



Supporting Information

for

Three-component reactions of aromatic amines, 1,3-dicarbonyl compounds, and α -bromoacetaldehyde acetal to access *N*-(hetero)aryl-4,5-unsubstituted pyrroles

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Experimental procedures and copies of NMR spectra

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1. General remarks

Methyl acetoacetate, ethyl acetoacetate, and acetylacetone were purchased from Sinopharm Chemical Reagent Co., Ltd. Aniline (**1a**), bromoacetaldehyde diethyl acetal, and benzyl acetoacetate were purchased from Accela Chem Bio Co., Ltd. 2-Aminodiphenyl, 1-amino-2-methylbenzene, *p*-anisidine, and 2-chloroaniline were purchased from Accela Chem Bio Co., Ltd. 3-Fluoroaniline, 4-fluoro-2-methoxyaniline, 4-fluoroaniline, 4-chloroaniline, 4-bromoaniline, 5-amino-2-chloropyridine, and 5-bromo-2-chloropyridine were purchased from Energy Chemical Company. 4-Aminoacetophenone, 4-amino-3-methylbenzoic acid, 1-naphthylamine, and 3-amino-4,5-dimethylisoxazole were purchased from Alfa Aesar Chemical Company. ¹H and ¹³C NMR spectra were recorded on a Bruker AV-400 or Bruker AV-600 device. Chemical shifts are expressed in ppm relative to Me₄Si in CDCl₃ or DMSO-*d*₆. High-resolution mass spectra were obtained on a Bruker Compass Data Analysis 4.0 spectrometer.

2. Experimental section

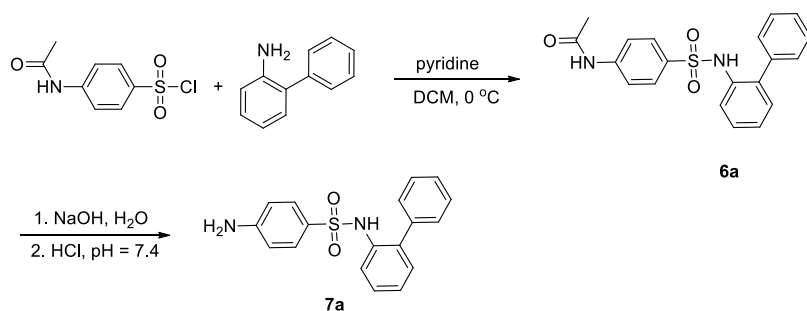
Typical procedure for the synthesis of *N*-(hetero)aryl-4,5-unsubstituted pyrrole derivatives

The reactions were conducted in a 10 mL V-type flask equipped with magnetic stirring. In a typical reaction, aniline (**1a**, 0.5 mmol) was mixed with **2a** (0.6 mmol), **3a** (0.6 mmol) and AlCl₃ (10 mol %) in acetonitrile (1.0 mL). The mixture was then stirred at 80 °C for 6 h. After the reaction (detected by TLC), the product was obtained by isolation with silica column chromatography (eluting solution:

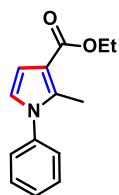
petroleum ether/ethyl acetate 20:1, v/v). The tests for the substrate scope were all performed with an analogous procedure.

Procedure for the synthesis of 7a [1,2].

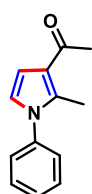
To a solution of [1,1'-biphenyl]-2-amine (1.0 equiv) in dichloromethane, pyridine (1.1 equiv) was added at 0 °C. Subsequently, a solution of 4-acetamidobenzene sulfonyl chloride (1.1 equiv) in dichloromethane was added dropwise at 0 °C and further stirred at room temperature overnight. The completion of the reaction was monitored by TLC, and the reaction mixture was quenched with saturated NaHCO₃, followed by extraction with DCM. The separated organic layer was dried over Na₂SO₄. Then, the mixture was concentrated under reduced pressure, and the residual mixture was subjected to an isolation by silica column chromatography (eluting solution: petroleum ether/ethyl acetate 10:1, v/v). The product **6a** was obtained in 80% yield. The obtained product **6a** was dissolved in 20% NaOH solution and the reaction mixtures were heated to reflux in an oil bath for 2 h. Then, the reaction solution was quenched with 2 M hydrochloric acid to pH 7.4, resulting in a large amount of a white solid forming. The crude product was obtained and washed with 5 × 10 mL water, then dried overnight in a vacuum desiccator, and the product **7a** was obtained in 82% yield.



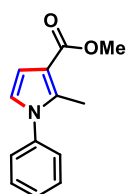
3. Characterization data of the compounds



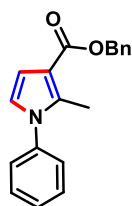
Ethyl 2-methyl-1-phenyl-1*H*-pyrrole-3-carboxylate (**4a**) [3]: yellow oil, ^1H NMR (600 MHz, CDCl_3 , TMS, 25 $^\circ\text{C}$) δ = 7.36 (t, J = 7.5 Hz, 2H), 7.32 – 7.27 (m, 1H), 7.16 (d, J = 7.7 Hz, 2H), 6.57 (q, J = 3.0 Hz, 2H), 4.20 (q, J = 7.1 Hz, 2H), 2.35 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (150 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ = 165.6, 139.2, 136.0, 129.3, 128.0, 126.3, 121.3, 113.3, 110.2, 59.4, 14.6, 12.2 ppm. HRMS (TOF, ESI): m/z calcd for $\text{C}_{14}\text{H}_{16}\text{NO}_2$, $[\text{M} + \text{H}]^+$ 230.1181, found 230.1185.



1-(2-Methyl-1-phenyl-1*H*-pyrrol-3-yl)ethanone (**4b**) [4]: yellow oil, ^1H NMR (600 MHz, CDCl_3 , TMS, 25 $^\circ\text{C}$) δ = 7.50 – 7.46 (m, 2H), 7.44 – 7.41 (m, 1H), 7.28 – 7.26 (m, 2H), 6.68 (d, J = 3.1 Hz, 1H), 6.62 (d, J = 3.1 Hz, 1H), 2.46 (s, 3H), 2.46 (s, 3H) ppm. ^{13}C NMR (150 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ = 195.4, 139.0, 135.7, 129.5, 128.3, 126.4, 122.1, 121.3, 110.6, 28.8, 12.9 ppm. HRMS (TOF, ESI): m/z calcd for $\text{C}_{13}\text{H}_{14}\text{NO}$, $[\text{M} + \text{H}]^+$ 200.1075, found 200.1077.

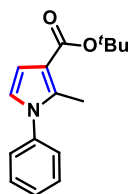


Methyl 2-methyl-1-phenyl-1*H*-pyrrole-3-carboxylate (**4c**): yellow oil, ^1H NMR (600 MHz, CDCl_3 , TMS, 25 $^\circ\text{C}$) δ = 7.49 – 7.46 (m, 2H), 7.43 – 7.40 (m, 1H), 7.28 – 7.26 (m, 2H), 6.67 (d, J = 3.1 Hz, 1H), 6.65 (d, J = 3.1 Hz, 1H), 3.83 (s, 3H), 2.44 (s, 3H) ppm. ^{13}C NMR (150 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ = 166.0, 139.2, 136.2, 129.3, 128.0, 126.3, 121.4, 113.0, 110.1, 50.9, 12.2 ppm. HRMS (TOF, ESI): m/z calcd for $\text{C}_{13}\text{H}_{14}\text{NO}_2$, $[\text{M} + \text{H}]^+$ 216.1025, found 216.1028.

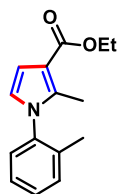


Benzyl 2-methyl-1-phenyl-1*H*-pyrrole-3-carboxylate (**4d**): yellow oil, ^1H NMR (600 MHz, CDCl_3 , TMS, 25 $^\circ\text{C}$) δ = 7.47 – 7.43 (m, 4H), 7.40 (t, J = 7.4 Hz, 1H), 7.36 (t, J = 7.5 Hz,

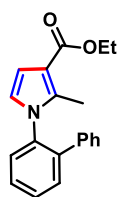
2H), 7.30 (t, $J = 7.3$ Hz, 1H), 7.25 (dd, $J = 12.7, 5.2$ Hz, 2H), 6.71 (d, $J = 3.1$ Hz, 1H), 6.66 (d, $J = 3.1$ Hz, 1H), 5.31 (s, 2H), 2.45 (s, 3H) ppm. ^{13}C NMR (150 MHz, CDCl_3 , 25 °C) $\delta = 165.3, 139.2, 137.1, 136.5, 129.3, 128.5, 128.1, 128.0, 127.9, 126.3, 121.5, 113.0, 110.4, 65.3, 12.3$ ppm. HRMS (TOF, ESI): m/z calcd for $\text{C}_{19}\text{H}_{18}\text{NO}_2$, $[\text{M} + \text{H}]^+$ 292.1338, found 292.1340.



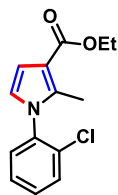
tert-Butyl 2-methyl-1-phenyl-1*H*-pyrrole-3-carboxylate (**4e**) [5]: yellow oil, ^1H NMR (600 MHz, CDCl_3 , TMS, 25 °C) $\delta = 7.48 - 7.44$ (m, 2H), 7.42 – 7.38 (m, 1H), 7.27 – 7.25 (m, 2H), 6.65 (d, $J = 3.1$ Hz, 1H), 6.63 (d, $J = 3.1$ Hz, 1H), 2.42 (s, 3H), 1.58 (s, 9H) ppm. ^{13}C NMR (150 MHz, CDCl_3 , 25 °C) $\delta = 165.1, 139.3, 135.4, 129.3, 127.9, 126.3, 121.0, 114.9, 110.4, 79.4, 28.5, 12.3$ ppm. HRMS (TOF, ESI): m/z calcd for $\text{C}_{16}\text{H}_{20}\text{NO}_2$, $[\text{M} + \text{H}]^+$ 258.1494, found 258.1495.



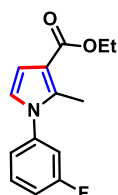
Ethyl 2-methyl-1-(*o*-tolyl)-1*H*-pyrrole-3-carboxylate (**4f**) [3]: yellow oil, ^1H NMR (600 MHz, CDCl_3 , TMS, 25 °C) $\delta = 7.37 - 7.32$ (m, 2H), 7.28 (t, $J = 7.3$ Hz, 1H), 7.16 (d, $J = 7.6$ Hz, 1H), 6.67 (t, $J = 7.9$ Hz, 1H), 6.52 (d, $J = 2.9$ Hz, 1H), 4.30 (q, $J = 7.0$ Hz, 2H), 2.01 (s, 3H), 1.37 (t, $J = 7.1$ Hz, 3H) ppm. ^{13}C NMR (150 MHz, CDCl_3 , 25 °C) $\delta = 165.7, 138.2, 136.5, 136.0, 130.9, 128.9, 127.9, 126.7, 120.9, 112.5, 109.9, 59.4, 17.2, 14.6, 11.6$ ppm. HRMS (TOF, ESI): m/z calcd for $\text{C}_{15}\text{H}_{18}\text{NO}_2$, $[\text{M} + \text{H}]^+$ 244.1332, found 244.1335.



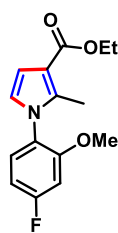
Ethyl 1-([1,1'-biphenyl]-2-yl)-2-methyl-1*H*-pyrrole-3-carboxylate (**4g**): yellow oil ^1H NMR (600 MHz, CDCl_3 , TMS, 25 °C) $\delta = 7.50$ (dtd, $J = 8.9, 7.7, 1.5$ Hz, 2H), 7.42 (td, $J = 7.5, 1.8$ Hz, 1H), 7.27 (dd, $J = 7.8, 1.0$ Hz, 1H), 7.25 – 7.20 (m, 3H), 7.06 – 7.02 (m, 2H), 6.56 (d, $J = 3.1$ Hz, 1H), 6.49 (d, $J = 3.1$ Hz, 1H), 4.22 (qd, $J = 7.1, 3.2$ Hz, 2H), 2.10 (s, 3H), 1.30 (t, $J = 7.1$ Hz, 3H) ppm. ^{13}C NMR (150 MHz, CDCl_3 , 25 °C) $\delta = 165.6, 139.6, 138.0, 136.8, 136.6, 131.0, 129.0, 128.6, 128.5, 128.2, 127.6, 121.7, 112.5, 110.1, 59.3, 14.5, 11.8$ ppm. HRMS (TOF, ESI): m/z calcd for $\text{C}_{20}\text{H}_{20}\text{NO}_2$, $[\text{M} + \text{H}]^+$ 306.1494, found 306.1498.



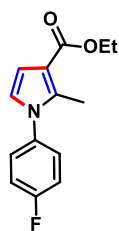
Ethyl 1-(2-chlorophenyl)-2-methyl-1*H*-pyrrole-3-carboxylate (**4h**) [3]: yellow oil, ^1H NMR (600 MHz, CDCl_3 , TMS, 25 $^\circ\text{C}$) δ = 7.53 (dd, J = 7.8, 1.1 Hz, 1H), 7.42 – 7.36 (m, 2H), 7.30 (dd, J = 7.6, 1.6 Hz, 1H), 6.70 (d, J = 3.1 Hz, 1H), 6.55 (d, J = 3.1 Hz, 1H), 4.30 (q, J = 7.1 Hz, 2H), 2.31 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (150 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ = 165.5, 137.0, 136.8, 132.7, 130.4, 130.2, 129.6, 127.7, 121.1, 112.9, 110.3, 59.5, 14.6, 11.6 ppm. HRMS (TOF, ESI): m/z calcd for $\text{C}_{14}\text{H}_{15}\text{ClNO}_2$, $[\text{M} + \text{H}]^+$ 264.0791, found 264.0792.



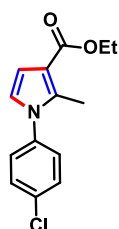
Ethyl 1-(3-fluorophenyl)-2-methyl-1*H*-pyrrole-3-carboxylate (**4i**): yellow oil, ^1H NMR (600 MHz, CDCl_3 , TMS, 25 $^\circ\text{C}$) δ = 7.44 (td, J = 8.1, 6.3 Hz, 1H), 7.12 (tdd, J = 8.4, 2.4, 0.7 Hz, 1H), 7.08 (dd, J = 7.9, 1.0 Hz, 1H), 7.01 (dt, J = 9.3, 2.2 Hz, 1H), 6.67 (dd, J = 7.3, 3.1 Hz, 2H), 4.30 (q, J = 7.1 Hz, 2H), 2.47 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (150 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ = 165.4, 162.7 (d, J = 247.5 Hz), 140.6 (d, J = 9.8 Hz), 135.8, 130.5 (d, J = 9.2 Hz), 122.0 (d, J = 3.2 Hz), 121.1, 115.0 (d, J = 21.0 Hz), 113.8 (d, J = 24.0 Hz), 113.7, 110.6, 59.5, 14.5, 12.2 ppm. ^{19}F NMR (565 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ = -110.8 ppm. HRMS (TOF, ESI): m/z calcd for $\text{C}_{14}\text{H}_{15}\text{FNO}_2$, $[\text{M} + \text{H}]^+$ 248.1087, found 248.1085.



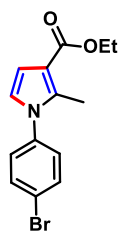
Ethyl 1-(4-fluoro-2-methoxyphenyl)-2-methyl-1*H*-pyrrole-3-carboxylate (**4j**): yellow oil, ^1H NMR (600 MHz, CDCl_3 , TMS, 25 $^\circ\text{C}$) δ = 7.15 (dd, J = 8.5, 6.2 Hz, 1H), 6.78 – 6.70 (m, 2H), 6.66 (d, J = 3.0 Hz, 1H), 6.52 (d, J = 3.0 Hz, 1H), 4.29 (q, J = 7.1 Hz, 2H), 3.78 (s, 3H), 2.29 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (150 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ = 165.6, 163.3 (d, J = 246.0 Hz), 156.2 (d, J = 10.6 Hz), 137.6, 129.7 (d, J = 10.4 Hz), 123.9 (d, J = 3.4 Hz), 121.6, 112.5, 109.9, 107.1 (d, J = 22.7 Hz), 100.3 (d, J = 27.2 Hz), 59.4, 56.0, 14.6, 11.6 ppm. ^{19}F NMR (565 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ = -109.0 ppm. HRMS (TOF, ESI): m/z calcd for $\text{C}_{15}\text{H}_{17}\text{FNO}_3$, $[\text{M} + \text{H}]^+$ 278.1192, found 278.1195.



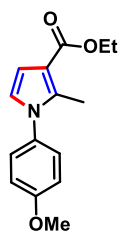
Ethyl 1-(4-fluorophenyl)-2-methyl-1*H*-pyrrole-3-carboxylate (**4k**): yellow oil, ^1H NMR (600 MHz, CDCl_3 , TMS, 25 $^\circ\text{C}$) δ = 7.27 – 7.23 (m, 2H), 7.18 – 7.14 (m, 2H), 6.66 (d, J = 3.1 Hz, 1H), 6.63 (d, J = 3.1 Hz, 1H), 4.30 (q, J = 7.1 Hz, 2H), 2.42 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (150 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ = 165.5, 162.5 (d, J = 246.0 Hz), 136.1, 135.2 (d, J = 3.1 Hz), 128.1 (d, J = 8.7 Hz), 121.4, 116.2 (d, J = 22.5 Hz), 113.4, 110.3, 59.5, 14.6, 12.1 ppm. ^{19}F NMR (565 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ = -113.2 ppm. HRMS (TOF, ESI): m/z calcd for $\text{C}_{14}\text{H}_{15}\text{FNO}_2$, $[\text{M} + \text{H}]^+$ 248.1087, found 248.1084.



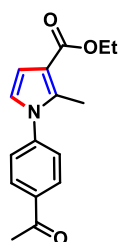
Ethyl 1-(4-chlorophenyl)-2-methyl-1*H*-pyrrole-3-carboxylate (**4l**) [3]: white solid, mp: 57 – 59 $^\circ\text{C}$, ^1H NMR (600 MHz, CDCl_3 , TMS, 25 $^\circ\text{C}$) δ = 7.46 – 7.44 (m, 1H), 7.44 – 7.43 (m, 1H), 7.23 – 7.22 (m, 1H), 7.21 – 7.19 (m, 1H), 6.67 (d, J = 3.1 Hz, 1H), 6.64 (d, J = 3.1 Hz, 1H), 4.30 (q, J = 7.1 Hz, 2H), 2.43 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (150 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ = 165.5, 137.7, 135.9, 133.9, 129.5, 127.5, 121.2, 113.7, 110.5, 77.3, 77.1, 59.5, 14.6, 12.2 ppm. HRMS (TOF, ESI): m/z calcd for $\text{C}_{14}\text{H}_{15}\text{ClNO}_2$, $[\text{M} + \text{H}]^+$ 264.0791, found 264.0792.



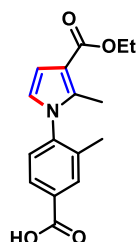
Ethyl 1-(4-bromophenyl)-2-methyl-1*H*-pyrrole-3-carboxylate (**4m**): yellow solid, 59 – 61 $^\circ\text{C}$, ^1H NMR (600 MHz, CDCl_3 , TMS, 25 $^\circ\text{C}$) δ = 7.59 (d, J = 8.5 Hz, 2H), 7.15 (d, J = 8.5 Hz, 2H), 6.67 (d, J = 3.1 Hz, 1H), 6.63 (d, J = 3.1 Hz, 1H), 4.29 (q, J = 7.1 Hz, 2H), 2.43 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (150 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ = 165.4, 138.2, 135.8, 132.5, 127.8, 121.8, 121.1, 113.7, 110.6, 59.5, 14.6, 12.2 ppm. HRMS (TOF, ESI): m/z calcd for $\text{C}_{14}\text{H}_{15}\text{BrNO}_2$, $[\text{M} + \text{H}]^+$ 308.0286, found 308.0289.



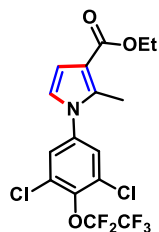
Ethyl 1-(4-methoxyphenyl)-2-methyl-1*H*-pyrrole-3-carboxylate (**4n**): yellow oil, ^1H NMR (600 MHz, CDCl_3 , TMS, 25 $^\circ\text{C}$) δ = 7.20 – 7.16 (m, 2H), 6.98 – 6.95 (m, 2H), 6.64 (d, J = 3.0 Hz, 1H), 6.62 (d, J = 3.1 Hz, 1H), 4.29 (q, J = 7.1 Hz, 2H), 3.85 (s, 3H), 2.40 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (150 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ = 165.6, 159.2, 136.3, 132.1, 127.5, 121.5, 114.4, 112.9, 109.8, 59.4, 55.6, 14.6, 12.1 ppm. HRMS (TOF, ESI): m/z calcd for $\text{C}_{15}\text{H}_{18}\text{NO}_3$, $[\text{M} + \text{H}]^+$ 260.1287, found 260.1285.



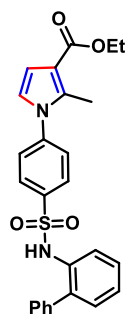
Ethyl 1-(4-acetylphenyl)-2-methyl-1*H*-pyrrole-3-carboxylate (**4o**): yellow solid, 55 – 57 $^\circ\text{C}$, ^1H NMR (600 MHz, CDCl_3 , TMS, 25 $^\circ\text{C}$) δ = 8.08 (d, J = 8.5 Hz, 2H), 7.39 (d, J = 8.5 Hz, 2H), 6.72 – 6.69 (m, 2H), 4.30 (q, J = 7.1 Hz, 2H), 2.66 (s, 3H), 2.49 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (150 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ = 196.8, 165.4, 143.0, 136.2, 135.7, 129.5, 126.0, 121.0, 114.3, 110.9, 59.6, 26.7, 14.5, 12.4 ppm. HRMS (TOF, ESI): m/z calcd for $\text{C}_{16}\text{H}_{18}\text{NO}_3$, $[\text{M} + \text{H}]^+$ 272.1287, found 272.1288.



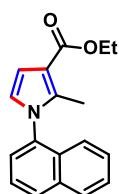
4-(3-(Ethoxycarbonyl)-2-methyl-1*H*-pyrrol-1-yl)-3-methylbenzoic acid (**4p**): yellow solid, 102 – 104 $^\circ\text{C}$, ^1H NMR (600 MHz, CDCl_3 , TMS, 25 $^\circ\text{C}$) δ = 10.44 (s, 1H), 8.10 (s, 1H), 8.04 (dd, J = 8.1, 1.5 Hz, 1H), 7.29 (d, J = 8.1 Hz, 1H), 6.73 (d, J = 3.1 Hz, 1H), 6.54 (d, J = 3.1 Hz, 1H), 4.32 (q, J = 7.1 Hz, 2H), 2.28 (s, 3H), 2.10 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (150 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ = 171.1, 165.8, 142.9, 136.5, 136.3, 132.9, 129.9, 128.7, 128.3, 120.6, 113.0, 110.6, 59.7, 20.9, 14.5, 11.7 ppm. HRMS (TOF, ESI): m/z calcd for $\text{C}_{16}\text{H}_{18}\text{NO}_4$, $[\text{M} + \text{H}]^+$ 288.1236, found 288.1239.



Ethyl 1-(3,5-dichloro-4-(perfluoroethoxy)phenyl)-2-methyl-1*H*-pyrrole-3-carboxylate (**4q**): yellow oil, ^1H NMR (600 MHz, CDCl_3 , TMS, 25 °C) δ = 7.36 (s, 2H), 6.69 (d, J = 3.1 Hz, 1H), 6.65 (d, J = 3.1 Hz, 1H), 4.30 (q, J = 7.1 Hz, 2H), 2.50 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (150 MHz, CDCl_3 , 25 °C) δ = 165.1, 141.5, 138.5, 135.7, 131.4, 126.9, 120.9, 117.1 (tt, J = 279.0, 28.8 Hz), 114.6, 111.3, 107.6 (tt, J = 252.7, 39.7 Hz), 59.7, 14.5, 12.2. ^{19}F NMR (565 MHz, CDCl_3 , 25 °C) δ = -86.15 (t, J = 6.0 Hz), -136.18 (t, J = 5.8 Hz) ppm. HRMS (TOF, ESI): m/z calcd for $\text{C}_{16}\text{H}_{13}\text{Cl}_2\text{F}_5\text{NO}_3$, $[\text{M} + \text{H}]^+$ 432.0193, found 432.0196.

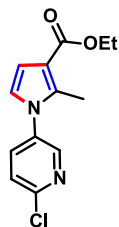


Ethyl 1-(4-(*N*-([1,1'-biphenyl]-2-yl)sulfamoyl)phenyl)-2-methyl-1*H*-pyrrole-3-carboxylate (**4r**): yellow oil, ^1H NMR (600 MHz, CDCl_3 , TMS, 25 °C) δ = 7.74 (d, J = 8.1 Hz, 1H), 7.63 (d, J = 8.4 Hz, 2H), 7.37 (dd, J = 17.8, 7.0 Hz, 4H), 7.29 (d, J = 8.4 Hz, 2H), 7.21 (t, J = 7.4 Hz, 1H), 7.14 (dd, J = 7.4, 1.0 Hz, 1H), 6.91 – 6.86 (m, 2H), 6.75 (s, 1H), 6.71 (d, J = 3.1 Hz, 1H), 6.67 (d, J = 3.1 Hz, 1H), 4.30 (q, J = 7.1 Hz, 2H), 2.47 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (150 MHz, CDCl_3 , 25 °C) δ = 165.3, 142.9, 138.4, 137.2, 135.5, 134.6, 133.1, 130.4, 129.2, 128.9, 128.7, 128.4, 128.3, 126.3, 125.7, 122.4, 120.9, 114.7, 111.3, 59.7, 14.5, 12.4 ppm. HRMS (TOF, ESI): m/z calcd for $\text{C}_{26}\text{H}_{25}\text{N}_2\text{O}_4\text{S}$, $[\text{M} + \text{H}]^+$ 461.1535, found 461.1537.

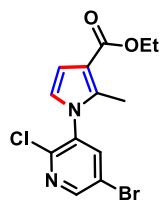


Ethyl 2-methyl-1-(naphthalen-1-yl)-1*H*-pyrrole-3-carboxylate (**4s**): yellow oil, ^1H NMR (600 MHz, CDCl_3 , TMS, 25 °C) δ = 7.83 (dd, J = 11.4, 8.3 Hz, 2H), 7.45 – 7.41 (m, 2H), 7.35 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H), 7.30 (dd, J = 7.2, 1.0 Hz, 1H), 7.15 (d, J = 8.2 Hz, 1H), 6.68 (d, J = 3.0 Hz, 1H), 6.59 (d, J = 3.0 Hz, 1H), 4.24 (q, J = 7.1 Hz, 2H), 2.15 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (150 MHz, CDCl_3 , 25 °C) δ = 165.8, 137.7, 135.7, 134.1, 130.8, 129.3, 128.2, 127.5,

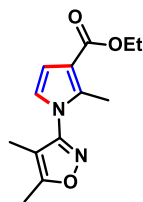
126.9, 125.3, 125.2, 122.9, 122.4, 112.8, 110.0, 59.5, 14.6, 11.8 ppm. HRMS (TOF, ESI): m/z calcd for $C_{18}H_{18}NO_2$, $[M + H]^+$ 280.1338, found 280.1336.



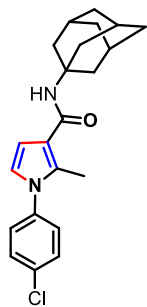
Ethyl 1-(6-chloropyridin-3-yl)-2-methyl-1*H*-pyrrole-3-carboxylate (**4t**): white solid, 65 – 67 °C, 1H NMR (600 MHz, $CDCl_3$, TMS, 25 °C) δ = 8.38 (d, J = 2.6 Hz, 1H), 7.62 (dd, J = 8.4, 2.8 Hz, 1H), 7.53 – 7.47 (m, 1H), 6.71 (d, J = 3.1 Hz, 1H), 6.66 (d, J = 3.1 Hz, 1H), 4.30 (q, J = 7.1 Hz, 2H), 2.46 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C) δ = 165.1, 150.6, 147.3, 146.9, 136.2, 128.6, 124.8, 121.1, 114.6, 111.3, 59.7, 14.5, 12.0 ppm. HRMS (TOF, ESI): m/z calcd for $C_{13}H_{14}ClN_2O_2$, $[M + H]^+$ 265.0744, found 265.0747.



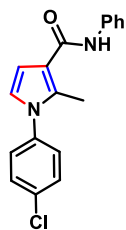
Ethyl 1-(5-bromo-2-chloropyridin-3-yl)-2-methyl-1*H*-pyrrole-3-carboxylate (**4u**): yellow oil, 1H NMR (600 MHz, $CDCl_3$, TMS, 25 °C) δ = 8.57 (d, J = 2.3 Hz, 1H), 7.89 (d, J = 2.3 Hz, 1H), 6.71 (d, J = 3.2 Hz, 1H), 6.58 (d, J = 3.2 Hz, 1H), 4.30 (q, J = 7.0 Hz, 2H), 2.35 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C) δ = 165.0, 150.7, 148.5, 140.5, 136.7, 134.4, 120.9, 118.8, 114.0, 111.4, 59.7, 14.5, 11.7 ppm. HRMS (TOF, ESI): m/z calcd for $C_{13}H_{13}BrClN_2O_2$, $[M + H]^+$ 342.9849, found 343.9851.



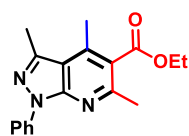
Ethyl 1-(4,5-dimethylisoxazol-3-yl)-2-methyl-1*H*-pyrrole-3-carboxylate (**4v**): yellow oil, 1H NMR (600 MHz, $CDCl_3$, TMS, 25 °C) δ = 6.61 (d, J = 2.8 Hz, 1H), 6.56 (d, J = 2.8 Hz, 1H), 4.21 (q, J = 7.0 Hz, 2H), 2.40 (s, 3H), 2.34 (s, 3H), 1.77 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C) δ = 168.1, 165.2, 159.2, 136.8, 120.2, 114.3, 111.3, 107.0, 59.6, 14.5, 11.8, 11.5, 6.4 ppm. HRMS (TOF, ESI): m/z calcd for $C_{13}H_{17}N_2O_3$, $[M + H]^+$ 249.1239, found 249.1238.



N-((3*s*,5*s*,7*s*)-Adamantan-1-yl)-1-(4-chlorophenyl)-2-methyl-1*H*-pyrrole-3-carboxamide (**4x**): yellow solid, 163 – 165 °C, ¹H NMR (600 MHz, CDCl₃, TMS, 25 °C) δ = 7.43 (d, *J* = 8.5 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 2H), 6.63 (d, *J* = 3.0 Hz, 1H), 6.31 (d, *J* = 3.0 Hz, 1H), 5.53 (s, 1H), 2.43 (s, 3H), 2.14 – 2.10 (m, 9H), 1.75 – 1.68 (m, 6H) ppm. ¹³C NMR (150 MHz, CDCl₃, 25 °C) δ = 165.2, 137.8, 133.7, 133.4, 129.5, 127.5, 120.7, 117.4, 107.2, 51.8, 42.0, 36.5, 29.6, 12.0 ppm. HRMS (TOF, ESI): *m/z* calcd for C₂₂H₂₆ClN₂O, [M + H]⁺ 369.1734, found 369.1738.



1-(4-Chlorophenyl)-2-methyl-*N*-phenyl-1*H*-pyrrole-3-carboxamide (**4y**): yellow solid, 152 – 154 °C, ¹H NMR (600 MHz, CDCl₃, TMS, 25 °C) δ = 7.61 (d, *J* = 7.8 Hz, 2H), 7.55 (s, 1H), 7.46 (d, *J* = 8.6 Hz, 2H), 7.35 (t, *J* = 7.9 Hz, 2H), 7.24 (d, *J* = 8.6 Hz, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 6.71 (d, *J* = 3.1 Hz, 1H), 6.48 (d, *J* = 2.1 Hz, 1H), 2.49 (s, 3H) ppm. ¹³C NMR (150 MHz, CDCl₃, 25 °C) δ = 163.8, 138.4, 137.5, 134.9, 134.0, 129.6, 129.0, 127.5, 123.9, 121.3, 120.0, 116.4, 107.0, 12.1 ppm. HRMS (TOF, ESI): *m/z* calcd for C₁₈H₁₆ClN₂O, [M + H]⁺ 311.0951, found 311.0955.



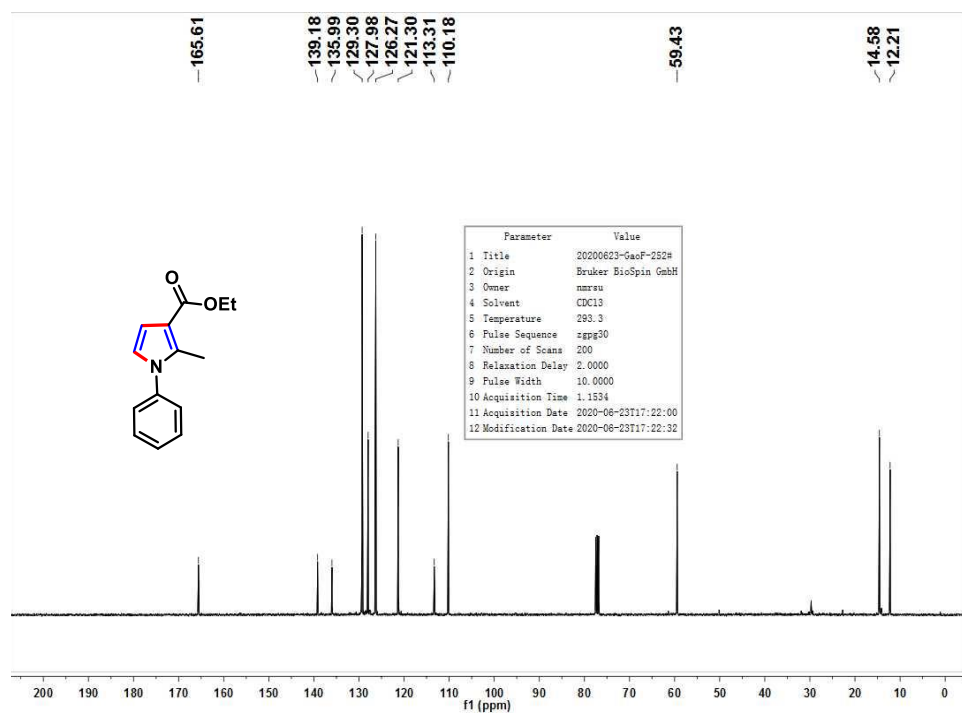
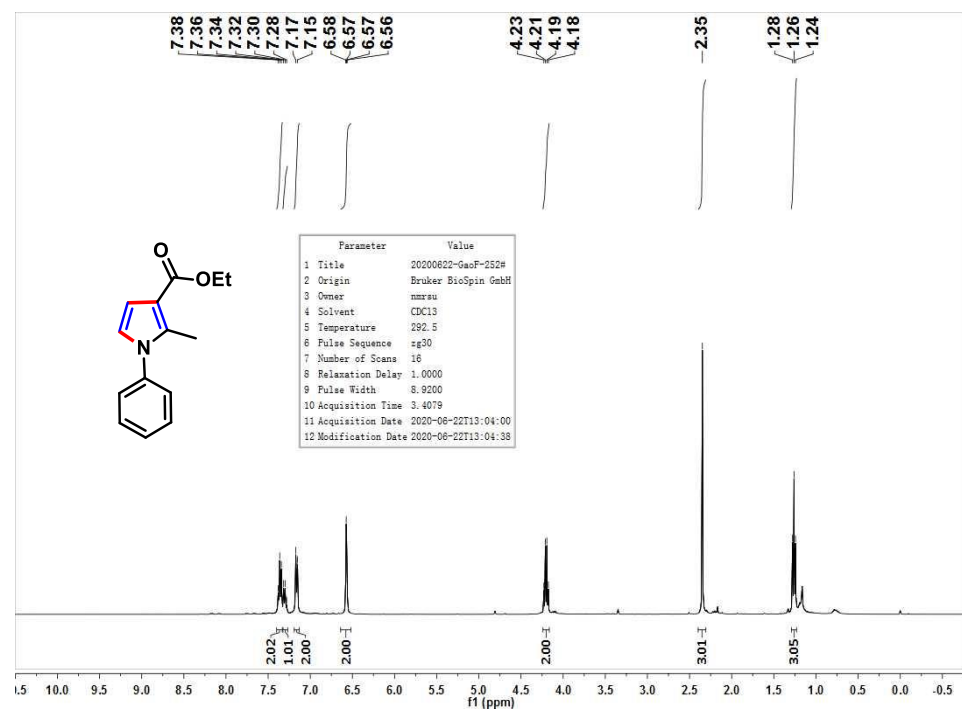
Ethyl 3,4,6-trimethyl-1-phenyl-1*H*-pyrazolo[3,4-*b*]pyridine-5-carboxylate (**5a**): colourless oil, ¹H NMR (600 MHz, CDCl₃, TMS, 25 °C) δ = 8.25 (d, *J* = 8.0 Hz, 2H), 7.49 (t, *J* = 7.9 Hz, 2H), 7.26 (t, *J* = 7.4 Hz, 1H), 4.45 (q, *J* = 7.1 Hz, 2H), 2.74 (s, 3H), 2.68 (s, 3H), 2.66 (s, 3H), 1.43 (t, *J* = 7.1 Hz, 3H) ppm. ¹³C NMR (150 MHz, CDCl₃, 25 °C) δ = 169.3, 155.8, 150.1, 143.2, 140.9, 139.4, 129.0, 125.6, 124.2, 121.1, 114.2, 61.5, 24.0, 16.5, 15.7, 14.3 ppm. HRMS (TOF, ESI): *m/z* calcd for C₁₈H₂₀N₃O₂, [M + H]⁺ 310.1556, found 310.1558.

4. References

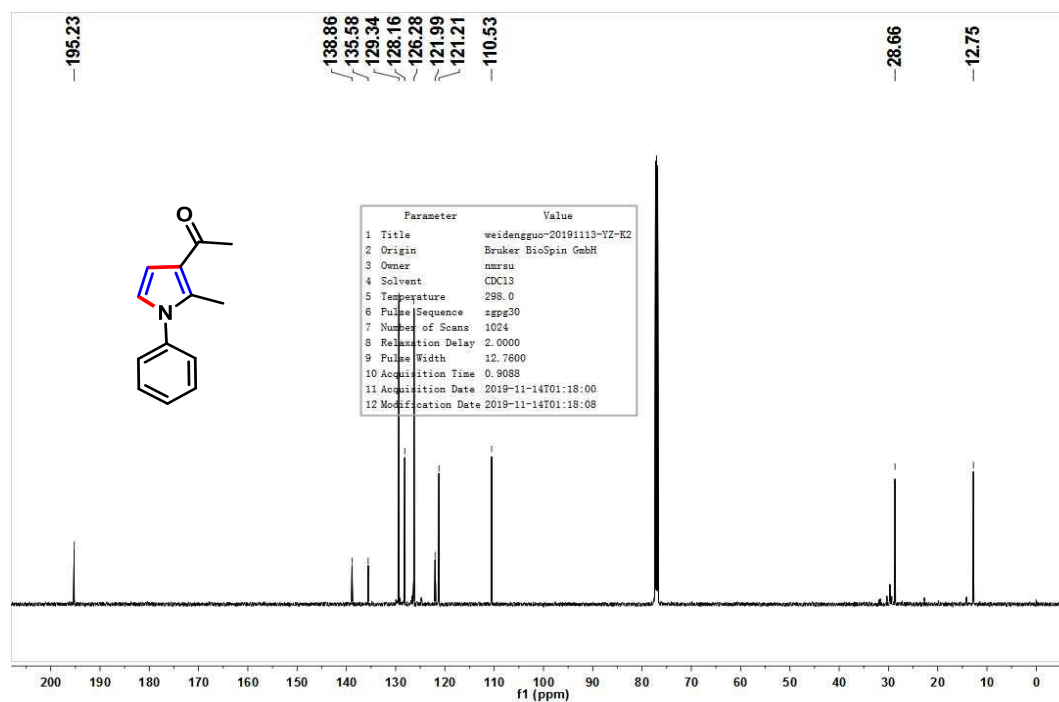
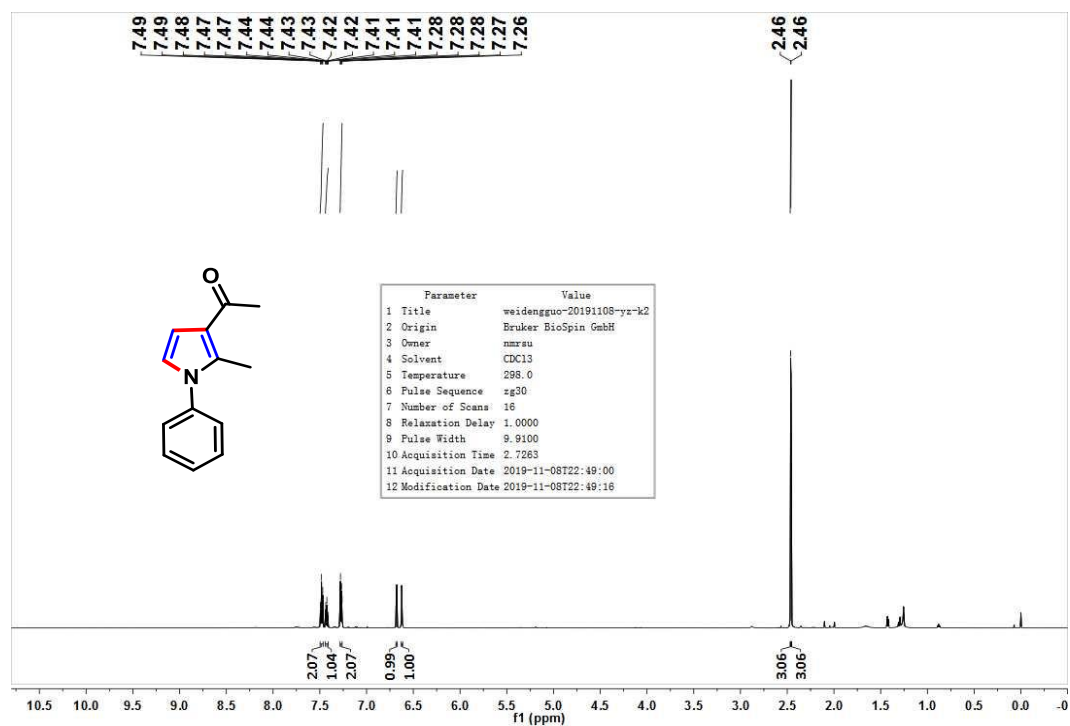
- (1) Kalsi, D.; Sundararaju, B., *Org. Lett.* **2015**, *17*, 6118–6121.
- (2) Wang, L.; Li, L.; Zhou, Z. -H.; Jiang, Z. -Y.; You, Q. -D.; Xu, X. -L., *Eur. J. Med. Chem.* **2018**, *143*, 724–731.
- (3) Zhang, Z.; Zhang, W.; Li, J.; Liu, Q.; Liu, T.; Zhang, G., *J. Org. Chem.* **2014**, *79*, 11226–11233.
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- (5) Tracey, M. R.; Hsung, R. P.; Lambeth, R. H., *Synthesis*. **2004**, 918–922.

5. ^1H NMR and ^{13}C NMR spectra

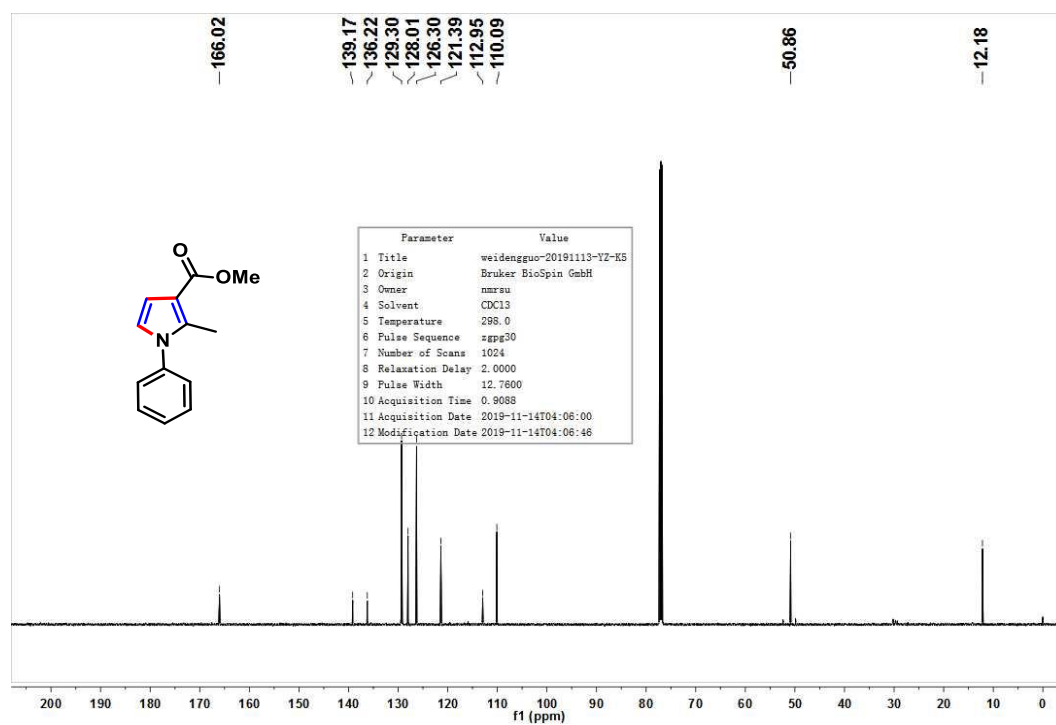
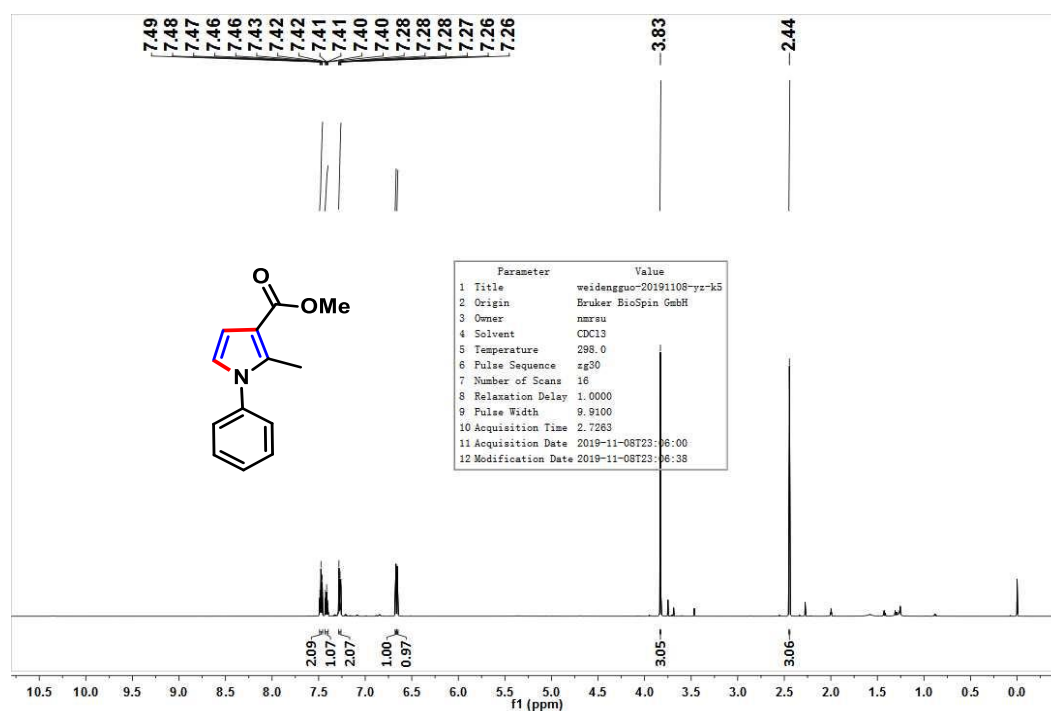
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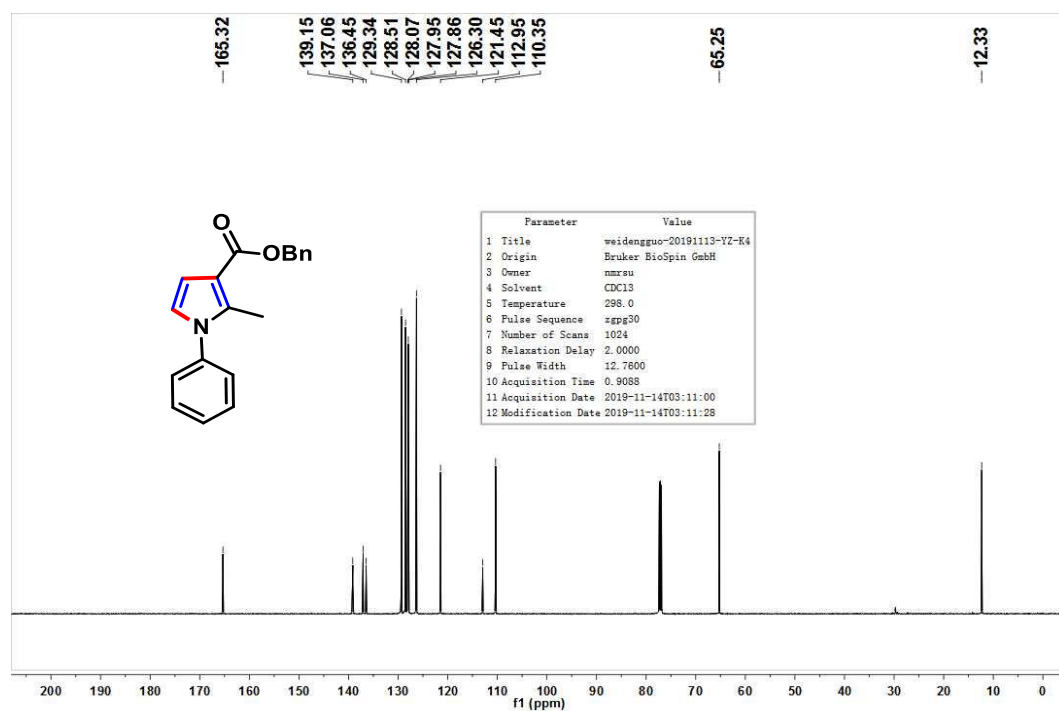
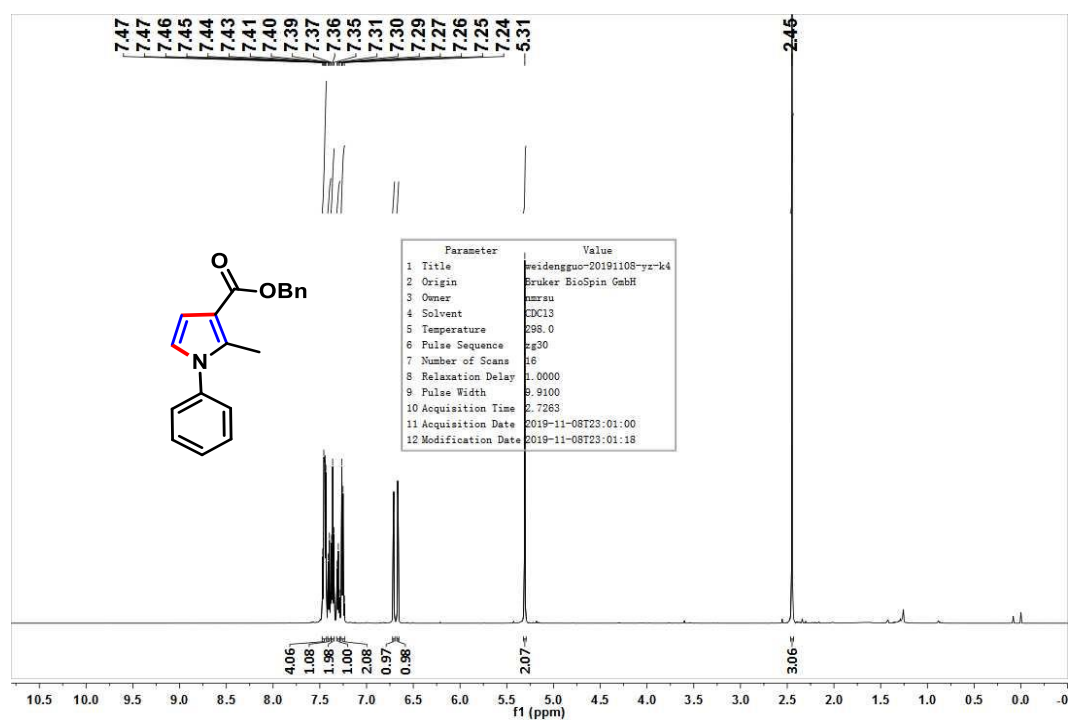
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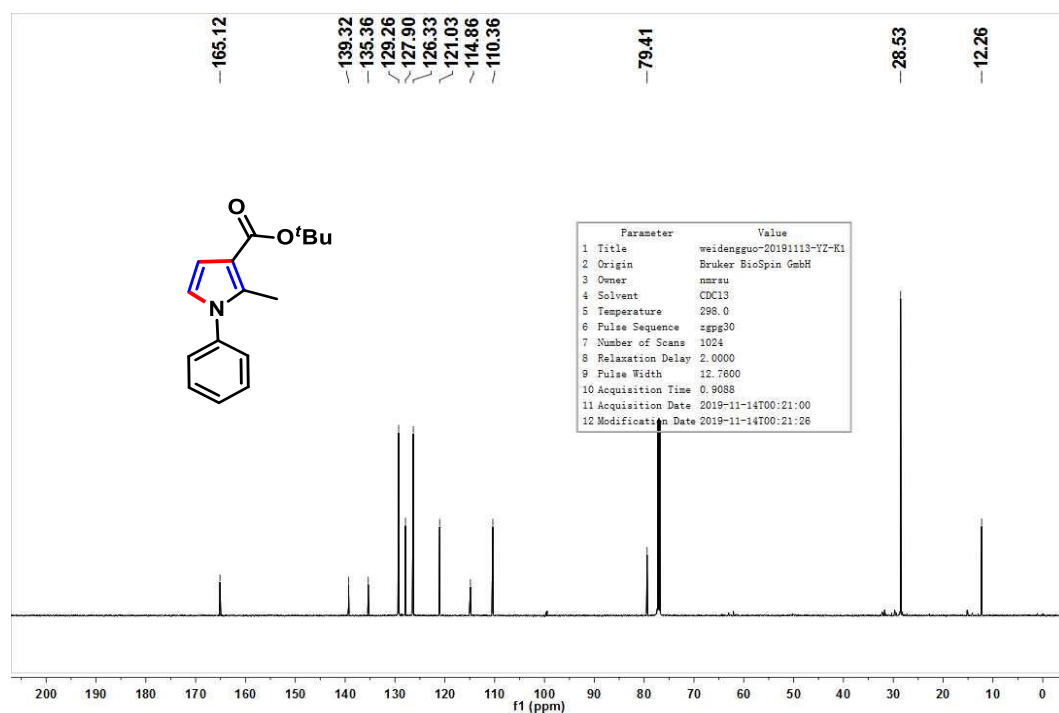
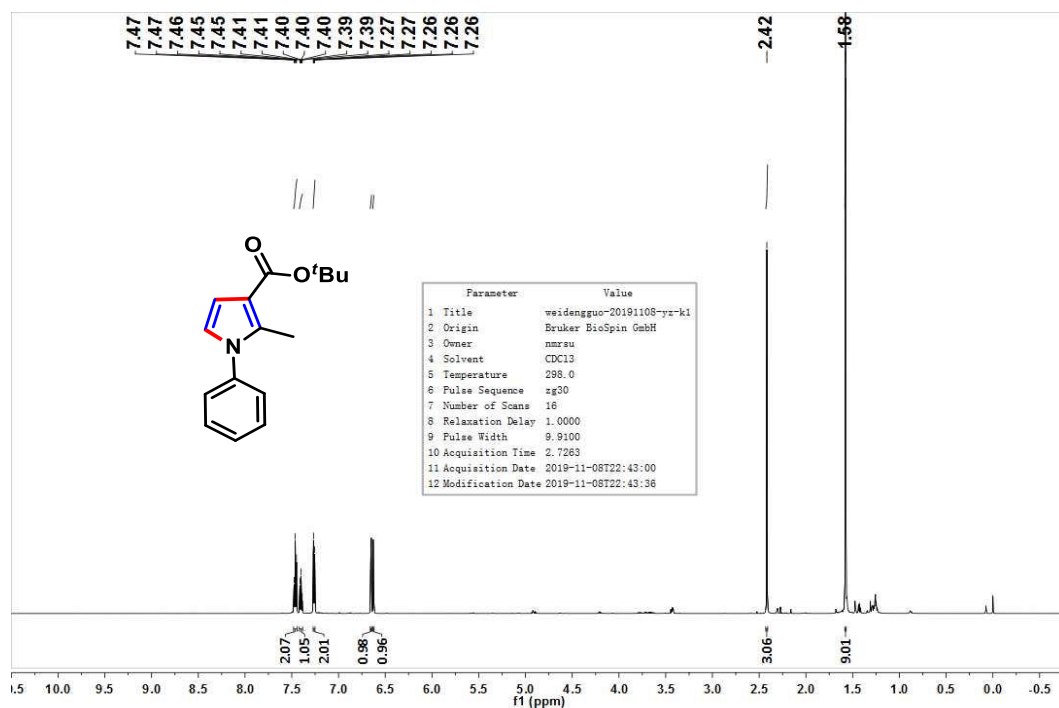
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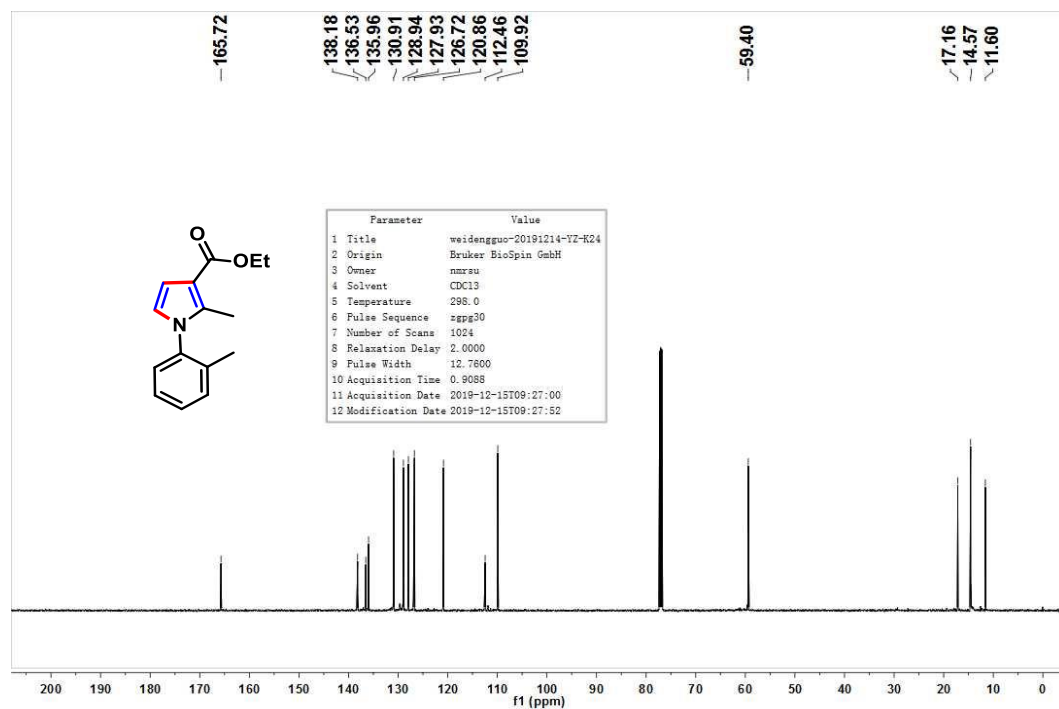
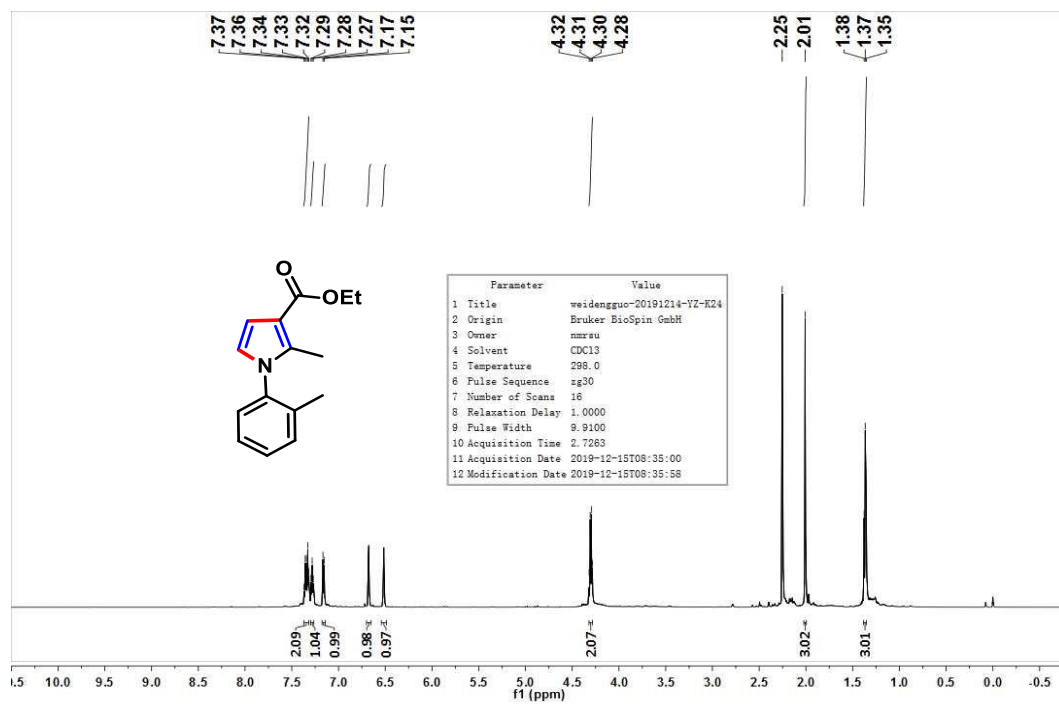
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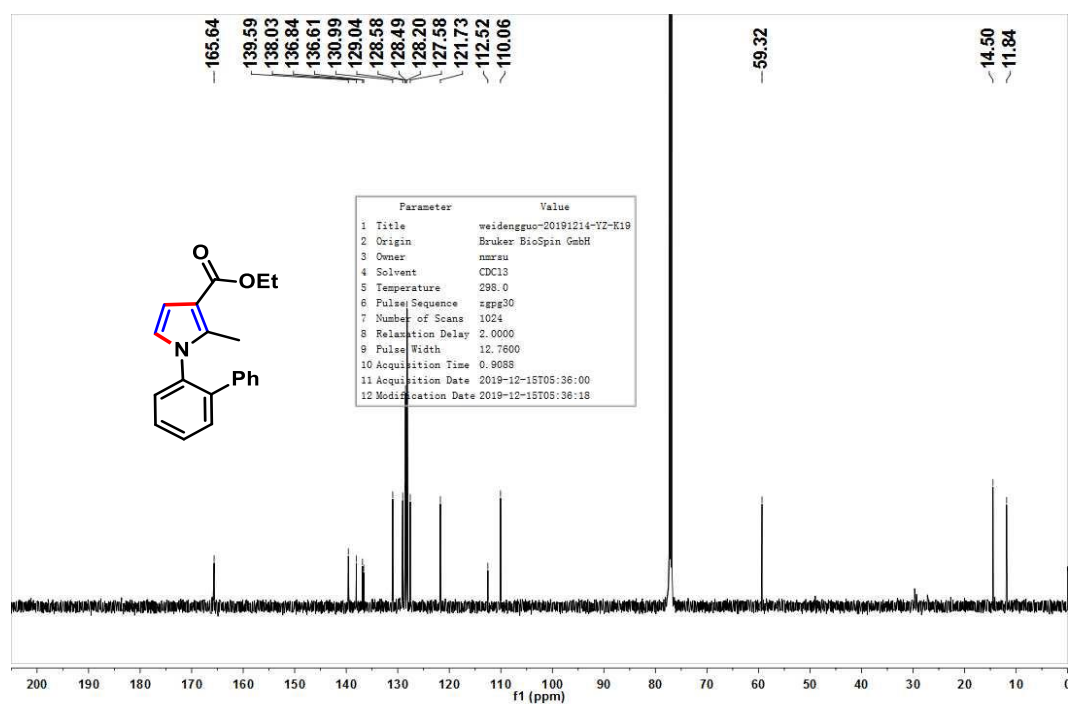
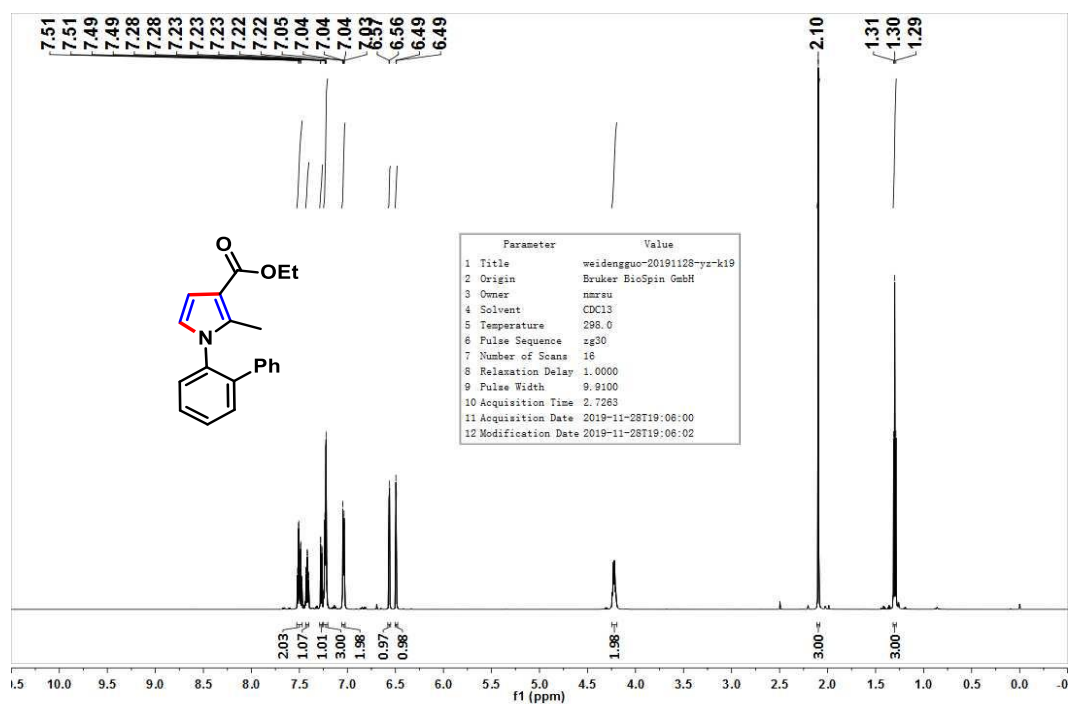
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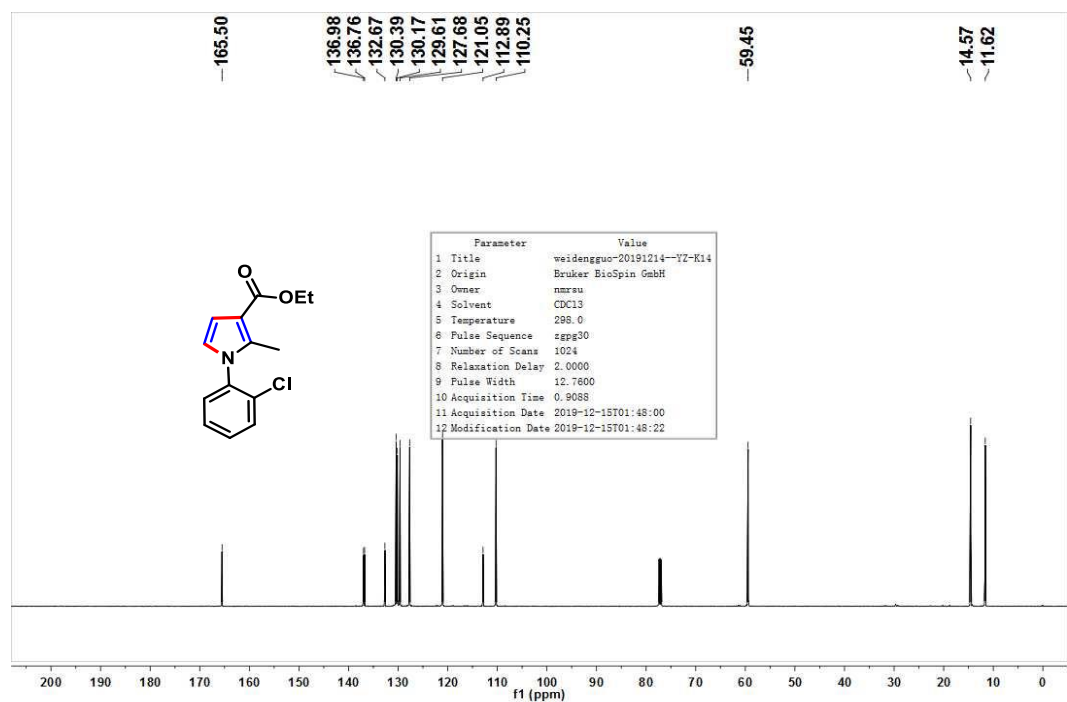
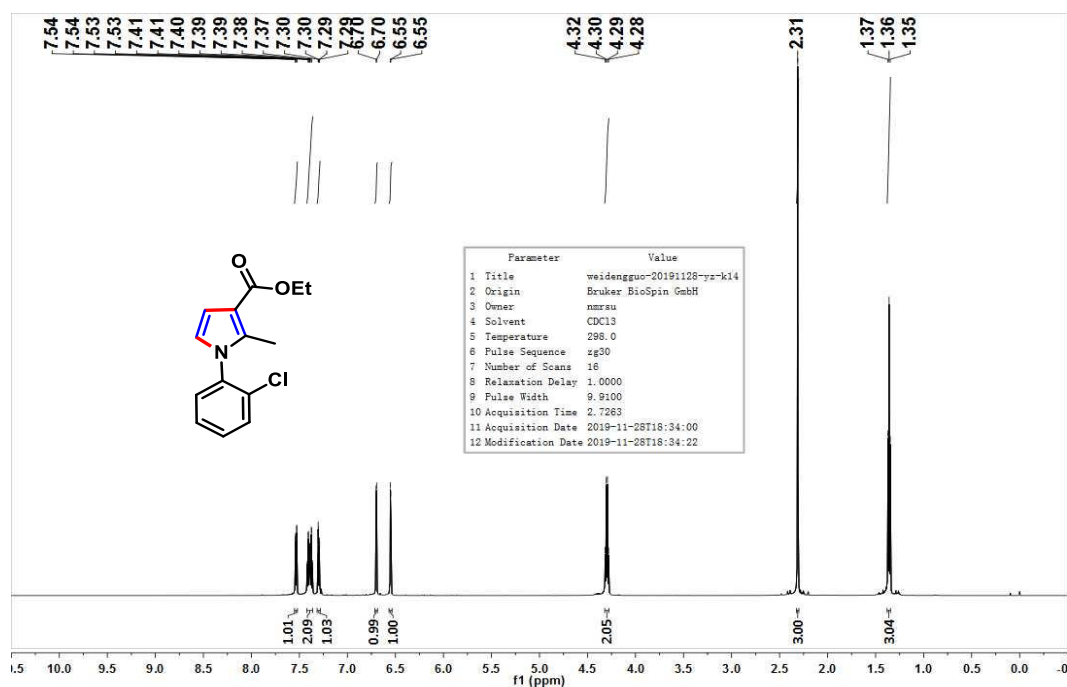
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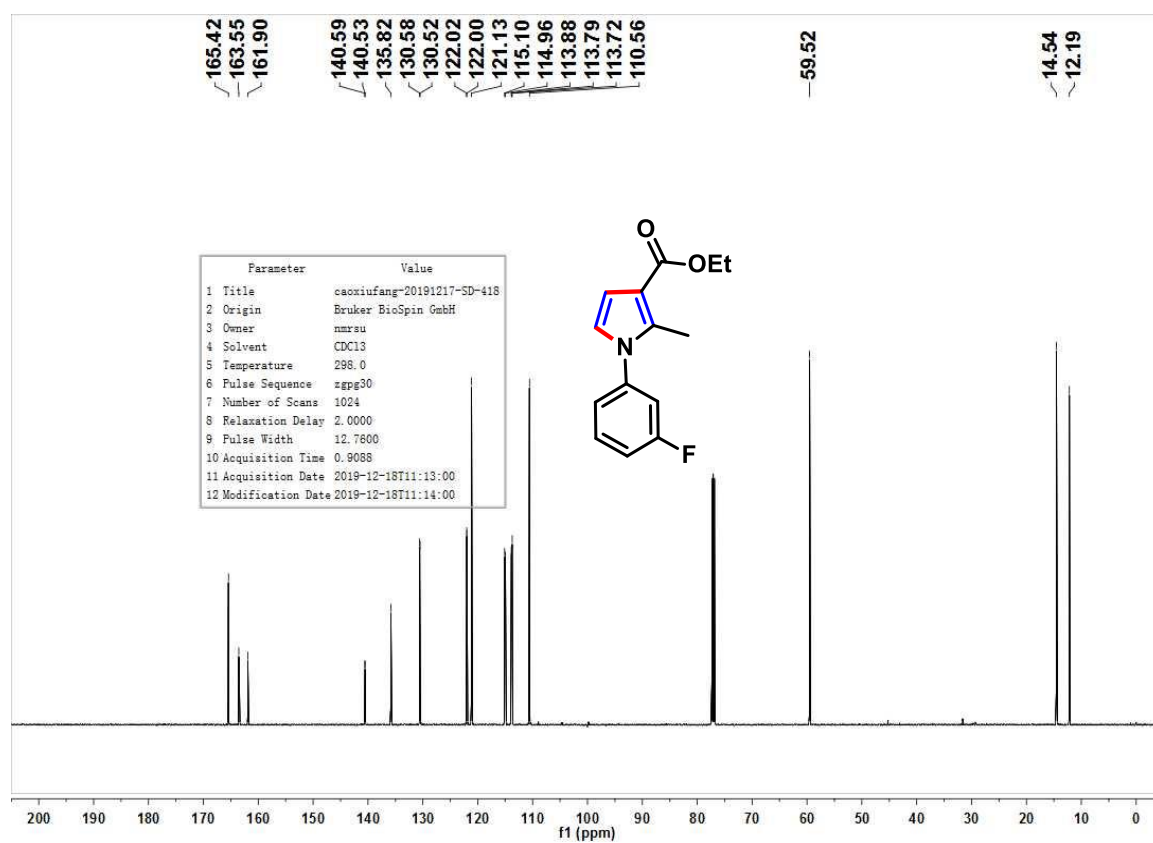
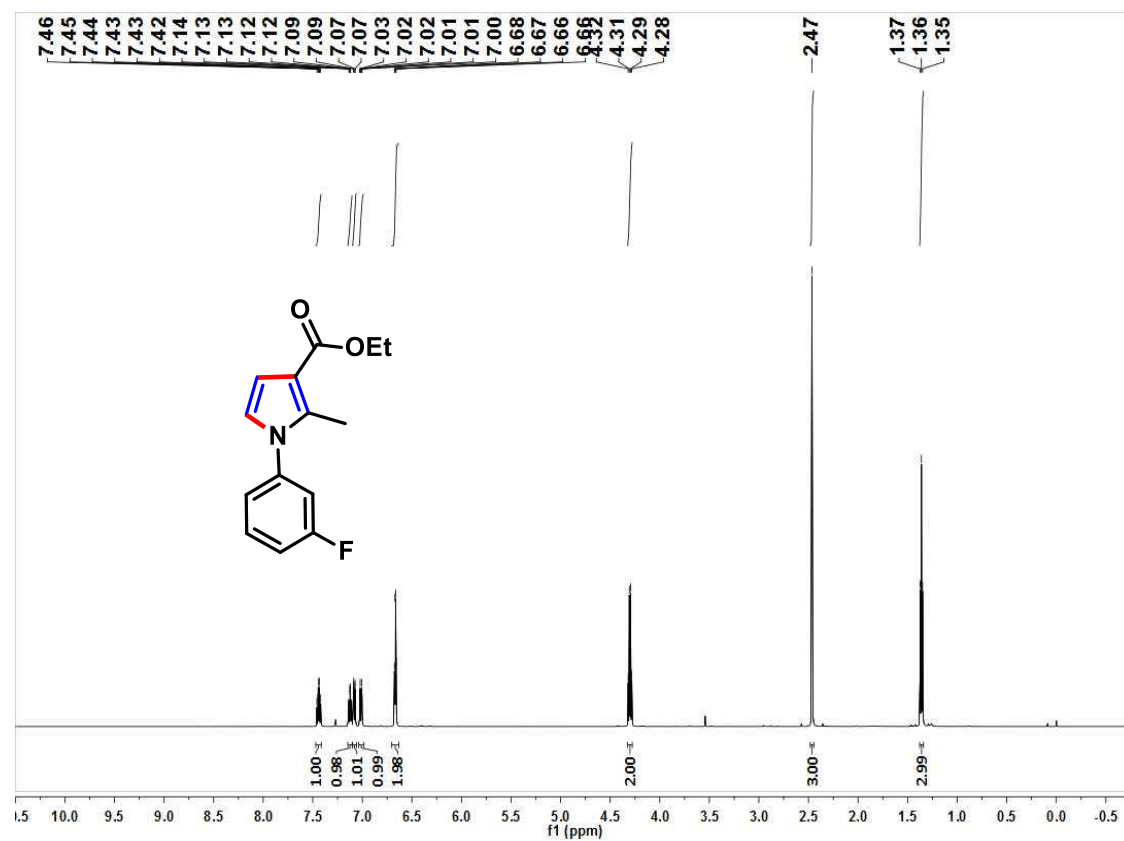
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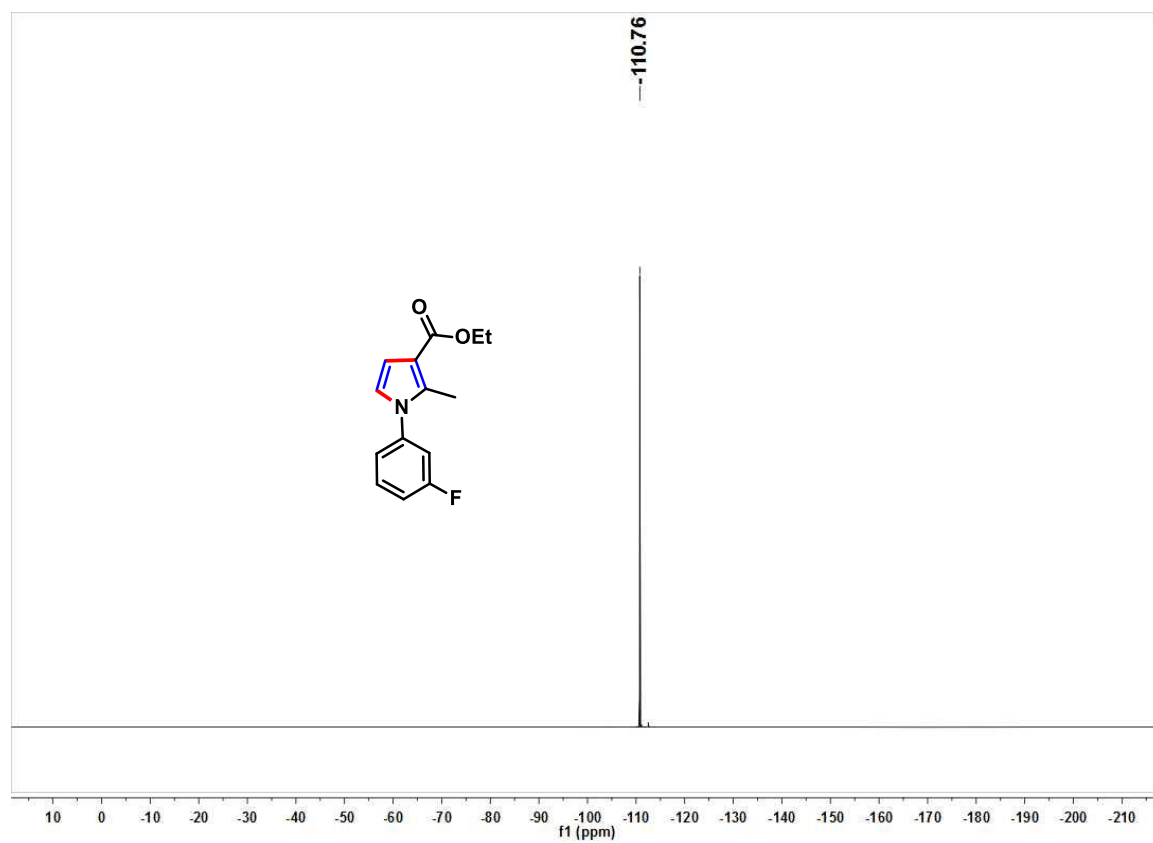


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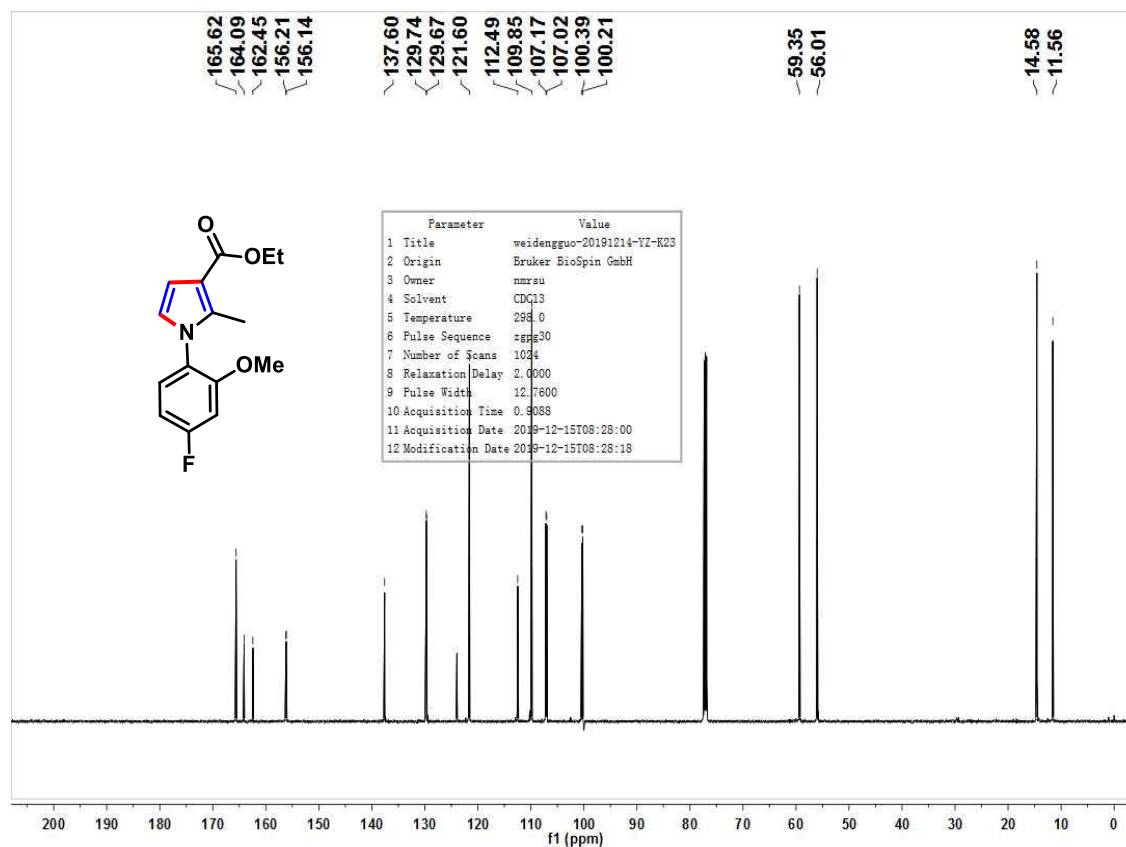
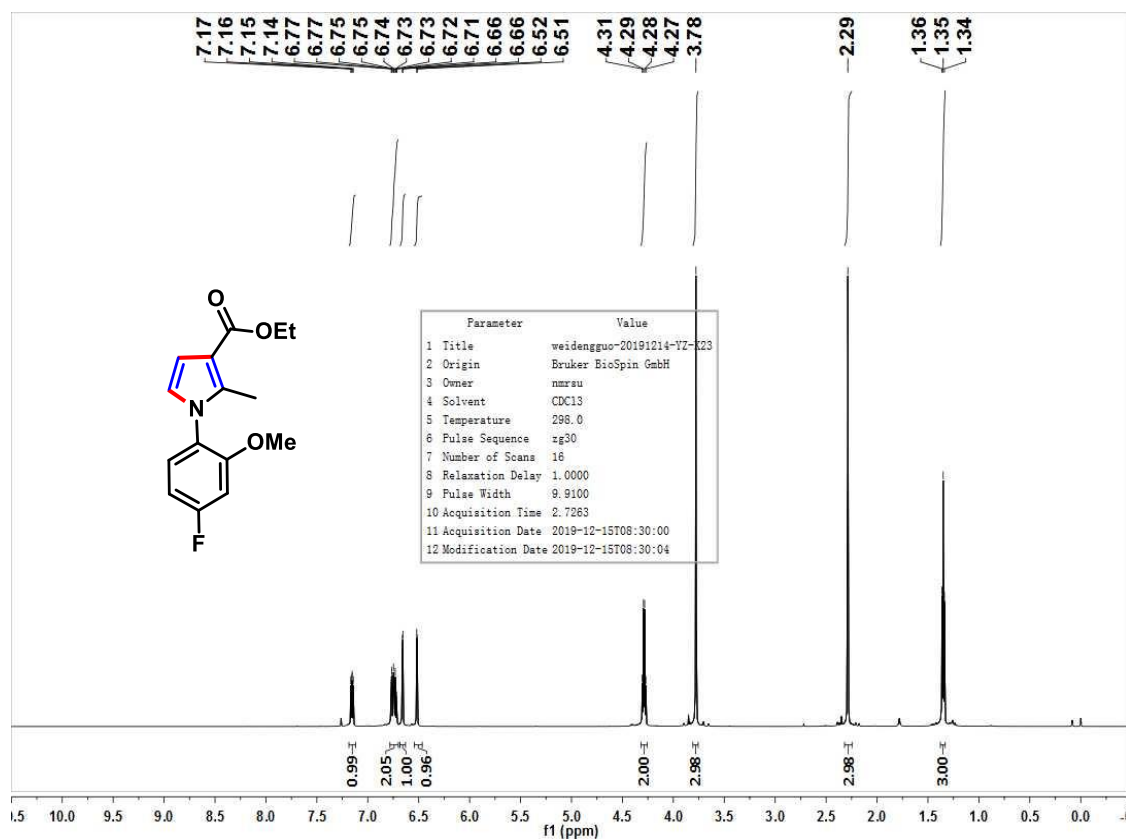


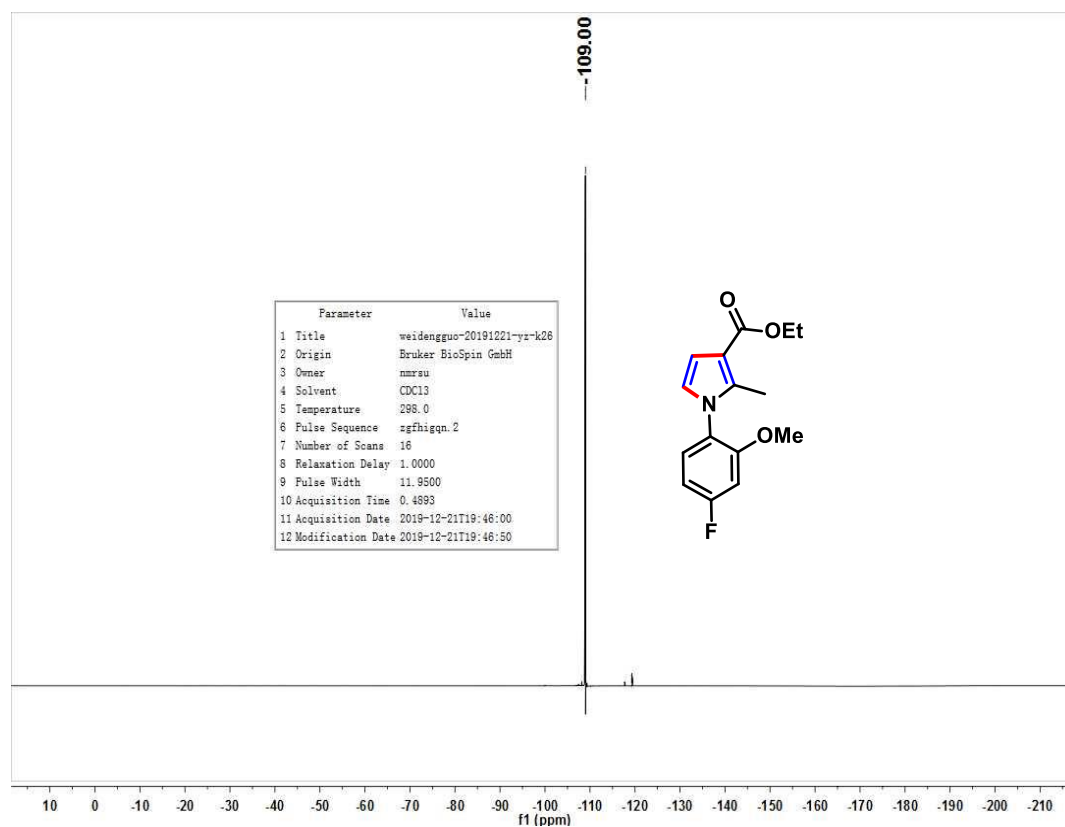
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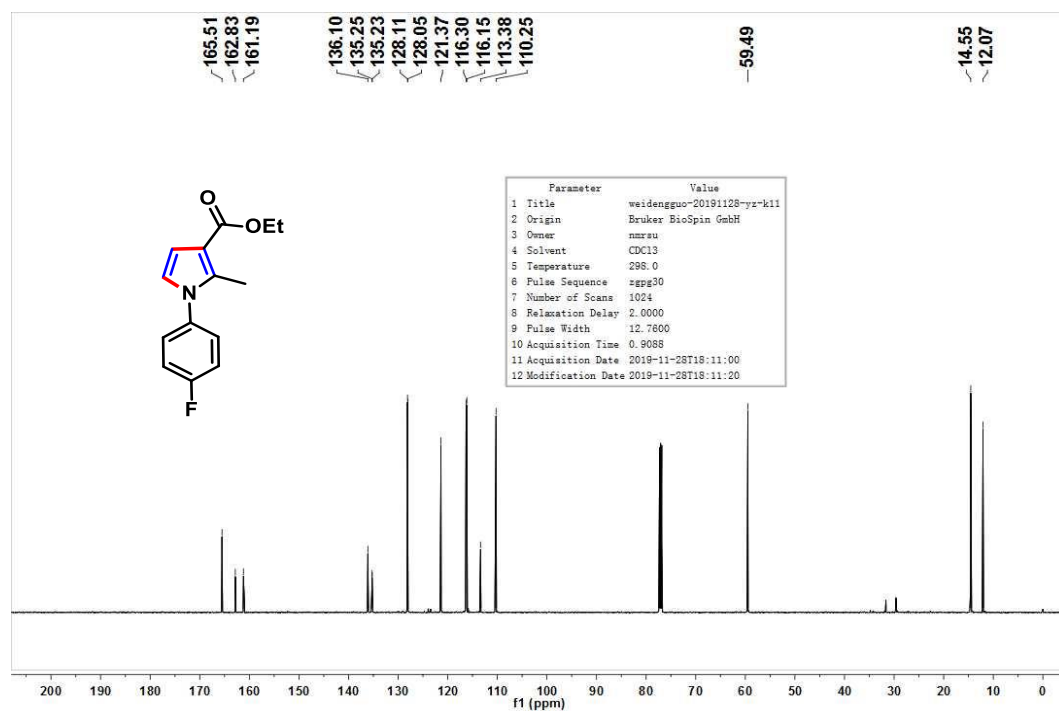
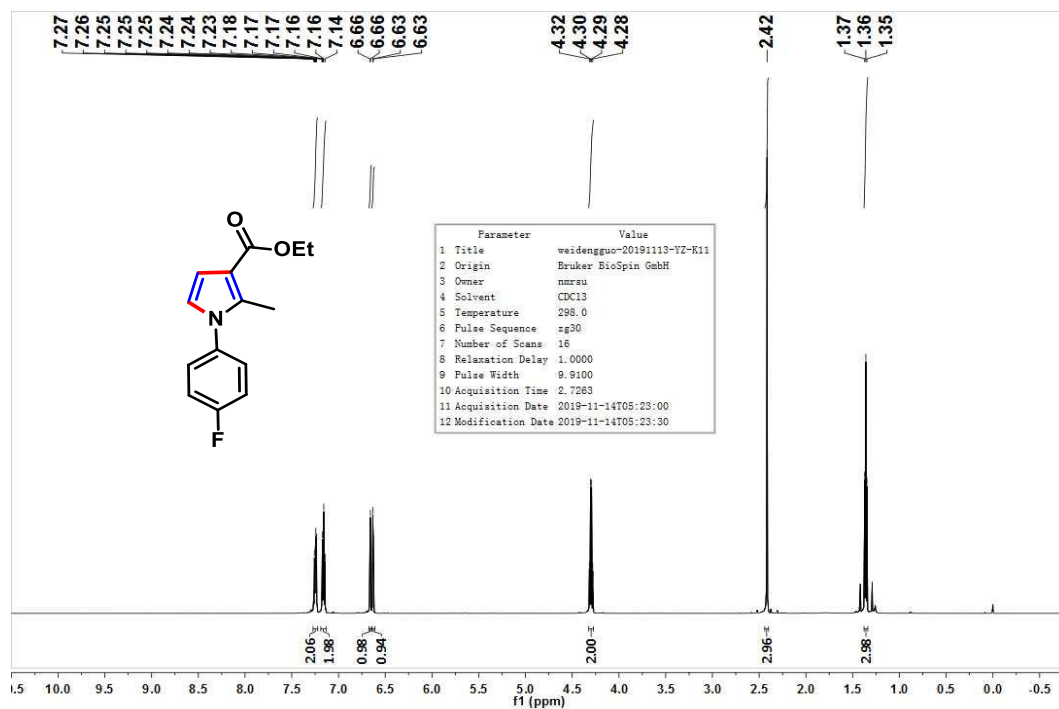


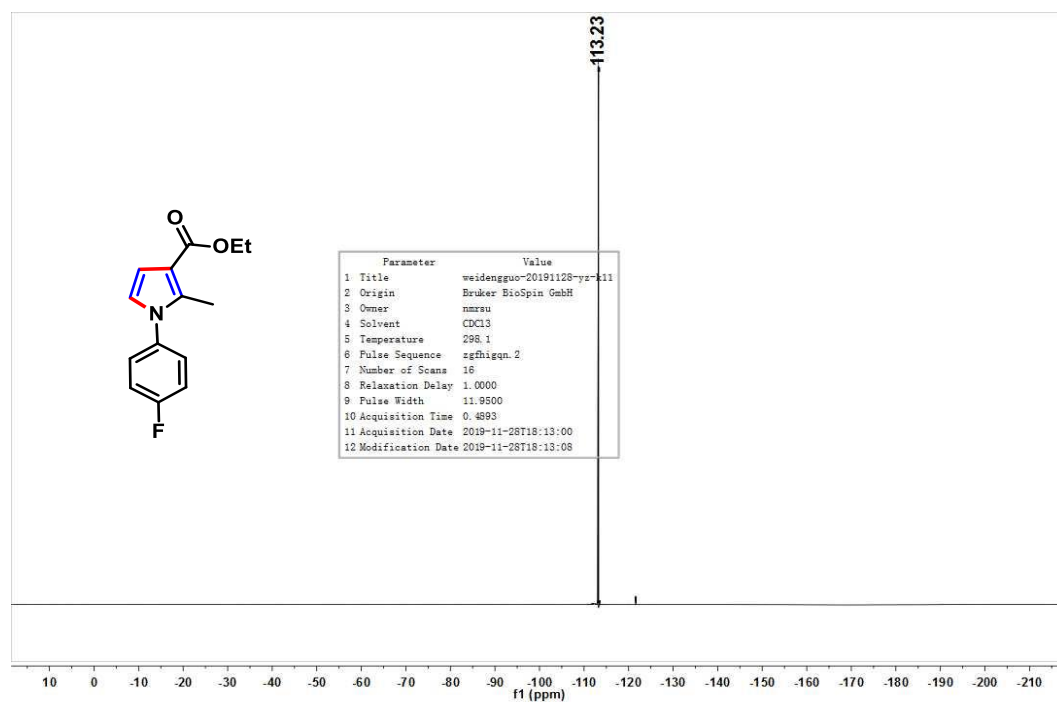
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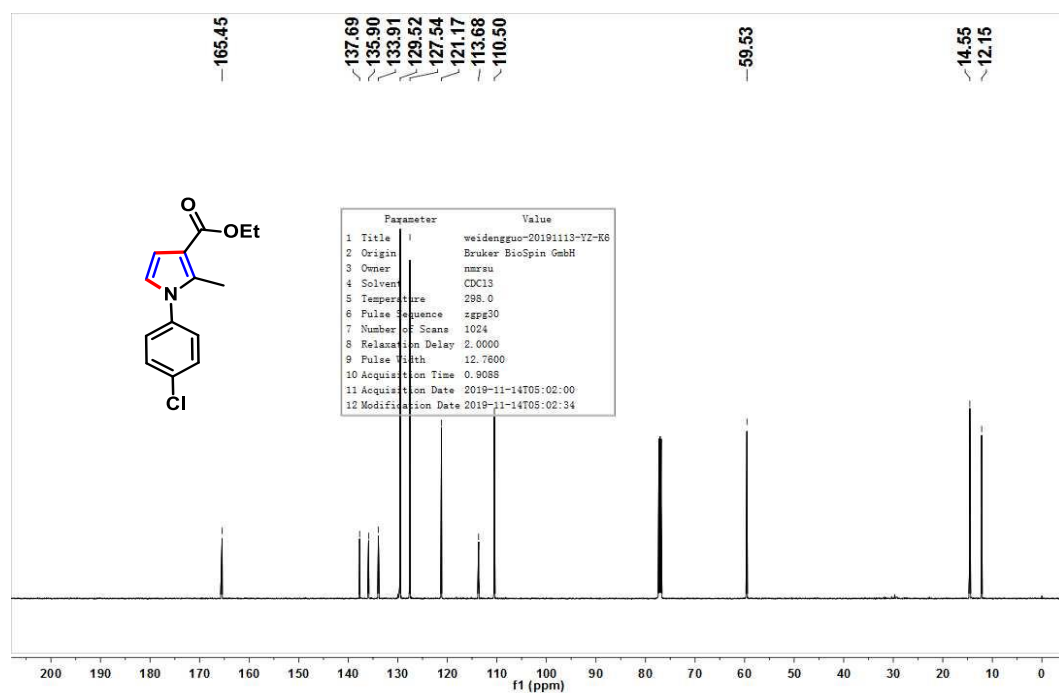
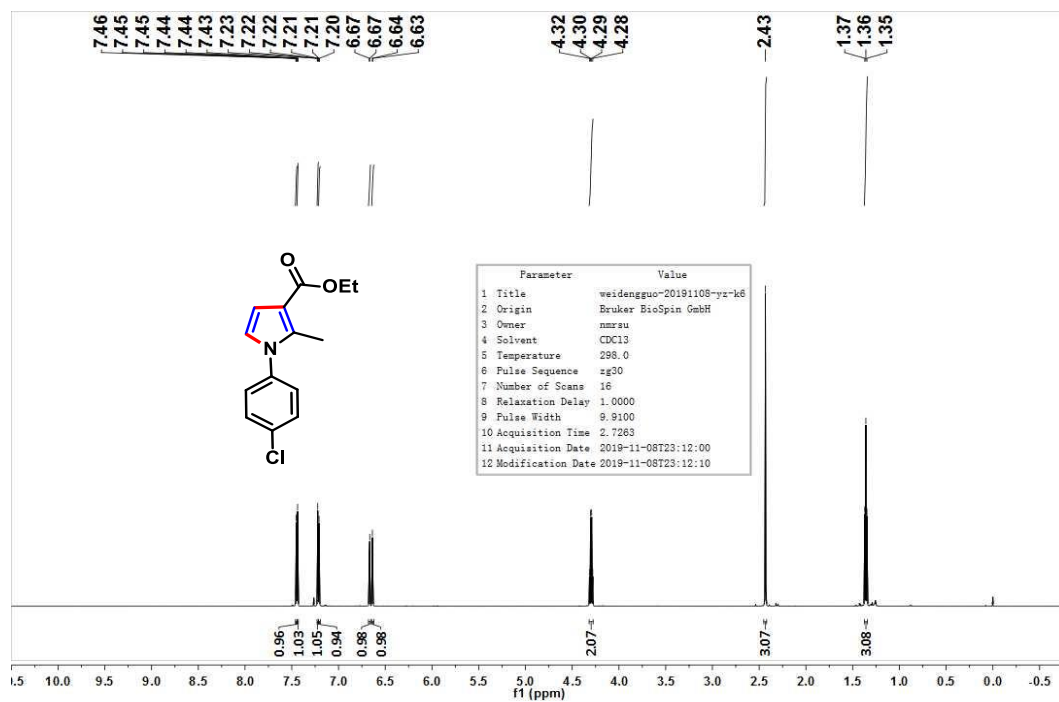




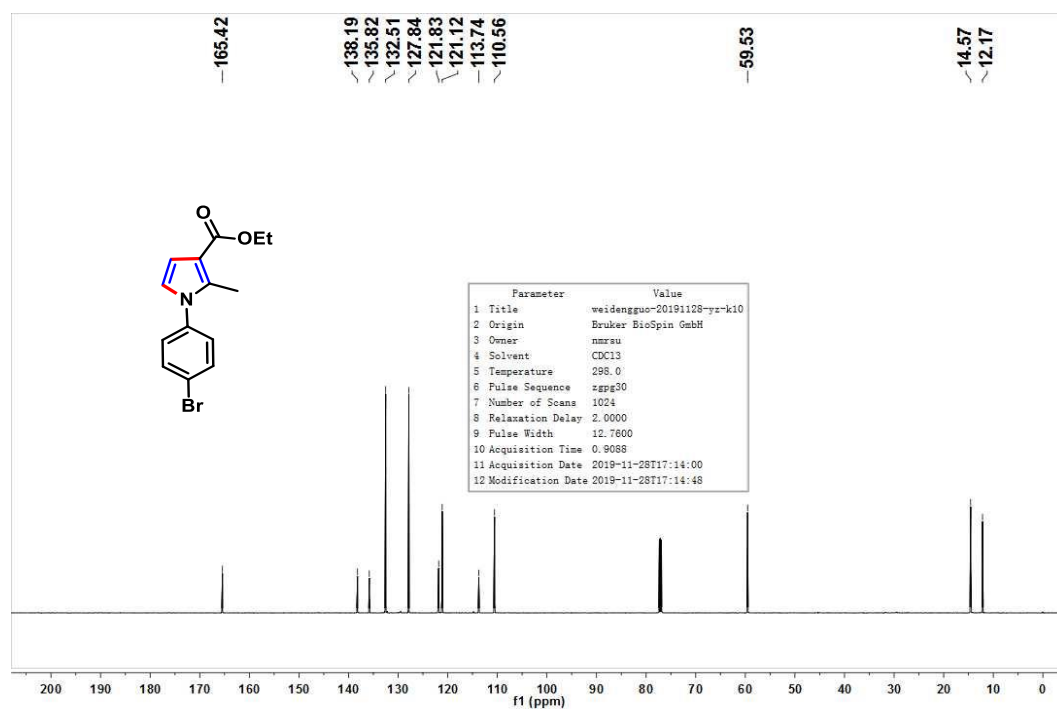
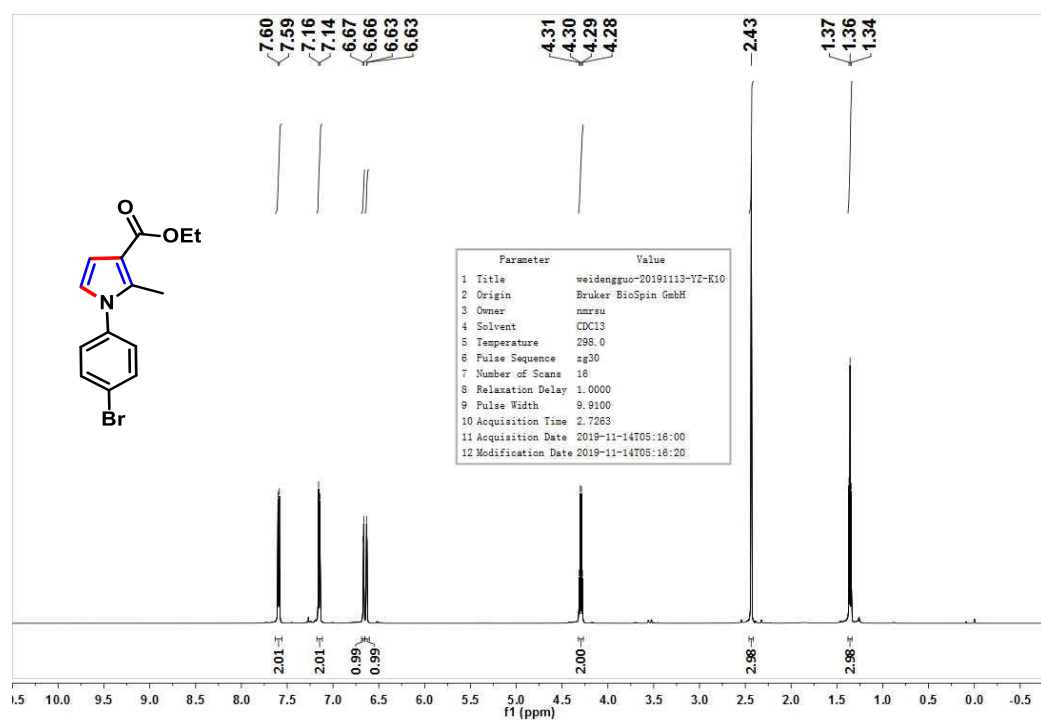
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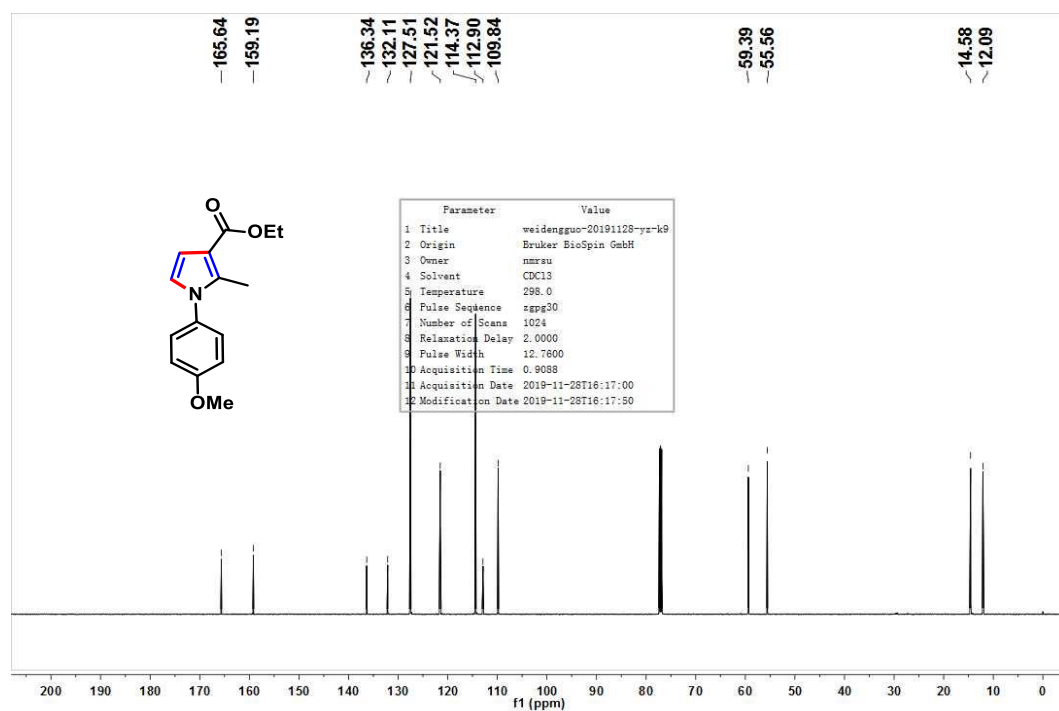
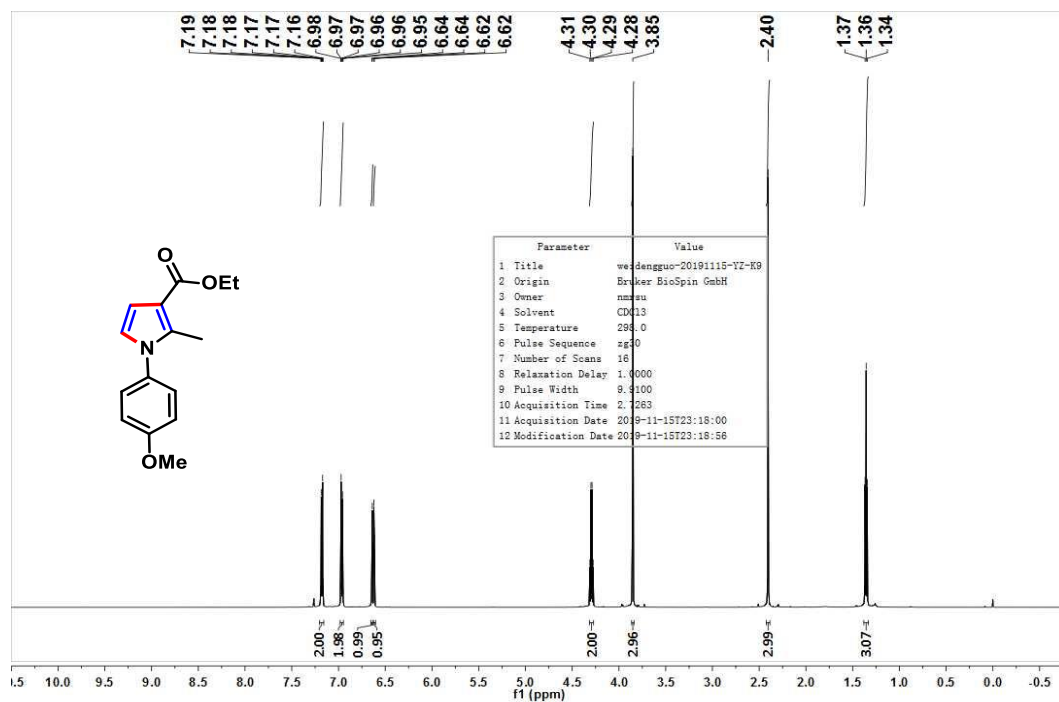


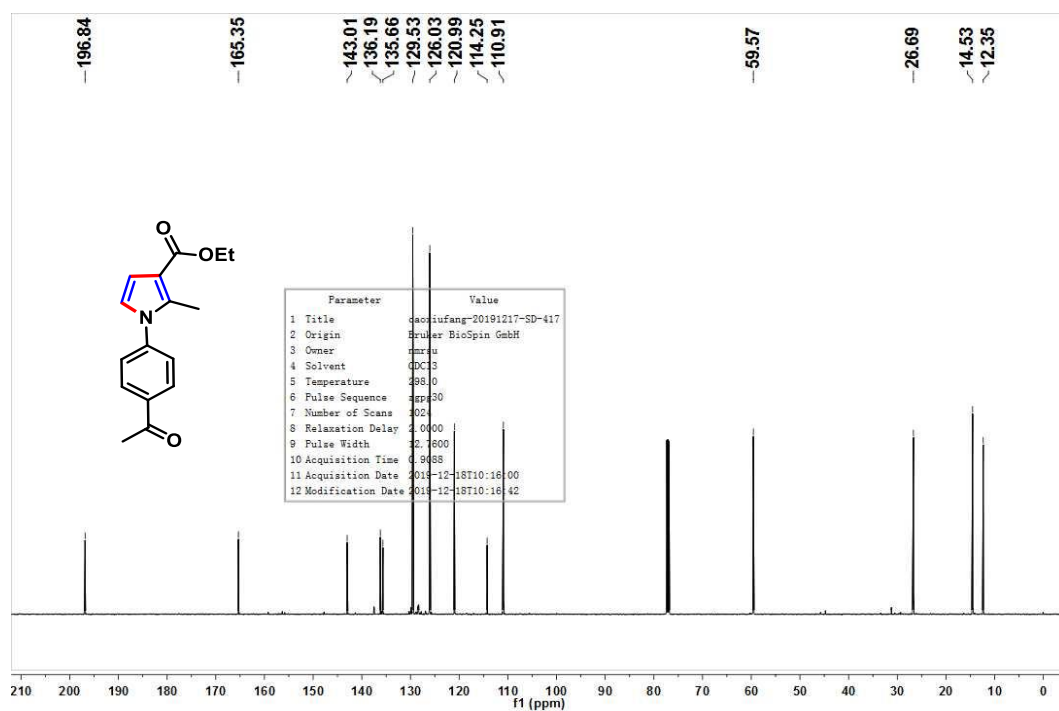
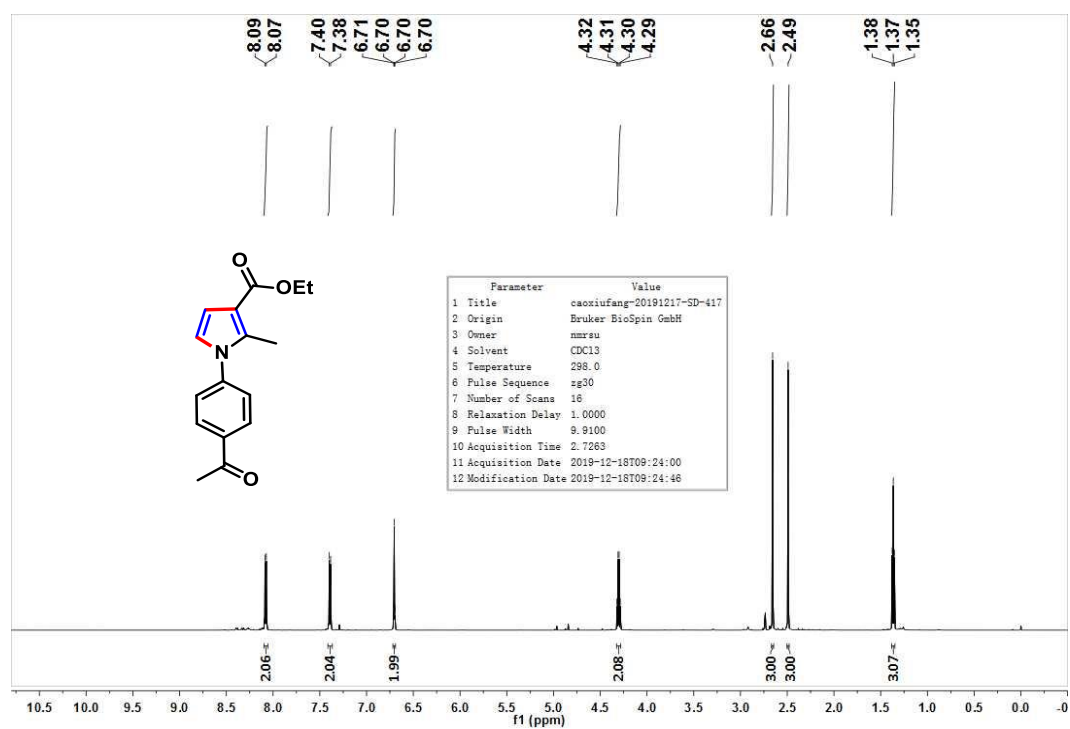


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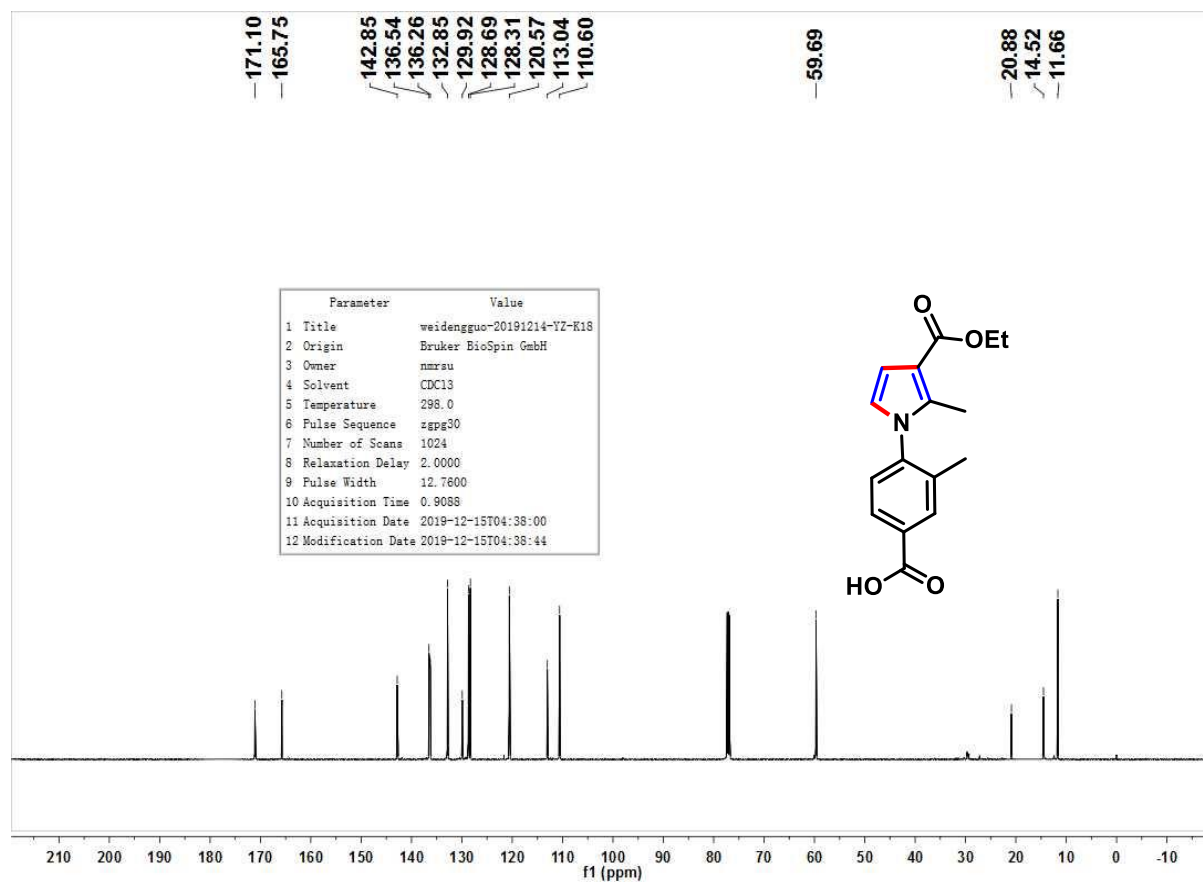
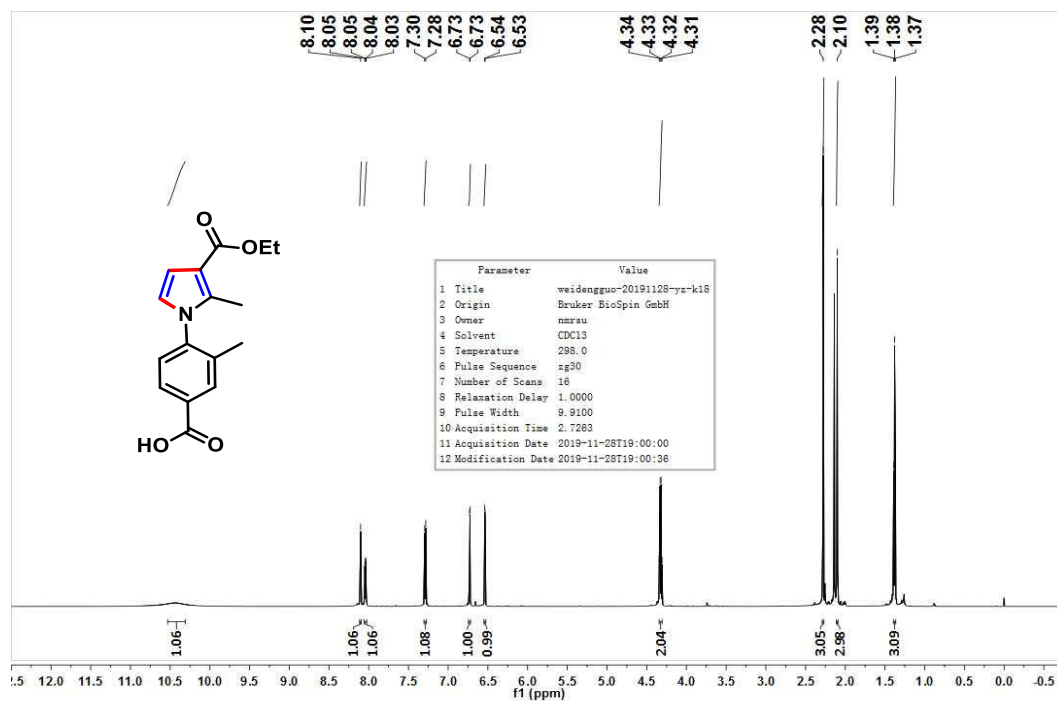


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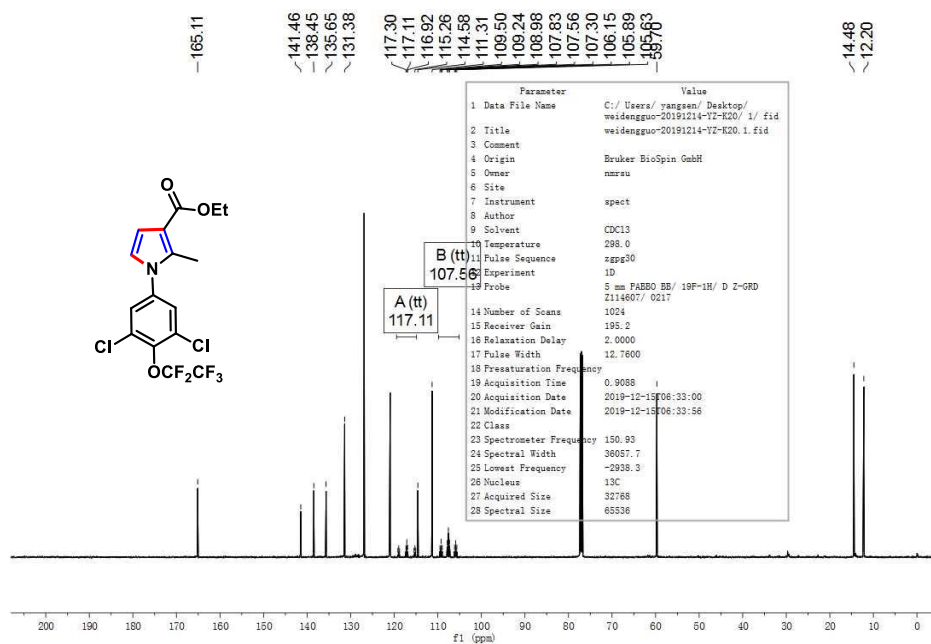
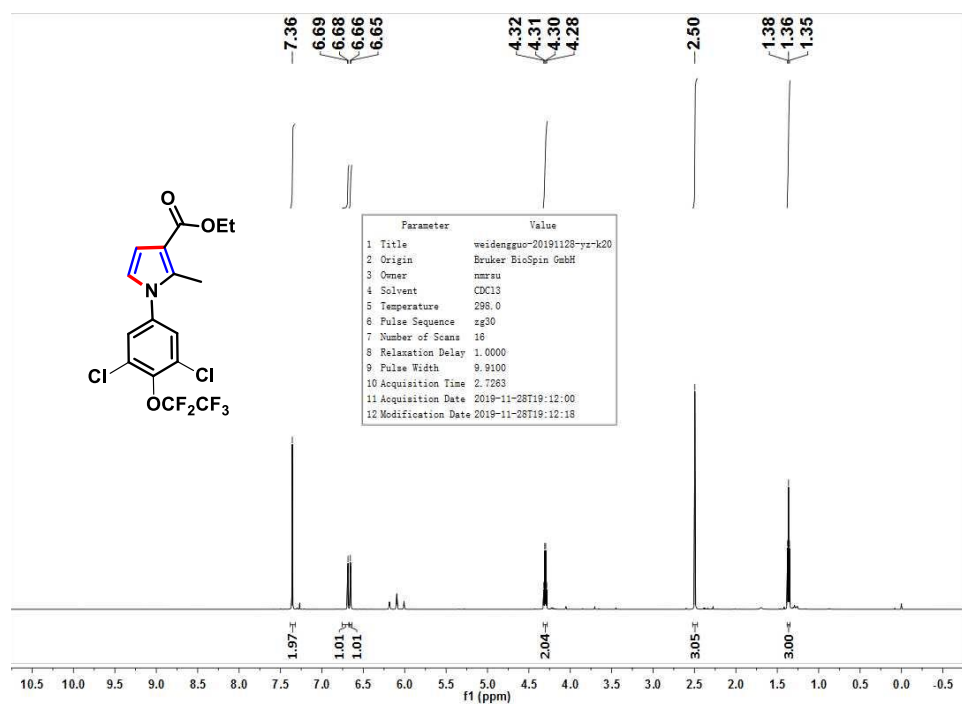


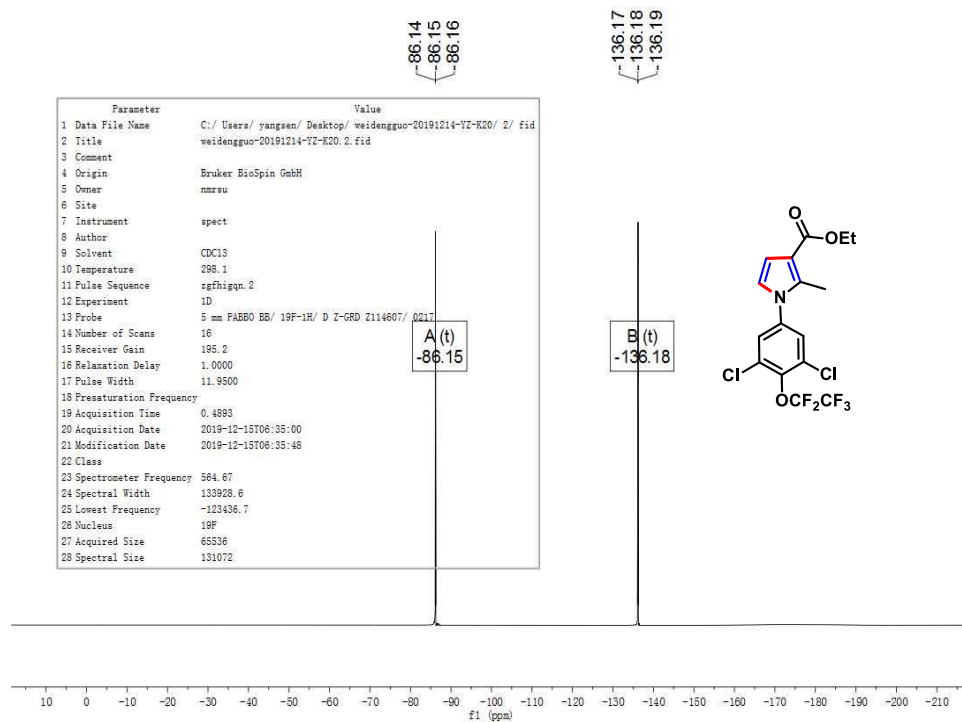


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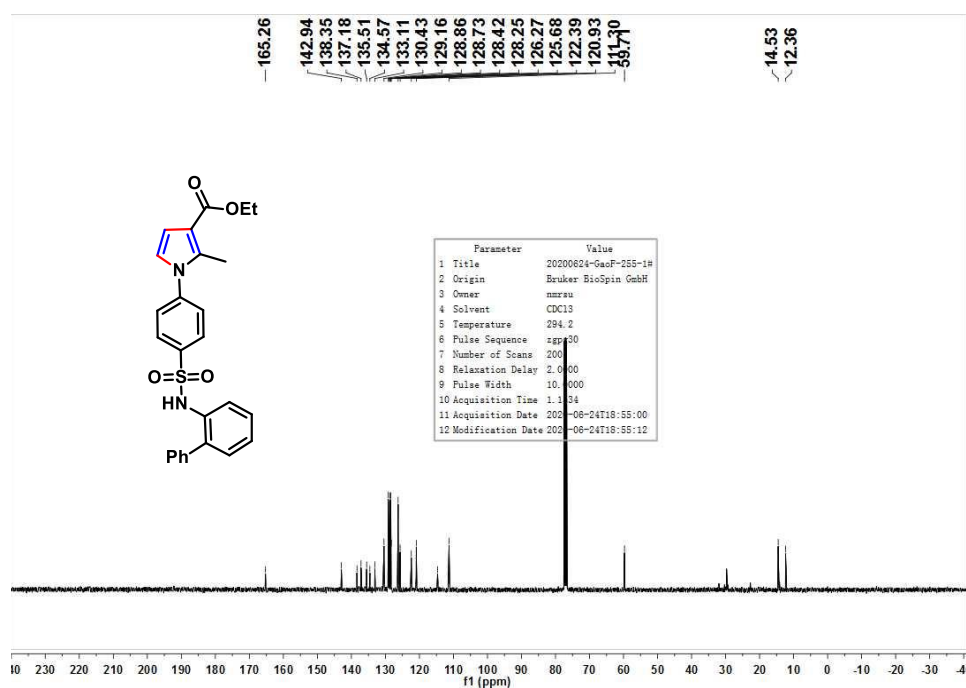
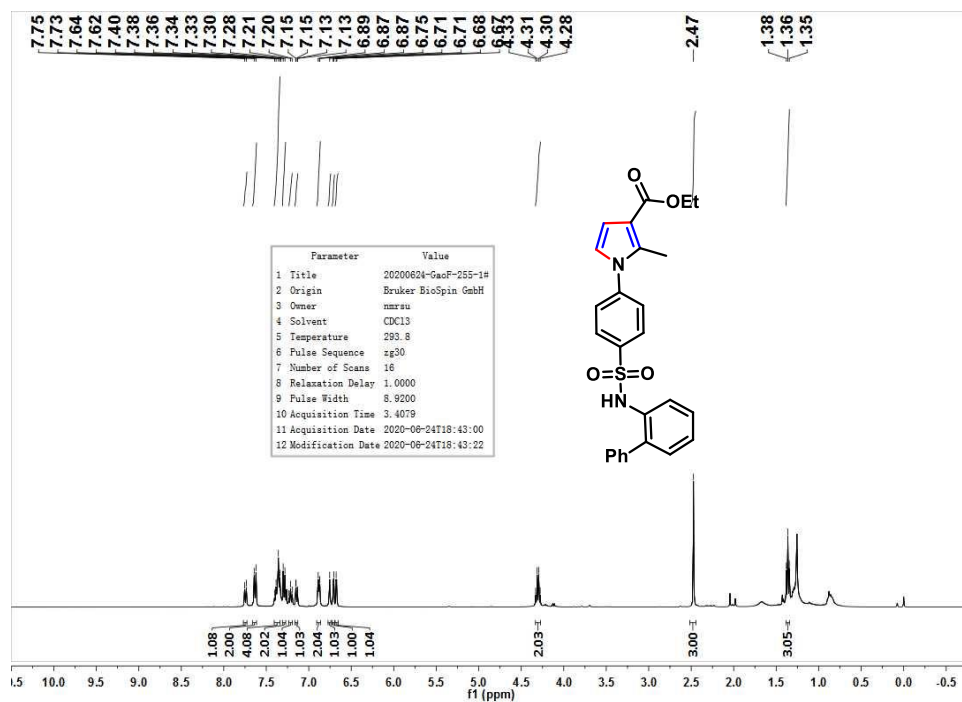


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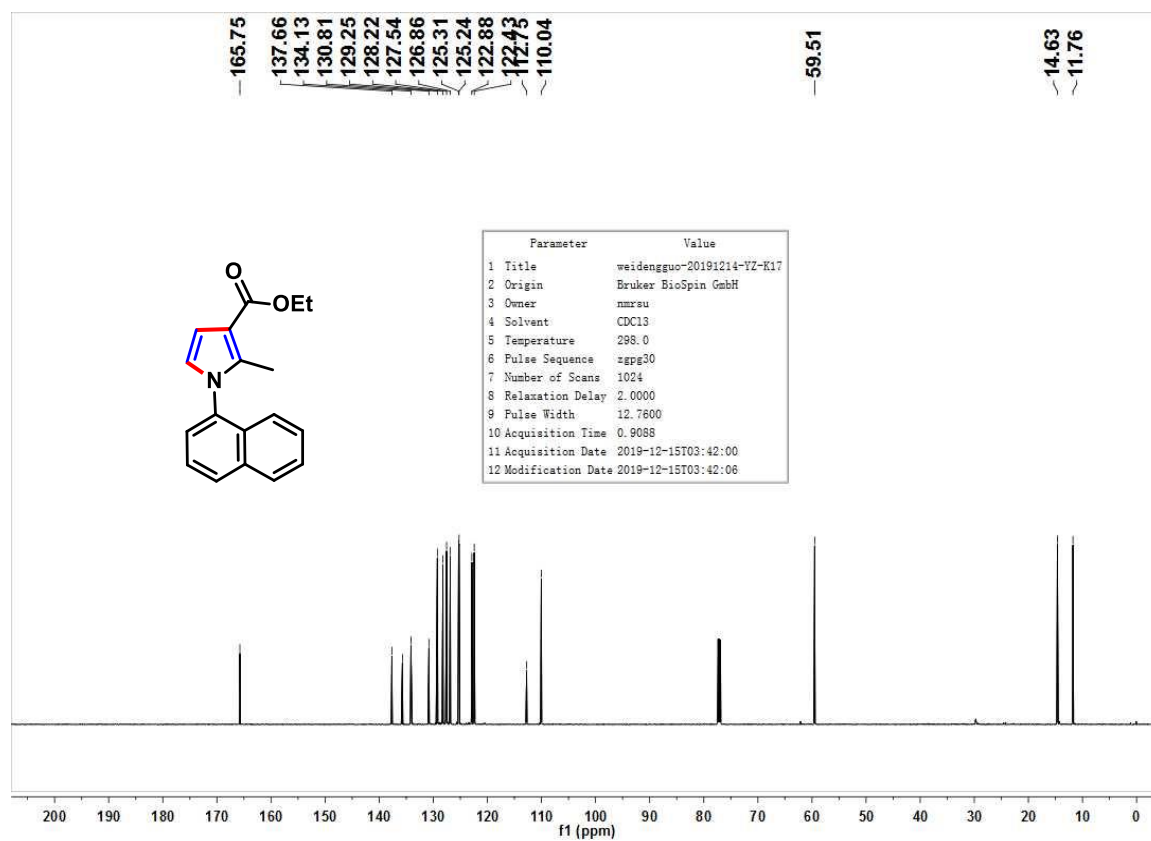
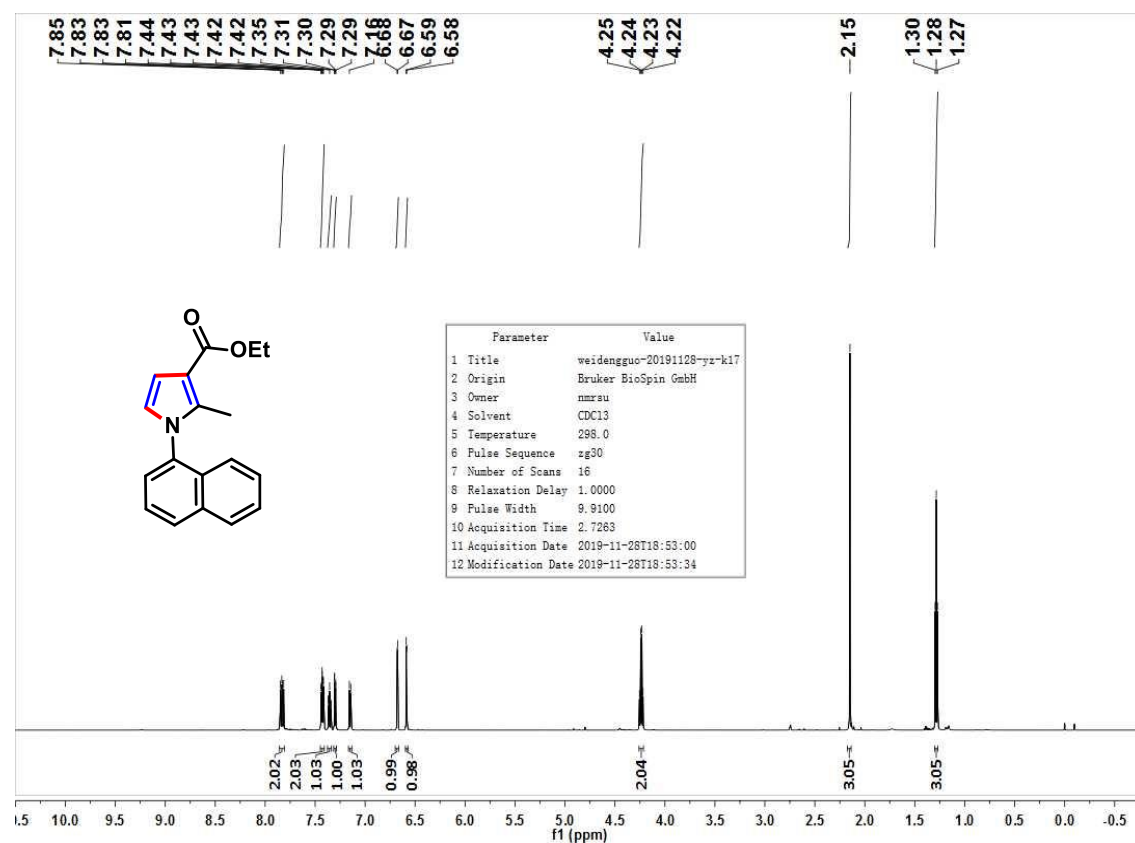




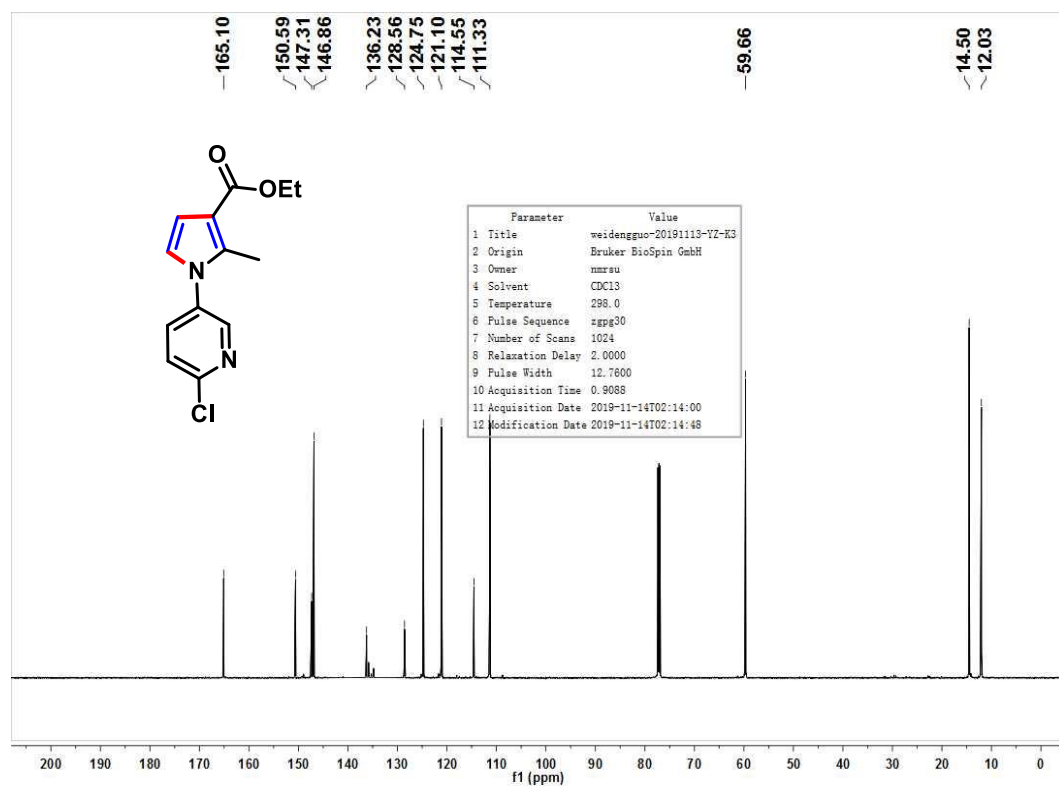
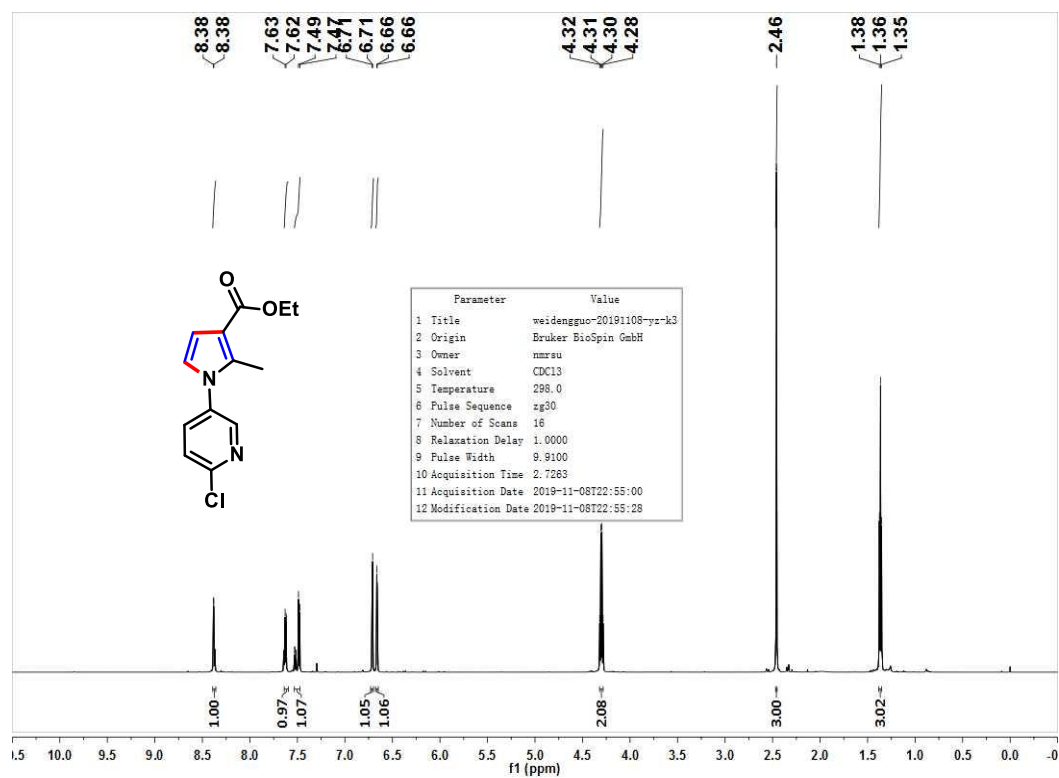
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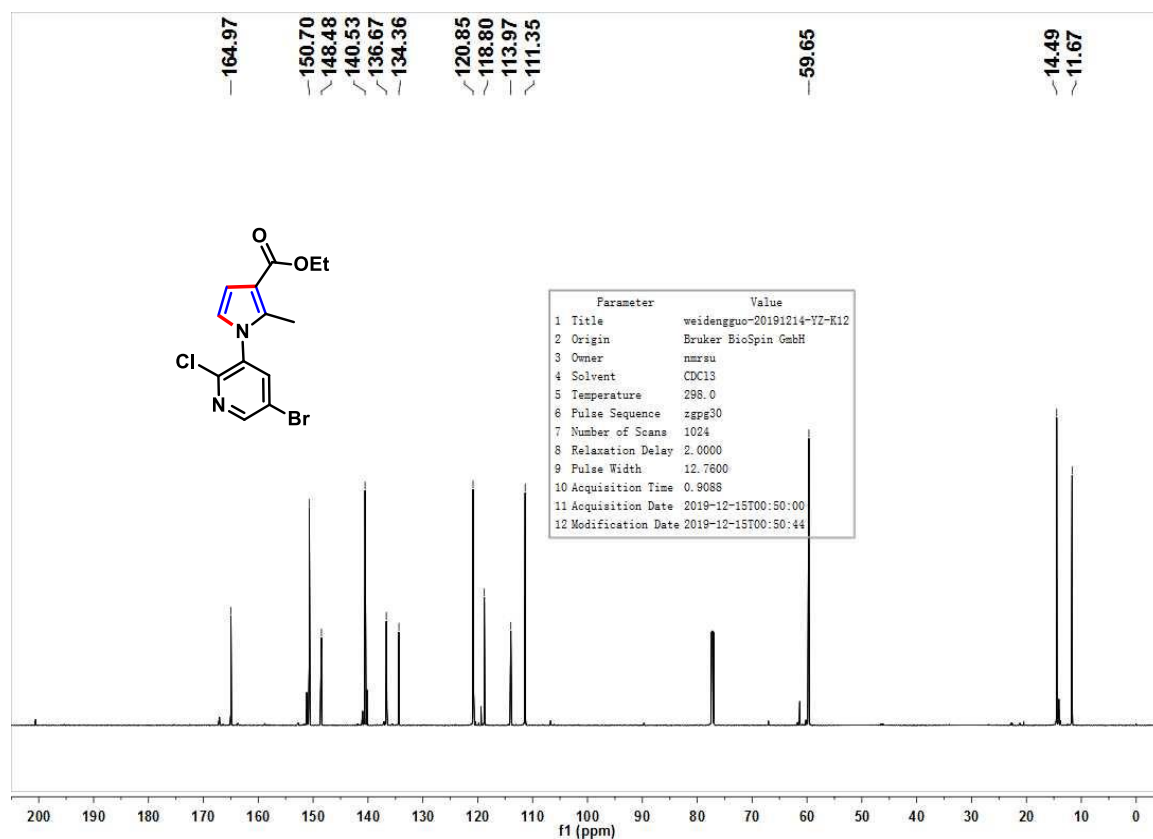
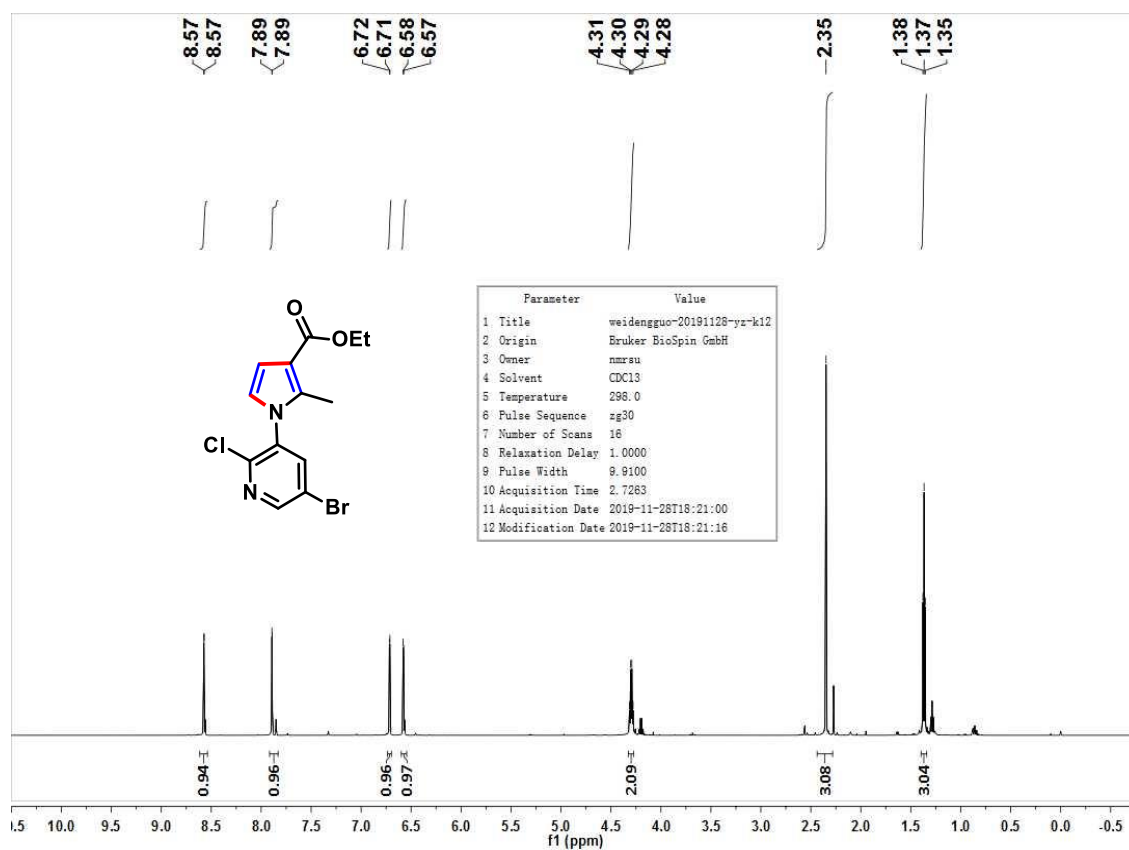
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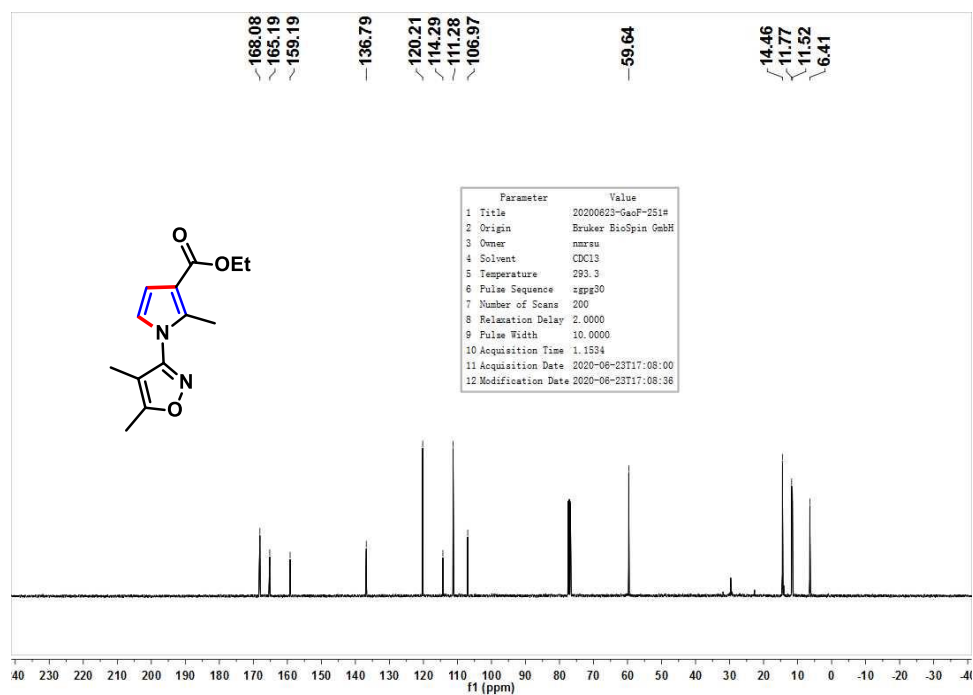
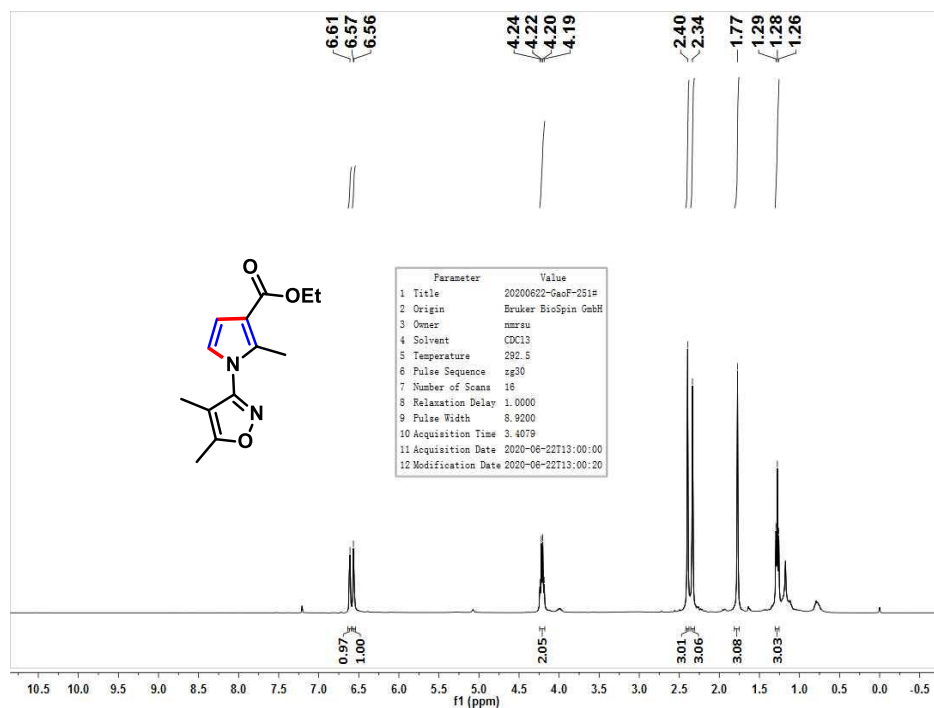
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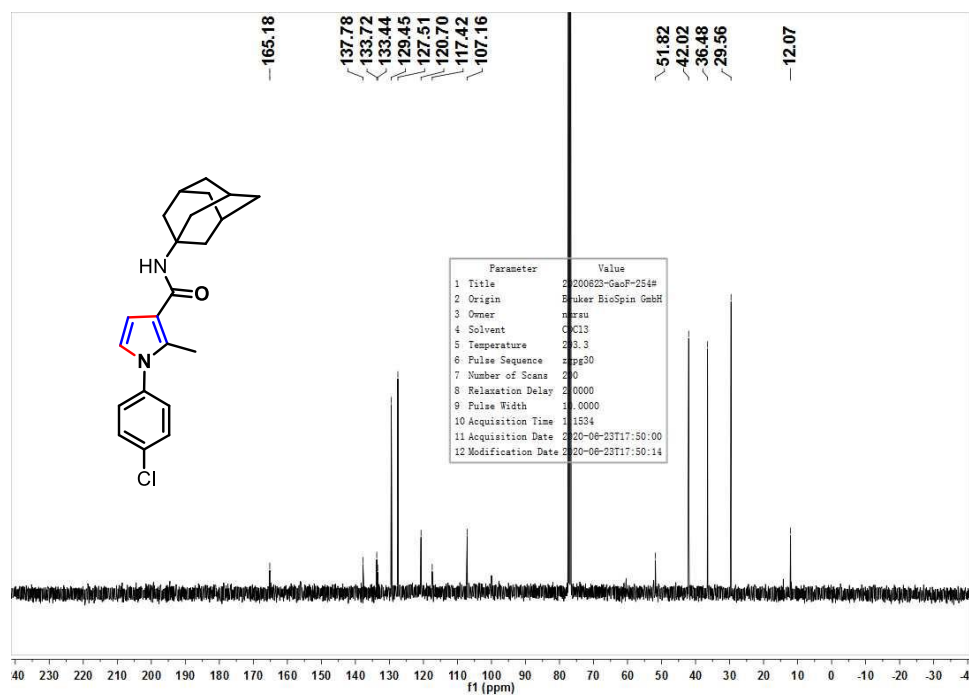
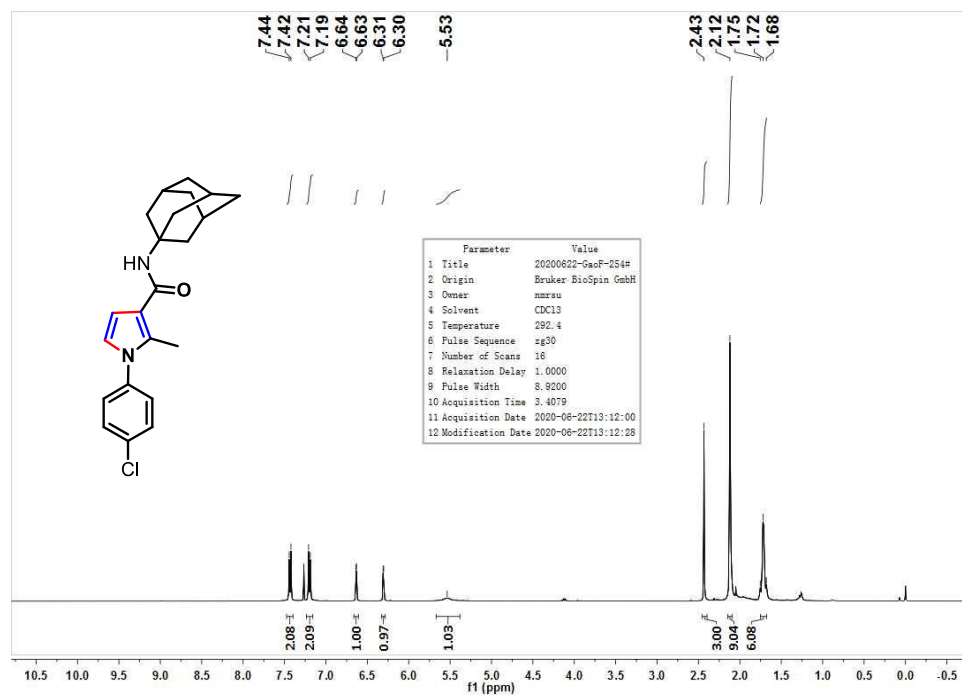
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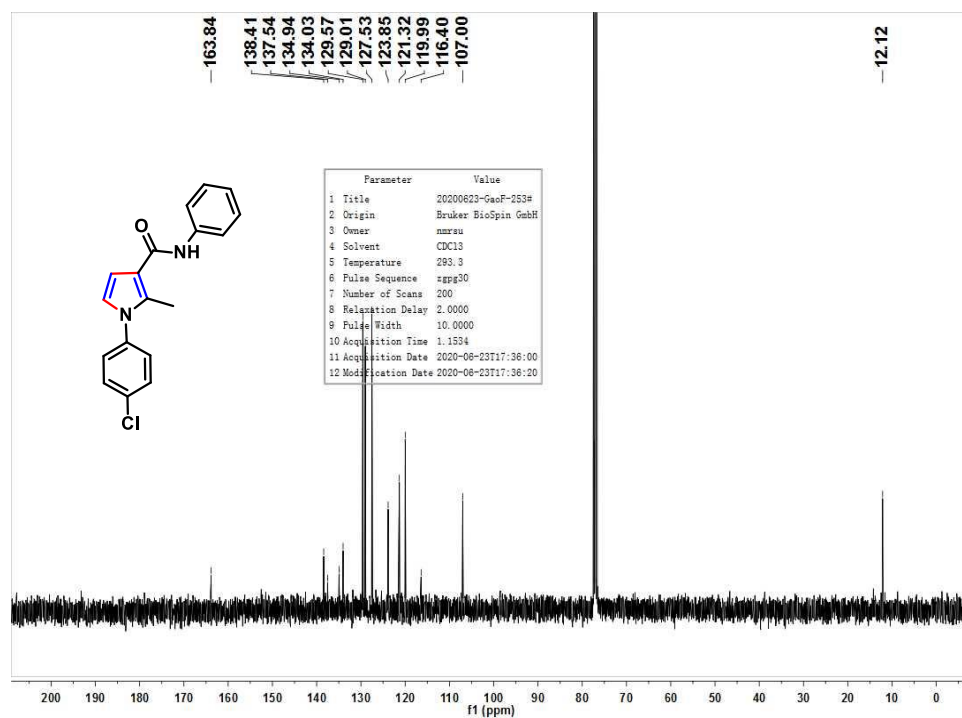
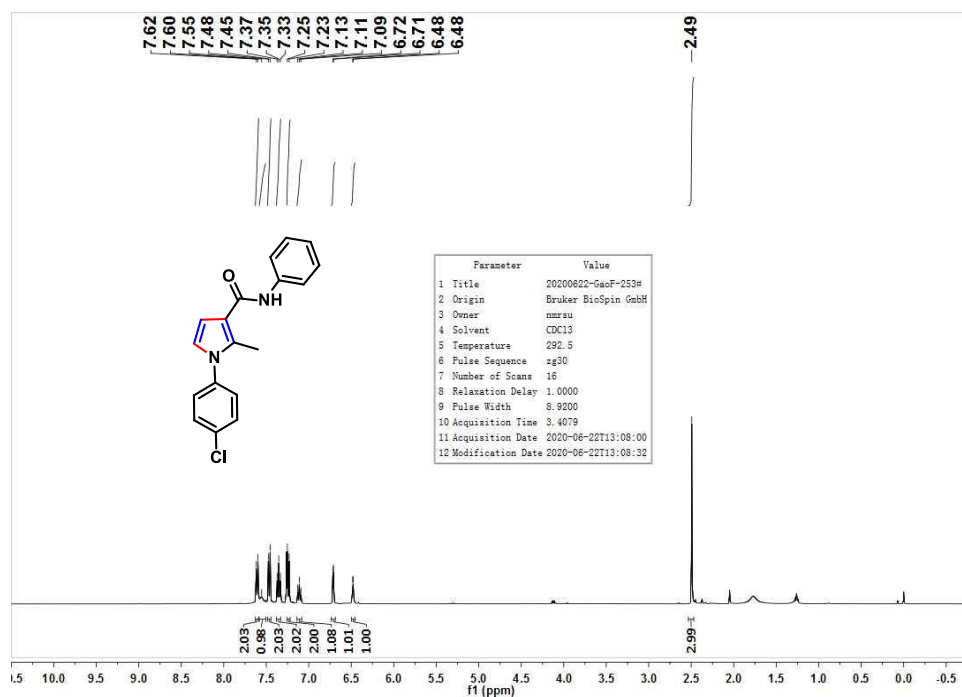
4v



4x



4y



5a

