Supporting Information

Pd-Catalyzed Cross-Coupling of Carboxylic Acids with Nitroethane via Combination of Decarboxylation and Dehydrogenation

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General comments

All reactions were carried out under N_2 atmosphere. The reagents used for experiments were purchased from Sigma-Aldrich, Acros and Alfa Aesar and used as received unless otherwise noted. 1,4-dioxane was distilled from sodium and benzophenone under nitrogen. DMSO was distilled from CaH_2 under nitrogen and stored under nitrogen. ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) and ^{19}F NMR (377 MHz) spectra were recorded respectively using a Burker AVANCE 400 spectrometer. Elemental analysis, Mass spectra, Gas chromatography (GC) and Gas chromatography-mass spectra (GC-MS) were performed by the analysis center of our institute.

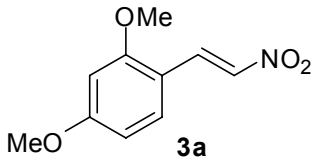
Products

General procedure:

In a glove box, the Schlenk tube equipped with a stir bar was charged with $Pd(OOCF_3)_2$ (0.02 mmol, 0.1 equiv), Ag_2CO_3 (0.4 mmol, 2.0 equiv), PivOH (0.5 mmol, 2.5 equiv) and benzoic acid (0.2 mmol, 1.0 equiv). The tube was fitted with a rubber septum and remove out of the glove box. The nitroethane (1.4 mmol, 7.0 equiv), DMSO (0.2 mL) and 1,4-dioxane (2.0 mL) were added in turn to the Schlenk tube though the rubber septum using syringes, and then the septum was replaced by a Teflon screwcap under a nitrogen flow. The reaction mixture was stirred at 100 °C for 24 h. Upon completion, the reaction mixture was diluted with 10 mL of ethyl acetate, filtered through a pad of silica gel, followed by washing the pad of the silica gel with the same solvent (20 mL). The filtrate was washed with saturated aqueous solution of Na_2CO_3 (30 mL) and then with water (3 × 15 mL). The organic phase was dried over Na_2SO_4, filtered, concentrated under reduced pressure. The residue was then purified by chromatography on silica gel to provide the corresponding product.

Characterization

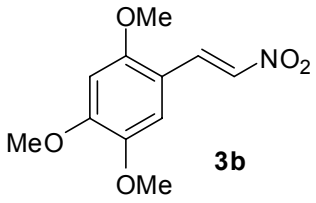
(*E*)-2,4-dimethoxy-β-nitrostyrene



3a

The reaction was performed following the general procedure with $Pd(OOCCF_3)_2$ (0.0066 g, 0.02 mmol), Ag_2CO_3 (0.1103 g, 0.4 mmol), PivOH (0.0512 g, 0.5 mmol), 2.4-dimethoxybenzoic acid (0.0364 g, 0.2 mmol), nitroethane (0.1 mL, 1.4 mmol), DMSO (0.2 mL) and 1,4-dioxane (2 mL). The reaction mixture was stirred at 100 °C for 24 h. After extraction and concentration, the reaction mixture was purified by column chromatography on silica gel (20% ethyl acetate/petroleum ether) afforded a yellow solid (71% yield). This compound is known.[1] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 13.5 Hz, 1H), 7.81 (d, *J* = 13.5 Hz, 1H), 7.36 (d, *J* = 8.6 Hz, 1H), 6.54 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.47 (d, *J* = 2.3 Hz, 1H), 3.91 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.44, 161.25, 135.98, 135.75, 134.35, 112.39, 105.98, 98.64, 55.66.

(*E*)-2,4,5-trimethoxy-β-nitrostyrene

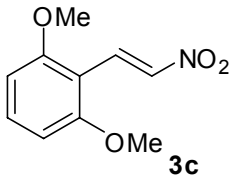


3b

The reaction was performed following the general procedure with $Pd(OOCCF_3)_2$ (0.0066 g, 0.02 mmol), Ag_2CO_3 (0.1103 g, 0.4 mmol), PivOH (0.0512 g, 0.5 mmol), 2.4.5-trimethoxybenzoic acid (0.0424 g, 0.2 mmol), nitroethane (0.1 mL, 1.4 mmol), DMSO (0.2 mL) and 1,4-dioxane (2.0mL). The reaction mixture was stirred at 100 °C

for 24 h. After extraction and concentration, the reaction mixture was purified by column chromatography on silica gel (20% ethyl acetate/petroleum ether) afforded a reddish-orange solid (70% yield). This compound is known.[1] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 13.5 Hz, 1H), 7.76 (d, *J* = 13.5 Hz, 1H), 6.88 (s, 1H), 6.51 (s, 1H), 3.95 (s, 3H), 3.93 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.78, 153.95, 143.41, 135.87, 135.37, 113.69, 110.45, 96.39, 56.53, 56.18, 56.16.

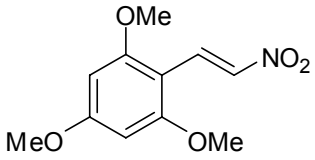
(*E*)-2,6-dimethoxy-β-nitrostyrene



3c

The reaction was performed following the general procedure with $Pd(OOCF_3)_2$ (0.0066 g, 0.02 mmol), Ag_2CO_3 (0.1103 g, 0.4 mmol), PivOH (0.0512 g, 0.5 mmol) 2.6-dimethoxybenzoic acid (0.0364 g, 0.2 mmol), nitroethane (0.1 mL,1.4 mmol), DMSO (0.3 mL) and 1,4-dioxane (2.0 mL). The reaction mixture was stirred at 80 °C for 24 h. After extraction and concentration, the reaction mixture was purified by column chromatography on silica gel (10% ethyl acetate/petroleum ether) afforded a yellow solid (74% yield). This compound is known.[2] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55 (d, J = 13.6 Hz, 1H), 8.07 (d, J = 13.6 Hz, 1H), 7.38 (t, J = 8.4 Hz, 1H), 6.58 (d, J = 8.5 Hz, 2H), 3.93 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.72, 138.88, 133.61, 129.83, 108.60, 103.69, 55.99. Anal. Calcd. For $C_{10}H_{11}NO_4$: C, 57.41; H, 5.30; N, 6.70, Found: C, 57.63; H, 5.28; N, 6.50.

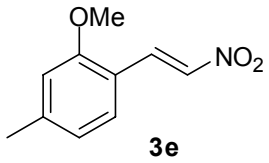
(*E*)-2,4,6-trimethoxy-β-nitrostyrene



3d

The reaction was performed following the general procedure with $Pd(OOCCF_3)_2$ (0.0066 g, 0.02 mmol), Ag_2CO_3 (0.1103 g, 0.4 mmol), PivOH(0.0512 g, 0.5 mmol), 2,4,6-trimethoxybenzoic acid (0.0424 g, 0.2 mmol), nitroethane (0.1 mL, 1.4 mmol), DMSO (0.8 mL) and 1,4-dioxane (1.2 mL). The reaction mixture was stirred at 100 °C for 24 h. After extraction and concentration, the reaction mixture was purified by column chromatography on silica gel (10% ethyl acetate/petroleum ether) afforded a yellow solid (28% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (d, J = 13.5 Hz, 1H), 7.98 (d, J = 13.5 Hz, 1H), 6.12 (s, 2H), 3.91 (s, 6H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.97, 162.14, 136.31, 130.28, 102.27, 90.59, 55.92, 55.56. Anal. Calcd. for $C_{11}H_{13}NO_5$: C, 55.23; H, 5.48; N, 5.86. Found: C, 55.42; H, 5.43; N, 5.73.

(*E*)-2-methoxy-4-methyl-β-nitrostyrene

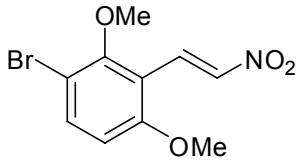


3e

The reaction was performed following the general procedure with $Pd(OOCCF_3)_2$ (0.0066 g, 0.02 mmol), Ag_2CO_3 (0.1103 g, 0.4 mmol), PivOH (0.0512 g, 0.5 mmol) 2-methoxy-4-methylbenzoic acid (0.0332 g, 0.2 mmol), nitroethane (0.1 mL,1.4 mmol), DMSO (0.1 mL) and 1,4-dioxane (2.0 mL). The reaction mixture was stirred at 120 °C for 24 h. After extraction and concentration, the reaction mixture was purified by column chromatography on silica gel (5% ethyl acetate/petroleum ether) afforded a yellow solid (65% yield). This compound is known.[3] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 13.5 Hz, 1H), 7.85 (d, *J* = 13.5 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 1H), 6.83 (d, *J* = 7.7 Hz, 1H), 6.78 (s, 1H), 3.93 (s, 3H), 2.41 (s, 3H); ^{13}C NMR

(100MHz, $CDCl_3$): δ 159.55, 144.84 , 137.44, 135.65, 132.50, 122.04, 116.51, 112.20, 55.55, 22.12.

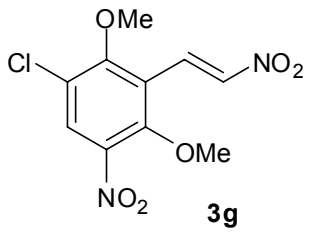
(*E*)-3-bromo-2,6-dimethoxy-β-nitrostyrene



3f

The reaction was performed following the general procedure with $Pd(OOCCF_3)_2$ (0.0066 g, 0.02 mmol), Ag_2CO_3 (0.1103 g, 0.4 mmol), 3-bromo-2,6-dimethoxybenzoic acid (0.0522 g, 0.2 mmol), nitroethane (0.1 mL, 1.4 mmol), DMSO (0.1 mL) and 1,4-dioxane (2.0 mL). The reaction mixture was stirred at 100 °C for 24 h. After extraction and concentration, the reaction mixture was purified by column chromatography on silica gel (5% ethyl acetate/petroleum ether) afforded a yellow solid (52% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 13.7 Hz, 1H), 8.08 (d, *J* = 13.7 Hz, 1H), 7.59 (d, *J* = 9.0 Hz, 1H), 6.67 (d, *J* = 9.0 Hz, 1H), 3.94 (s, 3H), 3.88 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ 159.72, 158.14, 140.56, 136.48, 129.21, 115.30, 108.67, 108.49, 61.76, 56.30. Anal. Calcd. for $C_{10}H_{10}BrNO_4$: C, 41.69; H, 3.50; N, 4.86; Found: C, 41.99; H, 3.42; N, 4.49.

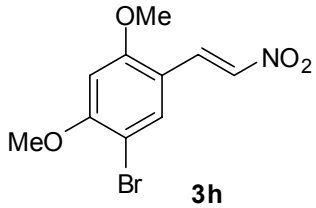
(*E*)-3-chloro-2,6-dimethoxy-5-nitro-β-nitrostyrene



3g

The reaction was performed following the general procedure with $Pd(CH_3CN)_2Cl_2$ (0.0104 g, 0.04 mmol), Ag_2CO_3 (0.1103 g, 0.4 mmol) 3-chloro-2,6-dimethoxy-5-nitrobenzoic acid (0.0523 g, 0.2 mmol), nitroethane(0.1 mL,1.4 mmol), DMSO (0.04 mL) and 1,4-dioxane (2.0 mL). The reaction mixture was stirred at 100 °C for 24 h. After extraction and concentration, the reaction mixture was purified by column chromatography on silica gel (10% ethyl acetate/petroleum ether) afforded an orange yellow solid (40% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 13.8 Hz, 1H), 8.05 (s, 1H), 8.04 (d, *J* = 13.8 Hz, 1H), 4.00 (s, 3H), 3.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.15, 153.33, 142.54, 140.01, 129.36, 127.37, 123.96, 122.15, 63.57, 61.71. Anal. Calcd. For $C_{10}H_9ClN_2O_6$: C, 41.61; H, 3.14; N, 9.71; Found: C, 41.79; H, 3.05; N, 9.60.

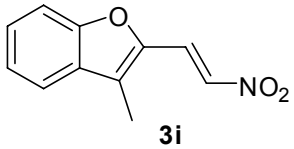
(*E*)-5-bromo-2,4-dimethoxy-β-nitrostyrene



3h

The reaction was performed following the general procedure with $Pd(OOCCF_3)_2$ (0.0066 g, 0.02 mmol), Ag_2CO_3 (0.1103 g, 0.4 mmol), PivOH (0.0512 g, 0.5 mmol) 5-bromo-2,4-dimethoxybenzoic acid (0.0522 g, 0.2 mmol), nitroethane (0.1 mL, 1.4 mmol), DMSO (0.1 mL) and 1,4-dioxane (2.0 ml). The reaction mixture was stirred at 100 °C for 24 h. After extraction and concentration, the reaction mixture was purified by column chromatography on silica gel (10% ethyl acetate/petroleum ether) afforded a yellow solid (73% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, J = 13.5 Hz, 1H), 7.76 (d, J = 13.5 Hz, 1H), 7.61 (s, 1H), 6.48 (s, 1H), 3.97 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.51, 159.83, 136.75, 135.87, 134.06, 113.12, 103.02, 95.98, 56.52, 56.03; Anal. Calcd. For $C_{10}H_{10}BrNO_4$: C, 41.69; H, 3.50; N, 4.86. Found: C, 42.17; H, 3.57; N, 4.64.

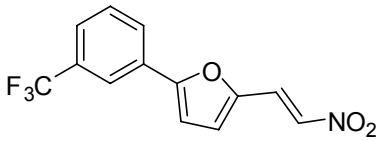
(*E*)-3-methyl-2-(2-nitro-vinyl)benzofuran



3i

The reaction was performed following the general procedure with $Pd(OOCF_3)_2$ (0.0066 g, 0.02 mmol), Ag_2CO_3 (0.1103 g, 0.4 mmol), PivOH (0.0512 g, 0.5 mmol) 3-methylbenzofuran-2-carboxylicacid (0.0352 g, 0.2 mmol), nitroethane(0.1 mL, 1.4 mmol), DMSO (0.2 mL) and 1,4-dioxane (2.0 mL). The reaction mixture was stirred at 100 °C for 24 h. After extraction and concentration, the reaction mixture was purified by column chromatography on silica gel (pure petroleum ether) afforded a orange-yellow solid (68% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 13.0 Hz, 1H), 7.67 (d, *J* = 13.0 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.48 – 7.44 (m, 2H), 7.34 – 7.27 (m, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.40, 144.45, 135.67, 129.32, 128.40, 126.58, 123.89, 123.45, 120.64, 111.57, 8.73; Anal. Calcd. For $C_{11}H_9NO_3$: C, 65.02; H, 4.46; N, 6.89, Found: C, 64.63; H, 4.47; N, 6.37.

(*E*)-2-(2-nitro-vinyl)-5-(3-(trifluoromethyl)phenyl)furan

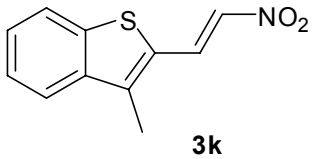


3j

The reaction was performed following the general procedure with $Pd(OOCCF_3)_2$ (0.0066 g, 0.02 mmol), Ag_2CO_3 (0.1103 g, 0.4 mmol), PivOH (0.0512 g, 0.5 mmol) 5-[3-(trifluoromethyl)phenyl]-2-furancarboxylic acid (0.0352 g, 0.2mmol), nitroethane (0.1 mL, 1.4 mmol), DMSO (0.2 mL) and 1,4-dioxane (2.0 mL). The reaction mixture was stirred at 100 °C for 24 h. After extraction and concentration, the

reaction mixture was purified by column chromatography on silica gel (1% ether /petroleum ether) afforded a orange-yellow solid (25% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (s, 1H), 7.92 (d, *J* = 7.7 Hz, 1H), 7.80 (d, *J* = 13.2 Hz, 1H), 7.68 – 7.55 (m, 3H), 7.00 (d, *J* = 3.7 Hz, 1H), 6.92 (d, *J* = 3.7 Hz, 1H), ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.93 (s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.51, 146.70, 134.87, 131.84, 131.52, 129.80, 129.64, 127.72, 125.79–125.66 (m), 124.94, 122.15, 121.53–121.32 (m), 109.76. Anal. Calcd. For $C_{13}H_8F_3NO_3$: C, 55.13; H, 2.85; N, 4.95. Found: C, 55.27; H, 2.63; N, 4.79.

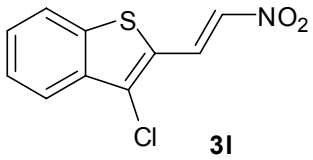
(*E*)-3-methyl-2-(2-nitrovinyl)benzothiophene



3k

The reaction was performed following the general procedure with $Pd(OOCCF_3)_2$ (0.0066 g, 0.02 mmol), Ag_2CO_3 (0.1103 g, 0.4 mmol), PivOH (0.0512 g,0.5 mmol) 3-methylbenzo[b]thiophene-2-carboxylic acid (0.0384 g, 0.2 mmol), nitroethane (0.1 mL,1.4 mmol), DMSO (0.1 mL) and 1,4-dioxane (2.0 mL). The reaction mixture was stirred at 110 °C for 24 h. After extraction and concentration, the reaction mixture was purified by column chromatography on silica gel (1% ether/petroleum ether) afforded a yellow solid (67% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (d, *J* = 13.2 Hz, 1H), 7.86-7.72 (m, 2H), 7.52–7.39 (m, 3H), 2.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.61, 140.00, 139.92, 136.38, 130.83, 128.20, 127.97, 125.06, 123.37, 122.65, 12.52. Anal. Calcd. for $C_{11}H_9NO_2S$: C, 60.26; H, 4.14; N, 6.39; Found: C, 59.94; H, 3.73; N, 6.06.

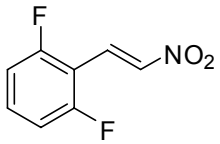
(*E*)-3-chloro-2-(2-nitrovinyl)benzothiophene



3l

The reaction was performed following the general procedure with $Pd(OOCCF_3)_2$ (0.0066 g, 0.02 mmol), Ag_2CO_3 (0.1103 g, 0.4 mmol), 3-chlorobenzo[b]thiophene-2-carboxylic acid (0.0425 g, 0.2 mmol), nitroethane (0.1 mL, 1.4 mmol), DMSO (0.1 mL) and 1,4-dioxane (2.0 mL). The reaction mixture was stirred at 110 °C for 24 h. After extraction and concentration, the reaction mixture was purified by column chromatography on silica gel (2% ethyl acetate/petroleum ether) afforded a yellow solid (64% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (d, J = 13.5 Hz, 1H), 7.89 – 7.85 (m, 1H), 7.80 – 7.77 (m, 1H), 7.55 – 7.46 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.96, 137.63, 136.44, 129.52, 129.03, 128.73, 126.85, 125.96, 123.26, 122.78. Anal. Calcd. for $C_{10}H_6ClNO_2S$: C, 50.11; H, 2.52; N, 5.84; Found: C, 50.21; H, 2.51; N, 5.64.

(*E*)-2,6-difluoro-β-nitrostyrene

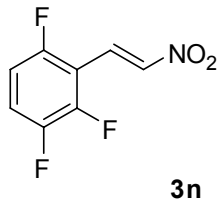


3m

The reaction was performed following the general procedure with $Pd(CH_3CN)_2Cl_2$ (0.0104 g, 0.04 mmol), Ag_2CO_3 (0.1103 g, 0.4 mmol), 2,6-Difluorobenzoic acid (0.0316 g, 0.2 mmol), nitroethane (0.1 mL, 1.4 mmol), DMSO (0.04 mL) and 1,4-dioxane (2.0 mL). The reaction mixture was stirred at 110 °C for 24 h. After extraction and concentration, the reaction mixture was purified by column chromatography on silica gel (5% ether /petroleum ether) afforded a orange-yellow solid (63% yield). This compound is known.[4] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, J = 13.9 Hz, 1H), 7.84 (d, J = 13.9 Hz, 1H), 7.50 – 7.41 (m, 1H), 7.03 (t, J = 8.7 Hz,

2H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -107.06 (s); ^{13}C NMR (100MHz, $CDCl_3$): δ 162.13 (d, J = 6.2 Hz), 159.57 (d, J = 6.2 Hz), 140.15 (t, J = 10.3 Hz), 132.50 (t, J = 11.2 Hz), 124.32 (t, J = 2.4 Hz), 111.09-111.35 (m), 107.67 (t, J = 15.5 Hz).

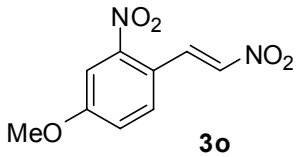
(E)-2,3,6-trifluoro-β-nitrostyrene



3n

The reaction was performed following the general procedure with $Pd(CH_3CN)_2Cl_2$ (0.0104 g, 0.04 mmol), Ag_2CO_3 (0.1103 g, 0.4 mmol), 2,4,6-trifluorobenzoic acid (0.0352 g, 0.2 mmol), nitroethane (0.1 mL, 1.4 mmol), DMSO (0.04 mL) and 1,4-dioxane (2.0 mL). The reaction mixture was stirred at 110 °C for 24 h. After extraction and concentration, the reaction mixture was purified by column chromatography on silica gel (5% ether /petroleum ether) afforded an orange-yellow solid (60% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, *J* = 14.0 Hz, 1H), 7.86 (d, *J* = 14.0 Hz, 1H), 7.36 – 7.26 (m, 1H), 7.04 – 6.96 (m, 1H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -112.24 (d, *J* = 15.5 Hz), -130.75 (d, *J* = 19.9 Hz), -140.33 (dd, *J* = 19.9, 15.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.28 – 157.11 (m), 154.78 – 154.58 (m), 149.84 – 149.52 (m), 147.65 – 147.42 (m), 147.27 – 146.94 (m), 145.18 – 144.94 (m), 140.90 (t, *J* = 10.1 Hz), 123.67 – 123.49 (m), 119.40 – 118.99 (m), 110.93 – 110.45 (m), 109.52 – 109.02 (m). Anal. Calcd. for $C_8H_4F_3NO_2$: C, 47.31; H, 1.98; N, 6.90 ; Found: C, 47.22; H, 2.24; N, 6.87.

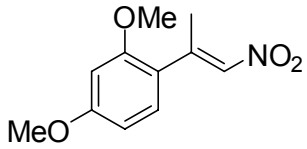
(*E*)-4-methoxy-2-nitro-β-nitrostyrene



3o

The reaction was performed following the general procedure with $Pd(CH_3CN)_2Cl_2$ (0.0104 g, 0.04 mmol), Ag_2CO_3 (0.1103 g, 0.4 mmol), 4-methoxy-2-nitrobenzoic acid (0.0394 g, 0.2 mmol), nitroethane (0.1 mL, 1.4 mmol), DMSO (0.04 ml) and 1,4-dioxane (2.0 mL). The reaction mixture was stirred at 130 °C for 24h. After extraction and concentration, the reaction mixture was purified by column chromatography on silica gel (20% ethyl acetate/petroleum ether) afforded a light-yellow solid (53% yield). ^{1}H NMR (400 MHz, Acetone): δ 8.40 (d, J = 13.5 Hz, 1H), 7.97 (d, J = 8.8 Hz, 1H), 7.88 (d, J = 13.5 Hz, 1H), 7.69 (d, J = 2.6 Hz, 1H), 7.41 (dd, J = 8.8, 2.6 Hz, 1H), 4.02 (s, 3H); ^{13}C NMR (100 MHz, Acetone): δ 205.29, 162.41, 139.03, 134.17, 131.06, 119.79, 117.43, 110.42, 56.01. Anal. Calcd. for $C_9H_8N_2O_5$: C, 48.22; H, 3.60; N, 12.50; Found: C, 48.99; H, 3.67; N, 12.02.

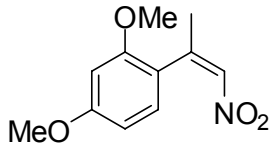
((E)-1-Methyl-2-nitro-vinyl)-2,4-dimethoxybenzene



The reaction was performed following the general procedure with $Pd(OOCCF_3)_2$ (0.0066 g, 0.02 mmol), Ag_2CO_3 (0.1103 g, 0.4 mmol), PivOH (0.0512 g, 0.5 mmol), 2.4-dimethoxybenzoic acid (0.0364 g, 0.2 mmol), 1-nitropropane (0.125 mL, 1.4 mmol), DMSO (0.2 mL) and 1,4-dioxane (2 mL). The reaction mixture was stirred at 100 °C for 24 h. After extraction and concentration, the reaction mixture was purified by column chromatography on silica gel (10% ether /petroleum ether) afforded a yellow solid (15% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, J = 1.1 Hz, 1H), 7.12 (d, J = 9.1 Hz, 1H), 6.50 (m, 2H), 3.84 (s, 3H), 3.83 (s, 3H), 2.55 (d, J = 1.1 Hz,

3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 162.25, 158.15, 149.62, 137.18, 129.90, 120.73, 104.59, 99.20, 55.55, 55.50, 19.97.

((Z)-1-Methyl-2-nitro-vinyl)-2,4-dimethoxybenzene



The reaction was performed following the general procedure with $Pd(OOCCF_3)_2$ (0.0066 g, 0.02 mmol), Ag_2CO_3 (0.1103 g, 0.4 mmol), PivOH (0.0512 g, 0.5 mmol), 2.4-dimethoxybenzoic acid (0.0364 g, 0.2 mmol), 1-nitropropane (0.125 mL, 1.4 mmol), DMSO (0.2 mL) and 1,4-dioxane (2 mL). The reaction mixture was stirred at 100 °C for 24 h. After extraction and concentration, the reaction mixture was purified by column chromatography on silica gel (10% ether /petroleum ether) afforded a yellow solid (9 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, J = 1.1 Hz, 1H), 7.01 (d, J = 8.4 Hz, 1H), 6.52 (dd, J = 8.4 Hz, 2.3 Hz, 1H), 6.48 (d, J = 2.3 Hz, 1H), 3.83 (s, 3H), 3.76 (s, 3H), 2.14 (d, J = 1.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.33, 156.60, 144.39, 135.03, 128.04, 118.68, 104.45, 98.65, 55.24, 55.18, 23.04.

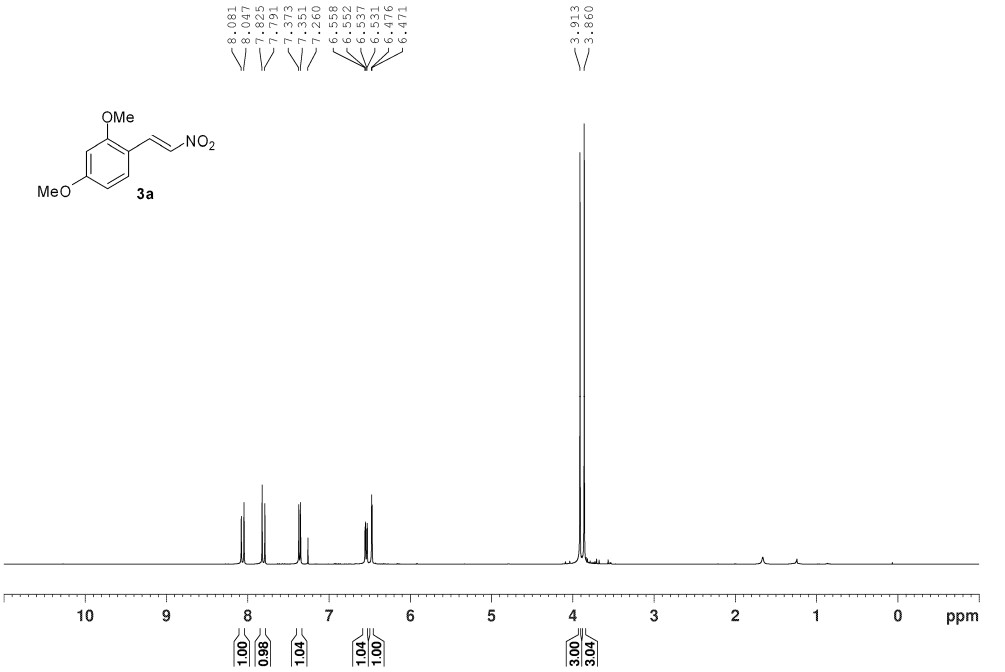
References:

(1) Buechi, G.; Mak, C.-P. *J. Org. Chem*. **1977***, 42,* 1784.

(2) Rao, A. S.; Srinivas, P. V.; Babu, S.; Rao, J. M. *Tetrahedron Lett.* **2005**, *46*, 8141.

(3) Gore, M. P.; Gould, S. J.; Weller, D. D. *J. Org. Chem*. **1992**, *57*, 2774.

(4) Jacobo, R.; Cota, A.; Rogel, E.; Garcia, J. D.; Rivero, I. A.; Hellberg, L. H.; Somanathan, R. *J. Fluorine Chem.* **1994**, *67*, 253.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6.471
3.913
3.860
OMe
NO2
MeO
3a
10
9
8
7
6
5
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3
2
1
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ppm
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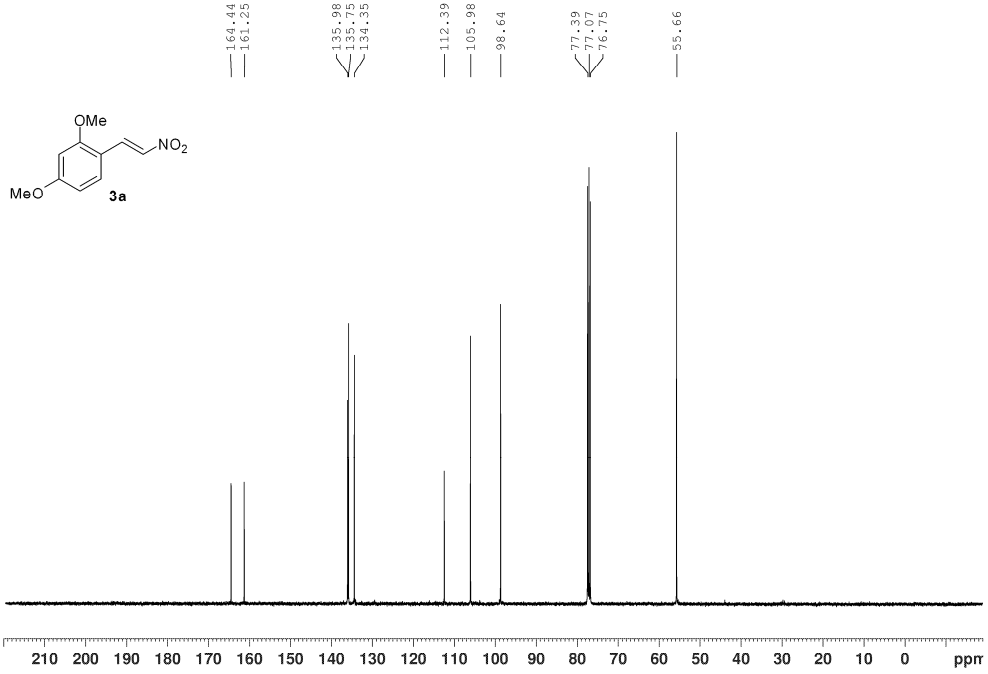
1.04
1.04
1.00
3.00
3.04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98.64
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NO2
MeO
3a
210
200
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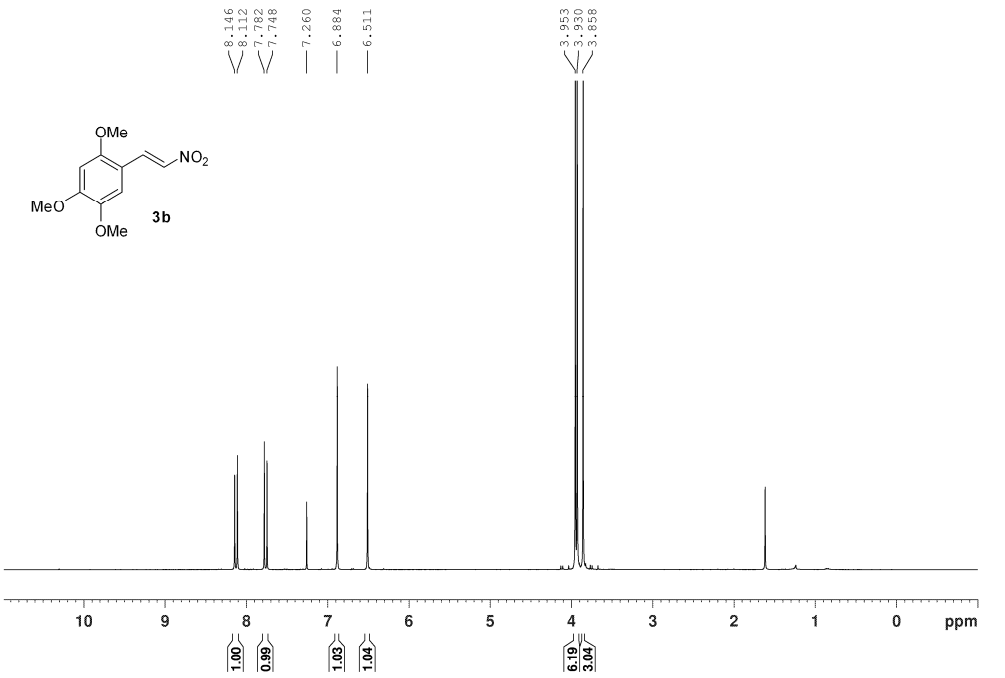
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3b
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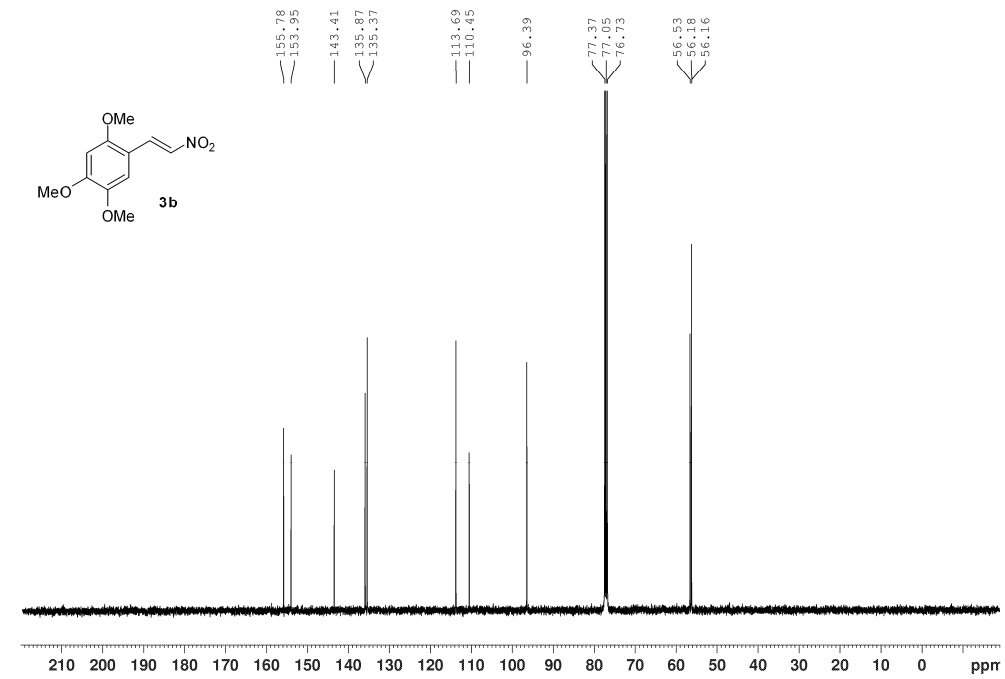
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56.18
56.16
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NO2
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OMe
3b
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200
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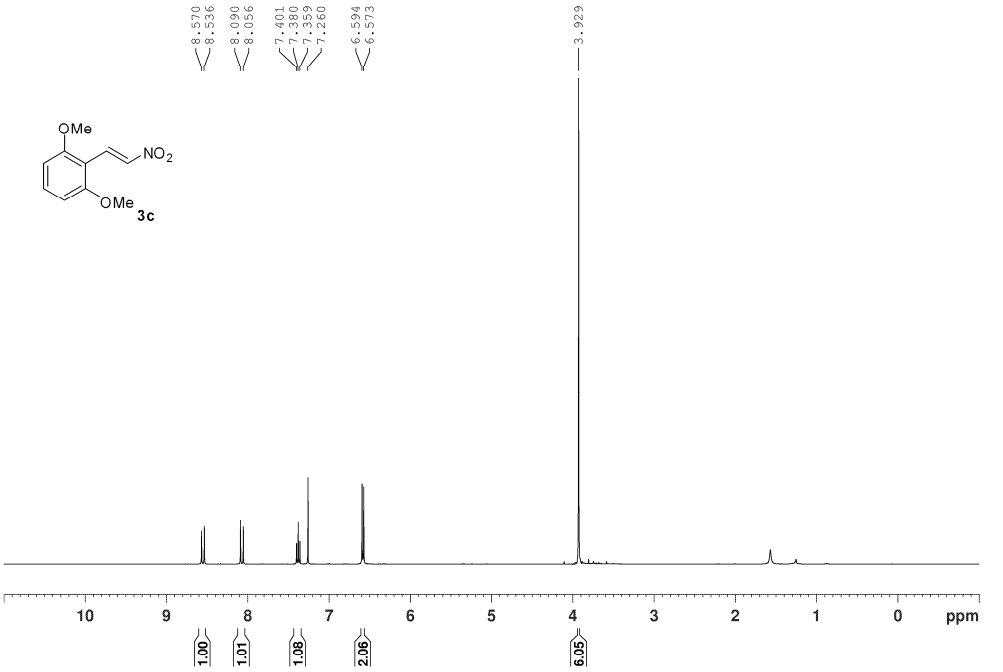
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3c
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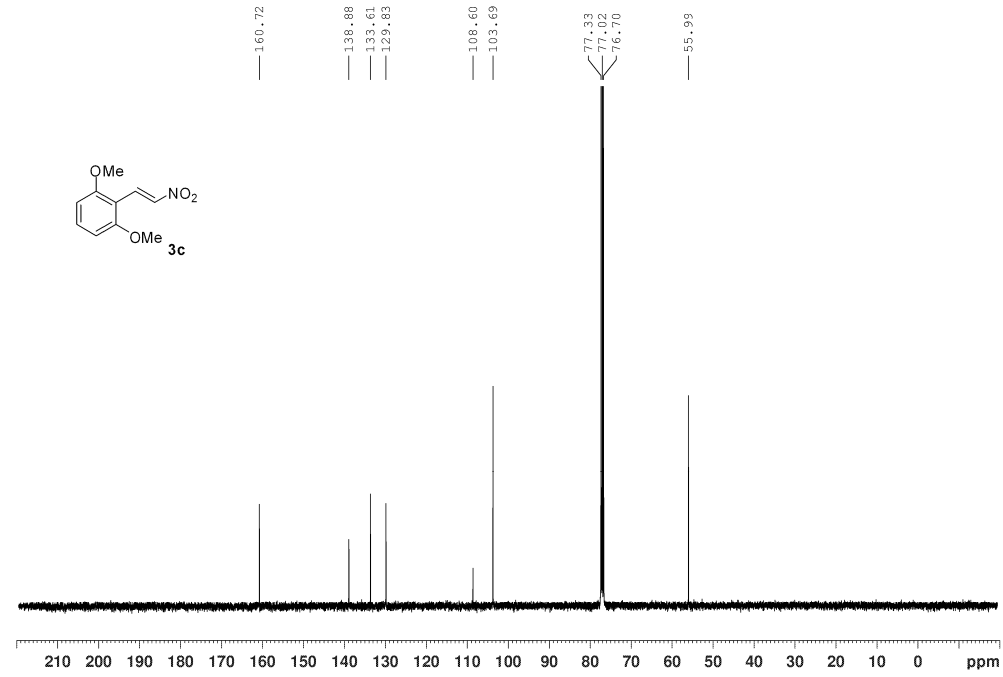
2.06
6.05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OMe
3c
210
200
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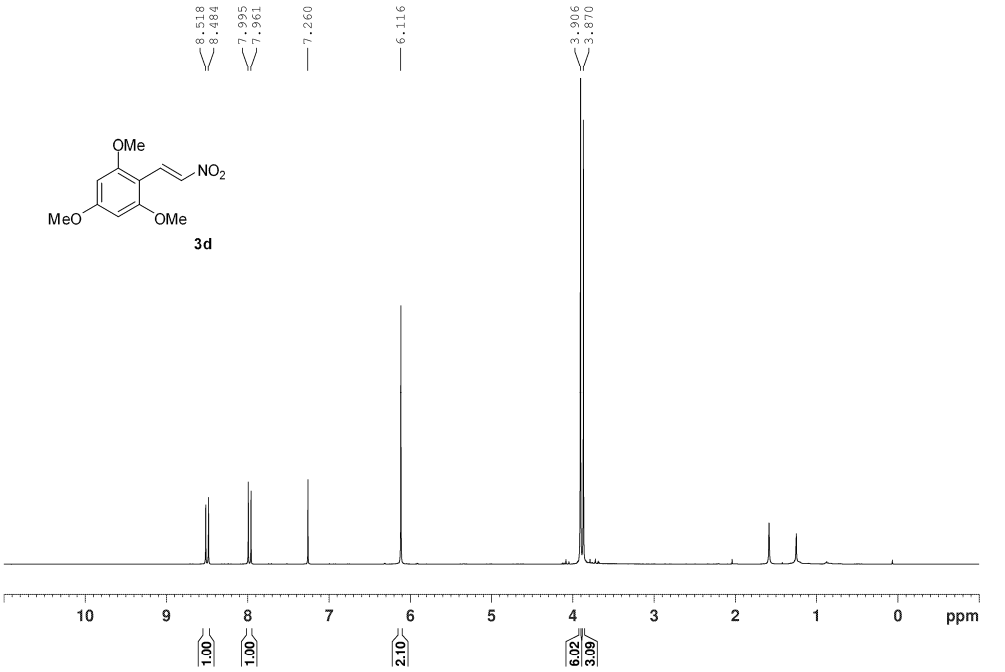
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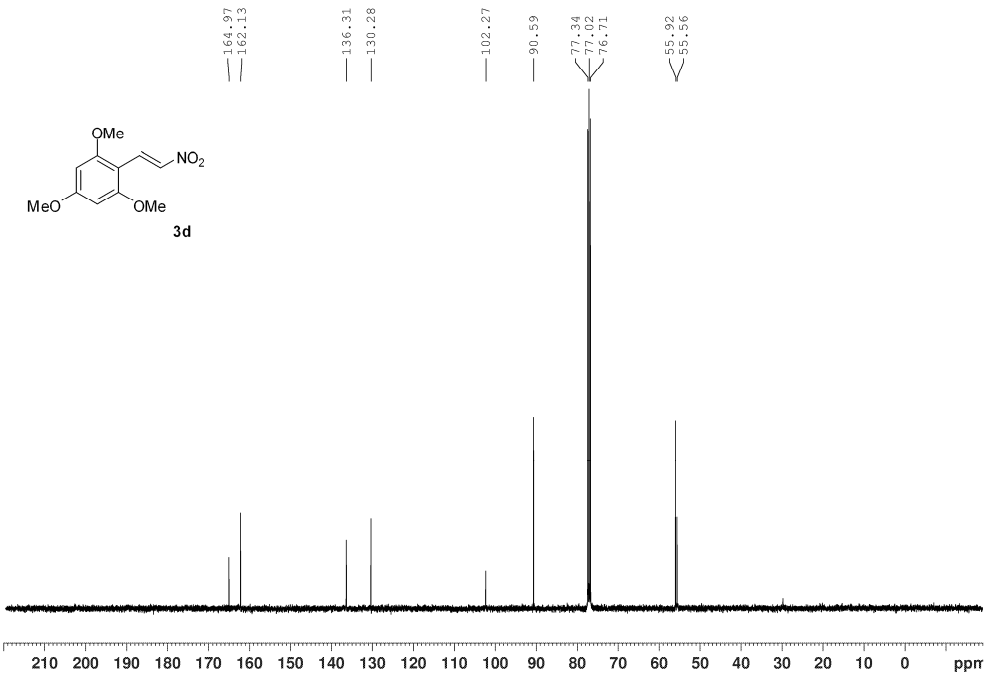
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OMe
3d
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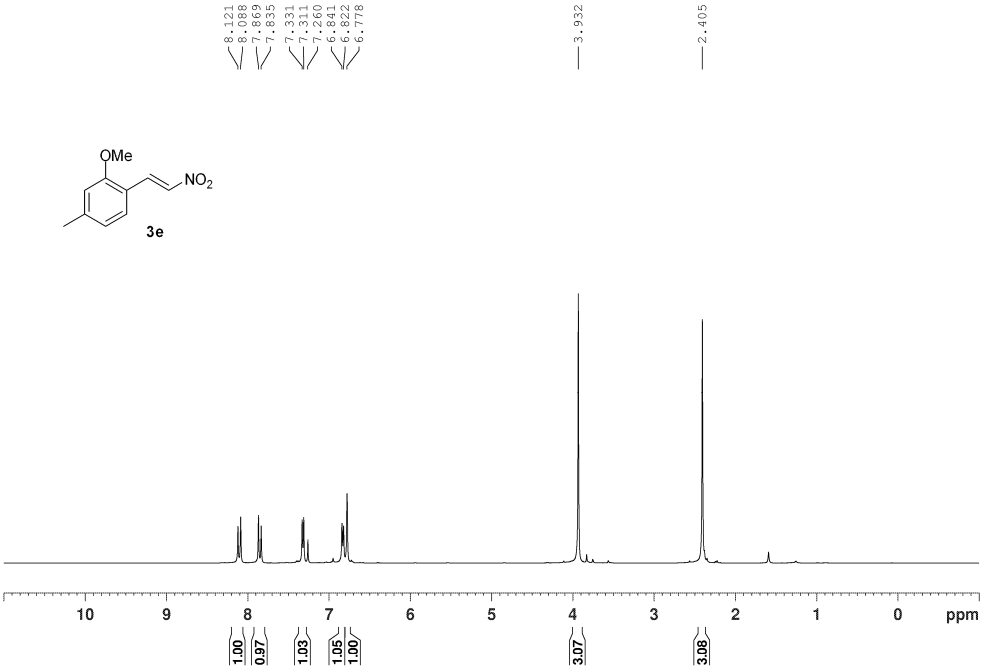
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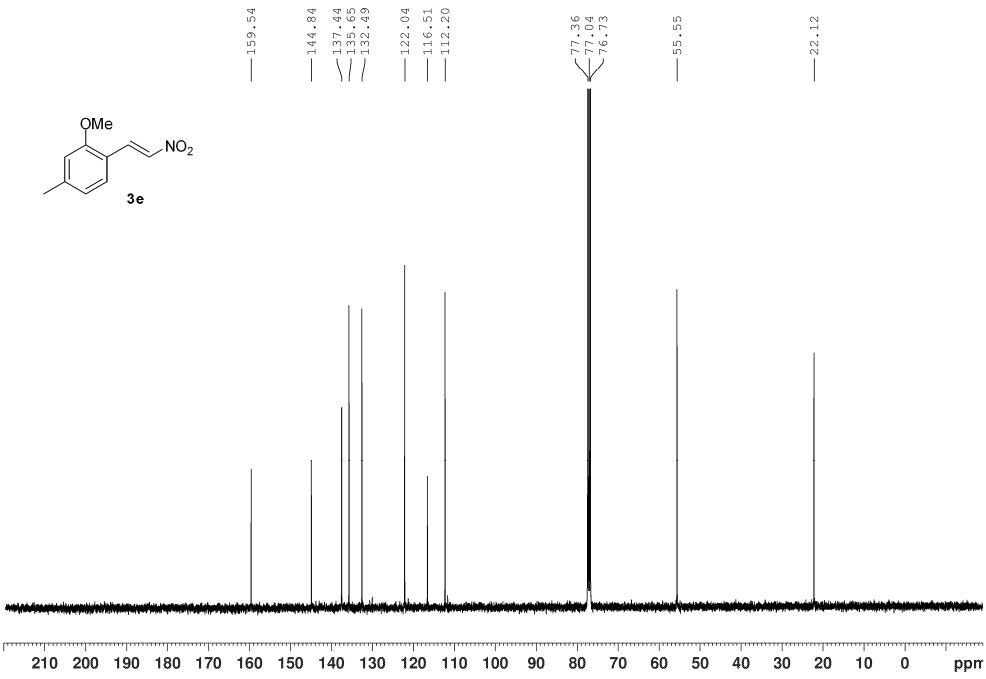
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NO2
3e
210
200
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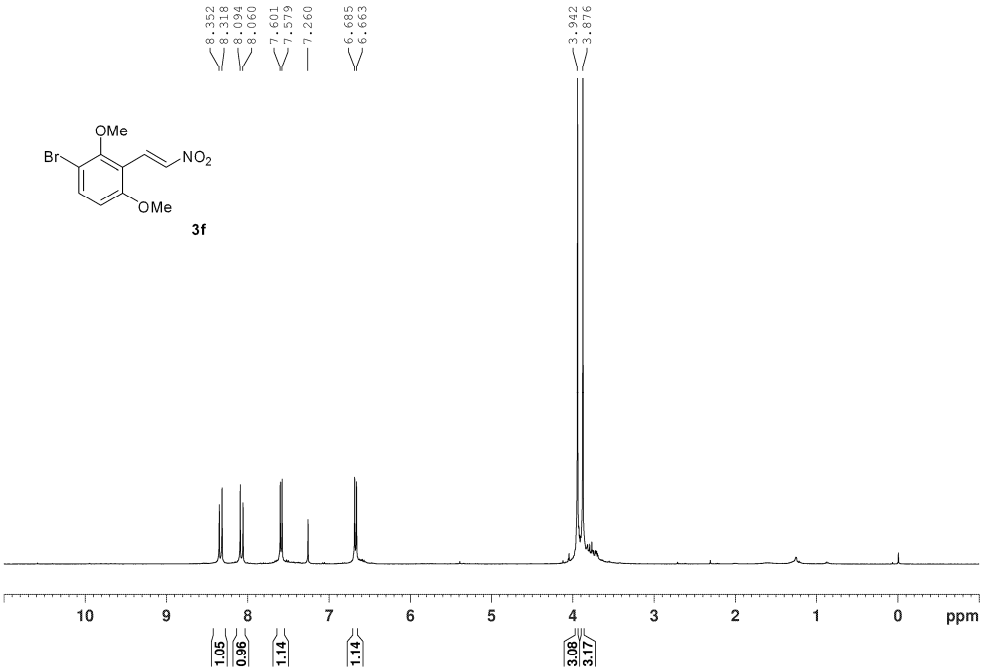
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3f
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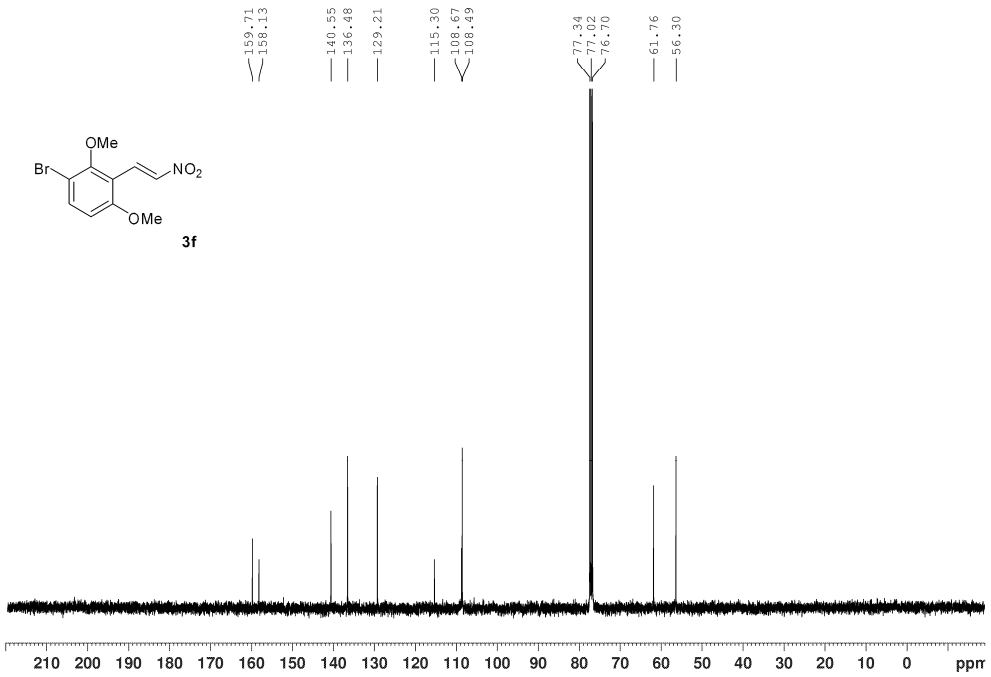
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3f
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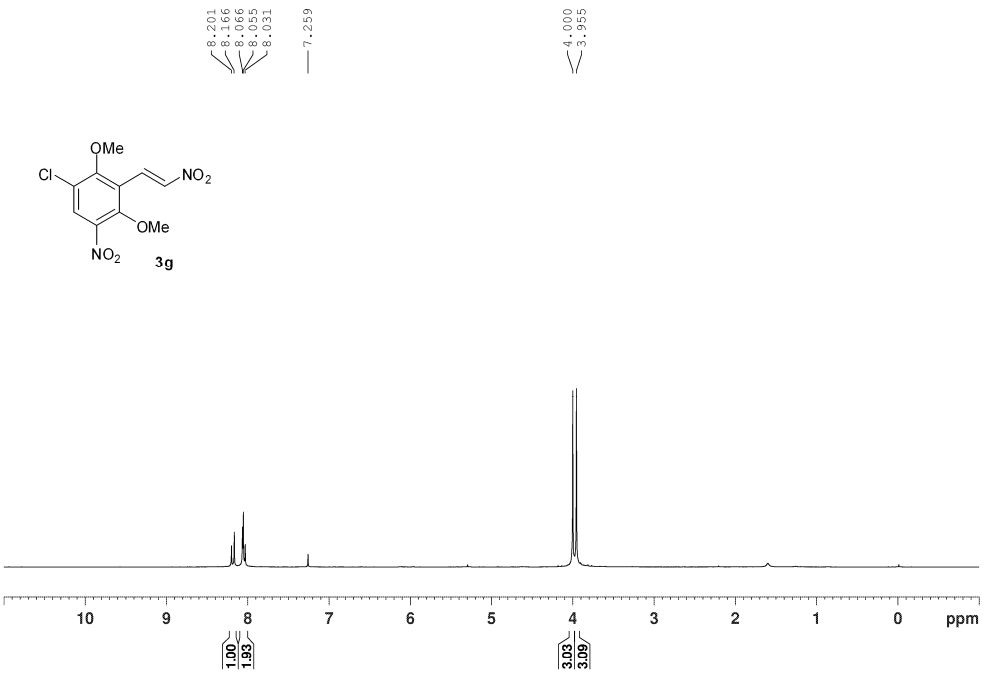
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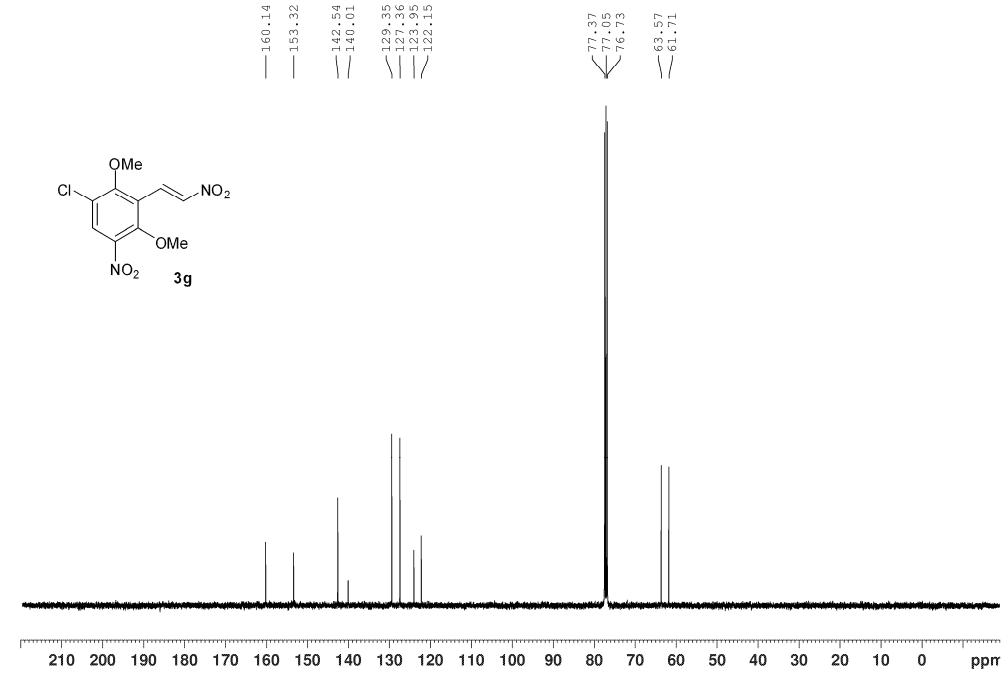
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Cl
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3g
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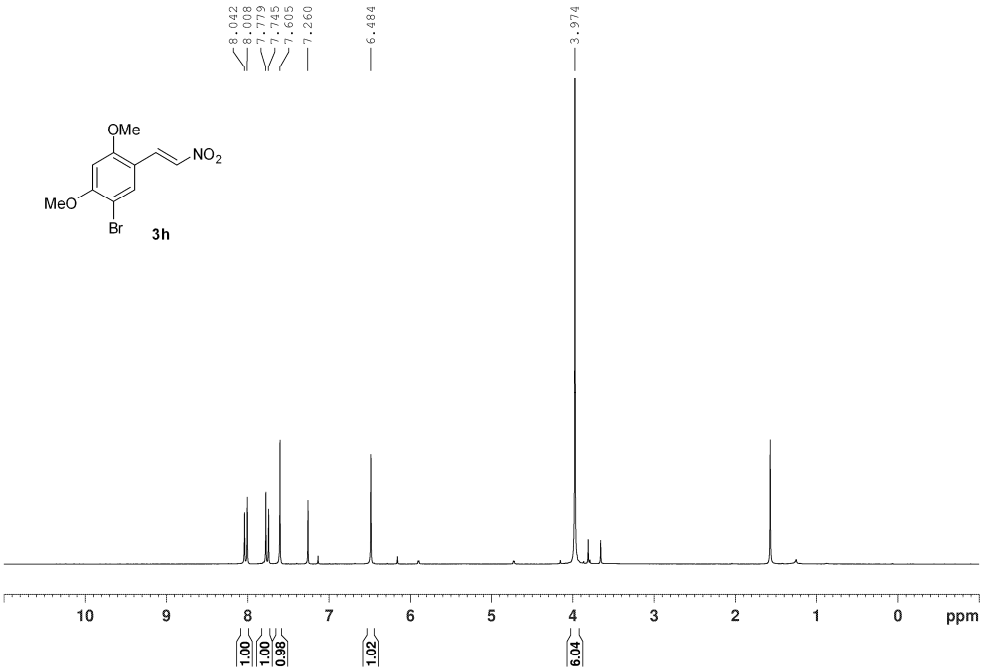
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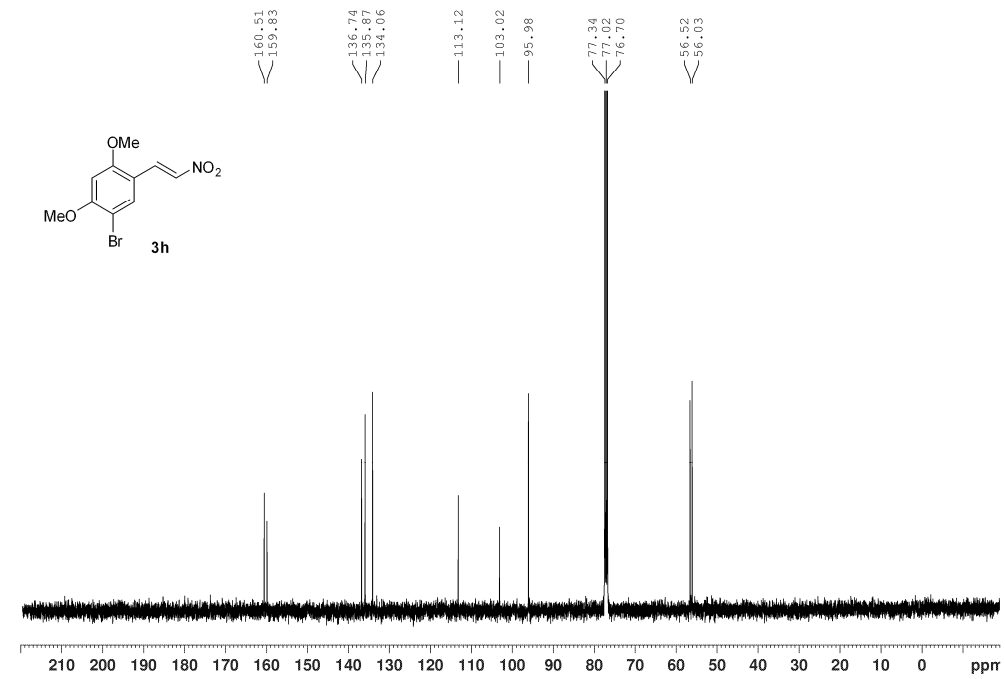
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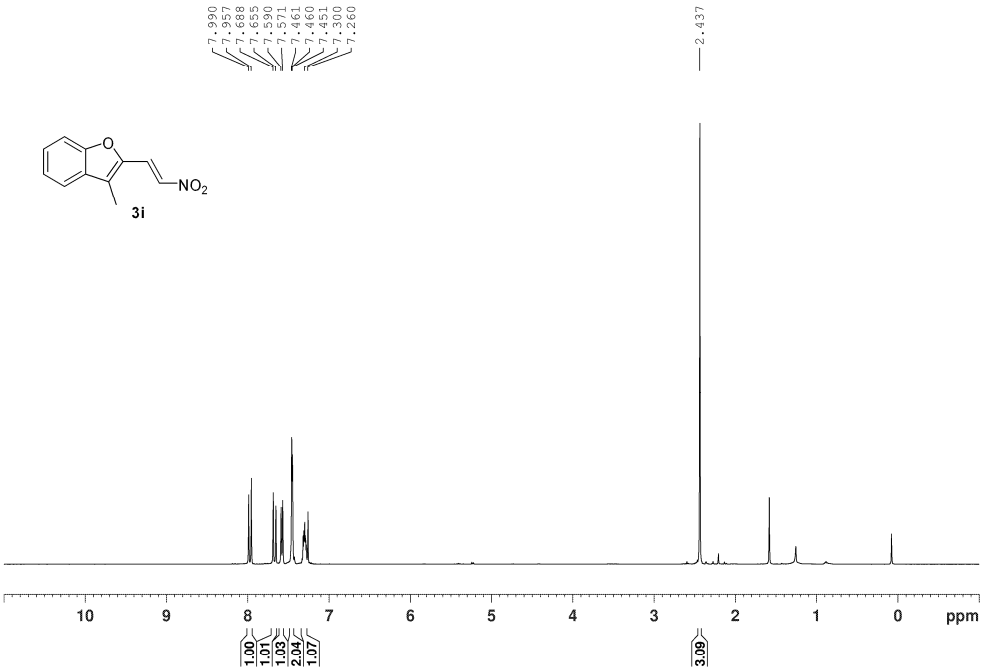
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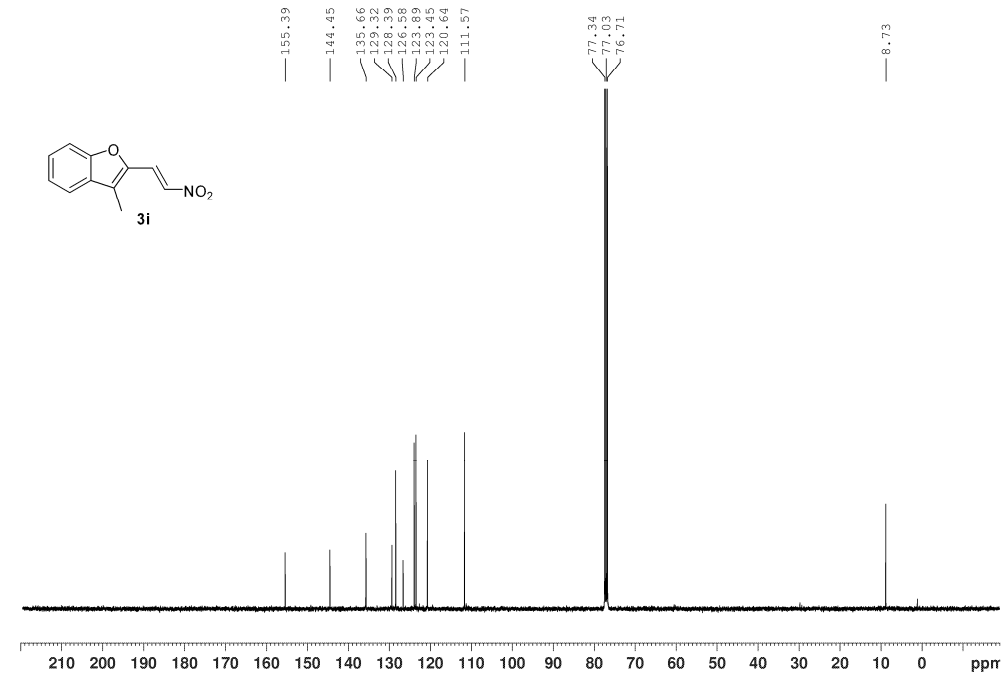
3.09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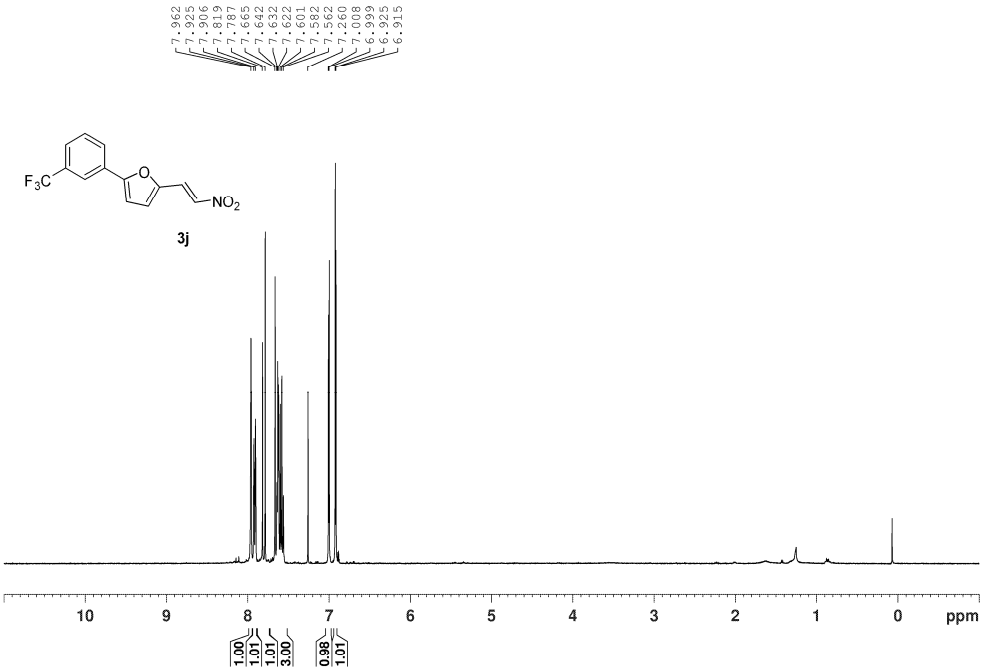
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6.925
6.915
F3C
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NO2
3j
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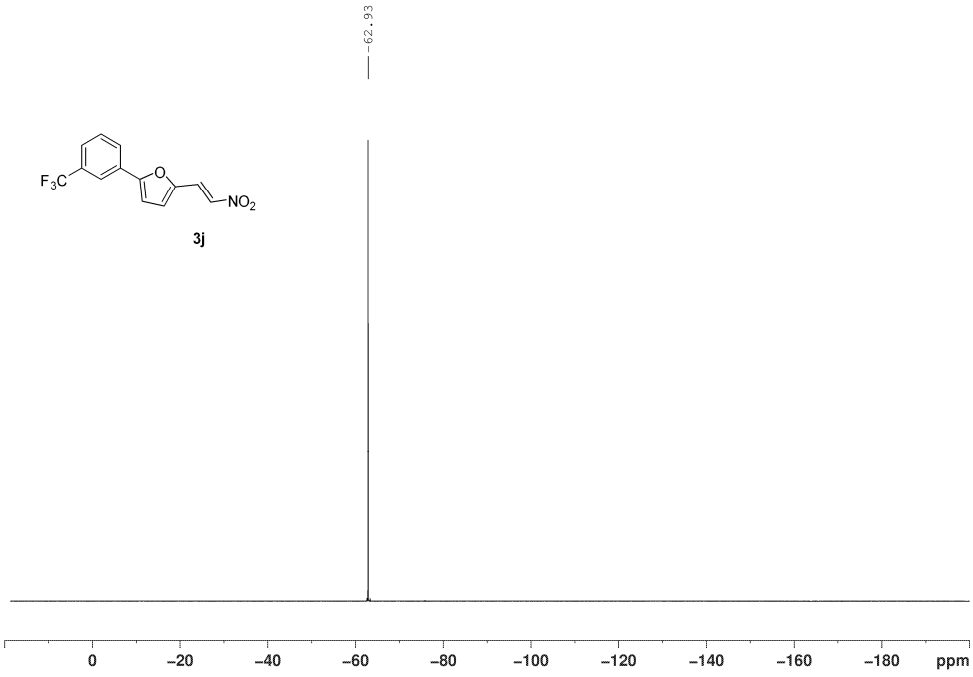
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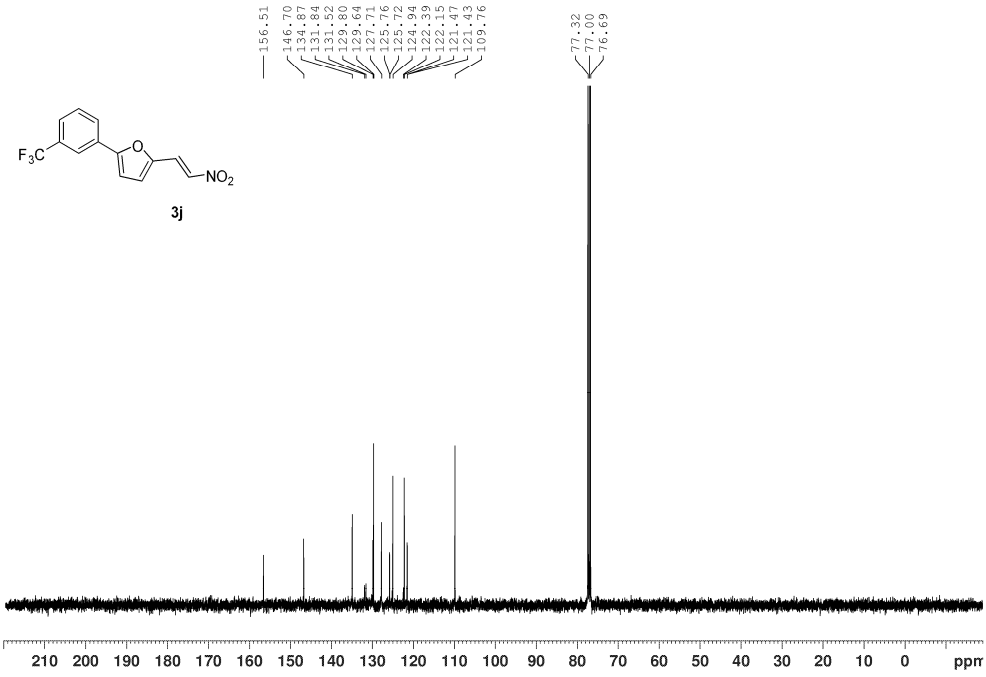
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O
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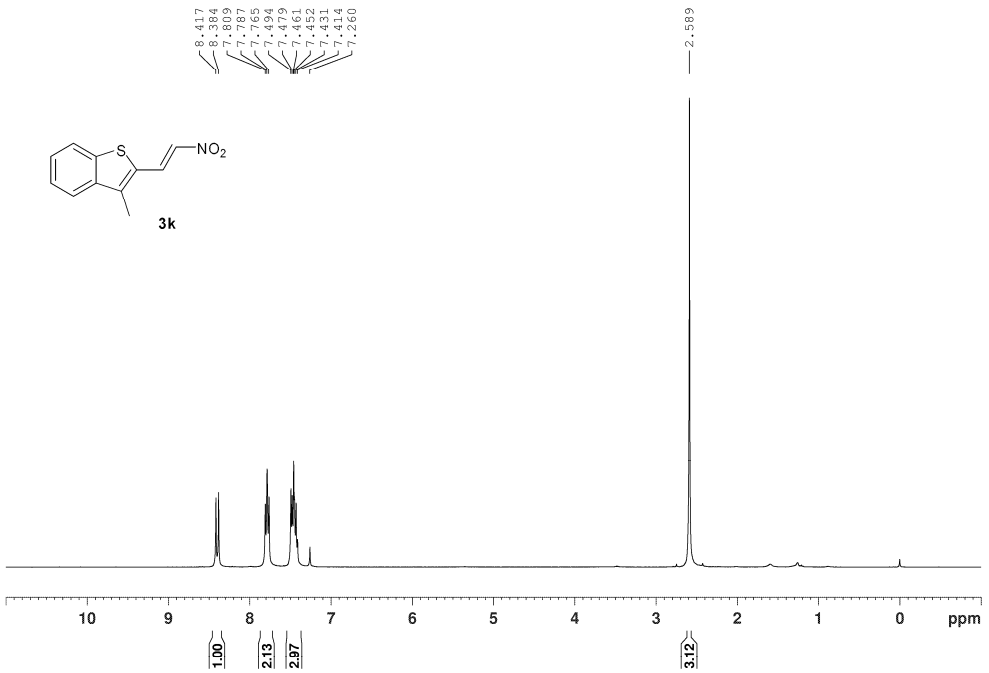
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S
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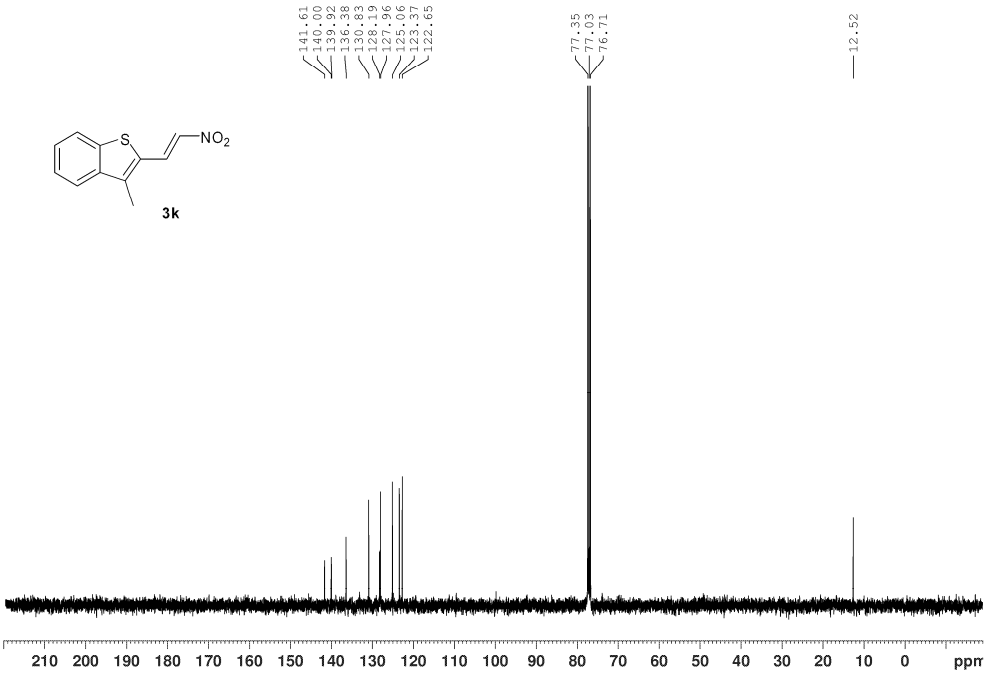
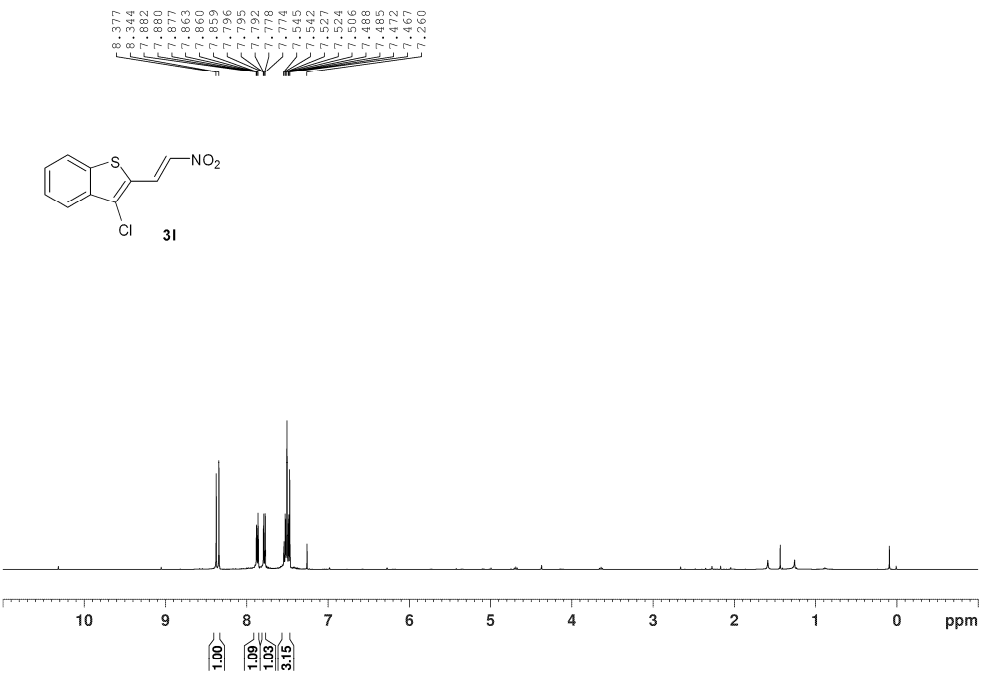
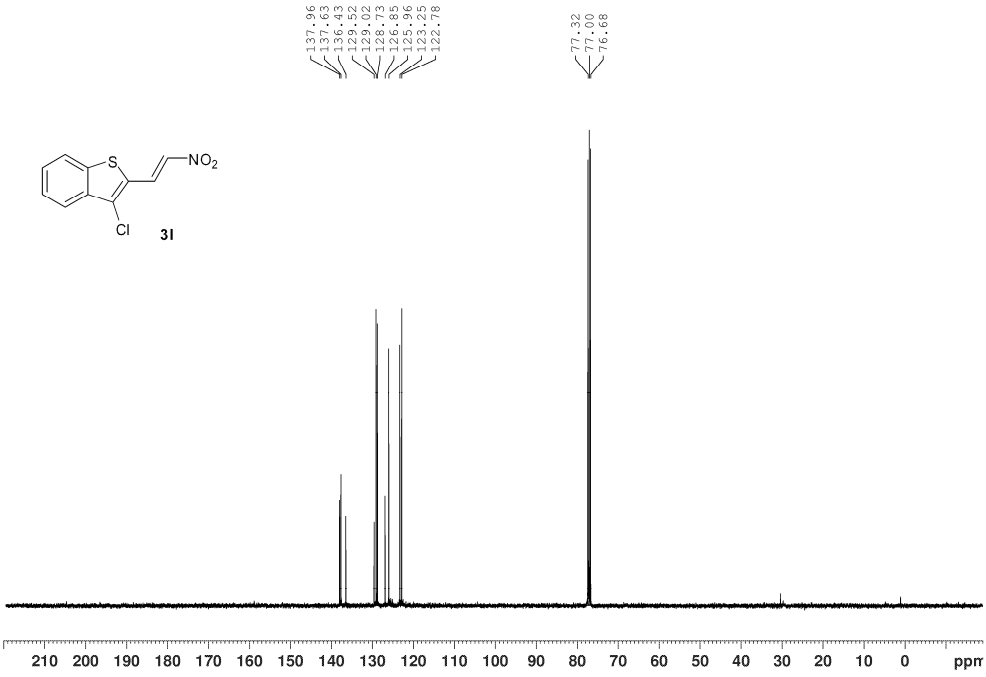
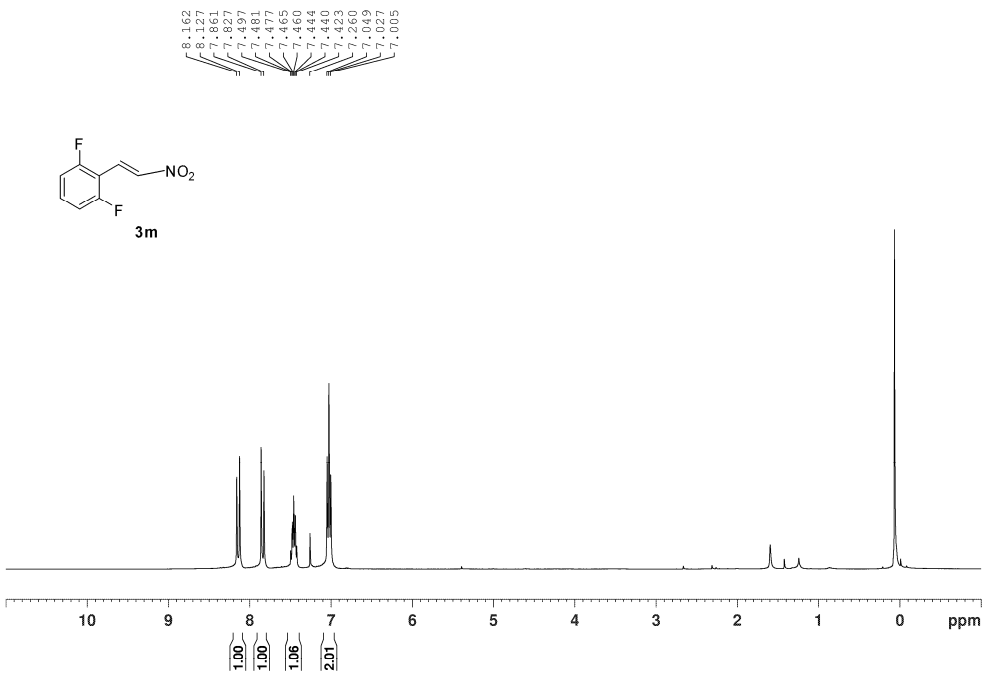
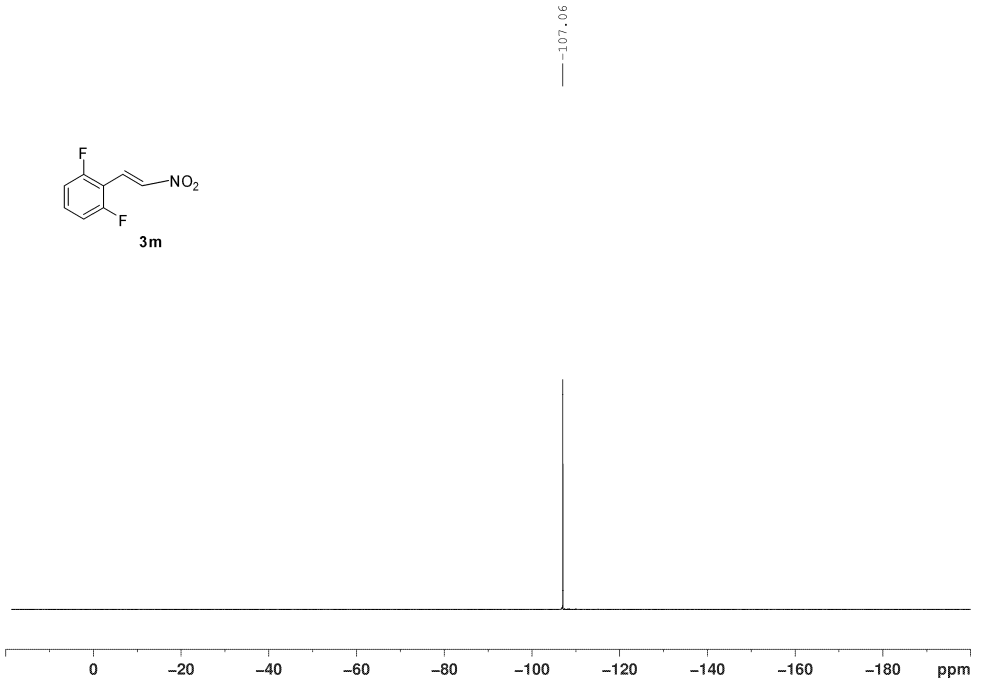
1.00
2.13
2.97
3.12

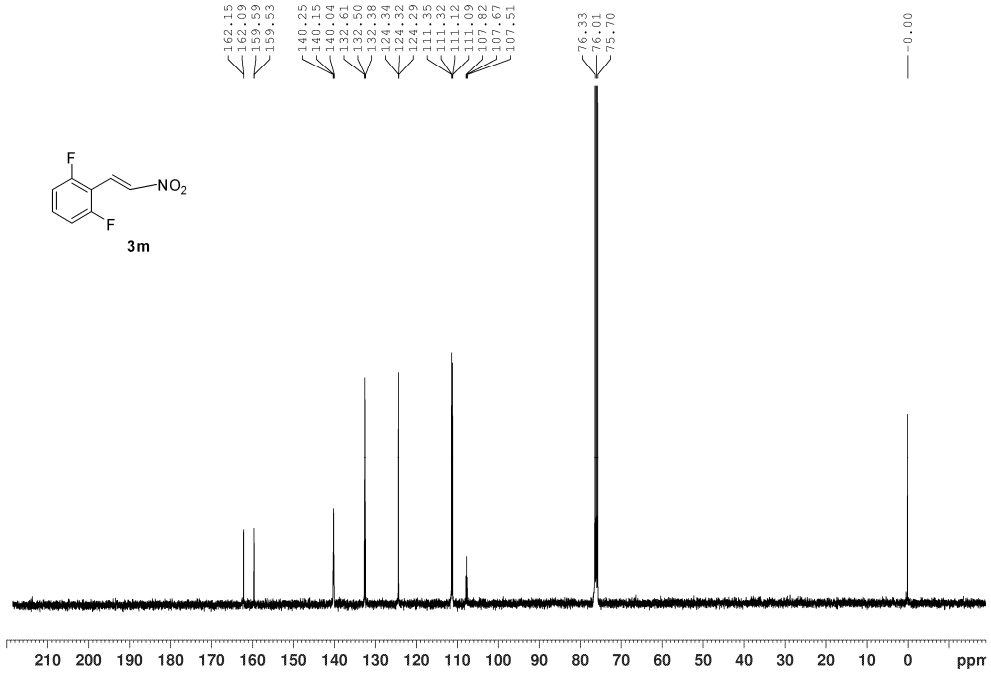

141.61
140.00
139.92
136.38
130.83
128.19
127.96
125.06
123.37
122.65
77.35
77.03
76.71
12.52
S
NO2
3k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

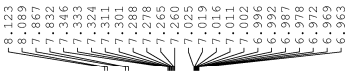

8.377
8.344
7.882
7.880
7.877
7.863
7.860
7.859
7.796
7.795
7.792
7.778
7.774
7.545
7.542
7.527
7.524
7.506
7.488
7.485
7.472
7.467
7.260
S
NO2
Cl
3l
10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
1.09
1.03
3.15

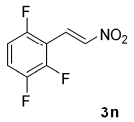

137.96
137.63
136.43
129.52
129.02
128.73
126.85
125.96
123.25
122.78
77.32
77.00
76.68
S
NO2
Cl
3l
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


8.162
8.127
7.861
7.827
7.497
7.481
7.477
7.465
7.460
7.444
7.440
7.423
7.260
7.049
7.027
7.005
F
NO2
F
3m
10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
1.00
1.06
2.01

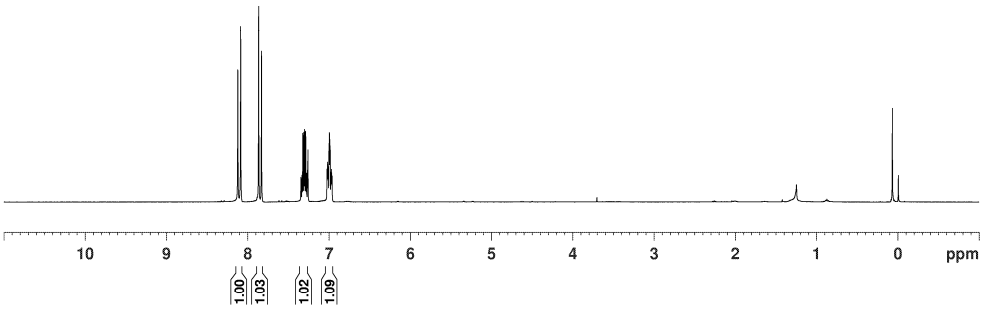

-107.06
F
NO2
F
3m
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

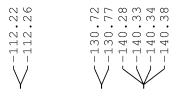

162.15
162.09
159.59
159.53
140.25
140.15
140.04
132.61
132.50
132.38
124.34
124.32
124.29
111.35
111.32
111.12
111.09
107.82
107.67
107.51
76.33
76.01
75.70
-0.00
F
NO2
F
3m
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

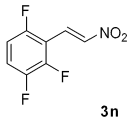

8.123
8.089
7.867
7.832
7.346
7.333
7.324
7.311
7.301
7.288
7.278
7.265
7.260
7.025
7.019
7.016
7.011
7.002
6.996
6.992
6.987
6.978
6.972
6.969
6.963


F
NO2
F
F

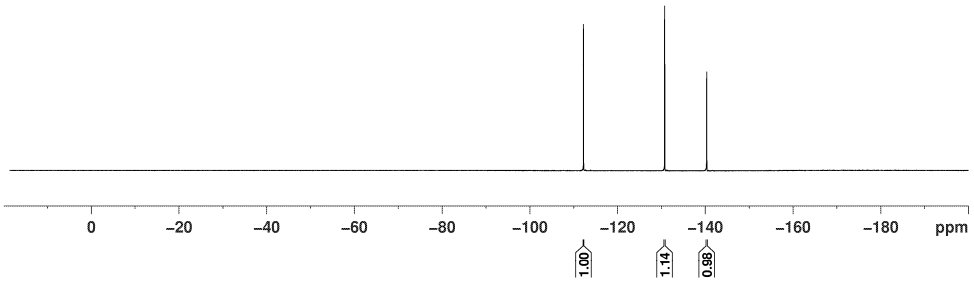
3n

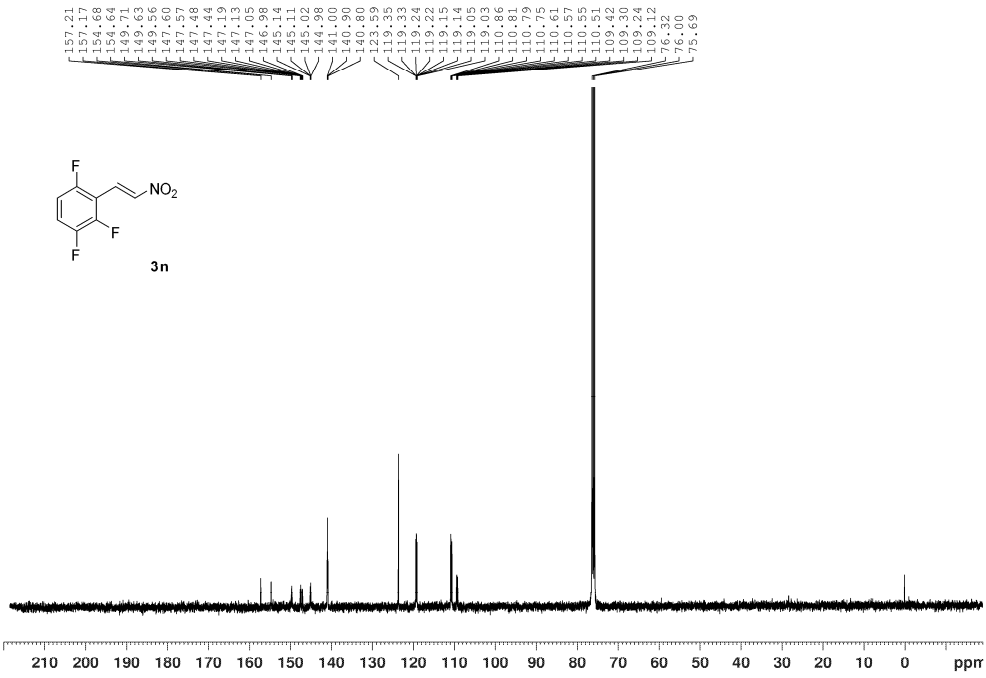

10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.03
1.02
1.09

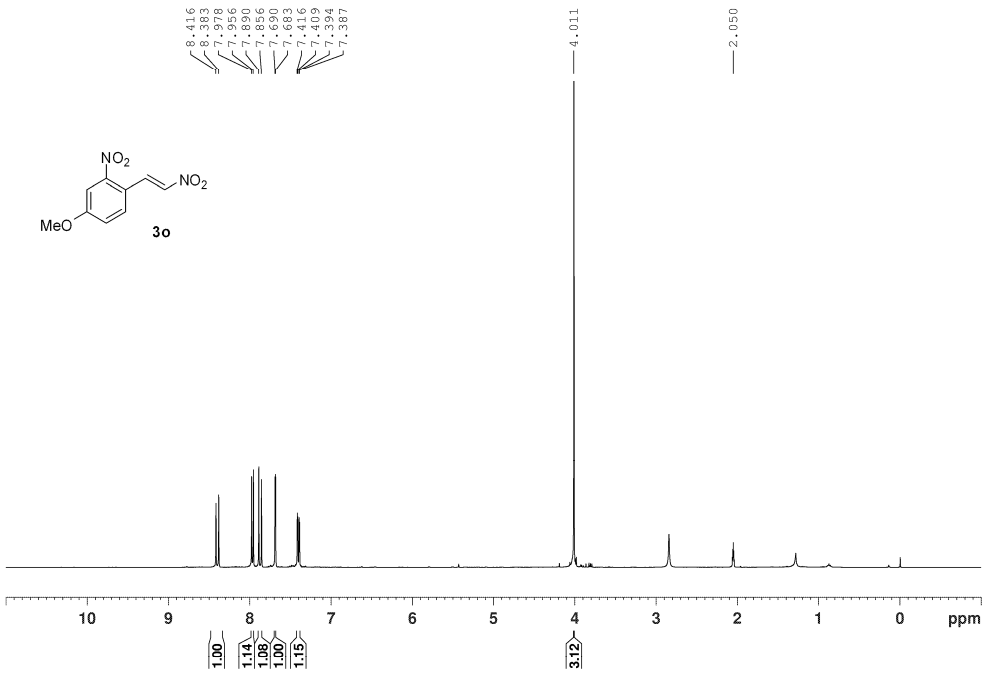

112.22
112.26
130.72
130.77
140.28
140.33
140.34
140.38

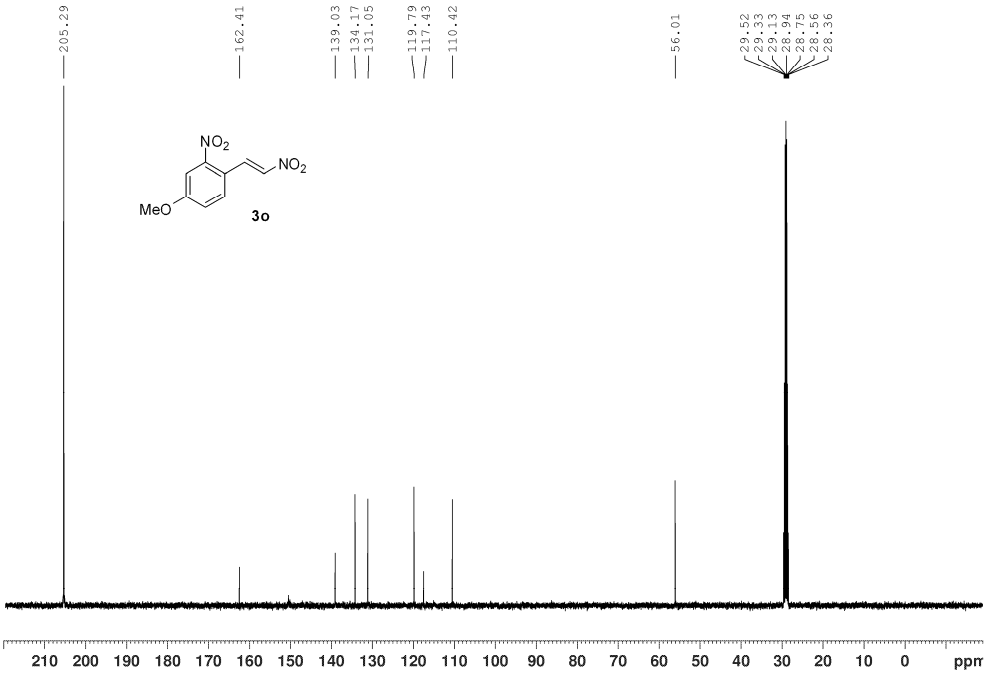

F
NO2
F
F

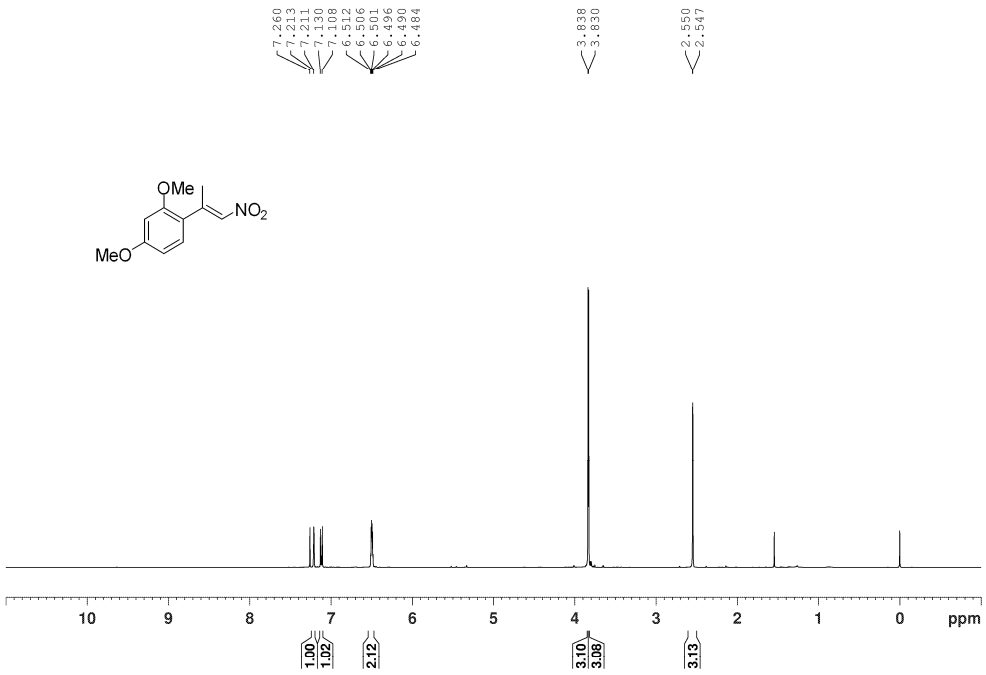
3n

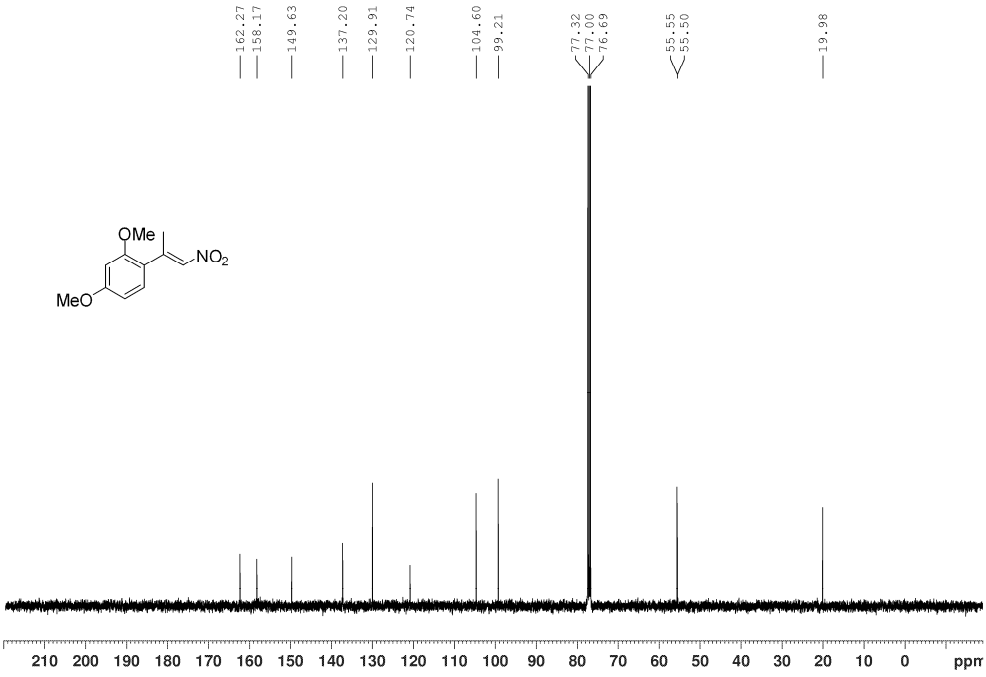

0
−20
−40
−60
−80
−100
−120
−140
−160
−180
ppm
1.00
1.14
0.98

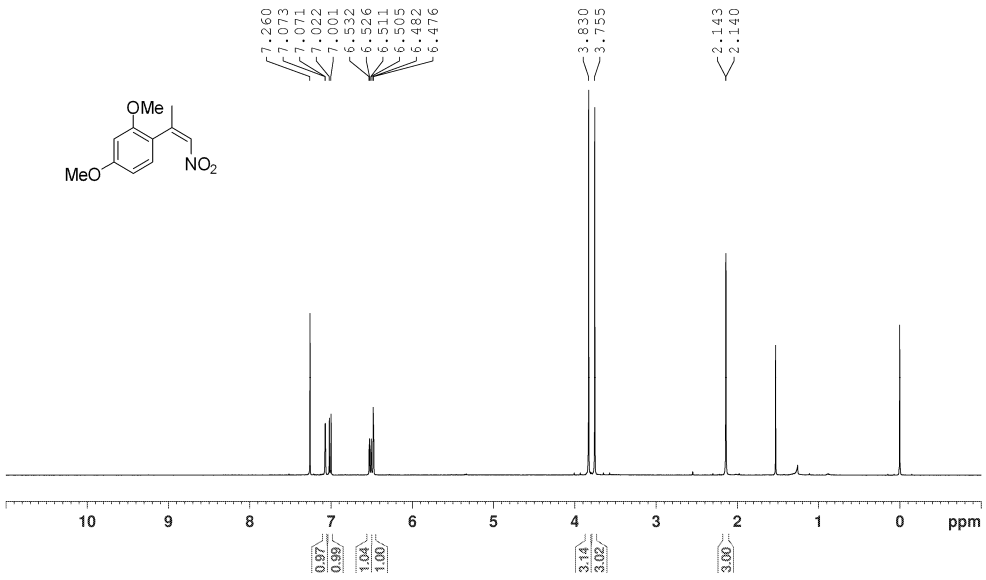

157.21
157.17
154.68
154.64
149.71
149.63
149.56
147.60
147.57
147.48
147.44
147.19
147.13
147.05
146.98
145.14
145.11
145.02
144.98
141.00
140.90
140.80
123.59
119.35
119.33
119.24
119.22
119.15
119.14
119.05
119.03
110.86
110.81
110.79
110.75
110.61
110.57
110.55
110.51
109.42
109.30
109.24
109.12
76.32
76.00
75.69
F
NO2
F
F
3n
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

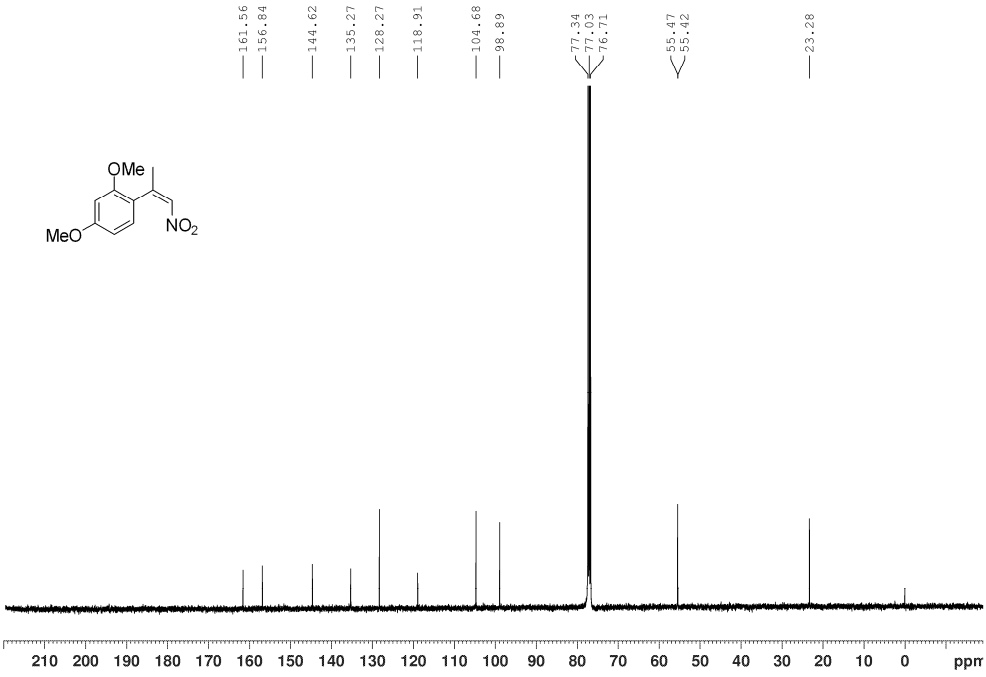

8.416
8.383
7.978
7.956
7.890
7.856
7.690
7.683
7.416
7.409
7.394
7.387
4.011
2.050
NO2
NO2
MeO
3o
10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
1.14
1.08
1.00
1.15
3.12


205.29
162.41
139.03
134.17
131.05
119.79
117.43
110.42
56.01
29.52
29.33
29.13
28.94
28.75
28.56
28.36
NO2
NO2
MeO
3o
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.260
7.213
7.211
7.130
7.108
6.512
6.506
6.501
6.496
6.490
6.484
3.838
3.830
2.550
2.547
OMe
NO2
MeO
10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
1.02
2.12
3.10
3.08
3.13


162.27
158.17
149.63
137.20
129.91
120.74
104.60
99.21
77.32
77.00
76.69
55.55
55.50
19.98
OMe
NO2
MeO
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.260
7.073
7.071
7.022
7.001
6.532
6.526
6.511
6.505
6.482
6.476
3.830
3.755
2.143
2.140
OMe
NO2
MeO
10 9 8 7 6 5 4 3 2 1 0 ppm
0.97
0.99
1.04
1.00
3.14
3.02
3.00


161.56
156.84
144.62
135.27
128.27
118.91
104.68
98.89
77.34
77.03
76.71
55.47
55.42
23.28
OMe
MeO
NO2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm