Electronic Supplementary Material (ESI) for ChemComm.

Ruthenium-Catalyzed *ortho* Alkenylation of Aromatic Nitriles with Activated Alkenes via C-H Bond Activation

Mallu Chenna Reddy and Masilamani Jeganmohan*

Department of Chemistry, Indian Institute of Science Education and Research, Pune 411021, India

Email: mjeganmohan@iiserpune.ac.in

Electronic Supplementary Information (ESI)

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General Procedure for the Coupling of Aromatic Nitriles with Alkenes Catalyzed by Ruthenium Complex.

Substituted nitriles **1** (75 mg, 1.0 equiv), [{$RuCl_2$(*p*-cymene)}$_2$] (5 mol %), AgOAc (2.0 equiv), $AgSbF_6$ (20 mol %) were taken in a 15-mL pressure tube equipped with a magnetic stirrer and septum. (Note: $AgSbF_6$ and AgOAc are moisture sensitive. Thus, $AgSbF_6$ and AgOAc were taken inside the nitrogen glove box). The tube was evacuated and purged with nitrogen gas three times. To the tube were then added liquid alkenes **2** (4.0 equiv), if nitrile **1** is liquid (75 mg, 1.0 equiv), dry acetic acid solvent (3.0 mL) via syringes, allowed the reaction mixture to stir at room temperature for few seconds and again the tube was evacuated and purged with nitrogen gas three times. Then, the septum was taken out and immediately a screw cap was used to cover the tube. Then, the reaction mixture was allowed to stir at 120 °C for 14 h. After cooling to ambient temperature, the reaction mixture was diluted with CH_2Cl_2, filtered through Celite and silica gel, and the filtrate was concentrated. The crude residue was purified through a silica gel column using hexanes and ethyl acetate as eluent to give pure **4**.

Note: For the preparation of compounds **4bi** AcOH solvent (3.0 mL) was not used. Instead, 1,2-dichloroethane (3.0 mL) and pivalic acid (0.5 mL) were added. 2.0 equiv of phenyl vinyl sulfone (**2i**) was used.

Note: Dry AcOH solvent is crucial for the reaction. If AcOH is contaminated with water, the yield of alkenylation product **4** was decreased and benzamide formation **3** is increased. Thus, Dry AcOH is crucial in order to get the more yield of **4**.

Note: For the preparation of compounds **4ka**, **4ma**, **4nb**, **4oa** and **4og**, the reaction was done for 16 h.

General Procedure for the Coupling of Heteroaromatic Nitriles with Alkenes Catalyzed by Ruthenium Complex.

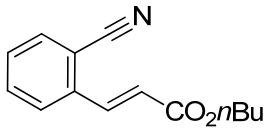
[{$RuCl_2$(*p*-cymene)}$_2$] (5 mol %), $Cu(OAc)_2{\cdot}H_2O$ (1.0 equiv), $AgSbF_6$ (20 mol %) were taken in a 15-mL pressure tube equipped with a magnetic stirrer and septum. (Note: $AgSbF_6$ is moisture sensitive. Thus, $AgSbF_6$ was taken inside the nitrogen glove box). The tube was evacuated and purged with nitrogen gas three times. To the tube were then added liquid alkenes **2** (6.0 equiv), heteroaromatic nitrile **1** (75 mg, 1.0 equiv), 1,2-dichloroethane (1.5 mL) and dry acetic acid (1.5 mL) via syringes, allowed the reaction mixture to stir at room

temperature for few seconds and again the tube was evacuated and purged with nitrogen gas three times. Then, the septum was taken out and immediately a screw cap was used to cover the tube. Then, the reaction mixture was allowed to stir at 120 °C for 16 h. After cooling to ambient temperature, the reaction mixture was diluted with CH_2Cl_2, filtered through Celite and silica gel, and the filtrate was concentrated. The crude residue was purified through a silica gel column using hexanes and ethyl acetate as eluent to give pure **5**.

The same procedure was used for synthesizing compound **4pa,** but the solvent is only 1,2-dichloroethane (3.0 mL) and pivalic acid (0.5 mL) and no AcOH was added. In addition, the oxidant is AgOAc (2.0 equiv) instead of $Cu(OAc)_2 \cdot H_2O$.

Spectral Data of all Compounds

Butyl (*E*)-3-(2-cyanophenyl)acrylate (4aa).



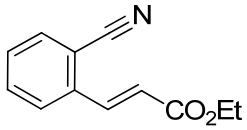
Orange oil; eluent (15% ethyl acetate in hexanes). The reaction scale is 75 mg, 126 mg of **4aa** was isolated and yield is 75%. The reaction was done for 14 h at 120 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.94 (d, *J* = 16.0 Hz, 1 H), 7.72 (d, *J* = 7.6 Hz, 1 H), 7.68 (d, *J* = 7.6 Hz, 1 H), 7.61 (t, *J* = 7.6 Hz, 1 H), 7.46 (t, *J* = 7.6 Hz, 1 H), 6.59 (d, *J* = 16.0 Hz, 1 H), 4.21 (t, *J* = 6.4 Hz, 2 H), 1.71 - 1.64 (m, 2 H), 1.46 - 1.37 (m, 2 H), 0.94 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.8, 139.2, 137.2, 133.4, 132.9, 129.9, 126.9, 122.9, 116.9, 112.5, 64.7, 30.5, 19.0, 13.6.

HRMS (ESI): calc. for [($C_{14}H_{15}NO_2$)Na] (M+Na) 252.1000, measured 252.0998.

Ethyl (*E*)-3-(2-cyanophenyl)acrylate (4ab).



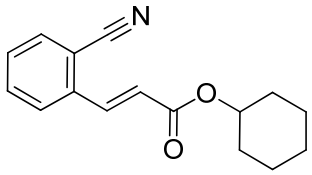
White solid; eluent (15% ethyl acetate in hexanes). The reaction scale is 75 mg, 94mg of **4ab** was isolated and yield is 64%. The reaction was done for 14 h at 120 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.91 (d, *J* = 16.0 Hz, 1 H), 7.70 (d, *J* = 7.8 Hz, 1 H), 7.66 (d, *J* = 7.8 Hz, 1 H), 7.60 (t, *J* = 7.8 Hz, 1 H), 7.45 (t, *J* = 7.8 Hz, 1 H), 6.57 (d, *J* = 16.0 Hz, 1 H), 4.21 (q, *J* = 7.2 Hz, 2 H), 0.94 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.6, 139.1, 137.1, 133.3, 132.9, 129.9, 126.8, 122.9, 116.9, 112.4, 60.8, 14.1.

HRMS (ESI): calc. for [($C_{12}H_{11}NO_2$)Na] (M+Na) 224.0687, measured 224.0685.

Cyclohexyl (*E*)-3-(2-cyanophenyl)acrylate (4ac).



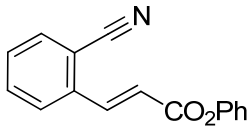
Colorless oil; eluent (15% ethyl acetate in hexanes). The reaction scale is 75 mg, 147 mg of **4ac** was isolated and yield is 79%. The reaction was done for 14 h at 120 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.93 (d, *J* = 16.0 Hz, 1 H), 7.72 – 7.58 (m, 4 H), 7.45 (t, *J* = 7.6 Hz, 1 H), 4.92 – 4.85 (m, 1 H), 1.92 – 1.73 (m, 4 H), 1.56 – 1.22 (m, 6 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.2, 138.9, 137.5, 133.5, 132.9, 129.9, 126.9, 123.7, 117.1, 112.6, 73.3, 31.6, 25.33, 23.7.

HRMS (ESI): calc. for [($C_{16}H_{17}NO_2$)Na] (M+Na) 278.1157, measured 278.1157.

Phenyl (*E*)-3-(2-cyanophenyl)acrylate (4ad).



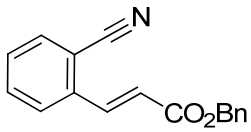
White solid; eluent (15% ethyl acetate in hexanes). The reaction scale is 75 mg, 125 mg of **4ad** was isolated and yield is 69%. The reaction was done for 14 h at 120 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.16 (d, *J* = 16.0 Hz, 1 H), 7.80 (d, *J* = 8.0 Hz, 1 H), 7.74 (d, *J* = 7.6 Hz, 1 H), 7.66 (t, *J* = 8.0 Hz, 1 H), 7.52 (t, *J* = 7.6 Hz, 1 H), 7.44 – 7.39 (m, 2 H), 7.28 - 7.17 (m, 3 H), 6.81 (d, *J* = 16.0 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.2, 150.6, 141.1, 137.0, 133.6, 133.0, 130.4, 129.4, 127.3, 125.9, 122.3, 121.5, 117.0, 112.9.

HRMS (ESI): calc. for [($C_{16}H_{11}NO_2$)Na] (M+Na) 272.0687, measured 272.0693.

Benzyl (*E*)-3-(2-cyanophenyl)acrylate (4ae).



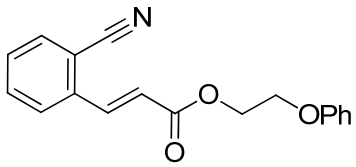
Colorless oil; eluent (15% ethyl acetate in hexanes). The reaction scale is 75 mg, 129 mg of **4ae** was isolated and yield is 67%. The reaction was done for 14 h at 120 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.03 (d, *J* = 16.0 Hz, 1 H), 7.74 – 7.70 (m, 2 H), 7.62 (t, *J* = 7.6 Hz, 1 H), 7.50 – 7.33 (m, 6 H), 6.66 (d, *J* = 16.0 Hz, 1 H), 5.29 (s, 2 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.6, 139.9, 137.3, 135.7, 133.5, 132.9, 130.1, 128.6, 128.3, 128.3, 127.0, 122.8, 117.0, 112.8, 66.7.

HRMS (ESI): calc. for [($C_{17}H_{13}NO_2$)Na] (M+Na) 286.0844, measured 286.0851.

2-Phenoxyethyl (*E*)-3-(2-cyanophenyl)acrylate (4af).



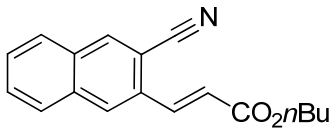
Light greenish color oil; eluent (20% ethyl acetate in hexanes). The reaction scale is 75 mg, 126 mg of **4af** was isolated and yield is 59%. The reaction was done for 14 h at 120 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.02 (d, *J* = 15.6 Hz, 1 H), 7.74 – 7.70 (m, 2 H), 7.63 (t, *J* = 8.0 Hz, 1 H), 7.49 (t, *J* = 8.0 Hz, 1 H), 7.33 – 7.29 (m, 2 H), 7.00 – 6.92 (m, 3 H), 6.66 (d, *J* = 15.6 Hz, 1 H), 4.60 (t, *J* = 4.8 Hz, 2 H), 4.27 (t, *J* = 4.8 Hz, 2 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.7, 158.4, 140.1, 137.2, 133.5, 132.9, 130.1, 129.5, 127.0, 122.5, 121.2, 116.9, 114.7, 112.8, 65.8, 63.3.

HRMS (ESI): calc. for [($C_{18}H_{15}NO_3$)Na] (M+Na) 316.0950, measured 316.0962.

Butyl (*E*)-3-(3-cyanonaphthalen-2-yl)acrylate (4ba).



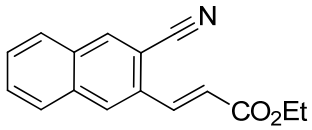
Light yellow semisolid; eluent (15% ethyl acetate in hexanes). The reaction scale is 75 mg, 102 mg of **4ba** was isolated and yield is 75%. The reaction was done for 14 h at 120 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.28 (s, 1 H), 8.16 (s, 1 H), 8.06 (d, *J* = 16.0 Hz, 1 H), 7.90 (t, *J* = 7.6 Hz, 2 H), 7.70 – 7.61 (m, 2 H), 6.76 (d, *J* = 16.0 Hz, 1 H), 4.26 (t, *J* = 6.8 Hz, 2 H), 1.76 - 1.69 (m, 2 H), 1.51 - 1.42 (m, 2 H), 0.98 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.1, 139.9, 135.8, 134.4, 132.4, 131.6, 129.7, 128.6, 128.6, 128.2, 127.8, 122.4, 117.6, 109.4, 64.8, 30.7, 19.2, 13.7.

HRMS (ESI): calc. for $[C_{18}H_{17}NO_2)H]$ (M+H) 280.1338, measured 280.1337.

Ethyl (*E*)-3-(3-cyanonaphthalen-2-yl)acrylate (4bb).



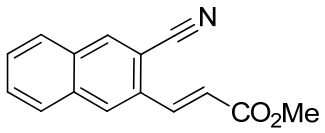
White semisolid; eluent (15% ethyl acetate in hexanes). The reaction scale is 75 mg, 80 mg of **4bb** was isolated and yield is 65%. The reaction was done for 14 h at 120 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.29 (s, 1 H), 8.16 (s, 1 H), 8.06 (d, *J* = 16.0 Hz, 1 H), 7.90 (t, *J* = 7.6 Hz, 2 H), 7.70 – 7.62 (m, 2 H), 6.76 (d, *J* = 16.0 Hz, 1 H), 4.32 (q, *J* = 7.2 Hz, 2 H), 1.37 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.1, 139.9, 135.9, 134.4, 132.4, 131.6, 129.7, 128.64, 128.59, 128.2, 127.8, 122.4, 117.7, 109.4, 60.9, 14.3.

HRMS (ESI): calc. for $[(C_{16}H_{13}NO_2)H]$ (M+H) 252.1025, measured 252.1025.

Methyl (*E*)-3-(3-cyanonaphthalen-2-yl)acrylate (4bg).



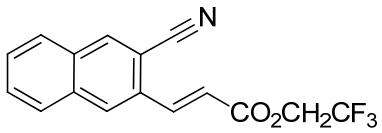
Colorless solid; eluent (25% ethyl acetate in hexanes). The reaction scale is 75 mg, 72mg of **4bg** was isolated and yield is 62%. The reaction was done for 14 h at 120 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.23 (s, 1 H), 8.12 (s, 1 H), 8.04 (d, *J* = 16.0 Hz, 1 H), 7.87 (t, *J* = 8.0 Hz, 2 H), 7.68 – 7.60 (m, 2 H), 6.73 (d, *J* = 16.0 Hz, 1 H), 3.84 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.4, 140.1, 135.7, 134.2, 132.3, 131.3, 129.7, 128.62, 128.5, 128.1, 127.7, 121.8, 117.5, 109.3, 51.9.

HRMS (ESI): calc. for [($C_{15}H_{11}NO_2$)Na] (M+Na) 260.0687, measured 260.0690.

2,2,2-Trifluoroethyl (*E*)-3-(3-cyanonaphthalen-2-yl)acrylate (4bh).



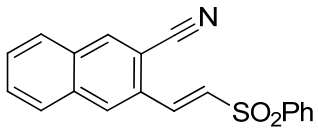
Colorless semisolid; eluent (20% ethyl acetate in hexanes). The reaction scale is 75 mg, 86 mg of **4bh** was isolated and yield is 57%. The reaction was done for 14 h at 120 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.28 (s, 1 H), 8.18 (s, 1 H), 8.15 (d, *J* = 16.0 Hz, 1 H), 7.91 (t, *J* = 8.4 Hz, 2 H), 7.72 – 7.64 (m, 2 H), 6.82 (d, *J* = 16.0 Hz, 1 H), 4.65 (q, *J* = 8.4 Hz, 2 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.3, 142.4, 135.9, 134.2, 132.6, 130.8, 129.9, 129.0, 128.7, 128.3, 128.2, 122.94 (q, *J* = 276 Hz, CH_2 of –O-CH_2-CF_3), 119.8, 117.4, 109.3, 60.55 (q, *J* = 36 Hz, CF_3 of –O-CH_2-CF_3).

HRMS (ESI): calc. for [($C_{16}H_{10}F_3NO_2$)Na] (M+Na) 328.0561, measured 328.0570.

(*E*)-3-(2-(Phenylsulfonyl)vinyl)-2-naphthonitrile (4bi).



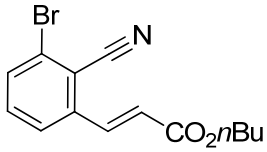
Light yellow semisolid; eluent (40% ethyl acetate in hexanes). The reaction scale is 75 mg, 81 mg of **4bi** was isolated and yield is 52%. The reaction was done for 14 h at 120 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.30 (s, 1 H), 8.10 (s, 1 H), 8.04 – 8.00 (m, 3 H), 7.91 – 7.89 (m, 2 H), 7.73 – 7.65 (m, 3 H), 7.62 – 7.56 (m, 2 H), 7.32 (d, *J* = 15.2 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.1, 138.1, 136.3, 134.2, 133.7, 132.7, 131.5, 130.1, 129.7, 129.5, 129.3, 129.3, 128.7, 128.3, 127.9, 117.4, 108.9.

HRMS (ESI): calc. for [($C_{19}H_{13}NO_2S$)H] (M+H) 320.0745, measured 320.0740.

Butyl (*E*)-3-(3-bromo-2-cyanophenyl)acrylate (4ca).



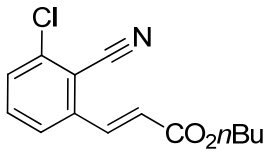
Light yellow semisolid; eluent (12% ethyl acetate in hexanes). The reaction scale is 75 mg, 65 mg of **4ca** was isolated and yield is 51%. The reaction was done for 14 h at 120 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.95 (d, *J* = 16.0 Hz, 1 H), 7.71 – 7.66 (m, 2 H), 7.47 (t, *J* = 7.6 Hz, 1 H), 6.59 (d, *J* = 16.0 Hz, 1 H), 4.25 (t, *J* = 6.8 Hz, 2 H), 1.74 - 1.67 (m, 2 H), 1.49 - 1.40 (m, 2 H), 0.97 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.5, 140.1, 138.8, 133.8, 133.5, 126.7, 125.4, 124.4, 115.8, 115.4, 65.0, 30.6, 19.1, 13.7.

HRMS (ESI): calc. for [($C_{14}H_{14}BrNO_2$)Na] (M+Na) 330.0106, measured 330.0110.

Butyl (*E*)-3-(3-chloro-2-cyanophenyl)acrylate (4da).



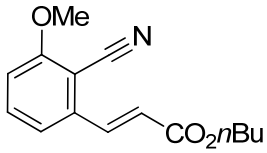
Light yellow oil; eluent (15% ethyl acetate in hexanes). The reaction scale is 75 mg, 72 mg of **4da** was isolated and yield is 50%. The reaction was done for 14 h at 120 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.94 (d, *J* = 16.0 Hz, 1 H), 7.63 (dd, *J* = 7.6, 2.0 Hz, 1 H), 7.57 – 7.53 (m, 2 H), 6.61 (d, *J* = 16.0 Hz, 1 H), 4.25 (t, *J* = 6.8 Hz, 2 H), 1.74 - 1.67 (m, 2 H), 1.49 - 1.40 (m, 2 H), 0.97 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.6, 139.8, 138.6, 138.2, 133.4, 130.6, 124.9, 124.5, 114.2, 113.5, 65.1, 30.6, 19.1, 13.7.

HRMS (ESI): calc. for [($C_{14}H_{14}ClNO_2$)Na] (M+Na) 286.0611, measured 286.0612.

Butyl (*E*)-3-(2-cyano-3-methoxyphenyl)acrylate (4ea).



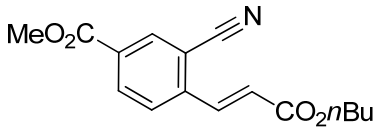
Light yellow oil; eluent (25% ethyl acetate in hexanes). The reaction scale is 75 mg, 69 mg of **4ea** was isolated and yield is 47%. The reaction was done for 14 h at 120 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.91 (d, *J* = 16.0 Hz, 1 H), 7.53 (t, *J* = 8.0 Hz, 1 H), 7.27 (d, *J* = 8.8 Hz, 1 H), 6.98 (d, *J* = 8.4 Hz, 1 H), 6.59 (d, *J* = 16.0 Hz, 1 H), 4.22 (t, *J* = 6.8 Hz, 2 H), 3.95 (s, 3 H), 1.73 - 1.65 (m, 2 H), 1.48 - 1.38 (m, 2 H), 0.96 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.92, 161.97, 139.4, 138.9, 133.9, 123.4, 118.7, 114.5, 111.9, 102.1, 64.8, 56.3, 30.6, 19.1, 13.7.

HRMS (ESI): calc. for [($C_{15}H_{17}NO_3$)Na] (M+Na) 282.1106, measured 282.1108.

Methyl (*E*)-4-(3-butoxy-3-oxoprop-1-en-1-yl)-3-cyanobenzoate (4fa).



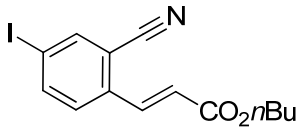
Yellow solid; eluent (20% ethyl acetate in hexanes). The reaction scale is 75 mg, 71 mg of **4fa** was isolated and yield is 53%. The reaction was done for 14 h at 120 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.36 (d, *J* = 1.6 Hz, 1 H), 8.25 (dd, *J* = 8.0, 1.6 Hz, 1 H), 7.97 (d, *J* = 16.0 Hz, 1 H), 7.81 (d, *J* = 8.0 Hz, 1 H), 6.69 (d, *J* = 16.0 Hz, 1 H), 4.25 (t, *J* = 6.8 Hz, 2 H), 3.97 (s, 3 H), 1.74 - 1.67 (m, 2 H), 1.49 - 1.39 (m, 2 H), 0.96 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.4, 164.6, 141.1, 138.2, 134.6, 133.6, 131.6, 127.2, 125.2, 116.2, 112.9, 65.1, 52.8, 30.6, 19.1, 13.7.

HRMS (ESI): calc. for [($C_{16}H_{17}NO_4$)Na] (M+Na) 310.1055, measured 310.1059.

Butyl (*E*)-3-(2-cyano-4-iodophenyl)acrylate (4ga).



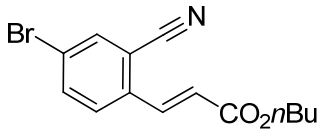
Yellow semisolid; eluent (15% ethyl acetate in hexanes). The reaction scale is 75 mg, 56 mg of **4ga** was isolated and yield is 48%. The reaction was done for 14 h at 120 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.03 (d, *J* = 1.8 Hz, 1 H), 7.94 (dd, *J* = 8.4, 1.8 Hz, 1 H), 7.87 (d, *J* = 15.6 Hz, 1 H), 7.45 (d, *J* = 8.4 Hz, 1 H), 6.62 (d, *J* = 15.6 Hz, 1 H), 4.24 (t, *J* = 6.8 Hz, 2 H), 1.74 - 1.67 (m, 2 H), 1.48 - 1.39 (m, 2 H), 0.97 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.7, 142.1, 141.7, 138.3, 136.8, 128.1, 123.6, 115.5, 114.2, 94.9, 65.0, 30.6, 19.1, 13.7.

HRMS (ESI): calc. for [($C_{14}H_{14}INO_2$)Na] (M+Na) 377.9967, measured 377.9966.

Butyl (*E*)-3-(4-bromo-2-cyanophenyl)acrylate (4ha).



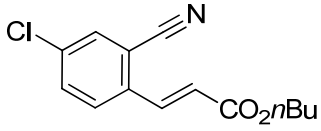
Colorless semisolid; eluent (15% ethyl acetate in hexanes). The reaction scale is 75 mg, 57 mg of **4ha** was isolated and yield is 45%. The reaction was done for 14 h at 120 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.89 (d, *J* = 16.0 Hz, 1 H), 7.84 (d, *J* = 2.0 Hz, 1 H), 7.75 (dd, *J* = 8.4, 2.0 Hz, 1 H), 7.60 (d, *J* = 8.4 Hz, 1 H), 6.61 (d, *J* = 16.0 Hz, 1 H), 4.24 (t, *J* = 6.8 Hz, 2 H), 1.74 - 1.66 (m, 2 H), 1.48 - 1.39 (m, 2 H), 0.97 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.7, 138.2, 136.3, 135.9, 128.2, 123.8, 123.7, 115.7, 114.2, 65.0, 30.6, 19.1, 13.7.

HRMS (ESI): calc. for [($C_{14}H_{14}BrNO_2$)Na] (M+Na) 330.0106, measured 330.0107.

Butyl (*E*)-3-(4-chloro-2-cyanophenyl)acrylate (4ia).



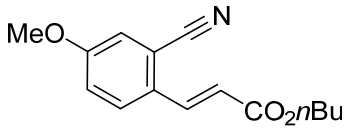
Colorless oil; eluent (15% ethyl acetate in hexanes). The reaction scale is 75 mg, 64 mg of **4ia** was isolated and yield is 44%. The reaction was done for 14 h at 120 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.90 (d, *J* = 16.0 Hz, 1 H), 7.69 – 7.67 (m, 2 H), 7.59 (dd, *J* = 8.8, 2.0 Hz, 1 H), 6.59 (d, *J* = 16.0 Hz, 1 H), 4.24 (t, *J* = 6.8 Hz, 2 H), 1.73 - 1.66 (m, 2 H), 1.48 - 1.39 (m, 2 H), 0.96 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.6, 138.1, 136.1, 135.9, 133.4, 133.0, 128.2, 123.6, 115.8, 114.0, 64.9, 30.6, 19.1, 13.7.

HRMS (ESI): calc. for [($C_{14}H_{14}ClNO_2$)Na] (M+Na) 286.0611, measured 286.0616.

Butyl (*E*)-3-(2-cyano-4-methoxyphenyl)acrylate (4ja).



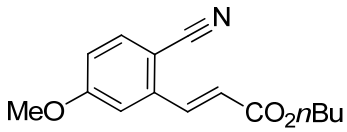
Off-white solid; eluent (25% ethyl acetate in hexanes). The reaction scale is 75 mg, 61 mg of **4ja** was isolated and yield is 42%. The reaction was done for 14 h at 120 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.87 (d, *J* = 16.0 Hz,1 H), 7.64(d, *J* = 8.8 Hz,1 H), 7.13 – 7.11 (m, 2 H), 6.46 (d, *J* = 16.0 Hz,1 H), 4.19 (t, *J* = 6.8 Hz, 2 H), 3.85(s, 3 H), 1.70 - 1.63 (m,2 H), 1.46 - 1.36 (m, 2 H), 0.94 (t, *J* = 7.2 Hz,3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.2, 160.5, 138.9, 129.7, 128.3, 120.4, 119.7, 117.4, 116.8, 113.7, 64.6, 55.7, 30.6, 19.0, 13.6.

HRMS (ESI): calc. for [($C_{15}H_{17}NO_3$)Na] (M+Na) 282.1106, measured 282.1093.

Butyl (*E*)-3-(2-cyano-5-methoxyphenyl)acrylate (4ka).



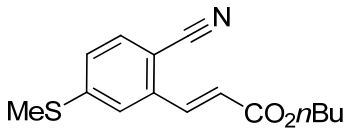
Colorless solid; eluent (25% ethyl acetate in hexanes). The reaction scale is 75 mg, 61 mg of **4ka** was isolated and yield is 42%. The reaction was done for 16 h at 120 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.92 (d, *J* = 16.0 Hz, 1 H), 7.63 (d, *J* = 8.4 Hz, 1 H), 7.17 (d, *J* = 2.4 Hz, 1 H), 6.98 (dd, *J* = 8.4, 2.4 Hz, 1 H), 6.58 (d, *J* = 16.0 Hz, 1 H), 4.24 (t, *J* = 6.8 Hz, 2 H), 3.89 (s, 3 H), 1.74 - 1.67 (m, 2 H), 1.49 - 1.39 (m, 2 H), 0.97 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.9, 162.8, 139.5, 139.3, 135.1, 123.1, 117.5, 116.1, 112.1, 104.5, 64.9, 55.7, 30.6, 19.1, 13.7.

HRMS (ESI): calc. for [($C_{15}H_{17}NO_3$)Na] (M+Na) 282.1106, measured 282.1102.

Butyl (*E*)-3-(2-cyano-5-(methylthio)phenyl)acrylate (4la).



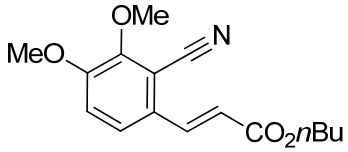
White semisolid; eluent (15% ethyl acetate in hexanes). The reaction scale is 75 mg, 79mg of **4la** was isolated and yield is 57%. The reaction was done for 14 h at 120 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.88 (d, *J* = 16.0 Hz, 1 H), 7.56 (d, *J* = 8.4 Hz, 1 H), 7.45 (d, *J* = 2.0 Hz, 1 H), 7.24 (dd, *J* = 8.4, 2.0 Hz, 1 H), 6.59 (d, *J* = 16.0 Hz, 1 H), 4.22 (t, *J* = 6.8 Hz, 2 H), 2.53 (s, 3 H), 1.72 - 1.65 (m, 2 H), 1.47 - 1.38 (m, 2 H), 0.95 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.7, 146.6, 139.0, 137.4, 133.3, 126.2, 123.3, 122.9, 117.3, 107.9, 64.9, 30.6, 19.1, 14.6, 13.7

HRMS (ESI): calc. for [($C_{15}H_{17}NO_2S$)Na] (M+Na) 298.0878, measured 298.0880.

Butyl (*E*)-3-(2-cyano-3,4-dimethoxyphenyl)acrylate (4ma).



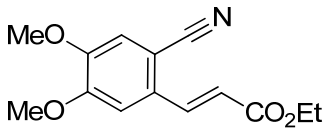
Colorless semisolid; eluent (30% ethyl acetate in hexanes). The reaction scale is 75 mg, 50 mg of **4ma** was isolated and yield is 38%. The reaction was done for 16 h at 120 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.84 (d, *J* = 16.0 Hz, 1 H), 7.41 (d, *J* = 8.8 Hz, 1 H), 7.12 (d, *J* = 8.8 Hz, 1 H), 6.50 (d, *J* = 16.0 Hz, 1 H), 4.21 (t, *J* = 6.8 Hz, 2 H), 4.02 (s, 3 H), 3.93 (s, 3 H), 1.72 - 1.64 (m, 2 H), 1.48 - 1.38 (m, 2 H), 0.96 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.3, 153.5, 152.1, 139.2, 129.7, 122.9, 120.8, 116.4, 114.3, 107.9, 64.7, 61.8, 56.2, 30.7, 19.1, 13.7.

HRMS (ESI): calc. for [($C_{16}H_{19}NO_4$)Na] (M+Na) 312.1212, measured 312.1212.

Ethyl (*E*)-3-(2-cyano-4,5-dimethoxyphenyl)acrylate (4nb).



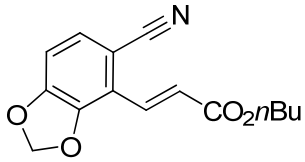
White solid; eluent (30% ethyl acetate in hexanes). The reaction scale is 75 mg, 35 mg of **4nb** was isolated and yield is 29%. The reaction was done for 16 h at 120 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.91 (d, *J* = 15.6 Hz, 1 H), 7.12 (s, 1 H), 7.08 (s, 1 H), 6.49 (d, *J* = 15.6 Hz, 1 H), 4.29 (q, *J* = 7.2 Hz, 2 H), 3.97 (s, 3 H), 3.94 (s, 3 H), 1.35 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.1, 152.7, 150.5, 139.3, 131.7, 120.9, 117.4, 114.3, 108.3, 105.2, 60.9, 56.3, 56.2, 14.3.

HRMS (ESI): calc. for [($C_{14}H_{15}NO_4$)Na] (M+Na) 284.0899, measured 284.0896.

Butyl (*E*)-3-(5-cyanobenzo[*d*][1,3]dioxol-4-yl)acrylate (4oa).



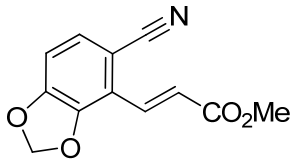
Colorless semisolid; eluent (30% ethyl acetate in hexanes). The reaction scale is 75 mg, 72 mg of **4oa** was isolated and yield is 52%. The reaction was done for 16 h at 120 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80 (d, *J* = 16.0 Hz, 1 H), 7.28 (d, *J* = 8.0 Hz, 1 H), 6.91 – 6.85 (m, 2 H), 6.20 (s, 2 H), 4.23 (t, *J* = 6.8 Hz, 2 H), 1.73 - 1.66 (m, 2 H), 1.48 - 1.39 (m, 2 H), 0.96 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.4, 151.5, 147.0, 134.8, 129.3, 125.7, 119.1, 117.2, 109.4, 105.8, 102.8, 64.8, 30.6, 19.1, 13.7.

HRMS (ESI): calc. for [($C_{15}H_{15}NO_4$)Na] (M+Na) 296.0899, measured 296.0900.

Methyl (*E*)-3-(5-cyanobenzo[*d*][1,3]dioxol-4-yl)acrylate (4og).



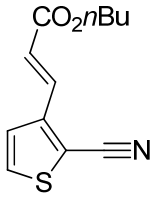
Colorless semisolid; eluent (30% ethyl acetate in hexanes). The reaction scale is 75 mg, 57 mg of **4og** was isolated and yield is 48%. The reaction was done for 16 h at 120 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.82 (d, *J* = 16.0 Hz, 1 H), 7.29 (d, *J* = 8.0 Hz, 1 H), 6.91 (d, *J* = 16.0 Hz, 1 H), 6.87 (d, *J* = 8.0 Hz, 1 H), 6.20 (s, 2 H), 3.83 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.7, 151.6, 147.1, 135.0, 129.3, 125.2, 118.9, 117.2, 109.5, 105.8, 102.8, 51.9.

HRMS (ESI): calc. for [($C_{12}H_9NO_4$)Na] (M+Na) 254.0429, measured 254.0432.

Butyl (*E*)-3-(2-cyanothiophen-3-yl)acrylate (4pa).



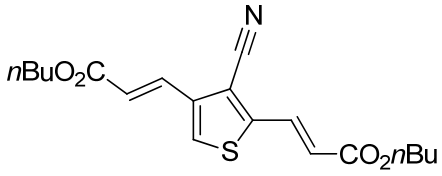
Brown oil; eluent (15% ethyl acetate in hexanes). The reaction scale is 75 mg, 86mg of **4pa** was isolated and yield is 53%. The reaction was done for 16 h at 120 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.75 (d, *J* = 16.0 Hz, 1 H), 7.59 (d, *J* = 5.2 Hz, 1 H), 7.33 (d, *J* = 5.2 Hz, 1 H), 6.51 (d, *J* = 16.0 Hz, 1 H), 4.23 (t, *J* = 6.4 Hz, 2 H), 1.73 - 1.66 (m, 2 H), 1.48 - 1.39 (m, 2 H), 0.96 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.1, 145.8, 133.7, 132.5, 125.7, 123.2, 113.0, 109.9, 64.9, 30.6, 19.1, 13.7.

HRMS (ESI): calc. for [($C_{12}H_{13}NO_2S$)Na] (M+Na) 258.0565, measured 258.0565.

Dibutyl 3,3'-(3-cyanothiophene-2,4-diyl)(2*E*,2'*E*)-diacrylate (5qa).



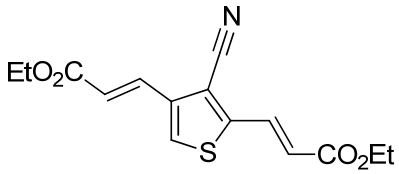
Off-white solid; eluent (20% ethyl acetate in hexanes). The reaction scale is 75 mg, 141 mg of **5qa** was isolated and yield is 56%. The reaction was done for 16 h at 120 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.88 (d, *J* = 15.8 Hz, 1 H), 7.61 (d, *J* = 16.2 Hz, 1 H), 7.57 (s, 1 H), 6.66 (d, *J* = 16.2 Hz, 1 H), 6.50 (d, *J* = 15.8 Hz, 1 H), 4.25 - 4.19 (m, 4 H), 1.73 - 1.65 (m, 4 H), 1.47 - 1.38 (m, 4 H), 0.98 – 0.94 (m, 6 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.2, 165.3, 149.6, 138.2, 133.7, 132.3, 127.9, 123.1, 121.8, 113.4, 110.9, 65.1, 64.9, 30.61, 30.58, 19.1, 13.7.

HRMS (ESI): calc. for [($C_{19}H_{23}NO_4S$)H] (M+H) 362.1426, measured 362.1429.

Dimethyl 3,3'-(3-cyanothiophene-2,4-diyl)(2*E*,2'*E*)-diacrylate (5qb).



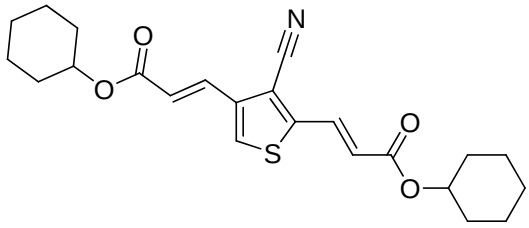
Off-white solid; eluent (25% ethyl acetate in hexanes). The reaction scale is 75 mg, 136 mg of **5qb** was isolated and yield is 65%. The reaction was done for 16 h at 120 °C.

^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.43 (s, 1 H), 7.68 (d, *J* = 16.0 Hz, 1 H), 7.53 (d, *J* = 16.0 Hz, 1 H), 6.71 (d, *J* = 16.0 Hz, 1 H), 6.64 (d, *J* = 16.0 Hz, 1 H), 4.24 - 4.17 (m, 4 H), 1.28 - 1.24 (m, 6 H).

^{13}C NMR (DMSO-d_6, 100 MHz): δ 165.6, 165.0, 148.8, 136.8, 134.0, 132.10, 132.07, 122.5, 120.7, 113.8, 110.2, 60.9, 60.5, 14.13, 14.10.

HRMS (ESI): calc. for [($C_{15}H_{15}NO_4S$)H] (M+H) 306.0800, measured 306.0799.

Dicyclohexyl 3,3'-(3-cyanothiophene-2,4-diyl)(2*E*,2'*E*)-diacrylate (5qc).



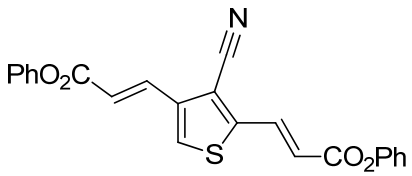
Colorless solid; eluent (20% ethyl acetate in hexanes). The reaction scale is 75 mg, 136 mg of **5qc** was isolated and yield is 48%. The reaction was done for 16 h at 120 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.87 (d, *J* = 15.6 Hz, 1 H), 7.60 (d, *J* = 16.0 Hz, 1 H), 7.55 (s, 1 H), 6.65 (d, *J* = 16.0 Hz, 1 H), 6.50 (d, *J* = 15.6 Hz, 1 H), 4.94 - 4.84 (m, 2 H), 1.97 - 1.90 (m, 4 H), 1.78 - 1.72 (m, 4 H), 1.59 – 1.51 (m, 4 H), 1.48 – 1.41 (m, 4 H), 1.39 - 1.27 (m, 4 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.6, 164.7, 149.8, 138.3, 133.5, 132.1, 127.7, 123.7, 122.3, 113.4, 110.8, 73.8, 73.4, 31.6, 25.3, 23.8.

HRMS (ESI): calc. for [($C_{23}H_{27}NO_4S$)H] (M+H) 414.1739, measured 414.1740.

Diphenyl 3,3'-(3-cyanothiophene-2,4-diyl)(2*E*,2'*E*)-diacrylate (5qd).



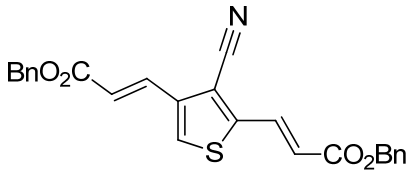
Pale yellow solid; eluent (30% ethyl acetate in hexanes). The reaction scale is 75 mg, 135 mg of **5qd** was isolated and yield is 49%. The reaction was done for 16 h at 120 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.09 (d, *J* = 16.0 Hz, 1 H), 7.81 (d, *J* = 16.0 Hz, 1 H), 7.69 (s, 1 H), 7.44 – 7.39 (m, 4 H), 7.29 – 7.24 (m, 2 H), 7.18 – 7.16 (m, 4 H), 6.90 (d, *J* = 16.0 Hz, 1 H), 6.73 (d, *J* = 16.0 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.5, 163.6, 150.6, 150.4, 149.3, 138.1, 135.4, 133.9, 129.5, 129.5, 129.2, 126.1, 125.9, 122.3, 121.4, 121.4, 121.1, 113.3, 111.4.

HRMS (ESI): calc. for [($C_{23}H_{15}NO_4S$)Na] (M+Na) 424.0619, measured 424.0627.

Dibenzyl 3,3'-(3-cyanothiophene-2,4-diyl)(2*E*,2'*E*)-diacrylate (5qe).



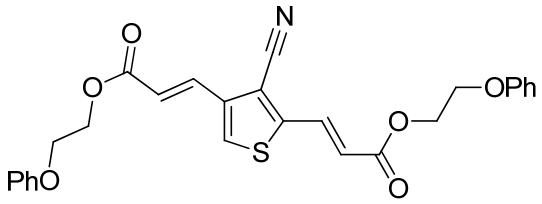
Greenish color solid; eluent (30% ethyl acetate in hexanes). The reaction scale is 75 mg, 139 mg of **5qe** was isolated and yield is 47%. The reaction was done for 16 h at 120 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.93 (d, *J* = 16.0 Hz, 1 H), 7.66 (d, *J* = 16.4 Hz, 1 H), 7.56 (s, 1 H), 7.43 – 7.34 (m, 10 H), 6.71 (d, *J* = 16.4 Hz, 1 H), 6.55 (d, *J* = 16.0 Hz, 1 H), 5.28 (s, 2 H), 5.26 (s, 2 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.9, 165.0, 149.5, 138.2, 135.7, 135.4, 134.3, 132.8, 128.7, 128.6, 128.5, 128.4, 128.4, 128.1, 122.8, 121.5, 113.3, 111.1, 67.0, 66.8.

HRMS (ESI): calc. for [($C_{25}H_{19}NO_4S$)Na] (M+Na) 452.0932, measured 452.0942.

Bis(2-phenoxyethyl) 3,3'-(3-cyanothiophene-2,4-diyl)(2*E*,2'*E*)-diacrylate (5qf).



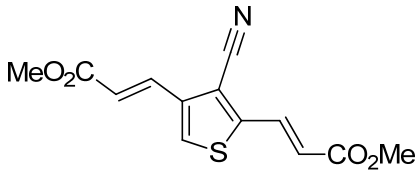
Light yellow solid; eluent (40% ethyl acetate in hexanes). The reaction scale is 75 mg, 151 mg of **5qf** was isolated and yield is 45%. The reaction was done for 16 h at 120 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.93 (d, *J* = 16.0 Hz, 1 H), 7.66 (d, *J* = 16.4 Hz, 1 H), 7.58 (s, 1 H), 7.33 – 7.29 (m, 4 H), 7.00 – 6.93 (m, 6 H), 6.71 (d, *J* = 16.4 Hz, 1 H), 6.56 (d, *J* = 16.0 Hz, 1 H), 4.61 – 4.57 (m, 4 H), 4.27 – 4.25 (m, 4 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.9, 165.1, 158.4, 158.37, 149.38, 138.2, 134.4, 132.9, 129.5, 129.5, 128.3, 122.5, 121.3, 121.2, 114.7, 114.7, 113.3, 111.2, 65.8, 65.7, 63.6, 63.3.

HRMS (ESI): calc. for [($C_{27}H_{23}NO_6S$)Na] (M+Na) 512.1144, measured 512.1149.

Dimethyl 3,3'-(3-cyanothiophene-2,4-diyl)(2*E*,2'*E*)-diacrylate (5qg).



Off-white solid; eluent (25% ethyl acetate in hexanes). The reaction scale is 75 mg, 131 mg of **5qg** was isolated and yield is 69%. The reaction was done for 16 h at 120 °C.

^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.44 (s, 1 H), 7.69 (d, *J* = 15.6 Hz, 1 H), 7.54 (d, *J* = 16.4 Hz, 1 H), 6.75 - 6.65 (m, 2 H), 3.76 (s, 3 H), 3.74 (s, 3 H).

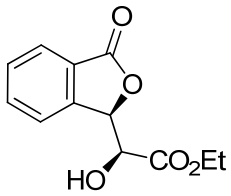
^{13}C NMR (DMSO-d_6, 100 MHz): δ 166.1, 165.5, 148.7, 136.7, 134.2, 132.2, 122.2, 120.4, 113.8, 110.3, 52.1, 51.9.

HRMS (ESI): calc. for [($C_{13}H_{11}NO_4S$)Na] (M+Na) 300.0306, measured 300.0305.

Procedure for the Preparation of Compound 6.[1]

A 50 mL RB flask was charged with $K_3Fe(CN)_6$ (0.988 g, 3 mmol), K_2CO_3 (0.414 g, 3 mmol), *tert*-BuOH (2.5 mL), THF (2.5 mL) and H_2O (5 mL) and stirred for 10 min. Subsequently, $(DHQD)_2PHAL$ (0.008 g, 1 mol%) and $K_2OsO_4 \cdot 2H_2O$ (0.002 g, 0.5 mol%) were added and the stirring continued for additional 30 min. To this reaction mixture, **4ab** (1 mmol) was added and allowed to stir for 7 h at 25 °C. After completion of reaction (as monitored by TLC), sodium bisulphite (1.0 g) was added slowly at 0 °C. The organic layer was separated, aqueous layer extracted with ethyl acetate (3 × 10 ml) and the combined organic layers washed with brine (15 mL), dried over anhydrous sodium sulphate and concentrated under reduced pressure to yield the crude product. The crude residue was purified through a silica gel column using hexanes and ethyl acetate as eluent to give pure **6**.

Ethyl (*S*)-2-hydroxy-2-((*R*)-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (6).[1]



Colorless solid; eluent (75% ethyl acetate in hexanes). The reaction scale is 201 mg, 219 mg of **6** was isolated and yield is 93%. The reaction was done for 7 h at 25 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.50 – 7.44 (m, 2 H), 7.38 (d, *J* = 7.6 Hz, 1 H), 7.19 (t, *J* = 7.6 Hz, 1 H), 5.78 (d, *J* = 2.08 Hz, 1 H), 4.63 (d, *J* = 2.08 Hz, 1 H), 4.29 (d, *J* = 7.2 Hz, 2 H), 1.29 (t, *J* = 7.2 Hz, 3 H).

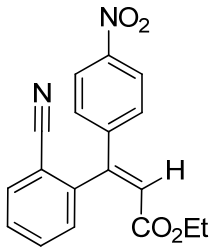
^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.4, 167.9, 143.2, 132.1, 129.5, 128.9, 123.9, 121.4, 83.9, 71.9, 62.0, 14.1.

HRMS (ESI): calc. for [($C_{12}H_{12}O_5$)Na] (M+Na) 259.0582, measured 259.0583.

Procedure for the Preparation of Compound 8a-b.[2,3]

$Pd(OAc)_2$ (0.0327 mmol, 10 mol%) and silver(I) oxide (0.3275 mmol, 1.0 equiv) were taken in a 15-mL pressure tube equipped with a magnetic stirrer and septum. The tube was evacuated and purged with nitrogen gas three times. To the tube were then added trifluoroacetic acid (2.0 mL), **4** (75 mg, 0.3275 mmol) and aryl iodide **7** (0.655 mmol). Again the tube was evacuated and purged with nitrogen gas three times and the reaction mixture was stirred at 110 °C for 12 h. The mixture was filtered through a short Celite pad and washed with dichloromethane several times. The filtrate was concentrated by vacuum and separated on a silica gel column using hexane/EtOAc as eluent to give the corresponding pure biphenyl-2-carbonitrile derivatives **8a-b**.

Ethyl (*Z*)-3-(2-cyanophenyl)-3-(4-nitrophenyl)acrylate (8a).

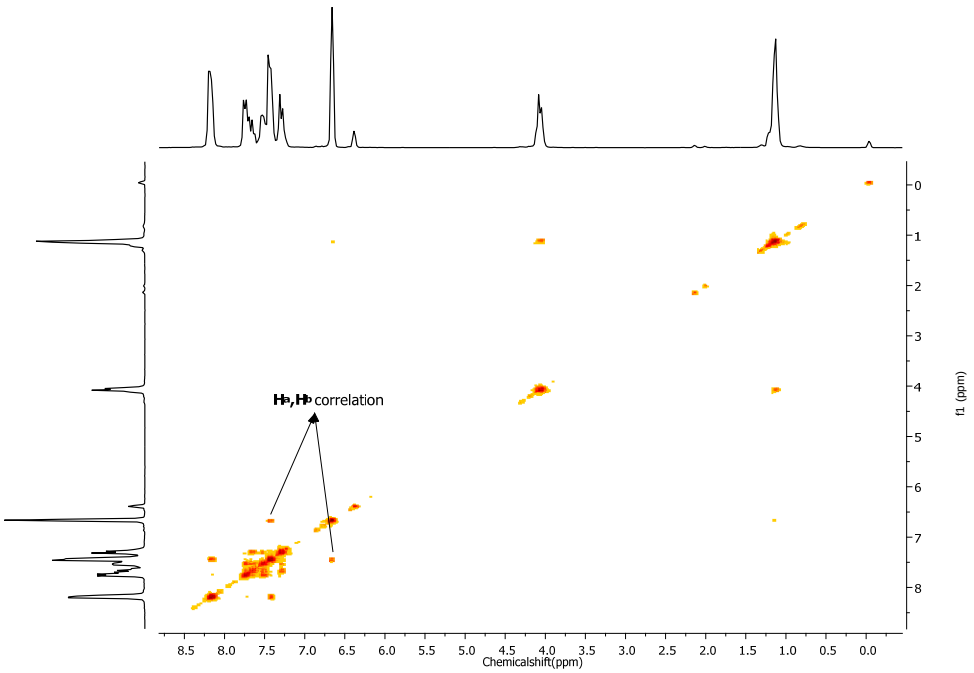


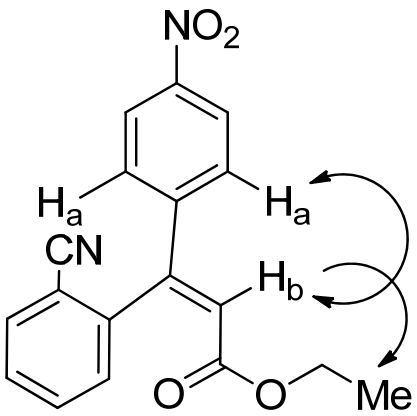
Yellow solid; eluent (30% ethyl acetate in hexanes). The reaction scale is 75 mg, 98 mg of **8a** was isolated and yield is 82%. The reaction was done for 12 h at 110 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.20 (d, *J* = 8.8 Hz, 2 H), 7.77 (d, *J* = 7.6 Hz, 1 H), 7.69 (d, *J* = 7.6 Hz, 1 H), 7.55 (d, *J* = 7.6 Hz, 1 H), 7.46 (d, *J* = 8.8 Hz, 2 H), 7.32 (d, *J* = 7.6 Hz, 1 H), 6.69 (s, 1 H), 4.10 (q, *J* = 7.2 Hz, 2 H), 1.16 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.3, 149.9, 148.3, 144.5, 141.7, 132.8, 132.7, 129.4, 128.8, 128.5, 123.9, 123.2, 117.1, 112.3, 60.8, 13.9.

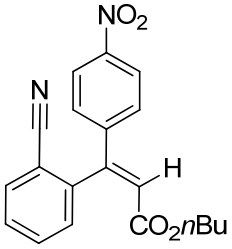
HRMS (ESI): calc. for [($C_{18}H_{14}N_2O_4$)Na] (M+Na) 345.0851, measured 345.0846.





There is a NOE correlation between Ha (δ 7.46, d) and Hb (δ 6.69, s). There is also a weak signal between Hb and methyl group of ester moiety (δ 1.16, t). But, there is no signal between Ha and ethyl ester group. This clearly indicates that the stereochemistry of compound **8a** is correct.

Butyl (*Z*)-3-(2-cyanophenyl)-3-(4-nitrophenyl)acrylate (8b).

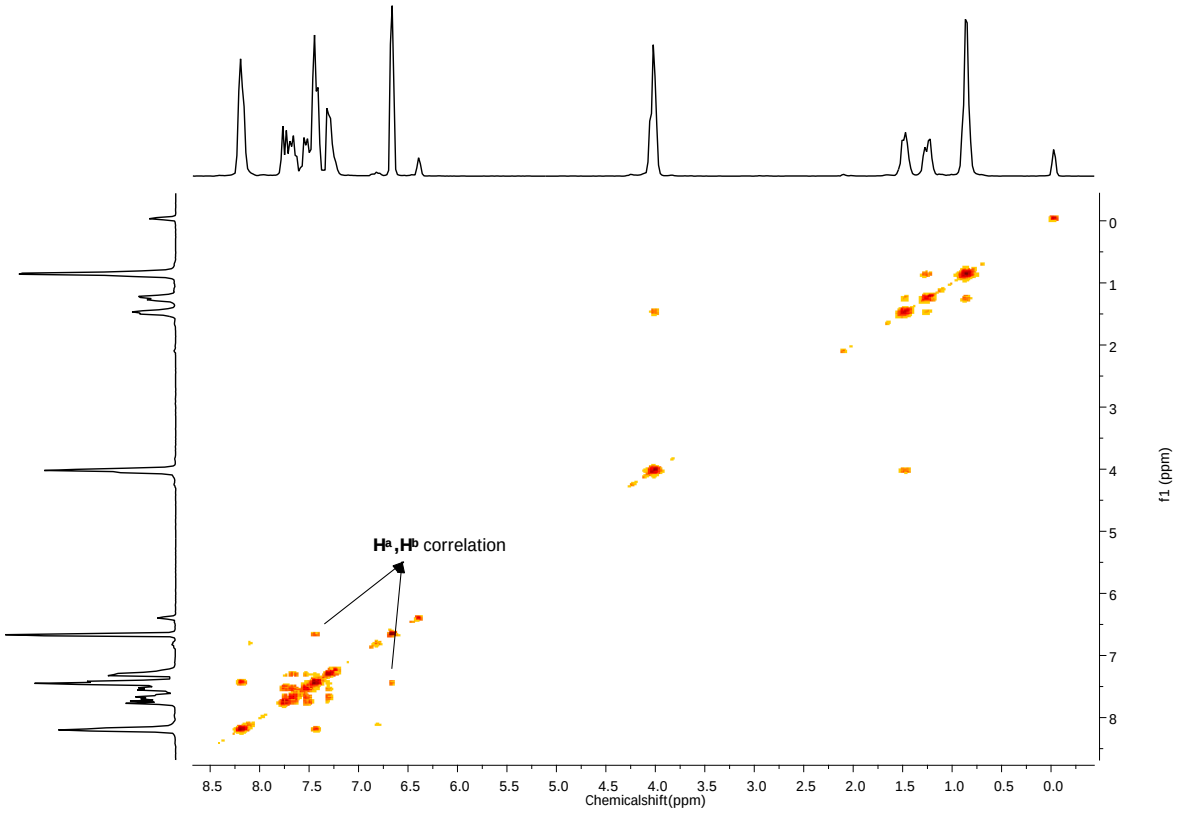


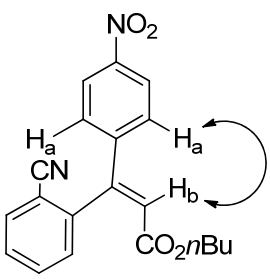
Yellow oil; eluent (30% ethyl acetate in hexanes). The reaction scale is 75 mg, 100 mg of **8b** was isolated and yield is 87%. The reaction was done for 12 h at 110 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.21 (d, *J* = 8.8 Hz, 2 H), 7.77 (d, *J* = 7.6 Hz, 1 H), 7.69 (d, *J* = 7.6 Hz, 1 H), 7.55 (d, *J* = 7.6 Hz, 1 H), 7.46 (d, *J* = 8.8 Hz, 2 H), 7.32 (d, *J* = 7.6 Hz, 1 H), 6.69 (s, 1 H), 4.04 (t, *J* = 6.8 Hz, 2 H), 1.54 - 1.47 (m, 2 H), 1.33 - 1.24 (m, 2 H), 0.89 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.5, 149.9, 148.3, 144.5, 141.7, 132.9, 132.7, 129.4, 128.8, 128.6, 123.9, 123.3, 117.2, 112.4, 64.9, 30.3, 18.9, 13.6.

HRMS (ESI): calc. for [($C_{20}H_{18}N_2O_4$)Na] (M+Na) 373.1164, measured 373.1161.



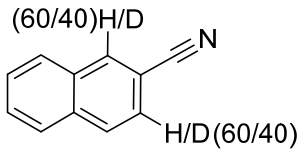


There is a NOE correlation between Ha (δ 6.69, s) and Hb (δ7.46, d). This clearly indicates that the stereochemistry of compound **8b** is correct.

Procedure for the preparation of 2-Naphthonitrile (*D*-1b).

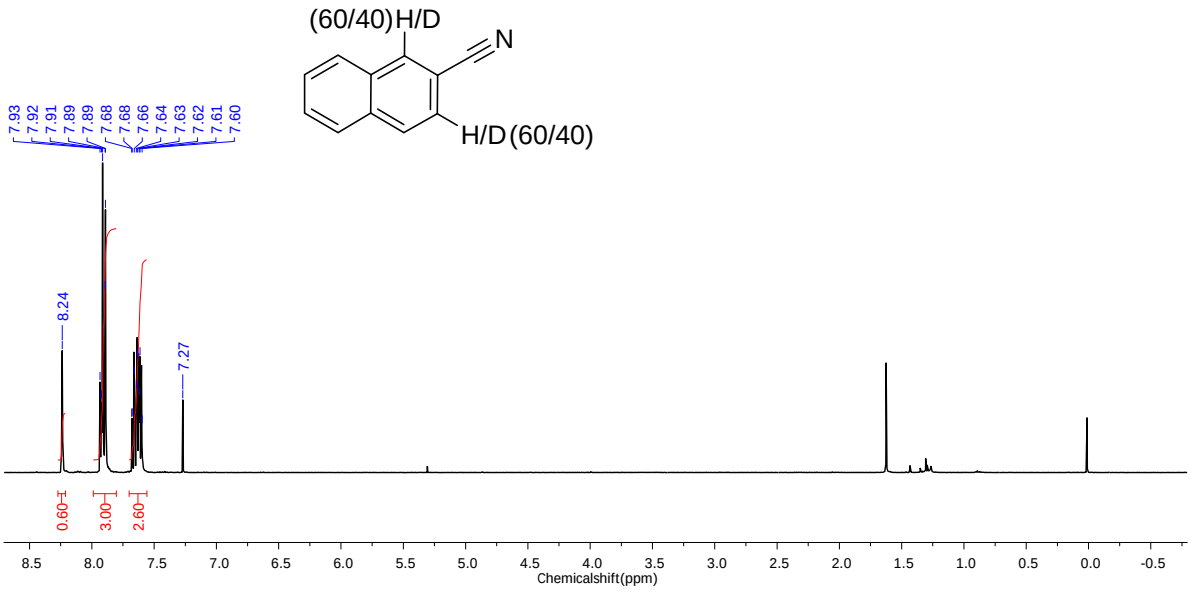
Substituted nitrile **1b** (75 mg, 1.0 equiv), [{$RuCl_2$(*p*-cymene)}$_2$] (5 mol %), AgOAc (2.0 equiv), $AgSbF_6$ (20 mol %) were taken in a 15-mL pressure tube equipped with a magnetic stirrer and septum. (Note: $AgSbF_6$ and AgOAc are moisture sensitive. Thus, $AgSbF_6$ and AgOAc were taken inside the nitrogen glove box). The tube was evacuated and purged with nitrogen gas three times. To the tube were then added CD_3COOD (0.4 mL) and DCE (3.0 mL) via syringes, allowed the reaction mixture to stir at room temperature for few seconds and again the tube was evacuated and purged with nitrogen gas three times. Then, the septum was taken out and immediately a screw cap was used to cover the tube. Then, the reaction mixture was allowed to stir at 120 °C for 14 h. After cooling to ambient temperature, the reaction mixture was diluted with CH_2Cl_2, filtered through Celite and silica gel, and the filtrate was concentrated. The crude residue was purified through a silica gel column using hexanes and ethyl acetate as eluent to give pure ***D*-1b**.

2-Naphthonitrile (*D*-1b).



Colorless solid; eluent (10% ethyl acetate in hexanes). The reaction scale is 75 mg, 70 mg of ***D*-1b** was isolated .The reaction was done for 16 h at 120 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.24 (s, 0.6 H), 7.93 – 7.89 (m, 3 H), 7.68 – 7.60 (m, 2.6 H).



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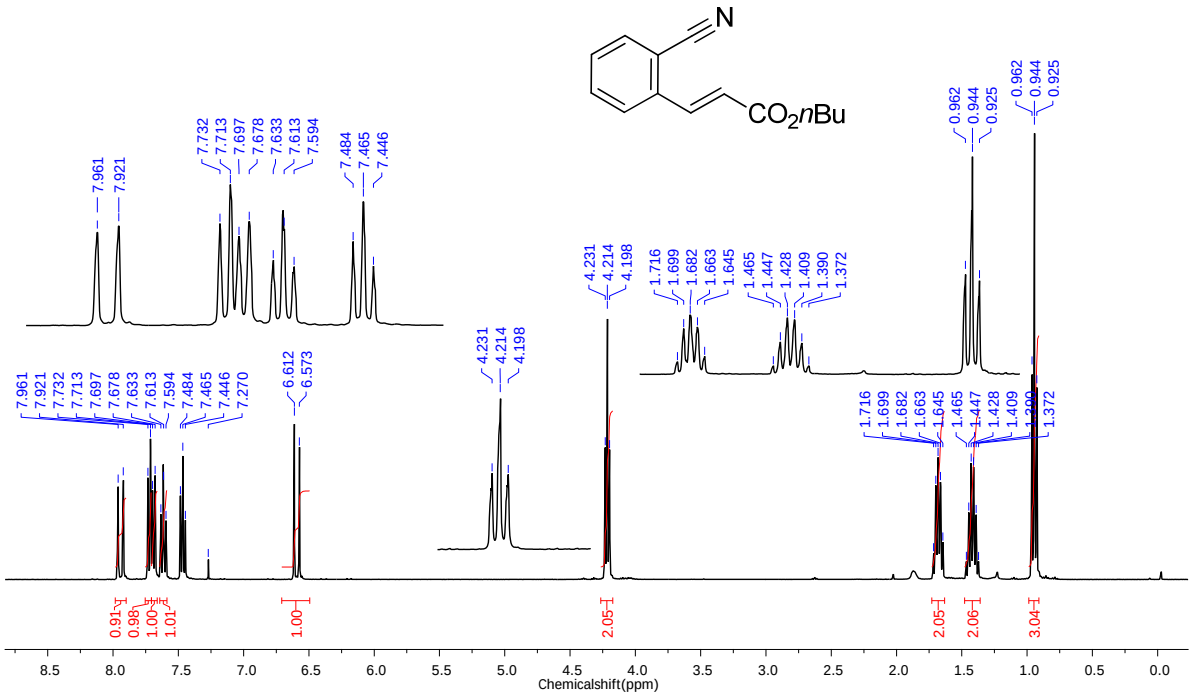
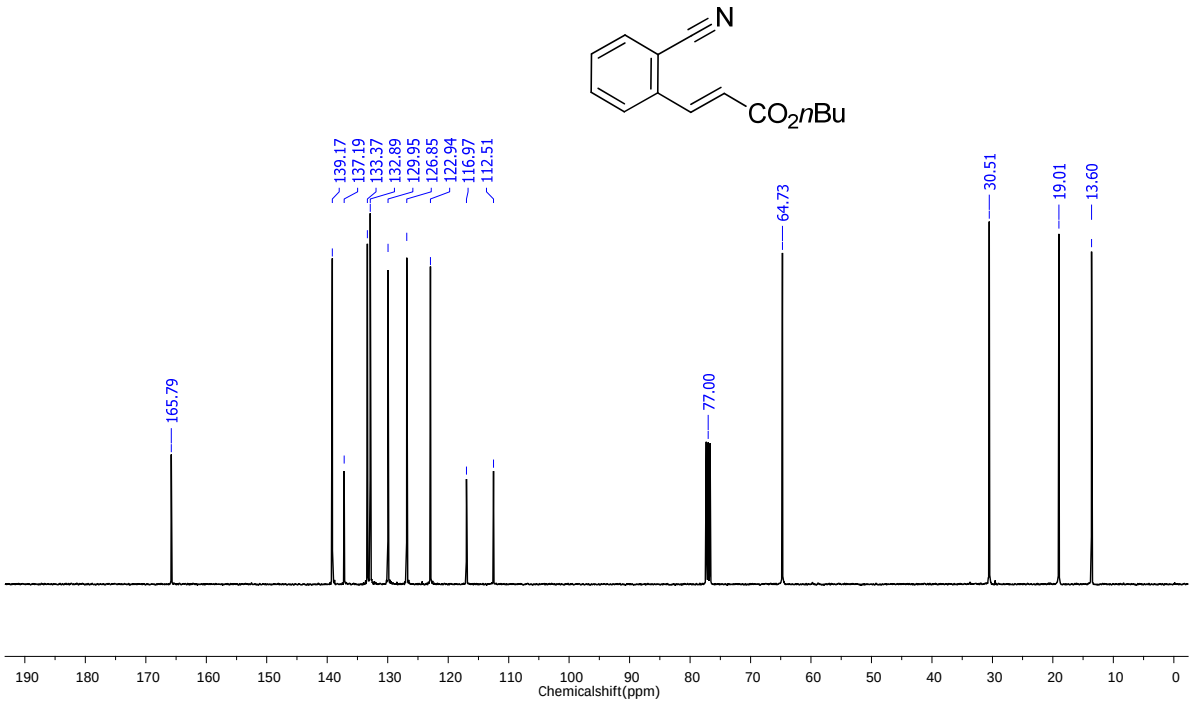
(1) Reddy, R. S.;Kiran, I. N. C.;Sudalai, A. *Org. Biomol.Chem.* **2012**, *10*, 3655

(2) Battistuzzi, G.; Cacchi, S.; Fabrizi, G. *Synlett.* **2002**, *3*, 439.

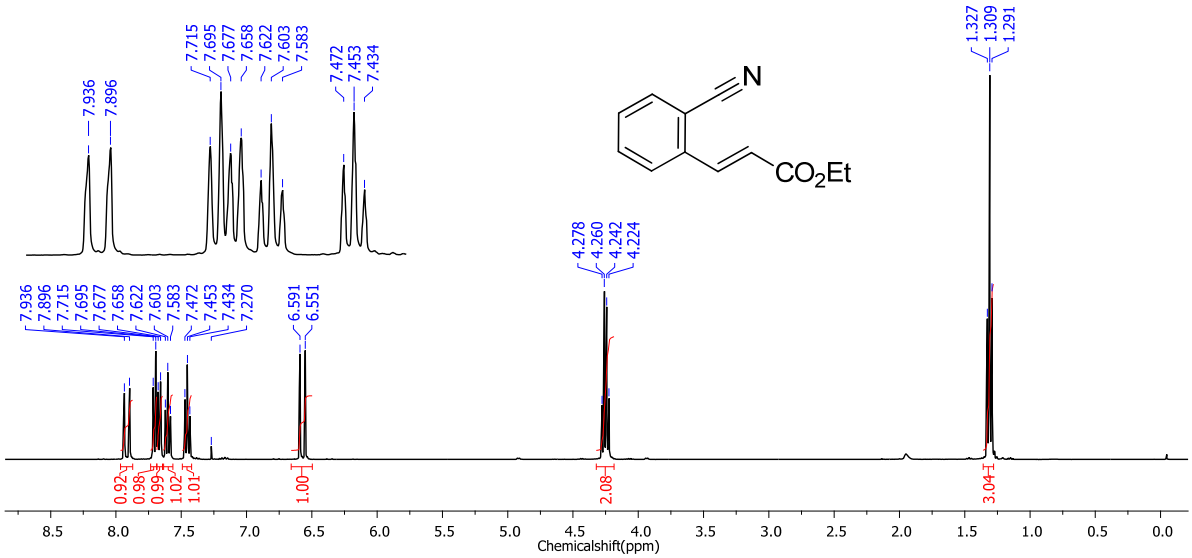
(3) Li, W.;Xu, Z.; Sun, P.; Jiang, X.; Fang, M. *Org. Lett.***2011**, *13*, 1286.

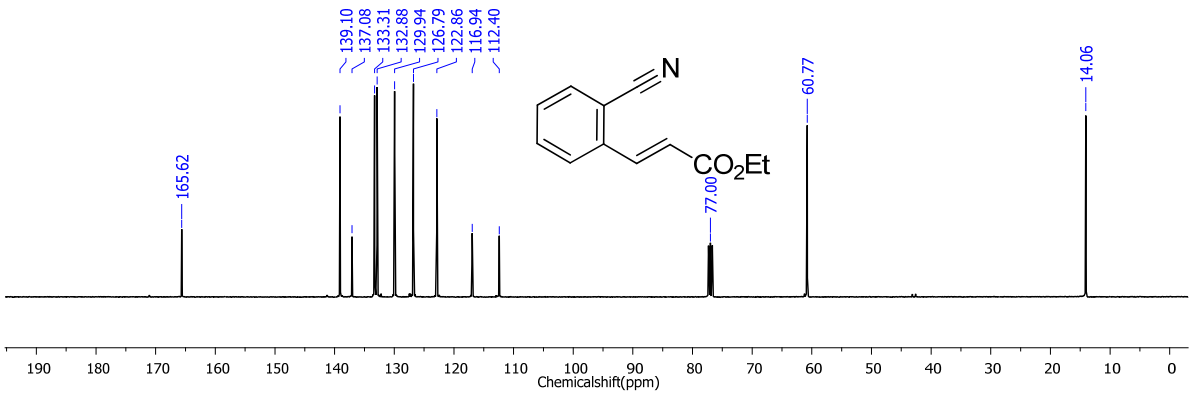
^{1}H and ^{13}C NMR Spectra of Compound **4aa**.

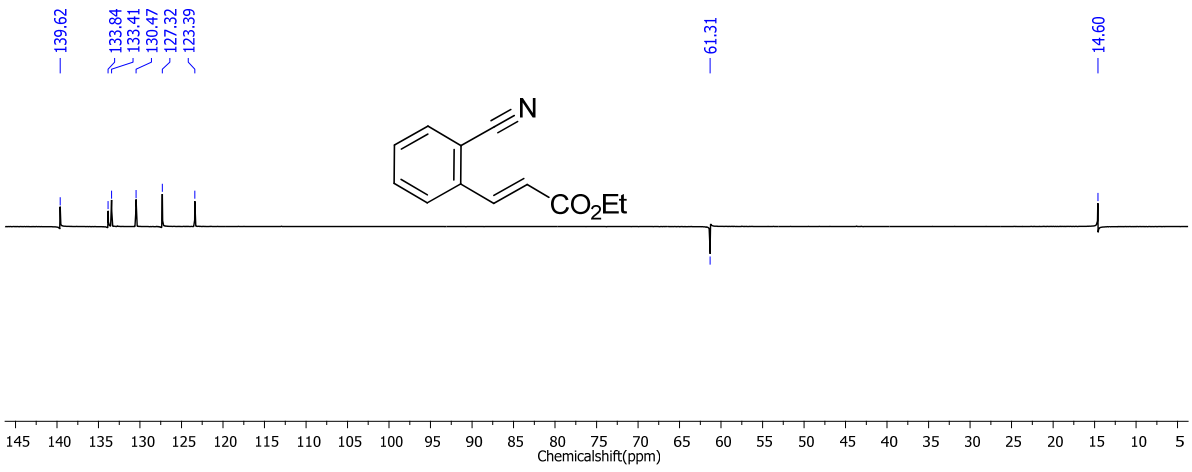




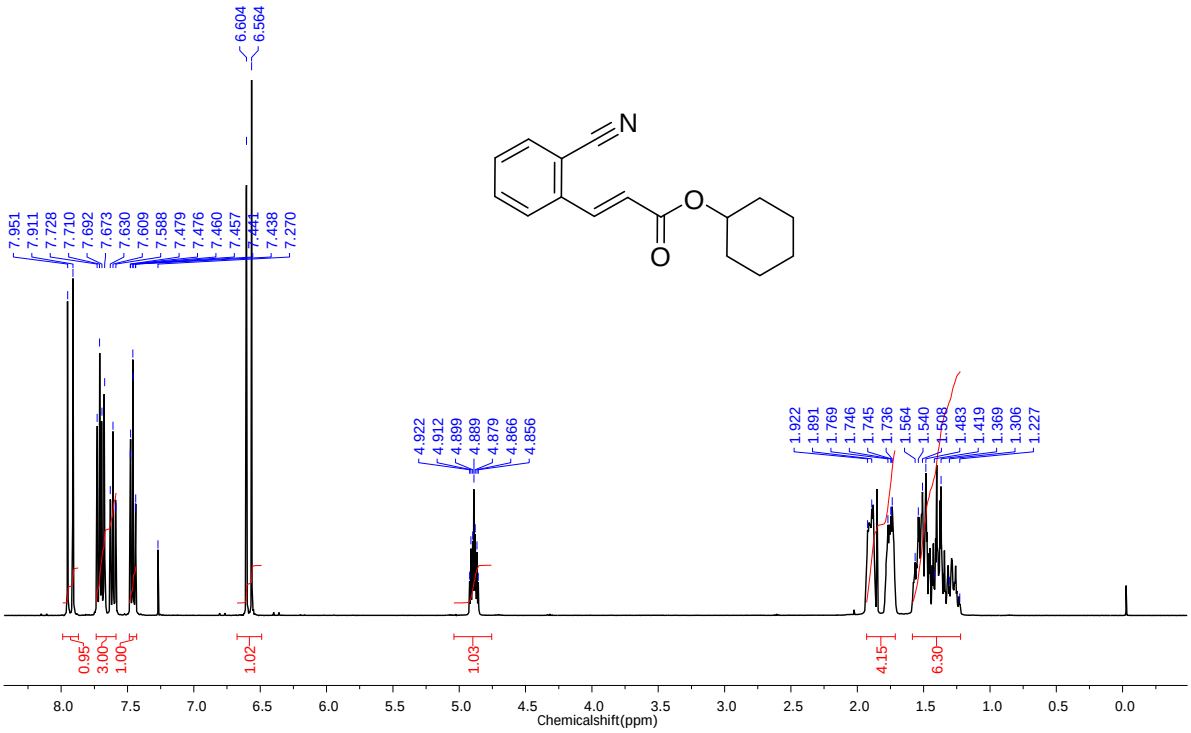
^{1}H and ^{13}C NMR Spectra of Compound **4ab**.

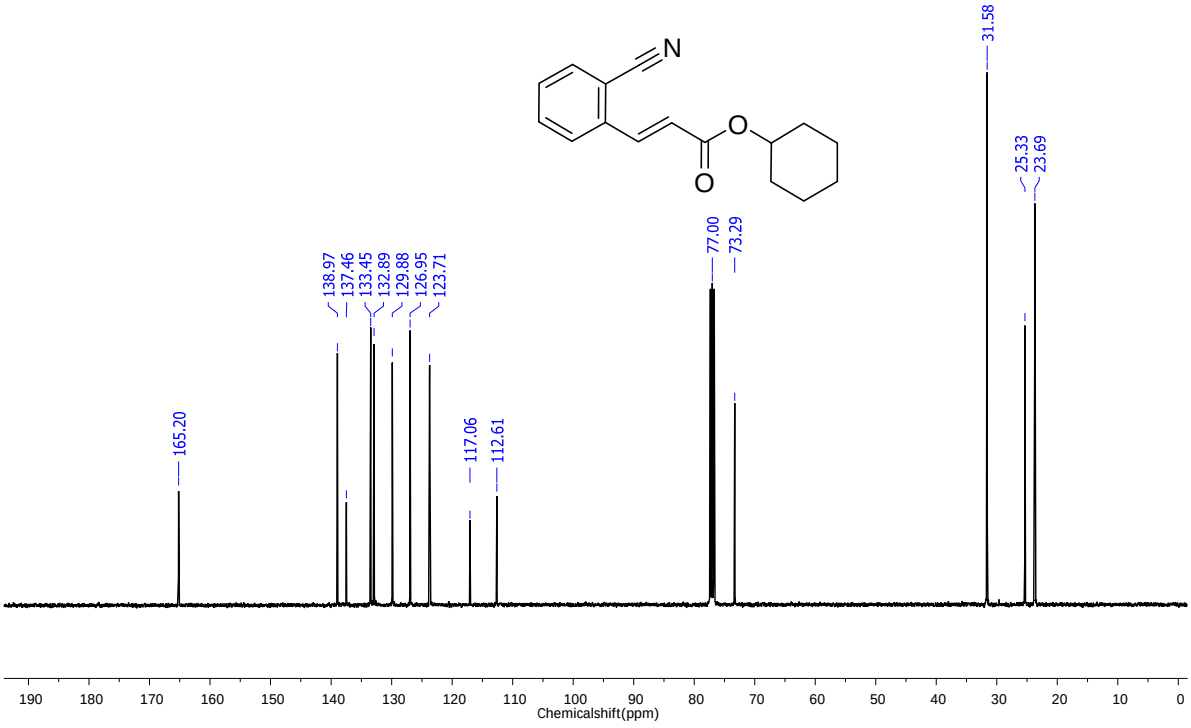




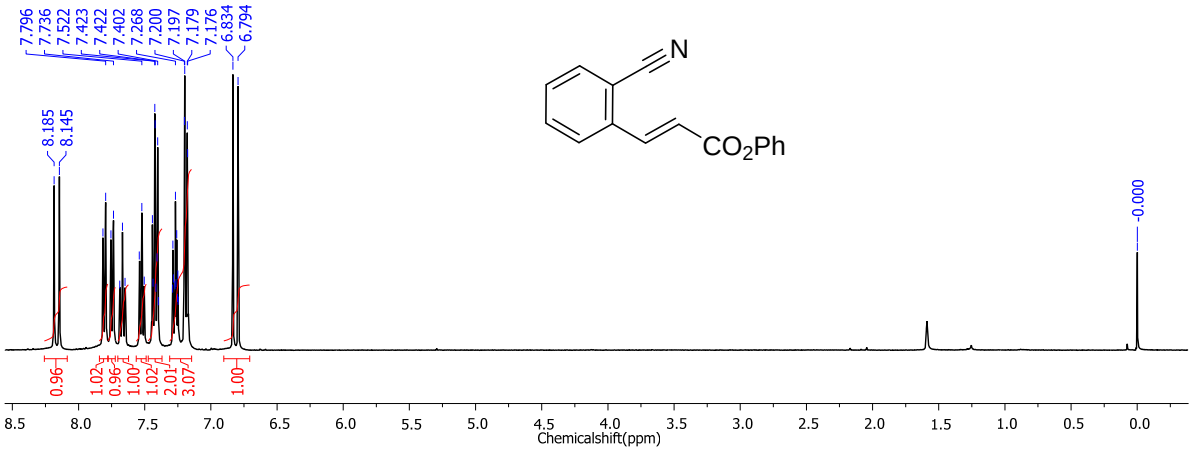


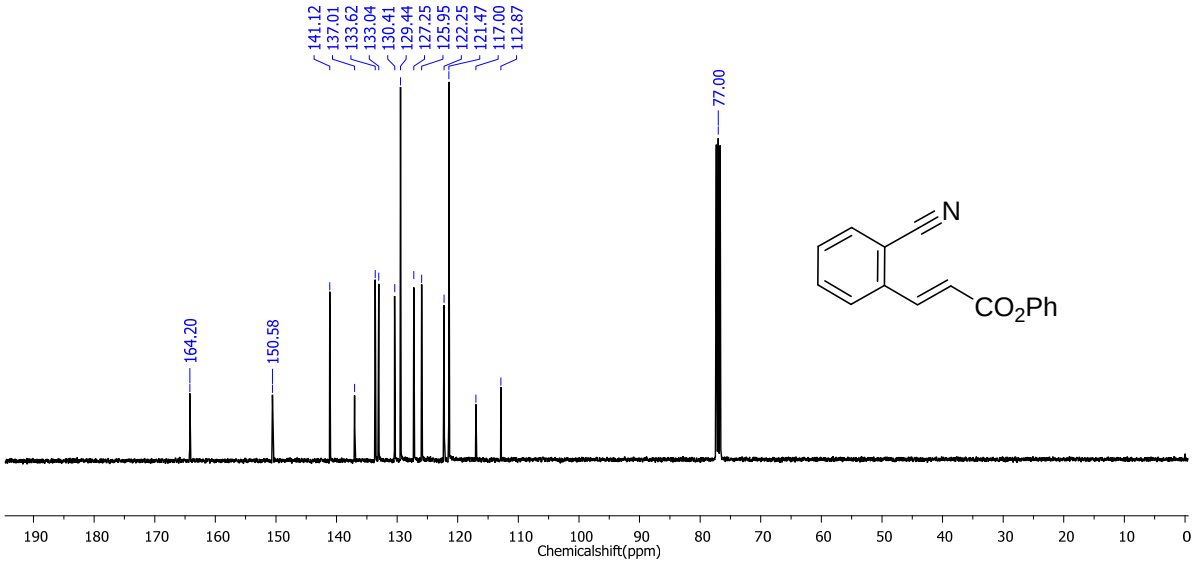
^{1}H and ^{13}C NMR Spectra of Compound **4ac**.

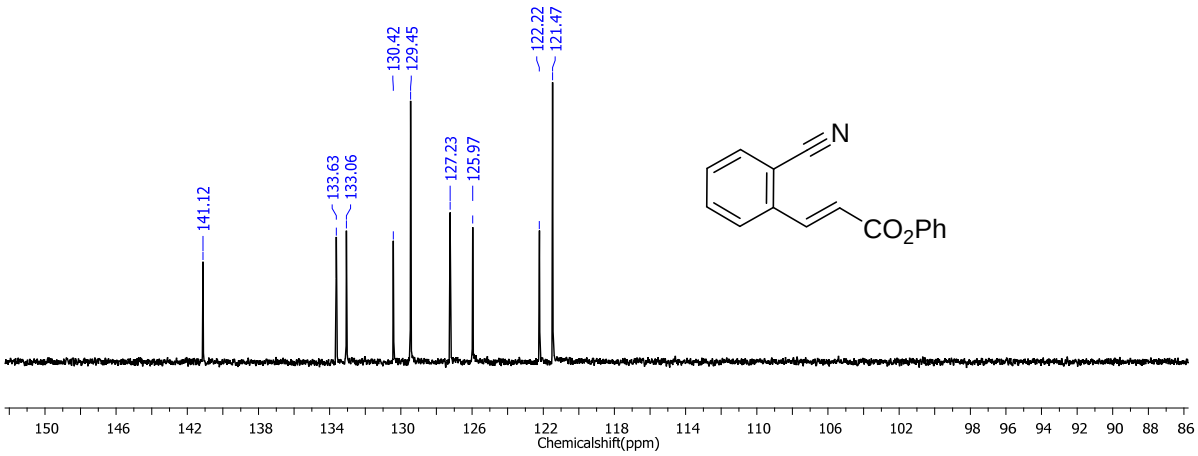




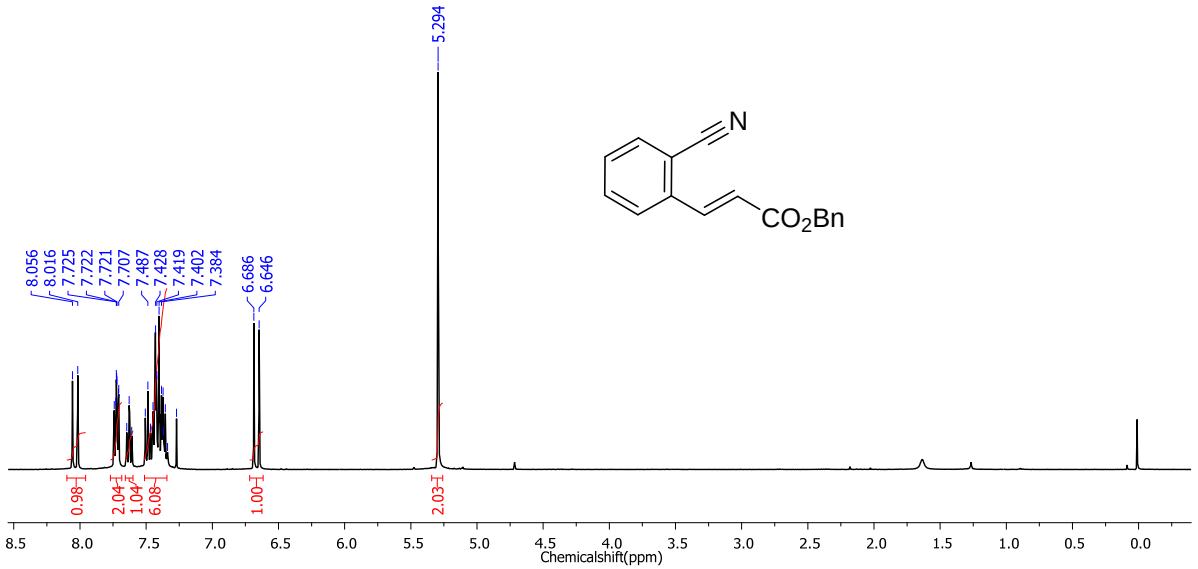
^{1}H and ^{13}C NMR Spectra of Compound **4ad**.

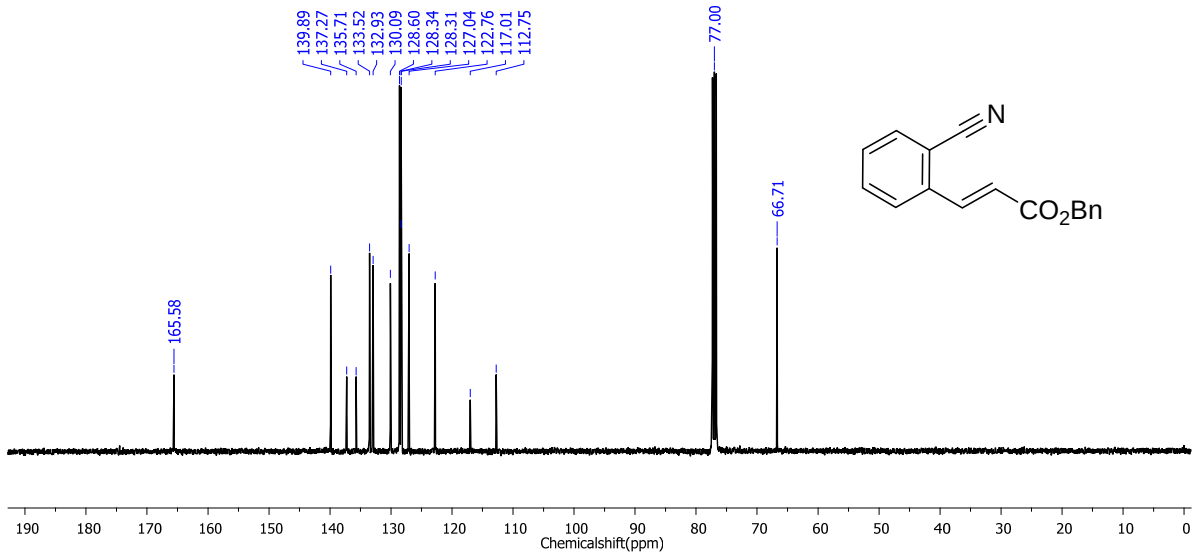


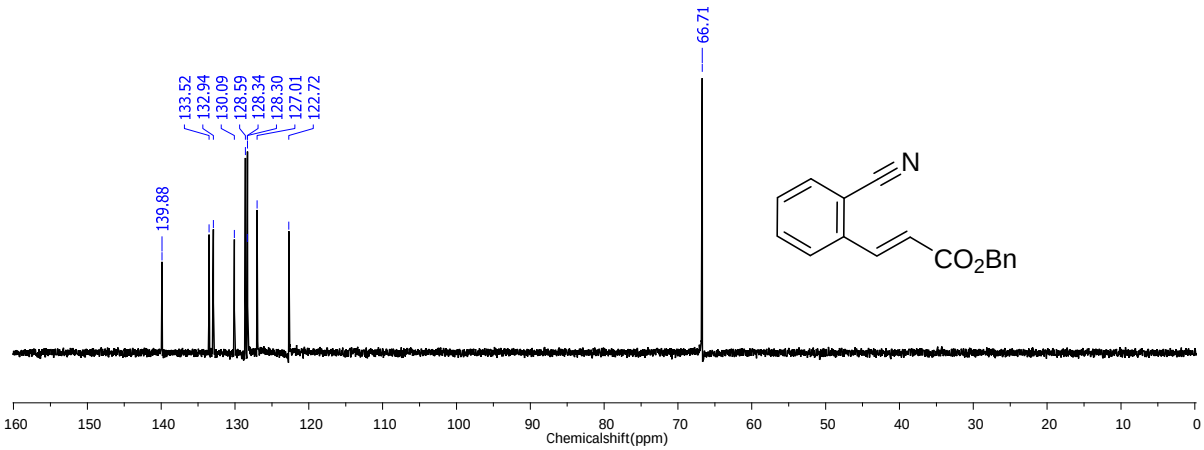




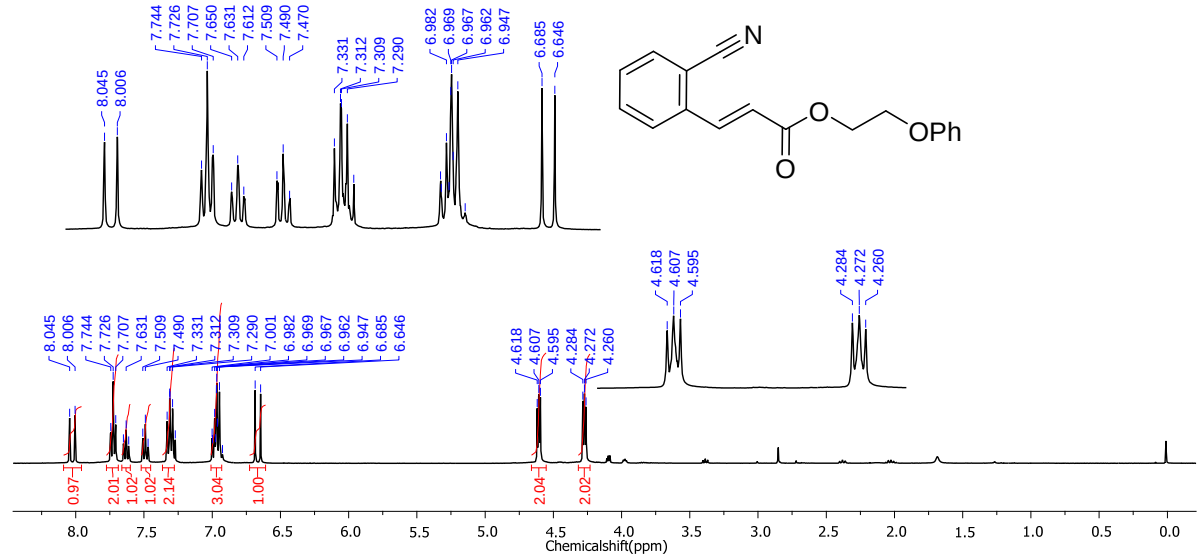
^{1}H and ^{13}C NMR Spectra of Compound **4ae**.

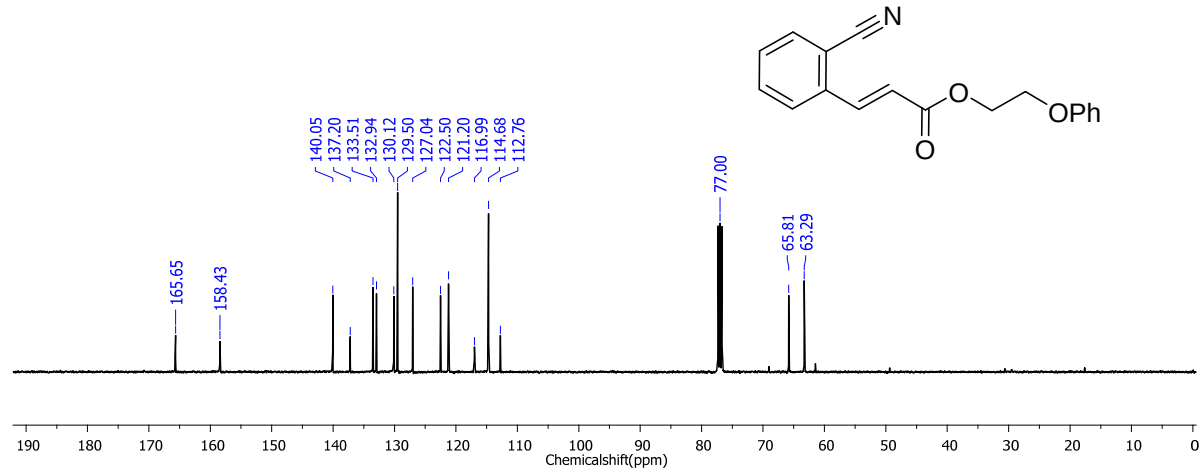


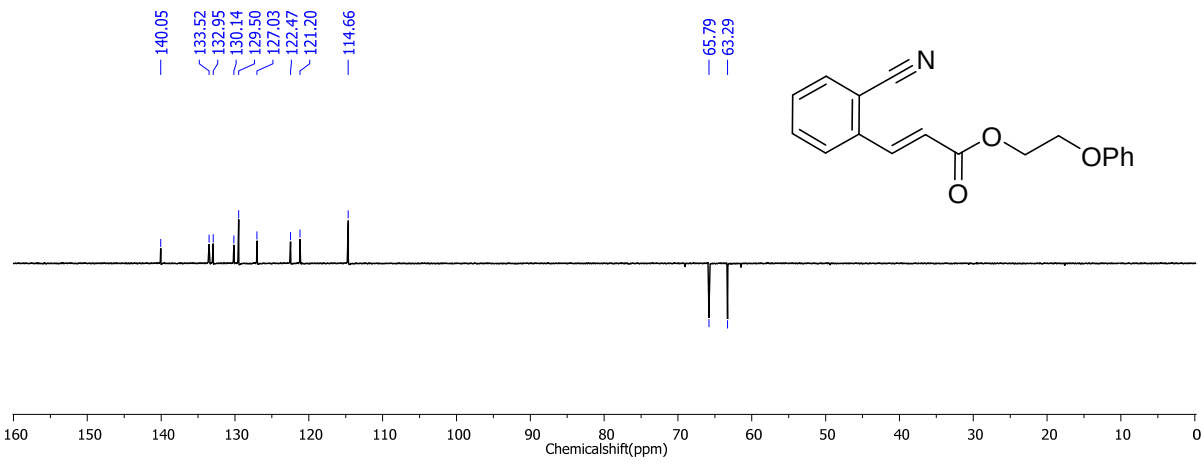




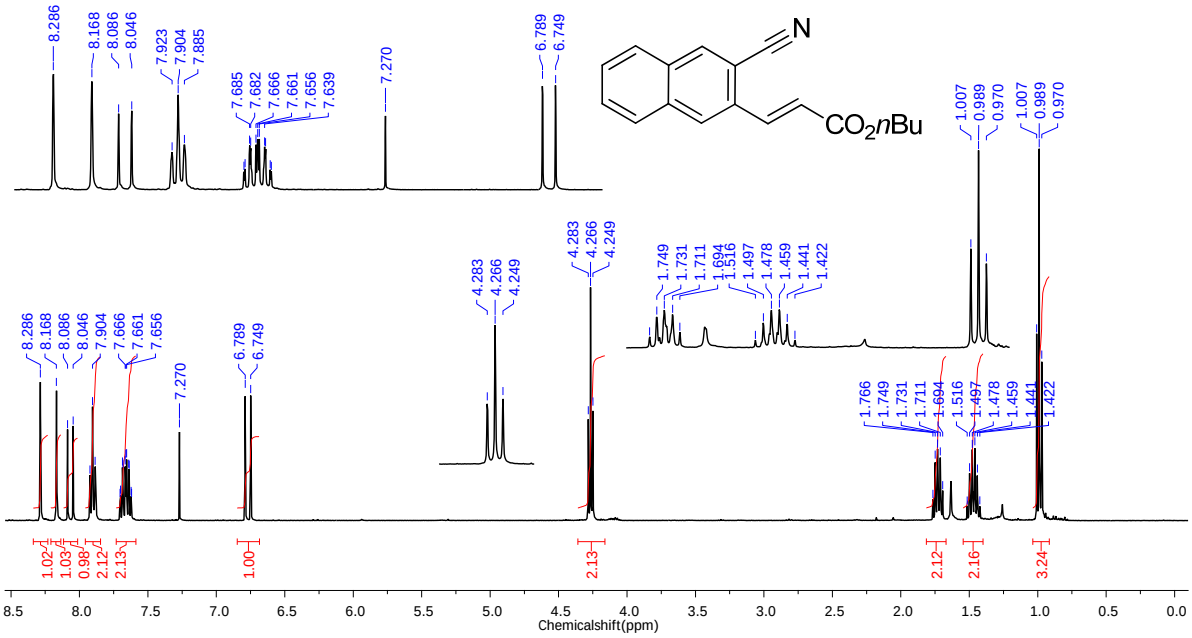
^{1}H and ^{13}C NMR Spectra of Compound **4af**.

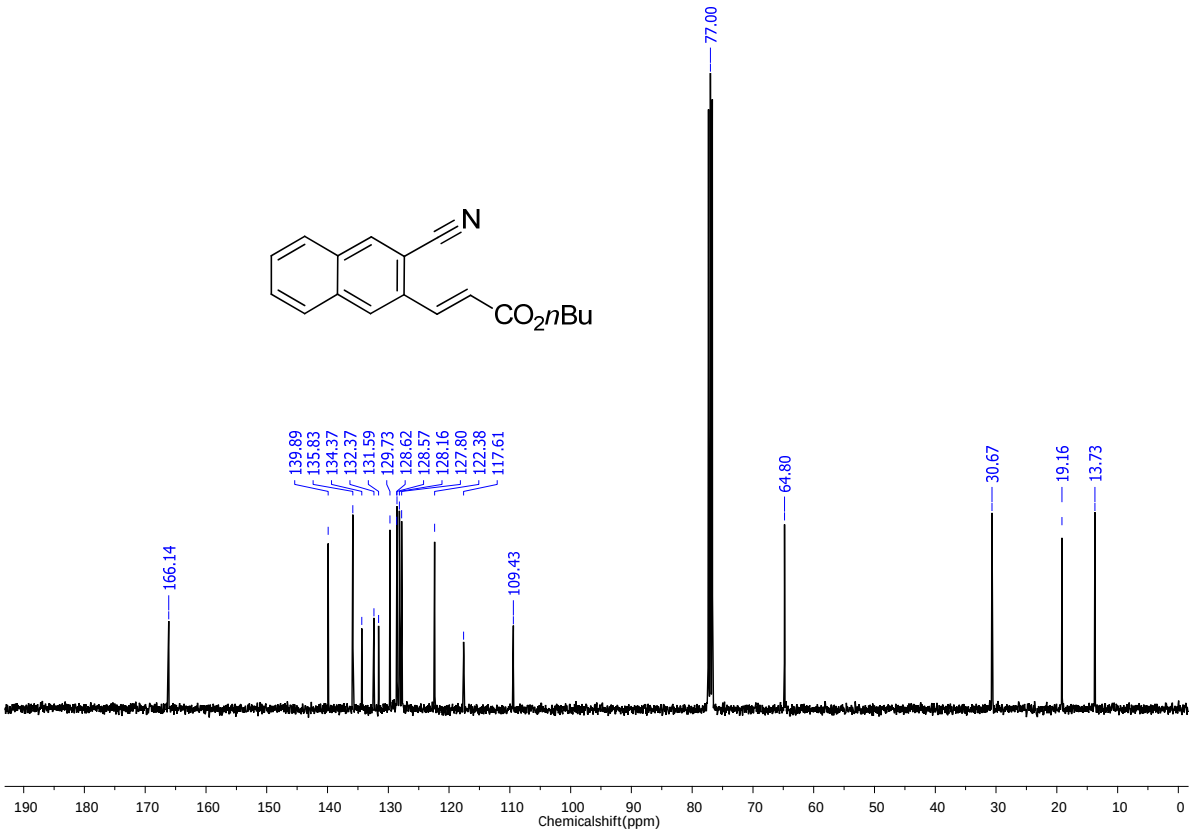




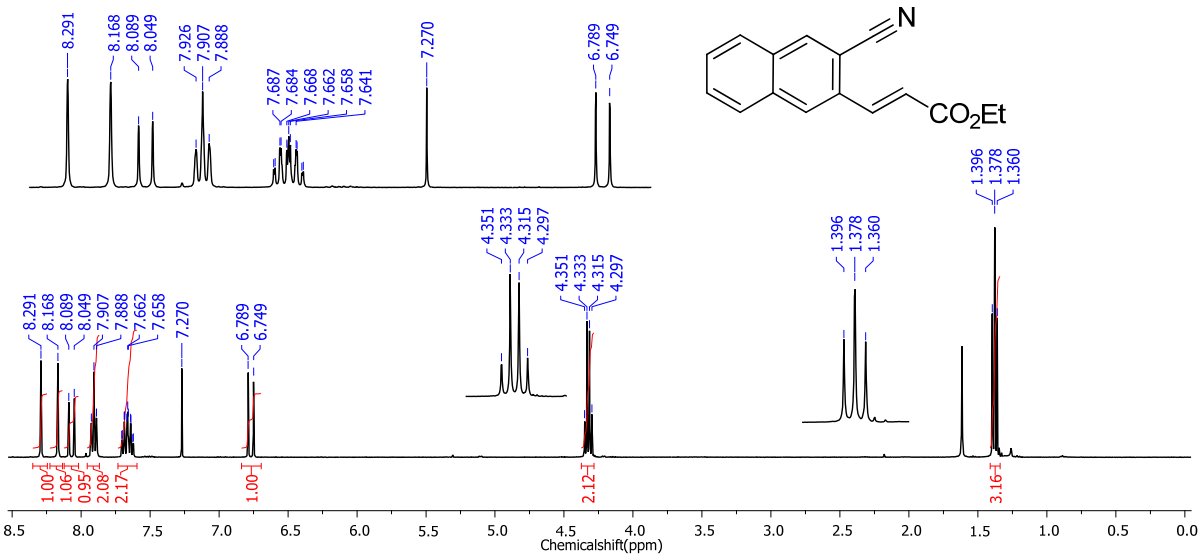


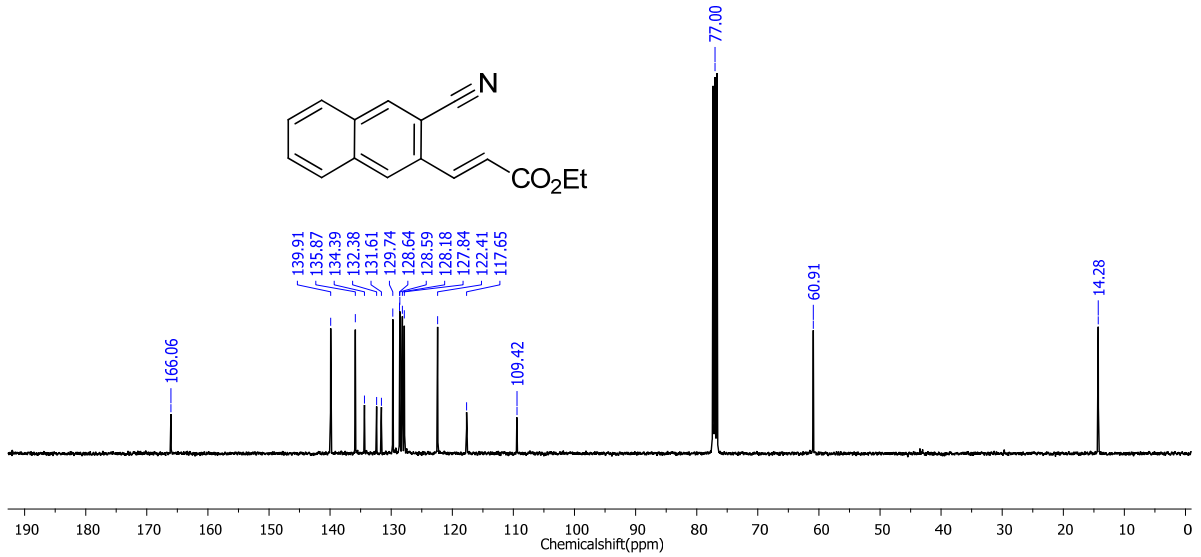
^{1}H and ^{13}C NMR Spectra of Compound **4ba**.

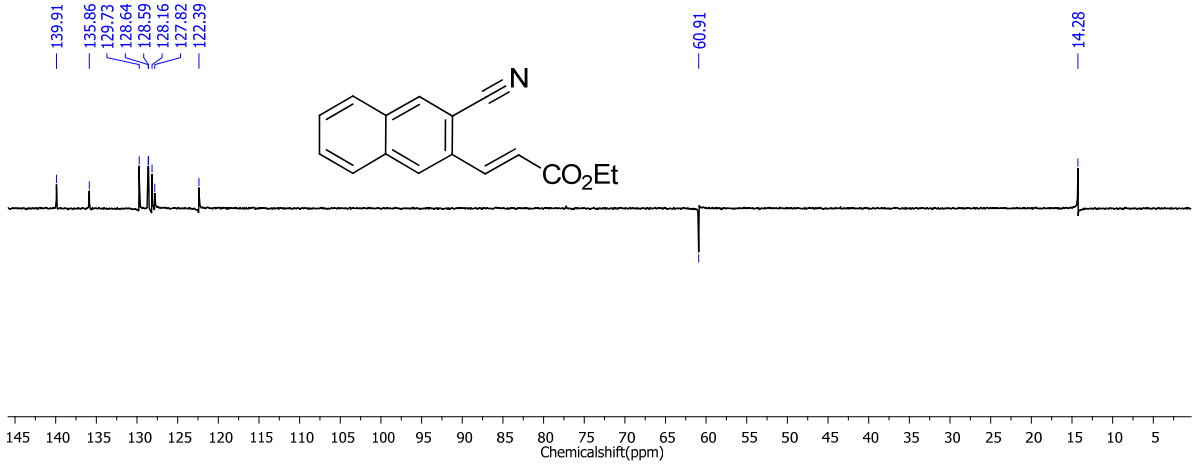




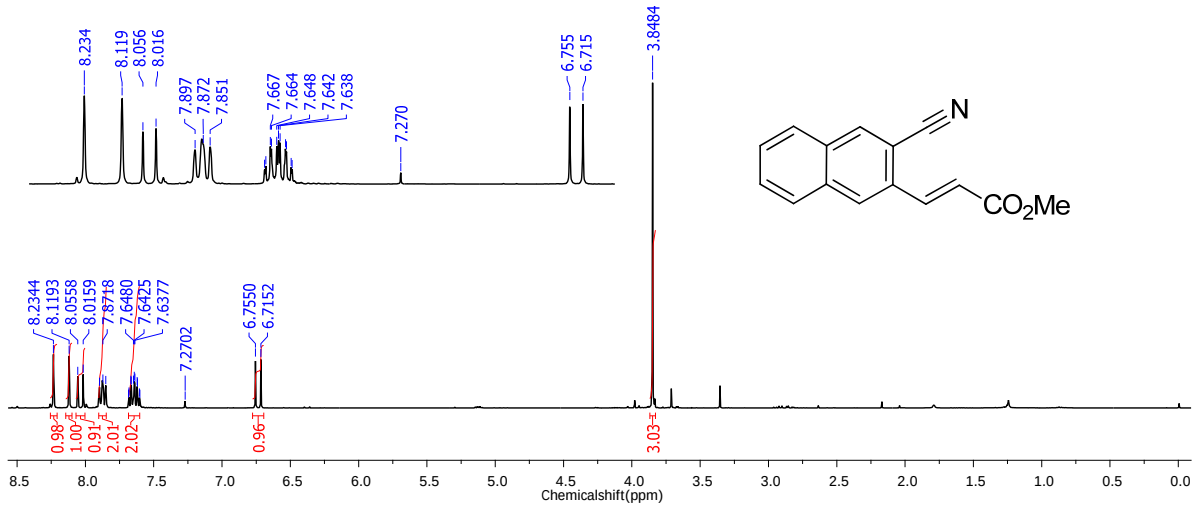
^{1}H and ^{13}C NMR Spectra of Compound **4bb**.

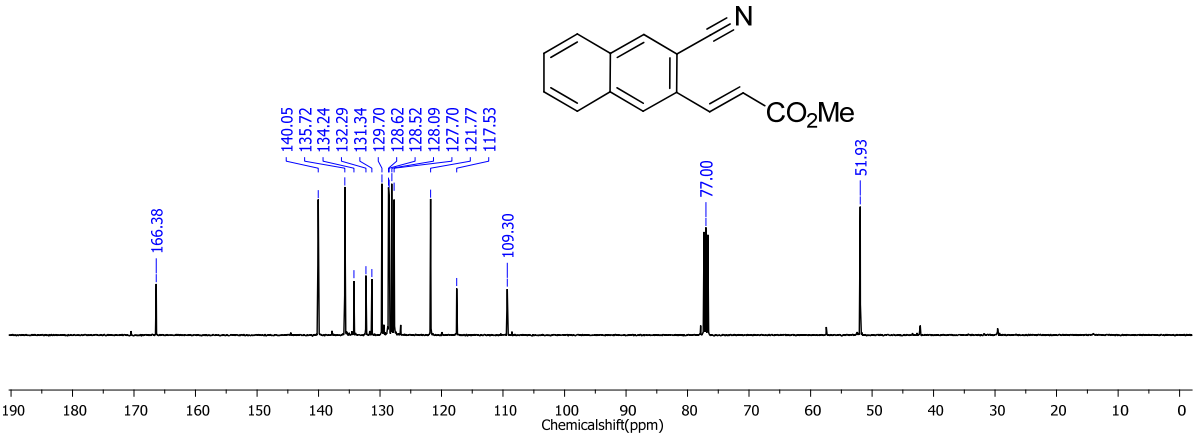


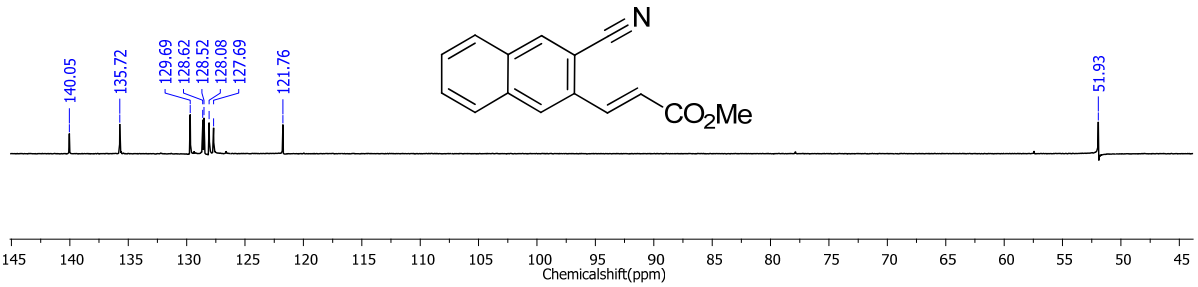




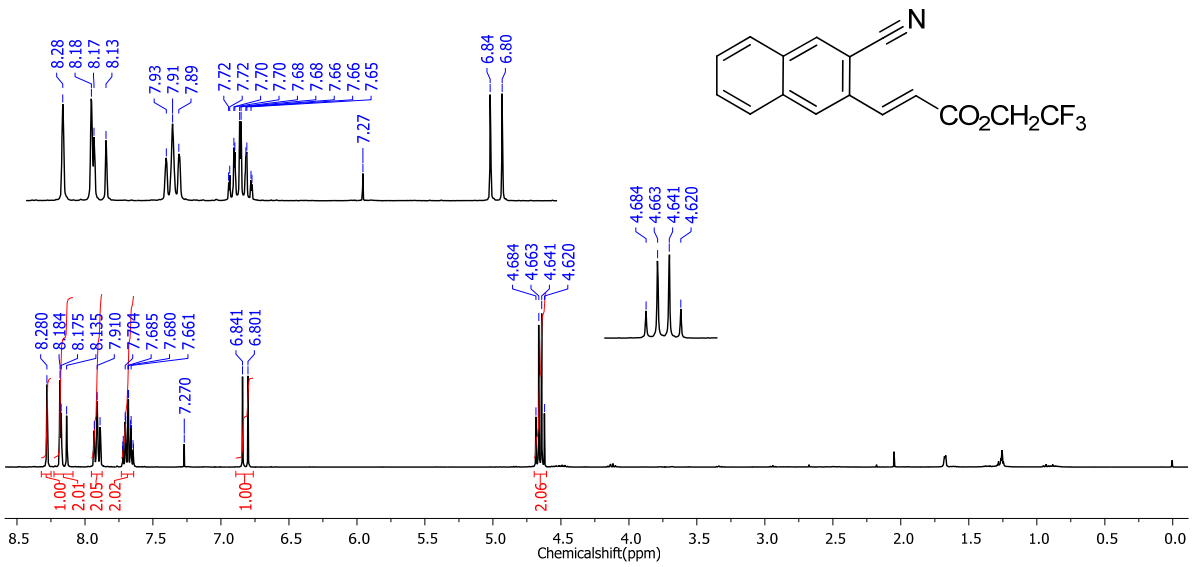
^{1}H and ^{13}C NMR Spectra of Compound **4bg**.

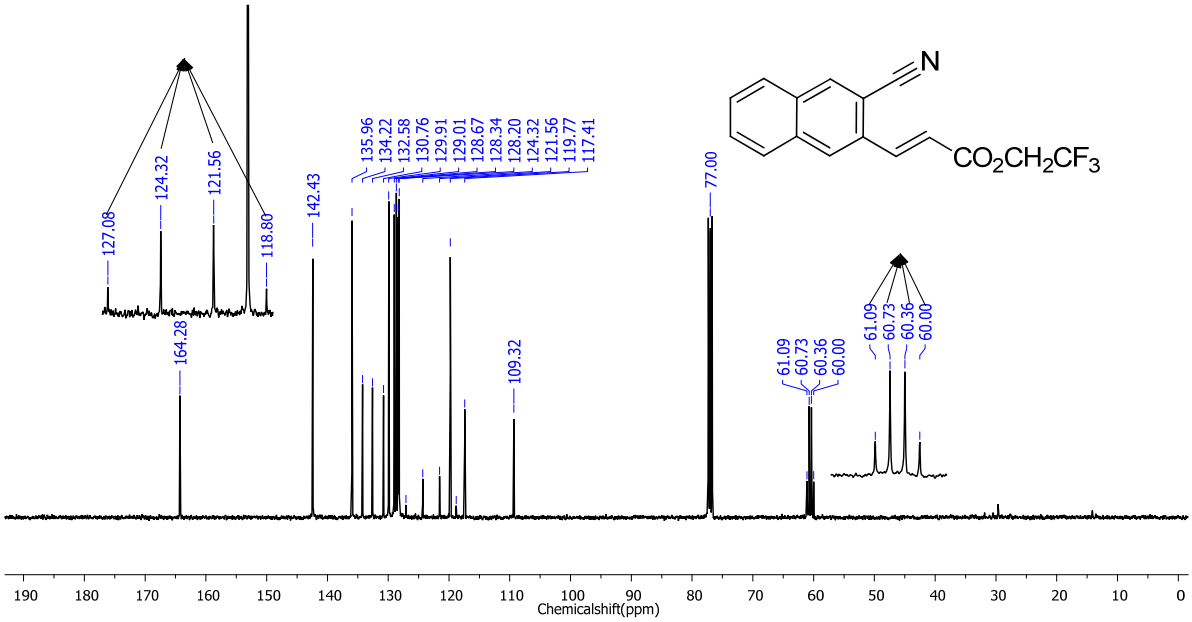


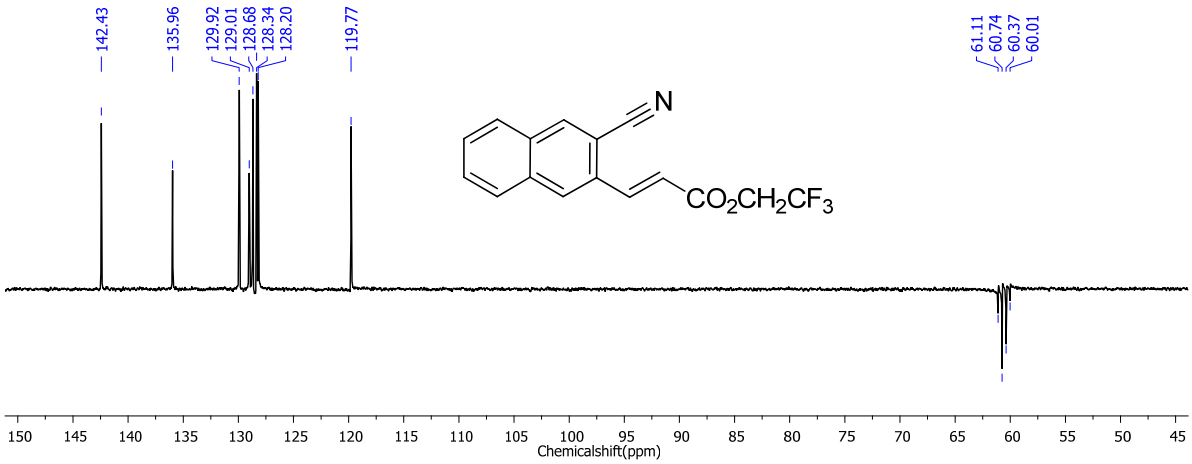




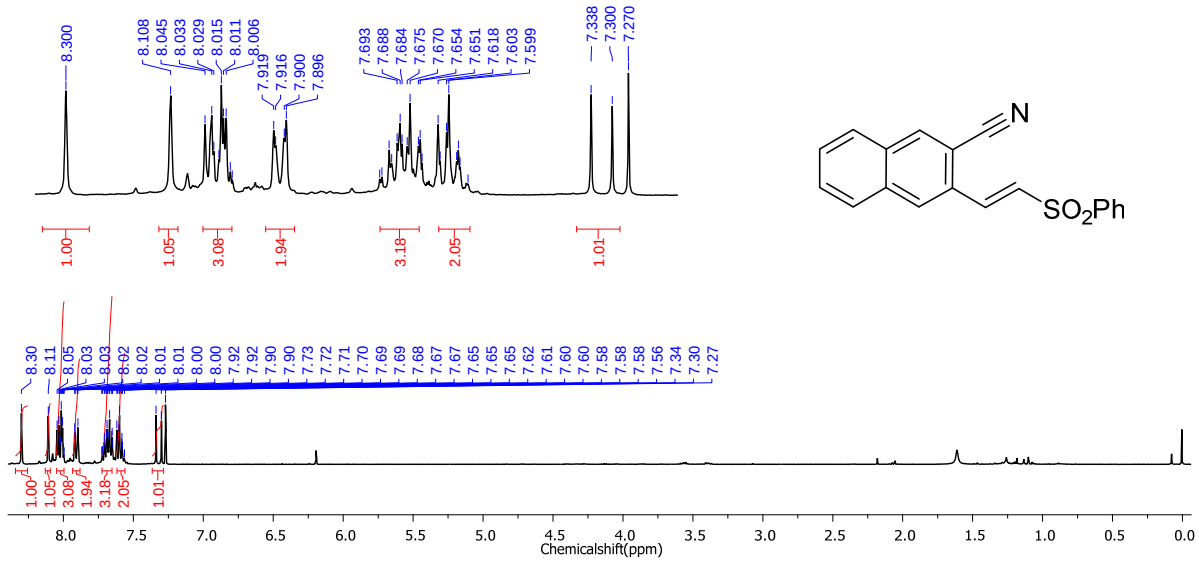
^{1}H and ^{13}C NMR Spectra of Compound **4bh**.

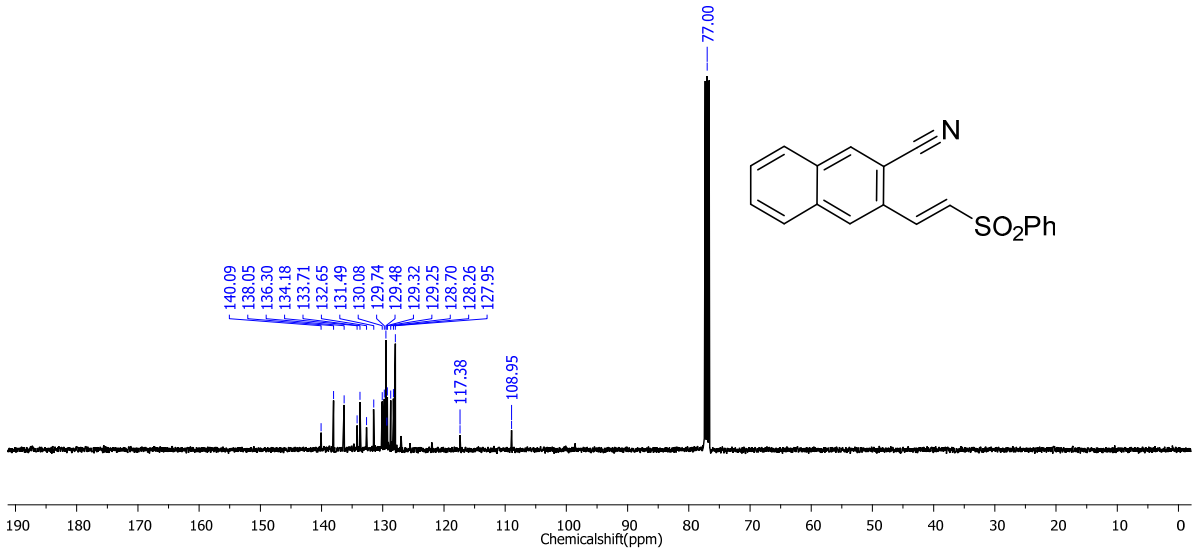


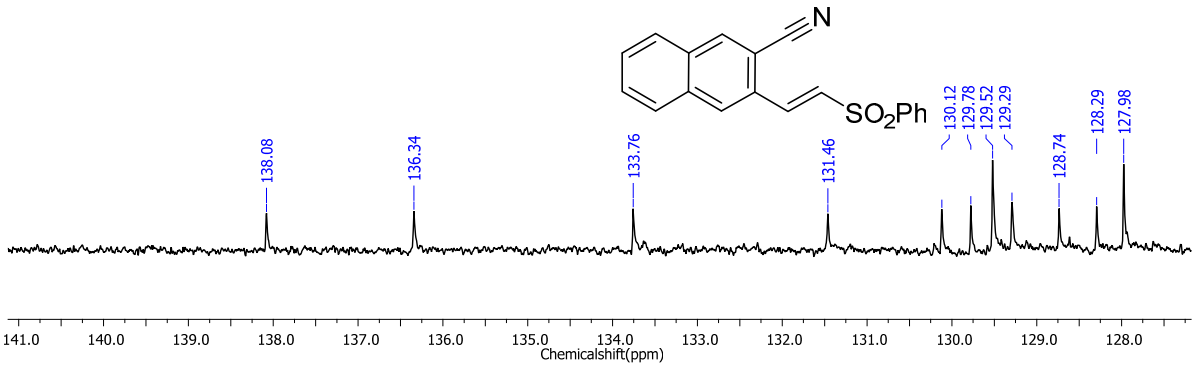




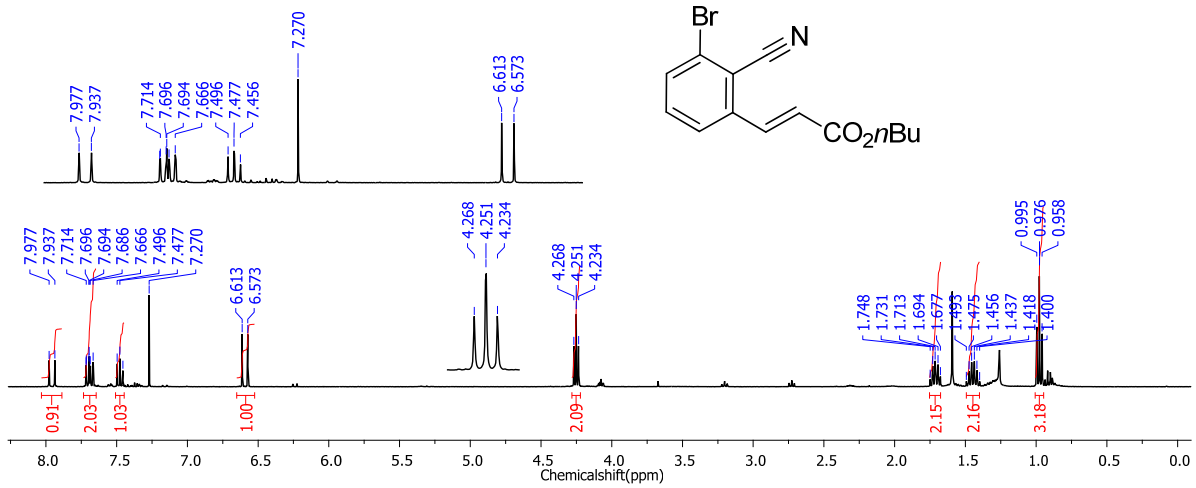
^{1}H and ^{13}C NMR Spectra of Compound **4bi**.

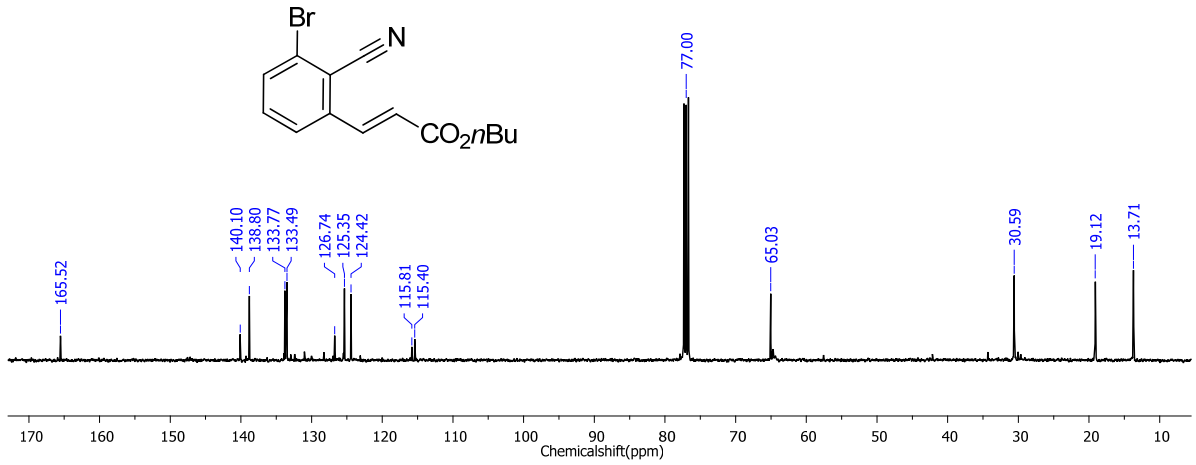


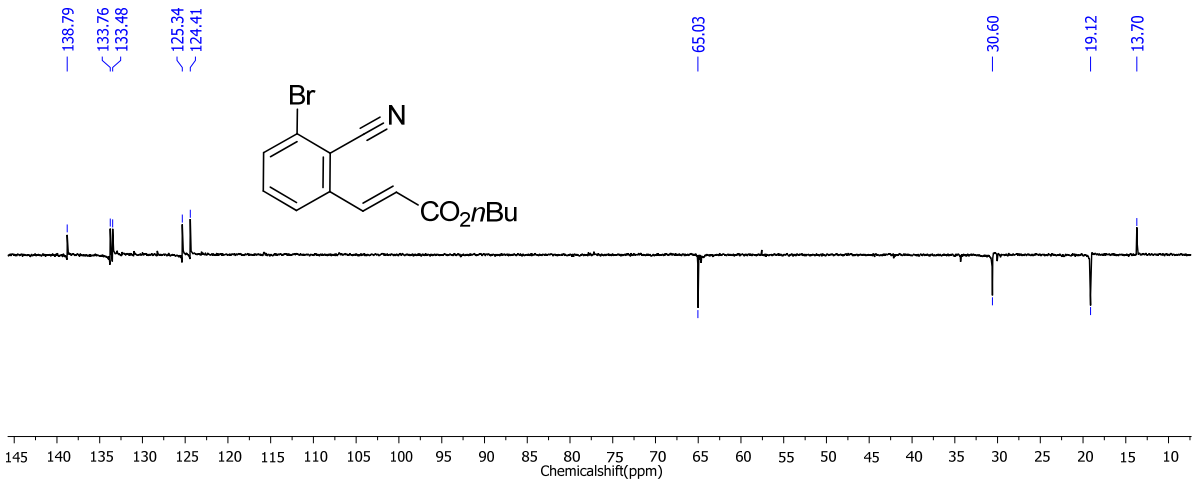




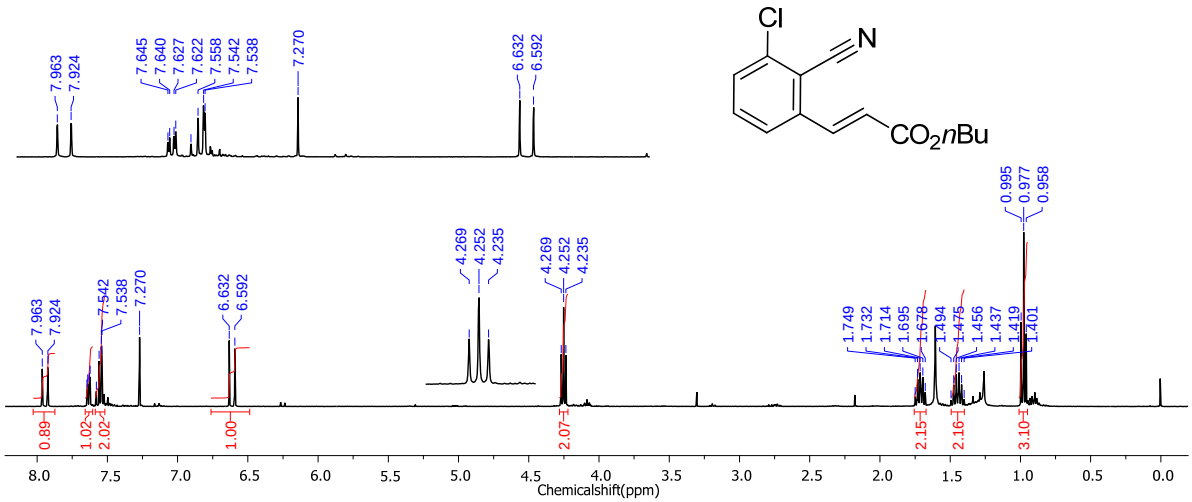
^{1}H and ^{13}C NMR Spectra of Compound **4ca**.

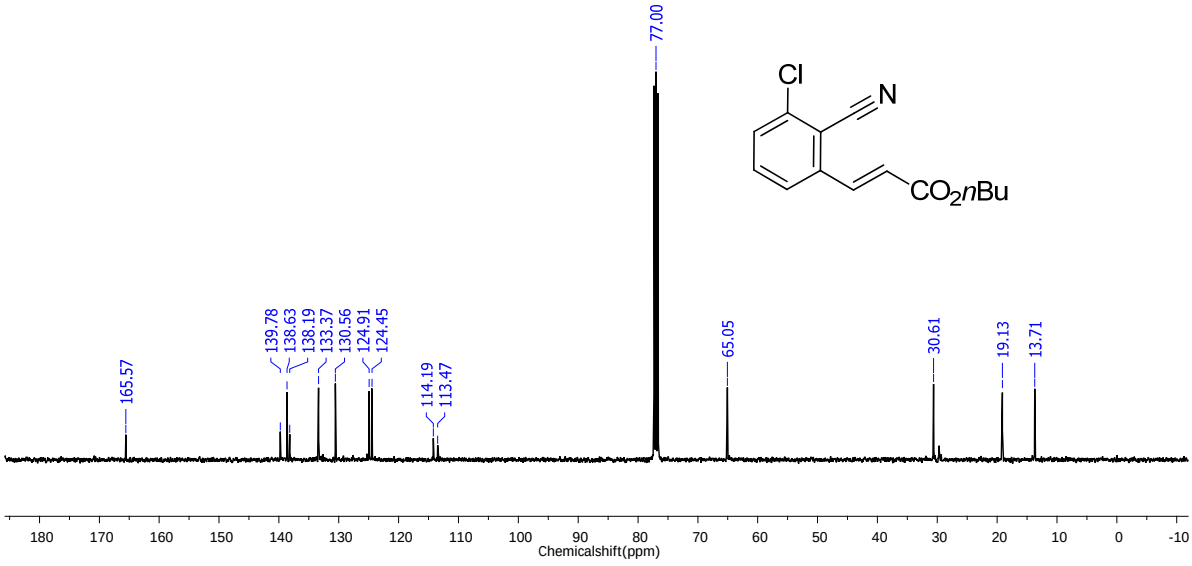


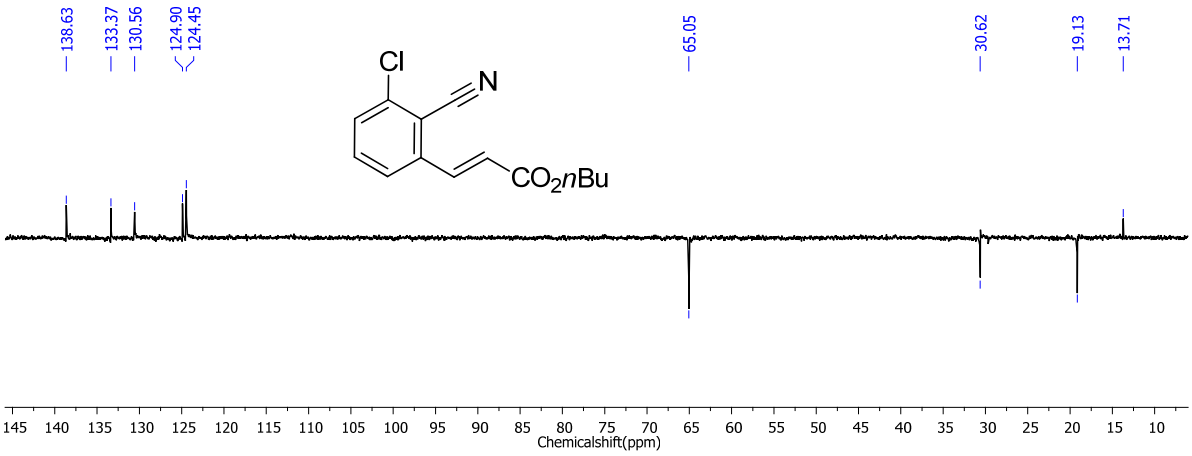




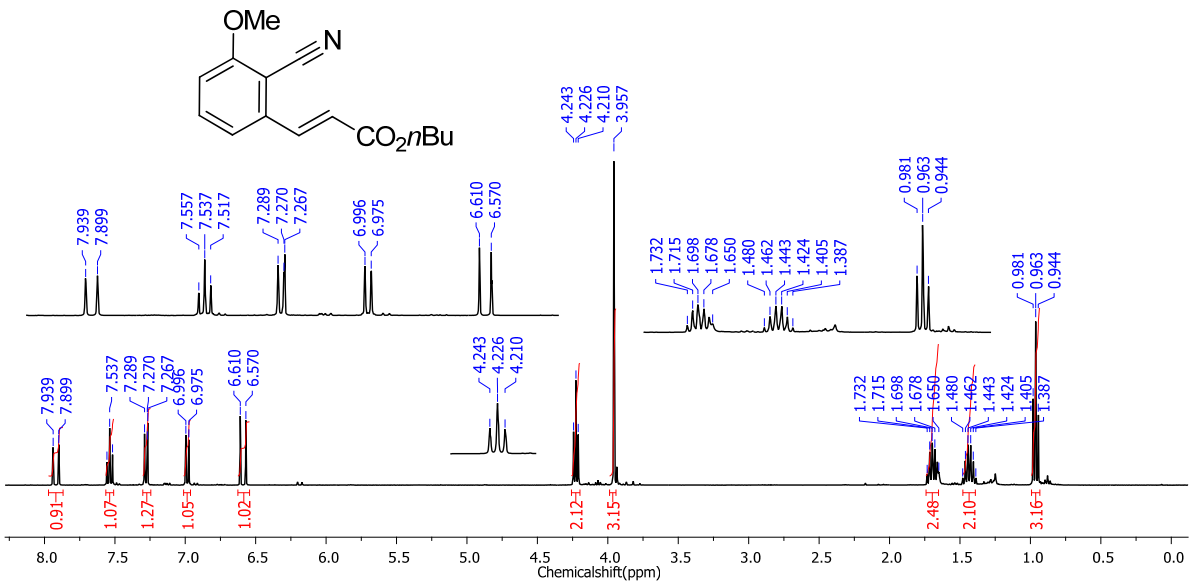
^{1}H and ^{13}C NMR Spectra of Compound **4da**.

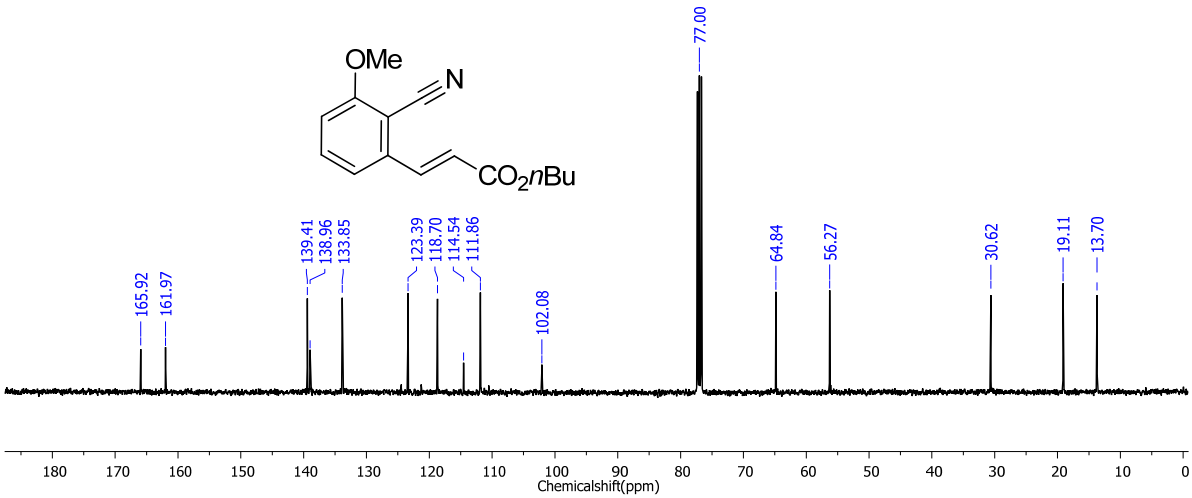


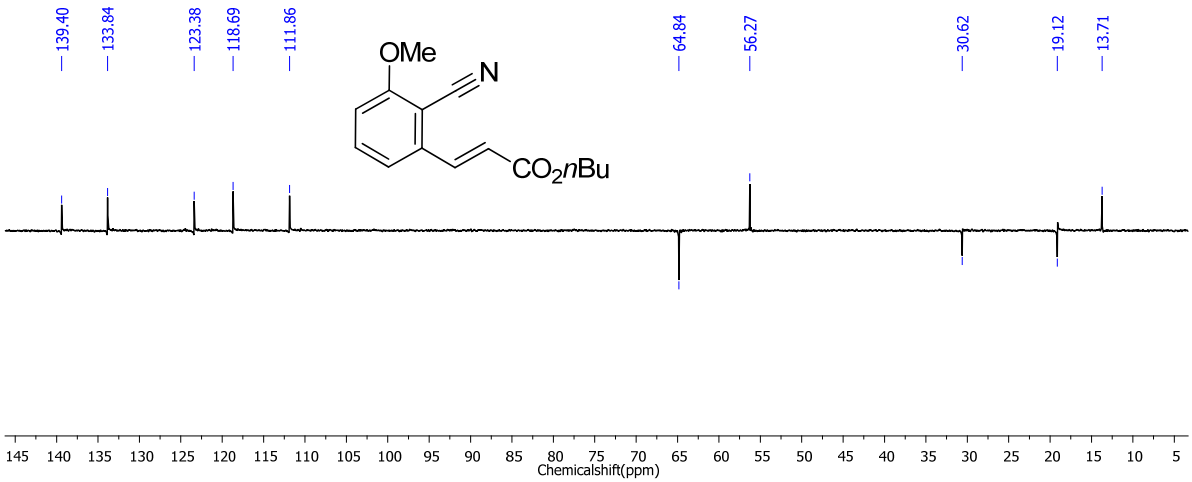




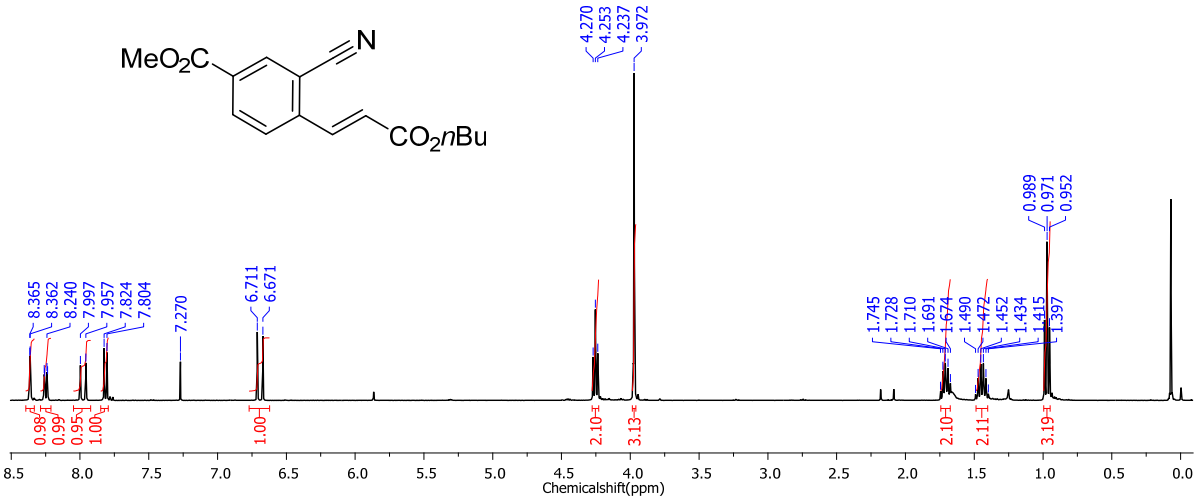
^{1}H and ^{13}C NMR Spectra of Compound **4ea**.

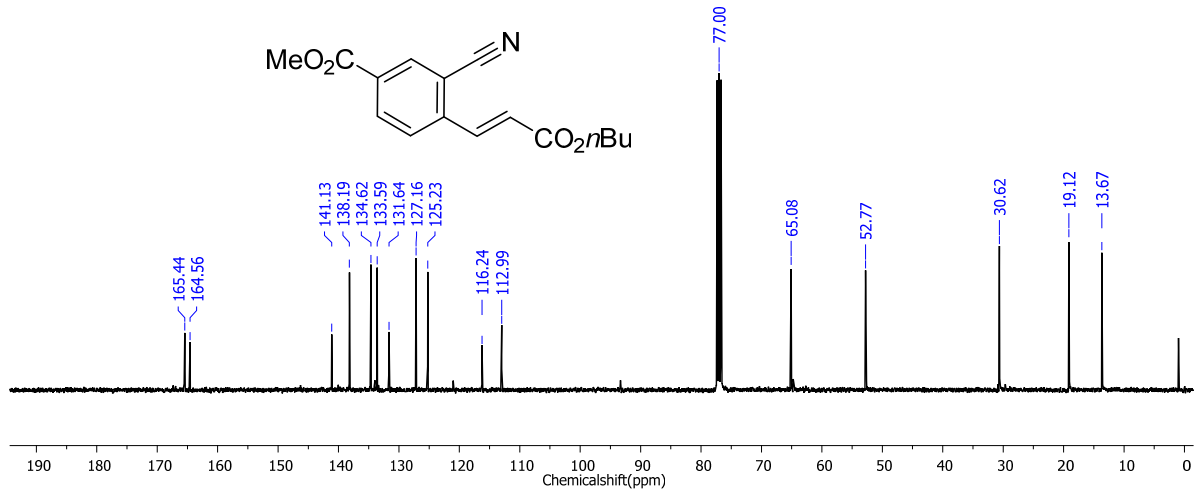


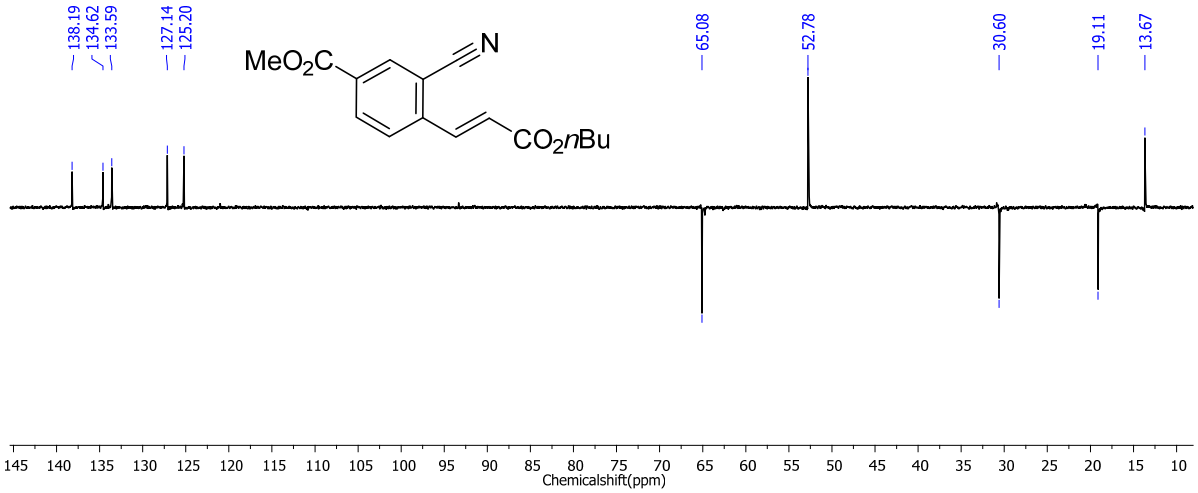




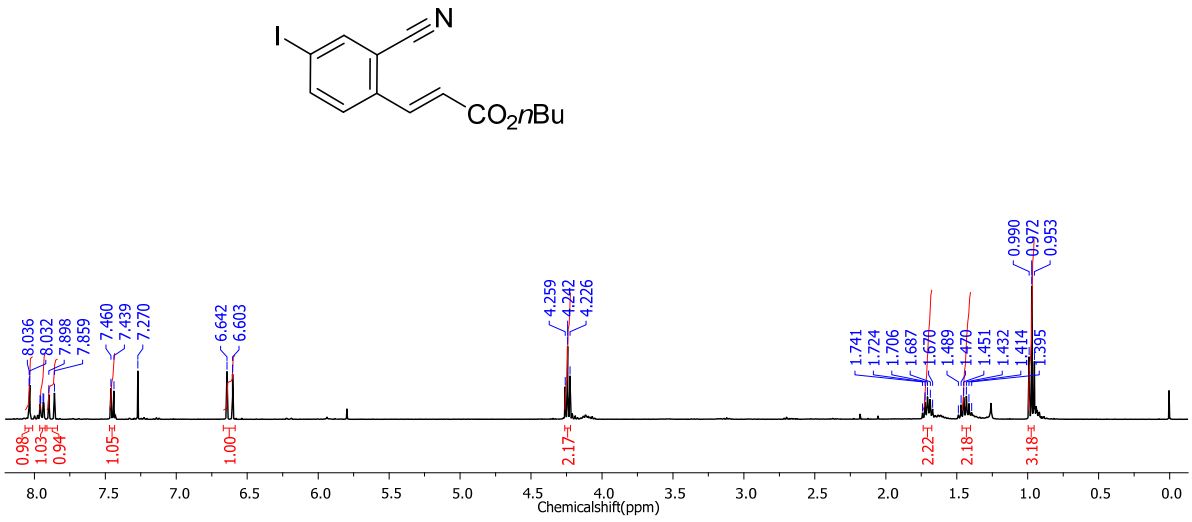
^{1}H and ^{13}C NMR Spectra of Compound **4fa**.

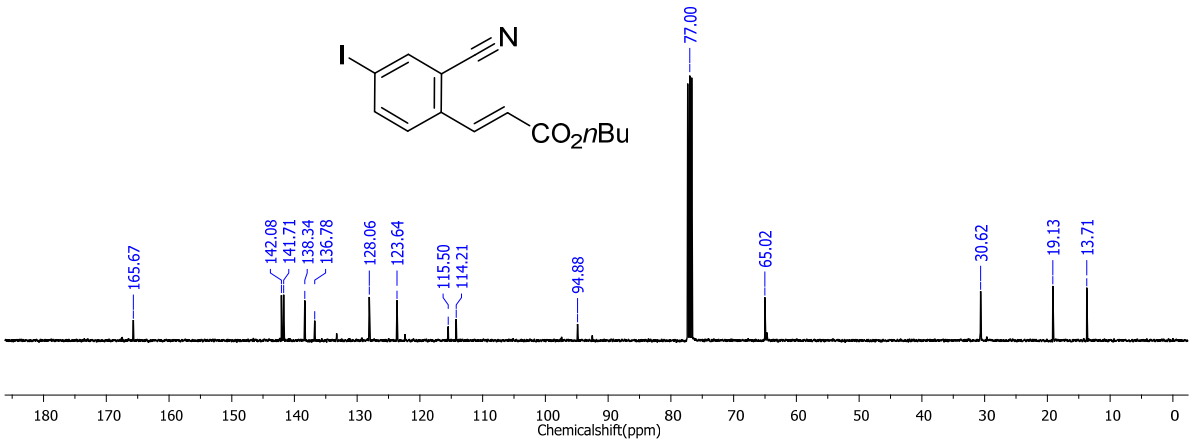


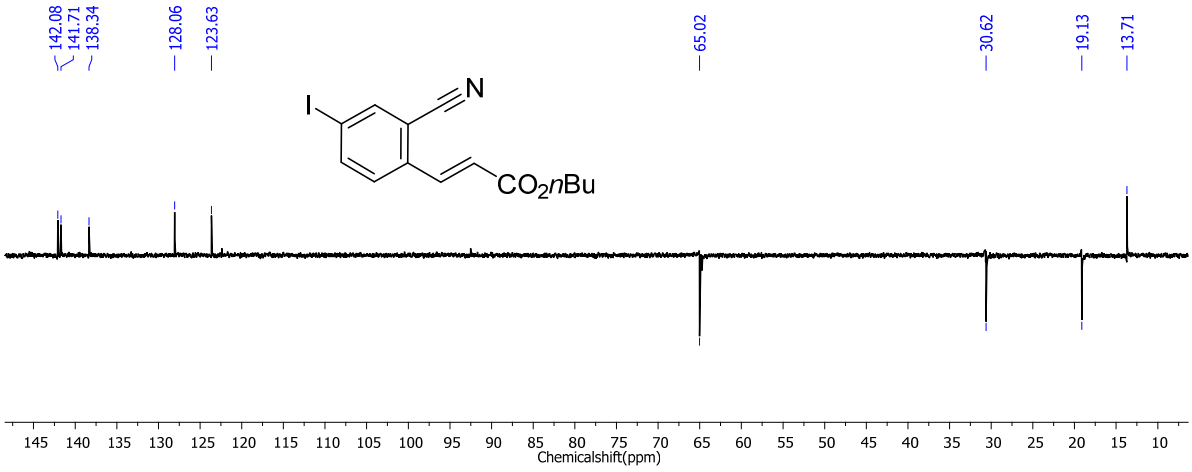




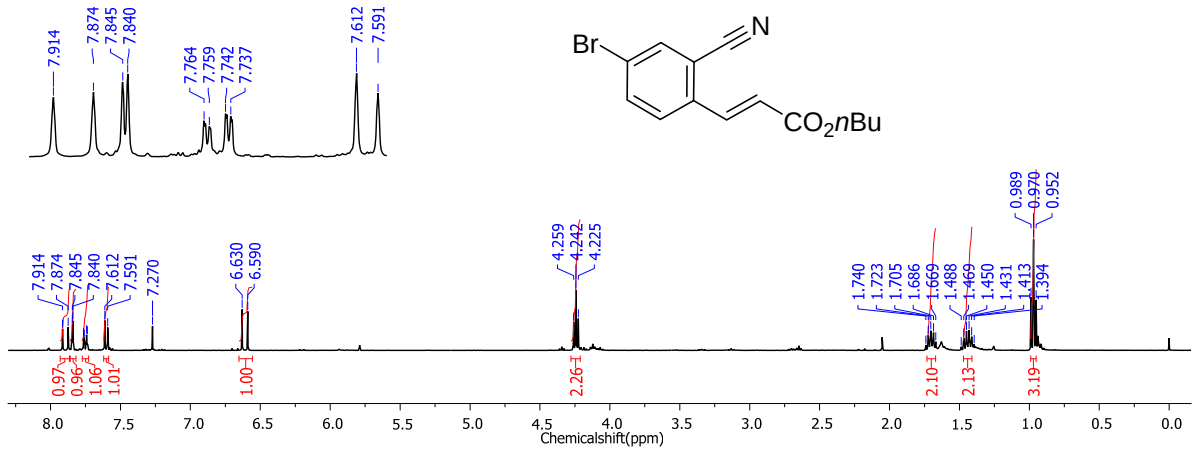
^{1}H and ^{13}C NMR Spectra of Compound **4ga**.

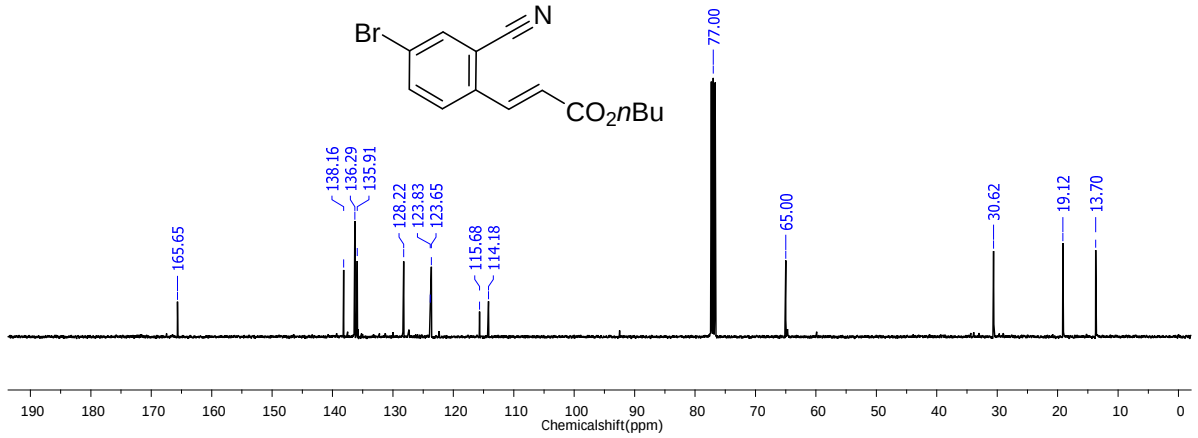


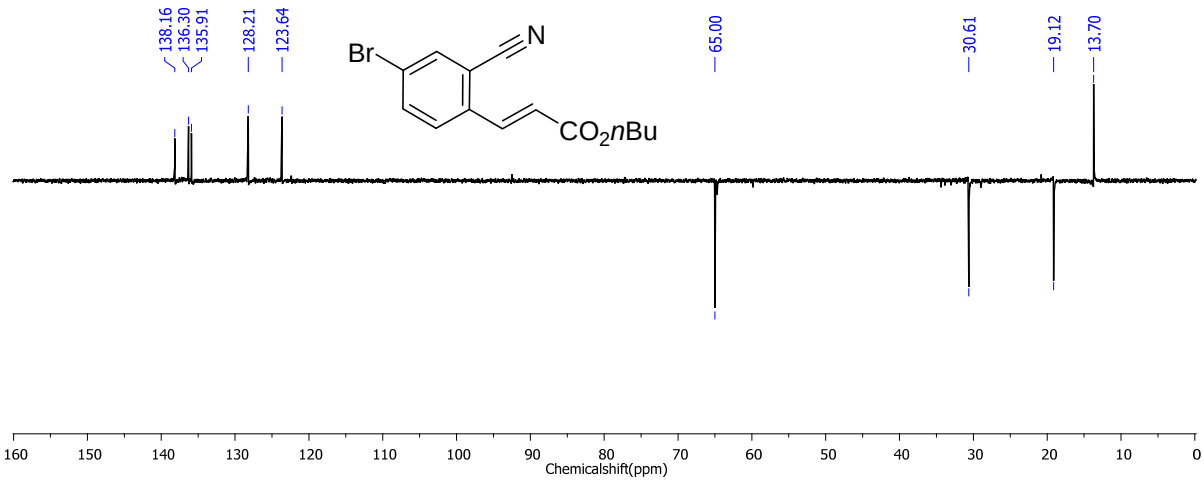




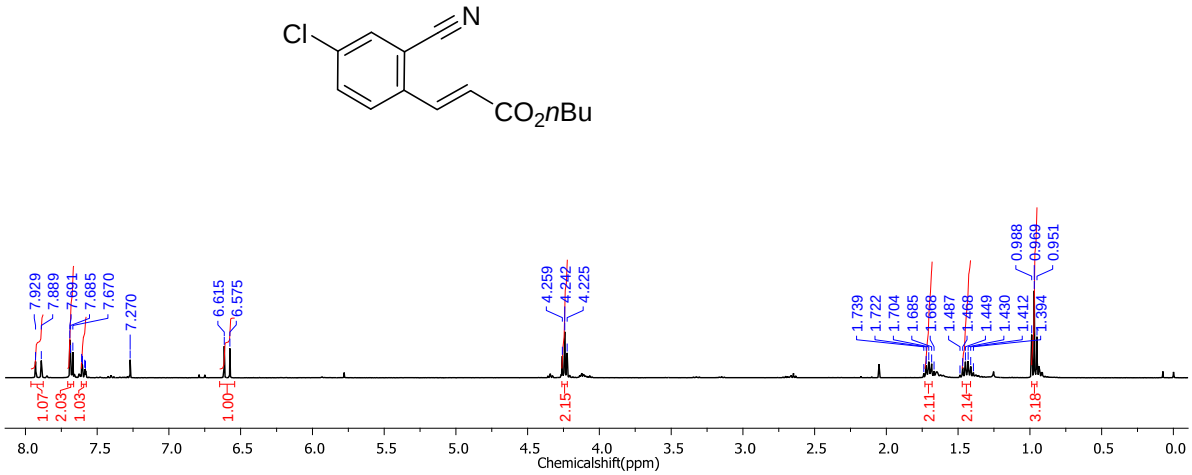
^{1}H and ^{13}C NMR Spectra of Compound **4ha**.

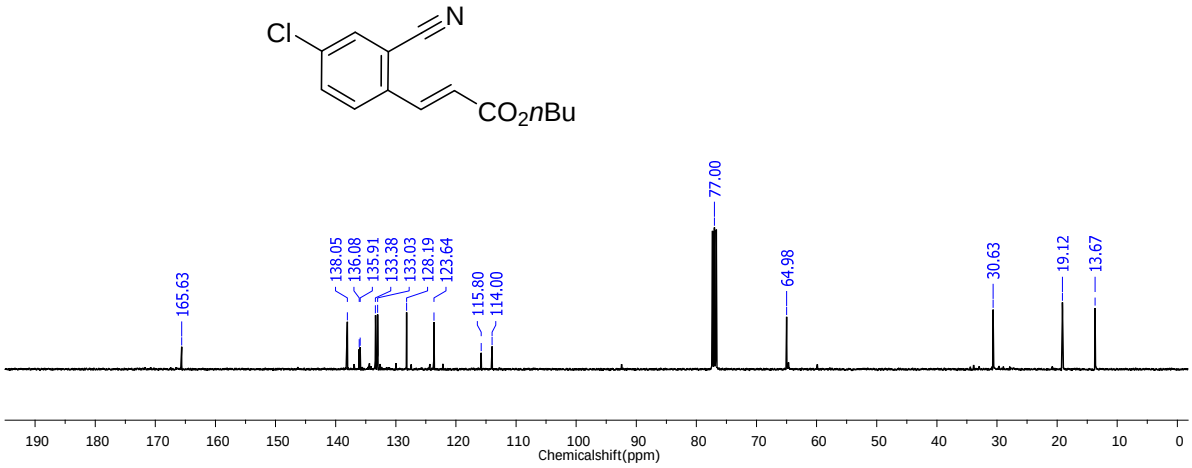


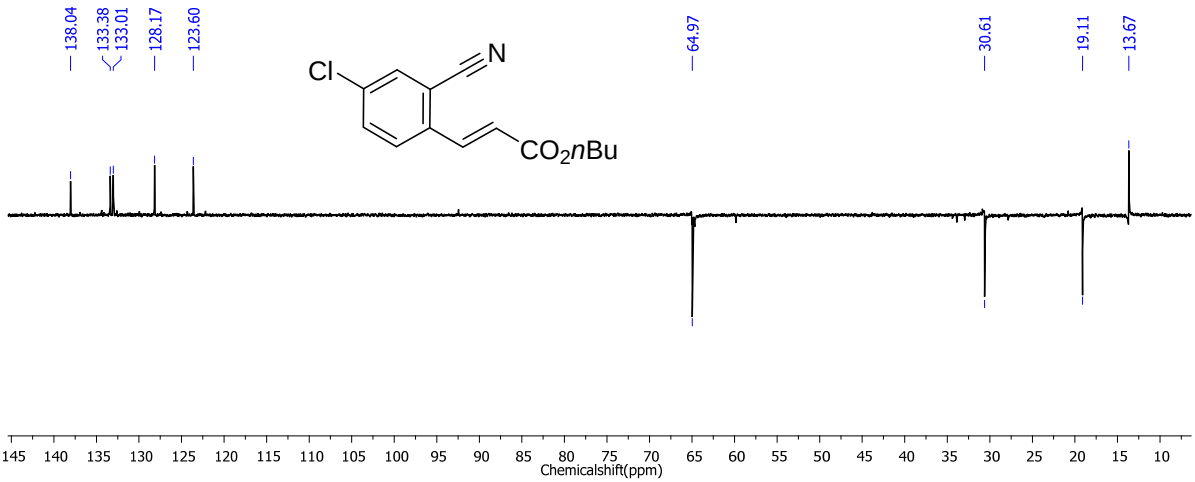




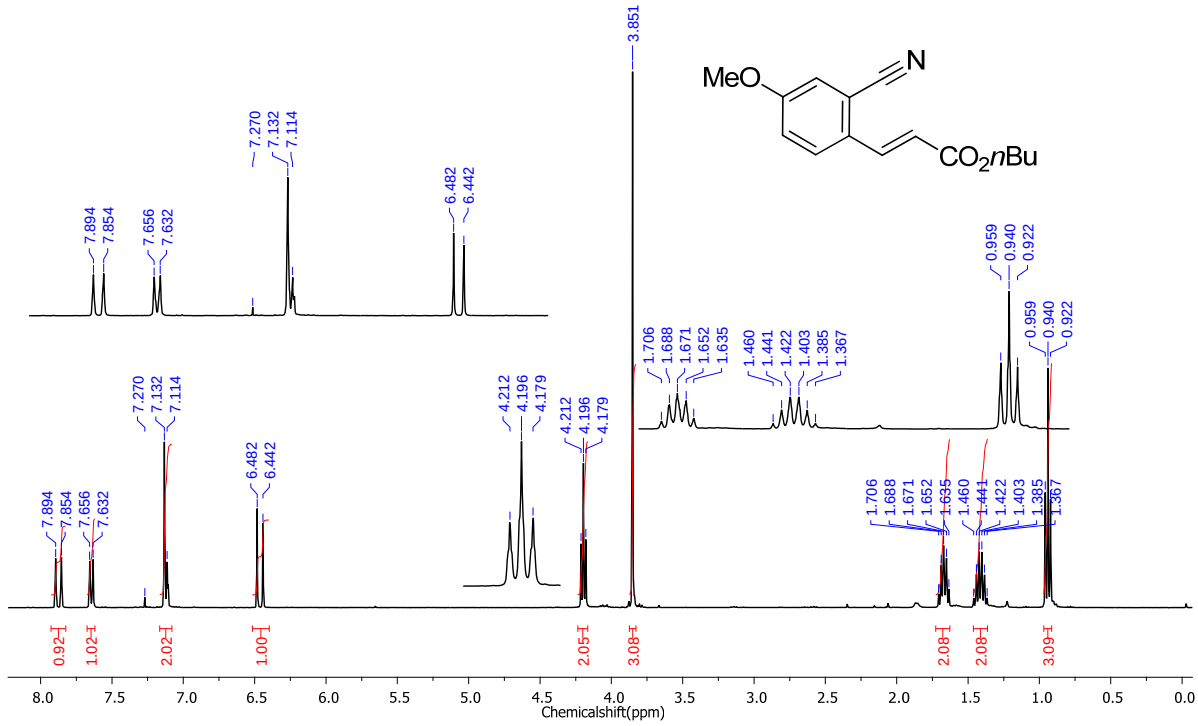
^{1}H and ^{13}C NMR Spectra of Compound **4ia**.

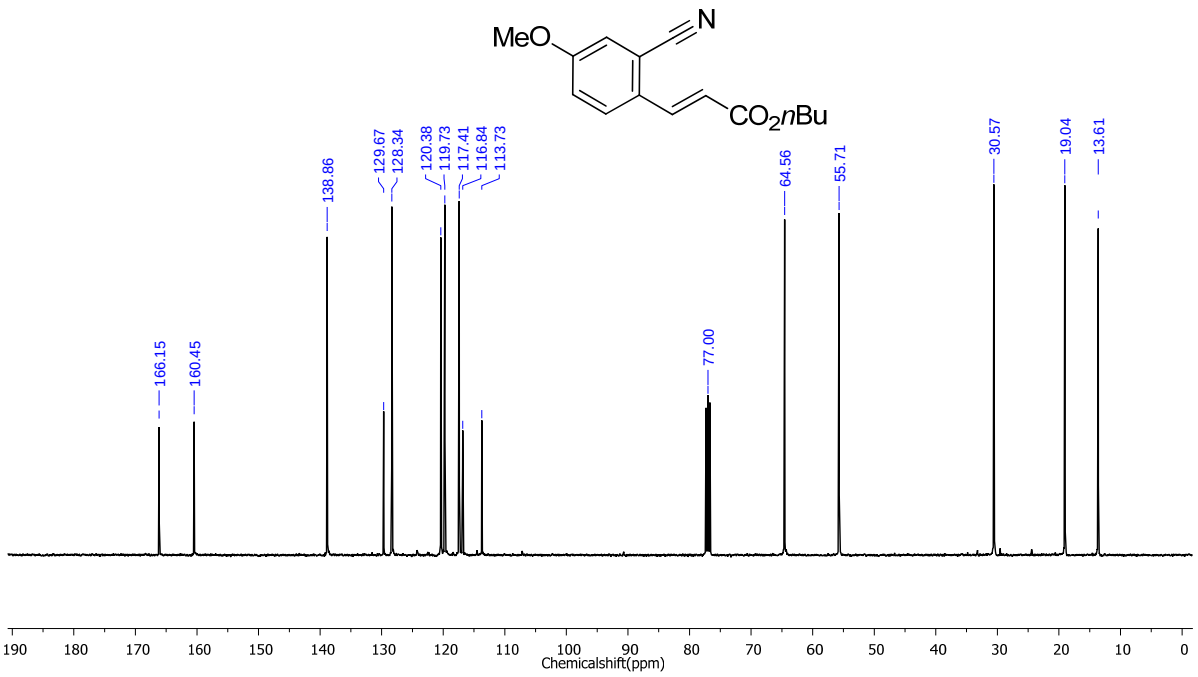






^{1}H and ^{13}C NMR Spectra of Compound **4ja**.





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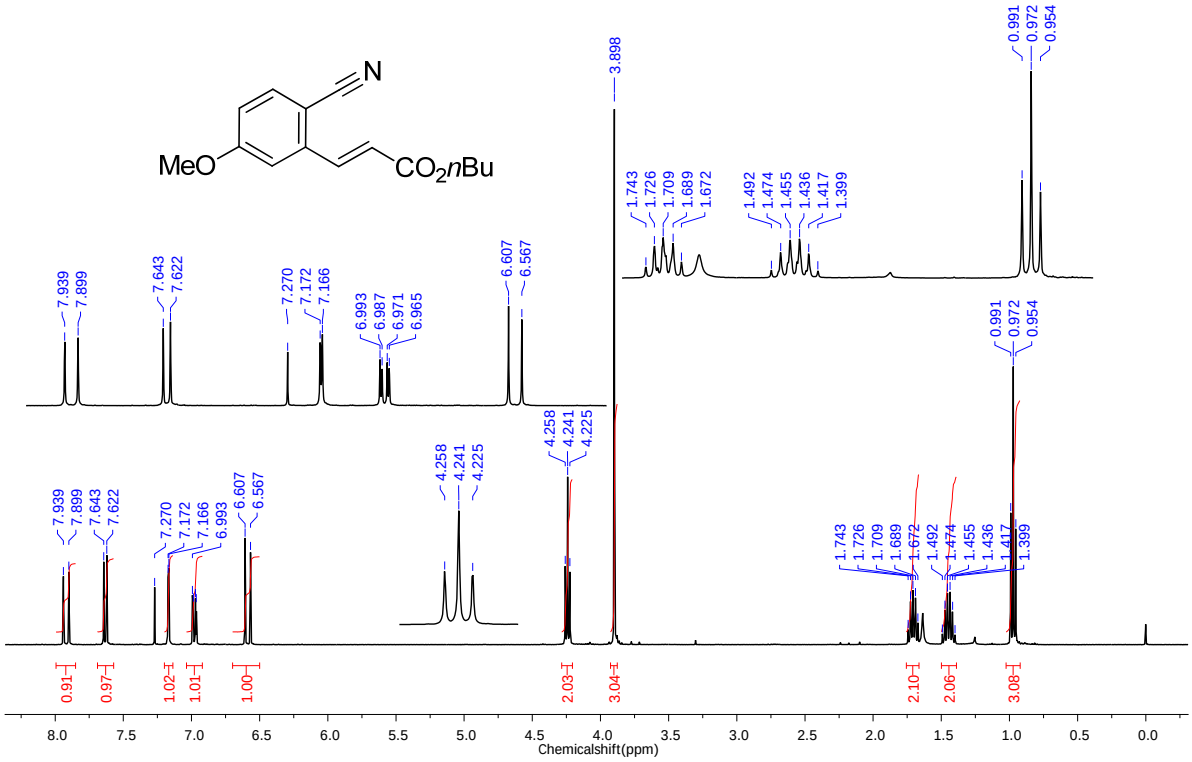
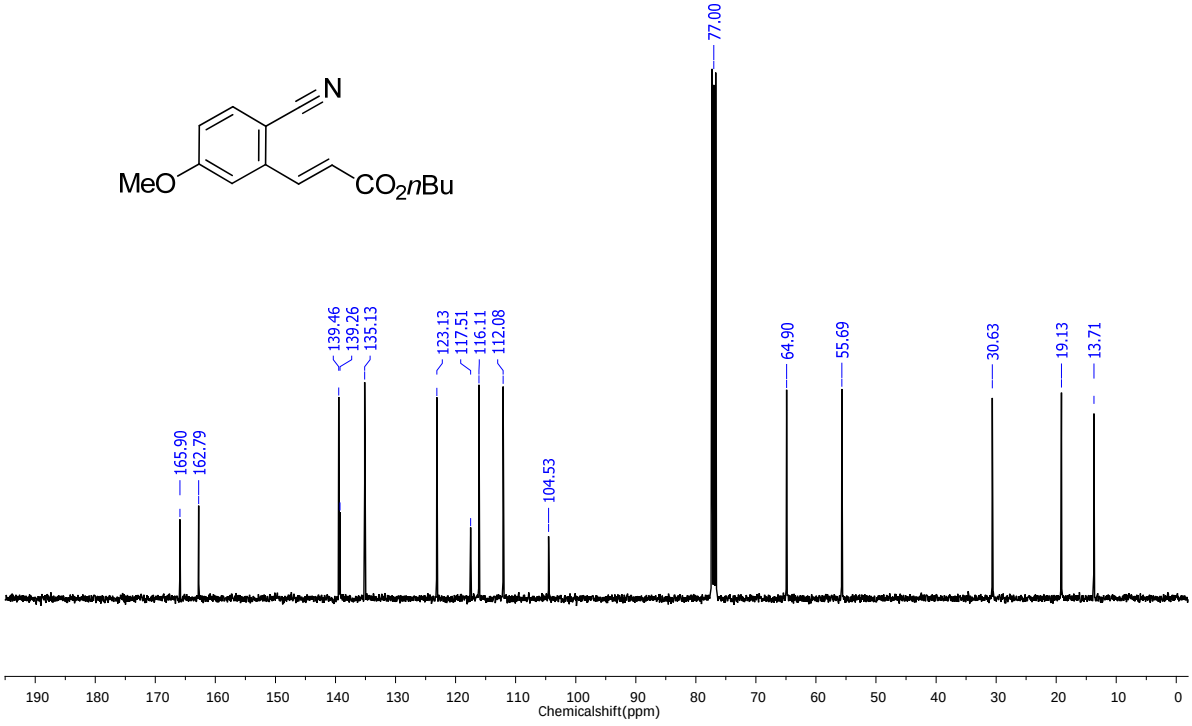
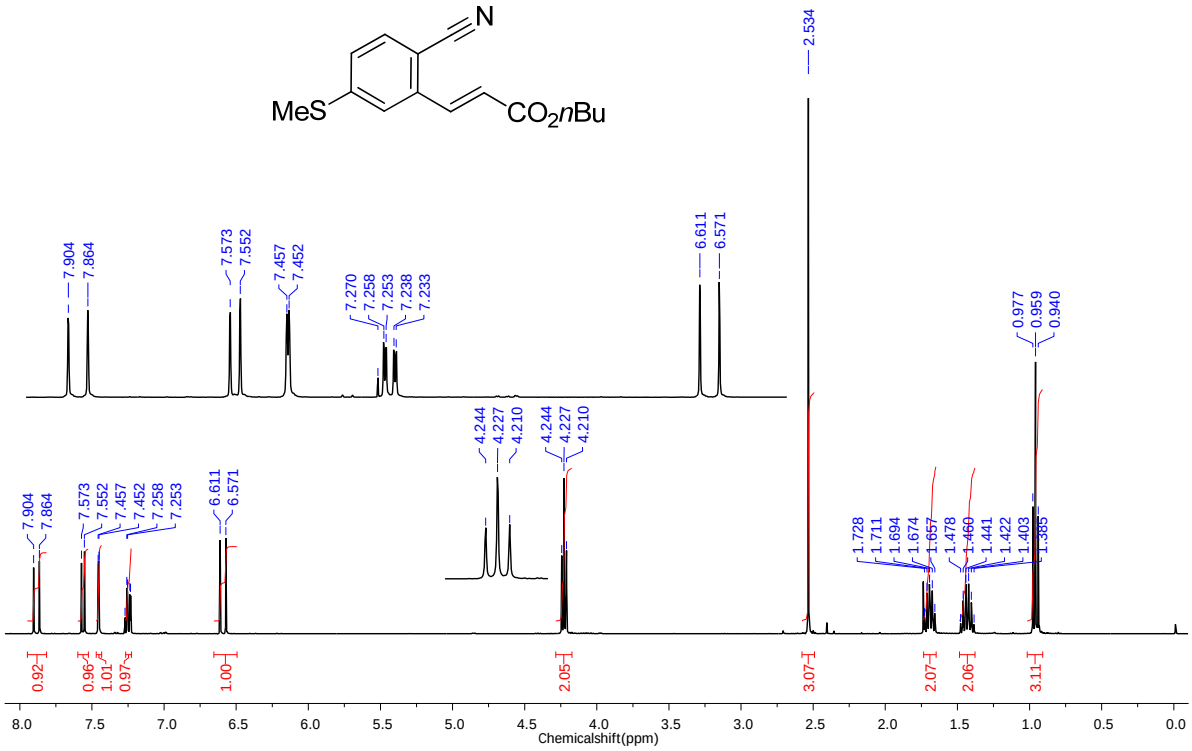
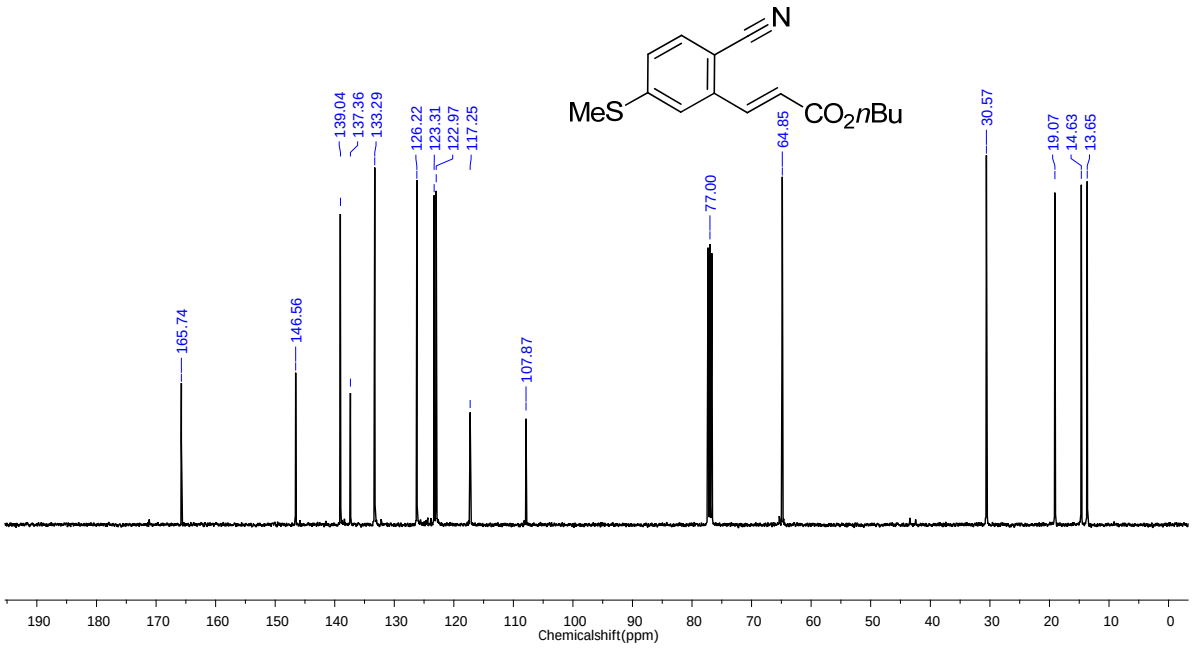


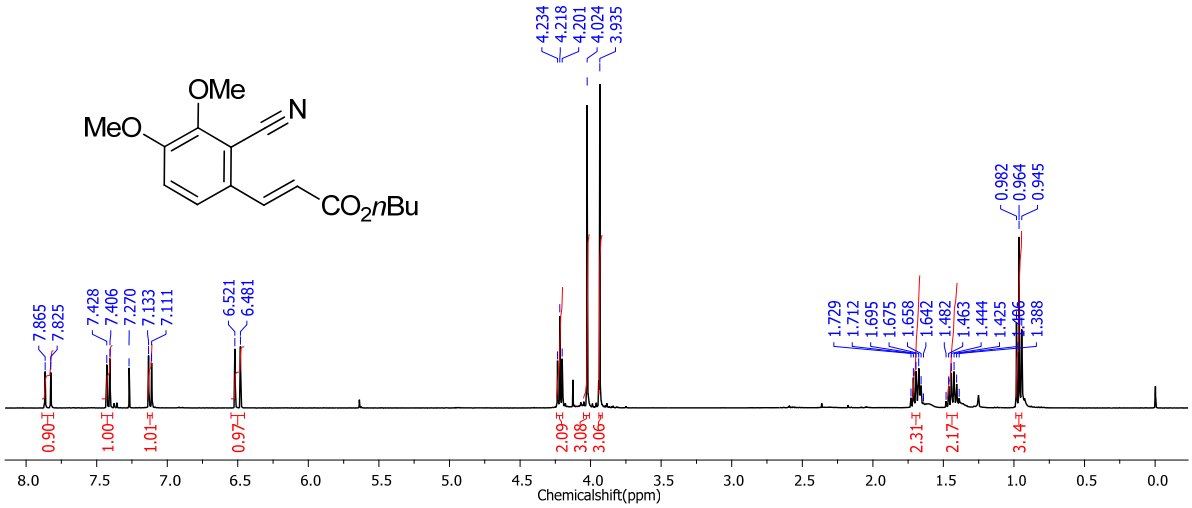


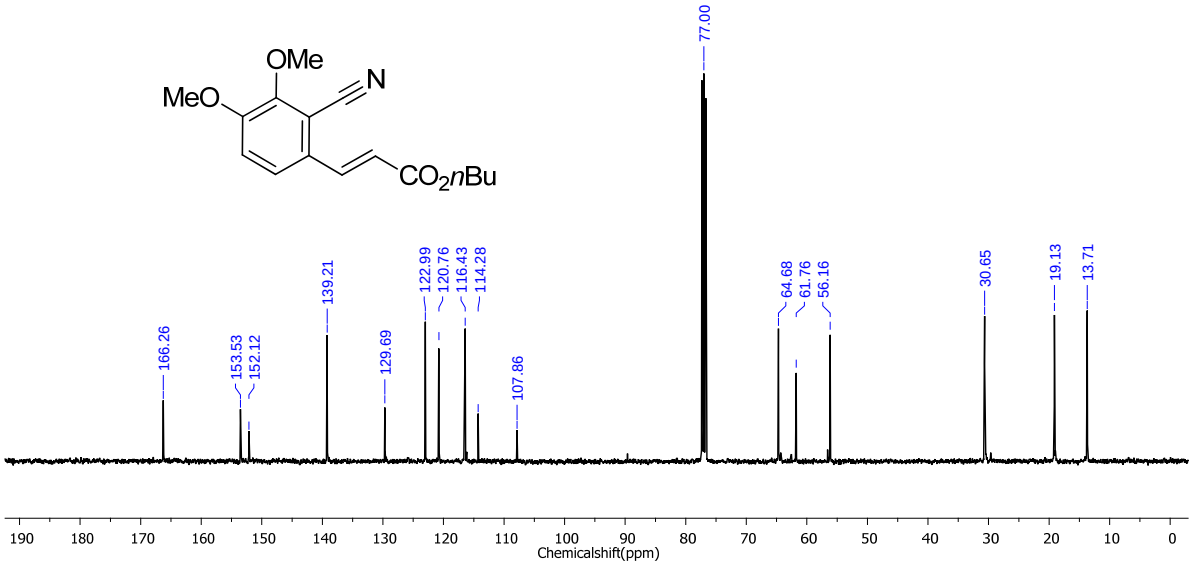
^{1}H and ^{13}C NMR Spectra of Compound **4la**.

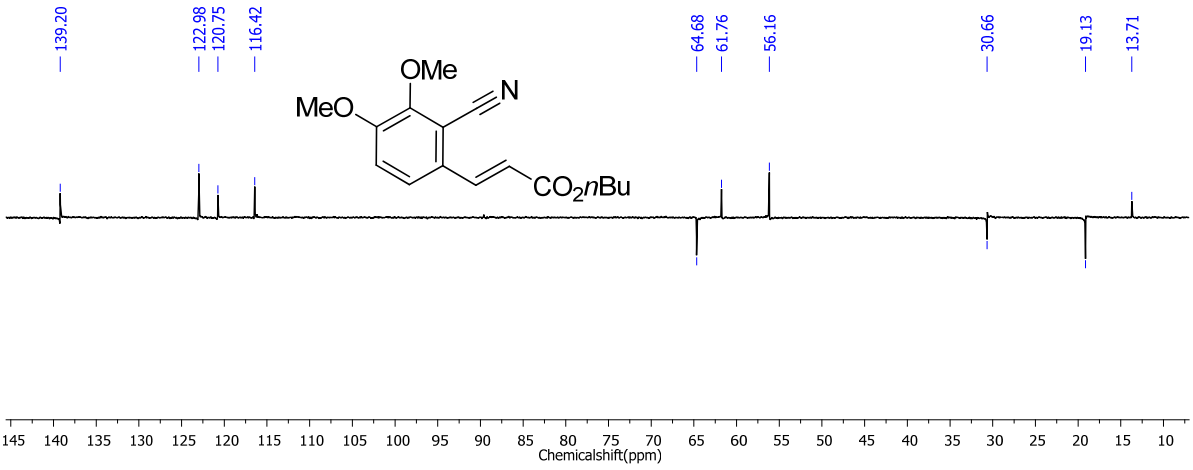




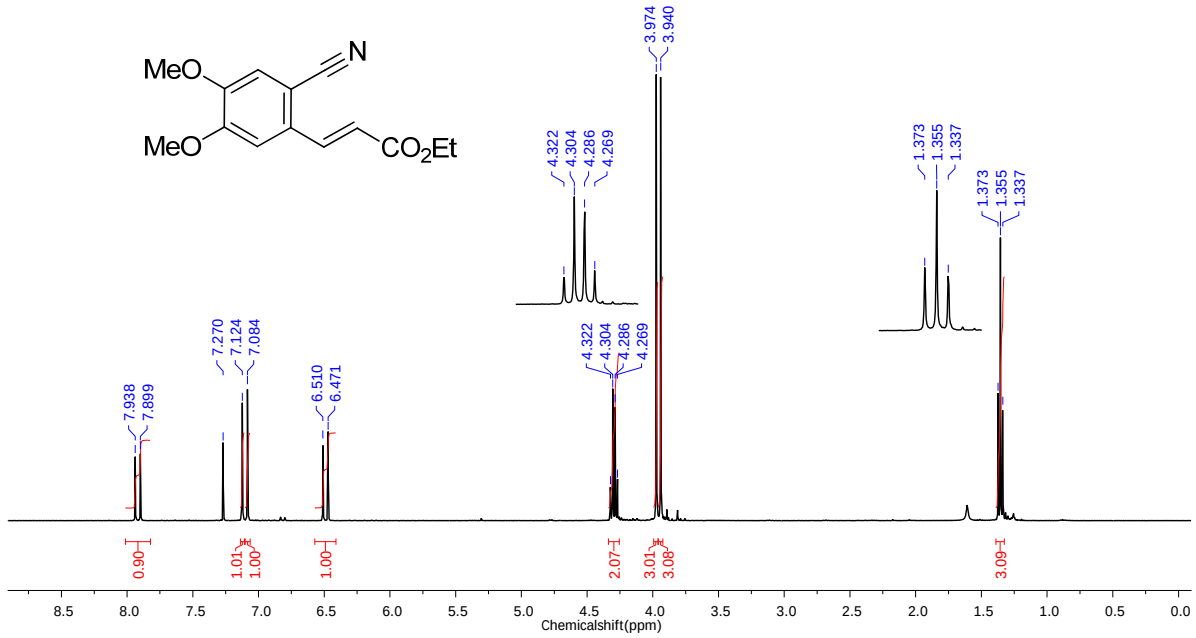
^{1}H and ^{13}C NMR Spectra of Compound **4ma**.

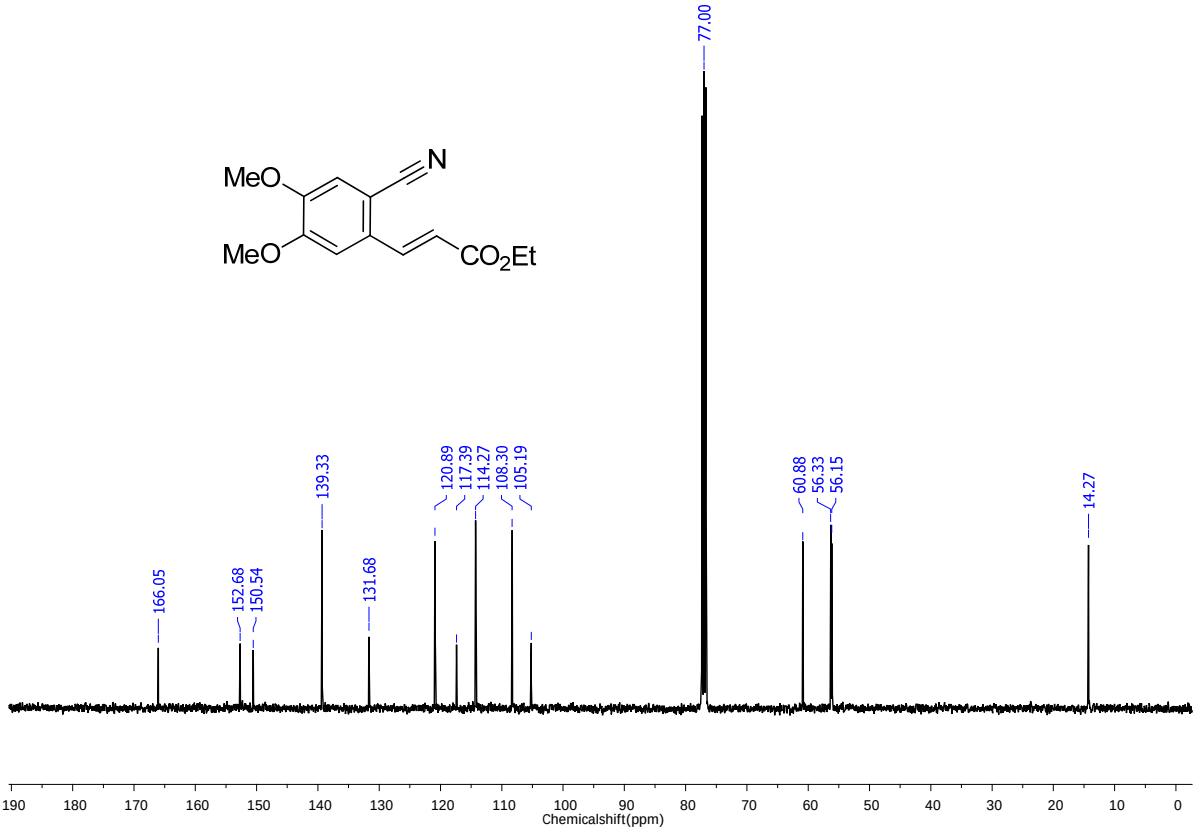




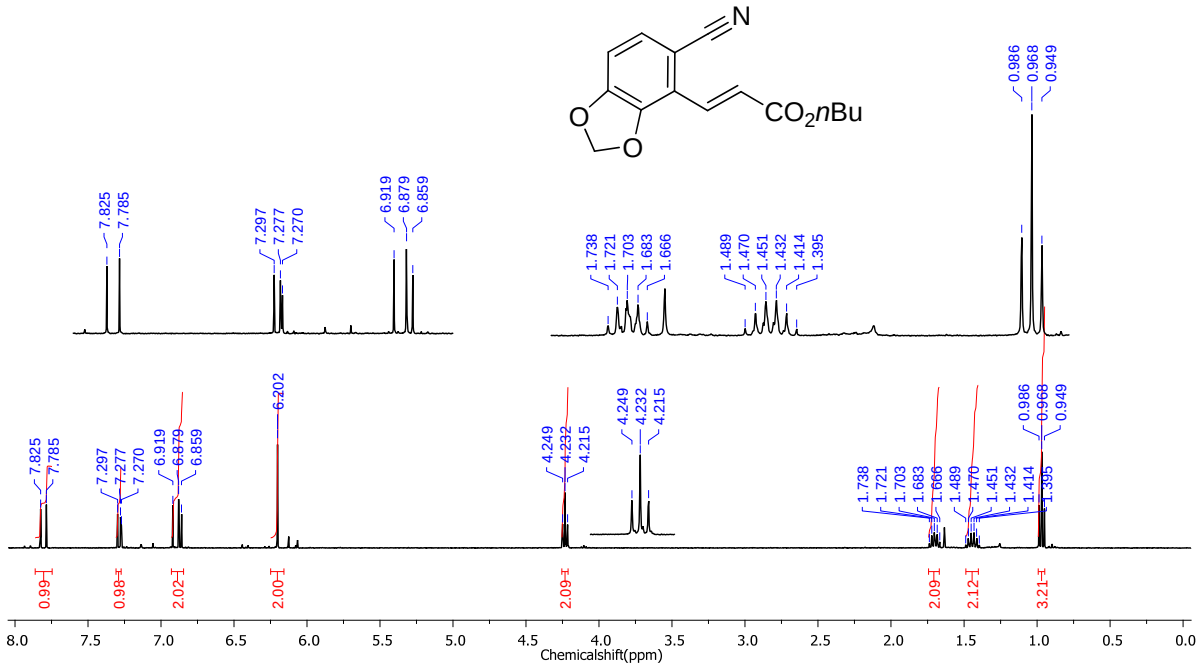


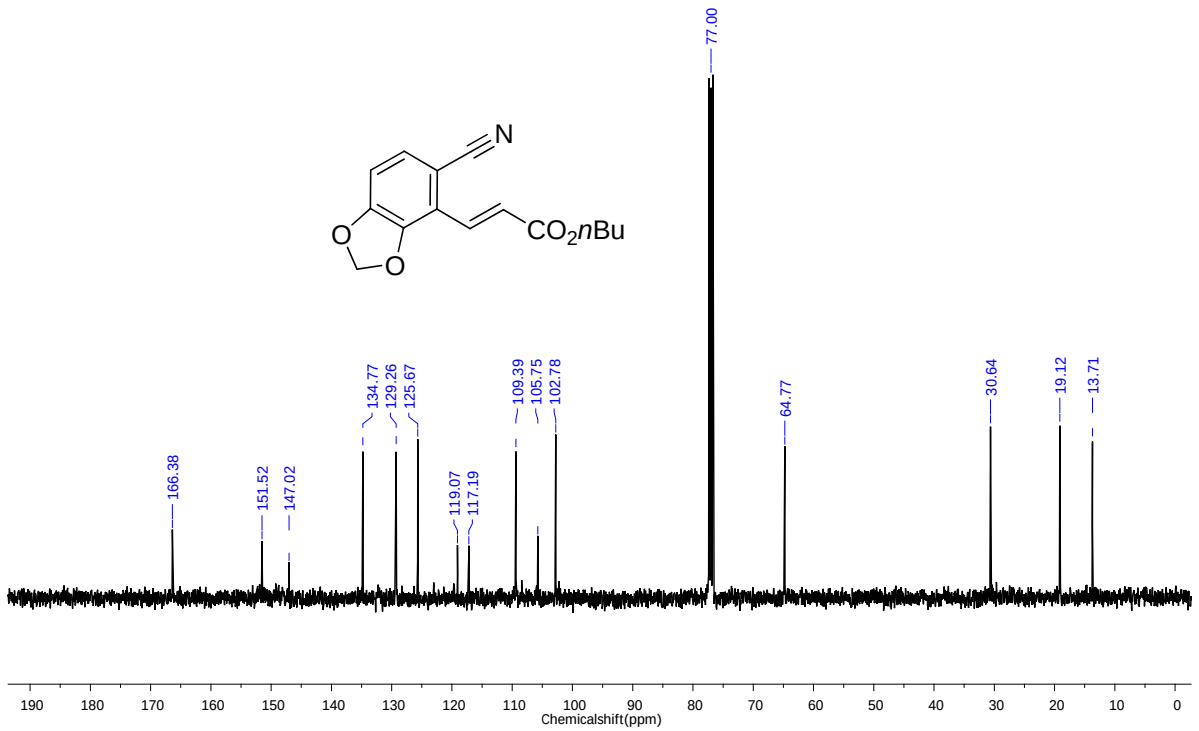
^{1}H and ^{13}C NMR Spectra of Compound **4nb**.



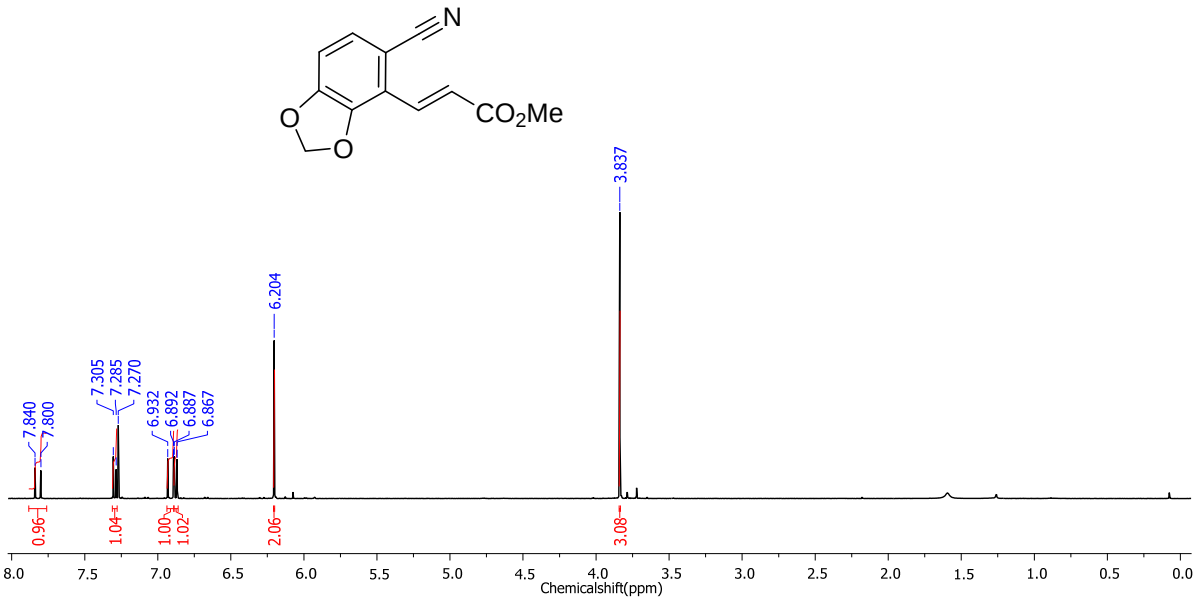


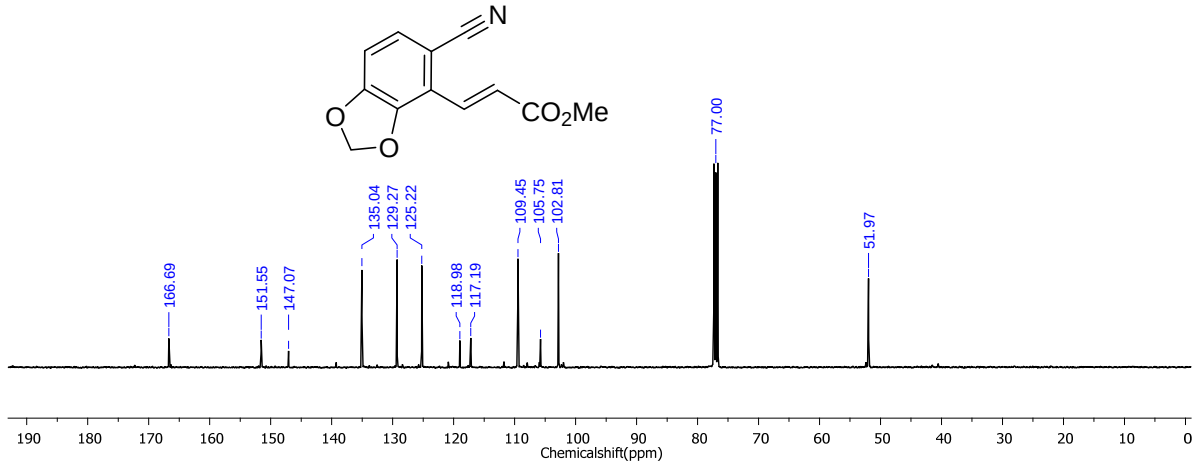
^{1}H and ^{13}C NMR Spectra of Compound **4oa**.

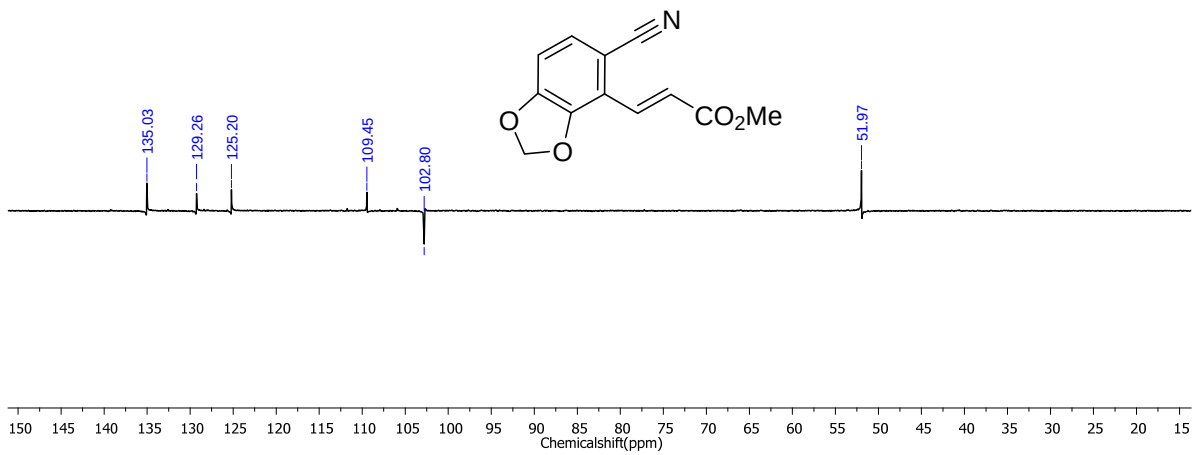




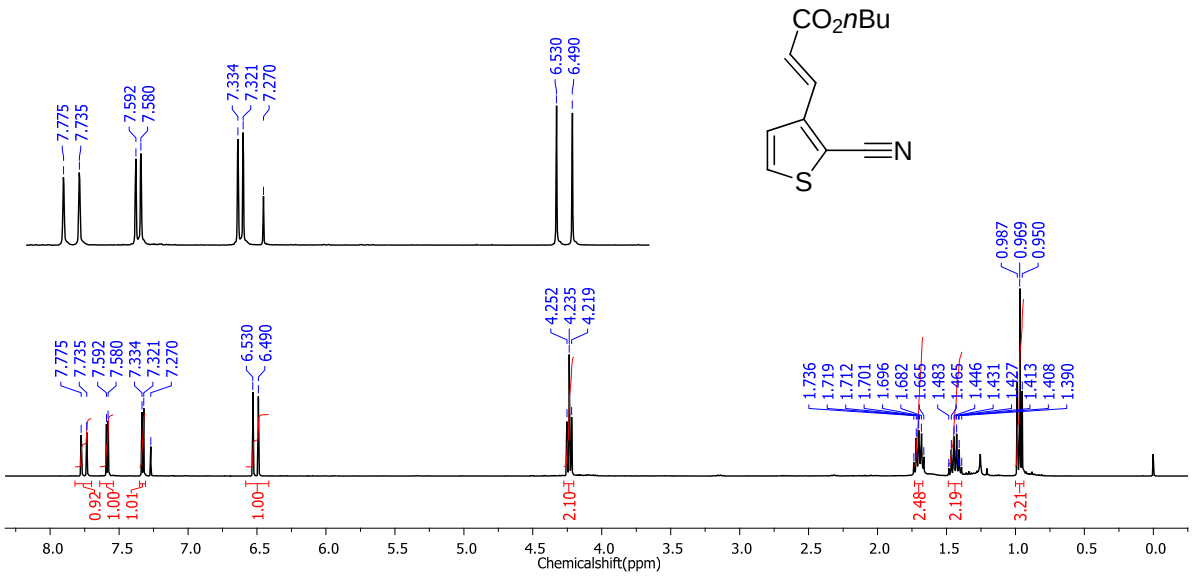
^{1}H and ^{13}C NMR Spectra of Compound **4og**.

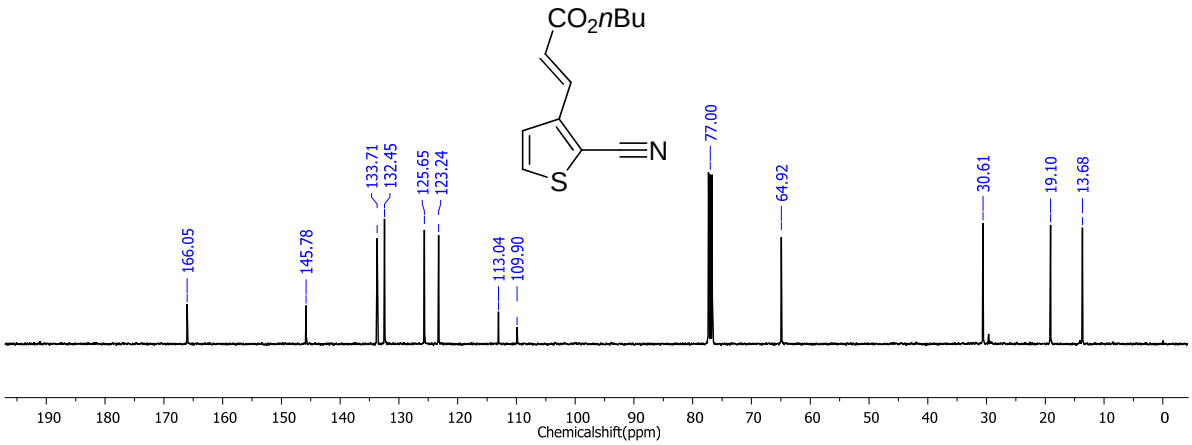


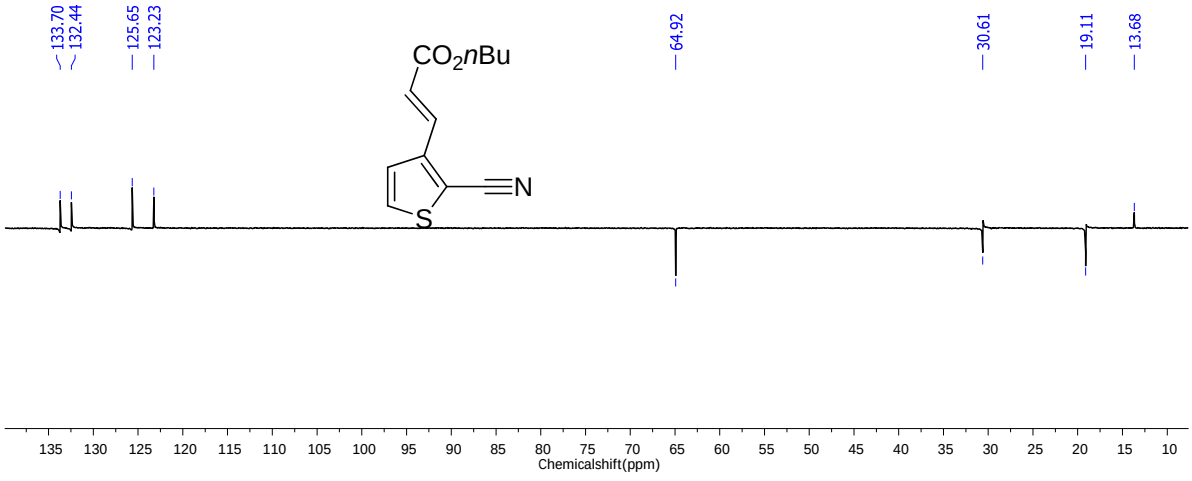




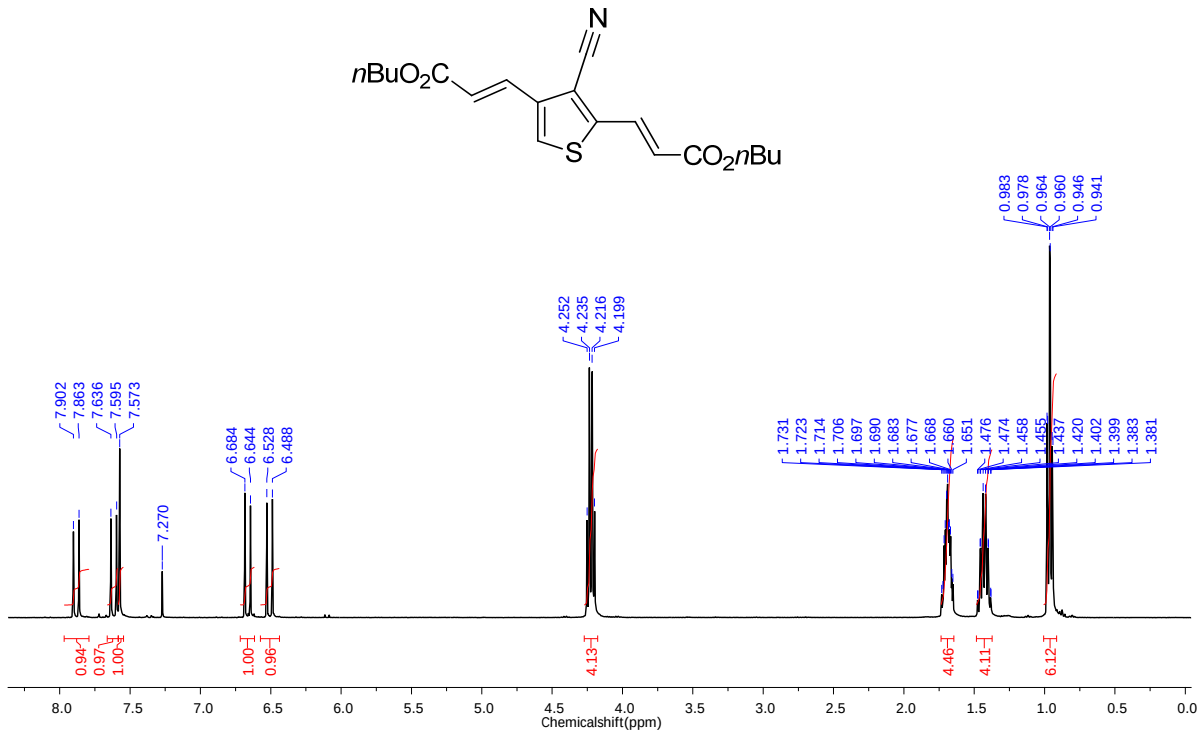
^{1}H and ^{13}C NMR Spectra of Compound **4pa**.

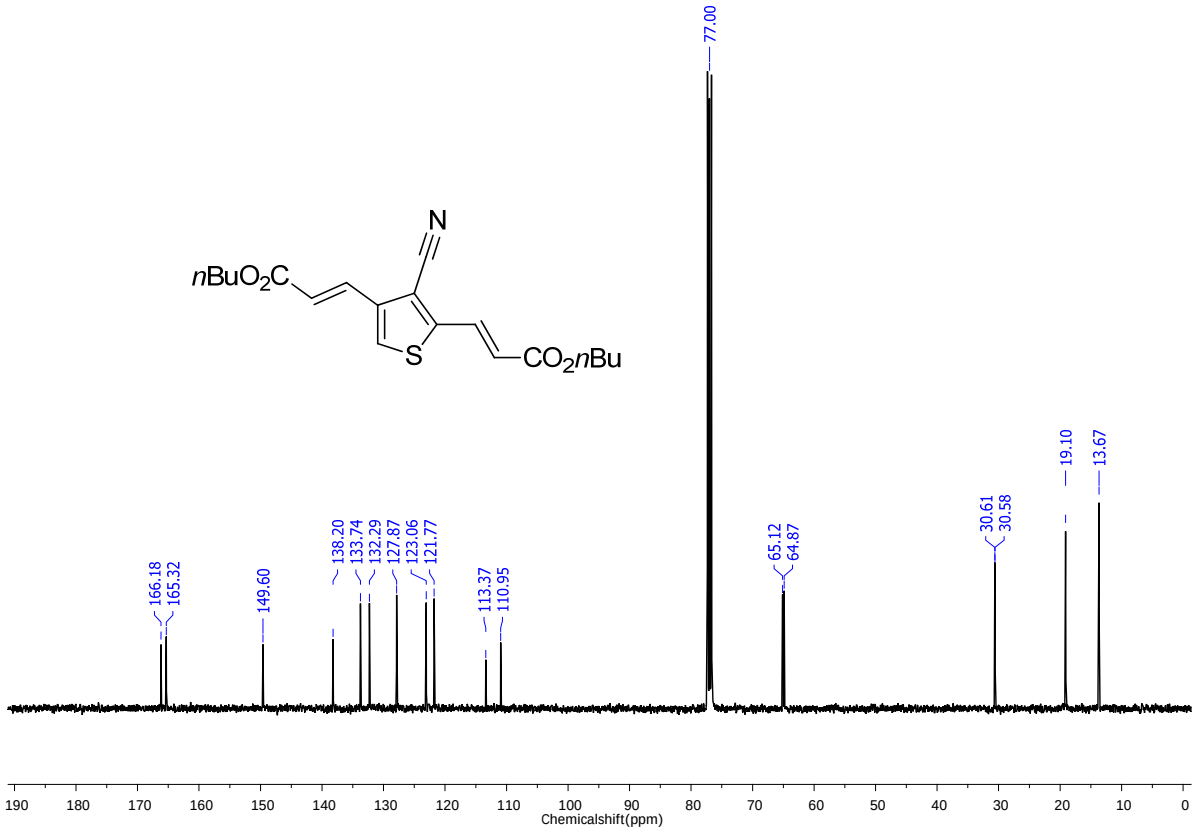




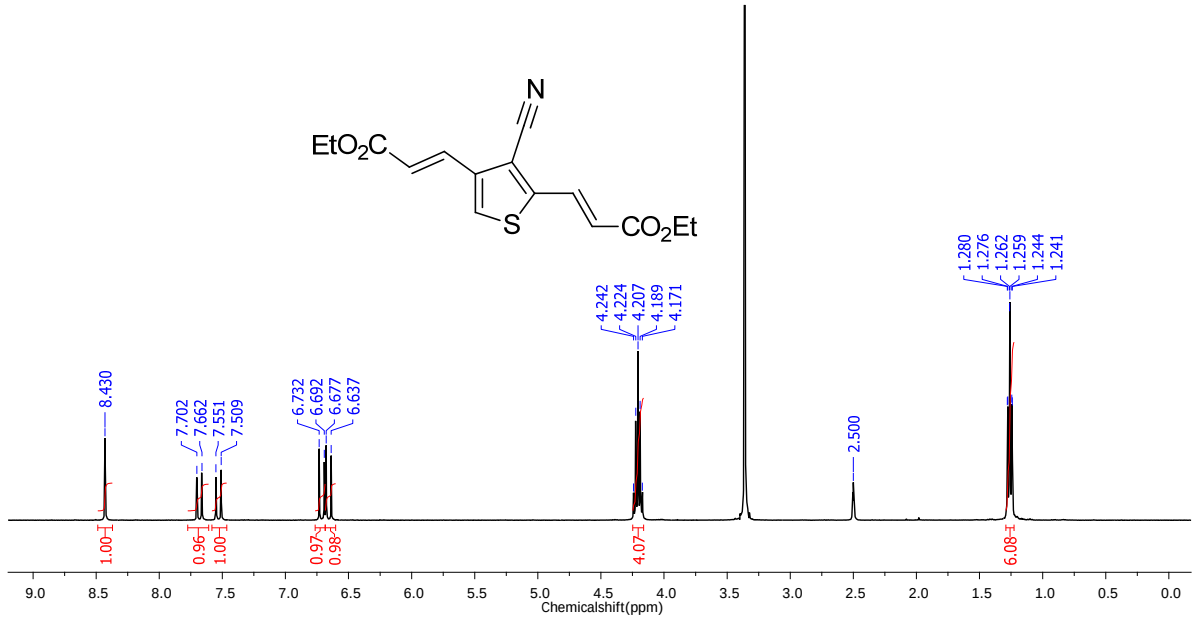


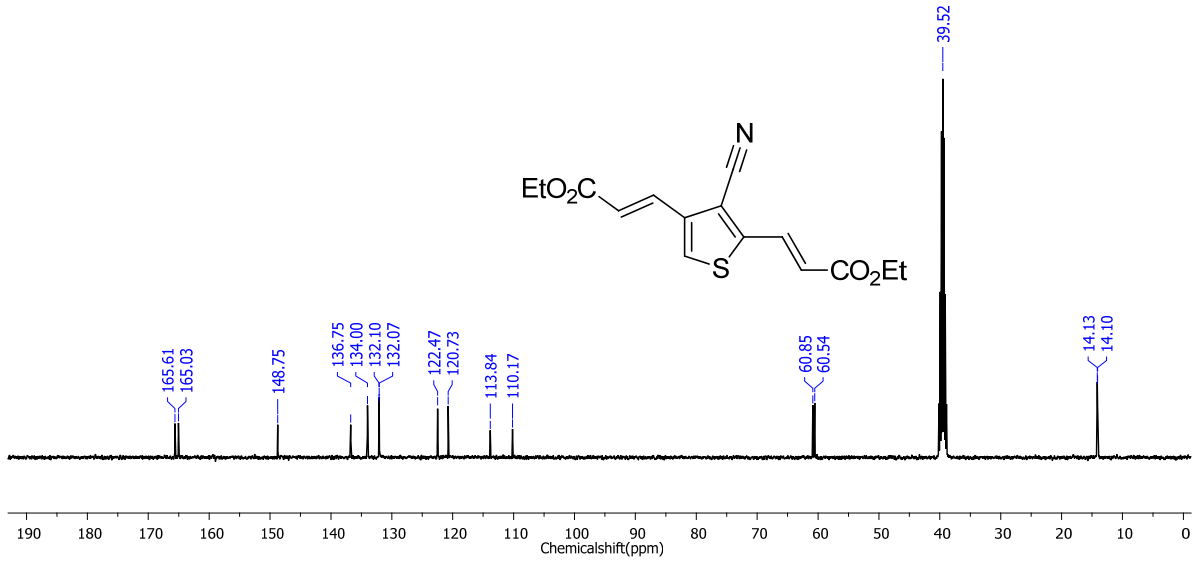
^{1}H and ^{13}C NMR Spectra of Compound **5qa**.

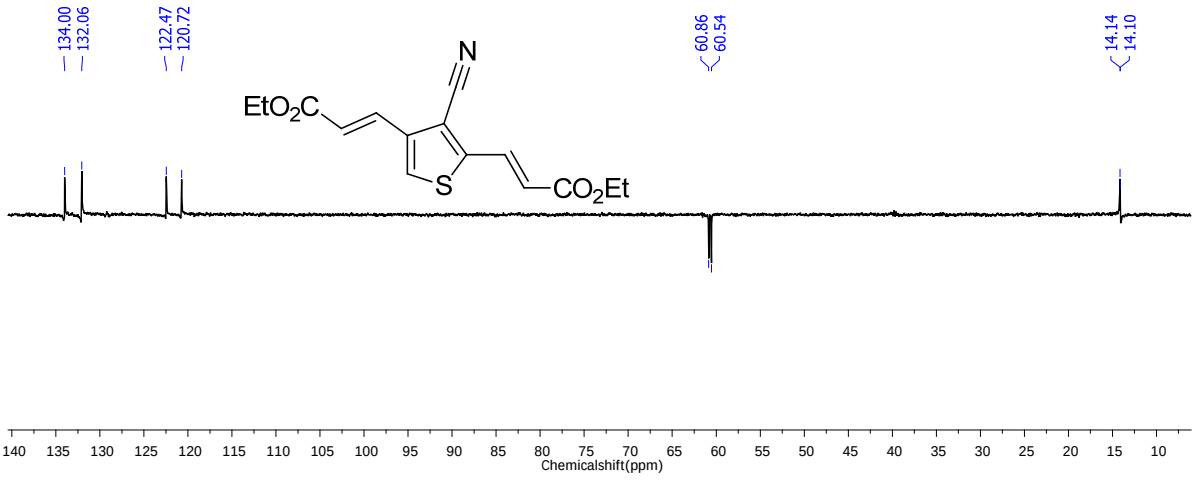




^{1}H and ^{13}C NMR Spectra of Compound **5qb**.







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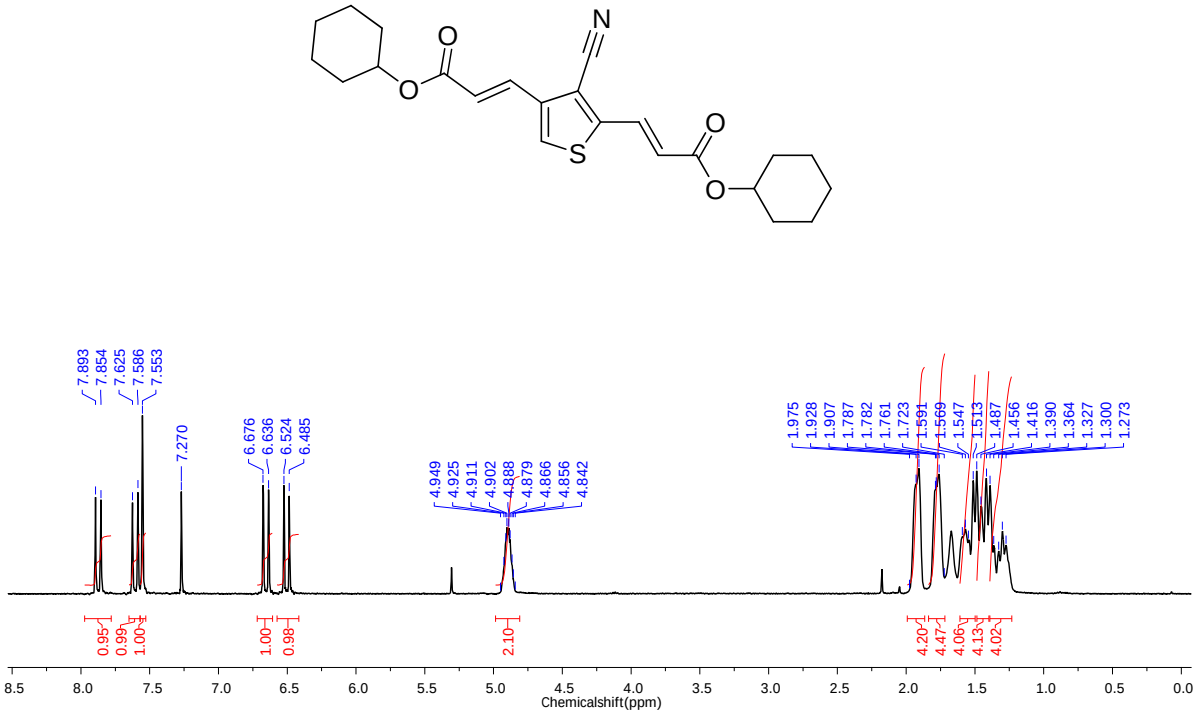

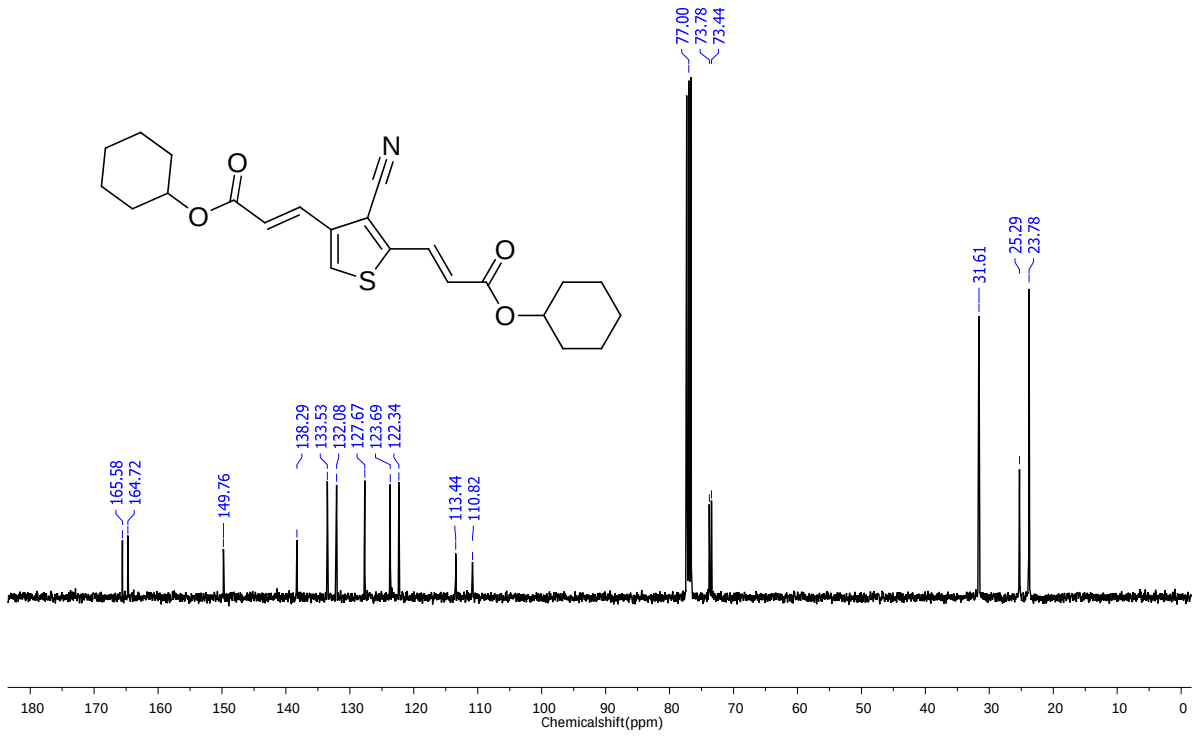

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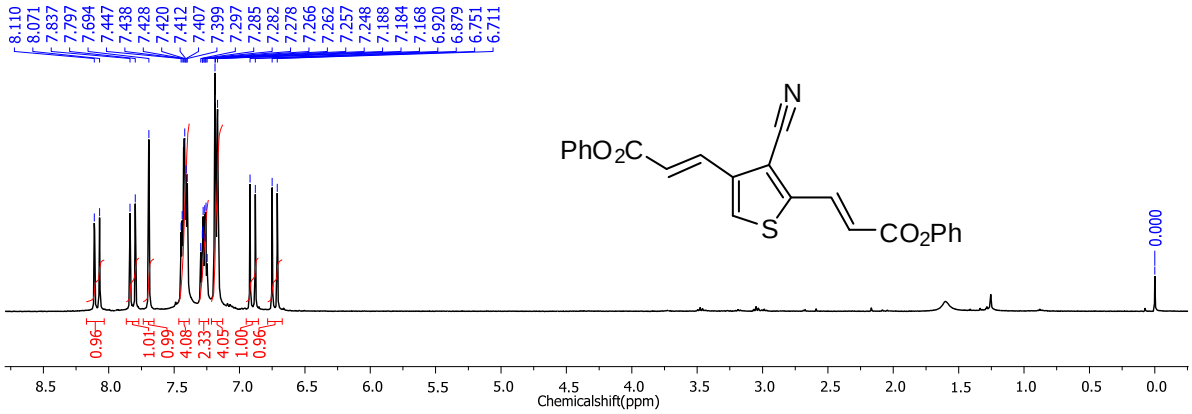

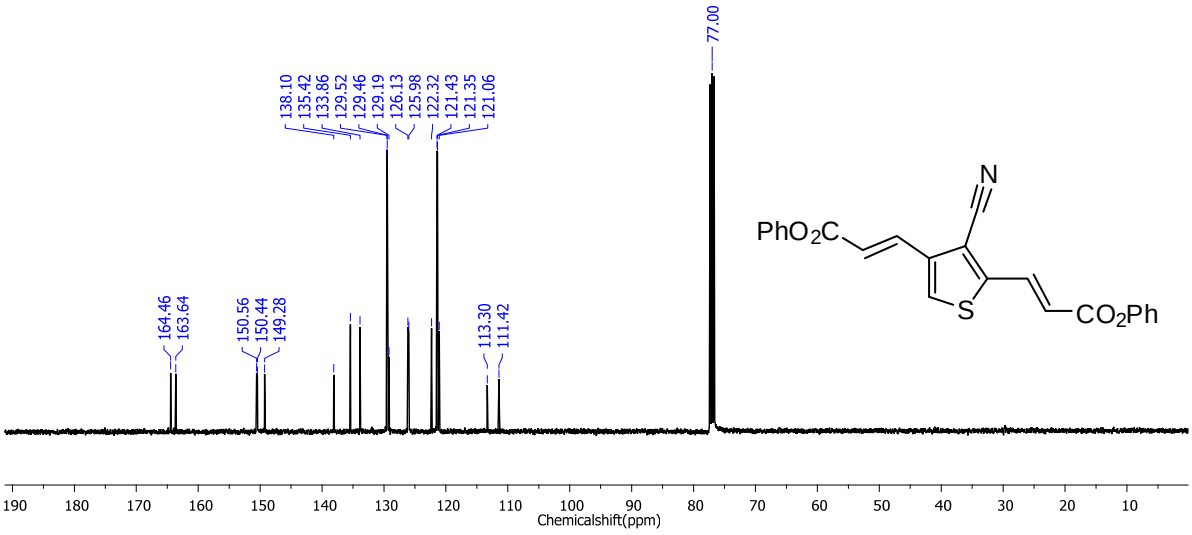

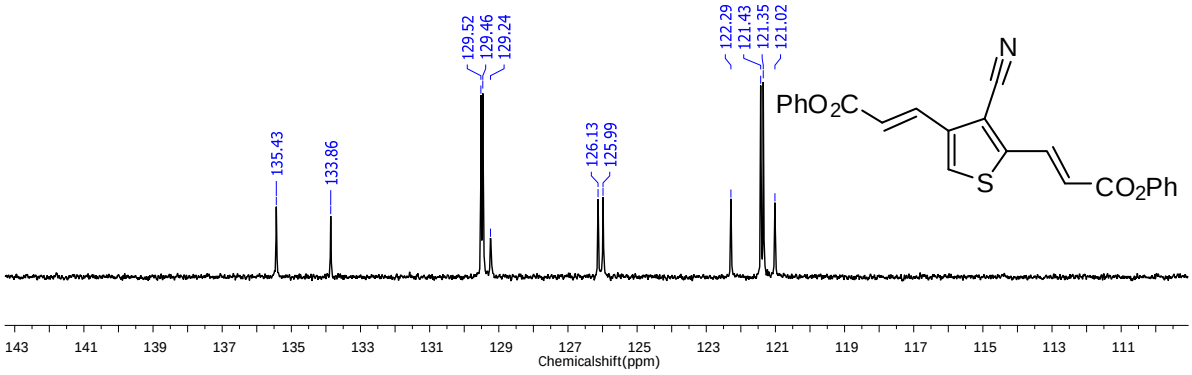

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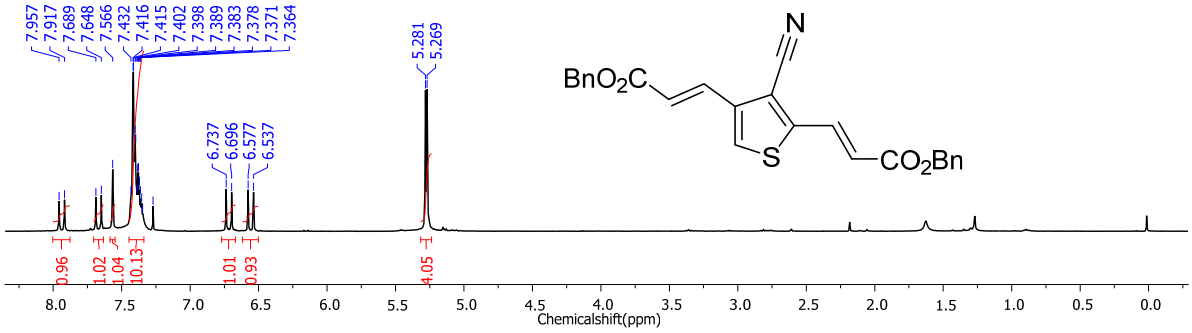
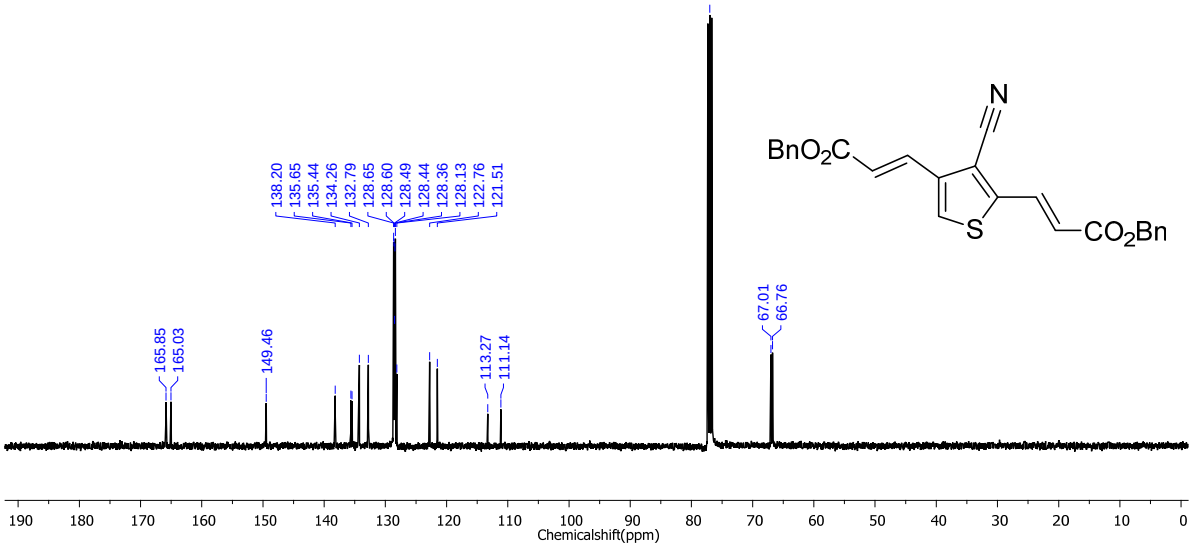
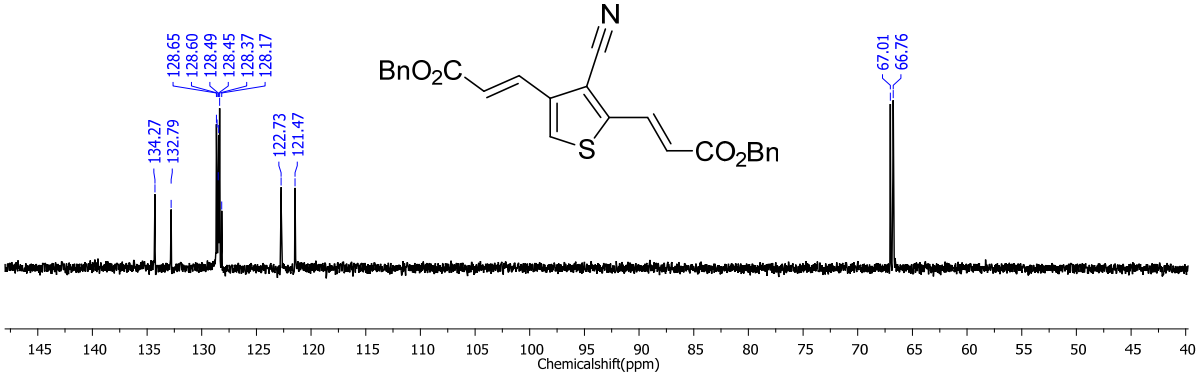
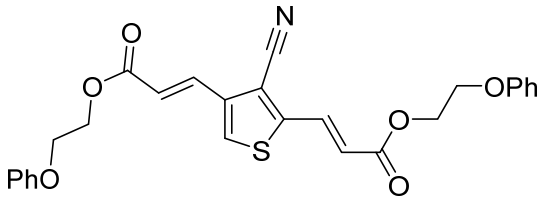
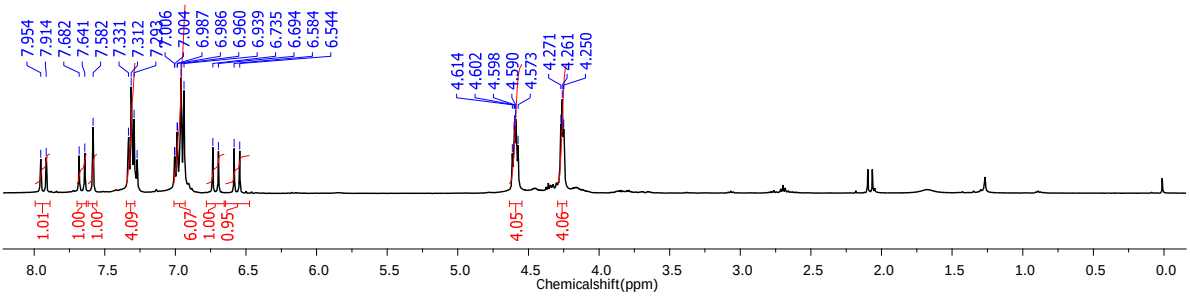


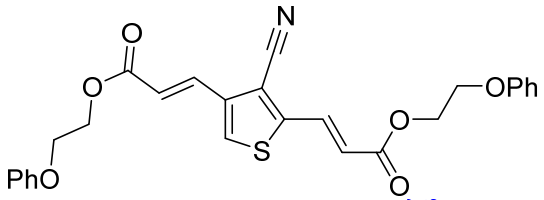


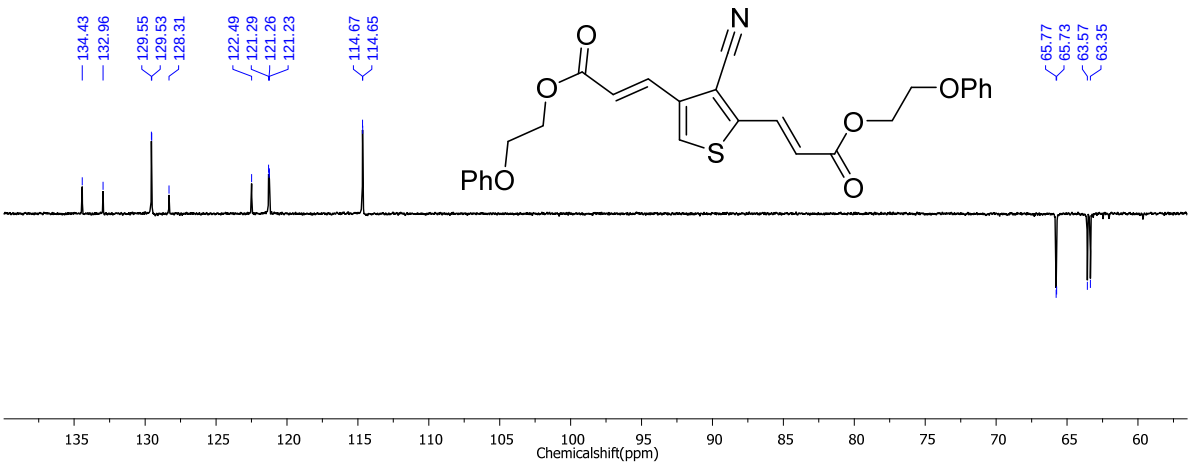


^{1}H and ^{13}C NMR Spectra of Compound **5qf**.

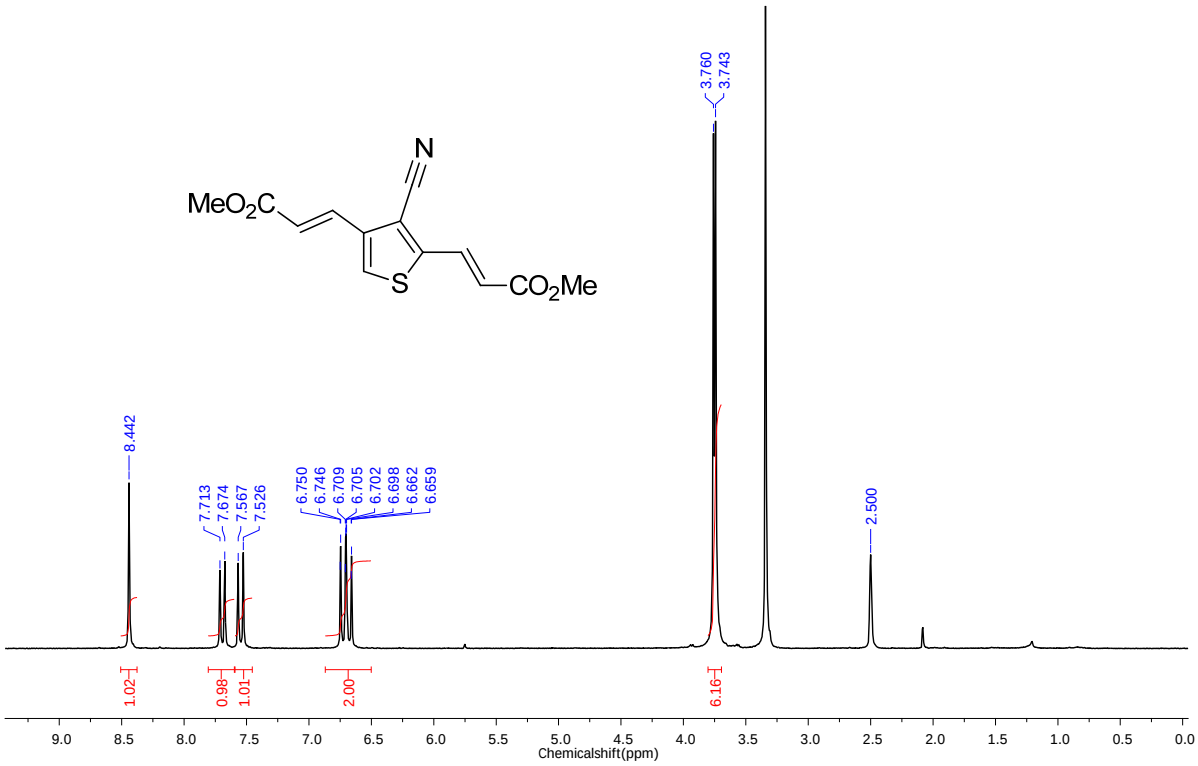


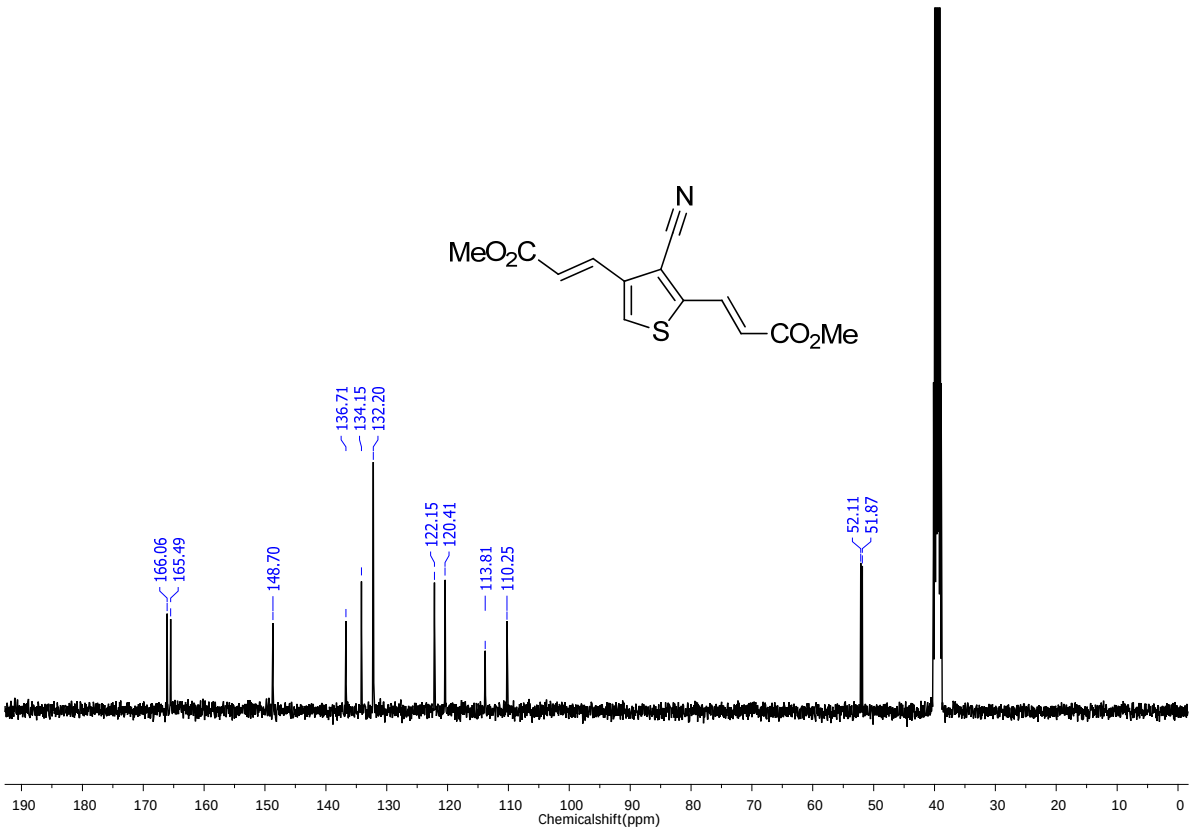




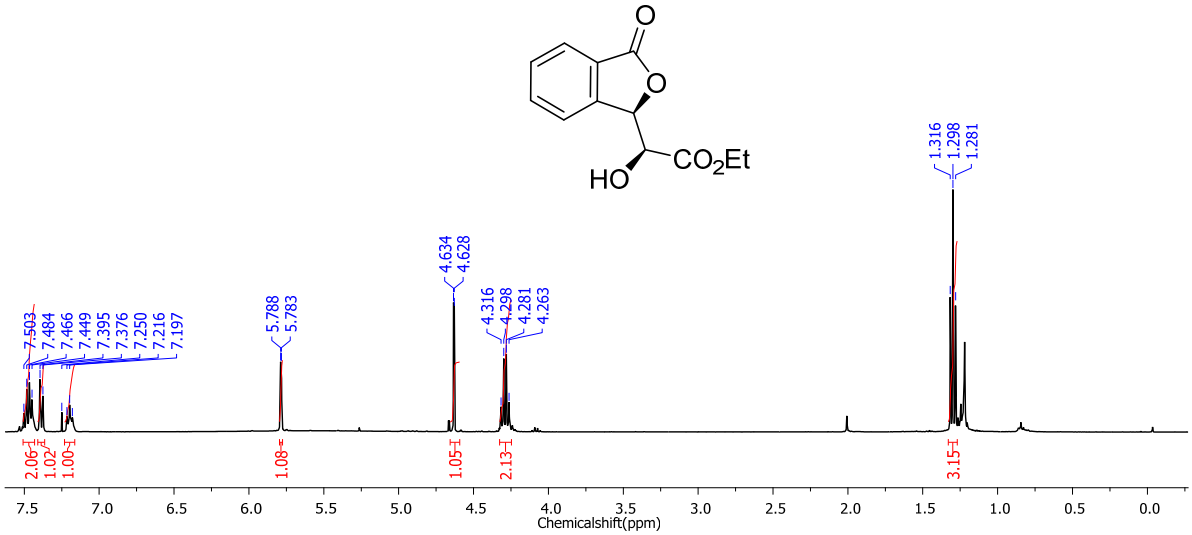


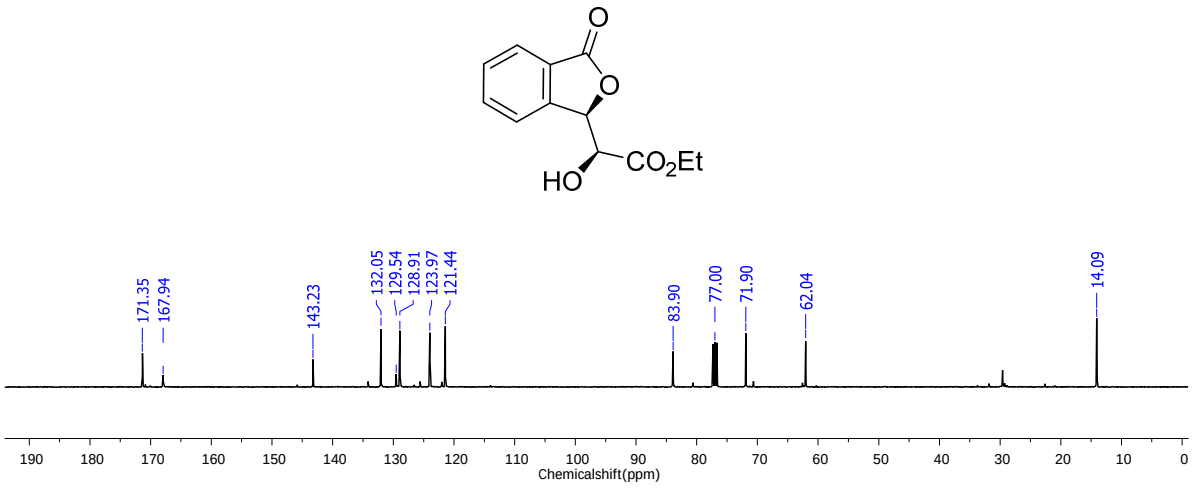
^{1}H and ^{13}C NMR Spectra of Compound **5qg**.

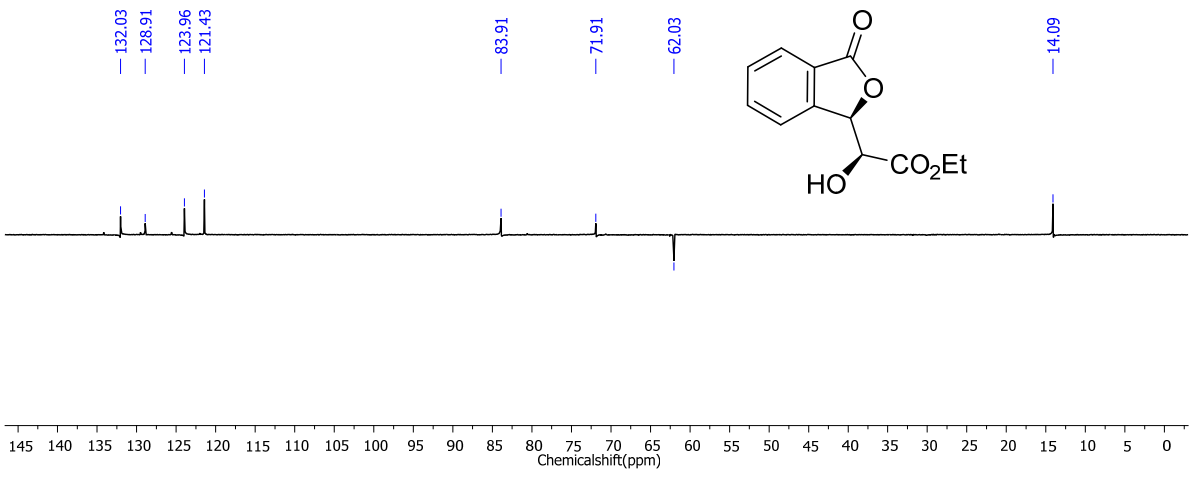




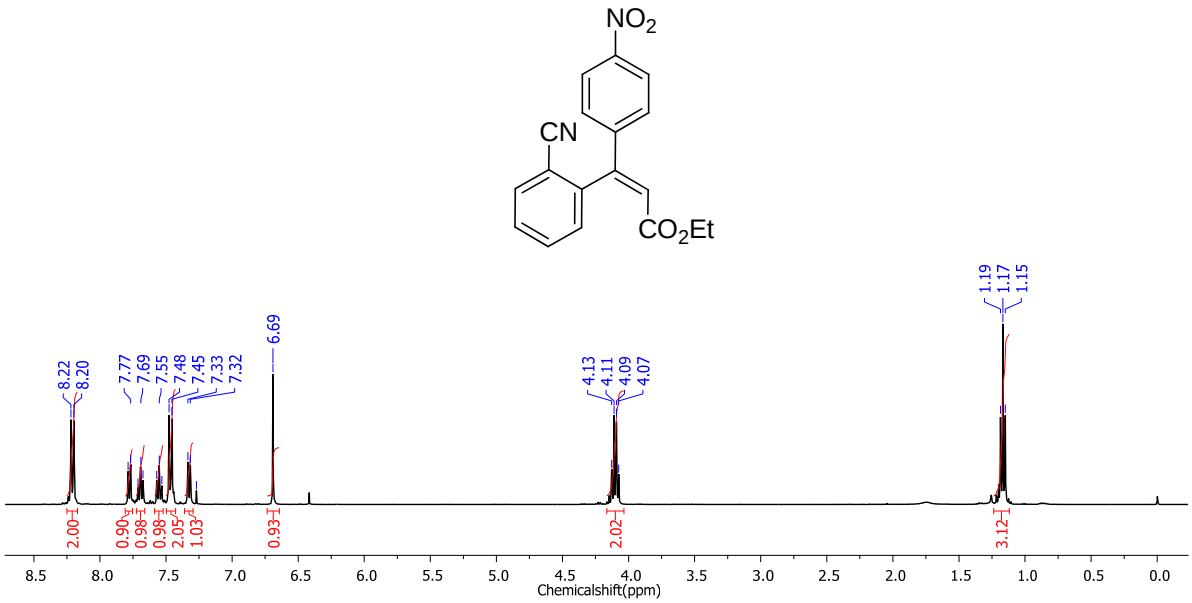
^{1}H and ^{13}C NMR Spectra of Compound **6**.

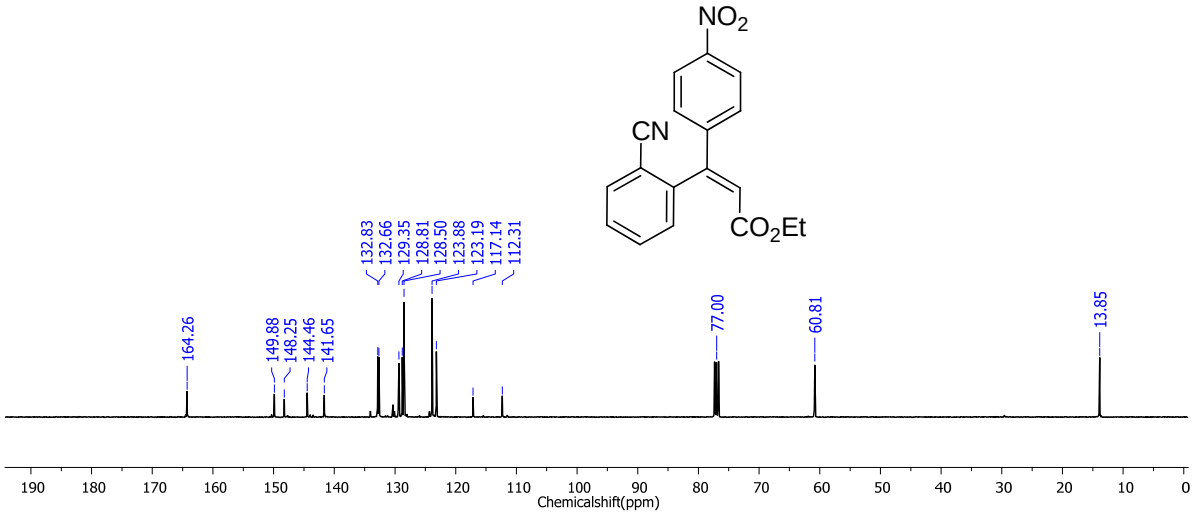


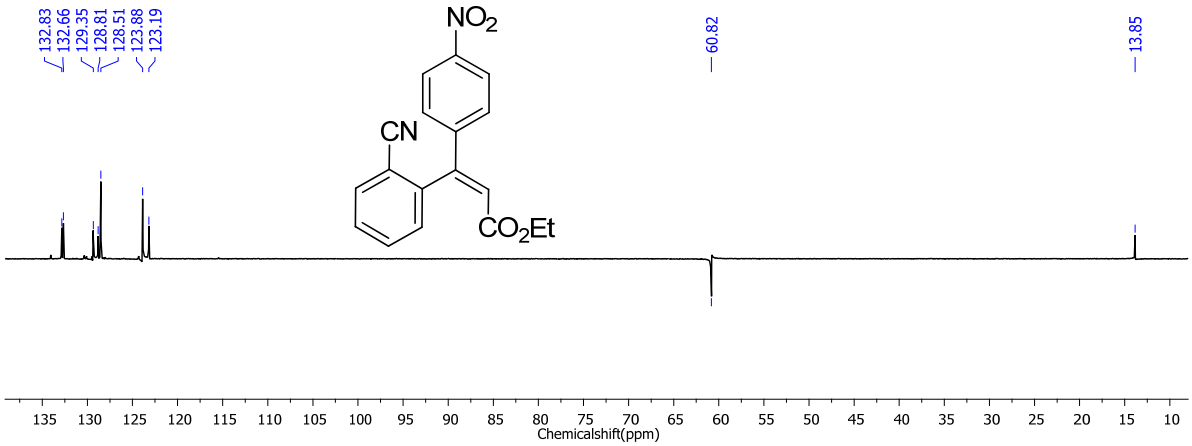




^{1}H and ^{13}C NMR Spectra of Compound **8a**.







^{1}H and ^{13}C NMR Spectra of Compound **8b**.