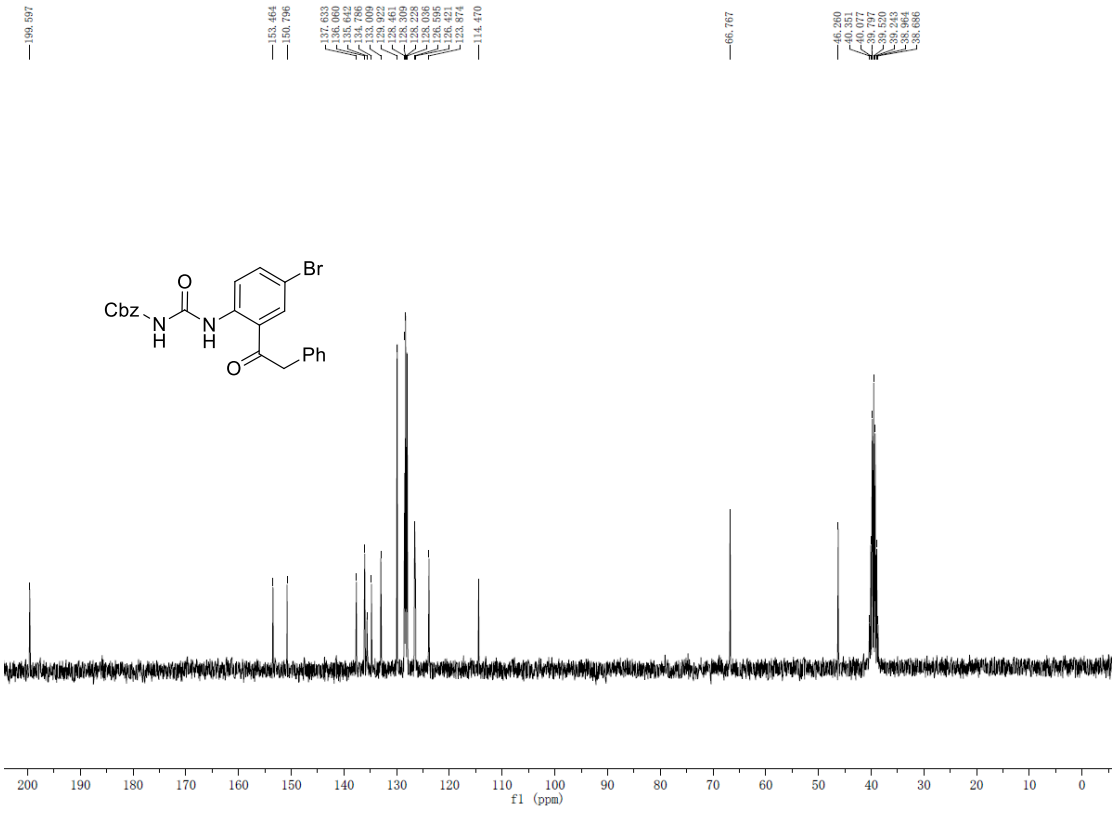
^{1}H NMR and ^{13}C NMR of **5k**





^{1}H NMR and ^{13}C NMR of **5l**





^{1}H NMR and ^{13}C NMR of **6**