Supporting Information

Domino Cyclization and Oxidation Approach for One-Pot Access to Thiazoles and Benzothiazoles

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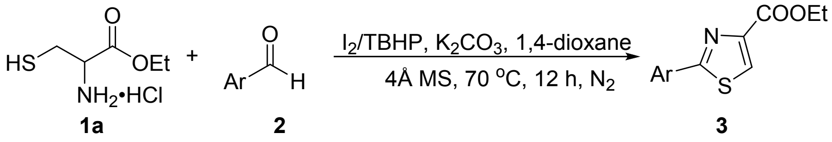
I. General Methods.

All reactions were carried out in schlenk tubes. The reactions were monitored by thin-layer chromatography on silica gel 60-F254 coated 0.2 mm plates. Visualization was accomplished by UV light (254 nm). The crude products were purified by flash column chromatography using silica gel (normal phase, 200-300 mesh. ^{1}H NMR spectra were recorded on a 400 MHz spectrometer at ambient temperature. Data were reported as follows: (1) chemical shift in parts per million (δ, ppm) from $CDCl_3$ (7.26 ppm), DMSO-d_6 (2.50 ppm); (2) multiplicity (s = singlet, br = broad, d = doublet, t = triplet, q = quartet, and m = multiplet); (3) coupling constants (Hz). ^{13}C NMR spectra were recorded on a 100 MHz spectrometer at ambient temperature. Chemical shifts were reported in ppm from $CDCl_3$ (77.10 ppm), DMSO-d_6 (39.52 ppm). Melting points were obtained on a melting point apparatus and the data are uncorrected. HR-MS analyses were carried out using a time-of-flight (TOF)-MS instrument with an electrospray ionization (ESI) source. All commercial materials were used as received unless otherwise noted. 4Å molecular sieves (powder) were activated at 100 ^{o}C

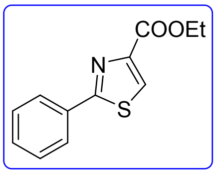
II. Analytical Characterization Data of Products

1) General procedure A:



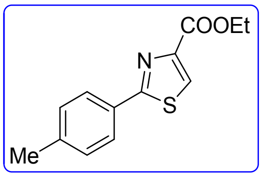
A mixture of L-cysteine ethyl ester hydrochloride (**1a**, 0.8 mmol, 0.1486 g, 4.0 equiv.), benzaldehyde (0.2 mmol, 0.0212 g, 1.0 equiv.), K_2CO_3 (0.6 mmol, 0.0828 g, 3.0 equiv.), I_2 (0.06 mmol, 0.0152 g, 0.3 equiv.), 4Å molecular sieve (0.4 g) was charged in a schlenk tube and purged with nitrogen gas for three times. 1,4-Dioxane (1 mL), and TBHP (70% in cyclohexane, 0.8 mmol, 0.1029 g, 4 equiv.) were then added slowly to the mixture at room temperature. The mixture was stirred at 70 ^{o}C for 12 hours. The resultant solution was quenched with aqueous saturated sodium thiosulfate solution (4 mL) and extracted with ethyl acetate (3×30 mL). The organic phase was combined and washed with brine (3×30 mL), dried over anhydrous sodium sulfate, filtered and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography (petroleum ether (PE) and ethyl acetate (EA) as the eluent).

Ethyl 2-phenylthiazole-4-carboxylate (3a)



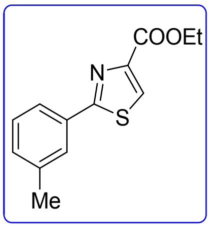
Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=25:1 as the eluent) to give **3a** (88% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (s, 1H), 8.01-7.99 (m, 2H), 7.44-7.43 (m, 3H), 4.44 (q, J = 7.1 Hz, 2H), 1.43 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 161.5, 148.1, 132.8, 130.7, 128.9, 127.1, 127.0, 61.5, 14.4. HRMS (ESI): Calcd for $C_{12}H_{12}NO_2S^+$ $[M+H]^+$ 234.0583, found 234.0582.

Ethyl 2-(p-tolyl)thiazole-4-carboxylate (3b)



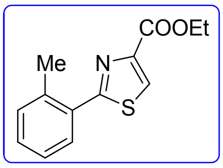
Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=25:1 as the eluent) to give **3b** (79% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (s, 1H), 7.89 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 4.44 (q, J = 7.1 Hz, 2H), 2.39 (s, 3H), 1.42 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.1, 161.5, 147.9, 141.1, 130.2, 129.6, 126.9, 126.7, 61.5, 21.5, 14.4. HRMS (ESI): Calcd for $C_{13}H_{14}NO_2S^+$ $[M+H]^+$ 248.0740, found 248.0739.

Ethyl 2-(m-tolyl)thiazole-4-carboxylate (3c)



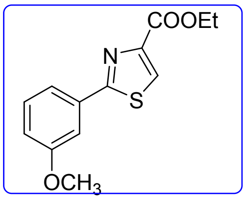
Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=25:1 as the eluent) to give **3c** (73% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (s, 1H), 7.86 (s, 1H), 7.77 (d, J = 7.6 Hz, 1H), 7.32 (t, J = 7.6 Hz, 1H), 7.25 (d, J = 7.6 Hz, 1H), 4.45 (q, J = 7.1 Hz, 2H), 2.41 (s, 3H), 1.43 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.1, 161.5, 148.0, 138.8, 132.7, 131.5, 128.8, 127.5, 126.9, 124.2, 61.5, 21.3, 14.4. HRMS (ESI): Calcd for $C_{13}H_{14}NO_2S^+$ $[M+H]^+$ 248.0740, found 248.0740.

Ethyl 2-(o-tolyl)thiazole-4-carboxylate (3d)



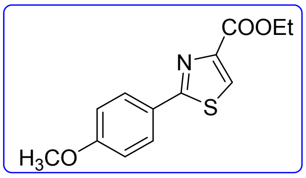
Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=20:1 as the eluent) to give **3d** (83% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (s, 1H), 7.69(d, J = 7.52 Hz, 1H), 7.36-7.25 (m, 3H), 4.44 (q, J = 7.1 Hz, 2H), 2.58 (s, 3H), 1.42 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 161.6, 147.5, 136.8, 132.4, 131.4, 130.2, 129.9, 127.7, 126.1, 61.4, 21.3, 14.4. HRMS (ESI): Calcd for $C_{13}H_{14}NO_2S^+$ $[M+H]^+$ 248.0740, found 248.0740.

Ethyl 2-(3-methoxyphenyl)thiazole-4-carboxylate (3e)



Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=15:1 as the eluent) to give **3e** (95% yield) as a white solid. Mp 58 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (s, 1H), 7.58-7.53 (m, 2H), 7.34 (t, J = 8.0 Hz, 1H), 7.00-6.98 (m, 1H), 4.44 (q, J = 7.1 Hz, 2H), 3.88 (s, 3H), 1.43 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.7, 161.4, 160.0, 147.9, 134.0, 129.9, 127.2, 119.6, 117.0, 111.6, 61.5, 55.5, 14.4. HRMS (ESI): Calcd for $C_{13}H_{14}NO_3S^+$ $[M+H]^+$ 264.0689, found 264.0690.

Ethyl 2-(4-methoxyphenyl)thiazole-4-carboxylate (3f)



Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=15:1 as the eluent) to give **3f** (85% yield) as a white solid. Mp 96 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.08 (s, 1H), 7.95-7.93 (m, 2H), 6.95 (d, J = 8.8 Hz, 2H), 4.44 (q, J = 7.1 Hz, 2H), 3.85 (s, 3H), 1.42 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 168.7, 161.6, 161.5, 147.8, 128.5, 126.3, 125.7, 114.3, 61.4, 55.4, 14.4. HRMS (ESI): Calcd for $C_{13}H_{14}NO_3S^+$ [M+H]$^+$ 264.0689; found 264.0689.

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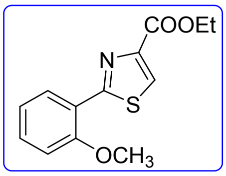
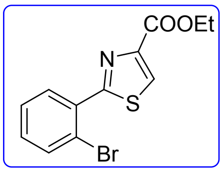
Ethyl 2-(2-methoxyphenyl)thiazole-4-carboxylate (3g)



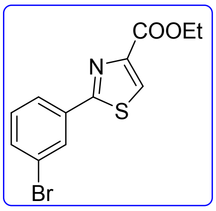
Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=15:1 as the eluent) to give **3g** (89% yield) as a yellow oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.52 (dd, J = 7.8, 1.4 Hz, 1H), 8.20 (s, 1H), 7.44-7.39 (m, 1H), 7.09 (t, J = 7.6 Hz, 1H), 7.03 (d, J = 8.3 Hz, 1H), 4.45 (q, J = 7.1 Hz, 2H), 4.03 (s, 3H), 1.43 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 163.0, 161.9, 156.52, 146.1, 131.3, 129.1, 127.9, 121.6, 121.1, 111.2, 61.3, 55.6, 14.4. HRMS (ESI): Calcd for $C_{13}H_{14}NO_3S^+$ [M+H]$^+$ 264.0689, found 264.0688.

Ethyl 2-(2-bromophenyl)thiazole-4-carboxylate (3h)



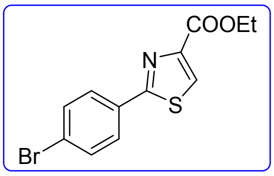
Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=20:1 as the eluent) to give **3h** (66% yield) as a yellow oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.30 (s, 1H), 8.11 (dd, J = 7.8, 1.7 Hz, 1H), 7.69 (dd, J = 8.0, 1.0 Hz, 1H), 7.42 (td, J = 7.8, 1.2 Hz, 1H), 7.30 (td, J = 7.8, 1.5 Hz, 1H), 4.46 (q, J = 7.1 Hz, 2H), 1.43 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 165.7, 161.5, 146.9, 133.9, 133.5, 132.1, 131.1, 128.5, 127.7, 121.8, 61.5, 14.4. HRMS (ESI): Calcd for $C_{12}H_{11}BrNO_2S^+$ [M+H]$^+$ 311.9688, found 311.9691.

2-(3-bromophenyl)-4-(ethylperoxy)thiazole (3i)



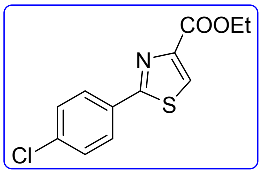
Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=20:1 as the eluent) to give **3i** (56% yield) as a white solid. Mp 72 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (t, *J* = 1.8 Hz, 1H), 8.18 (s, 1H), 7.93-7.88 (m, 1H), 7.58 (ddd, *J* = 8.0, 1.8, 0.9 Hz, 1H), 7.33 (t, *J* = 7.9 Hz, 1H), 4.46 (q, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 161.3, 148.3, 134.6, 133.6, 130.5, 129.8, 127.5, 125.6, 123.2, 61.6, 14.4. HRMS (ESI): Calcd for $C_{12}H_{11}BrNO_2S^+$ $[M+H]^+$ 311.9688, found 311.9690.

Ethyl 2-(4-bromophenyl)thiazole-4-carboxylate (3j)



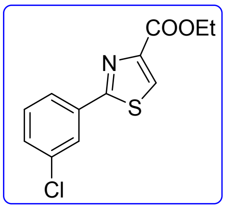
Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=20:1 as the eluent) to give **3j** (81% yield) as a yellow solid. Mp 99 °C. ^{1}H NMR (400 MHz, CDCl3): δ 8.18 (s, 1H), 7.90-7.88 (m, 2H), 7.61-7.58 (m, 2H), 4.46 (q, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.6, 161.3, 148.3, 132.2, 131.7, 128.4, 127.2, 125.1, 61.6, 14.4. HRMS (ESI): Calcd for $C_{12}H_{11}BrNO_2S^+$ $[M+H]^+$ 311.9688, found 311.9690.

Ethyl 2-(4-chlorophenyl)thiazole-4-carboxylate (3k)



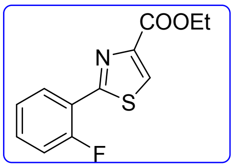
Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=15:1 as the eluent) to give **3k** (72% yield) as a white solid. Mp 90 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (s, 1H), 7.95 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 4.45 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl3): *δ* 167.5, 161.3, 148.3, 136.8, 131.3, 129.2, 128.2, 127.2, 61.6, 14.4. HRMS (ESI): Calcd for $C_{12}H_{11}ClNO_2S^+$ $[M+H]^+$ 268.0194, found 268.0198.

Ethyl 2-(3-chlorophenyl)thiazole-4-carboxylate (3l)



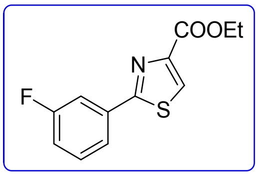
Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=15:1 as the eluent) to give **3l** (75% yield) as a yellow solid. Mp 66 °C. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.18 (s, 1H), 8.04 (t, *J* = 1.6 Hz, 1H), 7.86 (dt, *J* = 7.3, 1.5 Hz, 1H), 7.44-7.36 (m, 2H), 4.46 (q, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl3): *δ* 167.1, 161.3, 148.3, 135.2, 134.4, 130.6, 130.2, 127.5, 126.9, 125.1, 61.6, 14.4. HRMS (ESI): Calcd for $C_{12}H_{11}ClNO_2S^+$ $[M+H]^+$ 268.0194, found 268.0197.

Ethyl 2-(2-fluorophenyl)thiazole-4-carboxylate (3m)



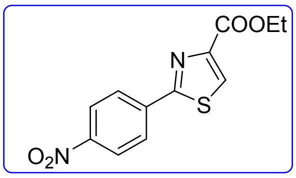
Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=15:1 as the eluent) to give **3m** (65% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (td, *J* = 7.7, 1.4 Hz, 1H), 8.27 (s, 1H), 7.45-7.39 (m, 1H), 7.29-7.24 (m, 1H), 7.20 (dd, *J* = 11.1, 9Hz, 1H), 4.456 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.5, 161.2 (d, *J* = 4.9 Hz), 160.1 (d, *J* = 250.4 Hz), 146.94, 131.83 (d, *J* = 8.6 Hz), 129.39, 128.25 (d, *J* = 9.1 Hz), 124.69 (d, *J* = 3.0 Hz), 120.63 (d, *J* = 11.2 Hz), 116.02 (d, *J* = 21.5 Hz), 61.50, 14.37. HRMS (ESI): Calcd for $C_{12}H_{11}FNO_2S^+$ $[M+H]^+$ 252.0489, found 252.0489.

Ethyl 2-(3-fluorophenyl)thiazole-4-carboxylate (3n)



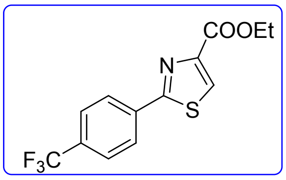
Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=15:1 as the eluent) to give **3n** (62% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (s, 1H), 7.76 (d, J = 7.3 Hz, 2H), 7.42 (dd, J = 13.9, 7.7 Hz, 1H), 7.20-7.08 (m, 1H), 4.45 (q, J = 7.1 Hz, 2H), 1.43 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.3, 163.0(d, J = 245.8 Hz), 161.3, 148.3, 134.78 (d, J = 8.1 Hz), 130.6 (d, J = 8.2 Hz), 127.5, 122.7 (d, J = 2.0 Hz), 117.6 (d, J = 2.2 Hz), 113.9 (d, J = 24.0 Hz), 61.60, 14.36. HRMS (ESI): Calcd for $C_{12}H_{11}FNO_2S^+$ $[M+H]^+$ 252.0489, found 252.0492.

Ethyl 2-(4-nitrophenyl)thiazole-4-carboxylate (3o)



Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=15:1 as the eluent) to give **3o** (49% yield) as a white solid. Mp 143 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, J = 8.9 Hz, 2H), 8.28 (s, 1H), 8.20 (d, J = 8.9 Hz, 2H), 4.47 (q, J = 7.1 Hz, 2H), 1.45 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 161.1, 148.9, 148.9, 138.2, 128.6, 127.7, 124.4, 61.8, 14.4. HRMS (ESI): Calcd for $C_{12}H_{11}N_2O_4S^+$ $[M+H]^+$ 279.0434, found 279.0435.

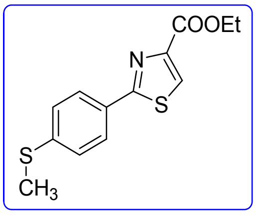
Ethyl 2-(4-(trifluoromethyl)phenyl)thiazole-4-carboxylate (3p)



Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=15:1 as the eluent) to give **3p** (44% yield) as a white solid. Mp 99 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (s, 1H), 8.14 (d, J = 8.1 Hz, 2H), 7.72 (d, J = 8.2 Hz, 2H), 4.47 (q, J = 7.1 Hz, 2H), 1.44 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 161.2, 148.6, 135.9, 132.5, 132.2, 127.9, 127.3, 126.0 (d, J = 4.0

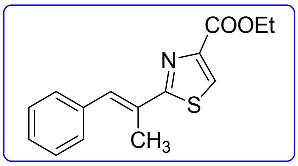
Hz), 61.7, 14.4. HRMS (ESI): Calcd for $C_{13}H_{11}F_3NO_2S^+$ $[M+H]^+$ 302.0457, found 302.0454.

Ethyl 2-(4-(methylthio)phenyl)-4,5-dihydrothiazole-4-carboxylate (3q)



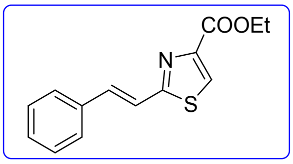
Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=15:1 as the eluent) to give **3q** (78% yield) as a yellow solid. Mp 80 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.11 (s, 1H), 7.91 (dd, J = 6.8, 1.7 Hz, 2H), 7.27 (d, J = 8.5 Hz, 2H), 4.44 (q, J = 7.1 Hz, 2H), 2.52 (s, 3H), 1.43 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.4, 161.5, 148.0, 142.4, 129.4, 127.2, 126.6, 125.9, 61.5, 15.2, 14.4. HRMS (ESI): Calcd for $C_{12}H_{15}NO_2S_2^+$ $[M+H]^+$ 280.0460, found 280.0460.

Ethyl (E)-2-(1-phenylprop-1-en-2-yl)thiazole-4-carboxylate (3r)



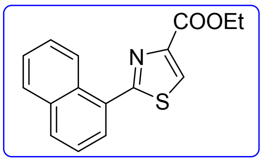
Following the general procedure A, the crude product was purified by silica gel flash chromatography(PE: EA=15:1 as the eluent) to give **3r** (49% yield) as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ 8.08 (s, 1H), 7.54 (s, 1H), 7.43-7.38 (m, 4H), 7.31-7.28 (m, 1H), 4.43 (q, J = 7.1 Hz, 2H), 2.45 (s, 3H), 1.42 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 160.5, 146.6, 135.3, 131.3, 129.7, 128.5, 127.4, 126.8, 125.4, 60.4, 15.7, 13.3. HRMS (ESI): Calcd for $C_{15}H_{16}NO_2S^+$ $[M+H]^+$ 274.0896, found 274.0898.

Ethyl (E)-2-styrylthiazole-4-carboxylate (3s)



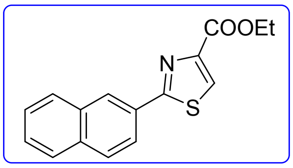
Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=15:1 as the eluent) to give **3s** (58% yield) as a yellow oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.08 (s, 1H), 7.52(d, J = 7.0 Hz, 2H), 7.41-7.35 (m, 5H), 7.32-7.31 (m, 1H), 4.44 (q, J = 7.1 Hz, 2H), 1.43 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 167.7, 161.4, 147.8, 136.3, 135.3, 129.4, 128.9, 127.2, 126.4, 121.2, 61.6, 14.4. HRMS (ESI): Calcd for $C_{14}H_{14}NO_2S^+$ [M+H]$^+$ 260.0740, found 260.0741.

Ethyl 2-(naphthalen-1-yl)thiazole-4-carboxylate (3t)



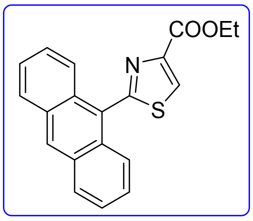
Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=25:1 as the eluent) to give **3t** (64% yield) as a yellow oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.74 (d, J = 8.3 Hz, 1H), 8.32 (s, 1H), 7.98 (d, J = 8.2 Hz, 1H), 7.93 (d, J = 8.3 Hz, 1H), 7.84 (dd, J = 7.1, 0.7 Hz, 1H), 7.64-7.52 (m, 3H), 4.51 (q, J = 7.1 Hz, 2H), 1.47 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 168.0, 161.60, 147.9, 133.9, 131.0, 130.6, 130.1, 128.9, 128.4, 128.0, 127.7, 126.5, 125.6, 124.9, 61.5, 14.4. HRMS (ESI): Calcd for $C_{16}H_{14}NO_2S^+$ [M+H]$^+$ 284.0740, found 284.0739

Ethyl 2-(naphthalen-2-yl)thiazole-4-carboxylate (3u)



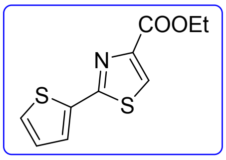
Following the general procedure A, the crude product was purified by silica gel flash chromatography(PE: EA=15:1 as the eluent) to give **3u** (83% yield) as a yellow solid. Mp 75 ^{o}C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.52 (s, 1H), 8.19 (s, 1H), 8.10 (dd, J = 8.5, 1.28 Hz, 1H), 7.95-7.85 (m, 3H), 7.55-7.52 (m, 2H), 4.47 (q, J = 7.1 Hz, 2H), 1.45 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 168.9, 161.5, 148.2, 134.4, 133.1, 130.1, 128.8, 128.7, 127.9, 127.4, 127.2, 126.9, 126.7, 124.1, 61.6, 14.4. HRMS (ESI): Calcd for $C_{16}H_{14}NO_2S^+$ [M+H]$^+$ 284.0740, found 284.0740.

Ethyl 2-(anthracen-9-yl)thiazole-4-carboxylate (3v)



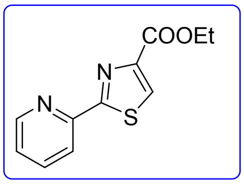
Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=15:1 as the eluent) to give **3v** (91% yield) as a yellow oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.59 (s, 1H), 8.55 (s, 1H), 8.03 (d, J = 7.9 Hz, 2H), 7.68 (d, J = 8.4, 2H), 7.49-7.42 (m, 4H), 4.49 (q, J = 7.1 Hz, 2H), 1.44 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 165.9, 161.6, 148.0, 131.3, 130.9, 129.8, 128.5, 126.9, 126.2, 125.5, 125.4, 61.6, 14.4. HRMS (ESI): Calcd for $C_{20}H_{16}N_1O_2S^+$ [M+H]$^+$ 334.0896, found 334.0898.

Ethyl 2-(thiophen-2-yl)thiazole-4-carboxylate (3w)



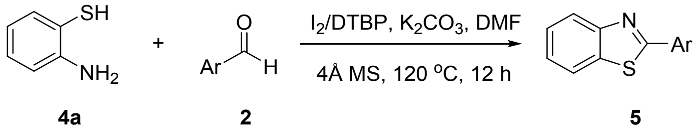
Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=15:1 as the eluent) to give **3w** (66% yield) as a yellow oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.07 (s, 1H), 7.58 (d, J = 3.6 Hz, 1H), 7.44 (d, J = 5.0 Hz, 1H), 7.09 (t, J = 4.3 Hz, 1H), 4.43 (q, J = 7.1 Hz, 2H), 1.42 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 162.4, 161.2, 147.8, 136.3, 128.7, 127.9, 127.68, 126.3, 61.5, 14.3. HRMS (ESI): Calcd for $C_{10}H_{10}NO_2S_2^+$ [M+H]$^+$ 240.0147, found 240.0154.

Ethyl 2-(pyridin-2-yl)thiazole-4-carboxylate (3x)



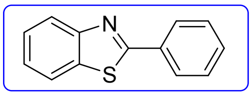
Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=15:1 as the eluent) to give **3x** (30% yield) as a yellow oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.62 (d, J = 4.6 Hz, 1H), 8.33 (d, J = 7.9 Hz, 1H), 8.25 (s, 1H), 7.82 (td, J = 7.6, 1.24 Hz, 1H), 7.36 (td, J = 6.6, 1.4 Hz, 1H), 4.45 (t, J = 7.1 Hz, 2H), 1.42 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 169.9, 161.5, 150.5, 149.4, 148.3, 137.1, 129.5, 125.1, 120.3, 61.5, 14.4. HRMS (ESI): Calcd for $C_{11}H_{11}N_2O_2S^+$ $[M+H]^+$ 235.0536, found 235.0536.

2) General procedure B:



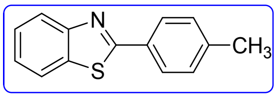
A mixture of 2-aminothiophenol (**4a**, 0.8 mmol, 0.108 g, 4.0 equiv.), benzaldehyde (0.2 mmol, 0.0212 g, 1.0 equiv.), potassium carbonate (K_2CO_3, 0.6 mmol, 0.0828 g, 3.0 equiv.), iodine (I_2, 0.06 mmol, 0.0152 g, 0.3 equiv.), 4Å molecular sieve (0.4 g) was charged with DMF (0.2 mL) in a pressure bottle, di-*tert*-butyl peroxide (DTBP, 0.8 mmol, 0.1169 g, 4 equiv.) was then added slowly to the mixture at room temperature. The mixture was stirred at 120 °C for 12 hours. The resultant solution was quenched with aqueous saturated sodium thiosulfate solution (4 mL) and extracted with ethyl acetate (3×30 mL). The organic phase was combined and washed with brine (3×30 mL), dried over anhydrous sodium sulfate, filtered and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography (petroleum ether (PE) and ethyl acetate (EA) as the eluent).

2-phenylbenzo[d]thiazole (5a)



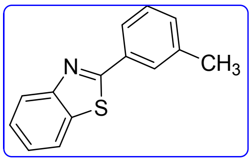
Following the general procedure B, the crude product was purified by silica gel flash chromatography (PE: EA=40:1 as the eluent) to give **5a** (99% yield) as a purple solid. Mp 112 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.09-8.06 (m, 3H), 7.88 (d, J = 8.0 Hz, 1H), 7.50-7.47 (m, 4H), 7.36 (t, J = 7.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 153.1, 134.0, 132.6, 129.9, 127.9, 126.5, 125.3, 124.1, 122.2, 120.6. HRMS (ESI): Calcd for $C_{13}H_{10}NS^+$ $[M+H]^+$ 212.0528, found 212.0528.

2-(p-tolyl)benzo[d]thiazole (5b)



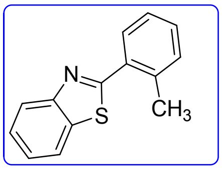
Following the general procedure B, the crude product was purified by silica gel flash chromatography (PE: EA=30:1 as the eluent) to give **5b** (98% yield) as a purple solid. Mp 84 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, J = 8.2 Hz, 1H), 7.97 (d, J = 8.2 Hz, 2H), 7.86 (dd, J = 8.0, 0.4 Hz, 1H), 7.48-7.44(m, 1H), 7.37-7.33 (m, 1H), 7.27 (d, J = 7.9 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 153.1, 140.4, 133.9, 129.9, 128.7, 126.4, 125.2, 123.9, 122.0, 120.5, 20.5. HRMS (ESI): Calcd for $C_{14}H_{12}NS^+$ $[M+H]^+$ 226.0685, found 226.0685.

2-(m-tolyl)benzo[d]thiazole (5c)



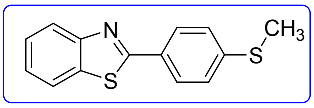
Following the general procedure B, the crude product was purified by silica gel flash chromatography (PE: EA=50:1 as the eluent) to give **5c** (98% yield) as a white solid. Mp 60 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, J = 8.2 Hz, 1H), 7.90-7.88 (m, 1H), 7.75 (dd, J = 7.5, 0.8 Hz, 1H), 7.51-7.26 (m, 1H), 7.40-7.26 (m, 4H), 2.65 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 152.8, 136.2, 134.5, 132.0, 130.5, 129.5, 128.9, 125.1, 125.0, 124.0, 122.3, 120.3, 20.3. HRMS (ESI): Calcd for $C_{14}H_{12}NS^+$ $[M+H]^+$ 226.0685, found 226.0684.

2-(o-tolyl)benzo[d]thiazole (5d)



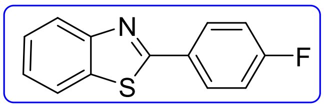
Following the general procedure B, the crude product was purified by silica gel flash chromatography(PE: EA=40:1 as the eluent) to give **5d** (99% yield) as a orange solid. Mp 56 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J = 8.1 Hz, 1H), 7.92 (s, 1H), 7.85 (t, J = 7.1 Hz, 2H), 7.49-7.44 (m, 1H), 7.35 (t, J = 7.7 Hz, 2H), 7.27 (d, J = 7.6 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 153.1, 137.8, 134.0, 132.5, 130.7, 127.9, 126.9, 125.2, 124.0, 123.8, 122.1, 120.5, 20.3. HRMS (ESI): Calcd for $C_{14}H_{12}NS^+$ $[M+H]^+$ 226.0685, found 226.0685.

2-(4-(methylthio)phenyl)benzo[d]thiazole (5e)



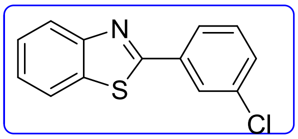
Following the general procedure B, the crude product was purified by silica gel flash chromatography (PE: EA=40:1 as the eluent) to give **5e** (77% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, J = 8.1 Hz, 1H), 8.02-7.99 (m, 2H), 7.89 (d, J = 8.1 Hz, 1H), 7.52-7.48 (m, 1H), 7.40-7.36 (m, 1H), 7.33 (d, J = 8.4 Hz, 2H), 2.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.6, 154.2, 142.8, 134.9, 130.1, 127.8, 126.34, 125.9, 125.2, 123.1, 121.6, 15.2. HRMS (ESI): Calcd for $C_{14}H_{12}NS_2^+$ $[M+H]^+$ 258.0406, found 258.0413.

2-(4-fluorophenyl)benzo[d]thiazole (5f)



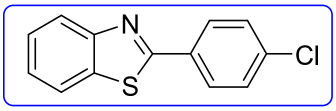
Following the general procedure B, the crude product was purified by silica gel flash chromatography (PE: EA=40:1 as the eluent) to give **5f** (45% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07-8.04 (m, 3H), 7.86 (dd, J = 8.0, 0.4 Hz, 1H), 7.49-7.45 (m, 1H), 7.38-7.33 (m, 1H), 7.17-7.12 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.73, 164.47 (d, J = 251 Hz), 154.12, 135.08, 129.97 (d, J = 3.3 Hz), 129.53 (d, J = 8.0 Hz), 126.43, 125.26, 123.22, 121.63, 116.16 (d, J = 22.0 Hz). HRMS (ESI): Calcd for $C_{13}H_9FNS^+$ [M+H]$^+$ 230.0434, found 230.0437.

2-(3-chlorophenyl)benzo[d]thiazole (5g)



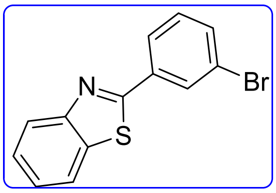
Following the general procedure B, the crude product was purified by silica gel flash chromatography (PE: EA=40:1 as the eluent) to give **5g** (59% yield) as a yellow solid. Mp 95 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08-8.04 (m, 2H), 7.89-7.83 (m, 2H), 7.49-7.45 (m, 1H), 7.42-7.34 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2, 154.0, 135.3, 135.2, 135.1, 130.8, 130.2, 127.4, 126.5, 125.7, 125.6, 123.5, 121.7. HRMS (ESI): Calcd for $C_{13}H_9ClNS^+$ [M+H]$^+$ 246.0139, found 246.0135.

2-(4-chlorophenyl)benzo[d]thiazole (5h)



Following the general procedure B, the crude product was purified by silica gel flash chromatography (PE: EA=40:1 as the eluent) to give **5h** (83% yield) as a yellow solid. Mp 120 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J = 8.2 Hz, 1H), 8.01 (d, J = 8.5 Hz, 2H), 7.88 (d, J = 8.0 Hz, 1H), 7.51-7.44 (m, 3H), 7.38 (t, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.60, 154.1, 137.0, 135.1, 132.2, 129.3, 128.7, 126.5, 125.4, 123.3, 121.7. HRMS (ESI): Calcd for $C_{13}H_9ClNS^+$ [M+H]$^+$ 246.0139, found 246.0135.

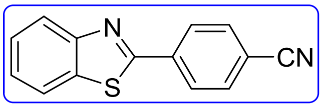
2-(3-bromophenyl)benzo[d]thiazole (5i)



Following the general procedure B, the crude product was purified by silica gel flash chromatography (PE: EA=50:1 as the eluent) to give **5i** (79% yield) as a white solid. Mp 100 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (t, J = 1.7 Hz, 1H), 8.06 (d, J = 8.1 Hz, 1H), 7.95

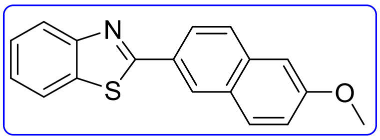
(d, *J* = 7.8, Hz, 1H), 7.87 (d, *J* = 7.7 Hz, 1H), 7.58 (ddd, *J* = 8.0, 1.7, 0.8 Hz, 1H), 7.50-7.46 (m, 1H), 7.40 (m, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): *δ* 165.0, 152.9, 134.4, 134.0, 132.7, 129.4, 129.2, 125.5, 125.1, 124.5, 122.4, 122.1, 120.6. HRMS (ESI): Calcd for $C_{13}H_9BrNS^+$ [M+H]$^+$ 289.9634, found 289.9627.

4-(benzo[d]thiazol-2-yl)benzonitrile (5j)



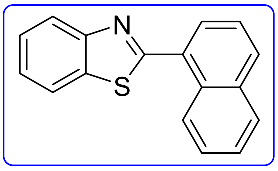
Following the general procedure B, the crude product was purified by silica gel flash chromatography (PE: EA=30:1 as the eluent) to give **5j** (54% yield) as a white solid. ^{1}H NMR ^{1}H NMR (400 MHz, CDCl$_3$): δ 9.01 (s, 1H), 8.21 (d, *J* = 8.4 Hz, 1H), 8.15 (d, *J* = 8.2 Hz, 1H), 8.12 (d, *J* = 8.2 Hz, 1H), 7.99-7.94 (m, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.56-7.51 (m, 1H), 7.45 (t, *J* = 7.5 Hz, 1H)**.** ^{13}C NMR (100 MHz, CDCl$_3$): δ 153.9, 132.8, 127.9, 126.9, 126.2, 126.1, 125.6, 123.8, 123.7, 121.9, 121.8. HR-MS (ESI): Calcd for $C_{14}H_9N_2S^+$ [M+H]$^+$ requires 237.0481; found 237.0485.

2-(6-methoxynaphthalen-2-yl)benzo[d]thiazole (5k)



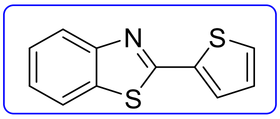
Following the general procedure B, the crude product was purified by silica gel flash chromatography (PE: EA=30:1 as the eluent) to give **5k** (94% yield) as a white solid. ^{1}H NMR (400 MHz, DMSO-*d*$_6$): *δ* 8.61 (s, 1H), 8.17-8.15 (m, 2H), 8.07 (d, *J* = 8.5 Hz, 2H), 7.98 (d, *J* = 8.6 Hz, 1H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.42 (s, 1H), 7.27 (dd, *J* = 8.9, 1.6 Hz, 1H), 3.91 (s, 3H). ^{13}C NMR (100 MHz, DMSO-*d*$_6$): *δ* 167.5, 158.8, 153.7, 135.8, 134.4, 130.5, 128.2, 128.1, 127.8, 127.2, 126.6, 125.4, 124.5, 122.7, 122.3, 119.7, 106.2, 55.4. HRMS (ESI): Calcd for $C_{18}H_{14}NOS^+$ [M+H]$^+$ 292.0791, found 292.0789.

2-(naphthalen-2-yl)benzo[d]thiazole (5l)



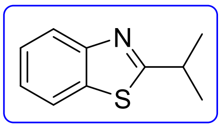
Following the general procedure B, the crude product was purified by silica gel flash chromatography (PE: EA=30:1 as the eluent) to give **5l** (87% yield) as a white solid. Mp 126 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55 (s, 1H), 8.20 (dd, J = 8.5, 1.6 Hz, 1H), 8.11 (d, J = 8.1 Hz, 1H), 7.96-7.85 (m, 4H), 7.54-7.48 (m, 3H), 7.38 (t, J = 7.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 153.2, 134.1, 133.6, 132.1, 129.9, 127.8, 127.8, 126.8, 126.5, 126.4, 125.8, 125.3, 124.2, 123.4, 122.2, 120.6. HRMS (ESI): Calcd for $C_{17}H_{12}NS^+$ $[M+H]^+$ 262.0685, found 262.0684.

2-(thiophen-2-yl)benzo[d]thiazole (5m)



Following the general procedure B, the crude product was purified by silica gel flash chromatography (PE: EA=40:1 as the eluent) to give **5m** (75% yield) as a white solid. Mp 99 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, J = 8.2 Hz, 1H), 7.83 (d, J = 7.9 Hz, 1H), 7.64 (d, J = 3.7 Hz, 1H), 7.47 (dd, J = 13.4, 5.1 Hz, 2H), 7.35 (t, J = 7.9 Hz, 1H), 7.13-7.11 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.4, 153.7, 137.4, 134.7, 129.3, 128.6, 128.0, 126.4, 125.2, 123.0, 121.5. HRMS (ESI): Calcd for $C_{11}H_8NS_2^+$ $[M+H]^+$ 218.0093, found 218.0089

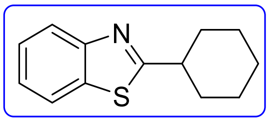
2-isopropylbenzo[d]thiazole (5n)



Following the general procedure B, the crude product was purified by silica gel flash chromatography (PE: EA=40:1 as the eluent) to give **5n** (90% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, J = 8.1 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.44 (t, J = 7.4 Hz, 1H), 7.32 (t, J = 7.4 Hz, 1H), 3.47-3.36 (m, 1H), 1.48 (d, J = 6.9 Hz, 6H). ^{13}C NMR (100

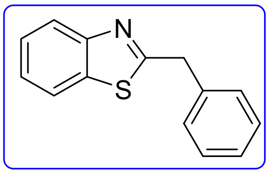
MHz, $CDCl_3$): δ 178.6, 153.2, 134.7, 125.8, 124.6, 122.6, 121.6, 34.1, 22.9. HRMS (ESI): Calcd for $C_{10}H_{12}NS^+$ $[M+H]^+$ 178.0685, found 178.0685

2-cyclohexylbenzo[d]thiazole (5o)



Following the general procedure B, the crude product was purified by silica gel flash chromatography (PE: EA=30:1 as the eluent) to give **5o** (91% yield) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.1 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.43 (td, *J* = 8.0, 0.64 Hz, 1H), 7.31 (t, *J* = 7.9 Hz, 1H), 3.10 (tt, *J* = 11.6, 3.4 Hz, 1H), 2.19 (d, *J* = 11.8 Hz, 2H), 1.89 (dt, *J* = 13, 2.9 Hz, 2H), 1.77-1.74 (m, 1H), 1.64 (qd, *J* = 12.36, 2.9 Hz, 2H) 1.44 (qt, *J* = 12.8, 3.2 Hz, 2H), 1.31 (qt, *J* = 12.4, 2.8 Hz, 1H) ^{13}C NMR (400 MHz, $CDCl_3$): δ 177.6, 153.1, 134.6, 125.8, 124.5, 122.6, 121.6, 43.5, 33.4, 26.1, 25.8. HRMS (ESI): Calcd for $C_{14}H_{18}NS^+$ $[M+H]^+$ 218.0998, found 218.0998.

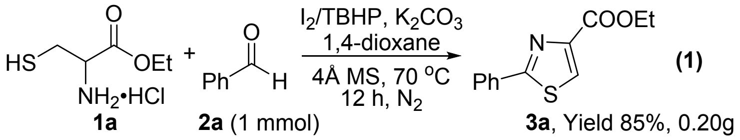
2-benzylbenzo[d]thiazole (5p)

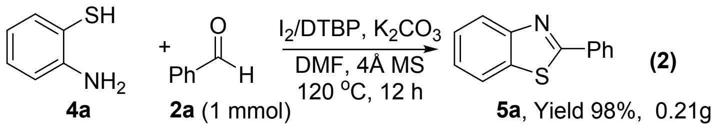


Following the general procedure B, the crude product was purified by silica gel flash chromatography (PE: EA=30:1 as the eluent) to give **5p** (84% yield) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.16 Hz, 1H), 7.76 (d, *J* = 7.96 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.37-7.27 (m, 6H), 7.42 (s, 2H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 171.2, 153.3, 137.2, 135.7, 129.2, 128.9, 127.4, 126.0, 124.8, 122.8, 121. 6, 40.7. HRMS (ESI): Calcd for $C_{14}H_{12}NOS^+$ $[M+H]^+$ 226.0685, found 226.0686.

III. Scale-up Synthesis and Synthetic Applications

a) Scale-up Synthesis



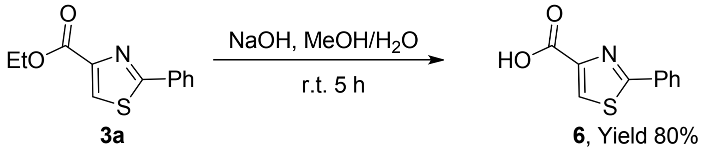


A mixture of L-cysteine ethyl ester hydrochloride (4 mmol, 0.743 g, 4.0 equiv.), benzaldehyde (1 mmol, 0.106 g, 1.0 equiv.), potassium carbonate (Na_2CO_3, 3 mmol, 0.414 g, 3.0 equiv.), iodine (I_2, 0.3 mmol, 0.076 g, 0.3 equiv.), and molecular sieve (MS, 2g) in 5 mL 1,4-dioxane in a schlenk tube, tert-butyl hydroperoxide (TBHP, 70% in cyclohexane, 4 mmol, 0.5145 g, 4 equiv.) was added slowly to the mixture at room temperature under nitrogen atmosphere, then the mixture was stirred at 70 ^{o}C for 12 hours. The resultant solution was quenched with saturated sodium thiosulfate (4 mL) and extracted with ethyl acetate (3×30 mL), the organic phase was combined and washed with brine (3×30 mL), dried over anhydrous sodium sulfate, filtered and concentrated in vacuo. the crude product was purified by silica gel flash chromatography (PE: EA=25:1 as the eluent) to give **3a** (85% yield) as a yellow oil.

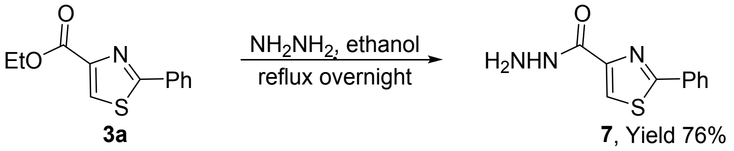
A mixture of 2-aminothiophenol (4 mmol, 0.54 g, 4.0 equiv.), benzaldehyde (1 mmol, 0.053 g, 1.0 equiv.), potassium carbonate (K_2CO_3, 3 mmol, 0.414 g, 3.0 equiv.), iodine (0.3 mmol, 0.076 g, 0.3 equiv.), and molecular sieve (2 g) in 1 mL N, N-dimethylformamide (DMF) in a pressure bottle, di-t-butyl peroxide (DTBP, 4 mmol, 0.5845 g, 4 equiv.) was added slowly to the mixture at room temperature, then the mixture was stirred at 120 ^{o}C for 12 hours. The resultant solution was quenched with saturated sodium thiosulfate (4 mL) and extracted with ethyl acetate (3×30 mL), the organic phase was combined and washed with brine (3×30 mL), dried over anhydrous sodium sulfate, filtered and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography (petroleum ether (PE) and ethyl acetate

(EA) as the eluent). the crude product was purified by silica gel flash chromatography (PE: EA=40:1 as the eluent) to give **5a** (98% yield) as a purple solid.

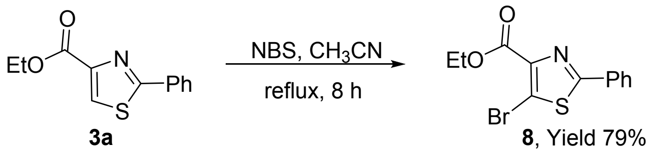
b) Synthetic Applications



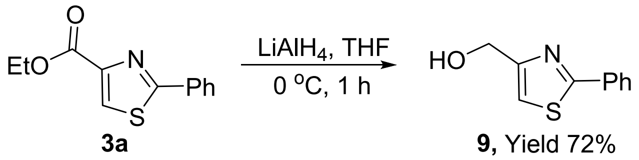
To a solution of **3a** (0.2 mmol, 47 mg, 1 equiv.) in methanol (0.5 mL), sodium hydroxide solution (2 mol/L, 0.2 ml, 2 equiv.) was added at room temperature. The mixture was kept stirring for 5 h. The methanol was removed in vacuo. The resultant mixture was adjusted to pH=5-6 with hydrochloric acid solution (1 mol/L). The solid was filtered and dried to give the product **6** (80%) as a yellow solid. ^{1}H NMR (400 MHz, DMSO) δ 13.16 (s, 1H), 8.51 (s, 1H), 8.02-7.96 (m, 2H), 7.59-7.51 (m, 3H). ^{13}C NMR (100 MHz, DMSO-d^6) δ 167.88, 162.56, 148.67, 132.97, 131.23, 129.81, 129.23, 126.87. For characterization data, also see: S. N. Thore, S. V. Gupta and K. G. Baheti, *Med. Chem. Res.,* 2013, 22, 3802.



To a solution of **3a** (0.5 mmol, 117 mg, 1 equiv.) in ethanol (2 mL), hydrazine hydrate ($NH_2NH_2 \cdot H_2O$, 1.5 mmol, 89mg, 3 equiv.) was added at room temperature. The mixture was refluxed overnight. The solvent was removed in vacuo, and the crude solid was recrystallized from dichloromethane/ethanol (4:1) to give the product **7** (76%) as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 8.14 (s, 1H), 7.99-7.94 (m, 2H), 7.58-7.45 (m, 3H), 4.14 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.65, 161.83, 149.04, 132.72, 130.77, 129.12, 126.64, 123.13.

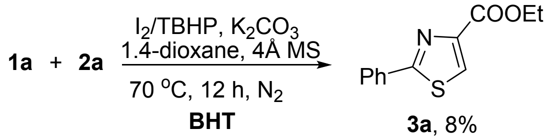


To a solution of **3a** (1 mmol, 0.23 g, 1 equiv.) in acetonitrile (3 mL), N-bromosuccinmide was added (NBS, 2 mmol, 0.36g, 2 equiv.) at room temperature. The mixture was refluxed for 8 h. The reaction was quenched with saturated sodium bicarbonate solution and extracted with ethyl acetate, dried over sodium sulfate, filtered and concentrated in vacuo. The crude product was purified by silica gel flash chromatography (PE:EA=30:1 as the eluent) to give product **8** (79%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90-7.96 (m, 2H), 7.53-7.45 (m, 3H), 4.49 (q, J = 7.1 Hz, 2H), 1.47 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.88, 161.13, 144.38, 132.29, 131.08, 129.10, 126.68, 116.35, 61.83, 14.32.



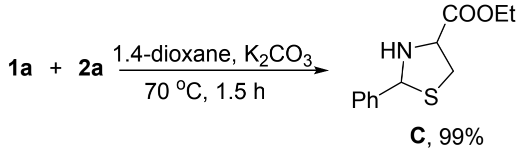
Lithium aluminium hydride (0.2 mmol, 77 mg, 1 equiv.) was dissolved in minimum amount of THF in a schlenk tube and cooled to 0 °C under N_2 atmosphere. To this was added drop-wise a solution of **3a** (0.14 mmol, 0.032g, 1.4 equiv.) in THF and stirred the recation mixture for an hour. After completion of reaction, the reaction mixture was quenched with 10% sodium carbonate solution at 0 °C and extracted with ethyl acetate. Organic layers were collected, dried over sodium sulphate and concentrated. The crude product was purified by silica gel flash chromatography (PE:EA=2:1 as the eluent) to give product **9** (72%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93-7.91 (m, 2H), 7.43-7.41 (m, 3H), 7.17 (s, 1H), 4.82 (s, 1H), 2.90 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 157.3, 133.5, 130.2, 129.0, 126.6, 114.6, 61.2.

IV. Mechanistic Experiments



3a, 8%

(1)

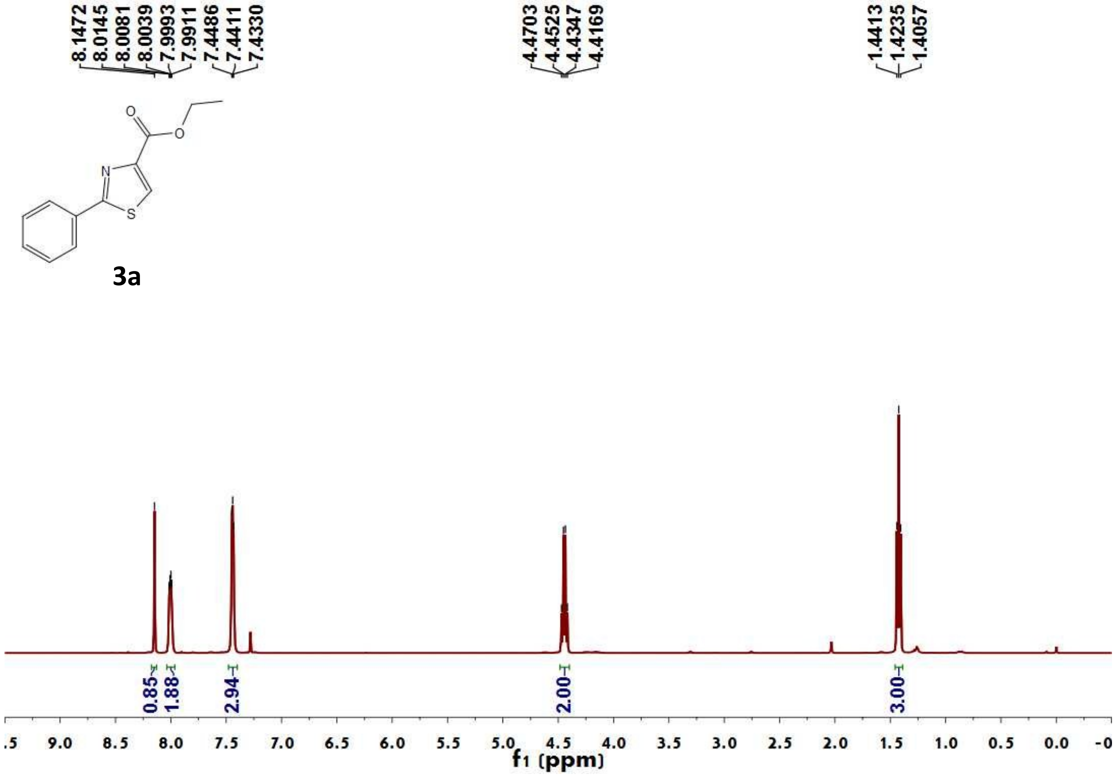


C, 99%

(2)

A mixture of L-cysteine ethyl ester hydrochloride (**1a**, 0.8 mmol, 0.1486 g, 4.0 equiv.), benzaldehyde (0.2 mmol, 0.0212 g, 1.0 equiv.), potassium carbonate (Na_2CO_3, 0.6 mmol, 0.0828 g, 3.0 equiv.) in 1 mL 1,4-dioxane in a schlenk tube under nitrogen atmosphere, then the mixture was stirred at 70 °C for 1.5 hours. The resultant solution was extracted with ethyl acetate (3×30 mL), the organic phase was combined and washed with brine (3×30 mL), dried over anhydrous sodium sulfate, filtered and concentrated in vacuo. The crude product was purified by silica gel flash chromatography (PE:EA=10:1 as the eluent) to give product **C** (99%) as a yellow oil. For characterization data of compound **C**, see: C. Saiz, P. Wiof, E. Manta and G. Mahler, *Org. Lett.,* 2009, **11**, 3170.

V. Spectrum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4.4347
4.4169
1.4413
1.4235
1.4057
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O
N
S
3a
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1.88
2.94
2.00
3.00
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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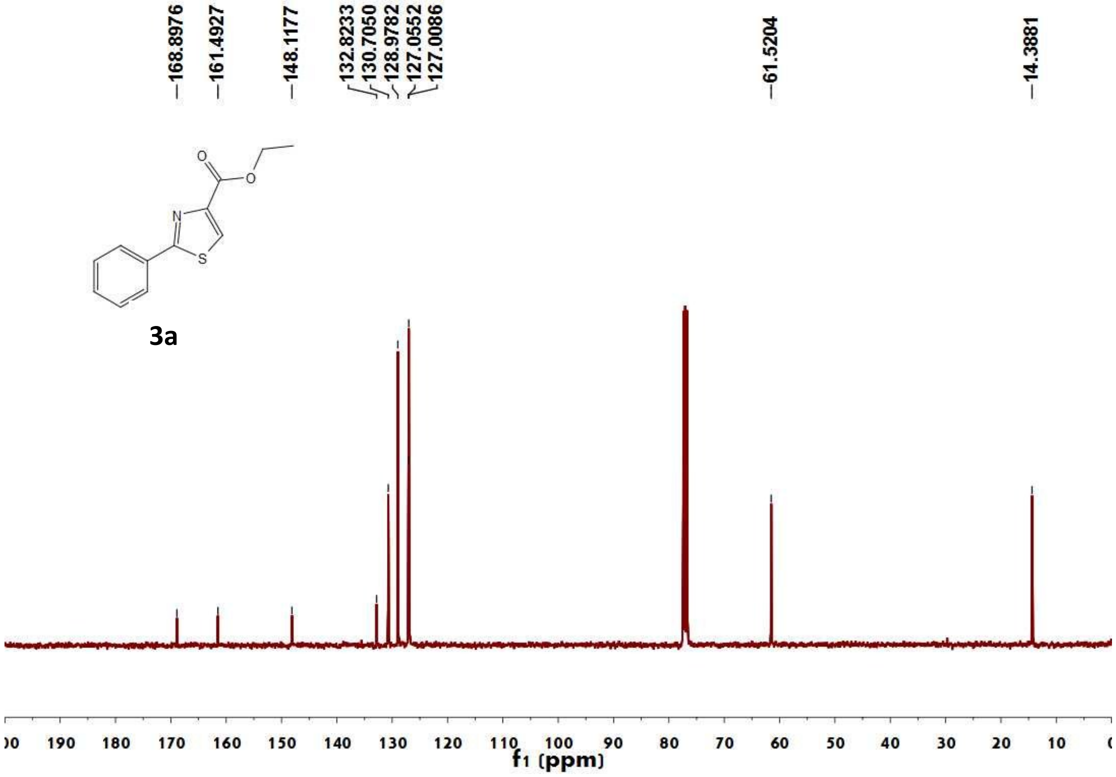
f1 (ppm)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N
S
3a
00
190
180
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110
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90
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70
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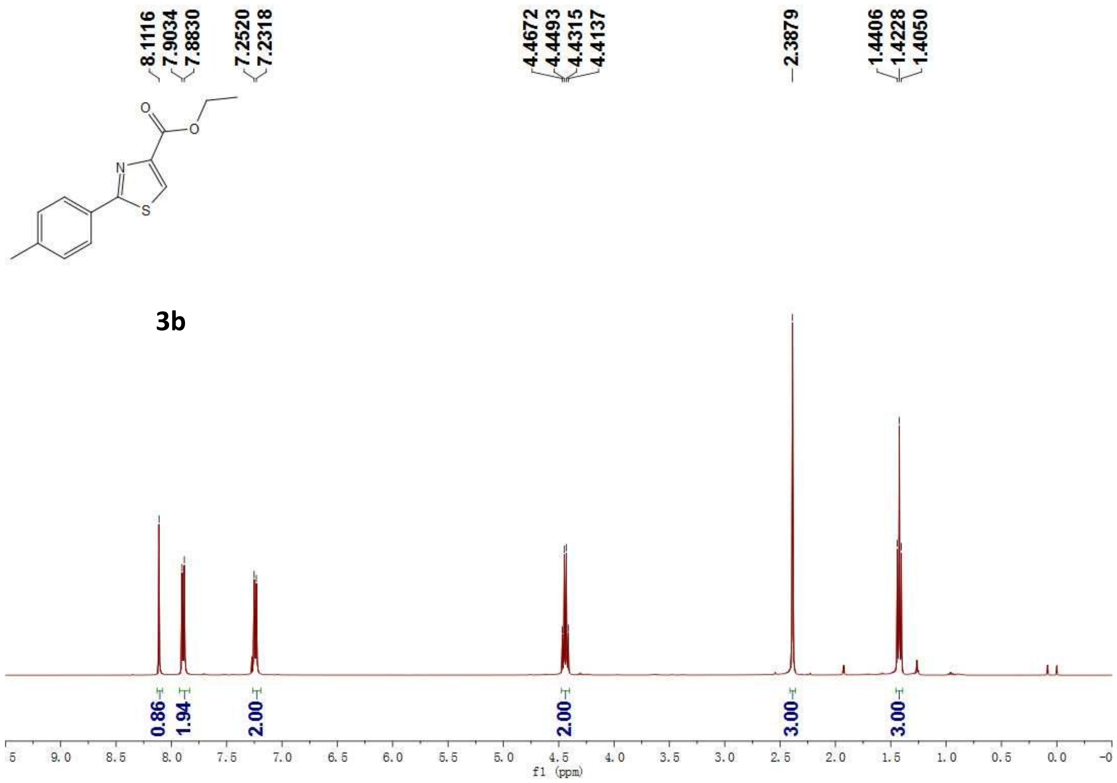
50
40
30
20
10
(
f1 (ppm)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2.00
2.00
3.00
3.00
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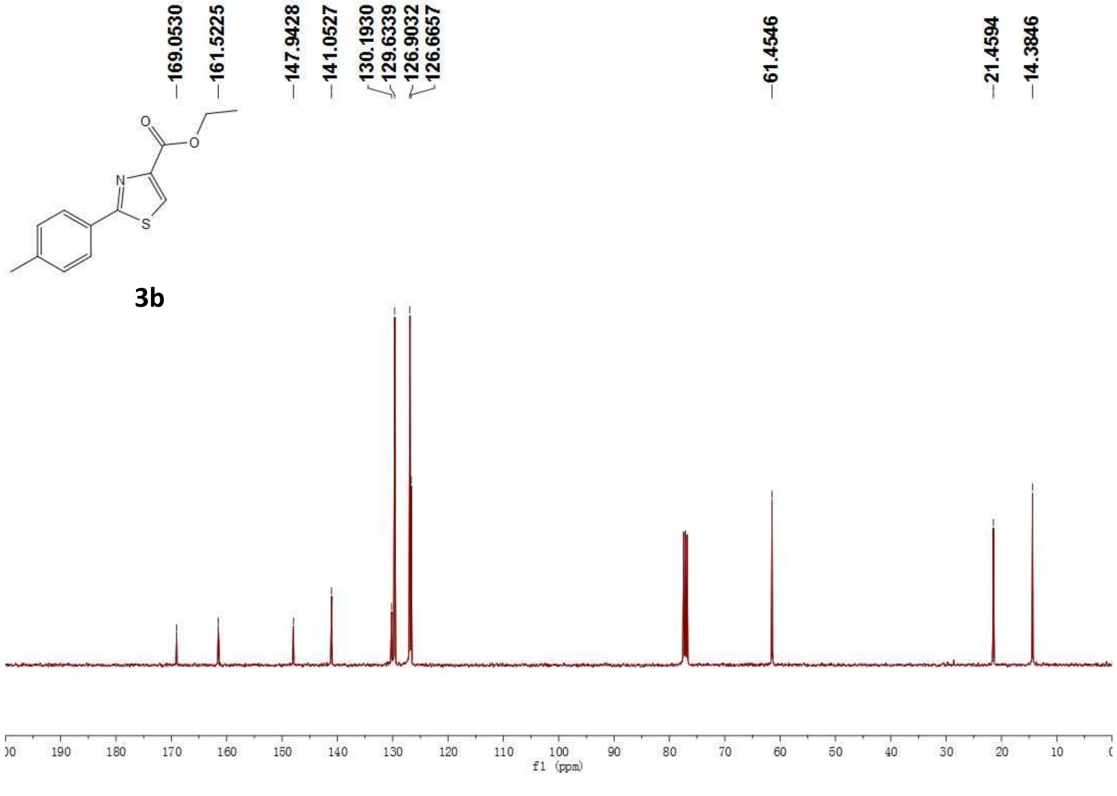
f1 (ppm)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130.1930
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14.3846
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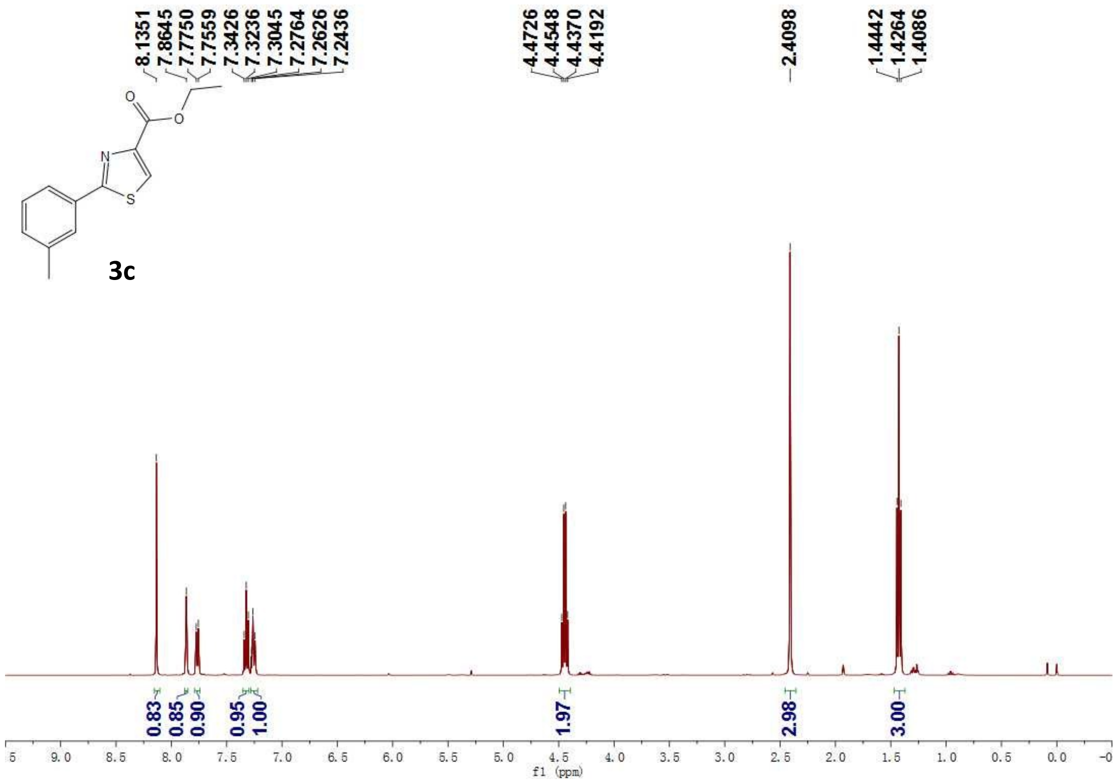
f1 (ppm)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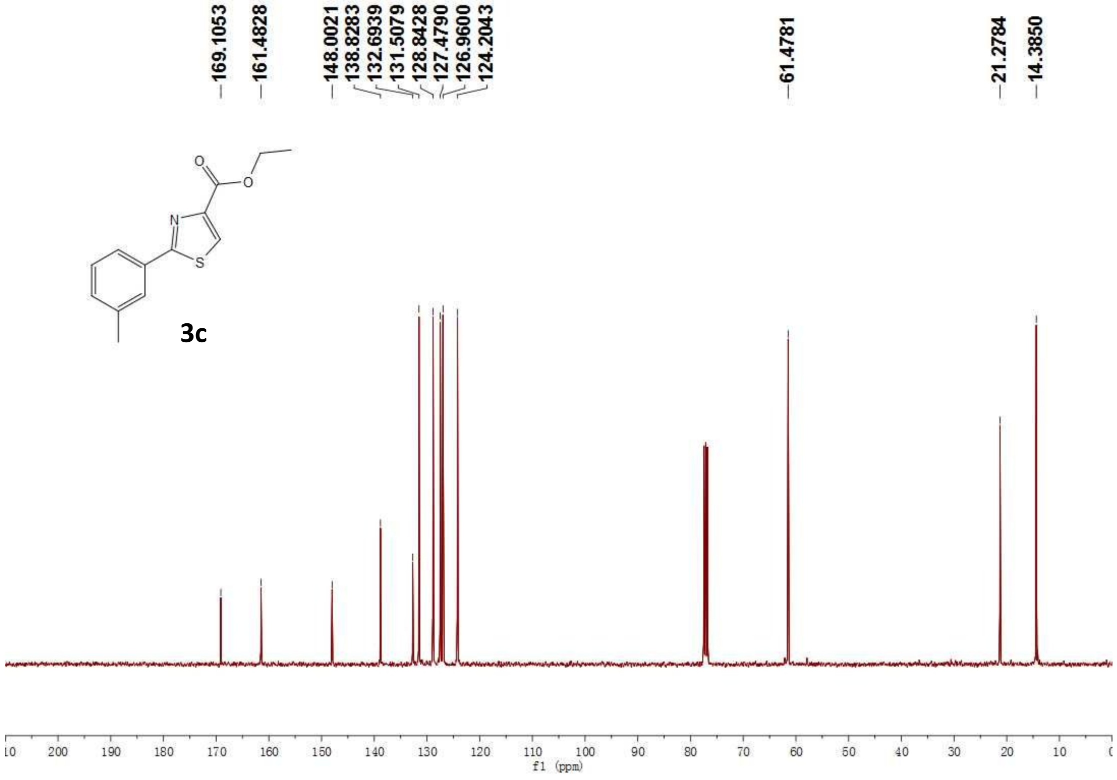
f1 (ppm)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O
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S
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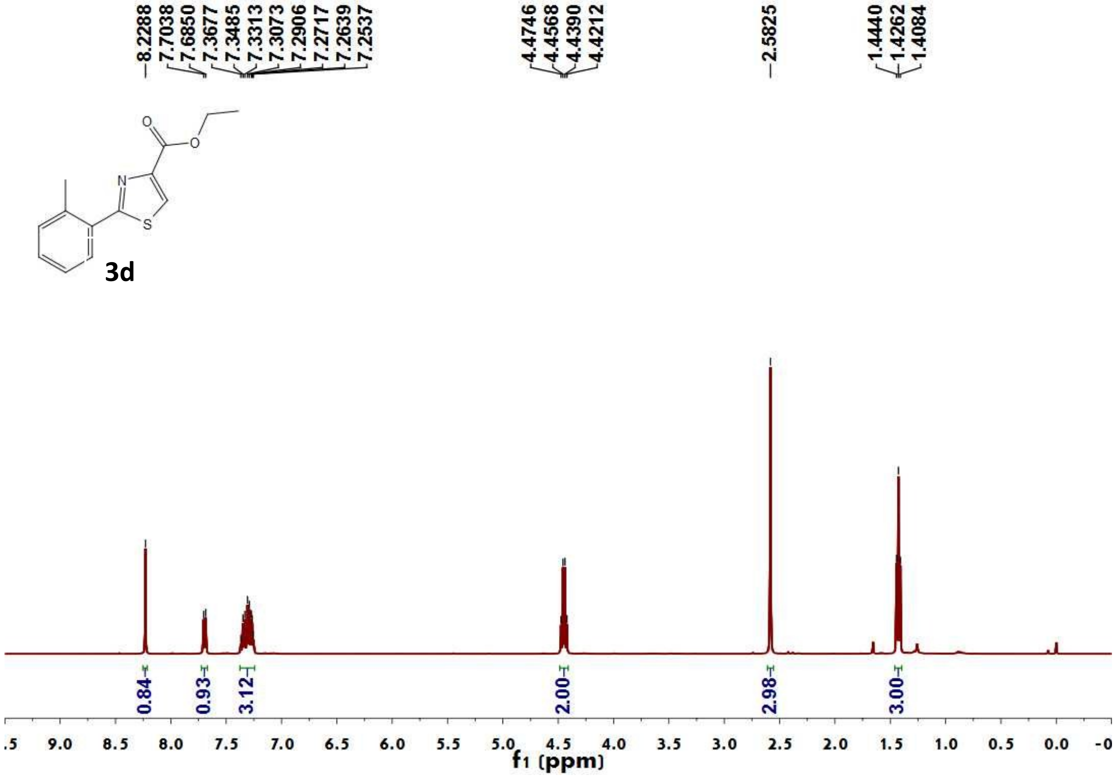
f1 (ppm)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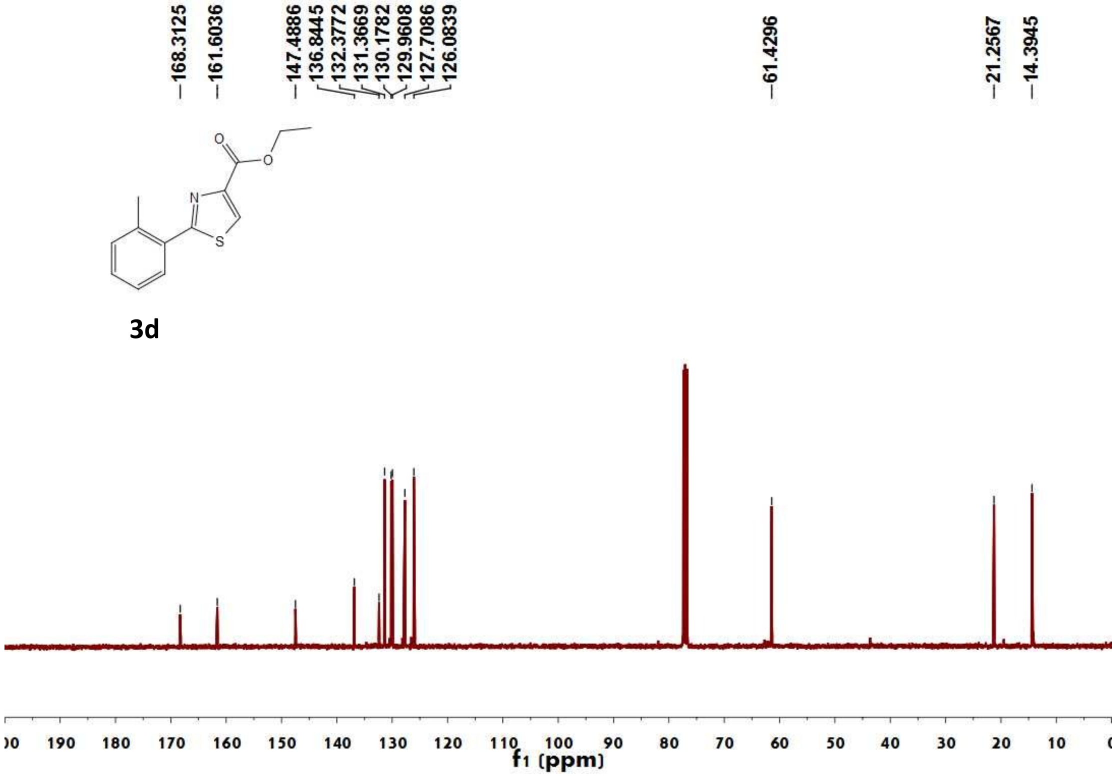
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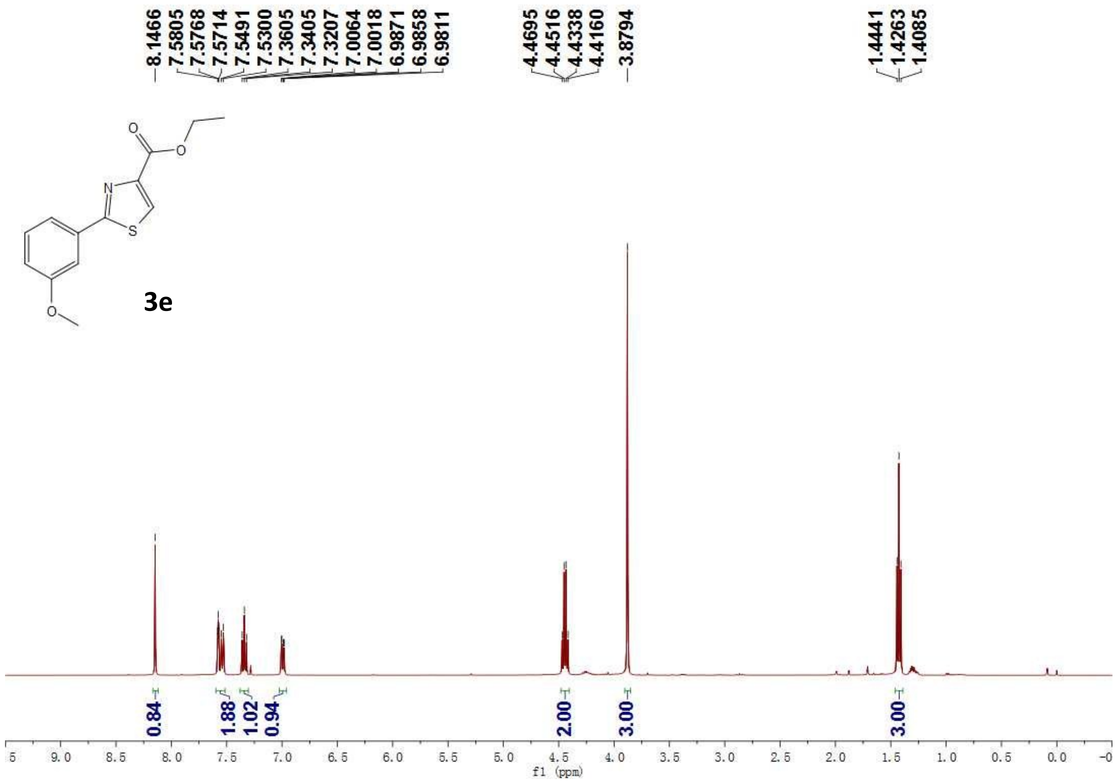
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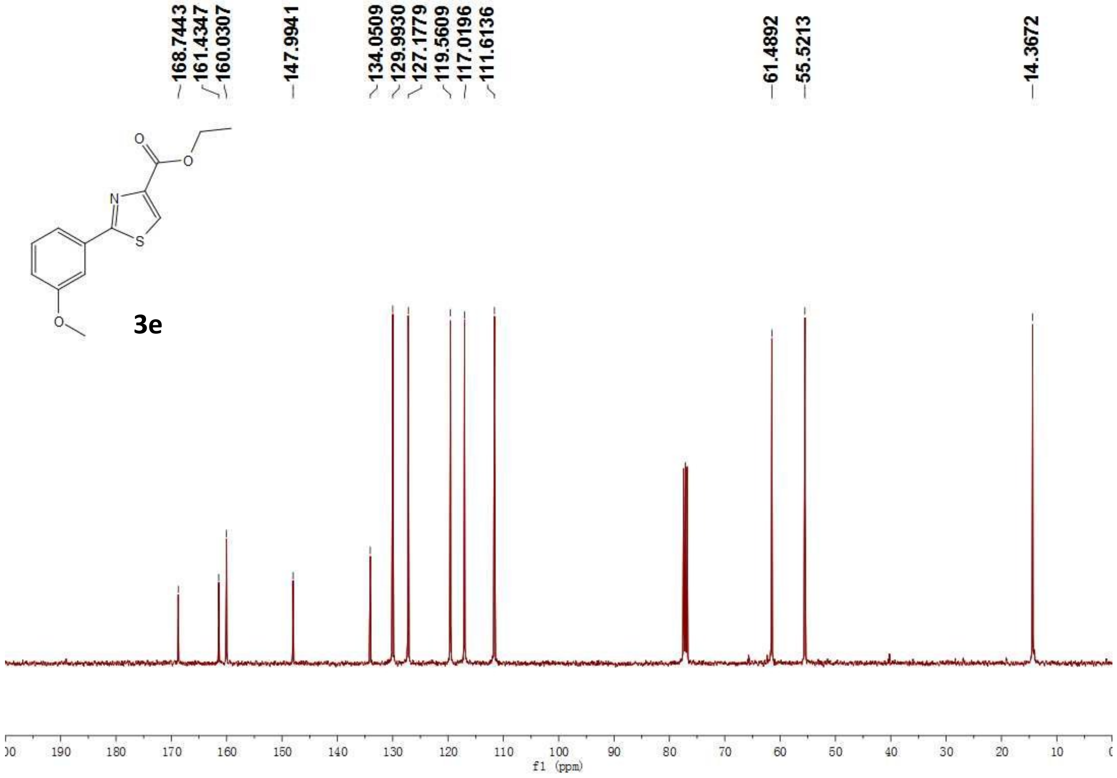
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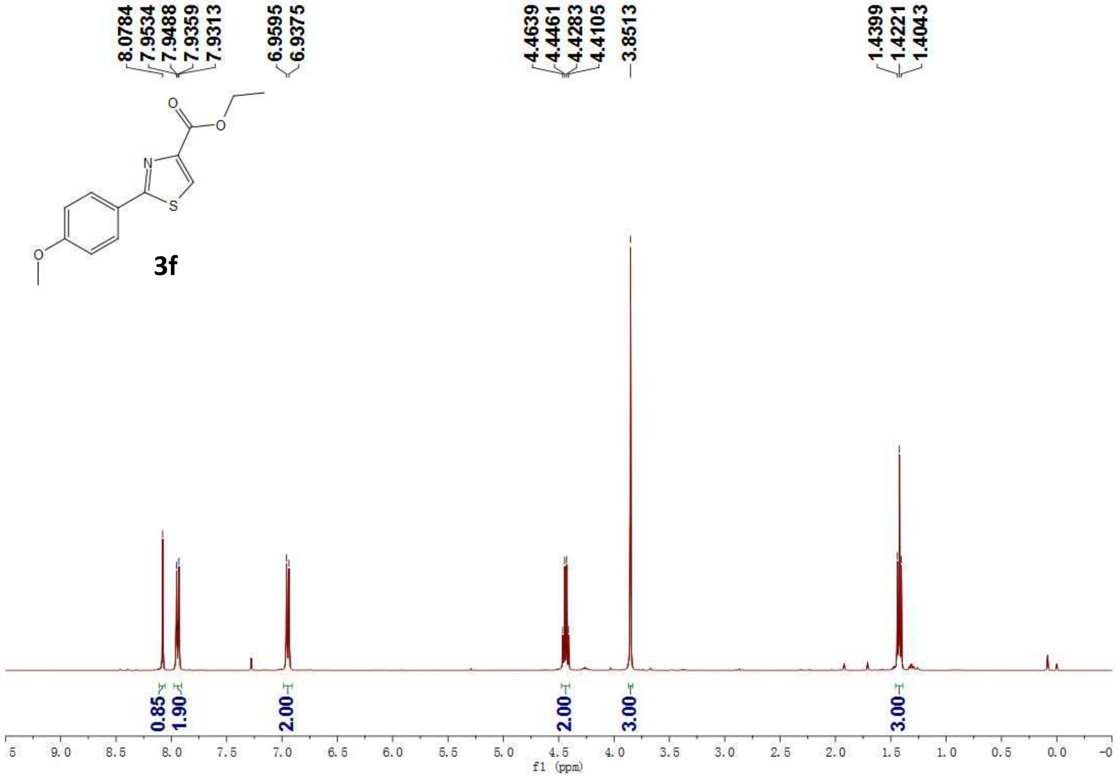

3f

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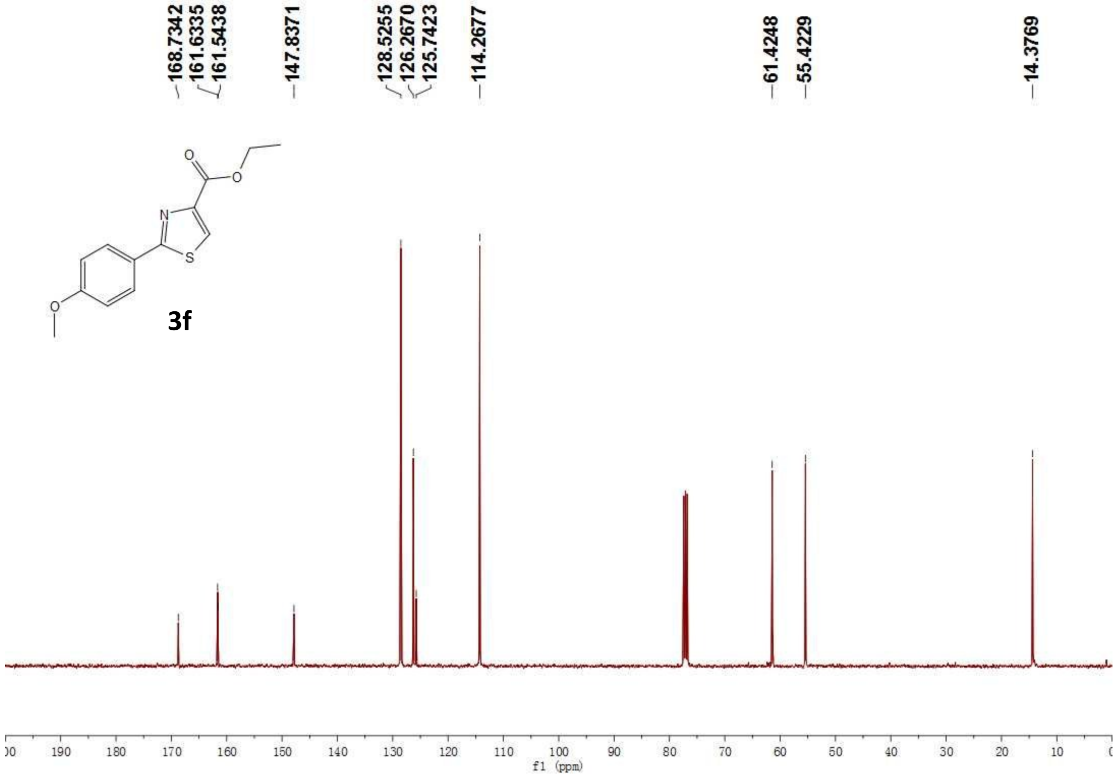

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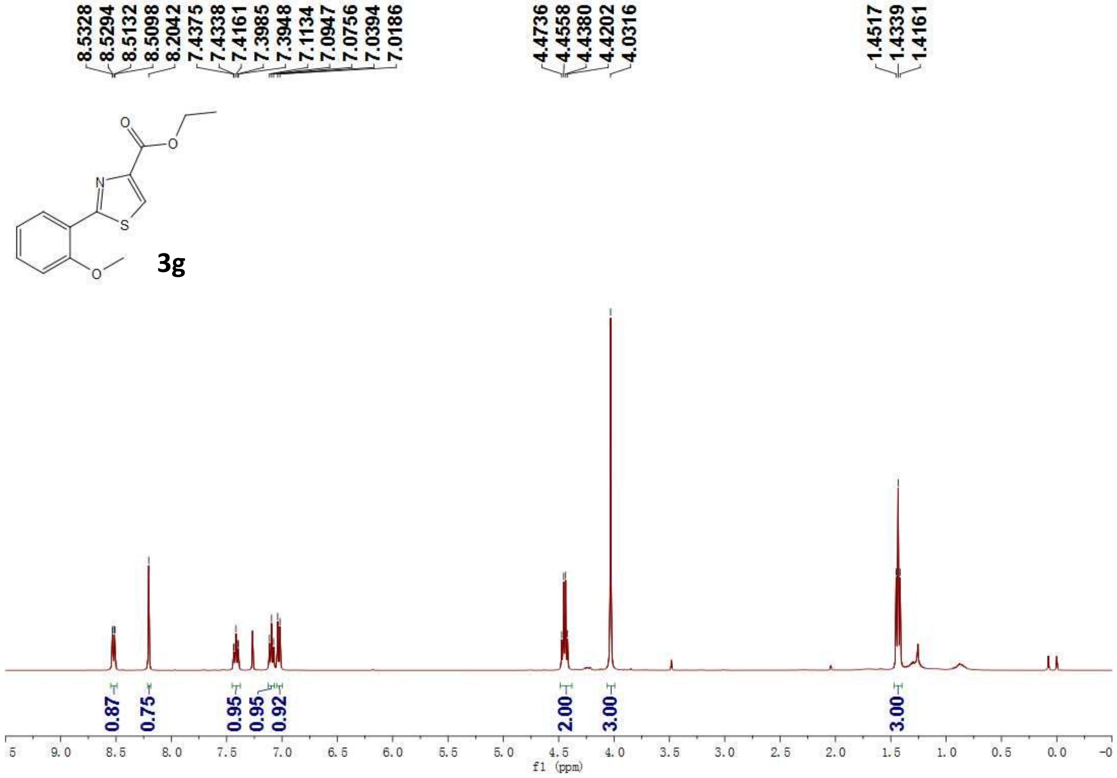
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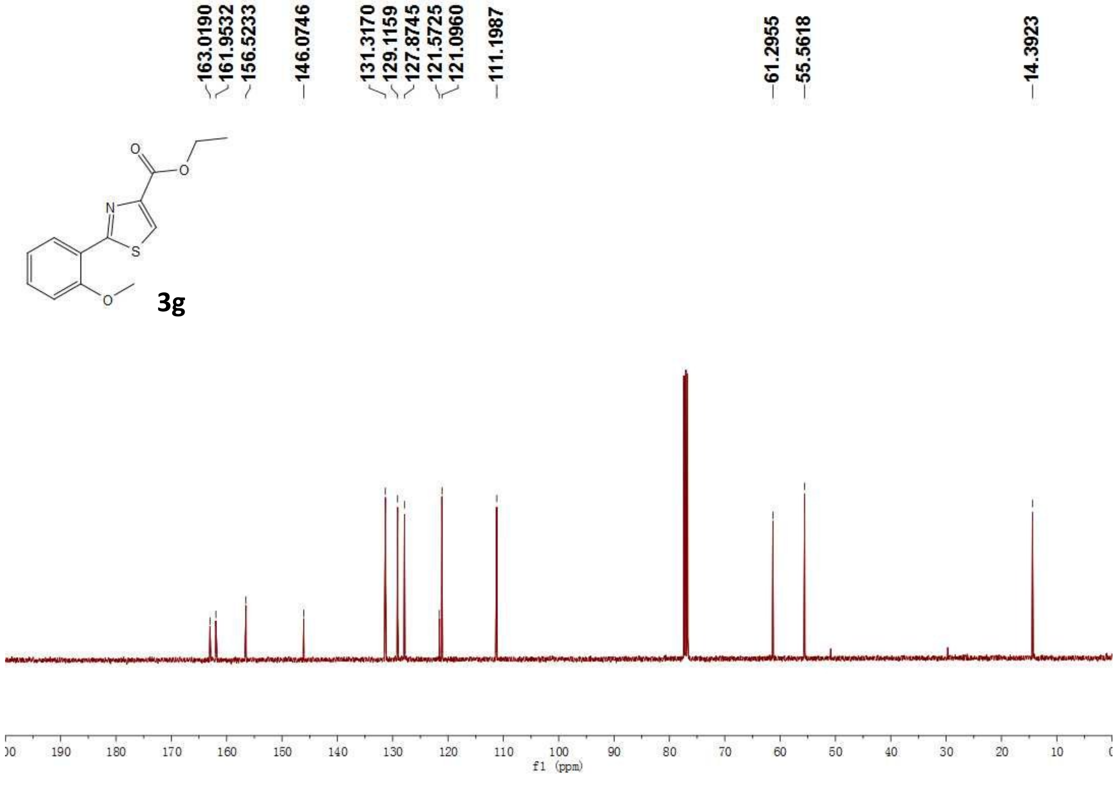
3g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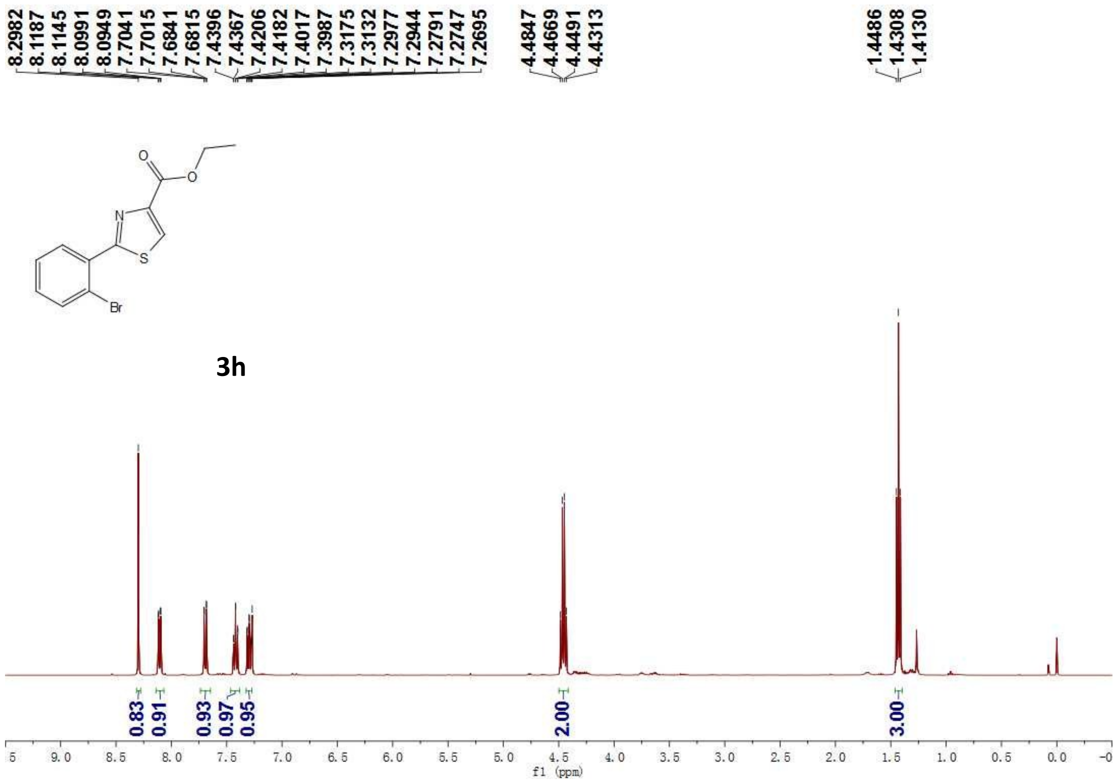
111.1987
61.2955
55.5618
14.3923
O
O
N
S
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

3g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8.1145
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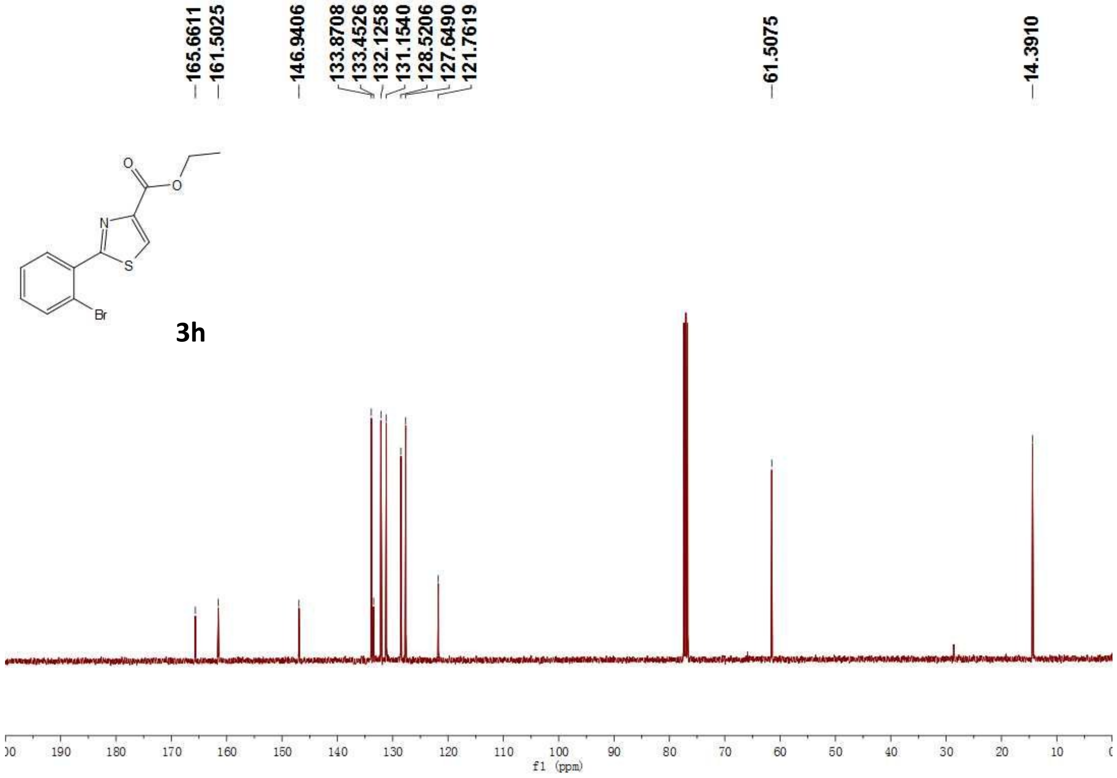
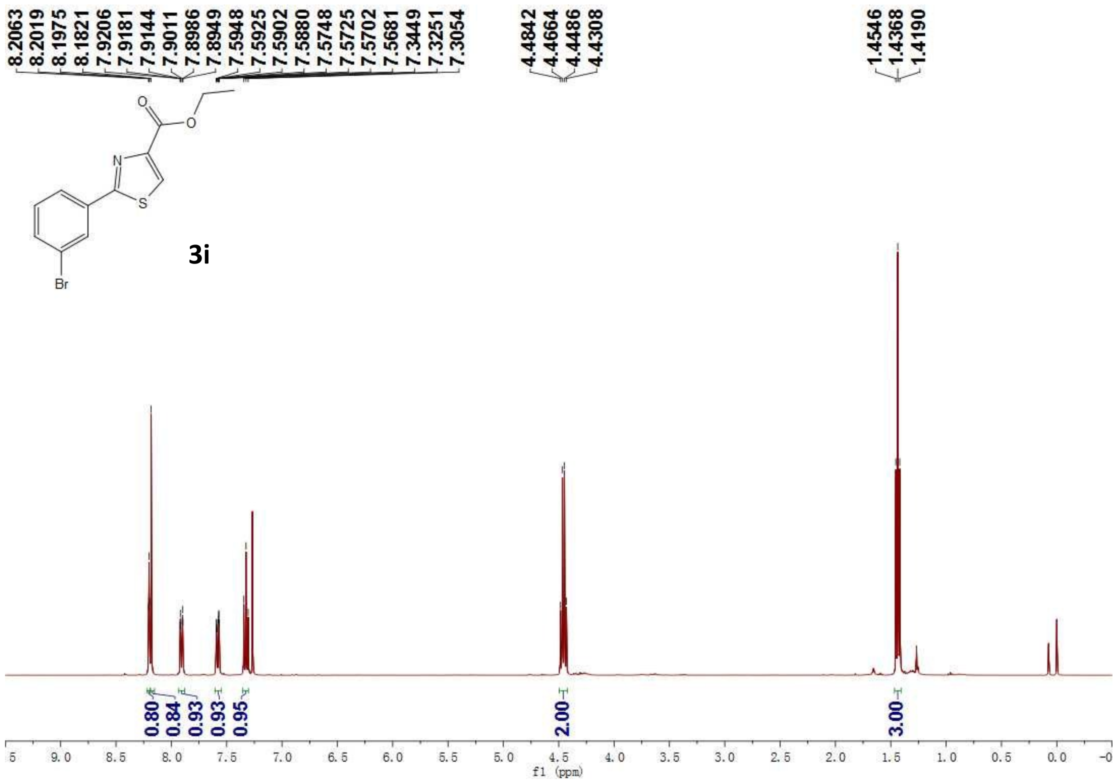
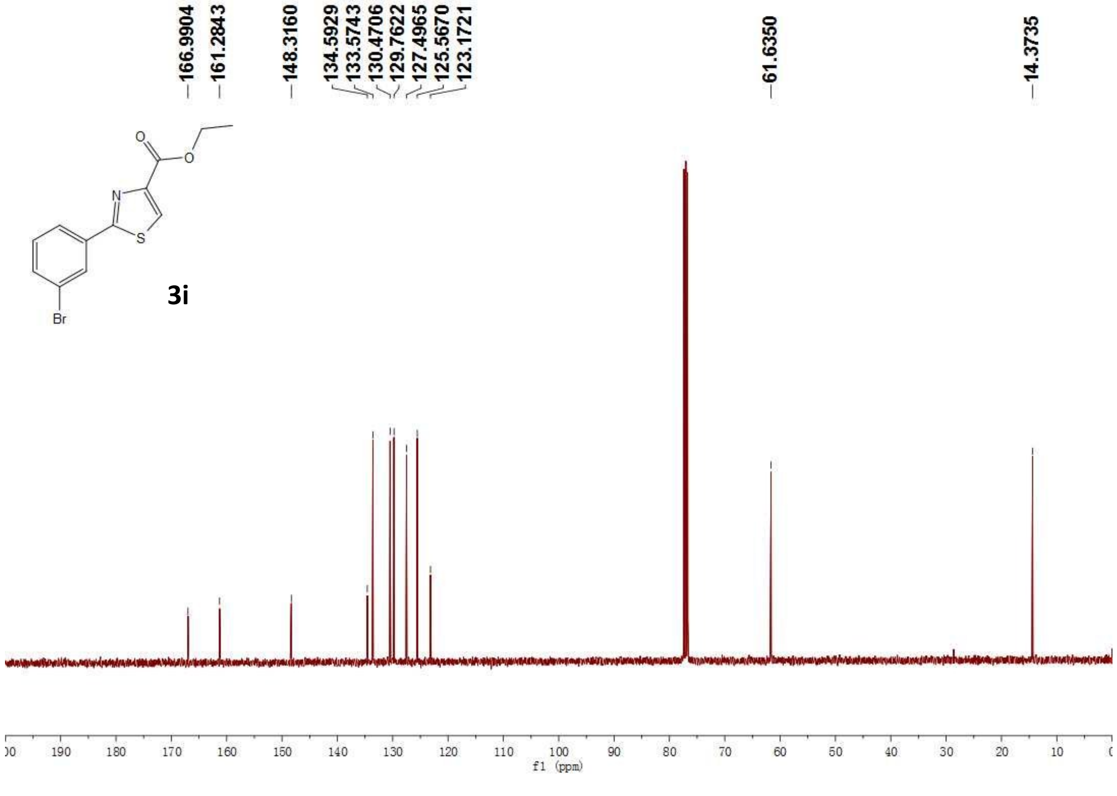
8.0949
7.7041
7.7015
7.6841
7.6815
7.4396
7.4367
7.4206
7.4182
7.4017
7.3987
7.3175
7.3132
7.2977
7.2944
7.2791
7.2747
7.2695
4.4847
4.4669
4.4491
4.4313
1.4486
1.4308
1.4130
O
O
N
S
Br
0.83
0.91
0.93
0.97
0.95
2.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3h


165.6611
161.5025
146.9406
133.8708
133.4526
132.1258
131.1540
128.5206
127.6490
121.7619
61.5075
14.3910
O
O
N
S
Br
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

3h


8.2063
8.2019
8.1975
8.1821
7.9206
7.9181
7.9144
7.9011
7.8986
7.8949
7.5948
7.5925
7.5902
7.5880
7.5748
7.5725
7.5702
7.5681
7.3449
7.3251
7.3054
4.4842
4.4664
4.4486
4.4308
1.4546
1.4368
1.4190
O
O
N
S
Br
3i
0.80
0.84
0.93
0.93
0.95
2.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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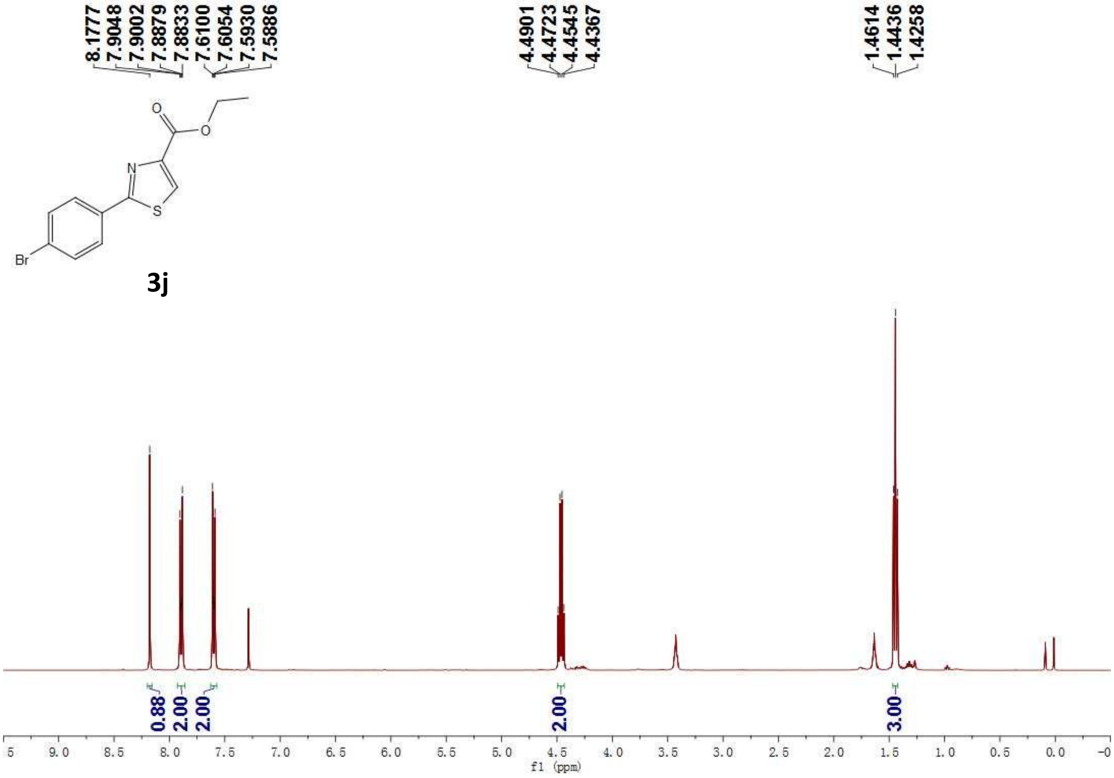
148.3160
134.5929
133.5743
130.4706
129.7622
127.4965
125.5670
123.1721
61.6350
14.3735
O
O
N
S
Br
3i
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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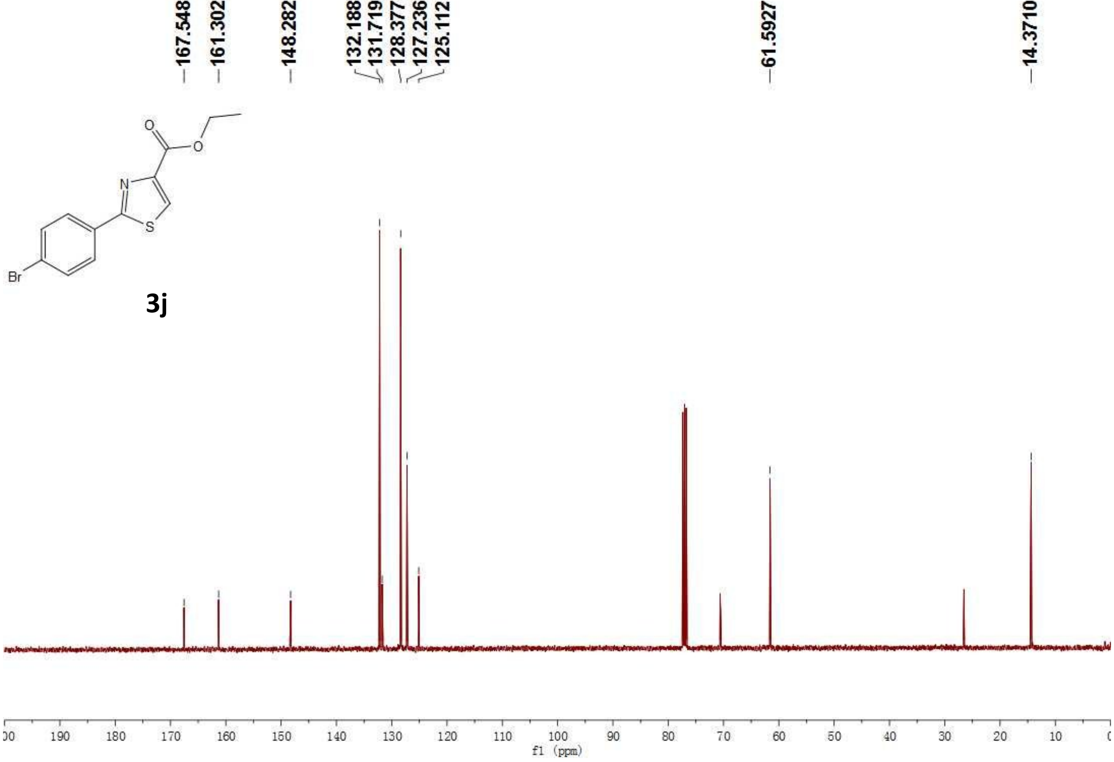
7.9002
7.8879
7.8833
7.6100
7.6054
7.5930
7.5886
4.4901
4.4723
4.4545
4.4367
1.4614
1.4436
1.4258
O
O
N
S
Br
0.88
2.00
2.00
2.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3j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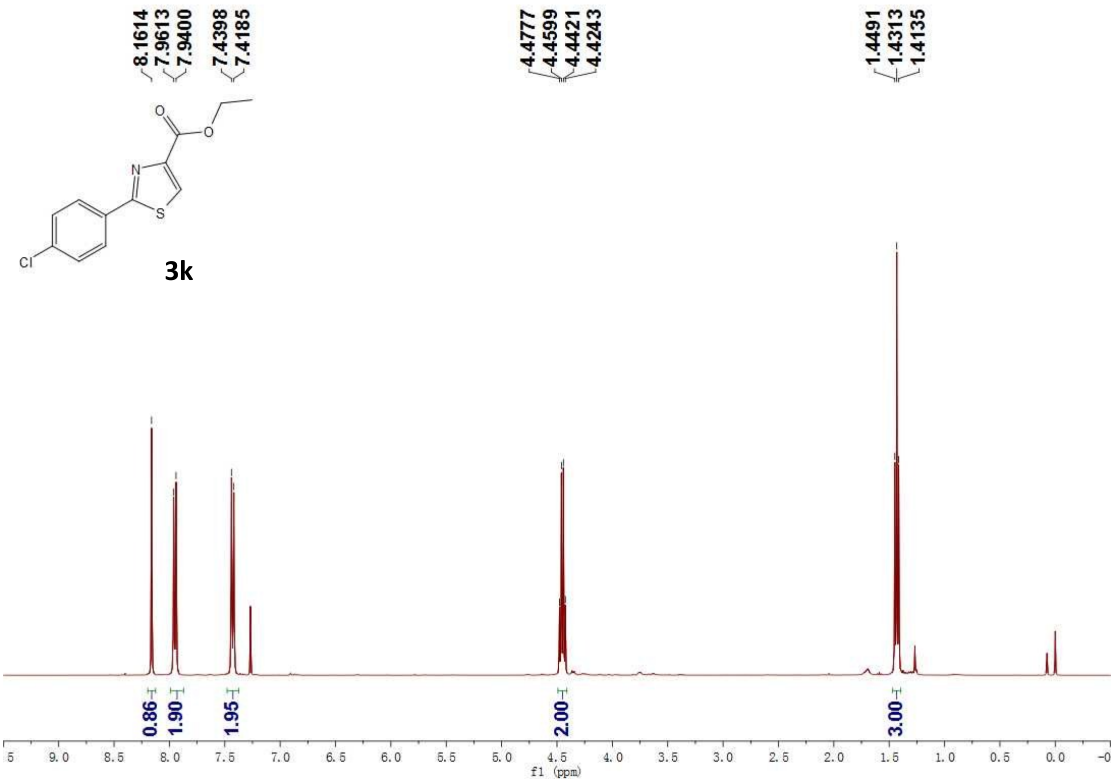
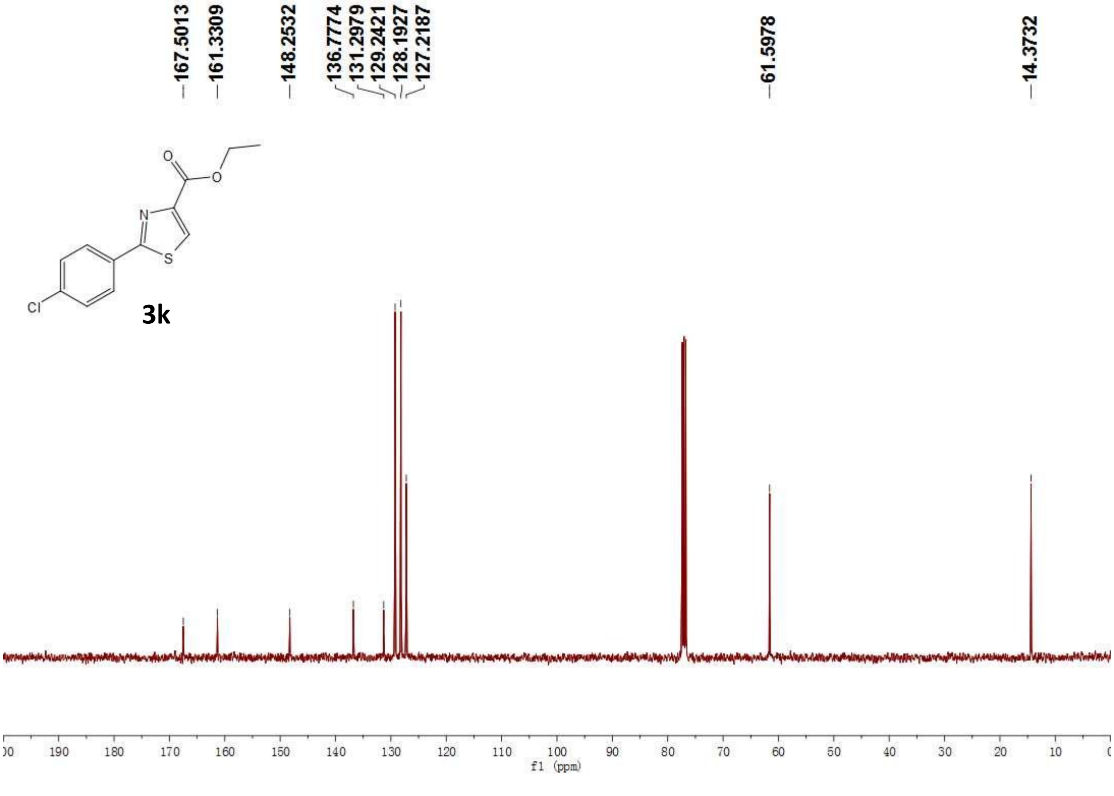
161.3024
148.2827
132.1888
131.7196
128.3774
127.2366
125.1127
61.5927
14.3710
O
O
N
S
Br
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

3j


8.1614
7.9613
7.9400
7.4398
7.4185
4.4777
4.4599
4.4421
4.4243
1.4491
1.4313
1.4135
O
O
N
S
Cl
3k
0.86
1.90
1.95
2.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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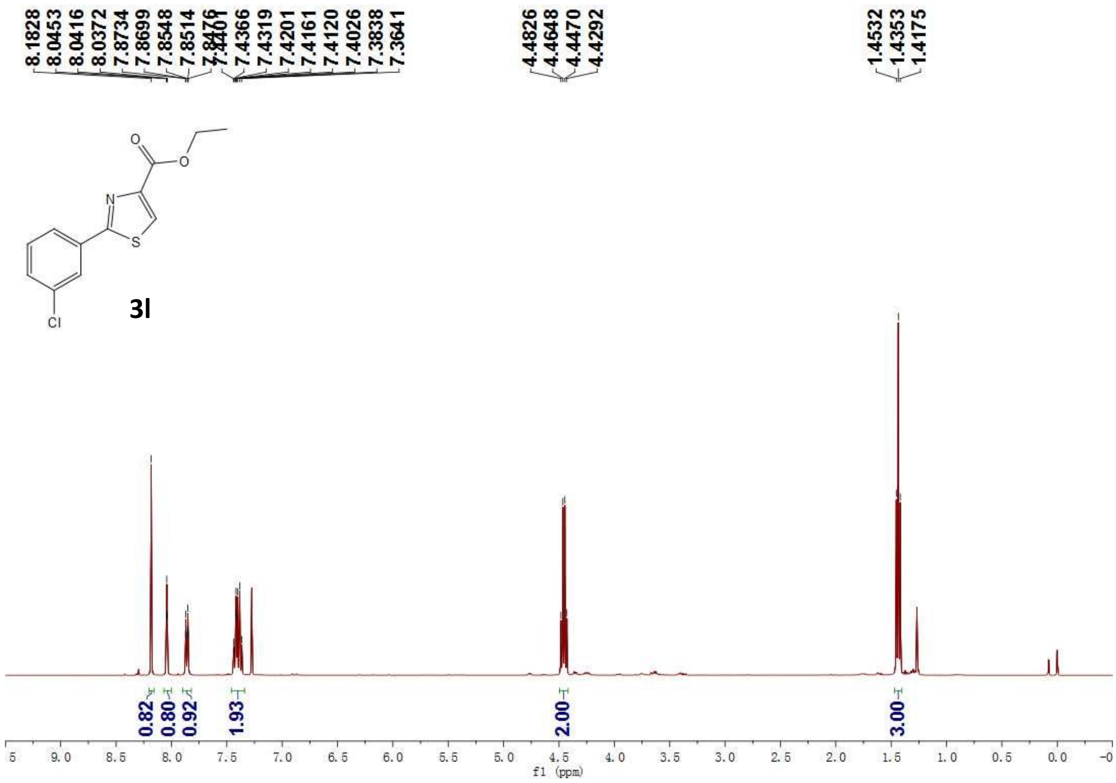
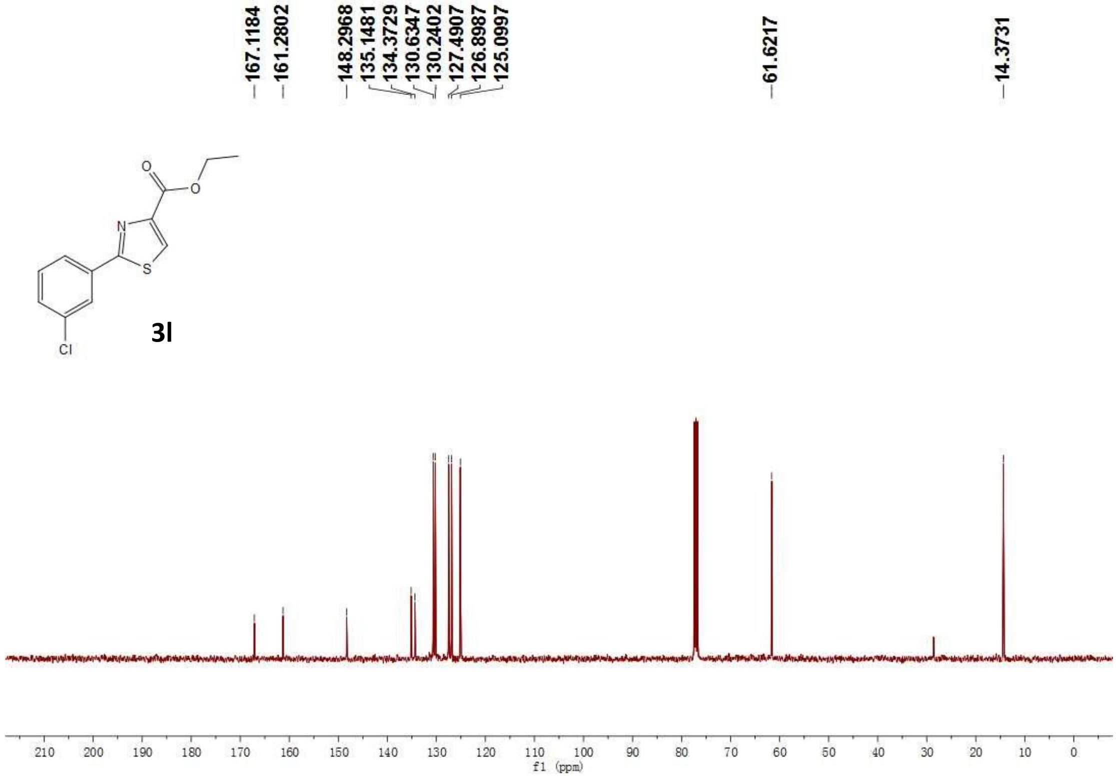
161.3309
148.2532
136.7774
131.2979
129.2421
128.1927
127.2187
61.5978
14.3732
O
O
N
S
Cl
3k
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



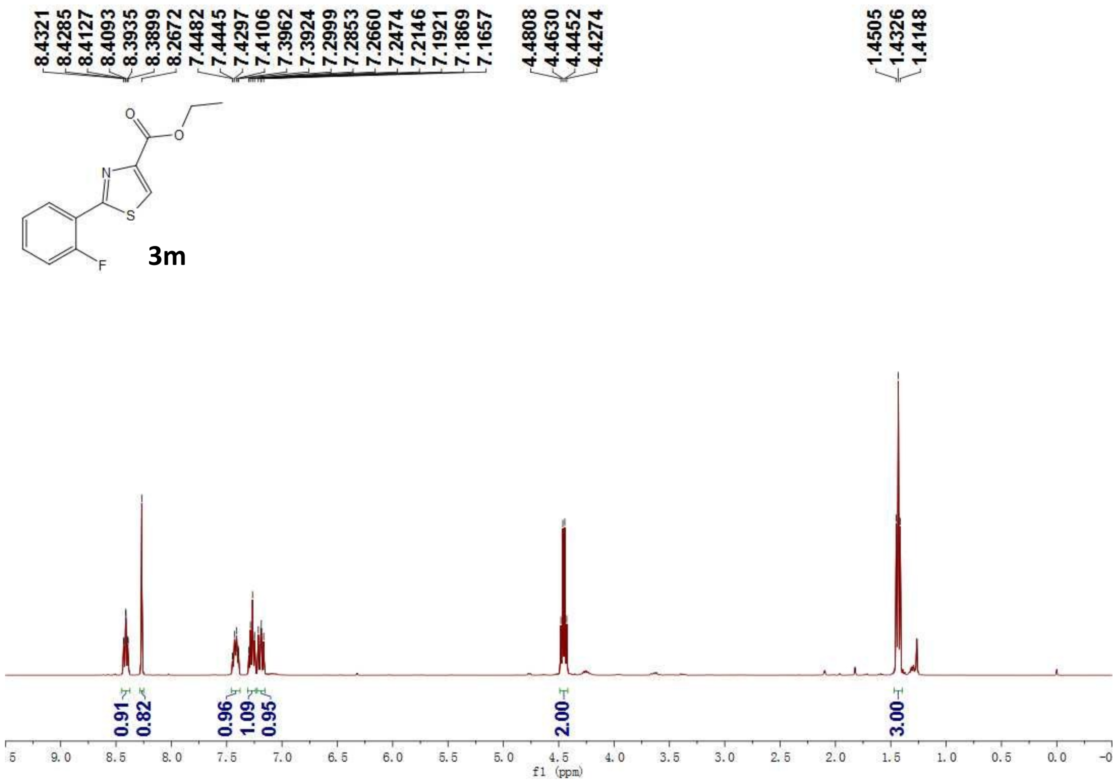
3l

8.1828
8.0453
8.0416
8.0372
7.8734
7.8699
7.8548
7.8514
7.8476
7.4401
7.4366
7.4319
7.4201
7.4161
7.4120
7.4026
7.3838
7.3641
4.4826
4.4648
4.4470
4.4292
1.4532
1.4353
1.4175
O
O
N
S
Cl
0.82
0.80
0.92
1.93
2.00
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)



3l

167.1184
161.2802
148.2968
135.1481
134.3729
130.6347
130.2402
127.4907
126.8987
125.0997
61.6217
14.3731
O
O
N
S
Cl
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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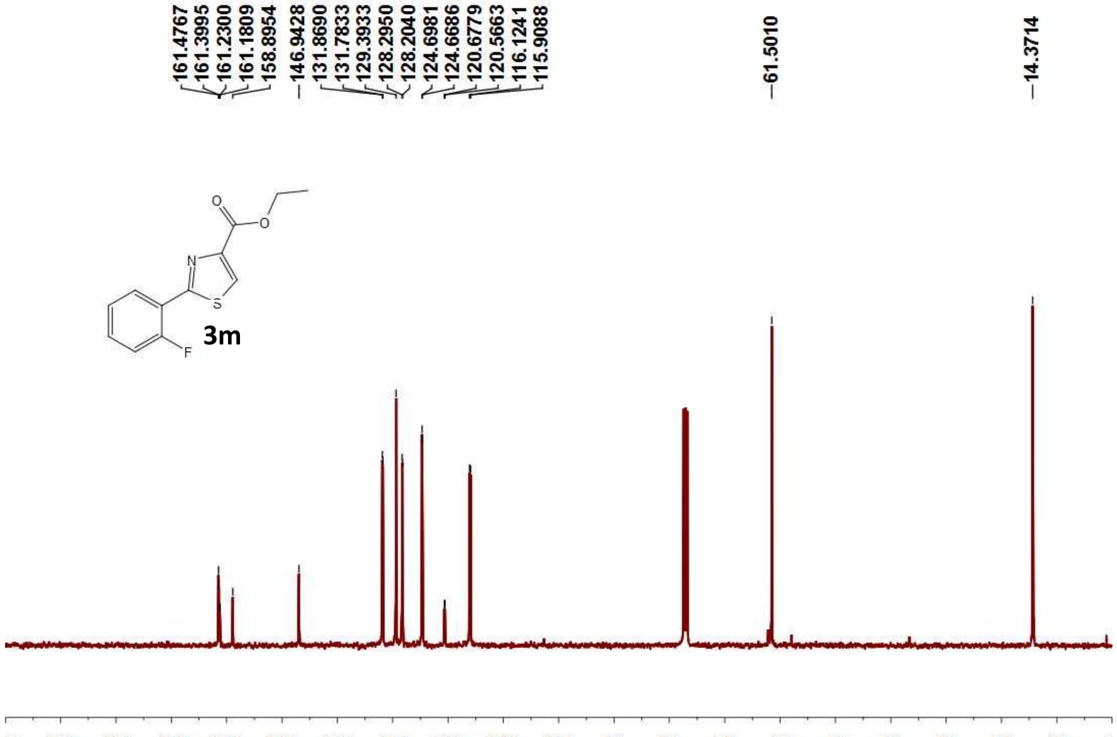
8.4285
8.4127
8.4093
8.3935
8.3899
8.2672
7.4482
7.4445
7.4297
7.4106
7.3962
7.3924
7.2999
7.2853
7.2660
7.2474
7.2146
7.1921
7.1869
7.1657
4.4808
4.4630
4.4452
4.4274
1.4505
1.4326
1.4148
O
O
N
S
F
3m
0.91
0.82
0.96
1.09
0.95
2.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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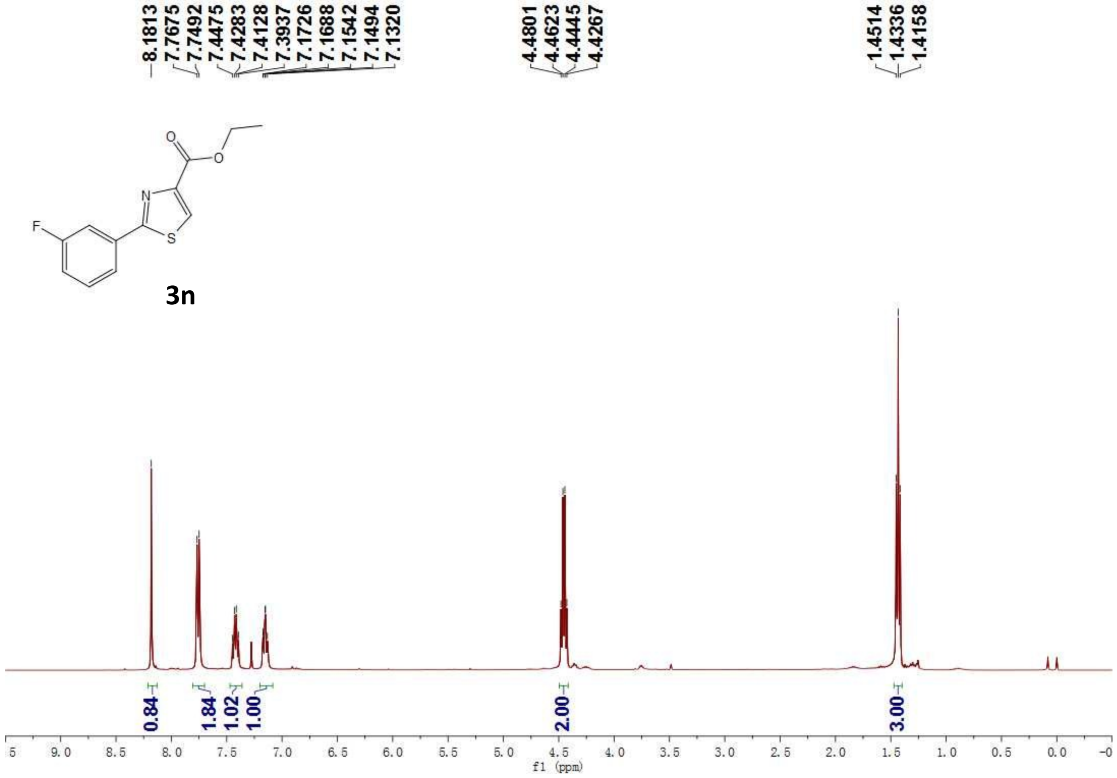
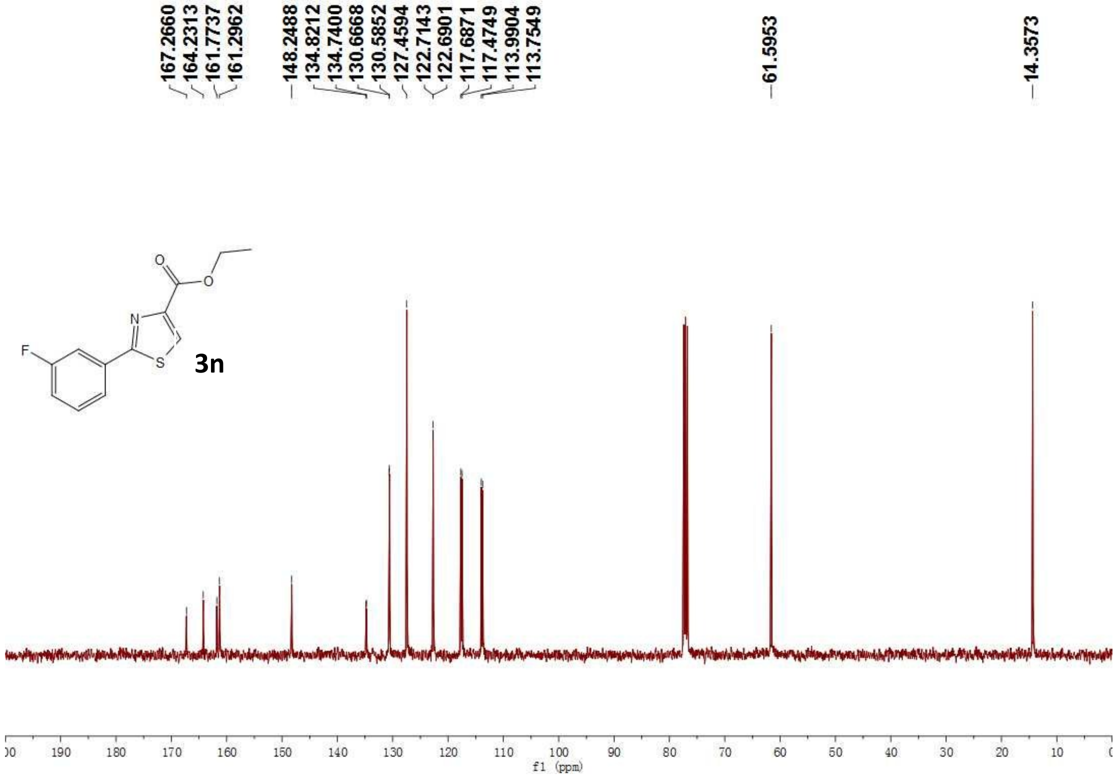
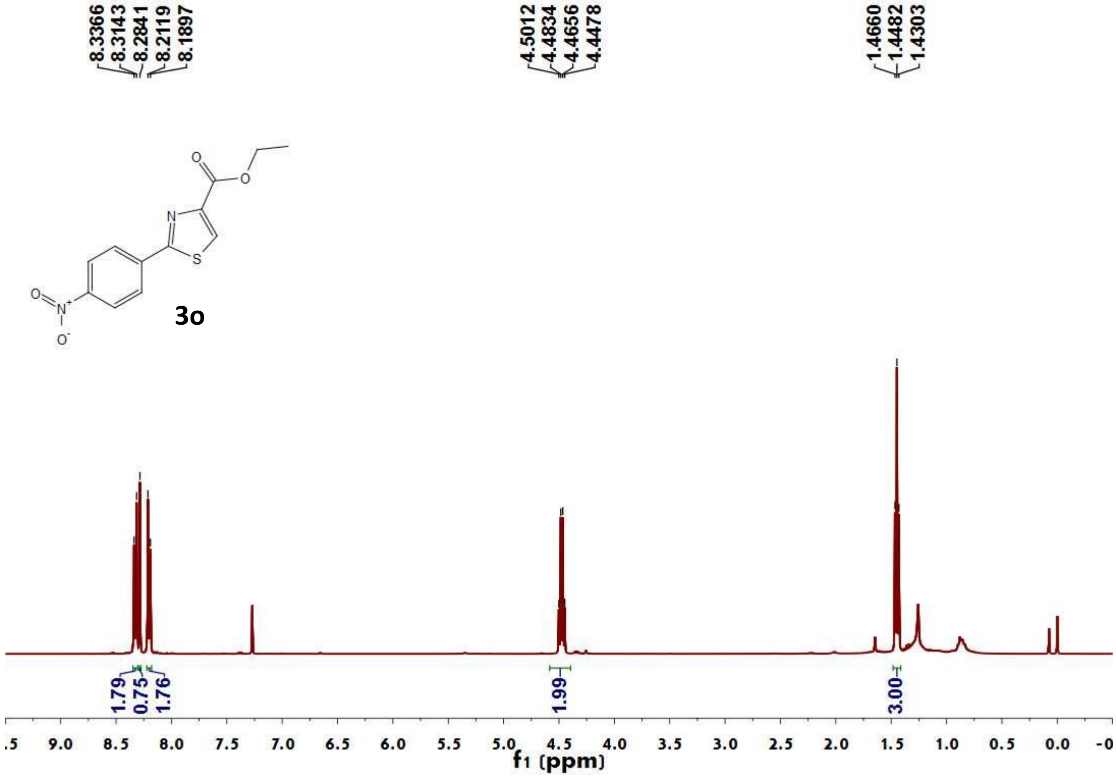
161.3995
161.2300
161.1809
158.8954
146.9428
131.8690
131.7833
129.3933
128.2950
128.2040
124.6981
124.6686
120.6779
120.5663
116.1241
115.9088
61.5010
14.3714
O
O
N
S
F
3m
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.1813
7.7675
7.7492
7.4475
7.4283
7.4128
7.3937
7.1726
7.1688
7.1542
7.1494
7.1320
4.4801
4.4623
4.4445
4.4267
1.4514
1.4336
1.4158
O
O
N
S
F
0.84
1.84
1.02
1.00
2.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3n


167.2660
164.2313
161.7737
161.2962
148.2488
134.8212
134.7400
130.6668
130.5852
127.4594
122.7143
122.6901
117.6871
117.4749
113.9904
113.7549
61.5953
14.3573
O
O
N
S
F
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

3n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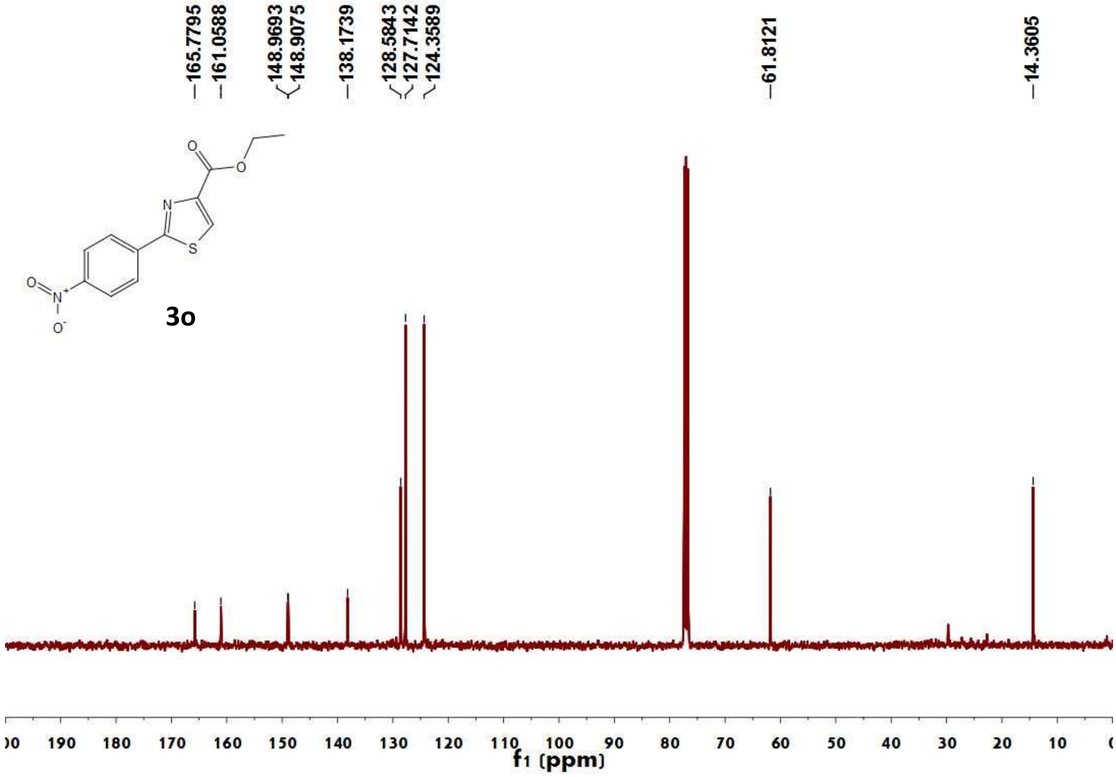
8.3143
8.2841
8.2119
8.1897
4.5012
4.4834
4.4656
4.4478
1.4660
1.4482
1.4303
O
O
N
S
O
N+
O-
3o
1.79
0.75
1.76
1.99
3.00
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)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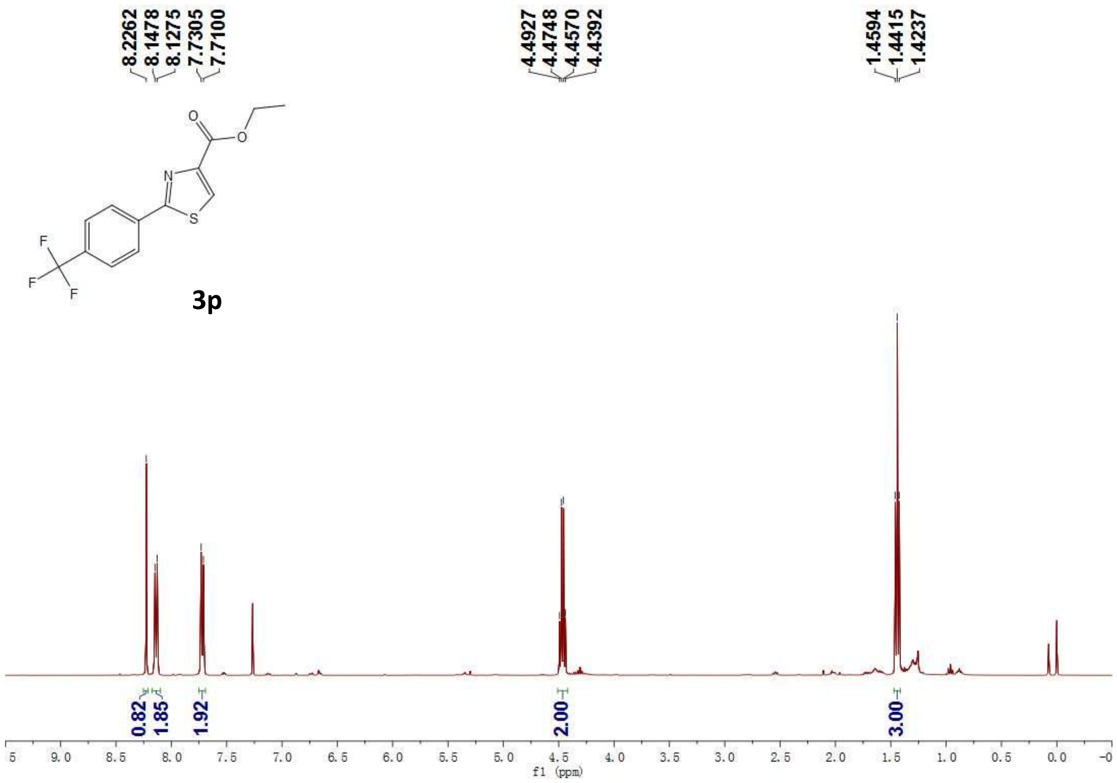
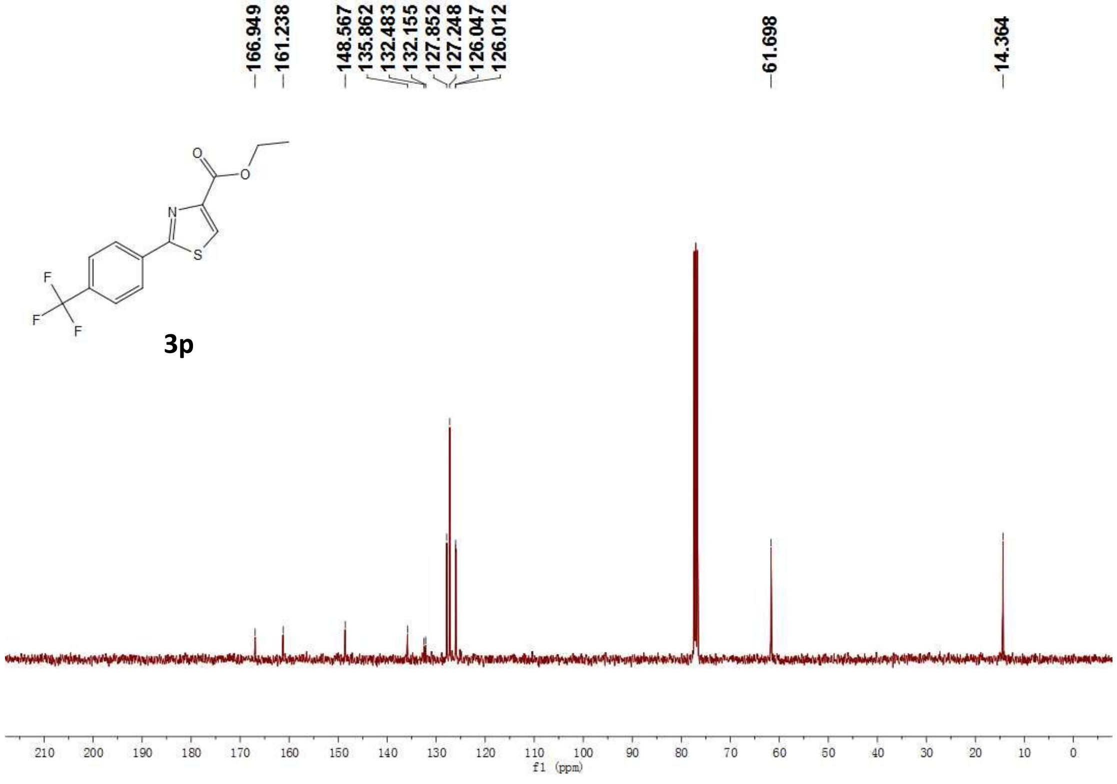
148.9693
148.9075
138.1739
128.5843
127.7142
124.3589
61.8121
14.3605
O
O
N
S
O
N+
O-
3o
)0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(
f1 (ppm)


8.2262
8.1478
8.1275
7.7305
7.7100
4.4927
4.4748
4.4570
4.4392
1.4594
1.4415
1.4237
O
O
N
S
F
F
F
3p
0.82
1.85
1.92
2.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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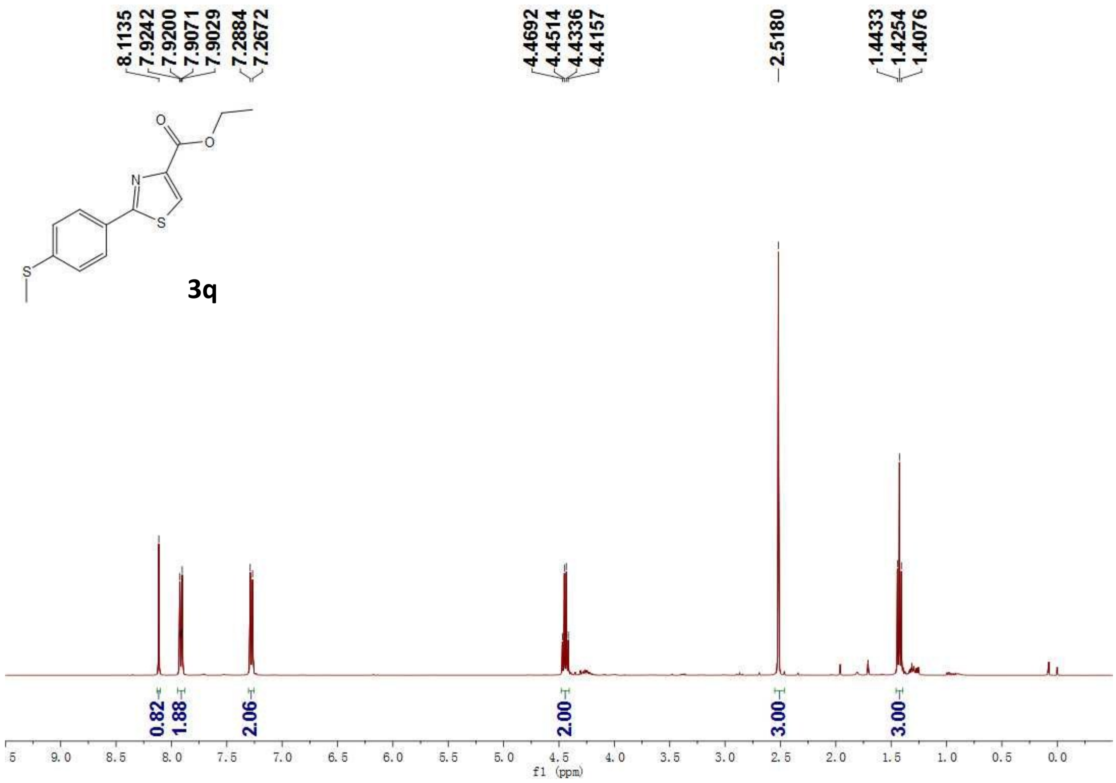
148.567
135.862
132.483
132.155
127.852
127.248
126.047
126.012
61.698
14.364
O
O
N
S
F
F
F
3p
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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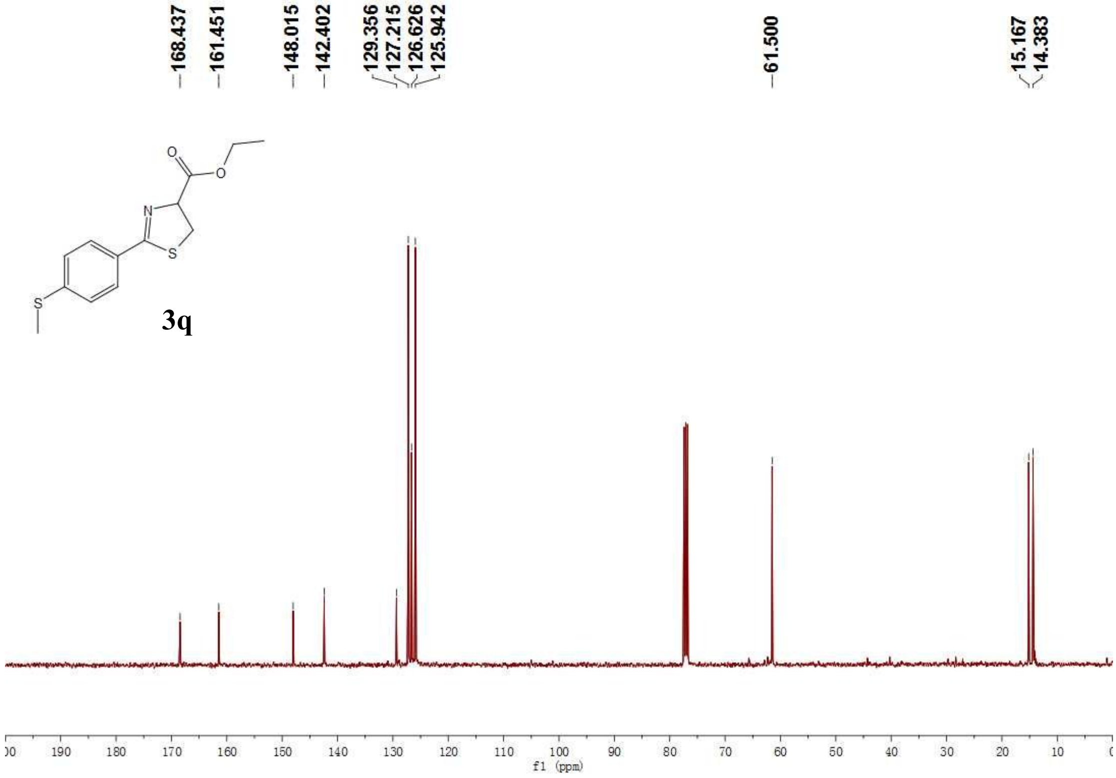
7.9200
7.9071
7.9029
7.2884
7.2672
4.4692
4.4514
4.4336
4.4157
2.5180
1.4433
1.4254
1.4076
3q
0.82
1.88
2.06
2.00
3.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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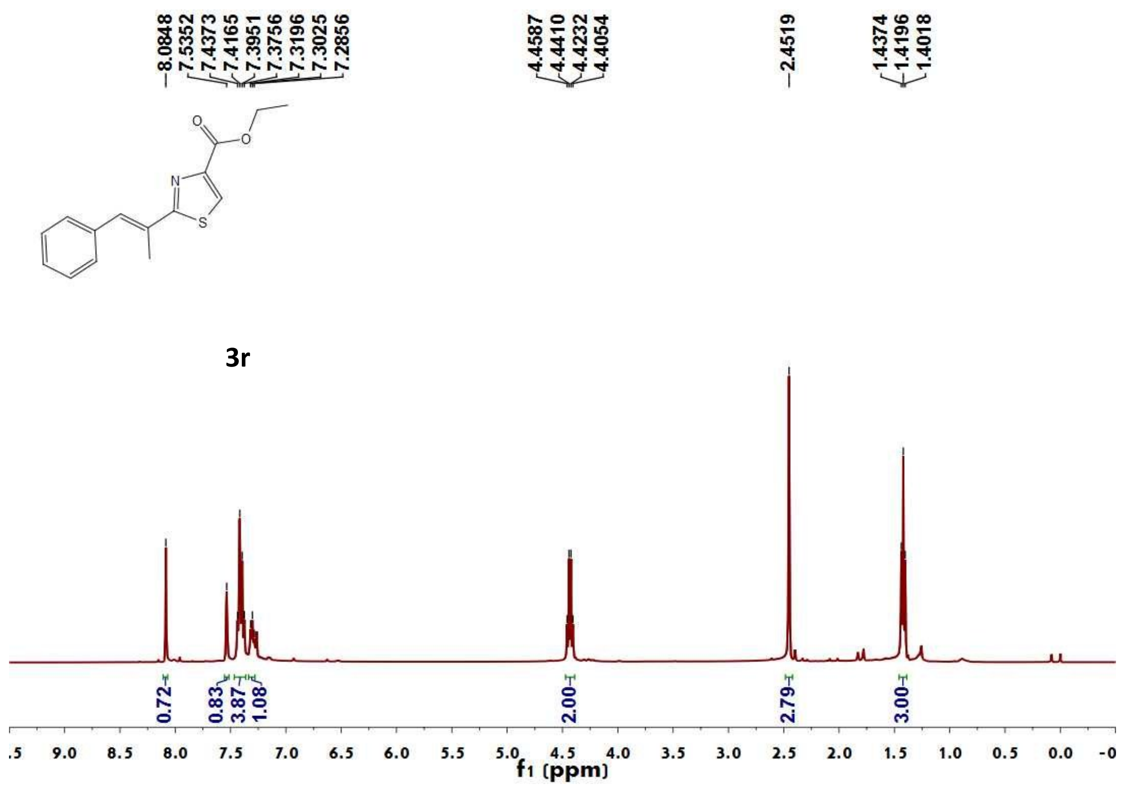
148.015
142.402
129.356
127.215
126.626
125.942
61.500
15.167
14.383
3q
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



3r

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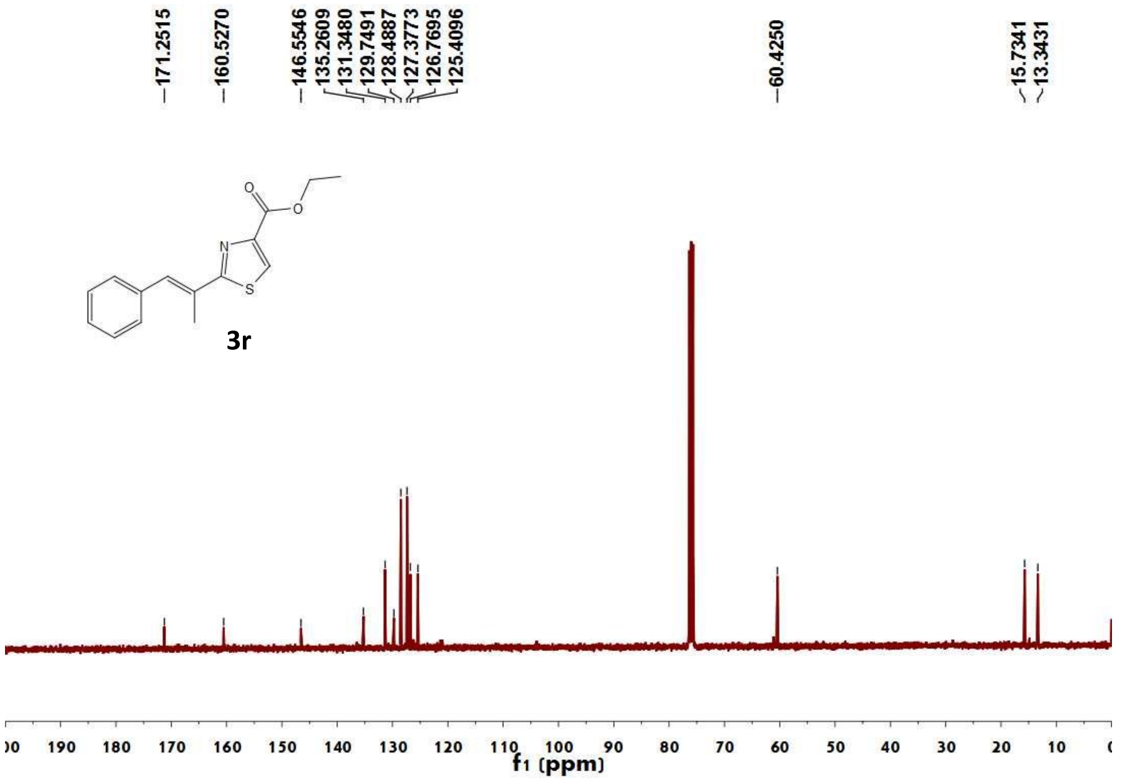
7.4373
7.4165
7.3951
7.3756
7.3196
7.3025
7.2856
4.4587
4.4410
4.4232
4.4054
2.4519
1.4374
1.4196
1.4018
O
O
N
S
0.72
0.83
3.87
1.08
2.00
2.79
3.00
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)



3r

171.2515
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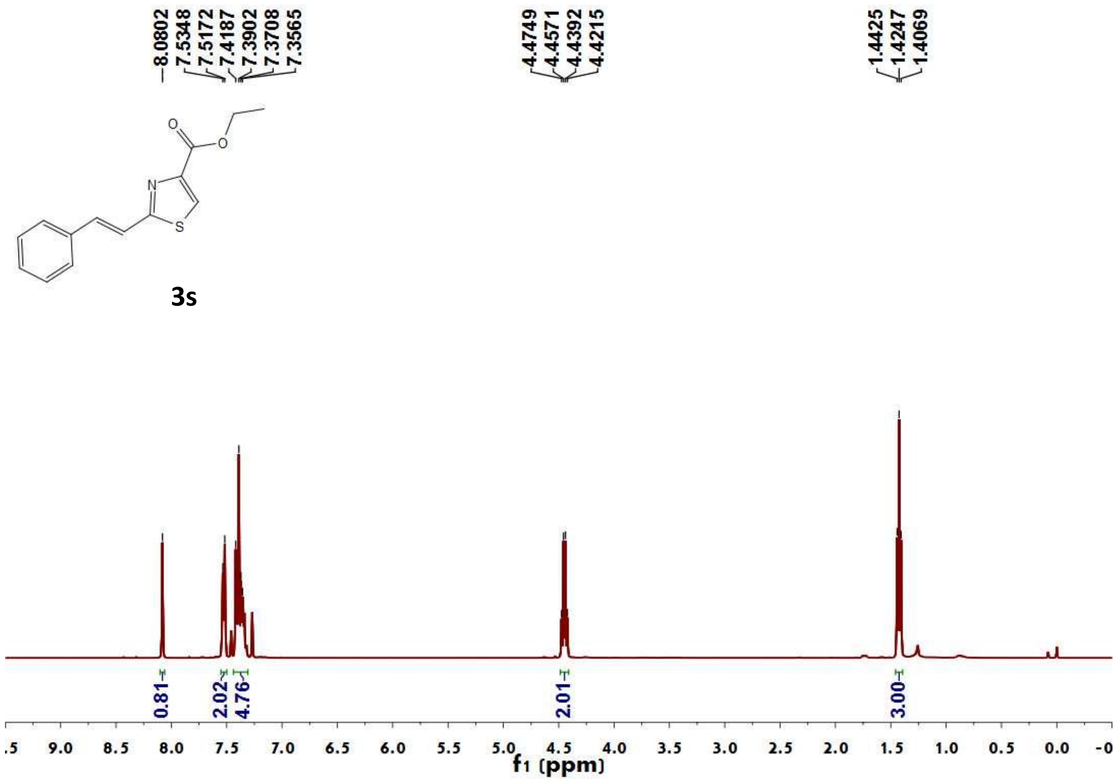
131.3480
129.7491
128.4887
127.3773
126.7695
125.4096
60.4250
15.7341
13.3431
O
O
N
S
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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7.5172
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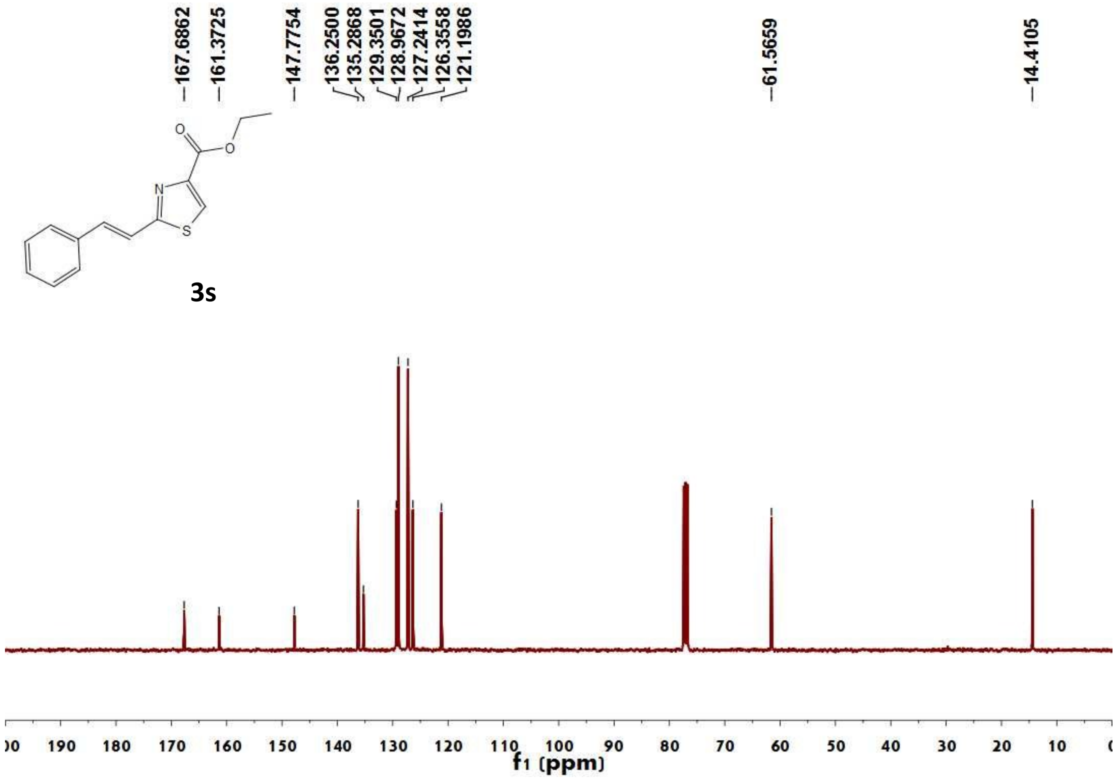
7.3902
7.3708
7.3565
4.4749
4.4571
4.4392
4.4215
1.4425
1.4247
1.4069
O
O
N
S
3s
0.81
2.02
4.76
2.01
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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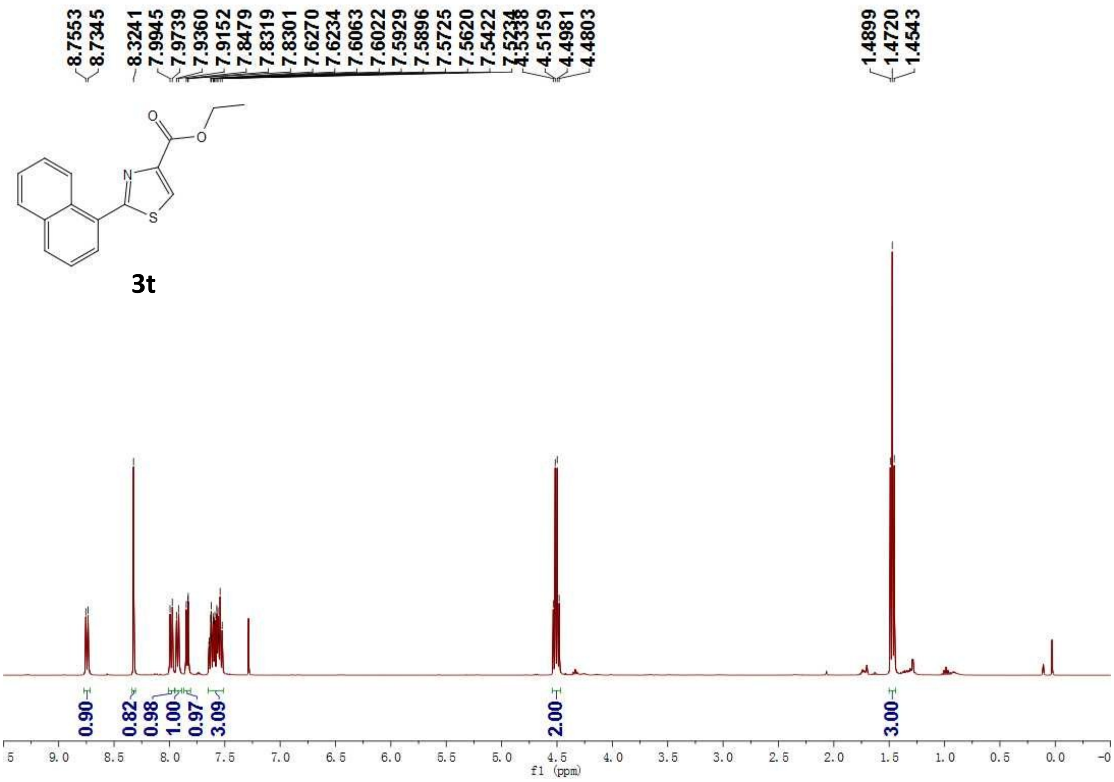
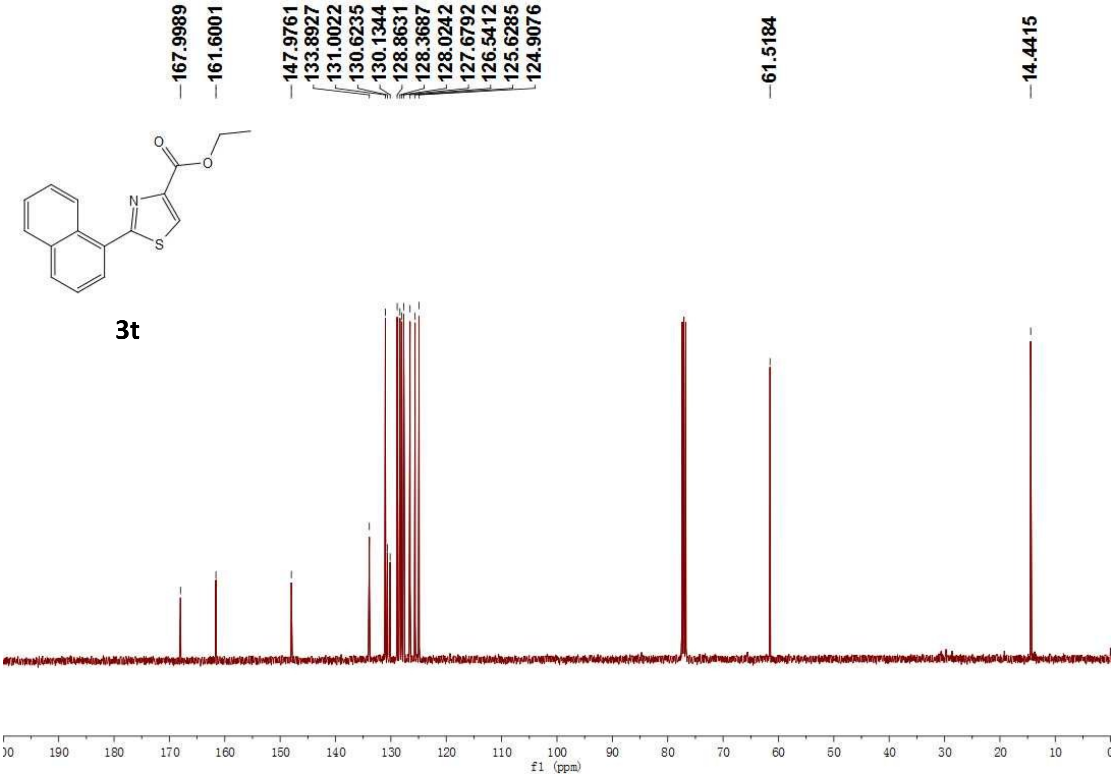
147.7754
136.2500
135.2868
129.3501
128.9672
127.2414
126.3558
121.1986
61.5659
14.4105
O
O
N
S
3s
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.7553
8.7345
8.3241
7.9945
7.9739
7.9360
7.9152
7.8479
7.8319
7.8301
7.6270
7.6234
7.6063
7.6022
7.5929
7.5896
7.5725
7.5620
7.5422
7.5234
4.5338
4.5159
4.4981
4.4803
1.4899
1.4720
1.4543
O
O
N
S
0.90
0.82
0.98
1.00
0.97
3.09
2.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3t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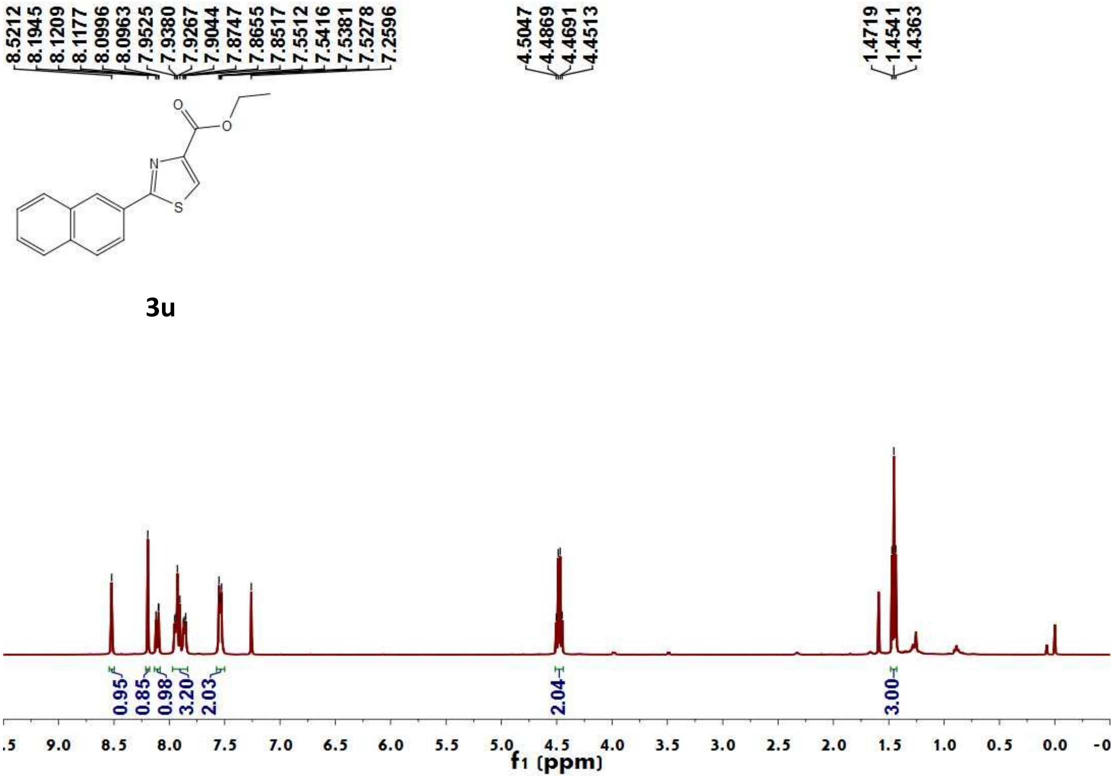
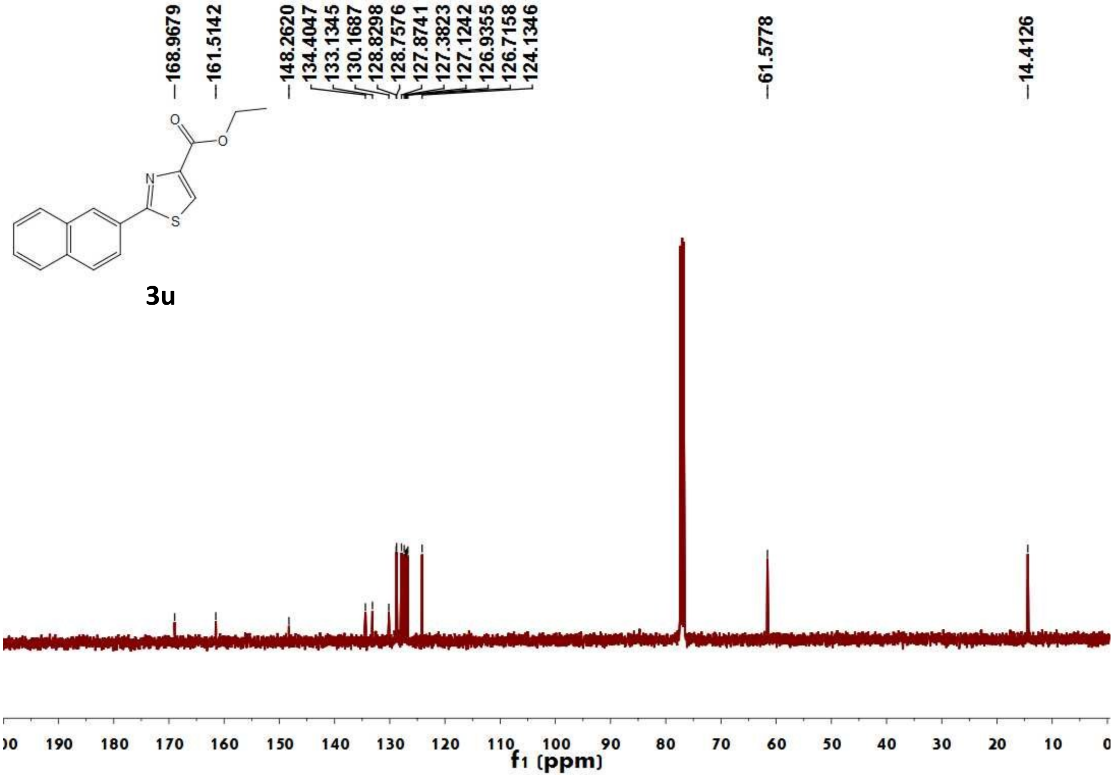
147.9761
133.8927
131.0022
130.6235
130.1344
128.8631
128.3687
128.0242
127.6792
126.5412
125.6285
124.9076
61.5184
14.4415
O
O
N
S
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

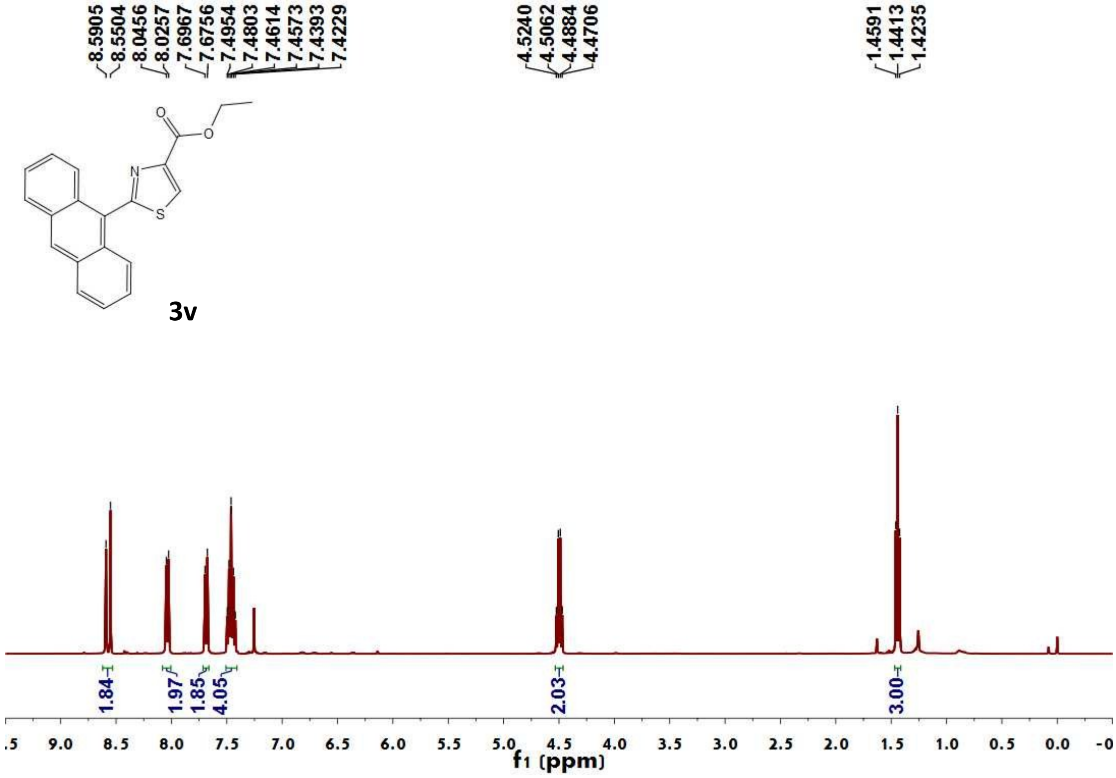
3t

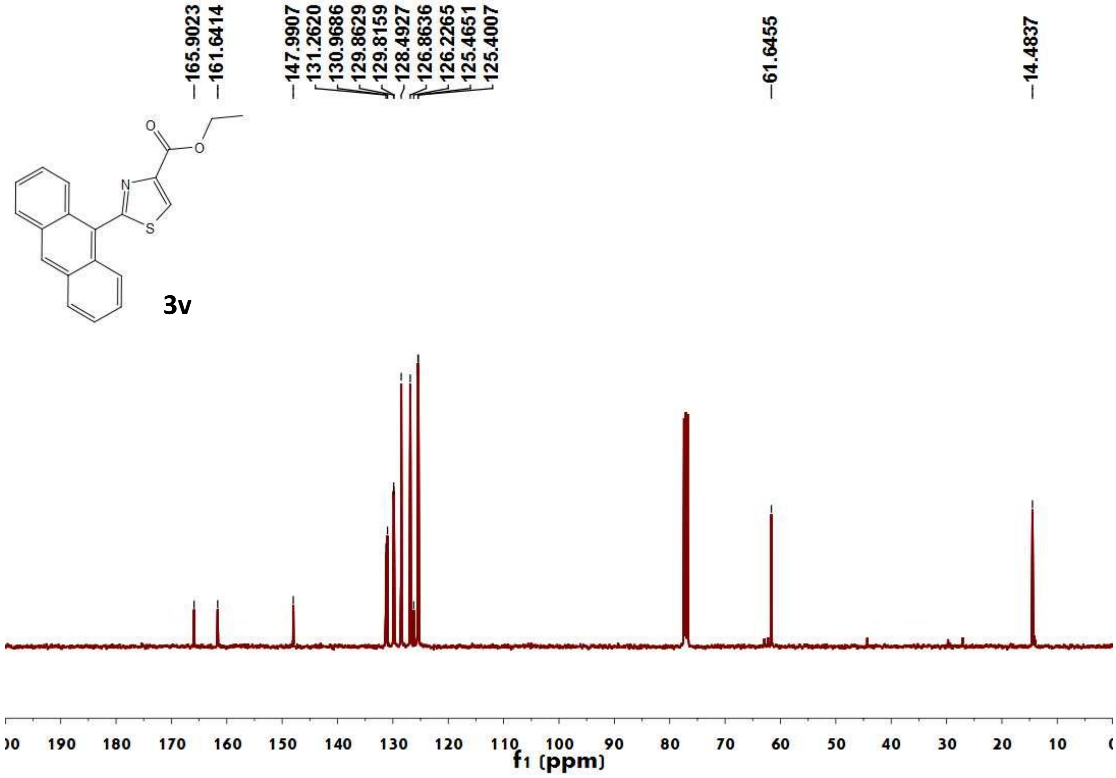

3u

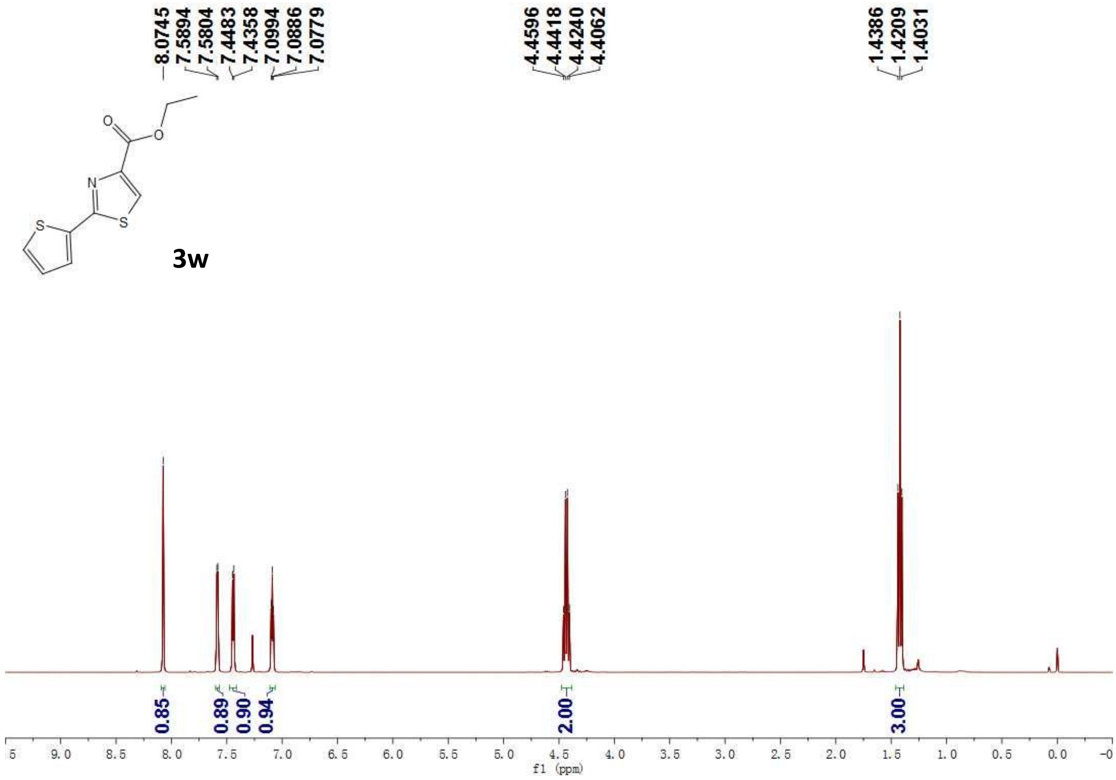
8.5212
8.1945
8.1209
8.1177
8.0996
8.0963
7.9525
7.9380
7.9267
7.9044
7.8747
7.8655
7.8517
7.5512
7.5416
7.5381
7.5278
7.2596
4.5047
4.4869
4.4691
4.4513
1.4719
1.4541
1.4363
O
O
N
S
0.95
0.85
0.98
3.20
2.03
2.04
3.00
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

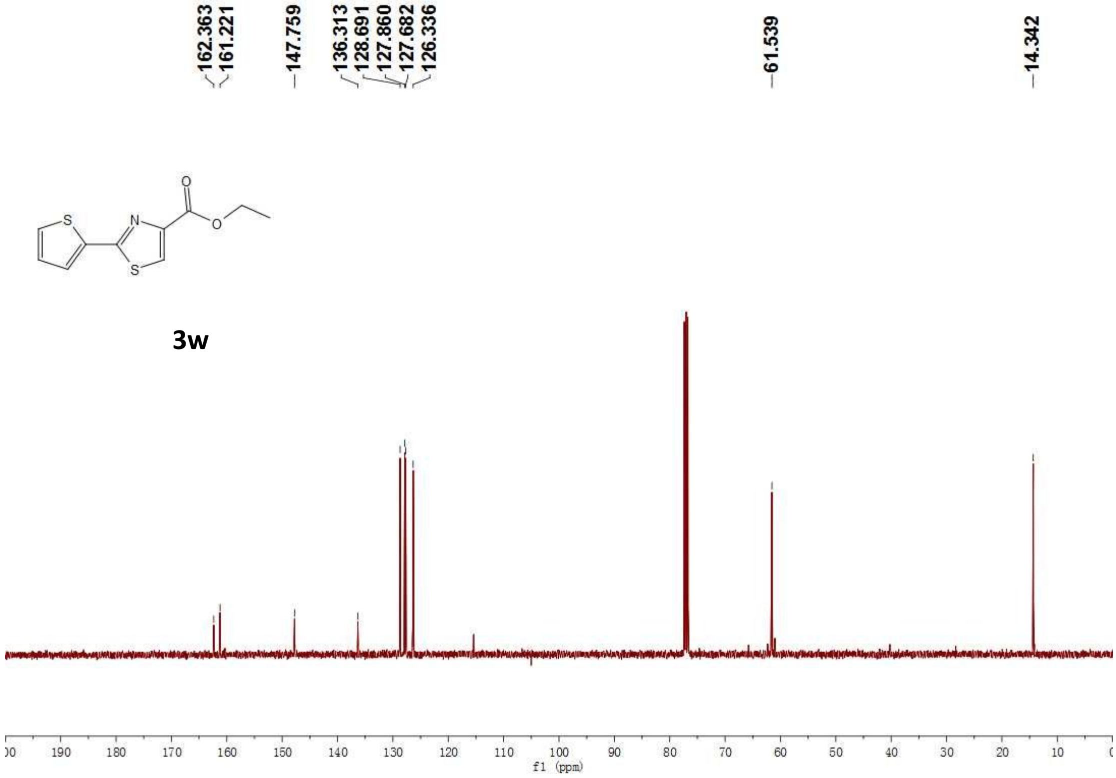

3u

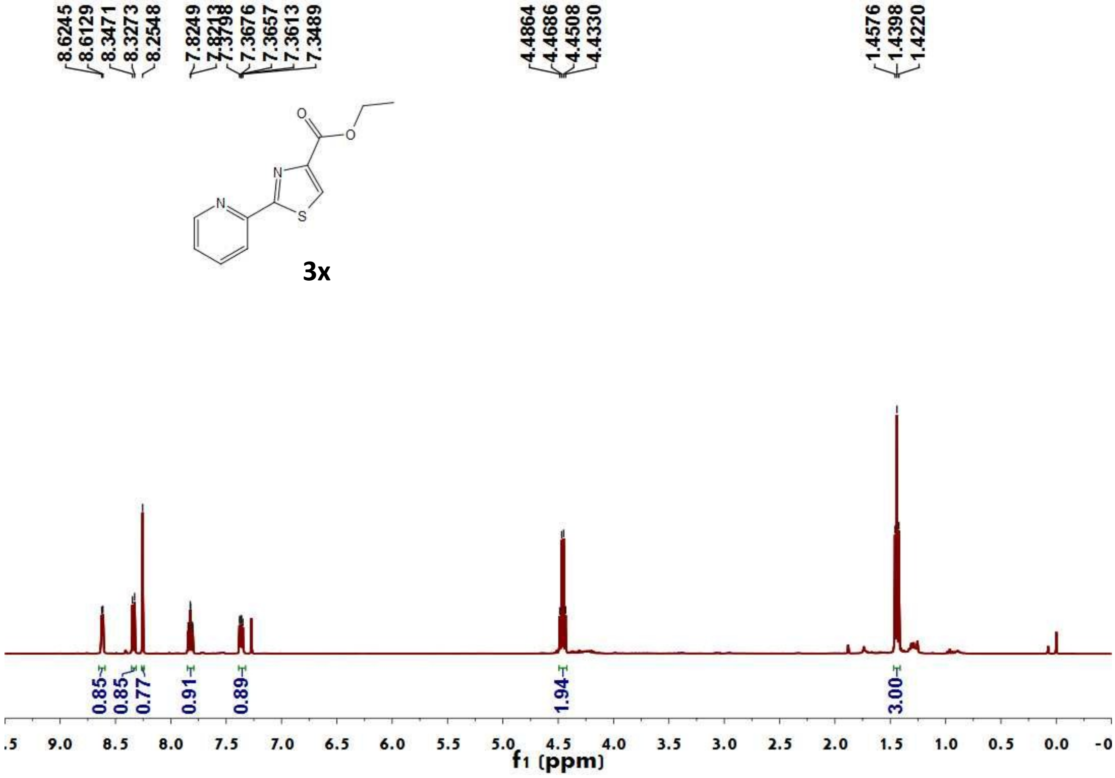
168.9679
161.5142
148.2620
134.4047
133.1345
130.1687
128.8298
128.7576
127.8741
127.3823
127.1242
126.9355
126.7158
124.1346
61.5778
14.4126
O
O
N
S
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

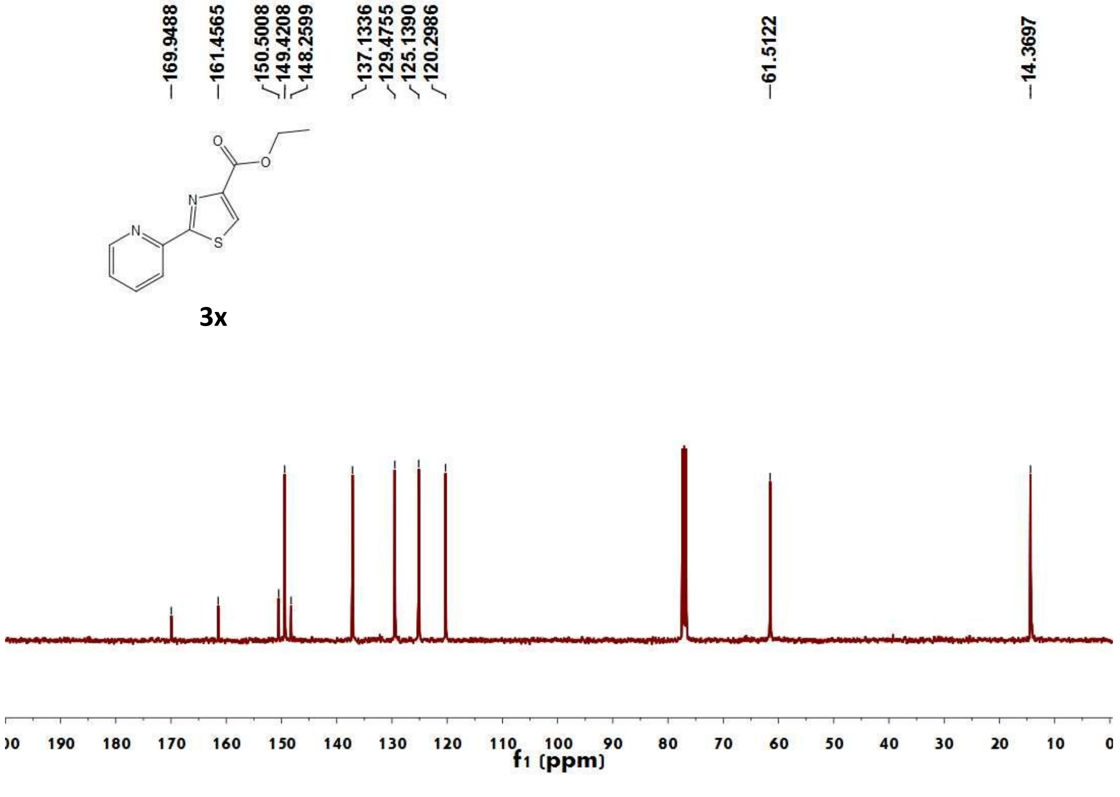

3v
8.5905
8.5504
8.0456
8.0257
7.6967
7.6756
7.4954
7.4803
7.4614
7.4573
7.4393
7.4229
4.5240
4.5062
4.4884
4.4706
1.4591
1.4413
1.4235
O
O
N
S
1.84
1.97
1.85
4.05
2.03
3.00
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

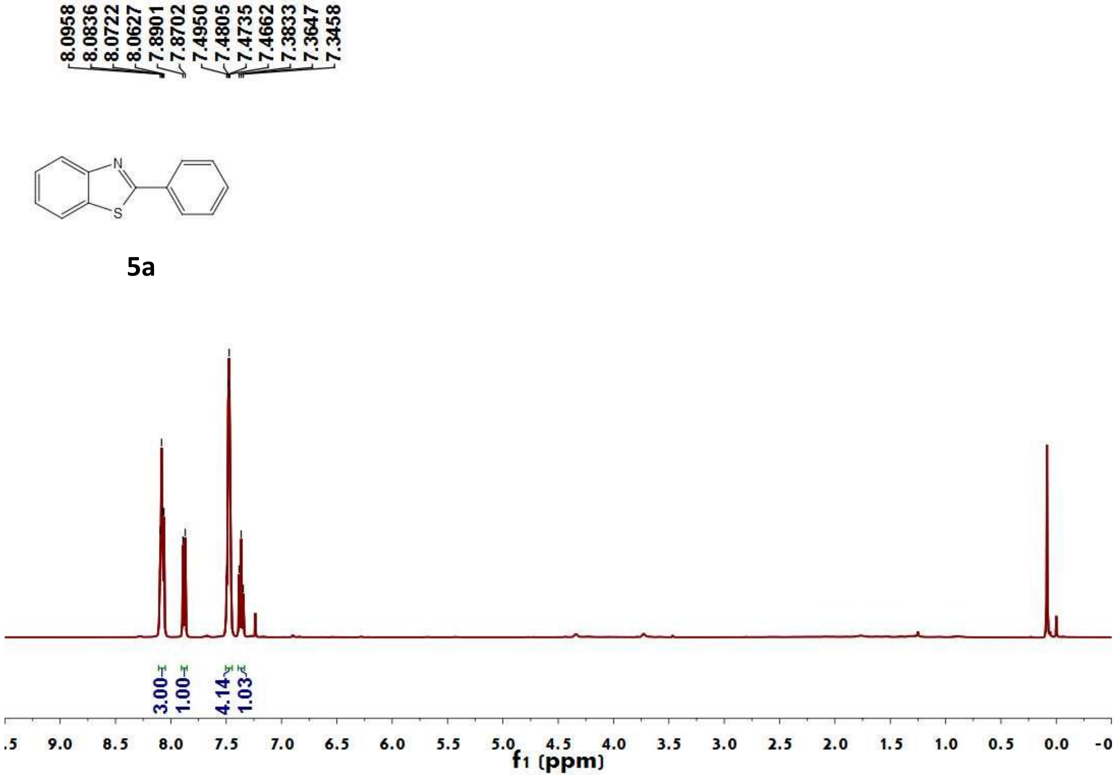

3v
165.9023
161.6414
147.9907
131.2620
130.9686
129.8629
129.8159
128.4927
126.8636
126.2265
125.4651
125.4007
61.6455
14.4837
O
O
N
S
)0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(
f1 (ppm)


3w
8.0745
7.5894
7.5804
7.4483
7.4358
7.0994
7.0886
7.0779
4.4596
4.4418
4.4240
4.4062
1.4386
1.4209
1.4031
O
O
N
S
S
0.85
0.89
0.90
0.94
2.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

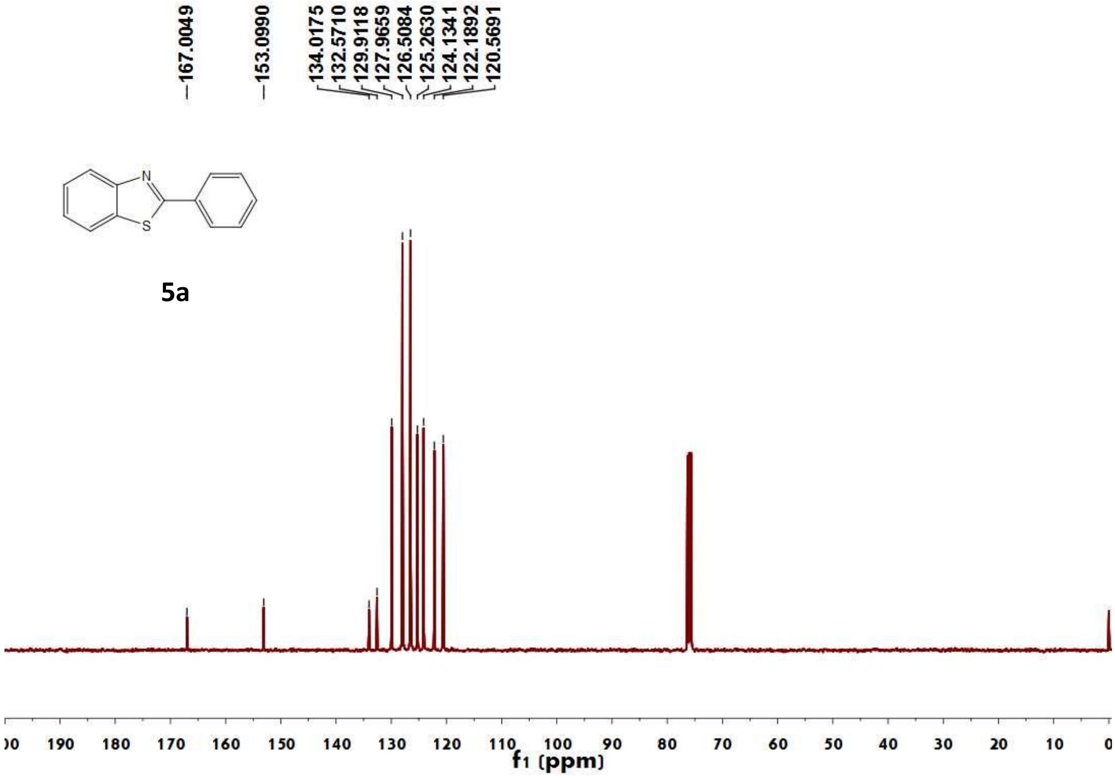

3w
162.363
161.221
147.759
136.313
128.691
127.860
127.682
126.336
61.539
14.342
O
O
N
S
S
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.6245
8.6129
8.3471
8.3273
8.2548
7.8249
7.8213
7.3798
7.3676
7.3657
7.3613
7.3489
4.4864
4.4686
4.4508
4.4330
1.4576
1.4398
1.4220
O
O
N
S
N
3x
0.85
0.85
0.77
0.91
0.89
1.94
3.00
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

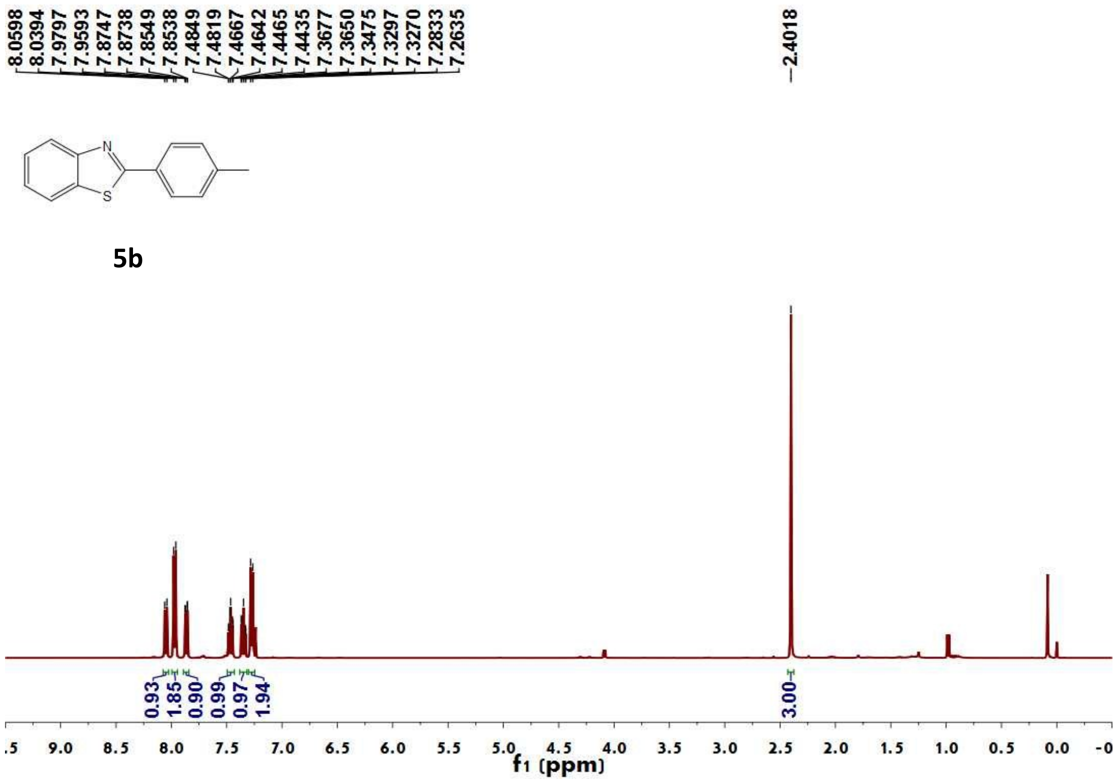

169.9488
161.4565
150.5008
149.4208
148.2599
137.1336
129.4755
125.1390
120.2986
61.5122
14.3697
O
O
N
S
N
3x
)0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


5a

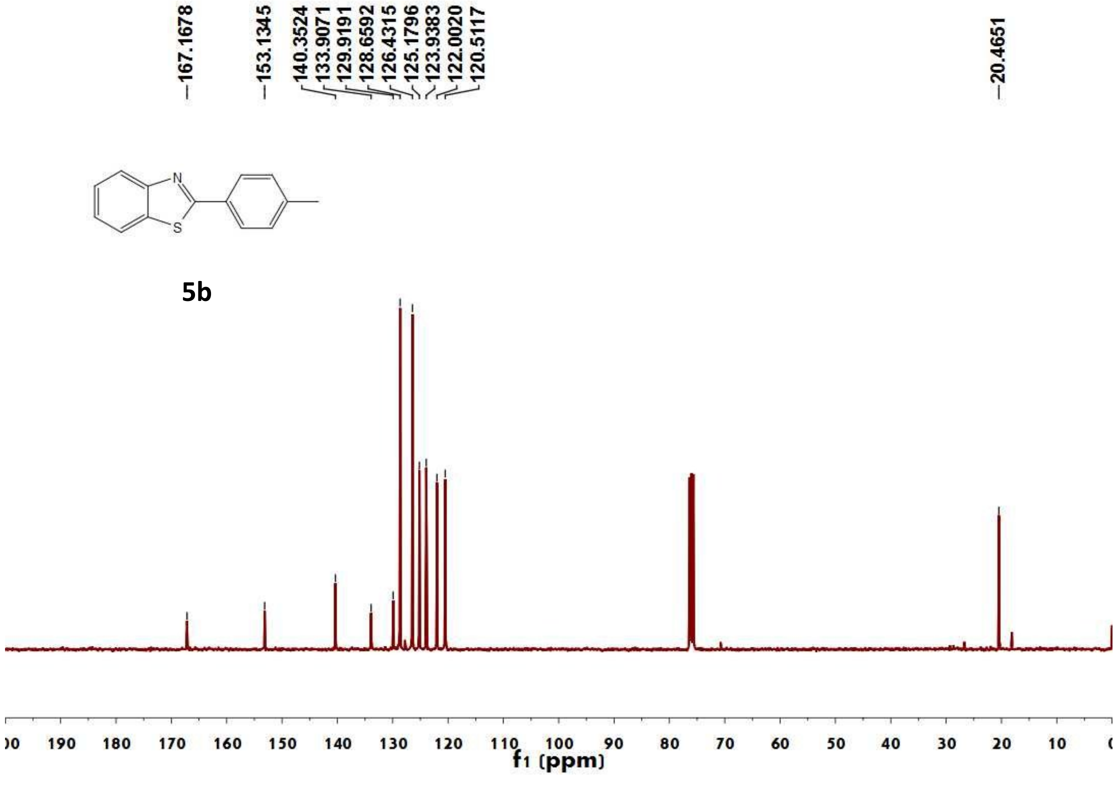
8.0958
8.0836
8.0722
8.0627
7.8901
7.8702
7.4950
7.4805
7.4735
7.4662
7.3833
7.3647
7.3458
N
S
3.00
1.00
4.14
1.03
.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)


5a

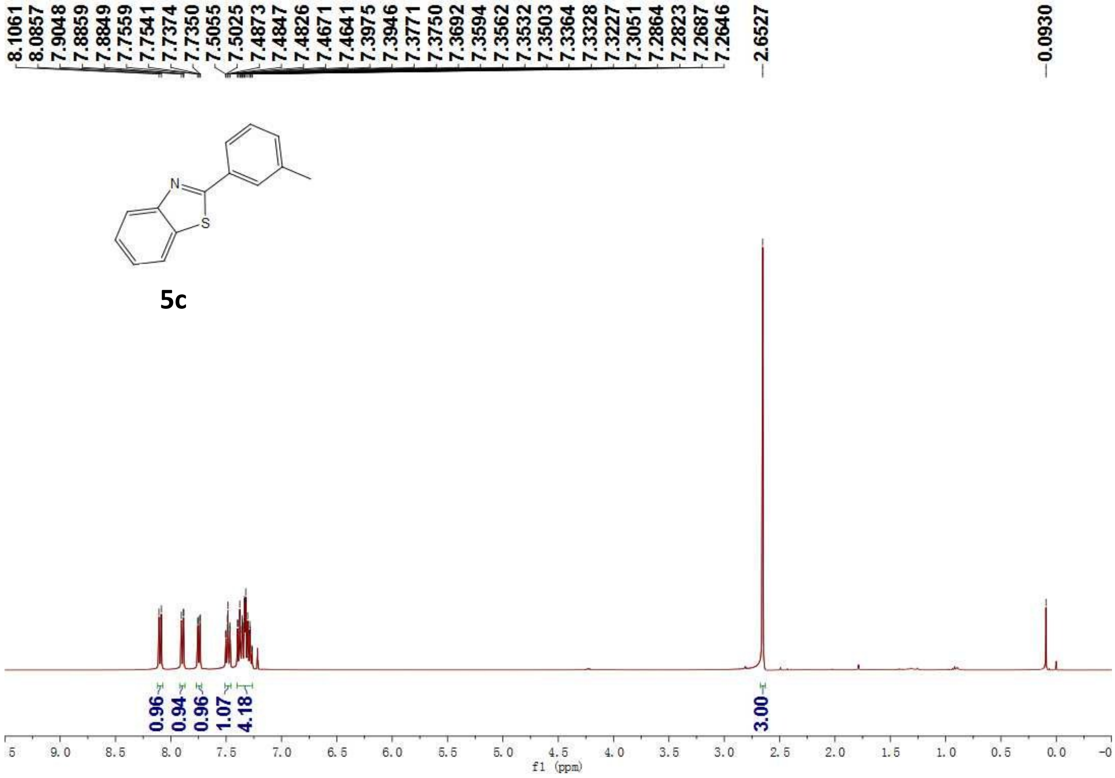
167.0049
153.0990
134.0175
132.5710
129.9118
127.9659
126.5084
125.2630
124.1341
122.1892
120.5691
N
S
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

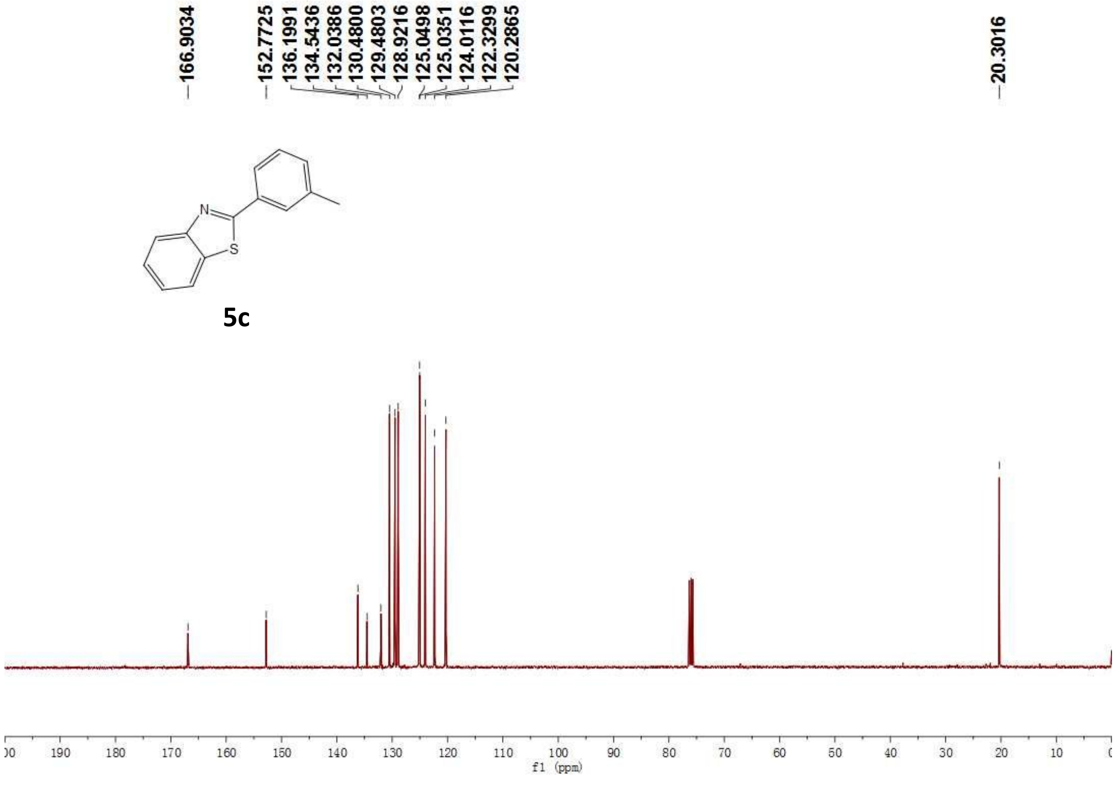

8.0598
8.0394
7.9797
7.9593
7.8747
7.8738
7.8549
7.8538
7.4849
7.4819
7.4667
7.4642
7.4465
7.4435
7.3677
7.3650
7.3475
7.3297
7.3270
7.2833
7.2635
2.4018
N
S
0.93
1.85
0.90
0.99
0.97
1.94
3.00
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

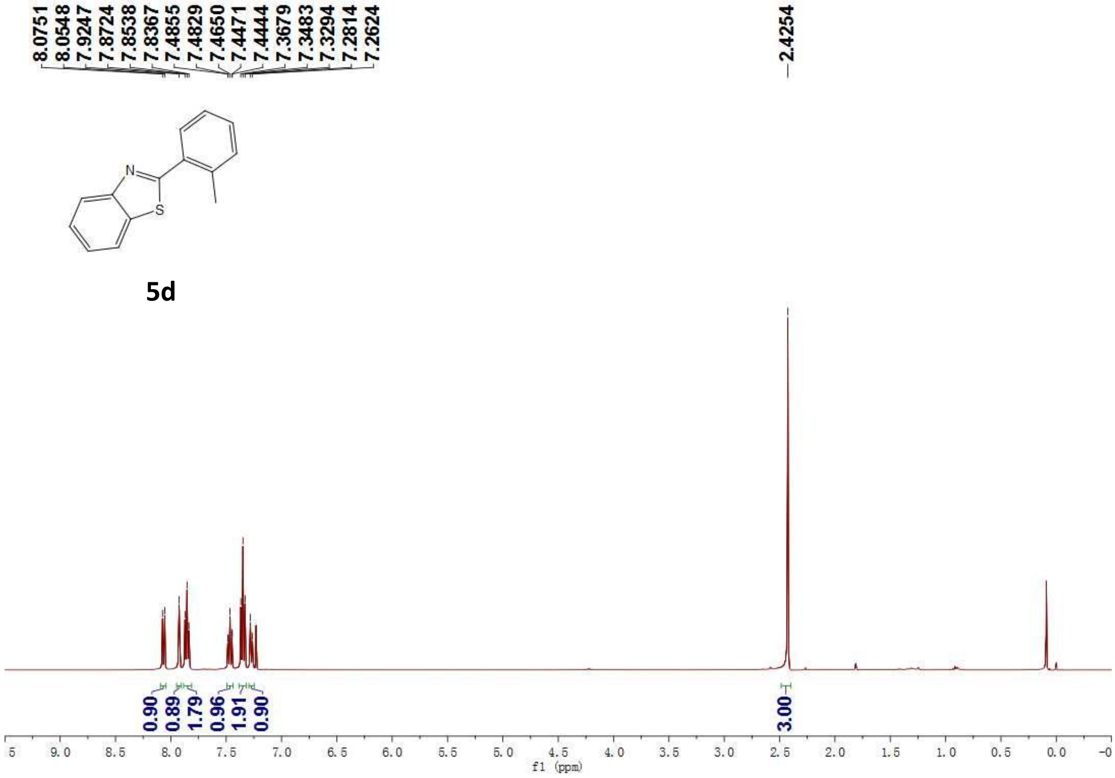
5b


167.1678
153.1345
140.3524
133.9071
129.9191
128.6592
126.4315
125.1796
123.9383
122.0020
120.5117
20.4651
N
S
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(
f1 (ppm)

5b


8.1061
8.0857
7.9048
7.8859
7.8849
7.7559
7.7541
7.7374
7.7350
7.5055
7.5025
7.4873
7.4847
7.4826
7.4671
7.4641
7.3975
7.3946
7.3771
7.3750
7.3692
7.3594
7.3562
7.3532
7.3503
7.3364
7.3328
7.3227
7.3051
7.2864
7.2823
7.2687
7.2646
2.6527
0.0930
N
S
5c
0.96
0.94
0.96
1.07
4.18
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


166.9034
152.7725
136.1991
134.5436
132.0386
130.4800
129.4803
128.9216
125.0498
125.0351
124.0116
122.3299
120.2865
20.3016
N
S
5c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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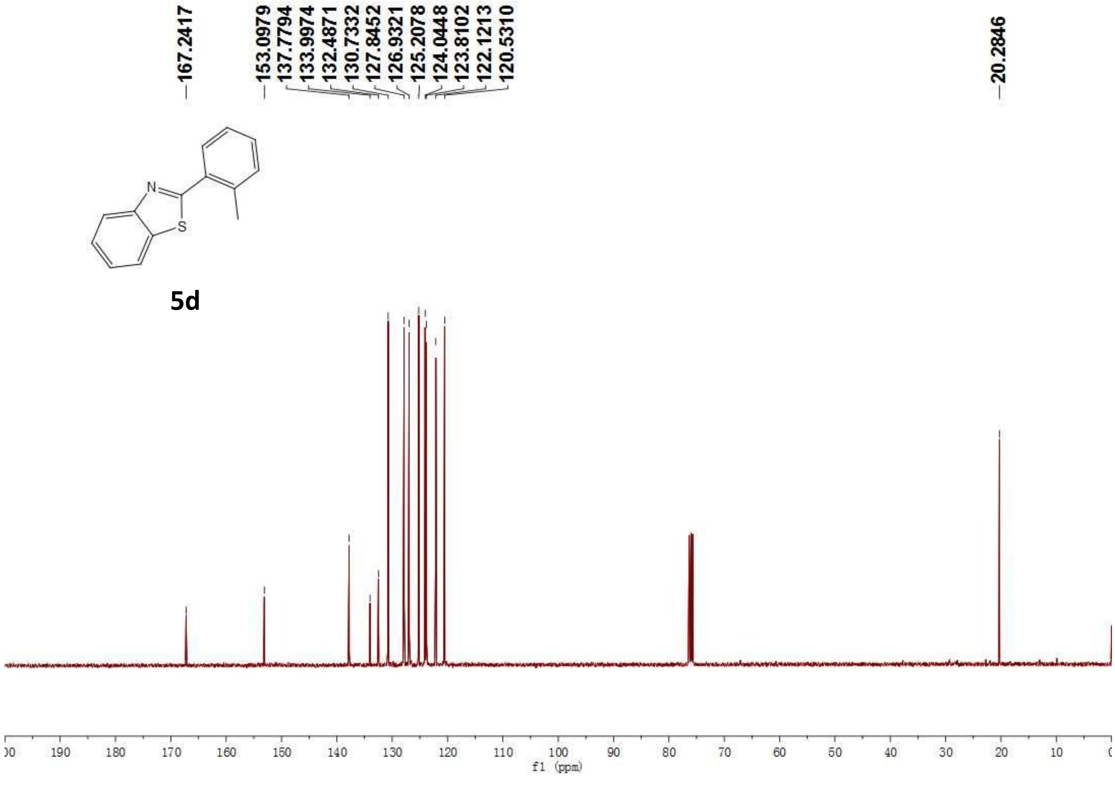
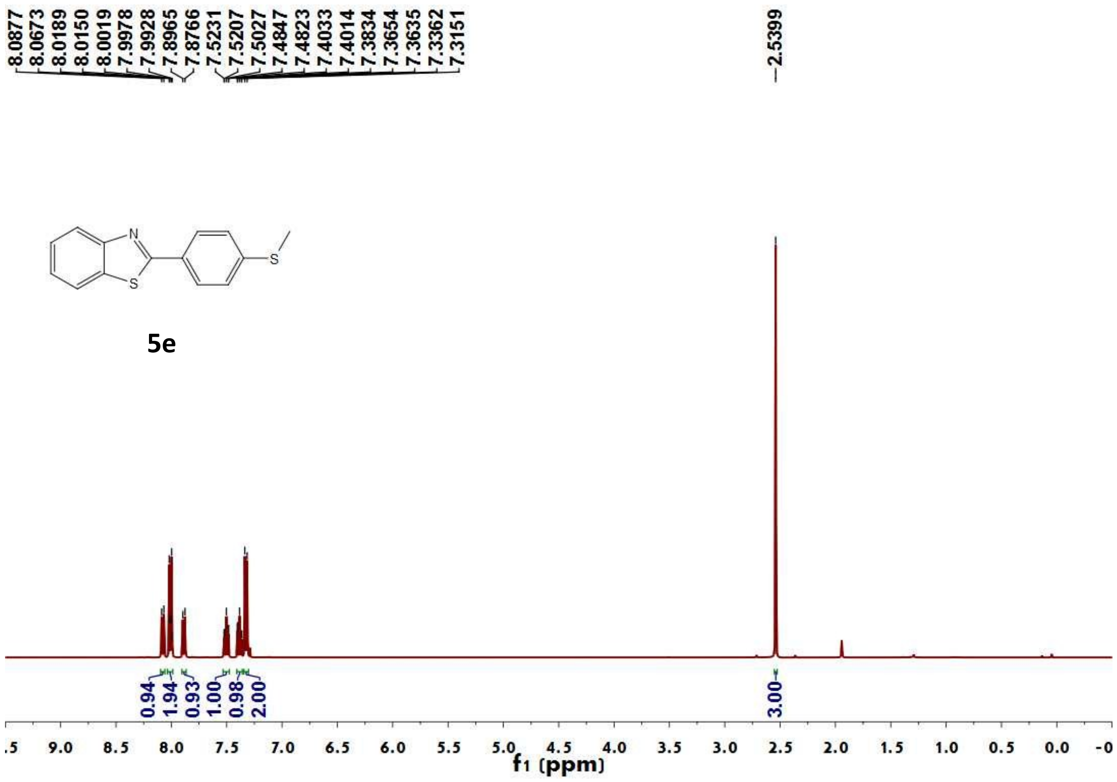
7.9247
7.8724
7.8538
7.8367
7.4855
7.4829
7.4650
7.4471
7.4444
7.3679
7.3483
7.3294
7.2814
7.2624
2.4254
N
S
0.90
0.89
1.79
0.96
1.91
0.90
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

5d


167.2417
153.0979
137.7794
133.9974
132.4871
130.7332
127.8452
126.9321
125.2078
124.0448
123.8102
122.1213
120.5310
20.2846
N
S
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

5d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8.0150
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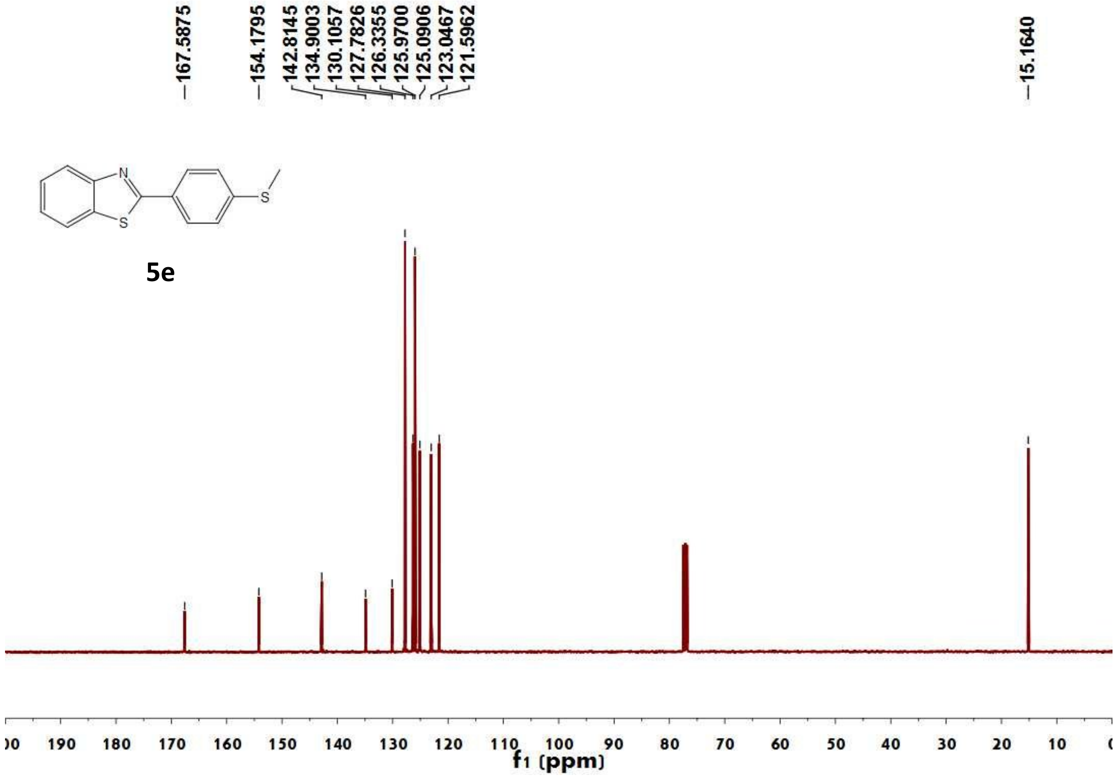
7.9928
7.8965
7.8766
7.5231
7.5207
7.5027
7.4847
7.4823
7.4033
7.4014
7.3834
7.3654
7.3635
7.3362
7.3151
2.5399
N
S
S
5e
0.94
1.94
0.93
1.00
0.98
2.00
3.00
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)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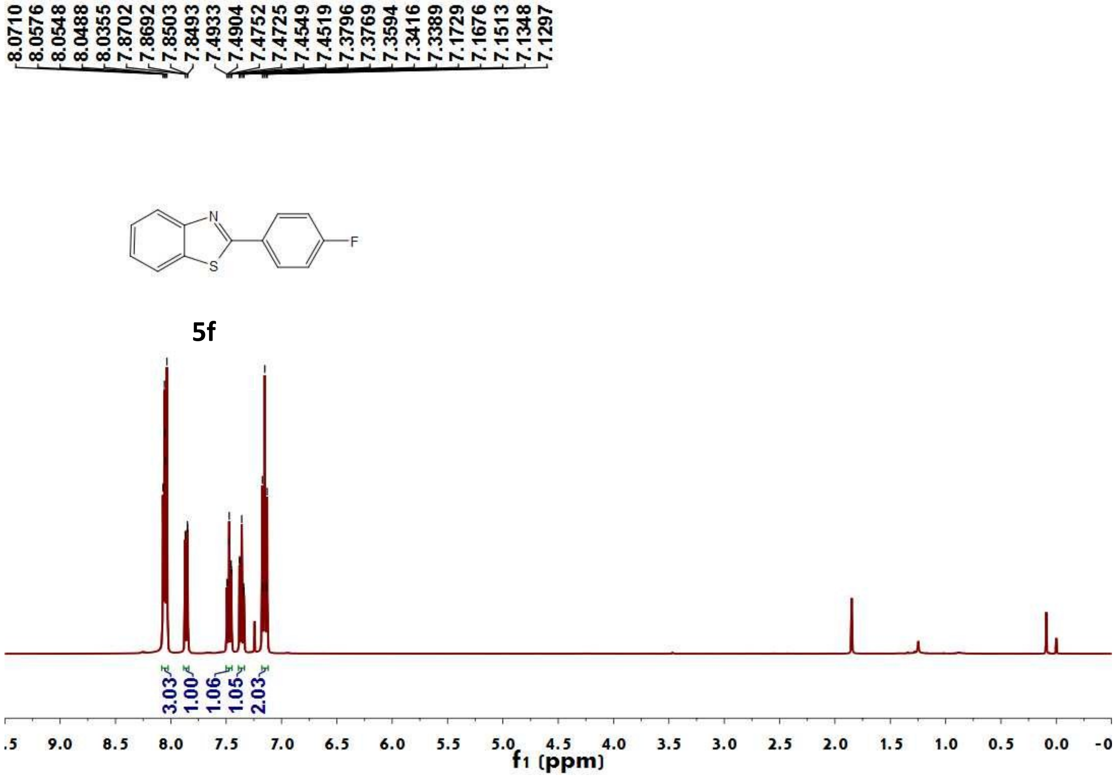
154.1795
142.8145
134.9003
130.1057
127.7826
126.3355
125.9700
125.0906
123.0467
121.5962
15.1640
N
S
S
5e
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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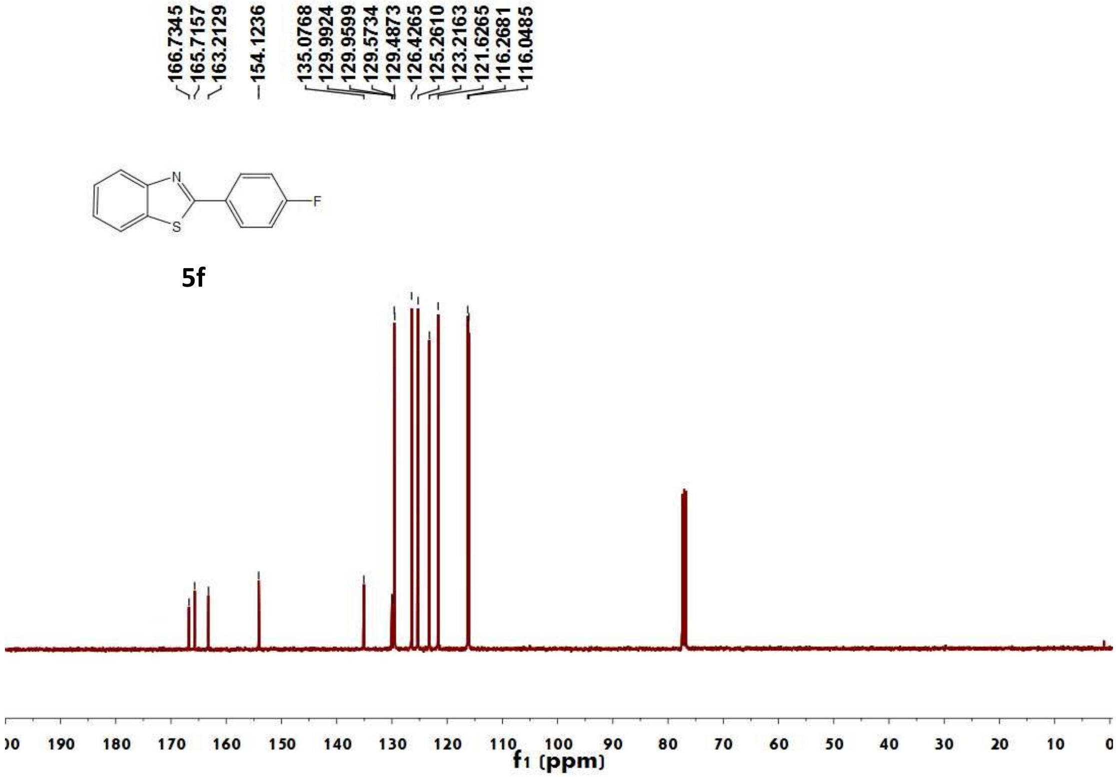
8.0576
8.0548
8.0488
8.0355
7.8702
7.8692
7.8503
7.8493
7.4933
7.4904
7.4752
7.4725
7.4549
7.4519
7.3796
7.3769
7.3594
7.3416
7.3389
7.1729
7.1676
7.1513
7.1348
7.1297
N
S
F
5f
3.03
1.00
1.06
1.05
2.03
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)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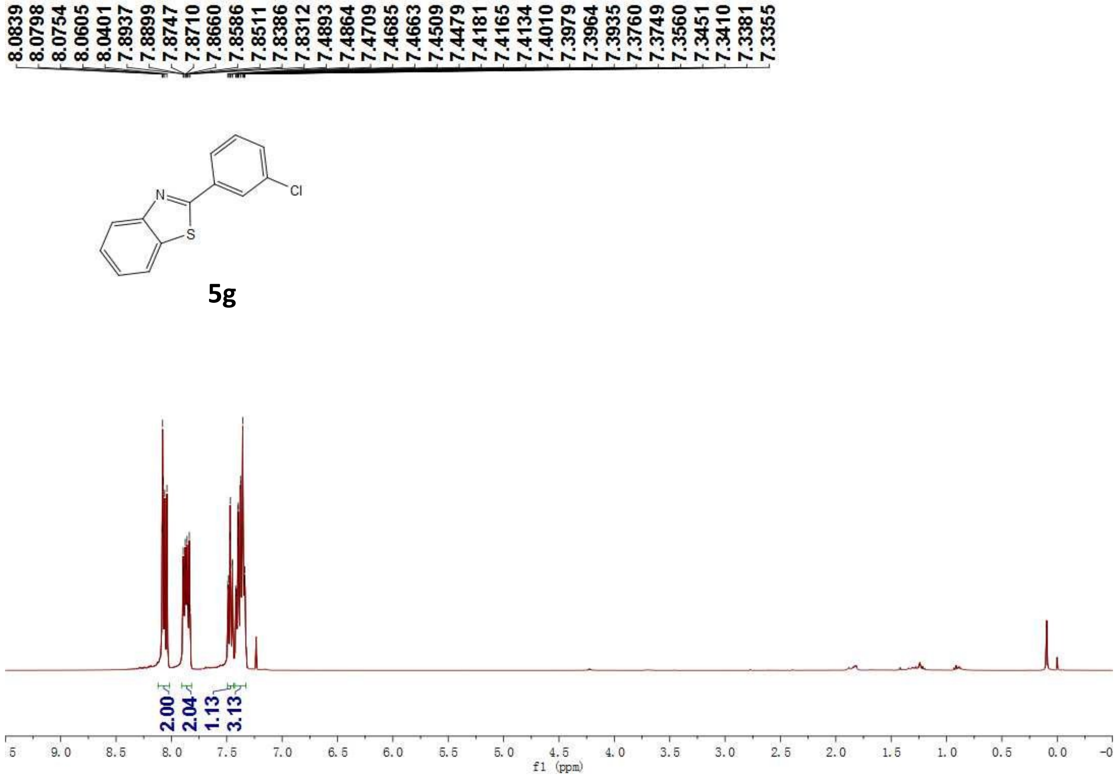
165.7157
163.2129
154.1236
135.0768
129.9924
129.9599
129.5734
129.4873
126.4265
125.2610
123.2163
121.6265
116.2681
116.0485
N
S
F
5f
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.0754
8.0605
8.0401
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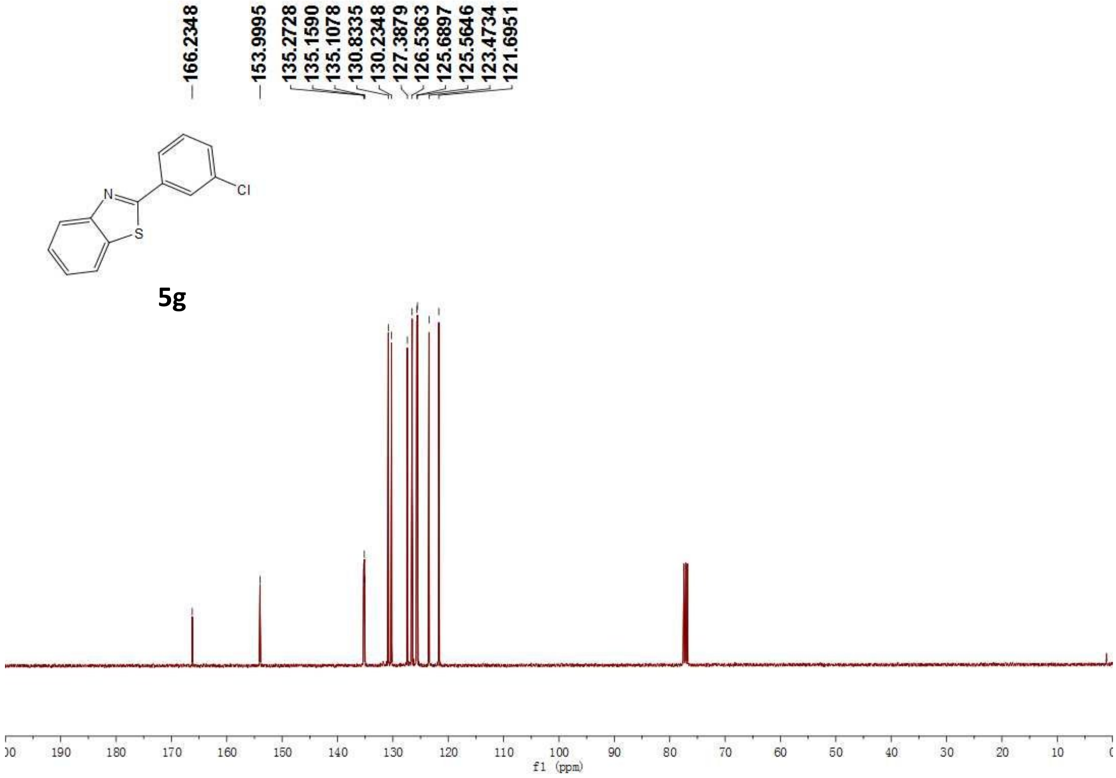
7.8899
7.8747
7.8710
7.8660
7.8586
7.8511
7.8386
7.8312
7.4893
7.4864
7.4709
7.4685
7.4663
7.4509
7.4479
7.4181
7.4165
7.4134
7.4010
7.3979
7.3964
7.3935
7.3760
7.3749
7.3560
7.3451
7.3410
7.3381
7.3355
N
S
Cl
2.00
2.04
1.13
3.13
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

5g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135.2728
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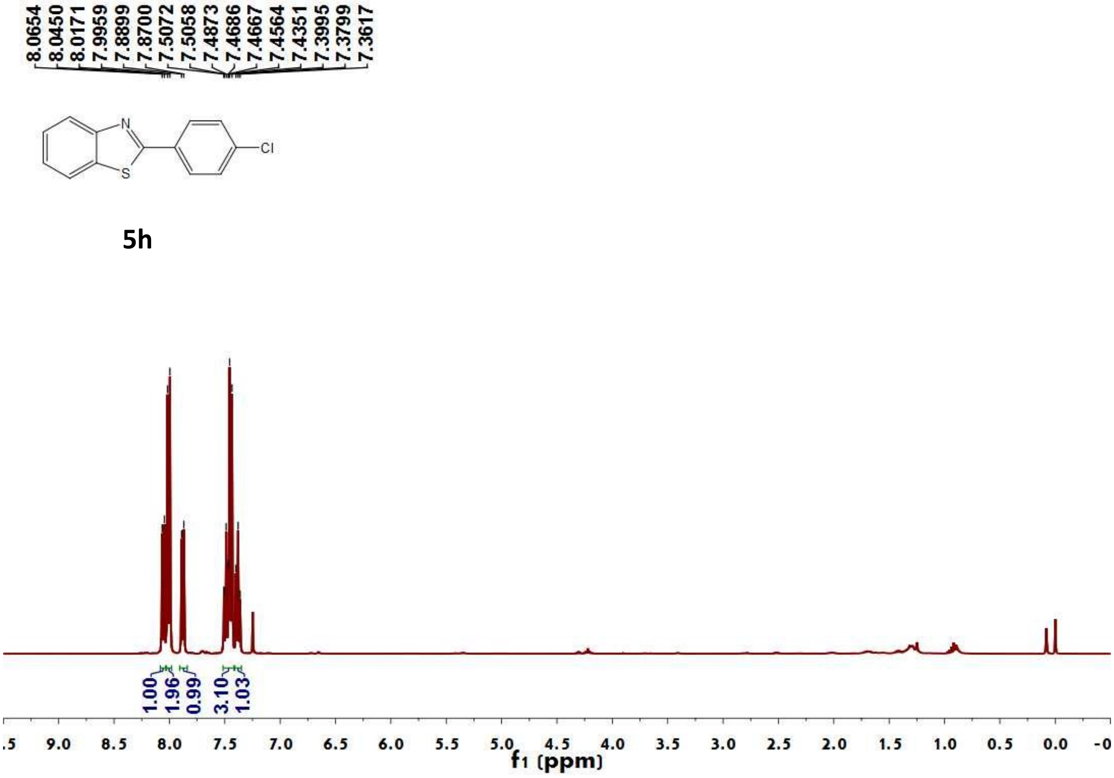
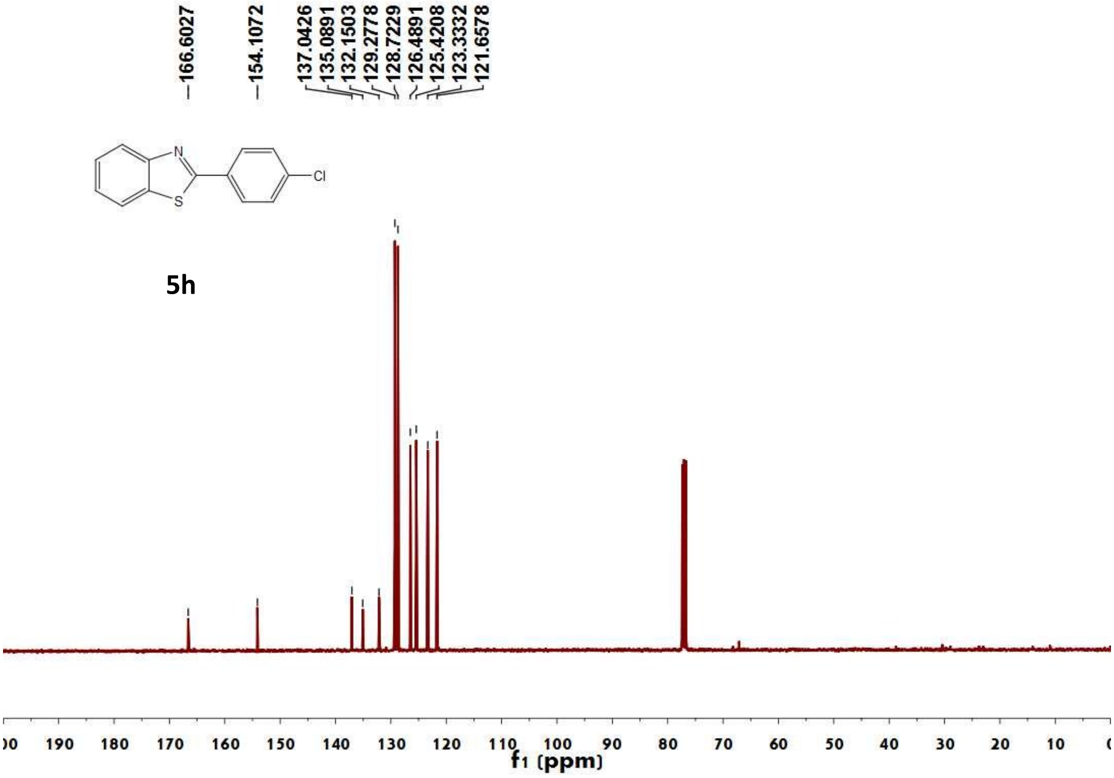
135.1078
130.8335
130.2348
127.3879
126.5363
125.6897
125.5646
123.4734
121.6951
N
S
Cl
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

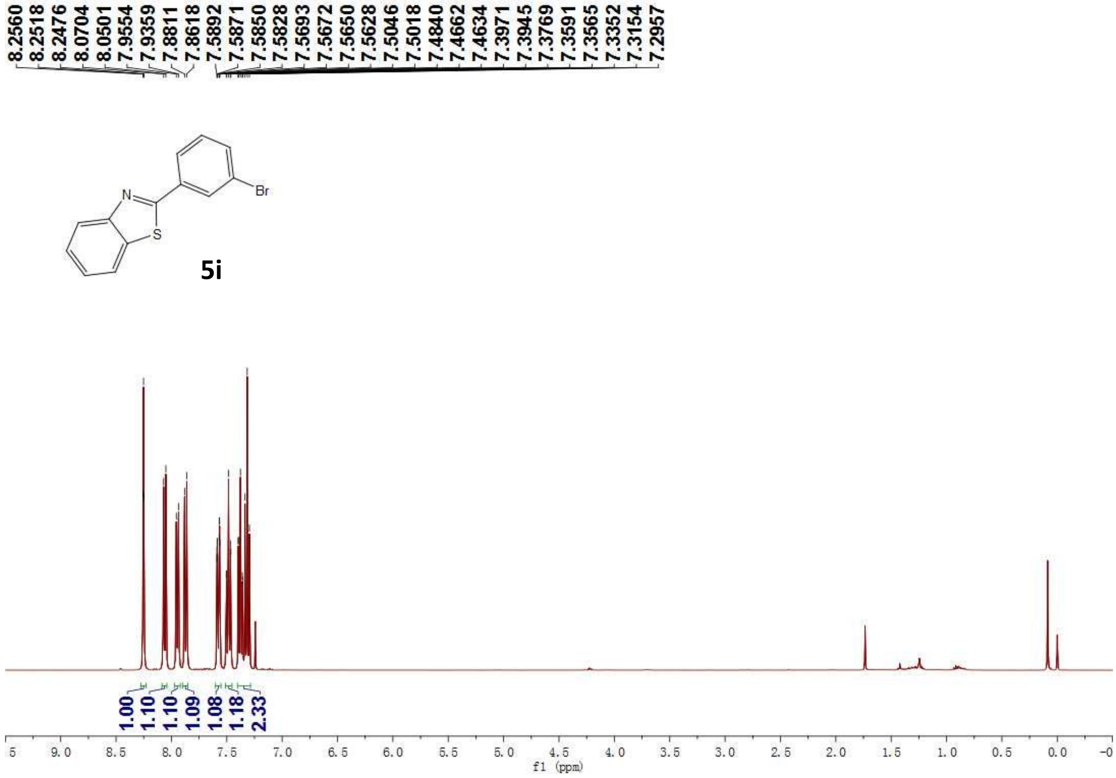
5g


8.0654
8.0450
8.0171
7.9959
7.8889
7.8700
7.5072
7.5058
7.4873
7.4686
7.4667
7.4564
7.4351
7.3995
7.3799
7.3617
N
S
Cl
1.00
1.96
0.99
3.10
1.03
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

5h


166.6027
154.1072
137.0426
135.0891
132.1503
129.2778
128.7229
126.4891
125.4208
123.3332
121.6578
N
S
Cl
)0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(
f1 (ppm)

5h



5i

8.2560
8.2518
8.2476
8.0704
8.0501
7.9554
7.9359
7.8811
7.8618
7.5892
7.5871
7.5850
7.5828
7.5693
7.5672
7.5650
7.5628
7.5046
7.5018
7.4840
7.4662
7.4634
7.3971
7.3945
7.3769
7.3591
7.3565
7.3352
7.3154
7.2957
N
S
Br
1.00
1.10
1.10
1.09
1.08
1.18
2.33
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.5
3.0
2.5
2.0
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1.0
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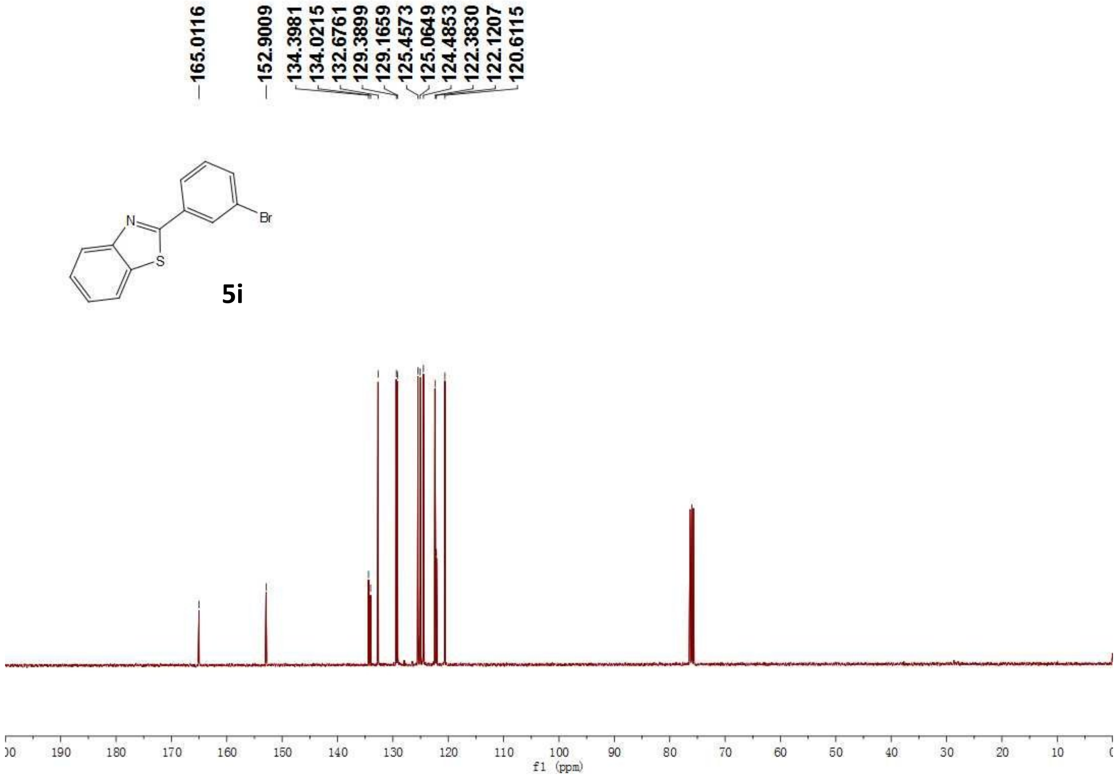
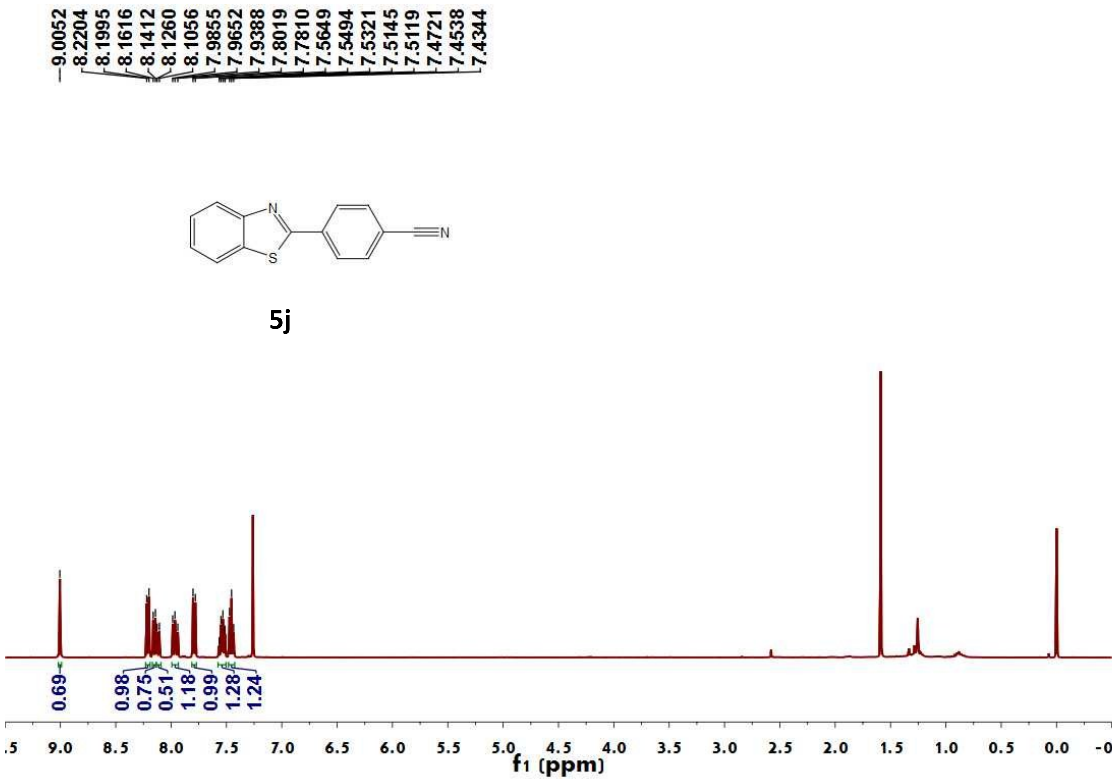
0.0
f1 (ppm)



5i

165.0116
152.9009
134.3981
134.0215
132.6761
129.3899
129.1659
125.4573
125.0649
124.4853
122.3830
122.1207
120.6115
N
S
Br
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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8.1995
8.1616
8.1412
8.1260
8.1056
7.9855
7.9652
7.9388
7.8019
7.7810
7.5649
7.5494
7.5321
7.5145
7.5119
7.4721
7.4538
7.4344
N
S
N
0.69
0.98
0.75
0.51
1.18
0.99
1.28
1.24
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
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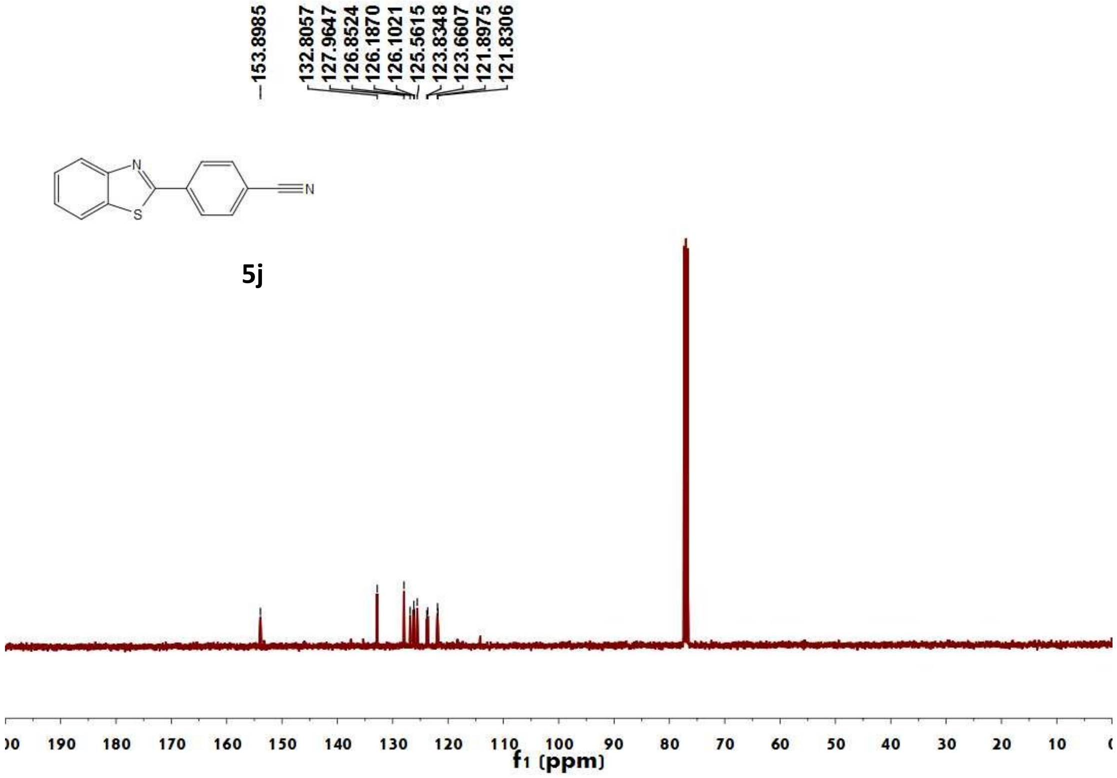
f1 (ppm)

5j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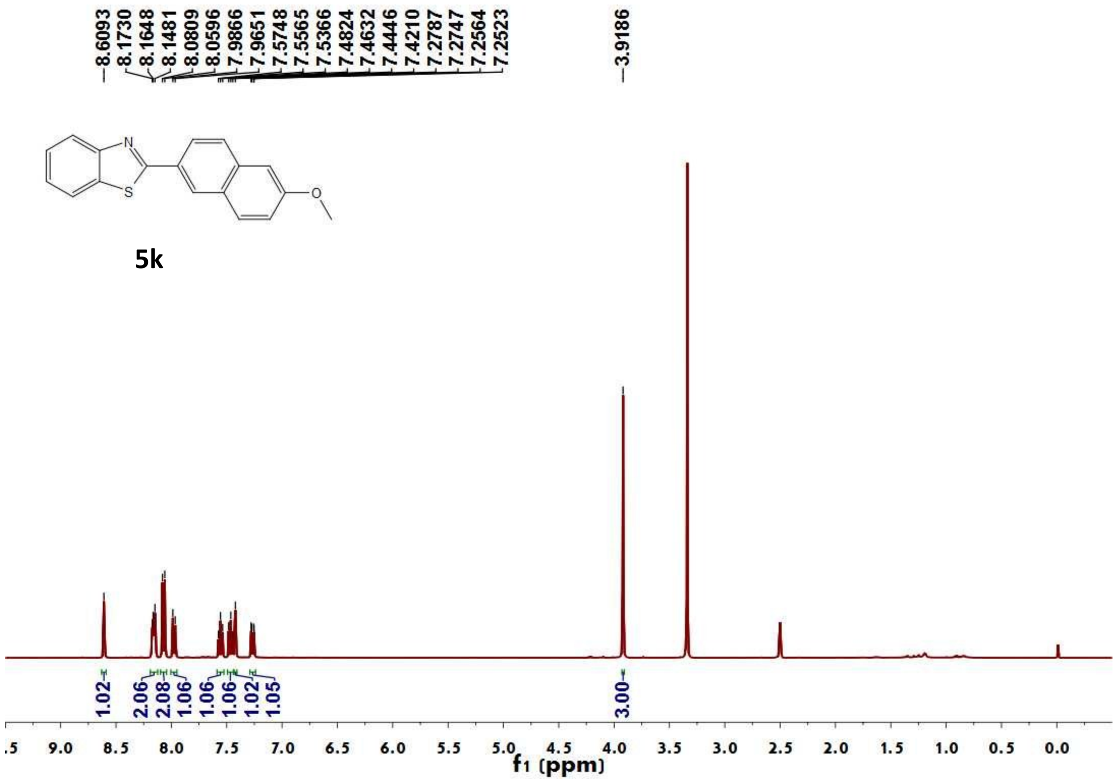
132.8057
127.9647
126.8524
126.1870
126.1021
125.5615
123.8348
123.6607
121.8975
121.8306
N
S
N
)0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(
f1 (ppm)

5j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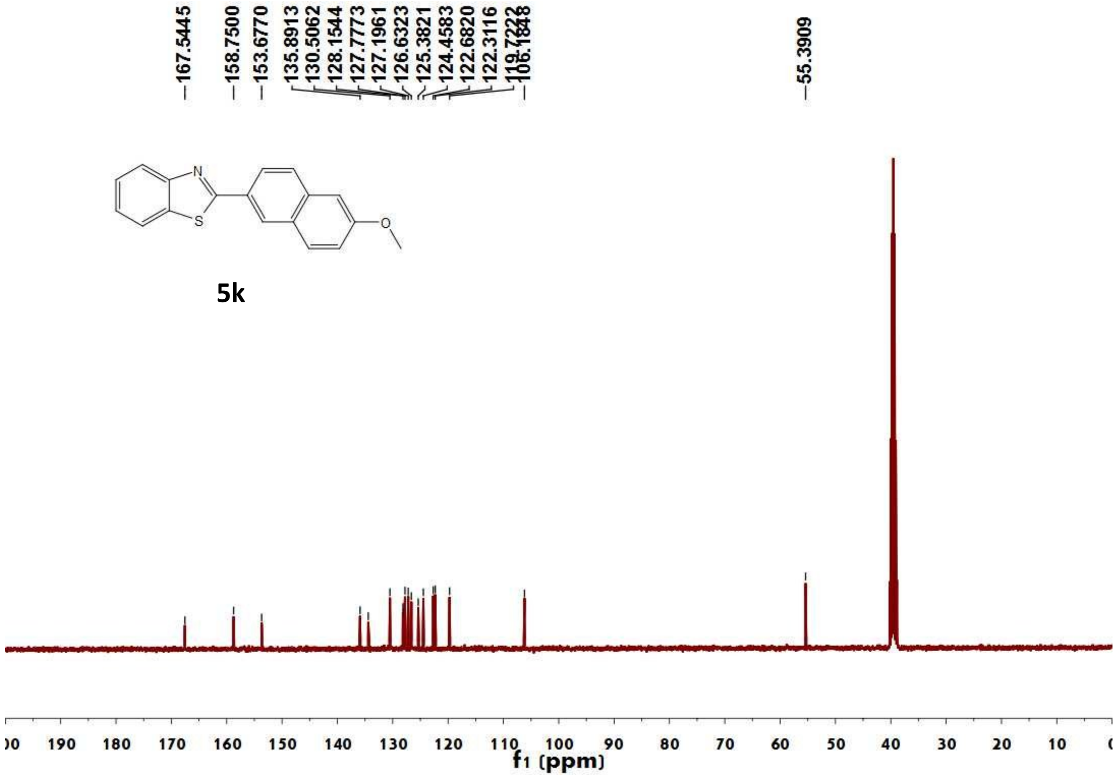
8.1730
8.1648
8.1481
8.0809
8.0596
7.9866
7.9651
7.5748
7.5565
7.5366
7.4824
7.4632
7.4446
7.4210
7.2787
7.2747
7.2564
7.2523
3.9186
N
S
O
1.02
2.06
2.08
1.06
1.06
1.06
1.02
1.05
3.00
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

5k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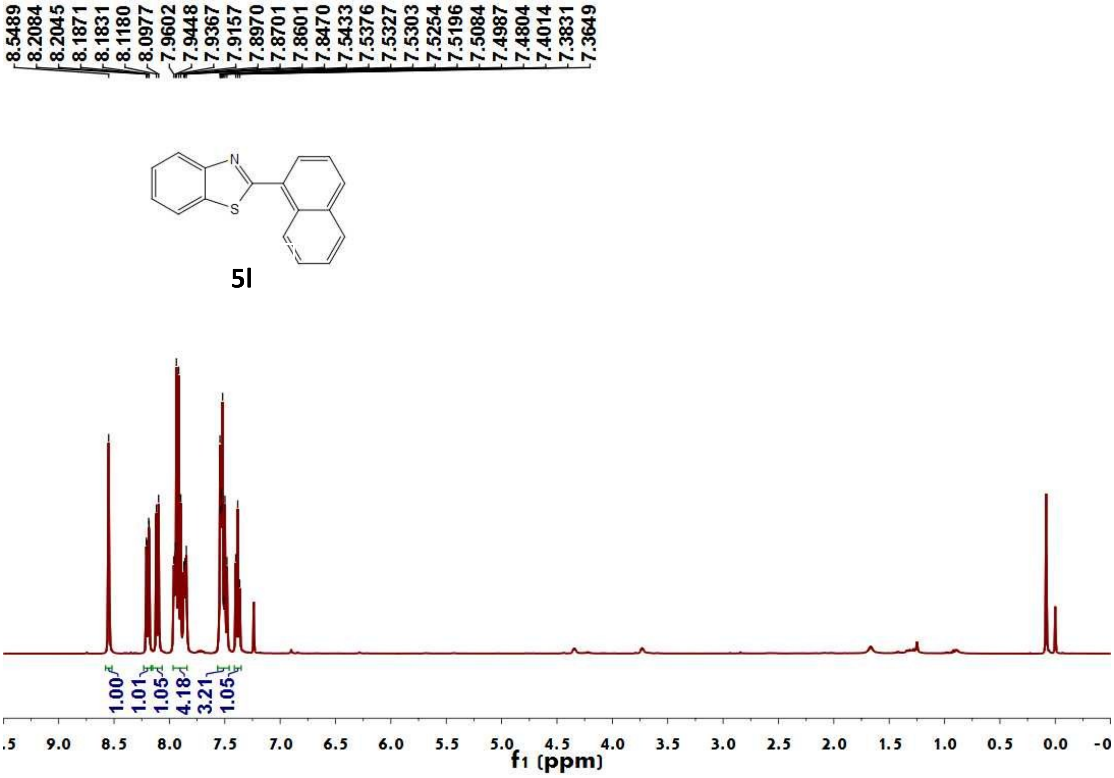
158.7500
153.6770
135.8913
130.5062
128.1544
127.7773
127.1961
126.6323
125.3821
124.4583
122.6820
122.3116
119.7222
106.1848
55.3909
N
S
O
)0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

5k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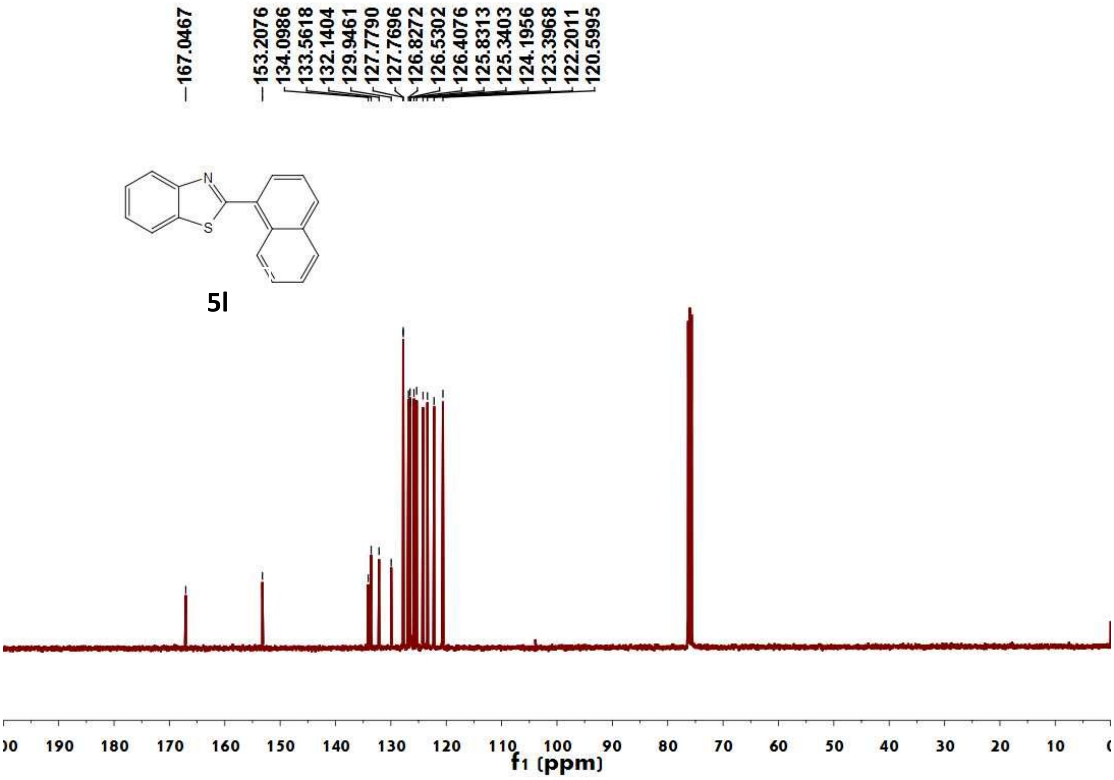
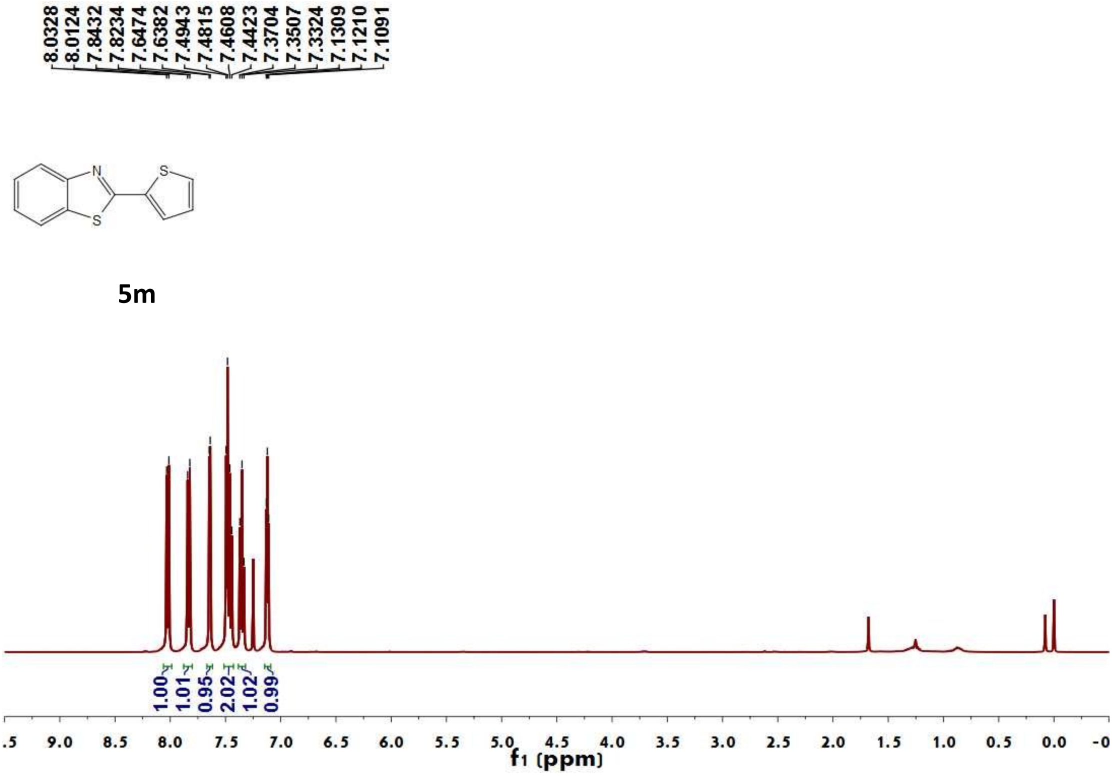
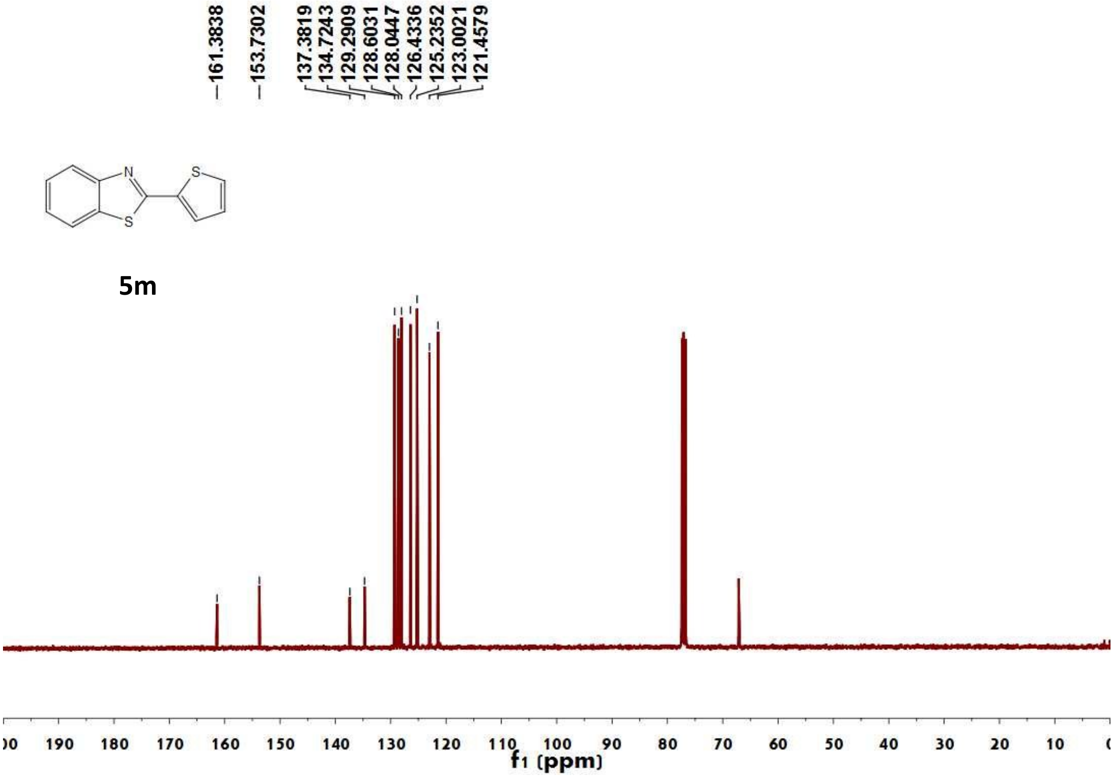
8.2084
8.2045
8.1871
8.1831
8.1180
8.0977
7.9602
7.9448
7.9367
7.9157
7.8970
7.8701
7.8601
7.8470
7.5433
7.5376
7.5327
7.5303
7.5254
7.5196
7.5084
7.4987
7.4804
7.4014
7.3831
7.3649
N
S
5l
1.00
1.01
1.05
4.18
3.21
1.05
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

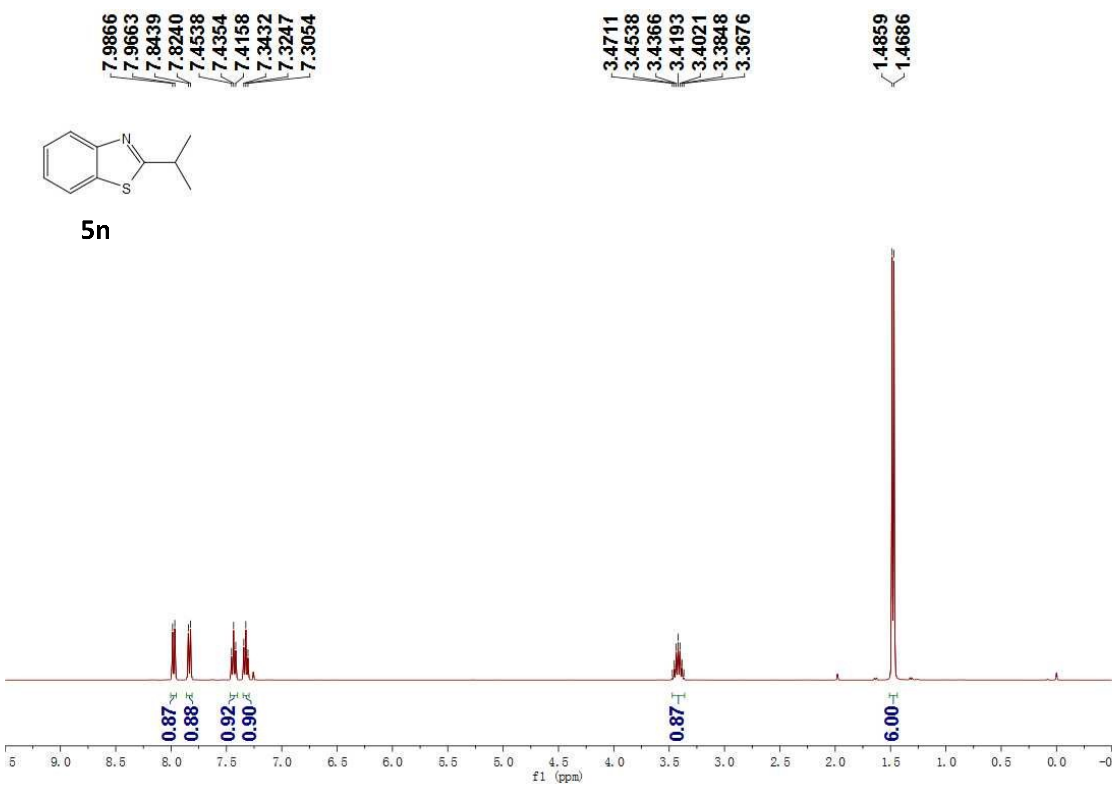

167.0467
153.2076
134.0986
133.5618
132.1404
129.9461
127.7790
127.7696
126.8272
126.5302
126.4076
125.8313
125.3403
124.1956
123.3968
122.2011
120.5995
N
S
5l
)0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(
f1 (ppm)


8.0328
8.0124
7.8432
7.8234
7.6474
7.6382
7.4943
7.4815
7.4608
7.4423
7.3704
7.3507
7.3324
7.1309
7.1210
7.1091
N
S
S
1.00
1.01
0.95
2.02
1.02
0.99
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

5m


161.3838
153.7302
137.3819
134.7243
129.2909
128.6031
128.0447
126.4336
125.2352
123.0021
121.4579
N
S
S
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

5m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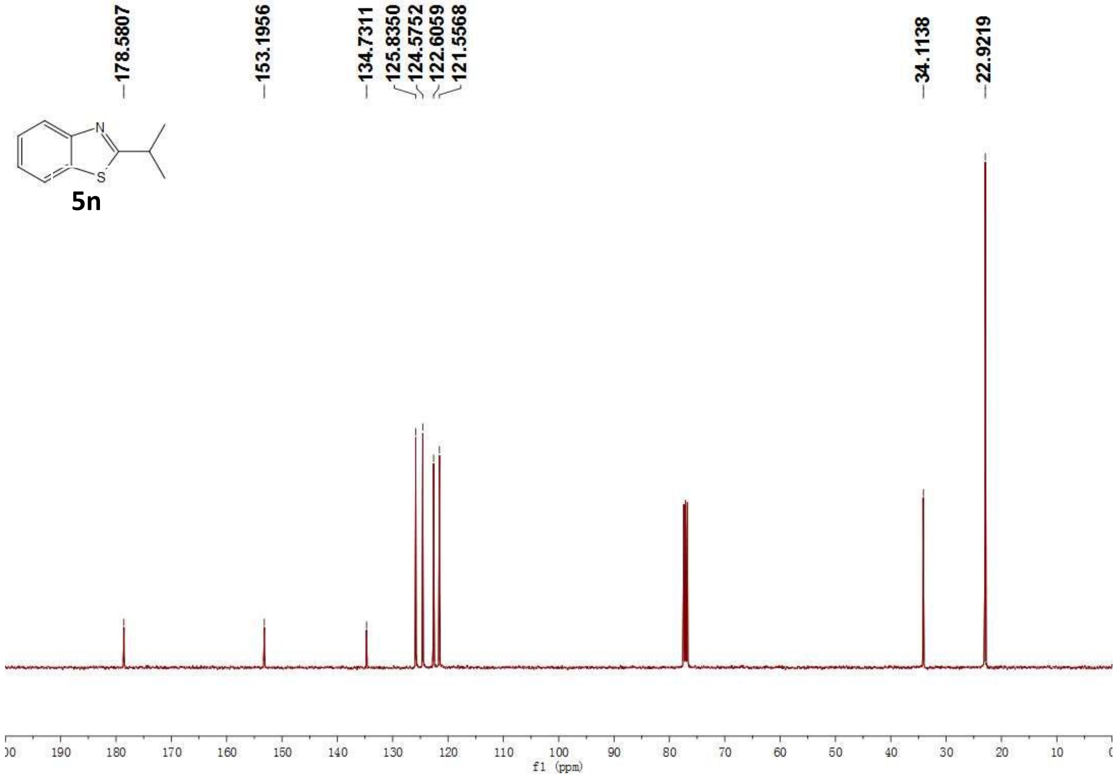
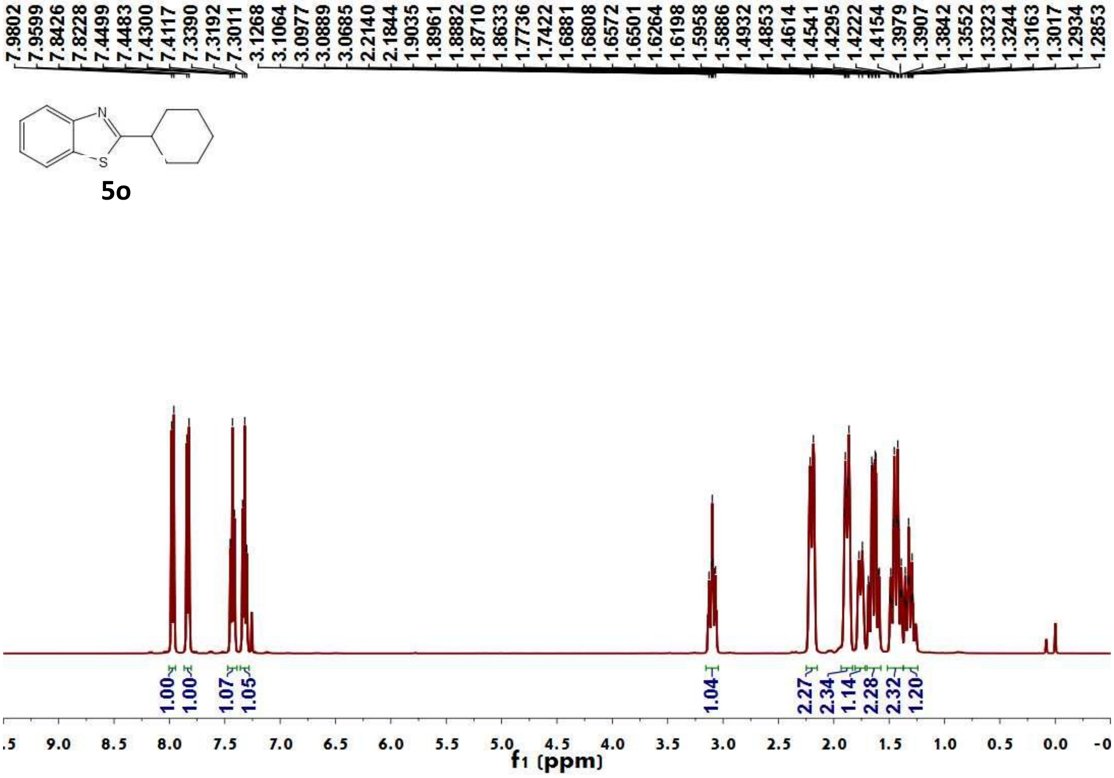
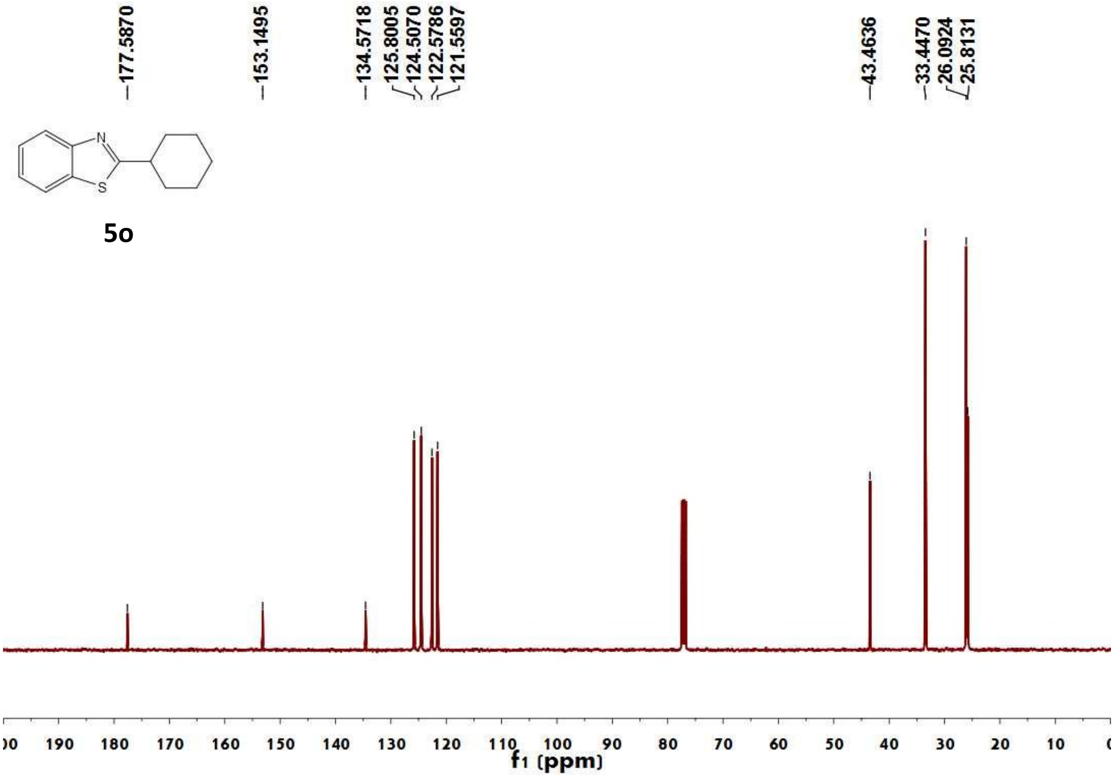
7.8439
7.8240
7.4538
7.4354
7.4158
7.3432
7.3247
7.3054
3.4711
3.4538
3.4366
3.4193
3.4021
3.3848
3.3676
1.4859
1.4686
N
S
5n
0.87
0.88
0.92
0.90
0.87
6.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


178.5807
153.1956
134.7311
125.8350
124.5752
122.6059
121.5568
34.1138
22.9219
N
S
5n
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



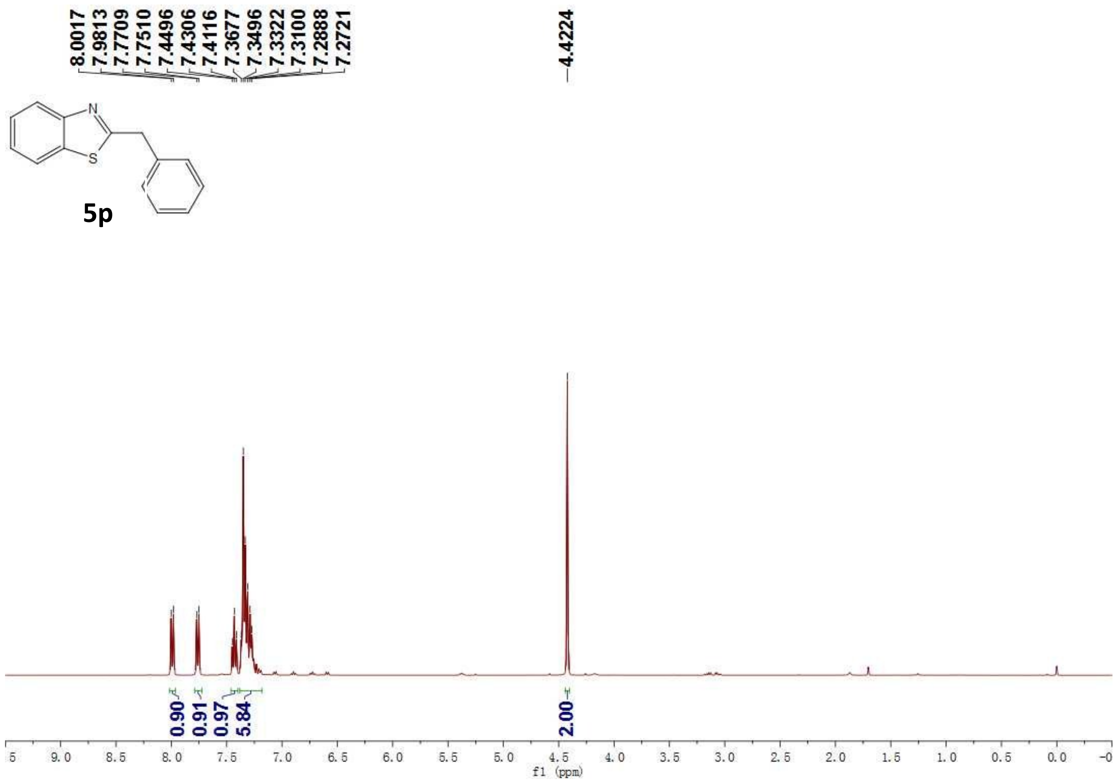
5o

7.9802
7.9599
7.8426
7.8228
7.4499
7.4483
7.4300
7.4117
7.3390
7.3192
7.3011
3.1268
3.1064
3.0977
3.0889
3.0685
2.2140
2.1844
1.9035
1.8961
1.8882
1.8710
1.8633
1.7736
1.7422
1.6881
1.6808
1.6572
1.6501
1.6264
1.6198
1.5958
1.5886
1.4932
1.4853
1.4614
1.4541
1.4295
1.4222
1.4154
1.3979
1.3907
1.3842
1.3552
1.3323
1.3244
1.3163
1.3017
1.2934
1.2853
N
S
1.00
1.00
1.07
1.05
1.04
2.27
2.34
1.14
2.28
2.32
1.20
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)



5o

177.5870
153.1495
134.5718
125.8005
124.5070
122.5786
121.5597
43.4636
33.4470
26.0924
25.8131
N
S
)0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.0017
7.9813
7.7709
7.7510
7.4496
7.4306
7.4116
7.3677
7.3496
7.3322
7.3100
7.2888
7.2721
4.4224
N
S
5p
0.90
0.91
0.97
5.84
2.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.5
3.0
2.5
2.0
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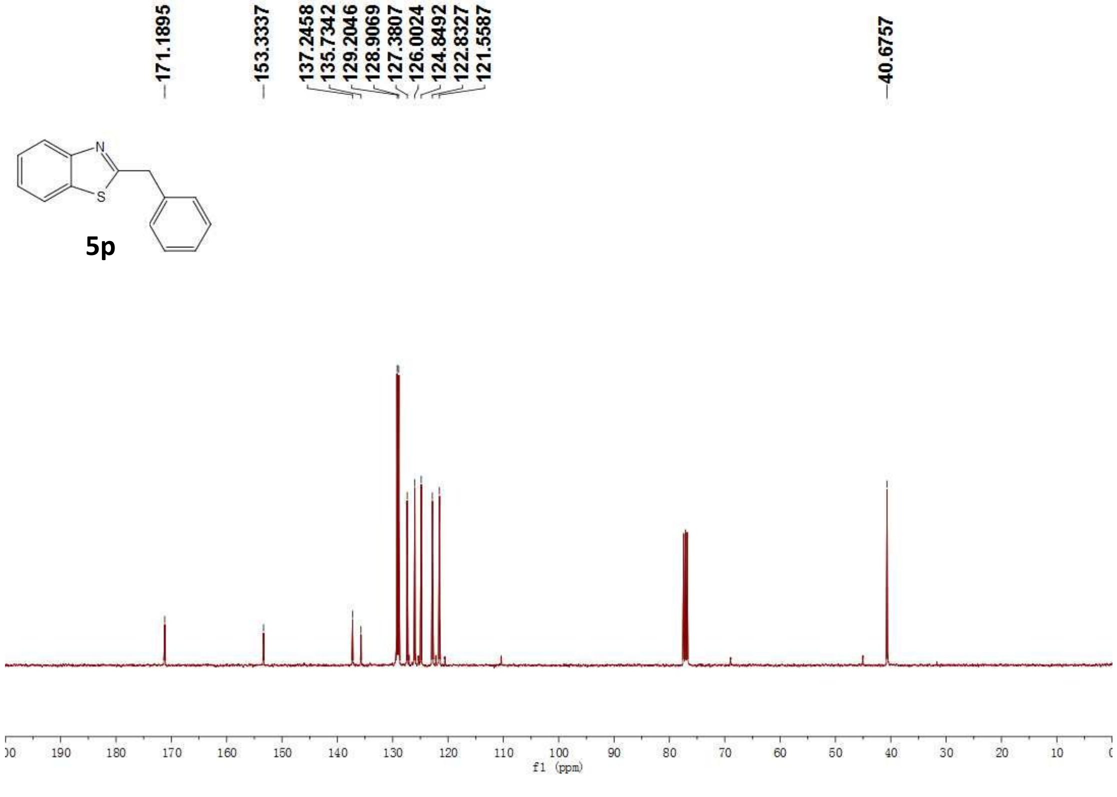
1.0
0.5
0.0
f1 (ppm)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137.2458
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128.9069
127.3807
126.0024
124.8492
122.8327
121.5587
40.6757
N
S
5p
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)