SUPPORTING INFORMATION

Manganese-Catalyzed Direct C2-Allylation of Indoles

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Lan Wu*[a] and Jia Li[a]

Contents

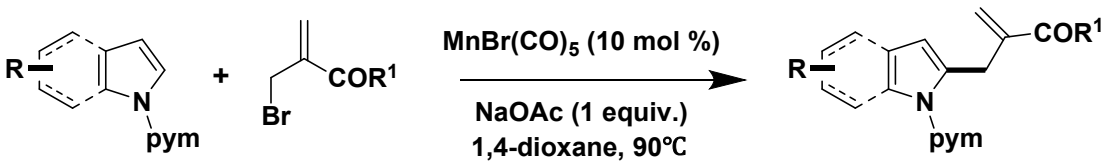
1. General Information

All reactions were carried out under an atmosphere of air atmosphere with dry solvents in flame-dried glassware unless otherwise noted. Anhydrous solvent were purchased from J&K® and used as received. Reactions were monitored by TLC on silica gel plates (GF254), and the analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gel plates. ^{1}H NMR, ^{13}C NMR spectra were recorded on a Bruker AVANCE Ⅲ–400 spectrometer at room temperature. Chemical shifts (δ) are reported in ppm downfield from tetramethylsilane. Abbreviations for signal couplings are: s, singlet; d, doublet; t, triplet; m, multiplet. High resolution mass spectras were obtained on a high–resolution mass spectrometer in the ESI mode. N-(pyrimidin-2-yl)-1H-indoles were prepared according to literature procedures[1]. All other reagents were purchased from commercial sources and used

[1] N. Sauermann, M. J. Gonzalez, L. Ackermann, *Org. Lett.* **2015**, *17*, 5316–5319.

as received.

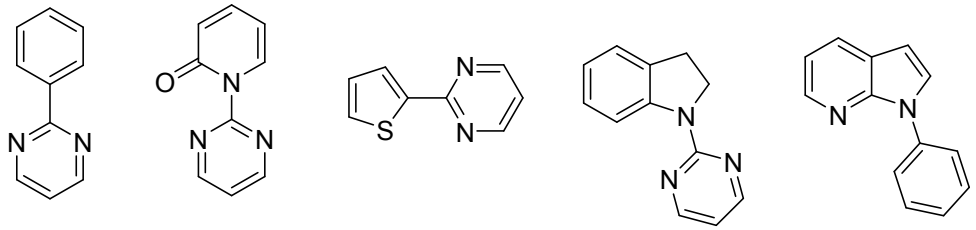
2. General procedure



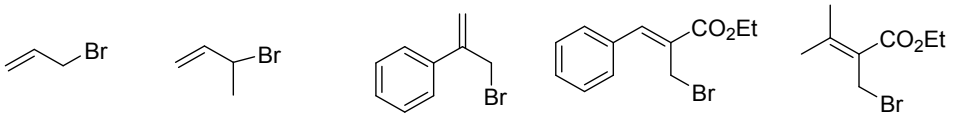
An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, **1a** (0.1 mmol), **2a** (2 equiv, 0.2 mmol), $MnBr(CO)_5$ (10 mol %, 0.01 mmol, 2.7 mg) and NaOAc (1.0 equiv, 0.1 mmol, 8.7 mg). 1.0 ml 1,4-dioxane was added with syringe under air and the reaction mixture was stirred at 90 ℃ and monitored by TLC. After the reaction was finished, the mixture was concentrated under vacuum to remove 1,4-dioxane, and the residue was purified by chromatography on silica gel to afford the product.

3. Extensive substrate test

More substrates with structures other than DG-protected indoles and ethyl 2-(bromomethyl) acrylate were tested under the standard conditions, but most of them fail to deliver the corresponding products.

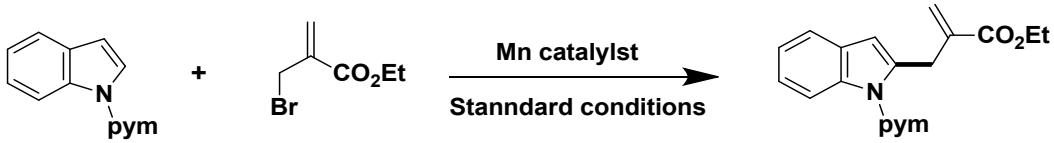


Failed



Failed

4. Gram-scale test



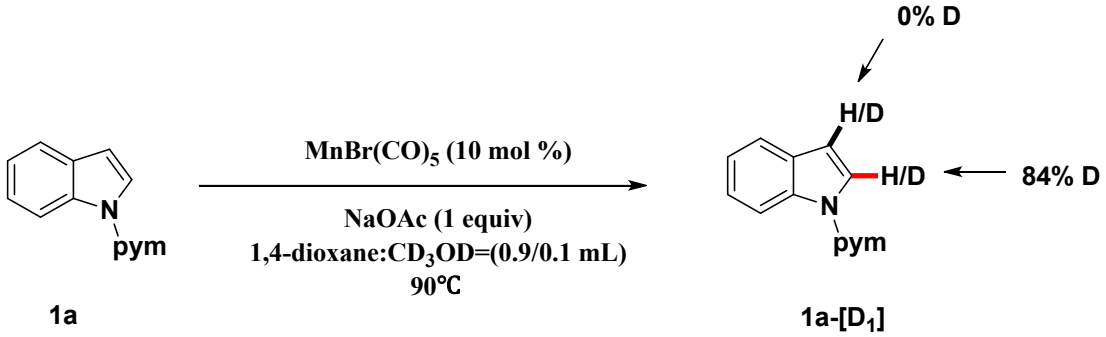
1a (10 mmol, 1.95 g) **2a** (20 mmol, 3.82 g) **3a** (1.90 g, 62%)

An oven-dried flsk (250 mL) was equipped with a magnetic stir bar, **1a** (10.0 mmol),

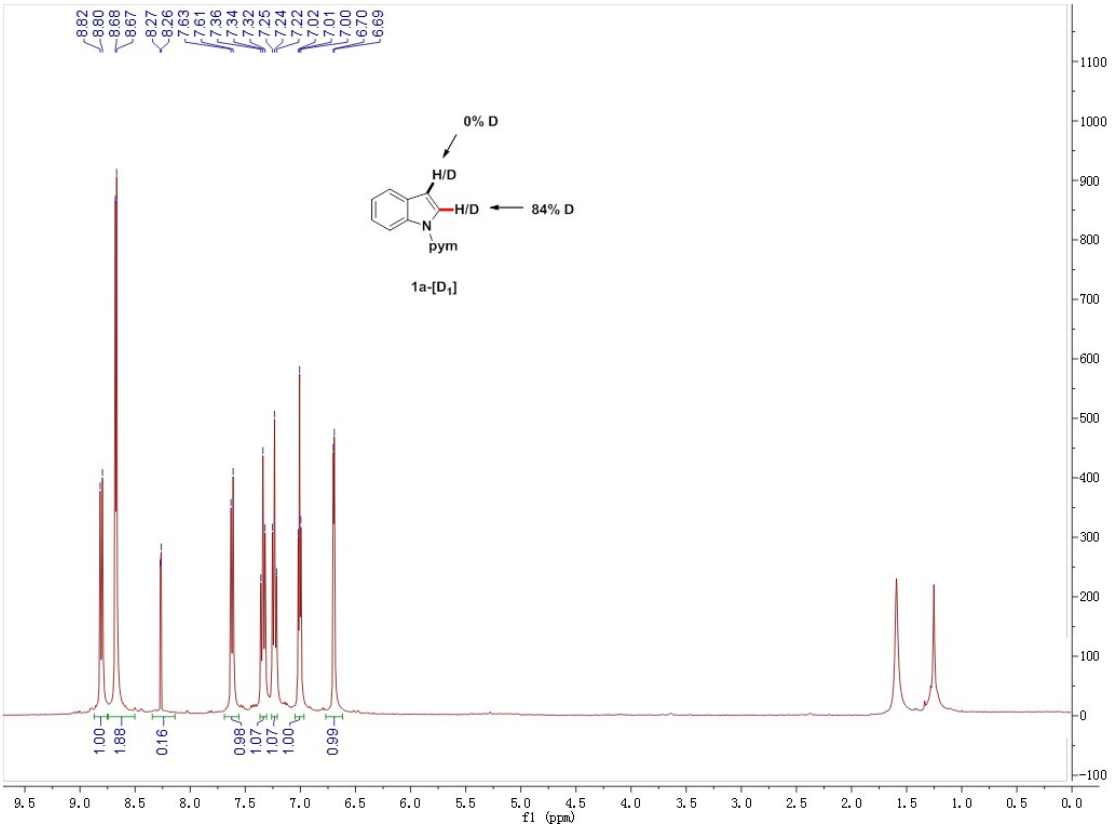
2a (2 equiv, 20.0 mmol), $MnBr(CO)_5$ (10 mol %, 1.0 mmol) and NaOAc (1.0 equiv, 10.0 mmol). 100 ml 1,4-dioxane was added with syringe under air and the reaction mixture was stirred at 90 ℃ and monitored by TLC. After the reaction was finished, the mixture was concentrated under vacuum to remove 1,4-dioxane, and the residue was purified by chromatography on silica gel to afford the product.

5. Machanism studies

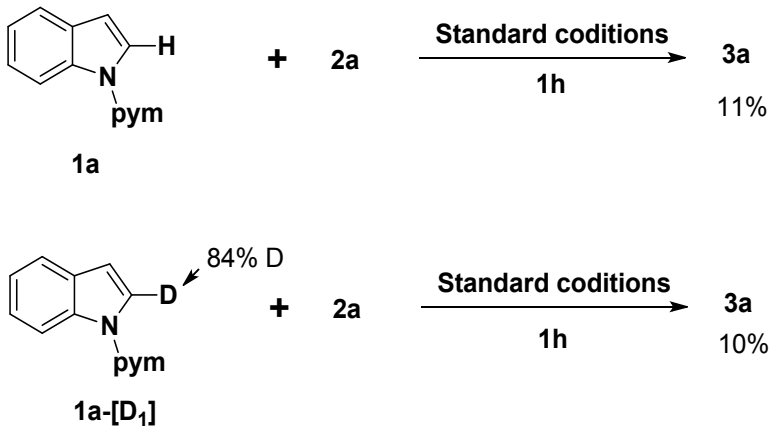
(a) H/D exchange experiment



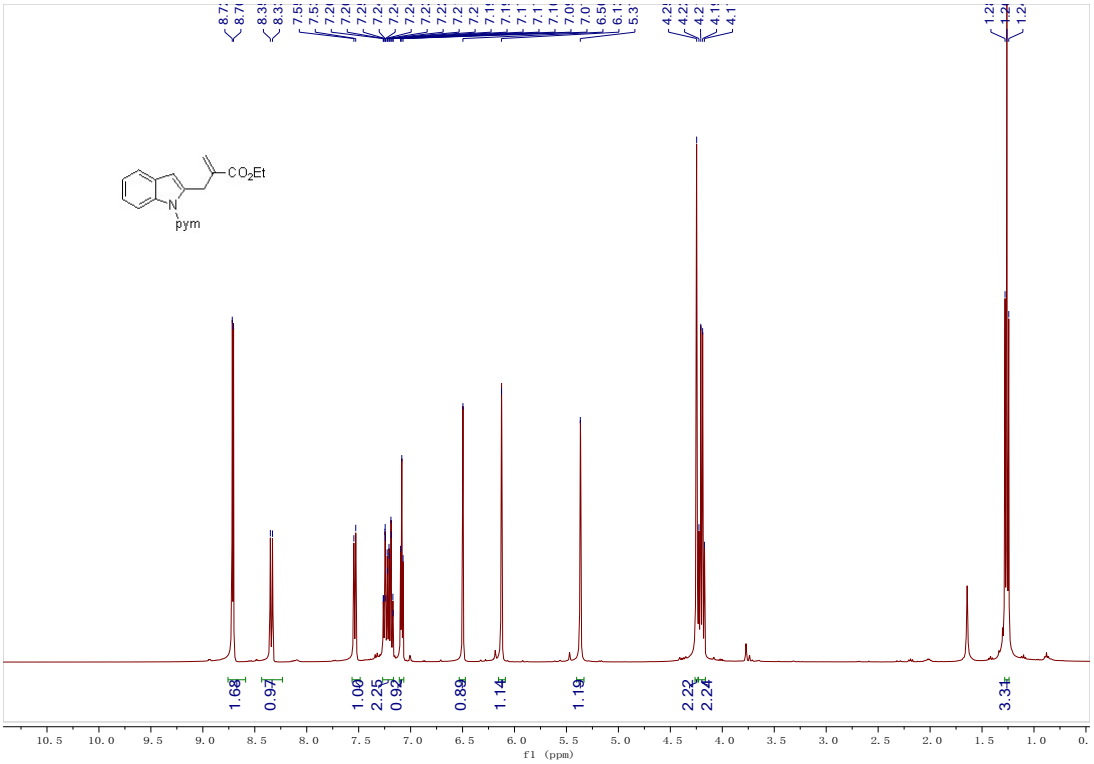
An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, **1a** (0.1 mmol), $MnBr(CO)_5$ (10 mol %, 0.01 mmol, 2.7 mg) and NaOAc (1.0 equiv, 0.1 mmol, 8.7 mg). 0.9 mL 1,4-dioxane, 0.1 mL CD_3OD was added with syringe under Ar and the mixture was stirred at 90 ℃ overnight. After the reaction was finished, the mixture was filtered and concentrated under vacuum to remove the solvent, and the residue collected without further purification.



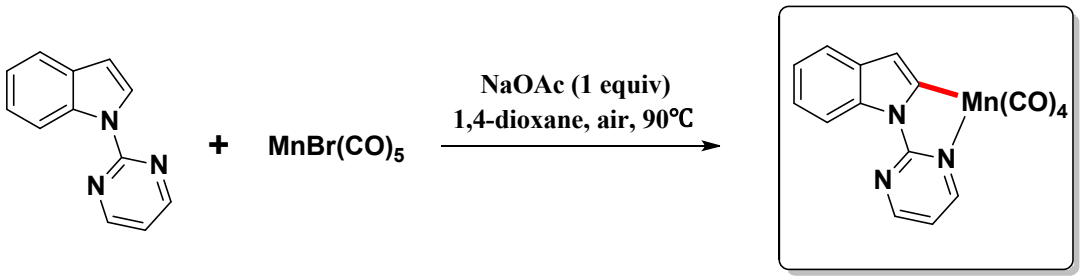
(b) KIE experiment



Two oven-dried Schlenk tube (10 mL) were added with **1a** (0.1 mmol) and **1a-[D1]** (0.1 mmol), respectively, and were both added with **2a** (2 equiv, 0.2 mmol), $MnBr(CO)_5$ (10 mol %, 0.01 mmol, 2.7 mg) and NaOAc (1.0 equiv, 0.1 mmol, 8.7 mg). 1.0 ml 1,4-dioxane under air. The reaction mixture was stirred at 90 ℃ for 1 hour. After the reaction was finished, the mixture was concentrated under vacuum to remove 1,4-dioxane, and the residue was purified by chromatography on silica gel to afford **3a**. Yield of **3a** is 10% for 1a and 11% for 1a-[D_1] (K_H/K_D = 1.1).



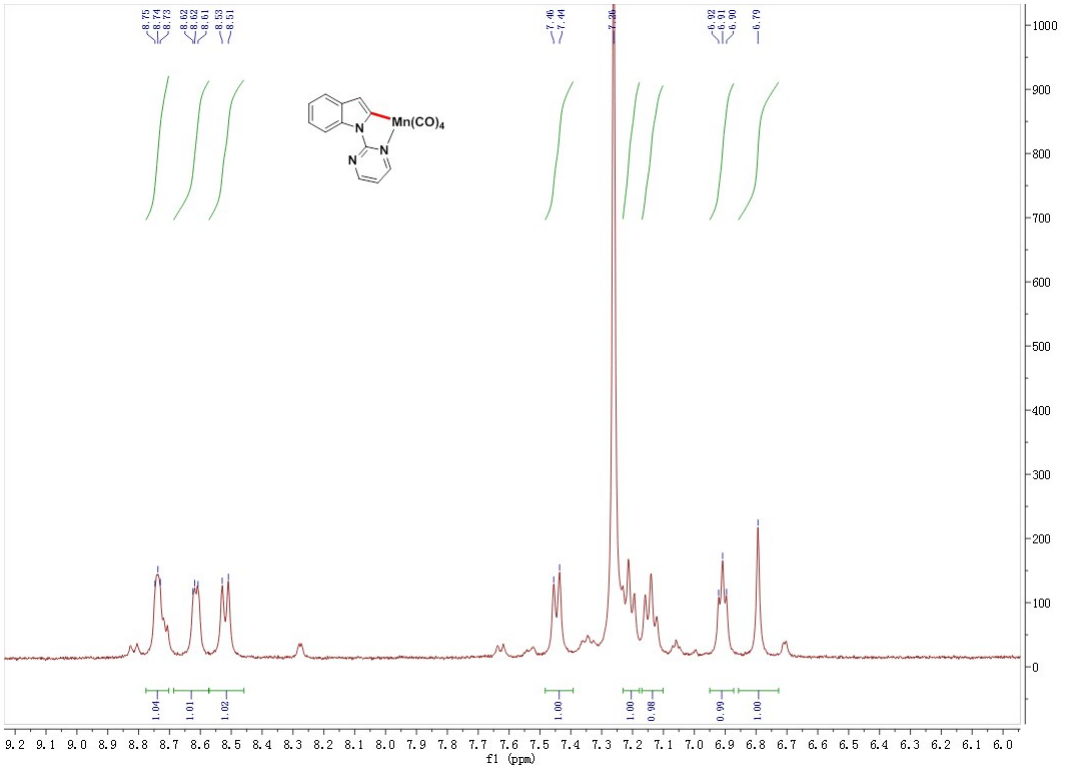
(c) Preparation of complex 4



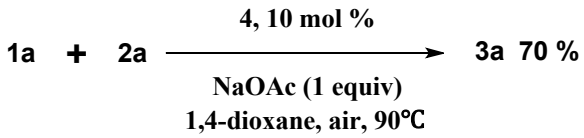
1a **4, 55 %**

An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, **1a** (0.1 mmol), $MnBr(CO)_5$ (1.0 equiv, 0.1 mmol) and NaOAc (1.0 equiv, 0.1 mmol). 1.0 ml 1,4-dioxane was added with syringe under air and the reaction mixture was stirred at 90 ℃. After the reaction was finished, the mixture was concentrated under vacuum to remove 1,4-dioxane, and the residue was purified by chromatography on silica gel to afford **4**.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.73 (dd, J = 4.8, 2.4 Hz, 1H), 8.62 (dd, J = 5.6, 2.4 Hz, 1H), 8.52 (d, J = 8.0 Hz, 1H), 7.44 (d, *J* = 7.5 Hz, 1H), 7.20 (dd, *J* = 7.5, 7.3 Hz, 1H), 7.12 (dd, *J* = 7.5, 7.2, 1H), 6.90 (t, *J* = 5.2 Hz, 1H), 6.79 (s, 1H). NMR data is in accordance with the previous literature[2].

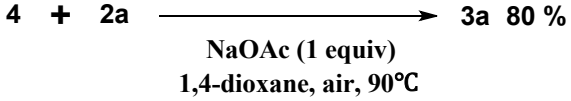


(d) 4 as catalyst



An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, **1a** (0.1 mmol), **2a** (2 equiv, 0.2 mmol), **4** (10 mol %, 0.01 mmol, 2.7 mg) and NaOAc (1.0 equiv, 0.1 mmol, 8.7 mg). 1.0 ml 1,4-dioxane was added with syringe under air and the reaction mixture was stirred at 90 ℃ and monitored by TLC. After the reaction was finished, the mixture was concentrated under vacuum to remove 1,4-dioxane, and the residue was purified by chromatography on silica gel to afford **3a**.

(e) stoichiometric addition with complex 4

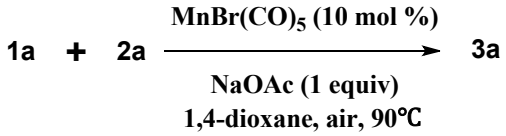


An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, **4** (0.1

[2] Z. Ruan, N. Sauermann, E. Manoni and L. Ackermann, *Angew. Chem. Int. Ed.,* 2017, **56**, 3172.

mmol), **2a** (2 equiv, 0.2 mmol) and NaOAc (1.0 equiv, 0.1 mmol, 8.7 mg). 1.0 ml 1,4-dioxane was added with syringe under air and the reaction mixture was stirred at 90 ℃ and monitored by TLC. After the reaction was finished, the mixture was concentrated under vacuum to remove 1,4-dioxane, and the residue was purified by chromatography on silica gel to afford **3a**.

(f) Radical scavenger experiments

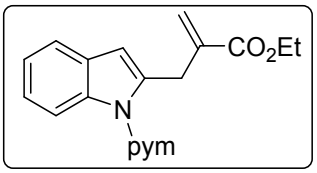


Standard conditions: 73 %
With TEMPO (1 equiv): 65 %
With BHT (1 equiv): 68 %

An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, **1a** (0.1 mmol), **2a** (2 equiv, 0.2 mmol), $MnBr(CO)_5$ (10 mol %, 0.01 mmol, 2.7 mg) and NaOAc (1.0 equiv, 0.1 mmol, 8.7 mg), Radical scavenger (1.0 equiv, 0.1 mmol), 1.0 ml 1,4-dioxane was added with syringe under air and the reaction mixture was stirred at 90 ℃ and monitored by TLC. After the reaction was finished, the mixture was concentrated under vacuum to remove 1,4-dioxane, and the residue was purified by chromatography on silica gel to afford the product.

6. Characterization data for new compounds

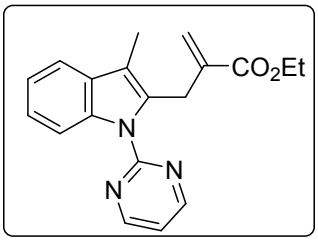
Ethyl 2-((1-(pyrimidin-2-yl)-1H-indol-2-yl) methyl) acrylate 3a



The reaction was carried out according to the general procedure (16 h). The residue was purified by flash column chromatography (9:1 petroleum ether: ethyl acetate) to afford **3a** (22.4 mg, 73 % yield) as yellow liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.71(d, *J*=4.8 Hz, 2H), 8.34(d, *J*=8.4 Hz, 1H), 7.54(d, *J*=7.2 Hz, 1H), 7.17-7.26(m, 2H), 7.08(t, *J*=8.4 Hz, 1H), 6.50(s, 1H), 6.13(s, 1H), 5.37(s, 1H), 4.25(s, 2H), 4.20(q, *J*=7.2 Hz, 2 H), 1.26(t, *J*=7.2 Hz, 3H) ^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.1, 167.0, 158.0, 139.1, 138.2, 137.1, 129.1, 125.6, 122.9, 121.9, 119.9, 117.0, 114.3, 108.0, 60.8, 31.8, 14.3. HRMS (ESI)

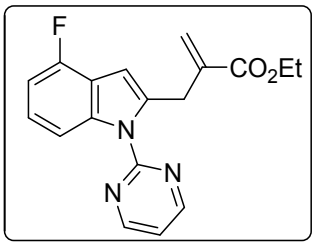
Calcd for $[M+H]^+$: 308.1394, found: 308.1397.

Ethyl 2-((3-methyl-1-(pyrimidin-2-yl)-1H-indol-2-yl) methyl) acrylate 3b



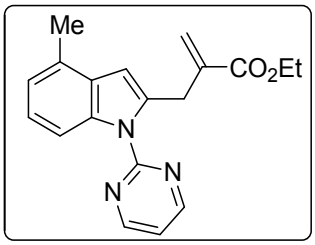
The reaction was carried out according to the general procedure (16 h). The residue was purified by flash column chromatography (10:1 petroleum ether: ethyl acetate) to afford **3b** (24.1mg, 75 % yield) as yellow liquid. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.66(d, *J*=8.4 Hz, 2H), 8.32-8.35(m, 1H), 7.53-7.55(m, 1H), 7.21-7.28(m, 2H), 7.02(t, *J*=4.8 Hz, 1H), 6.03(s, 1H), 5.12(s, 1H), 4.12(s, 2H), 4.23(q, *J*=7.2 Hz, 2H), 2.29(s, 3H), 1.30(t, *J*=7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.1, 158.0, 138.9, 136.2, 133.0, 130.3, 124.48, 123.2, 121.6, 118.2, 115.1, 60.7, 28.3, 14.3, 8.8. HRMS (ESI) Calcd for $[M+Na]^+$: 344.1369, found: 344.1372.

Ethyl 2-((4-fluoro-1-(pyrimidin-2-yl)-1H-indol-2-yl)methyl)acrylate 3c



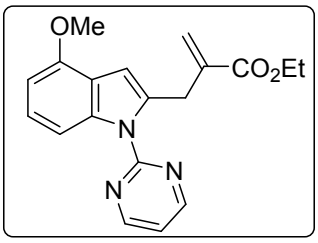
The reaction was carried out according to the general procedure (16 h). The residue was purified by flash column chromatography (10:1 petroleum ether: ethyl acetate) to afford **3c** (23.0 mg, 71 % yield) as yellow liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.72(d, *J*=4.8 Hz, 2H), 8.32-8.24(m, 2H), 7.92(dd, J_1=8.8 Hz, J_2=2.0 Hz, 1H), 7.13(t, *J*=4.8 Hz, 1H), 6.54(s, 1H), 6.13(s, 1H), 5.37(d, *J*=1.4 Hz, 2H), 4.23(s, 2H), 4.18(q, *J*=7.2 Hz, 2H), 1.24(t, *J*=7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 169.9, 157.5, 156.5(d, *J*=220.6 Hz), 140.0, 138.8, 133.4, 129.8(d, *J*=10.0 Hz), 125.6, 117.0, 115.5(d, *J*=10.0 Hz), 110.3, 107.6(d, *J*=4.0 Hz), 105.1, 104.9, 60.7, 32.0, 14.2. HRMS (ESI) Calcd for $[M+H]^+$: 326.1299, found: 326.1297.

Ethyl 2-((4-methyl-1-(pyrimidin-2-yl)-1H-indol-2-yl)methyl)acrylate 3d



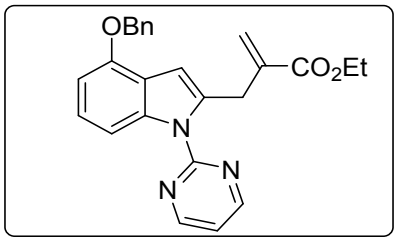
The reaction was carried out according to the general procedure (16 h). The residue was purified by flash column chromatography (10:1 petroleum ether: ethyl acetate) to afford **3d** (24.1 mg, 75 % yield) as yellow liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.72(d, *J*=4.8 Hz, 2H), 7.93(d, *J*=8.4 Hz, 1H), 7.17(t, *J*=8.4 Hz, 1H), 7.09(t, *J*=4.8 Hz, 1H), 6.65(d, *J*=7.9 Hz, 1H), 6.63(s, 1H), 6.13(s, 1H), 5.37(s, 1H), 4.23(s, 2H), 4.20(q, *J*=7.2 Hz, 2H), 2.59(s, 3H), 1.27(t, *J*=7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 169.9, 157.9, 151.4, 139.0, 138.4, 136.6, 128.4, 127.3, 125.5, 123.5, 119.7, 117.0, 107.8, 105.0, 69.9, 31.6, 21.4, 14.2. HRMS (ESI) Calcd for $[M+H]^{+}$: 322.1550, found: 322.1554.

Ethyl 2-((4-methoxy-1-(pyrimidin-2-yl)-1H-indol-2-yl) methyl) acrylate 3e



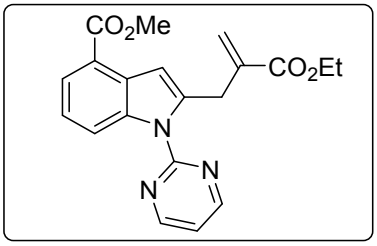
The reaction was carried out according to the general procedure (16 h). The residue was purified by flash column chromatography (10:1 petroleum ether: ethyl acetate) to afford **3e** (25.2 mg, 75 % yield) as yellow liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.71(d, *J*=4.8 Hz, 2H), 7.93(d, *J*=8.4 Hz, 1H), 7.16(t, *J*=8.0 Hz, 1H), 7.08(t, *J*=4.8 Hz, 1H), 6.62-6.65(m, 2H), 6.12(s, 1H), 5.36(s, 1H), 4.22(s, 2H), 4.19(q, J=7.2 Hz, 2H), 3.95(s, 3H), 1.26(t, *J*=7.2 Hz, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 167.0, 158.0, 152.4, 139.1, 138.4, 136.7, 125.6, 123.6, 119.2, 117.1, 107.6, 104.8, 102.2, 60.7, 55.4, 31.7, 14.3. HRMS (ESI) Calcd for $[M+H]^{+}$: 337.1426, found: 337.1430.

Ethyl 2-((4-(benzyloxy)-1-(pyrimidin-2-yl)-1H-indol-2-yl) methyl) acrylate 3f



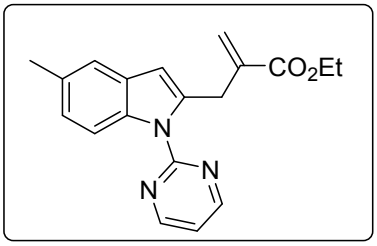
The reaction was carried out according to the general procedure (16 h). The residue was purified by flash column chromatography (10:1 petroleum ether: ethyl acetate) to afford **3f** (34.2 mg, 83 % yield) as yellow liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.68(d, *J*=4.8 Hz, 2H), 7.94(d, *J*=8.4 Hz, 1H), 7.48-7.50(m, 2H), 7.36-7.40(m, 2H), 7.31-7.33(m, 1H), 7.14(t, *J*=8.0 Hz, 1H), 7.05(t, *J*=4.8 Hz, 1H), 6.68-6.70(m, 2H), 6.11(s, 1H), 5.35(s, 1H), 5.21(s, 2H), 4.23(s, 2H), 4.19(q, *J*=6.8 Hz, 2H), 1.25(t, *J*=6.8 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.0, 158.0, 151.6, 139.2, 138.5, 137.5, 136.7, 128.5, 127.8, 125.6, 123.6, 119.9, 117.1, 107.9, 105.2, 103.8, 70.1, 60.7, 31.7, 14.3. HRMS (ESI) Calcd for $[M+H]^{+}$: 413.1739, found: 413.1740.

Methyl 2-(2-(ethoxycarbonyl) allyl)-1-(pyrimidin-2-yl)-1H-indole-4-carboxylate 3g



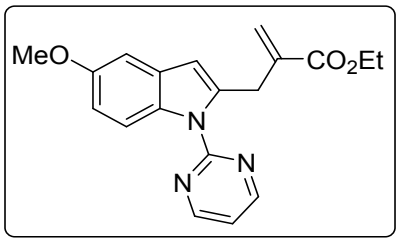
The reaction was carried out according to the general procedure (16 h). The residue was purified by flash column chromatography (6:1 petroleum ether: ethyl acetate) to afford **3g** (26.6 mg, 73 % yield) as faint yellow liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.74(d, *J*=4.8 Hz, 2H), 8.31(d, *J*=8.8 Hz, 1H), 8.27(d, *J*=1.6 Hz, 1H), 7.94(dd, J_1=8.8 Hz, J_2=2.0 Hz, 1H), 7.14(t, *J*=4.8 Hz, 1H), 6.56(s, 1H), 6.15(s, 1H), 5.38(s, 1H), 4.24(s, 2H), 4.19(q, *J*=7.2 Hz, 2H), 3.93(s, 3H), 1.25(t, *J*=7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.8, 166.8, 158.1, 157.7, 139.9, 139.6, 138.7, 128.7, 125.9, 124.2, 123.7, 122.4, 117.7, 113.9, 108.2, 60.8, 51.9, 31.8, 14.2. HRMS (ESI) Calcd for $[M+H]^{+}$: 365.1376, found: 365.1378.

Ethyl 2-((5-methyl-1-(pyrimidin-2-yl)-1H-indol-2-yl) methyl) acrylate 3h



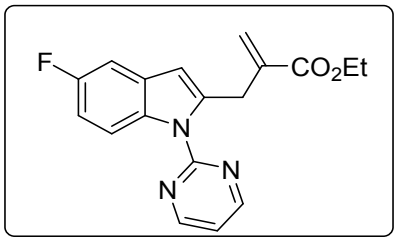
The reaction was carried out according to the general procedure (16 h). The residue was purified by flash column chromatography (9:1 petroleum ether: ethyl acetate) to afford **3h** (27.2 mg, 85 % yield) as yellow liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.66(d, *J*=4.8 Hz, 2H), 8.25(d, *J*=8.8 Hz, 1H), 7.31(s, 1H), 7.06(dd, J_1=8.4 Hz, J_2=1.6 Hz, 1H), 7.02(t, *J*=4.8 Hz, 1H), 6.41(s, 1H), 6.11(s, 1H), 5.34(s, 1H), 4.22(s, 2H), 4.19(q, *J*=6.8 Hz, 2H), 2.43(s, 3H), 1.25(t, *J*=6.8 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.1, 157.9, 139.3, 138.3, 135.4, 131.3, 129.4, 125.4, 124.3, 119.8, 114.3, 107.9, 60.7, 32.0, 21.4, 14.3. HRMS (ESI) Calcd for $[M+Na]^+$: 344.1369, found: 344.1372.

Ethyl 2-((5-methoxy-1-(pyrimidin-2-yl)-1H-indol-2-yl) methyl) acrylate 3i



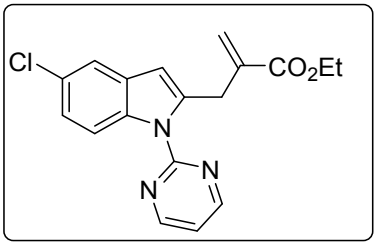
The reaction was carried out according to the general procedure (16 h). The residue was purified by flash column chromatography (9:1 petroleum ether: ethyl acetate) to afford **3i** (26.9 mg, 80 % yield) as yellow liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.67(d, *J*=4.8 Hz, 2H), 8.31(d, *J*=9.2 Hz, 1H), 7.04(t, *J*=4.8 Hz, 1H), 7.01(d, *J*=2.4 Hz, 1H), 6.87(dd, J_1=9.2 Hz, J_2=2.8 Hz, 1H), 6.42(s, 1H), 6.12(s, 1H), 5.36(s, 1H), 4.24(s, 2H), 4.20(q, *J*=7.2 Hz, 2H), 3.86(s, 3H), 1.26(t, *J*=7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.0, 157.9, 155.4, 139.2, 131.9, 129.9, 125.5, 116.7, 115.6, 111.8, 108.1, 102.3, 60.7, 55.7, 32.1, 14.3. HRMS (ESI) Calcd for $[M+H]^+$: 337.1426, found: 337.1432.

Ethyl 2-((5-fluoro-1-(pyrimidin-2-yl)-1H-indol-2-yl) methyl) acrylate 3j



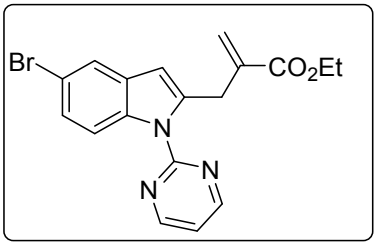
The reaction was carried out according to the general procedure (16 h). The residue was purified by flash column chromatography (9:1 petroleum ether: ethyl acetate) to afford **3j** (22.4 mg, 69 % yield) as yellow liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.70(d, *J*=4.8 Hz, 2H), 8.31(dd, *J*=4.8 Hz, 1H), 7.17(dd, J_1=8.8 Hz, J_2=2.8 Hz, 1H), 7.09(t, *J*=4.8 Hz, 1H), 6.93-6.98(m, 1H), 6.44(s, 1H), 6.14(s, 1H), 5.37(s, 1H), 4.24(s, 2H), 4.20(q, *J*=7.2 Hz, 2H), 1.26 (t, *J*=7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.9, 159.0(d, *J*=220.6 Hz), 158.0, 157.8, 140.1, 138.9, 133.4, 129.9(d, *J*=10.1 Hz), 125.7, 117.1, 115.5(d, *J*= 9.0 Hz), 107.7(d, *J*=4.0 Hz), 105.2, 104.9, 60.8, 32.1, 14.2. HRMS (ESI) Calcd for $[M+H]^+$: 325.1227, found: 325.1230.

Ethyl 2-((5-chloro-1-(pyrimidin-2-yl)-1H-indol-2-yl) methyl) acrylate 3k



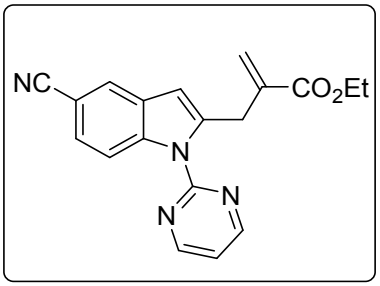
The reaction was carried out according to the general procedure (16 h). The residue was purified by flash column chromatography (9:1 petroleum ether: ethyl acetate) to afford **3k** (25.5 mg, 75 % yield) as yellow liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.69(d， *J*=4.8 Hz, 2H), 8.27(d, *J*=8.8 Hz, 1H), 7.48(d, *J*=2.0 Hz, 1H), 7.17(dd, J_1=8.8 Hz, J_2=2.0 Hz, 1H), 7.09(t, *J*=4.8 Hz, 1H), 6.41(s, 1H), 6.14(s, 1H), 5.36(s, 1H), 4.23(s, 2H), 4.20(q, *J*=7.2 Hz, 2H), 1.25(t, *J*=7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.9, 158.0, 139.9, 138.8, 135.4, 130.3, 127.4, 125.8, 122.9, 119.3, 117.3, 115.7, 107.2, 60.8, 32.0, 14.3. HRMS (ESI) Calcd for $[M+Na]^+$: 341.0931, found: 341.0930.

Ethyl 2-((5-bromo-1-(pyrimidin-2-yl)-1H-indol-2-yl) methyl) acrylate 3l



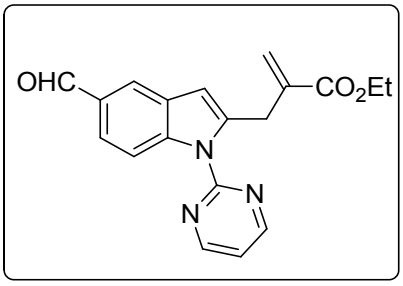
The reaction was carried out according to the general procedure (16 h). The residue was purified by flash column chromatography (9:1 petroleum ether: ethyl acetate) to afford **3l** (25.0 mg, 65 % yield) as yellow liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.72(d, *J*=4.8 Hz, 2H), 8.23(d, *J*=9.2 Hz, 1H), 7.65(d, *J*=2.0 Hz, 1H), 7.31(dd, J_1=10.8 Hz, J_2=2.0 Hz, 1H), 7.12(t, *J*=4.8 Hz, 1H), 6.42(s, 1H), 6.14(s, 1H), 6.37(s, 1. H), 4.22(s, 2H), 4.20(q, *J*=7.2 Hz, 2H), 1.26(t, *J*=7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.8, 158.1, 139.7, 138.8, 135.7, 130.9, 125.6, 122.4, 117.3, 116.0, 115.1, 107.1, 60.8, 31.9, 14.2. HRMS (ESI) Calcd for $[M+Na]^+$: 385.0426, found: 385.0430.

Ethyl 2-((5-cyano-1-(pyrimidin-2-yl)-1H-indol-2-yl) methyl) acrylate 3m



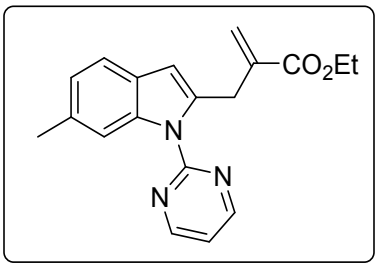
The reaction was carried out according to the general procedure (16 h). The residue was purified by flash column chromatography (10:1 petroleum ether: ethyl acetate) to afford **3m** (14.3 mg, 43 % yield) as colorless liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.79(d, *J*=4.8 Hz, 2H), 8.36(d, *J*=8.4 Hz, 1H), 7.87(s, 1H), 7.47(dd, J_1=1.6 Hz, J_2=8.8 Hz, 1H), 7.23(t, *J*=4.8 Hz, 1H), 6.54(s, 1H), 6.17(s, 1H), 5.40(s, 1H), 4.25(s, 2H), 4.20(q, *J*=7.2 Hz, 2H), 1.26(t, *J*=7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.6, 158.3, 157.5, 141.1, 138.8, 138.4, 128.9, 125.9, 124.9, 120.4, 118.1, 115.1, 107.3, 105.0, 60.9, 31.8, 14.2. HRMS (ESI) Calcd for $[M+Na]^+$: 332.1273, found: 332.1281.

Ethyl 2-((5-formyl-1-(pyrimidin-2-yl)-1H-indol-2-yl)methyl)acrylate 3n



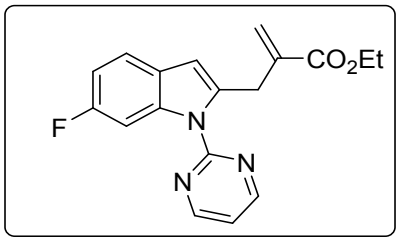
The reaction was carried out according to the general procedure (16 h). The residue was purified by flash column chromatography (10:1 petroleum ether: ethyl acetate) to afford **3n** (13.8 mg, 41 % yield) as yellow liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.88(s, 1H), 8.70(d， *J*=4.8 Hz, 2H), 8.28(d, *J*=8.8 Hz, 1H), 7.49(d, *J*=2.0 Hz, 1H), 7.18(dd, J_1=8.8 Hz, J_2=2.0 Hz, 1H), 7.12-7.07(m, 1H), 6.42(s, 1H), 6.15(s, 1H), 5.37(s, 1H), 4.24(s, 2H), 4.20(q, *J*=7.2 Hz, 2H), 1.26(t, *J*=7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 190.6, 166.6, 158.2, 157.4, 142.6, 138.3, 135.8, 132.3, 126.1, 124.9, 120.7, 120.5, 117.8, 107.8, 105.3 60.9, 32.1, 14.2. HRMS (ESI) Calcd for $[M+H]^+$: 336.1343, found: 336.1347.

Ethyl 2-((6-methyl-1-(pyrimidin-2-yl)-1H-indol-2-yl) methyl) acrylate 3o



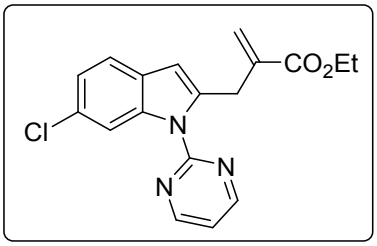
The reaction was carried out according to the general procedure (16 h). The residue was purified by flash column chromatography (9:1 petroleum ether: ethyl acetate) to afford **3o** (22.4 mg, 70 % yield) as yellow liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.70(d, *J*=4.8 Hz, 2H), 8.14(s, 1H), 7.41(d, *J*=8.0 Hz, 1H), 7.06(t, *J*=4.8 Hz, 1H), 7.01-7.03(m, 1H), 6.44(s, 1H), 6.10(s, 1H), 5.34(s, 1H), 4.21(s, 2H), 4.19(q, *J*=6.8 Hz, 2H), 2.48(s, 3H), 1.25(t, *J*=7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.0, 158.0, 139.3, 137.4, 132.7, 126.9, 125.4, 123.4, 119.5, 116.9, 114.3, 107.9, 60.7, 31.8, 22.1, 14.3. HRMS (ESI) Calcd for $[M+Na]^+$: 344.1369, found: 344.1370.

Ethyl 2-((6-fluoro-1-(pyrimidin-2-yl)-1H-indol-2-yl) methyl) acrylate 3p



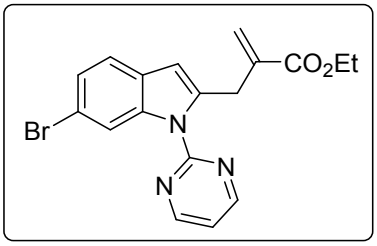
The reaction was carried out according to the general procedure (16 h). The residue was purified by flash column chromatography (9:1 petroleum ether: ethyl acetate) to afford **3p** (21.1 mg, 65 % yield) as yellow liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.71(d, *J*=4.8 Hz, 2H), 8.15(dd, J_1=7.2 Hz, J_2=2.4 Hz, 1H), 7.42(dd, J_1=8.8 Hz, J_2=5.6 Hz, 1H), 7.09(t, *J*=4.8 Hz, 1H), 6.93-6.98(m, 1H), 6.45(s, 1H), 6.13(s, 1H), 5.36(s, 1H), 4.23(s, 2H), 4.20(q, *J*=7.2 Hz, 2H), 1.26(t, *J*=7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.9, 160.5 (d, *J*=235.6 Hz), 158.0, 157.9, 139.1, 138.8(d, *J*=3.8 Hz), 137.1 (d, *J*=12.8 Hz), 125.6, 125.4, 120.2 (d, *J*=9.8 Hz), 117.2, 110.1(d, *J*=19.6 Hz), 107.7, 101.9(d, *J*=28.7 Hz), 60.8, 32.0, 14.2. HRMS (ESI) Calcd for $[M+H]^+$: 325.1227, found: 325.1230.

Ethyl 2-((6-chloro-1-(pyrimidin-2-yl)-1H-indol-2-yl) methyl) acrylate 3q



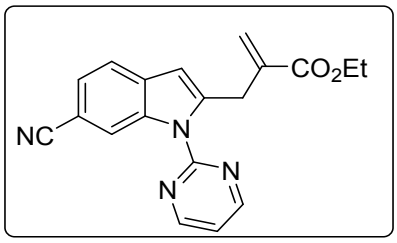
The reaction was carried out according to the general procedure (16 h). The residue was purified by flash column chromatography (9:1 petroleum ether: ethyl acetate) to afford **3q** (25.5 mg, 75 % yield) as yellow liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.72(d, *J*=4.8 Hz, 2H), 8.40(d, *J*=1.6 Hz, 1H), 7.42(d, *J*=8.4 Hz, 1H), 7.16(dd, J_1=8.4 Hz, J_2=2.0 Hz, 1H), 7.12(t, *J*=4.8 Hz, 1H), 6.45(s, 1H), 6.13(s, 1H), 5.37(s, 1H), 4.23(s, 2H), 4.20(q, *J*=7.2 Hz, 2H), 1.26(t, *J*=7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.9, 158.1, 157.8, 138.9, 137.3, 128.7, 127.6, 125.7, 122.4, 120.5, 117.3, 11.7, 107.7, 60.8, 32.0, 14.2. HRMS (ESI) Calcd for $[M+Na]^+$: 341.0931, found: 341.0928.

Ethyl 2-((6-bromo-1-(pyrimidin-2-yl)-1H-indol-2-yl) methyl) acrylate 3r



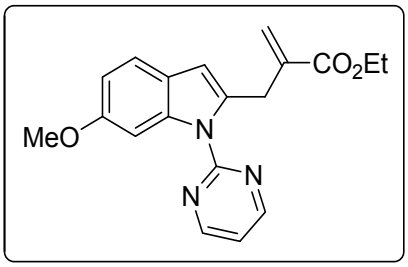
The reaction was carried out according to the general procedure (16 h). The residue was purified by flash column chromatography (9:1 petroleum ether: ethyl acetate) to afford **3r** (23.1 mg, 60 % yield) as faint yellow liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.72(d, *J*=4.8 Hz, 2H), 8.55(d, *J*=1.2 Hz, 1H), 7.38(d, *J*=8.0 Hz, 1H), 7.30(dd, J_1=8.4 Hz, J_2=1.6 Hz, 1H), 7.12(t, *J*=4.8 Hz, 1H), 6.45(s, 1H), 6.13(s, 1H), 5.36(s, 1H), 4.22(s, 2H), 4.19(q, *J*=7.2 Hz, 3H), 1.25(t, *J*=7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.9, 158.1, 157.8, 138.8, 137.7, 128.0, 125.7, 125.1, 121.0, 117.4, 116.5, 107.7, 60.8, 31.9, 14.2. HRMS (ESI) Calcd for $[M+Na]^+$: 385.0426, found: 385.0420.

Ethyl 2-((6-cyano-1-(pyrimidin-2-yl)-1H-indol-2-yl) methyl) acrylate 3s



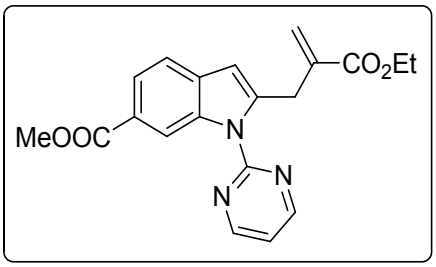
The reaction was carried out according to the general procedure (16 h). The residue was purified by flash column chromatography (9:1 petroleum ether: ethyl acetate) to afford **3s** (13.2 mg, 40 % yield) as colorless liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.78(d, *J*=4.8 Hz, 2H), 8.76(s, 1H), 7.58(d, *J*=8.0 Hz, 1H), 7.43(dd, J_1=8.0 Hz, J_2=1.2 Hz, 1H), 7.22(t, *J*=4.8 Hz, 1H), 6.54(s, 1H), 6.19(s, 1H), 5.41(s, 1H), 4.29(s, 2H), 4.20(q, *J*=7.2 Hz, 2H), 1.26(t, *J*=7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.7, 158.3, 157.5, 142.7, 138.4, 135.9, 132.4, 126.2, 125.0, 120.8, 120.5, 119.5, 117.9, 107.9, 105.4, 60.9, 32.1, 14.2. HRMS (ESI) Calcd for $[M+Na]^+$: 332.1273, found: 332.1280.

Ethyl 2-((6-methoxy-1-(pyrimidin-2-yl)-1H-indol-2-yl)methyl)acrylate 3t



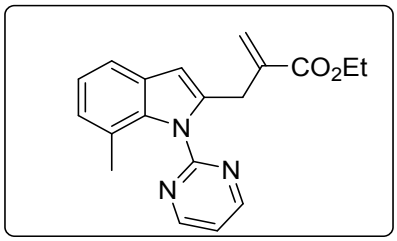
The reaction was carried out according to the general procedure (16 h). The residue was purified by flash column chromatography (9:1 petroleum ether: ethyl acetate) to afford **3t** (23.0 mg, 68 % yield) as yellow liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.69(d, *J*=4.8 Hz, 2H), 8.10(s, 1H), 7.41(d, *J*=8.0 Hz, 1H), 7.07(t, *J*=4.8 Hz, 1H), 7.04(t, *J*=7.2 Hz, 1H), 6.44(s, 1H), 6.10(s, 1H), 5.34(s, 1H), 4.21(s, 2H), 4.19(q, *J*=6.8 Hz, 2H), 3.83(s, 3H), 1.27(t, *J*=7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.8, 158.0, 157.7, 138.8, 137.3, 128.7, 127.6, 125.6, 122.4, 120.5, 117.2, 114.6, 107.6, 60.5, 56.3, 31.9, 22.1, 14.2. HRMS (ESI) Calcd for $[M+H]^{+}$: 338.1499, found: 338.1496.

Methyl 2-(2-(ethoxycarbonyl)allyl)-1-(pyrimidin-2-yl)-1H-indole-6-carboxylate 3u



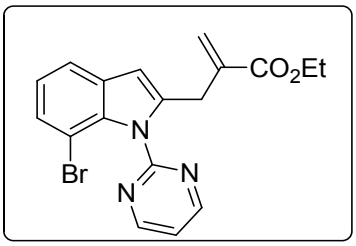
The reaction was carried out according to the general procedure (16 h). The residue was purified by flash column chromatography (9:1 petroleum ether: ethyl acetate) to afford **3u** (16.4 mg, 45 % yield) as yellow liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.73(d, *J*=4.8 Hz, 2H), 8.41(s, 1H), 7.43(d, *J*=8.0 Hz, 1H), 7.19-7.15(m, 1H), 7.12(t, *J*=4.8 Hz, 1H), 6.46(s, 1H), 6.14(s, 1H), 5.37(s, 1H), 4.25(s, 2H), 4.20(q, *J*=6.8 Hz, 2H), 3.89(s, 3H), 1.26(t, *J*=7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 169.7, 166.9, 157.9, 139.1, 137.4, 137.3, 132.6, 126.8, 125.3, 123.3, 119.4, 116.8, 114.2, 107.8, 60.6, 50.9, 31.7, 14.2. HRMS (ESI) Calcd for $[M+Na]^{+}$: 366.1448, found: 366.1445.

Ethyl 2-((7-methyl-1-(pyrimidin-2-yl)-1H-indol-2-yl) methyl) acrylate 3v



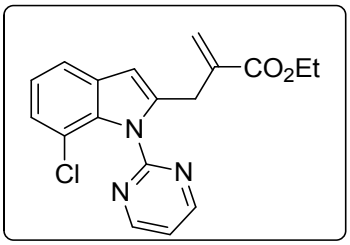
The reaction was carried out according to the general procedure (16 h). The residue was purified by flash column chromatography (9:1 petroleum ether: ethyl acetate) to afford **3v** (22.4 mg, 70 % yield) as yellow liquid. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.80(d, J=4.8 Hz, 2H), 7.43(d, *J*=7.6 Hz, 1H), 7.24(t, *J*=4.8 Hz, 1H), 7.08(t, *J*=7.6 Hz, 1H), 6.96(d, *J*=7.2 Hz, 1H), 6.46(s, 1H), 6.08(s, 1H), 5.30(s, 1H), 4.15(q, *J*=7.2 Hz, 2H), 3.84(s, 2H), 1.97(s, 3H), 1.24(t, *J*=7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.6, 158.6, 158.3, 138.3, 138.0, 136.6, 129.5, 126.3, 125.4, 122.0, 121.4, 119.0, 118.1, 105.7, 60.8, 29.7, 20.2, 14.2. HRMS (ESI) Calcd for $[M+Na]^{+}$: 344.1369, found: 344.1370.

Ethyl 2-((7-bromo-1-(pyrimidin-2-yl)-1H-indol-2-yl)methyl)acrylate 3w



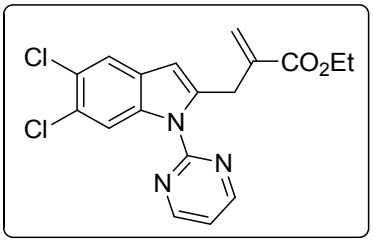
The reaction was carried out according to the general procedure (16 h). The residue was purified by flash column chromatography (9:1 petroleum ether: ethyl acetate) to afford **3w** (25.0 mg, 65 % yield) as yellow liquid. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.81(d, J=4.8 Hz, 2H), 7.44(d, *J*=7.6 Hz, 1H), 7.25(t, *J*=4.8 Hz, 1H), 7.09(t, *J*=7.6 Hz, 1H), 6.98(d, *J*=7.2 Hz, 1H), 6.47(s, 1H), 6.09(s, 1H), 5.31(q, *J*=1.5 Hz, 1H), 4.16(q, *J*=7.2 Hz, 2H), 3.85(s, 2H), 1.24(t, *J*=7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.5, 158.5, 158.2, 138.2, 137.9, 136.6, 129.4, 126.2, 125.3, 121.9, 121.4, 118.9, 118.0, 105.6, 60.7, 30.1, 14.1. HRMS (ESI) Calcd for $[M+H]^{+}$: 386.0499, found: 386.0497.

Ethyl 2-((7-chloro-1-(pyrimidin-2-yl)-1H-indol-2-yl)methyl)acrylate 3x



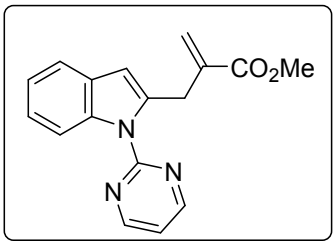
The reaction was carried out according to the general procedure (16 h). The residue was purified by flash column chromatography (9:1 petroleum ether: ethyl acetate) to afford **3x** (21.4 mg, 63 % yield) as yellow liquid. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.80(d, J=4.8 Hz, 2H), 7.45(d, *J*=7.6 Hz, 1H), 7.24(t, *J*=4.8 Hz, 1H), 7.09(t, *J*=7.6 Hz, 1H), 6.98(d, *J*=7.2 Hz, 1H), 6.46(s, 1H), 6.08(s, 1H), 5.31(q, *J*=1.5 Hz, 1H), 4.15(q, *J*=7.2 Hz, 2H), 3.83(s, 2H), 1.24(t, *J*=7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.7, 158.7, 158.2, 138.3, 137.8, 136.8, 129.4, 126.2, 125.5, 121.9, 121.4, 118.8, 118.0, 105.6, 60.7, 29.9, 14.1. HRMS (ESI) Calcd for $[M+H]^{+}$: 342.1004, found: 342.1004.

Ethyl 2-((5,6-dichloro-1-(pyrimidin-2-yl)-1H-indol-2-yl)methyl)acrylate 3y



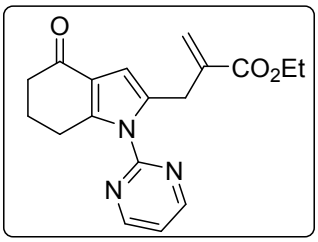
The reaction was carried out according to the general procedure (16 h). The residue was purified by flash column chromatography (9:1 petroleum ether: ethyl acetate) to afford **3y** (22.9 mg, 61 % yield) as yellow liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.74(d, *J*=4.8 Hz, 2H), 8.42(d, *J*=1.6 Hz, 1H), 7.44(d, *J*=8.4 Hz, 1H), 7.18(dd, J_1=8.4 Hz, J_2=2.0 Hz, 1H), 7.13(t, *J*=4.8 Hz, 1H), 6.47(s, 1H), 6.15(s, 1H), 5.38(s, 1H), 4.24(s, 2H), 4.21(q, *J*=7.2 Hz, 2H), 1.27(t, *J*=7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.7, 157.9, 139.8, 138.7, 135.3, 130.2, 127.3, 125.7, 122.8, 119.2, 117.2, 115.5, 107.1, 60.7, 31.9, 14.2. HRMS (ESI) Calcd for $[M+Na]^{+}$: 376.0614, found: 376.0617.

Methyl 2-((1-(pyrimidin-2-yl)-1H-indol-2-yl) methyl) acrylate 3z



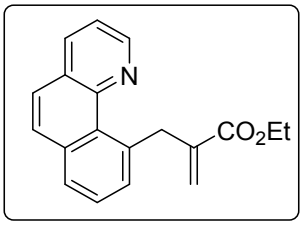
The reaction was carried out according to the general procedure (16 h). The residue was purified by flash column chromatography (10:1 petroleum ether: ethyl acetate) to afford **3z** (24.0 mg, 82 % yield) as colorless liquid. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.70(d, *J*=4.8 Hz, 2H), 8.34(d, *J*=8.4 Hz, 1H), 7.53(d, *J*=7.2 Hz, 1H), 7.17-7.26(m, 2H), 7.07(t, *J*=4.8 Hz, 1H), 6.94(s, 1H), 6.13(s, 1H), 5.39(s, 1H), 4.25(s, 2H), 3.73(s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.5, 158.0, 138.8, 138.2, 137.1, 129.1, 123.0, 122.0, 120.0, 117.0, 114.4, 108.0, 52.0, 31.9. HRMS (ESI) Calcd for $[M+Na]^{+}$: 316.1056, found: 316.1060.

Ethyl 2-((4-oxo-1-(pyrimidin-2-yl)-4, 5, 6, 7-tetrahydro-1H-indol-2-yl) methyl) acrylate 3aa



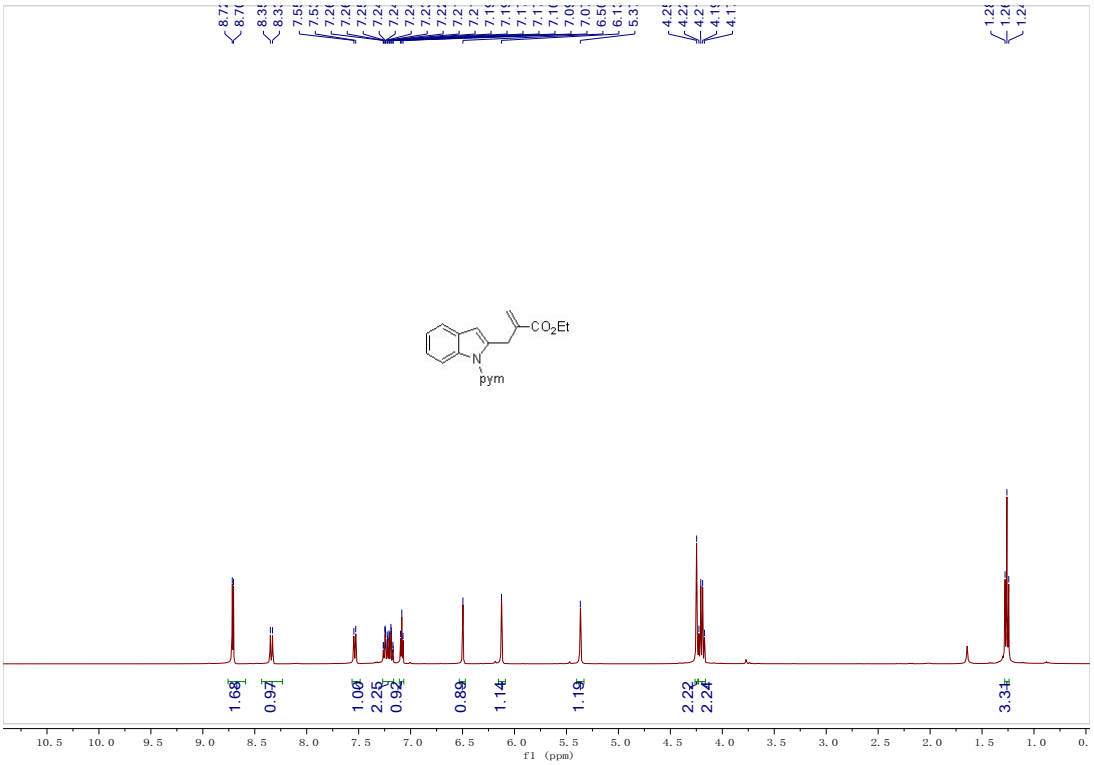
The reaction was carried out according to the general procedure (16 h). The residue was purified by flash column chromatography (9:1 petroleum ether: ethyl acetate) to afford **3aa** (21.1 mg, 65 % yield) as brown liquid. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.77(d, *J*=4.8 Hz, 1H), 7.28(d, *J*=4.8 Hz, 1H), 6.46(s, 1H), 6.09(s, 1H), 5.35(s, 1H), 4.16(q, *J*=6.8 Hz, 2H), 3.91(s, 2H), 3.01(t, *J*=6.4 Hz, 2H), 2.50-2.53(m, 2H), 2.09-2.15(m, 2H), 1.26(t, *J*=6.8 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 194.9, 166.6, 158.4, 156.9, 145.6, 138.5, 132.9, 125.8, 121.7, 119.0, 107.3, 60.8, 37.8, 30.1, 24.6, 23.9, 14.2. HRMS (ESI) Calcd for $[M+Na]^{+}$: 348.1319, found: 348.1322.

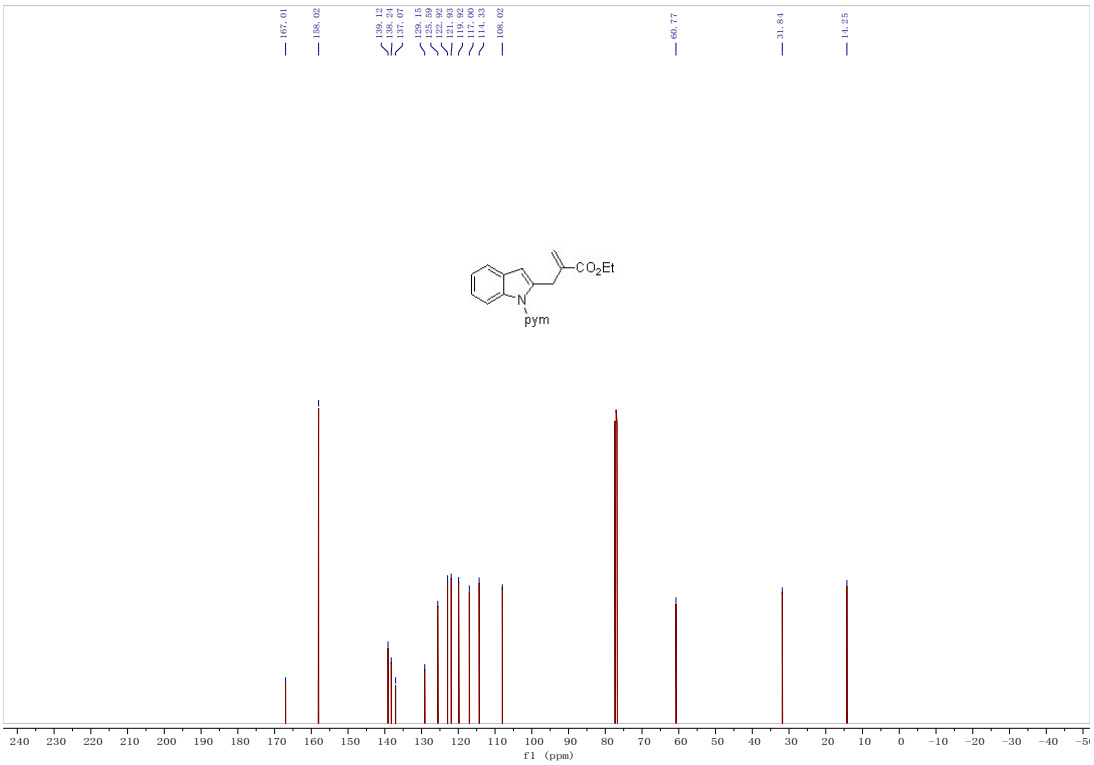
Ethyl 2-(benzo[h]quinolin-10-ylmethyl) acrylate 3bb

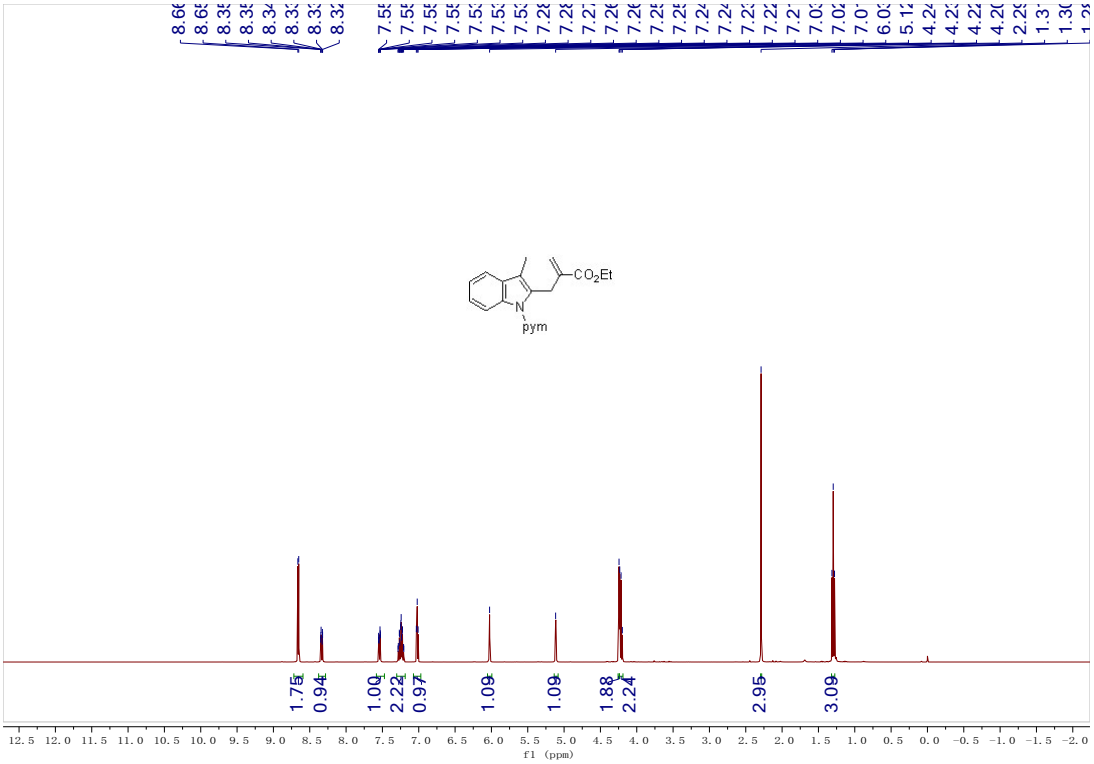


The reaction was carried out according to the general procedure (16 h). The residue was purified by flash column chromatography (15:1 petroleum ether: ethyl acetate) to afford **3bb** (14.5 mg, 50 % yield) as colorless liquid. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.84(dd, J_1=4.4 Hz, J_2=2.0 Hz, 1H), 8.11(dd, J_1=8.0 Hz, J_2=1.6 Hz, 1H), 7.85(dd, J_1=8.4 Hz, J_2=3.2 Hz, 1H), 7.80(d, J=8.8 Hz, 1H), 7.60-7.65(m, 2H), 7.54(dd, J_1=4.4 Hz, J_2=0.8 Hz, 1H), 7.43(dd, J_1=8.0 Hz, J_2=4.4 Hz, 1H), 5.95(s, 1H), 4.94(s, 1H), 4.81(s, 2H), 3.65(q, J=7.2 Hz, 2H), 3.16 (t, J=7.2 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-d) δ 168.3, 147.5, 147.1, 142.5, 138.5, 135.5, 135.4, 132.0, 129.2, 128.7, 127.8, 127.3, 125.7, 122.8, 120.8, 60.5, 39.7, 14.5. HRMS (ESI) Calcd for $[M+Na]^+$: 314.1151, found: 314.1150.

7. NMR Spectra for products



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pym
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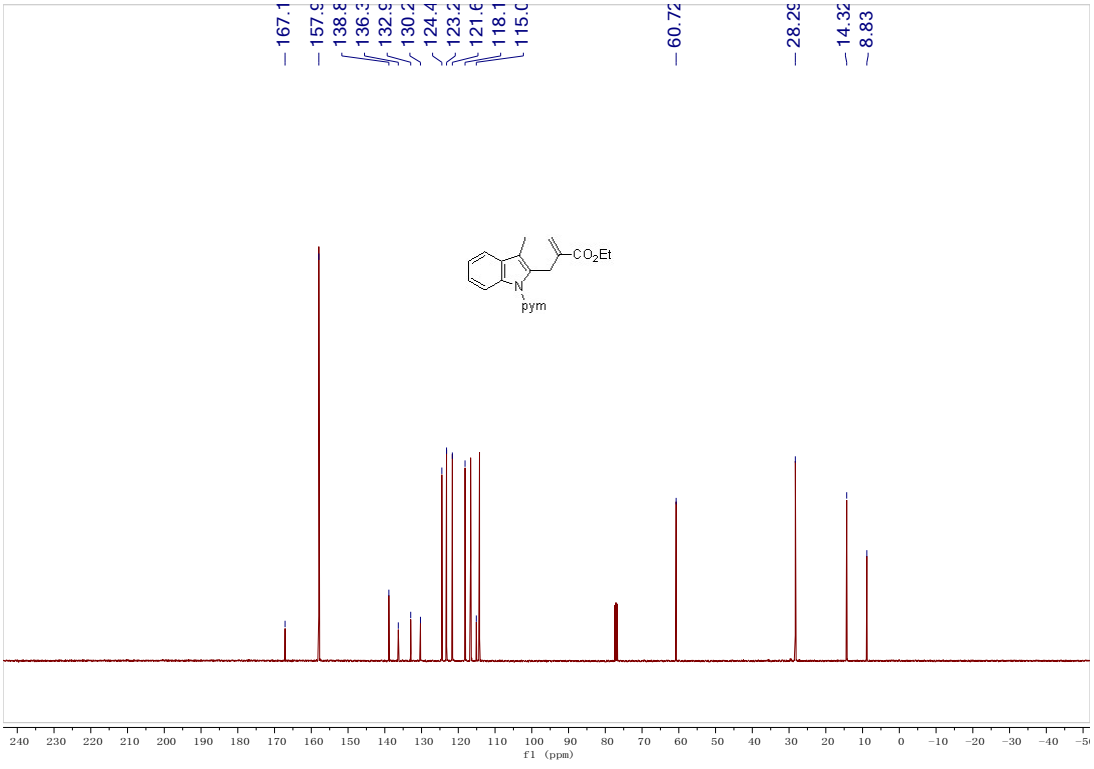
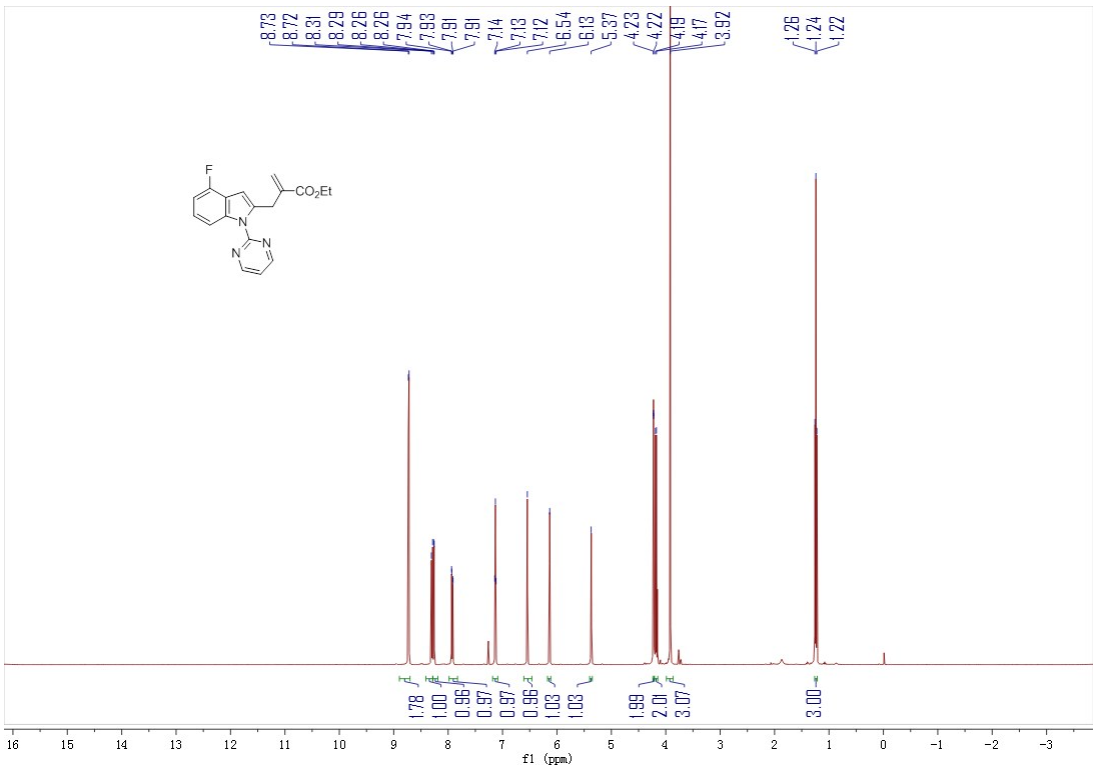
2.22
0.97
1.09
1.09
1.88
2.24
2.95
3.09
f1 (ppm)


167.1
157.9
138.8
136.3
132.9
130.2
124.4
123.2
121.6
118.1
115.0
60.72
28.29
14.32
8.83
CO2Et
pym
f1 (ppm)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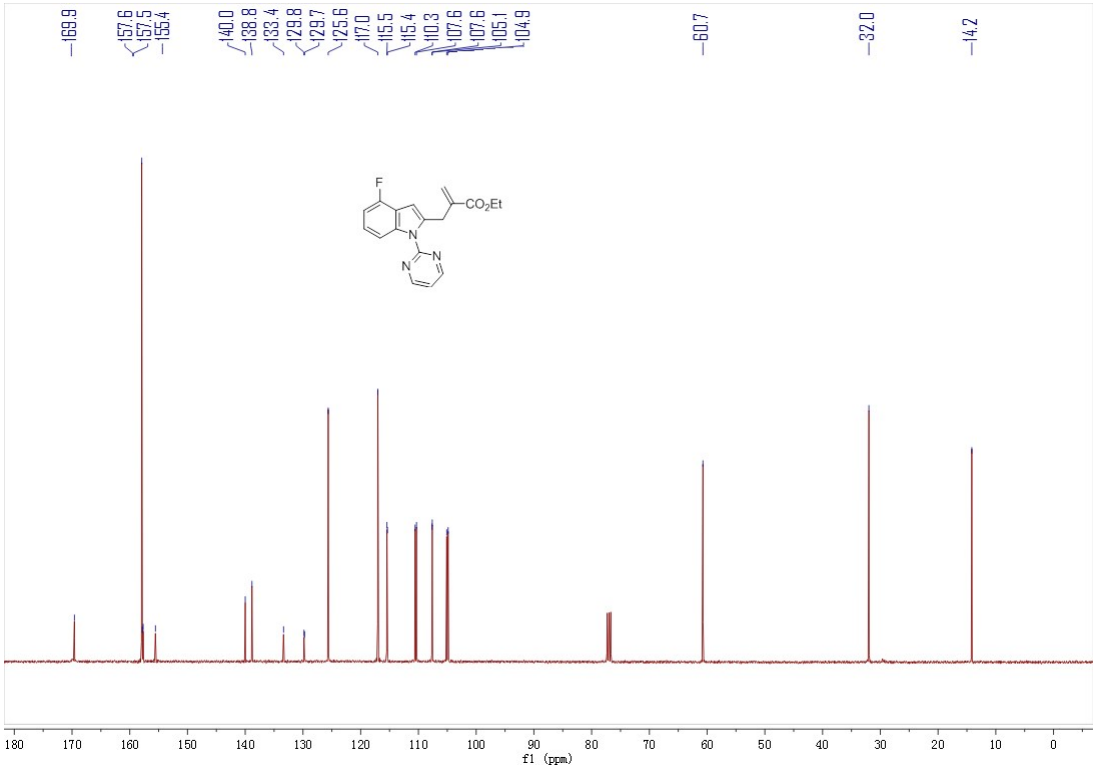
8.72
8.31
8.29
8.26
8.26
7.94
7.93
7.91
7.91
7.14
7.13
7.12
6.54
6.13
5.37
4.23
4.22
4.19
4.17
3.92
1.26
1.24
1.22
F
CO2Et
N
N
1.78
1.00
0.96
0.97
0.97
0.96
1.03
1.03
1.99
2.01
3.07
3.00
f1 (ppm)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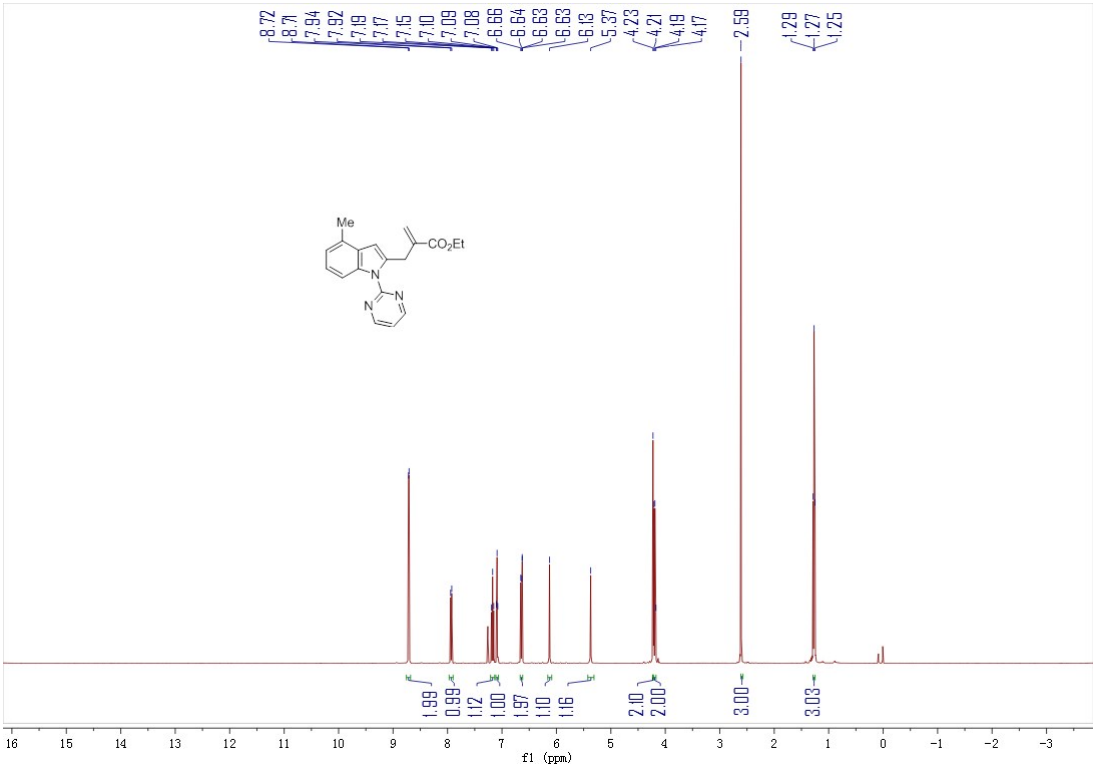
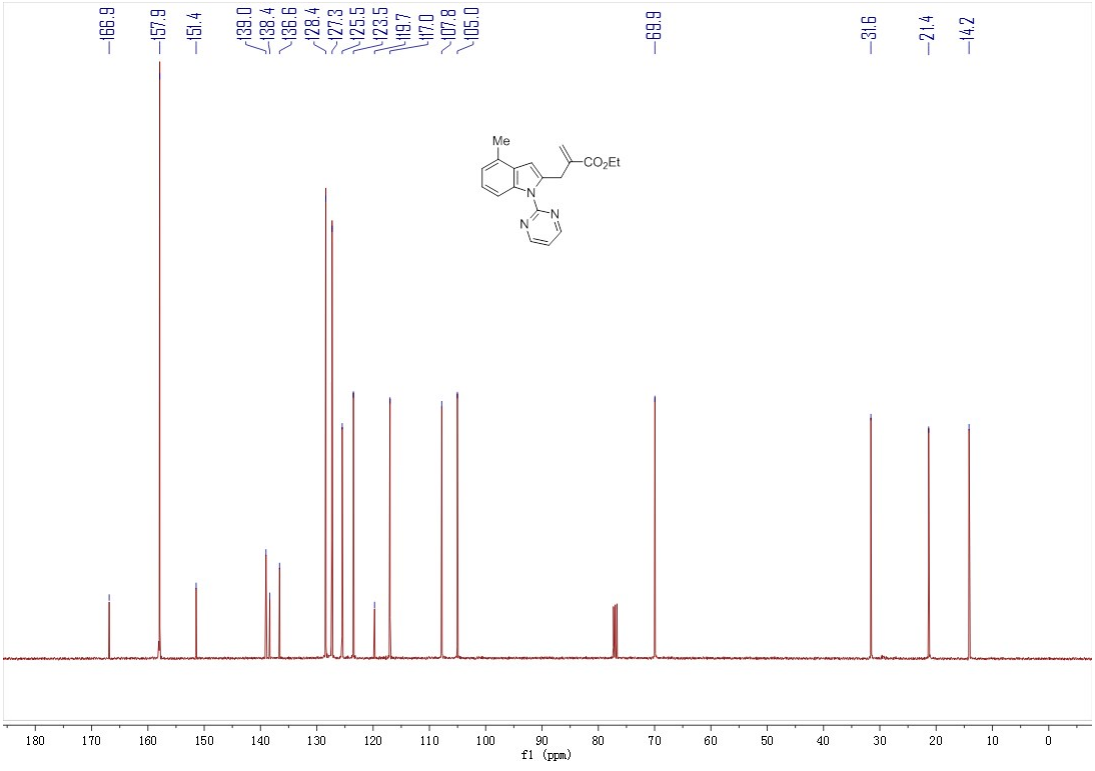
157.6
157.5
155.4
140.0
138.8
133.4
129.8
129.7
125.6
117.0
115.5
115.4
110.3
107.6
107.6
105.1
104.9
60.7
32.0
14.2
F
CO2Et
N
N
f1 (ppm)


8.72
8.71
7.94
7.92
7.19
7.17
7.15
7.10
7.09
7.08
6.66
6.64
6.63
6.63
6.13
5.37
4.23
4.21
4.19
4.17
2.59
1.29
1.27
1.25
Me
CO2Et
N
N
1.99
0.99
1.12
1.00
1.97
1.10
1.16
2.10
2.00
3.00
3.03
f1 (ppm)


166.9
157.9
151.4
139.0
138.4
136.6
128.4
127.3
125.5
123.5
119.7
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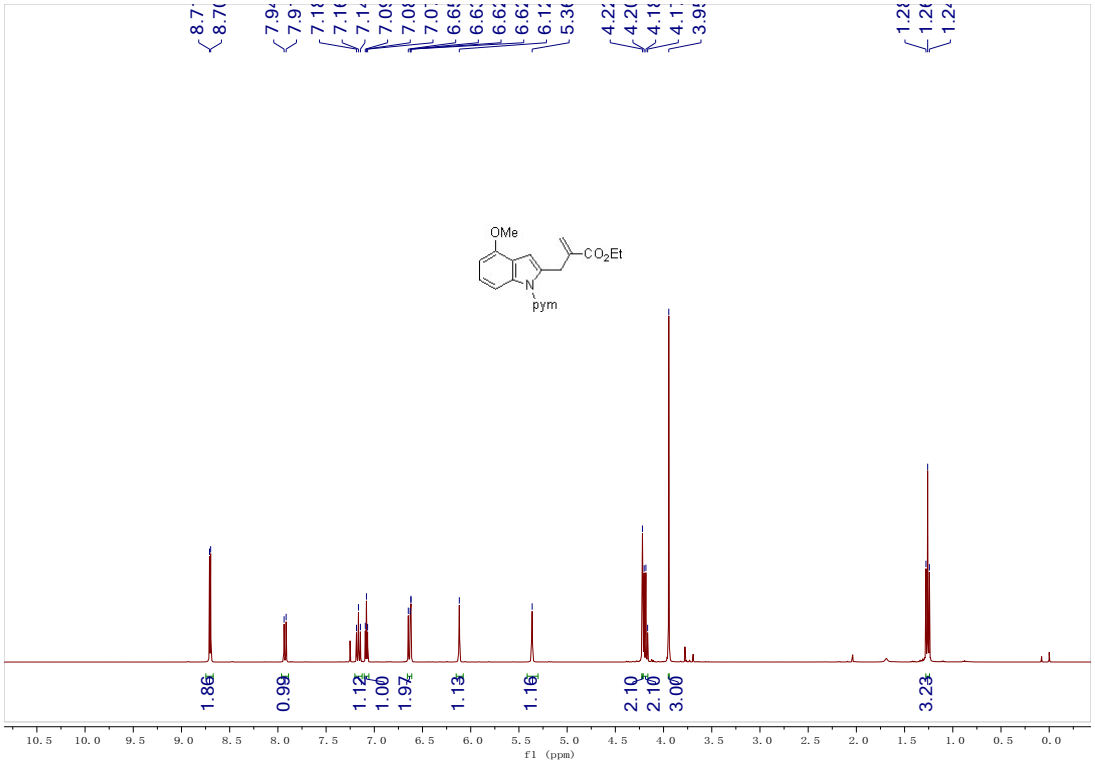
107.8
105.0
69.9
31.6
21.4
14.2
Me
CO2Et
N
N
f1 (ppm)


OMe
CO2Et
N
pym
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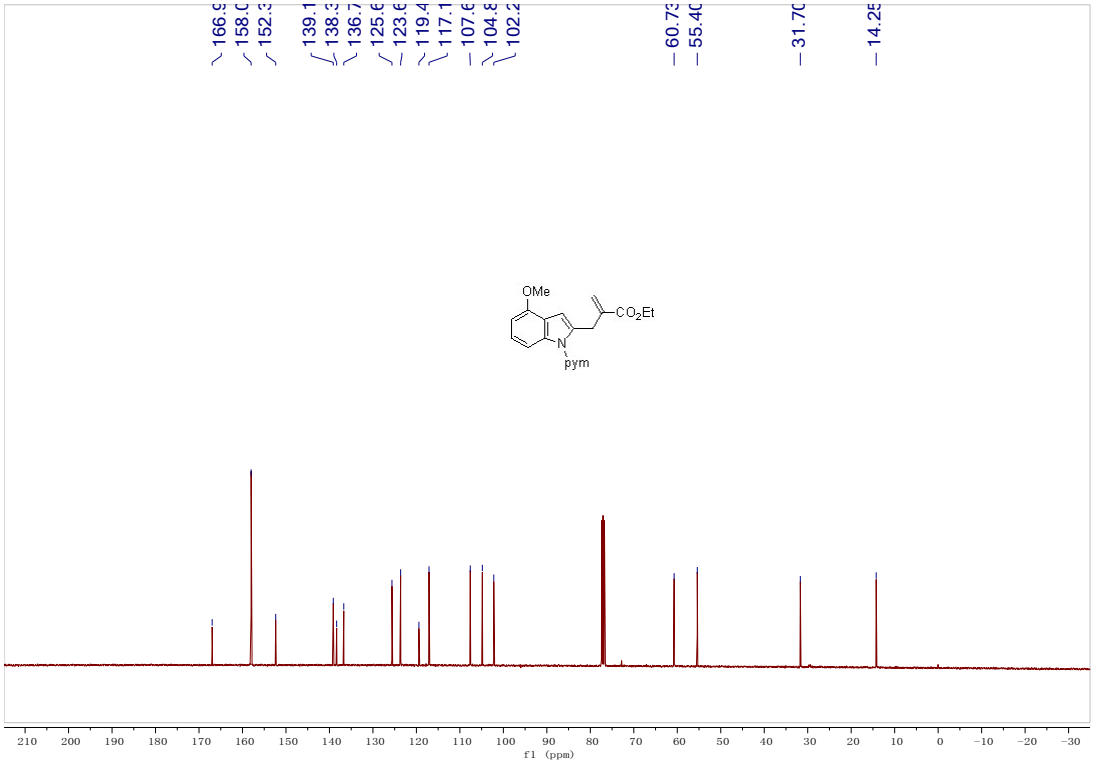
1.00
1.97
1.13
1.16
2.10
2.10
3.00
3.23
f1 (ppm)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CO2Et
N
pym
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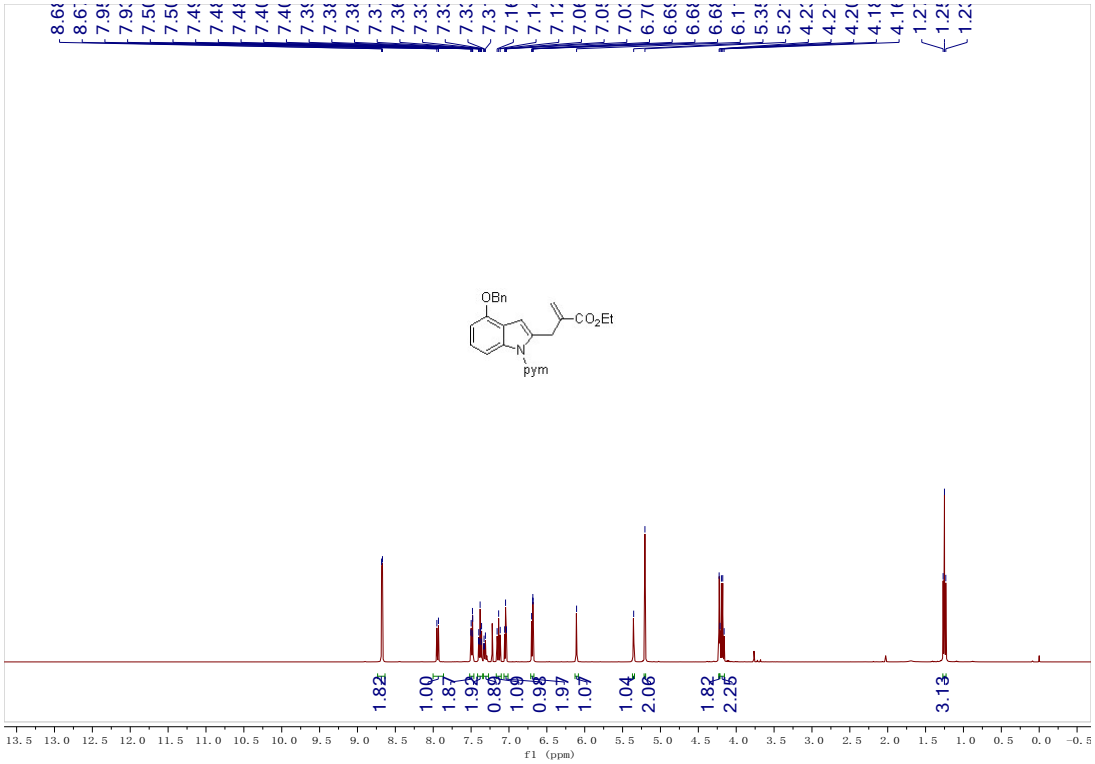
55.40
31.70
14.25
f1 (ppm)


OBn
CO2Et
pym
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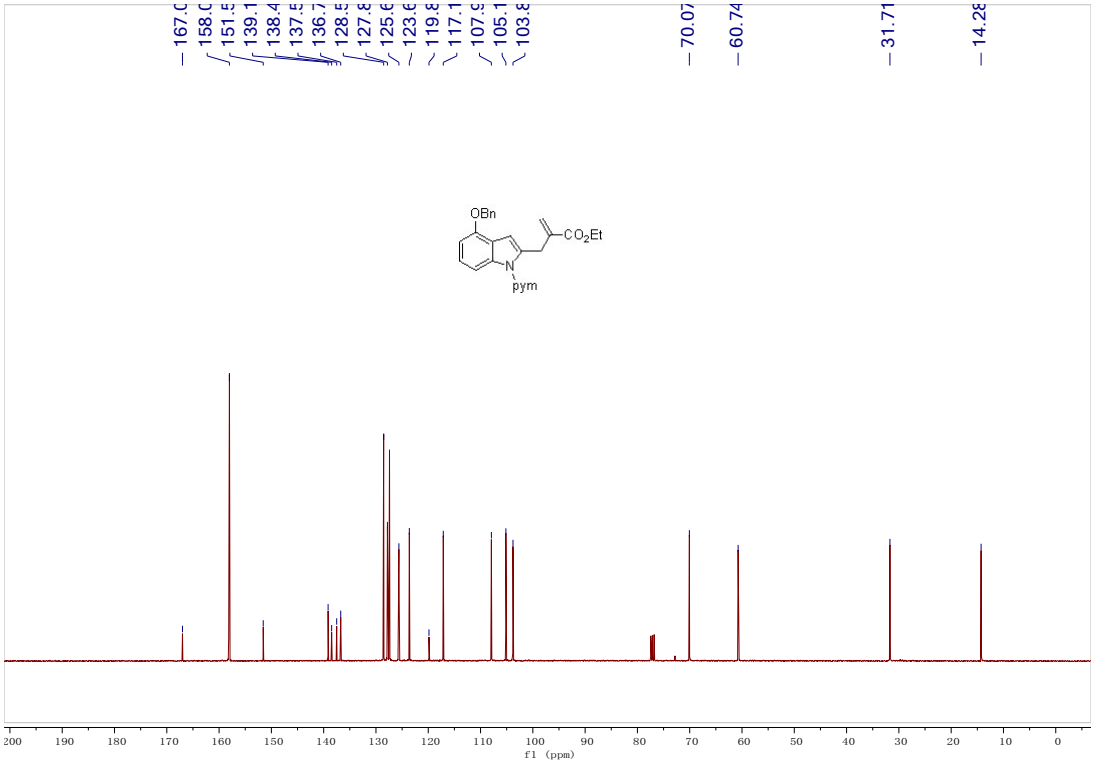
1.00
1.87
1.92
0.89
1.09
0.98
1.97
1.07
1.04
2.06
1.82
2.25
3.13
f1 (ppm)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151.5
139.1
138.4
137.5
136.7
128.5
127.8
125.6
123.6
119.8
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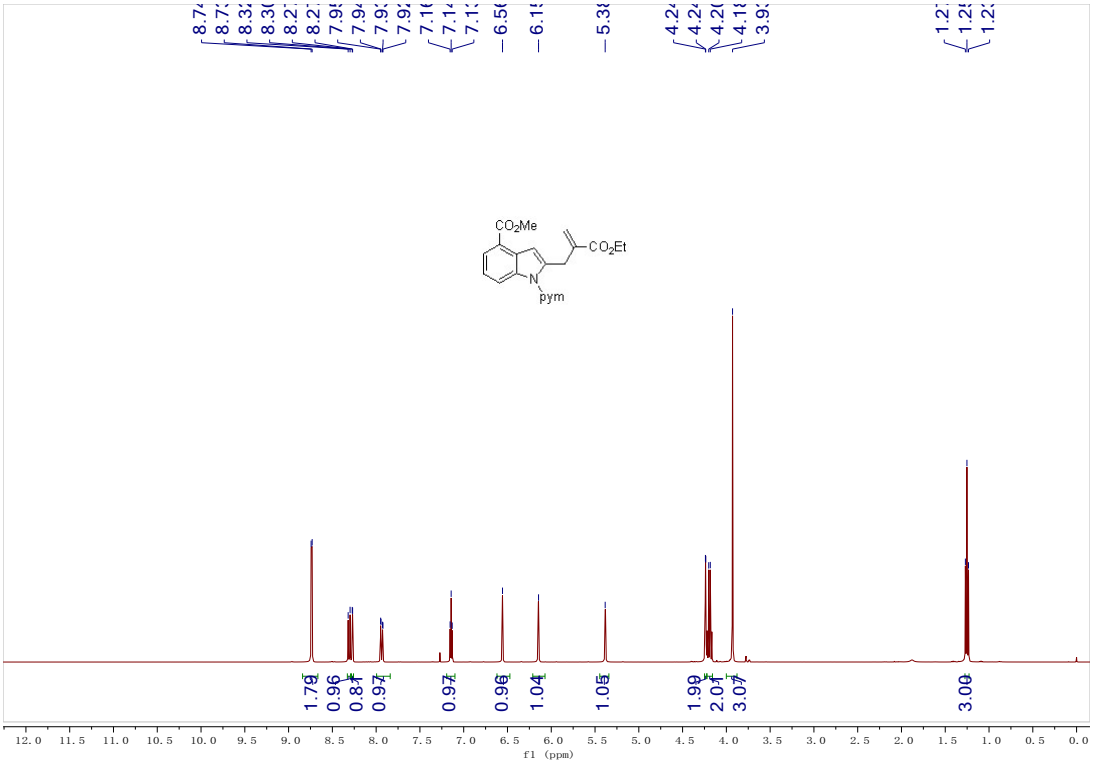
107.9
105.1
103.8
70.07
60.74
31.71
14.28
OBn
CO2Et
pym
f1 (ppm)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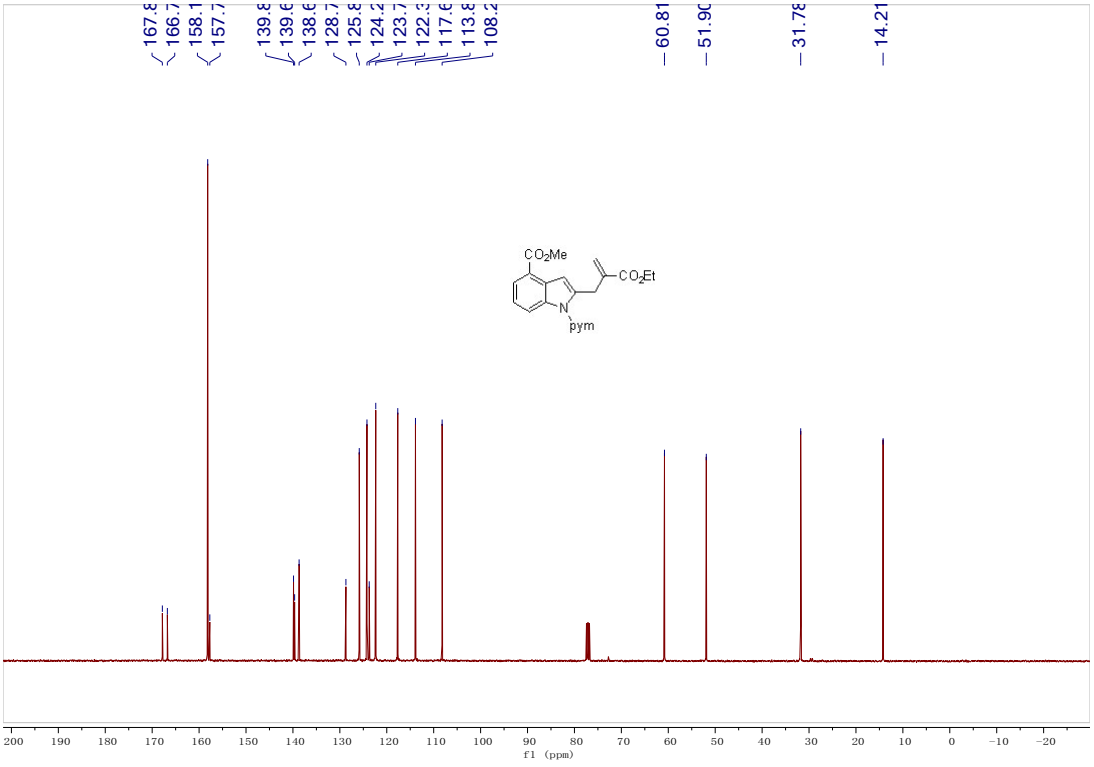
CO2Et
N
pym
f1 (ppm)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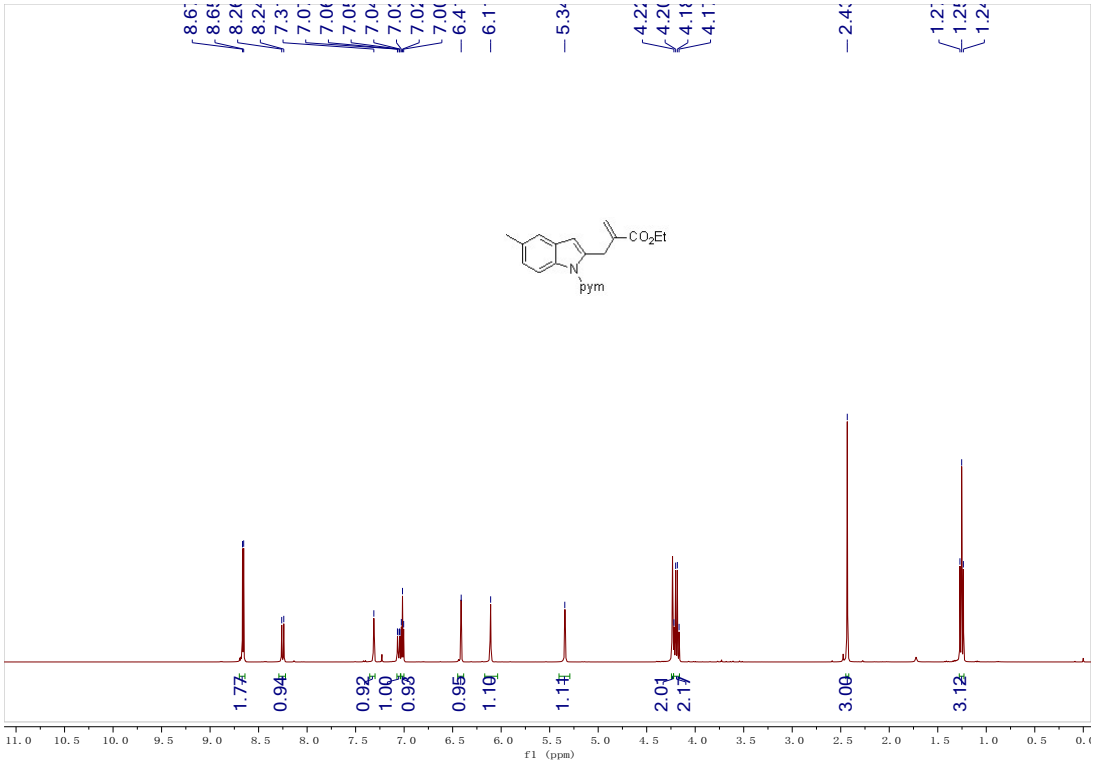
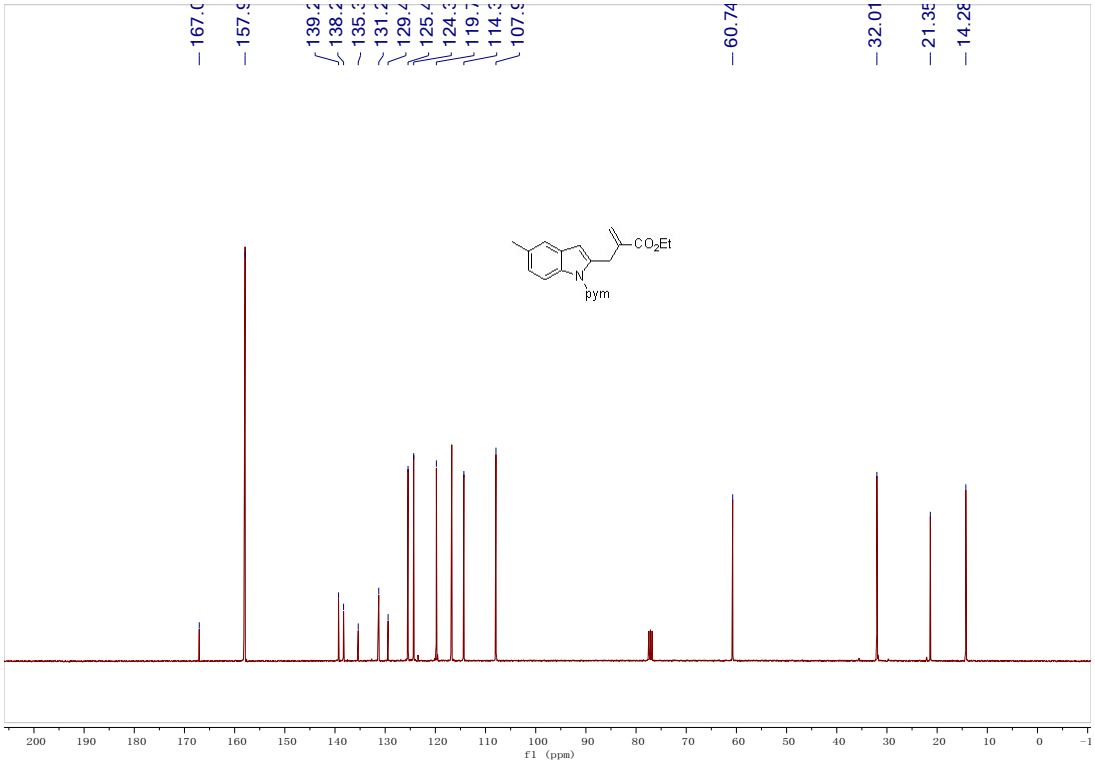
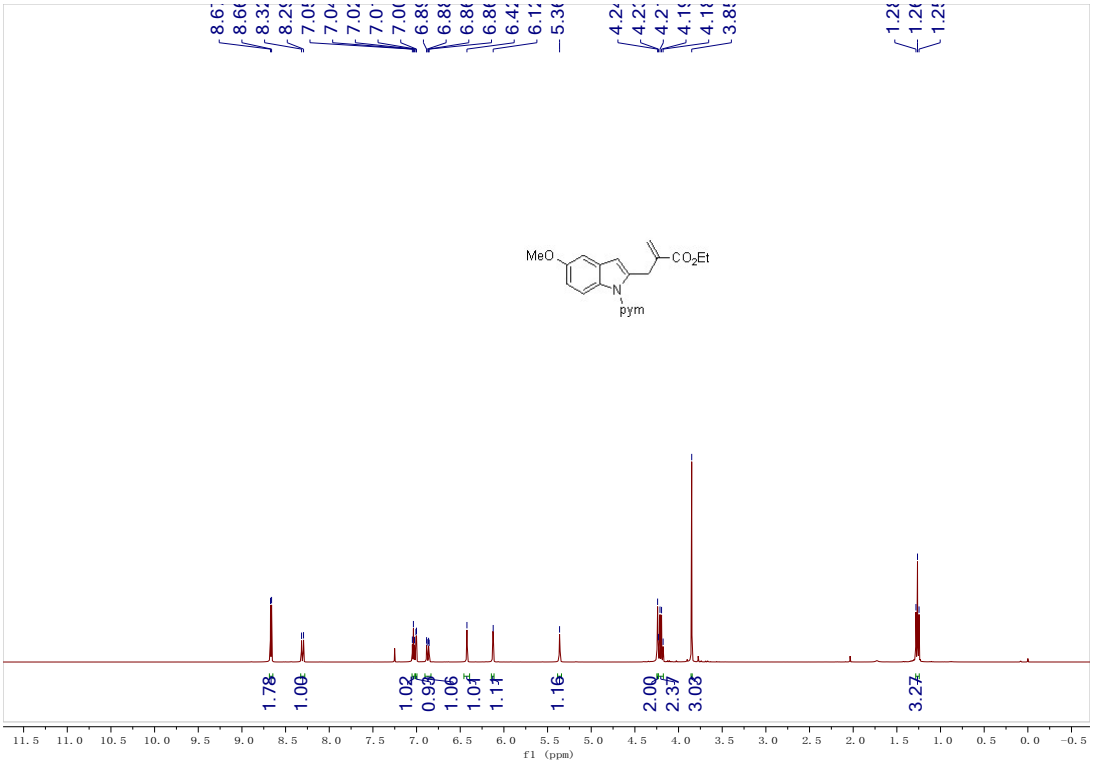
CO2Et
N
pym
f1 (ppm)


CO2Et
pym
f1 (ppm)


CO2Et
pym
f1 (ppm)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1.11
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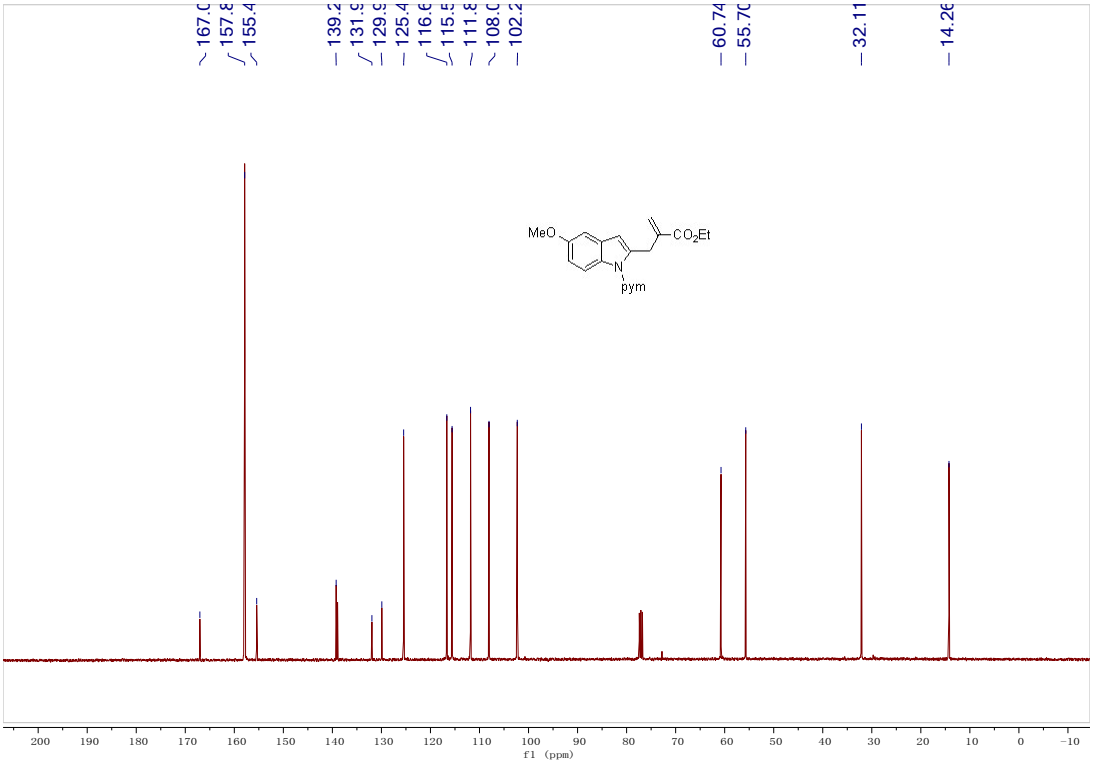
3.27
f1 (ppm)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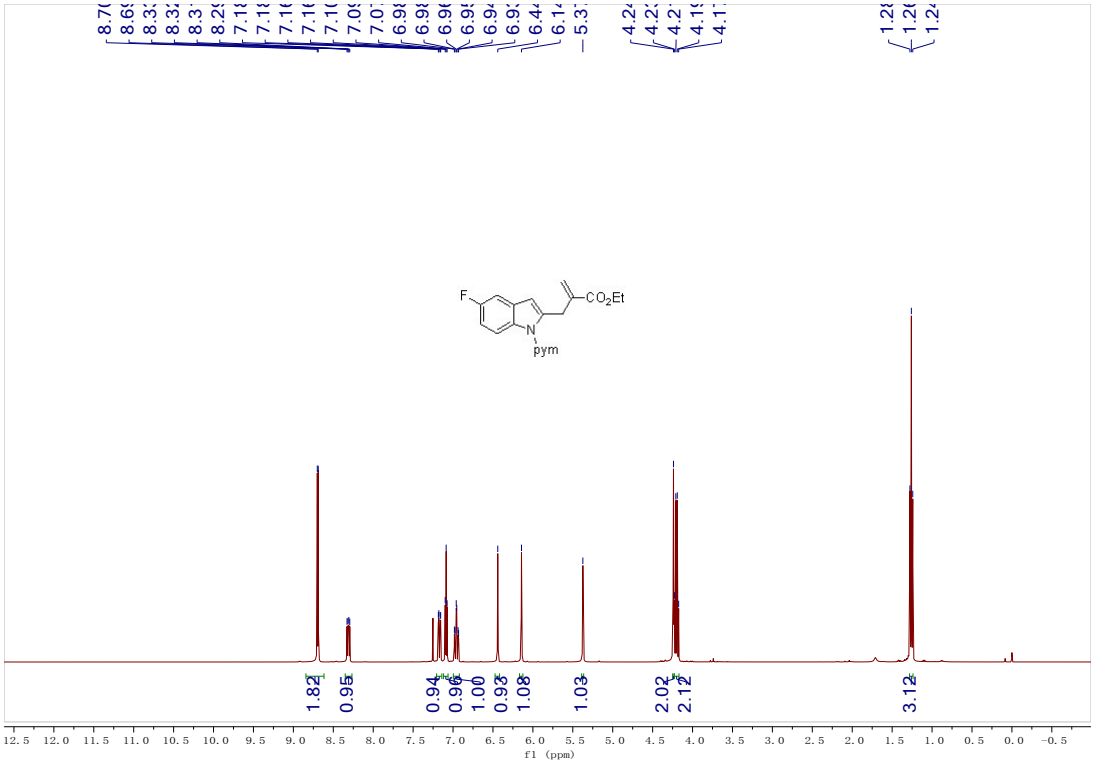
N
pym
f1 (ppm)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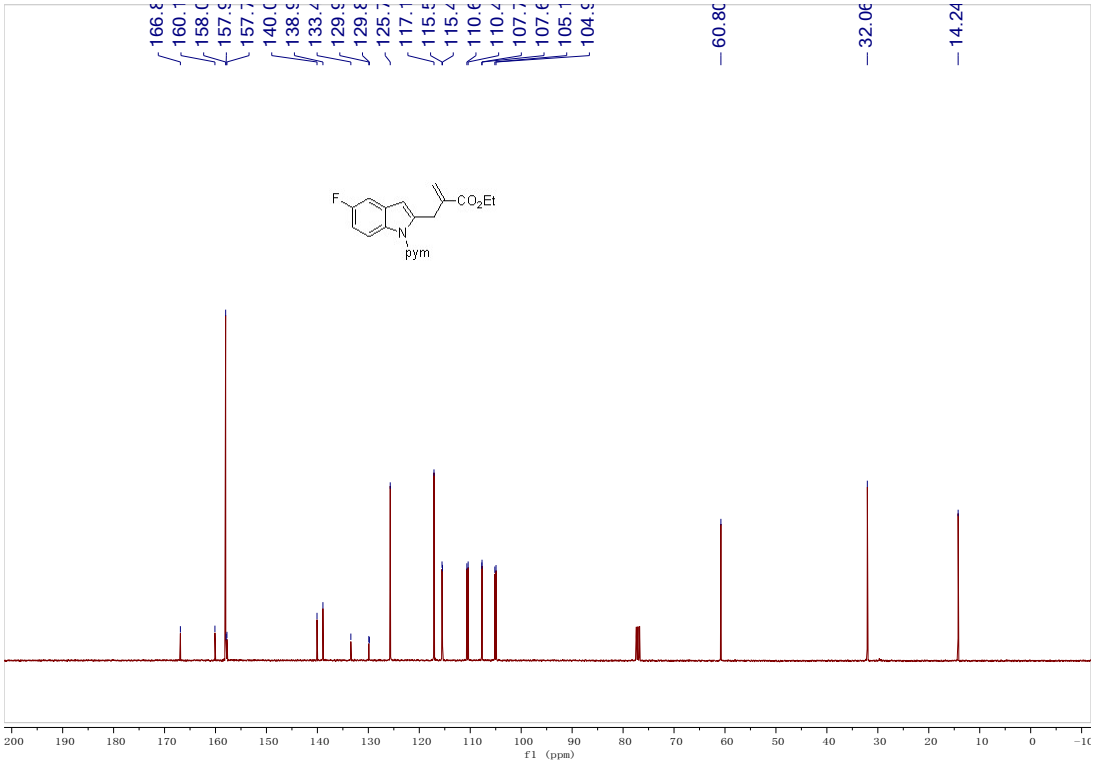
3.12
f1 (ppm)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pym
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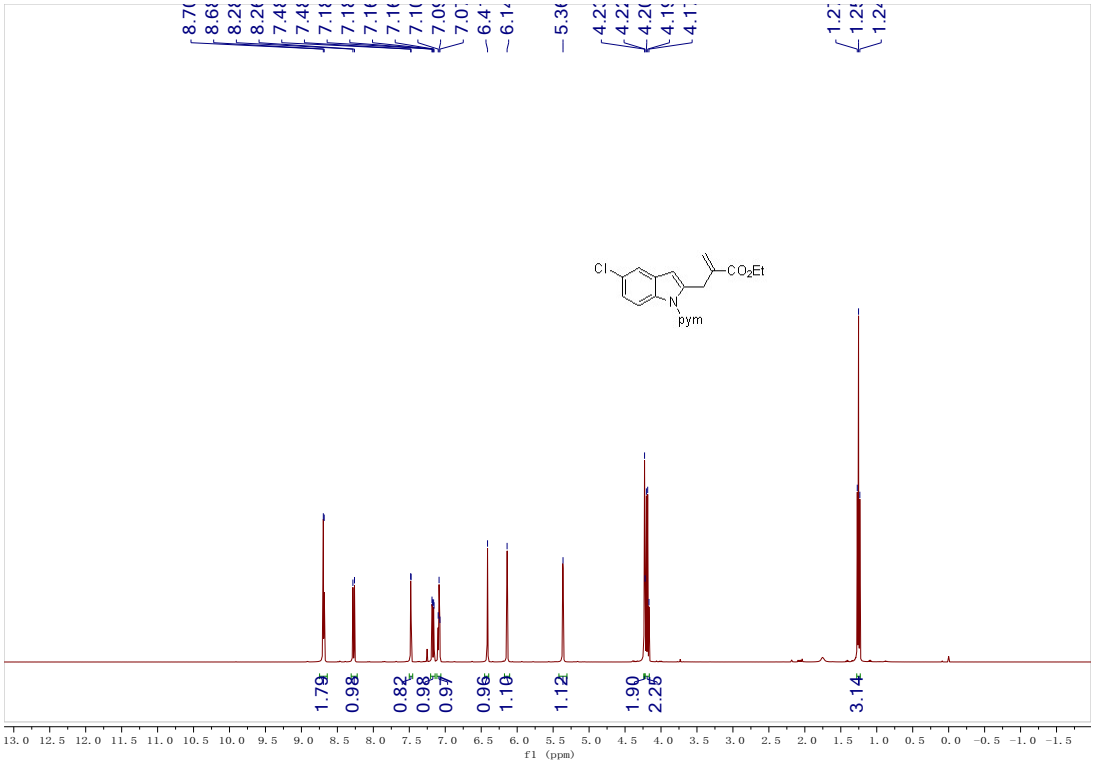
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CO2Et
N
pym
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0.98
0.97
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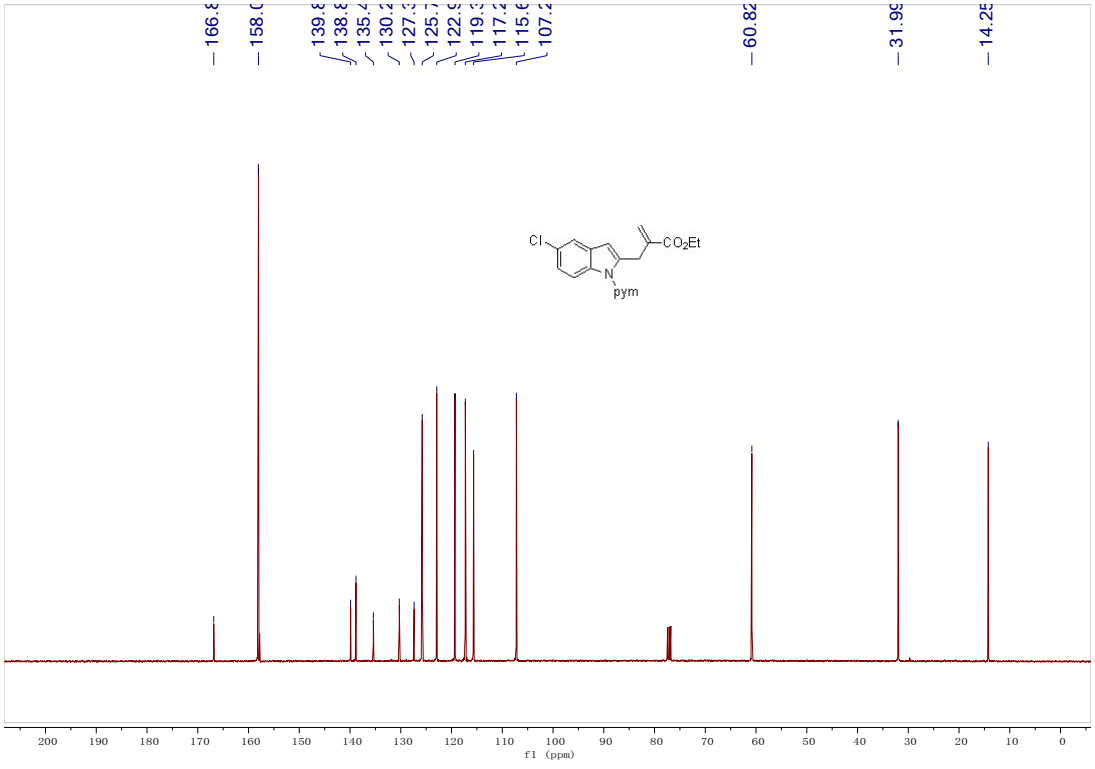
1.10
1.12
1.90
2.25
3.14
f1 (ppm)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130.2
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122.9
119.3
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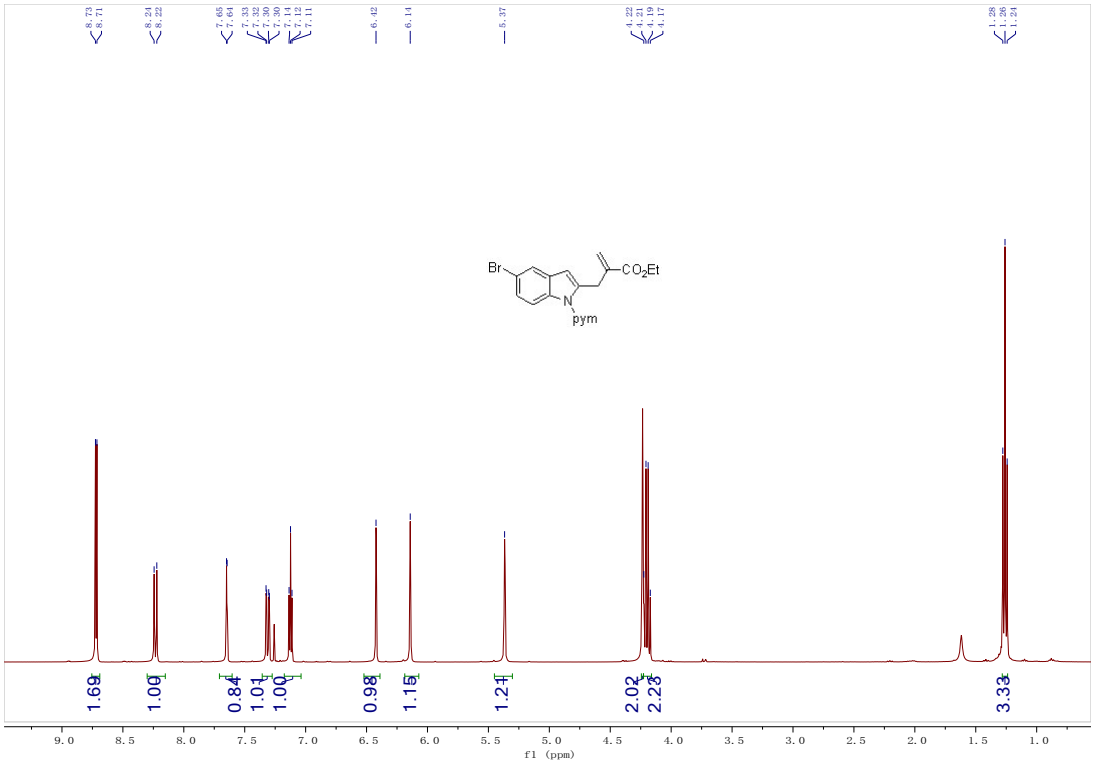
115.6
107.2
60.82
31.99
14.25
Cl
CO2Et
N
pym
f1 (ppm)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4.22
4.21
4.19
4.17
1.28
1.26
1.24
Br
CO2Et
N
pym
1.69
1.00
0.84
1.01
1.00
0.98
1.15
1.21
2.02
2.23
3.33
9.0
8.5
8.0
7.5
7.0
6.5
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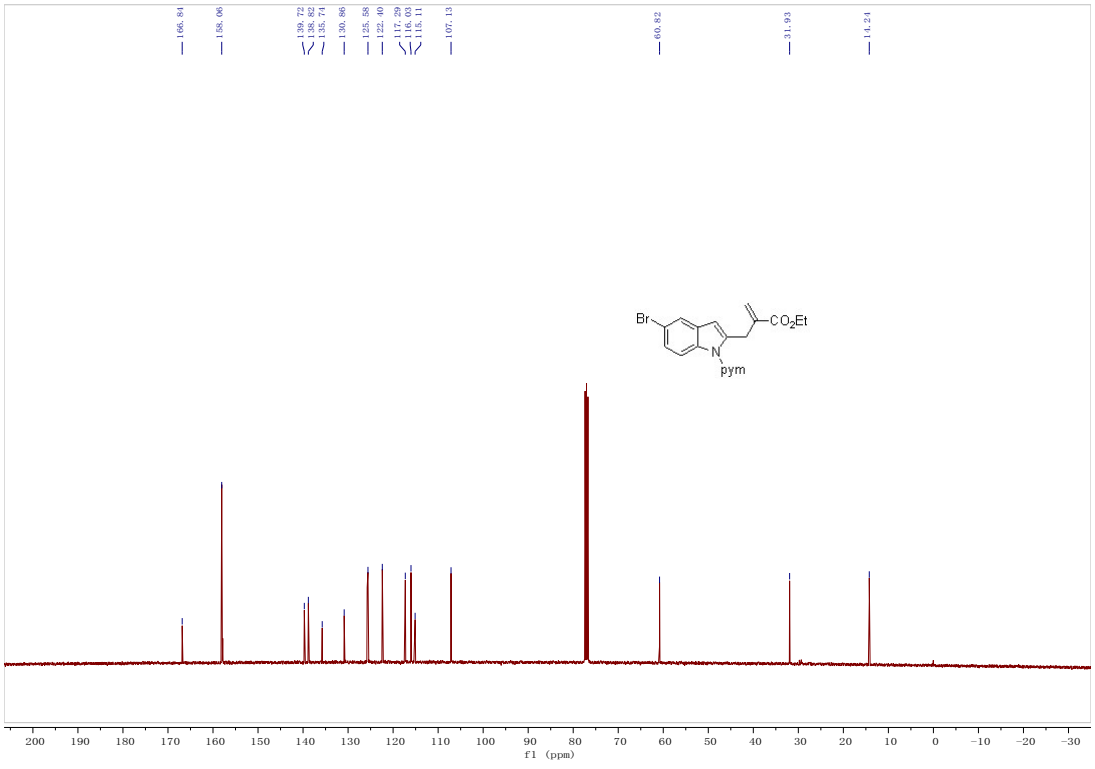
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116.03
115.11
107.13
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31.93
14.24
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CO2Et
N
pym
200
190
180
170
160
150
140
130
120
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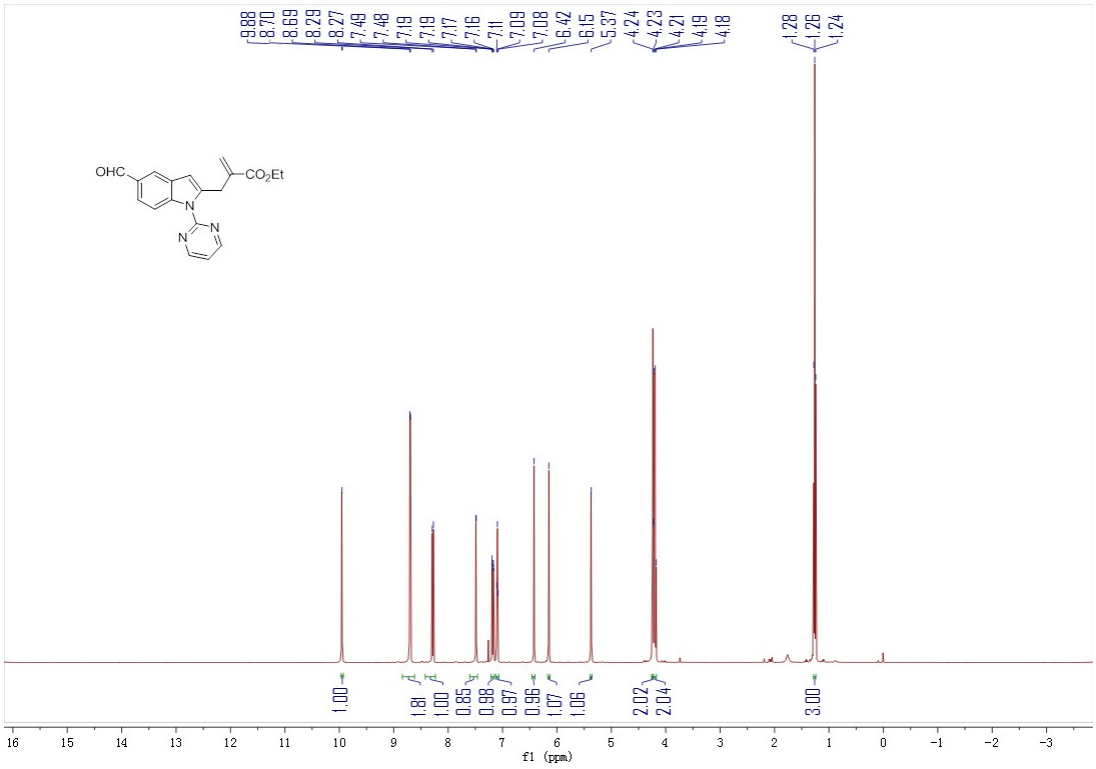
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
f1 (ppm)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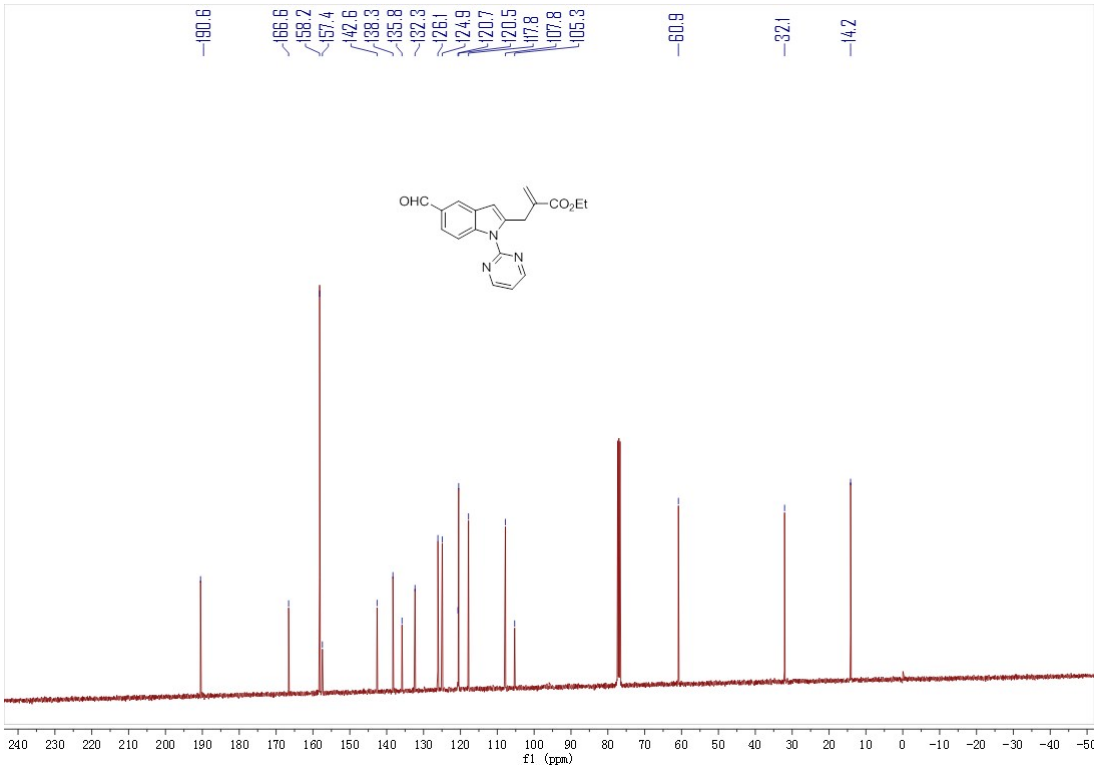
7.09
7.08
6.42
6.15
5.37
4.24
4.23
4.21
4.19
4.18
1.28
1.26
1.24
OHC
CO2Et
N
N
1.00
1.81
1.00
0.85
0.98
0.97
0.96
1.07
1.06
2.02
2.04
3.00
f1 (ppm)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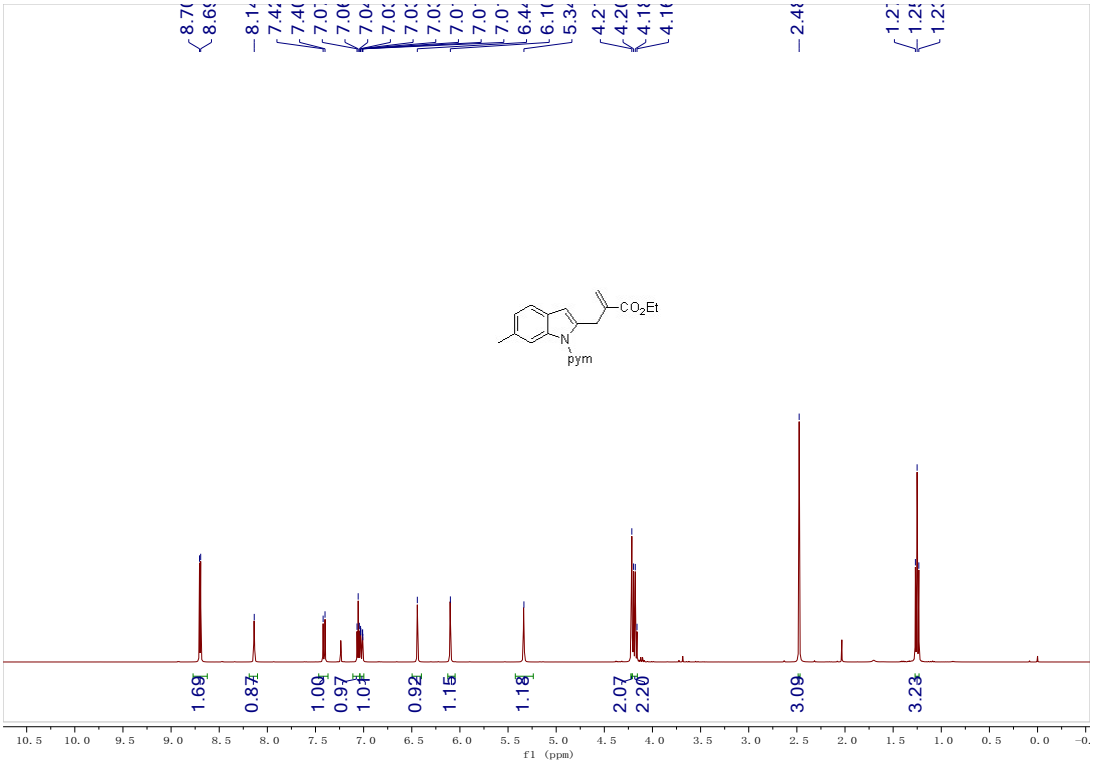
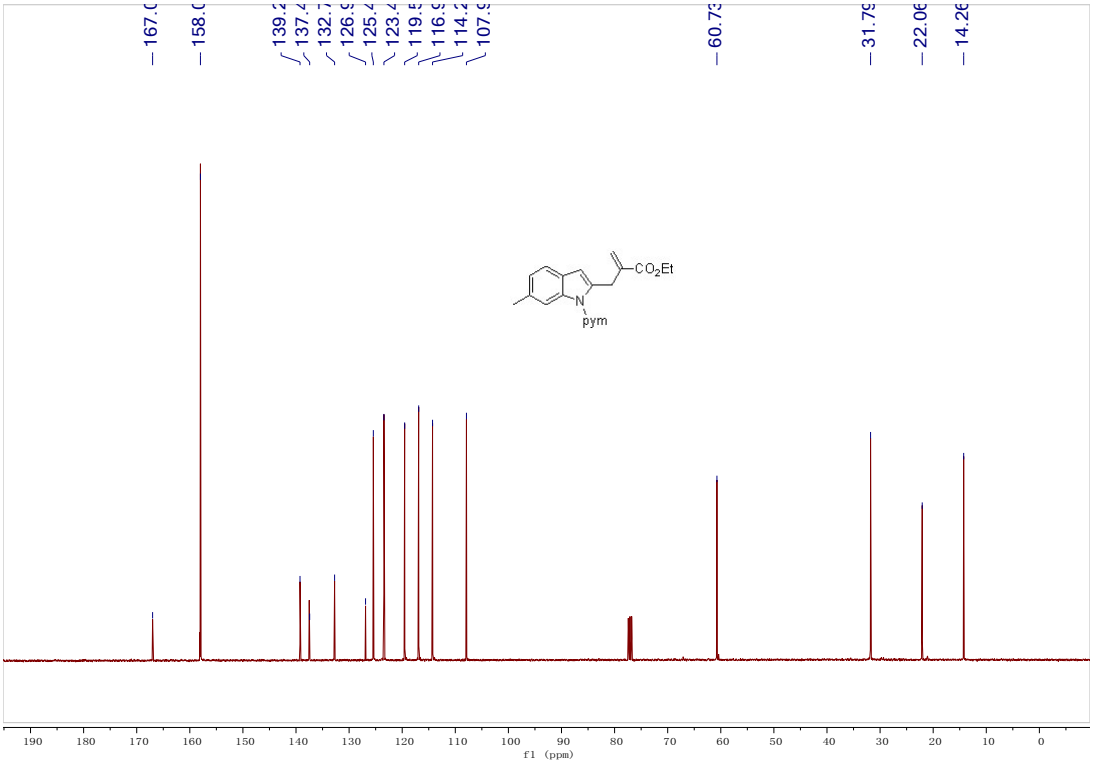
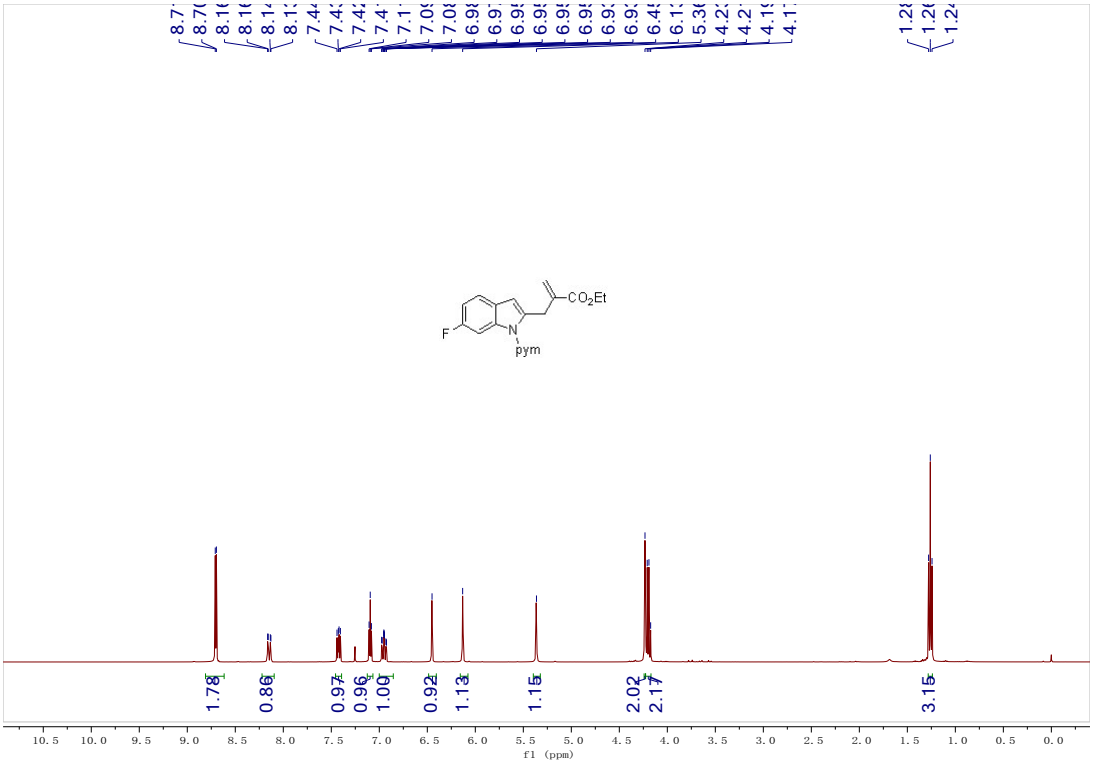
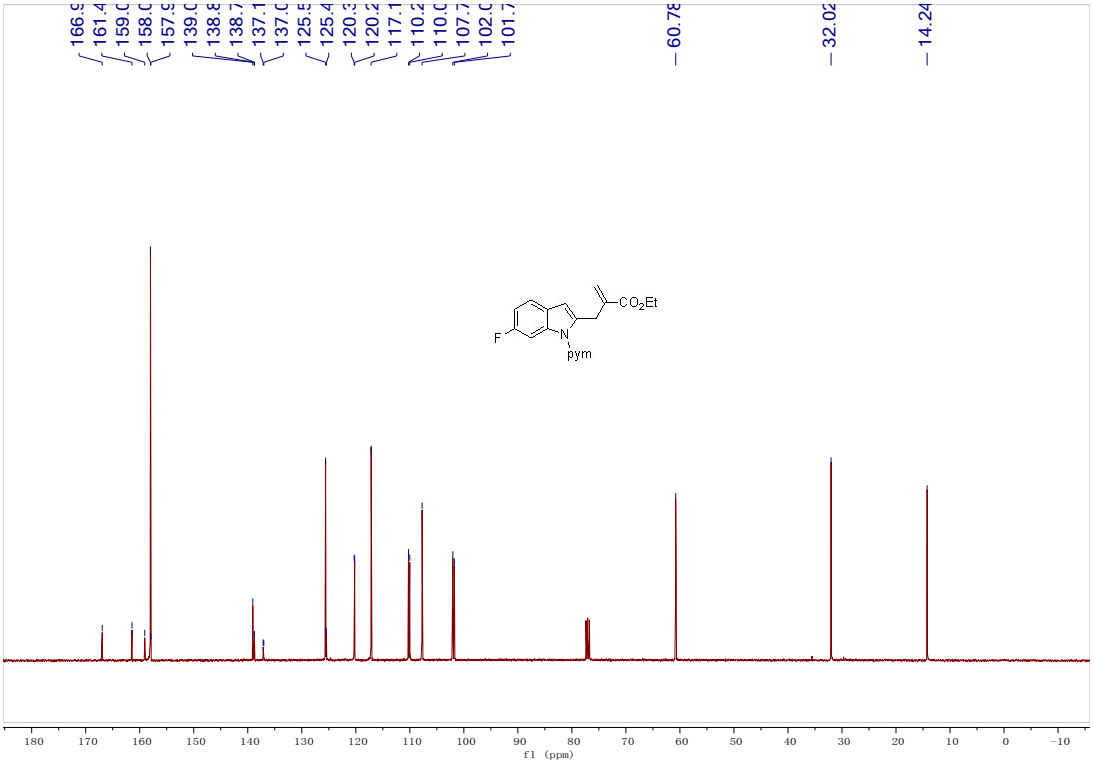
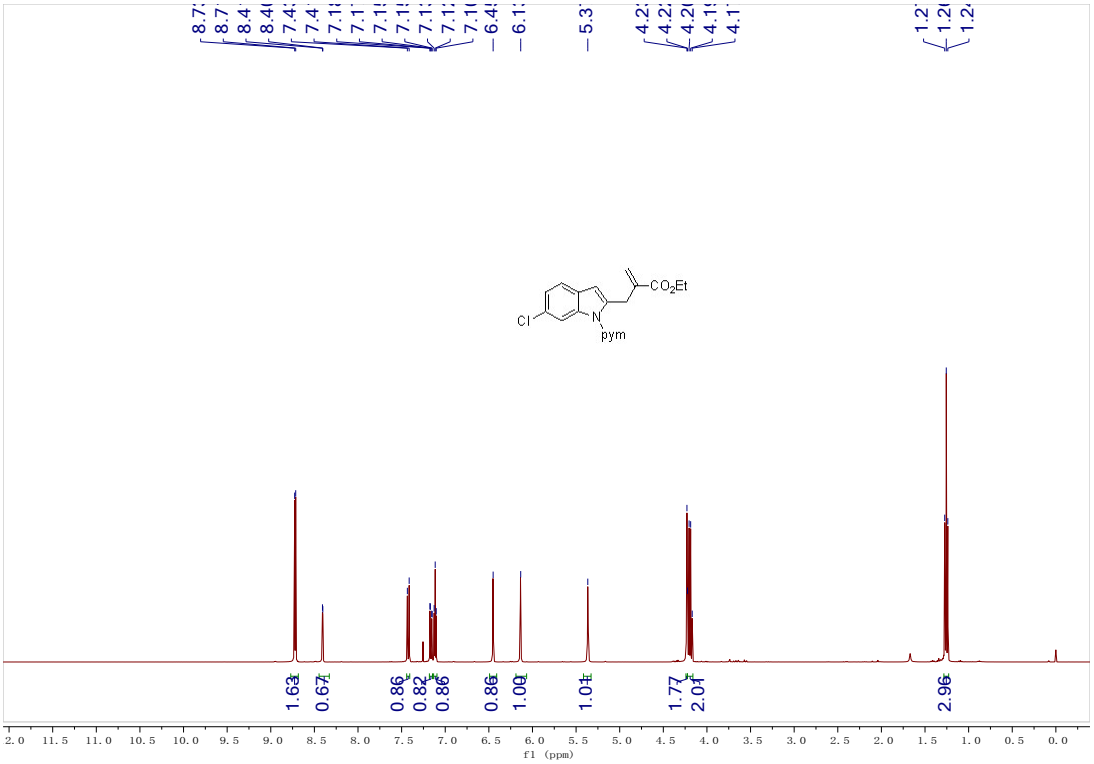
166.6
158.2
157.4
142.6
138.3
135.8
132.3
126.1
124.9
120.7
120.5
117.8
107.8
105.3
60.9
32.1
14.2
OHC
CO2Et
N
N
f1 (ppm)

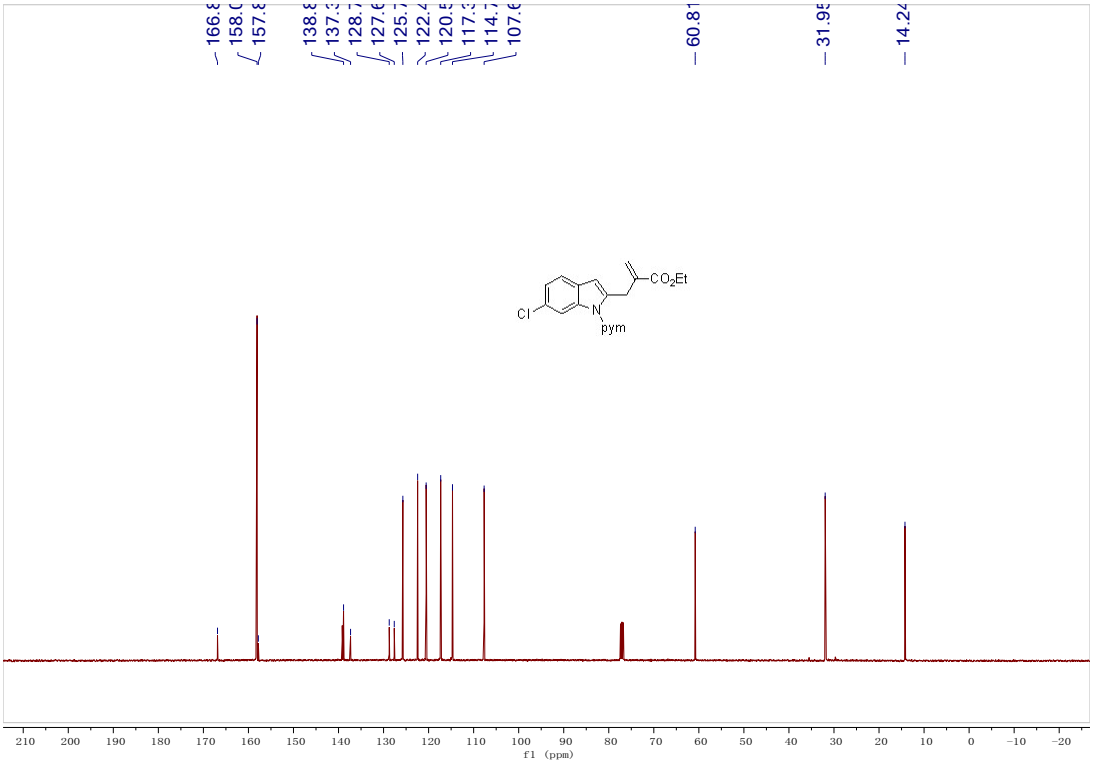

CO2Et
N
pym
f1 (ppm)

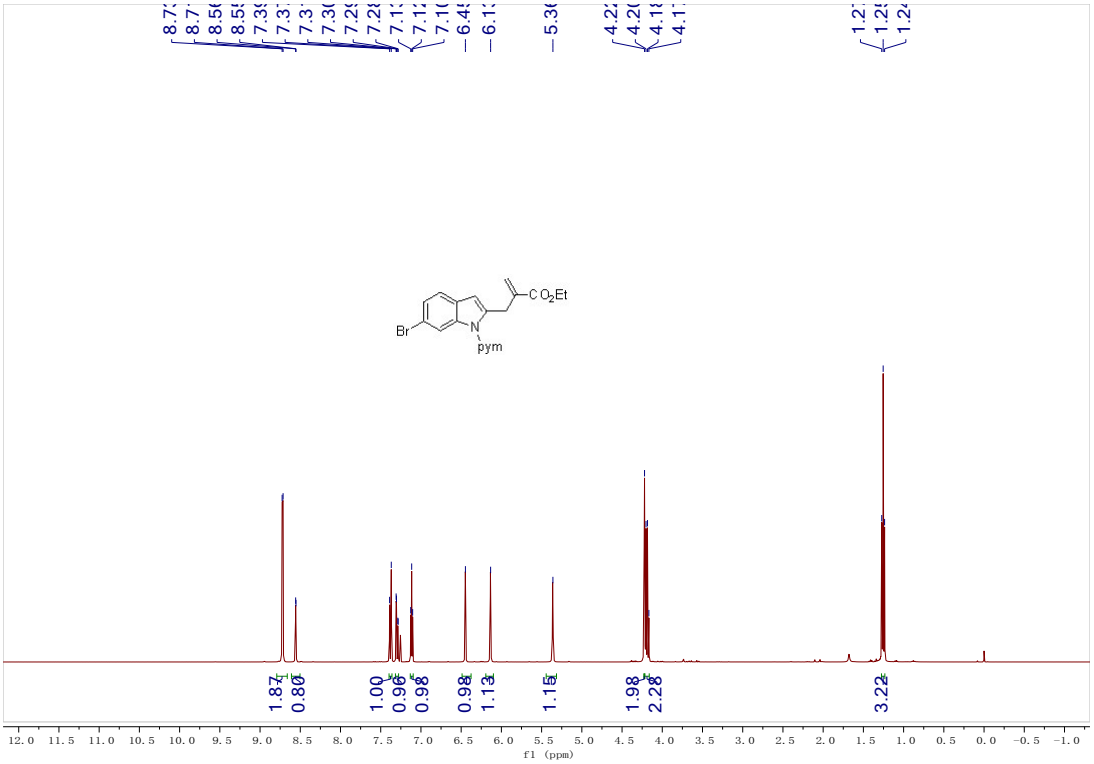

CO2Et
N
pym
f1 (ppm)

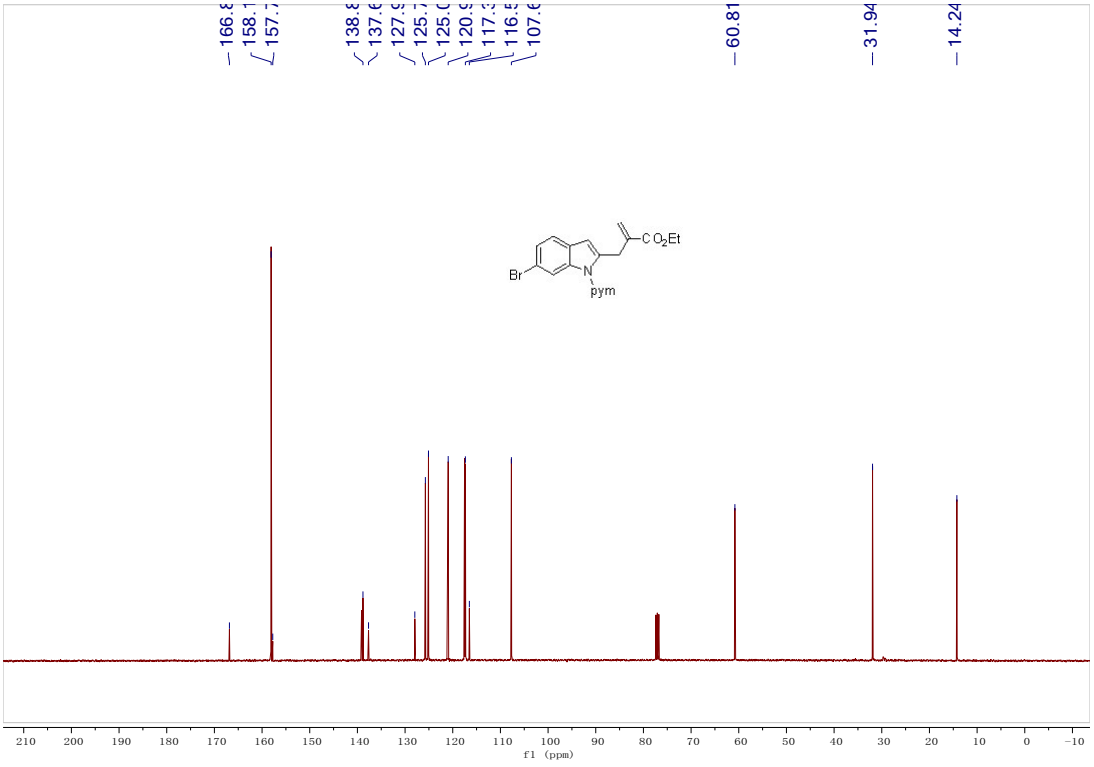

CO2Et
F
N
pym
f1 (ppm)

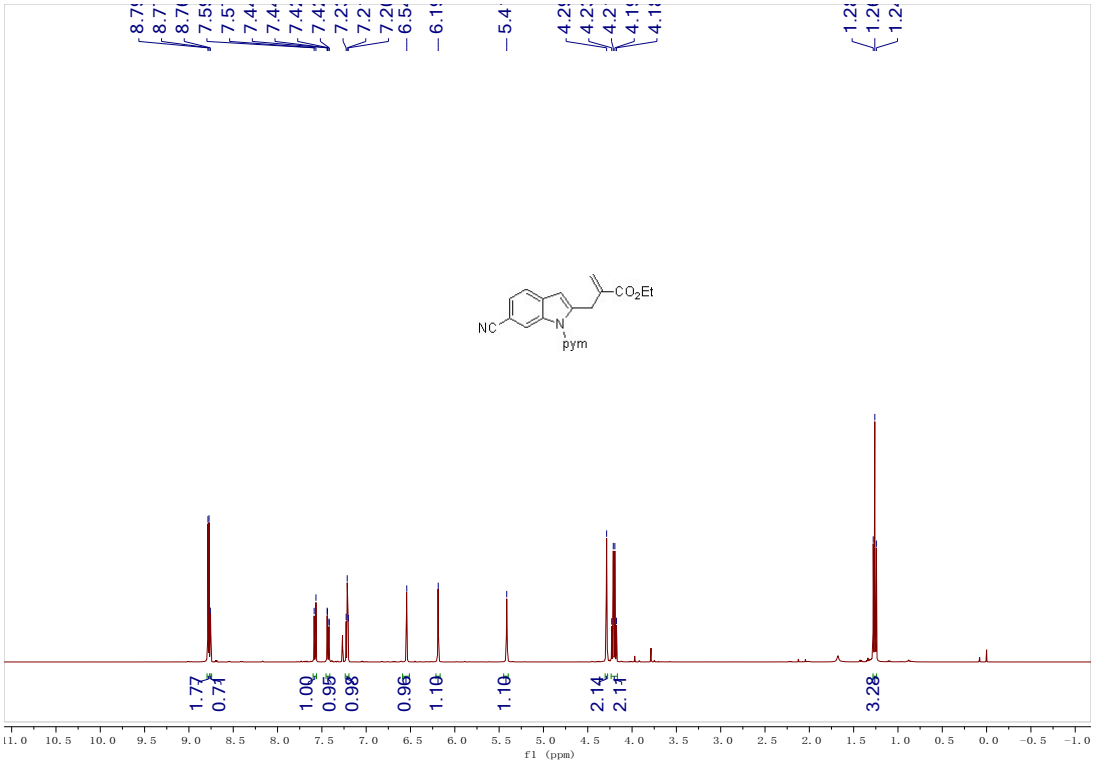

CO2Et
F
N
pym
f1 (ppm)

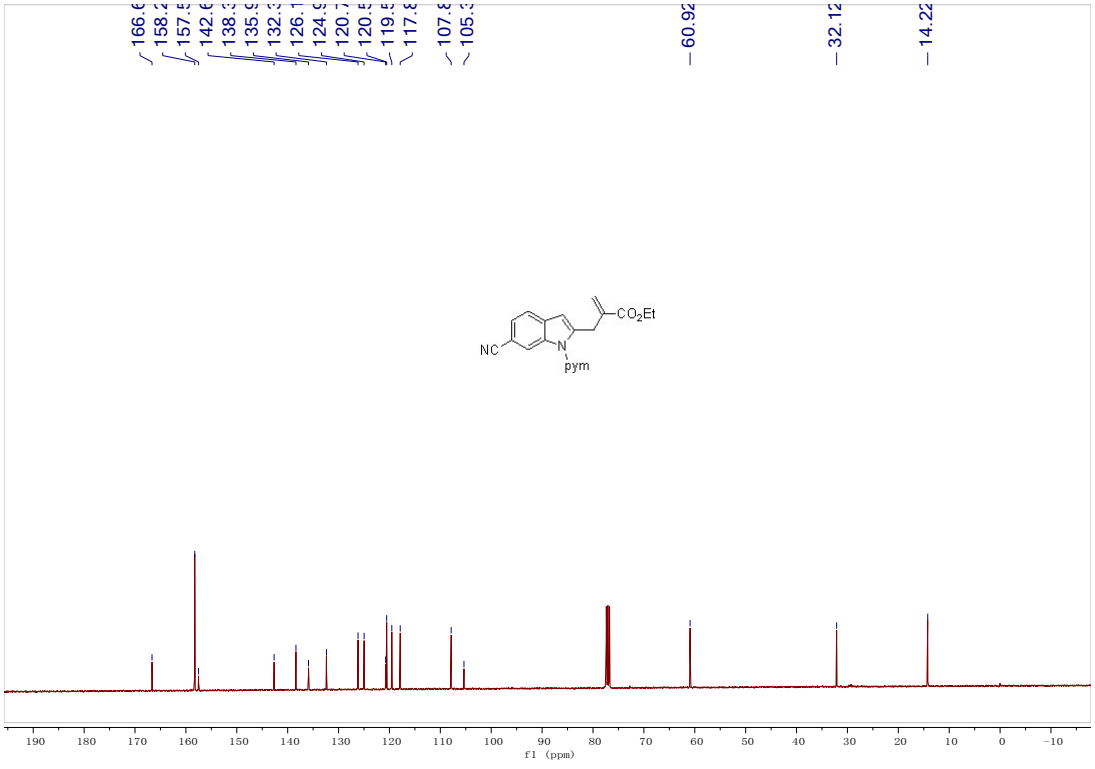

CO2Et
Cl
N
pym
1.63
0.67
0.86
0.82
0.86
0.86
1.00
1.01
1.77
2.01
2.96
f1 (ppm)

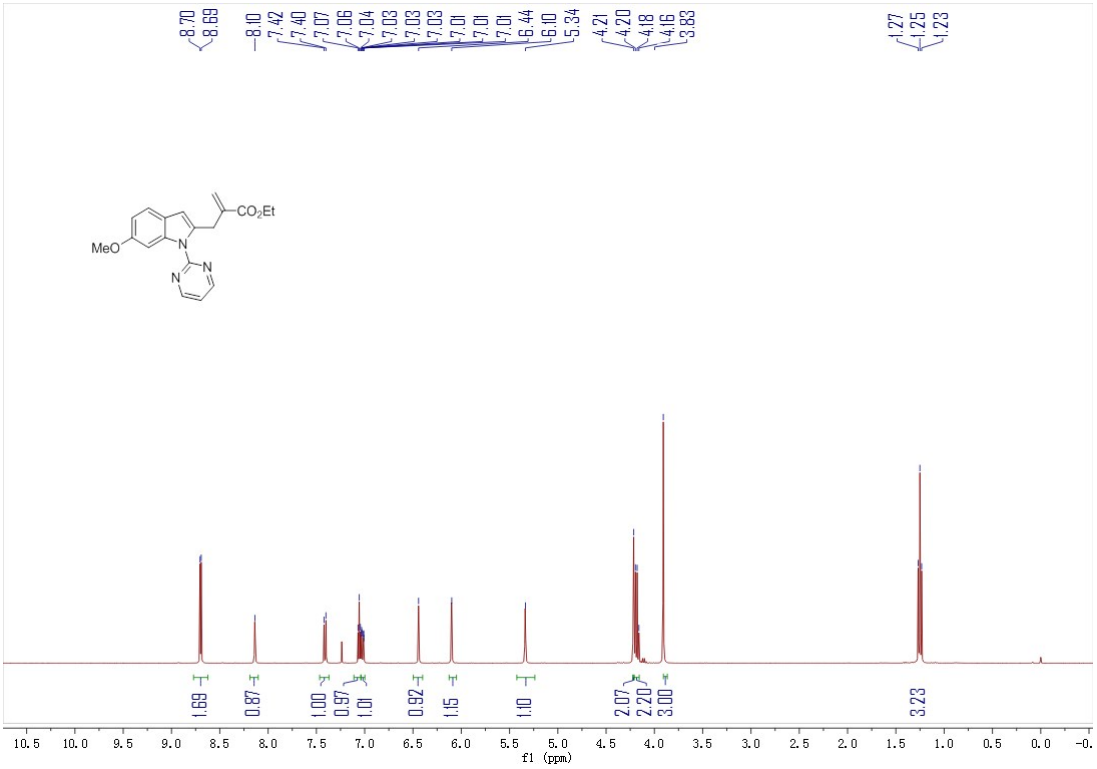

CO2Et
Cl
N
pym
f1 (ppm)


Br
N
pym
CO2Et
1.87
0.80
1.00
0.96
0.98
0.98
1.13
1.15
1.98
2.28
3.22
f1 (ppm)


Br
N
pym
CO2Et
60.81
31.94
14.24
f1 (ppm)


NC
CO2Et
pym
f1 (ppm)


NC
CO2Et
pym
f1 (ppm)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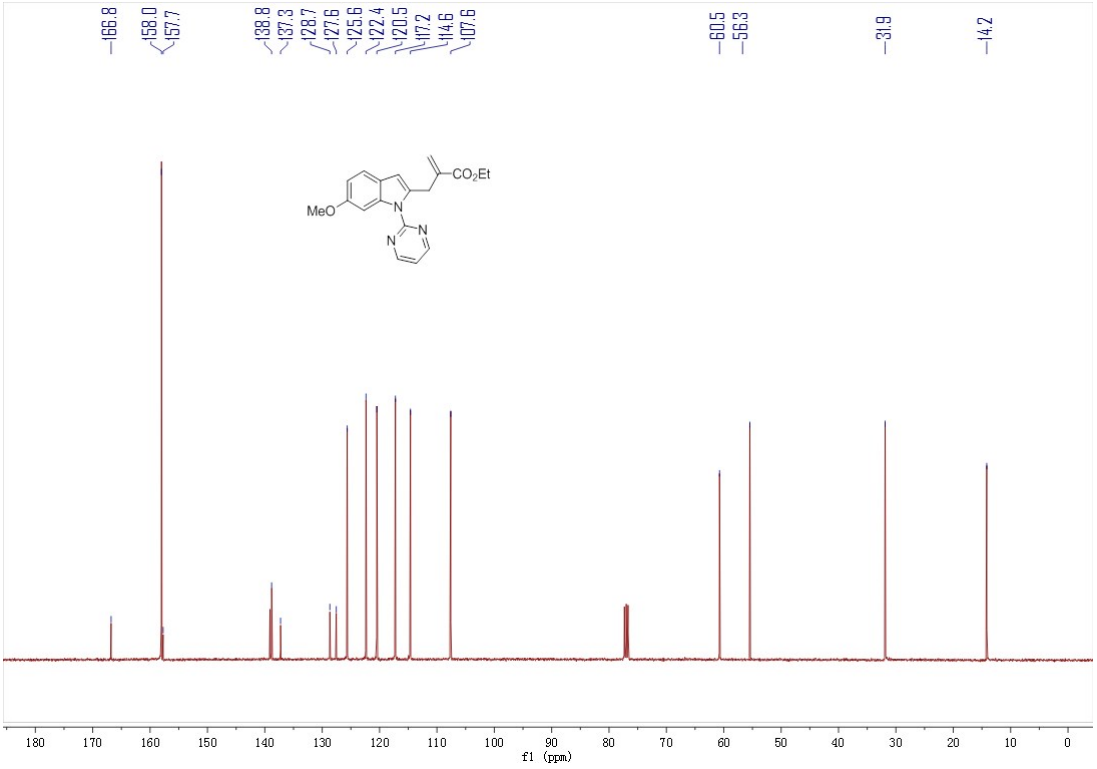
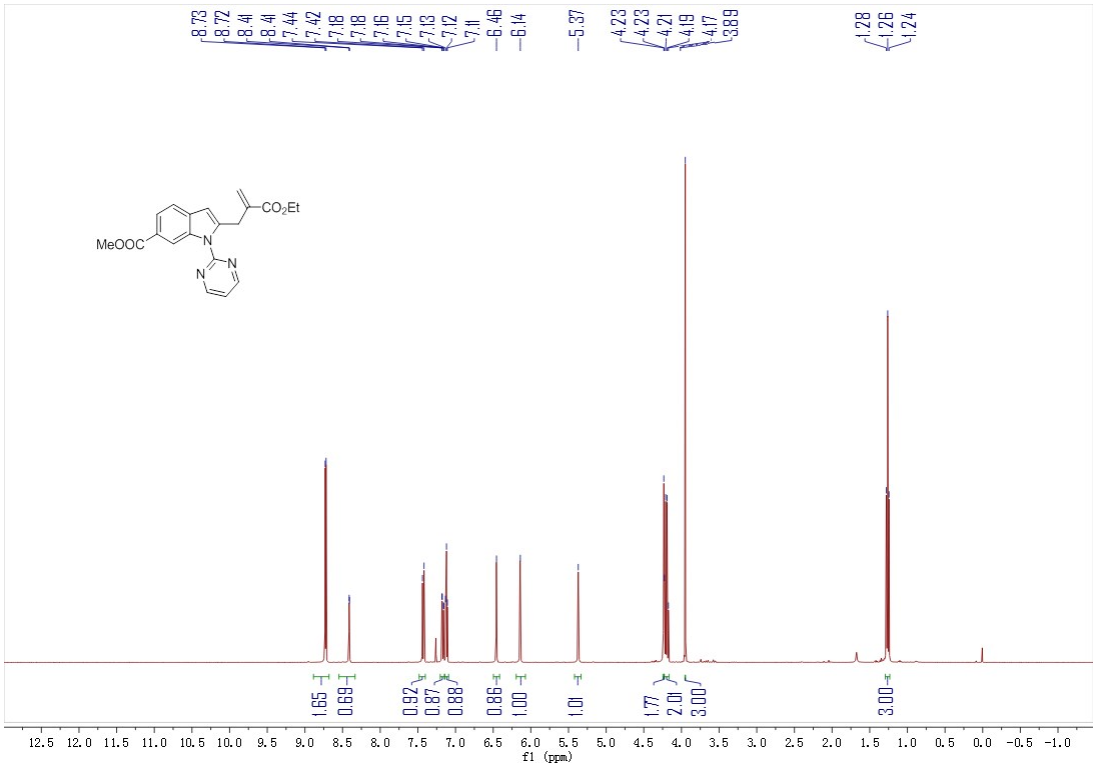
8.69
8.10
7.42
7.40
7.07
7.06
7.04
7.03
7.03
7.03
7.01
7.01
7.01
6.44
6.10
5.34
4.21
4.20
4.18
4.16
3.83
1.27
1.25
1.23
CO2Et
MeO
N
N
1.69
0.87
1.00
0.97
1.01
0.92
1.15
1.10
2.07
2.20
3.00
3.23
f1 (ppm)


166.8
158.0
157.7
138.8
137.3
128.7
127.6
125.6
122.4
120.5
117.2
114.6
107.6
60.5
56.3
31.9
14.2
CO2Et
MeO
N
N
f1 (ppm)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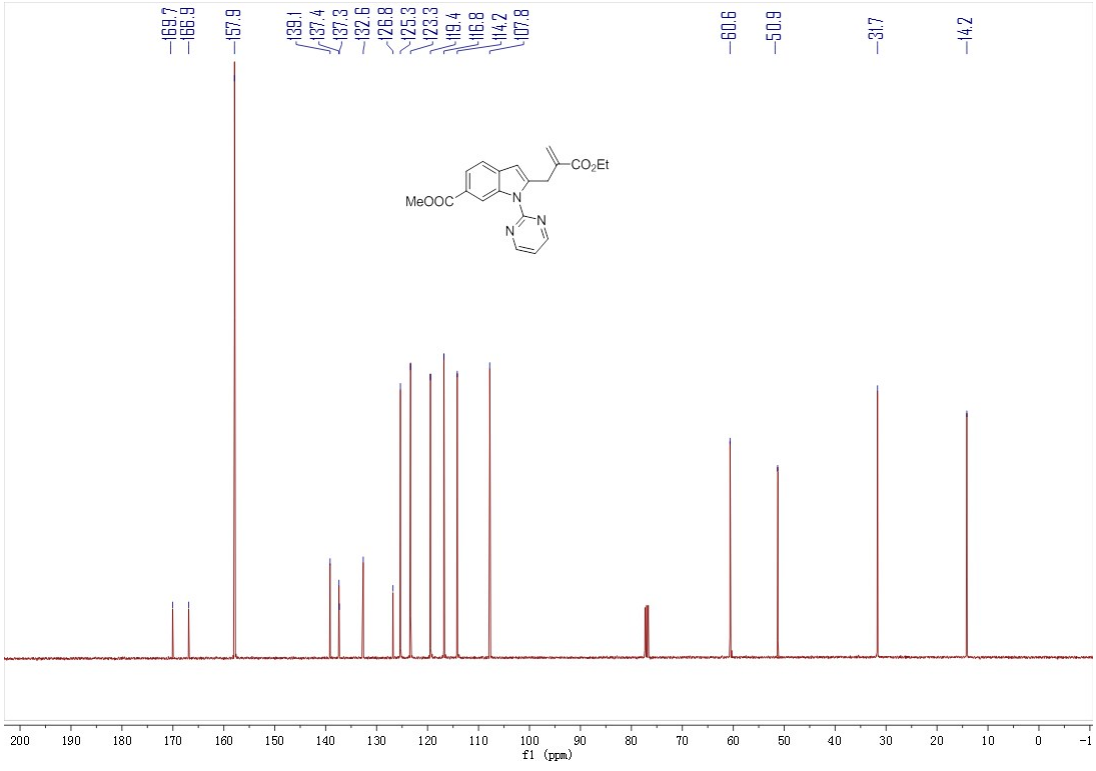
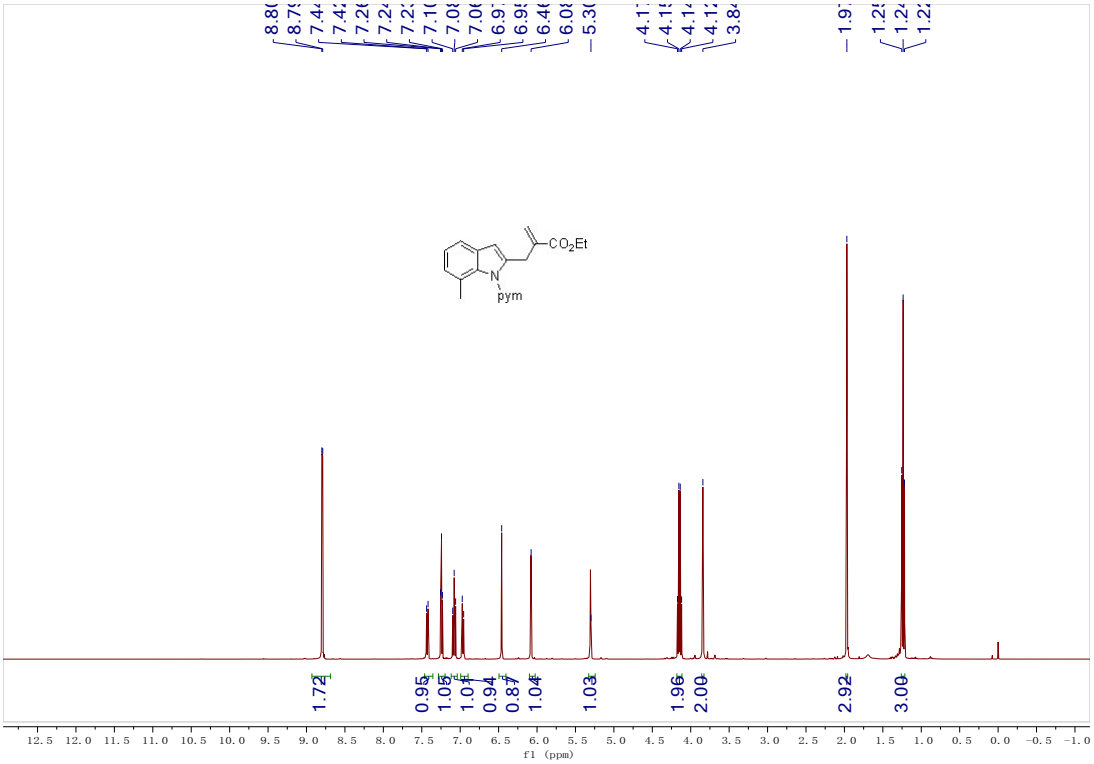
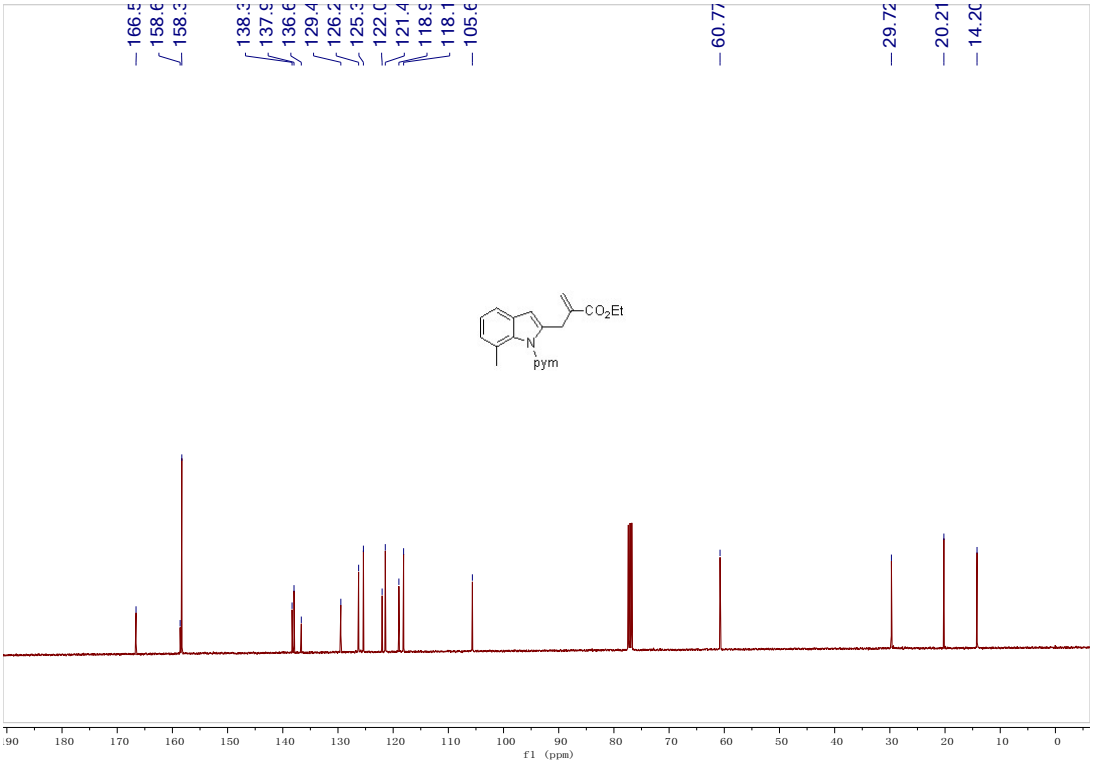
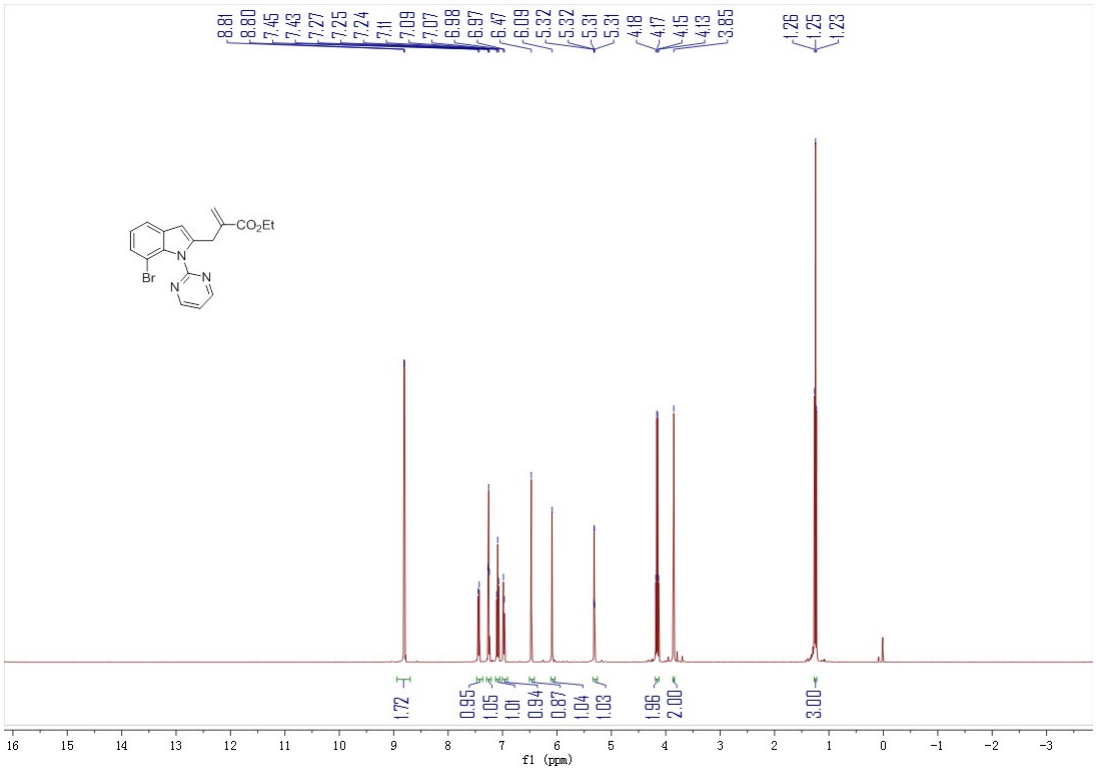
8.72
8.41
8.40
7.44
7.42
7.18
7.16
7.15
7.13
7.12
7.11
6.46
6.14
5.37
4.23
4.23
4.21
4.19
4.17
3.89
1.28
1.26
1.24
MeOOC
CO2Et
N
N
1.65
0.69
0.92
0.87
0.88
0.86
1.00
1.01
1.77
2.01
3.00
3.00
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


169.7
166.9
157.9
139.1
137.4
137.3
132.6
126.8
125.3
123.3
119.4
116.8
114.2
107.8
60.6
50.9
31.7
14.2
MeOOC
CO2Et
N
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


CO2Et
N
pym
1.72
0.95
1.05
1.01
0.94
0.87
1.04
1.03
1.96
2.00
2.92
3.00
f1 (ppm)


CO2Et
N
pym
f1 (ppm)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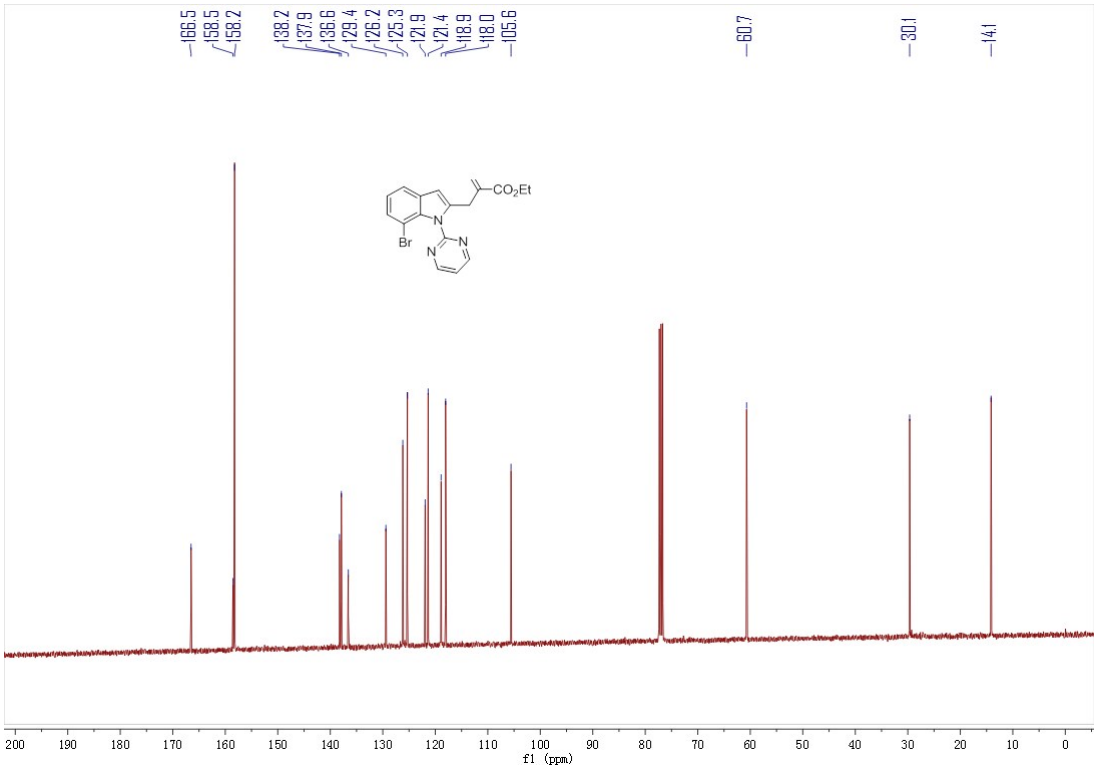
7.27
7.25
7.24
7.11
7.09
7.07
6.98
6.97
6.47
6.09
5.32
5.32
5.31
5.31
4.18
4.17
4.15
4.13
3.85
1.26
1.25
1.23
CO2Et
Br
N
N
1.72
0.95
1.05
1.01
0.94
0.87
1.04
1.03
1.96
2.00
3.00
f1 (ppm)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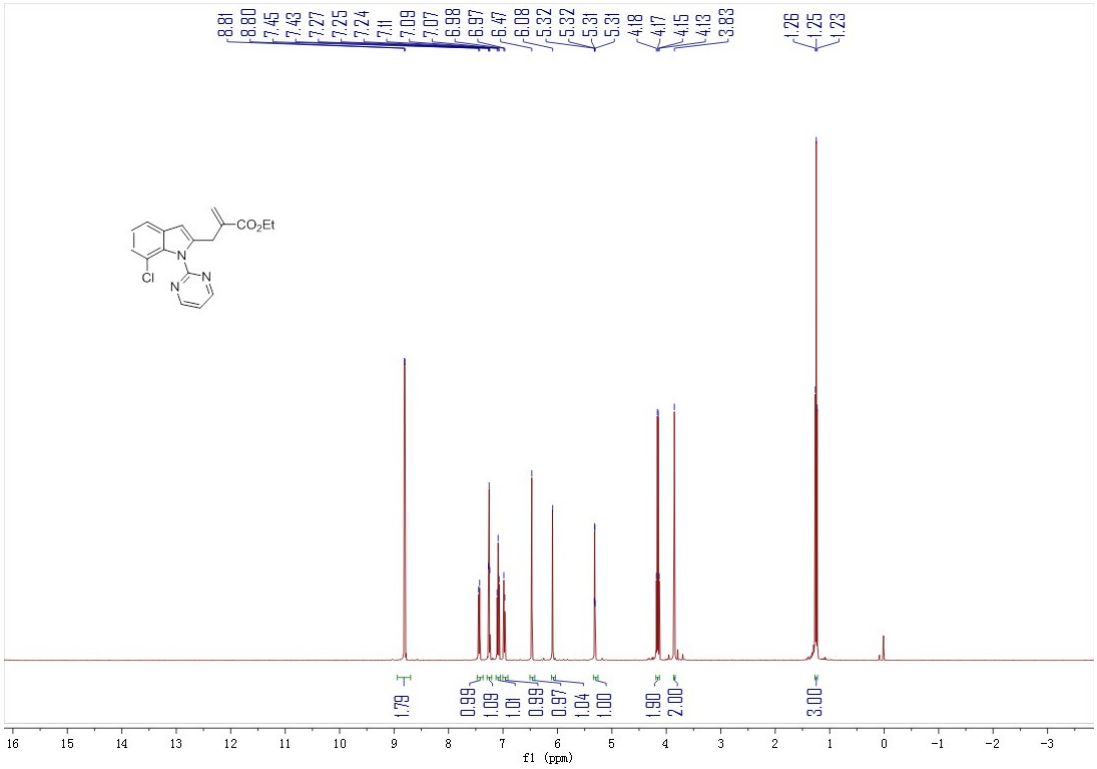
158.5
158.2
138.2
137.9
136.6
129.4
126.2
125.3
121.9
121.4
118.9
118.0
105.6
60.7
30.1
14.1
CO2Et
Br
N
N
f1 (ppm)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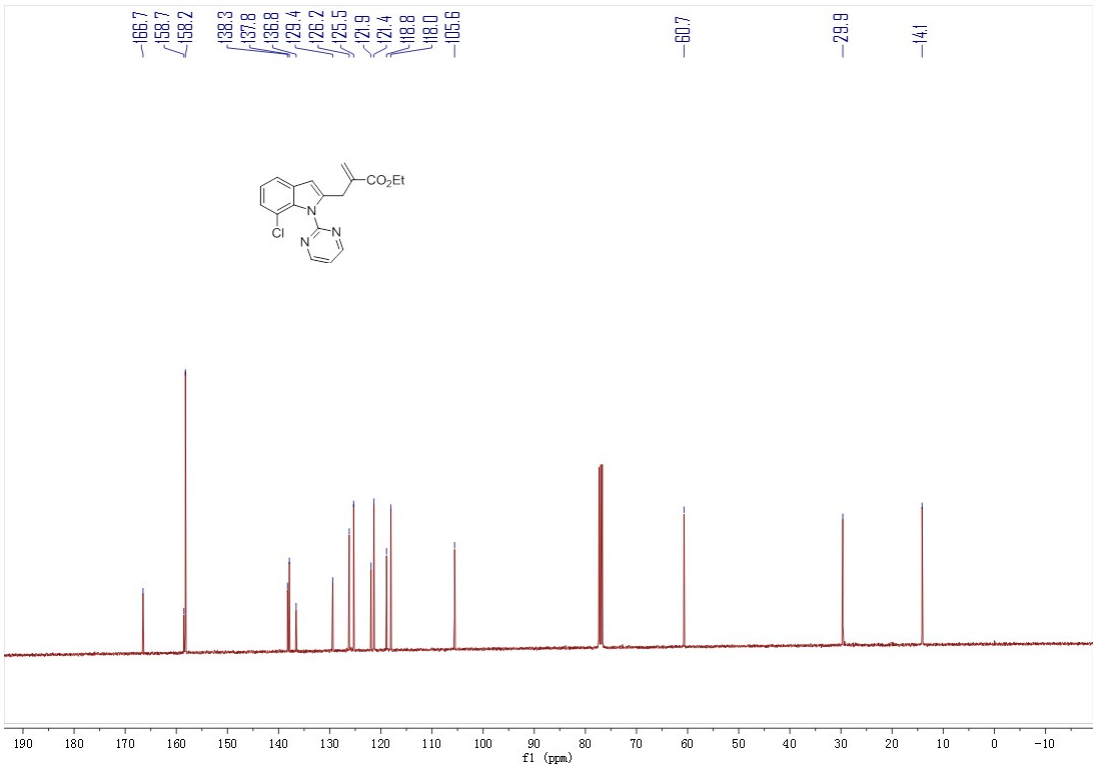
8.80
7.45
7.43
7.27
7.25
7.24
7.11
7.09
7.07
6.98
6.97
6.47
6.08
5.32
5.32
5.31
5.31
4.18
4.17
4.15
4.13
3.83
1.26
1.25
1.23
CO2Et
Cl
N
N
1.79
0.99
1.09
1.01
0.99
0.97
1.04
1.00
1.90
2.00
3.00
f1 (ppm)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158.7
158.2
138.3
137.8
136.8
129.4
126.2
125.5
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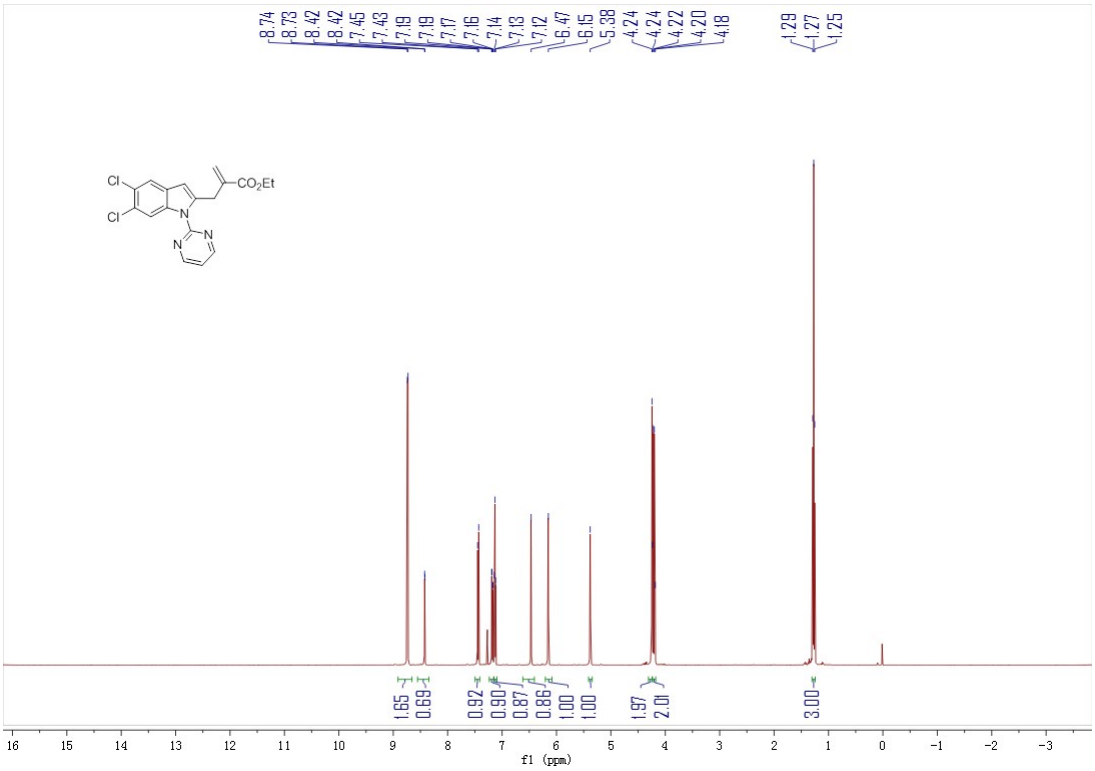
118.8
118.0
105.6
60.7
29.9
14.1
CO2Et
Cl
N
N
f1 (ppm)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7.16
7.14
7.13
7.12
6.47
6.15
5.38
4.24
4.24
4.22
4.20
4.18
1.29
1.27
1.25
Cl
Cl
CO2Et
N
N
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0.90
0.87
0.86
1.00
1.00
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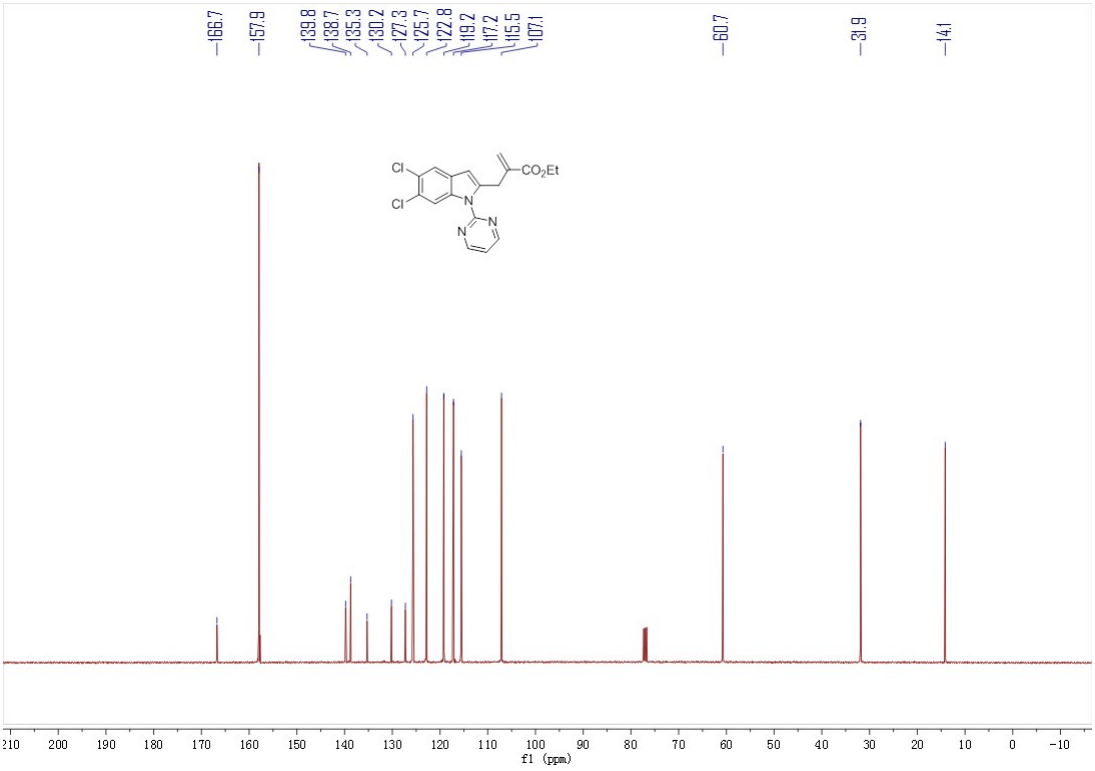
2.01
3.00
f1 (ppm)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157.9
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138.7
135.3
130.2
127.3
125.7
122.8
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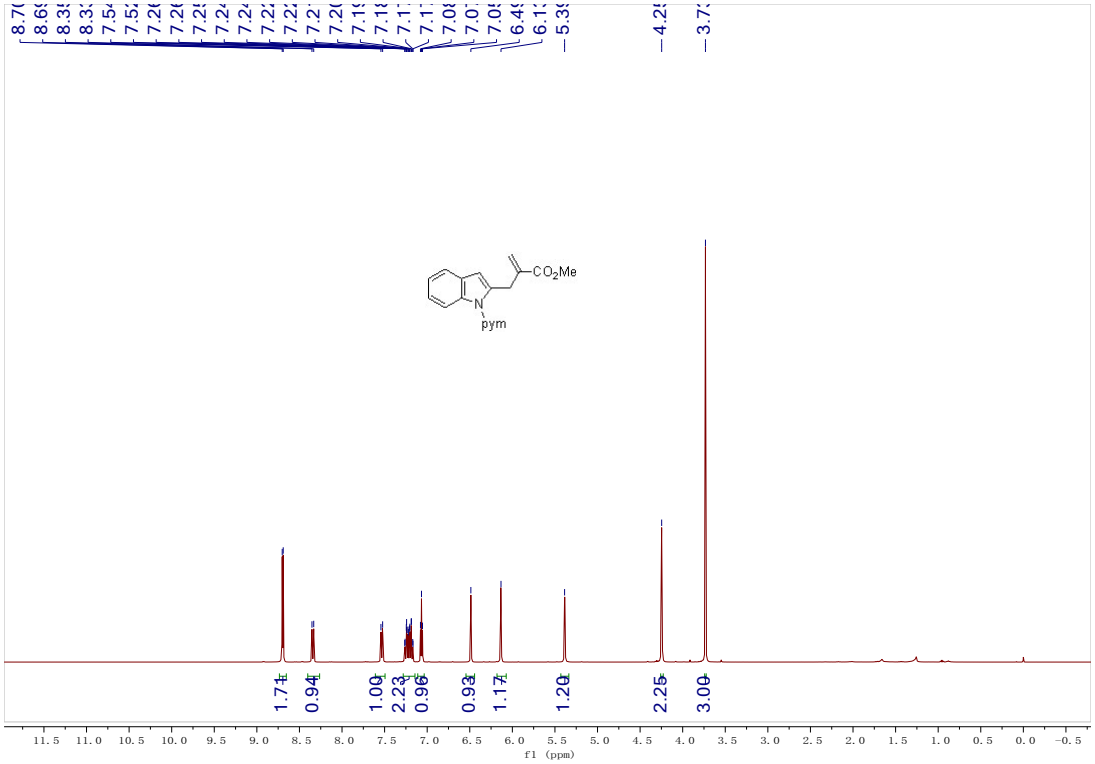
117.2
115.5
107.1
60.7
31.9
14.1
Cl
Cl
CO2Et
N
N
f1 (ppm)


CO2Me
N
pym
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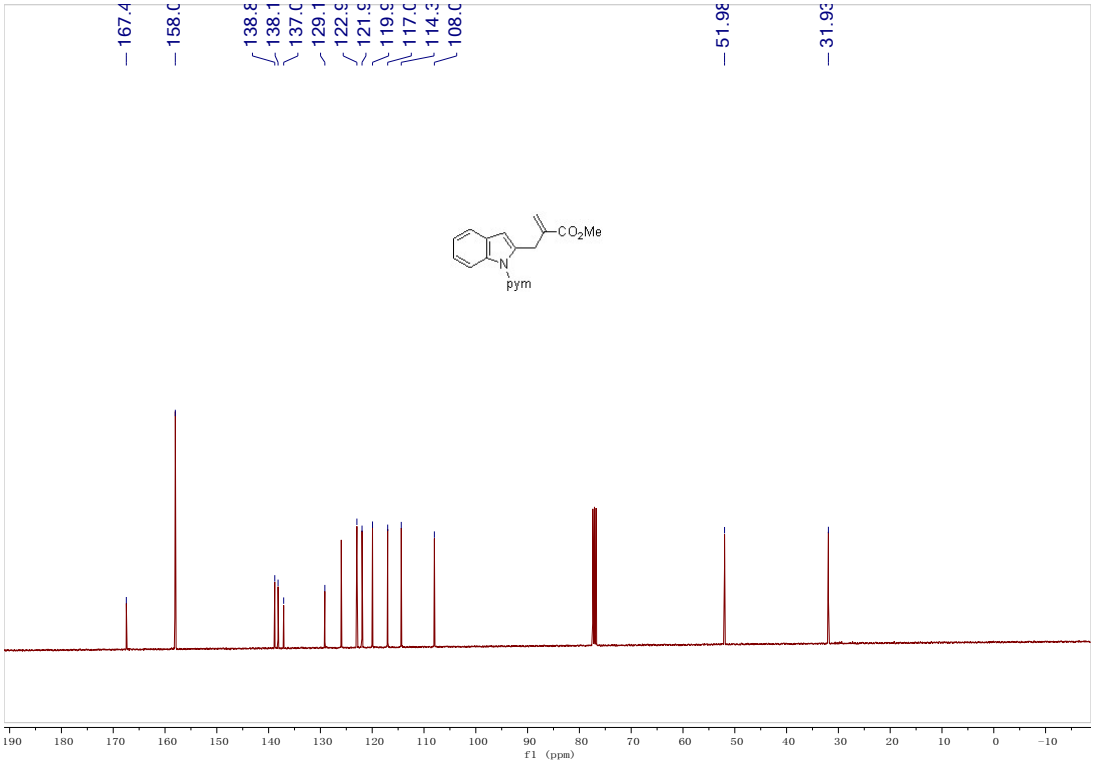
1.00
2.23
0.96
0.93
1.17
1.20
2.25
3.00
f1 (ppm)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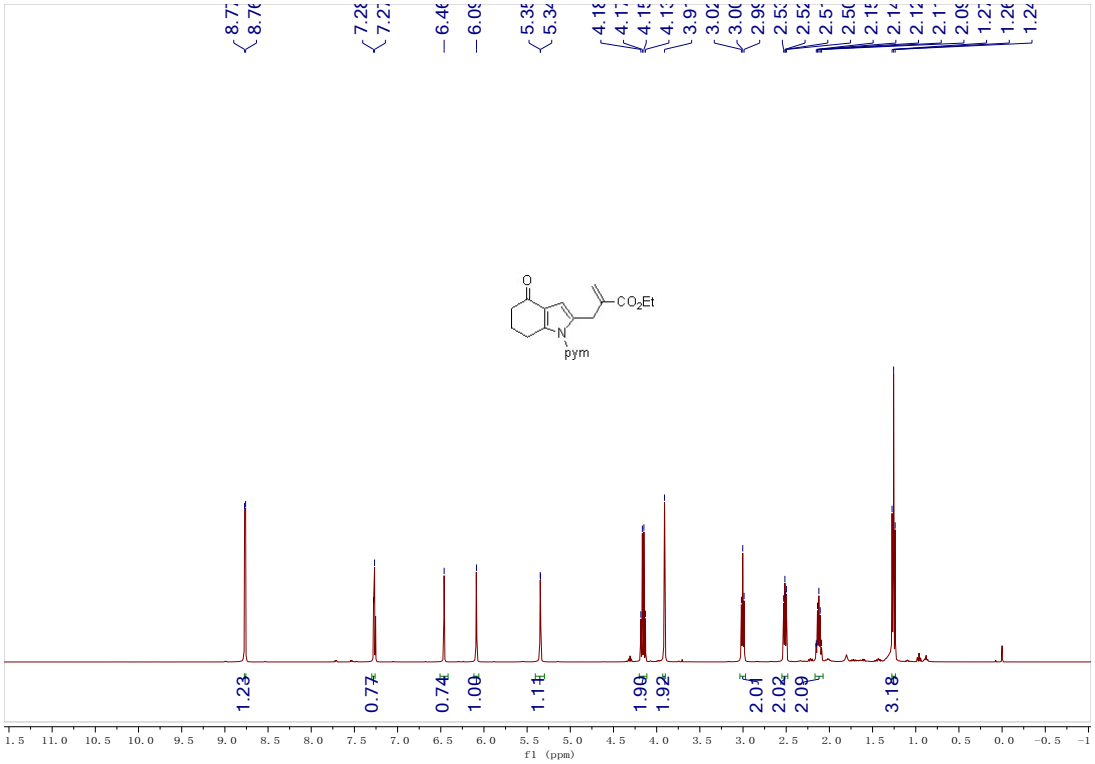
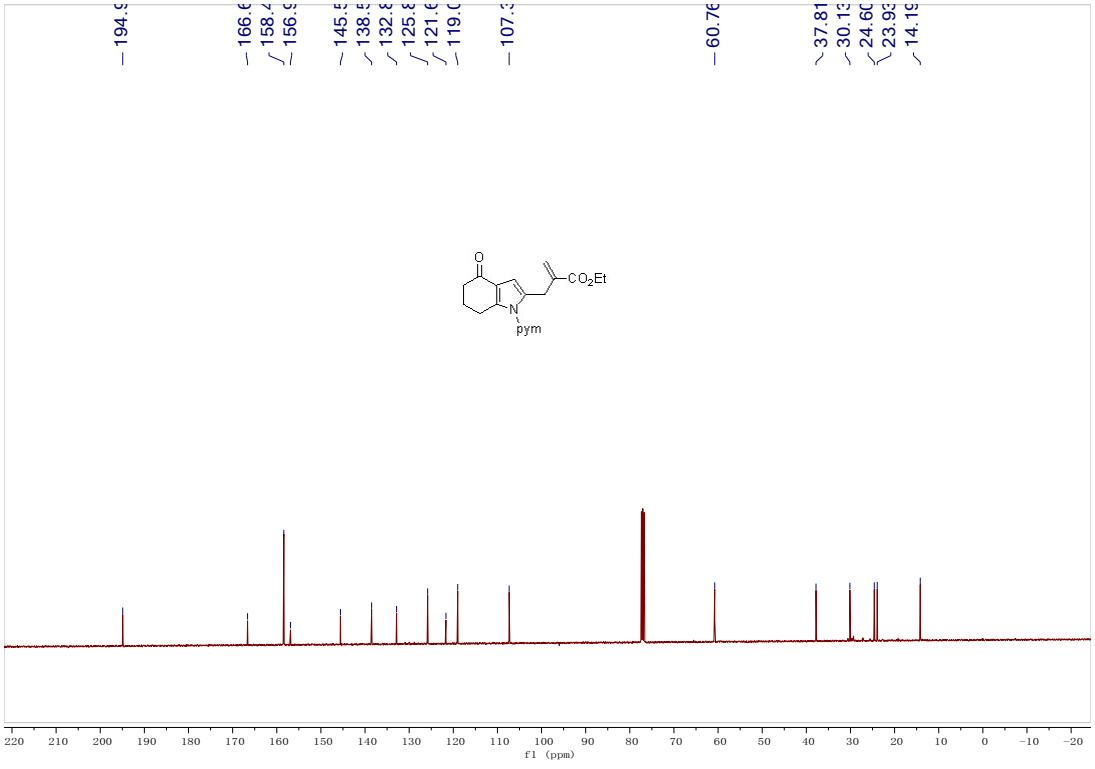
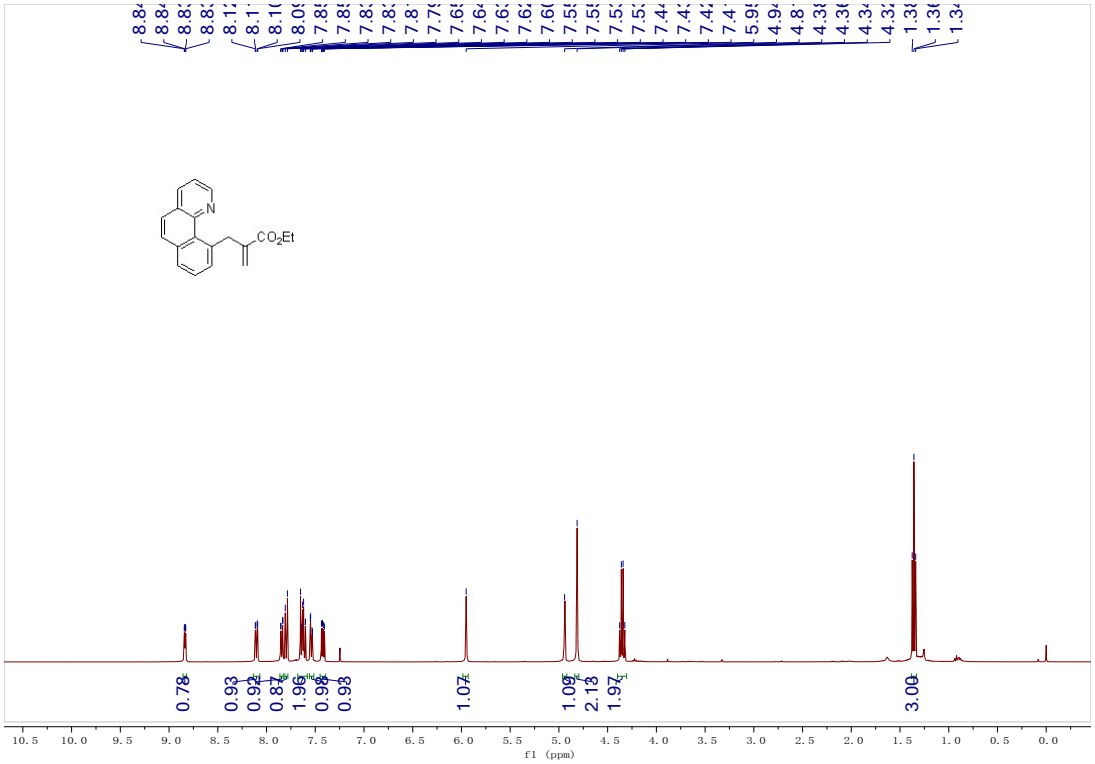
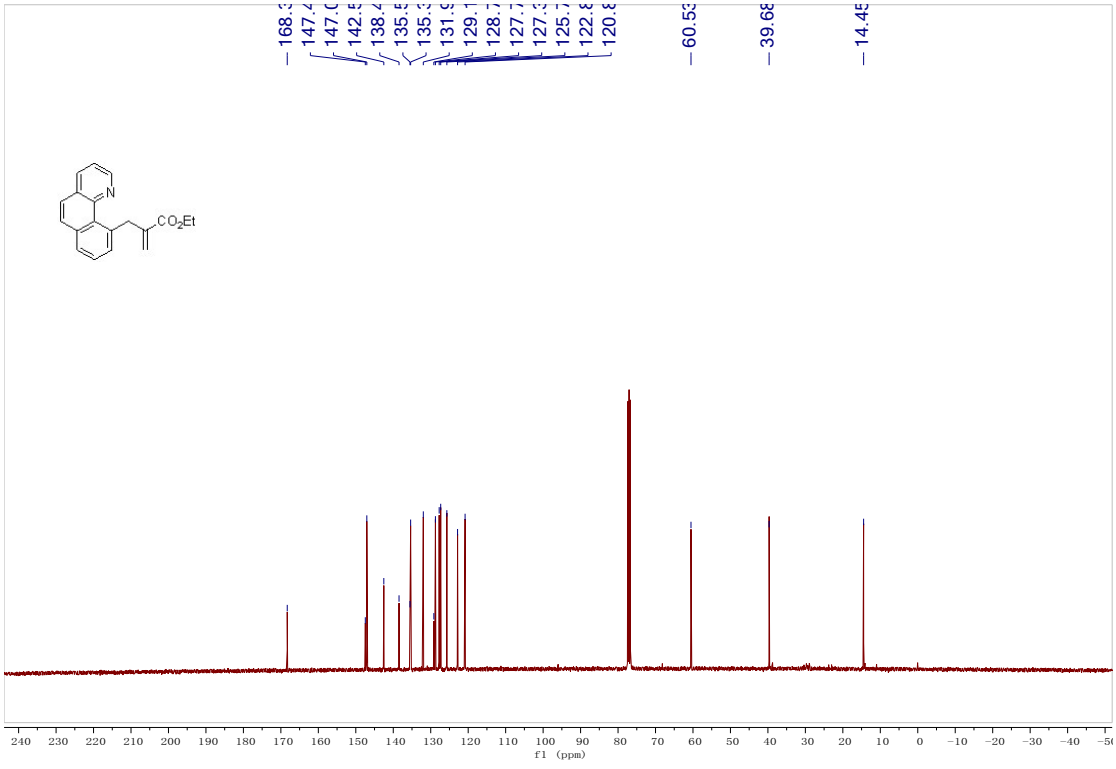
138.8
138.1
137.0
129.1
122.9
121.9
119.9
117.0
114.3
108.0
51.98
31.93
CO2Me
N
pym
f1 (ppm)


O
CO2Et
N
pym
f1 (ppm)


O
CO2Et
N
pym
f1 (ppm)


CO2Et
f1 (ppm)


CO2Et
f1 (ppm)