Supporting Information

Transition-metal-free and facile synthesis of 3-alkynylpyrrole-2, 4-dicarboxylates from methylene isocyanides and propiolaldehyde

Xiaoli Huo[a, b, †], Xiaojuan Chen[a, †], Liya Yu[a], Chong Zhang[a, b], Linghui Zeng[a, b], Huajian Zhu[a, b], Jiaan Shao[a, b, *], Liping Fu[c, *], Jiankang Zhang[a, b, *]

[a] *School of Medicine, Zhejiang University City College, Hangzhou, Zhejiang 310015, PR China*

[b] *College of Pharmaceutical Sciences, Zhejiang University, Hangzhou, 310058, PR China*

[c] *Department of Pharmacy, Shaoxing Hospital of Traditional Chinese Medicine, Shaoxing, Zhejiang 312000, PR China*

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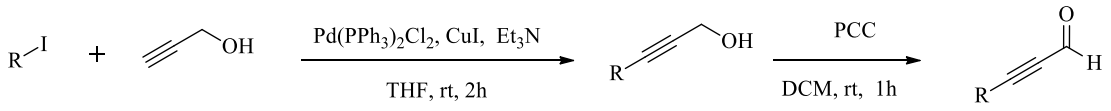
1. General Experimental

All reactions were carried out in test tube under air atmosphere. Chemicals were purchased from commercial suppliers and used without further purification. Purification of reaction products were carried out by chromatography using silica gel (200-300 mesh). High resolution MS data were recorded on a Agilent 6200 Series TOF spectrometer. NMR spectra were recorded on AVIII for ^{1}H NMR at 400 MHz and for ^{13}C NMR at 100 MHz. For ^{1}H NMR, tetramethylsilane (TMS) was served as internal standard (δ). The spectra data presented here are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constant(s) in Hertz. For ^{13}C NMR TMS was used as internal standard and spectra were obtained with complete proton decoupling. The starting materials propiolaldehyde (**1**) were prepared according to literature with modification (*J. Organometallic Chem.*, **2009**, 694, 566-570).

General procedure for the synthesis of propiolaldehyde (1)

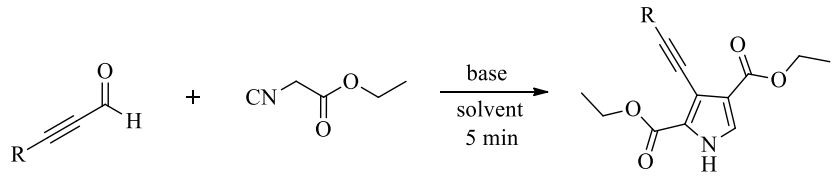


S1 **S2** **S3** **1**

To a two-necked round bottom flask, a mixture of **S1** (20 mmol), $Pd(PPh_3)_2Cl_2$ (0.015 equiv), CuI (0.015 equiv) in 50 mL of THF was added Et_3N (4.0 equiv) and dropwise added prop-2-yn-1-ol **S2** (1.1 equiv). The reaction was carried out under nitrogen at room temperature for 2h. After completion of the reaction, the reaction mixture was dried under reduced pressure to give the crude product. The propiolalcohol was purified by chromatography on silica gel to obtain **S3**.

To a stirred solution of **S3** (20 mmol) in 50 mL of DCM was added PCC (2.0 equiv) and Celite. The reaction was carried out under nitrogen at room temperature for 1h. The mixture was quickly filtered through a Celite pad and the solid residue was rinsed with more DCM. The filtrate was concentrated in *vacuo* and purified quickly by chromatography to afford the product **1**.

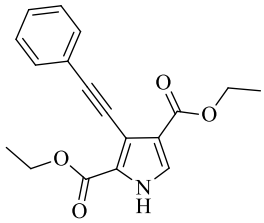
General procedure for the preparation of target compounds 3



1 **2a** **3**

To a solution of ethyl 2-isocyanoacetate (1.25 mmol, 2.5 equiv) in 3 mL of acetone was added DBU (0.75 mmol, 1.5 equiv) at 10 ℃, afterwards, corresponding propiolaldehyde (0.5 mmol) in 2 mL of acetone was added dropwise, and the reaction was proceeded for 5 minutes. After completion, the solvent was quenched by the addition of HCl (1N, 0.75ml), extracted with DCM. Then the organic layers was combined, dried with sodium sulfate and concentrated in *vacuo*. The target compounds **3** were obtained after purification on silica.

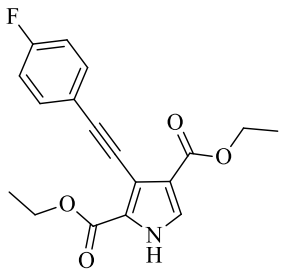
Characterization data for target compounds 3



diethyl 3-(phenylethynyl)-1H-pyrrole-2,4-dicarboxylate (**3a**)

White solid, yield: 75%. m.p.: 99.1 – 100.1 ℃.

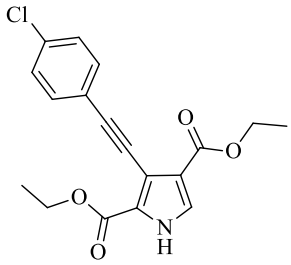
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.80 (s, 1H), 7.58 - 7.54 (m, 3H), 7.37 - 7.33 (m, 3H), 4.42 (q, J = 7.2 Hz, 2H), 4.35 (q, J = 7.2 Hz, 2H), 1.43 (t, J = 7.2 Hz, 3H), 1.38 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 160.6, 131.6, 128.3, 127.0, 125.7, 123.8, 119.5, 111.0, 96.2, 82.1, 61.3, 60.3, 14.43, 14.41. HRMS calcd for $C_{18}H_{17}NO_4$ $[M+H]^+$: 312.1236, found 312.1245.



diethyl 3-((4-fluorophenyl)ethynyl)-1H-pyrrole-2,4-dicarboxylate (**3b**)

White solid, yield: 66%. m.p.: 85.7 – 86.8 ℃.

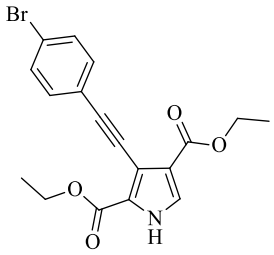
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.66 (s, 1H), 7.57 - 7.54 (m, 3H), 7.05 (t, J = 8.8 Hz, 2H), 4.41(q, J = 7.2 Hz, 2H), 4.35 (q, J = 7.2 Hz, 2H), 1.42 (t, J = 7.2 Hz, 3H), 1.38 (t, J = 7.2Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6 (161.3) (d, J = 248 Hz), 163.2, 160.4, 133.5 (133.4) (d, J = 9 Hz), 126.9, 125.7, 119.84 (119.81) (d, J = 3 Hz), 119.4, 115.7 (115.5) (d, J = 22 Hz), 110.9, 95.1, 81.8, 61.3, 60.3, 14.5, 14.4. HRMS calcd for $C_{18}H_{16}FNO_4$ $[M+H]^+$: 330.1142, found 330.1152.



diethyl 3-((4-chlorophenyl)ethynyl)-1H-pyrrole-2,4-dicarboxylate (**3c**)

White solid, yield: 64%. m.p.: 131.9 – 140.8 ℃.

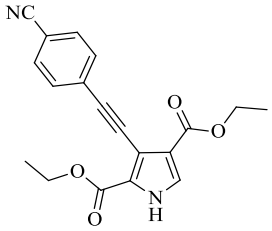
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.67 (s, 1H), 7.55 (d, J = 3.2 Hz, 1H), 7.50 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 4.41 (q, J = 7.2 Hz, 2H), 4.35 (q, J = 7.2 Hz, 2H), 1.42 (t, J = 7.2 Hz, 3H), 1.37 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 160.4, 134.3, 132.8, 128.7, 126.9, 125.8, 122.2, 119.5, 110.7, 94.9, 83.1, 61.3, 60.3, 14.5, 14.4. HRMS calcd for $C_{18}H_{16}ClNO_4$ $[M+H]^+$: 346.0846, found 346.0837.



diethyl 3-((4-bromophenyl)ethynyl)-1H-pyrrole-2,4-dicarboxylate (**3d**)

White solid, yield: 54%. m.p.: 161.1 – 162.2 ℃.

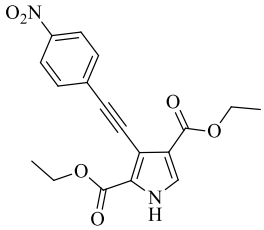
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.61 (s, 1H), 7.54 (d, J = 3.2 Hz, 1H), 7.49 - 7.42 (m, 4H), 4.41(q, J = 7.2 Hz, 2H), 4.35 (q, J = 7.2 Hz, 2H), 1.41 (t, J = 7.2 Hz, 3H), 1.37 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 160.3, 133.0, 131.6, 126.8, 125.8, 122.7, 122.5, 119.5, 110.7, 95.0, 83.3, 61.3, 60.3, 14.44, 14.42. HRMS calcd for $C_{18}H_{16}BrNO_4$ $[M+H]^+$: 390.0341, found 390.0332.



diethyl 3-((4-cyanophenyl)ethynyl)-1H-pyrrole-2,4-dicarboxylate (**3e**)

White solid, yield: 31%. m.p.: 165.8 – 166.7 ℃.

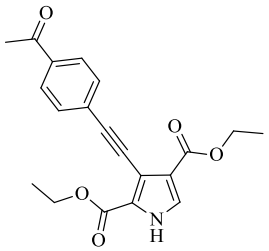
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.72 (s, 1H), 7.64 (s, 4H), 7.56 (d, J = 3.2 Hz, 1H), 4.42 (q, J = 7.2 Hz, 2H), 4.35 (q, J = 7.2 Hz, 2H), 1.44 (t, J = 7.2 Hz, 3H), 1.38 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 126.9, 160.1, 132.0, 132.0, 128.7, 126.9, 126.2, 119.6, 118.6, 111.4, 110.0, 94.2, 86.6, 61.4, 60.4, 14.44, 14.43. HRMS calcd for $C_{19}H_{16}N_2O_4$ $[M+H]^+$: 337.1188, found 337.1179.



diethyl 3-((4-nitrophenyl)ethynyl)-1H-pyrrole-2,4-dicarboxylate (**3f**)

White solid, yield: 24%. m.p.: 172.1 – 173.0 ℃.

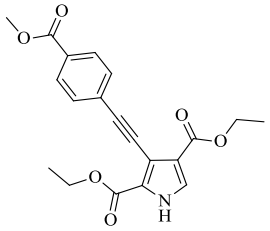
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.70 (s, 1H), 8.23 (d, J = 8.0 Hz, 2H), 7.71 (d, J = 8.4 Hz, 2H), 7.57 (s, 1H), 4.43 (q, J = 6.8 Hz, 2H), 4.35 (q, J = 6.8 Hz, 2H), 1.43 (t, J = 7.2 Hz, 3H), 1.38 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 160.0, 147.0, 132.2, 130.7, 126.9, 126.3, 123.7, 119.7, 109.9, 93.9, 87.6, 61.5, 60.5, 14.5. HRMS calcd for $C_{18}H_{16}N_2O_6$ $[M+H]^+$: 357.1087, found 357.1078.



diethyl 3-((4-acetylphenyl)ethynyl)-1H-pyrrole-2,4-dicarboxylate (**3g**)

White solid, yield: 39%. m.p.: 145.8 – 146.6 ℃.

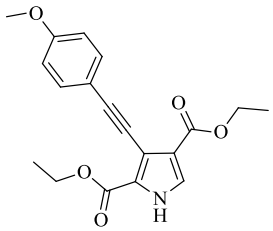
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.63 (s, 1H), 7.95 (d, J = 8.0 Hz, 2H), 7.65 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 3.2 Hz, 1H), 4.42 (q, J = 7.2 Hz, 2H), 4.36 (q, J = 7.2 Hz, 2H), 2.62 (s, 3H), 1.43 (t, J = 7.2 Hz, 3H), 1.38 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 163.1, 160.3, 136.2, 131.7, 128.7, 128.3, 126.9, 126.1, 119.6, 110.3, 95.1, 85.53, 61.4, 60.4, 26.7, 14.5, 14.4. HRMS calcd for $C_{20}H_{19}NO_5$ $[M+H]^+$: 354.1341, found 354.1347.



diethyl 3-((4-(methoxycarbonyl)phenyl)ethynyl)-1H-pyrrole-2,4-dicarboxylate (**3h**)

White solid, yield: 42%. m.p.: 154.0 – 155.1 ℃.

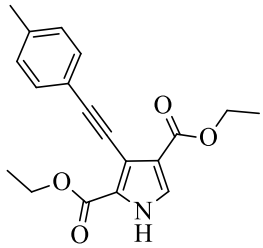
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.73 (s, 1H), 8.02 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 3.2 Hz, 1H), 4.42 (q, J = 7.2 Hz, 2H), 4.36 (q, J = 7.2 Hz, 2H), 3.93 (s, 3H), 1.42 (t, J = 7.2 Hz, 3H), 1.38 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 163.1, 160.3, 131.5, 129.5, 129.5, 128.5, 126.9, 126.1, 119.6, 110.4, 95.2, 85.2, 61.4, 60.4, 52.3, 14.44, 14.41. HRMS calcd for $C_{20}H_{19}NO_6$ $[M+H]^+$: 370.1291, found 370.1300.



diethyl 3-((4-methoxyphenyl)ethynyl)-1H-pyrrole-2,4-dicarboxylate (**3k**)

White solid, yield: 56%. m.p.: 133.3 – 134.3 ℃.

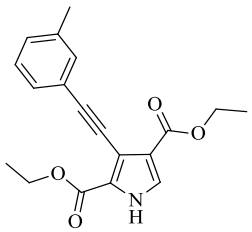
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.71 (s, 1H), 7.55 – 7.50 (m, 3H), 6.88 (d, J = 8.4 Hz, 2H), 4.41 (q, J = 7.2 Hz, 2H), 4.36 (q, J = 7.2 Hz, 2H), 3.83 (s, 3H), 1.43 (t, J = 7.2 Hz, 3H), 1.38 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 160.6, 159.7, 133.1, 126.9, 125.4, 115.9, 114.0, 111.4, 110.4, 96.4, 80.8, 61.2, 60.3, 55.3, 14.5, 14.4. HRMS calcd for $C_{19}H_{19}NO_5$ $[M+H]^+$: 342.1341, found 342.1331.



diethyl 3-(p-tolylethynyl)-1H-pyrrole-2,4-dicarboxylate (**3j**)

White solid, yield: 56%. m.p.: 123.3 – 124.2 ℃.

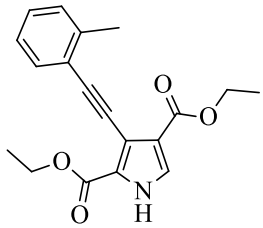
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.60 (s, 1H), 7.55 (d, J = 3.6 Hz, 1H), 7.47 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 4.41 (q, J = 7.2 Hz, 2H), 4.35 (q, J = 7.2 Hz, 2H), 2.37 (s, 3H), 1.43 (t, J = 7.2 Hz, 3H), 1.38 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 160.6, 138.4, 131.5, 129.1, 126.9, 125.6, 120.7, 119.4, 111.2, 96.5, 81.4, 61.3, 60.3, 21.6, 14.5, 14.4. HRMS calcd for $C_{20}H_{19}NO_5$ $[M+H]^+$: 326.1392, found 326.1383.



diethyl 3-(m-tolylethynyl)-1H-pyrrole-2,4-dicarboxylate (**3m**)

White solid, yield: 70%. m.p.: 110.3 – 110.9 ℃.

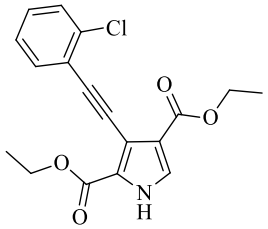
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.74 (s, 1H), 7.54 (d, J = 3.2 Hz, 1H), 7.40 – 7.37 (m, 2H), 7.24 (t, J = 7.6 Hz, 1H), 7.14 (d, J = 7.6 Hz, 1H), 4.42 (q, J = 7.2 Hz, 2H), 4.36 (q, J = 7.2 Hz, 2H), 2.35 (s, 3H), 1.43 (t, J = 7.2 Hz, 3H), 1.38 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 160.6, 137.9, 132.2, 129.2, 128.7, 128.2, 126.9, 125.7, 123.5, 119.4, 111.1, 96.4, 81.72, 61.3, 60.3, 21.3, 14.44, 14.42. HRMS calcd for $C_{20}H_{19}NO_5$ $[M+H]^+$: 326.1392, found 326.1387.



diethyl 3-(o-tolylethynyl)-1H-pyrrole-2,4-dicarboxylate (**3o**)

White solid, yield: 71%. m.p.: 79.2 – 80.3 ℃.

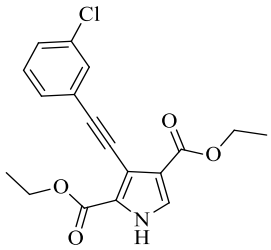
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.66 (s, 1H), 7.56 (d, J = 6.8 Hz, 2H), 7.24 – 7.17 (m, 3H), 4.43 (q, J = 7.2 Hz, 2H), 4.36 (q, J = 7.2 Hz, 2H), 2.60 (s, 3H), 1.40 (t, J = 7.2 Hz, 3H), 1.36 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 160.5, 140.4, 132.2, 129.4, 128.3, 126.9, 125.5, 125.4, 123.5, 119.5, 111.1, 95.4, 85.6, 61.2, 60.2, 20.7, 14.53, 14.50. HRMS calcd for $C_{20}H_{19}NO_5$ $[M+H]^+$: 326.1392, found 326.1402.



diethyl 3-((2-chlorophenyl)ethynyl)-1H-pyrrole-2,4-dicarboxylate (**3n**)

White solid, yield: 65%. m.p.: 110.1 – 111.1 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.71 (s, 1H), 7.65 – 7.63 (m, 1H), 7.56 (d, J = 3.6 Hz, 1H), 7.44 – 7.41 (m, 1H), 7.28 – 7.24 (m, 2H), 4.43 (q, J = 7.2 Hz, 2H), 4.36 (q, J = 7.2 Hz, 2H), 1.41 – 1.34 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 160.5, 135.6, 133.8, 129.3, 129.3, 126.9, 126.4, 126.1, 123.7, 119.8, 110.3, 92.7, 87.0, 61.4, 60.4, 14.5. HRMS calcd for $C_{18}H_{16}ClNO_4$ $[M+H]^+$: 346.0846, found 346.0854.

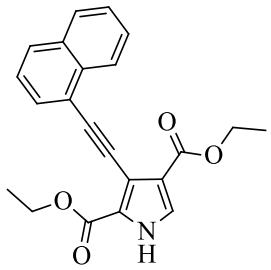


diethyl 3-((3-chlorophenyl)ethynyl)-1H-pyrrole-2,4-dicarboxylate (**3l**)

White solid, yield: 66%. m.p.: 93.7 – 94.1 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.69 (s, 1H), 7.55 (d, J = 3.2 Hz, 2H), 7.46 – 7.44 (m, 1H), 7.32 – 7.27 (m, 2H), 4.42 (q, J = 7.2 Hz, 2H), 4.36 (q, J = 7.2 Hz, 2H), 1.43 (t, J = 7.2 Hz, 3H), 1.38 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 160.4, 134.1, 131.4, 129.7, 129.5, 128.5, 126.9, 126.0, 125.4, 119.6, 110.5, 94.5, 83.3, 61.4, 60.4, 14.44, 14.42. HRMS calcd for $C_{18}H_{16}ClNO_4$

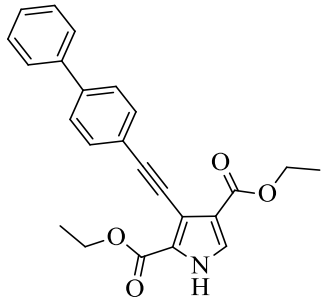
$[M+H]^+$: 346.0846, found346.0855.



diethyl 3-([1,1'-biphenyl]-4-ylethynyl)-1H-pyrrole-2,4-dicarboxylate (**3p**)

White solid, yield: 74%. m.p.: 64.8 – 65.7 ℃.

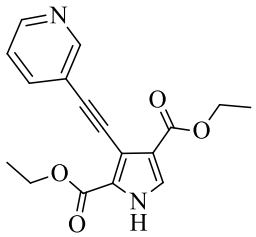
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.79 (s, 1H), 8.72 (d, J = 8.4 Hz, 1H), 7.87 – 7.81 (m, 3H), 7.61 – 7.44 (m, 4H), 4.48 (q, J = 7.2 Hz, 2H), 4.40 (q, J = 7.2 Hz, 2H), 1.43 (t, J = 7.2 Hz, 3H), 1.38 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 160.7, 133.6, 133.2, 130.5, 128.8, 128.1, 127.1, 126.8, 126.6, 126.4, 125.7, 125.3, 121.6, 119.6, 111.0, 94.5, 86.9, 61.4, 60.4, 14.6, 14.5. HRMS calcd for $C_{22}H_{19}NO_4$ $[M+H]^+$: 362.1392, found 362.1383.



diethyl 3-([1,1'-biphenyl]-4-ylethynyl)-1H-pyrrole-2,4-dicarboxylate (**3i**)

White solid, yield: 36%. m.p.: 160.2 – 161.9 ℃.

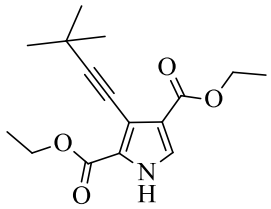
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.71 (s, 1H), 7.65 – 7.55 (m, 7H), 7.45 (t, J = 7.6 Hz, 2H), 7.36 (t, J = 7.2 Hz, 1H), 4.43 (q, J = 7.2 Hz, 2H), 4.37 (q, J = 7.2 Hz, 2H), 1.45 (t, J = 7.2 Hz, 3H) , 1.40 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 160.6, 141.0, 140.4, 132.0, 128.9, 127.6, 127.0, 127.0, 125.7, 122.7, 119.5, 111.0, 96.1, 82.8, 61.3, 60.3, 14.48, 14.47. HRMS calcd for $C_{24}H_{21}NO_4$ $[M+H]^+$: 388.1549, found 388.1540.



diethyl 3-(pyridin-3-ylethynyl)-1H-pyrrole-2,4-dicarboxylate (**3q**)

White solid, yield: 40%. m.p.: 108.2 – 109.1 ℃.

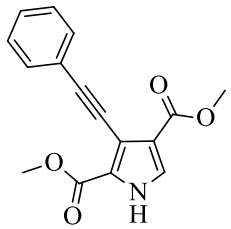
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.93 (s, 1H), 8.84 (s, 1H), 8.59 (d, J = 4.0 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 3.2 Hz, 1H), 7.33 (dd, J = 7.6, 5.2 Hz, 1H), 4.45 (q, J = 7.2 Hz, 2H), 4.39 (q, J = 7.2 Hz, 2H), 1.47 – 1.39 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 160.2, 152.1, 148.5, 138.5, 126.9, 126.1, 123.1, 121.0, 119.6, 110.1, 92.4, 85.5, 61.3, 60.4, 14.5, 14.4. HRMS calcd for $C_{17}H_{16}N_2O_4$ $[M+H]^+$: 313.1188, found 313.1180.



diethyl 3-(3,3-dimethylbut-1-yn-1-yl)-1H-pyrrole-2,4-dicarboxylate (**3r**)

White solid, yield: 48%. m.p.: 114.8 – 116.2 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.67 (s, 1H), 7.50 (d, J = 3.2 Hz, 1H), 4.39 (q, J = 7.2 Hz, 2H), 4.33 (q, J = 7.2 Hz, 2H), 1.42 (t, J = 7.2 Hz, 3H), 1.39 – 1.36 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 161.0, 127.0, 125.4, 119.4, 111.5, 105.6, 71.4, 61.1, 60.2, 30.9, 28.5, 14.5. HRMS calcd for $C_{16}H_{21}NO_4$ $[M+H]^+$: 292.1549, found 292.1558.

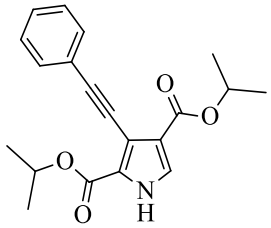


dimethyl 3-(phenylethynyl)-1H-pyrrole-2,4-dicarboxylate (**3s**)

White solid, yield: 81%. m.p.: 141.2 – 142.4 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.78 (s, 1H), 7.59 – 7.55 (m, 3H), 7.35 – 7.34 (m, 3H), 3.97 (s, 3H),

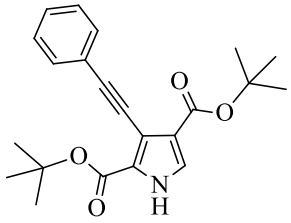
3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 160.9, 131.7, 128.4, 128.3, 127.1, 125.5, 123.6, 119.1, 111.3, 96.5, 81.9, 52.1, 51.5. HRMS calcd for $C_{16}H_{13}NO_4$ $[M+H]^+$: 284.0923, found 284.0915.



diisopropyl 3-(phenylethynyl)-1H-pyrrole-2,4-dicarboxylate (**3t**)

White solid, yield: 75%. m.p.: 113.0 – 1141 ℃.

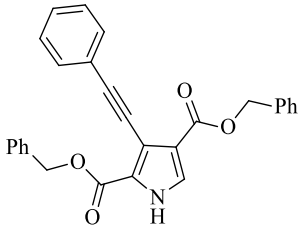
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.66 (s, 1H), 7.59 – 7.57 (m, 2H), 7.52 (d, J = 3.2 Hz, 1H), 7.37 – 7.32 (m, 3H), 5.30 – 5.21 (m, 2H), 1.39 (d, J = 6.4 Hz, 6H), 1.35 (d, J = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 160.2, 131.5, 128.3, 128.2, 126.7, 126.1, 123.9, 112.0, 110.7, 95.9, 82.3, 69.0, 67.6, 22.14, 22.12. HRMS calcd for $C_{20}H_{21}NO_4$ $[M+H]^+$: 340.1549, found 340.1541.



di-tert-butyl 3-(phenylethynyl)-1H-pyrrole-2,4-dicarboxylate (**3u**)

White solid, yield: 73%. m.p.: 118.2 – 119.2 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.68 (s, 1H), 7.57 – 7.54 (m, 2H), 7.46 (d, J = 7.2 Hz, 1H), 7.36 – 7.30 (m, 3H), 1.58 (s, 9H), 1.57 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 162.3, 133.7, 130.4, 130.2, 129.1, 128.5, 126.2, 123.3, 111.9, 97.5, 84.9, 84.5, 82.8, 30.6. HRMS calcd for $C_{22}H_{25}NO_4$ $[M+H]^+$: 368.1862, found 368.1870.

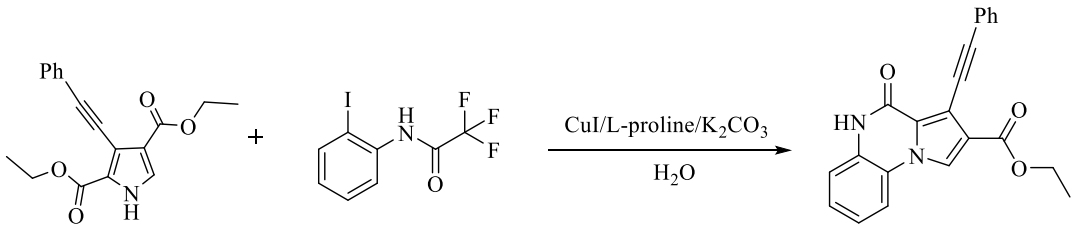


dibenzyl 3-(phenylethynyl)-1H-pyrrole-2,4-dicarboxylate (**3v**)

White solid, yield: 56%. m.p.: 126.3 – 127.4 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.64 (s, 1H), 7.58 (d, J = 3.6 Hz, 1H), 7.47 – 7.44 (m, 4H), 7.30 – 7.27 (m, 7H), 7.21 – 7.17 (t, J = 3.2 Hz, 2H), 7.13 – 7.11 (m, 2H), 5.39 (s, 2H), 5.34 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 160.5, 136.1, 135.4, 131.7, 128.7, 128.6, 128.3, 128.2, 128.2, 128.1, 127.6, 125.4, 123.4, 119.3, 111.3, 96.7, 81.9, 67.1, 66.2. HRMS calcd for $C_{28}H_{21}NO_4$ $[M+H]^+$: 436.1549, found 436.1543.

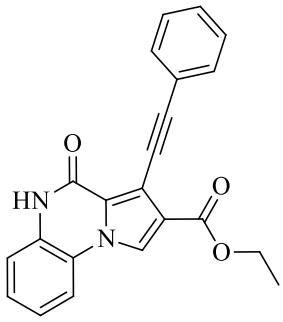
Procedure for the preparation of target compound 5



3a **4** **5**

A stirred mixture of **3a** (2 mmol), **4** (6 mmol, 3.0 equiv), CuI (0.2mmol, 0.1 equiv), *L*-proline (0.4mmol, 0.2 equiv) and K_2CO_3 (6mmol, 3.0 equiv) was first stirred in DMSO (6 mL) at 120℃ under nitrogen (*Organic Letters*, **2018**, 20, 2603 – 2606). The mixture was left standing overnight, to which 6 mL of H_2O was added and stirred at 100℃ for another 6h. Once completion, the mixture was poured into 50 mL of H_2O, and the precipitate **5** was filtrated and washed with DCM.

Characterization data for target compound 5



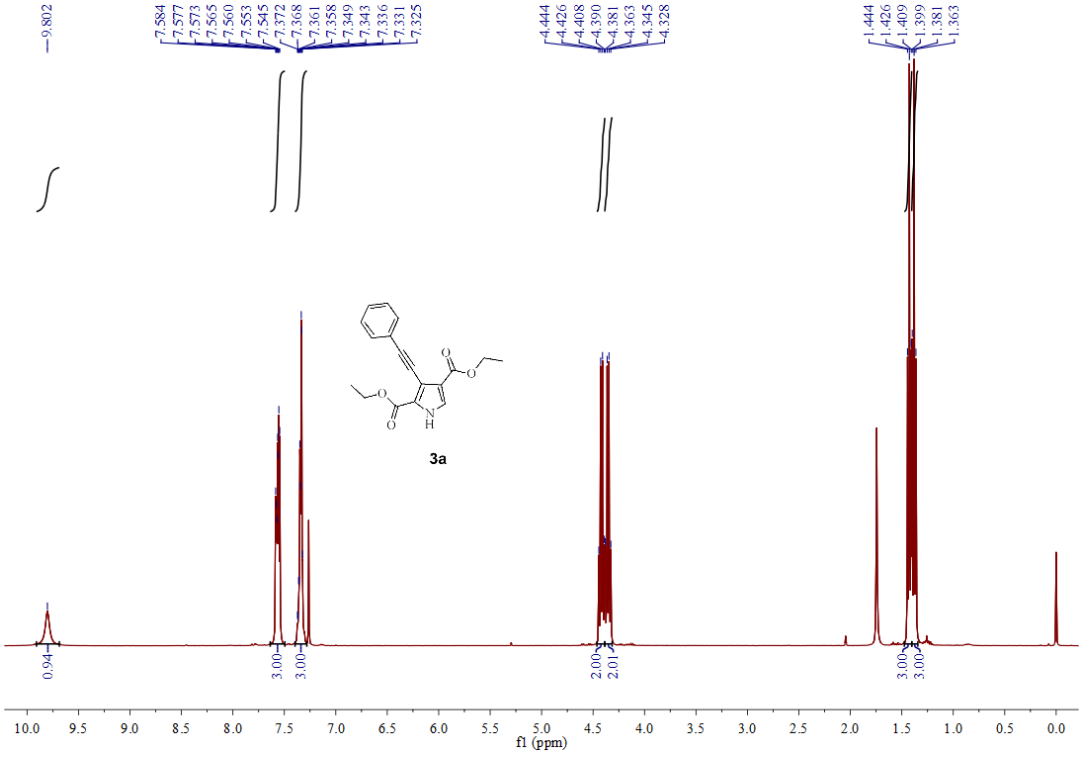
ethyl 4-oxo-3-(phenylethynyl)-4,5-dihydropyrrolo[1,2-a]quinoxaline-2-carboxylate (**5**)

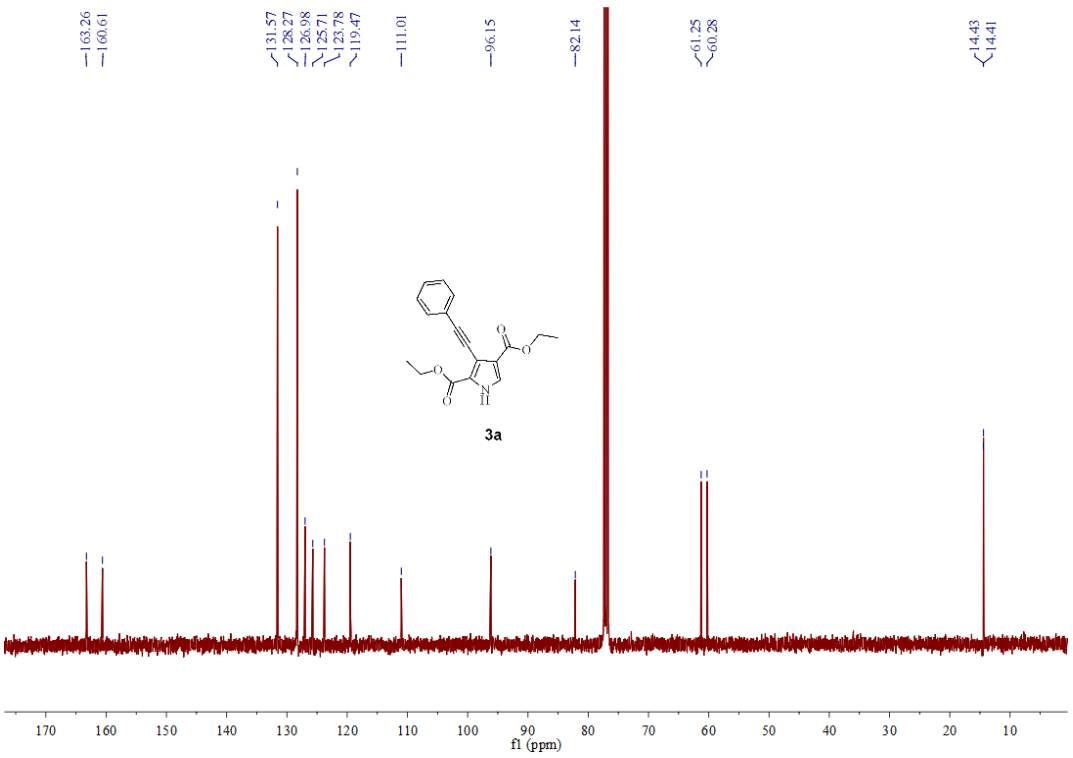
White solid, yield: 31%.

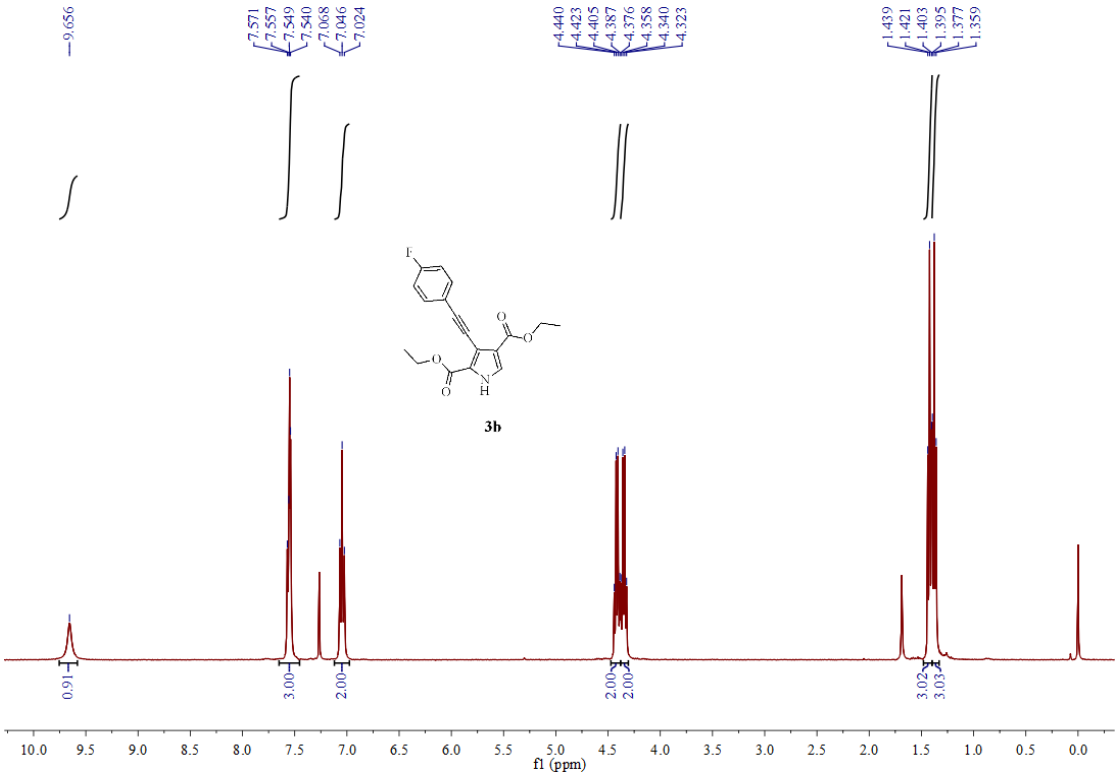
^{1}H NMR (400 MHz, DMSO-*d*6) δ 11.49 (s, 1H), 8.84 (s, 1H), 8.31 (d, J = 7.6 Hz, 1H), 7.57 – 7.55 (m, 2H), 7.50 – 7.33 (m, 5H), 7.27 – 7.23 (m, 1H), 4.35 (q, J = 7.2 Hz, 2H), 1.36 (t, J = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, DMSO-*d*6) δ 162.3, 154.1, 131.1, 129.3, 128.7, 128.5, 127.3, 125.2, 123.3, 122.8, 122.0, 121.7, 119.7, 116.5, 116.0, 107.1, 95.0, 83.0, 60.1, 14.3. HRMS calcd for $C_{22}H_{16}N_2O_3$ $[M+H]^+$: 357.1239, found 357.1246.

2. ^{1}H and ^{13}C NMR spectra for target compounds



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7.549
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7.068
7.046
7.024
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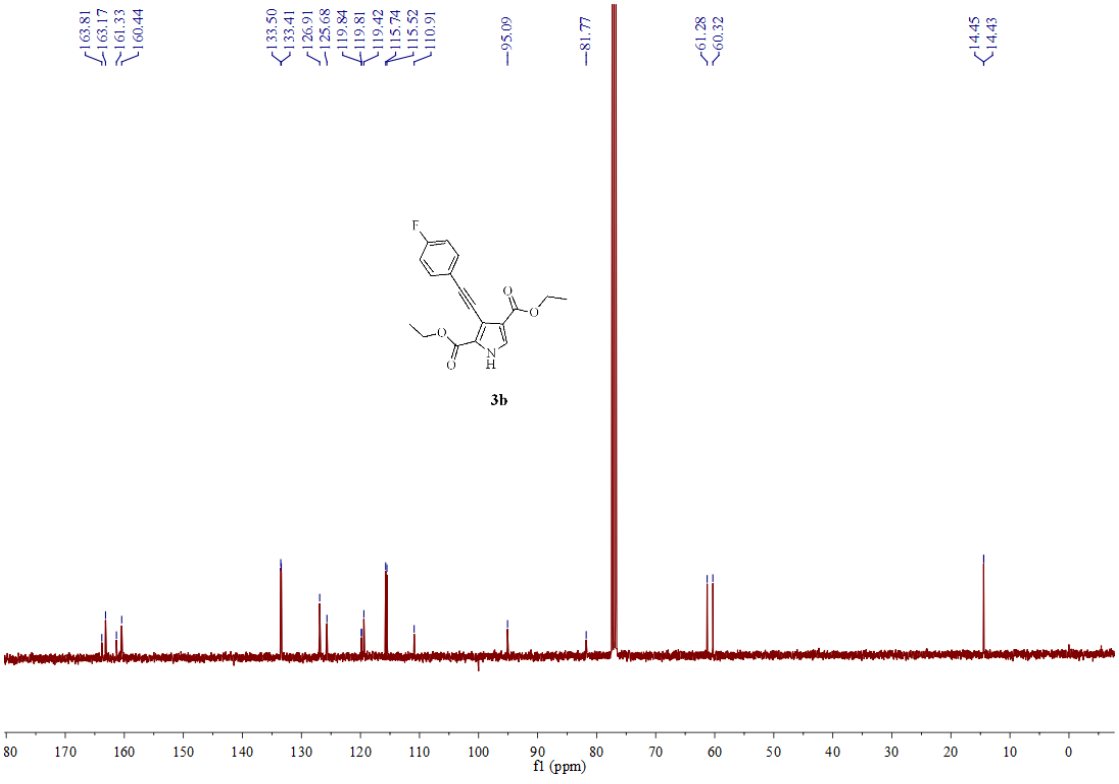
4.423
4.405
4.387
4.376
4.358
4.340
4.323
1.439
1.421
1.403
1.395
1.377
1.359
F
O
O
O
O
N
H
0.91
3.00
2.00
2.00
2.00
3.02
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

3b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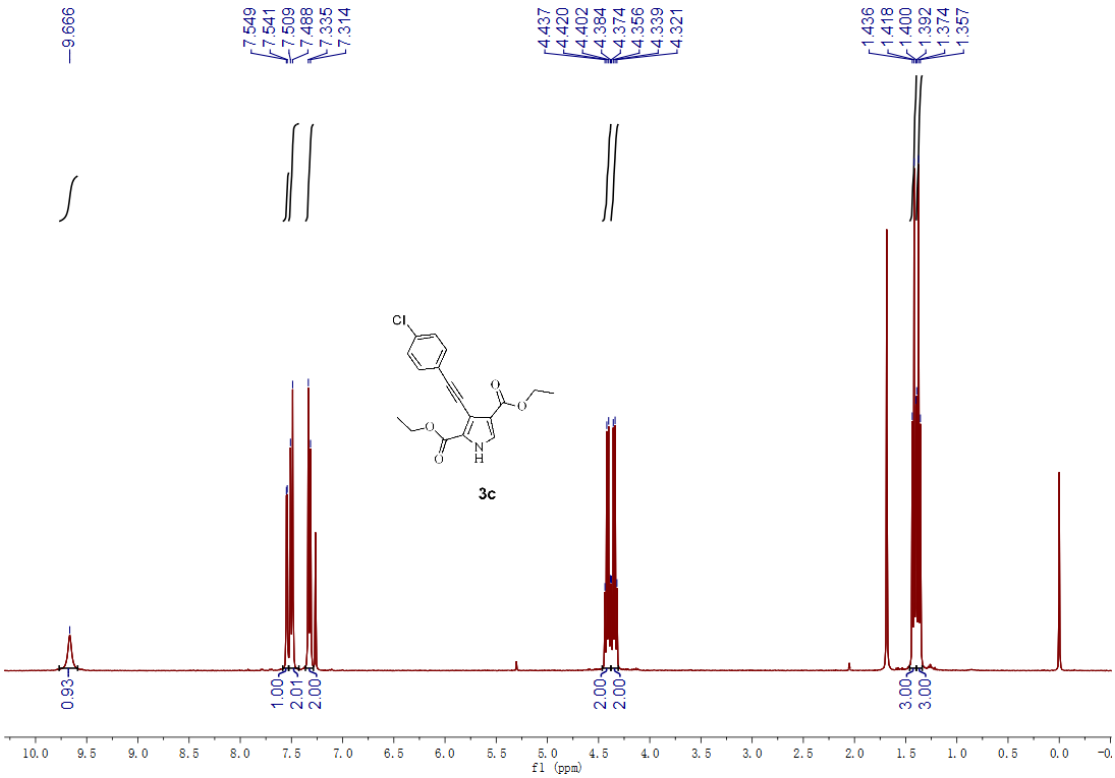
163.17
161.33
160.44
133.50
133.41
126.91
125.68
119.84
119.81
119.42
115.74
115.52
110.91
95.09
81.77
61.28
60.32
14.45
14.43
F
O
O
O
O
N
H
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3b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7.488
7.335
7.314
4.437
4.420
4.402
4.384
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4.356
4.339
4.321
1.436
1.418
1.400
1.392
1.374
1.357
Cl
O
O
O
O
N
H
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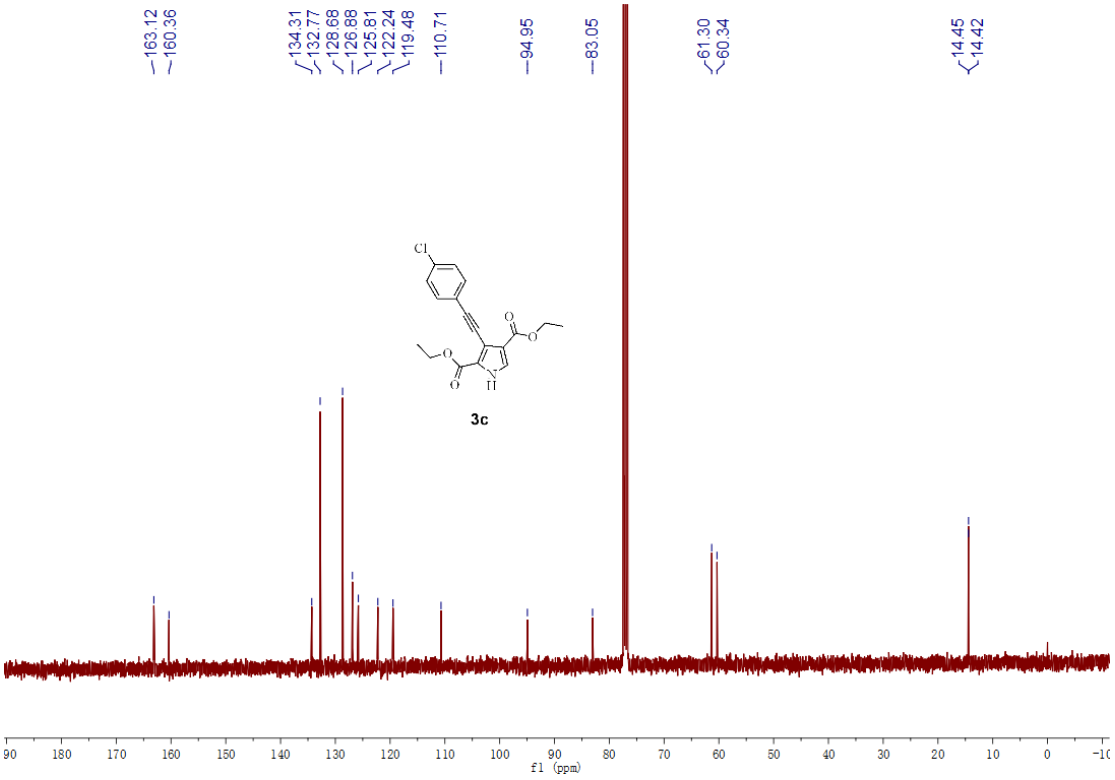
3.00
3.00
f1 (ppm)


163.12
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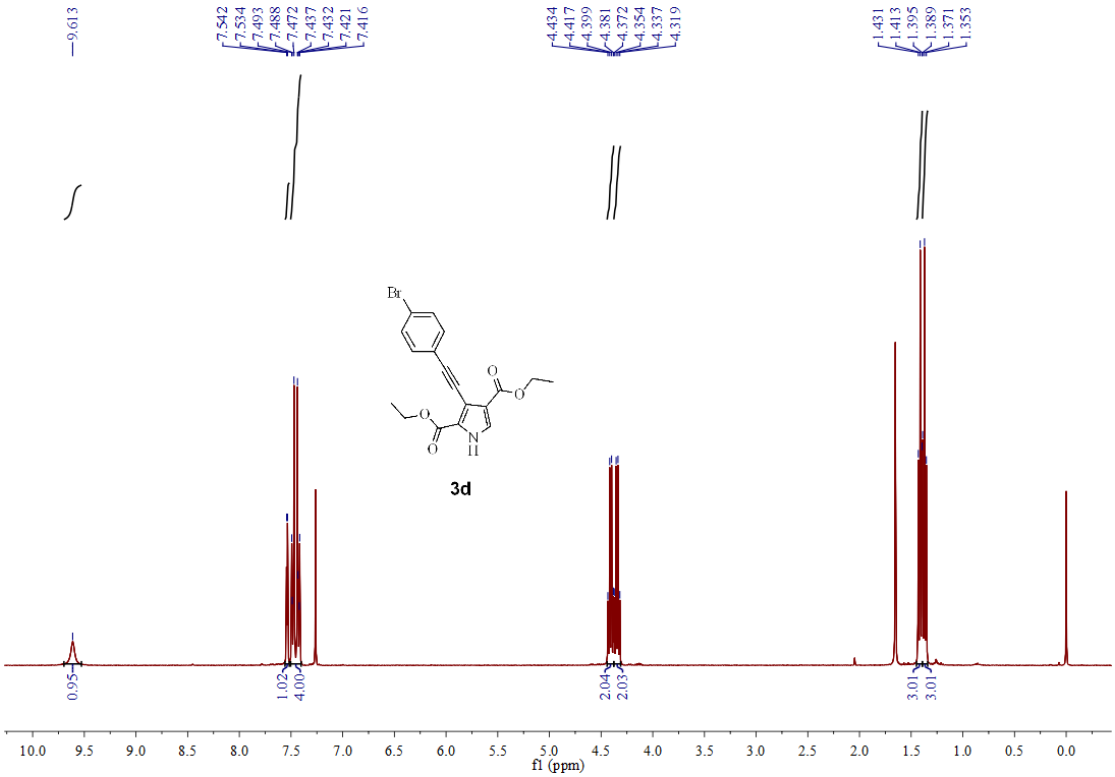
134.31
132.77
128.68
126.88
125.81
122.24
119.48
110.71
94.95
83.05
61.30
60.34
14.45
14.42
Cl
O
O
O
O
N
H
3c
f1 (ppm)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7.488
7.472
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7.421
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4.399
4.381
4.372
4.354
4.337
4.319
1.431
1.413
1.395
1.389
1.371
1.353
Br
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O
O
O
N
H
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4.00
2.04
2.03
3.01
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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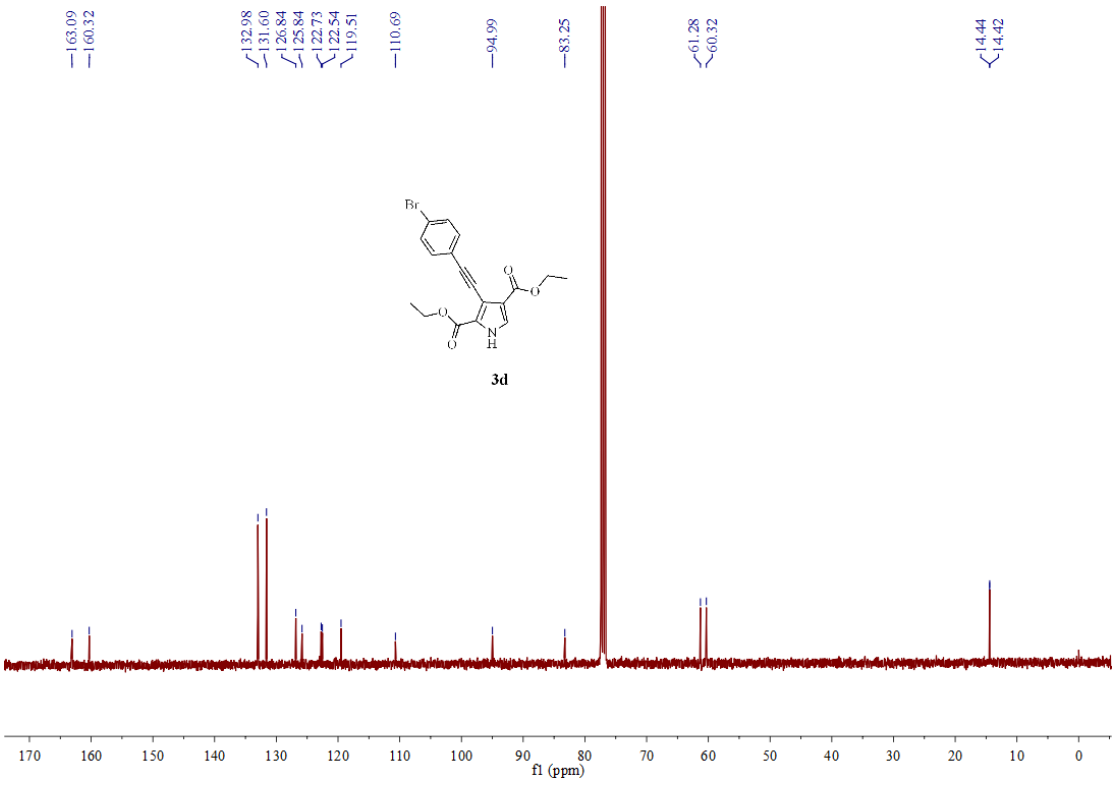
f1 (ppm)

3d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125.84
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61.28
60.32
14.44
14.42
Br
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O
O
O
N
H
170
160
150
140
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120
110
100
90
80
70
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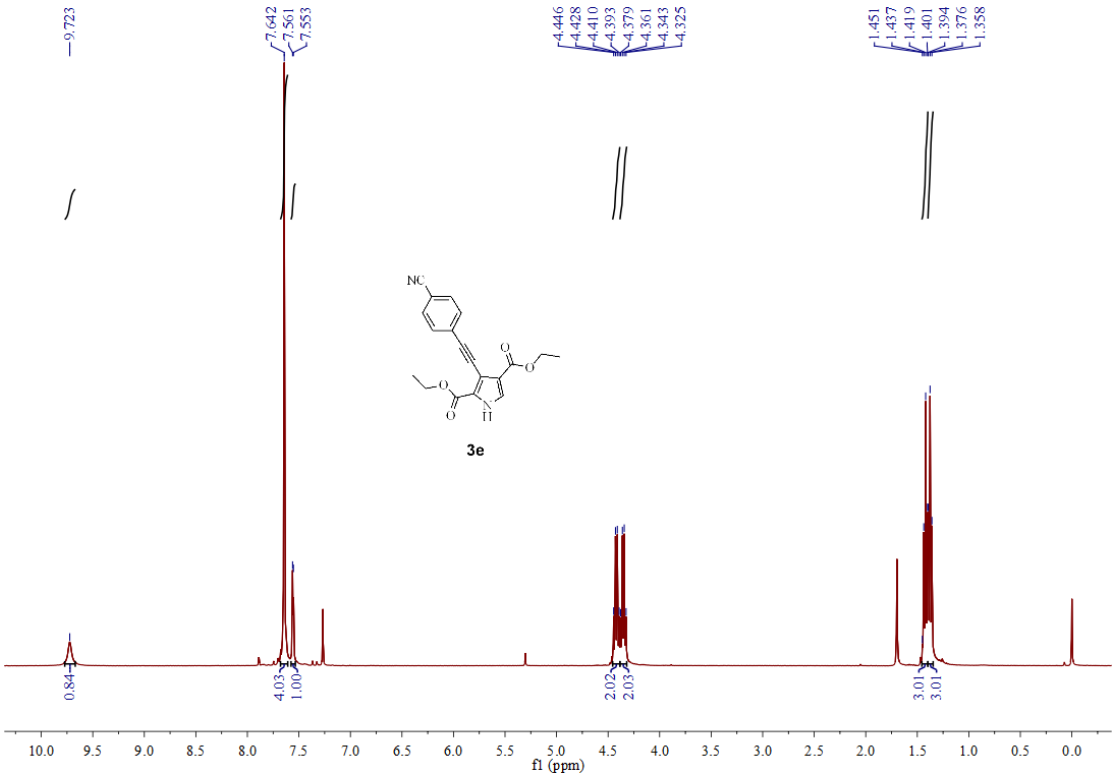
40
30
20
10
0
f1 (ppm)

3d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1.437
1.419
1.401
1.394
1.376
1.358
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O
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N
H
3e
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4.03
1.00
2.02
2.03
3.01
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.0
2.5
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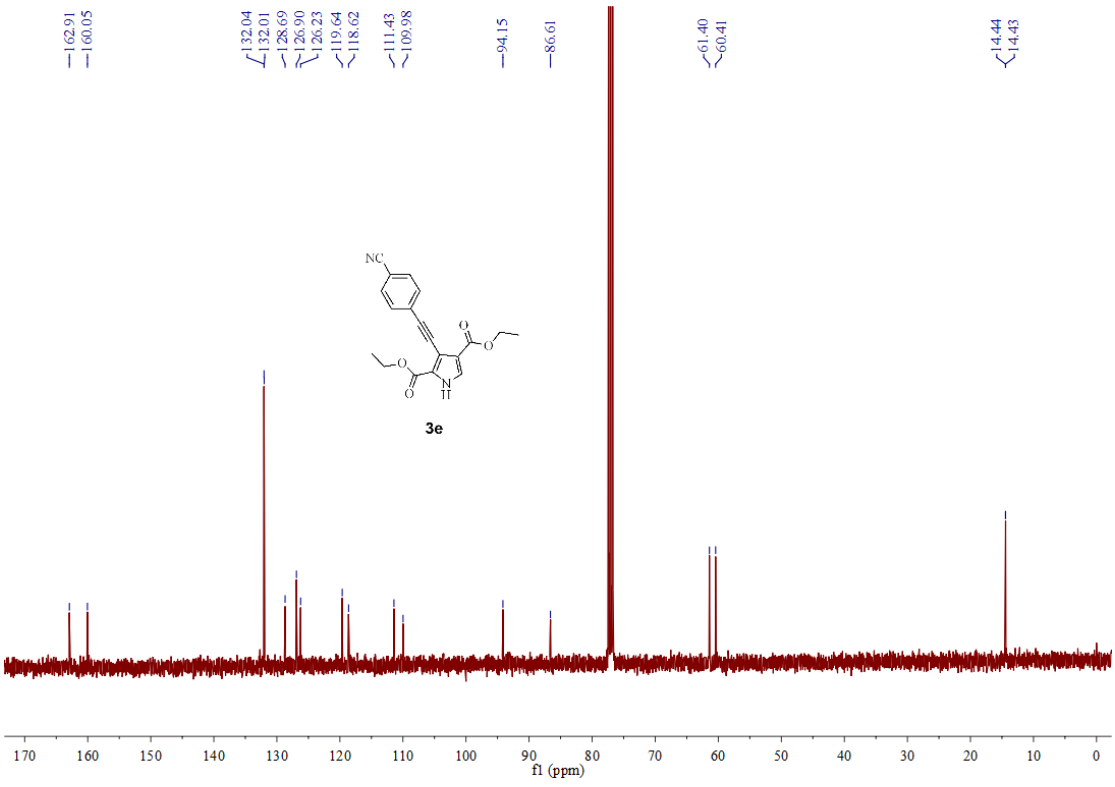
0.0
f1 (ppm)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132.01
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126.90
126.23
119.64
118.62
111.43
109.98
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14.43
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N
H
3e
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160
150
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130
120
110
100
90
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50
40
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10
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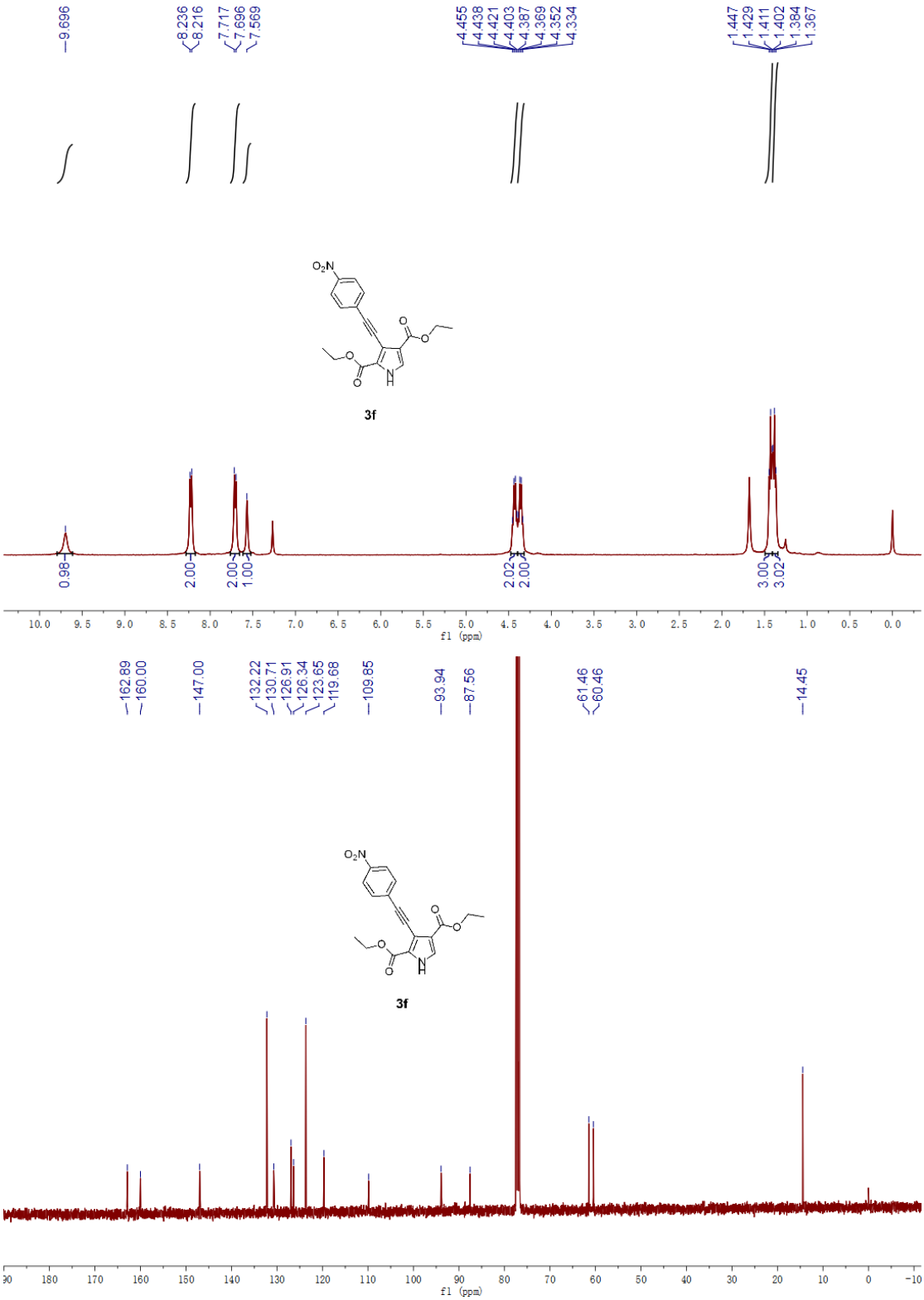
f1 (ppm)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4.438
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4.403
4.387
4.369
4.352
4.334
1.447
1.429
1.411
1.402
1.384
1.367
O2N
3f
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2.00
2.00
1.00
2.02
2.00
3.00
3.02
f1 (ppm)
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160.00
147.00
132.22
130.71
126.91
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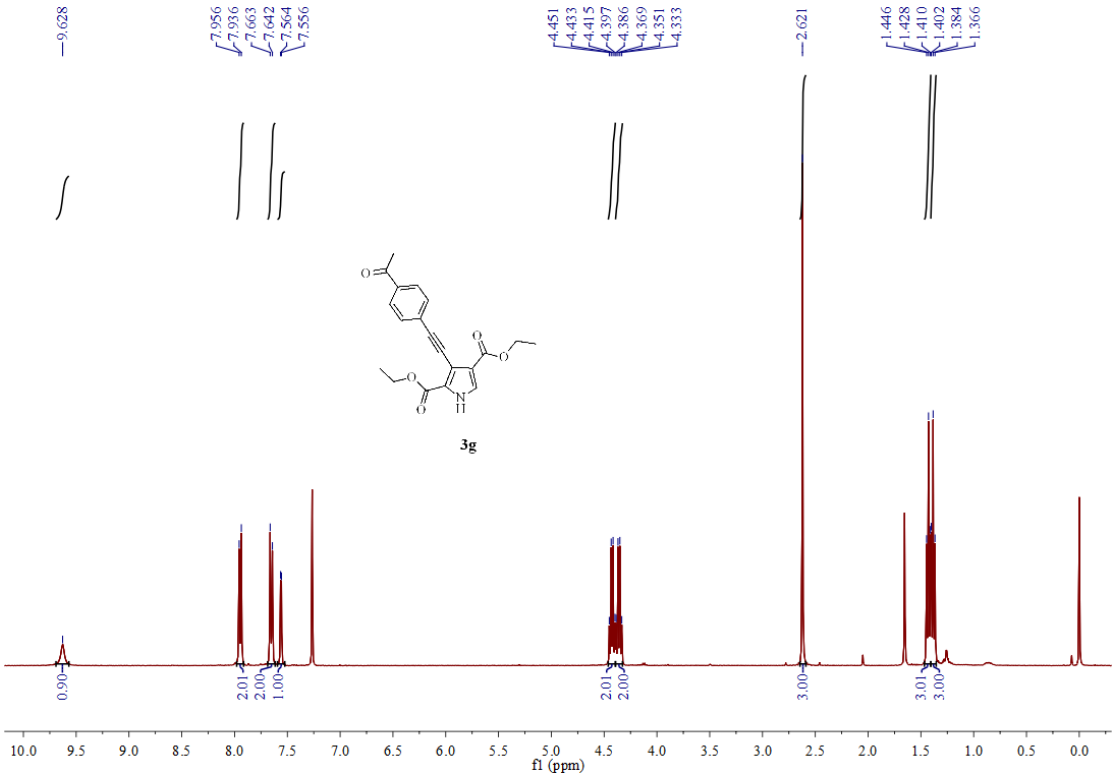
60.46
14.45
O2N
3f
f1 (ppm)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4.351
4.333
2.621
1.446
1.428
1.410
1.402
1.384
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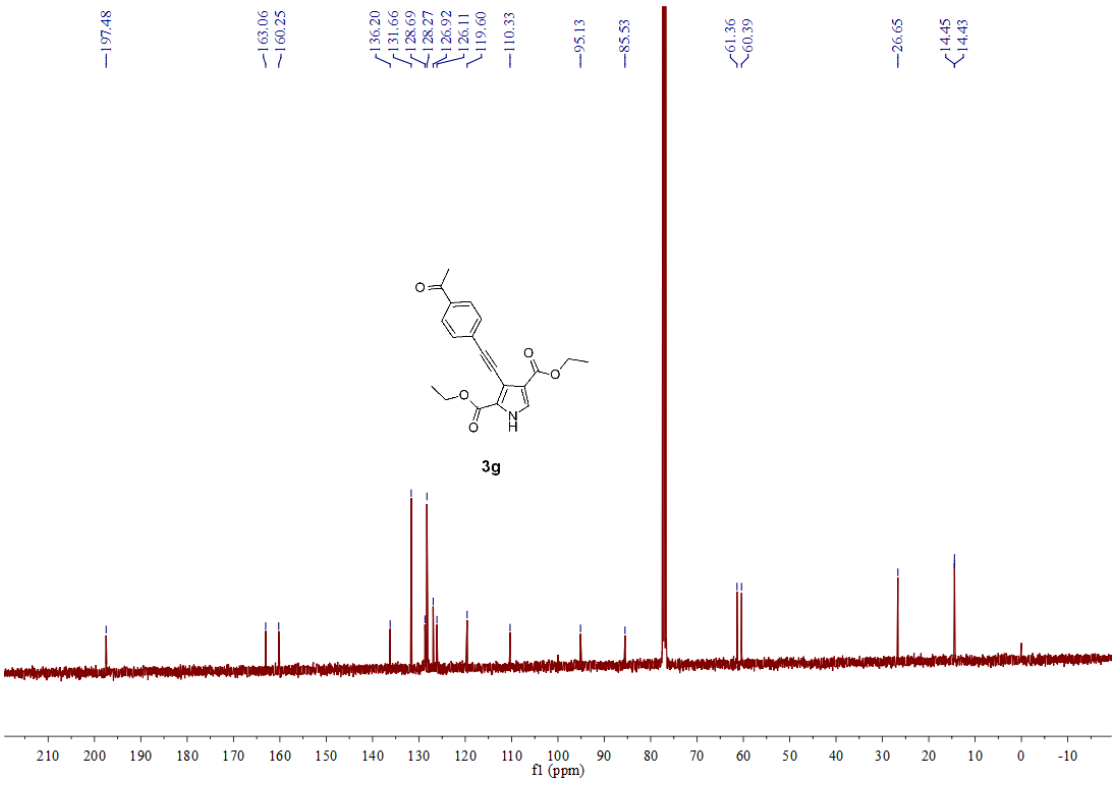
3.00
3.01
3.00
f1 (ppm)

3g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131.66
128.69
128.27
126.92
126.11
119.60
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95.13
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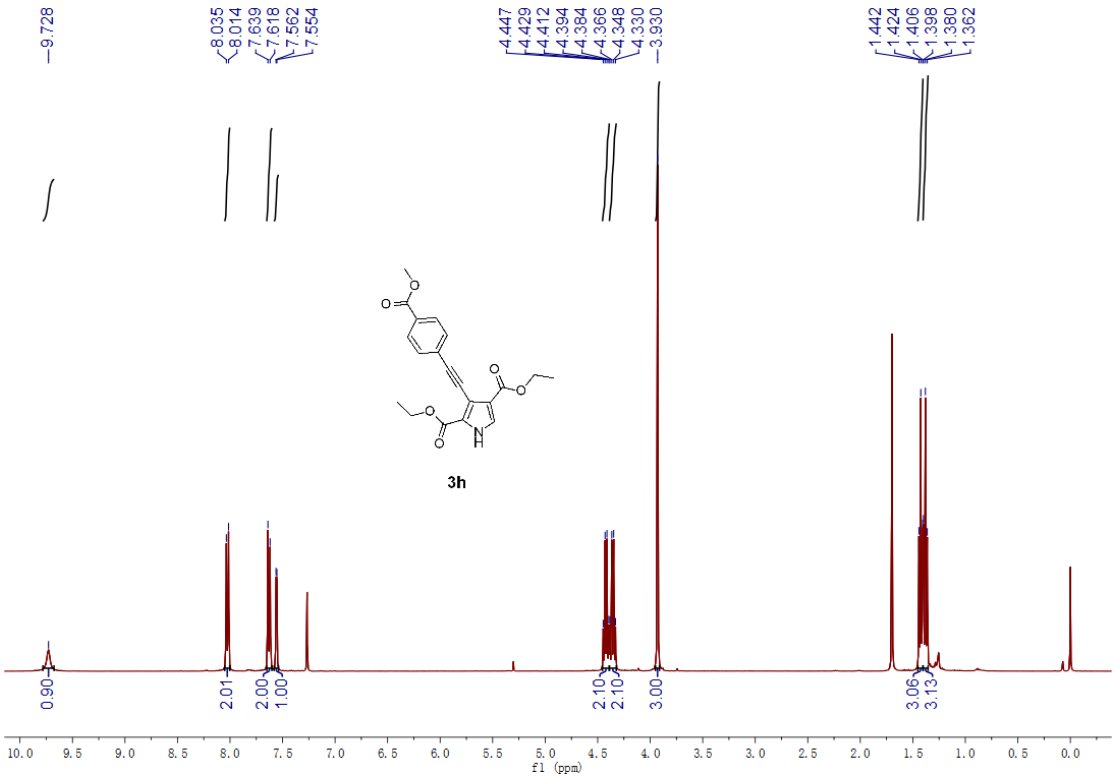
26.65
14.45
14.43
f1 (ppm)

3g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4.348
4.330
3.930
1.442
1.424
1.406
1.398
1.380
1.362
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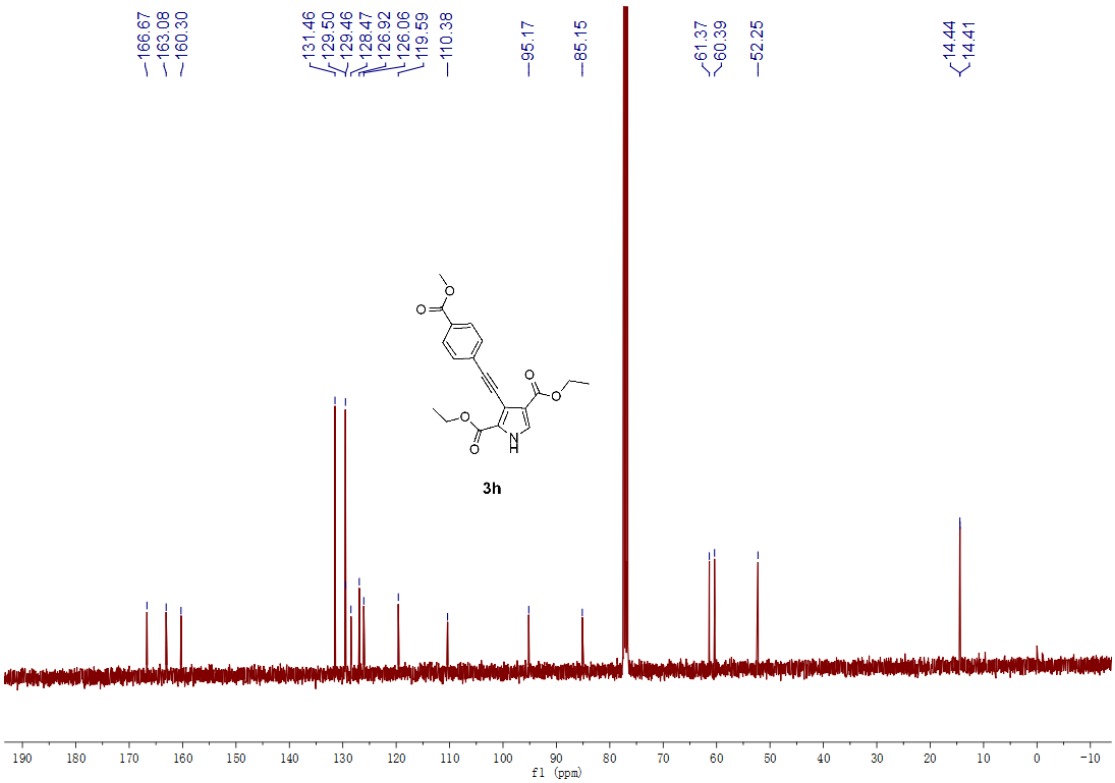
1.00
2.10
2.10
3.00
3.06
3.13
f1 (ppm)

3h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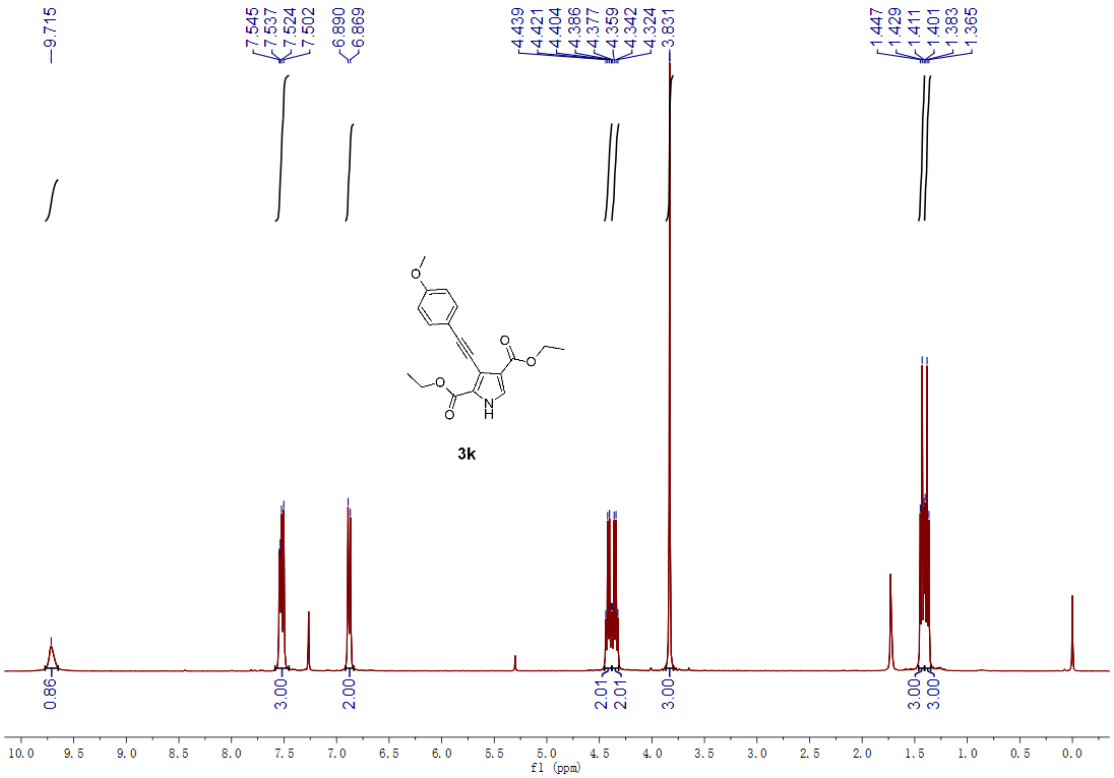
14.41
f1 (ppm)

3h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4.377
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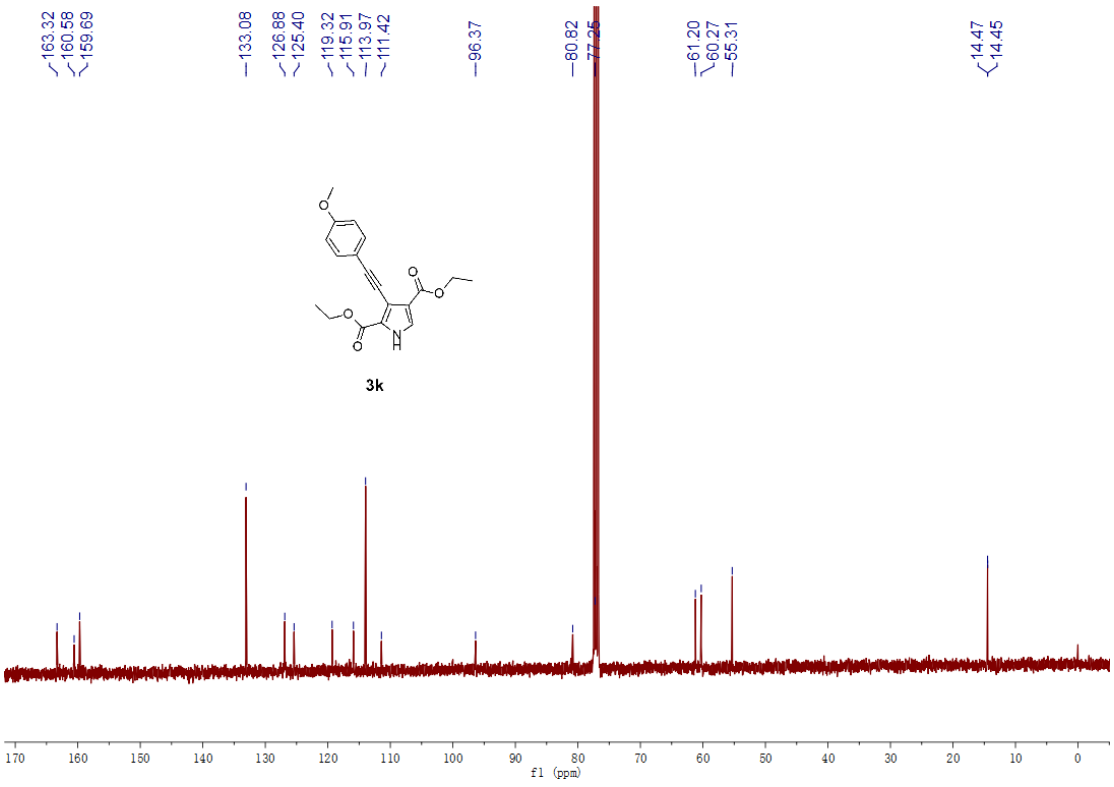
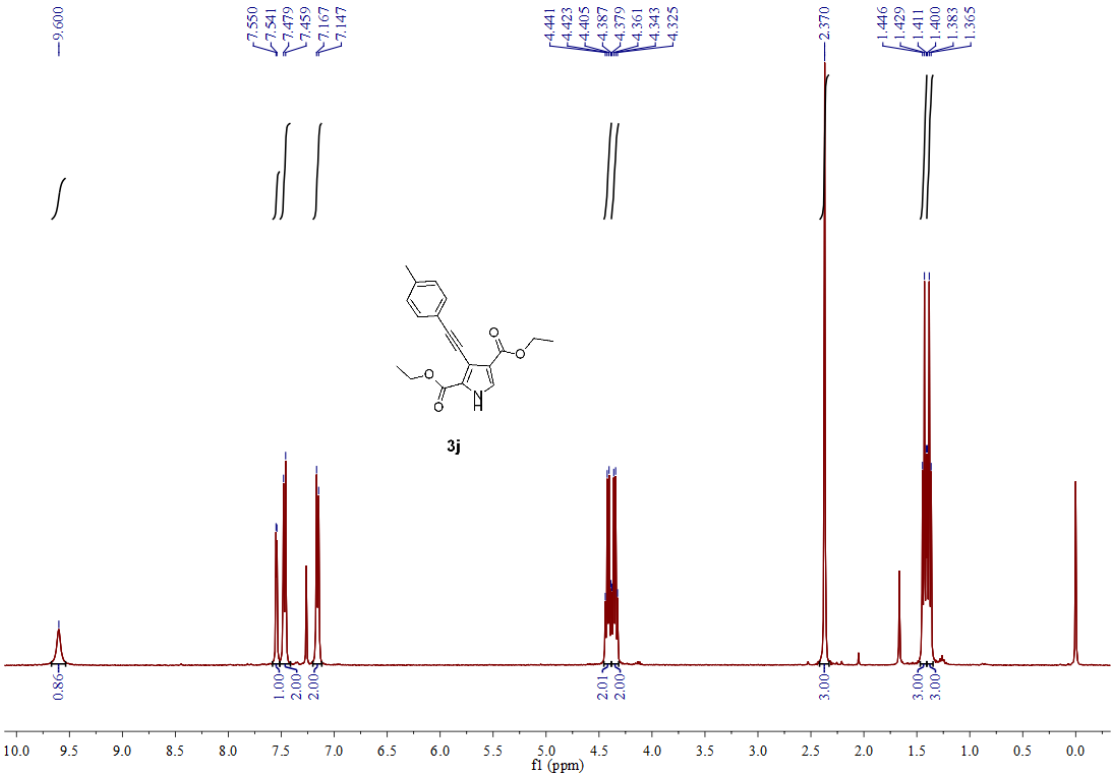
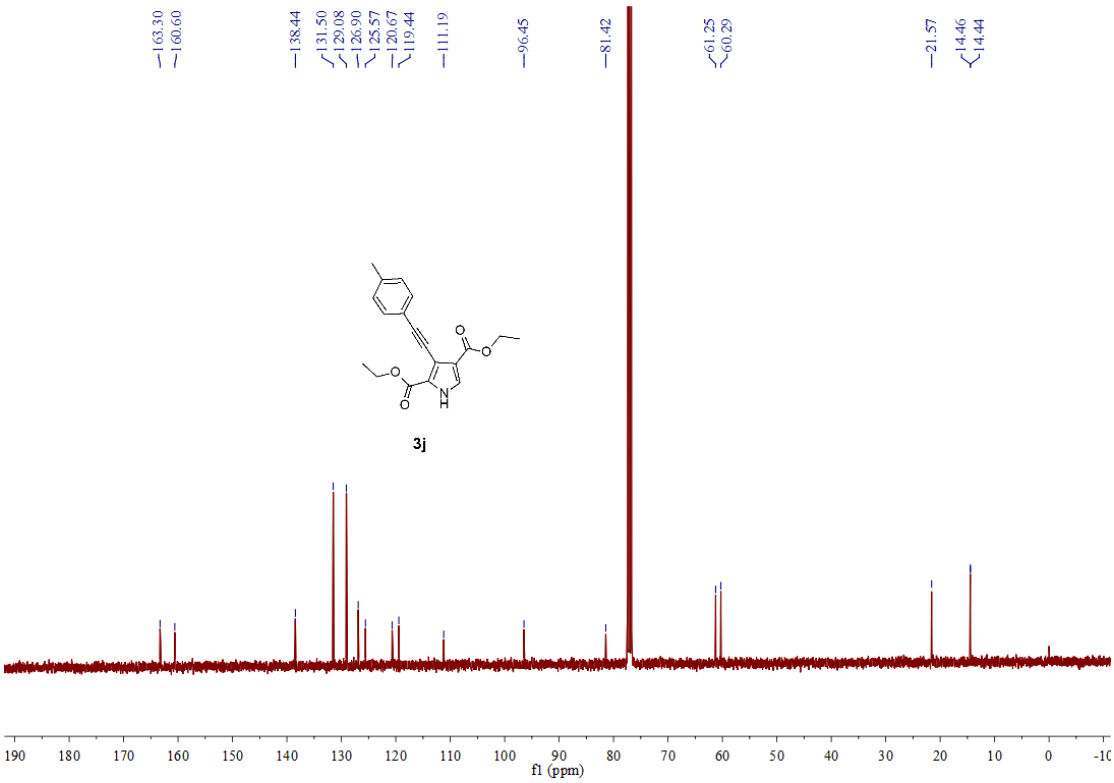
4.342
4.324
3.831
1.447
1.429
1.411
1.401
1.383
1.365
3k
0.86
3.00
2.00
2.01
2.01
3.00
3.00
3.00
f1 (ppm)

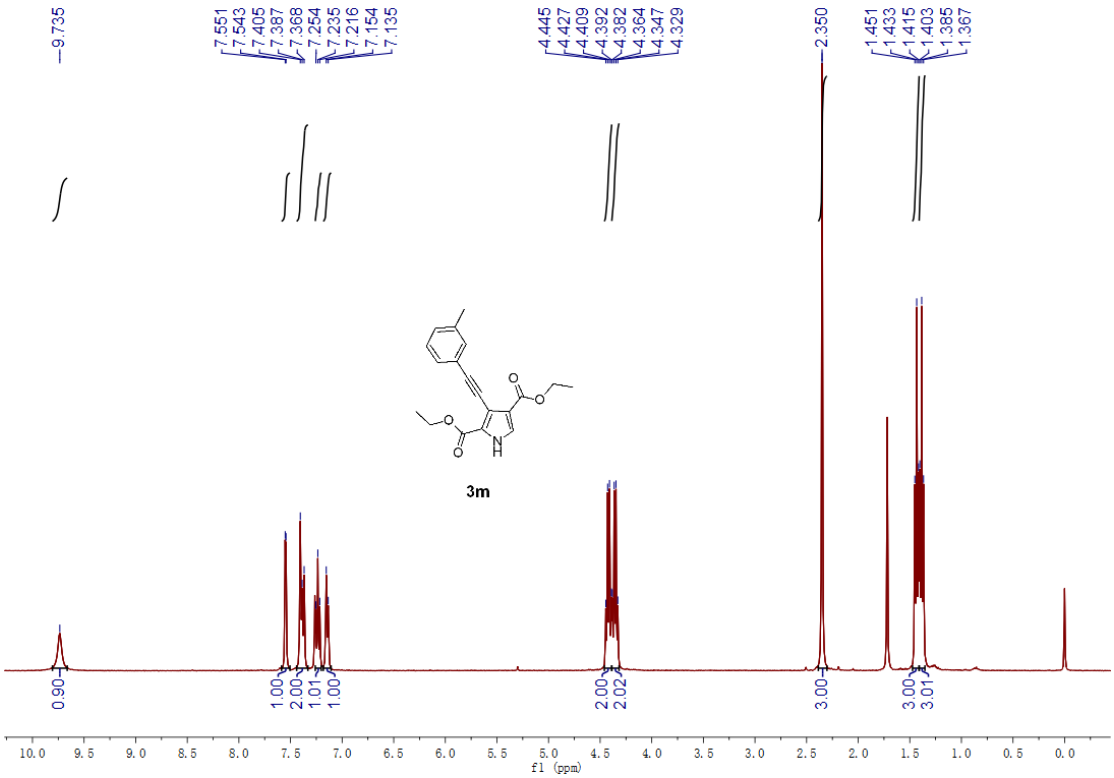

163.32
160.58
159.69
133.08
126.88
125.40
119.32
115.91
113.97
111.42
96.37
80.82
77.26
61.20
60.27
55.31
14.47
14.45
3k
f1 (ppm)


9.600
7.550
7.541
7.479
7.459
7.167
7.147
4.441
4.423
4.405
4.387
4.379
4.361
4.343
4.325
2.370
1.446
1.429
1.411
1.400
1.383
1.365
0.86
1.00
2.00
2.00
2.01
2.00
3.00
3.00
3.00
f1 (ppm)

3j


163.30
160.60
138.44
131.50
129.08
126.90
125.57
120.67
119.44
111.19
96.45
81.42
61.25
60.29
21.57
14.46
14.44
f1 (ppm)

3j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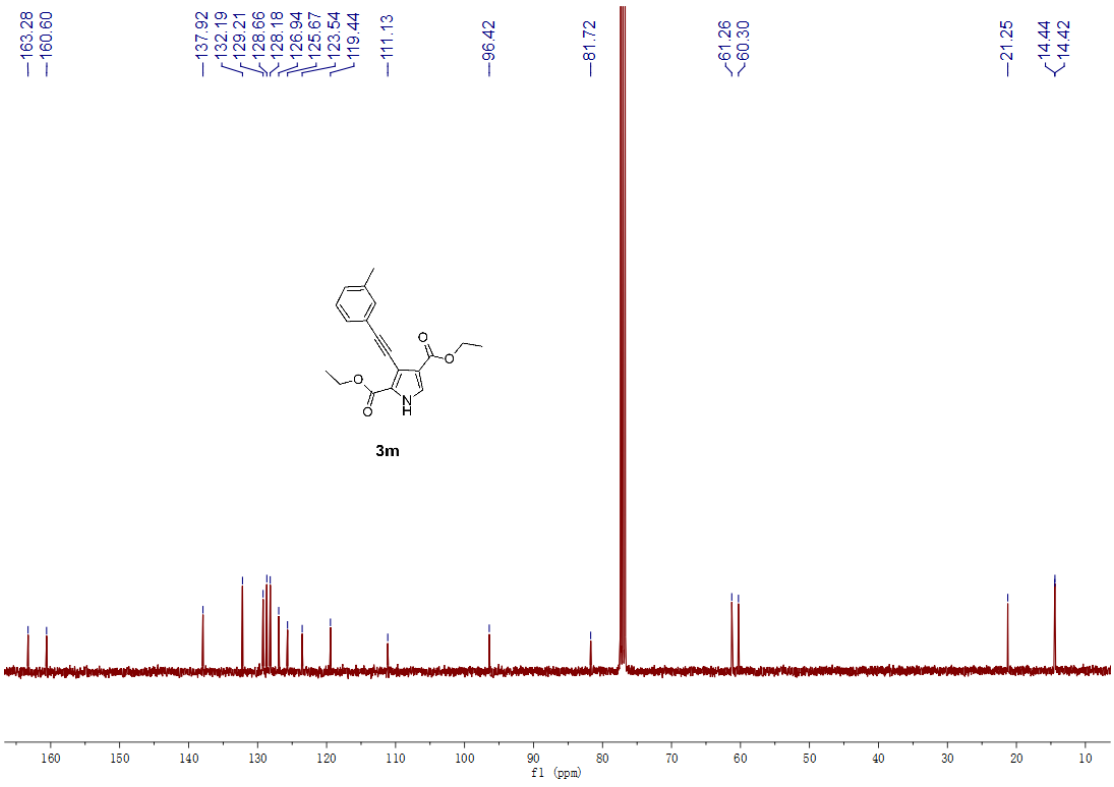
7.543
7.405
7.387
7.368
7.254
7.235
7.216
7.154
7.135
4.445
4.427
4.409
4.392
4.382
4.364
4.347
4.329
2.350
1.451
1.433
1.415
1.403
1.385
1.367
3m
0.90
1.00
2.00
1.01
1.00
2.00
2.02
3.00
3.00
3.01
f1 (ppm)


163.28
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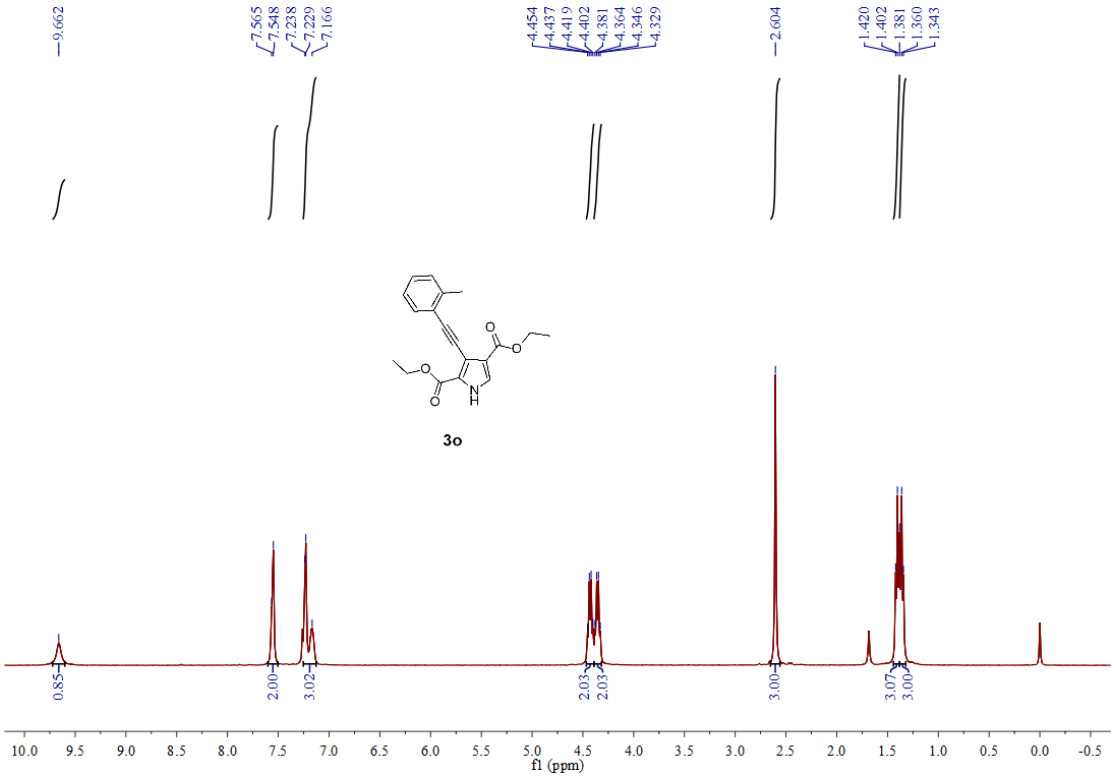
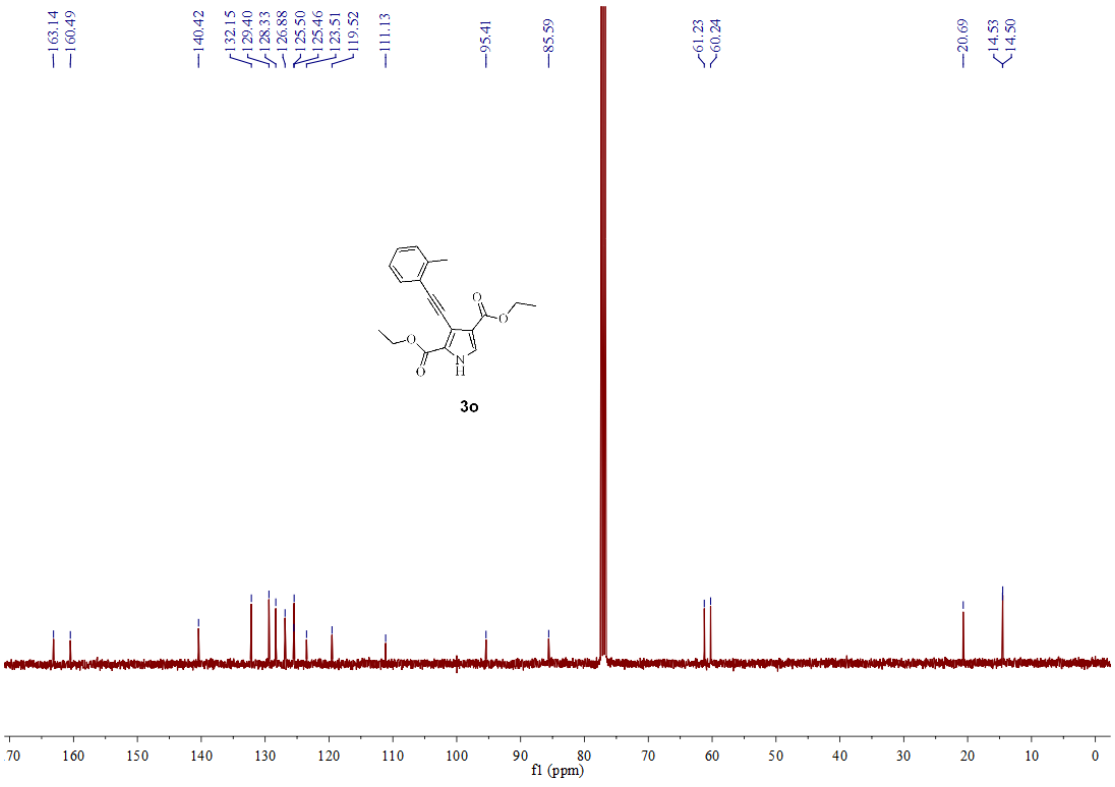
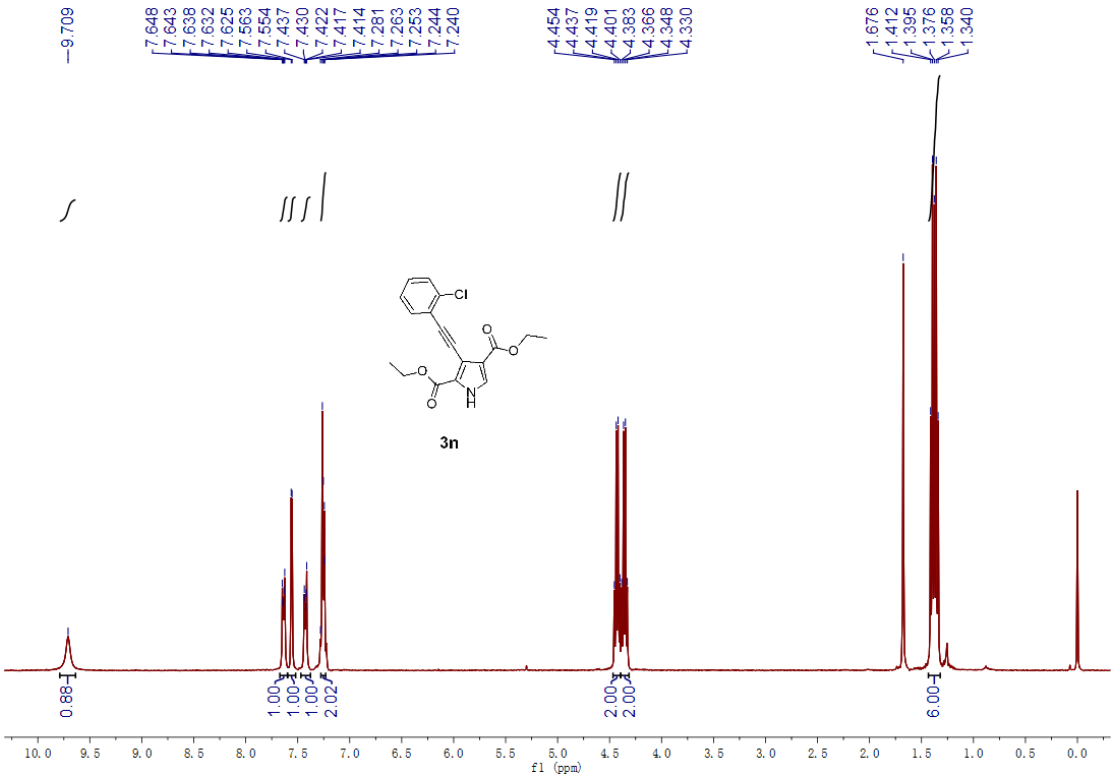
137.92
132.19
129.21
128.66
128.18
126.94
125.67
123.54
119.44
111.13
96.42
81.72
61.26
60.30
21.25
14.44
14.42
3m
f1 (ppm)


9.662
7.565
7.548
7.238
7.229
7.166
4.454
4.437
4.419
4.402
4.381
4.364
4.346
4.329
2.604
1.420
1.402
1.381
1.360
1.343
3o
0.85
2.00
3.02
2.03
2.03
3.00
3.07
3.00
f1 (ppm)


163.14
160.49
140.42
132.15
129.40
128.33
126.88
125.50
125.46
123.51
119.52
111.13
95.41
85.59
61.23
60.24
20.69
14.53
14.50
3o
f1 (ppm)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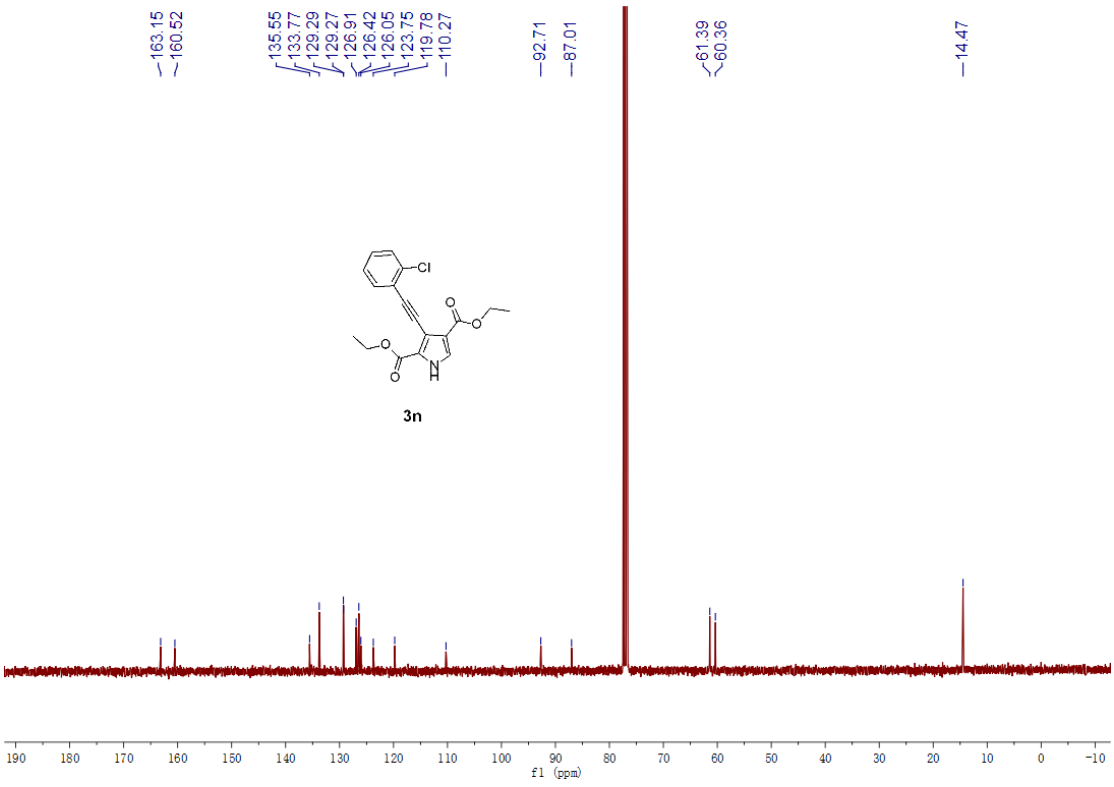
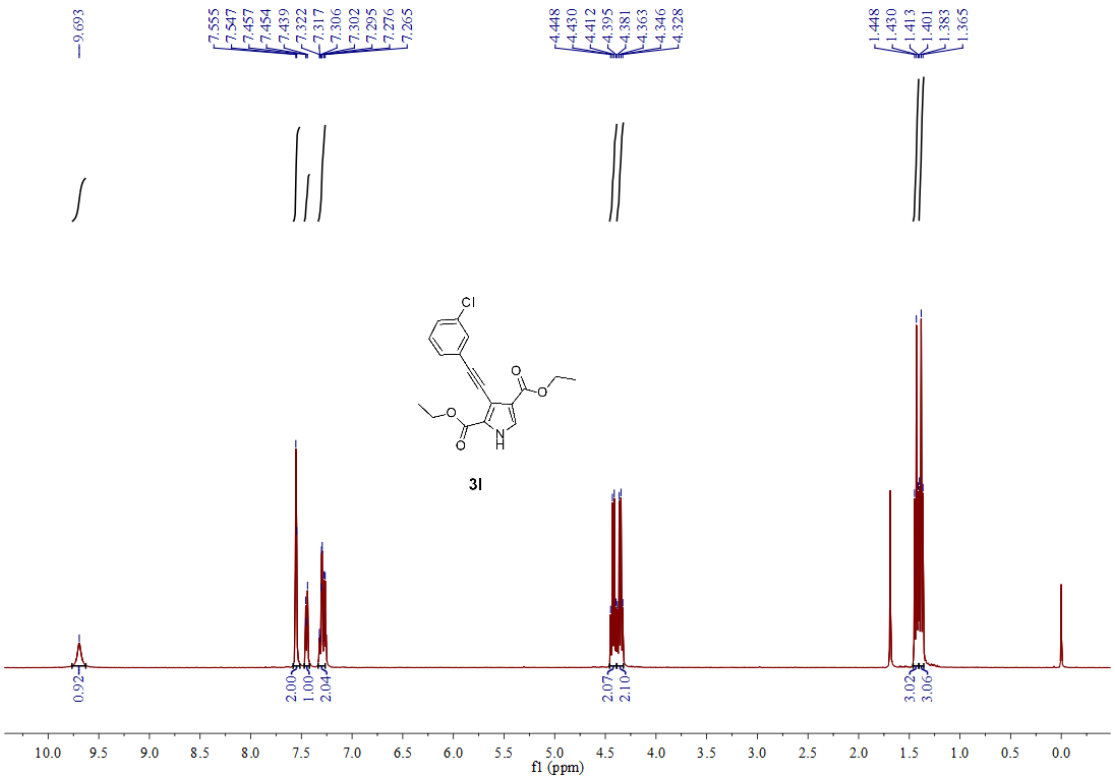
7.648
7.643
7.638
7.632
7.625
7.563
7.554
7.437
7.430
7.422
7.417
7.414
7.281
7.263
7.253
7.244
7.240
4.454
4.437
4.419
4.401
4.383
4.366
4.348
4.330
1.676
1.412
1.395
1.376
1.358
1.340
Cl
O
O
O
O
N
H
3n
0.88
1.00
1.00
1.00
2.02
2.00
2.00
6.00
f1 (ppm)


163.15
160.52
135.55
133.77
129.29
129.27
126.91
126.42
126.05
123.75
119.78
110.27
92.71
87.01
61.39
60.36
14.47
Cl
O
O
O
O
N
H
3n
f1 (ppm)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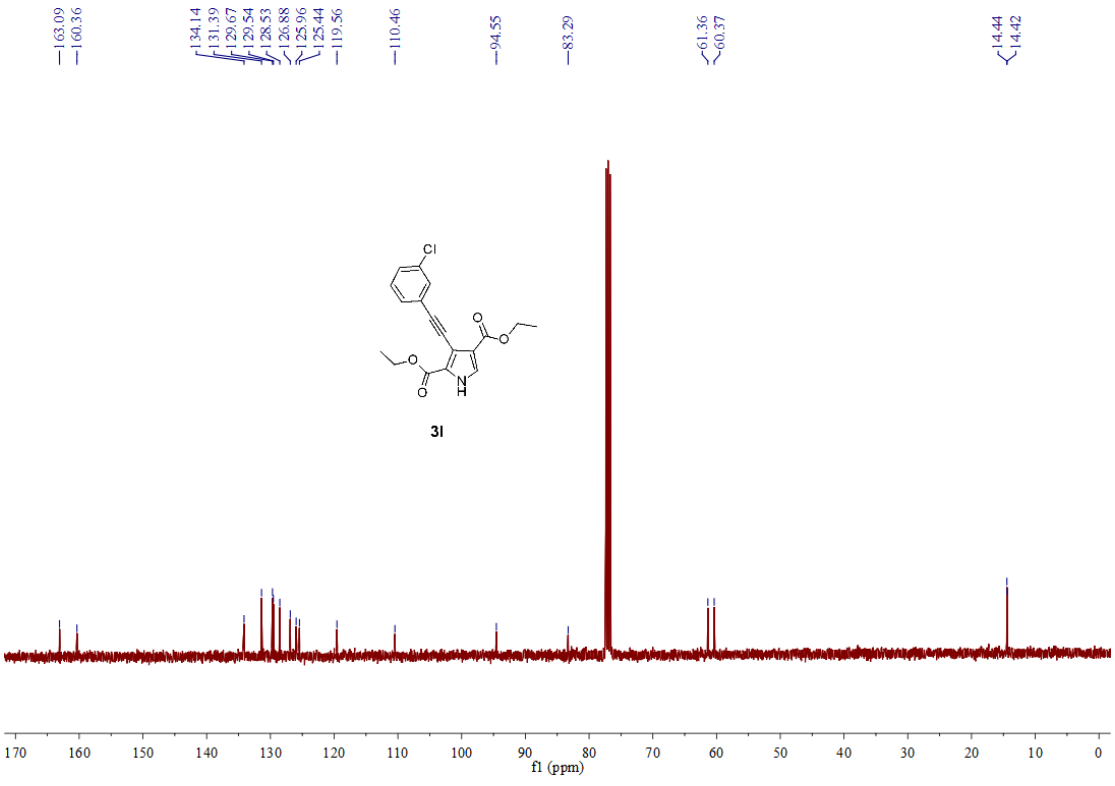
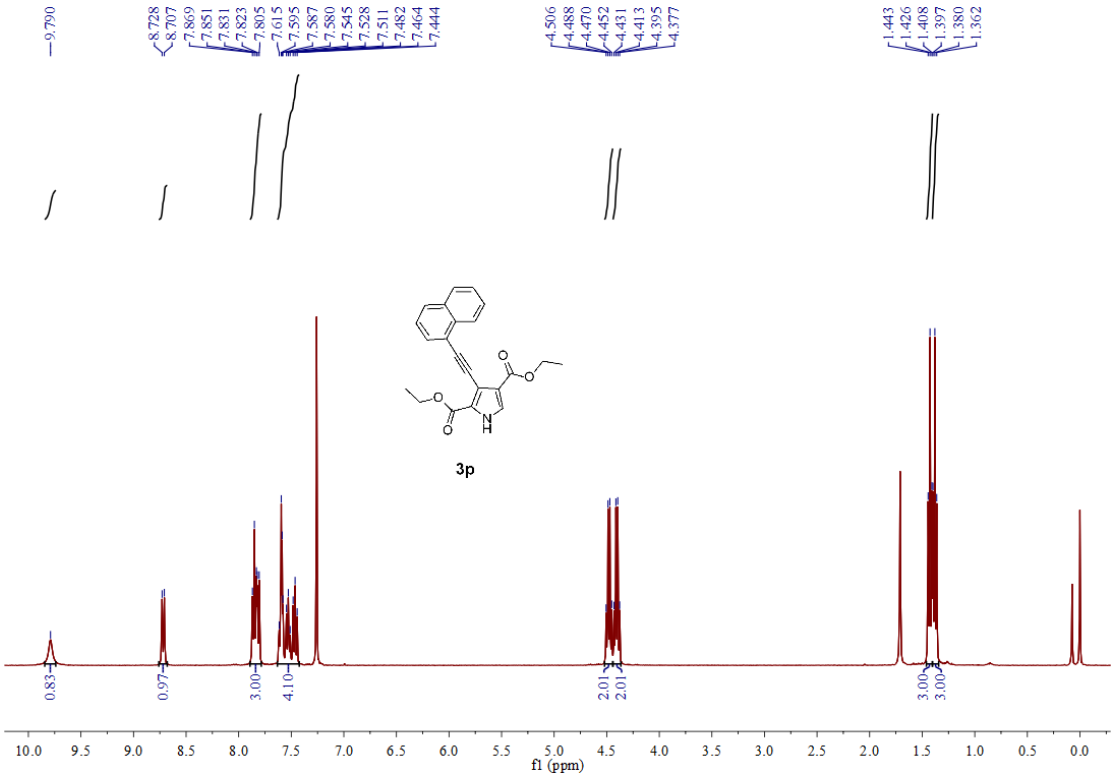
7.547
7.457
7.454
7.439
7.322
7.317
7.306
7.302
7.295
7.276
7.265
4.448
4.430
4.412
4.395
4.381
4.363
4.346
4.328
1.448
1.430
1.413
1.401
1.383
1.365
Cl
O
O
O
O
H
N
3l
0.92
2.00
1.00
2.04
2.07
2.10
3.02
3.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


163.09
160.36
134.14
131.39
129.67
129.54
128.53
126.88
125.96
125.44
119.56
110.46
94.55
83.29
61.36
60.37
14.44
14.42
Cl
O
O
O
O
H
N
3l
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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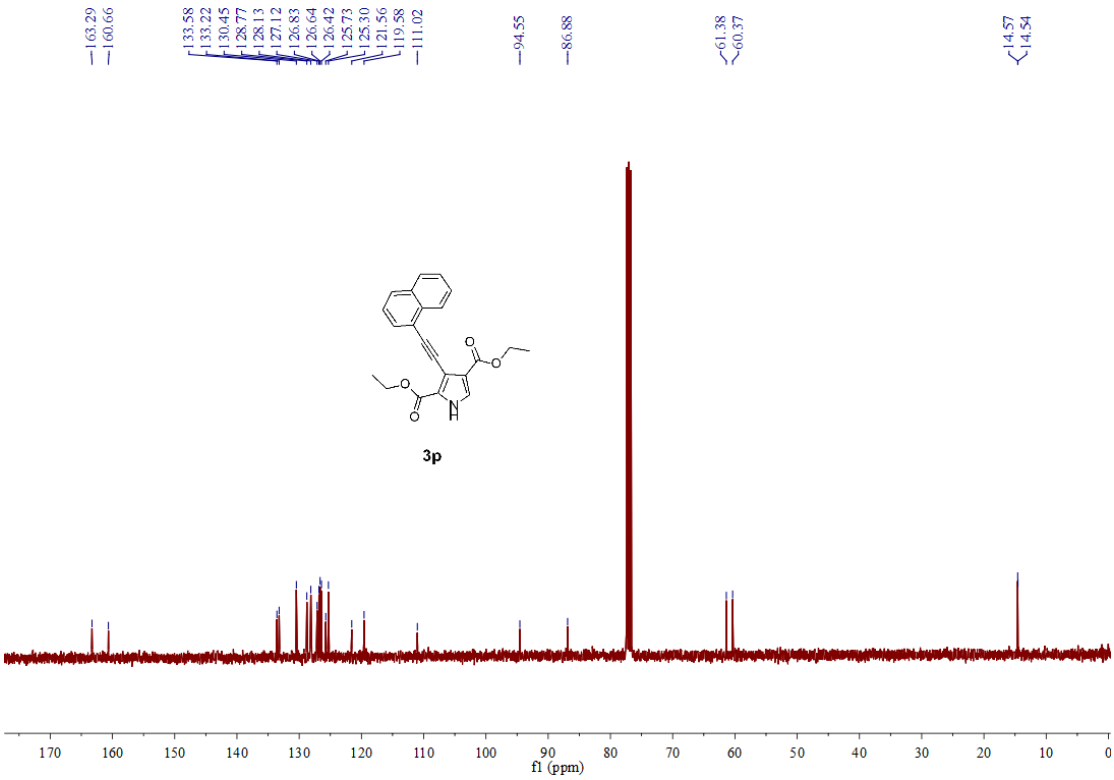
8.728
8.707
7.869
7.851
7.831
7.823
7.805
7.615
7.595
7.587
7.580
7.545
7.528
7.511
7.482
7.464
7.444
4.506
4.488
4.470
4.452
4.431
4.413
4.395
4.377
1.443
1.426
1.408
1.397
1.380
1.362
3p
0.83
0.97
3.00
4.10
2.01
2.01
3.00
3.00
f1 (ppm)


163.29
160.66
133.58
133.22
130.45
128.77
128.13
127.12
126.83
126.64
126.42
125.73
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111.02
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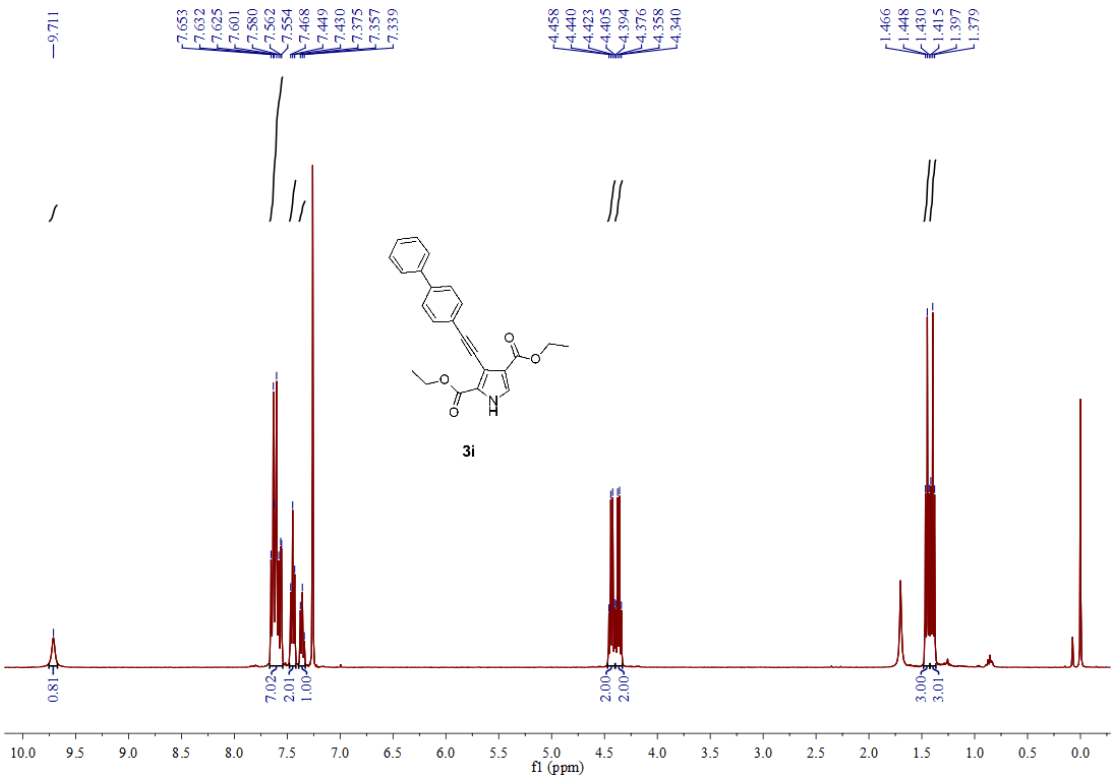
60.37
14.57
14.54
3p
f1 (ppm)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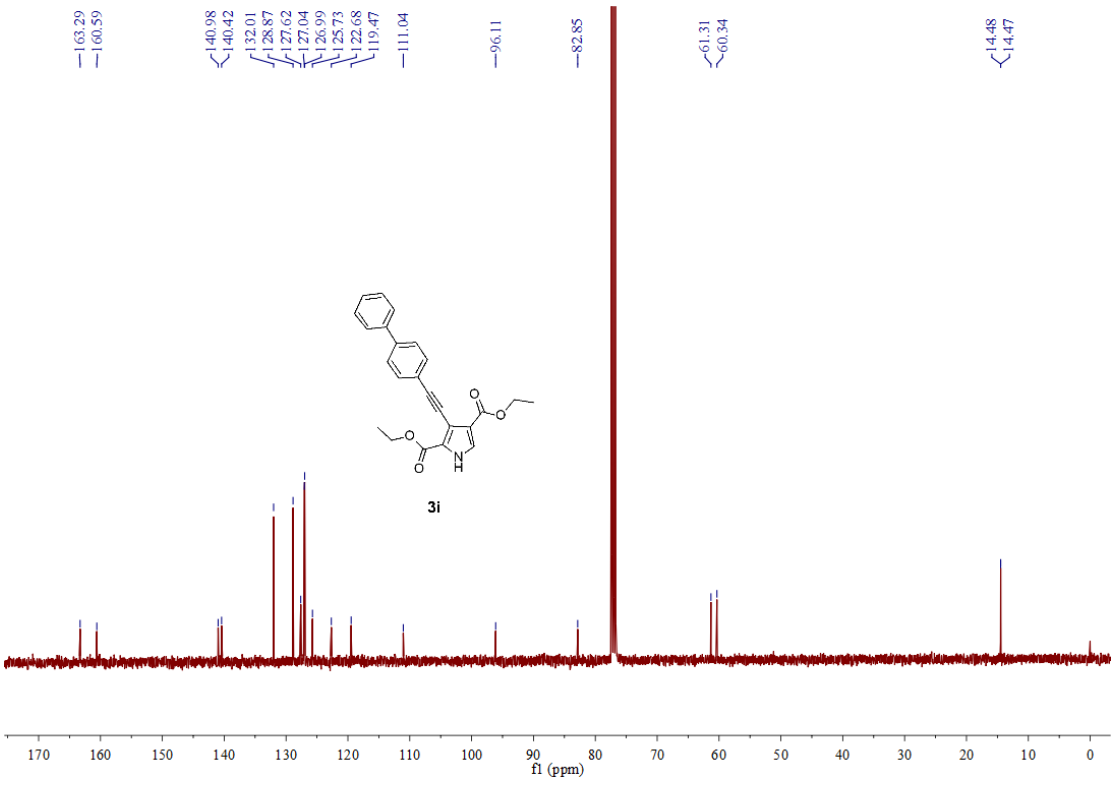
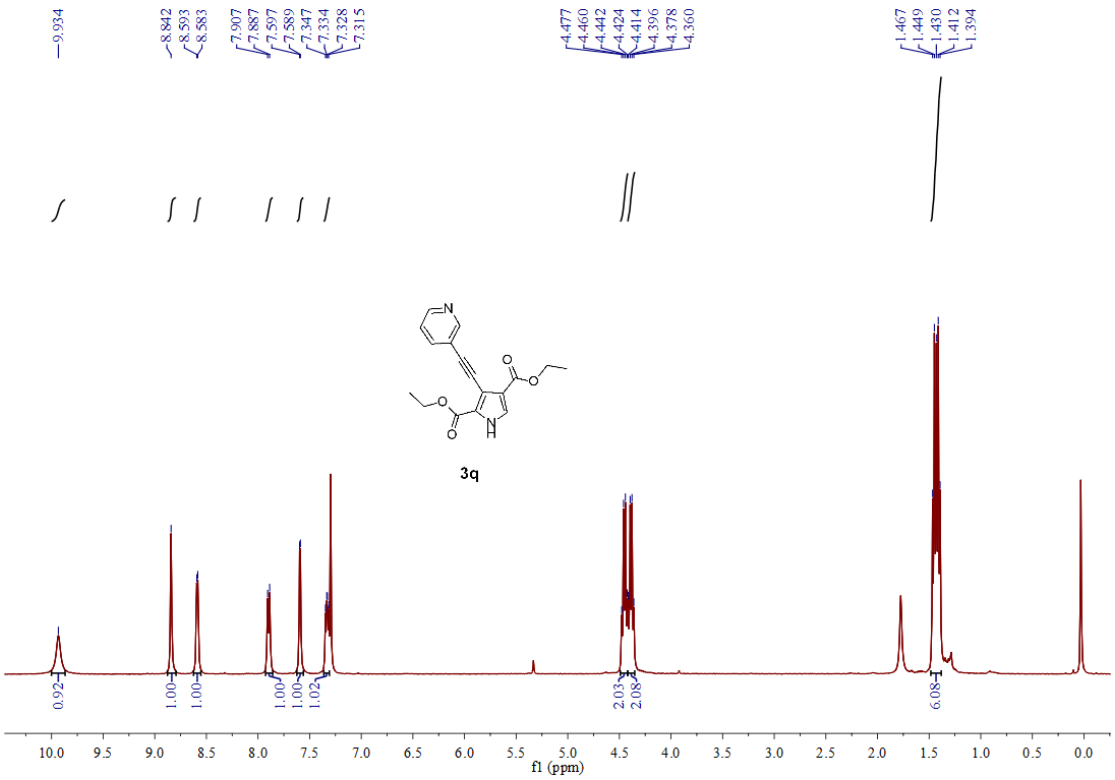
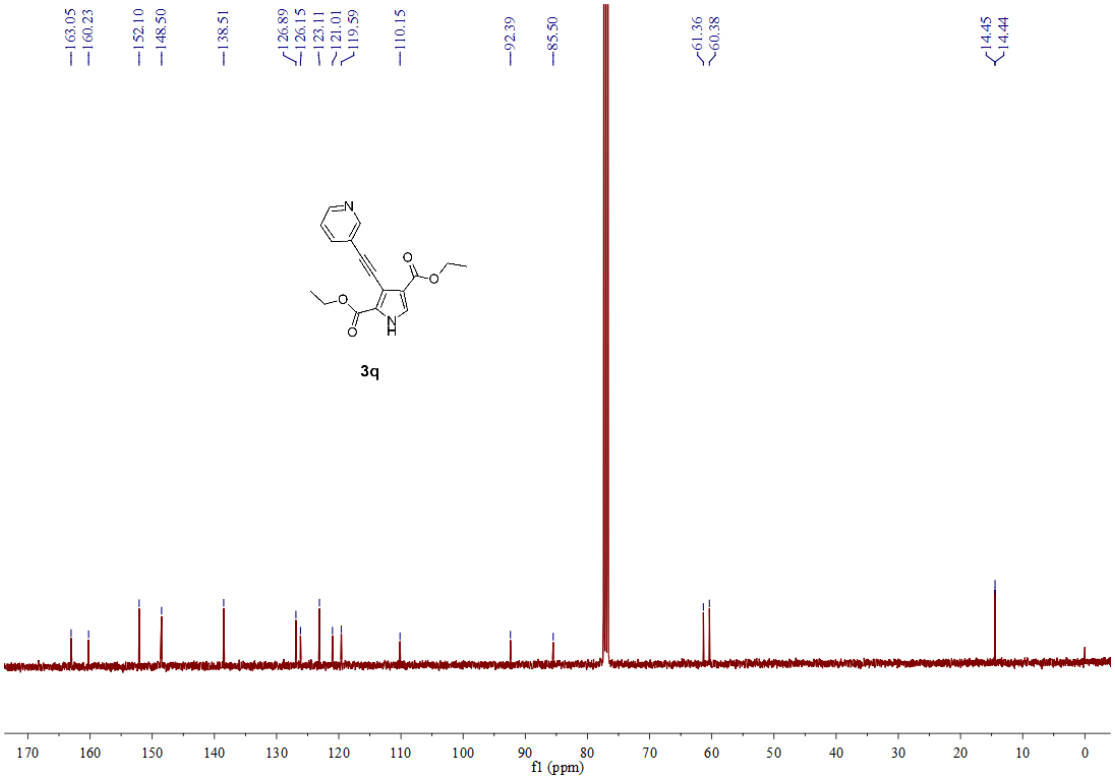
7.625
7.601
7.580
7.562
7.554
7.468
7.449
7.430
7.375
7.357
7.339
4.458
4.440
4.423
4.405
4.394
4.376
4.358
4.340
1.466
1.448
1.430
1.415
1.397
1.379
0.81
7.02
2.01
1.00
2.00
2.00
3.00
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

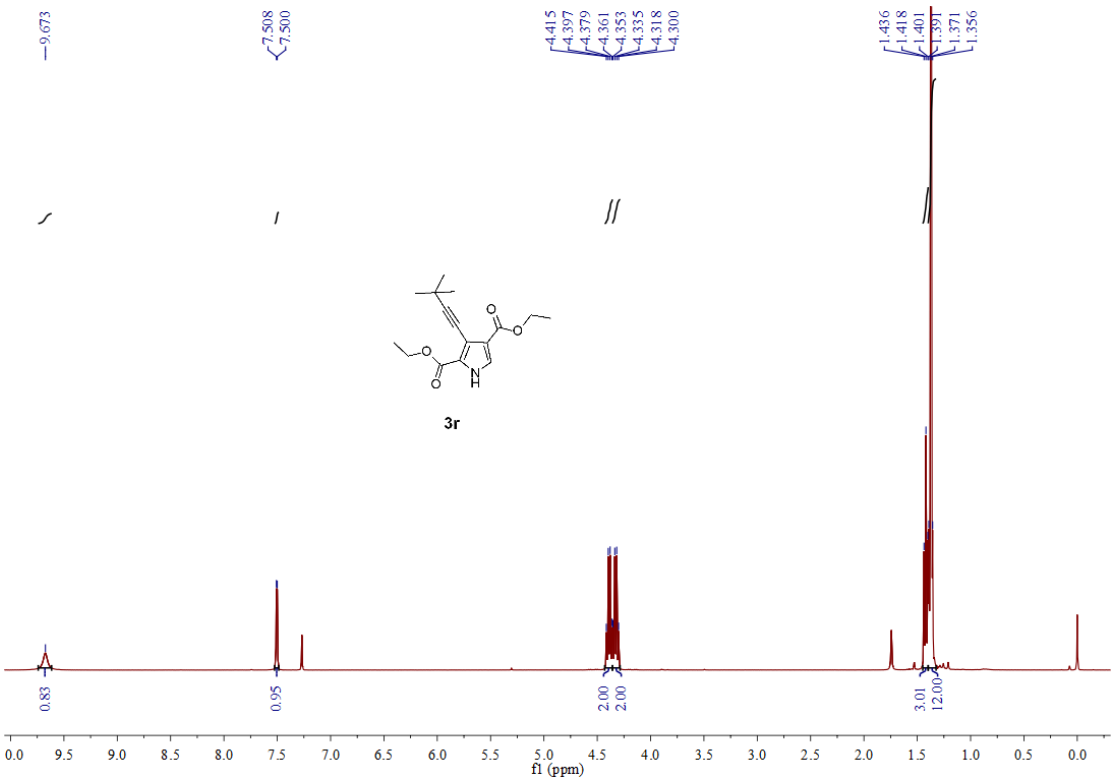
3i


163.29
160.59
140.98
140.42
132.01
128.87
127.62
127.04
126.99
125.73
122.68
119.47
111.04
96.11
82.85
61.31
60.34
14.48
14.47
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

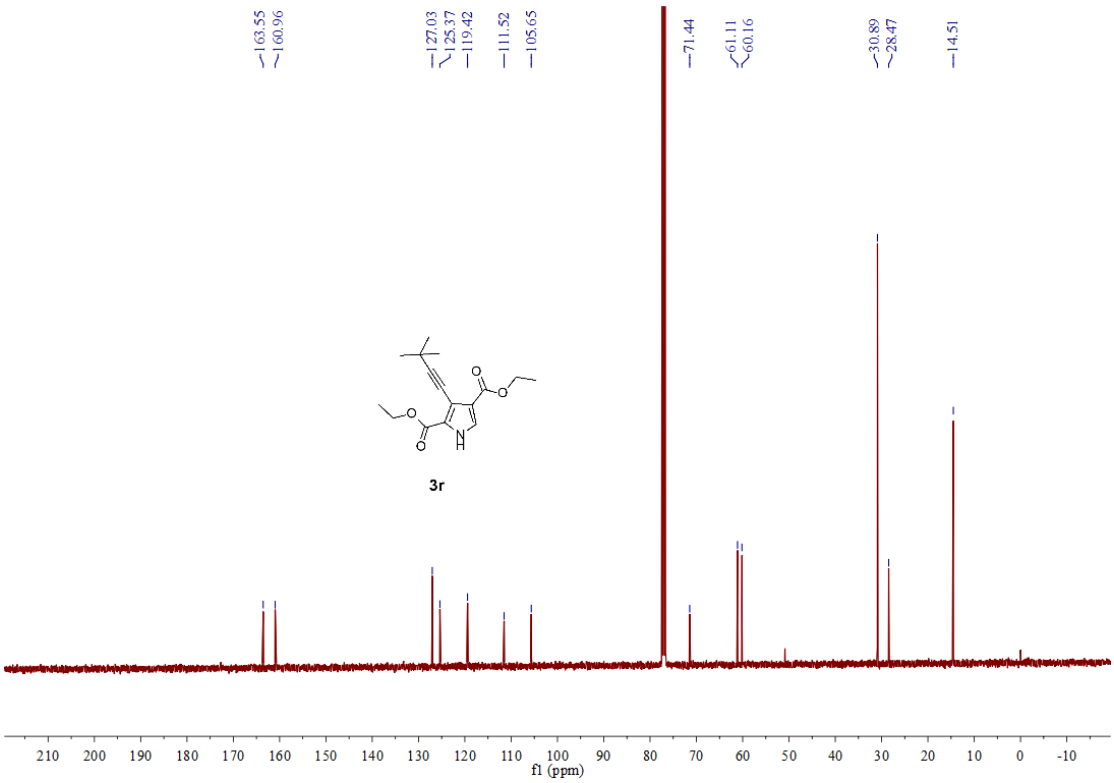
3i


9.934
8.842
8.593
8.583
7.907
7.887
7.597
7.589
7.347
7.334
7.328
7.315
4.477
4.460
4.442
4.424
4.414
4.396
4.378
4.360
1.467
1.449
1.430
1.412
1.394
3q
0.92
1.00
1.00
1.00
1.00
1.02
2.03
2.08
6.08
f1 (ppm)

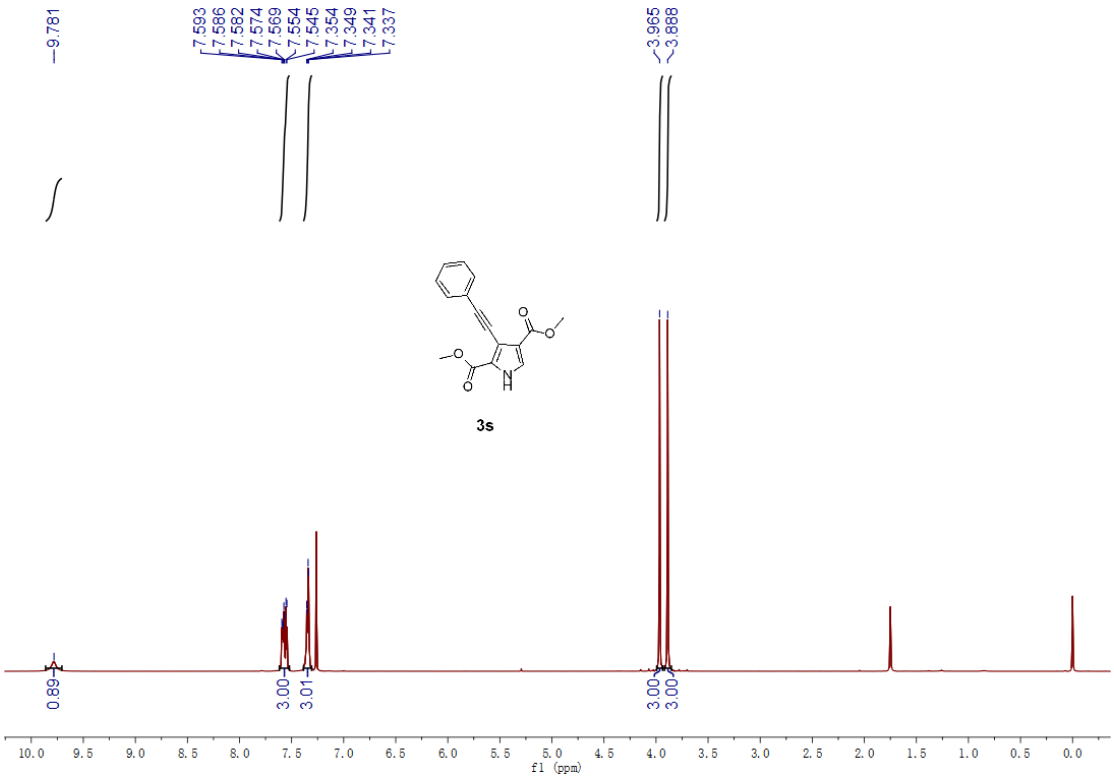

163.05
160.23
152.10
148.50
138.51
126.89
126.15
123.11
121.01
119.59
110.15
92.39
85.50
61.36
60.38
14.45
14.44
3q
f1 (ppm)


9.673
7.508
7.500
4.415
4.397
4.379
4.361
4.353
4.335
4.318
4.300
1.436
1.418
1.401
1.391
1.371
1.356
0.83
0.95
2.00
2.00
3.01
12.00
f1 (ppm)

3r


163.55
160.96
127.03
125.37
119.42
111.52
105.65
71.44
61.11
60.16
30.89
28.47
14.51
f1 (ppm)

3r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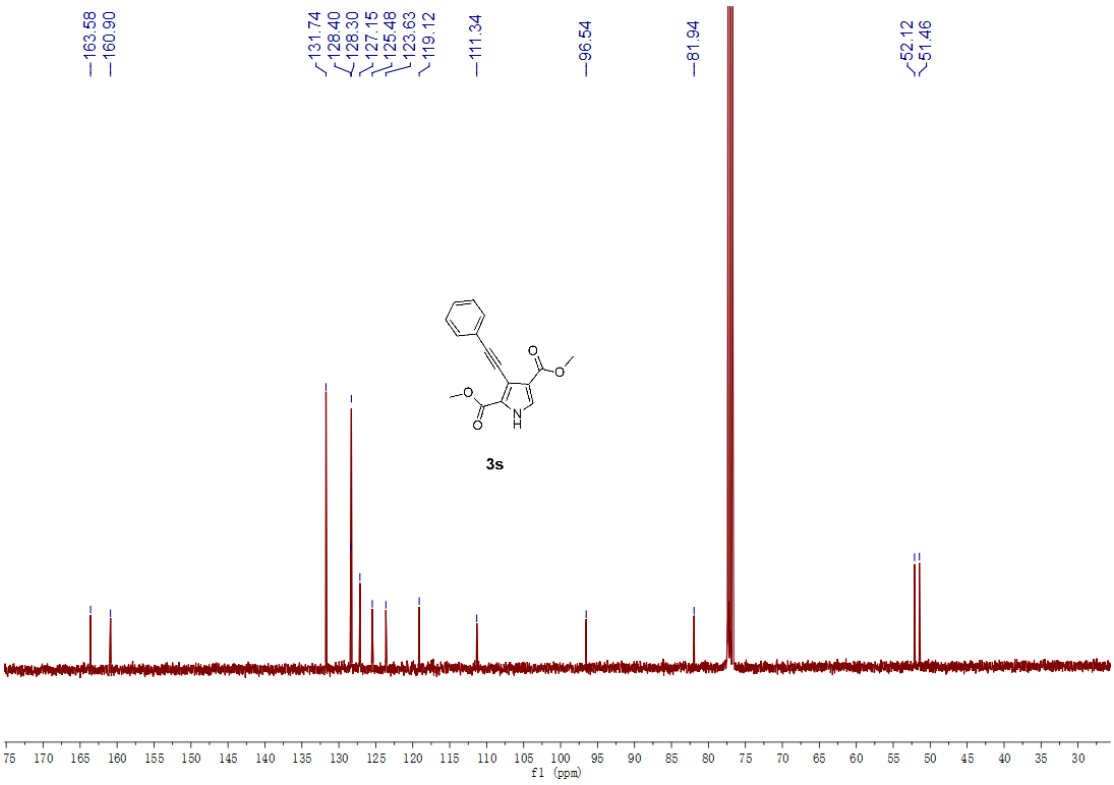
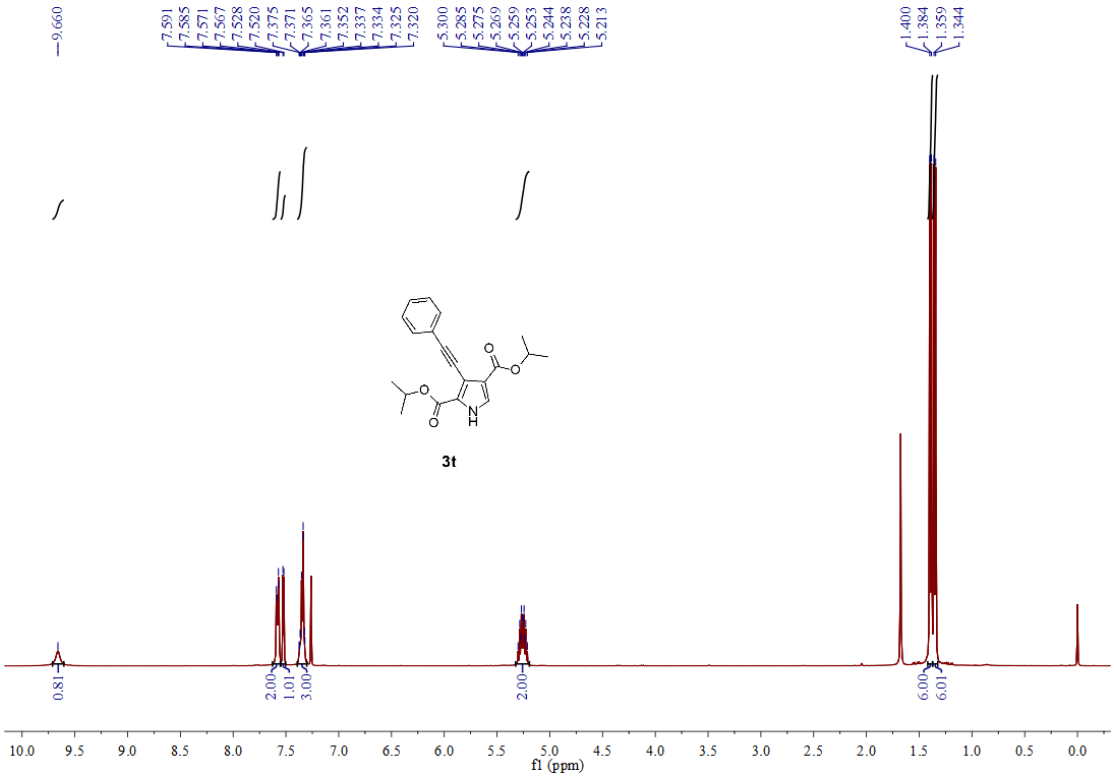
7.582
7.574
7.569
7.554
7.545
7.354
7.349
7.341
7.337
3.965
3.888
3s
0.89
3.00
3.01
3.00
3.00
f1 (ppm)


163.58
160.90
131.74
128.40
128.30
127.15
125.48
123.63
119.12
111.34
96.54
81.94
52.12
51.46
3s
f1 (ppm)


9.660
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7.585
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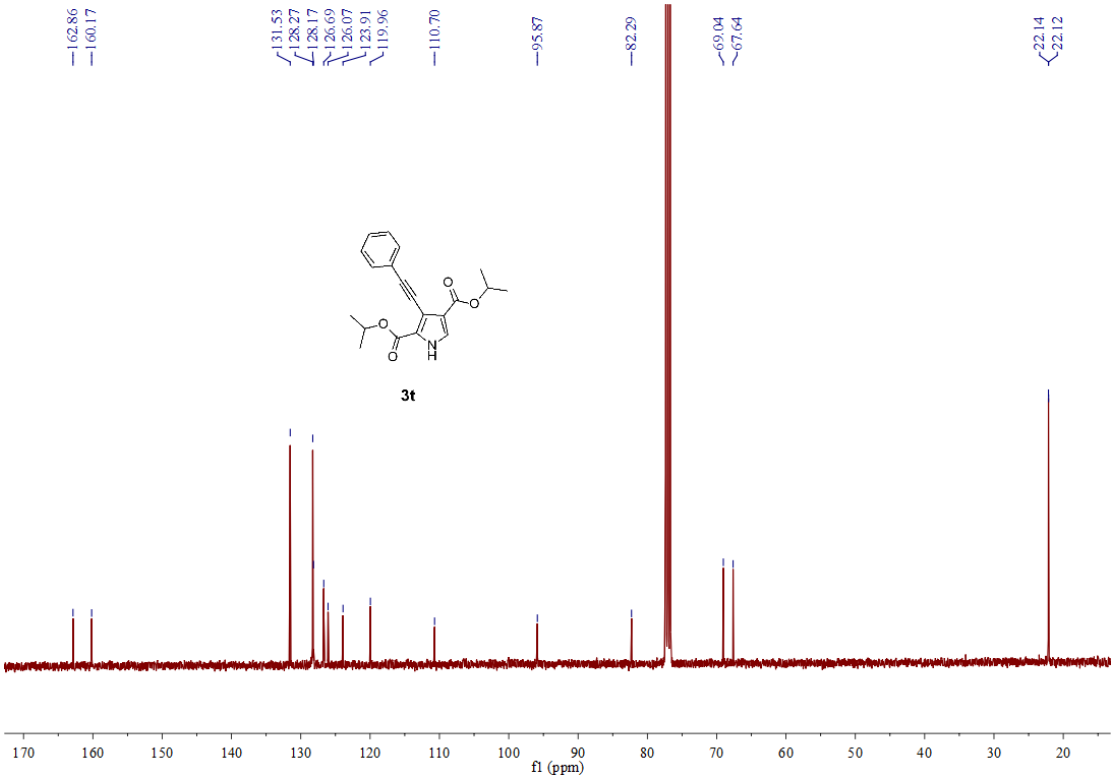
7.567
7.528
7.520
7.375
7.371
7.365
7.361
7.352
7.337
7.334
7.325
7.320
5.300
5.285
5.275
5.269
5.259
5.253
5.244
5.238
5.228
5.213
1.400
1.384
1.359
1.344
3t
0.81
2.00
1.01
3.00
2.00
6.00
6.01
f1 (ppm)


162.86
160.17
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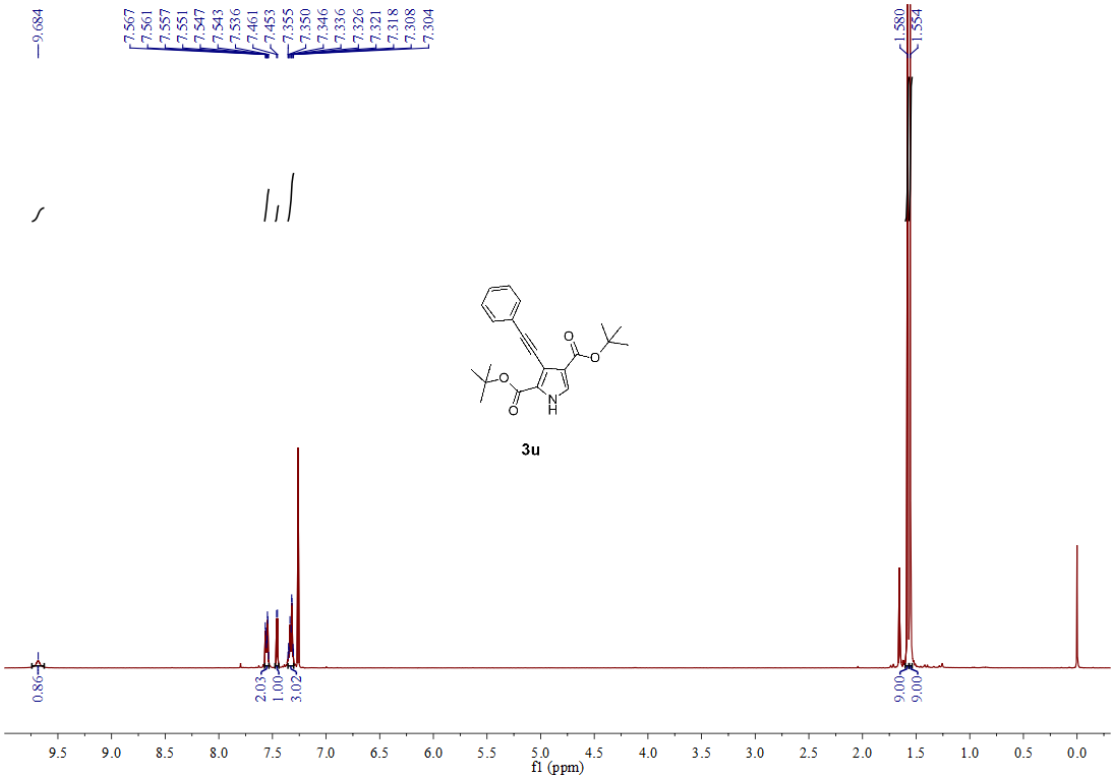
128.27
128.17
126.69
126.07
123.91
119.96
110.70
95.87
82.29
69.04
67.64
22.14
22.12
3t
f1 (ppm)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7.547
7.543
7.536
7.461
7.453
7.355
7.350
7.346
7.336
7.326
7.321
7.318
7.308
7.304
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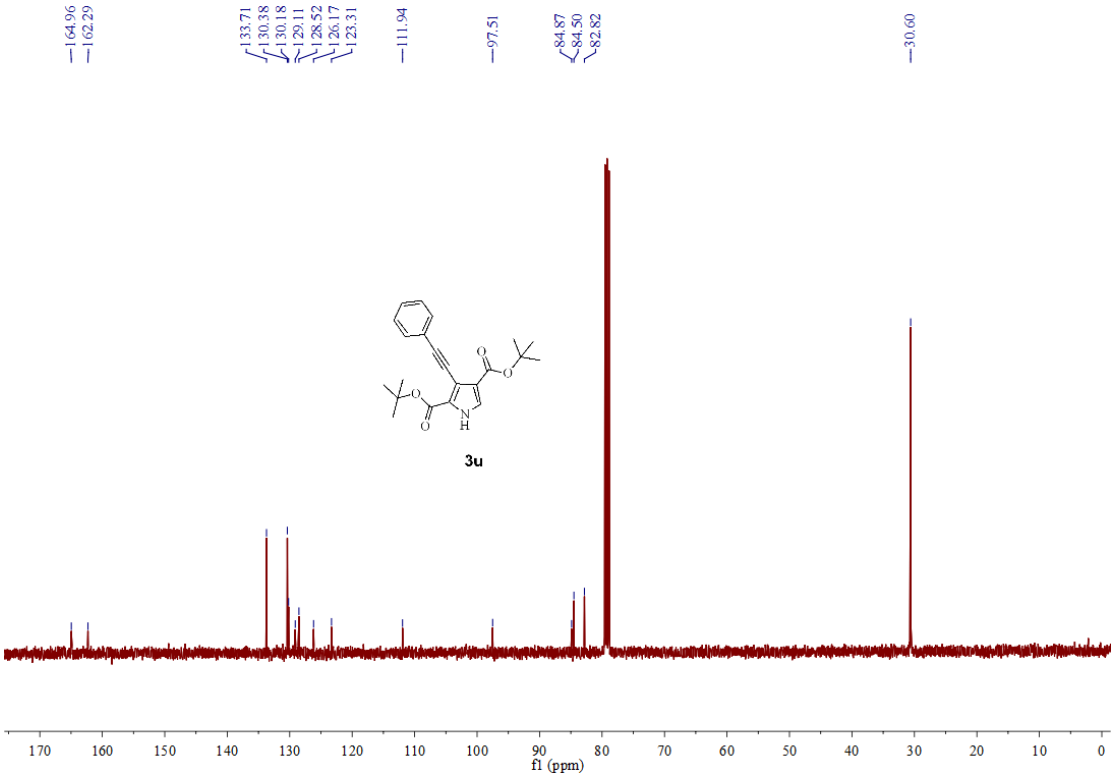
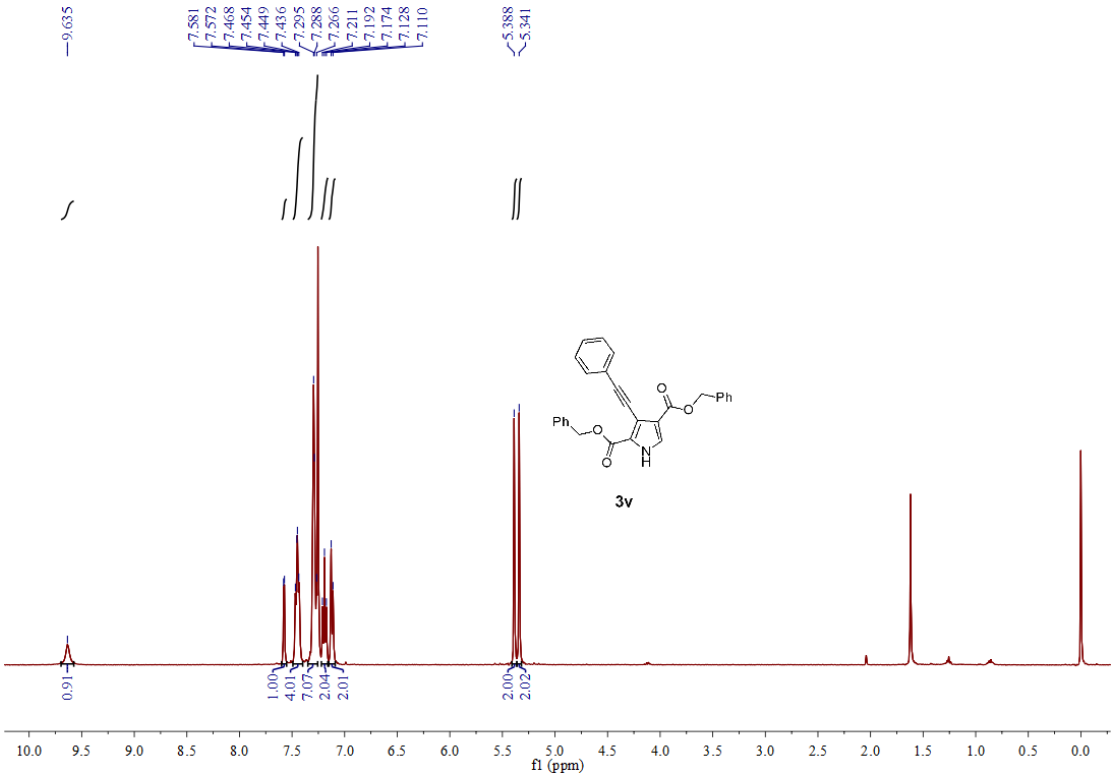
1.554
0.86
2.03
1.00
3.02
9.00
9.00
f1 (ppm)

3u


164.96
162.29
133.71
130.38
130.18
129.11
128.52
126.17
123.31
111.94
97.51
84.87
84.50
82.82
30.60
f1 (ppm)

3u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7.454
7.449
7.436
7.295
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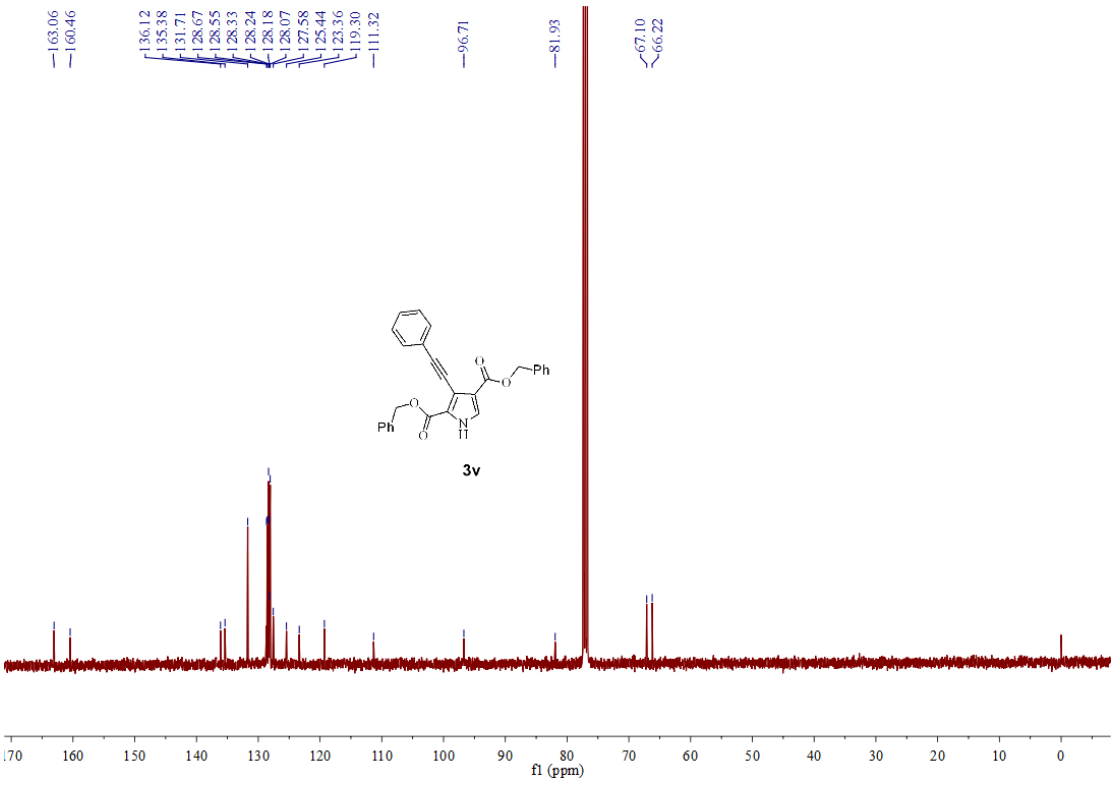
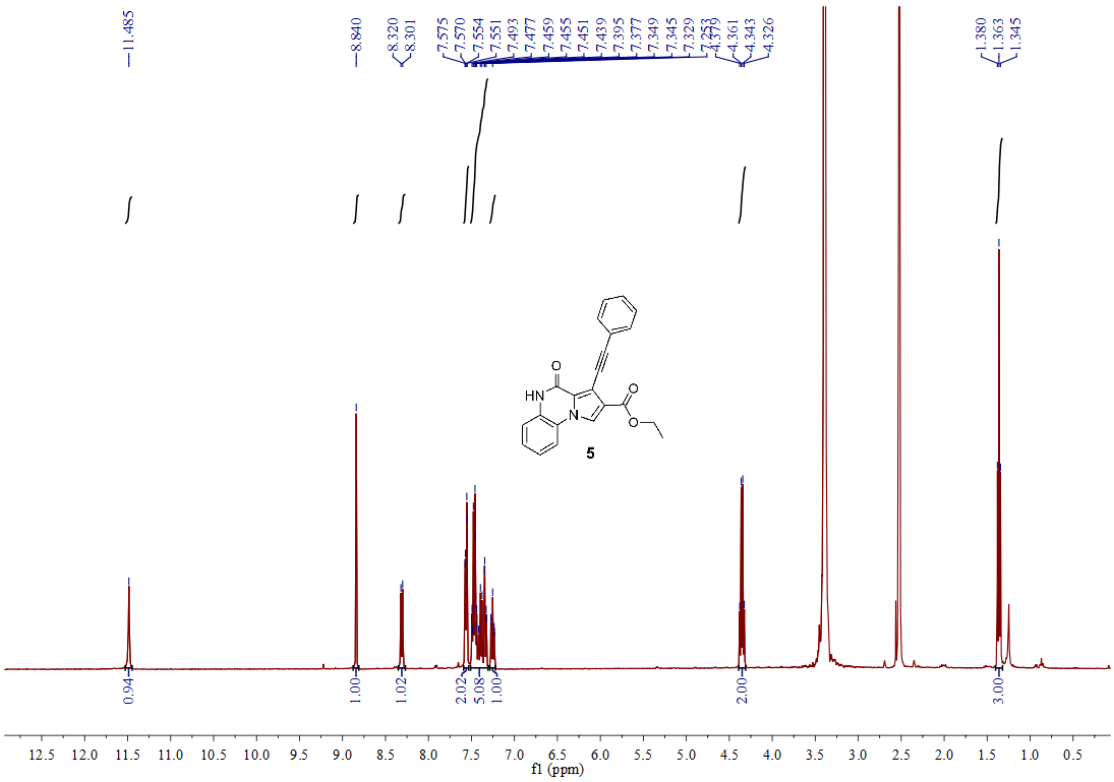
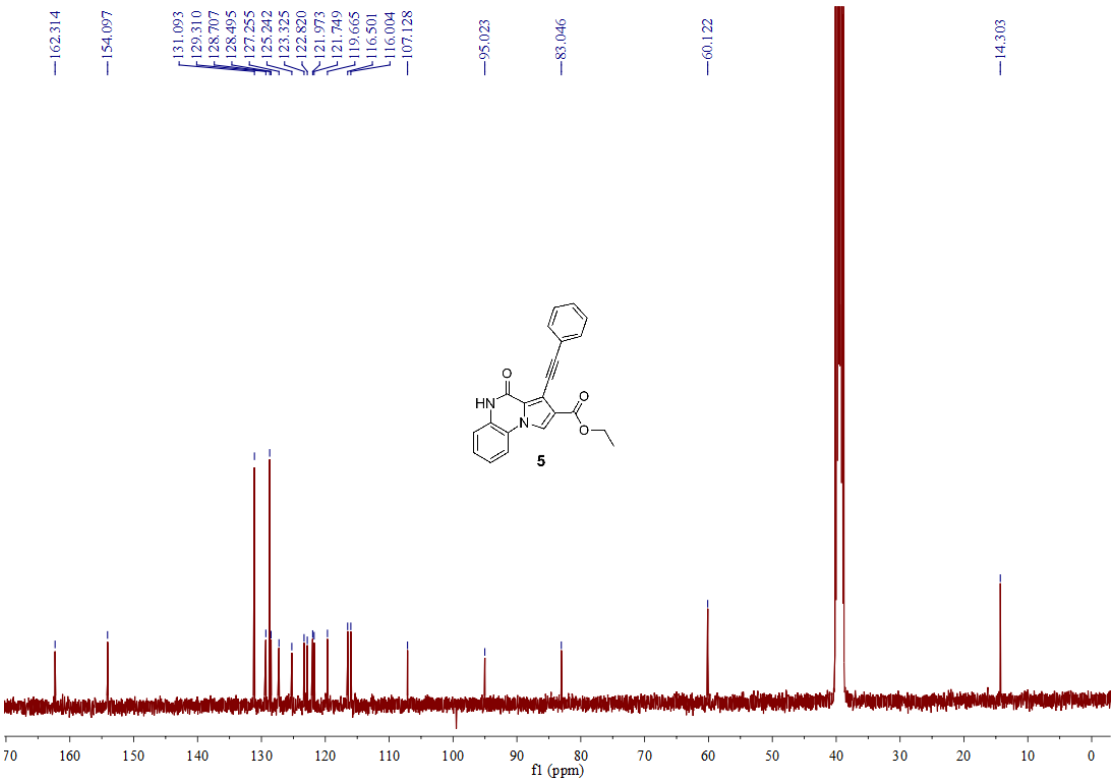
7.266
7.211
7.192
7.174
7.128
7.110
5.388
5.341
Ph
Ph
3v
0.91
1.00
4.01
7.07
2.04
2.01
2.00
2.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


163.06
160.46
136.12
135.38
131.71
128.67
128.55
128.33
128.24
128.18
128.07
127.58
125.44
123.36
119.30
111.32
96.71
81.93
67.10
66.22
Ph
Ph
3v
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


11.485
8.840
8.320
8.301
7.575
7.570
7.554
7.551
7.493
7.477
7.459
7.455
7.451
7.439
7.395
7.377
7.349
7.345
7.329
4.361
4.343
4.326
1.380
1.363
1.345
0.94
1.00
1.02
2.02
5.08
1.00
2.00
3.00
f1 (ppm)
5


162.314
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131.093
129.310
128.707
128.495
127.255
125.242
123.325
122.820
121.973
121.749
119.665
116.501
116.004
107.128
95.023
83.046
60.122
14.303
f1 (ppm)
5