

Supporting Information

**Synthesis of (*E*)-Nitroolefins via Decarboxylative Nitration using *t*-Butylnitrite
(*t*-BuONO) and TEMPO**

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General Consideration:

Reagent Information. Unless otherwise stated, all reactions were carried out under air in screw cap reaction tubes. All the solvents were bought from Aldrich insure-seal bottle and were used as received. *tert*-butylnitrite and TEMPO were purchased from Aldrich. Molecular sieves (4Å; particle size 2–3 μ) were bought from Aldrich. Molecular sieves were always kept in oven in small amount before use. All the cinnamic acids were bought from Aldrich and alfaAesar For column chromatography, silica gel (60–120 mesh or 100–200 mesh) obtained from SRL Co. were used. A gradient elution using pet ether and ethyl acetate was performed, based on Merck aluminium TLC sheets (silica gel 60F₂₅₄).

Analytical Information. All isolated compound are characterized by ¹H NMR, ¹³C NMR spectroscopy and Gas chromatography mass spectra (GC–MS). Copies of the ¹H NMR, ¹³C NMR can be found in the Supporting Information. Unless otherwise stated, all Nuclear Magnetic Resonance spectra were recorded on a Bruker 400 MHz instrument. Some Nuclear Magnetic Resonance was taken on a Varian 400 MHz instrument. All ¹H NMR experiments are reported in units, parts per million (ppm), and were measured relative to the signals for residual chloroform (7.26 ppm) in the deuterated solvent, unless otherwise stated. All ¹³C NMR spectra were reported in ppm relative to deuteriochloroform (77.23 ppm), unless otherwise stated, and all were obtained with ¹H decoupling. All GC analyses were performed on a Agilent 7890A GC system with an FID detector using a J & W DB–1 column (10 m, 0.1 mm I.D.) using *n*-decane as the internal standard. All GCMS analysis was done by Agilent 7890A GC system connected with 5975C inert XL EI/CI MSD (with triple axis detector). Melting point of the compounds was determined using a Buchi B-545 melting point apparatus.

Description of Reaction Tube:

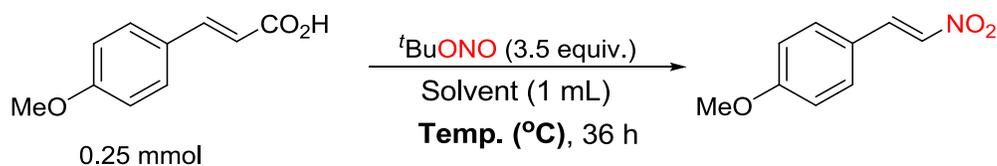


Fig. 1. Pictorial description of reaction tube for nitration of olefin: Fisherbrand Disposable Borosilicate Glass Tubes (16*125mm) with Threaded End (Fisher Scientific Order No.

1495935A) [left]; Kimble Black Phenolic Screw Thread Closures with Open Tops (Fisher Scientific Order No. 033407E) [middle]; Thermo Scientific National PTFE/Silicone Septa for Sample Screw Thread Caps (Fisher Scientific Order No. 03394A) [right].

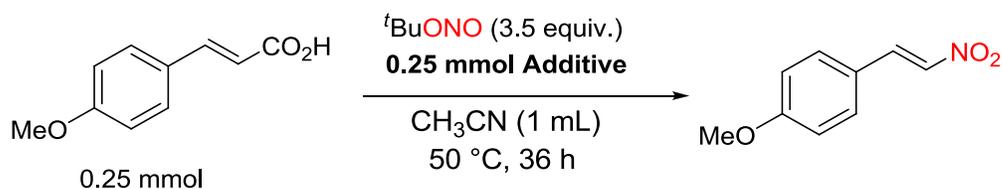
Optimization details for nitroolefin synthesis:

Table 1: Optimization by varying temperature under air



Entry	Solvent (1 mL)	Temperature ($^{\circ}\text{C}$)	GC Yield (%)
1	DCE	rt	0
2	DCE	50	17
3	DCE	60	21
4	DCE	70	17
5	CH_3CN	rt	13
6	CH_3CN	50	41
7	CH_3CN	60	18
8	CH_3CN	70	20

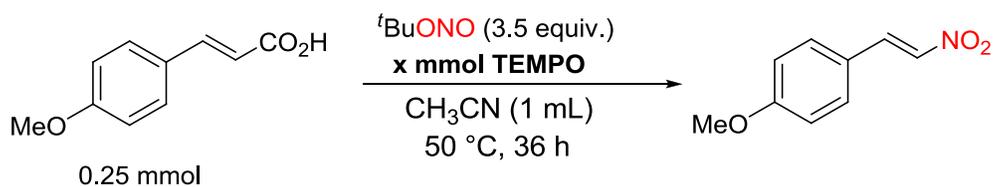
Table 2: Optimization varying different additive under air



Entry	Additive (0.25 mmol)	GC Yield (%)
1	AIBN	26

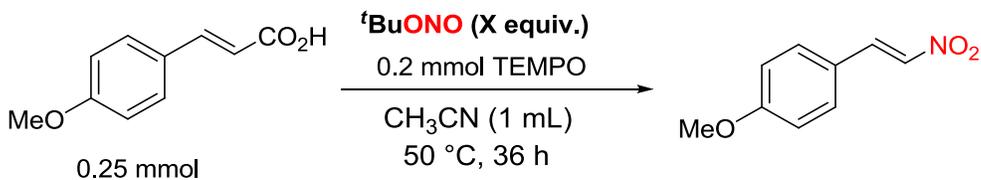
2	Benzimidazole	9
3	Benzoquinone	12
4	TEMPO	74
5	-	42

Table 3: Optimization varying amount of TEMPO under air



Entry	TEMPO (mmol)	GC Yield (%)
1	0.15	90
2	0.20	96
3	0.25	75
4	0.30	70
5	0.40	61

Table 4: Optimization of amount of nitrate source under air

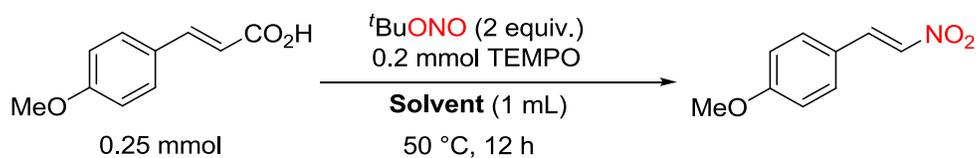


Entry	^t BuONO (equiv.)	GC Yield (%)
1	1.2	51
2	1.5	92

3	2.0	99
4	2.5	83
5	3.0	78
6	3.5	74
7	2.0	98^a

All the reactions are carried out under air. ^a under O₂ atmosphere.

Table 5: Optimization of solvent under air



Entry	Solvent (1mL)	GC Yield (%)
1	Benzene	17
2	Toluene	18
3	1,2,3-TCP	40
4	TFT	22
5	THF	18
6	Cyclohexane	16
7	Dioxane	40
8	DCE	60
9	MeCN	99
10	ⁿ BuCN	72
11	Vinyl nitrile	0

Table 6: Optimization of time under air

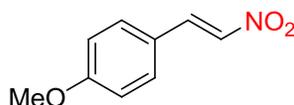


Entry	Time (h)	GC Yield (%)
1	3	95/99
2	4	92
3	6	95
2	12	95
3	18	95
4	24	88
5	36	86

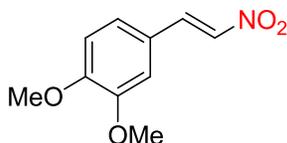
General Procedure for nitration of Cinnamic acids with $t\text{BuONO}$ and TEMPO under air using CH_3CN as the solvent.

An oven-dried screw cap test tube was charged with a magnetic stir-bar, TEMPO (0.2 mmol, 32 mg) and cinnamic acid derivative (0.25 mmol) under air atmosphere. $t\text{BuONO}$ (0.5 mmol, 60 μL) and the solvent (MeCN, 1 mL) were added by microliter syringe and laboratory syringe respectively. The reaction tube was placed in a preheated oil bath at $50\text{ }^\circ\text{C}$ and the reaction mixture was stirred vigorously for 3-24h. Then the reaction mixture was cooled to room temperature. The reaction mixture was filtered through a celite bed filter. Celite bed was washed with ethyl acetate as the washing solvent. Finally organic extract was concentrated and was purified by column chromatography using silica gel column (60-120/100-200 mesh size) and petroleum-ether / ethyl acetate as the eluent.

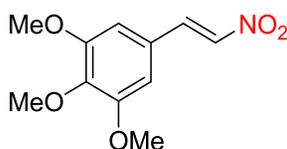
Characterization Data of Synthesized Nitroolefins:



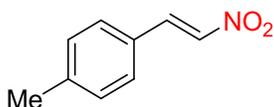
(E)-1-methoxy-2-(2-nitrovinyl) benzene (Table 2, entry 2a).¹ Nitration was done by the general procedure with (*E*)-3-(4-methoxyphenyl) acrylic acid (0.25mmol, 45 mg) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/ petroleum ether (2:98 v/v); crystalline (needle shape) yellow solid; isolated yield: 95% (43 mg). ¹H NMR (400 MHz, Chloroform-d) δ 3.86 (s, 3H), 6.92 – 6.97 (d, *J* = 8.8 Hz, 2H), 7.47 – 7.53 (m, 3H), 7.92 – 7.98 (d, *J* = 13.6 Hz, 1H). ¹³C NMR (101 MHz, Chloroform-d) δ 55.59, 114.97, 122.54, 131.28, 135.00, 139.13, 163.02. GC-MS (*m/z*): 179.1 [M]⁺. M. Pt. 89-92 °C (CHCl₃); Lit :86°C (EtOH)¹⁰.



(E)-1,2-dimethoxy-4-(2-nitrovinyl)benzene (Table 2, entry 2b).⁷ Nitration was done by the general procedure with (*E*)-3-(3,4-dimethoxyphenyl) acrylic acid (0.25mmol, 52 mg) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/ petroleum ether (2:98 v/v); crystalline (plate shape) yellow solid; isolated yield: 87% (45.5 mg). ¹H NMR (400 MHz, Chloroform-d) δ 3.93 (s, 3H), 3.95 (s, 3H), 6.87 – 6.97 (d, *J* = 8.3 Hz, 1H), 6.99 – 7.04 (d, *J* = 2.0 Hz, 1H), 7.14 – 7.20 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.48 – 7.57 (d, *J* = 13.6 Hz, 1H), 7.92 – 8.00 (d, *J* = 13.6 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 56.21, 56.30, 110.40, 111.52, 111.53, 124.83, 124.85, 135.35, 135.36, 139.52. GC-MS (*m/z*): 209.1 [3.88 (s, 3H), M]⁺. M. Pt. 138 °C (CHCl₃); Lit: 144.5 °C (EtOH)¹¹.

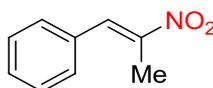


(E)-1,2,3-trimethoxy-5-(2-nitrovinyl)benzene (Table 2, entry 2c).¹ Nitration was done by the general procedure with (*E*)-3-(3,4,5-trimethoxyphenyl) acrylic acid (0.25mmol, 60mg) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/ petroleum ether (5:95 v/v); yellow solid powder; isolated yield: 80% (48 mg). ¹H NMR (400 MHz, Chloroform-d) δ 3.89 (s, 3H), 3.90 (s, 6H), 6.74 – 6.78 (s, 2H), 7.51 – 7.57 (d, *J* = 13.6 Hz, 1H), 7.90 – 7.95 (d, *J* = 13.6 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 56.44, 61.24, 100.15, 106.55, 125.47, 136.53, 139.51, 141.87, 153.83. GC-MS (*m/z*): 239.1 [M]⁺. M. Pt. 121 °C (CHCl₃).

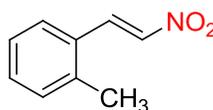


(E)-1-methyl-4-(2-nitrovinyl) benzene (Table 2, entry 2d).² Nitration was done by the general procedure with *p*-methylcinnamic acid (0.25mmol, 41 mg) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120).

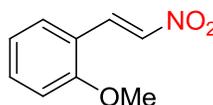
Eluent: ethyl acetate/ petroleum ether (1:99 v/v); yellow solid; isolated yield: 77% (31 mg). $^1\text{H NMR}$ (400 MHz, Chloroform-d) 2.43(s, 3H), 7.25 – 7.30 (m, 2H), 7.44 – 7.48 (m, 2H), 7.55 – 7.61 (d, $J = 13.7$ Hz, 1H), 7.97 – 8.03 (d, $J = 13.6$ Hz, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 21.84, 127.41, 129.36, 130.30, 136.41, 139.35, 143.29. GC-MS (m/z): 163.10 $[\text{M}]^+$. M. Pt. 106 °C (CHCl_3); Lit : 108 °C¹²



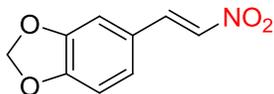
(Z)-2-(2-nitroprop-1-enyl) benzene (Table 2, entry 2e).⁴ Nitration was done by the general procedure with (*E*)-2-methyl-3-phenylacrylic acid (0.25mmol, 41 mg) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/ petroleum ether (1:99 v/v); yellow liquid; isolated yield: 72% (29 mg)[E:Z = 4:1]. $^1\text{H NMR}$ (400 MHz, Chloroform-d) δ 2.45 (d, $J = 1.1$ Hz, 3H), 7.39 – 7.49 (m, 5H), 8.08 – 8.11 (m, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 14.24, 129.09, 130.11, 130.15, 132.59, 133.76, 147.92. GC-MS (m/z): 163.08 $[\text{M}]^+$.



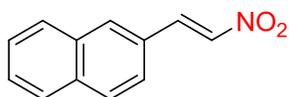
(E)-1-methyl-2-(2-nitrovinyl) benzene (Table 2, entry 2f).⁶ Nitration was done by the general procedure with *o*-methylcinnamic acid (0.25mmol, 41 mg) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/ petroleum ether (1:99 v/v); light yellow liquid; isolated yield: 71% (29 mg). $^1\text{H NMR}$ (400 MHz, Chloroform-d) δ 2.48 (s, 3H), 7.23 – 7.32 (m, 2H), 7.36 – 7.43 (dd, $J = 7.5, 1.4$ Hz, 1H), 7.46 – 7.57 (d, $J = 13.5$ Hz, 1H), 8.26 – 8.35 (d, $J = 13.6$ Hz, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 20.14, 126.95, 127.54, 129.11, 131.57, 132.13, 136.97, 137.80, 139.42. GC-MS (m/z): 163.10 $[\text{M}]^+$.



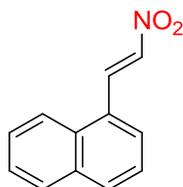
(E)-1-methoxy-2-(2-nitrovinyl) benzene (Table 2, entry 2g).² Nitration was done by the general procedure with *o*-methoxycinnamic acid (0.25mmol, 45 mg) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/ petroleum ether (3:97 v/v); deep yellow solid; isolated yield: 75% (34 mg). $^1\text{H NMR}$ (400 MHz, Chloroform-d) δ 3.94(s, 3H), 6.95 – 7.04 (m, 2H), 7.42 – 7.48 (m, 2H), 7.85 – 7.90 (d, $J = 13.6$ Hz, 1H), 8.10 – 8.15 (d, $J = 13.6$ Hz, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 55.79, 111.51, 119.25, 121.26, 132.65, 133.64, 135.69, 138.40, 159.65. GC-MS (m/z): 179.1 $[\text{M}]^+$. M. Pt. 84 °C (CHCl_3); Lit: 86 °C¹³.



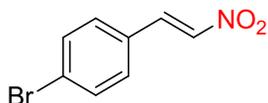
(E)-5-(2-nitrovinyl) benzo[d][1,3] dioxole (Table 2, entry 2h).¹ Nitration was done by the general procedure with (*E*)-3-(benzo[d][1,3]dioxol-5-yl) acrylic acid (0.25 mmol, 48 mg) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/ petroleum ether (1:99 v/v); orange yellow solid; isolated yield: 85% (41mg). ¹H NMR (400 MHz, Chloroform-d) δ 6.06 (s, 2H), 6.79 – 7.12 (m, 3H), 7.42 – 7.51 (d, *J* = 13.6 Hz, 1H), 7.87 – 7.96 (d, *J* = 13.6 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 102.27, 107.16, 109.26, 124.36, 126.88, 135.55, 139.33, 148.95, 151.58. GC-MS (m/z): 193.0 [M]⁺. M. Pt. 139 °C (CHCl₃); Lit: 144.5 °C (MeOH)¹⁴.



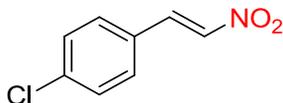
(E)-2-(2-nitrovinyl) naphthalene (Table 2, entry 2i).³ Nitration was done by the general procedure with (*E*)-3-(naphthalen-2-yl)acrylic acid (0.25 mmol, 49.5 mg) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/ petroleum ether (1:99 v/v); crystalline (needle shape); isolated yield: 70% (35 mg). ¹H NMR (400 MHz, Chloroform-d) δ 7.53 – 7.67 (m, 3H), 7.64 – 7.77 (d, *J* = 13.6 Hz, 1H), 7.84 – 7.97 (m, 3H), 7.97 – 8.09 (m, 1H), 8.12 – 8.24 (d, *J* = 13.7 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 76.91, 77.23, 77.55, 123.50, 127.49, 127.72, 128.15, 128.60, 129.04, 129.57, 132.54, 133.33, 135.10, 137.32, 139.48. m. p. 128–130 °C. M. Pt. 130 °C (CHCl₃); Lit: 132 °C (MeOH)¹⁴.



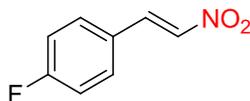
(E)-1-(2-nitrovinyl) naphthalene (Table 2, entry 2j).¹ Nitration was done by the general procedure with (*E*)-3-(naphthalen-1-yl)acrylic acid (0.25 mmol, 50 mg) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/ petroleum ether (1:99 v/v); yellow solid (plate shape); isolated yield: 70% (35 mg). ¹H NMR (400 MHz, Chloroform-d) δ 7.47 – 7.54 (dd, *J* = 8.2, 7.3 Hz, 1H), 7.55 – 7.67 (m, 3H), 7.70 – 7.76 (m, 1H), 7.88 – 7.95 (m, 1H), 7.96 – 8.04 (d, *J* = 8.2 Hz, 1H), 8.06 – 8.15 (m, 1H), 8.75 – 8.86 (d, *J* = 13.4 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 123.09, 125.55, 126.53, 126.94, 127.89, 129.21, 131.69, 132.72, 133.89, 136.23, 138.58. M. Pt. 84 °C (CHCl₃); Lit: 86 °C¹⁵.



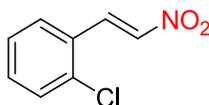
(E)-1-bromo-4-(2-nitrovinyl)benzene (Table 2, entry 2k).⁵ Nitration was done by the general procedure with *p*-bromocinnamic acid (0.25 mmol, 56.5 mg) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/ petroleum ether (1:99 v/v); crystalline (needle shape) yellow solid; isolated yield: 46% (26mg). ¹H NMR (400 MHz, Chloroform-d) δ 7.40 – 7.41 (d, *J* = 2.0 Hz, 1H), 7.42 – 7.43 (d, *J* = 2.0 Hz, 1H), 7.57 – 7.62 (m, 3H), 7.92 – 7.97 (d, *J* = 13.7 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 127.01, 129.12, 130.60, 132.95, 137.64, 138.01. GC-MS (*m/z*): 226.9 [M]⁺. M. Pt. 141 °C (CHCl₃); Lit :147°C¹⁶.



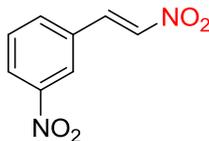
(E)-1-chloro-4-(2-nitrovinyl) benzene (Table 2, entry 2l).⁸ Nitration was done by general procedure with (*E*)-3-(4-chlorophenyl) acrylic (0.25 mmol, 45.5 mg) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/ petroleum ether (2:98 v/v); crystalline (needle shape) light yellowish solid; isolated yield: 44% (20 mg). ¹H NMR (400 MHz, Chloroform-d) δ 7.41 – 7.46 (m, 2H), 7.47 – 7.51 (m, 2H), 7.54 – 7.59 (d, *J* = 13.7 Hz, 1H), 7.94 – 7.99 (d, *J* = 13.7 Hz, 1H). ¹³C NMR (101 MHz, Chloroform-d) δ 128.65, 129.87, 130.42, 137.53, 137.85, 138.43, 77.51, 77.20, 76.88. GC-MS (*m/z*): 183.1 [M]⁺. M. Pt. 112 °C (CHCl₃); Lit: 113 °C¹⁷.



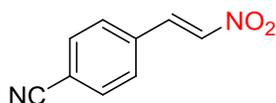
(E)-1-fluoro-4-(2-nitrovinyl) benzene (Table 2, entry 2m).⁸ Nitration was done by general procedure A with (*E*)-3-(4-fluorophenyl) acrylic (0.25 mmol, 41.5 mg) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/ petroleum ether (2:98 v/v); light yellow solid; isolated yield: 43% (18 mg). ¹H NMR (400 MHz, Chloroform-d) δ 7.09 – 7.21 (m, 2H), 7.51 – 7.55 (m, 1H), 7.55 – 7.60 (m, 2H), 7.88 – 8.22 (d, *J* = 13.7 Hz, 1H). ¹³C NMR (101 MHz, Chloroform-d) δ 116.90, 117.12, 131.53, 137.04, 138.04, 166.41. GC-MS (*m/z*): 167.1 [M]⁺. M. Pt. 98 °C (CHCl₃); Lit : 101 °C (Ethyl acetate)¹⁸.



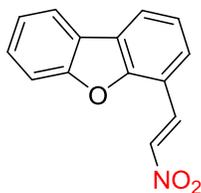
(E)-1-chloro-2-(2-nitrovinyl) benzene (Table 2, entry 2n).⁸ Nitration was done by general procedure with (*E*)-3-(2-chlorophenyl) acrylic acid (0.25 mmol, 41.5 mg) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/ petroleum ether (2:98 v/v); light yellow solid; isolated yield: 41% (19 mg). ¹H NMR (400 MHz, Chloroform-d) δ 7.30 – 7.36 (td, *J* = 7.5, 7.5, 1.4 Hz, 1H), 7.39 – 7.45 (td, *J* = 8.0, 7.7, 1.7 Hz, 1H), 7.46 – 7.50 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.56 – 7.61 (m, 2H), 8.38 (d, *J* = 13.7 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 127.65, 128.60, 128.74, 130.86, 133.03, 135.24, 136.15, 138.93.]⁺. M. Pt. 44 °C (CHCl₃); Lit: 48 °C¹².



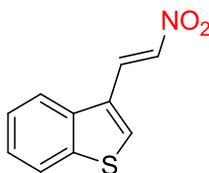
(E)-1-nitro-3-(2-nitrovinyl) benzene (Table 2, entry 2o)⁸. Nitration was done by general procedure with (*E*)-3-(3-nitrophenyl) acrylic acid (0.5 mmol, 83 mg) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/ petroleum ether (2:98 v/v); yellow solid; isolated yield: 34% (33 mg). ¹H NMR (400 MHz, Chloroform-d) δ 7.66 – 7.72 (m, 2H), 7.89 (d, *J* = 7.9 Hz, 1H), 8.06 (d, *J* = 13.8 Hz, 1H), 8.34 – 8.37 (ddd, *J* = 8.2, 2.2, 1.0 Hz, 1H), 8.43 (t, *J* = 2.0, 2.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 123.66, 126.39, 130.80, 131.97, 134.65, 136.45, 139.44, 148.95. GC-MS (*m/z*): 194.1 [M]⁺; M. Pt. 126 °C (CHCl₃); Lit: 125 °C⁸.



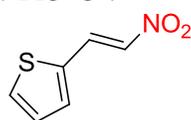
(E)-4-(2-nitrovinyl) benzonitrile (Table 2, entry 2o)⁸. Nitration was done by general procedure with (*E*)-3-(4-cyanophenyl) acrylic acid (0.25 mmol, 43.25 mg) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/ petroleum ether (2:98 v/v); yellow solid; isolated yield: 36% (16.5 mg). ¹H NMR (400 MHz, Chloroform-d) δ 7.62 (d, *J* = 13.8 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.72 – 7.80 (m, 2H), 7.99 (d, *J* = 13.7 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 115.32, 117.96, 129.56, 133.17, 134.48, 136.75, 139.61. GC-MS (*m/z*): 174.1 [M]⁺;]+. M. Pt. 185 °C (CHCl₃); Lit: 187 °C¹²



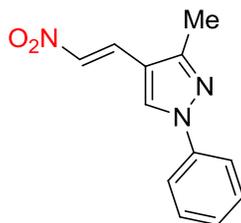
(E)-4-(2-nitrovinyl)dibenzo[*b,d*]furan (Table 3, entry 3a)⁸. Nitration was done by the general procedure with (*E*)-3-(dibenzo[*b,d*]furan-4-yl)acrylic acid (0.25 mmol, 59 mg) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/ petroleum ether (1:99 v/v); yellow solid; isolated yield: 78% (47 mg). ¹H NMR (400 MHz, Chloroform-d) δ 7.39 – 7.48 (m, 2H), 7.52 – 7.61 (m, 2H), 7.66 – 7.72 (d, *J* = 8.4 Hz, 1H), 7.97 – 8.03 (m, 1H), 8.06 – 8.11 (dd, *J* = 7.7, 1.3 Hz, 1H), 8.19 – 8.25 (d, *J* = 13.6 Hz, 1H), 8.34 – 8.41 (d, *J* = 13.6 Hz, 1H). ¹³C NMR (101 MHz, Chloroform-d) δ 112.18, 115.47, 121.06, 123.24, 123.60, 123.86, 124.48, 125.52, 128.27, 130.66, 134.36, 139.91, 154.44, 156.21. GC-MS (*m/z*): 239.06 [M]⁺. M. Pt. 123 °C (CHCl₃); Lit: 124 °C⁸.



(E)-3-(2-nitrovinyl)benzo[*b*]thiophene (Table 3, entry 3b).⁸ Nitration was done by the general procedure with (*E*)-3-(benzo[*b*]thiophen-3-yl)acrylic acid (0.25mmol, 51 mg) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/ petroleum ether (1:99 v/v); yellow solid; isolated yield: 81% (41mg). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.57 (m, 2H), 7.74 – 7.80 (d, *J* = 13.8 Hz, 1H), 7.91 – 7.99 (m, 3H), 8.27 – 8.33 (d, *J* = 13.8, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 122.23, 123.54, 125.90, 125.92, 127.30, 131.32, 133.09, 136.60, 136.89, 140.71. GC-MS (*m/z*): 205.02 [M]⁺. M. Pt. 112–113 °C (CHCl₃); Lit: 113 °C⁸.

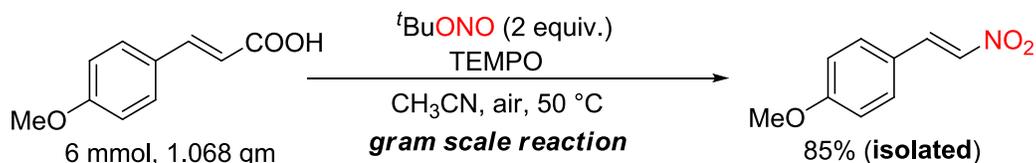


(E)-2-(2-nitrovinyl) thiophene (Table 3, entry 3c).⁹ Nitration was done by the general procedure with (*E*)-3-(thiophen-2-yl)acrylic acid (0.25mmol, 38 mg) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/ petroleum ether (1:99 v/v); orange yellow solid; isolated yield: 54% (21 mg). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.13 – 7.18 (dd, *J* = 5.1, 3.7 Hz, 1H), 7.45 – 7.48 (m, 2H), 7.49 – 7.52 (s, 1H), 7.55 – 7.59 (dt, *J* = 5.0, 1.0, 1.0 Hz, 1H), 8.13 – 8.19 (d, *J* = 13.4, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 129.08, 131.82, 132.31, 133.97, 134.86, 135.55. M. Pt. 75 °C (CHCl₃); Lit: 79 °C (Ethanol)¹⁹.



(E)-3-methyl-4-(2-nitrovinyl)-1-phenyl-1H-pyrazole (Table 3, entry 3d).⁸ Nitration was done by the general procedure with (*E*)-3-(3-methyl-1-phenyl-1H-pyrazol-4-yl)acrylic acid (0.25 mmol, 57 mg) as the substrate. Pure nitrated product was isolated by column chromatography through a silica gel column (mesh 60–120). Eluent: ethyl acetate/ petroleum ether (1:99 v/v); deep yellow solid; isolated yield: 74% (42 mg). ¹H NMR (400 MHz, Chloroform-*d*) δ 2.49 (s, 3H), 7.33 – 7.38 (m, 1H), 7.45 – 7.53 (m, 3H), 7.65 – 7.69 (m, 2H), 8.00 – 8.06 (d, *J* = 13.7, Hz, 1H), 8.15 – 8.17 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 13.53, 113.63, 119.50, 127.75, 129.01, 129.88, 130.22, 135.12, 139.16, 151.47. GC-MS (*m/z*): 229.09 [M]⁺. M. Pt. 143–144 °C (CHCl₃); Lit: 144 °C⁸.

Gram scale reaction with 4-methoxycinnamic acids:



An oven-dried round bottom flask was fitted with a reflux condenser and charged with a magnetic stir-bar, TEMPO (4.8 mmol, 750 mg) and 4-methoxycinnamic acid (6 mmol, 1.086g) under air atmosphere. The solvent (MeCN, 25 mL) and $t\text{BuONO}$ (12 mmol, 1.424 mL) were added by laboratory syringe and micro liter syringe respectively. The round bottom flask was placed in a preheated oil bath at $50\text{ }^\circ\text{C}$ and the reaction mixture was stirred vigorously for 12 h. Then the reaction mixture was cooled to room temperature. Then the reaction mixture was filtered through a celite bed filter. Celite bed was washed with ethyl acetate as the washing solvent. Finally organic extract was concentrated and was purified by column chromatography using silica gel column (60-120 mesh size) with ethyl acetate/petroleum-ether (1:99 v/v) as the eluent. Crystalline yellow solid; isolated yield: 85% (0.9179g).

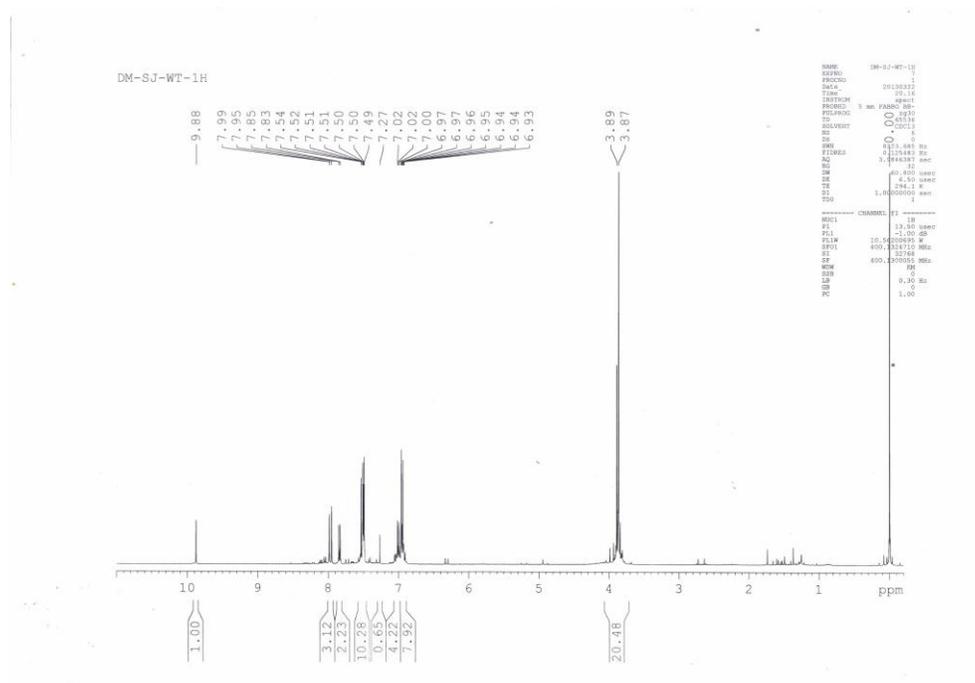
Determination of E/Z ratio w.r.t time with 4-methoxycinnamic acids without TEMPO



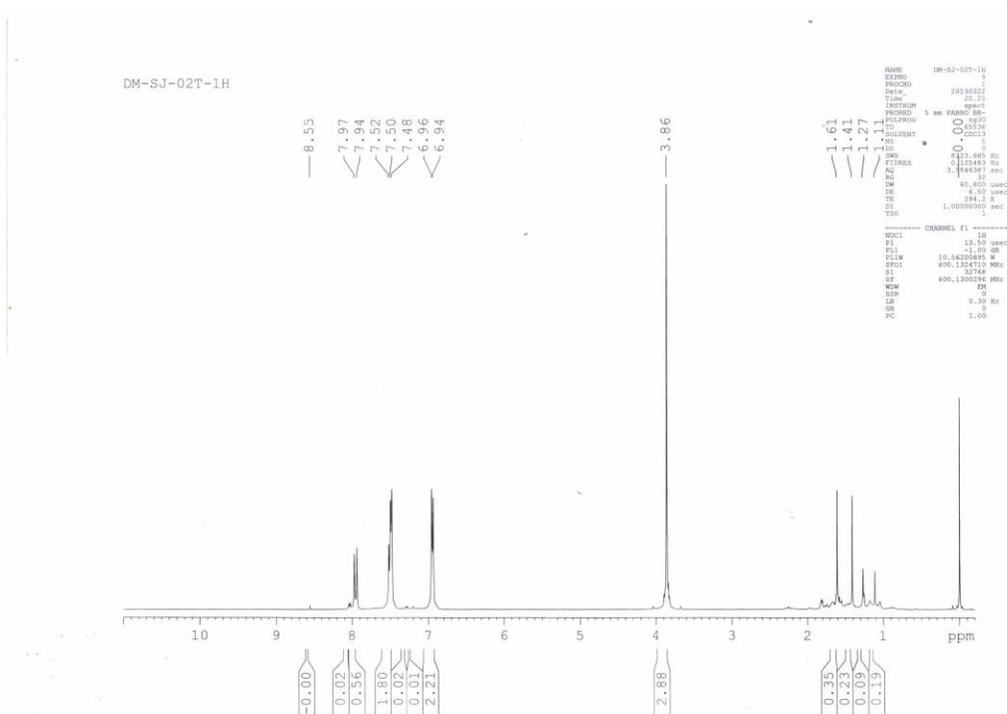
An oven-dried screw cap test tube was charged with a magnetic stir-bar and 4-methoxycinnamic acid (0.25 mmol, 45 mg) under air atmosphere in absence of TEMPO. $t\text{BuONO}$ (0.5 mmol, 60 μL) and the solvent (MeCN, 1 mL) were added by microliter syringe and laboratory syringe respectively. The reaction tube was placed in a preheated oil bath at $50\text{ }^\circ\text{C}$ and the reaction mixture was stirred vigorously for 1-4 h. Then the reaction mixture was cooled to room temperature. Reaction mixture was passed through flash column and dried. ^1H NMR of the crude reaction mixture was taken and resulted in the formation of E and Z products are given in the bellow.

Without TEMPO				With TEMPO
Entry	Time (h)	GC Yield (%)	E/Z ratio	GC Yield (%) [<i>E</i> only]
1	1	40	1 : 1.19	65
2	2	41	1 : 1.14	77
3	3	42	1 : 1.15	95
4	4	42	1 : 1.13	99

¹H NMR of crude reaction mixture of with 4-methoxycinnamic acids without TEMPO (after 12 h)

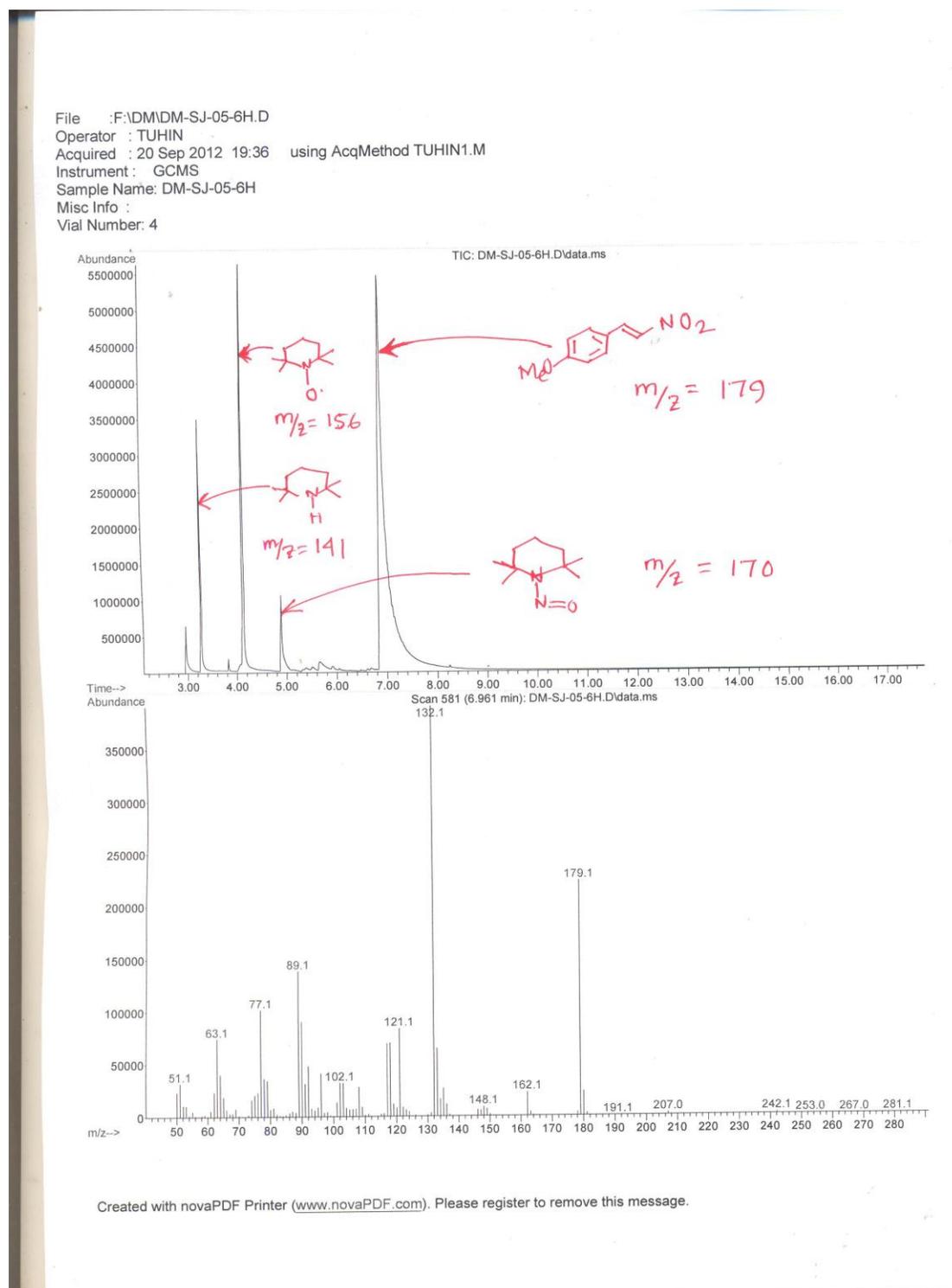


¹H NMR of crude reaction mixture of with 4-methoxycinnamic acids with TEMPO (after 12 h)



Identification of TEMPO by-products by GC-MS:

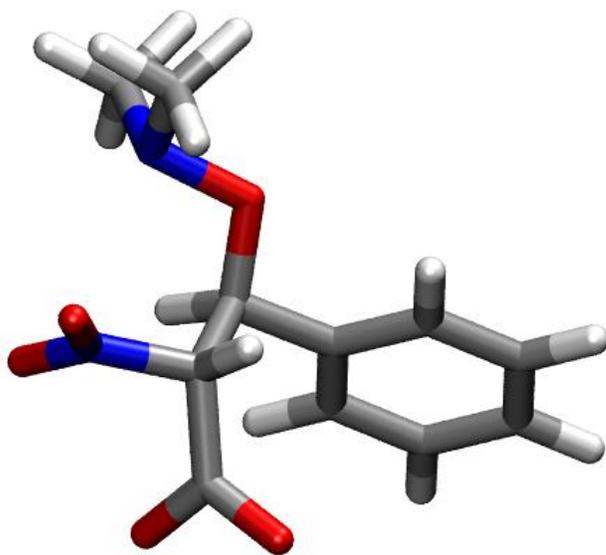
TEMPO by-products were checked by GC-MS after running our standard reaction mixture and the resulted by-products were found, GC-MS (m/z): 141.1, 156.2 170.2 [M]⁺.



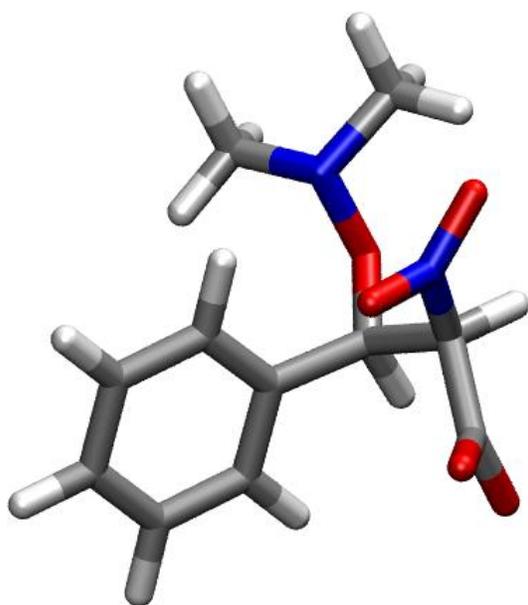
Computational Studies

Two model systems were constructed to investigate the relative stabilities of the two reactive intermediates, **2** and **3** using density functional theory (DFT) calculations. In the two model systems, TEMPO was replaced by O-N(CH₃)₂ for computational considerations. Such a simplification of the original system is not expected to alter the qualitative trends of the computed relative energies. Geometry optimizations were performed on doublet spin state of the two model systems using the hybrid DFT B3LYP functional using the 6-31G* basis set. Intermediate **2** was found to be more stable than **3** by 5.0 kcal/mol. Such a difference of 5.0 kcal/mol is large enough to differentiate the two intermediates, and to drive all of the reaction via **2** leading to the formation of the *E*-isomer, and precluding the formation of the *Z*-isomer.

Intermediate 2 (with Me₂NO, instead of TEMPO)



Intermediate 3 (with Me₂NO, instead of TEMPO)

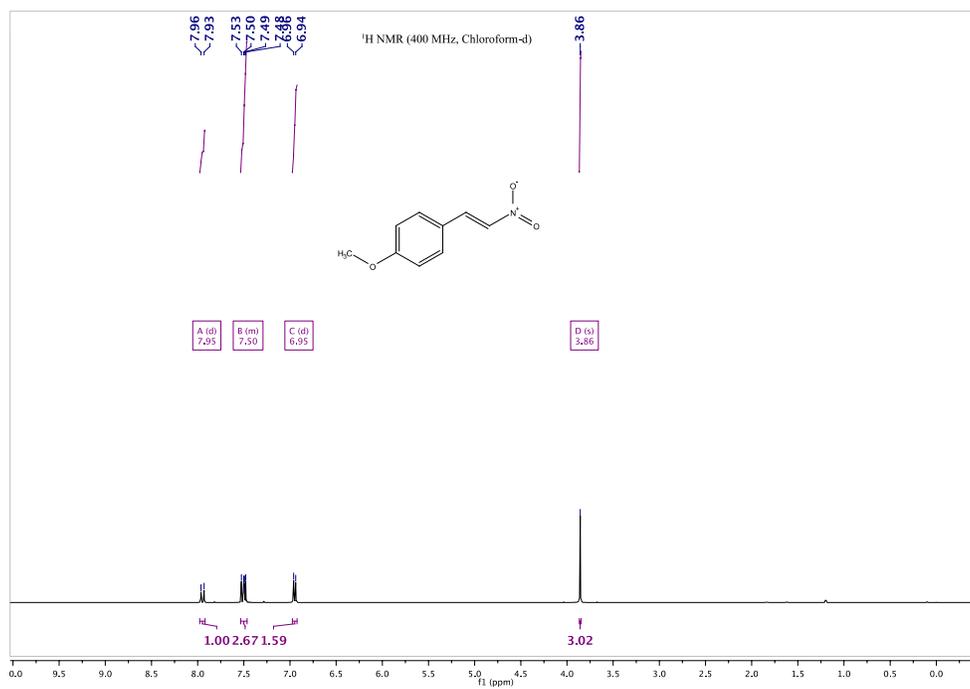


References:

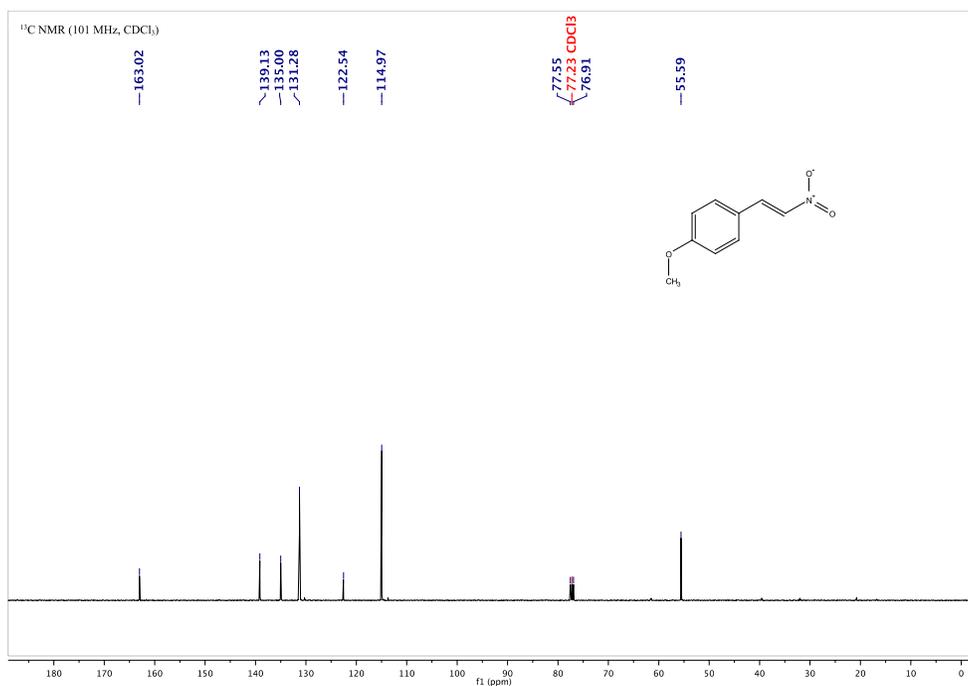
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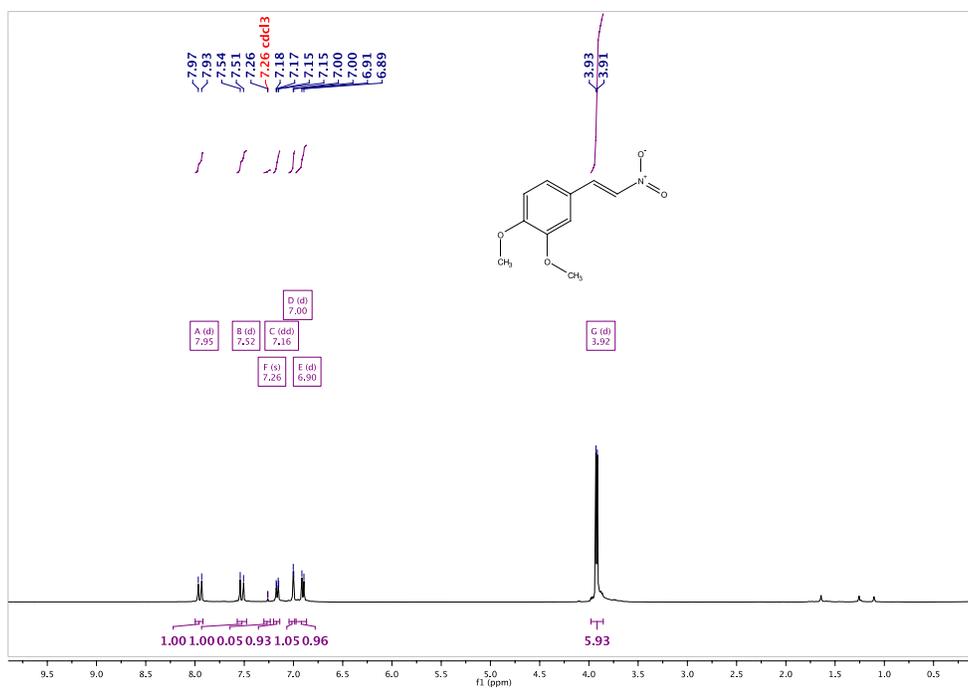
2a_ ¹H NMR



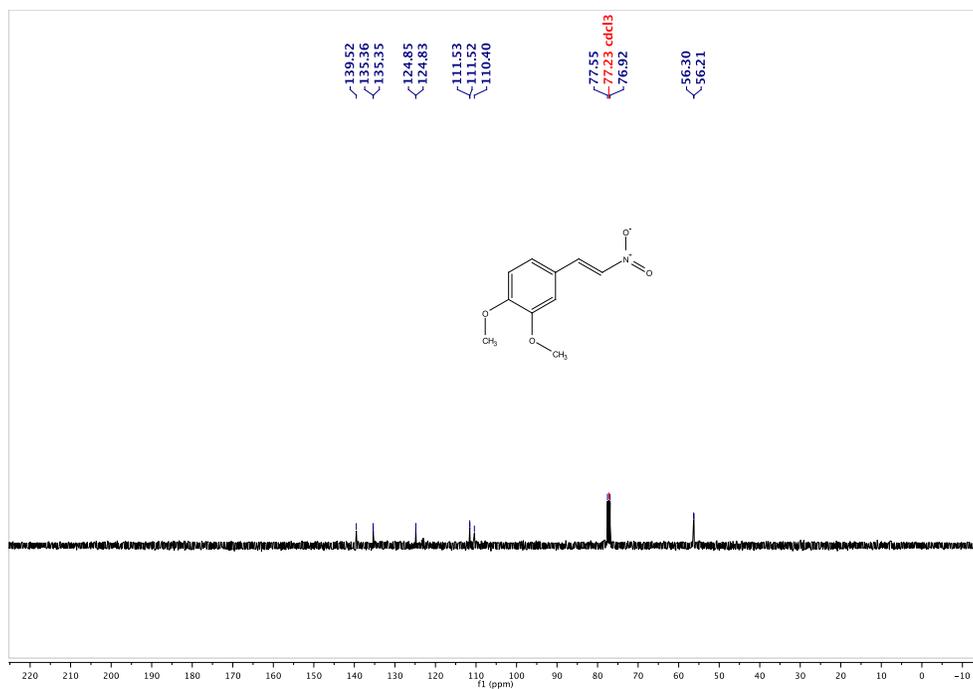
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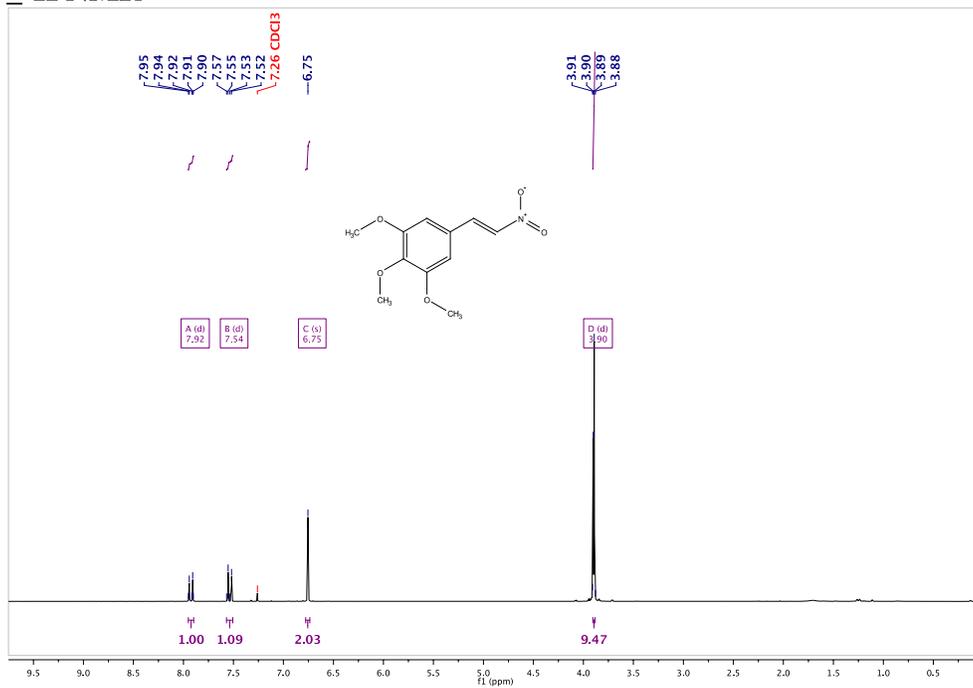
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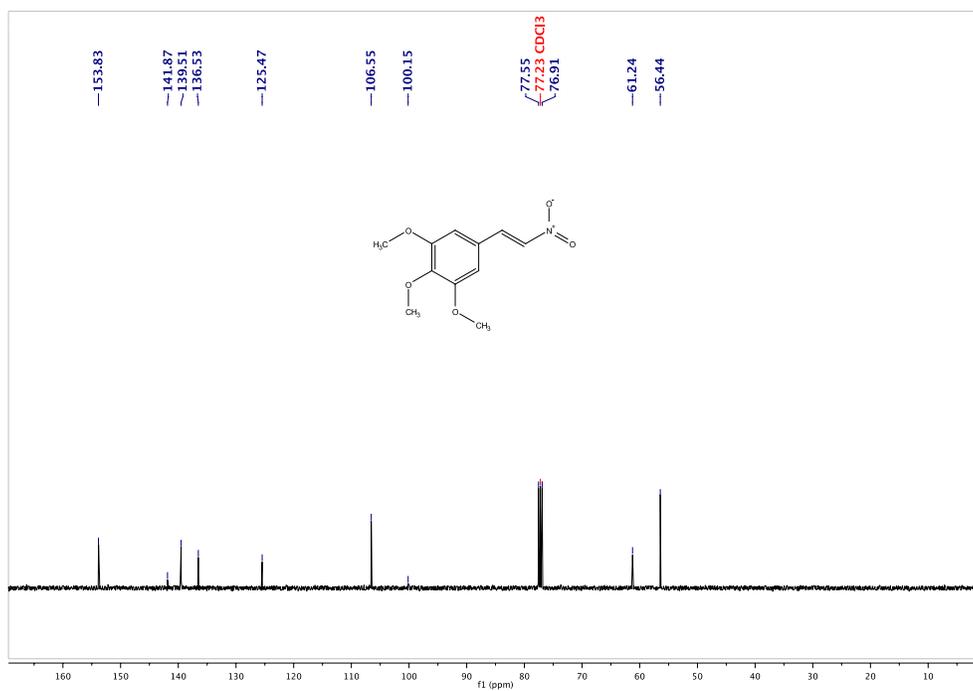
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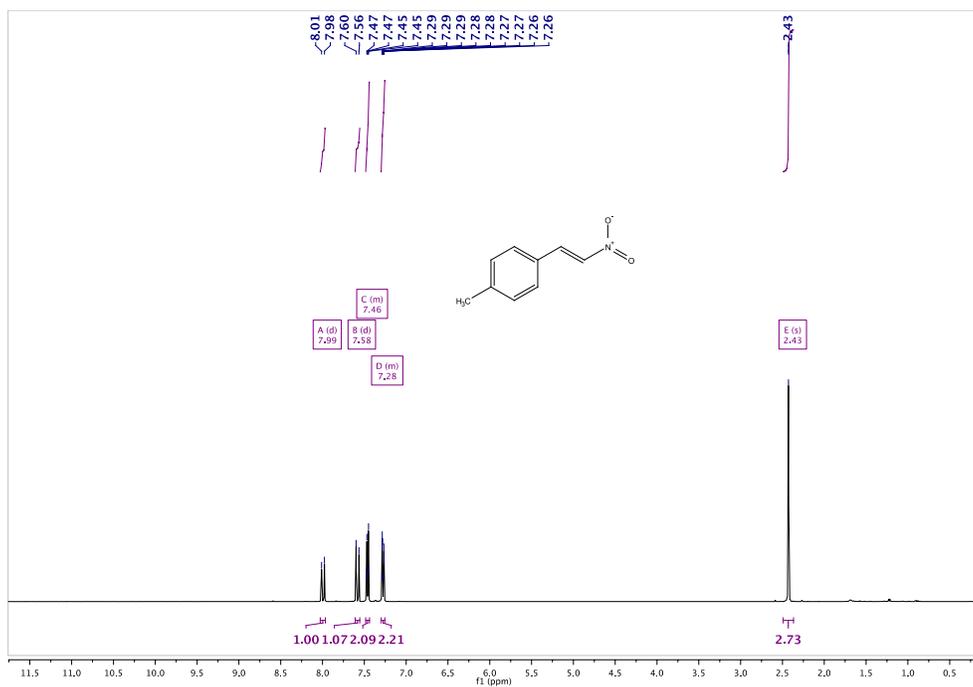
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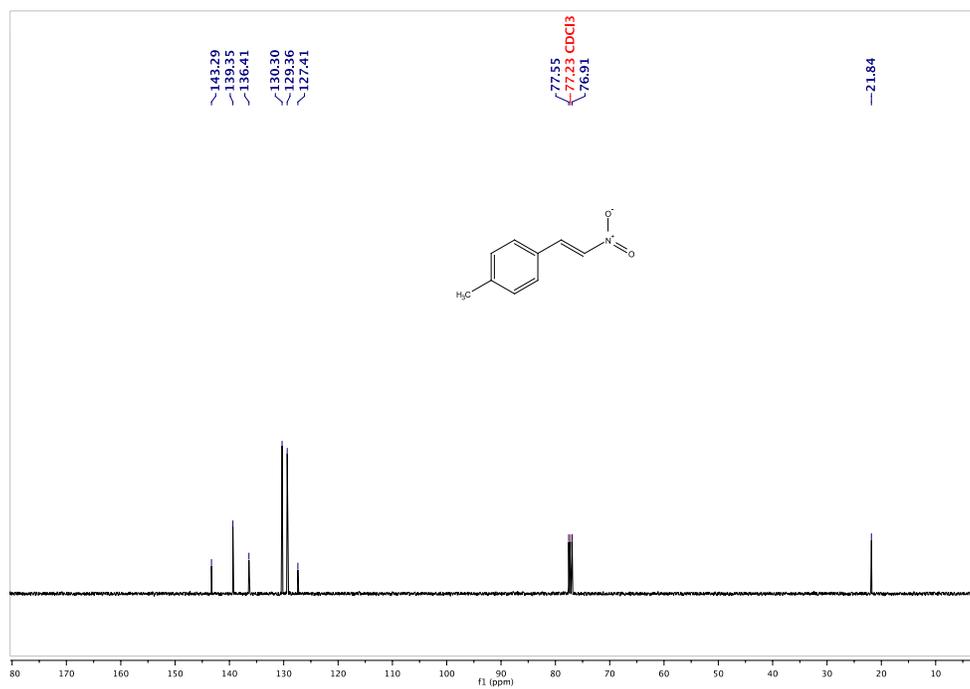
2c **¹³C NMR**



2d ^1H NMR



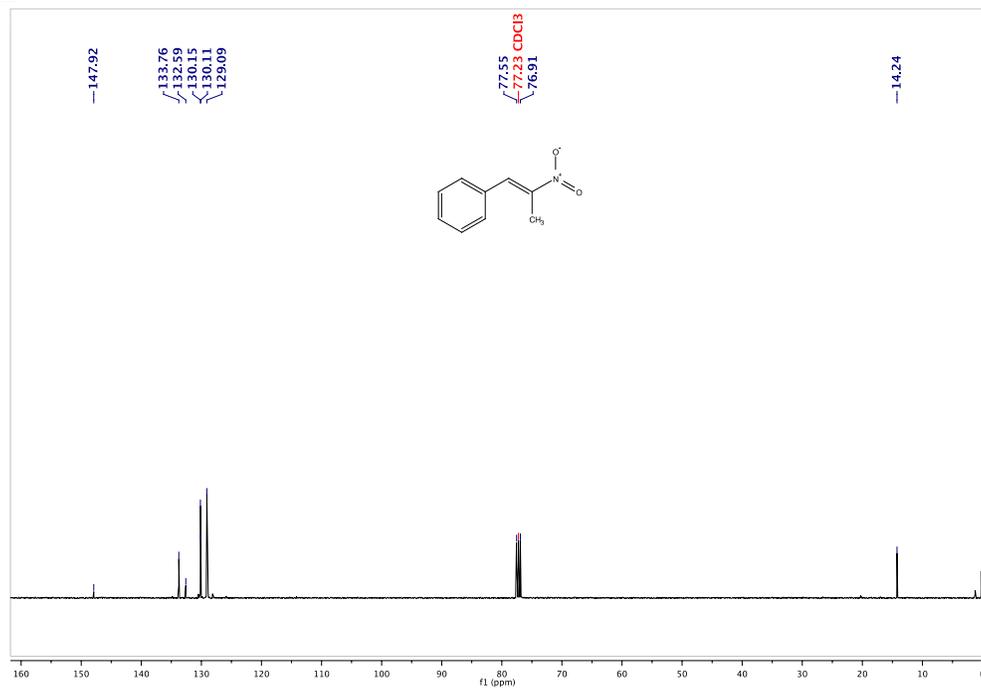
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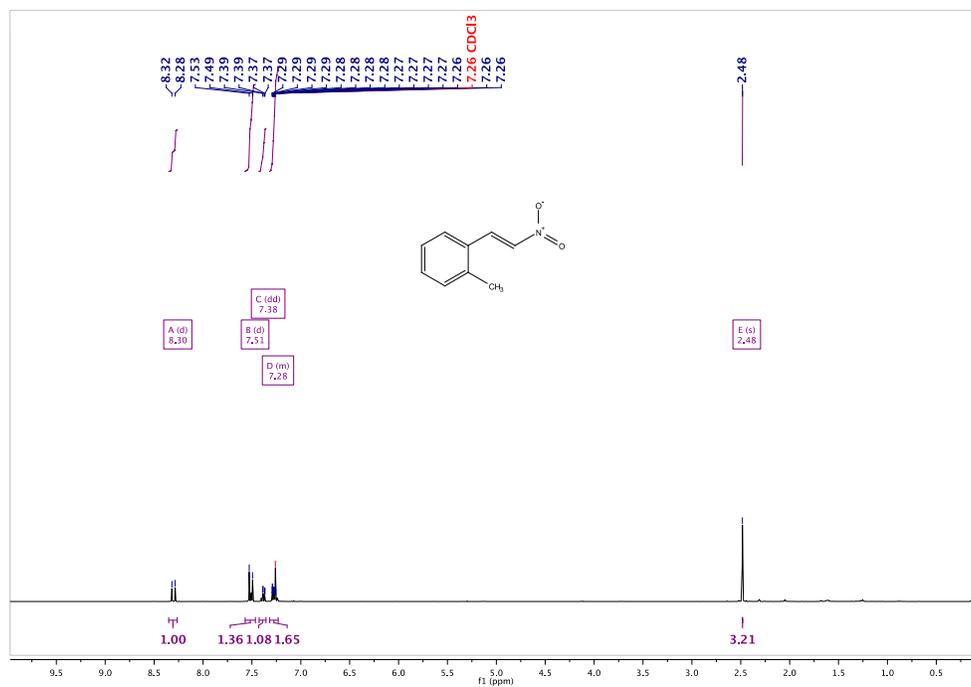
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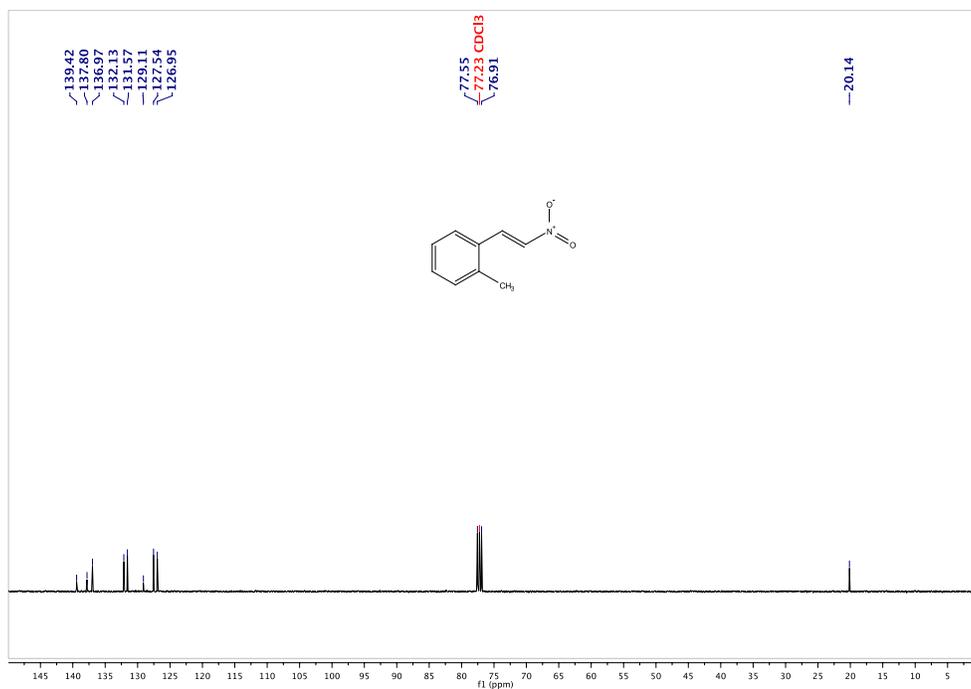
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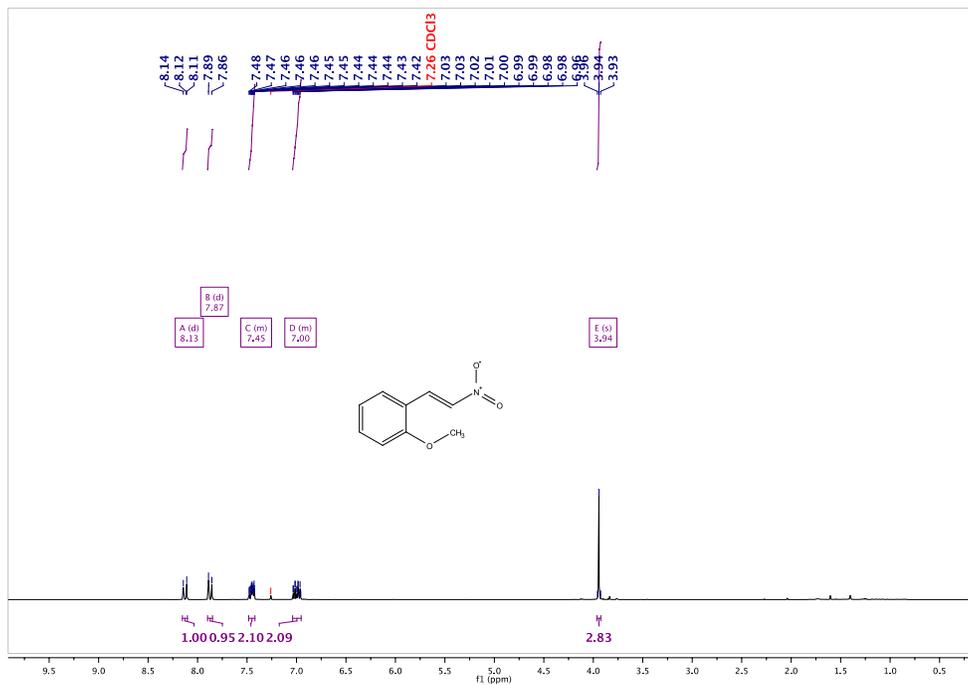
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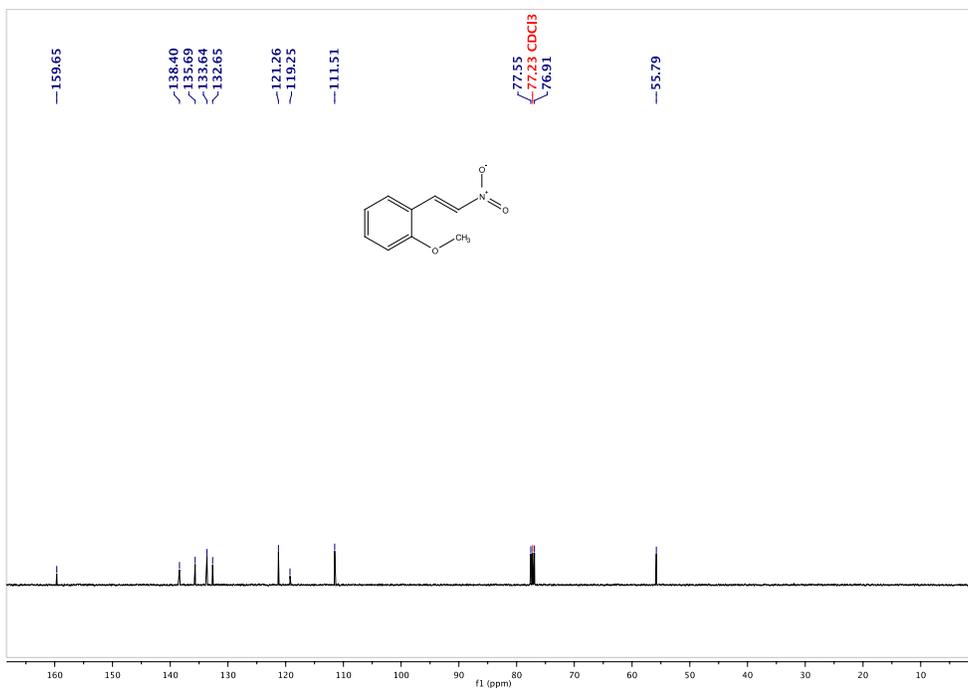
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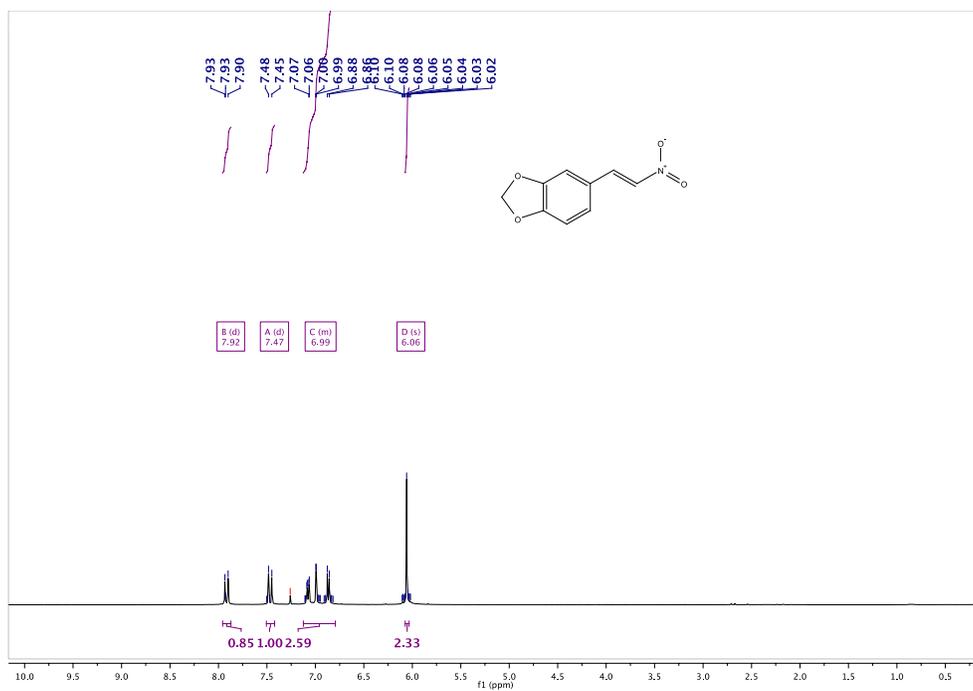
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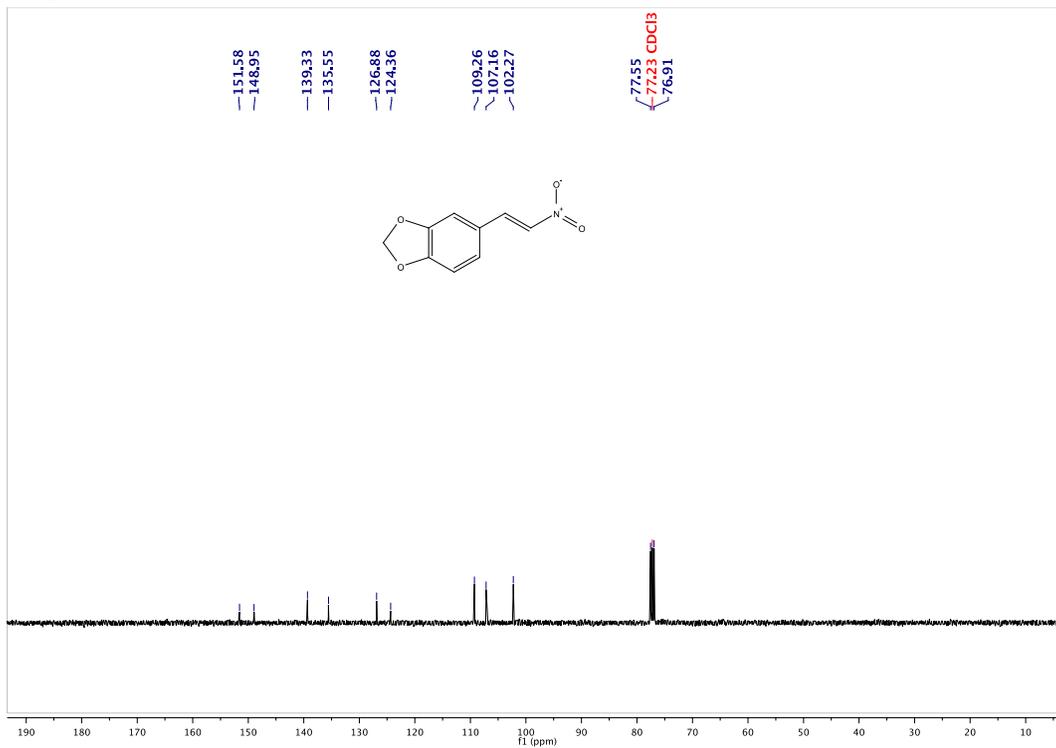
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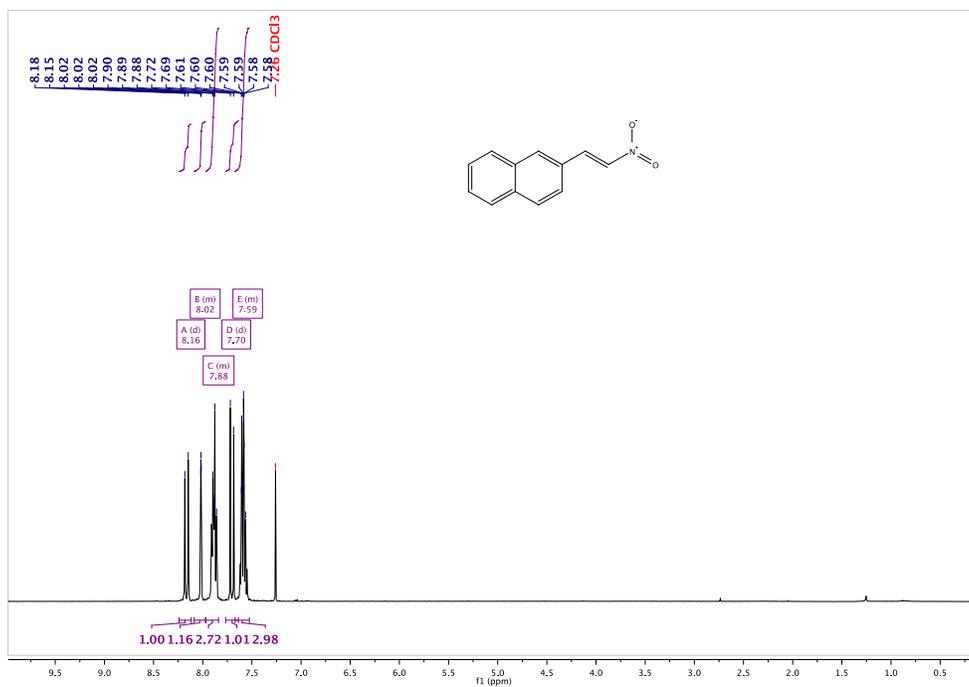
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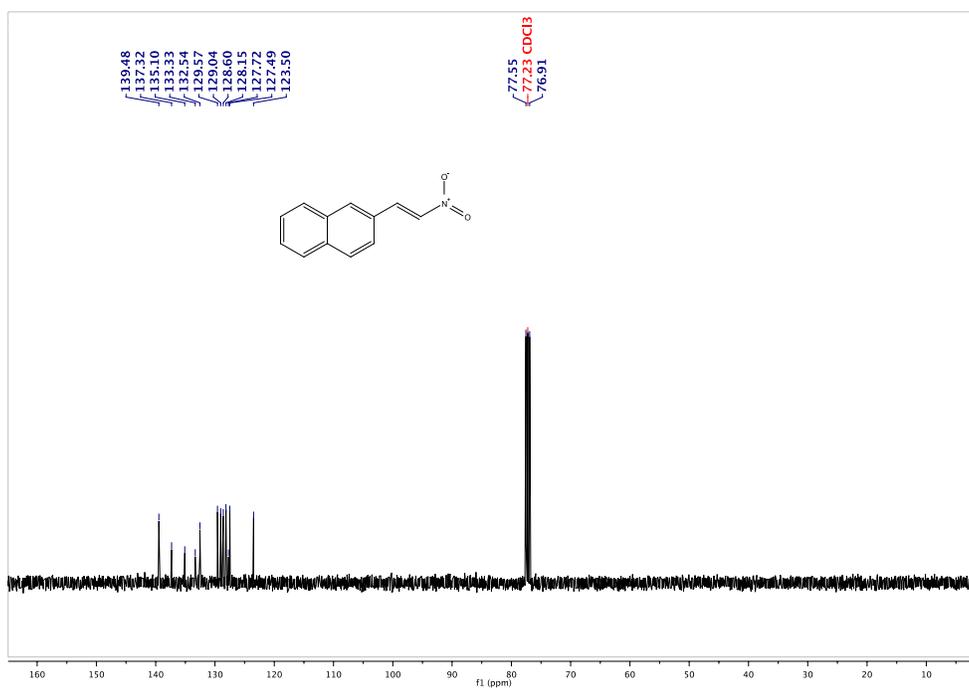
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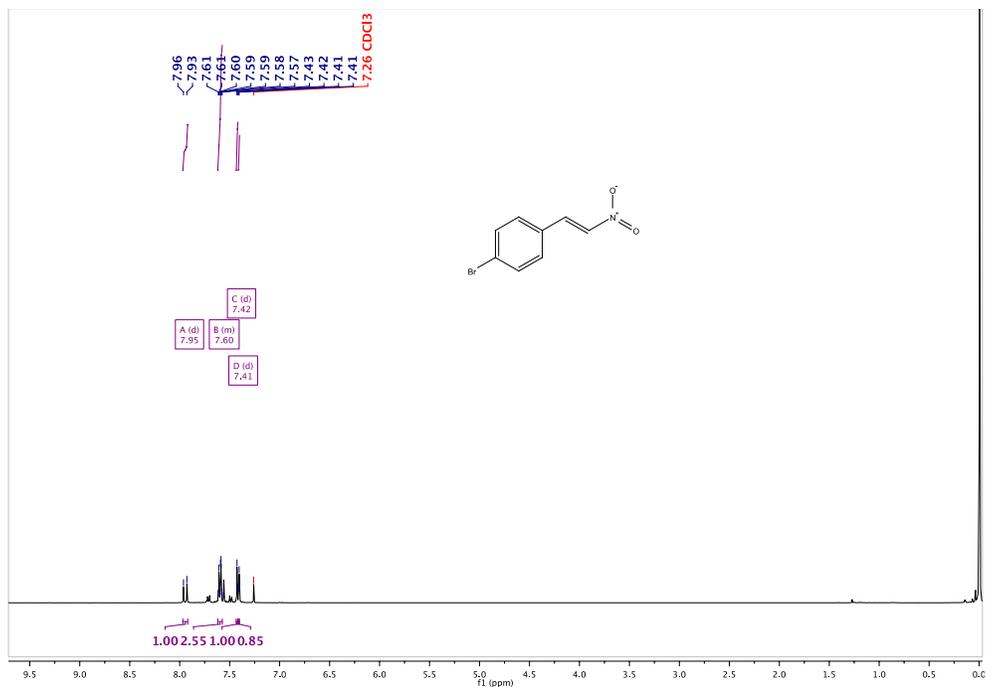
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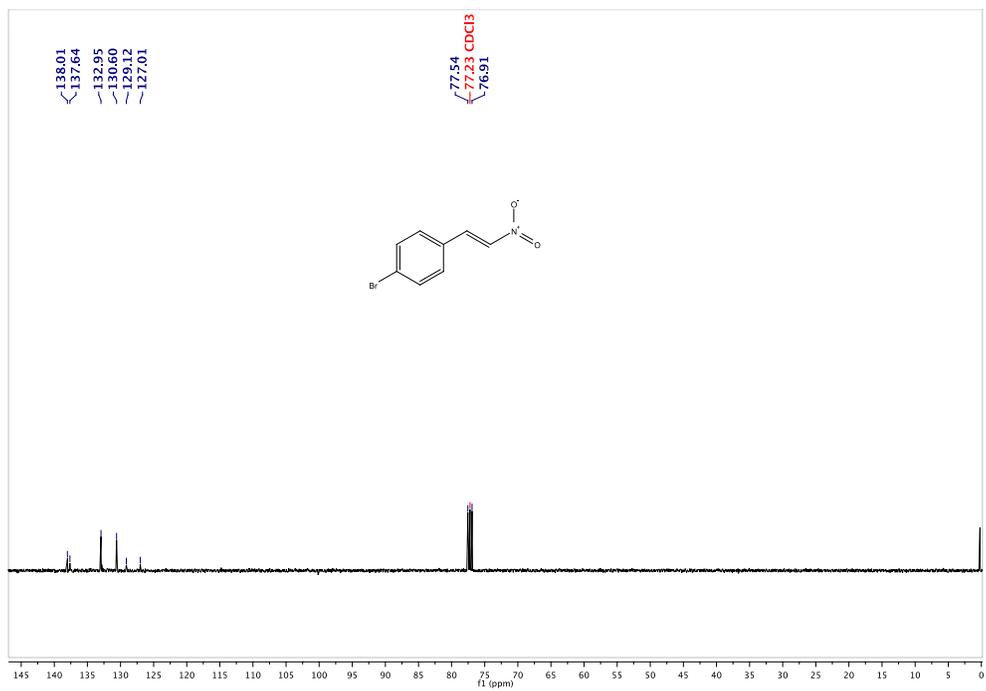
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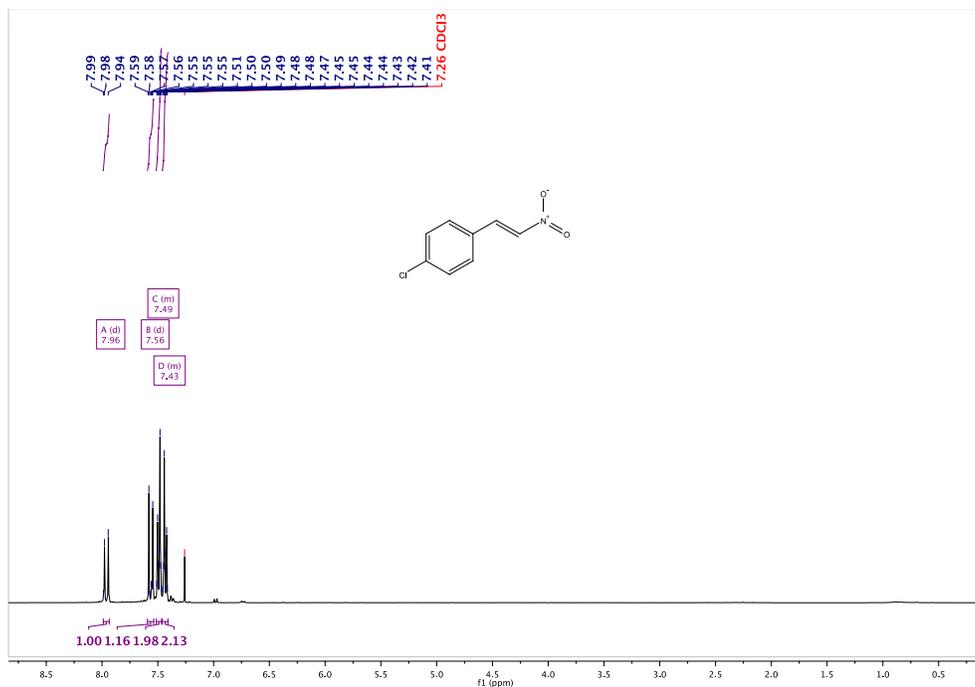
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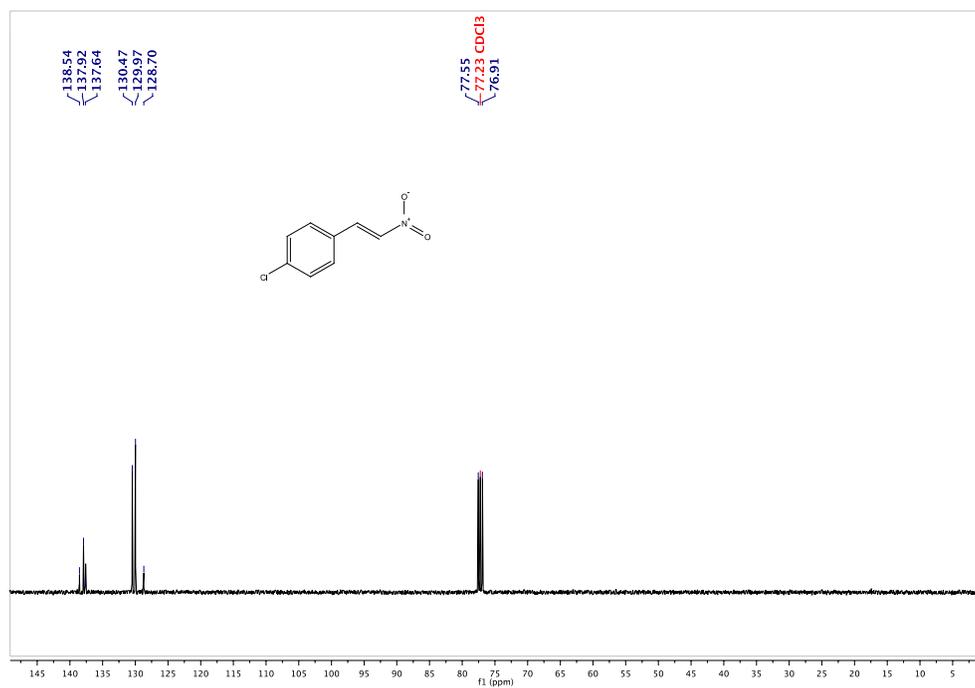
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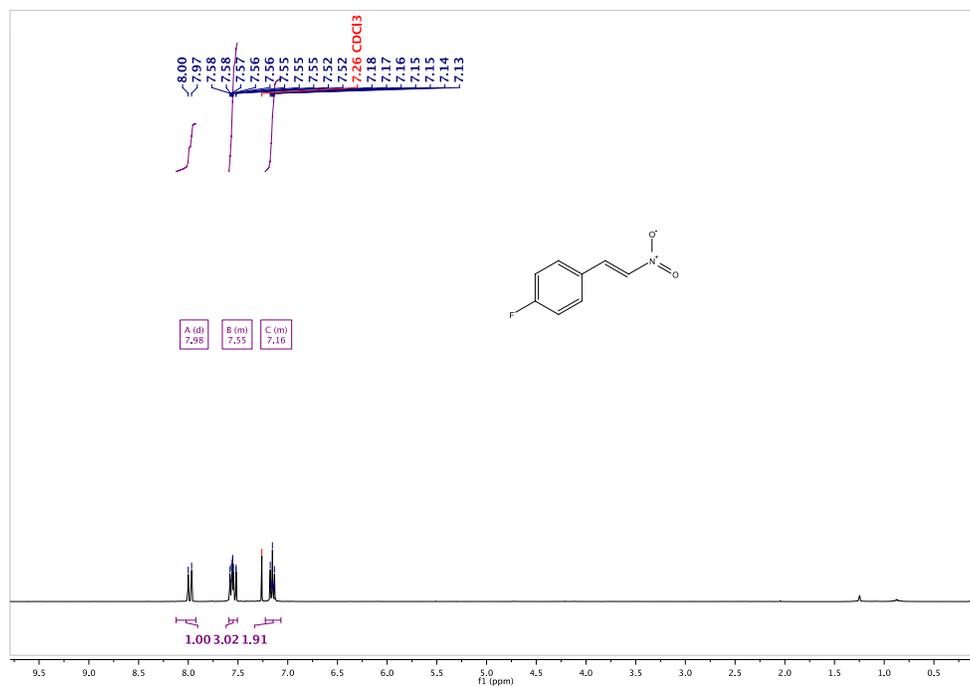
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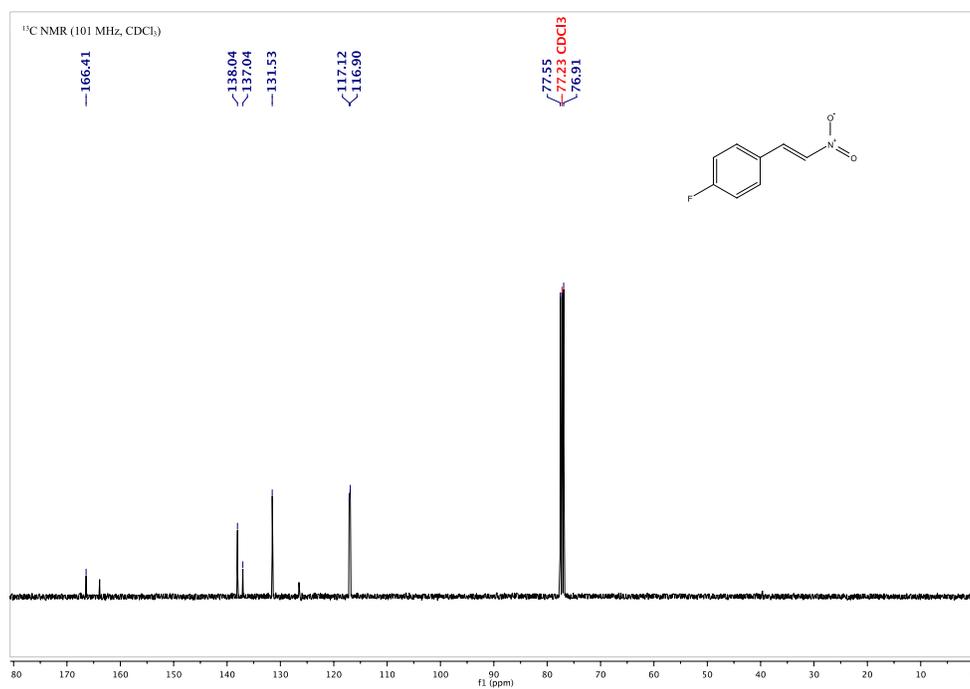
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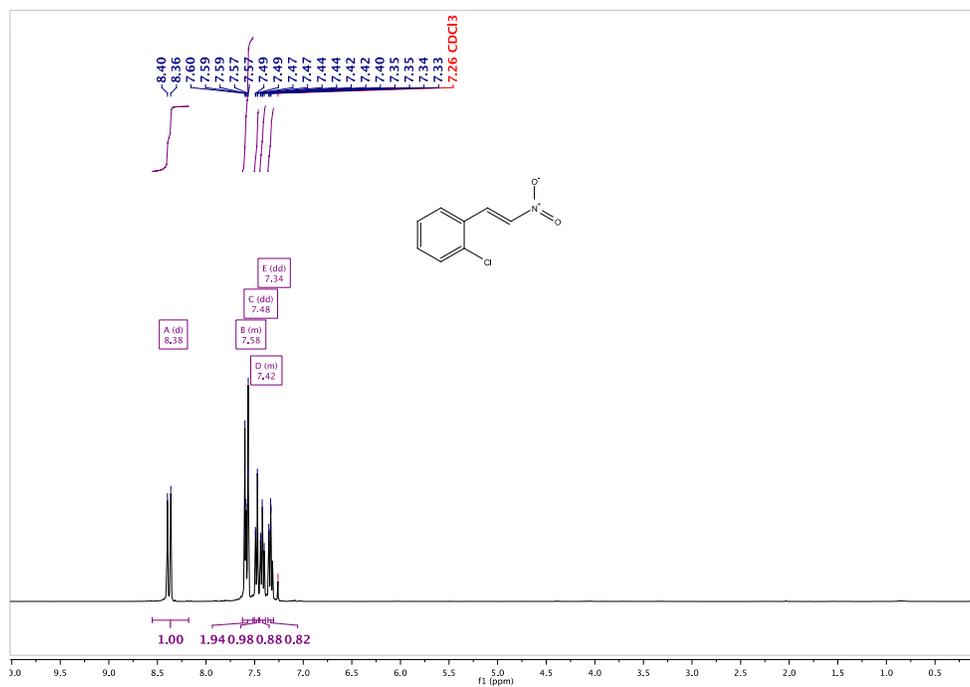
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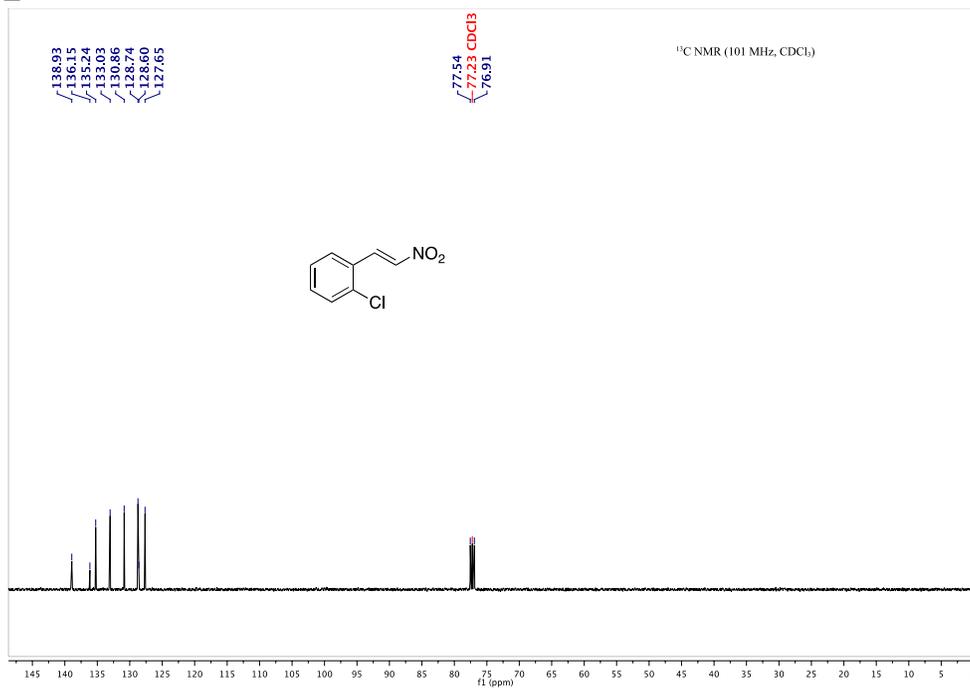
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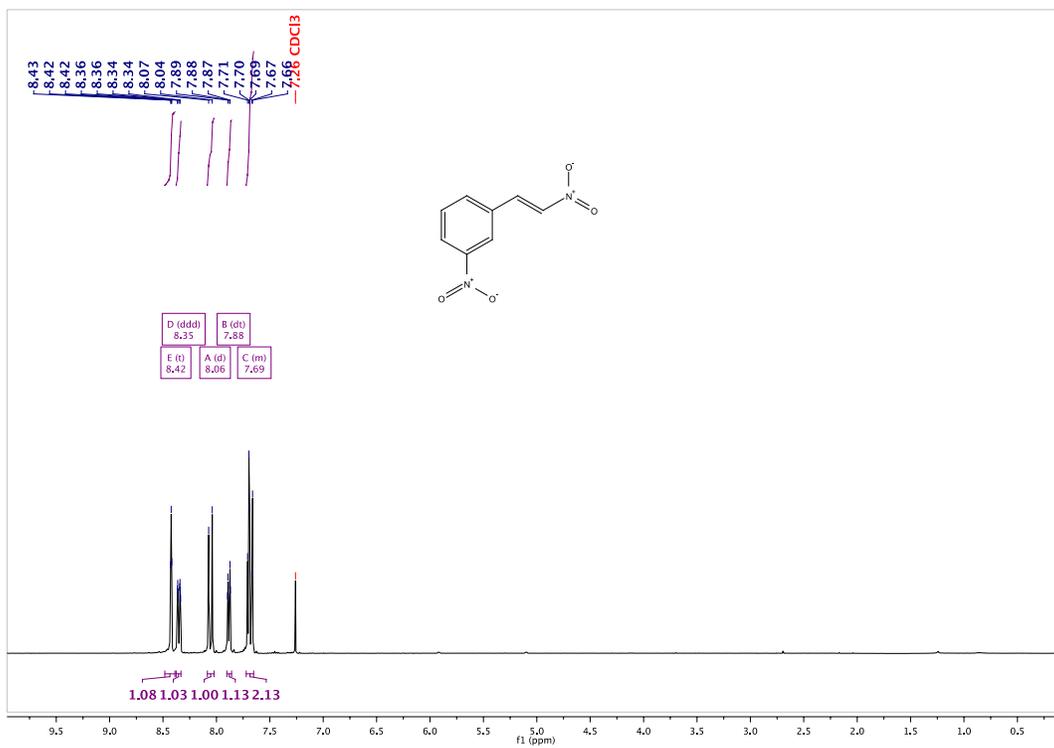
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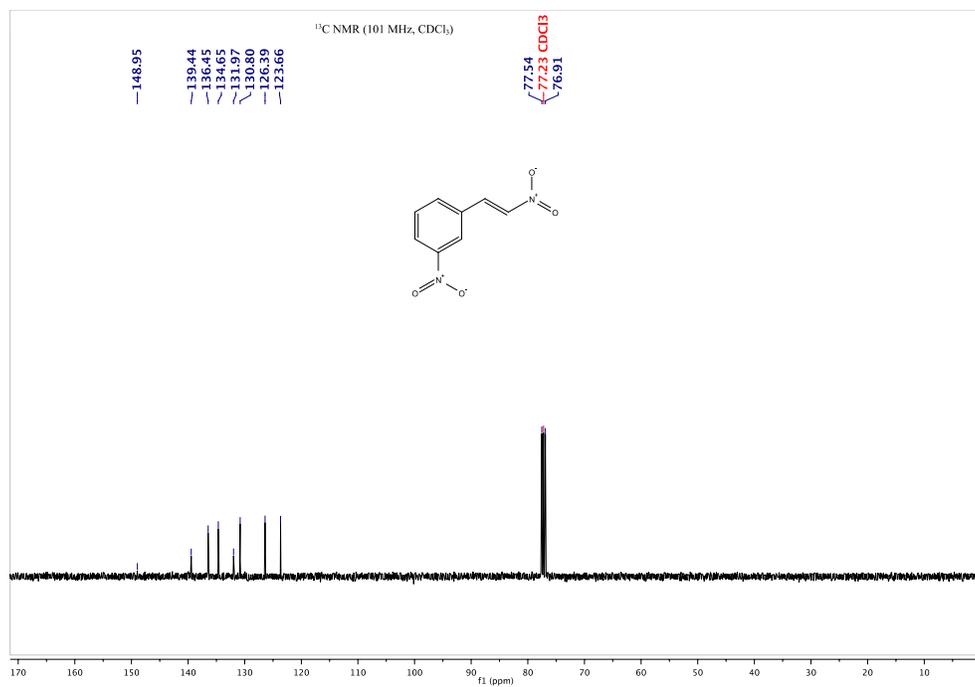
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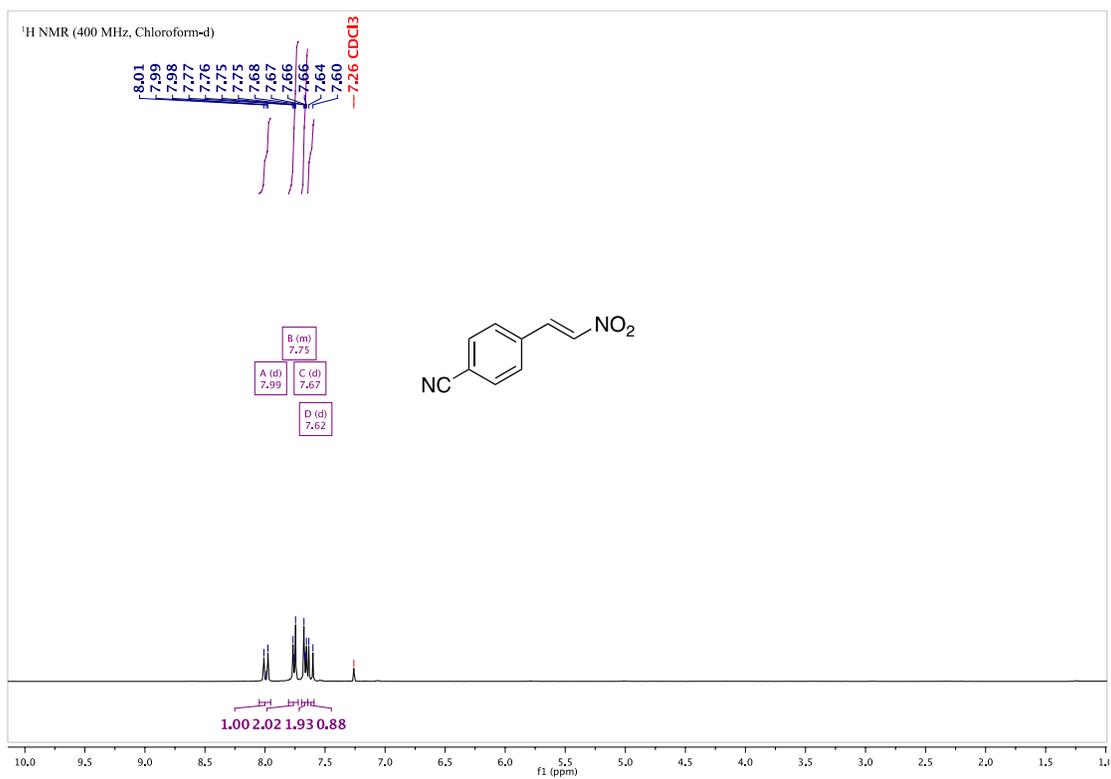
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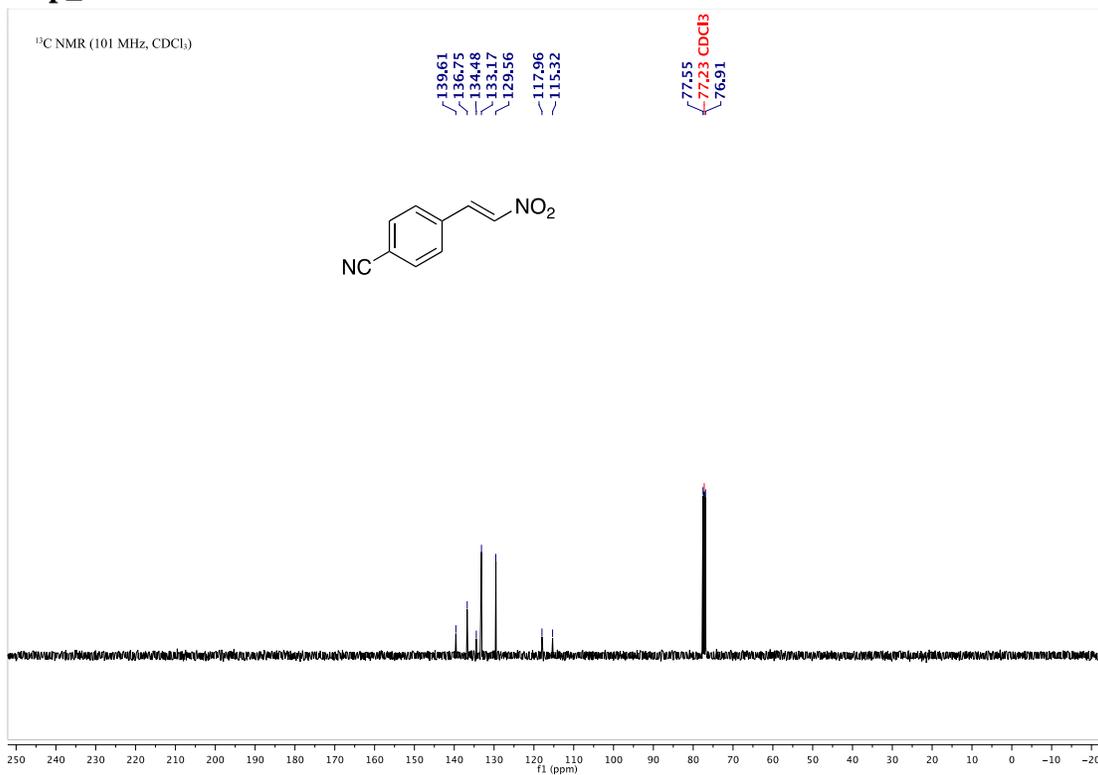
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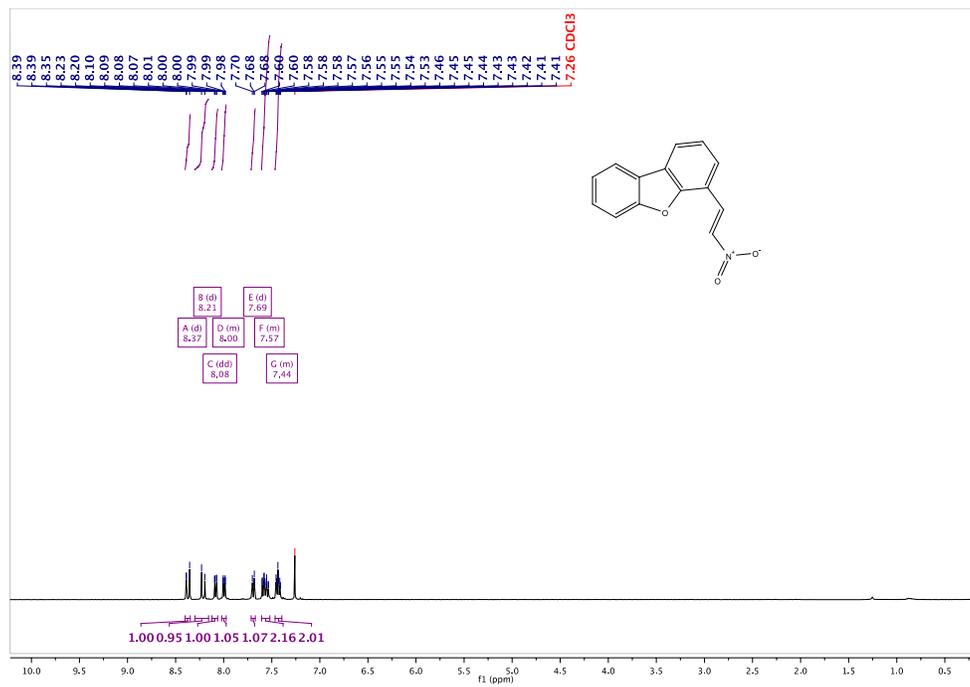
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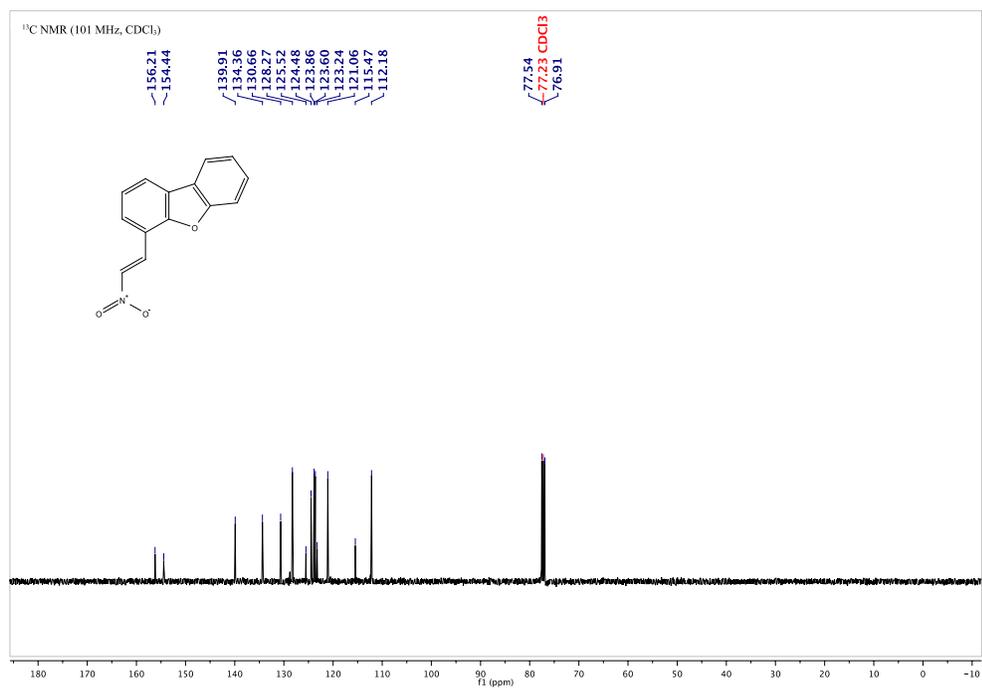
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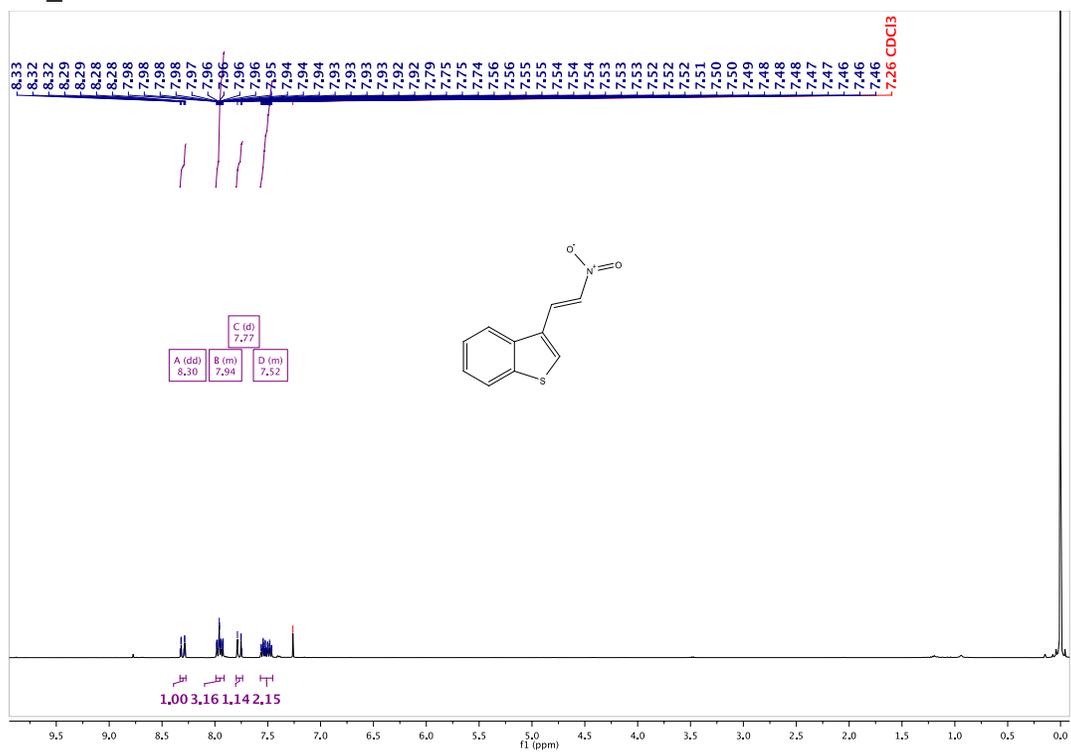
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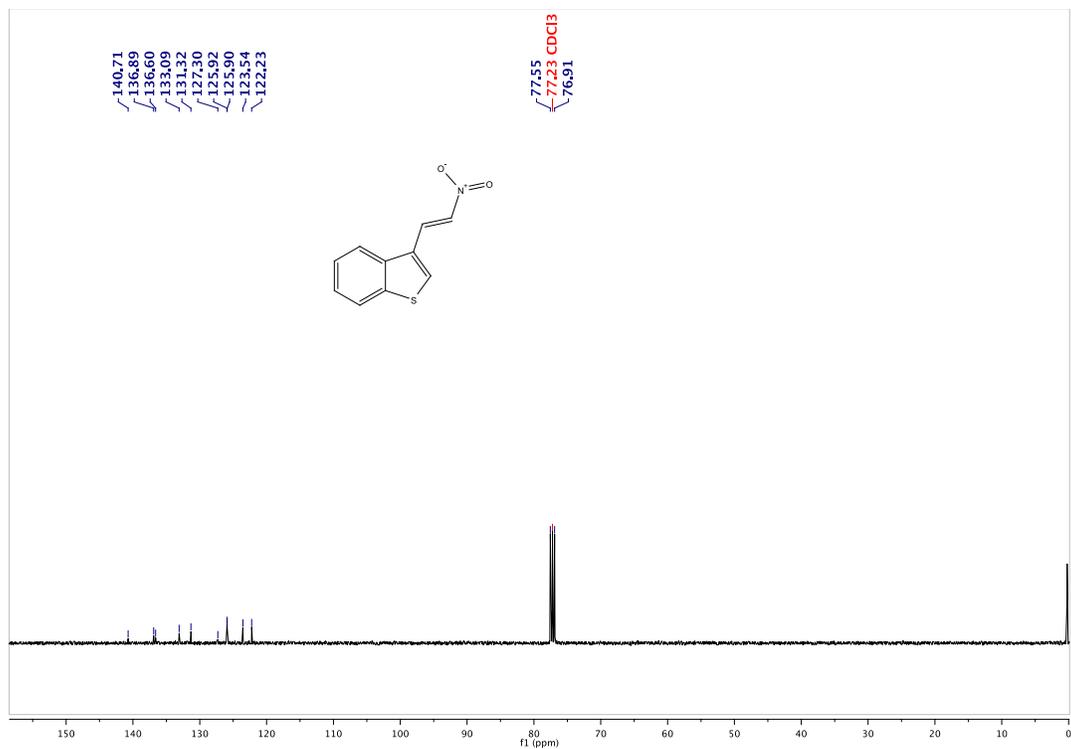
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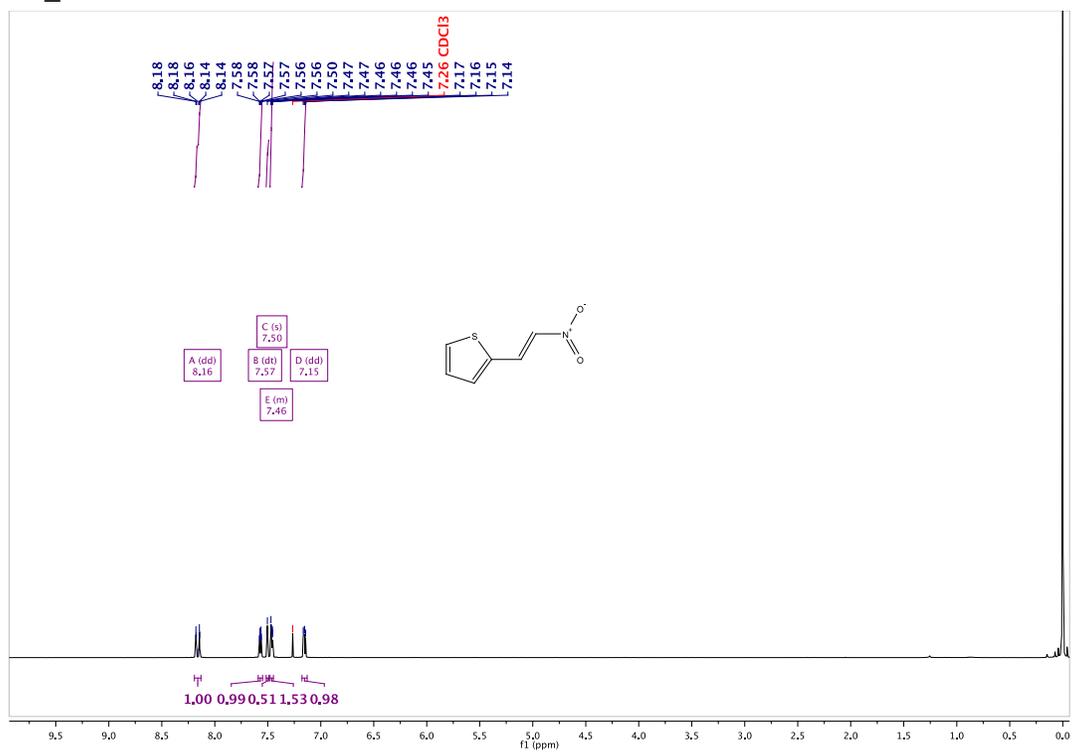
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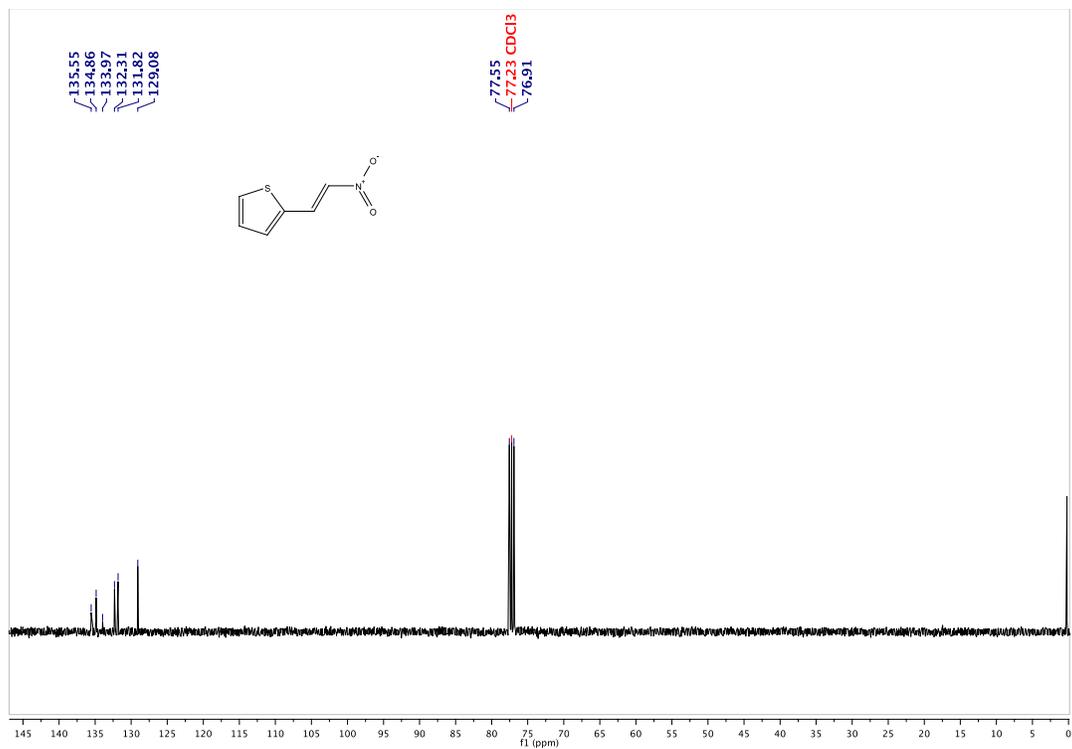
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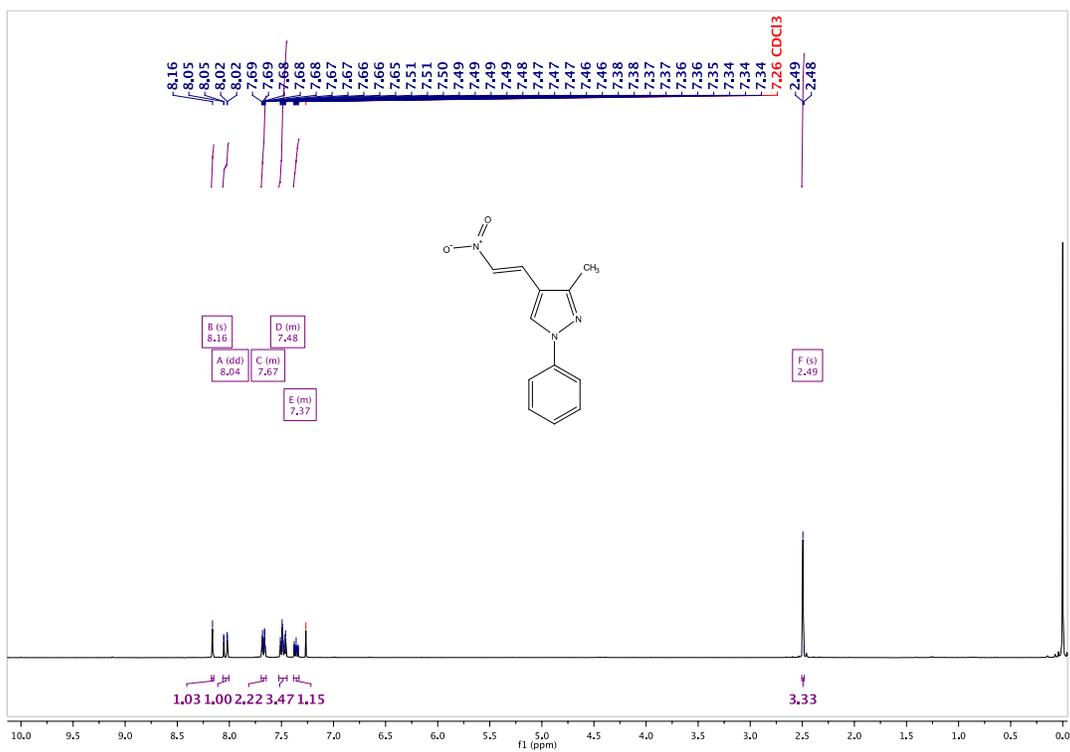
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3c_ ¹³C NMR



3d_ ¹H NMR



3d_ ¹³C NMR

