Brønsted acid promoted addition-cyclization and C-C bond cleavage for the convenient and efficient synthesis of 2-amino-5-aroylmethylthiazole derivatives

Supporting Information

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1. General experimental:

All substrates and reagents were purchased from commercial suppliers and used without further purification. TLC analysis was performed using pre-coated glass plates. Column chromatography was performed using silica gel (200–300 mesh). IR spectra were recorded on a Perkin-Elmer PE-983 infrared spectrometer as KBr pellets with absorption in cm^{-1}. ^1H spectra were recorded in $CDCl_3$ or CD_3COCD_3 on 400/600 MHz NMR spectrometers and resonances (δ) are given in ppm relative to tetramethylsilane. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz) and integration. ^{13}C spectra were recorded in $CDCl_3$ or DMSO on 100/150 MHz NMR spectrometers and resonances (*δ*) are given in ppm. HRMS were obtained on an Apex-Ultra MS equipped with ESI or APCI source. Melting points were determined without correction. The structures of **3ah** were confirmed by X-ray diffraction.

2. Additional optimization table entries - other solvents:

Entry	Catalyst (mmol)	Solvent	Temp (^oC)	Yield(%)
1	HCl(1.5)	MeOH	reflux	78
2	HCl(1.5)	^{i}PrOH	reflux	52
3	HCl(1.5)	^{t}BuOH	reflux	43

3. General experimental procedures for preparation of 3aa-3av, 3ba, 4aa from 1,4-enediones 1 and thioureas 2 (3aa as an example):

General procedure: A mixture of 2-benzoyl-1,4-diphenylbut-2-ene-1,4-dione **1a** (340 mg, 1.0 mmol), thiourea **2a** (76 mg, 1.0 mmol) and 36% hydrochloric acid (130 μL, 1.5 mmol) in 5 mL of EtOH was stirred at reflux for 3 h. After the reaction completed, the mixture was neutralized with saturated aqueous $NaHCO_3$ and extracted with EtOAc (3 × 30 mL), the combined organic extracts were then washed with brine. After drying over Na_2SO_4 and concentrated under reduced pressure, the crude product

was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc = 3:1) to afford a yellow solid **3aa** (262.0 mg, 89%).

4. General experimental procedures for preparation of 5 from 3ad

General procedure: 2-(2-amino-4-(4-methoxyphenyl)thiazol-5-yl)-1-phenylethanone **3ad** (260.1mg, 0.8 mmol) was dissolved in 4 mL of trifluoroacetic acid. Triethylsilane (4 mL) was added and the mixture was stirred for 72 h at ambient temperature. Then the solution was evaporated and the mixture was neutralized with saturated aqueous $NaHCO_3$ and extracted with EtOAc (3 × 30 mL), the combined organic extracts were then washed with brine. After drying over Na_2SO_4 and concentrated under reduced pressure, the crude product was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc = 5:1) to afford a yellow solid **5** (95.6 mg, 37%).

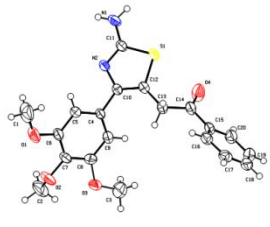
5. General experimental procedures for preparation of 6a-6c from 3

General procedure: A mixture of 2-(2-amino-4-phenylthiazol-5-yl)- 1-phenylethanone **3aa** (29.5 mg, 0.1mmol), o-phenylenediamine (10.8 mg, 0.1 mmol), iodine (27.9.mg, 0.11 mmol), and CuO (8.8 mg, 0.11 mmol) in methanol (2 mL) was heated at reflux for 0.5 h. Then the solvent was removed under reduce pressure, and added 20 mL water to the residue, extracted with EtOAc three times(3× 50 mL). The extract was washed with 10% $Na_2S_2O_3$, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure, the crude product was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc = 2:1) to afford a yellow solid **6a** (35.4 mg, 93%).

6. General experimental procedures for preparation of 7a-7b from 3(6a as an example):

General procedure: A mixture of 2-(2-amino-4-phenylthiazol-5-yl)- 1-phenylethan-one **3aa** (29.5 mg, 0.1mmol), thiourea (7.6 mg, 0.1 mmol), iodine (27.9.mg, 0.11 mmol), and CuO (8.8 mg, 0.11 mmol) in methanol (2 mL) was heated at reflux for 0.5 h. Then the solvent was removed under reduce pressure, and added 20 mL water to the residue, extracted with EtOAc three times(3× 50 mL). The extract was washed with 10% $Na_2S_2O_3$, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure, the crude product was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc = 3:1) to afford a yellow solid **7a** (32.9 mg, 94%).

7. Crystallographic data and molecular structure of compound 3ah



Crystal Data for Compound **3ah**: $C_{20}H_{20}N_2O_4$, MW = 384.45, triclinic, a = 12.7896(14) Å, b = 13.3917(15) Å, c = 13.4480(15) Å, α = 68.542(2)°, β = 63.471(1)°, γ = 76.053(2)°, V = 1909.6(4) $Å^3$, T = 296(2) K, space group P-1, Z=4, m(Mo–Ka) = 0.198 mm^{-1}, 17504 reflections measured, 9161 unique, which were used in all calculations. The final wR2 (F2) was 0.1323. CCDC 1013833 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

8. Spectroscopic Data：

8.3.1 *2-(2-amino-4-phenylthiazol-5-yl)-1-phenylethanone (**3aa**)*. Yield 89%; yellow solid; m.p. 178-179℃; IR (KBr): 3400, 3284, 3092, 1674, 1634, 1597, 1530, 1445, 1335, 1280, 1175 cm^{-1}; ^1H NMR (600 MHz, CDCl3): δ (ppm) 7.91 (d, *J*=8.4 Hz, 2H), 7.58 (t, *J*=7.8 Hz, 1H), 7.49 (d, *J*=7.8 Hz, 2H), 7.44 (t, *J*=7.8 Hz, 2H), 7.40 (t, *J*=7.8 Hz, 2H), 7.34 (t, *J*=7.8 Hz, 1H), 5.11 (s, 2H), 4.42(t, 2H); ^{13}C NMR (100 MHz, CDCl3): δ (ppm) 196.2, 166.8, 146.8, 135.6, 133.7, 128.7, 128.6, 128.4, 128.3, 128.2, 113.5, 36.8; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{17}H_{15}N_2OS$: 295.0900; found: 295.0897.

8.3.2 *2-(2-amino-4-(p-tolyl)thiazol-5-yl)-1-phenylethanone (**3ab**)*. Yield 92%; yellow solid; m.p. 169-171℃; IR (KBr): 3417, 3275, 3110, 2916, 1667, 1626, 1537, 1280 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.91 (d, *J*=7.8 Hz, 2H), 7.57 (t, *J*=7.2Hz, 1H), 7.44 (t, *J*=7.8 Hz, 2H), 7.37 (d, *J* =7.8 Hz, 2H), 7.20 (d, *J*=7.8 Hz, 2H), 5.12 (s, 2H), 4.41 (s, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 196.5, 166.2, 148.8, 137.5, 135.8, 133.4, 132.0, 129.1, 128.7, 128.4, 128.3, 113.3, 37.0, 21.2; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{18}H_{17}N_2OS$: 309.1056; found: 309.1053.

8.3.3 *2-(4-([1,1'-biphenyl]-4-yl)-2-aminothiazol-5-yl)-1-phenylethanone (**3ac**)*. Yield 84%; yellow solid; m.p. 182-183℃; IR (KBr): 3434, 3267, 3066, 1694, 1626, 1530, 1329, 1211, 1181, 1121, 849, 690 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.95 (d, *J*=7.8 Hz, 2H), 7.64-7.62 (m, 4H), 7.60-7.56 (m, 3H), 7.47-7.44 (m, 4H), 7.36 (t, *J*=7.2 Hz, 1H), 5.10 (s, 2H), 4.48 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 196.4, 166.1, 148.4, 140.53, 140.47, 135.8, 133.8, 133.6, 128.9, 128.8, 128.7, 128.4, 127.4, 127.2, 127.0, 114.1, 37.0; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{23}H_{19}N_2OS$: 371.1213; found: 371.1207.

8.3.4 *2-(2-amino-4-(4-methoxyphenyl)thiazol-5-yl)-1-phenylethanone (**3ad**)*. Yield 95%; yellow solid; m.p. 160-161℃; IR (KBr): 3399, 3269, 3099, 1664, 1621, 1534, 1502, 1448, 1284, 1248, 1171 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.91 (d, *J*=7.8 Hz, 2H), 7.58 (t, *J*=7.2 Hz, 1H), 7.46-7.42 (m, 4H), 6.93 (d, *J*=8.4 Hz, 2H), 5.07 (s, 2H), 4.40 (s, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 196.5, 166.1, 159.1, 148.4, 135.7, 133.5, 129.7, 128.7, 128.3, 127.3, 113.8, 112.7, 55.2, 37.0; HRMS (APCI): *m/z* $[M + H]^+$ calcd for $C_{18}H_{17}N_2O_2S$: 325.1005; found: 325.0999.

8.3.5 *2-(2-amino-4-(3-methoxyphenyl)thiazol-5-yl)-1-phenylethanone (**3ae**). Yield 81%*; yellow solid; m.p. 200-201℃; IR (KBr): 3370, 3298, 3069, 2962, 1687, 1645, 1599, 1534, 1326, 787, 693 cm^{-1}; ^1H NMR (600 MHz, CD_3COCD_3): δ (ppm) 8.01 (d, *J*=7.8 Hz, 2H), 7.65 (t, *J*=7.8 Hz, 1H), 7.52 (t, *J*=7.8 Hz, 2H), 7.28 (t, *J*=7.8 Hz, 1H), 7.13-7.11 (m, 2H), 6.87 (d, *J*=7.8 Hz, 1H), 6.28-6.27 (m, 2H), 4.55 (s, 2H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 197.1, 166.3, 159.1, 147.3, 136.6, 135.9, 133.7, 129.4, 128.9, 128.3, 120.3, 113.3, 113.1, 112.3, 54.9, 36.9; HRMS (APCI): *m/z* $[M + H]^+$ calcd for $C_{18}H_{17}N_2O_2S$: 325.1005; found: 325.0999.

8.3.6 *2-(2-amino-4-(4-ethoxyphenyl)thiazol-5-yl)-1-phenylethanone* ***(3af)***. Yield 88%; yellow solid; m.p. 168-169℃; IR(KBr): 3401, 3271, 3098, 2976, 1663, 1627, 1530, 1503, 1339, 1309, 1288, 1246, 1173, 1121, 1051 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.91 (d, *J*=7.2 Hz, 2H), 7.58 (t, *J*=7.2 Hz, 1H), 7.45 (t, *J*=7.8 Hz, 2H), 7.41 (d, *J*=9.0 Hz, 2H), 6.91 (d, *J*=8.4 Hz, 2H), 5.02 (s, 2H), 4.40 (s, 2H), 4.07-4.04 (m, 2H), 1.43 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 196.5, 165.9, 158.6, 148.6, 135.8, 133.5, 129.7, 128.7, 128.4, 127.2,114.4, 112.9, 63.4, 37.0, 14.8; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{19}H_{19}N_2O_2S$: 339.1162; found: 339.1158.

8.3.7 *2-(2-amino-4-(3,4-dimethoxyphenyl)thiazol-5-yl)-1-phenylethanone* ***(3ag)***. Yield 91%; yellow solid; m.p. 166-168℃; IR (KBr): 3381, 3288, 3117, 3002, 2933, 2833, 1688, 1635, 1514, 1352, 1329, 1257, 1227 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.92 (d, *J*=6.6 Hz, 2H), 7.59 (t, *J*=7.8 Hz, 1H), 7.46 (t, *J*=7.2 Hz, 2H), 7.06 (s, 1H), 7.01 (d, *J*=7.8 Hz, 1H), 6.87 (d, *J*=7.8 Hz, 1H), 5.01 (s, 2H), 4.42 (s, 2H), 3.90 (s, 3H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 196.6, 165.9, 148.71, 148.66, 148.5, 135.8, 133.6, 128.7, 128.3, 127.5, 120.8, 111.6, 110.8, 55.8, 55.7, 37.0; HRMS (APCI): *m/z* $[M + H]^+$ calcd for $C_{19}H_{19}N_2O_3S$: 355.1111; found: 355.1105.

8.3.8 *2-(2-amino-4-(3,4,5-trimethoxyphenyl)thiazol-5-yl)-1-phenylethanone* ***(3ah)***. Yield 93% (357.5 mg); red solid; m.p. 179-181℃; IR (KBr): 3411, 3370, 3281, 2937, 1683, 1620, 1590, 1530, 1503, 1412, 1356, 1232, 1131, 1033, 994 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.94 (d, *J*=7.8 Hz, 2H), 7.60 (t, *J*=7.8 Hz, 1H), 7.47 (t, *J*=7.8 Hz, 2H), 6.70 (s, 2H), 5.13 (s, 2H), 4.42 (s, 2H), 3.86 (s, 3H), 3.76 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 196.6, 166.1, 153.0, 148.7, 137.5, 135.7, 133.6, 130.3, 128.7, 128.2, 113.4, 105.4, 60.8, 55.9, 36.9; HRMS (APCI): *m/z* $[M + H]^+$ calcd for $C_{20}H_{21}N_2O_4S$: 385.1217; found: 385.1213.

8.3.9 *2-(2-amino-4-(benzo[d][1,3]dioxol-5-yl)thiazol-5-yl)-1-phenylethanone* ***(3ai)***. Yield 82% (277.5 mg); yellow solid; m.p. 156-158℃; IR (KBr): 3420, 3094, 2895, 1689, 1643, 1535, 1484, 1328, 1236, 1039 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.93 (d, *J*=7.2 Hz, 2H), 7.59 (t, *J*=7.2 Hz, 1H), 7.46 (t, *J*=7.8 Hz, 2H), 7.00 (s, 1H), 6.94 (d, *J*=7.8 Hz, 1H), 6.82 (d, *J*=7.8 Hz, 1H), 5.98 (s, 2H), 4.99 (s, 2H), 4.40 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 196.4, 165.9, 165.8, 148.4, 147.6, 147.2, 135.7, 133.6, 128.7, 128.3, 122.2, 113.3, 109.1, 108.3, 101.1, 37.0; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{18}H_{15}N_2O_3S$: 339.0798; found: 339.0793.

8.3.10 *2-(2-amino-4-(4-chlorophenyl)thiazol-5-yl)-1-phenylethanone* ***(3aj)***. Yield 90%; yellow solid; m.p. 204-206℃; IR (KBr): 3431, 3282, 3008, 1689, 1632, 1533, 1329, 1213, 841 cm^{-1}; ^1H NMR (600 MHz, CD_3COCD_3): δ (ppm) 8.02 (d, *J*=7.8 Hz, 2H), 7.65 (t, *J*=7.2 Hz, 1H), 7.59 (d, *J*=8.4 Hz, 2H), 7.53 (t, *J*=7.8 Hz, 2H), 7.41 (d, *J*=8.4 Hz, 2H), 6.33-6.31 (m, 2H), 4.56 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 196.9, 166.5, 146.3, 135.84, 135.82, 134.1, 133.6, 131.8, 129.7, 128.8, 128.4, 112.8, 36.7; HRMS (APCI): *m/z* $[M + H]^+$ calcd for $C_{17}H_{14}ClN_2OS$: 329.0510; found: 329.0505.

8.3.11 *2-(2-amino-4-(3-chlorophenyl)thiazol-5-yl)-1-phenylethanone (**3ak**)*. Yield 86%; yellow solid; m.p. 119-120℃; IR (KBr): 3417, 3283, 3130, 1675, 1633, 1524, 1331,1216, 798, 690 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.92 (d, *J*=7.8 Hz, 2H), 7.60 (t, *J*=7.2 Hz, 1H), 7.52 (s, 1H), 7.47 (t, *J*=7.8 Hz, 2H), 7.36-7.31 (m, 3H), 5.08 (s, 2H), 4.41 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 196.2, 166.5, 147.1, 136.5 135.6, 134.3, 133.7, 129.7, 128.7, 128.6, 128.3, 127.9, 126.5, 114.7, 36.7; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{17}H_{14}ClN_2OS$: 329.0510; found: 329.0507.

8.3.12 *2-(2-amino-4-(2-chlorophenyl)thiazol-5-yl)-1-phenylethanone (**3al**)*. Yield 78%; yellow solid; m.p. 209-210℃; IR (KBr): 3430, 3281, 3087, 1688, 1632, 1533, 1330, 1212, 1071, 841, 804, 691 cm^{-1}; ^1H NMR (600 MHz, CD_3COCD_3): δ (ppm) 8.02 (d, *J*=7.8 Hz, 2H), 7.65 (t, *J*=7.2 Hz, 1H), 7.60-7.59 (m, 2H), 7.53 (t, *J*=7.8 Hz, 2H), 7.41-7.40 (m, 2H), 6.34-6.32 (m, 2H), 4.56 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 196.9, 166.5, 146.3, 135.8, 134.1, 133.7, 131.8, 129.7, 128.9, 128.4, 128.3, 112.8, 112.7, 36.7; HRMS (APCI): *m/z* $[M + H]^+$ calcd for $C_{17}H_{14}ClN_2OS$: 329.0510; found: 329.0505.

8.3.13 *2-(2-amino-4-(4-bromophenyl)thiazol-5-yl)-1-phenylethanone (**3am**)*. Yield 85%; yellow solid; m.p. 214-215℃; IR (KBr): 3429, 3277, 3082, 1690, 1631, 1532, 1328, 1212, 837 cm^{-1}; ^1H NMR (600 MHz, CD_3COCD_3): δ (ppm) 8.02 (d, *J*=7.2 Hz, 2H), 7.65 (t, *J*=7.2 Hz, 1H), 7.56-7.52 (m, 6H), 6.33-6.32 (m, 2H), 4.56 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 196.8, 166.5, 146.3, 135.8, 134.5, 133.7, 131.3, 130.0, 128.9, 128.3, 120.5, 112.8, 36.7; HRMS (APCI): *m/z* $[M + H]^+$ calcd for $C_{17}H_{14}BrN_2OS$: 373.0005; found: 373.0006.

8.3.14 *2-(2-amino-4-(3-bromophenyl)thiazol-5-yl)-1-phenylethanone (**3an**)*. Yield 83%; yellow solid; m.p. 141-142℃; IR (KBr): 3440, 3257, 3067, 2914, 2687, 1684, 1620, 1526, 1327, 1213, 687 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.92 (d, *J*=7.8 Hz, 2H), 7.68 (s, 1H), 7.60 (t, *J*=7.8 Hz, 1H), 7.48-7.46 (m, 3H), 7.39 (d, *J*=7.8 Hz, 1H), 7.27-7.24 (m, 1H), 5.21 (s, 2H), 4.40 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 196.2, 166.4, 147.0, 136.7, 135.6, 133.7, 131.5, 130.8, 130.0, 128.8, 128.3, 126.9, 122.5, 114.7, 36.7; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{17}H_{14}BrN_2OS$: 373.0005; found: 373.0000.

8.3.15 *2-(2-amino-4-(4-fluorophenyl)thiazol-5-yl)-1-phenylethanone (**3ao**)*. Yield 83%; yellow solid; m.p. 175-176℃; IR (KBr): 3433, 3280, 3083, 1688, 1632, 1534, 1502, 1332, 1215, 1071, 844 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.92 (d, *J*=7.8 Hz, 2H), 7.60 (t, *J*=7.8 Hz, 1H), 7.47-7.45 (m, 4H), 7.08 (t, *J*=9.0 Hz, 2H), 5.12 (s, 2H), 4.38 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 196.3, 166.1, 163.6, 161.1, 147.8, 135.7, 133.7, 130.9, 130.3, 130.2, 128.8, 128.3, 115.5, 115.3, 113.9, 36.8; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{17}H_{14}FN_2OS$: 313.0805; found: 313.0802.

8.3.16 *2-(2-amino-4-(2-fluorophenyl)thiazol-5-yl)-1-phenylethanone (**3ap**)*. Yield 87%; yellow solid; m.p. 132-134℃; IR (KBr): 3412, 3392, 3289, 3101, 1671, 1637, 1580,

1534, 1486, 1448, 1334, 1286, 1219, 1175, 762, 715; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.89 (d, *J*=7.8 Hz, 2H), 7.57 (t, *J*=7.2 Hz, 1H), 7.48 (t, *J*=7.8 Hz, 1H), 7.44 (t, *J*=7.8 Hz, 2H), 7.37-7.33 (m, 1H), 7.20 (t, *J*=7.8 Hz, 1H), 7.13 (t, *J*=9.6 Hz, 1H), 5.08 (s, 2H), 4.29 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 196.5, 167.1, 160.3, 157.9, 141.8, 135.9, 133.5, 131.6, 129.93, 129.86, 128.8, 128.1, 124.4, 123.1, 122.9, 116.1, 114.5, 36.7; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{17}H_{14}FN_2OS$: 313.0805; found: 313.0802.

8.3.17 *2-(2-amino-4-(naphthalen-1-yl)thiazol-5-yl)-1-phenylethanone* ***(3aq)***. Yield 90% (310.0 mg); yellow solid; m.p. 144-145℃; IR (KBr): 3439, 3282, 3129, 1677, 1628, 1526, 1278 ; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.88-7.85 (m, 3H), 7.71 (d, *J*=7.2 Hz, 2H), 7.49-7.42 (m, 5H), 7.28 (t, *J*=7.8 Hz, 2H), 5.17 (s, 2H), 4.18 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 196.4, 166.6, 147.5, 135.6, 133.7, 133.3, 132.2, 132.1, 128.7, 128.4, 128.2, 128.1, 127.7, 126.3, 126.0, 125.9, 125.1, 115.8, 36.9; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{21}H_{17}N_2OS$: 345.1056; found: 345.1052.

8.3.18 *2-(2-amino-4-(naphthalen-2-yl)thiazol-5-yl)-1-phenylethanone* ***(3ar)***. Yield 89%; yellow solid; m.p. 170-171℃; IR (KBr): 3439, 3264, 3094, 1678, 1623, 1531, 1311, 1274, 1174, 708 ; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.92-7.84 (m, 5H), 7.78 (d, *J*=7.8 Hz, 1H), 7.64 (d, *J*=8.4 Hz, 1H), 7.56 (t, *J*=7.2 Hz, 1H), 7.50-7.46 (m, 2H), 7.42 (t, *J*=7.8 Hz, 2H), 5.18 (s, 2H), 4.47 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 196.5, 166.4, 148.6, 135.8, 133.5, 133.2, 132.7, 132.3, 128.7, 128.3, 128.1, 127.6, 127.5, 127.4, 126.5, 126.2, 126.1, 114.2, 37.0; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{21}H_{17}N_2OS$: 345.1056; found: 345.1052.

8.3.19 *2-(2-amino-4-(thiophen-2-yl)thiazol-5-yl)-1-phenylethanone* ***(3as)***. Yield 77%; yellow solid; m.p. 185-186℃; IR (KBr): 3393, 3289, 3124, 1675, 1635, 1531, 1282, 691 ; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.00 (d, *J*=7.8 Hz, 2H), 7.61 (t, *J*=7.8 Hz, 1H), 7.49 (t, *J*=7.8 Hz, 2H), 7.31 (d, *J*=4.8 Hz, 1H), 7.22 (d, *J*=3.0 Hz, 1H), 7.05 (t, *J*=4.2 Hz,, 1H), 5.03 (s, 2H), 4.56 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 195.7, 165.9, 141.8, 137.53, 137.48, 135.8, 133.7, 128.8, 128.3, 127.4, 125.4, 113.3, 37.1; HRMS (APCI): *m/z* $[M + H]^+$ calcd for $C_{15}H_{13}N_2OS_2$: 301.0464; found: 301.0461.

8.3.20 *2-(2-amino-4-(benzofuran-2-yl)thiazol-5-yl)-1-phenylethanone* ***(3at)***. Yield 87%; yellow solid; m.p. 201-203℃; IR (KBr): 3406, 3278, 3135, 1687, 1627, 1532, 1449, 1337, 1254, 1214, 1187, 754 cm^{-1}; ^{1}H NMR (600 MHz, CD_3COCD_3): δ (ppm) 8.17 (d, *J*=7.2 Hz, 2H), 7.69 (t, *J*=7.8 Hz, 1H), 7.60-7.58 (m, 3H), 7.24-7.20 (m, 3H), 7.01 (s, 1H), 6.47-6.45 (m, 2H), 4.93 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 196.9, 166.7, 153.8, 152.8, 137.3, 136.4, 133.5, 128.9, 128.3, 128.1, 124.3, 123.2, 121.2, 115.9, 110.7, 103.3, 36.1; HRMS (APCI): *m/z* $[M + H]^+$ calcd for $C_{19}H_{15}N_2O_2S$: 335.0849; found: 335.0845.

8.3.21 *2-(2-amino-4-methylthiazol-5-yl)-1-phenylethanone* ***(3au)***. Yield 93%; yellow solid; m.p. 171-172℃; IR (KBr): 3445, 3260, 3064, 2728, 1690, 1623, 1592, 1526, 1330, 1215, 1109, 765 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.00 (d, *J*=7.8 Hz,

2H), 7.60 (t, *J*=7.2 Hz, 1H), 7.49 (t, *J*=7.8 Hz, 2H), 4.92 (s, 2H), 4.25 (s, 2H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 196.8, 166.2, 144.5, 136.0, 133.3, 128.7, 128.3, 109.4, 35.9, 14.8; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{12}H_{13}N_2O_2S$: 233.0743; found: 233.0743.

8.3.22 *2-(2-amino-4-phenylthiazol-5-yl)-1-(4-methoxyphenyl)ethanone (**3av**)*. Yield 82%; yellow solid; m.p. 188-189℃; IR (KBr): 3438, 3273, 3069, 1680, 1631, 1596, 1528, 1329, 1262, 1229, 1166 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.89 (d, *J*=8.4 Hz, 2H), 7.50 (d, *J*=7.8 Hz, 2H), 7.40 (t, *J*=7.8 Hz, 2H), 7.34 (t, *J*=7.2 Hz, 1H), 6.90 (d, *J*=9.0 Hz, 2H), 5.06 (s, 2H), 4.37 (s, 2H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 194.9, 166.0, 163.8, 148.5, 134.8, 130.7, 128.7, 128.53, 128.47, 127.8, 114.5, 113.8, 55.5, 36.6; HRMS (APCI): *m/z* $[M + H]^+$ calcd for $C_{18}H_{17}N_2O_2S$: 325.1005; found: 325.1005.

8.3.23 *1-phenyl-2-(4-phenyl-2-(phenylamino)thiazol-5-yl)ethanone (**3ba**)*. Yield 93%; yellow solid; m.p. 142-143℃; IR (KBr): 3442, 3154, 3057, 2928, 2848, 1687, 1560, 1216, 756, 690 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.92 (d, *J*=7.8 Hz, 2H), 7.59 (t, *J*=7.2 Hz, 1H), 7.55 (d, *J*=7.8 Hz, 2H), 7.45 (t, *J*=7.8 Hz, 2H), 7.41 (t, *J*=7.8 Hz, 2H), 7.36 (t, *J*=7.2 Hz, 1H), 7.31-7.26 (m, 5H), 7.04 (t, *J* =6.6 Hz, 1H), 4.48 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 196.4, 164.4, 148.4, 140.2, 135.7, 134.6, 133.6, 129.2, 128.7, 128.5, 128.3, 128.0, 122.8, 118.6, 112.3, 36.8; HRMS (APCI): *m/z* $[M + H]^+$ calcd for $C_{23}H_{19}N_2OS$: 371.1213; found: 371.1210.

8.3.24 *3-(2-amino-4-phenylthiazol-5-yl)-4-hydroxypent-3-en-2-one (**4aa**)*. Yield 52%; yellow solid; m.p. 177-178℃; IR (KBr): 3411, 3294, 3115, 1640, 1595, 1529, 1485, 1412, 1340, 927, 773, 741, 699 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 16.87 (s, 1H), 7.57 (d, *J*=7.6 Hz, 2H), 7.34 (t, *J*=7.2 Hz, 2H), 7.30-7.27 (m, 1H), 5.46 (s, 2H), 2.02 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 193.4, 166.6, 148.2, 134.6, 128.5, 127.8, 127.3, 115.9, 104.2, 24.0; HRMS (APCI): *m/z* $[M + H]^+$ calcd for $C_{14}H_{15}N_2O_2S$: 275.0849; found: 275.0844.

8.3.25 *4-(4-methoxyphenyl)-5-phenethylthiazol-2-amine (**5**)*. Yield 37%; yellow solid; m.p. 126-128℃; IR (KBr): 3409, 3083, 2929, 2839, 1610, 1532, 1503, 1331, 1246, 1175, 1023, 837, 700, 591cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.34 (d, *J*=8.4 Hz, 2H), 7.28 (t, *J*=9.0 Hz, 2H), 7.21 (t, *J*=7.2 Hz, 1H), 7.16 (d, *J*=7.2 Hz, 2H), 6.89 (d, *J*=8.4 Hz, 2H), 6.17 (s, 2H), 3.82 (s, 3H), 3.04 (t, *J*=7.8 Hz, 2H), 2.90 (t, *J*=7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 164.5, 158.9, 145.9, 140.6, 129.6, 128.42, 138.37, 127.6, 126.2, 121.5, 113.6, 55.2, 38.0, 28.9; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{18}H_{19}N_2OS$: 311.1213; found: 311.1212.

8.3.26 *4-phenyl-5-(3-phenylquinoxalin-2-yl)thiazol-2-amine (**6a**)*. Yield 93%; yellow solid; m.p. 127-128℃; IR (KBr): 3442, 3058, 2924, 1624, 1519, 1484, 1394, 1351, 766, 696cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.12-8.08 (m, 2H), 7.77-7.73 (m, 2H), 7.17 (t, *J*=7.2 Hz, 1H), 7.12-7.05 (m, 5H), 6.98 (t, *J*=7.8 Hz, 2H), 6.77 (d, *J*=6.9 Hz, 2H), 5.85 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 167.8, 154.4, 150.1,

146.9, 141.1, 140.8, 138.24, 138.16, 134.4, 130.0, 129.9, 129.2, 128.7, 128.2, 128.1, 127.93, 127.85, 127.8, 119.0; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{23}H_{17}N_4S$: 381.1168; found: 381.1165.

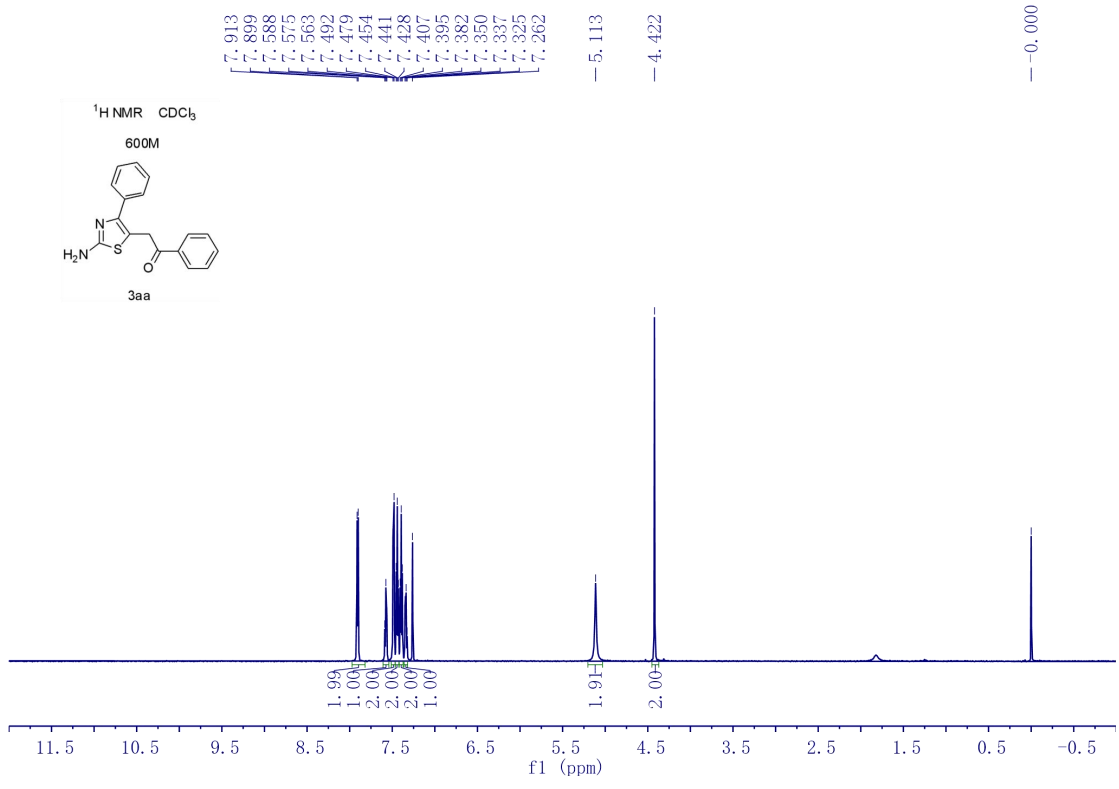
8.3.27 *5-(6,7-dimethyl-3-phenylquinoxalin-2-yl)-4-phenylthiazol-2-amine (**6b**)*. Yield 96%; yellow solid; m.p. 242-243℃; IR (KBr): 3458, 2922, 2852, 1620, 1535, 1483, 1352, 1020, 696cm^{-1}; ^{1}H NMR (600 MHz, DMSO-d_6): δ (ppm) 7.81 (d, J=8.4 Hz, 2H), 7.39 (s, 2H), 7.19 (t, J=7.2 Hz, 1H), 7.12-7.09 (m, 3H), 7.04 (d, J=7.2 Hz, 2H), 6.98 (t, J=7.8 Hz, 2H), 6.71 (d, J=8.4 Hz, 2H), 2.46 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6): δ (ppm) 168.0, 152.9, 149.0, 146.1, 140.8, 139.3, 139.2, 138.3, 134.7, 128.0, 127.9, 127.8, 127.6, 127.48, 127.45, 127.4, 127.19, 127.17, 116.7, 19.8; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{25}H_{21}N_4S$: 409.1487; found: 409.1497.

8.3.28 *4-methyl-5-(3-phenylquinoxalin-2-yl)thiazol-2-amine (**6c**)* Yield 87%; yellow oil; IR (KBr): 3443, 3310, 3181, 2923, 1622, 1509, 1343, 1077, 766, 698cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.14-8.12 (m, 1H), 8.09-8.07 (m, 1H), 7.76-7.73 (m, 2H), 7.69-7.68 (m, 2H), 7.43-7.42 (m, 3H), 5.53 (s, 2H), 1.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 167.8, 153.7, 148.2, 146.2, 141.0, 140.9, 138.8, 130.1, 130.0, 129.2, 129.11, 129.08, 128.7, 128.6, 118.6, 16.2; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{18}H_{15}N_4S$: 319.1017; found: 319.1008.

8.3.29 *4,4'-diphenyl-[5,5'-bithiazole]-2,2'-diamine (**7a**)* Yield 94%; brown solid; m.p. 124-125℃; IR (KBr): 3444, 3372, 3180, 2922, 1618, 1521, 1473, 1334, 1069, 920, 771, 696cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 7.62 (d, J=7.6 Hz, 4H), 7.28 (t, J=7.6 Hz, 4H), 7.23-7.20 (m, 6H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 167.2, 147.9, 134.6, 128.1, 127.5, 109.2; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{18}H_{15}N_4S_2$: 351.0738; found: 351.0732.

8.3.30 *4-(4-chlorophenyl)-4'-phenyl-[5,5'-bithiazole]-2,2'-diamine (**7b**)* Yield 93%; yellow solid; m.p. 268-269℃; IR (KBr): 3458, 3267, 3116, 1621, 1524, 1469, 1333, 918, 843, 697cm^{-1}; ^{1}H NMR (600 MHz, DMSO-d_6): δ (ppm) 7.60-7.57 (m, 4H), 7.35 (d, J=9.0 Hz, 2H), 7.28 (t, J=7.8 Hz, 2H), 7.24-7.20 (m, 5H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 167.4, 148.2, 146.7, 134.7, 133.5, 132.0, 129.2, 128.22, 128.15, 127.5, 110.0, 108.8; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{18}H_{15}ClN_4S_2$: 385.0348; found: 385.0338.

NMR Spectra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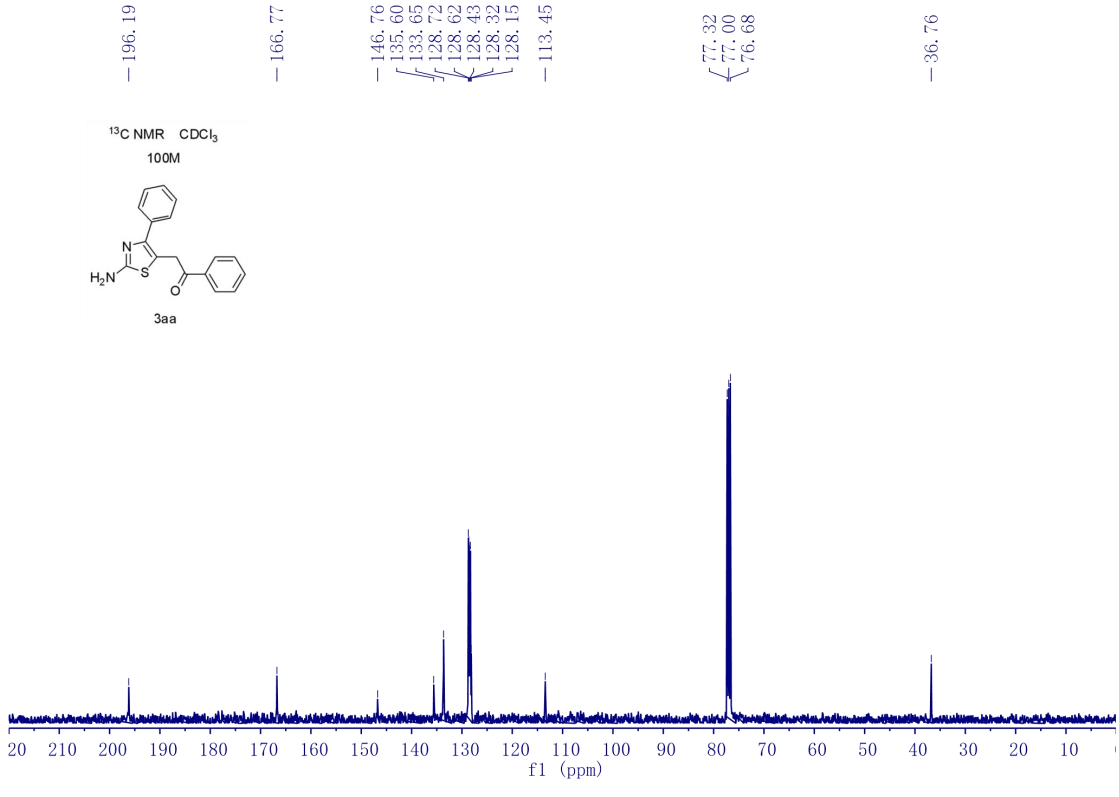
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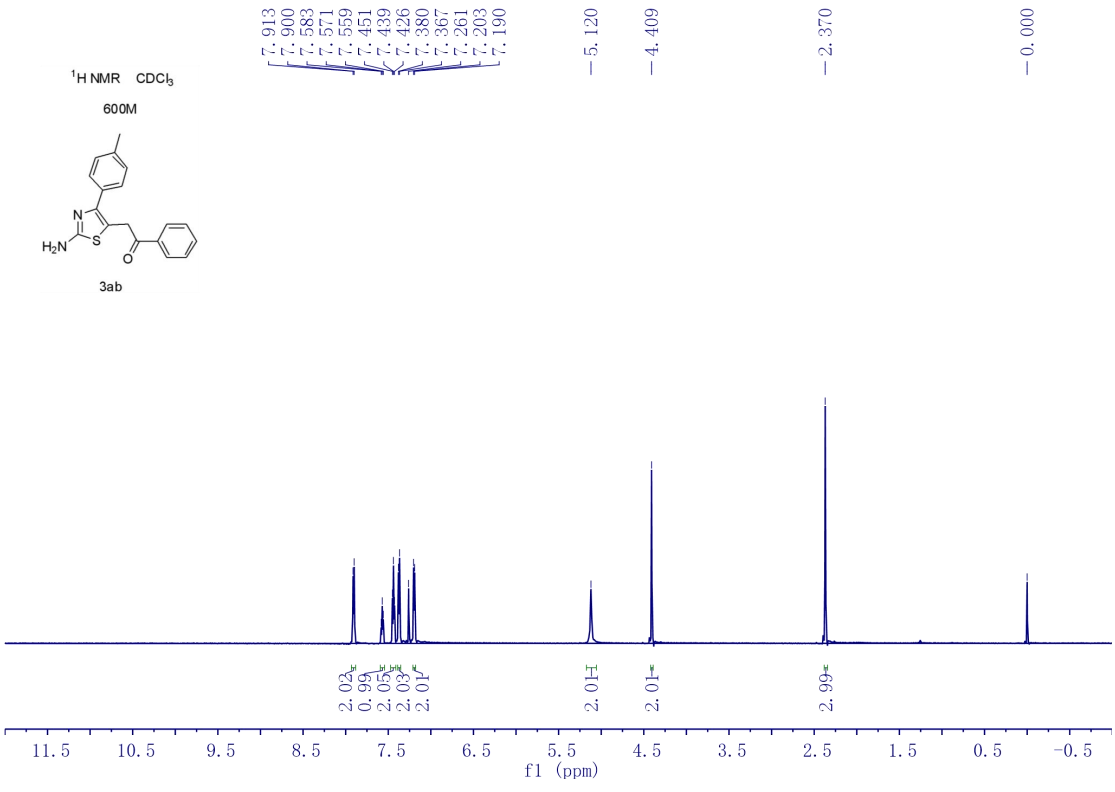
f1 (ppm)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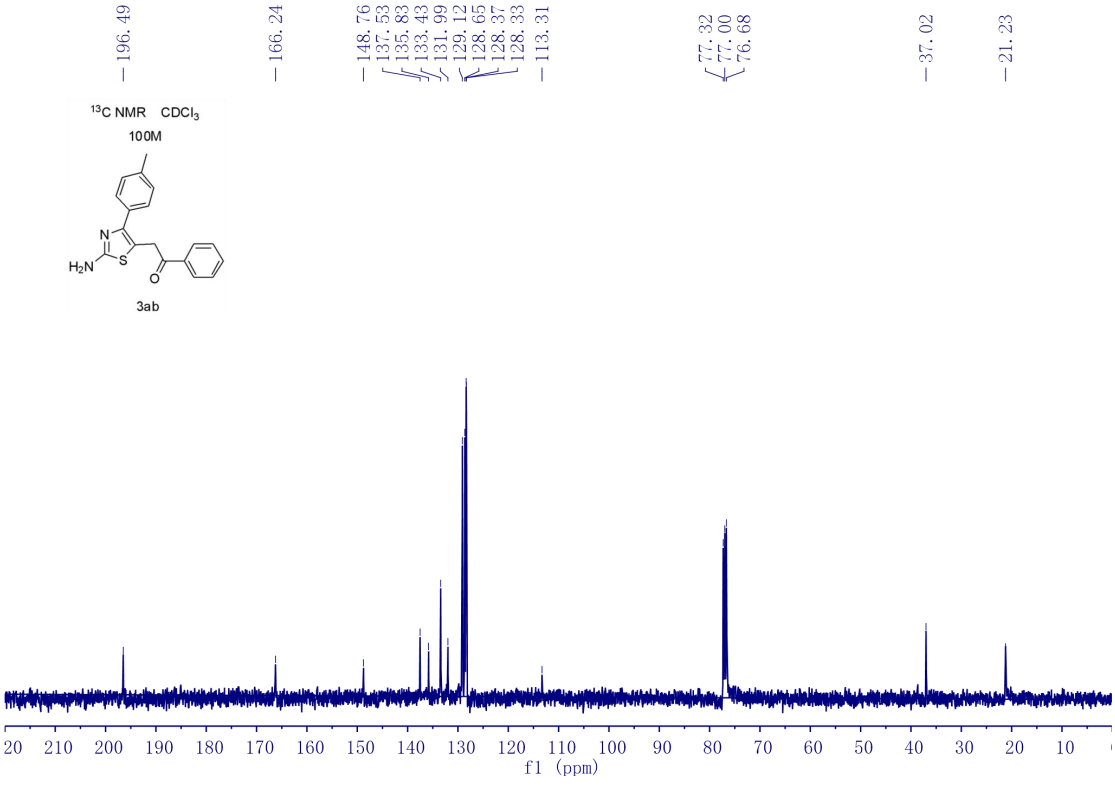
f1 (ppm)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13C NMR CDCl3
100M
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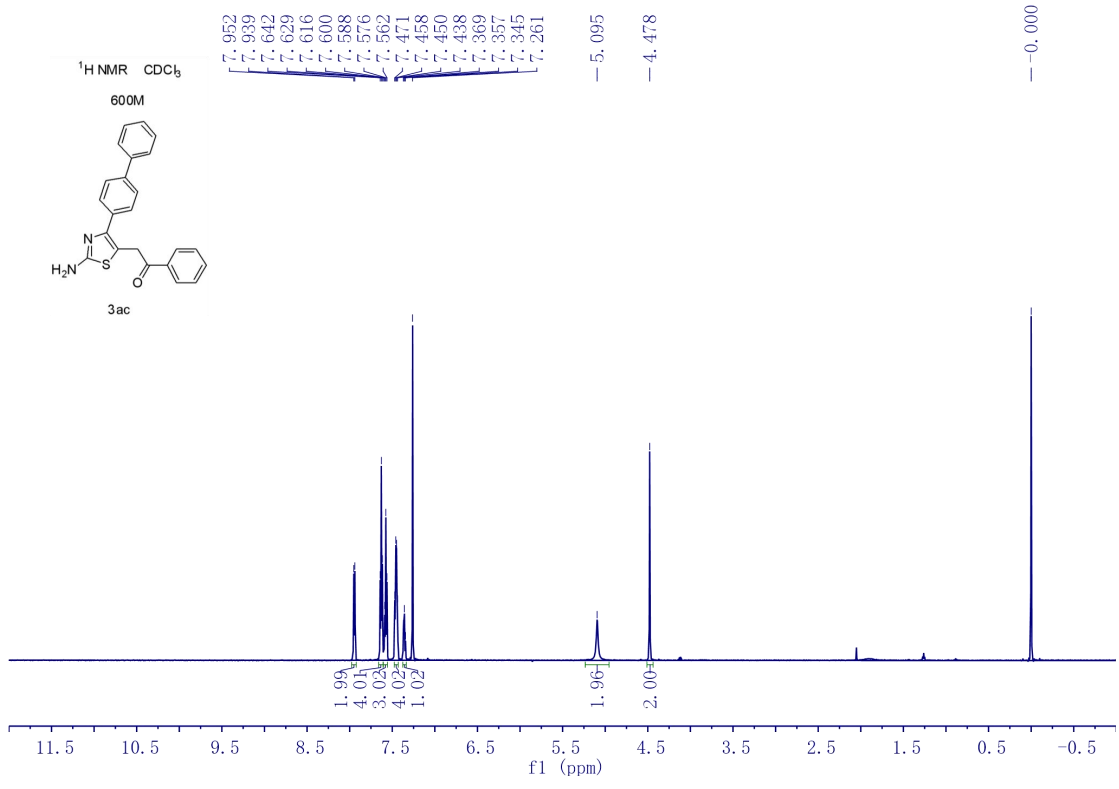
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4.01
3.02
4.02
1.02
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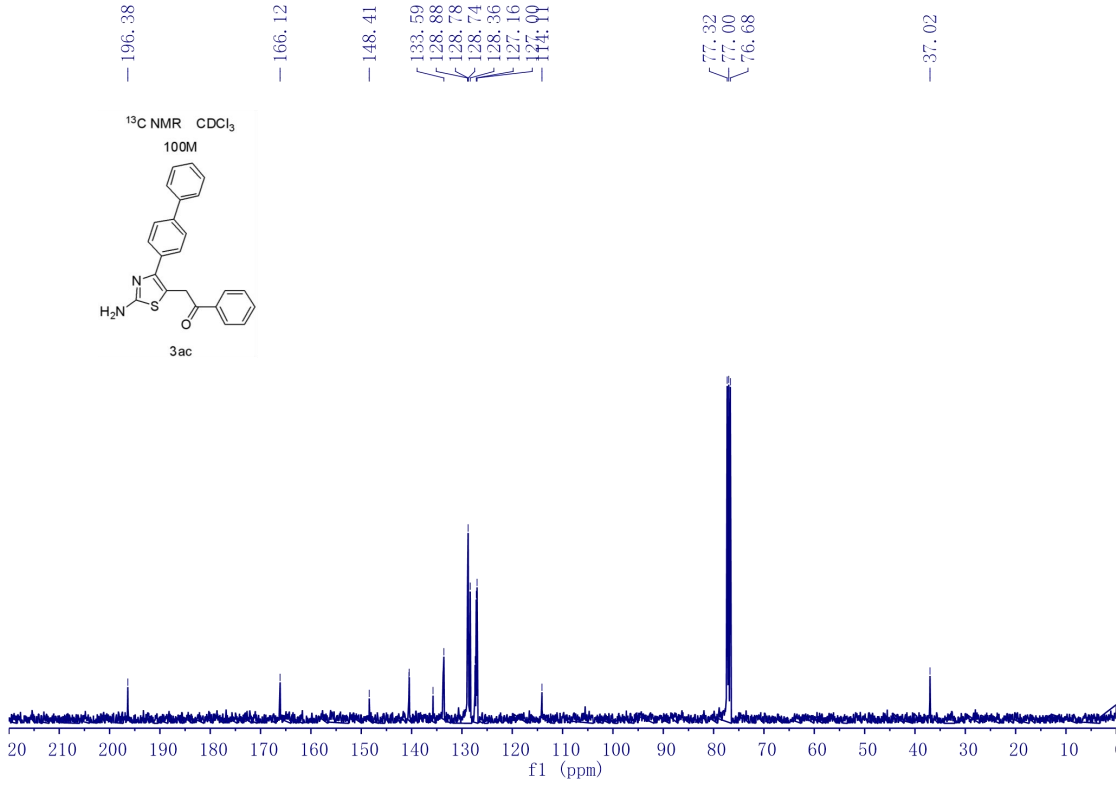
f1 (ppm)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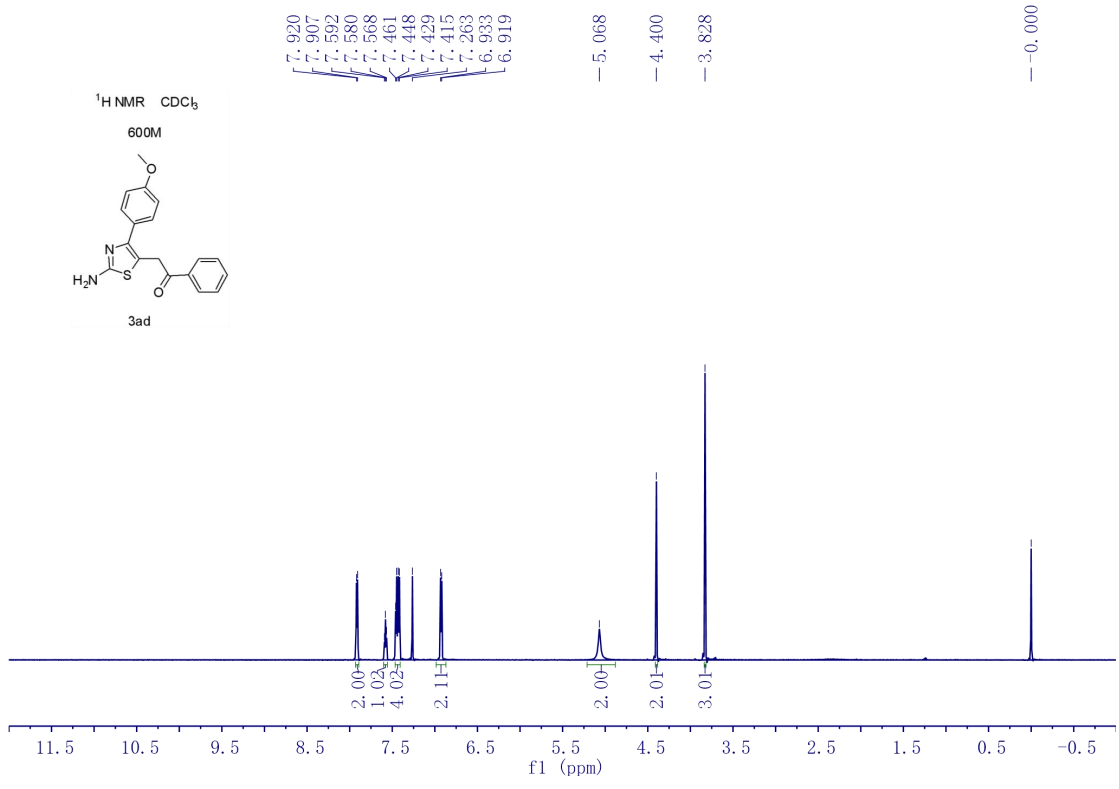
f1 (ppm)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4.02
2.11
2.00
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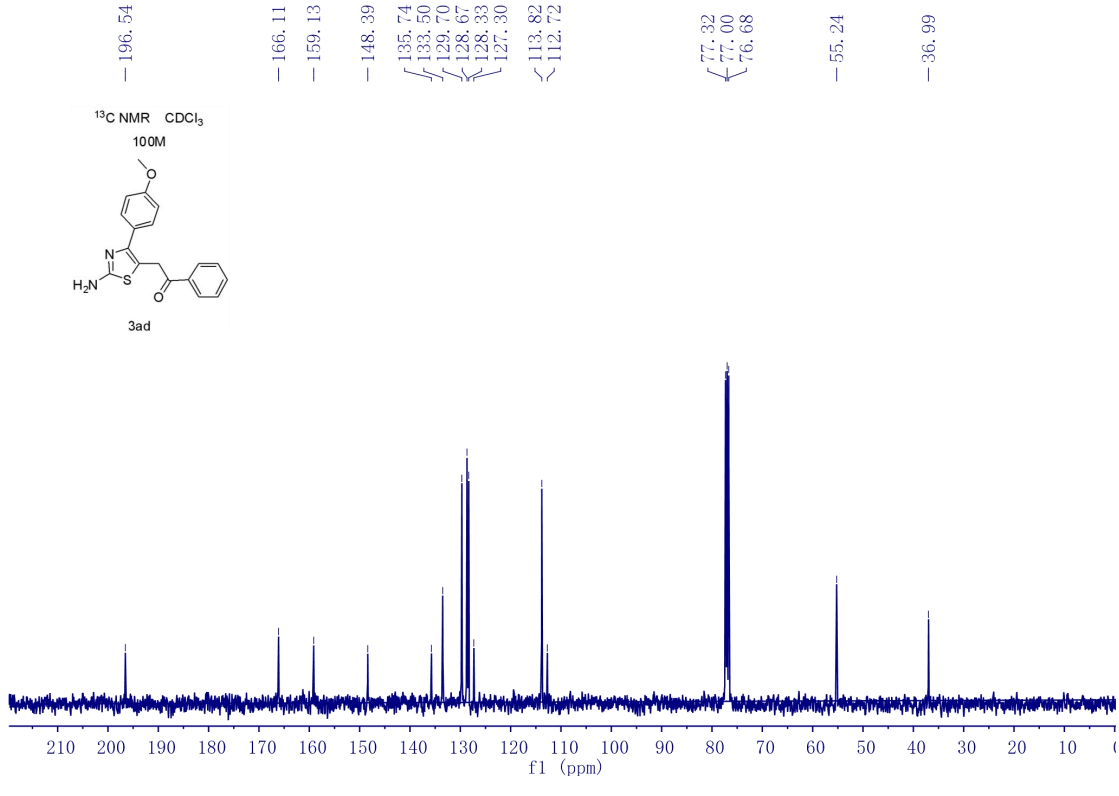
f1 (ppm)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100M
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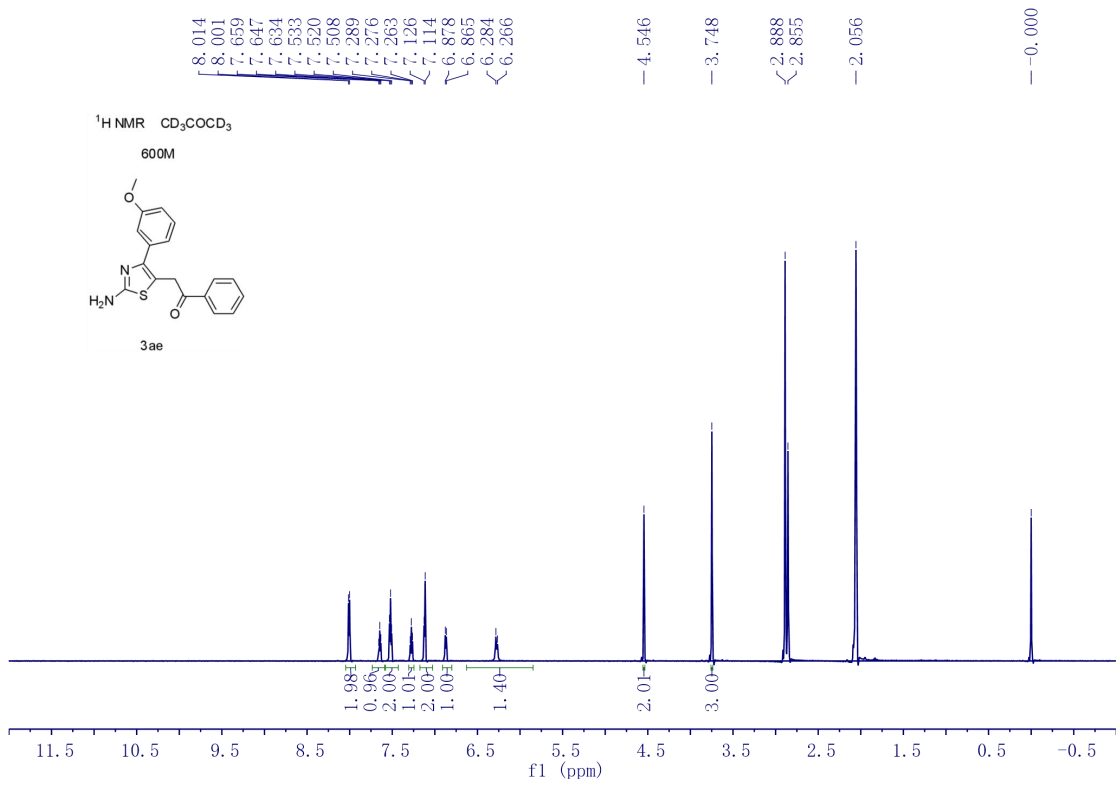
f1 (ppm)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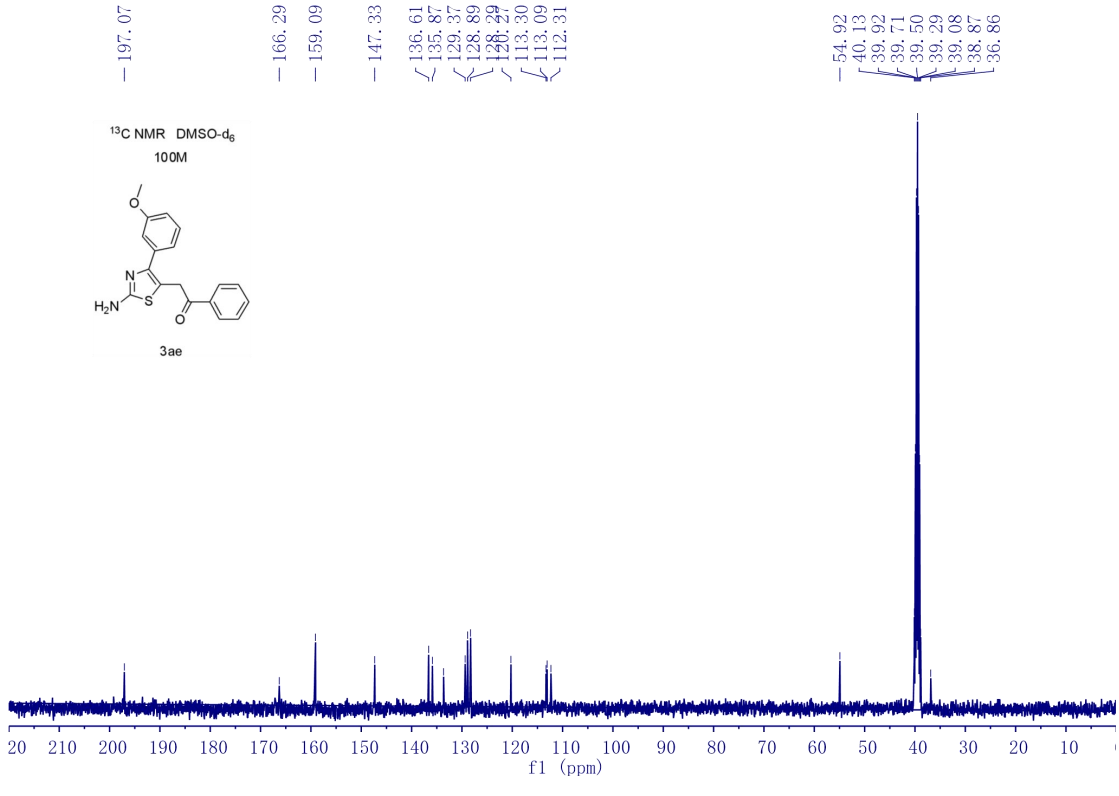
f1 (ppm)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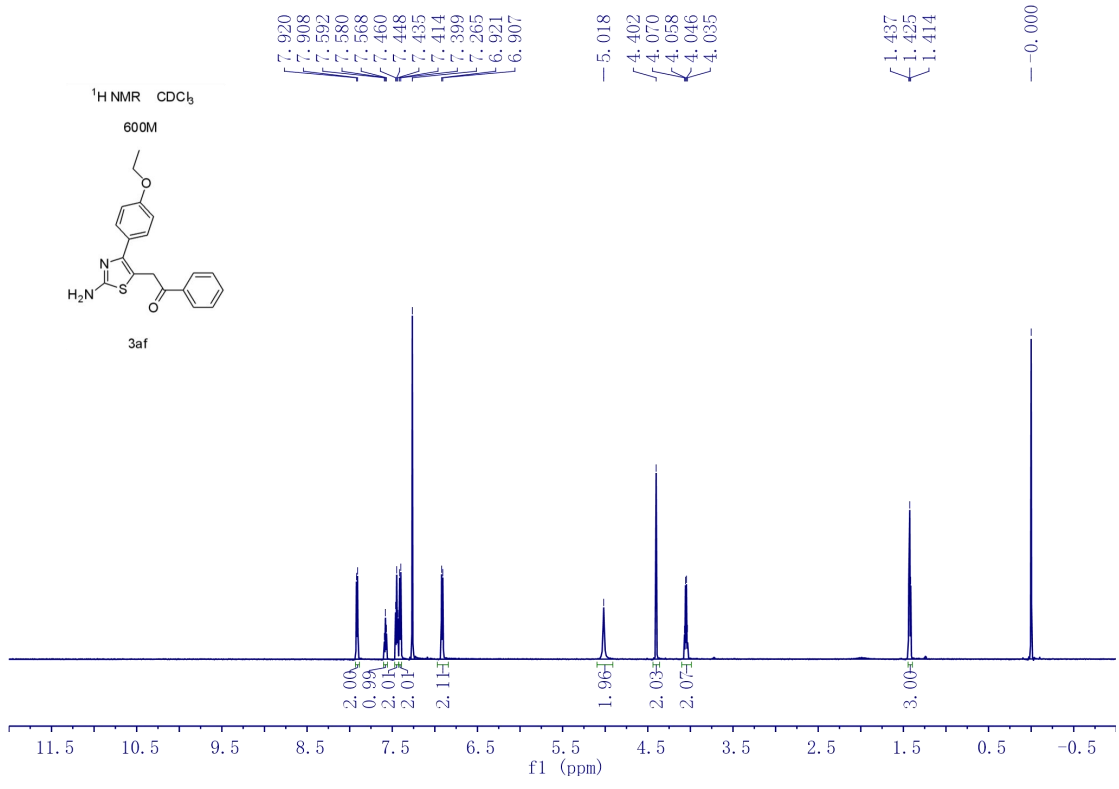
3ae
f1 (ppm)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4.035
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^{1}H NMR CDCl$_3$
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3af
2.00
0.99
2.01
2.01
2.11
1.96
2.03
2.07
3.00
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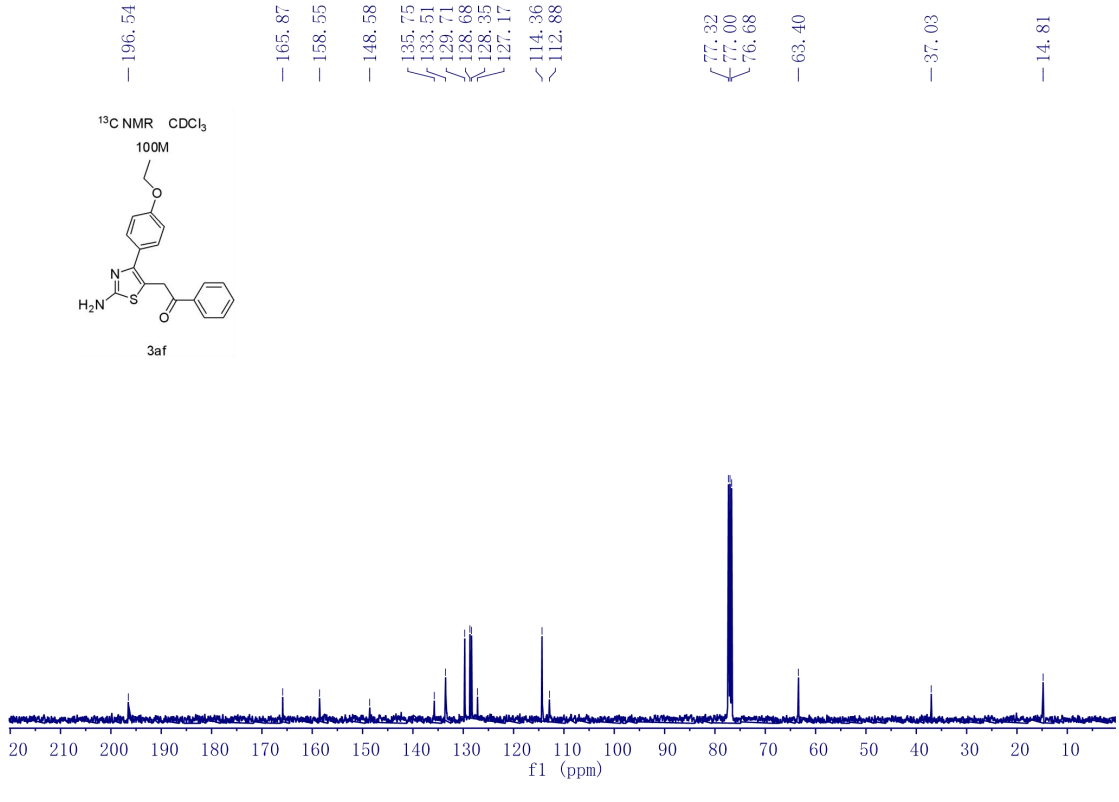
f1 (ppm)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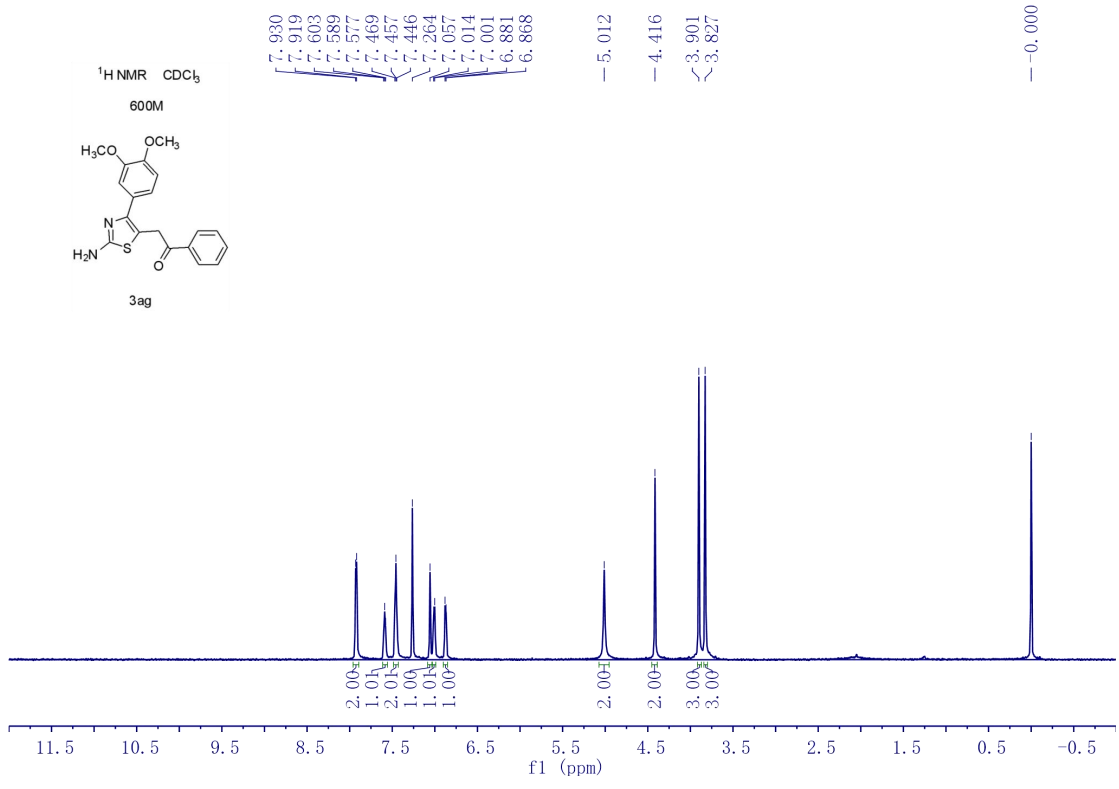
135.75
133.51
129.71
128.68
128.35
127.17
114.36
112.88
77.32
77.00
76.68
63.40
37.03
14.81
^{13}C NMR CDCl$_3$
100M
3af
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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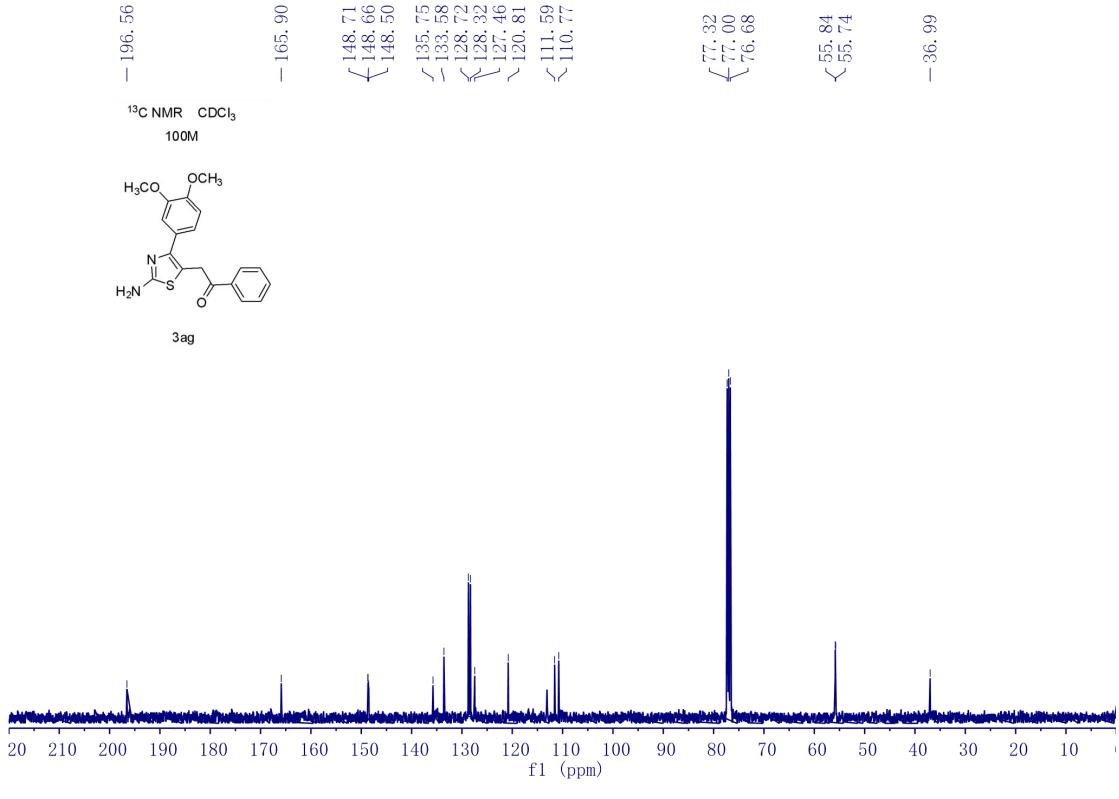
7.919
7.603
7.589
7.577
7.469
7.457
7.446
7.264
7.057
7.014
7.001
6.881
6.868
5.012
4.416
3.901
3.827
0.000
1H NMR CDCl3
600M
H3CO
OCH3
N
S
H2N
O
3ag
2.00
1.01
2.01
1.00
1.01
1.00
2.00
2.00
3.00
3.00
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)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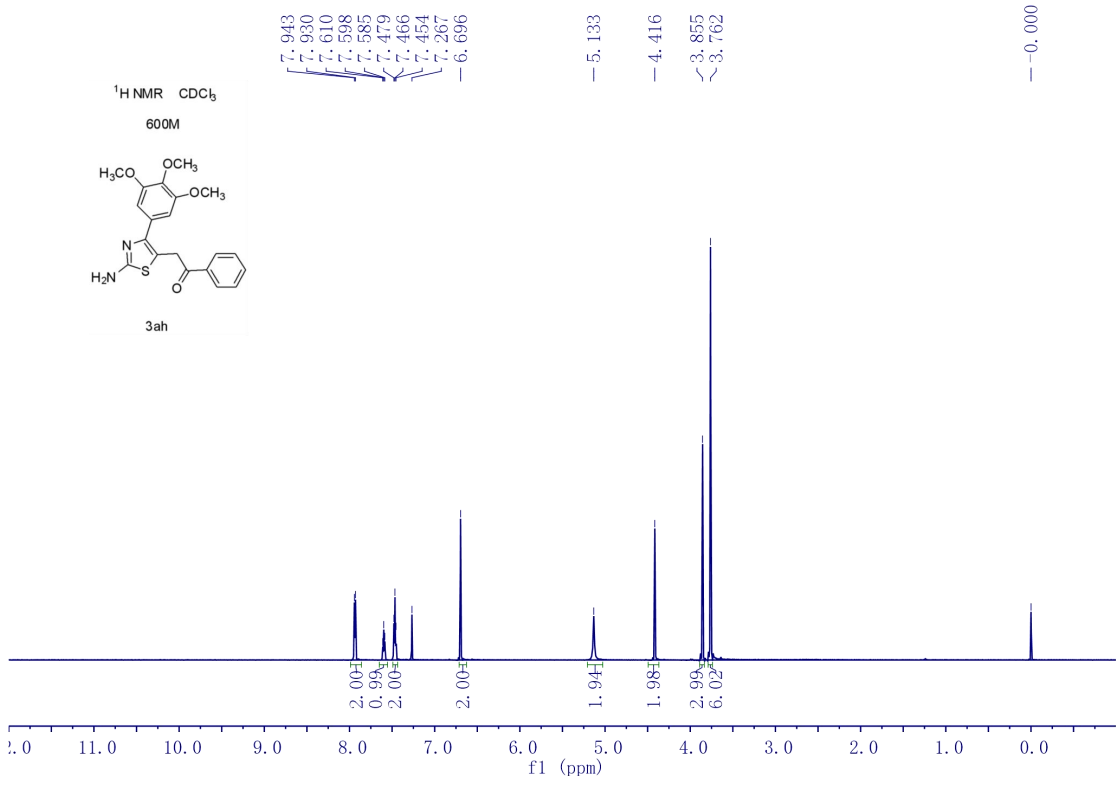
148.50
135.75
133.58
128.72
128.32
127.46
120.81
111.59
110.77
77.32
77.00
76.68
55.84
55.74
36.99
13C NMR CDCl3
100M
H3CO
OCH3
N
S
H2N
O
3ag
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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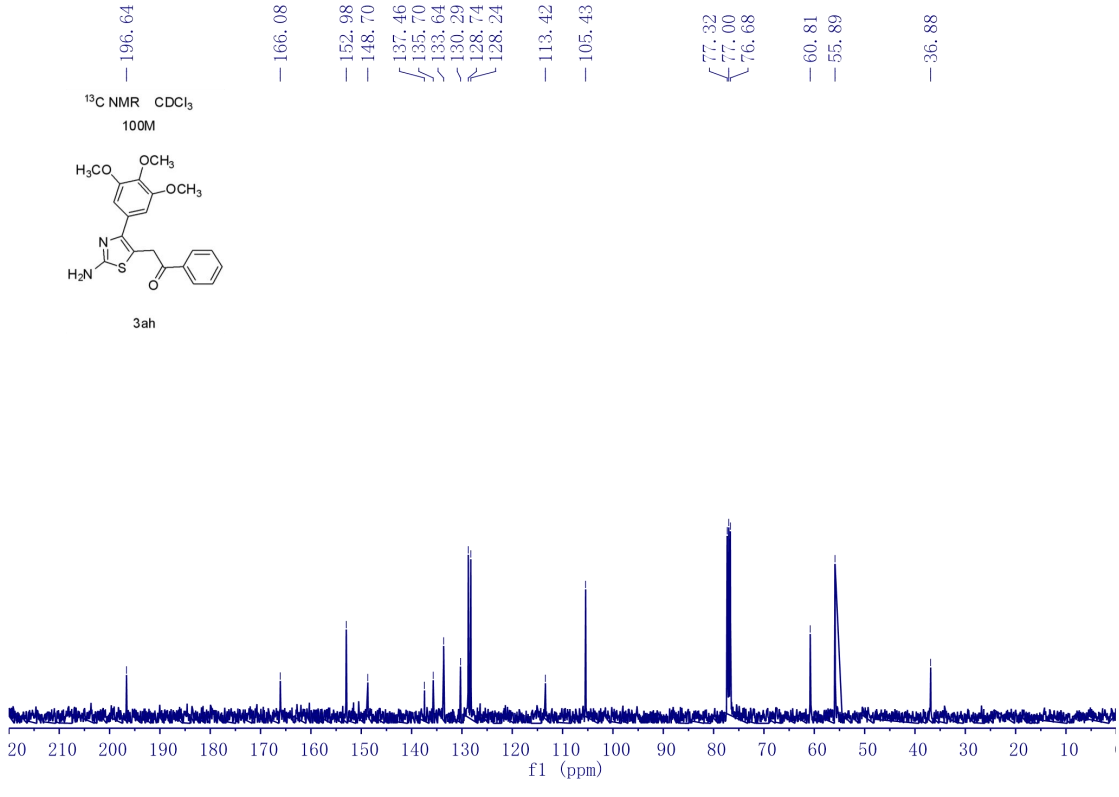
7.930
7.610
7.598
7.585
7.479
7.466
7.454
7.267
6.696
5.133
4.416
3.855
3.762
0.000
1H NMR CDCl3
600M
3ah
2.00
0.99
2.00
2.00
1.94
1.98
2.99
6.02
f1 (ppm)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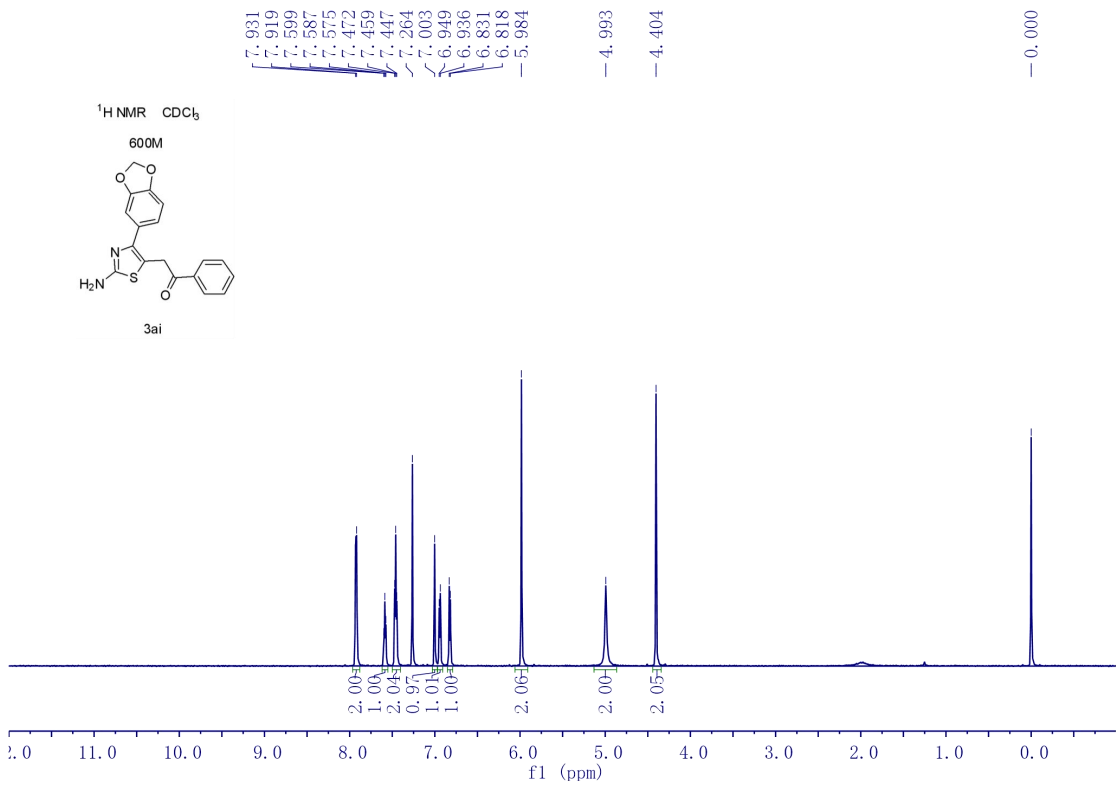
166.08
152.98
148.70
137.46
135.70
133.64
130.29
128.74
128.24
113.42
105.43
77.32
77.00
76.68
60.81
55.89
36.88
13C NMR CDCl3
100M
3ah
f1 (ppm)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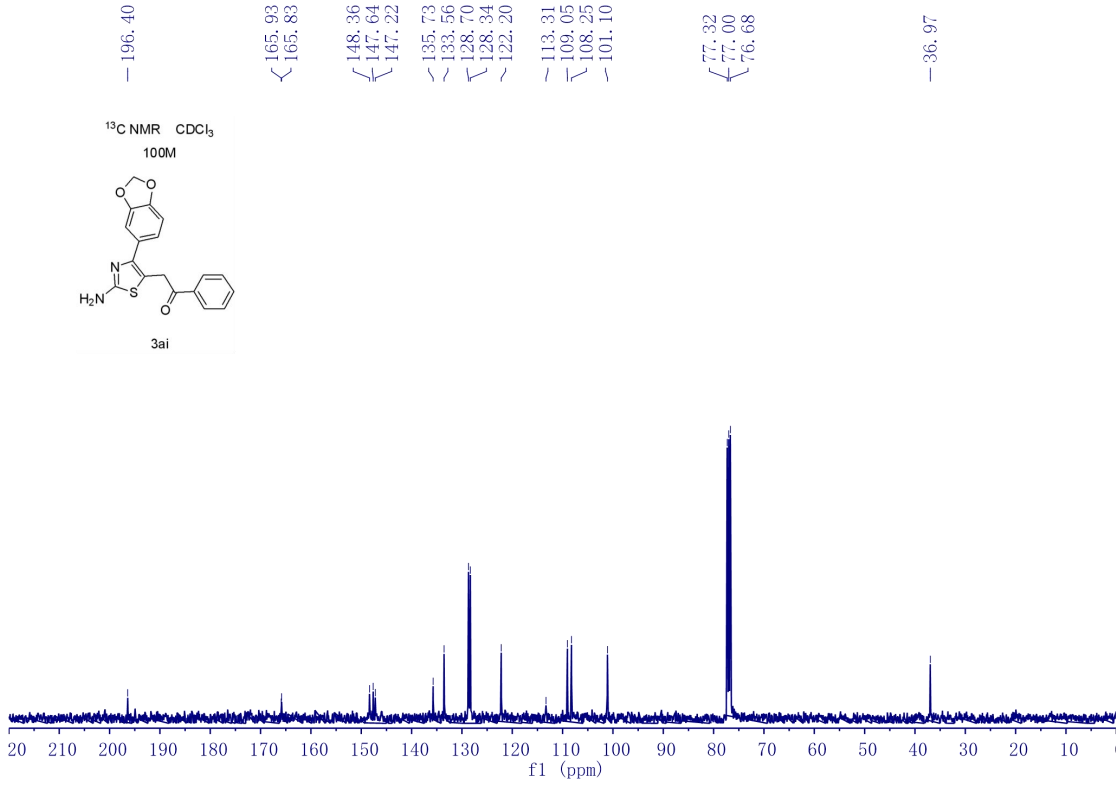
7.919
7.599
7.587
7.575
7.472
7.459
7.447
7.264
7.003
6.949
6.936
6.831
6.818
5.984
4.993
4.404
0.000
1H NMR CDCl3
600M
3ai
2.00
1.00
2.04
0.97
1.01
1.00
2.06
2.00
2.05
f1 (ppm)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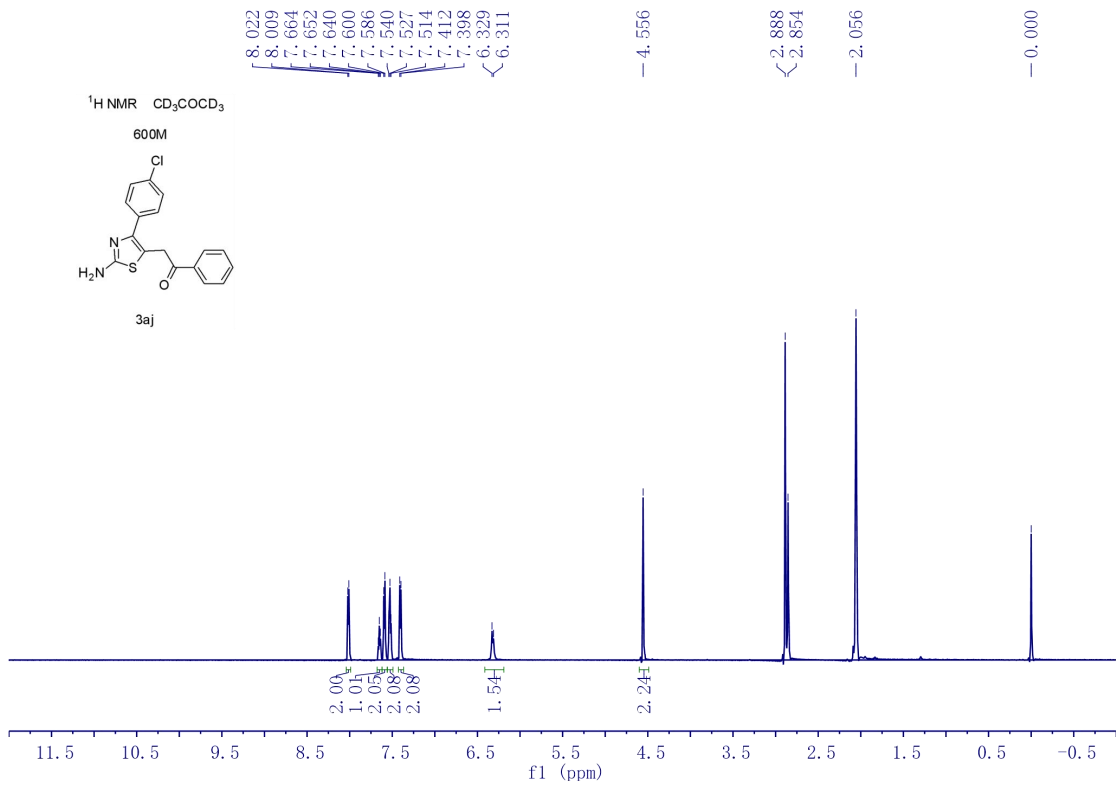
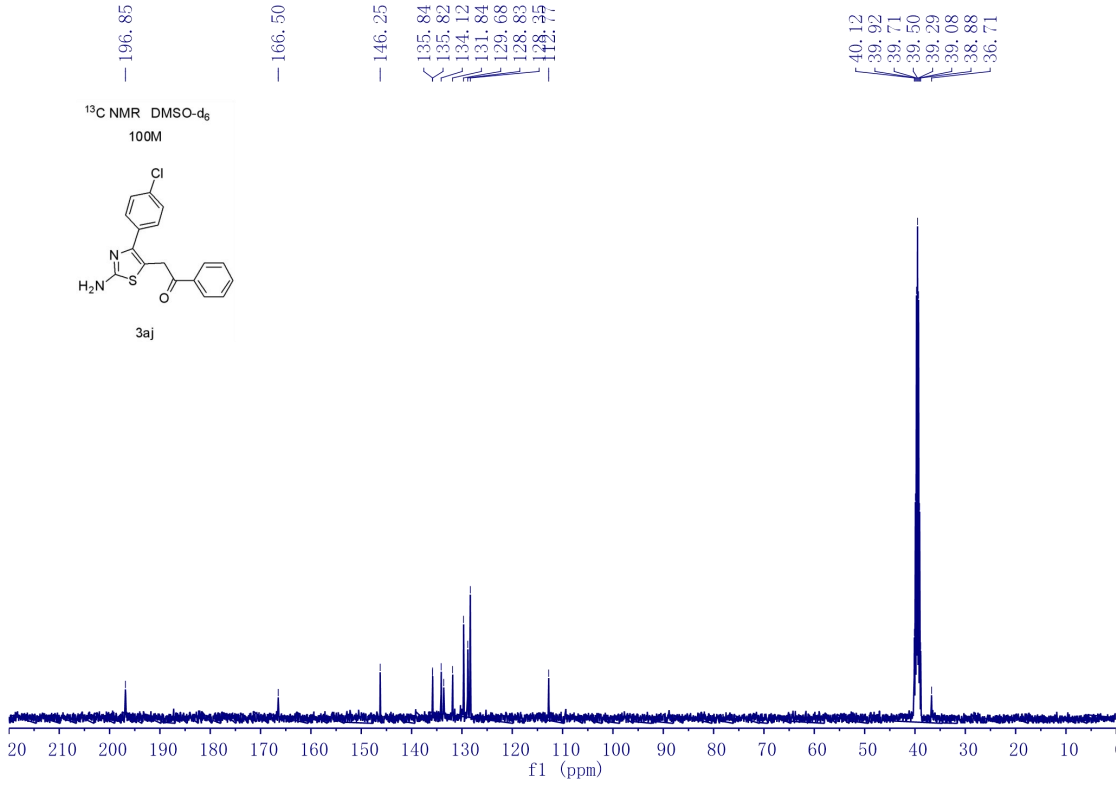
165.83
148.36
147.64
147.22
135.73
133.56
128.70
128.34
122.20
113.31
109.05
108.25
101.10
77.32
77.00
76.68
36.97
13C NMR CDCl3
100M
3ai
f1 (ppm)


8.022
8.009
7.664
7.652
7.640
7.600
7.586
7.540
7.527
7.514
7.412
7.398
6.329
6.311
4.556
2.888
2.854
2.056
0.000
1H NMR CD3COCD3
600M
Cl
N
S
H2N
O
3aj
2.00
1.01
2.05
2.08
2.08
1.54
2.24
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)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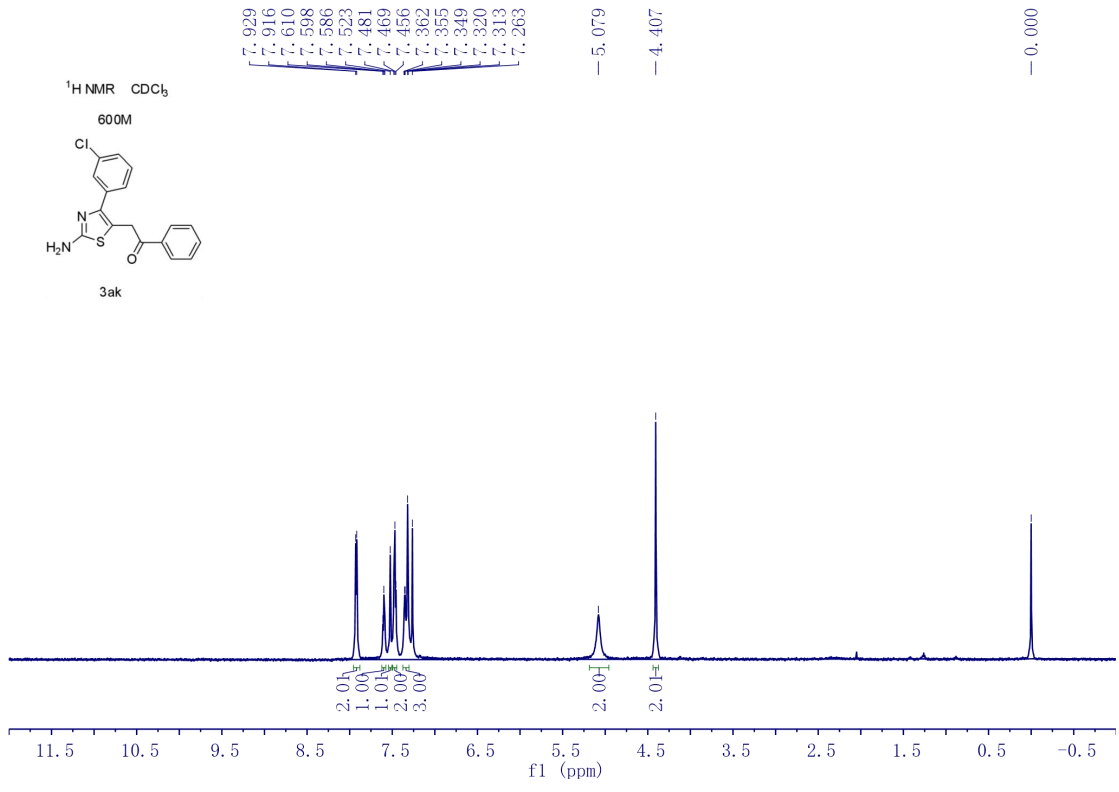
166.50
146.25
135.84
135.82
134.12
131.84
129.68
128.83
40.12
39.92
39.71
39.50
39.29
39.08
38.88
36.71
13C NMR DMSO-d6
100M
Cl
N
S
H2N
O
3aj
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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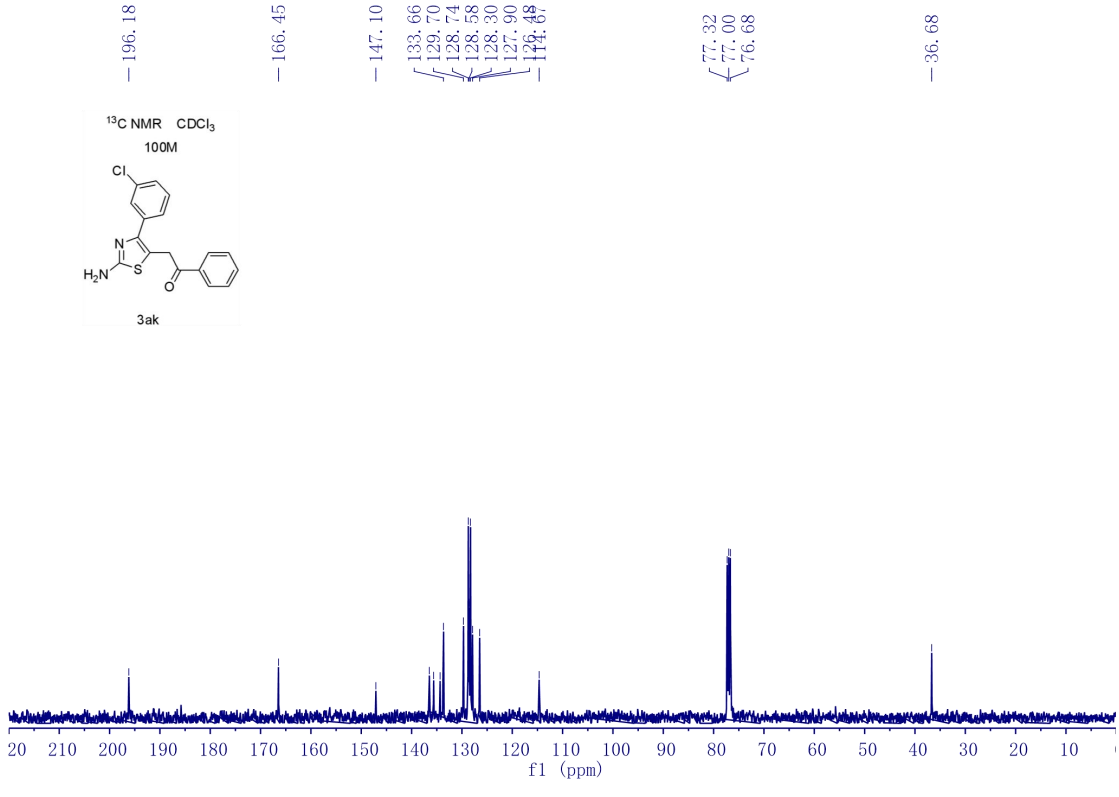
7.916
7.610
7.598
7.586
7.523
7.481
7.469
7.456
7.362
7.355
7.349
7.320
7.313
7.263
5.079
4.407
0.000
1H NMR CDCl3
600M
Cl
N
S
H2N
O
3ak
2.01
1.00
1.01
2.00
3.00
2.00
2.01
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)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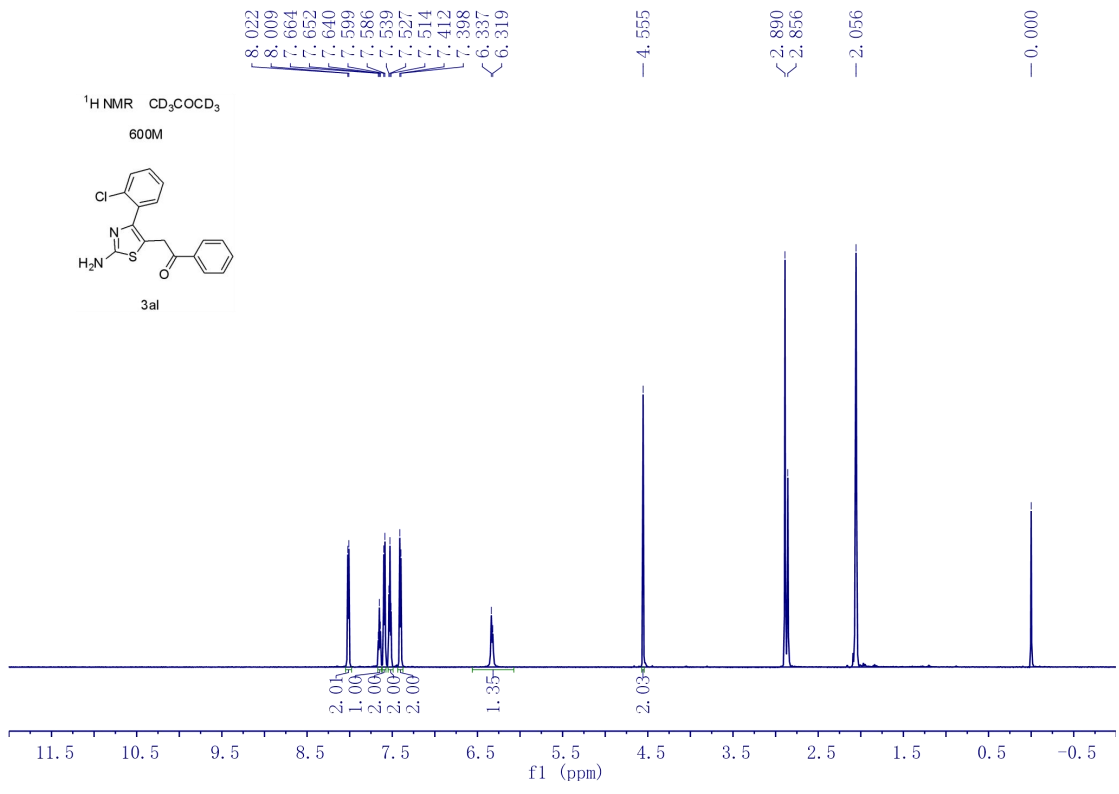
166.45
147.10
133.66
129.70
128.74
128.58
128.30
127.90
114.67
77.32
77.00
76.68
36.68
13C NMR CDCl3
100M
Cl
N
S
H2N
O
3ak
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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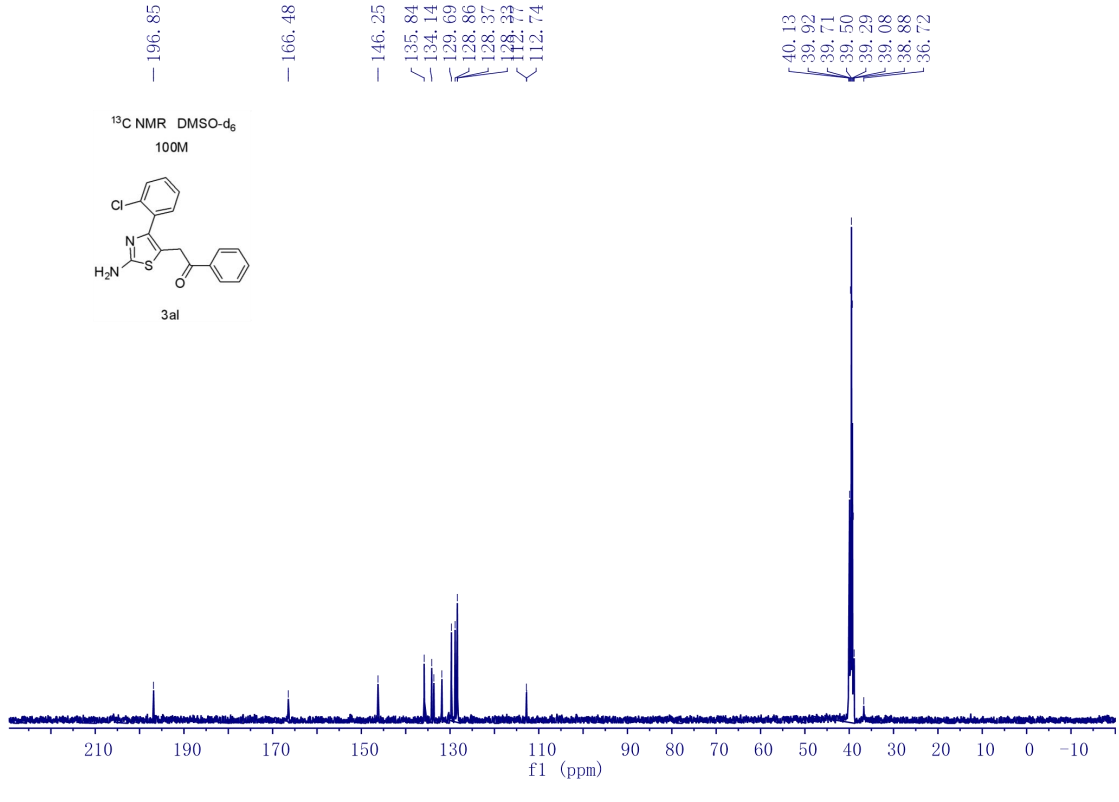
8.009
7.664
7.652
7.640
7.599
7.586
7.539
7.527
7.514
7.412
7.398
6.337
6.319
4.555
2.890
2.856
2.056
0.000
1H NMR CD3COCD3
600M
Cl
N
H2N
S
O
3al
2.01
1.00
2.00
2.00
2.00
1.35
2.03
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)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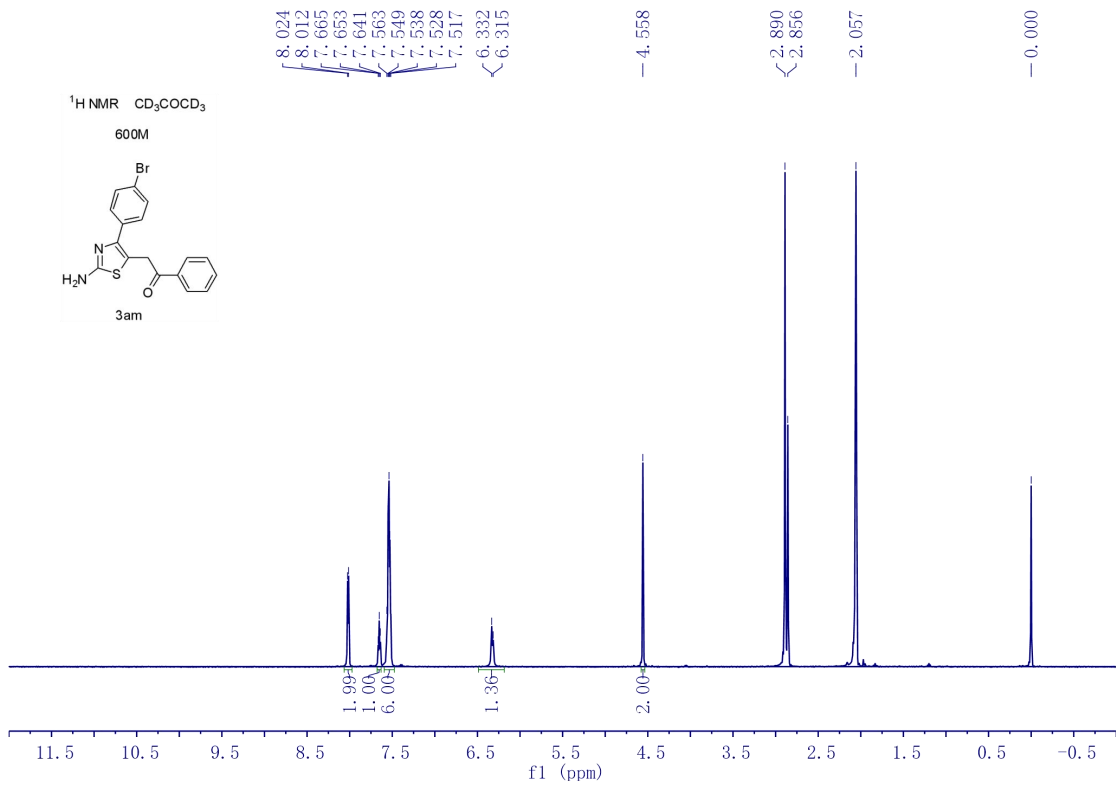
135.84
134.14
129.69
128.86
128.37
112.74
40.13
39.92
39.71
39.50
39.29
39.08
38.88
36.72
13C NMR DMSO-d6
100M
Cl
N
H2N
S
O
3al
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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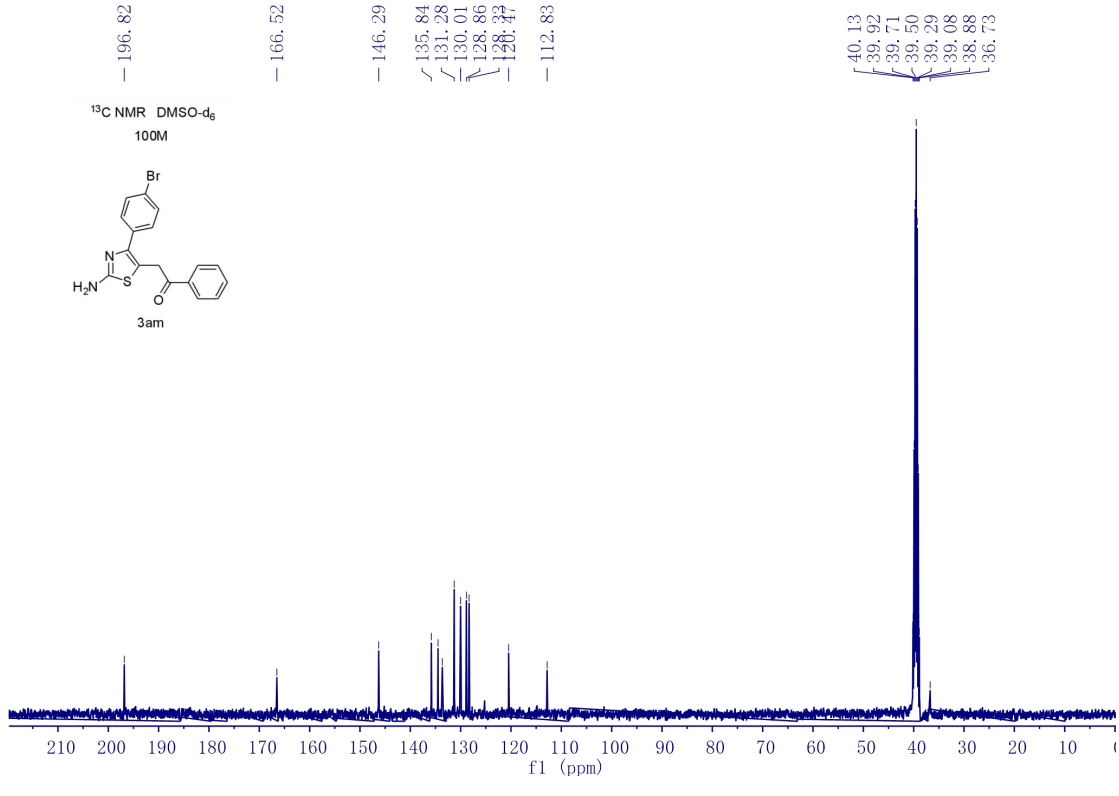
7.641
7.563
7.549
7.538
7.528
7.517
6.332
6.315
4.558
2.890
2.856
2.057
0.000
1H NMR CD3COCD3
600M
Br
N
S
H2N
O
3am
1.99
1.00
6.00
1.36
2.00
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)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131.28
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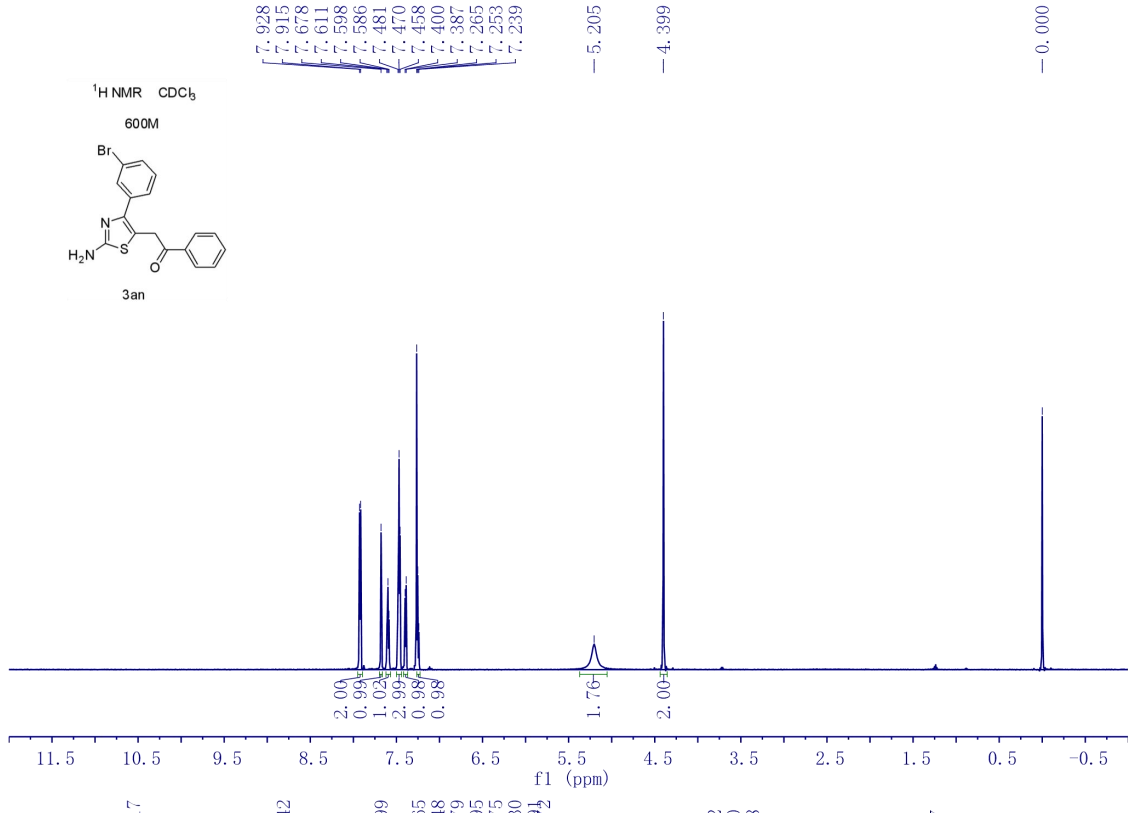
128.86
128.33
120.47
112.83
40.13
39.92
39.71
39.50
39.29
39.08
38.88
38.73
13C NMR DMSO-d6
100M
Br
N
S
H2N
O
3am
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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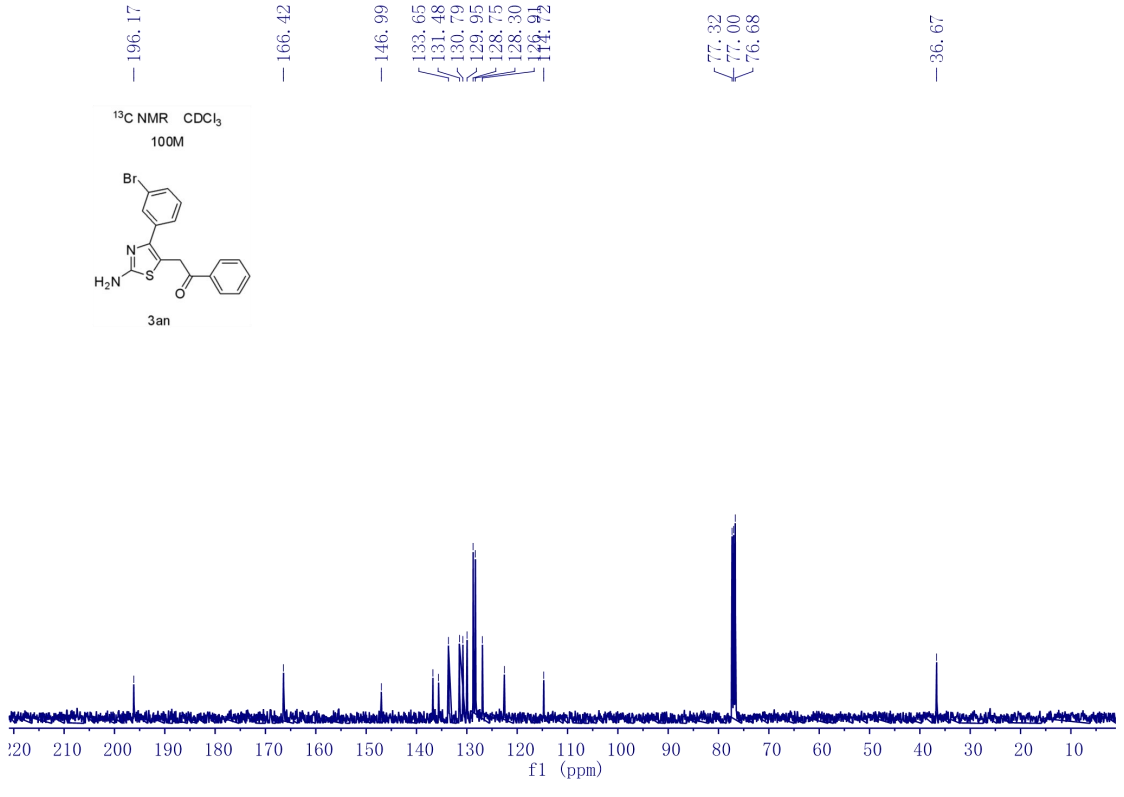
7.915
7.678
7.611
7.598
7.586
7.481
7.470
7.458
7.400
7.387
7.265
7.253
7.239
5.205
4.399
0.000
1H NMR CDCl3
600M
Br
N
S
H2N
O
3an
2.00
0.99
1.02
2.99
0.98
0.98
1.76
2.00
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)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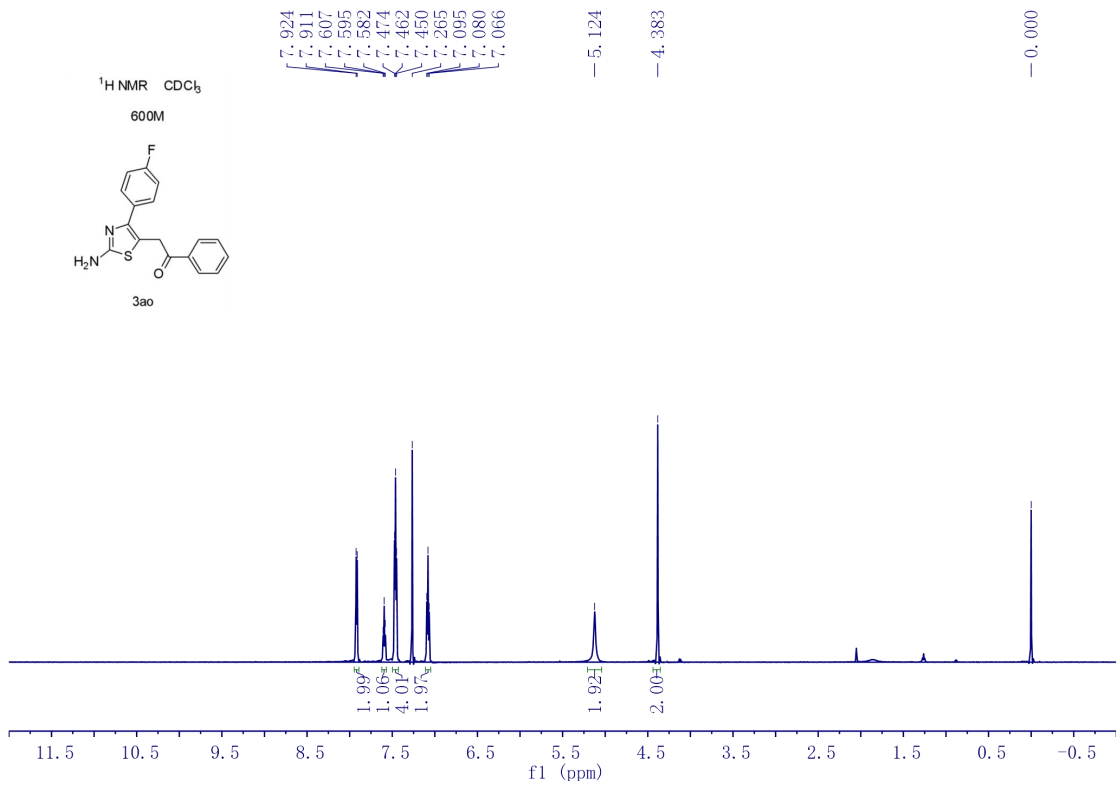
129.95
128.75
128.30
126.91
114.72
77.32
77.00
76.68
36.67
13C NMR CDCl3
100M
Br
N
S
H2N
O
3an
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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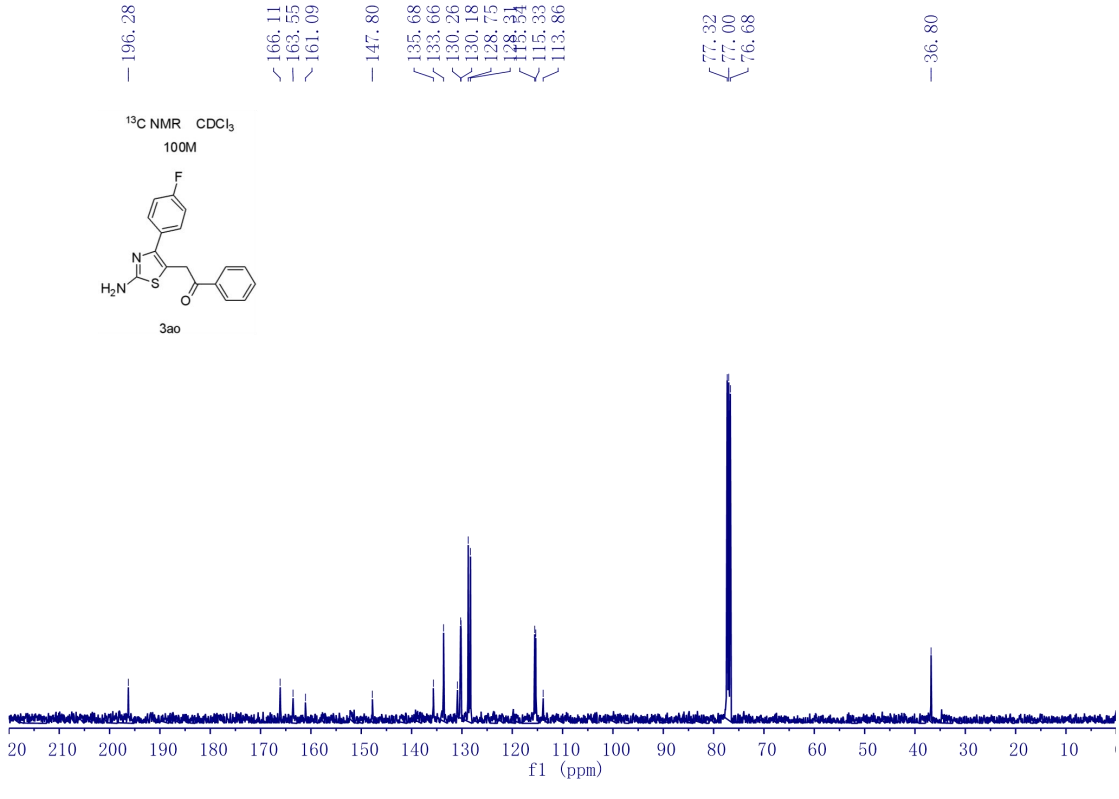
7.595
7.582
7.474
7.462
7.450
7.265
7.095
7.080
7.066
5.124
4.383
0.000
1H NMR CDCl3
600M
3ao
1.99
1.06
4.01
1.97
1.92
2.00
f1 (ppm)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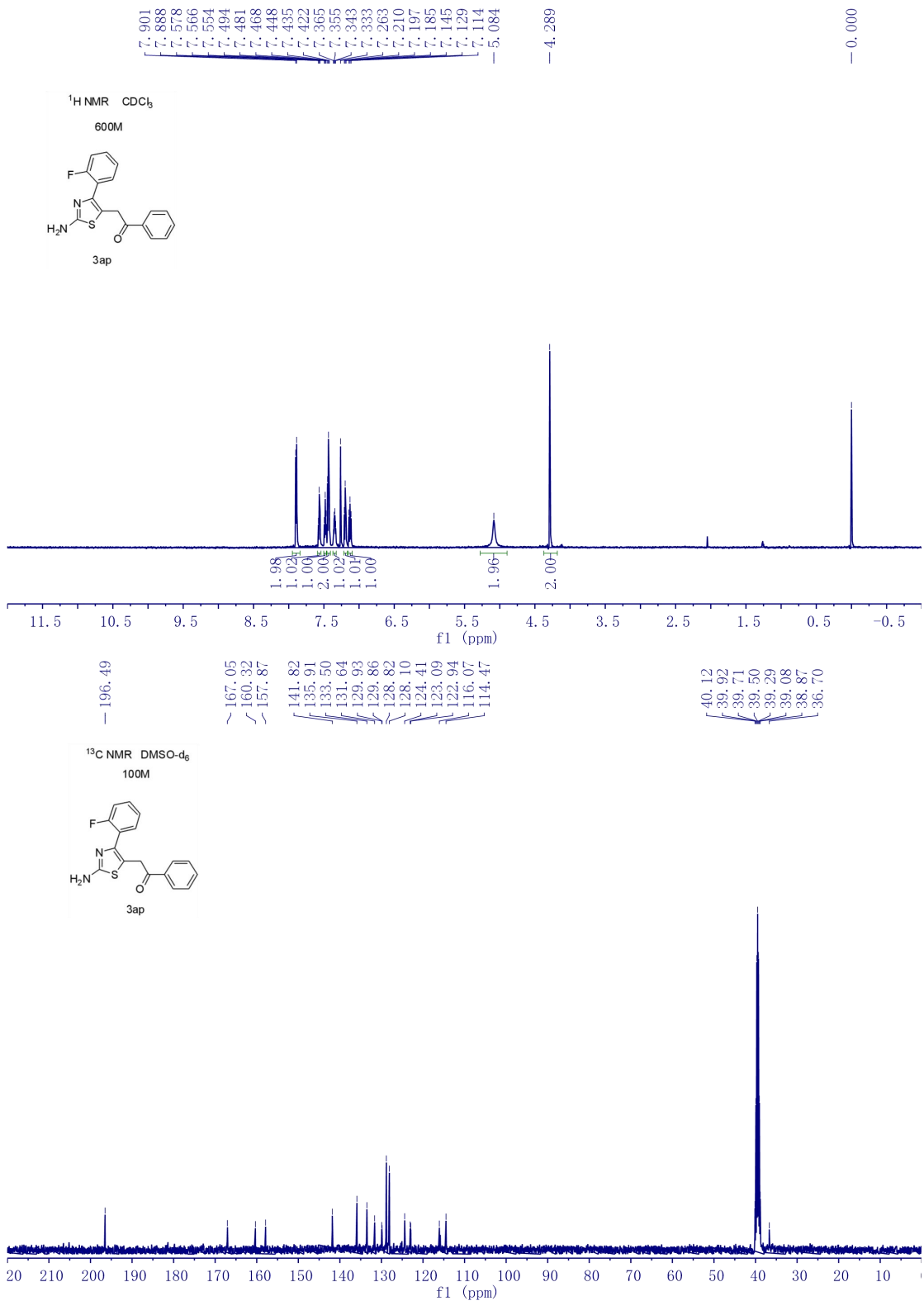
163.55
161.09
147.80
135.68
133.66
130.26
130.18
128.75
128.31
128.24
115.33
113.86
77.32
77.00
76.68
36.80
13C NMR CDCl3
100M
3ao
f1 (ppm)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7.578
7.566
7.554
7.494
7.481
7.468
7.448
7.435
7.422
7.365
7.355
7.343
7.333
7.263
7.210
7.197
7.185
7.145
7.129
7.114
5.084
4.289
0.000
1H NMR CDCl3
600M
3ap
1.98
1.02
1.00
2.00
1.02
1.01
1.00
1.96
2.00
f1 (ppm)
196.49
167.05
160.32
157.87
141.82
135.91
133.50
131.64
129.93
129.86
128.82
128.10
124.41
123.09
122.94
116.07
114.47
40.12
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39.50
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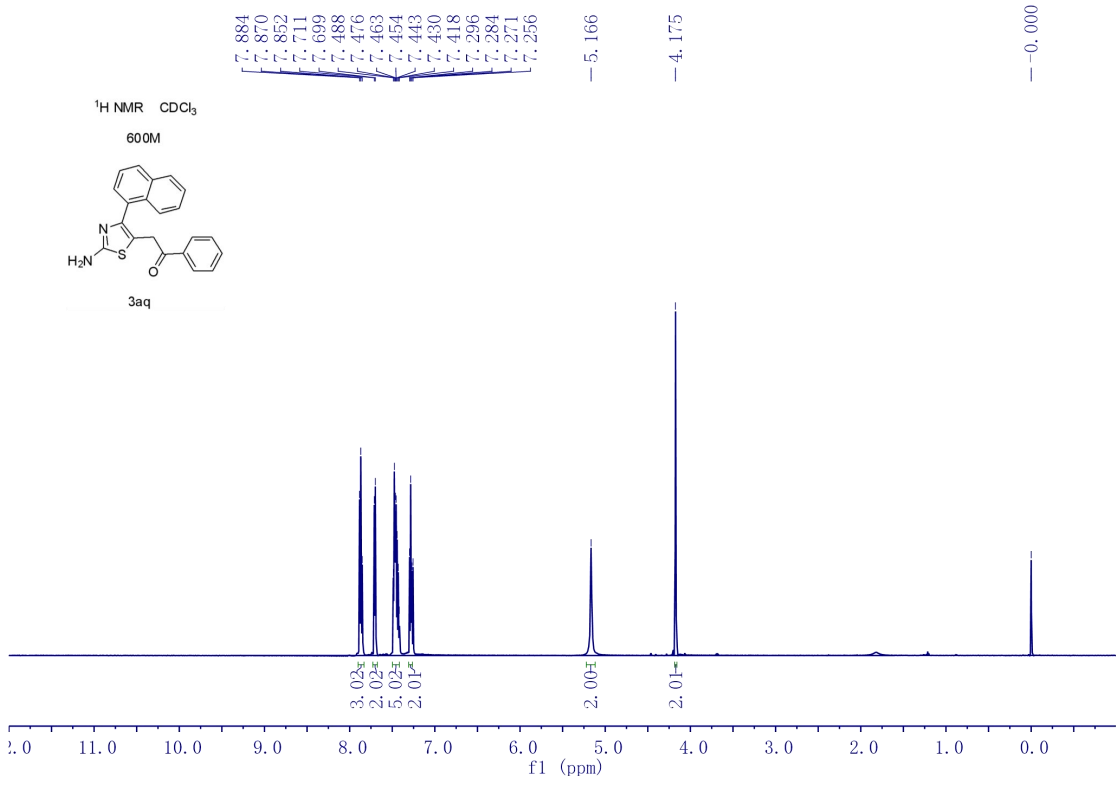
38.70
13C NMR DMSO-d6
100M
3ap
f1 (ppm)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7.852
7.711
7.699
7.488
7.476
7.463
7.454
7.443
7.430
7.418
7.296
7.284
7.271
7.256
5.166
4.175
0.000
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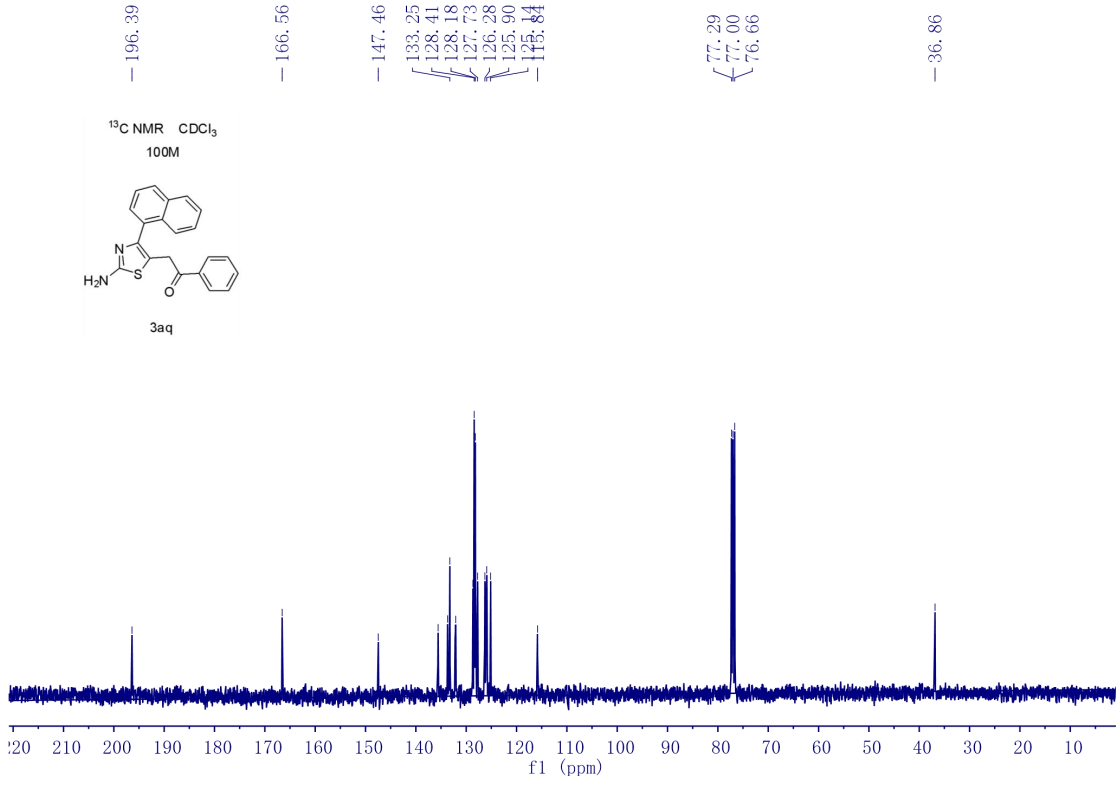
600M
3aq
3.02
2.02
5.02
2.01
2.00
2.01
f1 (ppm)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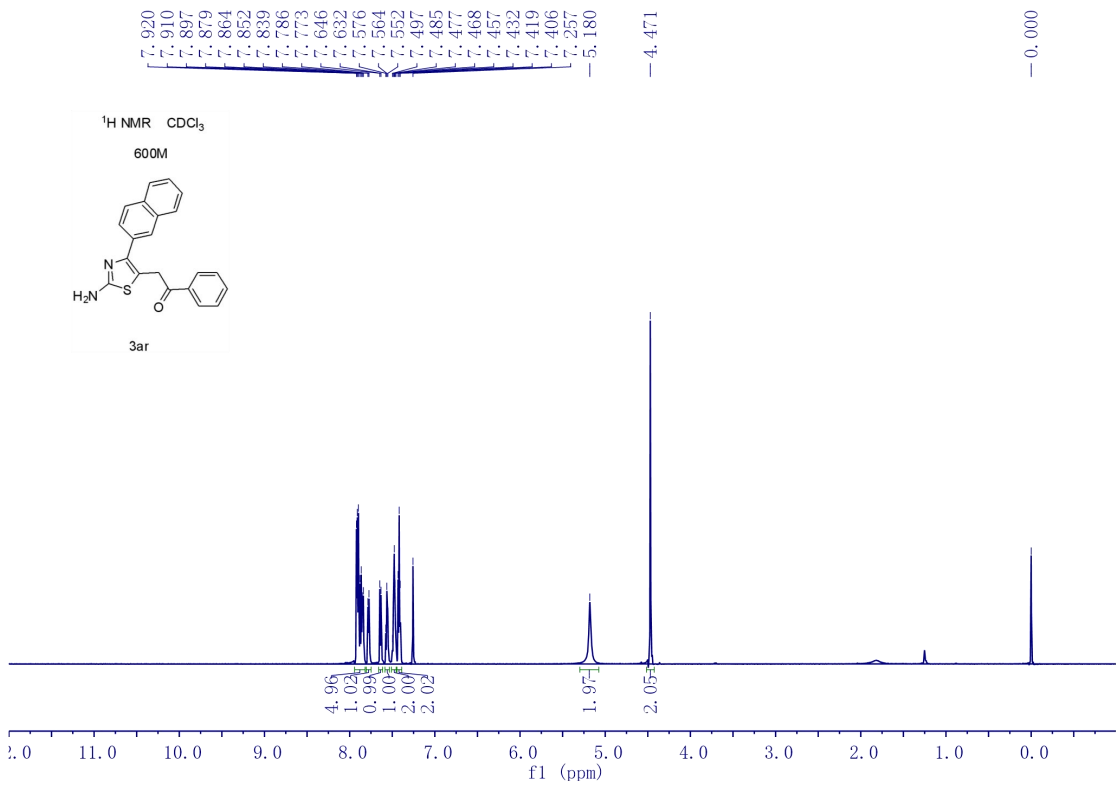
147.46
133.25
128.41
128.18
127.73
126.28
125.90
77.29
77.00
76.66
36.86
13C NMR CDCl3
100M
3aq
f1 (ppm)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7.879
7.864
7.852
7.839
7.786
7.773
7.646
7.632
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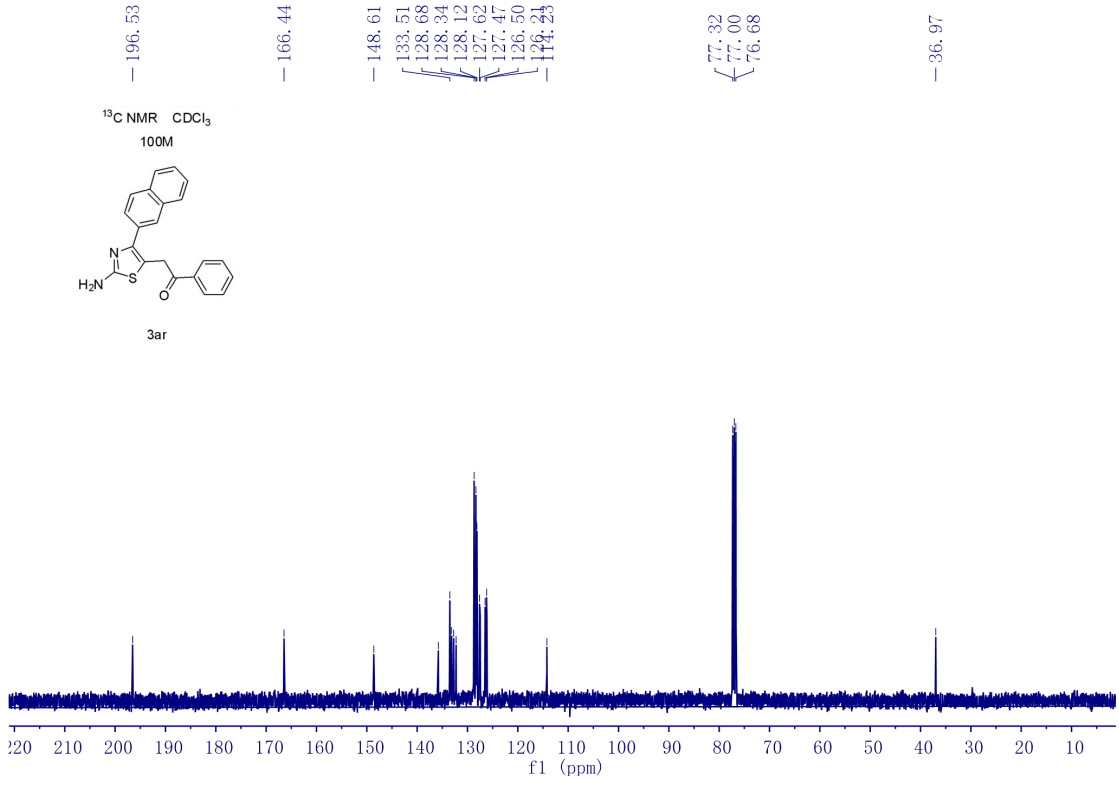
7.564
7.552
7.497
7.485
7.477
7.468
7.457
7.432
7.419
7.406
7.257
5.180
4.471
0.000
1H NMR CDCl3
600M
3ar
4.96
1.02
0.99
1.00
2.00
2.02
1.97
2.05
f1 (ppm)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128.34
128.12
127.62
127.47
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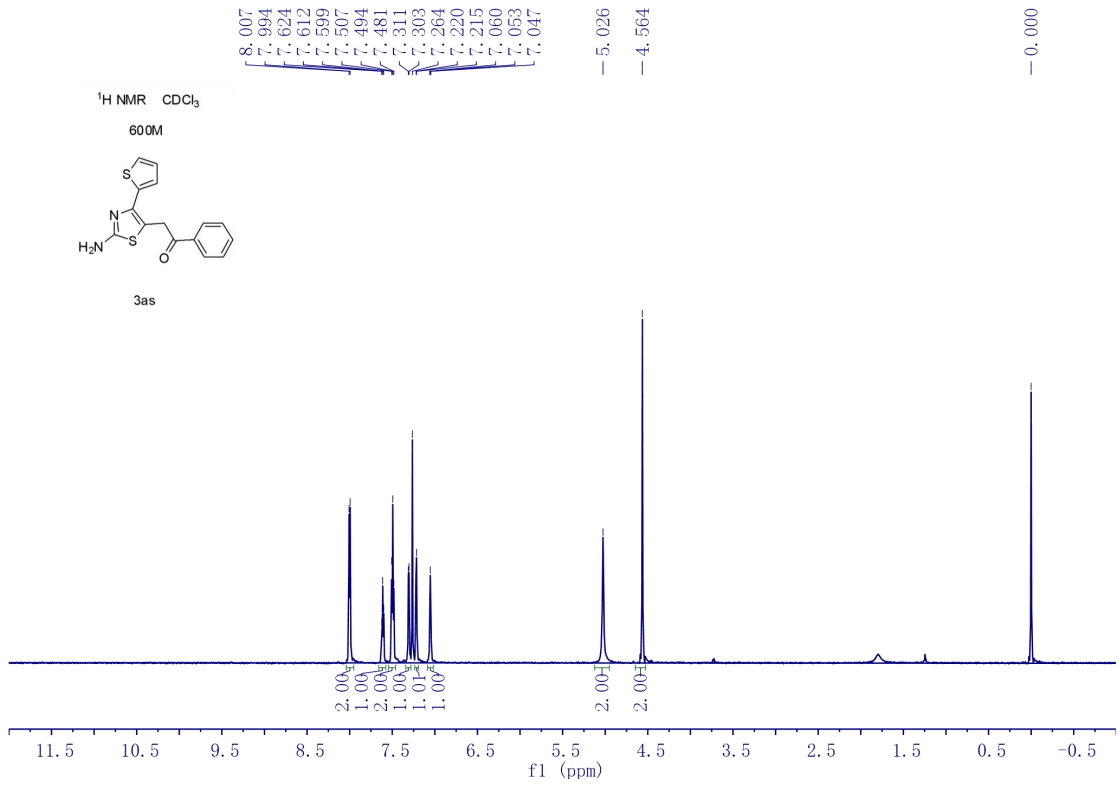
126.21
114.23
77.32
77.00
76.68
36.97
13C NMR CDCl3
100M
3ar
f1 (ppm)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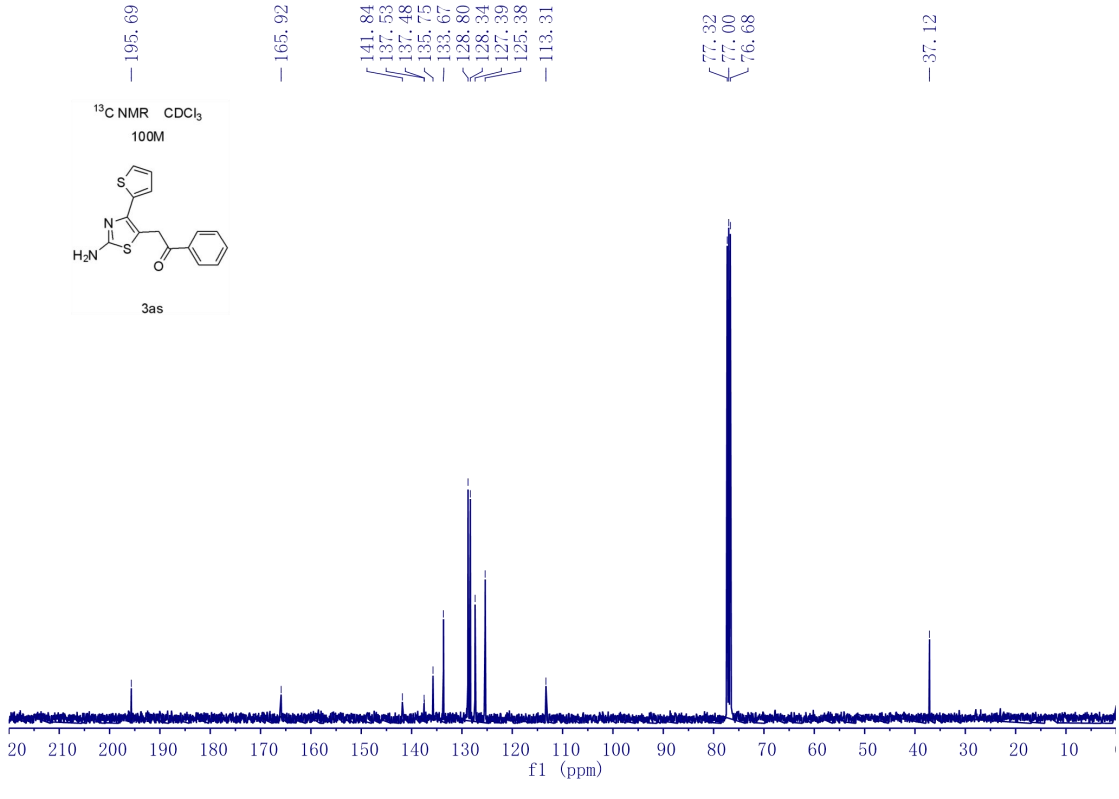
7.624
7.612
7.599
7.507
7.494
7.481
7.311
7.303
7.264
7.220
7.215
7.060
7.053
7.047
5.026
4.564
0.000
1H NMR CDCl3
600M
3as
2.00
1.00
2.00
1.00
1.01
1.00
2.00
2.00
f1 (ppm)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165.92
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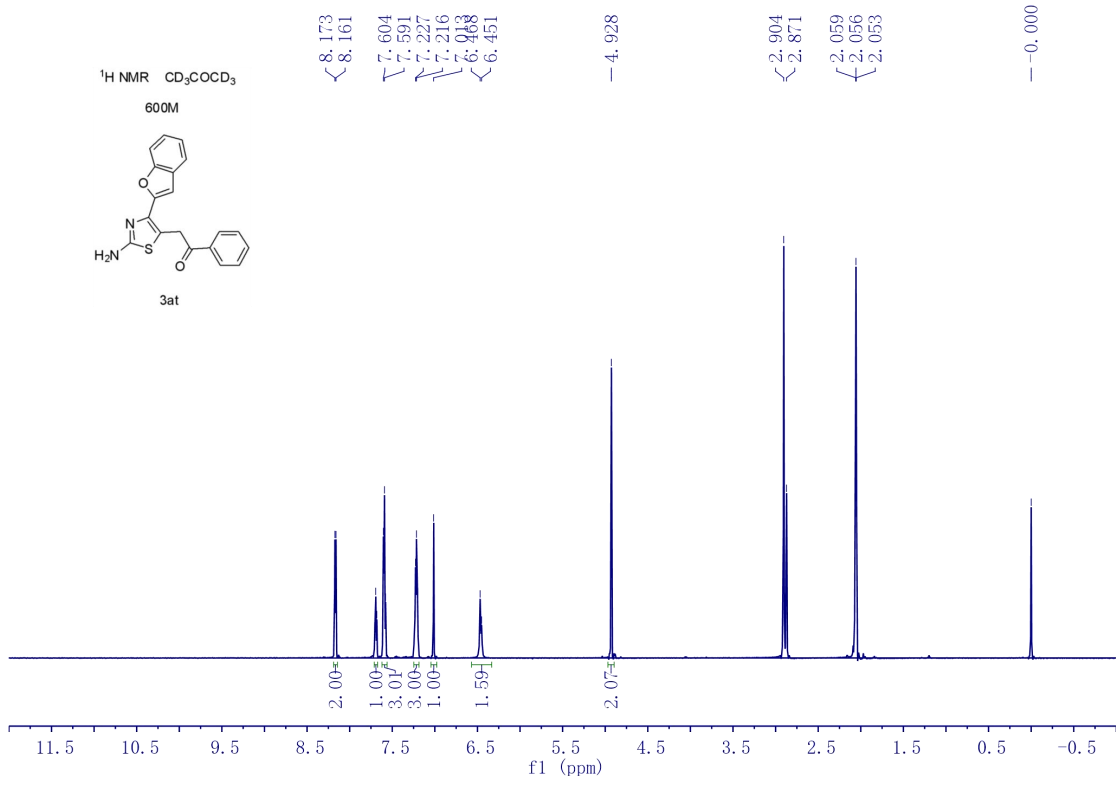
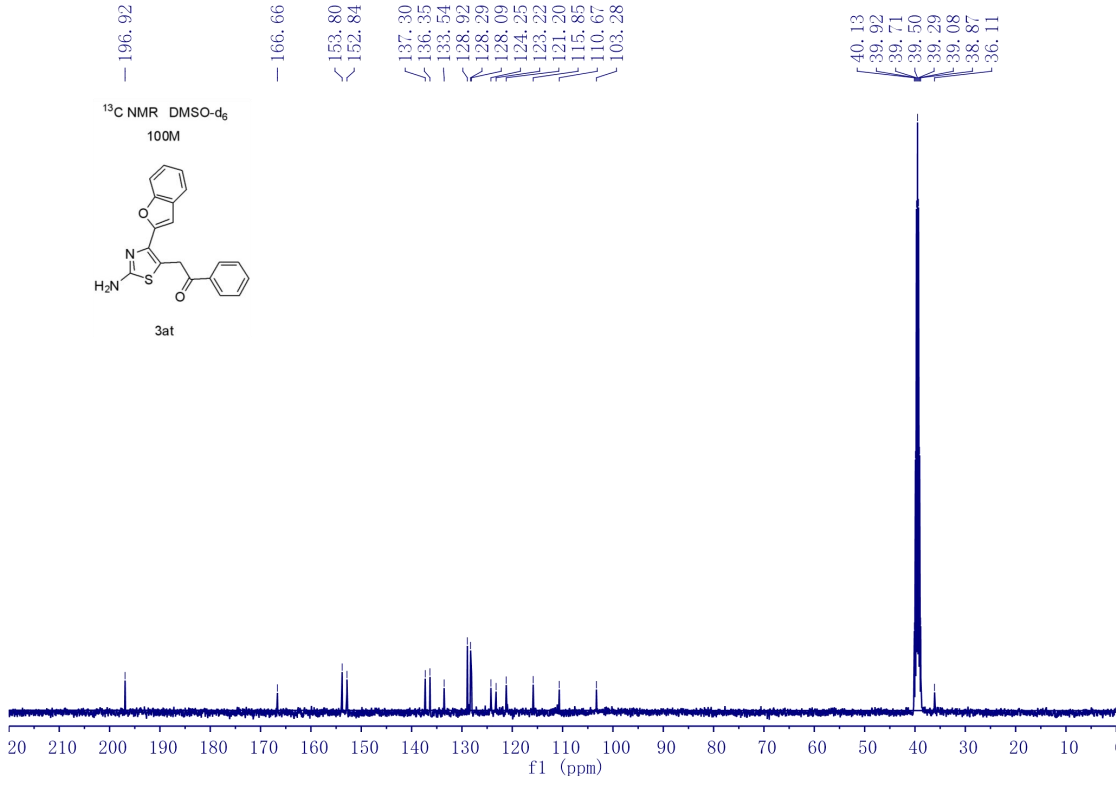
137.53
137.48
135.75
133.67
128.80
128.34
127.39
125.38
113.31
77.32
77.00
76.68
37.12
13C NMR CDCl3
100M
3as
f1 (ppm)



^{1}H NMR CD_3COCD_3

600M

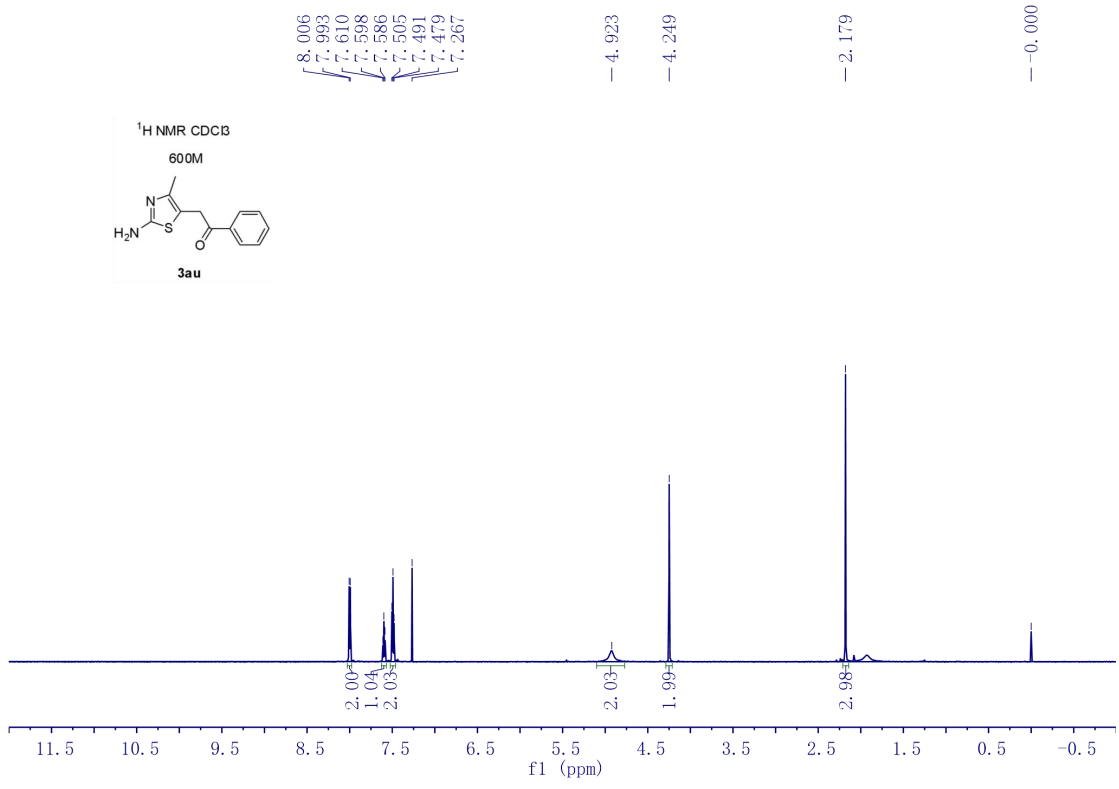
3at



^{13}C NMR DMSO-d_6

100M

3at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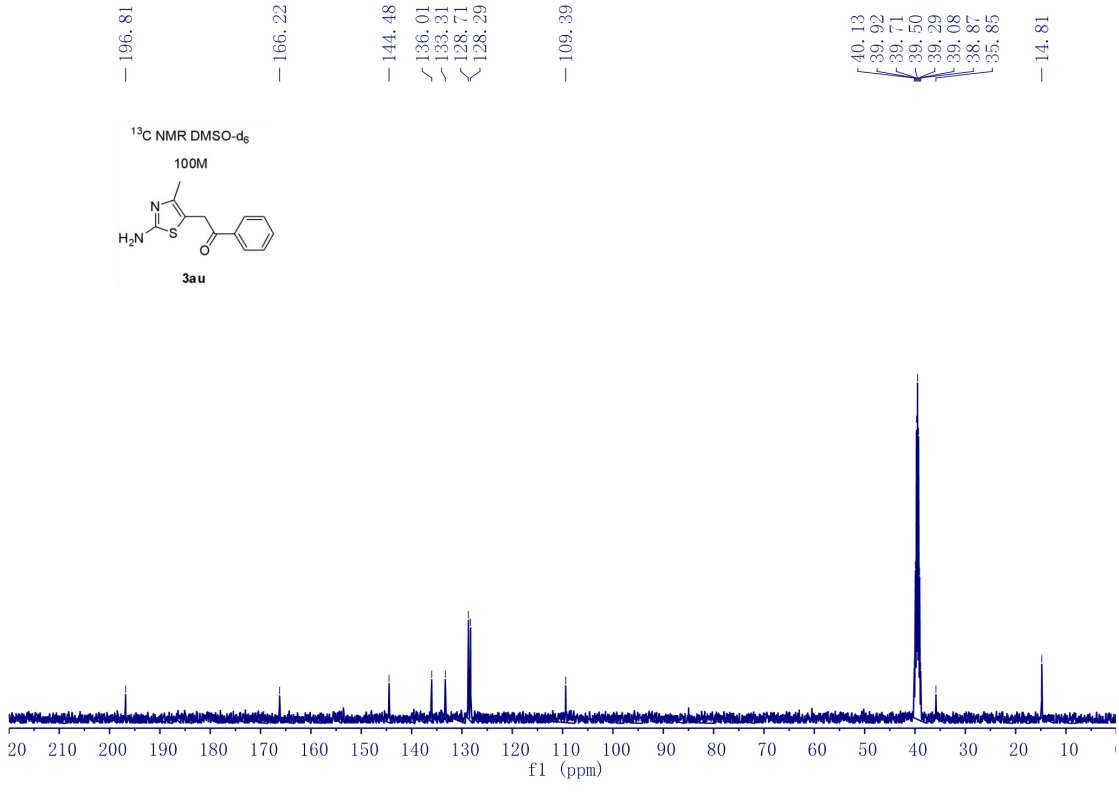
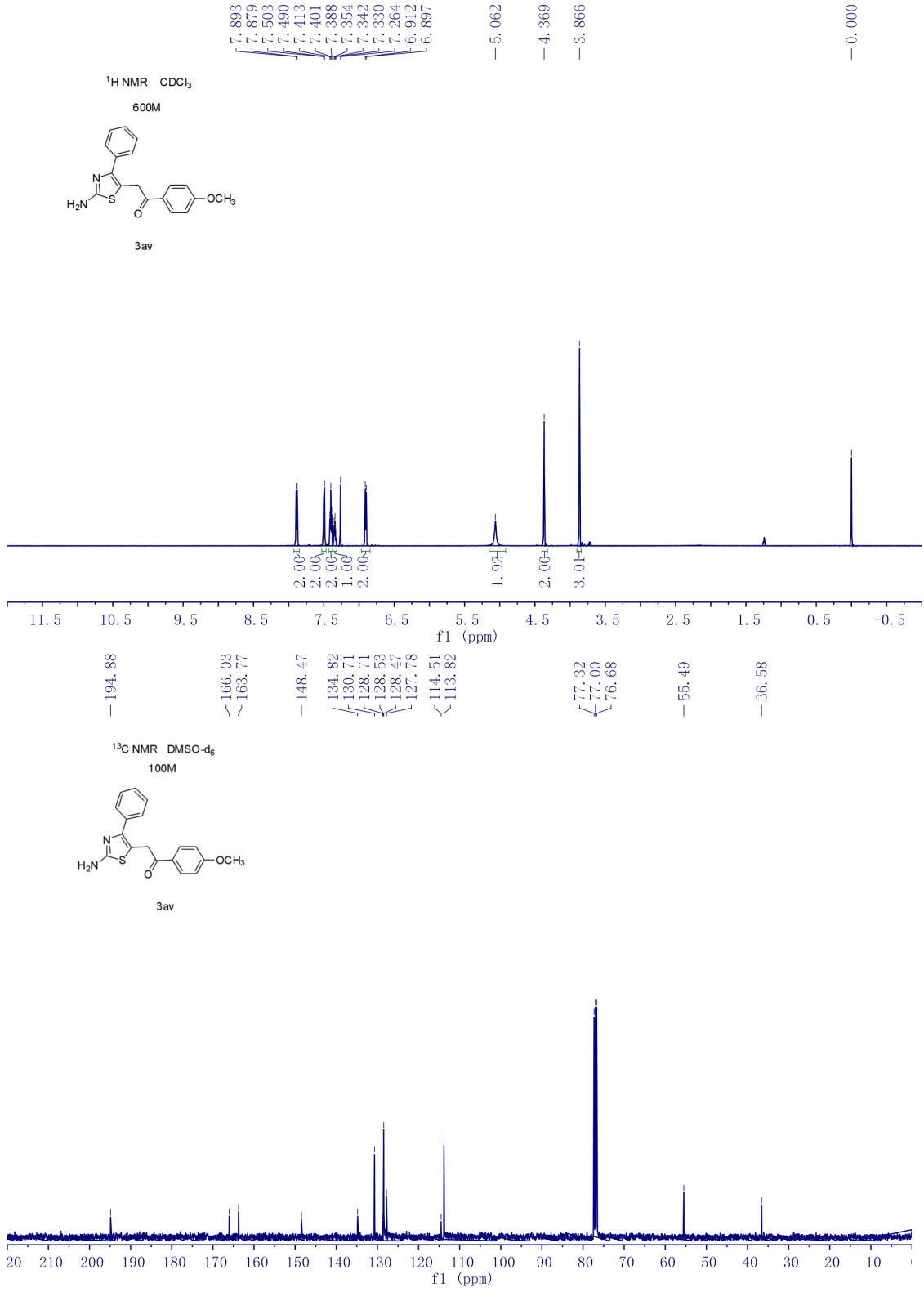
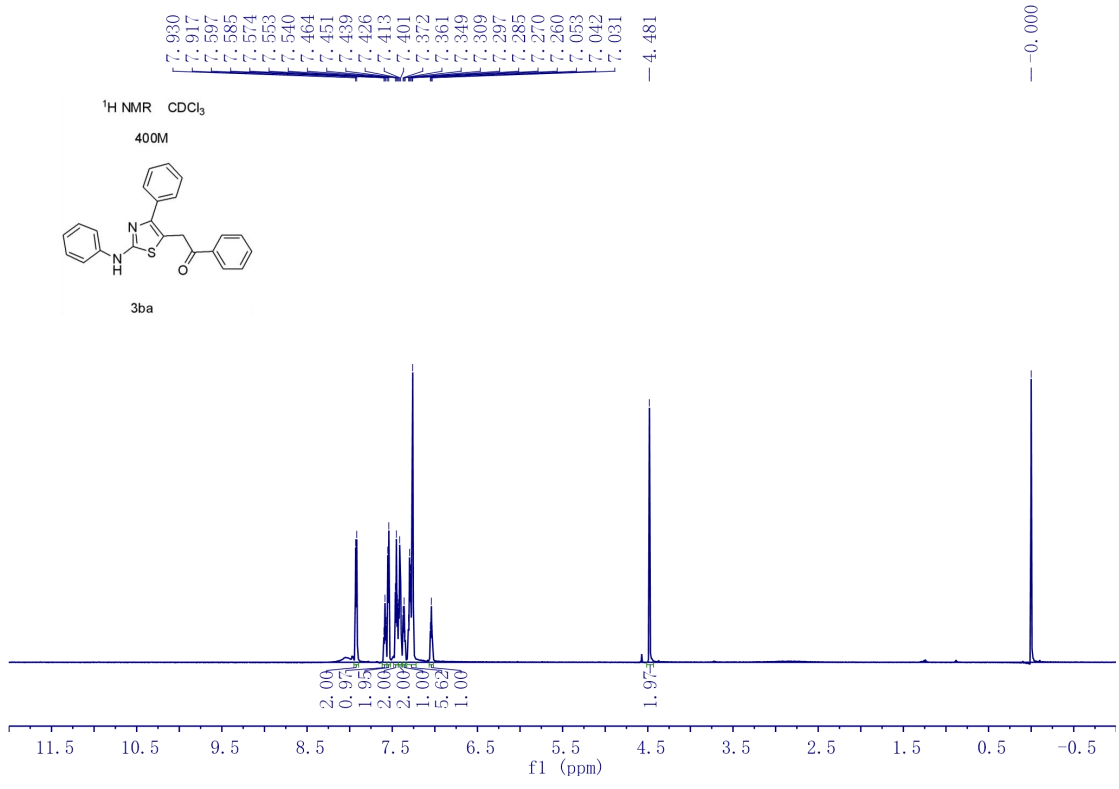
7.993
7.610
7.598
7.586
7.505
7.491
7.479
7.267
4.923
4.249
2.179
0.000
^{1}H NMR CDCl3
600M
3au
2.00
1.04
2.03
2.03
1.99
2.98
f1 (ppm)


196.81
166.22
144.48
136.01
133.31
128.71
128.29
109.39
40.13
39.92
39.71
39.50
39.29
39.08
38.87
35.85
14.81
^{13}C NMR DMSO-d$_6$
100M
3au
f1 (ppm)


7.893
7.879
7.503
7.490
7.413
7.401
7.388
7.354
7.342
7.330
7.264
6.912
6.897
5.062
4.369
3.866
0.000
1H NMR CDCl3
600M
3av
2.00
2.00
2.00
1.00
2.00
1.92
2.00
3.01
f1 (ppm)
194.88
166.03
163.77
148.47
134.82
130.71
128.71
128.53
128.47
127.78
114.51
113.82
77.32
77.00
76.68
55.49
36.58
13C NMR DMSO-d6
100M
3av
f1 (ppm)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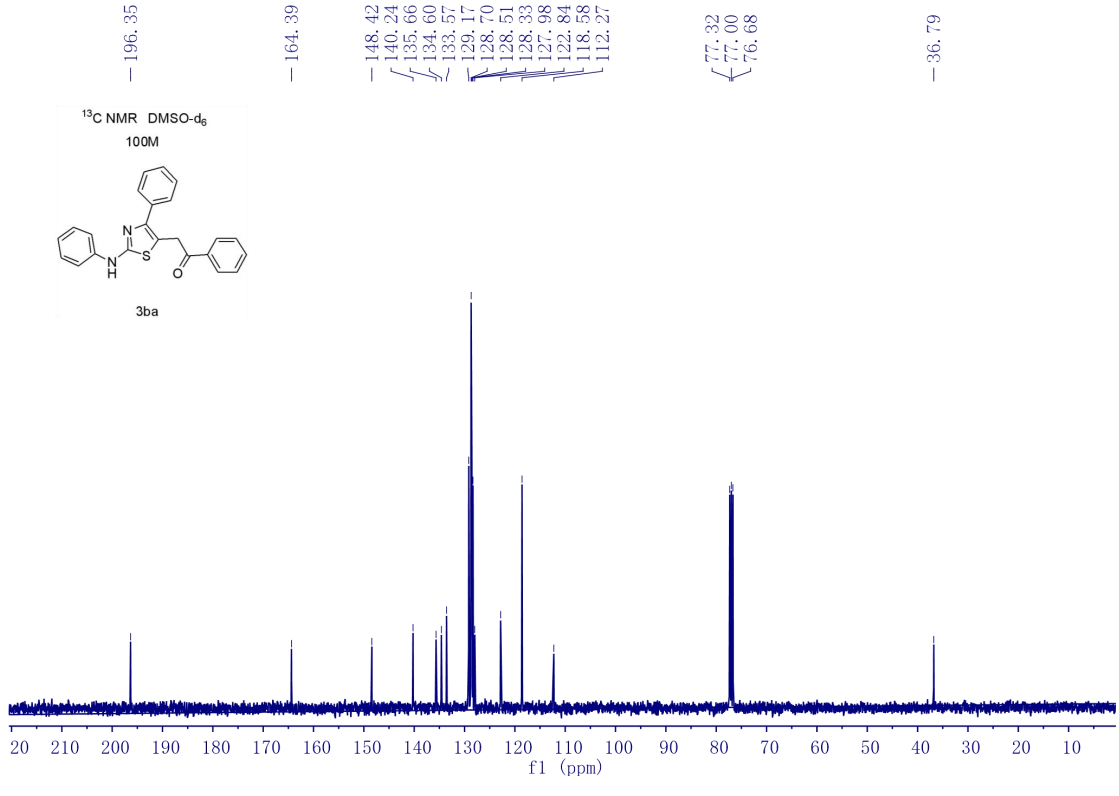
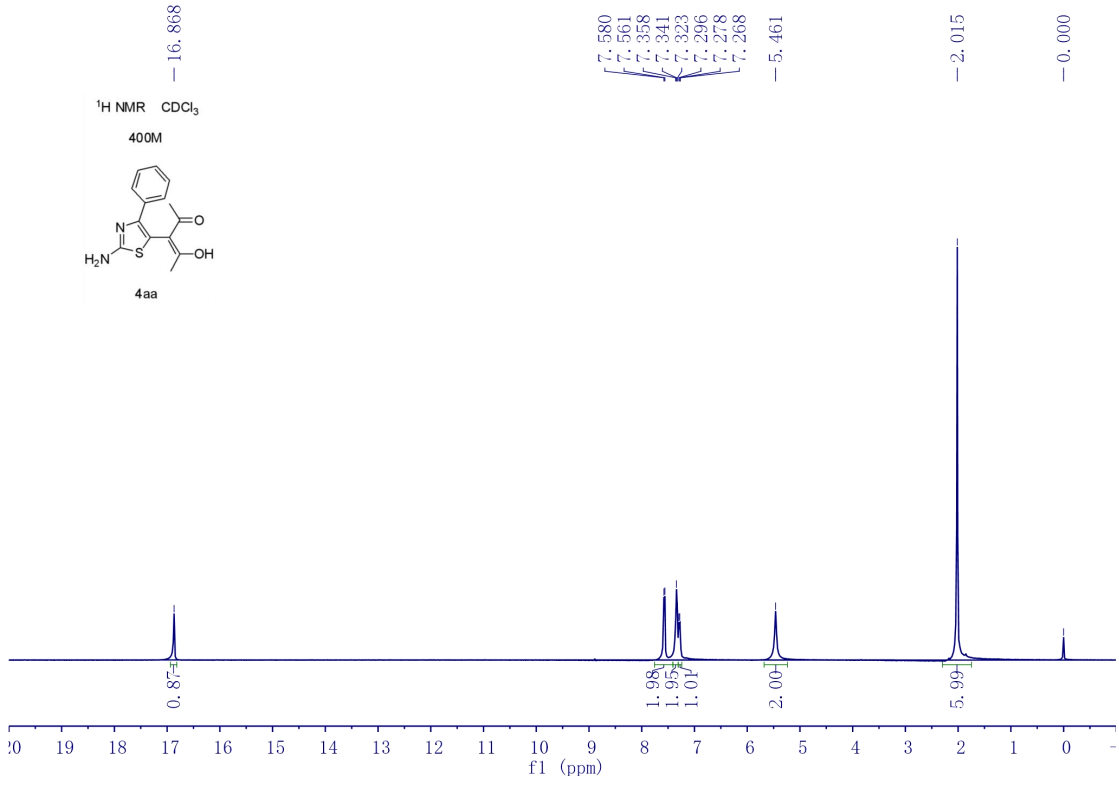
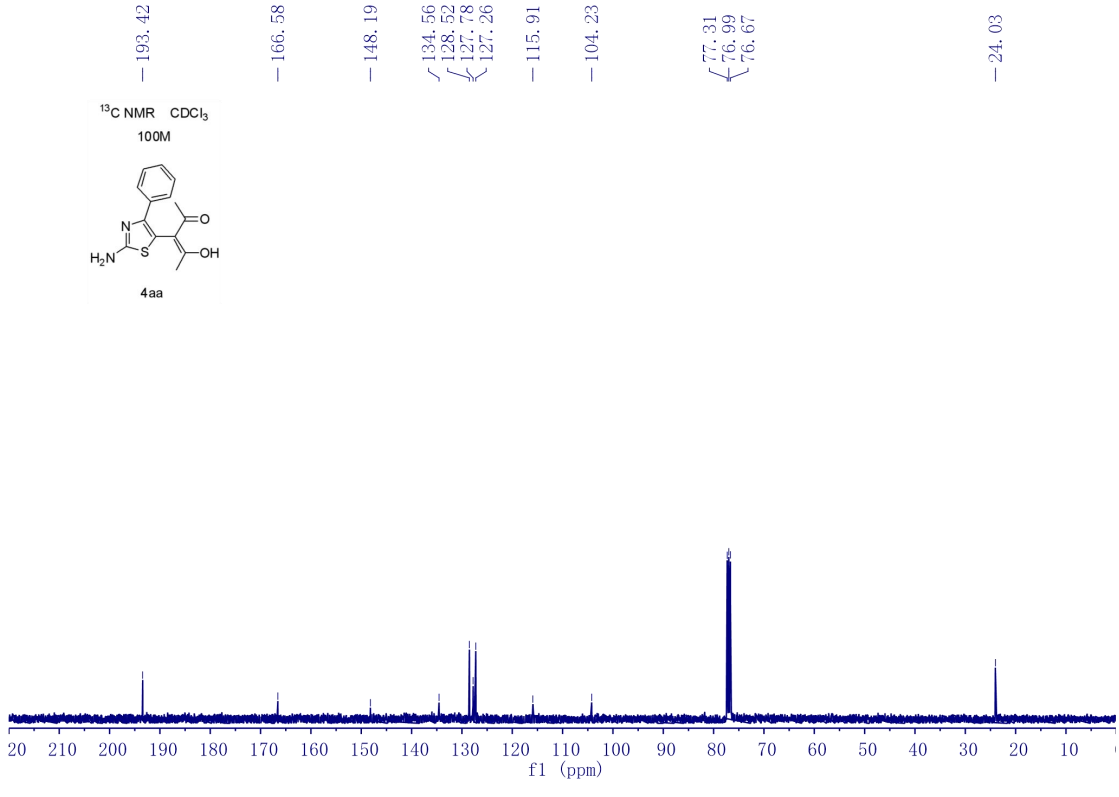
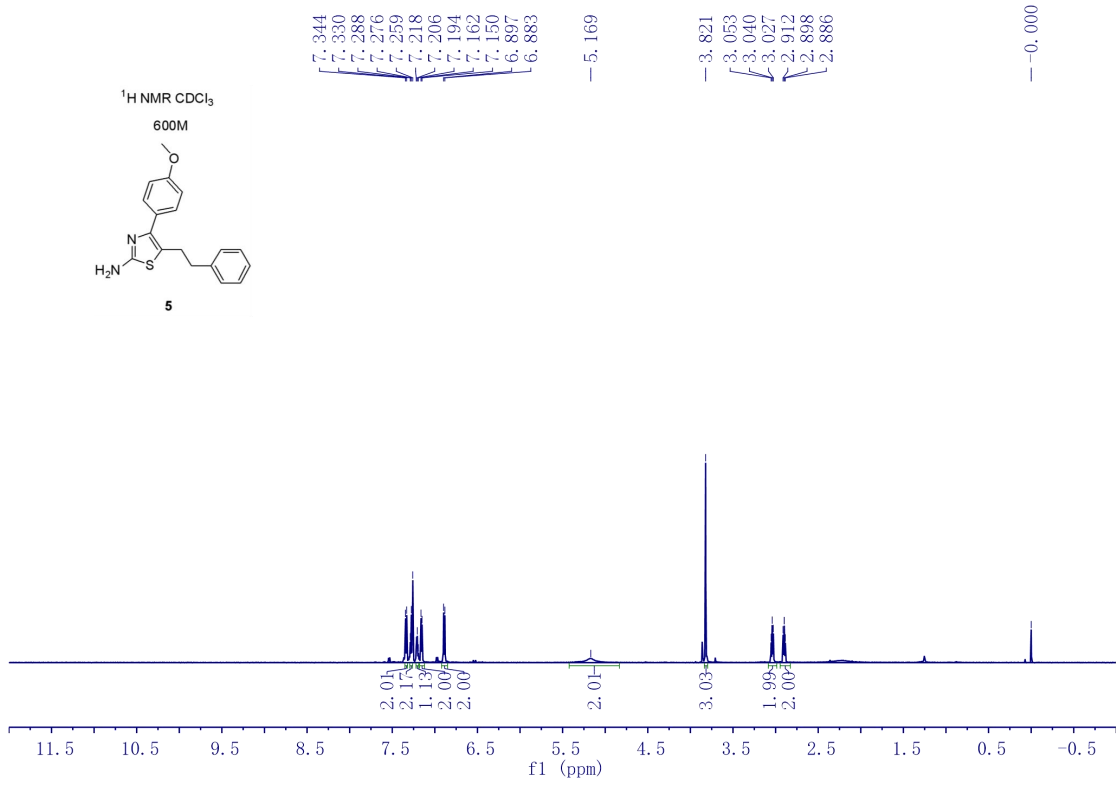
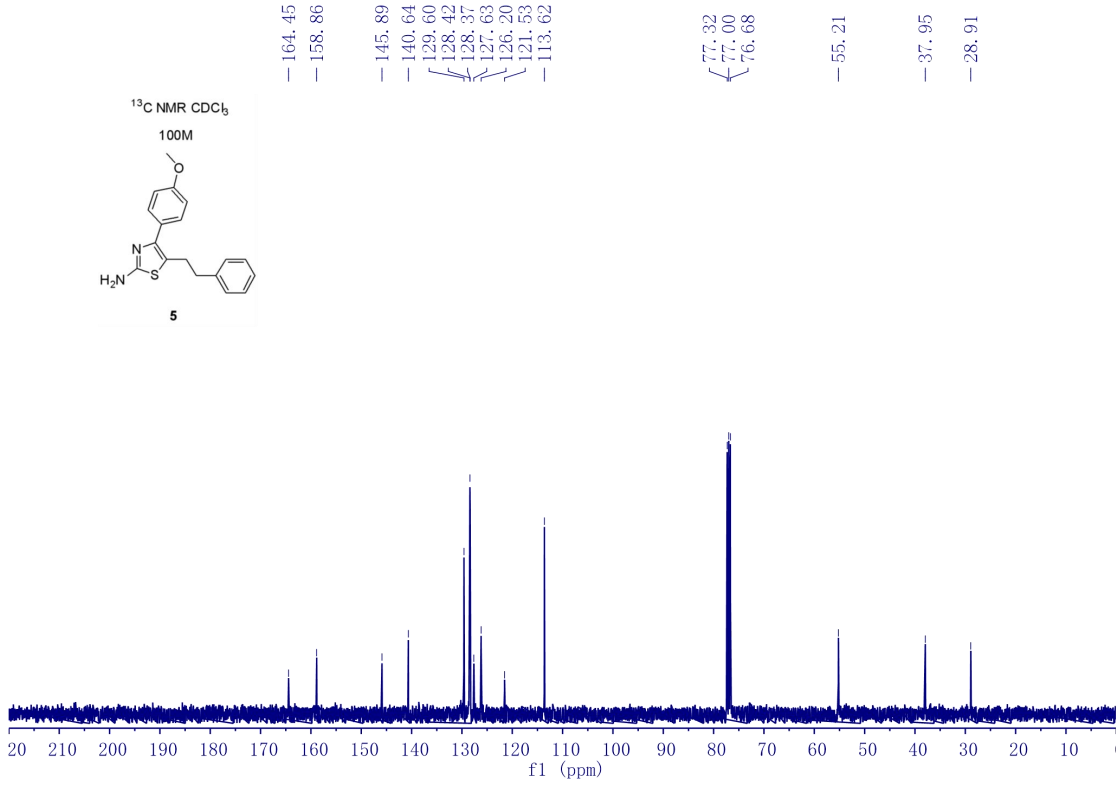
7.917
7.597
7.585
7.574
7.553
7.540
7.464
7.451
7.439
7.426
7.413
7.401
7.372
7.361
7.349
7.309
7.297
7.285
7.270
7.260
7.053
7.042
7.031
4.481
0.000
1H NMR CDCl3
400M
3ba
2.00
0.97
1.95
2.00
2.00
1.00
5.62
1.00
1.97
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

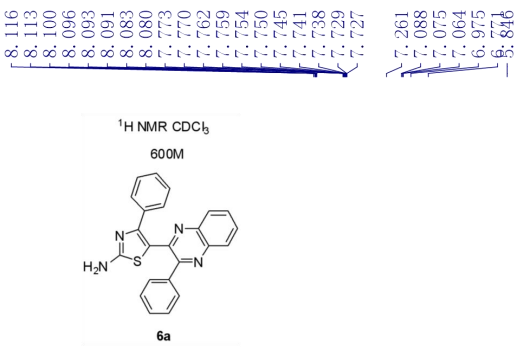

196.35
164.39
148.42
140.24
135.66
134.60
133.57
129.17
128.70
128.51
128.33
127.98
122.84
118.58
112.27
77.32
77.00
76.68
36.79
13C NMR DMSO-d6
100M
3ba
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

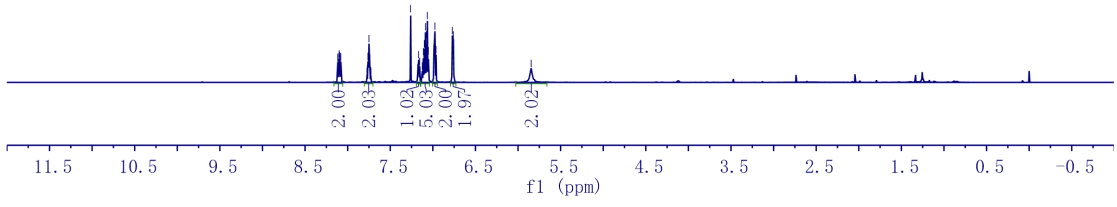

16.868
7.580
7.561
7.358
7.341
7.323
7.296
7.278
7.268
5.461
2.015
0.000
1H NMR CDCl3
400M
4aa
0.87
1.98
1.95
1.01
2.00
5.99
f1 (ppm)

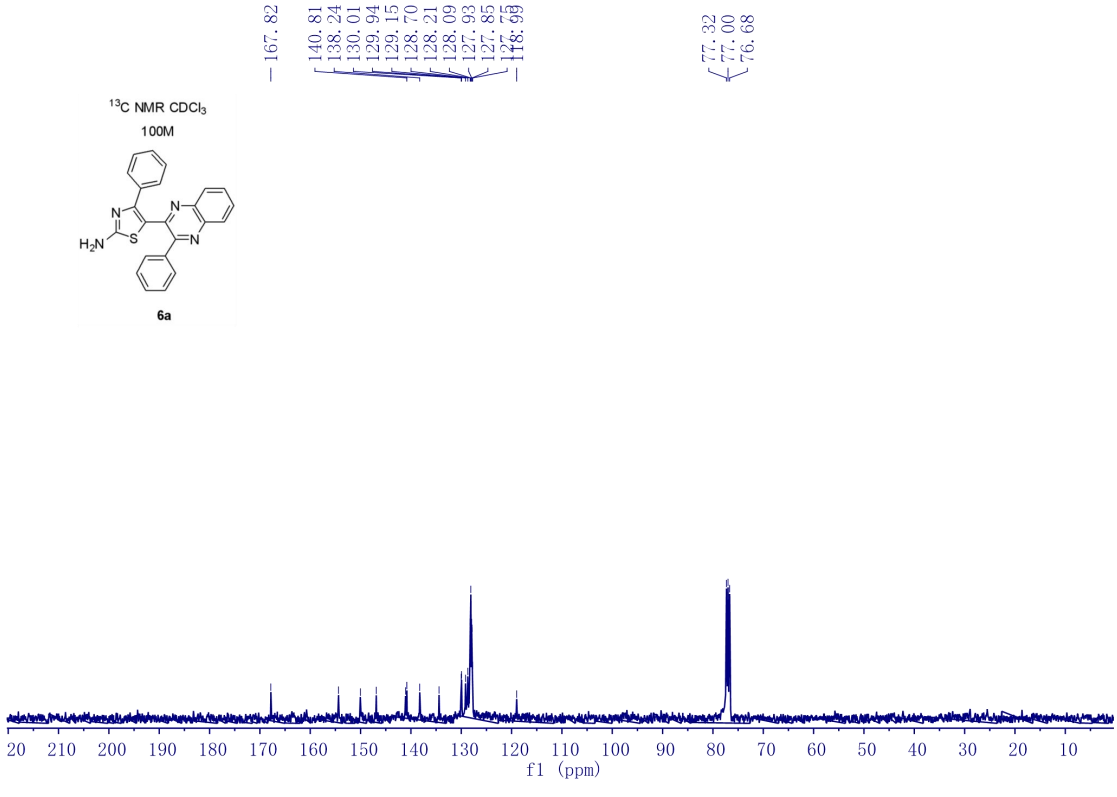

193.42
166.58
148.19
134.56
128.52
127.78
127.26
115.91
104.23
77.31
76.99
76.67
24.03
13C NMR CDCl3
100M
4aa
f1 (ppm)

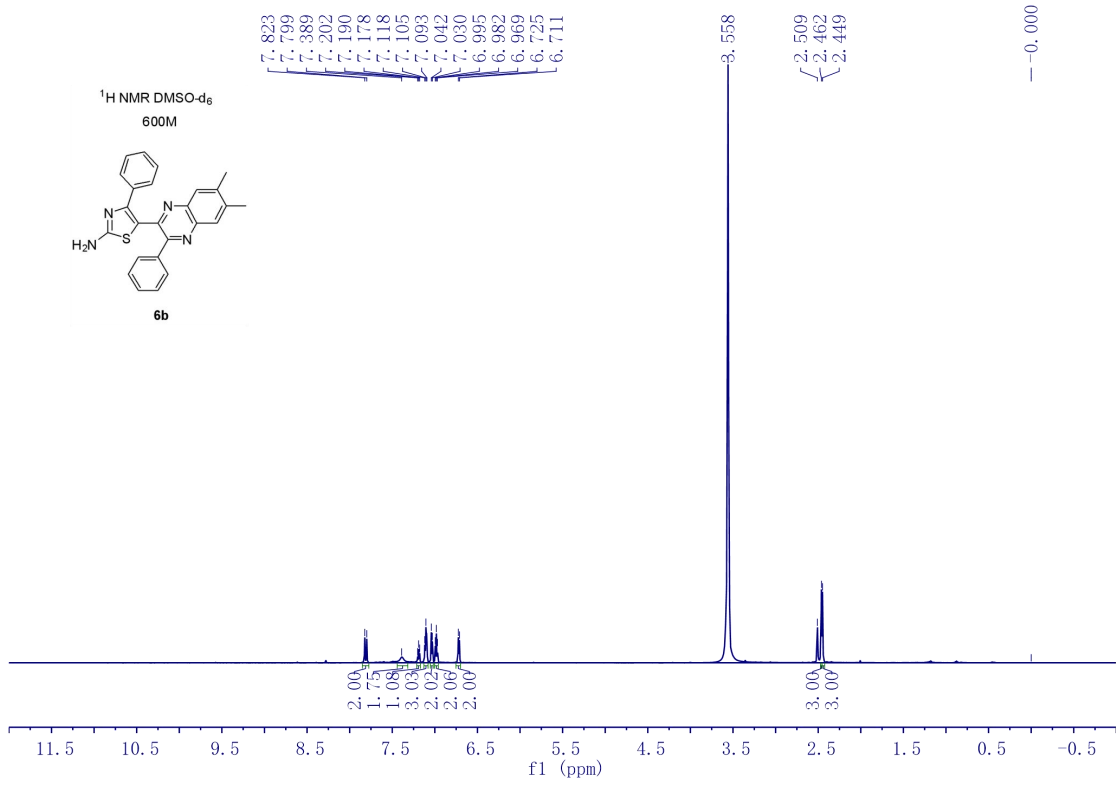

7.344
7.330
7.288
7.276
7.259
7.218
7.206
7.194
7.162
7.150
6.897
6.883
5.169
3.821
3.053
3.040
3.027
2.912
2.898
2.886
0.000
^{1}H NMR CDCl$_3$
600M
5
2.01
2.17
1.13
2.00
2.00
2.01
3.03
1.99
2.00
f1 (ppm)

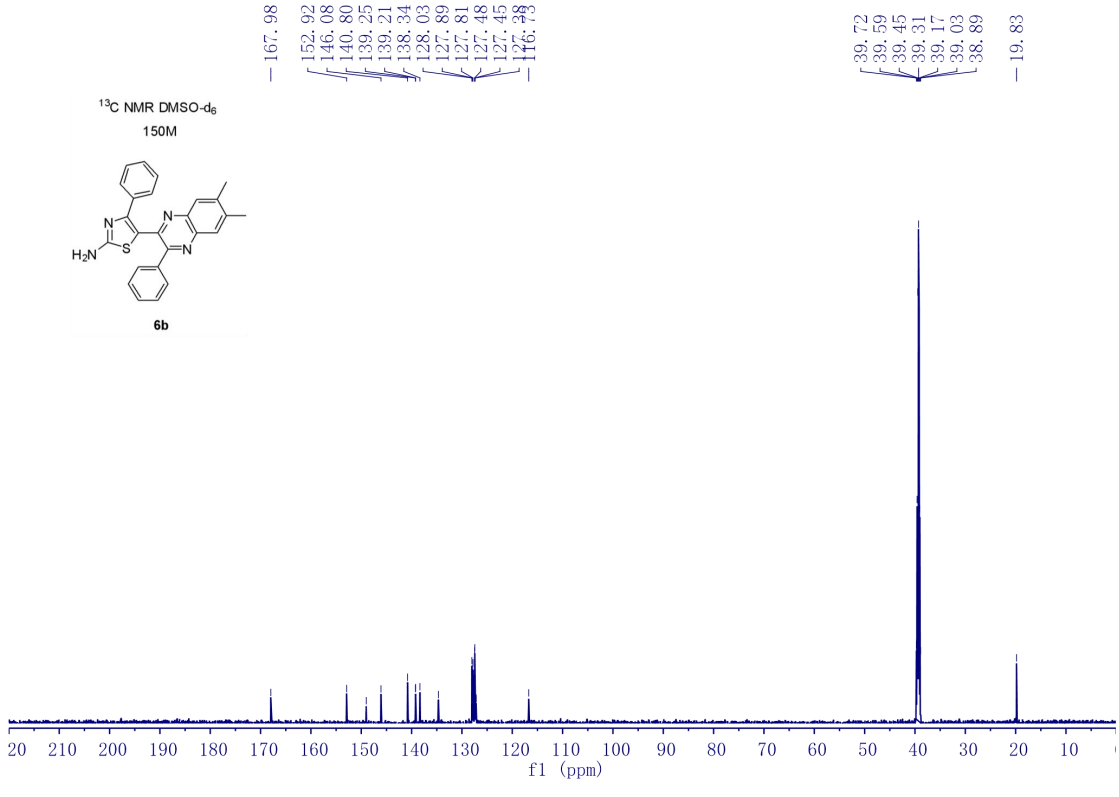

164.45
158.86
145.89
140.64
129.60
128.42
128.37
127.63
126.20
121.53
113.62
77.32
77.00
76.68
55.21
37.95
28.91
^{13}C NMR CDCl$_3$
100M
5
f1 (ppm)

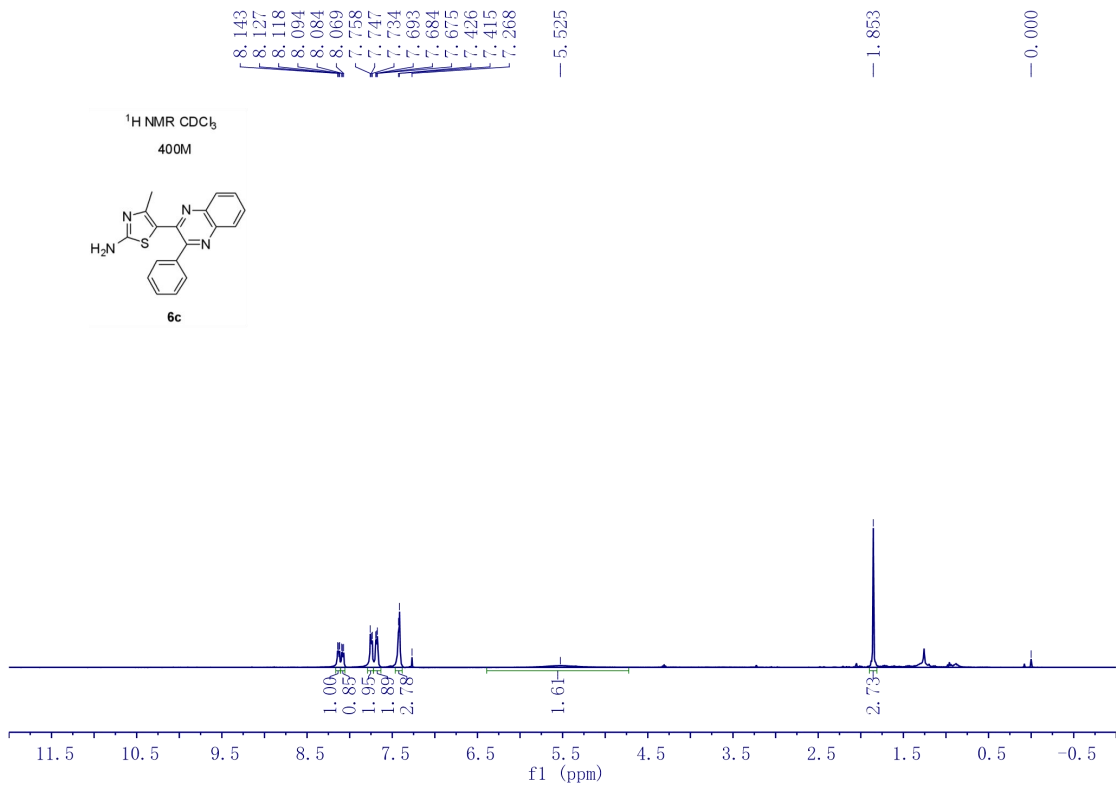

8.116
8.113
8.100
8.096
8.093
8.091
8.083
8.080
7.773
7.770
7.762
7.759
7.754
7.750
7.745
7.741
7.738
7.729
7.727
7.261
7.088
7.075
7.064
6.975
6.771
5.846
1H NMR CDCl3
600M
6a

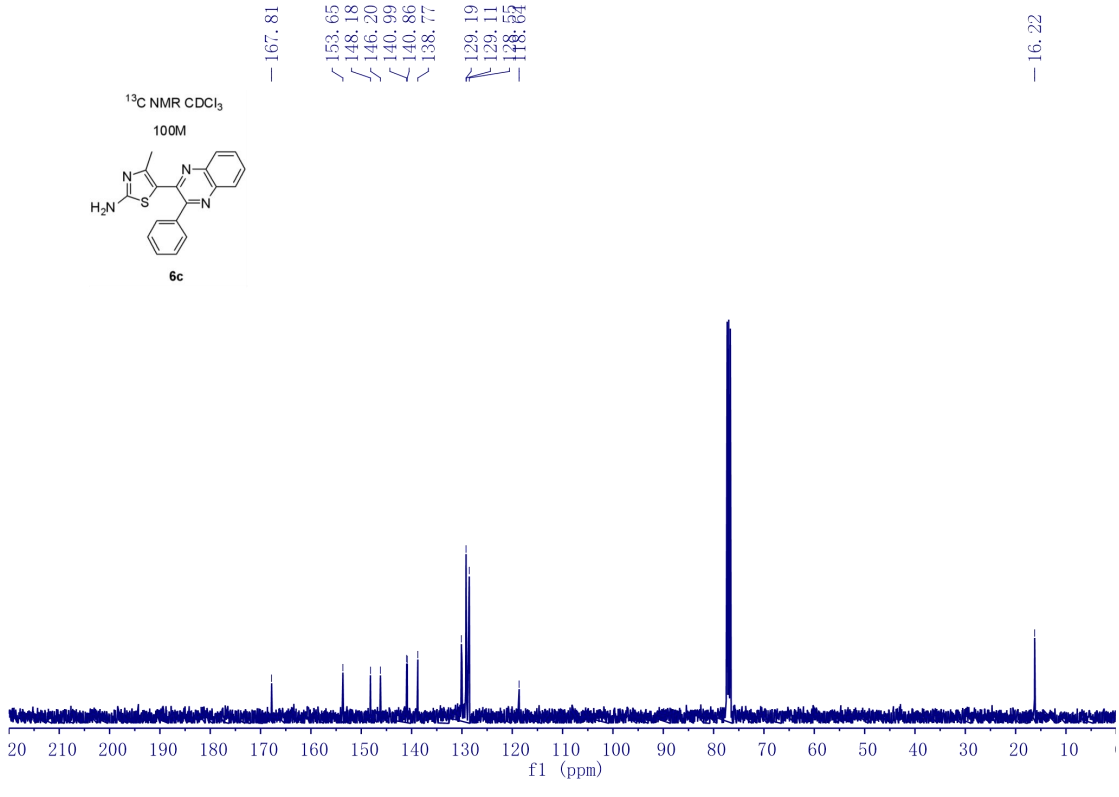

2.00
2.03
1.02
5.03
2.00
1.97
2.02
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

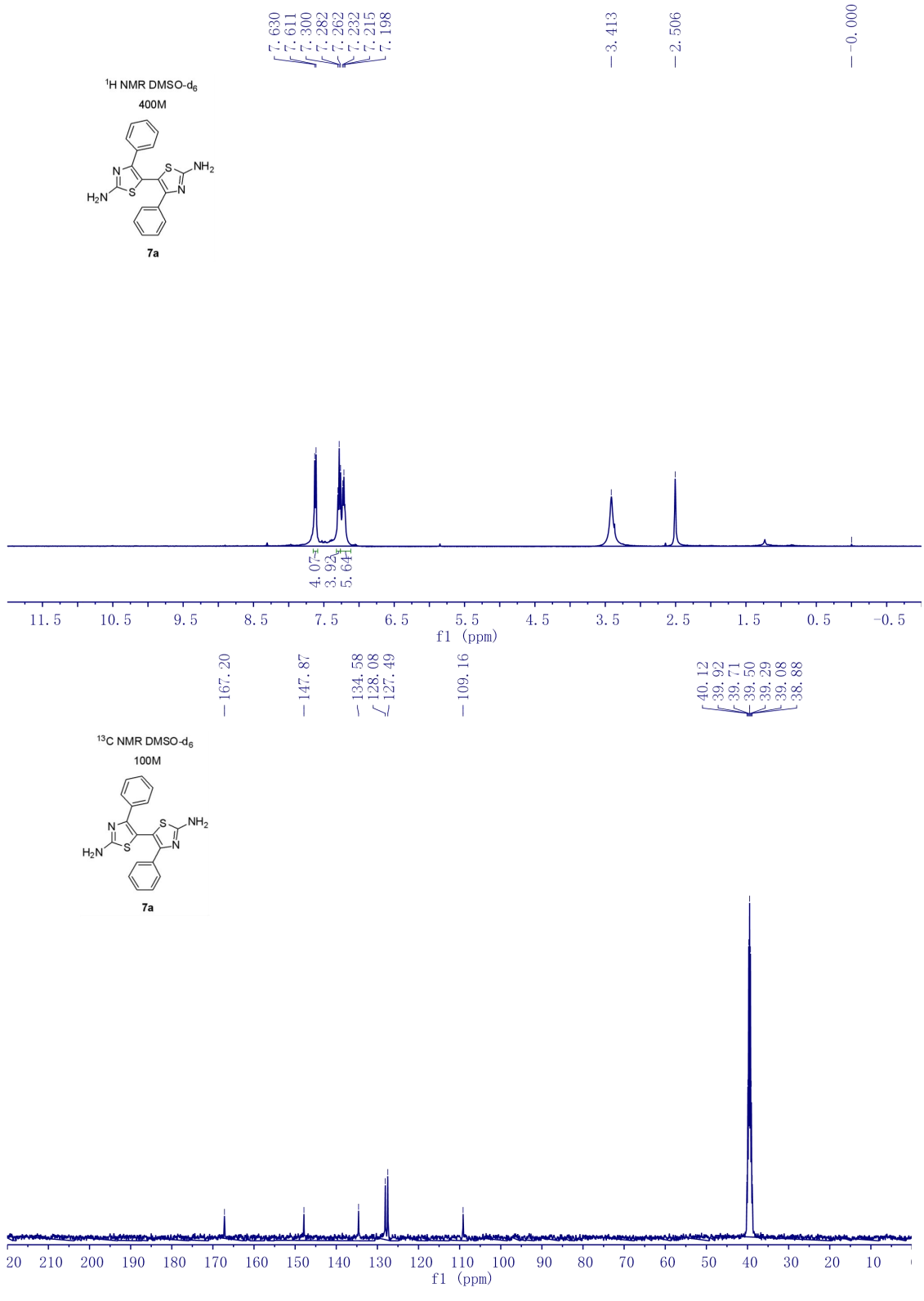

167.82
140.81
138.24
130.01
129.94
129.15
128.70
128.21
128.09
127.93
127.85
127.75
118.99
77.32
77.00
76.68
13C NMR CDCl3
100M
6a
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.823
7.799
7.389
7.202
7.190
7.178
7.118
7.105
7.093
7.042
7.030
6.995
6.982
6.969
6.725
6.711
3.558
2.509
2.462
2.449
0.000
^{1}H NMR DMSO-d$_6$
600M
6b
2.00
1.75
1.08
3.03
2.02
2.06
2.00
3.00
3.00
f1 (ppm)


167.98
152.92
146.08
140.80
139.25
139.21
138.34
128.03
127.89
127.81
127.48
127.45
116.73
39.72
39.59
39.45
39.31
39.17
39.03
38.89
19.83
^{13}C NMR DMSO-d$_6$
150M
6b
f1 (ppm)


8.143
8.127
8.118
8.094
8.084
8.069
7.758
7.747
7.734
7.693
7.684
7.675
7.426
7.415
7.268
5.525
1.853
0.000
1H NMR CDCl3
400M
6c
1.00
0.85
1.95
1.89
2.78
1.61
2.73
f1 (ppm)


167.81
153.65
148.18
146.20
140.99
140.86
138.77
129.19
129.11
128.55
118.64
16.22
13C NMR CDCl3
100M
6c
f1 (ppm)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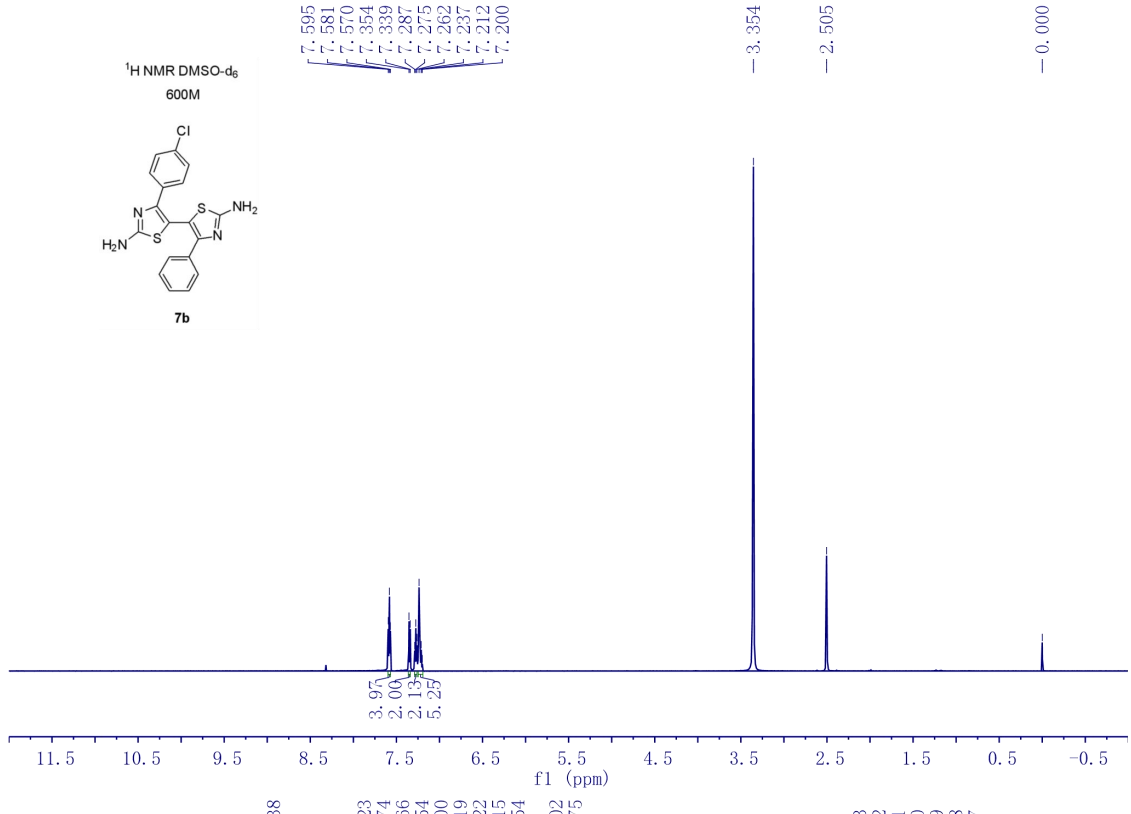
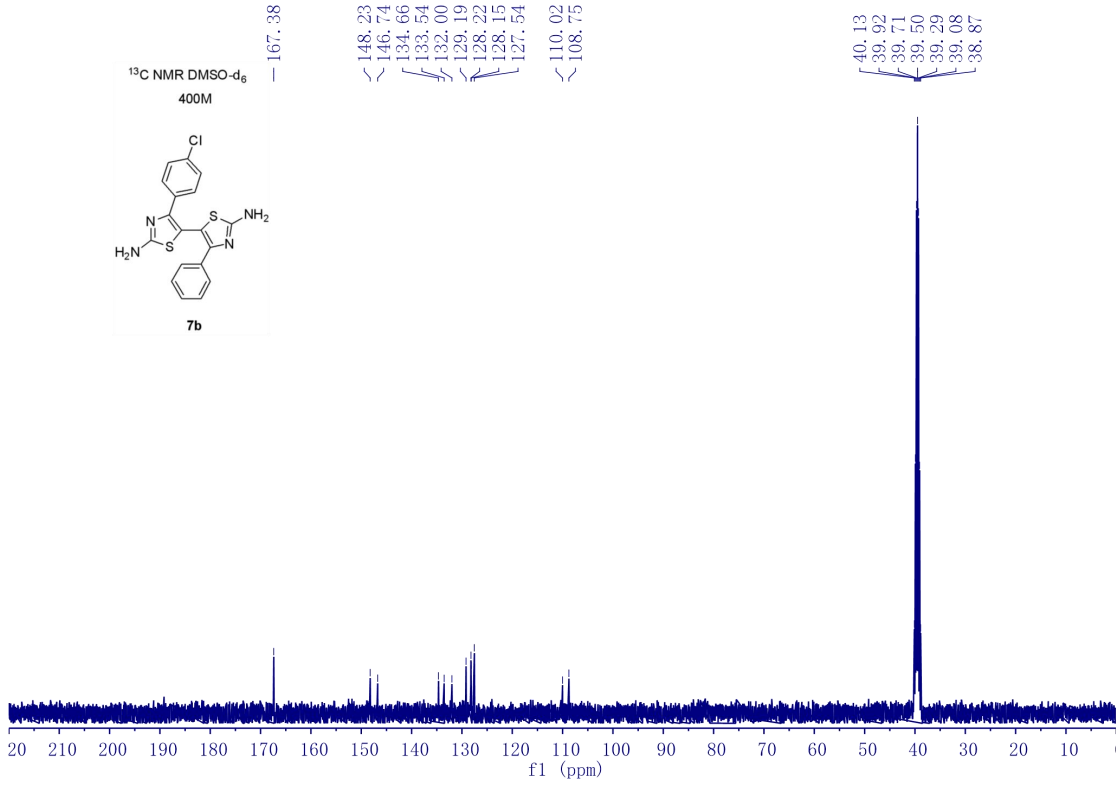
7.611
7.300
7.282
7.262
7.232
7.215
7.198
3.413
2.506
0.000
1H NMR DMSO-d6
400M
7a
4.07
3.92
5.64
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)
167.20
147.87
134.58
128.08
127.49
109.16
40.12
39.92
39.71
39.50
39.29
39.08
38.88
13C NMR DMSO-d6
100M
7a
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.595
7.581
7.570
7.354
7.339
7.287
7.275
7.262
7.237
7.212
7.200
3.354
2.505
0.000
1H NMR DMSO-d6
600M
Cl
N
S
NH2
H2N
7b
3.97
2.00
2.13
5.25
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)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148.23
146.74
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132.00
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128.22
128.15
127.54
110.02
108.75
40.13
39.92
39.71
39.50
39.29
39.08
38.87
13C NMR DMSO-d6
400M
Cl
N
S
NH2
H2N
7b
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)