Electronic Supplementary Material (ESI) for Chemical Communications.

Rhodium(III)-catalyzed regioselective distal *ortho* C-H alkenylation of *N*-benzyl/furanylmethylpyrazoles directed by *N*-coordinating heterocycles

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Supplementary Information

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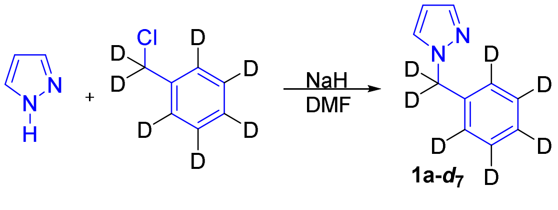
General remarks

All experiments were carried out under nitrogen unless stated otherwise. Merck precoated silica gel plates (Art. 5554) treated with a fluorescent indicator were used for analytical thin layer chromatography (TLC). Flash column chromatography was performed using silica gel 9385 (Merck). Melting points were determined using micro-cover glasses on a Fisher-Johns apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian VNS or DPX (600 or 300 MHz and 150 or 75 MHz, respectively) spectrometers. Chemical shifts for protons were reported as parts per million in δ scale using solvent residual peak ($CHCl_3$: 7.24 ppm) as an internal standard. Chemical shifts of ^{13}C NMR spectra were reported in ppm from the central peak of $CDCl_3$ (77.00 ppm) on the δ scale, and J values are given in Hz. Multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or overlap of nonequivalent resonances, and dd = doublet of doublets. Infrared (IR) spectra were recorded on a PerkinElmer Spectrum Two^{TM} IR spectrometer with frequencies expressed in cm^{-1}, and high-resolution mass spectrometry (HRMS) was carried out using a JEOL JMS-700 spectrometer at the Korea Basic Science Institute.

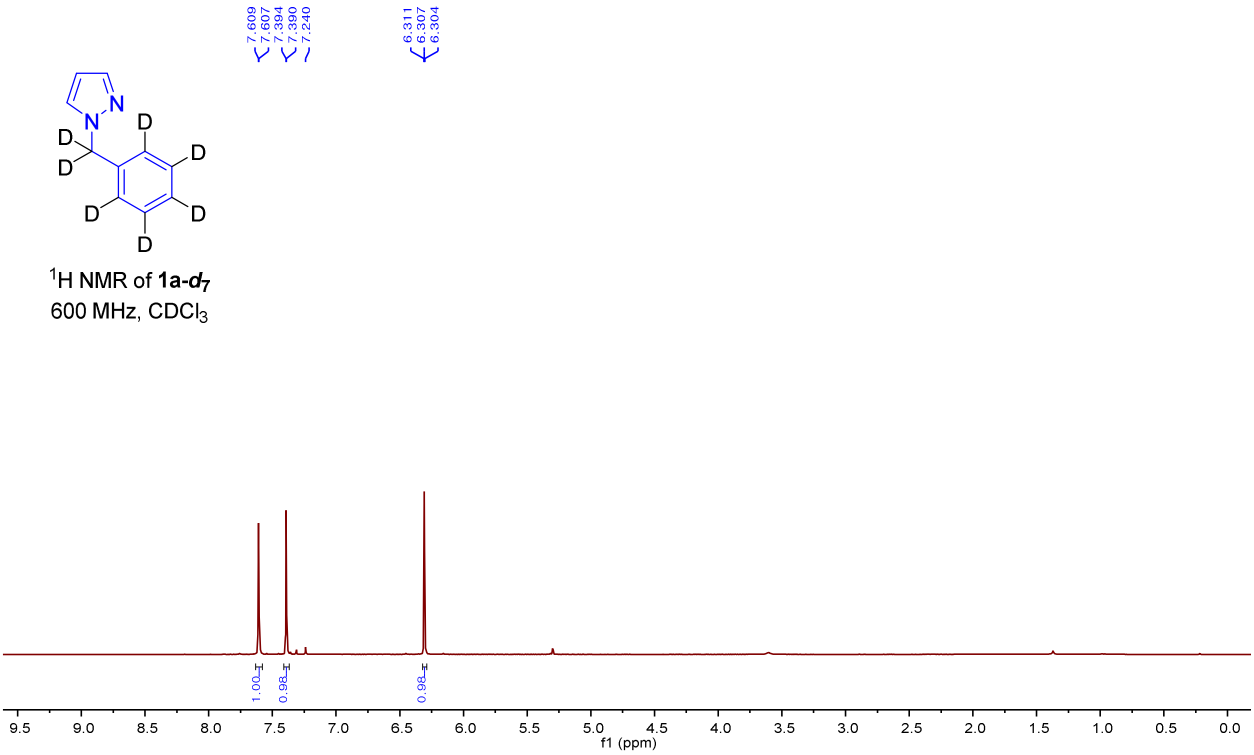
General procedure for the synthesis of alkenylated compounds (3-10)

A mixture of pyrazole derivatives **1** (0.5 mmol), acrylate **2** (1 mmol), $[RhCp^*Cl_2]_2$ (2.5 mol%), $AgSbF_6$ (10 mol%), and AgOAc (30 mol%) was stirred in DCE (5 mL) at 80 ºC for the described time. When the reaction was complete as indicated by TLC, the volatiles were removed *in vacuo* and the residue was purified by silica gel column chromatography (EtOAc/Hexanes) to obtain the desired products **3-10**.

Procedure for the synthesis of 1a-d_7



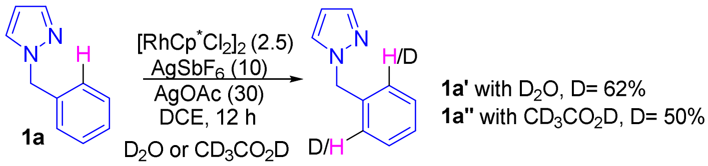
Benzyl bromide-d_7 (6 mmol) was added to a vigorously stirred suspension of pyrazole (5 mmol) and NaH (60% dispersion on oil, 12 mmol) in anhydrous DMF (15 mL) at 0 ºC. The mixture was stirred overnight at room temperature and quenched with a saturated solution of NH_4Cl. Distilled water was added and the aqueous layer was extracted with EtOAc (3 X 15 mL). The combined organic phases were dried over anhydrous $MgSO_4$, filtered and concentrated to obtain a compound **1a-*d*$_7$** as a colorless liquid.


^{1}H NMR of **1a-*d*$_7$**
600 MHz, $CDCl_3$

Mechanistic investigations

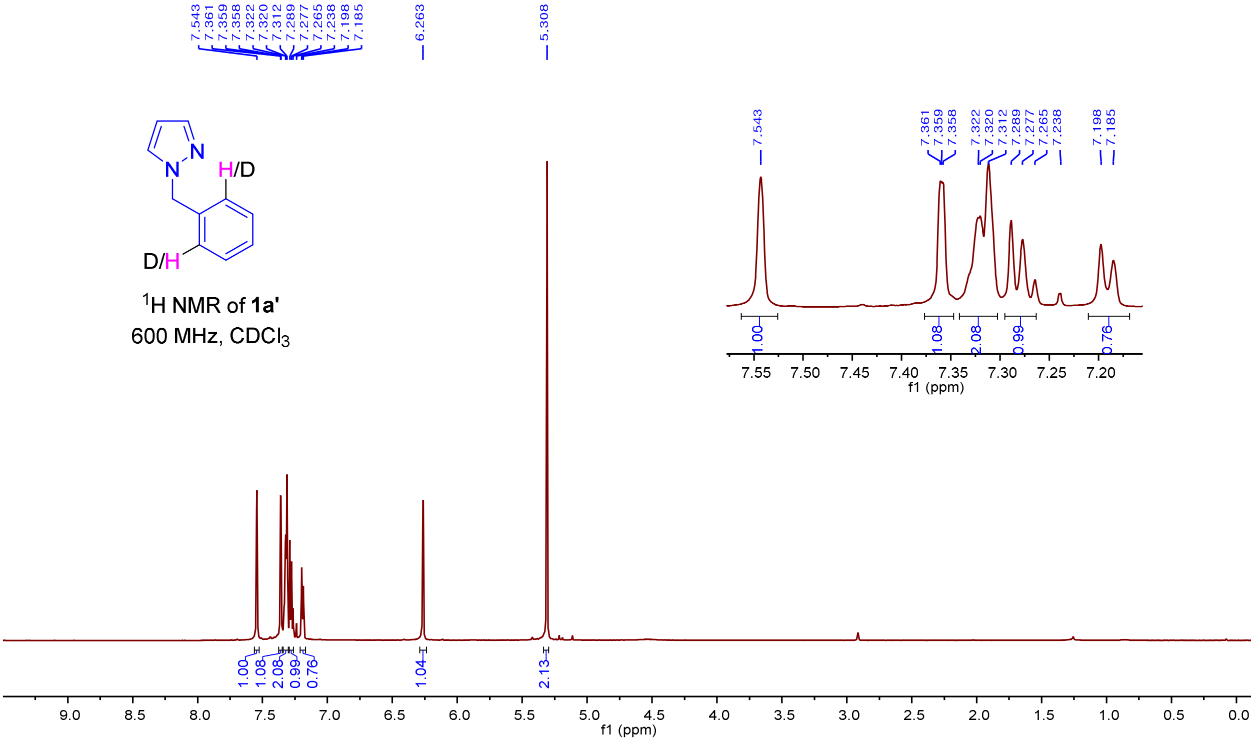
To probe the reaction mechanism of the C-H alkenylation reaction, control experiments were performed. The reaction of 1-benzyl-1*H*-pyrazole (**1a**) with **2a** using D_2O and CD_3CO_2D under standard reaction conditions provided 62 and 50% deuterated products at the *ortho*-positions of **1a'** and **1a''**, respectively (Scheme S1). The reaction of **1a** and its deuterated analog **1a-*d*$_7$** with **2a** under standard reaction conditions for 3 h provided a KIE value of 1.33, suggesting the C-H activation step is not a rate-determining step (Scheme S2).[1]

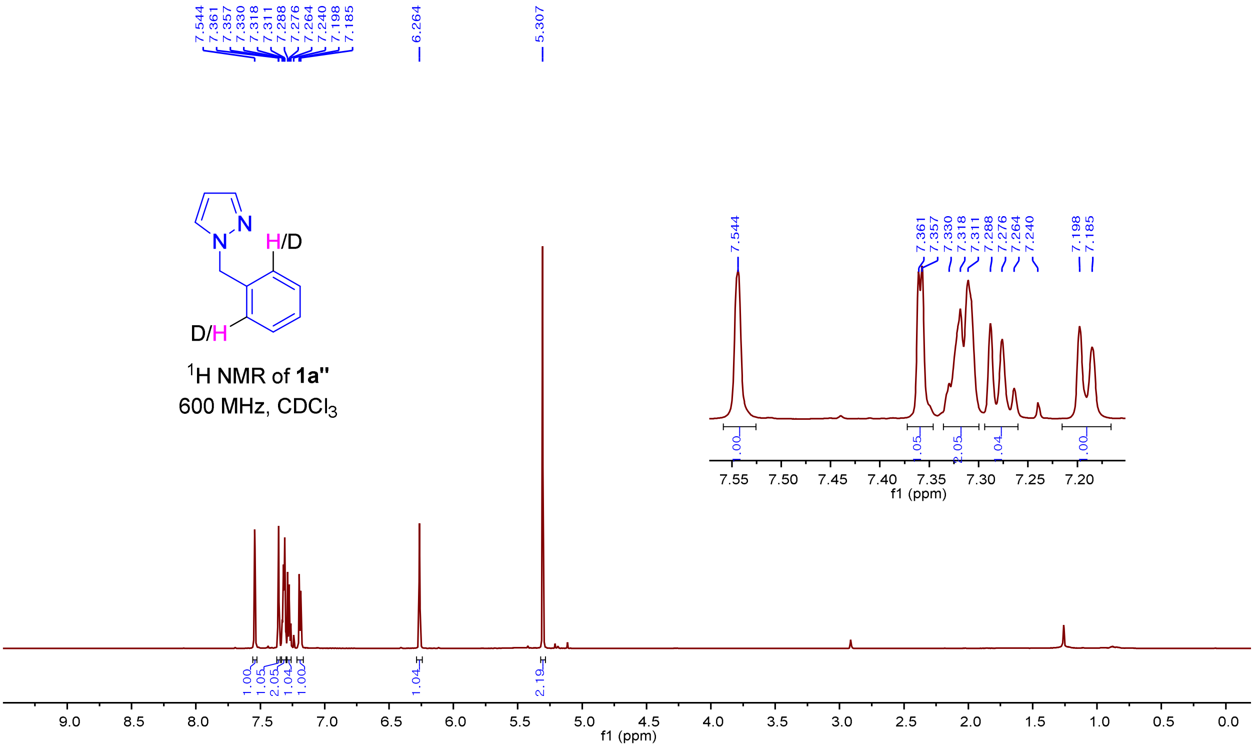
i) H/D exchange experiment



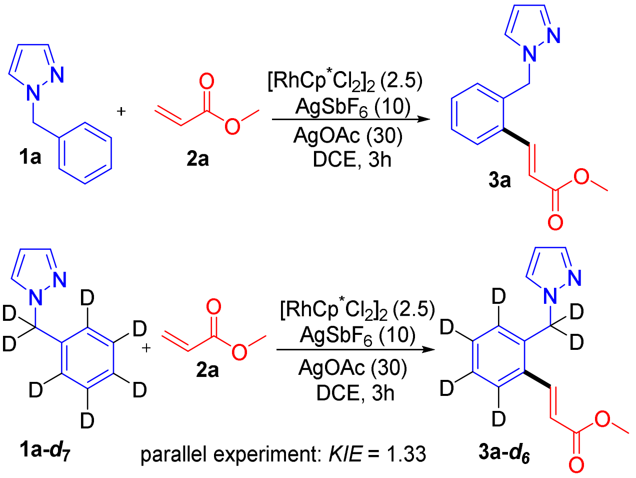
Scheme S1. Deuterium labelling study.

1-Benzyl-1*H*-pyrazole (**1a**, 0.2 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol%), $AgSbF_6$ (10 mol%), AgOAc (30 mol%), and D_2O or CD_3CO_2D (4 equiv) were stirred in DCE (3 mL) at 80 °C for described time. Then, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography (EtOAc/Hexanes) to afford **1a′** or **1a″**. C2-H was deuterated in 62% with D_2O and 50% deuterated with CD_3COD (See the following ^1H NMR spectra).



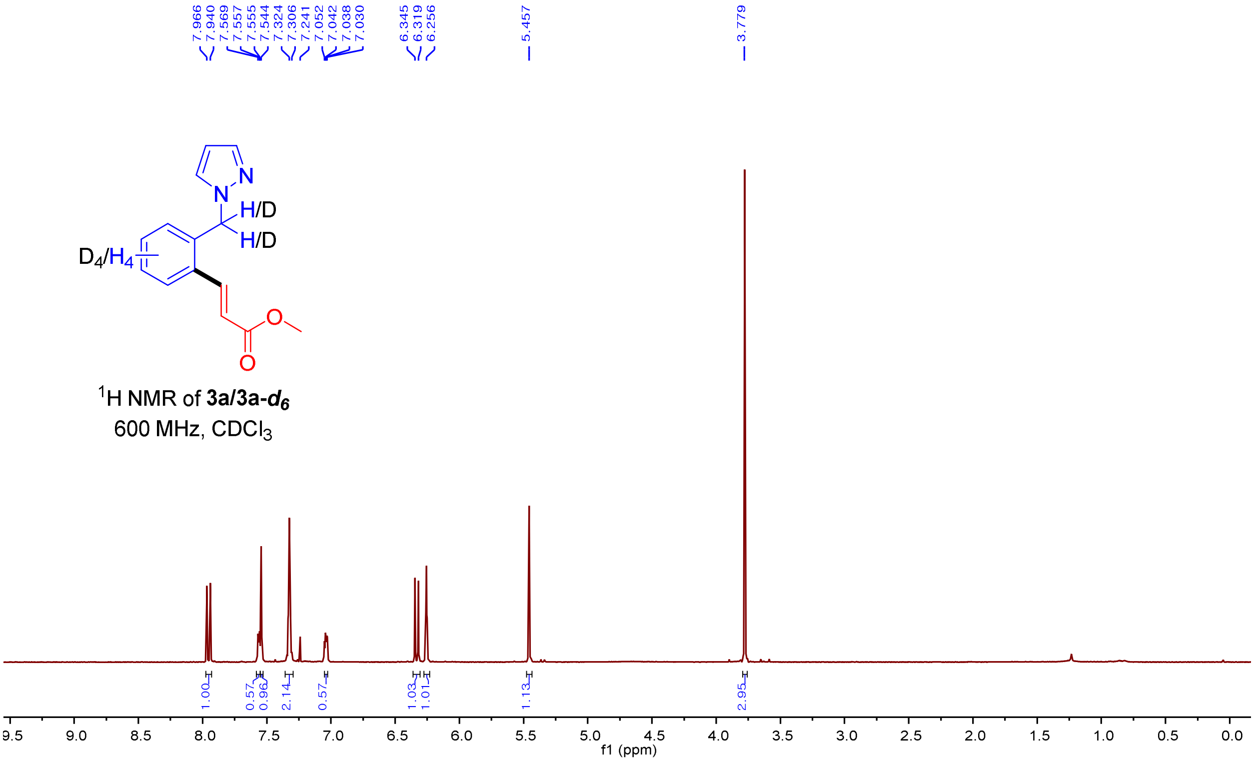


ii) KIE experiments



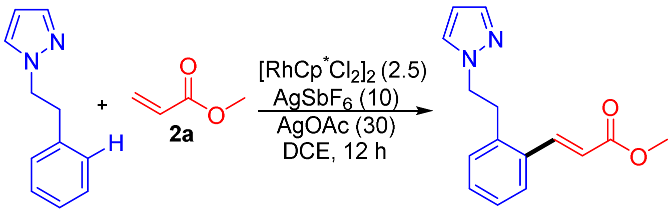
Scheme S2. Kinetic isotope effect experiment.

In a two different set of reactions, the reaction of **1a** or **1a-d_7** with **2a** was carried out at standard reaction condition for 3h. After that, both of the reaction mixtures were combined, and the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography (EtOAc/Hexanes) to afford the product. The KIE was calculated from ^{1}H NMR analysis.



^{1}H NMR of **3a/3a-d_6**
600 MHz, $CDCl_3$

iii) Reaction of extended tether

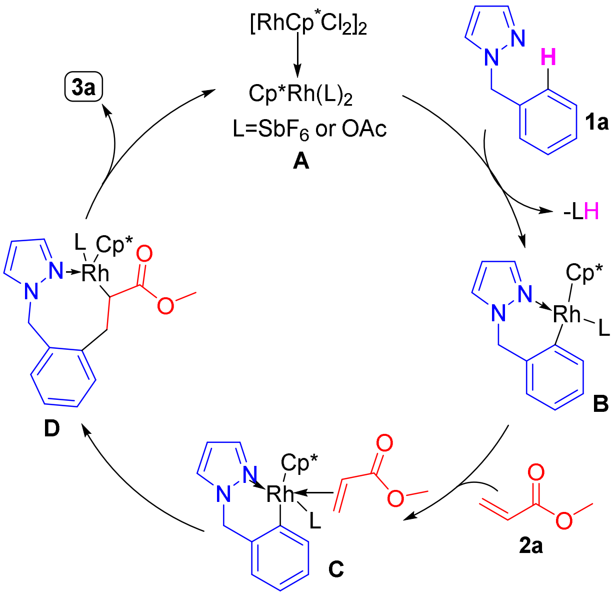


1y **2a** **11** not observed

Scheme S3. Reaction of extended tether.

To test the coordination ability of pyrazole in the current system, we have extended the tether and performed the reaction of 1-phenethyl-1*H*-pyrazole (**1y**) with **2a** under standard reaction condition. However, reaction failed to produce desired product **11**.

Reaction mechanism



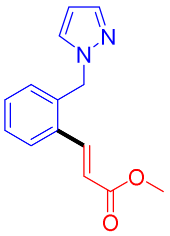
Scheme S4. Proposed reaction mechanism.

References:

1. (a) Kumar, P.; Kapur, M. *Org. Lett.* **2019**, *21*, 2134. (b) Pan, J.-L.; Liu, C.; Chen, C.; Liu, T.-Q.; Wang, M.; Sun, Z. l.; Zhang, S.-Yu. *Org. Lett.* **2019**, *8*, 2823.

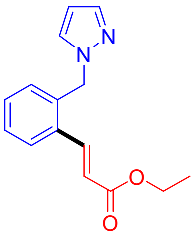
Characterization data of synthesized compounds

Methyl (*E*)-3-(2-((1*H*-pyrazol-1-yl)methyl)phenyl)acrylate (3a)



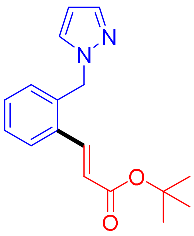
The title compound was prepared according to the general procedure. The product was obtained as a white solid. Yield: 88% (107 mg); mp 58-60 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (1H, d, *J* = 15.7 Hz), 7.53-7.50 (2H, m), 7.30-7.27 (3H, m), 6.98 (1H, dd, *J* = 6.6, 2.4 Hz), 6.31 (1H, d, *J* = 15.7 Hz), 6.22 (1H, s), 5.40 (2H, s), 3.74 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.6, 140.6, 139.5, 135.2, 133.0, 130.2, 129.2, 129.0, 128.4, 126.8, 120.6, 105.9, 53.0, 51.5; IR (ATR) 2951, 1698, 1631, 1318, 1167, 758 cm^{-1}; HRMS *m/z* (M$^+$) calcd for $C_{14}H_{14}N_2O_2$: 242.1055. Found: 242.1057.

Ethyl (*E*)-3-(2-((1*H*-pyrazol-1-yl)methyl)phenyl)acrylate (3b)



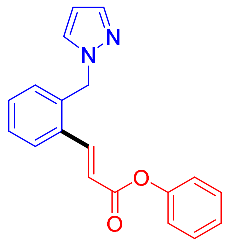
The title compound was prepared according to the general procedure. The product was obtained as a yellow liquid. Yield: 89% (114 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (1H, d, *J* = 15.7 Hz), 7.55-7.52 (2H, m), 7.34 (1H, s), 7.30-7.29 (2H, m), 7.01 (1H, t, *J* = 3.4 Hz), 6.31 (1H, d, *J* = 15.7 Hz), 6.25 (1H, s), 5.43 (2H, s), 4.22 (2H, q, *J* = 7.2 Hz), 1.29 (3H, t, *J* = 7.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.3, 140.4, 139.5, 135.2, 133.2, 130.2, 129.1, 128.5, 126.9, 126.8, 121.1, 106.1, 60.5, 53.1, 14.1; IR (ATR) 2979, 1707, 1633, 1270, 1311, 1175, 757 cm^{-1}; HRMS *m/z* (M$^+$) calcd for $C_{15}H_{16}N_2O_2$: 256.1212. Found: 256.1213.

tert-Butyl (*E*)-3-(2-((1*H*-pyrazol-1-yl)methyl)phenyl)acrylate (3c)



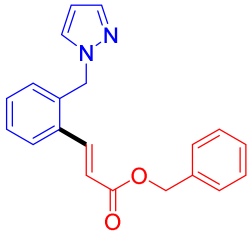
The title compound was prepared according to the general procedure. The product was obtained as a yellow liquid. Yield: 84% (119 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (1H, d, *J* = 15.8 Hz), 7.55 (2H, s), 7.33-7.30 (3H, m), 7.05-7.03 (1H, m), 6.26-6.24 (2H, m), 5.47 (2H, s), 1.51 (9H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.7, 139.5, 139.4, 135.1, 133.5, 130.0, 129.4, 129.1, 128.5, 126.9, 123.2, 106.0, 80.7, 53.2, 28.1; IR (ATR) 2974, 1763, 1632, 1317, 1149, 755 cm^{-1}; HRMS *m/z* (M$^+$) calcd for $C_{17}H_{20}N_2O_2$: 284.1525. Found: 284.1523.

Phenyl (*E*)-3-(2-((1*H*-pyrazol-1-yl)methyl)phenyl)acrylate (3d)



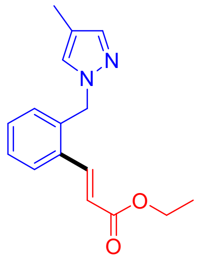
The title compound was prepared according to the general procedure. The product was obtained as a yellow liquid. Yield: 87% (132 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (1H, d, J = 15.8 Hz), 7.60 (1H, d, J = 8.7 Hz), 7.49 (1H, s), 7.34-7.30 (5H, m), 7.18-7.16 (1H, m), 7.09 (2H, d, J = 8.0 Hz), 7.02 (1H, d, J = 5.3 Hz), 6.47 (1H, d, J = 15.7 Hz), 6.21 (1H, s), 5.44 (2H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.8, 150.6, 142.3, 139.6, 135.5, 133.0, 130.7, 129.4, 129.4, 128.7, 127.1, 125.8, 121.5, 120.2, 106.1, 53.2; IR (ATR) 3065, 1724, 1192, 1137, 972, 752 cm^{-1}; HRMS *m/z* (M$^+$) calcd for $C_{19}H_{16}N_2O_2$: 304.1212. Found: 304.1208.

Benzyl (*E*)-3-(2-((1*H*-pyrazol-1-yl)methyl)phenyl)acrylate (3e)



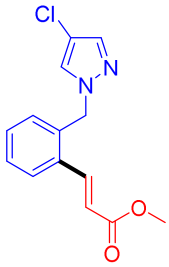
The title compound was prepared according to the general procedure. The product was obtained as a beige solid. Yield: 85% (135 mg); mp 67-69 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (1H, d, J = 15.7 Hz), 7.57 (1H, d, J = 7.5 Hz), 7.52 (1H, s), 7.40-7.36 (4H, m), 7.33-7.31 (4H, m), 7.04 (1H, d, J = 6.9 Hz), 6.39 (1H, d, J = 15.6 Hz), 6.24 (1H, s), 5.44 (2H, s), 5.23 (2H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.1, 141.0, 139.6, 135.8, 135.3, 133.1, 130.4, 129.3, 129.2, 128.6, 128.5, 128.2, 128.2, 126.9, 120.8, 106.0, 66.1, 53.2; IR (ATR) 2948, 1706, 1629, 1174, 748, 695 cm^{-1}; HRMS *m/z* (M$^+$) calcd for $C_{20}H_{18}N_2O_2$: 318.1368. Found: 318.1369.

Ethyl (*E*)-3-(2-((4-methyl-1*H*-pyrazol-1-yl)methyl)phenyl)acrylate (3f)



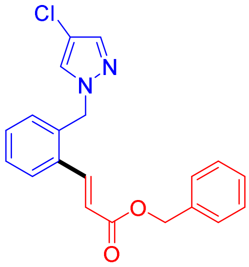
The title compound was prepared according to the general procedure. The product was obtained as a yellow liquid. Yield: 72% (97 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (1H, d, J = 15.7 Hz), 7.56 (1H, d, J = 9.1 Hz), 7.35 (1H, s), 7.32 (2H, t, J = 3.7 Hz), 7.09 (1H, s), 7.05 (1H, d, J = 8.1 Hz), 6.33 (1H, d, J = 15.7 Hz), 5.40 (2H, s), 4.25 (2H, q, J = 6.6 Hz), 2.03 (3H, s), 1.32 (3H, t, J = 7.1 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.4, 140.5, 139.6, 135.3, 133.2, 130.3, 129.3, 128.5, 128.3, 126.9, 121.3, 116.7, 60.6, 53.1, 14.2, 8.9; IR (ATR) 2930, 1707, 1633, 1311, 1270, 1172, 763 cm^{-1}; HRMS *m/z* (M$^+$) calcd for $C_{16}H_{18}N_2O_2$: 270.1368. Found: 270.1371.

Methyl (*E*)-3-(2-((4-chloro-1*H*-pyrazol-1-yl)methyl)phenyl)acrylate (3g)



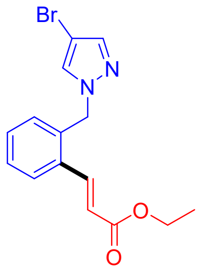
The title compound was prepared according to the general procedure. The product was obtained as a white solid. Yield: 91% (126 mg); mp 82-84 °C. ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.90 (1H, d, J = 15.7 Hz), 7.57-7.54 (1H, m), 7.41 (1H, s), 7.33-7.29 (2H, m), 7.25 (1H, s), 7.07-7.04 (1H, m), 6.32 (1H, d, J = 15.7 Hz), 5.34 (2H, s), 3.75 (3H, s); ^{13}C NMR (150 MHz, CDCl$_3$) δ 166.6, 140.3, 137.9, 134.3, 133.2, 130.3, 129.3, 128.8, 127.1, 127.0, 120.9, 110.2, 53.8, 51.6; IR (ATR) 2949, 1695, 1248, 1032, 766 cm^{-1}; HRMS *m/z* (M$^+$) calcd for $C_{14}H_{13}ClN_2O_2$: 276.0666. Found: 276.0664.

Benzyl (*E*)-3-(2-((4-chloro-1*H*-pyrazol-1-yl)methyl)phenyl)acrylate (3h)



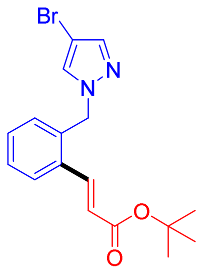
The title compound was prepared according to the general procedure. The product was obtained as a viscous liquid. Yield: 79% (139 mg); ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.87 (1H, d, J = 15.7 Hz), 7.50-7.48 (1H, m), 7.32-7.25 (7H, m), 7.16-7.15 (2H, m), 7.01-7.00 (1H, m), 6.30 (1H, d, J = 15.7 Hz), 5.28 (2H, s), 5.14 (2H, s); ^{13}C NMR (150 MHz, CDCl$_3$) δ 166.1, 140.7, 138.1, 135.8, 134.4, 134.3, 133.4, 130.5, 129.6, 129.0, 128.6, 128.3, 128.2, 127.2, 127.2, 121.1, 66.5, 54.0; IR (ATR) 3033, 2930, 1710, 1635, 1311, 1160, 972, 754 cm^{-1}; HRMS *m/z* (M$^+$) calcd for $C_{20}H_{17}ClN_2O_2$: 352.0979. Found: 352.0983.

Ethyl (*E*)-3-(2-((4-bromo-1*H*-pyrazol-1-yl)methyl)phenyl)acrylate (3i)



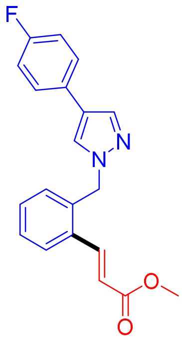
The title compound was prepared according to the general procedure. The product was obtained as a yellow liquid. Yield: 92% (154 mg); ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.91 (1H, d, J = 15.7 Hz), 7.58-7.57 (1H, m), 7.47 (1H, s), 7.35-7.33 (2H, m), 7.29 (1H, s), 7.09-7.07 (1H, m), 6.33 (1H, d, J = 15.7 Hz), 5.39 (2H, s), 4.24 (2H, q, J = 7.1 Hz), 1.31 (3H, t, J = 7.1 Hz); ^{13}C NMR (150 MHz, CDCl$_3$) δ 166.2, 140.1, 140.1, 134.3, 133.5, 130.3, 129.5, 129.3, 128.9, 127.1, 121.5, 93.5, 60.6, 53.9, 14.2; IR (ATR) 2979, 1706, 1633, 1310, 1271, 1176, 763 cm^{-1}; HRMS *m/z* (M$^+$) calcd for $C_{15}H_{15}BrN_2O_2$: 334.0317. Found: 334.0320.

tert-Butyl (_E_)-3-(2-((4-bromo-1_H_-pyrazol-1-yl)methyl)phenyl)acrylate (3j)



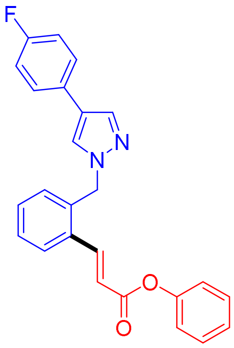
The title compound was prepared according to the general procedure. The product was obtained as a ivory solid. Yield: 90% (163 mg); mp 62-64 ºC. ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.80 (1H, d, J = 15.7 Hz), 7.56-7.55 (1H, m), 7.46 (1H, s), 7.32 (2H, t, J = 4.6 Hz), 7.29 (1H, s), 7.08-7.06 (1H, m), 6.25 (1H, d, J = 15.7 Hz), 5.37 (2H, s), 1.50 (9H, s); ^{13}C NMR (150 MHz, CDCl$_3$) δ 165.5, 140.1, 139.1, 134.1, 133.7, 130.1, 129.4, 129.3, 128.9, 127.1, 123.4, 93.4, 80.7, 53.9, 28.1; IR (ATR) 2974, 2929, 1703, 1632, 1313, 1144, 983, 760 cm^{-1}; HRMS _m/z_ (M$^+$) calcd for $C_{17}H_{19}BrN_2O_2$: 362.0630. Found: 362.0632.

Methyl (_E_)-3-(2-((4-(4-fluorophenyl)-1_H_-pyrazol-1-yl)methyl)phenyl)acrylate (3k)



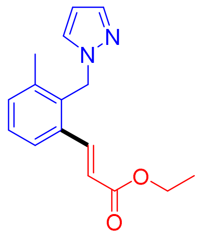
The title compound was prepared according to the general procedure. The product was obtained as a ivory liquid. Yield: 89% (150 mg); ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.14 (1H, d, J = 16.0 Hz), 7.60 (1H, dd, J = 8.6, 5.8 Hz), 7.40 (1H, d, J = 2.3 Hz), 7.38-7.35 (2H, m), 7.33-7.28 (4H, m), 7.10 (1H, td, J = 8.3, 2.7 Hz), 6.38-6.35 (2H, m), 5.36 (2H, s), 3.756 (3H, s); ^{13}C NMR (150 MHz, CDCl$_3$) δ 167.1, 162.2 (d, J = 246.0 Hz), 149.3, 143.3, 136.2, 134.7 (d, J = 7.5 Hz), 131.7 (d, J = 9 Hz), 130.3, 128.8, 128.1, 127.8, 119.7, 116.9 (d, J = 22.5 Hz), 113.3, 113.1, 107.1, 56.2, 51.6; IR (ATR) 2946, 1711, 1320, 1270, 1168, 715 cm^{-1}; HRMS _m/z_ (M$^+$) calcd for $C_{20}H_{17}FN_2O_2$: 336.1274. Found: 336.1276.

Phenyl (_E_)-3-(2-((4-(4-fluorophenyl)-1_H_-pyrazol-1-yl)methyl)phenyl)acrylate (3l)



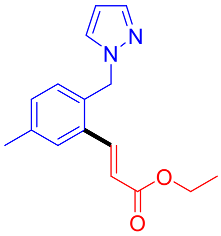
The title compound was prepared according to the general procedure. The product was obtained as a white solid. Yield: 85% (170 mg); mp 123-125 ºC. ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.38 (1H, d, J = 16.2 Hz), 7.66-7.63 (1H, m), 7.44-7.39 (4H, m), 7.31-7.25 (6H, m), 7.17-7.15 (3H, m), 6.59 (1H, d, J = 16.2 Hz), 6.42 (1H, s), 5.37 (2H, s); ^{13}C NMR (150 MHz, CDCl$_3$) δ 165.0, 162.2 (d, J = 246.0 Hz), 150.7, 149.3, 145.1 (d, J = 3.0 Hz), 136.1, 134.4, 131.7 (d, J = 9.0 Hz), 130.3, 129.3, 128.8, 128.1, 127.7, 125.7, 121.6, 119.2, 117.2 (d, J = 22.5 Hz), 113.4, 113.2, 107.0, 56.2; IR (ATR) 3061, 1708, 1497, 1267, 1195, 969, 703 cm^{-1}; HRMS _m/z_ (M$^+$) calcd for $C_{25}H_{19}FN_2O_2$: 398.1431. Found: 398.1429.

Ethyl (*E*)-3-(2-((1*H*-pyrazol-1-yl)methyl)-3-methylphenyl)acrylate (3m)



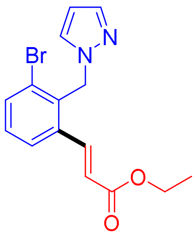
The title compound was prepared according to the general procedure. The product was obtained as a yellow solid. Yield: 74% (100 mg); mp 42-44 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (1H, d, *J* = 15.8 Hz), 7.50 (1H, s), 7.44 (1H, d, *J* = 7.6 Hz), 7.28-7.24 (2H, m), 7.07 (1H, s), 6.30 (1H, d, *J* = 14.5 Hz), 6.17 (1H, s), 5.44 (2H, s), 4.21 (2H, q, *J* = 7.2 Hz), 2.31 (3H, s), 1.29 (3H, t, *J* = 7.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.3, 141.7, 139.2, 139.1, 138.9, 135.3, 132.4, 128.9, 128.3, 125.2, 121.8, 105.5, 60.5, 49.2, 19.6, 14.2; IR (ATR) 2978, 1711, 1632, 1304, 1175, 745 cm^{-1}; HRMS *m/z* (M$^+$) calcd for $C_{16}H_{18}N_2O_2$: 270.1368. Found: 270.1371.

Ethyl (*E*)-3-(2-((1*H*-pyrazol-1-yl)methyl)-5-methylphenyl)acrylate (3n)



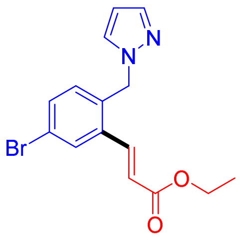
The title compound was prepared according to the general procedure. The product was obtained as a yellow liquid. Yield: 78% (105 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (1H, d, *J* = 15.5 Hz), 7.52 (1H, d, *J* = 1.8 Hz), 7.38 (1H, s), 7.30 (1H, d, *J* = 2.4), 7.14 (1H, d, *J* = 7.8 Hz), 6.97 (1H, d, *J* = 7.8 Hz), 6.32 (1H, d, *J* = 15.6 Hz), 6.23 (1H, t, *J* = 2.4 Hz), 5.41 (2H, s), 4.22 (2H, q, *J* = 6.6 Hz), 2.32 (3H, s), 1.30 (3H, t, *J* = 7.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.5, 140.6, 139.5, 138.4, 133.1, 132.3, 131.1, 129.5, 129.2, 127.5, 120.9, 105.9, 60.5, 52.9, 21.0, 14.2; IR (ATR) 2924, 1707, 1633, 1312, 1268, 1174, 750 cm^{-1}; HRMS *m/z* (M$^+$) calcd for $C_{16}H_{18}N_2O_2$: 270.1368. Found: 270.1370.

Ethyl (E)-3-(2-((1H-pyrazol-1-yl)methyl)-3-bromophenyl)acrylate (3o)



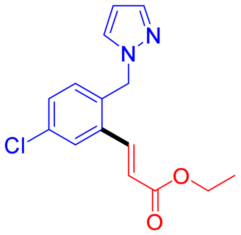
The title compound was prepared according to the general procedure. The product was obtained as a white solid. Yield: 67% (112 mg); mp 69-71 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (1H, d, *J* = 15.7 Hz), 7.63 (1H, d, *J* = 8.0 Hz), 7.51 (2H, d, *J* = 7.3 Hz), 7.32 (1H, d, *J* = 2.4 Hz), 7.22 (1H, t, *J* = 7.9 Hz), 6.28 (1H, d, *J* = 15.8 Hz), 6.20 (1H, t, *J* = 2.2 Hz), 5.59 (2H, d, *J* = 5.6 Hz), 4.23 (2H, q, *J* = 7.1 Hz), 1.29 (3H, t, *J* = 7.0 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.9, 141.1, 139.2, 137.8, 134.4, 133.2, 130.3, 129.1, 126.8, 126.7, 123.1, 105.6, 60.7, 52.2, 14.2; IR (ATR) 2982, 1696, 1625, 1269, 1183, 1040, 963, 746 cm^{-1}; HRMS *m/z* (M$^+$) calcd for $C_{15}H_{15}BrN_2O_2$: 334.0317. Found: 334.0319.

Ethyl (*E*)-3-(2-((1*H*-pyrazol-1-yl)methyl)-5-bromophenyl)acrylate (3p)



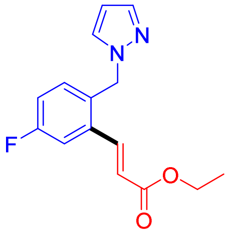
The title compound was prepared according to the general procedure. The product was obtained as a yellow solid. Yield: 69% (115 mg); mp 68-70 ºC. ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.83 (1H, d, *J* = 15.6 Hz), 7.66 (1H, s), 7.51(1H, s), 7.41 (1H, d, *J* = 8.2 Hz), 7.33 (1H, s), 6.86 (1H, d, *J* = 8.2 Hz), 6.31 (1H, d, *J* = 15.7 Hz), 6.25 (1H, s), 5.36 (2H, s), 4.23 (2H, q, *J* = 7.3 Hz), 1.30 (3H, t, *J* = 7.1 Hz); ^{13}C NMR (150 MHz, CDCl$_3$) δ 165.9, 139.9, 138.9, 135.1, 134.3, 133.0, 130.6, 129.7, 129.3, 123.7, 122.4, 106.2, 60.7, 52.6, 14.1; IR (ATR) 2977, 1710, 1634, 1309, 1173, 975, 753 cm^{-1}; HRMS *m/z* (M$^+$) calcd for $C_{15}H_{15}BrN_2O_2$: 334.0317. Found: 334.0320.

Ethyl (*E*)-3-(2-((1*H*-pyrazol-1-yl)methyl)-5-chlorophenyl)acrylate (3q)



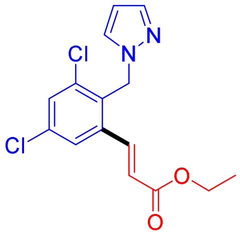
The title compound was prepared according to the general procedure. The product was obtained as a yellow semi-solid. Yield: 66% (96 mg); ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.85 (1H, d, *J* = 15.7 Hz), 7.52-7.51 (2H, m), 7.33 (1H, d, *J* = 2.3 Hz), 7.26 (1H, dd, *J* = 8.4, 1.8 Hz), 6.93 (1H, d, *J* = 8.3 Hz), 6.31 (1H, d, *J* = 15.8 Hz), 6.24 (1H, t, *J* = 3.0 Hz), 5.38 (2H, s), 4.22 (2H, q, *J* = 7.2 Hz), 1.29 (3H, t, *J* = 7.2 Hz); ^{13}C NMR (150 MHz, CDCl$_3$) δ 165.9, 139.8, 139.0, 134.8, 134.4, 133.7, 130.4, 130.0, 129.4, 126.8, 122.4, 106.2, 60.7, 52.5, 14.1; IR (ATR) 2979, 1709, 1634, 1310, 1175, 750 cm^{-1}; HRMS *m/z* (M$^+$) calcd for $C_{15}H_{15}ClN_2O_2$: 290.0822. Found: 290.0823.

Ethyl (*E*)-3-(2-((1*H*-pyrazol-1-yl)methyl)-5-fluorophenyl)acrylate (3r)



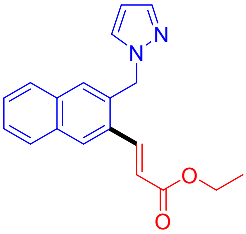
The title compound was prepared according to the general procedure. The product was obtained as a white solid. Yield: 65% (89 mg); mp 76-78 ºC. ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.88 (1H, d, *J* = 15.9 Hz), 7.52 (1H, s), 7.32 (1H, s), 7.24 (1H, d, *J* = 9.6 Hz), 7.02 (2H, d, *J* = 7.5 Hz), 6.31 (1H, d, *J* = 15.7 Hz), 6.24 (1H, s), 5.39 (2H, s), 4.23 (2H, q, *J* = 7.2 Hz), 1.30 (3H, t, *J* = 7.2 Hz); ^{13}C NMR (150 MHz, CDCl$_3$) δ 166.0, 163.4 (d, *J* = 246.0 Hz), 139.3, 139.3, 135.3 (d, *J* = 7.5 Hz), 131.2 (d, *J* = 9.0 Hz), 129.2, 122.3, 117.1 (d, *J* = 22.5 Hz), 113.6, 113.4, 106.1, 60.7, 52.5, 14.2; IR (ATR) 2980, 1697, 1322, 1191, 751 cm^{-1}; HRMS *m/z* (M$^+$) calcd for $C_{15}H_{15}FN_2O_2$: 274.1118. Found: 274.1115.

Ethyl (*E*)-3-(2-((1*H*-pyrazol-1-yl)methyl)-3,5-dichlorophenyl)acrylate (3s)



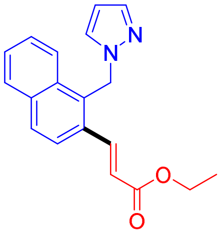
The title compound was prepared according to the general procedure. The product was obtained as a white solid. Yield: 63% (102 mg); mp 85-87 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (1H, d, *J* = 15.8 Hz), 7.50 (1H, s), 7.45 (2H, s), 7.35 (1H, s), 6.31 (1H, d, *J* = 15.7 Hz), 6.21 (1H, s), 5.51 (2H, s), 4.24 (2H, q, *J* = 7.1 Hz), 1.30 (3H, t, *J* = 7.1 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.6, 139.9, 139.6, 138.8, 136.8, 135.4, 130.5, 130.4, 129.2, 126.2, 124.1, 105.7, 60.9, 49.0, 14.2; IR (ATR) 2982, 1713, 1307, 1179, 859, 754 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{15}H_{14}Cl_2N_2O_2$: 324.0432. Found: 324.0428.

Ethyl (*E*)-3-(3-((1*H*-pyrazol-1-yl)methyl)naphthalen-2-yl)acrylate (3u)



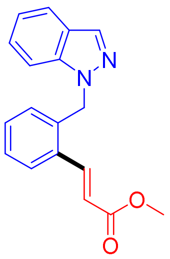
The title compound was prepared according to the general procedure. The product was obtained as a white solid. Yield: 89% (136 mg); mp 115-117 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (1H, s), 7.98 (1H, d, *J* = 15.7 Hz), 7.81-7.79 (1H, m), 7.73-7.71 (1H, m), 7.56 (1H, s), 7.48-7.46 (3H, m), 7.36 (1H, s), 6.43 (1H, d, *J* = 15.6 Hz), 6.27 (1H, s), 5.57 (2H, s), 4.26 (2H, q, *J* = 7.1 Hz), 1.33 (3H, t, *J* = 7.1 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.3, 140.9, 139.6, 133.6, 132.7, 132.3, 131.4, 129.4, 128.4, 128.0, 127.7, 127.3, 127.1, 126.8, 121.3, 106.0, 60.5, 53.9, 14.2; IR (ATR) 2984, 1696, 1309, 1183, 756 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{19}H_{18}N_2O_2$: 306.1368. Found: 306.1369.

Ethyl (*E*)-3-(1-((1*H*-pyrazol-1-yl)methyl)naphthalen-2-yl)acrylate (3v)



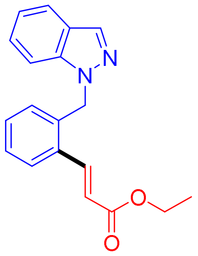
The title compound was prepared according to the general procedure. The product was obtained as a white solid. Yield: 71% (109 mg); mp 98-100 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.30 (1H, d, *J* = 15.7 Hz), 8.10 (1H, d, *J* = 7.1 Hz), 7.87-7.82 (2H, m), 7.70 (1H, d, *J* = 8.7 Hz), 7.54-7.50 (3H, m), 7.05 (1H, s), 6.51 (1H, d, *J* = 15.7 Hz), 6.14 (1H, s), 5.92 (2H, s), 4.27 (2H, q, *J* = 7.1 Hz), 1.33 (3H, t, *J* = 7.1 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) 166.4, 141.1, 139.1, 134.3, 132.6, 132.4, 130.0, 130.0, 128.6, 128.5, 127.7, 127.1, 124.3, 123.7, 122.6, 105.9, 60.7, 48.3, 14.3; IR (ATR) 2987, 1704, 1272, 1038, 743 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{19}H_{18}N_2O_2$: 306.1368. Found: 306.1365.

Methyl (*E*)-3-(2-((1*H*-indazol-1-yl)methyl)phenyl)acrylate (4a)



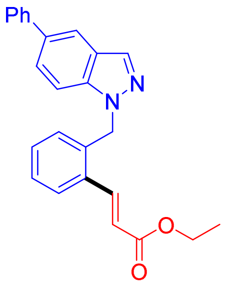
The title compound was prepared according to the general procedure. The product was obtained as a white solid. Yield: 91% (133 mg); mp 123-125 °C. ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.06 (1H, d, J = 15.7 Hz), 7.99 (1H, s), 7.68 (1H, d, J = 8.1 Hz), 7.50 (1H, d, J = 7.6 Hz), 7.28-7.16 (4H, m), 7.08 (1H, t, J = 7.3 Hz), 6.77 (1H, d, J = 7.6 Hz), 6.29 (1H, d, J = 15.7 Hz), 5.66 (2H, s), 3.73 (3H, s); ^{13}C NMR (150 MHz, CDCl$_3$) δ 166.8, 141.0, 139.6, 135.7, 133.7, 132.9, 130.2, 128.2, 128.1, 126.9, 126.5, 124.2, 121.1, 120.7, 120.6, 109.0, 51.7, 50.2; IR (ATR) 2953, 1700, 1273, 1208, 735 cm^{-1}; HRMS *m/z* (M$^+$) calcd for $C_{18}H_{16}N_2O_2$: 292.1212. Found: 292.1210.

Ethyl (*E*)-3-(2-((1*H*-indazol-1-yl)methyl)phenyl)acrylate (4b)



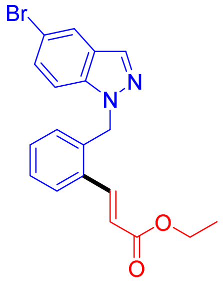
The title compound was prepared according to the general procedure. The product was obtained as a white solid. Yield: 90% (138 mg); mp 79-81 °C. ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.13 (1H, d, J = 15.7 Hz), 8.08 (1H, s), 7.76 (1H, d, J = 8.2 Hz), 7.59 (1H, d, J = 7.7 Hz), 7.36-7.15 (4H, m), 7.16 (1H, t, J = 7.3 Hz), 6.84 (1H, d, J = 7.5 Hz), 6.37 (1H, d, J = 15.7 Hz), 5.75 (2H, s), 4.28 (2H, q, J = 7.1 Hz), 1.34 (3H, t, J = 7.2 Hz); ^{13}C NMR (150 MHz, CDCl$_3$) δ 166.4, 140.6, 139.6, 135.6, 133.7, 132.9, 130.1, 128.1, 128.1, 126.9, 126.5, 124.2, 121.1, 121.1, 120.7, 109.0, 60.5, 50.2, 14.2; IR (ATR) 2985, 1700, 1628, 1310, 1178, 756 cm^{-1}; HRMS *m/z* (M$^+$) calcd for $C_{19}H_{18}N_2O_2$: 306.1368. Found: 306.1365.

Ethyl (*E*)-3-(2-((5-phenyl-1*H*-indazol-1-yl)methyl)phenyl)acrylate (4c)



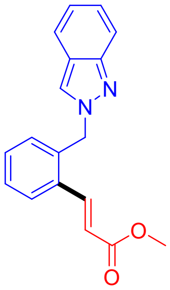
The title compound was prepared according to the general procedure. The product was obtained as a white solid. Yield: 90% (172 mg); mp 94-96 °C. ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.14 (1H, d, J = 15.8 Hz), 8.11 (1H, s), 7.92 (1H, s), 7.61-7.57 (4H, m), 7.43 (2H, t, J = 7.8 Hz), 7.36-7.24 (4H, m), 6.89 (1H, d, J = 7.4 Hz), 6.38 (1H, d, J = 15.7 Hz), 5.75 (2H, s), 4.27 (2H, q, J = 7.1 Hz), 1.33 (3H, t, J = 7.1 Hz); ^{13}C NMR (150 MHz, CDCl$_3$) δ 166.4, 141.2, 140.6, 139.1, 135.5, 134.3, 134.0, 132.9, 130.1, 128.7, 128.2, 128.1, 127.2, 126.9, 126.8, 126.6, 124.9, 121.2, 119.2, 109.3, 60.5, 50.4, 14.2; IR (ATR) 2957, 1710, 1631, 1313, 1181, 981, 758 cm^{-1}; HRMS *m/z* (M$^+$) calcd for $C_{25}H_{22}N_2O_2$: 382.1681. Found: 382.1682.

Ethyl (*E*)-3-(2-((5-bromo-1*H*-indazol-1-yl)methyl)phenyl)acrylate (4d)



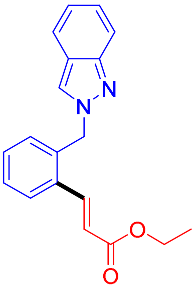
The title compound was prepared according to the general procedure. The product was obtained as a white liquid. Yield: 92% (177 mg). ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.06 (1H, d, *J* = 15.7 Hz), 7.99 (1H, s), 7.87 (1H, s), 7.58 (1H, d, *J* = 7.2 Hz), 7.39 (1H, d, *J* = 8.8 Hz), 7.30 (1H, t, *J* = 7.6 Hz), 7.26 (1H, t, *J* = 7.8 Hz), 7.17 (1H, d, *J* = 8.9 Hz), 6.85 (1H, d, *J* = 7.6 Hz), 6.34 (1H, d, *J* = 16.2 Hz), 5.71 (2H, s), 4.26 (2H, q, *J* = 7.4 Hz), 1.33 (3H, t, *J* = 7.1 Hz); ^{13}C NMR (150 MHz, CDCl$_3$) δ 166.3, 140.5, 138.3, 135.1, 133.0, 132.9, 130.2, 129.6, 128.3, 128.2, 127.1, 125.8, 123.5, 121.3, 113.9, 110.5, 60.6, 50.6, 14.2; IR (ATR) 2979, 1706, 1482, 1308, 1172, 1037, 793 cm^{-1}; HRMS *m/z* (M$^+$) calcd for $C_{19}H_{17}BrN_2O_2$: 384.0473. Found: 384.0475.

Methyl (*E*)-3-(2-((2*H*-indazol-2-yl)methyl)phenyl)acrylate (4e)



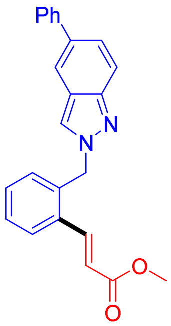
The title compound was prepared according to the general procedure. The product was obtained as a ivory solid. Yield: 94% (137 mg); mp 94-97 ºC. ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.01 (1H, d, *J* = 15.8 Hz), 7.81 (1H, s), 7.71 (1H, d, *J* = 8.8 Hz), 7.60 (2H, d, *J* = 8.3 Hz), 7.36-7.32 (2H, m), 7.28-7.25 (1H, m), 7.09-7.04 (2H, m), 6.36 (1H, d, *J* = 15.7 Hz), 5.74 (2H, s), 3.77 (3H, s); ^{13}C NMR (150 MHz, CDCl$_3$) δ 166.7, 148.8, 140.5, 134.4, 133.4, 130.5, 129.6, 129.0, 127.1, 126.2, 123.0, 122.0, 121.9, 121.2, 120.1, 117.4, 54.6, 51.8; IR (ATR) 3063, 1693, 1436, 1278, 757, 730 cm^{-1}; HRMS *m/z* (M$^+$) calcd for $C_{18}H_{16}N_2O_2$: 292.1212. Found: 292.1208.

Ethyl (*E*)-3-(2-((2*H*-indazol-2-yl)methyl)phenyl)acrylate (4f)



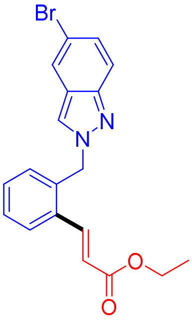
The title compound was prepared according to the general procedure. The product was obtained as a hazelnut solid. Yield: 92% (141 mg); mp 57-59 ºC. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.99 (1H, d, *J* = 15.7 Hz), 7.81 (1H, s), 7.70 (1H, d, *J* = 7.8 Hz), 7.59 (2H d, *J* = 8.0 Hz), 7.34-7.32 (2H, m), 7.28 (1H, d, *J* = 6.4 Hz), 7.09-7.03 (2H, m), 6.35 (1H, d, *J* = 15.5 Hz), 5.73 (2H, s), 4.22 (2H, q, *J* = 7.2 Hz), 1.29 (3H, t, *J* = 7.1 Hz); ^{13}C NMR (75 MHz, CDCl$_3$) δ 166.3, 148.6, 140.1, 134.2, 133.4, 130.4, 129.5, 128.9, 128.9, 127.0, 126.2, 123.1, 121.9, 121.6, 120.1, 117.3, 60.6, 54.6, 14.2; IR (ATR) 2927, 1704, 1267, 1159, 1036, 755 cm^{-1}; HRMS *m/z* (M$^+$) calcd for $C_{19}H_{18}N_2O_2$: 306.1368. Found: 306.1369.

Methyl (*E*)-3-(2-((5-phenyl-2*H*-indazol-2-yl)methyl)phenyl)acrylate (4g)



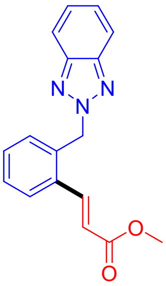
The title compound was prepared according to the general procedure. The product was obtained as a yellow viscous liquid. Yield: 89% (164 mg). ^{1}H NMR (600 MHz, $CDCl_3$) *δ* 8.03 (1H, d, *J* = 15.7 Hz), 7.86 (1H, s), 7.79-7.76 (2H, m), 7.60-7.55 (4H, m), 7.42 (2H, t, *J* = 7.8 Hz), 7.36-7.31 (3H, m), 7.12 (1H, d, *J* = 6.6 Hz), 6.37 (1H, d, *J* = 15.7 Hz), 5.75 (2H, s), 3.78 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.7, 148.1, 141.5, 140.4, 135.1, 134.2, 134.2, 133.3, 130.5, 129.6, 129.0, 128.6, 127.1, 127.1, 126.9, 126.9, 126.8, 123.6, 122.4, 121.2, 117.9, 117.7, 54.6, 51.7; IR (ATR) 3027, 1710, 1316, 1273, 1169, 976 cm^{-1}; HRMS *m/z* (M^{+}) calcd for $C_{24}H_{20}N_2O_2$: 368.1525. Found: 368.1527.

Ethyl (*E*)-3-(2-((5-bromo-2*H*-indazol-2-yl)methyl)phenyl)acrylate (4h)



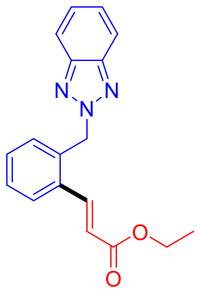
The title compound was prepared according to the general procedure. The product was obtained as a yellow viscous liquid. Yield: 92% (177 mg). ^{1}H NMR (600 MHz, $CDCl_3$) *δ* 7.95 (1H, d, *J* = 15.7 Hz), 7.75 (1H, s), 7.72 (1H, s), 7.59-7.56 (2H, m), 7.36-7.29 (3H, m), 7.10 (1H, d, *J* = 7.3 Hz), 6.33 (1H, d, *J* = 15.7 Hz), 5.70 (2H, s), 4.22 (2H, q, *J* = 7.2 Hz), 1.29 (3H, t, *J* = 7.1 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.2, 147.1, 140.0, 133.9, 133.5, 130.4, 129.7, 129.6, 129.1, 127.1, 123.1, 122.5, 122.2, 121.7, 119.2, 115.3, 60.6, 54.8, 14.2; IR (ATR) 2931, 1707, 1311, 1270, 1175, 1036 cm^{-1}; HRMS *m/z* (M^{+}) calcd for $C_{19}H_{17}BrN_2O_2$: 384.0473. Found: 384.0475.

Methyl (*E*)-3-(2-((2*H*-benzo[*d*][1,2,3]triazol-2-yl)methyl)phenyl)acrylate (5a)



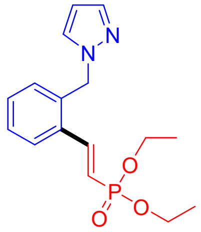
The title compound was prepared according to the general procedure. The product was obtained as a orange solid. Yield: 84% (123 mg); mp 109-111 °C. ^{1}H NMR (600 MHz, $CDCl_3$) *δ* 8.23 (1H, d, *J* = 15.8 Hz), 7.84 (2H, dd, *J* = 6.6, 3.1 Hz), 7.59-7.57 (1H, m), 7.35-7.32 (4H, m), 7.26-7.24 (1H, m), 6.37 (1H, d, *J* = 15.7 Hz), 6.00 (2H, s), 3.79 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) *δ* 166.8, 144.5, 141.0, 133.8, 133.5, 130.3, 130.0, 129.1, 127.1, 126.4, 121.2, 118.1, 57.3, 51.8; IR (ATR) 2924, 1709, 1632, 1318, 1168, 763 cm^{-1}; HRMS *m/z* (M^{+}) calcd for $C_{17}H_{15}N_3O_2$: 293.1164. Found: 293.1165.

Ethyl (*E*)-3-(2-((2*H*-benzo[*d*][1,2,3]triazol-2-yl)methyl)phenyl)acrylate (5b)



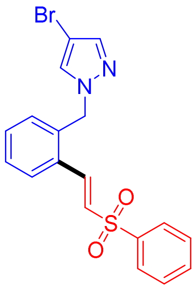
The title compound was prepared according to the general procedure. The product was obtained as a ivory solid. Yield: 85% (131 mg); mp 89-91 ºC. ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.21 (1H, d, *J* = 15.8 Hz), 7.84 (2H, dd, *J* = 6.6, 3.1 Hz), 7.59-7.58 (1H, m), 7.35-7.33 (4H, m), 7.25-7.23 (1H, m), 6.36 (1H, d, *J* = 15.7 Hz), 6.00 (2H, s), 4.25 (2H, q, *J* = 7.2 Hz), 1.32 (3H, t, *J* = 7.1 Hz); ^{13}C NMR (150 MHz, CDCl$_3$) δ 166.3, 144.5, 140.7, 133.9, 133.4, 130.2, 130.0, 129.1, 127.1, 126.4, 121.7, 118.1, 60.6, 57.4, 14.2; IR (ATR) 2986, 1702, 1636, 1313, 1180, 746 cm^{-1}; HRMS *m/z* (M$^+$) calcd for $C_{18}H_{17}N_3O_2$: 307.1321. Found: 307.1321.

Diethyl (*E*)-(2-((1*H*-pyrazol-1-yl)methyl)styryl)phosphonate (6a)



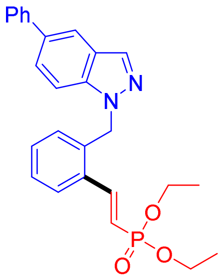
The title compound was prepared according to the general procedure. The product was obtained as a brown liquid. Yield: 86% (138 mg). ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.69 (1H, dd, *J* = 22.8, 17.4 Hz), 7.52-7.50 (1H, m), 7.47 (1H, s), 7.30-7.29 (3H, m), 7.04-7.02 (1H, m), 6.20 (1H, s), 6.14 (1H, t, *J* =17.4 Hz), 5.39 (2H, s), 4.08-3.99 (4H, m), 1.28 (6H, t, *J* = 7.1 Hz); ^{13}C NMR (150 MHz, CDCl$_3$) δ 144.5 (d, $J_{C\text{-}P}$ = 7.5 Hz), 139.4, 134.6, 133.9 (d, $J_{C\text{-}P}$ = 21.0 Hz), 130.2, 129.4 (d, $J_{C\text{-}P}$ = 6.0 Hz), 128.6, 128.1 (d, $J_{C\text{-}P}$ = 49.5 Hz), 126.7, 117.4 (d, $J_{C\text{-}P}$ = 189.0 Hz), 105.9, 61.9 (d, $J_{C\text{-}P}$ = 6.0 Hz), 53.1, 16.2 (d, $J_{C\text{-}P}$ = 6.0 Hz); IR (ATR) 2981, 1614, 1392, 1240, 1023, 963, 748 cm^{-1}; HRMS *m/z* (M$^+$) calcd for $C_{16}H_{21}N_2O_3P$: 320.1290. Found: 320.1292.

(*E*)-4-Bromo-1-(2-(2-(phenylsulfonyl)vinyl)benzyl)-1*H*-pyrazole (6b)



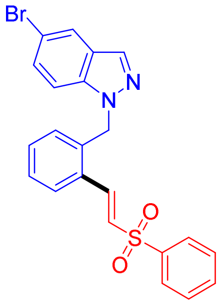
The title compound was prepared according to the general procedure. The product was obtained as a white solid. Yield: 88% (177 mg); mp 96-98 ºC. ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.91 (1H, d, *J* = 15.2 Hz), 7.85 (2H, d, *J* = 7.3 Hz), 7.59 (1H, t, *J* = 7.4 Hz), 7.52 (2H, t, *J* = 7.6 Hz), 7.48 (1H, d, *J* = 7.7 Hz), 7.42 (1H, s), 7.38 (1H, t, *J* = 7.5 Hz), 7.34-7.31 (2H, m), 7.18 (1H, d, *J* = 7.6 Hz), 6.77 (1H, d, *J* = 15.2 Hz), 5.38 (2H, s); ^{13}C NMR (150 MHz, CDCl$_3$) δ 140.2, 140.0, 138.2, 134.7, 133.4, 131.5, 131.2, 130.2, 130.1, 129.3, 129.2, 129.2, 127.6, 127.6, 93.5, 54.0; IR (ATR) 3047, 1600, 1300, 1140, 1077, 848, 748 cm^{-1}; HRMS *m/z* (M$^+$) calcd for $C_{18}H_{15}BrN_2O_2S$: 402.0038. Found: 402.0036.

Diethyl (*E*)-(2-((5-phenyl-1*H*-indazol-1-yl)methyl)styryl)phosphonate (7a)



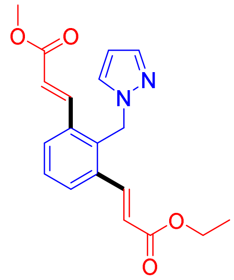
The title compound was prepared according to the general procedure. The product was obtained as a yellow liquid. Yield: 88% (196 mg). ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.10 (1H, s), 7.96-7.90 (2H, m), 7.61-7.57 (4H, m), 7.43 (2H, t, J = 7.7 Hz), 7.38 (1H, d, J = 8.7 Hz), 7.34-7.25 (3H, m), 6.94 (1H, d, J = 7.6 Hz), 6.22 (1H, t, J = 17.4 Hz), 5.74 (2H, s), 4.12-4.03 (4H, m), 1.32 (6H, t, J = 6.2 Hz); ^{13}C NMR (150 MHz, CDCl$_3$) δ 144.7 (d, $J_{C\text{-}P}$ = 7.5 Hz), 141.1, 139.1, 134.9, 134.5, 133.9, 133.7 (d, $J_{C\text{-}P}$ = 24.0 Hz), 130.2, 129.3, 128.7, 128.4, 128.3, 127.2, 126.8 (d, $J_{C\text{-}P}$ = 4.5 Hz), 126.8, 124.8, 119.1, 118.6 (d, $J_{C\text{-}P}$ = 189.0 Hz), 109.4, 61.9 (d, $J_{C\text{-}P}$ = 4.5 Hz), 50.4, 16.3 (d, $J_{C\text{-}P}$ = 6.0 Hz); IR (ATR) 2981, 1720, 1616, 1483, 1239, 1023, 962, 794 cm^{-1}; HRMS *m/z* (M$^+$) calcd for $C_{26}H_{27}N_2O_3P$: 446.1759. Found: 446.1758.

(*E*)-5-Bromo-1-(2-(2-(phenylsulfonyl)vinyl)benzyl)-1*H*-indazole (7b)



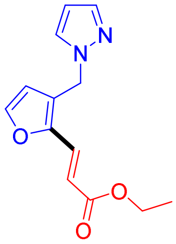
The title compound was prepared according to the general procedure. The product was obtained as a yellow solid. Yield: 82% (185 mg); mp 123-125 °C. ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.06 (1H, d, J = 15.2 Hz), 7.93 (1H, d, J = 1.0 Hz), 7.86 (1H, d, J = 1.7 Hz), 7.78 (2H, d, J = 7.2 Hz), 7.59 (1H, t, J = 7.5 Hz), 7.51-7.46 (3H, m), 7.41 (1H, dd, J = 8.9, 1.8 Hz), 7.33-7.27 (2H, m), 7.22 (1H, d, J = 8.9 Hz), 7.03 (1H, d, J = 7.5 Hz), 6.76 (1H, d, J = 15.1 Hz), 5.68 (2H, s); ^{13}C NMR (150 MHz, CDCl$_3$) δ 140.2, 138.6, 138.2, 135.6, 133.4, 133.0, 131.2, 131.1, 130.0, 129.8, 129.3, 129.2, 128.7, 127.6, 127.6, 125.8, 123.6, 114.0, 110.5, 50.7; IR (ATR) 2922, 1614, 1446, 1305, 1143, 1083, 750 cm^{-1}; HRMS *m/z* (M$^+$) calcd for $C_{22}H_{17}BrN_2O_2S$: 452.0194. Found: 452.0193.

Ethyl(*E*)-3-(2-((1*H*-pyrazol-1-yl)methyl)-3-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)phenyl)acrylate (8)



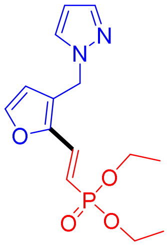
The title compound was prepared according to the general procedure. The product was obtained as a white solid. Yield: 71% (120 mg); mp 88-90 °C. ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.07-8.01 (2H, m), 7.57 (2H, d, J = 7.8 Hz), 7.49 (1H, s), 7.39 (1H, t, J = 7.8 Hz), 7.20 (1H, s), 6.31-6.27 (2H, m), 6.18 (1H, d, J = 1.8 Hz), 5.49 (2H, s), 4.21 (2H, q, J = 7.2 Hz), 3.75 (3H, s), 1.28 (3H, t, *J* = 7.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.5, 166.1, 141.3, 141.0, 139.6, 136.1, 136.0, 132.4, 129.3, 128.8, 128.7, 128.7, 122.7, 122.2, 105.8, 77.2, 51.8, 48.6, 14.1; IR (ATR) 2992, 2954, 1705, 1626, 1312, 1165, 739 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{19}H_{20}N_2O_4Na$: 363.1321. Found: 363.1318.

Ethyl (*E*)-3-(3-((1*H*-pyrazol-1-yl)methyl)furan-2-yl)acrylate (9a)



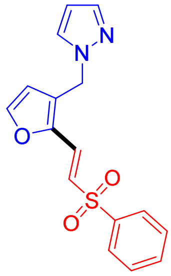
The title compound was prepared according to the general procedure. The product was obtained as a yellow liquid. Yield: 86% (106 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (1H, d, *J* = 1.8 Hz,), 7.42 (2H, m), 7.35 (1H, d, *J* = 2.2 Hz), 6.36-6.34 (2H, m), 6.26 (1H, s), 5.26 (2H, s), 4.23 (2H, q, *J* = 7.1 Hz), 1.30 (3H, t, *J* = 7.1 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.8, 147.6, 144.6, 139.6, 128.9, 127.7, 124.0, 117.1, 112.8, 106.2, 60.5, 46.3, 14.2; IR (ATR) 2974, 1748, 1224, 1022, 760 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{13}H_{14}N_2O_3$: 246.1004. Found: 246.1003.

Diethyl (*E*)-(2-(3-((1*H*-pyrazol-1-yl)methyl)furan-2-yl)vinyl)phosphonate (9b)



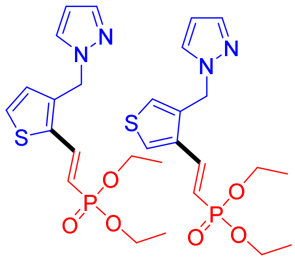
The title compound was prepared according to the general procedure. The product was obtained as a brown liquid. Yield: 62% (96 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (1H, s), 7.35 (2H, d, *J* = 6.2 Hz), 7.21 (1H, dd, *J* = 22.8, 17.4 Hz), 6.30 (1H, s), 6.21 (1H, s), 6.11 (1H, t, *J* = 17.4 Hz), 5.19 (2H, s), 4.07-4.01 (4H, m), 1.27 (6H, t, *J* = 7.1 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.3 (d, $J_{C\text{-}P}$ = 24.0 Hz), 144.2, 139.3, 131.9 (d, $J_{C\text{-}P}$ = 7.5 Hz), 128.9, 123.1, 112.6, 112.4 (d, $J_{C\text{-}P}$ = 192.0 Hz), 106.0, 61.7 (d, $J_{C\text{-}P}$ = 6.0 Hz), 46.0, 16.1 (d, $J_{C\text{-}P}$ = 7.5 Hz); IR (ATR) 3064, 1630, 1290, 1132, 745, 557 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{14}H_{19}N_2O_4P$: 310.1082. Found: 310.1084.

(*E*)-1-((2-(2-(phenylsulfonyl)vinyl)furan-3-yl)methyl)-1*H*-pyrazole (9c)



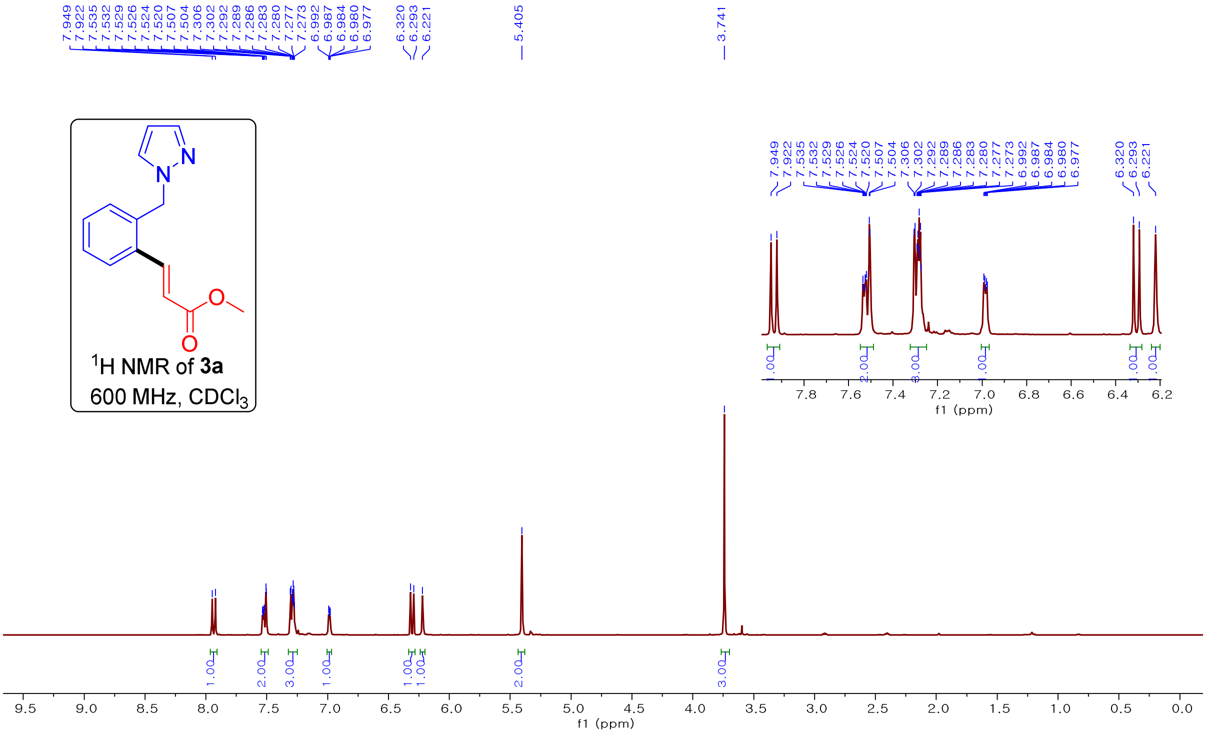
The title compound was prepared according to the general procedure. The product was obtained as an orange liquid. Yield: 72% (113 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (2H, d, *J* = 7.3 Hz), 7.59 (1H, t, *J* = 7.4 Hz), 7.53-7.51 (3H, m), 7.39-7.35 (3H, m), 6.77 (1H, d, *J* = 14.8 Hz), 6.36 (1H, d, *J* = 1.9 Hz), 6.28 (1H, s), 5.27 (2H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.4, 145.3, 140.6, 139.9, 133.3, 129.3, 129.1, 127.5, 126.5, 125.9, 125.7, 113.1, 106.4, 46.36; IR (ATR) 2974, 1707, 1268, 1172, 1040, 752 cm^{-1}; HRMS *m/z* $(M+H)^+$ calcd for $C_{16}H_{15}N_2O_3S$: 315.0803. Found: 315.0801.

Diethyl (*E*)-(2-(3-((1*H*-pyrazol-1-yl)methyl)thiophen-2-yl)vinyl)phosphonate (10a); Diethyl (*E*)-(2-(4-((1*H*-pyrazol-1-yl)methyl)thiophen-3-yl)vinyl)phosphonate (10a′)



The title compounds were prepared according to the general procedure. The product was obtained as a regioisomeric mixture (66:34). Combined yield: 73% (119 mg). For major isomer; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.64 (1H, dd, J = 22.2, 16.8 Hz), 7.50 (1H, s), 7.35 (1, s), 7.24 (1H, d, J = 4.8 Hz), 6.81 (1H, d, J = 5.4 Hz), 6.24 (1H, s), 6.01 (1H, t, J = 16.8 Hz), 5.36 (2H, s), 4.10-4.02 (4H, m), 1.31 (3H, t, J = 7.2 Hz); ^{13}C NMR (150 MHz, CDCl$_3$) δ 139.3 (d, $J_{\text{C-P}}$ = 15.6 Hz), 137.8, 137.7 (d, $J_{\text{C-P}}$ = 7.6 Hz), 135.4, 129.4 (d, $J_{\text{C-P}}$ = 1.8 Hz), 127.5, 114.3 (d, $J_{\text{C-P}}$ = 192.0 Hz), 106.2, 61.9 (d, $J_{\text{C-P}}$ = 5.5 Hz), 48.5, 16.3 (d, $J_{\text{C-P}}$ = 6.4 Hz); IR (ATR) 2982, 1607, 1231, 1080, 960, 754 cm^{-1}; HRMS *m/z* (M+H)$^+$ calcd for $C_{14}H_{19}N_2O_3PSNa$: 349.0752. Found: 349.0749.

^{1}H NMR and ^{13}C NMR spectra of synthesized compounds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6.992
6.987
6.984
6.980
6.977
6.320
6.293
6.221
5.405
3.741
N
N
O
O
^{1}H NMR of **3a**
600 MHz, CDCl$_3$
1.00
2.00
3.00
1.00
1.00
1.00
2.00
3.00
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
f1 (ppm)
9.5
9.0
8.5
8.0
7.5
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6.5
6.0
5.5
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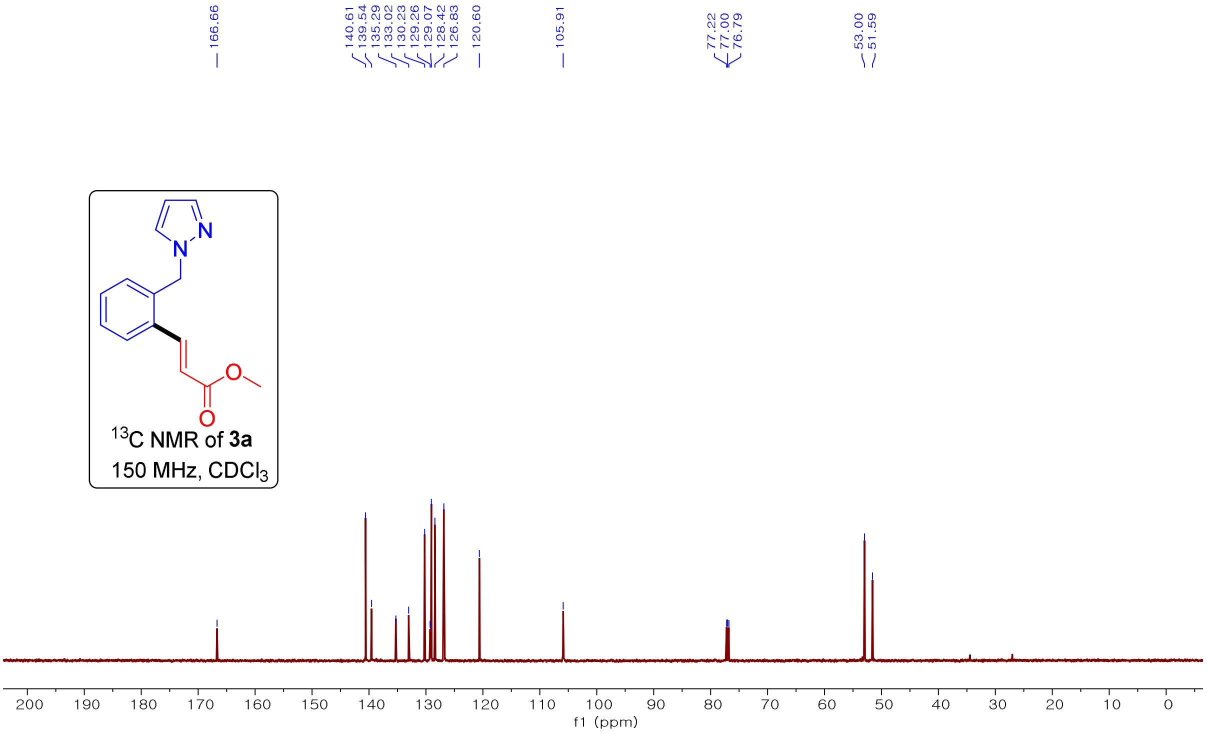
f1 (ppm)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77.00
76.79
53.00
51.59
N
N
O
O
^{13}C NMR of **3a**
150 MHz, CDCl$_3$
200
190
180
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140
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100
90
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50
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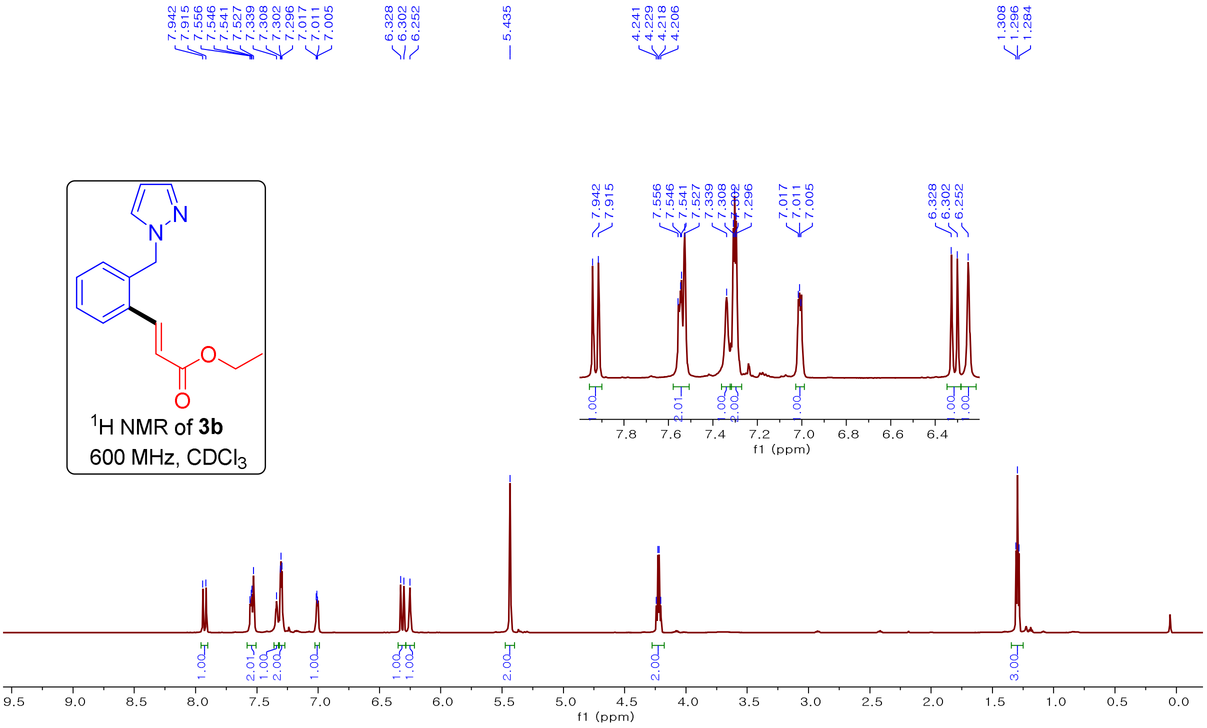
10
0
f1 (ppm)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6.328
6.302
6.252
5.435
4.241
4.229
4.218
4.206
1.308
1.296
1.284
N
N
O
O
^{1}H NMR of **3b**
600 MHz, $CDCl_3$
1.00
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1.00
2.00
1.00
1.00
1.00
2.00
2.00
3.00
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7.6
7.4
7.2
7.0
6.8
6.6
6.4
9.5
9.0
8.5
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6.5
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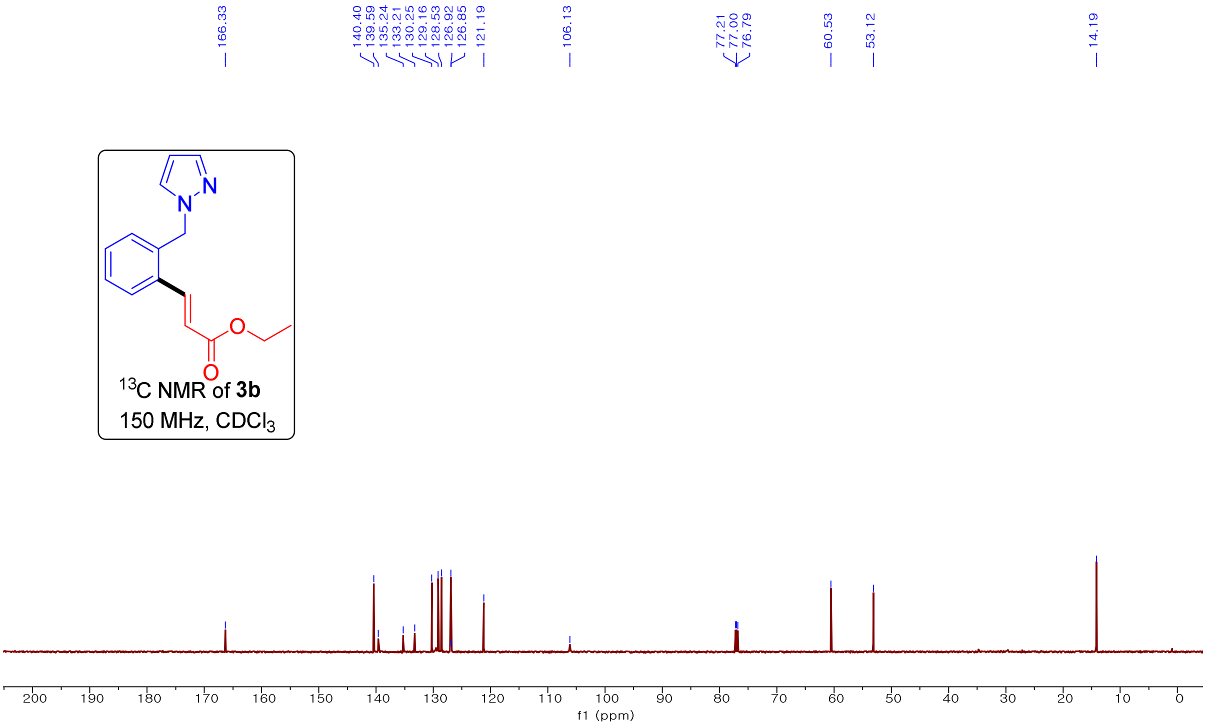
0.0
f1 (ppm)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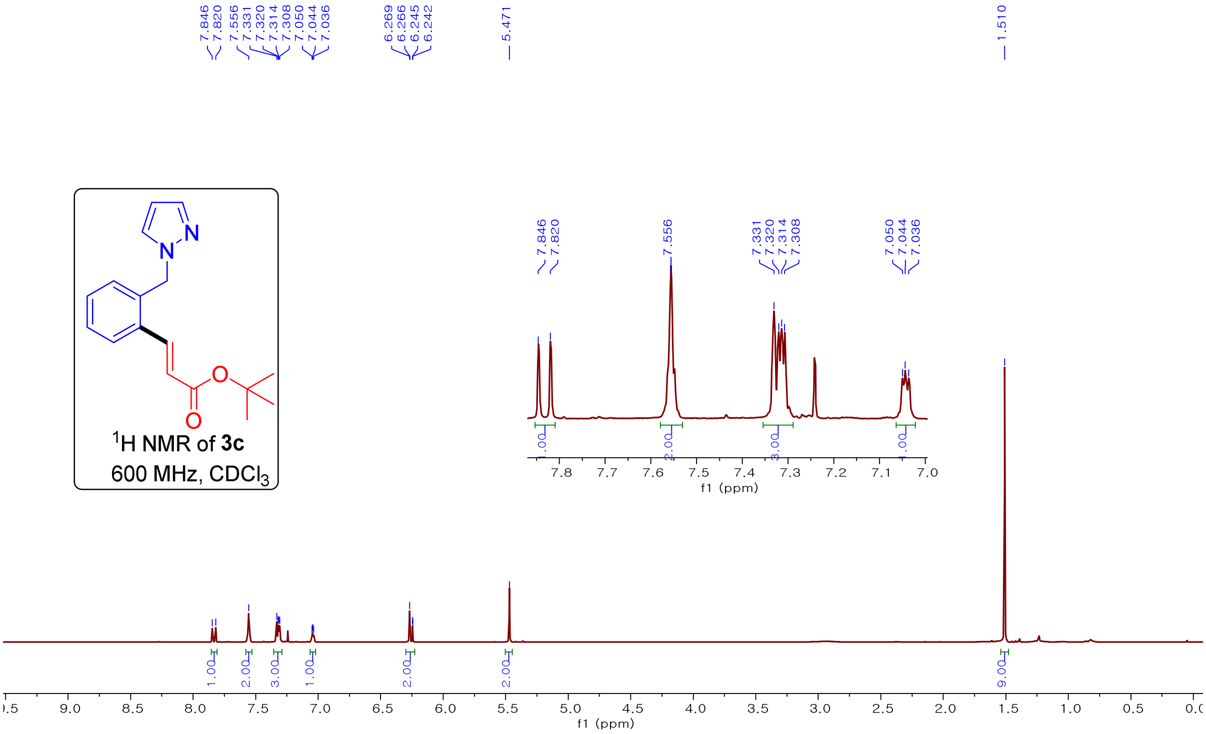
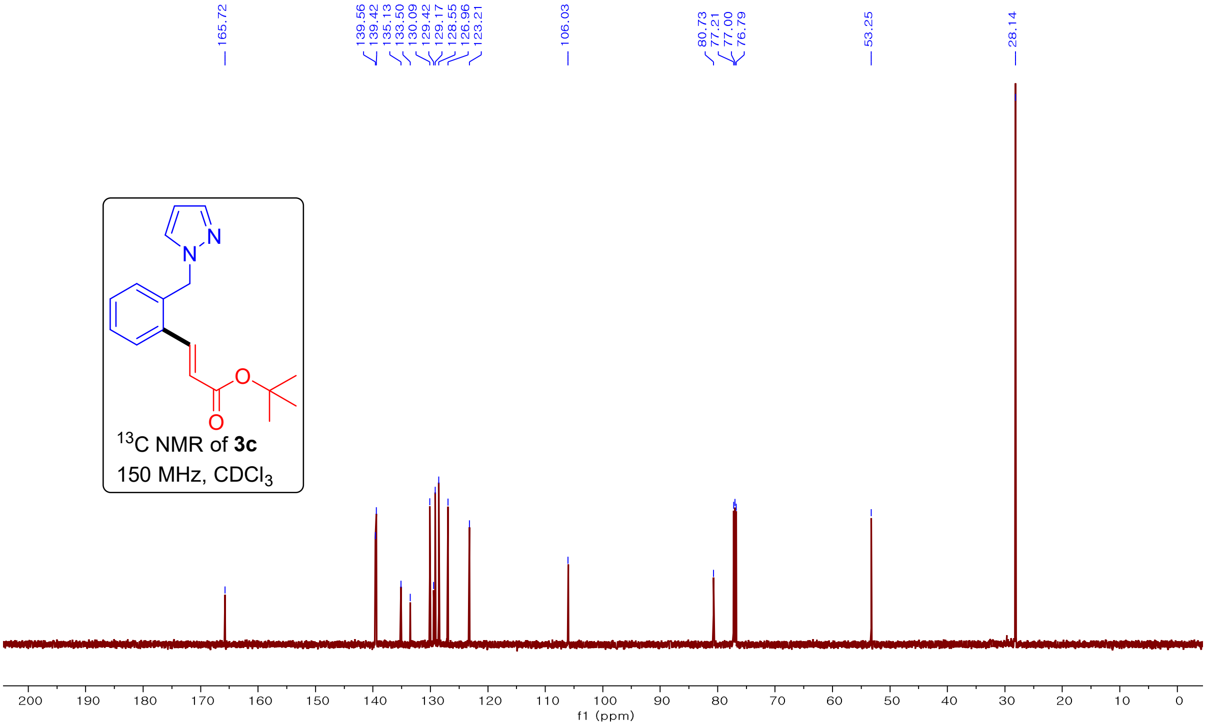
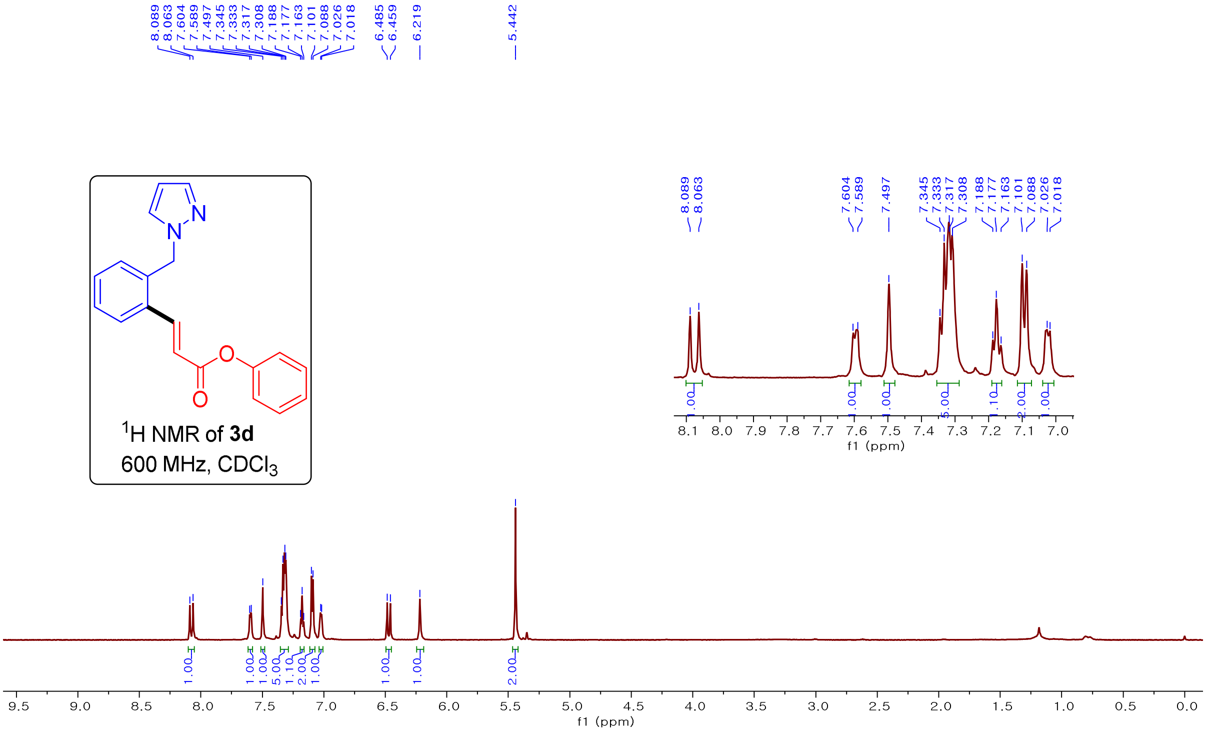
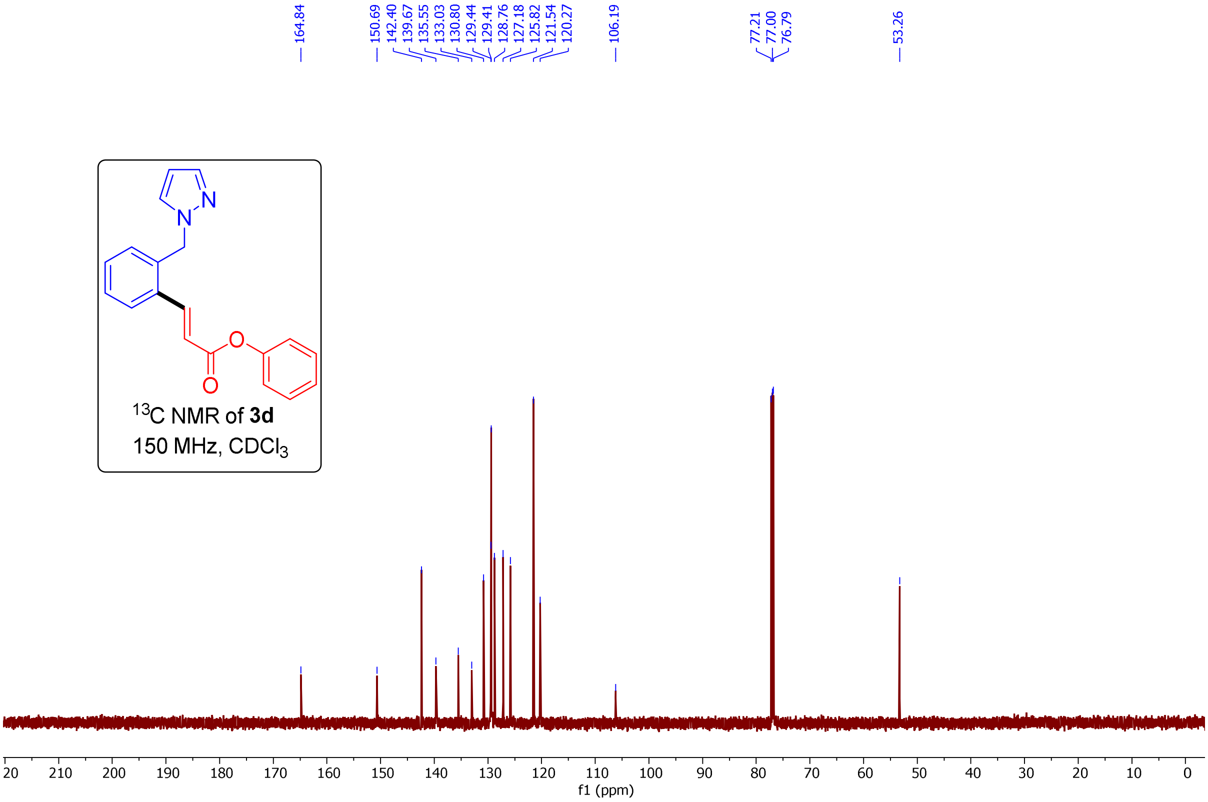
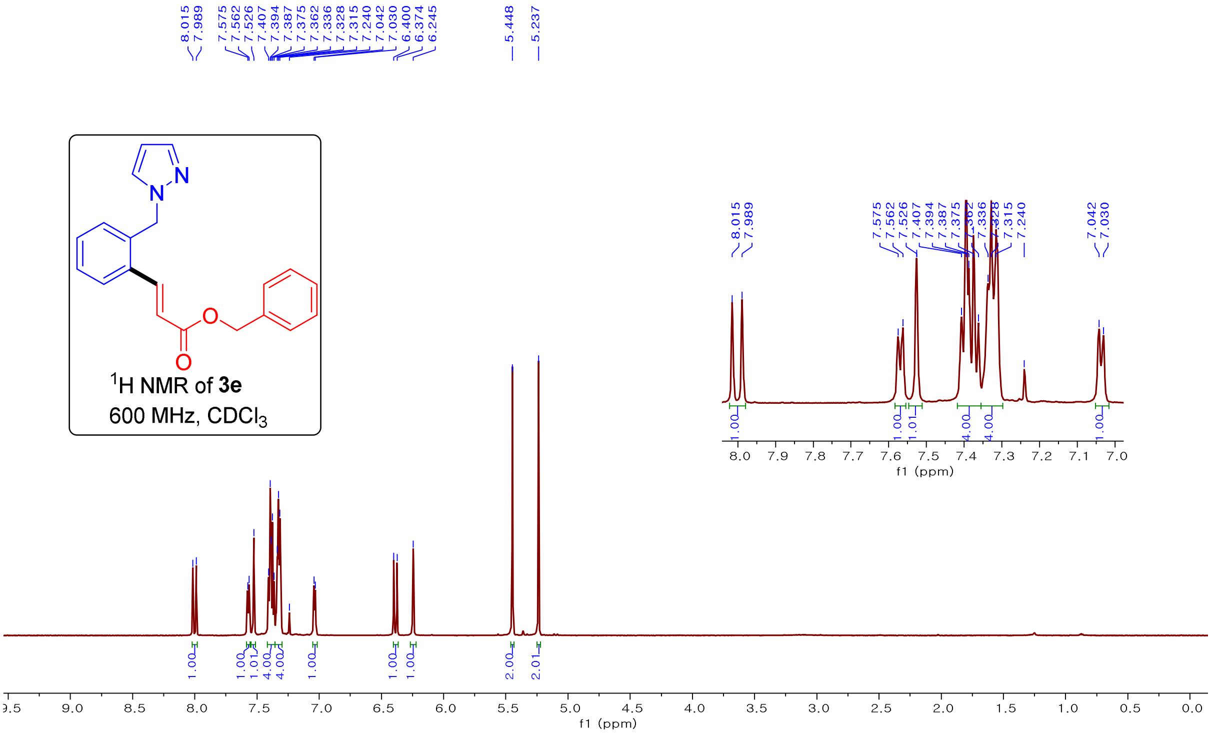
135.24
133.21
130.25
129.16
128.53
126.92
126.85
121.19
106.13
77.21
77.00
76.79
60.53
53.12
14.19
N
N
O
O
^{13}C NMR of **3b**
150 MHz, $CDCl_3$
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

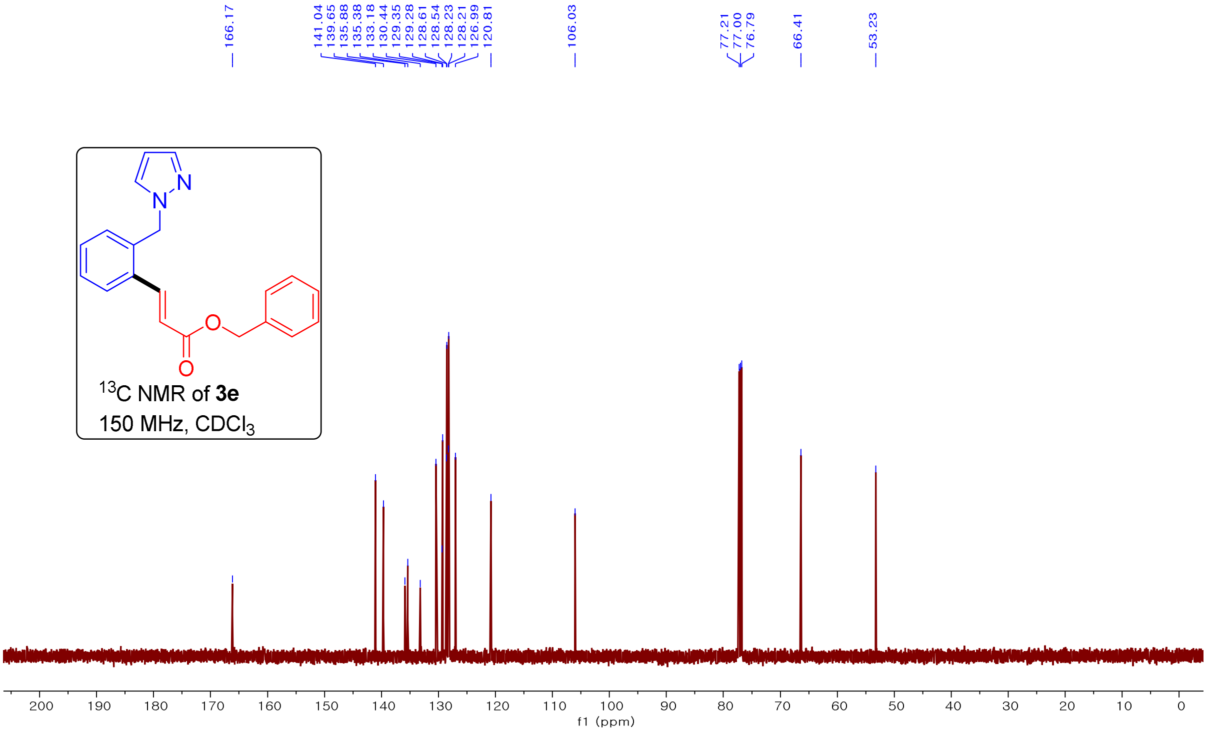

7.846
7.820
7.556
7.331
7.320
7.314
7.308
7.050
7.044
7.036
6.269
6.266
6.245
6.242
5.471
1.510
N
N
O
O
^{1}H NMR of **3c**
600 MHz, $CDCl_3$
1.00
2.00
3.00
1.00
2.00
2.00
9.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0

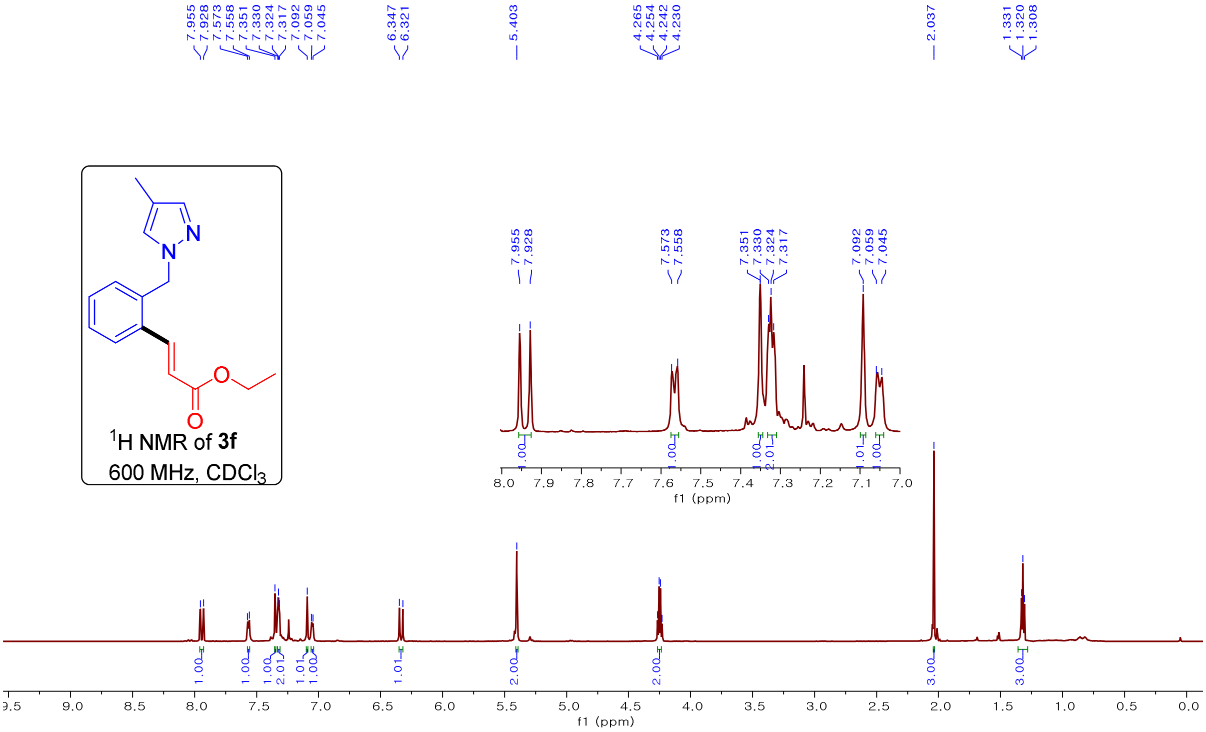

165.72
139.56
139.42
135.13
133.50
130.09
129.42
129.17
128.55
126.96
123.21
106.03
80.73
77.21
77.00
76.79
53.25
28.14
N
N
O
O
^{13}C NMR of **3c**
150 MHz, $CDCl_3$
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

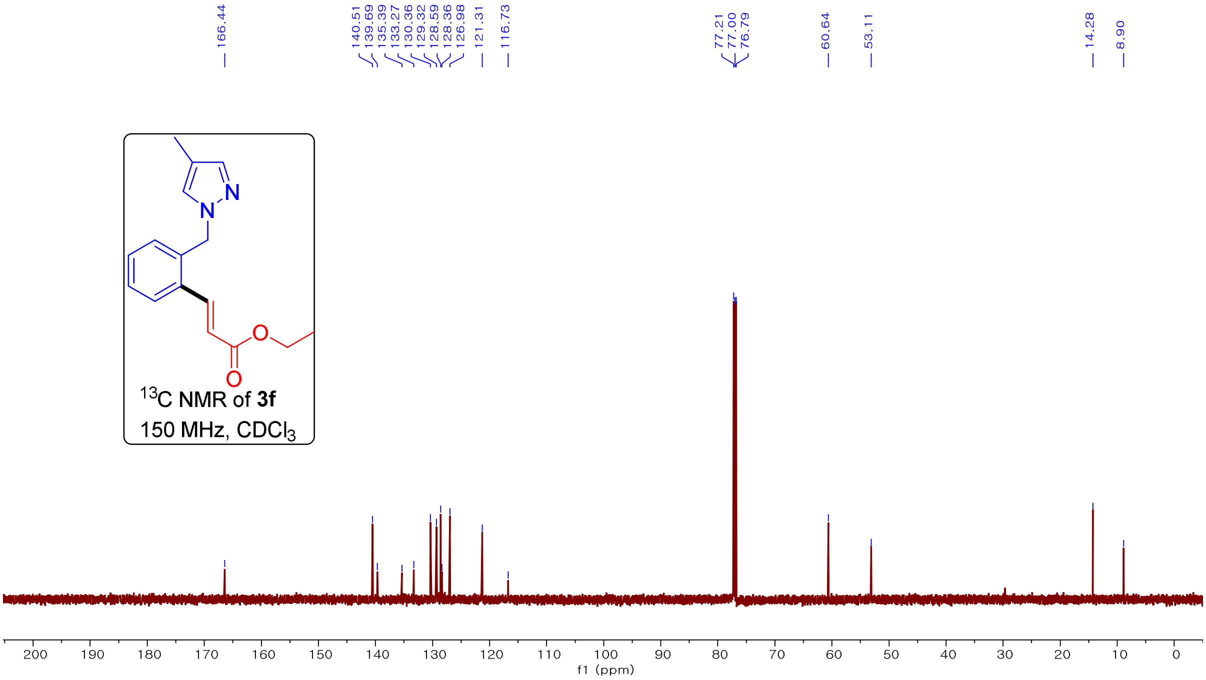

8.089
8.063
7.604
7.589
7.497
7.345
7.333
7.317
7.308
7.188
7.177
7.163
7.101
7.088
7.026
7.018
6.485
6.459
6.219
5.442
N
N
O
O
^{1}H NMR of **3d**
600 MHz, $CDCl_3$
1.00
5.00
1.10
2.00
f1 (ppm)

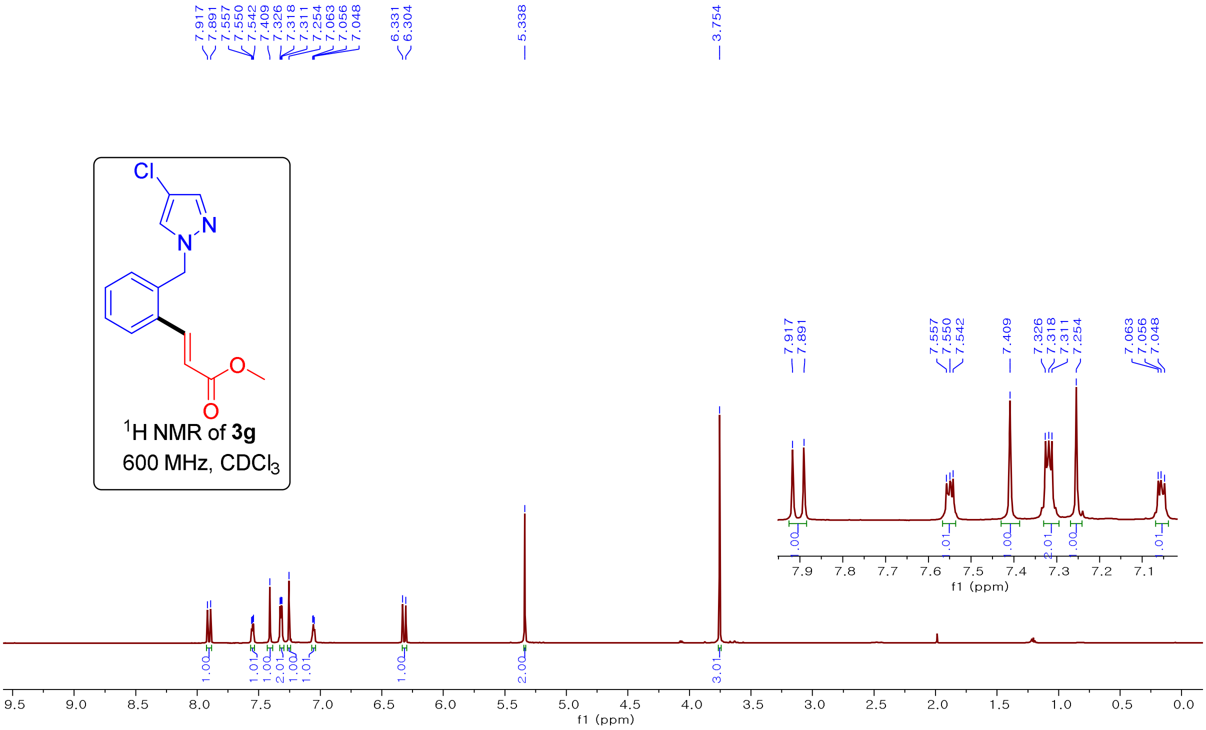

164.84
150.69
142.40
139.67
135.55
133.03
130.80
129.44
129.41
128.76
127.18
125.82
121.54
120.27
106.19
77.21
77.00
76.79
53.26
N
N
O
O
^{13}C NMR of **3d**
150 MHz, $CDCl_3$
f1 (ppm)

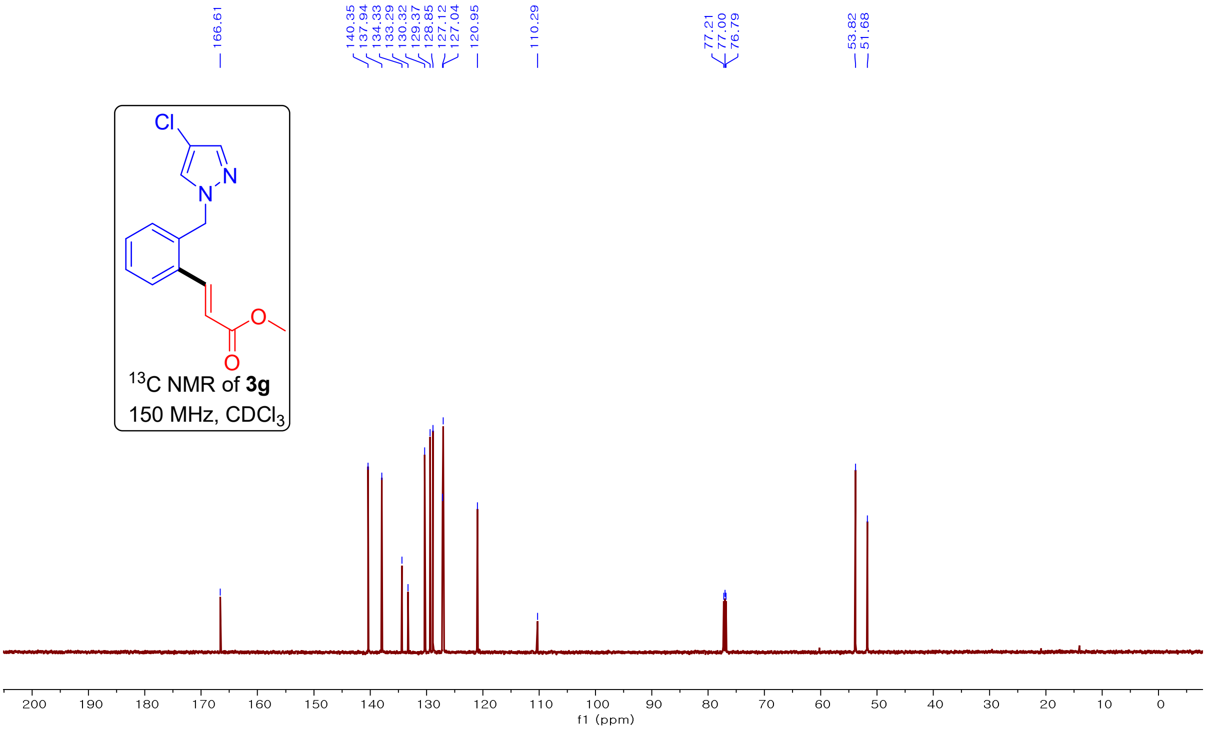

8.015
7.989
7.575
7.562
7.526
7.407
7.394
7.387
7.375
7.362
7.336
7.328
7.315
7.240
7.042
7.030
6.400
6.374
6.245
5.448
5.237
N
N
O
O
¹H NMR of 3e
600 MHz, CDCl₃
1.00
1.00
1.01
4.00
4.00
1.00
1.00
1.00
2.00
2.01
f1 (ppm)

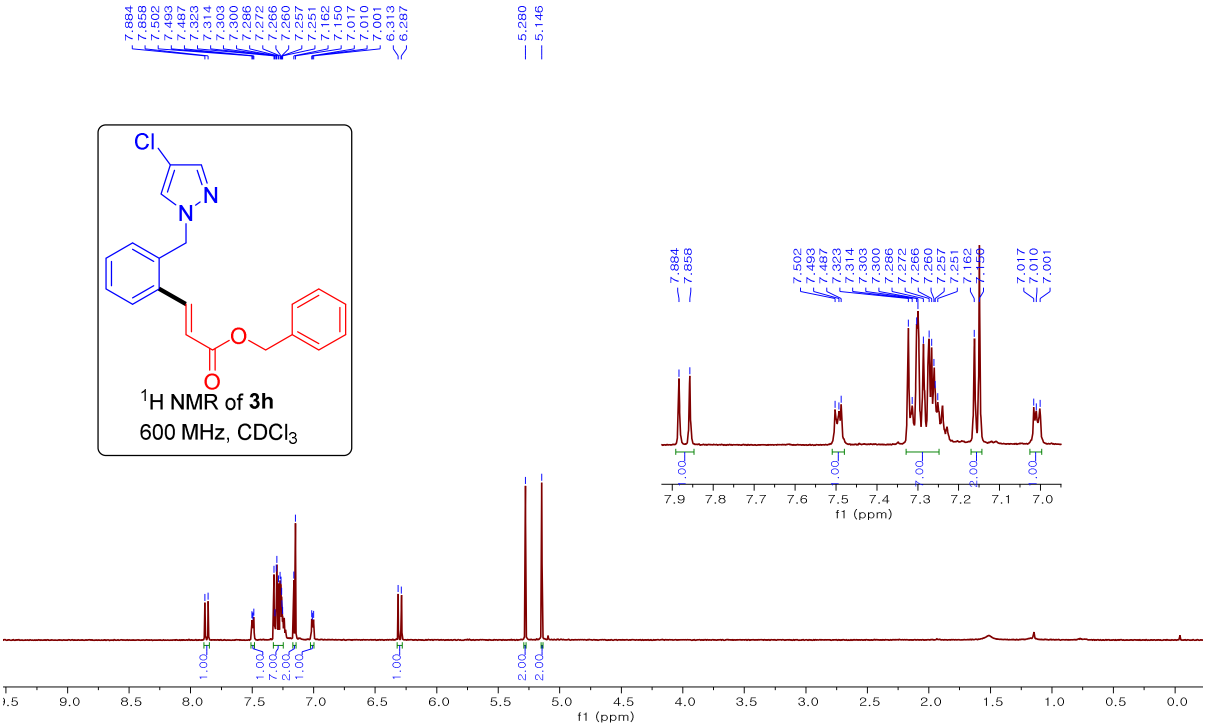

166.17
141.04
139.65
135.88
135.38
133.18
130.44
129.35
129.28
128.61
128.54
128.23
128.21
126.99
120.81
106.03
77.21
77.00
76.79
66.41
53.23
N
N
O
O
¹³C NMR of 3e
150 MHz, CDCl₃
f1 (ppm)

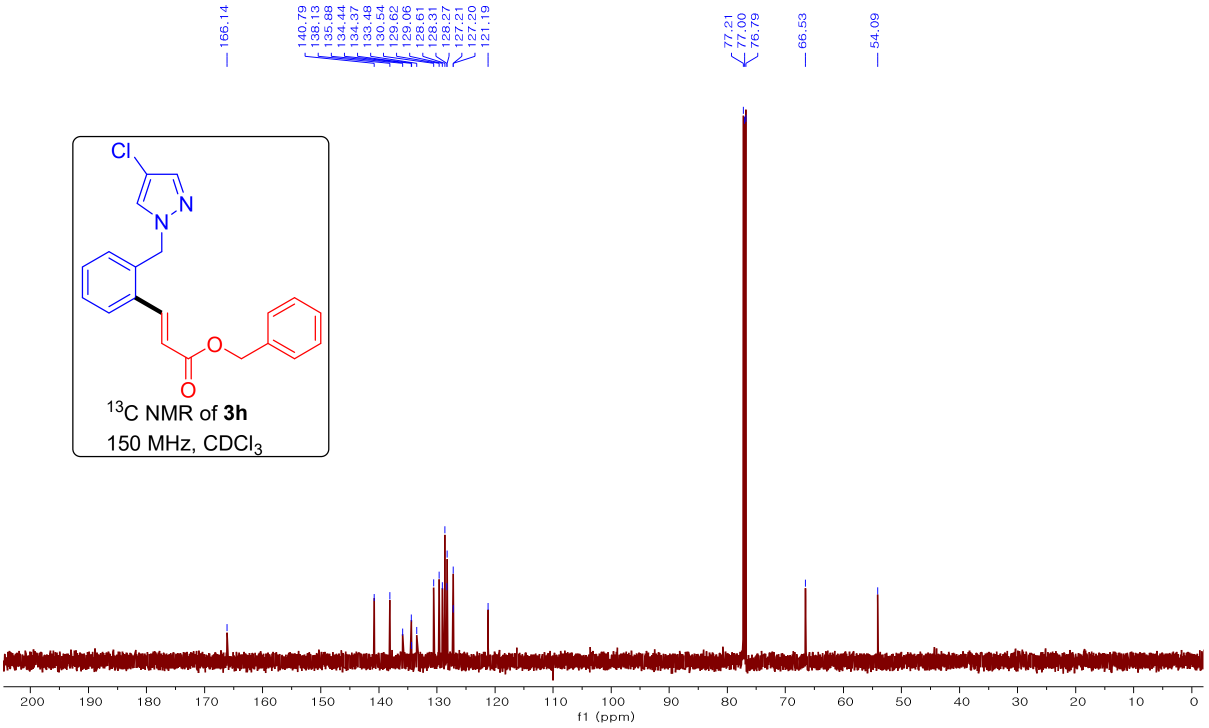

7.955
7.928
7.573
7.558
7.351
7.330
7.324
7.317
7.092
7.059
7.045
6.347
6.321
5.403
4.265
4.254
4.242
4.230
2.037
1.331
1.320
1.308
N
N
O
O
^{1}H NMR of **3f**
600 MHz, CDCl$_3$
1.00
1.00
1.00
2.01
1.01
1.00
1.01
2.00
2.00
3.00
3.00
f1 (ppm)

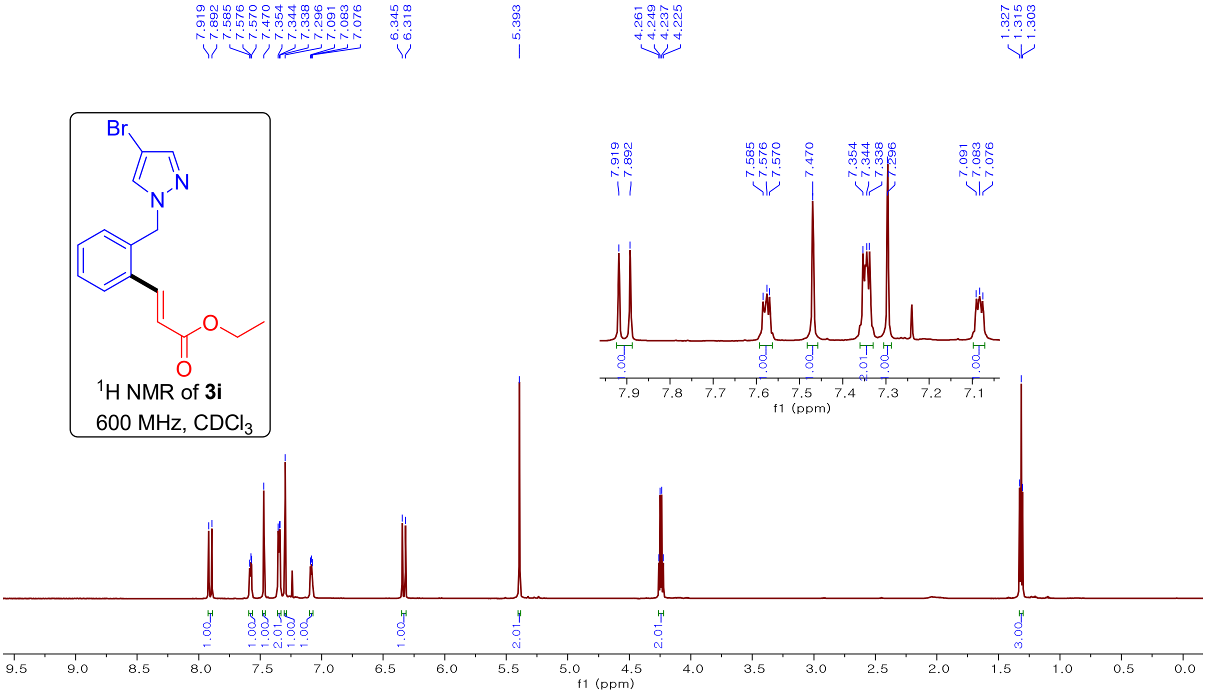

166.44
140.51
139.69
135.39
133.27
130.36
129.32
128.59
128.36
126.98
121.31
116.73
77.21
77.00
76.79
60.64
53.11
14.28
8.90
N
N
O
O
^{13}C NMR of **3f**
150 MHz, CDCl$_3$
f1 (ppm)


7.917
7.891
7.557
7.550
7.542
7.409
7.326
7.318
7.311
7.254
7.063
7.056
7.048
6.331
6.304
5.338
3.754
Cl
N
N
O
O
^{1}H NMR of **3g**
600 MHz, CDCl$_3$
1.00
1.01
1.00
2.01
1.00
1.01
1.00
2.00
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1
f1 (ppm)


166.61
140.35
137.94
134.33
133.29
130.32
129.37
128.85
127.12
127.04
120.95
110.29
77.21
77.00
76.79
53.82
51.68
Cl
N
N
O
O
^{13}C NMR of **3g**
150 MHz, CDCl$_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

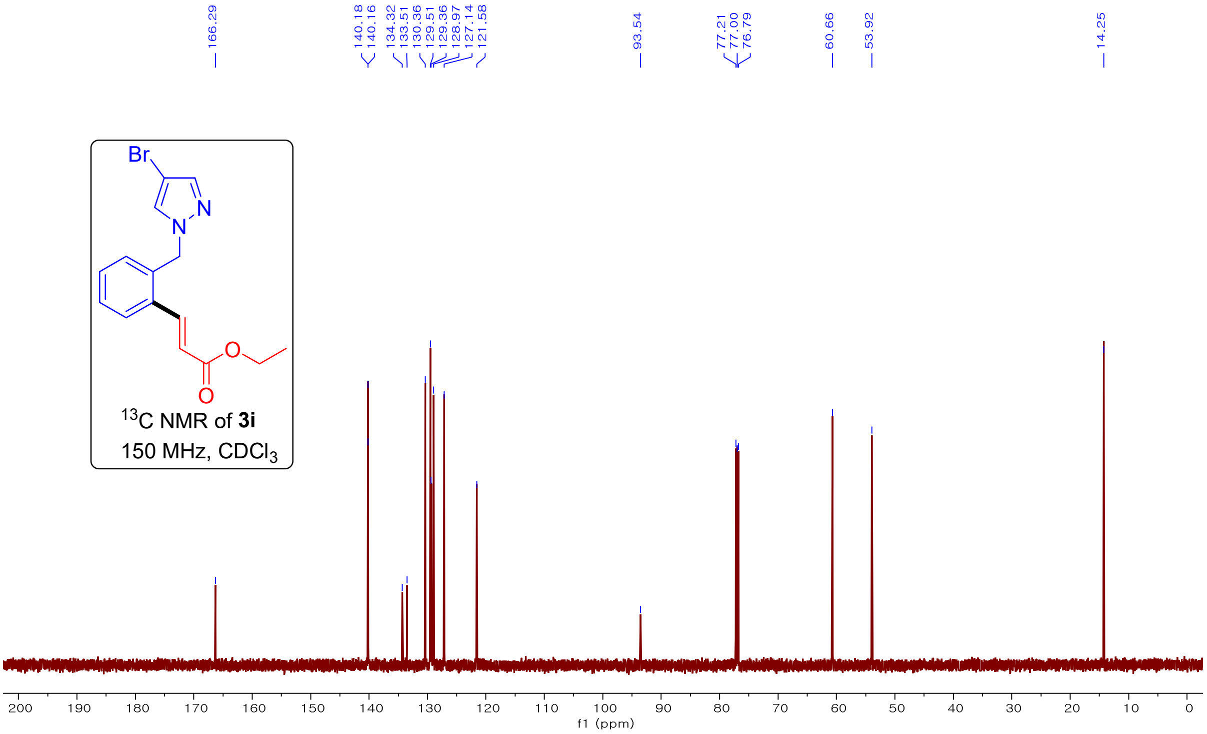

7.884
7.858
7.502
7.493
7.487
7.323
7.314
7.303
7.300
7.286
7.272
7.266
7.260
7.257
7.251
7.162
7.150
7.017
7.010
7.001
6.313
6.287
5.280
5.146
Cl
N
N
O
O
^{1}H NMR of 3h
600 MHz, $CDCl_3$
1.00
1.00
7.00
2.00
1.00
1.00
2.00
2.00
f1 (ppm)


166.14
140.79
138.13
135.88
134.44
134.37
133.48
130.54
129.62
129.06
128.61
128.31
128.27
127.21
127.20
121.19
77.21
77.00
76.79
66.53
54.09
Cl
N
N
O
O
^{13}C NMR of 3h
150 MHz, $CDCl_3$
f1 (ppm)



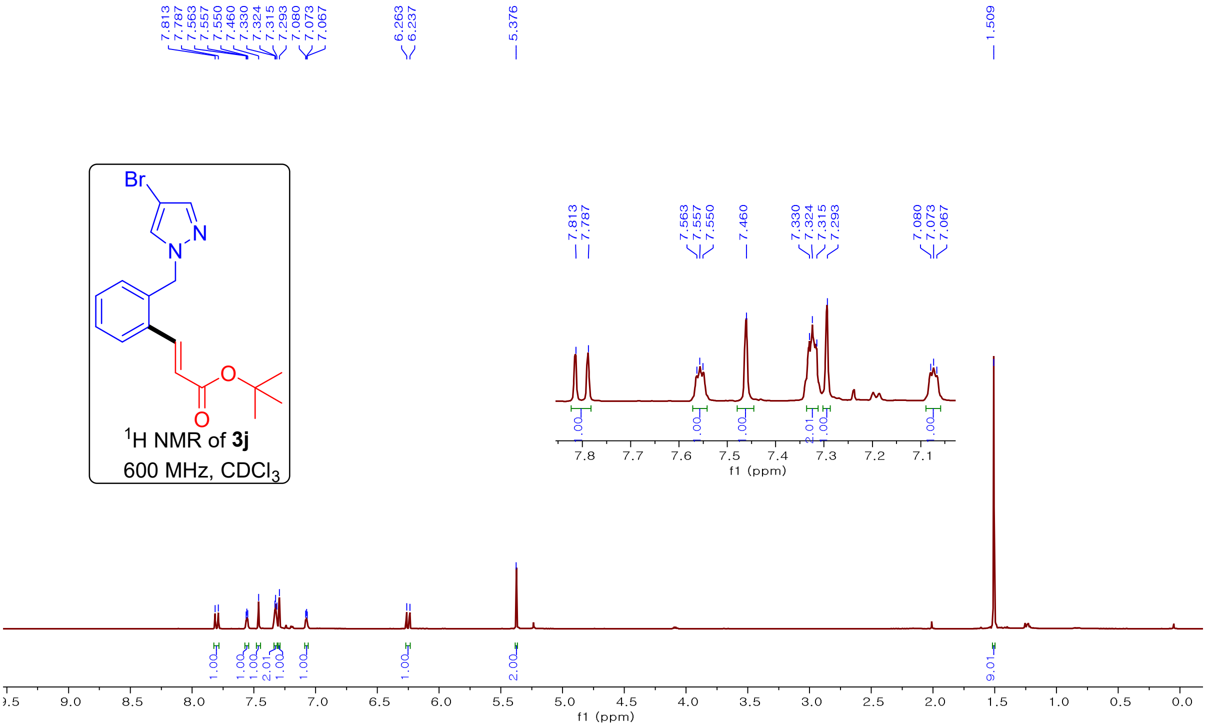
^{1}H NMR of **3i**

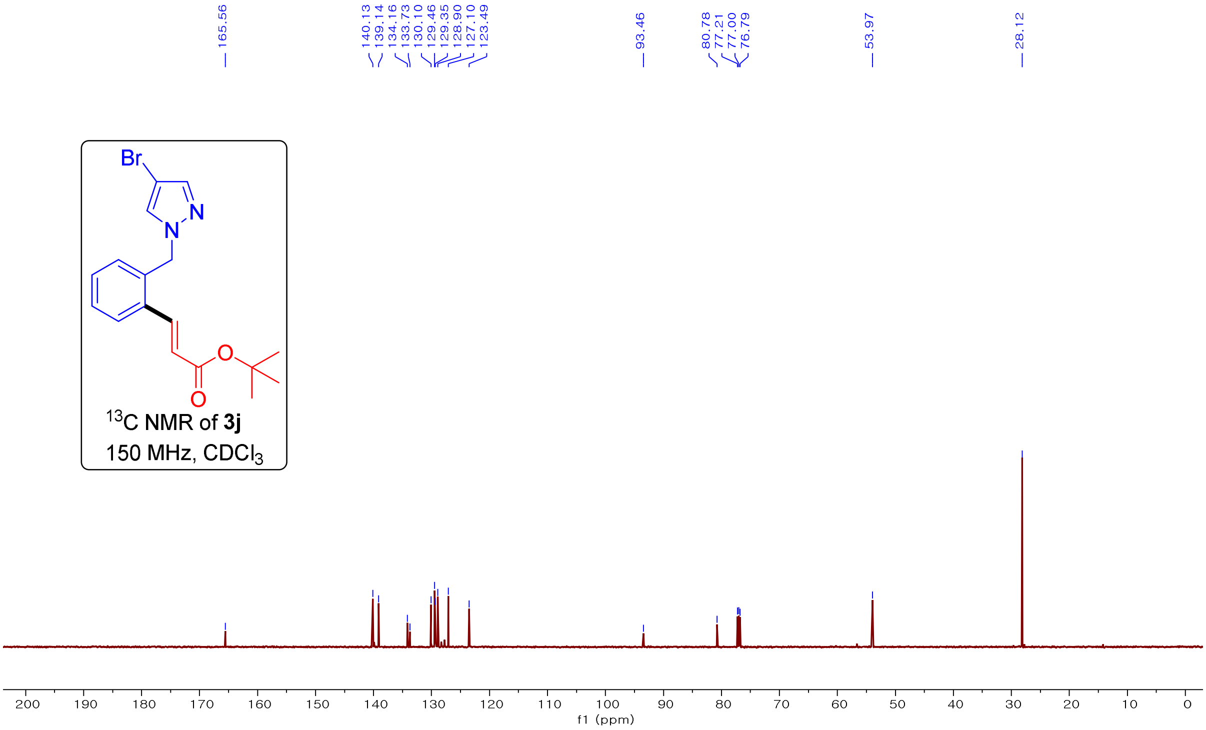
600 MHz, $CDCl_3$

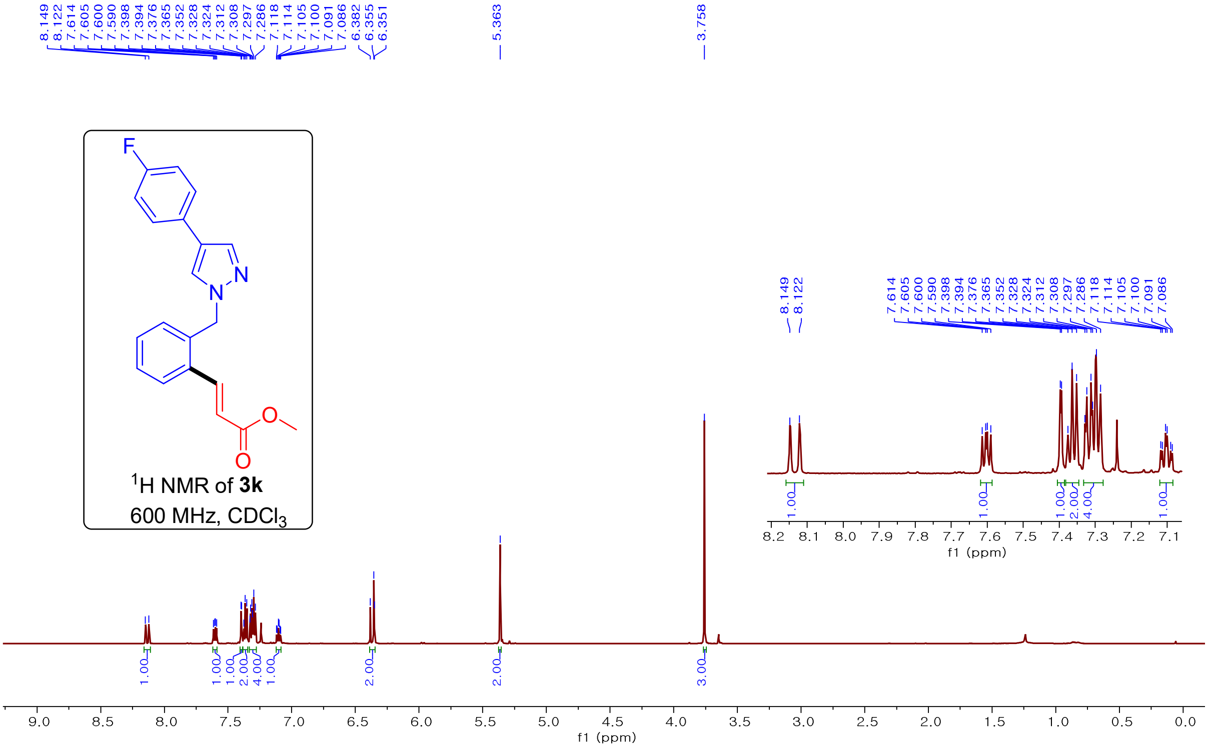


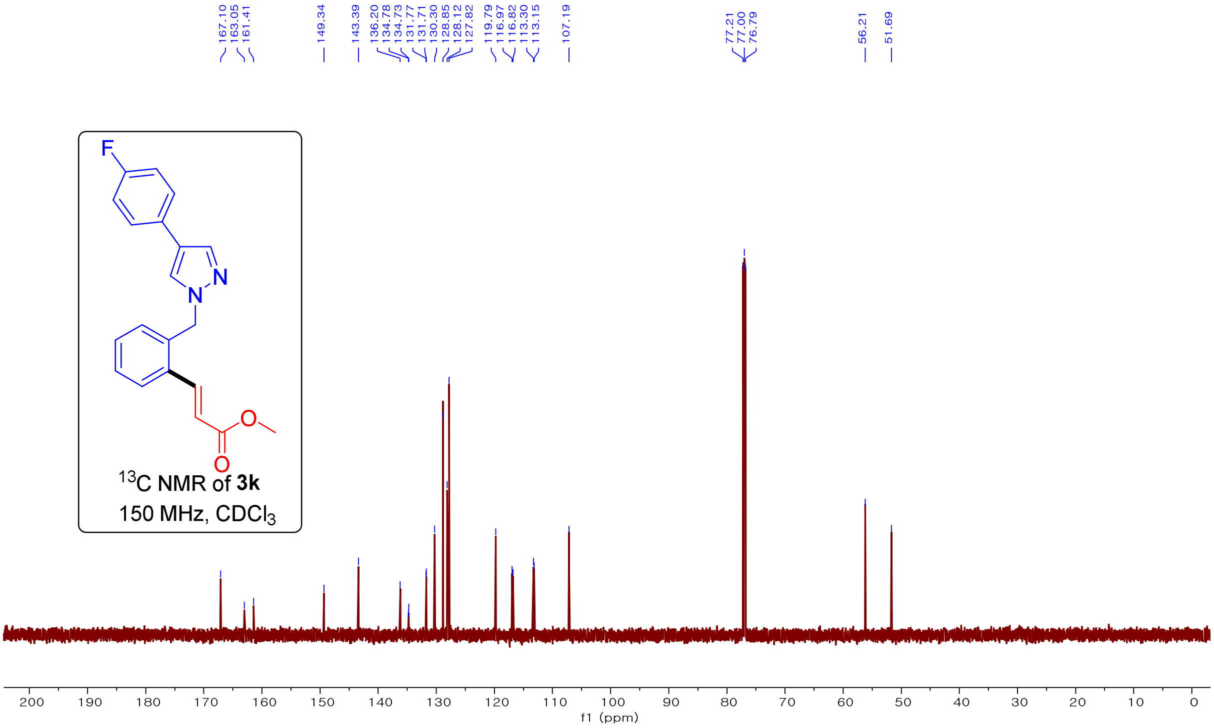
^{13}C NMR of **3i**

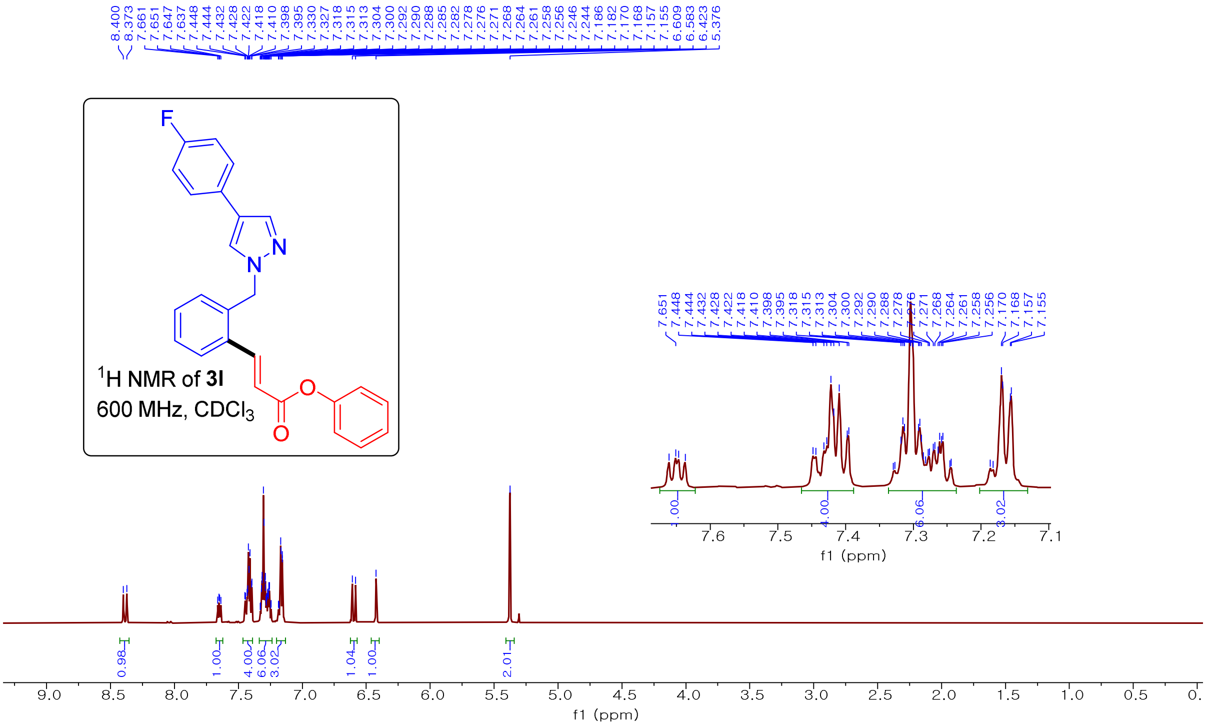
150 MHz, $CDCl_3$

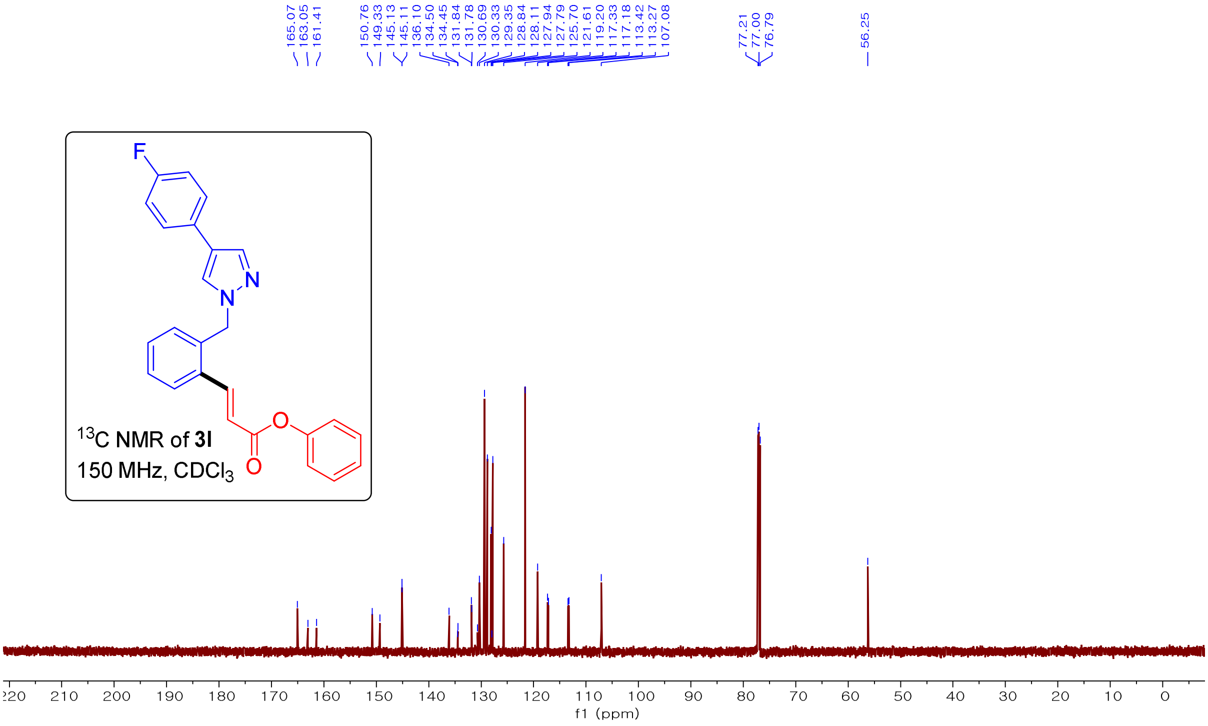

7.813
7.787
7.563
7.557
7.550
7.460
7.330
7.324
7.315
7.293
7.080
7.073
7.067
6.263
6.237
5.376
1.509
Br
N
N
O
O
^{1}H NMR of **3j**
600 MHz, CDCl$_3$
1.00
1.00
1.00
2.01
1.00
1.00
1.00
2.00
9.01
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
f1 (ppm)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

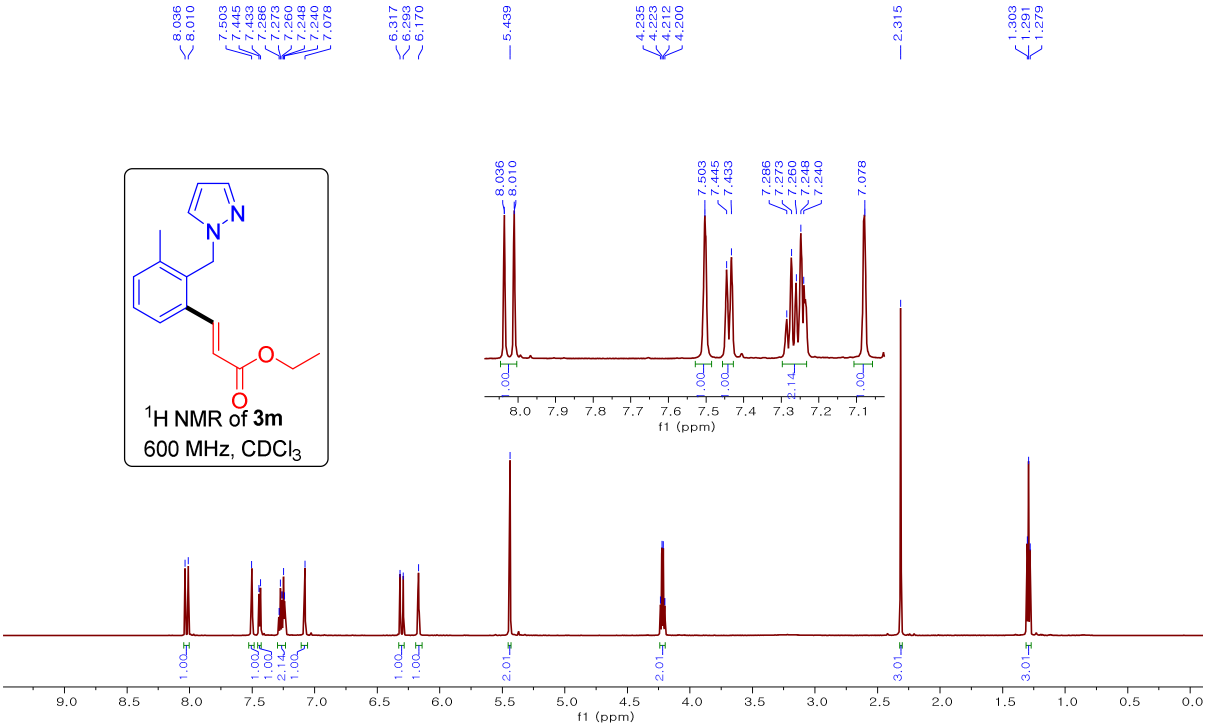

165.56
140.13
139.14
134.16
133.73
130.10
129.46
129.35
128.90
127.10
123.49
93.46
80.78
77.21
77.00
76.79
53.97
28.12
Br
N
N
O
O
^{13}C NMR of **3j**
150 MHz, CDCl$_3$
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

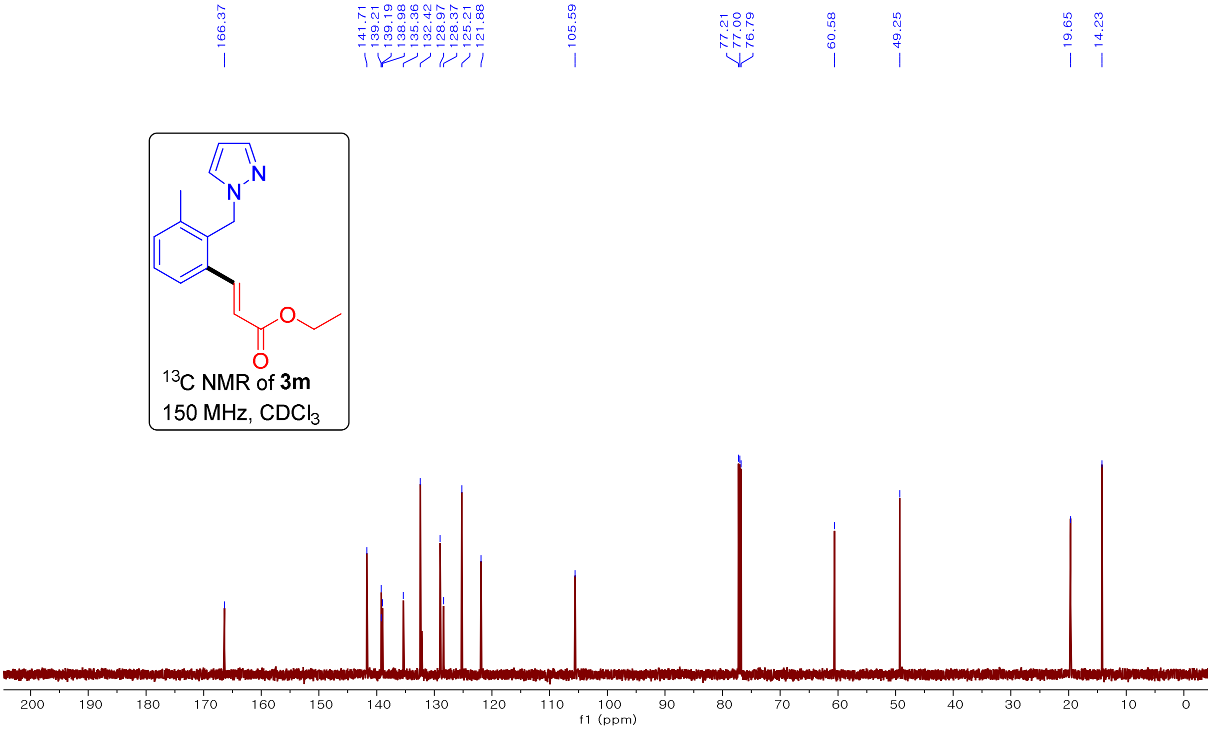

8.149
8.122
7.614
7.605
7.600
7.590
7.398
7.394
7.376
7.365
7.352
7.328
7.324
7.312
7.308
7.297
7.286
7.118
7.114
7.105
7.100
7.091
7.086
6.382
6.355
6.351
5.363
3.758
F
N
N
O
O
^{1}H NMR of **3k**
600 MHz, $CDCl_3$
1.00
1.00
1.00
2.00
4.00
1.00
2.00
2.00
3.00
f1 (ppm)

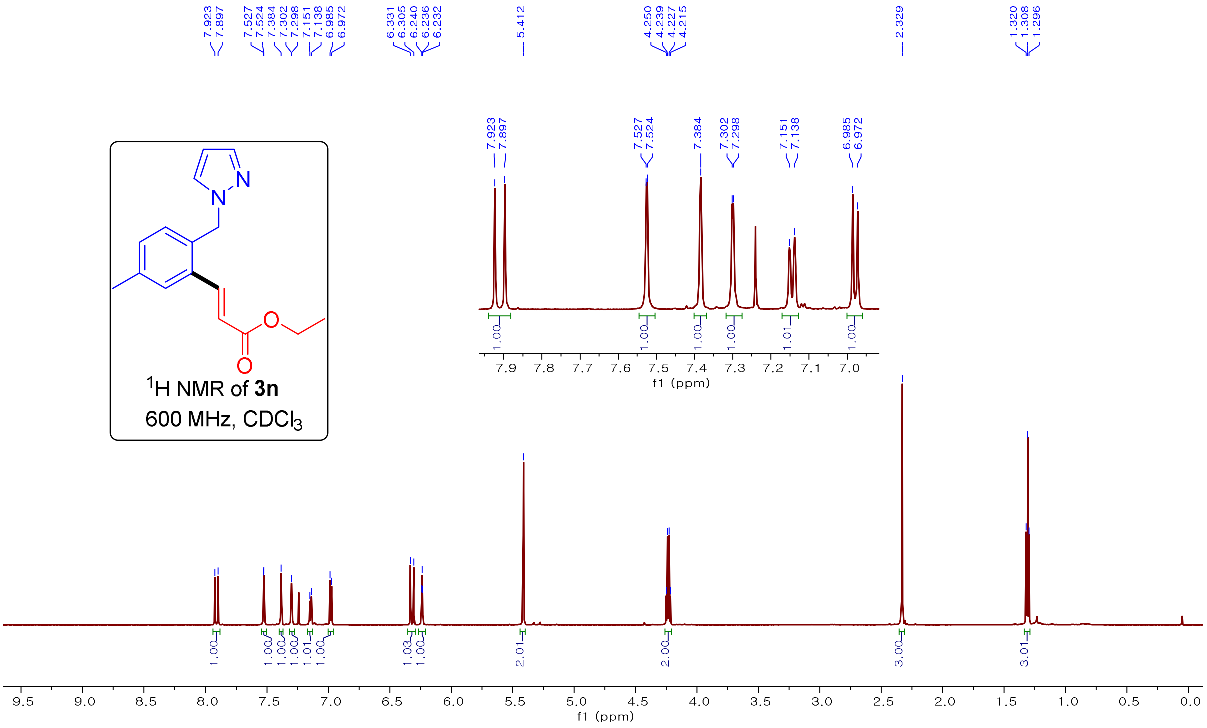

167.10
163.05
161.41
149.34
143.39
136.20
134.78
134.73
131.77
131.71
130.30
128.85
128.12
127.82
119.79
116.97
116.82
113.30
113.15
107.19
77.21
77.00
76.79
56.21
51.69
F
N
N
O
O
^{13}C NMR of **3k**
150 MHz, $CDCl_3$
f1 (ppm)

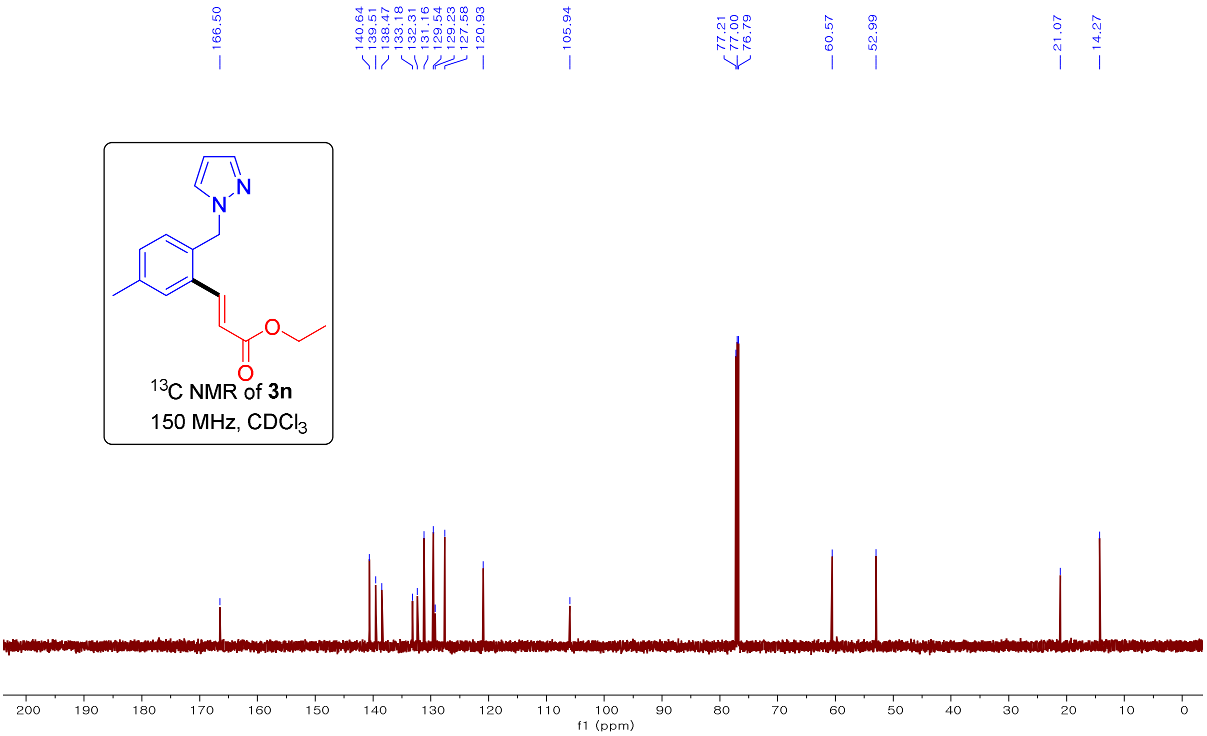

8.400
8.373
7.661
7.651
7.647
7.637
7.448
7.444
7.432
7.428
7.422
7.418
7.410
7.398
7.395
7.330
7.327
7.318
7.315
7.313
7.304
7.300
7.292
7.290
7.288
7.285
7.282
7.278
7.276
7.271
7.268
7.264
7.261
7.258
7.256
7.246
7.244
7.186
7.182
7.170
7.168
7.157
7.155
6.609
6.583
6.423
5.376
F
N
N
O
O
1H NMR of 3l
600 MHz, CDCl3
0.98
1.00
4.00
6.06
3.02
1.04
1.00
2.01
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.
f1 (ppm)
7.6
7.5
7.4
7.3
7.2
7.1
f1 (ppm)

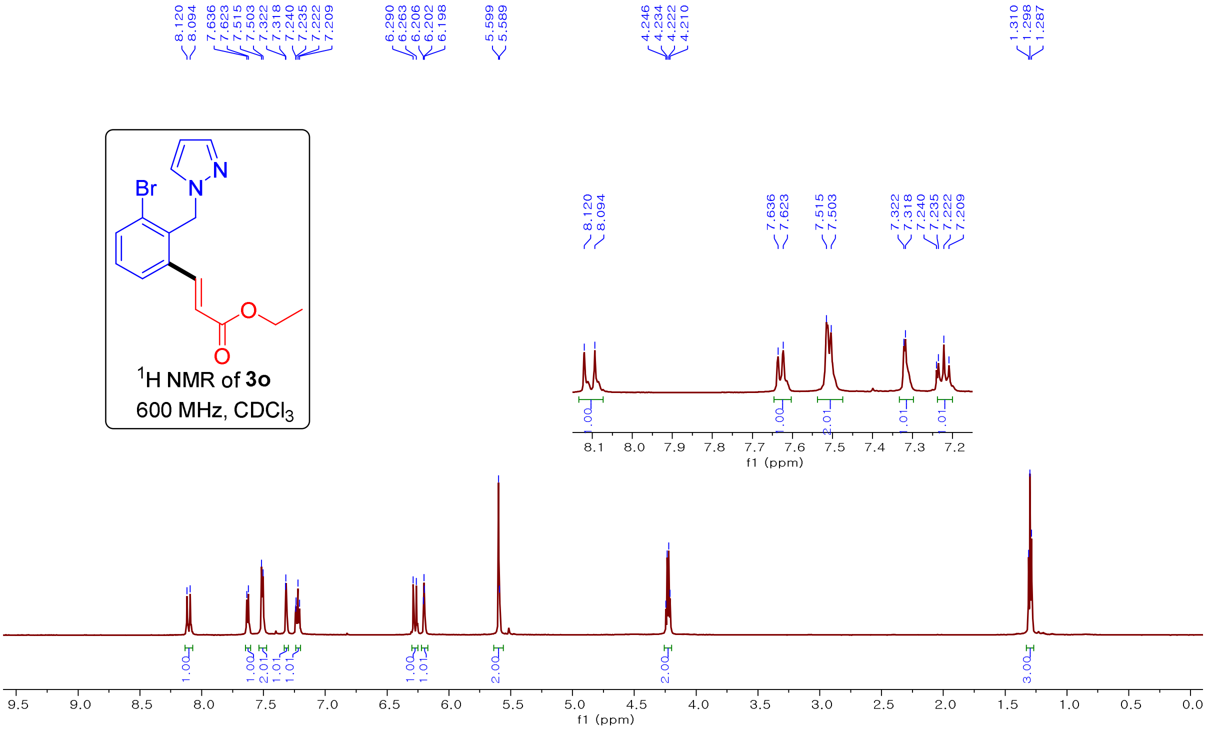

165.07
163.05
161.41
150.76
149.33
145.13
145.11
136.10
134.50
134.45
131.84
131.78
130.69
130.33
129.35
128.84
128.11
127.94
127.79
125.70
121.61
119.20
117.33
117.18
113.42
113.27
107.08
77.21
77.00
76.79
56.25
F
N
N
O
O
13C NMR of 3l
150 MHz, CDCl3
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

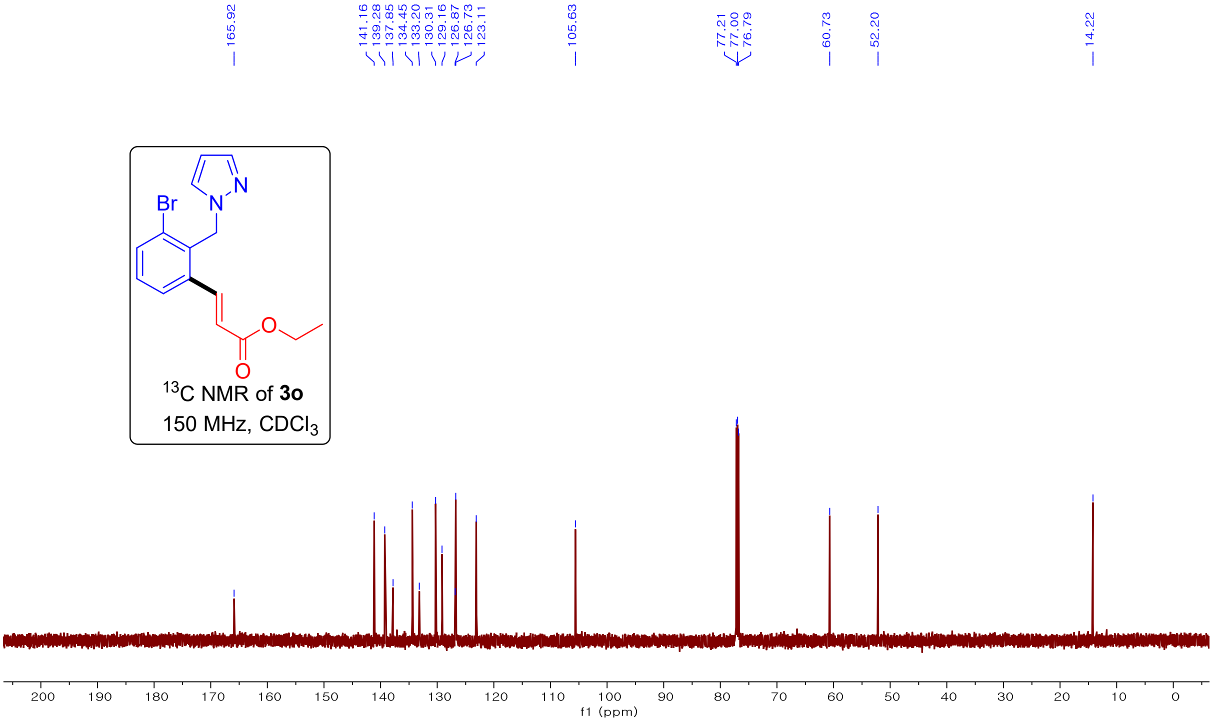

8.036
8.010
7.503
7.445
7.433
7.286
7.273
7.260
7.248
7.240
7.078
6.317
6.293
6.170
5.439
4.235
4.223
4.212
4.200
2.315
1.303
1.291
1.279
N
N
O
O
^{1}H NMR of **3m**
600 MHz, $CDCl_3$
1.00
1.00
1.00
2.14
1.00
1.00
1.00
2.01
2.01
3.01
3.01
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1
f1 (ppm)
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

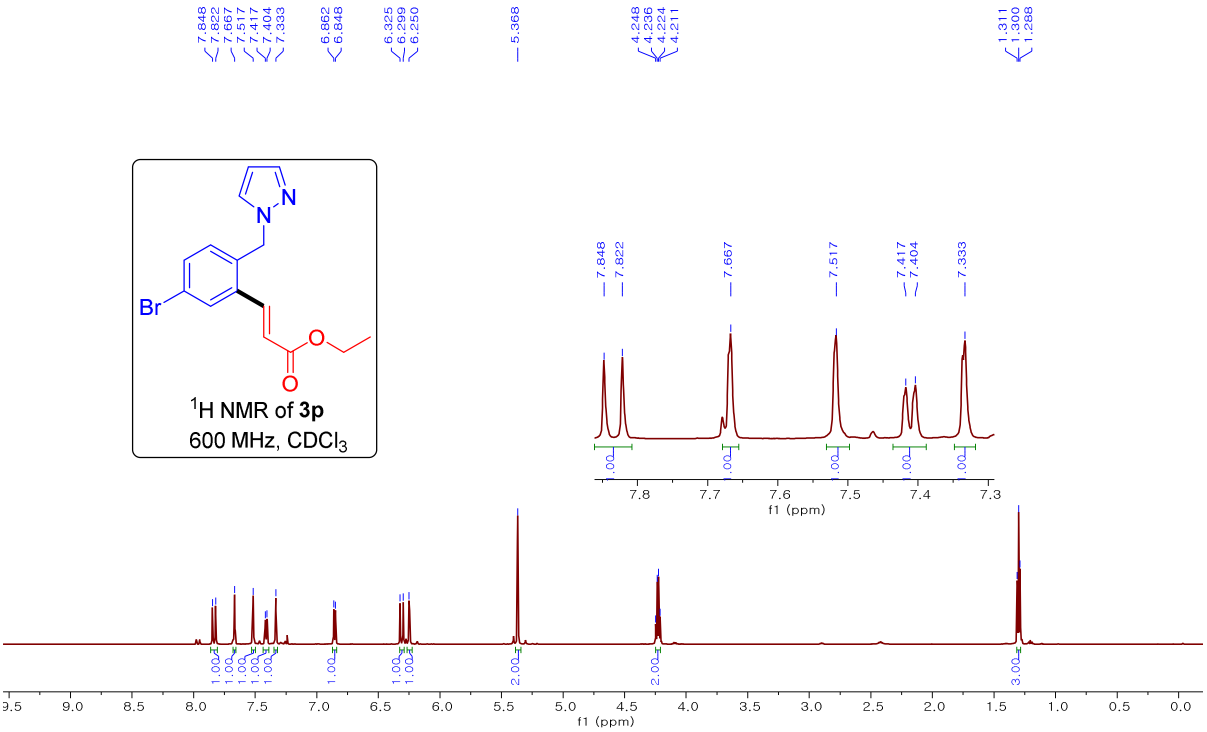

166.37
141.71
139.21
139.19
138.98
135.36
132.42
128.97
128.37
125.21
121.88
105.59
77.21
77.00
76.79
60.58
49.25
19.65
14.23
N
N
O
O
^{13}C NMR of **3m**
150 MHz, $CDCl_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

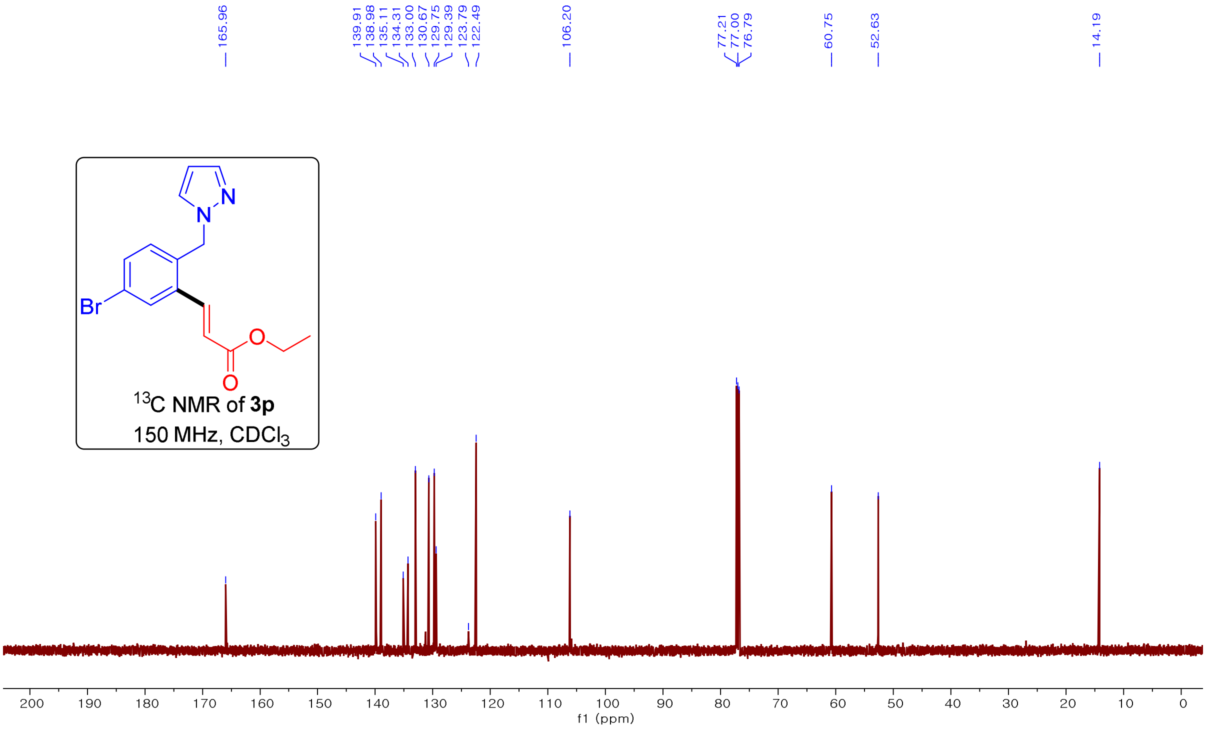

7.923
7.897
7.527
7.524
7.384
7.302
7.298
7.151
7.138
6.985
6.972
6.331
6.305
6.240
6.236
6.232
5.412
4.250
4.239
4.227
4.215
2.329
1.320
1.308
1.296
N
N
O
O
^{1}H NMR of **3n**
600 MHz, CDCl$_3$
1.00
1.00
1.00
1.00
1.01
1.00
1.03
1.00
2.01
2.00
3.00
3.01
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

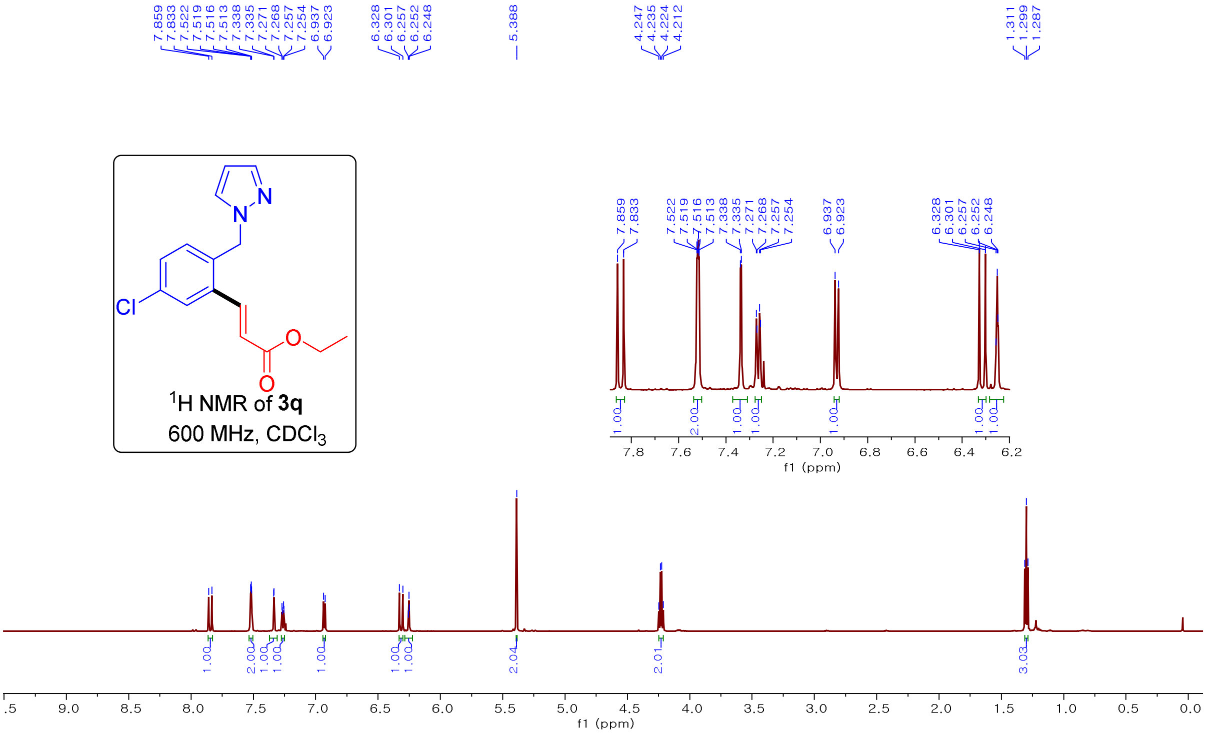

166.50
140.64
139.51
138.47
133.18
132.31
131.16
129.54
129.23
127.58
120.93
105.94
77.21
77.00
76.79
60.57
52.99
21.07
14.27
N
N
O
O
^{13}C NMR of **3n**
150 MHz, CDCl$_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.120
8.094
7.636
7.623
7.515
7.503
7.322
7.318
7.240
7.235
7.222
7.209
6.290
6.263
6.206
6.202
6.198
5.599
5.589
4.246
4.234
4.222
4.210
1.310
1.298
1.287
Br
N
N
O
O
^{1}H NMR of **3o**
600 MHz, CDCl$_3$
1.00
1.00
2.01
1.01
1.01
1.00
1.01
2.00
2.00
3.00
f1 (ppm)

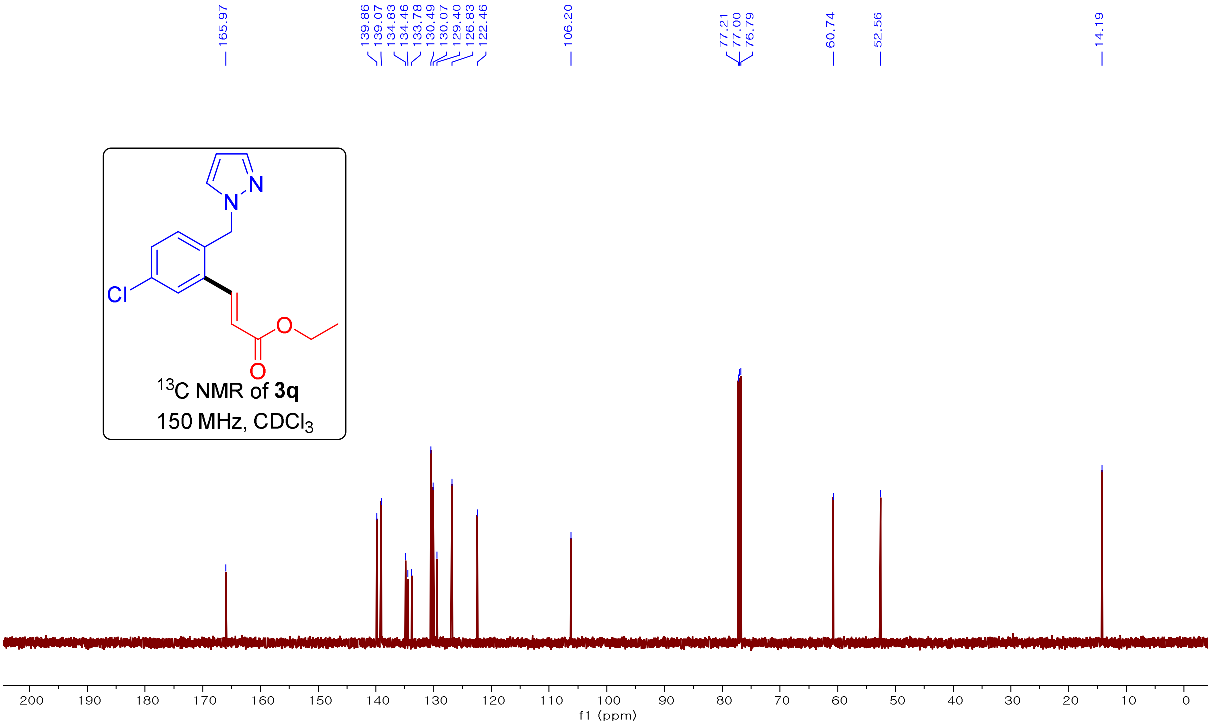

165.92
141.16
139.28
137.85
134.45
133.20
130.31
129.16
126.87
126.73
123.11
105.63
77.21
77.00
76.79
60.73
52.20
14.22
Br
N
N
O
O
^{13}C NMR of **3o**
150 MHz, CDCl$_3$
f1 (ppm)


7.848
7.822
7.667
7.517
7.417
7.404
7.333
6.862
6.848
6.325
6.299
6.250
5.368
4.248
4.236
4.224
4.211
1.311
1.300
1.288
Br
N
N
O
O
^{1}H NMR of **3p**
600 MHz, $CDCl_3$
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
2.00
2.00
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
7.8
7.7
7.6
7.5
7.4
7.3
f1 (ppm)

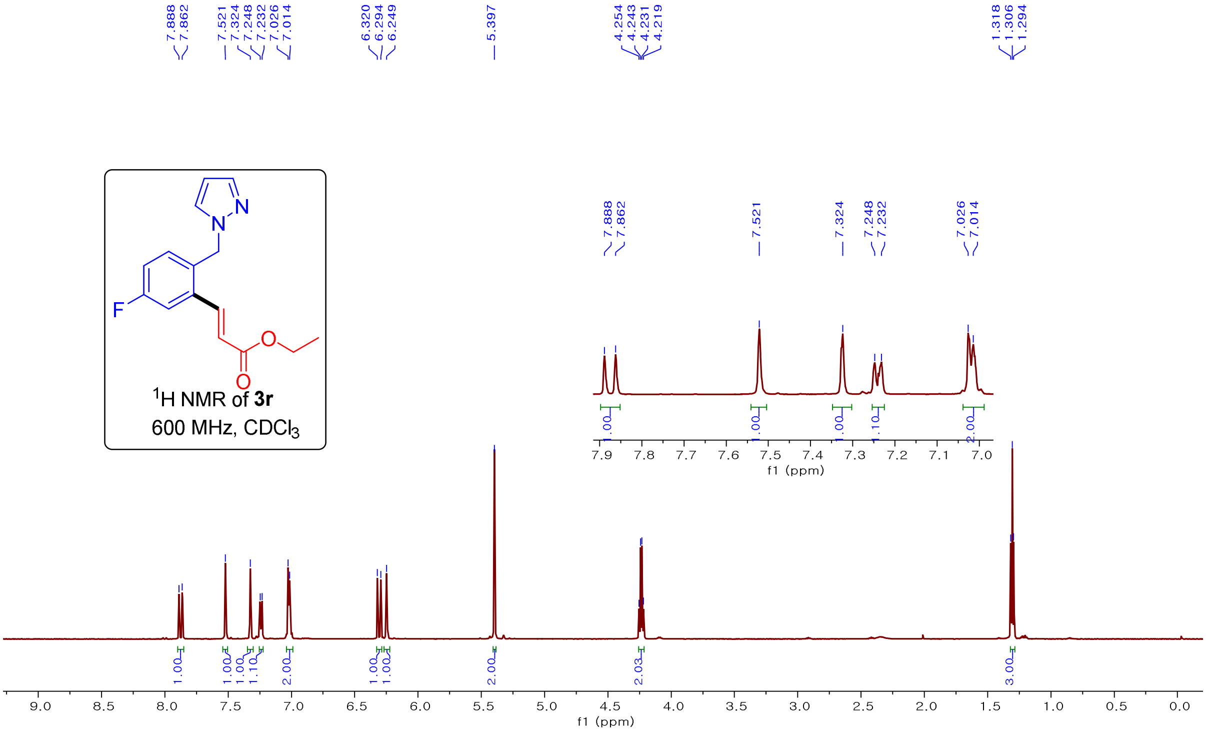

165.96
139.91
138.98
135.11
134.31
133.00
130.67
129.75
129.39
123.79
122.49
106.20
77.21
77.00
76.79
60.75
52.63
14.19
Br
N
N
O
O
^{13}C NMR of **3p**
150 MHz, $CDCl_3$
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

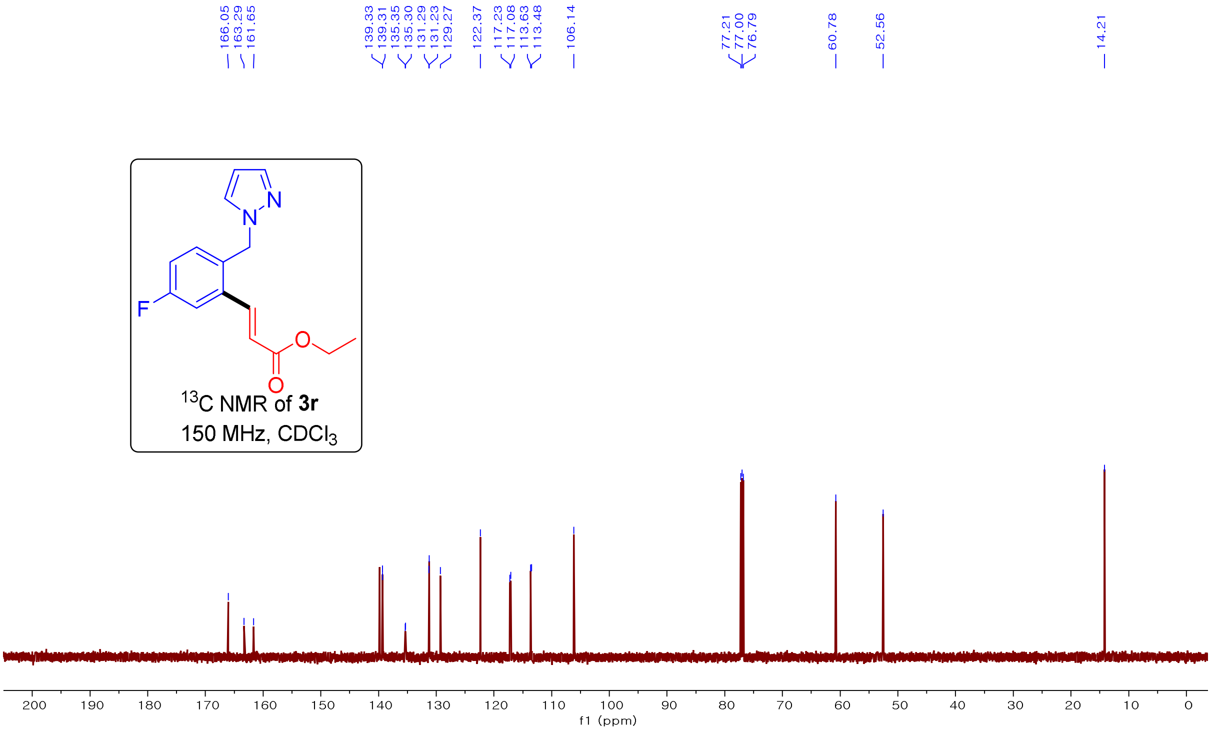


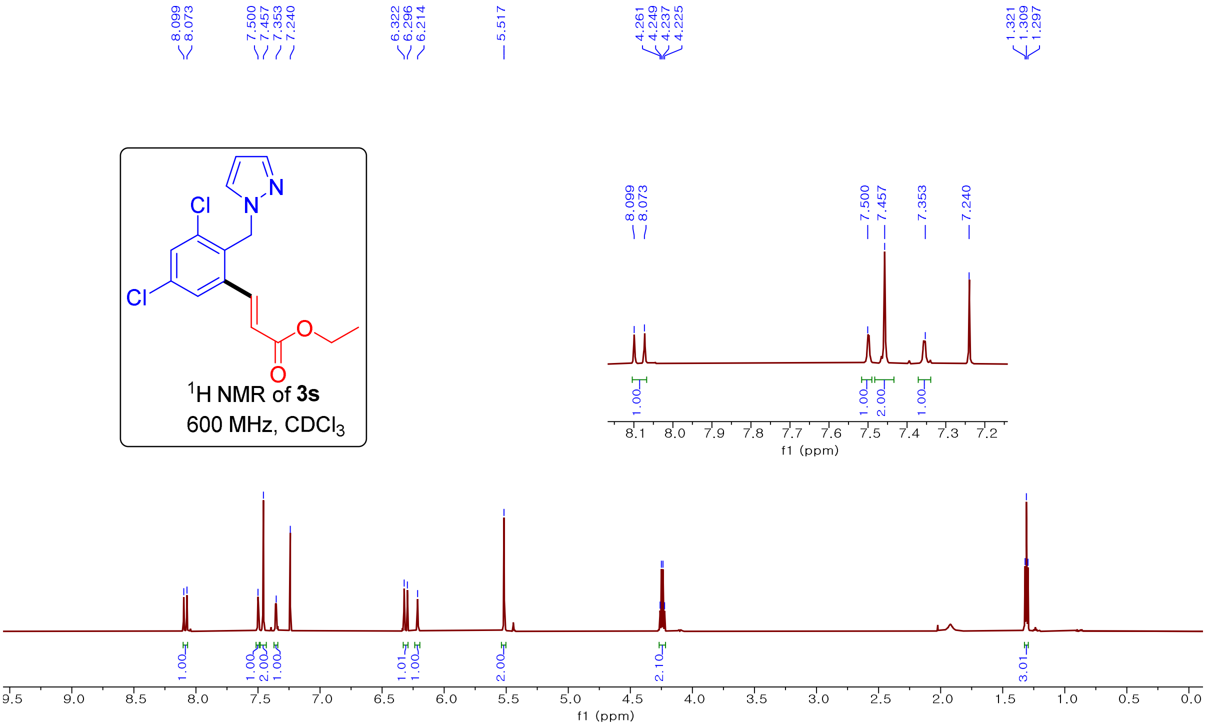
7.859
7.833
7.522
7.519
7.516
7.513
7.338
7.335
7.271
7.268
7.257
7.254
6.937
6.923
6.328
6.301
6.257
6.252
6.248
5.388
4.247
4.235
4.224
4.212
1.311
1.299
1.287
Cl
N
N
O
O
^{1}H NMR of **3q**
600 MHz, CDCl$_3$
1.00
2.00
1.00
1.00
1.00
1.00
1.00
2.04
2.01
3.03
f1 (ppm)

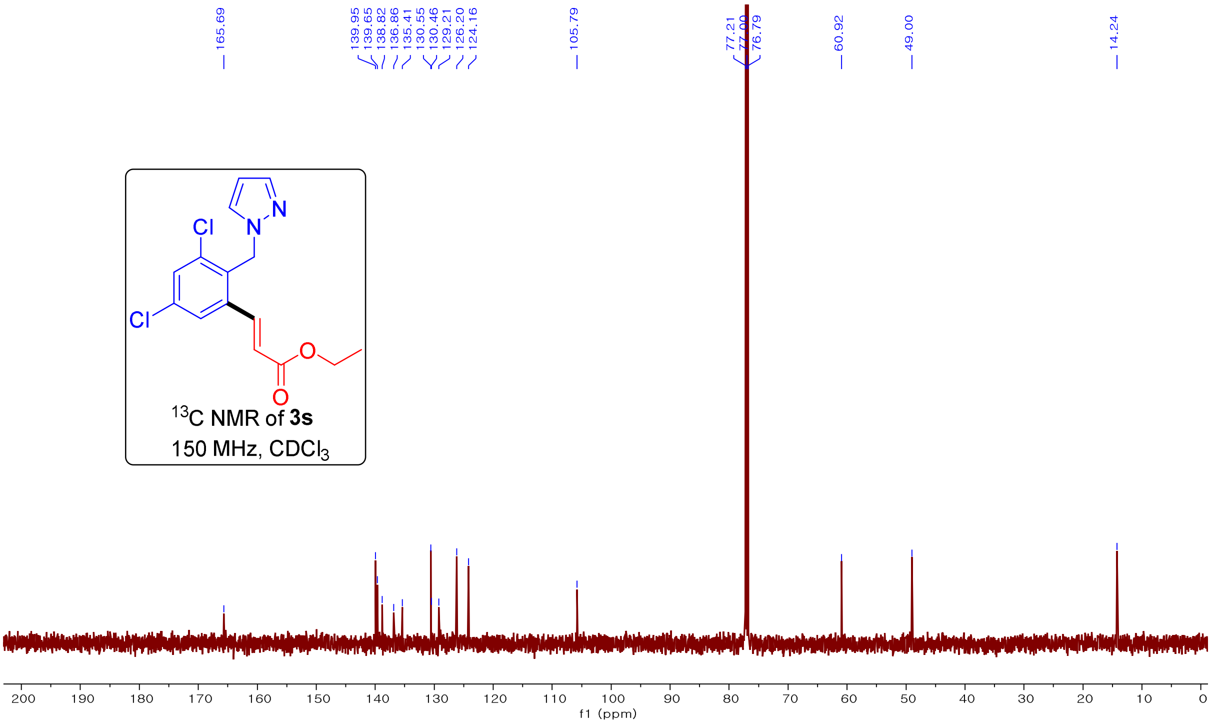


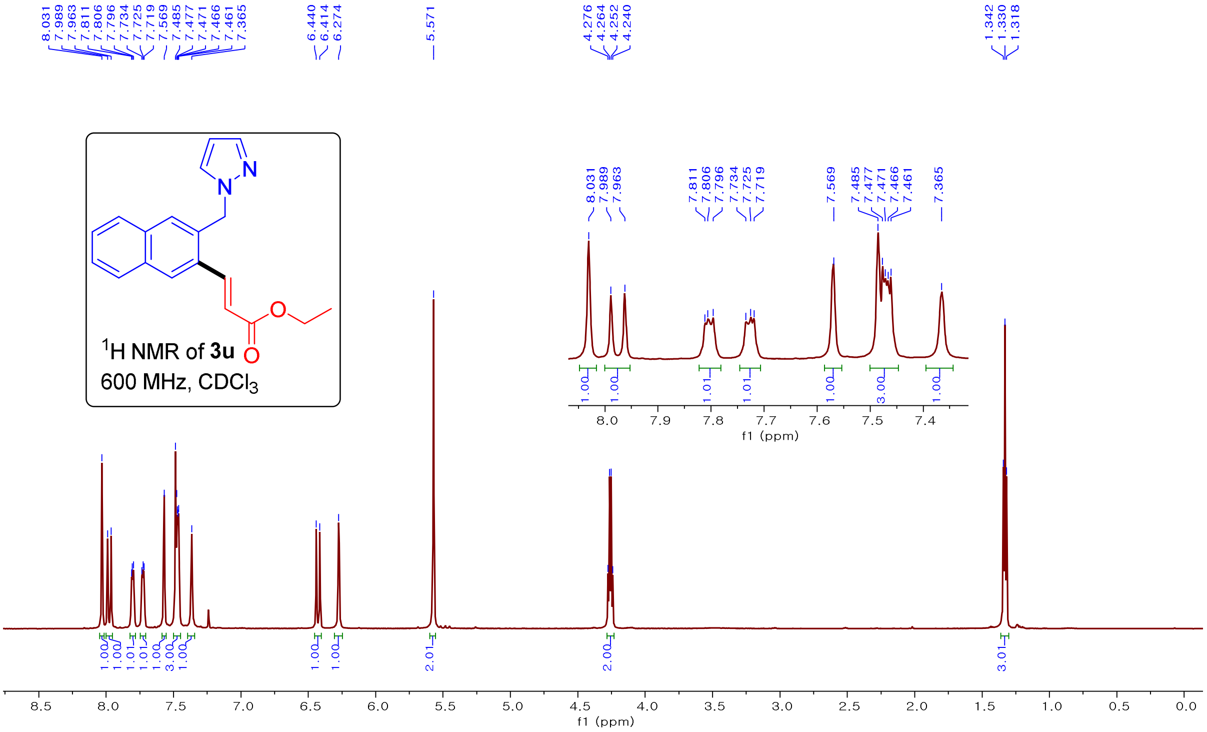
165.97
139.86
139.07
134.83
134.46
133.78
130.49
130.07
129.40
126.83
122.46
106.20
77.21
77.00
76.79
60.74
52.56
14.19
Cl
N
N
O
O
^{13}C NMR of **3q**
150 MHz, CDCl$_3$
f1 (ppm)


7.888
7.862
7.521
7.324
7.248
7.232
7.026
7.014
6.320
6.294
6.249
5.397
4.254
4.243
4.231
4.219
1.318
1.306
1.294
F
N
N
O
O
^{1}H NMR of **3r**
600 MHz, CDCl$_3$
1.00
1.00
1.00
1.10
2.00
1.00
1.00
2.00
2.03
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0

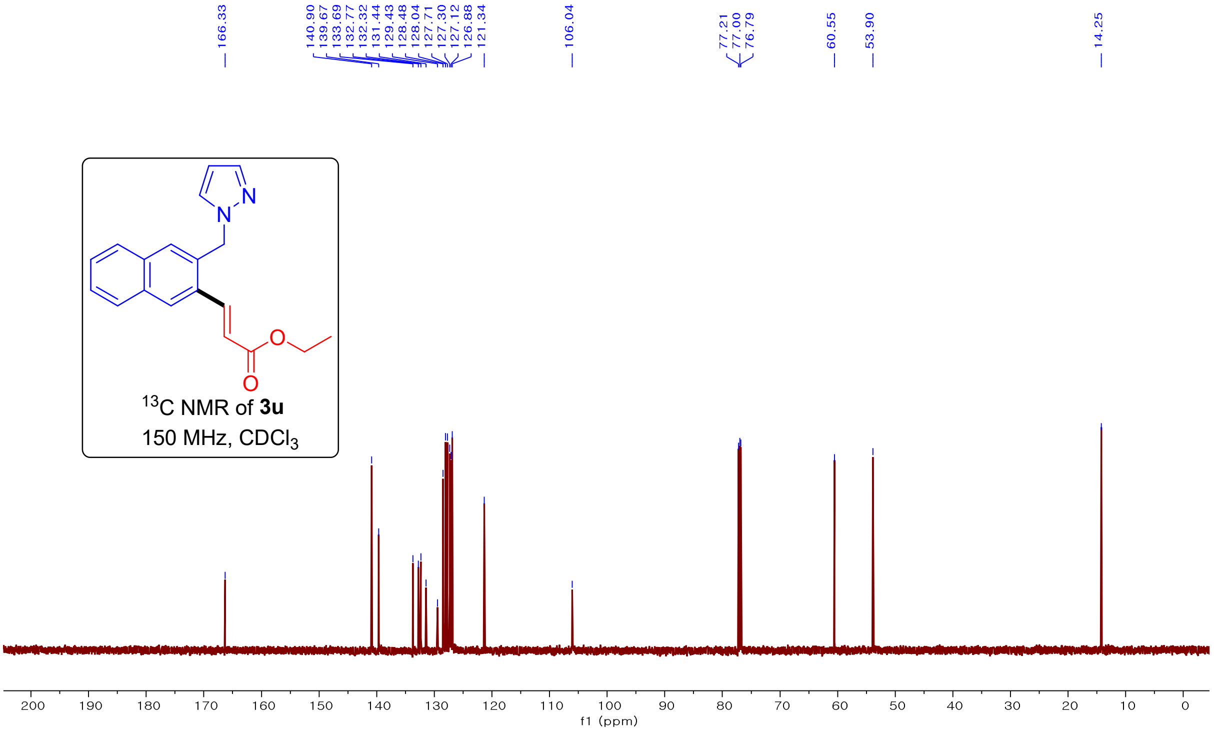

166.05
163.29
161.65
139.33
139.31
135.35
135.30
131.29
131.23
129.27
122.37
117.23
117.08
113.63
113.48
106.14
77.21
77.00
76.79
60.78
52.56
14.21
F
N
N
O
O
^{13}C NMR of **3r**
150 MHz, CDCl$_3$
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.099
8.073
7.500
7.457
7.353
7.240
6.322
6.296
6.214
5.517
4.261
4.249
4.237
4.225
1.321
1.309
1.297
Cl
N
N
Cl
O
O
^{1}H NMR of **3s**
600 MHz, $CDCl_3$
1.00
1.00
2.00
1.00
1.01
1.00
2.00
2.10
3.01
f1 (ppm)
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
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2

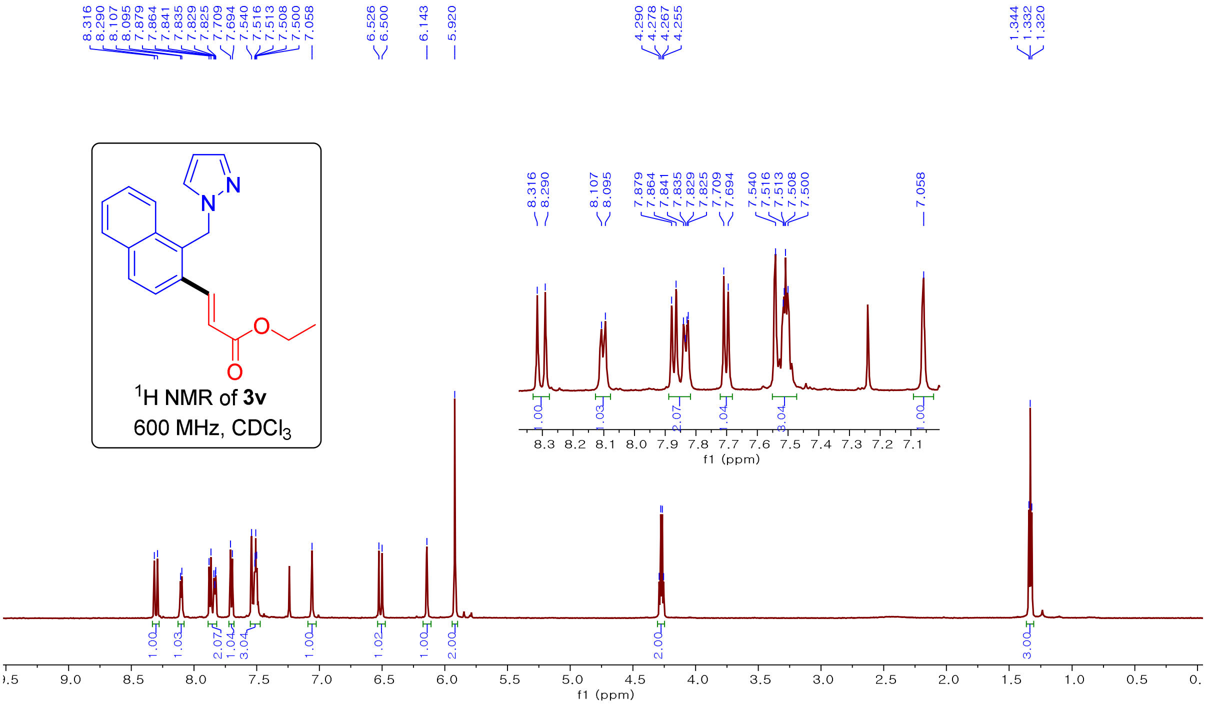

165.69
139.95
139.65
138.82
136.86
135.41
130.55
130.46
129.21
126.20
124.16
105.79
77.21
77.00
76.79
60.92
49.00
14.24
Cl
N
N
Cl
O
O
^{13}C NMR of **3s**
150 MHz, $CDCl_3$
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

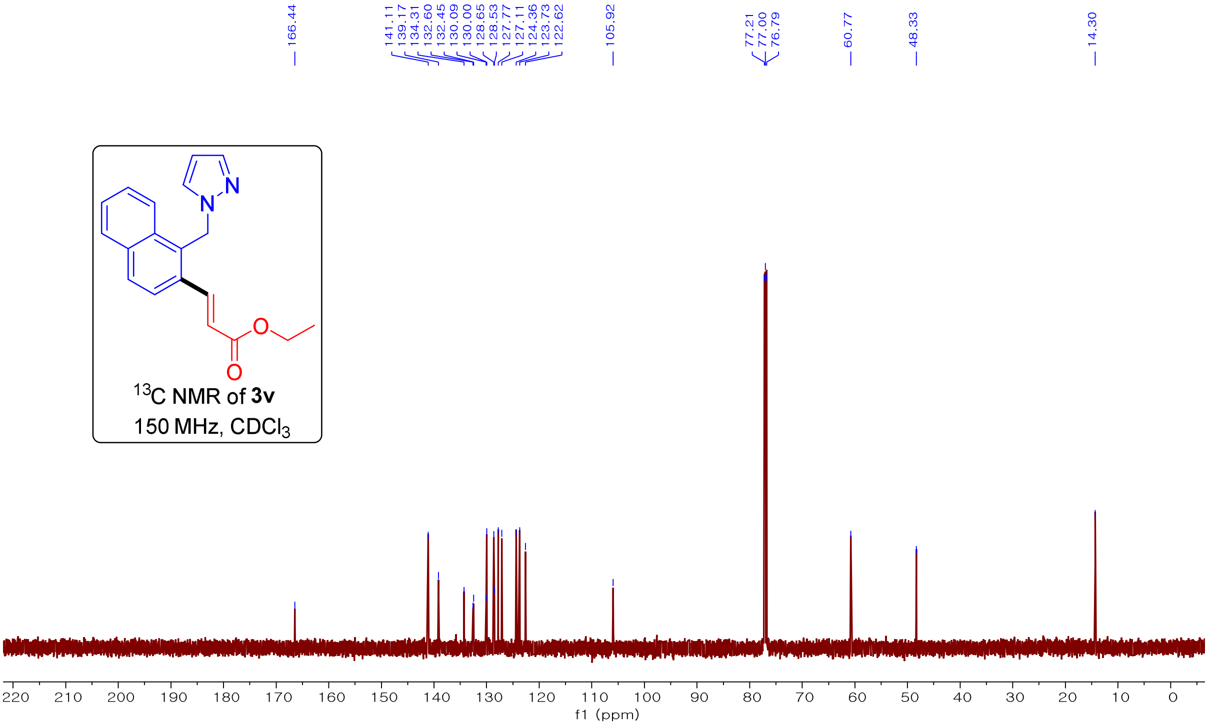


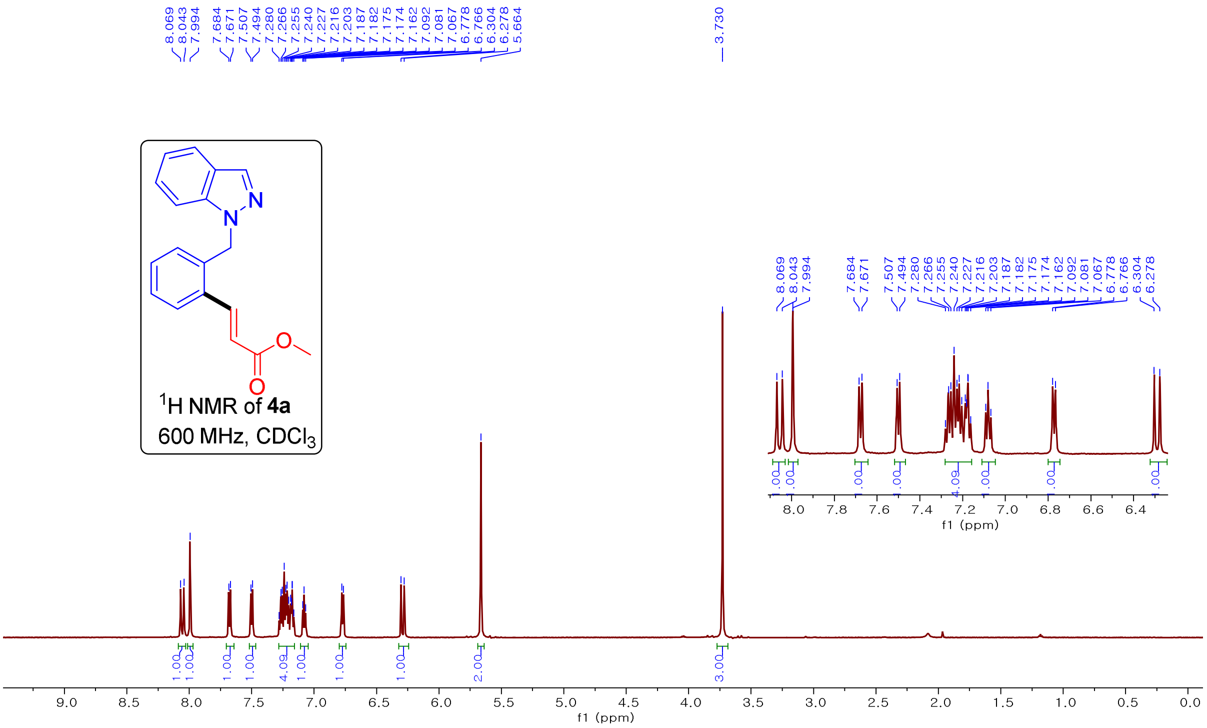
8.031
7.989
7.963
7.811
7.806
7.796
7.734
7.725
7.719
7.569
7.485
7.477
7.471
7.466
7.461
7.365
6.440
6.414
6.274
5.571
4.276
4.264
4.252
4.240
1.342
1.330
1.318
N
N
O
O
^{1}H NMR of **3u**
600 MHz, CDCl$_3$
1.00
1.00
1.01
1.01
1.00
3.00
1.00
8.0
7.9
7.8
7.7
7.6
7.5
7.4
f1 (ppm)
1.00
1.00
1.01
1.01
1.00
3.00
1.00
1.00
1.00
2.01
2.00
3.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

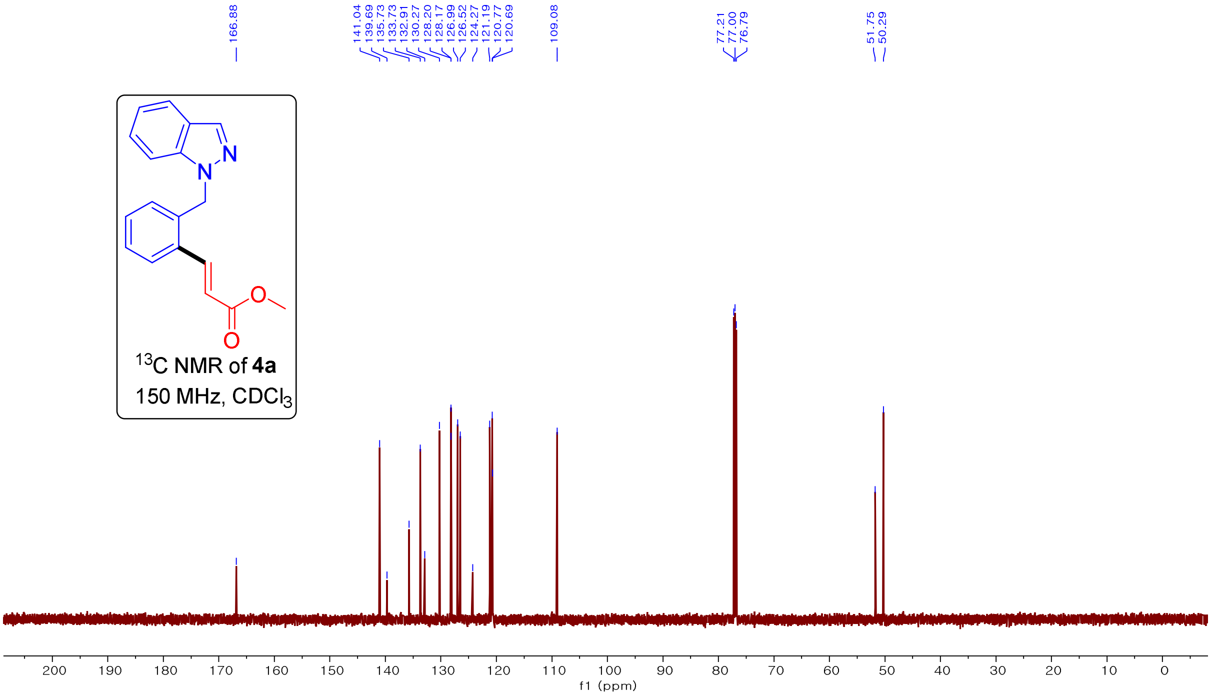


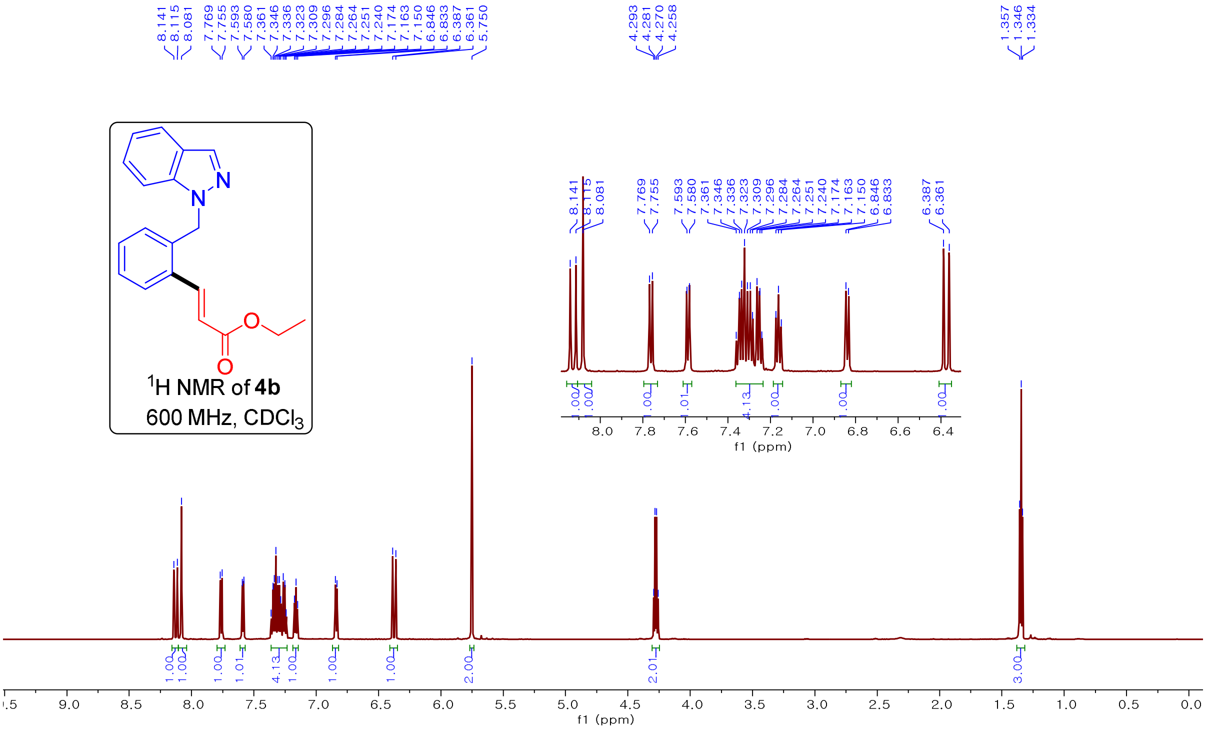
166.33
140.90
139.67
133.69
132.77
132.32
131.44
129.43
128.48
128.04
127.71
127.30
127.12
126.88
121.34
106.04
77.21
77.00
76.79
60.55
53.90
14.25
N
N
O
O
^{13}C NMR of **3u**
150 MHz, CDCl$_3$
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.316
8.290
8.107
8.095
7.879
7.864
7.841
7.835
7.829
7.825
7.709
7.694
7.540
7.516
7.513
7.508
7.500
7.058
6.526
6.500
6.143
5.920
4.290
4.278
4.267
4.255
1.344
1.332
1.320
N
N
O
O
^{1}H NMR of **3v**
600 MHz, CDCl$_3$
1.00
1.03
2.07
1.04
3.04
1.00
1.02
1.00
2.00
2.00
3.00
8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1
f1 (ppm)
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.
f1 (ppm)

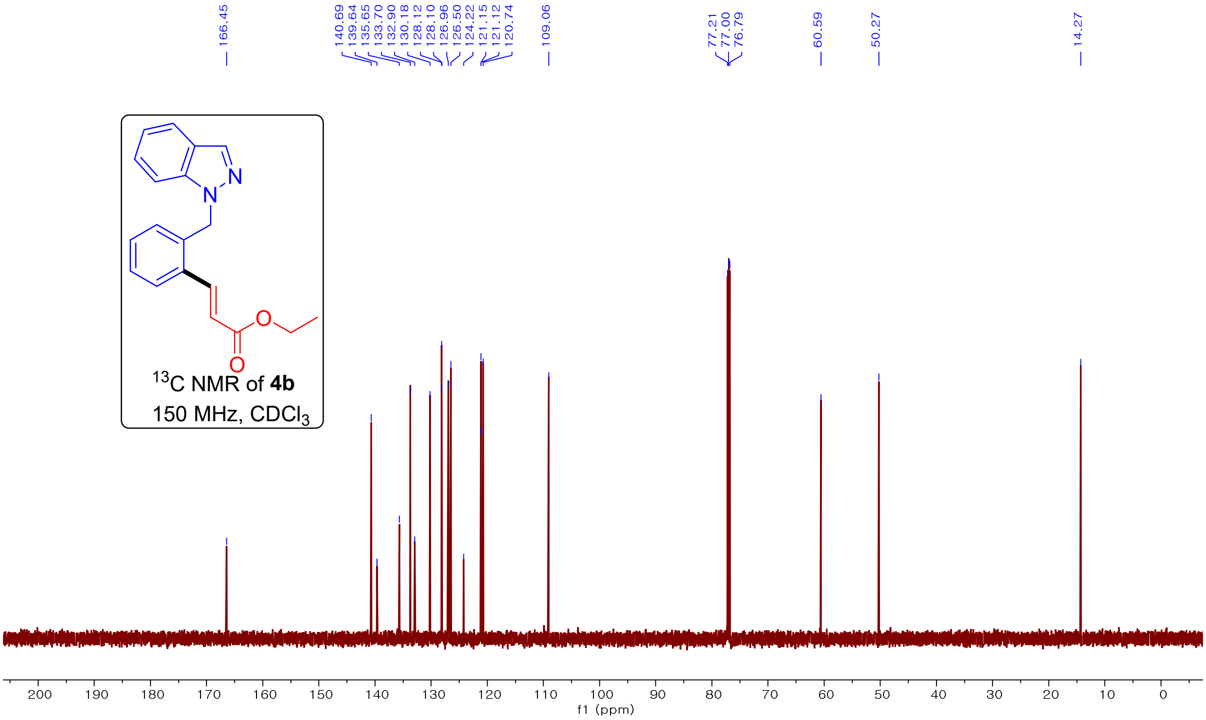

166.44
141.11
139.17
134.31
132.60
132.45
130.09
130.00
128.65
128.53
127.77
127.11
124.36
123.73
122.62
105.92
77.21
77.00
76.79
60.77
48.33
14.30
N
N
O
O
^{13}C NMR of **3v**
150 MHz, CDCl$_3$
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.069
8.043
7.994
7.684
7.671
7.507
7.494
7.280
7.266
7.255
7.240
7.227
7.216
7.203
7.187
7.182
7.175
7.174
7.162
7.092
7.081
7.067
6.778
6.766
6.304
6.278
5.664
3.730
N
N
O
O
^{1}H NMR of **4a**
600 MHz, CDCl$_3$
1.00
1.00
1.00
1.00
4.09
1.00
1.00
1.00
2.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4

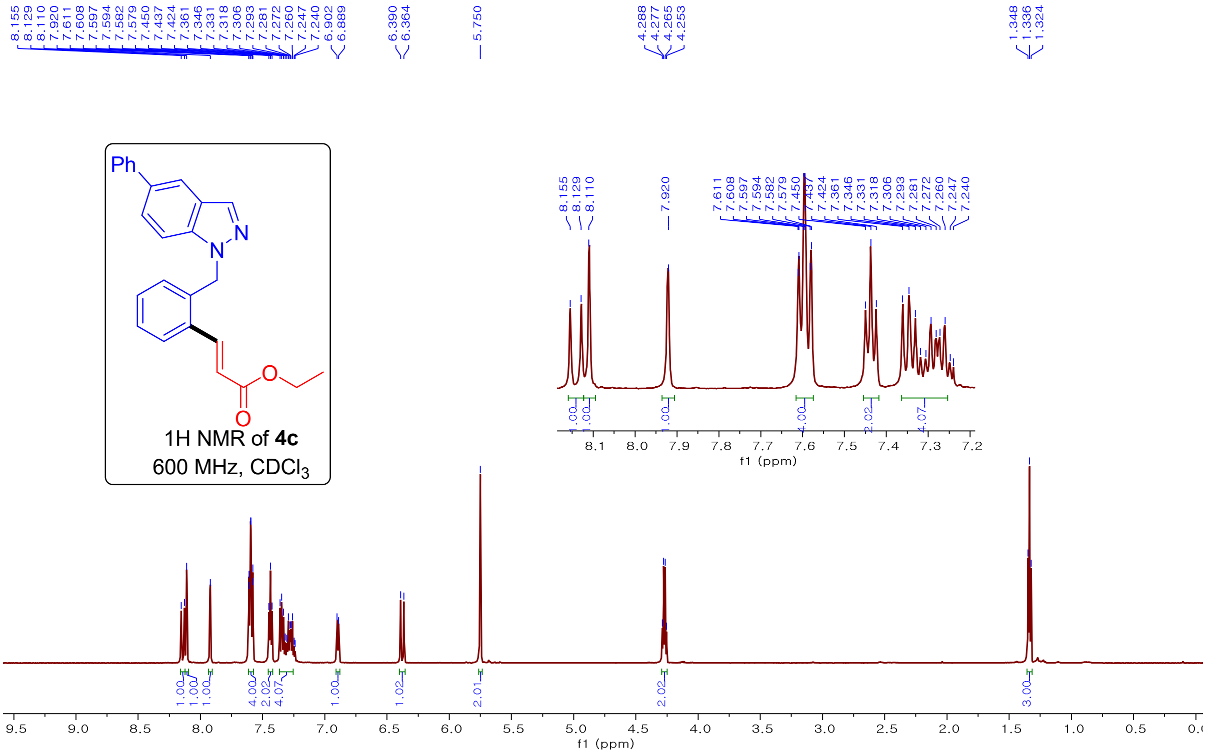

166.88
141.04
139.69
135.73
133.73
132.91
130.27
128.20
128.17
126.99
126.52
124.27
121.19
120.77
120.69
109.08
77.21
77.00
76.79
51.75
50.29
N
N
O
O
^{13}C NMR of **4a**
150 MHz, CDCl$_3$
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

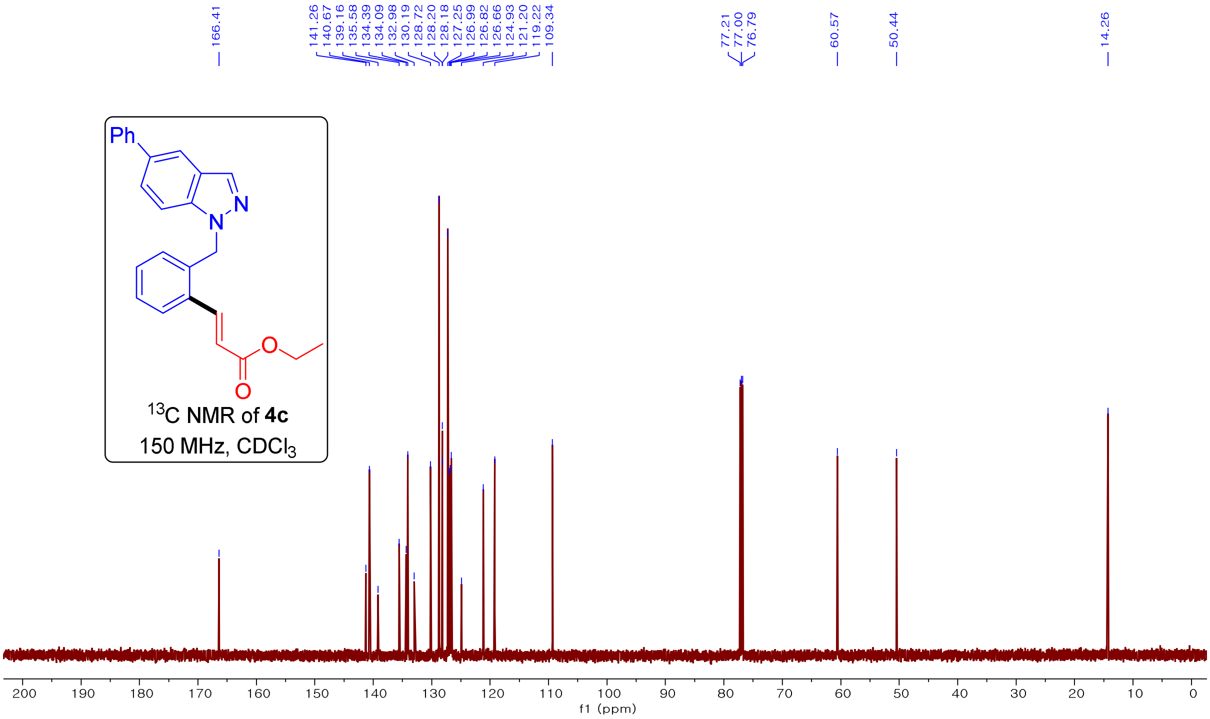


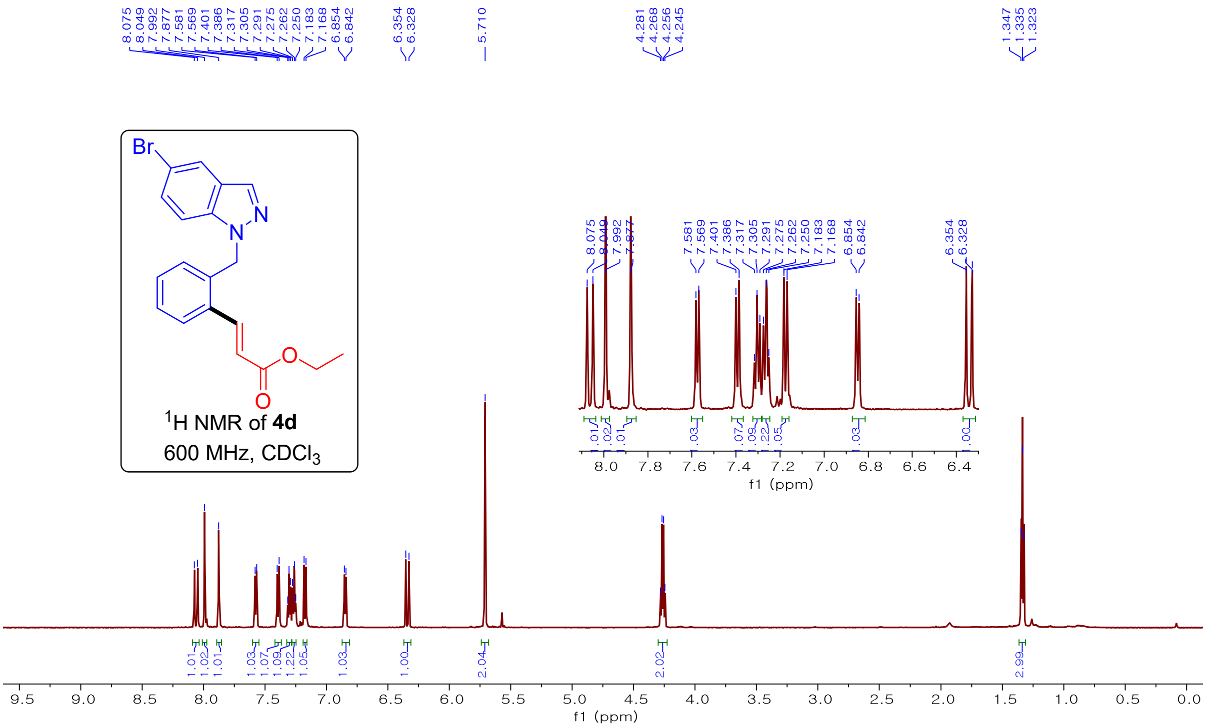
^{1}H NMR of **4b**
600 MHz, CDCl$_3$



^{13}C NMR of **4b**
150 MHz, CDCl$_3$

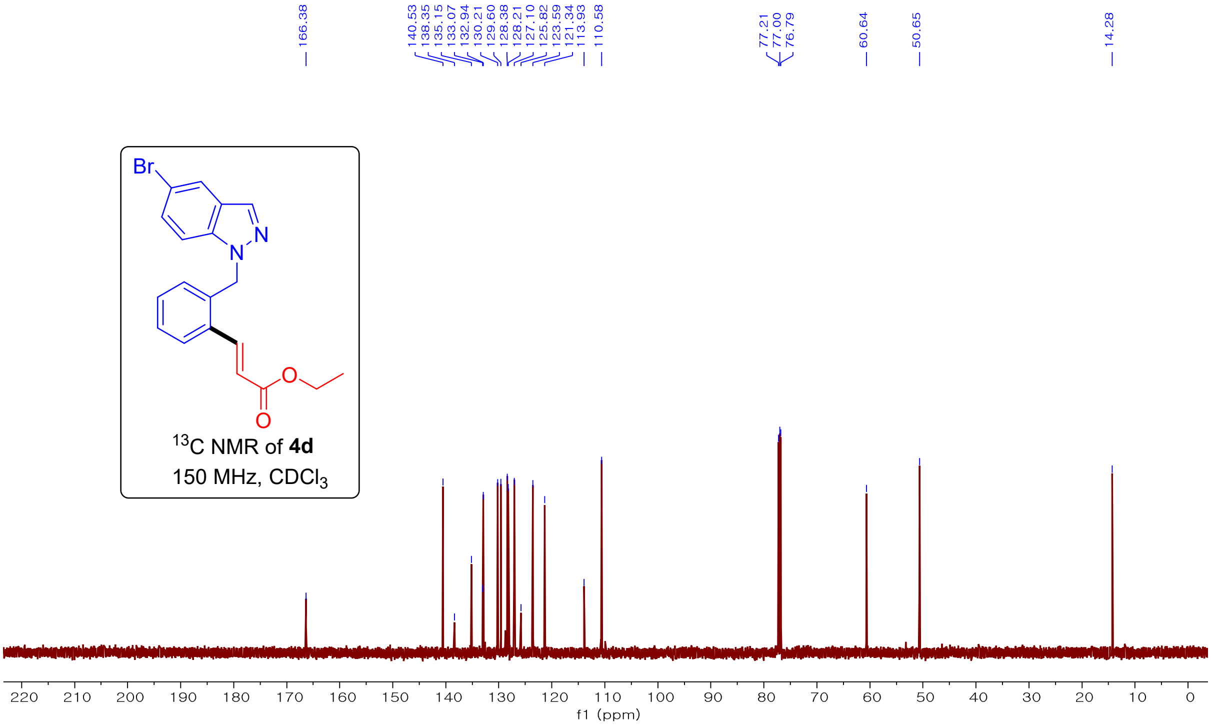

8.155
8.129
8.110
7.920
7.611
7.608
7.597
7.594
7.582
7.579
7.450
7.437
7.424
7.361
7.346
7.331
7.318
7.306
7.293
7.281
7.272
7.260
7.247
7.240
6.902
6.889
6.390
6.364
5.750
4.288
4.277
4.265
4.253
1.348
1.336
1.324
Ph
N
N
O
O
1H NMR of 4c
600 MHz, CDCl3
1.00
1.00
1.00
4.00
2.02
4.07
1.00
1.02
2.01
2.02
3.00
f1 (ppm)


166.41
141.26
140.67
139.16
135.58
134.39
134.09
132.98
130.19
128.72
128.20
128.18
127.25
126.99
126.82
126.66
124.93
121.20
119.22
109.34
77.21
77.00
76.79
60.57
50.44
14.26
Ph
N
N
O
O
13C NMR of 4c
150 MHz, CDCl3
f1 (ppm)



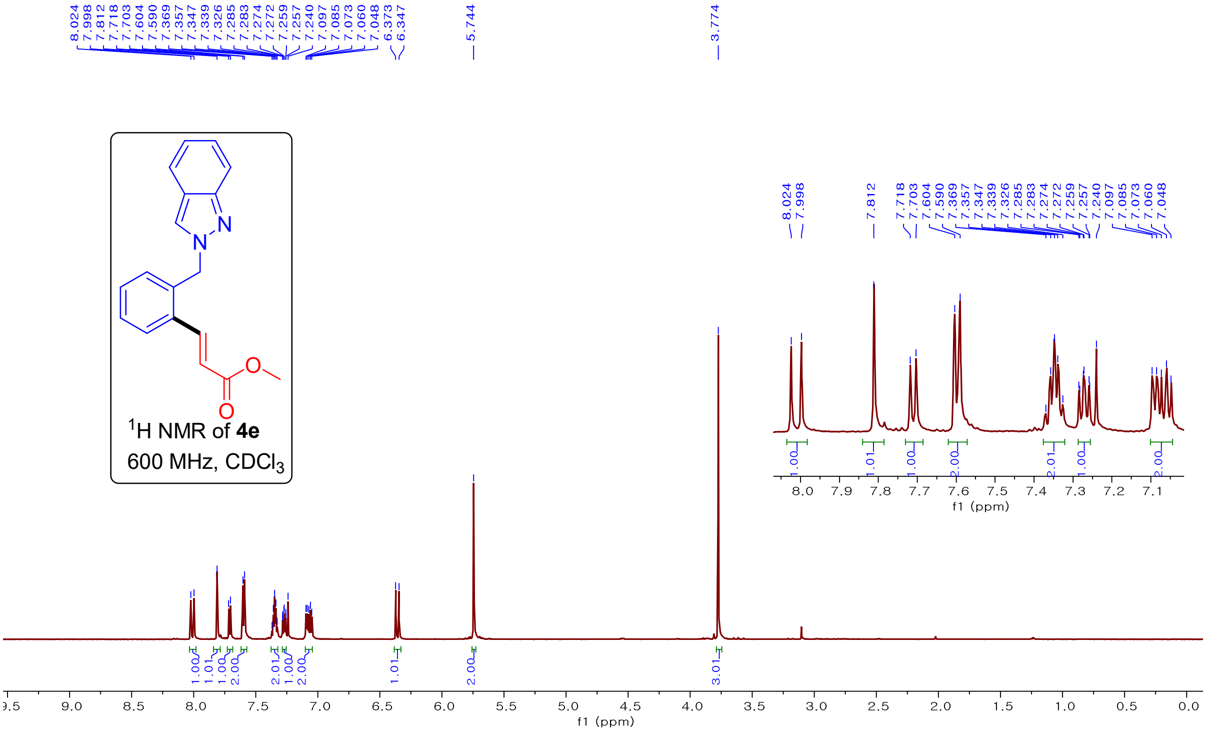
^{1}H NMR of **4d**

600 MHz, $CDCl_3$

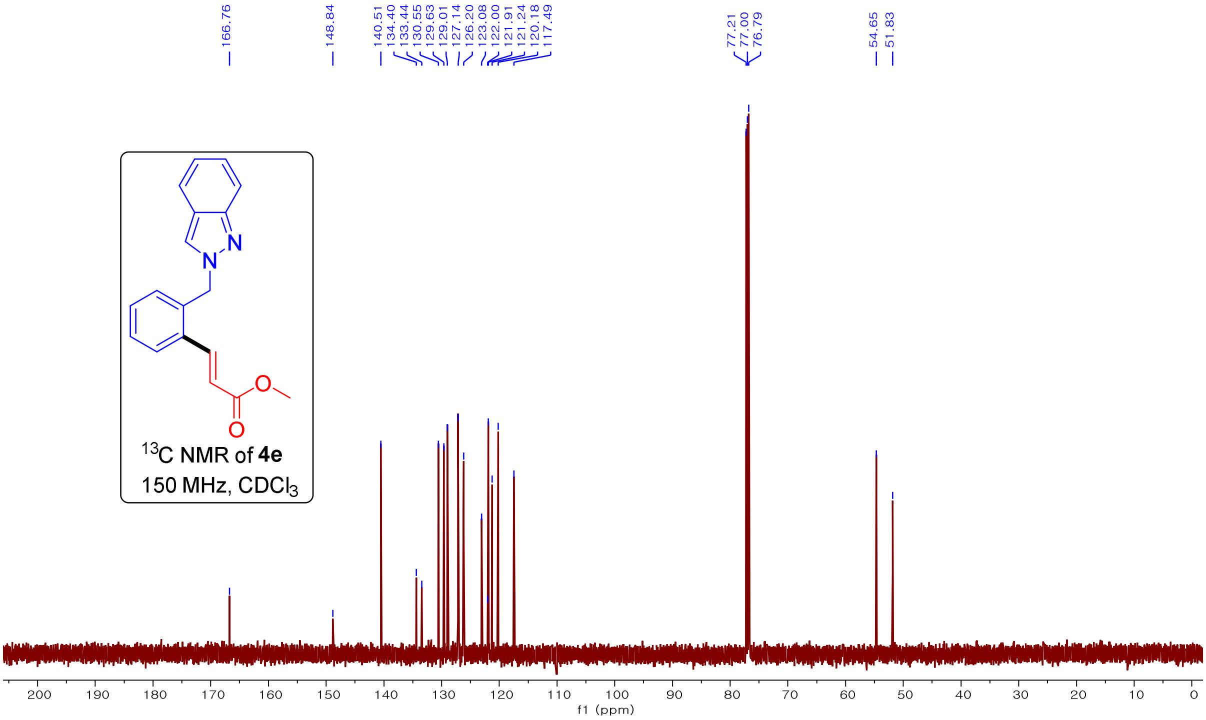


^{13}C NMR of **4d**

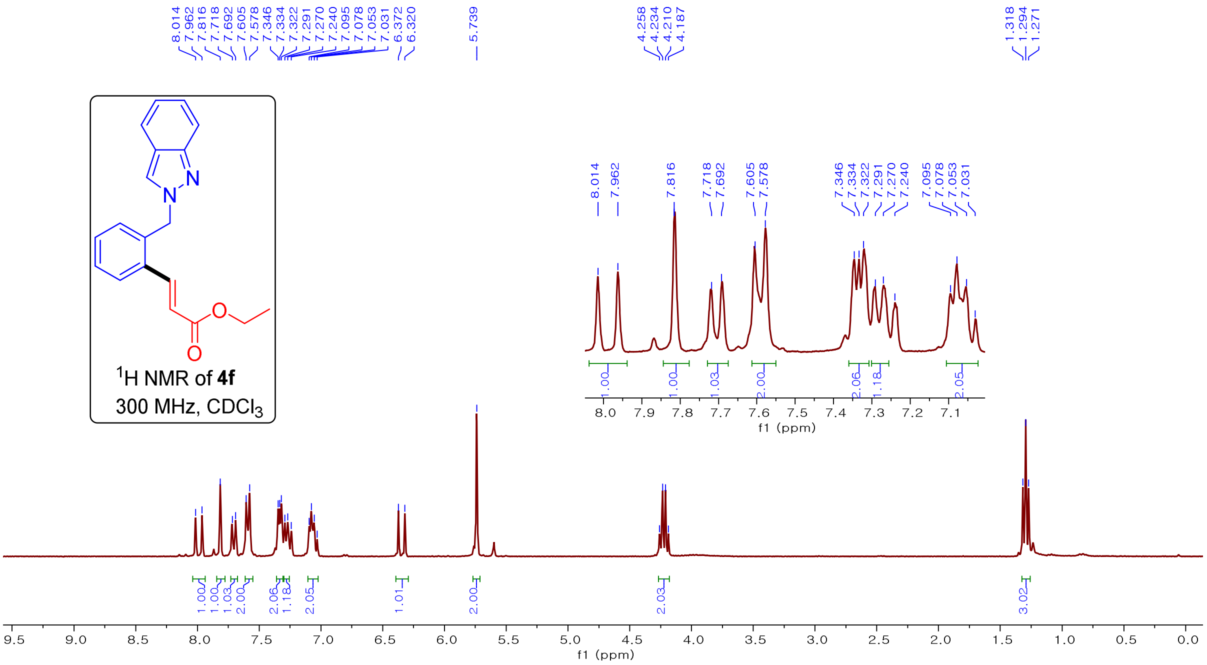
150 MHz, $CDCl_3$

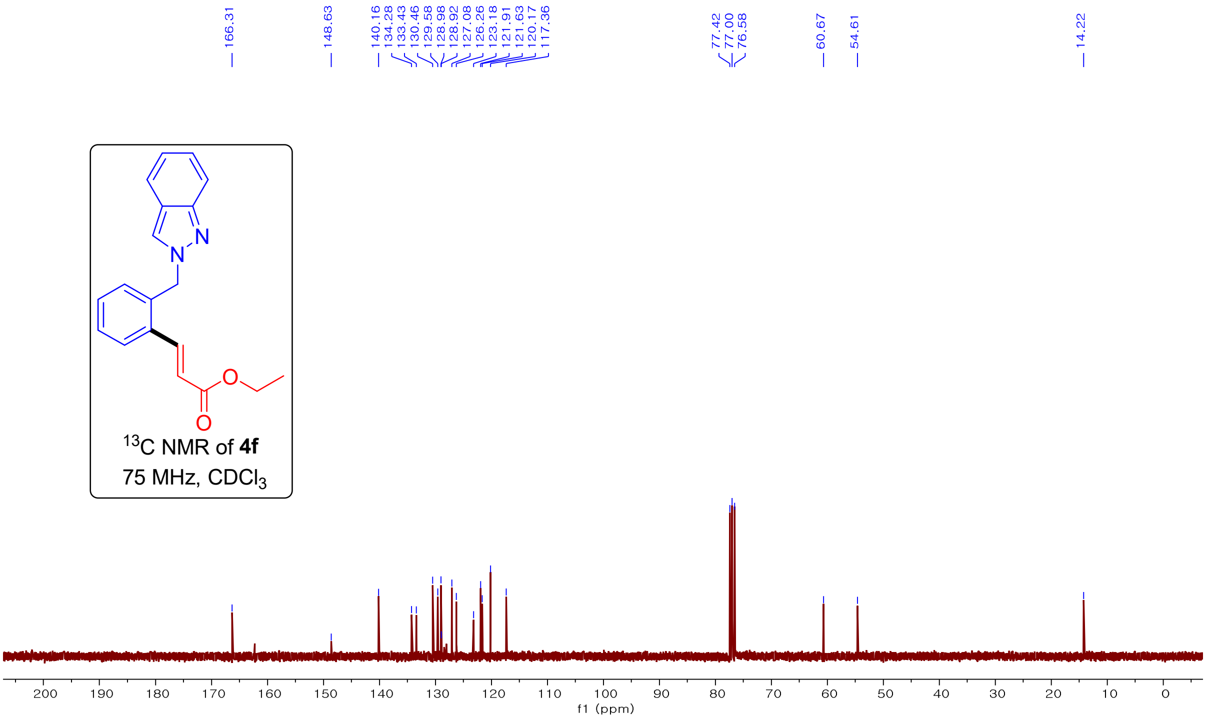


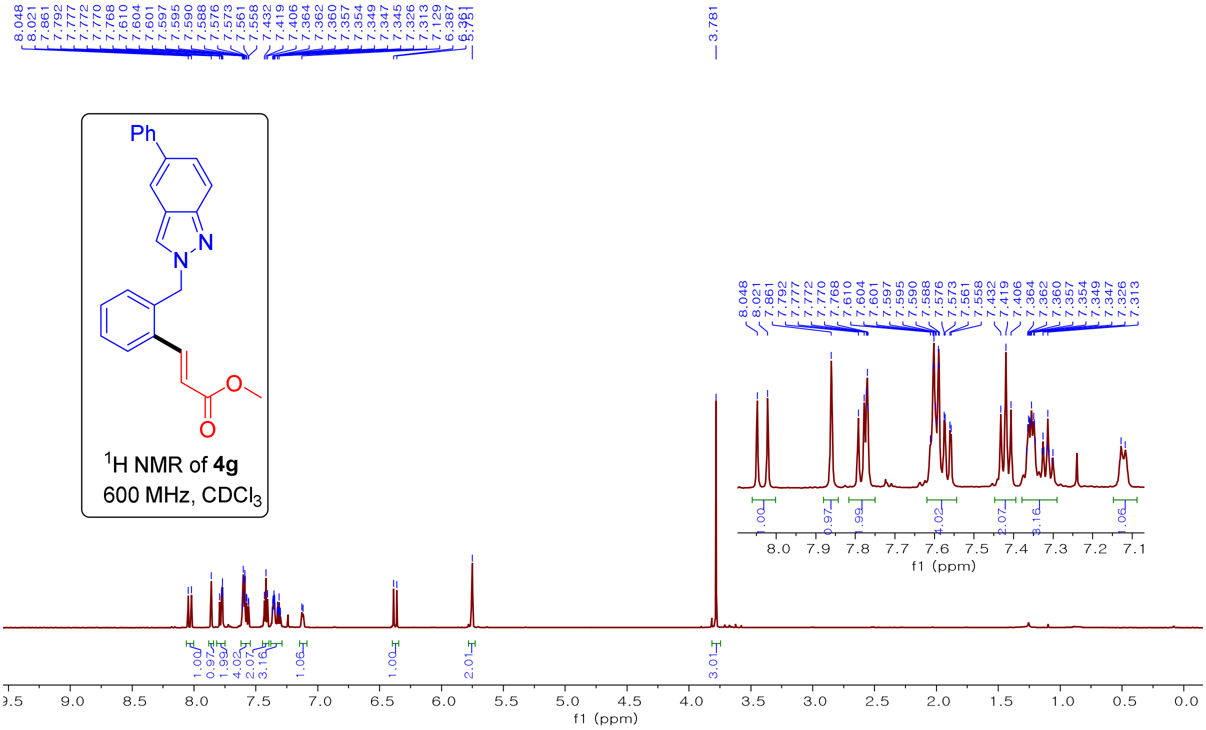
^{1}H NMR of **4e**
600 MHz, $CDCl_3$

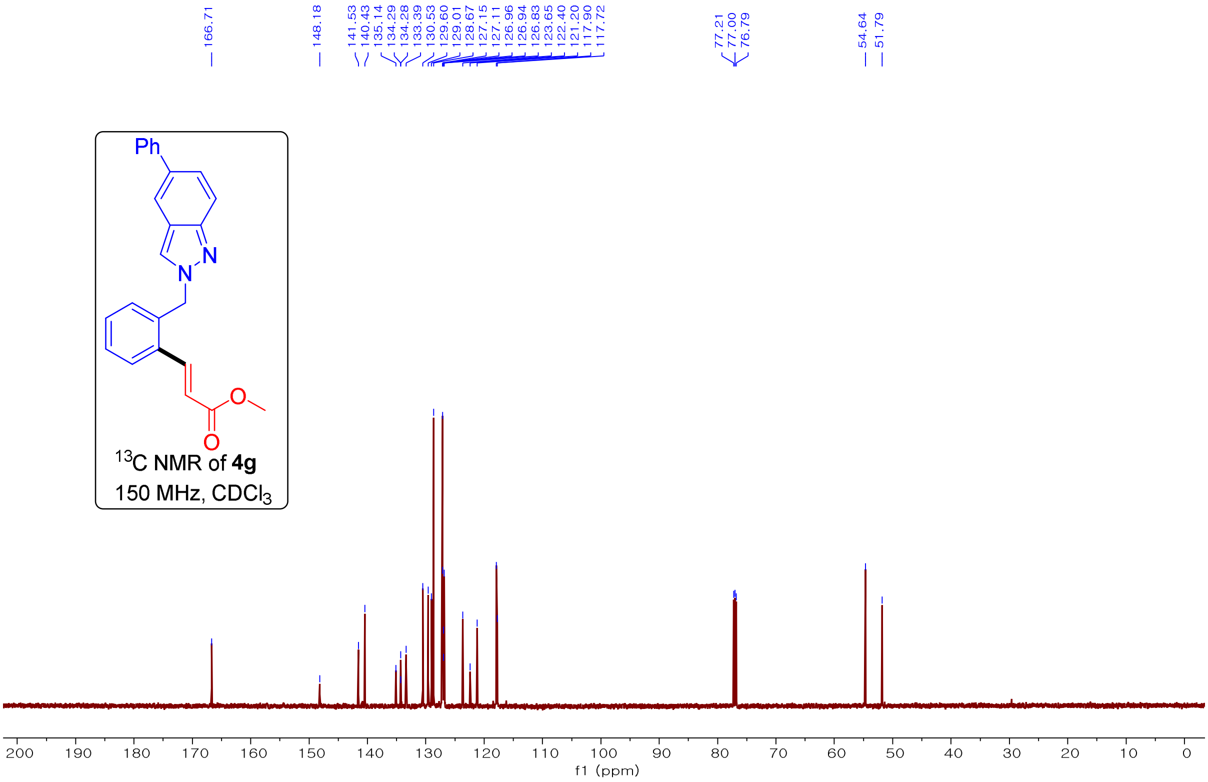


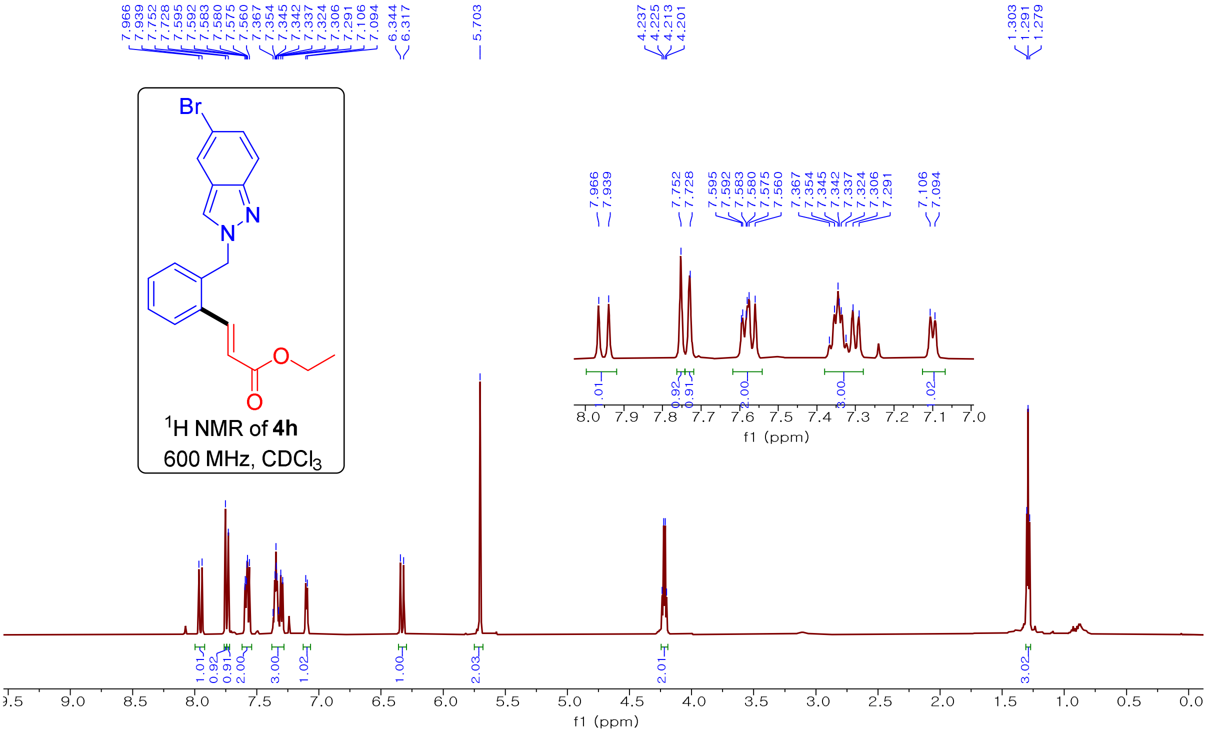
^{13}C NMR of **4e**
150 MHz, $CDCl_3$

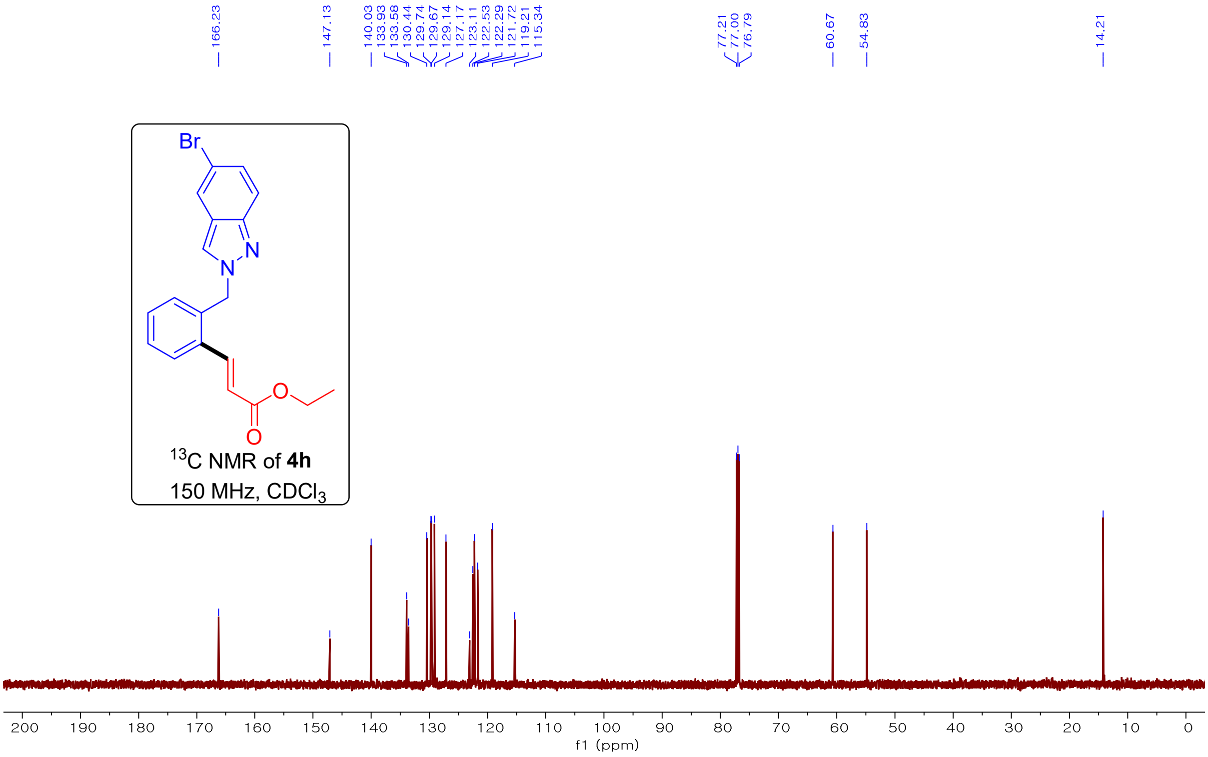

8.014
7.962
7.816
7.718
7.692
7.605
7.578
7.346
7.334
7.322
7.291
7.270
7.240
7.095
7.078
7.053
7.031
6.372
6.320
5.739
4.258
4.234
4.210
4.187
1.318
1.294
1.271
N
N
O
O
^{1}H NMR of **4f**
300 MHz, $CDCl_3$
1.00
1.00
1.03
2.00
2.06
1.18
2.05
1.01
2.00
2.03
3.02
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

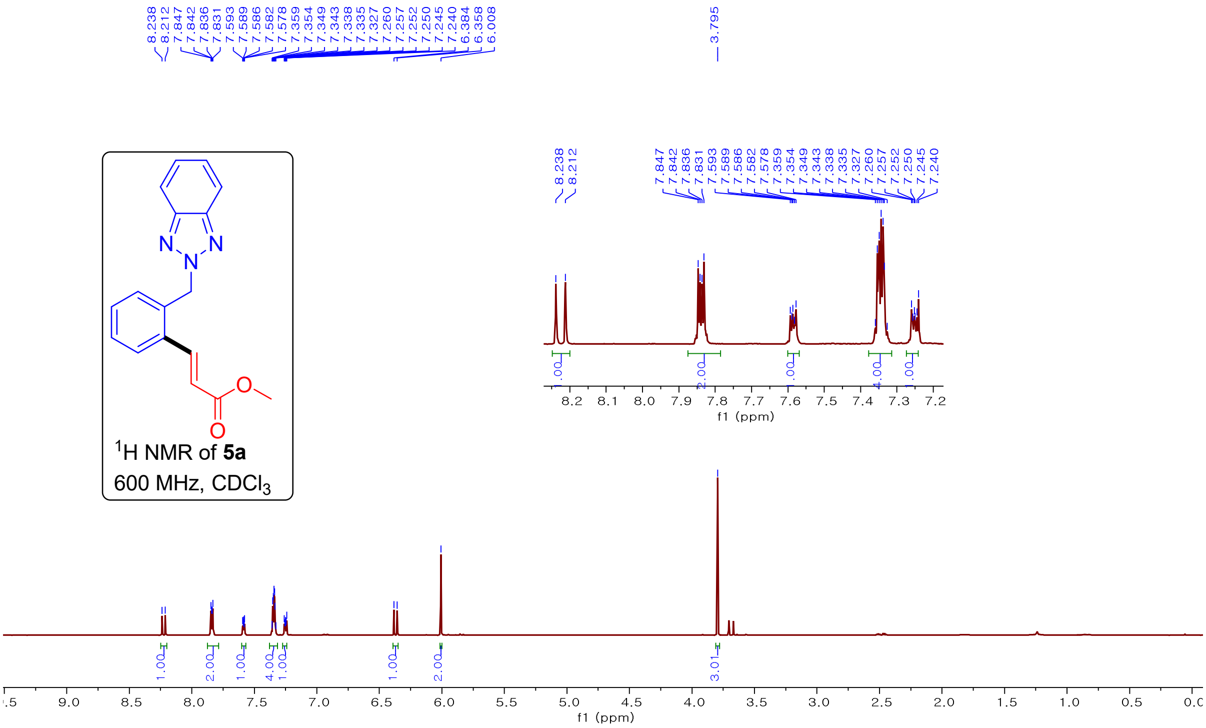

166.31
148.63
140.16
134.28
133.43
130.46
129.58
128.98
128.92
127.08
126.26
123.18
121.91
121.63
120.17
117.36
77.42
77.00
76.58
60.67
54.61
14.22
N
N
O
O
^{13}C NMR of **4f**
75 MHz, $CDCl_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.048
8.021
7.861
7.792
7.777
7.772
7.770
7.768
7.610
7.604
7.601
7.597
7.595
7.590
7.588
7.576
7.573
7.561
7.558
7.432
7.419
7.406
7.364
7.362
7.360
7.357
7.354
7.349
7.347
7.345
7.326
7.313
7.129
6.387
6.361
5.751
3.781
Ph
N
N
O
O
^{1}H NMR of **4g**
600 MHz, CDCl$_3$
1.00
0.97
1.99
4.02
2.07
3.16
1.06
1.00
2.01
3.01
f1 (ppm)

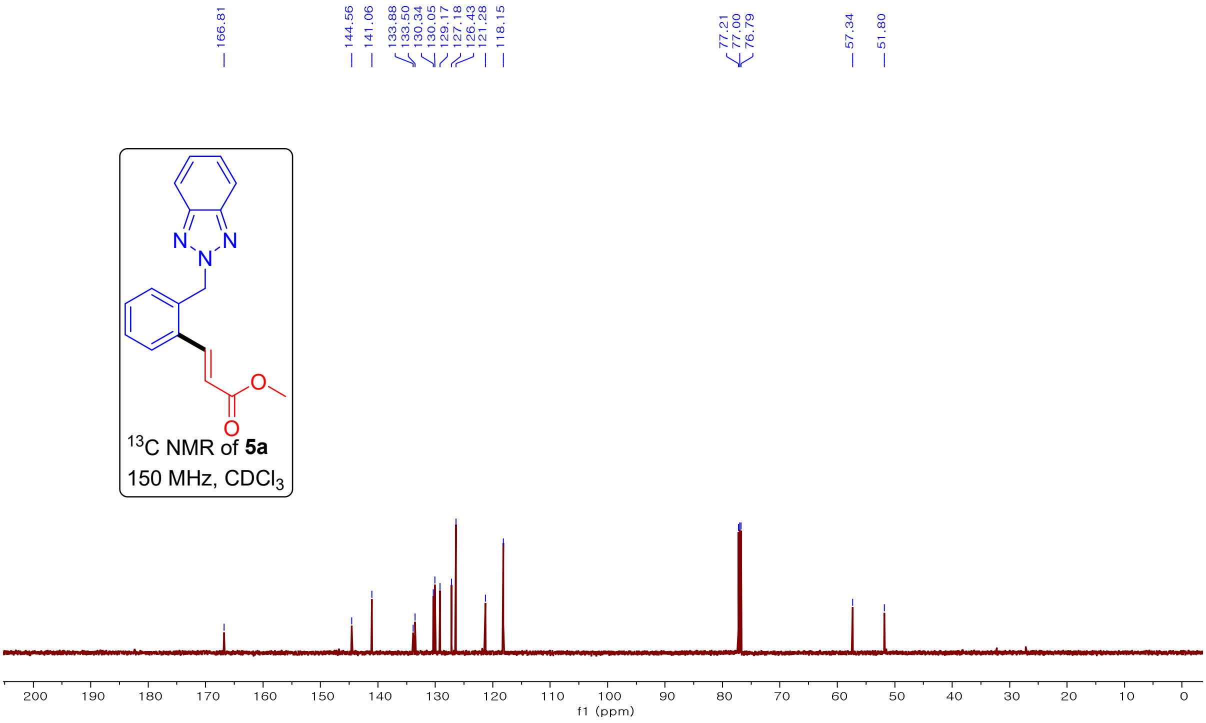

166.71
148.18
141.53
140.43
135.14
134.29
134.28
133.39
130.53
129.60
129.01
128.67
127.15
127.11
126.96
126.94
126.83
123.65
122.40
121.20
117.90
117.72
77.21
77.00
76.79
54.64
51.79
Ph
N
N
O
O
^{13}C NMR of **4g**
150 MHz, CDCl$_3$
f1 (ppm)


7.966
7.939
7.752
7.728
7.595
7.592
7.583
7.580
7.575
7.560
7.367
7.354
7.345
7.342
7.337
7.324
7.306
7.291
7.106
7.094
6.344
6.317
5.703
4.237
4.225
4.213
4.201
1.303
1.291
1.279
Br
N
N
O
O
^{1}H NMR of **4h**
600 MHz, CDCl$_3$
1.01
0.92
0.91
2.00
3.00
1.02
1.00
2.03
2.01
3.02
f1 (ppm)

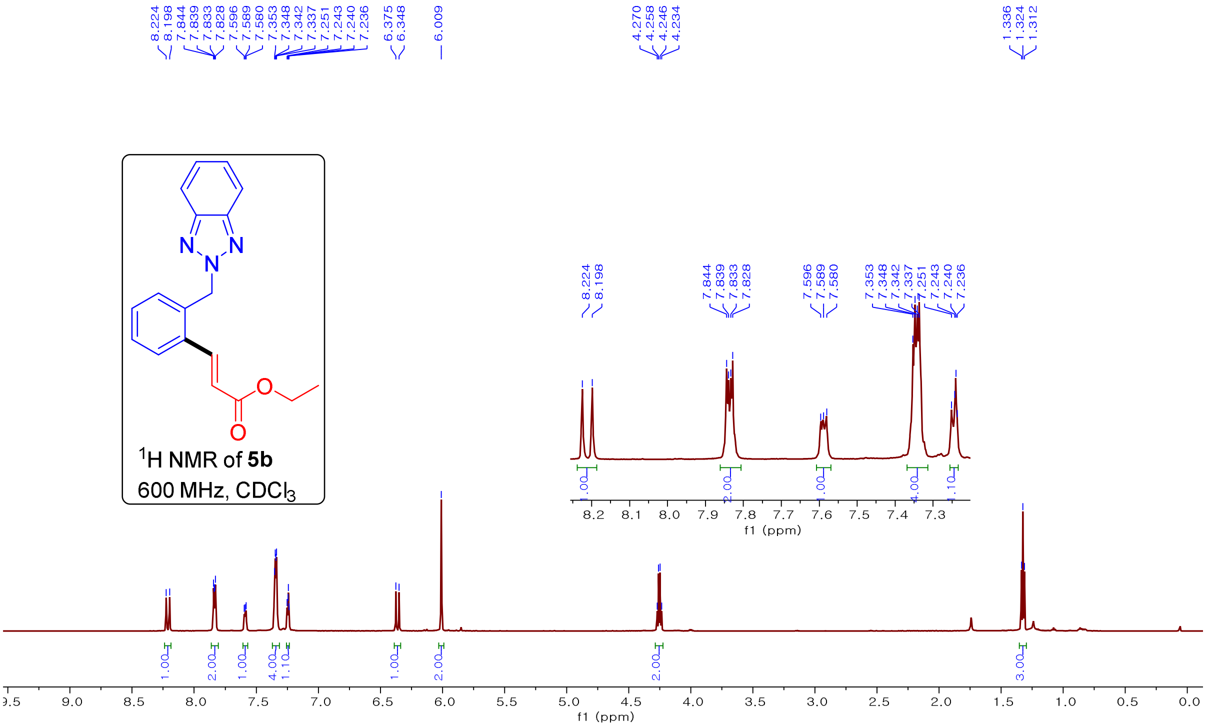

166.23
147.13
140.03
133.93
133.58
130.44
129.74
129.67
129.14
127.17
123.11
122.53
122.29
121.72
119.21
115.34
77.21
77.00
76.79
60.67
54.83
14.21
Br
N
N
O
O
^{13}C NMR of **4h**
150 MHz, CDCl$_3$
f1 (ppm)

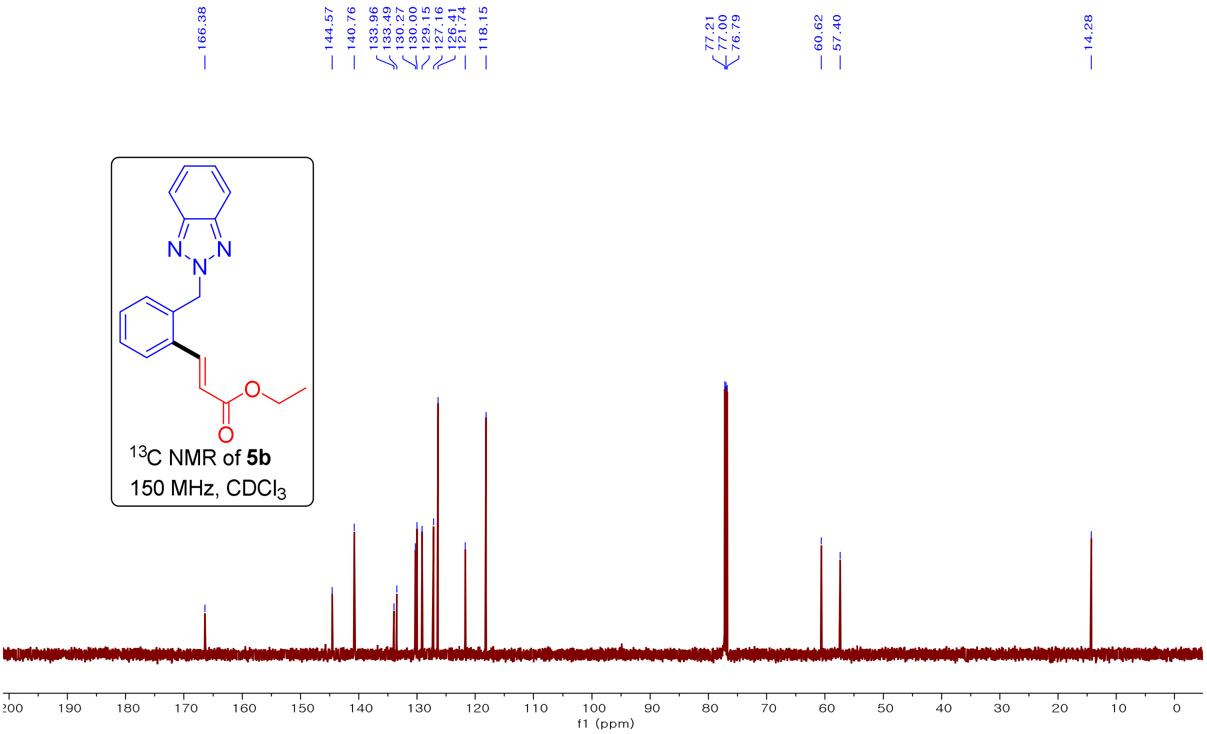


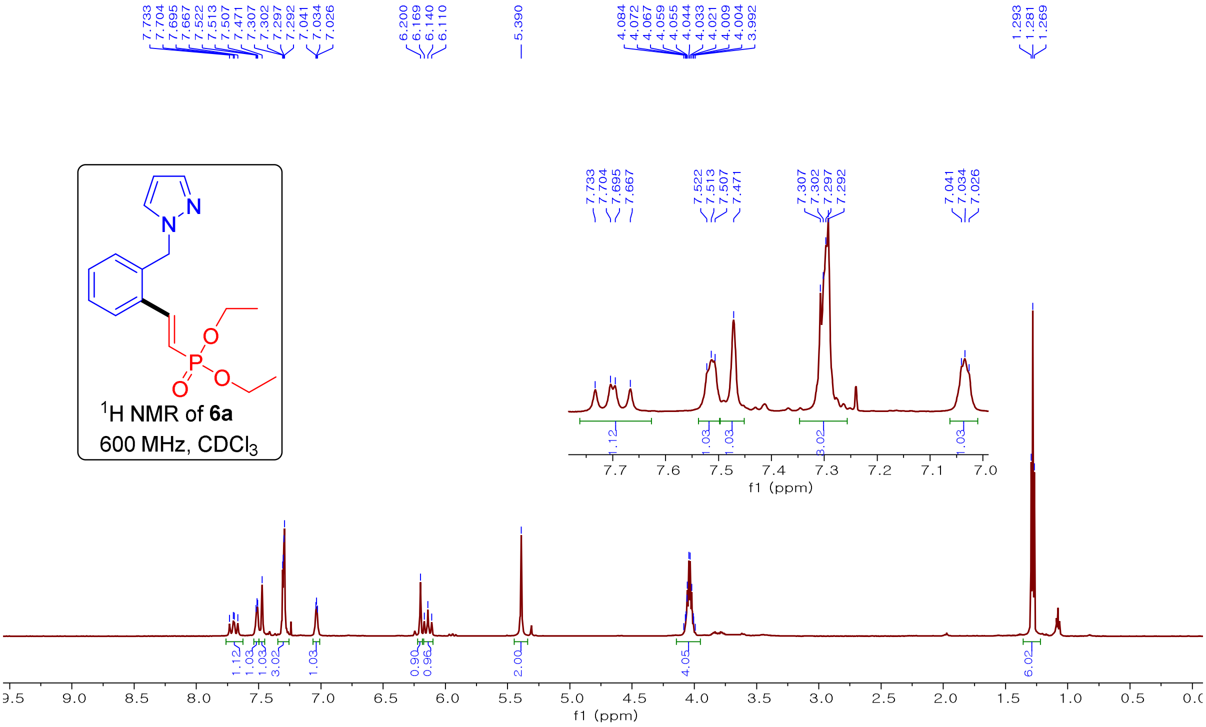
^{1}H NMR of **5a**
600 MHz, CDCl$_3$

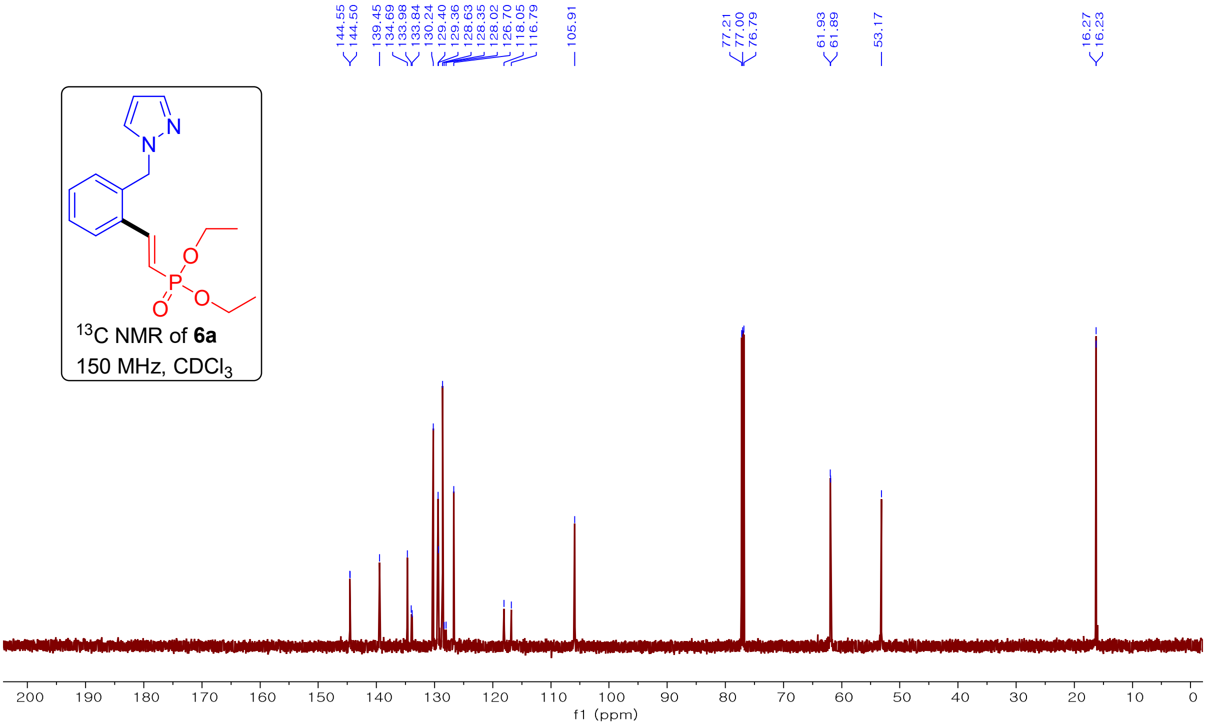


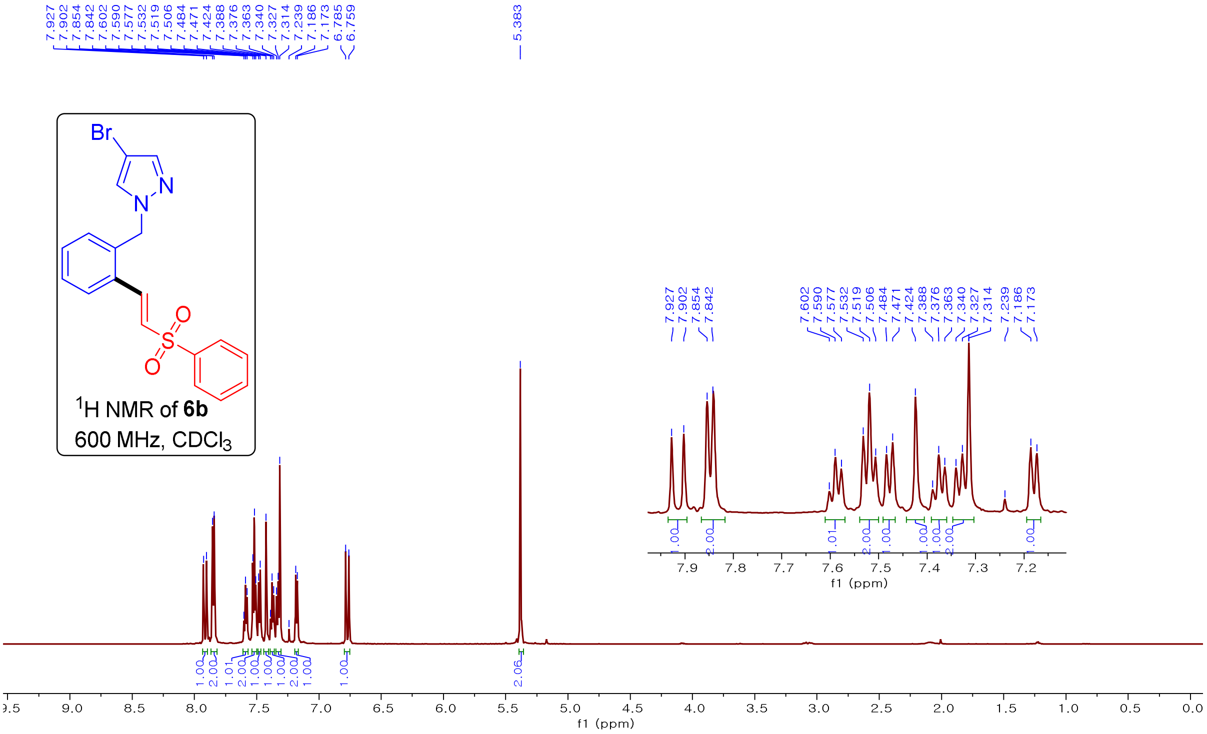
^{13}C NMR of **5a**
150 MHz, CDCl$_3$

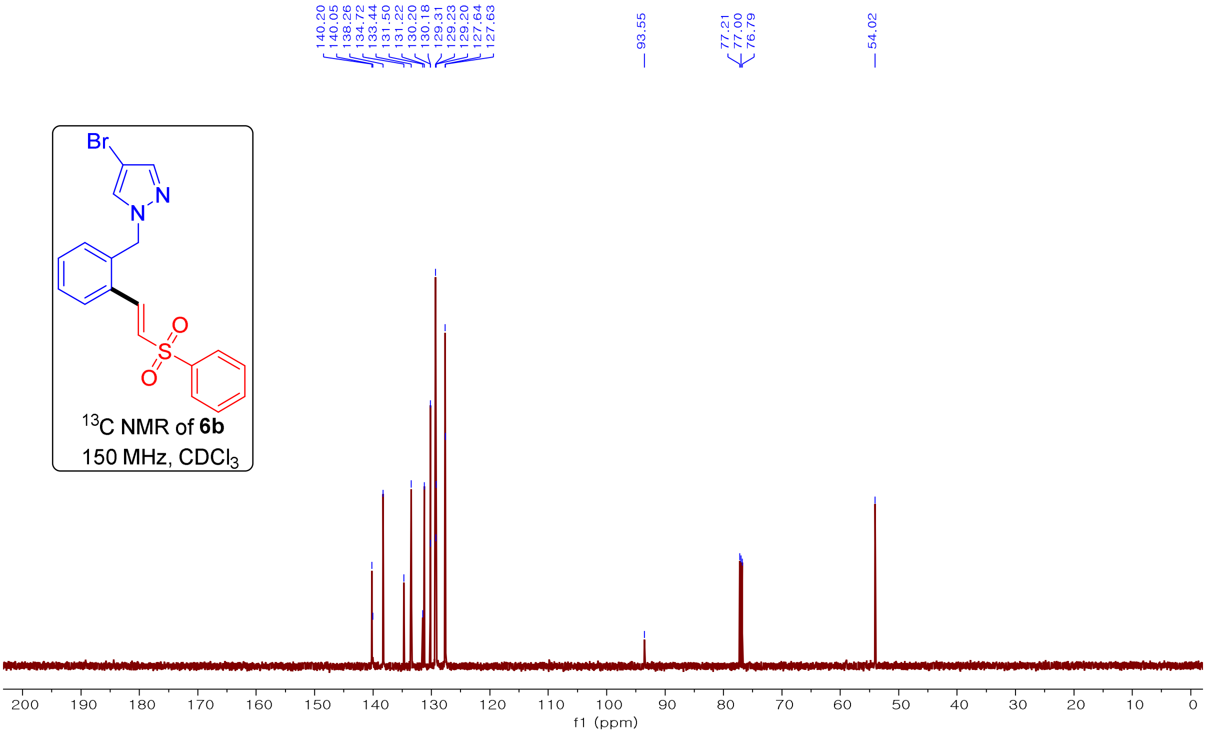

8.224
8.198
7.844
7.839
7.833
7.828
7.596
7.589
7.580
7.353
7.348
7.342
7.337
7.251
7.243
7.240
7.236
6.375
6.348
6.009
4.270
4.258
4.246
4.234
1.336
1.324
1.312
N
N
N
O
O
^{1}H NMR of **5b**
600 MHz, CDCl$_3$
1.00
2.00
1.00
4.00
1.10
1.00
2.00
2.00
3.00
f1 (ppm)
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

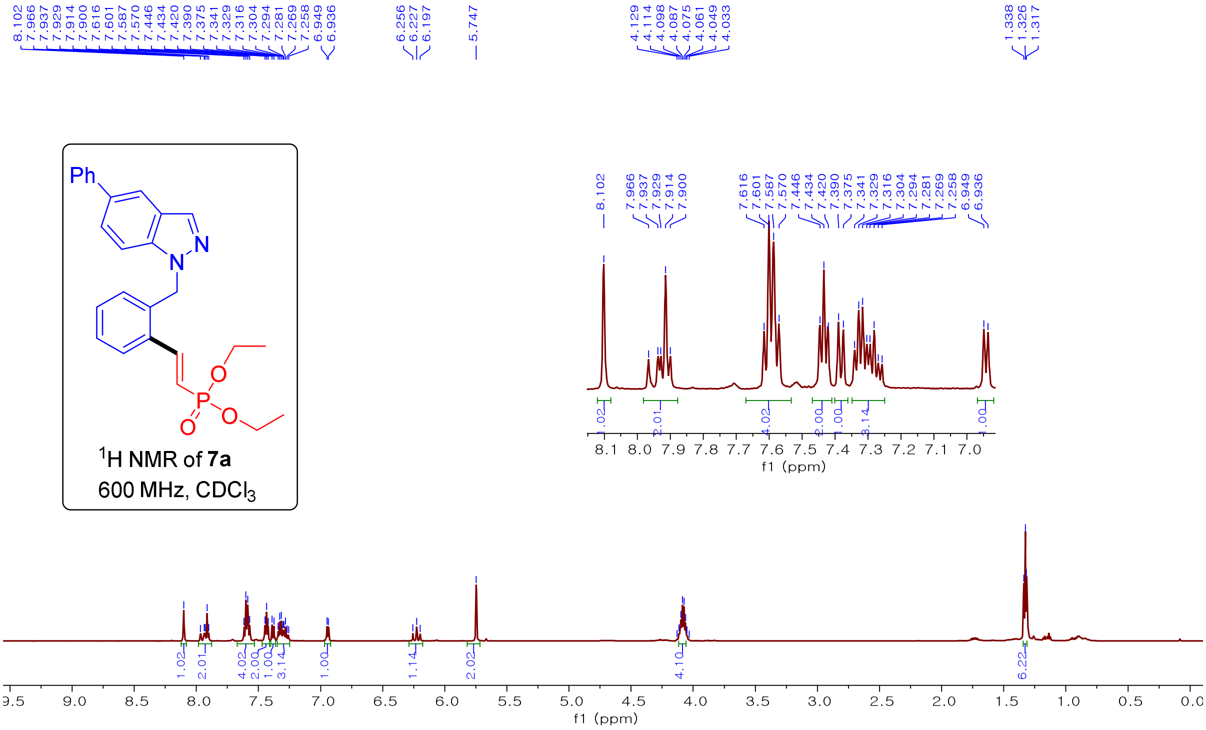

166.38
144.57
140.76
133.96
133.49
130.27
130.00
129.15
127.16
126.41
121.74
118.15
77.21
77.00
76.79
60.62
57.40
14.28
N
N
N
O
O
^{13}C NMR of **5b**
150 MHz, CDCl$_3$
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

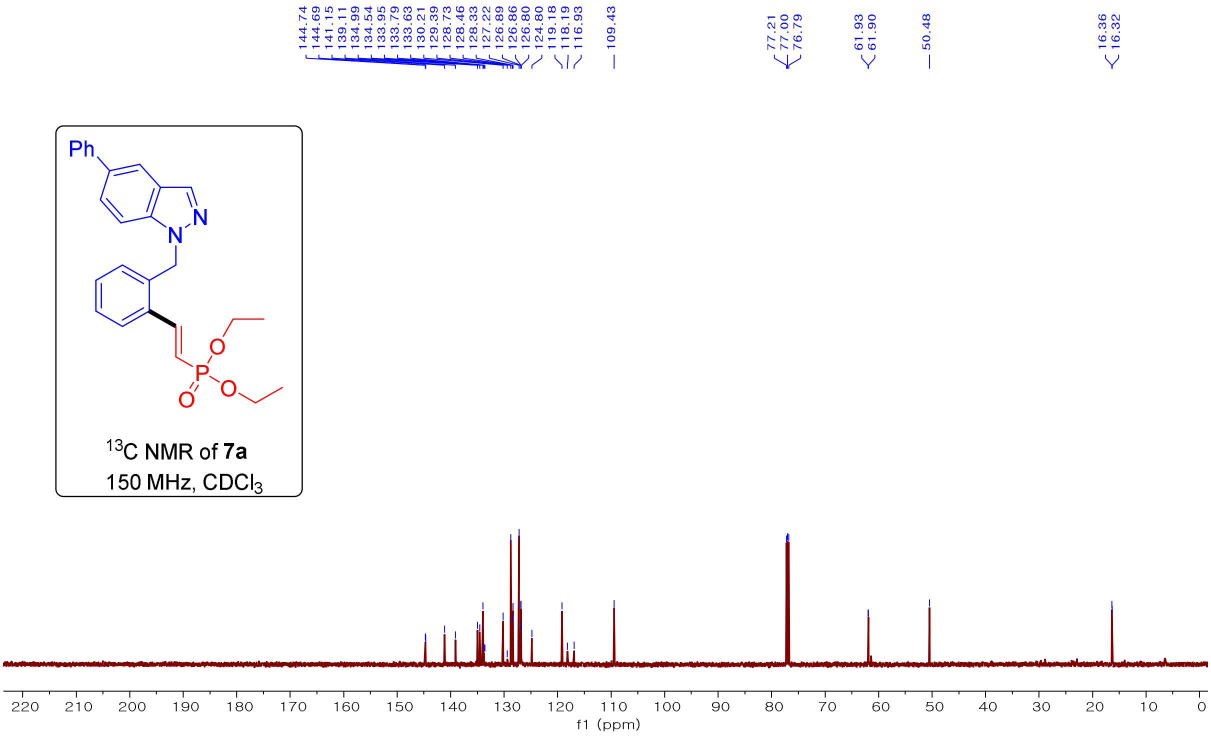

7.733
7.704
7.695
7.667
7.522
7.513
7.507
7.471
7.307
7.302
7.297
7.292
7.041
7.034
7.026
6.200
6.169
6.140
6.110
5.390
4.084
4.072
4.067
4.059
4.055
4.044
4.033
4.021
4.009
4.004
3.992
1.293
1.281
1.269
N
N
O
P
O
O
^{1}H NMR of **6a**
600 MHz, CDCl$_3$
1.12
1.03
1.03
3.02
1.03
0.90
0.96
2.00
4.05
6.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0

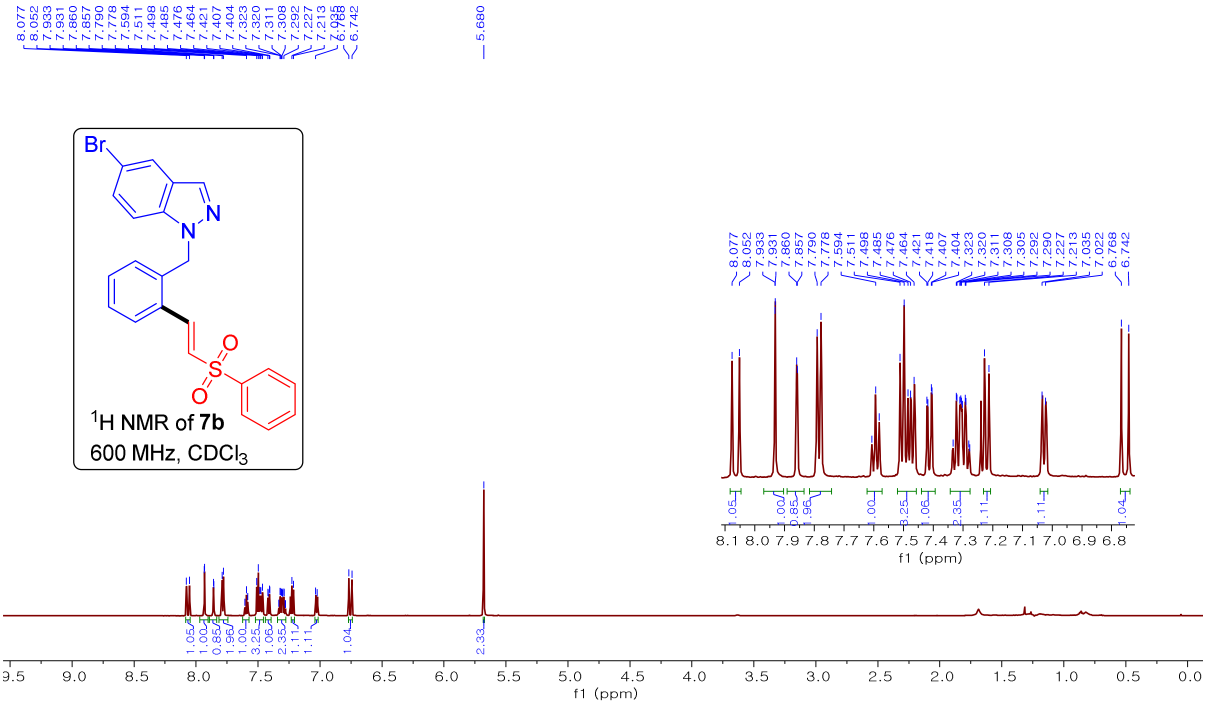

144.55
144.50
139.45
134.69
133.98
133.84
130.24
129.40
129.36
128.63
128.35
128.02
126.70
118.05
116.79
105.91
77.21
77.00
76.79
61.93
61.89
53.17
16.27
16.23
N
N
O
P
O
O
^{13}C NMR of **6a**
150 MHz, CDCl$_3$
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

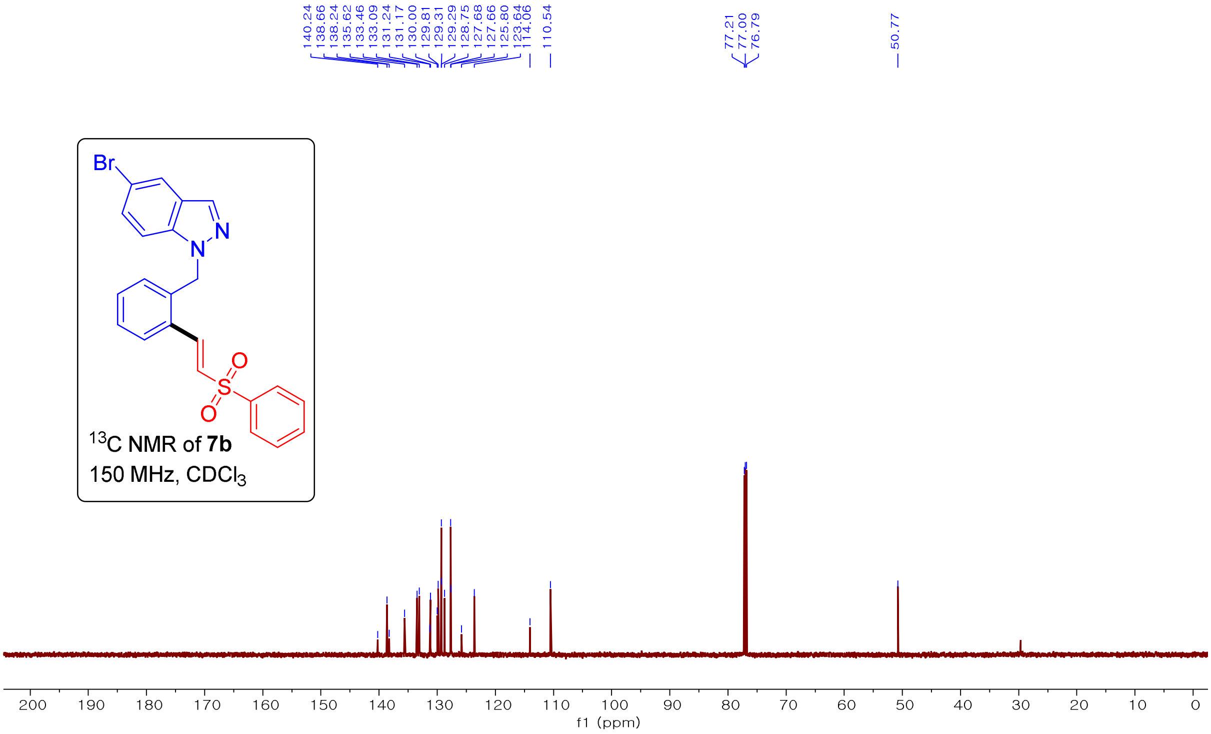

7.927
7.902
7.854
7.842
7.602
7.590
7.577
7.532
7.519
7.506
7.484
7.471
7.424
7.388
7.376
7.363
7.340
7.327
7.314
7.239
7.186
7.173
6.785
6.759
5.383
Br
N
N
O
S
O
^{1}H NMR of **6b**
600 MHz, $CDCl_3$
1.00
2.00
1.01
2.00
1.00
1.00
1.00
1.00
2.00
1.00
1.00
2.06
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

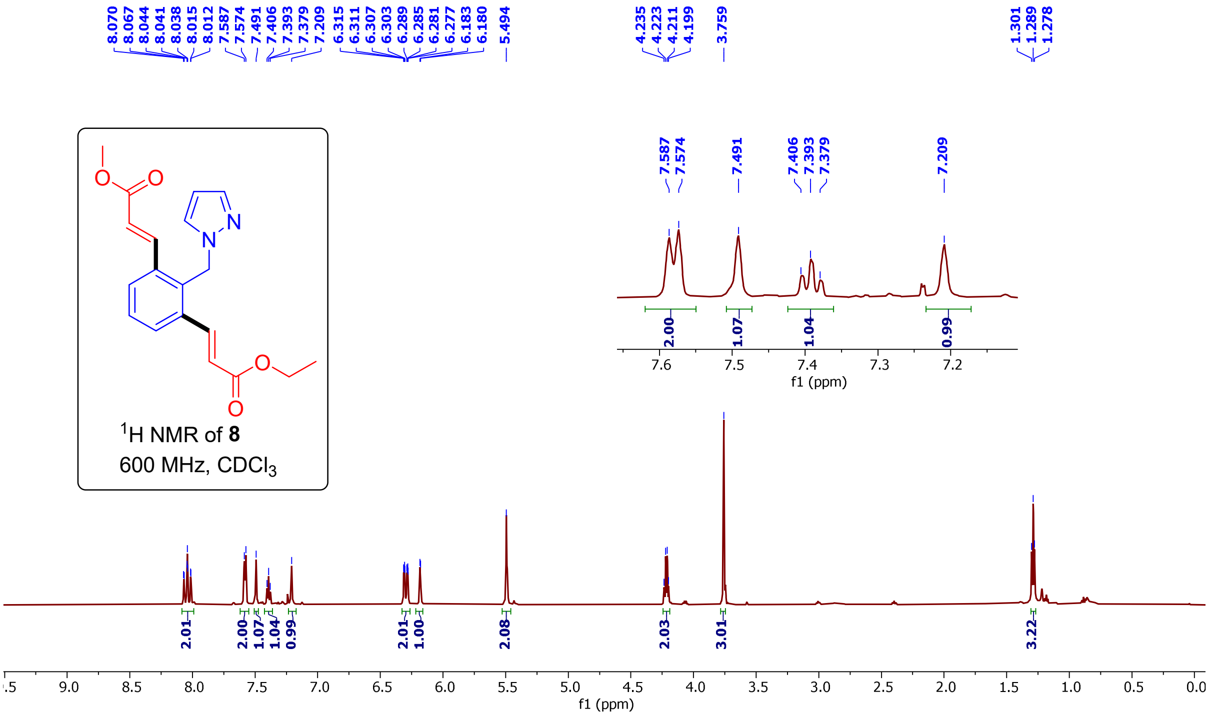

140.20
140.05
138.26
134.72
133.44
131.50
131.22
130.20
130.18
129.31
129.23
129.20
127.64
127.63
93.55
77.21
77.00
76.79
54.02
Br
N
N
O
S
O
^{13}C NMR of **6b**
150 MHz, $CDCl_3$
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

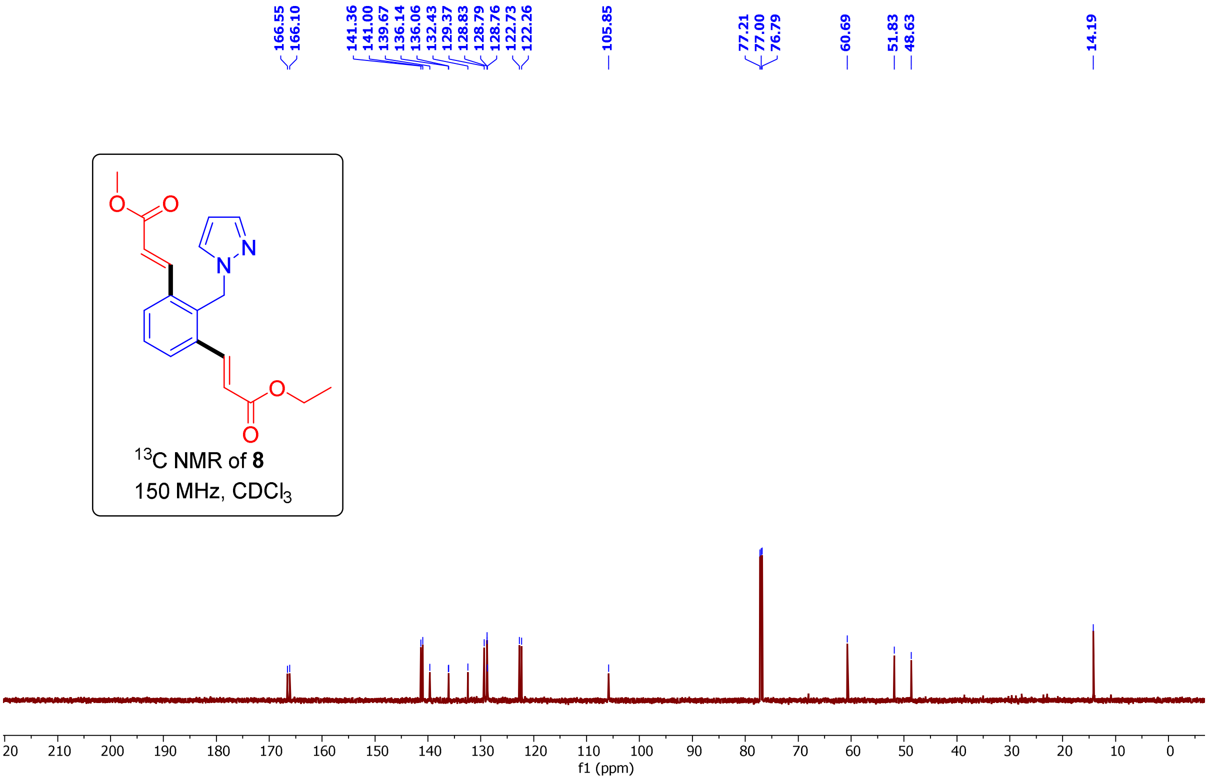

8.102 7.966 7.937 7.929 7.914 7.900 7.616 7.601 7.587 7.570 7.446 7.434 7.420 7.390 7.375 7.341 7.329 7.316 7.304 7.294 7.281 7.269 7.258 6.949 6.936
6.256 6.227 6.197
5.747
4.129 4.114 4.098 4.087 4.075 4.061 4.049 4.033
1.338 1.326 1.317
Ph
N
N
O
P
O
O
^{1}H NMR of **7a**
600 MHz, $CDCl_3$
1.02 2.01 4.02 2.00 1.00 3.14 1.00
8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)
1.02 2.01 4.02 2.00 1.00 3.14 1.00 1.14 2.02 4.10 6.22
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

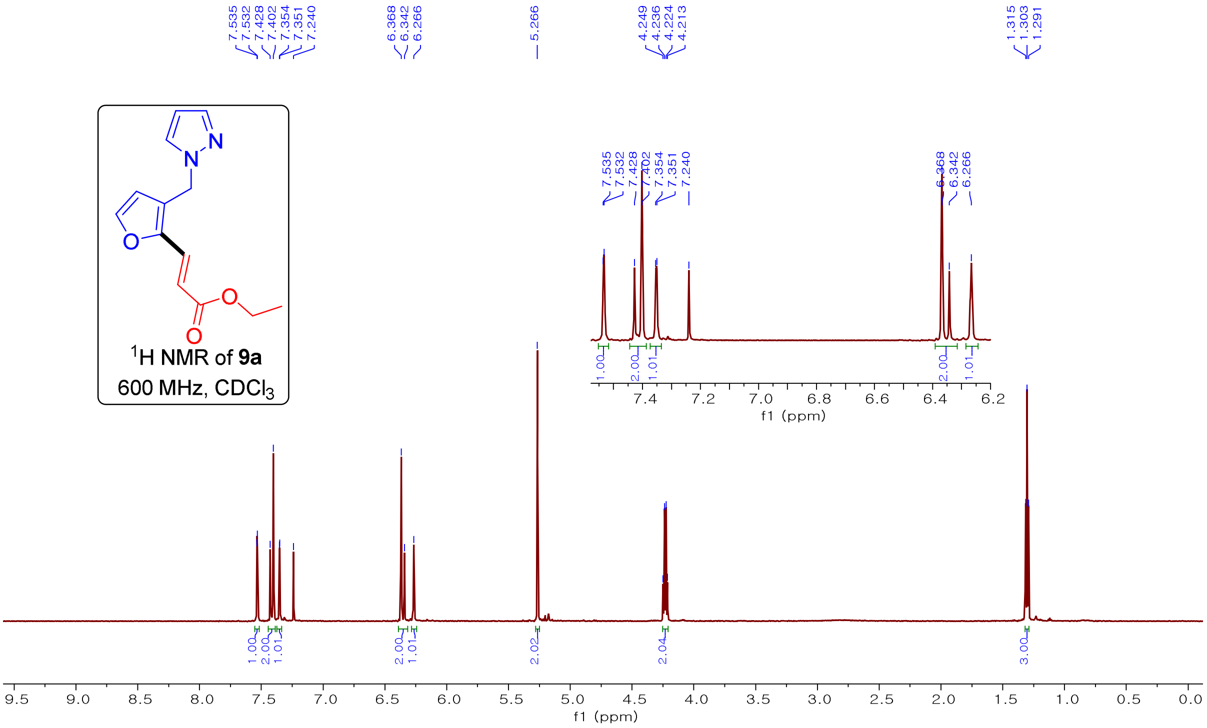

144.74 144.69 141.15 139.11 134.99 134.54 133.95 133.79 133.63 130.21 129.39 128.73 128.46 128.33 127.22 126.89 126.86 126.80 124.80 119.18 118.19 116.93
109.43
77.21 77.00 76.79
61.93 61.90
50.48
16.36 16.32
Ph
N
N
O
P
O
O
^{13}C NMR of **7a**
150 MHz, $CDCl_3$
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

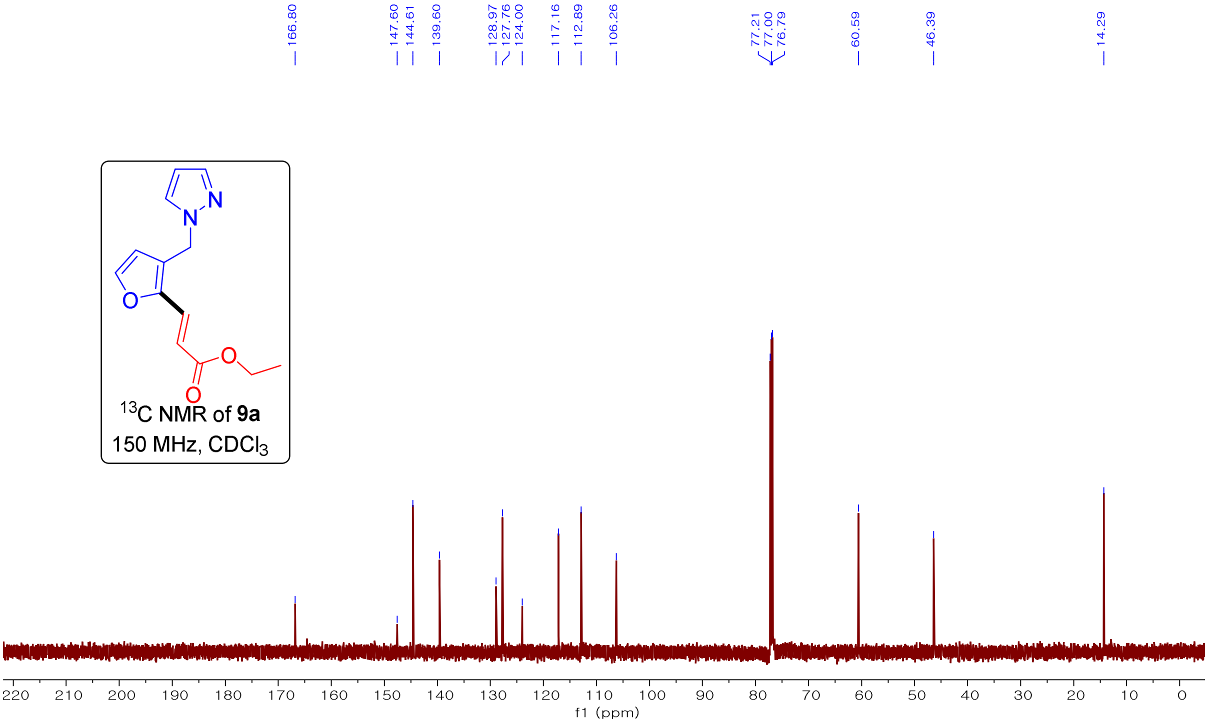

8.077
8.052
7.933
7.931
7.860
7.857
7.790
7.778
7.594
7.511
7.498
7.485
7.476
7.464
7.421
7.418
7.407
7.404
7.323
7.320
7.311
7.308
7.305
7.292
7.290
7.227
7.213
7.035
7.022
6.768
6.742
5.680
Br
N
N
^{1}H NMR of **7b**
600 MHz, CDCl$_3$
1.05
1.00
0.85
1.96
1.00
3.25
1.06
2.35
1.11
1.11
1.04
2.33
8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

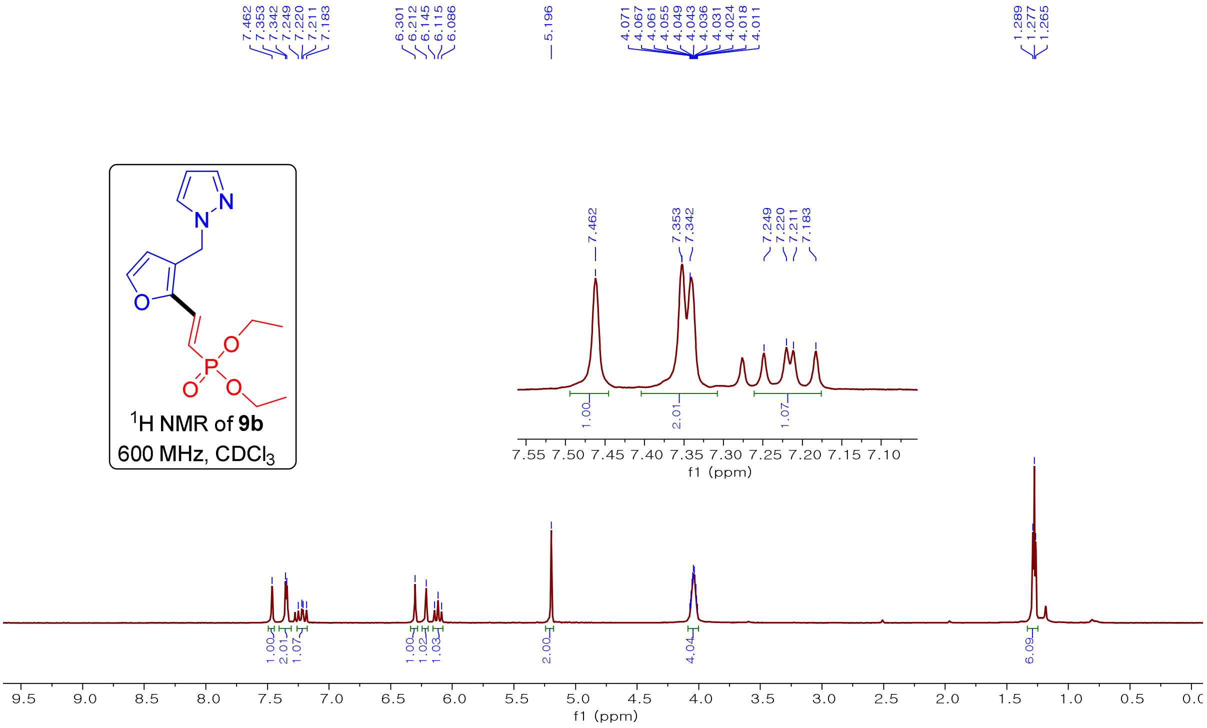

140.24
138.66
138.24
135.62
133.46
133.09
131.24
131.17
130.00
129.81
129.31
129.29
128.75
127.68
127.66
125.80
123.64
114.06
110.54
77.21
77.00
76.79
50.77
Br
N
N
S
O
O
^{13}C NMR of **7b**
150 MHz, CDCl$_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.070
8.067
8.044
8.041
8.038
8.015
8.012
7.587
7.574
7.491
7.406
7.393
7.379
7.209
6.315
6.311
6.307
6.303
6.289
6.285
6.281
6.277
6.183
6.180
5.494
4.235
4.223
4.211
4.199
3.759
1.301
1.289
1.278
^{1}H NMR of **8**
600 MHz, $CDCl_3$
2.00
1.07
1.04
0.99
2.01
2.00
1.07
1.04
0.99
2.01
1.00
2.08
2.03
3.01
3.22
f1 (ppm)

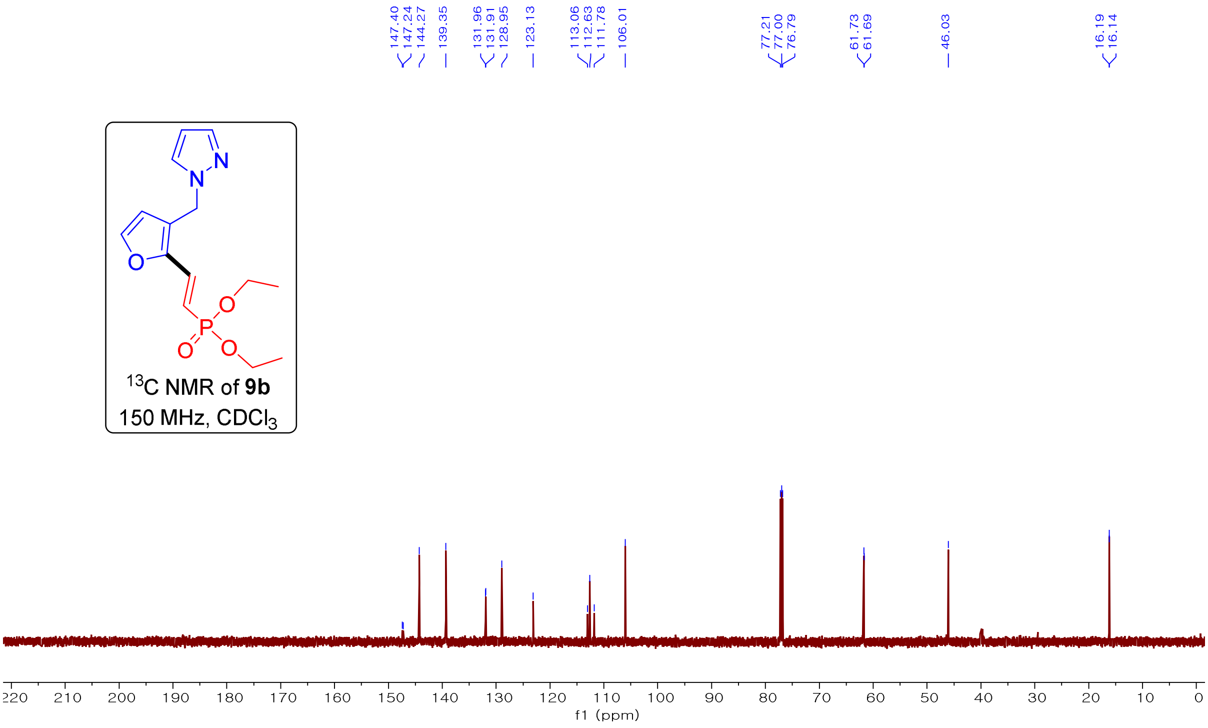

166.55
166.10
141.36
141.00
139.67
136.14
136.06
132.43
129.37
128.83
128.79
128.76
122.73
122.26
105.85
77.21
77.00
76.79
60.69
51.83
48.63
14.19
^{13}C NMR of **8**
150 MHz, $CDCl_3$
f1 (ppm)


7.535
7.532
7.428
7.402
7.354
7.351
7.240
6.368
6.342
6.266
5.266
4.249
4.236
4.224
4.213
1.315
1.303
1.291
N
N
O
O
O
^{1}H NMR of **9a**
600 MHz, CDCl$_3$
1.00
2.00
1.01
2.00
1.01
2.02
2.04
3.00
f1 (ppm)

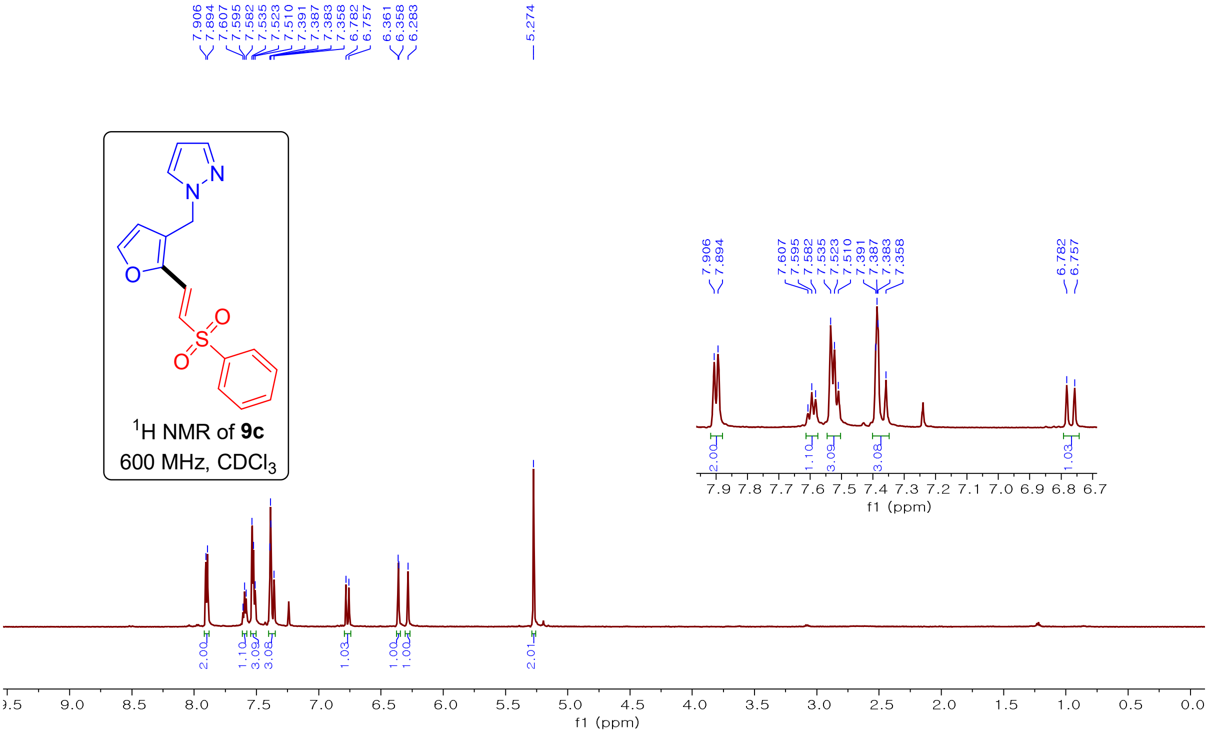

166.80
147.60
144.61
139.60
128.97
127.76
124.00
117.16
112.89
106.26
77.21
77.00
76.79
60.59
46.39
14.29
N
N
O
O
O
^{13}C NMR of **9a**
150 MHz, CDCl$_3$
f1 (ppm)

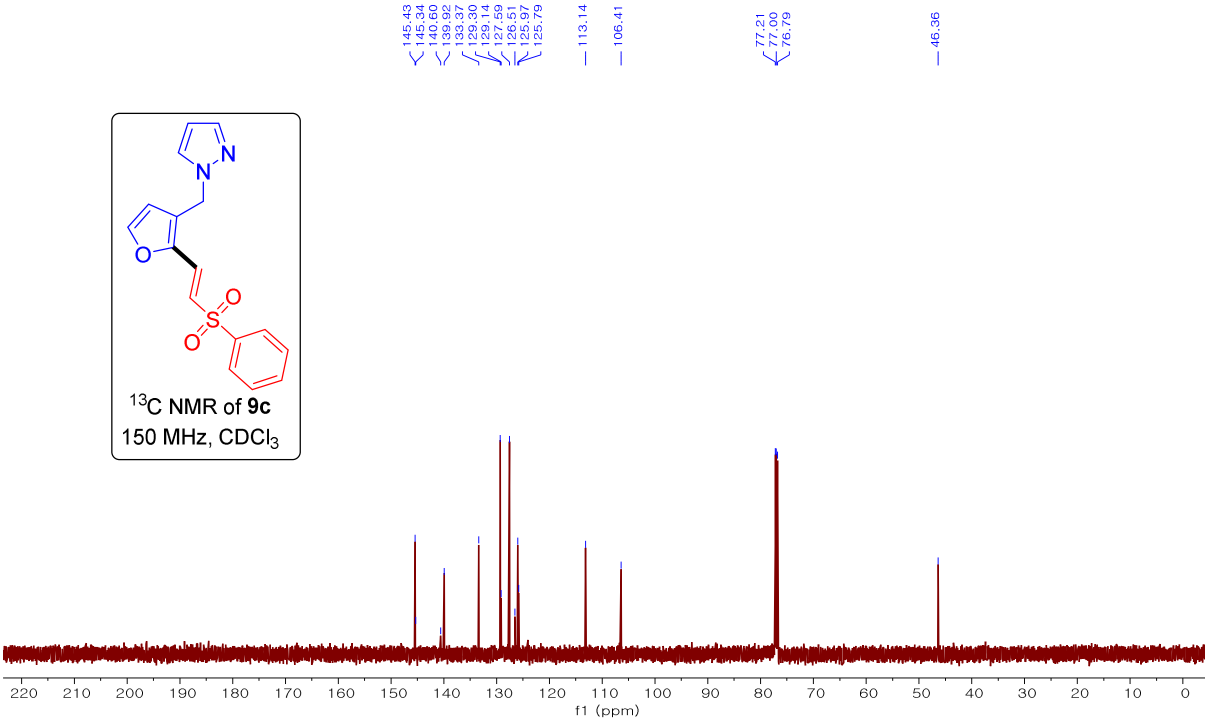


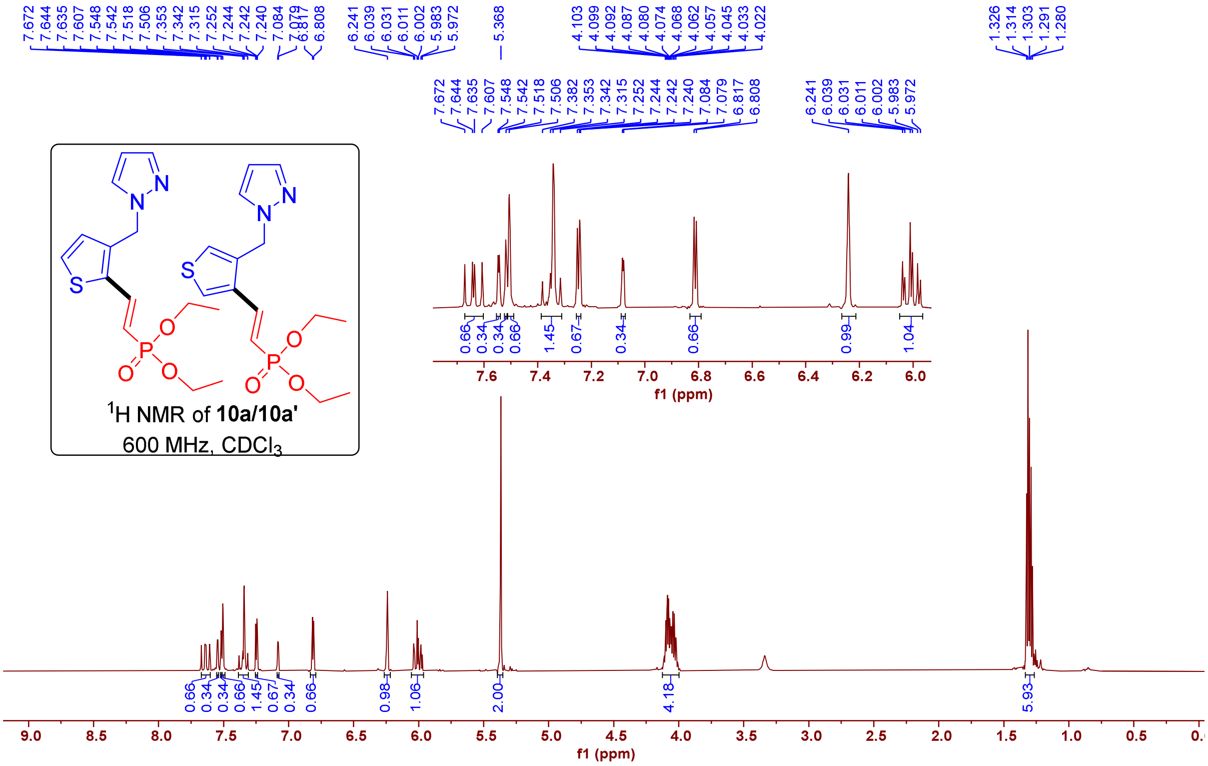
^{1}H NMR of **9b**
600 MHz, $CDCl_3$

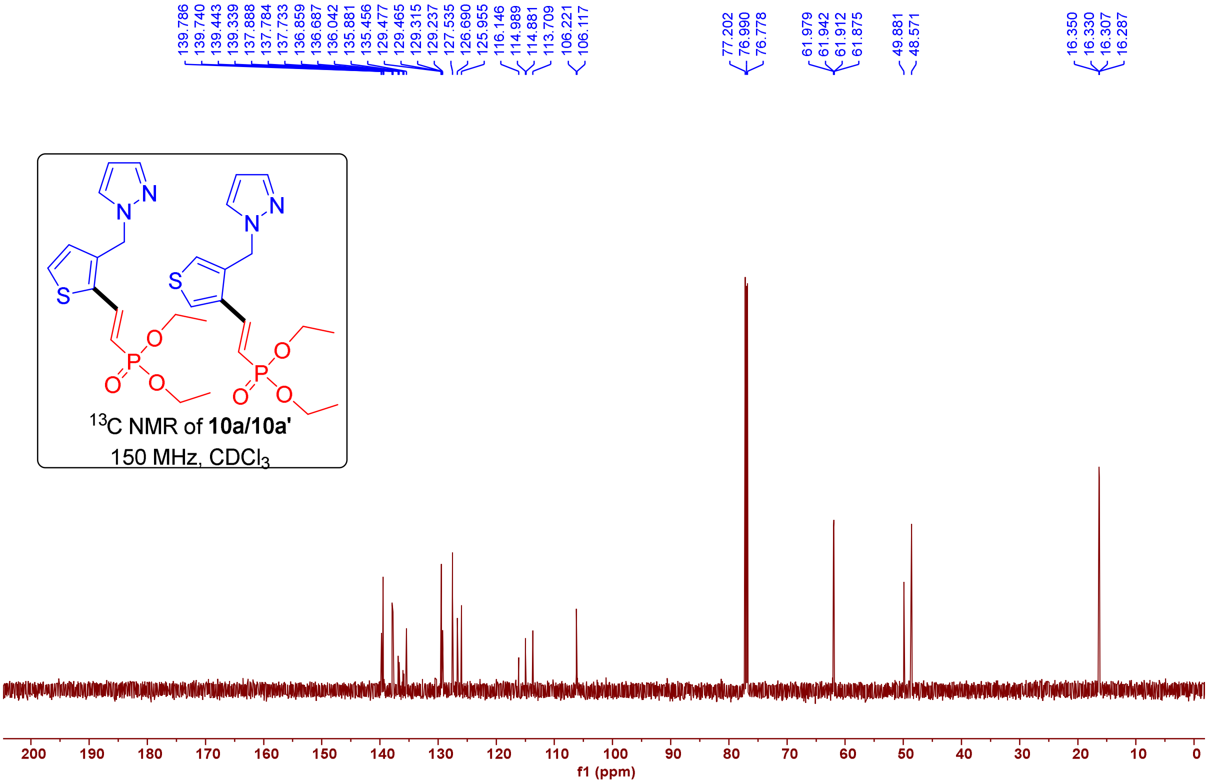


^{13}C NMR of **9b**
150 MHz, $CDCl_3$


7.906
7.894
7.607
7.595
7.582
7.535
7.523
7.510
7.391
7.387
7.383
7.358
6.782
6.757
6.361
6.358
6.283
5.274
N
N
O
S
O
O
^{1}H NMR of **9c**
600 MHz, $CDCl_3$
2.00
1.10
3.09
3.08
1.03
1.00
1.00
2.01
1.03
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7
f1 (ppm)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


145.43
145.34
140.60
139.92
133.37
129.30
129.14
127.59
126.51
125.97
125.79
113.14
106.41
77.21
77.00
76.79
46.36
N
N
O
S
O
O
^{13}C NMR of **9c**
150 MHz, $CDCl_3$
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


^{1}H NMR of **10a/10a'**
600 MHz, $CDCl_3$
7.672 7.644 7.635 7.607 7.548 7.542 7.518 7.506 7.353 7.342 7.315 7.252 7.244 7.242 7.240 7.084 7.079 6.817 6.808
6.241 6.039 6.031 6.011 6.002 5.983 5.972
5.368
4.103 4.099 4.092 4.087 4.080 4.074 4.068 4.062 4.057 4.045 4.033 4.022
1.326 1.314 1.303 1.291 1.280
0.66 0.34 0.34 0.66 1.45 0.67 0.34 0.66 0.98 1.06 2.00 4.18 5.93
0.66 0.34 0.34 0.66 1.45 0.67 0.34 0.66 0.99 1.04
f1 (ppm)


^{13}C NMR of **10a/10a'**
150 MHz, $CDCl_3$
139.786 139.740 139.443 139.339 137.888 137.784 137.733 136.859 136.687 136.042 135.881 135.456 129.477 129.465 129.315 129.237 127.535 126.690 125.955 116.146 114.989 114.881 113.709 106.221 106.117
77.202 76.990 76.778
61.979 61.942 61.912 61.875
49.881 48.571
16.350 16.330 16.307 16.287
f1 (ppm)

Crystal refinement data for compound 3a: Empirical Formula- $C_{14}H_{14}N_2O_2$, M = 242.27, Triclinic, Space group P-1, a = 8.868(5) Å, b = 8.948(5) Å, c = 10.107(6) Å, V = 637.1(6) Å^3, Z = 2, T = 173(2) K, ρ_{calcd} = 1.263 Mg/m^3, 2$\Theta_{max.}$ = 25.24^0, Refinement of 164 parameters on 2984 independent reflections out of 12629 collected reflections (R_{int} = 0.0434) led to R_1 = 0.0664 [I >2σ(I)], wR_2 = 0.1336 (all data) and S = 1.095 with the largest difference peak and hole of 0.200 and -0.174 e.Å^{-3} respectively. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (CCDC 1944051). The data can be obtained free of charge via the Internet at www.ccdc.cam.ac.uk/data_request/cif.

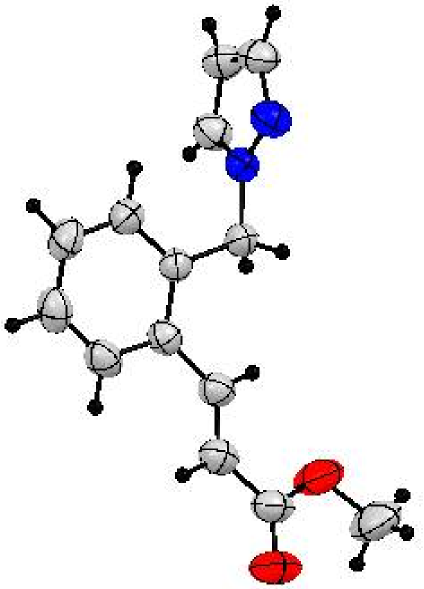


Figure S1. X-ray Structure of compound **3a**.

Table 1. Crystal data and structure refinement for 71a_re_a.

Identification code	71a_re_a	
Empirical formula	$C_{14}H_{14}N_2O_2$	
Formula weight	242.27	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.868(5) Å	α= 84.918(4)°.
	b = 8.948(5) Å	β= 66.058(4)°.
	c = 10.107(6) Å	γ = 61.274(4)°.
Volume	637.1(6) Å^3	
Z	2	
Density (calculated)	1.263 Mg/m^3	
Absorption coefficient	0.086 mm^{-1}	
F(000)	256	
Crystal size	0.200 x 0.200 x 0.200 mm^3	
Theta range for data collection	2.790 to 28.449°.	
Index ranges	-11<=h<=11, -11<=k<=11, -13<=l<=13	
Reflections collected	12629	
Independent reflections	2984 [R(int) = 0.0434]	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6507	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2984 / 0 / 164	
Goodness-of-fit on F^2	1.095	
Final R indices [I>2sigma(I)]	R1 = 0.0664, wR2 = 0.1336	
R indices (all data)	R1 = 0.1219, wR2 = 0.1556	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.200 and -0.174 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for 71a_re_a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	12(2)	5777(2)	6475(2)	49(1)
C(1)	7807(4)	-1226(4)	755(3)	100(1)
O(1)	7189(2)	-234(2)	2113(2)	89(1)
O(2)	10170(2)	-1353(2)	1790(2)	94(1)
N(2)	-634(3)	7431(2)	6219(2)	60(1)
C(2)	8516(3)	-384(3)	2500(2)	62(1)
C(5)	5109(3)	2965(3)	5957(2)	47(1)
C(4)	5946(3)	1811(3)	4608(2)	53(1)
C(3)	7750(3)	716(3)	3855(2)	61(1)
C(8)	3546(3)	5183(3)	8503(2)	64(1)
C(7)	5396(3)	3884(3)	7993(2)	65(1)
C(6)	6175(3)	2800(3)	6728(2)	59(1)
C(9)	2461(3)	5377(3)	7760(2)	56(1)
C(10)	3203(3)	4281(3)	6505(2)	45(1)
C(11)	1998(3)	4499(3)	5703(2)	53(1)
C(12)	-1339(3)	5539(3)	7537(2)	59(1)
C(13)	-2958(3)	7093(3)	7994(2)	63(1)
C(14)	-2447(3)	8210(3)	7152(3)	63(1)

Table 3. Bond lengths [Å] and angles [°] for 71a_re_a.

N(1)-C(12)	1.339(3)
N(1)-N(2)	1.350(2)
N(1)-C(11)	1.458(2)
C(1)-O(1)	1.453(3)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
O(1)-C(2)	1.330(3)
O(2)-C(2)	1.205(3)
N(2)-C(14)	1.329(3)
C(2)-C(3)	1.465(3)
C(5)-C(6)	1.402(3)
C(5)-C(10)	1.412(3)
C(5)-C(4)	1.472(3)
C(4)-C(3)	1.317(3)
C(4)-H(4)	0.9500
C(3)-H(3)	0.9500
C(8)-C(7)	1.377(3)
C(8)-C(9)	1.386(3)
C(8)-H(8)	0.9500
C(7)-C(6)	1.383(3)
C(7)-H(7)	0.9500
C(6)-H(6)	0.9500
C(9)-C(10)	1.388(3)
C(9)-H(9)	0.9500
C(10)-C(11)	1.520(3)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-C(13)	1.365(3)
C(12)-H(12)	0.9500
C(13)-C(14)	1.379(3)
C(13)-H(13)	0.9500
C(14)-H(14)	0.9500

C(12)-N(1)-N(2)	112.02(17)
C(12)-N(1)-C(11)	126.97(19)
N(2)-N(1)-C(11)	120.90(17)
O(1)-C(1)-H(1A)	109.5
O(1)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
O(1)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
C(2)-O(1)-C(1)	117.52(19)
C(14)-N(2)-N(1)	103.87(18)
O(2)-C(2)-O(1)	121.9(2)
O(2)-C(2)-C(3)	124.9(2)
O(1)-C(2)-C(3)	113.21(18)
C(6)-C(5)-C(10)	118.14(19)
C(6)-C(5)-C(4)	121.30(19)
C(10)-C(5)-C(4)	120.56(18)
C(3)-C(4)-C(5)	127.0(2)
C(3)-C(4)-H(4)	116.5
C(5)-C(4)-H(4)	116.5
C(4)-C(3)-C(2)	124.9(2)
C(4)-C(3)-H(3)	117.6
C(2)-C(3)-H(3)	117.6
C(7)-C(8)-C(9)	119.8(2)
C(7)-C(8)-H(8)	120.1
C(9)-C(8)-H(8)	120.1
C(8)-C(7)-C(6)	119.9(2)
C(8)-C(7)-H(7)	120.1
C(6)-C(7)-H(7)	120.1
C(7)-C(6)-C(5)	121.5(2)
C(7)-C(6)-H(6)	119.3
C(5)-C(6)-H(6)	119.3
C(8)-C(9)-C(10)	121.3(2)
C(8)-C(9)-H(9)	119.4
C(10)-C(9)-H(9)	119.4
C(9)-C(10)-C(5)	119.41(18)

C(9)-C(10)-C(11)	120.81(18)
C(5)-C(10)-C(11)	119.78(17)
N(1)-C(11)-C(10)	113.78(16)
N(1)-C(11)-H(11A)	108.8
C(10)-C(11)-H(11A)	108.8
N(1)-C(11)-H(11B)	108.8
C(10)-C(11)-H(11B)	108.8
H(11A)-C(11)-H(11B)	107.7
N(1)-C(12)-C(13)	107.2(2)
N(1)-C(12)-H(12)	126.4
C(13)-C(12)-H(12)	126.4
C(12)-C(13)-C(14)	104.6(2)
C(12)-C(13)-H(13)	127.7
C(14)-C(13)-H(13)	127.7
N(2)-C(14)-C(13)	112.3(2)
N(2)-C(14)-H(14)	123.9
C(13)-C(14)-H(14)	123.9

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x 10^3$) for 71a_re_a. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	45(1)	49(1)	50(1)	4(1)	-22(1)	-18(1)
C(1)	81(2)	103(2)	84(2)	-39(2)	-18(2)	-26(2)
O(1)	54(1)	99(1)	82(1)	-39(1)	-14(1)	-17(1)
O(2)	50(1)	85(1)	93(1)	-18(1)	-14(1)	-2(1)
N(2)	56(1)	52(1)	68(1)	13(1)	-27(1)	-23(1)
C(2)	45(1)	51(1)	66(1)	4(1)	-15(1)	-13(1)
C(5)	45(1)	49(1)	49(1)	9(1)	-21(1)	-24(1)
C(4)	44(1)	53(1)	59(1)	4(1)	-22(1)	-20(1)
C(3)	46(1)	62(2)	63(1)	2(1)	-22(1)	-19(1)
C(8)	72(2)	76(2)	52(1)	0(1)	-28(1)	-40(1)
C(7)	68(2)	86(2)	63(1)	15(1)	-39(1)	-45(1)
C(6)	48(1)	66(2)	66(1)	12(1)	-29(1)	-26(1)
C(9)	50(1)	60(1)	50(1)	0(1)	-20(1)	-22(1)
C(10)	44(1)	49(1)	43(1)	7(1)	-19(1)	-22(1)
C(11)	43(1)	59(1)	47(1)	-4(1)	-19(1)	-15(1)
C(12)	54(1)	57(1)	63(1)	16(1)	-25(1)	-26(1)
C(13)	45(1)	66(2)	62(1)	4(1)	-15(1)	-20(1)
C(14)	53(1)	49(1)	73(2)	0(1)	-25(1)	-14(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10 ^{3}) for 71a_re_a.

	x	y	z	U(eq)
H(1A)	6705	-1125	661	150
H(1B)	8664	-2436	756	150
H(1C)	8468	-786	-69	150
H(4)	5094	1863	4240	63
H(3)	8618	633	4218	73
H(8)	3014	5945	9361	77
H(7)	6136	3733	8510	78
H(6)	7461	1924	6374	70
H(9)	1186	6277	8116	67
H(11A)	2517	4837	4733	64
H(11B)	2088	3378	5543	64
H(12)	-1198	4486	7903	71
H(13)	-4167	7348	8730	76
H(14)	-3293	9400	7229	76

Table 6. Torsion angles [°] for 71a_re_a.

C(12)-N(1)-N(2)-C(14)	-0.7(2)
C(11)-N(1)-N(2)-C(14)	-177.14(18)
C(1)-O(1)-C(2)-O(2)	-2.8(4)
C(1)-O(1)-C(2)-C(3)	177.8(2)
C(6)-C(5)-C(4)-C(3)	-10.8(3)
C(10)-C(5)-C(4)-C(3)	168.8(2)
C(5)-C(4)-C(3)-C(2)	-178.8(2)
O(2)-C(2)-C(3)-C(4)	177.9(2)
O(1)-C(2)-C(3)-C(4)	-2.8(3)
C(9)-C(8)-C(7)-C(6)	1.3(4)
C(8)-C(7)-C(6)-C(5)	-1.4(3)
C(10)-C(5)-C(6)-C(7)	0.2(3)
C(4)-C(5)-C(6)-C(7)	179.8(2)
C(7)-C(8)-C(9)-C(10)	0.1(3)
C(8)-C(9)-C(10)-C(5)	-1.3(3)
C(8)-C(9)-C(10)-C(11)	179.69(19)
C(6)-C(5)-C(10)-C(9)	1.1(3)
C(4)-C(5)-C(10)-C(9)	-178.45(18)
C(6)-C(5)-C(10)-C(11)	-179.83(18)
C(4)-C(5)-C(10)-C(11)	0.6(3)
C(12)-N(1)-C(11)-C(10)	-83.7(3)
N(2)-N(1)-C(11)-C(10)	92.2(2)
C(9)-C(10)-C(11)-N(1)	-7.5(3)
C(5)-C(10)-C(11)-N(1)	173.51(18)
N(2)-N(1)-C(12)-C(13)	0.8(2)
C(11)-N(1)-C(12)-C(13)	176.96(19)
N(1)-C(12)-C(13)-C(14)	-0.5(3)
N(1)-N(2)-C(14)-C(13)	0.4(3)
C(12)-C(13)-C(14)-N(2)	0.1(3)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for 71a_re_a [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

Crystal refinement data for compound 4a: Empirical Formula- $C_{18} H_{16} N_2 O_2$, M = 292.33, Triclinic, Space group P-1, a = 7.423(5) Å, b = 10.929(7) Å, c = 10.931(7) Å, V = 730.2(8) Å^3, Z = 2, T = 173(2) K, ρ_{calcd} = 1.330 Mg/m^3, $2\Theta_{max.}$ = 25.24^0, Refinement of 200 parameters on 3554 independent reflections out of 16840 collected reflections (R_{int} = 0.0512) led to R_1 = 0.0576 [I >2σ(I)], wR_2 = 0.1104 (all data) and S = 1.062 with the largest difference peak and hole of 0.196 and -0.216 e.Å^{-3} respectively. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (CCDC 1944054). The data can be obtained free of charge via the Internet at www.ccdc.cam.ac.uk/data_request/cif.

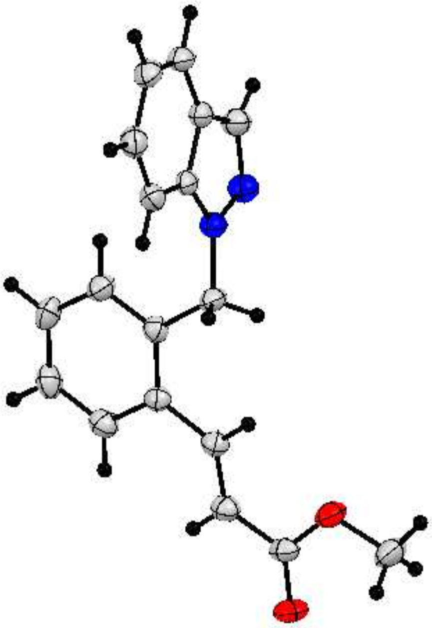


Figure S2. X-ray Structure of compound **4a**.

Table 1. Crystal data and structure refinement for 105_re_a.

Identification code	105_re_a	
Empirical formula	$C_{18} H_{16} N_2 O_2$	
Formula weight	292.33	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.423(5) Å	α= 106.755(4)°.
	b = 10.929(7) Å	β= 107.442(4)°.
	c = 10.931(7) Å	γ = 108.018(4)°.
Volume	730.2(8) Å^3	
Z	2	
Density (calculated)	1.330 Mg/m^3	
Absorption coefficient	0.088 mm^{-1}	
F(000)	308	
Crystal size	0.200 x 0.150 x 0.120 mm^3	
Theta range for data collection	2.979 to 28.489°.	
Index ranges	-9<=h<=9, -14<=k<=14, -14<=l<=14	
Reflections collected	16840	
Independent reflections	3454 [R(int) = 0.0512]	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6159	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3454 / 0 / 200	
Goodness-of-fit on F^2	1.062	
Final R indices [I>2sigma(I)]	R1 = 0.0576, wR2 = 0.1104	
R indices (all data)	R1 = 0.1008, wR2 = 0.1248	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.196 and -0.216 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for 105_re_a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	4932(2)	5852(1)	1751(1)	45(1)
C(1)	2579(3)	3092(2)	210(2)	46(1)
N(1)	7609(2)	1658(1)	6084(1)	32(1)
N(2)	9099(2)	1287(2)	5814(2)	38(1)
O(2)	4081(2)	3656(1)	1663(1)	39(1)
C(2)	5184(3)	5076(2)	2318(2)	32(1)
C(5)	8380(2)	5186(2)	5906(2)	28(1)
C(4)	6882(3)	4755(2)	4451(2)	31(1)
C(3)	6718(3)	5584(2)	3777(2)	33(1)
C(7)	11164(3)	7032(2)	8162(2)	38(1)
C(6)	9761(3)	6617(2)	6789(2)	36(1)
C(8)	11247(3)	6027(2)	8681(2)	38(1)
C(9)	9915(3)	4612(2)	7827(2)	34(1)
C(10)	8471(3)	4171(2)	6445(2)	28(1)
C(11)	6999(3)	2602(2)	5535(2)	34(1)
C(12)	6897(3)	1039(2)	6875(2)	29(1)
C(13)	5401(3)	1114(2)	7385(2)	34(1)
C(14)	5013(3)	322(2)	8132(2)	39(1)
C(15)	6068(3)	-522(2)	8382(2)	38(1)
C(16)	7552(3)	-579(2)	7896(2)	35(1)
C(17)	7991(3)	212(2)	7121(2)	31(1)
C(18)	9326(3)	426(2)	6431(2)	37(1)

Table 3. Bond lengths [Å] and angles [°] for 105_re_a.

O(1)-C(2)	1.2128(19)
C(1)-O(2)	1.447(2)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
N(1)-C(12)	1.370(2)
N(1)-N(2)	1.370(2)
N(1)-C(11)	1.454(2)
N(2)-C(18)	1.328(2)
O(2)-C(2)	1.346(2)
C(2)-C(3)	1.470(2)
C(5)-C(6)	1.405(2)
C(5)-C(10)	1.407(2)
C(5)-C(4)	1.474(2)
C(4)-C(3)	1.333(2)
C(4)-H(4)	0.9500
C(3)-H(3)	0.9500
C(7)-C(8)	1.383(3)
C(7)-C(6)	1.386(2)
C(7)-H(7)	0.9500
C(6)-H(6)	0.9500
C(8)-C(9)	1.381(2)
C(8)-H(8)	0.9500
C(9)-C(10)	1.397(2)
C(9)-H(9)	0.9500
C(10)-C(11)	1.526(2)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-C(13)	1.397(3)
C(12)-C(17)	1.418(2)
C(13)-C(14)	1.375(2)
C(13)-H(13)	0.9500
C(14)-C(15)	1.415(3)
C(14)-H(14)	0.9500

C(15)-C(16)	1.369(3)
C(15)-H(15)	0.9500
C(16)-C(17)	1.409(2)
C(16)-H(16)	0.9500
C(17)-C(18)	1.419(3)
C(18)-H(18)	0.9500
O(2)-C(1)-H(1A)	109.5
O(2)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
O(2)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
C(12)-N(1)-N(2)	111.56(13)
C(12)-N(1)-C(11)	129.10(15)
N(2)-N(1)-C(11)	119.34(14)
C(18)-N(2)-N(1)	106.03(14)
C(2)-O(2)-C(1)	115.83(13)
O(1)-C(2)-O(2)	122.96(16)
O(1)-C(2)-C(3)	123.68(16)
O(2)-C(2)-C(3)	113.36(13)
C(6)-C(5)-C(10)	118.27(15)
C(6)-C(5)-C(4)	120.94(15)
C(10)-C(5)-C(4)	120.79(15)
C(3)-C(4)-C(5)	127.16(16)
C(3)-C(4)-H(4)	116.4
C(5)-C(4)-H(4)	116.4
C(4)-C(3)-C(2)	124.12(16)
C(4)-C(3)-H(3)	117.9
C(2)-C(3)-H(3)	117.9
C(8)-C(7)-C(6)	119.99(16)
C(8)-C(7)-H(7)	120.0
C(6)-C(7)-H(7)	120.0
C(7)-C(6)-C(5)	121.32(16)
C(7)-C(6)-H(6)	119.3
C(5)-C(6)-H(6)	119.3
C(9)-C(8)-C(7)	119.61(16)

C(9)-C(8)-H(8)	120.2
C(7)-C(8)-H(8)	120.2
C(8)-C(9)-C(10)	121.40(16)
C(8)-C(9)-H(9)	119.3
C(10)-C(9)-H(9)	119.3
C(9)-C(10)-C(5)	119.40(15)
C(9)-C(10)-C(11)	120.16(14)
C(5)-C(10)-C(11)	120.44(14)
N(1)-C(11)-C(10)	113.93(14)
N(1)-C(11)-H(11A)	108.8
C(10)-C(11)-H(11A)	108.8
N(1)-C(11)-H(11B)	108.8
C(10)-C(11)-H(11B)	108.8
H(11A)-C(11)-H(11B)	107.7
N(1)-C(12)-C(13)	131.20(15)
N(1)-C(12)-C(17)	106.34(15)
C(13)-C(12)-C(17)	122.45(15)
C(14)-C(13)-C(12)	116.41(16)
C(14)-C(13)-H(13)	121.8
C(12)-C(13)-H(13)	121.8
C(13)-C(14)-C(15)	122.29(18)
C(13)-C(14)-H(14)	118.9
C(15)-C(14)-H(14)	118.9
C(16)-C(15)-C(14)	121.19(17)
C(16)-C(15)-H(15)	119.4
C(14)-C(15)-H(15)	119.4
C(15)-C(16)-C(17)	118.31(16)
C(15)-C(16)-H(16)	120.8
C(17)-C(16)-H(16)	120.8
C(16)-C(17)-C(12)	119.33(16)
C(16)-C(17)-C(18)	136.34(16)
C(12)-C(17)-C(18)	104.32(15)
N(2)-C(18)-C(17)	111.74(16)
N(2)-C(18)-H(18)	124.1
C(17)-C(18)-H(18)	124.1

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for 105_re_a. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	63(1)	45(1)	46(1)	33(1)	24(1)	33(1)
C(1)	50(1)	53(1)	32(1)	23(1)	10(1)	21(1)
N(1)	37(1)	27(1)	31(1)	14(1)	10(1)	13(1)
N(2)	41(1)	37(1)	38(1)	19(1)	17(1)	17(1)
O(2)	43(1)	37(1)	33(1)	21(1)	9(1)	15(1)
C(2)	38(1)	36(1)	37(1)	23(1)	20(1)	21(1)
C(5)	29(1)	27(1)	29(1)	13(1)	13(1)	11(1)
C(4)	33(1)	27(1)	33(1)	14(1)	14(1)	12(1)
C(3)	37(1)	29(1)	37(1)	18(1)	17(1)	15(1)
C(7)	36(1)	27(1)	34(1)	4(1)	10(1)	5(1)
C(6)	39(1)	27(1)	40(1)	15(1)	16(1)	13(1)
C(8)	34(1)	39(1)	26(1)	8(1)	6(1)	10(1)
C(9)	36(1)	34(1)	30(1)	16(1)	11(1)	14(1)
C(10)	28(1)	26(1)	28(1)	11(1)	12(1)	10(1)
C(11)	40(1)	28(1)	28(1)	15(1)	6(1)	12(1)
C(12)	34(1)	21(1)	22(1)	7(1)	5(1)	7(1)
C(13)	39(1)	27(1)	31(1)	9(1)	10(1)	15(1)
C(14)	45(1)	35(1)	33(1)	12(1)	18(1)	16(1)
C(15)	48(1)	34(1)	30(1)	17(1)	16(1)	14(1)
C(16)	43(1)	29(1)	31(1)	15(1)	9(1)	15(1)
C(17)	34(1)	25(1)	26(1)	9(1)	6(1)	10(1)
C(18)	39(1)	35(1)	38(1)	18(1)	13(1)	17(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 105_re_a.

	x	y	z	U(eq)
H(1A)	1835	2059	-161	69
H(1B)	3314	3334	-358	69
H(1C)	1571	3502	163	69
H(4)	5929	3780	3937	37
H(3)	7652	6564	4272	39
H(7)	12068	8008	8747	46
H(6)	9733	7314	6438	43
H(8)	12214	6307	9620	45
H(9)	9983	3925	8186	41
H(11A)	5571	2442	5450	41
H(11B)	6943	2356	4574	41
H(13)	4690	1680	7225	41
H(14)	4001	343	8492	46
H(15)	5740	-1058	8896	45
H(16)	8267	-1138	8077	42
H(18)	10267	5	6412	45

Table 6. Torsion angles [°] for 105_re_a.

C(12)-N(1)-N(2)-C(18)	0.21(17)
C(11)-N(1)-N(2)-C(18)	-179.73(14)
C(1)-O(2)-C(2)-O(1)	1.2(2)
C(1)-O(2)-C(2)-C(3)	-178.56(14)
C(6)-C(5)-C(4)-C(3)	4.3(3)
C(10)-C(5)-C(4)-C(3)	-175.34(17)
C(5)-C(4)-C(3)-C(2)	179.78(16)
O(1)-C(2)-C(3)-C(4)	173.91(18)
O(2)-C(2)-C(3)-C(4)	-6.4(2)
C(8)-C(7)-C(6)-C(5)	1.1(3)
C(10)-C(5)-C(6)-C(7)	-0.8(3)
C(4)-C(5)-C(6)-C(7)	179.51(16)
C(6)-C(7)-C(8)-C(9)	-0.5(3)
C(7)-C(8)-C(9)-C(10)	-0.3(3)
C(8)-C(9)-C(10)-C(5)	0.5(3)
C(8)-C(9)-C(10)-C(11)	-179.13(16)
C(6)-C(5)-C(10)-C(9)	0.0(2)
C(4)-C(5)-C(10)-C(9)	179.69(15)
C(6)-C(5)-C(10)-C(11)	179.68(15)
C(4)-C(5)-C(10)-C(11)	-0.6(2)
C(12)-N(1)-C(11)-C(10)	97.4(2)
N(2)-N(1)-C(11)-C(10)	-82.63(19)
C(9)-C(10)-C(11)-N(1)	-15.0(2)
C(5)-C(10)-C(11)-N(1)	165.35(15)
N(2)-N(1)-C(12)-C(13)	-179.76(16)
C(11)-N(1)-C(12)-C(13)	0.2(3)
N(2)-N(1)-C(12)-C(17)	-0.32(17)
C(11)-N(1)-C(12)-C(17)	179.62(14)
N(1)-C(12)-C(13)-C(14)	178.51(16)
C(17)-C(12)-C(13)-C(14)	-0.9(2)
C(12)-C(13)-C(14)-C(15)	0.3(2)
C(13)-C(14)-C(15)-C(16)	0.6(3)
C(14)-C(15)-C(16)-C(17)	-0.8(2)
C(15)-C(16)-C(17)-C(12)	0.2(2)

C(15)-C(16)-C(17)-C(18)	-178.60(19)
N(1)-C(12)-C(17)-C(16)	-178.85(14)
C(13)-C(12)-C(17)-C(16)	0.7(2)
N(1)-C(12)-C(17)-C(18)	0.29(17)
C(13)-C(12)-C(17)-C(18)	179.79(15)
N(1)-N(2)-C(18)-C(17)	-0.02(19)
C(16)-C(17)-C(18)-N(2)	178.74(18)
C(12)-C(17)-C(18)-N(2)	-0.17(19)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for 105_re_a [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)