Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Site-selective oxidative C−H sulfonylation of 8-acylaminoquinolines and anilides under metal-free conditions

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Supplementary Information

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EXPERIMENTAL SECTION

Instrumentation and chemicals

^{1}H NMR, ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer with $CDCl_3$ as the solvent and TMS as an internal standard, operating at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR. Melting points were measured by SGW X-4A microscopic apparatus. HRMS-ESI were measured by Q Exactive LC/HRMS spectrometer.

Dichloromethane, ethyl acetate and hexane were obtained from commercial sources and used for column chromatography without further purification. Other solvents were purified according to the standard methods. Other chemicals were obtained from commercial sources and used as received unless otherwise noted. All the 8-acylaminoquinolines and anilides were synthesized through the coupling between corresponding aryl or alkyl acids and 8-aminoquinoline or anilines according to literature procedures. [1–5]

General procedures

General procedure for the sulfonylation of 8-acylaminoquinolines or anilides. To a mixture of 8-acylaminoquinoline or anilide (0.2 mmol) in THF (2 mL), sulfonyl chloride (0.6 mmol), $PhI(OPiv)_2$ (0.8 mmol) were added. The resulting mixture was stirred at 75 °C for 8 h. After the reaction was completed, the mixture was added into H_2O (10 mL) and extracted with dichlormethane (15 mL) for three times. The combined organic layer was dried over anhydrous Na_2SO_4 and filtered. After removal of the solvent *in vacuo*, the residue was purified by column chromatography (ethyl acetate/hexane) to afford the pure product.

Characterization Data

***N*-(5-Tosylquinolin-8-yl)benzamide (3aa).**[1]

Yellow solid, mp 179–181 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.46 (s, 3H), 7.03 (d, J = 8.60 Hz, 1H), 7.32–7.34 (m, 2H), 7.49–7.61 (m, 4H), 7.76–7.68 (m, 2H), 8.05 (d, J = 7.36 Hz, 2H), 8.41 (d, J = 8.44 Hz, 1H), 8.79 (d, J = 8.56 Hz, 1H), 8.86–8.87 (m, 1H), 10.66 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.7, 115.3, 119.9, 122.2, 123.0, 127.3, 128.7, 128.9, 130.0, 131.4, 132.1, 132.2, 133.9, 134.9, 138.9, 139.7, 145.8, 149.0, 165.5.

4-Methoxy-N-(5-tosylquinolin-8-yl)benzamide (3ba).[1]

White solid, mp 179–181 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.45 (s, 3H), 3.89 (s, 3H), 7.02–7.04 (m, 2H), 7.31–7.33 (m, 2H), 7.49 (dd, J = 8.44 Hz, J = 4.16 Hz, 1H), 7.75–7.77 (m, 3H), 8.02 (d, J = 8.36 Hz, 2H), 8.38 (d, J = 8.44 Hz, 1H), 8.76 (d, J = 8.56 Hz, 1H), 8.84 (d, J = 3.68 Hz, 1H), 10.58 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.7, 55.5, 114.1, 115.0, 120.0, 122.2, 123.0, 127.8, 128.7, 129.2, 130.0, 132.1, 134.1, 138.9, 139.4, 144.9, 145.8, 148.9, 162.7, 165.0.

4-Fluoro-N-(5-tosylquinolin-8-yl)benzamide (3ca).[2]

Yellow solid, mp 172–174 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.46 (s, 3H), 7.03 (d, J = 8.60 Hz, 1H), 7.21–7.23 (m, 2H), 7.32–7.36 (m, 2H), 7.32 (dd, J = 8.44 Hz, J = 4.16 Hz, 1H), 7.77 (d, J = 7.92 Hz, 2H), 8.05–8.09 (m, 2H), 8.41 (d, J = 8.44 Hz, 1H), 8.76 (d, J = 8.60 Hz, 1H), 8.86 (d, J = 3.96 Hz, 1H), 10.61 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 115.3, 115.9 (d, J = 21.89 Hz), 119.9, 122.3, 123.1, 127.9, 128.7, 129.7 (d, J = 9.00 Hz), 130.0, 131.0 (d, J = 3.06 Hz), 131.5, 132.1, 133.7, 138.9, 139.7, 145.9, 149.0, 164.4, 165.1 (d, J = 251.38 Hz).

4-Chloro-*N*-(5-tosylquinolin-8-yl)benzamide (3da).

Light yellow solid, mp 159–161 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.46 (s, 3H), 7.03 (d, J = 8.56 Hz, 1H), 7.32–7.34 (m, 2H), 7.50–7.53 (m, 3H), 7.76–7.78 (m, 2H), 7.98–8.00 (m, 2H), 8.41 (d, J = 8.48 Hz, 1H), 8.76 (d, J = 8.56 Hz, 1H), 8.86 (d, J = 4.12 Hz, 1H), 10.62 (s,1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.7, 114.3, 118.9, 121.3, 122.0, 127.6, 127.7, 128.1, 129.0, 130.5, 131.0, 132.1, 132.6, 137.4, 137.8, 138.8, 144.8, 148.0, 163.3. HRMS-ESI (m/z): calcd for $C_{23}H_{18}ClN_2O_3S^+$, 437.0721, found 437.0725.

4-Bromo-*N*-(5-tosylquinolin-8-yl)benzamide (3ea).[1]

White solid, mp 182–183 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.46 (s, 3H), 7.03 (d, J = 8.60 Hz, 1H), 7.32–7.34 (m, 2H), 7.51 (dd, J = 8.40 Hz, J = 4.12 Hz, 1H), 7.67–7.69 (m, 2H), 7.76–7.78 (m, 2H), 7.90–7.92 (m, 2H), 8.40 (d, J = 8.44 Hz, 1H), 8.75 (d, J = 8.56 Hz, 1H), 8.86 (d, J = 3.04 Hz, 1H), 10.62 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.7, 115.4, 119.9, 122.3, 123.0, 126.9, 128.7, 128.9, 130.0, 131.5, 132.0, 132.1, 133.6, 133.7, 138.9, 139.8, 145.9, 149.1, 164.5.

N-(5-tosylquinolin-8-yl)-4-(trifluoromethyl)benzamide (3fa).[1]

White solid, mp 202–204 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.47 (s, 3H), 7.05 (d, J = 8.60 Hz, 1H), 7.33–7.35 (m, 2H), 7.53 (dd, J = 8.48 Hz, J = 4.20 Hz, 1H), 7.77–7.83 (m, 4H), 8.15–8.17 (m, 2H), 8.42 (d, J = 8.52 Hz, 1H), 8.78 (d, J = 8.60 Hz, 1H), 8.87 (d, J = 4.08 Hz, 1H), 10.69 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.8, 115.6, 119.9, 122.4, 123.1, 126.0 (q, J = 3.59 Hz), 127.8,

128.7, 130.0, 131.6, 132.1, 133.4, 133.7 (d, J = 32.51 Hz), 137.2, 138.1, 138.9, 140.0, 145.9, 149.1, 164.1.

***N*-(5-Tosylquinolin-8-yl)acetamide (3ga)**.[1]

White solid, mp 162–165 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.34 (s, 3H), 2.45 (s, 3H), 6.95 (d, J = 8.60 Hz, 1H), 7.31–7.33 (m, 2H), 7.48 (dd, J = 8.48 Hz, J = 4.20 Hz, 1H), 7.74–7.76 (m, 2H), 8.38 (d, J = 8.48 Hz, 1H), 8.61 (d, J = 8.56 Hz, 1H), 8.81 (d, J = 4.04 Hz, 1H), 9.72 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.7, 25.1, 115.1, 119.8, 122.2, 122.9, 128.7, 130.0, 131.4, 132.1, 133.8, 138.4, 139.5, 145.8, 148.8, 168.8.

***N*-(5-Tosylquinolin-8-yl)propionamide (3ha)**.[3]

Yellow solid, mp 152–154 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32 (t, J = 7.52 Hz, 3H), 2.45 (s, 3H), 2.59 (q, J = 7.52 Hz, 2H), 6.96 (d, J = 8.60 Hz, 1H), 7.33–7.34 (m, 2H), 7.48 (dd, J = 8.44 Hz, J = 4.16 Hz, 1H), 7.76–7.77 (m, 2H), 8.38 (d, J = 8.48 Hz, 1H), 8.63 (d, J = 8.60 Hz, 1H), 8.81 (d, J = 4.12 Hz, 1H), 9.75 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 9.7, 21.7, 31.2, 115.1, 119.9, 122.1, 122.9, 128.7, 130.0, 131.4, 132.1, 133.9, 138.5, 139.4, 145.8, 148.8, 172.6.

***N*-(5-Tosylquinolin-8-yl)butanamide (3ia)**.[3]

Yellow solid, mp 151–153 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05 (t, J = 7.36 Hz, 3H), 1.79–1.88 (m , 2H), 2.45 (s, 3H), 2.53 (t, J = 7.44 Hz, 2H), 6.95 (d, J = 8.60 Hz, 1H), 7.31–7.33 (m, 2H), 7.48 (dd, J = 8.44 Hz, J = 4.16 Hz, 1H), 7.74–7.76 (m, 2H), 8.38 (d, J = 8.48 Hz, 1H), 8.63 (d, J = 8.60 Hz, 1H), 8.81 (d, J = 4.00 Hz, 1H), 9.74 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.8, 18.0, 20.7, 39.1, 114.1, 118.8, 121.1, 121.9, 127.6, 128.9, 130.4, 131.1, 132.8, 137.4, 138.3, 144.8, 147.8, 170.8.

***N*-(5-Tosylquinolin-8-yl)hydrocinnamionamide (3ja)**.

Yellow solid, mp 187–189 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.45 (s, 3H), 2.87 (t, J = 8.04 Hz, 2H), 3.12 (t, J = 7.56 Hz, 2H), 6.96 (d, J = 8.60 Hz, 1H), 7.20–7.21 (m, 1H), 7.28–7.35 (m, 6H), 7.46 (dd, J = 8.48 Hz, J = 4.20 Hz, 1H), 7.74–7.76 (m, 2H), 8.36 (d, J = 8.48 Hz, 1H), 8.63 (d, J = 8.60 Hz, 1H), 8.77 (d, J = 4.08 Hz, 1H), 9.71 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.7, 30.3,

38.6, 114.2, 118.8, 121.1, 121.9, 125.3, 126.8, 127.3, 127.5, 127.6, 128.9, 130.3, 132.7, 137.4, 138.4, 139.5, 144.8, 147.7, 169.8. HRMS-ESI (m/z): calcd for $C_{25}H_{23}N_2O_3S^+$, 431.1424, found 431.1422.

***N*-(5-Tosylquinolin-8-yl)isobutyramide (3ka)**.[3]

Yellow solid, mp 185–187 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.35 (d, J = 6.84 Hz, 6H), 2.45 (s, 3H), 2.70–2.80 (m, 1H), 6.96 (d, J = 8.60 Hz, 1H), 7.31–7.33 (m, 2H), 7.48 (dd, J = 8.48 Hz, J = 4.16 Hz, 1H), 7.74–7.76 (m, 2H), 8.38 (d, J = 8.48 Hz, 1H), 8.64 (d, J = 8.60 Hz, 1H), 8.82 (d, J = 4.08 Hz, 1H), 9.83 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.7, 21.7, 37.1, 115.2, 119.9, 122.1, 123.0, 128.7, 130.0, 131.4, 132.1, 133.9, 138.6, 139.4, 145.8, 148.8, 175.8.

***N*-(5-Tosylquinolin-8-yl)cyclopropanecarboxamide (3la)**.[4]

White solid, mp 212–214 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.83–0.95 (m, 4H), 1.76–1.82 (m, 1H), 2.45 (s, 3H), 6.94 (d, J = 8.60 Hz, 1H), 7.30–7.32 (m, 2H), 7.48 (dd, J = 8.48 Hz, J = 4.20 Hz, 1H), 7.75–7.77 (m, 2H), 8.38 (d, J = 8.48 Hz, 1H), 8.58 (d, J = 8.60 Hz, 1H), 8.82 (d, J = 4.00 Hz, 1H), 9.95 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 8.3, 16.3, 21.7, 115.1, 119.9, 122.1, 123.0, 127.9, 128.7, 129.9, 130.0, 131.4, 134.0, 139.2, 145.8, 148.8, 172.4.

***N*-(5-(phenylsulfonyl)quinolin-8-yl)benzamide (3ad)**.[1]

White solid, mp 177–179 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07 (d, J = 8.56 Hz, 1H), 7.45–7.52 (m, 2H), 7.54–7.60 (m, 4H), 7.67–7.70 (m, 1H), 7.89–7.91 (m, 2H), 8.04–8.06 (m, 2H), 8.36 (d, J = 8.48 Hz, 1H), 8.80 (d, J = 8.60 Hz, 1H), 8.85 (d, J = 4.12 Hz, 1H), 10.65 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 115.3, 120.0, 122.3, 122.9, 127.3, 128.5, 128.6, 128.9, 129.4, 130.1, 131.3, 132.1, 134.0, 134.6, 138.9, 139.6, 149.0, 165.5.

***N*-(5-(4-Chlorophenylsulfonyl)quinolin-8-yl)benzamide (3af)**.[1]

White solid, mp 204–206 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10 (d, J = 8.56 Hz, 1H), 7.51–7.61 (m, 6H), 7.82–7.84 (m, 2H), 8.05–8.07 (m, 2H), 8.36 (d, J = 8.44 Hz, 1H), 8.83 (d, J = 8.56 Hz, 1H), 8.88 (d, J = 4.00 Hz, 1H), 10.66 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 115.3, 120.0, 122.4,

122.8, 127.3, 128.9, 129.8, 130.0, 131.2, 132.1, 133.6, 134.2, 134.7, 138.9, 139.4, 141.5, 149.1, 165.5.

4-Bromo-*N*-(5-(4-methoxyphenylsulfonyl)quinolin-8-yl)benzamide (**3eb**).

Yellow solid, mp 109–111 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.89 (s, 3H), 6.97–6.99 (m, 2H), 7.05 (d, J = 8.56 Hz, 1H), 7.52 (dd, J = 8.40 Hz, J = 4.12 Hz, 1H), 7.67–7.69 (m, 2H), 7.79–7.81 (m, 2H), 7.91–7.93 (m, 2H), 8.42 (d, J = 8.44 Hz, 1H), 8.76 (d, J = 8.60 Hz, 1H), 8.86 (d, J = 3.92 Hz, 1H), 10.62 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.8, 114.6, 115.5, 120.0, 122.3, 123.1, 126.2, 126.9, 128.9, 131.0, 131.6, 132.1, 133.5, 133.6, 138.8, 139.9, 149.0, 164.4, 164.5. HRMS-ESI (m/z): calcd for $C_{23}H_{18}BrN_2O_4S^+$, 497.0165, found 497.0166.

4-Bromo-*N*-(5-((2-methylphenyl)sulfonyl)quinolin-8-yl)benzamide (**3ec**).

Yellow solid, mp 98–100 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.84 (s, 3H), 6.83 (d, J = 8.56 Hz, 1H), 7.30–7.33 (m, 1H), 7.46–7.48 (m, 1H), 7.55–7.62 (m, 2H), 7.66–7.68 (m, 2H), 7.81–7.83 (m, 1H), 7.89–7.91 (m, 2H), 8.52 (d, J = 8.48 Hz, 1H), 8.69 (d, J = 8.56 Hz, 1H), 8.88 (d, J = 4.12 Hz, 1H), 10.61 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.7, 115.3, 119.4, 122.5, 123.3, 126.5, 126.9, 128.7, 128.9, 130.0, 130.6, 131.6, 132.1, 132.9, 133.6, 134.0, 134.6, 138.9, 139.8, 149.2, 164.5. HRMS-ESI (m/z): calcd for $C_{23}H_{18}BrN_2O_3S^+$, 481.0216, found 481.0220.

4-Bromo-*N*-(5-(phenylsulfonyl)quinolin-8yl)benzamide (**3ed**).

Yellow solid, mp 114–116 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07 (d, J = 8.60 Hz, 1H), 7.48–7.56 (m, 3H), 7.67–7.71 (m, 3H), 7.88–7.92 (m, 4H), 8.35–8.37 (m, 1H), 8.76 (d, J = 8.60 Hz, 1H), 8.85 (d, J = 4.08 Hz, 1H), 10.61 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 115.4, 120.0, 122.3, 122.9, 126.9, 128.6, 128.9, 129.4, 131.3, 132.1, 133.6, 133.7, 134.6, 135.1, 138.8, 139.7, 149.1, 164.5. HRMS-ESI (m/z): calcd for $C_{22}H_{16}BrN_2O_3S^+$, 467.0060, found 467.0057.

4-Bromo-*N*-(5-((4-fluorophenyl)sulfonyl)quinolin-8-yl)benzamide (**3ee**).

Yellow solid, mp 99–101 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11 (d, J = 8.60 Hz, 1H), 7..20–7.24 (m, 2H), 7.52 (dd, J = 8.44 Hz, J = 4.16 Hz, 1H), 7.67–7.69 (m, 2H), 7.91–7.93 (m, 4H), 8.35 (d, J = 8.48 Hz, 1H), 8.79 (d, J = 8.60 Hz, 1H), 8.86 (d, J = 3.92 Hz, 1H), 10.61 (s, 1H); ^{13}C NMR (100

MHz, $CDCl_3$): δ 114.3, 115.8 (d, J = 22.70 Hz), 118.9, 121.4, 121.8, 125.9, 127.8, 130.1 (d, J = 3.30 Hz), 130.2, 130.5 (d, J = 9.65 Hz), 131.1, 132.5, 132.8, 137.8, 138.5, 148.1, 163.4, 165.2 (d, J = 256.86 Hz). HRMS-ESI (m/z): calcd for $C_{22}H_{15}BrFN_2O_3S^+$, 484.9965, found 484.9970.

4-Bromo-*N*-(5-((4-chlorophenyl)sulfonyl)quinolin-8-yl)benzamide (**3ef**).

Yellow solid, mp 124–126 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10 (d, J = 8.60 Hz, 1H), 7.51–7.54 (m, 3H), 7.67–7.69 (m, 2H), 7.83 (d, J = 8.24 Hz, 2H), 7.90–7.93 (m, 2H), 8.36 (d, J = 8.44 Hz, 1H), 8.78 (d, J = 8.56 Hz, 1H), 8.87 (d, J = 3.80 Hz, 1H), 10.61 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 115.4, 120.0, 122.5, 122.9, 124.8, 127.0, 128.9, 129.8, 130.0, 131.2, 132.2, 133.6, 133.9, 138.9, 139.5, 141.5, 149.2, 164.5. HRMS-ESI (m/z): calcd for $C_{22}H_{15}BrClN_2O_3S^+$, 500.9670, found 500.9674.

4-Bromo-*N*-(5-(4-Bromophenylsulfonyl)quinolin-8-yl)benzamide (**3eg**).[6]

Yellow solid, mp 226–228 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10 (d, J = 8.60 Hz, 1H), 7.53 (dd, J = 8.48 Hz, J = 4.20 Hz, 1H), 7.68–7.70 (m, 4H), 7.74–7.76 (m, 2H), 7.91–7.93 (m, 2H), 8.36 (d, J = 8.48 Hz, 1H), 8.79 (d, J = 8.60 Hz, 1H), 8.87 (d, J = 4.12 Hz, 1H), 10.62 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 115.4, 119.9, 122.5, 122.8, 127.0, 128.9, 130.0, 130.1, 131.2, 132.2, 132.8, 133.6, 133.9, 134.1, 138.9, 139.5, 149.2, 164.5.

***N*-(5-Methyl-4-tosylylphenyl)acetamide** (**5aa**).

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ1.99 (s, 3H), 2.13 (s, 3H), 2.45 (s, 3H), 6.88–6.90 (m, 1H), 7.23 (d, J = 8.72 Hz, 1H), 7.31–7.33 (m, 2H), 7.37 (s, 1H), 7.70–7.72 (m, 2H), 7.82 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.7, 22.7, 24.6, 118.0, 122.4, 122.8, 128.4, 129.8, 132.5, 133.0, 136.5, 144.3, 145.4, 168.3. HRMS-ESI (m/z): calcd for $C_{16}H_{18}NO_3S^+$, 304.1002, found 304.0999.

***N*-(4-Tosylylphenyl)acetamide** (**5ba**).

Yellow solid, 99–101 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ2.13 (s, 3H), 2.44 (s, 3H), 6.87–6.89 (m, 2H), 7.30–7.32 (m, 2H), 7.43–7.45 (m, 2H), 7.67–7.68 (m, 2H), 7.93 (s, 1H); ^{13}C NMR (100 MHz,

$CDCl_3$): δ 21.7, 24.6, 120.5, 123.0, 128.6, 129.8, 132.2, 136.8, 145.4, 145.6, 168.2. HRMS-ESI (m/z): calcd for $C_{15}H_{16}NO_3S^+$, 290.0845, found 290.0840.

***N*-(2-Fluoro-4-tosylylphenyl)acetamide (5ca)**.

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.21 (s, 3H), 2.46 (s, 3H), 6.64 (d, J = 8.88 Hz, 1H), 6.92 (d, J = 11.12 Hz, 1H), 7.31–7.33 (m, 2H), 7.39 (s, 1H), 7.70 (d, J = 7.84 Hz, 2H), 8.23 (t, J = 8.88 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.7, 24.6, 110.1, 110.3, 118.4 (d, J = 3.63 Hz), 121.7, 124.8, 125.5 (d, J = 10.07 Hz), 128.6, 129.9, 131.9, 145.7, 168.4. HRMS-ESI (m/z): calcd for $C_{15}H_{15}FNO_3S^+$, 308.0751, found 308.0748.

***N*-(2-Chloro-4-tosylylphenyl)acetamide (5da)**.

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.23 (s, 3H), 2.46 (s, 3H), 6.77 (dd, J = 9.04 Hz, J = 1.72 Hz, 1H), 7.17 (d, J = 2.12 Hz, 1H), 7.32–7.34 (m, 2H), 7.57 (s, 1H), 7.69–7.71 (m, 2H), 8.30 (d, J = 9.04 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.8, 24.9, 121.6, 122.6, 123.4, 128.5, 128.6, 129.9, 132.0, 133.7, 144.9, 145.8, 168.2. HRMS-ESI (m/z): calcd for $C_{15}H_{15}ClNO_3S^+$, 324.0456, found 324.0455.

***N*-(2-Bromo-4-tosylylphenyl)acetamide (5ea)**.

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.23 (s, 3H), 2.46 (s, 3H), 6.81 (d, J = 8.96 Hz, 1H), 7.32–7.34 (m, 3H), 7.56 (s, 1H), 7.69–7.71 (m, 2H), 8.27 (d, J = 9.00 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.8, 112.6, 121.8, 122.2, 126.4, 128.5, 128.6, 129.9, 132.0, 134.8, 145.0, 145.8, 168.2. HRMS-ESI (m/z): calcd for $C_{15}H_{15}BrNO_3S^+$, 367.9951, found 367.9948.

***N*-(2-Methyl-4-tosylylphenyl)pyridylamide (5fa)**.

Yellow solid, mp 114–116 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.38 (s, 3H), 2.45 (s, 3H), 6.73 (d, J = 8.72 Hz, 1H), 7.01 (s, 1H), 7.31–7.33 (m, 2H), 7.48–7.51 (m, 1H), 7.71–7.73 (m, 2H), 7.90–7.94 (m, 1H), 8.21 (d, J = 8.88 Hz, 1H), 8.28 (d, J = 6.80 Hz, 1H), 8.62 (d, J = 4.48 Hz, 1H), 10.10 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.8, 21.7, 120.3, 121.7, 122.4, 124.4, 126.6, 127.9, 128.6, 129.8, 132.4, 134.9, 137.8, 145.3, 145.6, 148.2, 149.7, 161.9. HRMS-ESI (m/z): calcd for $C_{20}H_{19}N_2O_3S^+$, 367.1111, found 367.1095.

***N*-(2-Bromo-4-((2-methylphenyl)sulfonyl))acetamide (5ec)**.

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.22 (s, 3H), 2.77 (s, 3H), 6.83 (d, J = 8.92 Hz, 1H), 7.30–7.34 (m, 2H), 7.41–7.46 (m, 1H), 7.54–7.60 (m, 2H), 7.80–7.85 (m, 1H), 8.26 (d, J = 8.80 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.6, 112.7, 121.9, 126.2, 126.4, 128.6, 129.9, 130.7, 132.7, 133.7, 134.5, 134.8, 138.8, 144.9, 168.2. HRMS-ESI (m/z): calcd for $C_{15}H_{15}BrNO_3S^+$, 367.9951, found 367.9948.

***N*-(2-Bromo-4-(phenylsulfonyl))acetamide (5ed)**.

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.23 (s, 3H), 6.83 (d, J = 8.96 Hz, 1H), 7.29–7.30 (m, 1H), 7.55–7.57 (m, 2H), 7.68–7.72 (m, 2H), 7.83–7.85 (m, 2H), 8.28 (d, J = 9.00 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 112.7, 121.8, 122.2, 126.4, 128.4, 128.5, 129.3, 134.5, 134.9, 135.0, 144.9, 168.3. HRMS-ESI (m/z): calcd for $C_{14}H_{13}BrNO_3S^+$, 353.9794, found 353.9796.

***N*-(2-Bromo-4-((4-chlorophenyl)sulfonyl))acetamide (5ef)**.

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.24 (s, 3H), 6.86 (d, J = 9.00 Hz, 1H), 7.32 (d, J = 1.80 Hz, 1H), 7.52–7.54 (m, 2H), 7.58 (s, 1H), 7.76–7.78 (m, 2H), 8.31 (d, J = 9.00 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 112.8, 122.0, 126.3, 129.7, 129.9, 130.1, 133.1, 133.4, 135.1, 141.4, 144.7, 168.3. HRMS-ESI (m/z): calcd for $C_{14}H_{12}BrClNO_3S^+$, 387.9404, found 387.9408.

***N*-(2-Bromo-4-((4-bromophenyl)sulfonyl))acetamide (5eg)**.

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.24 (s, 3H), 6.86 (d, J = 8.96 Hz, 1H), 7.32 (s, 1H), 7.58 (s, 1H), 7.69–7.75 (m, 4H), 8.31 (d, J = 8.96 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 112.8, 122.0, 126.3, 129.9, 130.0, 132.7, 133.1, 133.9, 135.1, 144.2, 144.7, 168.3. HRMS-ESI (m/z): calcd for $C_{14}H_{12}Br_2NO_3S^+$, 431.8899, found 431.8896.

***N*-(2-Methyl-4-(2-methylphenyl)sulfonyl)pyridylamide (5fc)**.

Yellow solid, mp 116–118 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.36 (s, 3H), 2.79 (s, 3H), 6.75 (d, J = 8.96 Hz, 1H), 6.98 (s, 1H), 7.27–7.30 (m, 1H), 7.40–7.42 (m, 1H), 7.47–7.56 (m, 2H), 7.82 (d, J = 7.96 Hz, 1H), 7.89–7.93 (m, 1H), 8.20 (d, J = 8.88 Hz, 1H), 8.26 (d, J = 7.76 Hz, 1H), 8.60 (d, J

= 4.36 Hz, 1H), 10.08 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.8, 20.6, 120.0, 121.8, 122.4, 124.2, 126.2, 126.6, 129.6, 129.8, 130.7, 132.6, 134.2, 134.9, 137.7, 138.8, 145.5, 148.1, 149.8, 161.9. HRMS-ESI (m/z): calcd for $C_{20}H_{19}N_2O_3S^+$, 367.1111, found 367.1097.

***N*-(2-Methyl-4-Phenylsulfonyl)pyridylamide (5fd)**.

Yellow solid, mp 88–90 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.36 (s, 3H), 6.75 (d, J = 8.88 Hz, 1H), 7.48–7.58 (m, 4H), 7.84–7.93 (m, 4H), 8.23 (d, J = 8.88 Hz, 1H), 8.27 (d, J = 7.80 Hz, 1H), 8.61 (d, J = 4.64 Hz, 1H), 10.10 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.7, 120.3, 121.8, 122.4, 124.3, 126.7, 127.8, 128.6, 129.1, 133.9, 134.2, 135.0, 137.8, 145.5, 148.2, 149.7, 161.9. HRMS-ESI (m/z): calcd for $C_{19}H_{17}N_2O_3S^+$, 353.0954, found 353.0951.

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2. H. Qiao, S. Sun, F. Yang, Y. Zhu, W. Zhu, Y. Dong, Y. Wu, X. Kong, L. Jiang and Y. Wu, *Org. Lett.*, 2015, **17***,* 6086.
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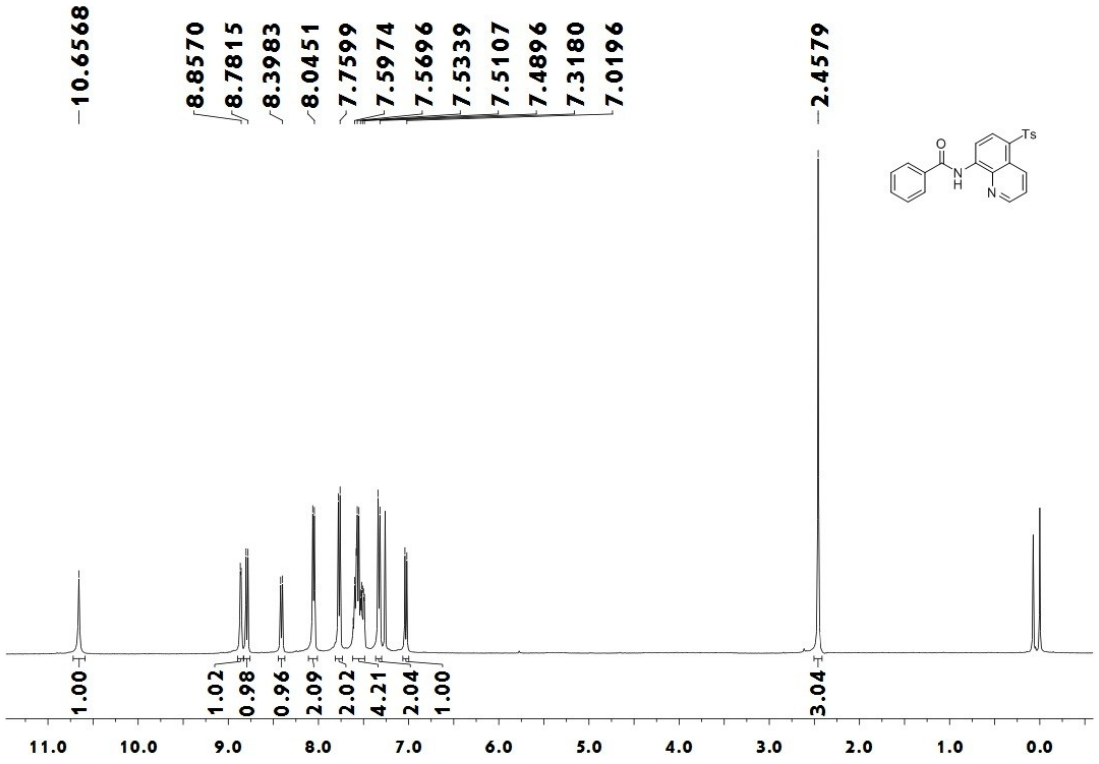
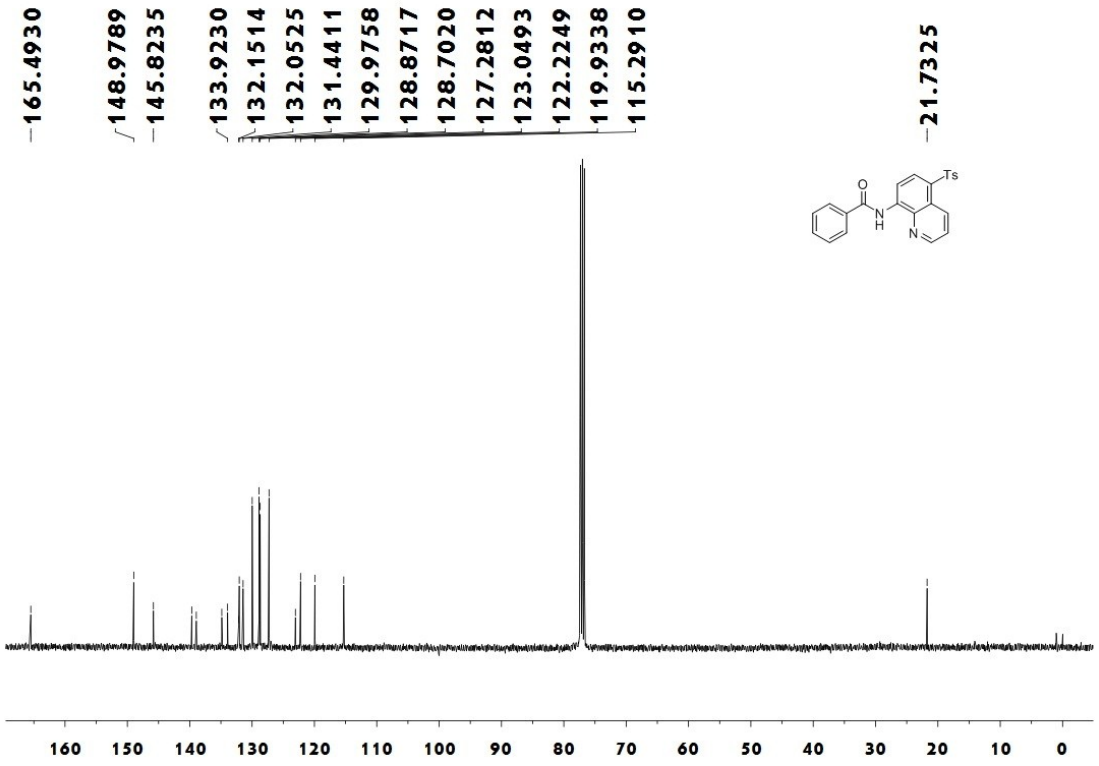
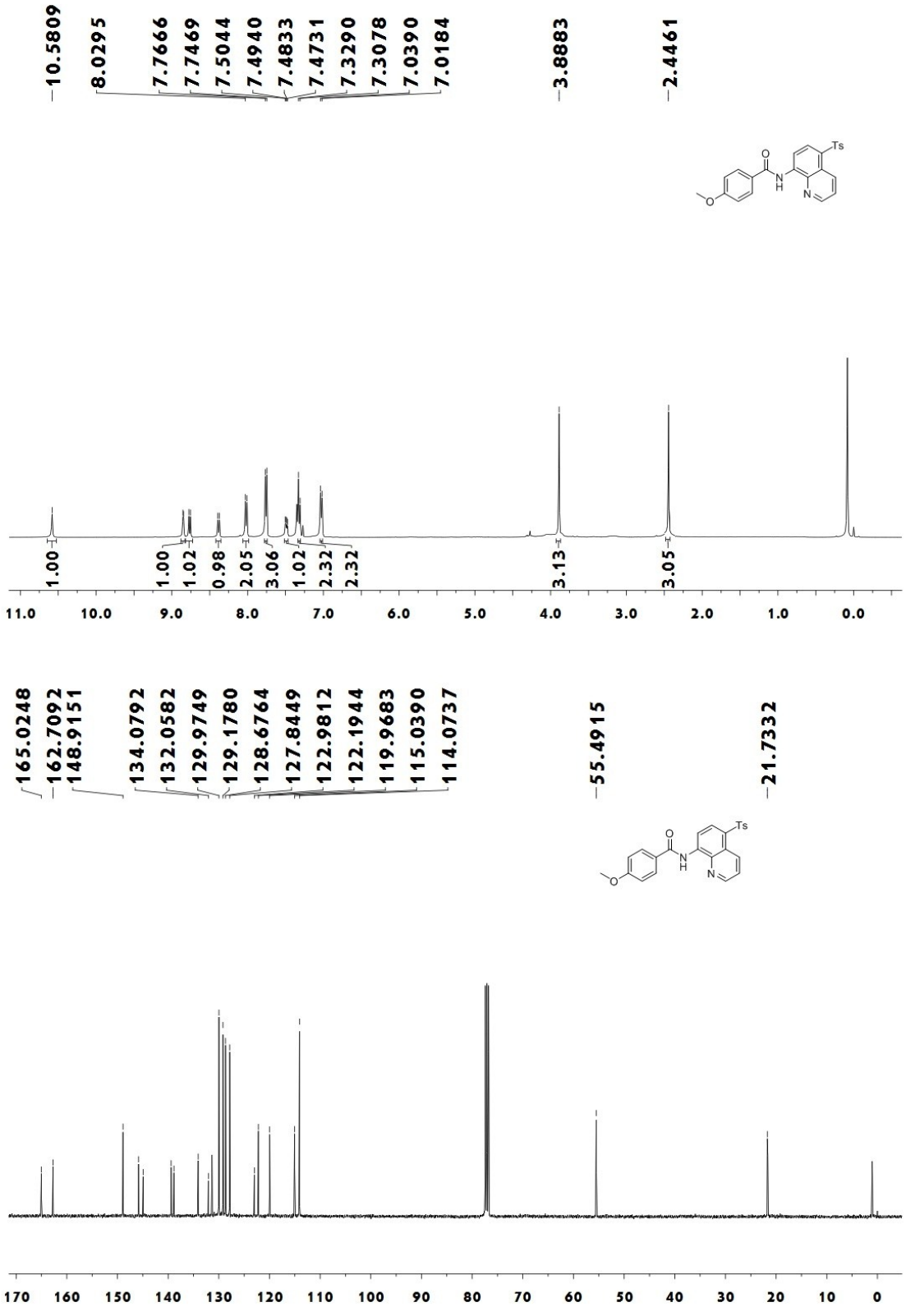
Copies of ^{1}H and ^{13}C NMR spectra

N-(5-Tosylquinolin-8-yl)benzamide (3aa)

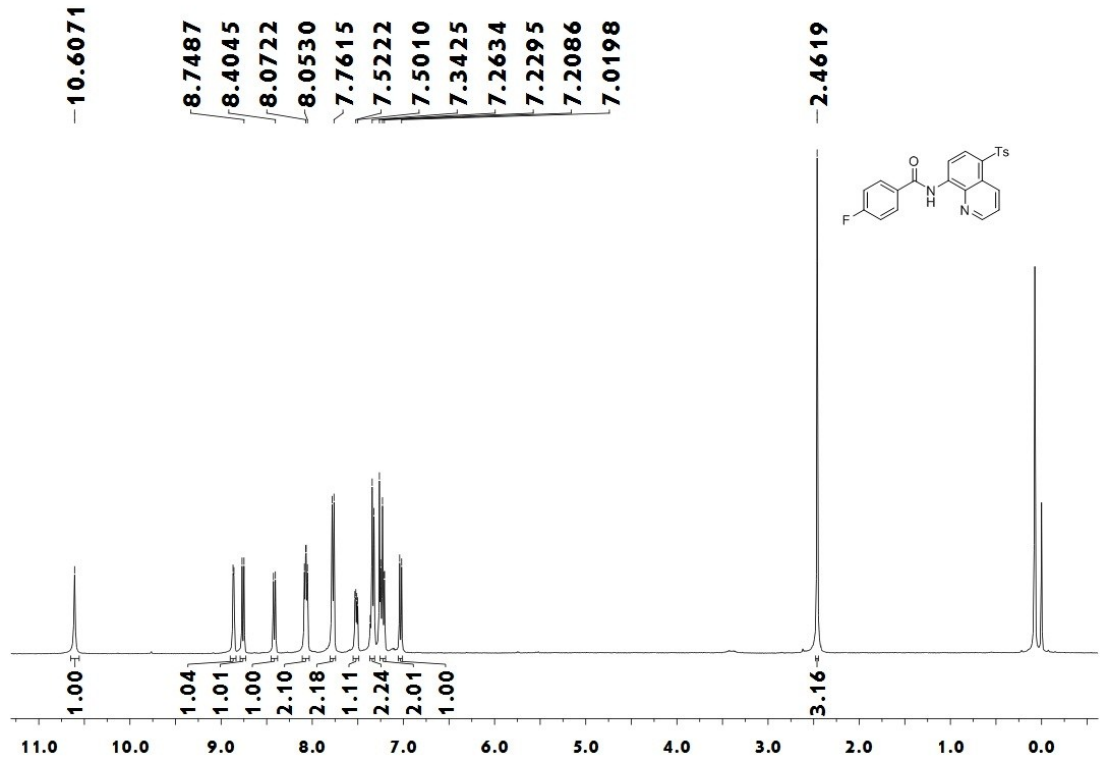


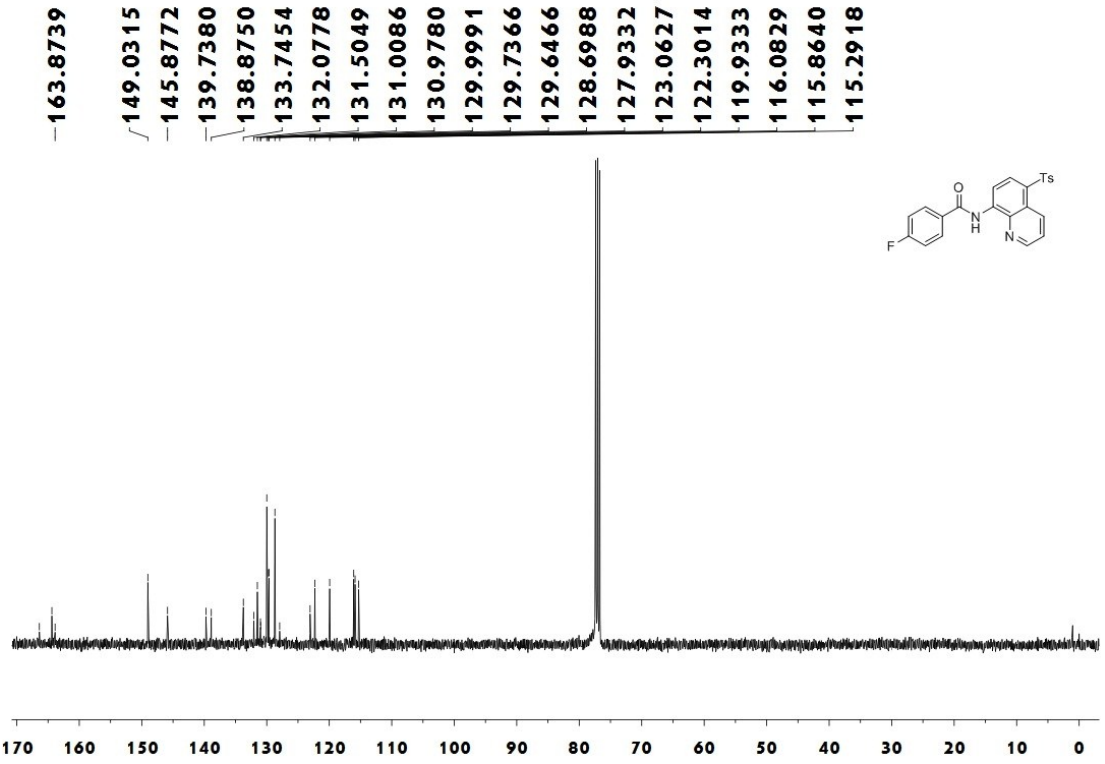


4-Methoxy-N-(5-Tosylquinolin-8-yl)benzamide (3ba)

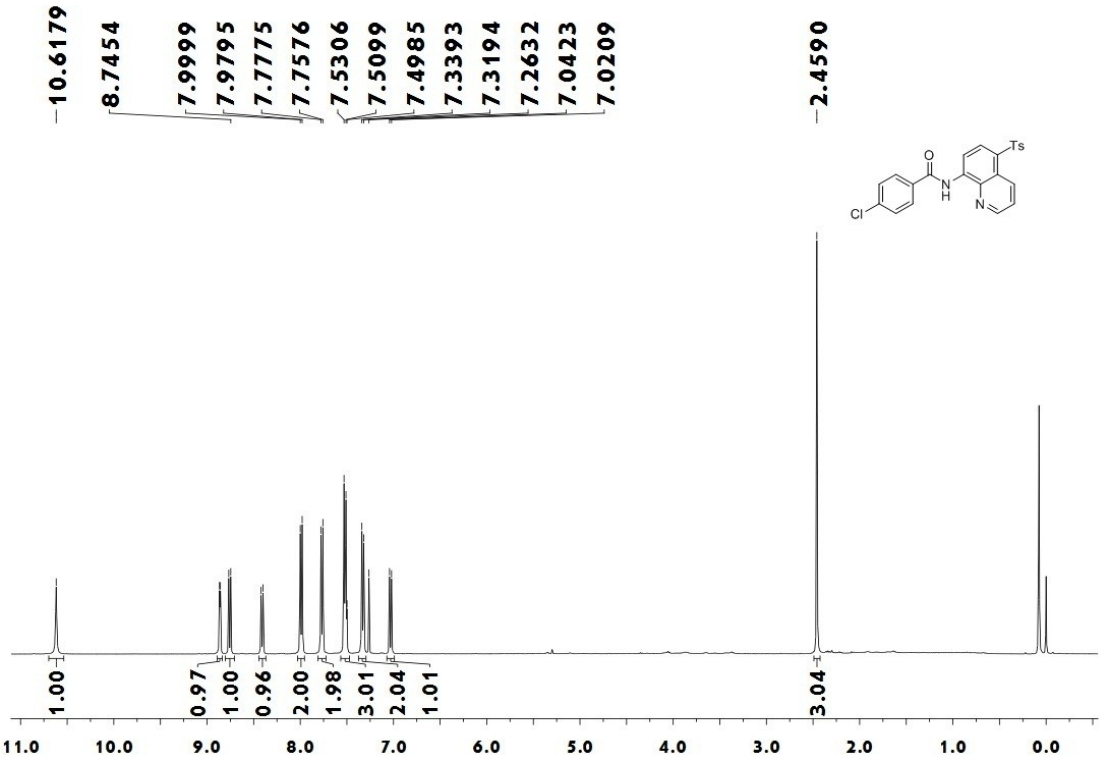


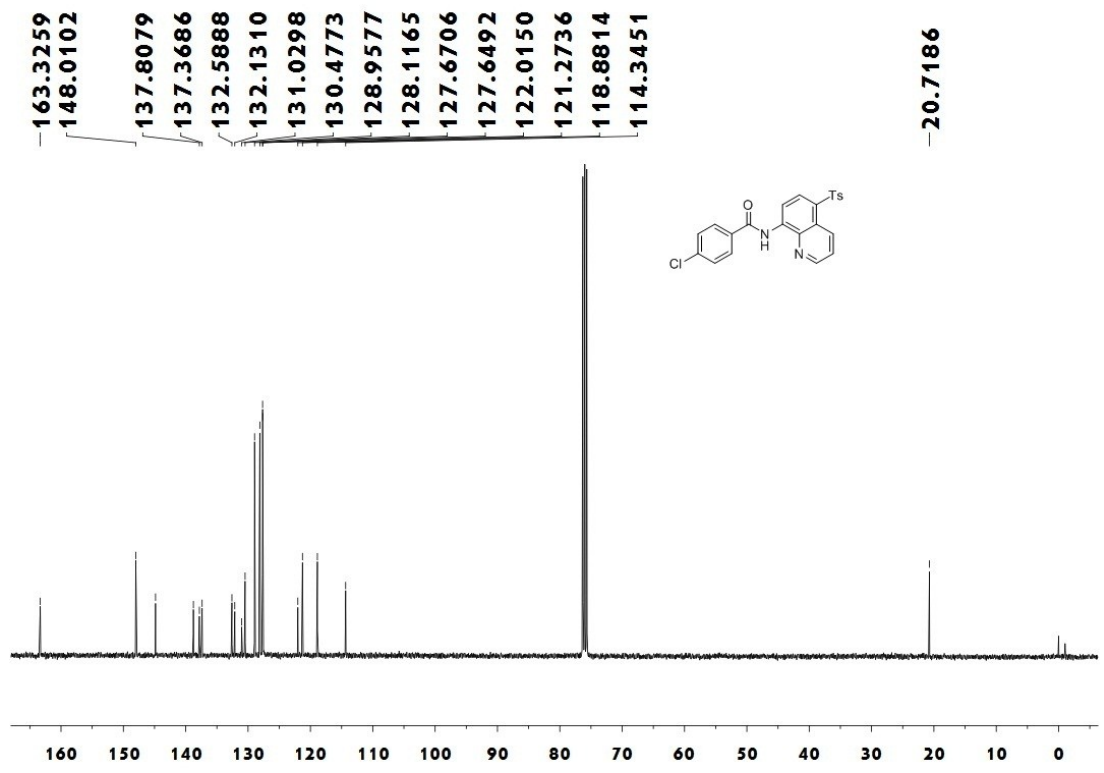
4-Fluoro-N-(5-Tosylquinolin-8-yl)benzamide (3ca)



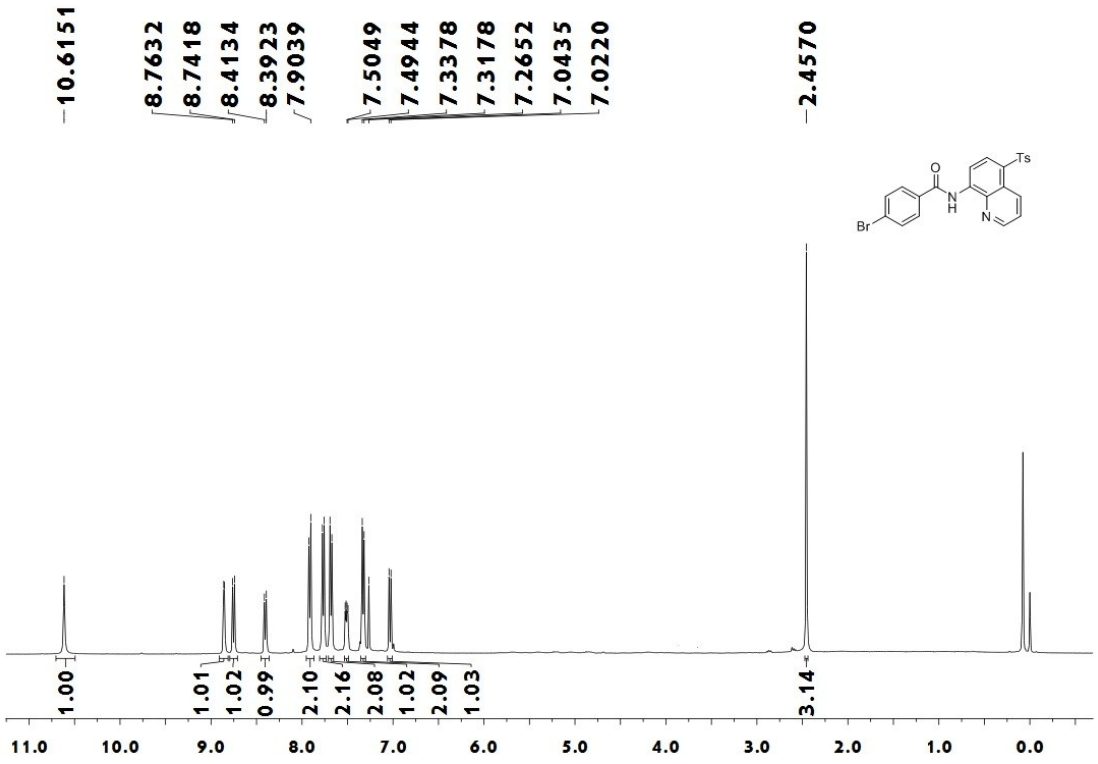


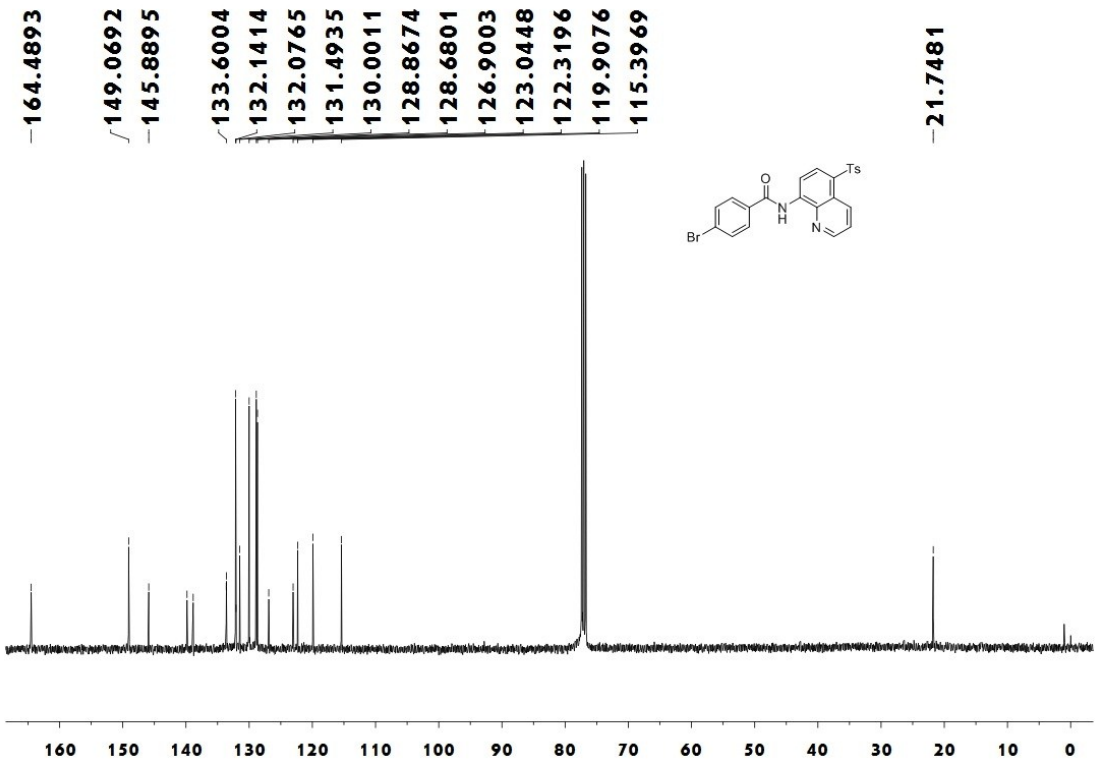
4-Chloro-N-(5-Tosylquinolin-8-yl)benzamide (3da)



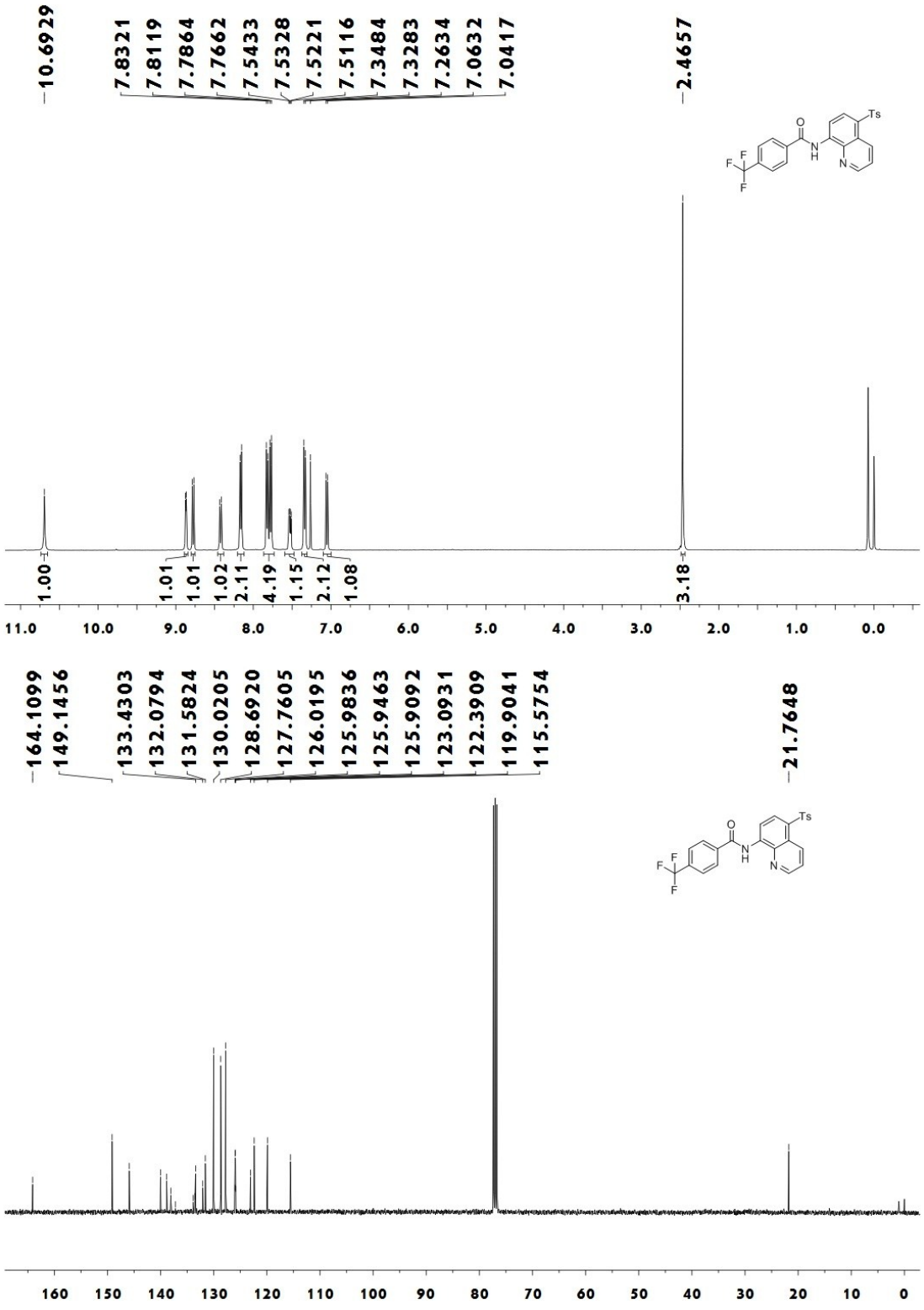


4-Bromo-N-(5-Tosylquinolin-8-yl)benzamide (3ea)

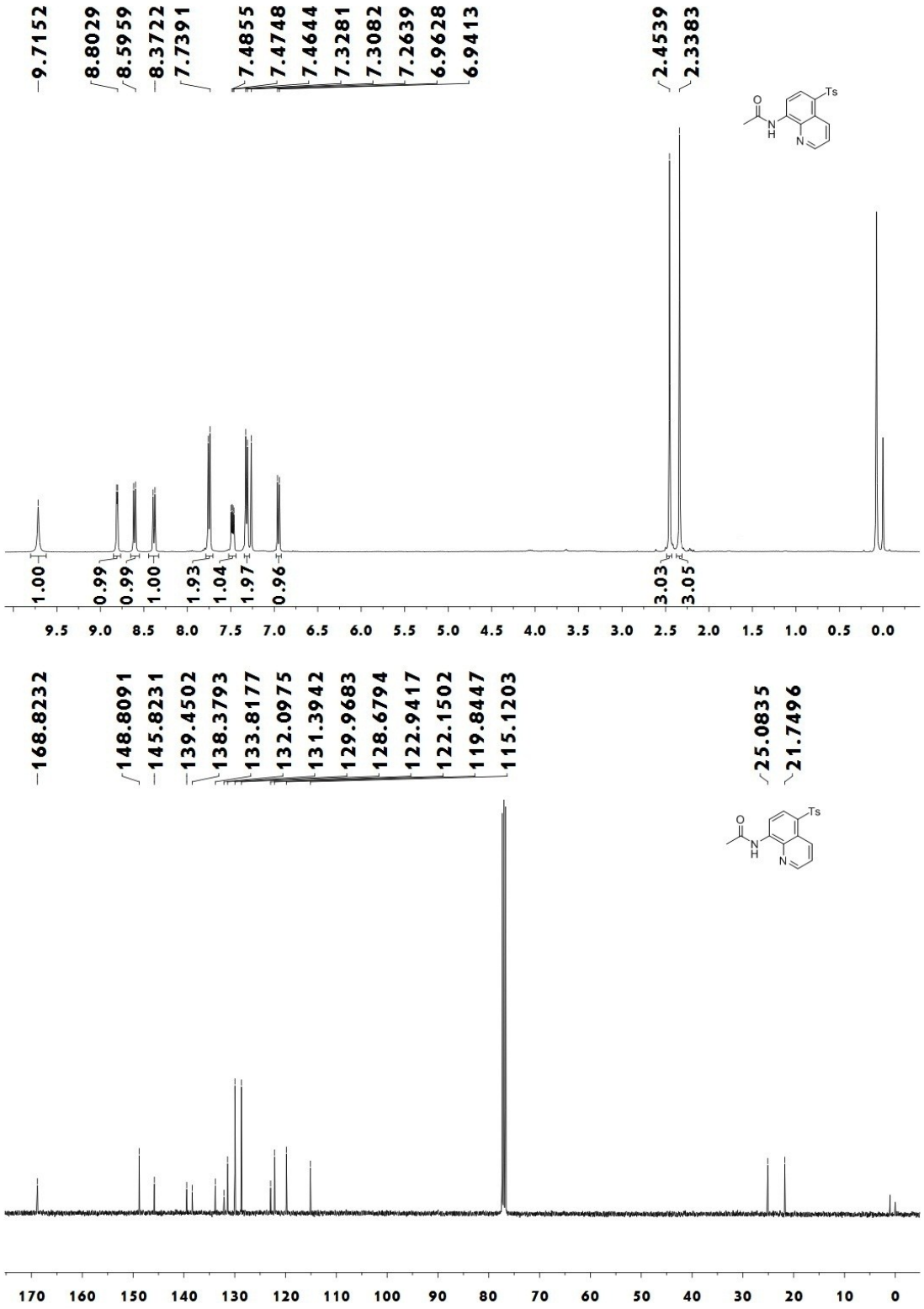




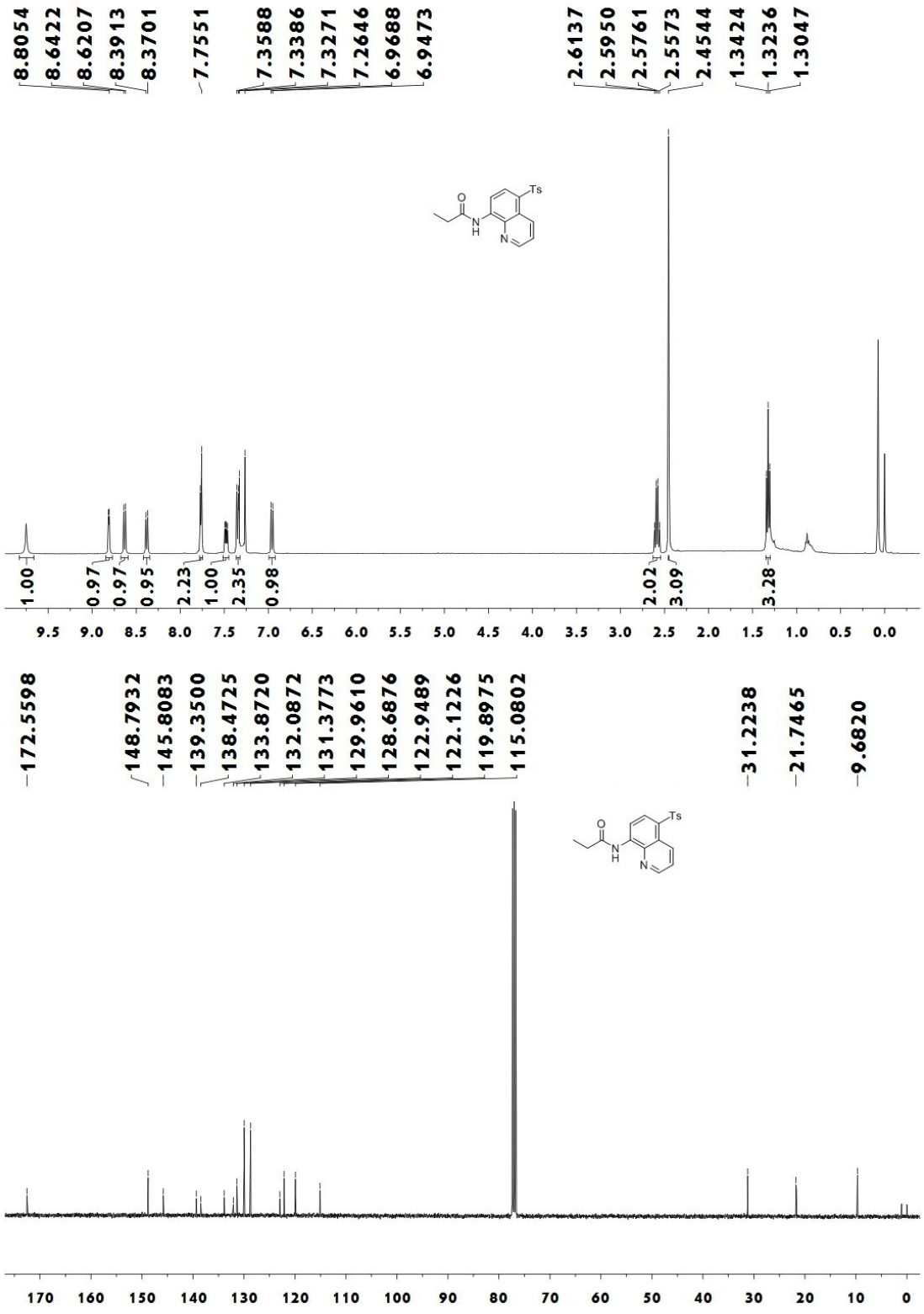
N-(5-Tosylquinolin-8-yl)-4-(trifluoromethyl)benzamide (3fa)



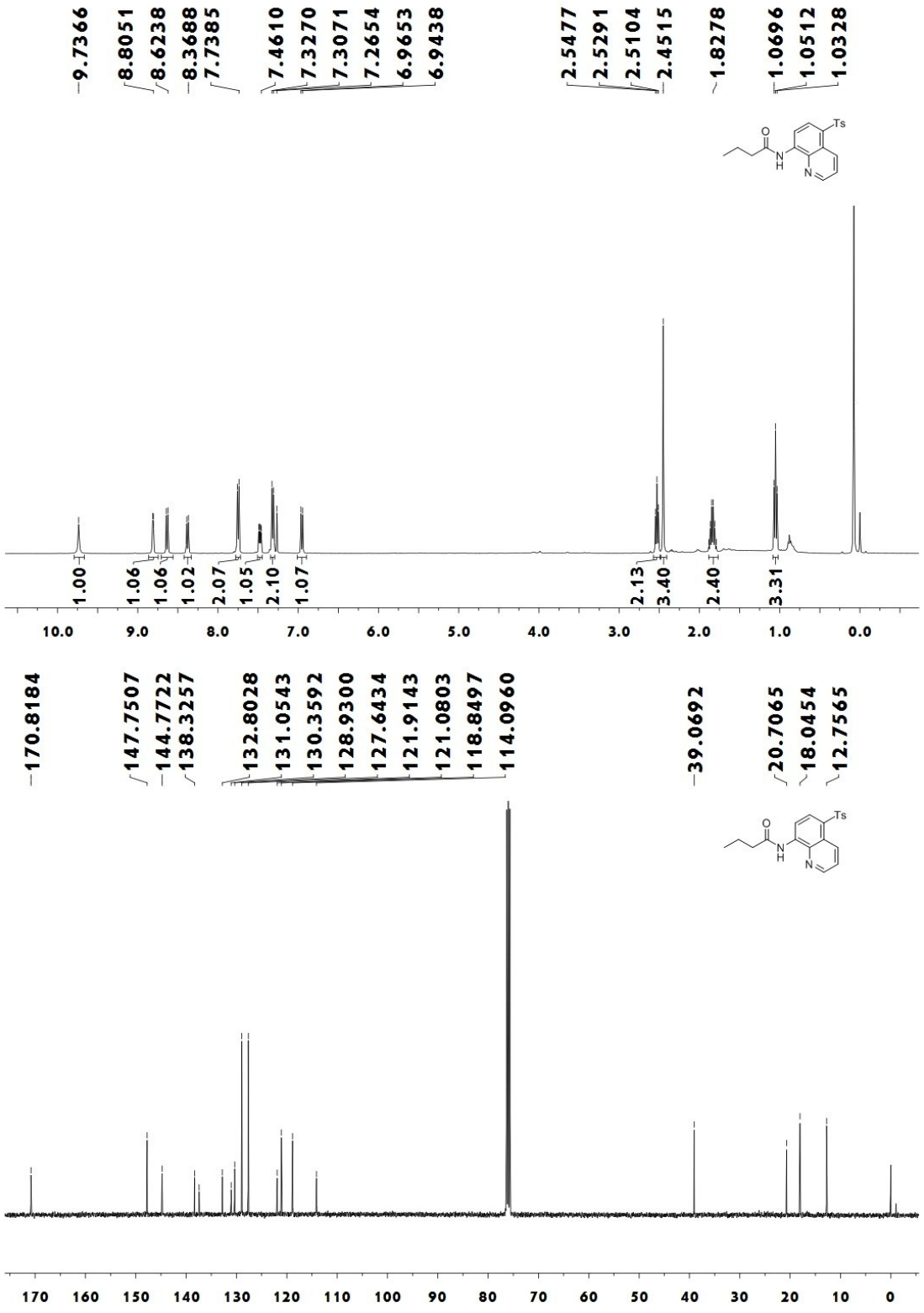
N-(5-Tosylquinolin-8-yl)acetamide (3ga)



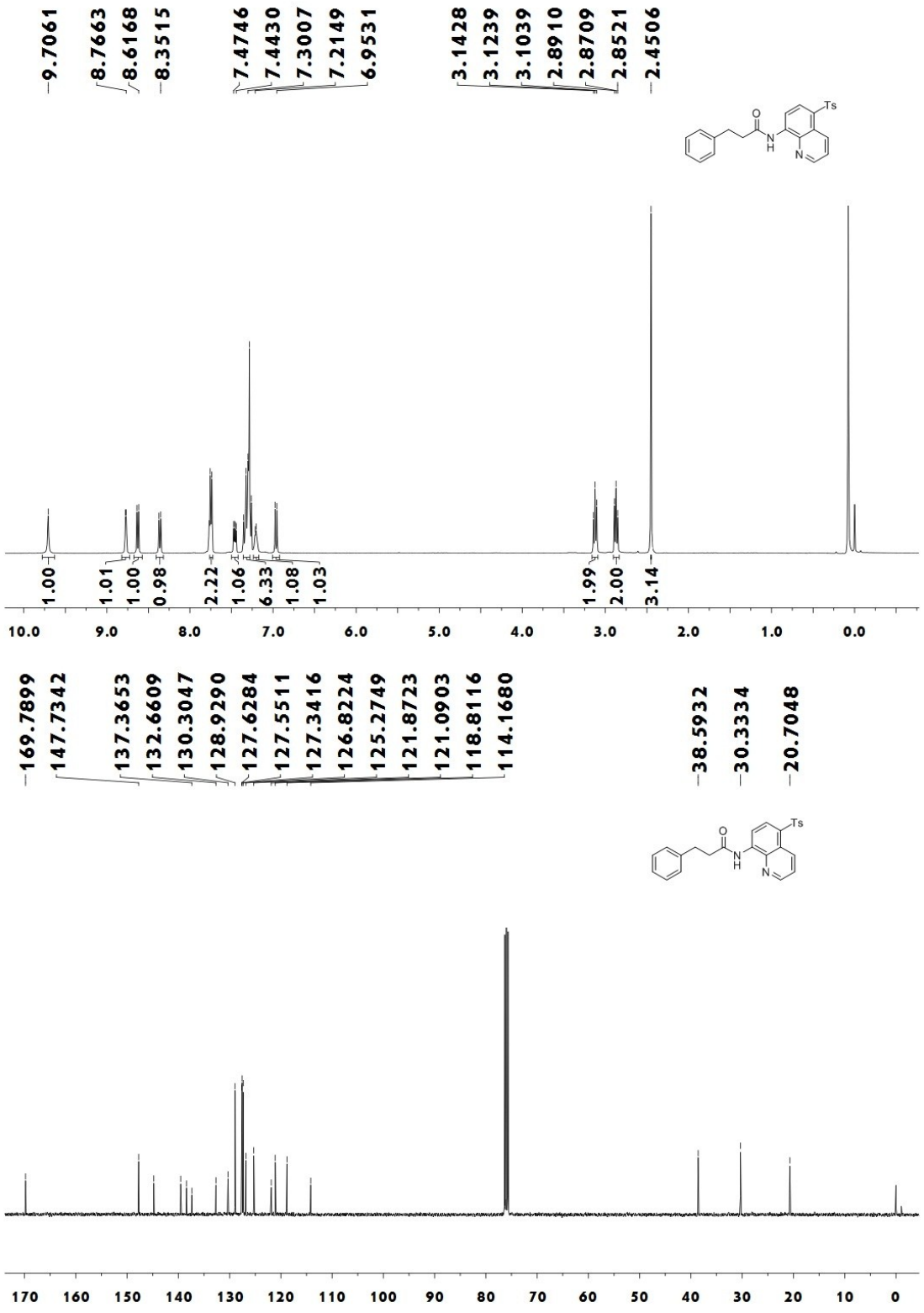
N-(5-Tosylquinolin-8-yl)propionamide (3ha)



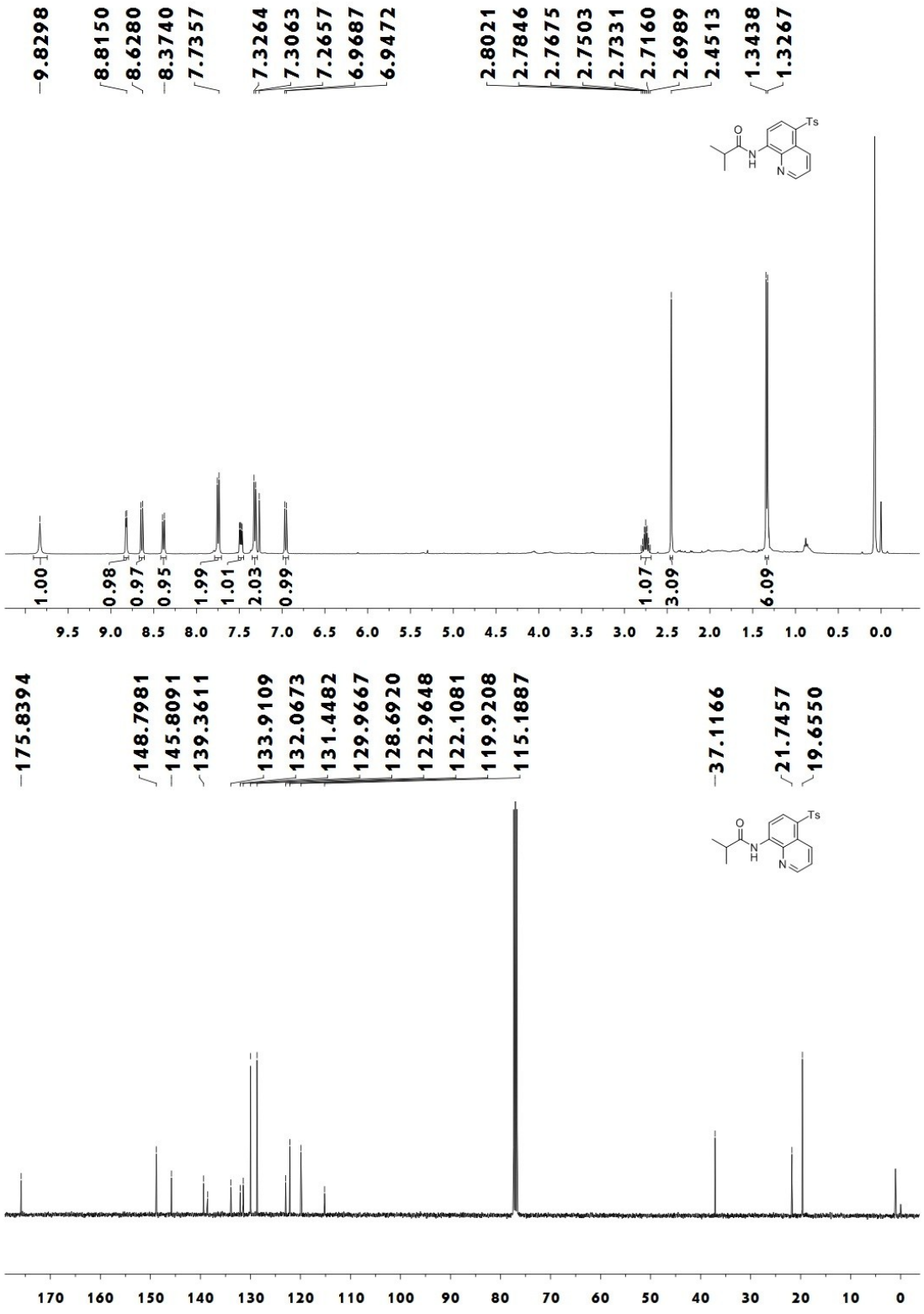
N-(5-Tosylquinolin-8-yl)butanamide (3ia)



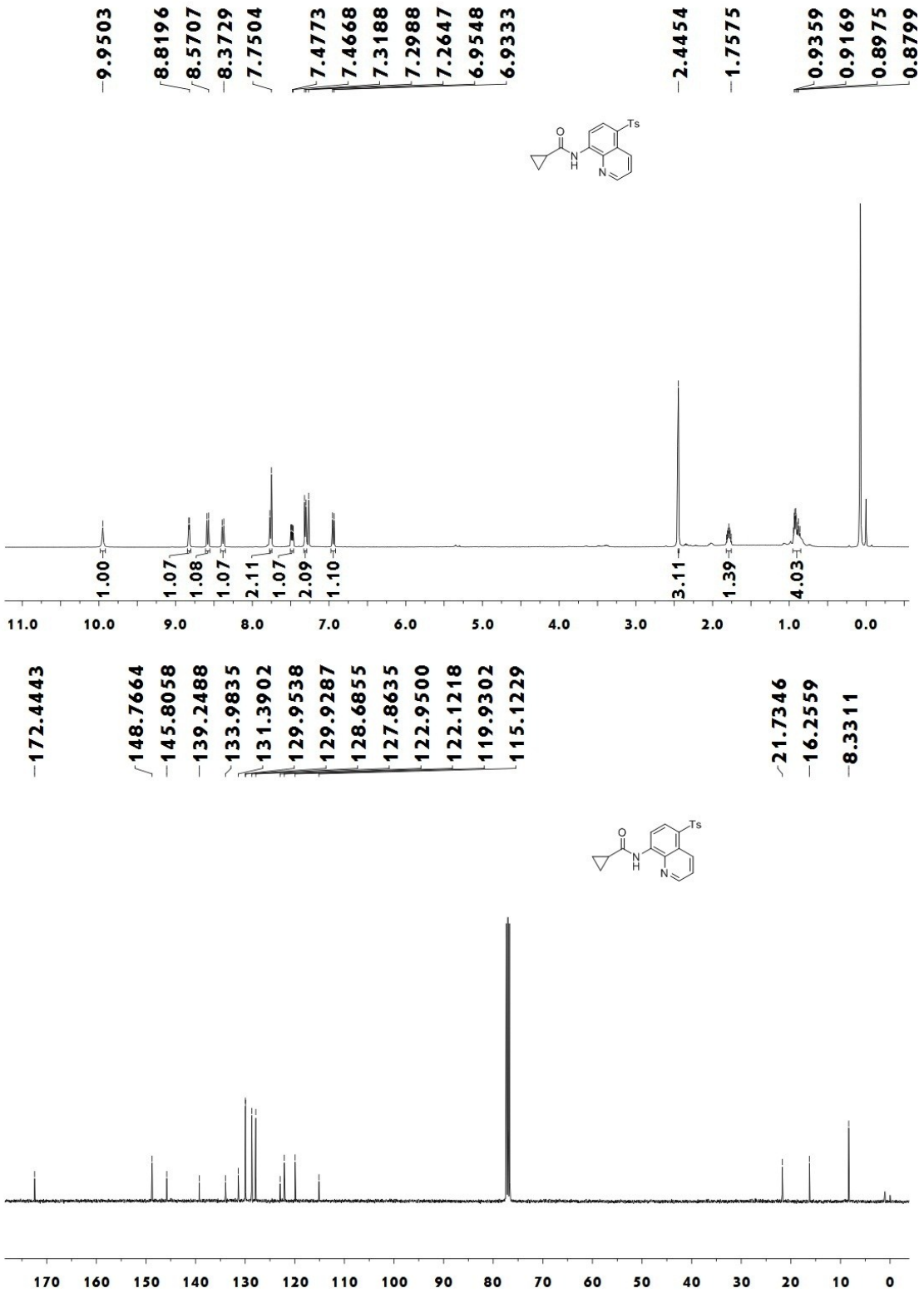
N-(5-Tosylquinolin-8-yl)hydrocinnamionamide (3ja)



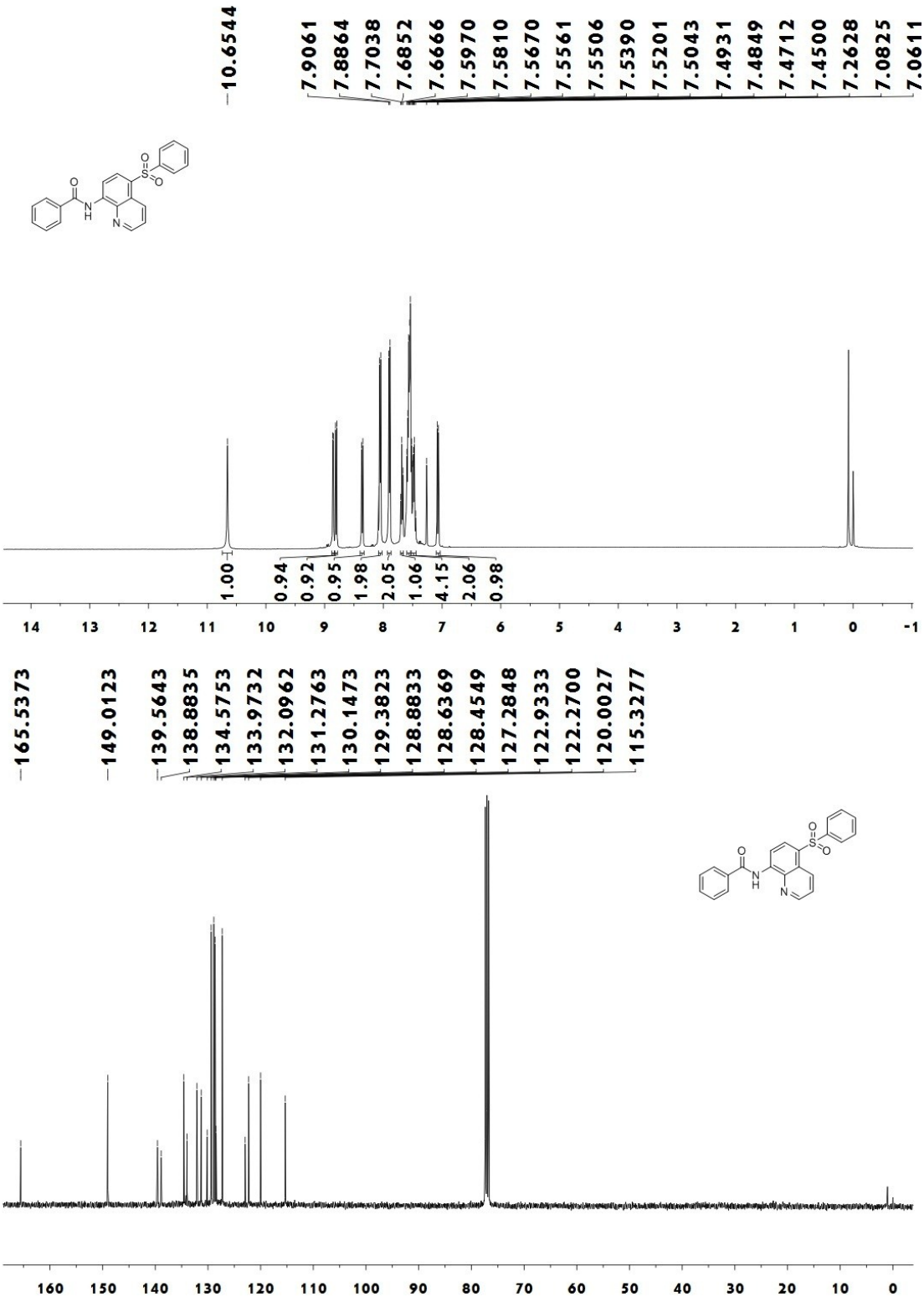
N-(5-Tosylquinolin-8-yl)isobutyramide (3ka)



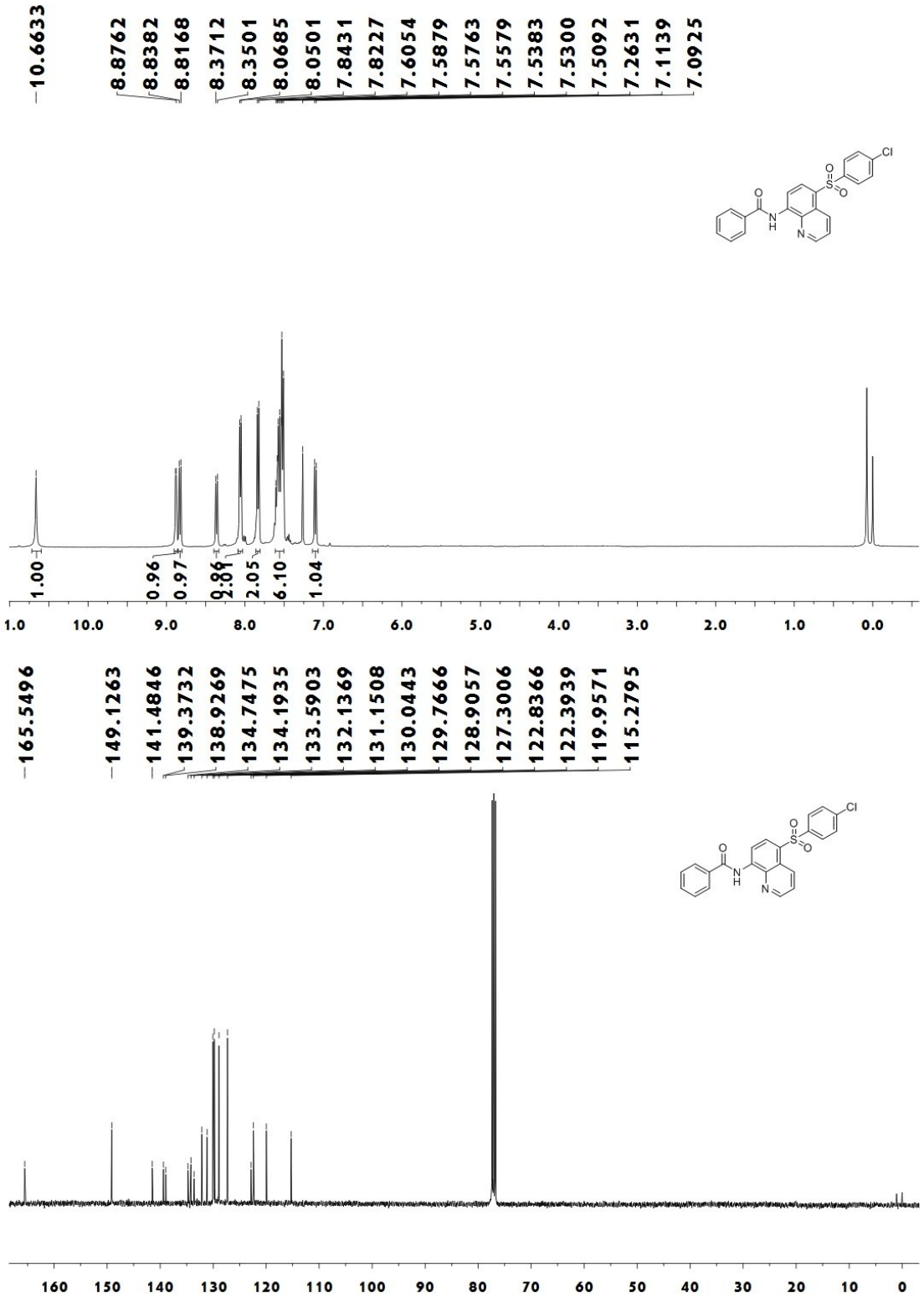
N-(5-Tosylquinolin-8-yl)cyclopropanecarboxamide (3la)



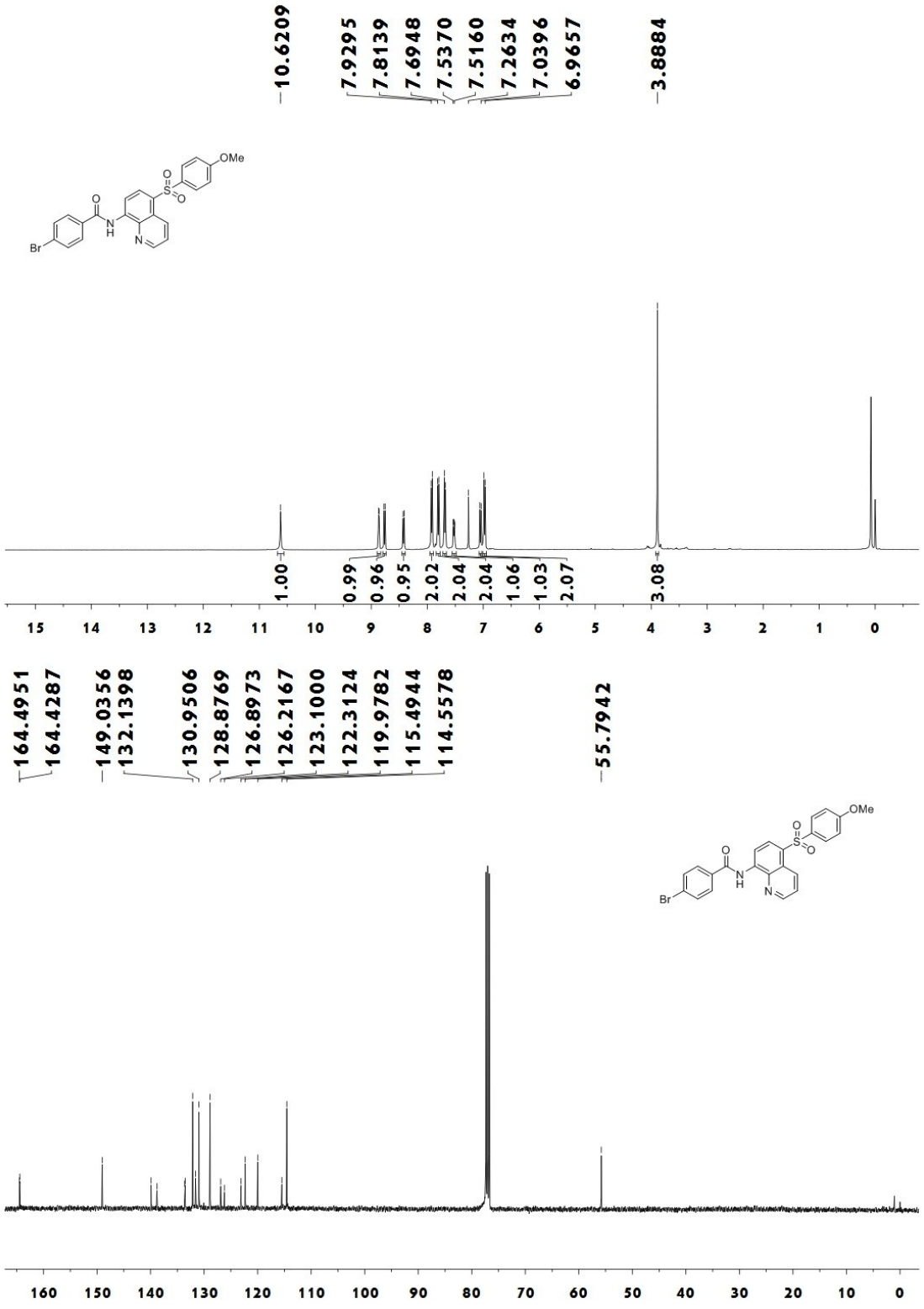
N-(5-(phenylsulfonyl)quinolin-8-yl)benzamide (3ad)



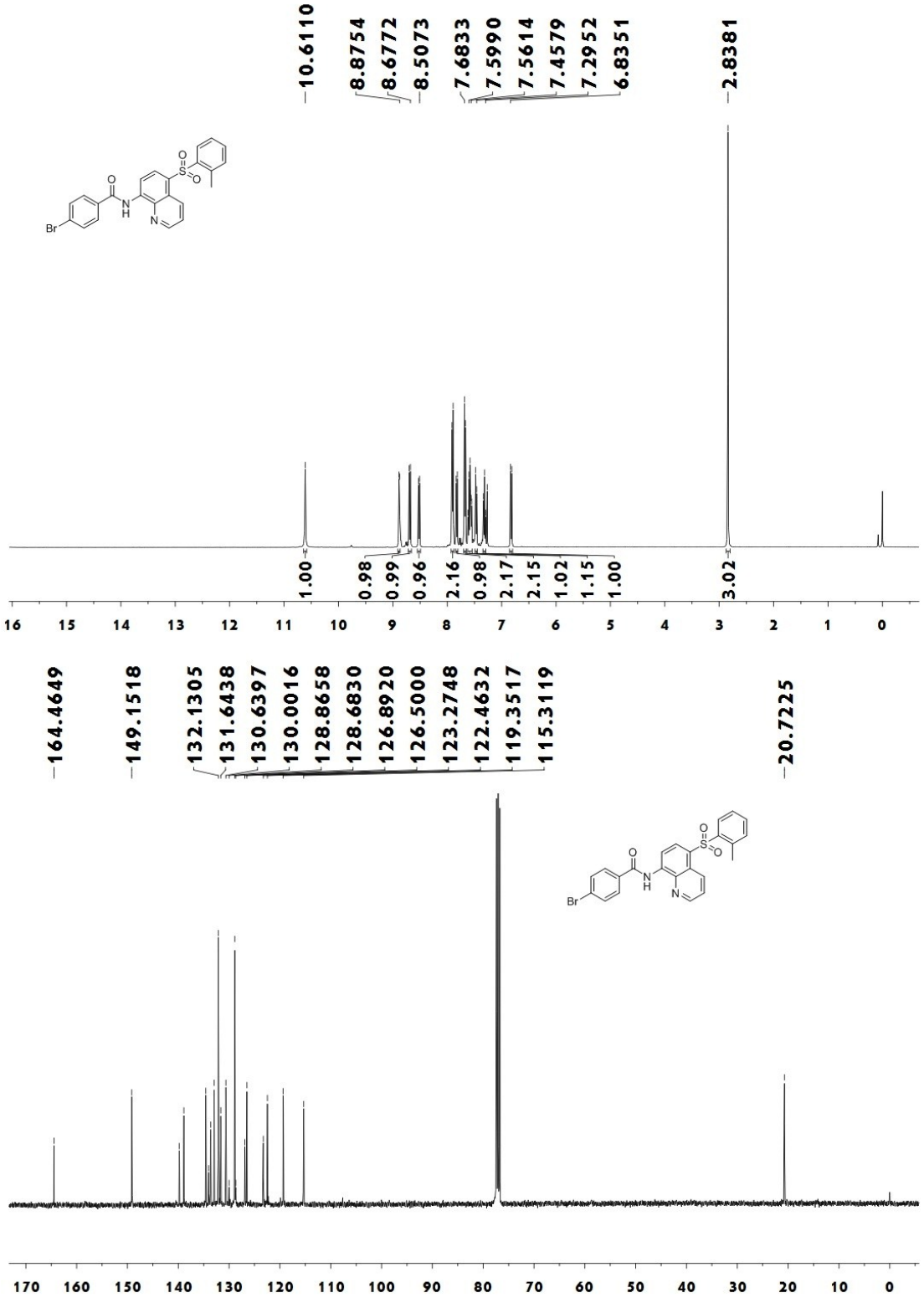
N-(5-(4-Chlorophenylsulfonyl)quinolin-8-yl)benzamide (3af)



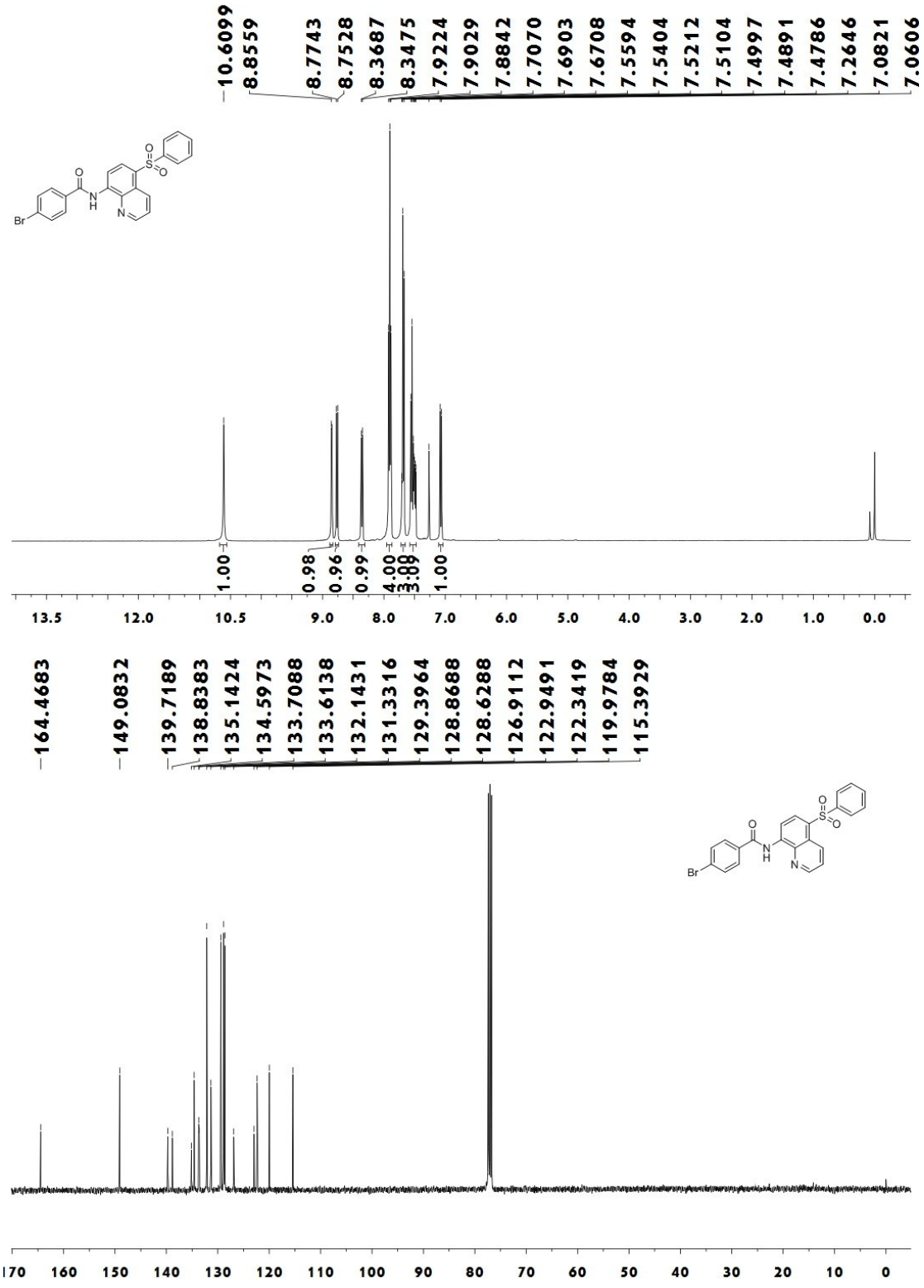
4-Bromo-*N*-(5-(4-Methoxyphenylsulfonyl)quinolin-8-yl)benzamide (3eb)



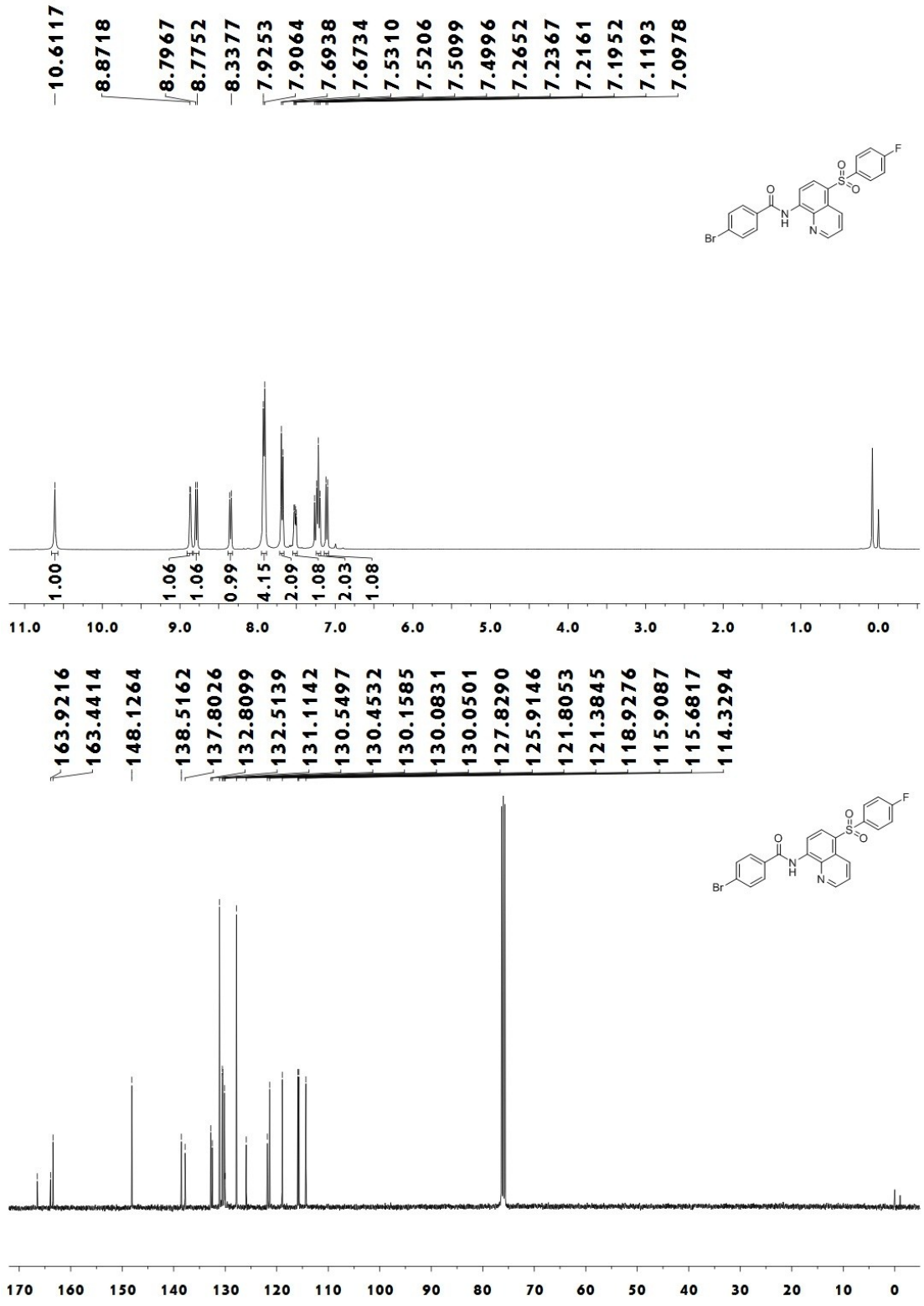
4-Bromo-N-(5-((2-Methylphenyl)sulfonyl)quinolin-8-yl)benzamide (3ec)



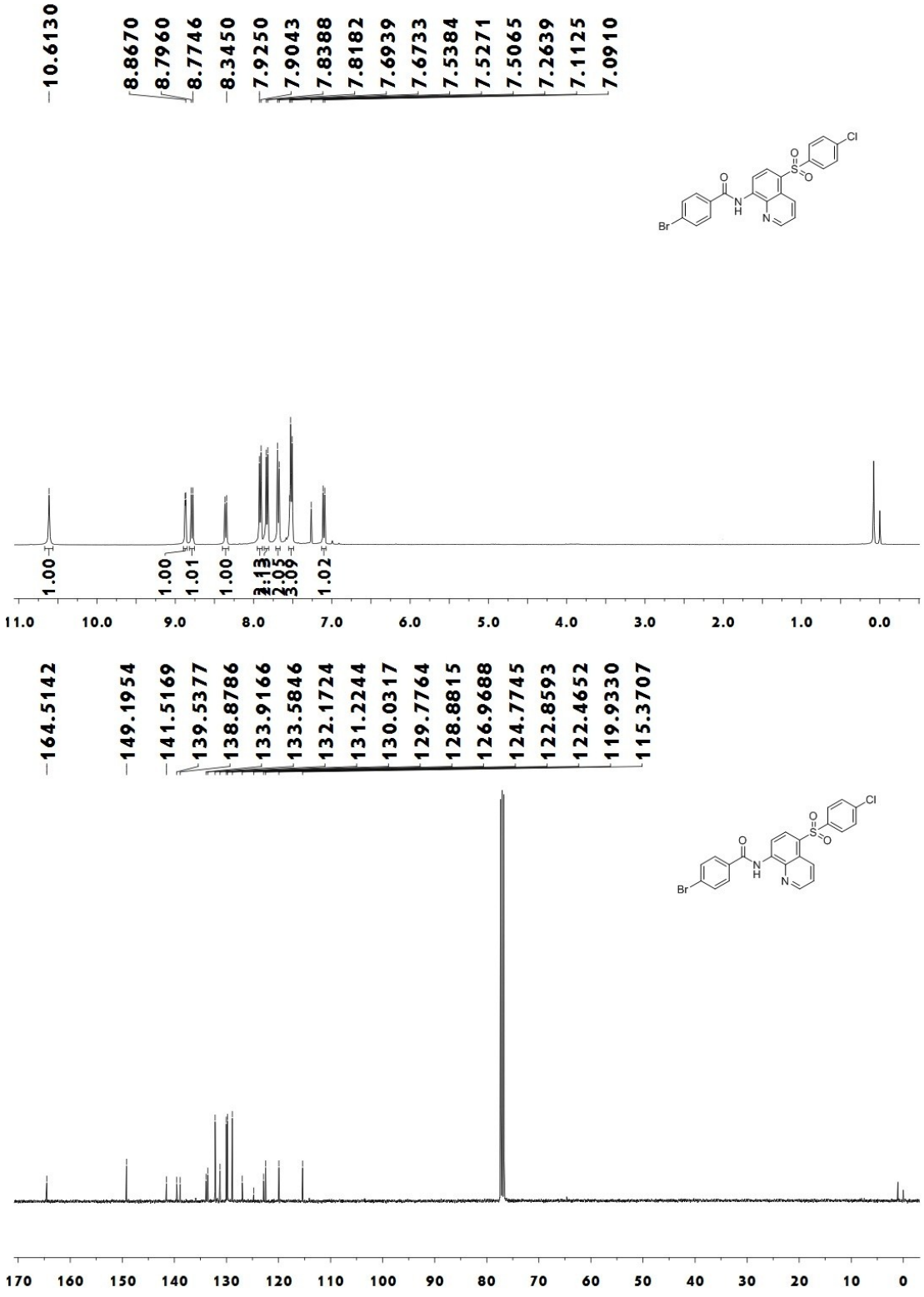
4-Bromo-N-(5-(Phenylsulfonyl)quinolin-8yl)benzamide (3ed)



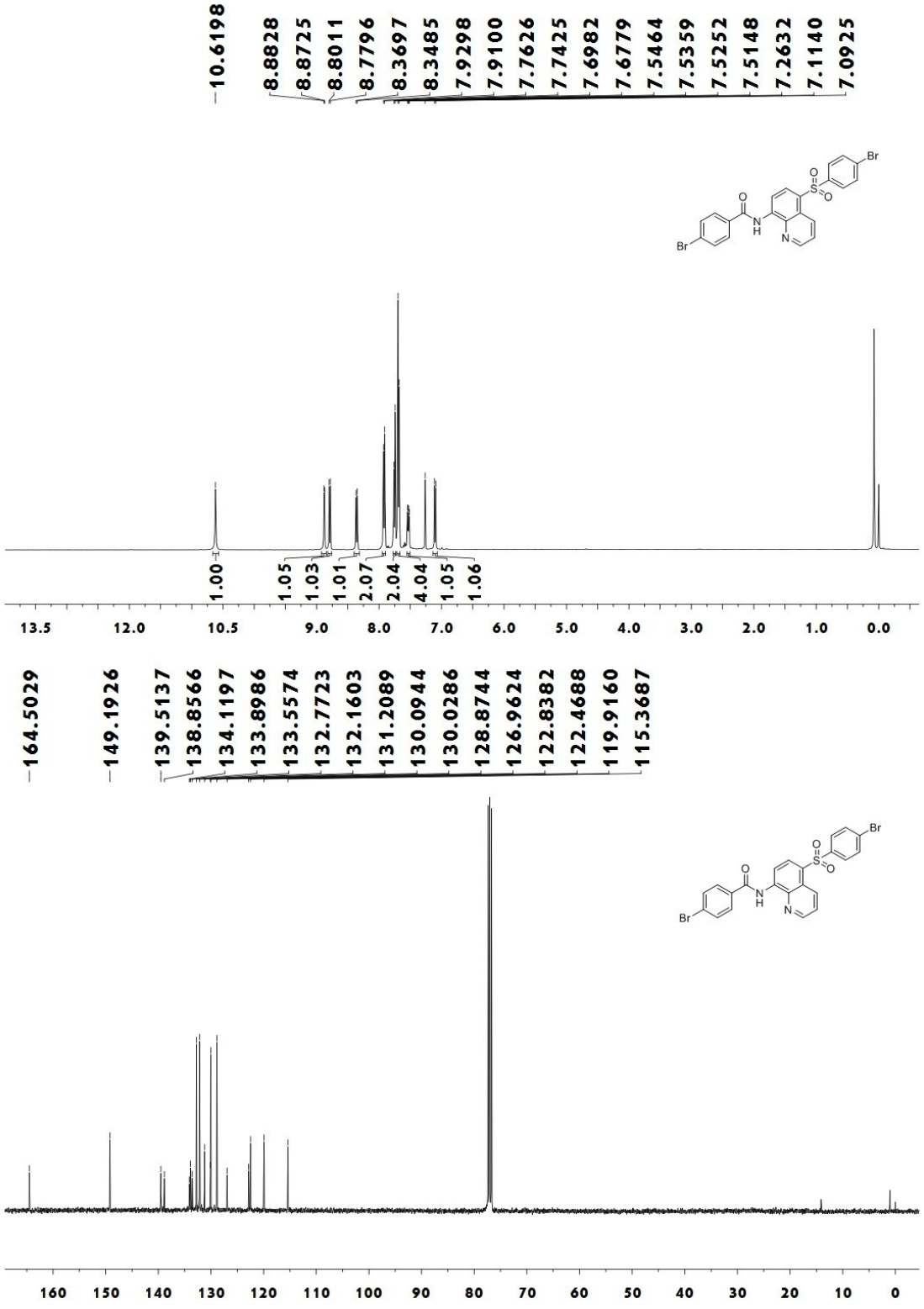
4-Bromo-N-(5-((4-Fluorophenyl)sulfonyl)quinolin-8-yl)benzamide (3ee)



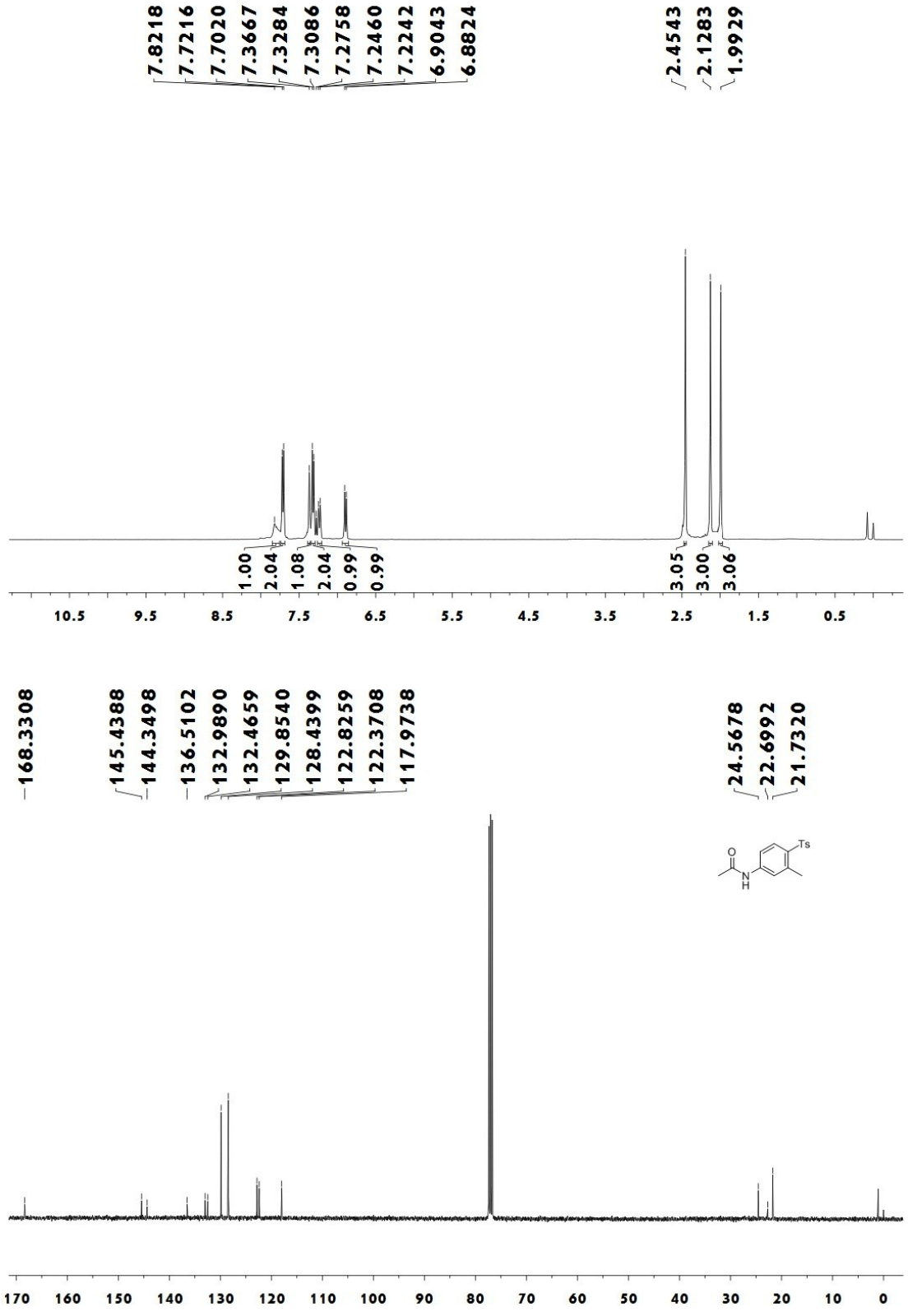
4-Bromo-N-(5-((4-Chlorophenyl)sulfonyl)quinolin-8-yl)benzamide (3ef)



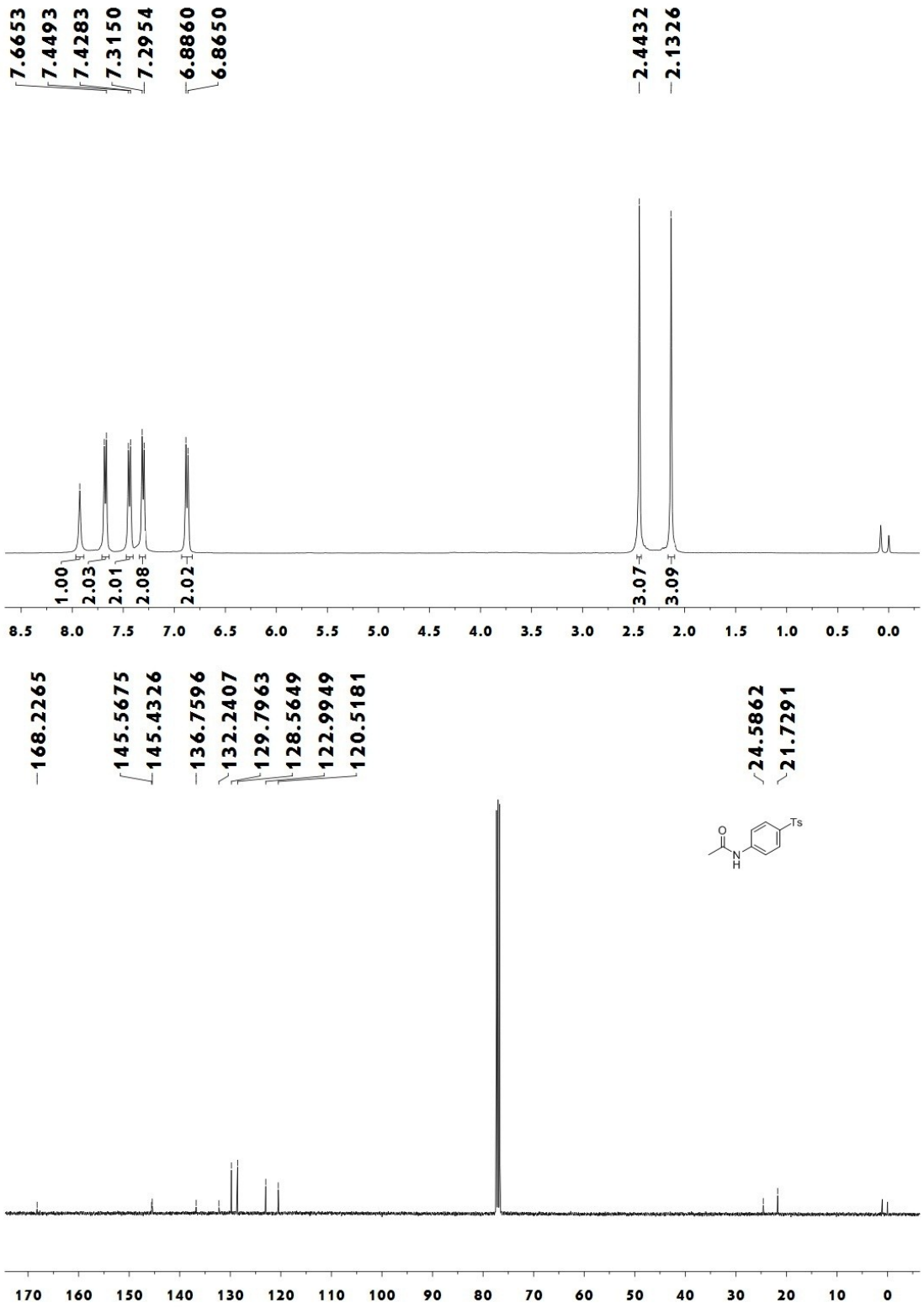
4-Bromo-*N*-(5-(4-Bromophenylsulfonyl)quinolin-8-yl)benzamide (3eg)

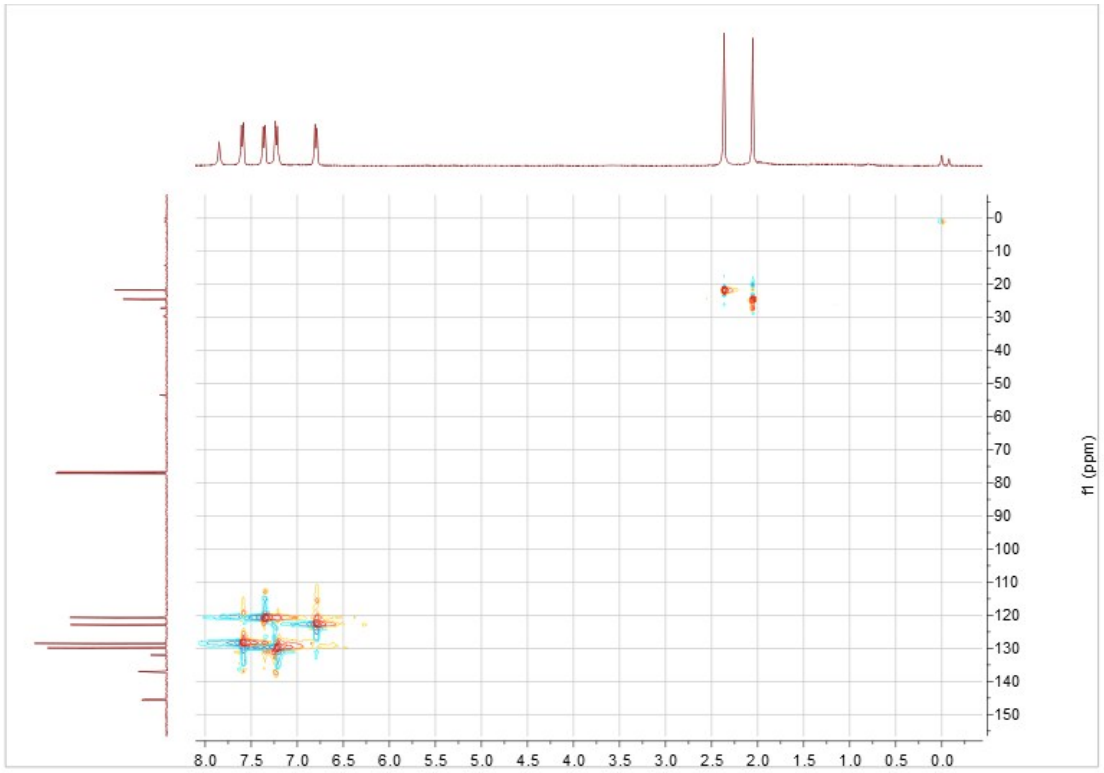


N-(5-Methyl-4-Tosylylphenyl)acetamide (**5aa**)



N-(4-Tosylylphenyl)acetamide (**5ba**)

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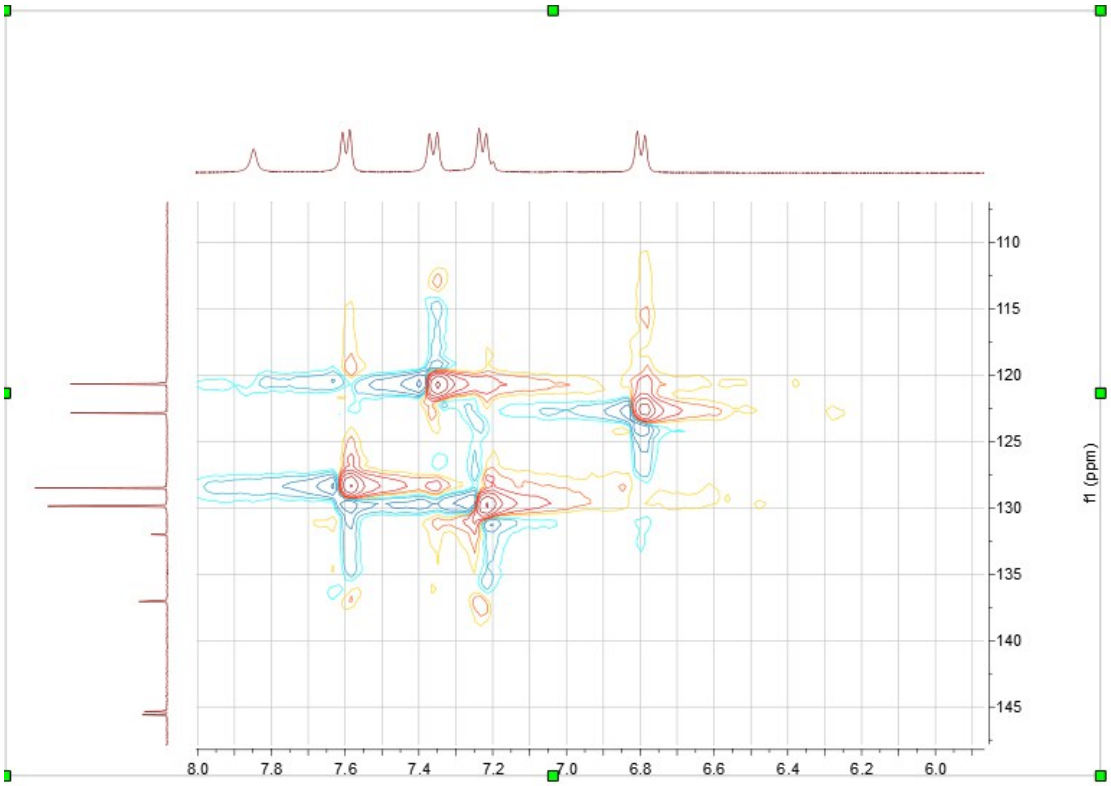
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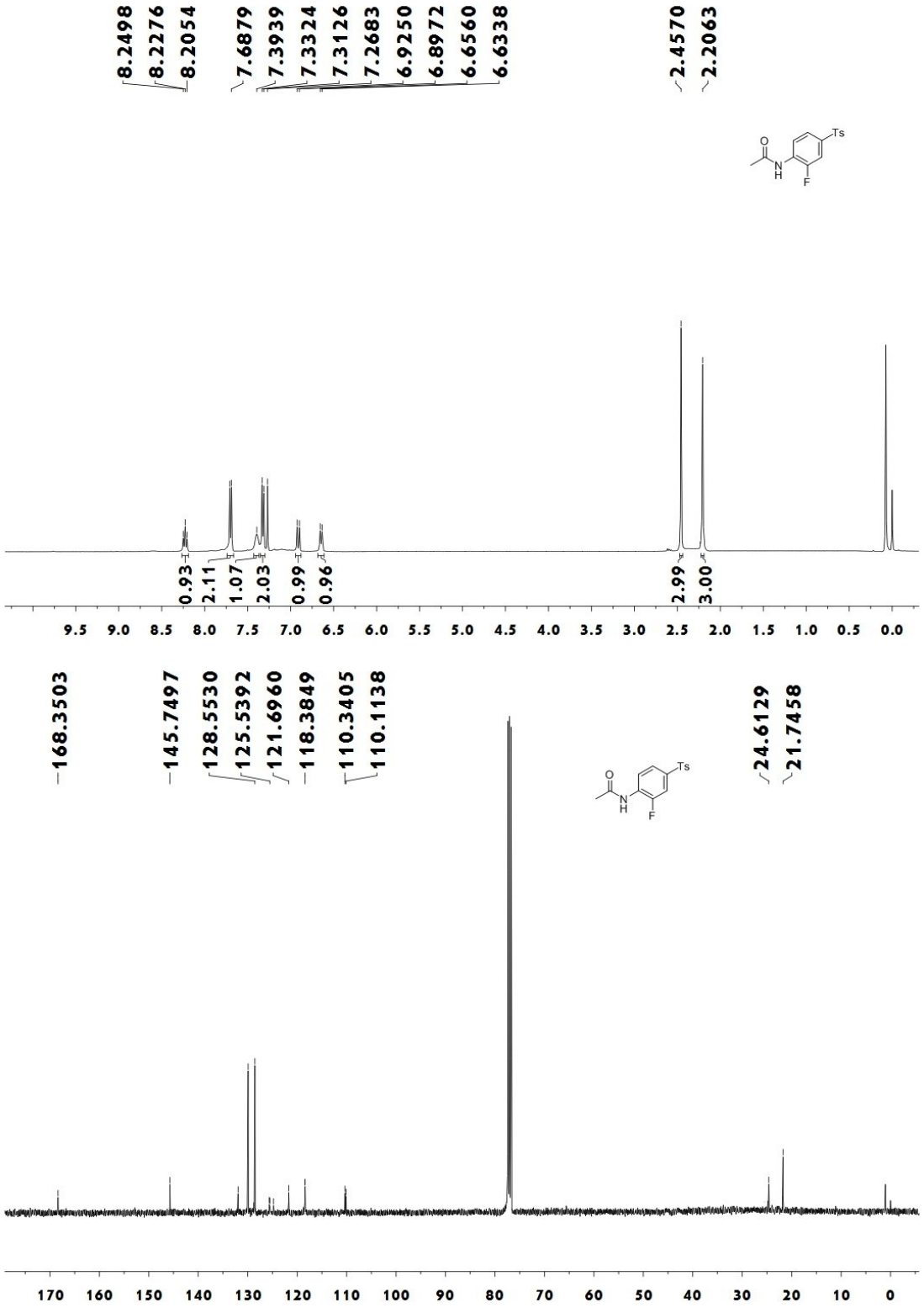
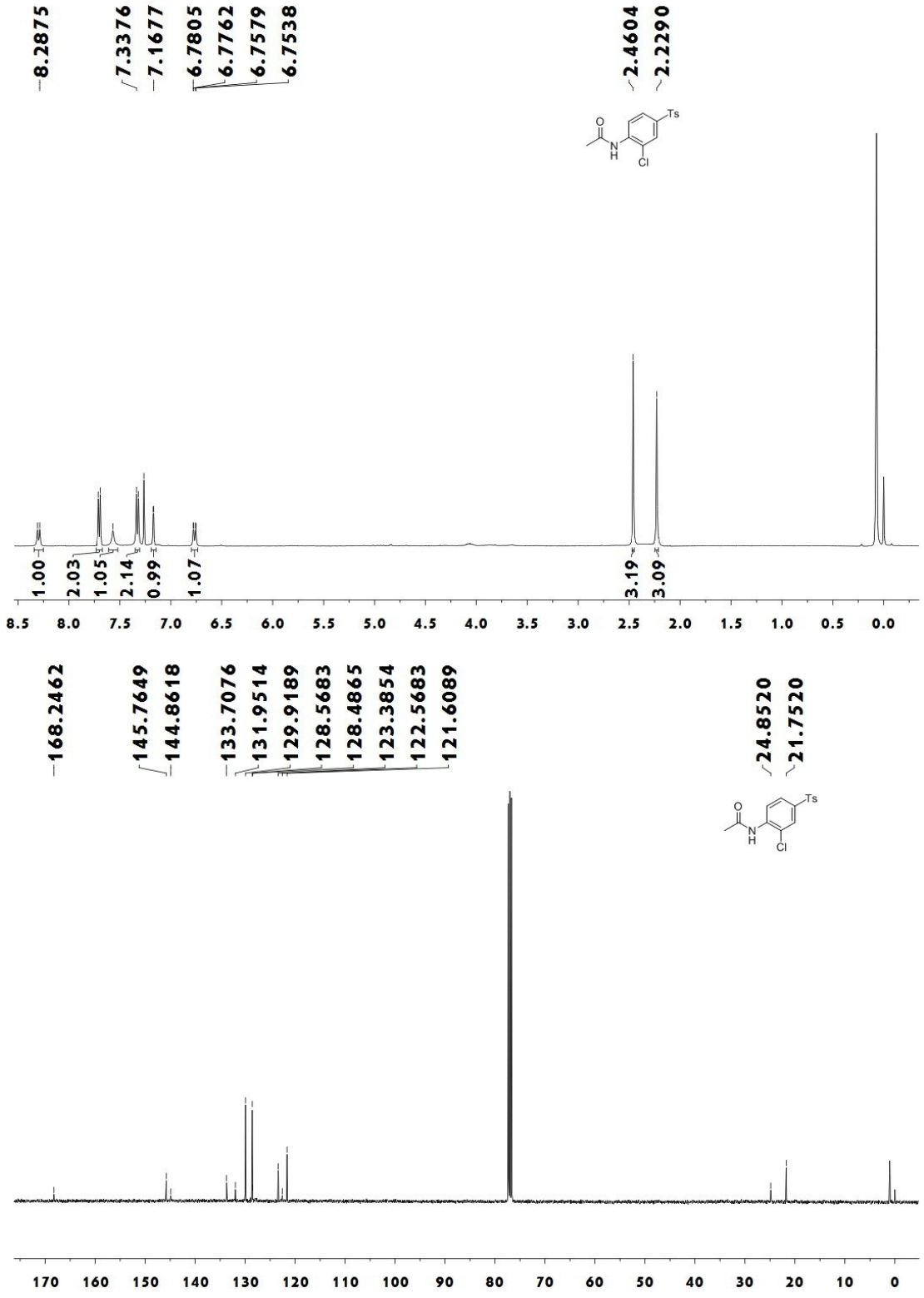
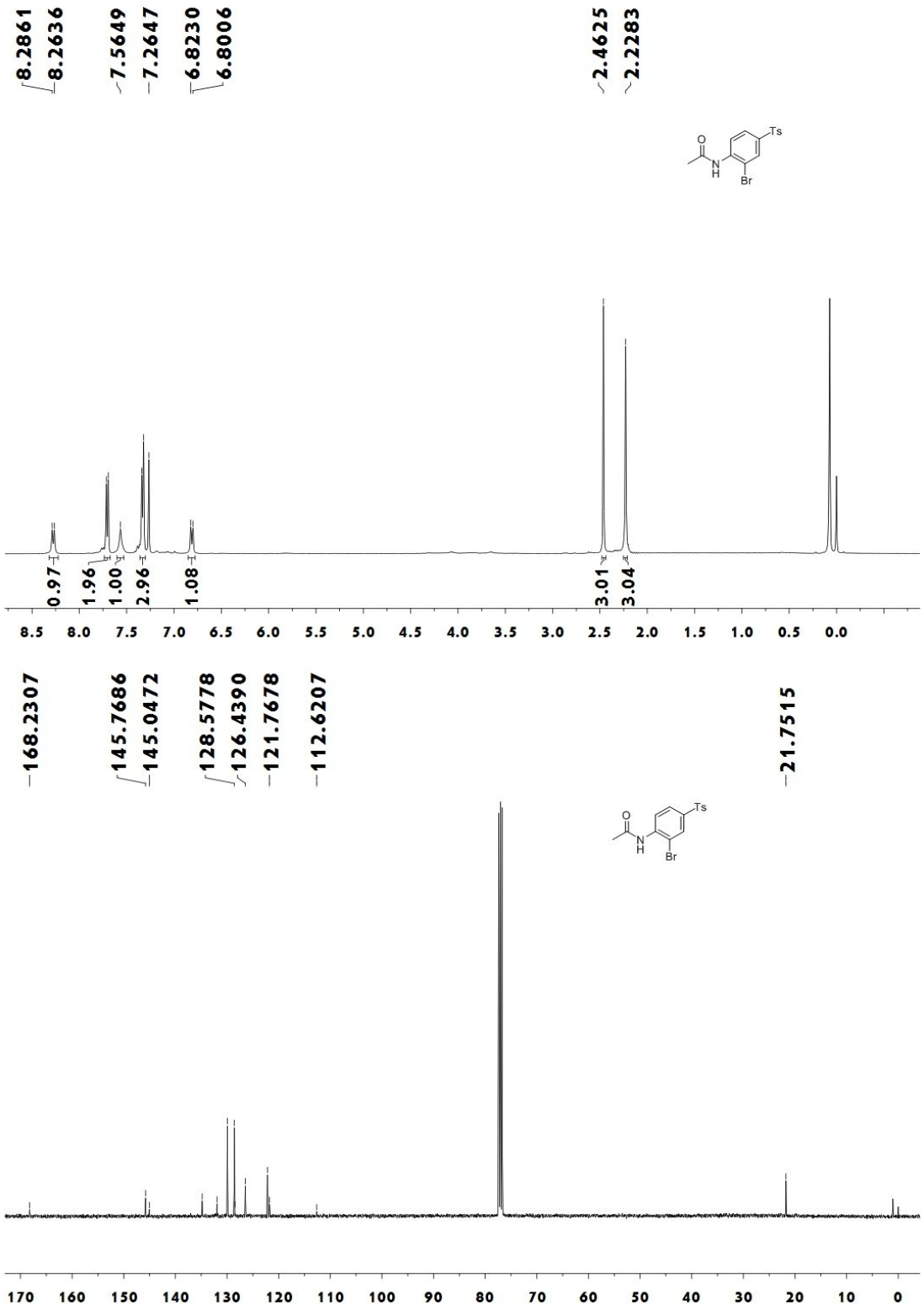
N-(2-Fluoro-4-Tosylylphenyl)acetamide (**5ca**)



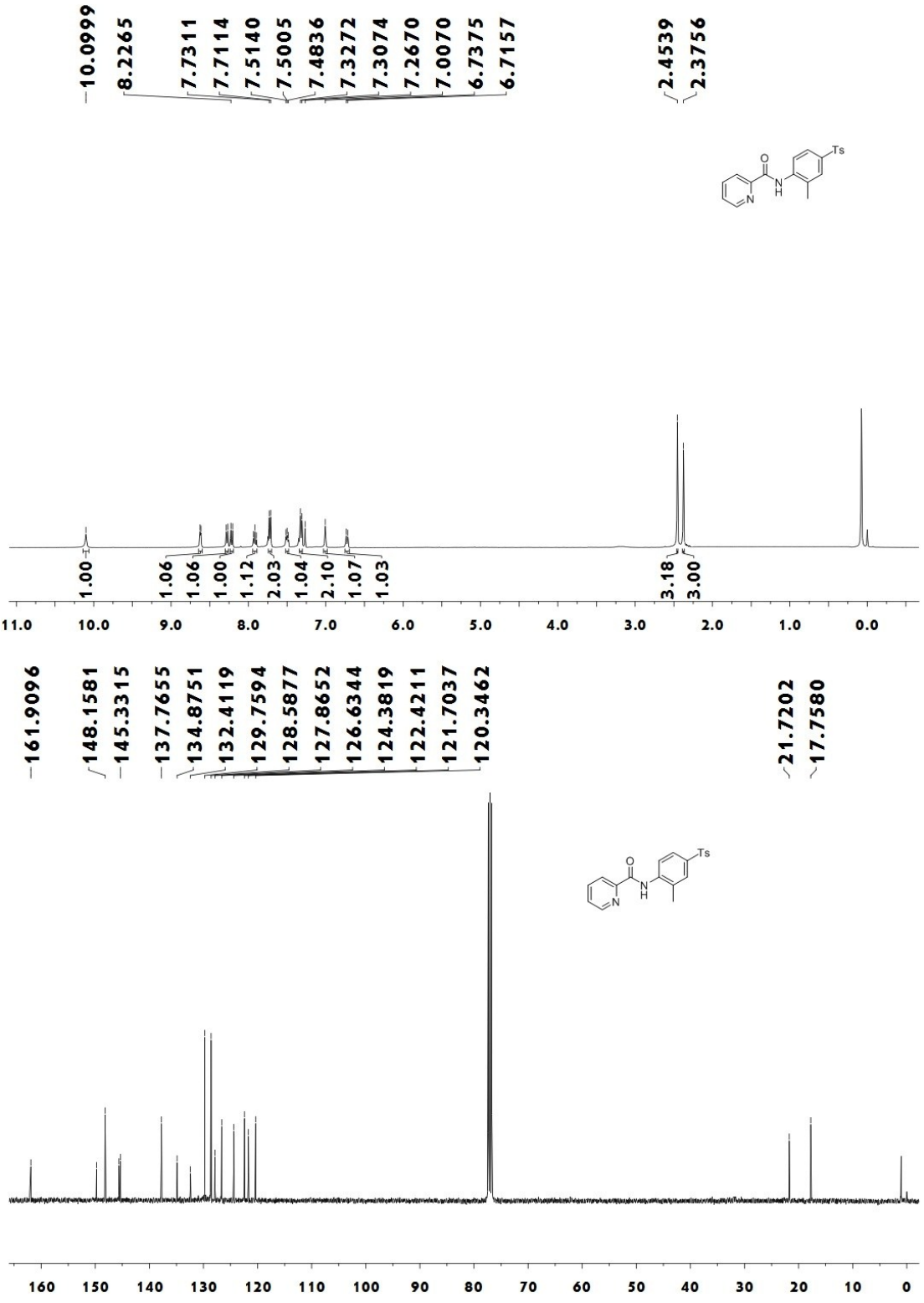
N-(2-Chloro-4-Tosylylphenyl)acetamide (**5da**)



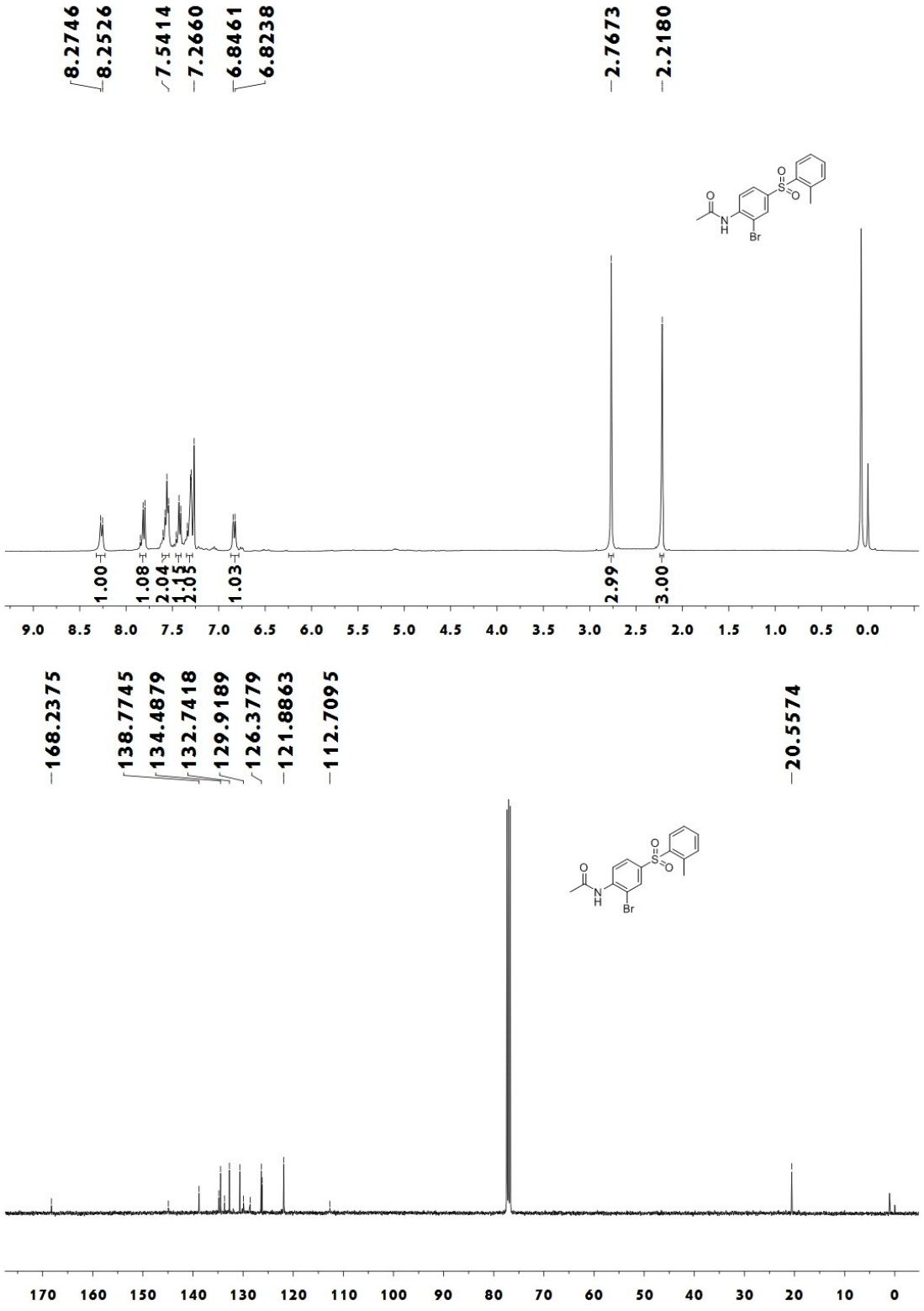
N-(2-Bromo-4-Tosylylphenyl)acetamide (**5ea**)



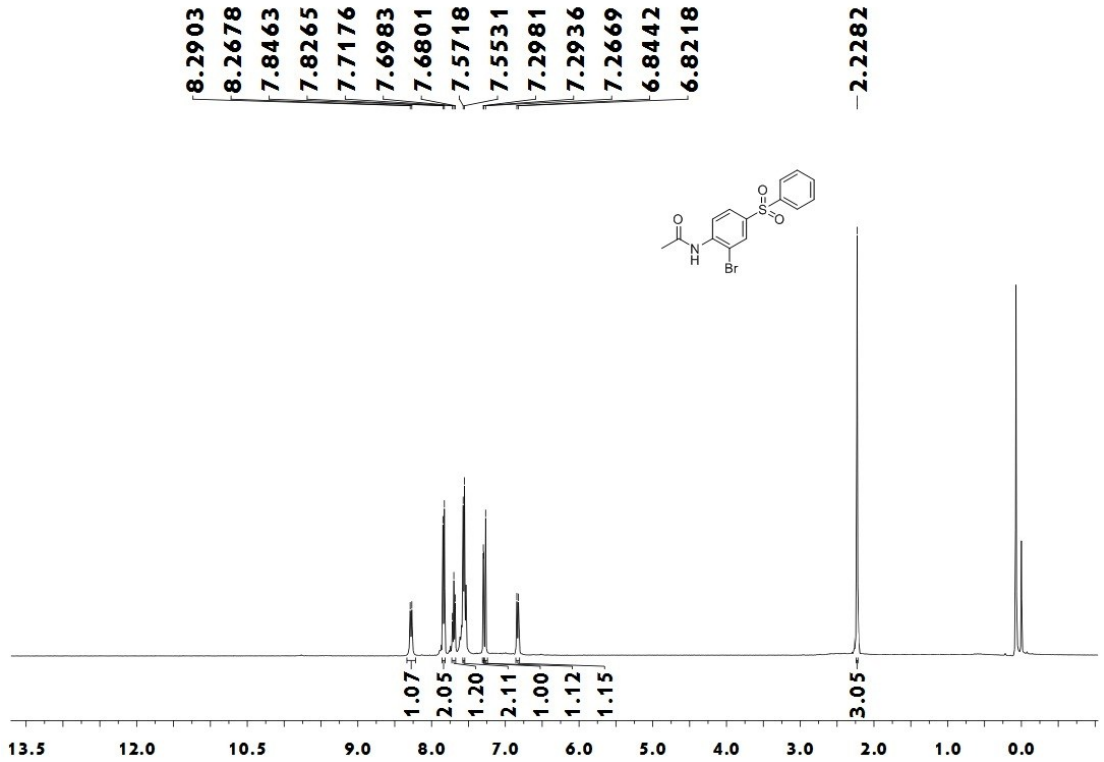
N-(2-Methyl-4-Tosylylphenyl)pyridylamide (**5fa**)

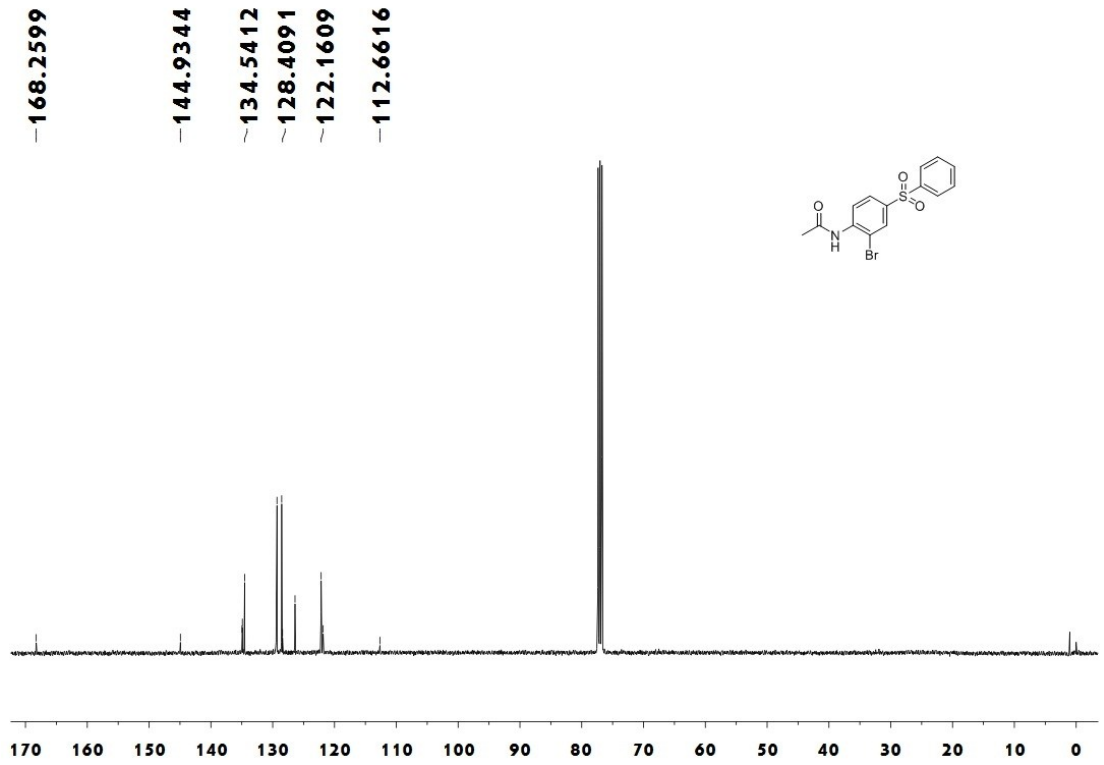


N-(2-Bromo-4-((2-Methylphenyl)sulfonyl))acetamide (**5ec**)

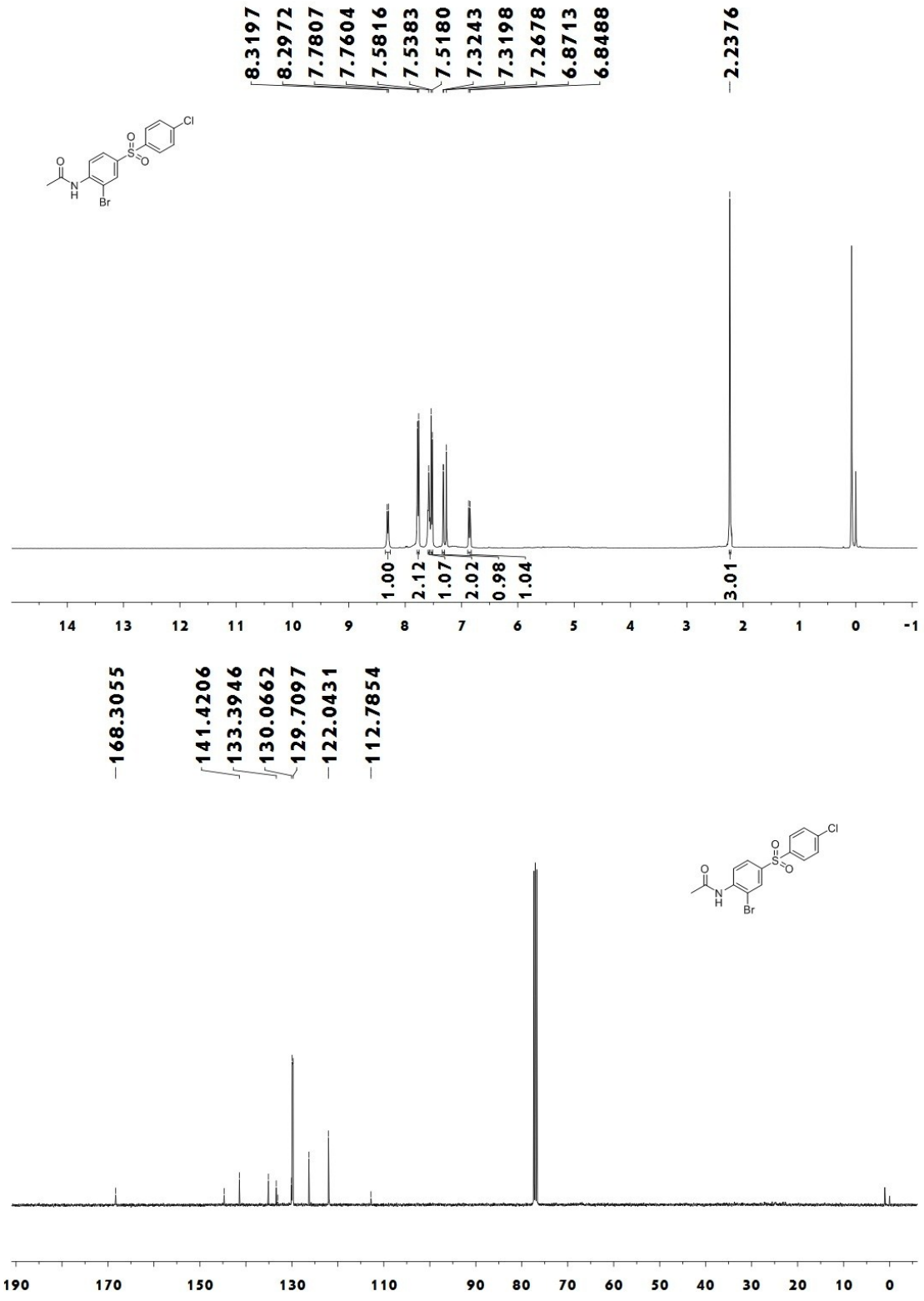


N-(2-Bromo-4-(Phenylsulfonyl))acetamide (**5ed**)

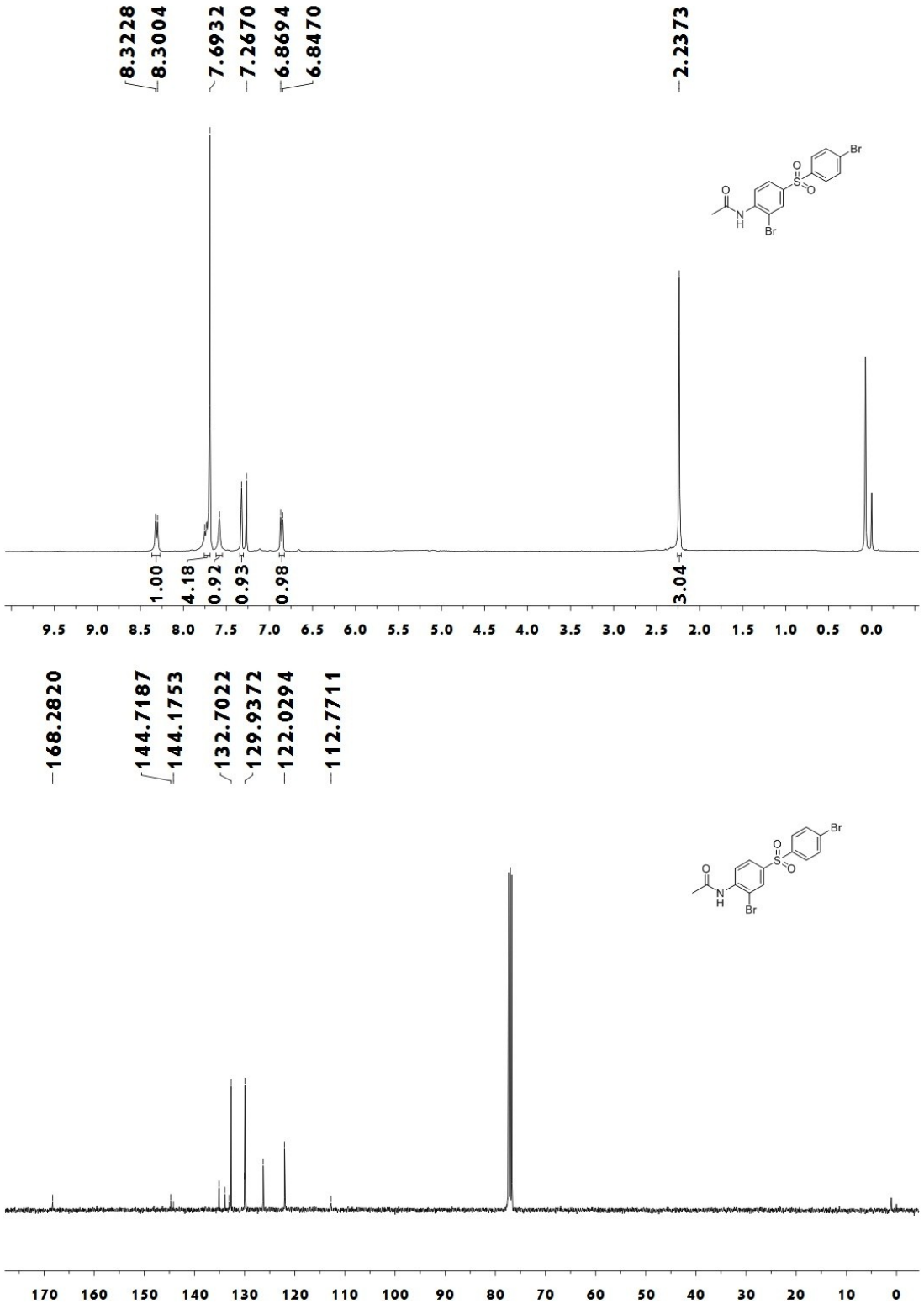




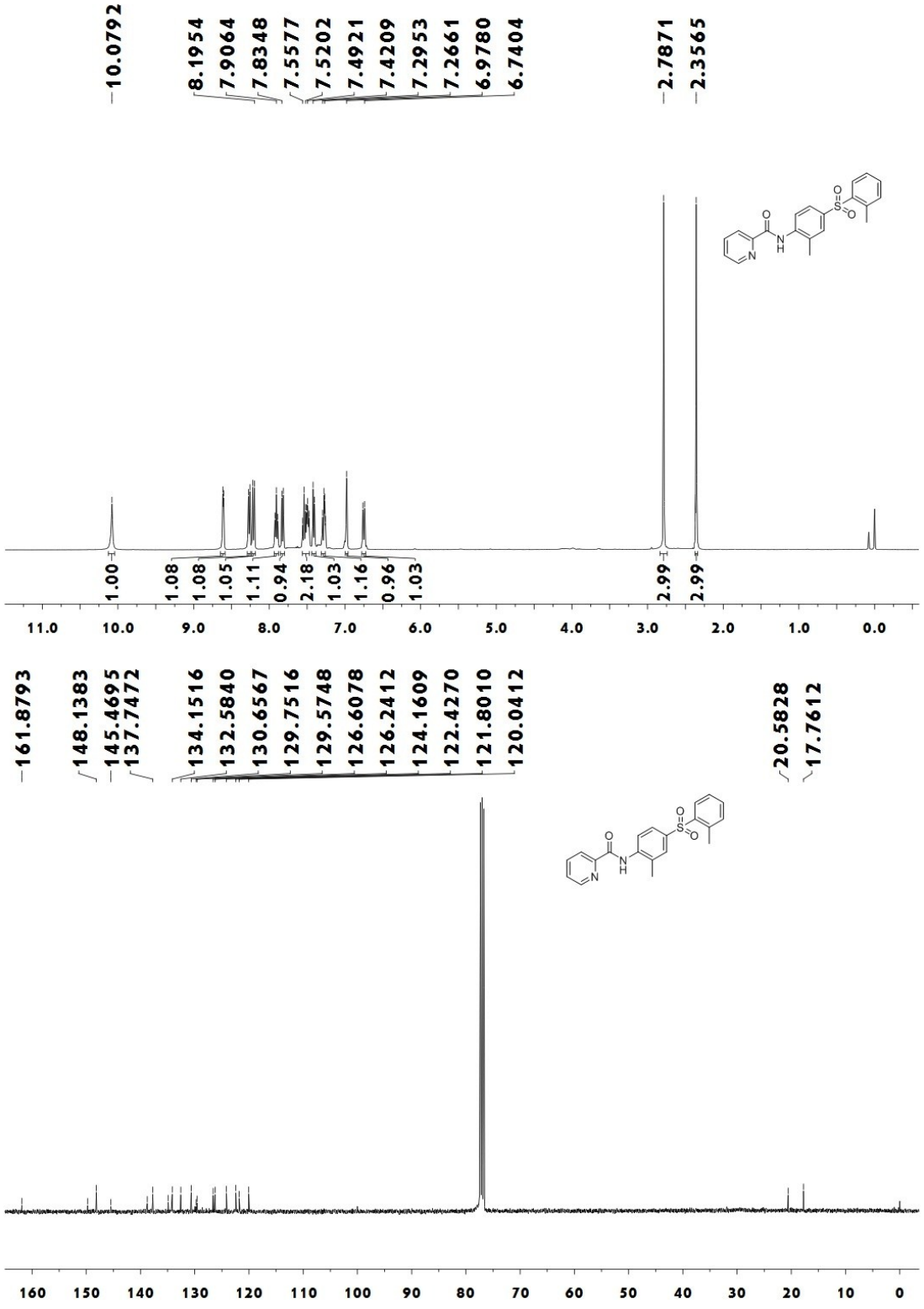
N-(2-Bromo-4-((4-Chlorophenyl)sulfonyl))acetamide (**5ef**)



N-(2-Bromo-4-((4-Bromophenyl)sulfonyl))acetamide (**5eg**)



N-(2-Methyl-4-(2-Methylphenyl)sulfonyl)pyridylamide (**5fc**)



N-(2-Methyl-4-Phenylsulfonyl)pyridylamide (**5fd**)