Supplementary Information (SI) for Organic & Biomolecular Chemistry.

Supporting Information

Copper-Catalyzed Tandem Cyclization Reaction of N-Acyl Enamines and Electron-Deficient Alkynes: Direct Synthesis of Alkynyl Substituted Pyridines

Ying Gao,[a] Ju-Yin Peng,[b] Yu-Na Zhang,[a]* Xiao-Liang Zhao,[b] and Yu-Long Zhao[b]*

[a] Department of Stomatology, NO. 964 Hospital, Changchun, Jilin 130021, China, E-mail: djlsyy964@139.com

[b] Jilin Province Key Laboratory of Organic Functional Molecular Design & Synthesis, Faculty of Chemistry, Northeast Normal University, Changchun 130024, China, E-mail: zhaoyl351@nenu.edu.cn

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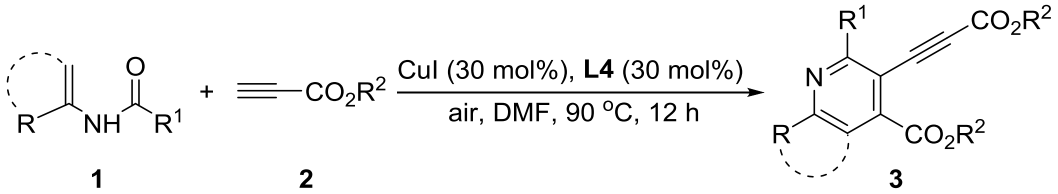
I. General Information:

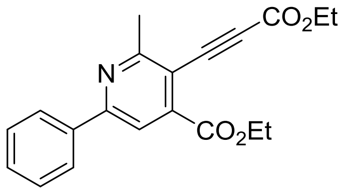
All reagents were commercial and were used without further purification. *N*-Acyl enamides **1** were synthesized according to known literature procedure.[1] Electron-deficient alkynes **2** were prepared according to the previous method reported.[2] Chromatography was carried on flash silica gel (300-400 mesh). All reactions were monitored by TLC, which was performed on percolated aluminum sheets of silica gel 60 (F254). Unless noted, the ^{1}H NMR spectra were recorded at 500 MHz, 600 MHz in $CDCl_3$, the ^{13}C NMR spectra were recorded at 151 MHz in $CDCl_3$ with TMS as internal standard, and the ^{19}F NMR spectra were recorded at 565 MHz in $CDCl_3$. All coupling constants (*J* values) were reported in Hertz (Hz). High-resolution mass spectra (HRMS) were obtained using a Bruker microTOF II focus spectrometer (ESI). The compound **3qa** was glued on a glass fiber. X-ray single-crystal data of **3qa** was collected by a Bruker D8 Venture diffractometer (Mo Kα radiation, $\lambda = 0.71073$ Å (Cu Kα radiation, $\lambda = 1.54178$ Å)) at 293(2) K, and IP technique in the range $2.19° < \theta < 27.48°$. Empirical absorption correction was applied. The structures were solved by the direct method and refined by the full-matrix least-squares method on F^2 using the SHELXS 97 crystallographic software package. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. Hydrogen atoms were located from difference Fourier maps.

II. General Procedure for the Preparation of 3 (3aa as example):



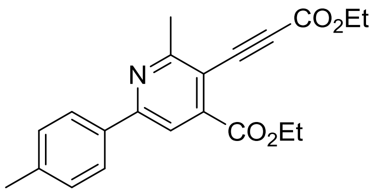
A sealed tube equipped with a magnetic stir bar was charged with **1a** (32.2 mg, 0.2 mmol), CuI (11.4 mg, 0.06 mmol) and 4,4'-dimethyl-2,2'-bipyridyl (11.1 mg, 0.06 mmol) in DMF (2.0 mL), then **2a** (58.9 mg, 0.6 mmol) was added. Subsequently, the reaction mixture was stirred at 90 ℃ (heating mantle) for 12 h. After the reaction was complete, the reaction mixture was diluted with 30 mL H_2O and extracted with CH_2Cl_2 (10 mL × 3). The combined organic extracts were washed with H_2O three times, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to yield the crude product, which was purified by silica gel column chromatography (EtOAc/PE = 1/10, V/V) to afford product **3aa** (58.7 mg, 87%) as a yellow solid.

Ethyl 3-(3-ethoxy-3-oxoprop-1-yn-1-yl)-2-methyl-6-phenylisonicotinate (3aa):



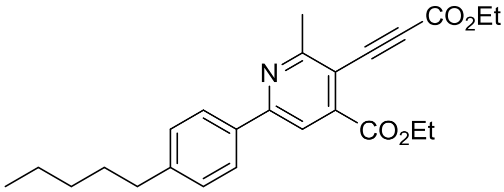
Yellow solid, mp: 47 – 48 ℃, 58.7 mg, 87% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 – 8.04 (m, 3H), 7.50 – 7.42 (m, 3H), 4.47 (q, *J* = 7.2 Hz, 2H), 4.33 (q, *J* = 7.1 Hz, 2H), 2.85 (s, 3H), 1.46 (t, *J* = 7.2 Hz, 3H), 1.37 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.85, 163.58, 157.18, 153.75, 141.82, 137.56, 130.10, 128.90, 127.22, 117.41, 112.28, 90.72, 81.66, 62.39, 62.20, 24.42, 14.11, 14.03. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{20}H_{19}NO_4Na^+$: 360.1206, found: 360.1209.

Ethyl 3-(3-ethoxy-3-oxoprop-1-yn-1-yl)-2-methyl-6-(*p*-tolyl)isonicotinate (3ba):



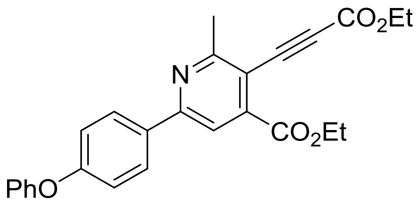
Yellow solid, mp: 51 – 52 ℃, 51.3 mg, 73% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.90 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 4.39 (q, *J* = 7.2 Hz, 2H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.77 (s, 3H), 2.33 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.97, 162.51, 156.23, 152.79, 140.77, 139.38, 133.81, 128.62, 126.11, 116.04, 110.81, 89.52, 80.82, 61.33, 61.13, 23.40, 20.35, 13.08, 13.00. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{21}H_{21}NO_4Na^+$: 374.1363, found: 374.1363.

Ethyl 3-(3-ethoxy-3-oxoprop-1-yn-1-yl)-2-methyl-6-(4-pentylphenyl)isonicotinate (3ca):



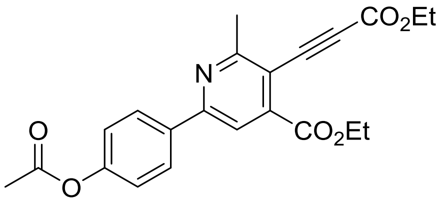
Yellow liquid, 57.1 mg, 70% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.98 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 4.47 (q, *J* = 7.1 Hz, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.84 (s, 3H), 2.65 (t, *J* = 7.7 Hz, 2H), 1.68 – 1.60 (m, 2H), 1.46 (t, *J* = 7.2 Hz, 3H), 1.39 – 1.30 (m, 7H), 0.89 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.99, 163.55, 157.37, 153.82, 145.44, 141.79, 135.07, 129.03, 127.18, 117.16, 111.83, 90.56, 81.86, 62.35, 62.16, 35.75, 31.43, 30.97, 24.42, 22.53, 14.10, 14.02. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{25}H_{29}NO_4Na^+$: 430.1989, found: 430.1987.

Ethyl 3-(3-ethoxy-3-oxoprop-1-yn-1-yl)-2-methyl-6-(4-phenoxyphenyl)isonicotinate (3da):



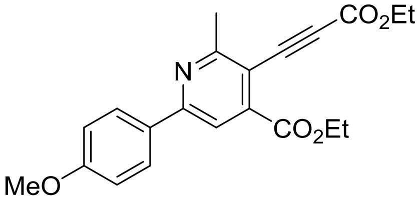
Yellow solid, mp: 77 – 78 ℃, 56.7 mg, 66% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.7 Hz, 2H), 8.02 (s, 1H), 7.37 (t, *J* = 7.9 Hz, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.05 – 7.10 (m, 4H), 4.47 (q, *J* = 7.1 Hz, 2H), 4.33 (q, *J* = 7.1 Hz, 2H), 2.84 (s, 3H), 1.46 (t, *J* = 7.1 Hz, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.95, 163.62, 159.41, 156.60, 156.44, 153.81, 141.86, 132.42, 129.90, 128.93, 123.92, 119.47, 118.68, 116.95, 111.81, 90.64, 81.78, 62.41, 62.20, 24.44, 14.12, 14.04. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{26}H_{23}NNaO_5^+$: 452.1468, found: 452.1477.

Ethyl 6-(4-acetoxyphenyl)-3-(3-ethoxy-3-oxoprop-1-yn-1-yl)-2-methylisonicotinate (3ea):



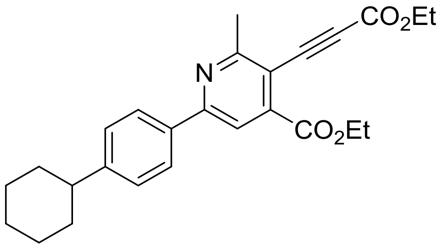
Yellow solid, mp: 60 – 61 ℃, 61.7 mg, 78% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.7 Hz, 2H), 8.06 (s, 1H), 7.24 (d, *J* = 8.7 Hz, 2H), 4.49 (q, *J* = 7.1 Hz, 2H), 4.34 (q, *J* = 7.1 Hz, 2H), 2.86 (s, 3H), 2.34 (s, 3H), 1.48 (t, *J* = 7.2 Hz, 3H), 1.38 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.08, 164.81, 163.63, 156.25, 153.73, 152.27, 141.94, 135.22, 128.45, 122.04, 117.22, 112.36, 90.79, 81.57, 62.41, 62.19, 24.37, 21.14, 14.08, 14.01. HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{22}H_{21}NO_6Na^+$: 418.1261, found: 418.1262.

Ethyl 3-(3-ethoxy-3-oxoprop-1-yn-1-yl)-6-(4-methoxyphenyl)-2-methylisonicotinate (3fa):



Yellow solid, mp: 52 – 53 ℃, 50.0 mg, 68% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 – 8.03 (m, 2H), 8.00 (s, 1H), 7.04 – 6.97 (m, 2H), 4.47 (q, *J* = 7.1 Hz, 2H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 3H), 2.83 (s, 3H), 1.46 (t, *J* = 7.1 Hz, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.04, 163.53, 161.40, 156.85, 153.87, 141.71, 130.13, 128.73, 116.60, 114.29, 111.26, 90.44, 81.99, 62.36, 62.17, 55.41, 24.45, 14.12, 14.04. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{21}H_{21}NNaO_5^+$: 390.1312, found: 390.1310.

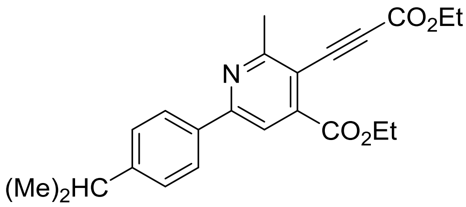
Ethyl 6-(4-cyclohexylphenyl)-3-(3-ethoxy-3-oxoprop-1-yn-1-yl)-2-methylisonico-tinate (3ga):



Yellow solid, mp: 35 – 36 ℃, 68.8 mg, 82% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.99 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 4.47 (q, *J* = 7.1 Hz, 2H), 4.33 (q, *J* = 7.1 Hz, 2H), 2.84 (s, 3H), 2.54 – 2.58 (m, 1H), 1.91 – 1.84 (m, 4H), 1.78 – 1.72 (m, 1H), 1.47 – 1.39 (m, 7H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.29 – 1.24 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.99, 163.56, 157.41, 153.82, 150.49, 141.77, 135.25, 127.44, 127.26, 117.18, 111.81, 90.56, 81.88, 62.36, 62.17, 44.48, 34.29, 26.83, 26.12, 24.43, 14.11, 14.03. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{26}H_{19}NNaO_4^+$: 442.1989, found: 442.1980.

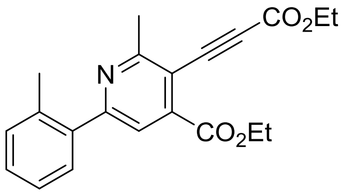
Ethyl 3-(3-ethoxy-3-oxoprop-1-yn-1-yl)-6-(4-isopropylphenyl)-2-methylisonico-

tinate (3ha):



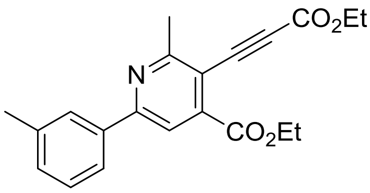
Yellow solid, mp: 37 – 38 ℃, 56.9 mg, 75% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (s, 1H), 8.02 – 7.98 (m, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 4.47 (q, *J* = 7.1 Hz, 2H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.01 – 2.94 (m, 1H), 2.85 (s, 3H), 1.46 (t, *J* = 7.1 Hz, 3H), 1.37 (t, *J* = 7.2 Hz, 3H), 1.29 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.01, 163.57, 157.39, 153.83, 151.30, 141.79, 135.30, 127.30, 127.05, 117.19, 111.85, 90.56, 81.86, 62.37, 62.17, 34.04, 24.44, 23.85, 14.11, 14.03. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{23}H_{25}NNaO_4^+$: 402.1676, found: 402.1681.

Ethyl 3-(3-ethoxy-3-oxoprop-1-yn-1-yl)-2-methyl-6-(o-tolyl)isonicotinate (3ia):



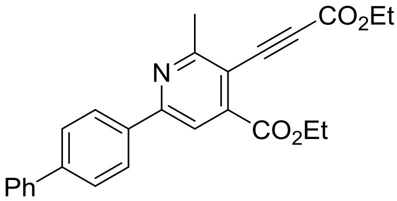
Yellow liquid, 51.3 mg, 73% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.37 – 7.33 (m, 1H), 7.28 – 7.23 (m, 1H), 7.23 – 7.20 (m, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.78 (s, 3H), 2.31 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.78, 163.11, 160.34, 153.74, 141.35, 138.79, 136.06, 131.12, 129.60, 129.15, 126.15, 121.17, 112.04, 90.53, 81.43, 62.39, 62.25, 24.32, 20.42, 14.11, 14.02. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{21}H_{21}NNaO_4^+$: 374.1363, found: 374.1363.

Ethyl 3-(3-ethoxy-3-oxoprop-1-yn-1-yl)-2-methyl-6-(m-tolyl)isonicotinate (3ja):



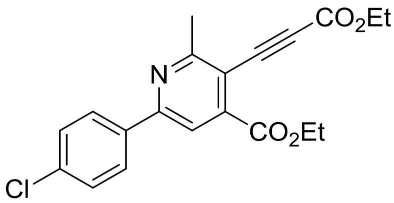
Yellow solid, mp: 42 – 43 ℃, 54.1 mg, 77% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.82 (s, 1H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.20 – 7.16 (m, 1H), 4.39 (q, *J* = 7.2 Hz, 2H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.78 (s, 3H), 2.36 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H), 1.29 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.94, 163.56, 157.44, 153.79, 141.78, 138.63, 137.54, 130.92, 128.82, 127.88, 124.39, 117.52, 112.16, 90.66, 81.72, 62.41, 62.21, 24.44, 21.53, 14.11, 14.04. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{21}H_{21}NNaO_4^+$: 374.1363, found: 374.1363.

Ethyl 6-([1,1'-biphenyl]-4-yl)-3-(3-ethoxy-3-oxoprop-1-yn-1-yl)-2-methylisonicotinate (3ka):



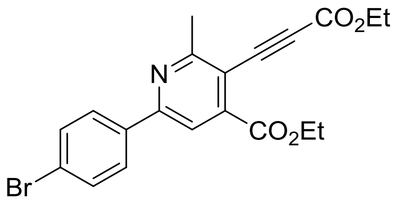
Yellow solid, mp: 67 – 68 ℃, 53.8 mg, 65% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 – 8.15 (m, 2H), 8.12 (s, 1H), 7.74 – 7.70 (m, 2H), 7.68 – 7.64 (m, 2H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.39 (d, *J* = 7.1 Hz, 1H), 4.49 (d, *J* = 7.2 Hz, 2H), 4.33 (d, *J* = 7.2 Hz, 2H), 2.87 (s, 3H), 1.47 (t, *J* = 7.1 Hz, 3H), 1.38 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.94, 163.68, 156.81, 153.80, 142.87, 141.88, 140.28, 136.46, 128.89, 127.80, 127.68, 127.60, 127.13, 117.32, 112.26, 90.77, 81.74, 62.44, 62.22, 24.47, 14.12, 14.05. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{26}H_{23}NNaO_4^+$: 436.1519, found: 436.1520.

Ethyl 6-(4-chlorophenyl)-3-(3-ethoxy-3-oxoprop-1-yn-1-yl)-2-methylisonicotinate (3la):



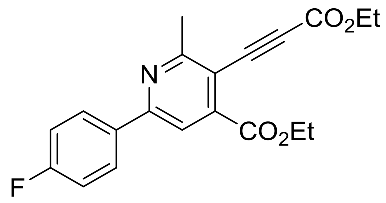
Yellow solid, mp: 82 – 83 ℃, 66.1 mg, 89% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (s, 3H), 7.46 (d, *J* = 8.6 Hz, 2H), 4.48 (q, *J* = 7.2 Hz, 2H), 4.33 (q, *J* = 7.1 Hz, 2H), 2.85 (s, 3H), 1.47 (t, *J* = 7.1 Hz, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.79, 163.72, 155.91, 153.72, 141.98, 136.38, 136.02, 129.15, 128.52, 117.20, 112.66, 90.90, 81.44, 62.50, 62.26, 29.71, 24.42, 14.10, 14.03. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{20}H_{18}ClNNaO_4^+$: 394.0817, found: 394.0816.

Ethyl 6-(4-bromophenyl)-3-(3-ethoxy-3-oxoprop-1-yn-1-yl)-2-methylisonicotinate (3ma):



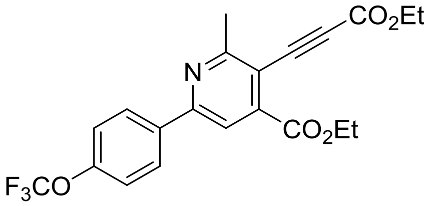
Yellow solid, mp: 90 – 91 ℃, 64.9 mg, 78% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.98 (d, *J* = 8.6 Hz, 2H), 7.63 (d, *J* = 8.6 Hz, 2H), 4.49 (q, *J* = 7.1 Hz, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 2.86 (s, 3H), 1.48 (t, *J* = 7.1 Hz, 3H), 1.39 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.75, 163.71, 155.93, 153.70, 142.00, 136.45, 132.08, 128.74, 124.79, 117.13, 112.71, 90.93, 81.43, 62.48, 62.23, 24.38, 14.09, 14.01. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{20}H_{18}BrNNaO_4^+$: 438.0311, found: 438.0305.

Ethyl 3-(3-ethoxy-3-oxoprop-1-yn-1-yl)-6-(4-fluorophenyl)-2-methylisonicotinate (3na):



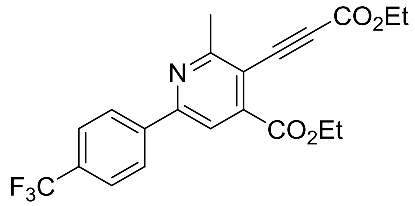
Yellow solid, mp: 74 – 75 ℃, 48.3 mg, 68% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 8.7, 5.4 Hz, 2H), 8.03 (s, 1H), 7.17 (t, *J* = 8.6 Hz, 2H), 4.48 (d, *J* = 7.2 Hz, 2H), 4.33 (d, *J* = 7.1 Hz, 2H), 2.85 (s, 3H), 1.47 (t, *J* = 7.2 Hz, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.83, 164.16 (d, *J* = 250.8 Hz), 163.66, 156.10, 153.74, 141.94, 133.78 (d, *J* = 3.0 Hz), 129.23 (d, *J* = 8.6 Hz), 117.08, 115.94 (d, *J* = 21.6 Hz), 112.28, 90.78, 81.52, 62.47, 62.23, 24.41, 14.10, 14.03. ^{19}F NMR (565 MHz, $CDCl_3$) δ -110.82 (t, *J* = 6.8 Hz). HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{20}H_{18}FNNaO_4^+$: 378.1112, found: 378.1107.

Ethyl 3-(3-ethoxy-3-oxoprop-1-yn-1-yl)-2-methyl-6-(4-(trifluoromethoxy)phenyl)isonicotinate (3oa):



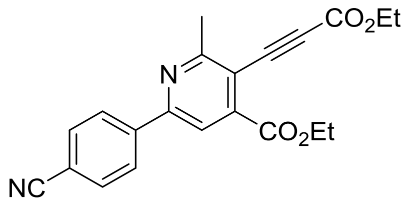
Yellow solid, mp: 37 – 38 ℃, 67.4 mg, 80% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 – 8.03 (m, 2H), 7.98 (s, 1H), 7.26 (d, *J* = 8.2 Hz, 2H), 4.41 (q, *J* = 7.2 Hz, 2H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.79 (s, 3H), 1.39 (t, *J* = 7.2 Hz, 3H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.74, 163.77, 155.72, 153.70, 150.63, 142.01, 136.18, 128.85, 121.13, 117.35, 112.79, 90.97, 81.34, 62.52, 62.28, 24.42, 14.10, 14.02. ^{19}F NMR (565 MHz, $CDCl_3$) δ -57.70. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{21}H_{18}F_3NNaO^+$: 444.1029, found: 444.1037.

Ethyl 3-(3-ethoxy-3-oxoprop-1-yn-1-yl)-2-methyl-6-(4-(trifluoromethyl)phenyl) isonicotinate (3pa):



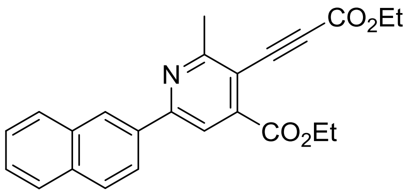
Yellow solid, mp: 42 – 43 ℃, 55.1 mg, 68% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 (d, J = 8.2 Hz, 2H), 8.04 (s, 1H), 7.68 (d, J = 8.2 Hz, 2H), 4.42 (q, J = 7.1 Hz, 2H), 4.27 (q, J = 7.1 Hz, 2H), 2.81 (s, 3H), 1.40 (t, J = 7.1 Hz, 3H), 1.31 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.66, 163.87, 155.51, 153.65, 142.09, 140.88, 131.76 (q, J = 32.2 Hz), 127.56, 125.85 (q, J = 3.9 Hz), 124.00 (q, J = 272.0 Hz), 117.79, 113.45, 91.20, 81.16, 62.59, 62.32, 24.44, 14.10, 14.03. ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.70. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{21}H_{18}F_3NNaO_4^+$: 428.1080, found: 428.1082.

Ethyl 6-(4-cyanophenyl)-3-(3-ethoxy-3-oxoprop-1-yn-1-yl)-2-methylisonicotinate (3qa):



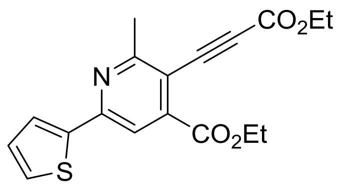
Yellow solid, mp: 93 – 97 ℃, 59.4 mg, 82% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 (d, J = 8.2 Hz, 2H), 8.11 (s, 1H), 7.79 (d, J = 8.2 Hz, 2H), 4.49 (q, J = 7.1 Hz, 2H), 4.34 (q, J = 7.1 Hz, 2H), 2.87 (s, 3H), 1.47 (t, J = 7.1 Hz, 3H), 1.38 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.47, 163.93, 154.69, 153.55, 142.12, 141.54, 132.65, 127.73, 118.52, 117.88, 113.88, 113.44, 91.45, 80.93, 62.64, 62.35, 24.41, 14.08, 14.01. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{21}H_{18}N_2NaO_4^+$: 385.1159, found: 385.1161.

Ethyl 3-(3-ethoxy-3-oxoprop-1-yn-1-yl)-2-methyl-6-(naphthalen-2-yl)isonicotinate (3ra):



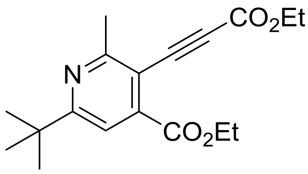
Yellow solid, mp: 102 – 103 ℃, 52.7 mg, 68% yield. ^1H NMR (600 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.17 – 8.12 (m, 2H), 7.92 – 7.87 (m, 2H), 7.83 – 7.79 (m, 1H), 7.50 – 7.45 (m, 2H), 4.43 (q, *J* = 7.2 Hz, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 2.84 (s, 3H), 1.42 (t, *J* = 7.2 Hz, 3H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.96, 163.66, 157.05, 153.79, 141.89, 134.85, 134.16, 133.36, 128.95, 128.66, 127.71, 127.25, 127.16, 126.53, 124.25, 117.62, 112.26, 90.80, 81.76, 62.43, 62.19, 24.45, 14.11, 14.05. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{24}H_{21}NNaO_4^+$: 410.1363, found: 410.1361.

Ethyl 3-(3-ethoxy-3-oxoprop-1-yn-1-yl)-2-methyl-6-(thiophen-2-yl)isonicotinate (3sa):



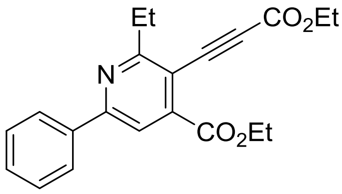
Yellow solid, mp: 67 – 68 ℃, 49.4 mg, 72% yield. ^1H NMR (600 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.68 (dd, *J* = 3.7, 1.0 Hz, 1H), 7.47 (dd, *J* = 5.0, 0.9 Hz, 1H), 7.12 (dd, *J* = 5.0, 3.8 Hz, 1H), 4.46 (q, *J* = 7.2 Hz, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 2.79 (s, 3H), 1.45 (t, *J* = 7.2 Hz, 3H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.73, 163.83, 153.78, 152.46, 143.42, 141.72, 129.67, 128.42, 126.67, 115.89, 111.68, 90.66, 81.70, 62.45, 62.18, 24.21, 14.10, 14.01. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{18}H_{17}NNaO_4S^+$: 366.0770, found: 366.0775.

Ethyl 6-(*tert*-butyl)-3-(3-ethoxy-3-oxoprop-1-yn-1-yl)-2-methylisonicotinate (3ta):



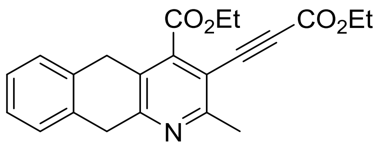
Yellow oli, 52.1 mg, 82% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (s, 1H), 4.44 (q, *J* = 7.1 Hz, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 2.76 (s, 3H), 1.44 (t, *J* = 7.2 Hz, 3H), 1.37 – 1.35 (m, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.50, 165.43, 162.42, 153.88, 141.36, 116.19, 110.77, 89.51, 81.97, 62.23, 62.11, 37.90, 29.81, 24.32, 14.10, 14.00. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{18}H_{23}NNaO_4^+$: 340.1519, found: 340.1520.

Ethyl 3-(3-ethoxy-3-oxoprop-1-yn-1-yl)-2-ethyl-6-phenylisonicotinate (3ua):



Yellow solid, mp: 52 – 53 ℃, 56.9 mg, 81% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 – 8.09 (m, 2H), 8.07 (s, 1H), 7.52 – 7.44 (m, 3H), 4.48 (q, *J* = 7.1 Hz, 2H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.20 (q, *J* = 7.5 Hz, 2H), 1.47 (t, *J* = 7.2 Hz, 3H), 1.42 (t, *J* = 7.5 Hz, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.95, 165.06, 157.16, 153.80, 142.13, 137.73, 130.08, 128.89, 127.25, 117.22, 111.60, 90.39, 81.46, 62.39, 62.19, 30.38, 14.11, 14.04, 12.77. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{21}H_{21}NNaO_4^+$: 374.1363, found: 374.1363.

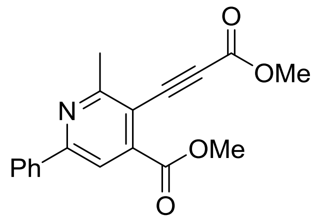
Ethyl 3-(3-ethoxy-3-oxoprop-1-yn-1-yl)-2-methyl-5,10-dihydrobenzo[g]quinoline-4-carboxylate (3va):



Yellow solid, mp: 46 – 47 ℃, 47.2 mg, 65% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ

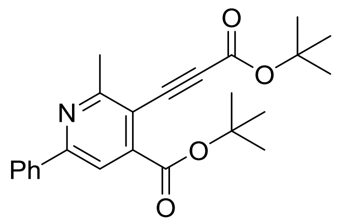
8.36 – 8.30 (m, 1H), 7.36 (td, *J* = 7.3, 6.4, 3.6 Hz, 2H), 7.26 – 7.17 (m, 1H), 4.49 (q, *J* = 7.1 Hz, 2H), 4.30 (q, *J* = 7.1 Hz, 2H), 2.92 (s, 4H), 2.78 (s, 3H), 1.46 (t, *J* = 7.1 Hz, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.24, 160.39, 153.61, 153.36, 143.72, 138.49, 133.47, 130.29, 127.79, 127.32, 125.98, 125.42, 110.60, 89.09, 62.33, 62.12, 27.37, 24.75, 23.81, 14.06. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{22}H_{21}NNaO_4^+$: 386.1363, found: 386.1366.

Methyl 3-(3-methoxy-3-oxoprop-1-yn-1-yl)-2-methyl-6-phenylisonicotinate (3ab):



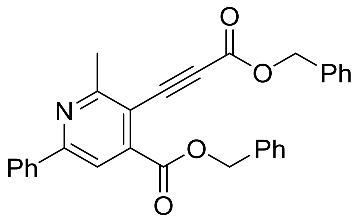
Yellow solid, mp: 39 – 40 ℃, 53.2 mg, 86% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 – 8.00 (m, 3H), 7.45 – 7.39 (m, 3H), 3.94 (s, 3H), 3.81 (s, 3H), 2.79 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.06, 162.71, 156.34, 153.18, 140.47, 136.54, 129.14, 127.92, 126.23, 116.42, 111.35, 89.38, 51.92, 51.90, 23.39. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{18}H_{15}NNaO_4^+$: 332.0893, found: 332.0901.

Tert-butyl 3-(3-(tert-butoxy)-3-oxoprop-1-yn-1-yl)-2-methyl-6-phenylisonicotinate (3ac):



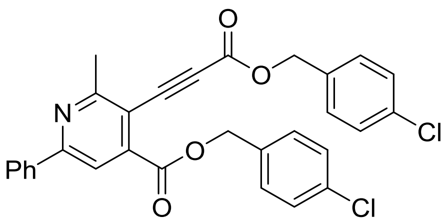
Yellow liquid, 50.4 mg, 64% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 – 7.96 (m, 2H), 7.88 (s, 1H), 7.39 (t, *J* = 7.3 Hz, 2H), 7.35 (d, *J* = 7.1 Hz, 1H), 2.75 (s, 3H), 1.58 (s, 9H), 1.47 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.65, 163.35, 157.00, 152.82, 143.79, 137.77, 129.95, 128.87, 127.20, 117.10, 112.07, 91.66, 83.82, 83.65, 79.65, 28.09, 28.01, 24.41. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{24}H_{27}NNaO_4^+$: 416.1832, found: 416.1841.

Benzyl 3-(3-(benzyloxy)-3-oxoprop-1-yn-1-yl)-2-methyl-6-phenylisonicotinate (3ad):



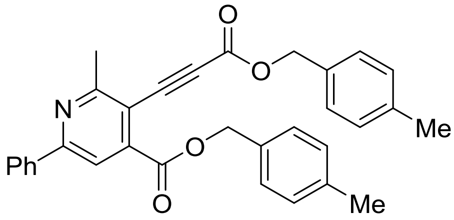
Yellow solid, mp: 52 – 53 ℃, 72.9 mg, 79% yield. ^1H NMR (500 MHz, $CDCl_3$) δ 8.09 (s, 1H), 8.08 – 8.04 (m, 2H), 7.48 (dd, *J* = 7.5, 3.1 Hz, 5H), 7.45 – 7.30 (m, 8H), 5.43 (s, 2H), 5.29 (s, 2H), 2.86 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.68, 163.70, 157.35, 153.56, 141.51, 137.54, 134.98, 134.90, 130.18, 128.95, 128.74, 128.70, 128.69, 128.66, 128.65, 128.59, 127.29, 117.53, 112.32, 90.64, 82.41, 68.08, 67.85, 24.49. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{30}H_{23}NNaO_4^+$: 484.1519, found: 484.1525.

4-Chlorobenzyl 3-(3-((4-chlorobenzyl)oxy)-3-oxoprop-1-yn-1-yl)-2-methyl-6-phenylisonicotinate (3ae):



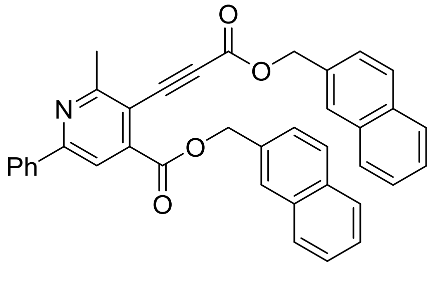
Yellow solid, mp: 65 – 66 ℃, 83.8 mg, 79% yield. ^1H NMR (500 MHz, $CDCl_3$) δ 8.09 – 8.05 (m, 3H), 7.51 – 7.46 (m, 3H), 7.42 – 7.34 (m, 6H), 7.32 (d, *J* = 8.4 Hz, 2H), 5.38 (s, 2H), 5.23 (s, 2H), 2.84 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.60, 163.79, 157.50, 153.35, 141.29, 137.45, 134.69, 134.56, 133.40, 130.26, 130.09, 130.02, 128.96, 128.92, 128.89, 127.27, 117.53, 112.10, 90.39, 82.63, 67.23, 66.98, 24.46. HRMS (ESI-TOF): [M + Na]$^+$ calculated for $C_{30}H_{21}Cl_2NNaO_4^+$: 552.0740, found: 552.0741.

4-Methylbenzyl 2-methyl-3-(3-((4-methylbenzyl)oxy)-3-oxoprop-1-yn-1-yl)-6-phenylisonicotinate (3af):



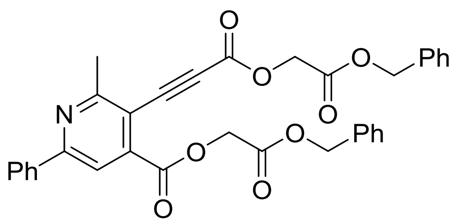
Yellow solid, mp: 57 – 58 ℃, 70.5 mg, 72% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, *J* = 9.4 Hz, 3H), 7.36 – 7.40 (m, 3H), 7.27 (d, *J* = 7.9 Hz, 2H), 7.24 (d, *J* = 7.9 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 7.06 (d, *J* = 7.8 Hz, 2H), 5.29 (s, 2H), 5.16 (s, 2H), 2.75 (s, 3H), 2.29 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.67, 162.59, 156.23, 152.58, 140.58, 137.51, 137.40, 136.53, 130.94, 130.86, 129.07, 128.30, 128.28, 127.87, 127.86, 127.77, 126.22, 116.44, 111.30, 89.62, 66.98, 66.76, 23.41, 20.22. HRMS (ESI-TOF): [M + Na]$^+$ calculated for $C_{32}H_{27}NNaO_4^+$: 512.1832, found: 512.1836.

Naphthalen-2-ylmethyl 2-methyl-3-(3-(naphthalen-2-ylmethoxy)-3-oxoprop-1-yn-1-yl)-6-phenylisonicotinate (3ag):



Yellow solid, mp: 96 – 97 ℃, 82.0 mg, 73% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.99 – 7.96 (m, 2H), 7.84 (s, 1H), 7.78 – 7.73 (m, 5H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.49 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.44 – 7.35 (m, 8H), 5.50 (s, 2H), 5.22 (s, 2H), 2.77 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.77, 163.71, 157.37, 153.55, 141.47, 137.53, 133.25, 133.14, 132.30, 132.22, 130.17, 128.94, 128.54, 128.49, 128.10, 128.07, 127.93, 127.74, 127.71, 127.27, 126.49, 126.45, 126.40, 126.35, 126.19, 126.02, 117.59, 112.30, 90.63, 82.50, 68.29, 67.92, 24.51. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{38}H_{27}NNaO_4^+$: 584.1832, found: 584.1840.

2-(Benzyloxy)-2-oxoethyl 3-(3-(2-(benzyloxy)-2-oxoethoxy)-3-oxoprop-1-yn-1-yl)-2-methyl-6-phenylisonicotinate (3ah):



Yellow solid, mp: 105 – 106 ℃, 90.1 mg, 78% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (s, 1H), 8.10 – 8.06 (m, 2H), 7.48 – 7.51 (m, 3H), 7.40 – 7.34 (m, 10H), 5.24 (d, *J* = 6.7 Hz, 4H), 4.98 (s, 2H), 4.80 (s, 2H), 2.88 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.94, 166.74, 163.96, 163.91, 157.73, 152.87, 140.71, 137.41, 134.96, 134.94, 130.31, 128.97, 128.68, 128.62, 128.46, 128.43, 127.35, 117.78, 112.18, 89.88, 83.47, 67.40, 67.35, 61.79, 61.72, 24.44. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{34}H_{27}NNaO_8^+$: 600.1629, found: 600.1628.

References:

1. (a) Zhao, M. N.; Ren, Z. H.; Wang, Y. Y.; Guan, Z. H. Pd-Catalyzed Oxidative Coupling of Enamides and Alkynes for Synthesis of Substituted Pyrroles. *Org. Lett.* **2014**, *16*, 608-611. (b) Selective Dehydrogenative Acylation of Enamides with Alldehydes Leading to Valuable *β*-Ketoenamides. *Org. Lett.* **2020**, *22*, 944-949.

2. (a) F. Chahdoura,; N. Lassauque,; D. Bourissou,; A. Amgoune. Gold-caatalyzed bis(stannylation) of propiolates. *Org. Chem. Front.* **2016**, *3*, 856-860. (b) Gao, G.; Kuang, Z.; Song, Q. Functionalized geminal-diborylalkanes from various electron-deficient alkynes and B_2pin_2. *Org. Chem. Front.* **2018**, *5*, 2249-2253.

III. ORTEP Drawing of Compound 3qa:

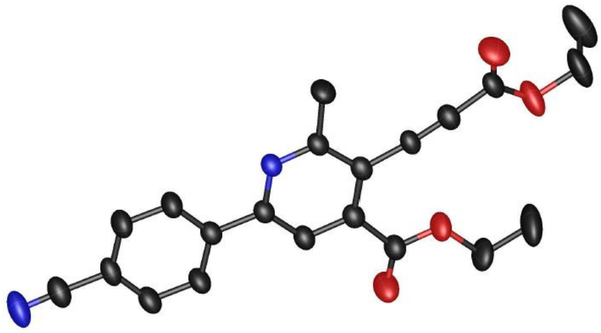


Figure 1. The ORTEP drawing of crystal 3qa (The ellipsoid contour percent probability level is 50%).

Method of Crystallization: The compounds **3qa** was recrystallized from mixed solvents of ethyl acetate and petroleum ether at 25 ˚C.

Introduction of crystal measuring instrument: X-ray single-crystal data of **3qa** was collected by a Bruker D8 Venture diffractometer (Mo Kα radiation, λ = 0.71073 Å (Cu Kα radiation, λ = 1.54178 Å)) at 293(2) K. The adsorption corrections were conducted by a multiscan technique. All the structures were solved via direct method and refined by the full-matrix least-squares technique using the SHELXL-2014 program. Anisotropic thermal parameters were used to refine the non-hydrogen atoms and hydrogen atoms were contained in calculated positions, refining with isotropic thermal parameters locating at those of the parent atoms.

IV. Copies of ^{1}H NMR, ^{13}C NMR and ^{19}F NMR Spectra of Compounds 3：

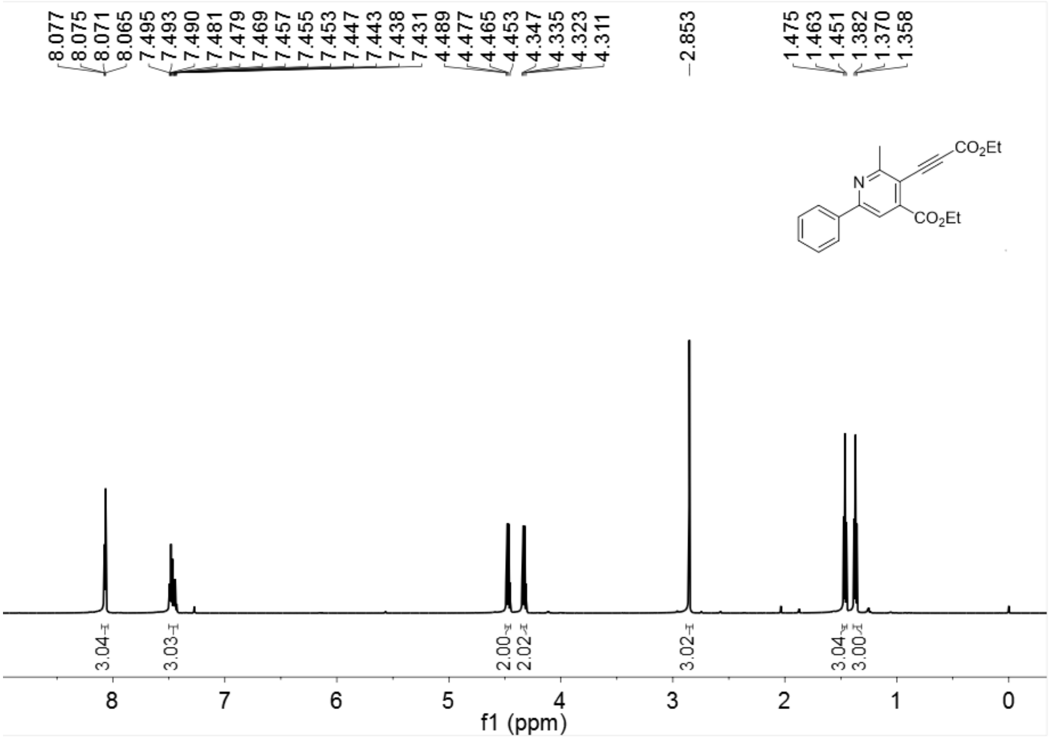


Figure 2. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3aa**

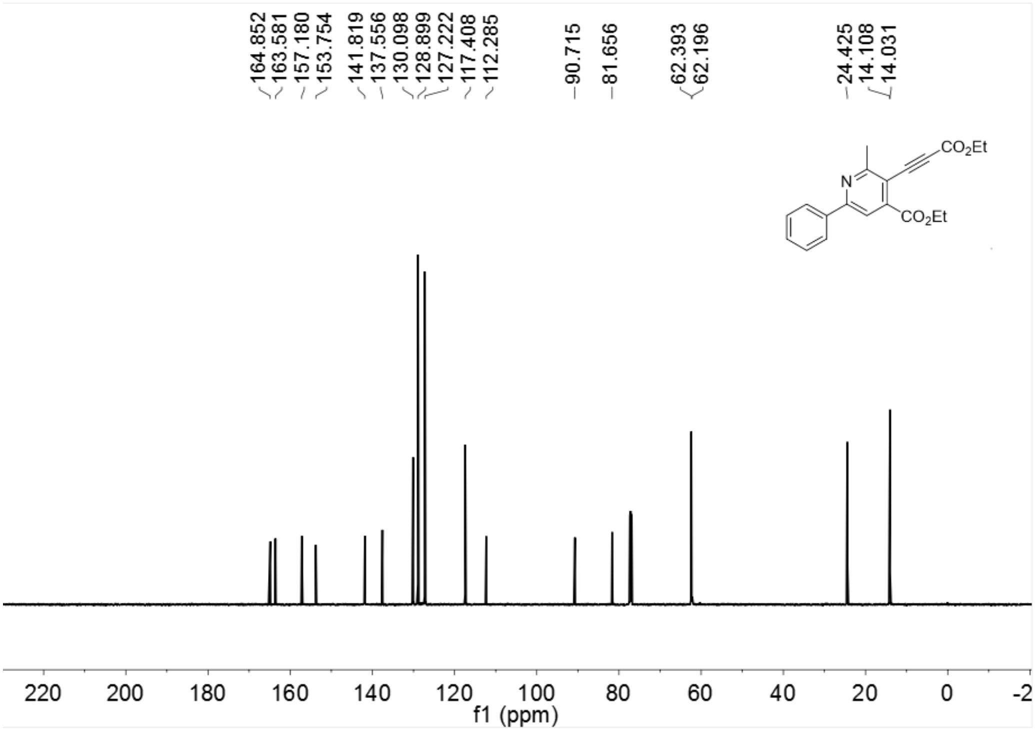


Figure 3. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3aa**

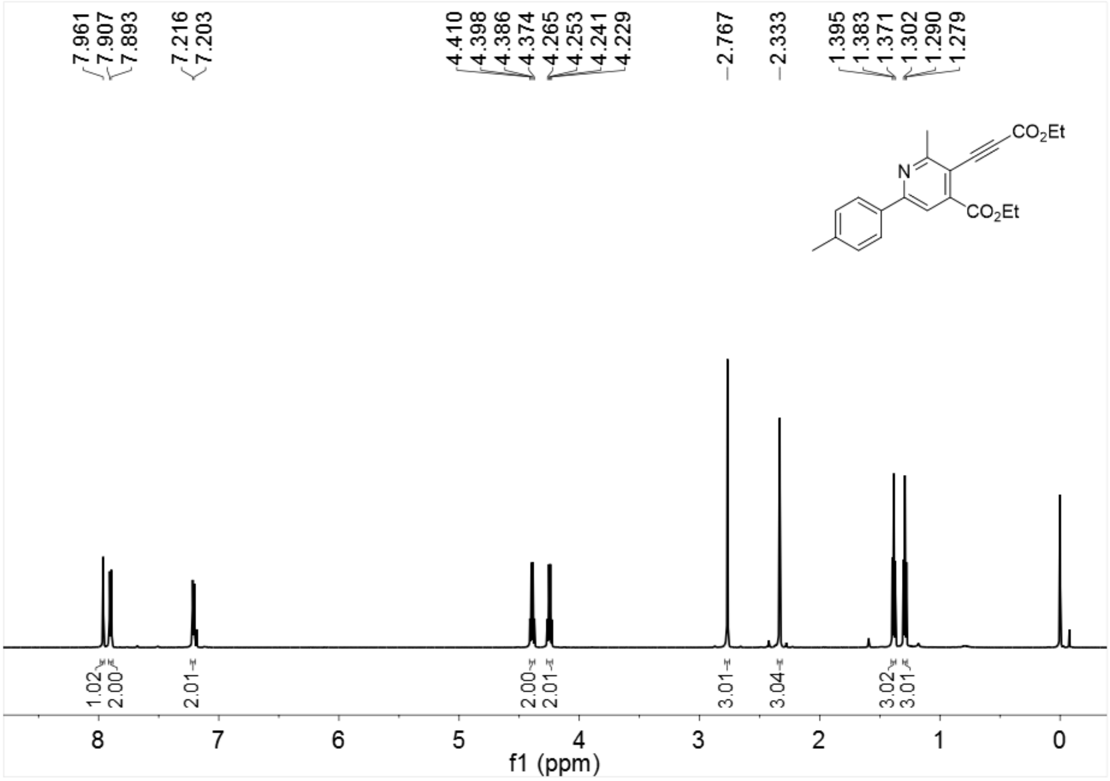


Figure 4. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3ba**

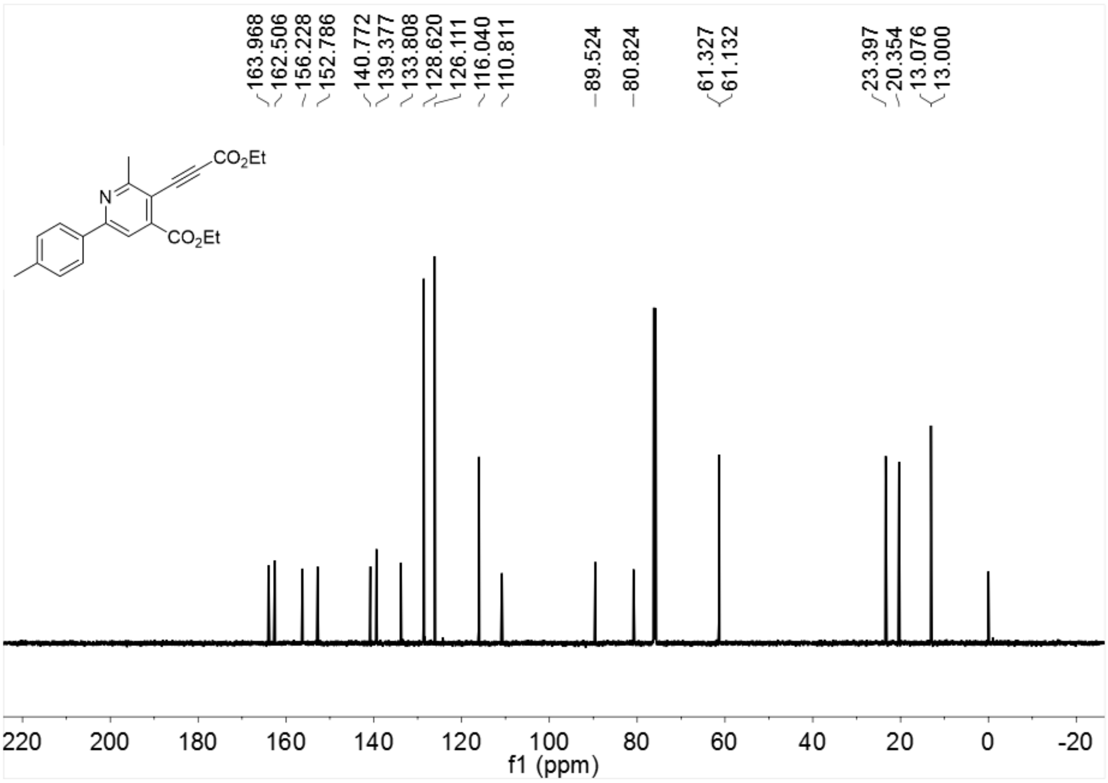


Figure 5. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ba**

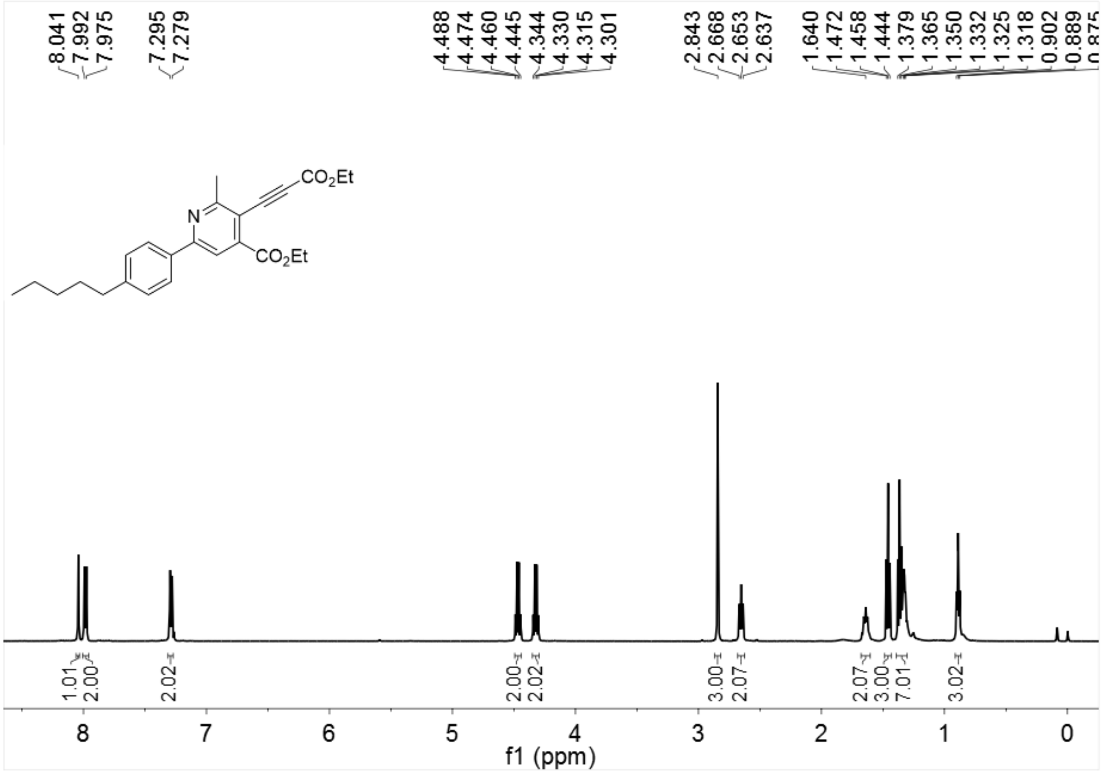


Figure 6. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3ca**

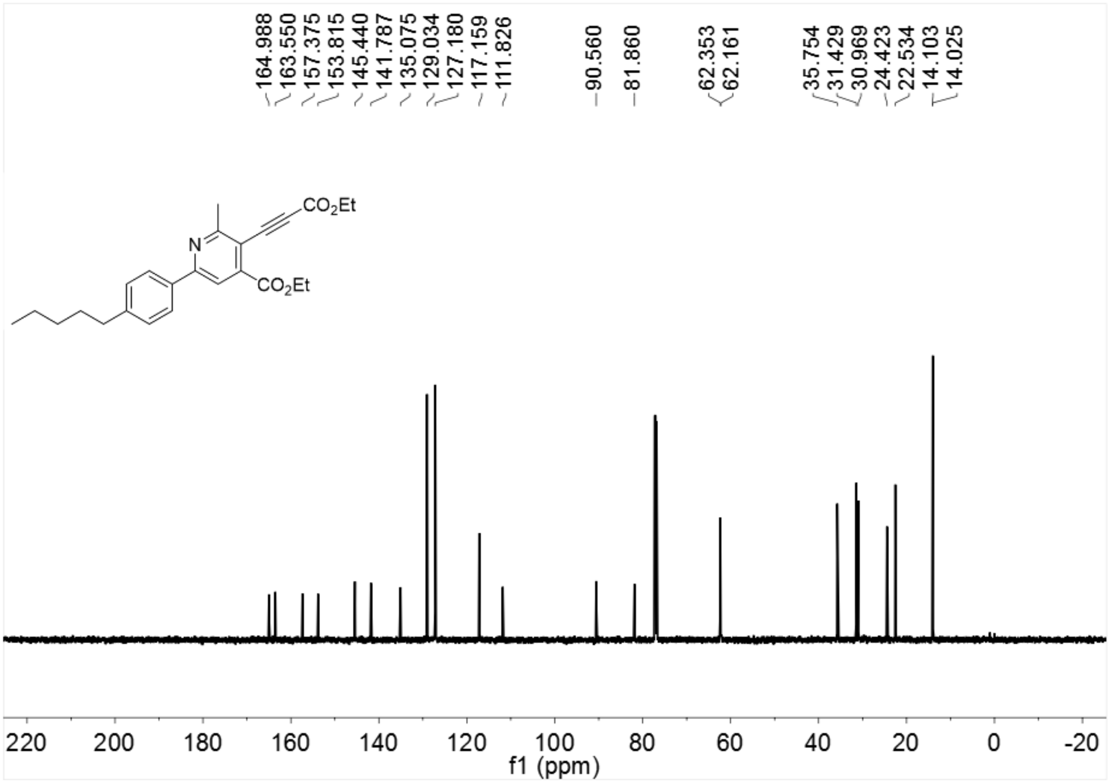


Figure 7. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ca**

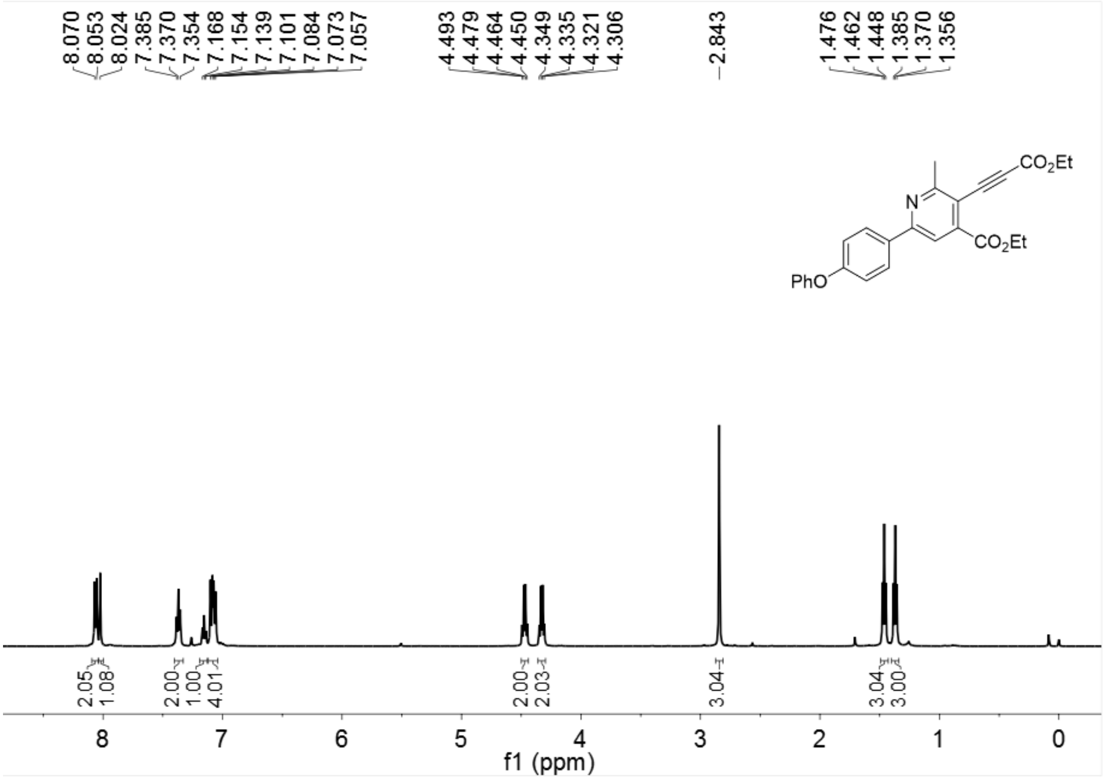


Figure 8. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3da**

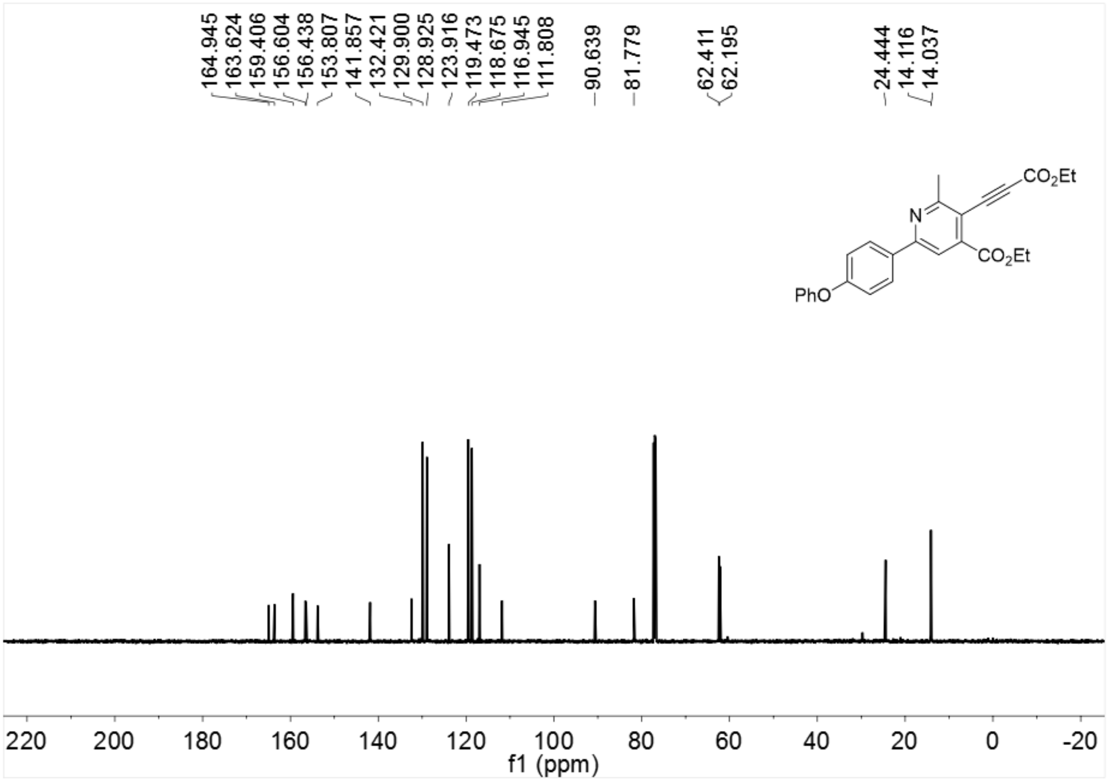


Figure 9. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3da**

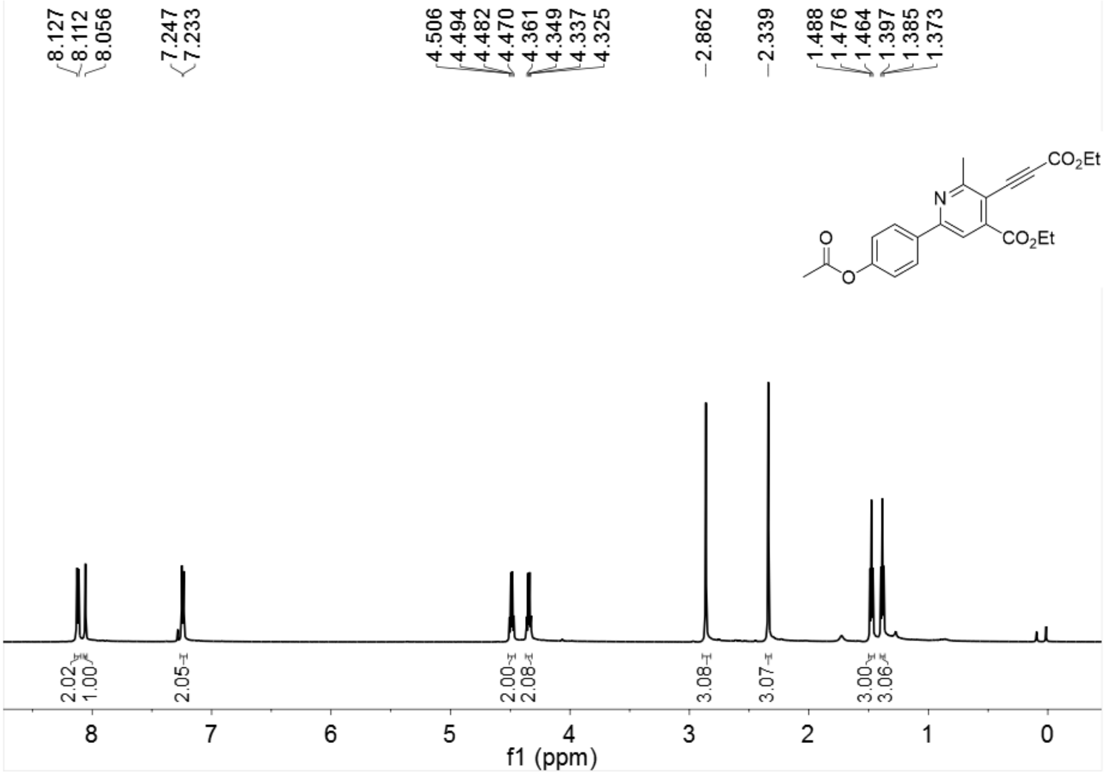


Figure 10. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3ea**

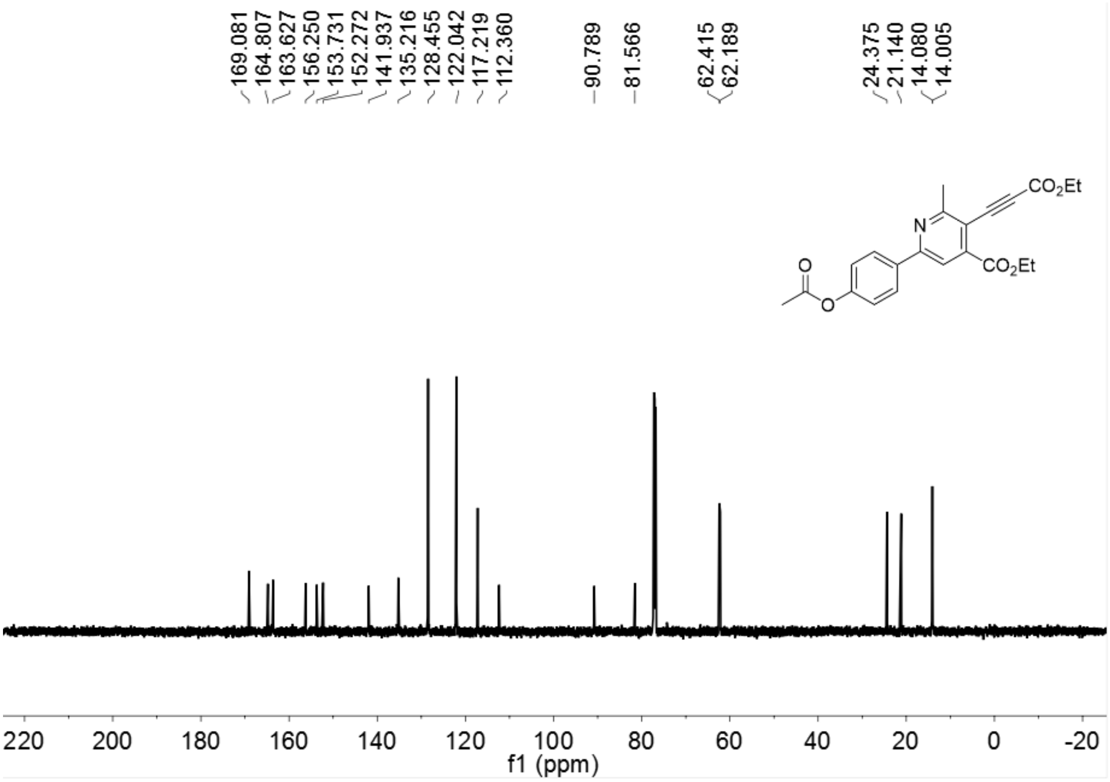


Figure 11. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ea**

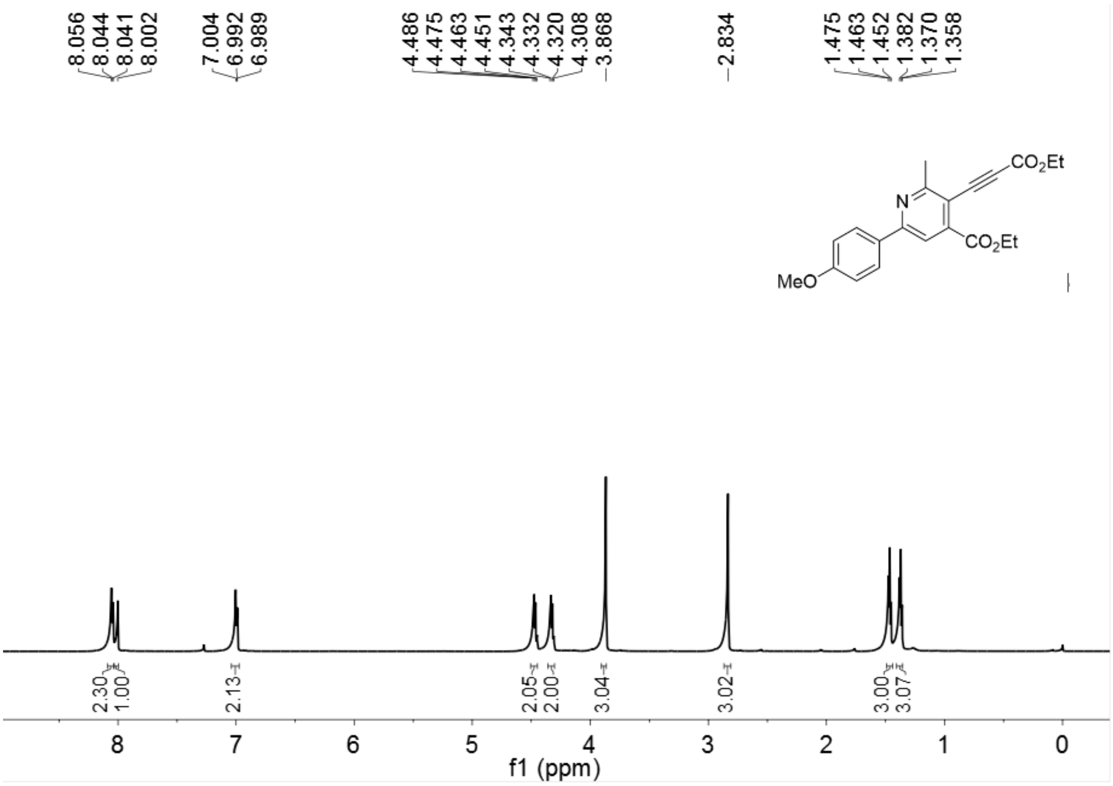


Figure 12. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3fa**

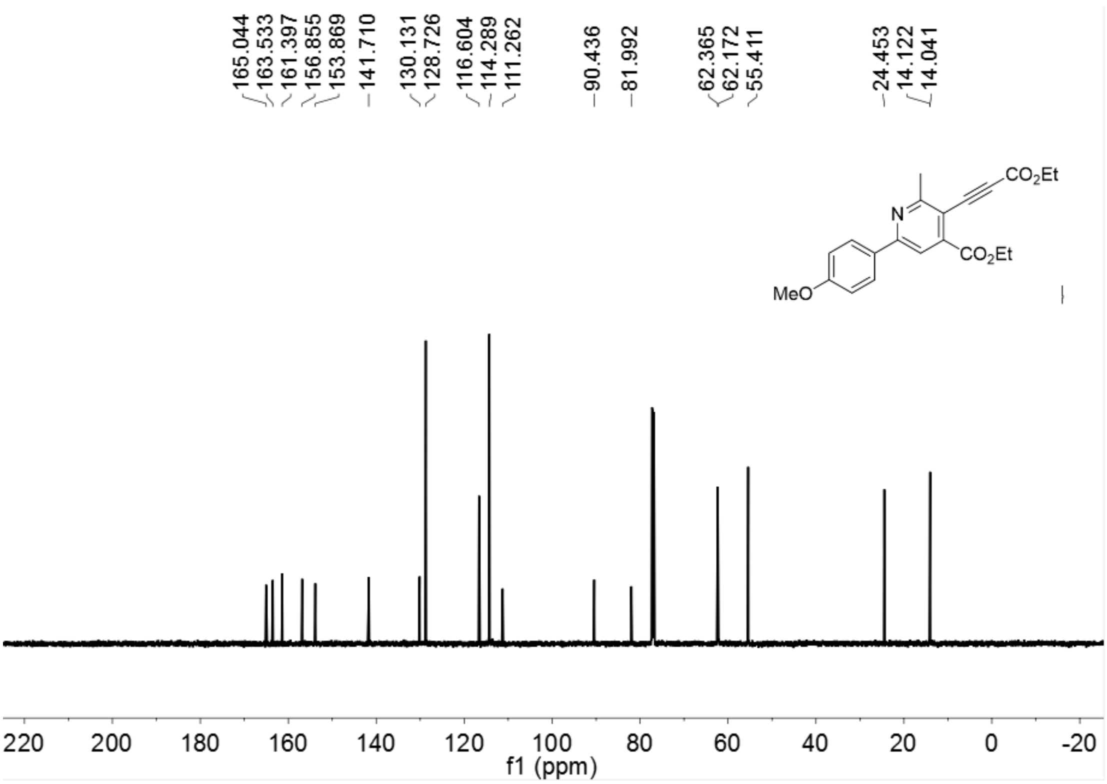


Figure 13. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3fa**

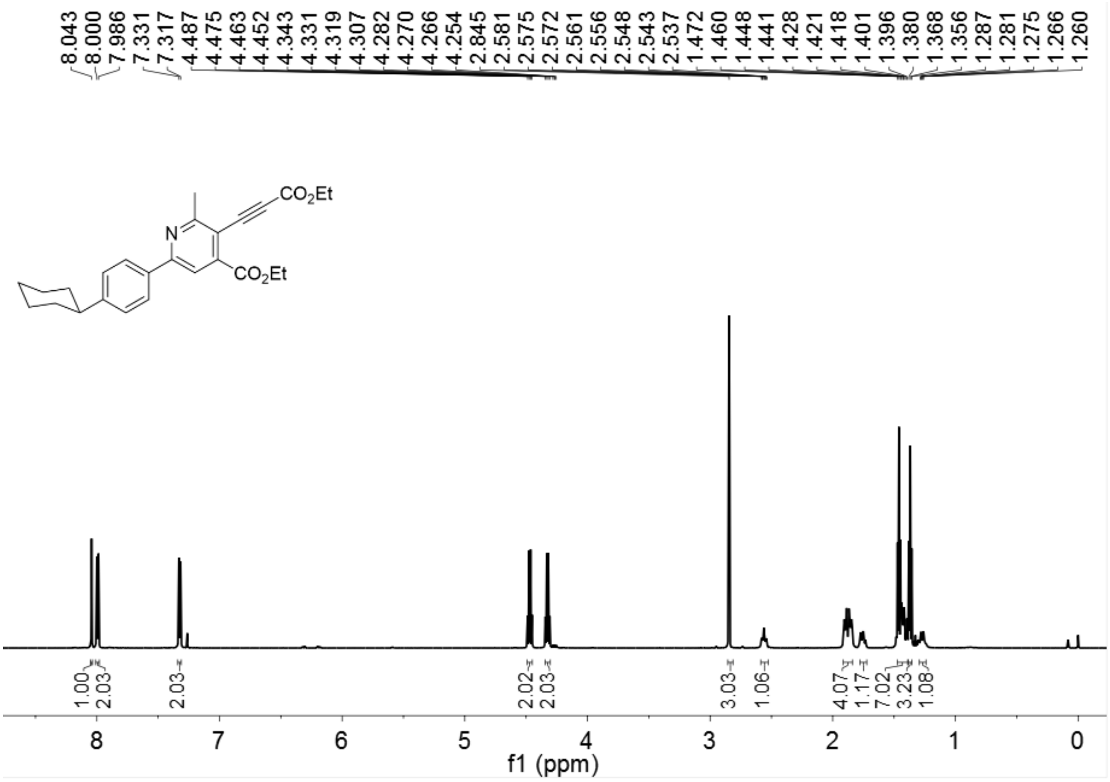


Figure 14. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3ga**

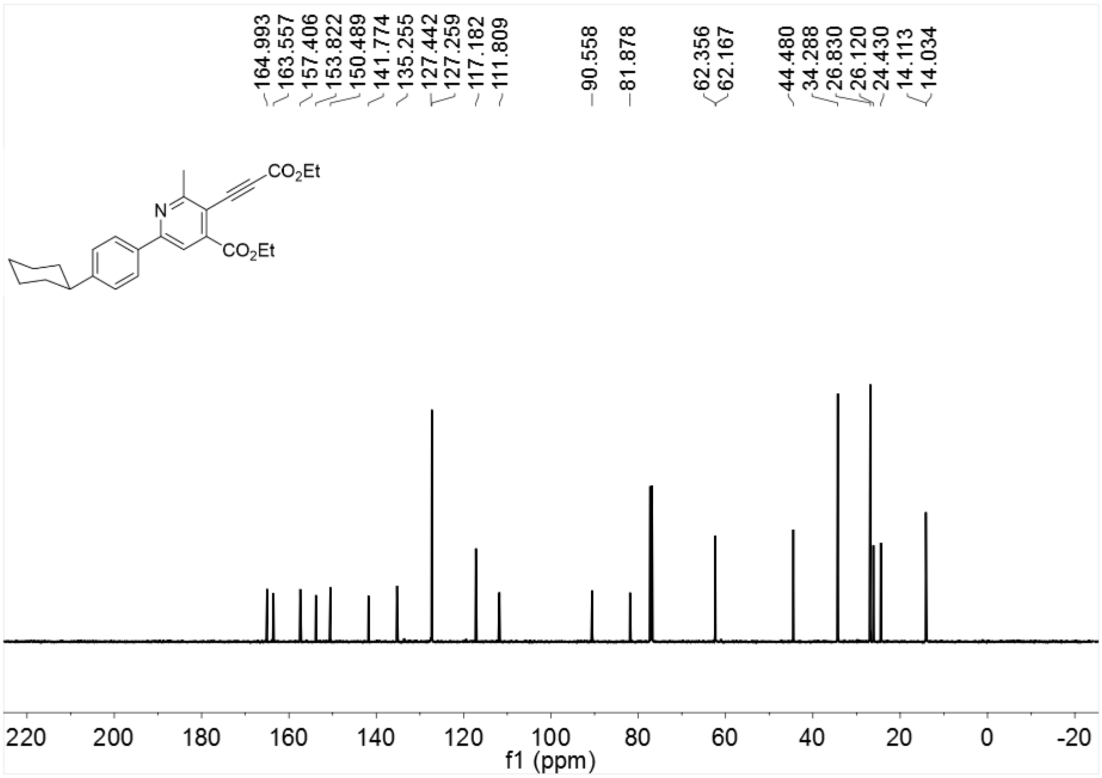


Figure 15. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ga**

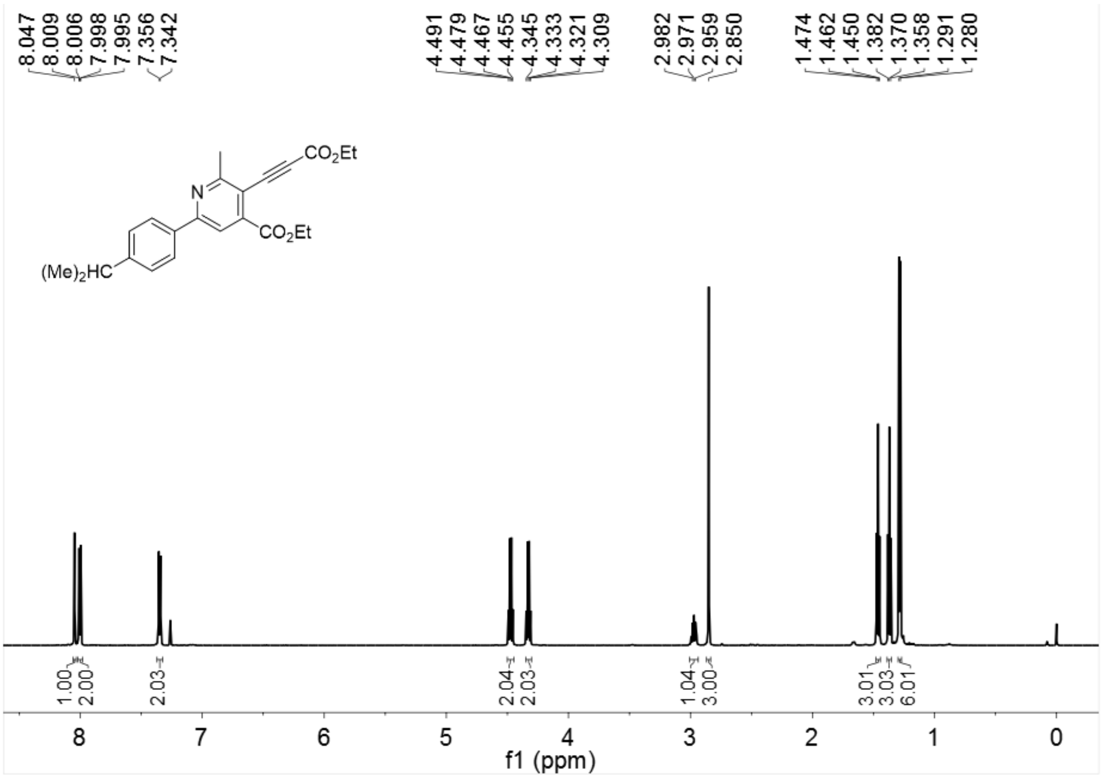


Figure 16. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3ha**

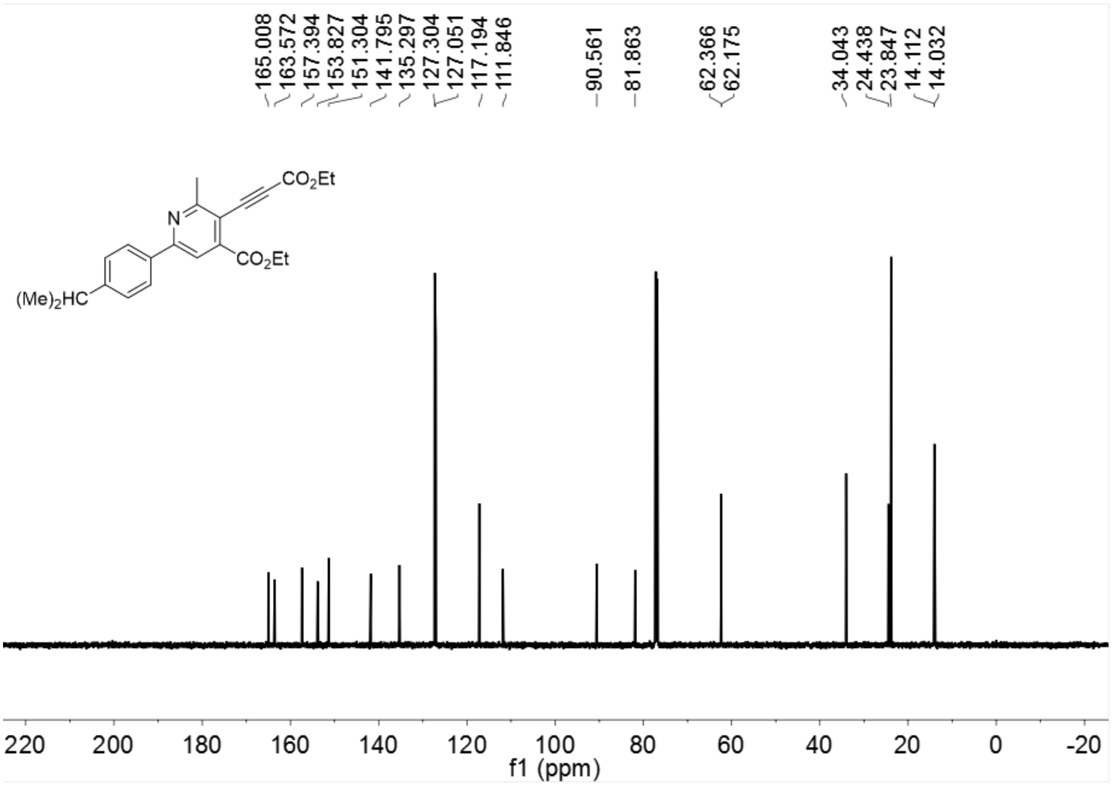


Figure 17. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ha**

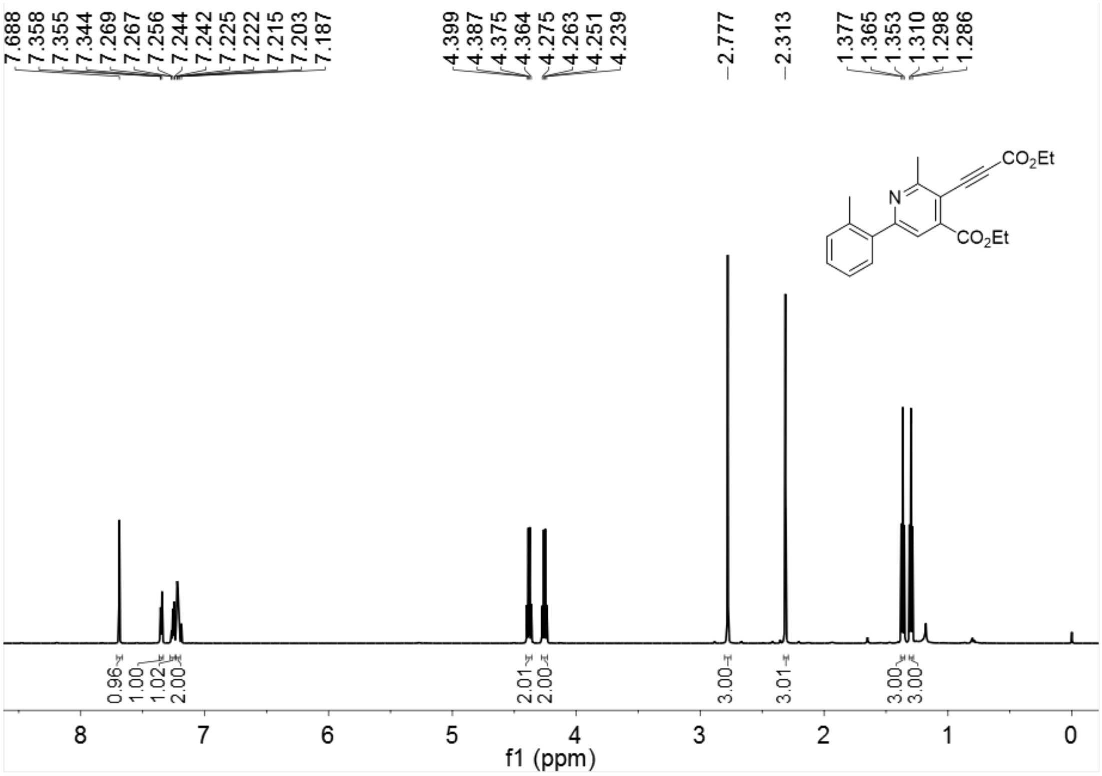


Figure 18. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3ia**

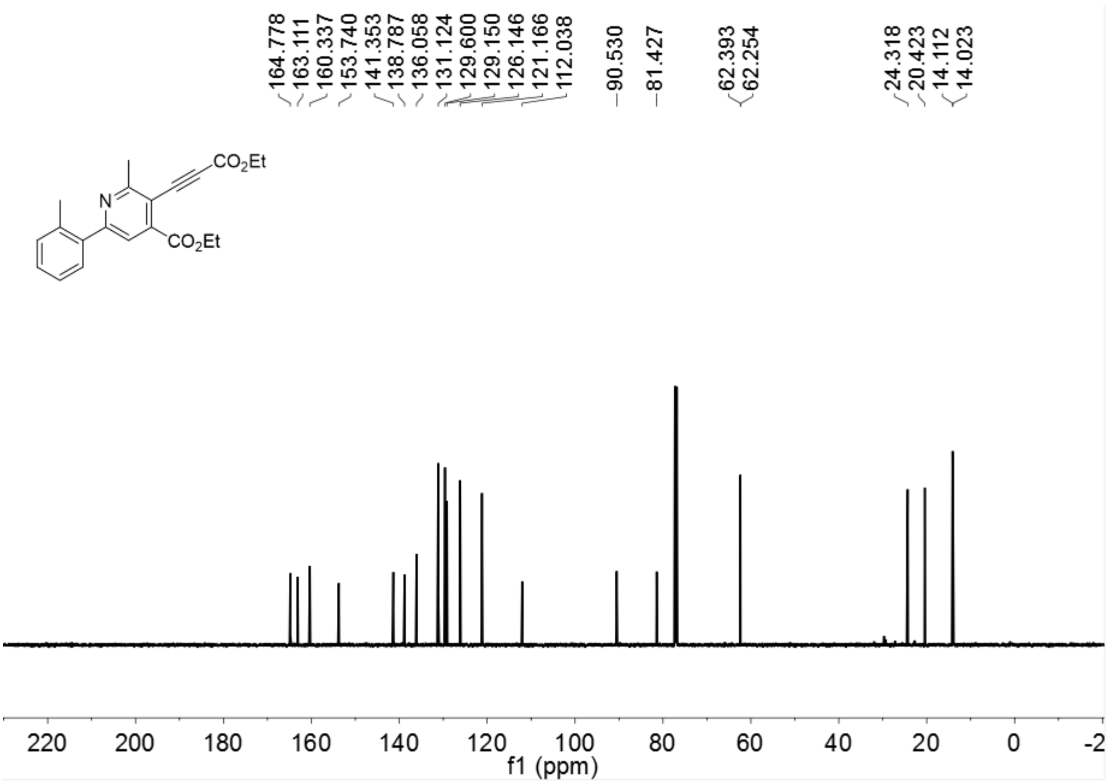


Figure 19. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ia**

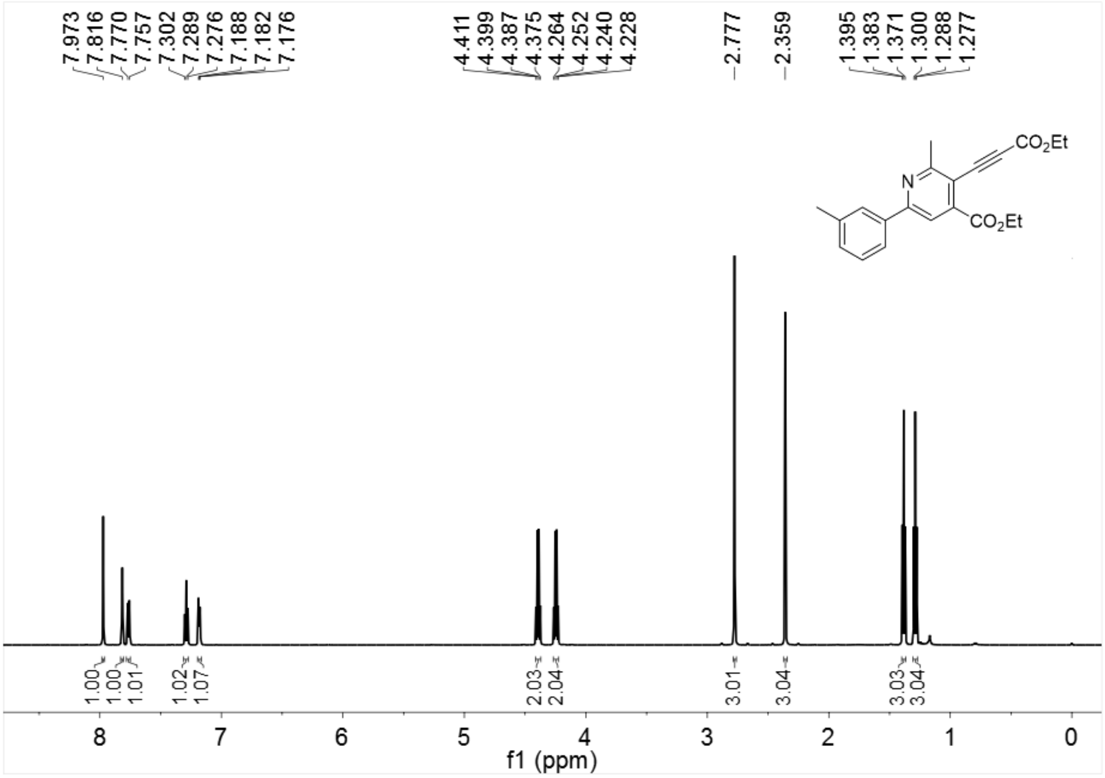


Figure 20. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3ja**

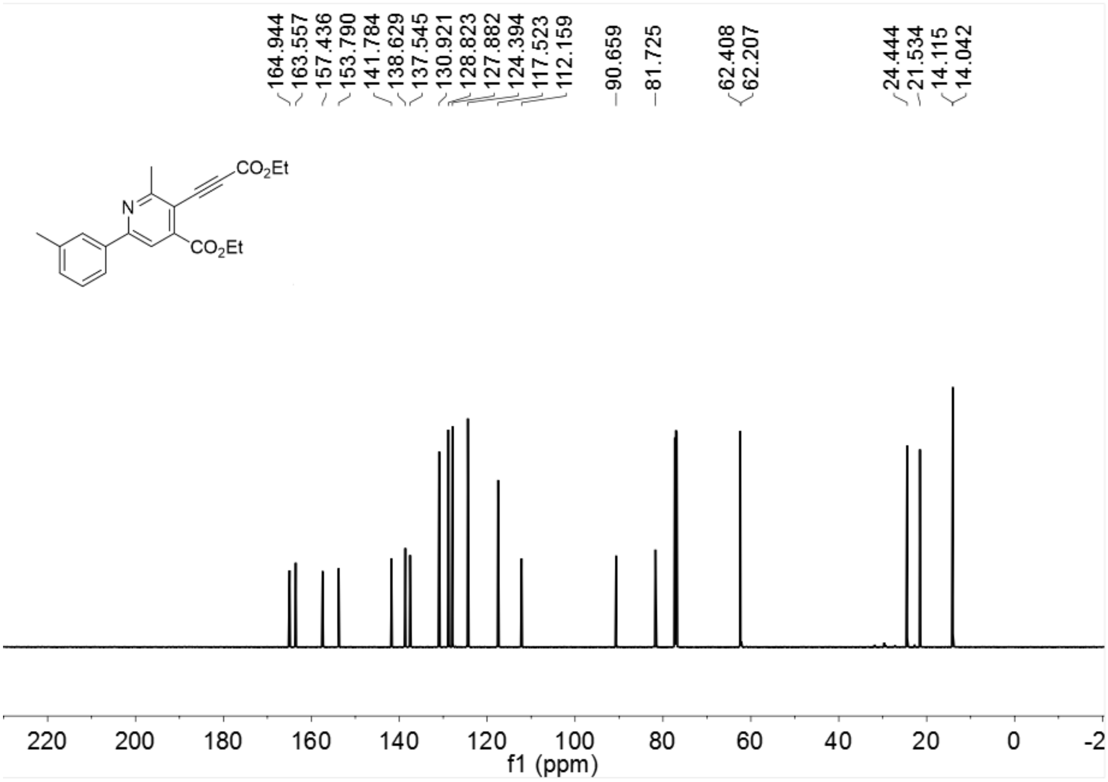


Figure 21. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ja**

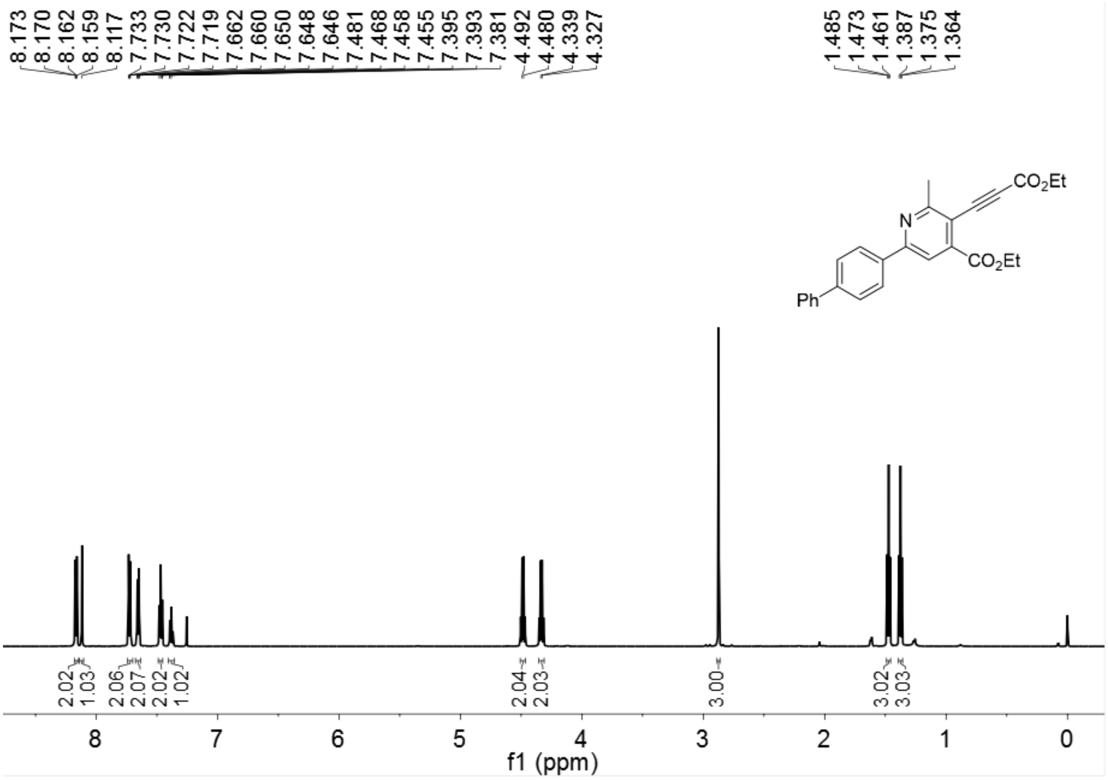


Figure 22. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3ka**

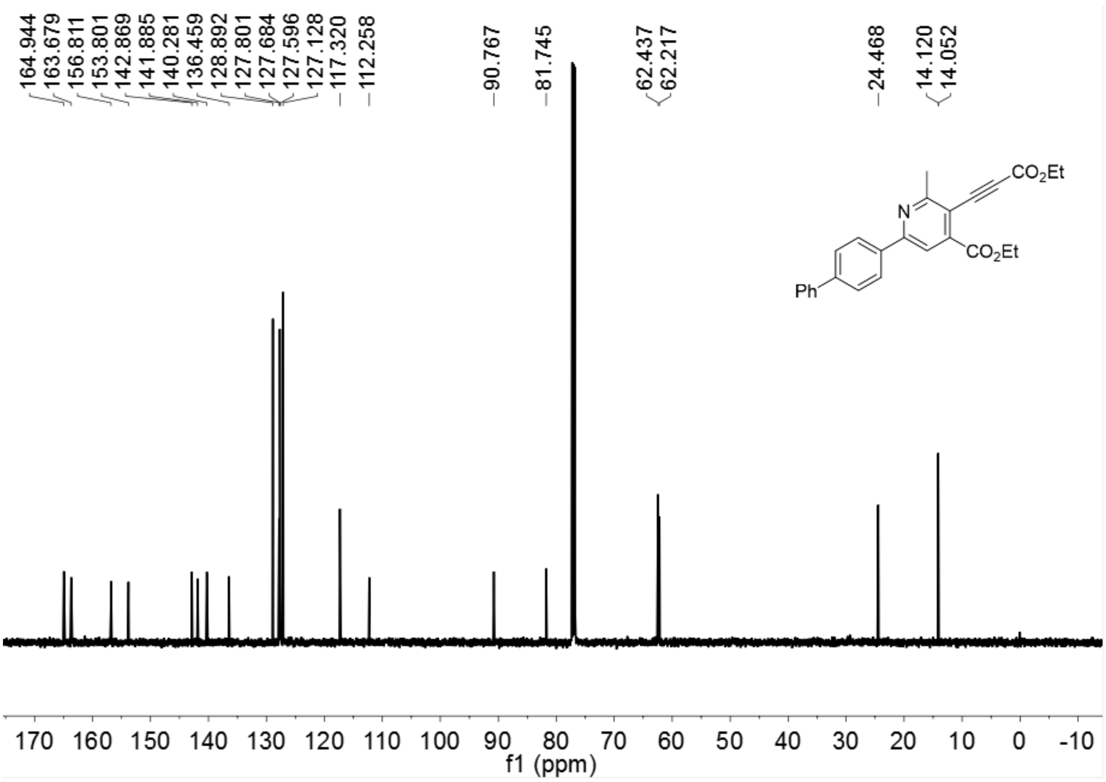


Figure 23. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ka**

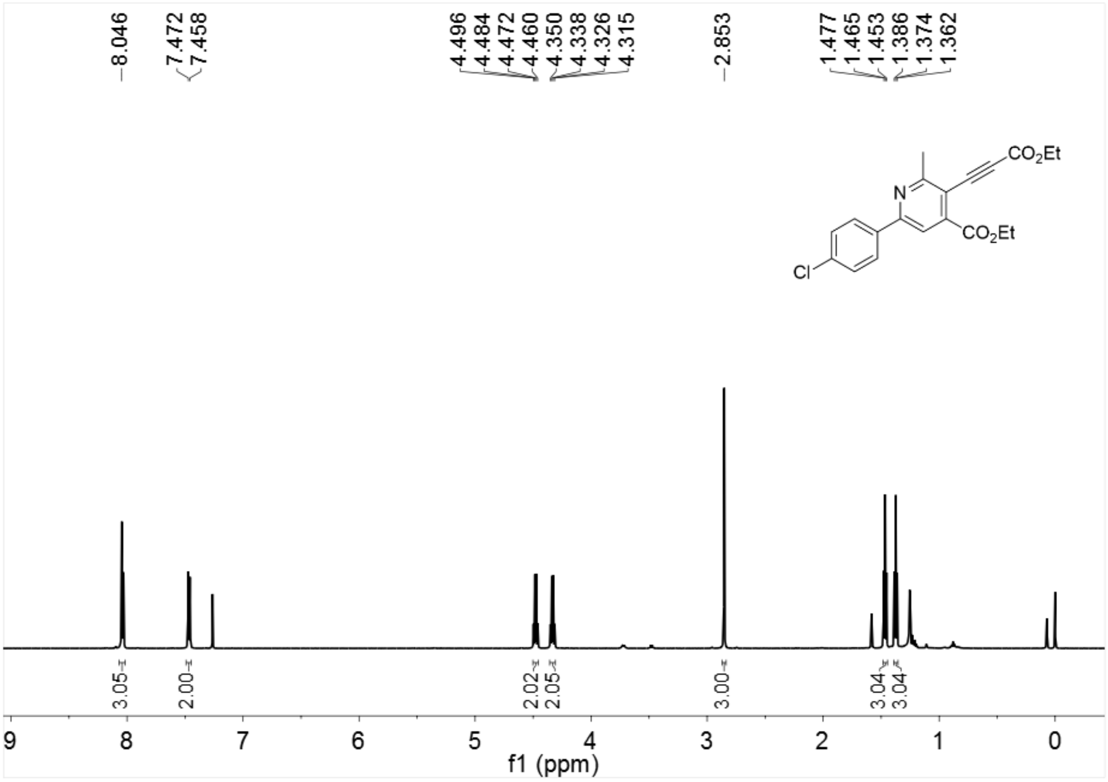


Figure 24. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3la**

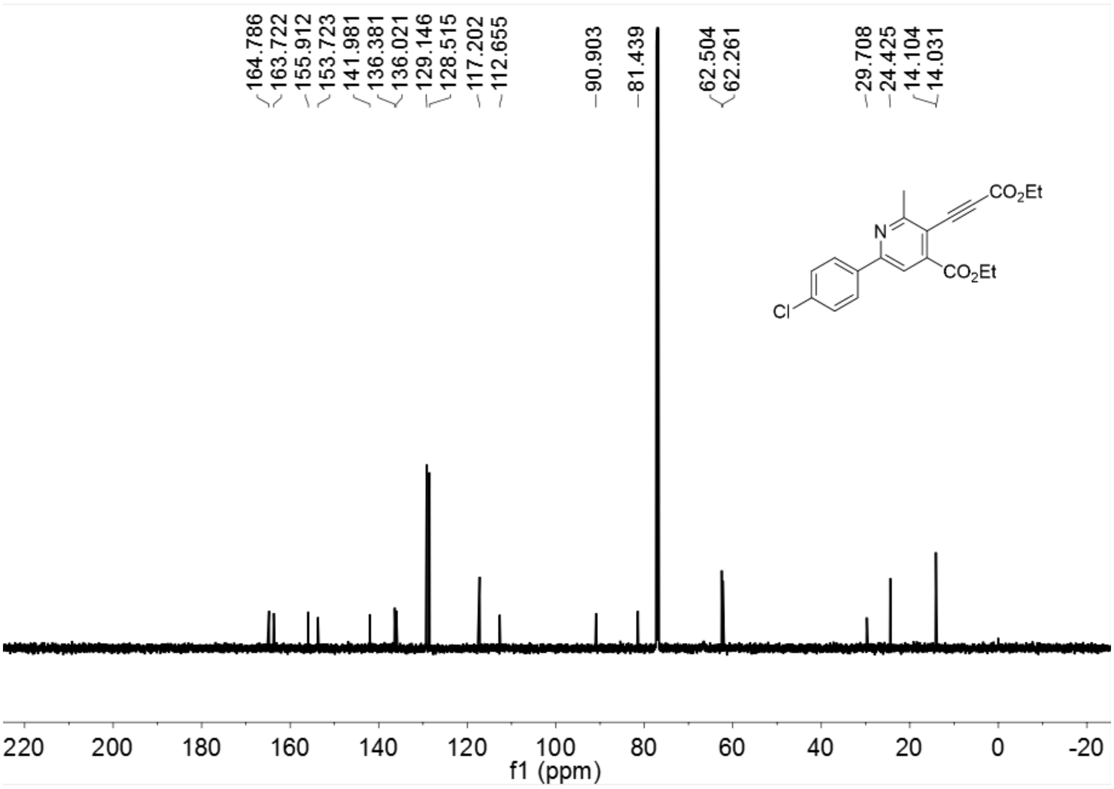


Figure 25. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3la**

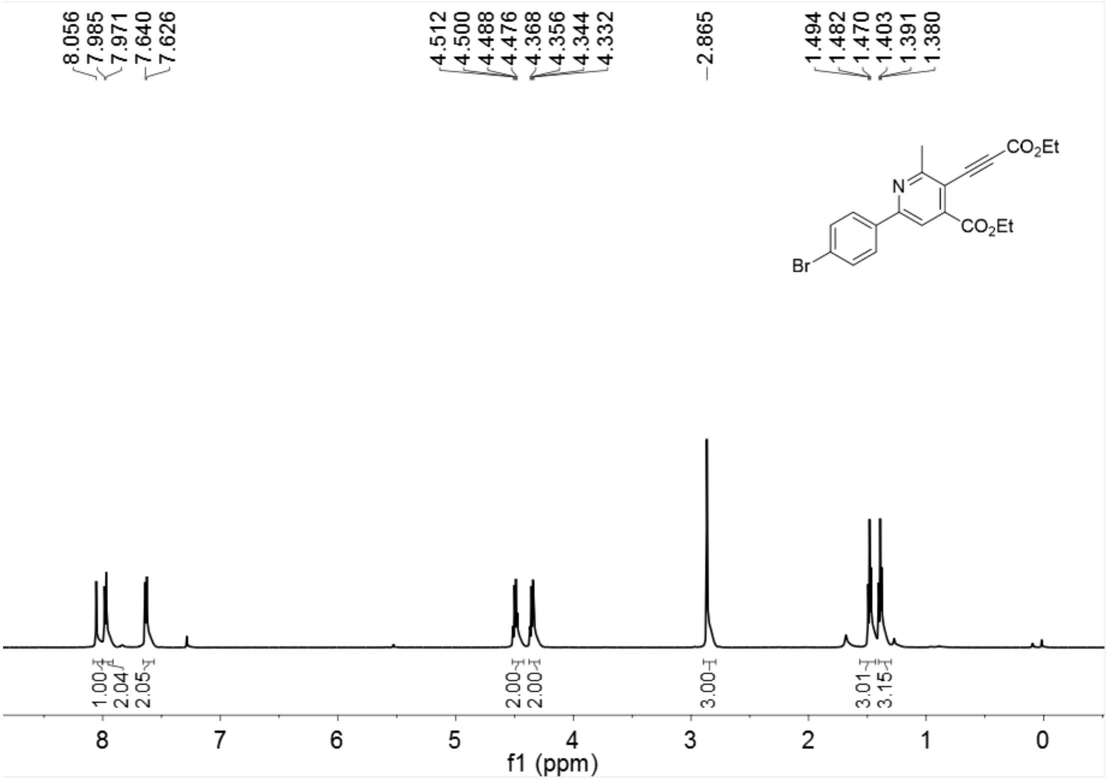


Figure 26. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3ma**

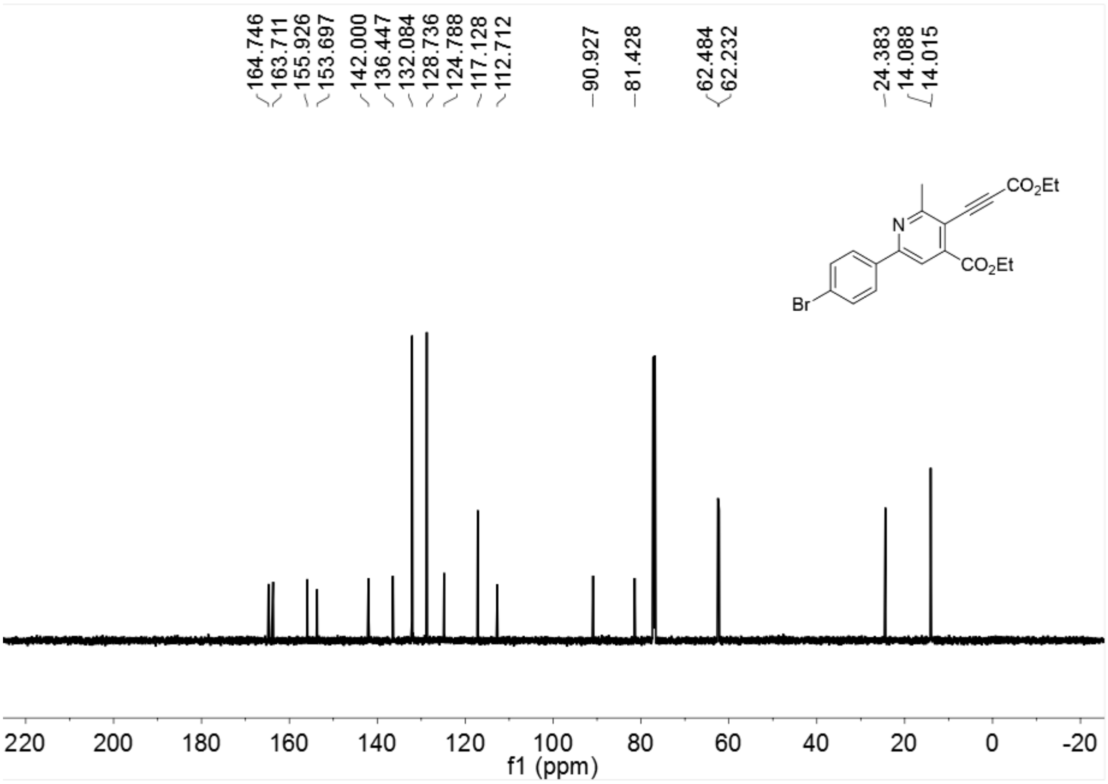


Figure 27. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ma**

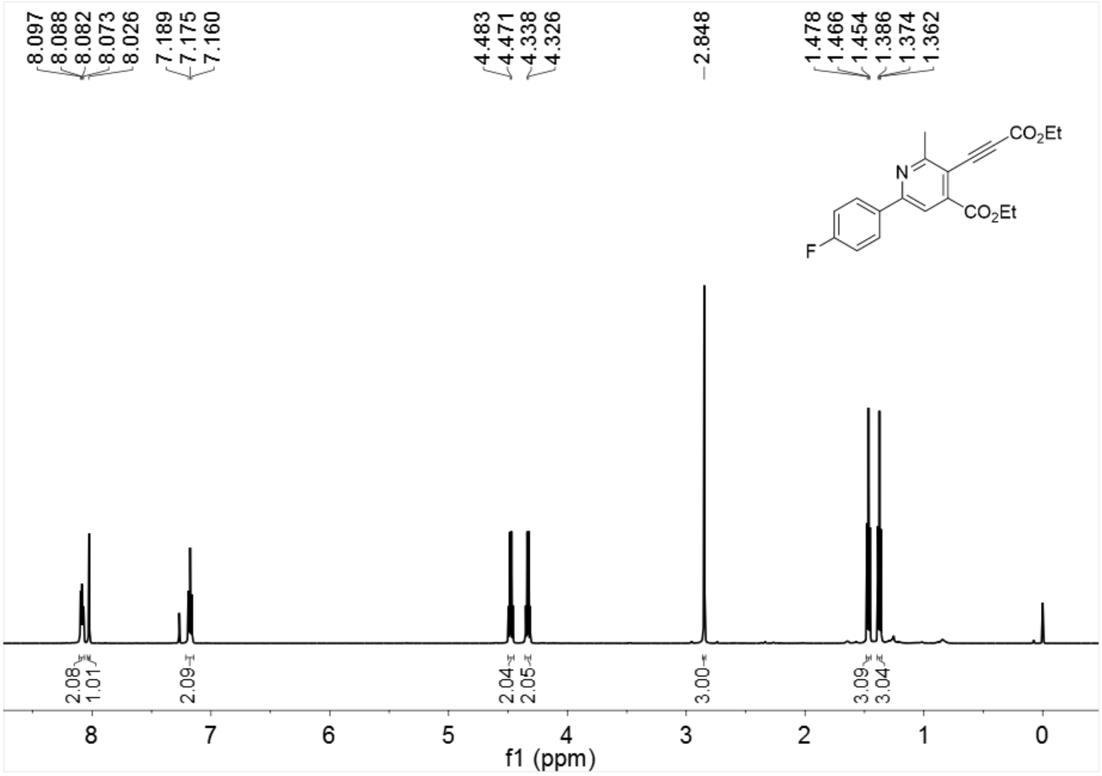


Figure 28. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3na**

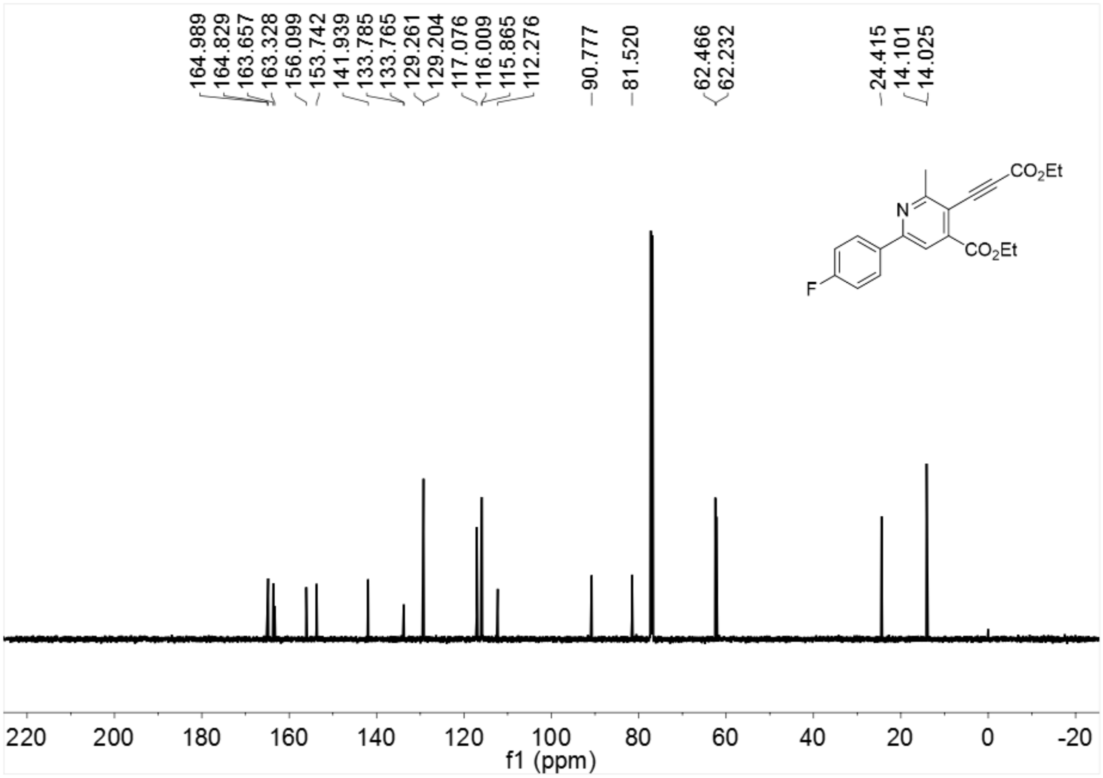


Figure 29. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3na**

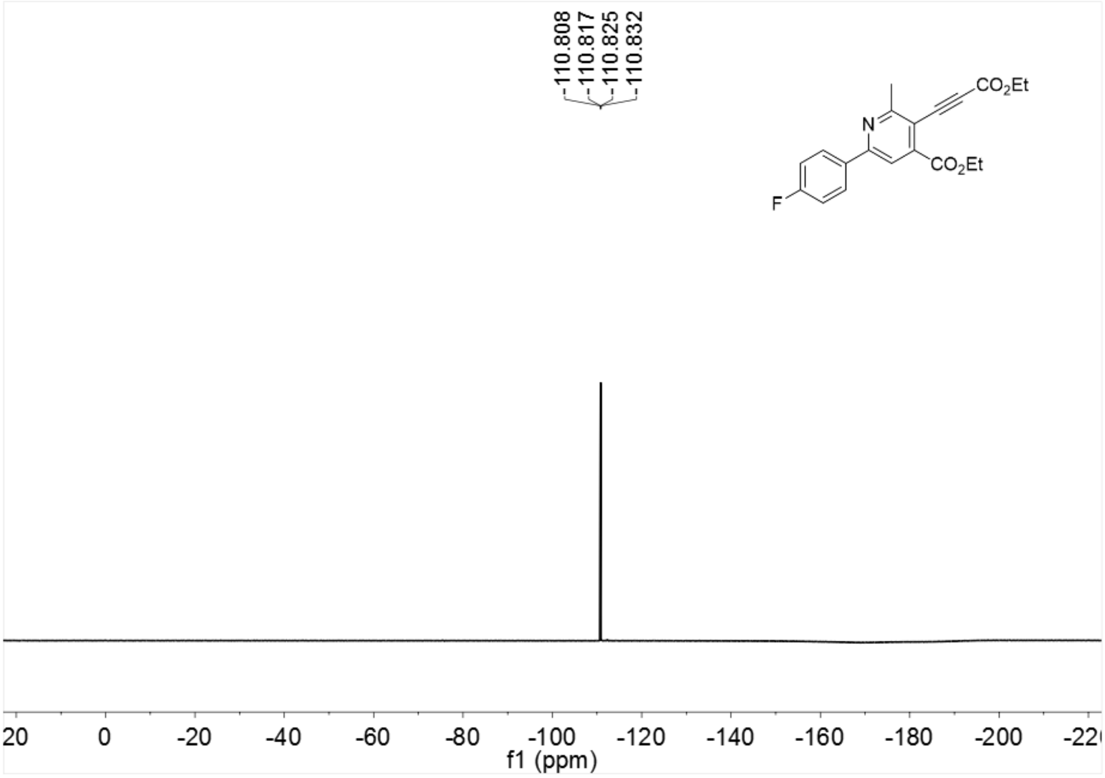


Figure 30. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **3na**

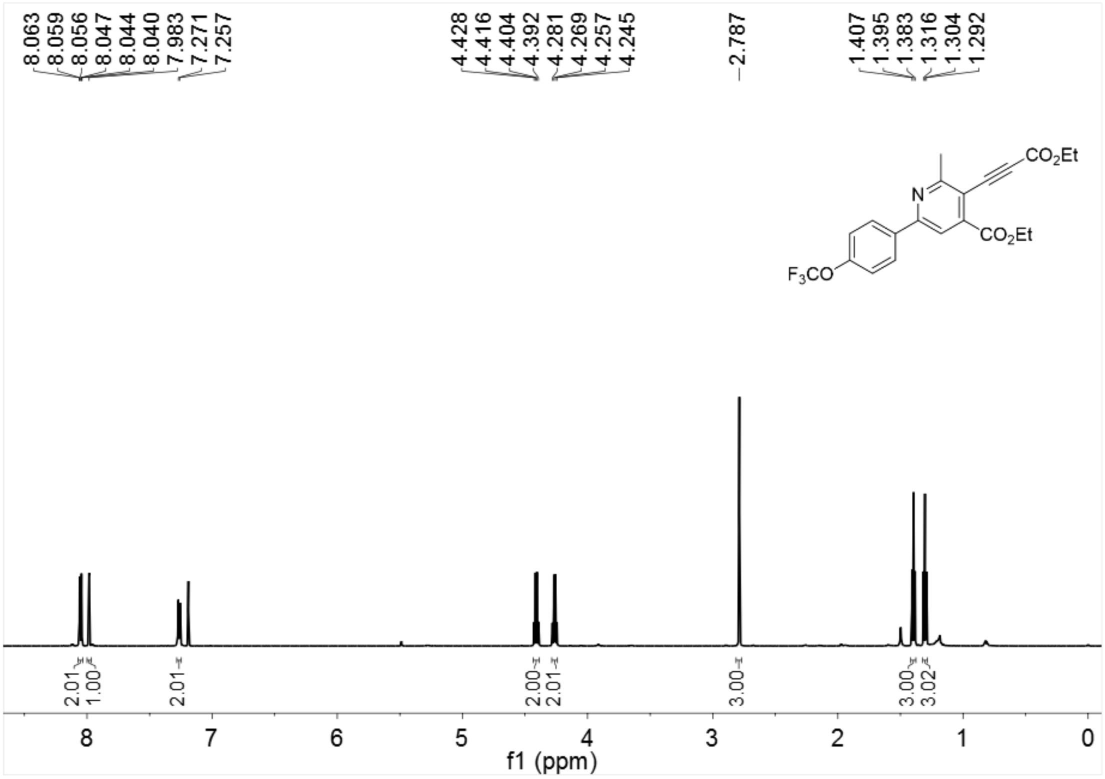


Figure 31. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3oa**

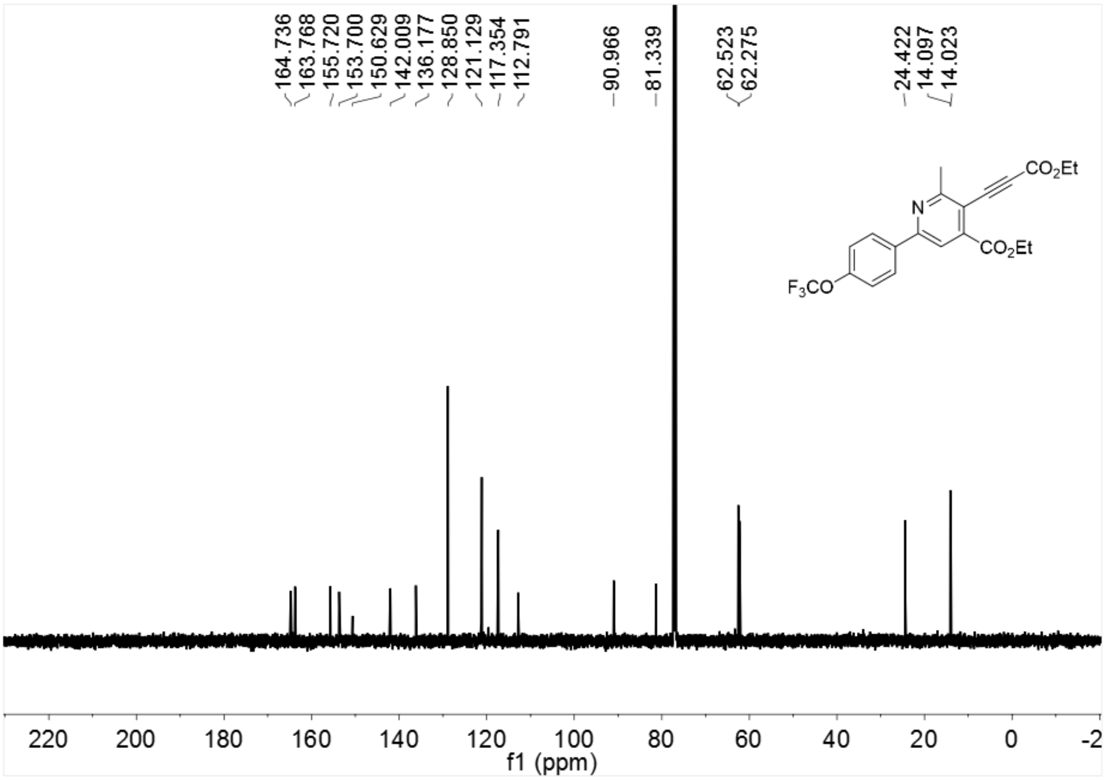


Figure 32. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3oa**

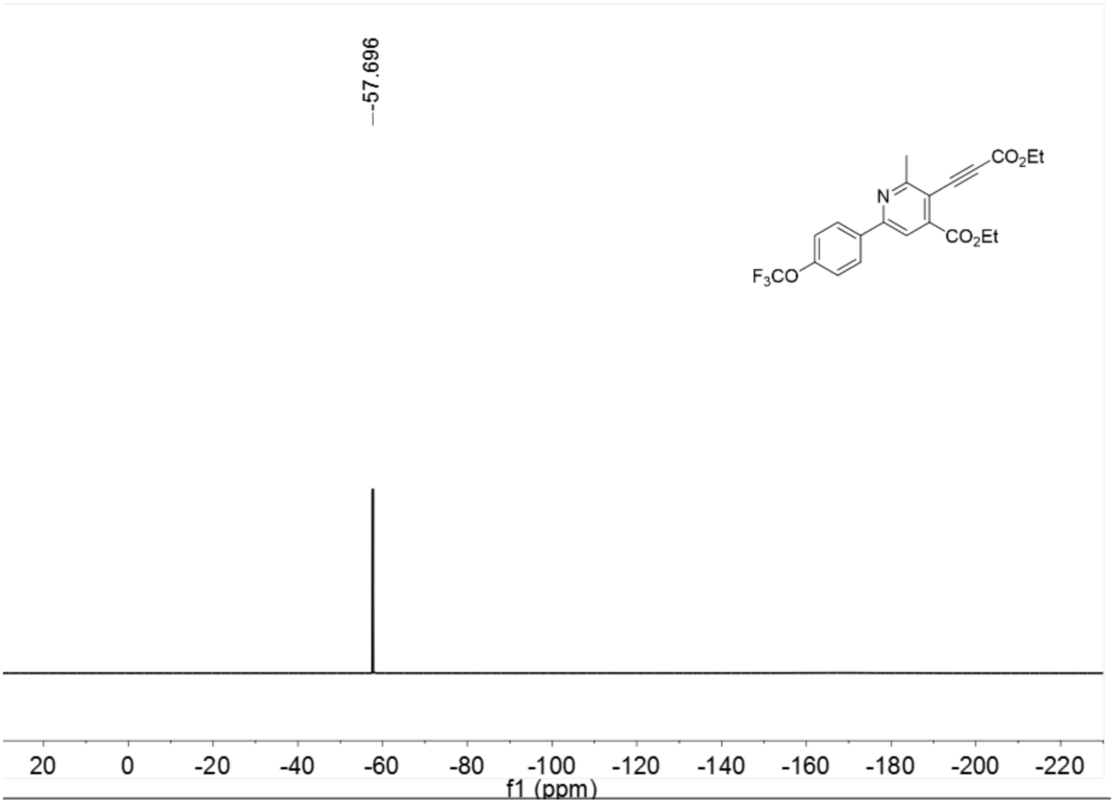


Figure 33. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **3oa**

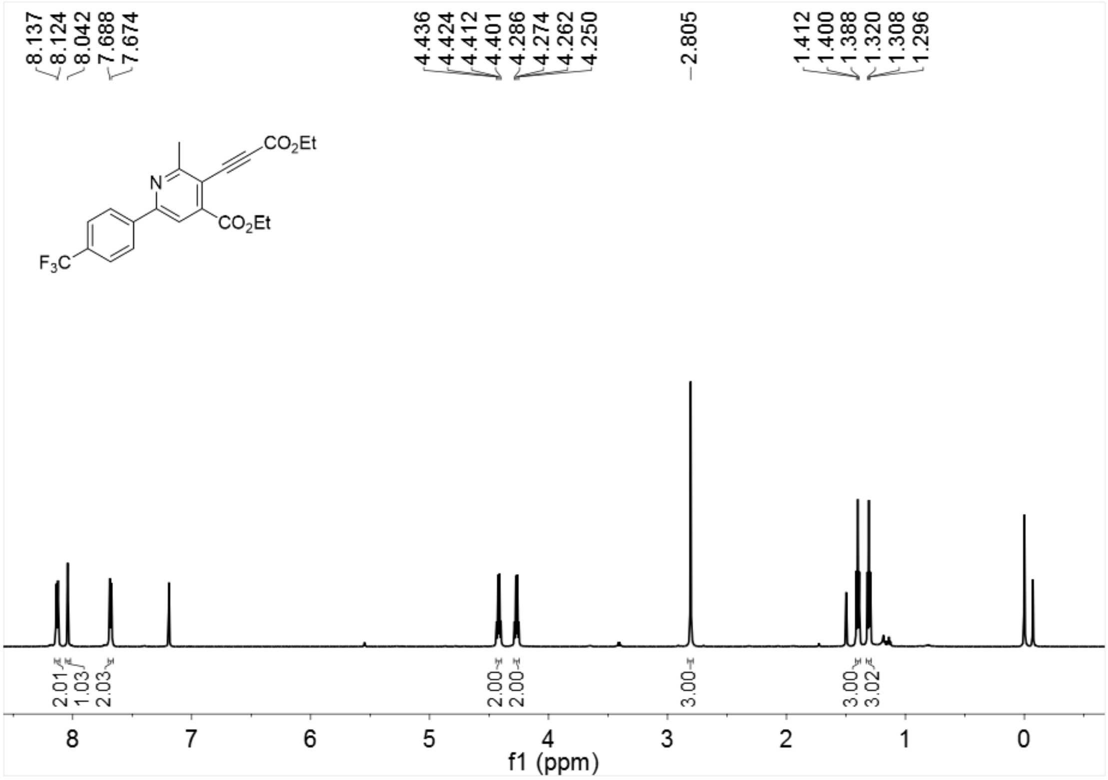


Figure 34. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3pa**

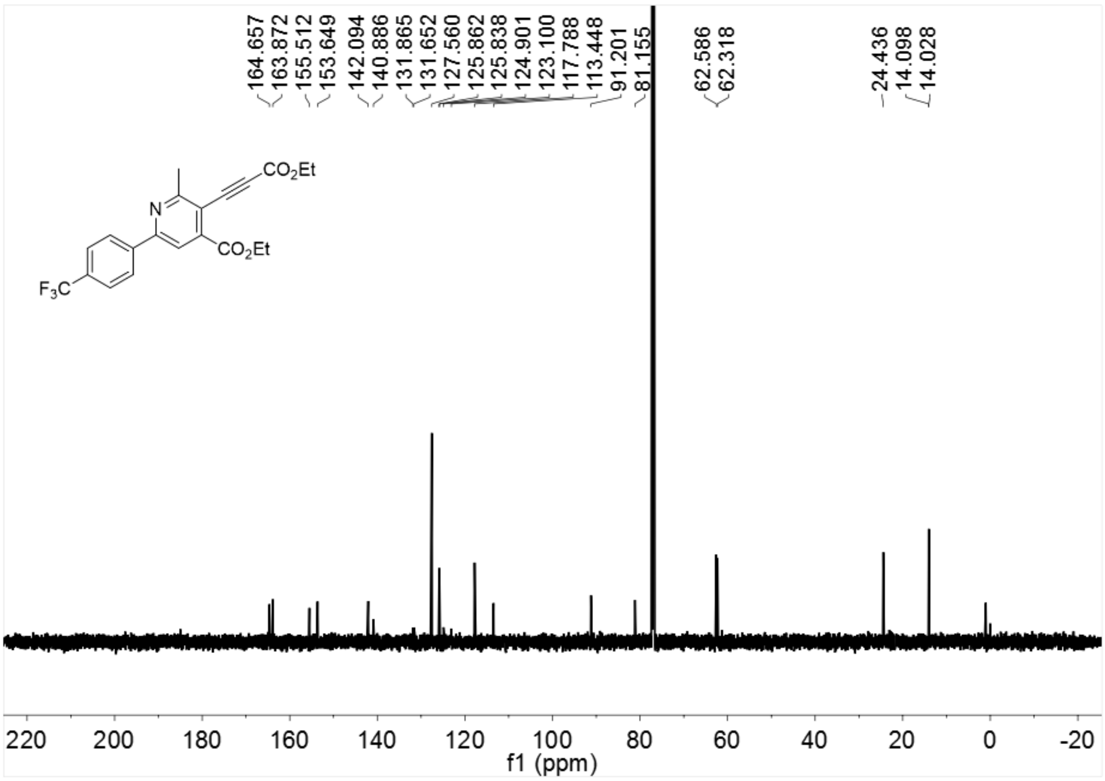


Figure 35. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3pa**

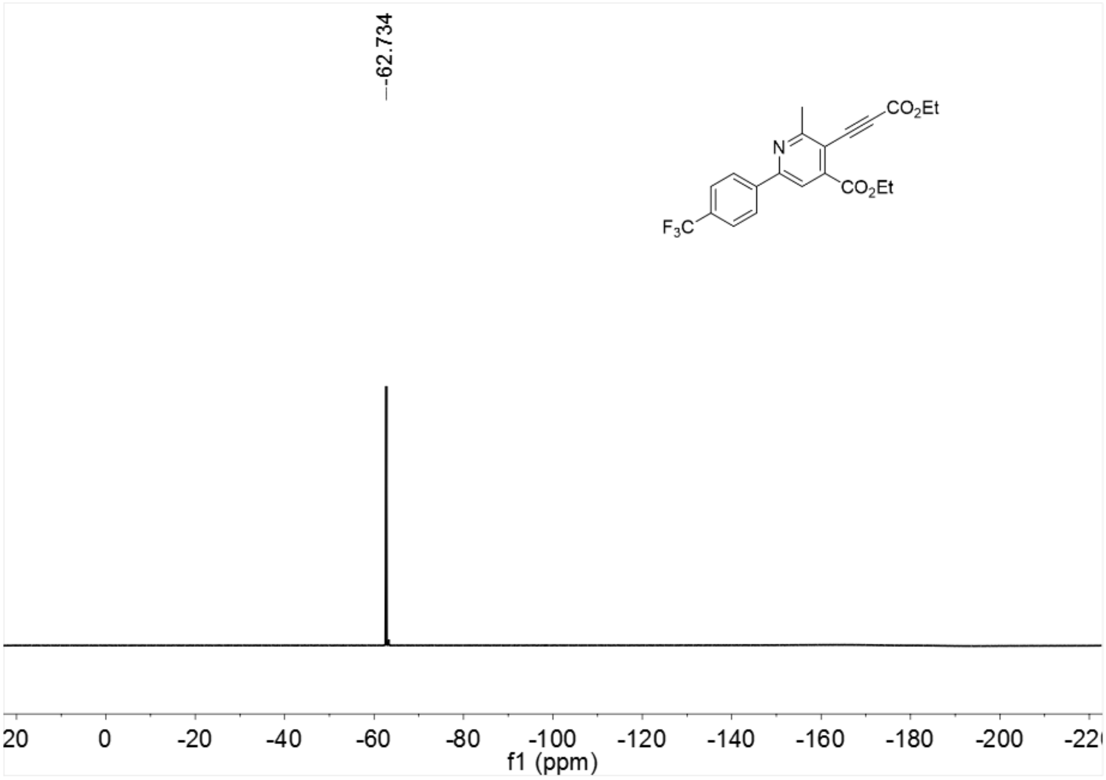


Figure 36. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **3pa**

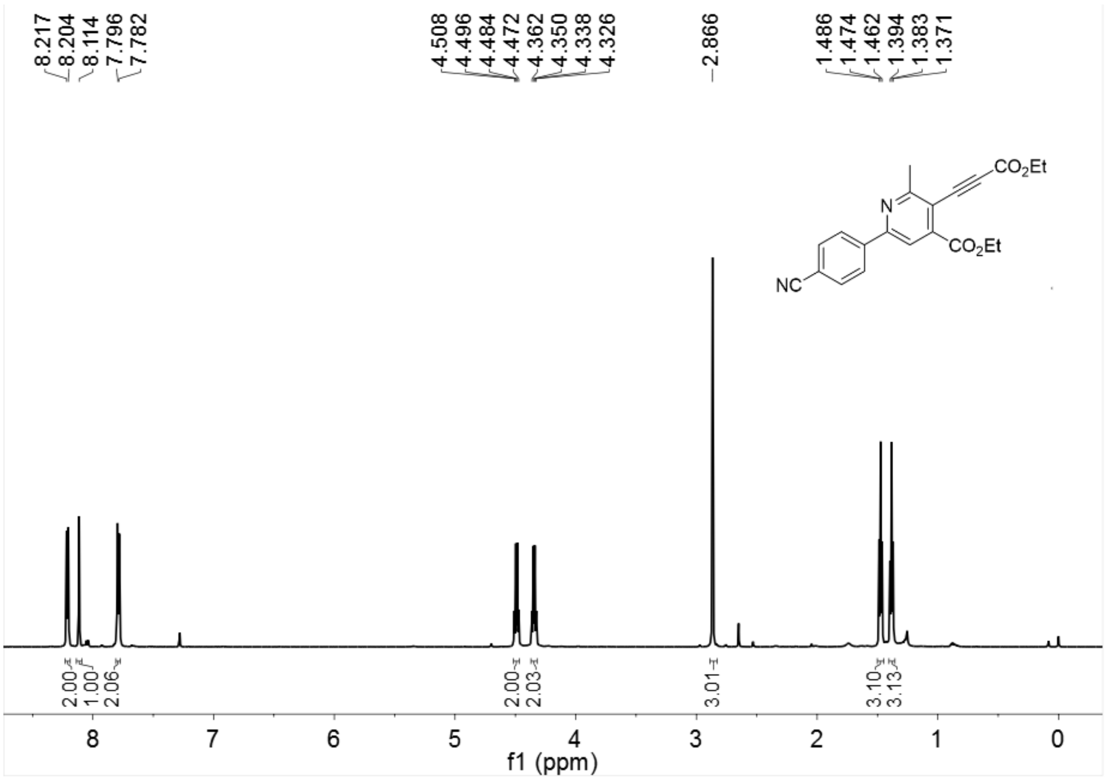


Figure 37. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3qa**

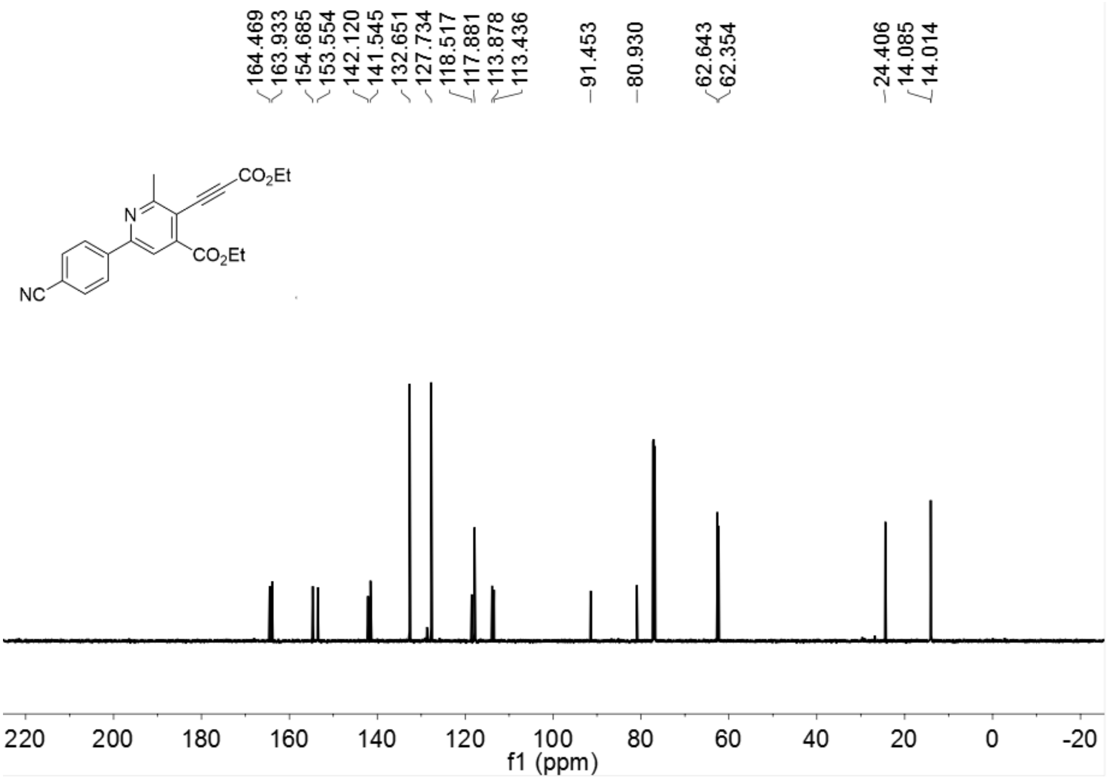


Figure 38. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3qa**

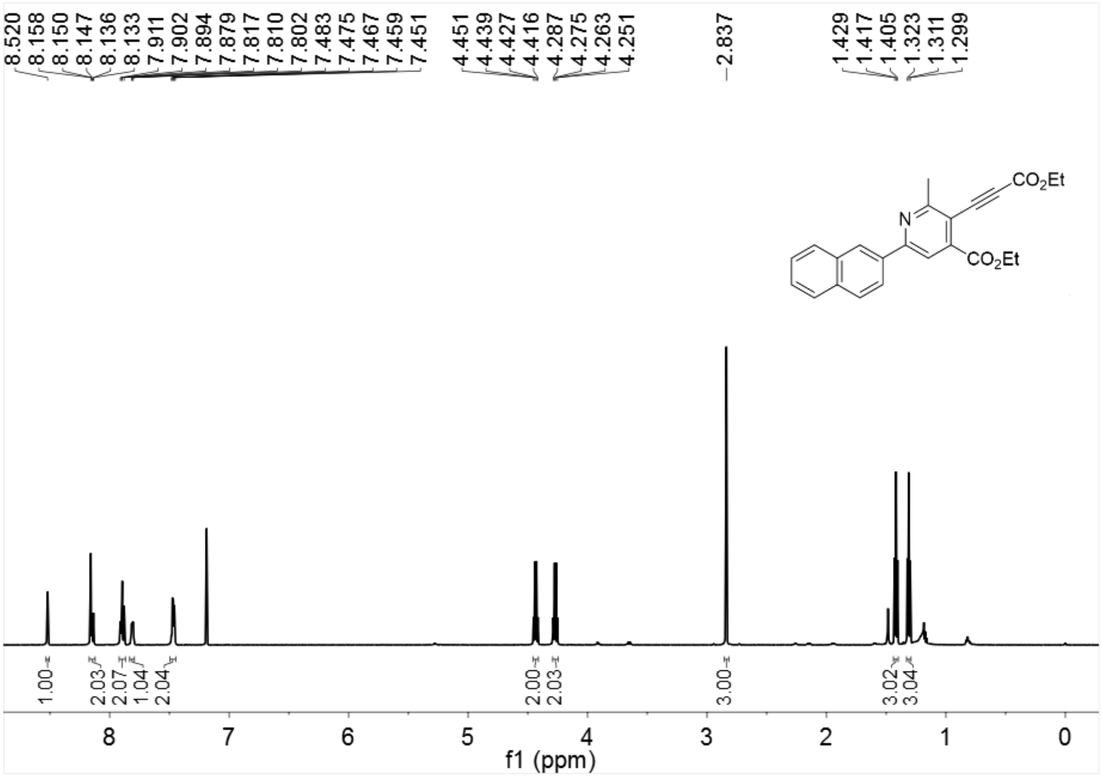


Figure 39. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3ra**

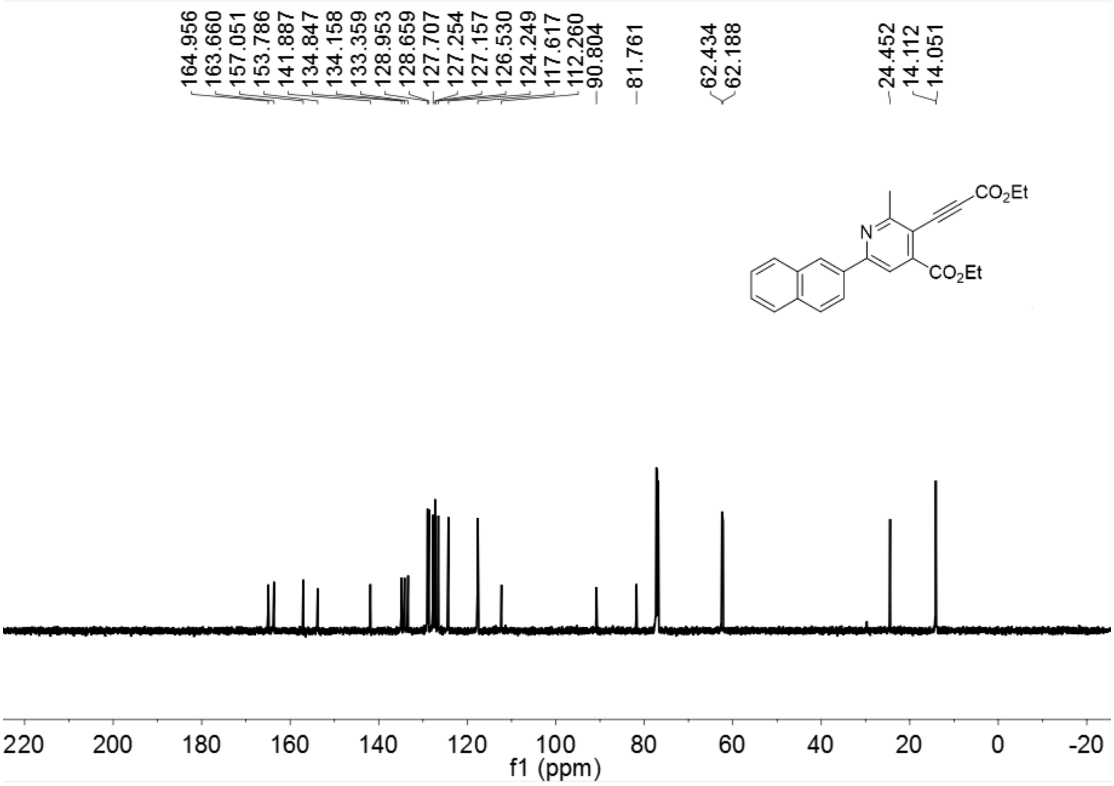


Figure 40. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ra**

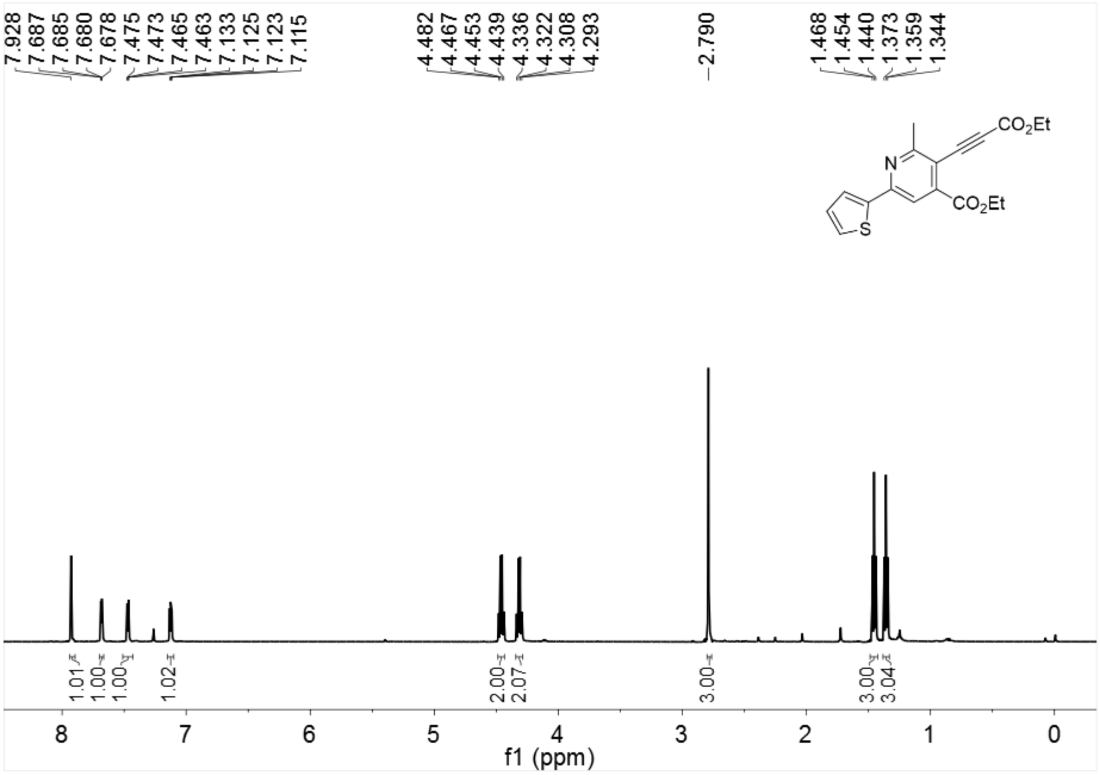


Figure 41. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3sa**

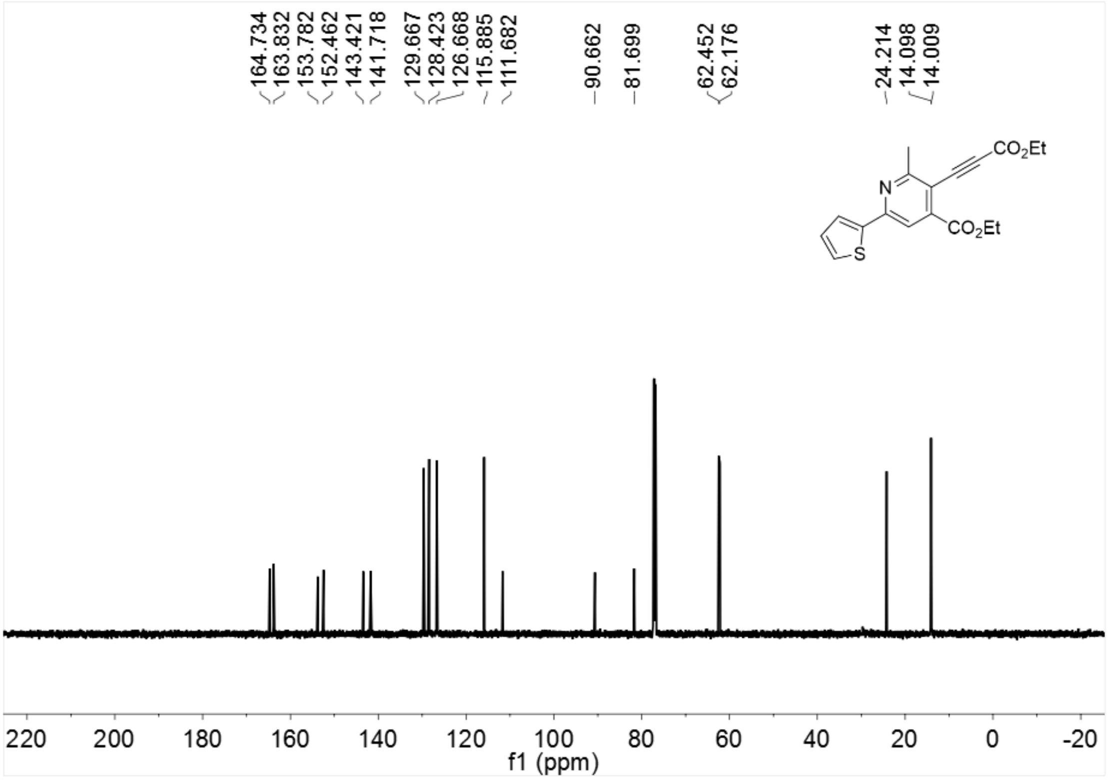


Figure 42. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3sa**

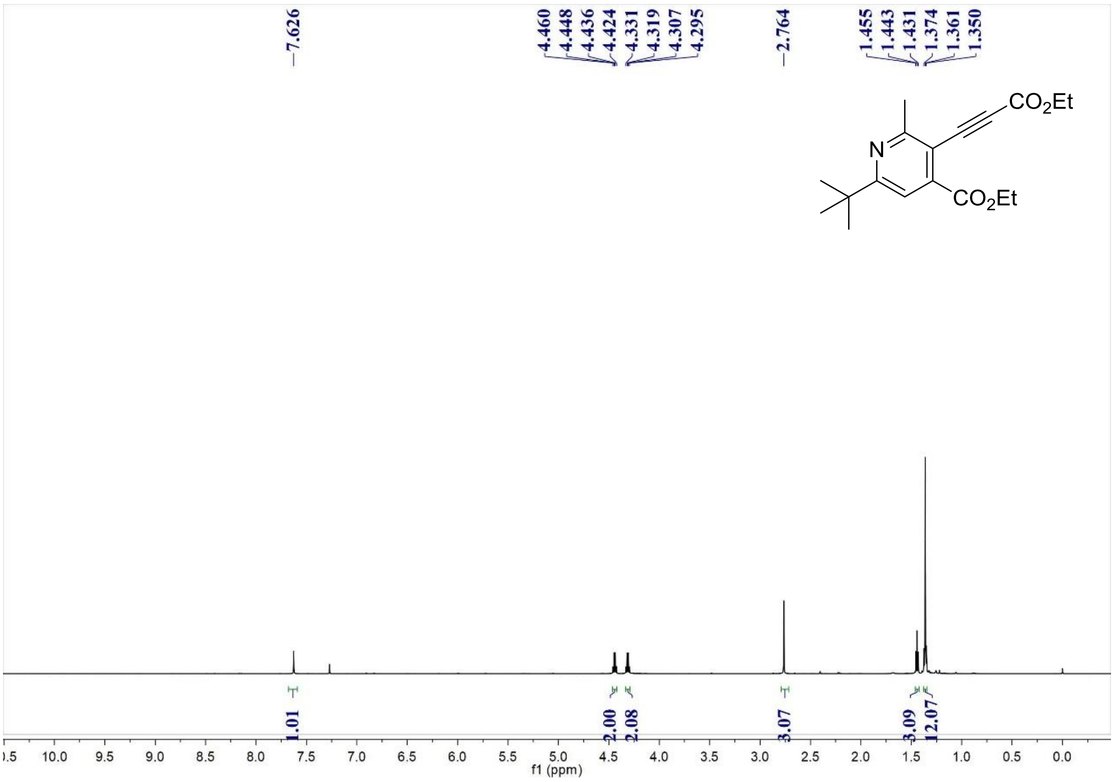


Figure 43. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3ta**

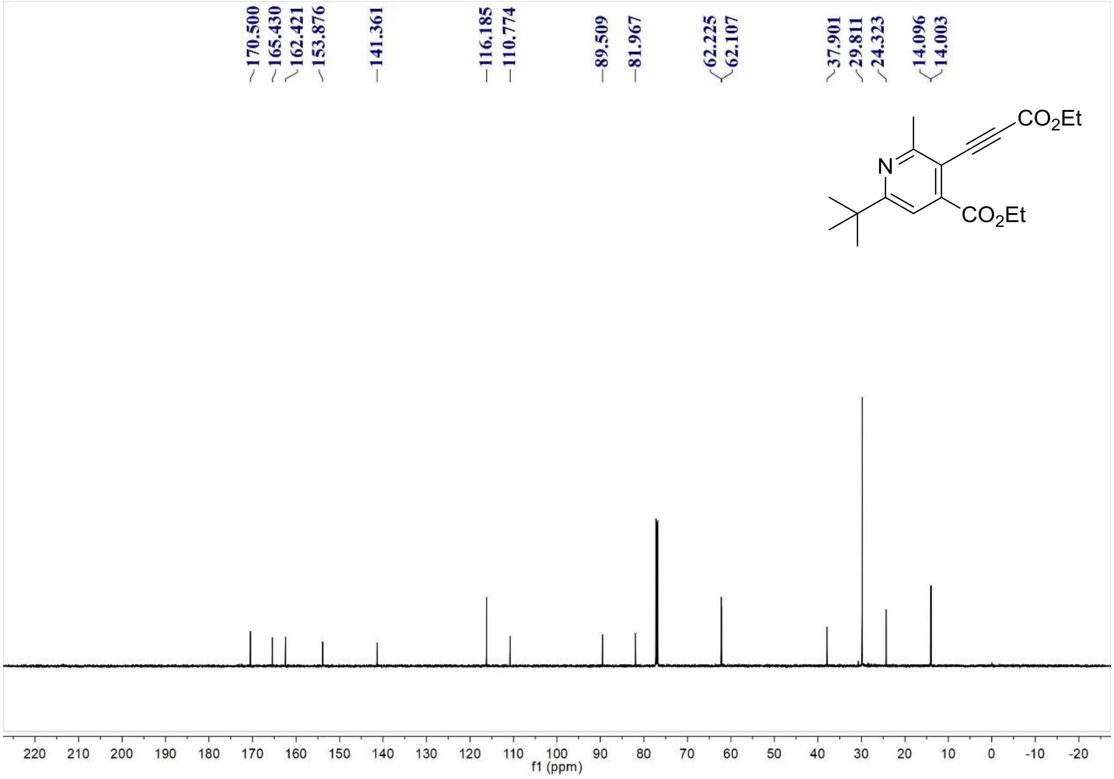


Figure 44. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ta**

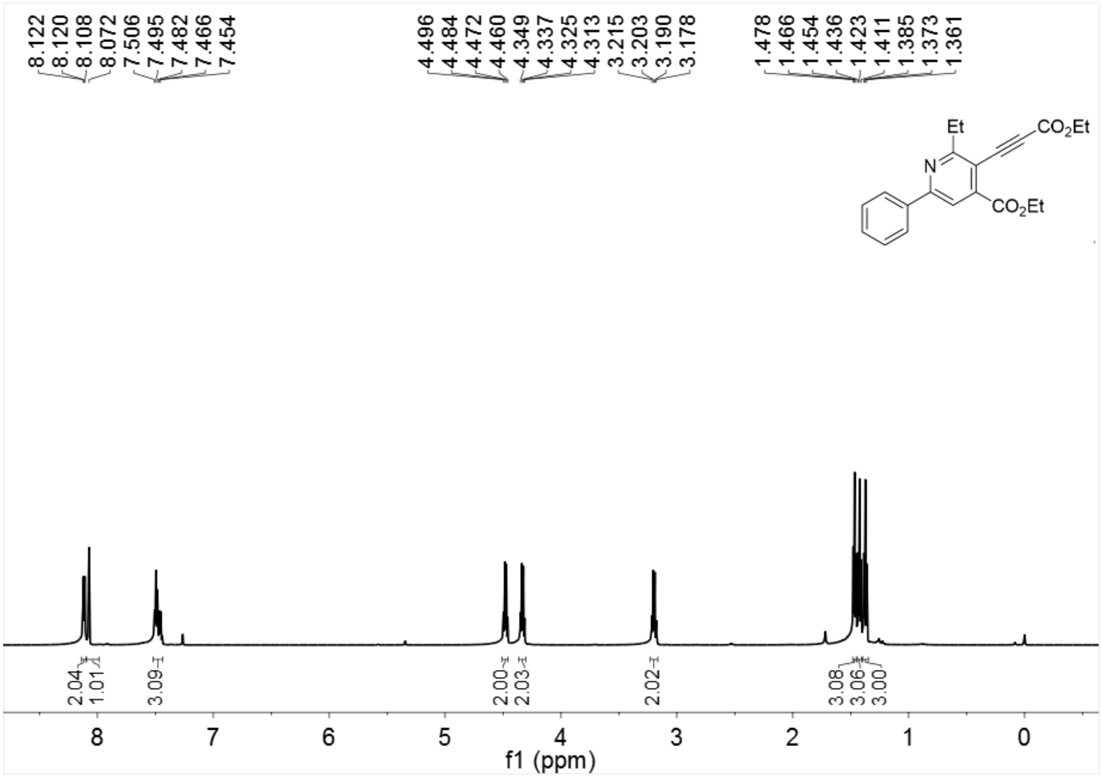


Figure 45. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3ua**

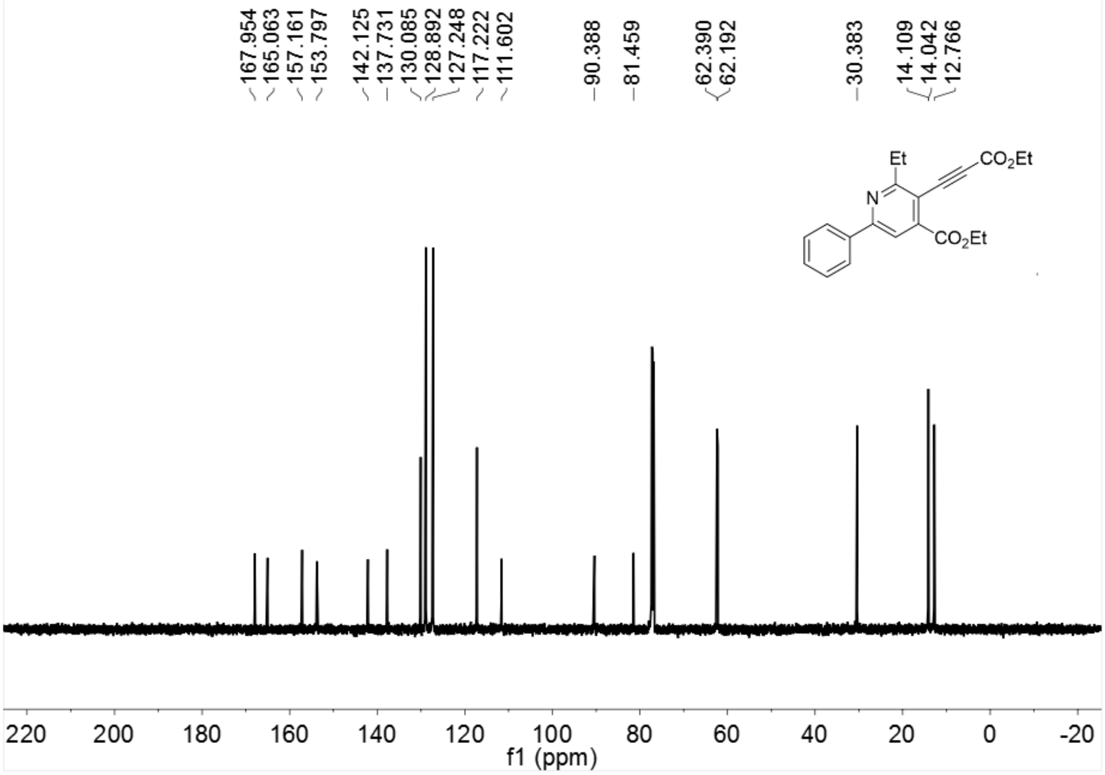


Figure 46. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ua**

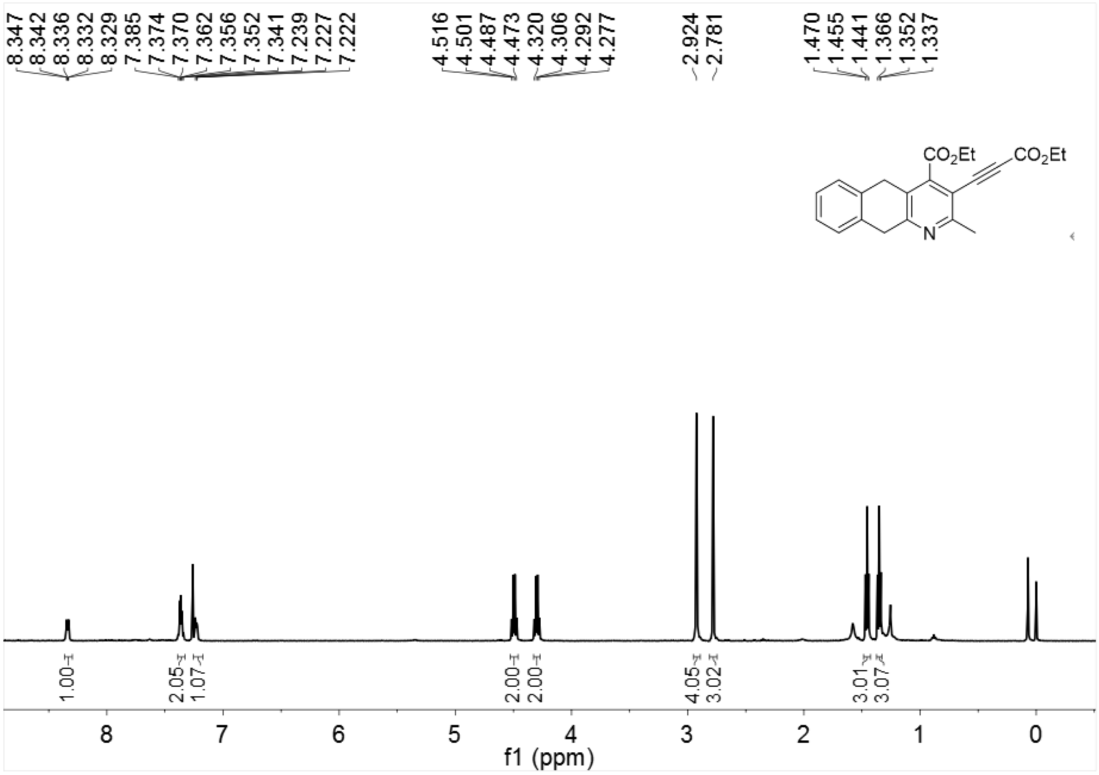


Figure 47. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3va**

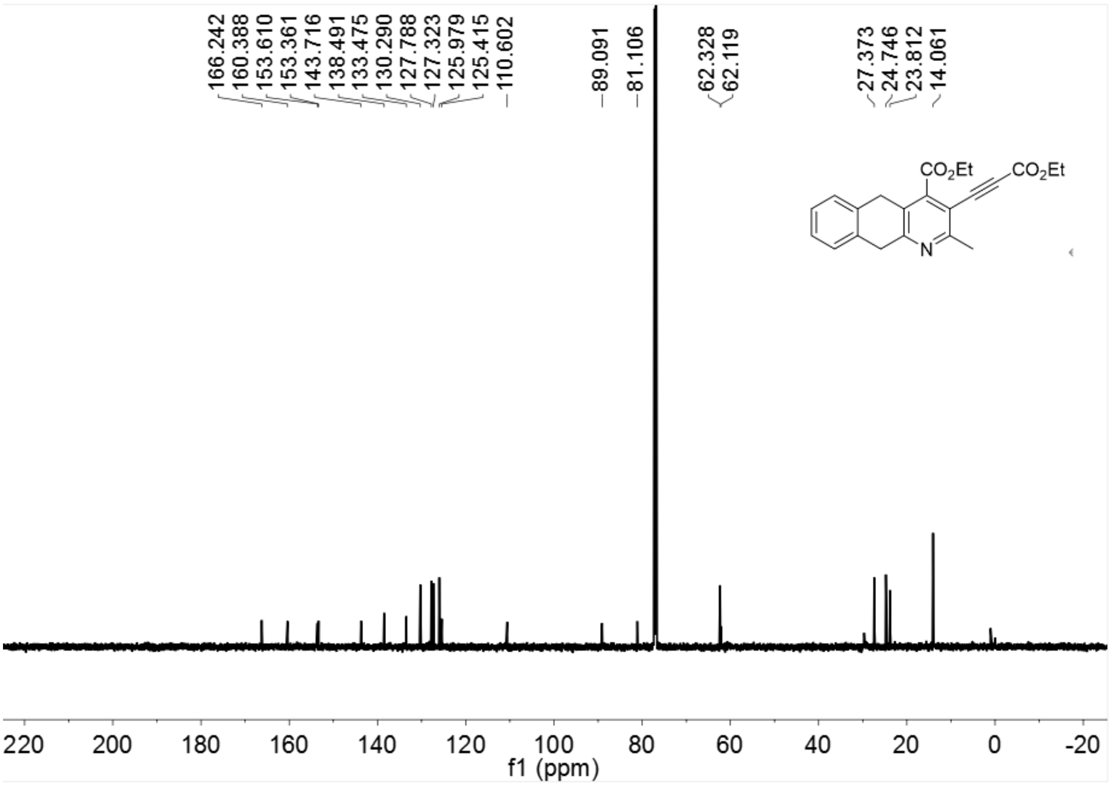


Figure 48. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3va**

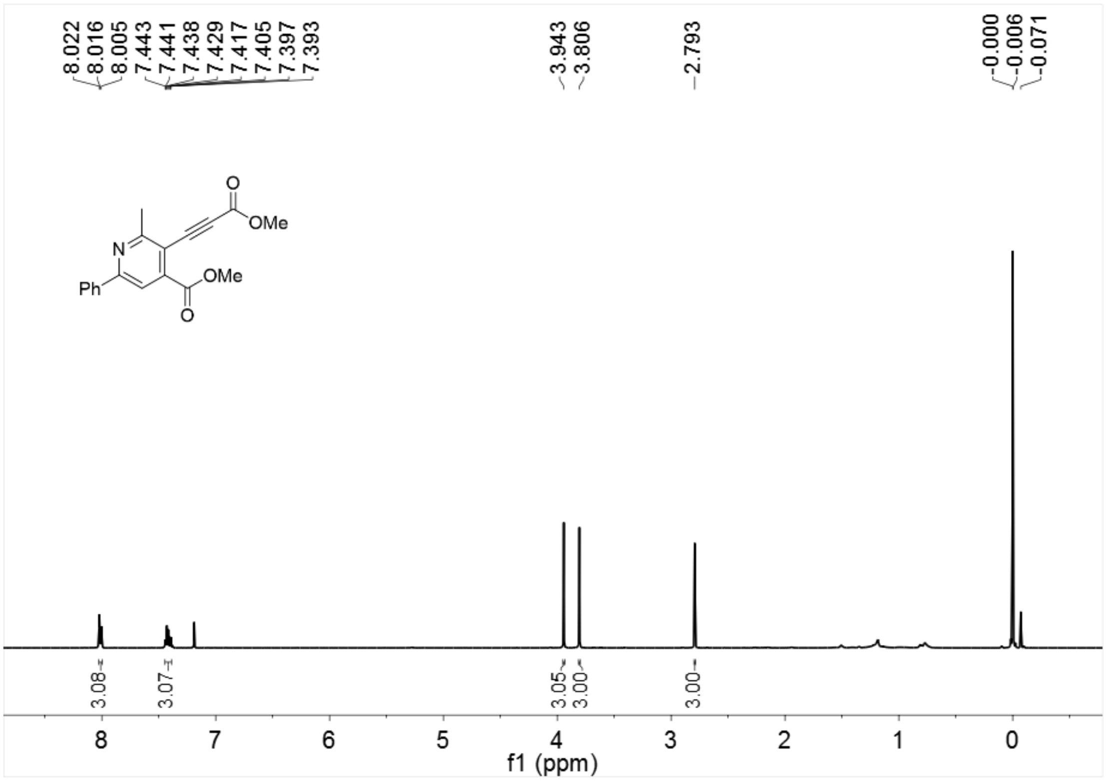


Figure 49. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3ab**

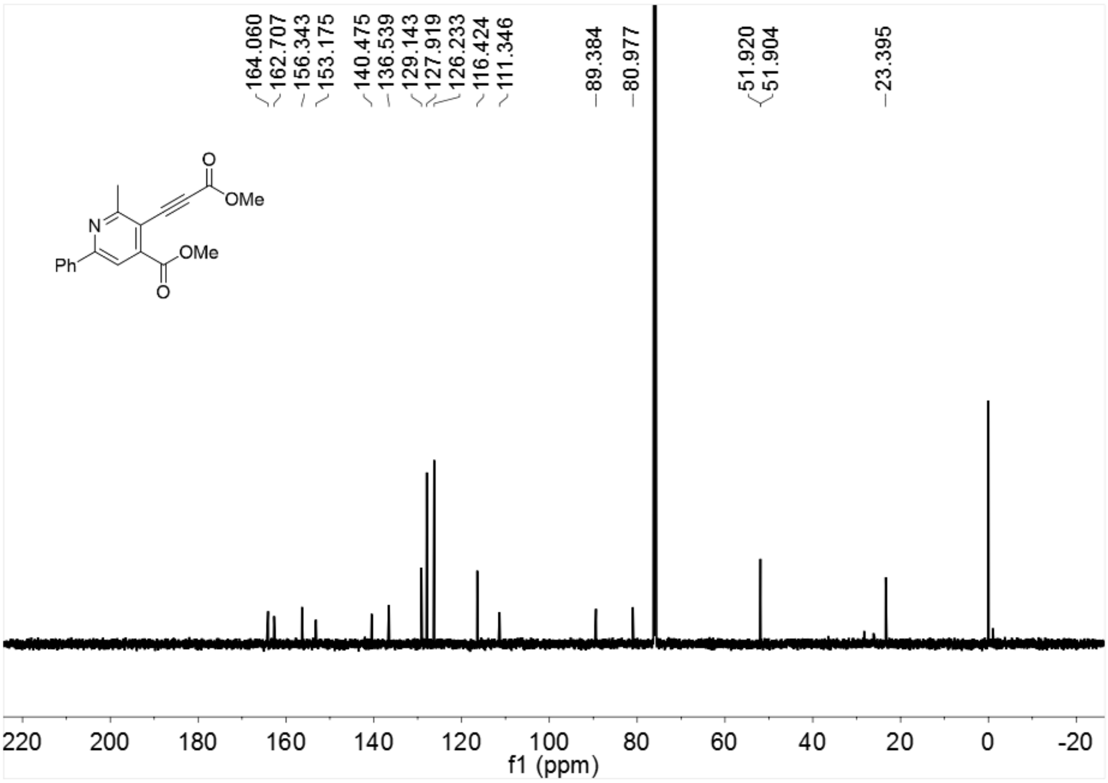


Figure 50. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ab**

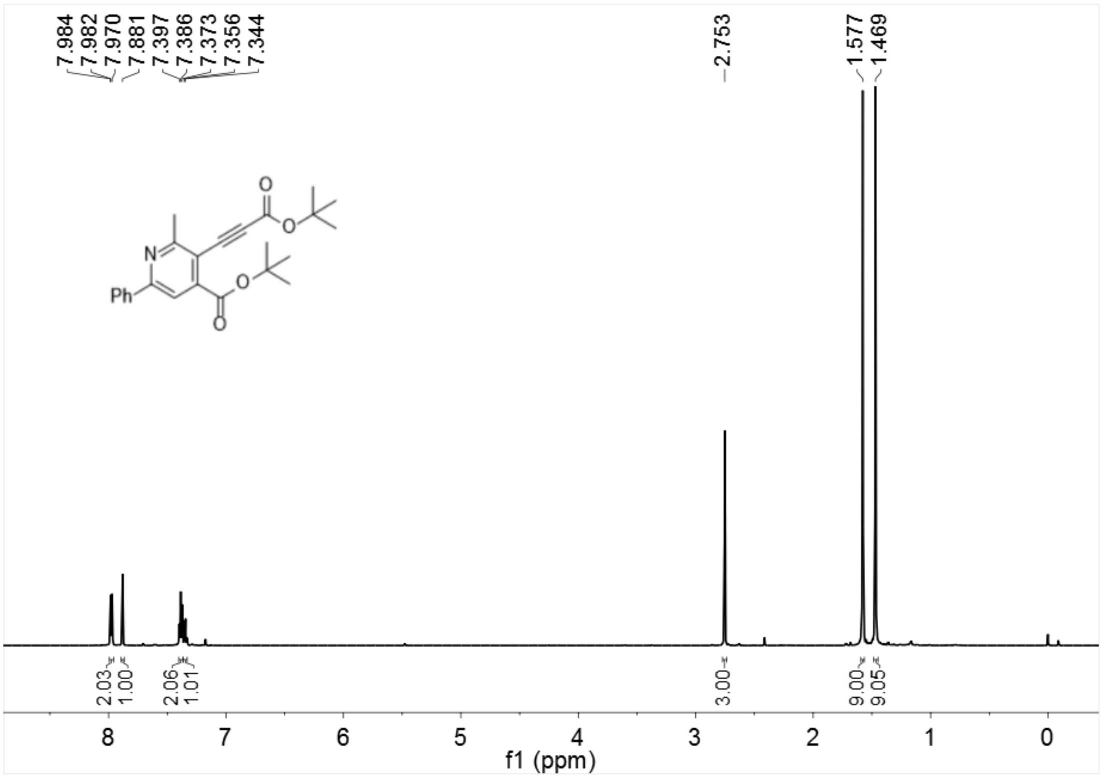


Figure 51. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3ac**

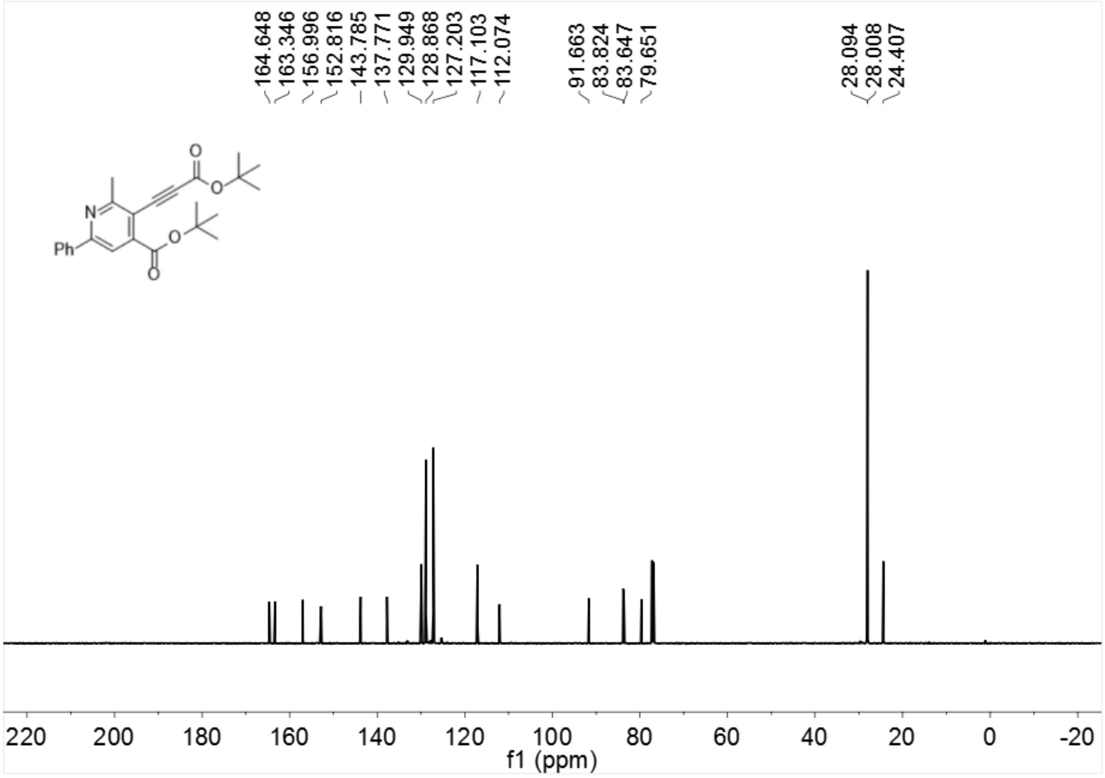


Figure 52. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ac**

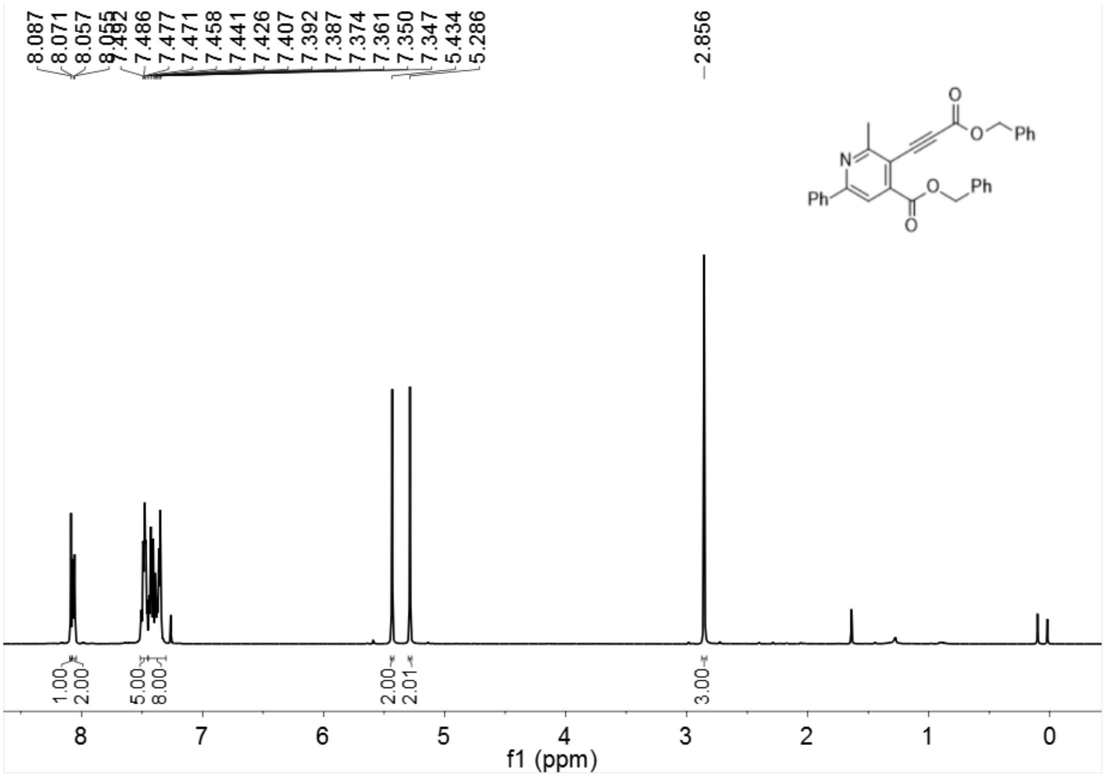


Figure 53. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3ad**

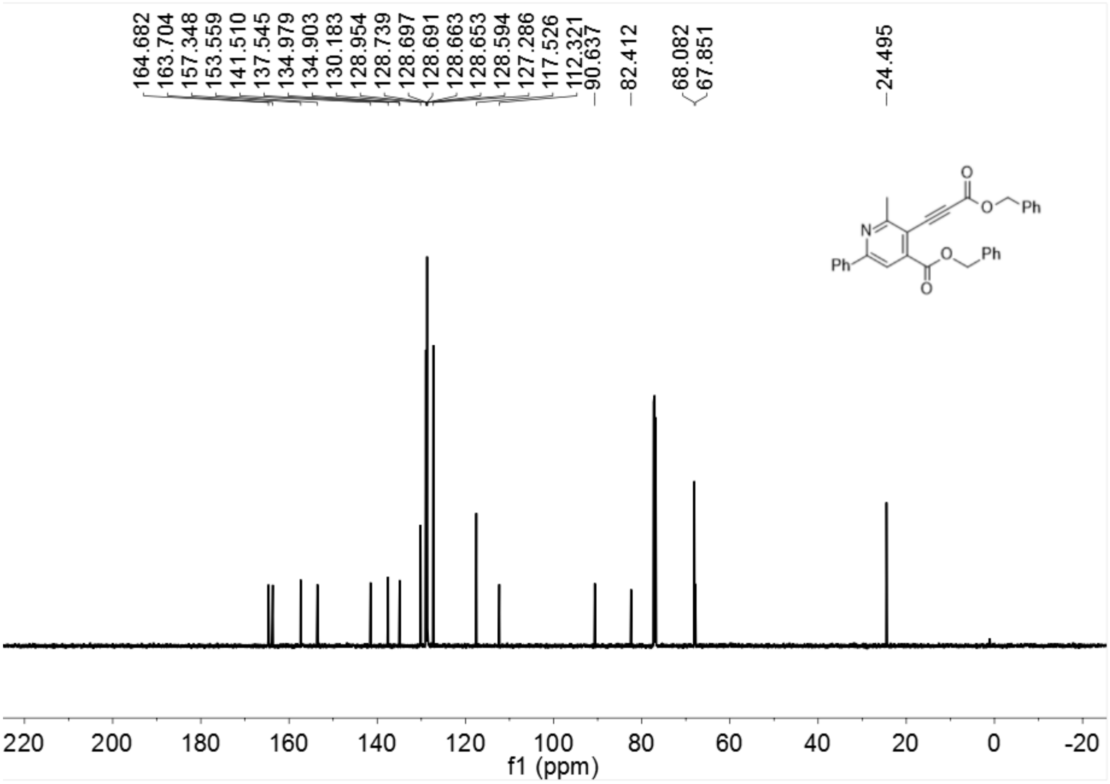


Figure 54. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ad**

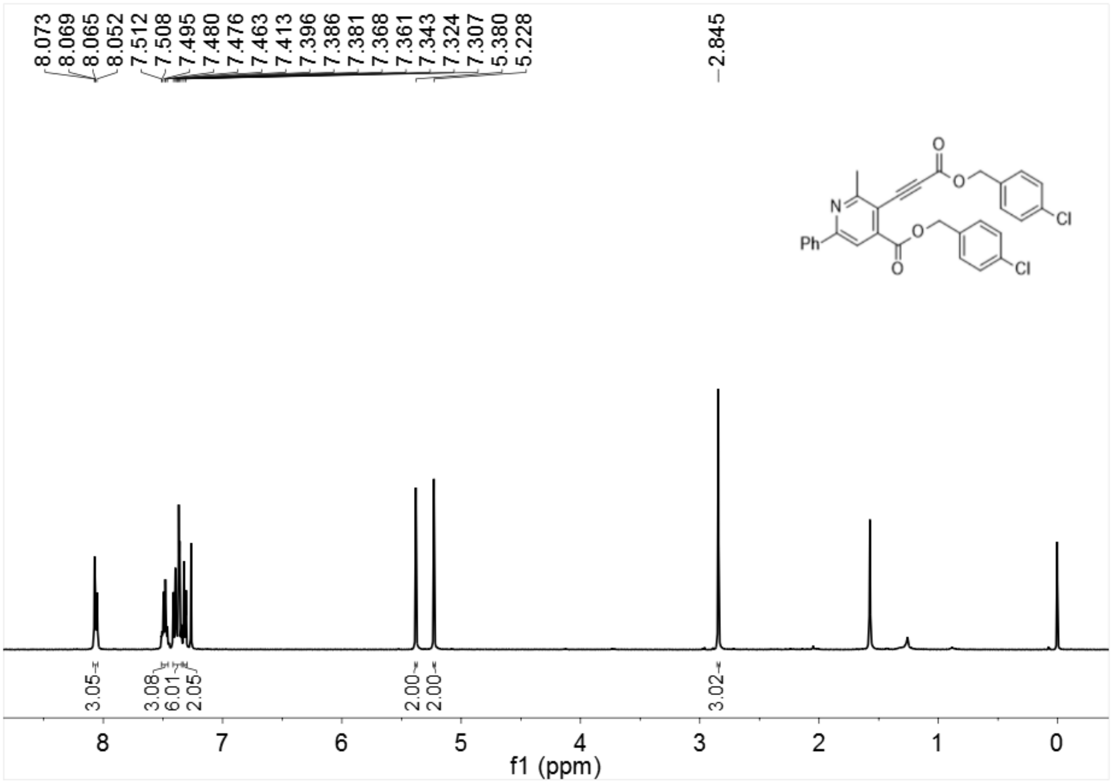


Figure 55. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3ae**

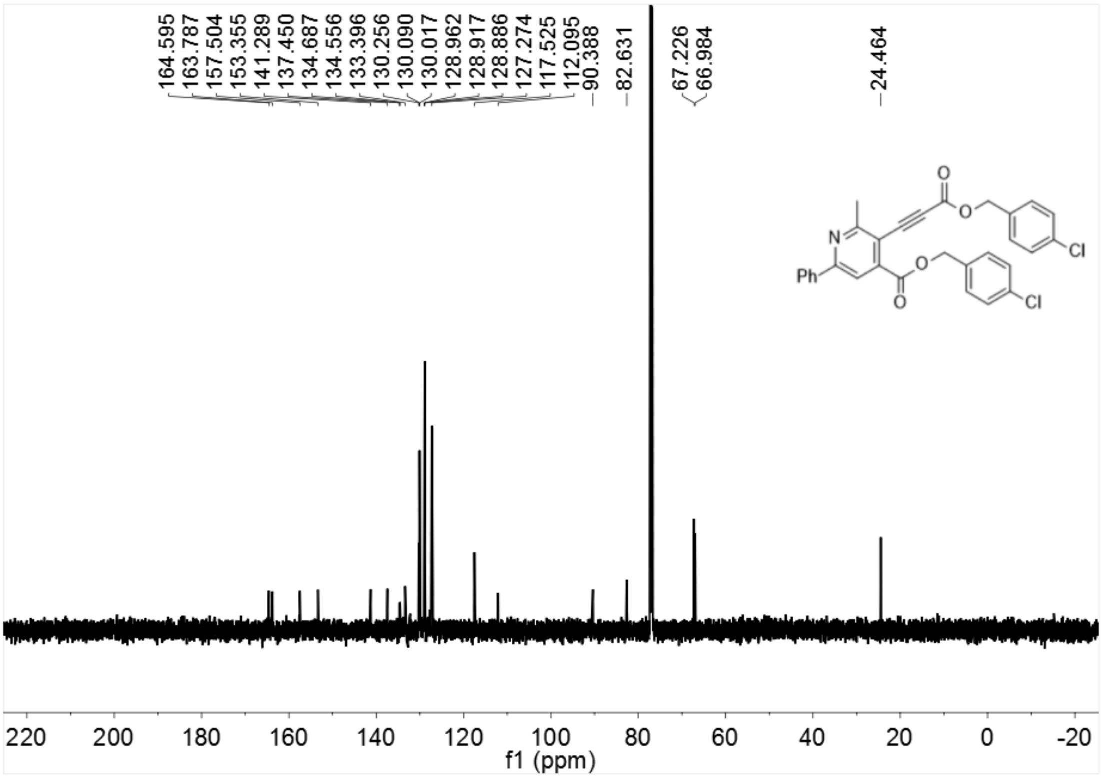


Figure 56. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ae**

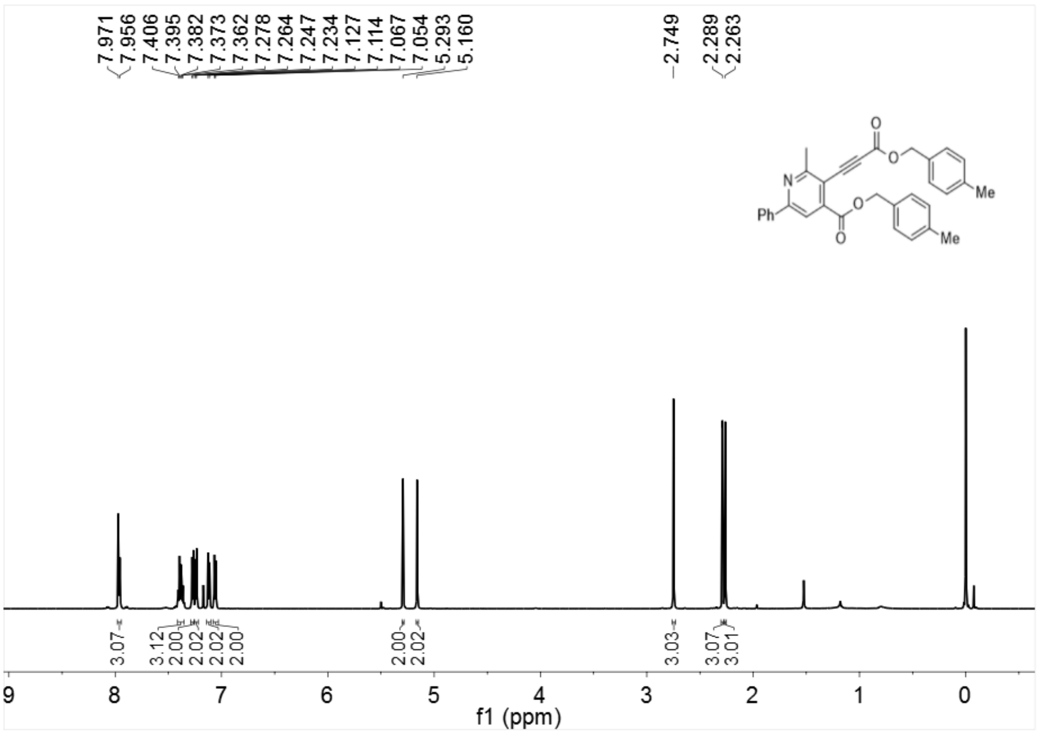


Figure 57. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3af**

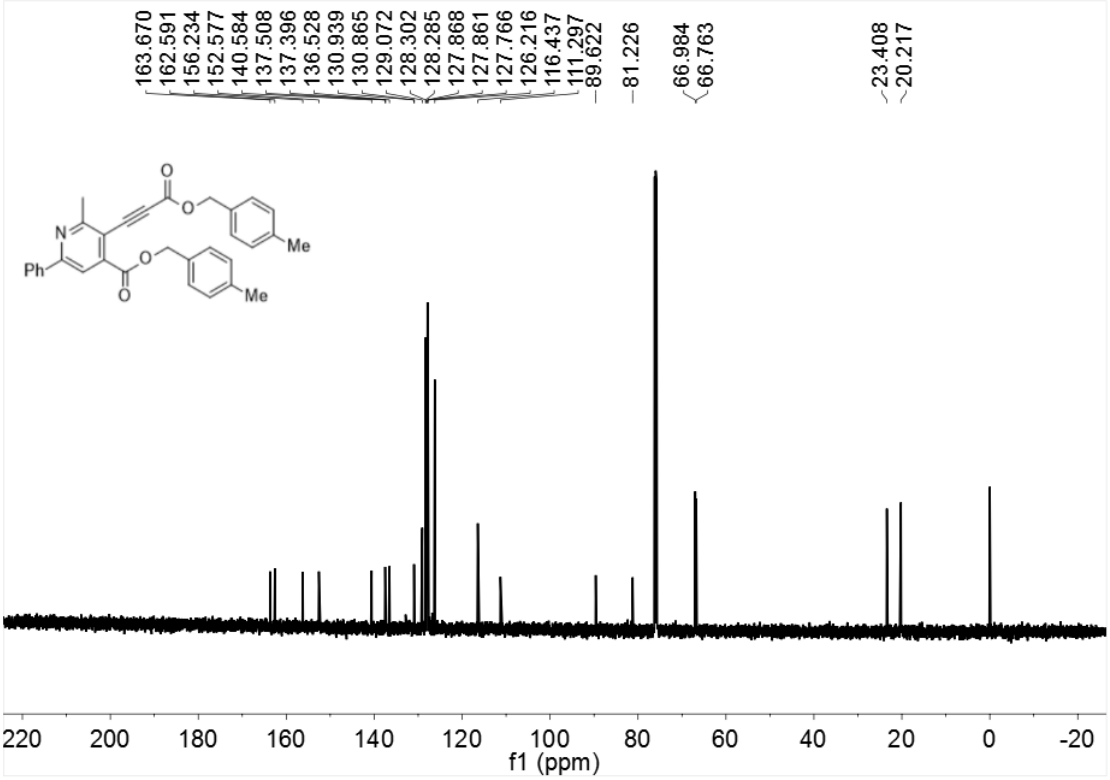


Figure 58. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3af**

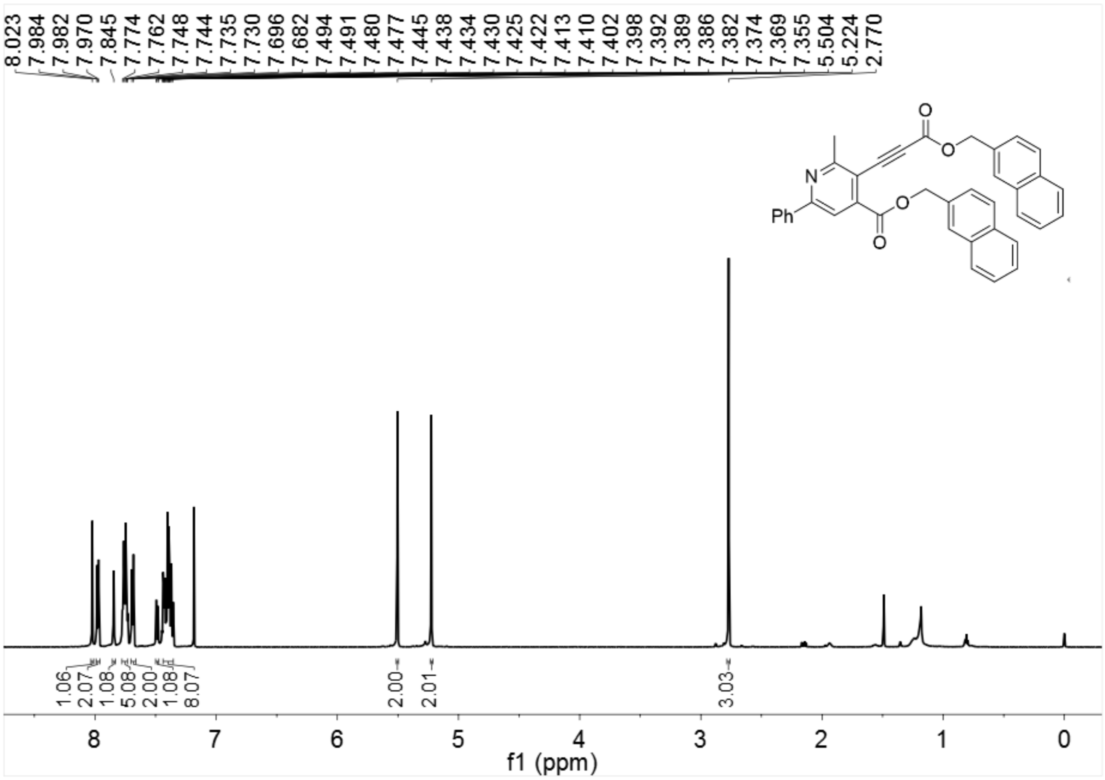


Figure 59. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3ag**

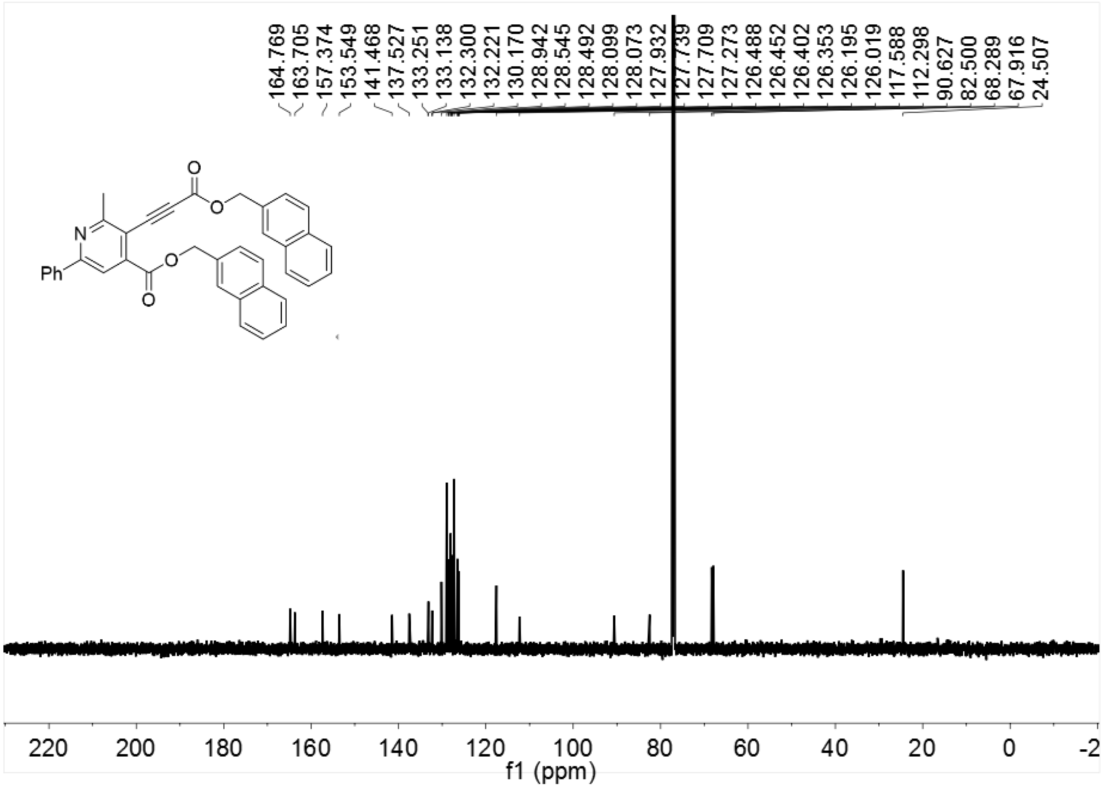


Figure 60. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ag**

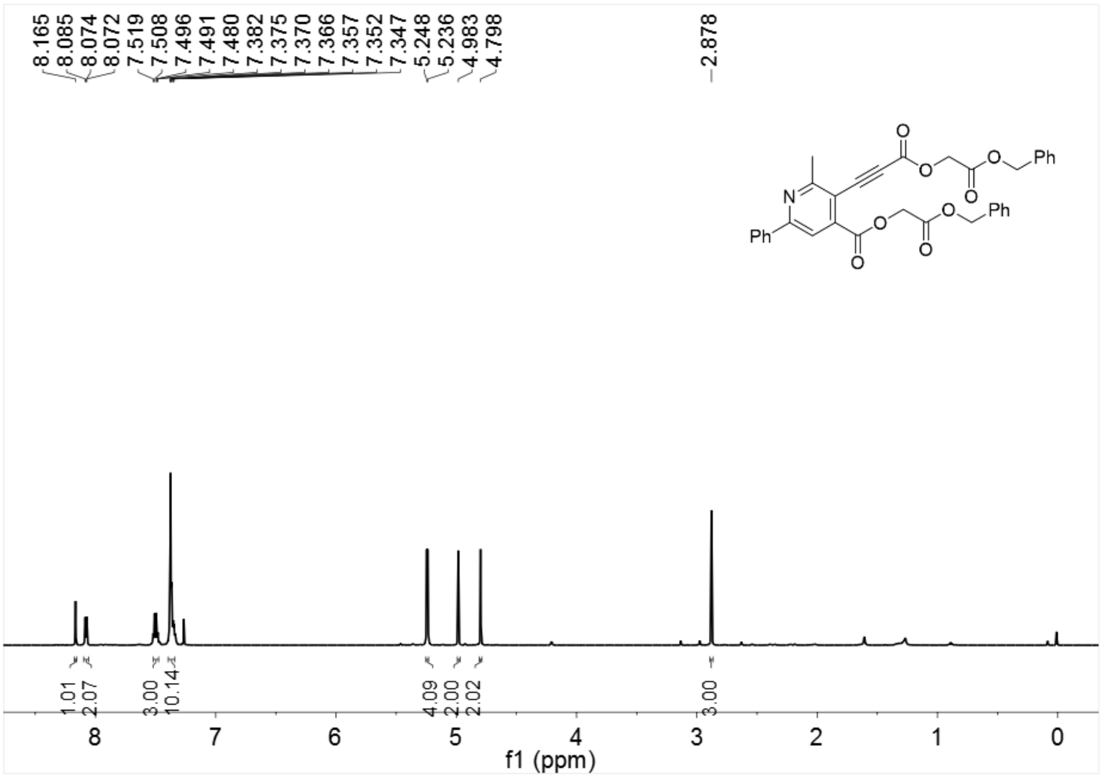


Figure 61. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3ah**

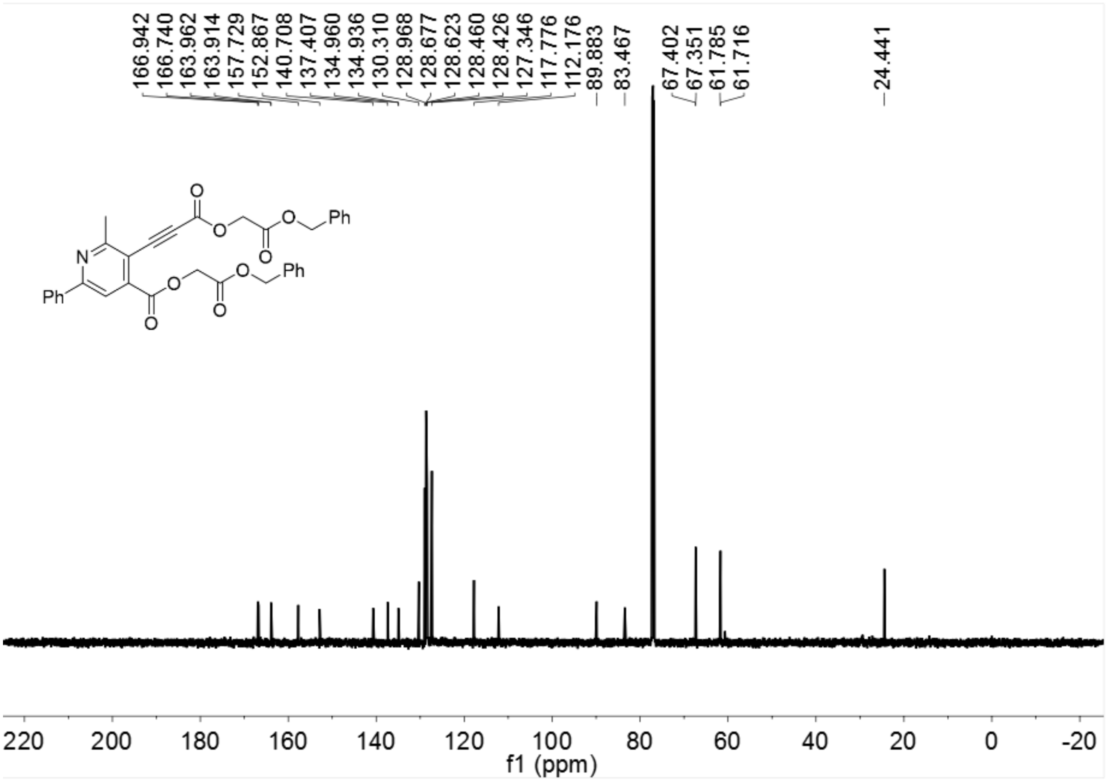


Figure 62. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3ah**