Electronic Supplementary Material (ESI) for RSC Advances.

SUPPORTING INFORMATION

Cinchona alkaloid and di-tert-butyldicarbonate-DMAP promoted efficient synthesis of (E)-nitroolefins

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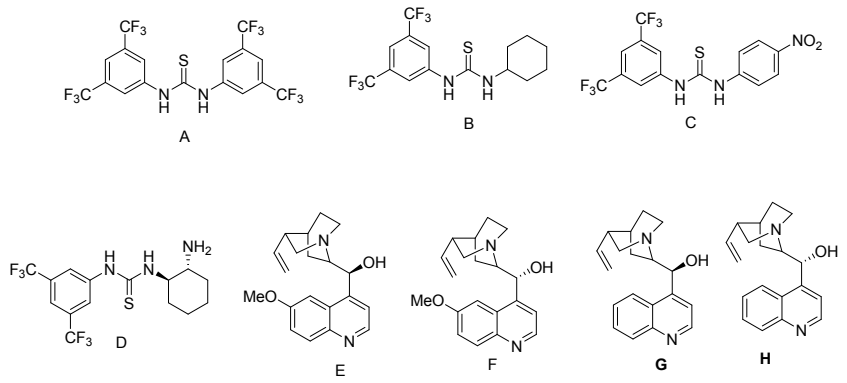
Experimental General:

All chemicals were purchased from Sigma Aldrich. All melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded in DMSO-d_6 using TMS as an internal standard on a Bruker avance spectrometer at 400 Mhz and 100 MHz respectively. Mass spectra were recorded using a JEOL GCMate-II – HR mass spectrometer. Analytical TLC was performed on precoated aluminium sheets of siliga gel G/UV-254 of 0.2 mm thickness (Merck, Germany). Elemental analyses were recorded using a ThermoFinnigan FLASH EA1112 CHN analyzer.

Strating materials: Catalysts and Arylidinemalononitriles:

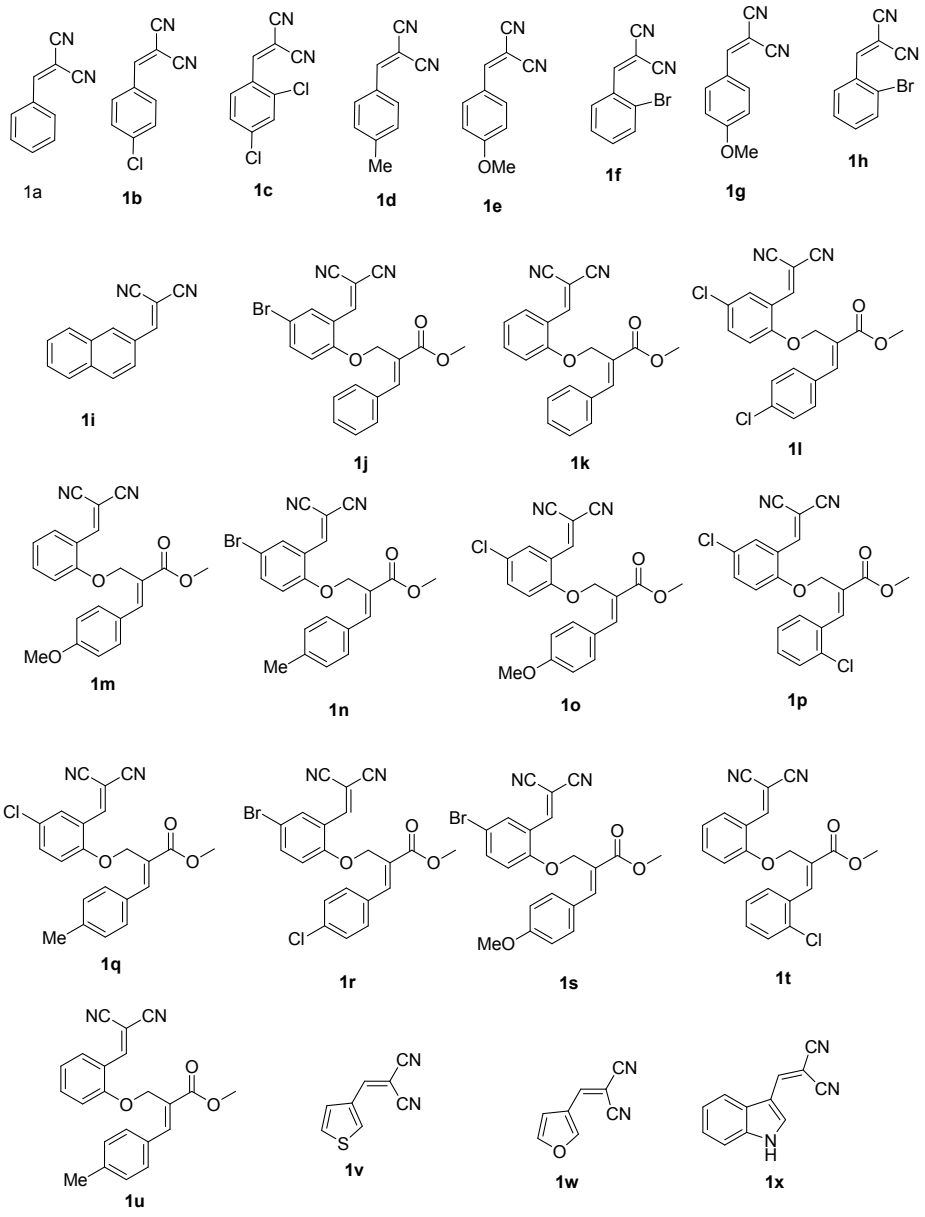
All commercially available chemicals were used as received, unless otherwise noted. Baylis-Hillmann aldehyde derivatives **6i-6x** were synthesized according to the literature procedure. [3]

Catalysts: Catalysts (A, B, C and D) were synthesized according to the literature procedure.[1, 2] & Catalyst E, F, G and H were purchased from Sigma Aldrich and used as such.



General procedure for the synthesis of Arylidinemalononitriles and (E)-methyl 2-((4-chloro-2-(2,2 dicyanovinyl)phenoxy)methyl)-3-(4-methoxyphenyl)acrylate derivatives:

Aldehyde (1 mmol), malononitrile (1 mmol) in ethanol (3 mL) and catalytic amount of water were charged in a 25 mL round bottomed flask and the resulting solution was stirred for 3-5 h at room temperature. The consumption of the starting material was monitored by TLC. The precipitated solid was filtred and washed with ethanol (5-7 mL), dried under vacuum to obtain pure **1a-x** in good yields (78-89 %). The identities of products were confirmed by NMR giving good agreement with the assigned structures.



1. A. Kaisuki and M. Seijiro, J. Am. Chem. Soc., 2011, 133, 16711.
2. D. Krzysztof, P. M. Anna and K. Piotr, Org. Lett., 2012, 14, 4222.
3. M. Bakthadoss, N. Sivakumar, G. Sivakumar and G. Murugan, Tetrahedron Lett., 2008, 49, 820-823

Optimization details of nitroolefin synthesis:

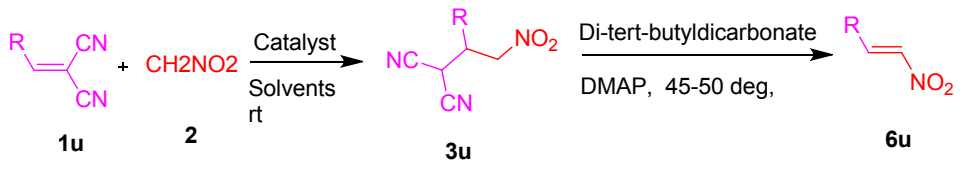
Entry	Catalyst (%)	Base (%)	Time (h)	Temp (°C)	Solvent (Toluene) yield (%)
					Toluene[a,b]
1.	--	DBU	7	50	--
2.	F	DBU	7	50	Trace
3.	F	DBU	7	90	Trace
4.	--	K-tOBu	7	50	Trace
5.	F	K-tOBu	7	90	Trace
6.	F	---	7	50	--
7.	F	---	7	90	---
8.	A	DBU	7	80	--
9.	A	DABCO	7	80	--
10.	B	DBU	7	80	--
11.	B	DABCO	10	80	--
12.	C	DBU	10	80	--
13.	C	DABCO	10	80	--
14.	-	DABCO	10	80	--
15.	F	DMAP	10	50	Trace
16.	Diethylamino ethanol	DMAP-Di-tert-butyldicarbonate	10	50	20
17.	Diethylamino ethanol	--	10	50	-
18	--	DMAP-Di-tert-butyldicarbonate	7	40	50
19.	--	DMAP-Di-tert-butyldicarbonate	7	90	40

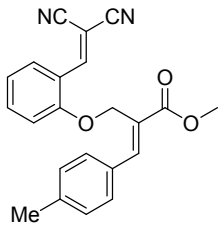
[a]The reaction was performed with arylidinemalononitile **1b** (0.1 mmol), nitromethane **2** (0.5 mmole), catalyst (10 mol %), Base (0.02 mmol) in 2 mL of solvents .[b] Isolated yields. [c]*E/Z* ratio is approximately >95/1). It was determined by NMR analysis of the crude products

General procedure for the preparation of E-nitroolefin derivatives:

A mixture of arylidine/heteroarylidinemalononitriles/(E)-methyl 2-((4-chloro-2-(2,2 dicyanovinyl)phenoxy)methyl)-3-(4-methoxyphenyl)acrylate derivatives **1(a-x)** (0.1 mmol), nitromethane **2** (5 mmol) in toluene (3 mL) and catalytic amount of cinchona alkaloid **F** (10 mol %) were charged in a 25 mL round bottomed flask and the resulting solution was stirred for 2-5 h at room temperature. The consumption of the starting material was monitored by TLC. After completition of the reaction, DMAP (0.02 mmol) and di-*tert*-butyldicarbonate (2.0 equiv) was then added to a stirred solution of corresponding crude product **3**. After stirring the reaction at 45-50 deg. for 2-3 hrs followed by TLC, the solvent was removed under reduced pressure and the residue was purified by column chromatography on siliga gel (3:97 % ethylacetate and petether) to afford pure products **6(a-x)** in average to good yields 65-90 %. The identities of products **6(a-x)** were confirmed by NMR and EI-HRMS, giving good agreement with the assigned structures.

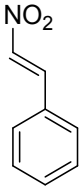
Isolation of intermediate 3u:



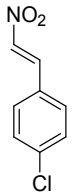
1u = 

3u: (E)-methyl 2-((2-(1,1-dicyano-3-nitropropan-2-yl)phenoxy)methyl)-3-(p-tolyl)acrylate: Isolated as yellow gelly semi solid, 95 %, ^{1}H NMR (400 MHz, $CDCl_3$) 8.00 (1 H, s), 7.36 – 7.22 (3 H, m), 7.19 (3 H, t, *J* 8.0), 6.97 (1 H, t, *J* 7.5), 6.87 (1 H, d, *J* 8.3), 4.96 (1 H, dd, *J* 13.7, 9.0), 4.89 (2 H, s), 4.78 (1 H, dd, *J* 13.7, 5.3), 4.61 (3 H, s), 4.24 (1 H, dd, *J* 14.3, 8.7), 3.82 (3 H, s), 2.32 (3 H, s) ppm. ^{13} C NMR: δ_C (100 MHz, $CDCl_3$) 167.64, 155.71, 146.51, 140.76, 131.46, 131.10, 130.10, 129.91, 129.53, 125.09, 122.16, 120.47, 112.85, 111.18, 111.15, 74.24, 63.70, 52.60, 24.77, 21.44 ppm.

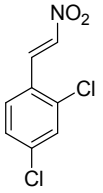
Characterisation data of the synthesized nitroolefins:



6a: (E)-(2-nitrovinyl) benzene: Isolated as yellow solid, 80 %, m.p: 57-58^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.93 (1 H, d, *J* = 13.7), 7.51 (1 H, d, *J* = 13.7), 7.49 – 7.45 (2 H, m), 7.44 – 7.34 (3 H, m) ppm. ^{13}C NMR δ_C (100 MHz, $CDCl_3$) 139.08, 137.15, 132.16, 130.10, 129.42, 129.16 ppm. EI-HRMS: Anal. Calcd for $C_8H_7NO_2$: 149.0477, Found: 149.0472. Elemental analysis: Anal. Calcd for $C_8H_7NO_2$: C, 64.42; H, 4.73; N, 9.39; O, 21.45 %. Found: C, 64.36; H, 4.79; N, 9.33; O, 21.49 %.

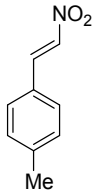


6b: (E)-1-chloro-4-(2-nitrovinyl) benzene: Isolated as yellow solid, 87 %, m.p: 111-112^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.96 (1 H, d, *J* = 13.7), 7.57 (1 H, d, *J* = 13.7), 7.53 – 7.47 (2 H, m), 7.47 – 7.40 (2 H, m) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 138.36, 137.71, 137.45, 130.29, 129.79, 128.55 ppm. EI-HRMS: Anal. Calcd for $C_8H_6ClNO_2$: 183.0087, Found: 183.0083. Elemental analysis: Anal. Calcd for $C_8H_6ClNO_2$: C, 52.34; H, 3.29; Cl, 19.31; N, 7.63; O, 17.43 %. Found: C, 52.30; H, 3.25; Cl, 19.38; N, 7.68; O, 17.37 %.

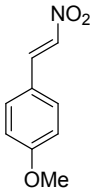


6c: (E)-2,4-dichloro-1-(2-nitrovinyl)benzene: Isolated as yellow solid, 85 %, m.p: 118-119^{o}C, ^{1}H NMR δ_H (400 MHz, $CDCl_3$) 8.33 (1 H, d, *J* = 13.7), 7.58 (1 H, d, *J* = 13.7), 7.55 – 7.49 (2 H, m), 7.34 (1 H, dd, *J* = 8.4, 1.9) ppm. ^{13}C NMR δ_C (101 MHz, $CDCl_3$) 139.05, 138.49, 136.68, 133.99, 130.69, 129.29, 128.04, 127.12 ppm. EI-HRMS: Anal. Calcd for $C_8H_5Cl_2NO_2$: 216.9697, Found: 216.9695. Elemental

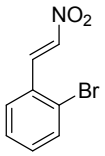
analysis: Anal. Calcd for $C_8 H_5 Cl_2 NO_2$: C, 44.07; H, 2.31; Cl, 32.52; N, 6.42; O, 14.68 %. Found: C, 44.0; H, 2.37; Cl, 32.45; N, 6.35; O, 14.61 %.



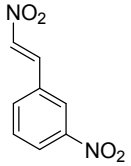
6d: (E)-1-methyl-4-(2-nitrovinyl) benzene: Isolated as yellow solid, 86 %, m.p: 105-106°C, ^{1}H NMR δ_H (400 MHz, $CDCl_3$) 7.98 (1 H, d, *J* = 13.6), 7.56 (1 H, d, *J* = 13.6), 7.44 (2 H, d, *J* = 8.1), 7.25 (2 H, d, *J* = 8.0), 2.41 (3 H, s) ppm. ^{13}C NMR δ_C (100 MHz, $CDCl_3$) 143.14, 139.20, 136.31, 130.17, 129.22, 127.31, 21.68 ppm. EI-HRMS: Anal. Calcd for $C_9H_9NO_2$: 163.0633, Found: 163.0630. Elemental analysis: Anal. Calcd for $C_9H_9NO_2$: C, 66.25; H, 5.56; N, 8.58; O, 14.68 %. Found: C, 66.20; H, 5.60; N, 8.51; O, 14.75 %.



6e: (E)-1-methoxy-4-(2-nitrovinyl) benzene: Isolated as yellow solid, 90 %, m.p: 90-92°C, ^{1}H NMR δ_H (400 MHz, $CDCl_3$) 7.96 (1 H, d, *J* = 13.6), 7.52 (1 H, d, *J* = 6.0), 7.51–7.48 (2 H, m), 6.99–6.92 (2 H, m), 3.86 (3 H, s) ppm. ^{13}C NMR δ_C (100 MHz, $CDCl_3$) 162.99, 139.07, 135.02, 131.21, 122.55, 114.95, 55.55 ppm. EI-HRMS: Anal. Calcd for $C_9 H_9 NO_3$: 179.0582, Found: 179.0580. Elemental analysis: Anal. Calcd for $C_9H_9NO_3$: C, 60.33; H, 5.06; N, 7.82; O, 26.79 %. Found: C, 60.39; H, 5.01; N, 7.75; O, 26.73 %.

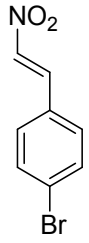


6f: (E)-1-bromo-2-(2-nitrovinyl) benzene: Isolated as yellow solid, 66 %, m.p: 140-142°C, ^{1}H NMR δ_H (400 MHz, $CDCl_3$) 8.40 (1 H, d, *J* = 13.7), 7.69 (1 H, dd, *J* = 7.8, 1.4), 7.63 – 7.49 (2 H, m), 7.44–7.26 (2 H, m) ppm. ^{13}C NMR δ_C (100 MHz, $CDCl_3$) 138.89, 137.60, 134.04, 132.92, 130.41, 128.49, 128.08, 126.35 ppm. EI-HRMS: Anal. Calcd for $C_8 H_6 Br NO_2$: 226. 9582 Found: 226.9581. Elemental analysis: Anal. Calcd for $C_8H_6BrNO_2$: C, 42.13; H, 2.65; Br, 35.04; N, 6.14; O, 14.03 %. Found: C, 42.19; H, 2.69; Br, 35.01; N, 6.19; O, 14.07 %.

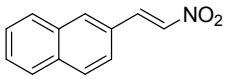


6g: (E)-1-nitro-3-(2-nitrovinyl) benzene Isolated as yellow solid, 60 %, m.p: 127-128°C, ^{1}H NMR δ_H (500 MHz,) 8.28–8.09 (3 H, m), 7.61 (1 H, dd, *J* = 4.9, 2.2). ppm. ^{13}C NMR δ_C (125 MHz, $CDCl_3$)

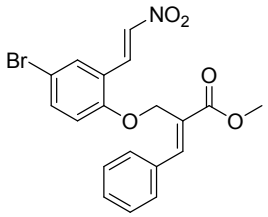
126.66, 126.39, 130.88, 131.97, 134.67, 148.95 ppm. EI-HRMS: Anal. Calcd for $C_8H_6N_2O_4$: 194.0328 Found: 194.0327. Elemental analysis: Anal. Calcd for $C_8H_6N_2O_4$: C, 49.49; H, 3.12; N, 14.43; O, 32.96 %. Found: C, 49.43; H, 3.17; N, 14.39; O, 32.91 %.



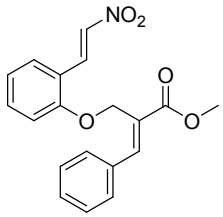
6h: (E)-1-bromo-4-(2-nitrovinyl) benzene: Isolated as yellow solid, 63 %, m.p: 143-145°C, δ_H (500 MHz,) 7.94 (1 H, d, *J* = 13.7), 7.58 (3 H, t, *J* = 10.8), 7.41 (2 H, d, *J* = 8.4) ppm. ^{13}C NMR δ_C (125 MHz, $CDCl_3$) 127.01, 129.13, 130.60, 132.95, 137.64,138.09 ppm. EI-HRMS: Anal. Calcd for $C_8H_6BrNO_2$: 226.9582 Found: 226.9580. Elemental analysis: Anal. Calcd for $C_8H_6BrNO_2$: C, 42.13; H, 2.65; Br, 35.04; N, 6.14; O, 14.03 %. Found: C, 42.09; H, 2.60; Br, 35.09; N, 6.10; O, 13.03 %.



6i: (E)-2-(2-nitrovinyl)naphthalene: Isolated as yellow solid, 73 %, m.p: 128-130°C, ^{1}H NMR δ_H (400 MHz, $CDCl_3$) 8.79 (1 H, d, *J* = 13.4), 8.09 (1 H, d, *J* = 8.4), 7.98 (1 H, d, *J* = 8.2), 7.94 – 7.85 (1 H, m), 7.71 (1 H, d, *J* = 7.2), 7.66 – 7.54 (3 H, m), 7.53 – 7.46 (1 H, m) ppm. ^{13}C NMR δ_C (100 MHz, $CDCl_3$) 138.50, 136.09, 133.79, 132.58, 131.59, 129.09, 127.76, 126.98, 126.82, 126.41, 125.43, 122.98 ppm. EI-HRMS: Anal. Calcd for $C_{12}H_9NO_2$: 199.0633, Found: 199.0632. Elemental analysis: Anal. Calcd for $C_{12}H_9NO_2$: C, 72.35; H, 4.55; N, 7.03; O, 16.06 %. Found: C, 72.30; H, 4.47; N, 6.05; O, 16.01 %.

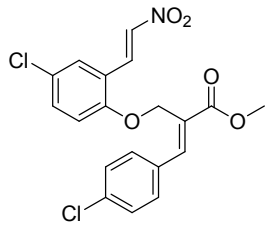


6j: (E)-methyl 2-((4-bromo-2-((E)-2-nitrovinyl)phenoxy)methyl)-3-phenylacrylate: Isolated as yellow solid, 81 %, m.p: 98-100°C, ^{1}H NMR δ_H (400 MHz, $CDCl_3$) 8.11 (1 H, s), 7.99 (1 H, d, *J* = 13.7), 7.71 (1 H, d, *J* = 13.7), 7.58 (1 H, d, *J* = 2.4), 7.51 (1 H, d, *J* = 2.5), 7.39 (5 H, s), 6.88 (1 H, d, *J* = 8.9), 4.99 (2 H, s), 3.89 (3 H, s). ^{13}C NMR δ_C (100 MHz, $CDCl_3$) 167.19, 157.14, 146.43, 139.11, 135.62, 134.12, 134.07, 133.57, 129.95, 129.40, 128.92, 126.08, 121.63, 114.77, 113.73, 64.07, 52.59 ppm. EI-HRMS: Anal. Calcd for $C_{19}H_{16}BrNO_5$: 417.0212, Found: 417.0210. Elemental analysis: Anal. Calcd for $C_{19}H_{16}BrNO_5$: C, 54.56; H, 3.86; Br, 19.10; N, 3.35; O, 19.13 %. Found: C, 54.51; H, 3.82; Br, 18.70; N, 3.31; O, 18.15 %.

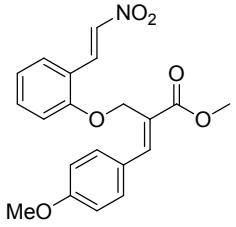


6k: (E)-methyl 2-((2-((E)-2-nitrovinyl)phenoxy)methyl)-3-phenylacrylate: Isolated as yellow solid, 83 %, m.p: 127-130°C, ^{1}H NMR δ_H (400 MHz, $CDCl_3$) 8.11 (1 H, t, *J* = 6.8), 7.78 (1 H, d, *J* = 13.6), 7.50 – 7.40 (2 H, m), 7.39 – 7.36 (1 H, m), 7.05 (1 H, t, *J* = 7.5), 6.99 (1 H, d, *J* = 8.4), 5.01 (1 H, s), 3.89 (2 H, s). ^{13}C NMR δ_C (100 MHz, $CDCl_3$) 167.34, 158.28, 146.22, 138.34, 135.28, 134.19, 133.38, 132.34, 129.84,

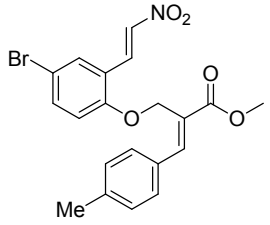
129.48, 128.88, 126.40, 121.62, 119.70, 112.96, 63.67, 52.55 ppm. EI-HRMS: Anal. Calcd for $C_{19}H_{17}NO_5$: 339.1107, Found: 339.1105. Elemental analysis: Anal. Calcd for $C_{19}H_{17}NO_5$: C, 67.25; H, 5.05; N, 4.13; O, 23.57 %. Found: C, 67.17; H, 5.01; N, 4.19; O, 23.51 %.



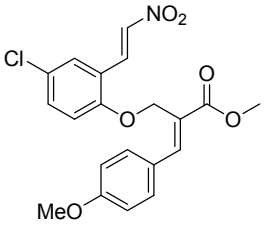
6l: (E)-methyl 2-((4-chloro-2-((E)-2-nitrovinyl)phenoxy)methyl)-3-(4-chlorophenyl)acrylate: Isolated as yellow solid, 70 %, m.p: 135-137°C, ^{1}H NMR δ_H (400 MHz, $CDCl_3$) 7.98–7.87 (1 H, m), 7.62 (1 H, d, *J* = 13.7), 7.37 (1 H, d, *J* = 2.5), 7.32–7.22 (3 H, m), 6.87 (1 H, d, *J* = 8.9), 4.88 (1 H, s), 3.81 (2 H, s). ^{13}C NMR δ_C (100 MHz, $CDCl_3$) 166.95, 156.49, 145.02, 139.06, 136.18, 133.51, 132.80, 132.47, 131.04, 130.69, 129.23, 126.85, 126.61, 121.11, 114.38, 64.02, 52.67 ppm. EI-HRMS: Anal. Calcd for $C_{19}H_{15}Cl_2NO_5$: 407.0327, Found: 407.0325. Elemental analysis: Anal. Calcd for $C_{19}H_{15}Cl_2NO_5$: C, 55.90; H, 3.70; Cl, 17.37; N, 3.43; O, 19.60 %. Found: C, 55.85; H, 3.66; Cl, 17.31; N, 3.49; O, 19.55 %.



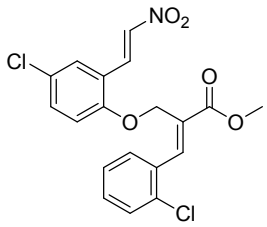
6m: (E)-methyl 3-(4-methoxyphenyl)-2-((2-((E)-2-nitrovinyl)phenoxy)methyl)acrylate: Isolated as yellow solid, 88 %, m.p: 108-110°C, ^{1}H NMR δ_H (400 MHz, $CDCl_3$) 8.24–8.01 (1 H, m), 7.77 (1 H, d, *J* = 13.6), 7.52–7.35 (2 H, m), 7.09–6.98 (1 H, m), 6.90 (1 H, d, *J* = 8.8), 5.04 (1 H, s), 3.87 (1 H, s), 3.81 (1 H, s). ^{13}C NMR δ_C (100 MHz, $CDCl_3$) 167.67, 161.12, 158.36, 146.17, 138.31, 135.30, 133.42, 132.34, 131.67, 126.66, 123.78, 121.57, 119.70, 114.40, 112.99, 63.82, 55.38, 52.42 ppm. EI-HRMS: Anal. Calcd for $C_{20}H_{19}NO_6$: 369.1212, Found: 369.1211. Elemental analysis: Anal. Calcd for $C_{20}H_{19}NO_6$: C, 65.03; H, 5.18; N, 3.79; O, 25.99 %. Found: C, 64.06; H, 5.12; N, 3.72; O, 26.06 %.



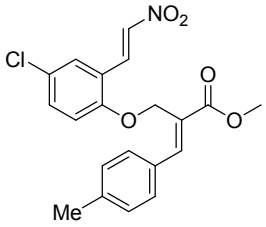
6n: (E)-methyl 2-((4-bromo-2-((E)-2-nitrovinyl)phenoxy)methyl)-3-(p-tolyl)acrylate: Isolated as yellow solid, 78 %, m.p: 123-140°C, ^{1}H NMR δ_H (400 MHz, $CDCl_3$) 8.14–7.92 (1 H, m), 7.71 (1 H, d, *J* = 13.6), 7.58 (1 H, d, *J* = 2.4), 7.50 (1 H, dd, *J* = 8.8, 2.5), 7.33–7.25 (1 H, m), 7.20 (1 H, d, *J* = 8.0), 6.90 (1 H, d, *J* = 8.9), 5.00 (1 H, s), 3.88 (2 H, s), 2.36 (2 H, s) ppm. ^{13}C NMR δ_C (100 MHz, $CDCl_3$) 167.36, 157.19, 146.61, 140.53, 139.11, 135.62, 134.15, 133.61, 131.22, 129.67, 129.58, 125.03, 121.62, 114.77, 113.66, 64.14, 52.52, 21.41ppm. EI-HRMS: Anal. Calcd for $C_{20}H_{18}BrNO_5$: 431.0368, Found: 431.0366. Elemental analysis: Anal. Calcd for $C_{20}H_{18}BrNO_5$: C, 55.57; H, 4.20; Br, 18.48; N, 3.24; O, 18.51 %. Found: C, 55.51; H, 4.17; Br, 18.43; N, 3.29; O, 18.43 %.



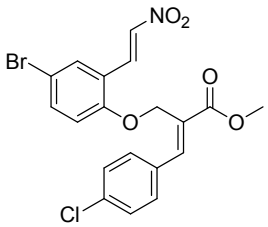
6o: (E)-methyl 2-((4-chloro-2-((E)-2-nitrovinyl)phenoxy)methyl)-3-(4-methoxyphenyl)acrylate: Isolated as yellow solid, 81 %, m.p: 140-142°C, ^{1}H NMR δ_{H} (400 MHz, $CDCl_3$) 8.08–7.96 (1 H, m), 7.71 (1 H, d, *J* = 13.7), 7.44 (1 H, d, *J* = 2.6), 7.39 (1 H, dd, *J* = 8.9, 2.7), 7.00 (1 H, d, *J* = 8.9), 6.91 (1 H, d, *J* = 8.8), 5.03 (1 H, s), 3.87 (1 H, s), 3.82 (2 H, s) ppm. ^{13}C NMR δ_{C} (100 MHz, $CDCl_3$) 167.57, 161.20, 156.74, 146.37, 139.11, 133.72, 132.76, 131.63, 131.18, 126.59, 126.53, 123.45, 121.13, 114.44, 114.42, 64.30, 55.40, 52.46 ppm. EI-HRMS: Anal. Calcd for C_{20} H_{18} Cl NO_6: 403.0823, Found: 403.0822. Elemental analysis: Anal. Calcd for $C_{20}H_{18}ClNO_6$: C, 59.49; H, 4.49; Cl, 8.78; N, 3.47; O, 23.77 %. Found: C, 59.43; H, 4.42; Cl, 8.74; N, 3.54; O, 23.70 %.



6p:(E)-methyl2-((4-chloro-2-((E)-2-nitrovinyl)phenoxy)methyl)-3-(2-chloro-phenyl)-acrylate: Isolated as yellow solid, 72 %, m.p: 136-138°C, ^{1}H NMR δ_{H} (400 MHz, $CDCl_3$) 8.15 (1 H, s), 7.97 (1 H, d, *J* = 13.7), 7.69 (1 H, d, *J* = 13.7), 7.47 – 7.39 (2 H, m), 7.33 (3 H, ddd, *J* = 8.6, 5.4, 2.0), 7.29–7.22 (1 H, m), 6.86 (1 H, d, *J* = 8.9), 4.91 (2 H, s), 3.91 (3 H, s) ppm. ^{13}C NMR δ_{C} (100 MHz, $CDCl_3$) 166.60, 156.47, 142.93, 139.03, 134.25, 133.54, 132.86, 132.71, 130.93, 130.85, 129.98, 129.90, 128.18, 127.02, 126.73, 121.12, 114.47, 64.34, 52.71ppm. EI-HRMS: Anal. Calcd for C_{19} H_{15} Cl_2 NO_5: 407.0327, Found: 407.0325. Elemental analysis: Anal. Calcd for $C_{19}H_{15}Cl_2NO_5$: C, 55.90; H, 3.70; Cl, 17.37; N, 3.43; O, 19.60 %. Found: C, 55.84; H, 3.64; Cl, 17.31; N, 3.49; O, 19.53 %.

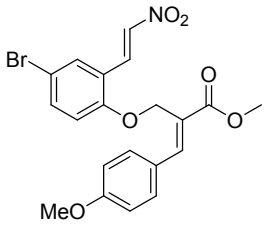


6q: (E)-methyl 2-((4-chloro-2-((E)-2-nitrovinyl)phenoxy)methyl)-3-(p-tolyl)acrylate: Isolated as yellow solid, 75 %, m.p: 149-151°C, ^{1}H NMR δ_{H} (400 MHz, $CDCl_3$) 8.09–7.94 (1 H, m), 7.72 (1 H, d, *J* = 13.7), 7.43 (1 H, d, *J* = 2.6), 7.37 (1 H, dd, *J* = 8.9, 2.6), 7.30 (1 H, d, *J* = 8.1), 7.20 (1 H, d, *J* = 8.0), 6.95 (1 H, d, *J* = 8.9), 5.00 (1 H, s), 3.88 (2 H, s), 2.36 (2 H, s) ppm. ^{13}C NMR δ_{C} (100 MHz, $CDCl_3$) 167.38, 156.71, 146.59, 140.52, 139.12, 133.71, 132.72, 131.23, 131.19, 129.67, 129.58, 126.58, 125.07, 121.13, 114.40, 64.21, 52.51, 21.41ppm. EI-HRMS: Anal. Calcd for C_{20} H_{18} Cl NO_5: 387.0874, Found: 387.0873. Elemental analysis: Anal. Calcd for $C_{20}H_{18}ClNO_5$: C, 61.94; H, 4.68; Cl, 9.14; N, 3.61; O, 20.63 %. Found: C, 61.99; H, 4.61; Cl, 9.19; N, 3.52; O, 20.55 %.

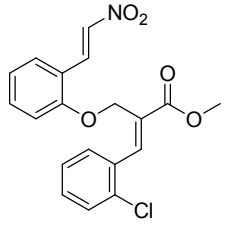


6r: (E)-methyl 2-((4-bromo-2-((E)-2-nitrovinyl)phenoxy)methyl)-3-(4-chlorophenyl)acrylate: Isolated as yellow solid, 81 %, m.p: 133-135°C, ^{1}H NMR δ_{H} (400 MHz, $CDCl_3$) 8.06–7.96 (1 H, m), 7.69 (1 H, d, *J* = 13.7), 7.59 (1 H, d, *J* = 2.4), 7.52 (1 H, dd, *J* = 8.8, 2.4), 7.41–7.30 (2 H, m), 6.89 (1 H, d, *J* = 8.9), 4.95 (1 H, s), 3.89 (2 H, s) ppm. ^{13}C NMR δ_{C} (100 MHz, $CDCl_3$) 166.93,

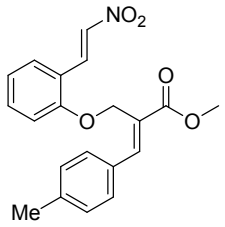
156.97, 145.06, 139.06, 136.21, 135.70, 134.02, 133.42, 132.45, 130.68, 129.24, 126.57, 121.60, 114.73, 113.95, 63.94, 52.68 ppm. EI-HRMS: Anal. Calcd for $C_{19}H_{15}BrClNO_5$: 450.9822, Found: 450.9820. Elemental analysis: Anal. Calcd for $C_{19}H_{15}BrClNO_5$: C, 50.41; H, 3.34; Br, 17.65; Cl, 7.83; N, 3.09; O, 17.67 %. Found: C, 50.35; H, 3.30; Br, 17.69; Cl, 7.88; N, 3.02; O, 17.61 %.



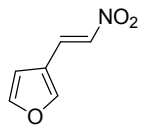
6s: (E)-methyl 2-((4-bromo-2-((E)-2-nitrovinyl)phenoxy)methyl)-3-(4-methoxyphenyl)acrylate: Isolated as yellow solid, 81 %, m.p: 148-150°C, ^{1}H NMR δ_H (400 MHz, $CDCl_3$) 8.05 (1 H, s), 7.99 (1 H, d, *J* = 13.7), 7.70 (1 H, d, *J* = 13.6), 7.57 (1 H, d, *J* = 2.4), 7.51 (1 H, dd, *J* = 8.8, 2.4), 7.38 (2 H, d, *J* = 8.7), 6.92 (3 H, dd, *J* = 16.2, 8.8), 5.02 (2 H, s), 3.87 (3 H, s), 3.82 (3 H, s) ppm. ^{13}C NMR: δ_C (100 MHz, $CDCl_3$) 167.55, 161.20, 157.22, 146.37, 139.08, 135.67, 134.12, 133.61, 131.64, 126.51, 123.41, 121.61, 114.81, 114.45, 113.66, 64.24, 55.40, 52.46 ppm. EI-HRMS: Anal. Calcd for $C_{20}H_{18}BrNO_6$: 447.0317, Found: 447.0315. Elemental analysis: Anal. Calcd for $C_{20}H_{18}BrNO_6$: C, 53.59; H, 4.05; Br, 17.83; N, 3.12; O, 21.42 %. Found: C, 53.51; H, 4.01; Br, 17.89; N, 3.05; O, 21.35 %.



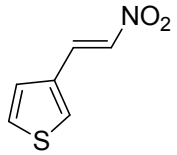
6t: (E)-methyl 3-(2-chlorophenyl)-2-((2-((E)-2-nitrovinyl)phenoxy)methyl)acrylate: Isolated as yellow solid, 86 %, m.p: 125-128°C, ^{1}HNMR δ_H (400 MHz, $CDCl_3$) 8.16 (1 H, s), 8.08 (1 H, d, *J* = 13.6), 7.75 (1 H, d, *J* = 13.6), 7.49–7.36 (4 H, m), 7.32 (1 H, m), 7.26–7.20 (1 H, m), 7.04 (1 H, t, *J* = 7.6), 6.92 (1 H, d, *J* = 8.4), 4.92 (2 H, s), 3.92 (3 H, s) ppm. ^{13}C NMR: δ_C (100 MHz, $CDCl_3$) 166.72, 156.52, 142.71, 141.53, 135.12, 134.88, 133.33, 132.05, 131.78, 130.74, 130.09, 129.83, 128.89, 128.46, 128.00, 126.99, 125.12, 121.69, 113.84, 113.03, 63.88, 49.48 ppm. EI-HRMS: Anal. Calcd for $C_{19}H_{16}ClNO_5$: 373.0717, Found: 373.0715. Elemental analysis: Anal. Calcd for $C_{19}H_{16}ClNO_5$: C, 61.05; H, 4.31; Cl, 9.48; N, 3.75; O, 21.40 %. Found: C, 61.0; H, 4.25; Cl, 9.42; N, 3.70; O, 21.33 %.



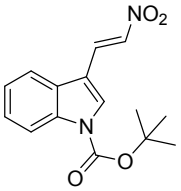
6u: (E)-methyl 2-((2-((E)-2-nitrovinyl)phenoxy)methyl)-3-(p-tolyl)acrylate: Isolated as yellow solid, 82 %, m.p: 118-120°C, ^{1}HNMR (400 MHz, $CDCl_3$) δ_H 8.10 (1 H, d, *J* = 14.8), 7.77 (1 H, d, *J* = 13.6), 7.44 (1 H, dd, *J* = 18.4, 8.0), 7.32 (1 H, d, *J* = 7.8), 7.25 (1 H, t, *J* = 7.5), 7.18 (2 H, d, *J* = 7.4), 7.03 (1 H, dd, *J* = 17.7, 8.1), 5.02 (1 H, s), 3.88 (2 H, s), 2.35 (3 H, s) ppm. ^{13}NMR: δ_C (100 MHz, $CDCl_3$) 167.50, 158.34, 146.36, 140.36, 138.34, 135.27, 133.35, 132.32, 131.35, 129.64, 129.62, 129.05, 128.23, 125.41, 125.31, 121.57, 119.72, 112.99, 63.76, 52.46, 21.39 ppm. EI-HRMS: Anal. Calcd for $C_{20}H_{19}NO_5$: 353.1263, Found: 353.1260. Elemental analysis: Anal. Calcd for $C_{20}H_{19}NO_5$: C, 67.98; H, 5.42; N, 3.96; O, 22.64 %. Found: C, 67.91; H, 5.48; N, 3.90; O, 22.60 %.



7v: (E)-3-(2-nitrovinyl)furan : Isolated as yellow solid, 75 %, m.p: 74-76^{o}C, ^{1}H NMR δ_{H} (400 MHz, $CDCl_3$) 7.94 (1 H, d, *J* = 13.5), 7.84–7.83 (1 H, m), 7.52 (1 H, t, *J* = 1.3), 7.41 (1 H, s), 7.37 (1 H, s), 7.26 (1 H, s), 6.57 (1 H, d, *J* 1.9). ^{13}C NMR δ_{C} (100 MHz, $CDCl_3$) 147.29, 145.37, 136.74, 129.53, 118.21, 107.25 ppm. EI-HRMS: Anal. Calcd for C_6 H_6 NO_3: 139.0269, Found: 139.0267. Elemental analysis: Anal. Calcd for $C_6H_6NO_3$: C, 51.80; H, 3.62; N, 10.07; O, 34.50 %. Found: C, 51.74; H, 3.67; N, 10.01; O, 34.45 %.

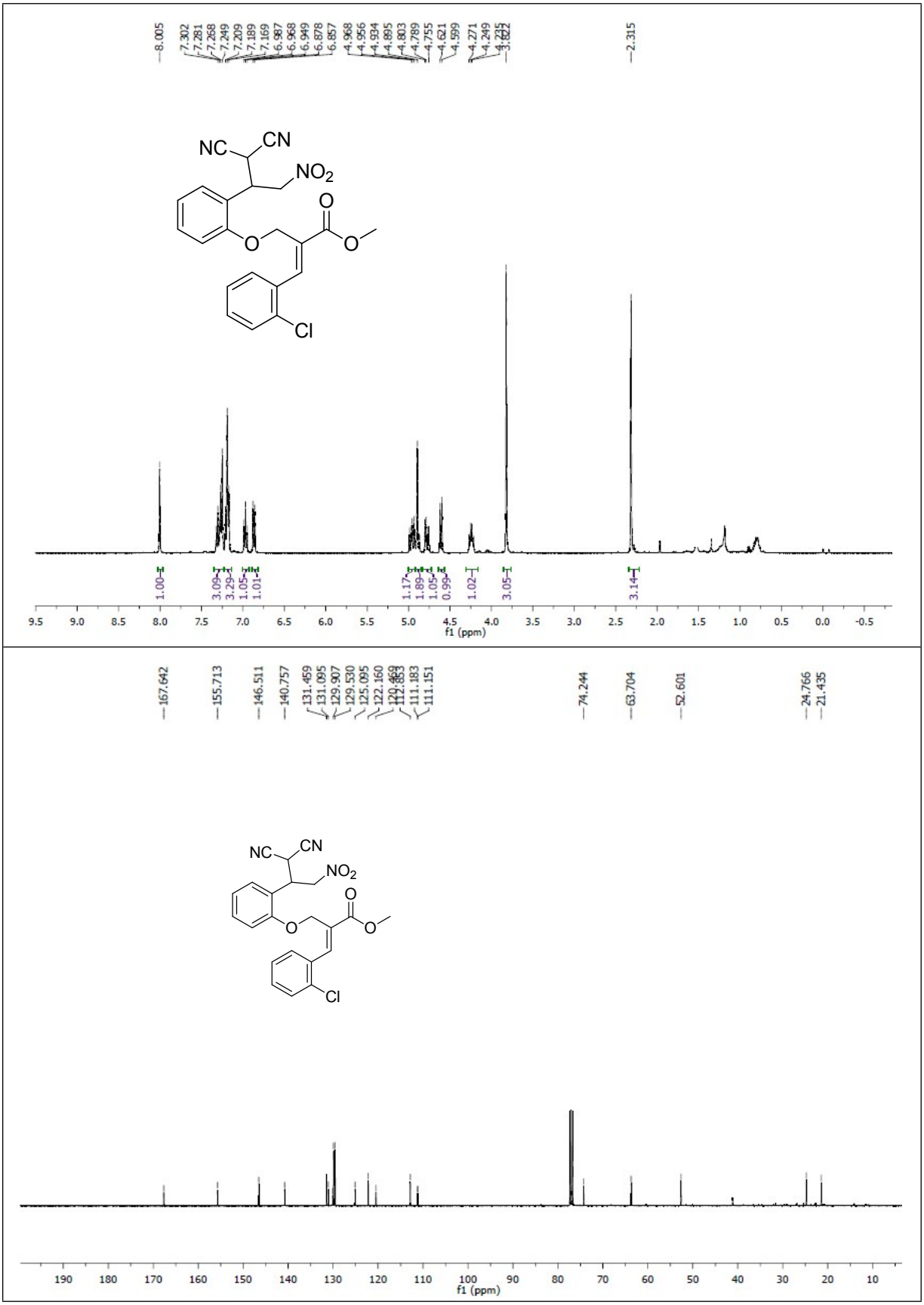


7w: (E)-3-(2-nitrovinyl)thiophene: Isolated as yellow solid, 89 %, m.p: 87-90^{o}C, ^{1}H NMR δ_{H} (400 MHz, $CDCl_3$) 8.15 (1 H, d, *J* = 13.4), 7.57 (1 H, d, *J* = 4.9), 7.51–7.43 (2 H, m), 7.15 (1 H, dd, *J* = 5.1, 3.7). ^{13}C NMR δ_{C} (100 MHz, $CDCl_3$) 135.39, 134.62, 133.79, 132.09, 131.63, 128.90 ppm. EI-HRMS: Anal. Calcd for $C_6H_5NO_2S$: 155.0041, Found: 155.0040. Elemental analysis: Anal. Calcd for $C_6H_5NO_2S$: C, 46.44; H, 3.25; N, 9.03; O, 20.62; S, 20.66 %. Found: C, 46.40; H, 3.21; N, 9.09; O, 20.55; S, 20.60 %.

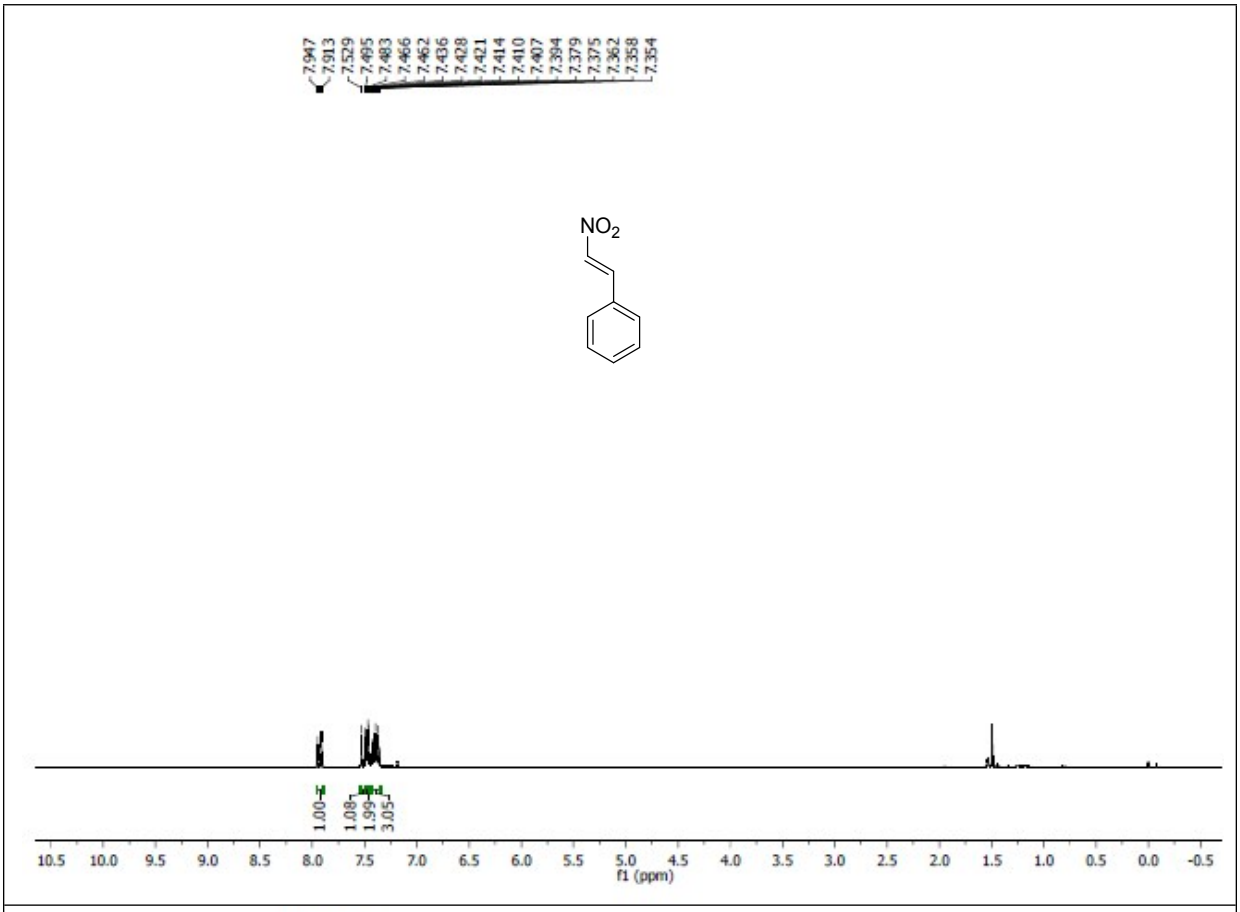


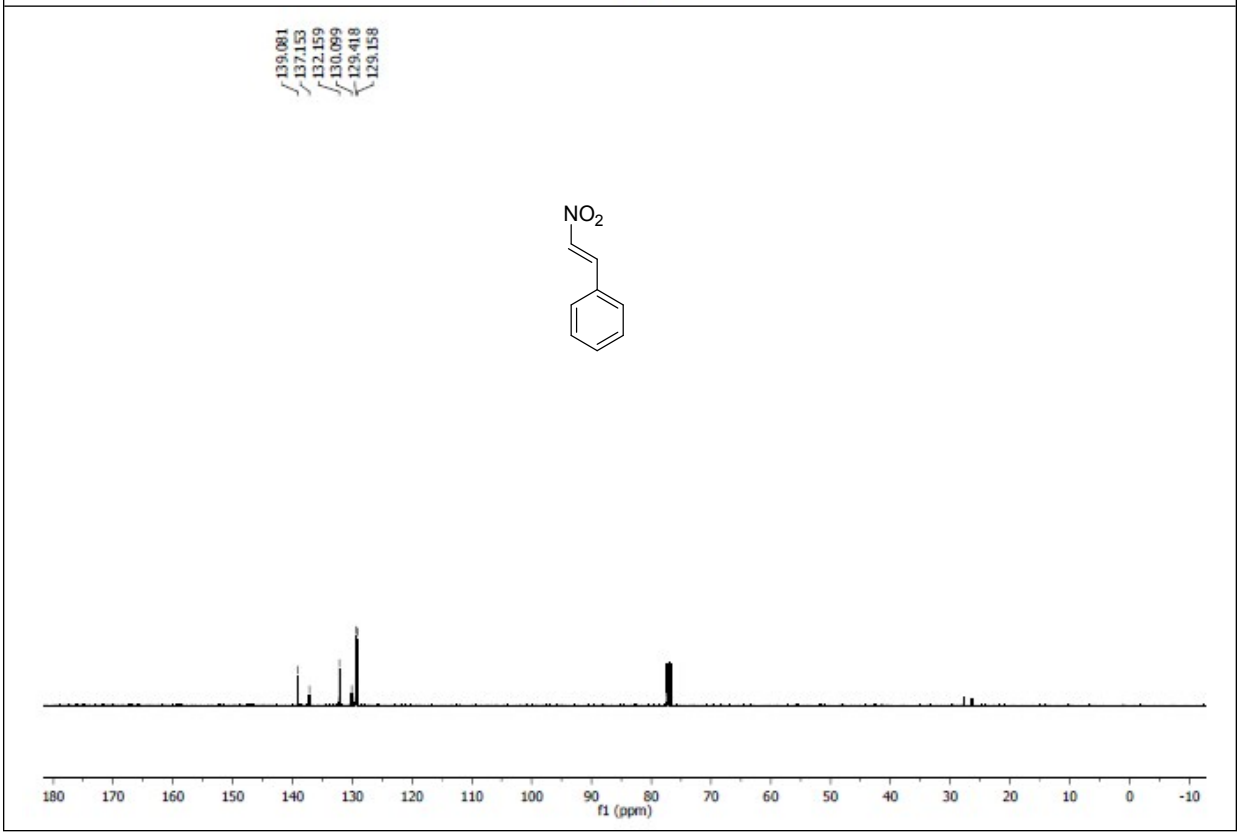
7x: (E)-tert-butyl 3-(2-nitrovinyl)-1H-indole-1-carboxylate: Isolated as yellow solid, 89 %, ^{1}H NMR : δ_{H} (400 MHz, $CDCl_3$) 8.23 (1 H, d, *J* = 8.1), 8.17 (1 H, d, *J* = 13.7), 8.03 (1 H, s), 7.78 (1 H, d, *J* = 13.7), 7.71 (1 H, dd, *J* = 7.2, 0.8), 7.41 (2 H, dtd, *J* = 20.7, 7.4, 1.2), 1.70 (9 H, s) ppm. ^{13}C NMR: δ_{C} (100 MHz, $CDCl_3$) 148.63, 136.40, 135.79, 132.19, 131.58, 126.85, 125.97, 124.26, 120.20, 115.93, 112.51, 85.58, 28.10 ppm. EI-HRMS: Anal. Calcd for C_{15} H_{16} N_2 O_4: 288.1110, Found: 288.1109. Elemental analysis: Anal. Calcd for $C_{15}H_{16}N_2O_4$: C, 62.49; H, 5.59; N, 9.72; O, 22.20; %. Found: C, 62.42; H, 5.53; N, 9.79; O, 22.14; %.

^{1}H and ^{13}C NMR Spectra of intermediate (6s)

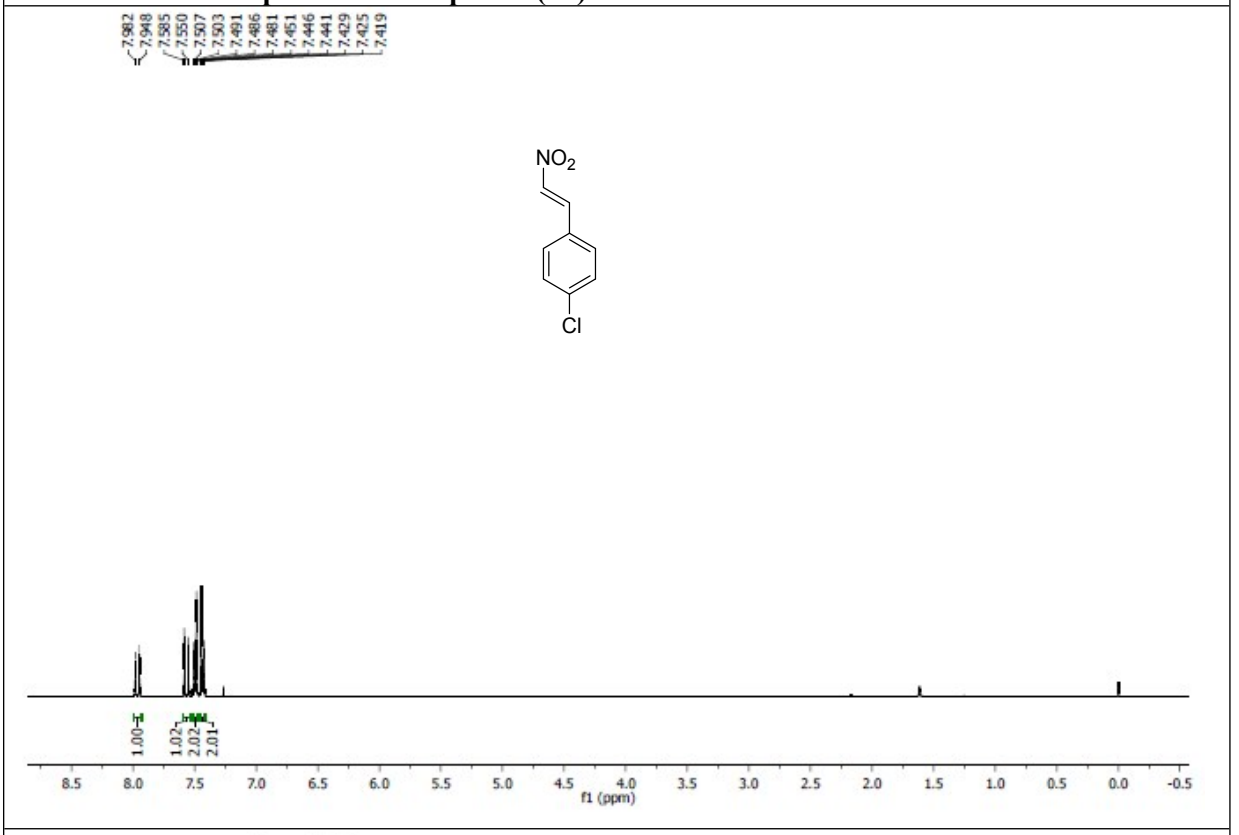


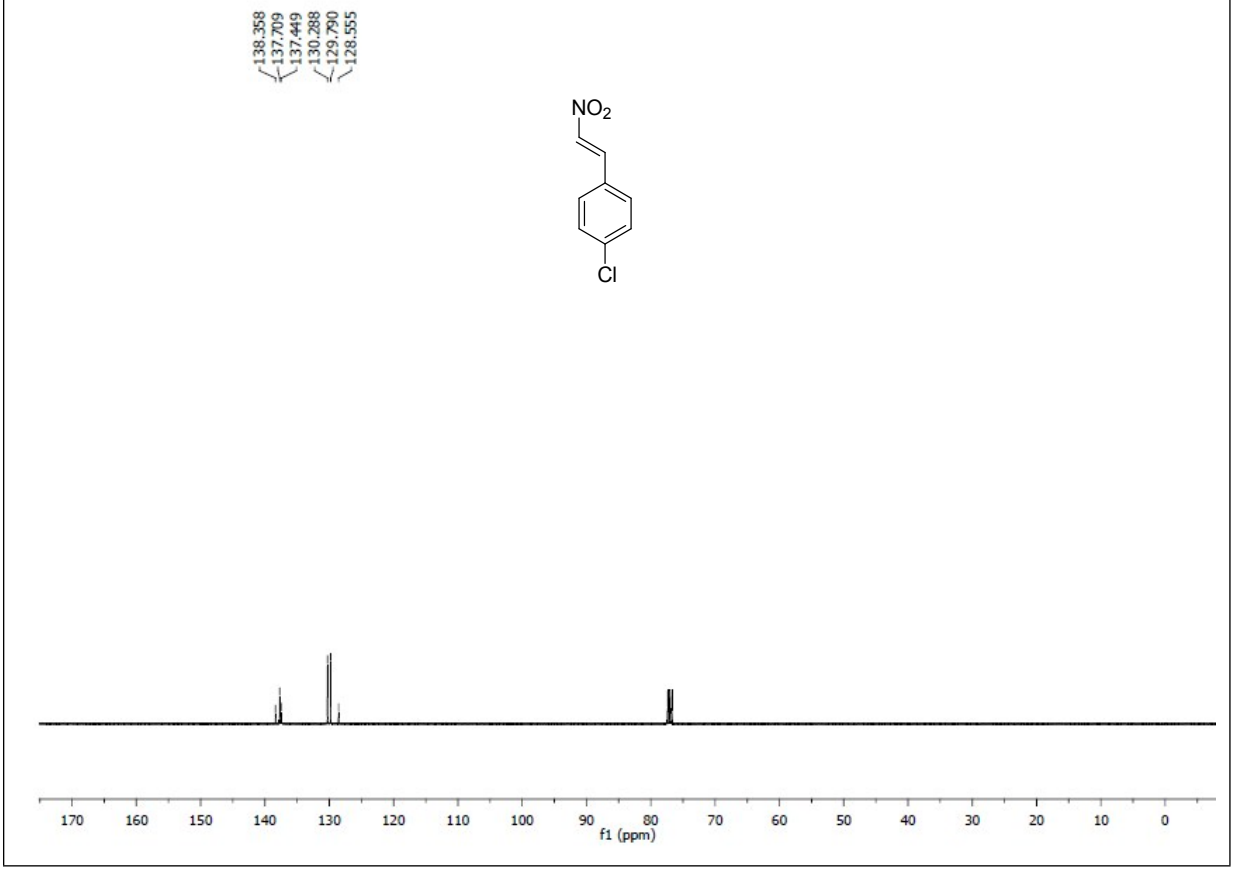
^{1}H and ^{13}C NMR Spectra of Compound (6a)


7.947
7.913
7.529
7.495
7.483
7.466
7.462
7.436
7.428
7.421
7.414
7.410
7.407
7.394
7.379
7.375
7.362
7.358
7.354
NO2
1.00
1.08
1.99
3.05
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

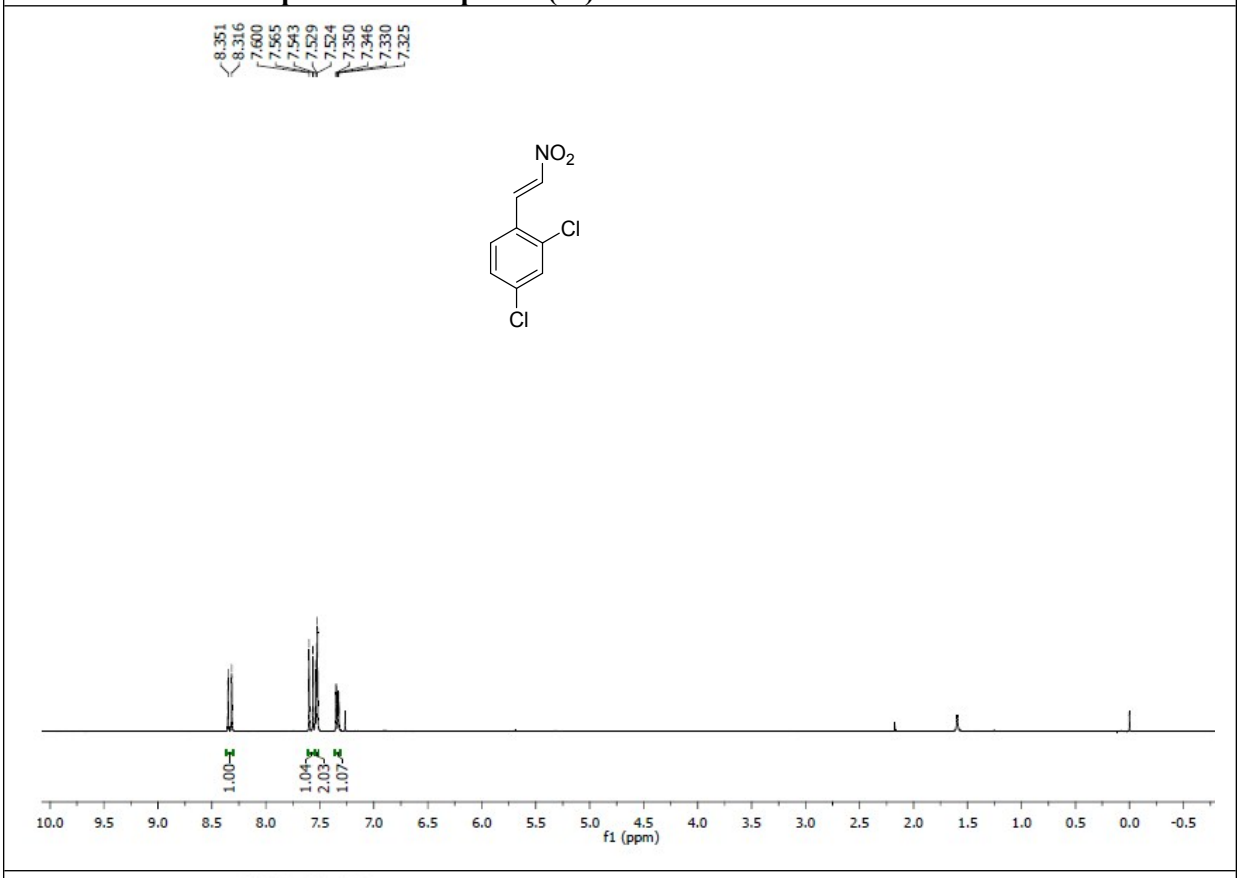

139.081
137.153
132.159
130.099
129.418
129.158
NO2
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

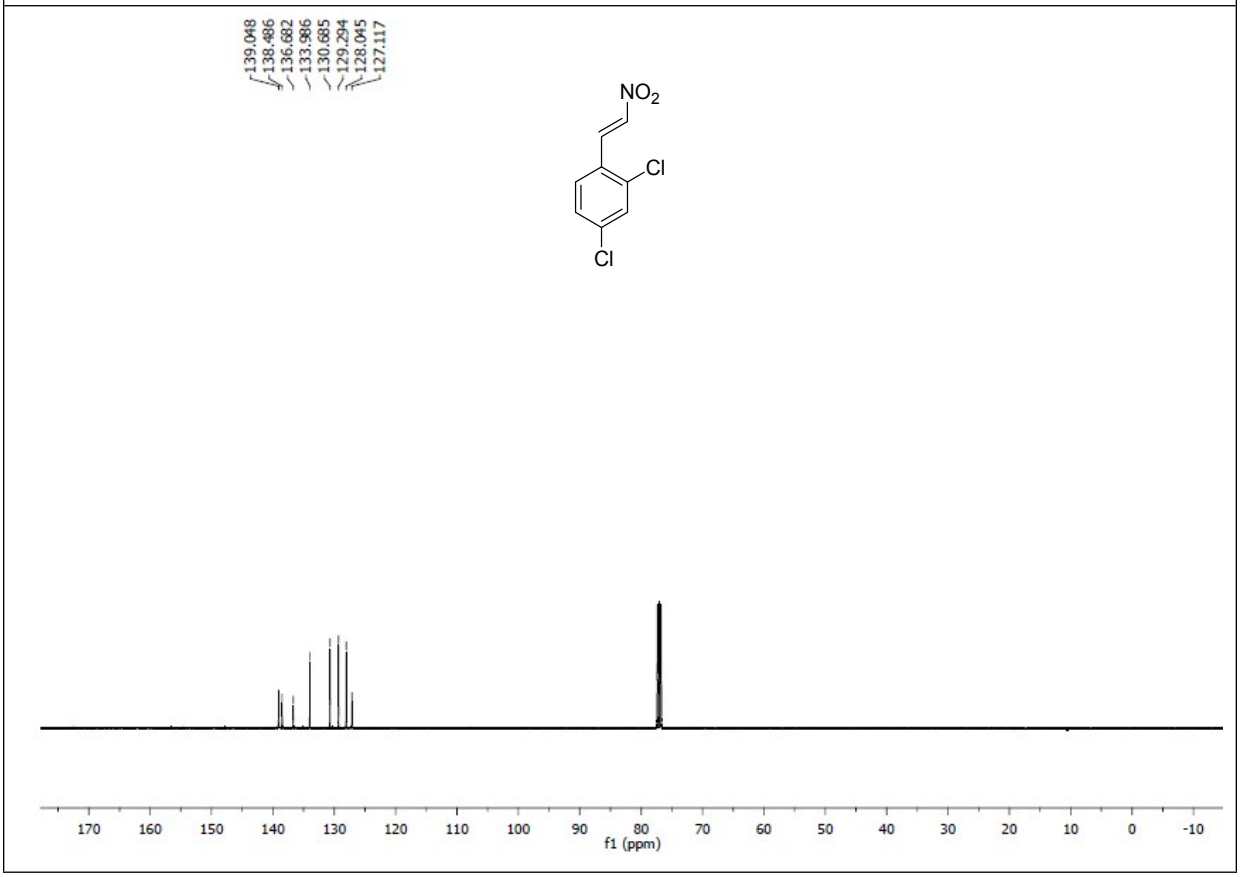
^{1}H and ^{13}C NMR Spectra of Compound (6b)



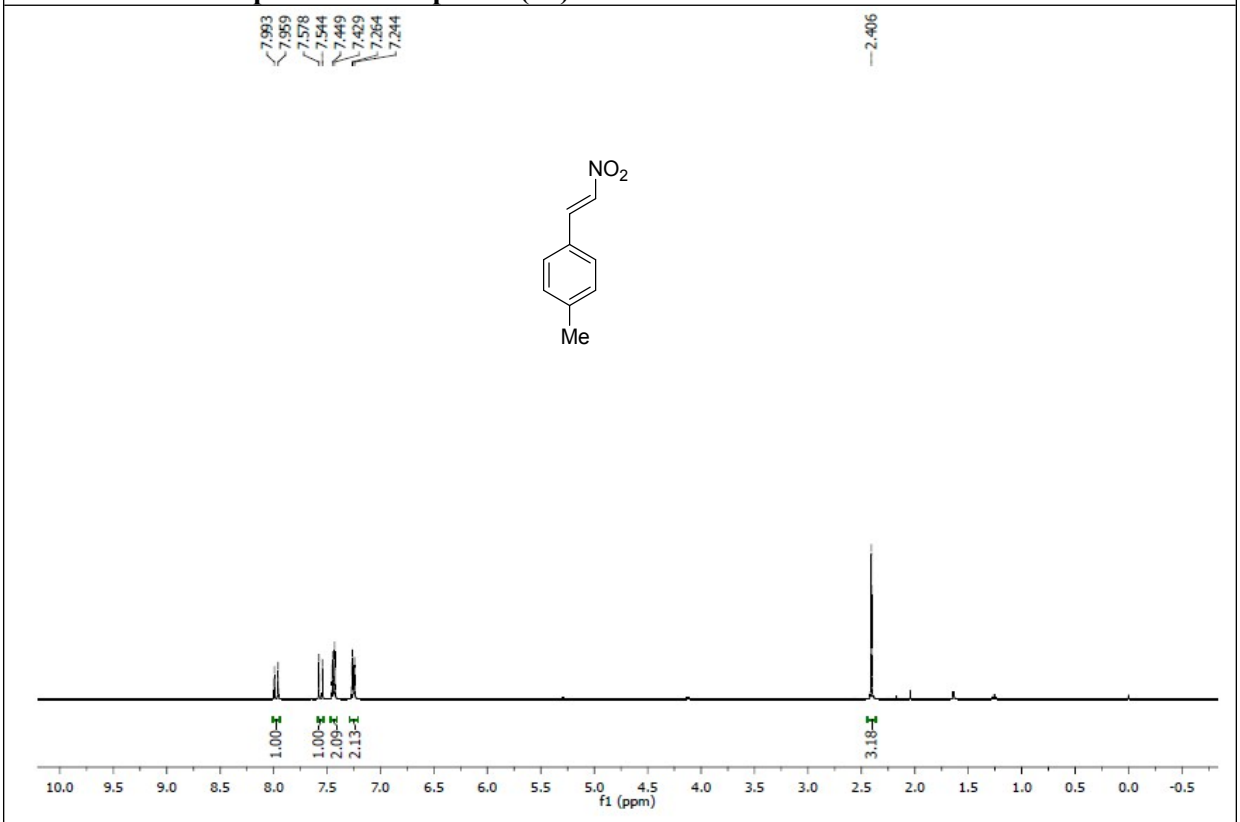


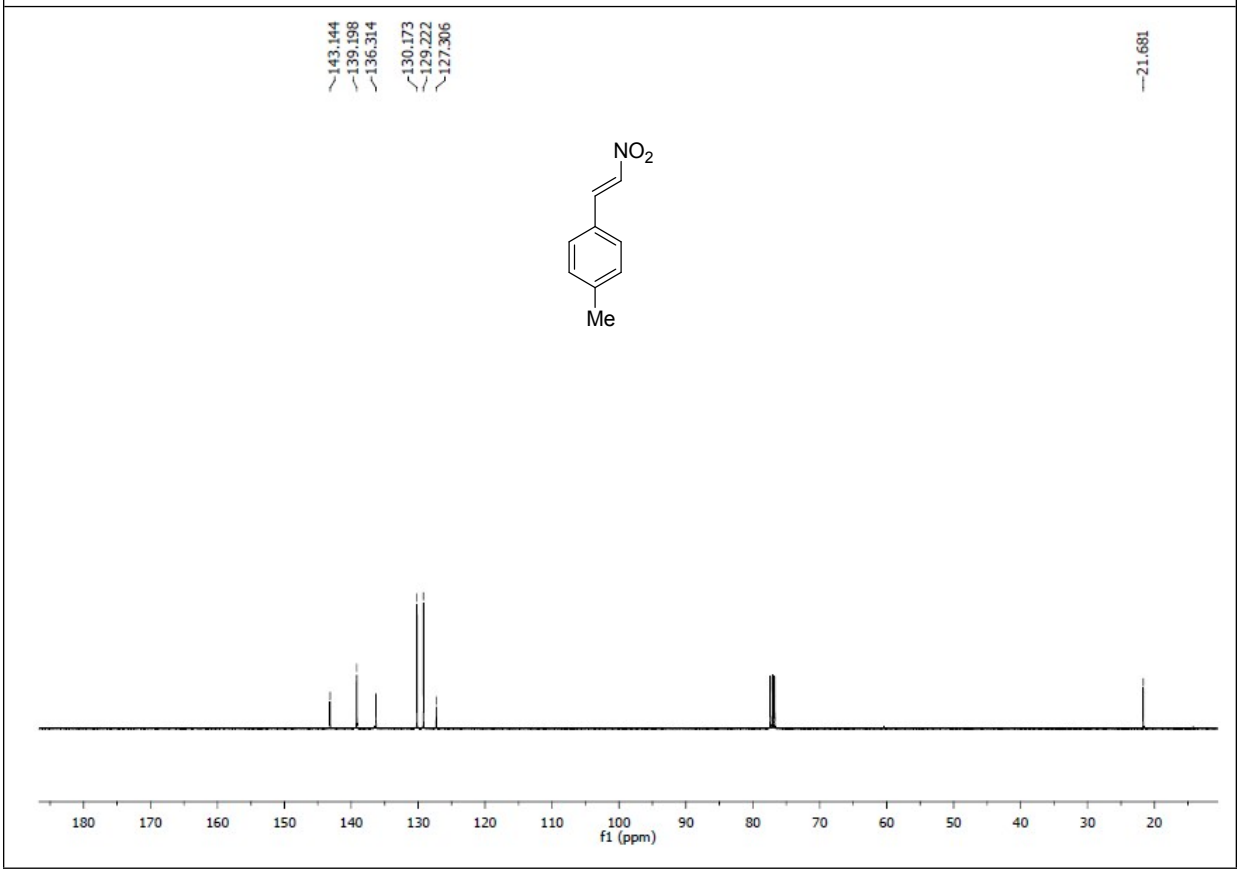
^{1}H and ^{13}C NMR Spectra of Compound (6c)



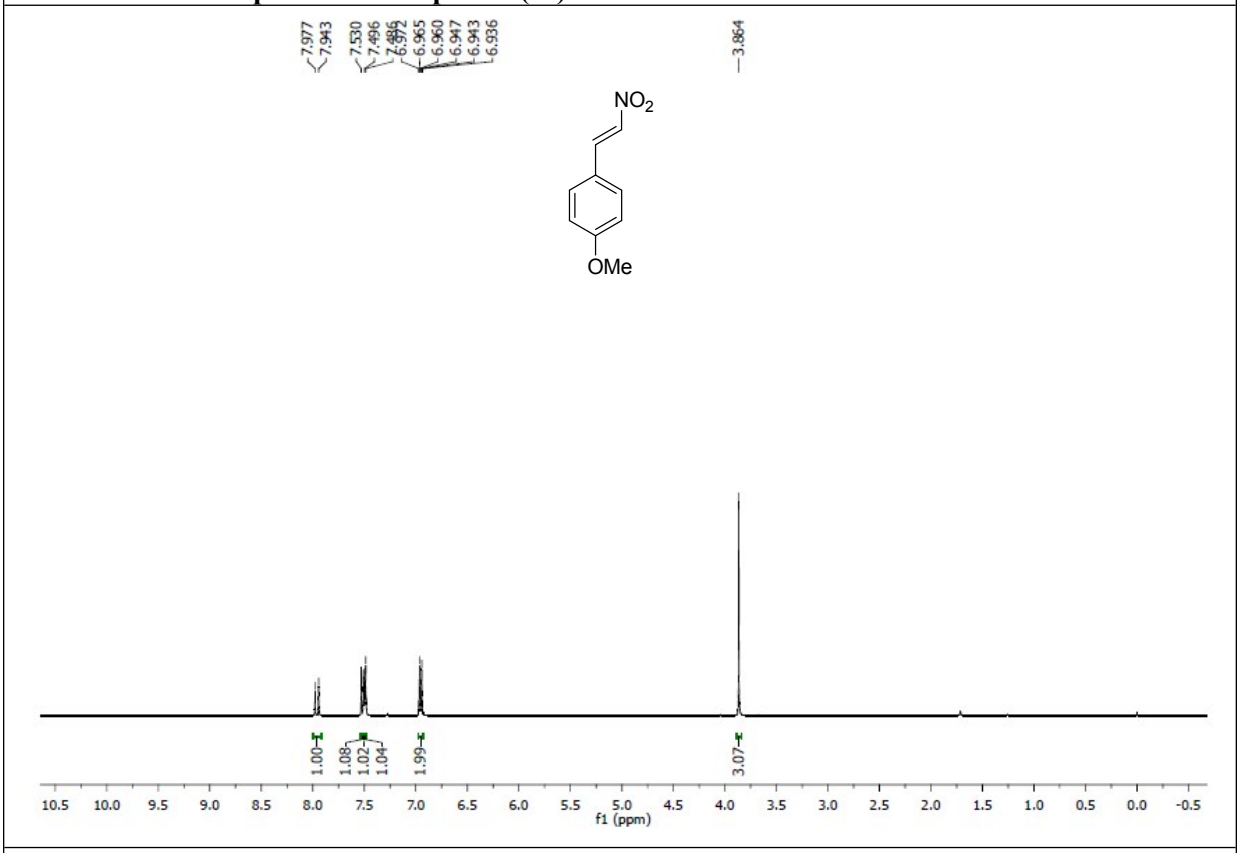


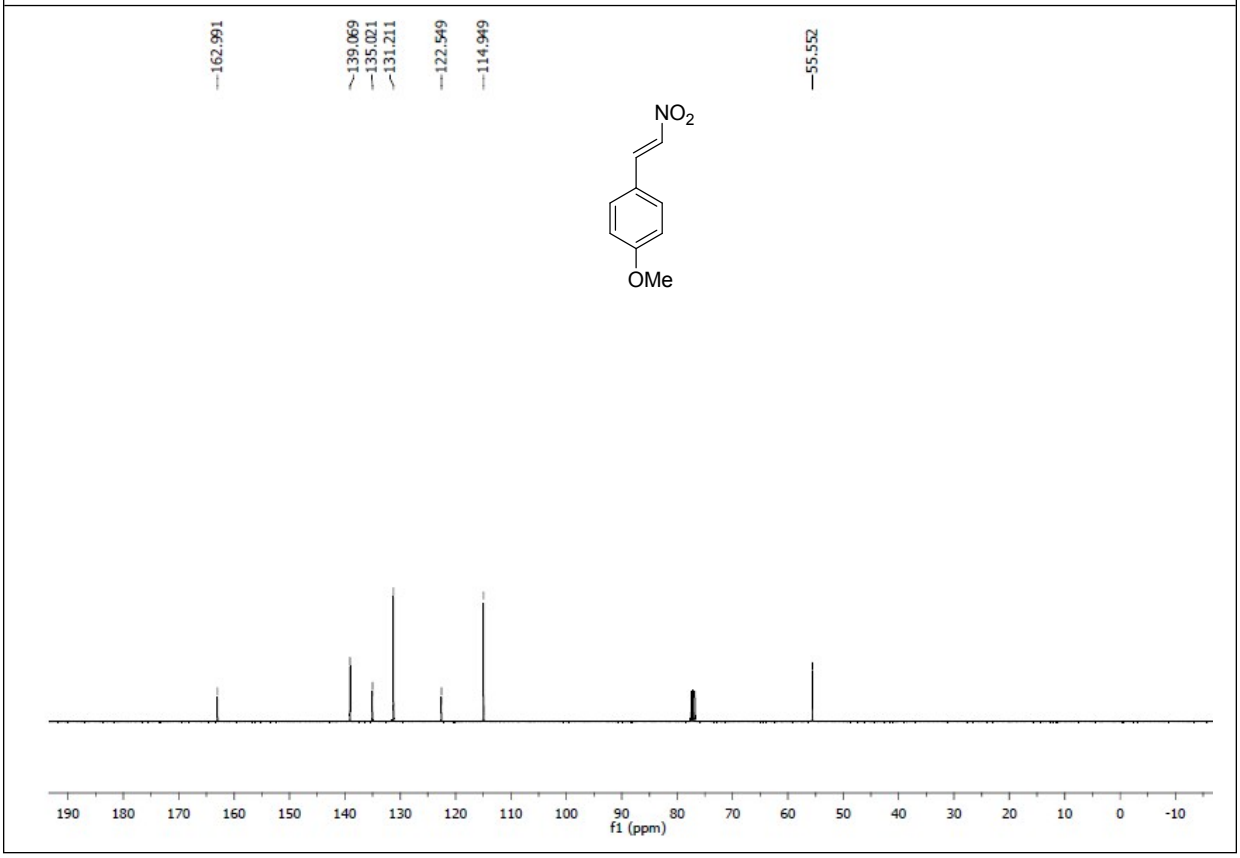
^{1}H and ^{13}C NMR Spectra of Compound (6d)



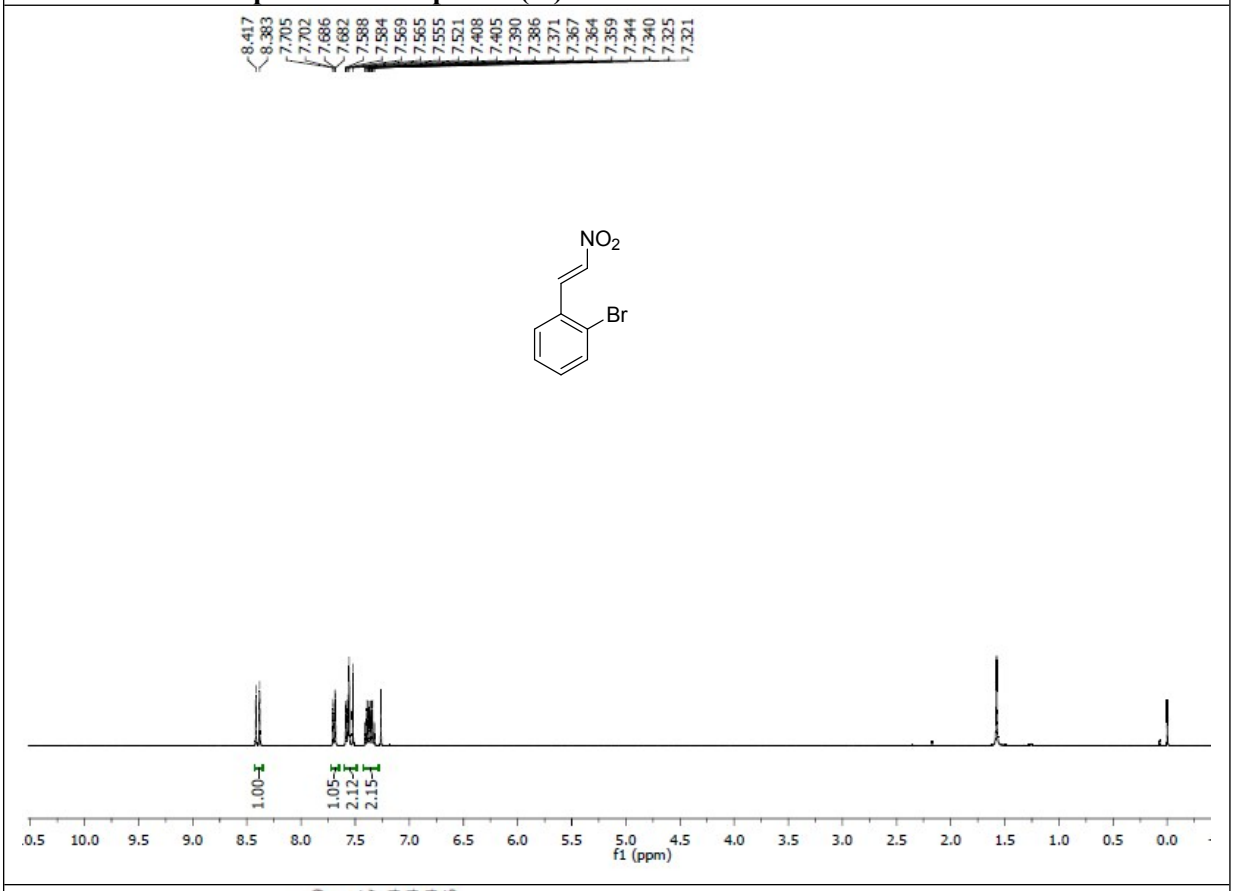


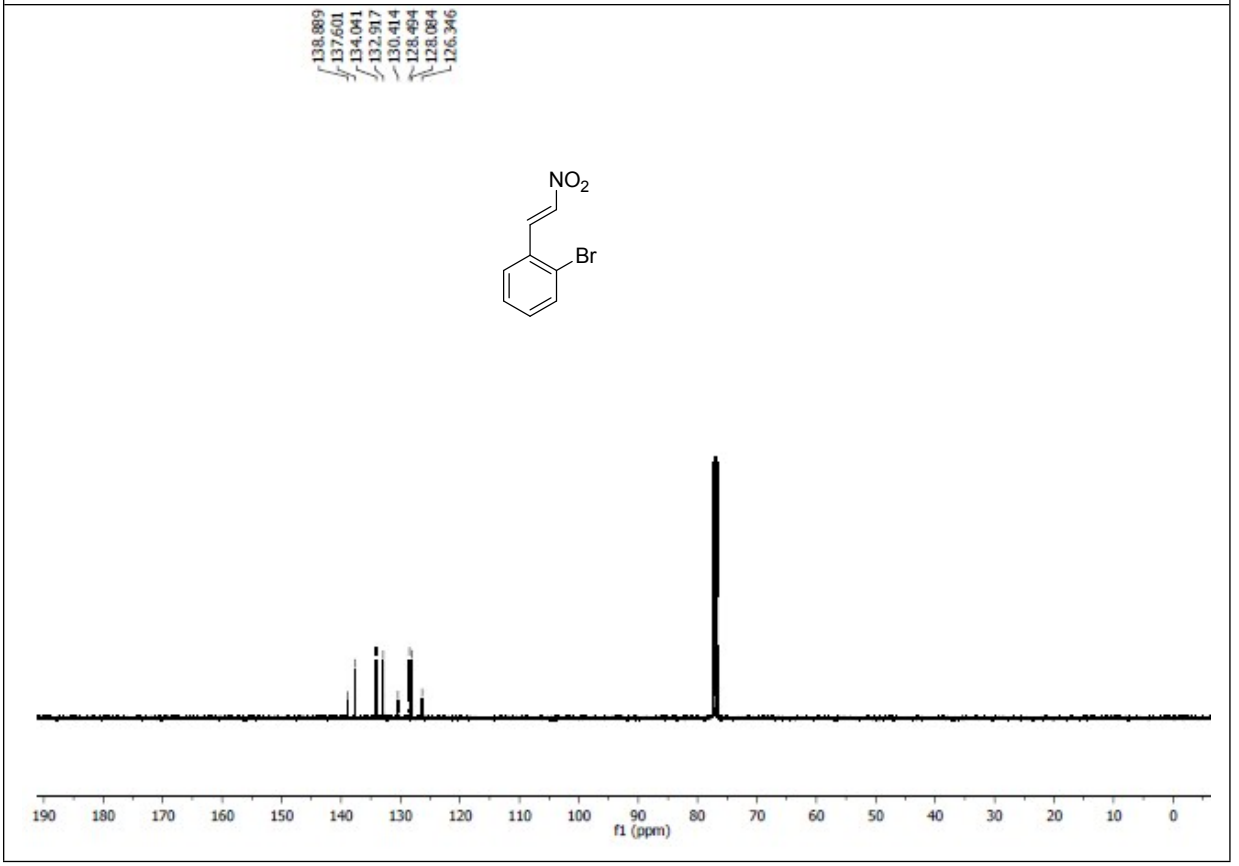
^{1}H and ^{13}C NMR Spectra of Compound (6e)



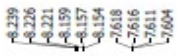


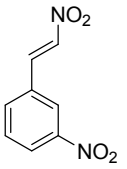
^{1}H and ^{13}C NMR Spectra of Compound (6f)

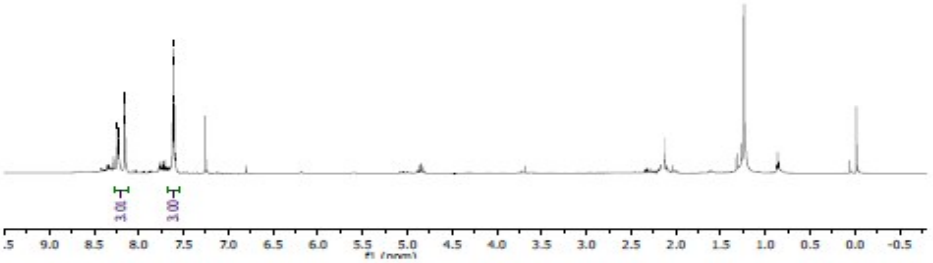


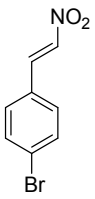


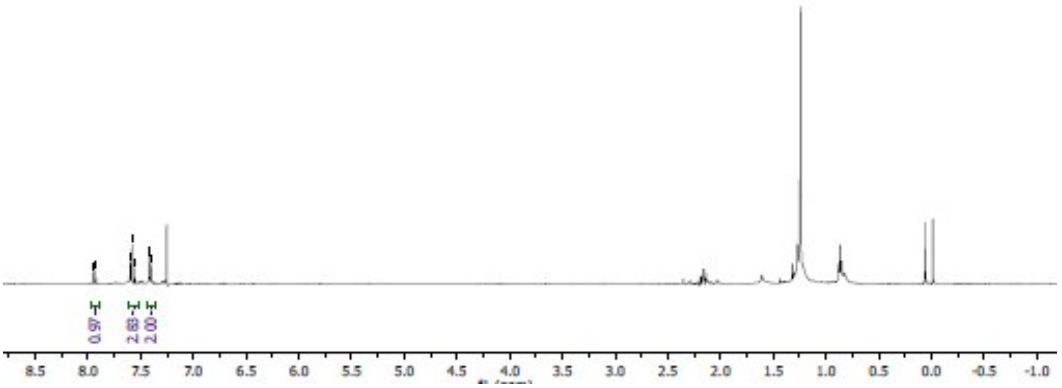
^{1}H Spectra's of Compound (6h & 6g)



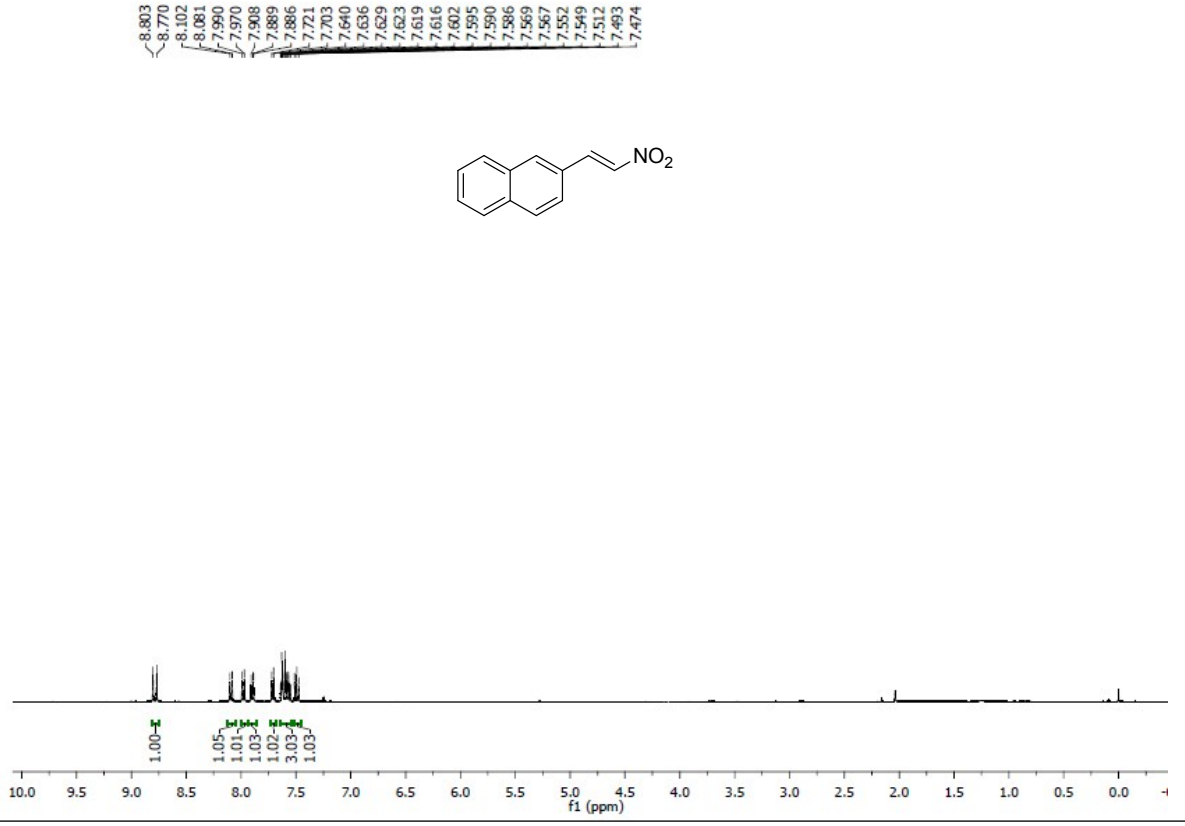


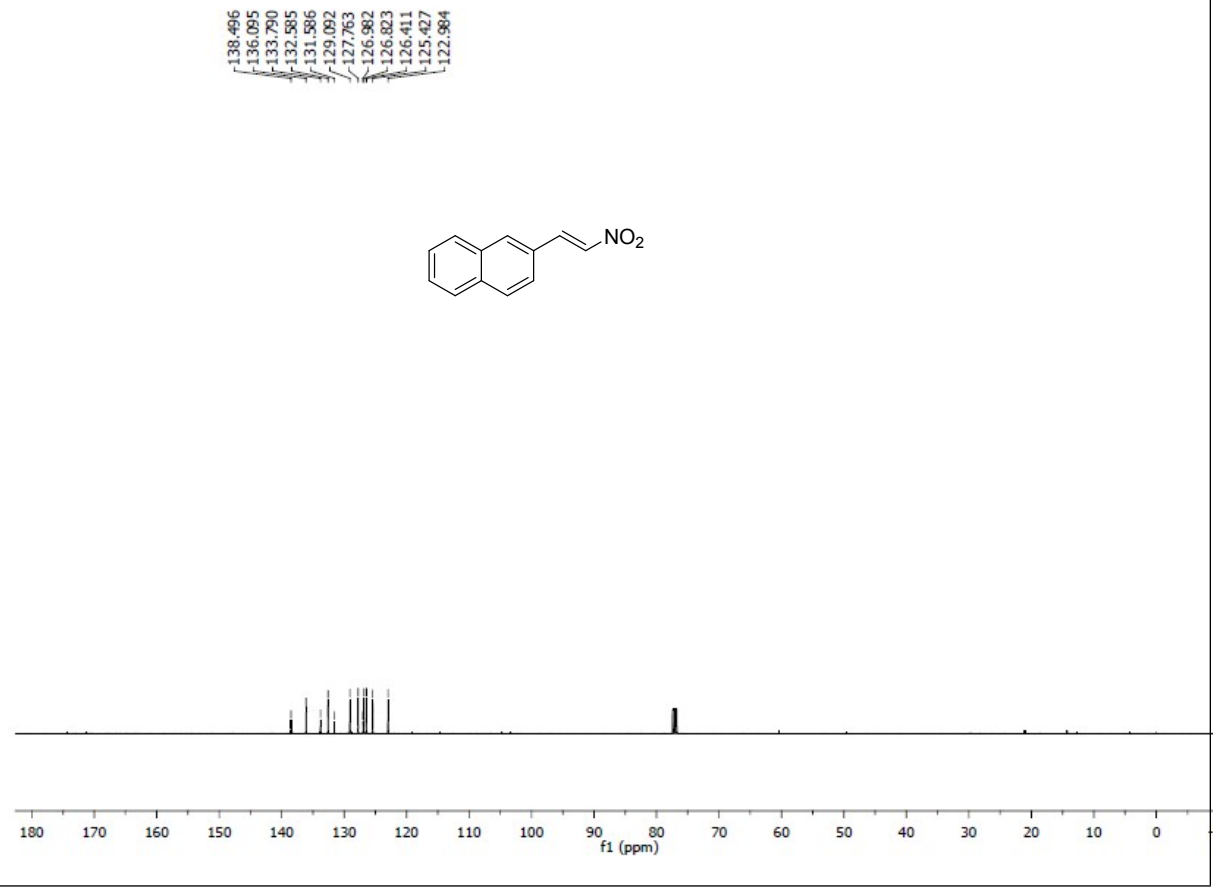




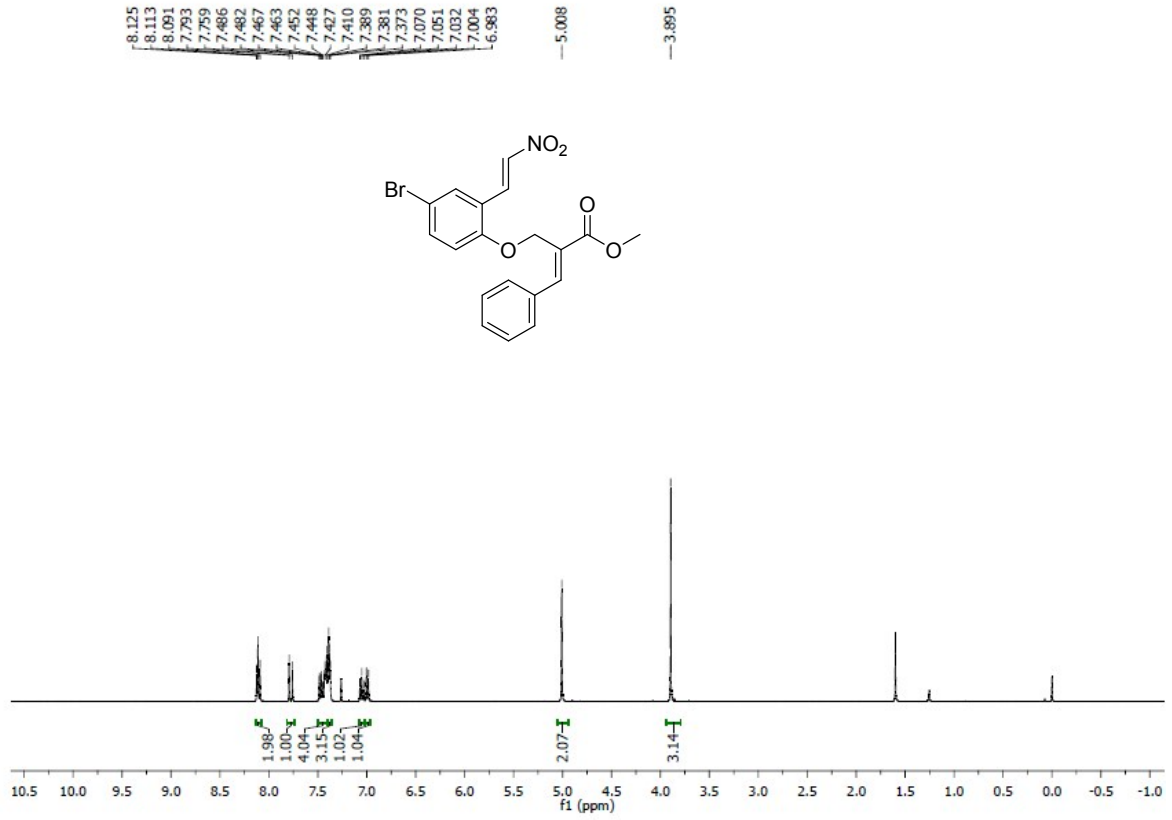


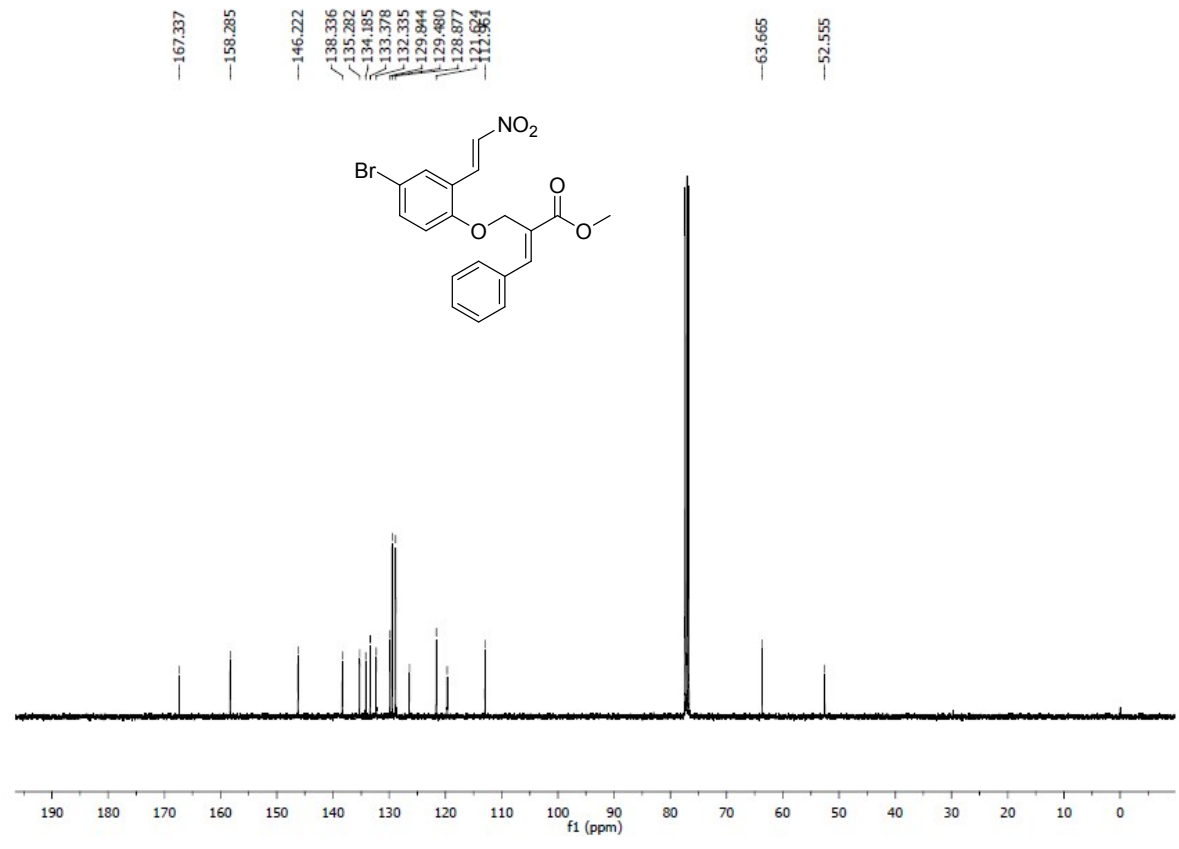
^{1}H and ^{13}C NMR Spectra of Compound (6i)



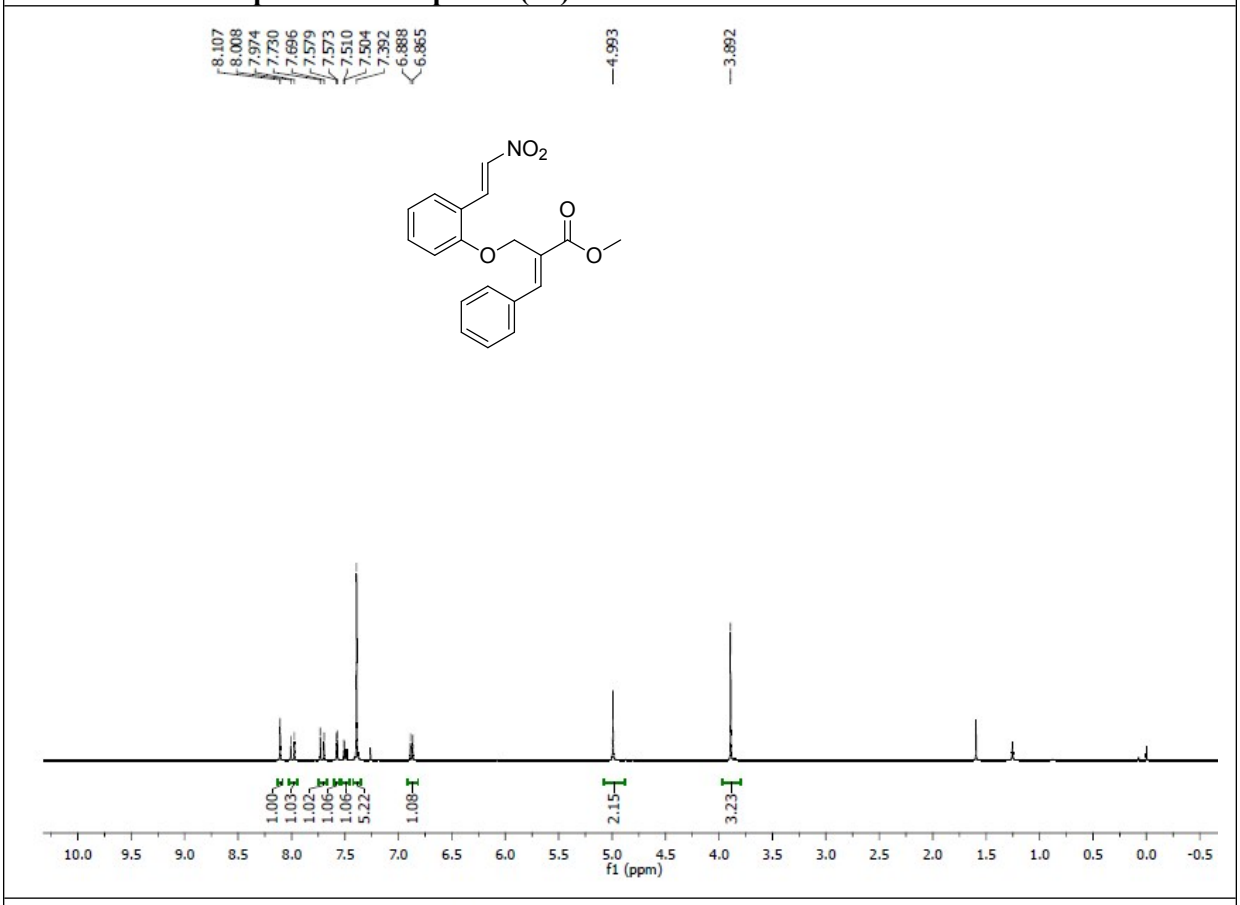


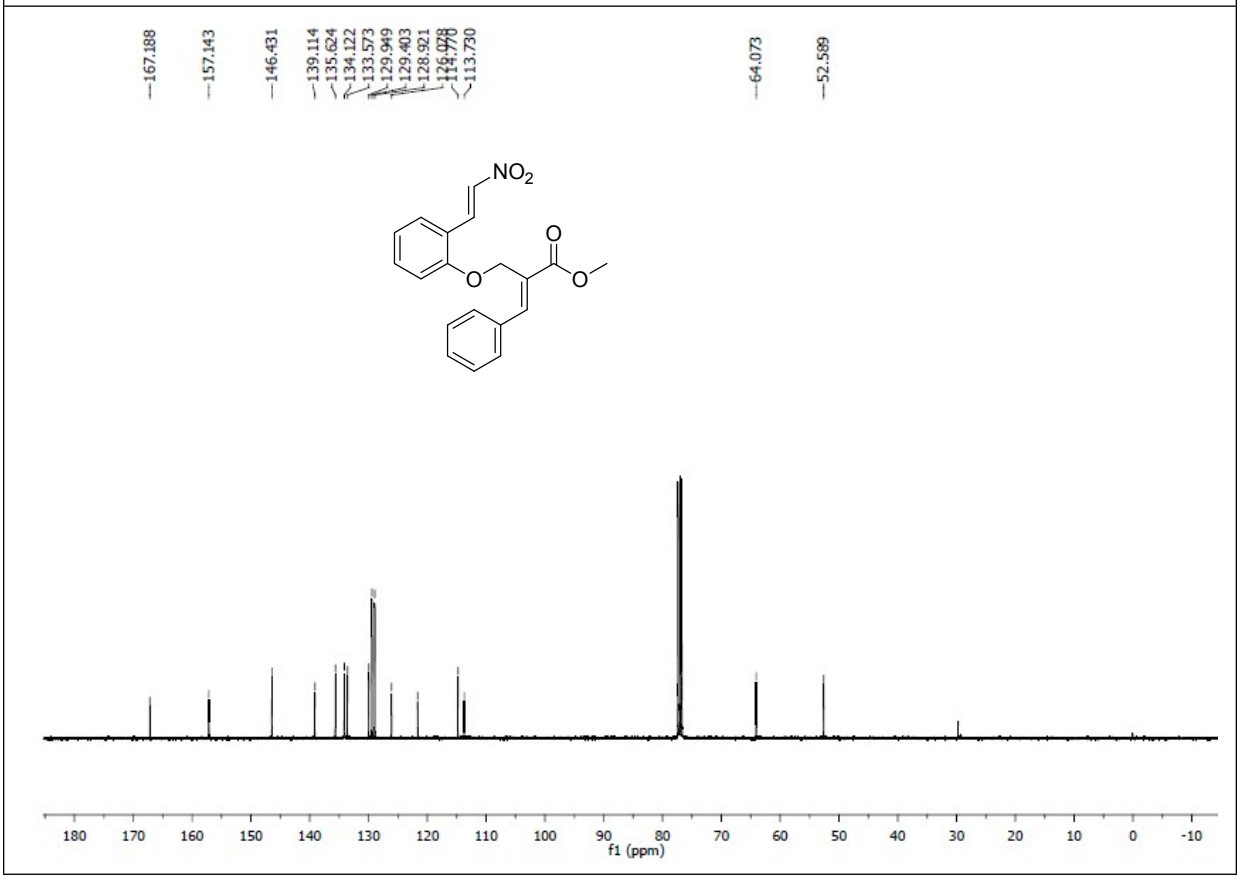
^{1}H and ^{13}C NMR Spectra of Compound (6j)



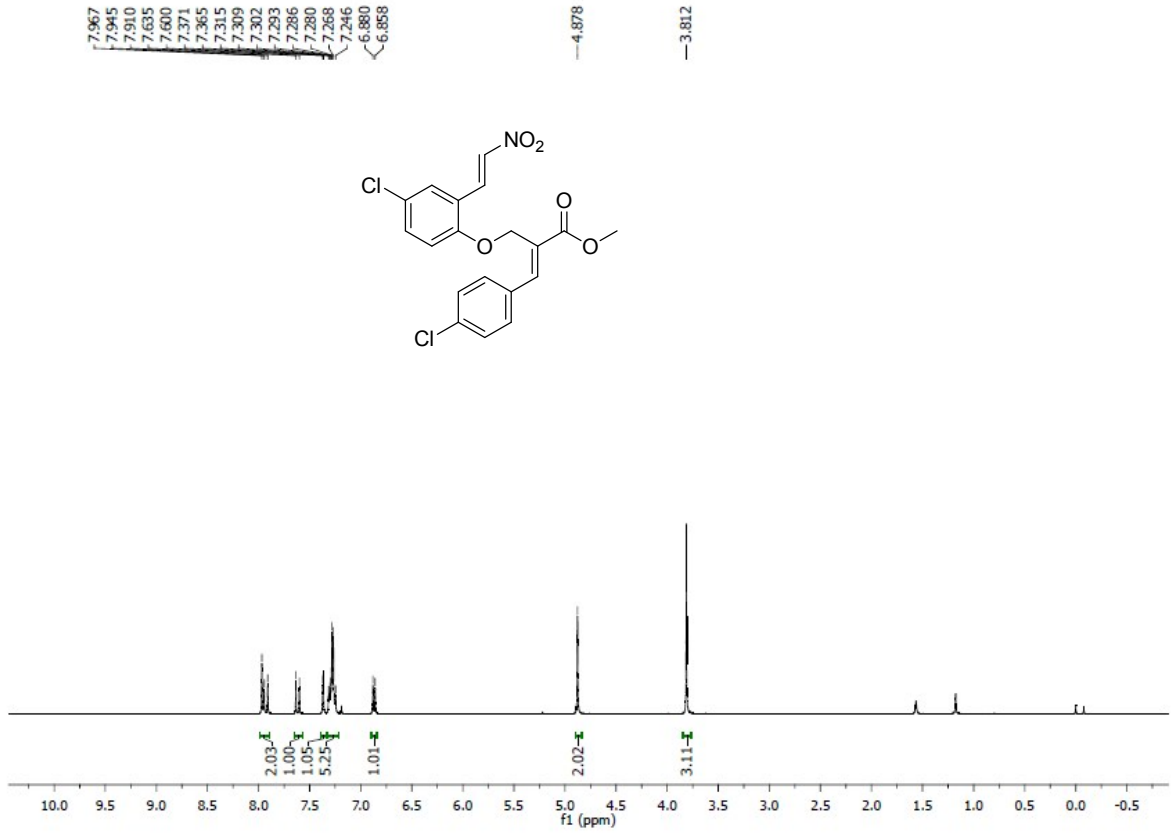


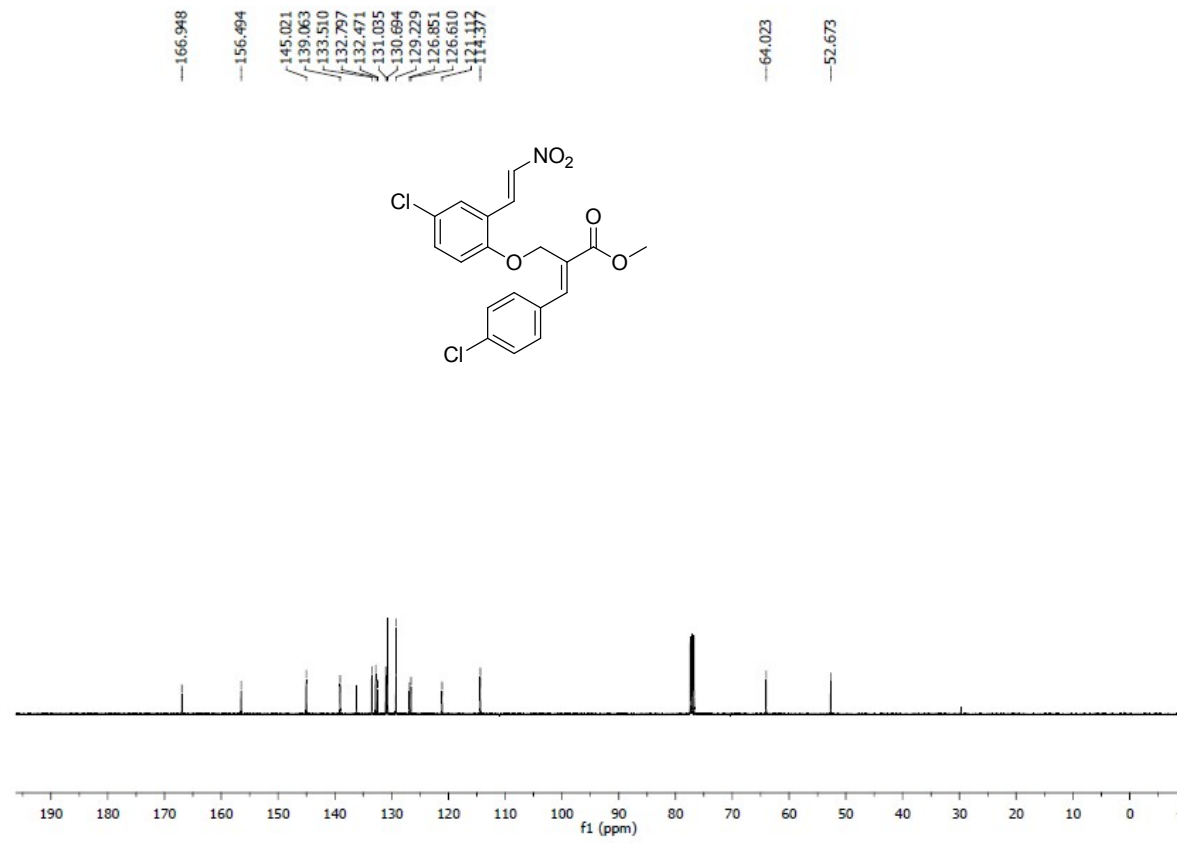
^{1}H and ^{13}C NMR Spectra of Compound (6k)



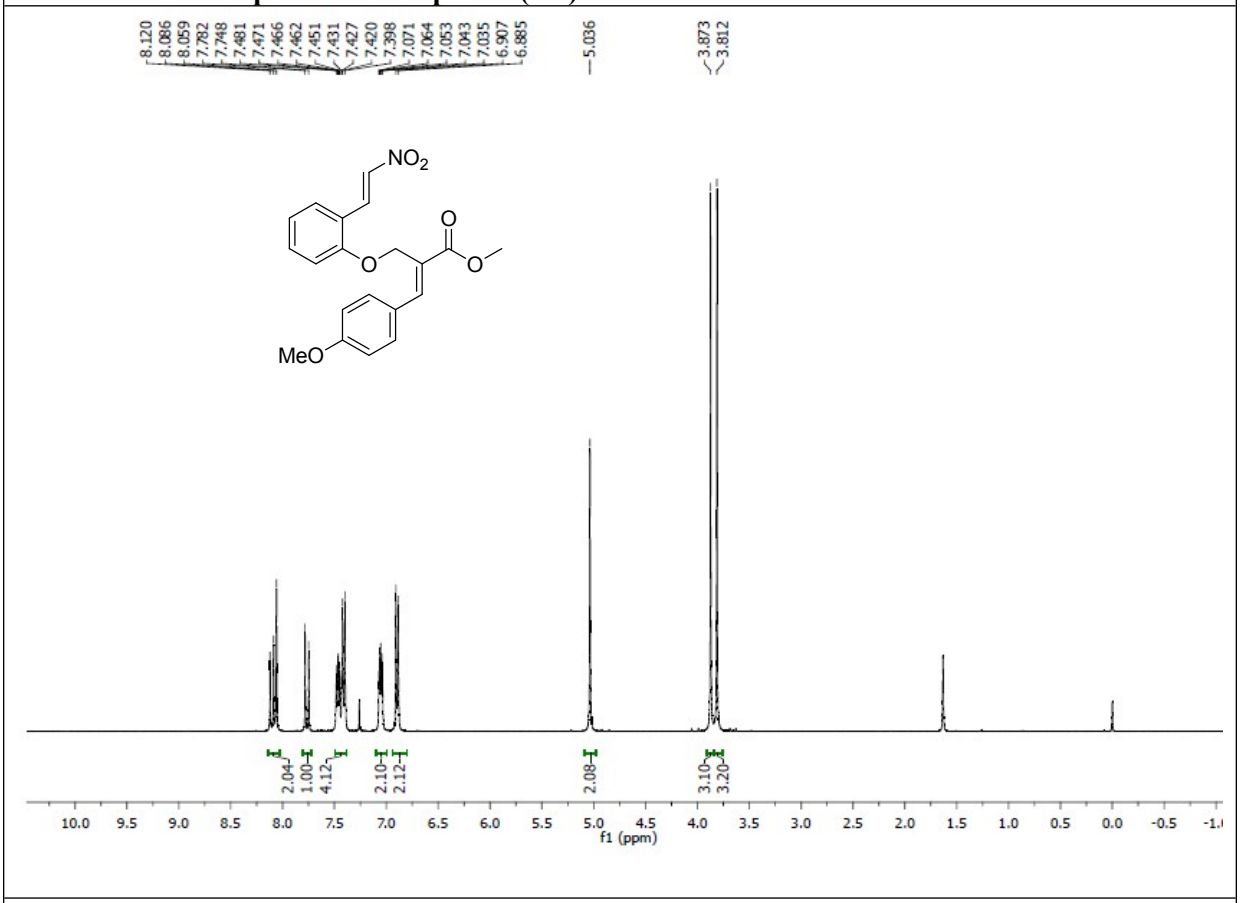


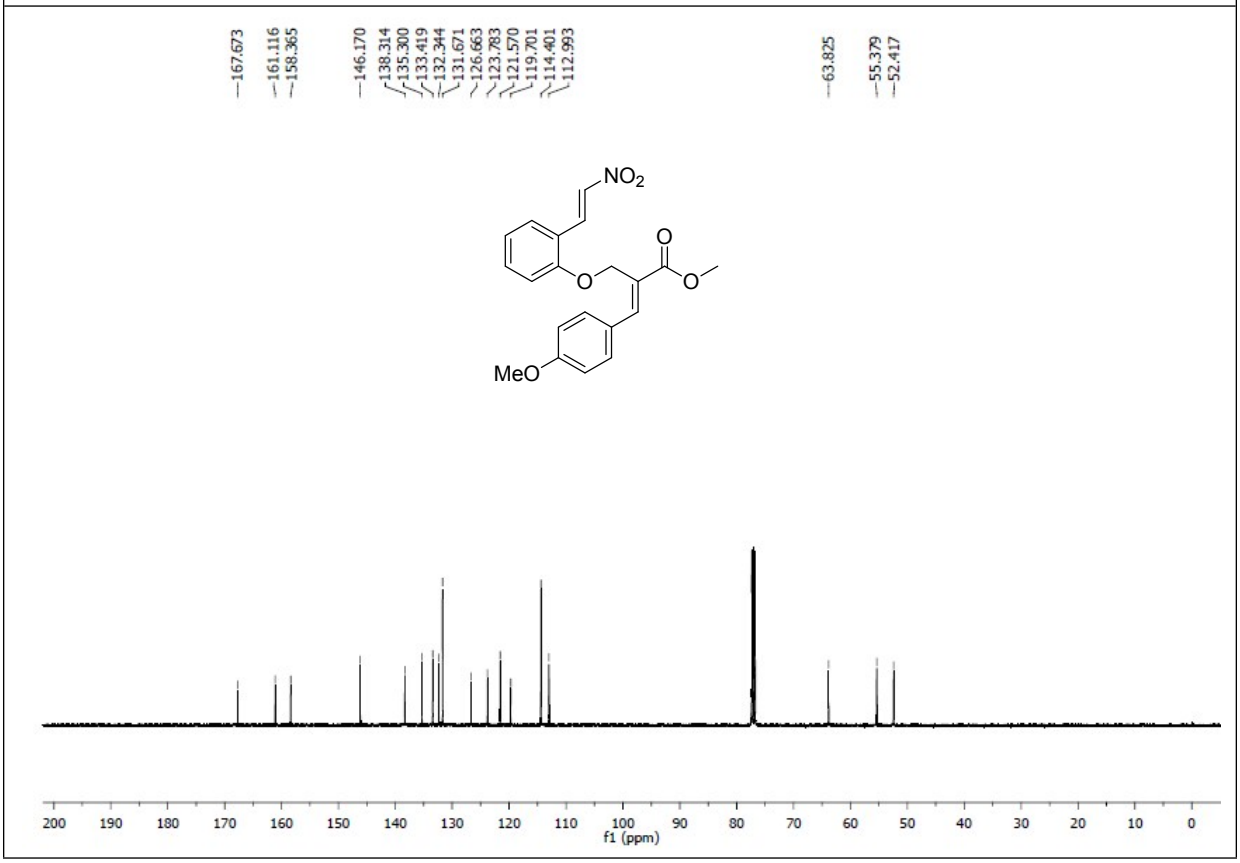
^{1}H and ^{13}C NMR Spectra of Compound (6l)



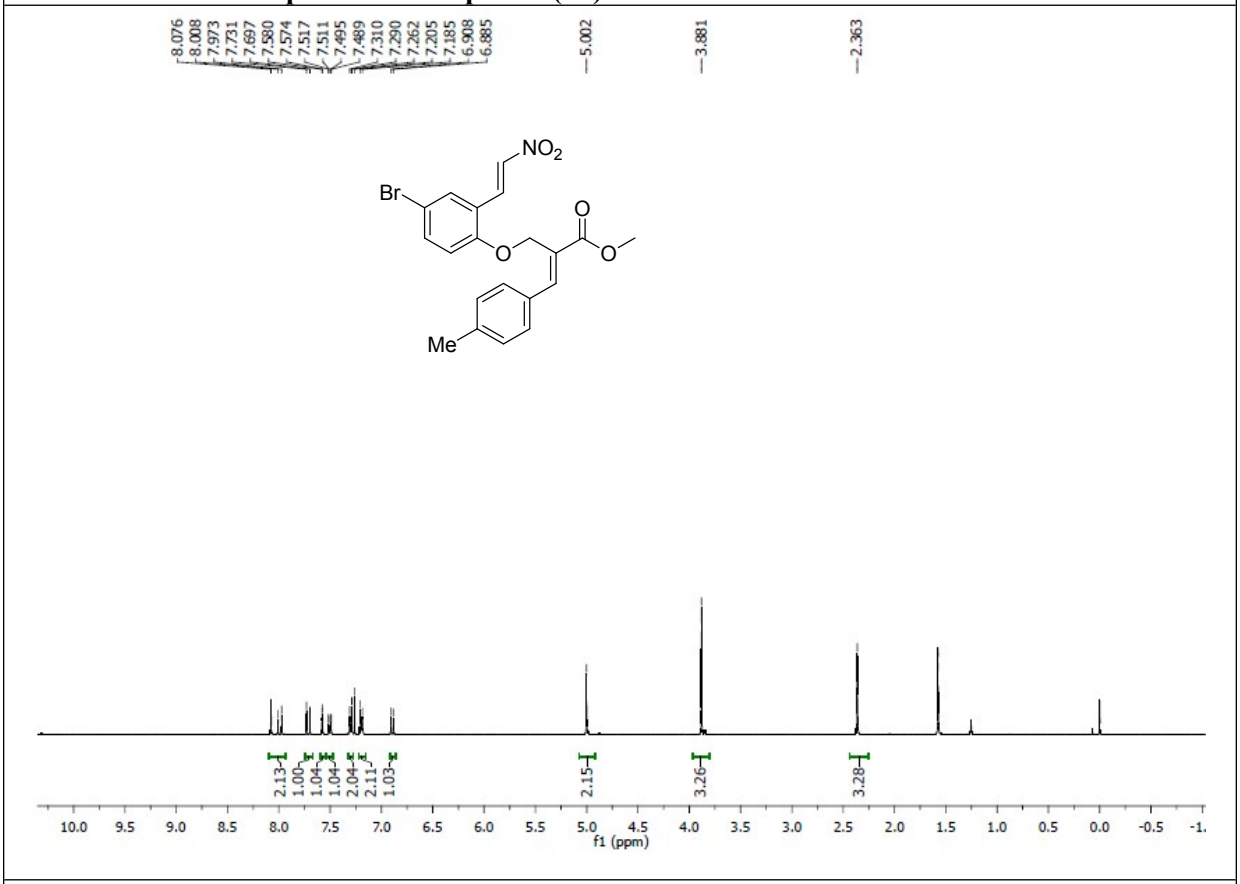


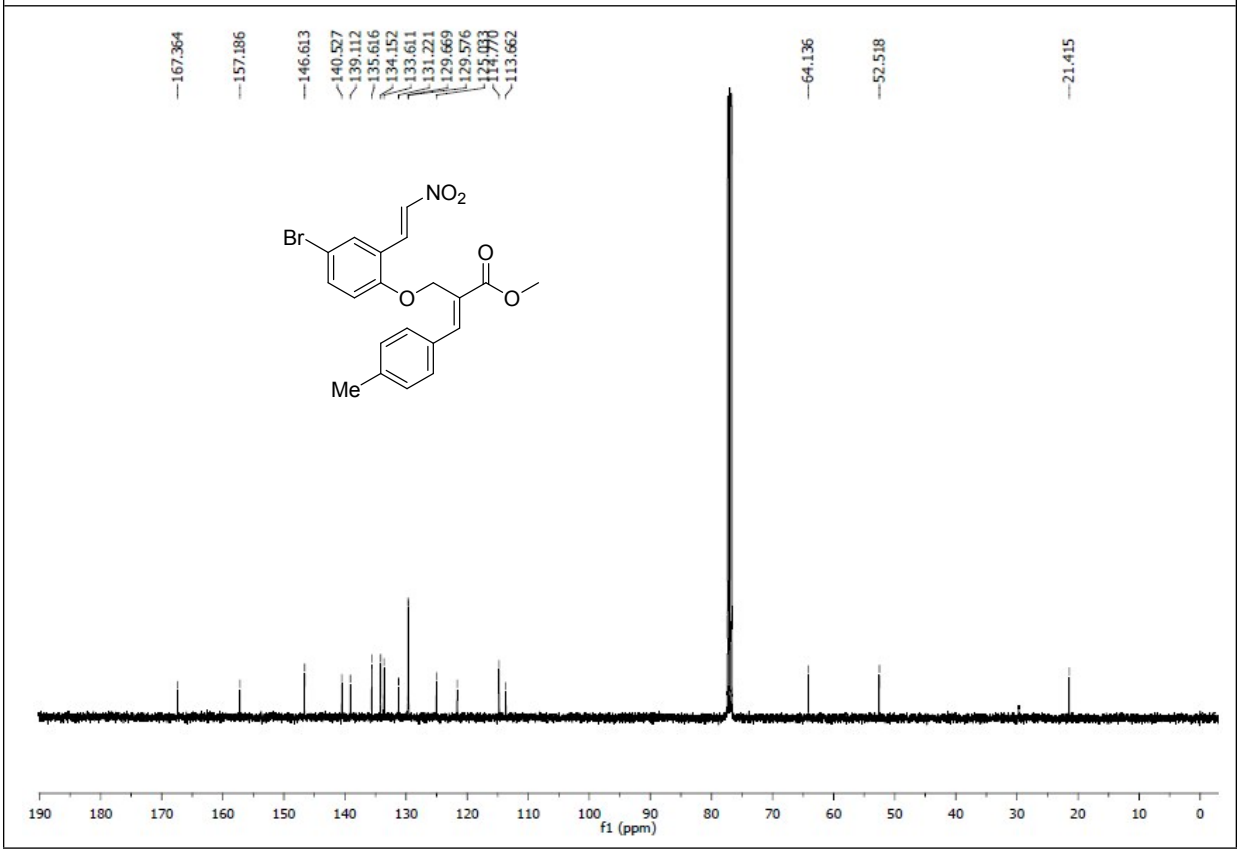
^{1}H and ^{13}C NMR Spectra of Compound (6m)



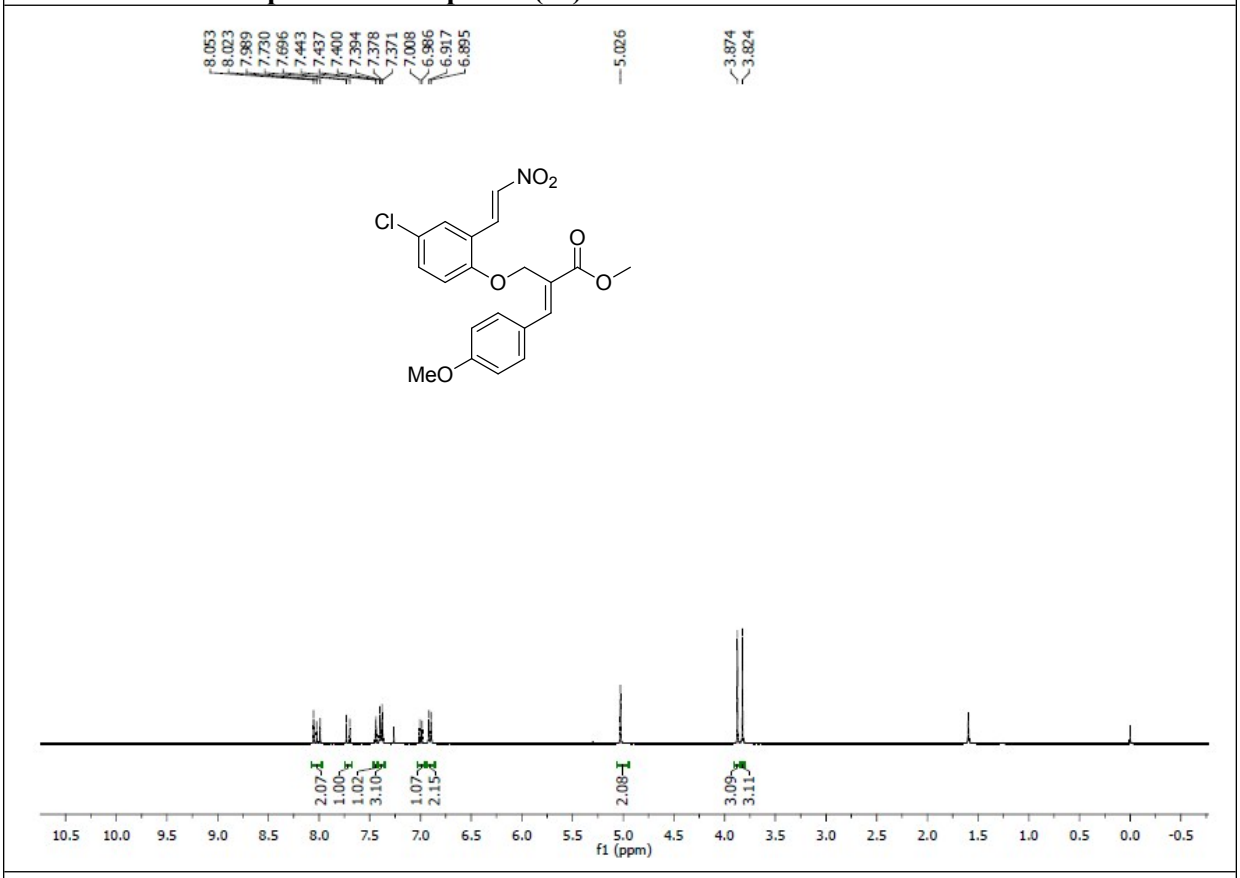


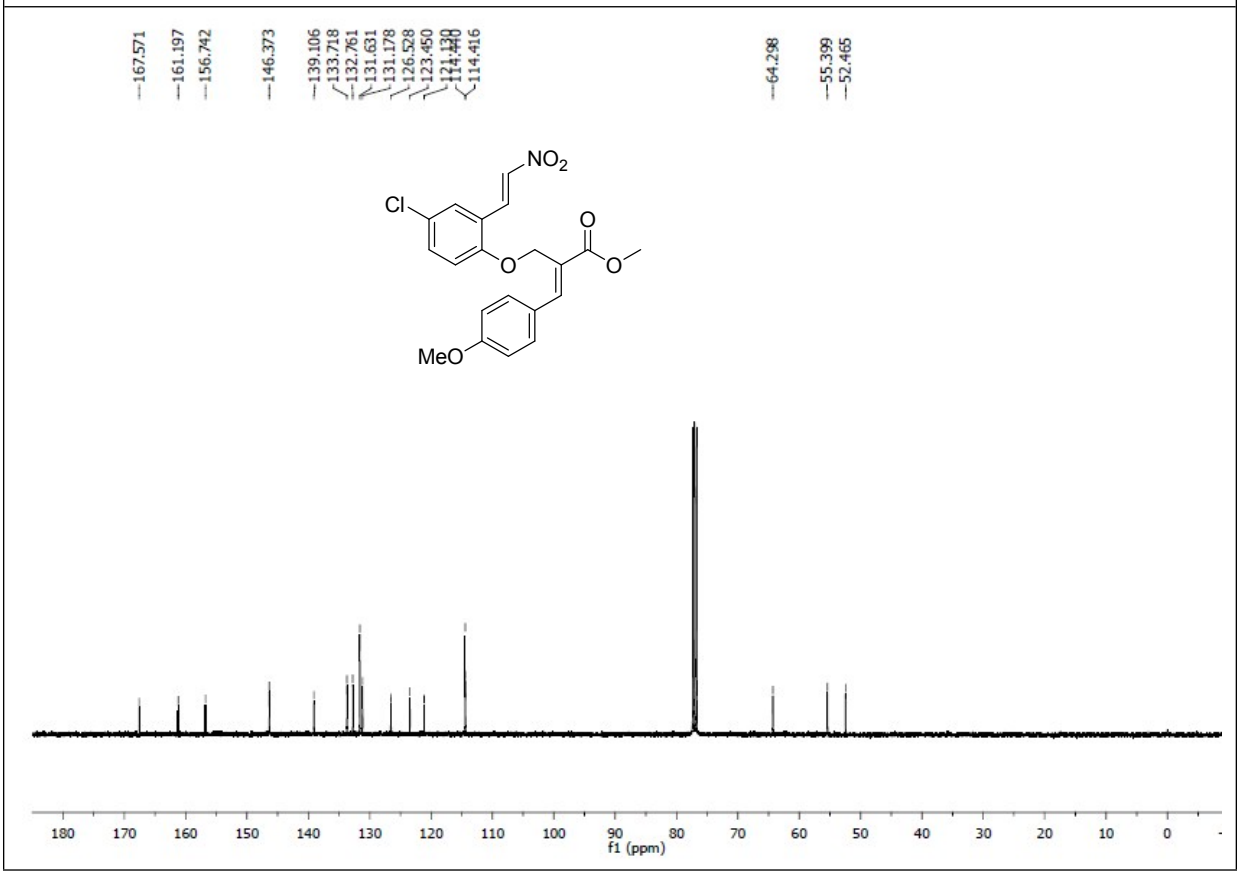
^{1}H and ^{13}C NMR Spectra of Compound (6n)



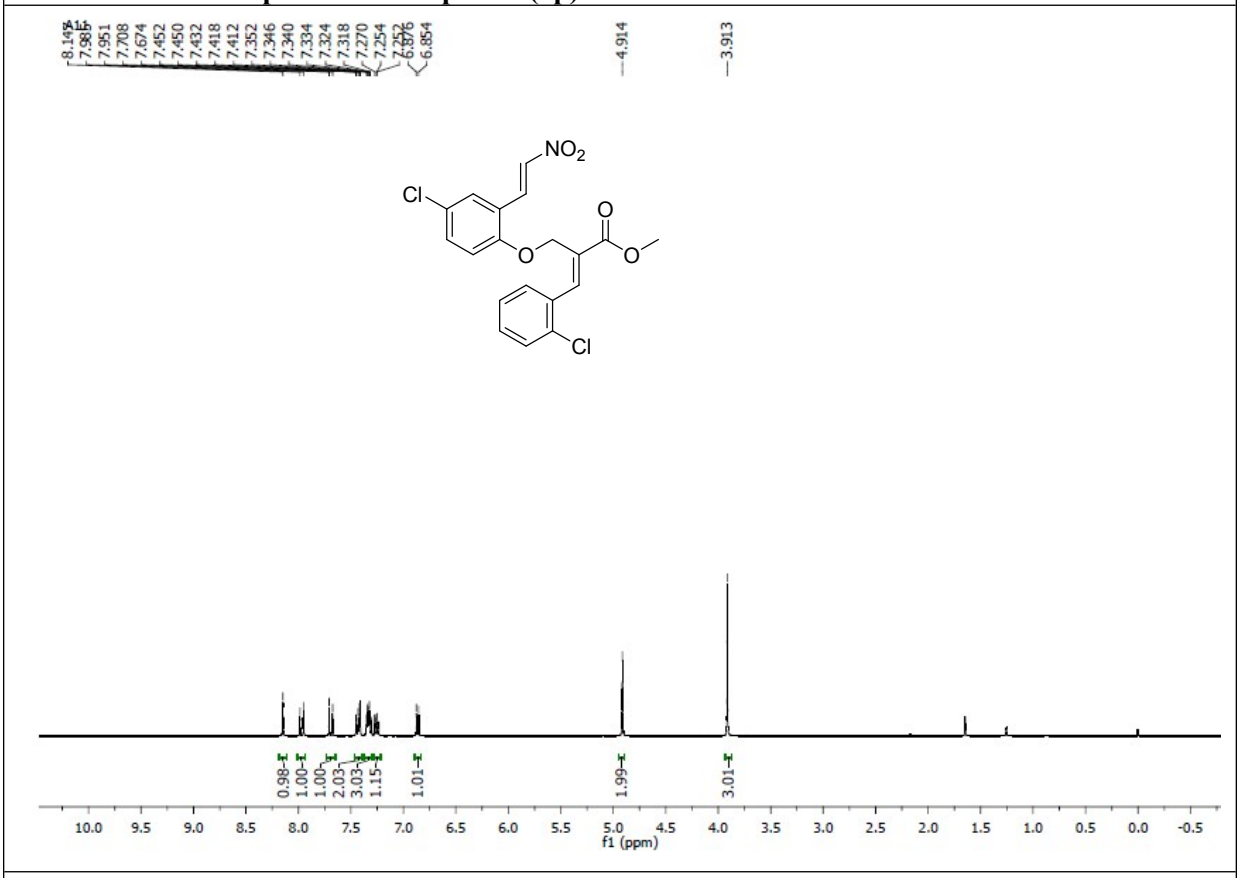


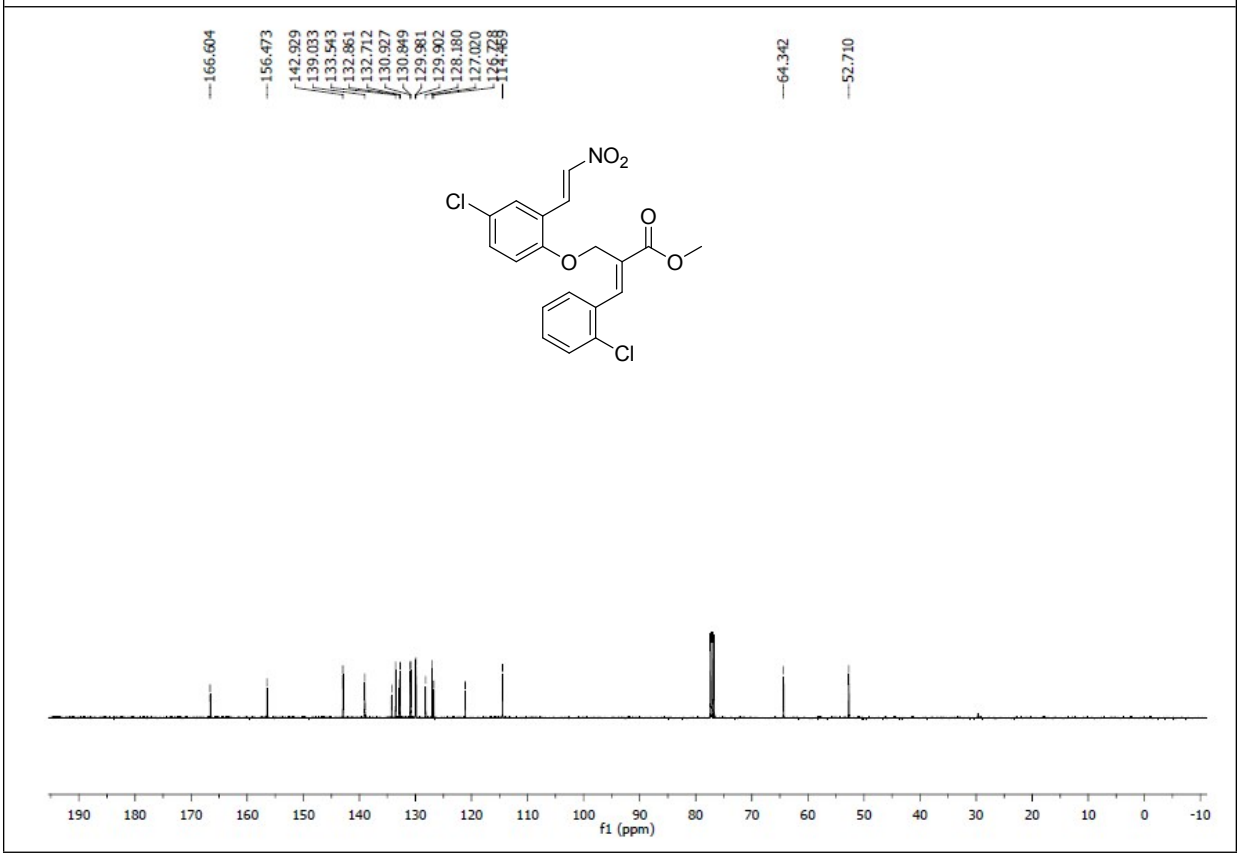
^{1}H and ^{13}C NMR Spectra of Compound (6o)



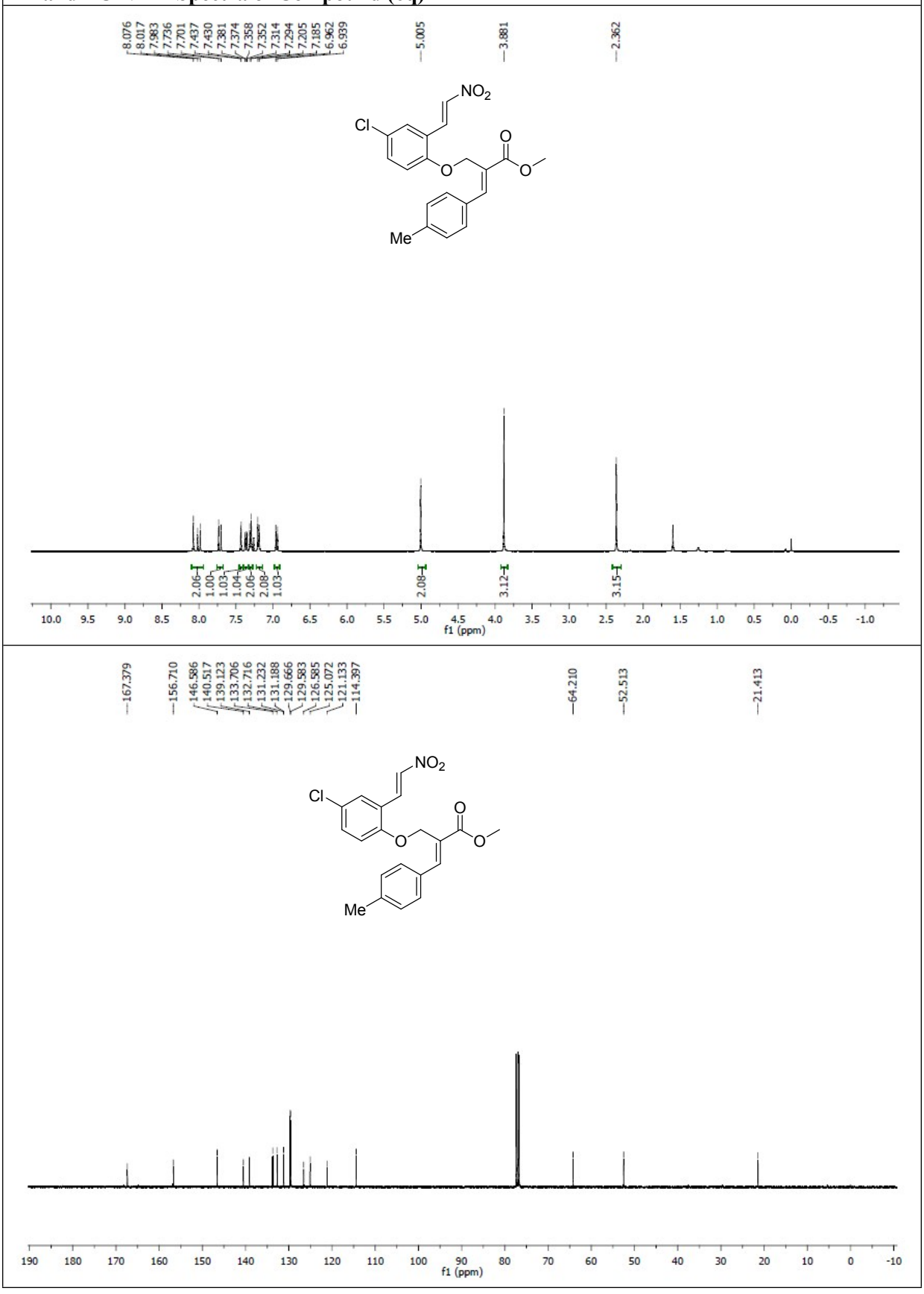


^{1}H and ^{13}C NMR Spectra of Compound (6p)

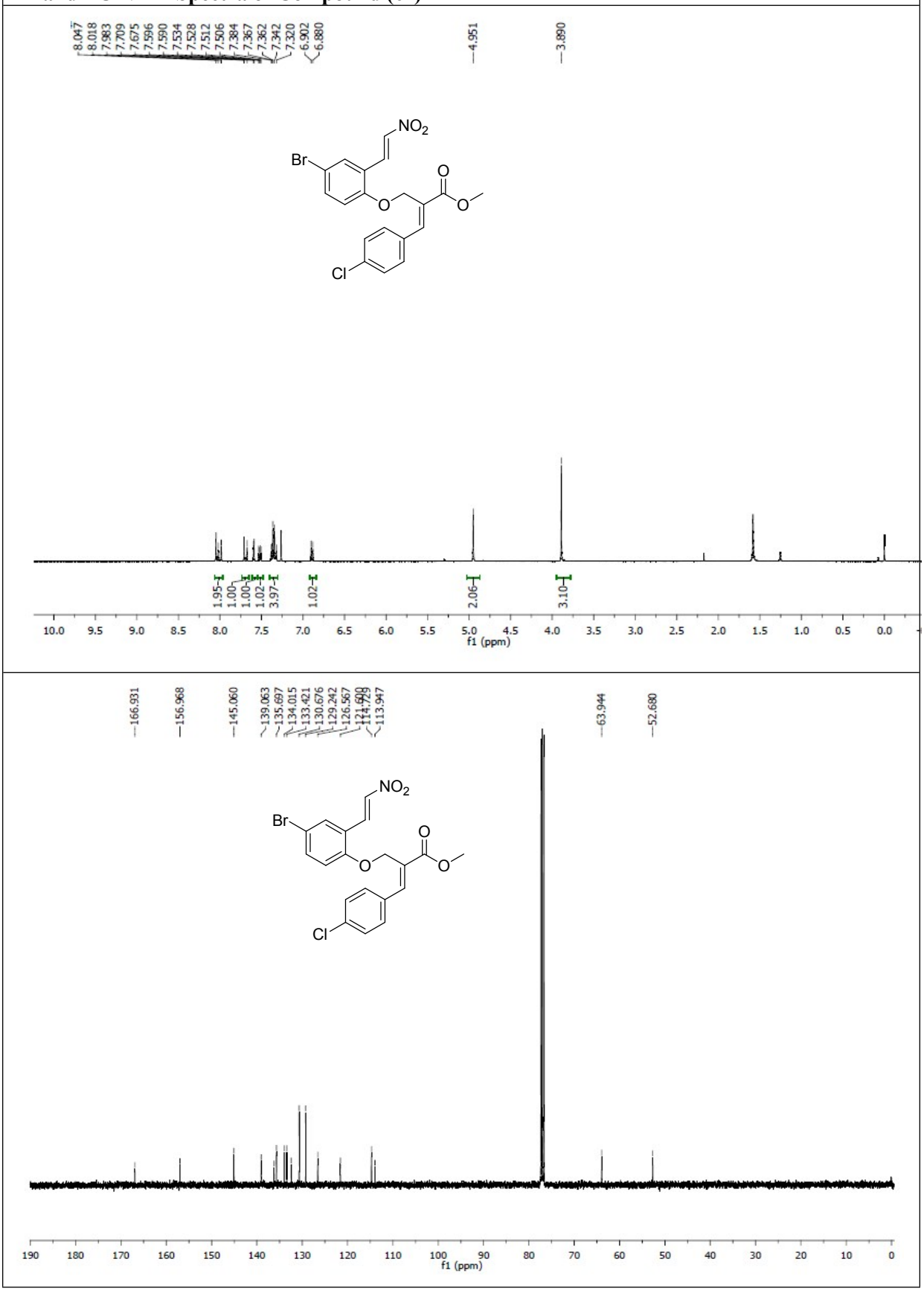




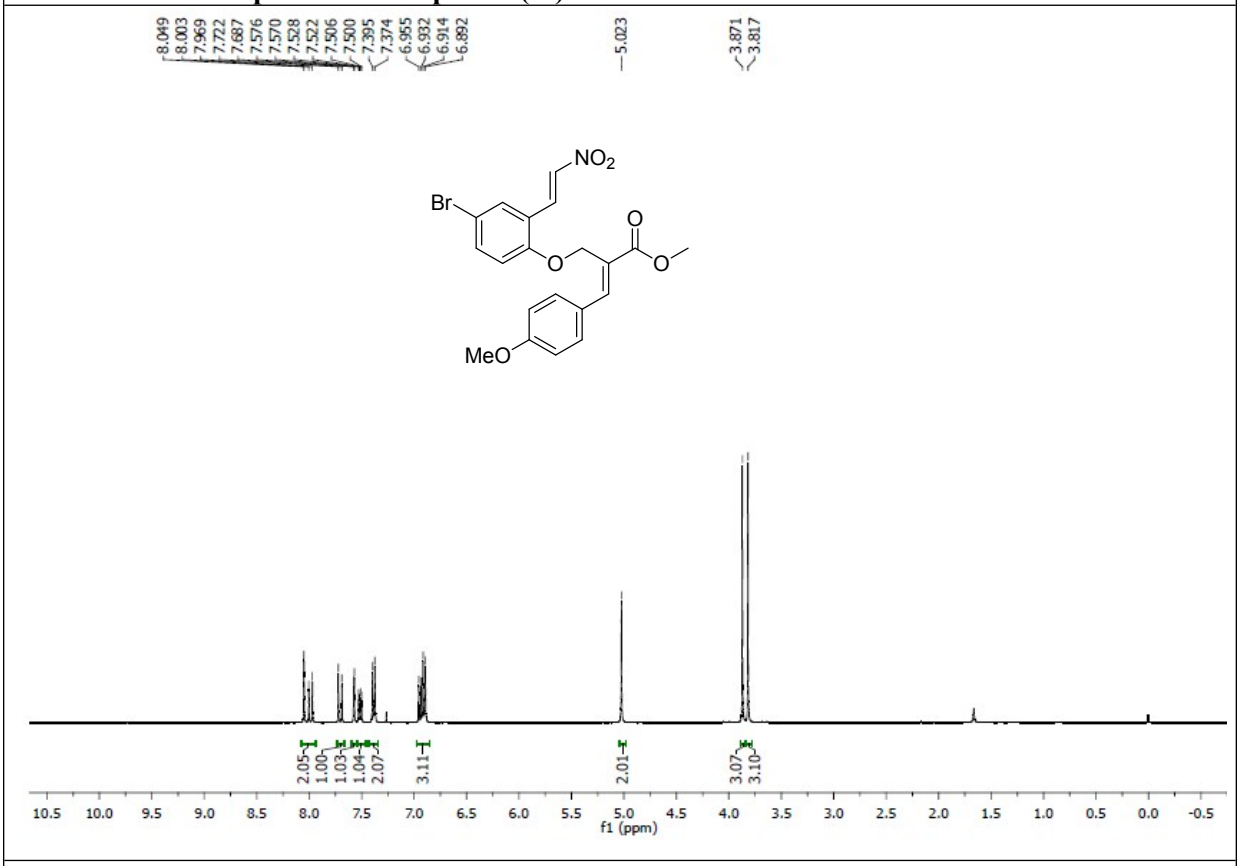
^{1}H and ^{13}C NMR Spectra of Compound (6q)

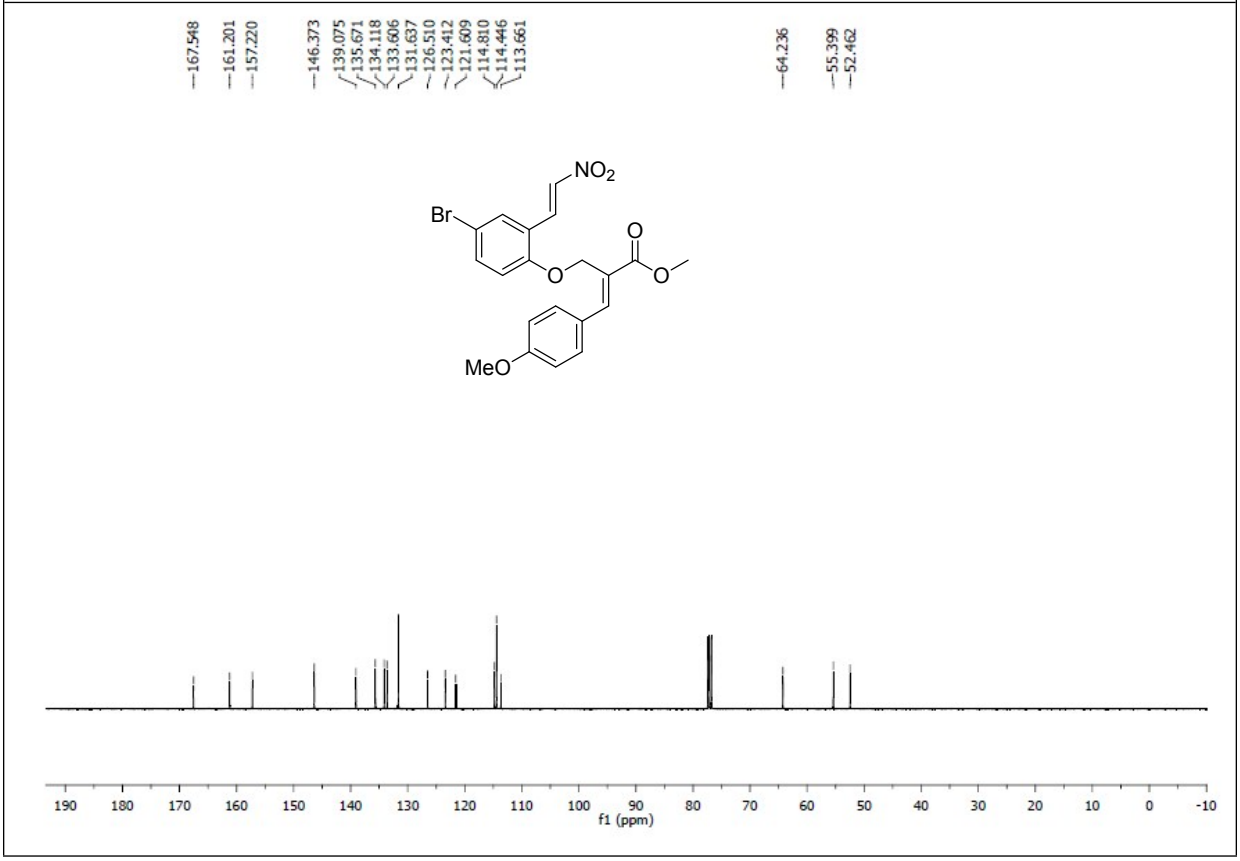


^{1}H and ^{13}C NMR Spectra of Compound (6r)



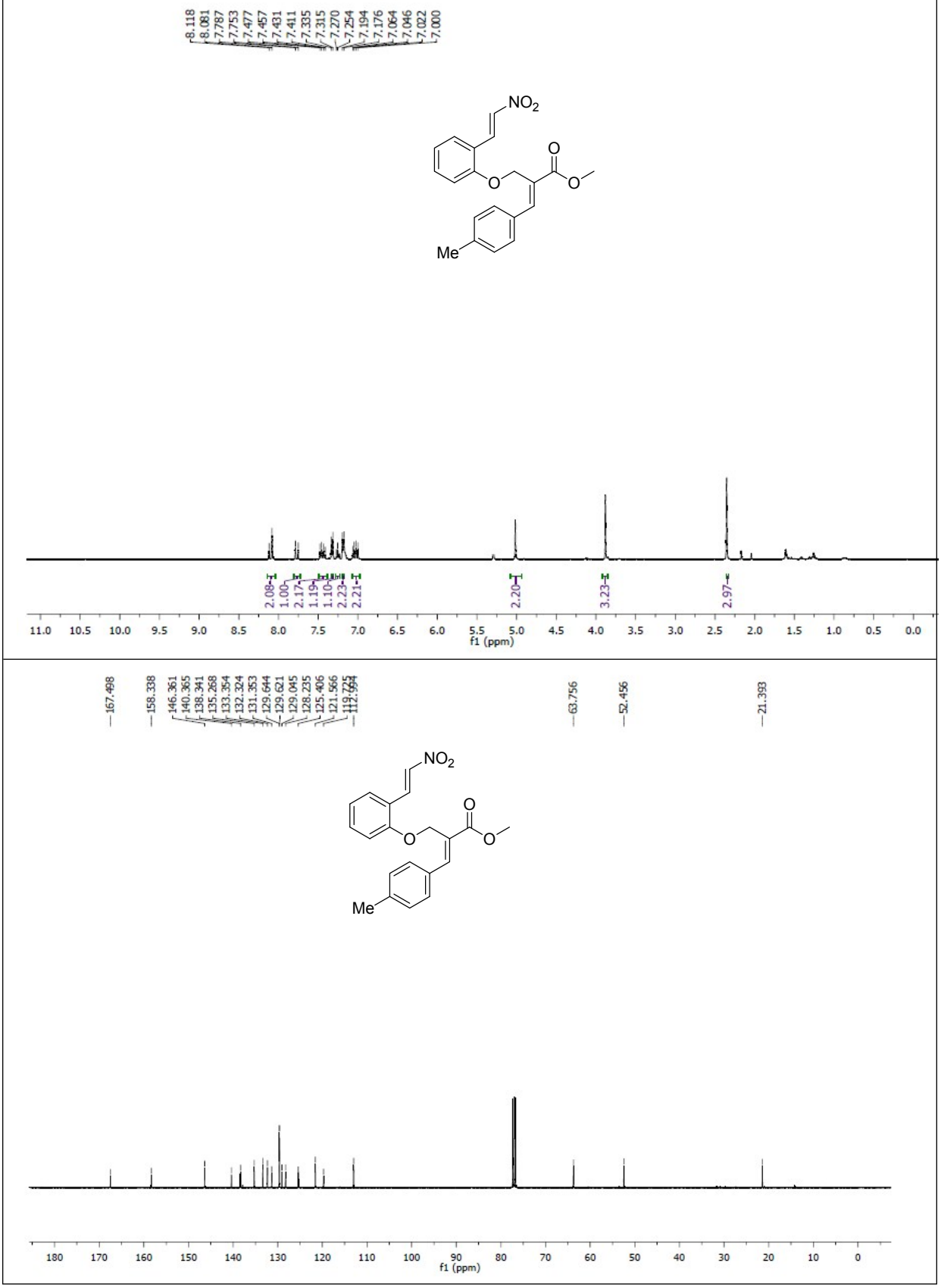
^{1}H and ^{13}C NMR Spectra of Compound (6s)



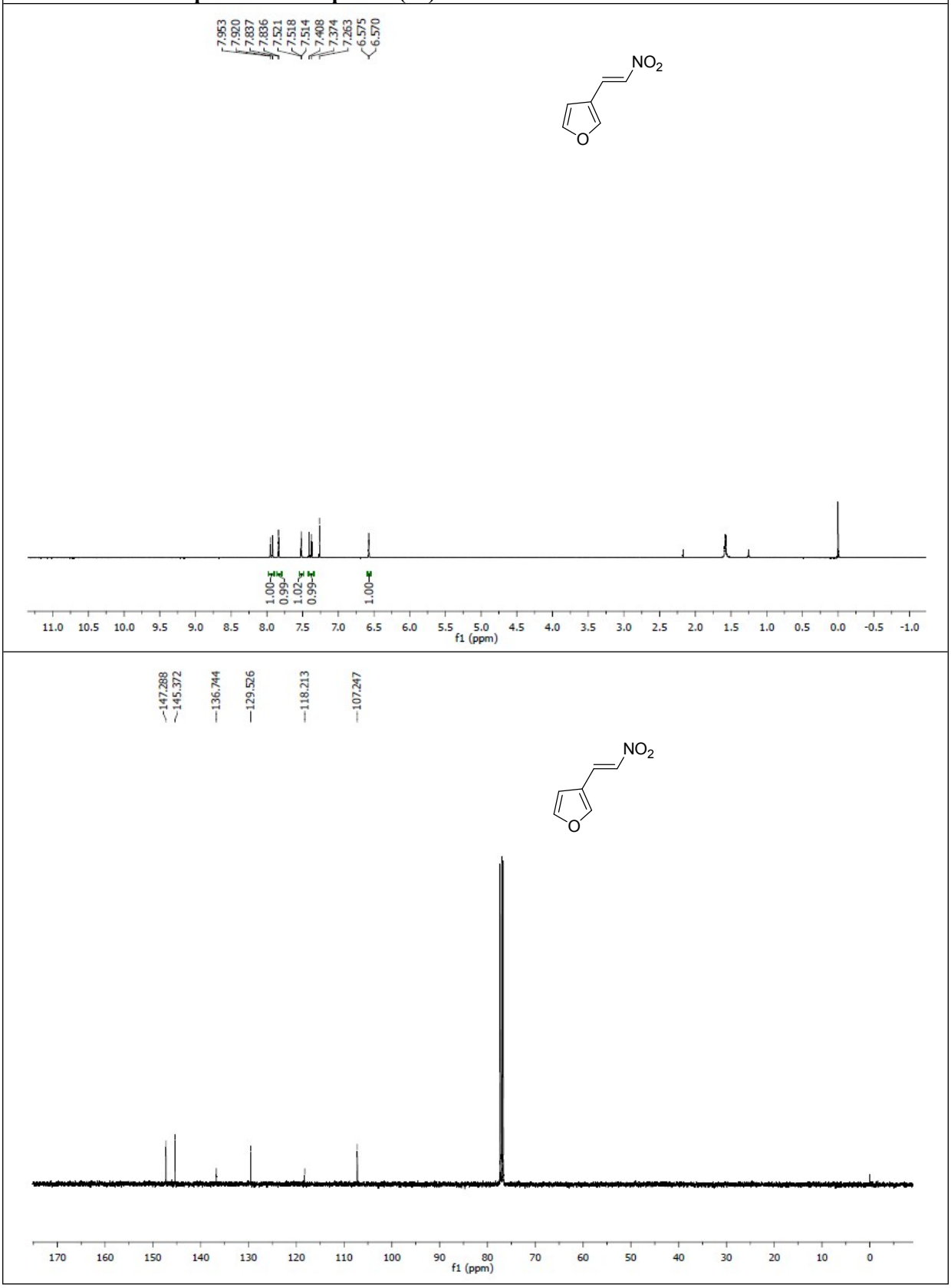


^{1}H and ^{13}C NMR Spectra of Compound (6t)

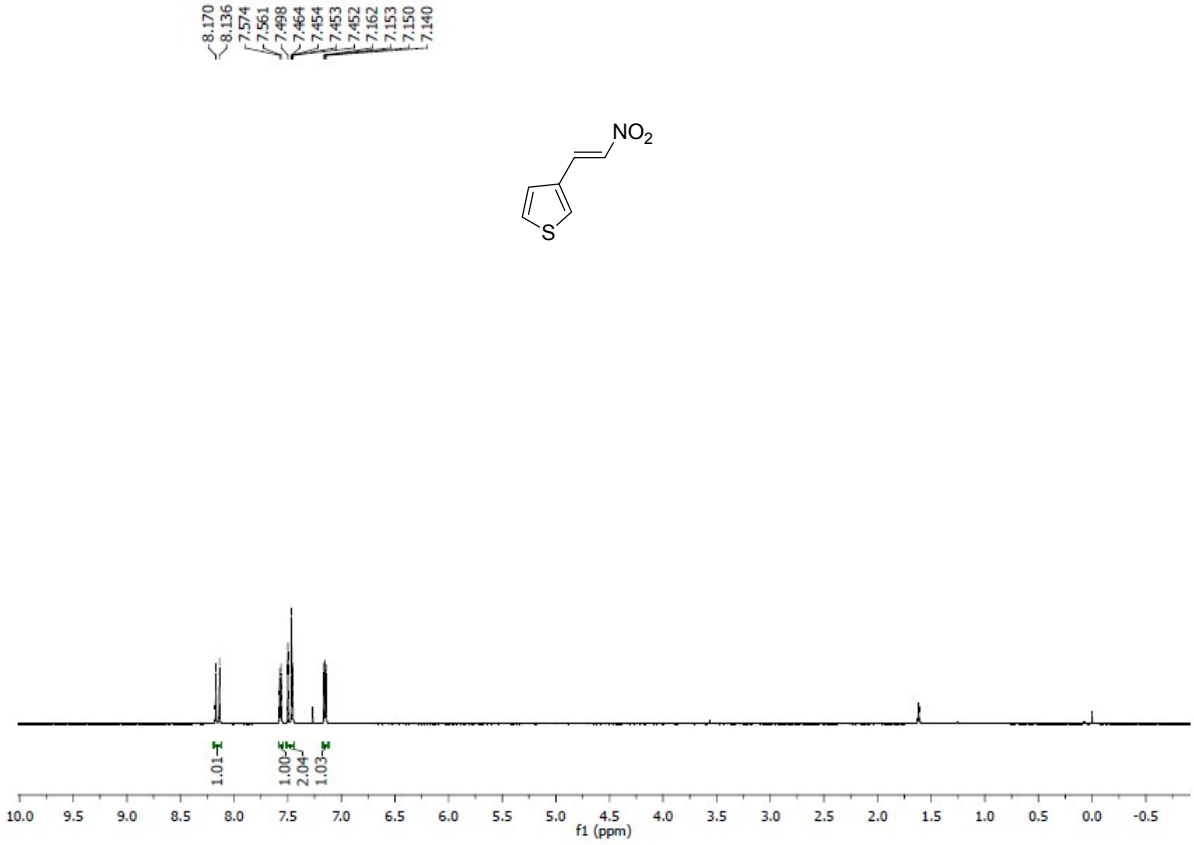
^{1}H and ^{13}C NMR Spectra of Compound (6u)

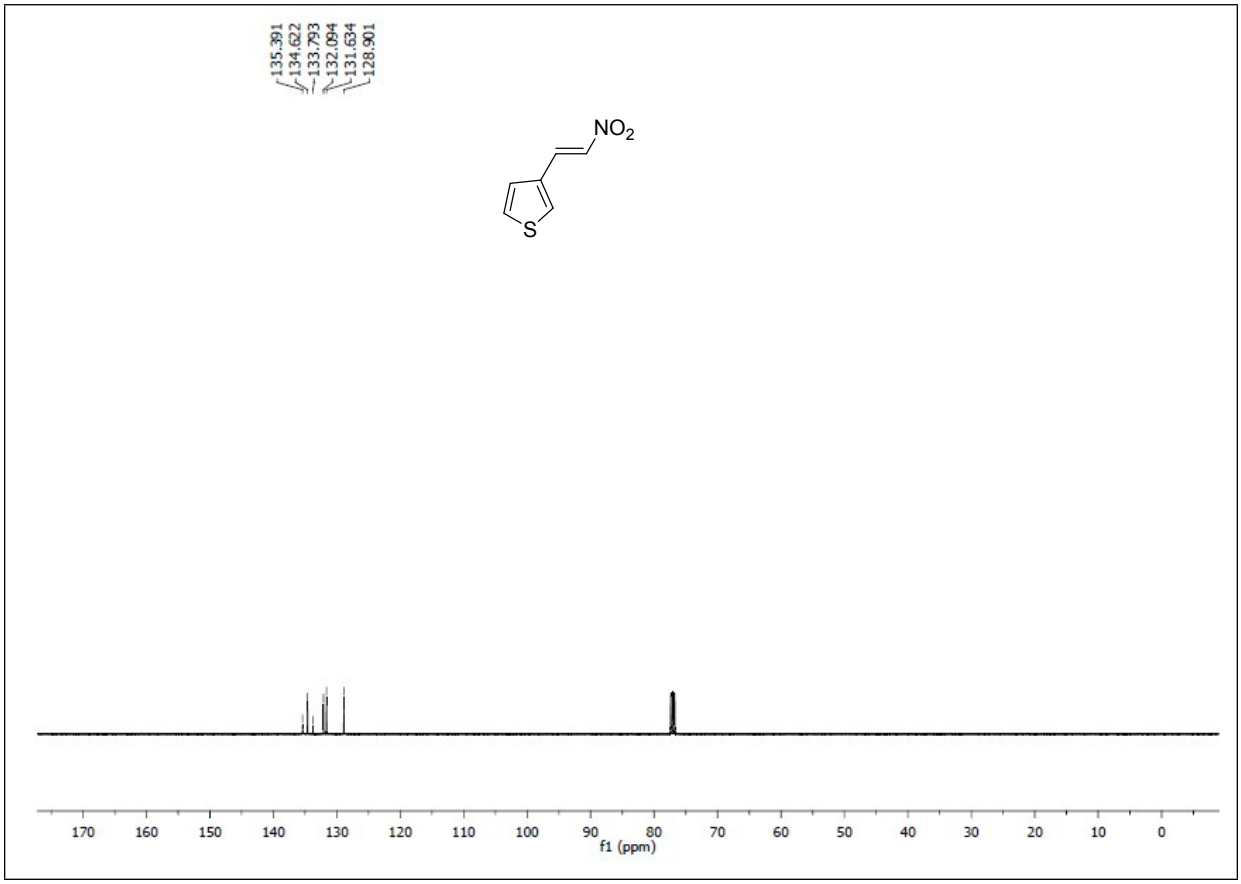


^{1}H and ^{13}C NMR Spectra of Compound (7v)

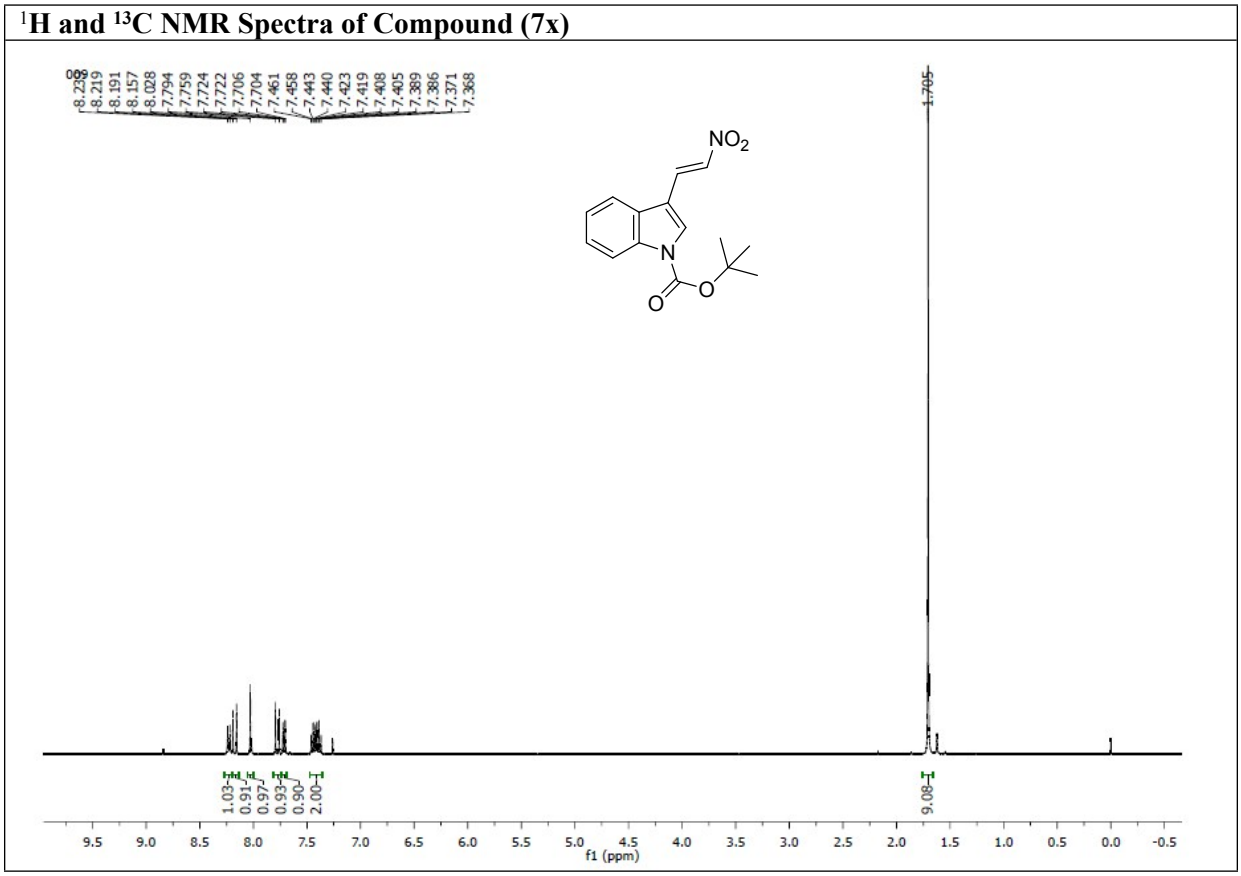


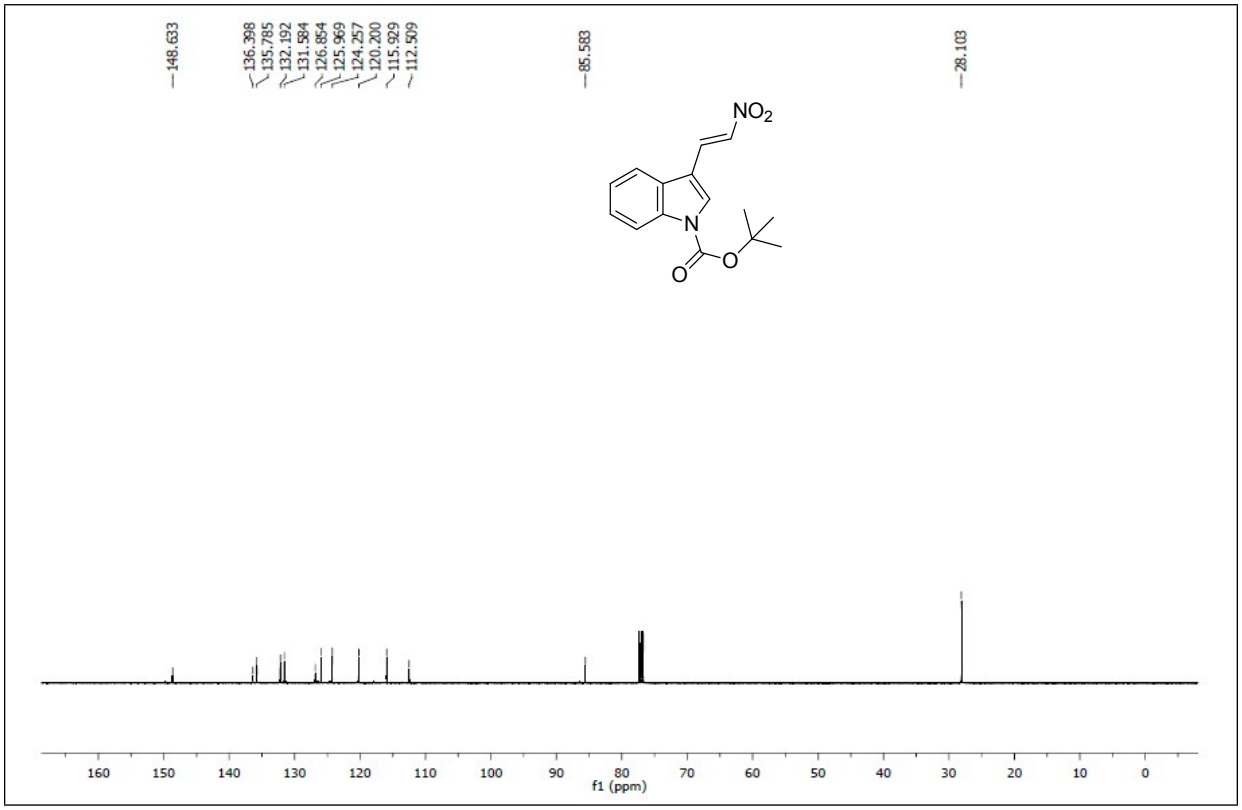
^{1}H and ^{13}C NMR Spectra of Compound (7w)





^{1}H and ^{13}C NMR Spectra of Compound (7x)

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f1 (ppm)