Supporting Information

Di-*tert*-butyl peroxide as an effective two-carbon unit in oxidative radical cyclization toward 7-methylazolo[1,5-*a*]pyrimidines

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1. General

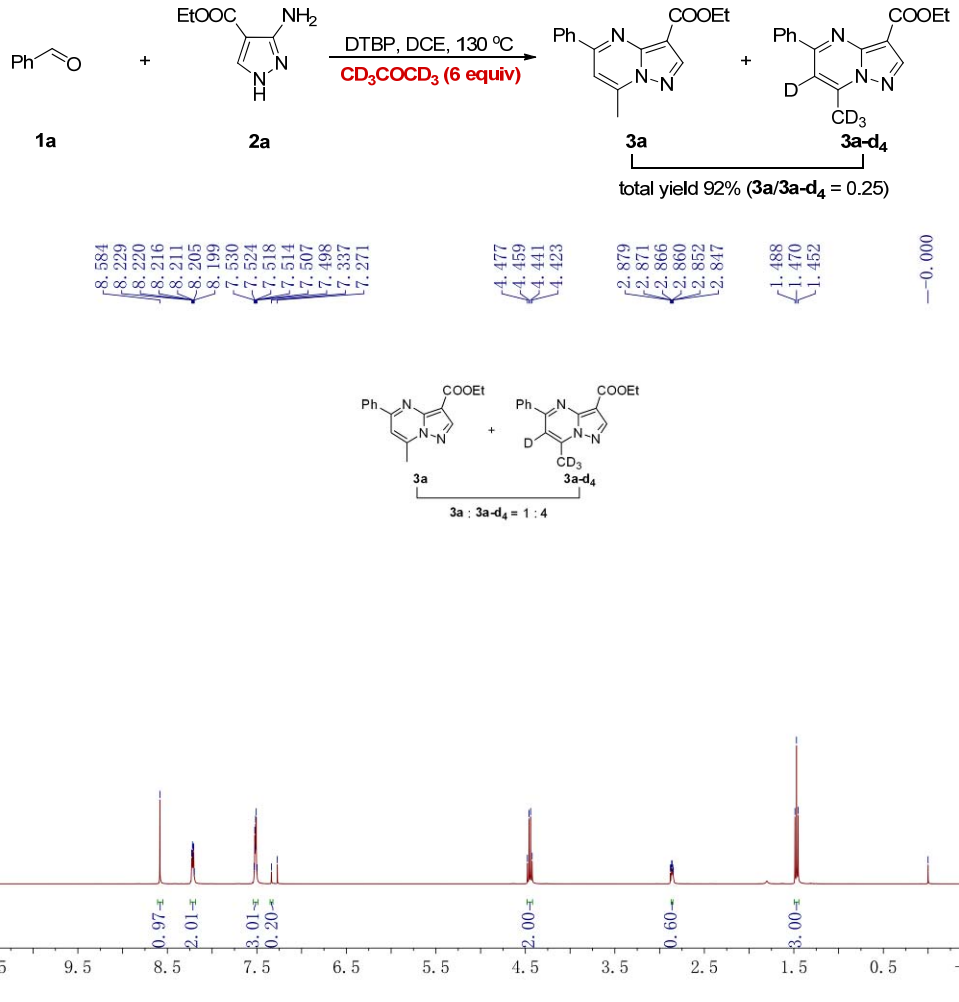
Substrates aromatic aldehydes (**1a**–**1ah**), 3(5)-aminoazoles (**2**), and reagents were commercially available and used without further purification. Aldehydes derivatives (**1ai**–**1al**) were synthesised using a reported procedure.[1] TLC analysis was performed using pre-coated glass plates. Column chromatography was performed using silica gel (200–300 mesh). ^{1}H spectra were recorded in $CDCl_3$ on 400 MHz NMR spectrometers and resonances (δ) are given in parts per million 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 $CDCl_3$ on 100 MHz NMR spectrometers and resonances (δ) are given in ppm. HRMS analysis of compounds was performed with a time-of-flight mass spectrometer (micrOTOF-Q, Bruker Daltonik, Germany) equipped with an electrospray ionization source. The X-ray crystal-structure determinations of **3a** were obtained on a Bruker SMART APEX CCD system. Melting points were determined using XT-4 apparatus and not corrected. All reactions were heated by a metal sand bath (WATTCAS, LAB-500, https://www.wattcas.com).

2. General procedure for the synthesis of compounds 4 (4aa as an example)

Benzaldehyde **1a** (53 mg, 0.5 mmol), ethyl 3-amino-1*H*-pyrazole-4-carboxylate **2a** (77.6 mg, 0.5 mmol), DTBP (219 mg, 1.5 mmol) and DCE (2.5 mL) were charged into a pressure tube (35 mL) and were stirred at 130 ºC for 10 h. After disappearance of the reactant (monitored by TLC), and added 50 mL water to the mixture, then extracted with EtOAc 3 times (3 × 50 mL), dried over anhydrous Na_2SO_4 and evaporation. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 8:1) to afford the product **3a** as a yellow solid (119.4 mg, 85% yield).

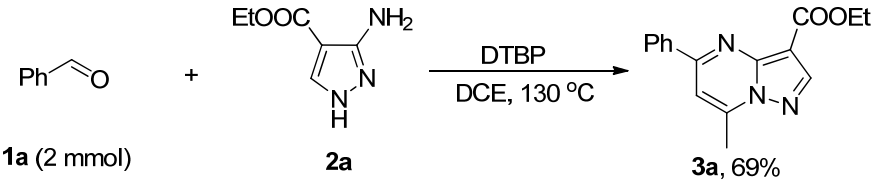
3. The D-labeling experiments and the spectrogram

Benzaldehyde **1a** (53 mg, 0.5 mmol), ethyl 3-amino-1*H*-pyrazole-4-carboxylate **2a** (77.6 mg, 0.5 mmol), DTBP (219 mg, 1.5 mmol), acetone-d_6 (192 mg, 3 mmol) and DCE (2.5 mL) were charged into a pressure tube (35 mL) and were stirred at 130 ºC for 10 h. After disappearance of the reactant (monitored by TLC), and added 50 mL water to the mixture, then extracted with EtOAc 3 times (3 × 50 mL), dried over anhydrous Na_2SO_4 and evaporation. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 8:1) to afford a mixture of **3a** and **3a-d$_4$** in a 92% total yield with 1 : 4 ratio. Then, the product was monitored by ^{1}H NMR (400 MHz), the spectral copies of ^{1}H NMR was listed in the following. This result reveals that the acetone molecule generated from DTBP was a real source of the methyl group and two-carbon unit of the product.



4. Experimental details

(1) The methodology applicable for scale-up synthesis (**3a** as an example)

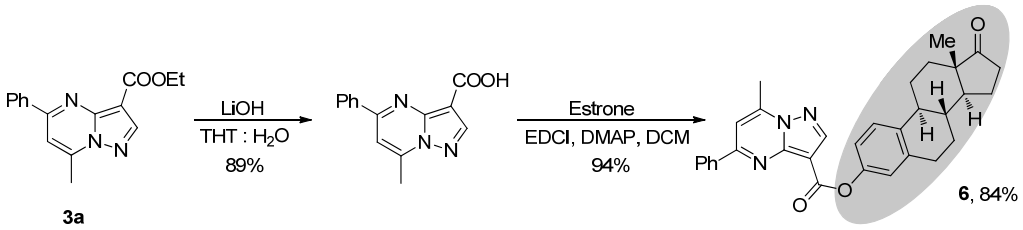


Benzaldehyde **1a** (212 mg, 2 mmol), ethyl 3-amino-1*H*-pyrazole-4-carboxylate **2a** (310 mg, 2 mmol), DTBP (876 mg, 6 mmol) and DCE (10 mL) were charged into a pressure tube (150 mL) and were stirred at 130 °C for 24 h. After disappearance of the reactant (monitored by TLC), and added 200 mL water to the mixture, then extracted with EtOAc 3 times (3 × 200 mL), dried over anhydrous Na_2SO_4 and evaporation. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 8:1) to afford the product **3a** as a yellow solid (388 mg, 69% yield).

(2) Experimental procedure for synthesis of compound **6**

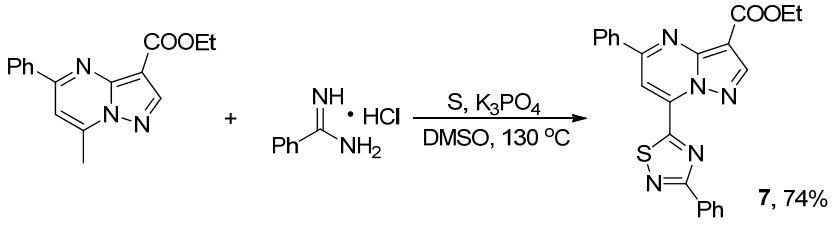
Ethyl 7-methyl-5-phenylpyrazolo[1,5-*a*]pyrimidine-3-carboxylate **3a** (140.5 mg, 0.5 mmol) and THF (2 mL) were charged into a pressure tube (15.0 mL). The mixture wasstirred at room temperature, then added LiOH (35.9 mg, 1.5 mmol) in water (2 mL) and stirred at same temperature for 12 h. Water was added and the solution was acidified with 6 M aqueous HCl to get precipitation, filtration and drying afforded 7-methyl-5-phenylpyrazolo[1,5-*a*]pyrimidine-3-carboxylic acid as a white solid (112.6 mg, 89% yield).

7-Methyl-5-phenylpyrazolo[1,5-*a*]pyrimidine-3-carboxylic acid (50.6 mg, 0.2 mmol)，estrone (54.1 g, 0.2 mmol), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (42.2 g, 1.1 mmol), *N*,*N*-dimethyl-4-aminopyridine (6.1 mg, 0.25 mmol) and CH_2Cl_2 (2 mL) were charged into a round-bottom flask (50 mL). After stirred at room temperature for 4 h, the reaction was quenched with 20 mL of saturated $NaHCO_3$ (aq.) and then extracted with CH_2Cl_2 (10 mL × 3). The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (petroleum ether/EtOAc = 2:1)to afford the product **6** as a white solid (95 mg, 94% yield).

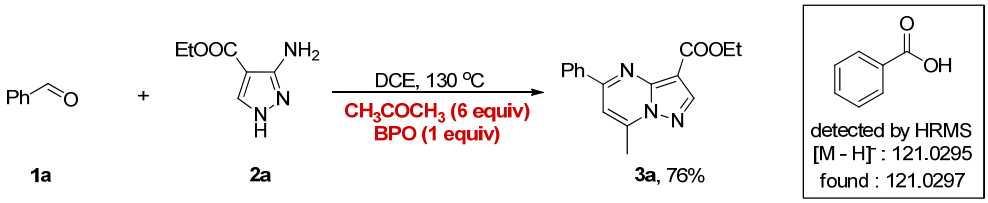


(3) Experimental procedure for synthesis of compound **7**

Using Deng' s group reported conditions,[2] A 35 mL pressure tube was charged with ethyl 7-methyl-5-phenylpyrazolo[1,5-*a*]pyrimidine-3-carboxylate **3a** (56.2 mg, 0.2 mmol)，benzimidamide hydrochloride (62.6 mg, 0.4 mmol), S (32 mg, 1.0 mmol), K_3PO_4 (127.4 mg, 0.6 mmol), and DMSO (0.6 mL) under air. The reaction vessel was stirred at 130 ºC for 12 h. After cooling to room temperature, the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 30:1) to yield the desired product **7** as white solid (63.2 mg, yield 74%).

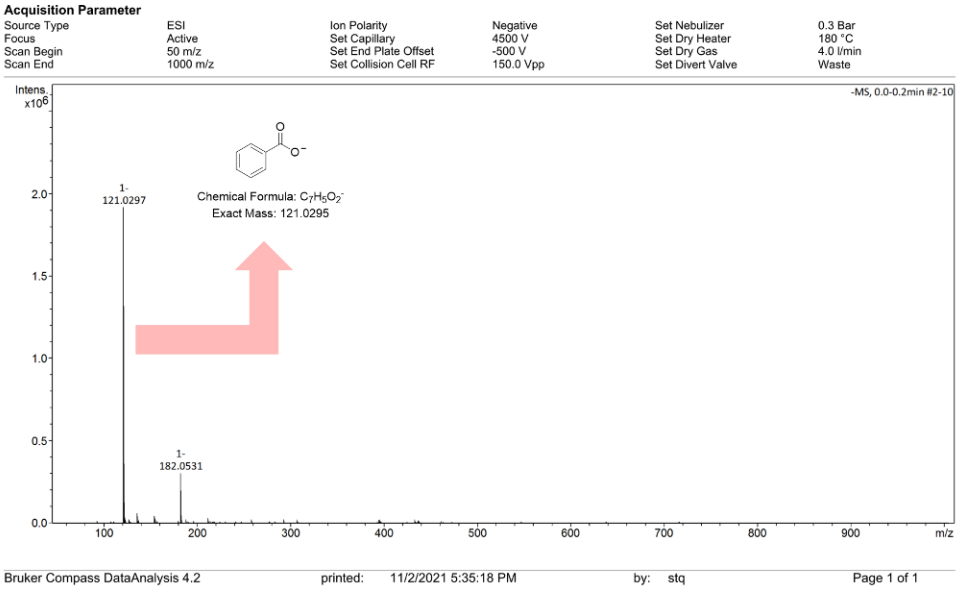


(4) the control experiment: (Scheme 5c)

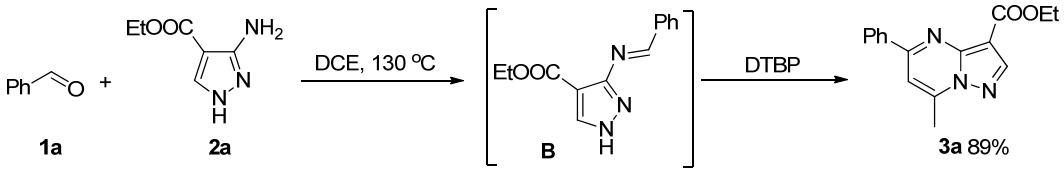


Benzaldehyde **1a** (53 mg, 0.5 mmol), ethyl 3-amino-1*H*-pyrazole-4-carboxylate **2a** (77.6 mg, 0.5 mmol), BPO (121 mg, 0.5 mmol), acetone (174 mg, 3 mmol) and DCE were charged

into a pressure tube (35 mL) and were stirred at 130 ºC for 10 h. After disappearance of the reactant (monitored by TLC), and added 50 mL water to the mixture, then extracted with EtOAc 3 times (3 × 50 mL), dried over anhydrous Na_2SO_4 and evaporation. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 8:1) to afford the product **3a** as a yellow solid (106.8 mg, 76% yield). Moreover, the formation of benzoic acid was proved by HRMS. HRMS (ESI): m/z $[M - H]^-$ calcd for $C_7H_5O_2$: 121.0295; found: 121.0297.

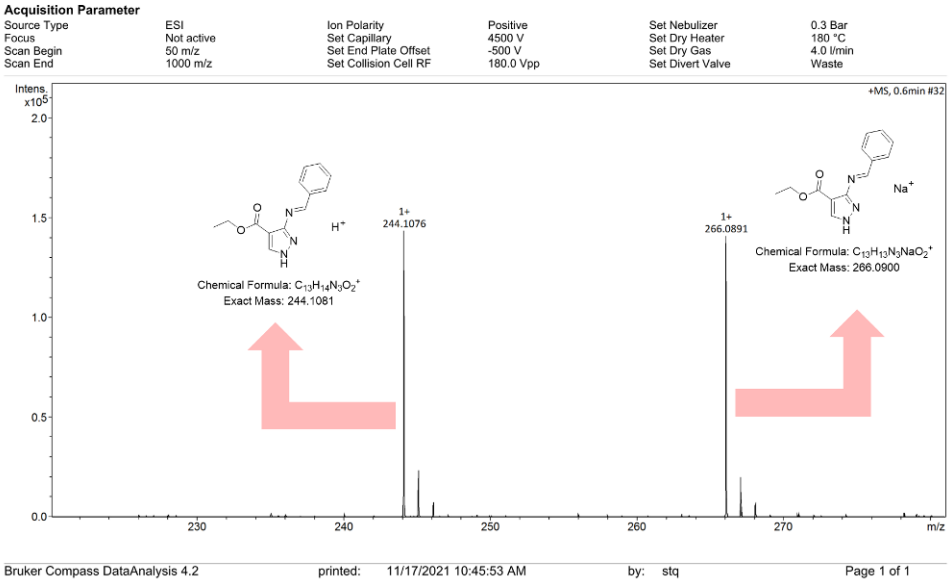


5. Studying the reaction mechanism

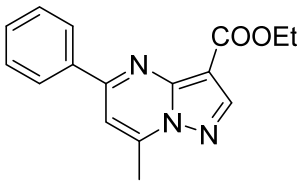


1a **2a** **B** **3a** 89%

Benzaldehyde **1a** (53 mg, 0.5 mmol), ethyl 3-amino-1*H*-pyrazole-4-carboxylate **2a** (77.6 mg, 0.5 mmol) and DCE (2.5 mL) were charged into a pressure tube (35 mL) and were stirred at 130 ºC for 5 h. The condensation imine (**B**) rather than annulation product (**3a**) was detected by HRMS. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{13}H_{14}N_3O_2$: 244.1081; found: 244.1076. $[M + Na]^+$ calcd for $C_{13}H_{13}N_3NaO_2$: 266.0900; found: 266.0891.Then, DTBP (219 mg, 1.5 mmol) was added without further purification, afterward, the mixture was stirred at 130 ºC for 10 h. Added 50 mL water to the mixture, then extracted with EtOAc 3 times (3 × 50 mL), dried over anhydrous Na_2SO_4 and evaporation. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 8:1) to afford the product **3a** as a yellow solid (125 mg, 89% yield).

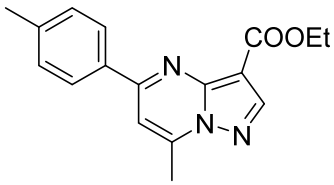


6. Characterization data for compounds



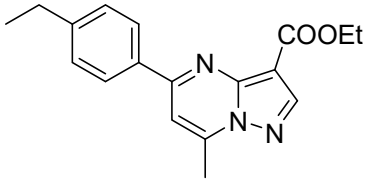
ethyl 7-methyl-5-phenylpyrazolo[1,5-*a*]pyrimidine-3-carboxylate (3a) (CAS: 140706-36-1):

Yield 85% (119.4 mg; petroleum ether/EtOAc = 8:1); yellow solid; mp 121–123 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.58 (s, 1H), 8.24–8.17 (m, 2H), 7.53–7.47 (m, 3H), 7.32 (s, 1H), 4.45 (q, J = 7.2 Hz, 2H), 2.86 (s, 3H), 1.47 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 162.8, 158.5, 147.8, 147.4, 147.1, 136.4, 130.9, 128.8, 127.5, 106.3, 102.9, 60.1, 17.6, 14.4; HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{16}H_{15}N_3NaO_2$: 304.1056; found: 304.1056.



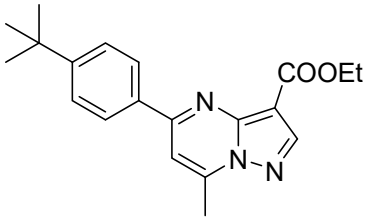
ethyl 7-methyl-5-(*p*-tolyl)pyrazolo[1,5-*a*]pyrimidine-3-carboxylate (3b):

Yield 84% (124 mg; petroleum ether/EtOAc = 10:1); orange solid; mp 119–121 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.56 (s, 1H), 8.10 (d, J = 8.4 Hz, 2H), 7.3–7.28 (m, 3H), 4.44 (q, J = 7.2 Hz, 2H), 2.84 (s, 3H), 2.42 (s, 3H), 1.47 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 162.9, 158.5, 147.9, 147.3, 146.8, 141.4, 133.6, 129.6, 127.5, 106.1, 102.7, 60.1, 21.4, 17.5, 14.4; HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{17}H_{17}N_3NaO_2$: 318.1213; found: 318.1214.



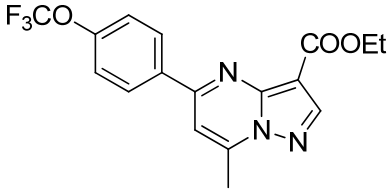
ethyl 5-(4-ethylphenyl)-7-methylpyrazolo[1,5-*a*]pyrimidine-3-carboxylate (3c) (CAS: 1403602-81-2):

Yield 80% (123.6 mg; petroleum ether/EtOAc = 10:1); yellow solid; mp 76–78 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.57 (s, 1H), 8.15 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 7.32 (s, 1H), 4.45 (q, J = 7.2 Hz, 2H), 2.87 (s, 3H), 2.73 (q, J = 7.6 Hz, 2H), 1.47 (t, J = 7.2 Hz, 3H), 1.29 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 162.9, 158.7, 148.0, 147.7, 147.4, 146.9, 134.0, 128.5, 127.7, 106.2, 102.8, 60.1, 28.8, 17.6, 15.3, 14.5; HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{18}H_{19}N_3NaO_2$: 332.1369; found: 332.1368.



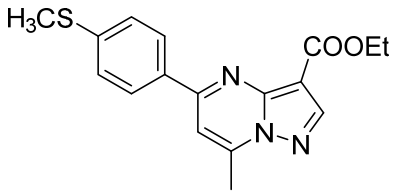
ethyl 5-(4-(*tert*-butyl)phenyl)-7-methylpyrazolo[1,5-*a*]pyrimidine-3-carboxylate (3d):

Yield 60% (101 mg; petroleum ether/EtOAc = 8:1); yellow solid; mp 139–141 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.57 (s, 1H), 8.15 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 8.4 Hz, 2H), 7.32 (s, 1H), 4.45 (q, J = 7.2 Hz, 2H), 2.87 (s, 3H), 1.47 (t, J = 7.0 Hz, 3H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm); 163.0, 158.6, 154.5, 147.9, 147.5, 146.9, 133.8, 127.4, 125.9, 106.2, 102.8, 60.1, 34.9, 31.1, 17.6, 14.5. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{20}H_{23}N_3NaO_2$: 360.1682; found: 360.1681.

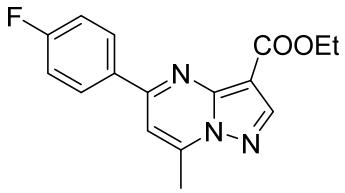


ethyl 7-methyl-5-(4-(trifluoromethoxy)phenyl)pyrazolo[1,5-*a*]pyrimidine-3-carboxylate (3e):

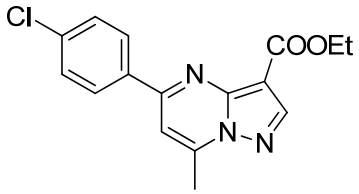
Yield 66% (120.5 mg; petroleum ether/EtOAc = 8:1); yellow solid; mp 129–132 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.59 (s, 1H), 8.29–8.22 (m, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.30 (s, 1H), 4.45 (q, J = 7.2 Hz, 2H), 2.89 (s, 3H), 1.46 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 162.8, 157.1, 151.2 (q, $J_{C\text{-}F}$ = 1.8 Hz), 147.8 (q, $J_{C\text{-}F}$ = 15.4 Hz), 147.7, 147.4, 135.1, 129.3, 120.3 (q, $J_{C\text{-}F}$ = 258.3 Hz), 121.0, 106.1, 103.2, 60.3, 17.7, 14.5; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{17}H_{15}F_3N_3O_3$: 366.1060; found: 366.1062.



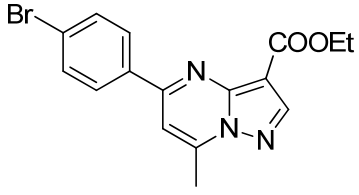
ethyl 7-methyl-5-(4-(methylthio)phenyl)pyrazolo[1,5-*a*]pyrimidine-3-carboxylate (3f):
Yield 72% (117.7 mg; petroleum ether/EtOAc = 10:1); yellow solid; mp 121–123 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.55 (s, 1H), 8.15–8.09 (m, 2H), 7.34–7.29 (m, 2H), 7.26 (s, 1H), 4.44 (q, J = 7.2 Hz, 2H), 2.85 (s, 3H), 2.54 (s, 3H), 1.47 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 162.8, 157.8, 147.9, 147.4, 146.9, 143.0, 132.7, 127.8, 125.7, 105.8, 102.7, 60.1, 17.6, 14.9, 14.5; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{17}H_{18}N_3O_2S$: 328.1114; found: 328.1116.



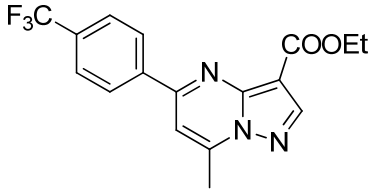
ethyl 5-(4-fluorophenyl)-7-methylpyrazolo[1,5-*a*]pyrimidine-3-carboxylate (3g):
Yield 80% (119.6 mg; petroleum ether/EtOAc = 12:1); white solid; mp 145–147 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.58 (s, 1H), 8.26–8.20 (m, 2H), 7.29 (s, 1H), 7.23–7.17 (m, 2H), 4.45 (q, J = 7.2 Hz, 2H), 2.88 (s, 3H), 1.46 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 164.7 (d, $J_{C\text{-}F}$ = 252.0 Hz), 162.8, 157.5, 147.9, 147.6, 147.2, 132.7 (d, $J_{C\text{-}F}$ = 3.0 Hz), 129.7 (d, $J_{C\text{-}F}$ = 8.8 Hz), 116.0 (d, $J_{C\text{-}F}$ = 21.8 Hz), 106.0, 103.0, 60.2, 17.6, 14.5; HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{16}H_{14}FN_3NaO_2$: 322.0962; found: 322.0963.



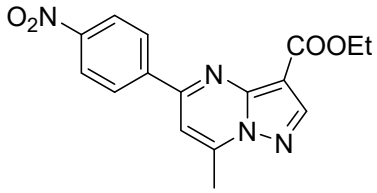
ethyl 5-(4-chlorophenyl)-7-methylpyrazolo[1,5-*a*]pyrimidine-3-carboxylate (3h) (CAS: 871571-83-4):
Yield 76% (120 mg; petroleum ether/EtOAc = 8:1); yellow solid; mp 117–119 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.59 (s, 1H), 8.20–8.14 (m, 2H), 7.52–7.46 (m, 2H), 7.30 (s, 1H), 4.45 (q, J = 7.2 Hz, 2H), 2.89 (s, 3H), 1.46 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 162.8, 157.3, 147.9, 147.6, 147.3, 137.3, 135.0, 129.2, 128.9, 106.0, 103.1, 60.2, 17.7, 14.5; HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{16}H_{14}ClN_3NaO_2$: 338.0667; found: 338.0665.



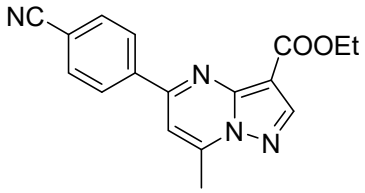
ethyl 5-(4-bromophenyl)-7-methylpyrazolo[1,5-*a*]pyrimidine-3-carboxylate (3i):
Yield 78% (140.4 mg; petroleum ether/EtOAc = 8:1); yellow solid; mp 145–147 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.58 (s, 1H), 8.08 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H), 7.28 (s, 1H), 4.44 (q, J = 7.2 Hz, 2H), 2.88 (s, 3H), 1.46 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 162.7, 157.3, 147.8, 147.6, 147.3, 135.3, 132.1, 129.0, 125.8, 105.9, 103.1, 60.2, 17.6, 14.5; HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{16}H_{14}BrN_3NaO_2$: 382.0162; found: 382.0164.



ethyl 7-methyl-5-(4-(trifluoromethyl)phenyl)pyrazolo[1,5-*a*]pyrimidine-3-carboxylate (3j):
Yield 68% (118.7 mg; petroleum ether/EtOAc = 8:1); white solid; mp 161–163 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.60 (s, 1H), 8.30 (d, J = 8.0 Hz, 2H), 7.75 (d, J = 8.0 Hz, 2H), 7.34 (s, 1H), 4.45 (q, J = 7.2 Hz, 2H), 2.89 (s, 3H), 1.47 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 162.6, 156.7, 147.7 (x 2), 147.6, 139.7, 132.4 (q, $J_{C\text{-}F}$ = 32.6 Hz), 127.8, 125.7 (q, $J_{C\text{-}F}$ = 3.7 Hz), 123.8 (q, $J_{C\text{-}F}$ = 272.4 Hz), 106.3, 103.3, 60.2, 17.6, 14.4; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{17}H_{15}F_3N_3O_2$: 350.1111; found: 350.1113.

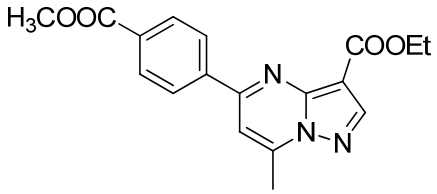


ethyl 7-methyl-5-(4-nitrophenyl)pyrazolo[1,5-*a*]pyrimidine-3-carboxylate (3k):
Yield 57% (92.9 mg; petroleum ether/EtOAc =3:1); yellow solid; mp 168–170 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.63 (s, 1H), 8.41–8.37 (m, 2H), 8.36–8.33 (m, 2H), 7.42 (s, 1H), 4.46 (q, J = 7.2 Hz, 2H), 2.94 (s, 3H), 1.47 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 162.5, 155.7, 149.0, 147.9(4), 147.8(6), 147.6, 142.2, 128.4, 124.0, 106.4, 103.6, 60.3, 17.7, 14.4; HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{16}H_{14}N_4NaO_4$: 349.0907; found: 349.0905.



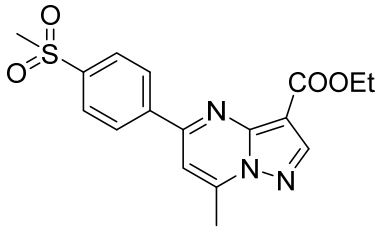
ethyl 5-(4-cyanophenyl)-7-methylpyrazolo[1,5-*a*]pyrimidine-3-carboxylate (3l):
Yield 80% (122.4 mg; petroleum ether/EtOAc = 8:1); light yellow solid; mp 180–182 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.54 (s, 1H), 8.25 (d, J = 8.8 Hz, 2H), 7.73 (d, J = 8.8 Hz, 2H), 7.28 (s, 1H), 4.37 (q, J = 7.2 Hz, 2H), 2.84 (s, 3H), 1.38 (t, J = 7.2 Hz, 3H); ^{13}C NMR

(100 MHz, $CDCl_3$): δ (ppm) 162.5, 156.1, 147.8(5), 147.8(3), 147.7, 140.5, 132.6, 128.1, 118.3, 114.2, 106.3, 103.5, 60.3, 17.7, 14.4; HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{17}H_{14}N_4NaO_2$: 329.1009; found: 329.1012.



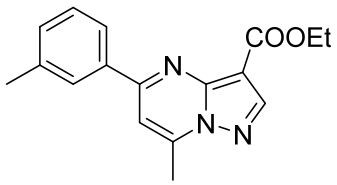
ethyl 5-(4-(methoxycarbonyl)phenyl)-7-methylpyrazolo[1,5-*a*]pyrimidine-3-carboxylate (3m):

Yield 70% (118.6 mg; petroleum ether/EtOAc = 5:1); yellow solid; mp 199–202 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.60 (s, 1H), 8.28 (d, J = 8.4 Hz, 2H), 8.16 (d, J = 8.4 Hz, 2H), 7.37 (s, 1H), 4.45 (q, J = 7.2 Hz, 2H), 3.97 (s, 3H), 2.90 (s, 3H), 1.47 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 166.5, 162.7, 157.2, 147.8, 147.7, 147.5, 140.5, 132.0, 130.0, 127.5, 106.5, 103.3, 60.3, 52.3, 17.6, 14.4; HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{18}N_3O_4$: 340.1292; found: 340.1293.



ethyl 7-methyl-5-(4-(methylsulfonyl)phenyl)pyrazolo[1,5-*a*]pyrimidine-3-carboxylate (3n):

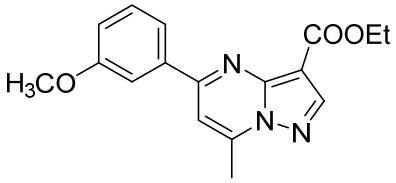
Yield 68% (122 mg; petroleum ether/EtOAc = 3:1); yellow solid; mp 173–175 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.60 (s, 1H), 8.39 (d, J = 8.8 Hz, 2H), 8.06 (d, J = 8.8 Hz, 2H), 7.40 (s, 1H), 4.44 (q, J = 7.2 Hz, 2H), 3.12 (s, 3H), 2.92 (s, 3H), 1.46 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 162.4, 156.1, 147.8, 147.7, 147.5, 141.9, 141.4, 128.4, 127.8, 106.4, 103.4, 60.2, 44.3, 17.6, 14.3; HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{17}H_{17}N_3NaO_4S$: 382.0832; found: 382.0829.



ethyl 7-methyl-5-(*m*-tolyl)pyrazolo[1,5-*a*]pyrimidine-3-carboxylate (3o):

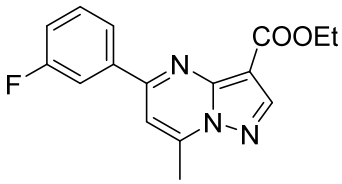
Yield 79% (116.5 mg; petroleum ether/EtOAc = 8:1); yellow solid; mp 91–94 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.58 (s, 1H), 8.07 (s, 1H), 7.97 (d, J = 7.6 Hz, 1H), 7.39 (t, J = 7.6 Hz, 1H), 7.30–7.34 (m, 2H), 4.45 (q, J = 7.2 Hz, 2H), 2.87 (s, 3H), 2.46 (s, 3H), 1.47 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 162.9, 158.8, 147.9, 147.4, 147.0, 138.6,

136.4, 131.8, 128.7, 128.2, 124.7, 106.4, 102.9, 60.1, 21.5, 17.6, 14.4; HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{17}H_{17}N_3NaO_2$: 318.1213; found: 318.1211.



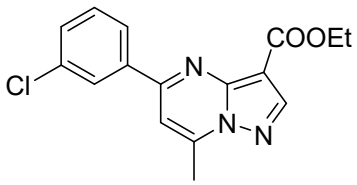
ethyl 5-(3-methoxyphenyl)-7-methylpyrazolo[1,5-*a*]pyrimidine-3-carboxylate (3p) (CAS: 2137500-65-1):

Yield 73% (113.5 mg; petroleum ether/EtOAc = 8:1); yellow solid; mp 100–102 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.59 (s, 1H), 7.84–7.82 (m, 1H), 7.75–7.70 (m, 1H), 7.41 (t, J = 8.0 Hz, 1H), 7.32 (s, 1H), 7.08–7.04 (m, 1H), 4.45 (q, J = 7.2 Hz, 2H), 3.92 (s, 3H), 2.88 (s, 3H), 1.47 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 162.9, 160.1, 158.3, 147.7, 147.6, 147.1, 137.9, 129.8, 120.0, 117.3, 112.3, 106.5, 103.0, 60.2, 55.4, 17.6, 14.5; HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{17}H_{18}N_3O_3$: 312.1343; found: 312.1342.



ethyl 5-(3-fluorophenyl)-7-methylpyrazolo[1,5-*a*]pyrimidine-3-carboxylate (3q) (CAS: 2137500-67-3):

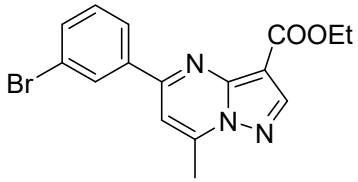
Yield 72% (107.6 mg; petroleum ether/EtOAc = 10:1); light yellow solid; mp 107–110 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.60 (s, 1H), 7.98–7.96 (m, 1H), 7.96–7.93 (m, 1H), 7.52–7.45 (m, 1H), 7.31 (s, 1H), 7.24–7.18 (m, 1H), 4.45 (q, J = 7.2 Hz, 2H), 2.90 (s, 3H), 1.47 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 163.2 (d, $J_{C\text{-}F}$ = 246.6 Hz), 162.8, 157.2 (d, $J_{C\text{-}F}$ = 2.7 Hz), 147.7(3), 147.7(0), 147.4, 138.8 (d, $J_{C\text{-}F}$ = 7.6 Hz), 130.5 (d, $J_{C\text{-}F}$ = 8.1 Hz), 123.2 (d, $J_{C\text{-}F}$ = 2.9 Hz), 117.0 (d, $J_{C\text{-}F}$ = 21.4 Hz), 114.6 (d, $J_{C\text{-}F}$ = 23.2 Hz), 106.3, 103.2, 60.3, 17.7, 14.5; HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{16}H_{15}FN_3O_2$: 300.1143; found: 300.1142.



ethyl 5-(3-chlorophenyl)-7-methylpyrazolo[1,5-*a*]pyrimidine-3-carboxylate (3r) (CAS: 2137500-77-5):

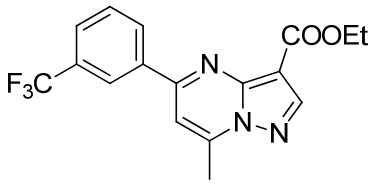
Yield 71% (112 mg; petroleum ether/EtOAc = 10:1); yellow solid; mp 108–111 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.60 (s, 1H), 8.21 (t, J = 1.6 Hz, 1H), 8.08 (dt, J = 7.2, 1.6 Hz, 1H), 7.50–7.47 (m, 1H), 7.47–7.42 (m, 1H), 7.31 (s, 1H), 4.45 (q, J = 7.2 Hz, 2H), 2.90 (s, 3H), 1.48 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 162.8, 157.0, 147.7(4),

147.6(9), 147.5, 138.3, 135.1, 130.9, 130.1, 127.7, 125.7, 106.2, 103.3, 60.3, 17.7, 14.4; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{16}H_{15}ClN_3O_2$: 316.0847; found: 316.0850.



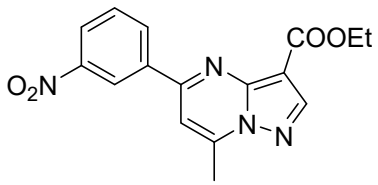
ethyl 5-(3-bromophenyl)-7-methylpyrazolo[1,5-*a*]pyrimidine-3-carboxylate (3s) (CAS: 2137501-07-4):

Yield 75% (135 mg; petroleum ether/EtOAc = 10:1); orange solid; mp 120–123 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.59 (s, 1H), 8.37–8.33 (m, 1H), 8.13–8.09 (m, 1H), 7.64–7.60 (m, 1H), 7.37 (t, J = 8.0 Hz, 1H), 7.29 (s, 1H), 4.45 (q, J = 7.2 Hz, 2H), 2.89 (s, 3H), 1.48 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 162.7, 156.8, 147.6(6), 147.6(5), 147.4, 138.5, 133.8, 130.5, 130.3, 126.1, 123.2, 106.1, 103.2, 60.3, 17.6, 14.4; HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{16}H_{14}BrN_3NaO_2$: 382.0162; found: 382.0161.



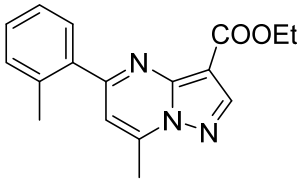
ethyl 7-methyl-5-(3-(trifluoromethyl)phenyl)pyrazolo[1,5-*a*]pyrimidine-3-carboxylate (3t):

Yield 74% (129 mg; petroleum ether/EtOAc = 10:1); yellow solid; mp 124–126 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.60 (s, 1H), 8.47 (s, 1H), 8.38 (d, J = 8.0 Hz, 1H), 7.75 (d, J = 7.6 Hz, 1H), 7.63 (t, J = 7.8 Hz, 1H), 7.35 (s, 1H), 4.45 (q, J = 7.2 Hz, 2H), 2.90 (s, 3H), 1.48 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 162.7, 156.6, 147.7, 147.6 (d, $J_{C\text{-}F}$ = 13.3 Hz), 137.2, 131.3 (q, $J_{C\text{-}F}$ = 32.6 Hz), 130.6, 129.4, 127.3 (q, $J_{C\text{-}F}$ = 3.6 Hz), 123.8 (q, $J_{C\text{-}F}$ = 272.5 Hz), 124.3 (q, $J_{C\text{-}F}$ = 3.9 Hz), 105.9, 103.3, 60.3, 17.6, 14.3; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{17}H_{15}F_3N_3O_2$: 350.1111; found: 350.1112.

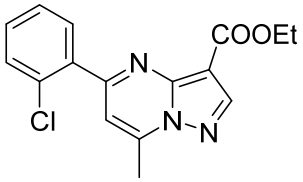


ethyl 7-methyl-5-(3-nitrophenyl)pyrazolo[1,5-*a*]pyrimidine-3-carboxylate (3u):

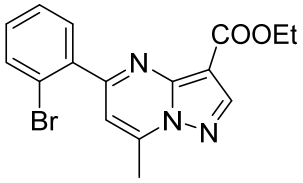
Yield 63% (102.7 mg; petroleum ether/EtOAc = 5:1); white solid; mp 212–214 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.01 (s, 1H), 8.69–8.60 (m, 2H), 8.40–8.34 (m, 1H), 7.73 (t, J = 8.0 Hz, 1H), 7.43 (s, 1H), 4.46 (q, J = 7.2 Hz, 2H), 2.95 (s, 3H), 1.50 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 162.7, 155.7, 148.7, 148.1, 148.0, 147.6, 138.3, 133.4, 130.1, 125.3, 122.3, 106.0, 103.6, 60.4, 17.7, 14.4; HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{16}H_{14}N_4NaO_4$: 349.0907; found: 349.0907.



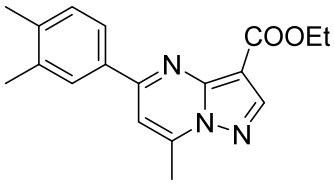
ethyl 7-methyl-5-(*o*-tolyl)pyrazolo[1,5-*a*]pyrimidine-3-carboxylate (3v):
Yield 75% (110.6 mg; petroleum ether/EtOAc = 8:1); yellow solid; mp 112–115 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.62 (s, 1H), 7.56 (d, J = 7.6 Hz, 1H), 7.39–7.29 (m, 3H), 7.07 (s, 1H), 4.42 (q, J = 7.2 Hz, 2H), 2.88 (s, 3H), 2.60 (s, 3H), 1.42 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 162.9, 161.9, 147.5, 147.3, 146.6, 137.6, 137.1, 131.5, 129.9, 129.7, 126.0, 110.2, 103.1, 60.2, 20.9, 17.5, 14.5; HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{17}H_{17}N_3NaO_2$: 318.1213; found: 318.1210.



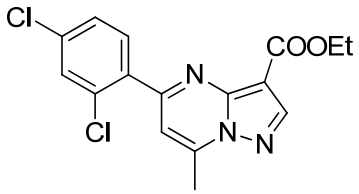
ethyl 5-(2-chlorophenyl)-7-methylpyrazolo[1,5-*a*]pyrimidine-3-carboxylate (3w):
Yield 67% (105.7 mg; petroleum ether/EtOAc = 8:1); light yellow solid; mp 182–184 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.62 (s, 1H), 7.87–7.82 (m, 1H), 7.52–7.47 (m, 1H), 7.44–7.39 (m, 2H), 7.34 (s, 1H), 4.42 (q, J = 7.2 Hz, 2H), 2.90 (s, 3H), 1.42 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 162.6, 158.9, 147.8, 147.4, 146.2, 137.1, 132.2(3), 132.1(5), 130.9, 130.3, 127.3, 111.0, 103.4, 60.2, 17.6, 14.5; HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{16}H_{14}ClN_3NaO_2$: 338.0667; found: 338.0665.



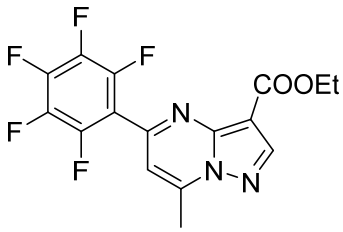
ethyl 5-(2-bromophenyl)-7-methylpyrazolo[1,5-*a*]pyrimidine-3-carboxylate (3x):
Yield 68% (122.4 mg; petroleum ether/EtOAc = 8:1); white solid; mp 177–179 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.62 (s, 1H), 7.77–7.73 (m, 1H), 7.70–7.66 (m, 1H), 7.47–7.41 (m, 1H), 7.35–7.29 (m, 2H), 4.42 (q, J = 7.2 Hz, 2H), 2.89 (s, 3H), 1.41 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 162.5, 160.1, 147.7, 147.3, 146.1, 139.0, 133.4, 132.0, 130.9, 127.7, 121.4, 111.0, 103.4, 60.2, 17.5, 14.4; HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{16}H_{14}BrN_3NaO_2$: 382.0162; found: 382.0162.



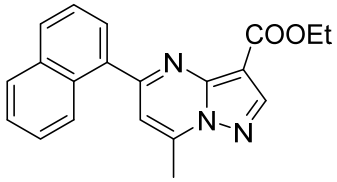
ethyl 5-(3,4-dimethylphenyl)-7-methylpyrazolo[1,5-*a*]pyrimidine-3-carboxylate (3y):
Yield 80% (123.6 mg; petroleum ether/EtOAc = 5:1); yellow solid; mp 98–101 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.48 (s, 1H), 7.96 (s, 1H), 7.84 (d, J = 7.6 Hz, 1H), 7.24 (s, 1H), 7.18 (d, J = 8.4 Hz, 1H), 4.37 (q, J = 7.2 Hz, 2H), 2.78 (s, 3H), 2.29 (s, 3H), 2.26 (s, 3H), 1.40 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 163.0, 158.8, 148.0, 147.4, 146.8, 140.3, 137.3, 134.0, 130.2, 128.7, 125.0, 106.2, 102.7, 60.1, 19.9, 19.8, 17.6, 14.5; HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{18}H_{19}N_3NaO_2$: 332.1369; found: 332.1367.



ethyl 5-(2,4-dichlorophenyl)-7-methylpyrazolo[1,5-*a*]pyrimidine-3-carboxylate (3z):
Yield 76% (133 mg; petroleum ether/EtOAc = 10:1); yellow solid; mp 195–197 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.62 (s, 1H), 7.81 (d, J = 8.4 Hz, 1H), 7.55–7.46 (m, 1H), 7.40 (dd, J = 8.4, 2.0 Hz, 1H), 7.32 (s, 1H), 4.42 (q, J = 7.2 Hz, 2H), 2.89 (s, 3H), 1.42 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 162.5, 157.7, 147.7, 147.4, 146.4, 136.4, 135.5, 133.0, 132.9, 130.0, 127.7, 110.6, 103.4, 60.2, 17.5, 14.4; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{16}H_{14}Cl_2N_3O_2$: 350.0458; found: 350.0456.

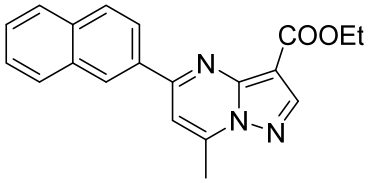


ethyl 7-methyl-5-(perfluorophenyl)pyrazolo[1,5-*a*]pyrimidine-3-carboxylate (3aa):
Yield 70% (129.8 mg; petroleum ether/EtOAc = 12:1); yellow solid; mp 147–149 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.67 (s, 1H), 7.06 (s, 1H), 4.42 (q, J = 7.2 Hz, 2H), 2.93 (s, 3H), 1.42 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 162.2, 148.9, 147.8, 147.4, 144.9 (dm, $J_{C\text{-}F}$ = 253.2 Hz), 142.0 (dm, $J_{C\text{-}F}$ = 257.4 Hz), 137.9 (dm, $J_{C\text{-}F}$ = 249.7 Hz), 113.8–113.4 (m), 110.8, 104.1, 60.4, 17.6, 14.4; HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{16}H_{10}F_5N_3NaO_2$: 394.0585; found: 394.0584.

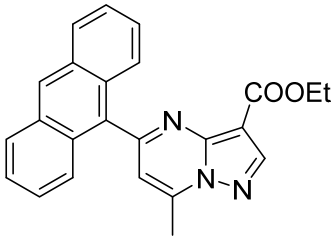


ethyl 7-methyl-5-(naphthalen-1-yl)pyrazolo[1,5-*a*]pyrimidine-3-carboxylate (3ab):
Yield 78% (129 mg; petroleum ether/EtOAc = 5:1); yellow solid; mp 113–115 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.66 (s, 1H), 8.55–8.50 (m, 1H), 7.98 (d, J = 8.4 Hz, 1H), 7.95–7.91 (m, 1H), 7.82 (dd, J = 7.2, 1.2 Hz, 1H), 7.60–7.53 (m, 3H), 7.24 (s, 1H), 4.42 (q, J

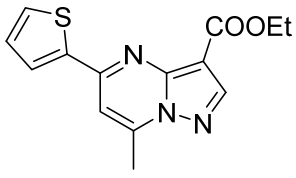
= 7.2 Hz, 2H), 2.91 (s, 3H), 1.41 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 162.9, 161.1, 147.6(1), 147.5(8), 146.7, 135.7, 134.0, 130.7, 130.6, 128.7, 128.5, 127.1, 126.2, 125.4, 125.1, 111.1, 103.4, 60.2, 17.5, 14.5; HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{20}H_{17}N_3NaO_2$: 354.1213; found: 354.1217.



ethyl 7-methyl-5-(naphthalen-2-yl)pyrazolo[1,5-*a*]pyrimidine-3-carboxylate (3ac):
Yield 80% (132.4 mg; petroleum ether/EtOAc = 8:1); yellow solid; mp 145–147 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.64 (s, 1H), 8.58 (s, 1H), 8.37 (dd, J = 8.8, 2.0 Hz, 1H), 7.99–7.92 (m, 2H), 7.90–7.85 (m, 1H), 7.58–7.51 (m, 2H), 7.45 (s, 1H), 4.47 (q, J = 7.2 Hz, 2H), 2.88 (s, 3H), 1.50 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 162.9, 158.4, 148.0, 147.5, 147.0, 134.5, 133.8, 133.1, 129.0, 128.7, 127.9, 127.7, 127.5, 126.6, 124.3, 106.4, 103.0, 60.2, 17.6, 14.5; HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{20}H_{17}N_3NaO_2$: 354.1213; found: 354.1216.

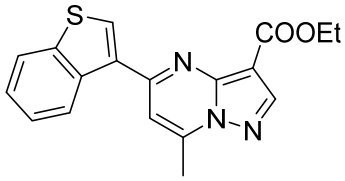


ethyl 5-(anthracen-9-yl)-7-methylpyrazolo[1,5-*a*]pyrimidine-3-carboxylate (3ad):
Yield 69% (131.4 mg; petroleum ether/EtOAc = 8:1); orange solid; mp 250–252 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.71 (s, 1H), 8.58 (s, 1H), 8.06 (d, J = 8.4 Hz, 2H), 7.77–7.72 (m, 2H), 7.50–7.45 (m, 2H), 7.42–7.38 (m, 2H), 7.10 (s, 1H), 4.36 (q, J = 7.2 Hz, 2H), 2.93 (s, 3H), 1.33 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 162.5, 161.1, 148.1, 147.5, 146.6, 132.6, 131.2, 129.6, 128.7, 128.6, 126.4, 125.5, 125.3, 113.4, 103.6, 60.1, 17.5, 14.4; HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{24}H_{19}N_3NaO_2$: 404.1369; found: 404.1366.

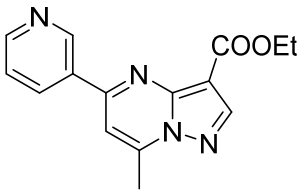


ethyl 7-methyl-5-(thiophen-2-yl)pyrazolo[1,5-*a*]pyrimidine-3-carboxylate (3ae):
Yield 61% (87.5 mg; petroleum ether/EtOAc = 5:1); brown solid; mp 142–144 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.53 (s, 1H), 7.75–7.72 (m, 1H), 7.57–7.54 (m, 1H), 7.16–7.10 (m, 2H), 4.43 (q, J = 7.2 Hz, 2H), 2.82 (s, 3H), 1.48 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 162.8, 153.7, 147.4, 147.3, 146.9, 142.5, 131.0, 128.3, 128.1, 105.2, 102.6,

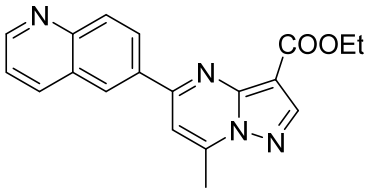
60.1, 17.4, 14.3; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{14}H_{14}N_3O_2S$: 288.0801; found: 288.0803.



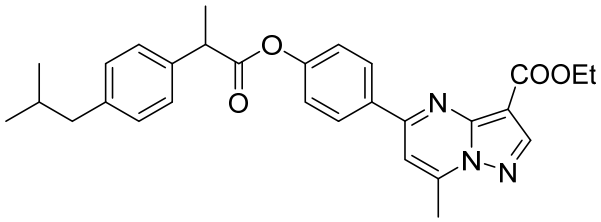
ethyl 5-(benzo[b]thiophen-3-yl)-7-methylpyrazolo[1,5-*a*]pyrimidine-3-carboxylate (3af):
Yield 62% (104.5 mg; petroleum ether/EtOAc = 5:1); orange solid; mp 179–181 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.37 (d, J = 8.4 Hz, 1H), 8.62 (s, 1H), 8.11 (s, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.58–7.53 (m, 1H), 7.48–7.44 (m, 1H), 7.27 (s, 1H), 4.49 (q, J = 7.2 Hz, 2H), 2.86 (s, 3H), 1.55 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 163.2, 155.4, 147.7, 147.2, 146.7, 140.7, 136.8, 133.5, 130.4, 126.1, 125.5, 125.2, 122.5, 107.5, 103.4, 60.4, 17.5, 14.6; HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{18}H_{15}N_3NaO_2S$: 360.0777; found: 360.0779.



ethyl 7-methyl-5-(pyridin-3-yl)pyrazolo[1,5-*a*]pyrimidine-3-carboxylate (3ag) (CAS: 2137500-39-9):
Yield 55% (77.5 mg; petroleum ether/EtOAc = 2:1); brown solid; mp 186–188 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.36 (s, 1H), 8.75 (dd, J = 4.8, 1.6 Hz, 1H), 8.65–8.56 (m, 2H), 7.51–7.46 (m, 1H), 7.37 (s, 1H), 4.45 (q, J = 7.2 Hz, 2H), 2.93 (s, 3H), 1.47 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 162.7, 156.1, 151.7, 148.6, 147.9, 147.8, 135.3, 132.4, 123.8, 106.0, 103.4, 60.3, 17.7, 14.5; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{15}H_{15}N_4O_2$: 283.1190; found: 283.1187.

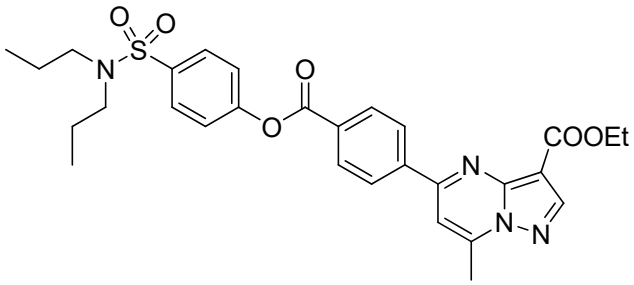


ethyl 7-methyl-5-(quinolin-6-yl)pyrazolo[1,5-*a*]pyrimidine-3-carboxylate (3ah):
Yield 65% (107.9 mg; petroleum ether/EtOAc = 2:1); white solid; mp 164–167 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.00 (dd, J = 4.4, 1.6 Hz, 1H), 8.74 (d, J = 2.0 Hz, 1H), 8.62 (s, 1H), 8.58 (dd, J = 8.8, 2.0 Hz, 1H), 8.34–8.30 (m, 1H), 8.25 (d, J = 8.8 Hz, 1H), 7.52–7.47 (m, 2H), 4.48 (q, J = 7.2 Hz, 2H), 2.95 (s, 3H), 1.50 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 162.8, 157.7, 151.8, 149.3, 148.0, 147.7, 147.4, 137.1, 134.6, 130.3, 128.1, 128.0, 127.9, 121.9, 106.5, 103.3, 60.3, 17.8, 14.6; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{19}H_{17}N_4O_2$: 333.1346; found: 333.1341.



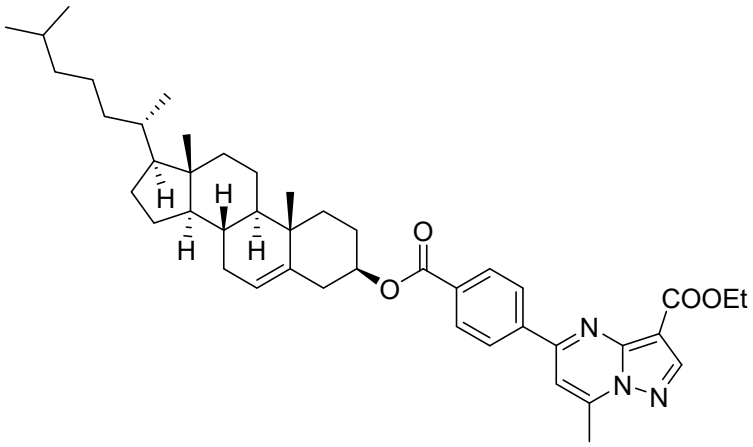
ethyl 5-(4-((2-(4-isobutylphenyl)propanoyl)oxy)phenyl)-7-methylpyrazolo[1,5-*a*]pyrimidine-3-carboxylate (3ai):

Yield 61% (148 mg; petroleum ether/EtOAc = 8:1); yellow solid; mp 42–45 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.58 (s, 1H), 8.21 (d, J = 8.8 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.29 (s, 1H), 7.17 (d, J = 8.8 Hz, 4H), 4.44 (q, J = 7.2 Hz, 2H), 3.97 (q, J = 7.2 Hz, 1H), 2.88 (s, 3H), 2.50–2.46 (m, 2H), 1.93–1.83 (m, 1H), 1.63 (d, J = 7.2 Hz, 3H), 1.45 (t, J = 7.2 Hz, 3H), 0.93 (s, 3H), 0.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 172.9, 162.9, 157.7, 153.2, 147.6, 147.2, 141.0, 137.0, 134.1, 131.7, 129.6, 128.8, 127.2, 122.0, 121.6, 106.2, 103.1, 60.2, 45.3, 45.0, 30.2, 22.4, 18.5, 17.7, 14.5; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{29}H_{32}N_3O_4$: 486.2387; found: 486.2387.



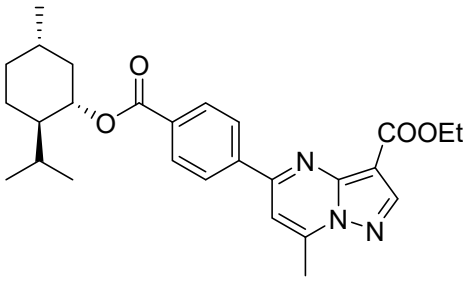
ethyl 5-(4-((4-(*N*,*N*-dipropylsulfamoyl)phenoxy)carbonyl)phenyl)-7-methylpyrazolo[1,5-*a*]pyrimidine-3-carboxylate (3aj):

Yield 50% (141 mg; petroleum ether/EtOAc = 10:1); white solid; mp 128–130 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.60 (s, 1H), 8.39–8.30 (m, 4H), 8.01–7.95 (m, 2H), 7.44–7.38 (m, 2H), 7.35 (s, 1H), 4.45 (q, J = 7.2 Hz, 2H), 3.17–3.11 (m, 4H), 2.91 (s, 3H), 1.62–1.54 (m, 4H), 1.47 (t, J = 7.2 Hz, 3H), 0.90 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 163.5, 162.8, 157.5, 152.8, 148.0, 147.6, 147.3, 145.1, 134.7, 132.5, 130.9, 129.1, 127.2, 122.1, 106.2, 103.1, 60.2, 49.9, 21.9, 17.7, 14.5, 11.2; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{29}H_{33}N_4O_6S$: 565.2115; found: 565.2119.



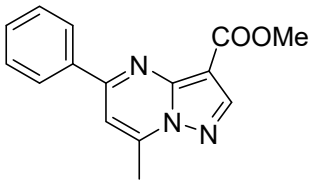
ethyl 5-(4-((((3*R*,8*R*,9*R*,10*S*,13*S*,14*R*,17*S*)-10,13-dimethyl-17-((*S*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-3-yl)oxy)carbonyl)phenyl)-7-methylpyrazolo[1,5-*a*]pyrimidine-3-carboxylate (3ak):

Yield 80% (277.2 mg; petroleum ether/EtOAc = 8:1); yellow solid; mp 109–112 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.60 (s, 1H), 8.28 (d, J = 8.4 Hz, 2H), 8.16 (d, J = 8.4 Hz, 2H), 7.38 (s, 1H), 5.43 (d, J = 4.0 Hz, 1H), 4.94–4.85 (m, 1H), 4.45 (q, J = 7.2 Hz, 2H), 2.91 (s, 3H), 2.50 (d, J = 7.6 Hz, 2H), 2.06–1.94 (m, 4H), 1.85–1.74 (m, 2H), 1.57–1.50 (m, 3H), 1.47 (t, J = 7.0 Hz, 5H), 1.42–1.30 (m, 4H), 1.26–1.21 (m, 2H), 1.20–1.13 (m, 3H), 1.11–1.06 (m, 5H), 1.03–0.96 (m, 3H), 0.93 (d, J = 6.8 Hz, 3H), 0.87 (dd, J = 6.4, 1.6 Hz, 7H), 0.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 165.4, 162.7, 157.3, 147.8, 147.7, 147.4, 140.3, 139.5, 132.8, 130.0, 127.5, 122.8, 106.5, 103.4, 75.0, 60.3, 56.6, 56.1, 50.0, 42.3, 39.7, 39.5, 38.2, 37.0, 36.6, 36.1, 35.8, 31.9, 31.8, 28.2, 28.0, 27.8, 24.3, 23.8, 22.8, 22.5, 21.0, 19.4, 18.7, 17.7, 14.5, 11.8; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{44}H_{60}N_3O_4$: 694.4578; found: 694.4572.

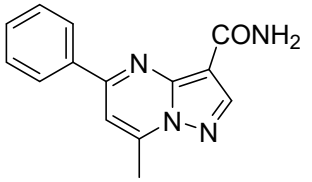


ethyl 5-(4-((((1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl)oxy)carbonyl)phenyl)-7-methylpyrazolo[1,5-*a*]pyrimidine-3-carboxylate (3al):

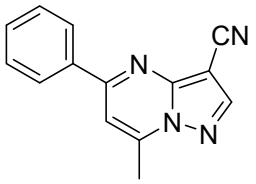
Yield 75% (173.6 mg; petroleum ether/EtOAc = 8:1); orange solid; mp 147–149 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.60 (s, 1H), 8.29 (d, J = 8.4 Hz, 2H), 8.17 (d, J = 8.0 Hz, 2H), 7.38 (s, 1H), 5.02–4.93 (m, 1H), 4.45 (q, J = 7.2 Hz, 2H), 2.91 (s, 3H), 2.19–2.13 (m, 1H), 2.02–1.94 (m, 1H), 1.79–1.72 (m, 2H), 1.65–1.55 (m, 2H), 1.47 (t, J = 7.2 Hz, 3H), 1.21–1.09(m, 2H), 0.95 (dd, J = 6.4, 2.0 Hz, 7H), 0.82 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 165.5, 162.7, 157.3, 147.8, 147.7, 147.4, 140.3, 132.7, 130.0, 127.5, 106.4, 103.4, 75.2, 60.2, 47.2, 40.9, 34.2, 31.4, 26.5, 23.6, 22.0, 20.7, 17.6, 16.5, 14.5; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{27}H_{34}N_3O_4$: 464.2544; found: 464.2545.



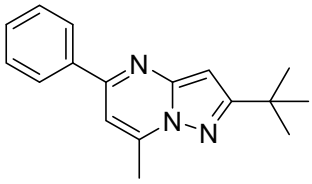
methyl 7-methyl-5-phenylpyrazolo[1,5-*a*]pyrimidine-3-carboxylate (3am):
Yield 72% (96 mg; petroleum ether/EtOAc = 10:1); white solid; mp 135–137 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.57 (s, 1H), 8.20–8.13 (m, 2H), 7.52–7.44 (m, 3H), 7.28 (s, 1H), 3.97 (s, 3H), 2.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 163.2, 158.6, 147.7, 147.5, 147.1, 136.3, 130.8, 128.8, 127.5, 106.3, 102.5, 51.4, 17.5; HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{15}H_{13}N_3NaO_2$: 290.0900; found: 290.0904.



7-methyl-5-phenylpyrazolo[1,5-*a*]pyrimidine-3-carboxamide (3an):
Yield 60% (75.6 mg; petroleum ether/EtOAc = 2:1); light yellow solid; mp 225–227 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.70 (s, 1H), 8.13–8.06 (m, 3H), 7.58–7.54 (m, 3H), 7.32 (s, 1H), 5.81 (s, 1H), 2.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 164.2, 157.9, 147.8, 146.8, 146.5, 136.3, 131.2, 129.1, 127.5, 106.2, 105.3, 17.6; HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{14}H_{12}N_4NaO$: 275.0903; found: 275.0900.

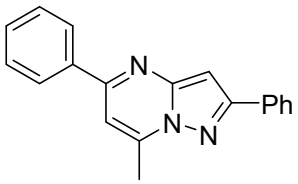


7-methyl-5-phenylpyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (3ao) (CAS: 140706-37-2):
Yield 79% (92.4 mg; petroleum ether/EtOAc = 12:1); light yellow solid; mp 157–160 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.34 (s, 1H), 8.16–8.11 (m, 2H), 7.53–7.47 (m, 3H), 7.36 (s, 1H), 2.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 159.0, 150.2, 147.6, 147.1, 135.6, 131.4, 128.9, 127.5, 113.3, 107.2, 82.6, 17.4; HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{14}H_{10}N_4Na$: 257.0798; found: 257.0796.

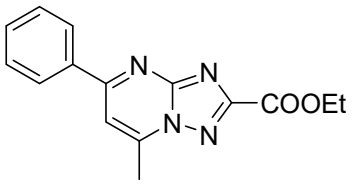


2-(*tert*-butyl)-7-methyl-5-phenylpyrazolo[1,5-*a*]pyrimidine (3ap) (CAS: 2699782-21-1):
Yield 61% (80.8 mg; petroleum ether/EtOAc = 100:1); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.08–8.06 (m, 1H), 8.06–8.04 (m, 1H), 7.52–7.46 (m, 3H), 7.05 (s, 1H), 6.57

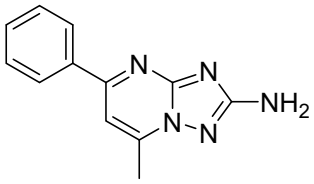
(s, 1H), 2.82 (s, 3H), 1.44 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 167.9, 155.1, 149.2, 145.7, 137.9, 129.8, 128.8, 127.2, 104.1, 93.0, 32.9, 30.5, 17.5; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{17}H_{20}N_3$: 266.1652; found: 266.1655.



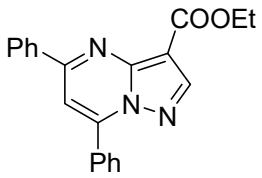
7-methyl-2,5-diphenylpyrazolo[1,5-*a*]pyrimidine (3aq) (CAS: 331978-87-1):
Yield 46% (65.5 mg; petroleum ether/EtOAc = 100:1); yellow solid; mp 110–113 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.12–8.08 (m, 2H), 8.07–8.02 (m, 2H), 7.53–7.46 (m, 5H), 7.43–7.39 (m, 1H), 7.15 (s, 1H), 7.02 (s, 1H), 2.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 156.2, 155.8, 150.0, 145.8, 137.6, 133.2, 130.1, 128.9, 128.9, 128.8, 127.2, 126.6, 105.0, 93.8, 17.6; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{19}H_{16}N_3$: 286.1339; found: 286.1338.



ethyl 7-methyl-5-phenyl-[1,2,4]triazolo[1,5-*a*]pyrimidine-2-carboxylate (3ar) (CAS: 1707085-17-3):
Yield 57% (80.4 mg; petroleum ether/EtOAc = 4:1); white solid; mp 172–174 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.22–8.18 (m, 2H), 7.56–7.51 (m, 4H), 4.58 (q, J = 7.2 Hz, 2H), 2.97 (s, 3H), 1.50 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 162.4, 160.4, 157.5, 155.7, 148.0, 135.8, 131.7, 129.1, 127.8, 108.5, 62.5, 17.6, 14.2; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{15}H_{15}N_4O_2$: 283.1190; found: 283.1189.

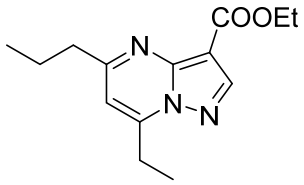


7-methyl-5-phenyl-[1,2,4]triazolo[1,5-*a*]pyrimidin-2-amine (3as) (CAS: 72966-18-8):
Yield 45% (50.6 mg; petroleum ether/EtOAc = 2:1); light brown solid; mp 202–205 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.16–8.13 (m, 2H), 7.52–7.48 (m, 3H), 7.26 (s, 1H), 4.73 (s, 2H), 2.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 166.7, 159.3, 155.8, 145.5, 136.7, 130.7, 128.9, 127.4, 105.5, 17.5; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{12}H_{12}N_5$: 226.1087; found: 226.1091.



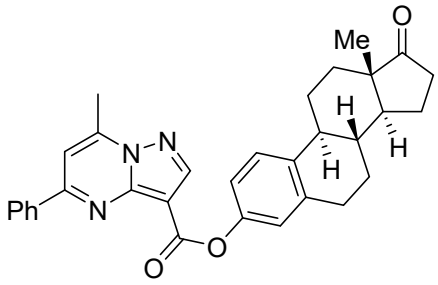
ethyl 5,7-diphenylpyrazolo[1,5-*a*]pyrimidine-3-carboxylate (4):

Yield 73% (125.2 mg; petroleum ether/EtOAc = 20:1); yellow solid; mp 92–95 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.60 (s, 1H), 8.29–8.24 (m, 2H), 8.05–8.00 (m, 2H), 7.62–7.58 (m, 3H), 7.54–7.50 (m, 4H), 4.47 (q, J = 7.2 Hz, 2H), 1.48 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 162.8, 158.9, 148.8, 147.8, 147.7, 136.5, 131.3, 131.1, 130.7, 129.4, 128.9, 128.8, 127.6, 106.3, 103.0, 60.2, 14.5; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{21}H_{18}N_3O_2$: 344.1394; found: 344.1393.



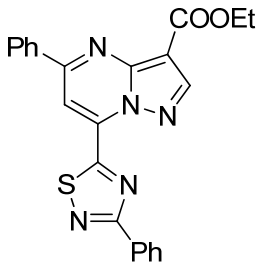
ethyl 7-ethyl-5-propylpyrazolo[1,5-*a*]pyrimidine-3-carboxylate (5):

Yield 67% (62.7 mg; petroleum ether/EtOAc = 5:1); light yellow solid; mp 50–52 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.60 (s, 1H), 8.53 (s, 1H), 4.44 (q, J = 7.2 Hz, 2H), 3.24–3.18 (m, 2H), 2.78 (q, J = 7.6 Hz, 2H), 1.87–1.77 (m, 2H), 1.42 (t, J = 7.2 Hz, 3H), 1.30 (t, J = 7.6 Hz, 3H), 1.09 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 162.8, 154.1, 148.0, 146.9, 146.7, 122.8, 102.6, 60.2, 29.1, 21.9, 20.4, 15.8, 14.6, 14.2; HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{14}H_{19}N_3NaO_2$: 284.1369; found: 284.1371.

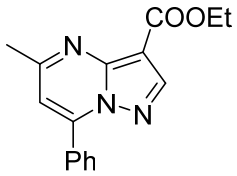


(8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl 7-methyl-5-phenylpyrazolo[1,5-*a*]pyrimidine-3-carboxylate (6):

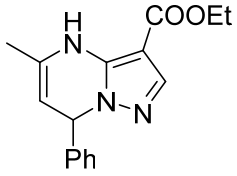
Yield 84% (84.8 mg; petroleum ether/EtOAc = 2:1); white solid; mp 221–223 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.71 (s, 1H), 8.24–8.17 (m, 2H), 7.50–7.44 (m, 3H), 7.37 (s, 1H), 7.33 (d, J = 8.4 Hz, 1H), 7.08 (dd, J = 8.4, 2.8 Hz, 1H), 7.06–7.02 (m, 1H), 2.99–2.91 (m, 2H), 2.89 (s, 3H), 2.56–2.47 (m, H), 2.46–2.38 (m, 1H), 2.35–2.26 (m, 1H), 2.20–2.10 (m, 1H), 2.10–1.95 (m, 3H), 1.67–1.43 (m, 6H), 0.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 220.8, 161.2, 158.8, 148.7, 148.3, 147.8, 147.3, 137.7, 137.0, 136.2, 131.0, 128.8, 127.6, 126.2, 122.0, 119.1, 106.5, 102.0, 50.3, 47.9, 44.1, 37.9, 35.8, 31.5, 29.3, 26.3, 25.7, 21.5, 17.6, 13.8; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{32}H_{32}N_3O_3$: 506.2438; found: 506.2436.



ethyl
5-phenyl-7-(3-phenyl-1,2,4-thiadiazol-5-yl)pyrazolo[1,5-*a*]pyrimidine-3-carboxylate (7):
Yield 74% (63.2mg; petroleum ether/EtOAc = 30:1); yellow solid; mp 238–240 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.77 (s, 1H), 8.67 (s, 1H), 8.46–8.42 (m, 2H), 8.41–8.35 (m, 2H), 7.62–7.51 (m, 6H), 4.49 (q, J = 7.2 Hz, 2H), 1.50 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 174.6, 172.6, 162.4, 159.3, 147.7, 147.5, 136.3, 136.2, 132.1, 131.6, 130.8, 129.2, 128.8, 128.3, 127.9, 104.5, 104.1, 60.6, 14.5; HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{23}H_{17}N_5NaO_2S$: 450.0995; found: 450.0990.



ethyl 5-methyl-7-phenylpyrazolo[1,5-*a*]pyrimidine-3-carboxylate (9):
Yield 81% (113.8 mg; petroleum ether/EtOAc = 5:1); yellow solid; mp 117–119 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.52 (s, 1H), 7.99–7.94 (m, 2H), 7.60–7.54 (m, 3H), 6.95 (s, 1H), 4.43 (q, J = 7.2 Hz, 2H), 2.77 (s, 3H), 1.43 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 162.8, 162.6, 148.8, 147.0, 146.9, 131.2, 130.2, 129.3, 128.6, 110.0, 101.9, 60.1, 25.3, 14.4; HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{16}H_{15}N_3NaO_2$: 304.1056; found: 304.1055.



ethyl 5-methyl-7-phenyl-4,7-dihydropyrazolo[1,5-a]pyrimidine-3-carboxylate **(11):**
Yield 88% (124.5 mg; petroleum ether/EtOAc = 30:1); white solid; mp 149–151 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.65 (s, 1H), 7.36–7.31 (m, 2H), 7.30–7.26 (m, 1H), 7.26–7.22 (m, 2H), 7.18 (s, 1H), 5.95–5.92 (m, 1H), 4.63–4.60 (m, 1H), 4.29 (q, J = 7.2 Hz, 2H), 1.97 (s, 3H), 1.35 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 164.3, 143.0, 142.0, 139.9, 129.6, 128.7, 128.1, 126.8, 97.1, 94.5, 60.4, 59.8, 18.9, 14.4; HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{16}H_{18}N_3O_2$: 284.1394; found: 284.1393.

7. Crystallographic data and molecular structure of 3a

The crystal of **3a** for X-ray diffraction study has been obtained through the dissolving of compound in $CHCl_3$, followed by slow evaporation of the solvent at room temperature. The crystal was kept at 296(2) during data collection. CCDC 2152909 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

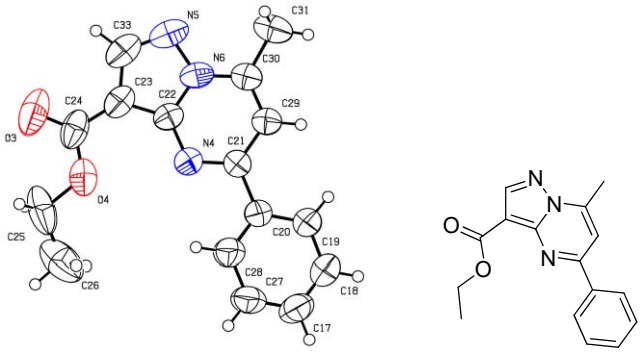


Figure S1. X-ray crystal structure of **3a**; the ellipsoids depicted at the 50% probability level.

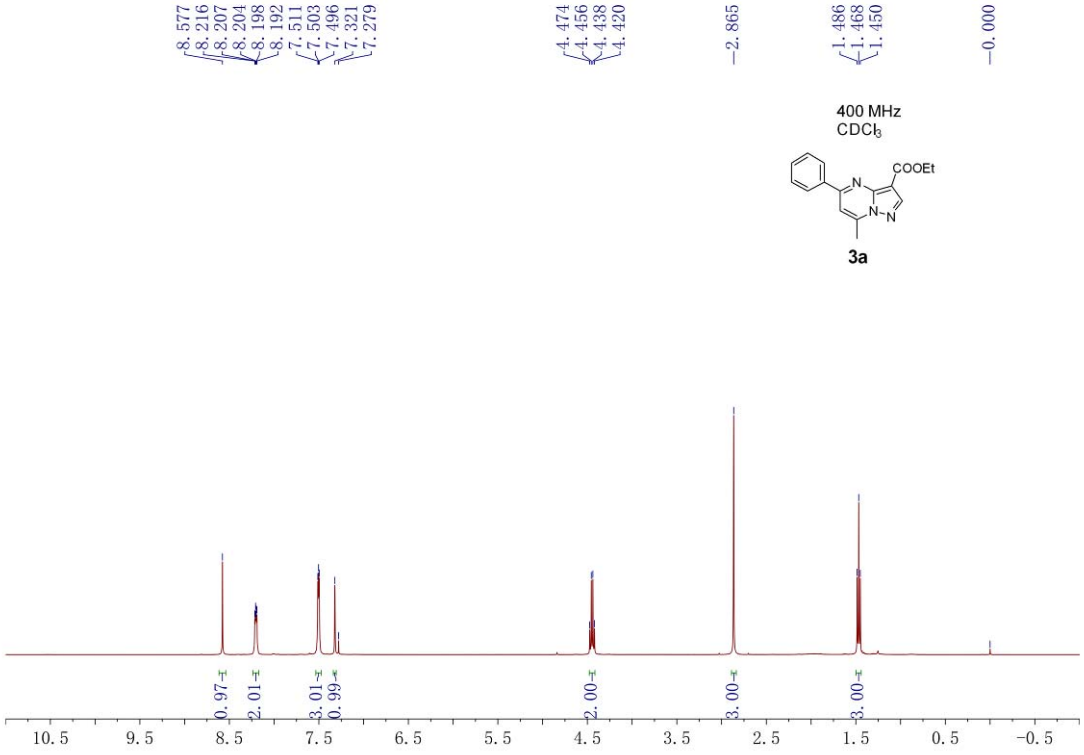
Empirical formula	$C_{32}H_{30}N_6O_4$		Absorption coefficient	0.088 mm^{-1}
Formula weight	562.62		F(000)	1184.0
Temperature	296(2) K		Crystal size	0.130 × 0.110 × 0.090 mm^3
Crystal system	monoclinic		Theta range for data collection	2.944 to 50.498°
Space group	$P2_1/c$		Reflections collected	14990
Unit cell dimensions	a = 7.521(2) Å	α = 90°	Independent reflections	5222 [R(int) = 0.0761]
	b = 18.826(6) Å	β = 97.770(4)°	Data / restraints / parameters	5222/0/383
	c = 20.597(6) Å	γ = 90°	Goodness-of-fit on F^2	1.021
Volume	2889.6(15) $Å^3$		Final R indices [I>2sigma(I)]	R_1 = 0.0705, wR_2 = 0.1599
Z	4		R indices (all data)	R_1 = 0.1669, wR_2 = 0.2063
Density (calculated)	1.293 Mg/m^3		Largest diff. peak and hole	0.15/-0.25 e.$Å^{-3}$

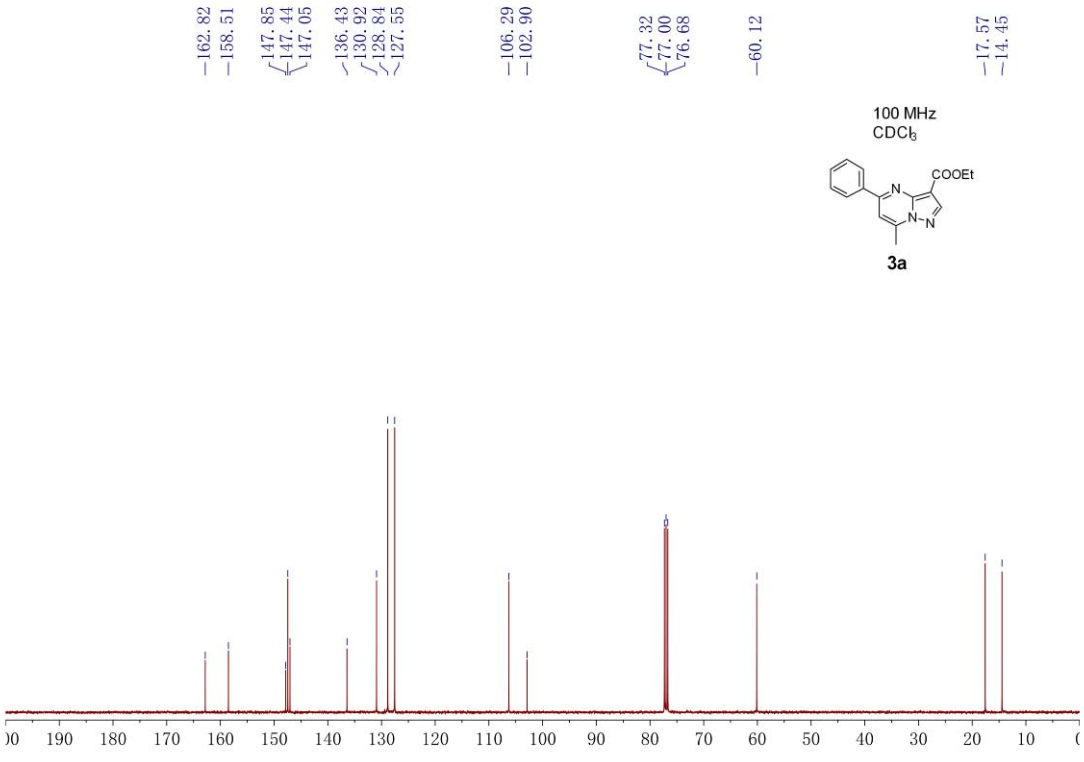
8. References

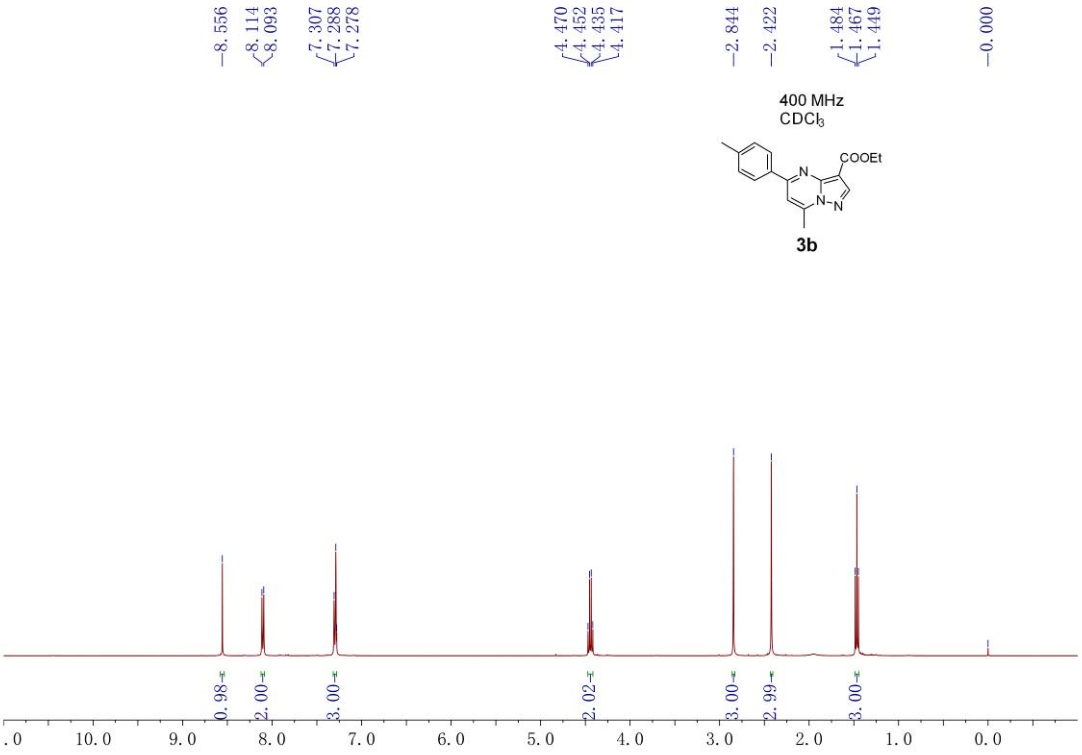
(1) X. Jiang, G. Wang, Z. Zheng, X. Yu, Y. Hong, H. Xia, C. Yu, Autocatalytic Synthesis of Thioesters via Thiocarbonylation of *gem*-Difluoroalkenes, *Org. Lett.*, 2020, **22**, 9762–9766.

(2) H. Xie, J. Cai, Z. Wang, H. Huang, G.-J. Deng, A Three-Component Approach to 3,5-Diaryl-1,2,4-thiadiazoles under Transition-Metal-Free Conditions, *Org. Lett.*, 2016, **18**, 2196−2199.

9. NMR spectra



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COOEt
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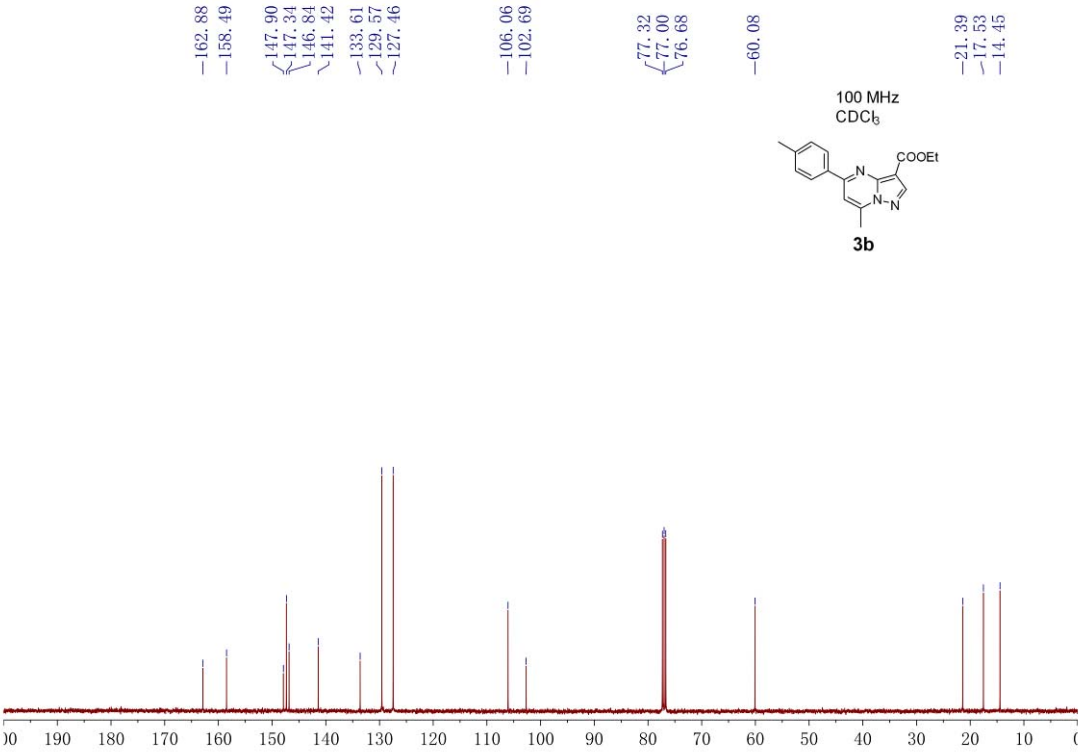
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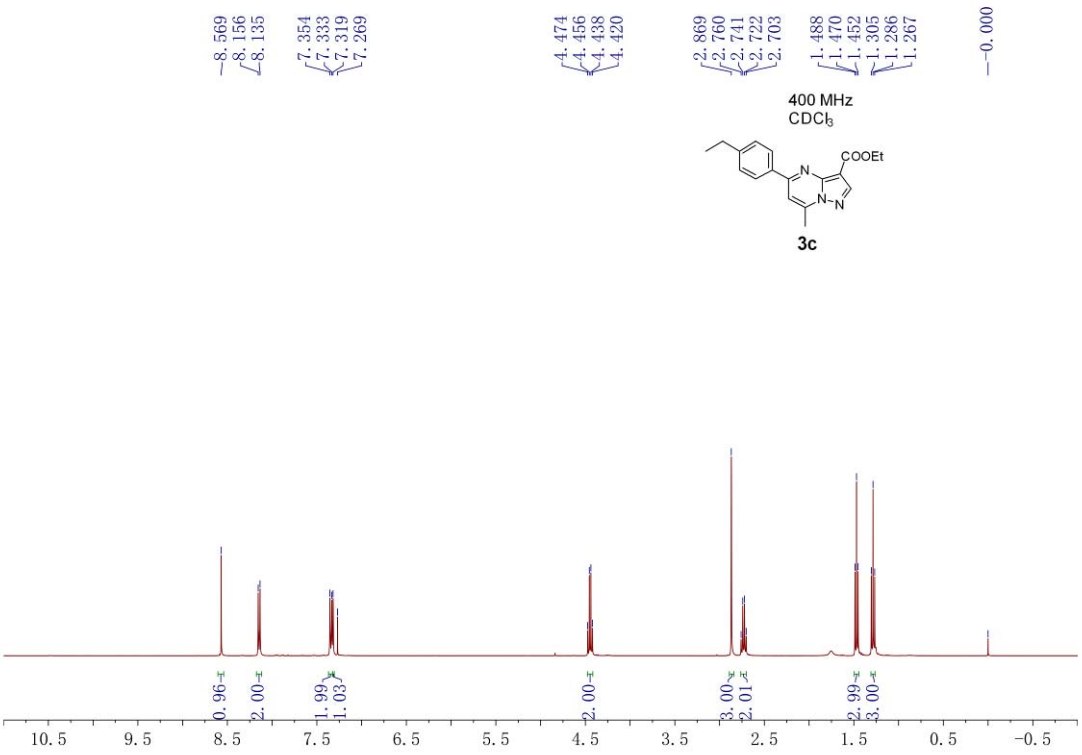
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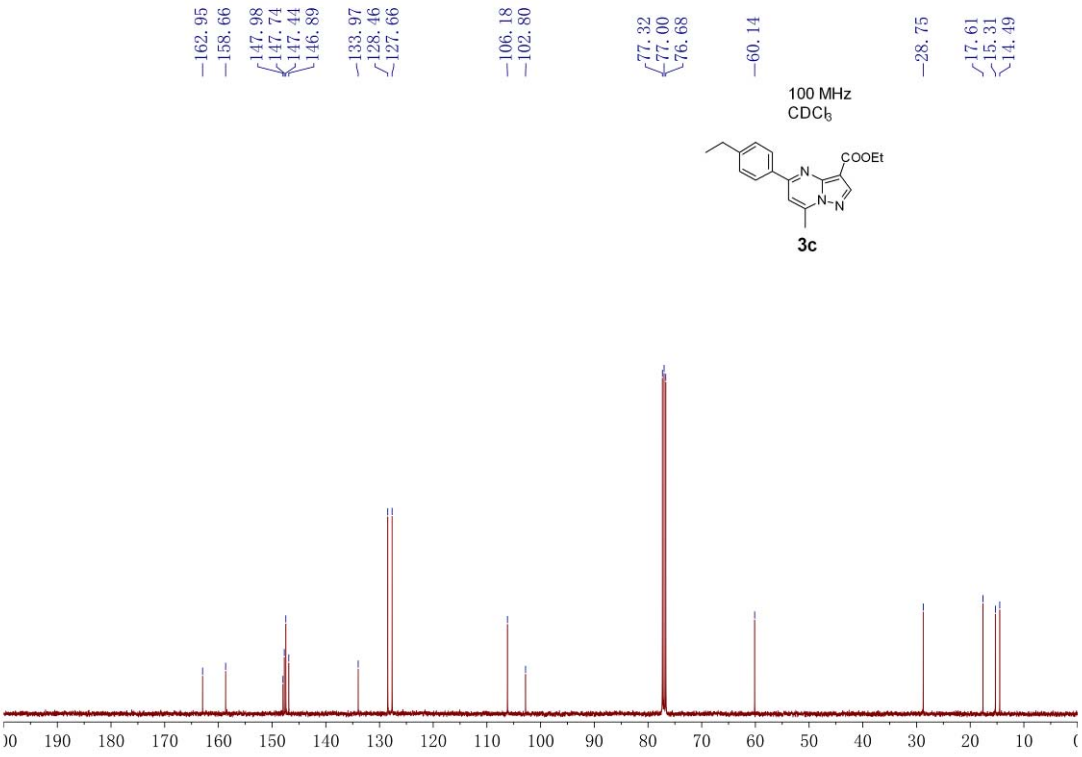
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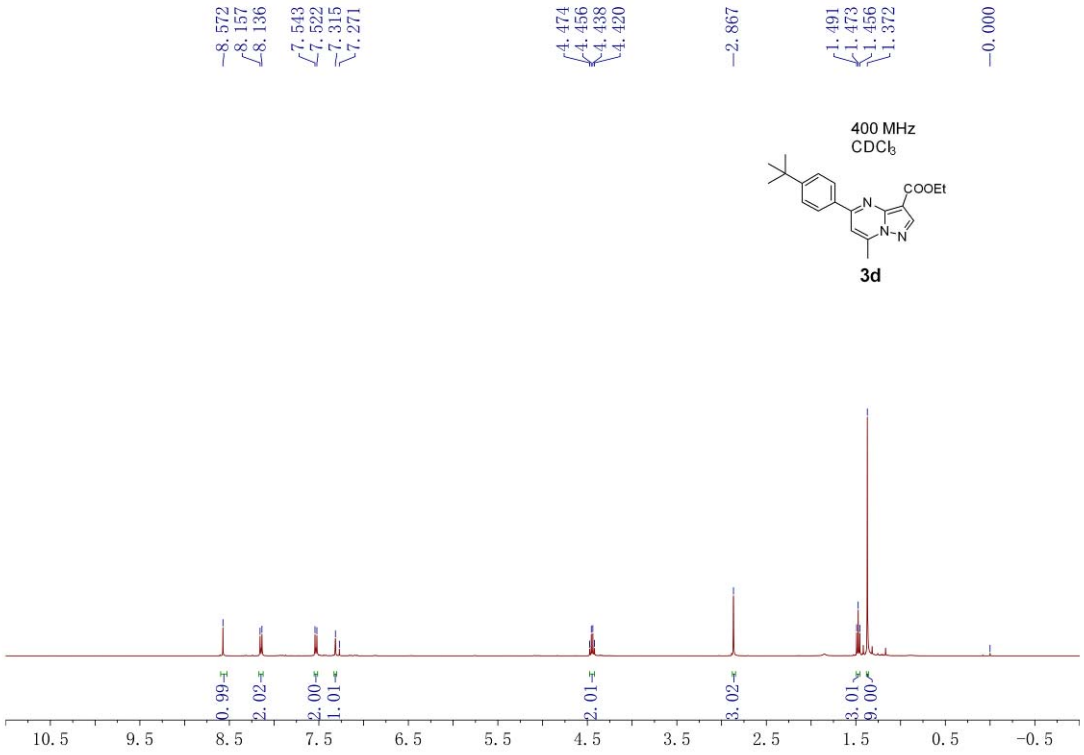
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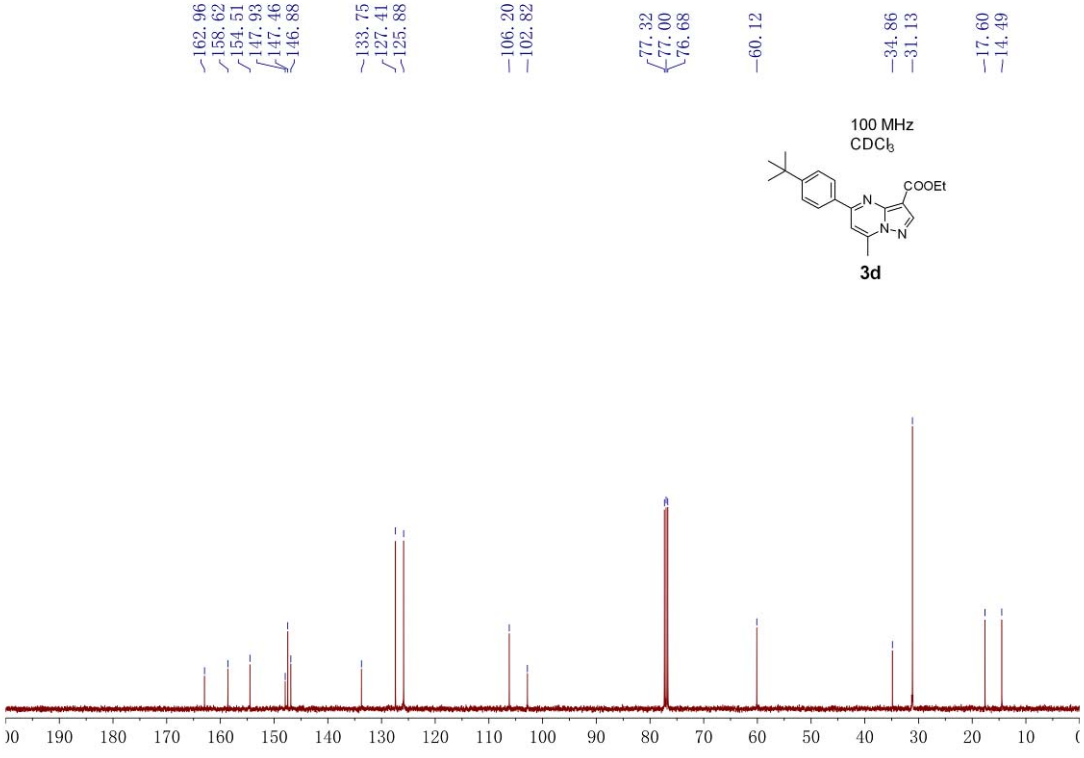
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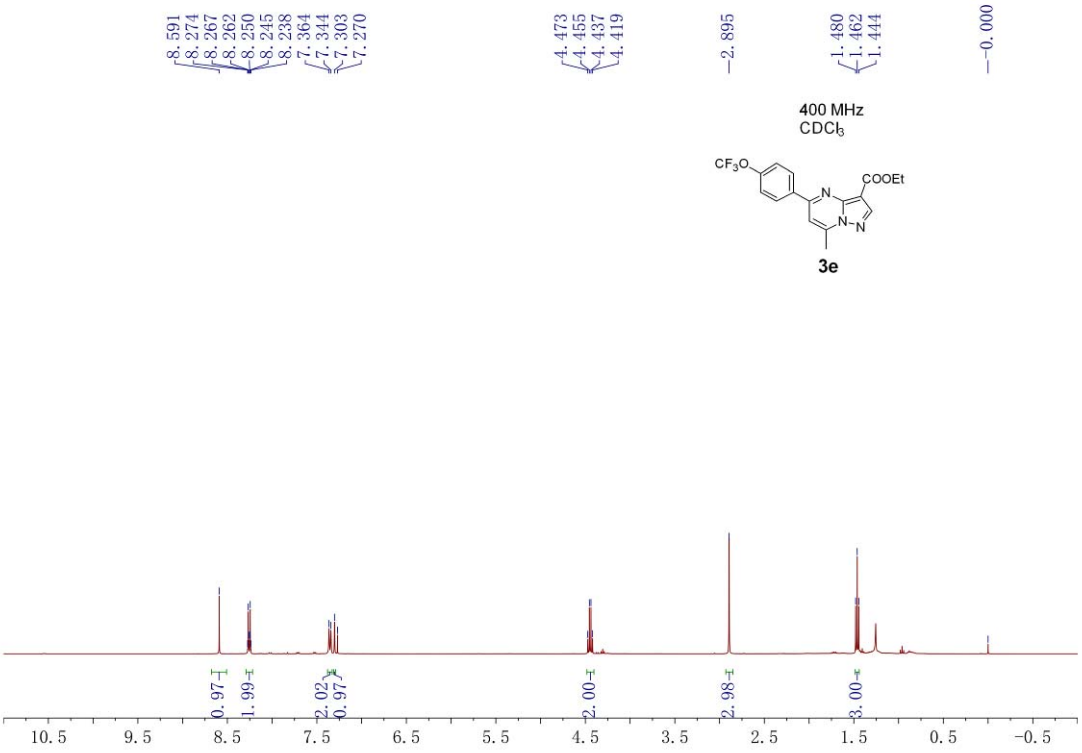
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1.99
2.02
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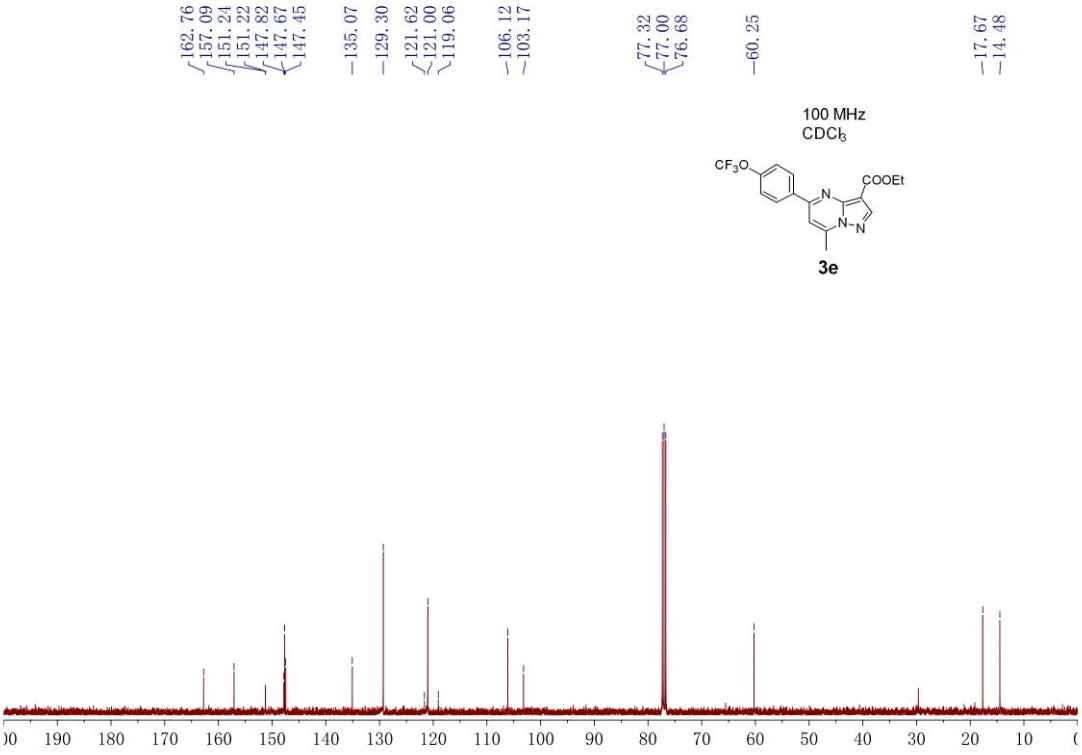
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14.48
100 MHz
CDCl3
CF3O
COOEt
N
N-N
3e
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160
150
140
130
120
110
100
90
80
70
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50
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30
20
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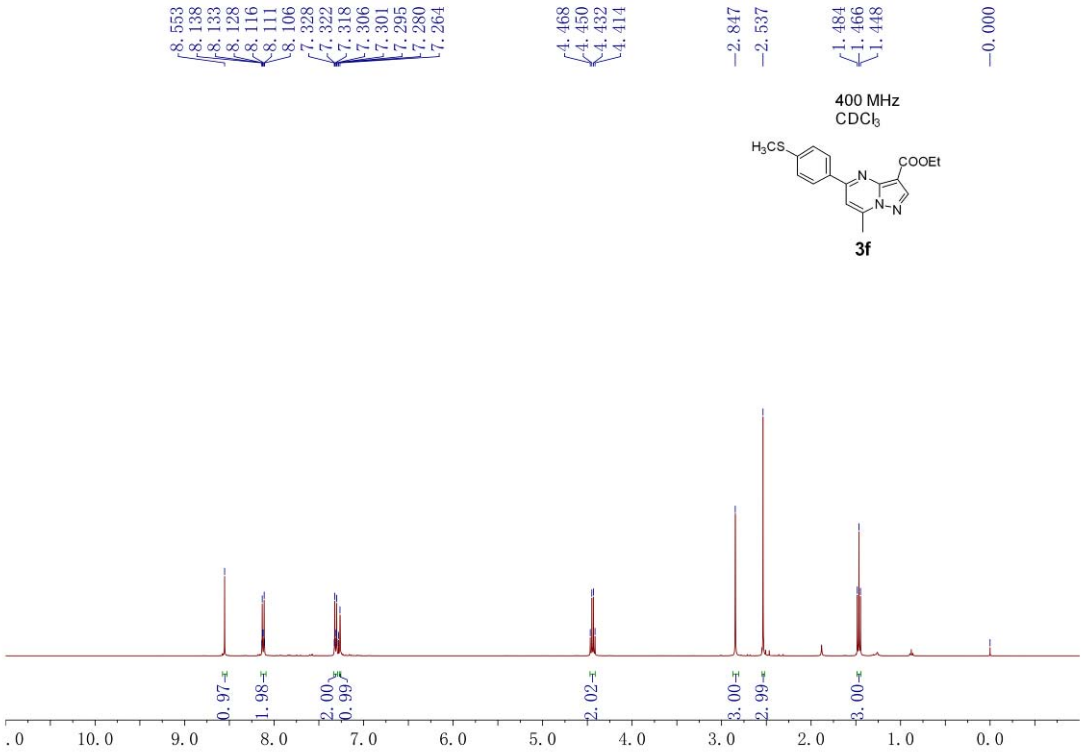
8.553
8.138
8.133
8.128
8.116
8.111
8.106
7.328
7.322
7.318
7.306
7.301
7.295
7.280
7.264
4.468
4.450
4.432
4.414
2.847
2.537
1.484
1.466
1.448
0.000
400 MHz
CDCl3
H3CS
COOEt
N
N-N
3f
0.97
1.98
2.00
0.99
2.02
3.00
2.99
3.00
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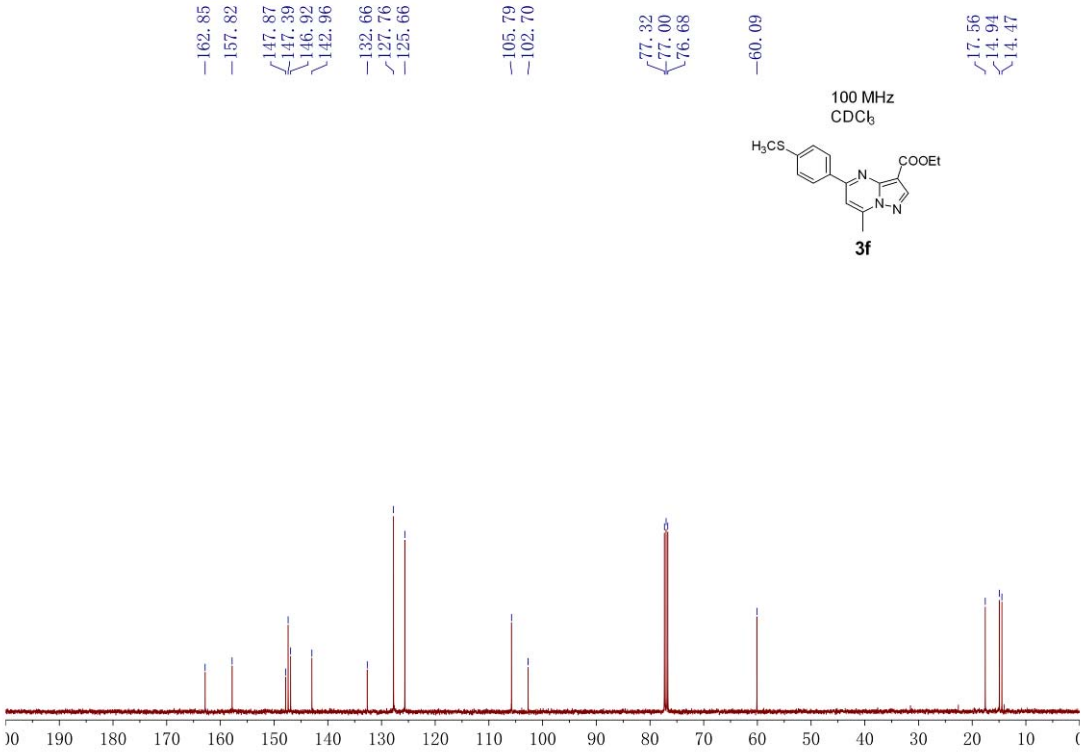
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0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157.82
147.87
147.39
146.92
142.96
132.66
127.76
125.66
105.79
102.70
77.32
77.00
76.68
60.09
17.56
14.94
14.47
100 MHz
CDCl3
H3CS
COOEt
N
N-N
3f
190
180
170
160
150
140
130
120
110
100
90
80
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40
30
20
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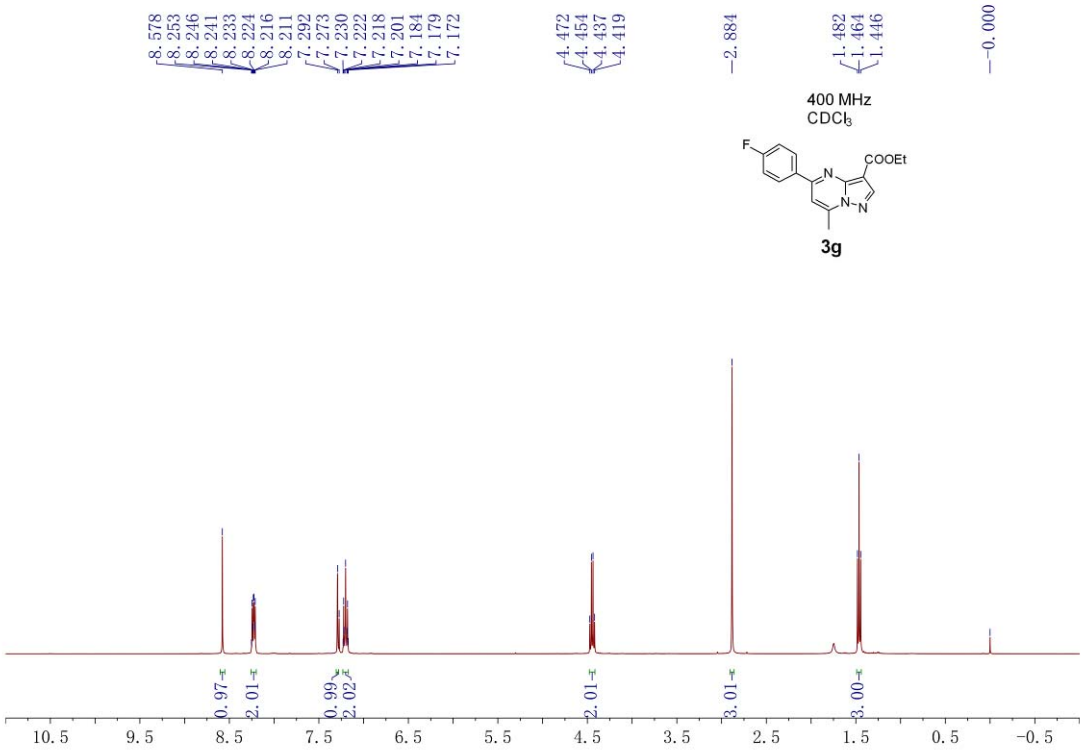
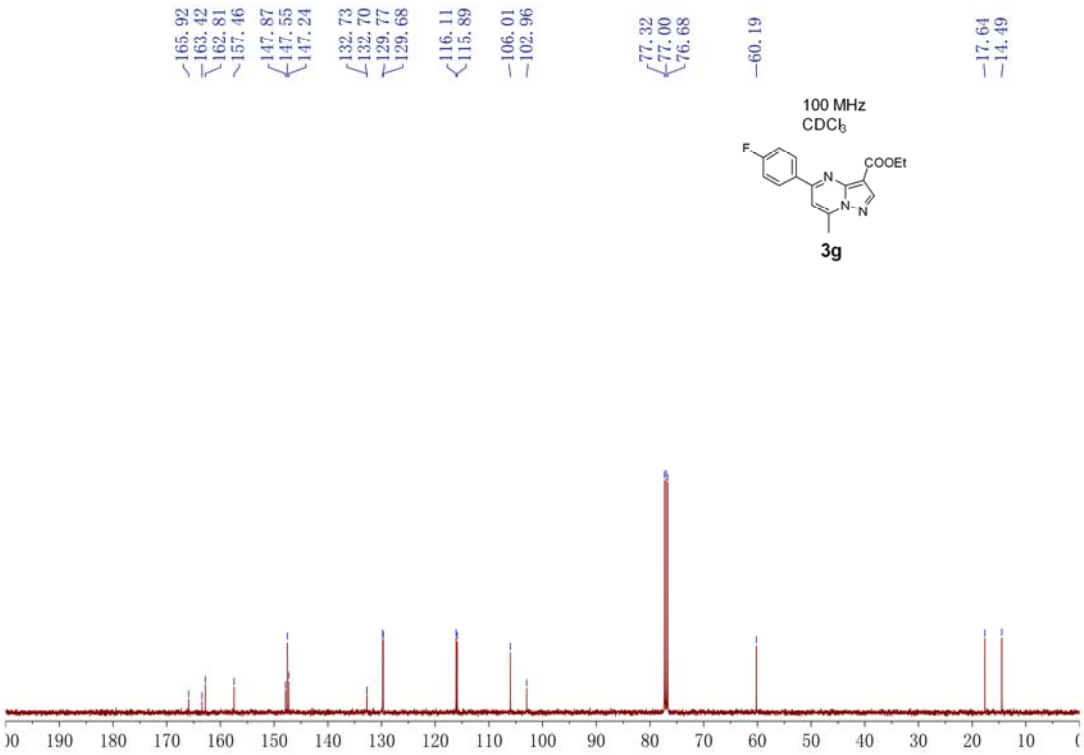

8.578
8.253
8.246
8.241
8.233
8.224
8.216
8.211
7.292
7.273
7.230
7.222
7.218
7.201
7.184
7.179
7.172
4.472
4.454
4.437
4.419
2.884
1.482
1.464
1.446
0.000
400 MHz
CDCl3
F
COOEt
N
N-N
3g
0.97
2.01
0.99
2.02
2.01
3.01
3.00
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5


165.92
163.42
162.81
157.46
147.87
147.55
147.24
132.73
132.70
129.77
129.68
116.11
115.89
106.01
102.96
77.32
77.00
76.68
60.19
17.64
14.49
100 MHz
CDCl3
F
COOEt
N
N-N
3g
190
180
170
160
150
140
130
120
110
100
90
80
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40
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20
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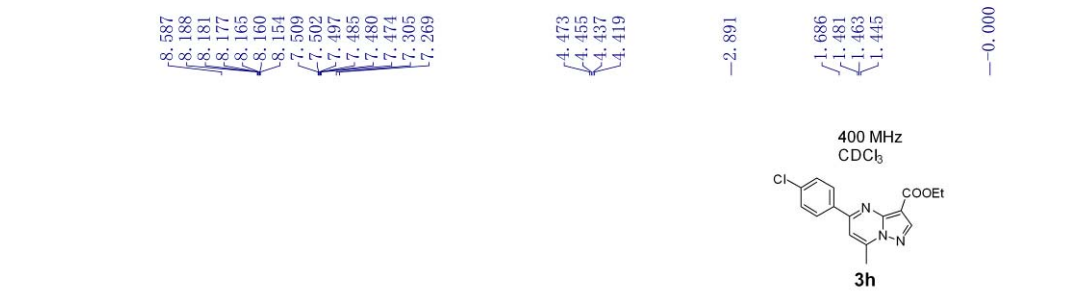
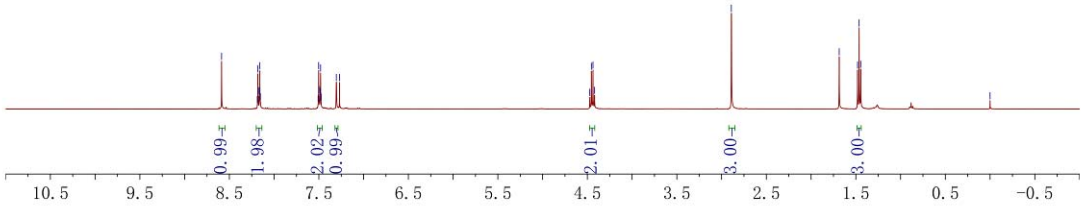
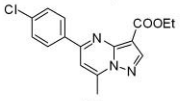


400 MHz
$CDCl_3$

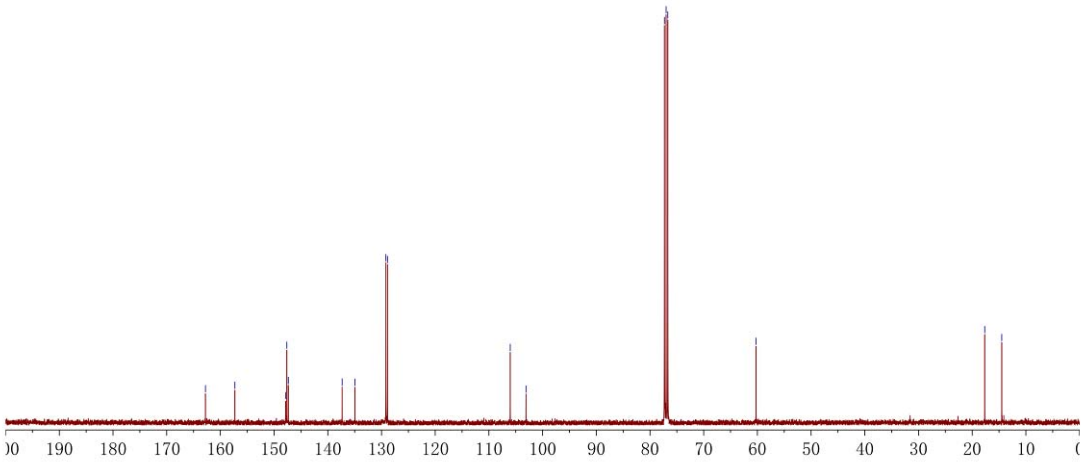
3h

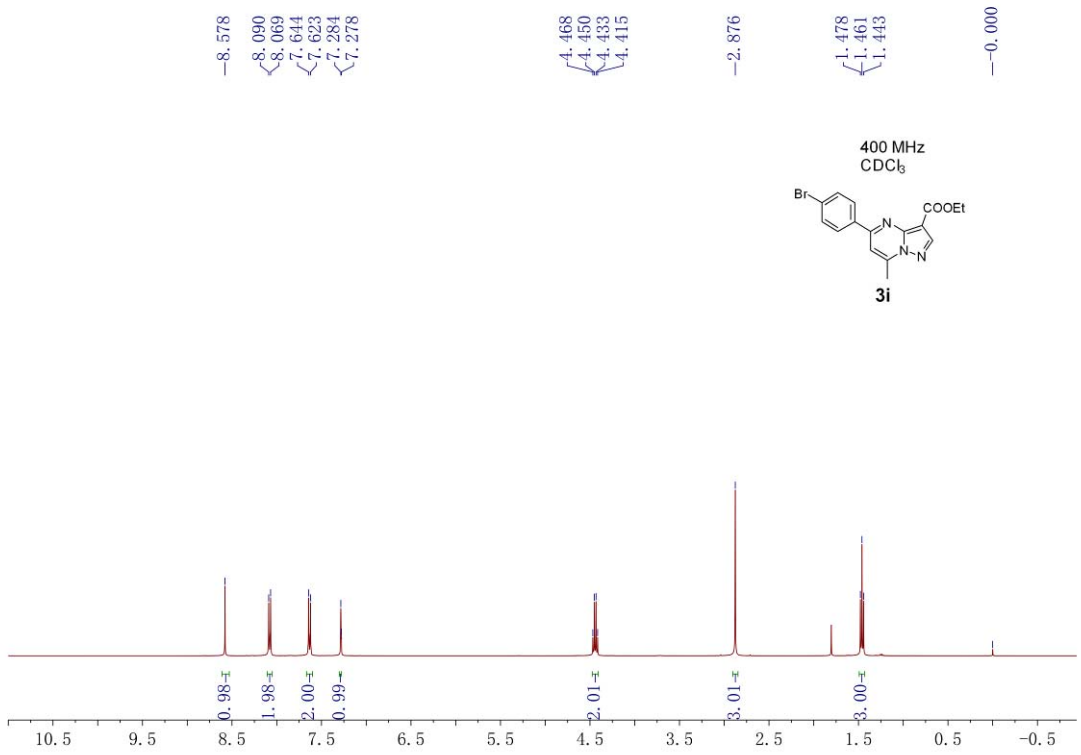


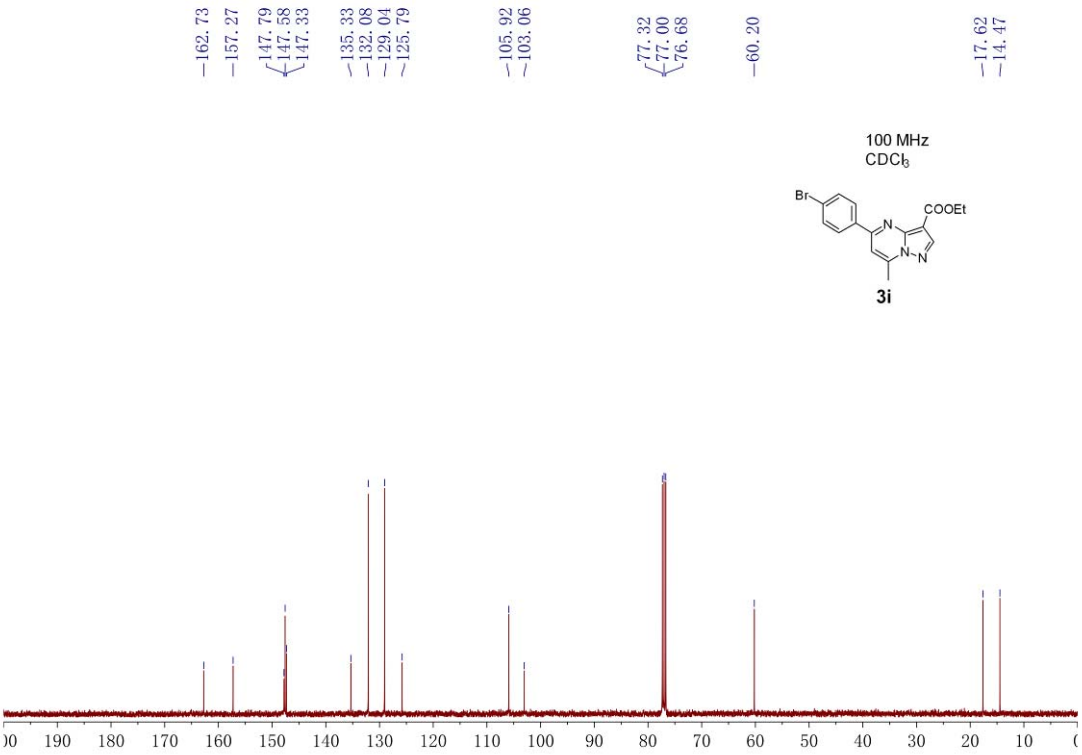
100 MHz
$CDCl_3$

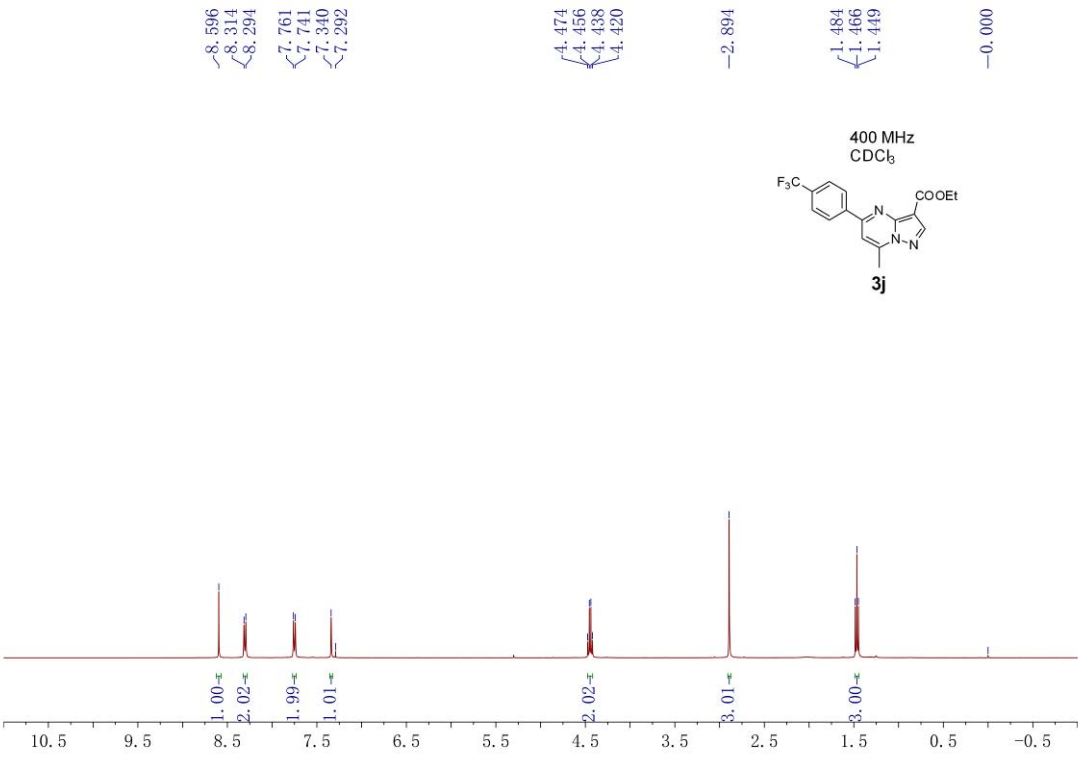


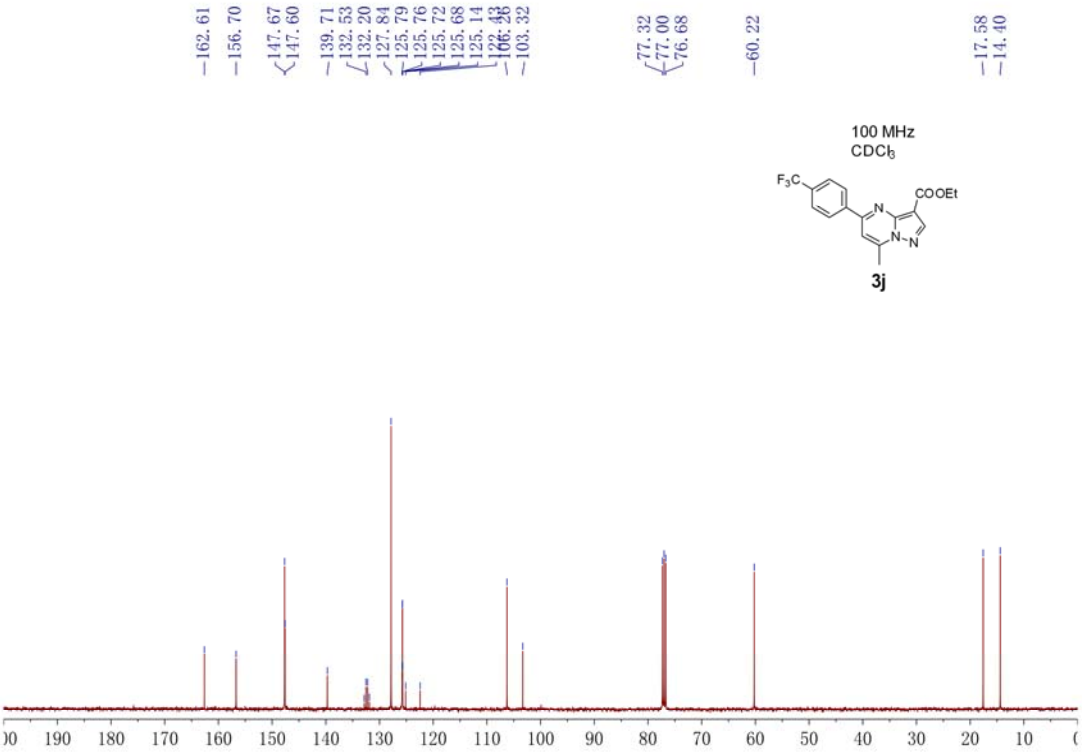
3h

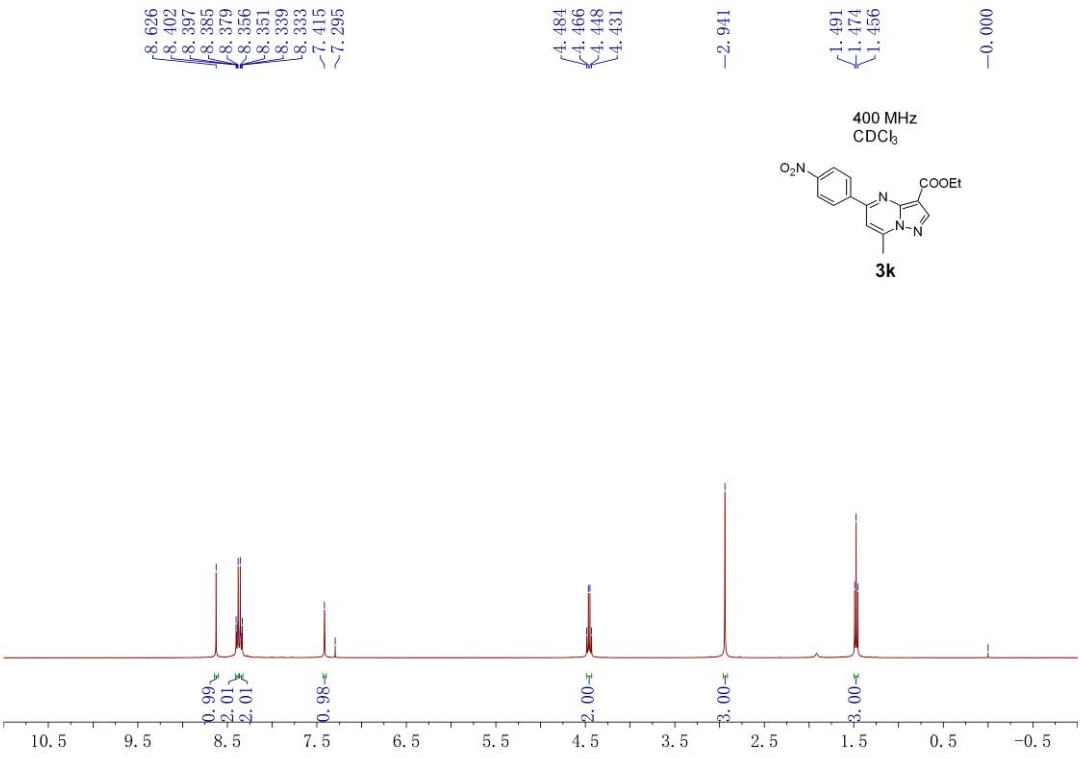


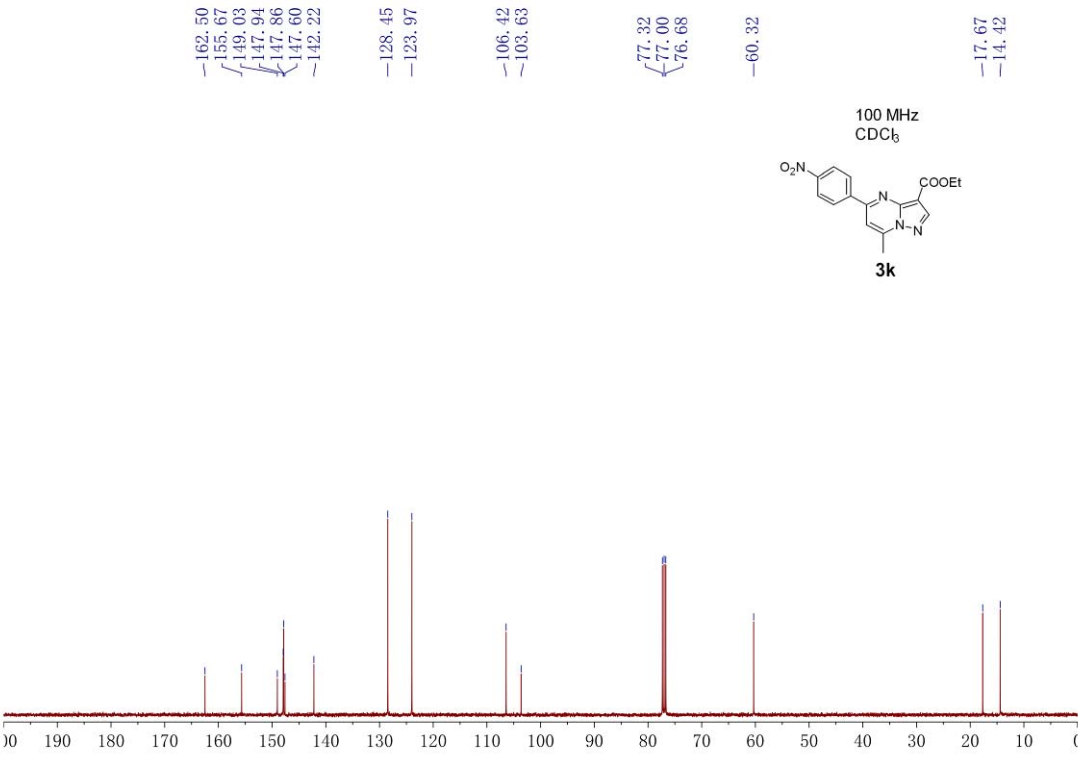

8.578
8.090
8.069
7.644
7.623
7.284
7.278
4.468
4.450
4.433
4.415
2.876
1.478
1.461
1.443
0.000
400 MHz
CDCl3
Br
COOEt
N
N
N
3i
0.98
1.98
2.00
0.99
2.01
3.01
3.00
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5

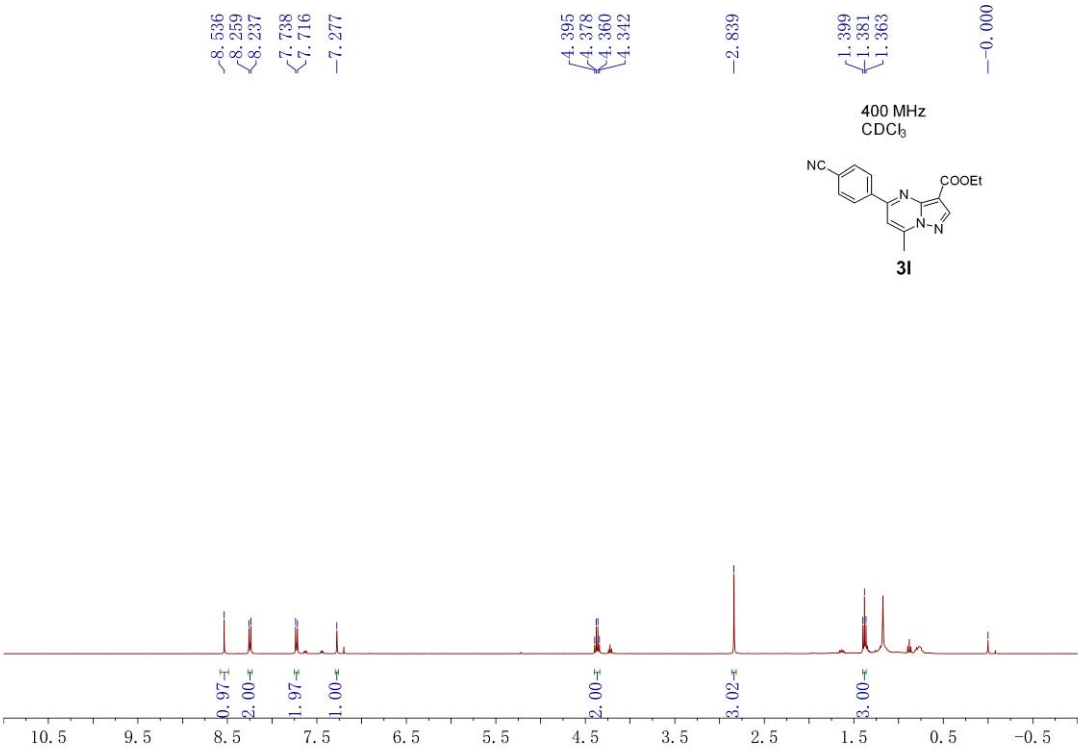

162.73
157.27
147.79
147.58
147.33
135.33
132.08
129.04
125.79
105.92
103.06
77.32
77.00
76.68
60.20
17.62
14.47
100 MHz
CDCl3
Br
COOEt
N
N
N
3i
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

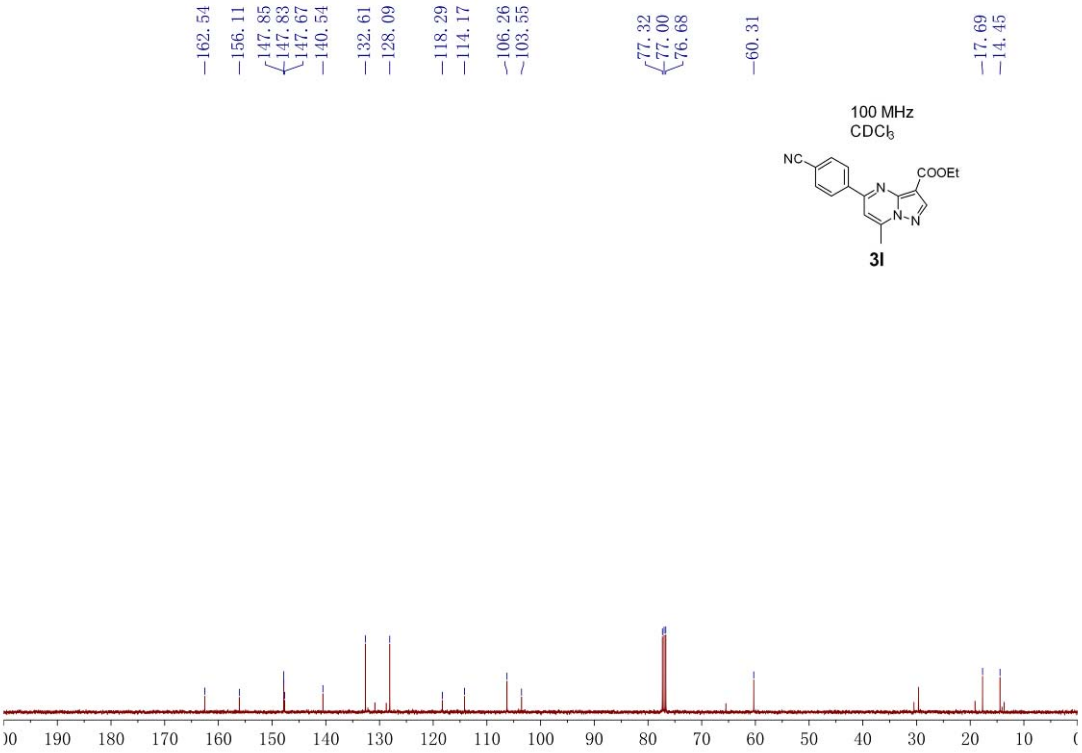

8.596
8.314
8.294
7.761
7.741
7.340
7.292
4.474
4.456
4.438
4.420
2.894
1.484
1.466
1.449
0.000
400 MHz
CDCl3
F3C
COOEt
N
N-N
3j
1.00
2.02
1.99
1.01
2.02
3.01
3.00
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5


162.61
156.70
147.67
147.60
139.71
132.53
132.20
127.84
125.79
125.76
125.72
125.68
125.14
103.32
77.32
77.00
76.68
60.22
17.58
14.40
100 MHz
CDCl3
F3C
COOEt
N
N-N
3j
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


8.626
8.402
8.397
8.385
8.379
8.356
8.351
8.339
8.333
7.415
7.295
4.484
4.466
4.448
4.431
2.941
1.491
1.474
1.456
0.000
400 MHz
CDCl3
O2N
COOEt
N
N-N
3k
0.99
2.01
2.01
0.98
2.00
3.00
3.00
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5


162.50
155.67
149.03
147.94
147.86
147.60
142.22
128.45
123.97
106.42
103.63
77.32
77.00
76.68
60.32
17.67
14.42
100 MHz
CDCl3
O2N
COOEt
N
N-N
3k
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


8.536
8.259
8.237
7.738
7.716
7.277
4.395
4.378
4.360
4.342
2.839
1.399
1.381
1.363
0.000
400 MHz
CDCl3
NC
COOEt
N
N-N
3l
0.97
2.00
1.97
1.00
2.00
3.02
3.00
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5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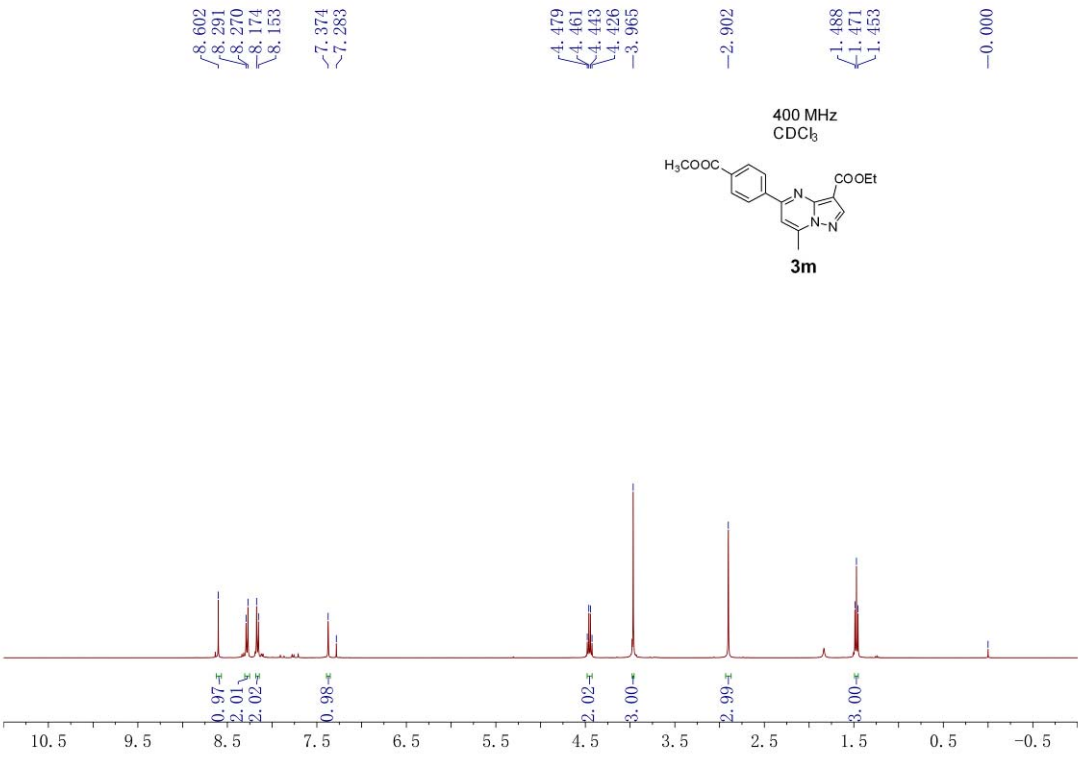
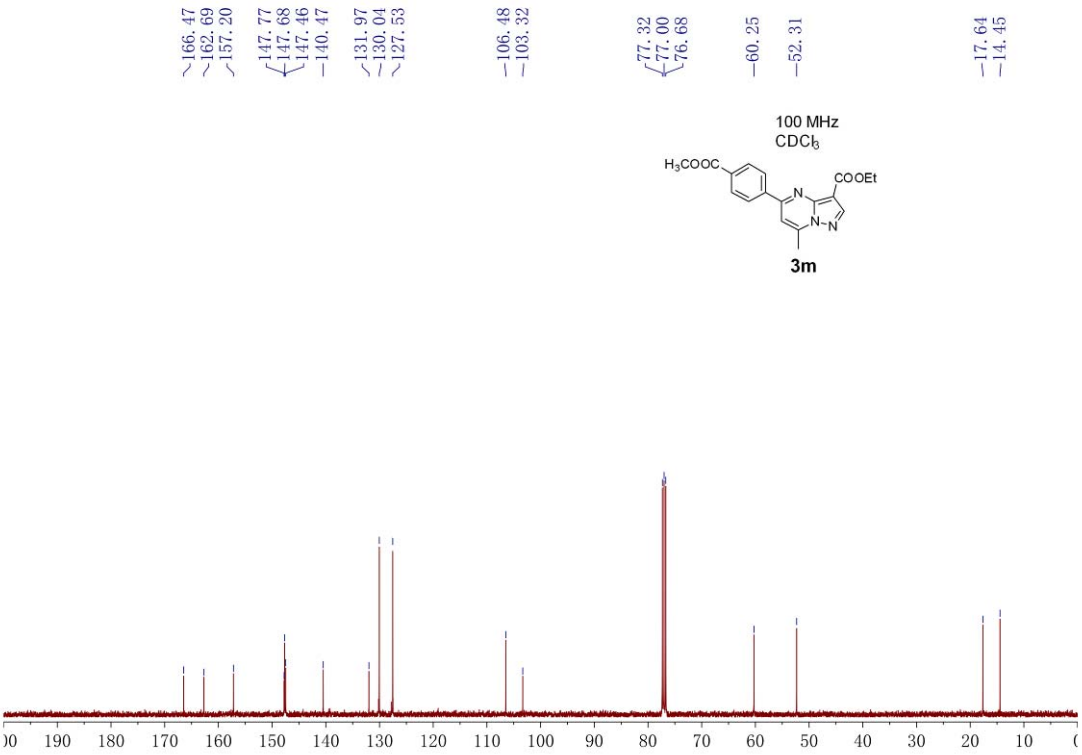
156.11
147.85
147.83
147.67
140.54
132.61
128.09
118.29
114.17
106.26
103.55
77.32
77.00
76.68
60.31
17.69
14.45
100 MHz
CDCl3
NC
COOEt
N
N-N
3l
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


8.602
8.291
8.270
8.174
8.153
7.374
7.283
4.479
4.461
4.443
4.426
3.965
2.902
1.488
1.471
1.453
0.000
400 MHz
CDCl3
H3COOC
COOEt
3m
0.97
2.01
2.02
0.98
2.02
3.00
2.99
3.00
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5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147.46
140.47
131.97
130.04
127.53
106.48
103.32
77.32
77.00
76.68
60.25
52.31
17.64
14.45
100 MHz
CDCl3
H3COOC
COOEt
3m
190
180
170
160
150
140
130
120
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80
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20
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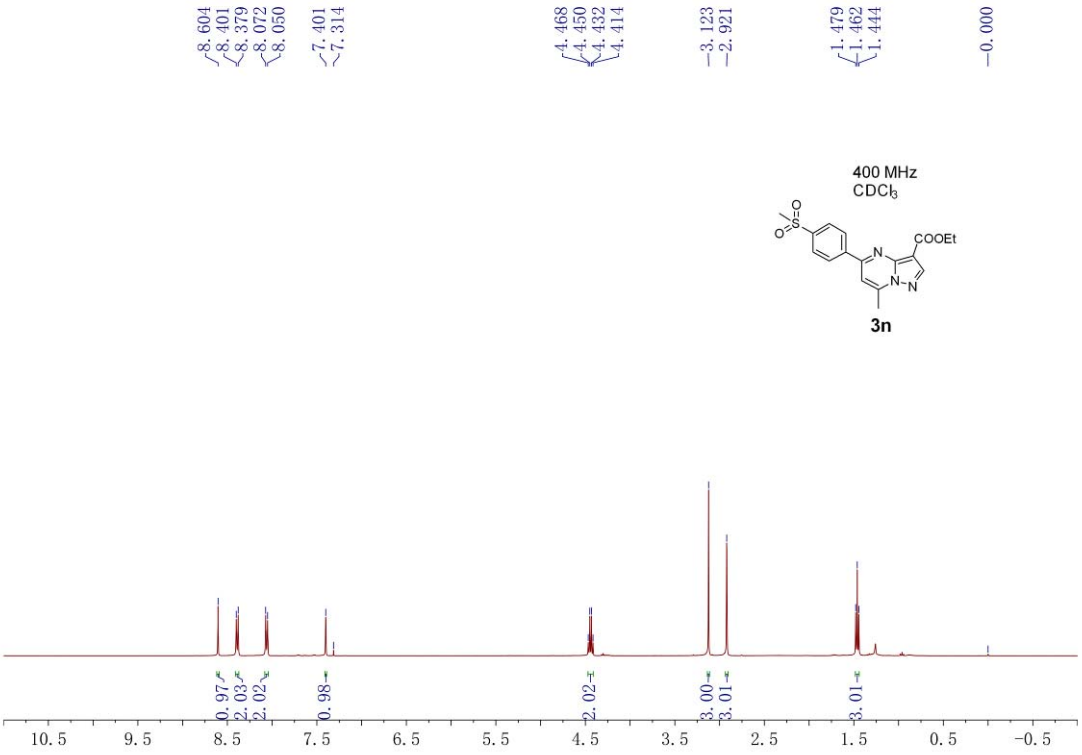
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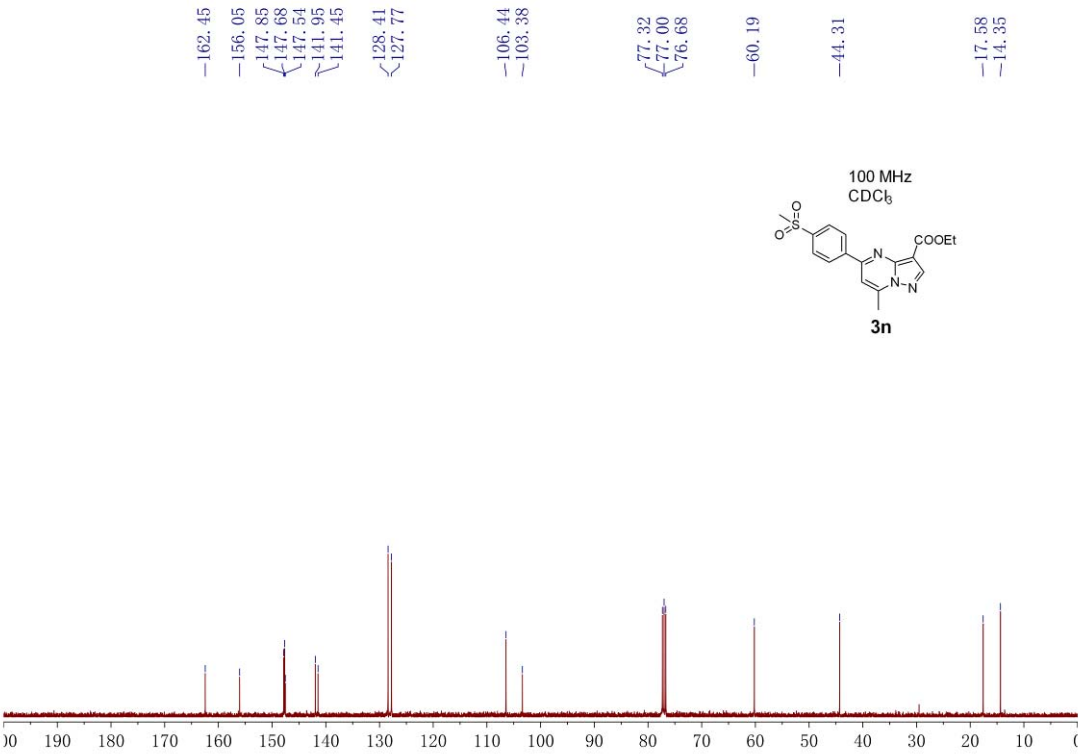
8.401
8.379
8.072
8.050
7.401
7.314
4.468
4.450
4.432
4.414
3.123
2.921
1.479
1.462
1.444
0.000
400 MHz
CDCl3
COOEt
3n
0.97
2.03
2.02
0.98
2.02
3.00
3.01
3.01
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5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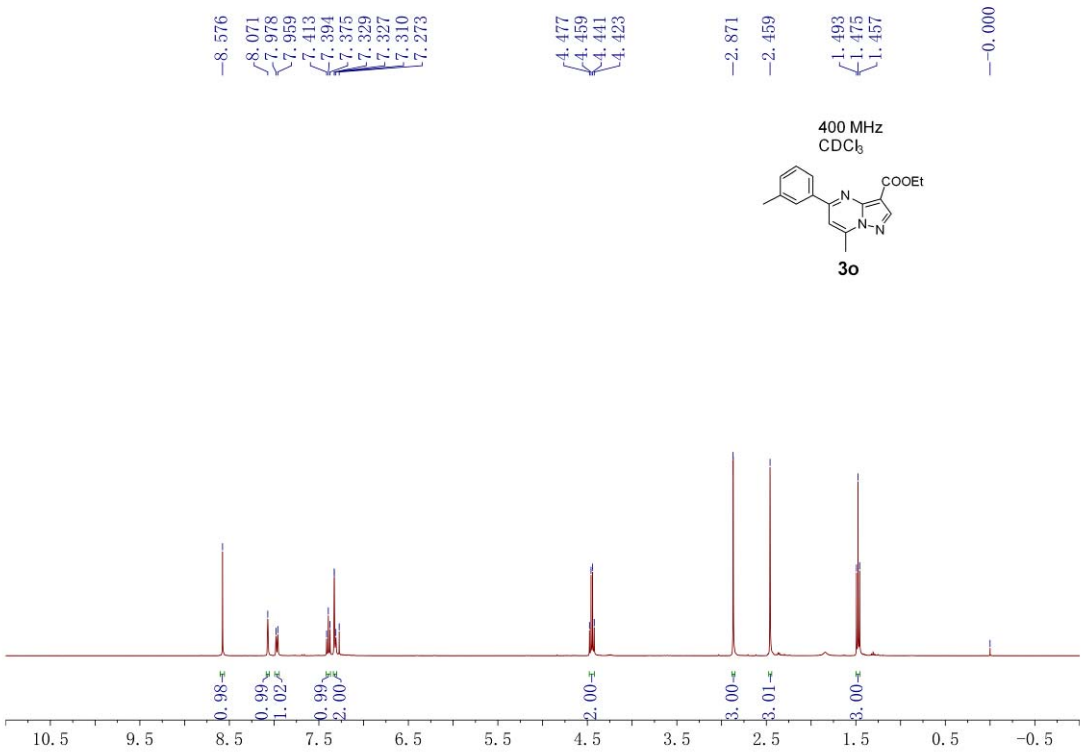
147.85
147.68
147.54
141.95
141.45
128.41
127.77
106.44
103.38
77.32
77.00
76.68
60.19
44.31
17.58
14.35
100 MHz
CDCl3
COOEt
3n
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10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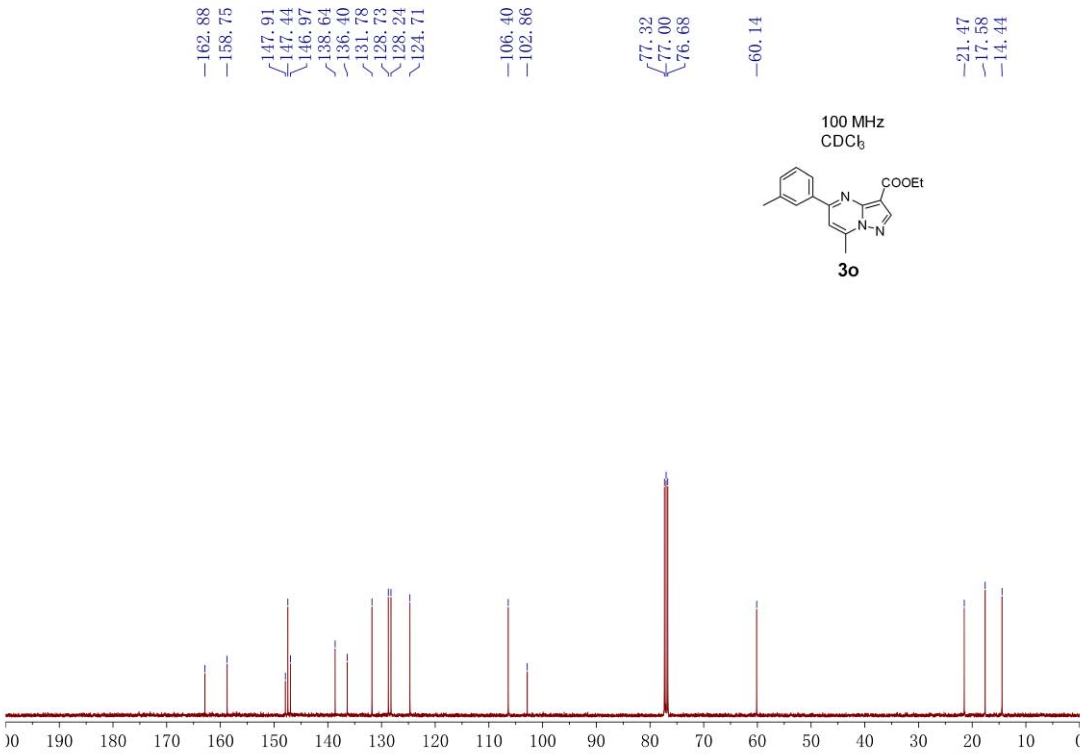
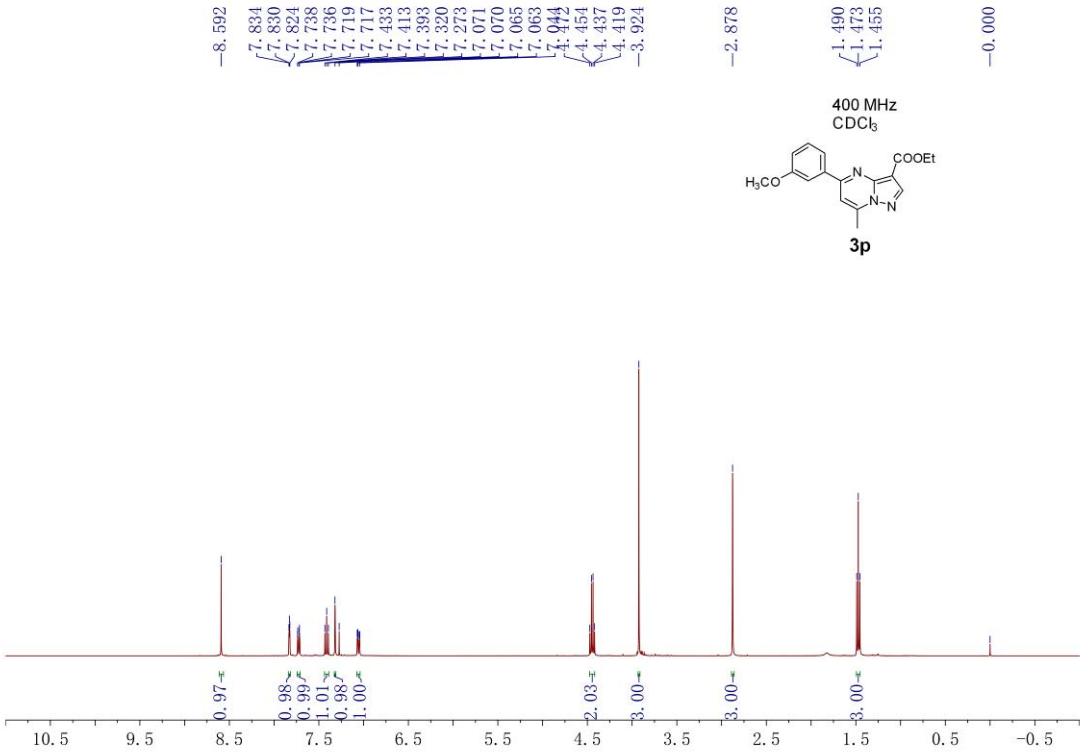
8.071
7.978
7.959
7.413
7.394
7.375
7.329
7.327
7.310
7.273
4.477
4.459
4.441
4.423
2.871
2.459
1.493
1.475
1.457
0.000
400 MHz
CDCl3
COOEt
3o
0.98
0.99
1.02
0.99
2.00
2.00
3.00
3.01
3.00
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5


162.88
158.75
147.91
147.44
146.97
138.64
136.40
131.78
128.73
128.24
124.71
106.40
102.86
77.32
77.00
76.68
60.14
21.47
17.58
14.44
100 MHz
CDCl3
COOEt
3o
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10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7.830
7.824
7.738
7.736
7.719
7.717
7.433
7.413
7.393
7.320
7.273
7.071
7.070
7.065
7.063
4.454
4.437
4.419
3.924
2.878
1.490
1.473
1.455
0.000
400 MHz
CDCl3
COOEt
H3CO
N
N-N
3p
0.97
0.98
0.99
1.01
0.98
1.00
2.03
3.00
3.00
3.00
10.5
9.5
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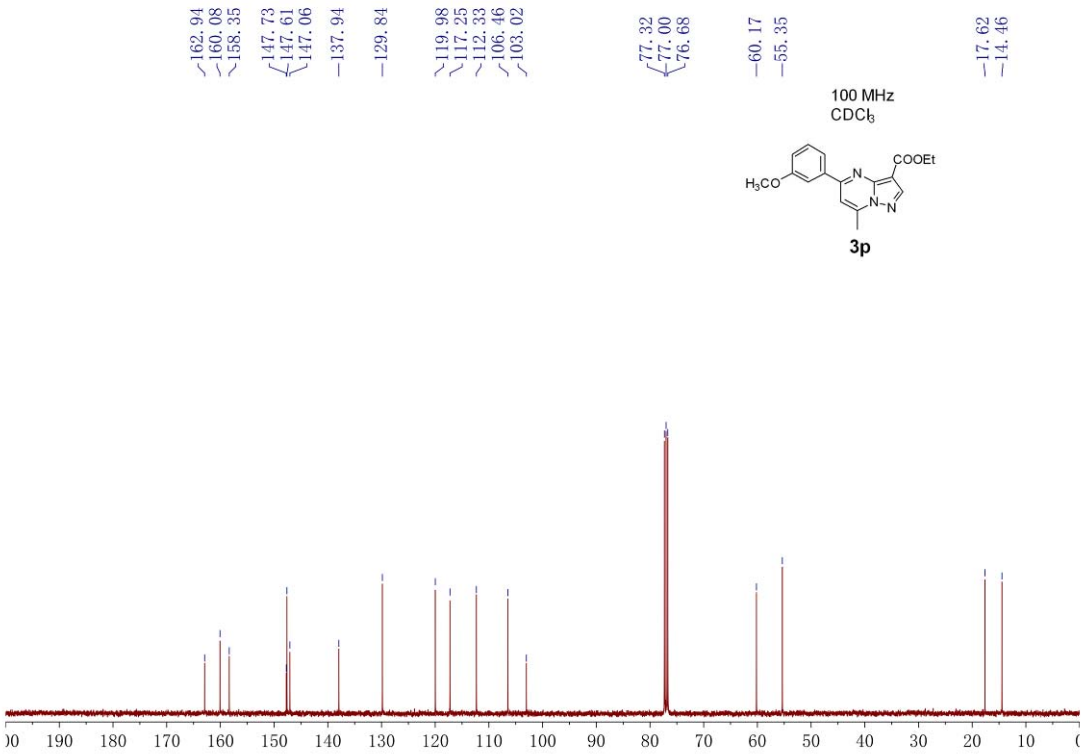
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5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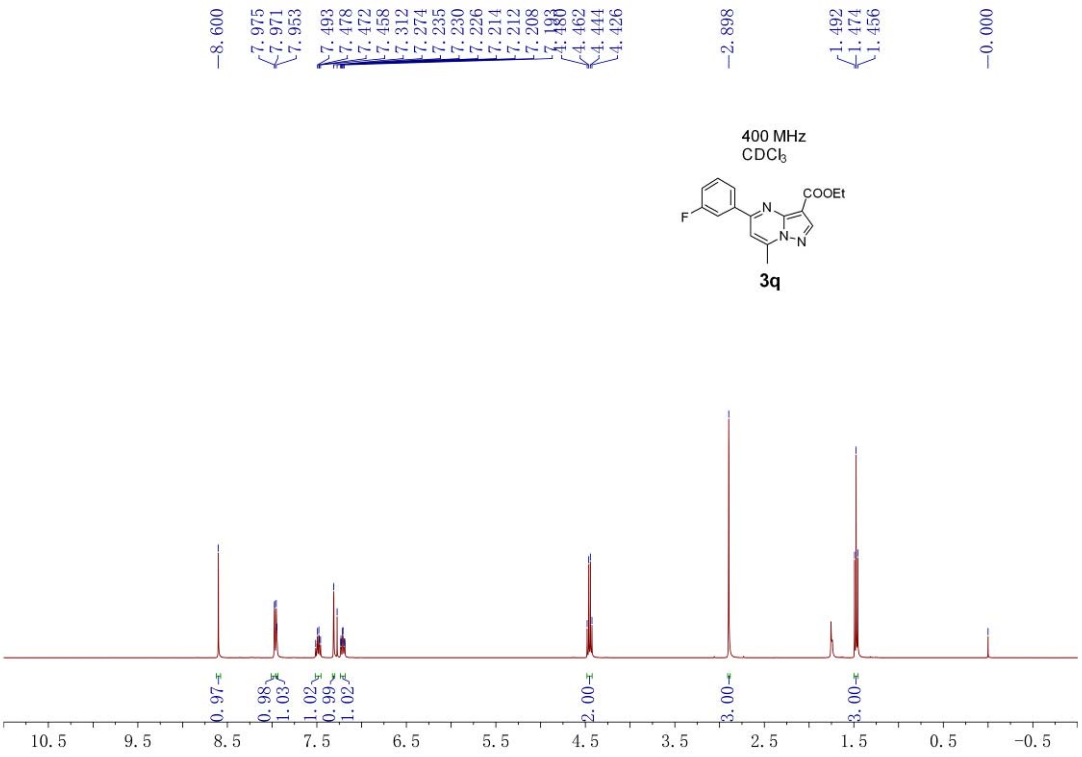
160.08
158.35
147.73
147.61
147.06
137.94
129.84
119.98
117.25
112.33
106.46
103.02
77.32
77.00
76.68
60.17
55.35
17.62
14.46
100 MHz
CDCl3
COOEt
H3CO
N
N-N
3p
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10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7.493
7.478
7.472
7.458
7.312
7.274
7.235
7.230
7.226
7.214
7.212
7.208
4.462
4.444
4.426
2.898
1.492
1.474
1.456
0.000
400 MHz
CDCl3
COOEt
F
N
N-N
3q
0.97
0.98
1.03
1.02
0.99
1.02
2.00
3.00
3.00
10.5
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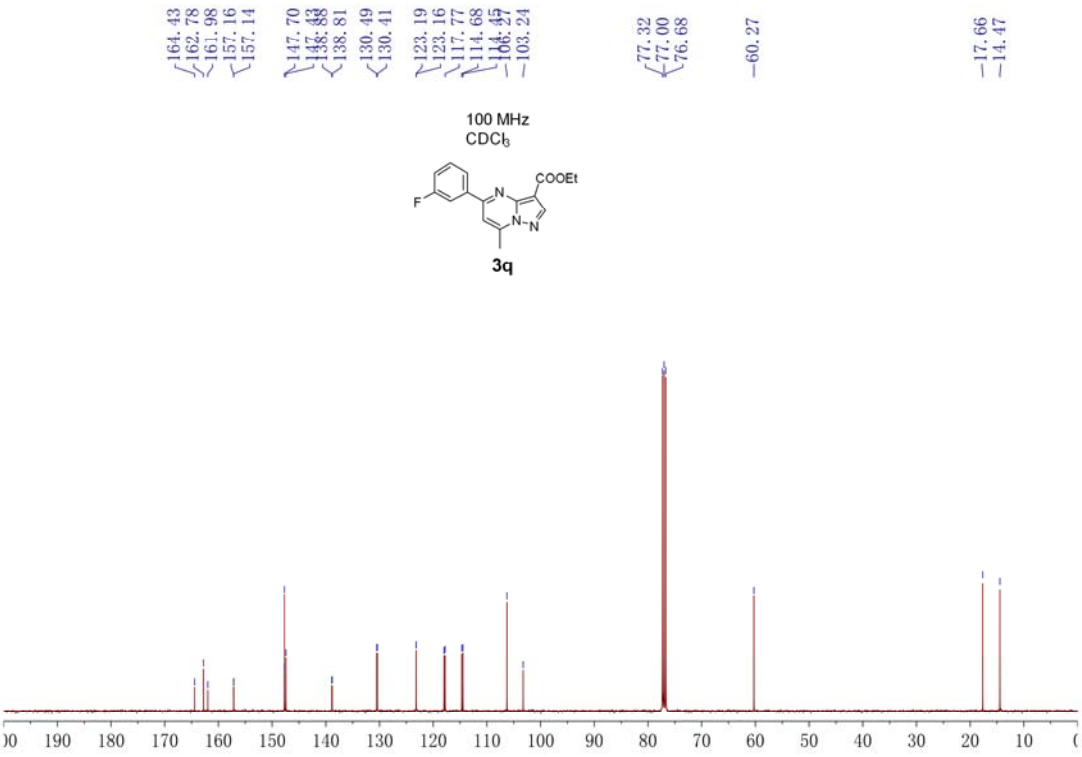
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5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157.16
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147.70
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130.49
130.41
123.19
123.16
117.77
114.68
103.24
77.32
77.00
76.68
60.27
17.66
14.47
100 MHz
CDCl3
COOEt
F
N
N-N
3q
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
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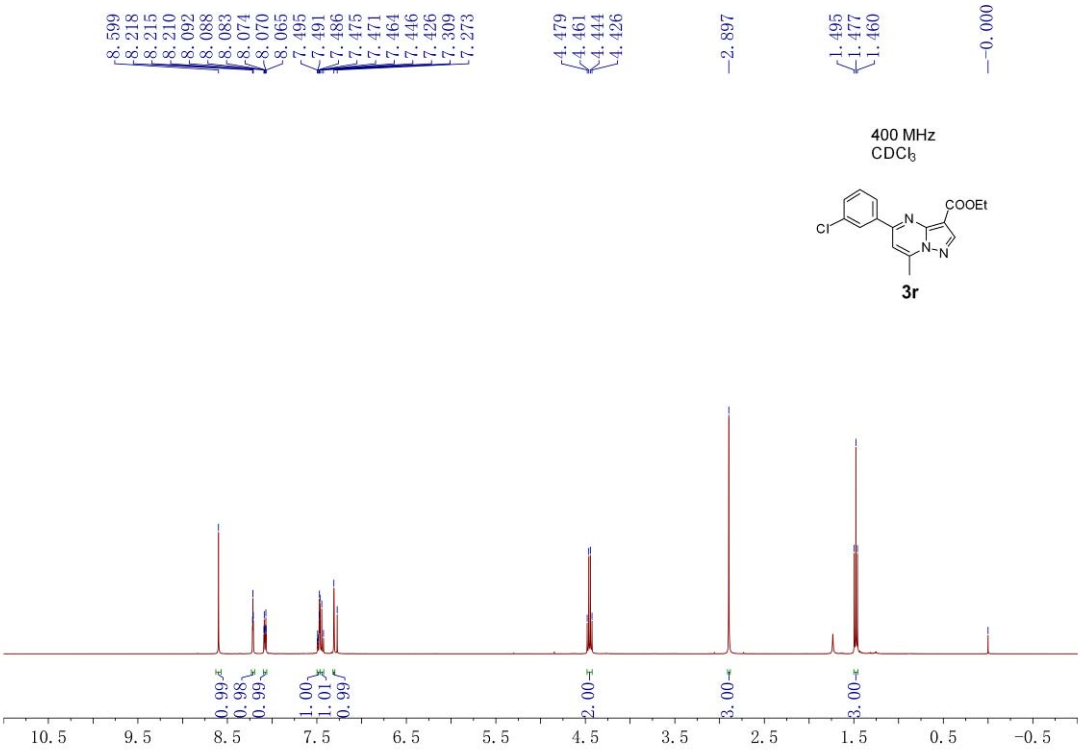
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8.218
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8.210
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8.088
8.083
8.074
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8.065
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7.491
7.486
7.475
7.471
7.464
7.446
7.426
7.309
7.273
4.479
4.461
4.444
4.426
2.897
1.495
1.477
1.460
0.000
400 MHz
CDCl3
COOEt
Cl
N
N-N
3r
0.99
0.98
0.99
1.00
1.01
0.99
2.00
3.00
3.00
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5.5
4.5
3.5
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1.5
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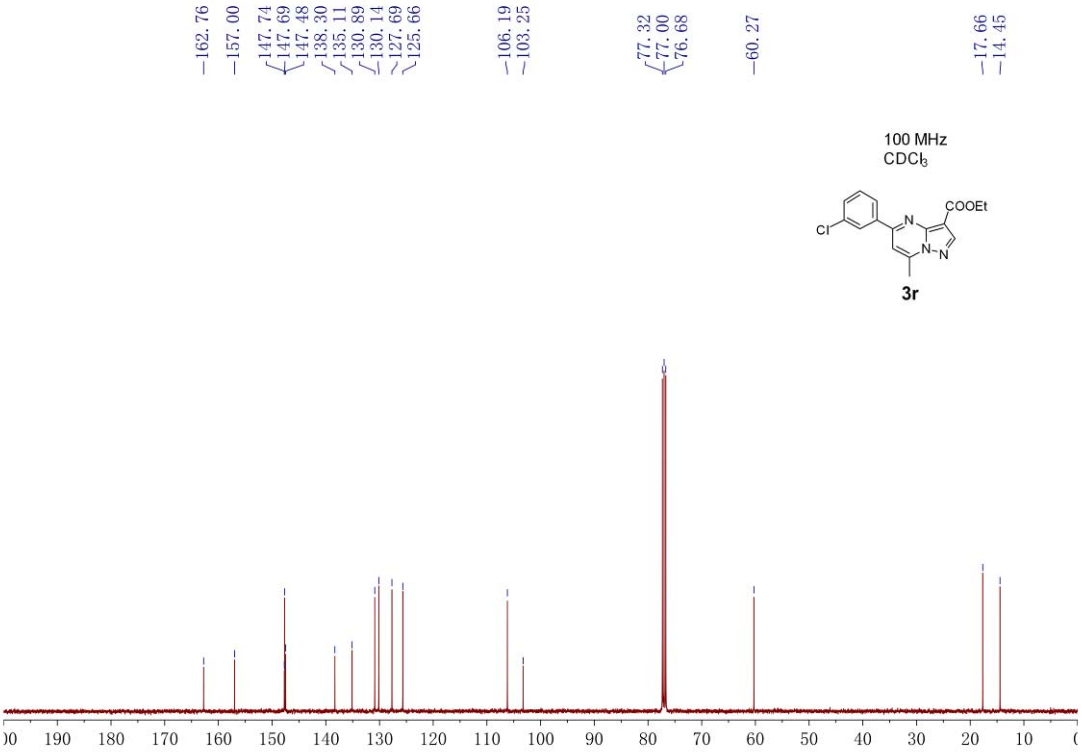
-0.5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130.89
130.14
127.69
125.66
106.19
103.25
77.32
77.00
76.68
60.27
17.66
14.45
100 MHz
CDCl3
COOEt
Cl
N
N-N
3r
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180
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160
150
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130
120
110
100
90
80
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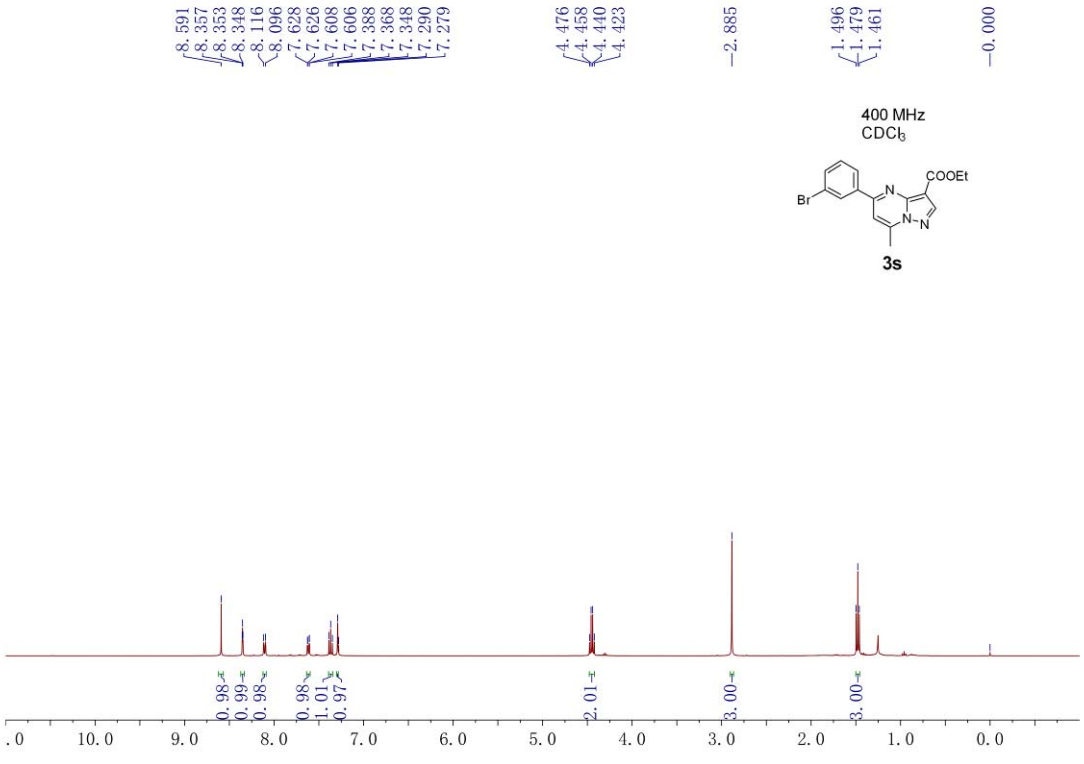
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8.096
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7.626
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7.606
7.388
7.368
7.348
7.290
7.279
4.476
4.458
4.440
4.423
2.885
1.496
1.479
1.461
0.000
400 MHz
CDCl3
COOEt
Br
N
N
N
3s
0.98
0.99
0.98
0.98
1.01
0.97
2.01
3.00
3.00
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4.0
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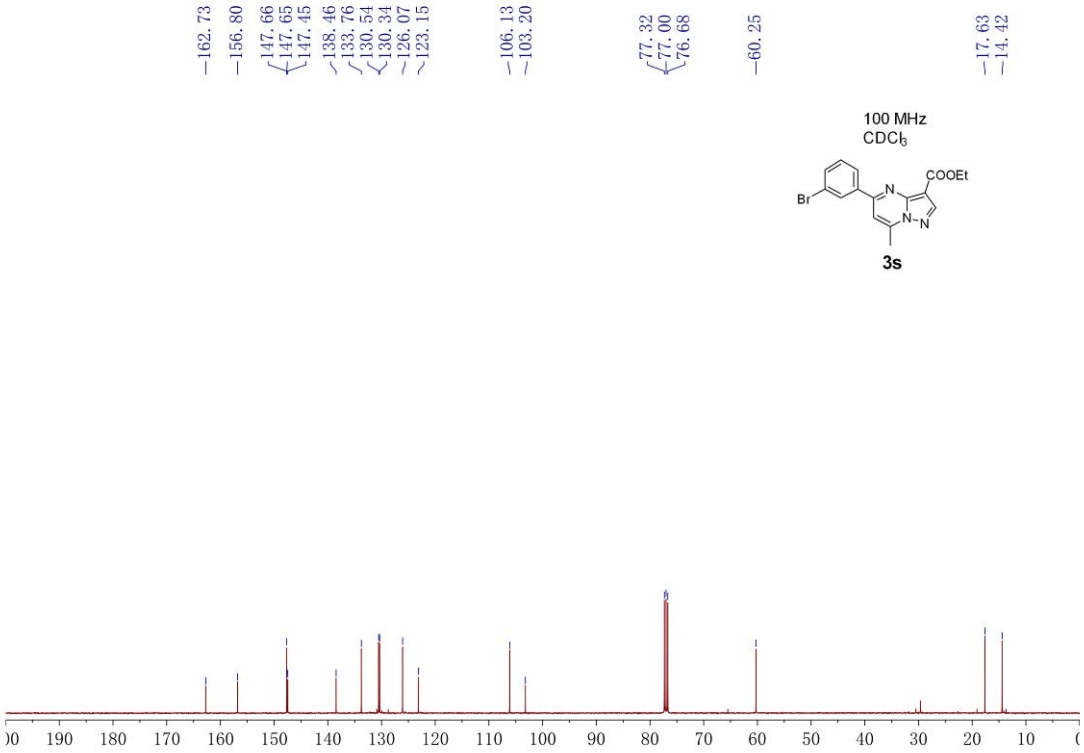
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130.54
130.34
126.07
123.15
106.13
103.20
77.32
77.00
76.68
60.25
17.63
14.42
100 MHz
CDCl3
COOEt
Br
N
N
N
3s
190
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120
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80
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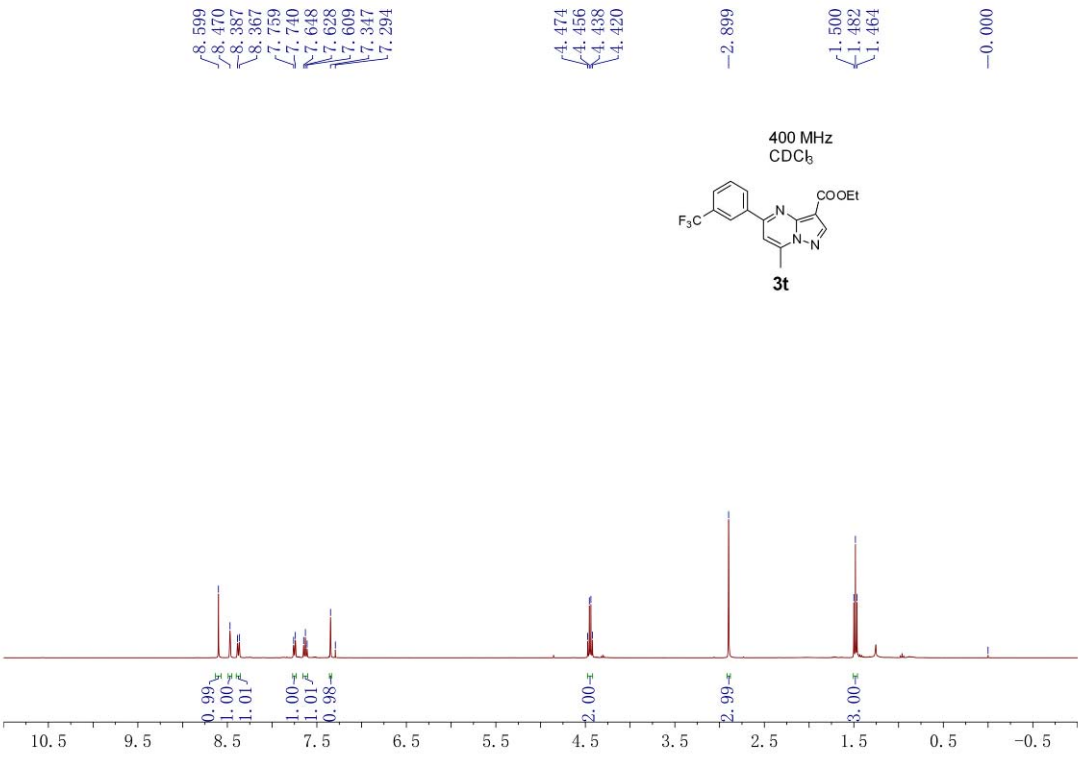
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8.387
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7.740
7.648
7.628
7.609
7.347
7.294
4.474
4.456
4.438
4.420
2.899
1.500
1.482
1.464
0.000
400 MHz
CDCl3
COOEt
F3C
N
N-N
3t
0.99
1.00
1.01
1.00
1.01
0.98
2.00
2.99
3.00
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5.5
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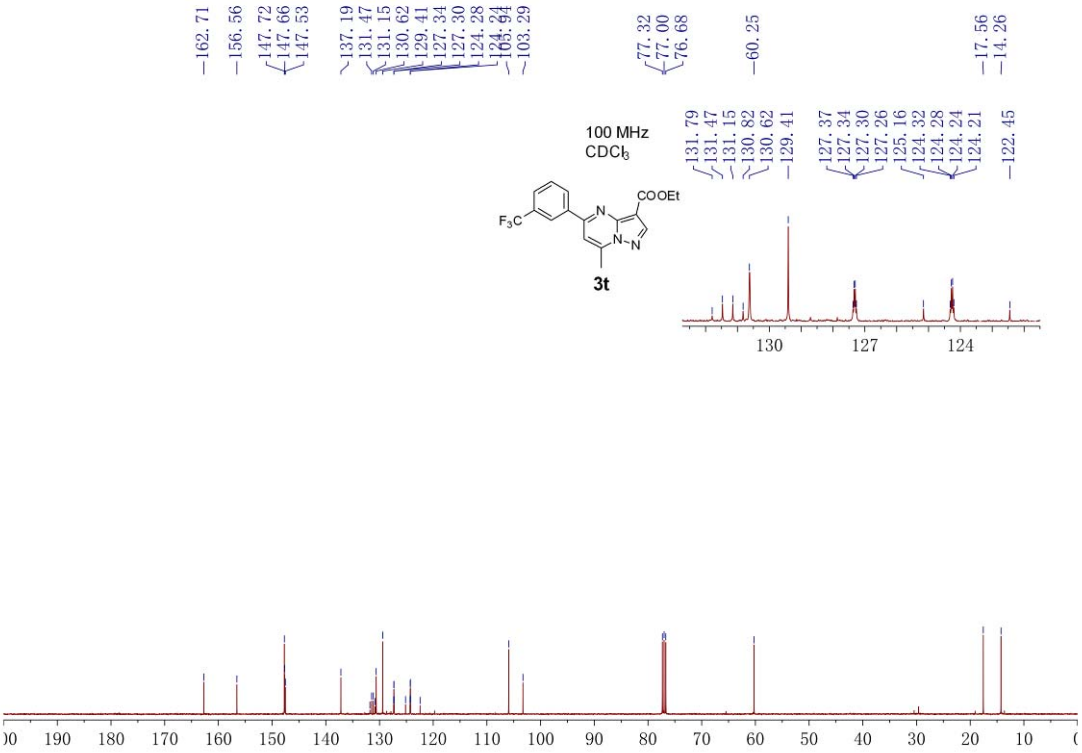
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127.34
127.30
124.28
124.24
124.21
103.29
77.32
77.00
76.68
60.25
17.56
14.26
100 MHz
CDCl3
COOEt
F3C
N
N-N
3t
131.79
131.47
131.15
130.82
130.62
129.41
127.37
127.34
127.30
127.26
125.16
124.32
124.28
124.24
124.21
122.45
130
127
124
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150
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120
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100
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80
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40
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20
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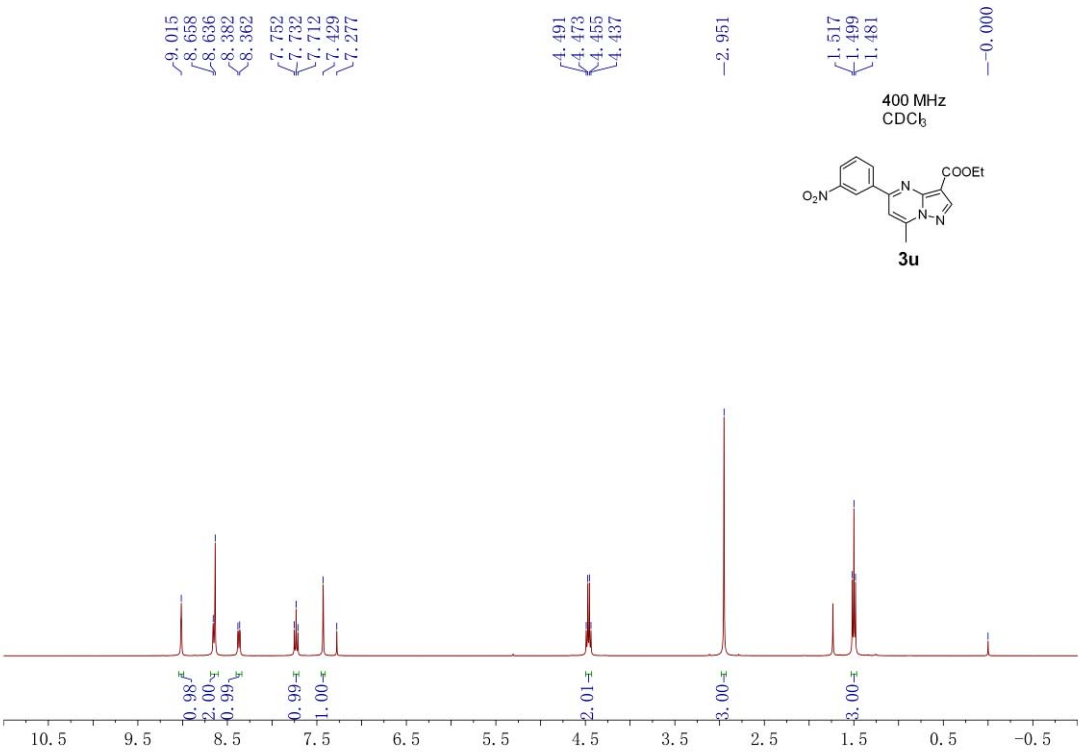
9.015
8.658
8.636
8.382
8.362
7.752
7.732
7.712
7.429
7.277
4.491
4.473
4.455
4.437
2.951
1.517
1.499
1.481
0.000
400 MHz
CDCl3
COOEt
O2N
N
N
3u
0.98
2.00
0.99
0.99
1.00
2.01
3.00
3.00
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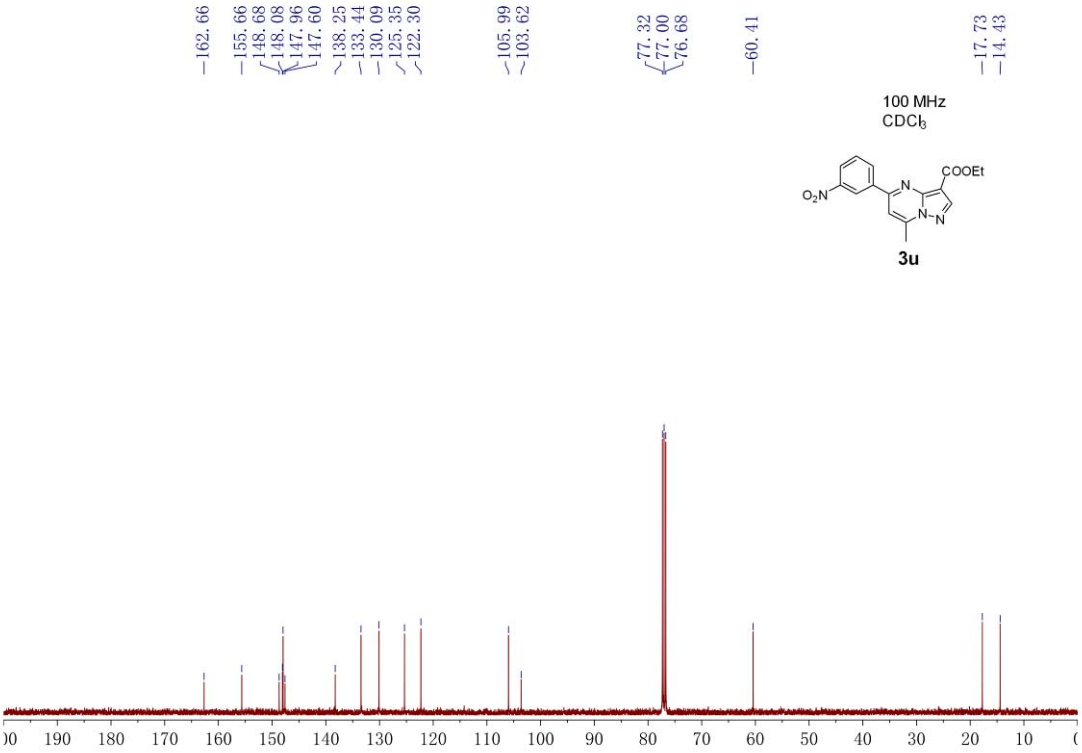
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5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133.44
130.09
125.35
122.30
105.99
103.62
77.32
77.00
76.68
60.41
17.73
14.43
100 MHz
CDCl3
COOEt
O2N
N
N
3u
190
180
170
160
150
140
130
120
110
100
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80
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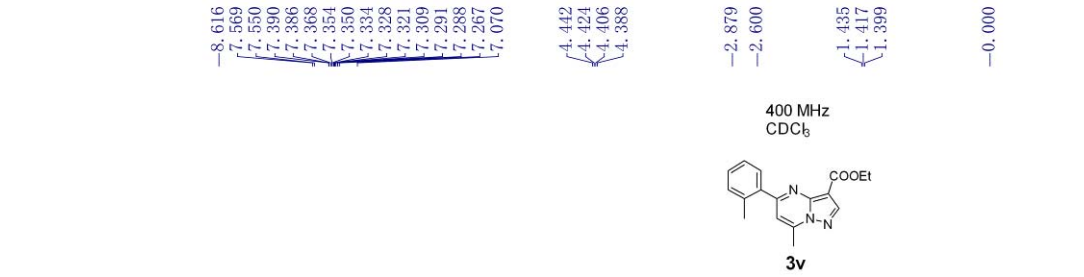
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7.350
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7.328
7.321
7.309
7.291
7.288
7.267
7.070
4.442
4.424
4.406
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1.435
1.417
1.399
0.000
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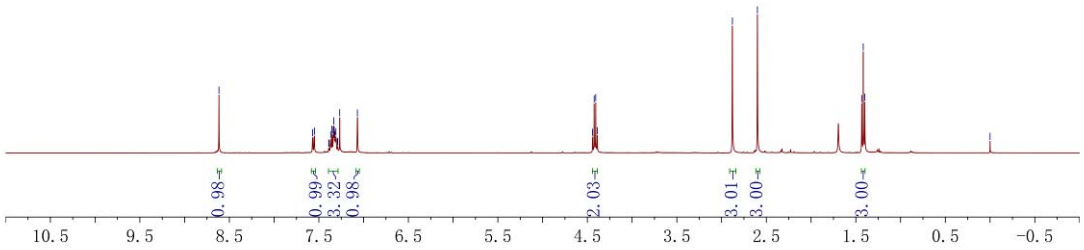
CDCl3
COOEt
N
N-N
3v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0.99
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0.98
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3.01
3.00
3.00
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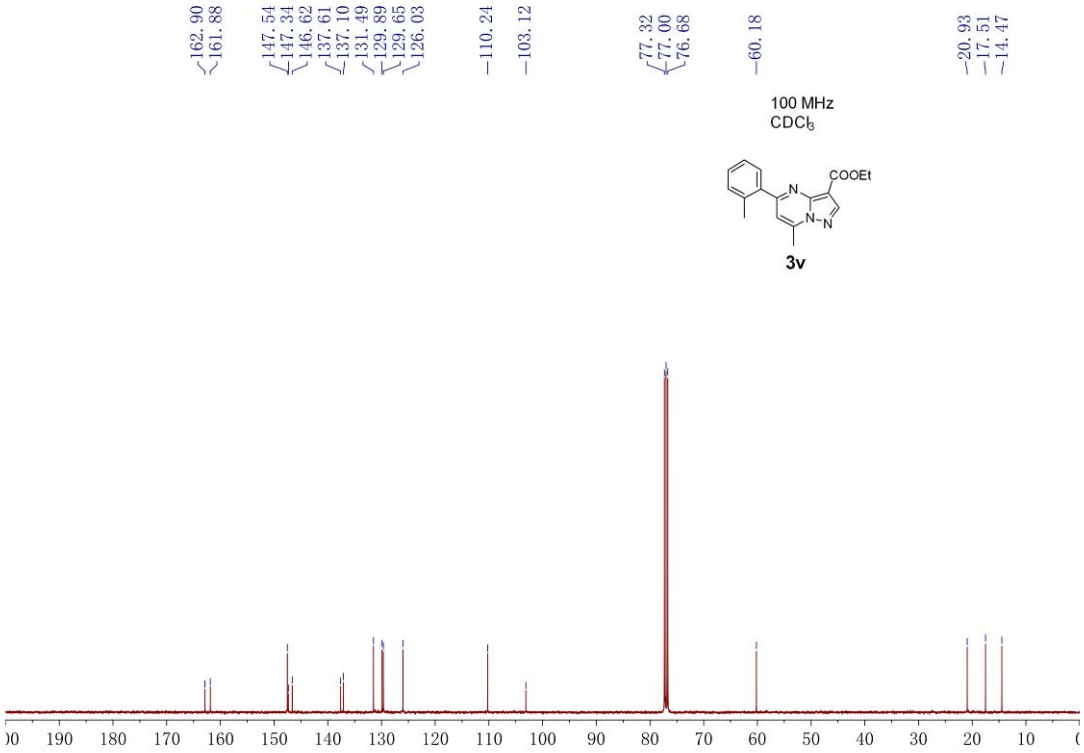
5.5
4.5
3.5
2.5
1.5
0.5
-0.5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129.89
129.65
126.03
110.24
103.12
77.32
77.00
76.68
60.18
20.93
17.51
14.47
100 MHz
CDCl3
COOEt
N
N-N
3v
190
180
170
160
150
140
130
120
110
100
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80
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60
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40
30
20
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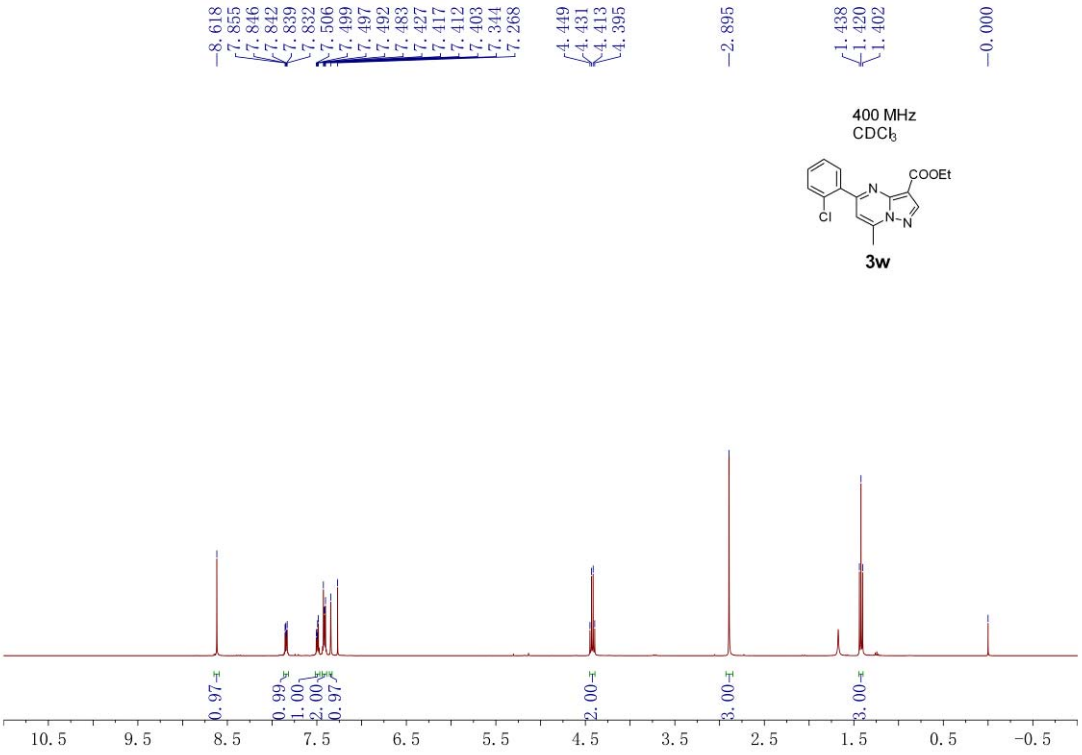
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7.839
7.832
7.506
7.499
7.497
7.492
7.483
7.427
7.417
7.412
7.403
7.344
7.268
4.449
4.431
4.413
4.395
2.895
1.438
1.420
1.402
0.000
400 MHz
CDCl3
COOEt
Cl
3w
0.97
0.99
1.00
2.00
0.97
2.00
3.00
3.00
10.5
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7.5
6.5
5.5
4.5
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2.5
1.5
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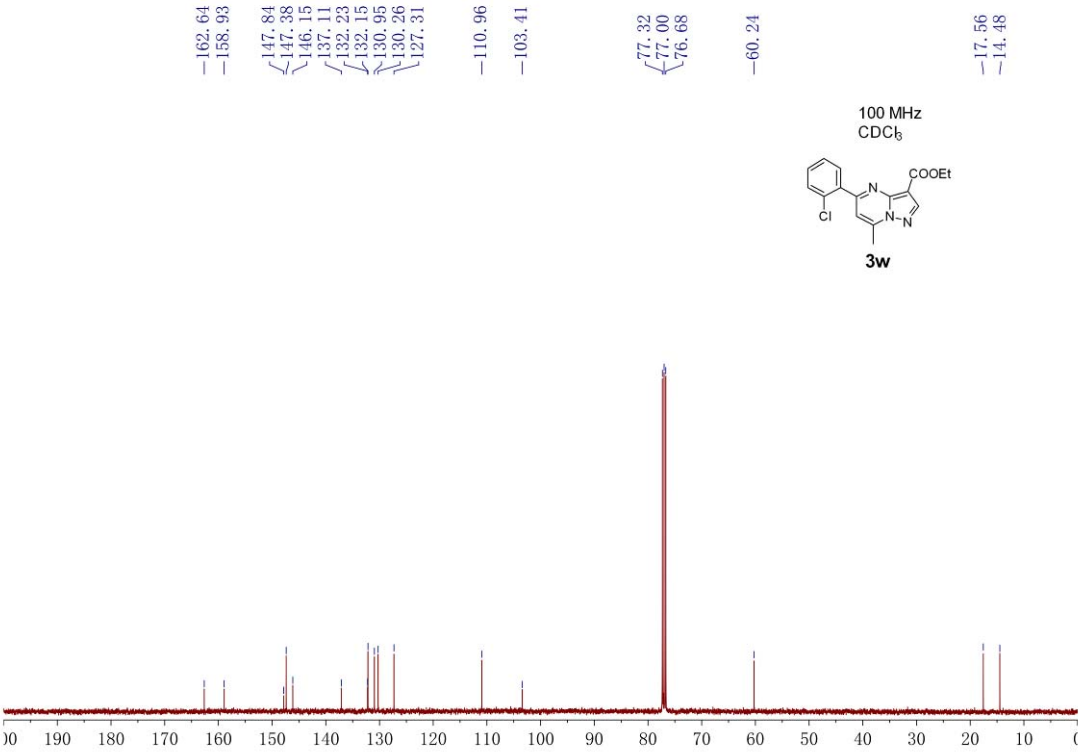
-0.5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132.15
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130.26
127.31
110.96
103.41
77.32
77.00
76.68
60.24
17.56
14.48
100 MHz
CDCl3
COOEt
Cl
3w
190
180
170
160
150
140
130
120
110
100
90
80
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30
20
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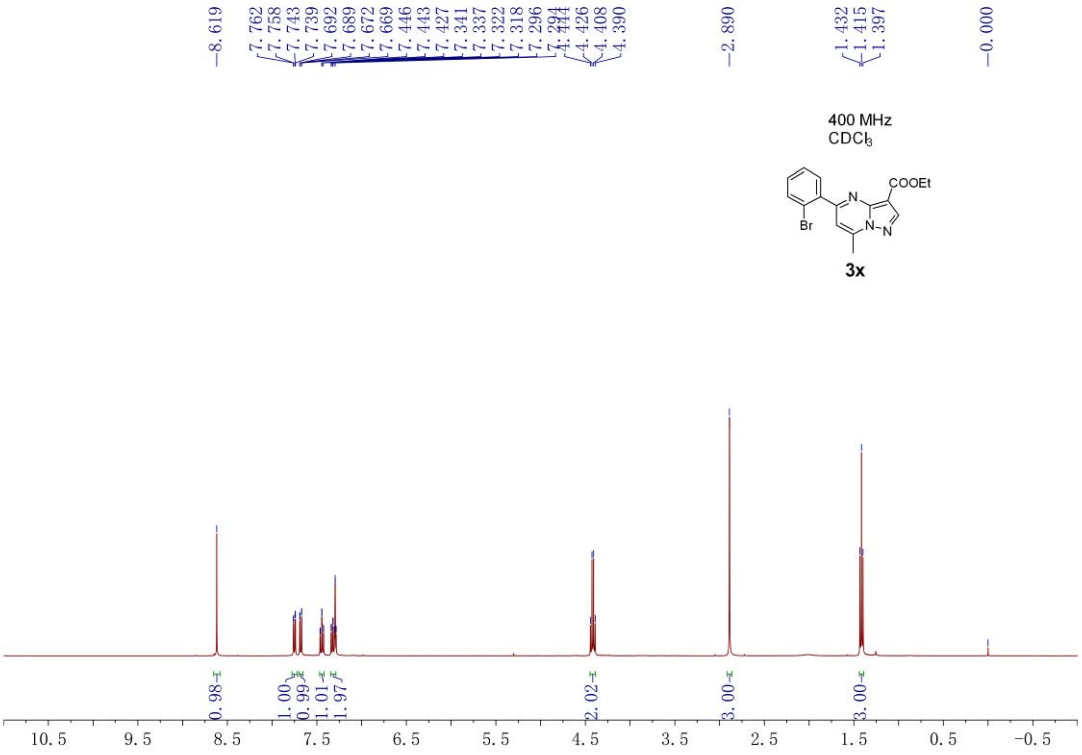
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7.739
7.692
7.689
7.672
7.669
7.446
7.443
7.427
7.341
7.337
7.322
7.318
7.296
7.294
4.426
4.408
4.390
2.890
1.432
1.415
1.397
0.000
400 MHz
CDCl3
COOEt
Br
N
N-N
3x
0.98
1.00
0.99
1.01
1.97
2.02
3.00
3.00
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6.5
5.5
4.5
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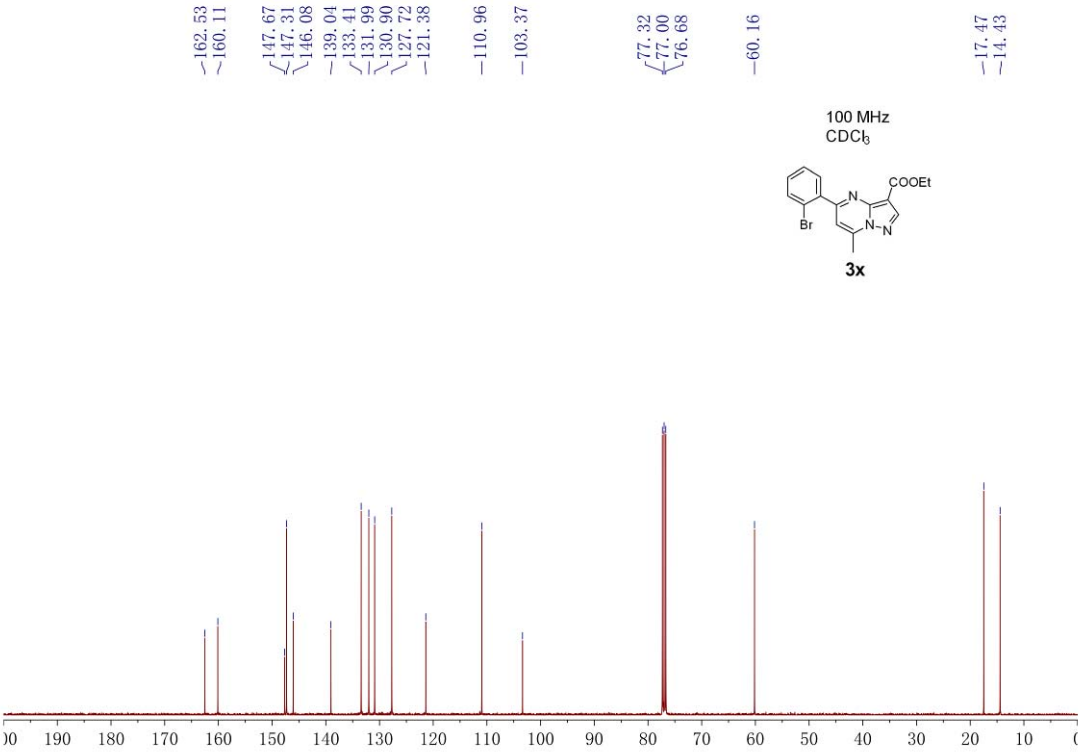
-0.5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127.72
121.38
110.96
103.37
77.32
77.00
76.68
60.16
17.47
14.43
100 MHz
CDCl3
COOEt
Br
N
N-N
3x
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180
170
160
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80
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20
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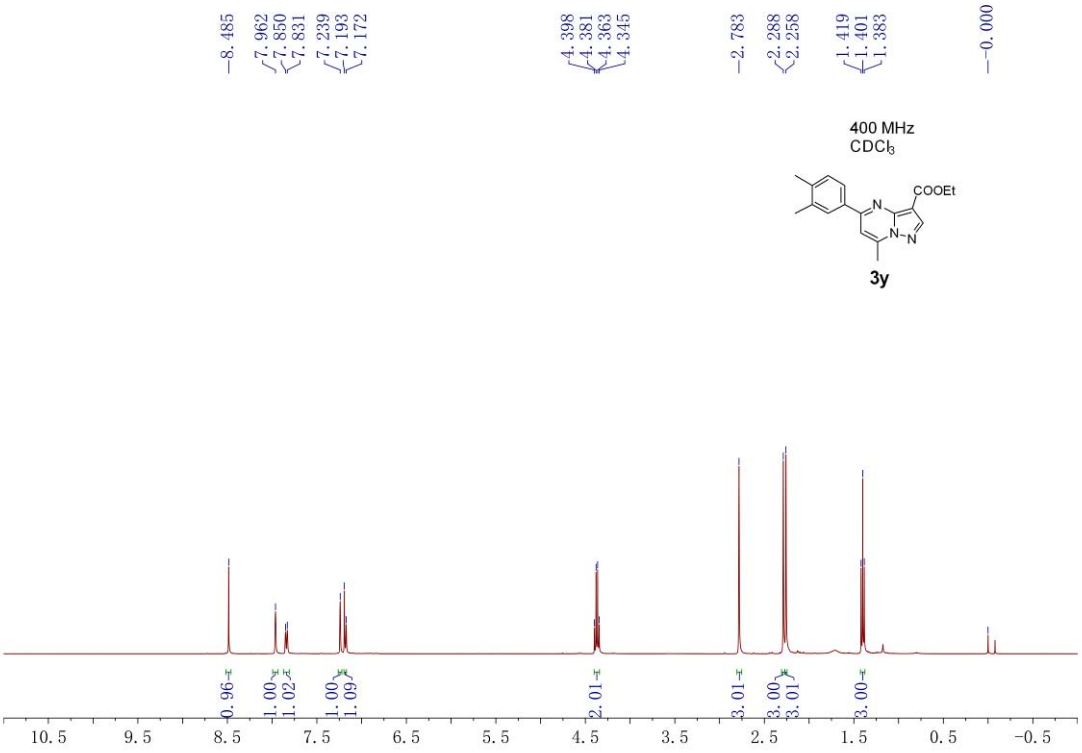
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4.363
4.345
2.783
2.288
2.258
1.419
1.401
1.383
0.000
400 MHz
CDCl3
COOEt
N
N-N
3y
0.96
1.00
1.02
1.00
1.09
2.01
3.01
3.00
3.01
3.00
10.5
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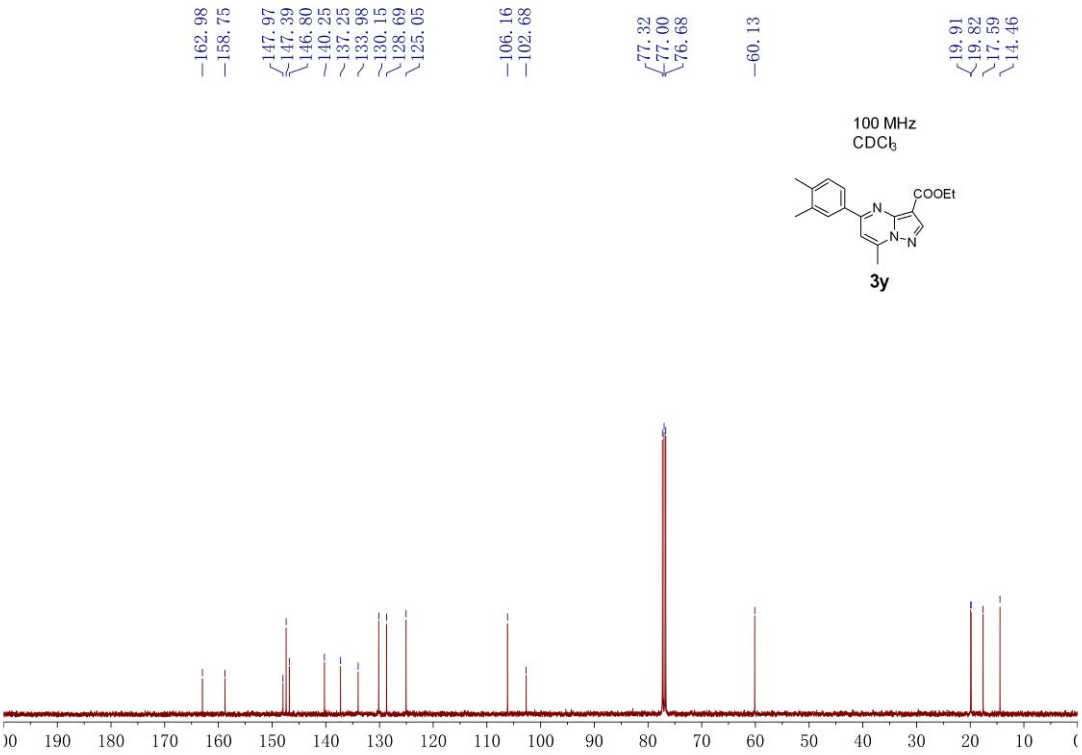
-0.5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130.15
128.69
125.05
106.16
102.68
77.32
77.00
76.68
60.13
19.91
19.82
17.59
14.46
100 MHz
CDCl3
COOEt
N
N-N
3y
190
180
170
160
150
140
130
120
110
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80
70
60
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40
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20
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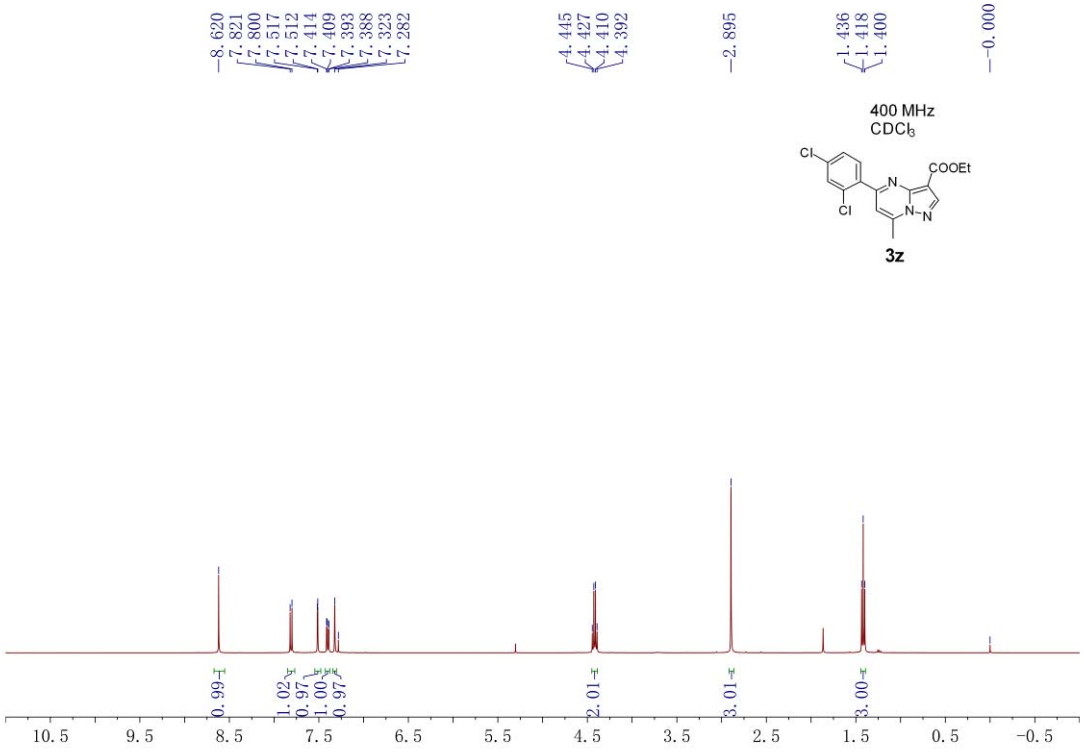
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7.517
7.512
7.414
7.409
7.393
7.388
7.323
7.282
4.445
4.427
4.410
4.392
2.895
1.436
1.418
1.400
0.000
400 MHz
CDCl3
COOEt
Cl
Cl
N
N
N
3z
0.99
1.02
0.97
1.00
0.97
2.01
3.01
3.00
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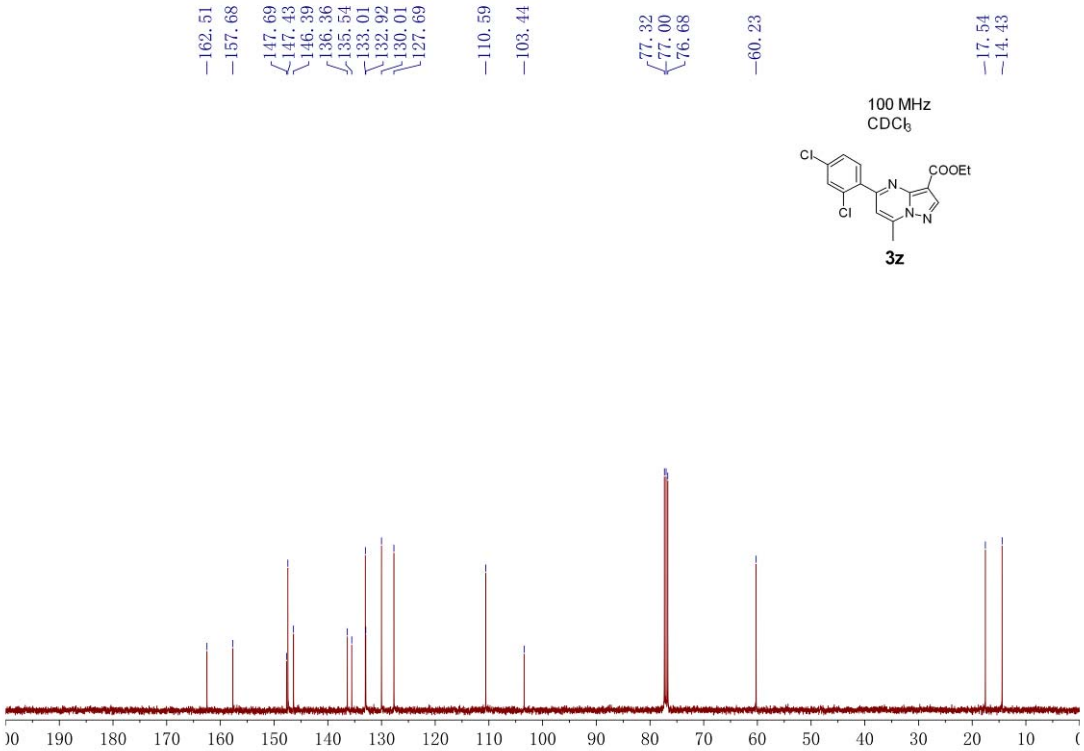
-0.5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132.92
130.01
127.69
110.59
103.44
77.32
77.00
76.68
60.23
17.54
14.43
100 MHz
CDCl3
COOEt
Cl
Cl
N
N
N
3z
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180
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160
150
140
130
120
110
100
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80
70
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20
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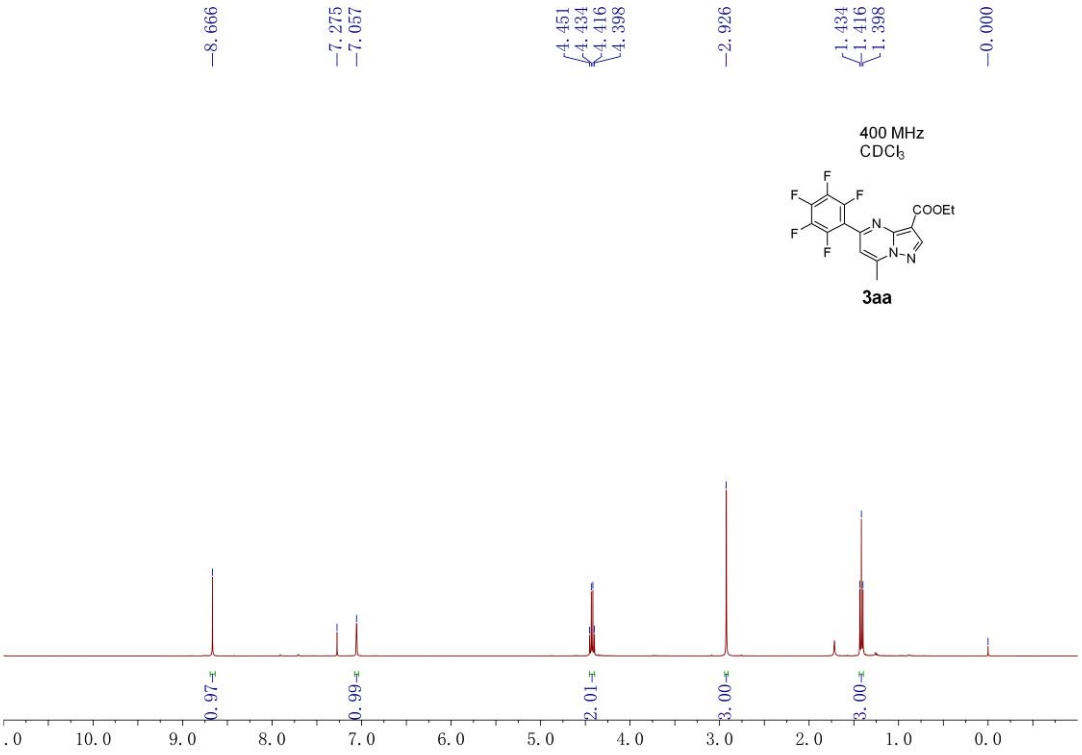
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7.275
7.057
4.451
4.434
4.416
4.398
2.926
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0.000
400 MHz
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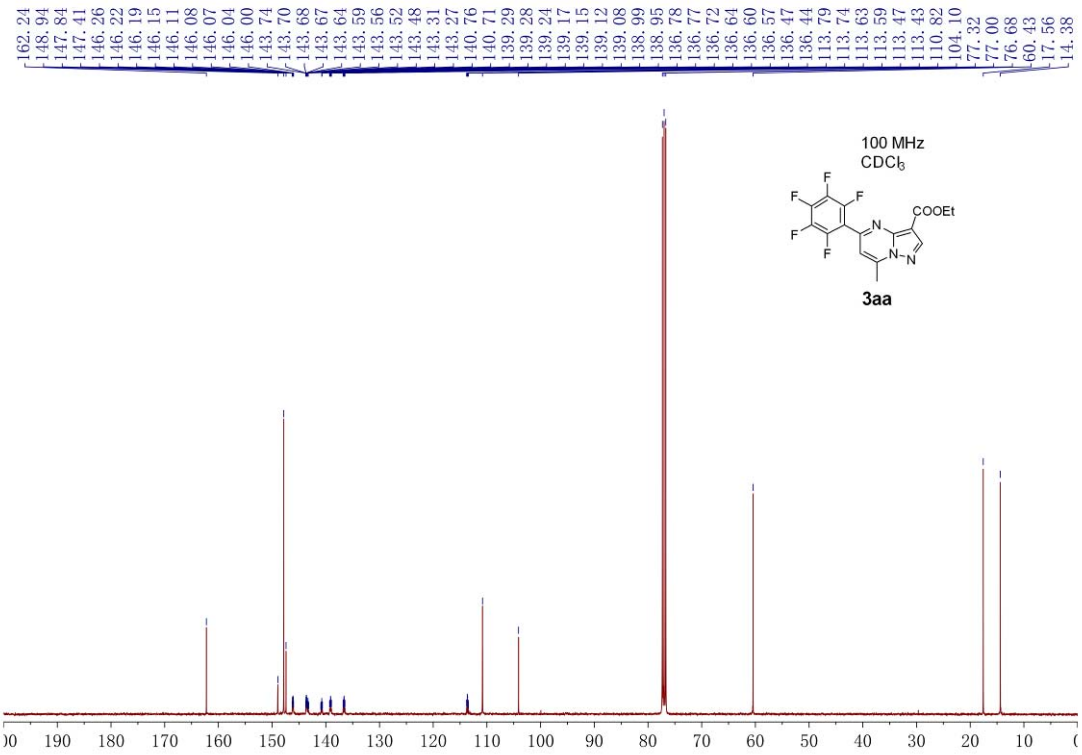
COOEt
3aa
0.97
0.99
2.01
3.00
3.00


100 MHz
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COOEt
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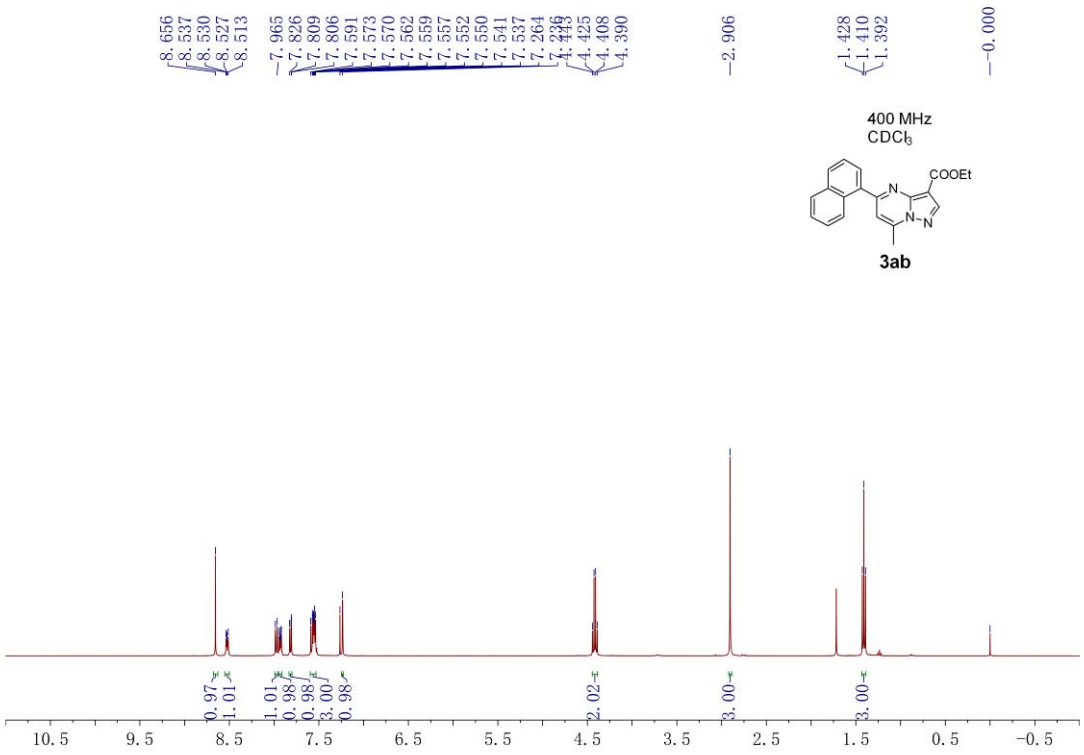
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8.527
8.513
7.965
7.826
7.809
7.806
7.591
7.573
7.570
7.562
7.559
7.557
7.552
7.550
7.541
7.537
7.264
7.236
4.425
4.408
4.390
2.906
1.428
1.410
1.392
0.000
400 MHz
CDCl3
COOEt
3ab
0.97
1.01
1.01
0.98
0.98
3.00
0.98
2.02
3.00
3.00
10.5
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5.5
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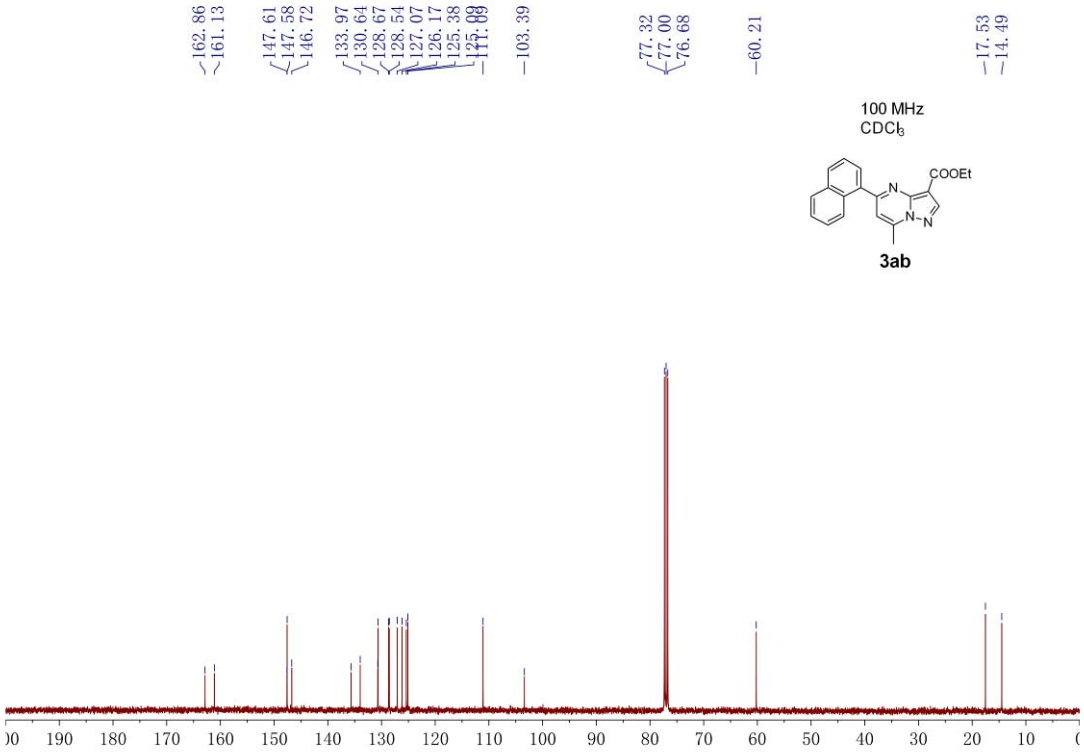
-0.5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130.64
128.67
128.54
127.07
126.17
125.38
103.39
77.32
77.00
76.68
60.21
17.53
14.49
100 MHz
CDCl3
COOEt
3ab
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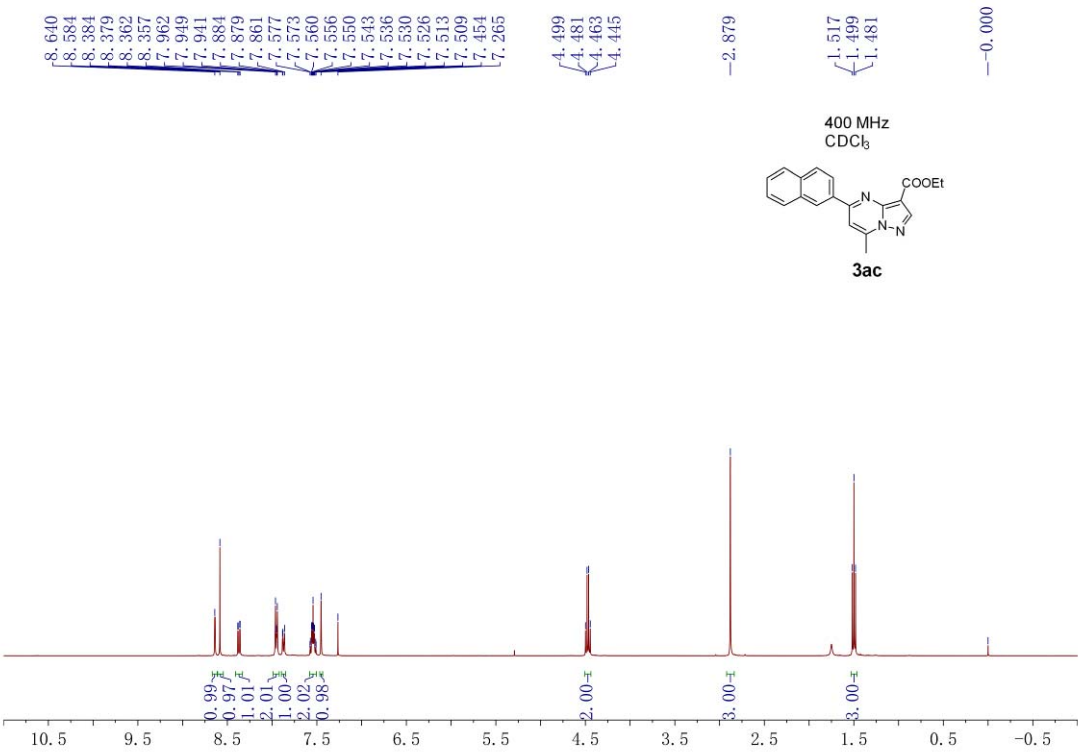
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7.884
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7.861
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7.573
7.560
7.556
7.550
7.543
7.536
7.530
7.526
7.513
7.509
7.454
7.265
4.499
4.481
4.463
4.445
2.879
1.517
1.499
1.481
0.000
400 MHz
CDCl3
COOEt
N
N-N
3ac
0.99
0.97
1.01
2.01
1.00
2.02
0.98
2.00
3.00
3.00
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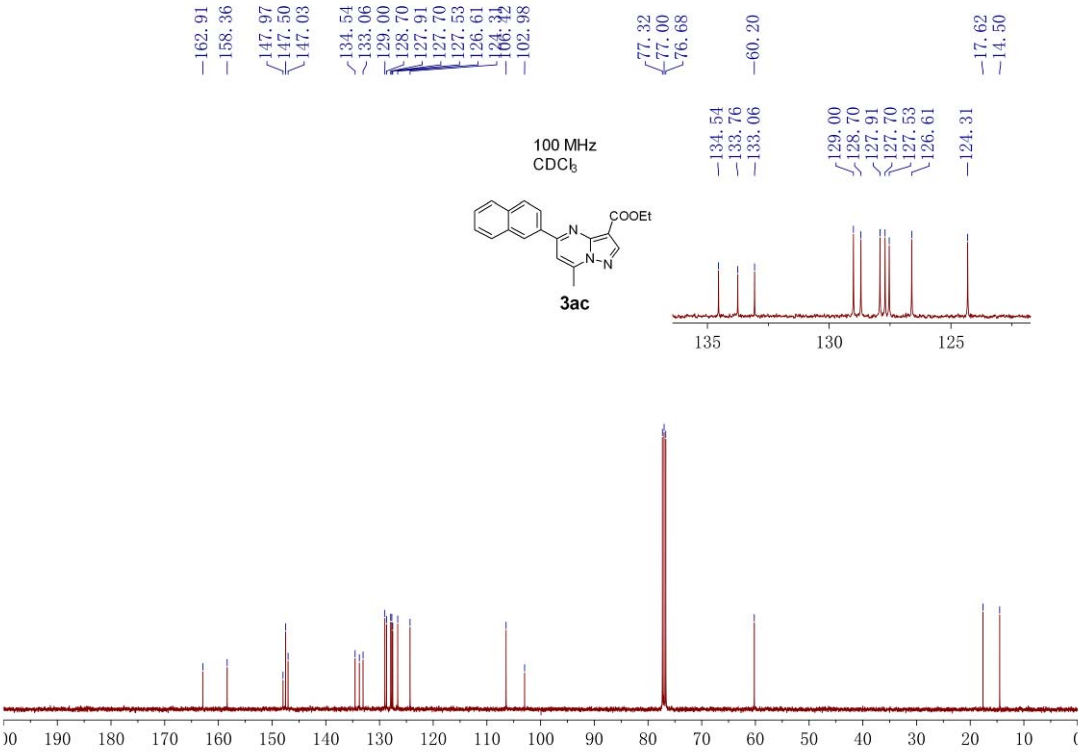
-0.5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133.06
129.00
128.70
127.91
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127.53
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124.31
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77.00
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60.20
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133.76
133.06
129.00
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127.91
127.70
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126.61
124.31
100 MHz
CDCl3
COOEt
N
N-N
3ac
135
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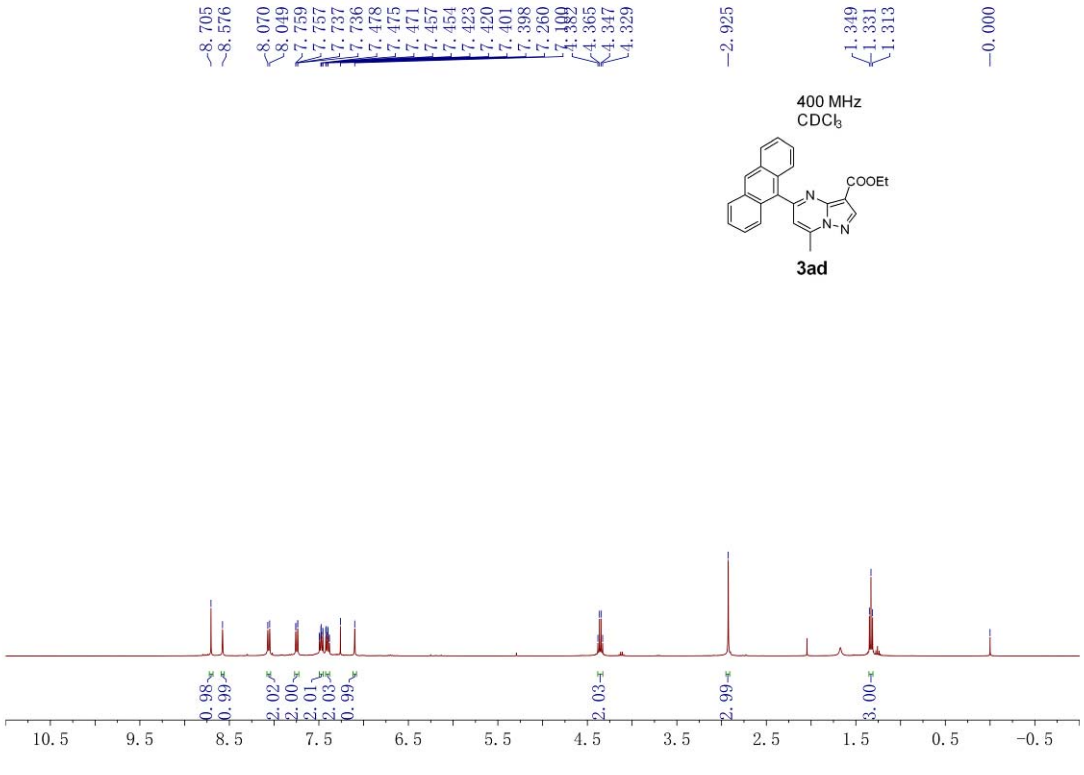
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7.454
7.423
7.420
7.401
7.398
7.260
4.365
4.347
4.329
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1.331
1.313
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400 MHz
CDCl3
COOEt
3ad
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0.99
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2.01
2.03
0.99
2.03
2.99
3.00
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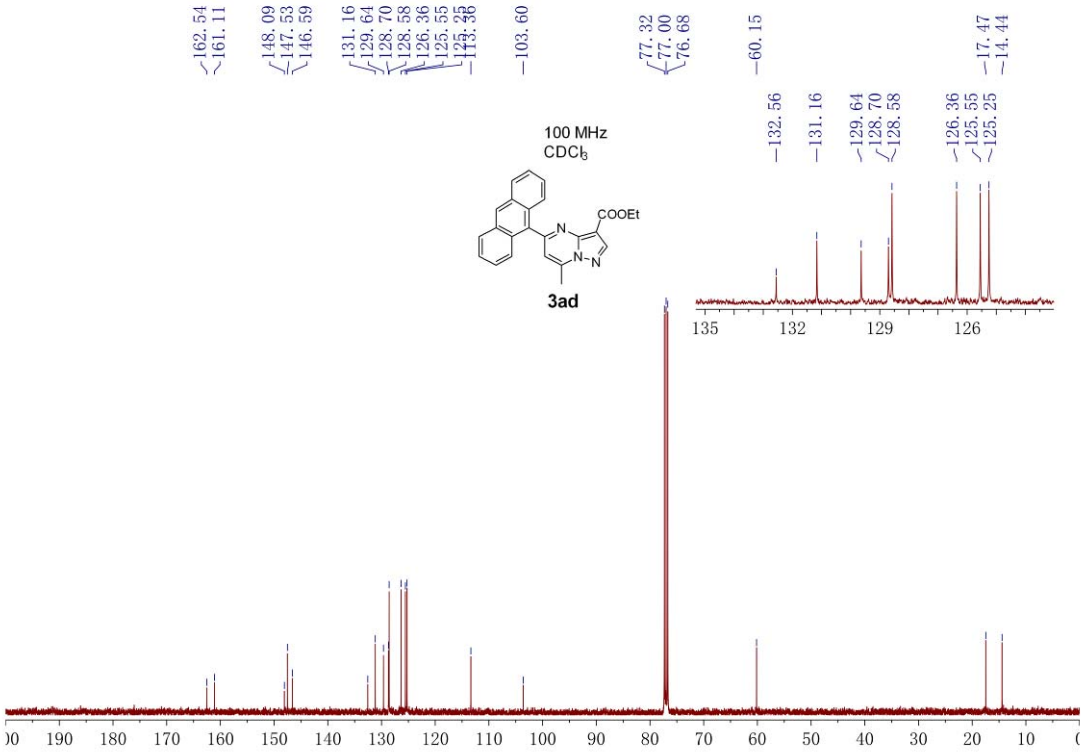
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77.00
76.68
60.15
17.47
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132.56
131.16
129.64
128.70
128.58
126.36
125.55
125.25
100 MHz
CDCl3
COOEt
3ad
135
132
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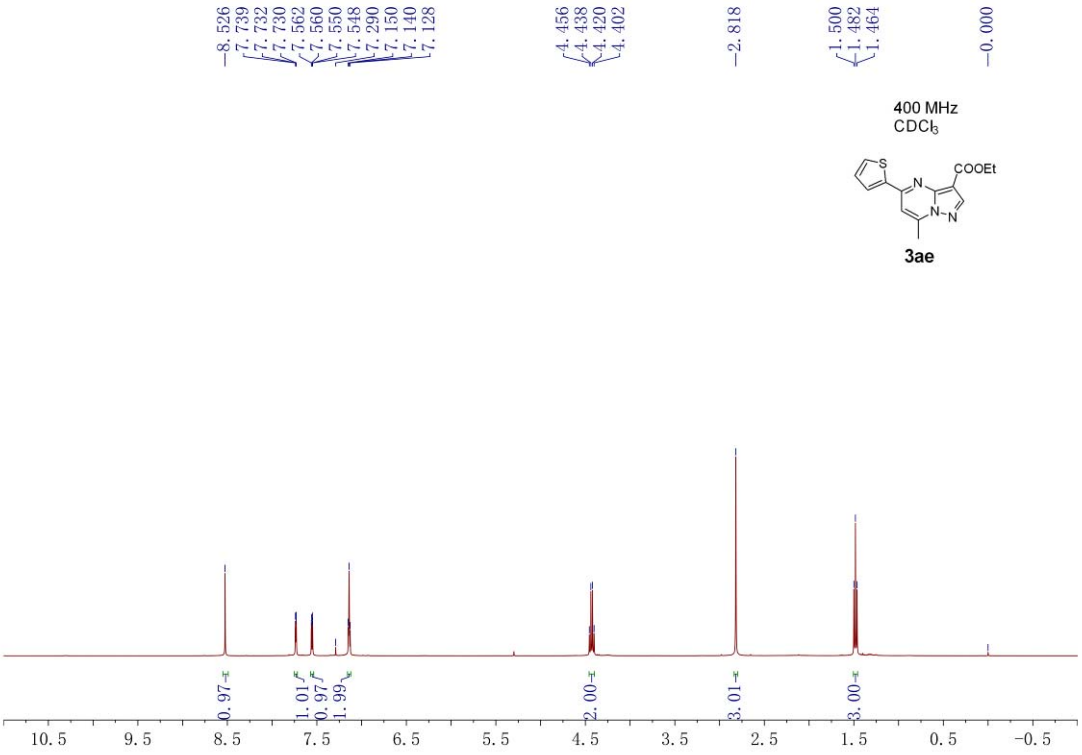
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7.548
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7.150
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4.456
4.438
4.420
4.402
2.818
1.500
1.482
1.464
0.000
400 MHz
CDCl3
COOEt
3ae
0.97
1.01
0.97
1.99
2.00
3.01
3.00
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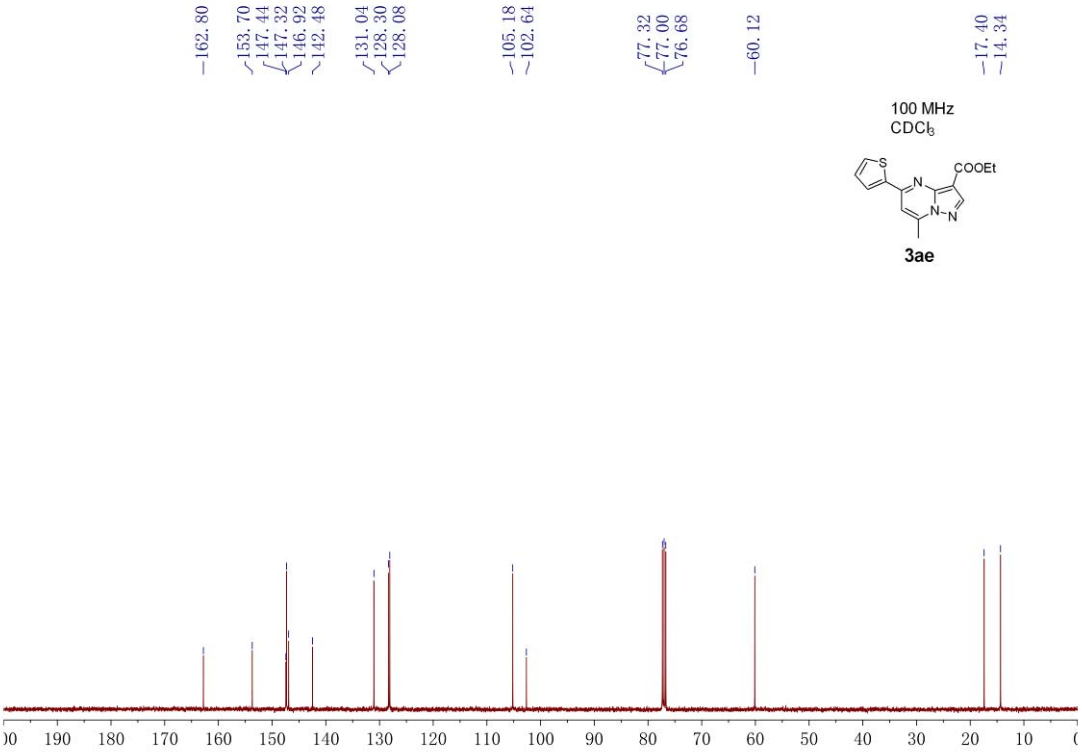
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76.68
60.12
17.40
14.34
100 MHz
CDCl3
COOEt
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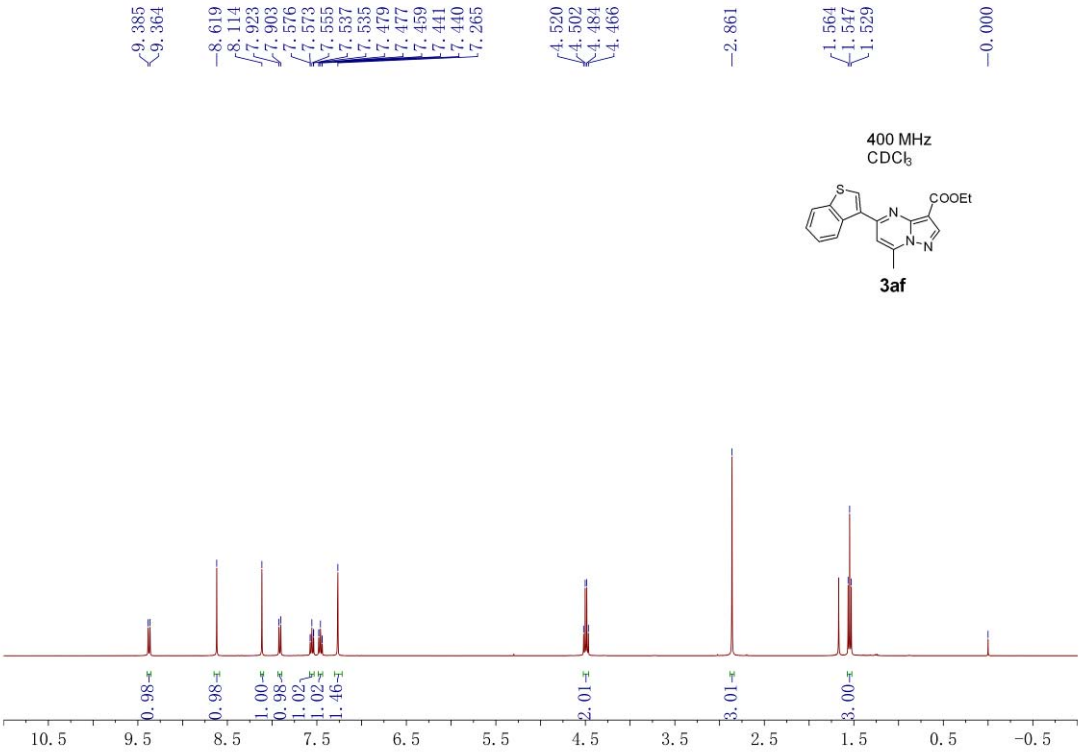
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8.114
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7.573
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7.537
7.535
7.479
7.477
7.459
7.441
7.440
7.265
4.520
4.502
4.484
4.466
2.861
1.564
1.547
1.529
0.000
400 MHz
CDCl3
COOEt
3af
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0.98
1.00
0.98
1.02
1.02
1.46
2.01
3.01
3.00
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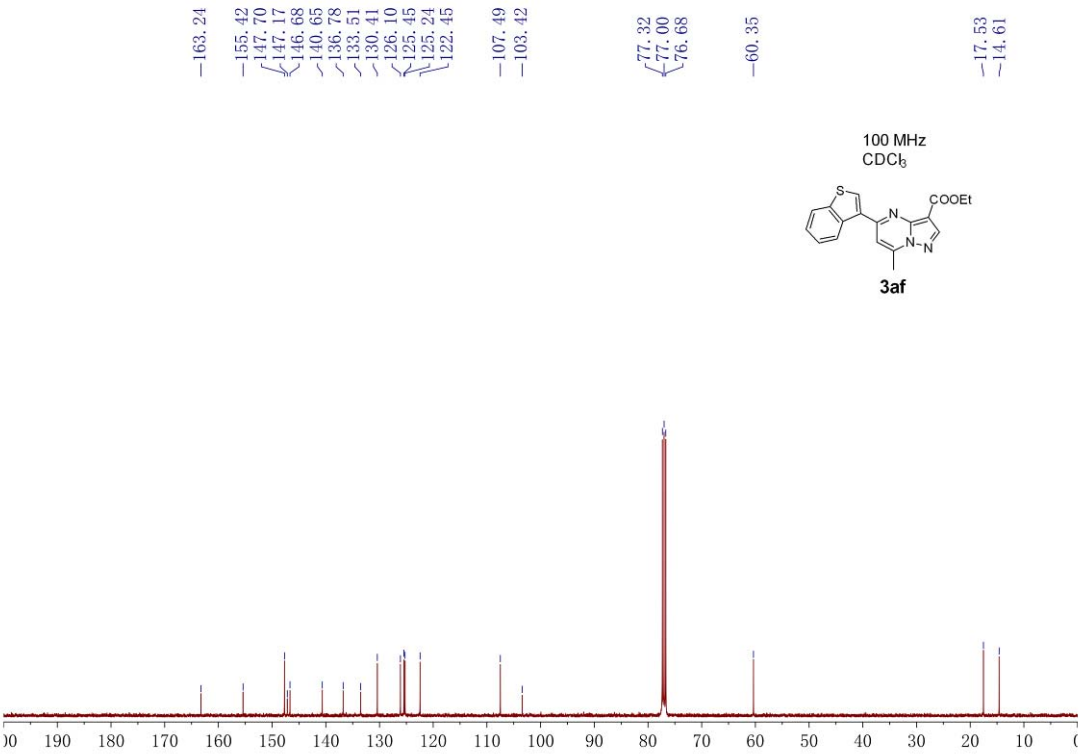
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125.24
122.45
107.49
103.42
77.32
77.00
76.68
60.35
17.53
14.61
100 MHz
CDCl3
COOEt
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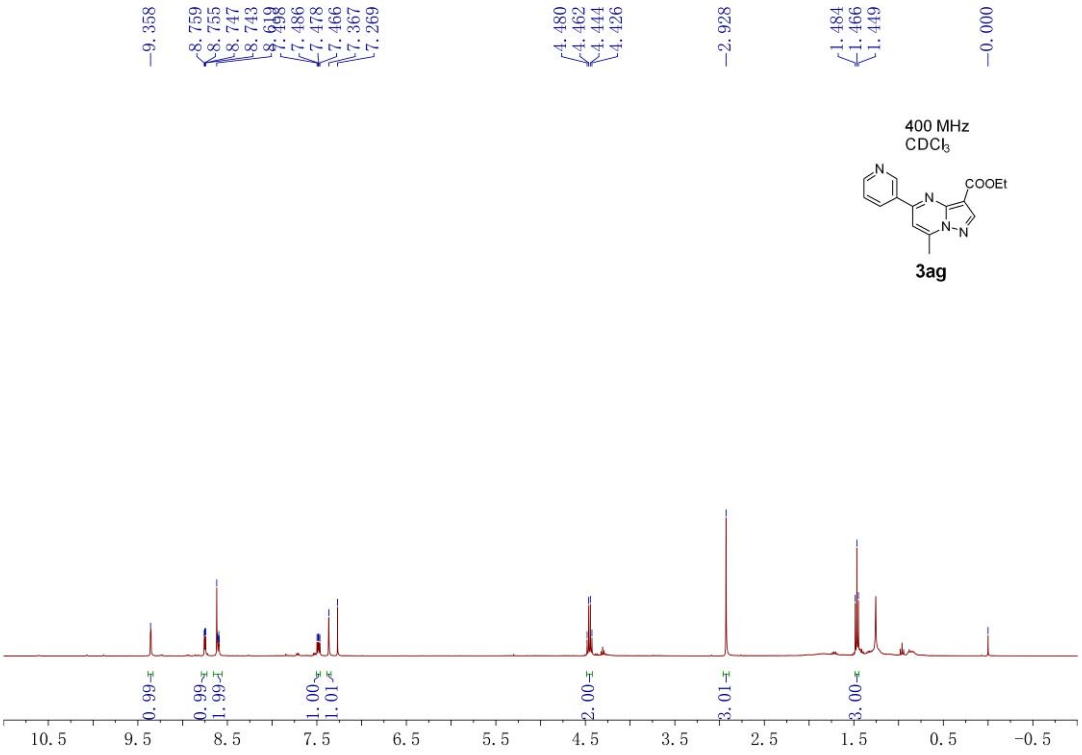
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7.478
7.466
7.367
7.269
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4.462
4.444
4.426
2.928
1.484
1.466
1.449
0.000
400 MHz
CDCl3
COOEt
3ag
0.99
0.99
1.99
1.00
1.01
2.00
3.01
3.00
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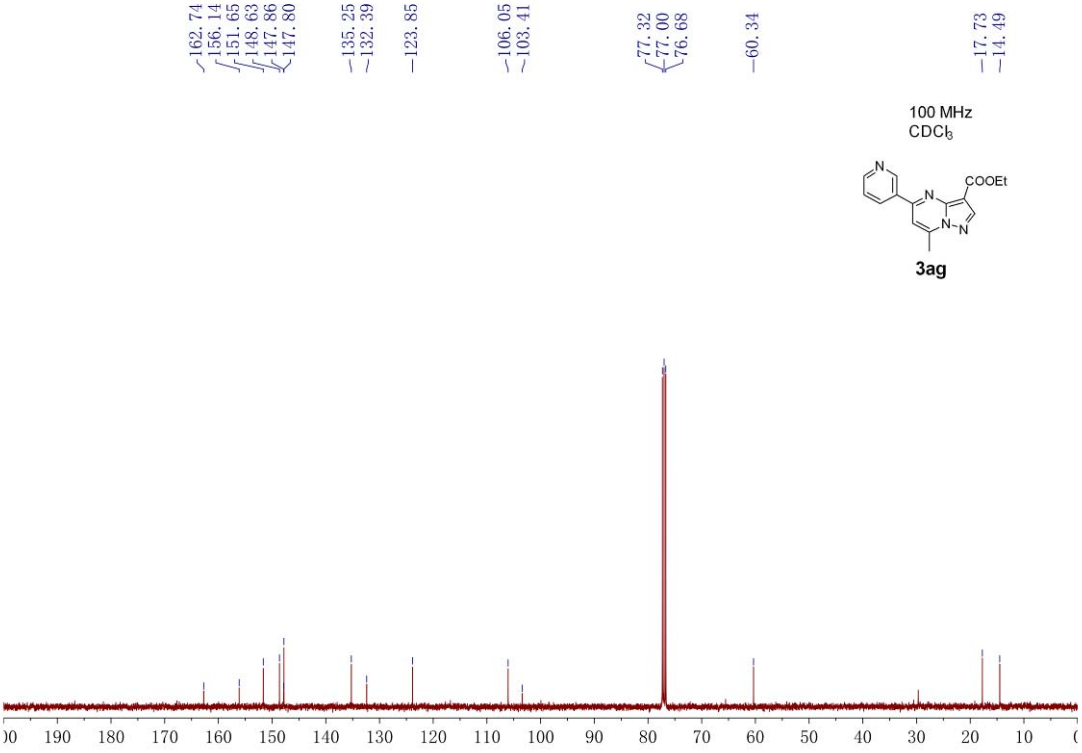
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132.39
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106.05
103.41
77.32
77.00
76.68
60.34
17.73
14.49
100 MHz
CDCl3
COOEt
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150
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80
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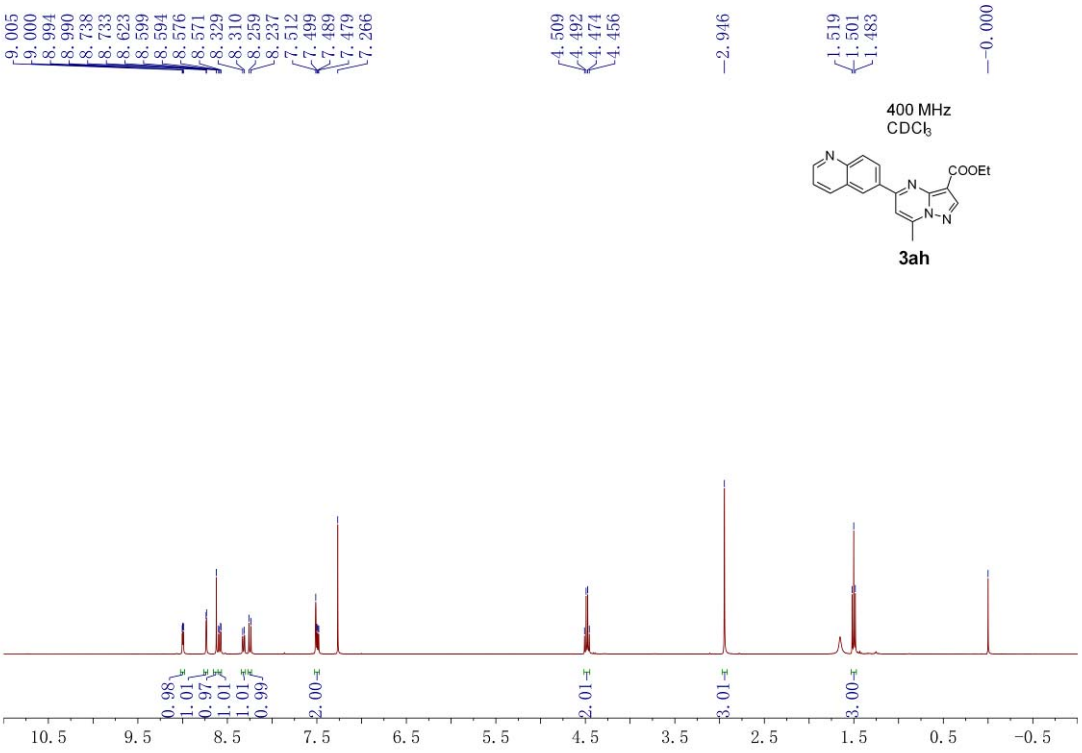
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8.599
8.594
8.576
8.571
8.329
8.310
8.259
8.237
7.512
7.499
7.489
7.479
7.266
4.509
4.492
4.474
4.456
2.946
1.519
1.501
1.483
0.000
400 MHz
CDCl3
COOEt
3ah
0.98
1.01
0.97
1.01
1.01
0.99
2.00
2.01
3.01
3.00
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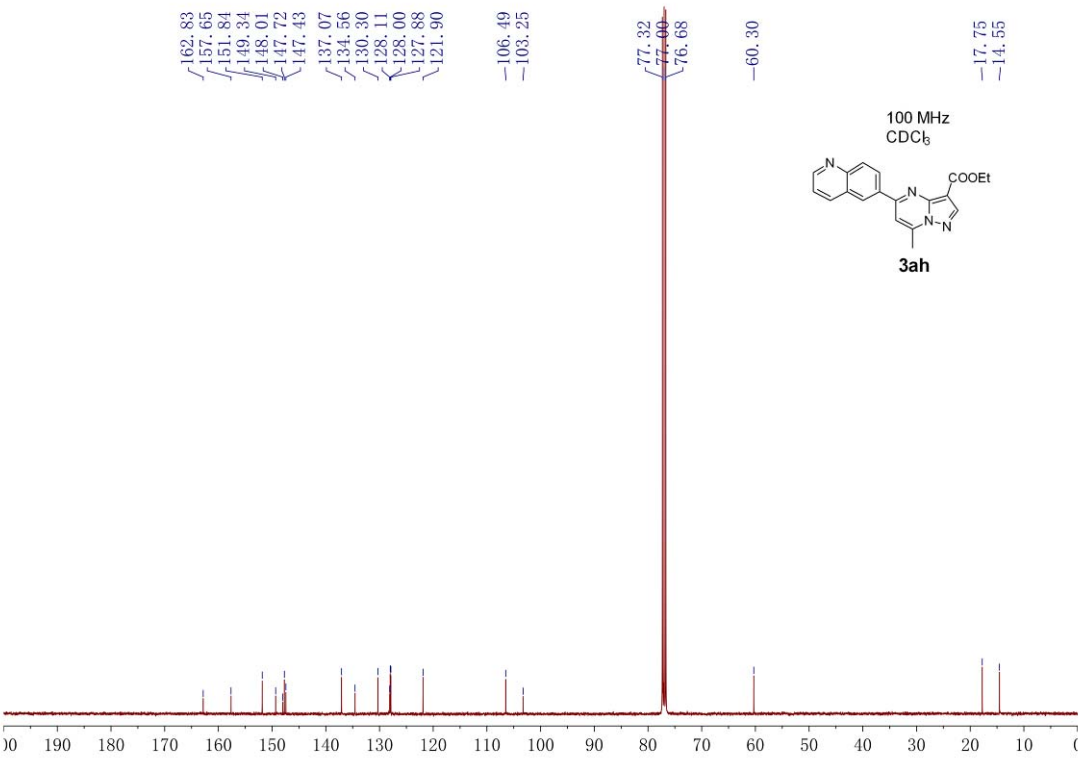
1.5
0.5
-0.5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127.88
121.90
106.49
103.25
77.32
77.00
76.68
60.30
17.75
14.55
100 MHz
CDCl3
COOEt
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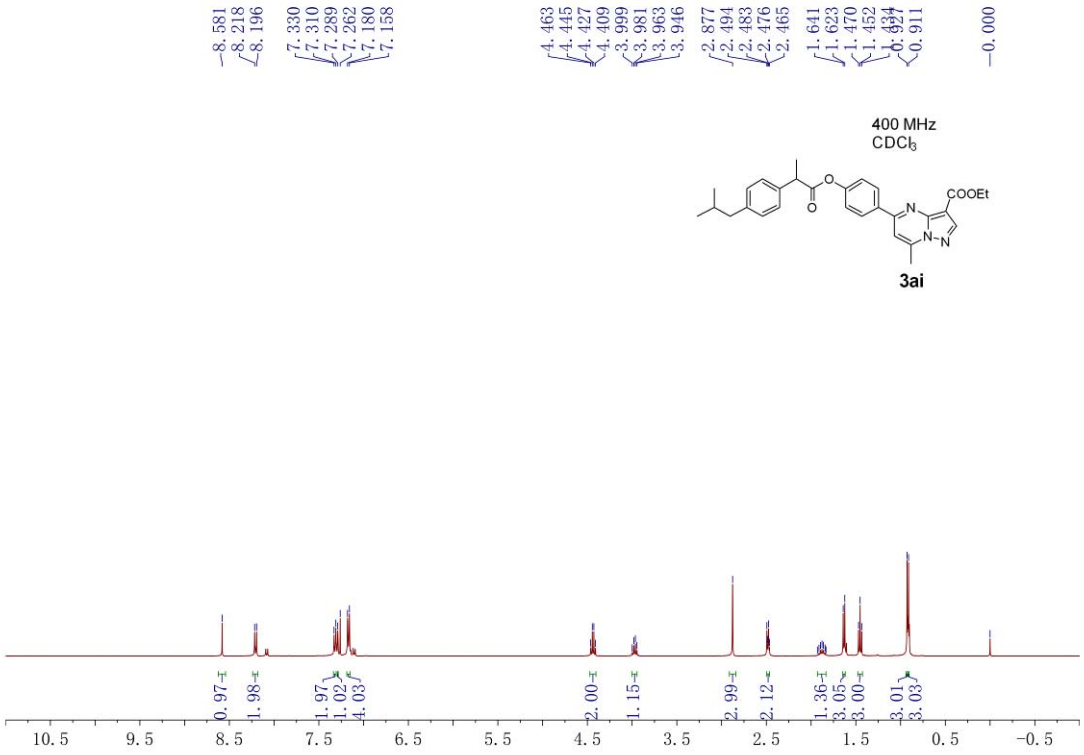
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7.180
7.158
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4.445
4.427
4.409
3.999
3.981
3.963
3.946
2.877
2.494
2.483
2.476
2.465
1.641
1.623
1.470
1.452
0.927
0.911
0.000
400 MHz
CDCl3
COOEt
3ai
0.97
1.98
1.97
1.02
4.03
2.00
1.15
2.99
2.12
1.36
3.05
3.00
3.01
3.03
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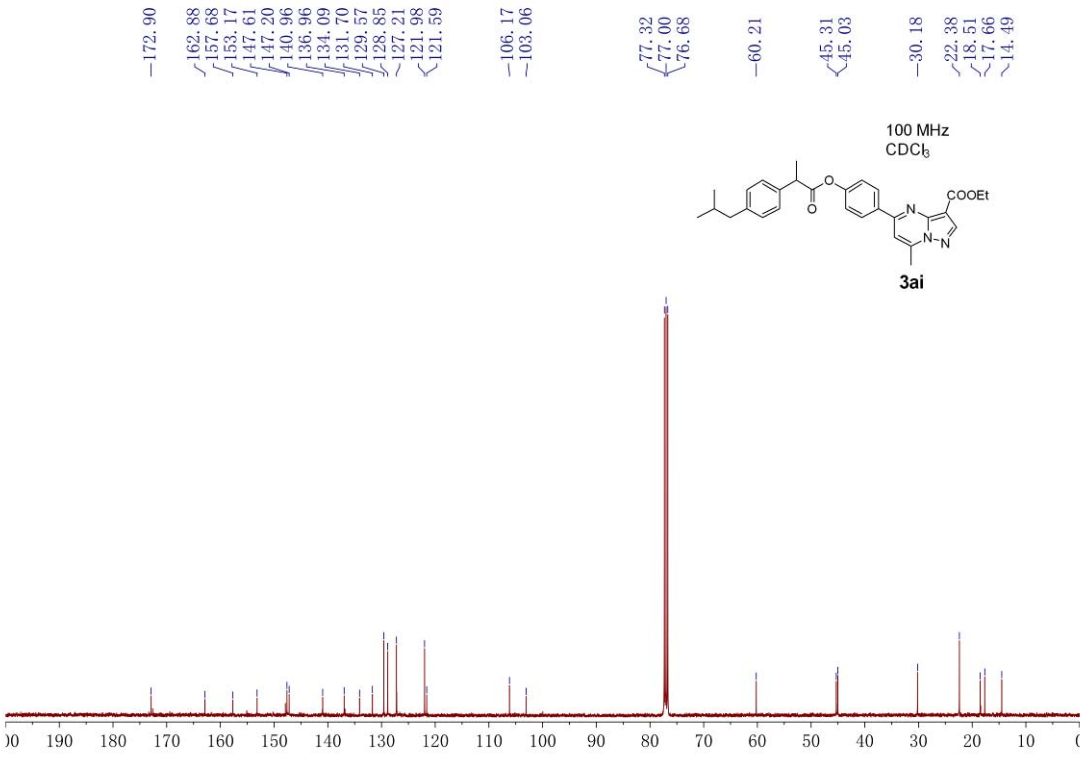
0.5
-0.5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127.21
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121.59
106.17
103.06
77.32
77.00
76.68
60.21
45.31
45.03
30.18
22.38
18.51
17.66
14.49
100 MHz
CDCl3
COOEt
3ai
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150
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20
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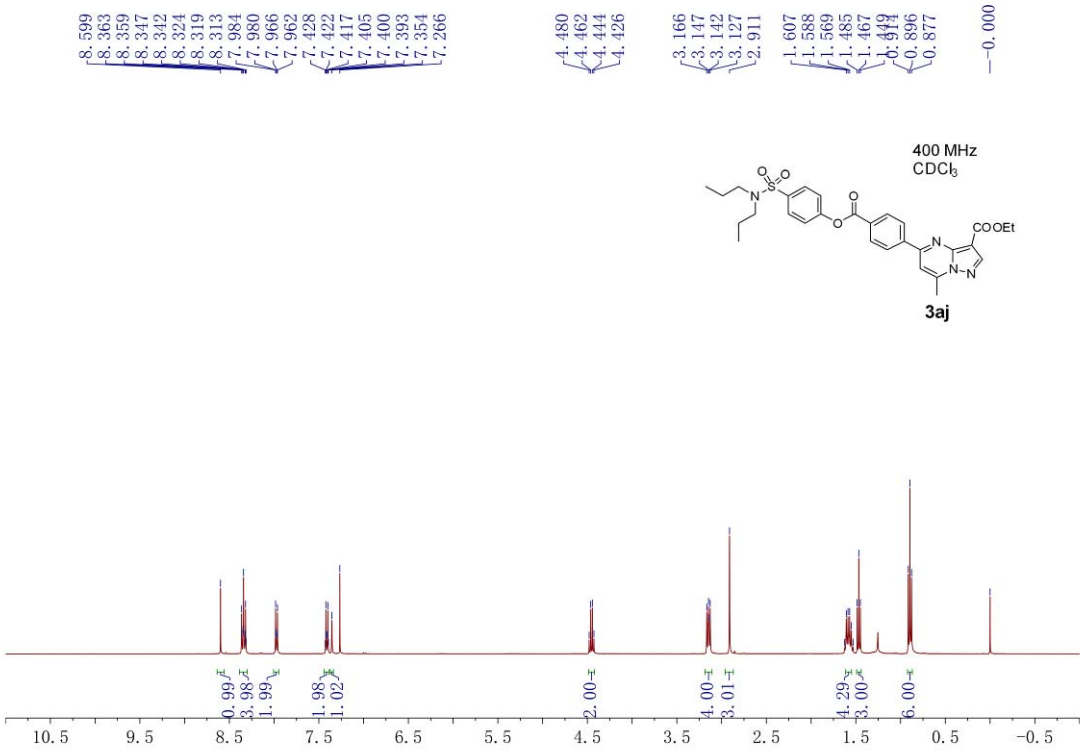
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7.400
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7.266
4.480
4.462
4.444
4.426
3.166
3.147
3.142
3.127
2.911
1.607
1.588
1.569
1.485
1.467
0.896
0.877
0.000
400 MHz
CDCl3
COOEt
3aj
0.99
3.98
1.99
1.98
1.02
2.00
4.00
3.01
4.29
3.00
6.00
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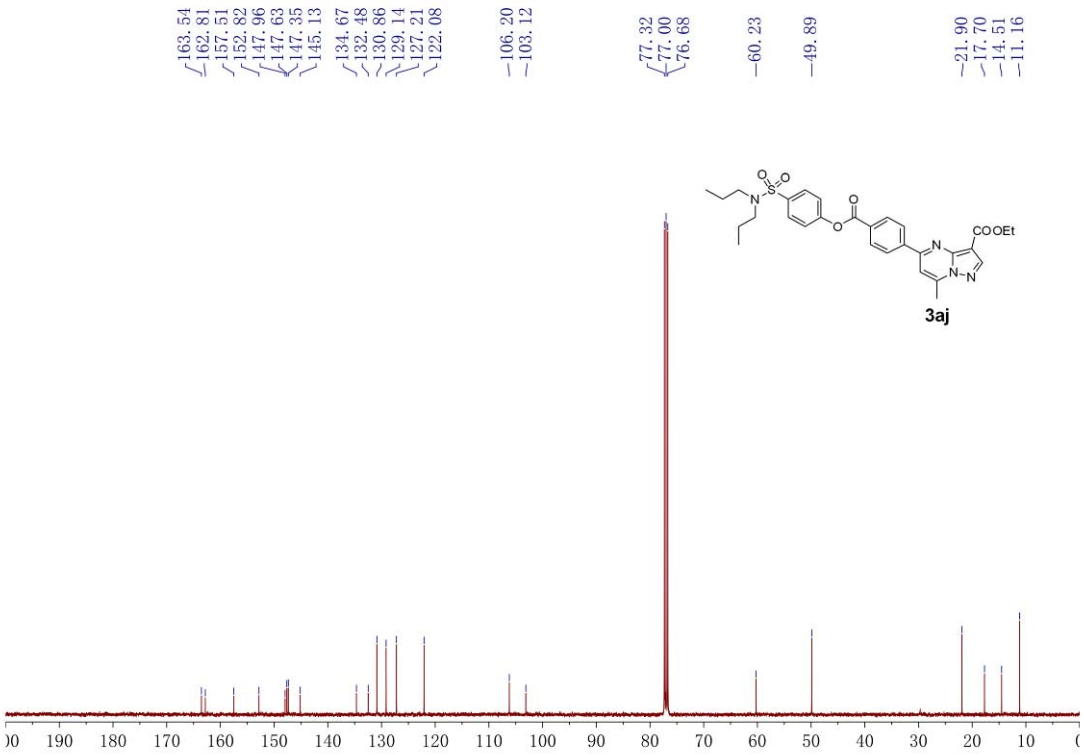
-0.5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127.21
122.08
106.20
103.12
77.32
77.00
76.68
60.23
49.89
21.90
17.70
14.51
11.16
COOEt
3aj
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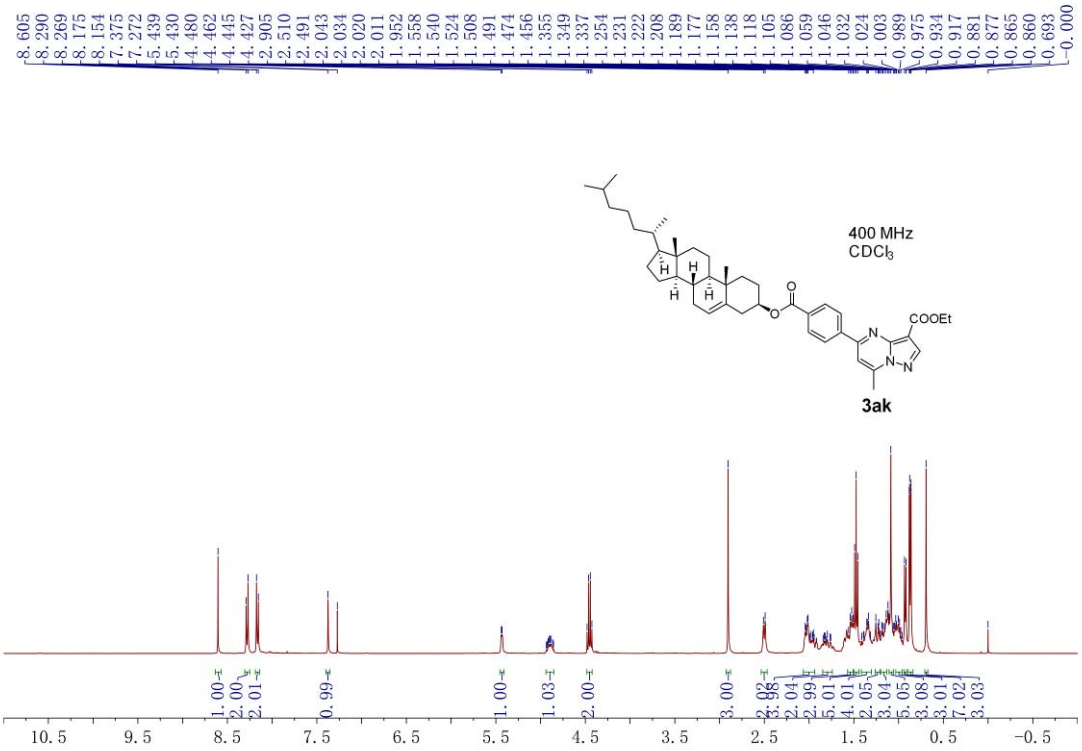
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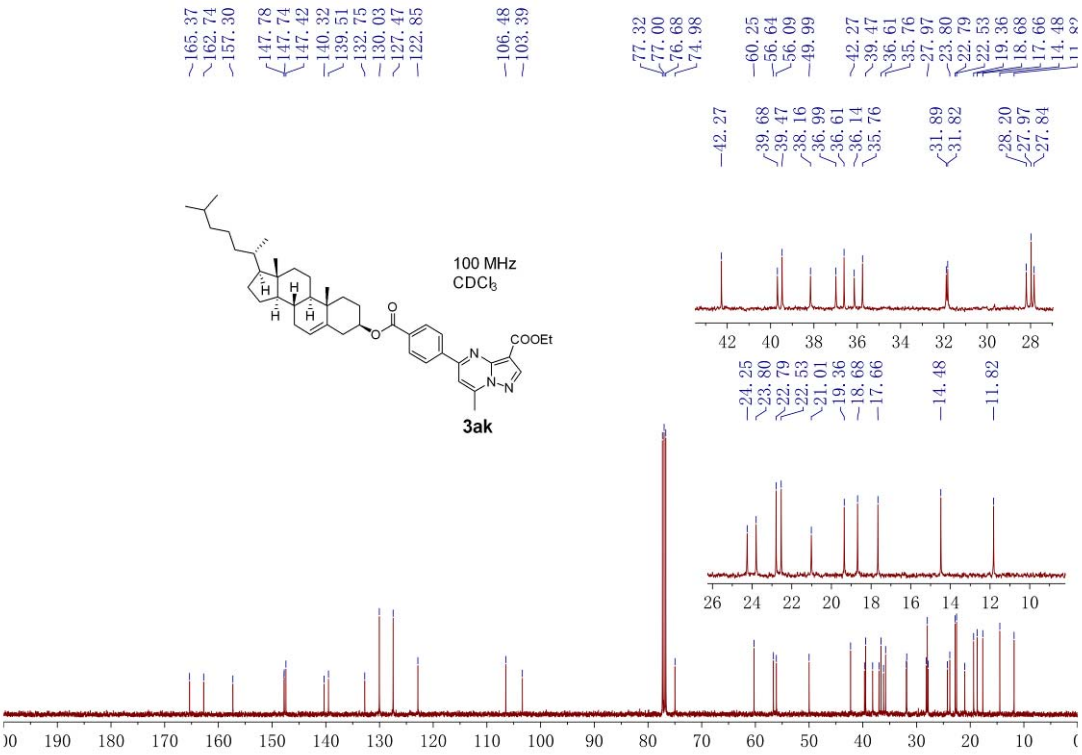
COOEt
3ak


100 MHz
CDCl3
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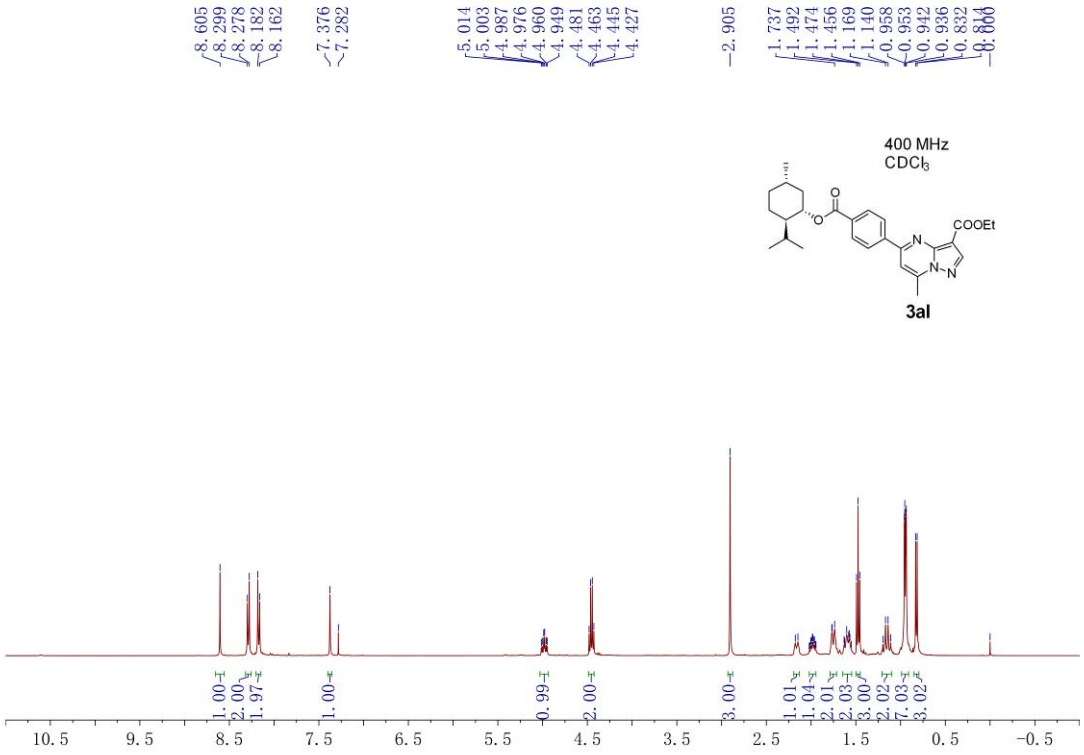
3ak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5.014
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4.949
4.481
4.463
4.445
4.427
2.905
1.737
1.492
1.474
1.456
1.169
1.140
0.958
0.953
0.942
0.936
0.832
400 MHz
CDCl3
COOEt
3al
1.00
2.00
1.97
1.00
0.99
2.00
3.00
1.01
1.04
2.01
2.03
3.00
2.02
7.03
3.02
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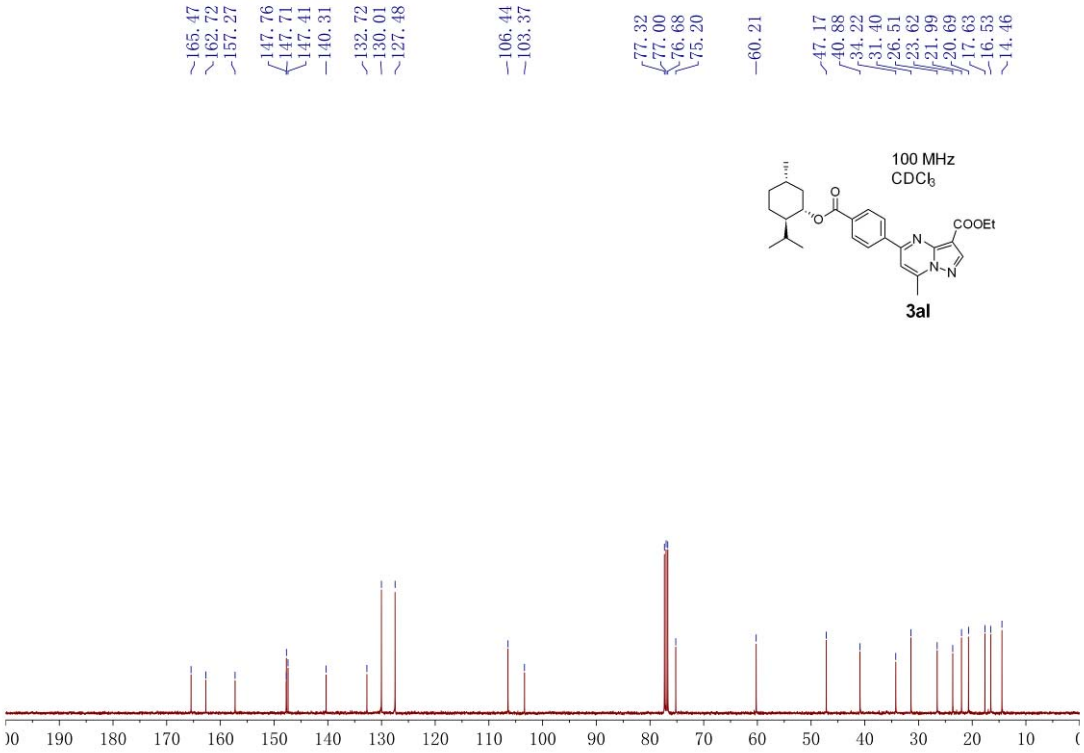
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77.00
76.68
75.20
60.21
47.17
40.88
34.22
31.40
26.51
23.62
21.99
20.69
17.63
16.53
14.46
100 MHz
CDCl3
COOEt
3al
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170
160
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120
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100
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80
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40
30
20
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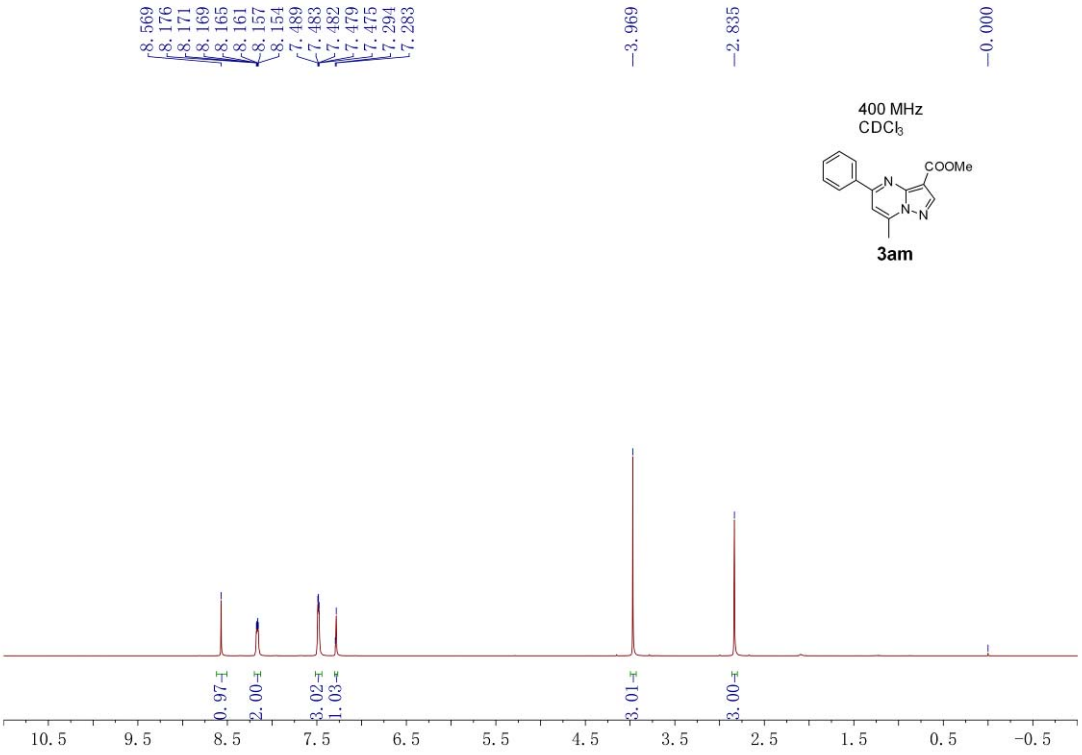
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8.154
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7.482
7.479
7.475
7.294
7.283
3.969
2.835
0.000
400 MHz
CDCl3
COOMe
3am
0.97
2.00
3.02
1.03
3.01
3.00
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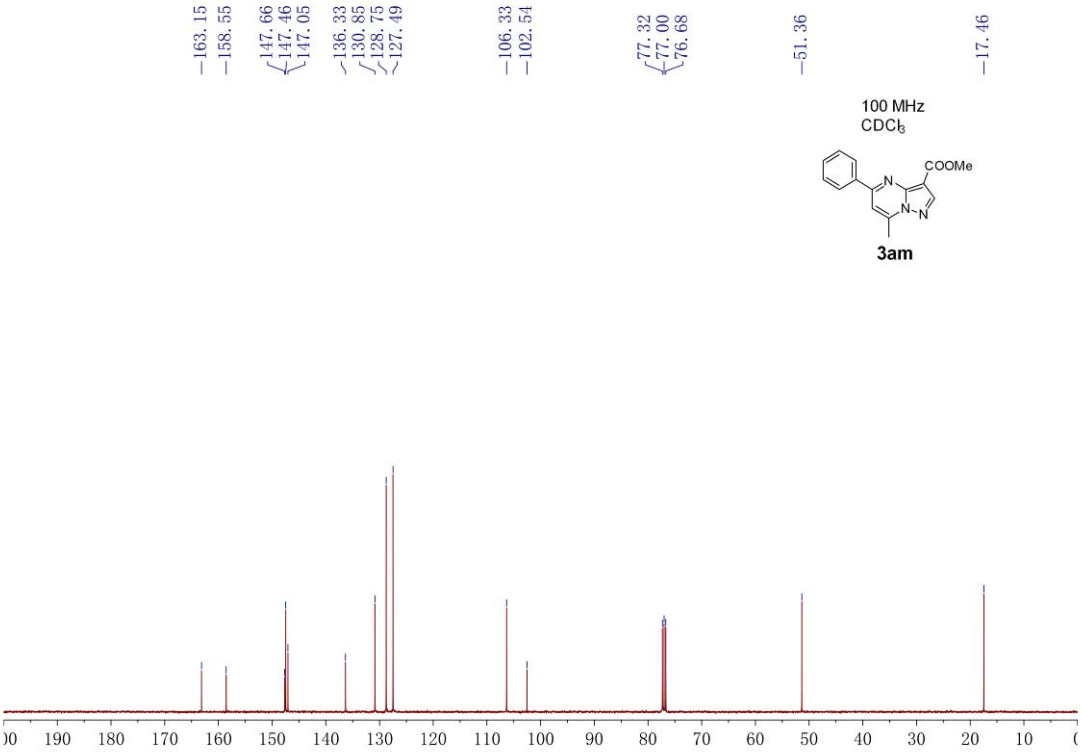
-0.5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106.33
102.54
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77.00
76.68
51.36
17.46
100 MHz
CDCl3
COOMe
3am
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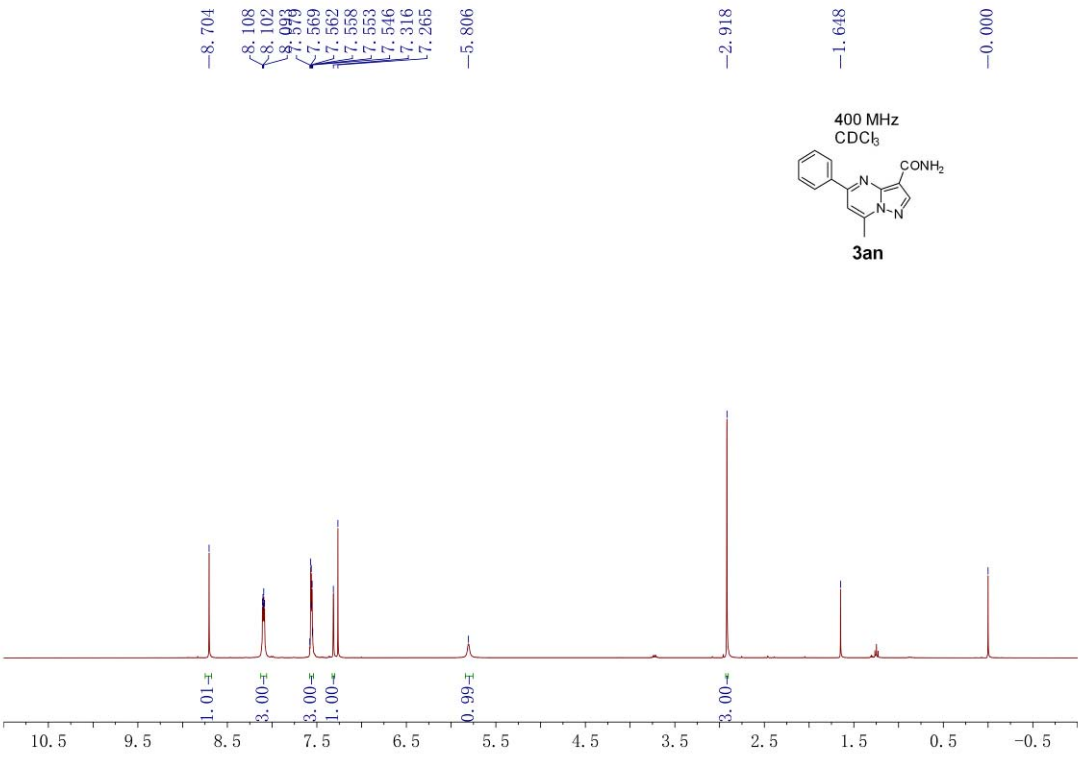
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7.546
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7.265
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0.000
400 MHz
CDCl3
CONH2
3an
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3.00
3.00
1.00
0.99
3.00
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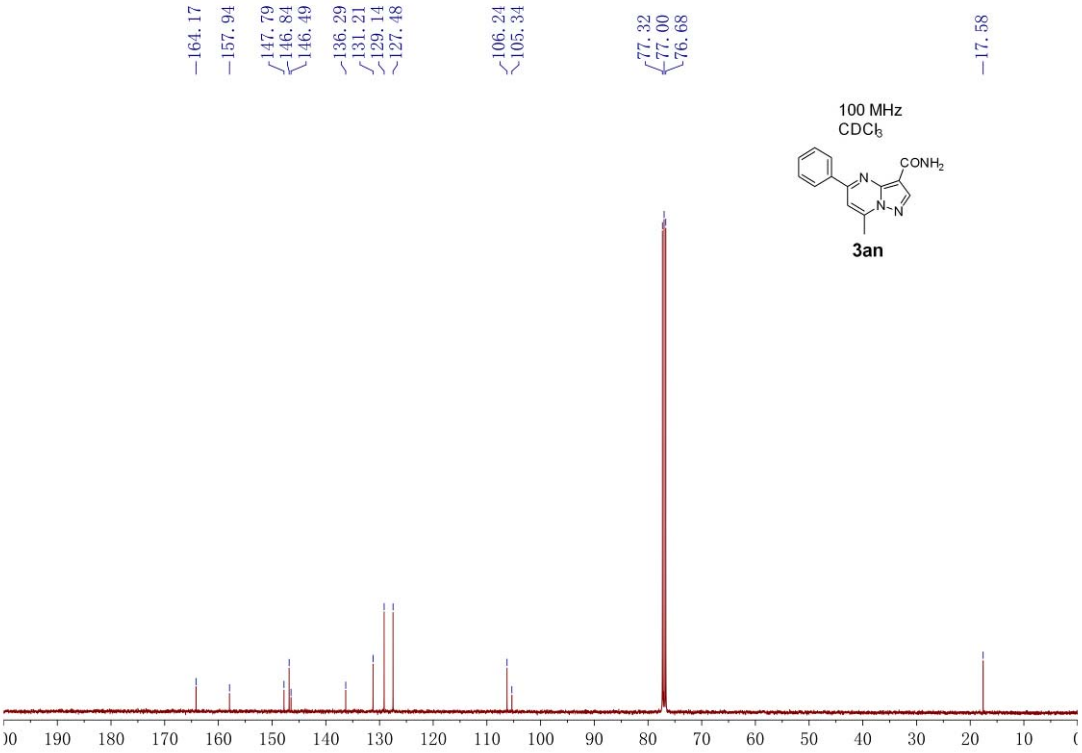
-0.5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129.14
127.48
106.24
105.34
77.32
77.00
76.68
17.58
100 MHz
CDCl3
CONH2
3an
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


8.337
8.150
8.146
8.137
8.132
8.126
7.523
7.518
7.511
7.507
7.500
7.492
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400 MHz
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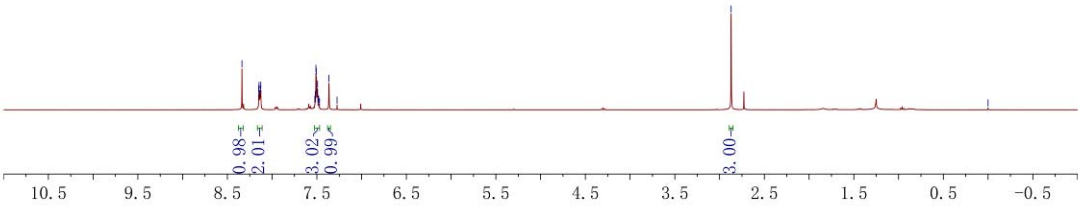
CN
N
N-N
3ao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0.99
3.00
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9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5


158.96
150.17
147.58
147.05
135.57
131.36
128.92
127.55
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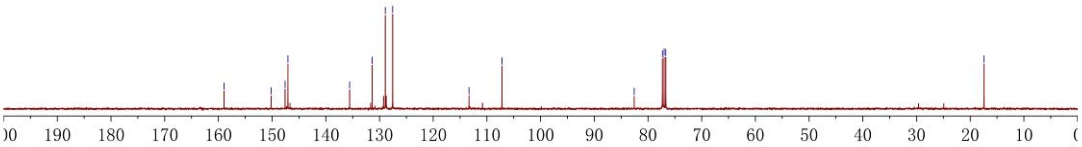
107.20
82.57
77.32
77.00
76.68
17.41
100 MHz
CDCl3
CN
N
N-N
3ao


190
180
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130
120
110
100
90
80
70
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40
30
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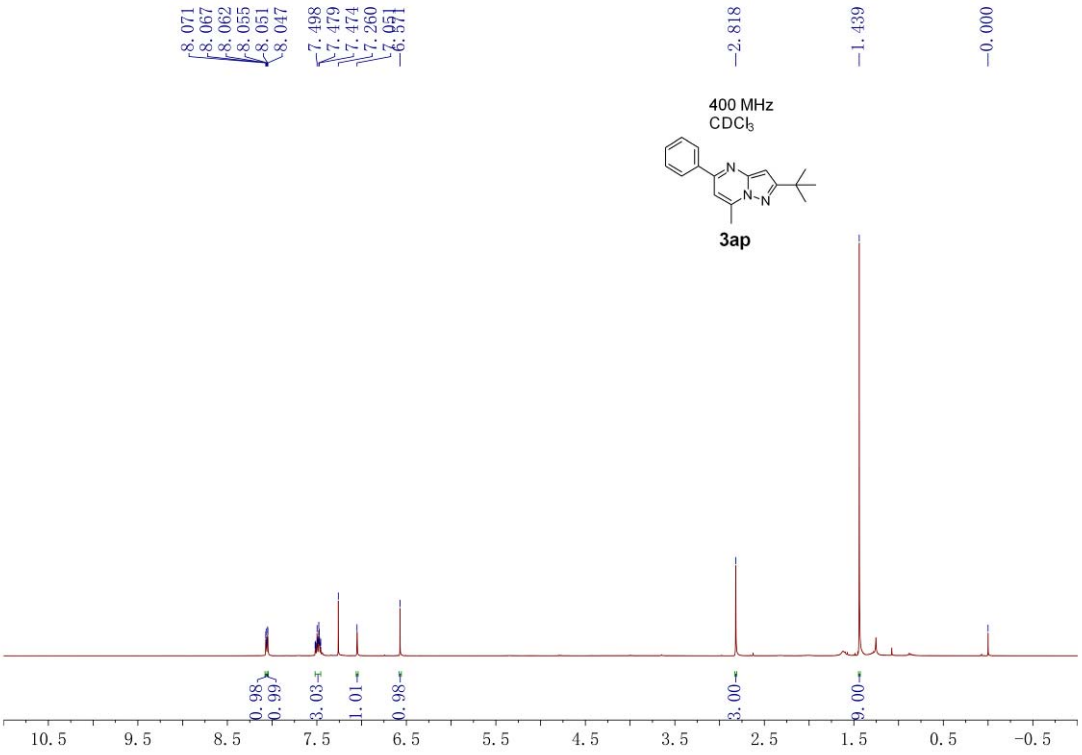
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8.067
8.062
8.055
8.051
8.047
7.498
7.479
7.474
7.260
6.571
2.818
1.439
0.000
400 MHz
CDCl3
3ap
0.98
0.99
3.03
1.01
0.98
3.00
9.00
10.5
9.5
8.5
7.5
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5.5
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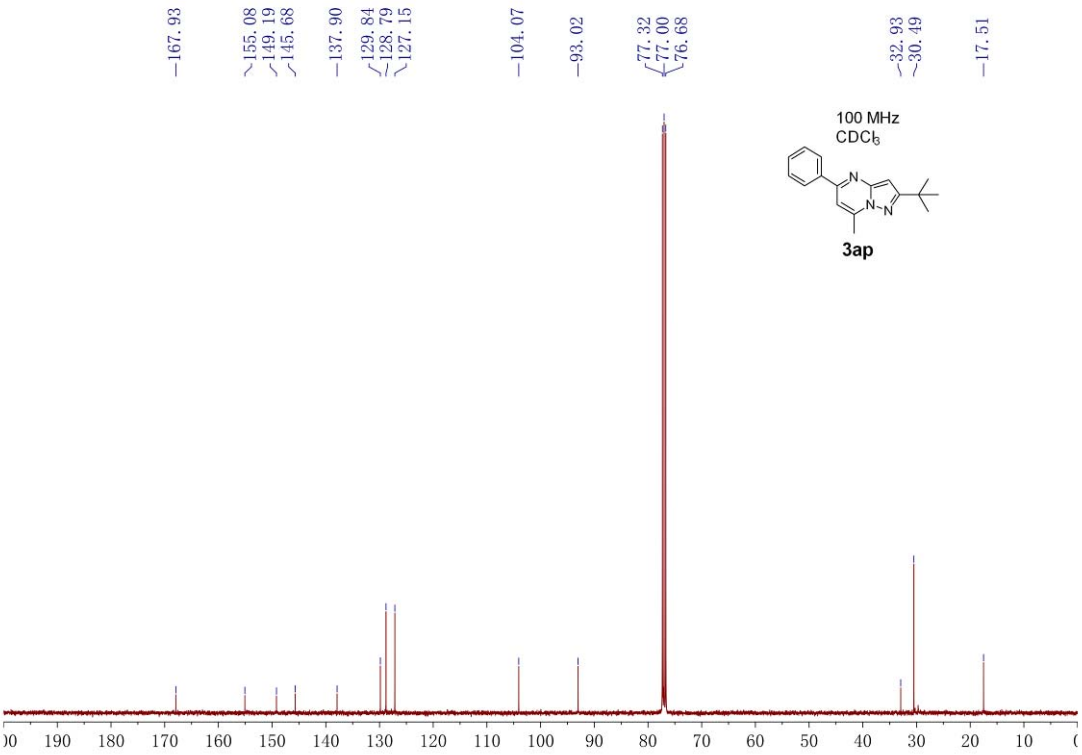
-0.5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149.19
145.68
137.90
129.84
128.79
127.15
104.07
93.02
77.32
77.00
76.68
32.93
30.49
17.51
100 MHz
CDCl3
3ap
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160
150
140
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120
110
100
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80
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30
20
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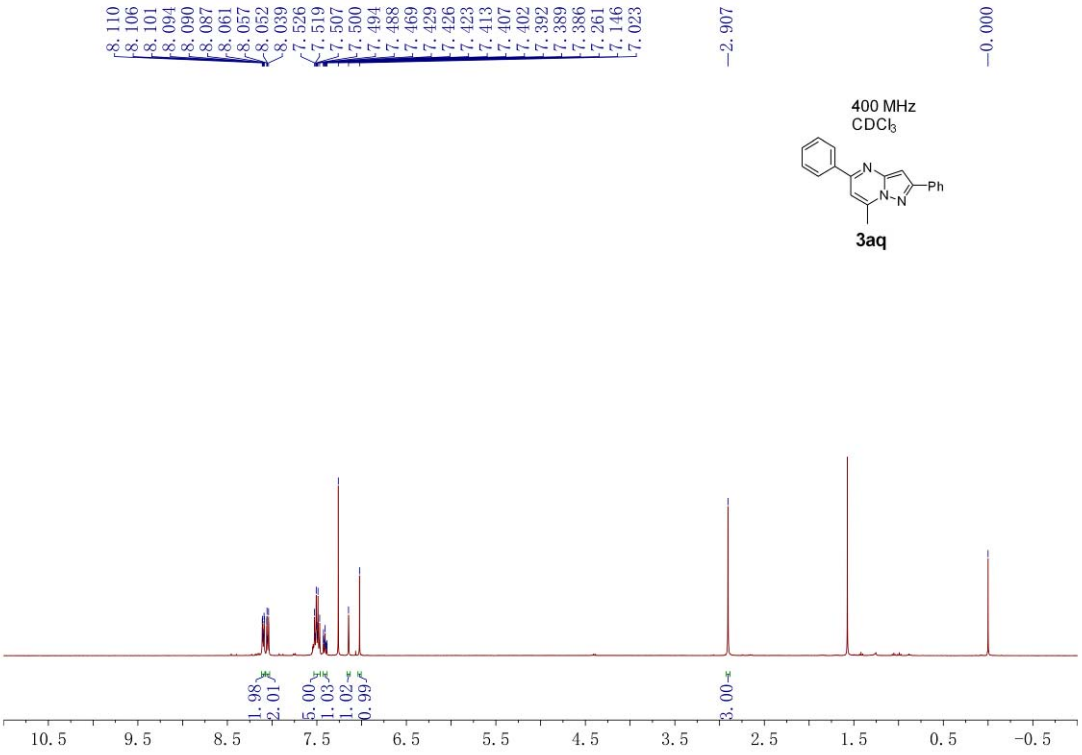
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8.106
8.101
8.094
8.090
8.087
8.061
8.057
8.052
8.039
7.526
7.519
7.507
7.500
7.494
7.488
7.469
7.429
7.426
7.423
7.413
7.407
7.402
7.392
7.389
7.386
7.261
7.146
7.023
2.907
0.000
400 MHz
CDCl3
Ph
3aq
1.98
2.01
5.00
1.03
1.02
0.99
3.00
10.5
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8.5
7.5
6.5
5.5
4.5
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2.5
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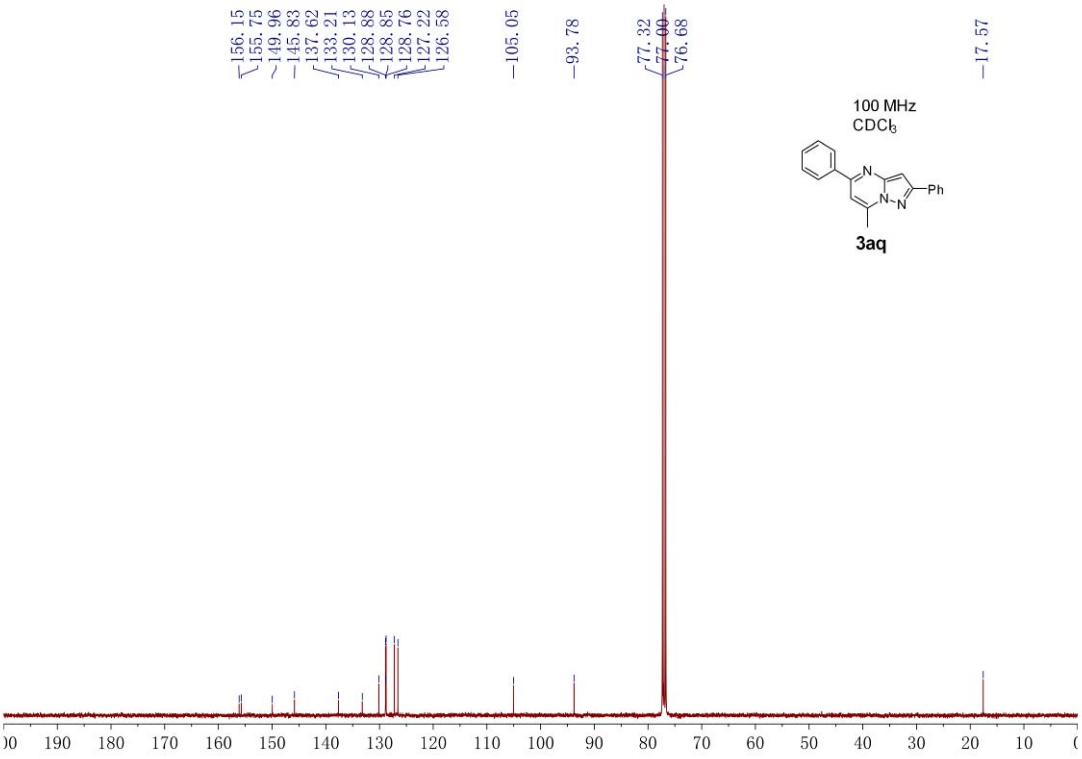
-0.5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149.96
145.83
137.62
133.21
130.13
128.88
128.85
128.76
127.22
126.58
105.05
93.78
77.32
77.00
76.68
17.57
100 MHz
CDCl3
Ph
3aq
190
180
170
160
150
140
130
120
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100
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80
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60
50
40
30
20
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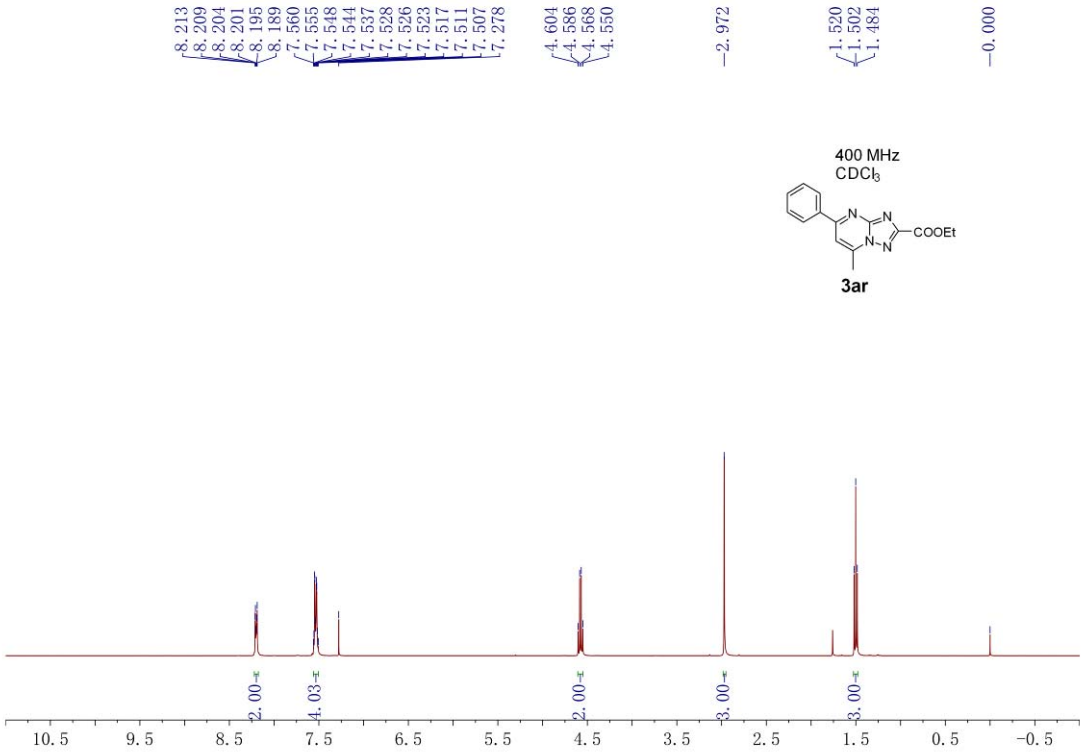
8.213
8.209
8.204
8.201
8.195
8.189
7.560
7.555
7.548
7.544
7.537
7.528
7.526
7.523
7.517
7.511
7.507
7.278
4.604
4.586
4.568
4.550
2.972
1.520
1.502
1.484
0.000
400 MHz
CDCl3
COOEt
3ar
2.00
4.03
2.00
3.00
3.00
10.5
9.5
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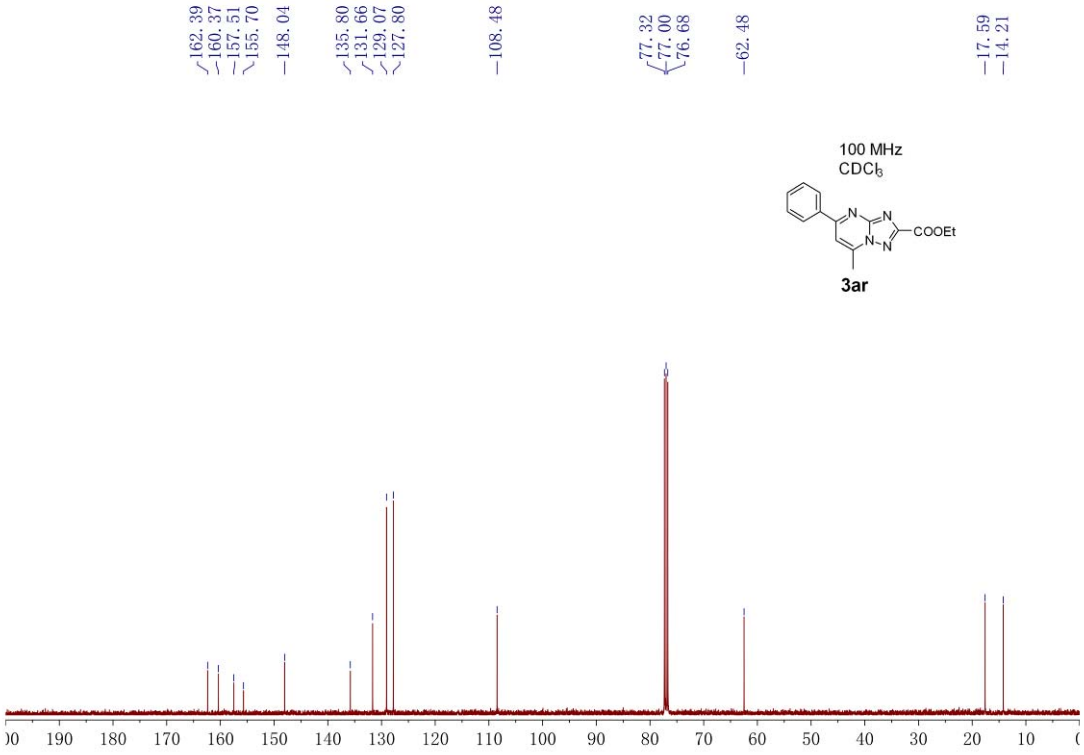
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5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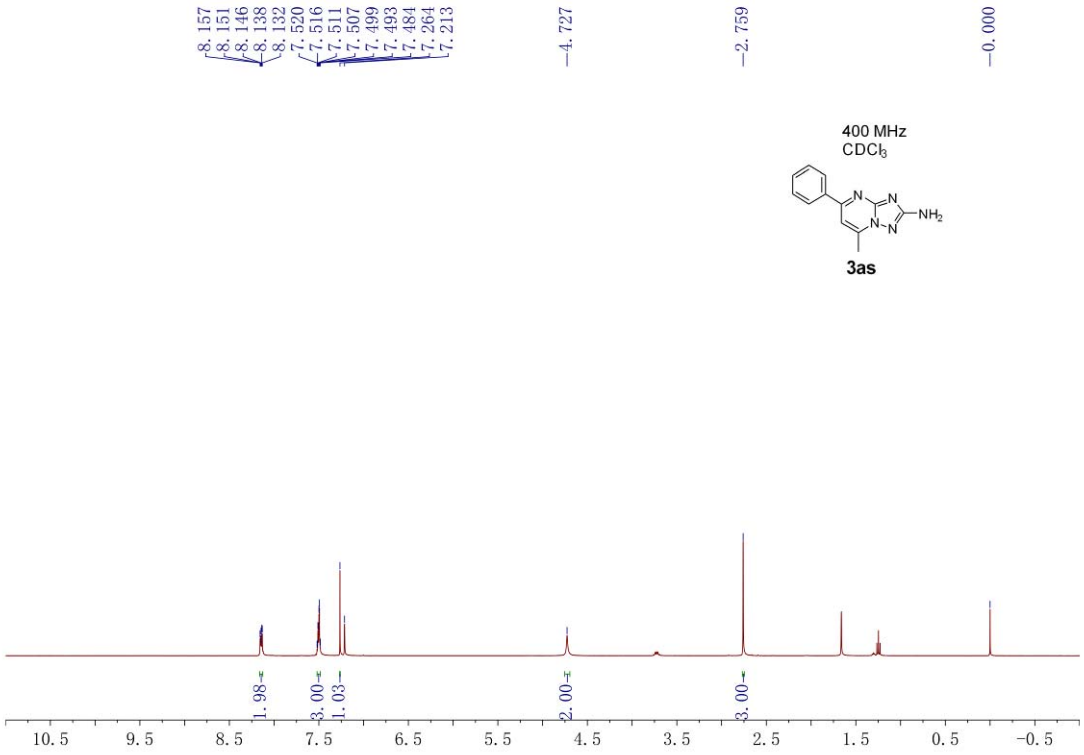
160.37
157.51
155.70
148.04
135.80
131.66
129.07
127.80
108.48
77.32
77.00
76.68
62.48
17.59
14.21
100 MHz
CDCl3
COOEt
3ar
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10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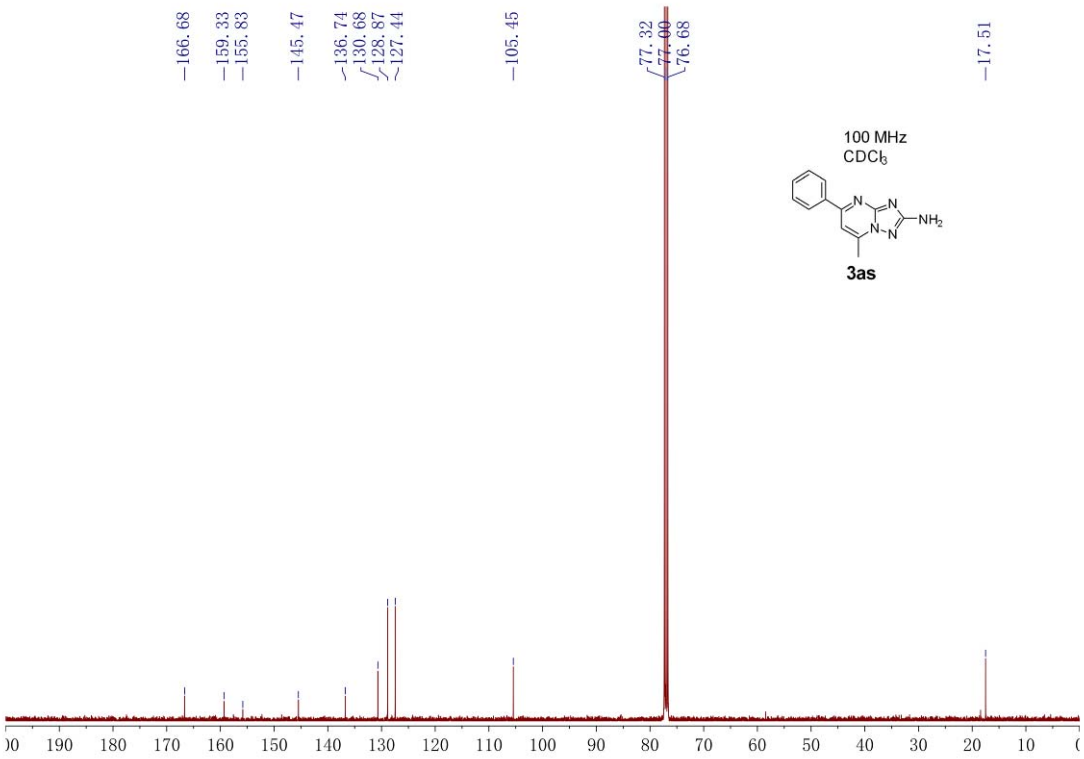
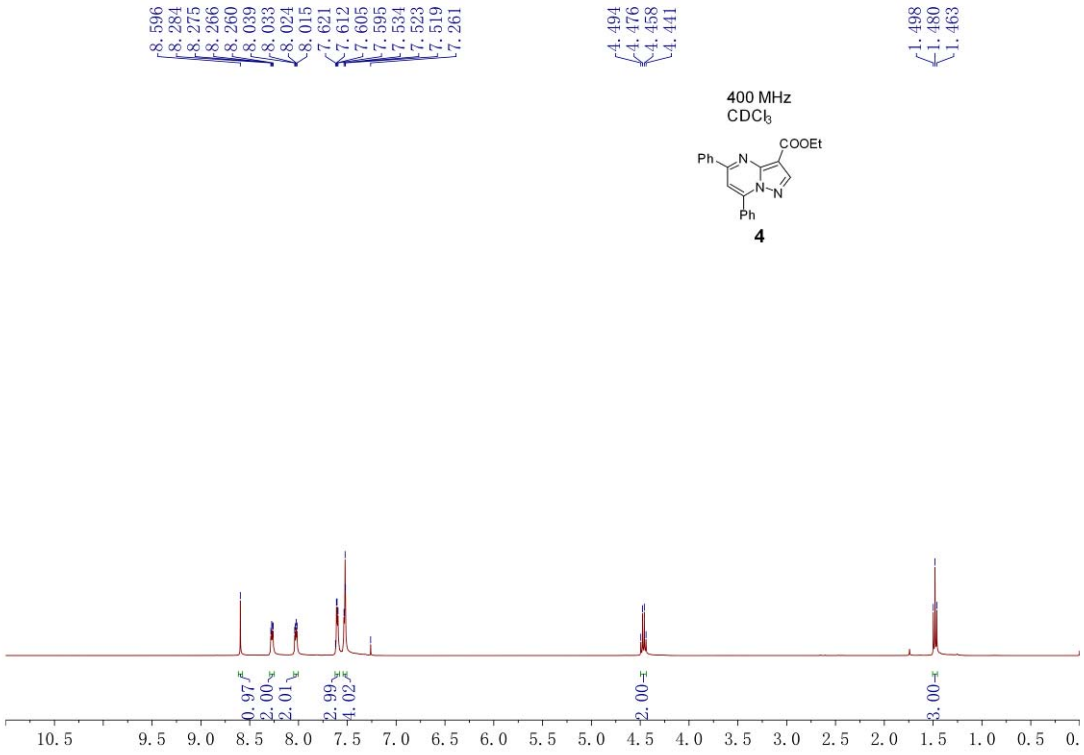
8.151
8.146
8.138
8.132
7.520
7.516
7.511
7.507
7.499
7.493
7.484
7.264
7.213
4.727
2.759
0.000
400 MHz
CDCl3
NH2
3as
1.98
3.00
1.03
2.00
3.00
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5


166.68
159.33
155.83
145.47
136.74
130.68
128.87
127.44
105.45
77.32
77.00
76.68
17.51
100 MHz
CDCl3
NH2
3as
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


8.596
8.284
8.275
8.266
8.260
8.039
8.033
8.024
8.015
7.621
7.612
7.605
7.595
7.534
7.523
7.519
7.261
4.494
4.476
4.458
4.441
1.498
1.480
1.463
400 MHz
CDCl3
COOEt
Ph
N
N
N
Ph
4
0.97
2.00
2.01
2.99
4.02
2.00
3.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.0
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3.0
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2.0
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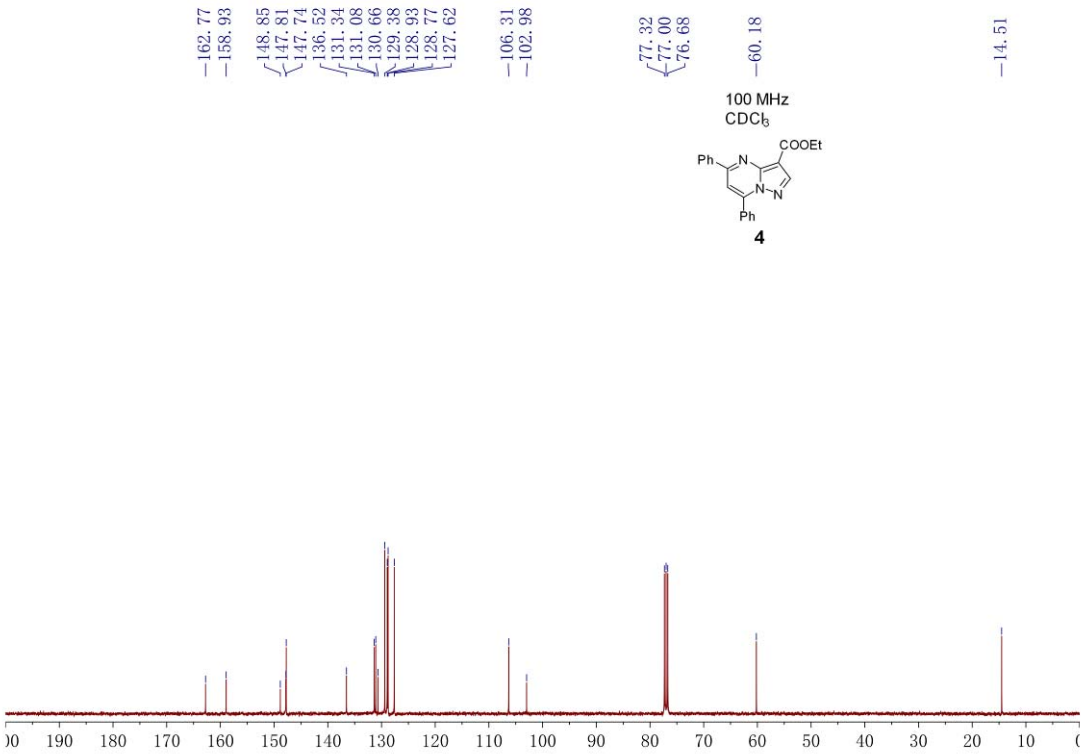
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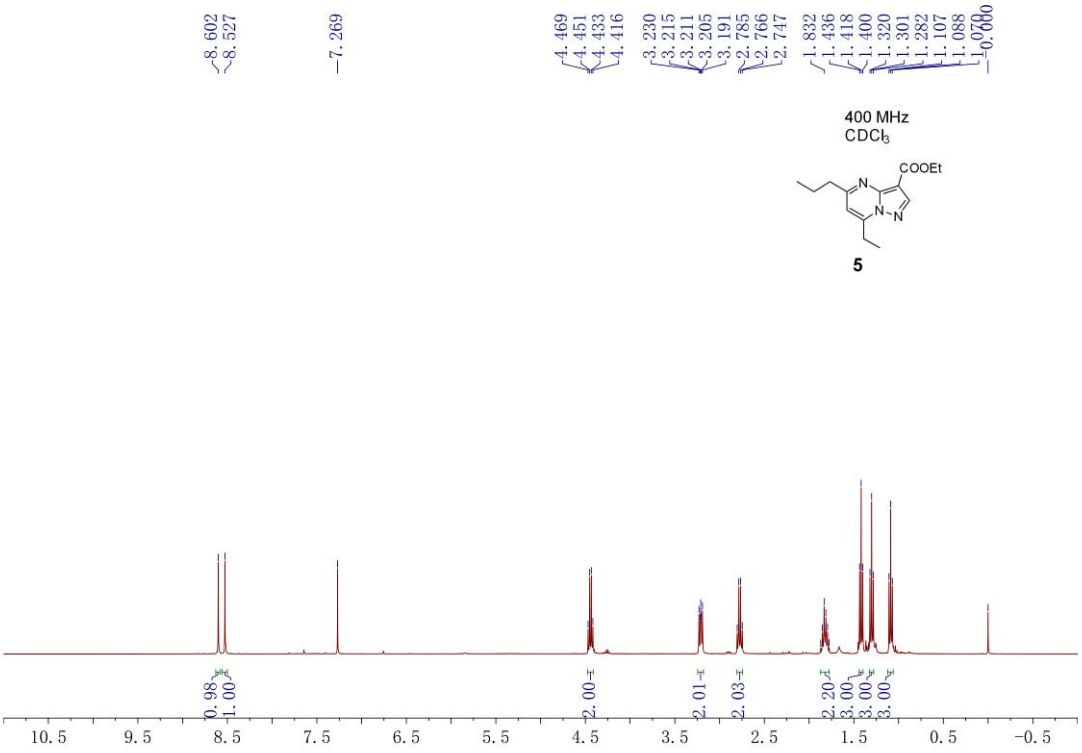
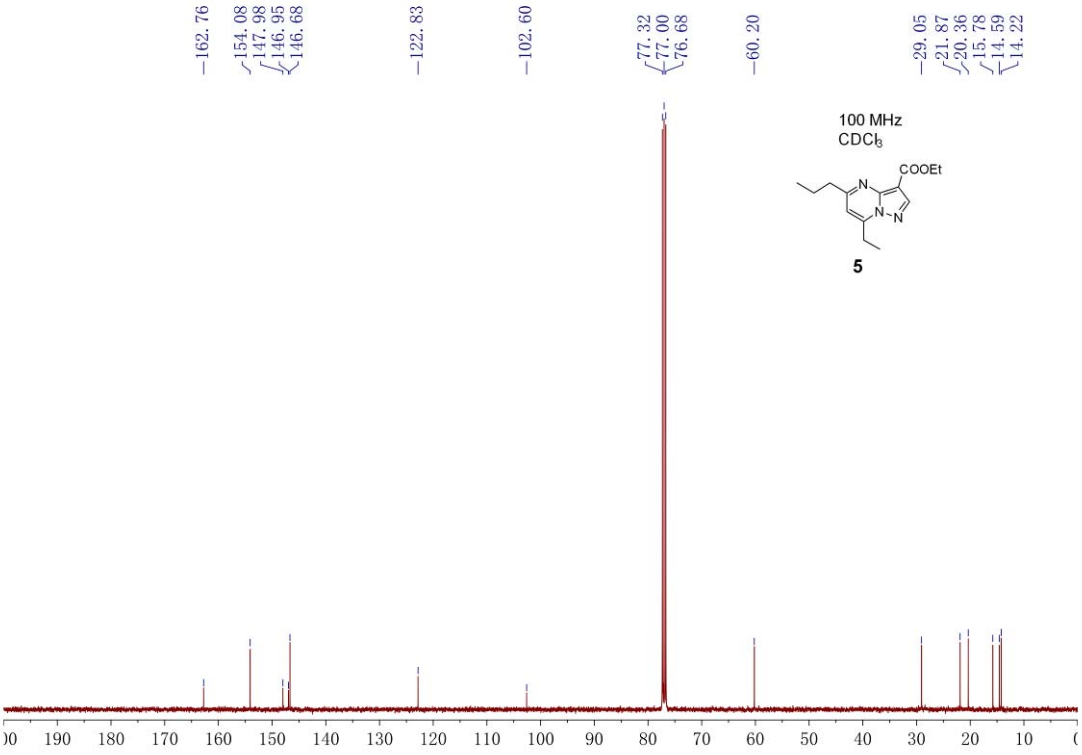
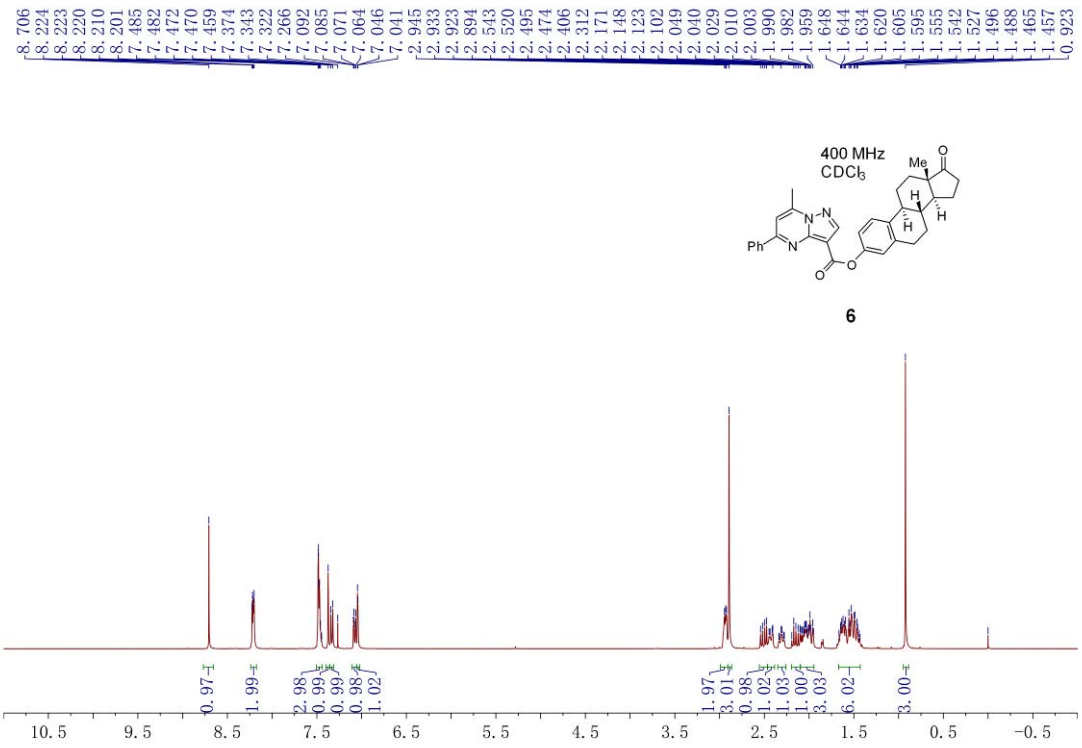
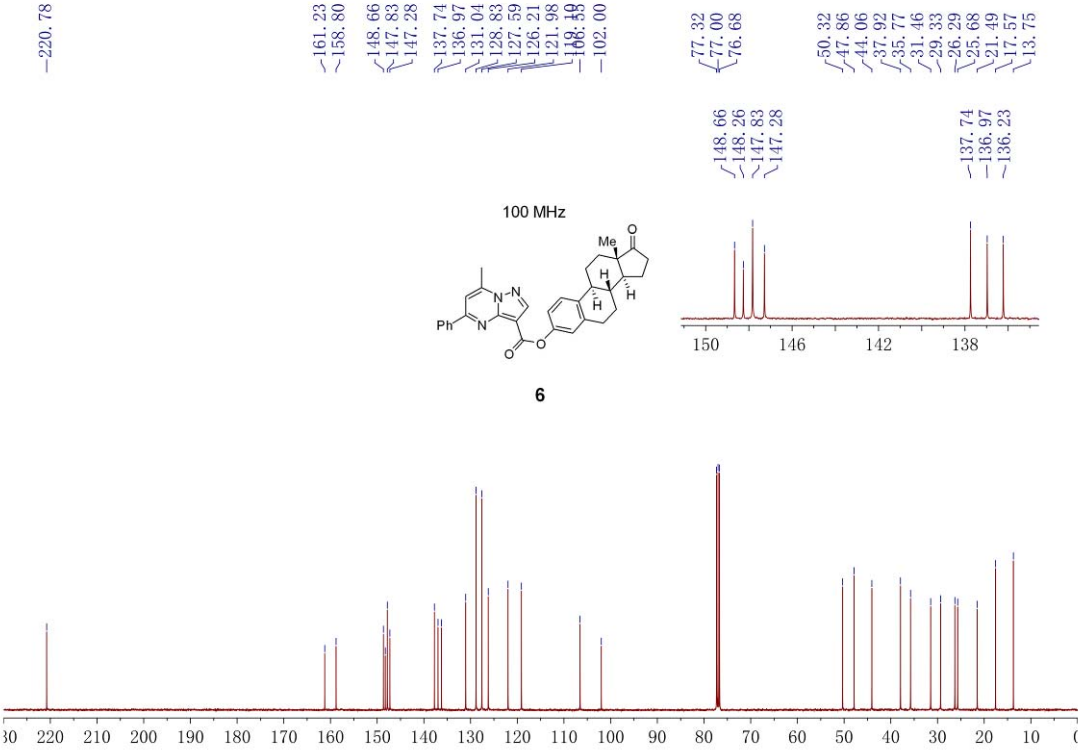
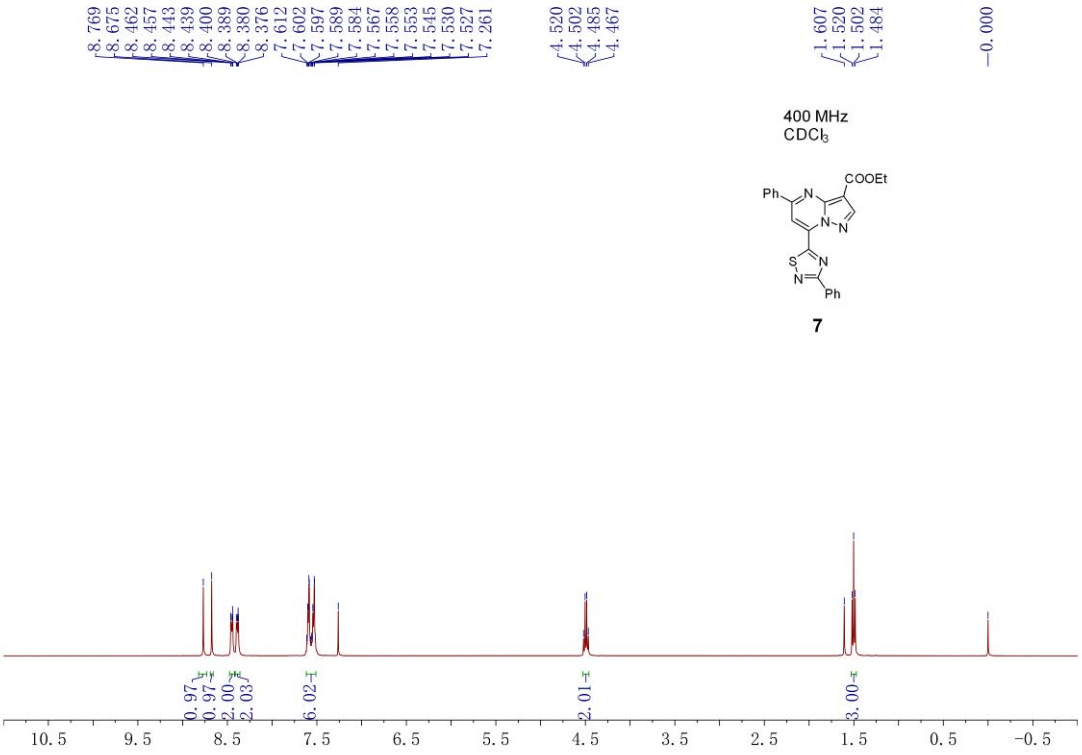
158.93
148.85
147.81
147.74
136.52
131.34
131.08
130.66
129.38
128.93
128.77
127.62
106.31
102.98
77.32
77.00
76.68
60.18
14.51
100 MHz
CDCl3
COOEt
Ph
N
N
N
Ph
4
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

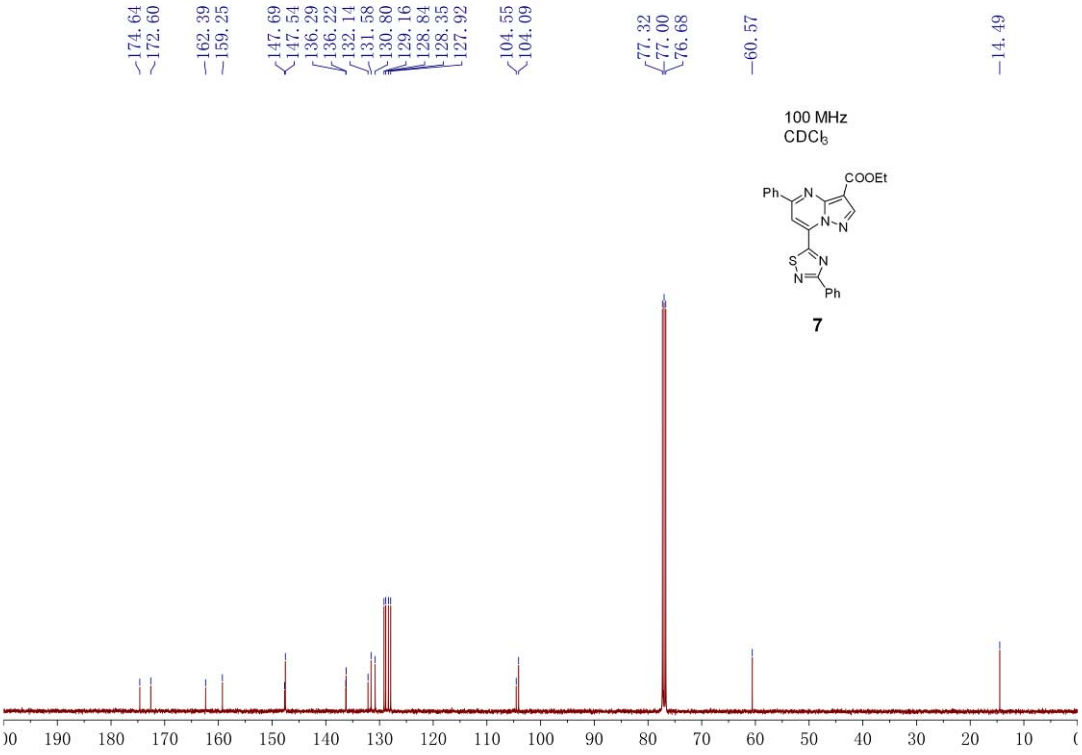

8.602
8.527
7.269
4.469
4.451
4.433
4.416
3.230
3.215
3.211
3.205
3.191
2.785
2.766
2.747
1.832
1.436
1.418
1.400
1.320
1.301
1.282
1.107
1.088
1.070
0.000
400 MHz
CDCl3
COOEt
5
0.98
1.00
2.00
2.01
2.03
2.20
3.00
3.00
3.00
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5


162.76
154.08
147.98
146.95
146.68
122.83
102.60
77.32
77.00
76.68
60.20
29.05
21.87
20.36
15.78
14.59
14.22
100 MHz
CDCl3
COOEt
5
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


400 MHz
CDCl3
Me
O
H
H
H
N
N
Ph
O
O
6
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5


100 MHz
Me
O
H
H
H
N
N
Ph
O
O
6
150
146
142
138
30
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


8.769
8.675
8.462
8.457
8.443
8.439
8.400
8.389
8.380
8.376
7.612
7.602
7.597
7.589
7.584
7.567
7.558
7.553
7.545
7.530
7.527
7.261
4.520
4.502
4.485
4.467
1.607
1.520
1.502
1.484
0.000
400 MHz
CDCl3
COOEt
Ph
N
N
N
S
N
Ph
7
0.97
0.97
2.00
2.03
6.02
2.01
3.00
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5


174.64
172.60
162.39
159.25
147.69
147.54
136.29
136.22
132.14
131.58
130.80
129.16
128.84
128.35
127.92
104.55
104.09
77.32
77.00
76.68
60.57
14.49
100 MHz
CDCl3
COOEt
Ph
N
N
N
S
N
Ph
7
190
180
170
160
150
140
130
120
110
100
90
80
70
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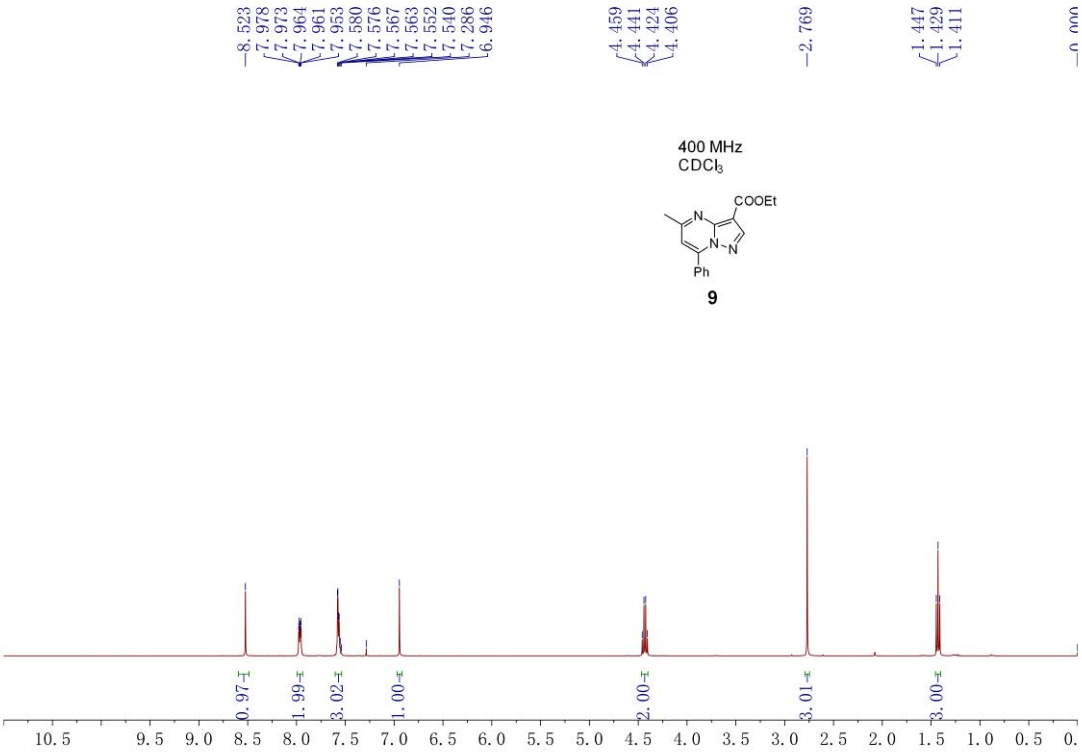
50
40
30
20
10


8.523
7.978
7.973
7.964
7.961
7.953
7.580
7.576
7.567
7.563
7.552
7.540
7.286
6.946
4.459
4.441
4.424
4.406
2.769
1.447
1.429
1.411
400 MHz
CDCl3
COOEt
Ph
9
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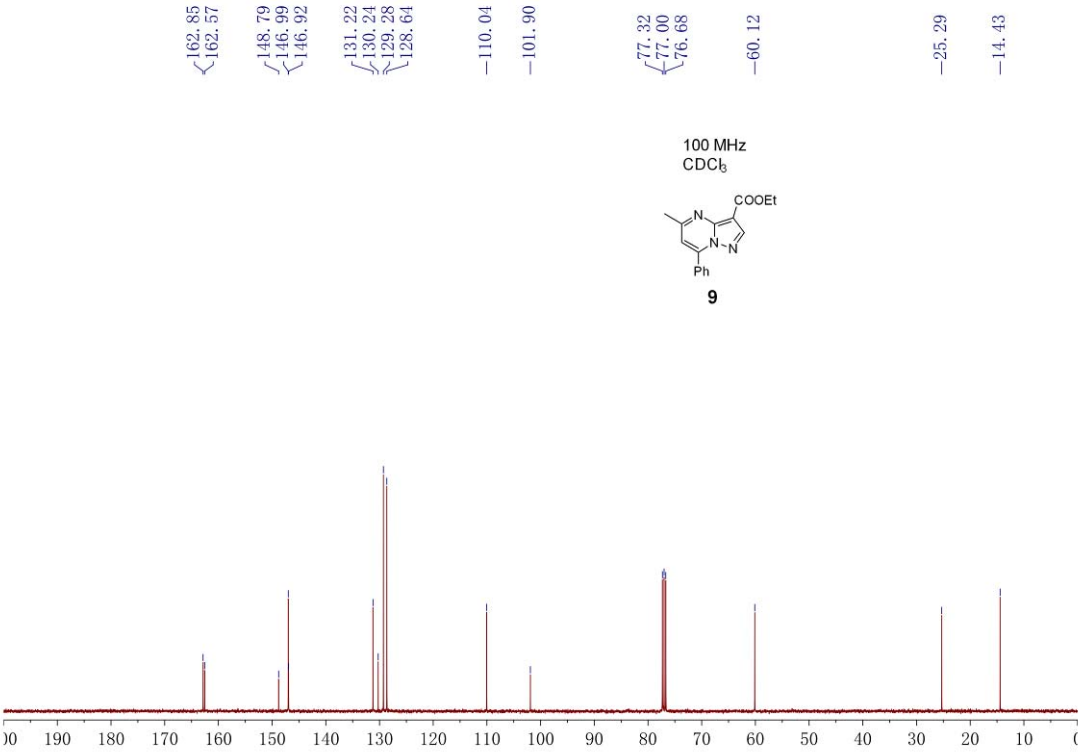
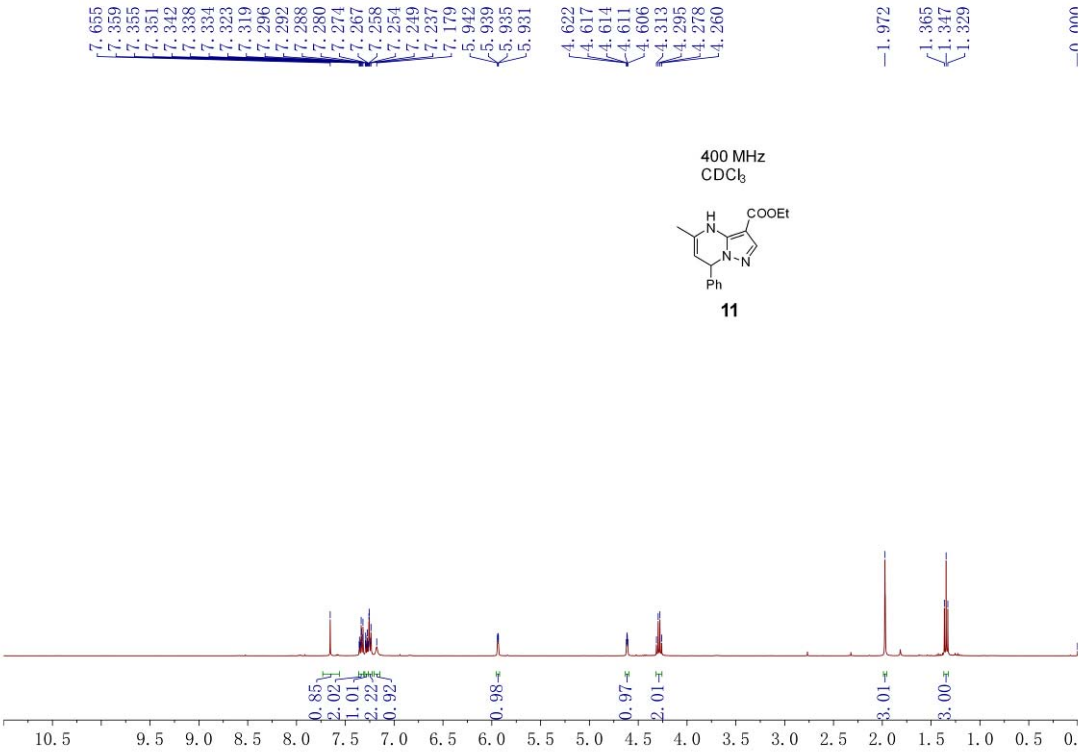
1.99
3.02
1.00
2.00
3.01
3.00


162.85
162.57
148.79
146.99
146.92
131.22
130.24
129.28
128.64
110.04
101.90
77.32
77.00
76.68
60.12
25.29
14.43
100 MHz
CDCl3
COOEt
Ph
9


7.655
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7.355
7.351
7.342
7.338
7.334
7.323
7.319
7.296
7.292
7.288
7.280
7.274
7.267
7.258
7.254
7.249
7.237
7.179
5.942
5.939
5.935
5.931
4.622
4.617
4.614
4.611
4.606
4.313
4.295
4.278
4.260
1.972
1.365
1.347
1.329
400 MHz
CDCl3
COOEt
Ph
11
0.85
2.02
1.01
2.22
0.92
0.98
0.97
2.01
3.01
3.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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5.5
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3.5
3.0
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2.0
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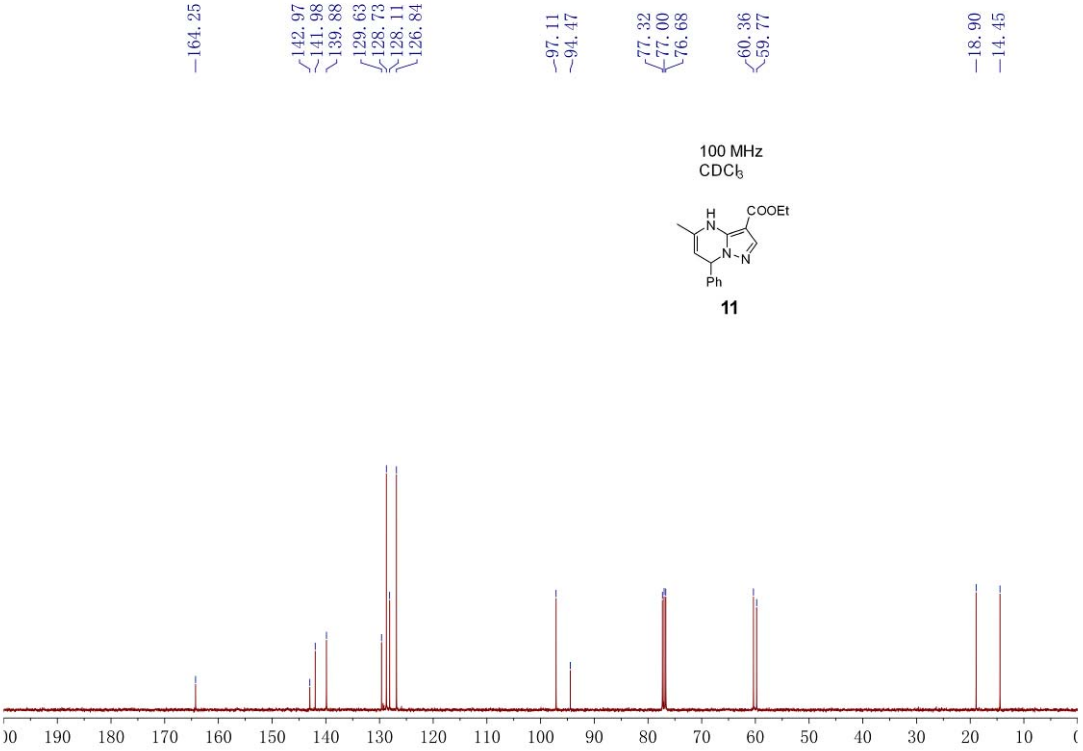
0.5


164.25
142.97
141.98
139.88
129.63
128.73
128.11
126.84
97.11
94.47
77.32
77.00
76.68
60.36
59.77
18.90
14.45
100 MHz
CDCl3
COOEt
Ph
11
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10