Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Rhodium-Catalyzed Coupling-Cyclization Reaction of Isocyanides and 2-Azidophenyloxyacrylates: Synthesis of *N*-(3-Substituted Benzo[*d*]oxazol-2(3*H*)-ylidene)amines and Dihydrobenzo[*d*]oxazoles

Ming Yang, Xue-Cen Xu, Yue Gong and Yu-Long Zhao*

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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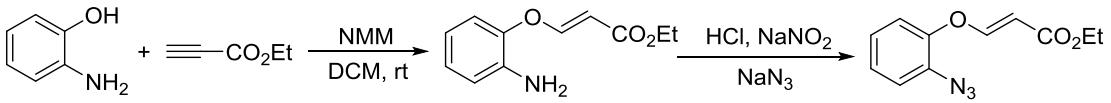
I. General Information:

All reagents were commercial and were used without further purification. Isocyanides **1** were prepared according to the previous reported method.[1] 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 471 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 compounds **3pa** and **4m** were glued on a glass fiber. X-ray single-crystal data of **3pa** and **4m** were 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, and IP technique in the range 2.19 ° < θ < 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 2 (2a as example):

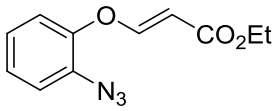


S1 **S2** **S3** **2a**

To a stirred solution of 2-Aminophenol **S1** (1.09 g, 10.0 mmol) in dry CH_2Cl_2 (25.0 mL) was added *N*-methyl morpholine (1.11 g, 11.0 mmol, 1.1 equiv) at 0 ^oC. The mixture was stirred for 10 min and ethyl propiolate **S2** (1.08 g, 11 mmol, 1.1 equiv) was added dropwise at 0 ^oC. The reaction mixture was stirred for additional 6-12 h at room temperature. The reaction progress was monitored by TLC. The organic layer was washed with brine, dried (Na_2SO_4) and concentrated under vacuum. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (50:1) as an eluent to afford **S3** in 85% yield.[2]

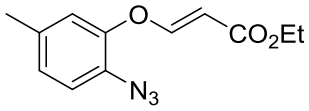
In a round-bottom flask equipped with a magnetic stirring bar, **S3** (10.0 mmol) was dissolved with HCl (6 N, 10.0 mL) in an ice bath. $NaNO_2$ (15.0 mmol) dissolved in 25.0 mL water was added dropwise. The reaction mixture was stirred for 30 min. Sodium azide (40.0 mmol) dissolved in 50 mL water was added dropwise. After this addition, the system was stirred for another 2-4 hours at room temperature. Then, the mixture was extracted with ethyl acetate and the combined organic extracts were washed with H_2O, dried (Na_2SO_4) and concentrated under vacuum. The residue was purified by silica gel column chromatography using PE/EtOAc (100:1) as an eluent to afford **2a** in 80% yield.[2]

Ethyl (*E*)-3-(2-azidophenoxy)acrylate (2a):



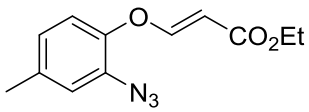
Yellow liquid, (**2a** was purified by PE/EtOAc = 100/1, V/V), 1.59 g, 68% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (d, J = 12.2 Hz, 1H), 7.19 – 7.22 (m, 1H) 7.11 – 7.17 (m, 2H), 7.07 (d, J = 7.9 Hz, 1H), 5.48 (d, J = 12.3 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 1.28 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.8, 159.3, 147.0, 131.1, 126.3, 125.8, 120.8, 120.3, 102.4, 60.2, 14.3. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{11}H_{11}N_3O_3Na^+$: 256.0693, found: 256.0696.

Ethyl (*E*)-3-(2-azido-5-methylphenoxy)acrylate (2b):



Yellow liquid, (**2b** was purified by PE/EtOAc = 100/1, V/V), 1.73 g, 70% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, J = 12.3 Hz, 1H), 6.90 – 6.97 (m, 3H), 5.43 (d, J = 12.3 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 2.33 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.9, 159.8, 144.7, 136.5, 130.6, 126.4, 121.0, 120.3, 101.9, 60.1, 20.8, 14.3. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{12}H_{13}N_3O_3Na^+$: 270.0849, found: 270.0846.

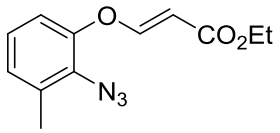
Ethyl (*E*)-3-(2-azido-4-methylphenoxy)acrylate (2c):



Yellow liquid, (**2c** was purified by PE/EtOAc = 100/1, V/V), 1.73 g, 70% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (d, J = 12.3 Hz, 1H), 7.00 (s, 2H), 6.88 (s, 1H), 5.47 (d, J = 12.2 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 2.33 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.9, 159.4, 146.7, 136.3, 128.1, 126.9, 120.8, 120.5, 102.3, 60.2, 20.8, 14.3. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{12}H_{13}N_3O_3Na^+$:

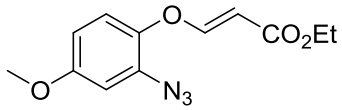
270.0849, found: 270.0859.

Ethyl (*E*)-3-(2-azido-3-methylphenoxy)acrylate (2d):



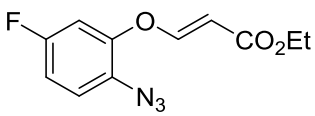
Yellow liquid, (**2d** was purified by PE/EtOAc = 100/1, V/V), 1.61 g, 65% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, J = 12.2 Hz, 1H), 7.02 (t, J = 7.8 Hz, 1H), 6.98 (d, J = 7.2 Hz, 1H), 6.89 (d, J = 7.9 Hz, 1H), 5.58 (d, J = 12.2 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 2.25 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.7, 158.7, 149.6, 132.7, 129.0, 127.4, 125.2, 116.7, 103.1, 60.2, 17.8, 14.3. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{12}H_{13}N_3O_3Na^+$: 270.0849, found: 270.0859.

Ethyl (*E*)-3-(2-azido-4-methoxyphenoxy)acrylate (2e):



Yellow liquid, (**2e** was purified by PE/EtOAc = 100/1, V/V), 1.92 g, 73% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, J = 12.3 Hz, 1H), 6.98 (d, J = 8.8 Hz, 1H), 6.65 (dd, J = 8.8, 2.8 Hz, 1H), 6.63 (d, J = 2.8 Hz, 1H), 5.38 (d, J = 12.3 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 3.80 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.9, 160.4, 157.8, 140.6, 132.0, 121.6, 110.8, 106.2, 101.5, 60.1, 55.7, 14.3. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{12}H_{13}N_3O_4Na^+$: 286.0798, found: 286.0799.

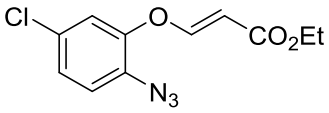
Ethyl (*E*)-3-(2-azido-5-fluorophenoxy)acrylate (2f):



White solid, (**2f** was purified by PE/EtOAc = 100/1, V/V), mp: 38 – 39 ℃, 1.58 g, 63% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (d, J = 12.2 Hz, 1H), 7.08 (dd, J = 8.8, 5.4 Hz, 1H), 6.94 (ddd, J = 10.1, 8.3, 2.7 Hz, 1H), 6.85 (dd, J = 8.6, 2.7 Hz, 1H), 5.55 (d,

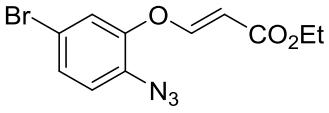
J = 12.2 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) *δ* 166.5, 159.8 (d, *J* = 247.9 Hz,), 158.1, 147.5 (d, *J* = 10.1 Hz), 127.1 (d, *J* = 3.3 Hz), 121.6 (d, *J* = 9.4 Hz), 113.0 (d, *J* = 22.7 Hz), 108.0 (d, *J* = 25.7 Hz), 103.5, 60.4, 14.3. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{11}H_{10}FN_3O_3Na^+$: 274.0598, found: 274.0593.

Ethyl (*E*)-3-(2-azido-5-chlorophenoxy)acrylate (2g):



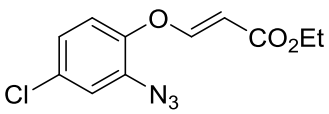
Yellow liquid, (**2g** was purified by PE/EtOAc = 100/1, V/V), 1.73 g, 65% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, *J* = 12.2 Hz, 1H), 7.18 (d, *J* = 8.6 Hz, 1H), 7.09 (s, 1H), 7.05 (d, *J* = 8.6 Hz, 1H), 5.53 (d, *J* = 12.2 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) *δ* 166.5, 158.2, 147.3, 130.7, 129.8, 126.3, 121.6, 120.5, 103.5, 60.4, 14.3. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{11}H_{10}ClN_3O_3Na^+$: 290.0303, found: 290.0296.

Ethyl (*E*)-3-(2-azido-5-bromophenoxy)acrylate (2h):



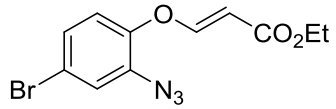
Yellow liquid. (**2h** was purified by PE/EtOAc = 100/1, V/V), 2.03 g, 65% yield. ^{1}H NMR (600 MHz, $CDCl_3$) *δ* 7.65 (d, *J* = 12.2 Hz, 1H), 7.32 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.22 (d, *J* = 1.9 Hz, 1H), 6.99 (d, *J* = 8.5 Hz, 1H), 5.53 (d, *J* = 12.2 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) *δ* 166.5, 158.3, 147.4, 130.4, 129.2, 123.3, 122.0, 117.7, 103.5, 60.4, 14.3. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{11}H_{10}BrN_3O_3Na^+$: 333.9798, found: 333.9801.

Ethyl (*E*)-3-(2-azido-4-chlorophenoxy)acrylate (2i):



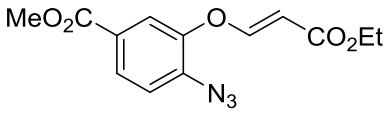
White solid, (**2i** was purified by PE/EtOAc = 100/1, V/V), mp: 38 – 39 ℃, 1.82 g, 68% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (d, J = 12.3 Hz, 1H), 7.13 – 7.09 (m, 2H), 7.01 (d, J = 9.4 Hz, 1H), 5.48 (d, J = 12.2 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 1.28 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.6, 158.8, 145.6, 132.4, 131.5, 125.7, 121.2, 120.9, 102.9, 60.3, 14.3. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{11}H_{10}ClN_3O_3Na^+$: 290.0303, found: 290.0298.

Ethyl (*E*)-3-(2-azido-4-bromophenoxy)acrylate (2j):



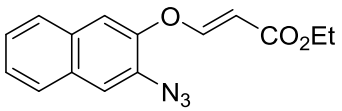
Red liquid, (**2j** was purified by PE/EtOAc = 100/1, V/V), 1.87 g, 60% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (d, J = 12.2 Hz, 1H), 7.24 – 7.29 (m, 2H), 6.95 (d, J = 9.3 Hz, 1H), 5.49 (d, J = 12.3 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 1.28 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.6, 158.6, 146.1, 132.6, 128.7, 123.8, 121.5, 118.7, 103.0, 60.3, 14.3. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{11}H_{10}BrN_3O_3Na^+$: 333.9798, found: 333.9790.

Methyl (*E*)-4-azido-3-((3-ethoxy-3-oxoprop-1-en-1-yl)oxy)benzoate (2k):



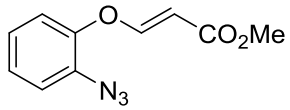
White solid, (**2k** was purified by PE/EtOAc = 80/1, V/V), mp: 48 – 50 ℃, 1.98 g, 68% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (dd, J = 8.3, 1.7 Hz, 1H), 7.74 (d, J = 1.7 Hz, 1H), 7.71 (d, J = 12.2 Hz, 1H), 7.16 (d, J = 8.4 Hz, 1H), 5.54 (d, J = 12.2 Hz, 1H), 4.21 (q, J = 7.1 Hz, 2H), 3.92 (s, 3H),1.29 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.5, 165.3, 158.3, 146.7, 135.7, 127.7, 127.5, 121.0, 120.5, 103.3, 60.3, 52.4, 14.2. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{13}H_{13}N_3O_5Na^+$: 314.0747, found: 314.0741.

Ethyl (*E*)-3-((3-azidonaphthalen-2-yl)oxy)acrylate (2l):



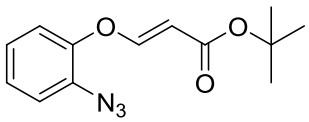
Red liquid, (**2l** was purified by PE/EtOAc = 70/1, V/V), 1.42 g, 50% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (d, J = 12.2 Hz, 1H), 7.75 – 7.70 (m, 2H), 7.51 (s, 1H), 7.43 – 7.49 (m, 3H), 5.60 (d, J = 12.2 Hz, 1H), 4.21 (q, J = 7.1 Hz, 2H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.8, 158.8, 146.2, 131.2, 131.1, 130.4, 127.2, 126.7, 126.6, 126.4, 118.2, 116.5, 103.2, 60.3, 14.3. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{15}H_{13}N_3O_3Na^+$: 306.0849, found: 306.0859.

Methyl (*E*)-3-(2-azidophenoxy)acrylate (2m):



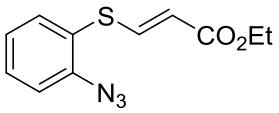
Yellow liquid, (**2m** was purified by PE/EtOAc = 100/1, V/V), 1.53 g, 70% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (d, J = 12.3 Hz, 1H), 7.21 (t, J = 7.7 Hz, 1H), 7.12 – 7.16 (m, 2H), 7.06 (d, J = 8.0 Hz, 1H), 5.50 (d, J = 12.3 Hz, 1H), 3.72 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.2, 159.5, 146.9, 131.1, 126.4, 125.8, 120.8, 120.2, 102.0, 51.4. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{10}H_9N_3O_3Na^+$: 242.0536, found: 242.0539.

Tert-butyl (*E*)-3-(2-azidophenoxy)acrylate (2n):



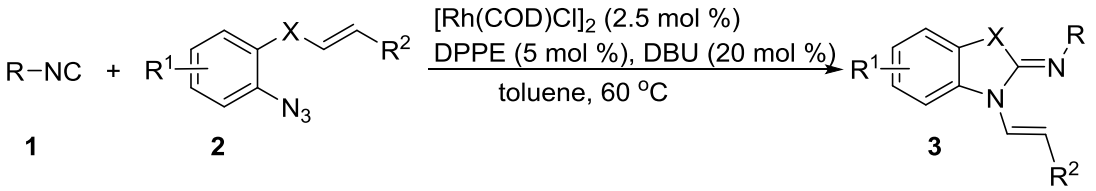
Yellow liquid, (**2n** was purified by PE/EtOAc = 100/1, V/V), 1.78 g, 68% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, J = 12.2 Hz, 1H), 7.19 (td, J = 7.7, 1.4 Hz, 1H), 7.16 – 7.10 (m, 2H), 7.06 (dd, J = 8.0, 1.2 Hz, 1H), 5.40 (d, J = 12.2 Hz, 1H), 1.48 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.1, 158.5, 147.1, 131.1, 126.2, 125.8, 120.8, 120.3, 104.1, 80.4, 28.2. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{13}H_{15}N_3O_3Na^+$: 284.1006, found: 284.1008.

(E)-Ethyl 3-((2-azidophenyl)thio)acrylate (2o):



Yellow liquid, (**2o** was purified by PE/EtOAc = 100/1, V/V), 1.12 g, 45% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.41 (td, *J* = 7.9, 1.5 Hz, 1H), 7.22 (dd, J = 8.0, 1.0 Hz, 1H), 7.15 (td, *J* = 7.6, 1.2 Hz, 1H), 7.09 (d, *J* = 10.0 Hz, 1H), 5.93 (d, *J* = 10.0 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.5, 149.1, 140.9, 134.1, 130.2, 126.7, 125.4, 119.0, 113.8, 60.4, 14.4. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{11}H_{11}N_3NaO_2S^+$: 272.0464, found: 272.0455.

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

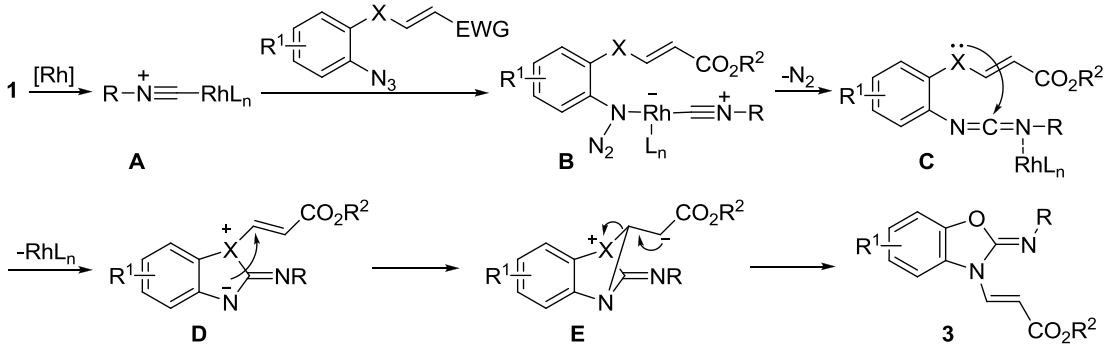


A sealed tube equipped with a magnetic stir bar was charged with $[Rh(COD)Cl]_2$ (2.5 mg, 0.005 mmol), DPPE (4.1 mg, 0.01 mmol) in toluene (2.0 mL), then **1a** (23.4 mg, 0.2 mmol), **2a** (46.6 mg, 0.2 mmol) and DBU (0.006 ml, 0.04 mmol) were added. Subsequently, the reaction mixture was stirred at 60 ℃ (heating mantle) for 5 h. After the reaction was complete, the solvent was removed under reduced pressure. The crude residue was purified by silica gel column chromatography (EtOAc/PE = 1/50, V/V) to afford pure product **3aa** (61.2 mg, 95%) as a white solid.

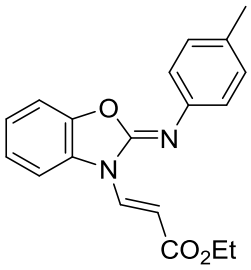
A gram-scale synthesis of compound 3aa:

An oven-dried vial equipped with a magnetic stir bar was charged with $[Rh(COD)Cl]_2$ (61.6 mg, 0.13 mmol), DPPE (99.6 mg, 0.25 mmol) in toluene (50.0 mL), then **1a** (0.59 g, 5.0 mmol), **2a** (1.17 g, 5.0 mmol) and DBU (0.149 ml, 1.0 mmol) were added. Subsequently, the reaction mixture was stirred at 60 ℃ (oil bath) for 12 h. After the reaction was complete, the solvent was removed under reduced pressure. The crude residue was purified by silica gel column chromatography (EtOAc/PE = 1/50, V/V) to afford pure product **3aa** (1.35 g, 84%) as a white solid.

Proposed mechanism for the formation of 3 without any base:

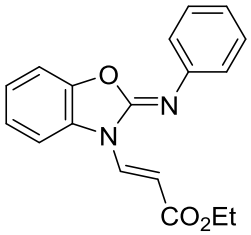


Ethyl (*E*)-3-((*Z*)-2-(*p*-tolylimino)benzo[*d*]oxazol-3(2*H*)-yl)acrylate (3aa):



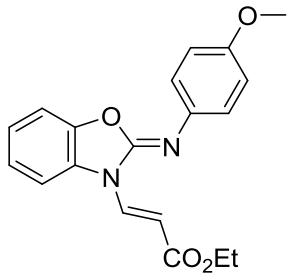
White solid, (**3aa** was purified by PE/EtOAc = 50/1, V/V), mp: 98 – 100 ℃, 61.2 mg, 95% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 (d, *J* = 14.4 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.17 (q, *J* = 8.4 Hz, 5H), 7.13 (q, *J* = 4.5, 3.7 Hz, 2H), 6.68 (d, *J* = 14.4 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.35 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.5, 144.7, 144.6, 141.7, 134.5, 133.5, 129.5, 129.3, 124.1, 123.8, 123.1, 110.0, 109.9, 104.8, 60.5, 21.0, 14.4. FT-IR (neat): (cm^{-1}) 3107, 2915, 2850, 1690, 1638, 1599, 1483, 1401, 1250, 967, 730. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{19}H_{18}N_2NaO_3^+$: 345.1210, found: 345.1208.

Ethyl (*E*)-3-((*Z*)-2-(phenylimino)benzo[*d*]oxazol-3(2*H*)-yl)acrylate (3ba):



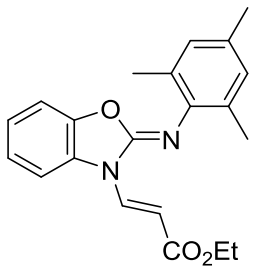
White solid, (**3ba** was purified by PE/EtOAc = 50/1, V/V), mp: 83 – 85 ℃, 55.5 mg, 90% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (d, *J* = 14.4 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.28 (dd, *J* = 19.2, 7.6 Hz, 3H), 7.20 (ddd, *J* = 8.0, 5.4, 3.4 Hz, 1H), 7.14 – 7.10 (m, 3H), 6.70 (d, *J* = 14.4 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.5, 144.9, 144.6, 144.4, 134.5, 129.3, 128.9, 124.2, 124.0, 123.8, 123.3, 110.0, 109.9, 105.0, 60.5, 14.4. FT-IR (neat): (cm^{-1}) 3100, 3070, 2977, 1692, 1638, 1586, 1487, 1357, 1228, 1139, 728. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{18}H_{16}N_2NaO_3^+$: 331.1053, found: 331.1051.

Ethyl (*E*)-3-((*Z*)-2-((4-methoxyphenyl)imino)benzo[*d*]oxazol-3(2*H*)-yl)acrylate (3ca):



White solid, (**3ca** was purified by PE/EtOAc = 50/1, V/V), mp: 94 – 95 ℃, 58.9 mg, 87% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (d, *J* = 14.3 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.29 – 7.26 (m, 2H), 7.20 (td, *J* = 7.5, 1.8 Hz, 1H), 7.17 – 7.13 (m, 2H), 6.92 – 6.89 (m, 2H), 6.69 (d, *J* = 14.4 Hz, 1H), 4.28 (d, *J* = 7.1 Hz, 2H), 3.82 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.6, 156.3, 144.7, 144.2, 137.3, 134.6, 129.3, 124.4, 124.2, 123.7, 114.1, 110.0, 110.0, 104.6, 60.5, 55.5, 14.4. FT-IR (neat): (cm^{-1}) 3064, 2951, 2837, 1702, 1635, 1601, 1485, 1359, 1234, 1133, 1029, 831, 736. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{19}H_{18}N_2NaO_4^+$: 361.1159, found: 361.1168.

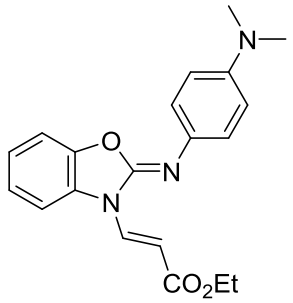
Ethyl (*E*)-3-((*Z*)-2-(mesitylimino)benzo[*d*]oxazol-3(2*H*)-yl)acrylate (3da):



White solid, (**3da** was purified by PE/EtOAc = 50/1, V/V), mp: 165 – 167 ℃, 62.4 mg, 89% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, *J* = 14.3 Hz, 1H), 7.22 (d, *J* = 7.9 Hz, 1H), 7.10 (d, *J* = 15.4 Hz, 1H), 7.01 (t, *J* = 7.7 Hz, 1H), 6.97 (d, *J* = 7.8 Hz, 1H), 6.82 (s, 2H), 6.72 (d, *J* = 14.3 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.21 (s, 3H), 2.06 (s, 6H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.6, 144.6, 143.9, 140.4, 134.4, 132.7, 129.8, 128.8, 128.6, 124.1, 123.7, 110.1, 109.7, 105.0,

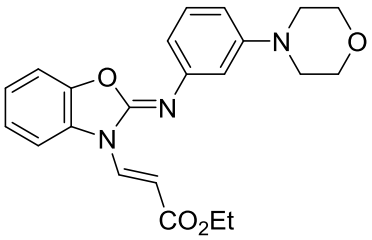
60.5, 20.8, 18.3, 14.4. FT-IR (neat): (cm^{-1}) 3109, 2977, 2912, 1702, 1614, 1489, 1400, 1357, 1250, 1131, 844, 730. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{21}H_{22}N_2NaO_3^+$: 373.1523, found: 373.1513.

Ethyl (*E*)-3-((*Z*)-2-((4-(dimethylamino)phenyl)imino)benzo[*d*]oxazol-3(2*H*)-yl)acrylate (3ea):



Yellow solid, (**3ea** was purified by PE/EtOAc = 50/1, V/V), mp: 162 – 164 ℃, 60.4 mg, 86% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 (d, *J* = 14.3 Hz, 1H), 7.29 – 7.26 (m, 3H), 7.16 (td, *J* = 7.6, 1.5 Hz, 1H), 7.14 – 7.09 (m, 2H), 6.75 (d, *J* = 8.9 Hz, 2H), 6.67 (d, *J* = 14.3 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.94 (s, 6H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.7, 147.8, 144.8, 143.4, 134.7, 133.7, 129.3, 124.4, 124.0, 123.6, 113.2, 109.9, 109.8, 104.1, 60.4, 41.0, 14.4. FT-IR (neat): (cm^{-1}) 3107, 2969, 2792, 1696, 1638, 1610, 1483, 1359, 1234, 1139, 812, 728. HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{20}H_{22}N_3O_3^+$: 352.1656, found: 352.1652.

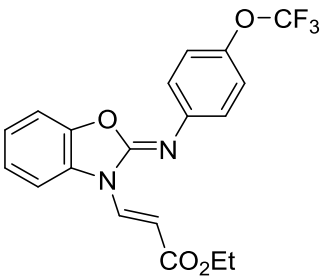
Ethyl (*E*)-3-((*Z*)-2-((3-morpholinophenyl)imino)benzo[*d*]oxazol-3(2*H*)-yl)acrylate (3fa):



White solid, (**3fa** was purified by PE/EtOAc = 50/1, V/V), mp: 135 – 137 ℃, 64.5 mg, 82% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (d, *J* = 14.4 Hz, 1H), 7.32 (d, *J* = 7.9

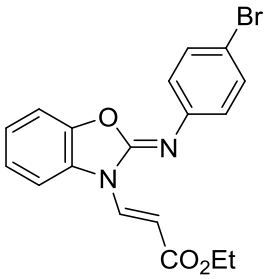
Hz, 1H), 7.27 – 7.25 (m, 1H), 7.21 (ddd, *J* = 8.0, 5.9, 3.0 Hz, 1H), 7.15 (q, *J* = 3.9, 2.8 Hz, 2H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.77 (t, *J* = 2.0 Hz, 1H), 6.72 – 6.67 (m, 2H, Ar), 4.28 (q, *J* = 7.1 Hz, 2H), 3.89 – 3.85 (m, 4H), 3.21 – 3.17 (m, 4H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.4, 152.1, 145.4, 144.9, 144.6, 134.5, 129.5, 129.3, 124.2, 123.8, 114.5, 111.6, 110.9, 110.1, 110.0, 105.0, 67.0, 60.5, 49.4, 14.4. FT-IR (neat): (cm^{-1}) 2994, 2954, 1689, 1642, 1580, 1357, 1228, 1170, 1040, 932, 734, 680. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{22}H_{23}N_3NaO_4^+$: 416.1581, found: 416.1577.

Ethyl (*E*)-3-((*Z*)-2-((4-(trifluoromethoxy)phenyl)imino)benzo[*d*]oxazol-3(2*H*)-yl) acrylate (3ga):



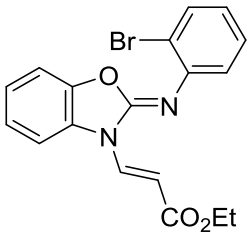
White solid, (**3ga** was purified by PE/EtOAc = 45/1, V/V), mp: 98 – 100 ℃, 68.3 mg, 87% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (d, *J* = 14.4 Hz, 1H), 7.32 (d, *J* = 7.9 Hz, 1H), 7.30 – 7.27 (m, 2H), 7.23 (dt, *J* = 8.1, 4.1 Hz, 1H), 7.19 (d, *J* = 8.6 Hz, 2H), 7.17 (q, *J* = 4.8, 4.1 Hz, 2H), 6.69 (d, *J* = 14.4 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.3, 145.4, 145.3, 144.4, 143.0, 134.26, 129.1, 124.5, 124.4, 124.0, 121.6, 120.6 (q, J = 256.4 Hz), 110.1, 110.0, 105.4, 60.6, 14.4. ^{19}F NMR (471 MHz, $CDCl_3$) δ -58.01. FT-IR (neat): (cm^{-1}) 3119, 3064, 2966, 1689, 1485, 1357, 1154, 846, 738, 674. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{19}H_{15}F_3N_2NaO_4^+$: 415.0876, found: 415.0869.

Ethyl (*E*)-3-((*Z*)-2-((4-bromophenyl)imino)benzo[*d*]oxazol-3(2*H*)-yl)acrylate (3ha):



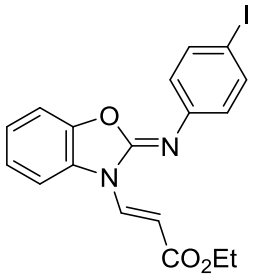
White solid, (**3ha** was purified by PE/EtOAc = 50/1, V/V), mp: 136 – 138 ℃, 65.8 mg, 85% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (d, *J* = 14.4 Hz, 1H), 7.44 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 1H), 7.21 (ddd, *J* = 8.0, 5.3, 3.5 Hz, 1H), 7.17 – 7.13 (m, 4H), 6.67 (d, *J* = 14.4 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.3, 145.2, 144.4, 143.4, 134.3, 131.9, 129.1, 125.2, 124.4, 124.0, 116.9, 110.1, 110.1, 105.3, 60.6, 14.4. FT-IR (neat): (cm^{-1}) 3117, 3061, 2988, 2899, 1700, 1627, 1575, 1482, 1400, 1278, 1176, 961, 816, 682. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{18}H_{15}BrN_2NaO_3^+$: 409.0158, found: 409.0150.

Ethyl (*E*)-3-((*Z*)-2-((2-bromophenyl)imino)benzo[*d*]oxazol-3(2*H*)-yl)acrylate (3ia):



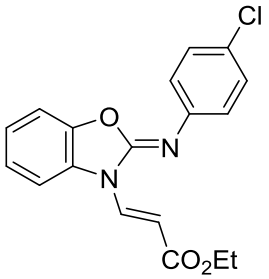
White solid, (**3ia** was purified by PE/EtOAc = 50/1, V/V), mp: 130 – 132 ℃, 70.5 mg, 91% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (d, *J* = 14.3 Hz, 1H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.32 (d, *J* = 7.9 Hz, 1H), 7.30 (d, *J* = 4.2 Hz, 2H), 7.22 (td, *J* = 8.1, 7.2, 2.6 Hz, 1H), 7.17 – 7.13 (m, 2H), 7.00 – 6.96 (m, 1H), 6.91 (d, *J* = 14.3 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.4, 145.6, 144.4, 143.6, 133.9, 132.9, 129.4, 127.9, 125.0, 124.4, 124.0, 123.5, 118.3, 110.2, 109.8, 106.2, 60.6, 14.4. FT-IR (neat): (cm^{-1}) 3109, 2919, 2850, 1702, 1638, 1608, 1487, 1355, 1273, 1137, 958, 732. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{18}H_{15}BrN_2NaO_3^+$: 409.0158, found: 409.0154.

Ethyl (*E*)-3-((*Z*)-2-((4-iodophenyl)imino)benzo[*d*]oxazol-3(2*H*)-yl)acrylate (3ja):



White solid, (**3ja** was purified by PE/EtOAc = 50/1, V/V), mp: 130 – 132 ℃, 69.5 mg, 80% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 14.4 Hz, 1H), 7.62 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.22 – 7.19 (m, 1H), 7.14 (d, *J* = 4.1 Hz, 2H), 7.03 (d, *J* = 8.6 Hz, 2H), 6.66 (d, *J* = 14.4 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.3, 145.2, 144.4, 144.1, 137.9, 134.3, 129.1, 125.6, 124.4, 124.0, 110.1, 110.1, 105.4, 87.7, 60.6, 14.4. FT-IR (neat): (cm^{-1}) 3118, 3059, 2991, 1700, 1619, 1528, 1437, 1323, 852, 760, 674. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{18}H_{15}IN_2NaO_3^+$: 457.0020, found: 457.0013.

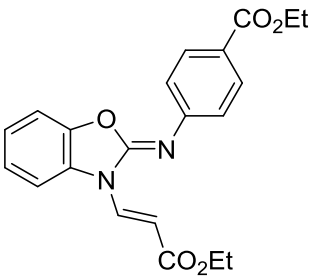
Ethyl (*E*)-3-((*Z*)-2-((4-chlorophenyl)imino)benzo[*d*]oxazol-3(2*H*)-yl)acrylate (3ka):



White solid, (**3ka** was purified by PE/EtOAc = 50/1, V/V), mp: 137 – 138 ℃, 63.1 mg, 92% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 14.4 Hz, 1H), 7.28 (d, *J* = 8.6 Hz, 3H), 7.23 – 7.18 (m, 3H), 7.14 (d, *J* = 3.3 Hz, 2H), 6.66 (d, *J* = 14.4 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.3, 145.1, 144.5, 142.8, 134.3, 129.1, 129.1, 128.9, 124.7, 124.4, 123.9, 110.0, 110.0, 105.3, 60.6, 14.4. FT-IR (neat): (cm^{-1}) 3115, 3059, 2925, 1694, 1612, 1489,

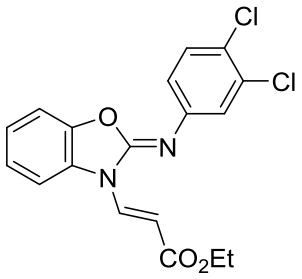
1360, 1249, 1135, 1085, 824, 738, 684. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{18}H_{15}ClN_2NaO_3^+$: 365.0663, found: 365.0665

Ethyl 4-(((*Z*)-3-((*E*)-3-ethoxy-3-oxoprop-1-en-1-yl)benzo[*d*]oxazol-2(3*H*)-ylidene) amin)benzoate (3la):



White solid, (**3la** was purified by PE/EtOAc = 50/1, V/V), mp: 134 – 135 ℃, 63.1 mg, 83% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (d, *J* = 14.4 Hz, 1H), 8.04 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 1H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.22 (dt, *J* = 8.1, 4.4 Hz, 1H), 7.16 (d, *J* = 4.2 Hz, 2H), 6.69 (d, *J* = 14.4 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 4.29 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.2, 166.4, 148.8, 145.6, 144.4, 134.2, 130.6, 129.0, 125.9, 124.5, 124.1, 123.2, 110.2, 110.1, 105.7, 60.7, 60.6, 14.4 (-$CH_2\underline{C}H_3$), 14.4. FT-IR (neat): (cm^{-1}) 3394, 3113, 2981, 1687, 1644, 1588, 1483, 1357, 1254, 1107, 950, 846, 732. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{21}H_{20}N_2NaO_5^+$: 403.1264, found: 403.1261.

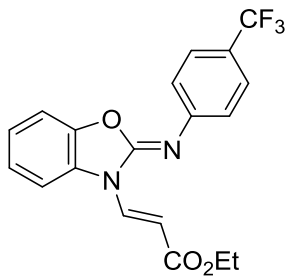
Ethyl (*E*)-3-((*Z*)-2-((3,4-dichlorophenyl)imino)benzo[*d*]oxazol-3(2*H*)-yl)acrylate (3ma):



White solid, (**3ma** was purified by PE/EtOAc = 45/1, V/V), mp: 125 – 127 ℃, 57.3

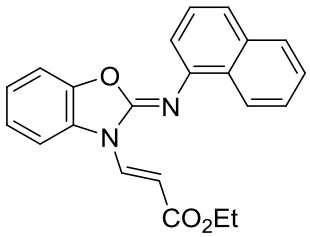
mg, 76% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 14.4 Hz, 1H), 7.40 (d, *J* = 2.4 Hz, 1H), 7.37 (d, *J* = 8.6 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.23 (td, *J* = 7.6, 1.7 Hz, 1H), 7.21 – 7.16 (m, 2H), 7.13 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.67 (d, *J* = 14.4 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.2, 145.7, 144.4, 143.9, 134.1, 132.4, 130.4, 129.0, 127.3, 125.3, 124.6, 124.1, 123.2, 110.2, 110.1, 105.8, 60.7, 14.4. FT-IR (neat): (cm^{-1}) 3105, 3055, 2979, 1707, 1644, 1610, 1487, 1360, 1260, 1195, 1146, 1021, 961, 803, 732. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{18}H_{14}Cl_2N_2NaO_3^+$: 399.0274, found: 399.0270.

Ethyl (*E*)-3-((*Z*)-2-((4-(trifluoromethyl)phenyl)imino)benzo[*d*]oxazol-3(2*H*)-yl)acrylate (3na):



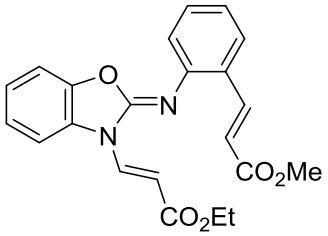
White solid, (**3na** was purified by PE/EtOAc = 45/1, V/V), mp: 125 – 127 ℃, 64.7 mg, 86% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 (d, *J* = 14.4 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 3H), 7.24 (dd, *J* = 8.0, 4.3 Hz, 1H), 7.18 (d, *J* = 4.2 Hz, 2H), 6.70 (d, *J* = 14.4 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.2, 147.7, 145.8, 144.4, 134.2, 126.1 (q, *J* = 3.6 Hz), 125.8 (q, *J* = 32.6 Hz), 124.5, 124.4 (q, *J* = 271.5 Hz), 124.1, 123.5, 121.7, 110.2, 110.1, 105.8, 60.7, 14.4. ^{19}F NMR (471 MHz, $CDCl_3$) δ -61.88. FT-IR (neat): (cm^{-1}) 3055, 2990, 2921, 1717, 1629, 1592, 1482, 1388, 1314, 1236, 1099, 963, 827, 741. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{19}H_{15}F_3N_2NaO_3^+$: 399.0927, found: 399.0920.

Ethyl (*E*)-3-((*Z*)-2-(naphthalen-1-ylimino)benzo[*d*]oxazol-3(2*H*)-yl)acrylate (3oa):



White solid, (**3na** was purified by PE/EtOAc = 40/1, V/V), mp: 132 – 134 ℃, 62.4 mg, 87% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.28 (d, *J* = 14.3 Hz, 1H), 8.27 – 8.22 (m, 1H), 7.87 – 7.82 (m, 1H), 7.64 (d, *J* = 8.2 Hz, 1H), 7.51 – 7.45 (m, 3H), 7.36 (dd, *J* = 18.1, 7.6 Hz, 2H), 7.21 (t, *J* = 7.7 Hz, 1H), 7.13 (t, *J* = 7.7 Hz, 1H), 7.10 (d, *J* = 7.7 Hz, 1H), 6.84 (d, *J* = 14.3 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.5, 145.3, 144.6, 141.0, 134.5, 134.3, 129.4, 128.8, 127.9, 126.1, 125.8, 125.6, 124.3, 124.0, 124.0, 117.3, 110.2, 110.0, 105.3, 60.6, 14.4. FT-IR (neat): (cm^{-1}) 3105, 3059, 2921, 1690, 1607, 1485, 1392, 1351, 1241, 1140, 861, 768, 734. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{22}H_{18}N_2NaO_3^+$: 381.1210, found: 381.1200.

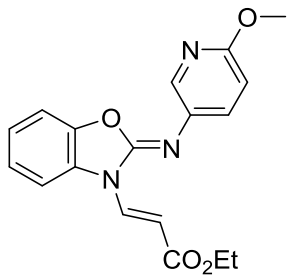
Ethyl (*E*)-3-((*Z*)-2-((2-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)phenyl)imino)benzo [*d*]oxazol-3(2*H*)-yl)acrylate (3pa):



White solid, (**3pa** was purified by PE/EtOAc = 50/1, V/V), mp: 170 – 172 ℃, 66.7 mg, 85% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 (d, *J* = 14.4 Hz, 1H), 8.10 (d, *J* = 16.1 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 7.9 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 2H), 7.14 (m, 3H), 6.74 (d, *J* = 14.4 Hz, 1H), 6.45 (d, *J* = 16.1 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.77 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.6, 167.3, 145.5, 144.4, 141.7, 134.2, 130.8, 129.4, 127.9, 127.1, 124.4, 124.2, 124.0, 123.0, 118.0, 110.2, 110.1, 105.8, 60.6, 51.6, 14.4.

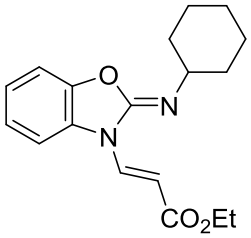
FT-IR (neat): (cm^{-1}) 3109, 3061, 2994, 2904, 1707, 1629, 1590, 1478, 1401, 1316, 1167, 1017, 872, 827, 730. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{22}H_{20}N_2NaO_5^+$: 415.1264, found: 415.1256.

Ethyl (*E*)-3-((*Z*)-2-((6-methoxypyridin-3-yl)imino)benzo[*d*]oxazol-3(2*H*)-yl)acrylate (3qa):



White solid, (**3qa** was purified by PE/EtOAc = 45/1, V/V), mp: 115 – 117 ℃, 59.0 mg, 87% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 (d, *J* = 2.6 Hz, 1H), 8.11 (d, *J* = 14.4 Hz, 1H), 7.61 (dd, *J* = 8.7, 2.7 Hz, 1H), 7.30 (d, *J* = 7.8 Hz, 1H), 7.21 (ddd, *J* = 8.0, 5.1, 3.7 Hz, 1H), 7.15 (d, *J* = 3.6 Hz, 2H), 6.74 (d, *J* = 8.7 Hz, 1H), 6.66 (d, *J* = 14.4 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.94 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.3, 160.8, 145.1, 144.4, 141.4, 134.5, 134.3, 134.3, 129.1, 124.4, 123.9, 110.4, 110.0, 110.0, 105.0, 60.5, 53.5, 14.4. FT-IR (neat): (cm^{-1}) 3085, 3038, 2982, 2899, 1707, 1625, 1590, 1483, 1374, 1278, 1172, 1129, 958, 814, 741. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{18}H_{17}N_3NaO_4^+$: 362.1111, found: 362.1108.

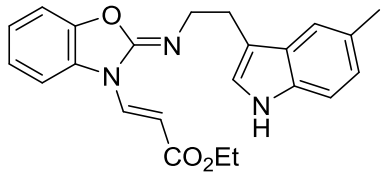
Ethyl (*E*)-3-((*Z*)-2-(cyclohexylimino)benzo[*d*]oxazol-3(2*H*)-yl)acrylate (3ra):



White solid, (**3ra** was purified by PE/EtOAc = 50/1, V/V), mp: 72 – 73 ℃, 53.4 mg, 85% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 14.2 Hz, 1H), 7.19 (d, *J* = 7.7

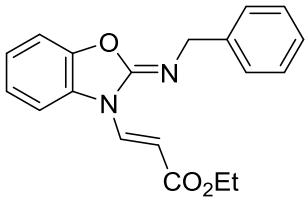
Hz, 1H), 7.12 (td, *J* = 7.8, 7.3, 2.1 Hz, 1H), 7.09 – 7.05 (m, 2H), 6.61 (d, *J* = 14.2 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.69 (td, *J* = 9.7, 4.9 Hz, 1H), 1.83 – 1.77 (m, 4H), 1.64 – 1.60 (m, 1H), 1.41 (dq, *J* = 21.5, 12.4, 11.0 Hz, 4H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.30 – 1.23 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.0, 144.9, 144.1, 134.8, 129.9, 123.5, 123.16, 109.4, 109.3, 103.2, 60.3, 55.4, 34.4, 25.9, 24.8, 14.4. FT-IR (neat): (cm^{-1}) 3036, 2979, 2917, 2848, 1705, 1633, 1607, 1489, 1353, 1271, 1206, 1133, 952, 838, 725, 674. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{18}H_{22}N_2NaO_3^+$: 337.1523, found: 337.1517.

Ethyl (*E*)-3-((*Z*)-2-((2-(5-methyl-1*H*-indol-3-yl)ethyl)imino)benzo[*d*]oxazol-3(2*H*) -yl) acrylate (3sa):



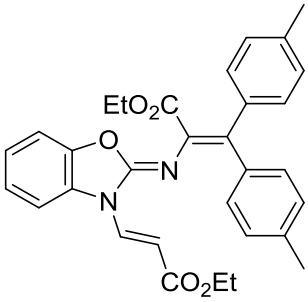
White solid, (**3sa** was purified by PE/EtOAc = 50/1, V/V), mp: 95 – 97 ℃, 58.4 mg, 75% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 14.2 Hz, 1H), 7.90 (s, 1H), 7.47 (s, 1H), 7.21 (d, *J* = 8.2 Hz, 1H), 7.15 (d, *J* = 7.8 Hz, 1H), 7.10 (td, *J* = 7.5, 1.6 Hz, 1H), 7.06 – 7.02 (m, 3H), 7.01 – 6.98 (m, 1H), 6.67 (d, *J* = 14.2 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.81 – 3.77 (m, 2H), 3.08 (t, *J* = 7.5 Hz, 2H), 2.46 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.0, 145.7, 144.8, 134.7, 134.6, 129.9, 128.3, 127.9, 123.7, 123.4, 123.26, 122.0, 118.7, 114.1, 110.7, 109.4, 109.4, 103.6, 60.4, 47.8, 27.2, 21.6, 14.5. FT-IR (neat): (cm^{-1}) 3303, 2899, 2844, 1724, 1679, 1636, 1607, 1485, 1347, 1275, 1241, 1150, 954, 848, 786, 732, 617, 425. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{23}H_{23}N_3NaO_3^+$: 412.1632, found: 412.1640.

Ethyl (*E*)-3-((*Z*)-2-(benzylimino)benzo[*d*]oxazol-3(2*H*)-yl)acrylate (3ta):



White solid, (**3ta** was purified by PE/EtOAc = 50/1, V/V), mp: 72 – 74 ℃, 25.5 mg, 40% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, J = 14.3 Hz, 1H), 7.49 (d, J = 7.4 Hz, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.30 (t, J = 7.5 Hz, 1H), 7.23 (d, J = 7.8 Hz, 1H), 7.18 – 7.10 (m, 3H), 6.71 (d, J = 14.3 Hz, 1H), 4.77 (s, 2H), 4.31 (q, J = 7.1 Hz, 2H), 1.38 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.72, 146.40, 144.73, 140.32, 134.51, 129.86, 128.38, 127.44, 126.67, 123.87, 123.38, 109.61, 109.56, 103.95, 60.37, 50.54, 14.44. FT-IR (neat): (cm^{-1}) 3115, 3025, 2979, 2859, 1702, 1610, 1487, 1346, 1245, 1137, 1057, 893, 598, 426. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{19}H_{18}N_2NaO_3^+$: 345.1210, found: 345.1215.

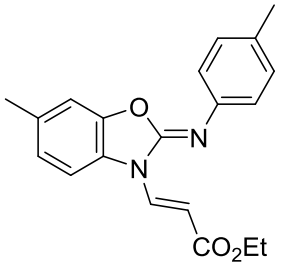
Ethyl 2-(((*Z*)-3-((*E*)-3-ethoxy-3-oxoprop-1-en-1-yl)benzo[*d*]oxazol-2(3*H*)-ylidene) amino)-3,3-di-*p*-tolylacrylate (3ua):



Yellow solid, (**3ua** was purified by PE/EtOAc = 45/1, V/V), mp: 160 – 161 ℃, 84.8 mg, 83% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 14.4 Hz, 1H), 7.26 (d, *J* = 7.9 Hz, 1H), 7.19 (t, *J* = 6.6 Hz, 3H), 7.17 – 7.12 (m, 4H), 7.09 (t, *J* = 6.3 Hz, 2H), 7.05 (d, *J* = 8.1 Hz, 2H), 6.52 (d, *J* = 14.4 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 4.05 (q, *J* = 7.1 Hz, 2H), 2.36 (s, 3H), 2.30 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.00 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.9, 167.2, 146.4, 144.7, 138.24, 137.4, 137.2, 137.1, 137.0, 133.9, 130.6, 130.4, 129.7, 129.5, 128.8, 128.7, 128.2, 124.3, 123.9,

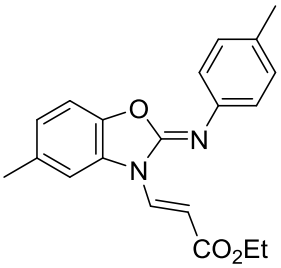
110.1, 110.0, 105.7, 60.8, 60.4, 21.3, 14.3, 13.7. FT-IR (neat): (cm^{-1}) 3027, 2966, 2913, 2858, 1687, 1636, 1605, 1482, 1362, 1278, 1133, 1023, 885, 818, 730. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{31}H_{30}N_2NaO_5^+$: 533.2047, found: 533.2040.

Ethyl (*E*)-3-((*Z*)-6-methyl-2-(*p*-tolylimino)benzo[*d*]oxazol-3(2*H*)-yl)acrylate (3ab):



White solid, (**3ab** was purified by PE/EtOAc = 50/1, V/V), mp: 110 – 112 ℃, 63.9 mg, 95% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (d, *J* = 14.4 Hz, 1H), 7.19 – 7.14 (m, 3H), 7.14 – 7.10 (m, 2H), 6.95 (d, *J* = 8.1 Hz, 1H), 6.92 (s, 1H), 6.55 (d, *J* = 14.4 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 2.34 (s, 6H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.5, 144.8, 141.7, 134.8, 134.1, 133.4, 129.5, 126.8, 124.4, 123.2, 110.6, 109.7, 104.0, 60.4, 21.4, 21.0, 14.4. FT-IR (neat): (cm^{-1}) 3053, 2986, 2917, 2848, 1692, 1629, 1498, 1349, 1249, 1150, 960, 825, 777. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{20}H_{20}N_2NaO_3^+$: 359.1366, found: 359.1362.

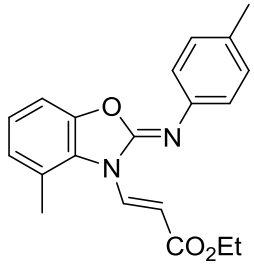
Ethyl (*E*)-3-((*Z*)-5-methyl-2-(*p*-tolylimino)benzo[*d*]oxazol-3(2*H*)-yl)acrylate (3ac):



White solid, (**3ac** was purified by PE/EtOAc = 50/1, V/V), mp: 133 – 135 ℃, 62.6 mg, 93% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 (d, *J* = 14.4 Hz, 1H), 7.19 – 7.14 (m, 4H), 7.12 (s, 1H), 7.01 (d, *J* = 8.1 Hz, 1H), 6.92 (d, *J* = 8.1 Hz, 1H), 6.66 (d, *J* = 14.4

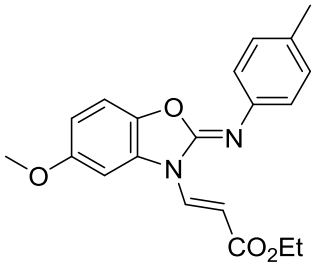
Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 2.41 (s, 3H), 2.35 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.6, 145.1, 142.7, 141.8, 134.7, 134.2, 133.5, 129.5, 129.2, 124.0, 123.1, 110.6, 109.5, 104.5, 60.5, 21.6, 21.0, 14.4. FT-IR (neat): (cm^{-1}) 3115, 3025, 2979, 1689, 1601, 1489, 1364, 1228, 1150, 1004, 958, 820, 667. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{20}H_{20}N_2NaO_3^+$: 359.1366, found: 359.1360.

Ethyl (*E*)-3-((*Z*)-4-methyl-2-(*p*-tolylimino)benzo[*d*]oxazol-3(2*H*)-yl)acrylate (3ad):



Yellow solid, (**3ad** was purified by PE/EtOAc = 50/1, V/V), mp: 93 – 95 ℃, 54.5 mg, 81% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.30 (d, *J* = 13.8 Hz, 1H), 7.34 (d, *J* = 13.8 Hz, 1H), 7.15 (s, 4H), 7.00 – 6.95 (m, 2H, Ar), 6.92 (d, *J* = 7.4 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.66 (s, 3H), 2.35 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.6, 145.0, 144.4, 142.1, 135.5, 133.4, 129.5, 127.8, 127.6, 123.5, 123.0, 121.0, 118.3, 108.0, 106.6, 60.3, 21.0, 19.2, 14.4. FT-IR (neat): (cm^{-1}) 3126, 2984, 2915, 1700, 1599, 1502, 1437, 1355, 1303, 1243, 1200, 1150, 1025, 805, 721. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{20}H_{20}N_2NaO_3^+$: 359.1366, found: 359.1362.

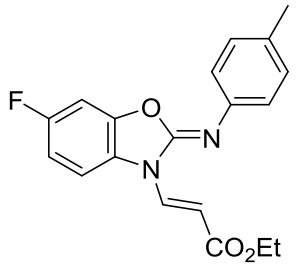
Ethyl (*E*)-3-((*Z*)-5-methoxy-2-(*p*-tolylimino)benzo[*d*]oxazol-3(2*H*)-yl)acrylate (3ae):



White solid, (**3ae** was purified by PE/EtOAc = 50/1, V/V), mp: 148 – 150 ℃, 63.4 mg,

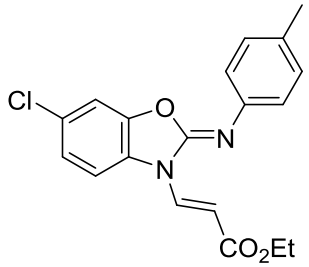
90% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, *J* = 14.3 Hz), 7.17 (dd, *J* = 8.0, 5.7 Hz, 4H), 7.02 (d, *J* = 8.7 Hz, 1H), 6.86 (d, *J* = 2.4 Hz, 1H), 6.71 (d, *J* = 14.3 Hz, 1H), 6.62 (dd, *J* = 8.7, 2.4 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 2.35 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.6, 156.9, 145.3, 141.7, 138.7, 134.4, 133.5, 130.0, 129.5, 123.1, 110.0, 107.9, 105.0, 97.4, 60.5, 56.2, 21.0, 14.4. FT-IR (neat): (cm^{-1}) 3104, 2982, 2919, 1703, 1597, 1489, 1338, 1252, 1139, 1032, 963, 783, 686. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{20}H_{20}N_2NaO_4^+$: 375.1315, found: 375.1318.

Ethyl (*E*)-3-((*Z*)-6-fluoro-2-(*p*-tolylimino)benzo[*d*]oxazol-3(2*H*)-yl)acrylate (3af):



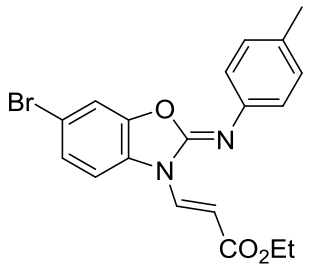
White solid, (**3af** was purified by PE/EtOAc = 50/1, V/V), mp: 106 – 108 ℃, 57.9 mg, 85% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 14.4 Hz, 1H), 7.22 – 7.19 (m, 1H), 7.15 (s, 4H), 6.92 (dd, *J* = 4.6, 2.3 Hz, 1H), 6.91 – 6.89 (m, 1H), 6.62 (d, *J* = 14.4 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.35 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.3, 159.3 (d, *J* = 244.3 Hz), 145.0 (d, *J* = 13.3 Hz), 144.4, 141.2, 134.4, 133.8, 129.5, 125.7 (d, *J* = 2.4 Hz), 123.1, 110.5 (d, *J* = 23.9 Hz), 110.1 (d, *J* = 9.4 Hz), 104.6, 99.4 (d, *J* = 28.8 Hz), 60.6, 21.0, 14.4. ^{19}F NMR (471 MHz, $CDCl_3$) δ -116.22. FT-IR (neat): (cm^{-1}) 3117, 3063, 2981, 1705, 1607, 1489, 1360, 1241, 1083, 1040, 947, 796. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{19}H_{17}FN_2NaO_3^+$: 363.1115, found: 363.1116.

Ethyl (*E*)-3-((*Z*)-6-chloro-2-(*p*-tolylimino)benzo[*d*]oxazol-3(2*H*)-yl)acrylate (3ag):



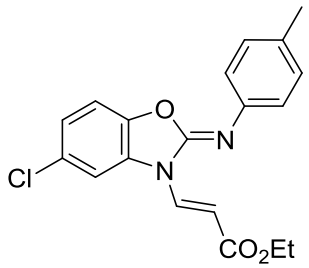
White solid, (**3ag** was purified by PE/EtOAc = 50/1, V/V), mp: 102 – 104 ℃, 64.2 mg, 90% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, *J* = 14.4 Hz, 1H), 7.19 (d, *J* = 8.4 Hz, 1H), 7.18 – 7.13 (m, 6H), 6.64 (d, *J* = 14.4 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.35 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.2, 145.0, 144.0, 141.1, 134.2, 133.9, 129.5, 129.2, 128.1, 124.1, 123.1, 110.9, 110.3, 105.2, 60.6, 21.0, 14.4. FT-IR (neat): (cm^{-1}) 3107, 2971, 2910, 1703, 1599, 1482, 1357, 1297, 1258, 1187, 1140, 945, 919, 805. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{19}H_{17}ClN_2NaO_3^+$: 379.0820, found: 379.0814.

Ethyl (*E*)-3-((*Z*)-6-bromo-2-(*p*-tolylimino)benzo[*d*]oxazol-3(2*H*)-yl)acrylate (3ah):



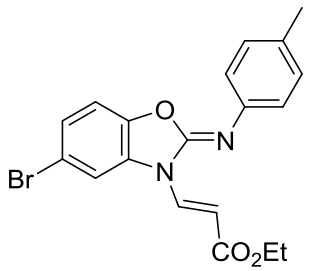
White solid, (**3ah** was purified by PE/EtOAc = 50/1, V/V), mp: 120 – 121 ℃, 70.6 mg, 88% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, *J* = 14.4 Hz, 1H), 7.33 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.29 (d, *J* = 1.6 Hz, 1H), 7.15 (d, *J* = 7.1 Hz, 5H), 6.65 (d, *J* = 14.4 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.35 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.3, 145.2, 143.8, 141.1, 134.1, 133.9, 129.5, 128.6, 127.0, 123.1, 116.0, 113.6, 110.8, 105.4, 60.6, 21.0, 14.4. FT-IR (neat): (cm^{-1}) 3102, 2973, 2913, 1702, 1593, 1478, 1353, 1290, 1262, 1193, 1150, 954, 907, 796. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{19}H_{17}BrN_2NaO_3^+$: 423.0315, found: 423.0316.

Ethyl (*E*)-3-((*Z*)-5-chloro-2-(*p*-tolylimino)benzo[*d*]oxazol-3(2*H*)-yl)acrylate (3ai):



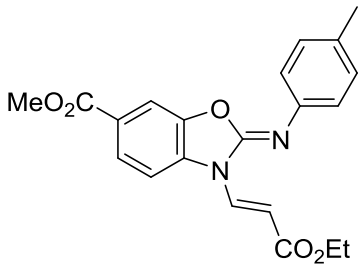
White solid, (**3ai** was purified by PE/EtOAc = 50/1, V/V), mp: 145 – 146 ℃, 62.1 mg, 87% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, *J* = 14.4 Hz, 1H), 7.27 (d, *J* = 1.9 Hz, 1H), 7.15 (s, 4H), 7.09 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.03 (d, *J* = 8.5 Hz, 1H), 6.64 (d, *J* = 14.4 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.34 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.1, 144.2, 143.2, 141.2, 134.0, 133.8, 130.3, 129.7, 129.5, 123.5, 123.1, 110.6, 110.4, 105.6, 60.6, 21.0, 14.4. FT-IR (neat): (cm^{-1}) 3107, 3074, 2954, 1702, 1597, 1478, 1366, 1297, 1245, 1036, 952, 805. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{19}H_{17}ClN_2NaO_3^+$: 379.0820, found: 379.0815.

Ethyl (*E*)-3-((*Z*)-5-bromo-2-(*p*-tolylimino)benzo[*d*]oxazol-3(2*H*)-yl)acrylate (3aj):



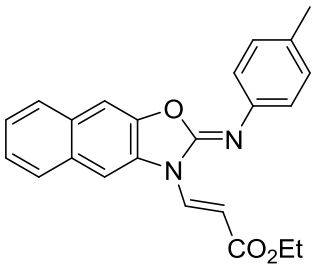
Yellow solid, (**3aj** was purified by PE/EtOAc = 50/1, V/V), mp: 122 – 124 ℃, 70.6 mg, 88% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, *J* = 14.4 Hz, 1H), 7.43 (d, *J* = 1.8 Hz, 1H), 7.26 (t, *J* = 3.3 Hz, 1H), 7.16 (s, 4H), 7.01 (d, *J* = 8.4 Hz, 1H), 6.65 (d, *J* = 14.4 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 2.35 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.1, 144.1, 143.7, 141.2, 134.0, 133.9, 130.6, 129.5, 126.5, 123.1, 116.7, 113.1, 111.1, 105.7, 60.7, 21.0, 14.4. FT-IR (neat): (cm^{-1}) 3105, 2951, 2921, 1703, 1605, 1480, 1252, 1135, 950, 790. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{19}H_{17}BrN_2NaO_3^+$: 423.0315, found: 423.0308.

Methyl (*Z*)-3-((*E*)-3-ethoxy-3-oxoprop-1-en-1-yl)-2-(*p*-tolylimino)-2,3-dihydroben -zo [*d*]oxazole-6-carboxylate (3ak):



White solid, (**3ak** was purified by PE/EtOAc = 50/1, V/V), mp: 134 – 135 ℃, 57.1 mg, 75% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 14.3 Hz, 1H), 7.96 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.79 (d, *J* = 1.2 Hz, 1H), 7.31 (d, *J* = 8.3 Hz, 1H), 7.21 – 7.15 (m, 4H), 6.79 (d, *J* = 14.3 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.92 (s, 3H), 2.36 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.2, 165.8, 144.4, 144.1, 141.0, 134.0, 133.9, 133.1, 129.6, 126.7, 125.9, 123.1, 110.9, 109.0, 106.4, 60.7, 52.4, 21.0, 14.4. FT-IR (neat): (cm^{-1}) 3109, 2975, 2949, 1698, 1605, 1506, 1446, 1360, 1265, 1146, 816, 755. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{21}H_{20}N_2NaO_5^+$: 403.1264, found: 403.1260.

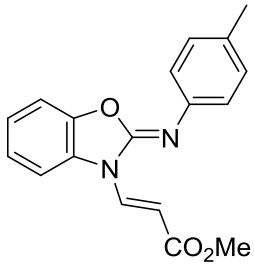
Ethyl (*E*)-3-((*Z*)-2-(*p*-tolylimino)naphtho[2,3-*d*]oxazol-3(2*H*)-yl)acrylate (3al):



White solid, (**3al** was purified by PE/EtOAc = 45/1, V/V), mp: 184 – 185 ℃, 41.7 mg, 56% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 (d, *J* = 14.4 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.62 (s, 1H), 7.46 (q, *J* = 6.6, 6.1 Hz, 3H), 7.23 – 7.18 (m, 4H), 6.71 (d, *J* = 14.4 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.37 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.4, 144.4, 144.1, 141.4, 134.7,

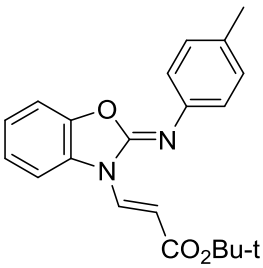
133.8, 130.8, 130.3, 129.6, 129.0, 127.7, 127.6, 125.8, 125.7, 123.2, 106.8, 106.0, 105.1, 60.6, 21.0, 14.4. FT-IR (neat): (cm^{-1}) 3059, 2953, 2917, 1696, 1599, 1459, 1236, 1036, 950, 799, 743. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{23}H_{20}N_2NaO_3^+$: 395.1366, found: 395.1364.

Methyl (*E*)-3-((*Z*)-2-(*p*-tolylimino)benzo[*d*]oxazol-3(2*H*)-yl)acrylate (3am):



White solid, (**3am** was purified by PE/EtOAc = 50/1, V/V), mp: 114 – 115 ℃, 56.7 mg, 92% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (d, *J* = 14.4 Hz, 1H), 7.30 (d, *J* = 7.9 Hz, 1H), 7.22 – 7.17 (m, 3H), 7.17 – 7.12 (m, 4H), 6.70 (d, *J* = 14.4 Hz, 1H), 3.82 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.9, 144.7, 144.6, 141.6, 134.7, 133.6, 129.5, 129.3, 124.2, 123.8, 123.1, 110.0, 109.9, 104.3, 51.7, 21.0. FT-IR (neat): (cm^{-1}) 3113, 2919, 1690, 1593, 1483, 1355, 1137, 975, 824, 730. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{18}H_{16}N_2NaO_3^+$: 331.1053, found: 331.1046.

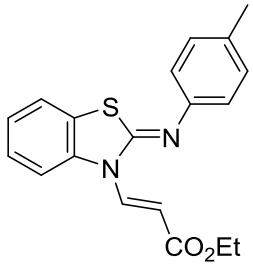
Tert-butyl (*E*)-3-((*Z*)-2-(*p*-tolylimino)benzo[*d*]oxazol-3(2*H*)-yl)acrylate (3an):



White solid, (**3an** was purified by PE/EtOAc = 50/1, V/V), mp: 163 – 165 ℃, 63.1 mg, 90% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (d, *J* = 14.4 Hz, 1H), 7.27 (d, *J* = 7.8 Hz, 1H), 7.19 – 7.14 (m, 5H), 7.11 (dd, *J* = 6.8, 1.2 Hz, 2H), 6.59 (d, *J* = 14.4 Hz, 1H), 2.35 (s, 3H), 1.55 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.8, 144.7, 144.6,

141.8, 133.8, 133.4, 129.5, 129.4, 124.1, 123.6, 123.1, 109.9, 109.9, 106.7, 80.6, 28.3, 21.0. FT-IR (neat): (cm^{-1}) 3091, 2973, 1687, 1607, 1478, 1353, 1250, 1135, 956, 740, 486. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{21}H_{22}N_2NaO_3^+$: 373.1523, found: 373.1514.

Ethyl (*E*)-3-((*Z*)-2-(*p*-tolylimino)benzo[*d*]thiazol-3(2*H*)-yl)acrylate (3ao):



White solid, (**3ao** was purified by PE/EtOAc = 50/1, V/V), mp: 123 – 125 ℃, 30.5 mg, 45% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 14.1 Hz, 1H), 7.35 – 7.29 (m, 2H), 7.28 (s, 1H), 7.23 – 7.18 (m, 3H), 7.14 (t, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 8.1 Hz, 2H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.36 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.3, 154.0, 147.8, 137.5, 135.5, 134.1, 130.2, 126.5, 124.0, 122.9, 122.6, 120.5, 111.1, 107.7, 60.5, 21.0, 14.4. FT-IR (neat): (cm^{-1}) 3124, 3029, 2979, 1703, 1648, 1500, 1472, 1349, 1264, 1144, 818, 741, 570. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{19}H_{18}N_2NaO_2S^+$: 361.0981, found: 361.0976.

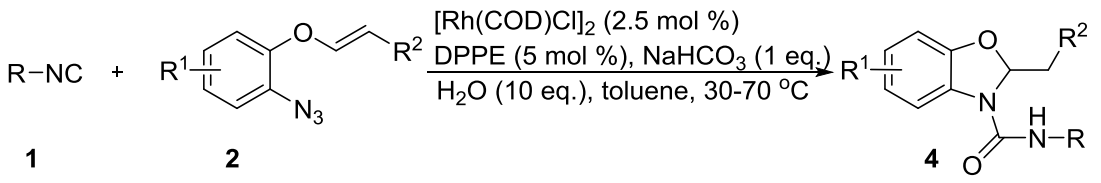
References:

1. (a) Zhang, Z.; Huang, B. L.; Qiao, G. Y.; Zhu, L.; Xiao, F.; Chen, F.; Fu, B.; Zhang, Z. H. Tandem Coupling of Azide with Isonitrile and Boronic Acid: Facile Access to Functionalized Amidines. *Angew. Chem., Int. Ed.* **2017**, *56*, 4320-4323. (b) Hu, Z.; Yuan, H.; Men, Y.; Liu, Q.; Zhang, J.; Xu, X. Cross-Cycloaddition of Two Different Isocyanides: Chemoselective Heterodimerization and [3+2]-Cyclization of 1,4-Diazabutatriene. *Angew. Chem., Int. Ed.* **2016**, *55*, 7077-7080. (c) Wang, R.; Zhang, Y.; Yu, S. Synthesis of isoquinolines via visible light-promoted insertion of vinyl isocyanides with diaryliodonium salts. *Chem. Commun.* **2014**, *50*,

6164-6167. (d) Liu, Y.; Chen, X. L.; Li, X. Y.; Zhu, S. S.; Li, S. J.; Song, Y.; Qu, L. B.; Yu, B. 4CzIPN-^{t}Bu-Catalyzed Proton-Coupled Electron Transfer for Photosynthesis of Phosphorylated *N*-Heteroaromatics. *J. Am. Chem. Soc.* **2021**, *143*, 964-972.

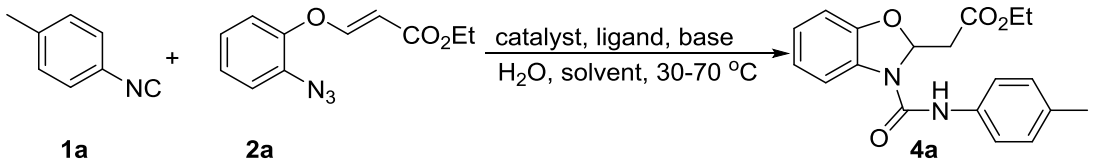
2. (a) Gharpure, S. J.; Naveen, S.; Samala, G.; Vishwakarma, D. S. Transition-Metal Acetate-Promoted Intramolecular Nitrene Insertion to Vinylogous Carbonates for Divergent Synthesis of Azirinobenzoxazoles and Benzoxazines. *Chem. Eur. J.* **2019**, *25*, 1456-1460. (b) Alt, I. T.; Plietker, B. Iron-Catalyzed Intramolecular C(sp^2)-H Amination. *Angew. Chem., Int. Ed.* **2016**, *55*, 1519-1522. (c) Necardo, C.; Alfano, A. I.; Del Grosso, E.; Pelliccia, S.; Galli, U.; Novellino, E.; Meneghetti, F.; Giustiniano, M.; Tron, G. C. Aryl Azides as Forgotten Electrophiles in the Van Leusen Reaction: A Multicomponent Transformation Affording 4-Tosyl-1-arylimidazoles. *J. Org. Chem.* **2019,** *84*, 16299-16307. (d) Su, S.; Hu, J.; Cui, Y.; Tang, C.; Chen, Y.; Li, J. A formal (5+1) annulation reaction from heterodimerization of two different isocyanides: stereoselective synthesis of 2H-benzo[*b*][1,4]oxazin-2-one. *Chem. Commun.* **2019,** *55*, 12243-12246.

IV. General Procedure for the Preparation of 4:



A sealed tube equipped with a magnetic stir bar was charged with $[Rh(COD)Cl]_2$ (2.5 mg, 0.005 mmol), DPPE (4.1 mg, 0.01 mmol) and $NaHCO_3$ (16.8 mg, 0.2 mmol) in toluene (2.0 mL), then **1a** (23.4 mg, 0.2 mmol), **2a** (46.6 mg, 0.2 mmol) and H_2O (0.036 mL, 2 mmol) were added. Subsequently, the reaction mixture was stirred at 30 ℃ for 72 h and then heated to 70 ℃ for 12 h. After the reaction was complete, the solvent was removed under reduced pressure. The crude residue was purified by silica gel column chromatography (EtOAc/PE = 1/40, V/V) to afford pure product **4a** (49.0 mg, 72%) as colorless liquid.

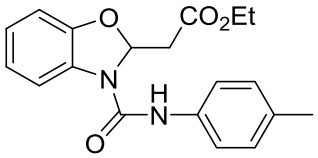
Table 1. Optimization of Reaction Conditions[a]



entry	catalyst (mol %)	ligand (mol %)	base (eq.)	H_2O (eq.)	solvent	yield[b] (%)
1	$[Rh(COD)Cl]_2$ (2.5)	---	---	---	toluene	10
2	$[Rh(COD)Cl]_2$ (2.5)	DPPE (5)	$NaHCO_3$ (1 eq.)	10 eq.	toluene	72[c]
3	$[Rh(COD)Cl]_2$ (1.5)	DPPE (5)	$NaHCO_3$ (1 eq.)	10 eq.	toluene	55
4	$Rh_2(OAc)_4$ (2.5)	DPPE (5)	$NaHCO_3$ (1 eq.)	10 eq.	toluene	36
5	$[Cp^*RhCl_2]_2$ (2.5)	DPPE (5)	$NaHCO_3$ (1 eq.)	10 eq.	toluene	43
6	$[Rh(COD)Cl]_2$ (2.5)	DPPP (5)	$NaHCO_3$ (1 eq.)	10 eq.	toluene	56
7	$[Rh(COD)Cl]_2$ (2.5)	DPPF (5)	$NaHCO_3$ (1 eq.)	10 eq.	toluene	48
8	$[Rh(COD)Cl]_2$ (2.5)	DPPE (5)	KH_2PO_4 (1 eq.)	10 eq.	toluene	40
9	$[Rh(COD)Cl]_2$ (2.5)	DPPE (5)	K_2HPO_4 (1 eq.)	10 eq.	toluene	52
10	$[Rh(COD)Cl]_2$ (2.5)	DPPE (5)	Na_2CO_3 (1 eq.)	10 eq.	toluene	52
11	$[Rh(COD)Cl]_2$ (2.5)	DPPE (5)	TfOK (1 eq.)	10 eq.	toluene	trace
12	$[Rh(COD)Cl]_2$ (2.5)	DPPE (5)	$NaHCO_3$ (1 eq.)	20 eq.	toluene	59
13	$[Rh(COD)Cl]_2$ (2.5)	DPPE (5)	$NaHCO_3$ (1 eq.)	10 eq.	toluene	59
14	$[Rh(COD)Cl]_2$ (2.5)	DPPE (5)	$NaHCO_3$ (1 eq.)	10 eq.	PhCl	62
15	$[Rh(COD)Cl]_2$ (2.5)	DPPE (5)	$NaHCO_3$ (1 eq.)	10 eq.	PhF	56
16	$[Rh(COD)Cl]_2$ (2.5)	DPPE (5)	$NaHCO_3$ (1 eq.)	10 eq.	xylene	65

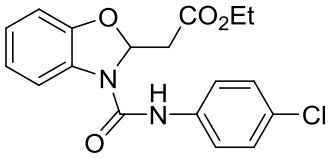
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), catalyst (0.003-0.005 mmol), ligand (0.01 mmol), addive (0.1-0.2 mmol), H_2O (2 mmol), solvent (2.0 mL), at 30 ℃ for 72 h and heated to 70 °C for 12 h in a sealed tube. $[Rh(COD)Cl]_2$ = Chloro(1,5-cyclooctadiene)-rhodium(I)dimer, $[Cp^*RhCl_2]_2$ = Bis[(pentamethylcyclopentadienyl)dichloro-rhodium]. DPPE = 1,2-Bis(diphenylphosphino)ethane, DPPP = 1,3-Bis(diphenylphosphino)propane, DPPF =1,1'-Bis(diphenylphosphino)ferrocene.[b] Estimated by ^1H NMR spectroscopy using CH_2Br_2 as an internal standard. [c] Isolated yield.

Ethyl 2-(3-(*p*-tolylcarbamoyl)-2,3-dihydrobenzo[*d*]oxazol-2-yl)acetate (4a):



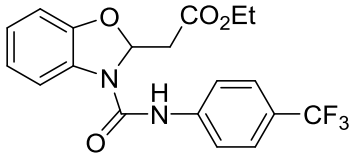
Colorless liquid, (**4a** was purified by PE/EtOAc = 40/1, V/V), 49.0 mg, 72% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.39 (d, *J* = 7.7 Hz, 1H), 7.37 (d, *J* = 8.3 Hz, 2H), 7.13 (d, *J* = 8.2 Hz, 2H), 6.98 (dt, *J* = 24.4, 7.6 Hz, 2H), 6.87 (d, *J* = 7.7 Hz, 1H), 6.62 (dd, *J* = 7.2, 4.1 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.08 (dd, *J* = 17.2, 7.2 Hz, 1H), 2.92 (dd, *J* = 17.2, 4.0 Hz, 1H), 2.31 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.4, 152.3, 150.2, 135.6, 133.2, 129.5, 129.3, 124.5, 121.6, 119.9, 116.7, 109.7, 90.8, 61.7, 40.6, 20.8, 14.1. FT-IR (neat): (cm^{-1}) 3297, 2915, 1735, 1646, 1592, 1528, 1476, 1377, 1323, 1226, 805, 741, 602. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{19}H_{20}N_2NaO_4^+$: 363.1315, found: 363.1311.

Ethyl 2-(3-((4-chlorophenyl)carbamoyl)-2,3-dihydrobenzo[*d*]oxazol-2-yl)acetate (4b):



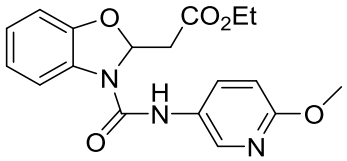
Yellow liquid, (**4b** was purified by PE/EtOAc = 40/1, V/V), 52.0 mg, 72% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.68 (s, 1H), 7.48 – 7.44 (m, 2H), 7.44 – 7.41 (m, 1H), 7.30 – 7.27 (m, 2H), 7.02 (td, *J* = 7.7, 1.2 Hz, 1H), 6.98 (td, *J* = 7.6, 1.0 Hz, 1H), 6.88 (d, *J* = 7.6 Hz, 1H), 6.59 (dd, *J* = 8.0, 3.3 Hz, 1H), 4.26 (q, *J* = 7.2 Hz, 2H), 3.09 (dd, *J* = 17.5, 8.0 Hz, 1H), 2.94 (dd, *J* = 17.5, 3.3 Hz, 1H), 1.30 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.9, 152.3, 150.1, 137.1, 129.0, 129.0, 128.5, 124.8, 121.7, 120.8, 117.5, 109.6, 90.5, 62.0, 40.5, 14.0. FT-IR (neat): (cm^{-1}) 3283, 2923, 1735, 1649, 1592, 1526, 1474, 1401, 1312, 1219, 1004, 797, 743, 611. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{18}H_{17}ClN_2NaO_4^+$: 383.0769, found: 383.0767.

Ethyl 2-(3-((4-(trifluoromethyl)phenyl)carbamoyl)-2,3-dihydrobenzo[*d*]oxazol-2-yl)acetate (4c):



Yellow liquid, (**4c** was purified by PE/EtOAc = 40/1, V/V), 45.7 mg, 58% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.02 (s, 1H), 7.64 (d, *J* = 8.6 Hz, 2H), 7.57 (d, *J* = 8.7 Hz, 2H), 7.45 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.04 (td, *J* = 7.7, 1.3 Hz, 1H), 6.99 (td, *J* = 7.7, 1.1 Hz, 1H), 6.88 (dd, *J* = 7.8, 0.9 Hz, 1H), 6.60 (dd, *J* = 8.3, 3.0 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.10 (dd, *J* = 17.7, 8.3 Hz, 1H), 2.95 (dd, *J* = 17.7, 3.0 Hz, 1H), 1.30 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.2, 152.3, 150.0, 141.8, 128.8, 126.2 (q, *J* = 3.9 Hz), 125.2 (q, *J* = 32.6 Hz), 125.0, 124.2 (q, *J* = 271.5 Hz), 121.8, 119.1, 117.9, 109.7, 90.4, 62.1, 40.5, 14.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ -61.97. FT-IR (neat): (cm^{-1}) 3281, 2981, 1728, 1640, 1483, 1407, 1308, 1241, 1112, 1012, 833, 747, 645. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{19}H_{17}F_3N_2NaO_4^+$: 417.1038, found: 417.1033.

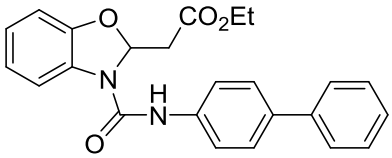
Ethyl 2-(3-((6-methoxypyridin-3-yl)carbamoyl)-2,3-dihydrobenzo[*d*]oxazol-2-yl)-acetate (4d):



Yellow liquid, (**4d** was purified by PE/EtOAc = 45/1, V/V), 46.5 mg, 65% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.18 (d, *J* = 2.7 Hz, 1H), 7.85 (dd, *J* = 8.9, 2.8 Hz, 1H), 7.42 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.02 (td, *J* = 7.7, 1.3 Hz, 1H), 6.97 (td, *J* = 7.6, 1.0 Hz, 1H), 6.87 (dd, *J* = 7.8, 0.9 Hz, 1H), 6.73 (d, *J* = 8.9 Hz, 1H), 6.61 (dd, *J* = 7.8, 3.5 Hz, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 3.92 (s, 3H), 3.09 (dd, *J* = 17.4, 7.8 Hz, 1H), 2.94 (dd, *J* = 17.4, 3.5 Hz, 1H), 1.29 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.8, 160.8, 152.7, 150.0, 138.5, 132.3, 129.1, 124.7, 121.7, 117.2, 110.6,

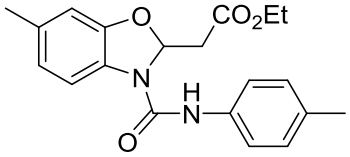
109.6, 90.5, 61.9, 53.5, 40.6, 14.0. FT-IR (neat): (cm^{-1}) 3258, 2915, 1737, 1635, 1478, 1374, 1249, 1180, 1017, 822, 745, 602. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{18}H_{19}N_3NaO_5^+$: 380.1217, found: 380.1208.

Ethyl 2-(3-([1,1'-biphenyl]-4-ylcarbamoyl)-2,3-dihydrobenzo[*d*]oxazol-2-yl)acetate (4e):



Colorless liquid, (**4e** was purified by PE/EtOAc = 40/1, V/V), 43.5 mg, 54% yield. ^1H NMR (600 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.57 (dd, *J* = 5.7, 2.5 Hz, 6H), 7.44 – 7.40 (m, 3H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.02 (td, *J* = 7.7, 1.3 Hz, 1H), 6.98 (td, *J* = 7.6, 1.1 Hz, 1H), 6.90 – 6.84 (m, 1H), 6.63 (dd, *J* = 7.6, 3.7 Hz, 1H), 4.26 (q, *J* = 7.2 Hz, 2H), 3.10 (dd, *J* = 17.3, 7.6 Hz, 1H), 2.94 (dd, *J* = 17.3, 3.7 Hz, 1H), 1.29 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.6, 152.3, 150.2, 140.7, 137.7, 136.5, 129.2, 128.8, 127.6, 127.0, 126.8, 124.7, 121.7, 120.0, 117.1, 109.7, 90.7, 61.8, 40.5, 14.1. FT-IR (neat): (cm^{-1}) 3262, 2919, 1735, 1636, 1482, 1241, 1174, 1012, 833, 756. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{24}H_{22}N_2NaO_4^+$: 425.1472, found: 425.1471.

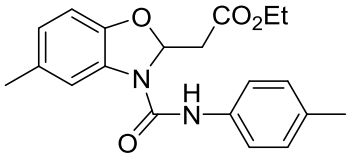
Ethyl 2-(6-methyl-3-(*p*-tolylcarbamoyl)-2,3-dihydrobenzo[*d*]oxazol-2-yl)acetate (4f):



Colorless liquid, (**4f** was purified by PE/EtOAc = 40/1, V/V), 48.2 mg, 68% yield. ^1H NMR (600 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 1H), 7.12 (d, *J* = 8.2 Hz, 2H), 6.76 (d, *J* = 7.9 Hz, 1H), 6.70 (s, 1H), 6.59 (dd, *J* = 7.0, 4.3 Hz, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 3.05 (dd, *J* = 17.1, 7.1 Hz, 1H), 2.89 (dd, *J* = 17.1, 4.3 Hz, 1H), 2.31 (s, 6H), 1.28 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$)

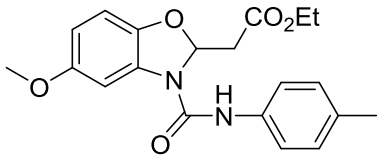
δ 171.2, 152.3, 150.4, 135.7, 134.8, 133.1, 129.5, 126.8, 121.9, 119.8, 116.1, 110.5, 91.0, 61.6, 40.5, 21.3, 20.8, 14.1. FT-IR (neat): (cm^{-1}) 3320, 2921, 1694, 1601, 1489, 1377, 1187, 1131, 1014, 807, 646. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{20}H_{22}N_2NaO_4^+$: 377.1472, found: 377.1480.

Ethyl 2-(5-methyl-3-(*p*-tolylcarbamoyl)-2,3-dihydrobenzo[*d*]oxazol-2-yl)acetate (4g):



Colorless liquid, (**4g** was purified by PE/EtOAc = 40/1, V/V), 49.6 mg, 70% yield. ^1H NMR (600 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.39 – 7.36 (m, 2H), 7.24 – 7.21 (m, 1H), 7.12 (d, *J* = 8.2 Hz, 2H), 6.80 – 6.78 (m, 1H), 6.74 (d, *J* = 8.0 Hz, 1H), 6.58 (dd, *J* = 7.3, 4.0 Hz, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 3.06 (dd, *J* = 17.2, 7.3 Hz, 1H), 2.90 (dd, *J* = 17.2, 4.0 Hz, 1H), 2.32 (d, *J* = 6.4 Hz, 6H), 1.28 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.4, 152.3, 148.1, 135.7, 133.1, 131.3, 129.5, 129.2, 124.7, 119.8, 117.5, 109.1, 90.9, 61.7, 40.5, 21.2, 20.8, 14.1. FT-IR (neat): (cm^{-1}) 3314, 2923, 1681, 1495, 1314, 1016, 805, 738. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{20}H_{22}N_2NaO_4^+$: 377.1472, found: 377.1472.

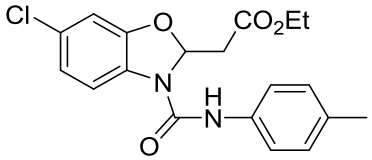
Ethyl 2-(5-methoxy-3-(*p*-tolylcarbamoyl)-2,3-dihydrobenzo[*d*]oxazol-2-yl)acetate (4h):



Yellow liquid, (**4h** was purified by PE/EtOAc = 40/1, V/V), 45.9 mg, 62% yield. ^1H NMR (600 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.2 Hz, 2H), 7.06 (d, *J* = 2.6 Hz, 1H), 6.74 (d, *J* = 8.6 Hz, 1H), 6.57 (dd, *J* = 7.3, 4.0 Hz, 1H), 6.50 (dd, *J* = 8.6, 2.6 Hz, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 3.77 (s, 3H), 3.08 (dd, *J* =

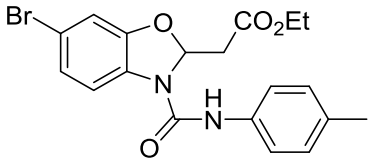
17.2, 7.3 Hz, 1H), 2.90 (dd, *J* = 17.2, 4.0 Hz, 1H), 2.31 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.5, 154.9, 152.1, 144.2, 135.6, 133.2, 130.1, 129.5, 120.0, 109.2, 108.7, 104.3, 91.2, 61.7, 56.1, 40.5, 20.8, 14.1. FT-IR (neat): (cm^{-1}) 3305, 2945, 1683, 1597, 1487, 1293, 1181, 1021, 799, 604. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{20}H_{22}N_2NaO_5^+$: 393.1421, found: 393.1417.

Ethyl 2-(6-chloro-3-(*p*-tolylcarbamoyl)-2,3-dihydrobenzo[*d*]oxazol-2-yl)acetate (4i):



Colorless liquid, (**4i** was purified by PE/EtOAc = 40/1, V/V), 54.0 mg, 72% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 1H), 7.12 (d, *J* = 8.3 Hz, 2H), 6.94 (dd, *J* = 8.3, 2.0 Hz, 1H), 6.86 (d, *J* = 2.0 Hz, 1H), 6.61 (dd, *J* = 8.0, 3.3 Hz, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 3.06 (dd, *J* = 17.5, 8.0 Hz, 1H), 2.93 (dd, *J* = 17.5, 3.3 Hz, 1H), 2.31 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.6, 152.3, 150.8, 135.6, 133.3, 129.5, 129.5, 128.4, 121.6, 119.8, 117.9, 110.3, 91.5, 62.0, 40.5, 20.8, 14.0. FT-IR (neat): (cm^{-1}) 3290, 2919, 1694, 1601, 1536, 1478, 1377, 1310, 1191, 1010, 961, 812. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{19}H_{19}ClN_2NaO_4^+$: 397.0926, found: 397.0920.

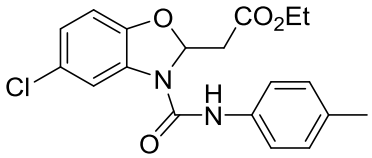
Ethyl 2-(6-bromo-3-(*p*-tolylcarbamoyl)-2,3-dihydrobenzo[*d*]oxazol-2-yl)acetate (4j):



Yellow liquid, (**4j** was purified by PE/EtOAc = 40/1, V/V), 46.1 mg, 55% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 1H), 7.12 (d, *J* = 8.3 Hz, 2H), 7.08 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.00 (d, *J* = 1.8 Hz, 1H),

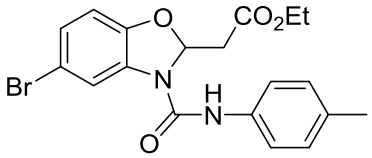
6.60 (dd, *J* = 8.0, 3.3 Hz, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 3.06 (dd, *J* = 17.5, 8.0 Hz, 1H), 2.93 (dd, *J* = 17.5, 3.3 Hz, 1H), 2.31 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.6, 152.2, 151.0, 135.6, 133.3, 129.5, 129.0, 124.5, 119.8, 118.4, 116.6, 113.0, 91.4, 62.0, 40.5, 20.8, 14.1. FT-IR (neat): (cm^{-1}) 3294, 2915, 1694, 1601, 1536, 1476, 1381, 1191, 1008, 960, 810. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{19}H_{19}BrN_2NaO_4^+$: 441.0420, found: 441.0422.

Ethyl 2-(5-chloro-3-(*p*-tolylcarbamoyl)-2,3-dihydrobenzo[*d*]oxazol-2-yl)acetate (4k):



Colorless liquid, (**4k** was purified by PE/EtOAc = 40/1, V/V), 48.7 mg, 65% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.45 (d, *J* = 2.1 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.3 Hz, 2H), 6.96 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.76 (d, *J* = 8.4 Hz, 1H), 6.61 (dd, *J* = 8.0, 3.3 Hz, 1H), 4.26 (q, *J* = 7.2 Hz, 2H), 3.07 (dd, *J* = 17.5, 8.0 Hz, 1H), 2.94 (dd, *J* = 17.5, 3.3 Hz, 1H), 2.32 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.6, 152.0, 148.8, 135.5, 133.4, 130.7, 129.5, 126.5, 124.1, 119.9, 117.9, 109.8, 91.4, 62.0, 40.6, 20.8, 14.0. FT-IR (neat): (cm^{-1}) 3299, 2923, 1690, 1603, 1517, 1478, 1375, 1293, 1016, 797, 686. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{19}H_{19}ClN_2NaO_4^+$: 397.0926, found: 397.0921.

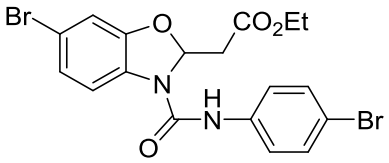
Ethyl 2-(5-bromo-3-(*p*-tolylcarbamoyl)-2,3-dihydrobenzo[*d*]oxazol-2-yl)acetate (4l):



Yellow liquid, (**4l** was purified by PE/EtOAc = 40/1, V/V), 48.6 mg, 58% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.60 (d, *J* = 1.9 Hz, 1H), 7.37 (d, *J* = 8.4 Hz,

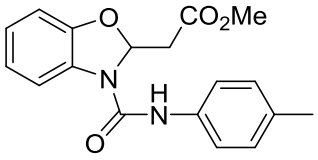
2H), 7.13 (d, *J* = 8.2 Hz, 2H), 7.10 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.72 (d, *J* = 8.4 Hz, 1H), 6.60 (dd, *J* = 8.0, 3.2 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.07 (dd, *J* = 17.5, 8.0 Hz, 1H), 2.94 (dd, *J* = 17.5, 3.2 Hz, 1H), 2.32 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.6, 152.0, 149.3, 135.5, 133.4, 131.0, 129.5, 127.1, 120.6, 119.9, 113.5, 110.5, 91.3, 62.0, 40.61, 20.8, 14.0. FT-IR (neat): (cm^{-1}) 3283, 2921, 1685, 1608, 1547, 1472, 1405, 1316, 1200, 1040, 801, 652. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{19}H_{19}BrN_2NaO_4^+$: 441.0420, found: 441.0423.

Ethyl 2-(6-bromo-3-((4-bromophenyl)carbamoyl)-2,3-dihydrobenzo[*d*]oxazol-2-yl)acetate (4m):



White solid, (**4m** was purified by PE/EtOAc = 40/1, V/V), mp: 114 – 116 °C, 54.2 mg, 56% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.89 (s, 1H), 7.61 (d, *J* = 1.8 Hz, 1H), 7.47 – 7.38 (m, 4H), 7.12 (dt, *J* = 8.4, 1.7 Hz, 1H), 6.73 (dd, *J* = 8.4, 1.2 Hz, 1H), 6.62 – 6.55 (m, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.08 (dd, *J* = 17.8, 8.5 Hz, 1H), 3.00 – 2.92 (m, 1H), 1.30 (td, *J* = 7.1, 1.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.14, 151.97, 149.20, 137.47, 131.92, 130.74, 127.38, 121.22, 121.19, 116.23, 113.56, 110.53, 91.05, 62.24, 40.60, 14.02. FT-IR (neat): (cm^{-1}) 3275, 3197, 3124, 2919, 1687, 1545, 1476, 1368, 1310, 1195, 796, 654, 501, 430. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{18}H_{16}Br_2N_2NaO_4^+$: 504.9369, found: 504.9359.

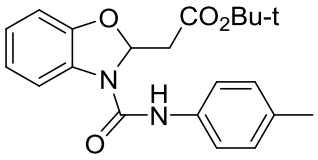
Methyl 2-(3-(*p*-tolylcarbamoyl)-2,3-dihydrobenzo[*d*]oxazol-2-yl)acetate (4n):



Colorless liquid, (**4n** was purified by PE/EtOAc = 40/1, V/V), 42.4 mg, 65% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.29 (dd, *J* = 8.6, 2.0 Hz, 3H), 7.05 (d, *J* =

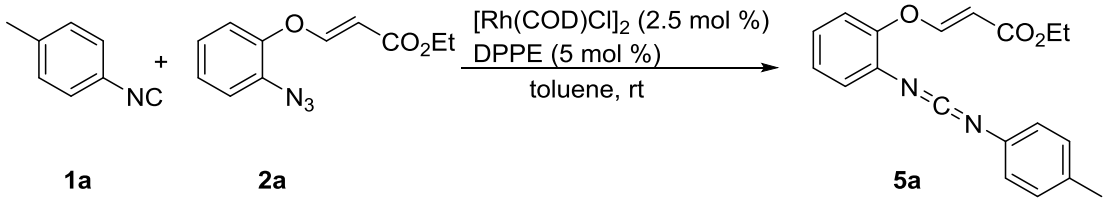
8.3 Hz, 2H), 6.93 (td, *J* = 7.7, 1.3 Hz, 1H), 6.89 (td, *J* = 7.6, 1.1 Hz, 1H), 6.82 – 6.78 (m, 1H), 6.55 (dd, *J* = 7.0, 4.4 Hz, 1H), 3.70 (s, 3H), 3.02 (dd, *J* = 17.1, 7.0 Hz, 1H), 2.85 (dd, *J* = 17.1, 4.4 Hz, 1H), 2.24 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.6, 152.1, 150.2, 135.6, 133.3, 129.5, 129.2, 124.6, 121.7, 119.9, 116.5, 109.7, 90.8, 52.5, 40.3, 20.8. FT-IR (neat): (cm^{-1}) 3299, 2923, 1687, 1595, 1517, 1480, 1318, 986, 807, 740, 510. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{18}H_{18}N_2NaO_4^+$: 349.1159, found: 349.1151.

Tert-butyl 2-(3-(*p*-tolylcarbamoyl)-2,3-dihydrobenzo[*d*]oxazol-2-yl)acetate (4o):



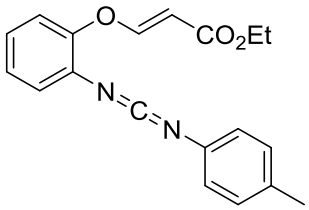
Colorless liquid, (**4o** was purified by PE/EtOAc = 40/1, V/V), 47.2 mg, 64% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.43 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.3 Hz, 2H), 6.99 (td, *J* = 7.7, 1.4 Hz, 1H), 6.95 (td, *J* = 7.6, 1.2 Hz, 1H), 6.85 (dd, *J* = 7.7, 1.1 Hz, 1H), 6.56 (dd, *J* = 7.7, 3.6 Hz, 1H), 3.01 (dd, *J* = 17.3, 7.7 Hz, 1H), 2.86 (dd, *J* = 17.3, 3.6 Hz, 1H), 2.31 (s, 3H), 1.48 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.0, 152.4, 150.2, 135.9, 133.0, 129.5, 129.4, 124.4, 121.5, 119.8, 117.2, 109.5, 90.8, 83.0, 41.7, 28.1, 20.8. FT-IR (neat): (cm^{-1}) 3297, 2977, 1687, 1599, 1517, 1482, 1374, 1316, 1144, 810, 736, 508. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{21}H_{24}N_2NaO_4^+$: 391.1628, found: 391.1620.

V. General Procedure for the Preparation of 5a:



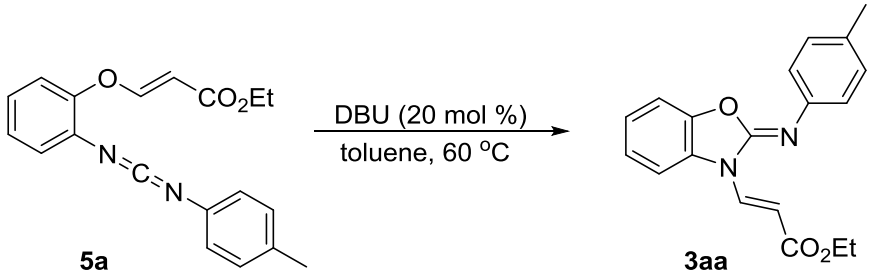
An oven-dried vial equipped with a magnetic stir bar was charged with **1a** (23.4 mg, 0.2 mmol), **2a** (46.6 mg, 0.2 mmol), $[Rh(COD)Cl]_2$ (2.5 mg, 0.005 mmol), DPPE (4.1 mg, 0.01 mmol), and toluene (2.0 mL) were added. The reaction was then stirred at room temperature for 0.5 h until arylisocyanide **1a** disappeared. The solvent was removed under reduced pressure. The crude residue was purified by silica gel column chromatography (EtOAc/PE = 1/60, V/V) to afford pure product **5a** (45.1 mg, 70%) as a yellow liquid.

Ethyl (*E*)-3-(2-(((*p*-tolylimino)methylene)amino)phenoxy)acrylate (5a):



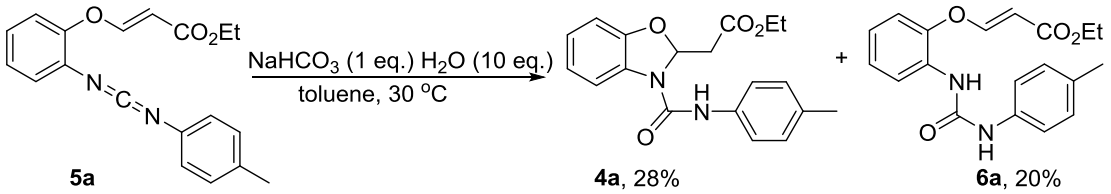
Yellow liquid, (**5a** was purified by PE/EtOAc = 60/1, V/V), 45.1 mg, 70% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (d, *J* = 12.2 Hz, 1H), 7.19 – 7.14 (m, 3H), 7.13 – 7.05 (m, 5H), 5.37 (d, *J* = 12.2 Hz, 1H), 4.15 (q, *J* = 6.9 Hz, 2H), 2.33 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.8, 158.7, 149.9, 135.4, 135.2, 135.1, 130.1, 126.3, 125.9, 125.9, 124.1, 118.7, 102.9, 60.1, 21.0, 14.3. FT-IR (neat): (cm^{-1}) 2934, 2110, 1713, 1491, 1232, 1103, 814; HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{19}H_{18}N_2NaO_3^+$: 345.1210, found: 345.1213.

VI. General Procedure from 5a to 3aa:



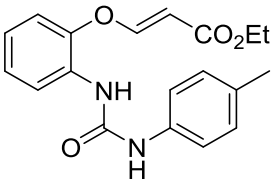
An oven-dried vial equipped with a magnetic stir bar was charged with **5a** (64.5 mg, 0.2 mmol), DBU (6.0 μL, 0.04 mmol), then toluene (2.0 mL) was added. The reaction was then stirred at 60 ^{o}C (heating mantle) for 4 h. After the reaction was complete, the solvent was removed under reduced pressure. The crude residue was purified by silica gel column chromatography (EtOAc/PE = 1/50, V/V) to afford pure product **3aa** (61.9 mg, 96%) as a white solid.

VII. General Procedure from 5a to 4a and 6a:



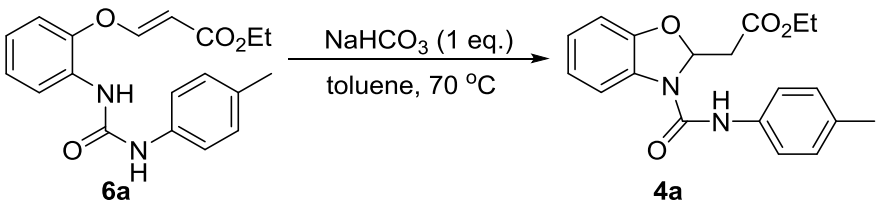
A Schlenck tube charged with **5a** (64.5 mg, 0.2 mmol), $NaHCO_3$ (16.8 mg, 0.2 mmol) in toluene (2.0 mL), then H_2O (0.036 mL, 2 mmol) was added. Subsequently, the reaction mixture was stirred at 30 ℃ (heating mantle) for 36 h. The solvent was removed under reduced pressure. The crude residue was purified by silica gel column chromatography to afford pure product **4a** (19.1 mg, 28%) as colorless liquid and pure product **6a** (13.6 mg, 20%) as white solid.

Ethyl (*E*)-3-(2-(3-(*p*-tolyl)ureido)phenoxy)acrylate (6a):



White solid, (**6a** was purified by PE/EtOAc = 40/1, V/V), mp: 118 – 120 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.25 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.65 (d, *J* = 12.2 Hz, 1H), 7.51 (s, 1H), 7.44 (s, 1H), 7.23 (d, *J* = 8.3 Hz, 2H), 7.16 – 7.13 (m, 1H), 7.10 (d, *J* = 8.2 Hz, 2H), 7.00 – 6.95 (m, 2H), 5.46 (d, *J* = 12.2 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 2.30 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.5, 159.4, 153.3, 144.3, 135.3, 134.1, 130.0, 129.8, 126.0, 123.0, 121.0, 117.7, 102.6, 60.6, 20.8, 14.3. FT-IR (neat): (cm^{-1}) 3299, 2919, 1707, 1642, 1593, 1549, 1452, 1312, 1217, 1129, 745, 628; HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{19}H_{20}N_2NaO_4^+$: 363.1315, found: 363.1306.

VIII. General Procedure from 6a to 4a：



An oven-dried vial equipped with a magnetic stir bar was charged with **6a** (68.1 mg, 0.2 mmol) and $NaHCO_3$ (16.8 mg, 0.2 mmol) in toluene (2.0 mL). The reaction was then stirred at 70 ^oC (heating mantle) for 12 h. After the reaction was complete, the solvent was removed under reduced pressure. The crude residue was purified by silica gel column chromatography (EtOAc/PE = 1/40, V/V) to afford pure product **4a** (53.1 mg, 78%) as colorless liquid.

IX. ORTEP Drawing of Compound 3pa and 4m:

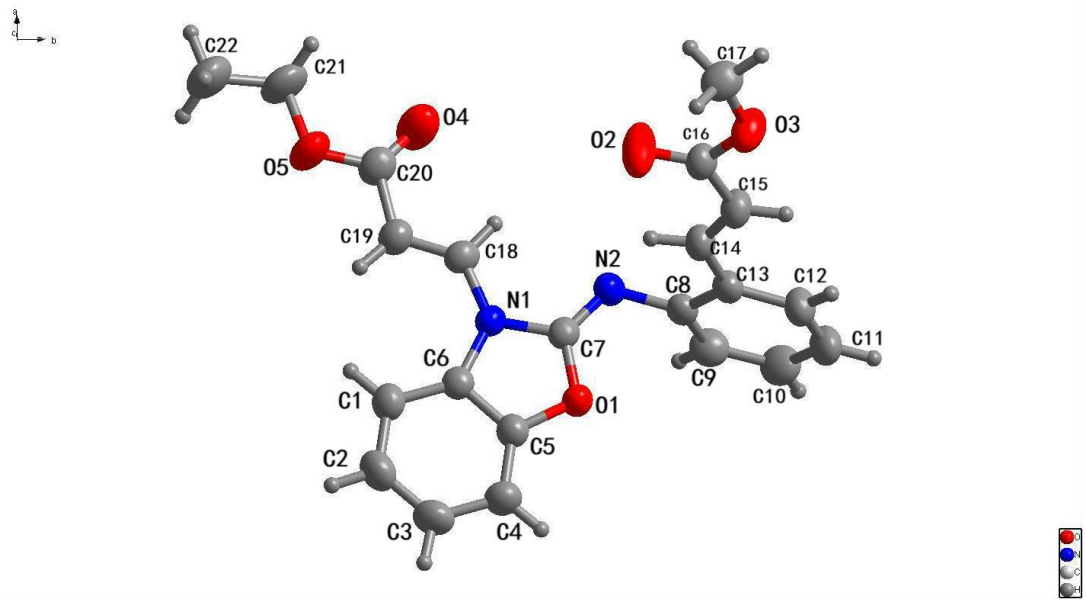


Figure 1. The ORTEP drawing of crystal 3pa (The ellipsoid contour percent probability level is 50%).

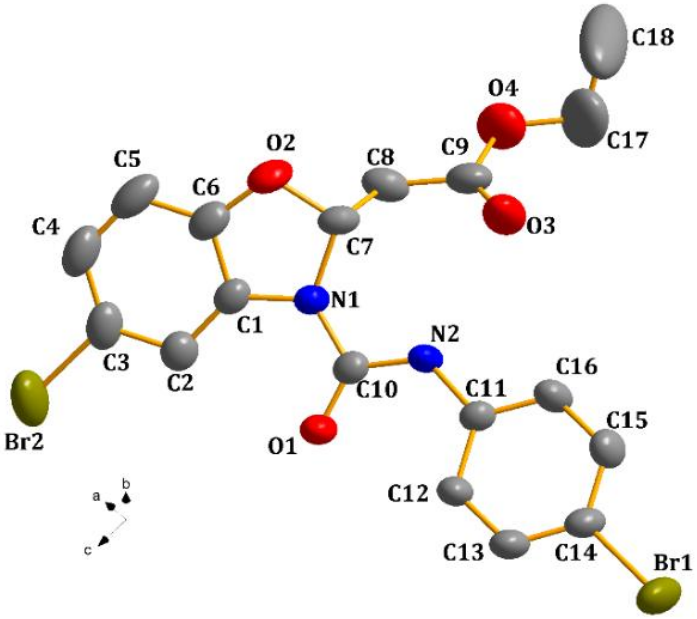


Figure 2. The ORTEP drawing of crystal 4m (The ellipsoid contour percent probability level is 50%).

Method of Crystallization: The compounds **3pa** and **4m** were recrystallized from mixed solvents of ethyl acetate and petroleum ether at 25 ˚C.

Introduction of crystal measuring instrument: X-ray single-crystal data of **3pa** and **4m** were 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.

X. Copies of ^{1}H NMR, ^{13}C NMR and ^{19}F NMR Spectra of Compounds 2-6：

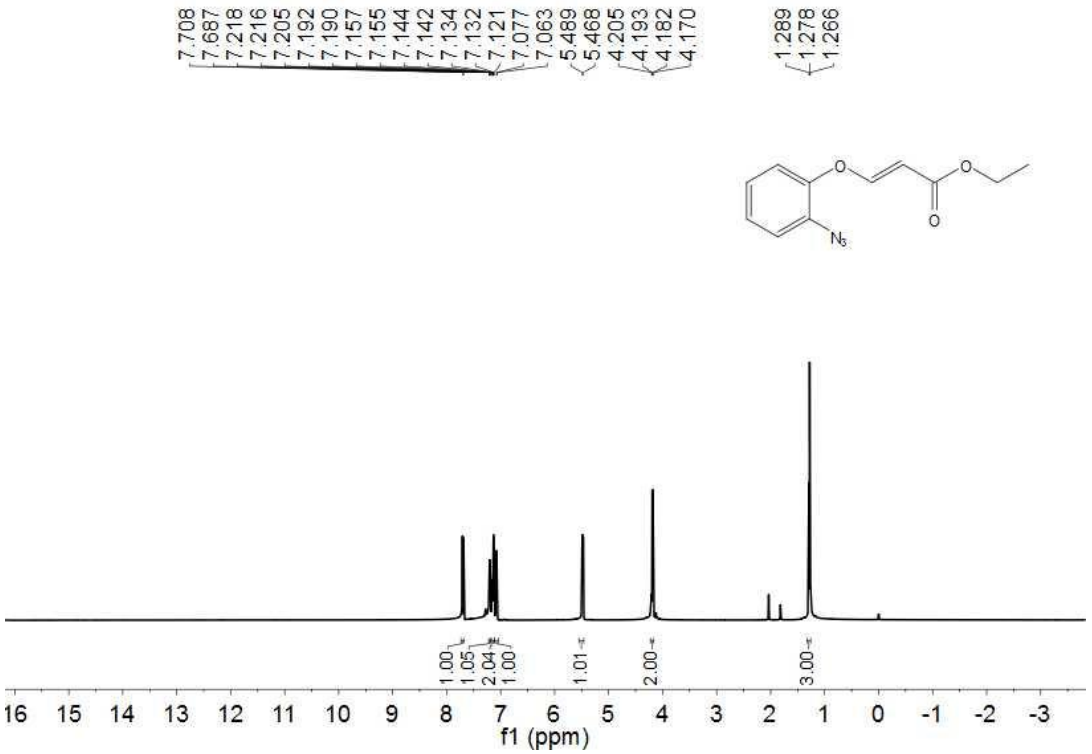


Figure 3. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **2a**

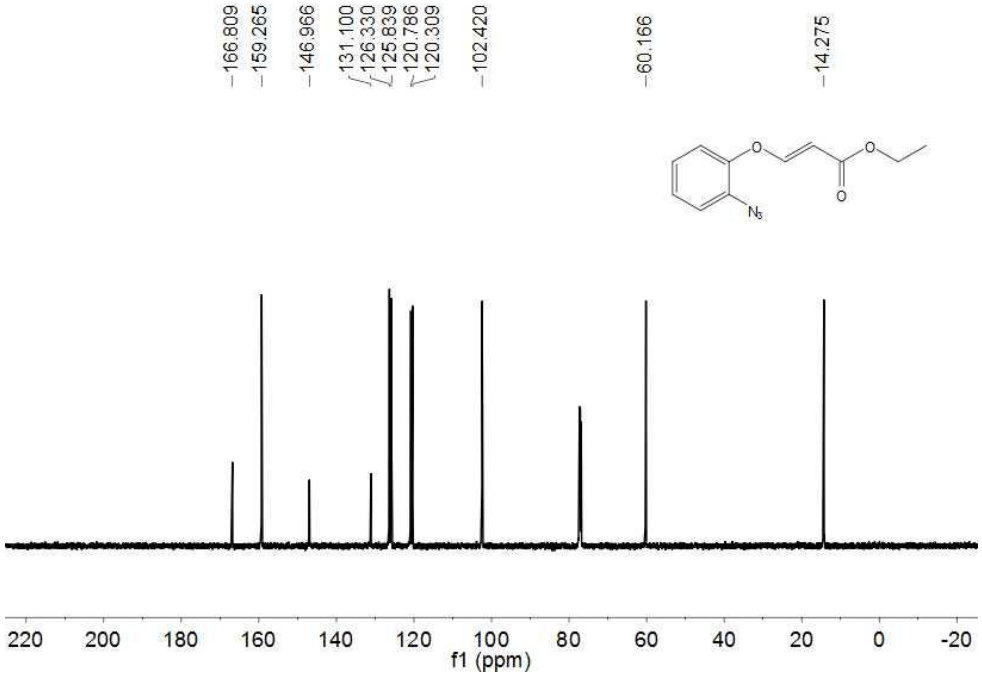


Figure 4. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **2a**

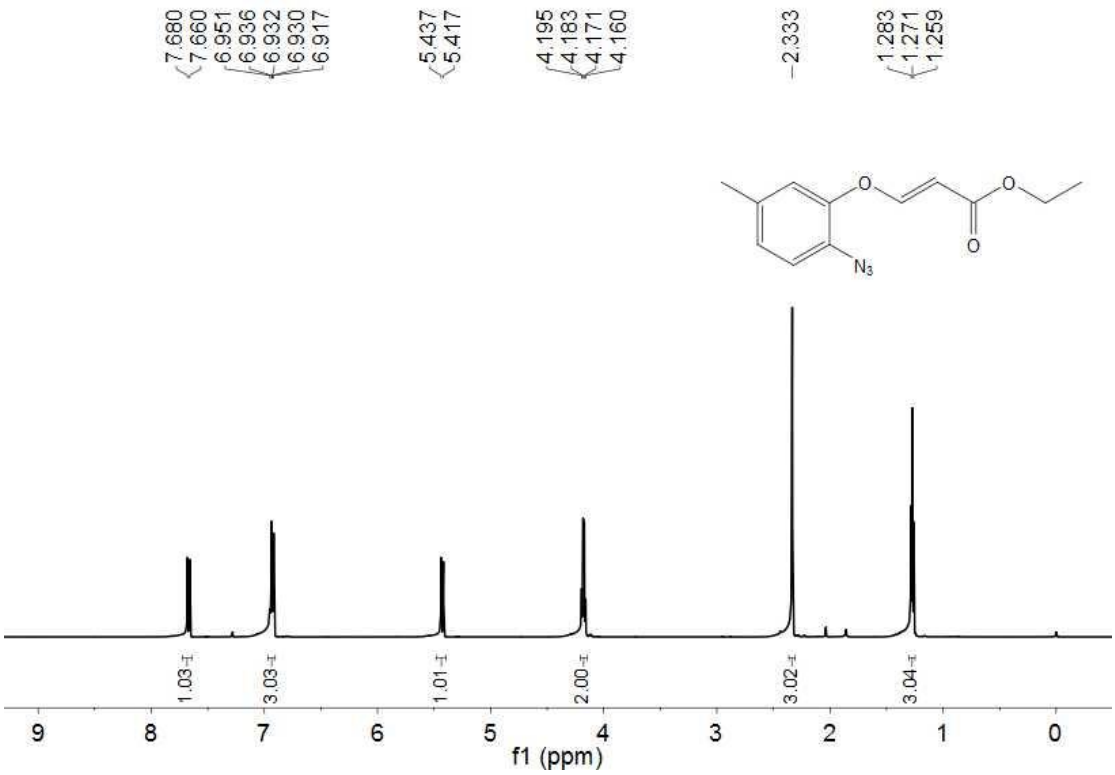


Figure 5. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **2b**

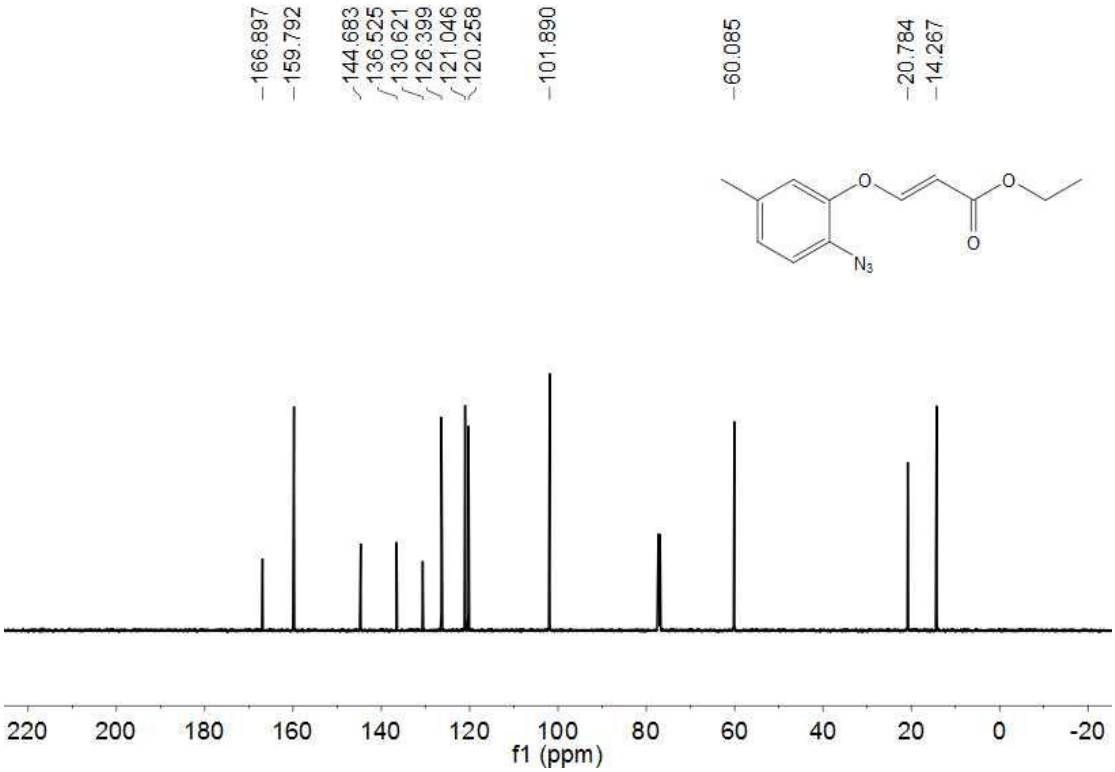


Figure 6. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **2b**

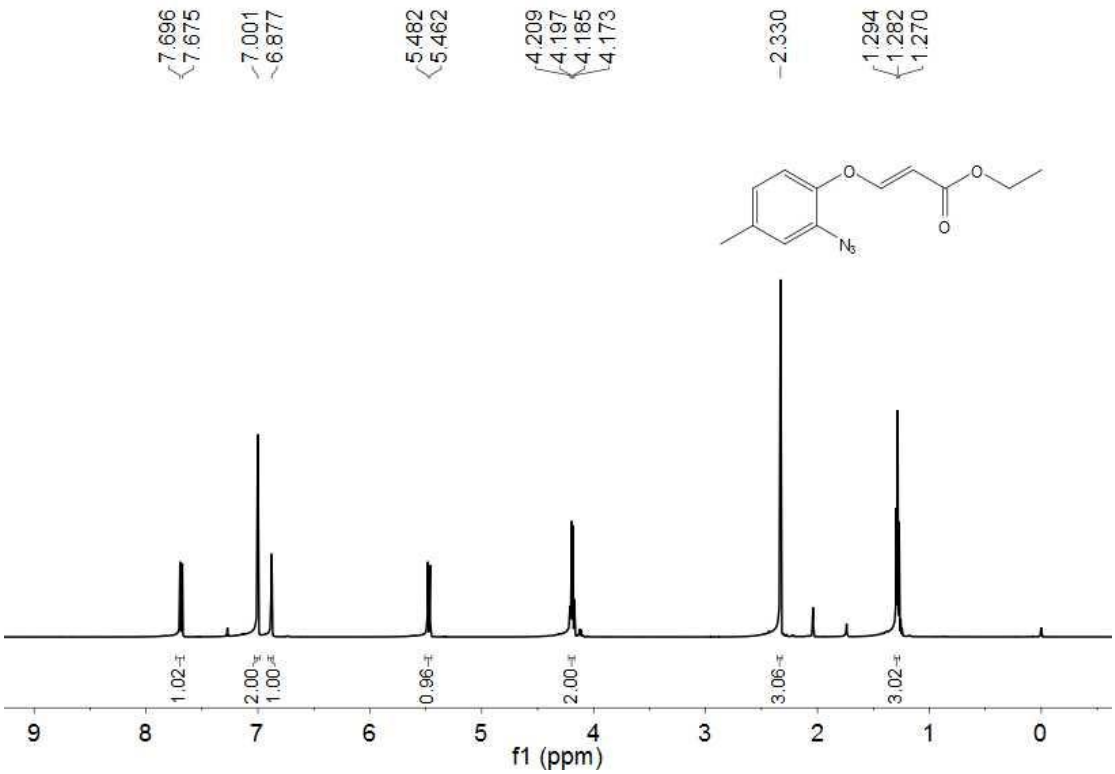


Figure 7. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **2c**

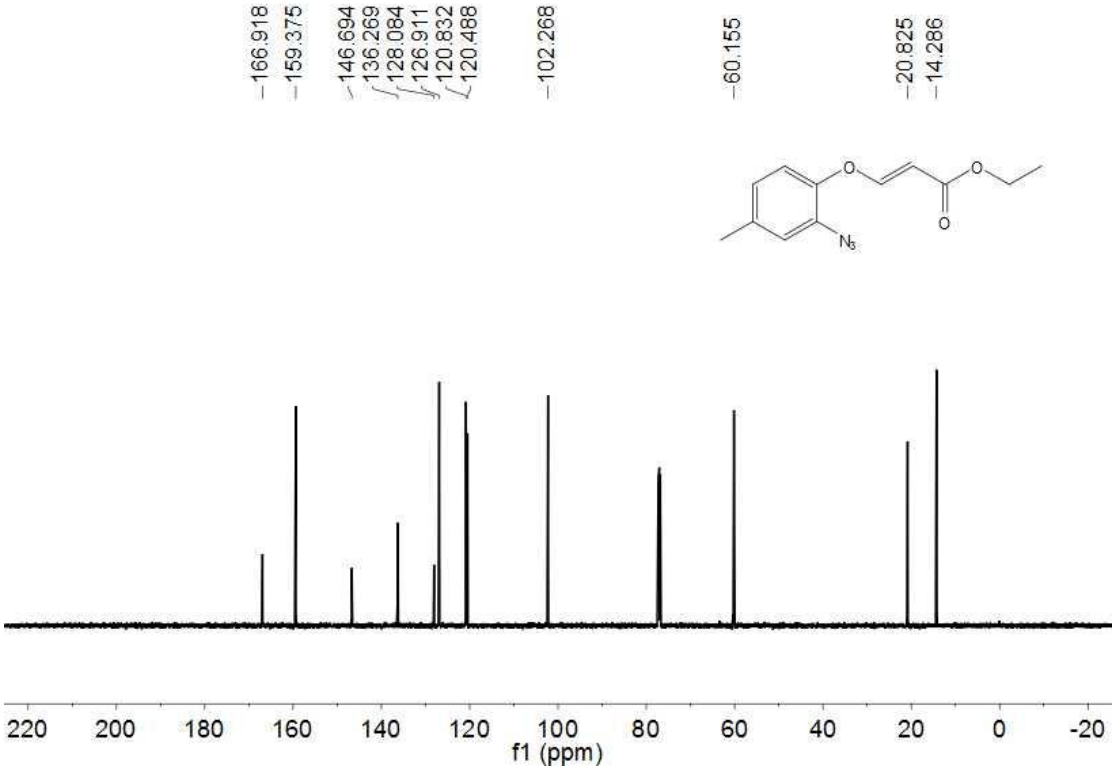


Figure 8. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **2c**

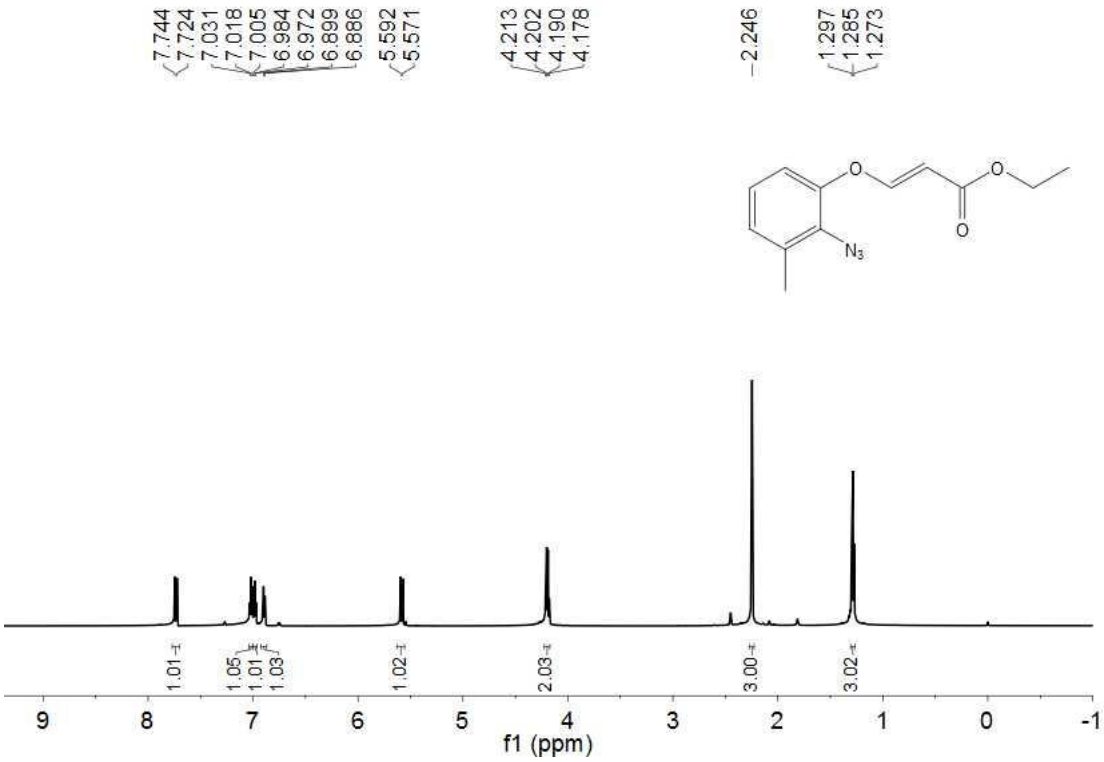


Figure 9. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **2d**

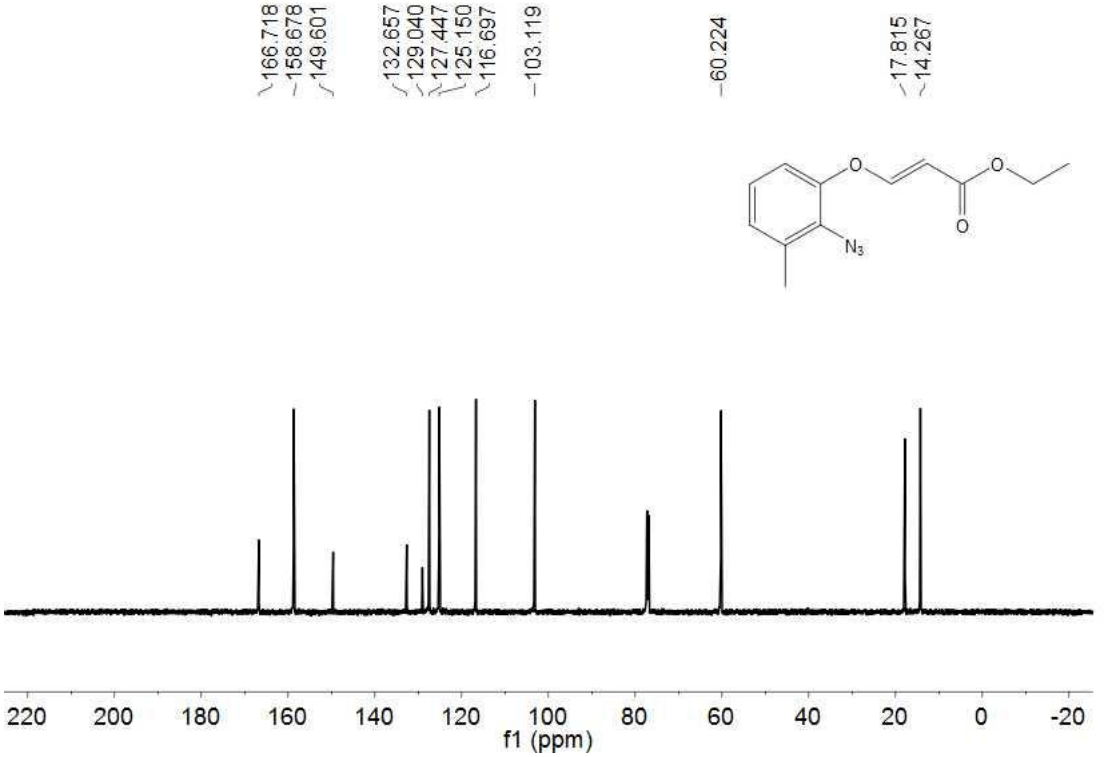


Figure 10. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **2d**

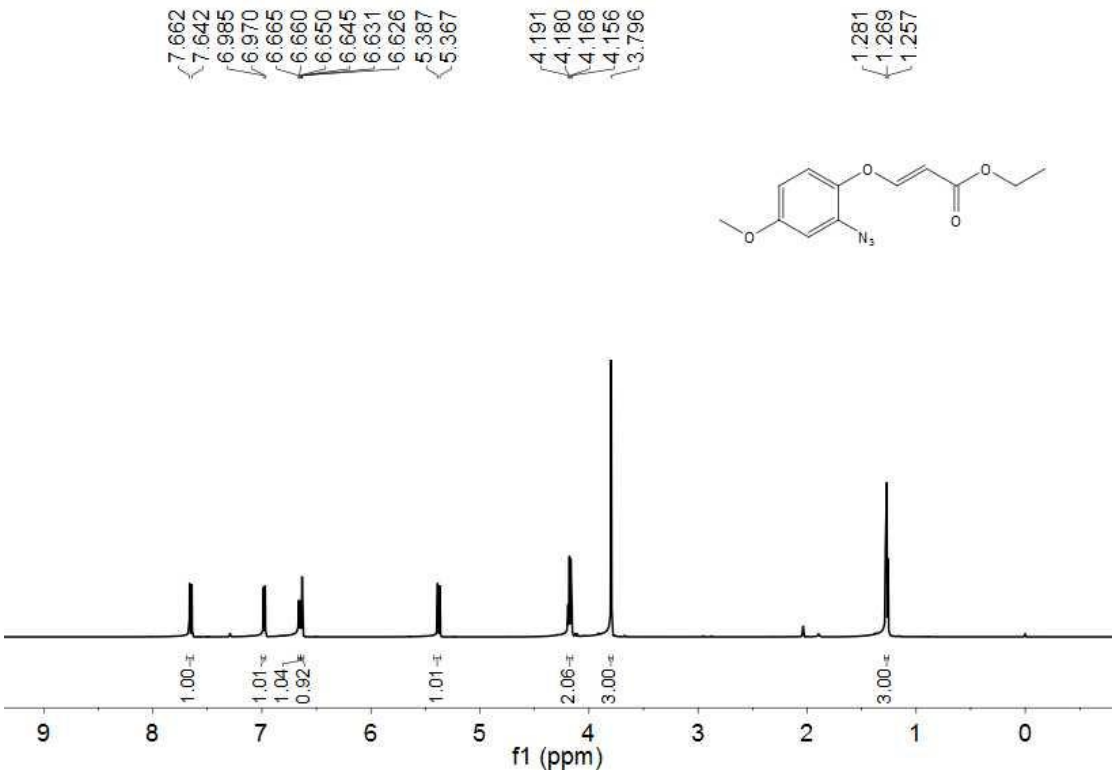


Figure 11. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **2e**

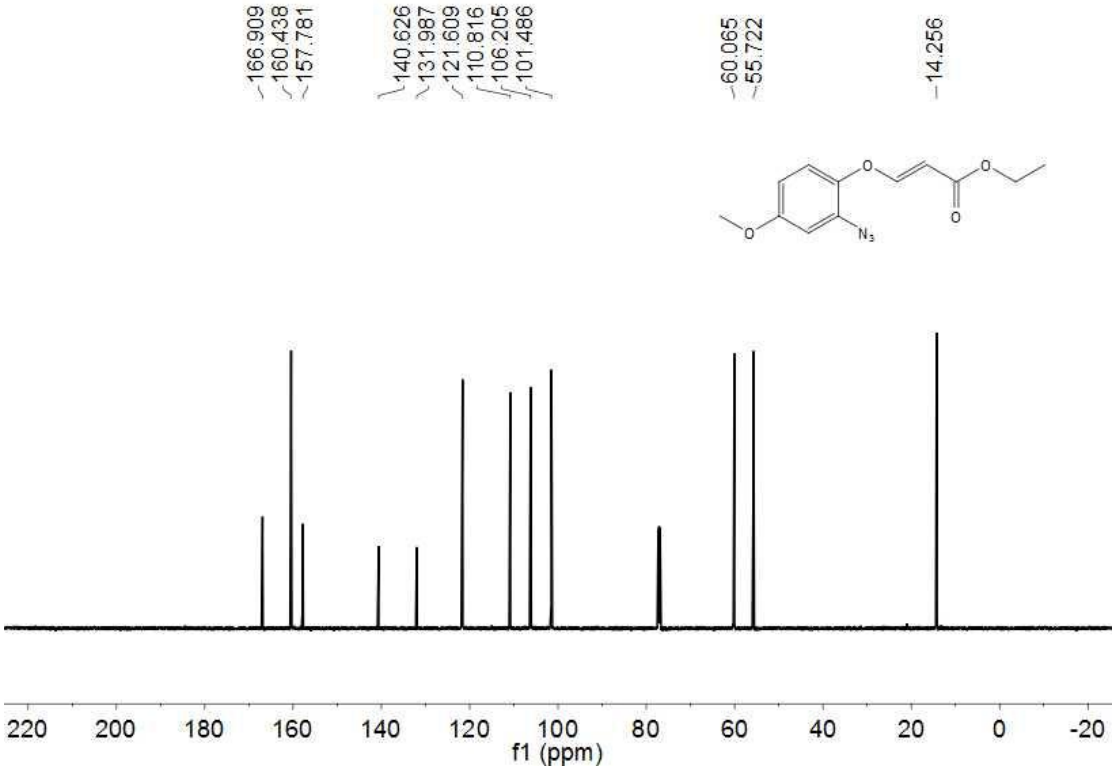


Figure 12. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **2e**

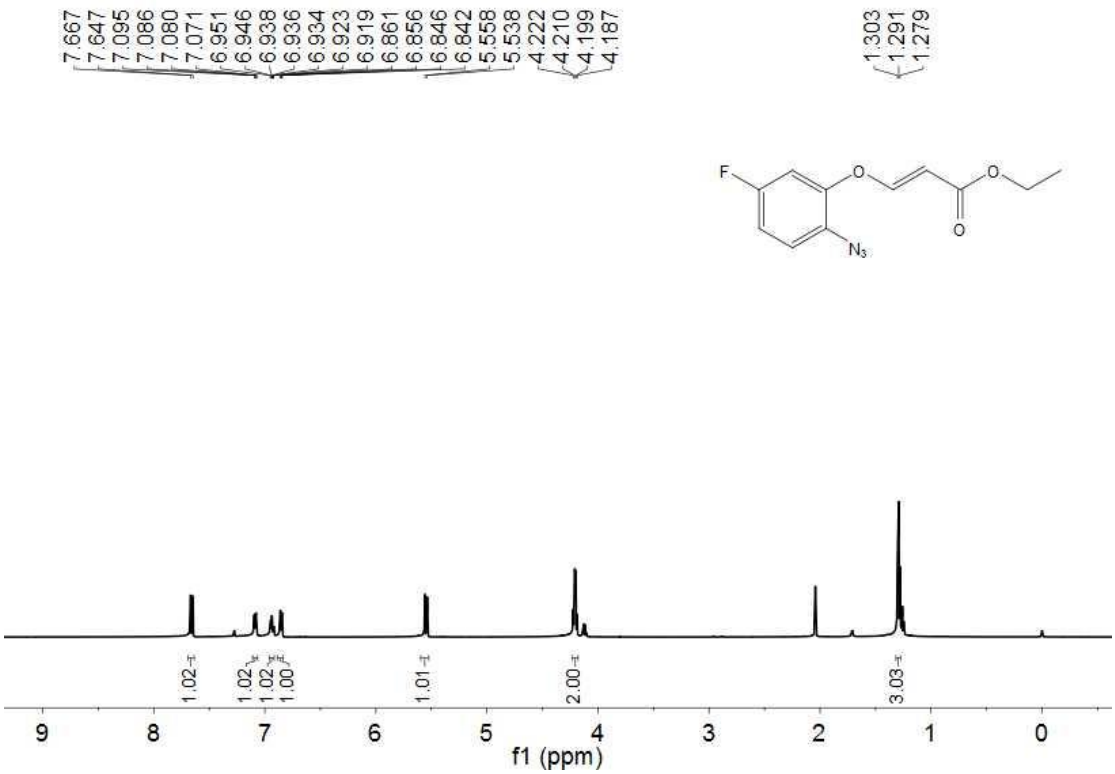


Figure 13. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **2f**

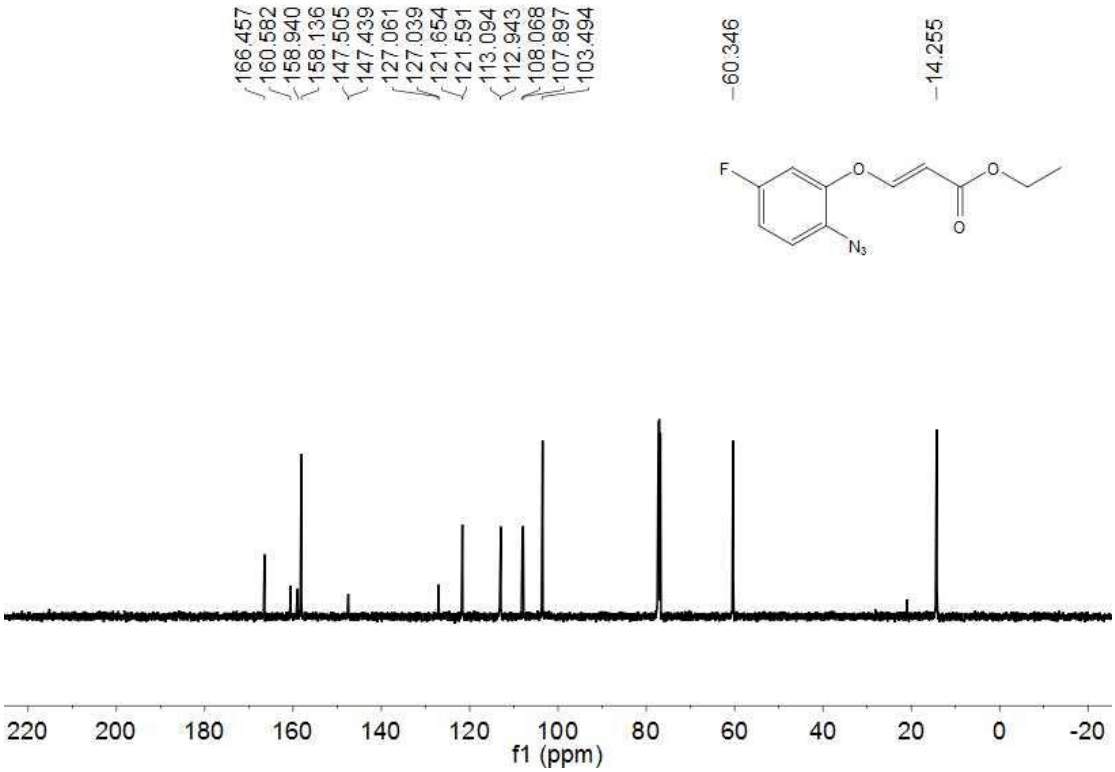


Figure 14. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **2f**

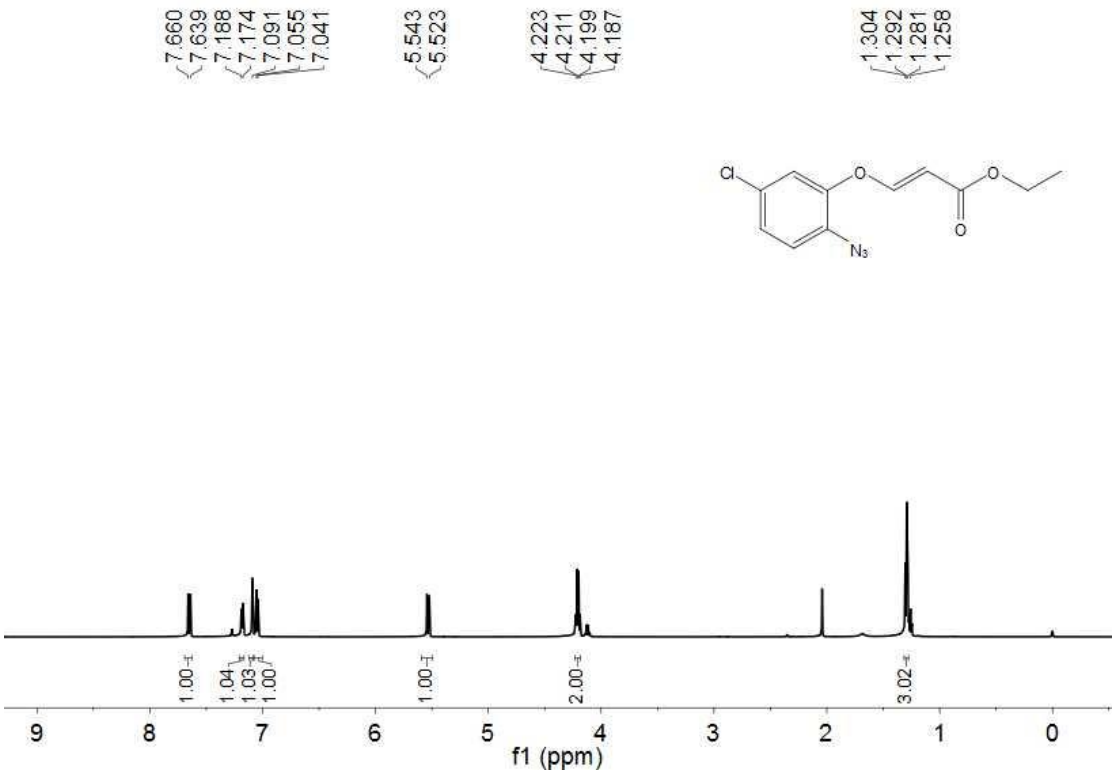


Figure 15. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **2g**

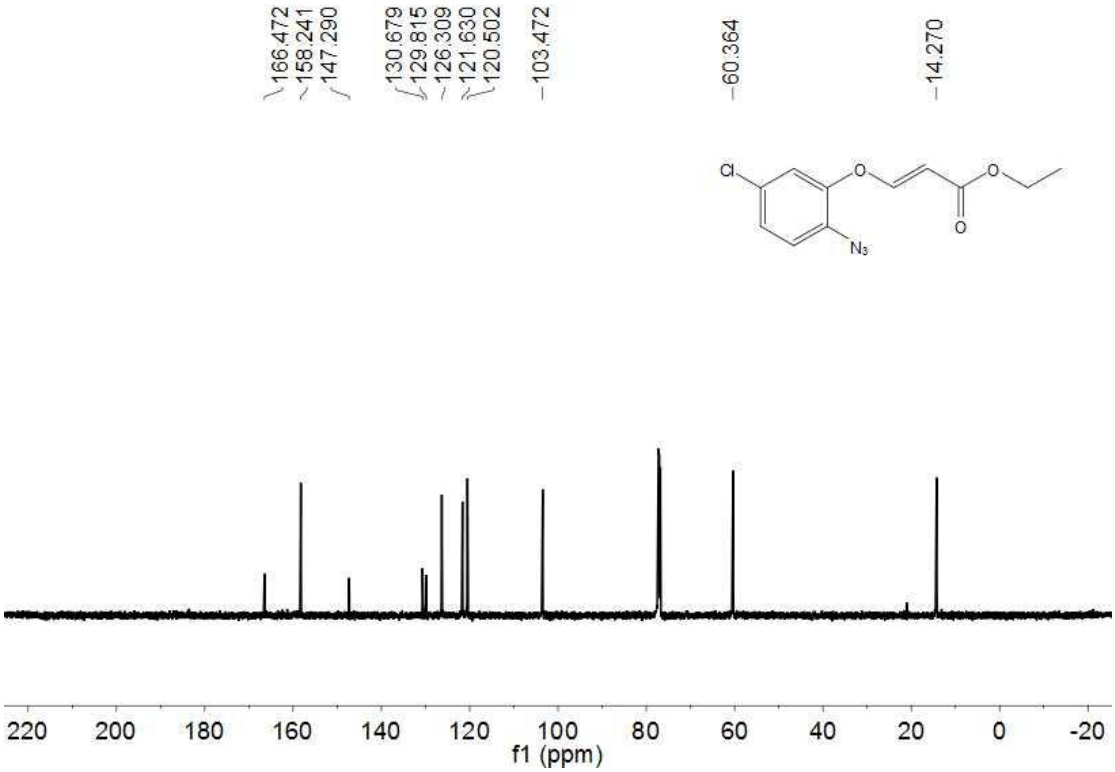


Figure 16. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **2g**

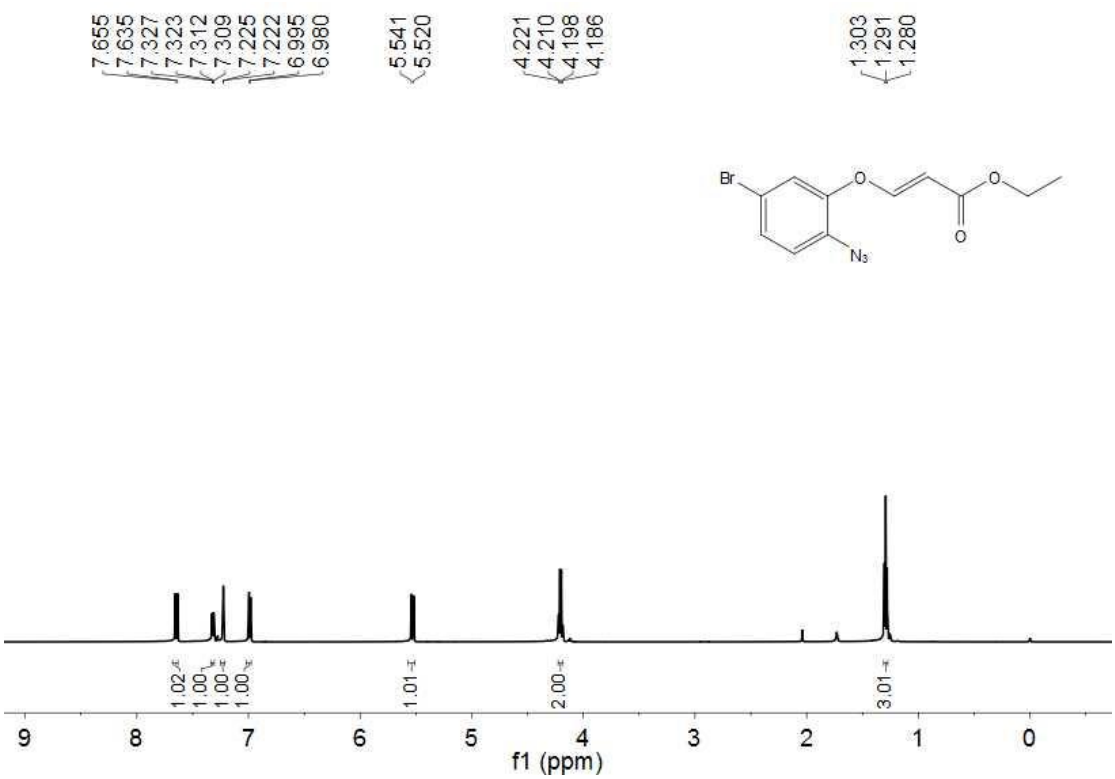


Figure 17. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **2h**

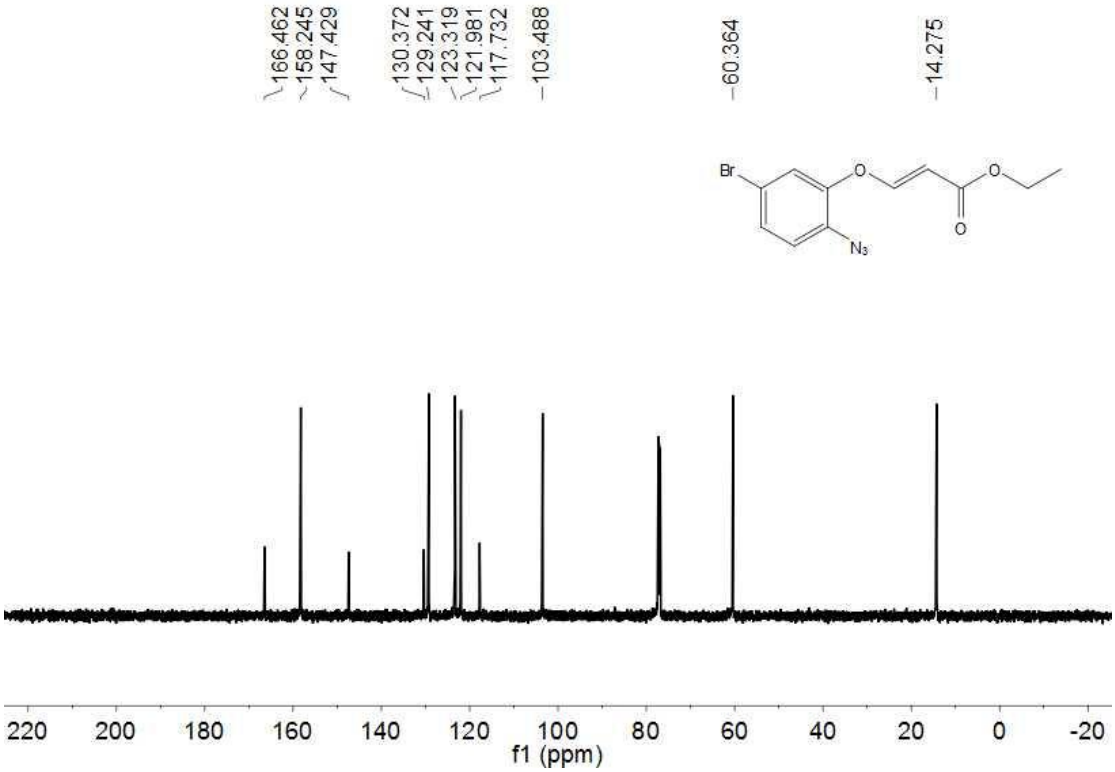


Figure 18. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **2h**

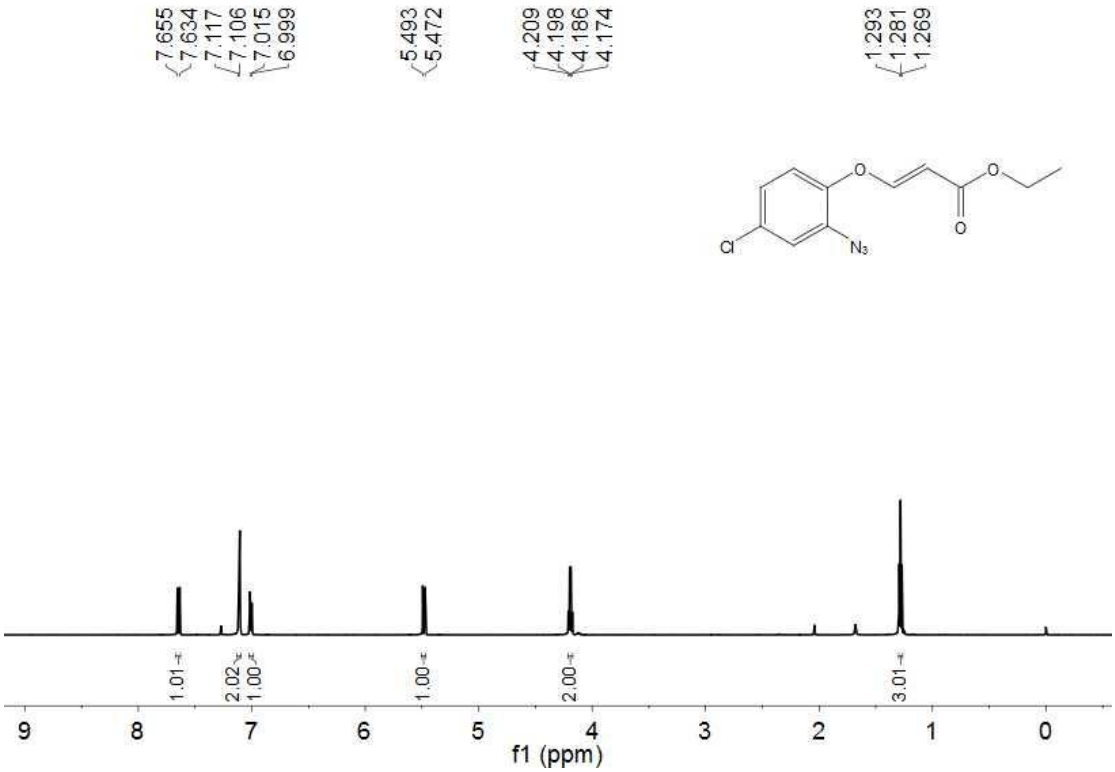


Figure 19. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **2i**

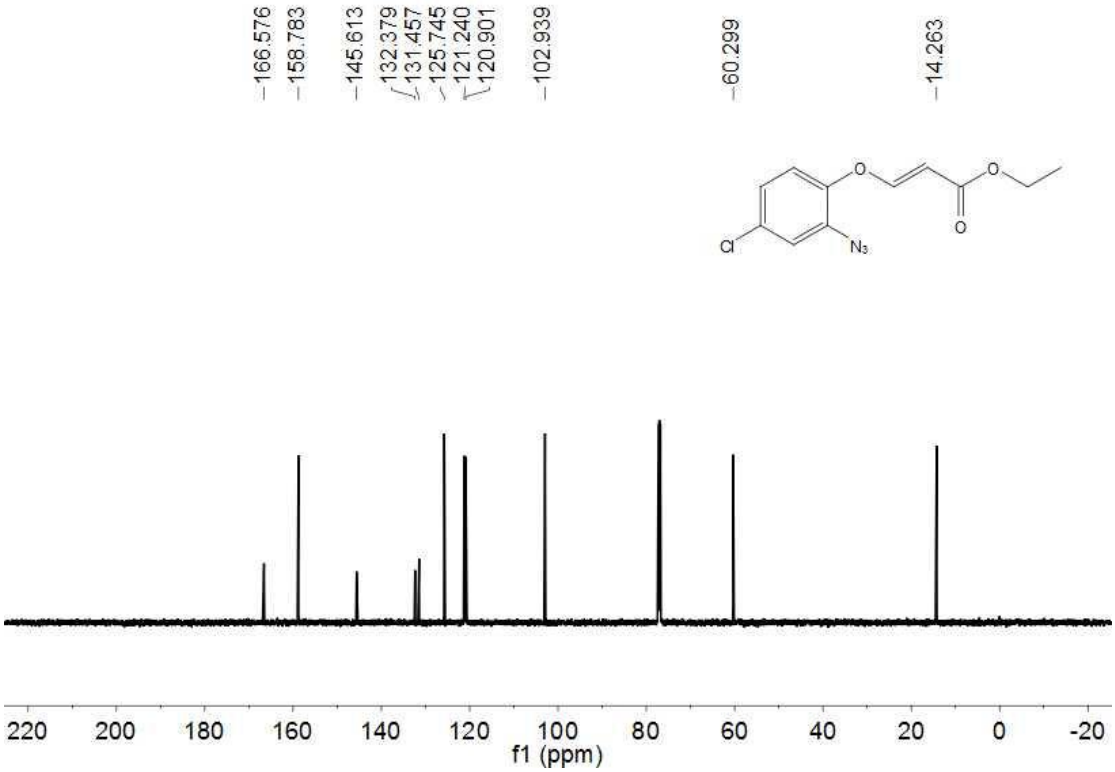


Figure 20. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **2i**

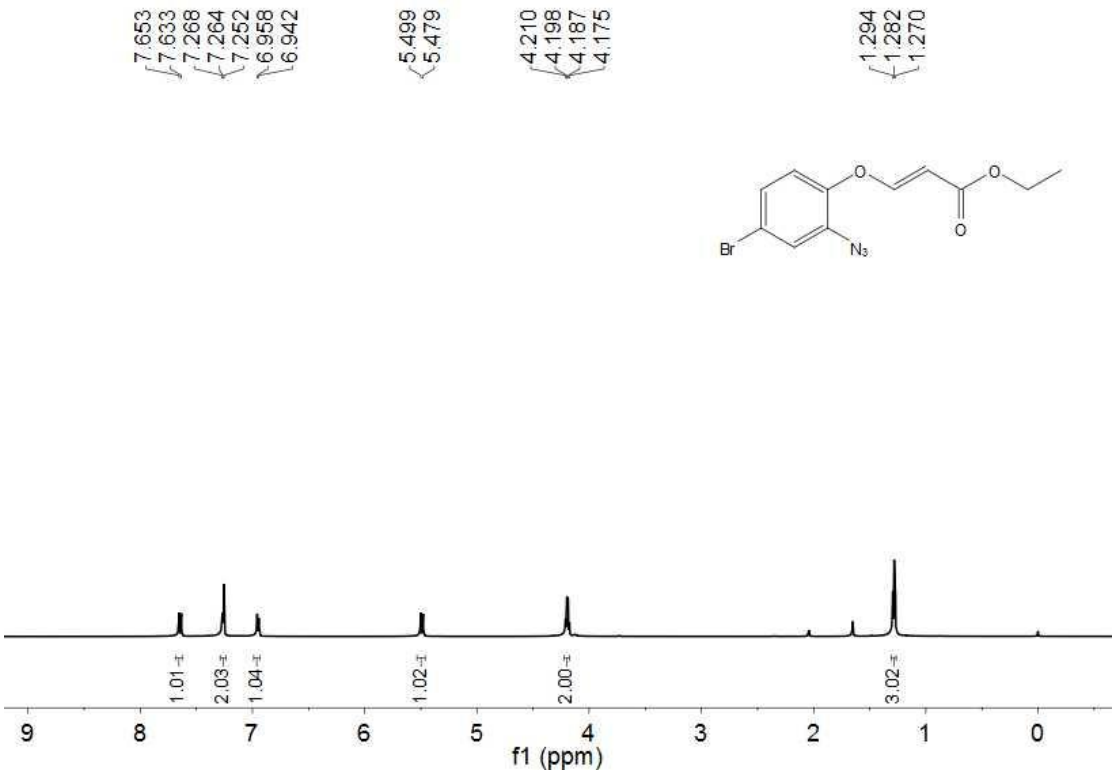


Figure 21. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **2j**

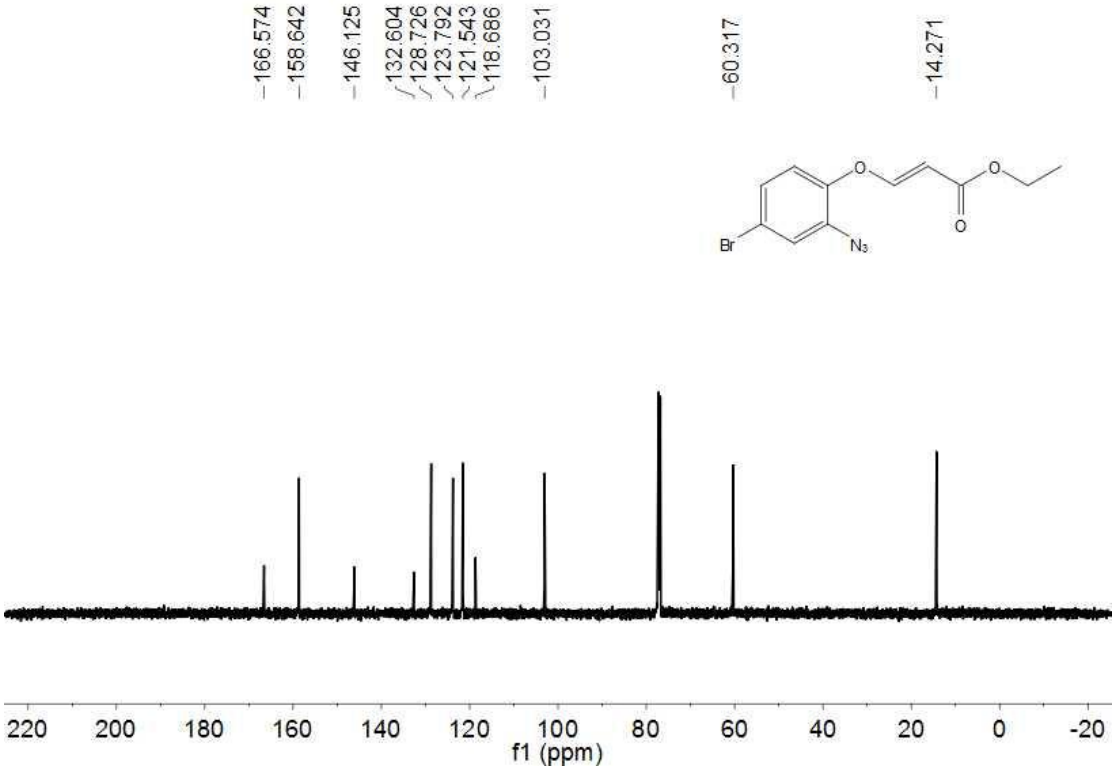


Figure 22. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **2j**

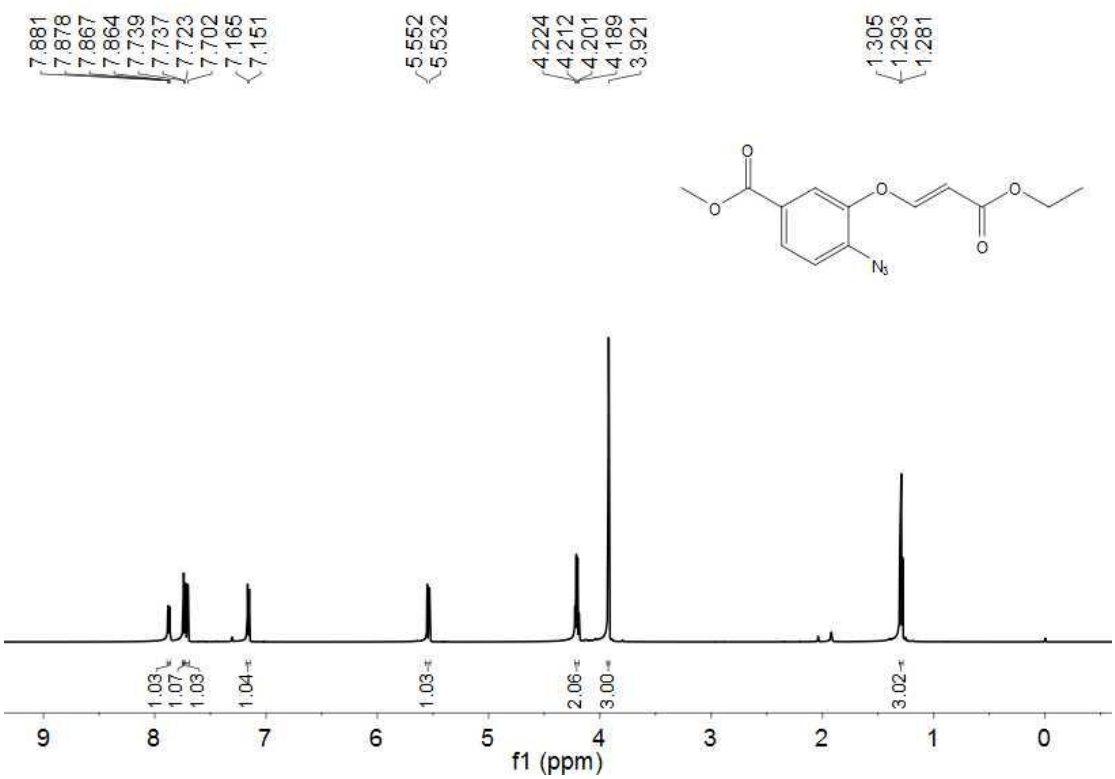


Figure 23. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **2k**

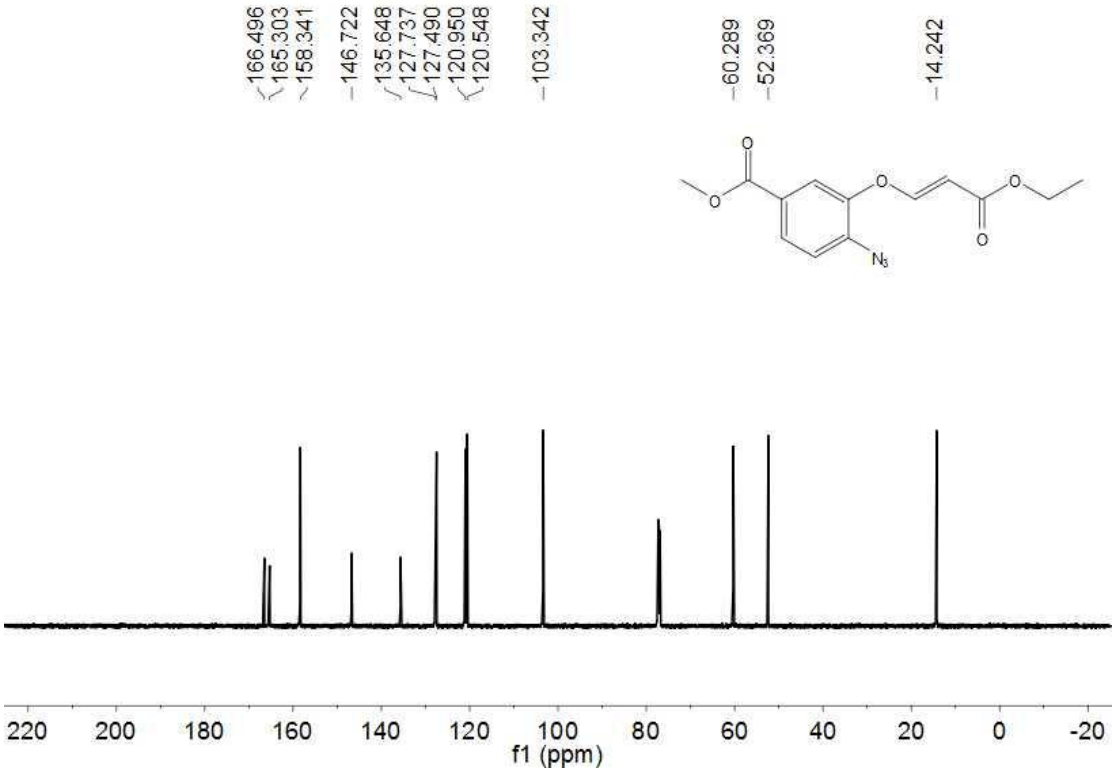


Figure 24. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **2k**

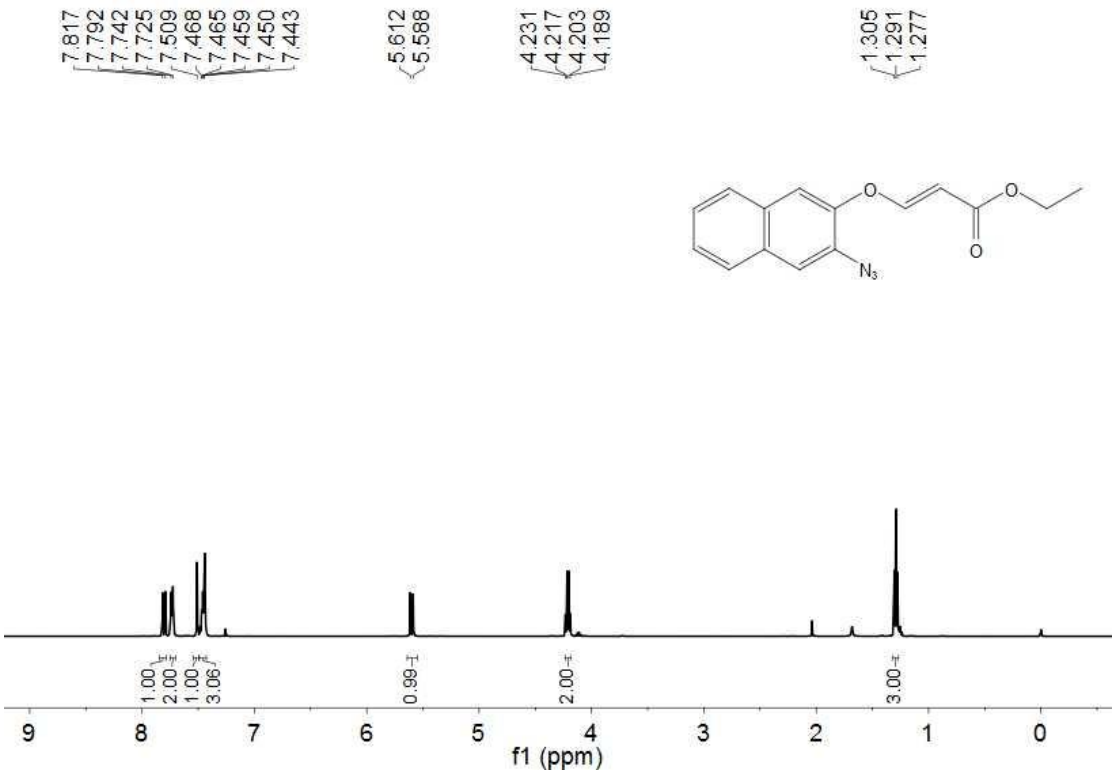


Figure 25. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **2l**

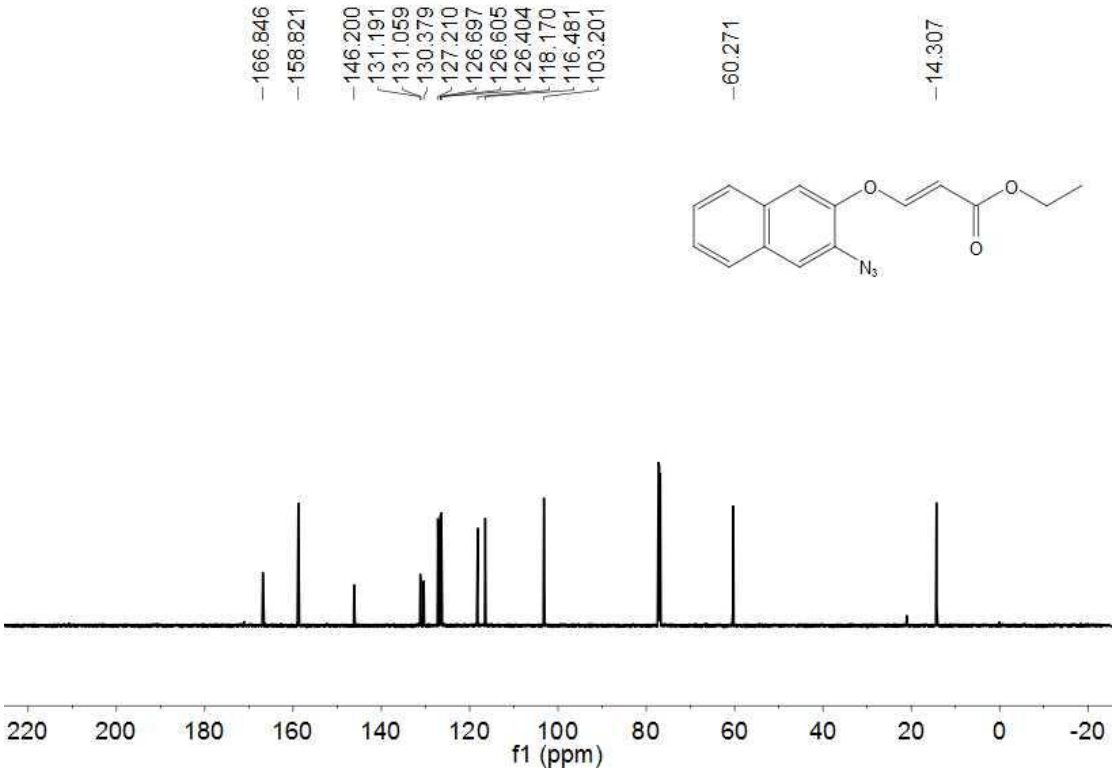


Figure 26. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **2l**

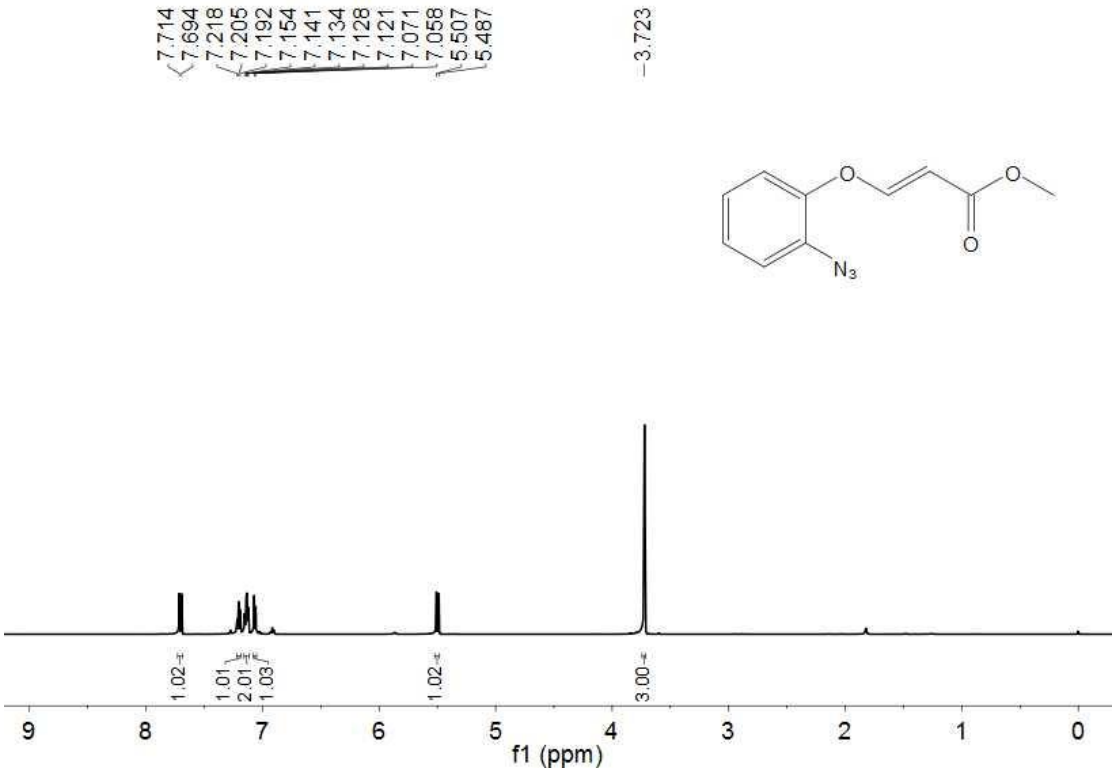


Figure 27. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **2m**

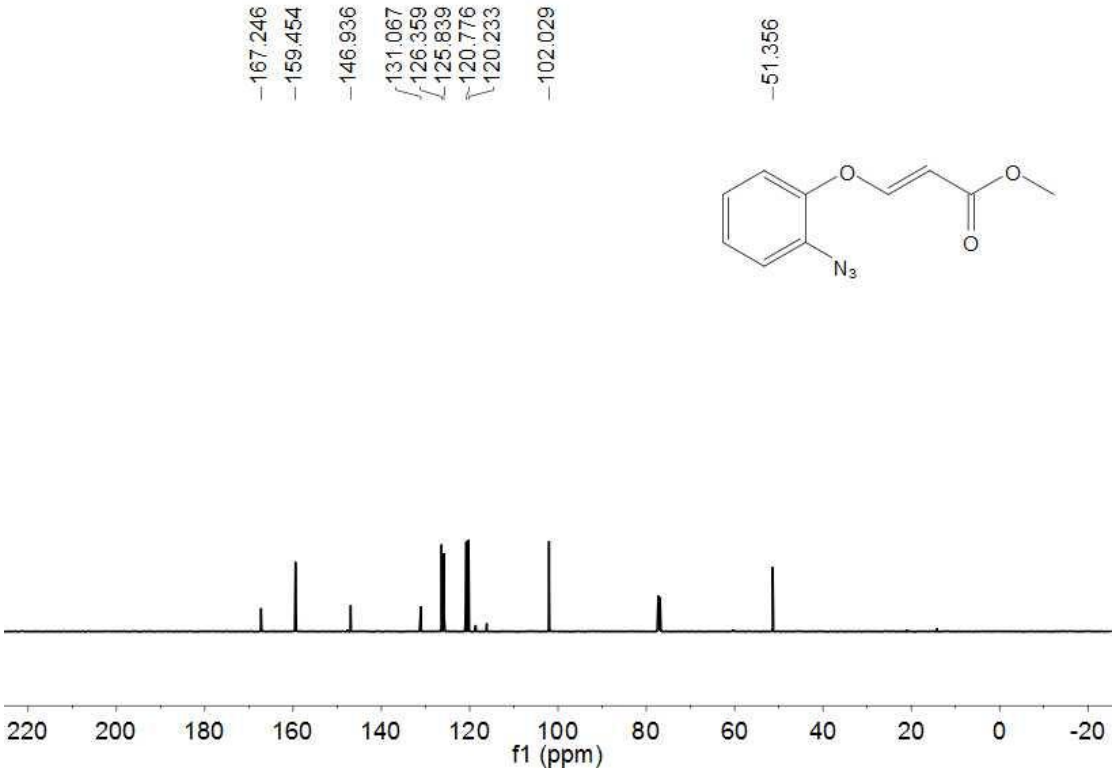


Figure 28. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **2m**

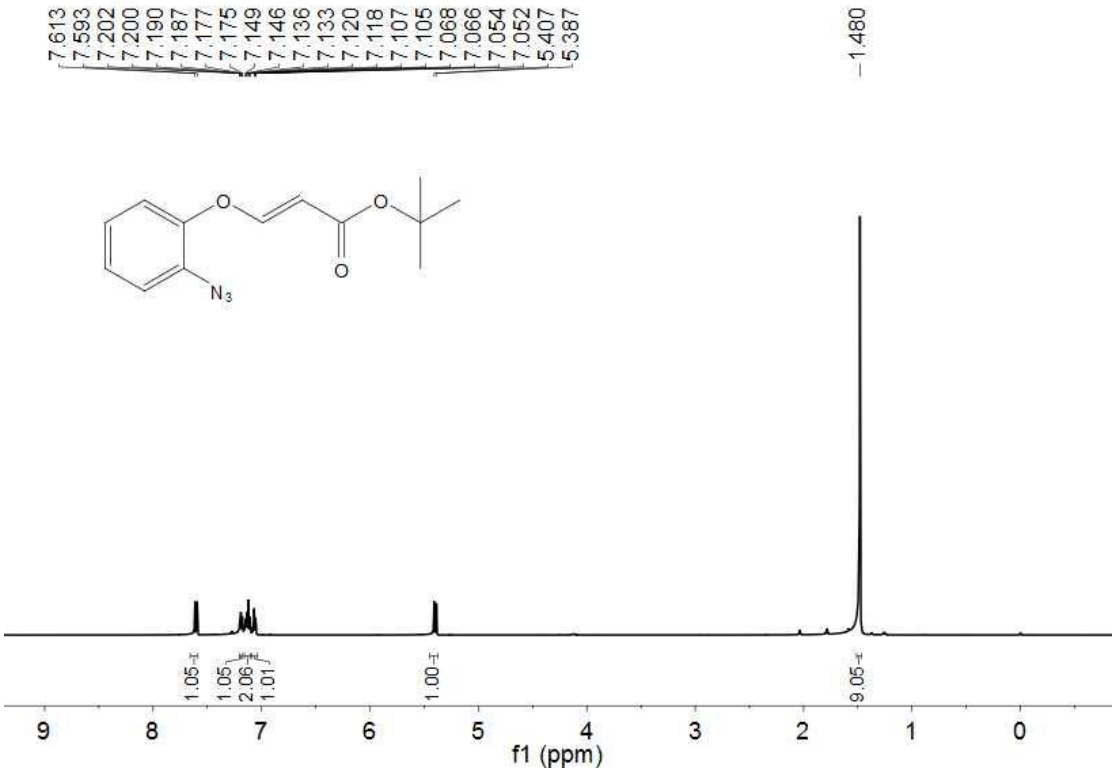


Figure 29. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **2n**

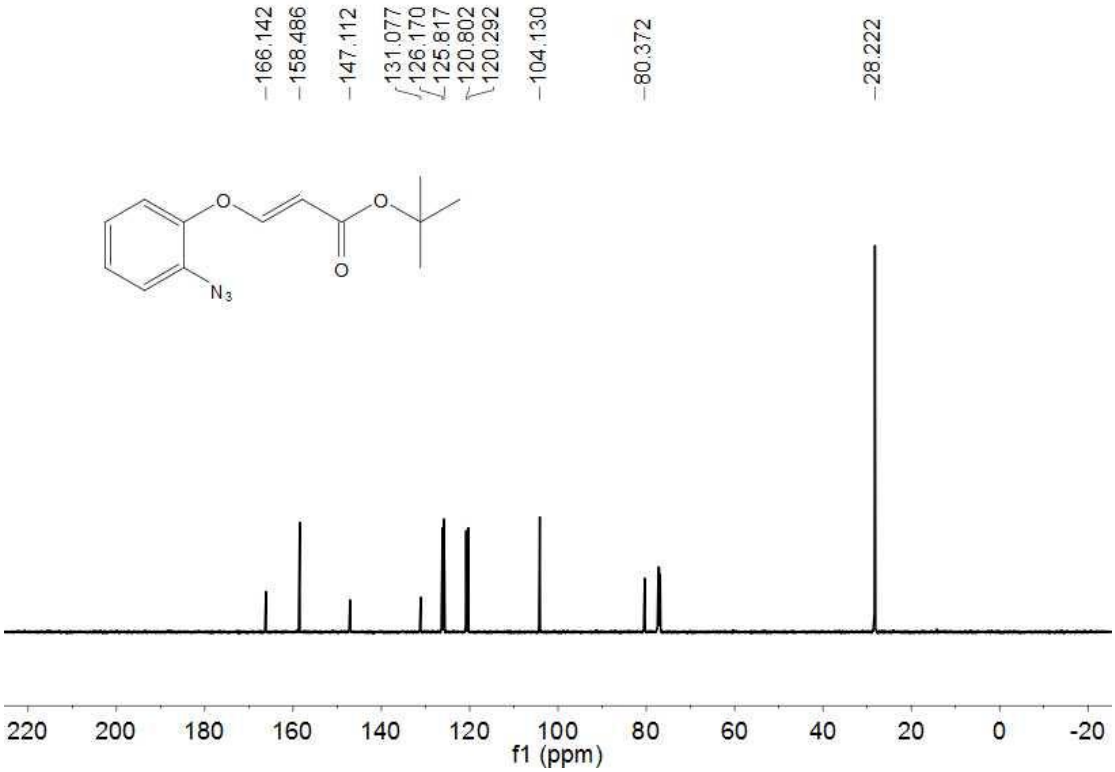


Figure 30. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **2n**

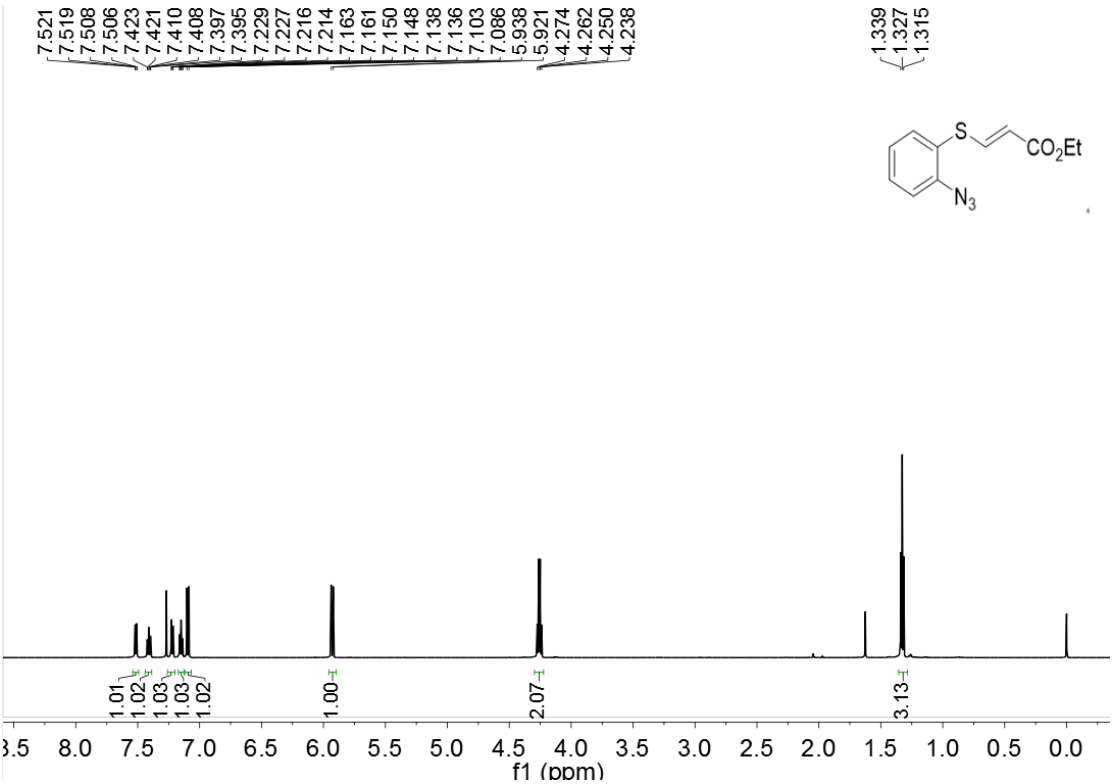


Figure 31. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **2o**

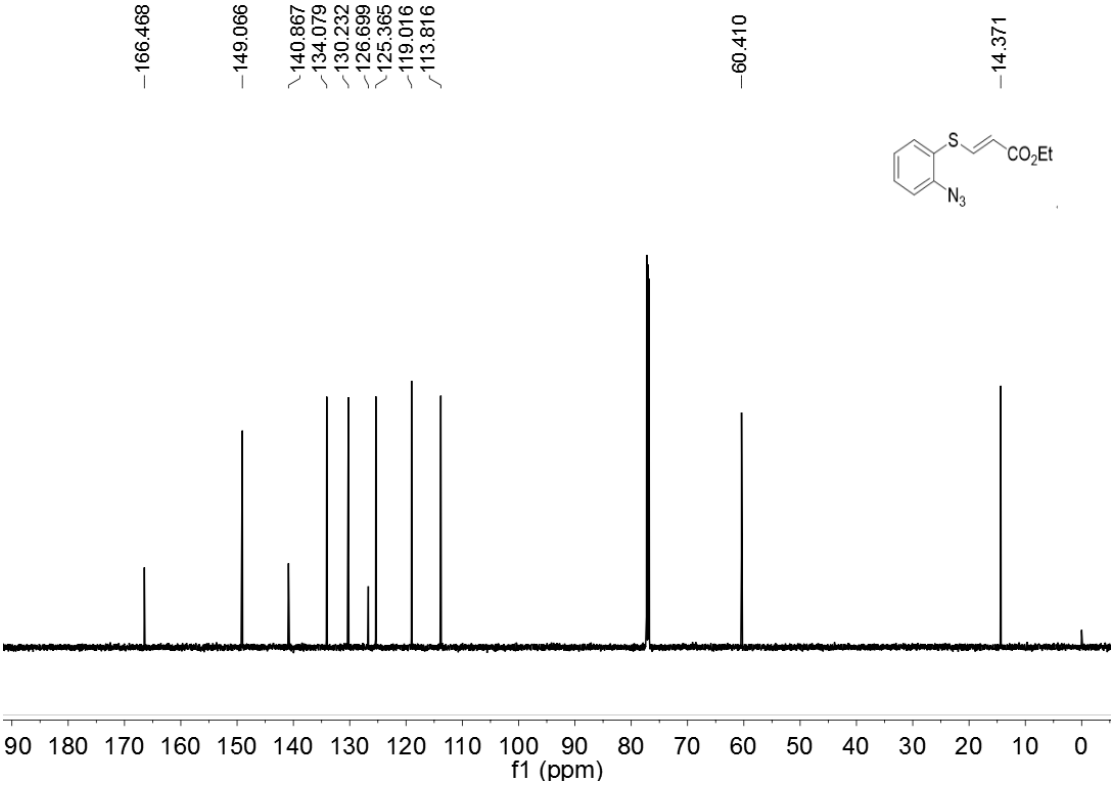


Figure 32. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **2n**

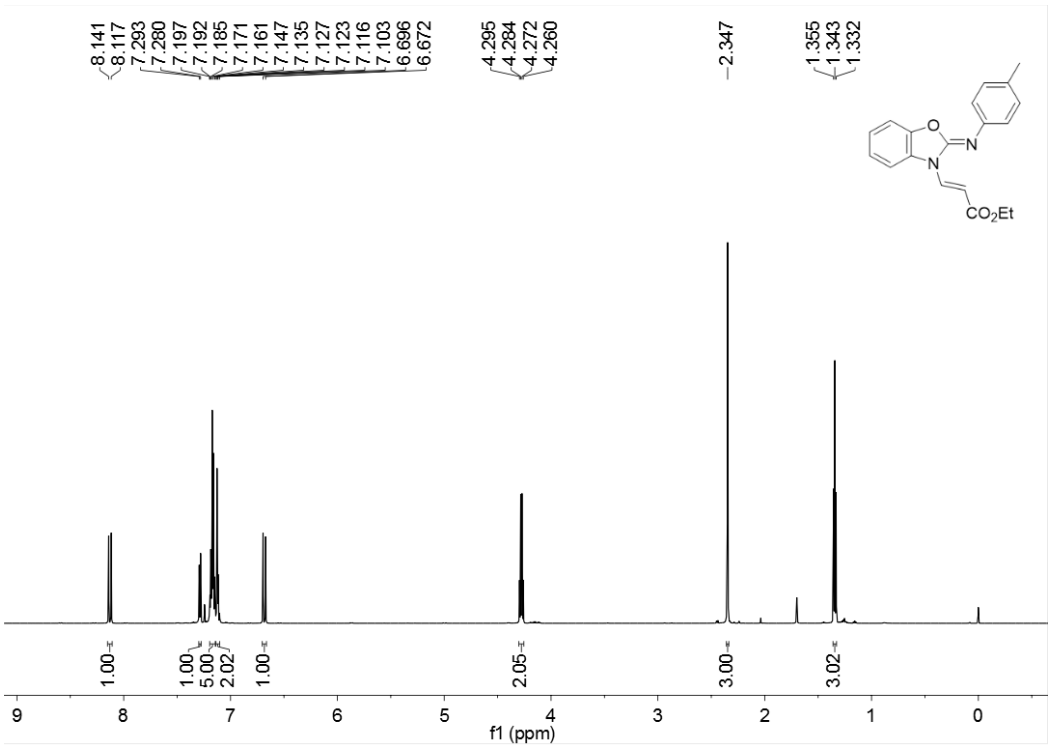


Figure 33. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3aa**

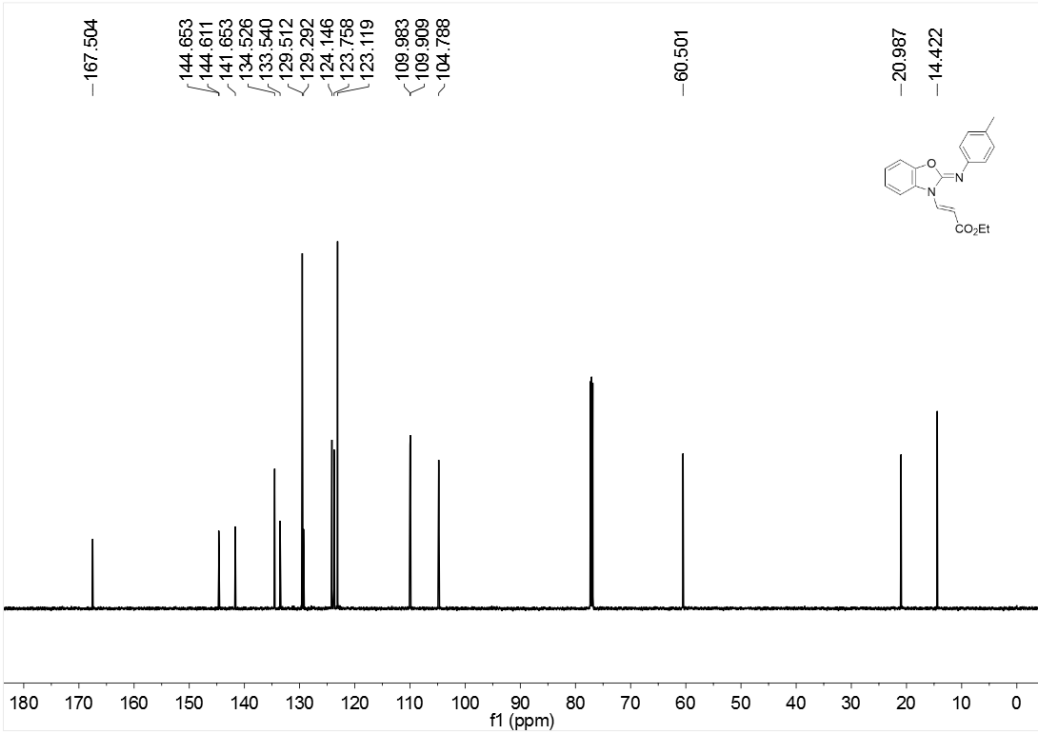


Figure 34. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3aa**

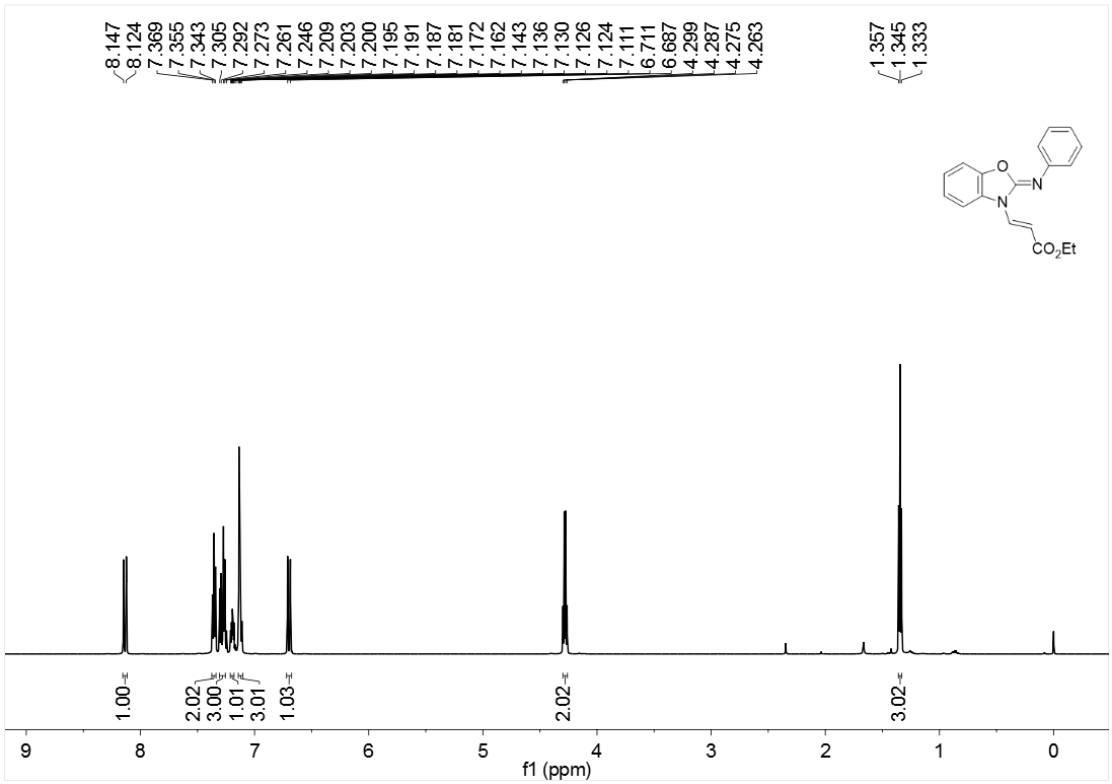


Figure 35. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3ba**

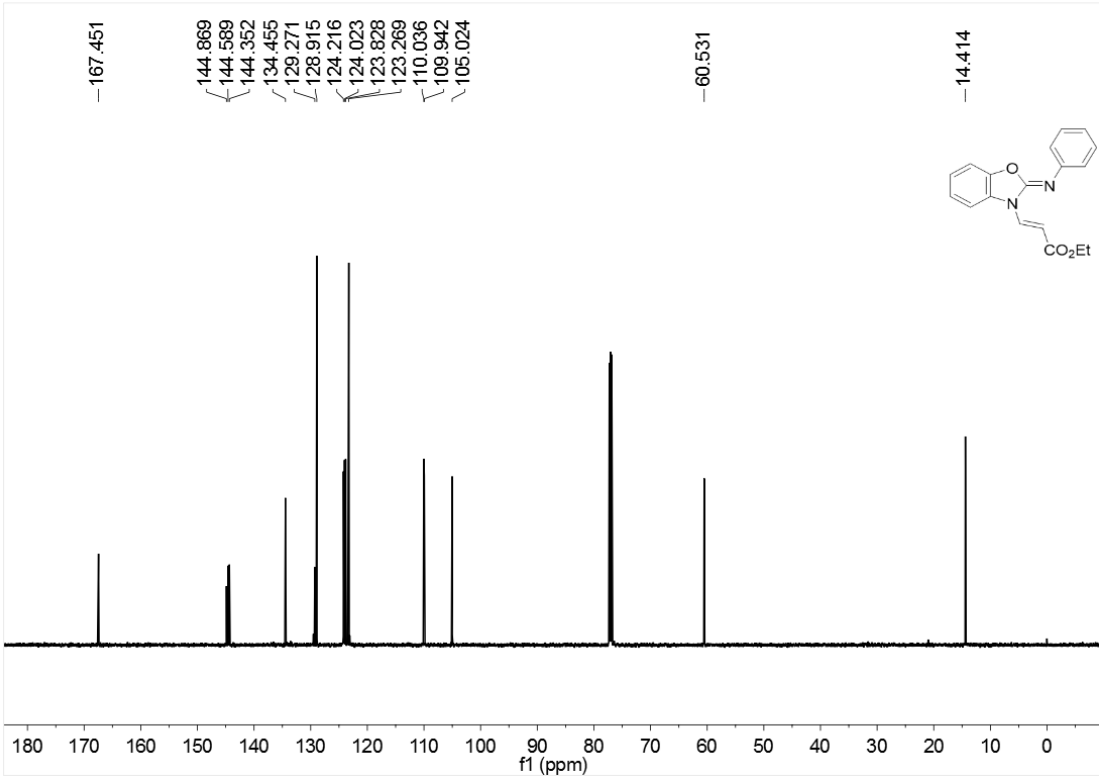


Figure 36. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ba**

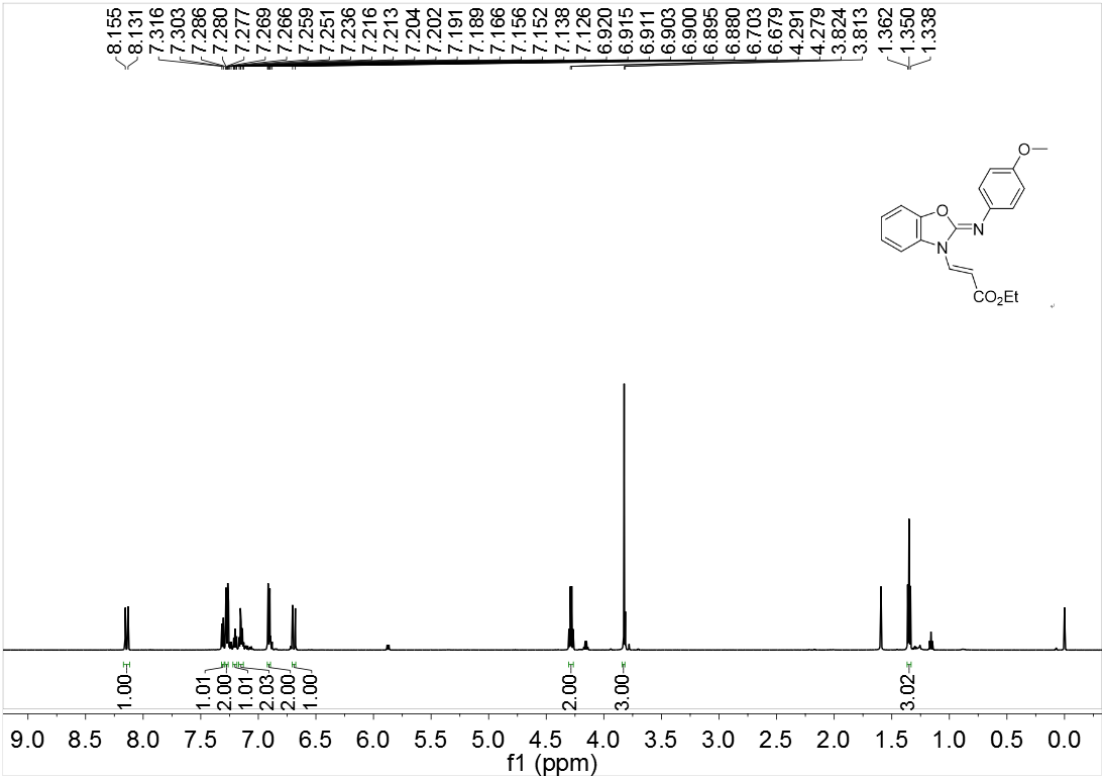


Figure 37. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3ca**

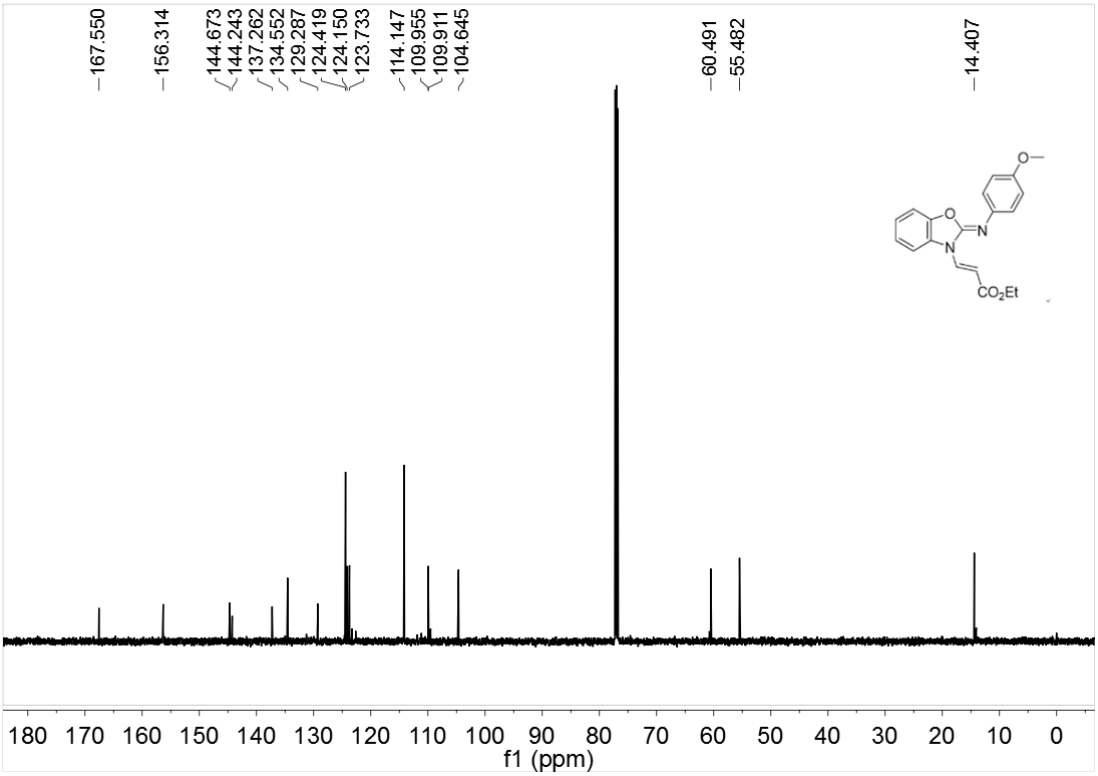


Figure 38. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ca**

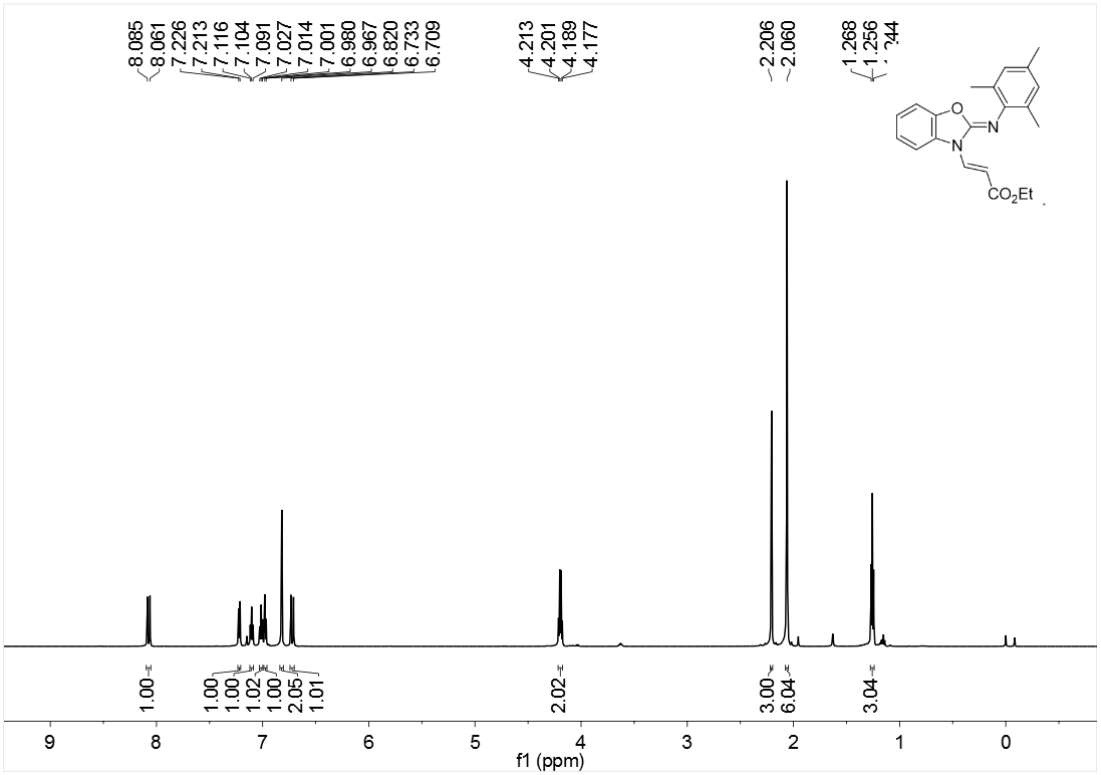


Figure 39. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3da**

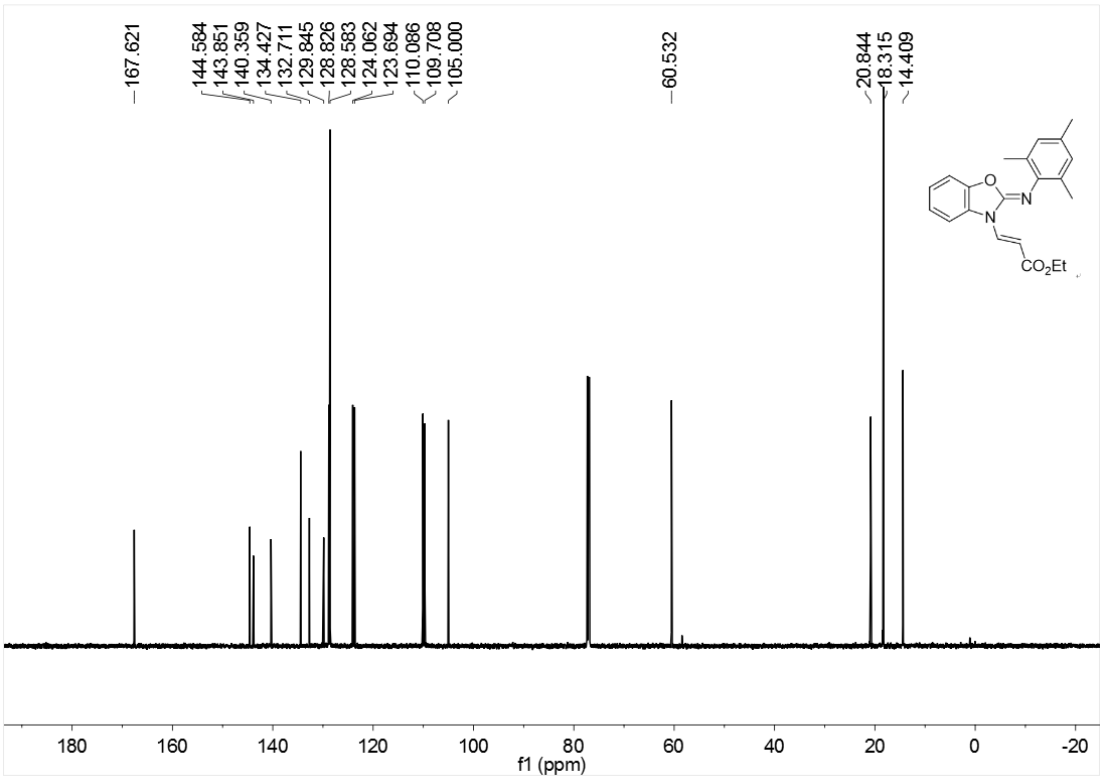


Figure 40. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3da**

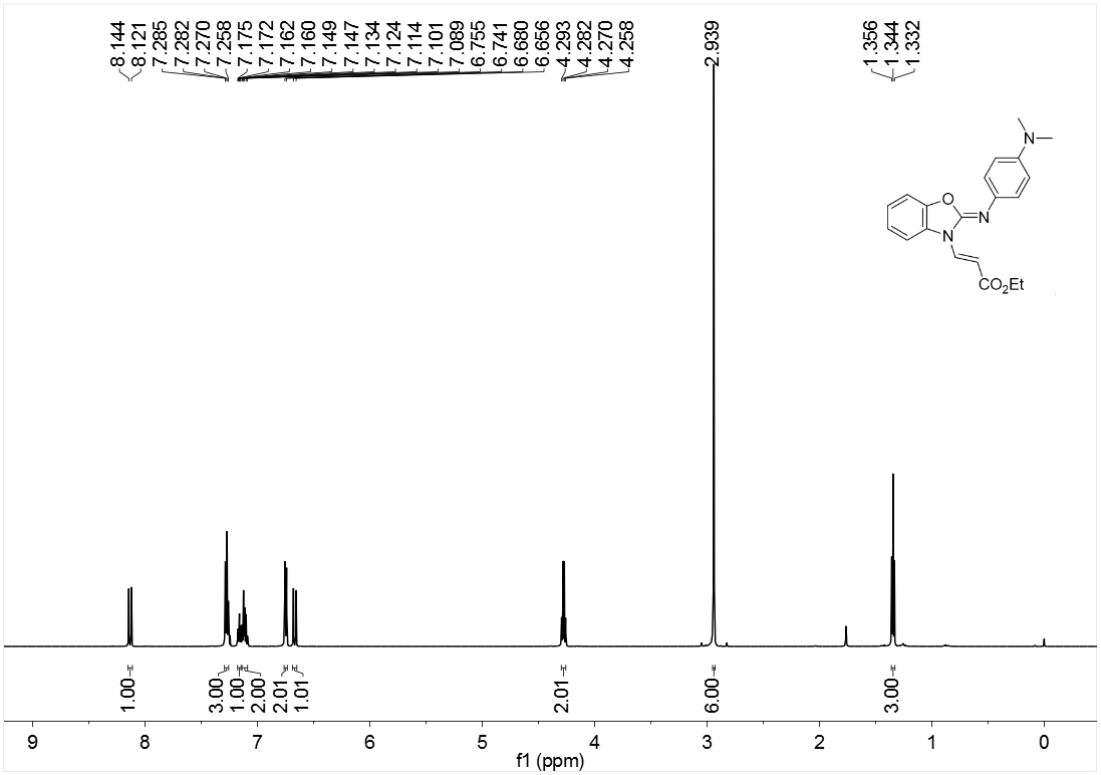


Figure 41. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3ea**

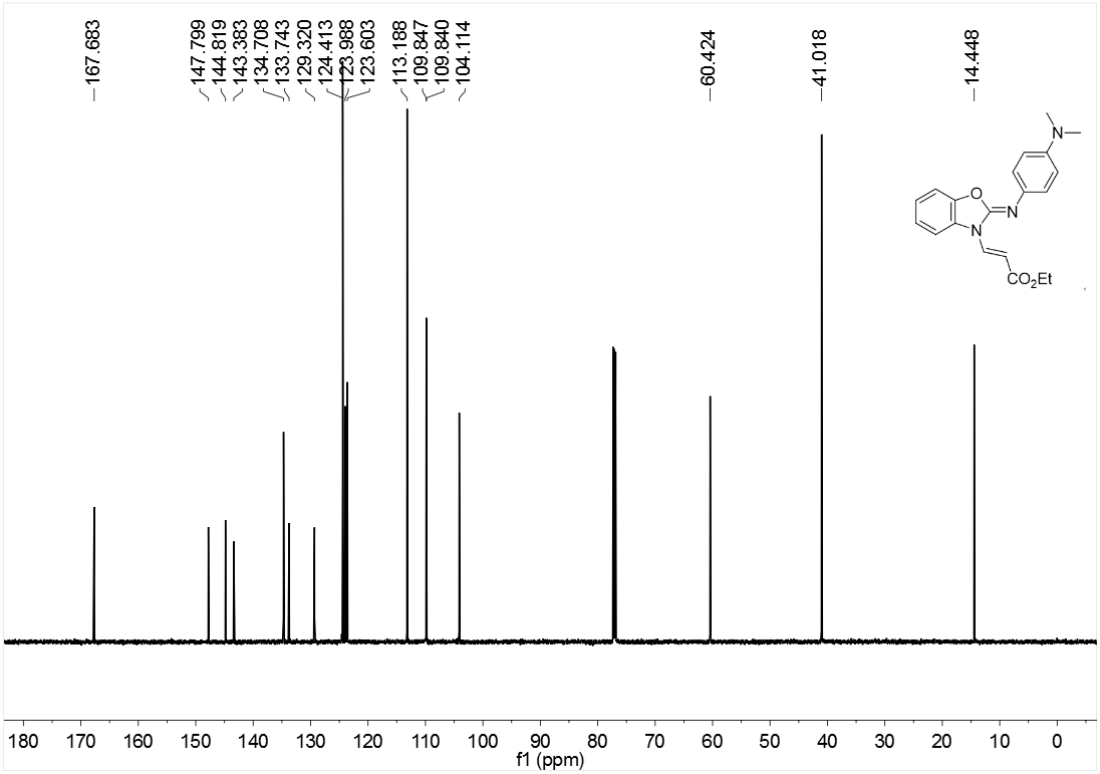


Figure 42. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ea**

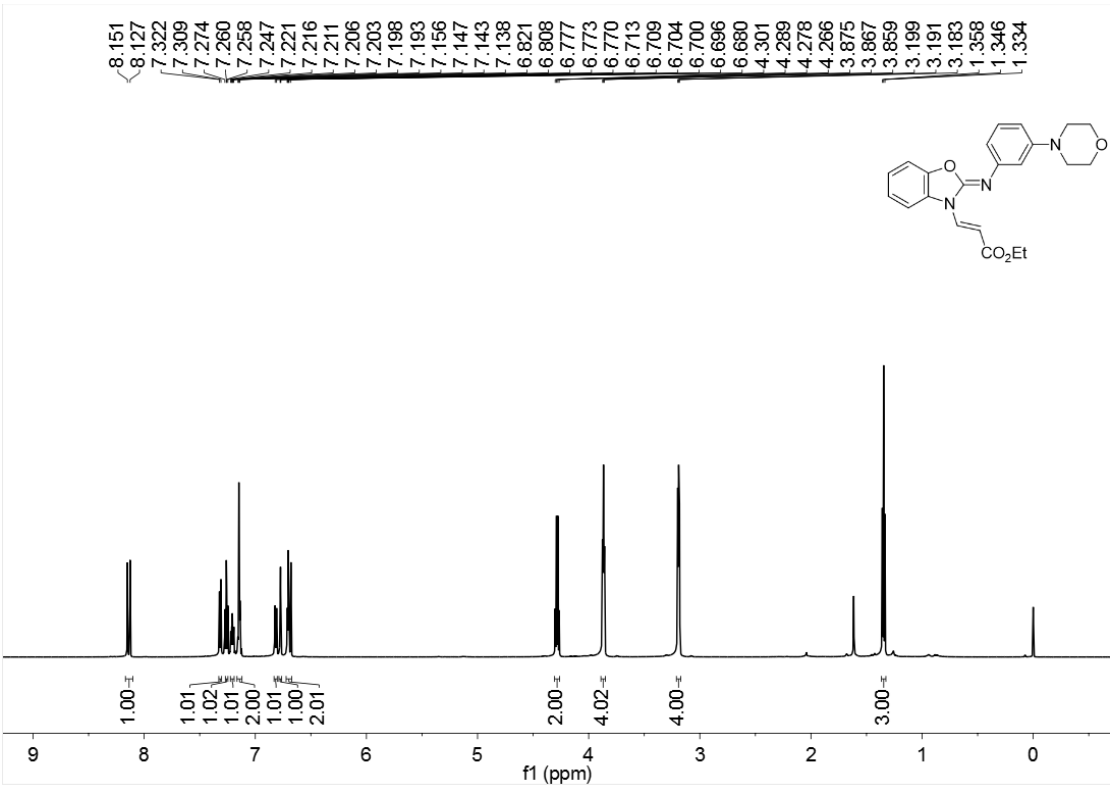


Figure 43. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3fa**

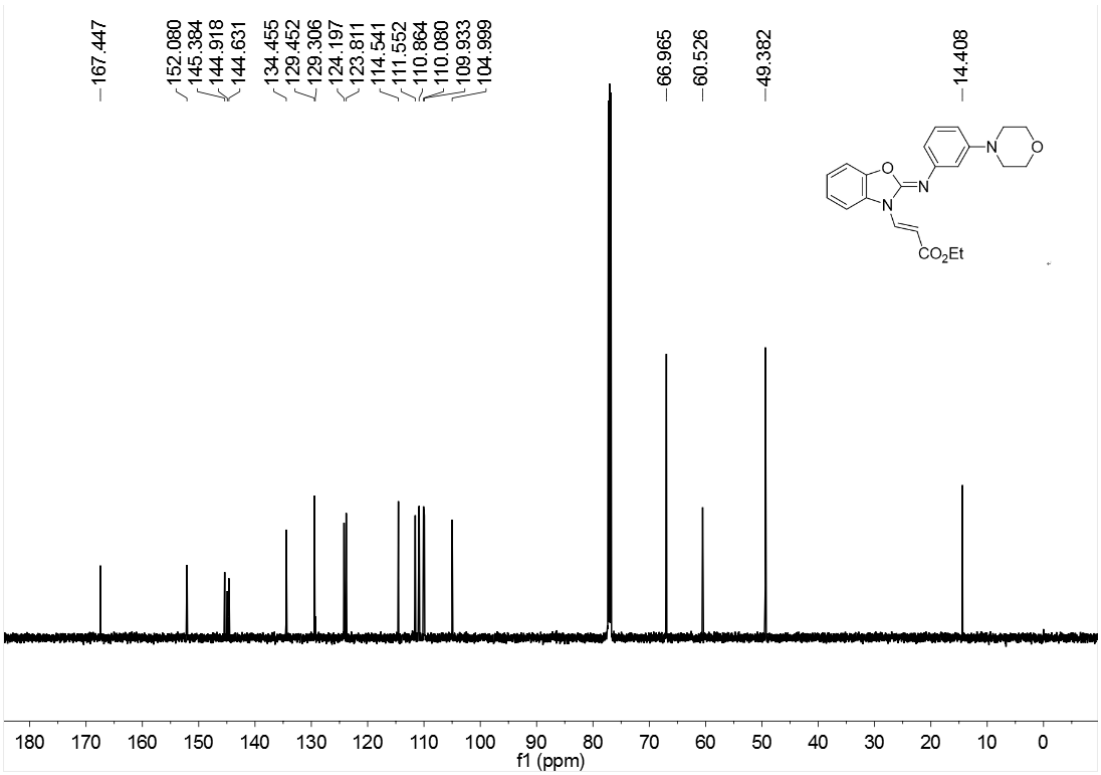


Figure 44. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3fa**

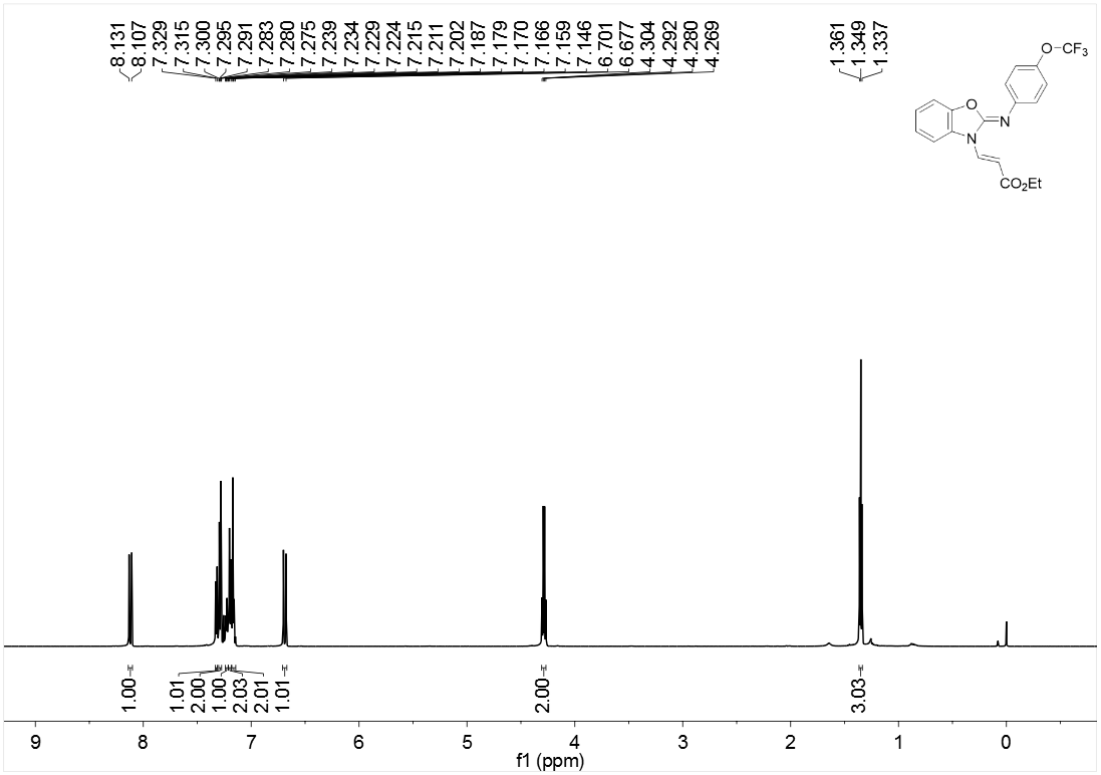


Figure 45. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3ga**

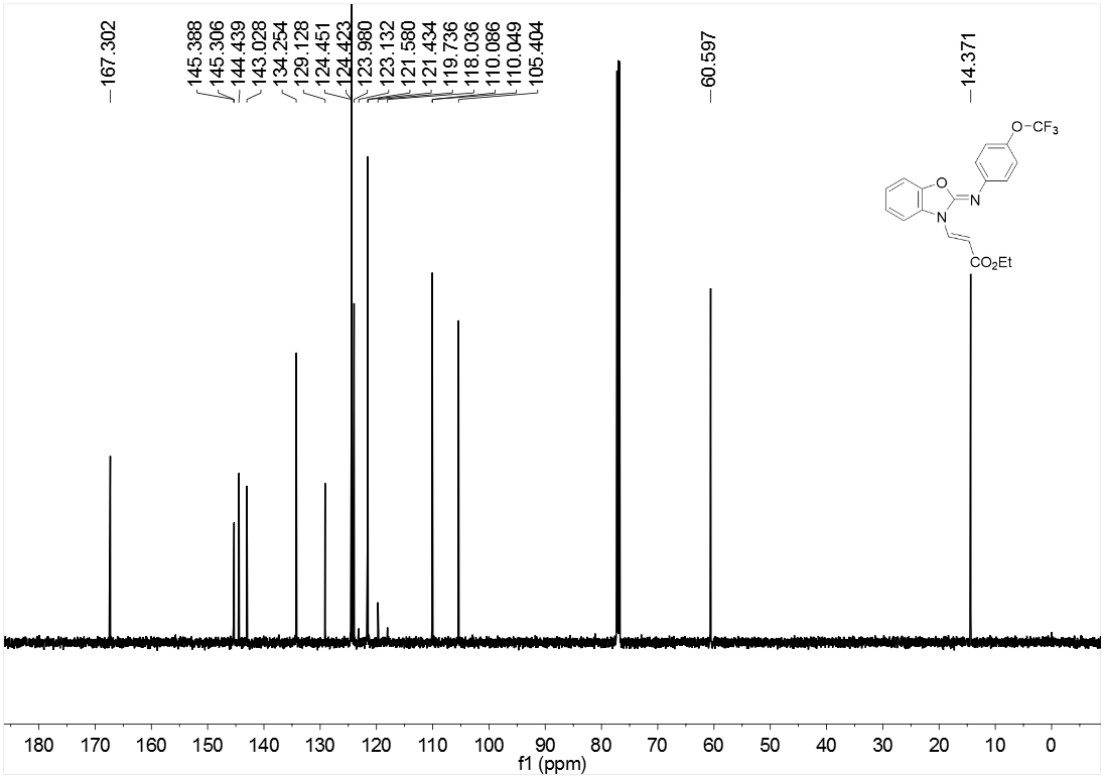


Figure 46. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ga**

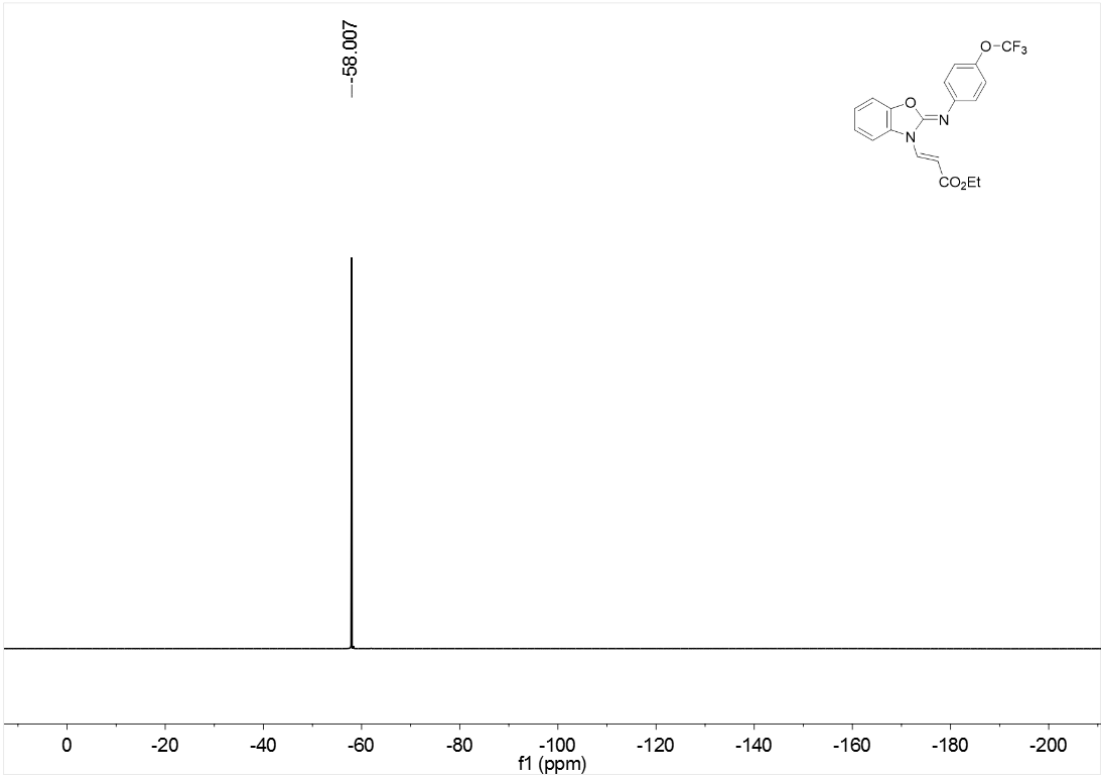


Figure 47. ^{19}F NMR spectrum (471 MHz, $CDCl_3$) of **3ga**

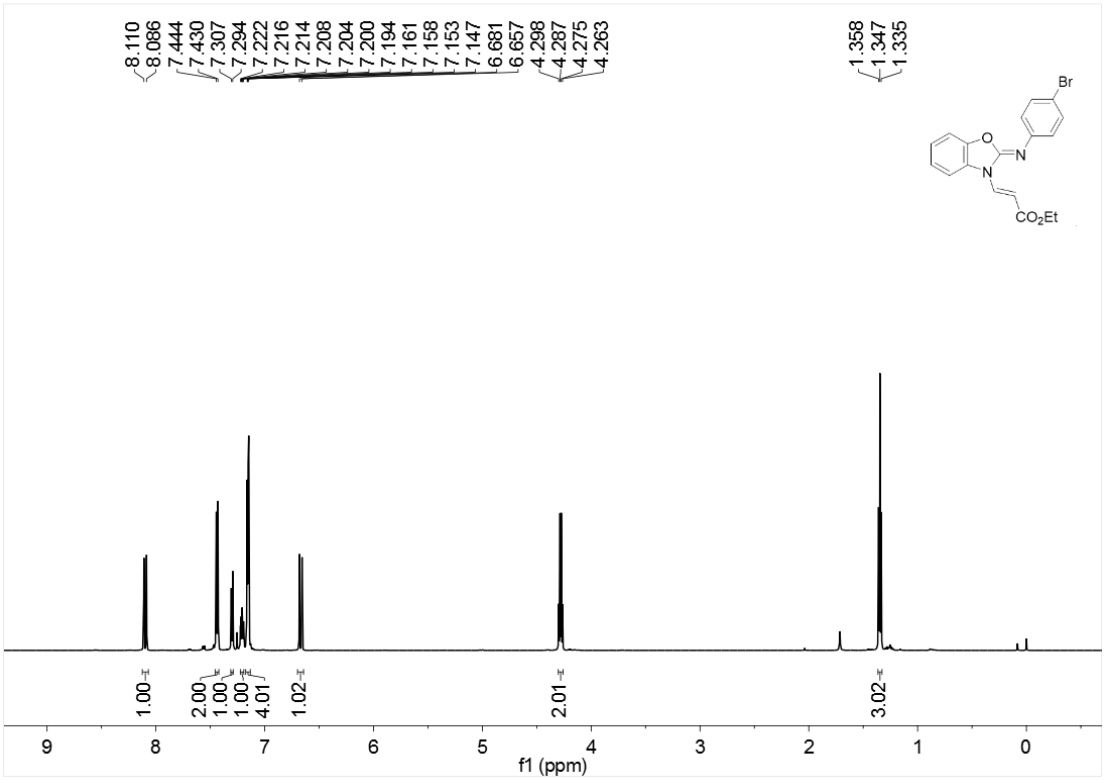


Figure 48. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3ha**

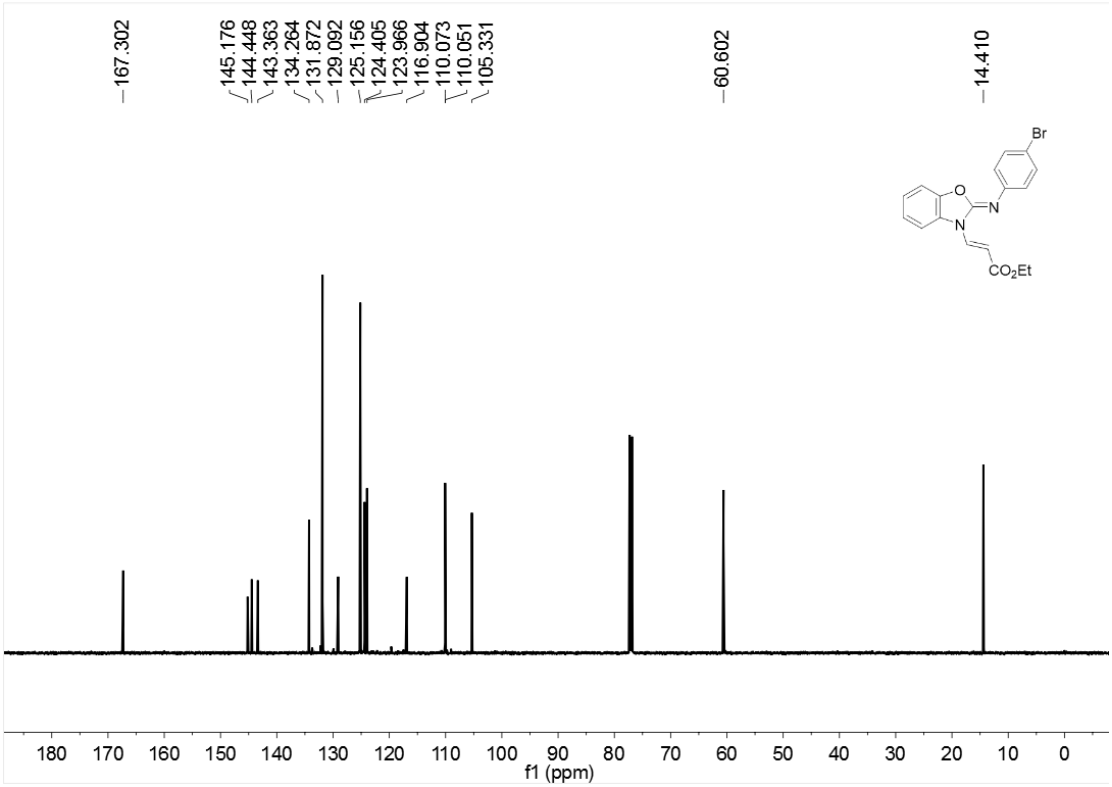


Figure 49. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ha**

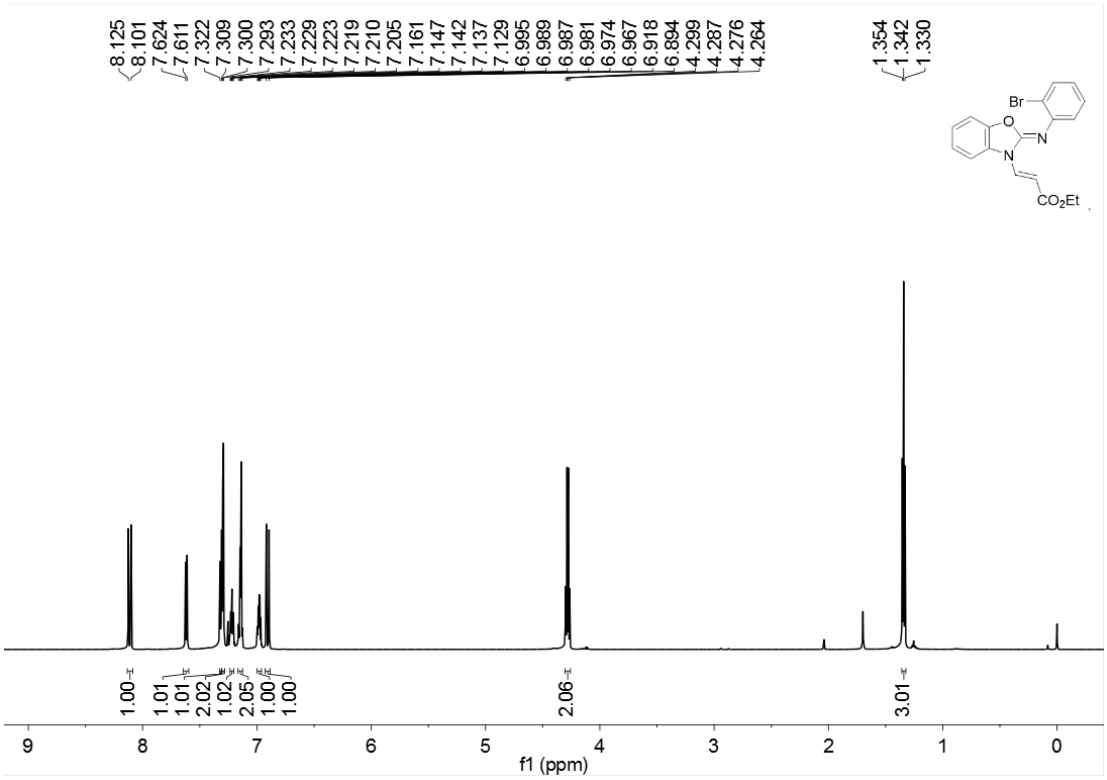


Figure 50. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3ia**

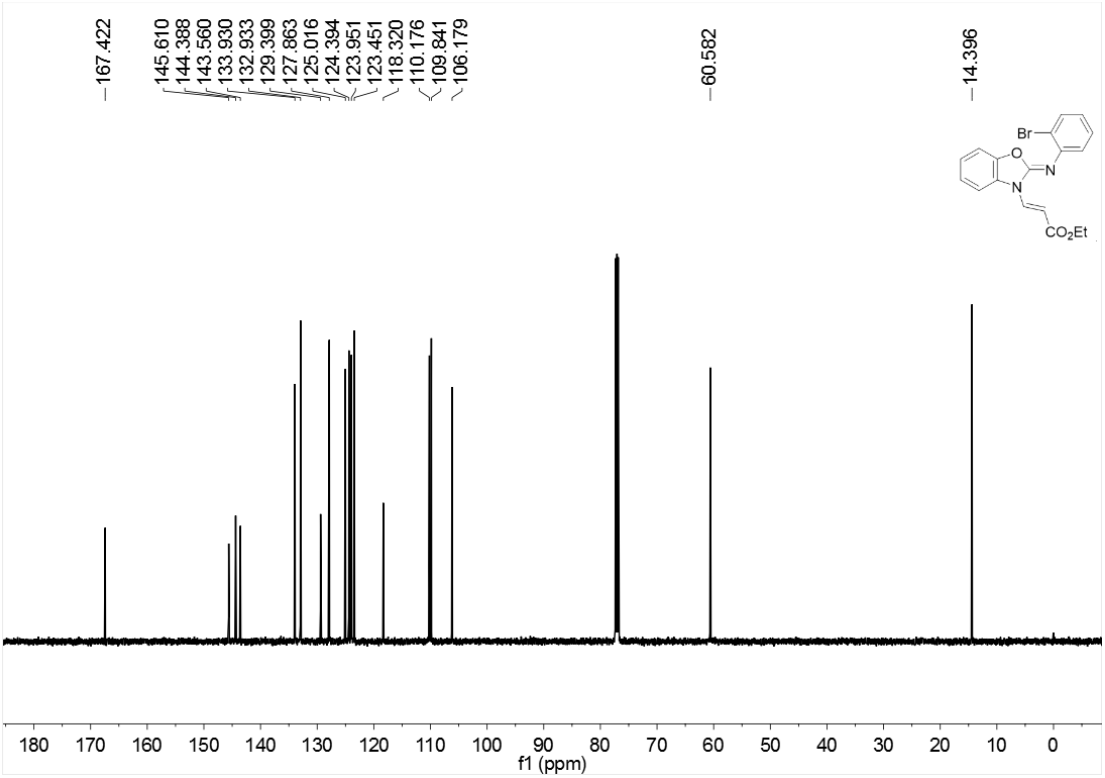


Figure 51. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ia**

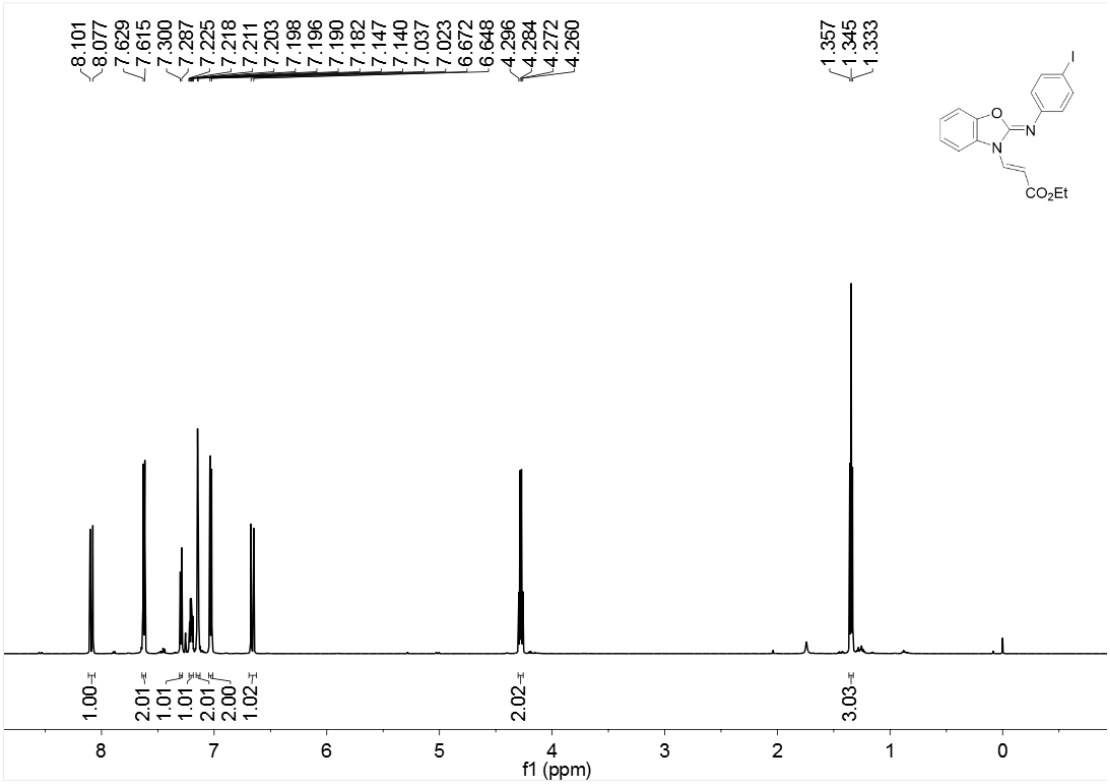


Figure 52. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3ja**

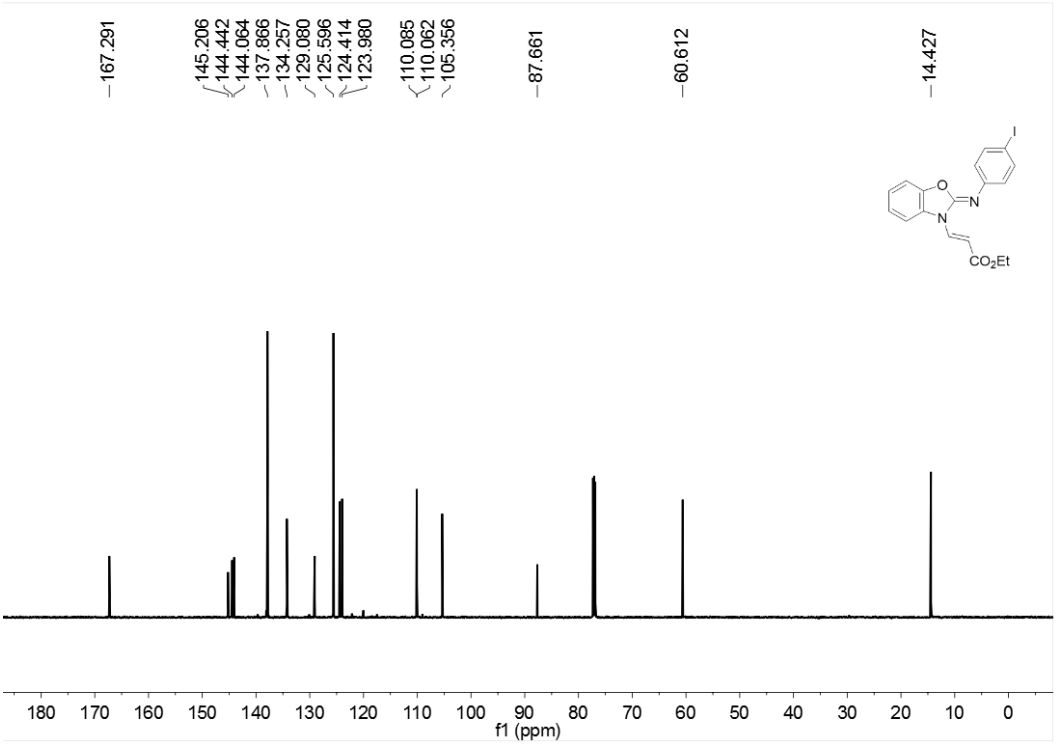


Figure 53. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ja**

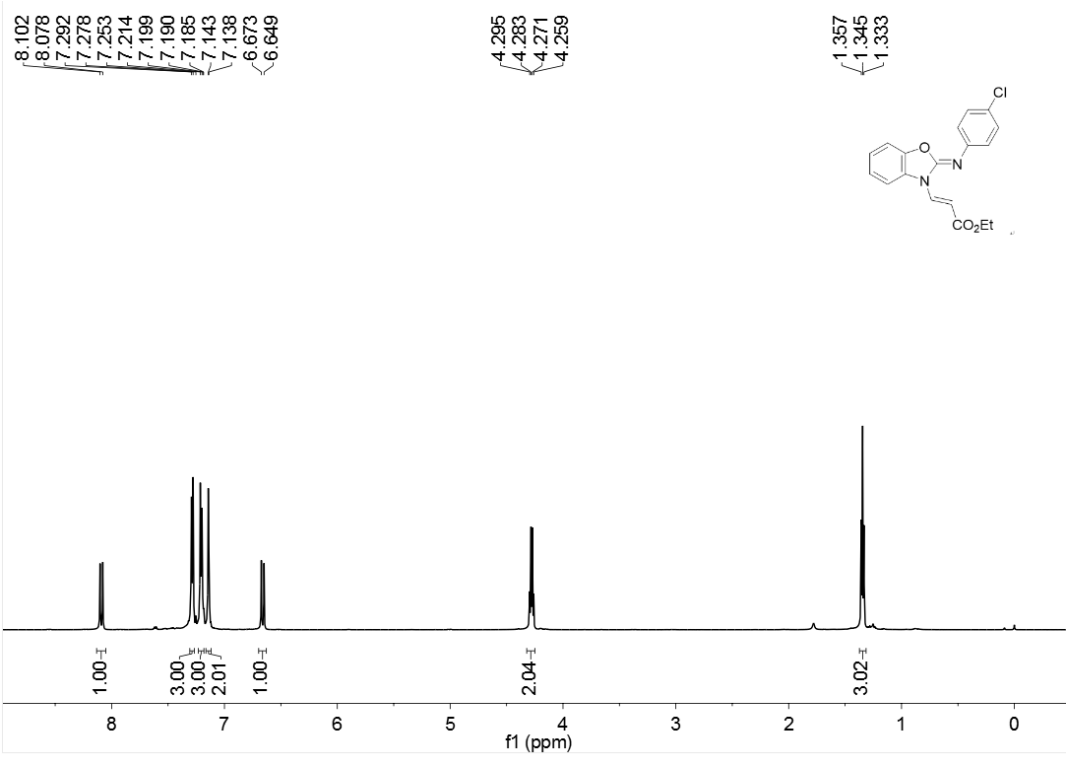


Figure 54. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3ka**

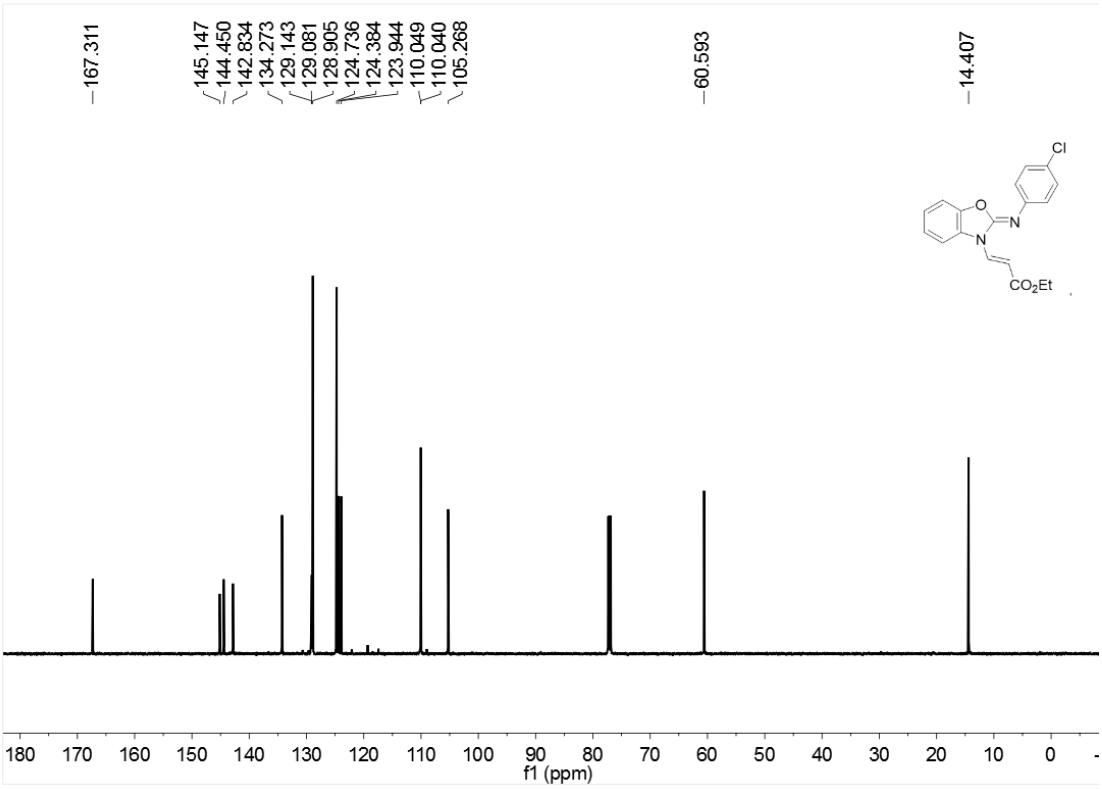


Figure 55. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ka**

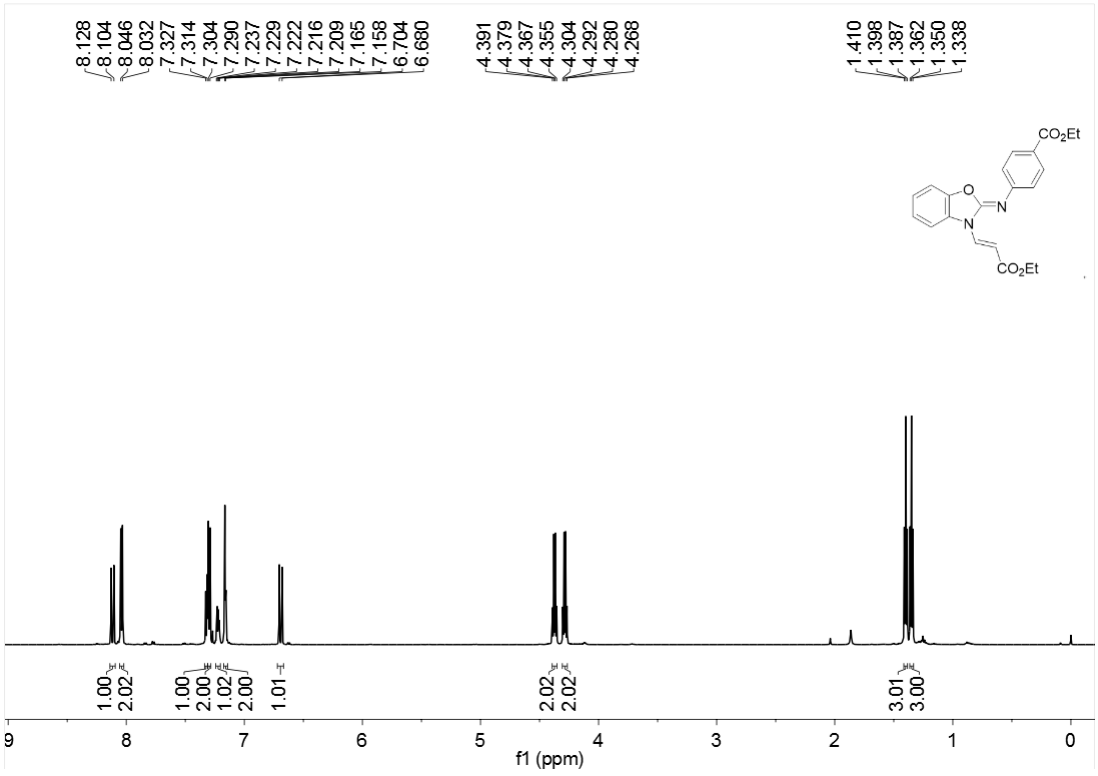


Figure 56. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3la**

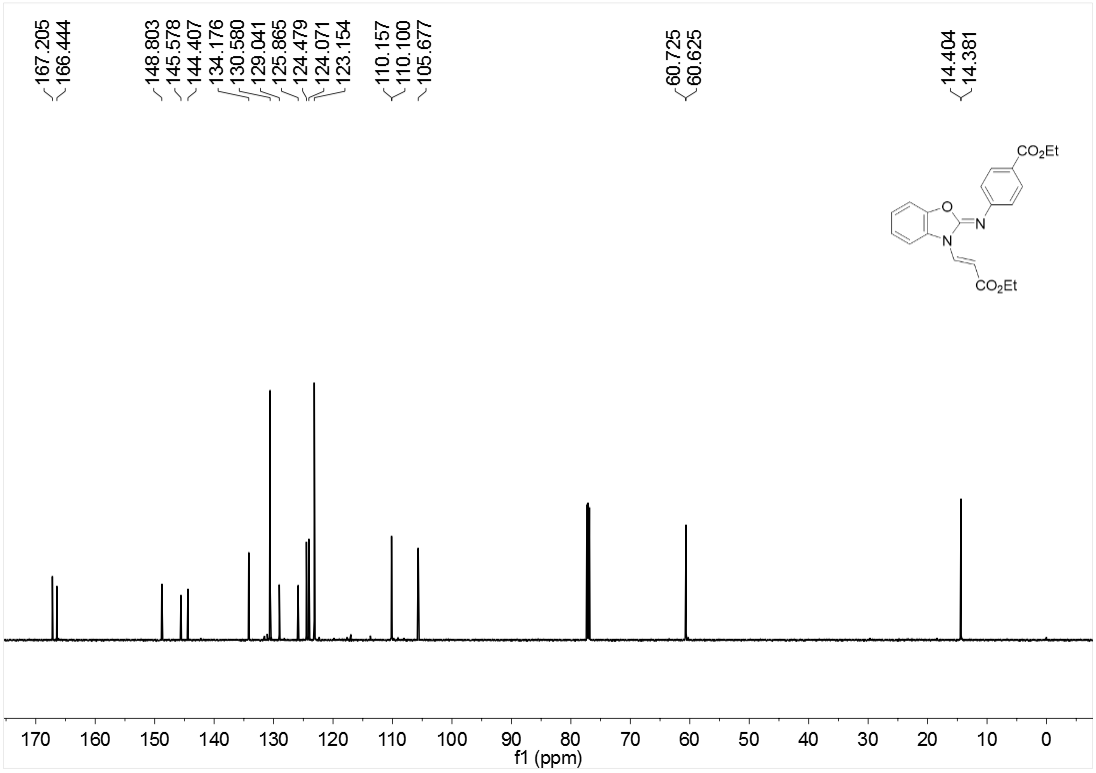


Figure 57. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3la**

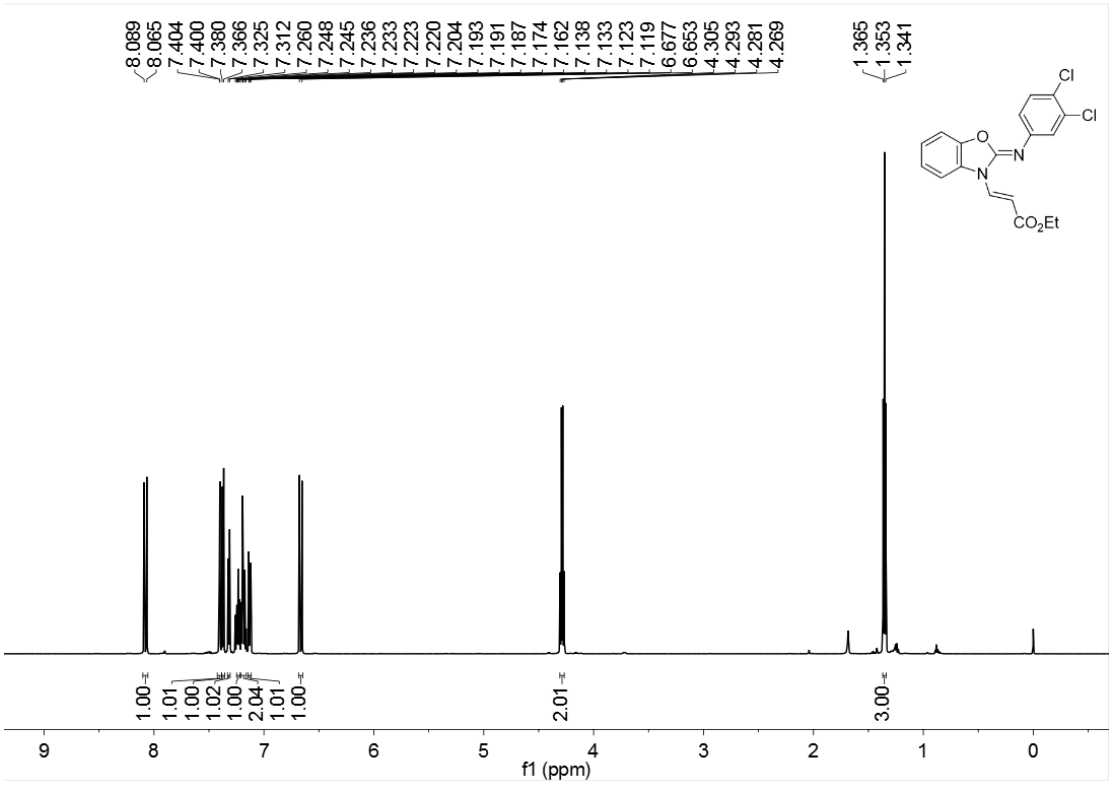


Figure 58. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3ma**

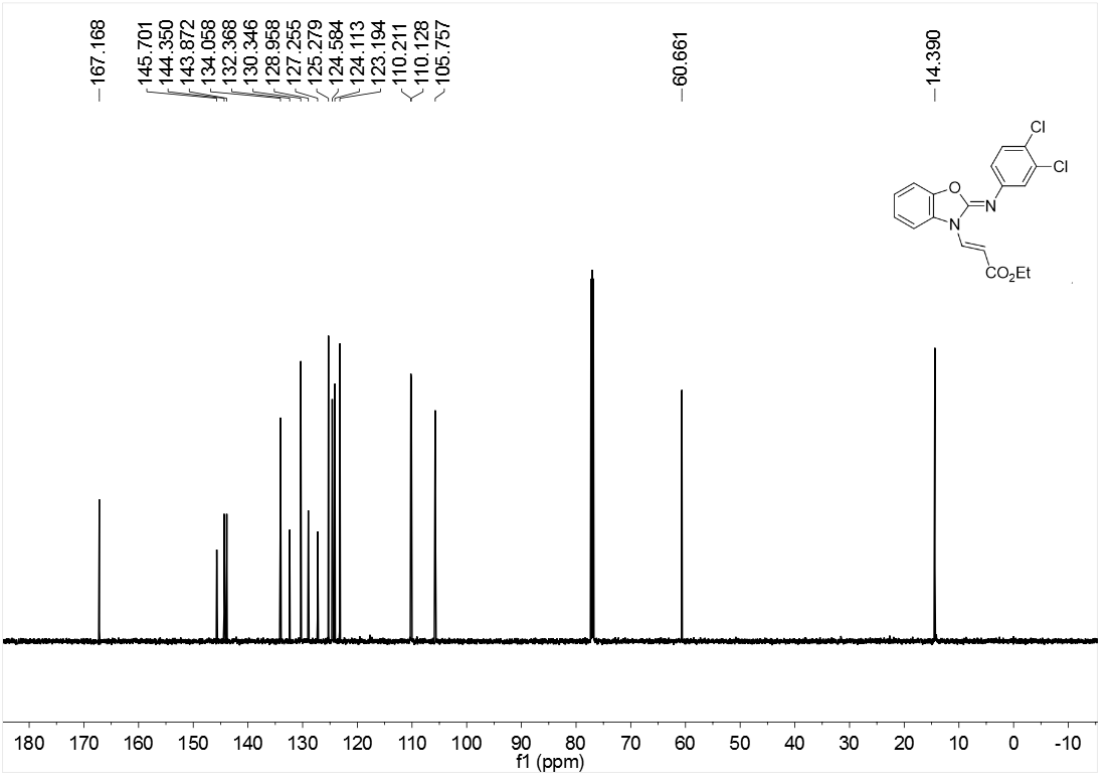


Figure 59. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ma**

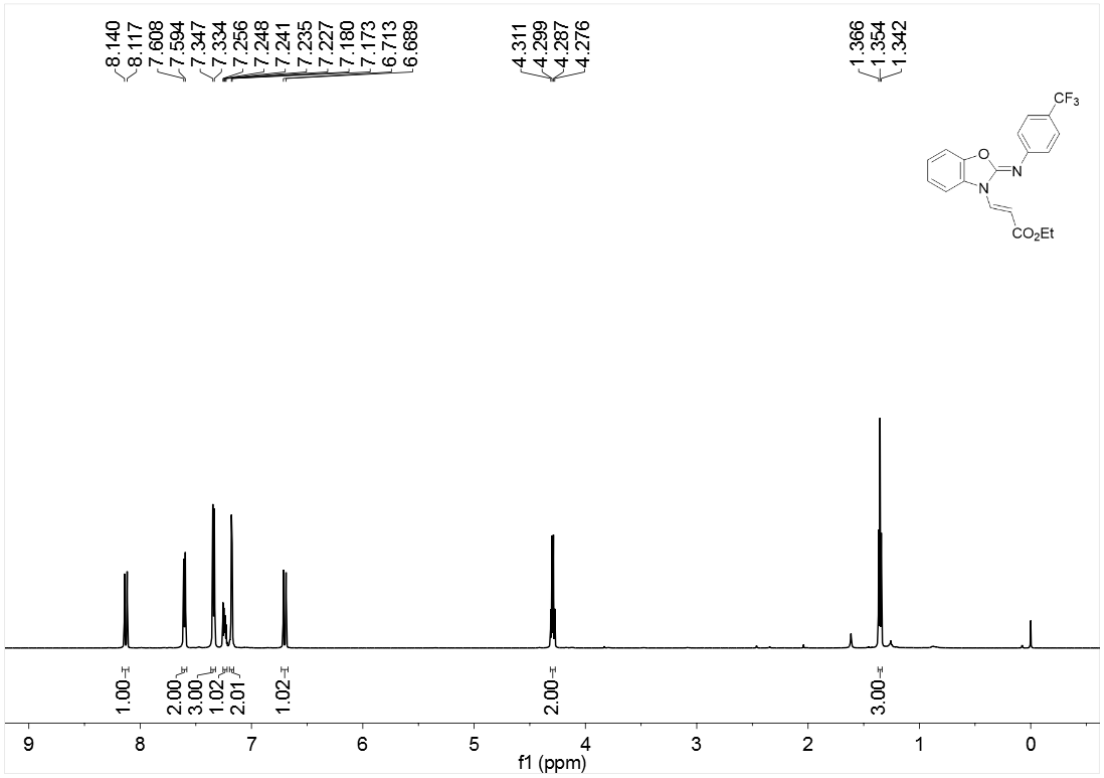


Figure 60. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3na**

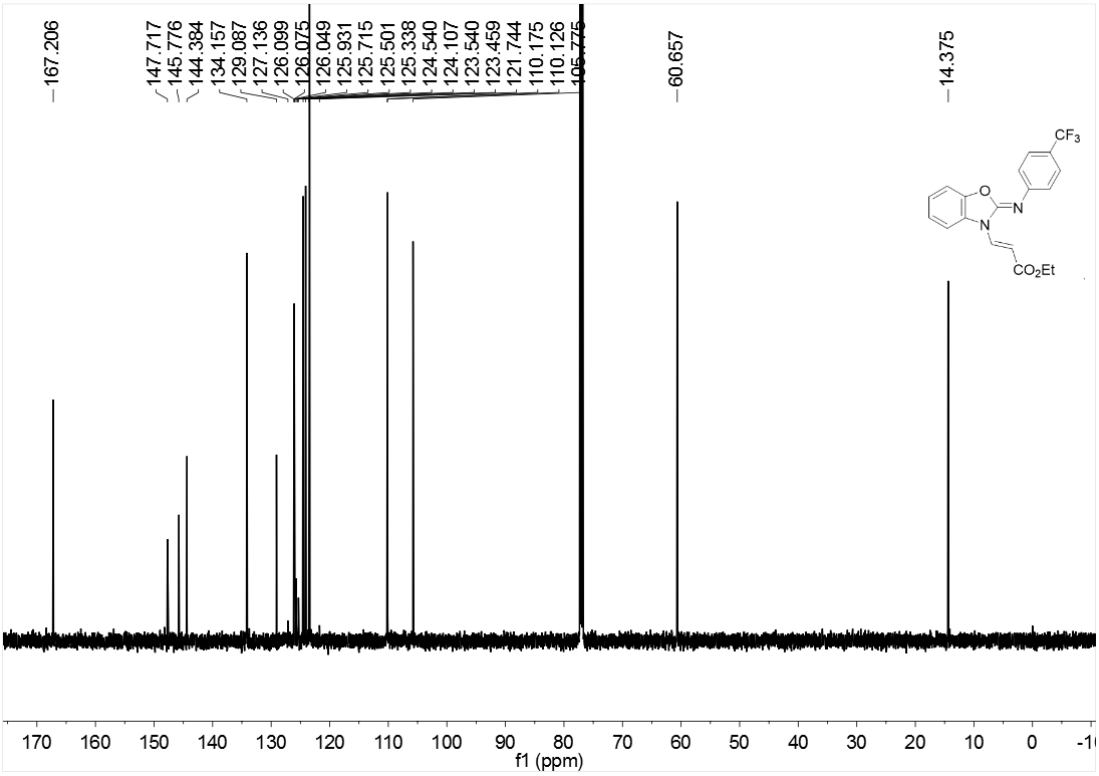


Figure 61. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3na**

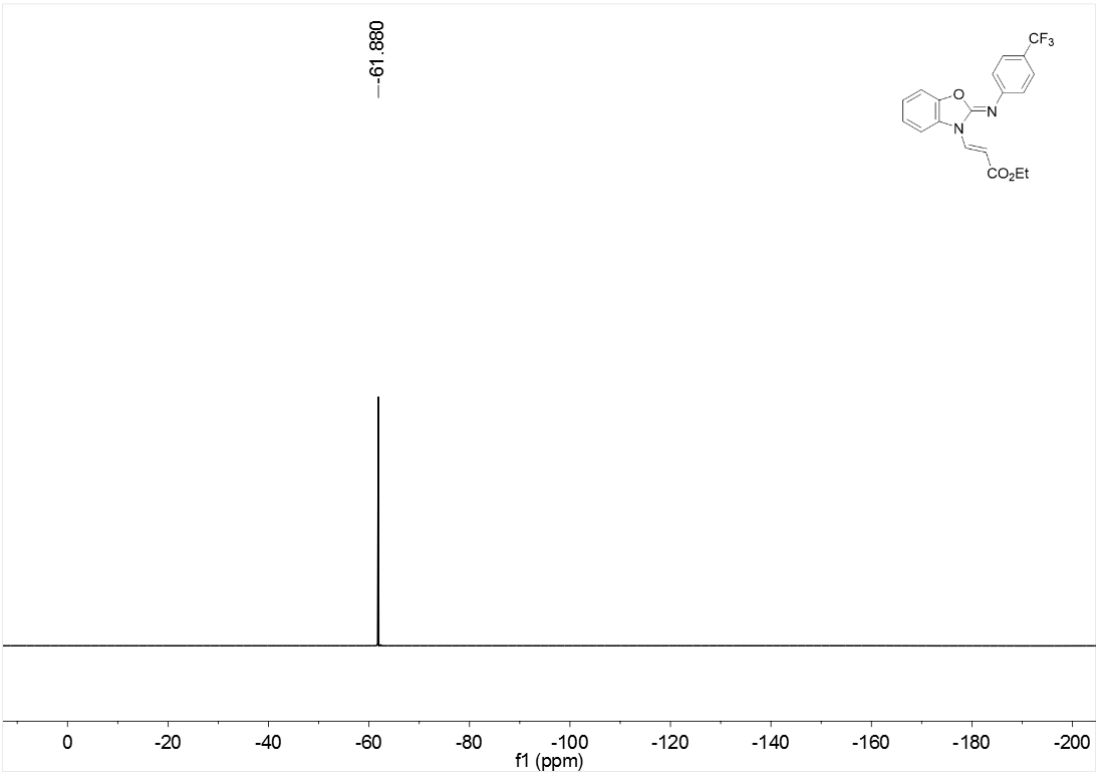


Figure 62. ^{19}F NMR spectrum (471 MHz, $CDCl_3$) of **3na**

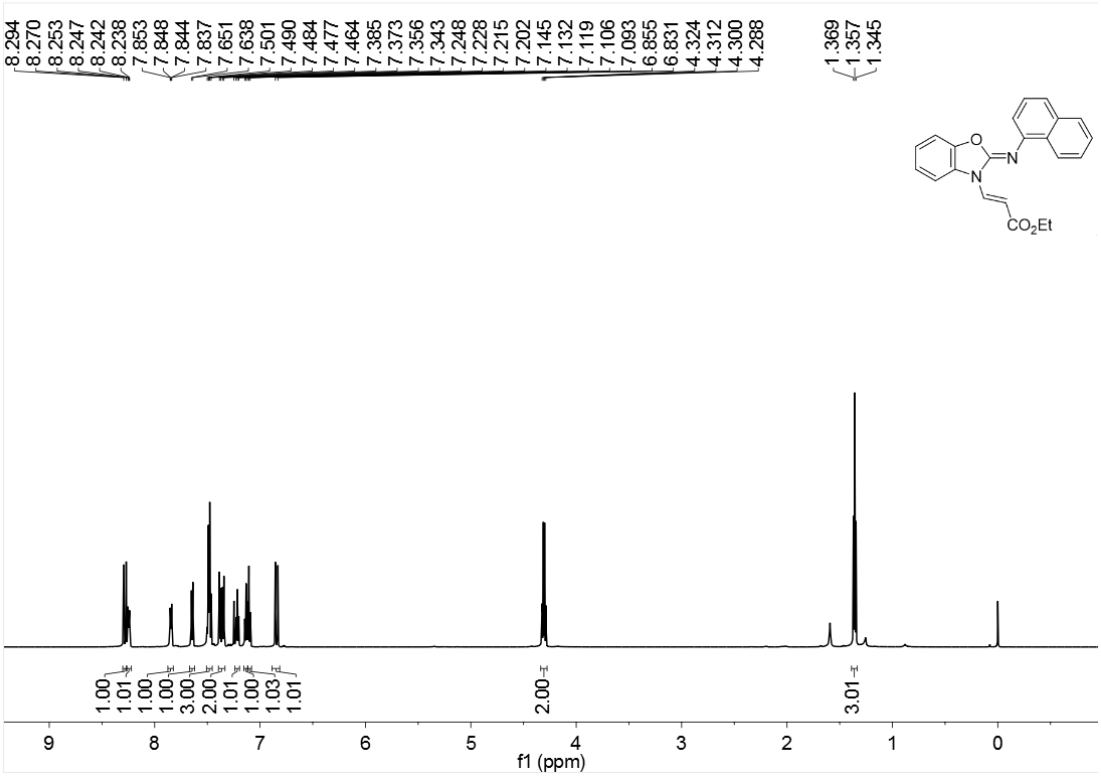


Figure 63. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3oa**

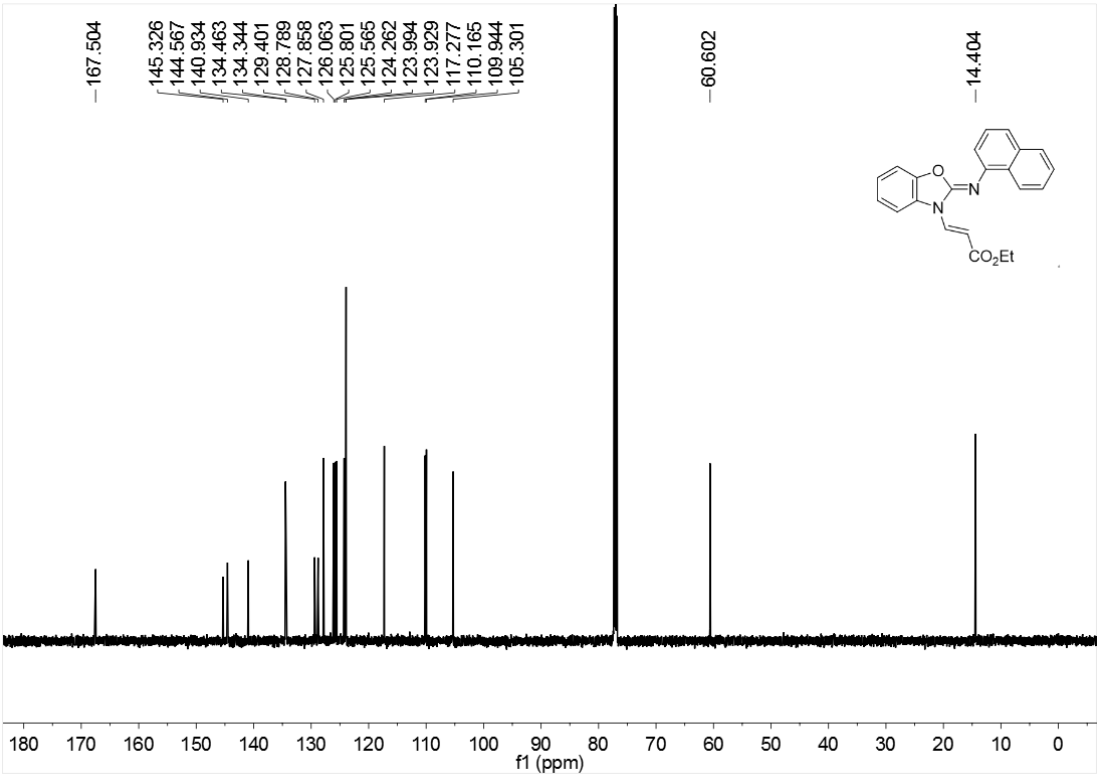


Figure 64. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3oa**

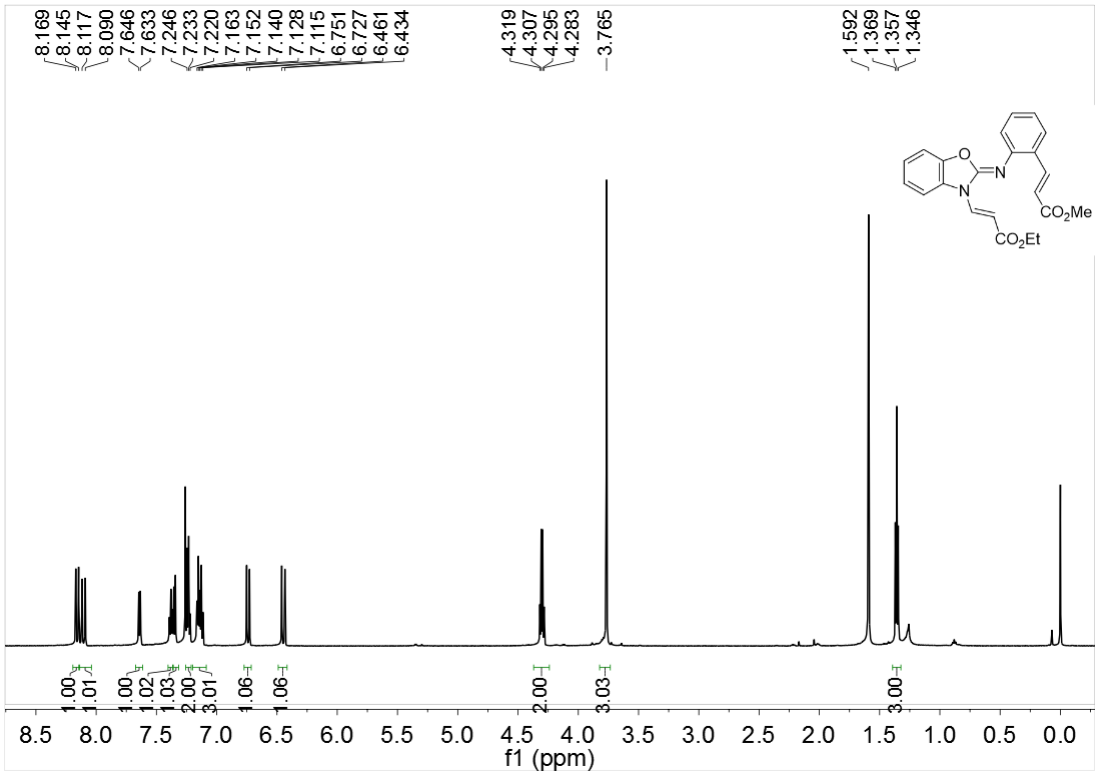


Figure 65. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3pa**

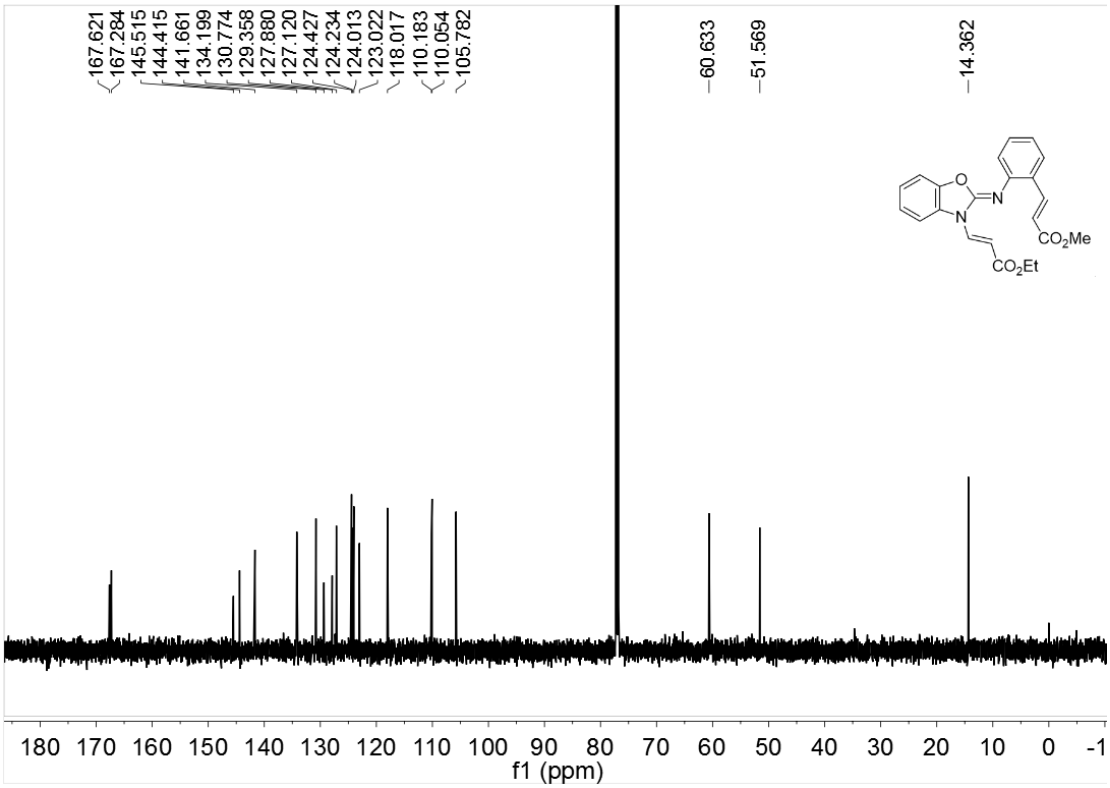


Figure 66. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3pa**

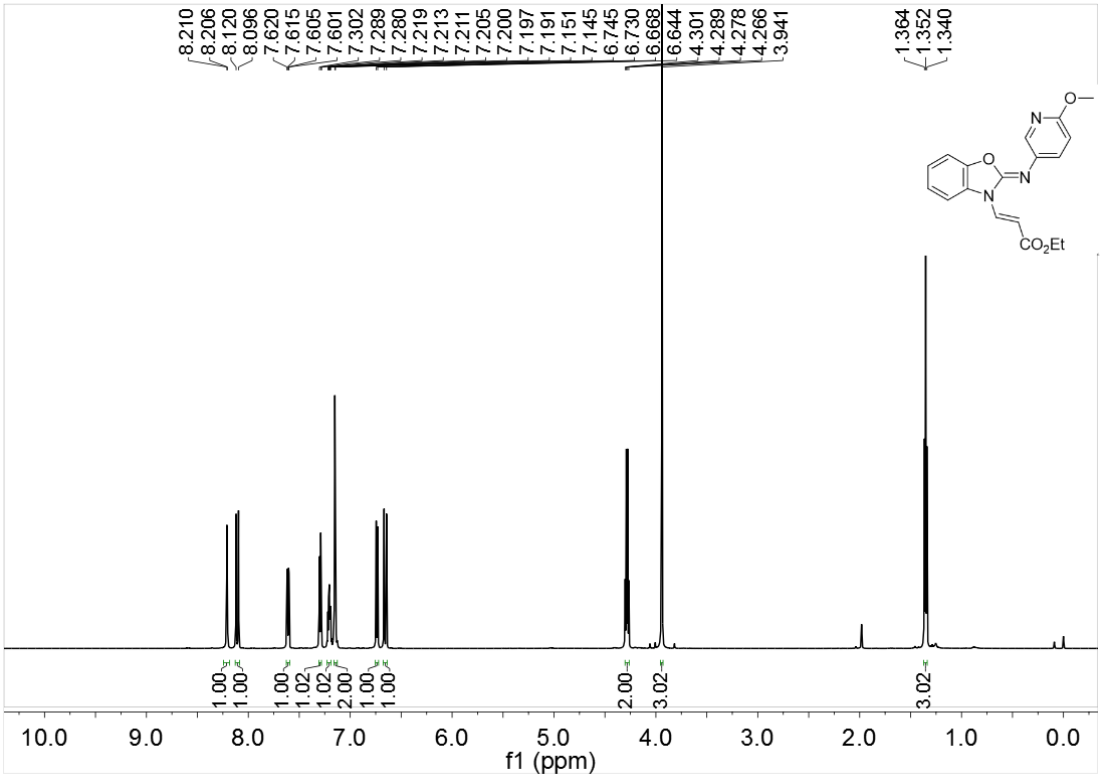


Figure 67. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3qa**

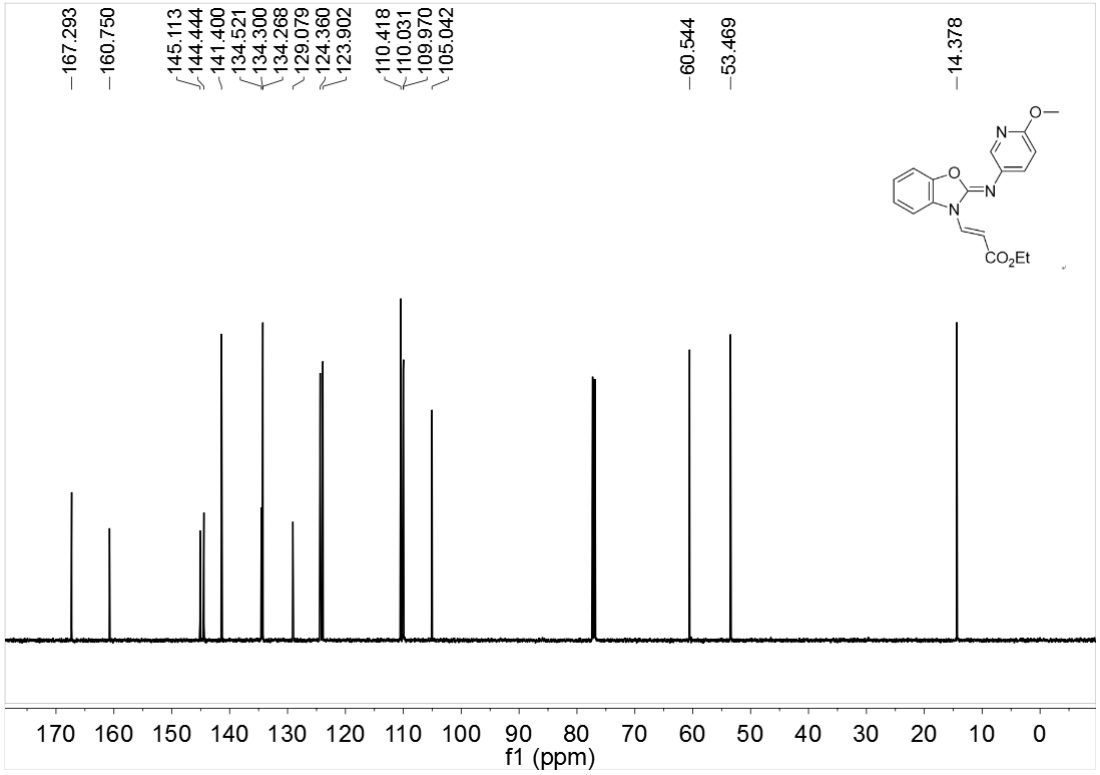


Figure 68. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3qa**

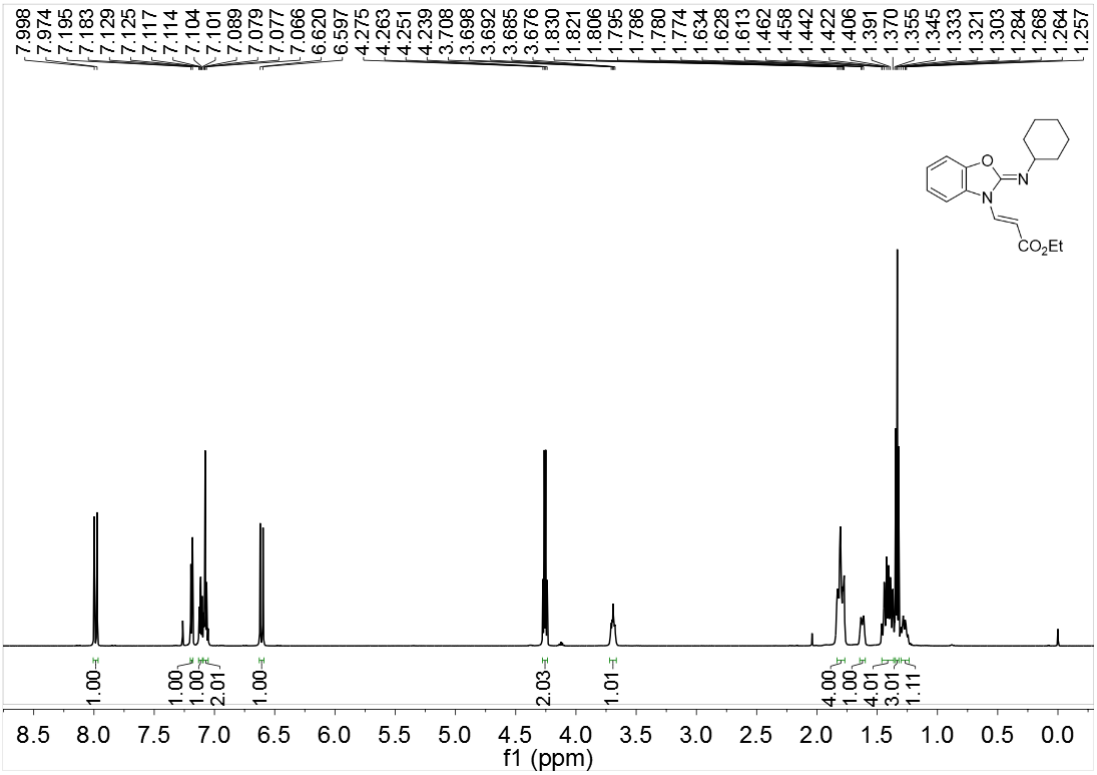


Figure 69. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3ra**

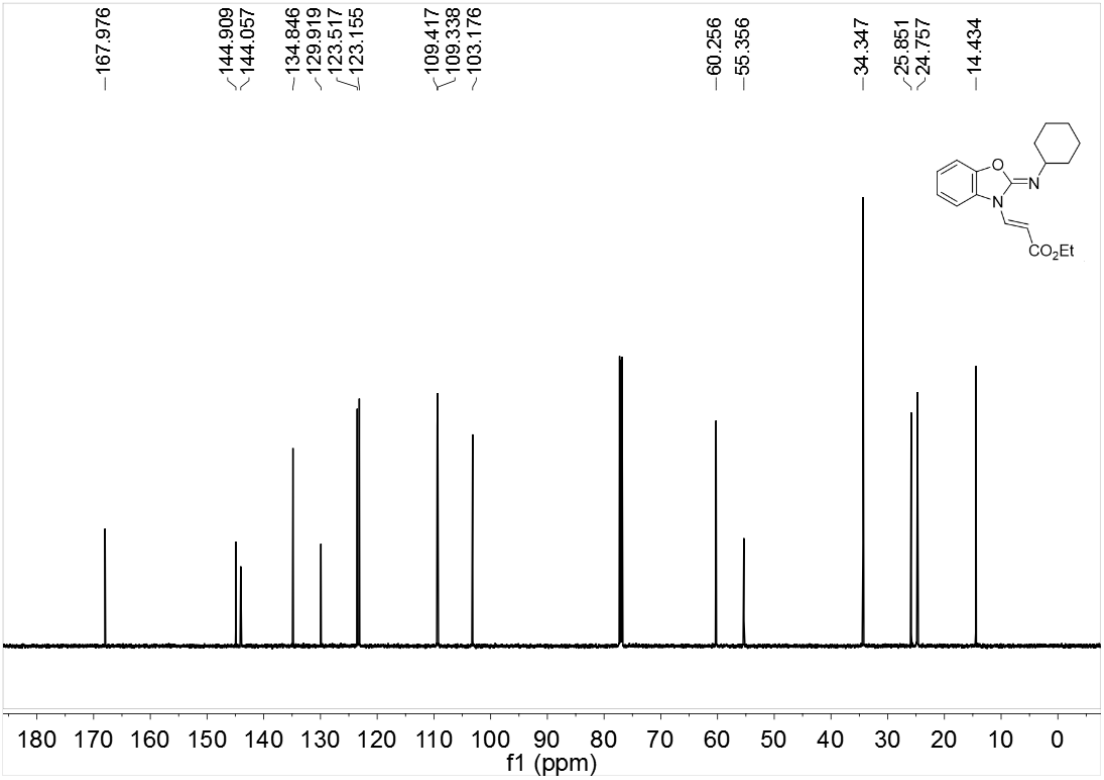


Figure 70. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ra**

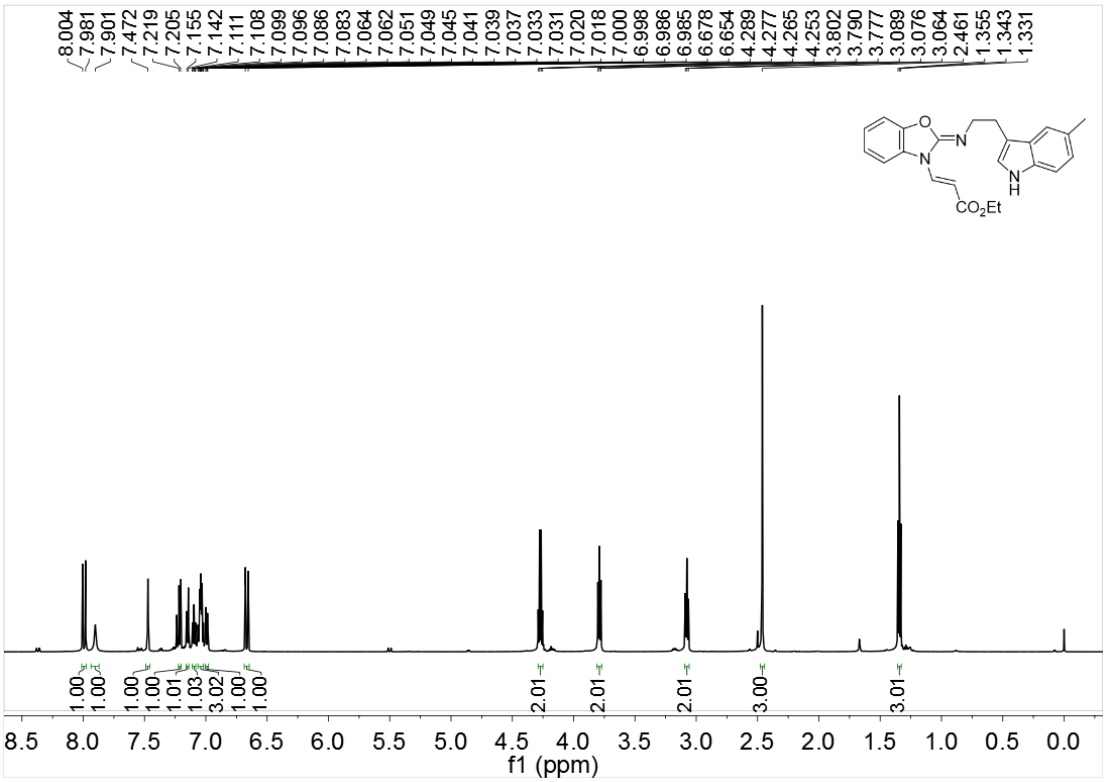


Figure 71. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3sa**

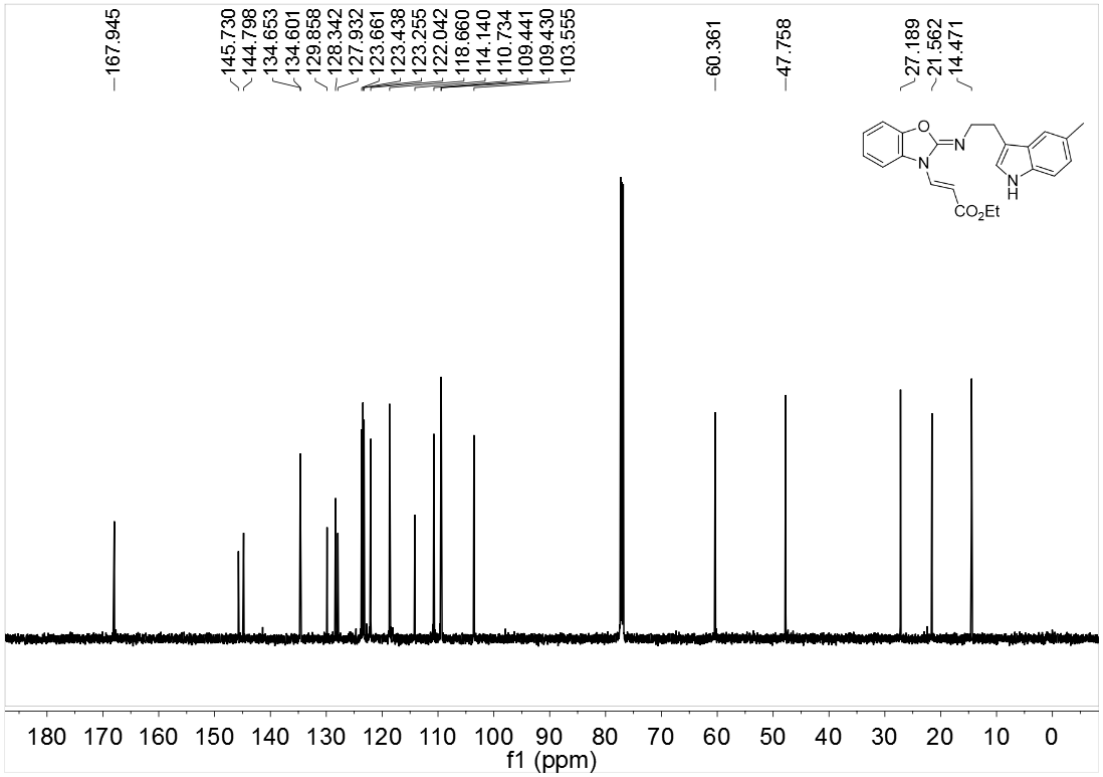


Figure 72. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3sa**

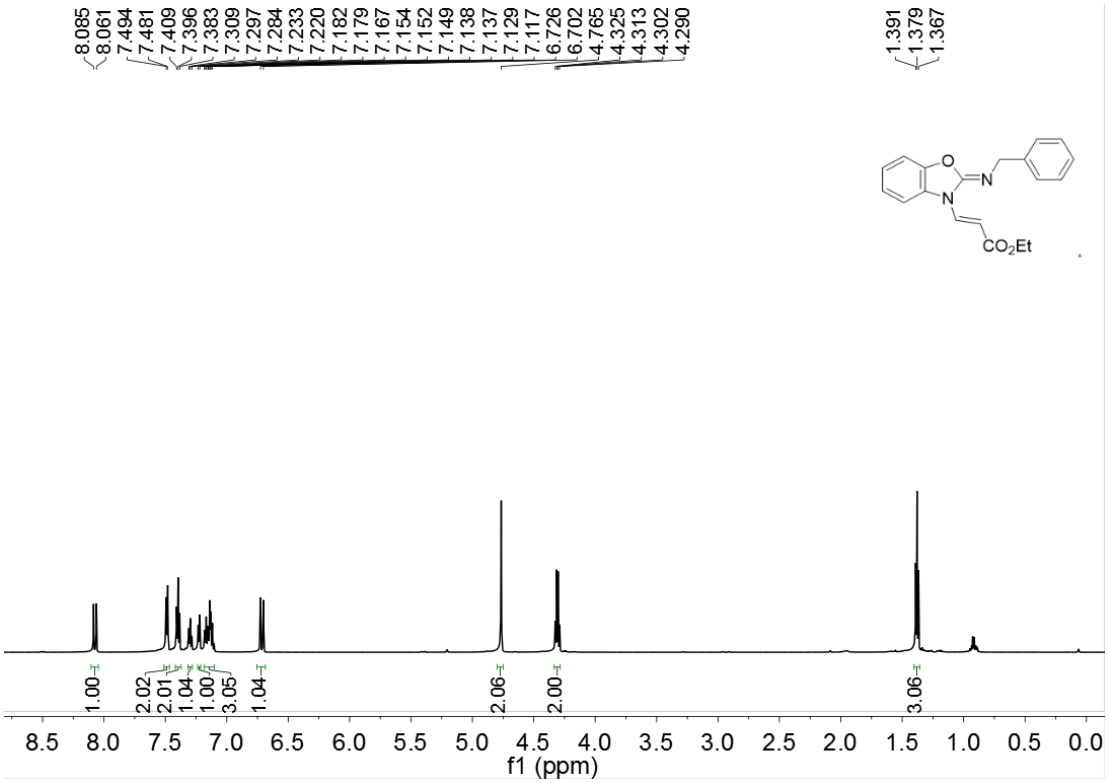


Figure 73. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3ta**

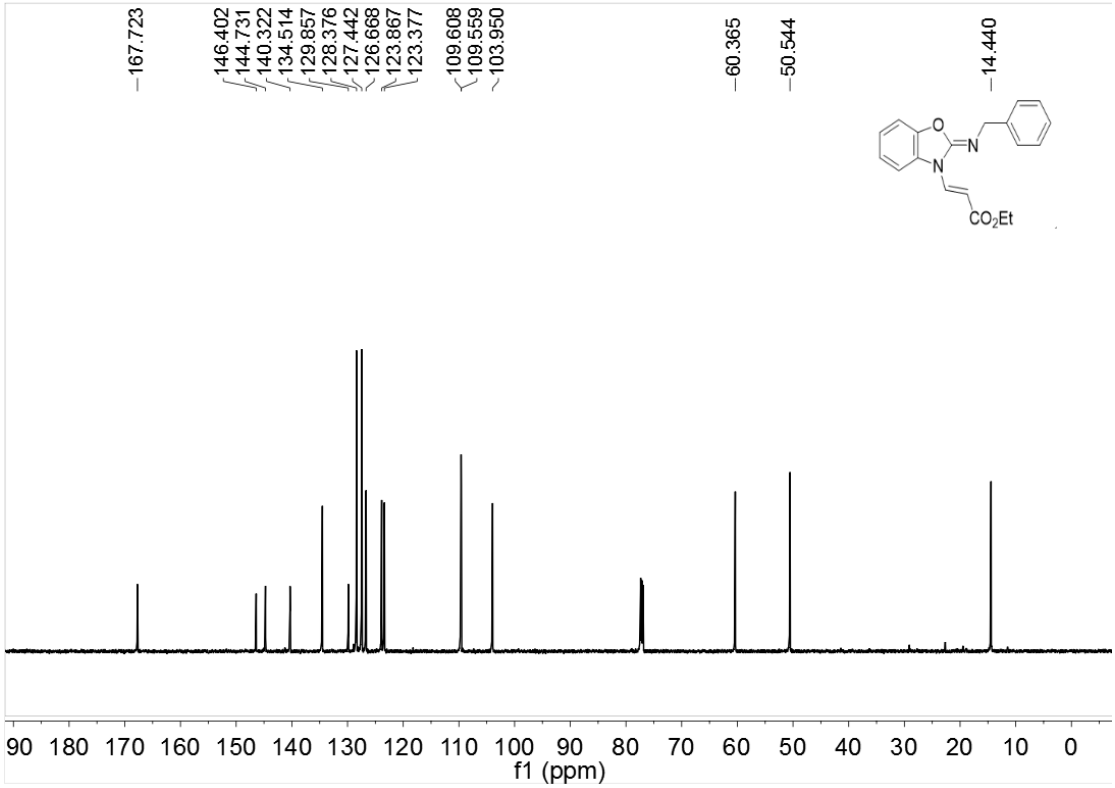


Figure 74. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ta**

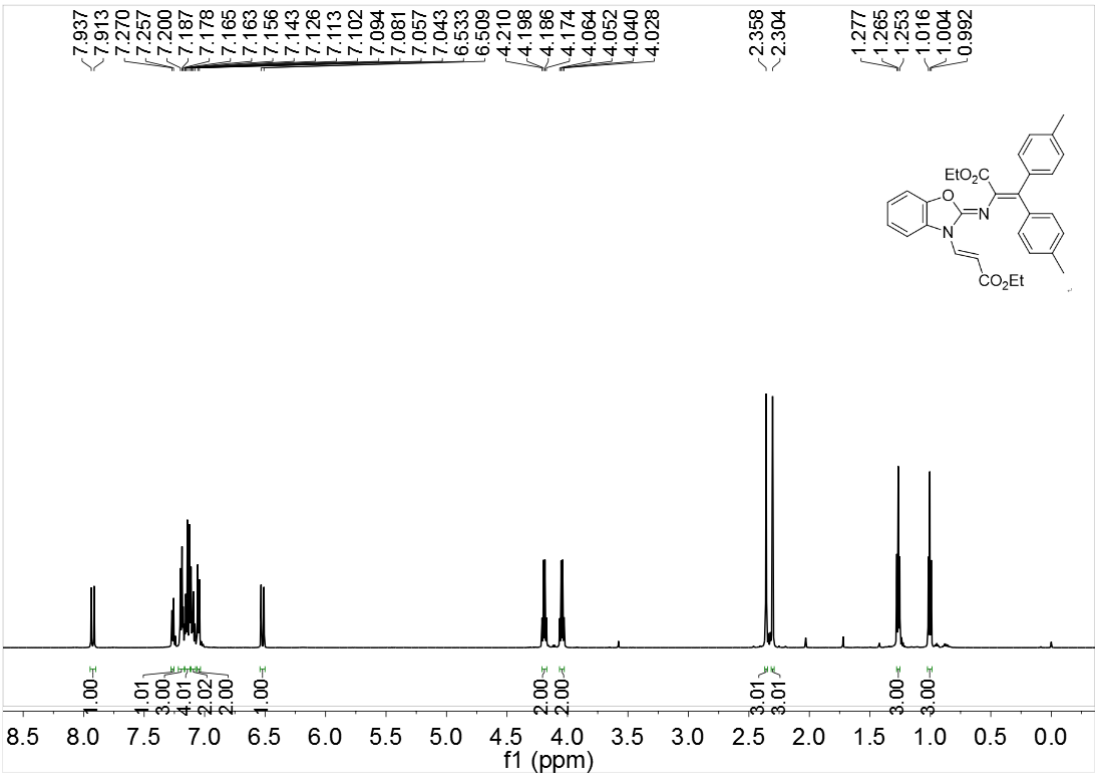


Figure 75. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3ua**

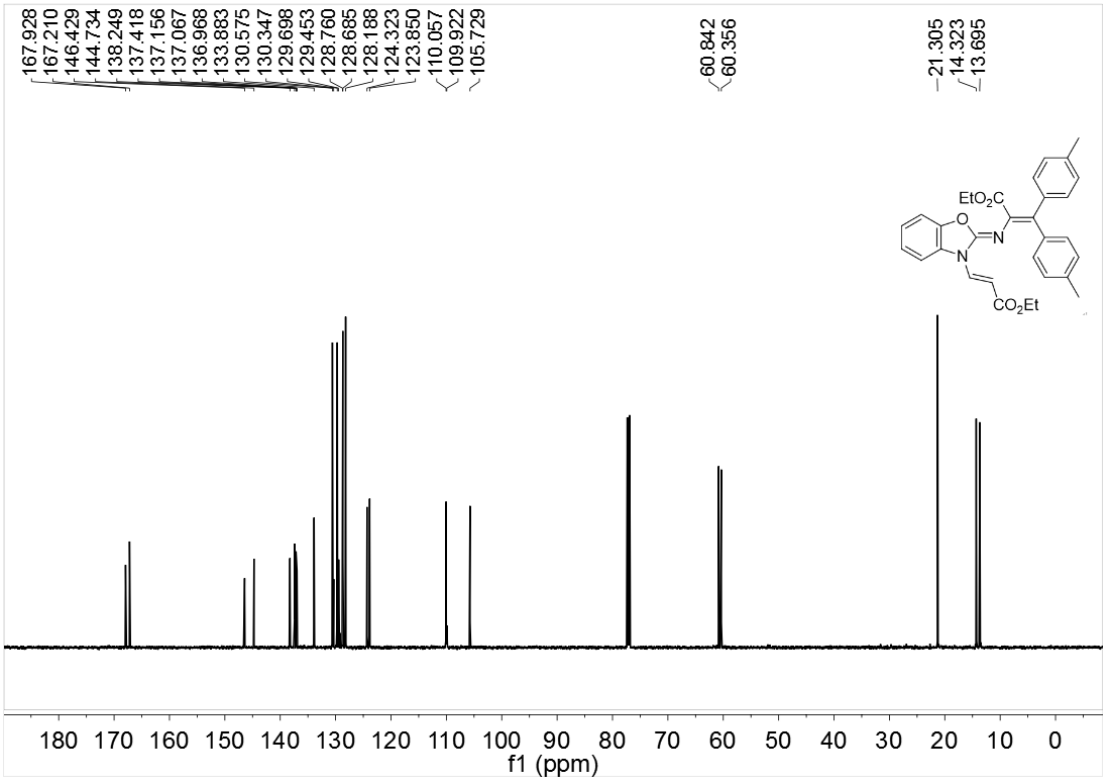


Figure 76. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ua**

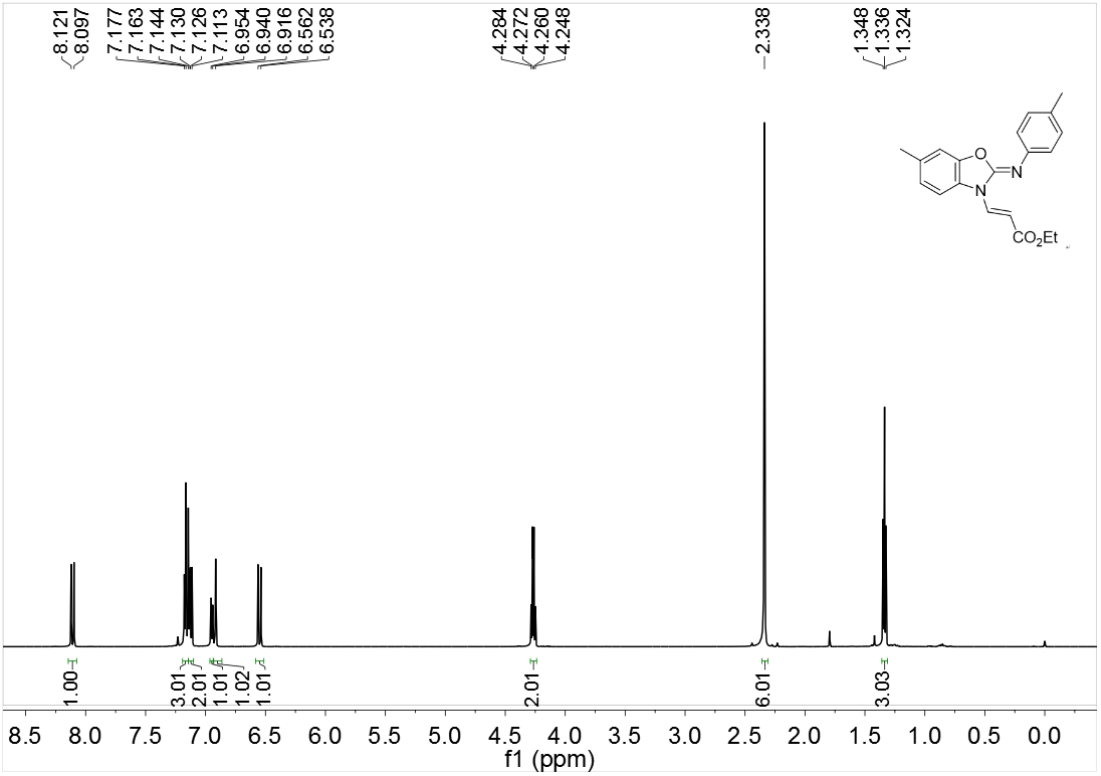


Figure 77. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3ab**

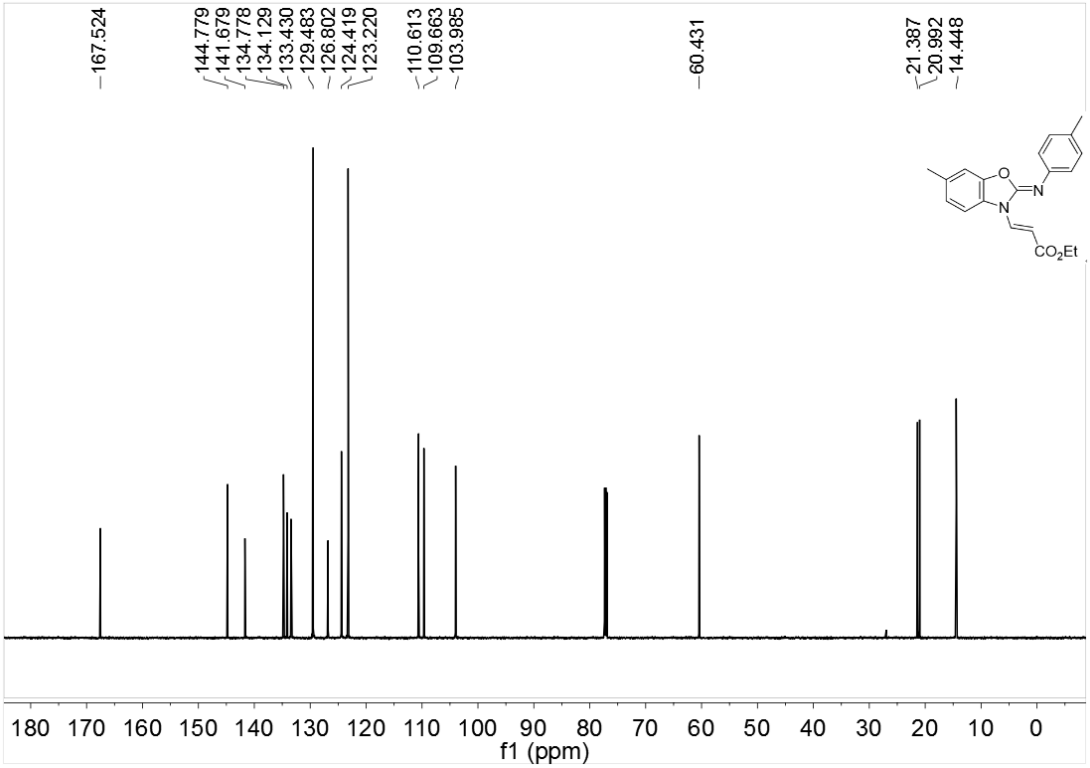


Figure 78. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ab**

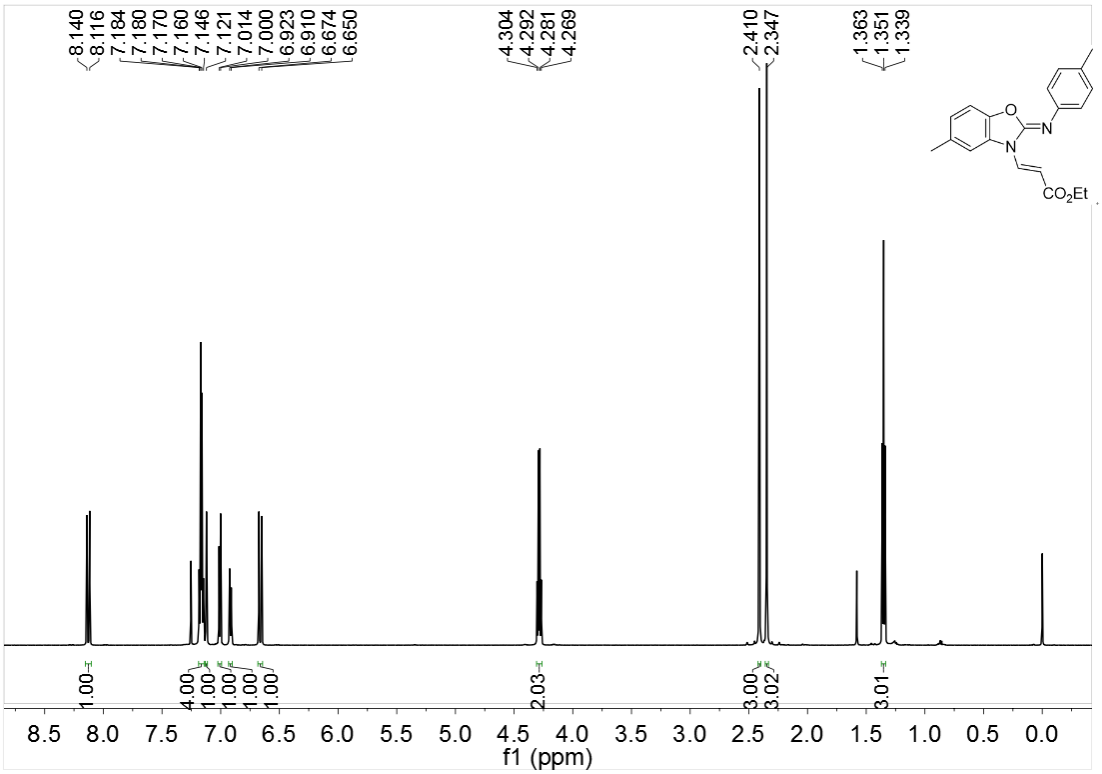


Figure 79. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3ac**

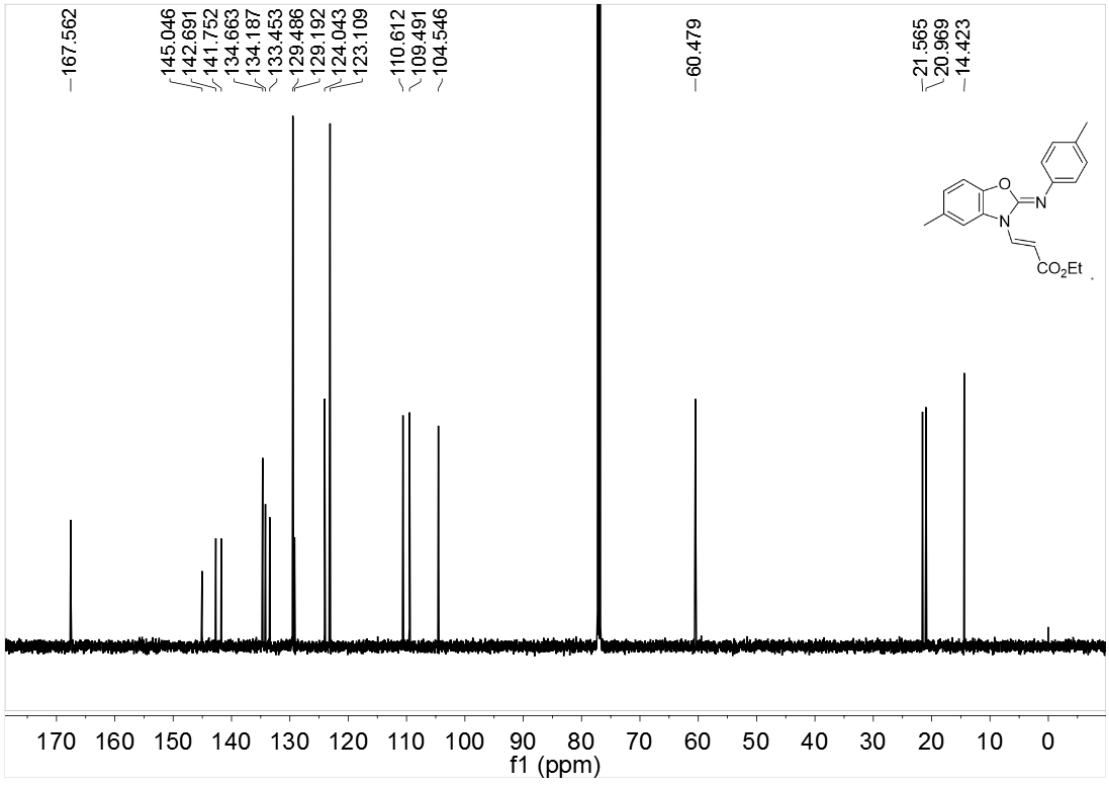


Figure 80. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ac**

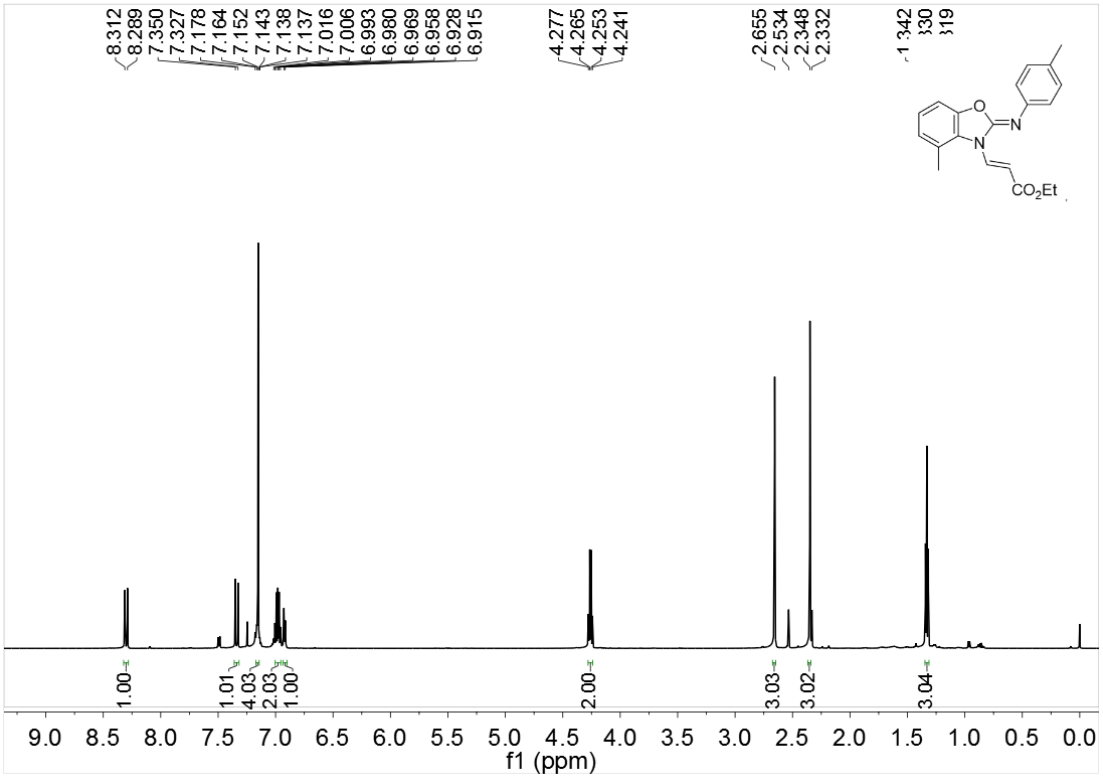


Figure 81. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3ad**

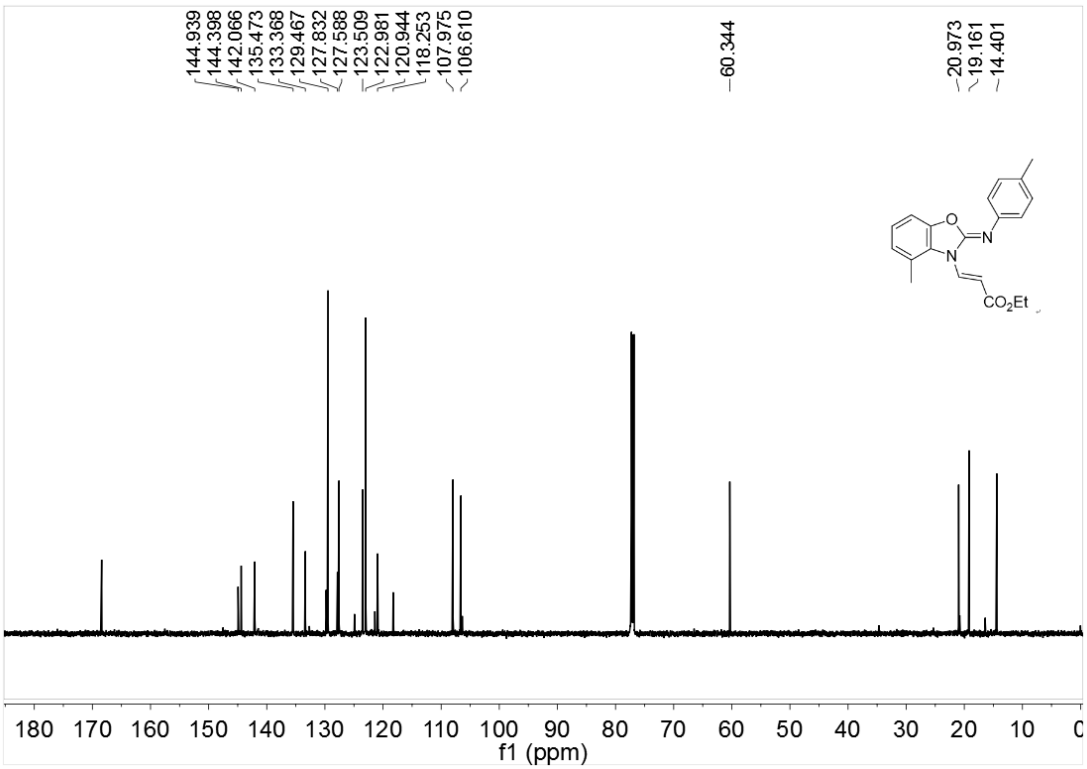


Figure 82. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ad**

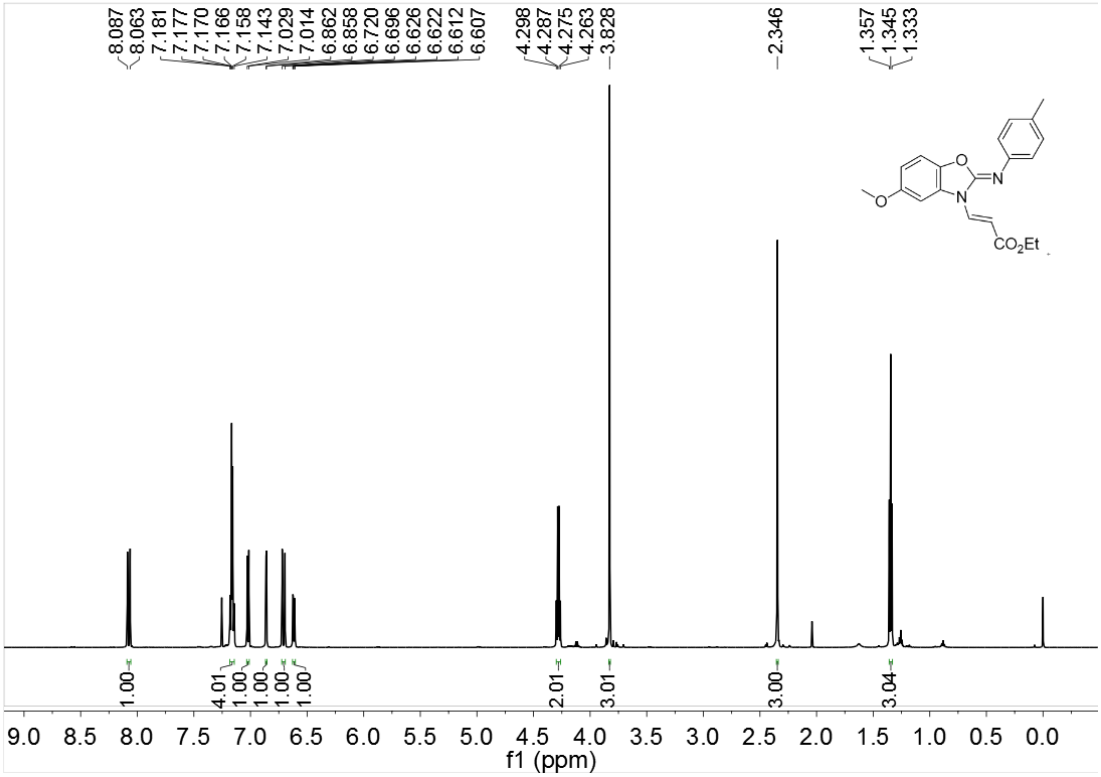


Figure 83. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3ae**

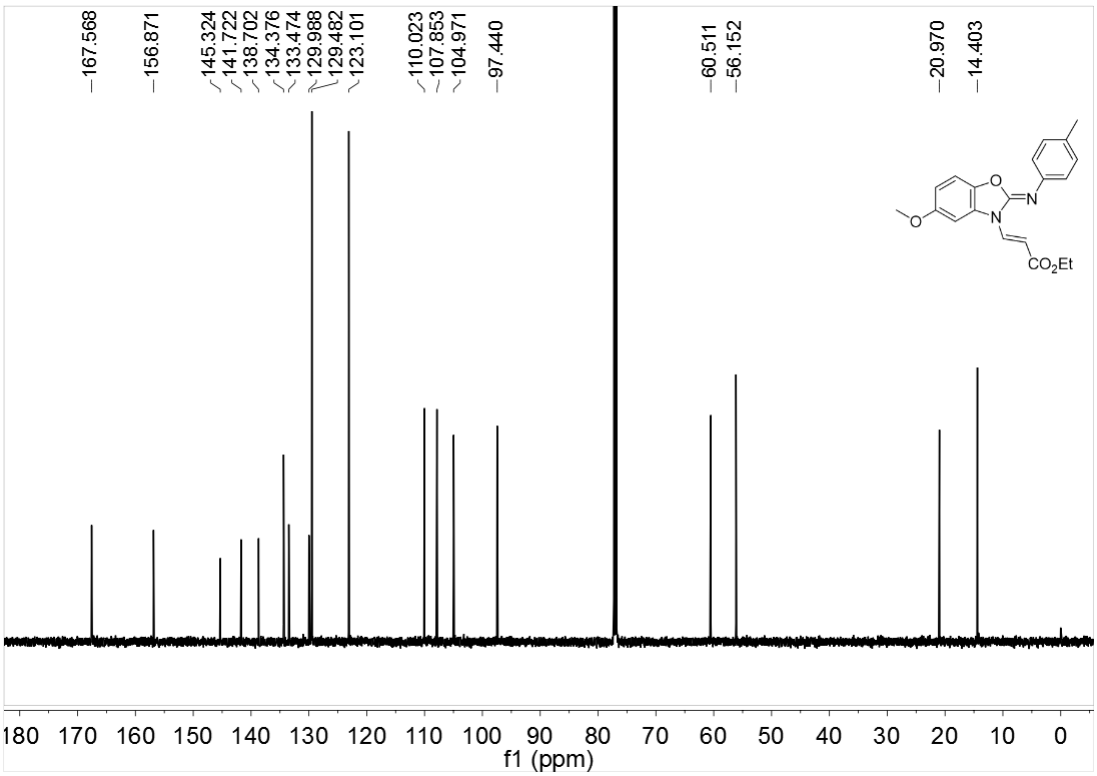


Figure 84. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ae**

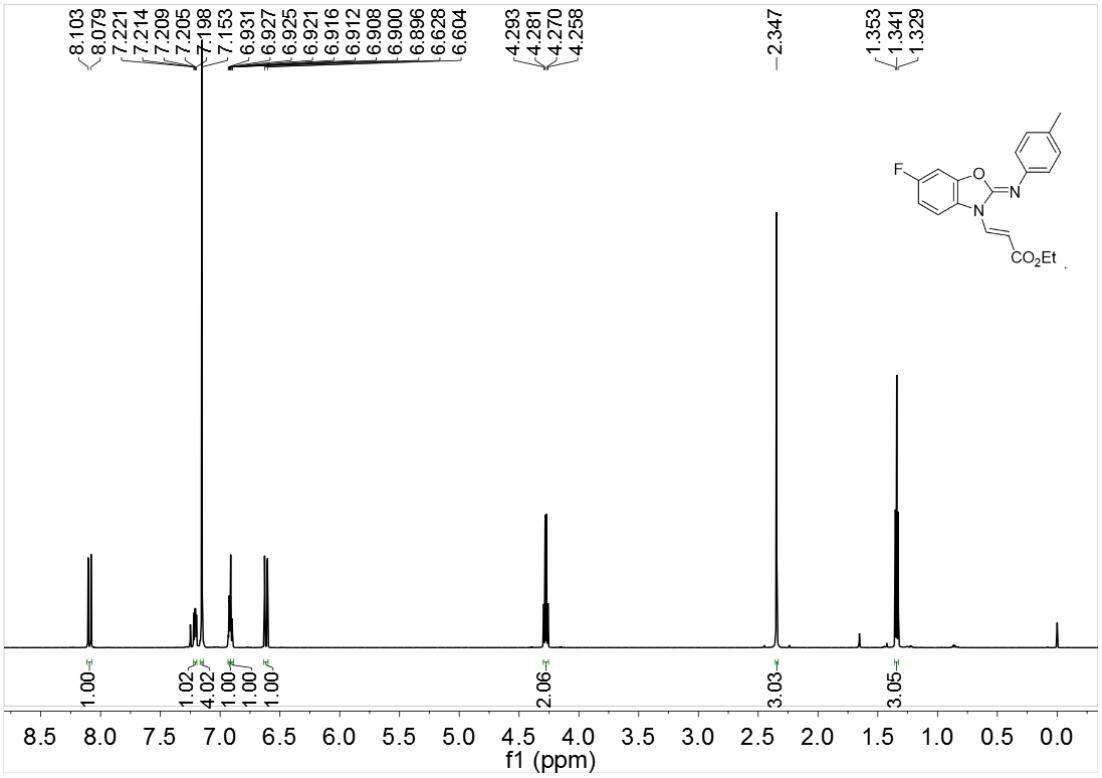


Figure 85. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3af**

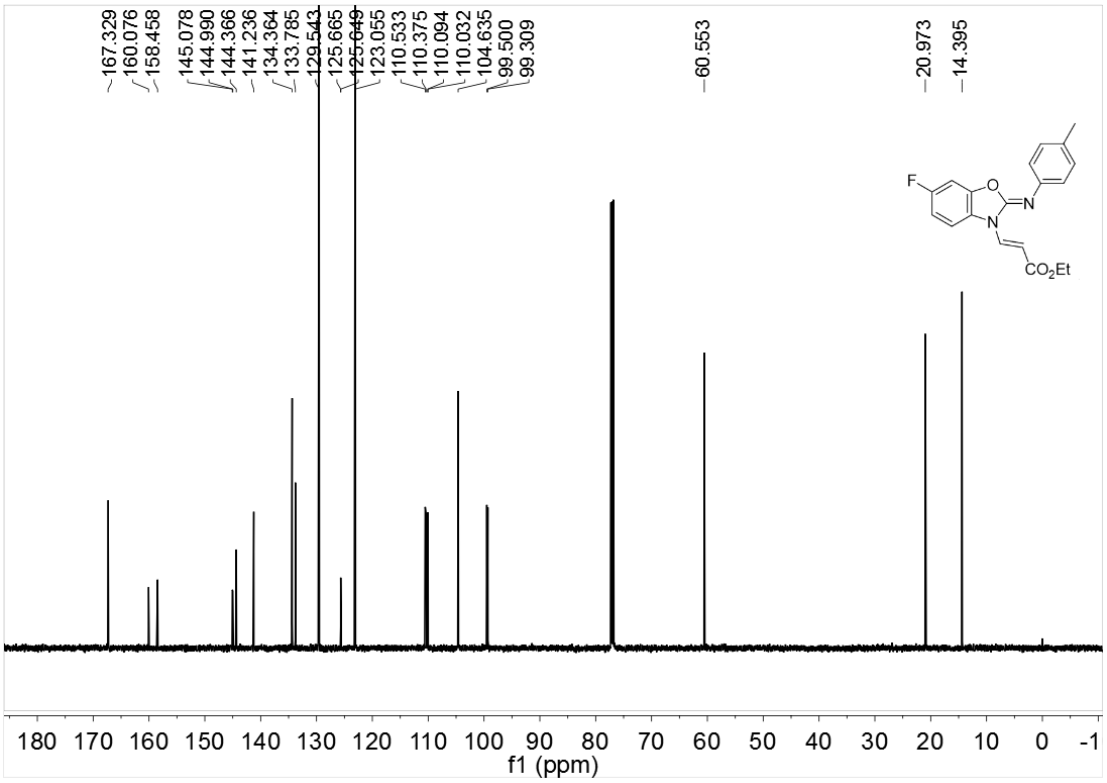


Figure 86. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3af**

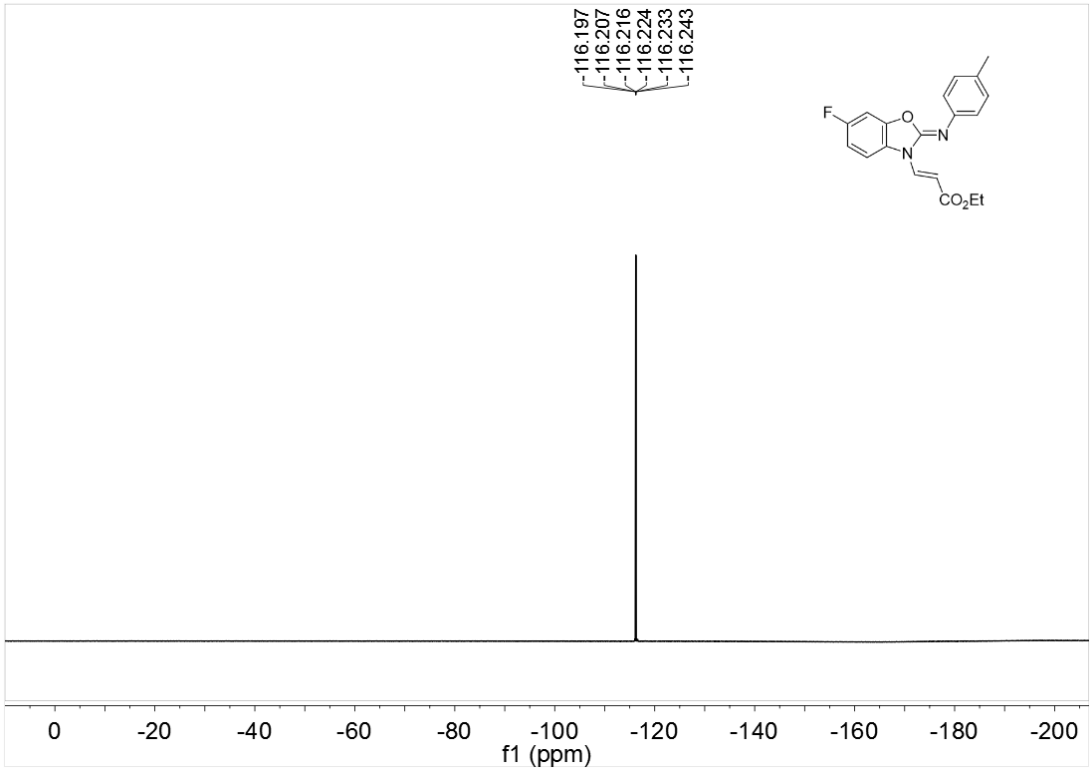


Figure 87. ^{19}F NMR spectrum (471 MHz, $CDCl_3$) of **3af**

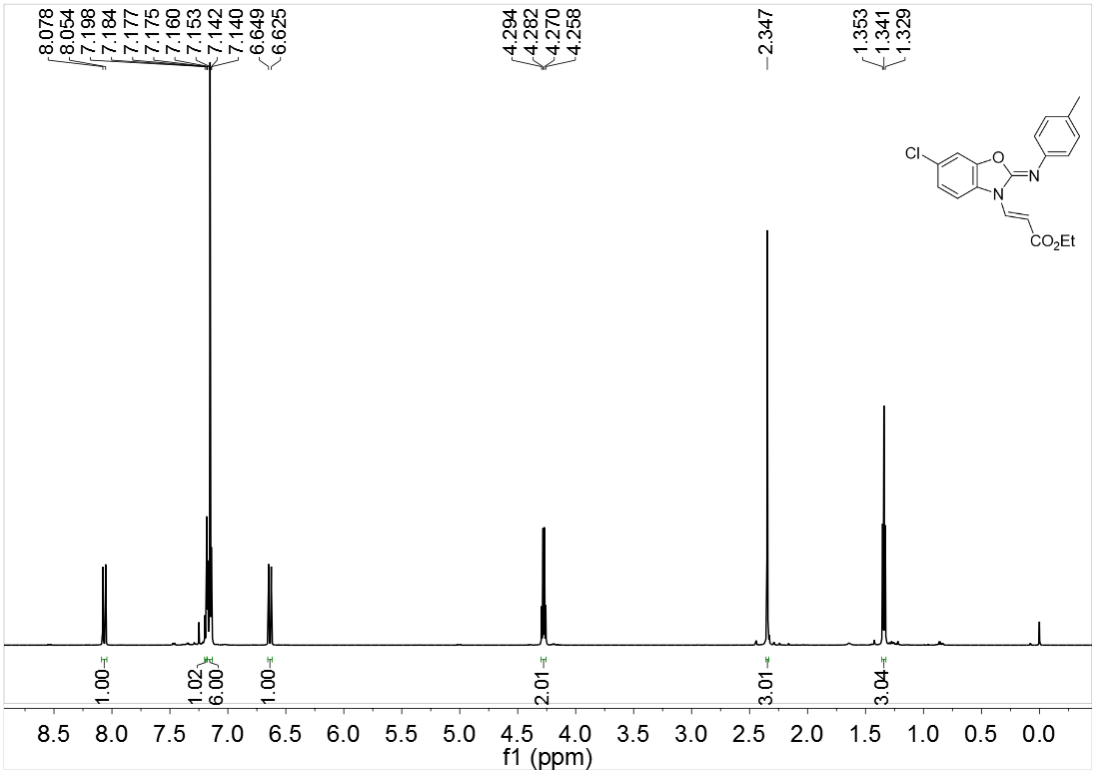


Figure 88. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3ag**

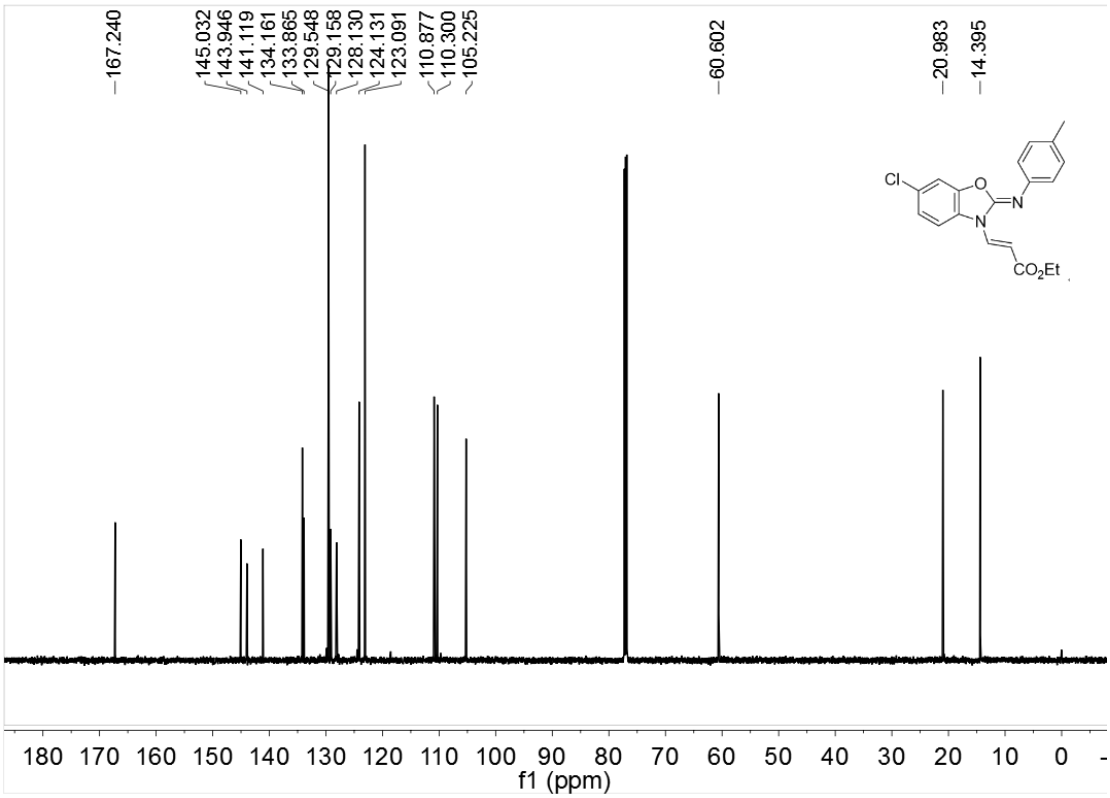


Figure 89. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ag**

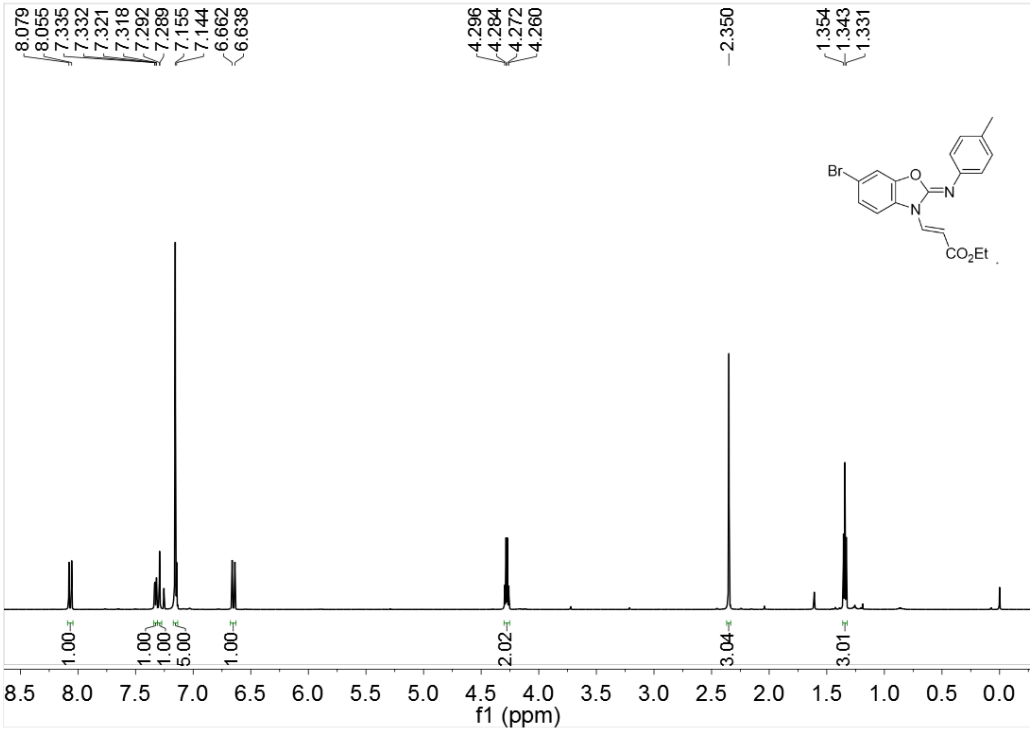


Figure 90. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3ah**

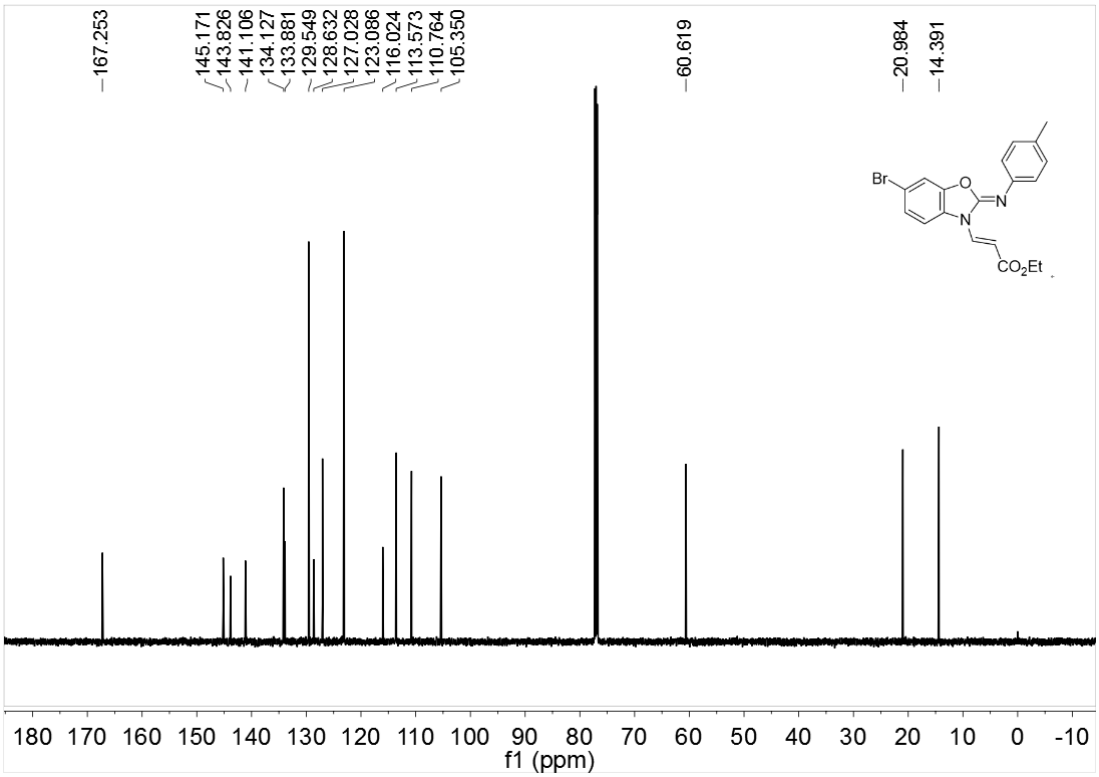


Figure 91. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ah**

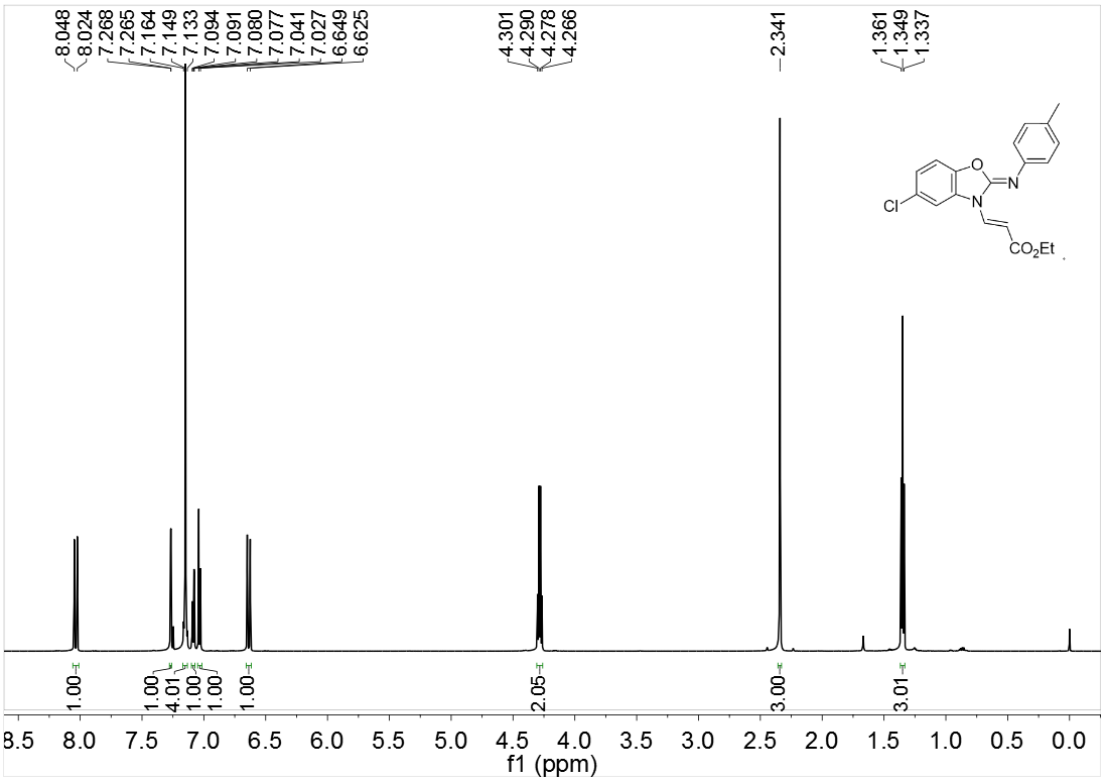


Figure 92. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3ai**

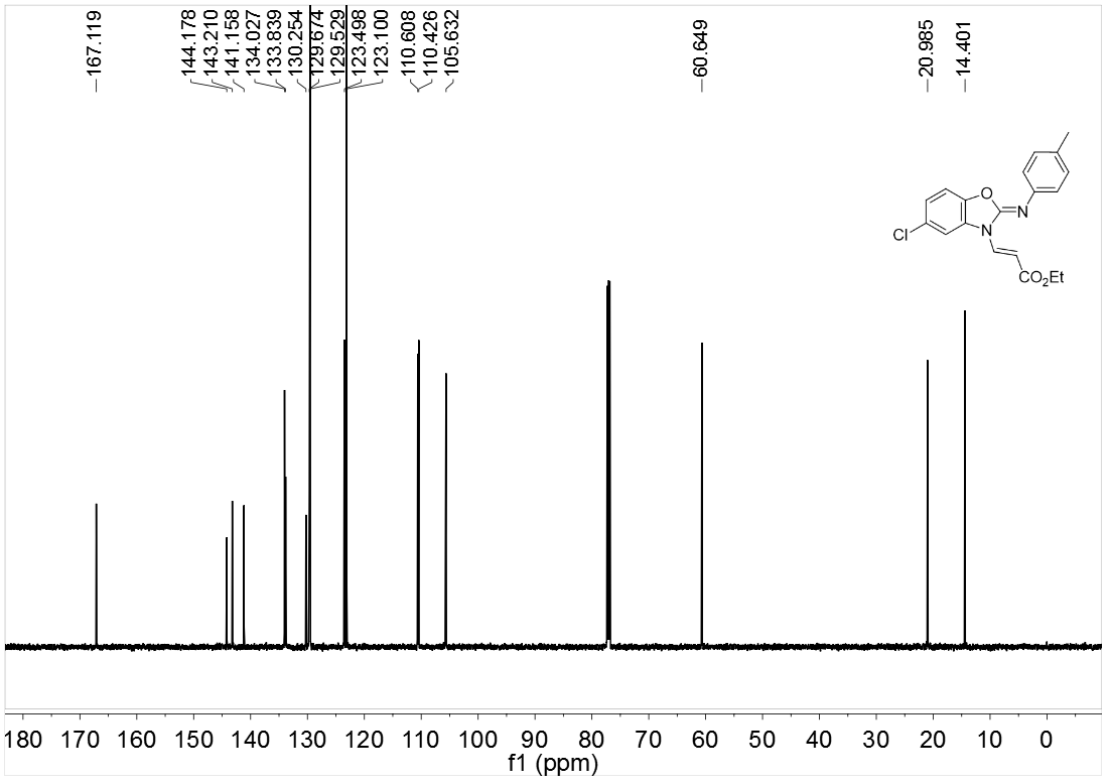


Figure 93. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ai**

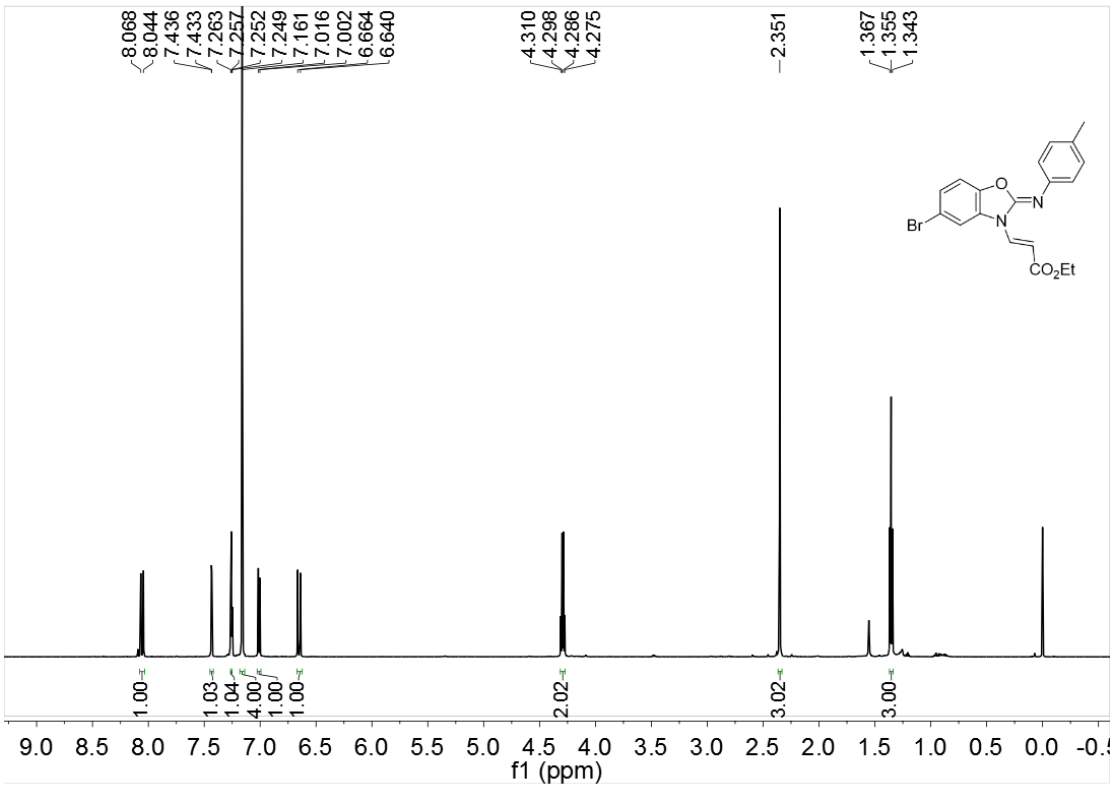


Figure 94. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3aj**

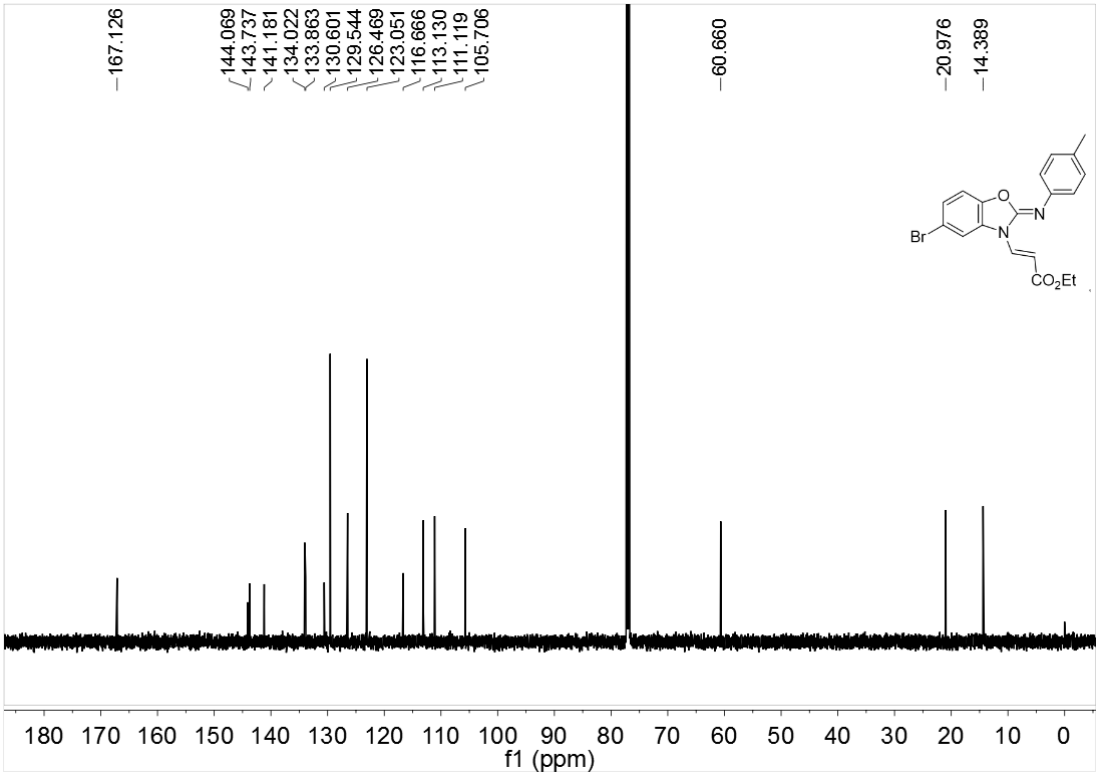


Figure 95. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3aj**

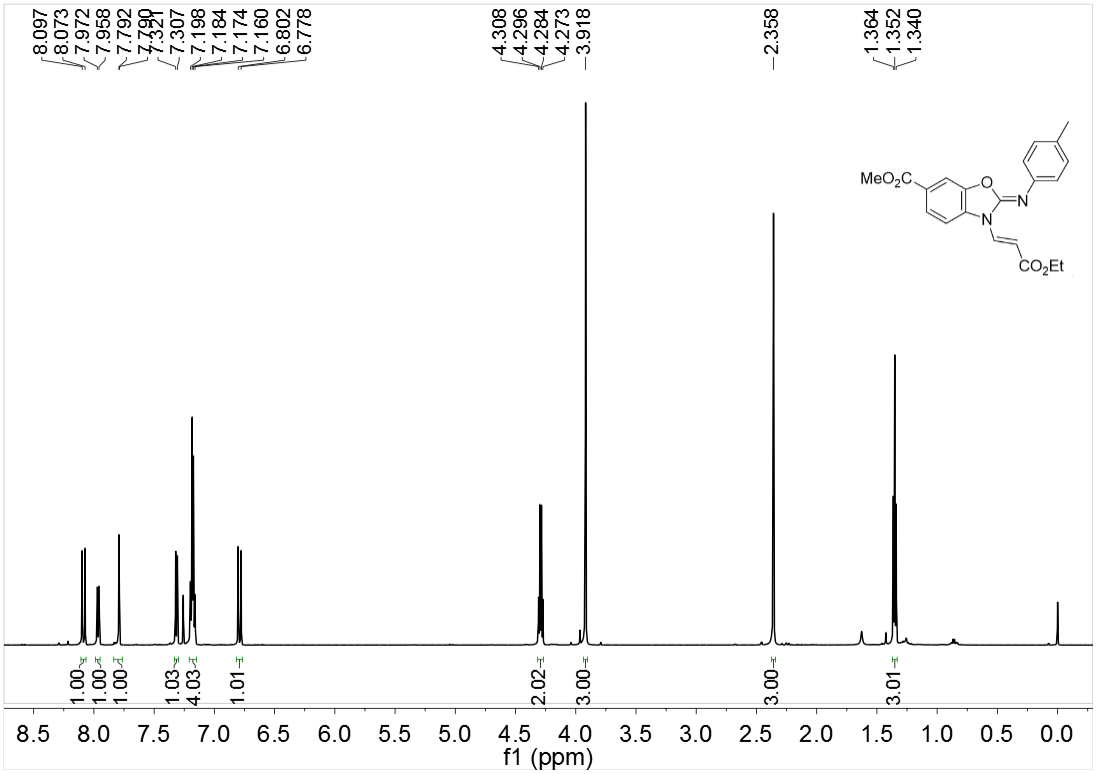


Figure 96. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3ak**

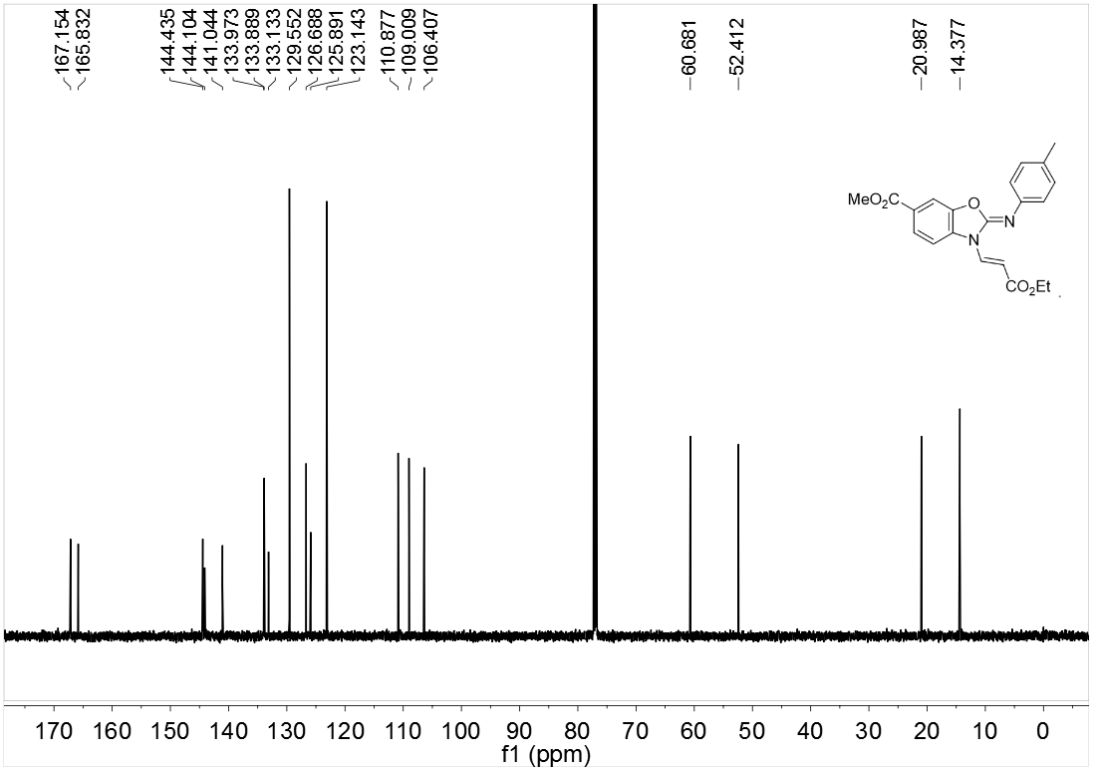


Figure 97. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ak**

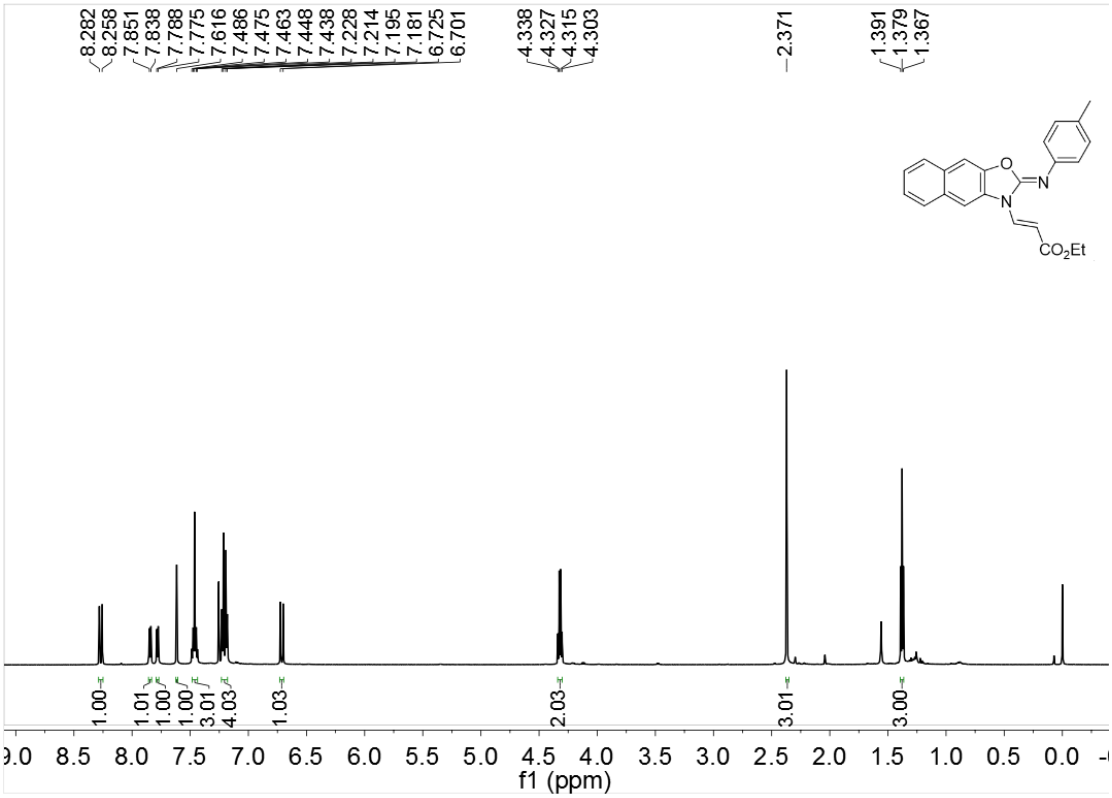


Figure 98. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3al**

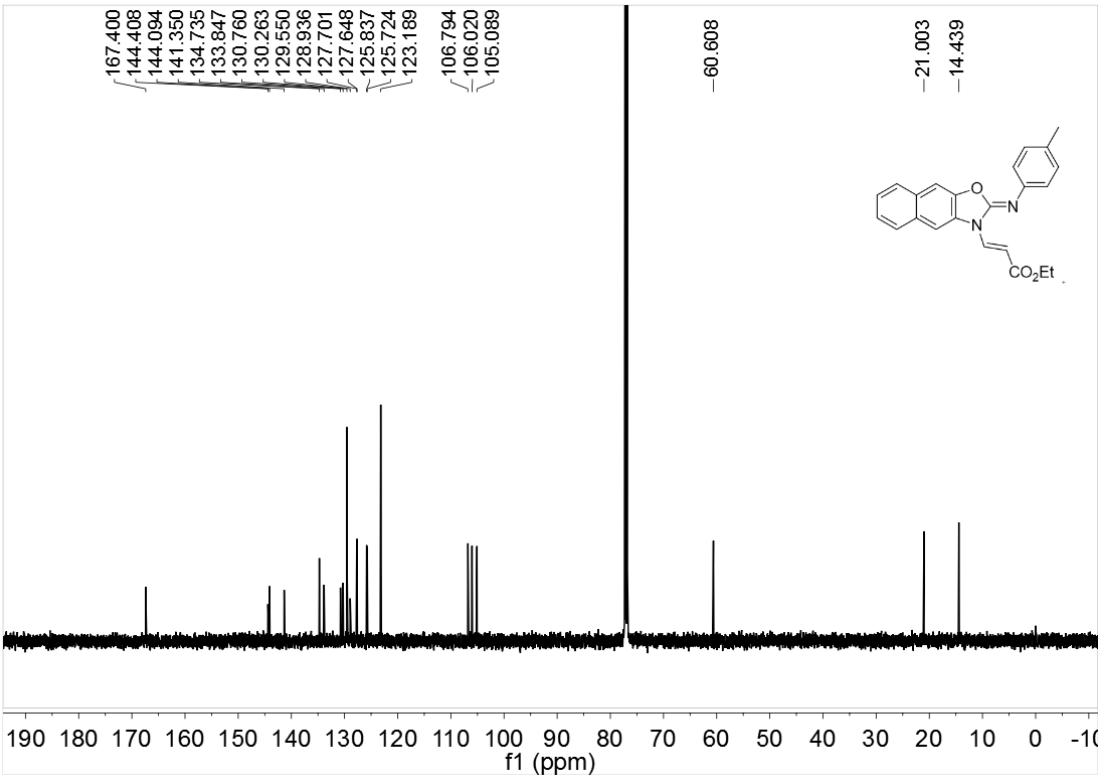


Figure 99. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3al**

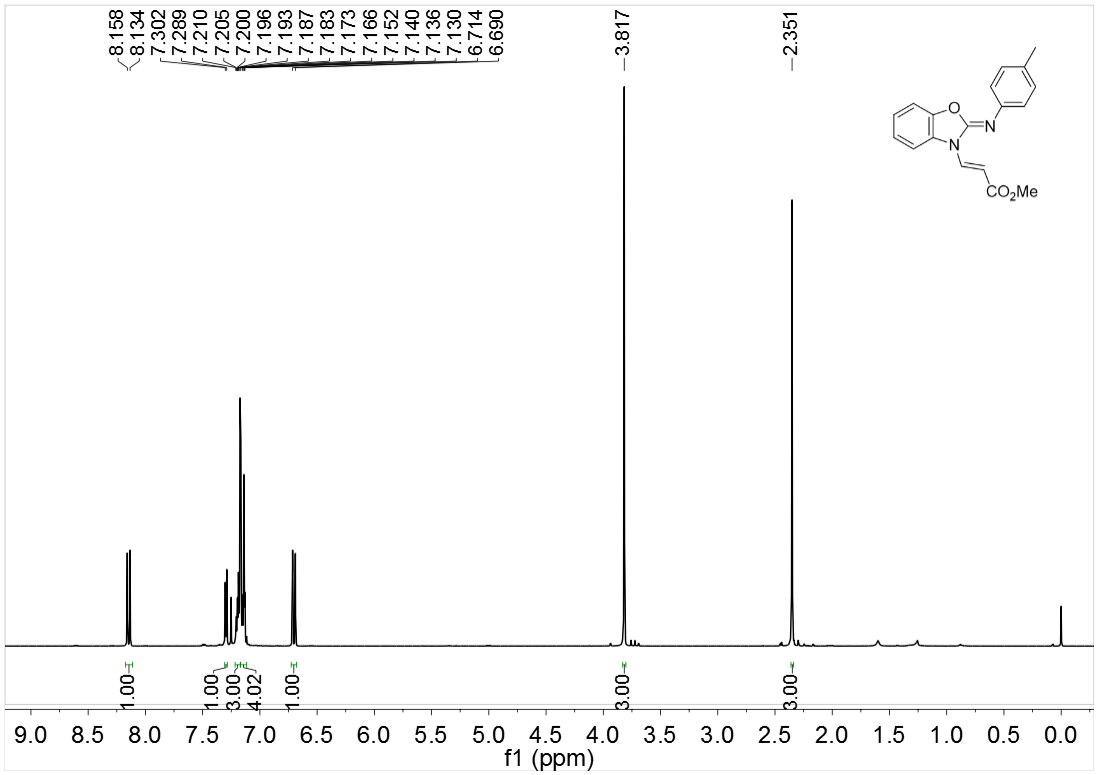


Figure 100. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3am**

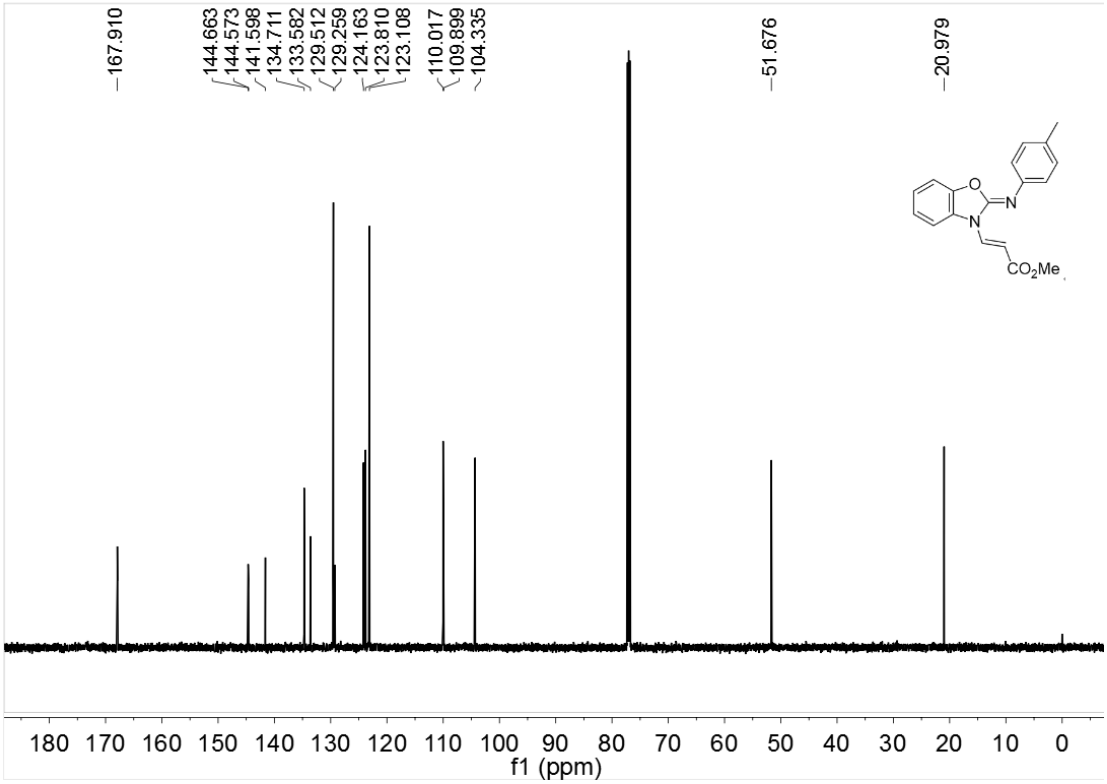


Figure 101. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3am**

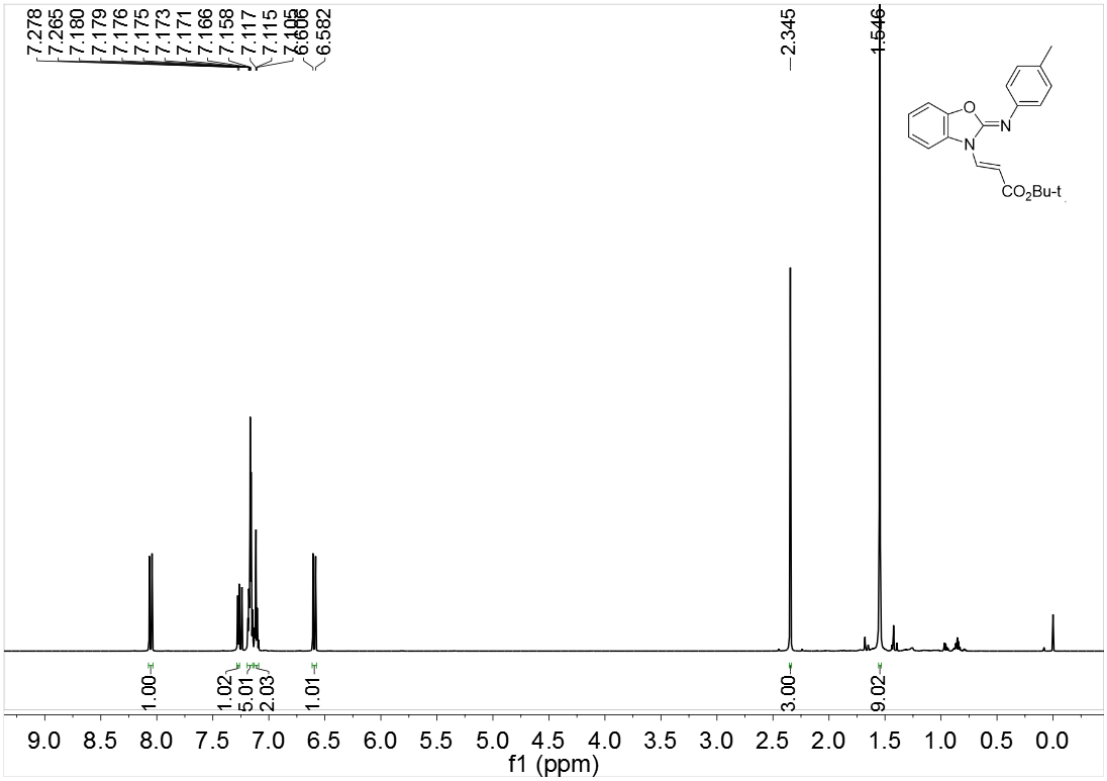


Figure 102. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3an**

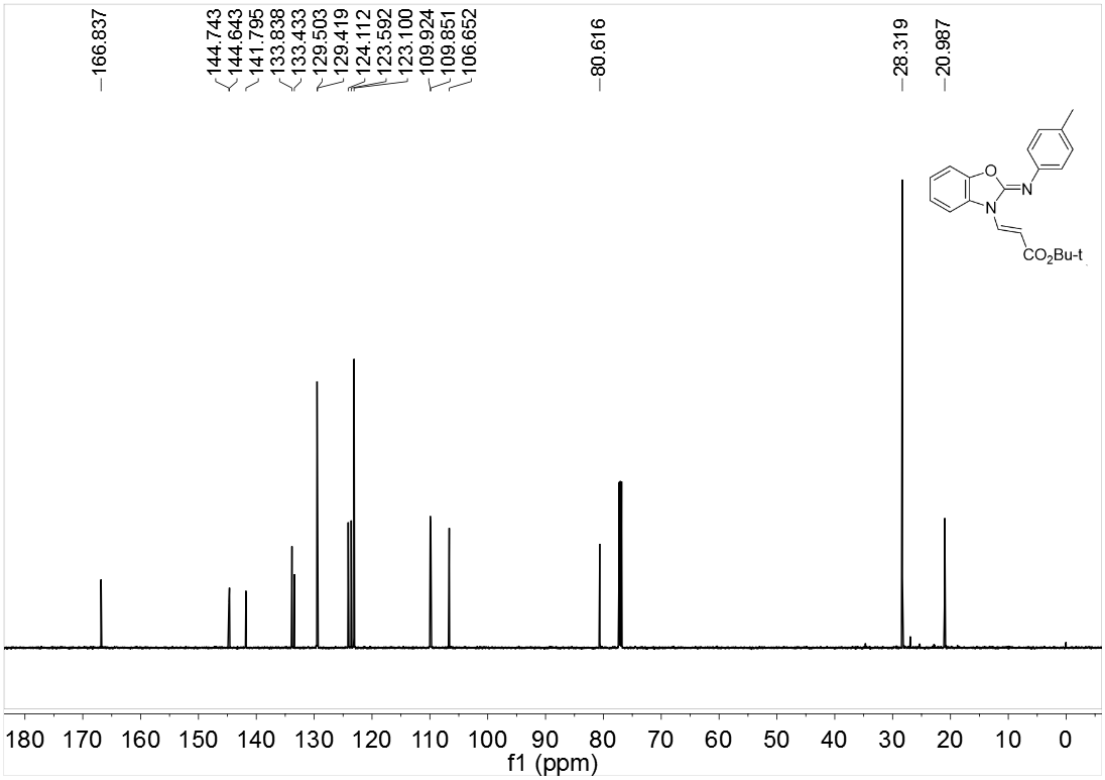


Figure 103. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3an**

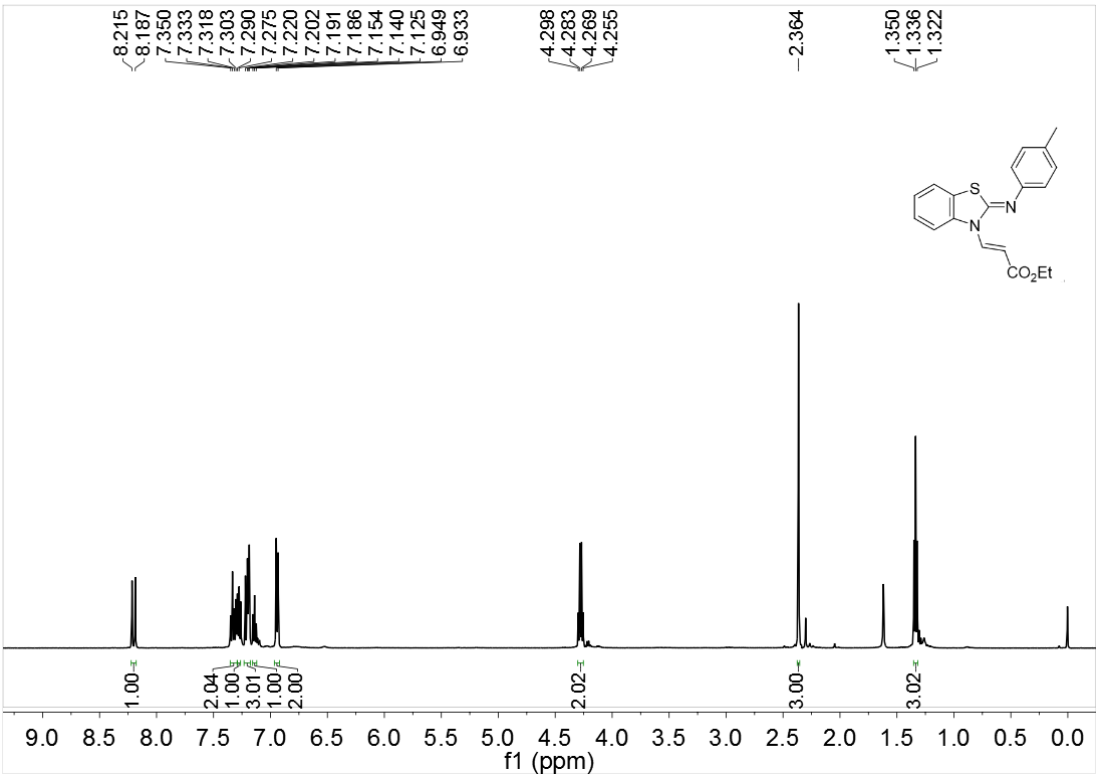


Figure 104. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3ao**

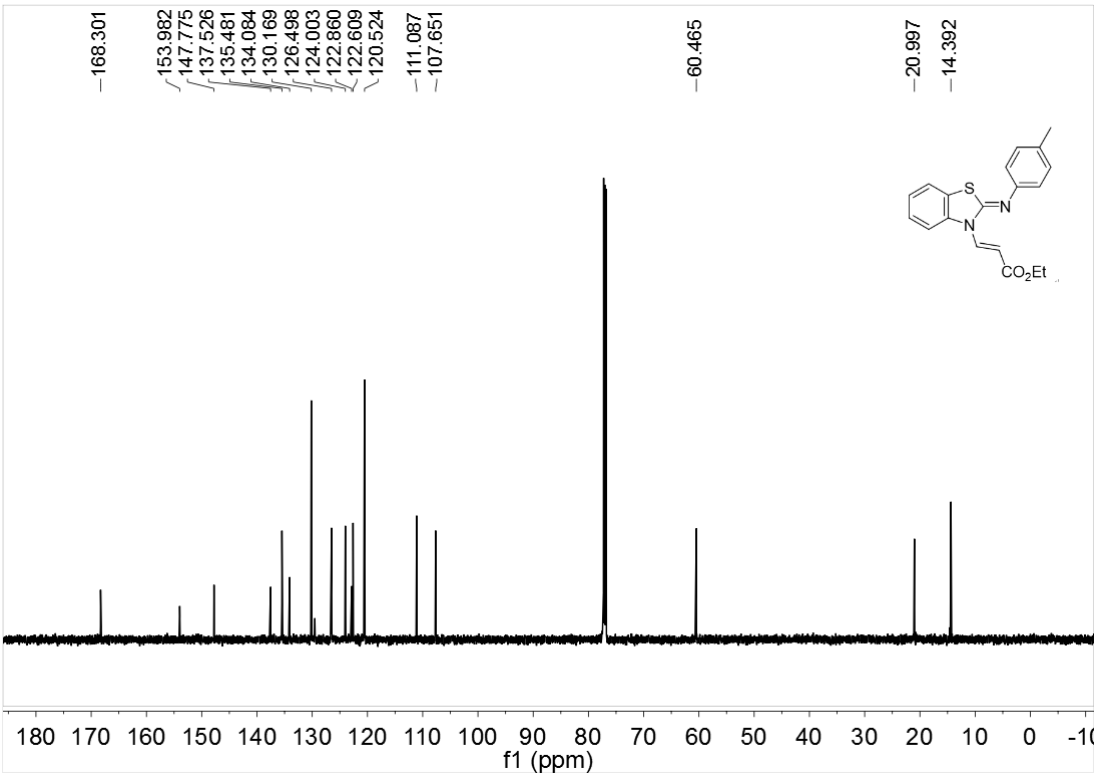


Figure 105. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ao**

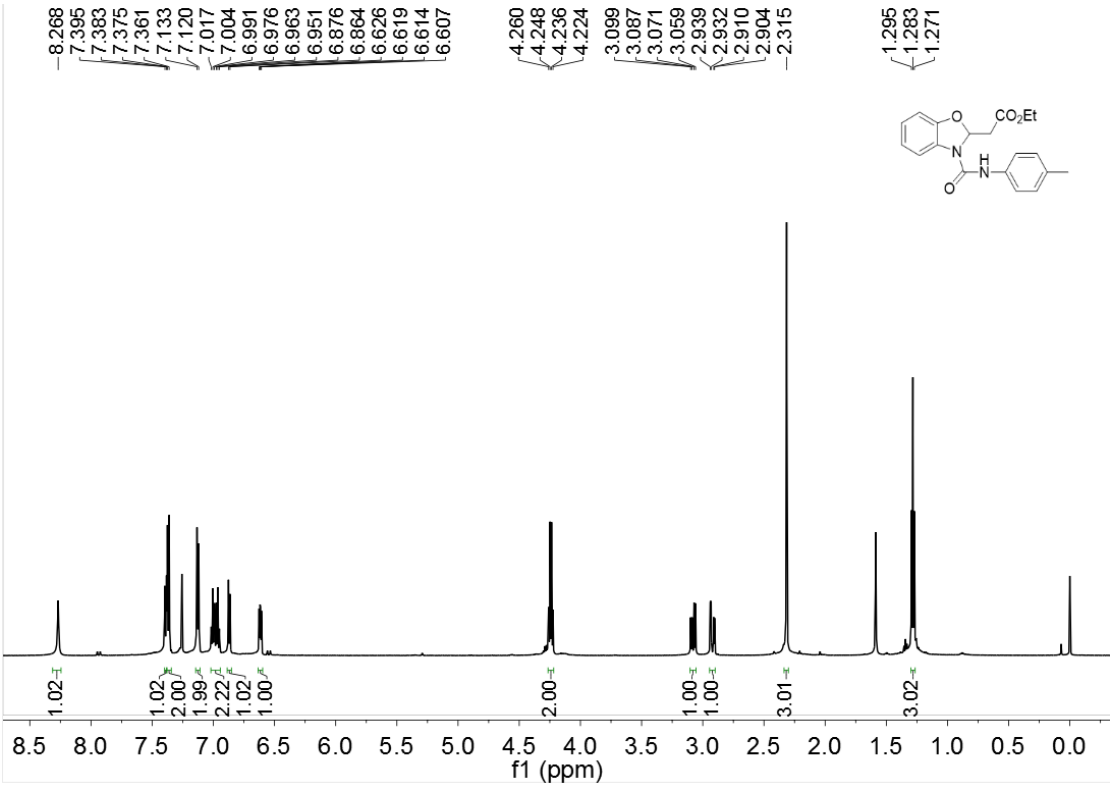


Figure 106. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **4a**

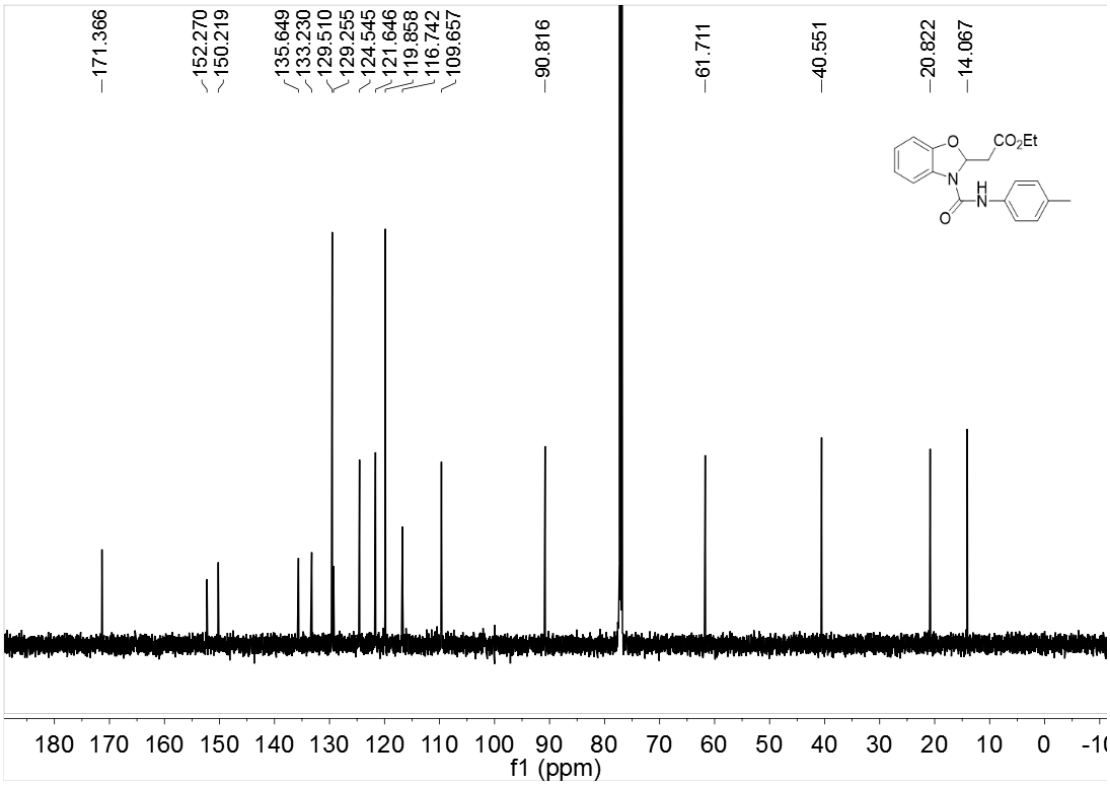


Figure 107. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4a**

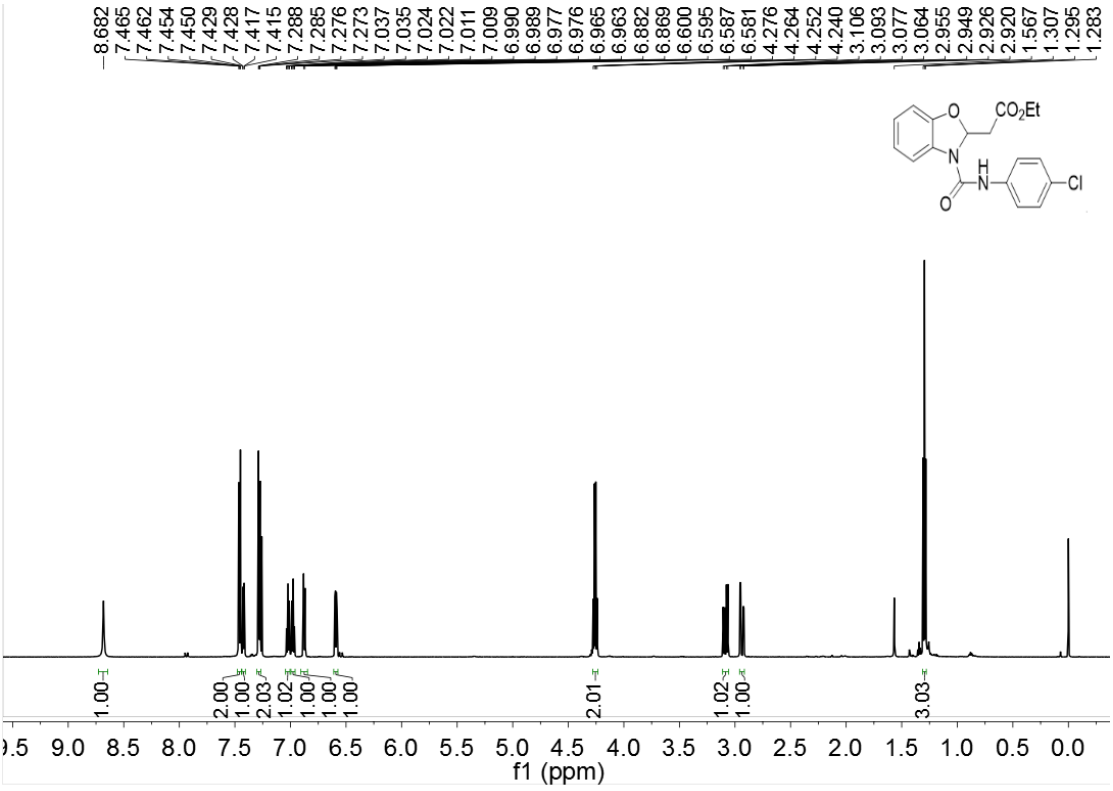


Figure 108. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **4b**

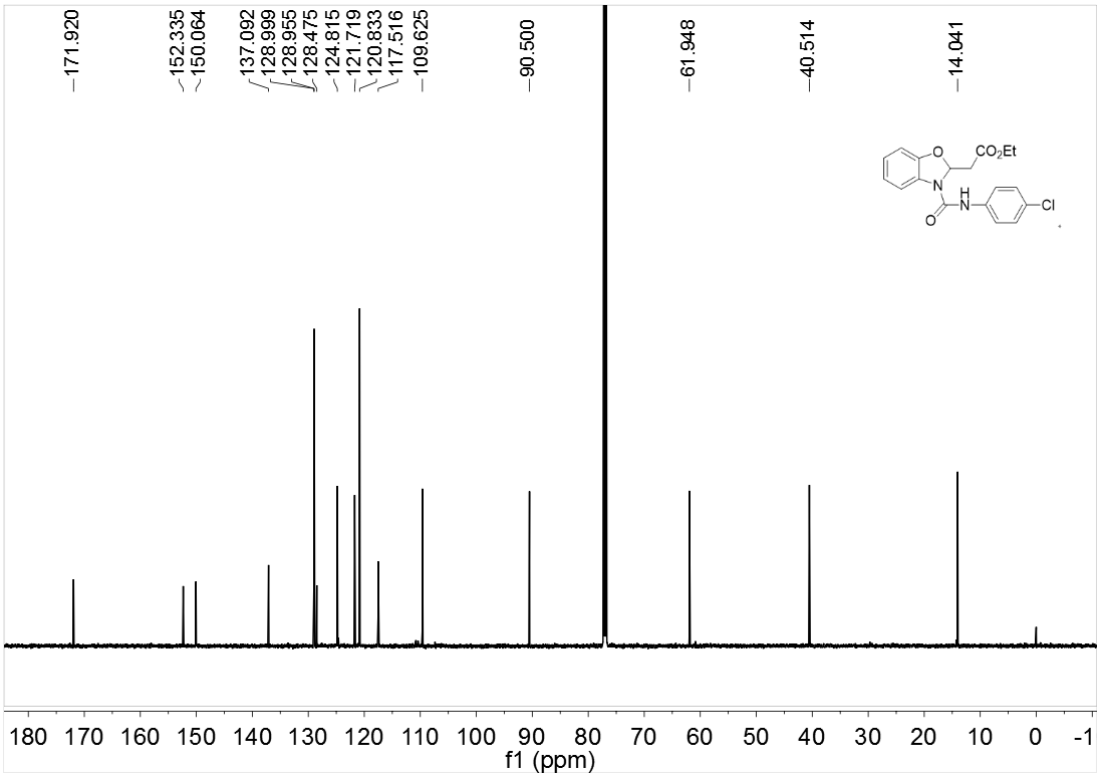


Figure 109. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4b**

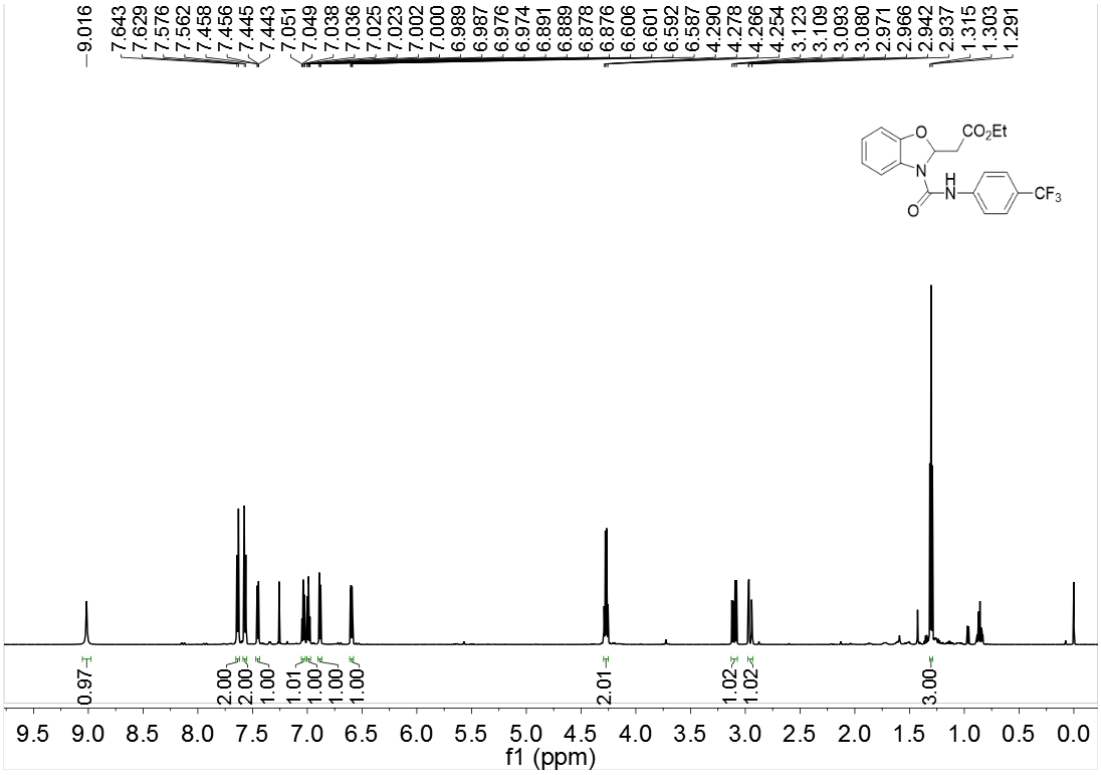


Figure 110. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **4c**

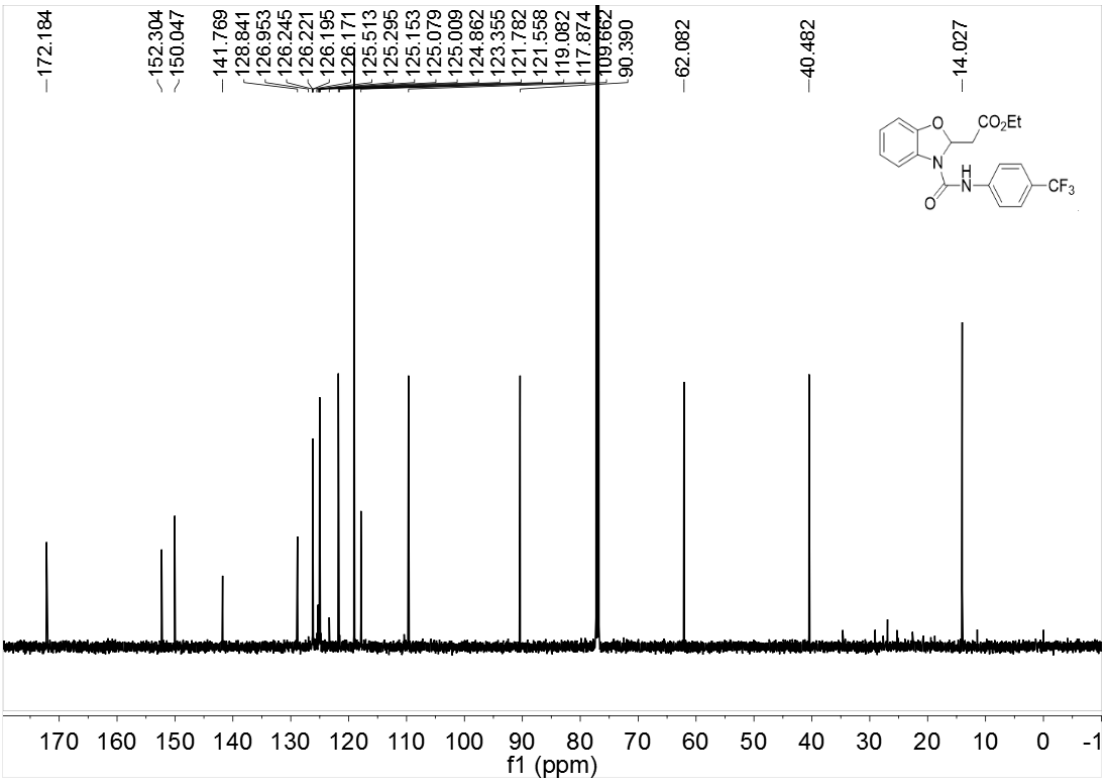


Figure 111. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4c**

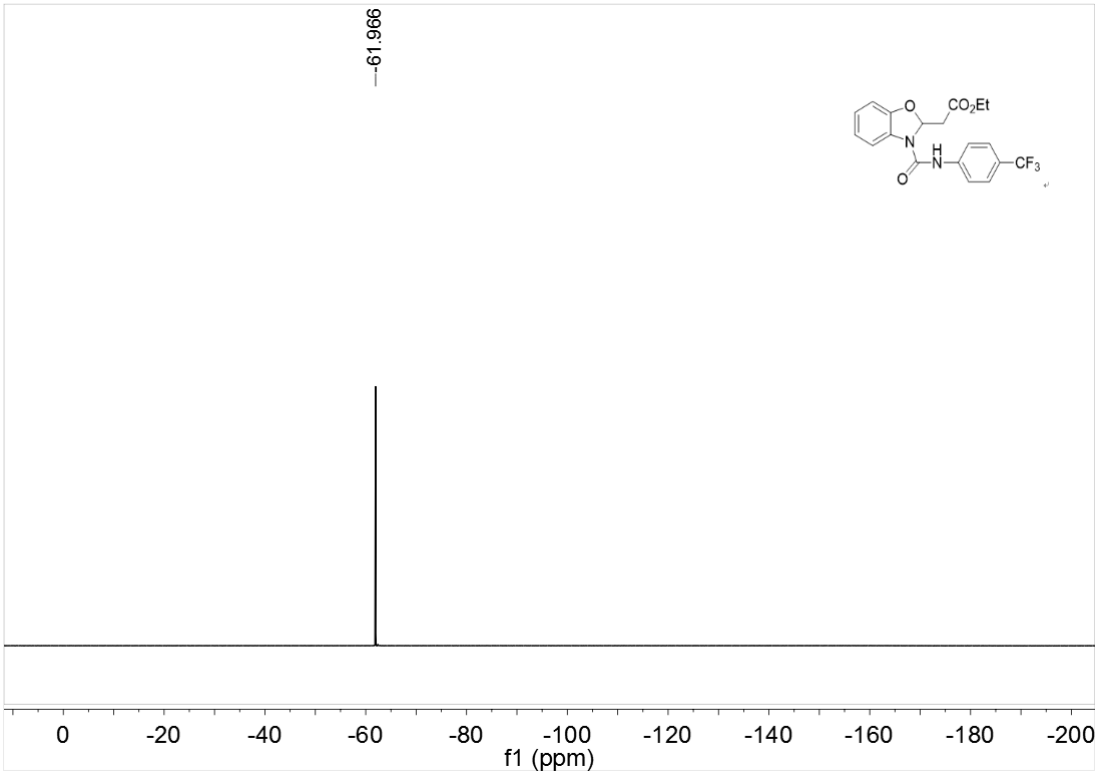


Figure 112. ^{19}F NMR spectrum (471 MHz, $CDCl_3$) of **4c**

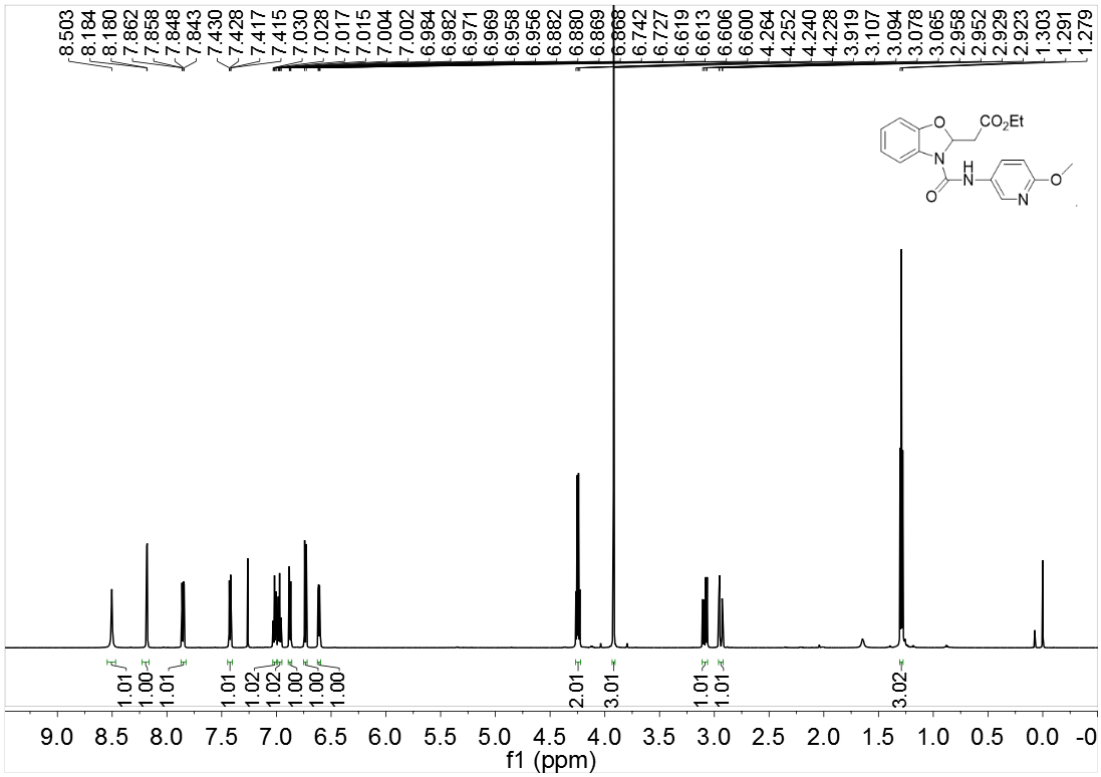


Figure 113. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **4d**

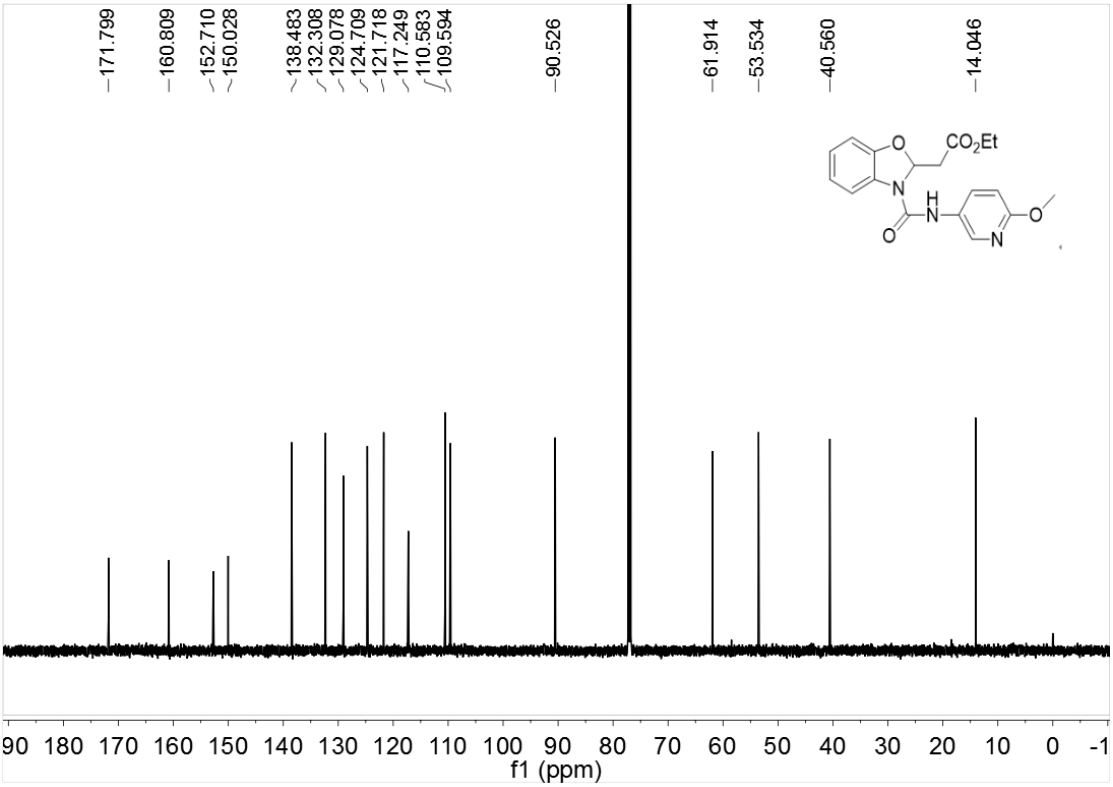


Figure 114. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4d**

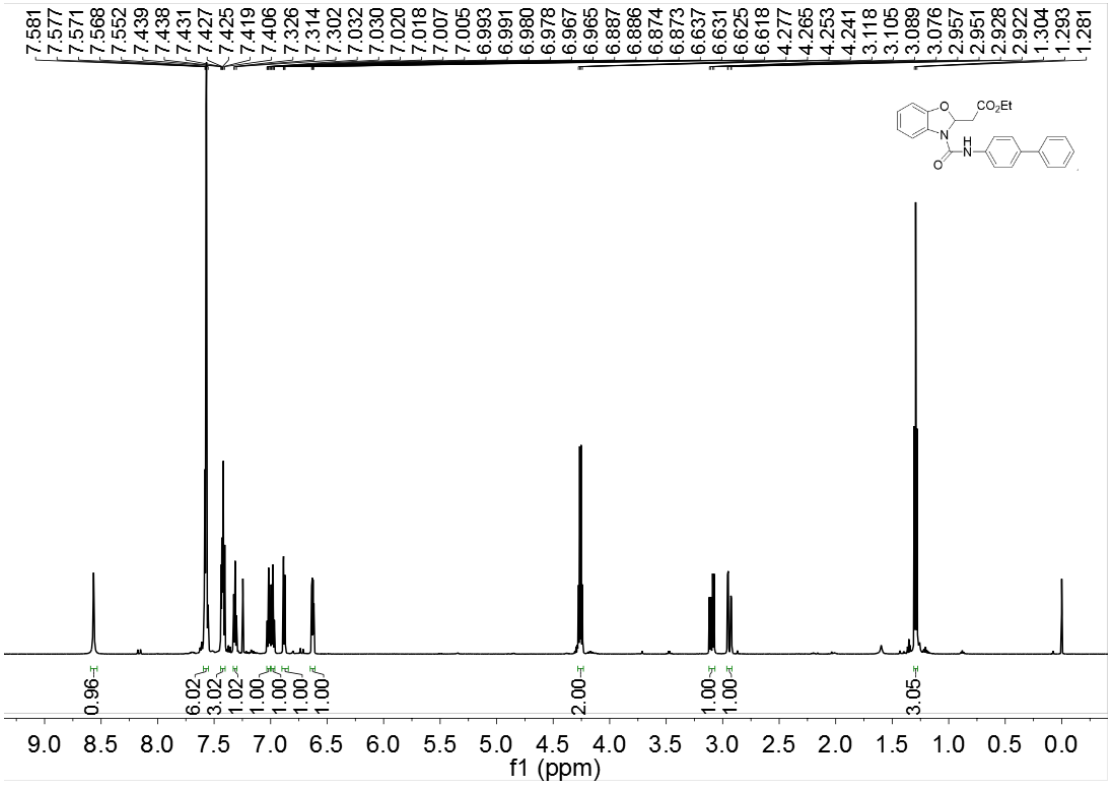


Figure 115. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **4e**

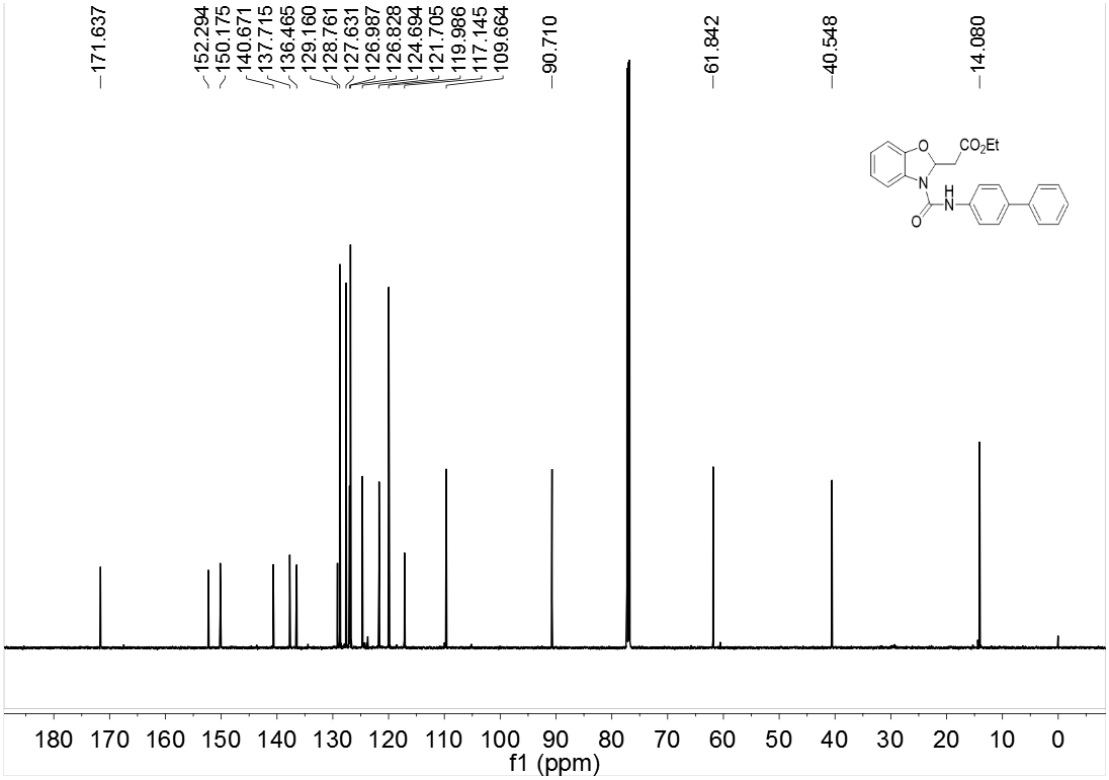


Figure 116. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4e**

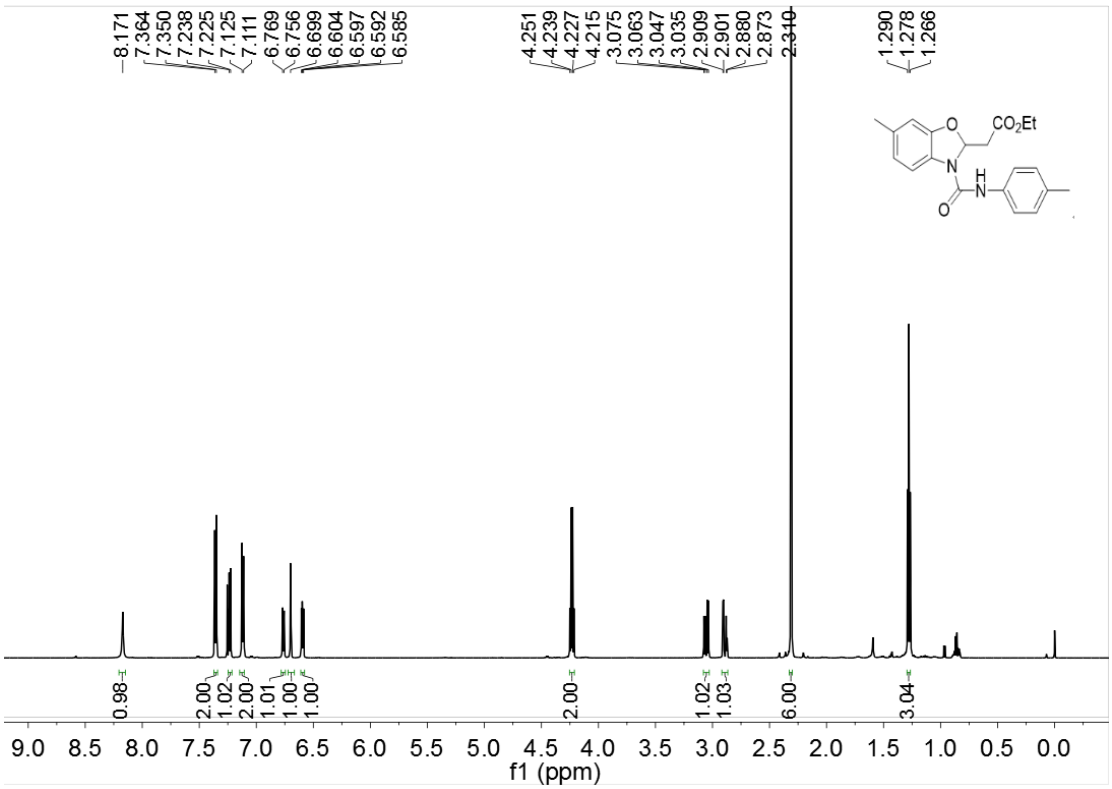


Figure 117. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **4f**

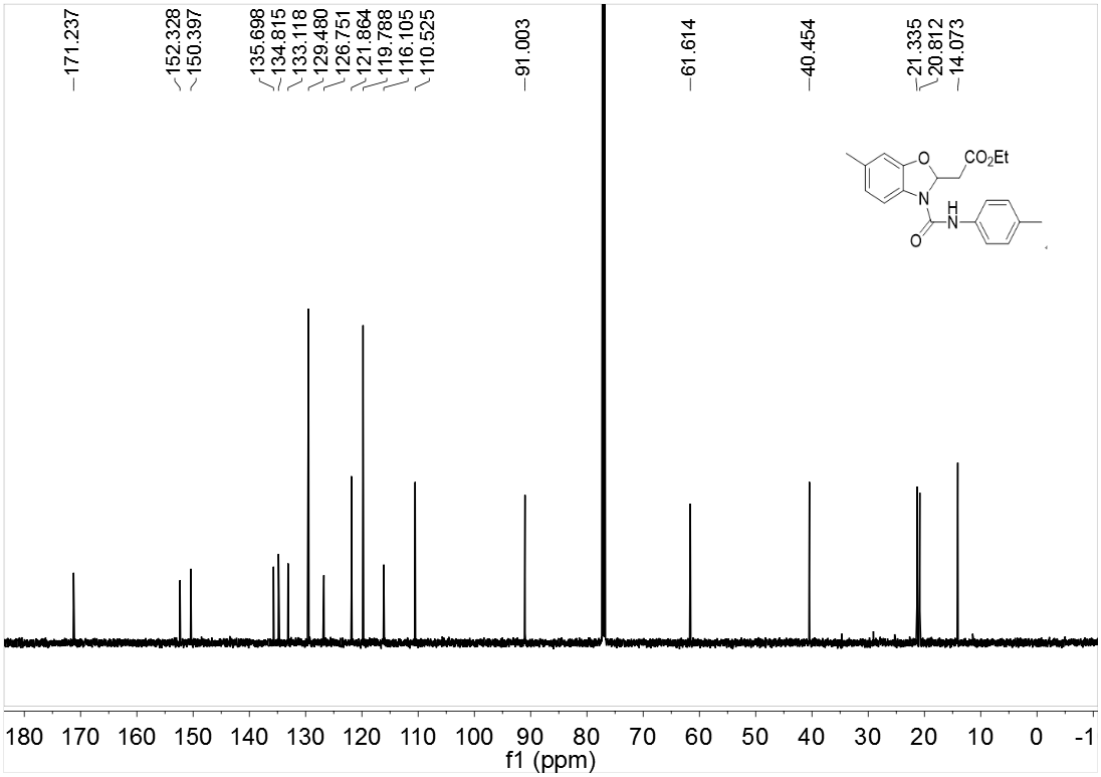


Figure 118. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4f**

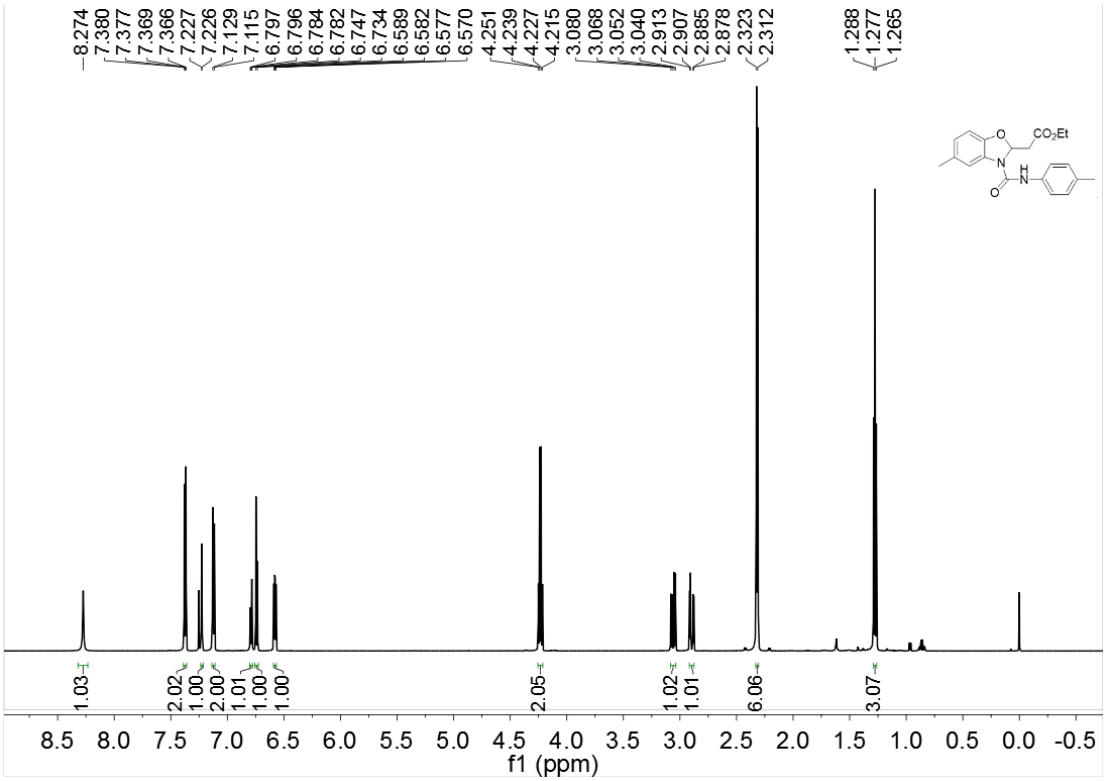


Figure 119. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **4g**

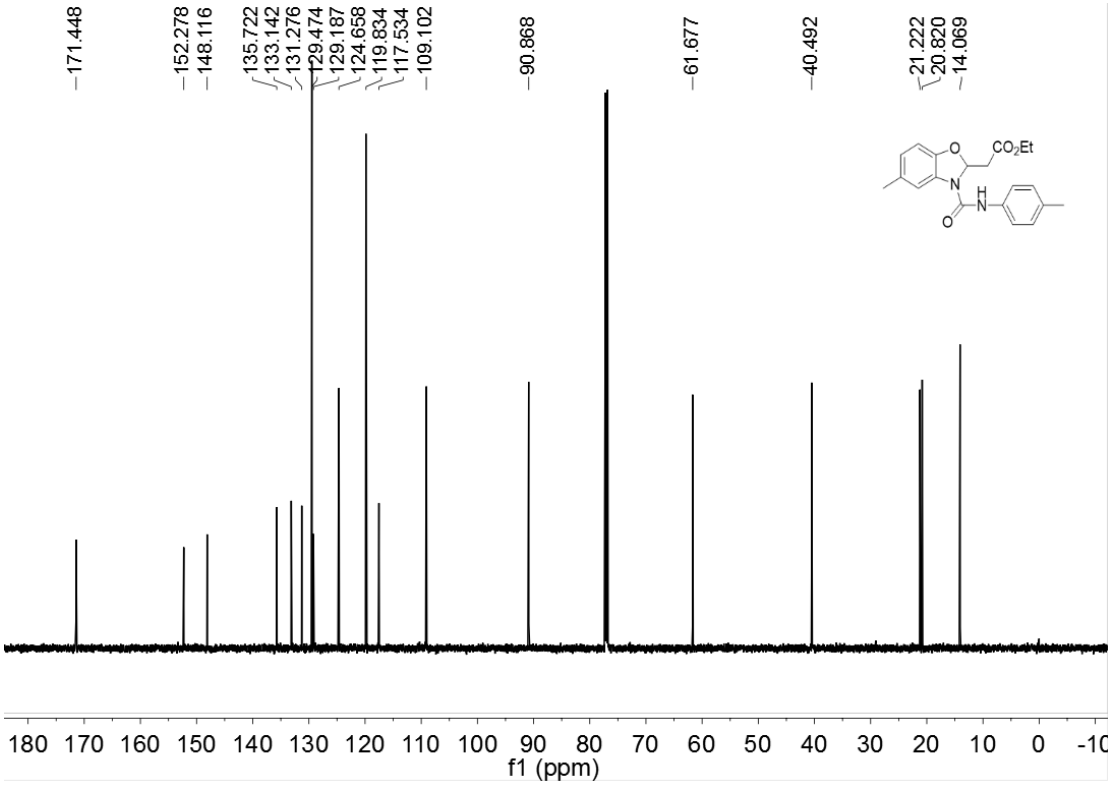


Figure 120. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4g**

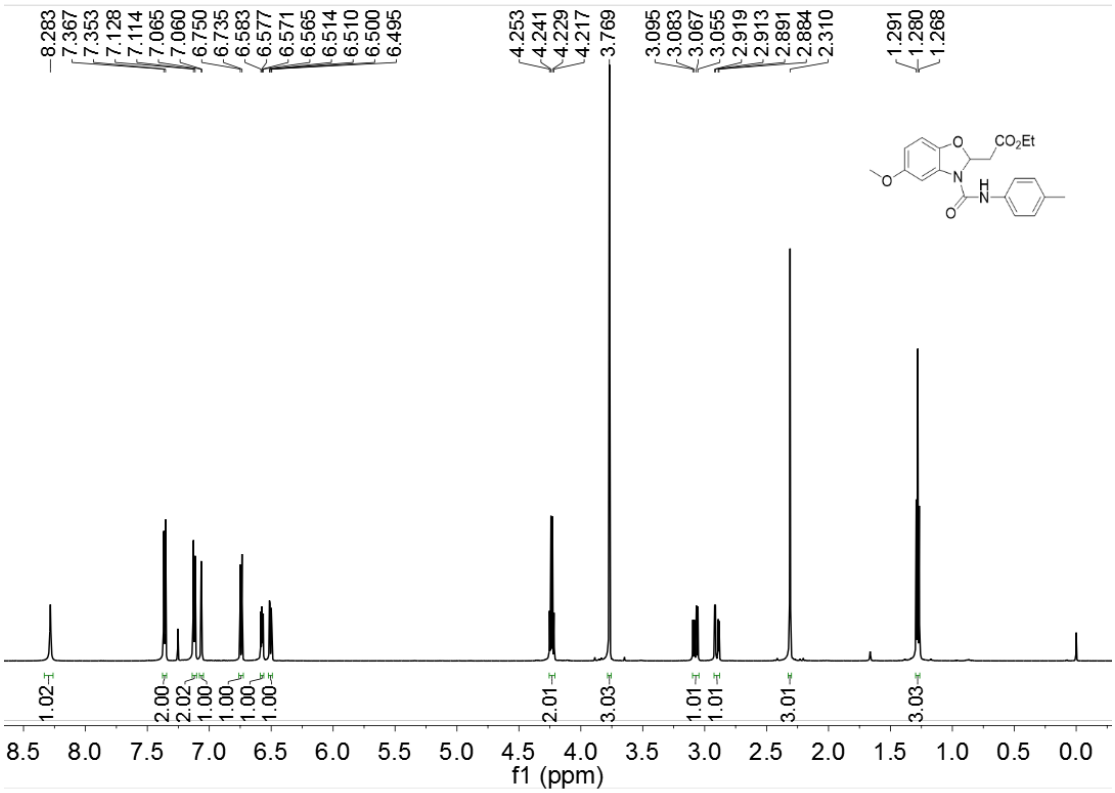


Figure 121. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **4h**

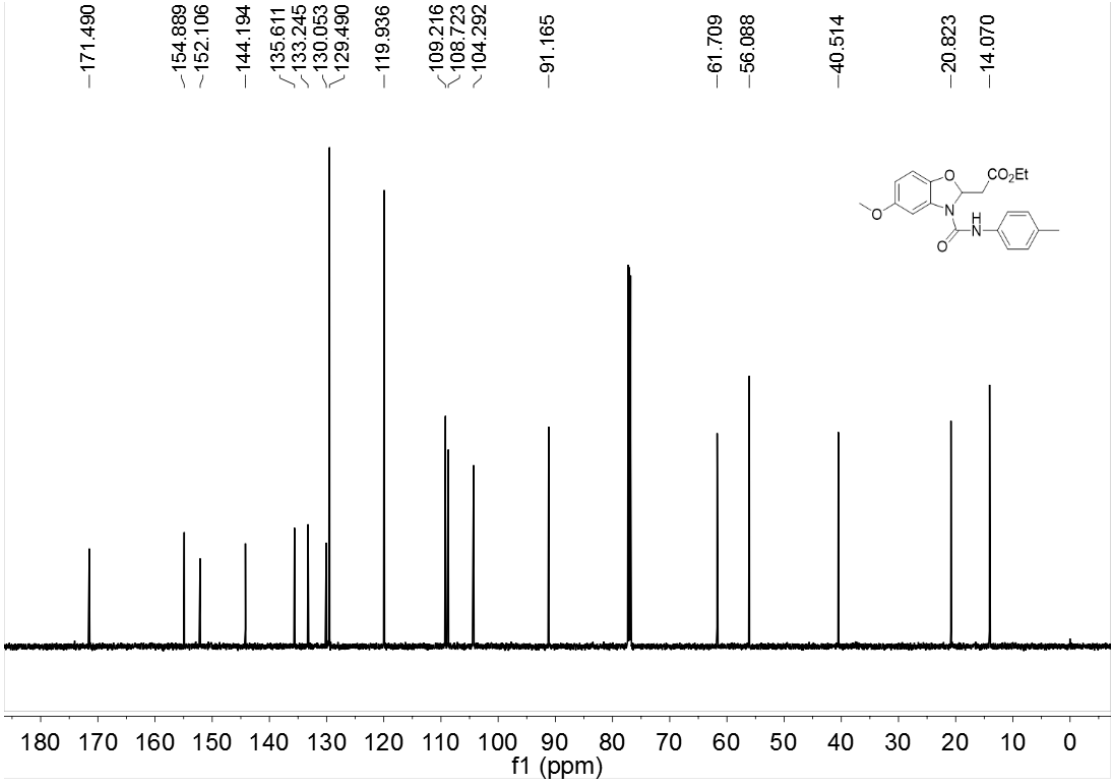


Figure 122. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4h**

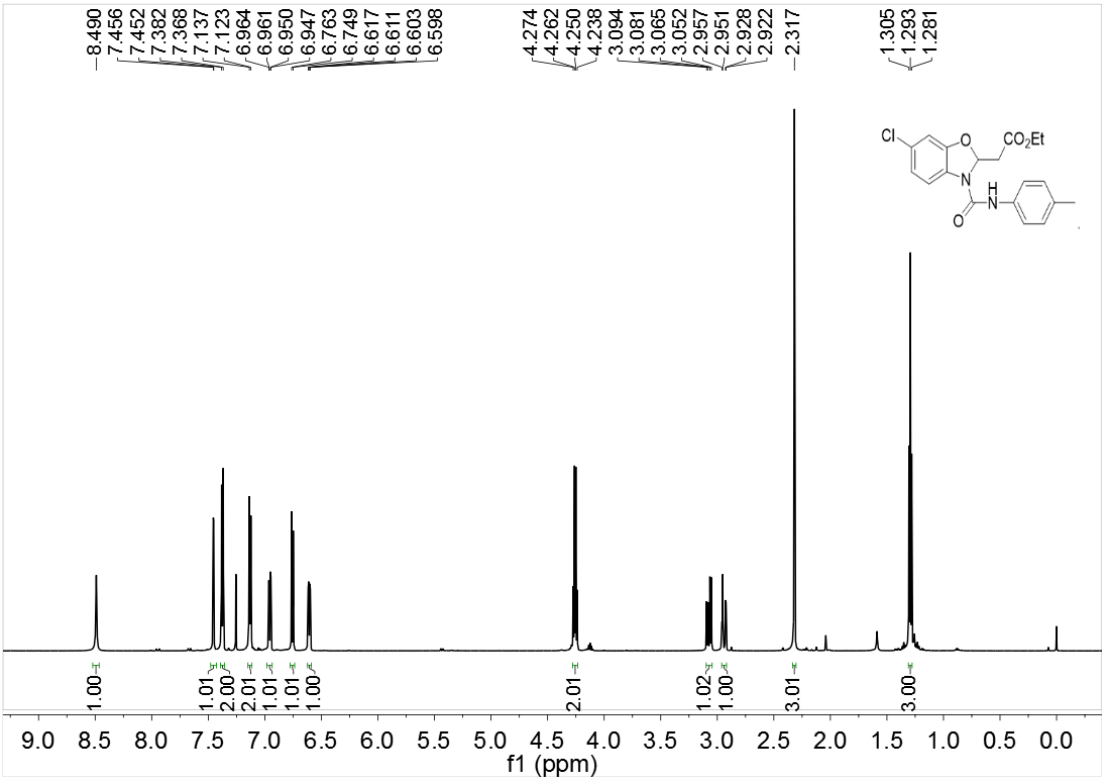


Figure 123. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **4i**

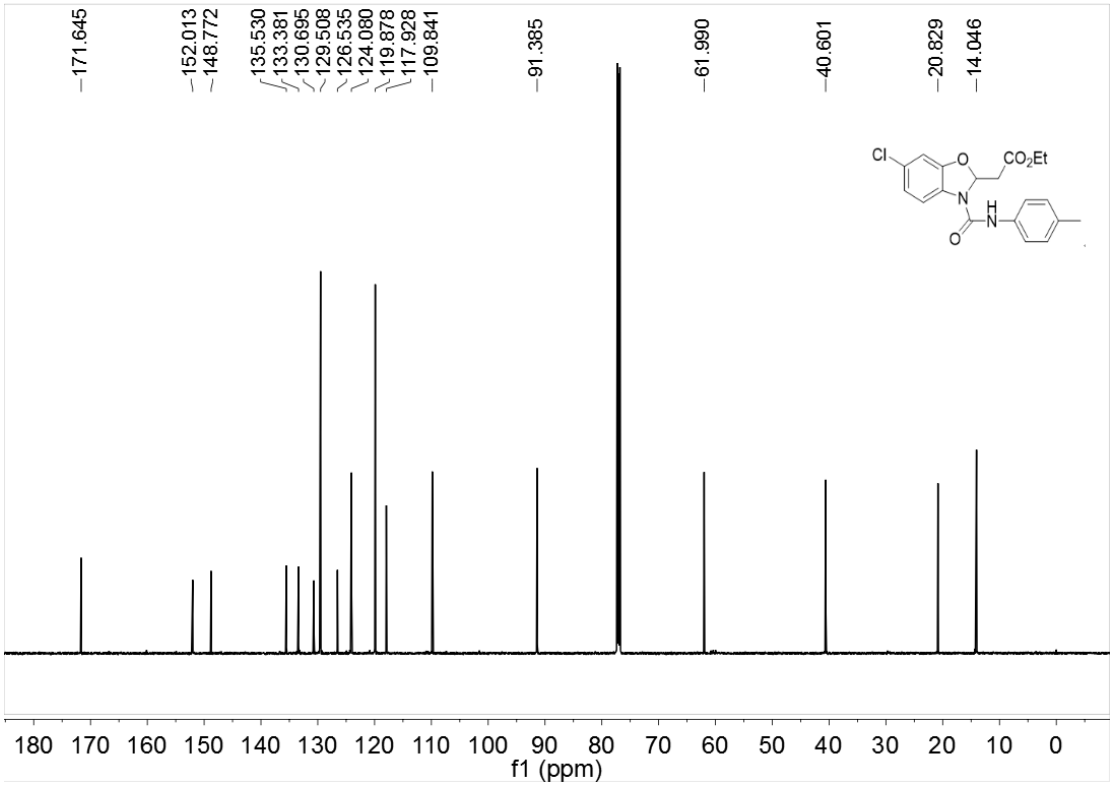


Figure 124. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4i**

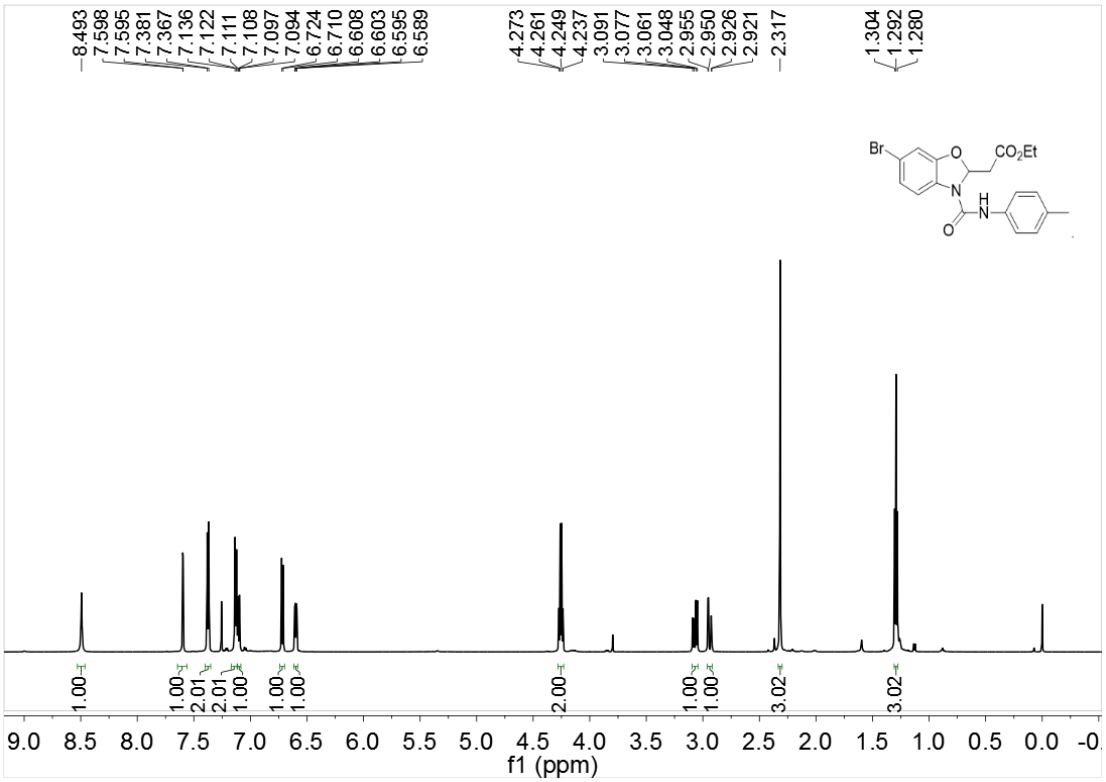


Figure 125. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **4j**

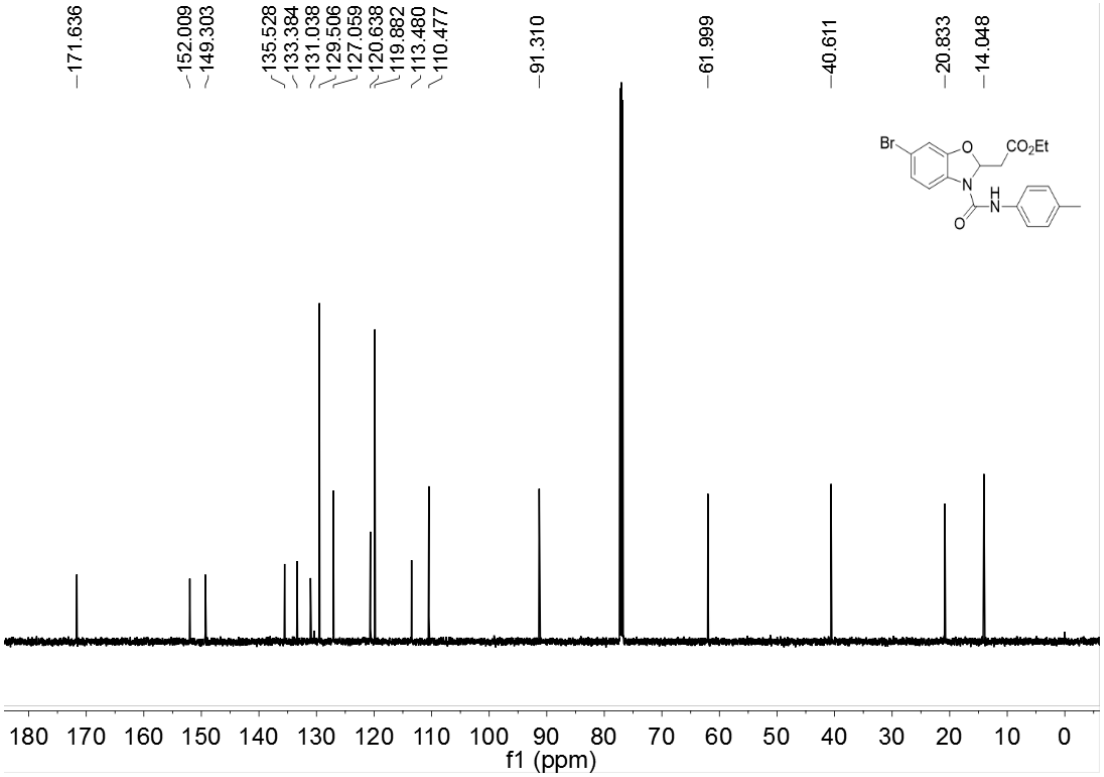


Figure 126. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4j**

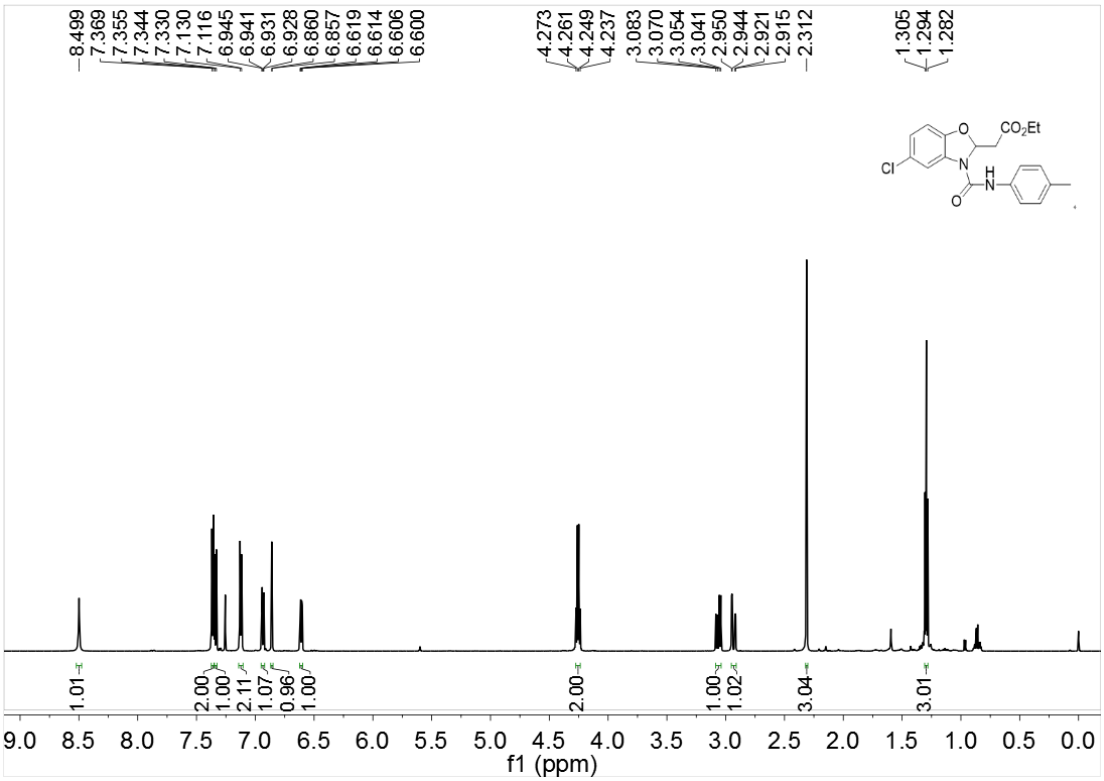


Figure 127. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **4k**

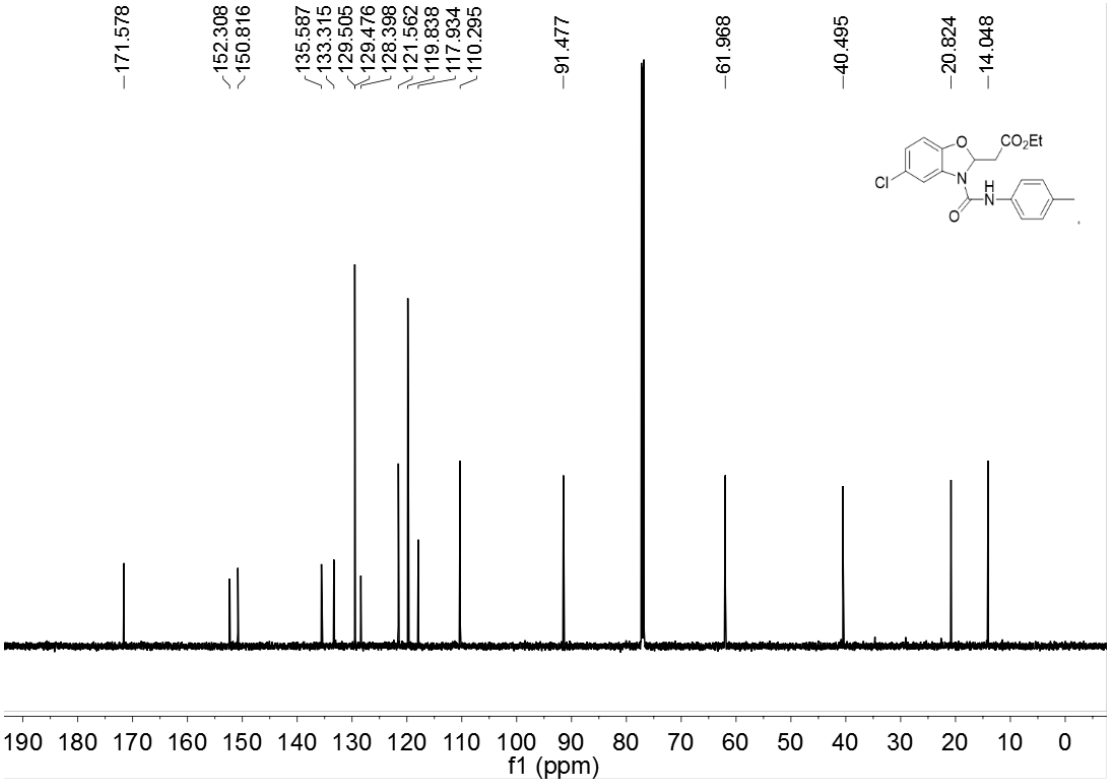


Figure 128. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4k**

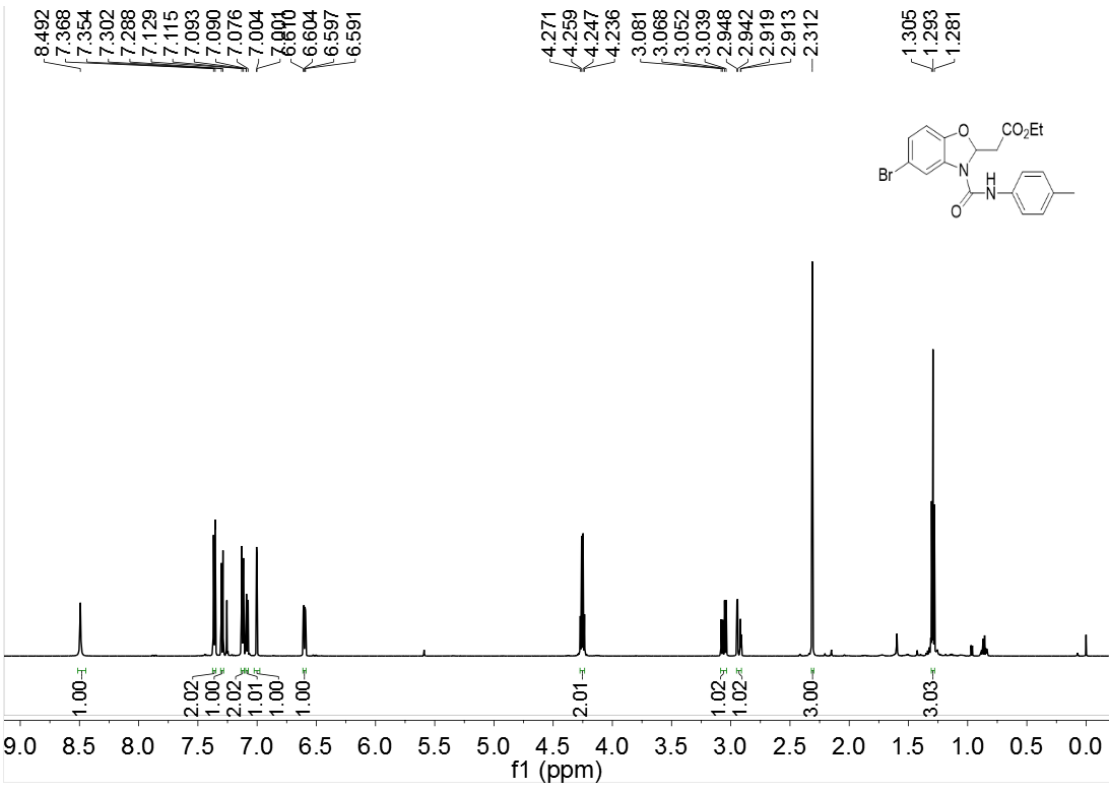


Figure 129. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **4l**

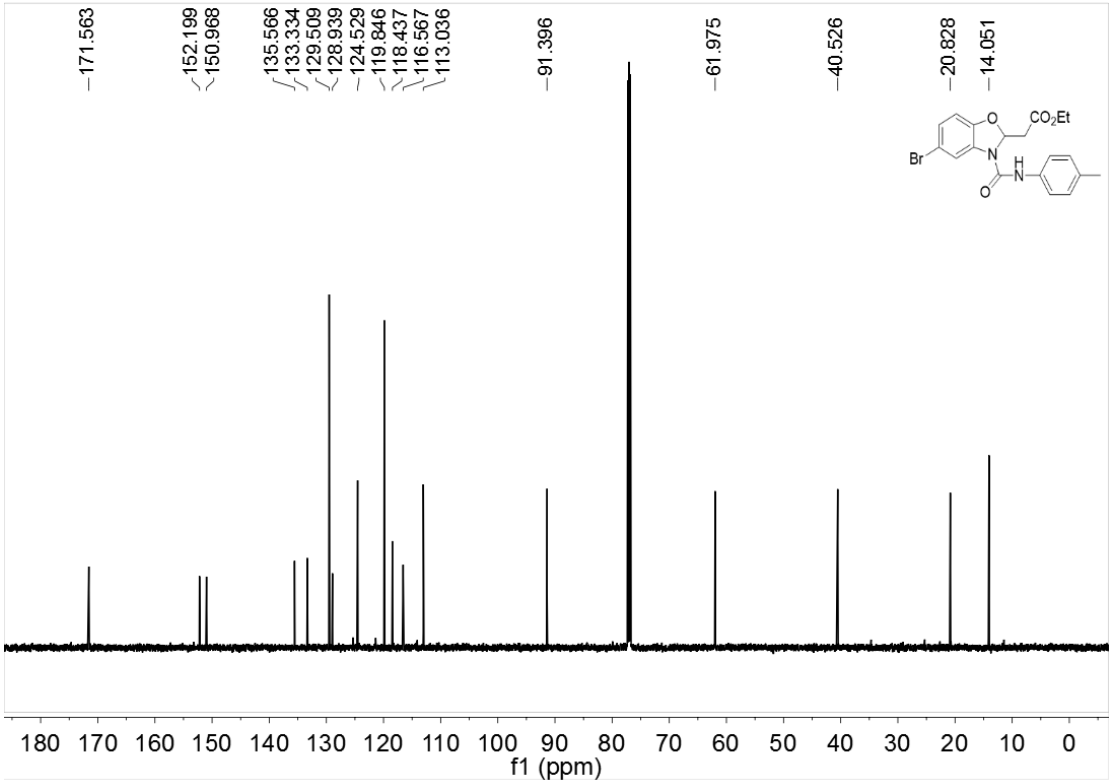


Figure 130. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4l**

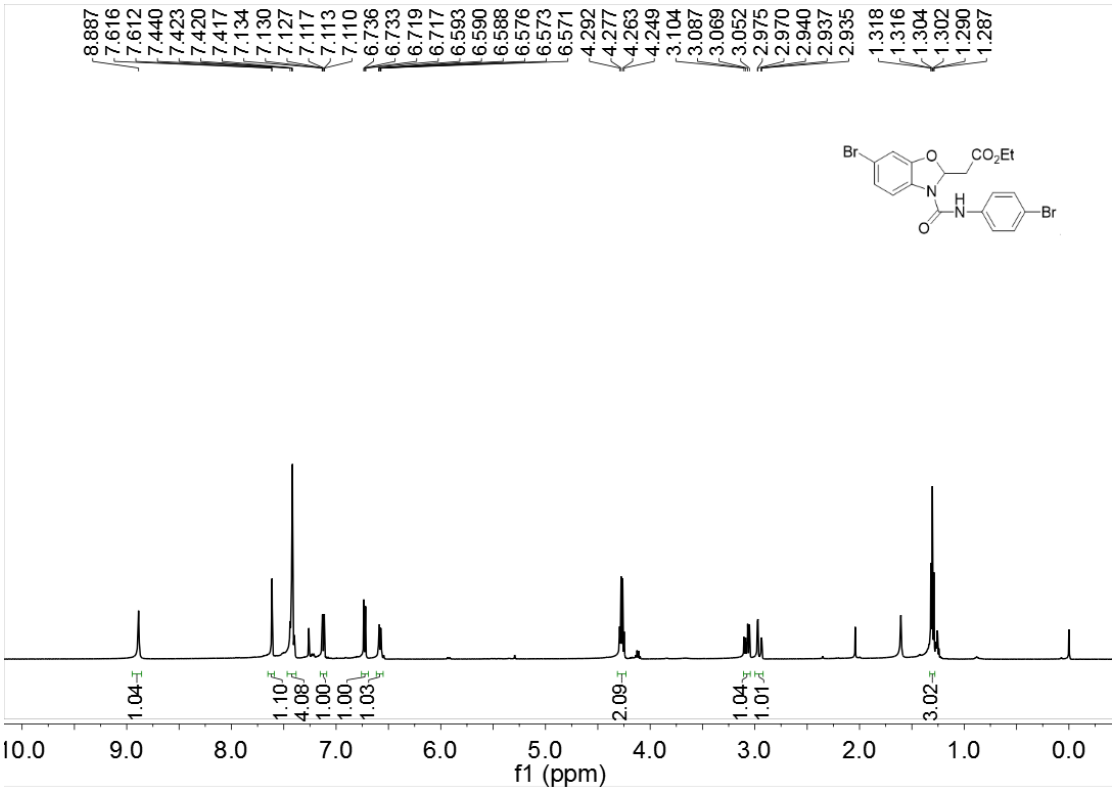


Figure 131. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **4m**

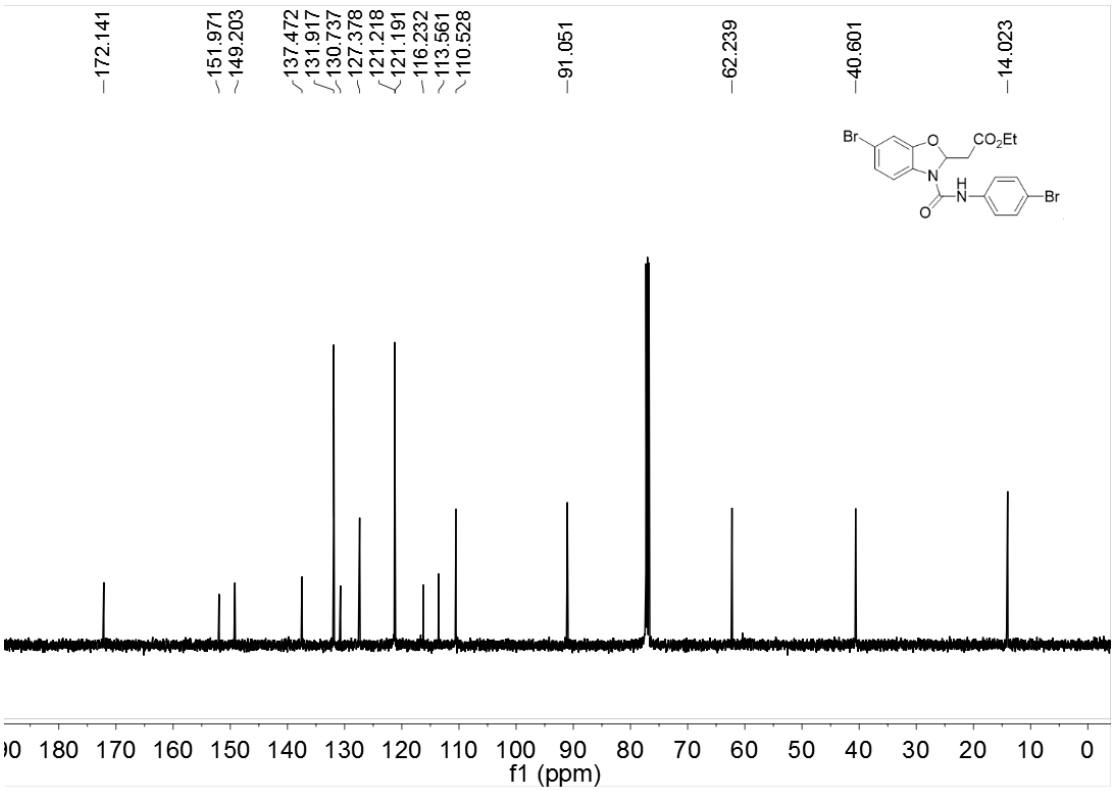


Figure 132. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4m**

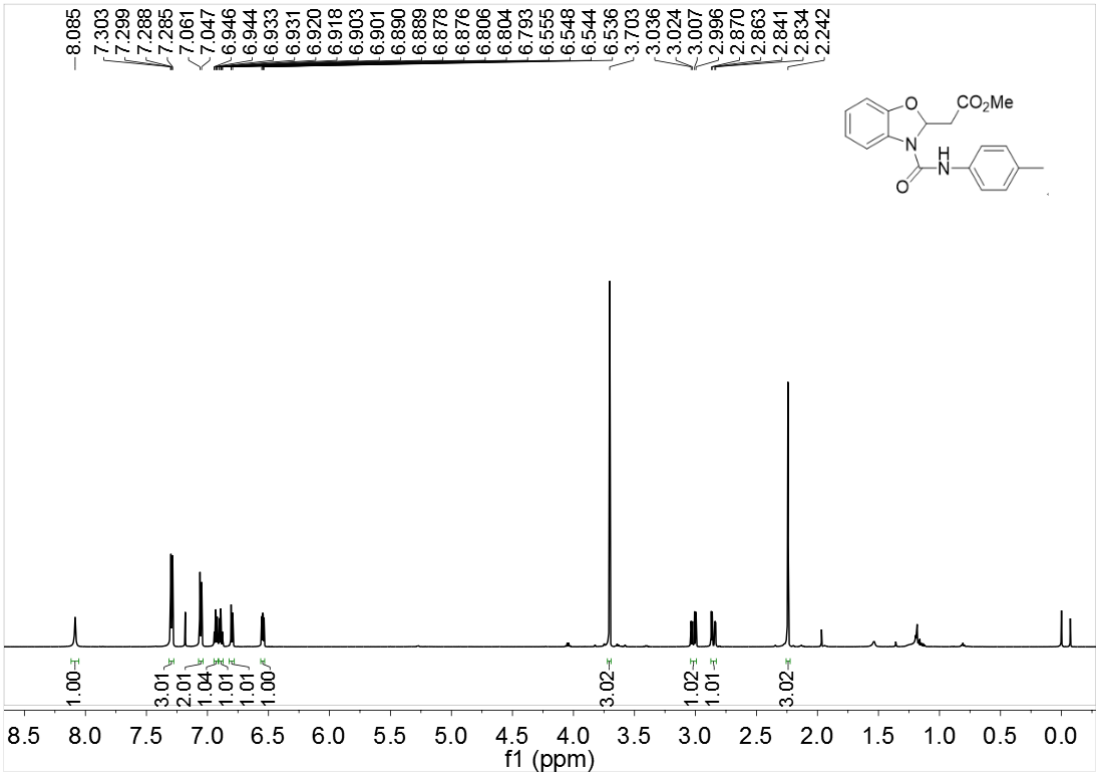


Figure 133. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **4n**

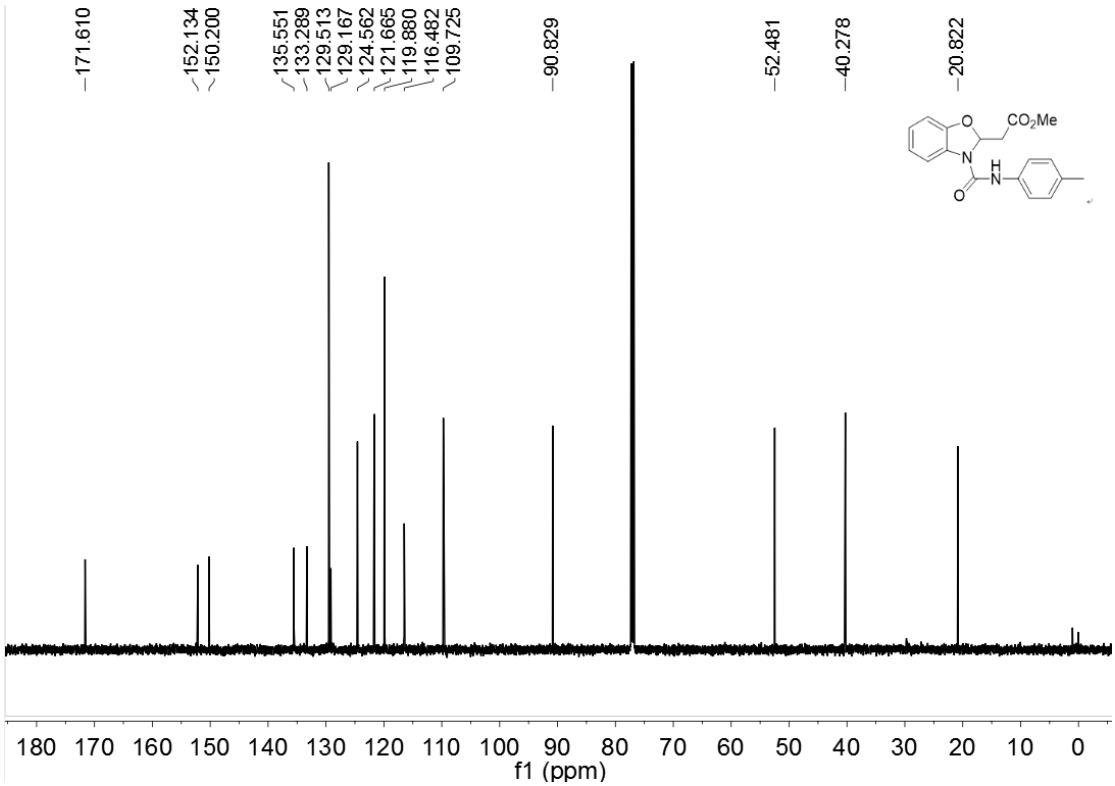


Figure 134. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4n**

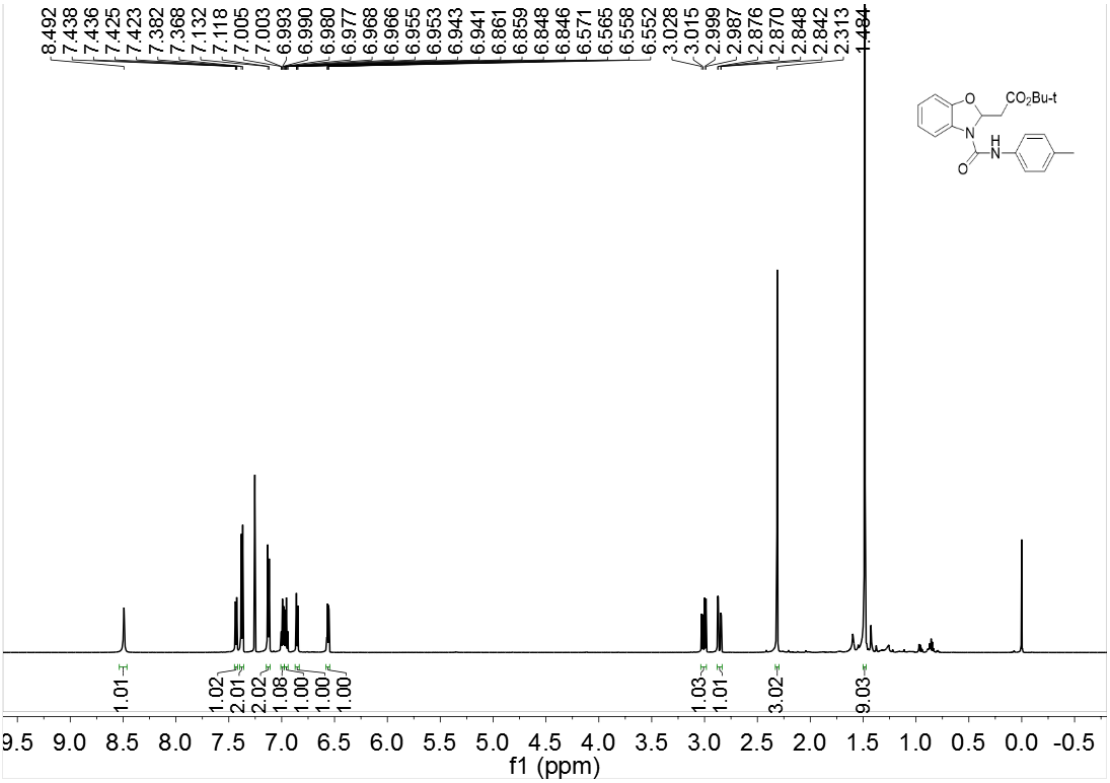


Figure 135. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **4o**

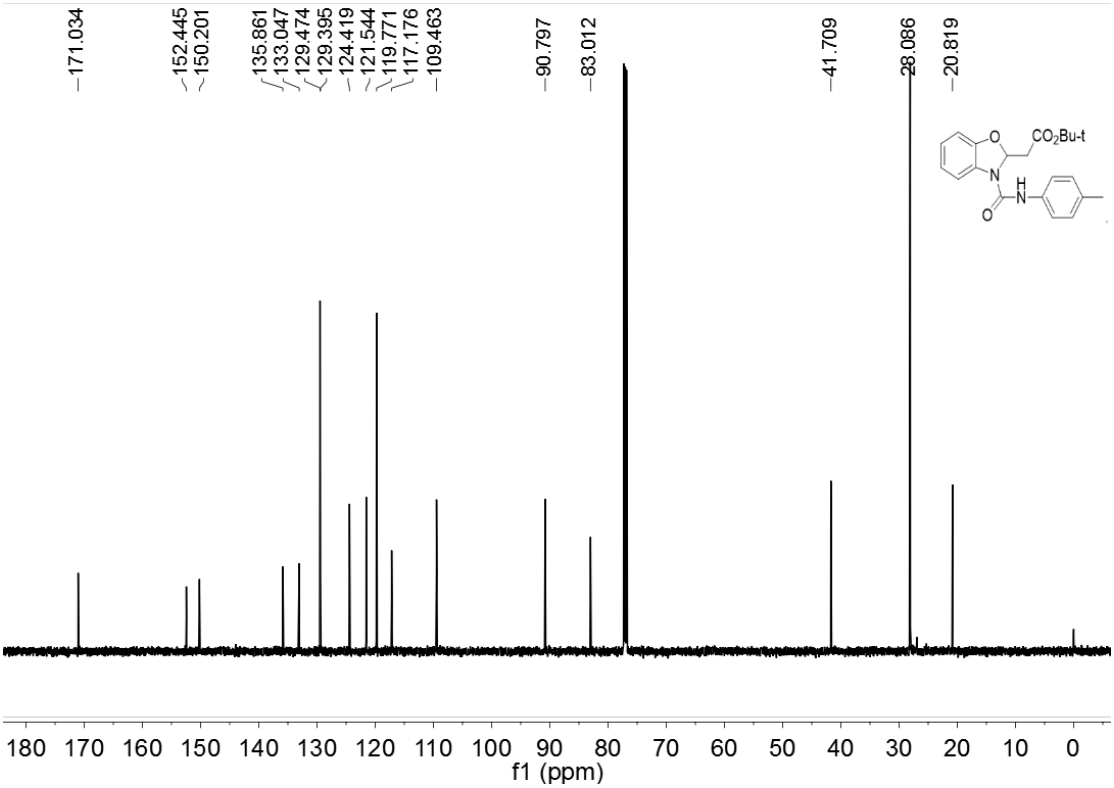


Figure 136. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4o**

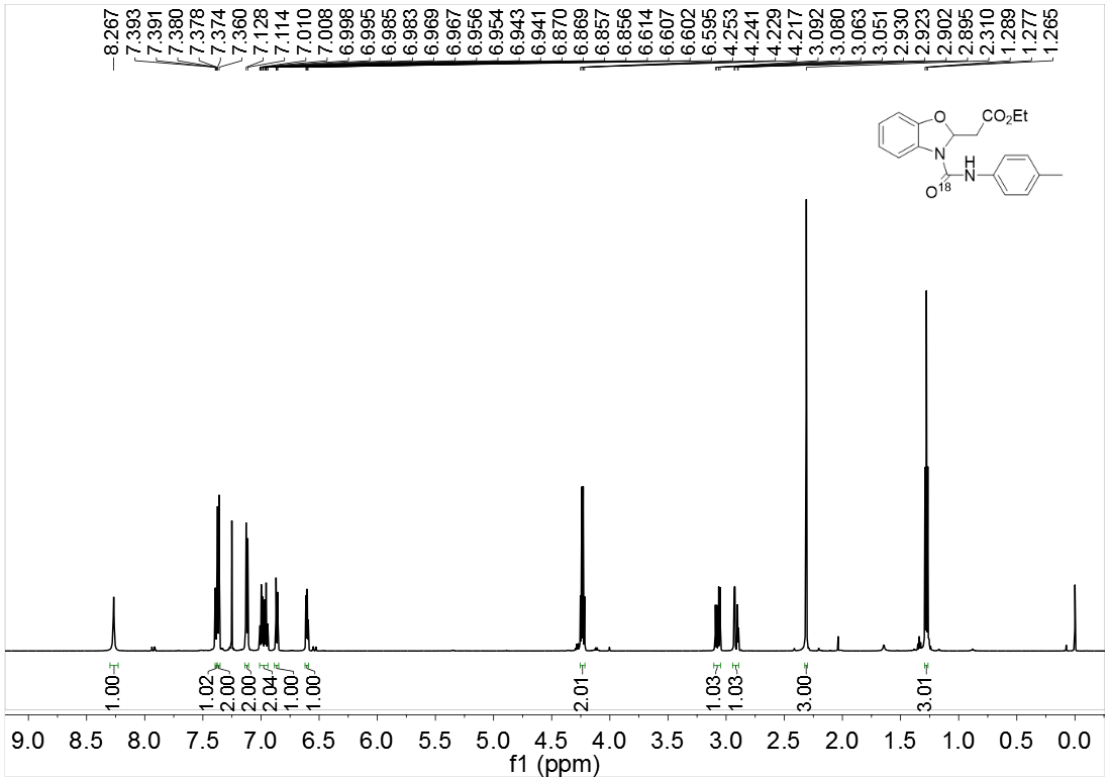


Figure 137. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **4a'**

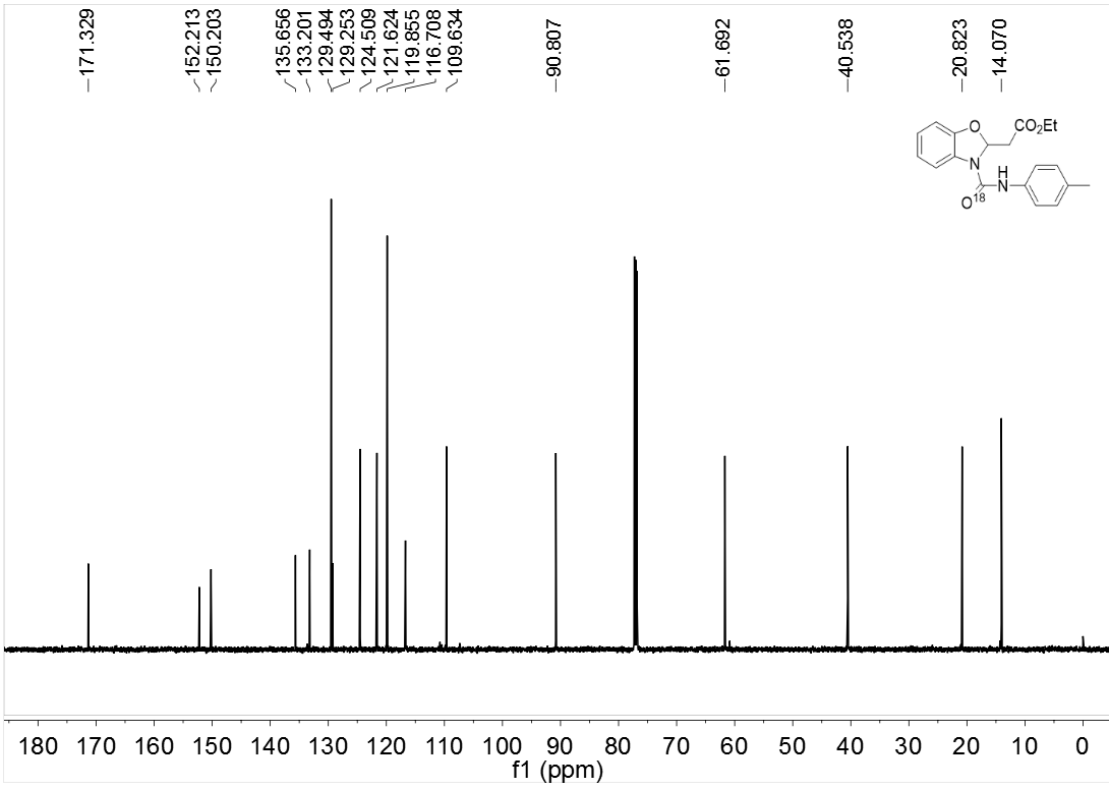


Figure 138. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4a'**

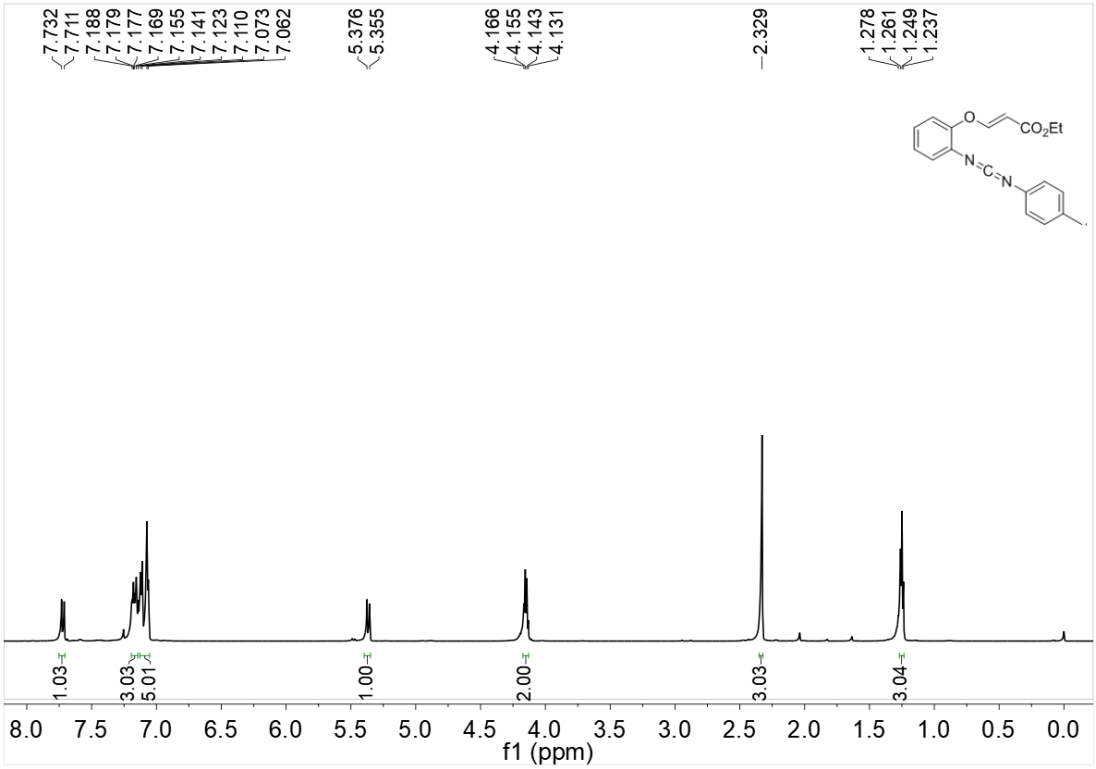


Figure 139. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **5a**

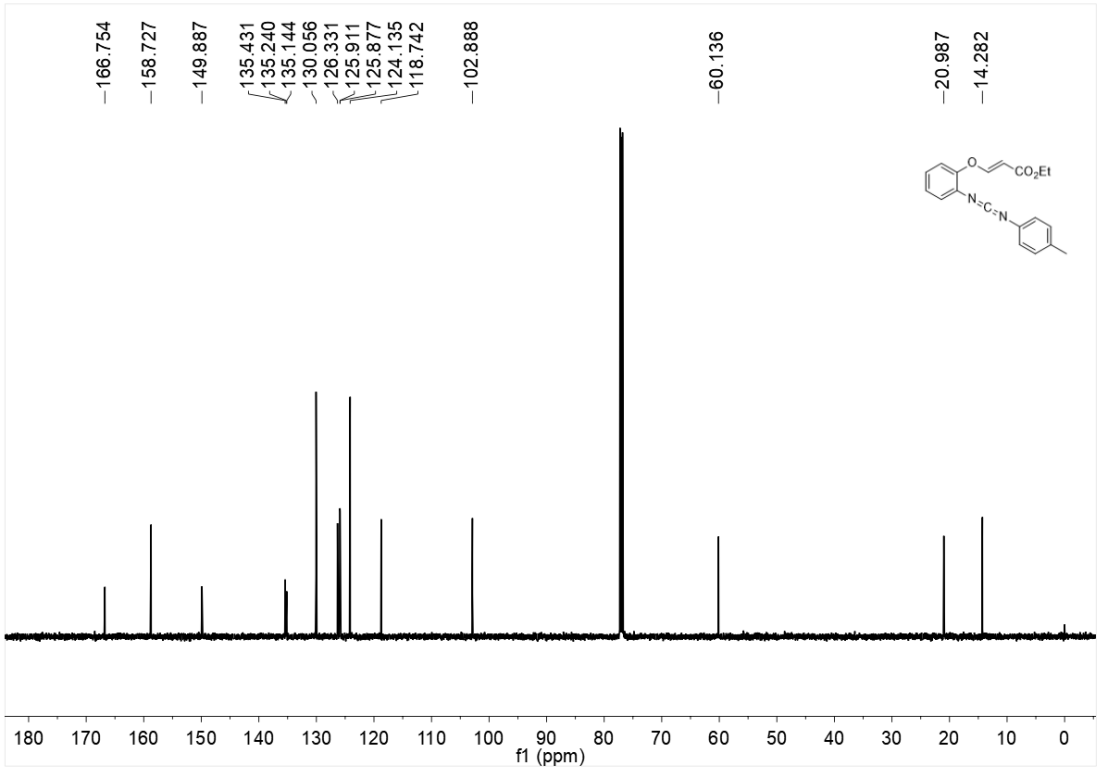


Figure 140. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **5a**

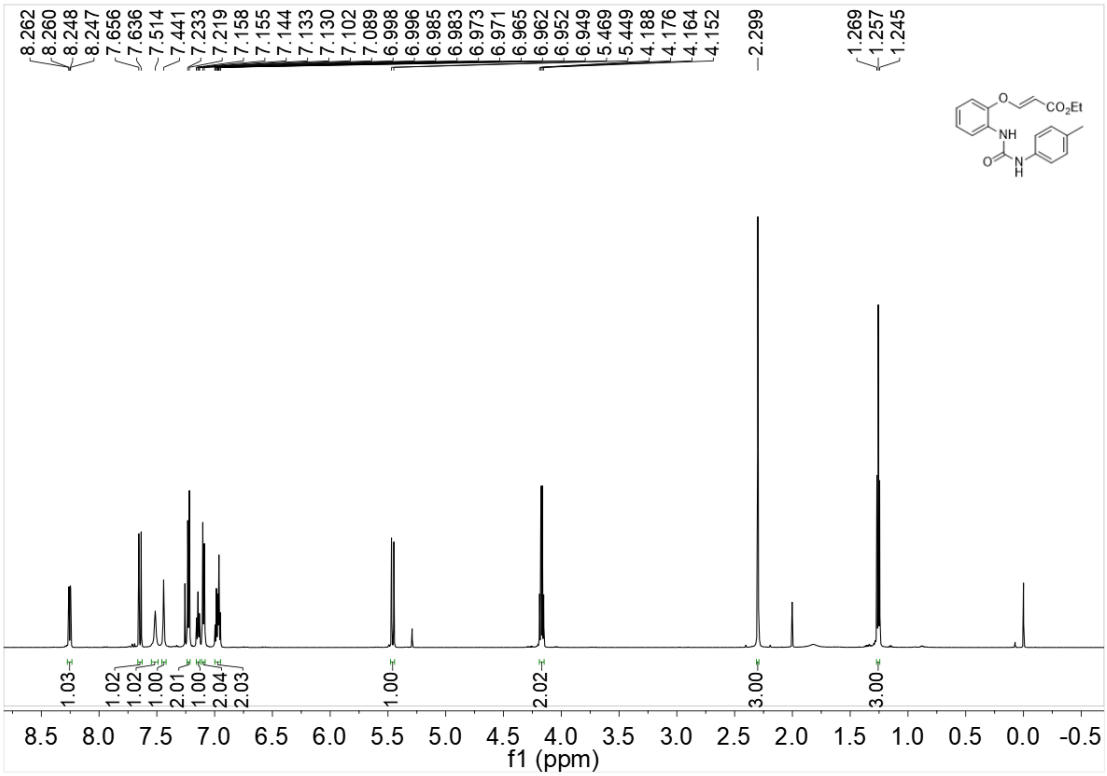


Figure 141. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **6a**

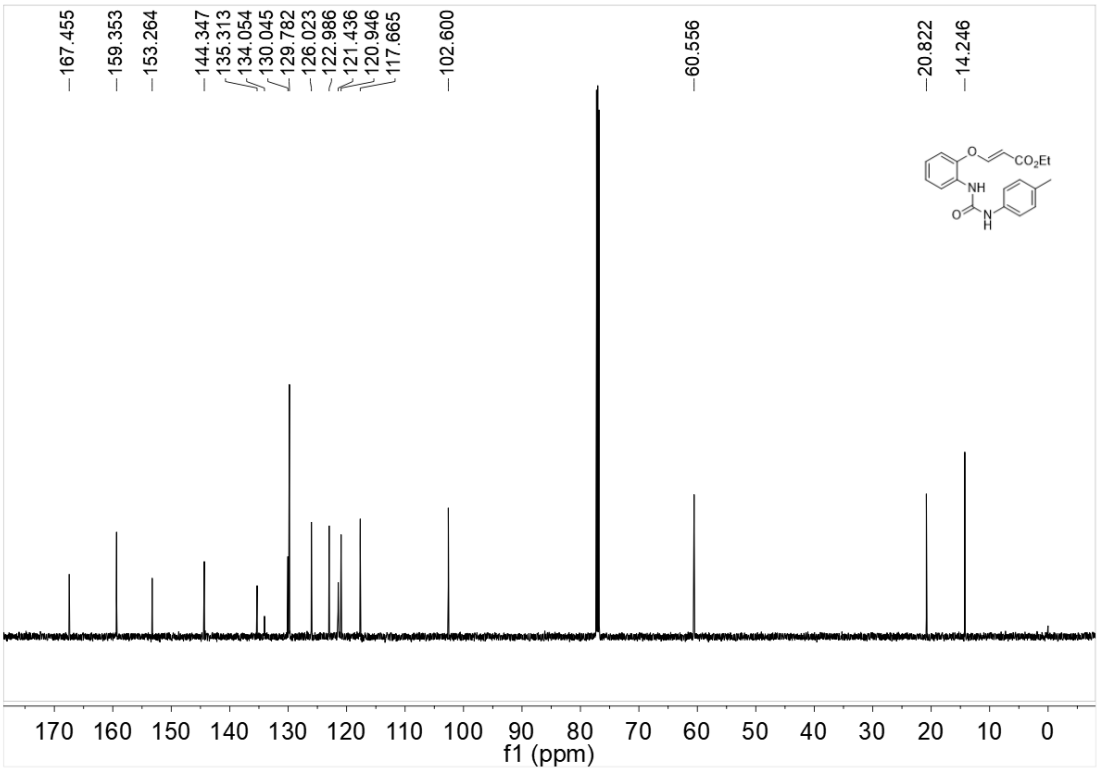
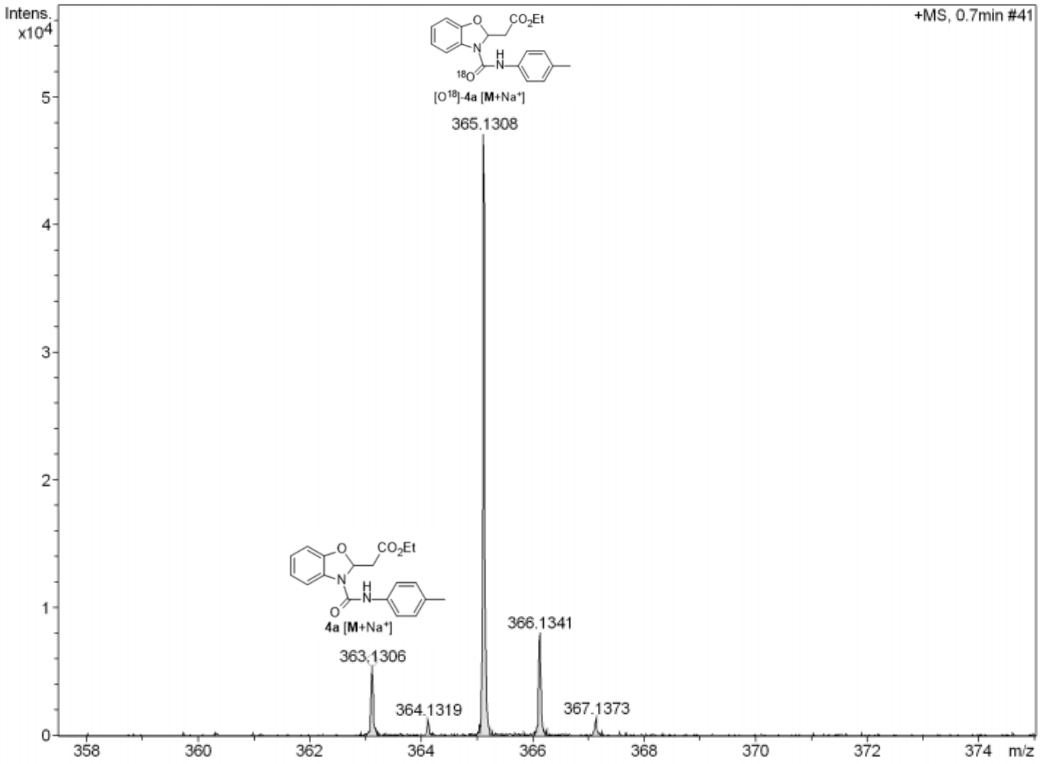


Figure 142. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **6a**

XI. Copy of HRMS Spectra of [O^{18}]-4a obtained by reaction with H_2O^{18}:

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	8.0 l/min
Scan End	1000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e¯ Conf	N-Rule
363.1306	1	C19H20N2NaO4	363.1315	-2.4	765.5	1	100.00	10.5	even	ok