Supporting Information

N-Nitroheterocycles: Bench-Stable Organic Reagents for Catalytic *ipso*-Nitration of Aryl- and Heteroarylboronic Acids

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1. General Information

1.1 Materials and methods

Starting materials are commercially available and were purchased from Sigma Aldrich or ABCR (Germany) unless otherwise noted. All commercially available aryl boronic acids were analyzed by ^{1}H NMR spectroscopy prior to use. Anhydrous acetonitrile was stored over pre-conditioned 3 Å mol sieves for at least 2 days prior to use. Hexafluoro-2-propanol (HFIP) was purchased from FluoroChem and used without further purification. Analytical thin layer chromatography (TLC) was performed on Merck silica gel 60 F254 TLC glass plates and visualized with 254 nm light and potassium permanganate or ceric ammonium molybdate staining solutions followed by heating. Purification of reaction products was carried out by flash chromatography using Brunschwig silica 32-63, 60Å under 0.3-0.5 bar overpressure. Medium pressure liquid chromatography (MPLC) was performed on a CombiFlash Rf200 System from Teledyne ISCO with built-in UV-detector and fraction collector or manually using silica gel SilicaFlash P60, 40-63 µm. Teledyne ISCO RediSep Rf flash columns used have a 0.035–0.070 mm particle size and 230–400 mesh. Normal phase preparative HPLC purification was conducted on a Teledyne Isco CombiFlash EZ Prep system using a Macherey-Nagel VP 250/21 Nucleosil 50-5 column.

GC-MS measurements were performed on an Agilent GC 7890A with an HP-5MS column (30 m x 250 µm x 0.25 µm), with a column flow of 1.7 ml/min using helium as carrier gas, and an Agilent mass spectrometer 5975C VL MSD operating in EI (70 eV) positive mode with scan rate from 30 to 600 m/z. Sample injection was done by an Agilent autosampler ALS 7693, 1 µl at <1 mg/ml in split mode (split ratio 100:1) with an injection port temperature of 280 °C. The standard method used consisted of the following temperature program: two min at 50 °C, ramp of 20 °C/min to 300 °C followed by a 2min hold time at 300 °C (16.5 min total time). For volatile analytes including gases, a similar method comprising a temperature program of four minutes at 40 °C then 20 °C/min to 240 °C was utilized. Gases were injected under manual conditions while solid and liquid analytes were dissolved in dichloromethane (1 -2 mg/mL). High resolution mass spectra were measured by the MS-service of the "Laboratorium für Organische Chemie der ETH Zürich". Values are given as m/z and the intensity I% of the base peak. High-resolution mass spectra (HRMS) were measured on: (a) Waters Micromass AutoSpec Ultima spectrometer (electron impact ion source, EBE triSector mass analyzer); (b) Bruker UltraFlex II (MALDI ion source, TOF mass analyzer); (c) Bruker maXis (ESI ion source, Qq-TOF mass analyzer).

NMR spectra were acquired on a Bruker AVIII HD 300 MHz and 400 MHz spectrometers, Bruker Neo 300 MHz and 400 MHz spectrometers, operating at the denoted spectrometer frequency given in MHz for the specified nucleus. All experiments were acquired at 298.0 K with a calibrated Bruker Variable

Temperature Controller unless otherwise noted. The chemical shifts are reported in parts per million (ppm) and coupling constants (*J*) are given in Hertz (Hz). ^{1}H NMR spectra are reported with the solvent resonance as the reference unless noted otherwise (CD_3CN at 1.94 ppm, $CDCl_3$ at 7.26 ppm, CD_3OD at 3.31 ppm, CD_2Cl_2 at 5.32 ppm, DMSO-d_6 at 2.50 ppm). Peaks are reported as (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or unresolved, br = broad signal, coupling constant(s) in Hz, integration). ^{13}C NMR spectra were recorded with ^{1}H-decoupling and are reported with the solvent resonance as the reference unless noted otherwise (CD_3CN at 1.32 ppm, $CDCl_3$ at 77.16 ppm, CD_3OD at 49.00 ppm, CD_2Cl_2 at 54.00 ppm, DMSO-d_6 at 39.52 ppm). For ^{19}F NMR, an appropriately calibrated tertiary reference was employed, calibrated according to the literature method for improved reproducibility where 0.00 ppm represents the signal of the second isotopologue of neat $CFCl_3$.[1] IR spectra were recorded on a Thermo Fischer Scientific Nicolet 6700 FTIR equipped with a PIKE technologies GladiATRTM or on a Perkin-Elmer BX II using ATR FT-IR technology. The peaks are reported as absorption maxima (cm^{-1}). High-resolution mass spectrometric data were obtained at the mass spectrometry service operated by the Laboratory of Organic Melting points were determined on a Büchi Melting Point B-540 apparatus in open capillaries.

1.2 High-intensity photoreactor and irradiation vessel

Photoreactors (Figure S1) were custom designed and built by the authors in coordination with the mechanical workshop in the Department of Chemistry and Applied Biosciences at ETH Zürich having blue LEDs, equally spaced in a circle design, powered by a 10.3A power supply, emitting 350 W of light with the measured UV-Vis spectrum (Figure 2). The LEDs were water cooled and further cooled by built-in fans to maintain an ambient temperature. Reactions were performed in normal 15 mL borosilicate glass at a distance of 3 cm from the light source (LEDs).

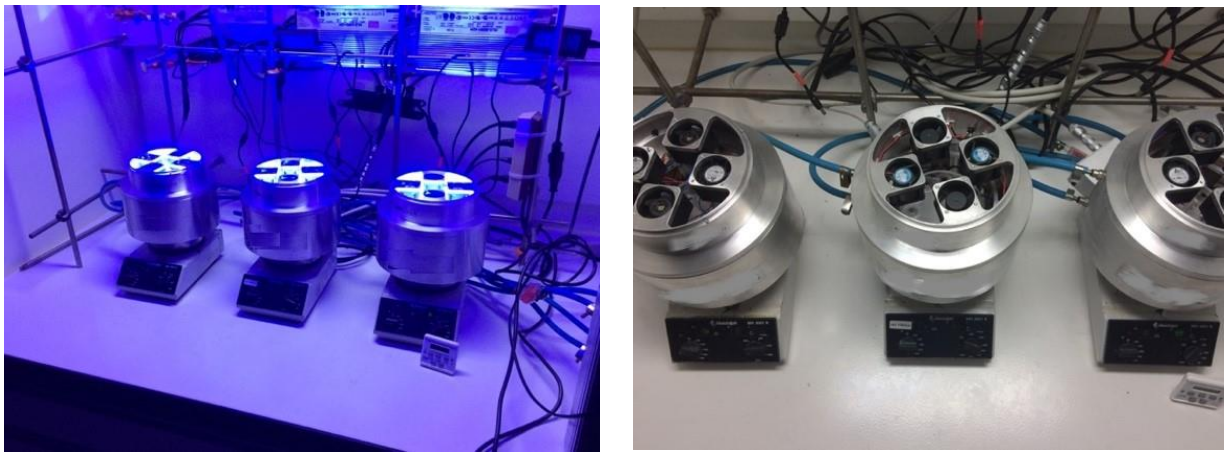


Figure S1. Custom high-intensity, blue LED photoreactors for reaction optimization and scale-up processes.

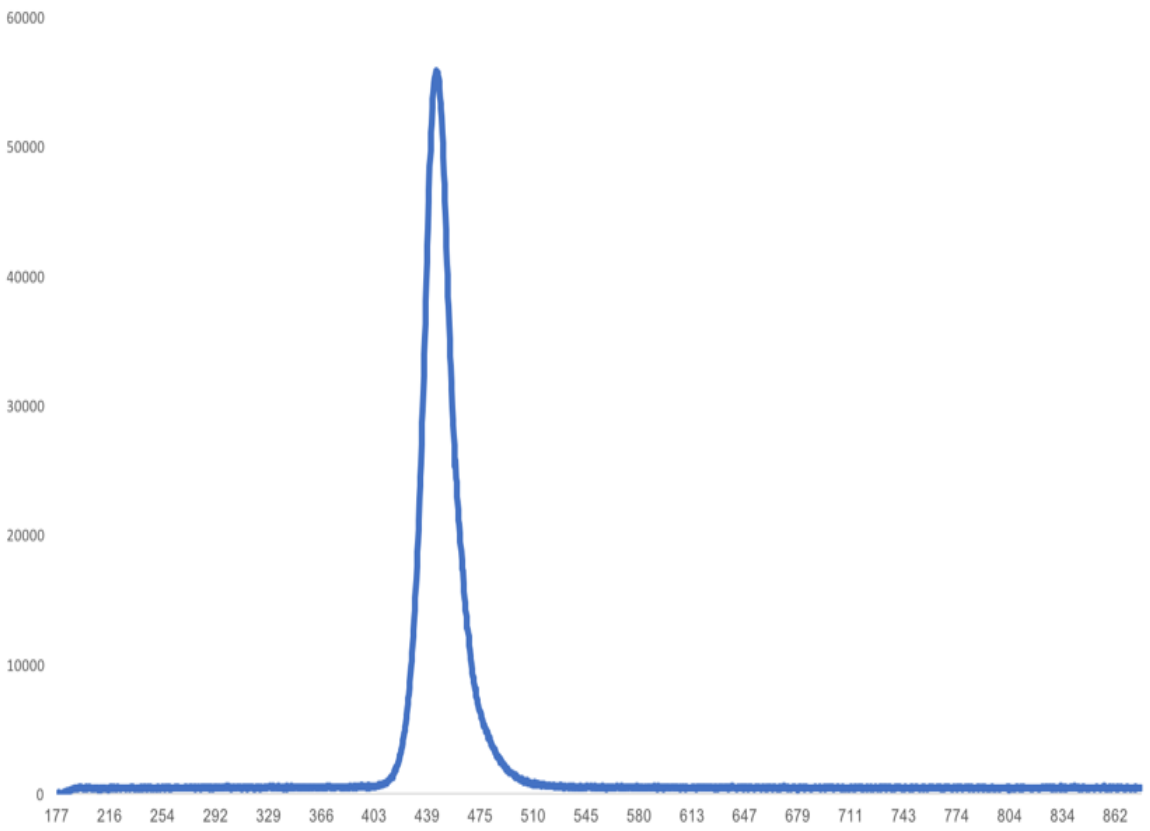
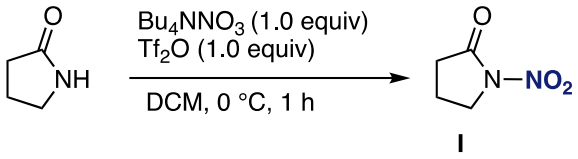


Figure S2. UV-Vis emission spectrum of high-intensity, blue LED photoreactors (λ_{max} = 446 nm, FWHM = 20 nm).

2. Experimental and Characterization Data

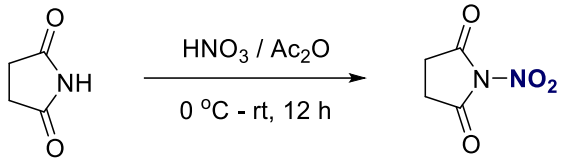
2.1 Synthesis of NO_2-transfer reagents I-IV



I

***N*-Nitropyrrolidinone (I)**:[2] Following the above reported procedure, Bu_4NNO_3 (1.52 g, 5 mmol) in anhydrous DCM (30 mL) was placed in a 100 mL three-necked round bottom flask equipped with a dropping funnel and nitrogen outlet. The system was placed under inert atmosphere and cooled to 0 °C using an ice bath. A 10-mL pressure equalizing dropping funnel was charged with triflic anhydride (1.41 g, 5 mmol). The triflic anhydride was added dropwise to the reaction mixture, and the mixture was stirred for 1 hour at 0 °C. In a dropping funnel was placed pyrrolidin-2-one (421 mg, 5 mmol) in 10 mL DCM, and the solution was added to the mixture during 10 minutes. The reaction mixture was slowly warmed to room temperature and kept for an additional 12 hours. After the reaction was completed, 25 mL of 5% $NaHCO_3$ was added and the solution was stirred for 30 minutes, and then extracted with DCM (3x30 mL). The solvent was removed and crude products were purified by column chromatography over silica gel as indicated. The product was isolated in 65% (422.5 mg) yield as a yellow solid.

Physical state: yellow solid (m.p. 55 ºC); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 4.14 (t, *J* = 7.1 Hz, 2H), 2.68 (t, *J* = 8.0 Hz, 2H), 2.13 (p, *J* = 7.6 Hz, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 167.7, 47.7, 30.9, 14.7; **IR** 1761, 1540, 1480 1459, 1414, 1365, 1269, 1227, 1138, 1026, 937, 890, 837, 802, 762, 688, 629, 591, 530, 466; **HRMS** (EI) m/z [M]+ Calcd for $C_4H_6N_2O_3$: 130.0378; Found 130.0376.

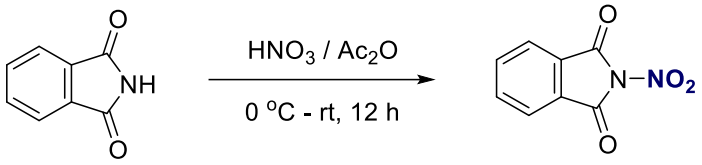


II

***N*–Nitrosuccinimide (II)**:[3] This is a modification of a known procedure. A 250 mL three-necked round bottomed flask equipped with a dropping funnel and a gas outlet connected to an aqueous sodium hydroxide solution trap, was charged with succinimide (15 g, 0.15 mol) and acetic anhydride (57 mL) and then cooled to 0 °C. Fuming nitric acid (99.5%-Sigma Aldrich) (57 mL) was slowly added with a dropping funnel behind a blast shield during 20-30 minutes. Importantly, dry air was rapidly bubbled through the reaction mixture to remove nitrogen oxide. The reaction was then warmed to room temperature and stirred

vigorously for 12 hours. After the reaction was completed, the mixture was cooled to 0 °C, and ice (150 g) and ice-water (200 ml) were added subsequently. The reaction was stirred for an additional 15 minutes leading to the formation of white precipitate. The precipitate was filtered, washed with ice-water (100 mL), and then dried under high-vacuum. The yield of glistening colorless crystalline plates was 10 g (64.5 mmol). Another 2.9 g crop was obtained by extraction of the filtrate with ether (3x30 mL). Recrystallization from absolute ethanol afforded a white crystalline solid with comparable purity in a total yield of 59% (12.7 g).

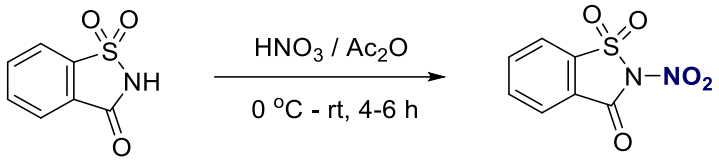
Physical state: white solid (m.p. 89 ºC); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 2.92 (s, 4H); **^{13}C NMR** (75 MHz, MeCN-*d_3*) δ 168, 27.5.; **IR (neat)**: 1746, 1593, 1423, 1407, 1301, 1264, 1234, 1145, 1047, 1003, 993, 808, 733, 626, 595, 540, 482 (no H_2O or EtOH observed); **HRMS** (ESI) m/z [M]+ Calcd for $C_4H_4N_2O_4$ 144.0171; Found 144.0157; **Elem. Anal.** (crystallized from toluene), Calcd for $C_4H_4N_2O_4$ [C] 33.34% [H] 2.80% [N] 19.44%, Found [C] 33.44 [H] 2.80% [N] 19.41%; Recrystallized from EtOH: Calcd for $C_4H_4N_2O_4$ [C] 33.34% [H] 2.80% [N] 19.44%, Found [C] 33.44 [H] 2.81% [N] 19.39%.



III

***N*–Nitrophthalimide** (**III**):[2] This is a modification of a known procedure. A 250 mL three-necked round bottomed flask equipped with a dropping funnel and a gas outlet connected to an aqueous sodium hydroxide solution trap, was charged with phthalimide (12.5 g, 0.085 mol) and acetic anhydride (40 mL). The mixture was cooled to 0 °C and fuming nitric acid (50 mL) (99.5% from Sigma Aldrich) was added slowly with a dropping funnel behind a blast shield. Importantly, dry air was rapidly bubbled through the reaction mixture to remove excess of nitrogen oxide. The reaction mixture was then warmed to room temperature over a period of 12 hours. After the reaction was completed, the mixture was placed in freezer at 4 °C for 12 hours. The ensuing precipitate was collected and recrystallized from chloroform affording *N*-nitrophthalimide as a white solid in 50% (8.16 g) yield.

Physical state: white solid (m.p. 205 °C, decomposition); **^{1}H NMR** (300 MHz, Acetonitrile-d_3) δ 8.07 – 7.90 (m, 4H); **^{13}C NMR** (75 MHz, Acetonitrile-d_3) δ 159.5, 137.5, 129.3, 126.1; **IR** 1750, 1598, 1578, 1465, 1242, 1208, 1164, 1132, 1106, 1058, 1009, 906, 858, 798, 787, 771, 744, 695, 666, 553, 532, 438. **HRMS** (ESI) m/z [M]+ Calcd for $C_8H_4N_2O_4$ 192.0171; Found 192.0162.

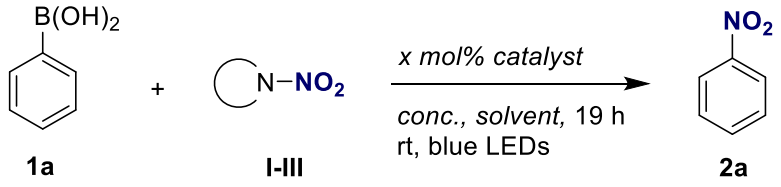


IV

***N*–Nitrosaccharin (IV)**:[4] In a 250 mL three necked round bottom flask equipped with a dropping funnel, air outlet and stirring bar was placed saccharin (10.0 g, 54.64 mmol) in acetic anhydride (25.7 mL, 0.27 mol). The solution was cooled to 0-5 °C with an ice-bath and fuming concentrated nitric acid (99.5% from Sigma Aldrich) (25.1 mL, 0.61 mol) was added dropwise to the solution during 30 minutes, while dry air was bubbled through the solution rapidly in order to remove excess nitrogen oxides. Saccharin completely dissolved once all nitric acid was added. The cooling bath was removed and the reaction mixture was stirred at room temperature during at least 4-6 hours with continuous bubbling of air through the liquid. The precipitate which had formed during the reaction was collected on a sintered glass filter and dried under high vacuum until dryness (11.8 g, 95% yield). Crystallization is possible from 1,4-dioxane or acetonitrile (long boiling time in these solvents can lead to partial decomposition of *N*-nitrosaccharin). The mother liquor was quenched with a cold solution of 1N NaOH.

^{1}H NMR (300 MHz, CD_3CN): δ = 8.05 (dt, *J* = 7.4, 1.5 Hz, 1H), 8.14 (dt, *J* = 6.1, 1.4 Hz, 1H), 8.16-8.23 (m, 2H); **^{13}C NMR** (75 MHz): δ = 121.7, 123.1, 126.5, 134.4, 135.9, 137.6, 151.7; **IR** (ATR, neat): 3097, 1781, 1717, 1601, 1463, 1292, 1176, 1068, 1007, 891, 758, 662, 582, 500; **HRMS** (EI) *m/z* calc'd for $C_7H_4N_2O_5S$: [M^+] 227.9836, found 227.9842; **Anal. calcd.** for $C_7H_4N_2O_5S$: C 36.85, H 1.77, N 12.28 found: C 36.88, H 1.87, N 12.41.

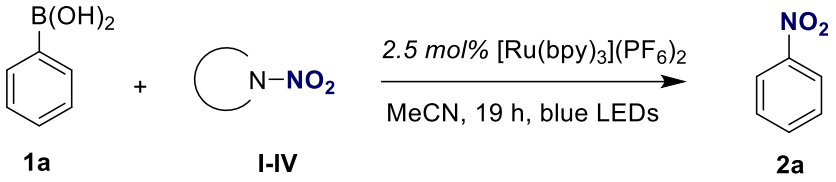
2.2 Development of reaction conditions (*a*) for the nitration of phenylboronic acid



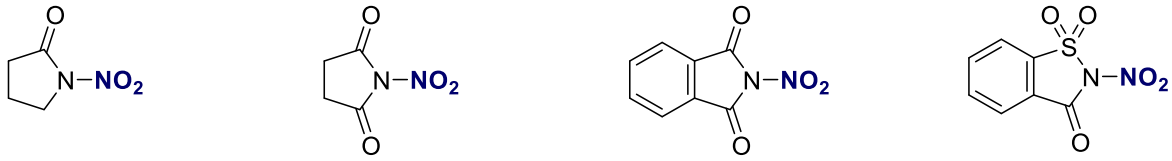
1a **I-III** **2a**

An oven-dried, 5 mL micro-vial was charged on the benchtop with a magnetic pTFE-coated stirbar, reagent, and photocatalyst (x mol%). The vial was sealed and the atmosphere was cycled 3x with Ar/vac. phenylboronic acid (**1a**) (30.5 mg, 0.25 mmol, 1.00 equiv) and anhydrous solvent (1 mL) was added with a plastic 1 mL syringe and then sparged with argon for 5 minutes. The reaction mixture was stirred and irradiated in the photoreactor at ambient conditions for 19 h. An internal standard of *n*-decane (48 μL, 1.00 equiv) was added with a microsyringe. An aliquot was analyzed by GC-MS to obtain the calibrated yields and characterization for the desired product.

2.2.1 Table S1: Effect of NO_2-transfer reagent

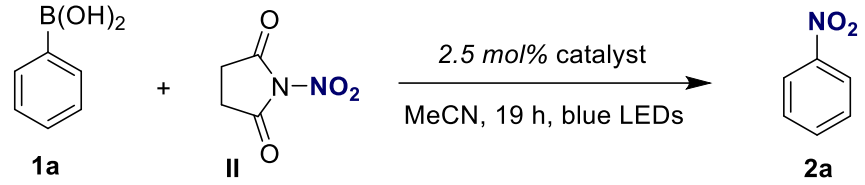


1a I-IV 2a

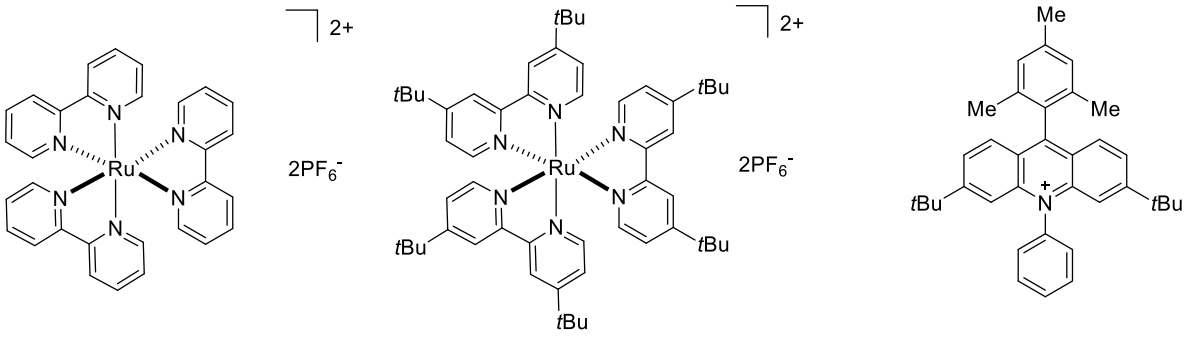


I	II	III	IV
0%	87%	55%	<5%

2.2.2 Table S2: Photocatalyst effect

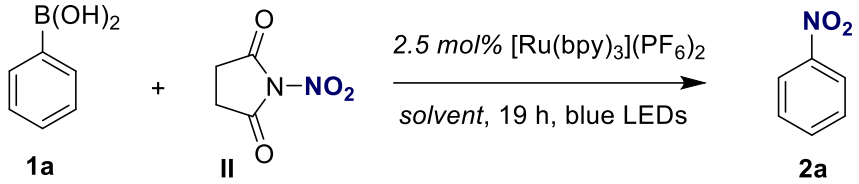


1a II 2a



90%	75%	0%

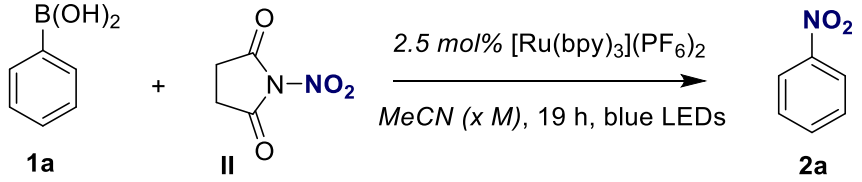
2.2.3 Table S3: Solvent effect



Entry	Solvent	Yield %[a]
1	DMF	57
2	DMSO	56
3	MeCN	89
4	THF	41
5	Acetone	71
6	1,4-dioxane	15
7	EtOAc	40
8	DCM	32

Conditions: [Ru] (2.5 mol%), **1a** (1.0 equiv), reagent **II** (2.0 equiv), solvent (0.5 M), blue LEDs, rt, 19 h.

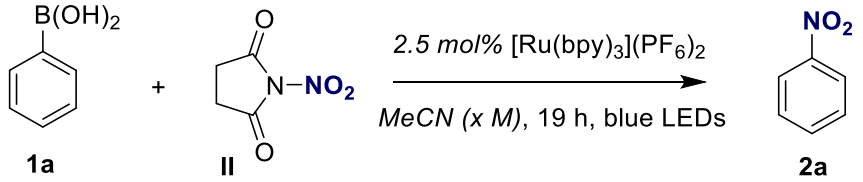
2.2.4 Table S4: Concentration effect



Entry	[1a] (M)	Yield %[a]
1	0.5	87
2	0.25	56
3	0.1	50

Conditions: [Ru] (2.5 mol%), **1a** (1.0 equiv), reagent **II** (2.0 equiv), MeCN (x M), blue LEDs, 19 h.

2.2.5 Table S5: Loading of NO_2-transfer reagent



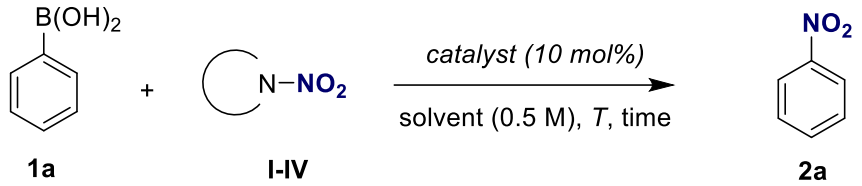
Entry	Reagent II	Yield %[a]
1	1.0 eq	52
2	2.0 eq	85
3	3.0 eq	86

Conditions: [Ru] (2.5 mol%), **1a** (x equiv), reagent **II** (2.0 equiv), MeCN (0.5 M), blue LEDs, 19 h.

2.3 Development of reaction conditions (*b*) for the nitration of phenylboronic acid

2.3.1 Table S6: Reagent, solvent and catalyst screening

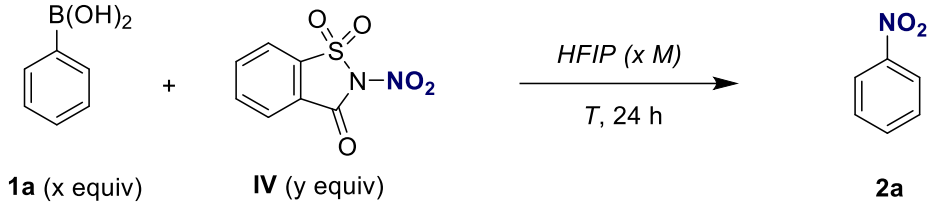
General procedure for the optimization of reaction conditions: An oven-dried crimp cap microvial equipped with a magnetic stirrer was cooled down to room temperature under high vacuum, filled with argon and charged with phenylboronic acid **1a** (61 mg, 0.5 mmol, 1 equiv), reagent (1.3 equiv) and catalyst (10 mol%). The vial was closed with a cap with septum using a crimper, connected to a Schlenk line via a needle and the solids were dried under vacuum for 5 min and the vial was refilled with argon. HFIP (1 mL, 0.5 M) was added via a plastic syringe. The reaction mixture was stirred at 85 °C in a metal heat block for 24 h. The reaction mixture was cooled down to room temperature and connected to Ar. An internal standard of *n*-decane (97.5 μL, 0.5 mmol, 1.0 equivalent) was added via a microsyringe, and the vial was vigorously agitated to ensure homogenous mixture. The vial was opened, an aliquot (0.2 mL) was filtered through a silica gel plug and rinsed with MeCN (2 mL). The yield was determined using GC-MS with *n*-decane as internal standard following calibration.



Entry	Reagent	Catalyst	Solvent	*T* [°C]	Time [h]	Yield [%][b]
1	**IV**	–	MeCN	80	19	39
2	**IV**	–	$MeNO_2$	80	19	54
3	**I**	–	MeCN	80	19	0
4	**II**	–	MeCN	80	19	0
5	**III**	–	MeCN	80	19	0
6[c]	**IV**	$Mg(ClO_4)_2$	MeCN	85	6	96
7	**IV**	$Mg(ClO_4)_2$	MeCN	85	6	73
8	**IV**	$Mg(ClO_4)_2$	MeCN	80	19	84
9	**IV**	$Mg(ClO_4)_2$	MeCN	85	19	75
10[d]	**IV**	$Mg(ClO_4)_2$	MeCN	85	6	61
11	**IV**	$Mg(ClO_4)_2$	MeCN:H_2O 9:1	85	6	0
12[c]	**IV**	$Zn(NTf_2)_2$	MeCN	85	6	93
13	**IV**	$Zn(NTf_2)_2$	MeCN	80	19	86
14	**IV**	$Cu(OTf)_2$	MeCN	85	6	0
15	**IV**	$AlCl_3$	MeCN	85	6	57
16[d]	**IV**	$Mg(ClO_4)_2$	$MeNO_2$	85	6	63
17[d]	**IV**	$Zn(NTf_2)_2$	$MeNO_2$	85	6	46
18[d]	**IV**	$Cu(OTf)_2$	$MeNO_2$	85	6	0
19[d]	**IV**	$AlCl_3$	$MeNO_2$	85	6	75

[a] Reaction conditions: phenylboronic acid **1a** (0.5 mmol, 1 equiv), reagent (0.65 mmol, 1.3 equiv), catalyst (0.05 mmol, 10 mol%), anhydrous solvent (1 mL). [b] Determined by GC–MS using *n*-decane as internal standard. [c] A different batch of **1a** was used. [d] Wet solvent was used.

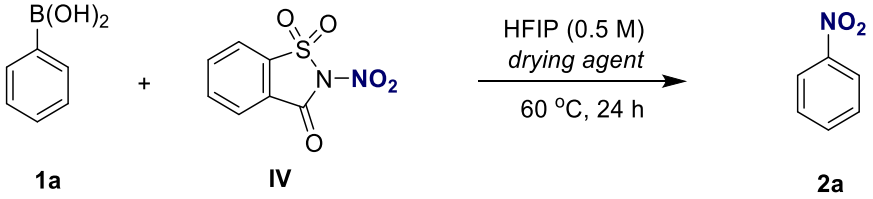
2.3.2 Table S7: Optimization of conditions in HFIP



Entry[a]	1a [equiv]	IV [equiv]	Conc. [M]	*T* [°C]	Yield [%][b]
1[c]	1.0	1.3	0.5	85	94
2[c]	**1.0**	**1.3**	**0.5**	**60**	**93**
3[d]	1.0	1.3	0.5	50	78
4	1.0	1.3	0.5	25	0
5	1.0	1.1	0.5	60	88
6	1.0	1.6	0.5	60	93
7	1.0	2.0	0.5	60	87
8	1.3	1.0	0.5	60	76
9	1.6	1.0	0.5	60	69
10	1.0	1.3	0.3	60	93
11	1.0	1.3	0.8	60	87
12	1.0	1.3	1.0	60	92

[a] Reaction conditions: **1a** (0.5 mmol), HFIP (conc.), temperature, 24 h.
[b] Determined by GC-MS using *n*-decane as internal standard. [c] Reaction time 19 h.

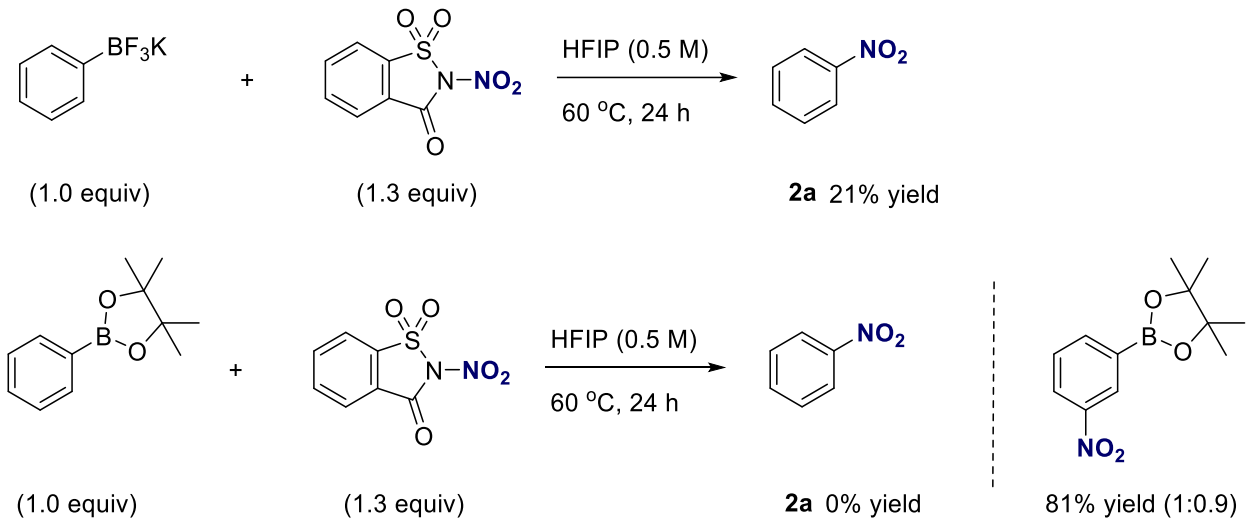
2.3.3 Table S8: Effect of drying agents



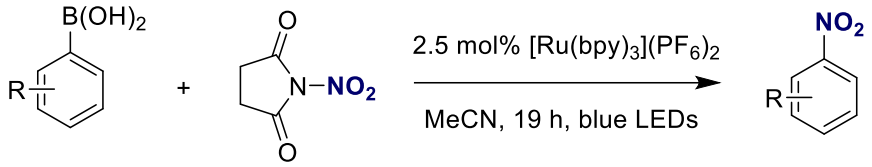
Entry[a]	Drying agent	Yield [%][b]
1[c]	–	99
2	3Å molecular sieves	25
3	Na_2SO_4 (4 equiv)	34
4	$MgSO_4$ (4 equiv)	62

[a] Reaction conditions: **1a** (0.5 mmol, 1.0 equiv), **IV** (1.3 equiv 0.65 mmol), HFIP (1 mL), drying agent (4 equiv).

2.3.3 Table S9: Screening of aryl boronic derivatives

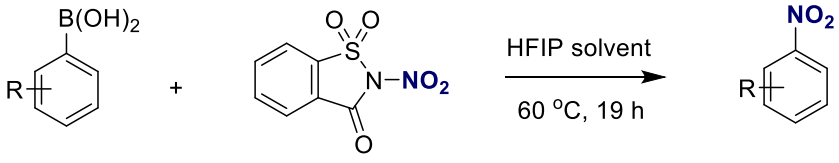


2.4 General procedure (GP) *a* for the photocatalytic *ipso*-nitration



A 10-mL glass microwave vial was charged with *N*-nitrosuccinimide **II** (1 mmol, 2.00 equiv), and photocatalyst (2.5 mol%). The contents of the vial were then subject to 3x argon/vacuum cycles. Anhydrous CH_3CN was added and the reaction mixture was sparged for 5 min with argon. Finally, the substrate was introduced to the reaction mixture. The obtained red solution was stirred at room temperature under blue LED irradiation. After 19 hours, water was added to the reaction mixture and the product was extracted with DCM (3x10 mL). The solvent was removed under reduced pressure, and the crude product were subsequently purified by flash column chromatography over silica gel (hexane/EA = 50:1).

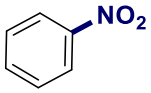
2.5 General procedure (GP) *b* for *ipso*-nitration in HFIP



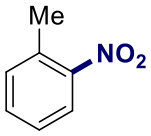
An oven-dried crimp cap microvial equipped with a magnetic stirrer was cooled down to rt under high vacuum, filled with argon and charged with arylboronic acid **1** (1 mmol, 1.0 equiv) and **IV** (296 mg, 1.3

mmol, 1.3 equiv) on a bench. The vial was closed with a cap with septum using a crimper, connected to a Schlenk line via a needle, evacuated for 5 min and then backfilled with Ar. HFIP (2 mL, 0.5M) was added, and the reaction was stirred at 60 °C in a metal heat block until complete consumption of aryl boronic acid. The vial was cooled to room temperature and the crude residue was concentrated on silica gel under reduced pressure (40 °C, 200 mbar). The product was purified by automated flash column chromatography as indicated.

2.6 Characterization data of nitro(hetero)arenes 2a-2an

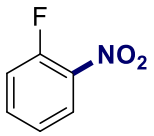


Nitrobenzene (**2a):** According to GP *a*, *N*-nitrosuccinimide (1.0 mmol, 2.00 equiv), phenylboronic acid (0.5 mmol, 1.00 equiv), $[Ru(bpy)_3](PF_6)_2$ (2.5 mol%) and MeCN (2.0 mL) were added to a 10-mL vial. The reaction was irradiated with blue LEDs as described in Section 2.4. Compound **2a** was isolated as a yellow oil 87% (54 mg). According to GP *b*, *N*-nitrosaccharin (1.3 mmol, 1.3 equiv), phenylboronic acid (0.5 mmol, 1.0 equiv) and HFIP (2 mL) were added to a 10-mL vial and the reaction was stirred in a metal heat block as described in Section 2.5. Compound **2a** was isolated as a yellow oil 93% (57 mg) after purification with flash column chromatography on silica gel (*n*-hexane:EtOAc, 99:1). Observed spectral data correspond to literature specifications [CAS: 98-95-3]. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.17 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.3 Hz, 2H), 2.53 (s, 3H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 146.1, 129.9, 123.6, 21.7.

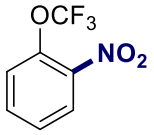


1-Methyl-2-nitrobenzene (2b): According to GP *a*, *N*-nitrosuccinimide (1.0 mmol, 2.00 equiv), o-tolylboronic acid (0.5 mmol, 1.00 equiv), $[Ru(bpy)_3](PF_6)_2$ (2.5 mol%) and MeCN (2.0 mL) were added to a 10-mL vial. The reaction was irradiated with blue LEDs as described in Section 2.4. Compound **2b** was isolated as a yellow solid 77% (53 mg). According to GP *b*, *N*-nitrosaccharin (1.3 mmol, 1.3 equiv), o-tolyllboronic acid (0.5 mmol, 1.0 equiv) and HFIP (2 mL) were added to a 10-mL vial and the reaction was stirred in a metal heat block as described in Section 2.5. Compound **2b** was isolated as a yellow solid 82% (56 mg) after purification with flash column chromatography on silica gel (*n*-hexane:EtOAc, 99:1). Observed spectral data correspond to literature specifications [CAS: 88-72-2]. **^{1}H NMR** (300 MHz,

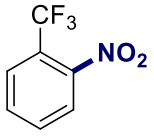
Chloroform-*d*) δ 7.99 – 7.90 (m, 1H), 7.53 – 7.44 (m, 1H), 7.37 – 7.28 (m, 2H), 2.58 (s, 3H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 148.2, 133.6, 133.1, 132.8, 126.9, 124.6, 20.4.



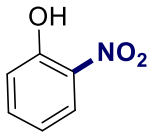
1-Fluoro-2-nitrobenzene (2c): According to GP *a*, *N*-nitrosuccinimide (1.0 mmol, 2.00 equiv), (2-fluorophenyl)boronic acid (0.5 mmol, 1.00 equiv), $[Ru(bpy)_3](PF_6)_2$ (2.5 mol%) and MeCN (2.0 mL) were added to a 10-mL vial. The reaction was irradiated with blue LEDs as described in Section 2.4. Compound **2c** was isolated as a yellow oil 68% (49 mg) after purification with flash column chromatography on silica gel (*n*-hexane:EtOAc, 99:1). Observed spectral data correspond to literature specifications [CAS: 1493-27-2]. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.23 – 8.05 (m, 1H), 7.76 – 7.60 (m, 1H), 7.54 – 7.25 (m, 2H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 155.6 (d, *J* = 264.8 Hz), 137.5, 135.6 (d, *J* = 8.6 Hz), 126.2 (d, *J* = 2.8 Hz), 124.6 (d, *J* = 4.4 Hz), 118.5 (d, *J* = 20.6 Hz); **^{19}F NMR** (282 MHz, Chloroform-*d*) δ -117.65.



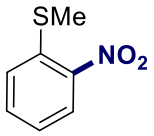
1-Nitro-2-(trifluoromethoxy)benzene (2d): According to GP *a*, *N*-nitrosuccinimide (1.0 mmol, 2.00 equiv), (2-(trifluoromethoxy)phenyl)boronic acid (0.5 mmol, 1.00 equiv), $[Ru(bpy)_3](PF_6)_2$ (2.5 mol%) and MeCN (2.0 mL) were added to a 10-mL vial. The reaction was irradiated with blue LEDs as described in Section 2.4. Compound **2d** was isolated as a yellow solid 78% (77 mg). According to GP *b*, *N*-nitrosaccharin (1.3 mmol, 1.3 equiv), (2-(trifluoromethoxy)phenyl)boronic acid (0.5 mmol, 1.0 equiv) and HFIP (2 mL) were added to a 10-mL vial and the reaction was stirred in a metal heat block as described in Section 2.5. Compound **2d** was isolated as a yellow solid 85% (84 mg) after purification with flash column chromatography on silica gel (*n*-hexane:EtOAc, 95:5). Observed spectral data correspond to literature specifications [CAS: 1644-88-8]. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.00 – 7.94 (m, 1H), 7.68 (td, *J* = 8.0, 1.6 Hz, 1H), 7.47 (t, *J* = 7.9 Hz, 2H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 142.9, 141.5 (q, *J* = 2.0 Hz), 134.4, 127.7, 126.1, 123.4 (m), 120.34 (q, *J* = 261.1 Hz); **^{19}F NMR** (282 MHz, Chloroform-*d*) δ -57.69.



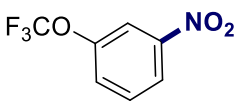
1-Nitro-2-(trifluoromethyl)benzene (2e): According to GP *a*, *N*-nitrosuccinimide (1.0 mmol, 2.00 equiv), (2-(trifluoromethyl)phenyl)boronic acid (0.5 mmol, 1.00 equiv), $[Ru(bpy)_3](PF_6)_2$ (2.5 mol%) and MeCN (2.0 mL) were added to a 10-mL vial. The reaction was irradiated with blue LEDs as described in Section 2.4. Compound **2e** was isolated as a yellow oil 82% (80 mg) after purification with flash column chromatography on silica gel (*n*-hexane:EtOAc, 95:5). Observed spectral data correspond to literature specifications [CAS: 384-22-5]. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.86 (ddd, *J* = 11.9, 5.3, 3.5 Hz, 2H), 7.74 (dd, *J* = 5.9, 3.5 Hz, 2H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 148.3, 133.1, 132.6, 127.9 (q, *J* = 5.2 Hz), 125.0, 123.8 (q, *J* = 33.7 Hz), 122.1 (q, *J* = 271.5 Hz); **^{19}F NMR** (282 MHz, Chloroform-*d*) δ -60.05.



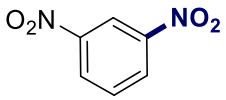
2-Nitrophenol (2f): According to GP *b*, *N*-nitrosacharin (1.3 mmol, 1.3 equiv), (2-hydroxyphenyl)boronic acid (0.5 mmol, 1.0 equiv) and HFIP (2 mL) were added to a 10-mL vial and the reaction was stirred in a metal heat block as described in Section 2.5. Compound **2f** was isolated as colorless oil 70% (49 mg) after purification with flash column chromatography on silica gel (*n*-hexane:EtOAc, 5:1). Observed spectral data correspond to literature specifications [CAS: 88-75-5]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 10.60 (s, 1H), 8.12 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.76 – 7.48 (m, 1H), 7.20 – 7.12 (m, 1H), 7.10 – 6.91 (m, 1H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 155.1, 137.5, 133.7, 125.1, 120.2, 119.9.



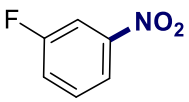
Methyl(2-nitrophenyl)sulfane (2g): According to GP *b*, *N*-nitrosacharin (1.3 mmol, 1.3 equiv), (2-(methylthio)phenyl)boronic acid (0.5 mmol, 1.0 equiv) and HFIP (2 mL) were added to a 10-mL vial and the reaction was stirred in a metal heat block as described in Section 2.5. Compound **2g** was isolated as colorless oil 72% (61 mg) after purification with flash column chromatography on silica gel (*n*-hexane:EtOAc, 95:5). Observed spectral data correspond to literature specifications [CAS: 3058-47-7]. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.32 (d, *J* = 8.3 Hz, 1H), 7.66 (t, *J* = 7.7 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.32 (t, *J* = 7.7 Hz, 1H), 2.57 (s, 3H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 145.5, 139.3, 133.7, 126.2, 125.7, 124.2, 16.0.



1-Methyl-2-nitrobenzene (2h): According to GP *a*, *N*-nitrosuccinimide (1.0 mmol, 2.00 equiv), (3-(trifluoromethoxy)phenyl)boronic acid (0.5 mmol, 1.00 equiv), $[Ru(bpy)_3](PF_6)_2$ (2.5 mol%) and MeCN (2.0 mL) were added to a 10-mL vial. The reaction was irradiated with blue LEDs as described in Section 2.4. Compound **2h** was isolated as a yellow oil 75% (77 mg) after purification with flash column chromatography on silica gel (*n*-hexane:EtOAc, 95:5). According to GP *b*, *N*-nitrosaccharin (1.3 mmol, 1.3 equiv), (3-(trifluoromethoxy)phenyl)boronic acid (0.5 mmol, 1.0 equiv) and HFIP (2 mL) were added to a 10-mL vial and the reaction was stirred in a metal heat block as described in Section 2.5. Compound **2h** was isolated as a yellow oil 85% (88 mg) after purification with flash column chromatography on silica gel (*n*-hexane:EtOAc, 95:5). Observed spectral data correspond to literature specifications [CAS: 2995-45-1]. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.25 – 8.04 (m, 2H), 7.71 – 7.52 (m, 2H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 149.6 (m), 149.2, 130.9, 127.0, 121.9, 120.4 (q, *J* = 259.7 Hz), 116.6.; **^{19}F NMR** (282 MHz, Chloroform-*d*) δ -58.22.

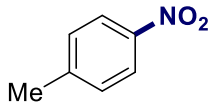


1,3-Dinitrobenzene (2i): According to GP *a*, *N*-nitrosaccharin (1.3 mmol, 1.3 equiv), (3-nitrophenyl)boronic acid (0.5 mmol, 1.0 equiv) and HFIP (2 mL) were added to a 10-mL vial and the reaction was stirred in a metal heat block as described in Section 2.5. Compound **2i** was isolated as colorless oil 45% (38 mg) after purification with flash column chromatography on silica gel (*n*-hexane:EtOAc, 10:1). Observed spectral data correspond to literature specifications [CAS: 99-65-0]. **^{1}H NMR** (300 MHz, Chloroform-*d*): *δ* 9.09 (t, *J* = 2.2 Hz, 1H, $C_{Ar}H$), 8.59 (dd, *J* = 8.2, 2.2 Hz, 2H, $C_{Ar}H$), 7.82 (t, *J* = 8.2 Hz, 1H, $C_{Ar}H$). **^{13}C NMR** (75 MHz, Chloroform-*d*): *δ* 148.7, 130.9, 129.0, 119.2. **GC-MS** (EI): *m/z* 168 (M^+).

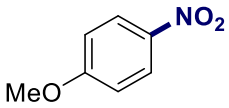


1-Fluoro-3-nitrobenzene (2j): According to GP *a*, *N*-nitrosuccinimide (1.0 mmol, 2.00 equiv), (3-fluorophenyl)boronic acid (0.5 mmol, 1.00 equiv), $[Ru(bpy)_3](PF_6)_2$ (2.5 mol%) and MeCN (2.0 mL) were added to a 10-mL vial. The reaction was irradiated with blue LEDs as described in Section 2.4. Compound **2j** was isolated as a yellow oil 75% (53 mg) after purification with flash column chromatography on silica gel (*n*-hexane:EtOAc, 99:1). According to GP *b*, *N*-nitrosaccharin (1.3 mmol, 1.3 equiv), (3-fluorophenyl)boronic acid (0.5 mmol, 1.0 equiv) and HFIP (2 mL) were added to a 10-mL vial and the reaction was stirred in a metal heat block as described in Section 2.5. Compound **2j** was isolated as a yellow oil 80% (56.5 mg) after purification with flash column chromatography on silica gel (*n*-hexane:EtOAc,

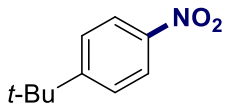
99:1). Observed spectral data correspond to literature specifications [CAS: 402-67-5]. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 8.2 Hz, 1H), 7.89 (dt, *J* = 8.6, 2.2 Hz, 1H), 7.56 (dd, *J* = 8.3, 5.6 Hz, 1H), 7.42 (td, *J* = 7.9, 1.8 Hz, 1H); **^{13}C NMR** (300 MHz, Chloroform-*d*) δ *δ* 162.5 (d, *J* = 251.2 Hz), 149.3 (m), 130.9 (d, *J* = 8.1 Hz), 122.0 (d, *J* = 21.4 Hz), 119.5 (d, *J* = 3.5 Hz), 111.5 (d, *J* = 26.4 Hz); **^{19}F NMR** (282 MHz, Chloroform-*d*) δ -109.13.



1-Methyl-4-nitrobenzene (2k): According to GP *a*, *N*-nitrosuccinimide (1.0 mmol, 2.00 equiv), *p*-tolylboronic acid (0.5 mmol, 1.00 equiv), $[Ru(bpy)_3](PF_6)_2$ (2.5 mol%) and MeCN (2.0 mL) were added to a 10-mL vial. The reaction was irradiated with blue LEDs as described in Section 2.4. Compound **2k** was isolated as a yellow oil 70% (48 mg) after purification with flash column chromatography on silica gel (*n*-hexane:EtOAc, 99:1). Observed spectral data correspond to literature specifications [CAS: 99-990]. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.17 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.3 Hz, 2H), 2.53 (s, 3H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 146.1, 129.9, 123.6, 21.7.

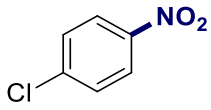


1-Methoxy-4-nitrobenzene (2l): According to GP *a*, *N*-nitrosuccinimide (1.0 mmol, 2.00 equiv), (4-methoxyphenyl)boronic acid (0.5 mmol, 1.00 equiv), $[Ru(bpy)_3](PF_6)_2$ (2.5 mol%) and MeCN (2.0 mL) were added to a 10-mL vial. The reaction was irradiated with blue LEDs as described in Section 2.4. Compound **2l** was isolated as a yellow oil 57% (43 mg) after purification with flash column chromatography on silica gel (*n*-hexane:EtOAc, 95:5). Observed spectral data correspond to literature specifications [CAS: 100-17-4]. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.20 (d, *J* = 9.2 Hz, 2H), 6.96 (d, *J* = 9.2 Hz, 2H), 3.91 (s, 3H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 165.2, 142.2, 126.5, 114.6, 56.51.

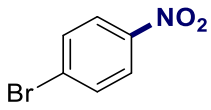


1-(*tert*-Butyl)-4-nitrobenzene (2m): According to GP *a*, *N*-nitrosuccinimide (1.0 mmol, 2.00 equiv), (4-(tert-butyl)phenyl)boronic acid (0.5 mmol, 1.00 equiv), $[Ru(bpy)_3](PF_6)_2$ (2.5 mol%) and MeCN (2.0 mL) were added to a 10-mL vial. The reaction was irradiated with blue LEDs as described in Section 2.4. Compound **2m** was isolated as a yellow oil 72% (65 mg). According to GP *b*, *N*-nitrosaccharin (1.3 mmol,

1.3 equiv), (4-(tert-butyl)phenyl)boronic acid (0.5 mmol, 1.0 equiv) and HFIP (2 mL) were added to a 10-mL vial and the reaction was stirred in a metal heat block as described in Section 2.5. Compound **2m** was isolated as a yellow oil 82% (74 mg) after purification with flash column chromatography on silica gel (*n*-hexane:EtOAc, 95:5). Observed spectral data correspond to literature specifications [CAS: 3282-56-2]. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.14 (d, *J* = 9.0 Hz, 2H), 7.53 (d, *J* = 9.0 Hz, 2H), 1.36 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 158.9, 146.1, 126.4, 123.5, 35.5, 31.2.

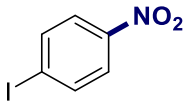


1-Chloro-4-nitrobenzene (2n): According to GP *a*, *N*-nitrosuccinimide (1.0 mmol, 2.00 equiv), (4-(chloro)phenyl)boronic acid (0.5 mmol, 1.00 equiv), $[Ru(bpy)_3](PF_6)_2$ (2.5 mol%) and MeCN (2.0 mL) were added to a 10-mL vial. The reaction was irradiated with blue LEDs as described in Section 2.4. Compound **2n** was isolated as a yellow oil 83% (65 mg) after purification with flash column chromatography on silica gel (*n*-hexane:EtOAc, 99:1). According to GP *b*, *N*-nitrosaccharin (1.3 mmol, 1.3 equiv), (4-(chloro)phenyl)boronic acid (0.5 mmol, 1.0 equiv) and HFIP (2 mL) were added to a 10-mL vial and the reaction was stirred in a metal heat block as described in Section 2.5. Compound **2n** was isolated as a yellow oil 99% (77.5 mg) after purification with flash column chromatography on silica gel (*n*-hexane:EtOAc, 95:5). Observed spectral data correspond to literature specifications [CAS: 100-00-5]. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.21 – 8.15 (m, 2H), 7.55 – 7.48 (m, 2H); **^{13}C NMR** (282 MHz, Chloroform-*d*) δ 146.7, 141.5, 129.7, 125.1.

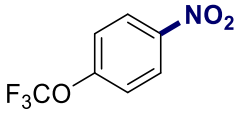


1-Bromo-4-nitrobenzene (2o): According to GP *a*, *N*-nitrosuccinimide (1.0 mmol, 2.00 equiv), (4-(bromo)phenyl)boronic acid (0.5 mmol, 1.00 equiv), $[Ru(bpy)_3](PF_6)_2$ (2.5 mol%) and MeCN (2.0 mL) were added to a 10-mL vial. The reaction was irradiated with blue LEDs as described in Section 2.4. Compound **2o** was isolated as a yellow oil 85% (86 mg). According to GP *b*, *N*-nitrosaccharin (1.3 mmol, 1.3 equiv), (4-(bromo)phenyl)boronic acid (0.5 mmol, 1.0 equiv) and HFIP (2 mL) were added to a 10-mL vial and the reaction was stirred in a metal heat block as described in Section 2.5. Compound **2o** was isolated as a yellow oil 96% (97 mg) after purification with flash column chromatography on silica gel (*n*-hexane:EtOAc, 95:5). Observed spectral data correspond to literature specifications [CAS: 586-78-7]. **^{1}H**

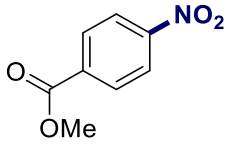
NMR (300 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 9.0 Hz, 2H), 7.68 (d, *J* = 9.0 Hz, 2H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 147.2, 132.7, 130.1, 125.1.



1-Iodo-4-nitrobenzene (2p): According to GP *b*, *N*-nitrosaccharin (1.3 mmol, 1.3 equiv), (4-iodophenyl)boronic acid (0.5 mmol, 1.0 equiv) and HFIP (2 mL) were added to a 10-mL vial and the reaction was stirred in a metal heat block as described in Section 2.5. Compound **2p** was isolated as yellow solid 91% (113 mg) after purification with flash column chromatography on silica gel (*n*-hexane:EtOAc, 99:1). Observed spectral data correspond to literature specifications [CAS: 639-98-6]. **Mp** 53-55°C; **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 9.0 Hz, 2H), 7.92 (d, *J* = 9.0 Hz, 2H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 147.8, 138.7, 124.9, 102.7.

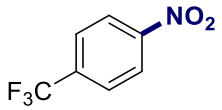


1-Nitro-4-(trifluoromethoxy)benzene (2q): According to GP *a*, *N*-nitrosuccinimide (1.0 mmol, 2.00 equiv), (4-(trifluoromethoxy)phenyl)boronic acid (0.5 mmol, 1.00 equiv), $[Ru(bpy)_3](PF_6)_2$ (2.5 mol%) and MeCN (2.0 mL) were added to a 10-mL vial. The reaction was irradiated with blue LEDs as described in Section 2.4. Compound **2q** was isolated as a yellow oil 80% (83 mg) after purification with flash column chromatography on silica gel (*n*-hexane:EtOAc, 95:5). According to GP *b*, *N*-nitrosaccharin (1.3 mmol, 1.3 equiv), (4-(trifluoromethoxy)phenyl)boronic acid (0.5 mmol, 1.0 equiv) and HFIP (2 mL) were added to a 10-mL vial and the reaction was stirred in a metal heat block as described in Section 2.5. Compound **2q** was isolated as a yellow oil 96% (100 mg) after purification with flash column chromatography on silica gel (*n*-hexane:EtOAc, 95:5). Observed spectral data correspond to literature specifications [CAS: 713-65-5]. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.30 (d, *J* = 9.2 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H); **^{13}C NMR** (75 MHz, Chloroform-*d*) *δ* 153.8 (q, *J* = 1.8 Hz), 146.0, 125.9, 121.1 (q, *J* = 1.4 Hz), 120.3 (q, *J* = 261.1 Hz); **^{19}F NMR** (282 MHz, Chloroform-*d*) δ -57.86.

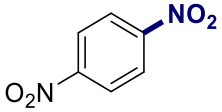


Methyl 4-nitrobenzoate (2r): According to GP *a*, *N*-nitrosuccinimide (1.0 mmol, 2.00 equiv), (4-(methoxycarbonyl)phenyl)boronic acid (0.5 mmol, 1.00 equiv), $[Ru(bpy)_3](PF_6)_2$ (2.5 mol%) and MeCN (2.0 mL) were added to a 10-mL vial. The reaction was irradiated with blue LEDs as described in Section

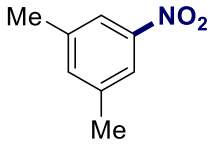
2.4. Compound **2q** was isolated as a yellow oil 88% (80 mg) after purification with flash column chromatography on silica gel (*n*-hexane:EtOAc, 95:5). According to GP *b*, *N*-nitrosaccharin (1.3 mmol, 1.3 equiv), (4-(methoxycarbonyl)phenyl)boronic acid (0.5 mmol, 1.0 equiv) and HFIP (2 mL) were added to a 10-mL vial and the reaction was stirred in a metal heat block as described in Section 2.5. Compound **2r** was isolated as a yellow oil 93% (85 mg) after purification with flash column chromatography on silica gel (*n*-hexane:EtOAc, 95:5). Observed spectral data correspond to literature specifications [CAS: 619-50-1]. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.26 (d, *J* = 8.9 Hz, 2H), 8.18 (d, *J* = 8.9 Hz, 2H), 3.96 (s, 3H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 165.7, 151.1, 136.0, 131.2, 124.0, 53.3.



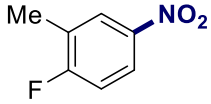
1-Nitro-4-(trifluoromethyl)benzene (2s): According to GP *a*, *N*-nitrosuccinimide (1.0 mmol, 2.00 equiv), (4-(trifluoromethyl)phenyl)boronic acid (0.5 mmol, 1.00 equiv), $[Ru(bpy)_3](PF_6)_2$ (2.5 mol%) and MeCN (2.0 mL) were added to a 10-mL vial. The reaction was irradiated with blue LEDs as described in Section 2.4. Compound **2s** was isolated as a yellow oil 81% (77 mg) after purification with flash column chromatography on silica gel (*n*-hexane:EtOAc, 95:5). According to GP *b*, *N*-nitrosaccharin (1.3 mmol, 1.3 equiv), (4-(trifluoromethyl)phenyl)boronic acid (0.5 mmol, 1.0 equiv) and HFIP (2 mL) were added to a 10-mL vial and the reaction was stirred in a metal heat block as described in Section 2.5. Compound **2s** was isolated as a yellow oil 74% (70 mg) after purification with flash column chromatography on silica gel (*n*-hexane:EtOAc, 95:5). Observed spectral data correspond to literature specifications [CAS: 402-54-0]. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.36 (d, *J* = 8.5 Hz, 2H), 7.84 (d, *J* = 8.6 Hz, 2H); **^{13}C NMR** (75 MHz, Chloroform-*d*) *δ* 150.0, 136.2 (q, *J* = 33.4 Hz), 126.8 (q, *J* = 3.7 Hz), 124.1, 123.1 (q, *J* = 273.2 Hz).; **^{19}F NMR** (282 MHz, Chloroform-*d*) δ -63.16.



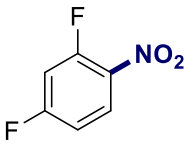
1,4-Dinitrobenzene (2t): According to GP *b*, *N*-nitrosaccharin (1.3 mmol, 1.3 equiv), (4-nitrophenyl)boronic acid (0.5 mmol, 1.0 equiv) and HFIP (2 mL) were added to a 10-mL vial and the reaction was stirred in a metal heat block as described in Section 2.5. Compound **2t** was isolated as yellow solid 51% (43 mg) after purification with flash column chromatography on silica gel (*n*-hexane:EtOAc, 10:1). Observed spectral data correspond to literature specifications [CAS: 100-25-4]. **R_f:** 0.59 (hexane:EtOAc 5:1). **^{1}H NMR** (300 MHz, Chloroform-*d*): *δ* 8.43 (s, 4H, $C_{Ar}H$). **^{13}C NMR** (75 MHz, Chloroform-*d*): *δ* 151.2, 125.0. **GC-MS** (EI): *m/z* 168 (M^+).



1,3-Dimethyl-5-nitrobenzene (2u): According to GP *a*, *N*-nitrosuccinimide (1.0 mmol, 2.00 equiv), (3,5-dimethylphenyl)boronic acid (0.5 mmol, 1.00 equiv), $[Ru(bpy)_3](PF_6)_2$ (2.5 mol%) and MeCN (2.0 mL) were added to a 10-mL vial. The reaction was irradiated with blue LEDs as described in Section 2.4. Compound **2u** was isolated as a yellow oil 73% (55 mg) after purification with flash column chromatography on silica gel (*n*-hexane:EtOAc, 99:1). Observed spectral data correspond to literature specifications [CAS: 603-71-4]. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.83 (s, 2H), 7.31 (s, 1H), 2.41 (s, 6H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 148.5, 139.6, 136.3, 121.2, 21.3.

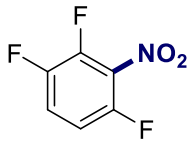


1-Fluoro-2-methyl-4-nitrobenzene (2v): According to GP *a*, *N*-nitrosuccinimide (1.0 mmol, 2.00 equiv), (4-fluoro-3-methylphenyl)boronic acid (0.5 mmol, 1.00 equiv), $[Ru(bpy)_3](PF_6)_2$ (2.5 mol%) and MeCN (2.0 mL) were added to a 10-mL vial. The reaction was irradiated with blue LEDs as described in Section 2.4. Compound **2v** was isolated as a yellow oil 85% (66 mg) after purification with flash column chromatography on silica gel (*n*-hexane:EtOAc, 20:1). Observed spectral data correspond to literature specifications [CAS: 455-88-9]. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.22 – 8.07 (m, 2H), 7.19 (t, *J* = 8.7 Hz, 1H), 2.43 (s, 3H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 167.1, 163.7, 144.5, 127.7, 127.6, 127.3, 127.1, 124.1, 123.9, 116.5, 116.2, 15.1; **^{19}F NMR** (282 MHz, Chloroform-*d*) δ -106.12.

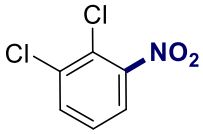


2,4-Difluoro-1-nitrobenzene (2w): According to GP *b*, *N*-nitrosaccharin (1.3 mmol, 1.3 equiv), (2,4-difluorophenyl)boronic acid (0.5 mmol, 1.0 equiv) and HFIP (2 mL) were added to a 10-mL vial and the reaction was stirred in a metal heat block as described in Section 2.5. Compound **2w** was isolated as yellow solid 90% (143 mg) after purification with flash column chromatography on silica gel (*n*-hexane:EtOAc, 99:1). Observed spectral data correspond to literature specifications [CAS: 446-35-5]. **R_f:** 0.38 (hexane:EtOAc 95:5). **^{1}H NMR** (300 MHz, Chloroform-*d*): *δ* 8.22 – 8.11 (m, 1H), 7.09 – 6.99 (m, 2H). **^{19}F NMR** (282 MHz, Chloroform-*d*): *δ* –97.49 (m, 1F), –110.80 (m, 1F). **^{13}C NMR** (75 MHz, Chloroform-*d*):

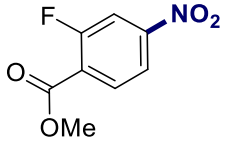
δ 165.9 (dd, J = 260.4, 11.2 Hz), 157.0 (dd, J = 268.3, 13.1 Hz), 134.4, 128.4 (dd, J = 11.0, 2.1 Hz), 112.3 (dd, J = 23.1, 4.2 Hz), 106.8 (dd, J = 26.6, 24.2 Hz). **GC-MS** (EI): *m/z* 159 (M^+).



1,2,4-Trifluoro-3-nitrobenzene (2x): According to GP *b*, *N*-nitrosaccharin (1.3 mmol, 1.3 equiv), (2,3,6-trifluorophenyl)boronic acid (0.5 mmol, 1.0 equiv) and HFIP (2 mL) were added to a 10-mL vial and the reaction was stirred in a metal heat block as described in Section 2.5. Compound **2x** was isolated as colorless oil 92% (81 mg) after purification with flash column chromatography on silica gel (*n*-hexane:EtOAc, 95:5). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.49 – 7.32 (m, 1H), 7.09 (t, J = 9.1 Hz, 1H); **^{13}C NMR** (75 MHz, Chloroform-*d*): 112.3 (ddd, J = 21.7, 6.4, 4.5 Hz), 120.2 (ddd, J = 19.4, 8.9, 1.5 Hz), 130.3 – 131.0 (m), 143.8 (ddd, J = 265, 17, 2.5 Hz), 147.2 (ddd, J = 262, 16, 2.5 Hz), 150.8 (dd, J = 255, 3 Hz); **^{19}F NMR** (282 MHz, Chloroform-*d*): δ -123.4 – -123.5 (m, 1F), -137.1 – -137.3 (m, 1F), -140.2 – -140.3 (m, 1F); **HRMS** (EI) m/z [M+] Calcd for $C_6H_2F_3NO_2$: 117.0032; Found 117.0033.

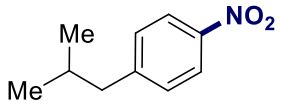


1,2-Dichloro-3-nitrobenzene (2y): According to GP *b*, *N*-nitrosaccharin (1.3 mmol, 1.3 equiv), (2,3-dichlorophenyl)boronic acid (0.5 mmol, 1.0 equiv) and HFIP (2 mL) were added to a 10-mL vial and the reaction was stirred in a metal heat block as described in Section 2.5. Compound **2y** was isolated as a white solid 96% (92 mg) after purification with flash column chromatography on silica gel (*n*-hexane:EtOAc, 95:5). Observed spectral data correspond to literature specifications [CAS: 3209-22-1]. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.79 – 7.61 (m, 2H), 7.37 (t, J = 8.1 Hz, 1H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 135.7, 133.7, 127.7, 125.9, 123.3.

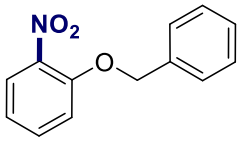


Methyl 2-fluoro-4-nitrobenzoate (2z): According to GP *b*, *N*-nitrosaccharin (1.3 mmol, 1.3 equiv), (2-fluoro-4-(methoxycarbonyl)phenyl)boronic acid (0.5 mmol, 1.0 equiv) and HFIP (2 mL) were added to a 10-mL vial and the reaction was stirred in a metal heat block as described in Section 2.5. Compound **2z** was isolated as a white solid 87% (86.5 mg) after purification with flash column chromatography on silica gel (*n*-hexane:EtOAc, 10:1). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.0 – 8.2 (m, 3H), 3.99 (s, 3H); **^{13}C**

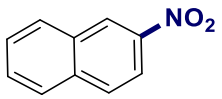
NMR (75 MHz, Chloroform-*d*) δ 165.12 – 161.12 (m), 159.66, 151.01 (d, *J* = 8.6 Hz), 133.27, 124.40 (d, *J* = 10.8 Hz), 118.5 (d, *J* = 4.5 Hz), 112.94 (d, *J* = 27.7 Hz), 53.08.



1-Isobutyl-4-nitrobenzene (2aa): According to GP *b*, *N*-nitrosaccharin (1.3 mmol, 1.3 equiv), (4-isobutylphenyl)boronic acid (0.5 mmol, 1.0 equiv) and HFIP (2 mL) were added to a 10-mL vial and the reaction was stirred in a metal heat block as described in Section 2.5. Compound **2aa** was isolated as a yellow oil 84% (75 mg) after purification with flash column chromatography on silica gel (*n*-hexane:EtOAc, 99:1). Observed spectral data correspond to literature specifications [CAS: 10342-60-6]. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.14 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 2.58 (d, *J* = 7.2 Hz, 2H), 1.99 – 1.85 (m, 1H), 0.92 (d, *J* = 6.6 Hz, 6H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 149.6, 129.8, 123.5, 45.2, 30.2, 22.3.

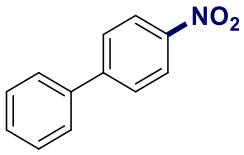


1-(Benzyloxy)-2-nitrobenzene (2ab): According to GP *b*, *N*-nitrosaccharin (1.3 mmol, 1.3 equiv), (2-(benzyloxy)phenyl)boronic acid (0.5 mmol, 1.0 equiv) and HFIP (2 mL) were added to a 10-mL vial and the reaction was stirred in a metal heat block as described in Section 2.5. Compound **2ab** was isolated as a colorless oil 82% (94 mg) after purification with flash column chromatography on silica gel (*n*-hexane:EtOAc, 10:1). Observed spectral data correspond to literature specifications [CAS: 4560-41-2]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.85 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.53 – 7.43 (m, 3H), 7.43 – 7.36 (m, 2H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 1H), 7.04 (t, *J* = 7.3 Hz, 1H), 5.24 (s, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 151.9, 135.6, 134.0, 128.7, 128.2, 126.9, 125.7, 120.6, 115.1, 71.1.

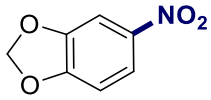


2-Nitronaphthalene (2ac): According to GP *b*, *N*-nitrosaccharin (1.3 mmol, 1.3 equiv), naphthalen-2-ylboronic acid (0.5 mmol, 1.0 equiv) and HFIP (2 mL) were added to a 10-mL vial and the reaction was stirred in a metal heat block as described in Section 2.5. Compound **2ac** was isolated as a yellow solid 84% (73 mg) after purification with flash column chromatography on silica gel (*n*-hexane:EtOAc, 99:1). Observed spectral data correspond to literature specifications [CAS: 581-89-5]. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.78 (s, 1H), 8.22 (d, *J* = 8.7 Hz, 1H), 7.98 (dd, *J* = 22.7, 8.2 Hz, 3H), 7.66 (dt, *J* = 14.8,

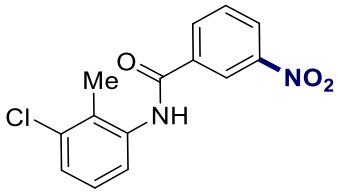
6.4 Hz, 2H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 145.6, 135.9, 131.9, 130.0, 129.8, 129.6, 127.9, 124.7, 119.3.



4-Nitro-1,1'-biphenyl (2ad): According to GP *a*, *N*-nitrosuccinimide (1.0 mmol, 2.00 equiv), [1,1'-biphenyl]-4-ylboronic acid (0.5 mmol, 1.00 equiv), $[Ru(bpy)_3](PF_6)_2$ (2.5 mol%) and MeCN (2.0 mL) were added to a 10-mL vial. The reaction was irradiated with blue LEDs as described in Section 2.4. Compound **2ad** was isolated as a yellow oil 72% (65 mg) after purification with flash column chromatography on silica gel (*n*-hexane:EtOAc, 20:1). Observed spectral data correspond to literature specifications [CAS: 92-93-3]. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.30 (d, *J* = 8.9 Hz, 2H), 7.74 (d, *J* = 8.9 Hz, 2H), 7.63 (dd, *J* = 8.1, 1.4 Hz, 2H), 7.48 (dd, *J* = 10.2, 7.1 Hz, 3H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 147.8, 147.2, 138.9, 129.3, 129.1, 127.9, 127.5, 124.2.

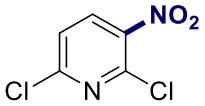


5-Nitrobenzo[d][1,3]dioxole (2ae): According to GP *b*, *N*-nitrosaccharin (1.3 mmol, 1.3 equiv), benzo[d][1,3]dioxol-5-ylboronic acid (0.5 mmol, 1.0 equiv) and HFIP (2 mL) were added to a 10-mL vial and the reaction was stirred in a metal heat block as described in Section 2.5. Compound **2ae** was isolated as a colorless oil 78% (65 mg) after purification with flash column chromatography on silica gel (*n*-hexane:EtOAc, 5:1). Observed spectral data correspond to literature specifications [CAS: 2620-44-2]. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.5 Hz, 1H), 7.84 – 7.61 (m, 1H), 6.94 (d, *J* = 8.6 Hz, 1H), 6.21 (s, 2H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 153.2, 148.2, 142.9, 119.9, 107.6, 104.5, 103.1.

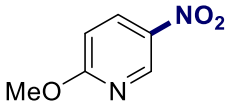


N-(3-chloro-2-methylphenyl)-3-nitrobenzamide (2af): According to GP *b*, *N*-nitrosaccharin (1.3 mmol, 1.3 equiv), (3-((3-chloro-2-methylphenyl)carbamoyl)phenyl)boronic acid (0.5 mmol, 1.0 equiv) and HFIP (2 mL) were added to a 10-mL vial and the reaction was stirred in a metal heat block as described in Section 2.5. Compound **2af** was isolated as a white solid 68% (99 mg) after purification with flash column chromatography on silica gel (*n*-hexane:EtOAc, 5:1). **^{1}H NMR** (300 MHz, DMSO-d_6) δ 10.51 (s, 1H), 8.82 (s, 1H), 8.44 (t, J = 7.9 Hz, 2H), 7.85 (t, J = 8.0 Hz, 1H), 7.33 (ddd, J = 24.2, 16.2, 7.7 Hz, 3H), 2.27 (s,

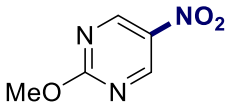
3H); **^{13}C NMR** (75 MHz, DMSO-d_6) δ 163.4, 147.8, 137.5, 135.5, 134.1, 133.9, 132.3, 130.2, 127.1, 126.9, 126.3, 125.9, 122.4, 15.3; **HRMS** (ESI) m/z [M+Na] Calcd for $C_{14}H_{11}CN_2NaO_3$: 313.035; Found 313.0352.



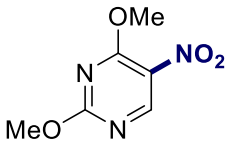
2,6-Dichloro-3-nitropyridine (2ag): According to GP *a*, *N*-nitrosuccinimide (1.0 mmol, 2.00 equiv), (2,6-dichloropyridin-3-yl)boronic acid (0.5 mmol, 1.00 equiv), $[Ru(bpy)_3](PF_6)_2$ (2.5 mol%) and MeCN (2.0 mL) were added to a 10-mL vial. The reaction was irradiated with blue LEDs as described in Section 2.4. Compound **2ag** was isolated as a white solid 65% (62 mg) after purification with flash column chromatography on silica gel (*n*-hexane:EtOAc, 9:1). Observed spectral data correspond to literature specifications [CAS: 16013-85-7]. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.31 (d, *J* = 8.4 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 1H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 153.52, 143.58, 136.58, 123.83.



2-Methoxy-5-nitropyridine (2ah): According to GP *a*, *N*-nitrosuccinimide (1.0 mmol, 2.00 equiv), (6-methoxypyridin-3-yl)boronic acid (0.5 mmol, 1.00 equiv), $[Ru(bpy)_3](PF_6)_2$ (2.5 mol%) and MeCN (2.0 mL) were added to a 10-mL vial. The reaction was irradiated with blue LEDs as described in Section 2.4. Compound **2ah** was isolated as a white solid 35% (27 mg) after purification with flash column chromatography on silica gel (*n*-hexane:EtOAc, 10:1). Observed spectral data correspond to literature specifications [CAS: 5446-92-4]. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.15 (d, *J* = 2.3 Hz, 1H), 8.41 (dd, *J* = 9.1, 2.6 Hz, 1H), 6.89 (d, *J* = 9.1 Hz, 1H), 4.12 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 167.4, 144.9, 133.9, 111.3, 54.9

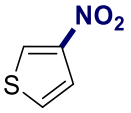


2-Methoxy-5-nitropyrimidine (2ai): According to GP *a*, *N*-nitrosuccinimide (1.0 mmol, 2.00 equiv), (2-methoxypyrimidin-5-yl)boronic acid (0.5 mmol, 1.00 equiv), $[Ru(bpy)_3](PF_6)_2$ (2.5 mol%) and MeCN (2.0 mL) were added to a 10-mL vial. The reaction was irradiated with blue LEDs as described in Section 2.4. Compound **2ai** was isolated as a white solid 70% (54 mg) after purification with flash column chromatography on silica gel (*n*-hexane:EtOAc, 10:1). Observed spectral data correspond to literature specifications [CAS: 14001-69-5]. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 9.35 (s, 2H), 4.21 (s, 3H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 167.4, 155.9, 138.3, 56.7.

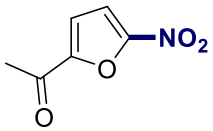


2,4-Dimethoxy-5-nitropyrimidine (2aj): According to GP *a*, *N*-nitrosuccinimide (1.0 mmol, 2.00 equiv), (2,4-dimethoxypyrimidin-5-yl)boronic acid (0.5 mmol, 1.00 equiv), $[Ru(bpy)_3](PF_6)_2$ (2.5 mol%) and MeCN (2.0 mL) were added to a 10-mL vial. The reaction was irradiated with blue LEDs as described in Section 2.4. Compound **2aj** was isolated as a white solid 69% (63 mg) after purification with flash column chromatography on silica gel (*n*-hexane:EtOAc, 10:1). Observed spectral data correspond to literature specifications [CAS: 30561-07-0]. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 9.09 (s, 1H), 4.19 (s, 3H), 4.12 (s, 3H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 166.2, 164.1, 158.3, 128.0, 56.3, 55.6.

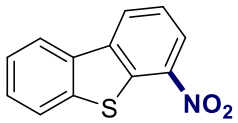
3,5-Dimethyl-4-nitroisoxazole (2ak): According to GP *a*, *N*-nitrosuccinimide (1.0 mmol, 2.00 equiv), (3,5-dimethylisoxazol-4-yl)boronic acid (0.5 mmol, 1.00 equiv), $[Ru(bpy)_3](PF_6)_2$ (2.5 mol%) and MeCN (2.0 mL) were added to a 10-mL vial. The reaction was irradiated with blue LEDs as described in Section 2.4. Compound **2ak** was isolated as a white solid 55% (39 mg) after purification with flash column chromatography on silica gel (*n*-hexane:EtOAc, 95:5). Observed spectral data correspond to literature specifications [CAS: 1123-49-5]. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 2.80 (s, 3H), 2.53 (s, 3H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 171.9, 155.6, 130.3, 13.9, 11.6.



3-Nitrothiophene (2al): According to GP *b*, *N*-nitrosaccharin (1.3 mmol, 1.3 equiv), thiophen-3-ylboronic acid (0.5 mmol, 1.0 equiv) and HFIP (2 mL) were added to a 10-mL vial and the reaction was stirred in a metal heat block as described in Section 2.5. Compound **2al** was isolated as a yellow oil 62% (40 mg) after purification with flash column chromatography on silica gel (*n*-hexane:EtOAc, 95:5). Observed spectral data correspond to literature specifications [CAS: 822-84-4]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.36 – 8.24 (m, 1H), 7.65 (dd, *J* = 5.4, 1.5 Hz, 1H), 7.36 (dd, *J* = 5.4, 3.4 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.0, 127.5, 126.9, 122.7.

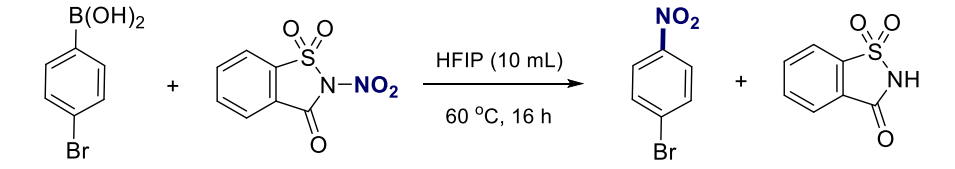


1-(5-Nitrofuran-2-yl)ethan-1-one (2am): According to GP *b*, *N*-nitrosaccharin (1.3 mmol, 1.3 equiv), (5-acetylfuran-2-yl)boronic acid (0.5 mmol, 1.0 equiv) and HFIP (2 mL) were added to a 10-mL vial and the reaction was stirred in a metal heat block as described in Section 2.5. Compound **2am** was isolated as a light yellow solid 68% (53 mg) after purification with flash column chromatography on silica gel (*n*-hexane:EtOAc, 95:5). Observed spectral data correspond to literature specifications [CAS: 1330049-33-6]. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 3.8 Hz, 1H), 7.20 (d, *J* = 3.8 Hz, 1H), 2.54 (s, 3H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 186.8, 151.9, 151.5, 116.7, 111.9, 26.3.



4-Nitrodibenzo[b,d]thiophene (2an): According to GP *b*, *N*-nitrosaccharin (1.3 mmol, 1.3 equiv), dibenzo[b,d]thiophen-4-ylboronic acid (0.5 mmol, 1.0 equiv) and HFIP (2 mL) were added to a 10-mL vial and the reaction was stirred in a metal heat block as described in Section 2.5. Compound **2an** was isolated as a yellow solid 71% (81 mg) after purification with flash column chromatography on silica gel (*n*-hexane:EtOAc, 95:5). Observed spectral data correspond to literature specifications [CAS: 157555-18-5]. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.50 (t, *J* = 8.5 Hz, 2H), 8.22 (d, *J* = 6.8 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.65 (t, *J* = 7.9 Hz, 1H), 7.61 – 7.47 (m, 2H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 143.0, 141.0, 138.9, 135.5, 133.9, 128.2, 127.3, 125.3, 124.8, 123.3, 122.8, 121.9.

2.7 Nitration of arylboronic acids: gram-scale reaction



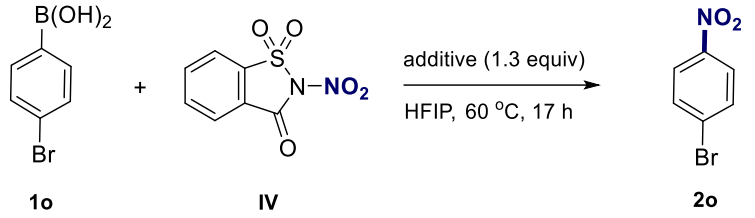
1o: 2.0 g, 10 mmol **IV**: 3.0 g, 13 mmol **2o**: 1.91 g, 95% **IVc**: 2.27 g, 95%

A 50 mL flame-dried Schlenk flask equipped with a stirbar was charged (4-bromophenyl)boronic acid **1o** (2.0 g, 10 mmol, 1.0 equiv) and **IV** (3.0 g, 13 mmol, 1.3 equiv). The flask evacuated for 5 min and then backfilled with Ar. HFIP (10 mL, 1M) was added, the tap was closed and the reaction was stirred as a suspension for 16 h at 60 °C. The solvent was removed under reduced pressure (40 °C, 200 mbar) to give a yellow solid. CH_2Cl_2 (10 mL) was added, and the mixture was sonicated for 2 min. The solid was collected on a glass frit, washed thoroughly with CH_2Cl_2 and dried on high vacuum to give pure saccharin (**IVc**) as a white solid (1.96 g). The filtrate (yellow solution) was loaded onto silica gel and purified by automated flash column chromatography (hexane; after complete elution of 1-bromo-4-nitrobenzene **2o**, the gradient was increased to 40% EtOAc in hexane to elute remaining saccharin). Saccharin obtained after column chromatography was washed CH_2Cl_2 to give a white solid (0.31 g). 1-Bromo-4-nitrobenzene **2o** was obtained as an off-white solid (1.91 g, 95%).

2.8 Mechanistic studies

2.8.1 Effect of radical scavengers on *ipso*-nitration of 1o in HFIP

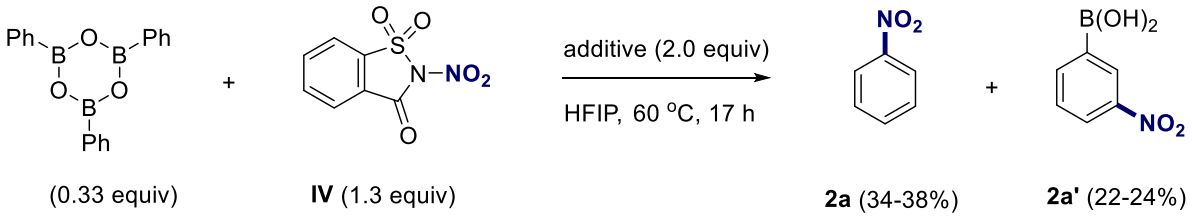
An oven-dried crimp cap microvial equipped with a magnetic stirrer was cooled down to rt under high vacuum, filled with argon and charged with arylboronic acid **1o** (1 mmol, 1.0 equiv) and **IV** (296 mg, 1.3 mmol, 1.3 equiv) on a bench. The vial was closed with a cap with septum using a crimper, connected to a Schlenk line via a needle, evacuated for 5 min and then backfilled with Ar. Radical scavenger (1.3 mmol, 1.3 equiv,) in HFIP (2 mL, 0.5M) was added, and the reaction was stirred at 60 °C in a metal heat block for 17 hours. The vial was cooled to room temperature and the crude residue was concentrated on silica gel under reduced pressure (40 °C, 200 mbar). The product was purified by automated flash column chromatography as indicated.



Entry	Radical scavenger	Isolated yield of 2n [%][b]
1	1,4-Dinitrobenzene	92
2	1,4-Benzoquinone	55
3	Styrene	49

[a] Reaction conditions: **1o** (1 mmol, 1 equiv), **IV** (1.3 equiv 0.65 mmol), radical scavenger (1.3 equiv), HFIP (2 mL). [b] Isolated yield.

2.8.2 Nitration of triphenylboroxine with IV in HFIP



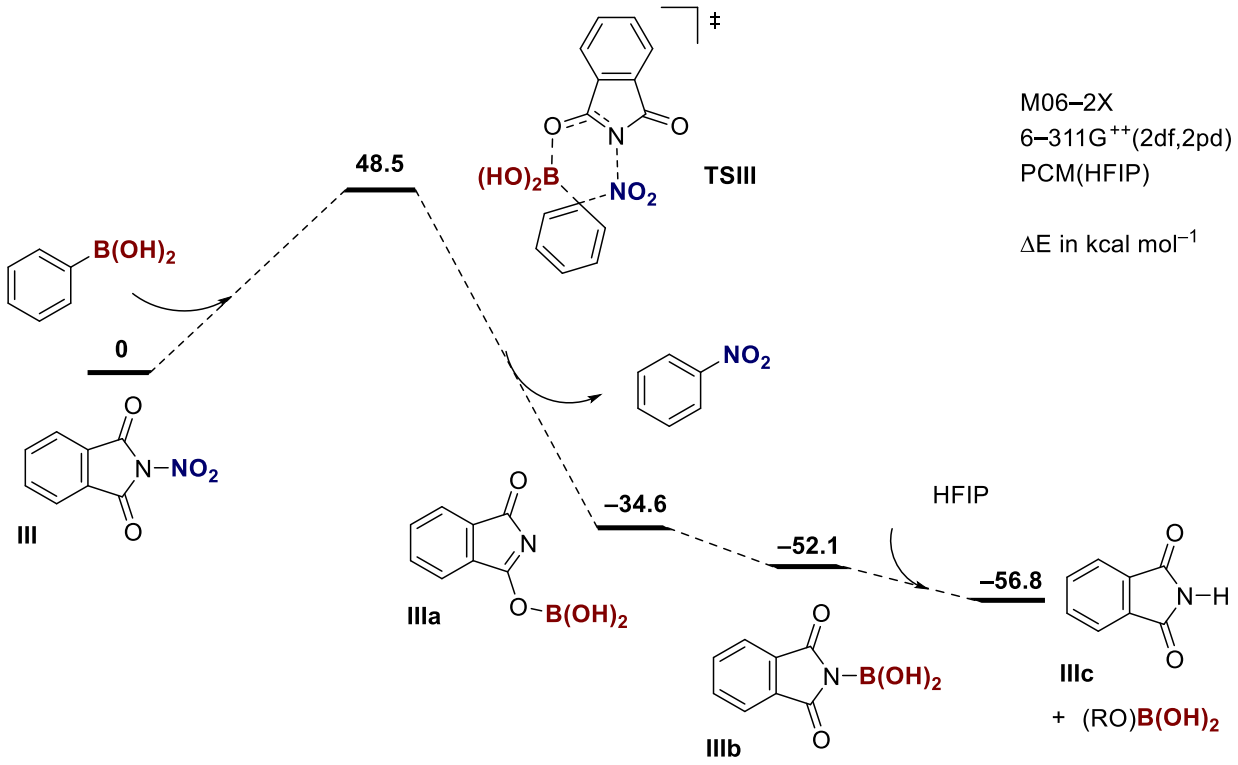
Experiment 1: triphenylboroxine (0.17 mmol, 1.0 equiv), **IV** (0.65 mmol, 3.8 equiv), HFIP (1 mL), 34% of **2a**, 22% of **2a'**; ***experiment 2***: triphenylboroxine (0.17 mmol, 1.0 equiv), **IV** (0.65 mmol, 3.8 equiv), HFIP (1 mL), $MgSO_4$ (2 equiv), 38% of **2a**, 24% of **2a'**. Yields were determined by GC and GC-MS using *n*-decane as internal standard. Addition of water in the end of the reaction had no effect on yields of **2a** and **2a'**.

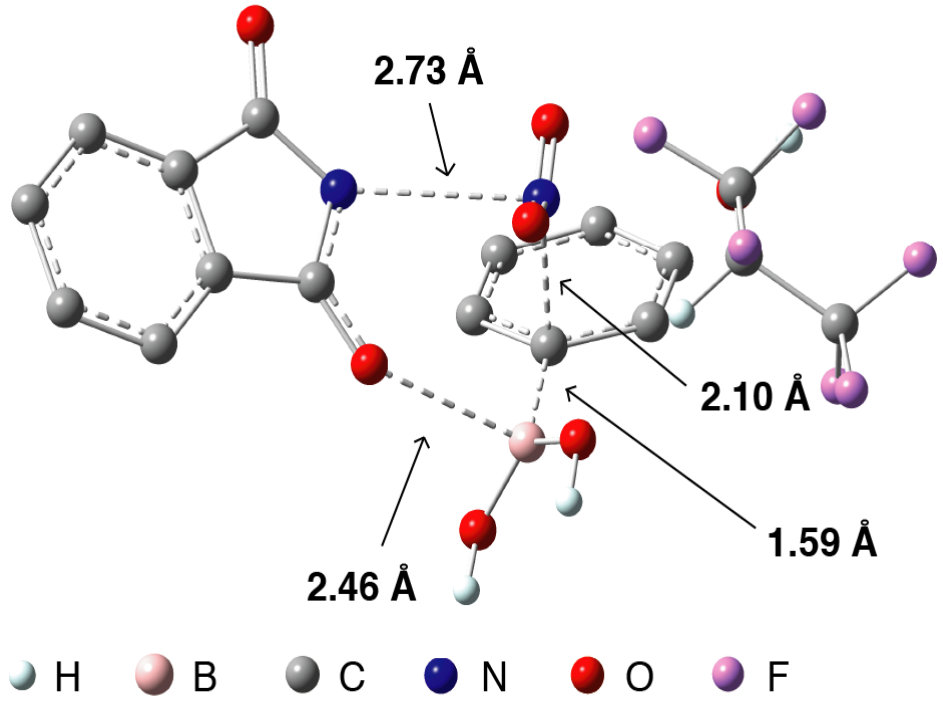
2.8.3 Density Functional Theory (DFT) calculations

All DFT calculations were performed with the Gaussian09 program package (Revision D.01).[5] The structures of all minima and transition states were fully optimized using the hybrid density functional M06–2X[6] with the ultrafine pruned (99,590) grid. The 6–311G++(2df,2pd) (or 6–311G++(d,p) where expressly stated) Pople basis set[7] was used for all the atoms. The implicit solvation model IEF–PCM was used as implemented in Gaussian, applying all the parameters of 2-propanol, apart from the dielectric constant (ε), which was modified to 16.70 (HFIP)[8] according to the literature for the description of HFIP as solvent[9,3] (or acetonitrile where expressly stated). Stationary points were characterized by vibrational analysis (only real frequencies for minima, one imaginary frequency for transition states (TSs)), and intrinsic reaction coordinate (IRC) calculations were carried out on the TSs in order to confirm their correct identification. Computed harmonic frequencies were used to calculate the thermal contribution to Gibbs free energy at 298 K and 1 atm. TSs were modelled according to the literature by substitution of benzene with phenyl boronic acid for nitrating agents (**III** and **IV**). Gibbs free energies and energies (G and E) are reported in Hartree, imaginary frequencies (ν) are reported in cm^{-1}.

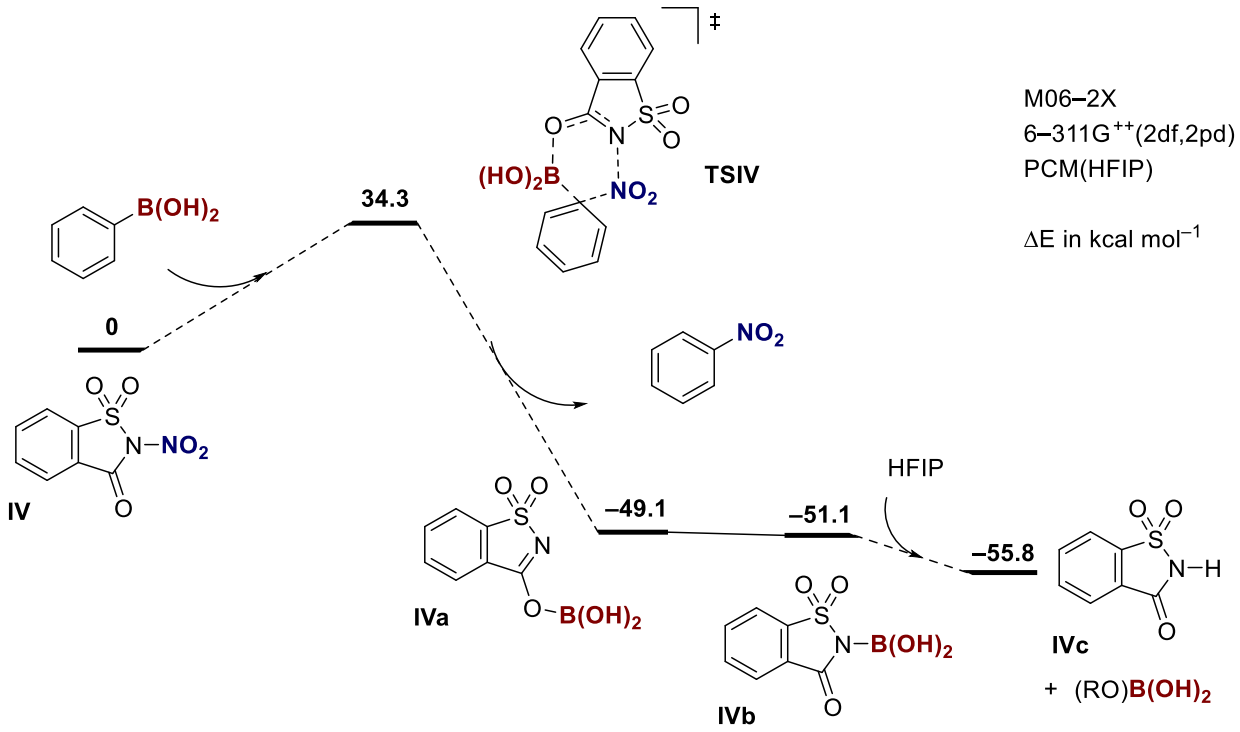
Results

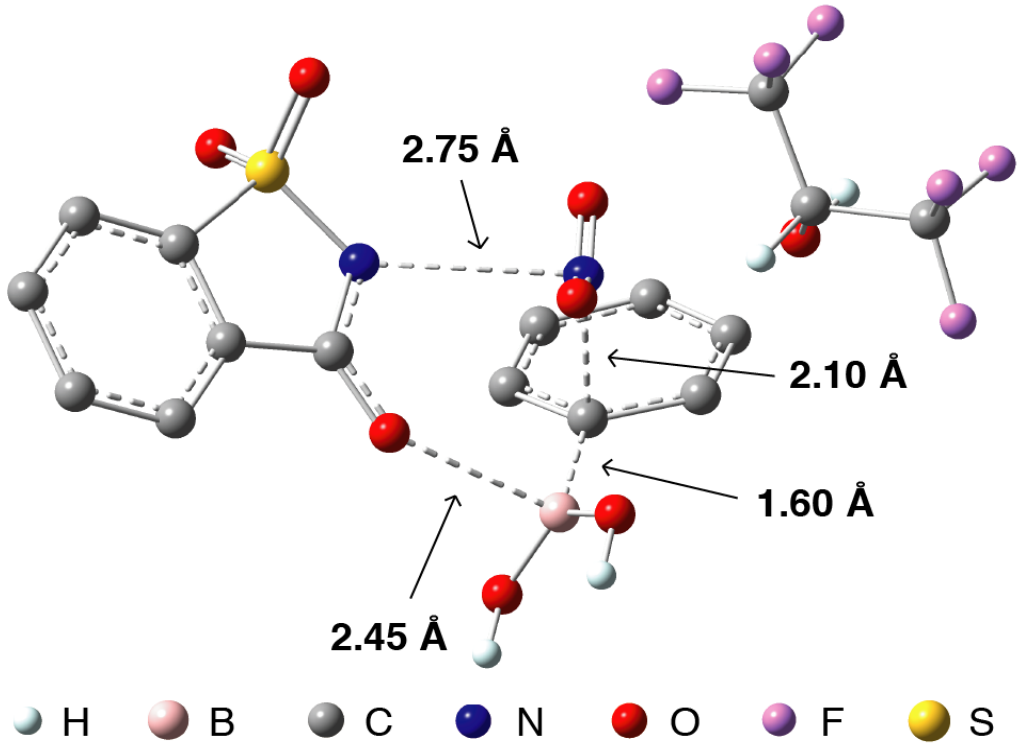
Ipso-nitration in HFIP with nitrating reagent III





Ipso-nitration in HFIP with nitrating reagent IV




2.75 Å
2.10 Å
1.60 Å
2.45 Å
H
B
C
N
O
F
S

18

III (G = –717.448344, E = –717.530064)

C	-1.19780500	0.89430900	-0.04710300
C	-1.09637800	-0.47914600	0.11044800
C	-2.21352800	-1.28263900	0.20844700
C	-3.45350900	-0.65422200	0.13853300
C	-3.55563600	0.72647100	-0.02144300
C	-2.42148200	1.52755300	-0.11830600
H	-2.12434100	-2.35236000	0.33120000
H	-4.35464900	-1.24621700	0.20897600
H	-4.53432600	1.18171400	-0.07017900
H	-2.49099300	2.59872400	-0.24114000
C	0.15598700	1.49146300	-0.12268200
O	2.89008100	1.47899900	0.44119900
O	0.48765100	2.62152300	-0.29013400
O	3.02028700	-0.46976500	-0.47040800
N	1.03407600	0.36566600	0.00777900
N	2.42526500	0.46623000	-0.00822300
C	0.33039300	-0.87474100	0.15541000
O	0.82489300	-1.94494200	0.31405000

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TSIII (G = –1915.327690, E = –1915.567940, □ = 169.79)

C	-0.32189100	-0.52130800	-0.60428800
C	2.34462700	-1.39920600	-0.42034800
C	0.45770400	-0.19735800	0.54874900
C	0.24409700	-1.18796800	-1.65702700
C	1.78740100	-0.72551500	0.63700500
C	1.58175700	-1.59910000	-1.57306100
H	-1.34926200	-0.18998600	-0.63521300
H	3.35988800	-1.76388200	-0.37229100
H	-0.32506000	-1.39703100	-2.55071700
H	2.35609400	-0.54947200	1.53988300
H	2.02981900	-2.10271500	-2.41945200
O	1.72118000	1.40062300	-1.28004900
O	1.05669800	2.41069100	0.52414400
N	1.24363600	1.58023800	-0.24899100
N	-1.13449700	2.40915200	-1.30941400
C	-1.87933400	2.52377000	-0.18296900
C	-3.00223100	3.50913300	-0.39679600
O	-1.68994300	1.92146400	0.87503700
C	-2.86890100	3.95274200	-1.69909900
C	-4.01049300	3.96593400	0.42463200
C	-3.73702300	4.87507100	-2.24194700
C	-4.89860100	4.90128800	-0.11123000
H	-4.11183700	3.61627300	1.44318800
C	-4.76415000	5.34851800	-1.42235200
H	-3.62803600	5.21998400	-3.26137400
H	-5.70396600	5.28614800	0.49924300
H	-5.46713200	6.07362400	-1.80890900
O	3.67159300	1.68103800	1.12526500
H	4.60336900	1.72436100	0.87471000
C	3.48056700	2.20378500	2.40282700
H	2.41945600	2.12424400	2.64673500
C	4.24510600	1.36960700	3.42912700
C	3.86206000	3.68295900	2.42901100
F	3.11257500	4.35008200	1.55636300
F	3.68459100	4.22856300	3.62719500
F	5.13944400	3.85556100	2.07867500
F	4.08347400	1.81756200	4.66833100
F	5.55222800	1.34874800	3.15974100
F	3.80821800	0.11065400	3.38734300
B	-0.27341600	0.20218700	1.90729200
O	-1.37613800	-0.53312600	2.20102200
H	-1.80859700	-0.32834200	3.03447700
O	0.42338400	0.99255200	2.76996700
H	0.00245600	1.16057200	3.61805300
C	-1.66421400	3.23444400	-2.26374800
O	-1.24698600	3.38632300	-3.40169400

20

IIIa (G = –689.016325, E = –689.118806)

N	-2.09530000	0.00013400	-1.16554900
C	-2.85035700	0.13997500	-0.13384100
C	-3.93262900	1.14272500	-0.28276100
O	-2.70571400	-0.48969300	1.01102600
O	0.80910700	-1.68956400	1.42549200
C	-3.77947300	1.63133800	-1.57037600
C	-4.92773100	1.58905300	0.55673000
C	-4.61890000	2.59286600	-2.08128000
C	-5.78628200	2.56818800	0.04900100
H	-5.04290900	1.20452400	1.56012500
C	-5.63566300	3.05956100	-1.24255200
H	-4.49931700	2.97224700	-3.08643700
H	-6.58275900	2.95098000	0.67121700
H	-6.31798800	3.81637500	-1.60285200
B	-2.01679300	-1.69769400	1.21343700
O	-2.00692300	-2.62416700	0.23608200
H	-1.55158800	-3.43497200	0.48096300
O	-1.45778300	-1.91019900	2.42498800
H	-1.52707800	-1.16900200	3.03302900
C	-2.59766400	0.90213400	-2.14636900
O	-2.12701400	1.03517600	-3.24204700

20

IIIb (G = –689.041022, E = –689.145914)

C	-2.77812100	0.18384700	0.03344200
C	-3.87396600	1.15305600	-0.24246500
O	-2.50842500	-0.33590100	1.07822100
C	-3.82486500	1.49677100	-1.58068200
C	-4.82412700	1.68146400	0.60723100
C	-4.72121000	2.38549800	-2.13937900
C	-5.73507100	2.57940900	0.05748700
H	-4.85721000	1.40862600	1.65241100
C	-5.68469700	2.92566400	-1.29257400
H	-4.67462000	2.64810500	-3.18662300
H	-6.49684800	3.01791000	0.68629200
H	-6.40799900	3.62602000	-1.68520700
N	-2.09864300	-0.01476600	-1.19462100
B	-0.93125800	-0.88436000	-1.43700400
O	-0.42685700	-1.58531200	-0.39705200
H	0.33129400	-2.11905000	-0.65397500
O	-0.39487200	-0.96263100	-2.67571900
H	-0.86134300	-0.40483800	-3.31511000
C	-2.69800600	0.75947800	-2.19982500
O	-2.33847600	0.79860100	-3.35317700

16

IIIc (G = –512.992849, E= –513.077064)

C	-1.20113800	0.87148300	-0.02570000
C	-1.12152000	-0.50807400	0.09268700
C	-2.25089900	-1.29508800	0.16655800
C	-3.48283800	-0.64514100	0.11741000
C	-3.56278300	0.74028500	-0.00124900
C	-2.41362000	1.52548700	-0.07523200
H	-2.18200800	-2.36975100	0.25866400
H	-4.39354600	-1.22438700	0.17242400
H	-4.53426900	1.21243700	-0.03626100
H	-2.46880500	2.60094800	-0.16721600
C	0.18755700	1.41500300	-0.07936800
O	0.54808500	2.55817600	-0.17994200
N	1.02055300	0.30601300	0.01256900
C	0.32055500	-0.89042000	0.11850400
O	0.81051600	-1.98517400	0.20998500
H	2.02815300	0.36275100	0.00209500

19

IV (G = –1152.706933, E = –1152.787048)

C	-1.19038800	0.84221300	-0.02395900
C	-1.16754900	-0.53624600	0.09479600
C	-2.31480300	-1.29907100	0.16762500
C	-3.52539600	-0.61724500	0.11547500
C	-3.56668600	0.76953500	-0.00459600
C	-2.39817700	1.51539100	-0.07552000
H	-2.27806700	-2.37444900	0.26111800
H	-4.44788000	-1.17666100	0.16980500
H	-4.52276200	1.27067800	-0.04263200
H	-2.41383600	2.59174800	-0.16812900
C	0.13911000	1.49148900	-0.08494200
O	2.90926400	1.73031900	-0.11464800
O	0.37128100	2.65433200	-0.18668000
O	3.11822200	-0.40956200	0.06160100
N	1.10665200	0.44731000	0.00174900
N	2.48590000	0.61512700	-0.01992000
S	0.46919200	-1.16896900	0.14125700

O	0.79826900	-1.89773200	-1.04052700
47			
TSIV (G = –2350.608769, E = –2350.847520, □ = 141.31)			
C	-0.29922400	-0.59580300	-0.68848700
C	2.37725000	-1.34786400	-0.24139000
C	0.31714400	-0.31963300	0.56932100
C	0.42590000	-1.15223100	-1.70510600
C	1.66032800	-0.77509400	0.78176700
C	1.76815300	-1.50439800	-1.48528300
H	-1.33405100	-0.31515200	-0.82248500
H	3.40080500	-1.65966600	-0.09444600
H	-0.01854700	-1.32308700	-2.67448800
H	2.10917600	-0.61807100	1.75375800
H	2.34001400	-1.92267300	-2.30295800
O	1.67722100	1.46441200	-1.00414200
O	0.91491100	2.27077100	0.86343400
N	1.15097200	1.52716500	0.01661700
N	-1.13606000	2.40608900	-1.22602500
C	-1.98458900	2.45225900	-0.18331500
S	-1.53173100	3.47330100	-2.36933700
C	-3.08096300	3.47404600	-0.35212600
O	-1.90322800	1.74824700	0.82468700
C	-2.96169500	4.14336600	-1.55218100
O	-1.92273100	2.81420600	-3.60151900
O	-0.51300600	4.49610000	-2.51781000
C	-4.11243900	3.77690900	0.51775400
C	-3.84111000	5.13009300	-1.94756900
C	-5.01362100	4.76822800	0.14296400
H	-4.20673600	3.25231900	1.45845900
C	-4.88006000	5.43595700	-1.07279200
H	-3.73234000	5.64462500	-2.89191300
H	-5.83068600	5.02685700	0.80176800
H	-5.59336600	6.20256400	-1.34095200
O	3.67171300	1.51273700	1.17846400
H	4.43520400	1.19614600	0.67792100
C	3.96091000	2.73295800	1.78339600
H	3.08648800	3.04929800	2.35263700
C	5.11957900	2.57096400	2.76763900
C	4.22612800	3.79527300	0.71515400
F	3.17012100	3.87795700	-0.09186700
F	4.44183600	4.99562500	1.23757800
F	5.28092900	3.46911300	-0.03467100
F	5.45493000	3.71931700	3.34376700
F	6.19987400	2.08141400	2.15422600
F	4.77671100	1.71221800	3.72311200
B	-0.59718700	-0.05650100	1.85018900
O	-1.71218100	-0.83067200	1.91734400
H	-2.25635500	-0.70761900	2.69993500
O	-0.04599600	0.65841900	2.86346100
H	-0.58348000	0.74473000	3.65542900
21			
IVa (G = –1124.296717, E = –1124.398166)			
N	-2.01863300	-0.05755100	-1.19232700
C	-2.81048200	0.14201400	-0.20605100
S	-2.44617900	0.94503900	-2.45670800
C	-3.87654400	1.15786500	-0.36039800
O	-2.72093800	-0.46361200	0.95951000
C	-3.80605300	1.72307400	-1.62030800
O	-2.90543500	0.14550200	-3.55978800
O	-1.37871000	1.87872000	-2.69346800
C	-4.84401900	1.55746500	0.54153300
C	-4.67797500	2.69830500	-2.04650700
C	-5.73632100	2.54416500	0.13248800
H	-4.90084400	1.11684300	1.52639900
C	-5.65495000	3.10457700	-1.13859900
H	-4.61240200	3.13088600	-3.03418300
H	-6.50546400	2.88144400	0.81208000
H	-6.36124500	3.86895200	-1.42921600
B	-2.07974500	-1.68481300	1.23293200
O	-1.90741900	-2.58077200	0.24388800
H	-1.50234900	-3.40241800	0.53683600
O	-1.72216400	-1.92714500	2.51219200
H	-1.89552600	-1.20393900	3.12120300
O	4.95254700	1.52236000	-2.12745300
12			
21			
IVb (G = –1124.298592, E = –1124.401408)			
C	-2.78004200	0.21777100	-0.03804200
S	-2.47699700	1.00099100	-2.48106100
C	-3.86809600	1.19105800	-0.32607200
O	-2.60845100	-0.34848000	1.00400800
C	-3.84772500	1.67687200	-1.61809500
O	-2.86256700	0.14684300	-3.57698900
O	-1.47992300	1.99916100	-2.74555300
C	-4.84652400	1.60937600	0.55813100
C	-4.76927200	2.58599300	-2.09581200
C	-5.79001500	2.52061900	0.10239000
H	-4.86423600	1.22884300	1.56934400
C	-5.75284400	3.00105900	-1.20546100
H	-4.73167700	2.95650100	-3.10970600
H	-6.56667900	2.86418900	0.77015900
H	-6.49946200	3.70898400	-1.53497600
N	-1.99460600	0.03570300	-1.19142800
B	-0.89178000	-0.93265300	-1.38000900
O	-0.27512500	-1.40481800	-0.27993000
H	0.40445700	-2.05457600	-0.48567000
O	-0.51097300	-1.30129200	-2.62577900
H	-1.09657600	-1.04980100	-3.34901000
17			
IVc (G = –948.252796, E = –948.334697)			
C	-1.20153400	0.84082600	-0.02351900
C	-1.17846500	-0.53735000	0.09483300
C	-2.32506000	-1.30003500	0.16738700
C	-3.53617800	-0.61719200	0.11535400
C	-3.57646300	0.76962900	-0.00407300
C	-2.40649900	1.51608700	-0.07486500
H	-2.28943300	-2.37572600	0.26047300
H	-4.45978400	-1.17512800	0.16924400
H	-4.53286600	1.27065400	-0.04176200
H	-2.42365800	2.59268600	-0.16704000
C	0.15775800	1.44469800	-0.08139100
O	0.42584500	2.61257700	-0.18575600
N	1.09044300	0.42767600	0.00776200
S	0.48506300	-1.12210800	0.13779400
O	0.82479100	-1.68101900	1.41618300
O	0.81904900	-1.88255200	-1.03376300
H	2.08645000	0.60085200	-0.01999000
16			
1a (G = –408.167104, E = –408.259986)			
C	1.98346900	0.28433200	1.36960300
C	3.07230900	0.08873500	0.52865200
C	3.47715700	1.10483400	-0.32741600
C	2.79164400	2.31189400	-0.33867000
C	1.69448700	2.53126000	0.49802500
C	1.30481900	1.49433500	1.35144200
H	1.66645000	-0.50556000	2.03684700
H	3.60406300	-0.85303800	0.54011300
H	4.32399000	0.95644300	-0.98324600
H	3.13040600	3.08672200	-1.01672100
H	0.45727400	1.64354300	2.00765200
B	0.90208900	3.88448000	0.50679800
O	1.19695800	4.94960500	-0.29482100
H	1.94122100	4.82317800	-0.88646400
O	-0.14865000	4.00704600	1.36697000
H	-0.58124200	4.86424300	1.30893400
14			
2a (G = –436.654962, E = –436.727137)			
C	0.75070200	-0.51355600	-1.81101100
C	2.13390300	-0.59581100	-1.80949900
C	2.85882400	0.57170200	-1.97756300
C	2.26111700	1.80916500	-2.14576100
C	0.87690300	1.87325200	-2.14463800
C	0.12517100	0.71625500	-1.97790300
H	0.16236800	-1.41020400	-1.68182900
H	2.64462100	-1.53733900	-1.68224500
H	2.86836000	2.69152900	-2.27305800
H	0.38651700	2.82699900	-2.27391000
H	-0.95420900	0.77328200	-1.97803400
N	4.32777100	0.49388200	-1.97724500
O	4.84015100	-0.59493600	-1.82673400

HFIP (G = –789.826835, E = –789.855141)

O	3.45942900	2.35362400	-1.29850200
H	4.03376700	1.77670800	-0.77969000
C	3.79921600	3.68362500	-1.08876700
H	3.13322100	4.30806400	-1.68357300
C	3.58970100	4.05891300	0.37898100
C	5.22710600	3.94814400	-1.56945200
F	5.32080900	3.66597200	-2.86580200
F	5.59439500	5.21366400	-1.39727100
F	6.10137100	3.17127300	-0.92424000
F	2.31590100	3.86810500	0.71058200
F	3.89254000	5.32907400	0.62596100
F	4.33335000	3.29167000	1.18042500

16

$(OCH(CF_3)_2)B(OH)_2$ (G = –965.880111, E = –965.929269)

O	3.38692000	2.34645300	-0.78281700
C	3.81980600	3.65699800	-0.86397400
H	3.05272700	4.22200200	-1.39507100
C	3.91560300	4.28514300	0.52656900
C	5.11700700	3.88789700	-1.66789900
F	5.24864800	2.96195300	-2.61077900
F	5.04660400	5.07839200	-2.27148600
F	6.22134600	3.89756700	-0.92827700
F	2.70597300	4.34579200	1.07933900
F	4.39614200	5.52641400	0.44683700
F	4.69508600	3.58869500	1.34648500
B	4.13722100	1.22730600	-0.47629500
O	3.41400100	0.07853000	-0.44332300
H	3.90975300	-0.71882500	-0.24607400
O	5.46785700	1.35770400	-0.25431800
H	5.95027900	0.55156400	-0.05844400

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Ru(III) (G = –1578.924253, E = –1579.351308)

(6–311G++(d,p), acetonitrile)

Ru	-0.00561200	-0.00602100	-0.00936300
C	0.18160100	2.33116200	-1.97477700
C	1.99131200	2.11478600	-0.51918400
C	0.72994200	3.46352200	-2.55398900
H	-0.76804000	1.93116000	-2.30800800
C	2.58814100	3.24829600	-1.05253700
C	1.95022600	3.92682200	-2.08281100
H	0.20120400	3.96355200	-3.35333200
H	3.53440500	3.60348200	-0.67067000
C	2.57373600	1.31528800	0.57888000
C	3.81039600	1.57445200	1.15230400
C	4.26563100	0.75363300	2.17604900
H	4.41540500	2.40030700	0.80694500
C	2.25798900	-0.51896000	1.98500300
C	3.48049400	-0.30867700	2.60128000
H	1.61011300	-1.33436500	2.28096900
H	3.80002100	-0.97109600	3.39349500
C	-0.72521100	2.21384200	1.96638000
C	-2.44183000	1.58153900	0.51852000
C	-1.52855100	3.16784100	2.56883000
H	0.29741200	2.05482000	2.28431900
C	-3.29458300	2.52197600	1.07907300
C	-2.83169100	3.32065700	2.11685700
H	-1.13034000	3.77165200	3.37215500
H	-4.30531000	2.63615200	0.71508900
C	-1.55776400	-1.72433100	1.99240600
C	-0.13861100	-2.90221100	0.56492000
C	-1.95467600	-2.88984300	2.62696100
H	-1.95088600	-0.75984500	2.28896200
C	-0.49907500	-4.10398300	1.15751100
C	-1.41407500	-4.09511500	2.20236300
H	-2.67207500	-2.84011100	3.43410200
H	-0.07596300	-5.03665400	0.81362200
C	-2.81882700	0.68285100	-0.59293100
C	-4.07756900	0.65974700	-1.17629500
C	-4.32677900	-0.23090700	-2.21246500
H	-4.85763200	1.32231900	-0.83067000
C	-2.08332800	-1.01376900	-2.01531300
C	-3.31759900	-1.08176200	-2.64004800
H	-1.26450300	-1.65548700	-2.31510100
H	-3.47136500	-1.79099400	-3.44123400
C	2.35268500	-3.65209400	-2.17868300
H	1.29614700	-4.87544300	-0.76743900
C	1.89230300	-1.31871600	-2.01235400
C	2.56918000	-2.35767500	-2.62930900
H	2.02464500	-0.29173500	-2.32876300
H	3.24833800	-2.14374000	-3.44263800
N	0.80121800	1.67266800	-0.98699600
N	1.03492500	-1.53239000	-1.00579800
N	-0.66651400	-1.73185100	0.99284100
N	-1.17553600	1.43832100	0.97204400
N	1.81617100	0.27718100	1.00297400
N	-1.84059000	-0.14883200	-1.02191100
H	2.40437100	4.81198300	-2.50925600
H	-3.48657300	4.05748600	2.56382700
H	-5.30411600	-0.25889900	-2.67683900
H	-1.70188500	-5.02489100	2.67599600
H	2.86607200	-4.48763600	-2.63678300
H	5.22810300	0.94348600	2.63338900

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Ru(II) (G = –1579.143430, E = –1579.569265)

(6–311G++(d,p), acetonitrile)

Ru	-0.00158100	-0.00742600	0.01119500
C	-1.96781400	1.06852200	2.12999500
C	-2.88238600	-0.40463100	0.58724100
C	-3.18942700	1.24014200	2.76331200
H	-1.07819800	1.58121300	2.47544300
C	-4.13835100	-0.27523500	1.17155700
C	-4.29268500	0.55636200	2.27185700
H	-3.26305000	1.89799200	3.61843800
H	-4.98926400	-0.81092800	0.77622300
C	-2.61539000	-1.27311800	-0.58572300
C	-3.58837800	-2.06480000	-1.18774900
C	-3.24678400	-2.84280500	-2.28511300
H	-4.60018100	-2.08095300	-0.80889900
C	-1.02128700	-2.00515000	-2.10551800
C	-1.94111500	-2.81423100	-2.75508300
H	0.00906700	-1.94711800	-2.43452600
H	-1.63067100	-3.40413300	-3.60657800
C	-1.25322800	1.89909300	-2.06353200
C	0.18748000	2.89823200	-0.54271500
C	-1.50131200	3.10754900	-2.69673100
H	-1.71854400	0.98068100	-2.40041600
C	-0.01722000	4.14303800	-1.12942000
C	-0.87060400	4.24784200	-2.21887000
H	-2.17388100	3.14229200	-3.54283200
H	0.47947000	5.02250900	-0.74573900
C	2.24193800	0.16833600	-2.09594400
C	2.41785800	-1.60473600	-0.60894300
C	3.41016600	-0.19757000	-2.74705800
H	1.66849600	1.03155700	-2.41119000
C	3.59693500	-2.02745900	-1.21478600
C	4.09760500	-1.31580600	-2.29610400
H	3.76334000	0.38728200	-3.58524600
H	4.12289900	-2.89853100	-0.85160700
C	1.08366900	2.68267200	0.61979100
C	1.80795300	3.70450900	1.22555300
C	2.61873900	3.40937200	2.31261200
H	1.74515000	4.71890300	0.85864500
C	1.94206500	1.13092300	2.11719200
C	2.68937100	2.10038200	2.76869700
H	1.96115800	0.09605300	2.43692200
H	3.30796400	1.82502800	3.61188600
C	1.80195800	-2.29817400	0.54897700
C	2.33540200	-3.44882000	1.12074500
C	1.69313900	-4.02795300	2.20611400
H	3.23873700	-3.89344500	0.72863500
C	0.05430900	-2.30014300	2.07630400
C	0.53207300	-3.44556100	2.69510400
H	-0.84680800	-1.80756800	2.42130000
H	-0.00111800	-3.86275100	3.53837600
N	-1.81423200	0.26767900	1.06959300
N	0.67121500	-1.73709200	1.03132400
N	1.75437900	-0.51578900	-1.05515700
N	-0.42916400	1.79289200	-1.01529200
N	-1.34642300	-1.25182700	-1.04916400

C	0.81870000	-2.78996600	-0.55515200
C	1.47027700	-3.87242400	-1.12899200
N	1.15674500	1.41130300	1.07129700
H	-1.03843800	5.20979100	-2.68620100
H	-5.26409800	0.66709600	2.73662000
H	-3.99342400	-3.46348400	-2.76384100
H	2.09722300	-4.92325200	2.66121000
H	5.01392900	-1.63331300	-2.77722100
H	3.18719900	4.19447400	2.79469200

3

NO_2 radical (G = –205.067273, E = –205.052447)

(6–311G++(d,p), acetonitrile)

N	-1.73356800	1.12878500	0.81665200
O	-2.45065400	2.06703000	0.81665200
O	-0.56246700	0.97688700	0.81665200

16

$PhB(OH)_2$ (G = –408.141397, E = –408.233439)

(6–311G++(d,p), acetonitrile)

C	1.96953100	0.27451900	1.35635200
C	3.07285600	0.08411400	0.52753500
C	3.49551300	1.11099900	-0.31248600
C	2.81229100	2.32335200	-0.32187800
C	1.69956600	2.53605000	0.50151500
C	1.29396300	1.49022800	1.34186700
H	1.63930600	-0.52330000	2.01134800
H	3.60233700	-0.86161300	0.53633600
H	4.35487100	0.96727100	-0.95674300
H	3.16828200	3.10708300	-0.98432100
H	0.43606800	1.63649100	1.98894900
B	0.90541500	3.88846900	0.51193600
O	1.15715200	4.93537300	-0.33096500
H	1.85802600	4.78189000	-0.96935700
O	-0.10477000	4.03350700	1.41933100
H	-0.54396500	4.88761800	1.34827700

14

$PhNO_2$ (G = –436.655200, E = –436.696694)

(6–311G++(d,p), acetonitrile)

C	-0.42503900	-1.21942800	0.00000800
C	-1.81394300	-1.20948500	0.00003000
C	-0.42506100	1.21945200	-0.00003400
C	-2.50506400	-0.00001400	0.00000500
H	-2.35513600	-2.14696500	0.00007400
C	-1.81395000	1.20947800	-0.00002700
H	0.13562700	2.14378300	-0.00004400
H	-3.58824100	-0.00000200	0.00003600
H	-2.35519100	2.14693000	-0.00003000
H	0.13568200	-2.14374100	0.00002700
C	0.23801800	0.00000600	-0.00001400
N	1.71170700	0.00000200	-0.00000100
O	2.28223500	1.07183300	0.00007200
O	2.28220700	-1.07184100	-0.00005600

19

$PhNO_2(B(OH)_2)$ cation (G = –612.979194, E = –613.080621)

(6–311G++(d,p), acetonitrile)

C	-0.56762000	0.68508600	-1.19328200
C	-1.93881200	0.73089600	-1.11843700
C	-0.47478900	0.41004700	1.27690900
C	-2.56966300	0.61026800	0.12589200
H	-2.52490600	0.89745700	-2.01180100
C	-1.84893600	0.45108200	1.31600200
H	0.13174700	0.33756500	2.17161700
H	-3.65063800	0.67140100	0.17322300
H	-2.36481300	0.40154100	2.26499900
H	-0.03077800	0.81438400	-2.12488900
C	0.17062500	0.39648700	-0.00277600
N	1.62833500	0.78679500	-0.02669500
O	2.16686900	0.95497400	1.03649100
O	2.14406500	0.88743100	-1.11129900
B	0.21224100	-1.41087300	-0.07636000
O	1.45636000	-1.79047000	0.16885400
H	1.66452500	-2.73215500	0.10836100
O	-0.93596300	-1.99966800	-0.35455200
H	-0.96015900	-2.96472600	-0.35464000
O	-2.45901800	-0.36389400	1.06158200
N	-2.10705600	-0.00181300	-1.20261600

19

$PhNO_2(B(OH)_2)$ radical (G = –613.166059, E = –613.264587)

(6–311G++(d,p), acetonitrile)

C	-0.68245800	0.20926400	-1.25135200
C	-2.04199000	0.14936800	-1.30545000
C	-0.83096600	-0.00492900	1.24215700
C	-2.82387800	0.02478000	-0.13491900
H	-2.53417900	0.20993400	-2.26916600
C	-2.18448000	-0.04047600	1.12684500
H	-0.34778800	-0.06502200	2.20896000
H	-3.90292300	-0.00534000	-0.20105900
H	-2.78735300	-0.12149900	2.02383500
H	-0.09142700	0.31021800	-2.15295100
C	0.05283800	0.07015700	0.04000600
N	1.03931400	1.25362100	0.22890200
O	1.63734600	1.29476600	1.28305400
O	1.19363800	2.03670300	-0.67726300
B	1.02108000	-1.22150200	-0.10981800
O	0.55825200	-2.38460700	0.39837500
H	1.10708300	-3.16130500	0.24520900
O	2.17304500	-1.01052800	-0.79001600
H	2.74334900	-1.77448000	-0.92497100

5

$B(OH)_2$ cation (G = –176.367519, E = –176.373707)

(6–311G++(d,p), acetonitrile)

B	0.00011300	-0.01026000	-0.00086600
O	-1.25443300	0.06139000	-0.07889900
H	-1.90434800	-0.47421500	0.40374600
O	1.25442700	0.05887600	0.08133400
H	1.90577200	-0.45935900	-0.41804800

5

$B(OH)_2$ radical (G = –176.523343, E = –176.529602)

(6–311G++(d,p), acetonitrile)

B	-0.00461400	0.51966800	-0.00004200
O	-1.13606100	-0.21986200	-0.00001500
H	-1.94623200	0.29823100	0.00017000
O	1.22760900	-0.01876600	0.00002400
H	1.23691400	-0.98754200	-0.00003600

11

NR_2 radical (G = –360.120705, E = –360.170230)

(6–311G++(d,p), acetonitrile)

C	-2.75563300	0.18161900	-0.02123000
O	-2.48023300	-0.35056600	1.05502300
N	-2.09657200	-0.01828500	-1.18928800
C	-2.67558500	0.72826900	-2.16192200
O	-2.31604500	0.77085400	-3.33944200
C	-3.86467600	1.54621200	-1.64128200
H	-4.75921600	1.27190500	-2.20292200
H	-3.67358600	2.60562300	-1.82041200
C	-3.92025400	1.16928800	-0.16873000
H	-3.76254300	2.00915300	0.51002200
H	-4.84657000	0.67412300	0.12740200

16

$(NR_2)B(OH)_2$ (G = –536.609849, E = –536.690781)

(6–311G++(d,p), acetonitrile)

C	-2.62640600	0.32299100	0.03258400
O	-2.16078500	-0.02944300	1.08612700
N	-2.09630400	-0.00186800	-1.22190600
B	-0.92265200	-0.89044000	-1.42830700
O	-0.86395200	-1.99898900	-0.65573800
H	-0.07218900	-2.53531100	-0.75992500
O	-0.03123500	-0.50199900	-2.36816600
H	0.69316900	-1.11357900	-2.53093600
C	-2.81016600	0.61362100	-2.25724600
O	-2.59262600	0.45256500	-3.43099200
C	-3.89596900	1.48424800	-1.65712300
H	-4.84582300	1.24248600	-2.13190600
H	-3.65764300	2.52264500	-1.89407600
C	-3.85106900	1.19485000	-0.16102000
H	-3.75646700	2.08148700	0.46427500
H	-4.71835300	0.63078600	0.18653400

16

$(NR_2)B(OH)_2$ radical anion (G = –536.666161, E = –536.744970)

(6–311G++(d,p), acetonitrile)

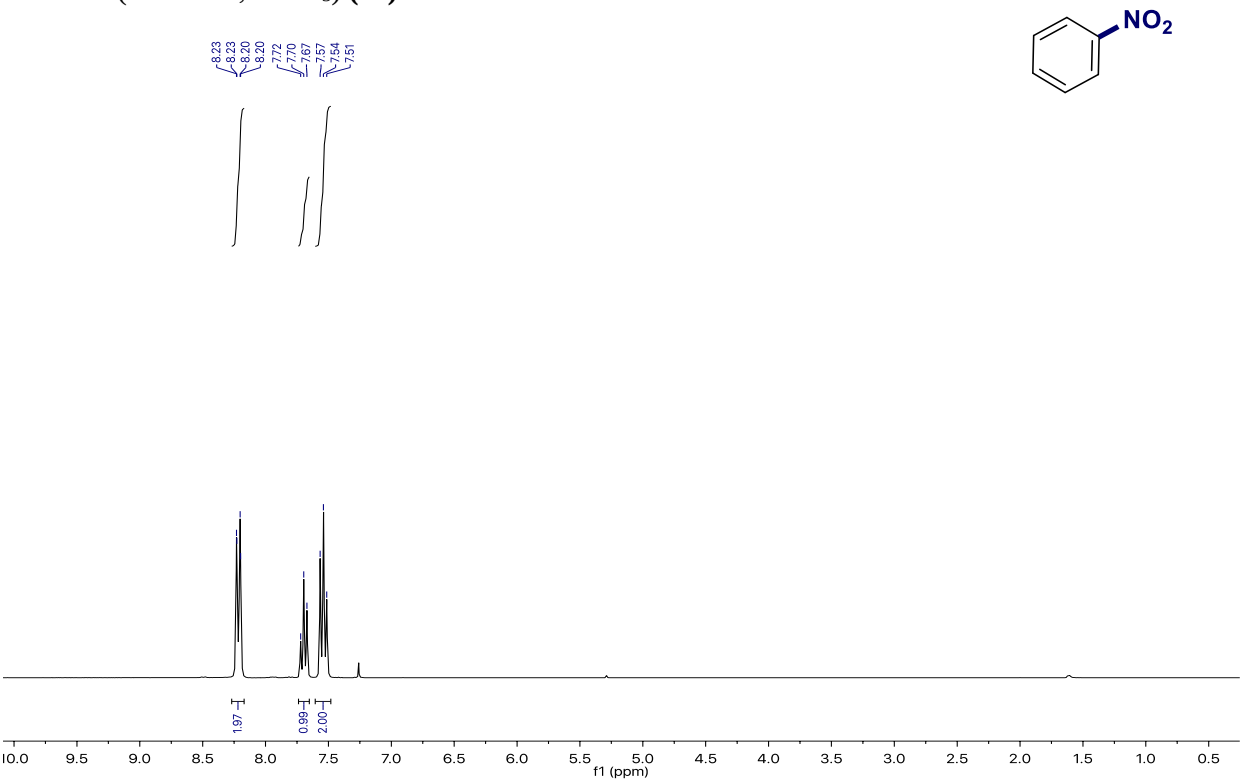
C	-2.72385600	0.18820600	-0.00280800

B	-0.95919300	-0.87433600	-1.41190500
O	-0.95526600	-2.10297800	-0.81155200
H	-0.14231000	-2.60383700	-0.92311900
O	0.06115900	-0.40578400	-2.19100900
H	0.76720800	-1.03681100	-2.35388800
C	-2.62045400	0.92518100	-2.25587600
O	-2.52482900	0.56061600	-3.47914400

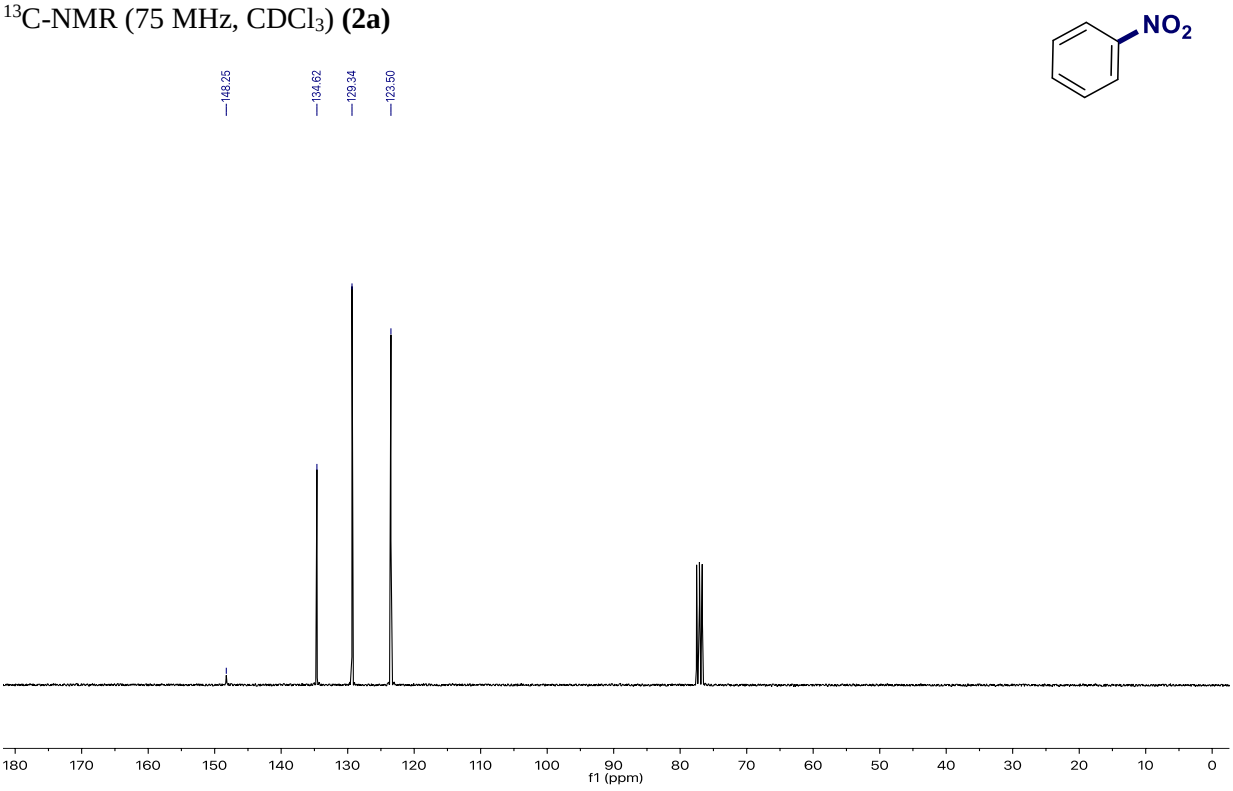
C	-3.93723600	1.42317400	-1.66713800
H	-4.73987900	0.74377100	-2.00088200
H	-4.19109300	2.42897300	-2.00206900
C	-3.74589700	1.30302800	-0.16071800
H	-3.28680500	2.20633000	0.25706200
H	-4.64394500	1.08422100	0.41626000

2.9 NMR spectra of isolated compounds

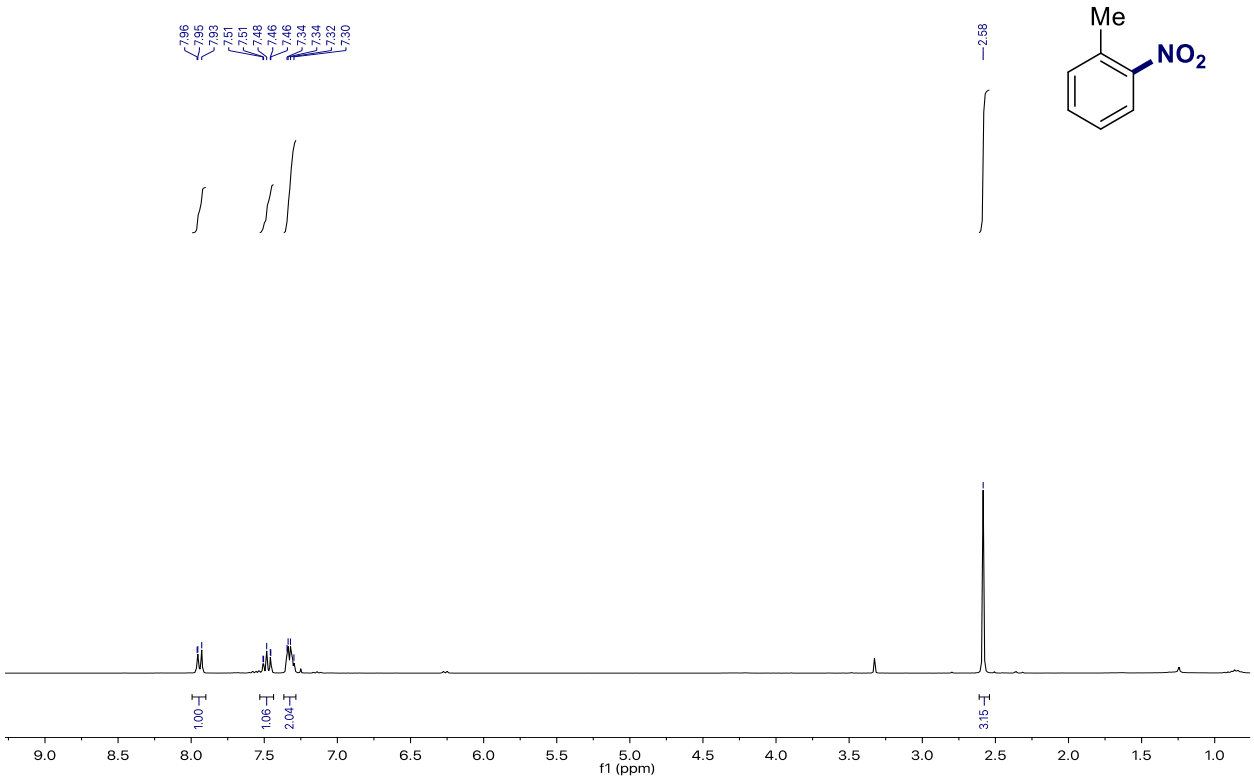
^{1}H-NMR (300 MHz, $CDCl_3$) **(2a)**



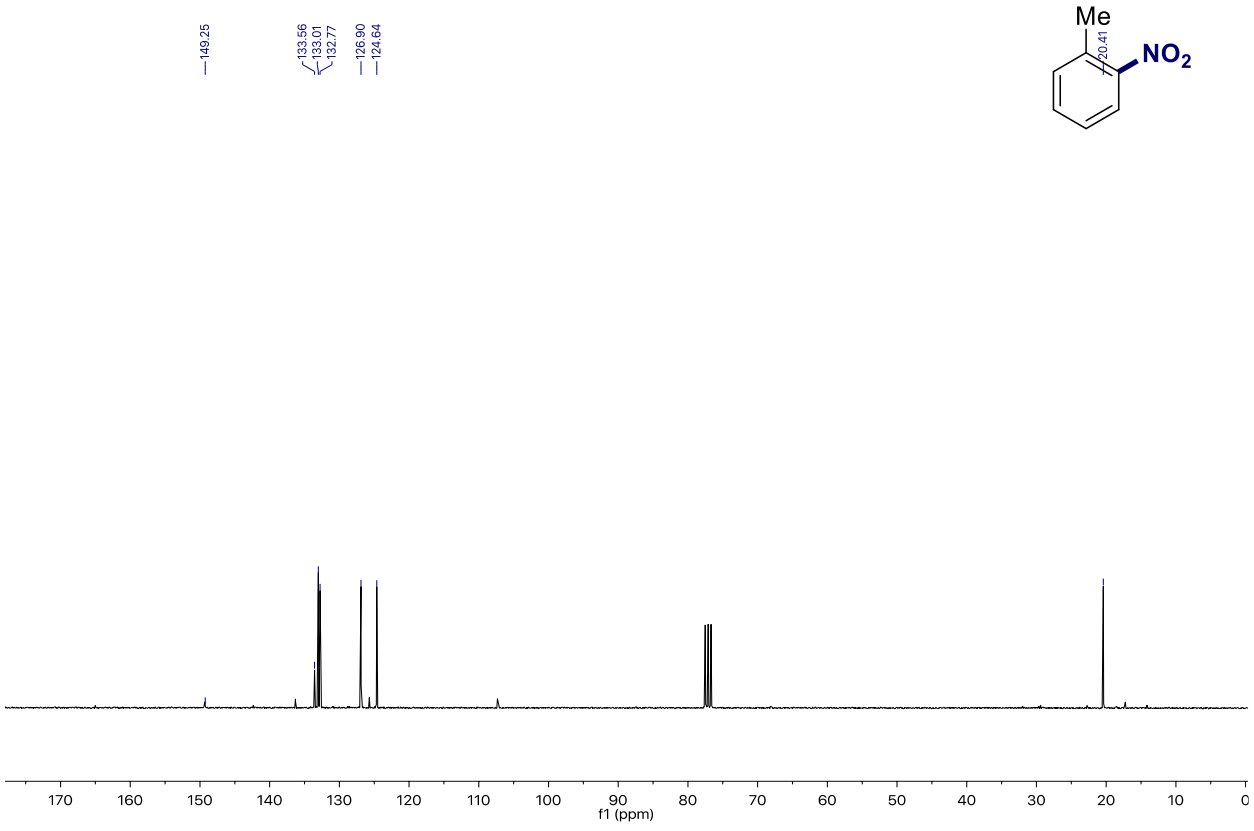
^{13}C-NMR (75 MHz, $CDCl_3$) **(2a)**



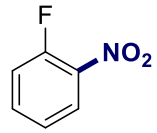
^{1}H-NMR (300 MHz, $CDCl_3$) **(2b)**



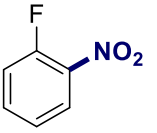
^{13}C-NMR (75 MHz, $CDCl_3$) **(2b)**



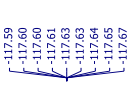
^{1}H-NMR (300 MHz, $CDCl_3$) **(2c)**

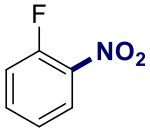


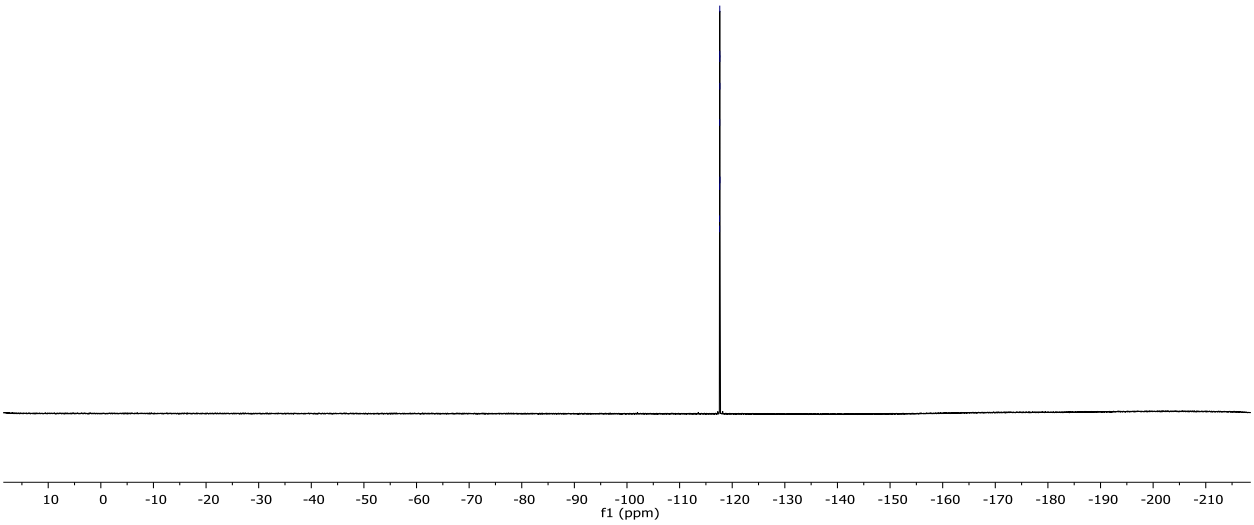
^{13}C-NMR (75 MHz, $CDCl_3$) **(2c)**



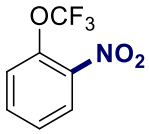
^{19}F-NMR (282 MHz, $CDCl_3$) **(2c)**

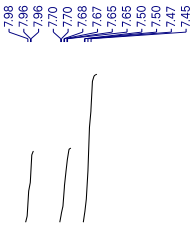


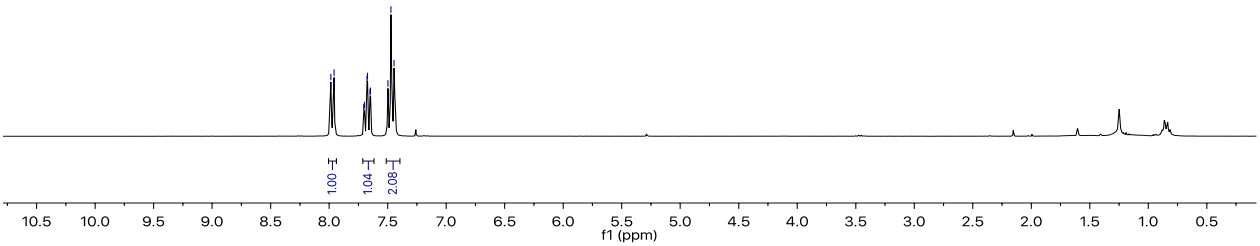




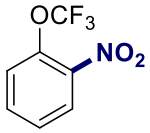
^{1}H-NMR (300 MHz, $CDCl_3$) **(2d)**



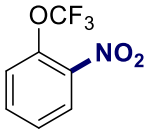




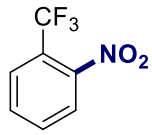
^{13}C-NMR (75 MHz, $CDCl_3$) **(2d)**



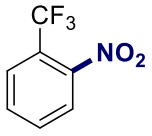
^{19}F-NMR (282 MHz, $CDCl_3$) **(2d)**



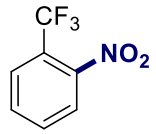
^{1}H-NMR (300 MHz, $CDCl_3$) **(2e)**



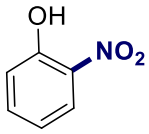
^{13}C-NMR (75 MHz, $CDCl_3$) **(2e)**



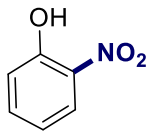
^{19}F-NMR (282 MHz, $CDCl_3$) **(2e)**



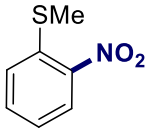
^{1}H-NMR (300 MHz, $CDCl_3$) **(2f)**



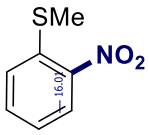
^{13}C-NMR (75 MHz, $CDCl_3$) **(2f)**



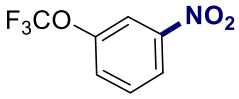
^{1}H-NMR (300 MHz, $CDCl_3$) **(2g)**



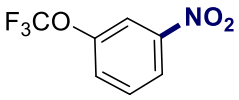
^{13}C-NMR (75 MHz, $CDCl_3$) **(2g)**



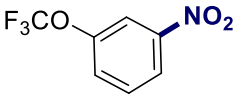
^{19}F-NMR (282 MHz, $CDCl_3$) **(2h)**



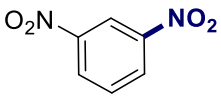
^{13}C-NMR (75 MHz, $CDCl_3$) **(2h)**

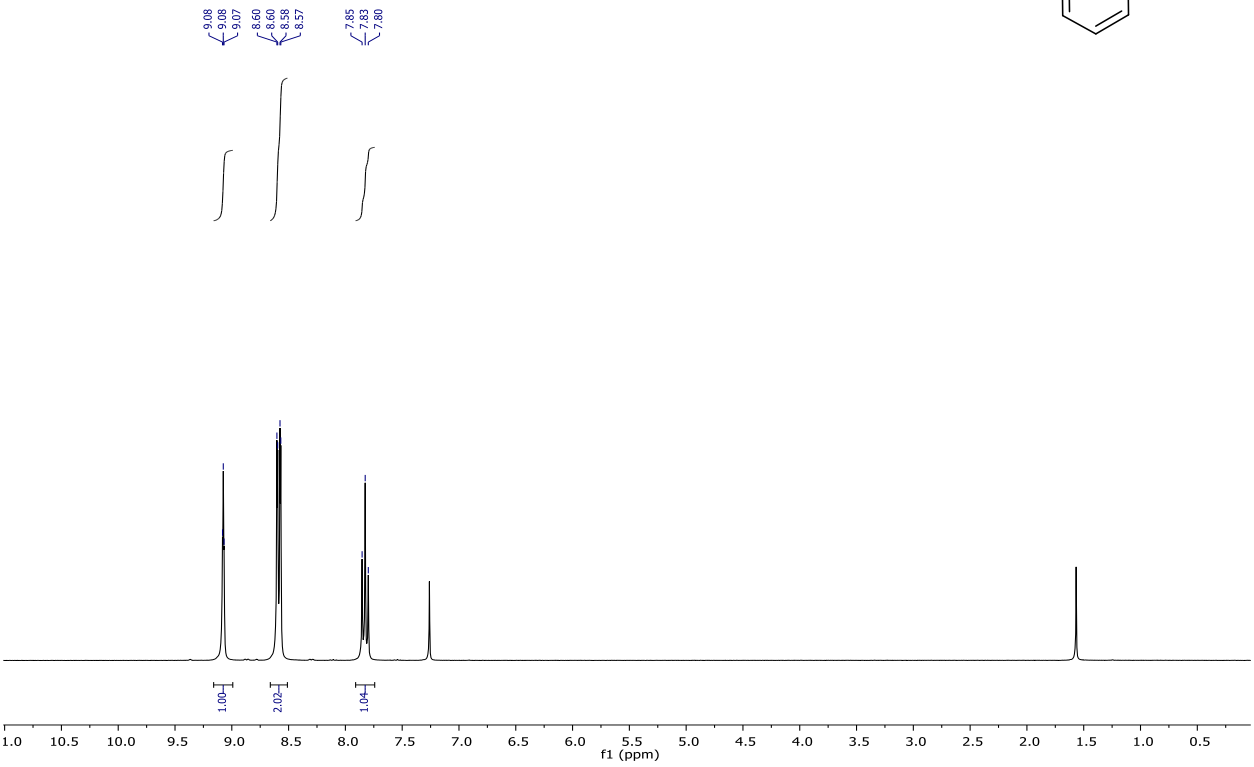


^{19}F-NMR (282 MHz, $CDCl_3$) **(2h)**

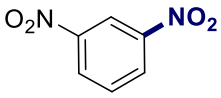


^{1}H-NMR (300 MHz, $CDCl_3$) **(2i)**

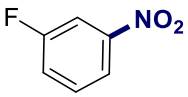


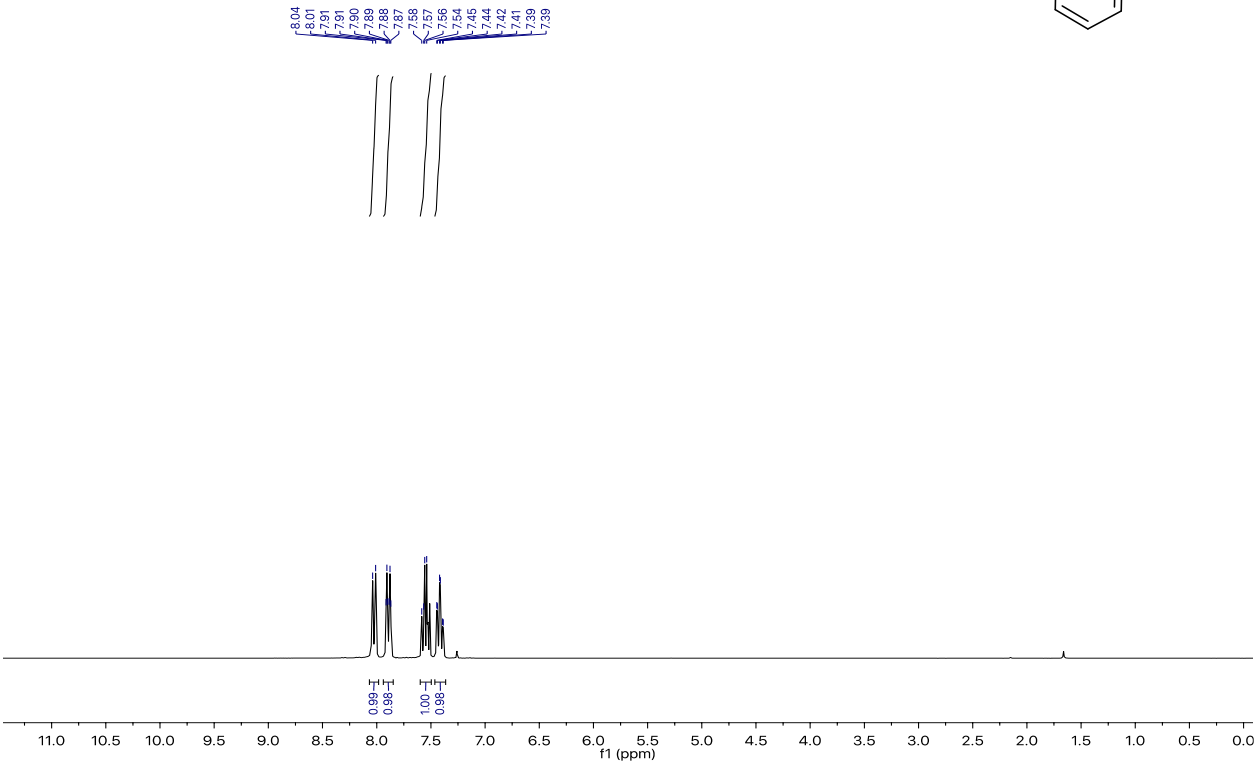


^{13}C-NMR (75 MHz, $CDCl_3$) **(2i)**

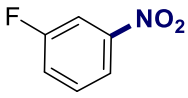


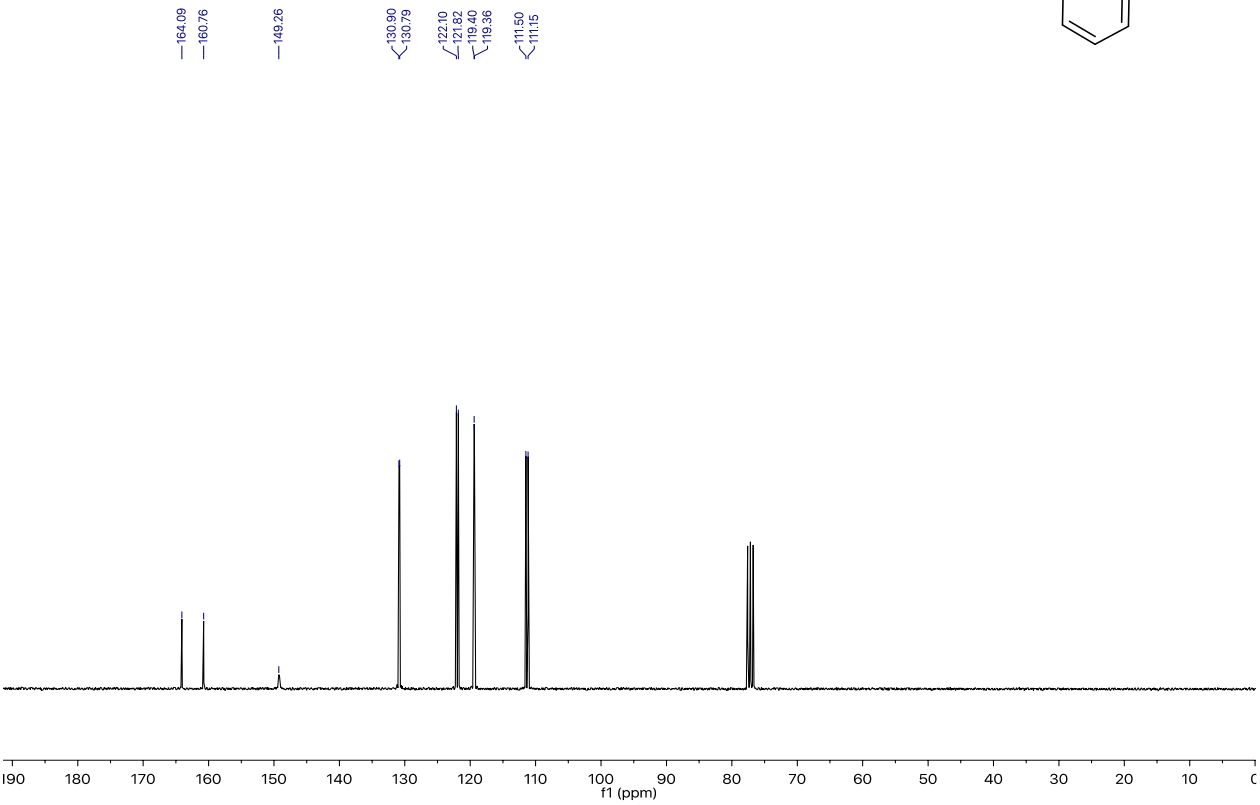
^{1}H-NMR (300 MHz, $CDCl_3$) **(2j)**



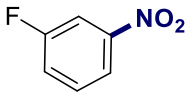


^{13}C-NMR (75 MHz, $CDCl_3$) **(2j)**

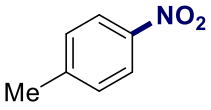




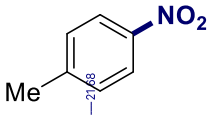
^{19}F-NMR (282 MHz, $CDCl_3$) (**2j**)

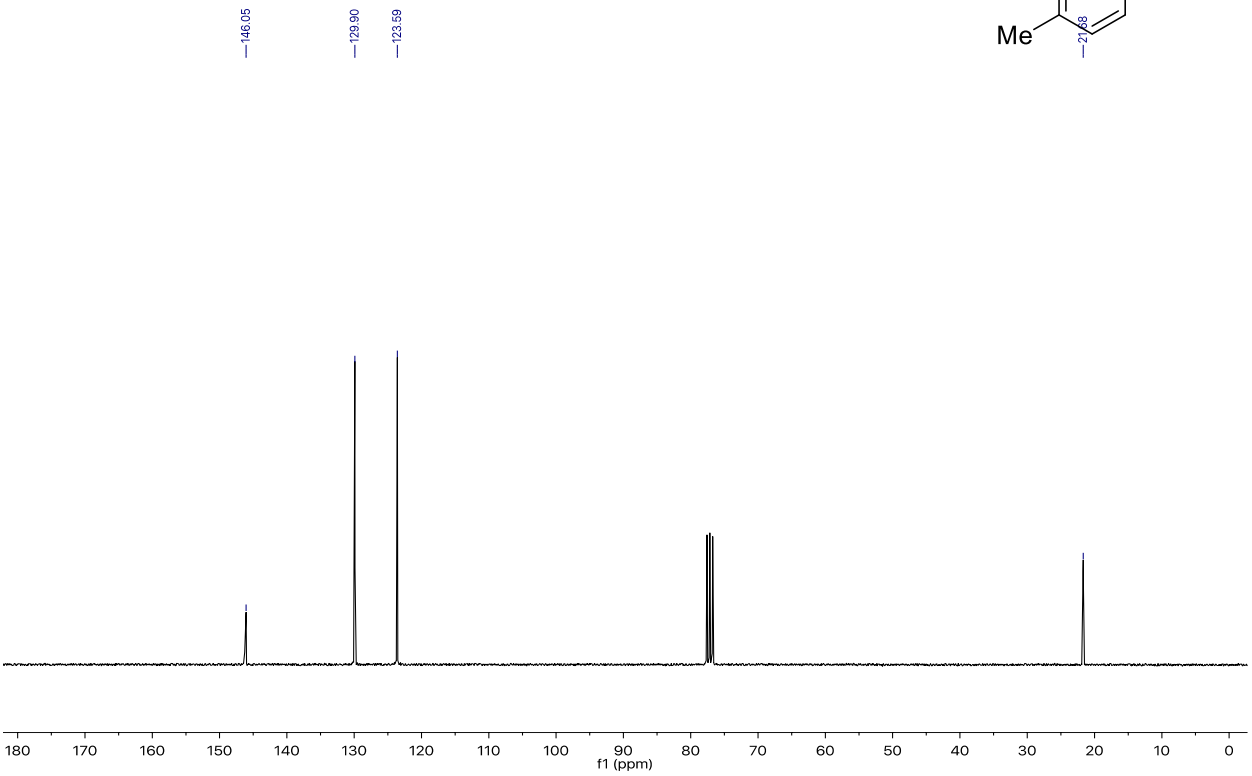


^{1}H-NMR (300 MHz, $CDCl_3$) **(2k)**

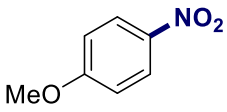


^{13}C-NMR (75 MHz, $CDCl_3$) **(2k)**

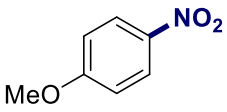


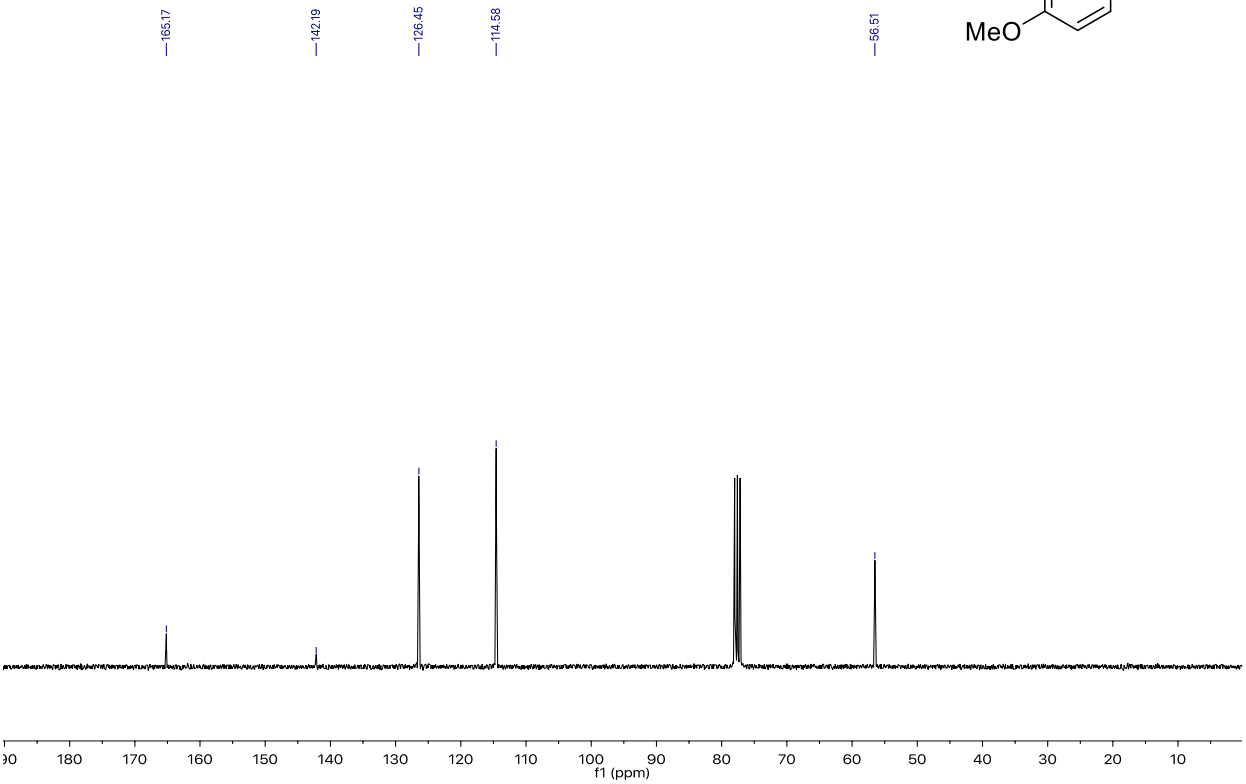


^{1}H-NMR (300 MHz, $CDCl_3$) **(2l)**

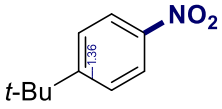


^{13}C-NMR (75 MHz, $CDCl_3$) **(2l)**

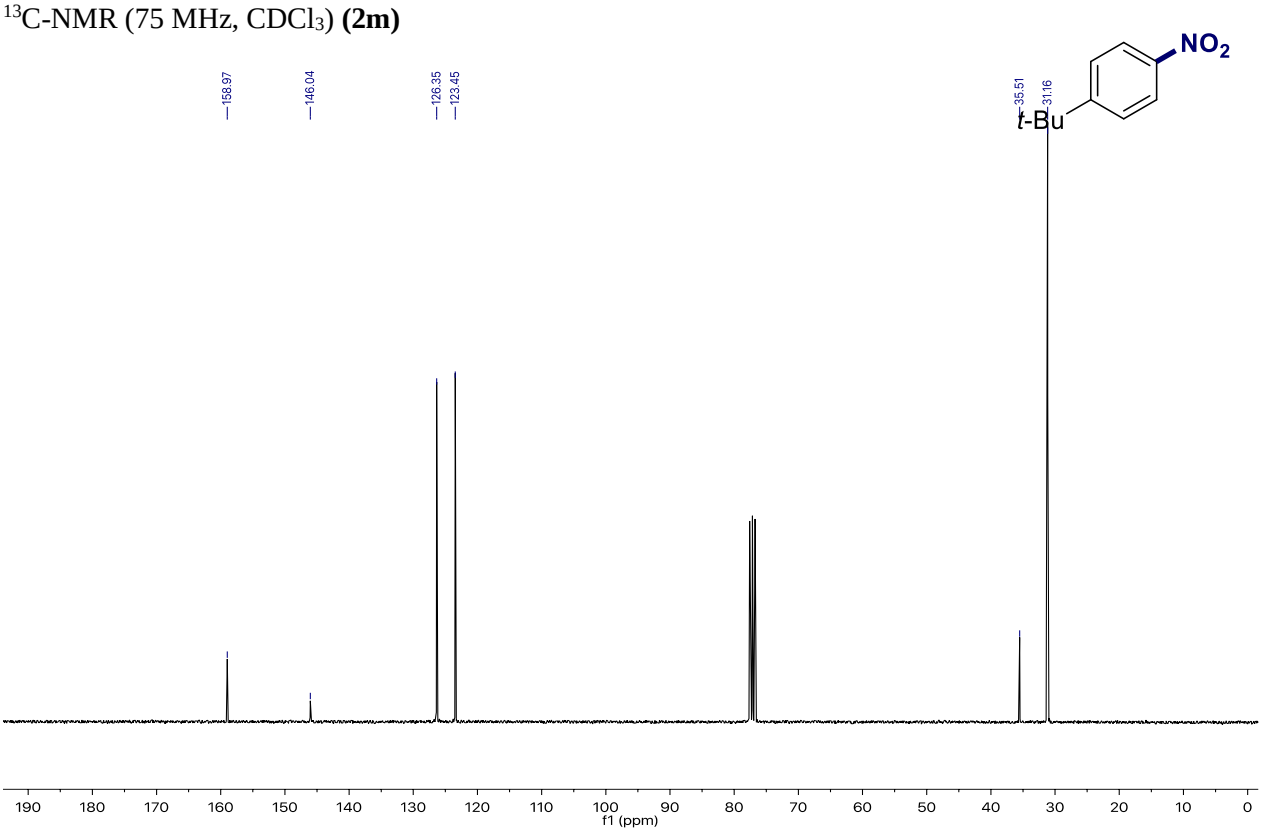




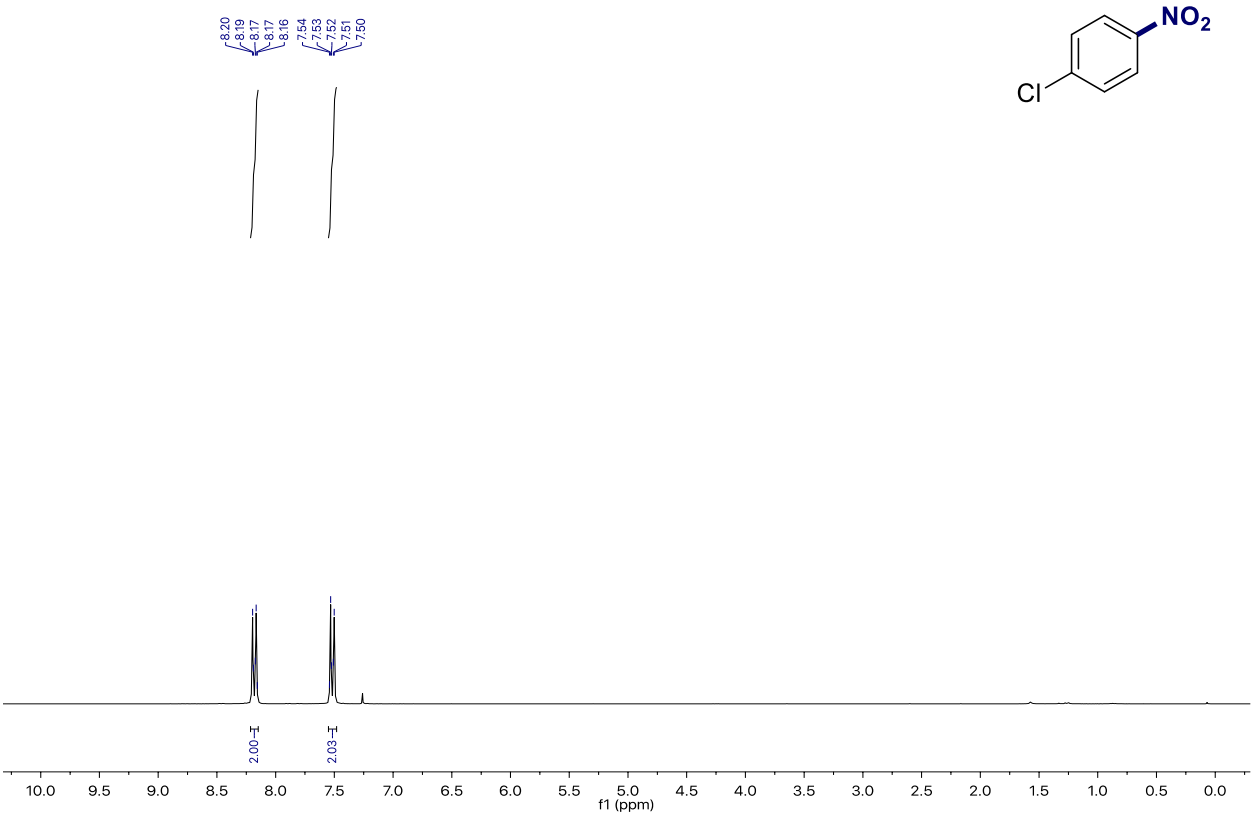
^{1}H-NMR (300 MHz, $CDCl_3$) **(2m)**



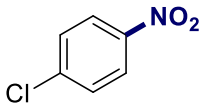
^{13}C-NMR (75 MHz, $CDCl_3$) **(2m)**

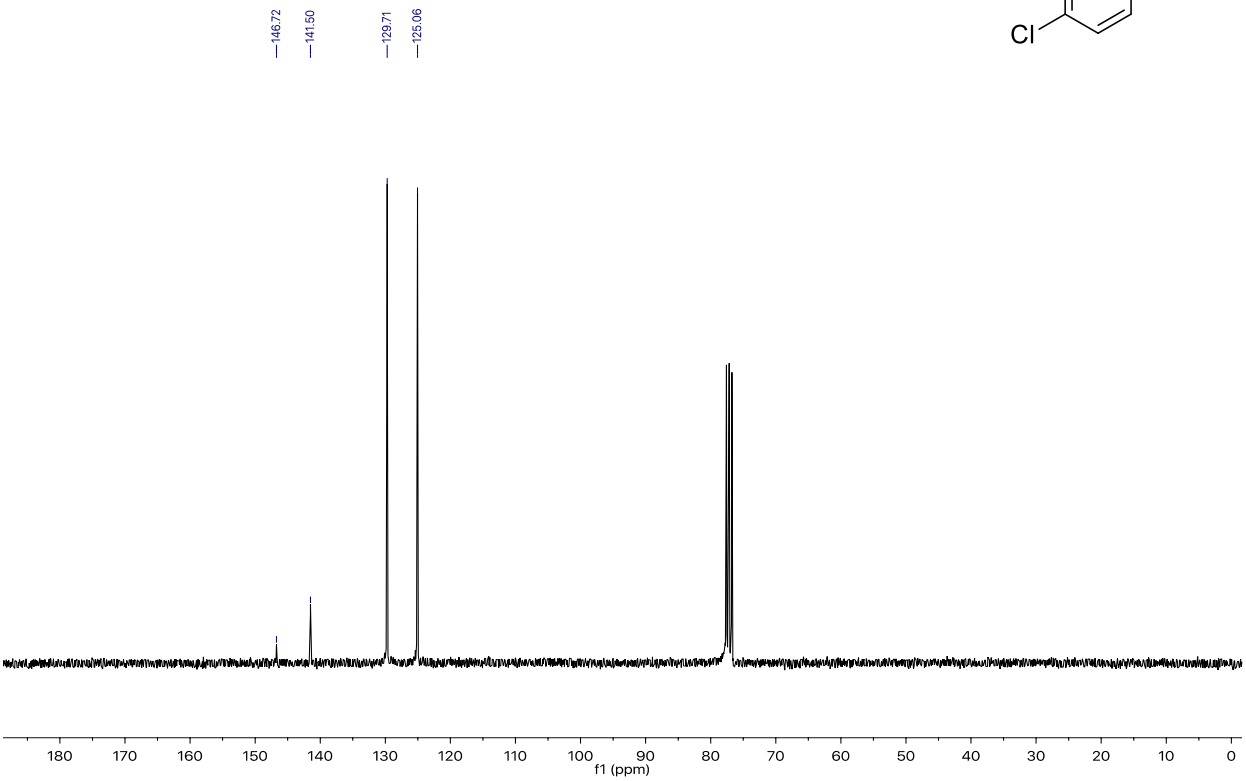


^{1}H-NMR (300 MHz, $CDCl_3$) **(2n)**

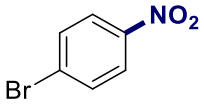


^{13}C-NMR (75 MHz, $CDCl_3$) **(2n)**

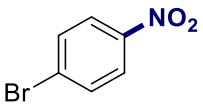




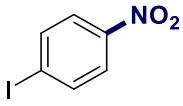
^{1}H-NMR (300 MHz, $CDCl_3$) **(2o)**



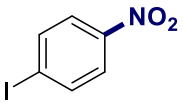
^{13}C-NMR (75 MHz, $CDCl_3$) **(2o)**

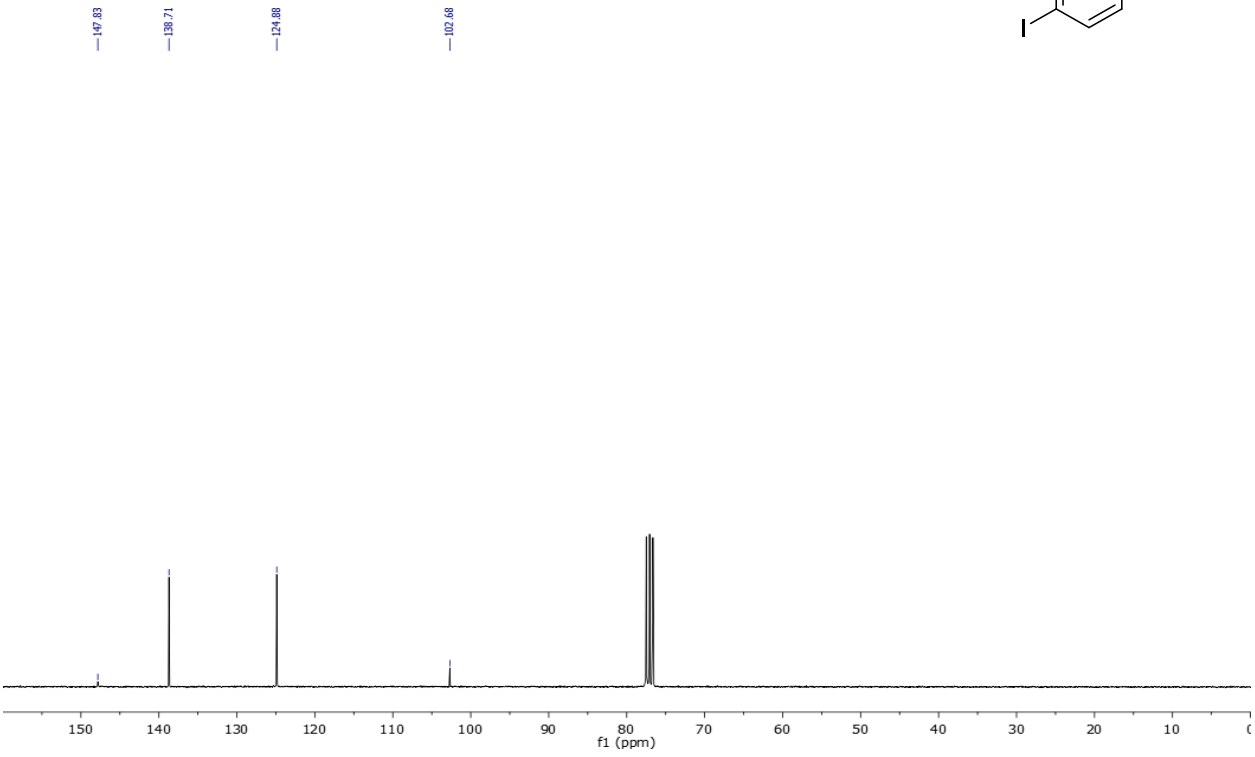


^{1}H-NMR (300 MHz, $CDCl_3$) **(2p)**

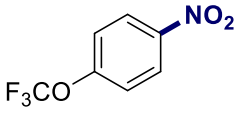


^{13}C-NMR (75 MHz, $CDCl_3$) **(2p)**

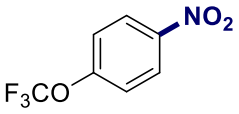


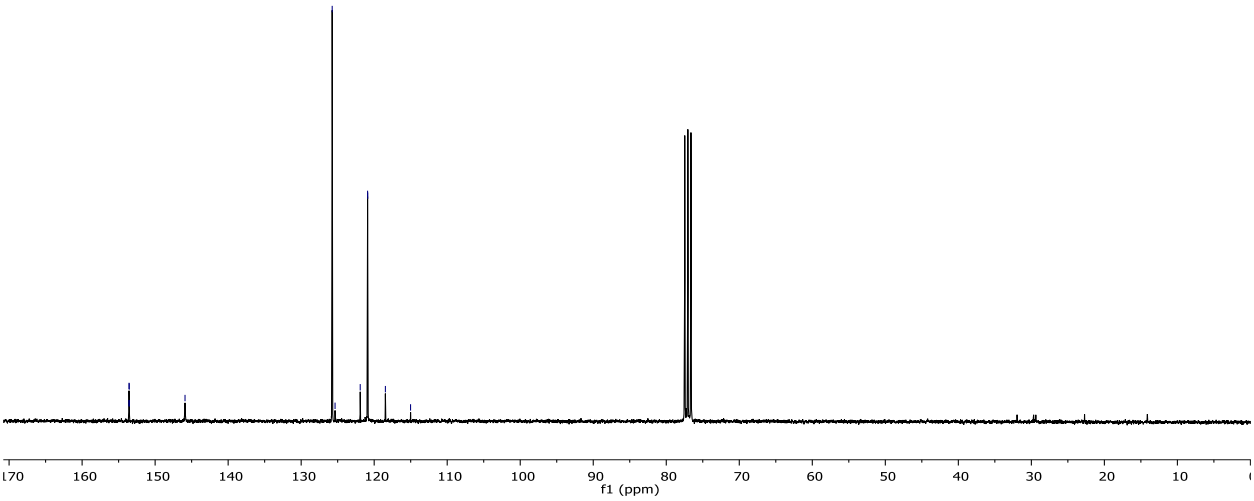


^{1}H-NMR (300 MHz, $CDCl_3$) **(2q)**

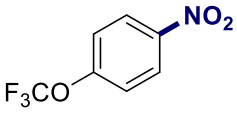


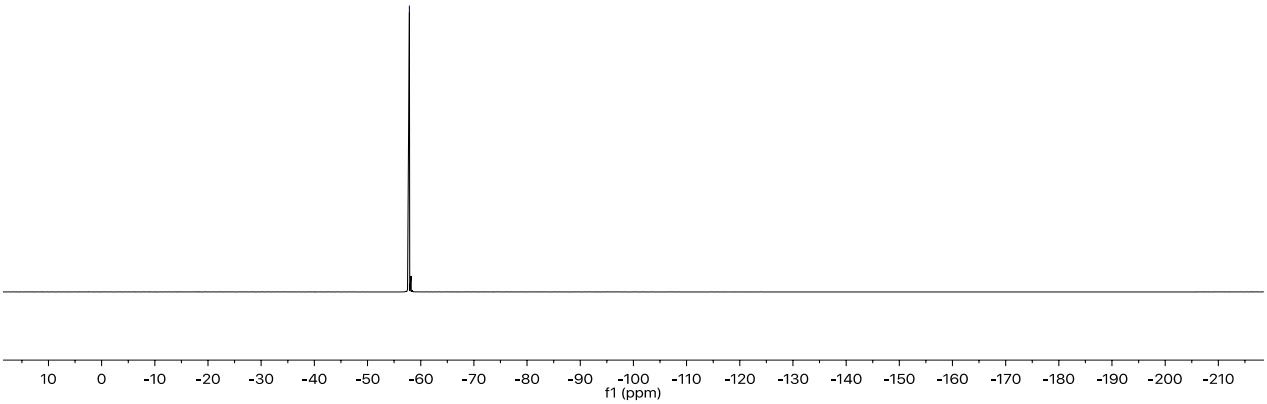
^{13}C-NMR (75 MHz, $CDCl_3$) **(2q)**



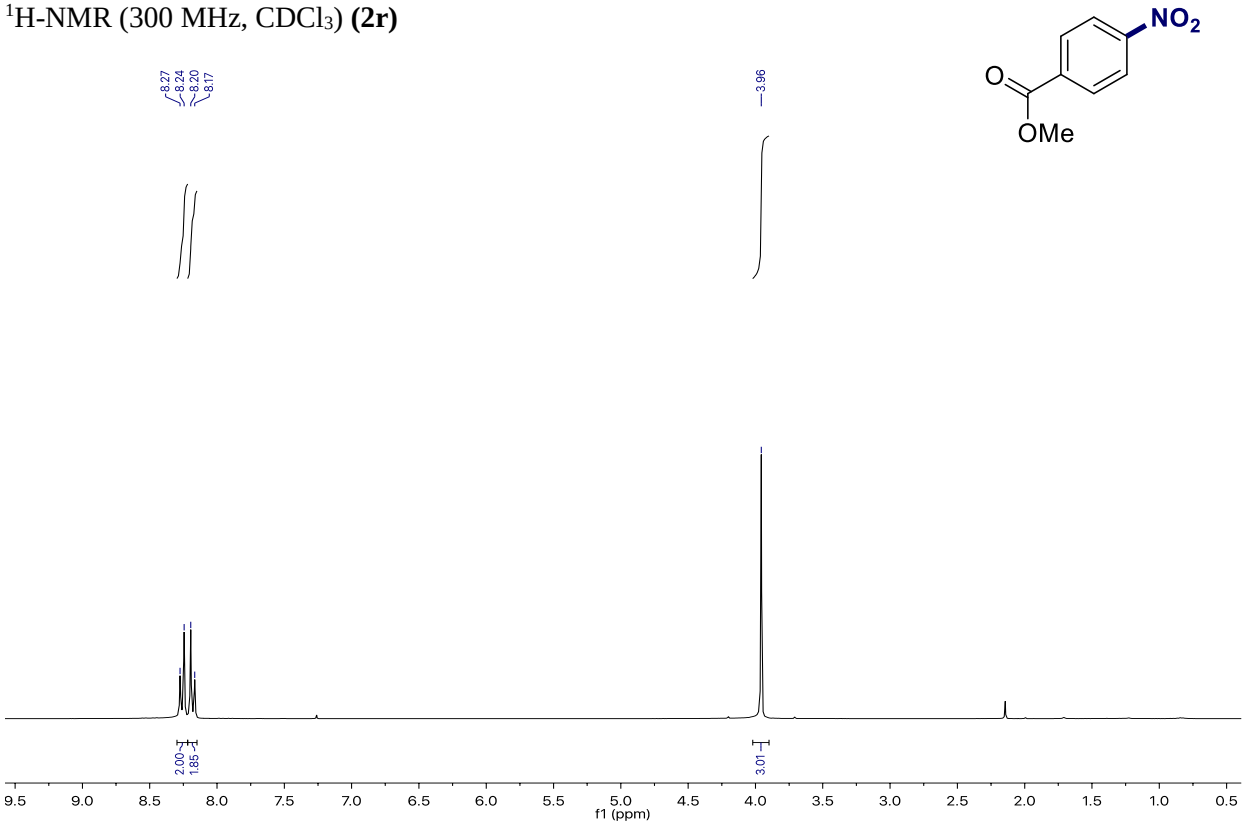


^{19}F-NMR (282 MHz, $CDCl_3$) **(2q)**

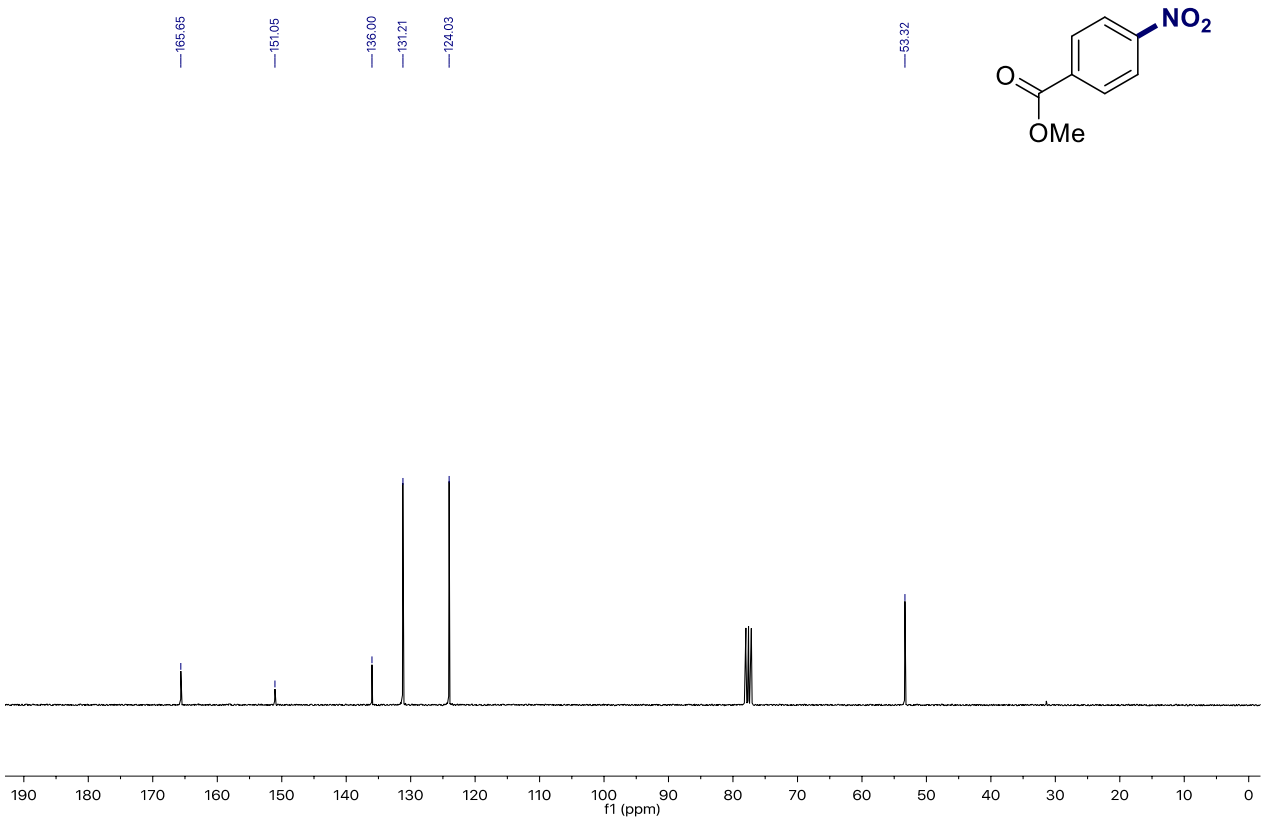




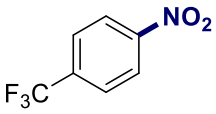
^{1}H-NMR (300 MHz, $CDCl_3$) **(2r)**

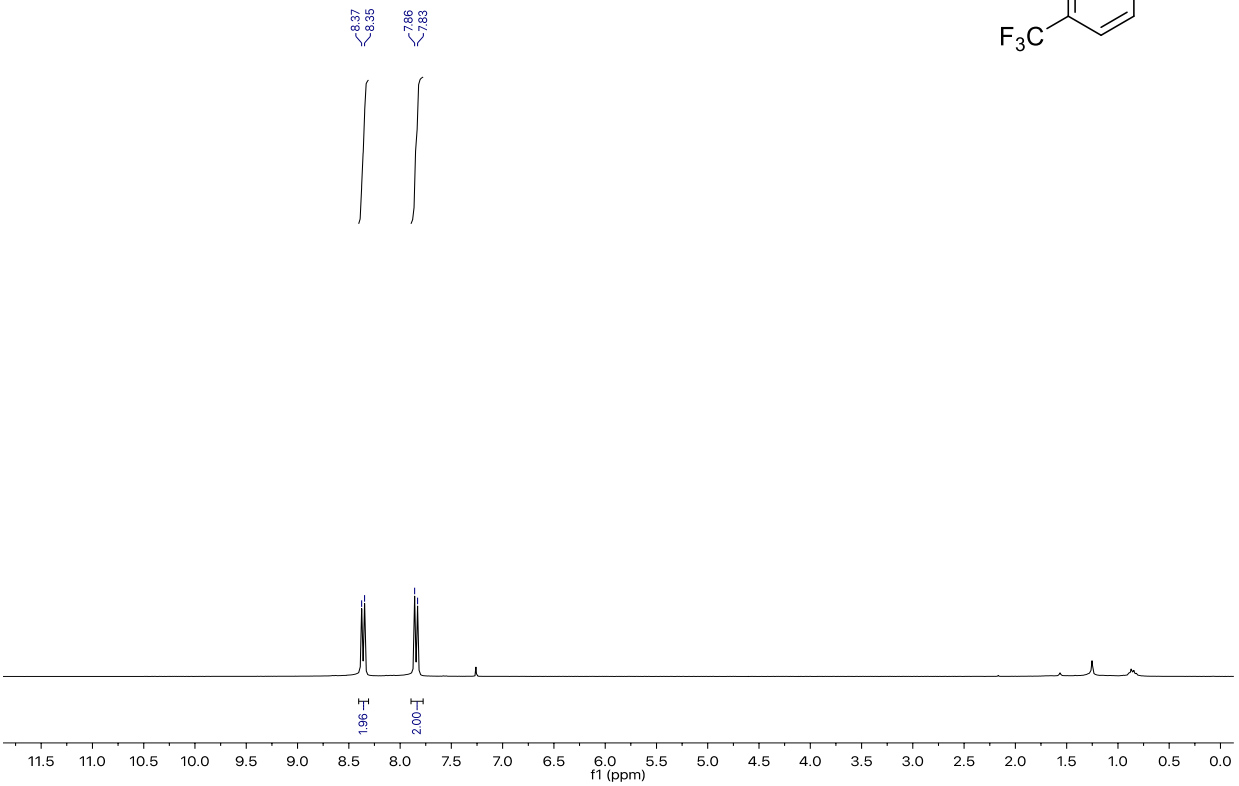


^{13}C-NMR (75 MHz, $CDCl_3$) **(2r)**

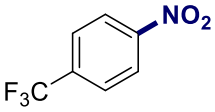


^{1}H-NMR (300 MHz, $CDCl_3$) **(2s)**

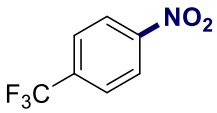


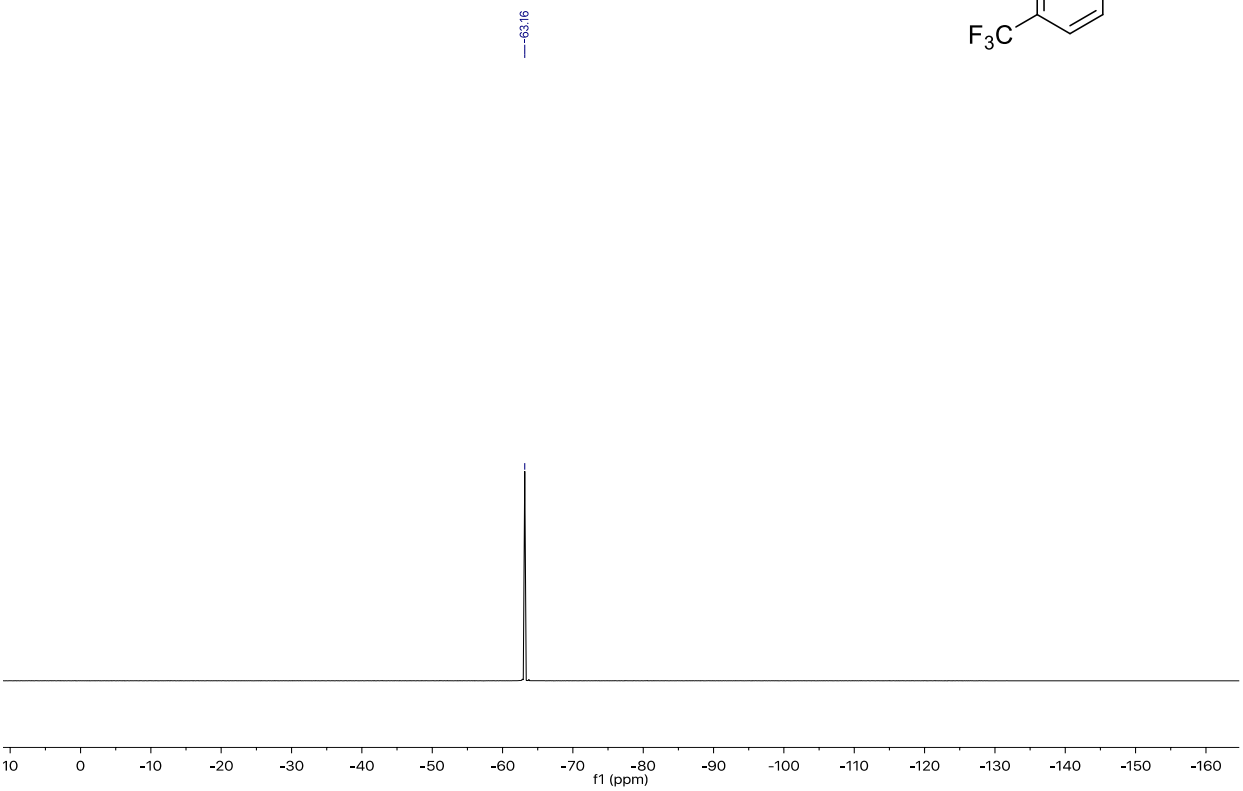


^{13}C-NMR (75 MHz, $CDCl_3$) **(2s)**

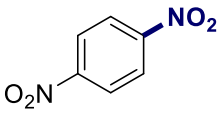


^{19}F-NMR (282 MHz, $CDCl_3$) **(2s)**

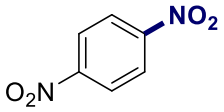


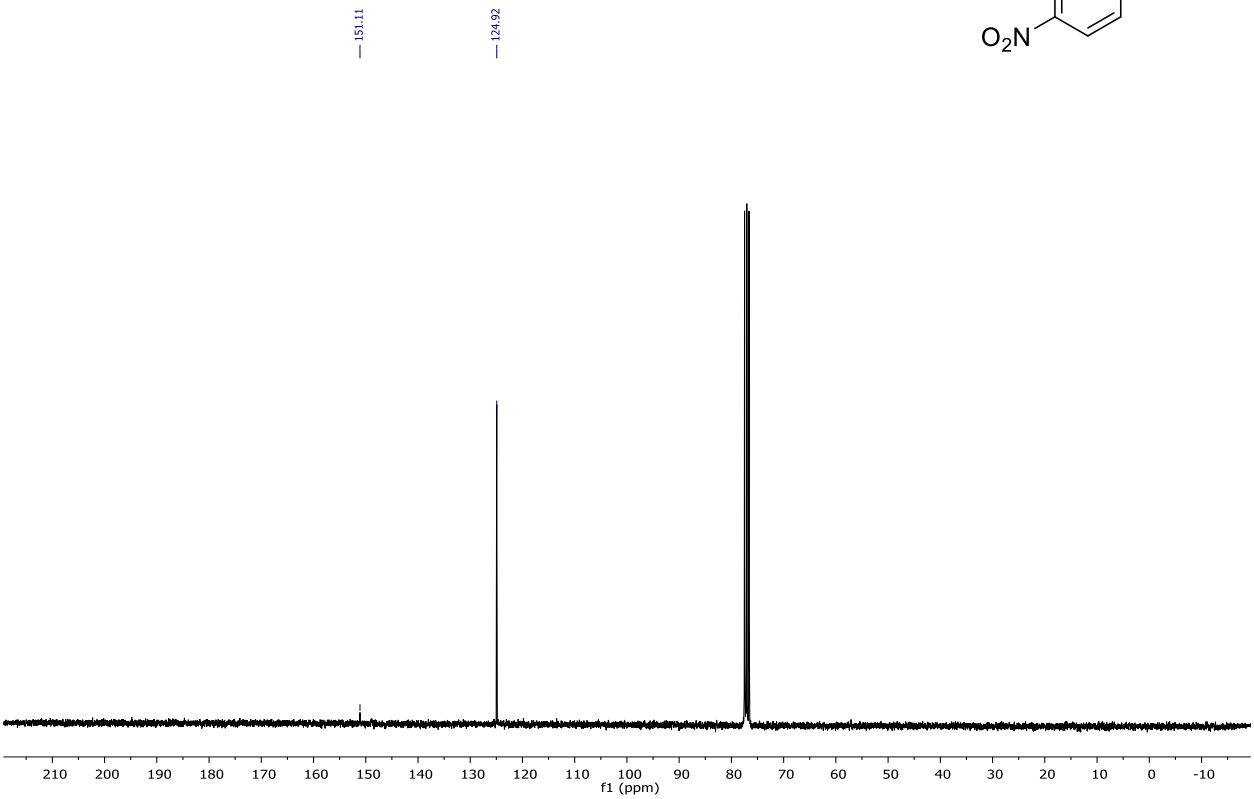


^{1}H-NMR (300 MHz, $CDCl_3$) **(2t)**

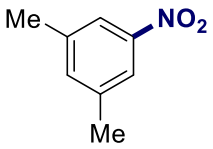


^{13}C-NMR (75 MHz, $CDCl_3$) **(2t)**

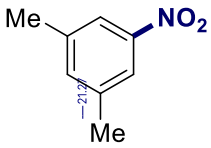




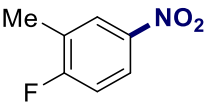
^{1}H-NMR (300 MHz, $CDCl_3$) **(2u)**



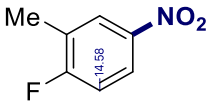
^{13}C-NMR (75 MHz, $CDCl_3$) **(2u)**

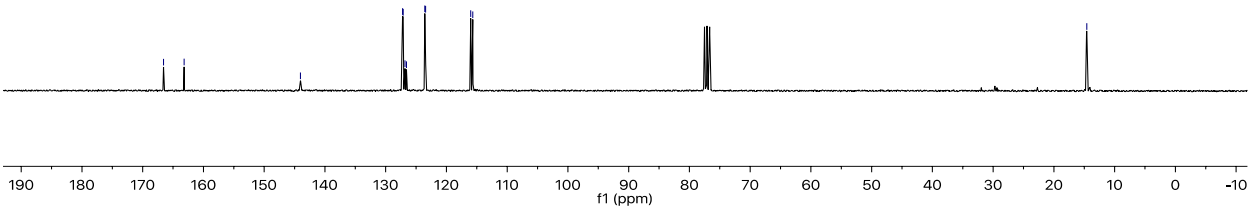


^{1}H-NMR (300 MHz, $CDCl_3$) **(2v)**

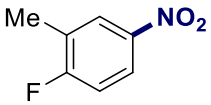


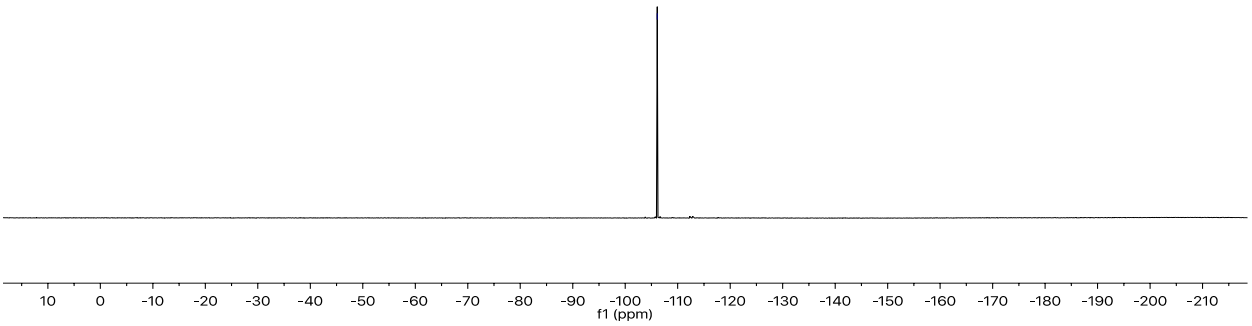
^{13}C-NMR (75 MHz, $CDCl_3$) **(2v)**



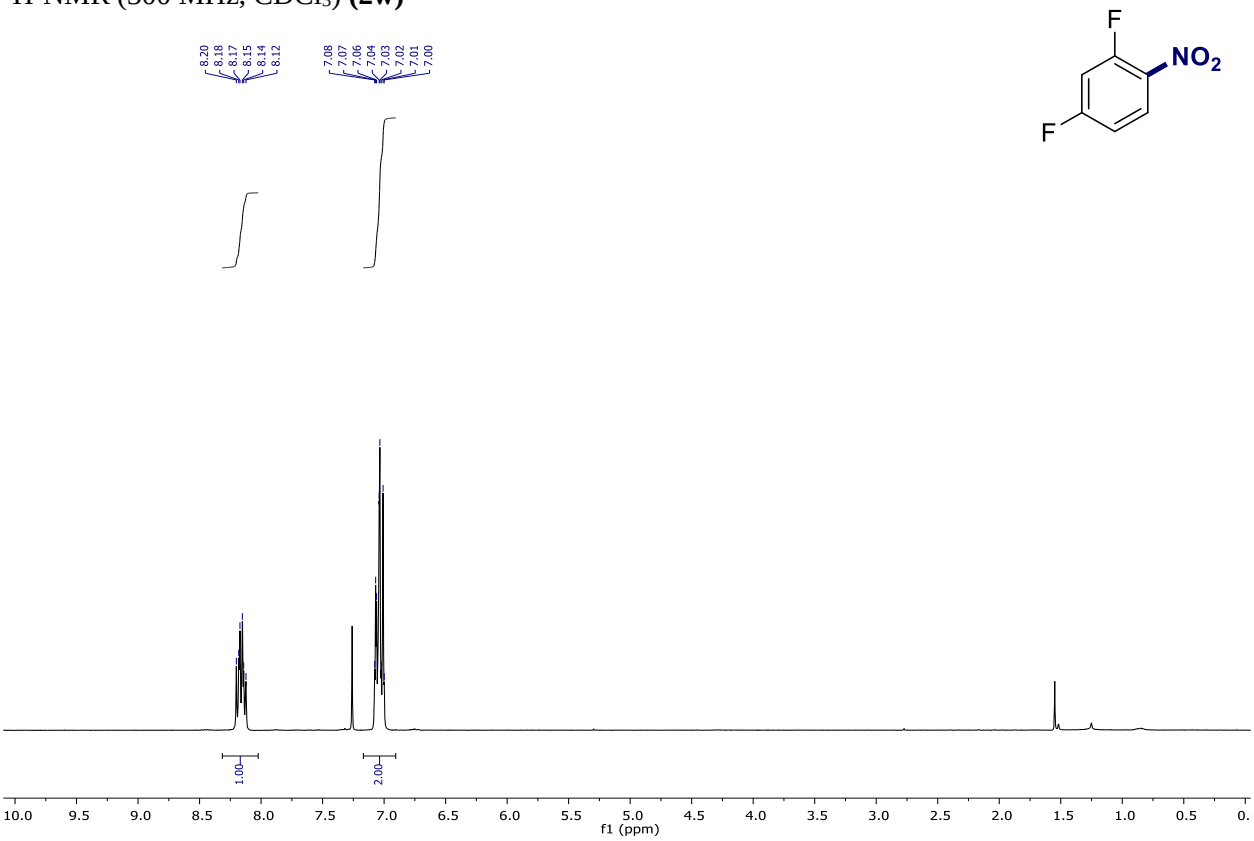


^{19}F-NMR (282 MHz, $CDCl_3$) **(2v)**

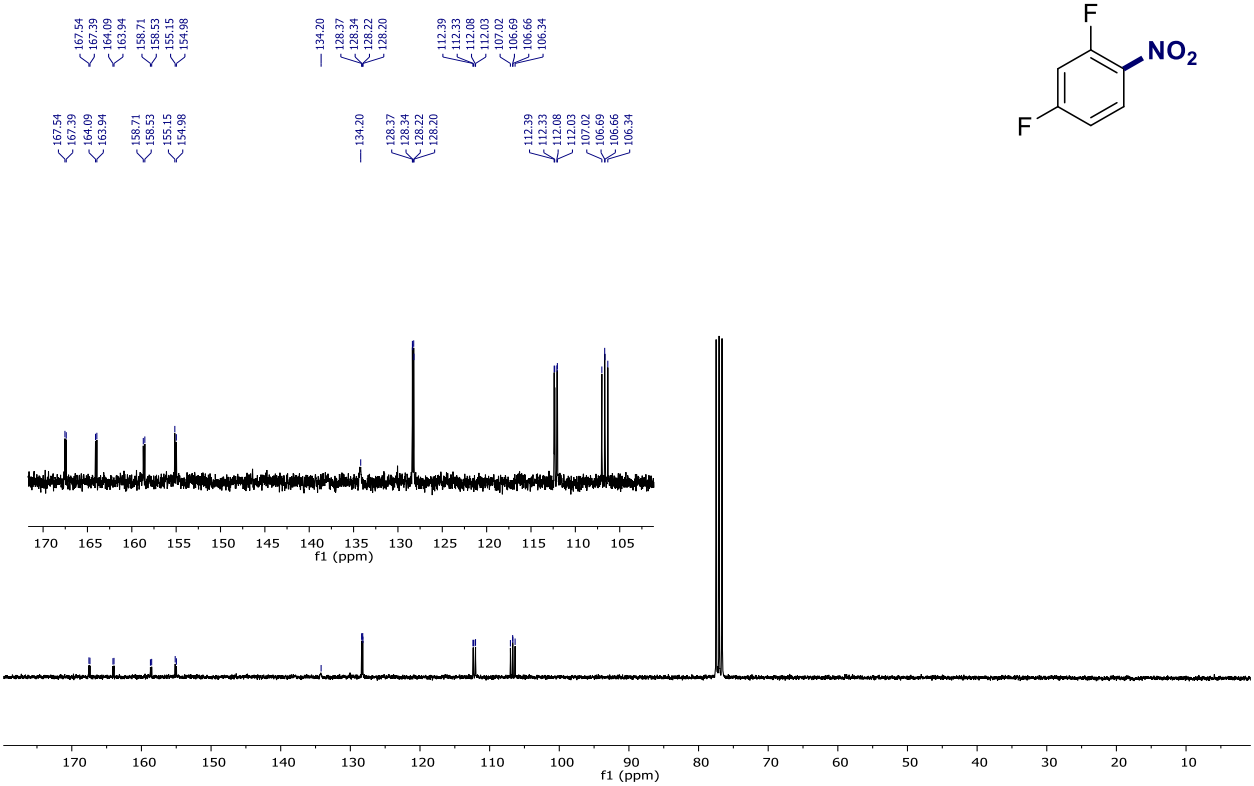




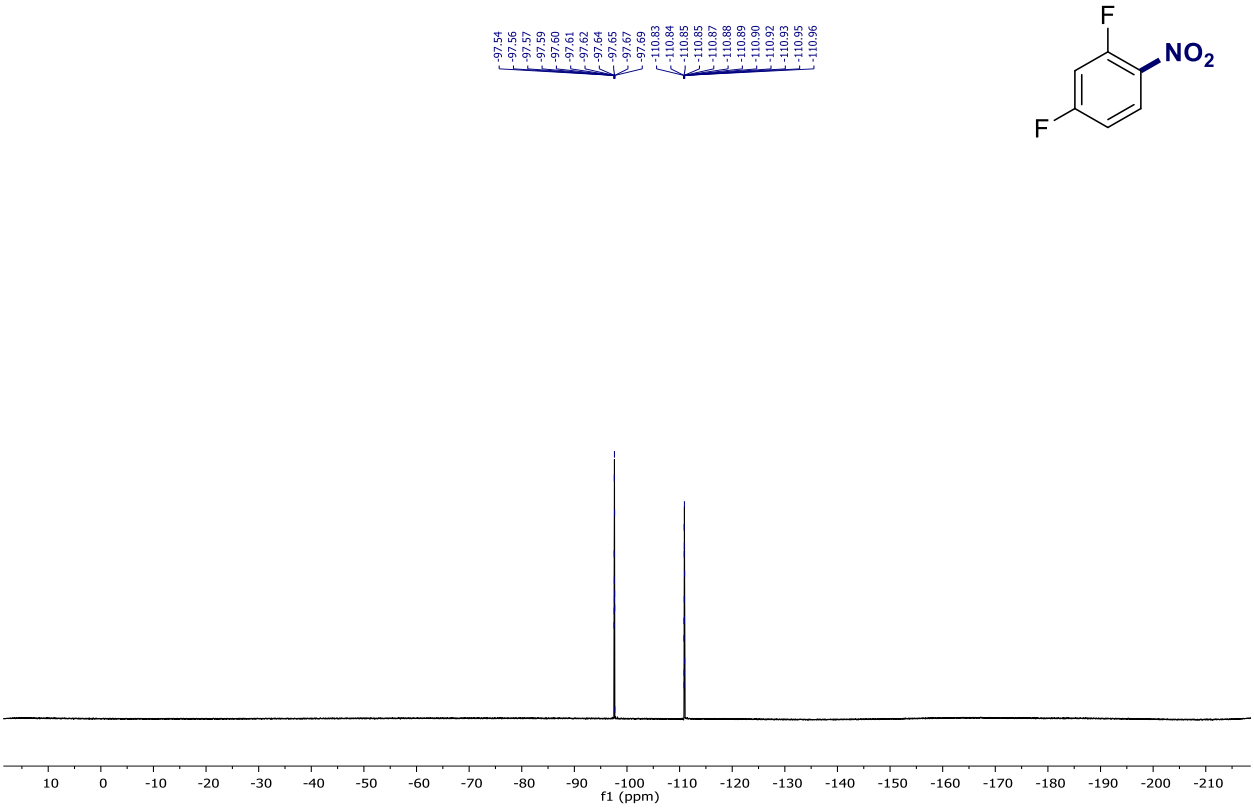
^{1}H-NMR (300 MHz, $CDCl_3$) **(2w)**



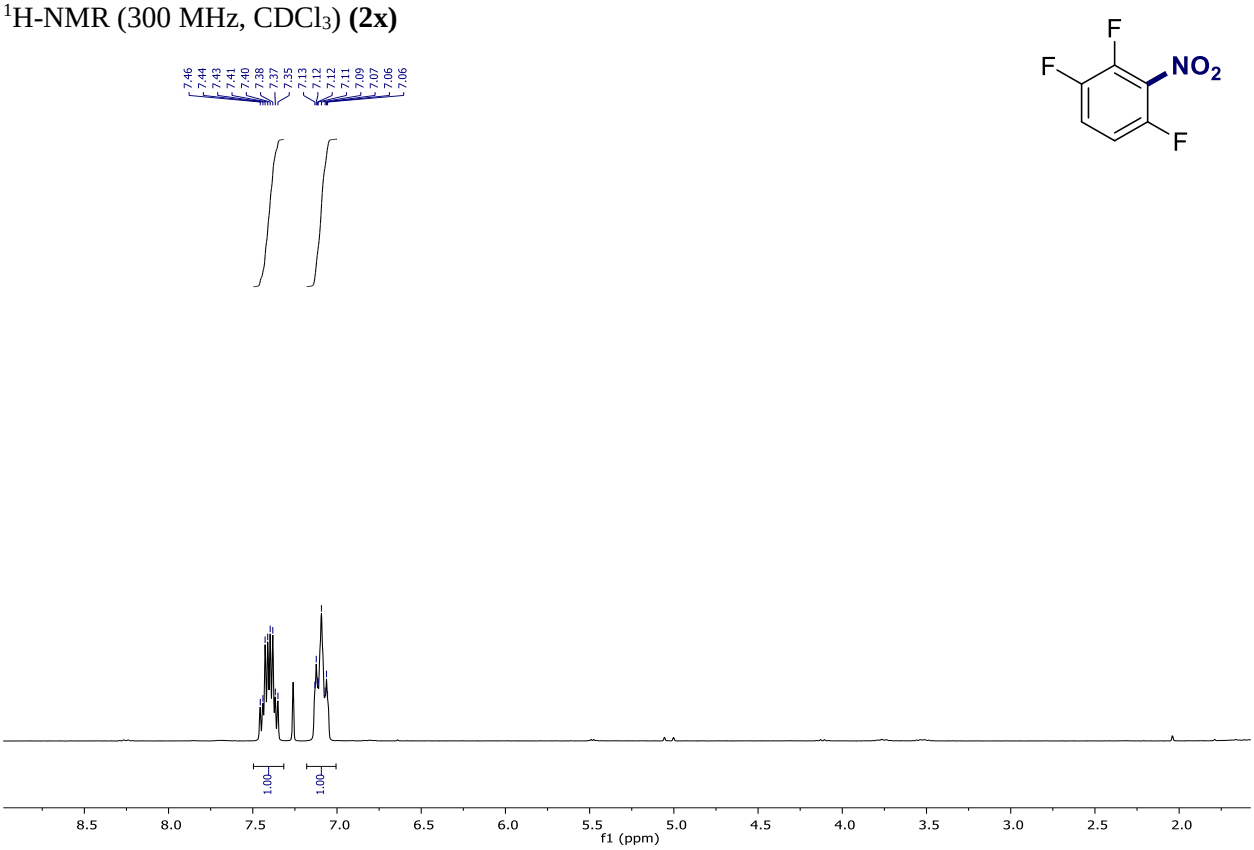
^{13}C-NMR (75 MHz, $CDCl_3$) **(2w)**



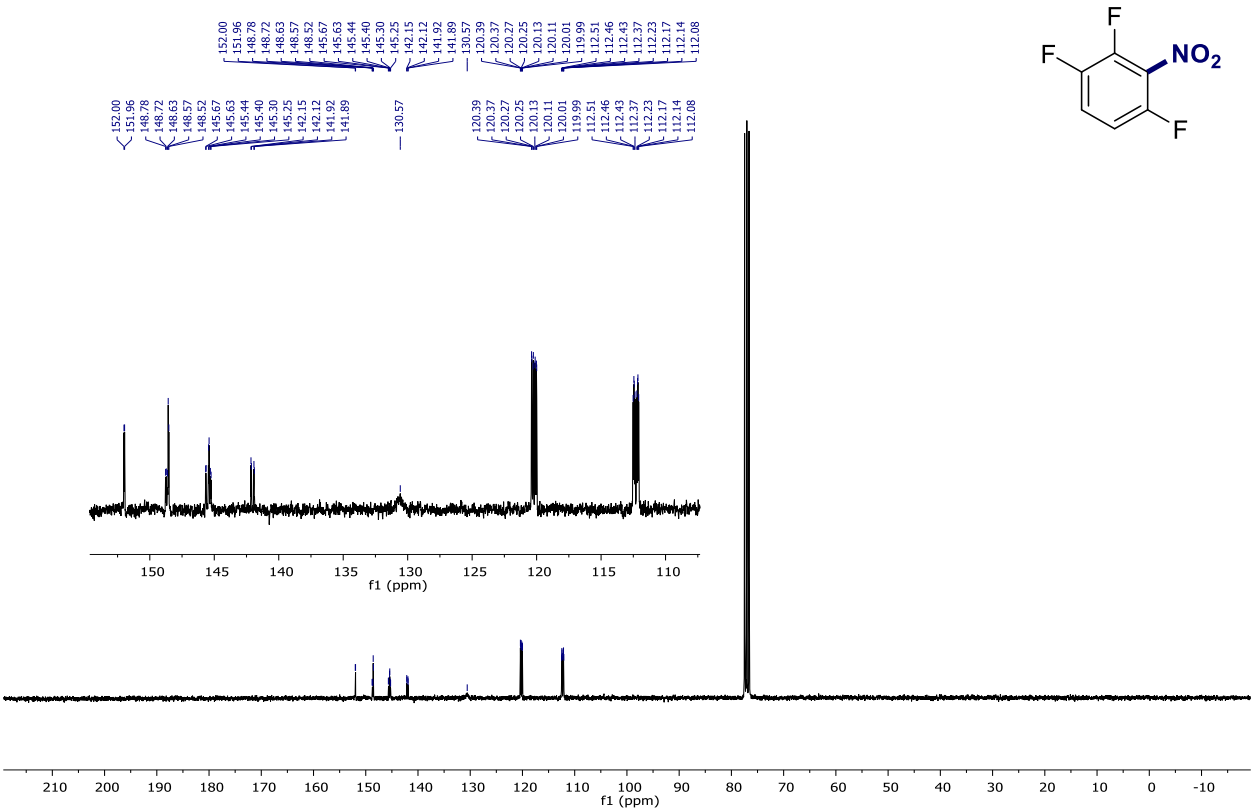
^{19}F-NMR (282 MHz, $CDCl_3$) **(2w)**



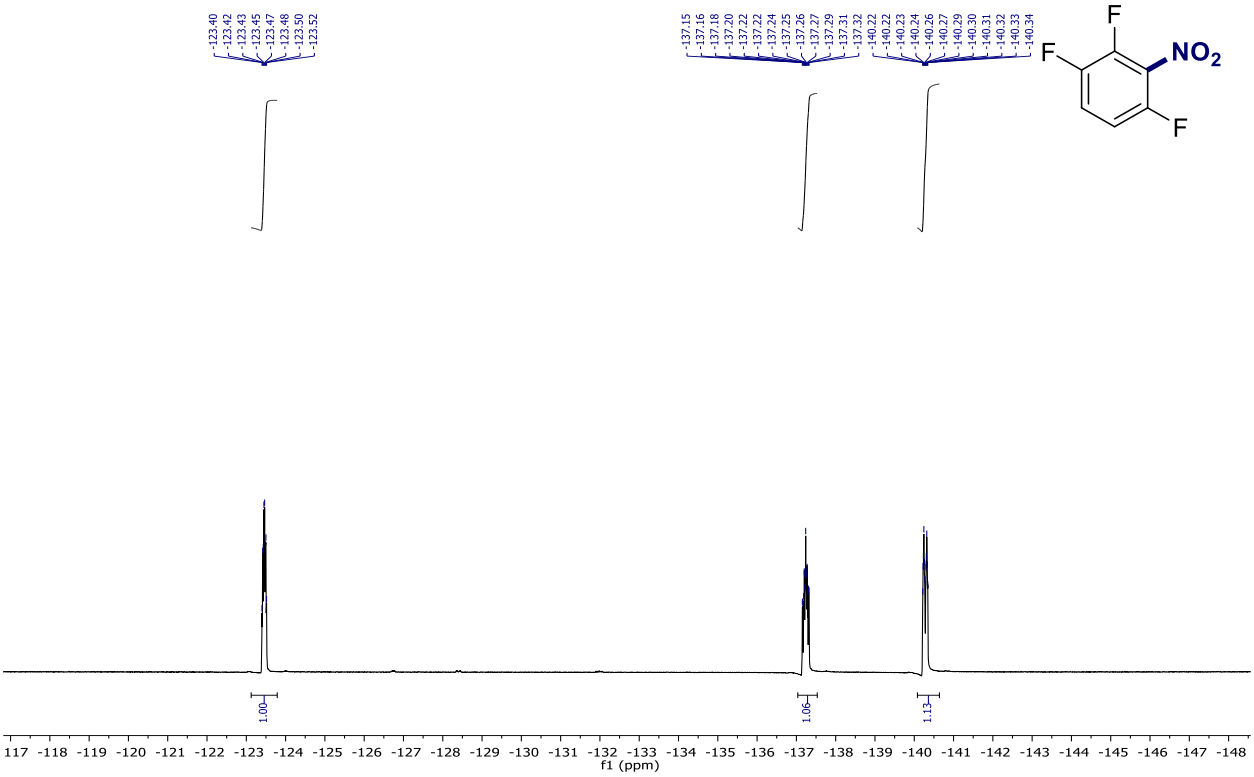
^{1}H-NMR (300 MHz, $CDCl_3$) **(2x)**



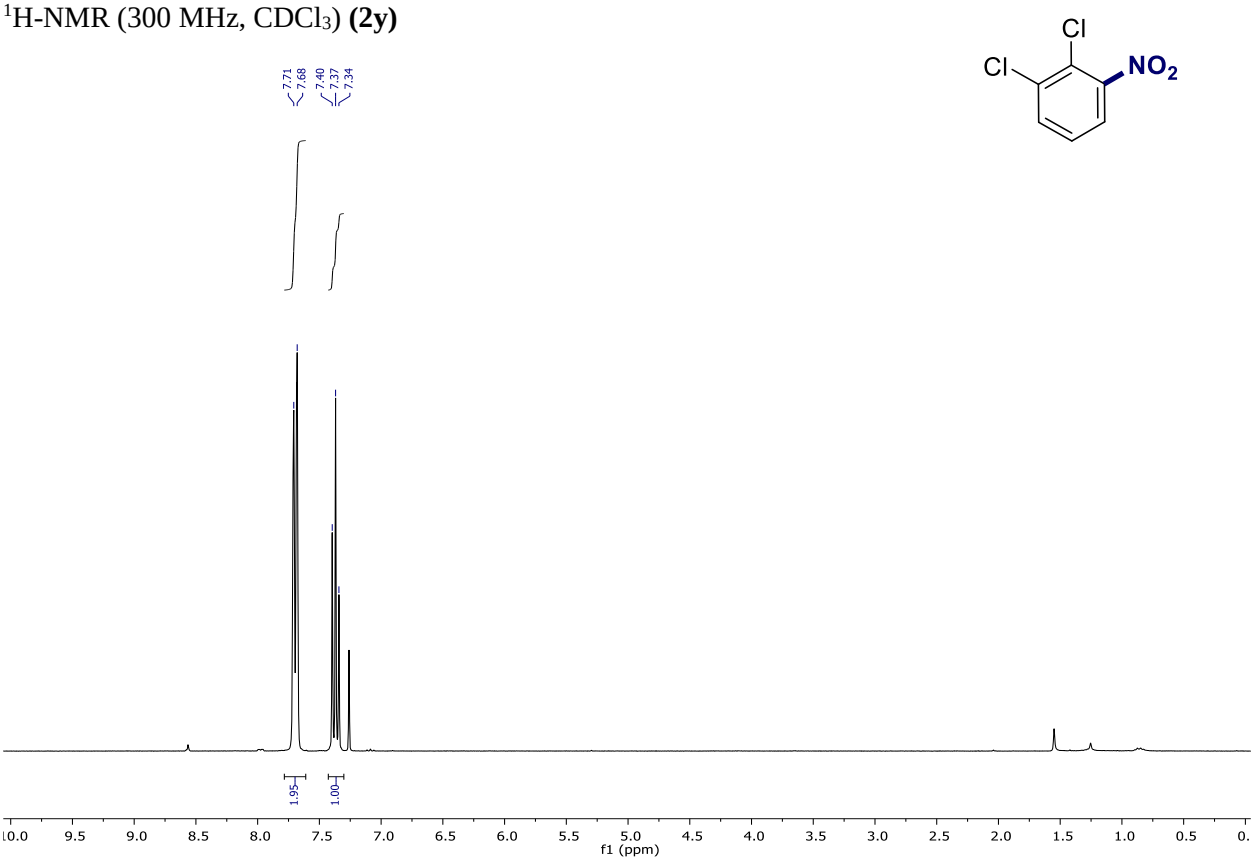
^{13}C-NMR (75 MHz, $CDCl_3$) **(2x)**



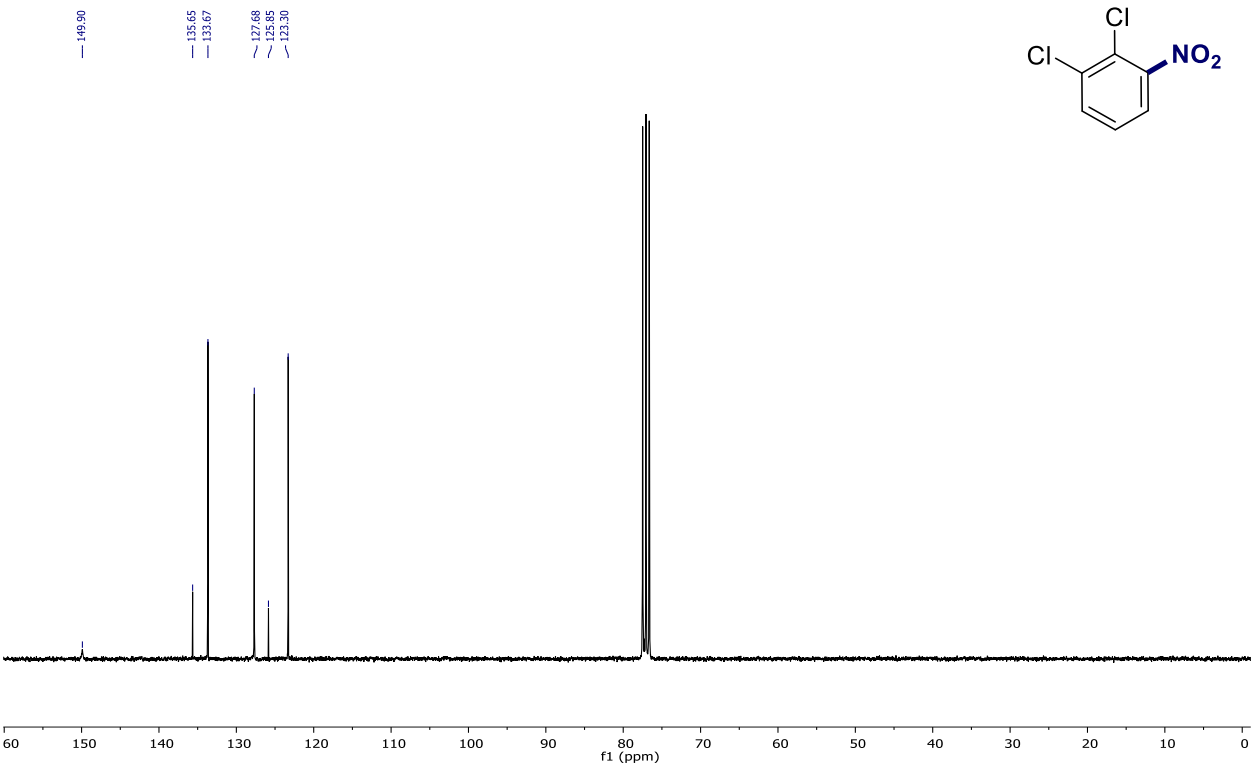
^{19}F-NMR (282 MHz, $CDCl_3$) **(2x)**



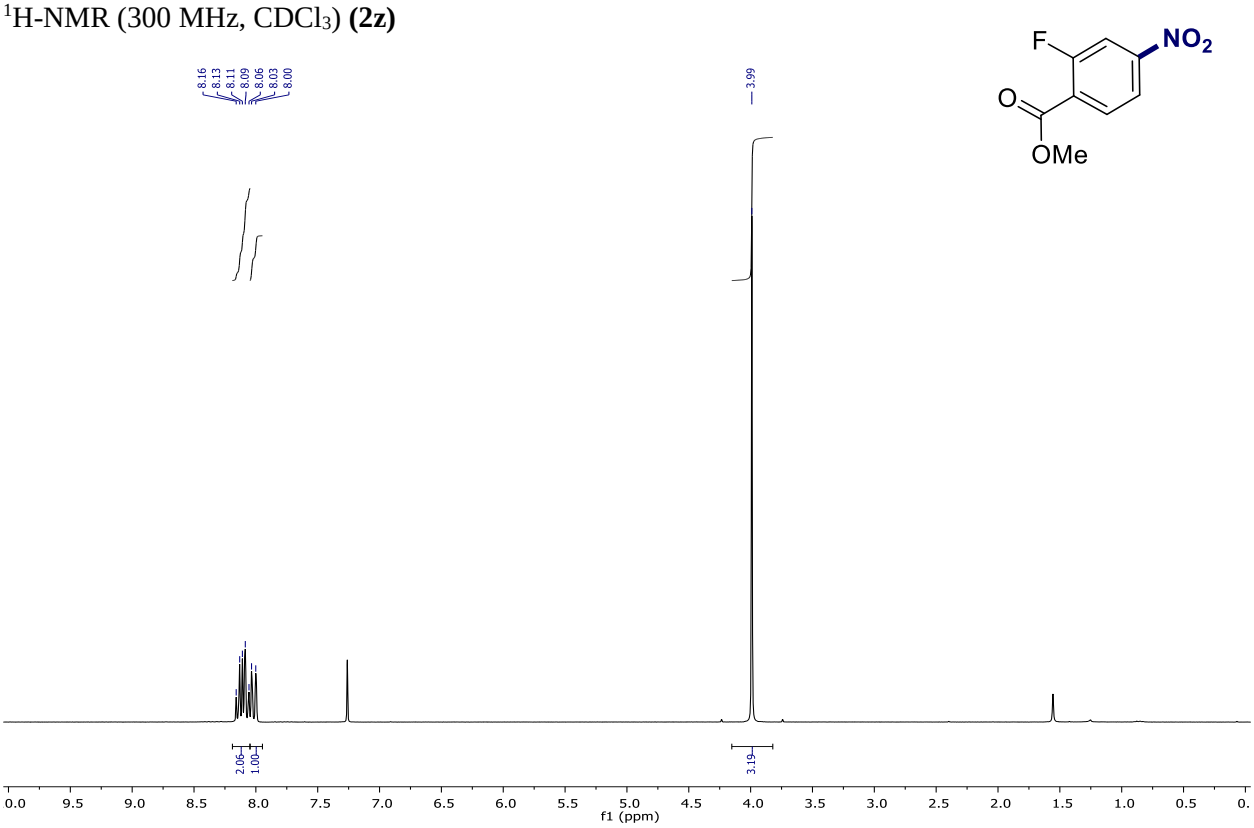
^{1}H-NMR (300 MHz, $CDCl_3$) **(2y)**



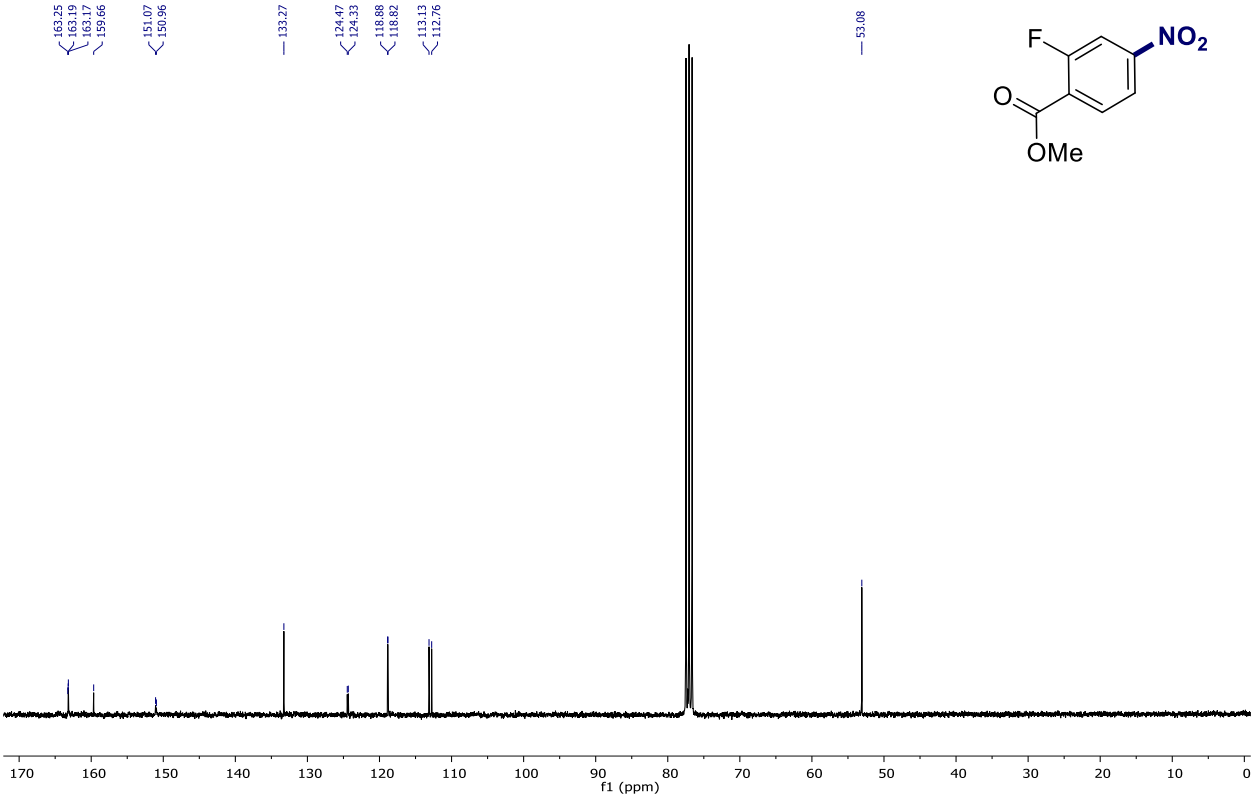
^{13}C-NMR (75 MHz, $CDCl_3$) **(2y)**



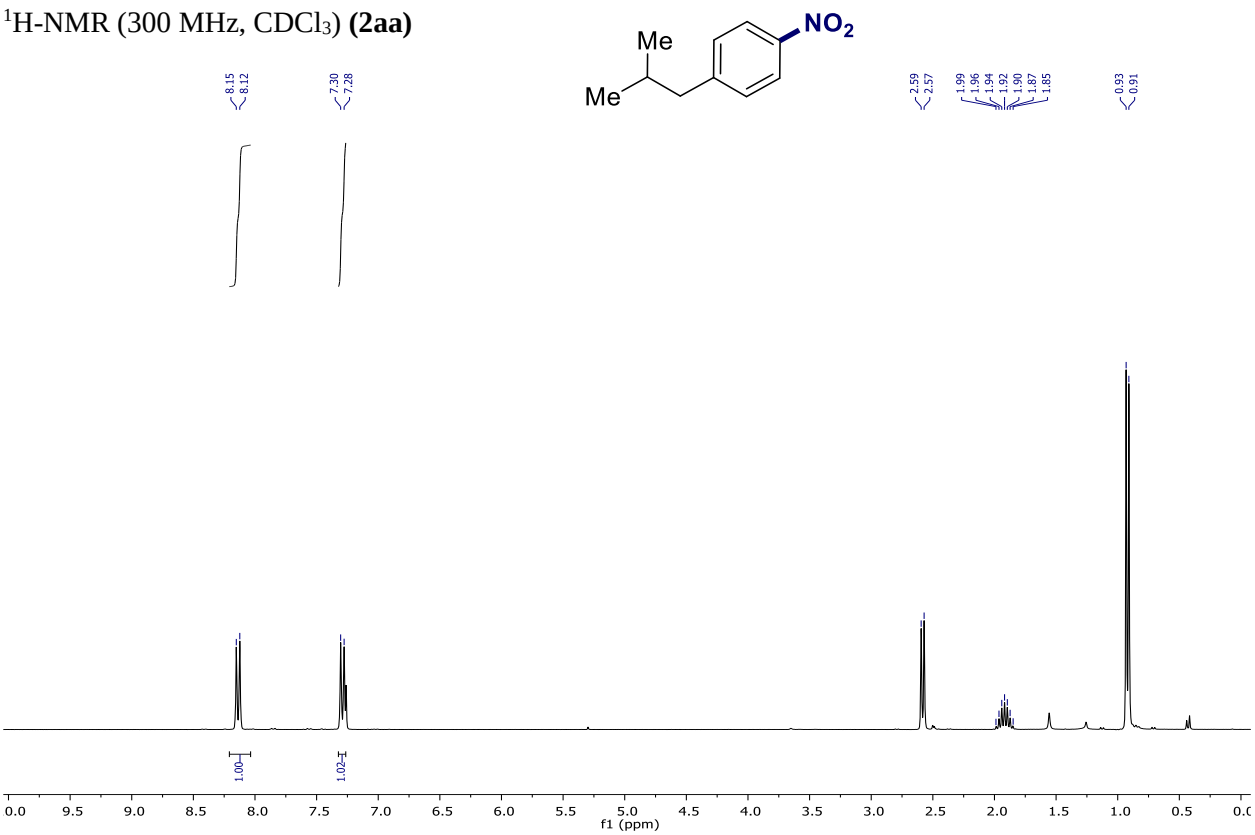
^{1}H-NMR (300 MHz, $CDCl_3$) **(2z)**



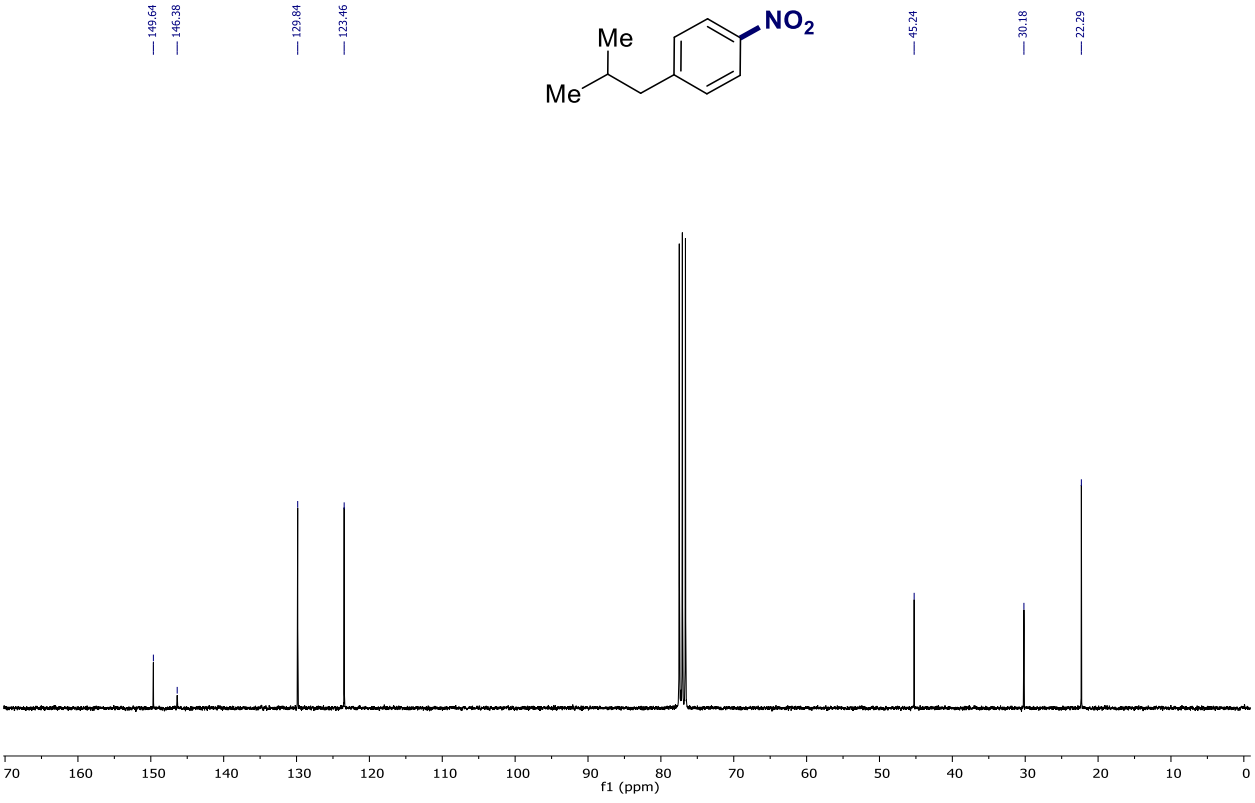
^{13}C-NMR (75 MHz, $CDCl_3$) **(2z)**



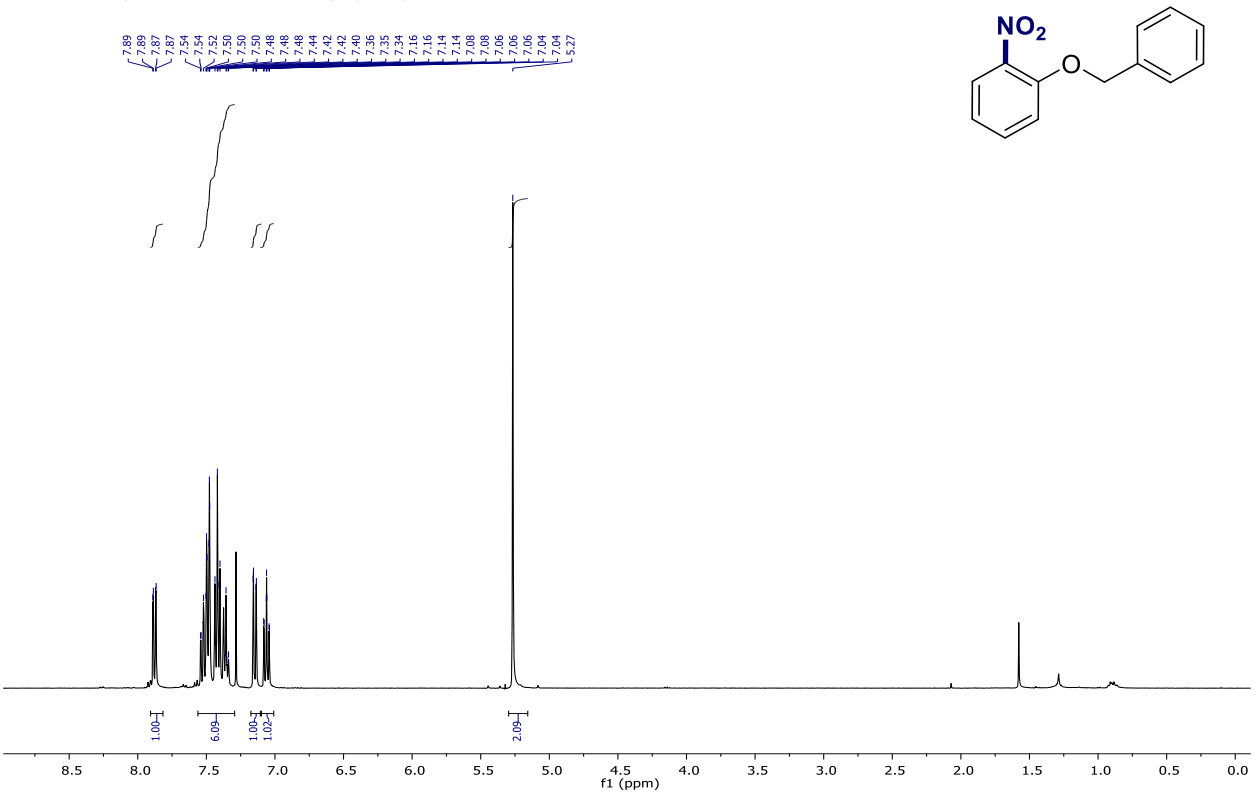
^{1}H-NMR (300 MHz, $CDCl_3$) **(2aa)**



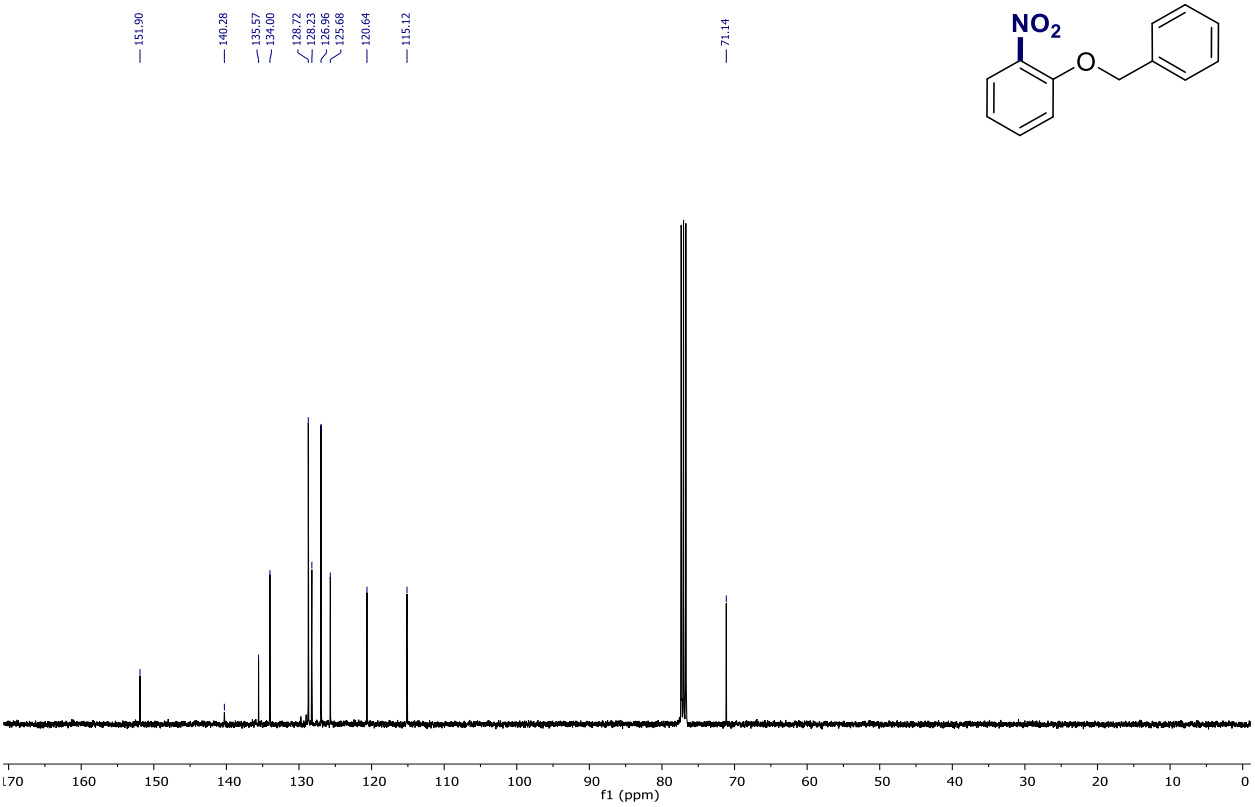
^{13}C-NMR (75 MHz, $CDCl_3$) **(2aa)**



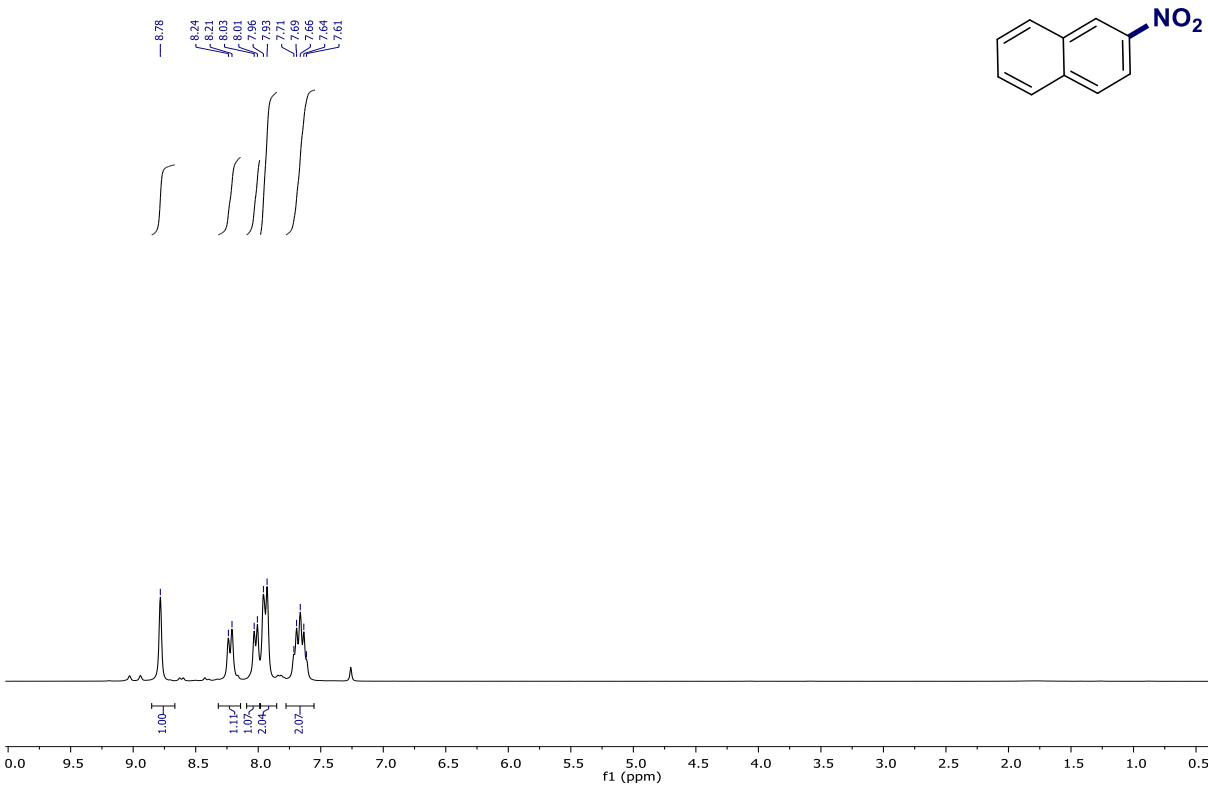
^{1}H-NMR (300 MHz, $CDCl_3$) **(2ab)**



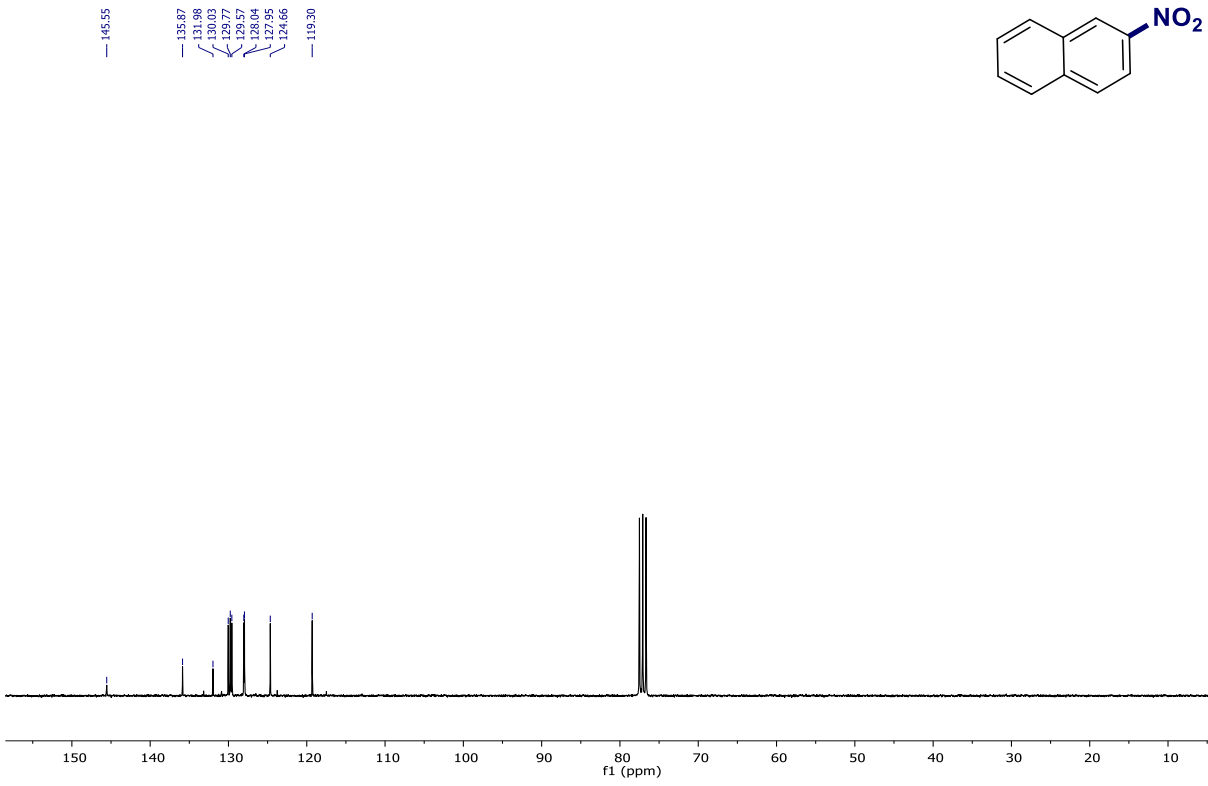
^{13}C-NMR (75 MHz, $CDCl_3$) **(2ab)**



^{1}H-NMR (300 MHz, $CDCl_3$) **(2ac)**



^{13}C-NMR (75 MHz, $CDCl_3$) **(2ac)**



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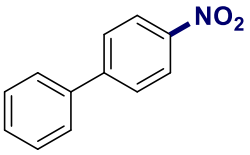

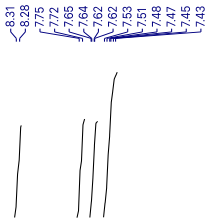

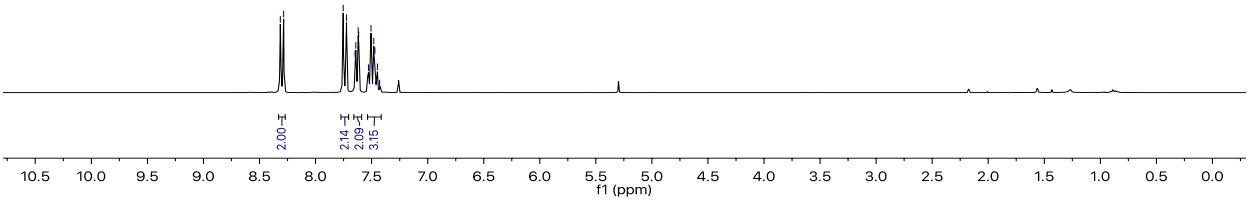

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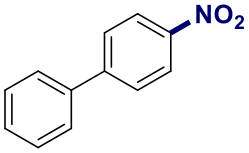
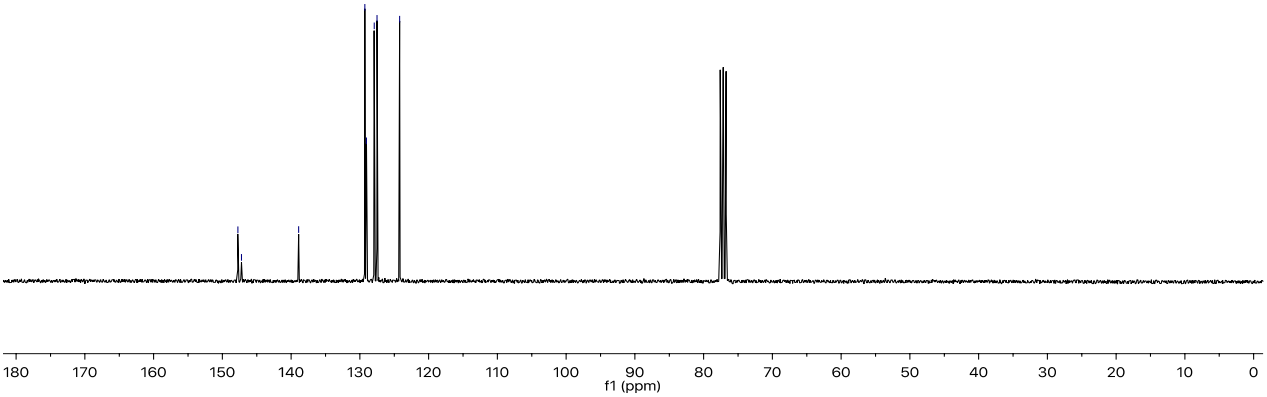
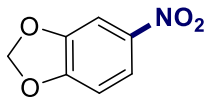
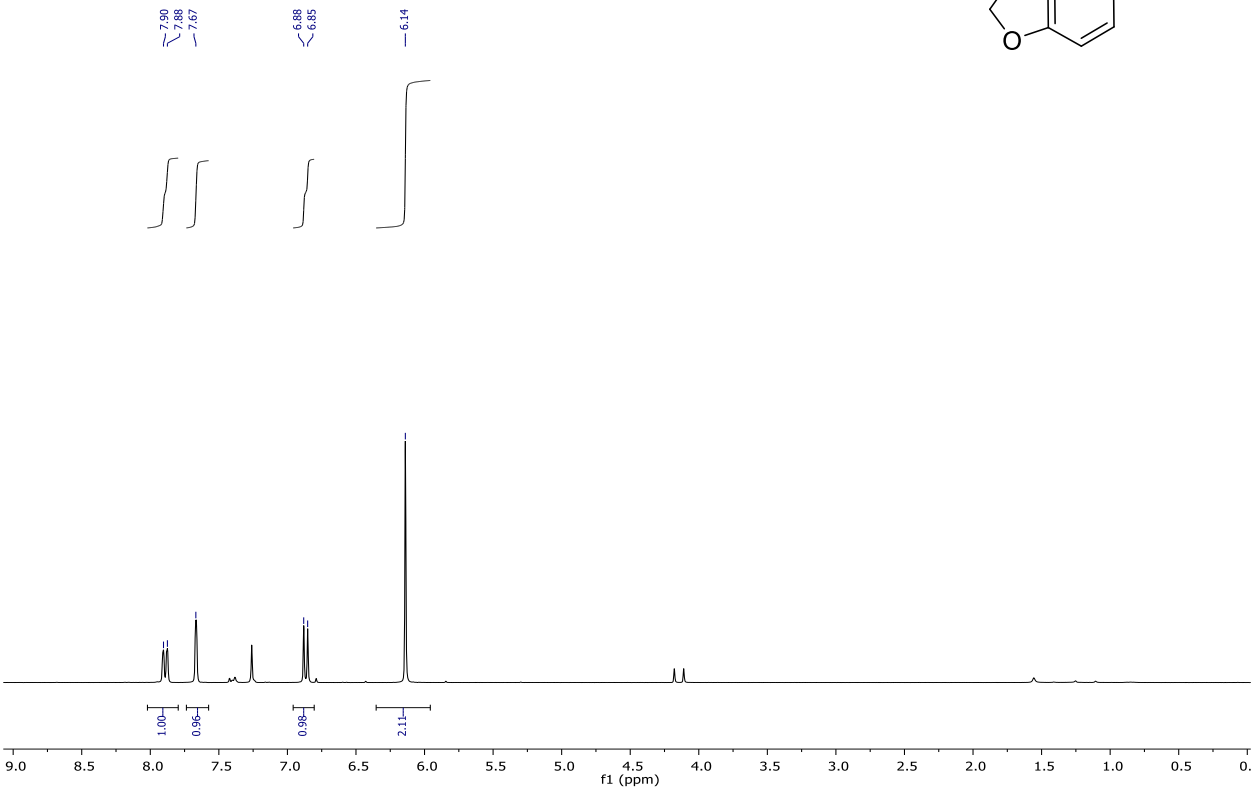


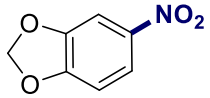


^{1}H-NMR (300 MHz, $CDCl_3$) **(2ae)**

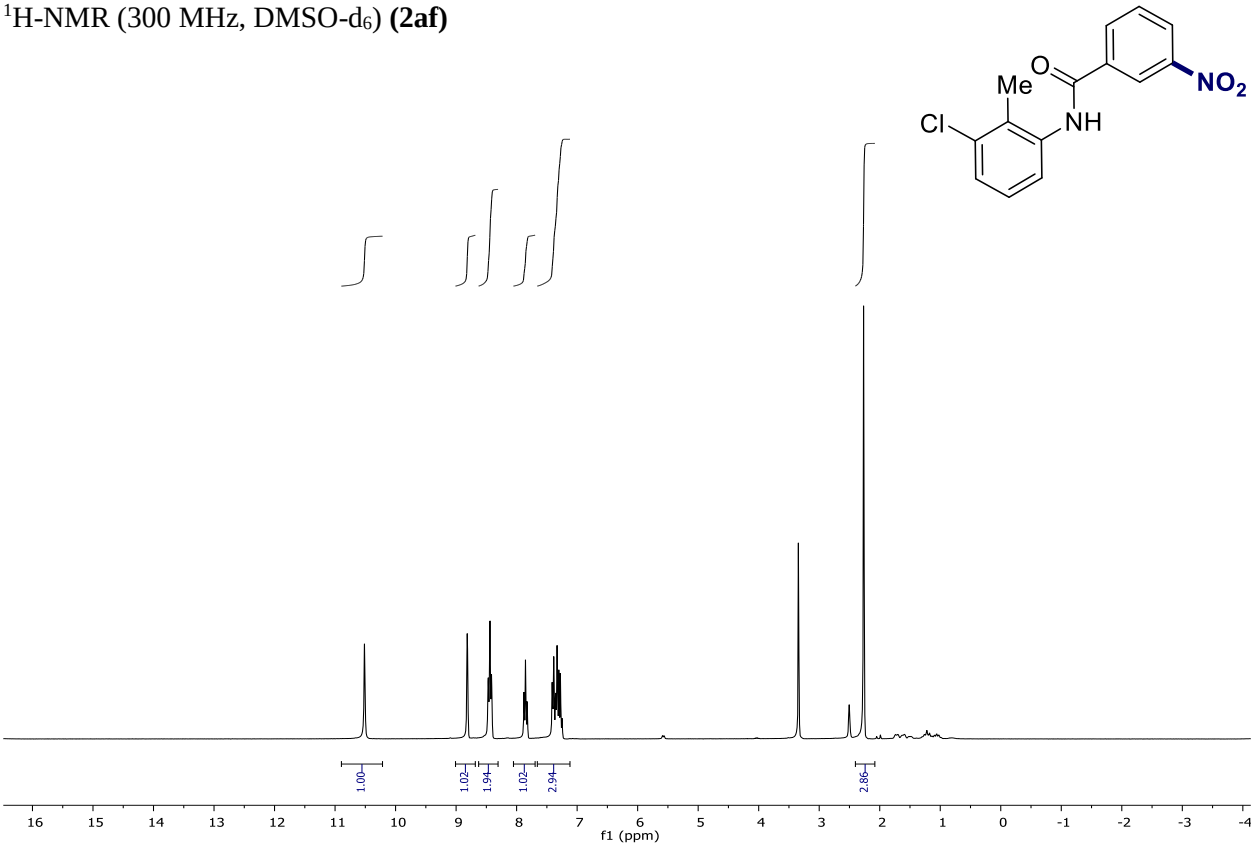




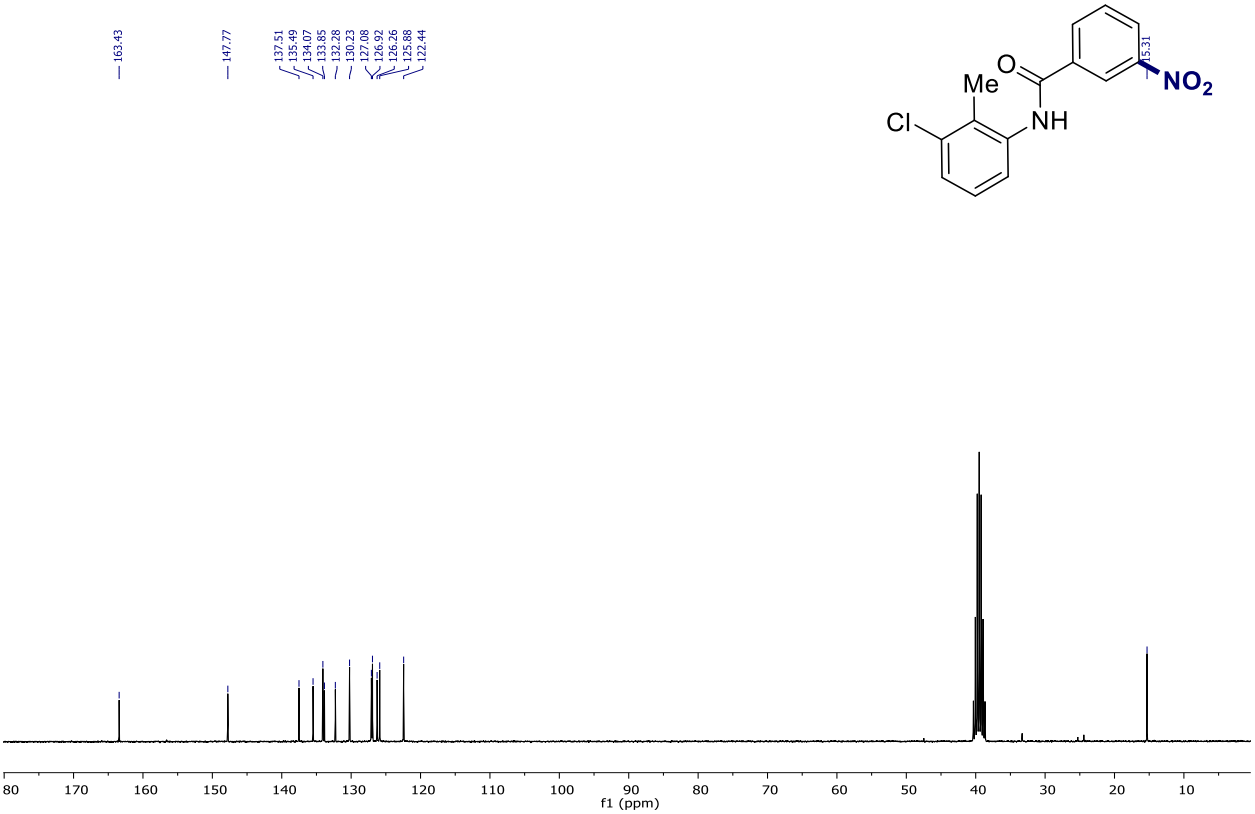
^{13}C-NMR (75 MHz, $CDCl_3$) **(2ae)**



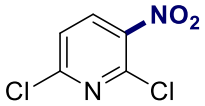
^{1}H-NMR (300 MHz, DMSO-d_6) **(2af)**



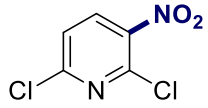
^{13}C-NMR (75 MHz, DMSO-d_6) **(2af)**



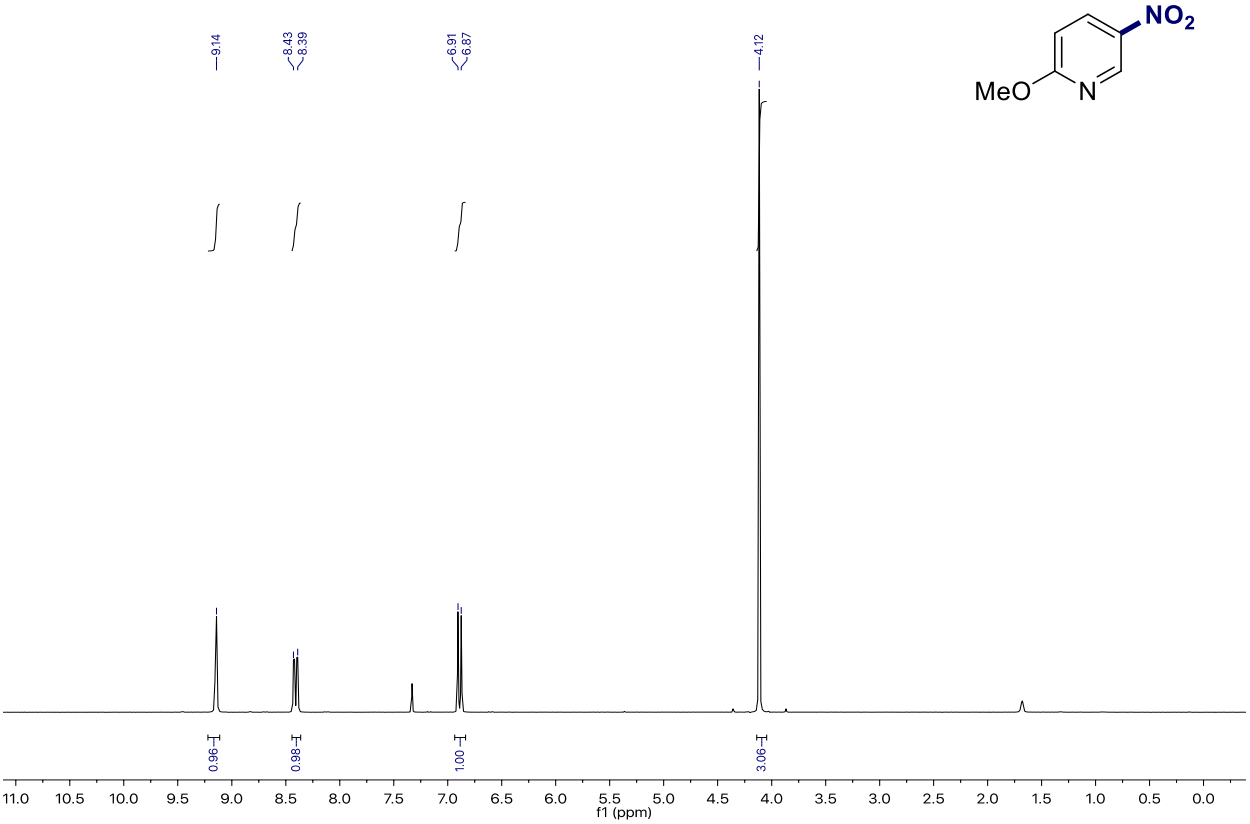
^{1}H-NMR (300 MHz, $CDCl_3$) **(2ag)**



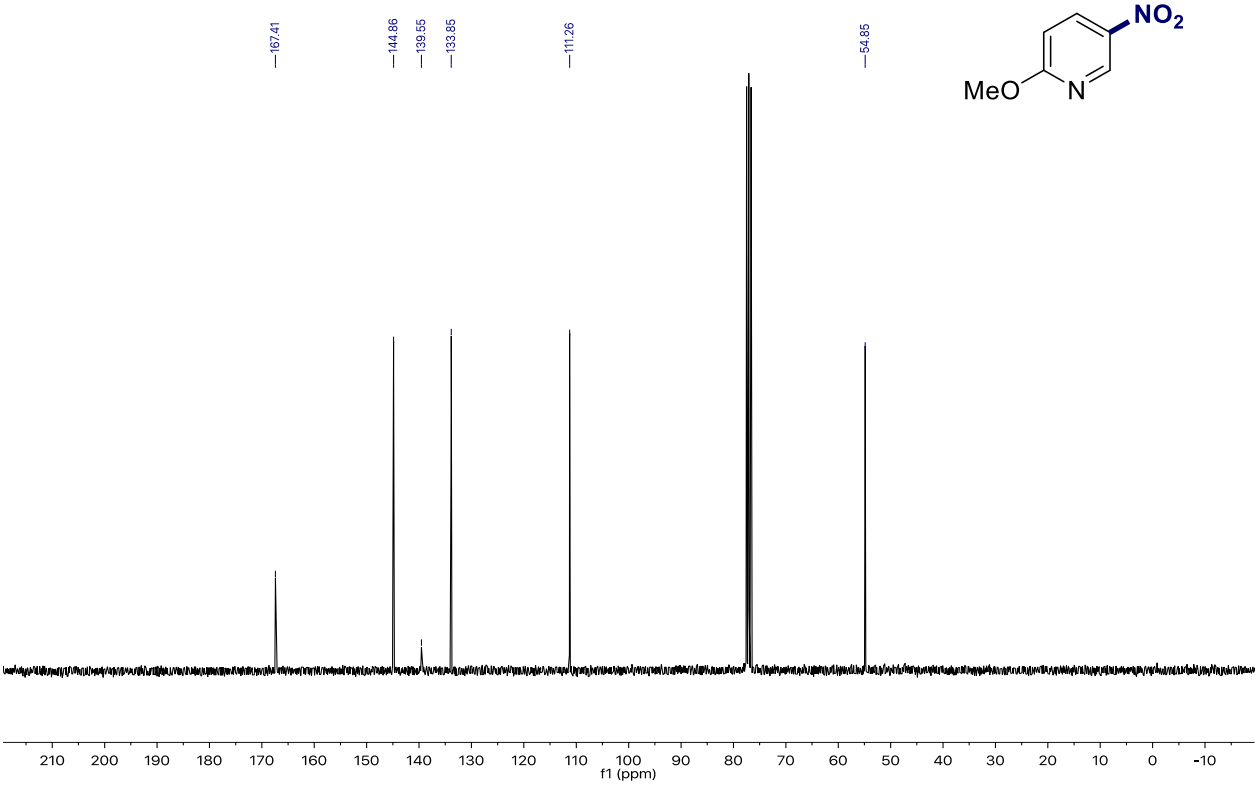
^{13}C-NMR (75 MHz, $CDCl_3$) **(2ag)**



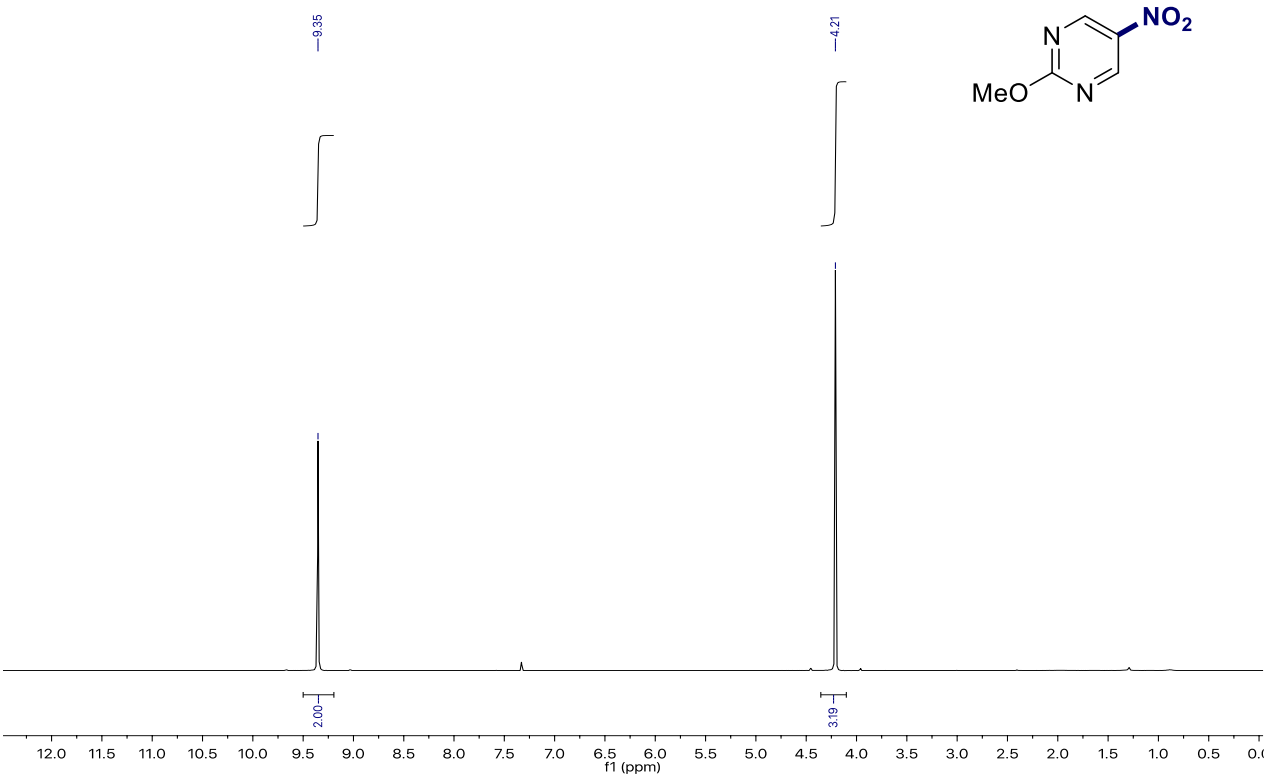
^{1}H-NMR (300 MHz $CDCl_3$) **(2ah)**



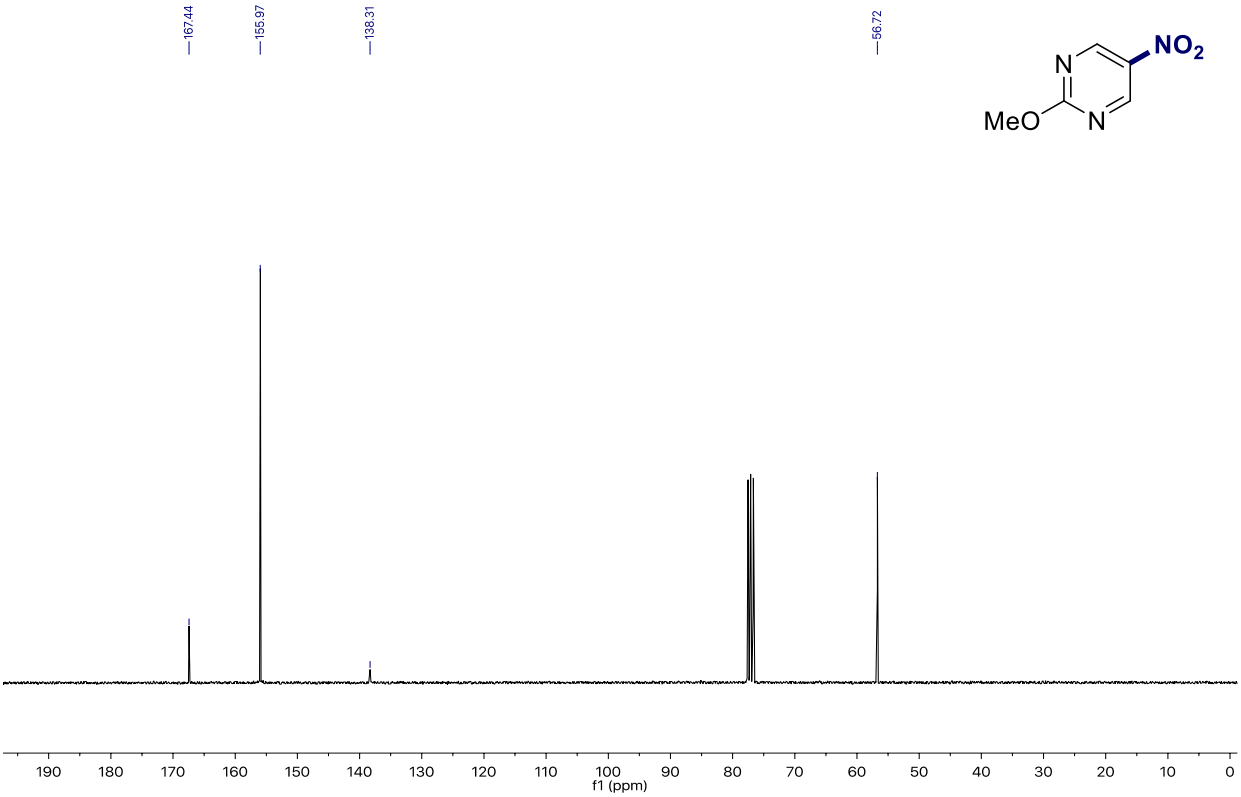
^{13}C-NMR (75 MHz, $CDCl_3$) **(2ah)**



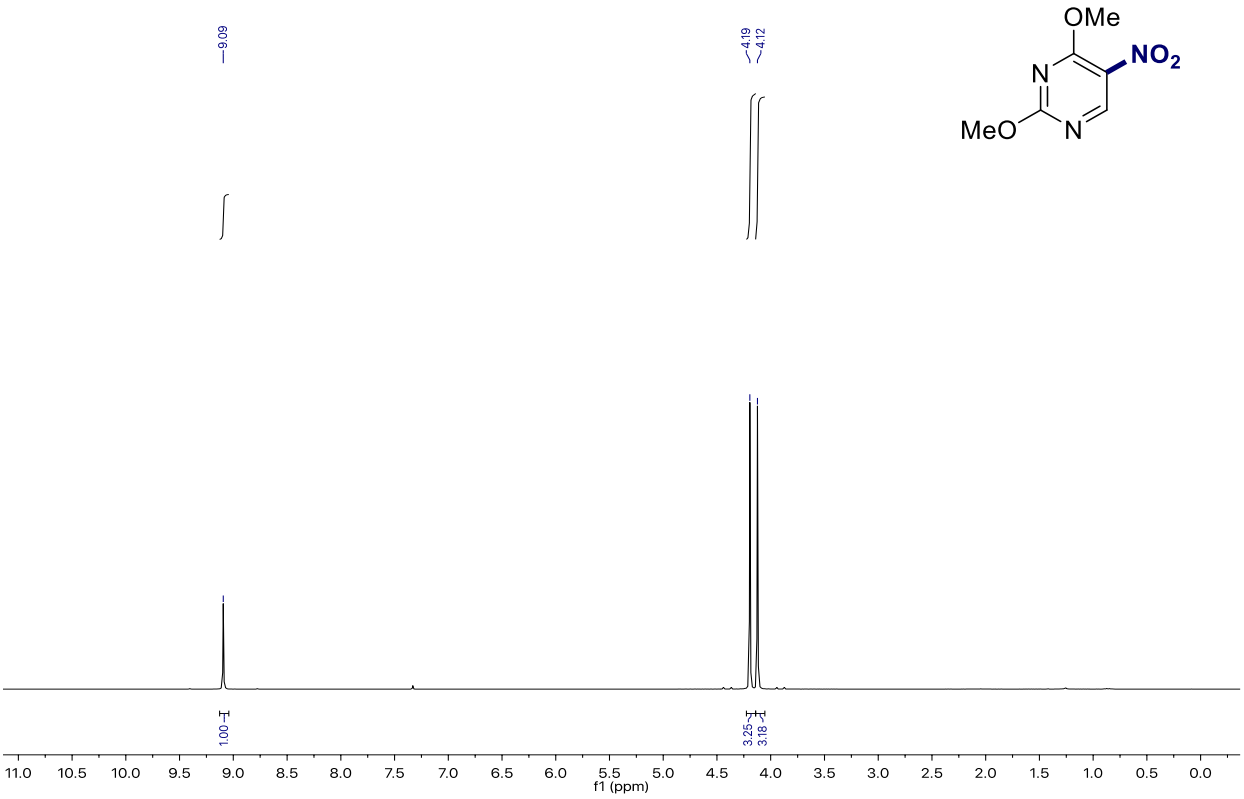
^{1}H-NMR (300 MHz, $CDCl_3$) **(2ai)**



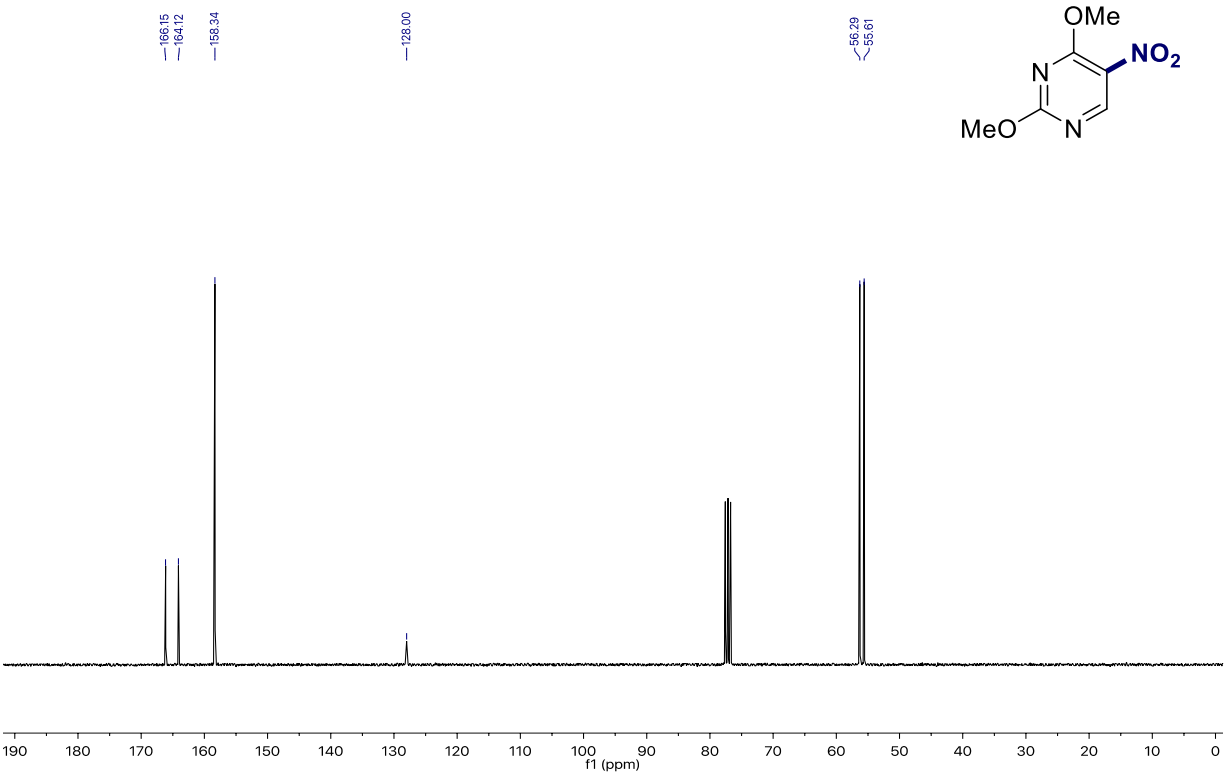
^{13}C-NMR (75 MHz, $CDCl_3$) **(2ai)**



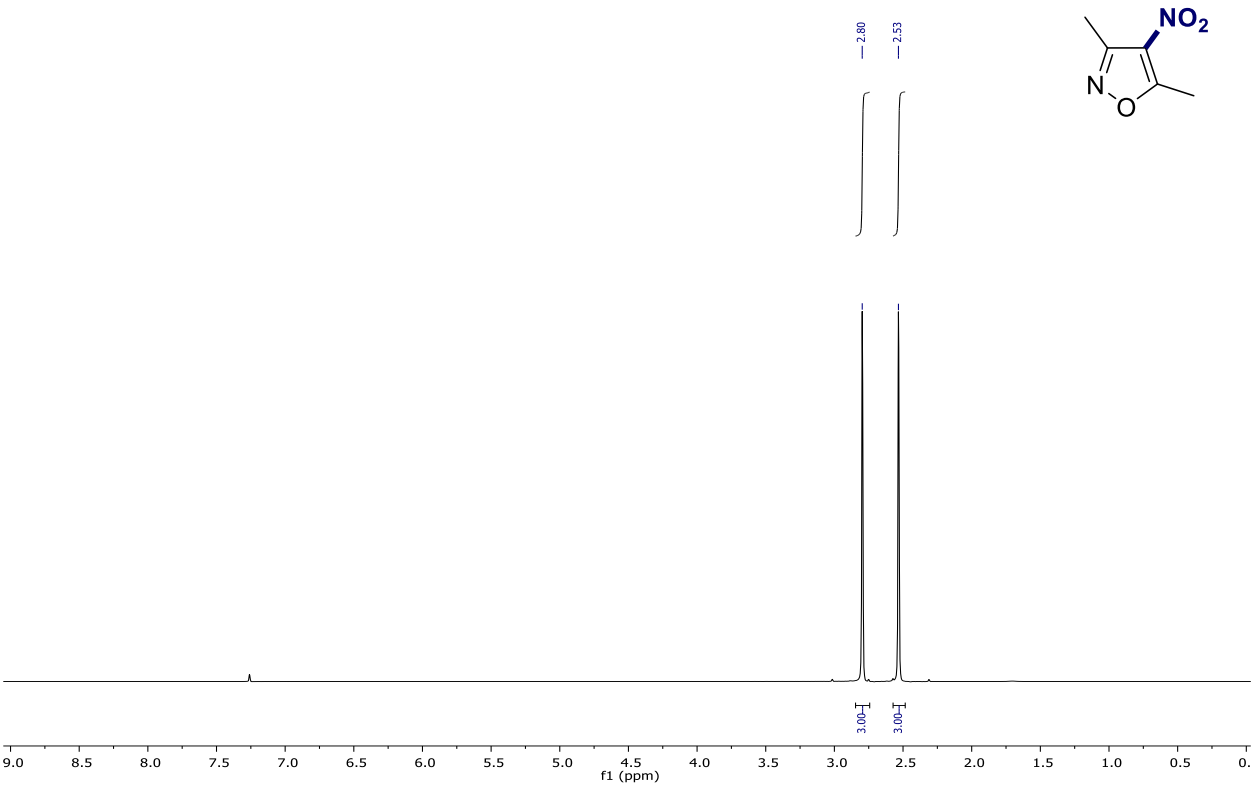
^{1}H-NMR (300 MHz, $CDCl_3$) **(2aj)**



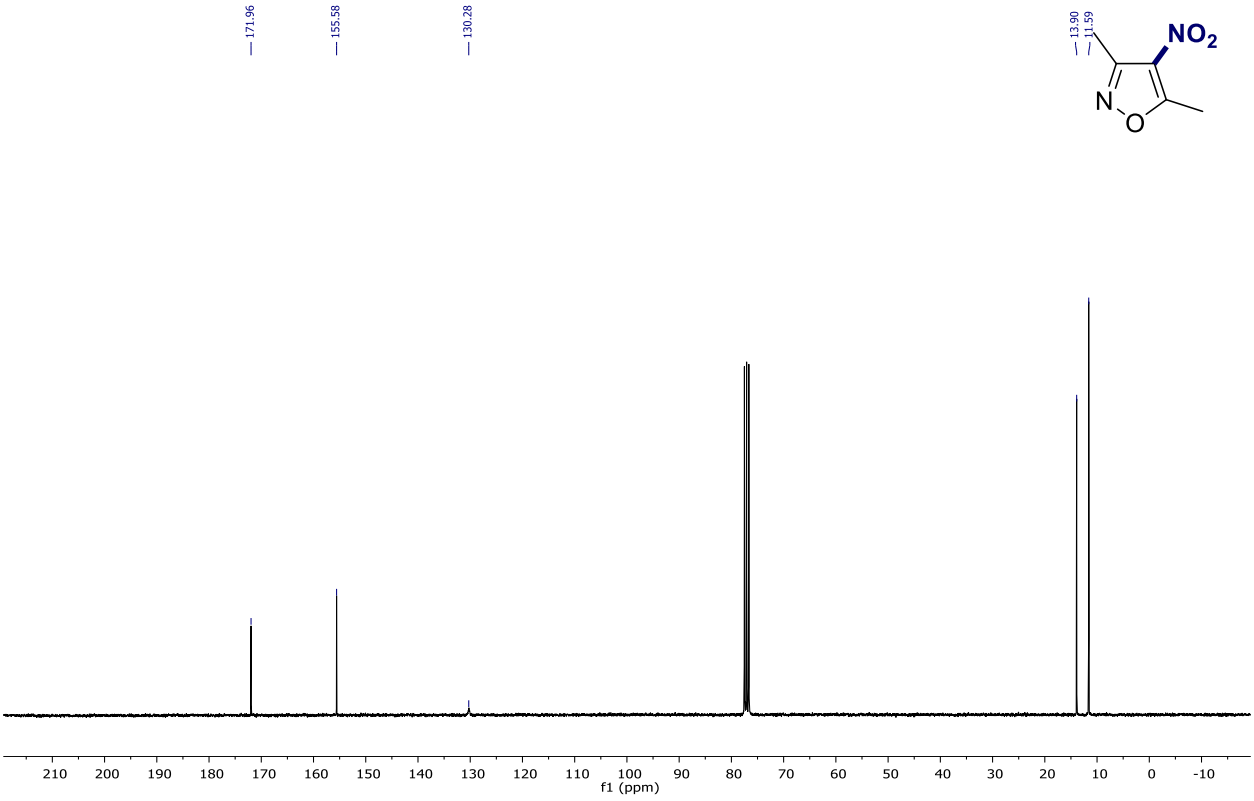
^{13}C-NMR (75 MHz, $CDCl_3$) **(2aj)**



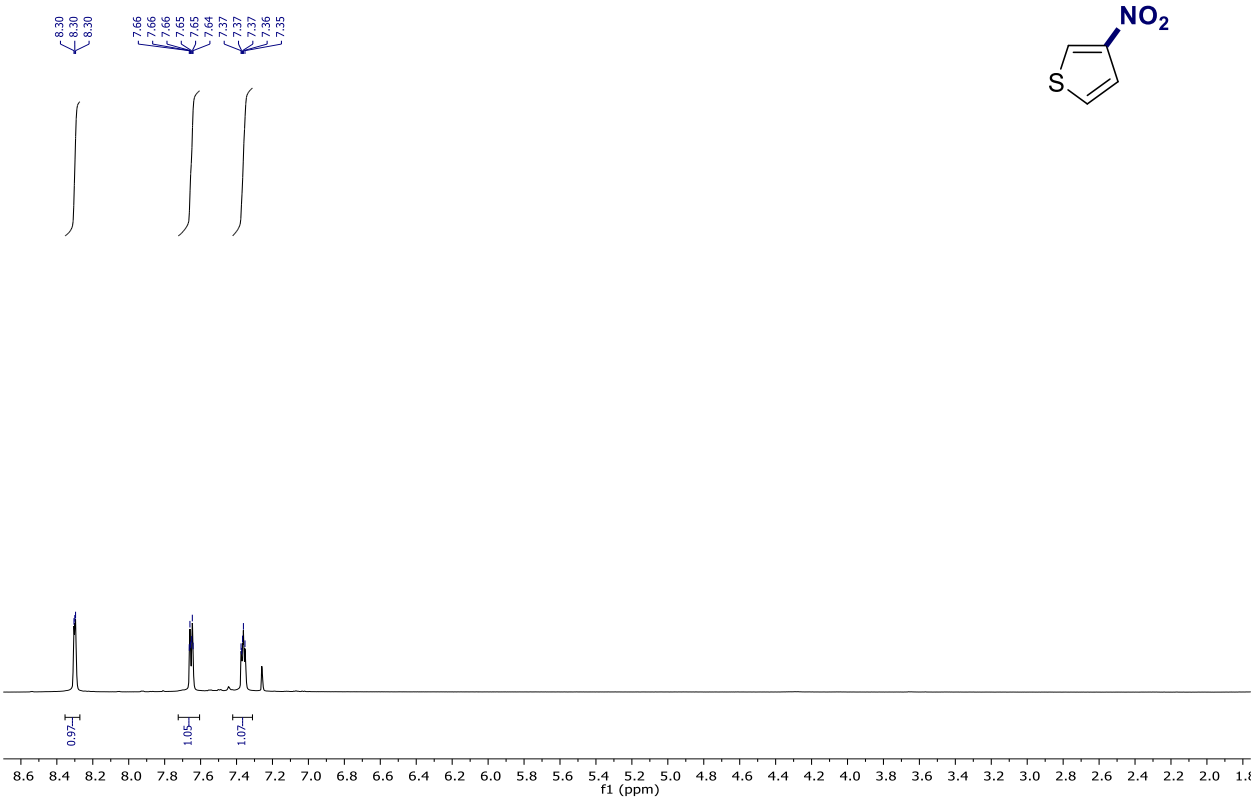
^{1}H-NMR (300 MHz, $CDCl_3$) **(2ak)**



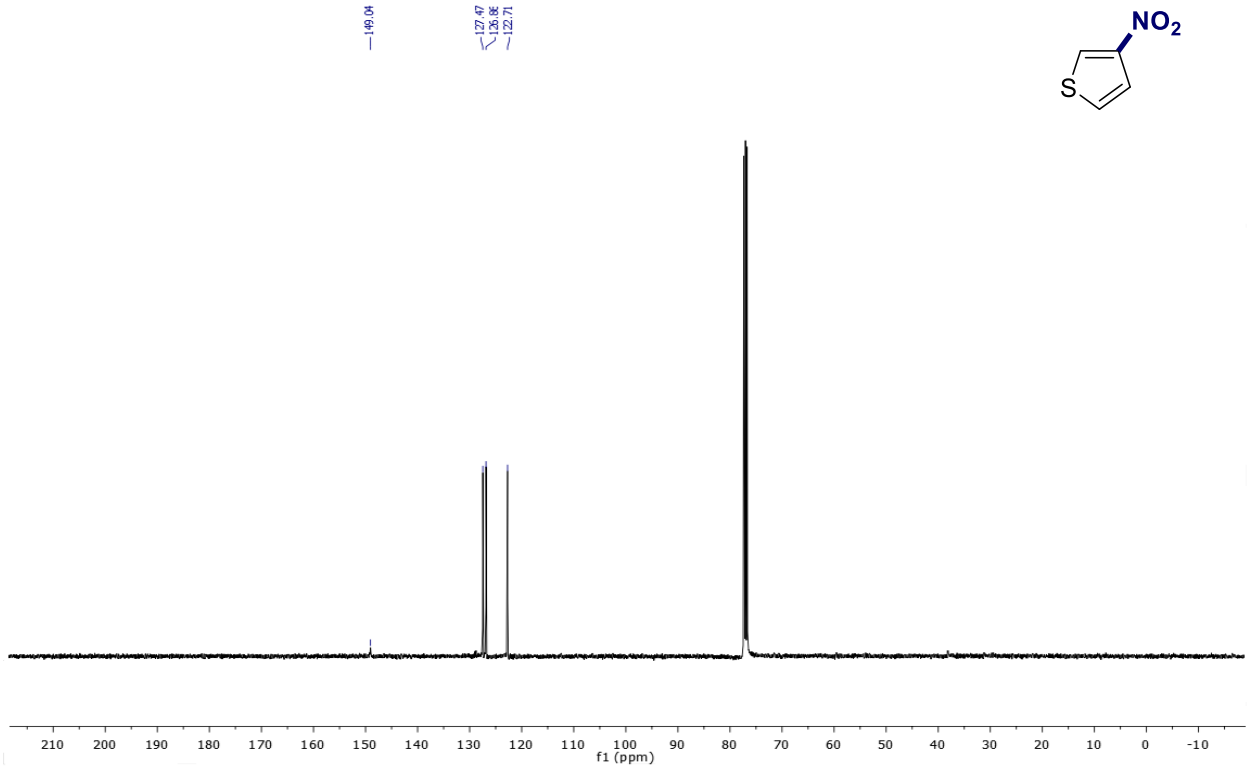
^{13}C-NMR (75 MHz, $CDCl_3$) **(2ak)**



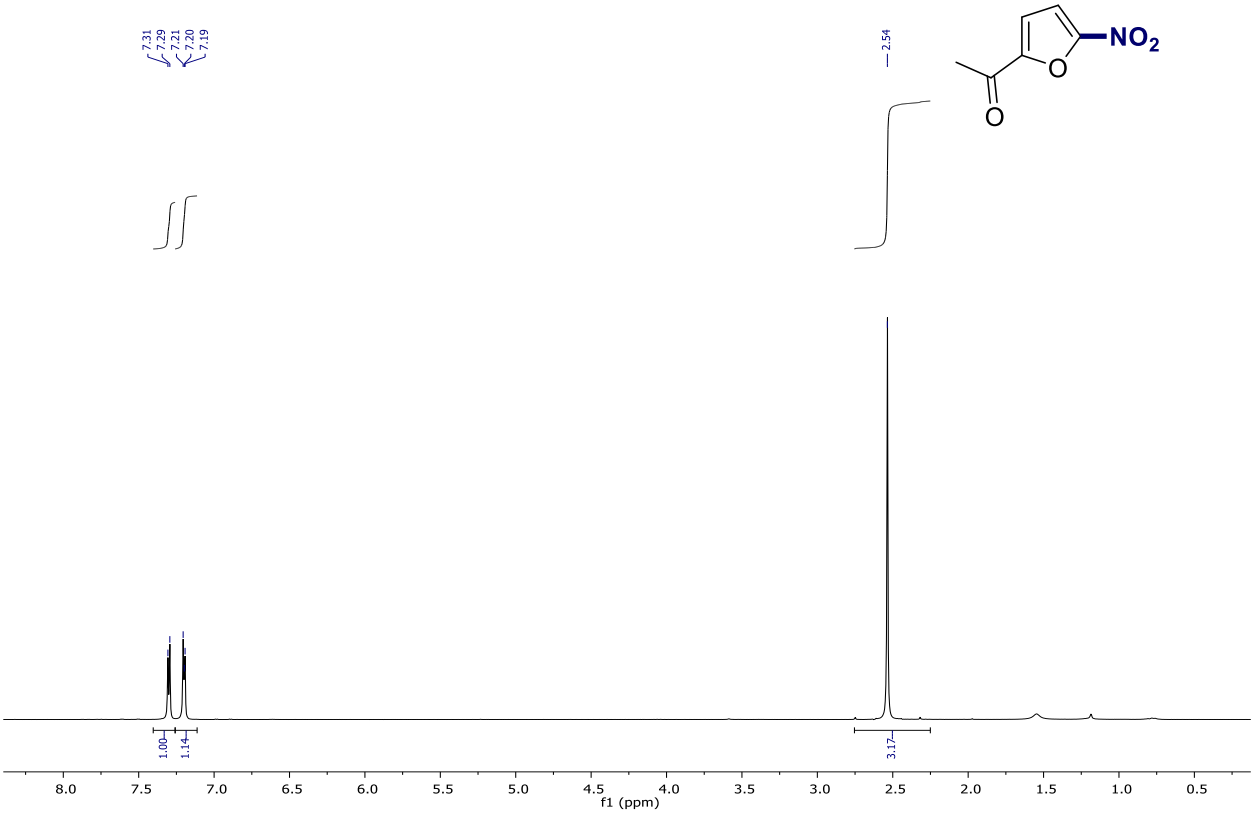
^{1}H-NMR (300 MHz, $CDCl_3$) **(2al)**



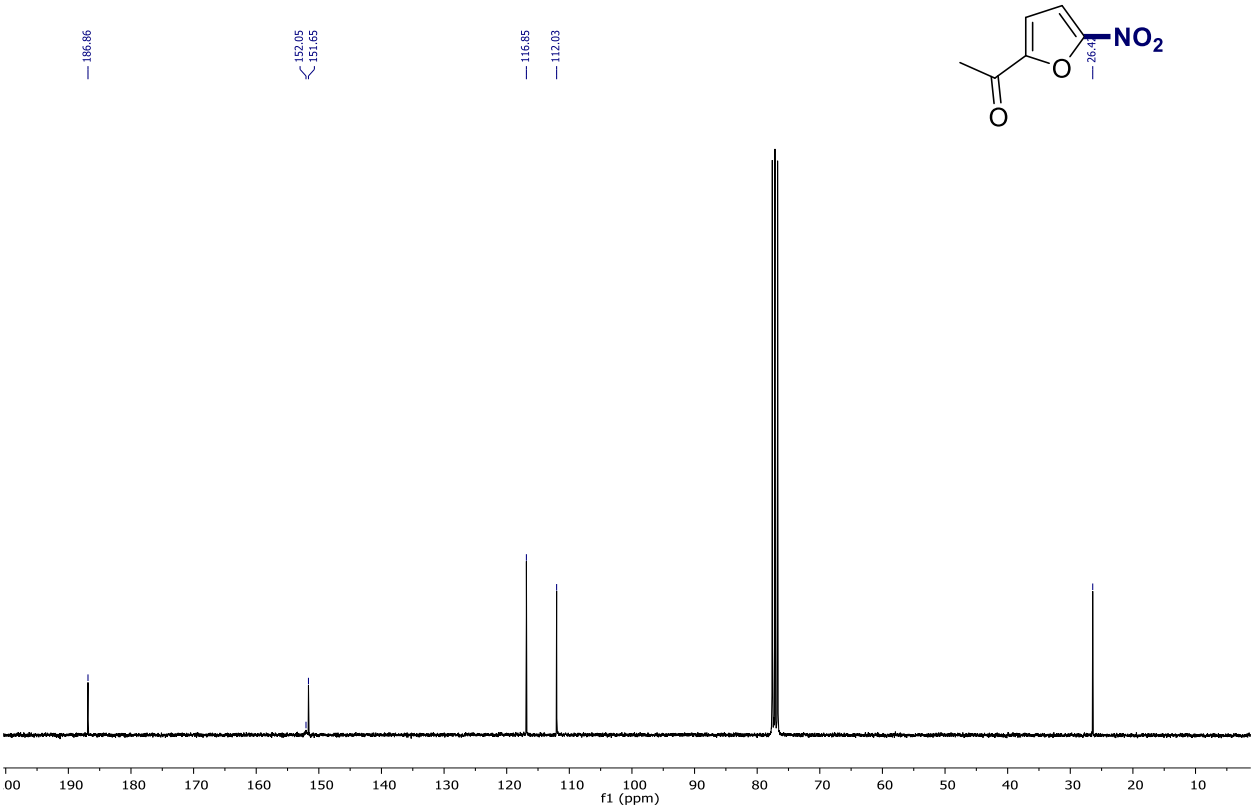
^{13}C-NMR (75 MHz, $CDCl_3$) **(2al)**



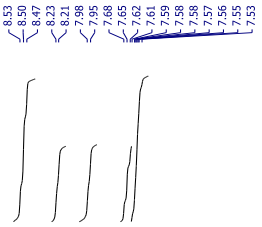
^{1}H-NMR (300 MHz, $CDCl_3$) **(2am)**

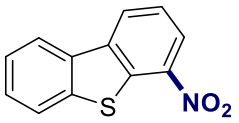


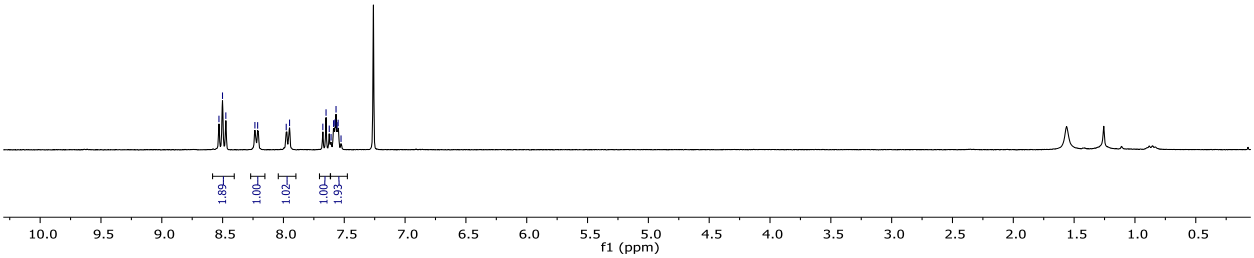
^{13}C-NMR (75 MHz, $CDCl_3$) **(2am)**



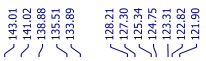
^{1}H-NMR (300 MHz, $CDCl_3$) **(2an)**

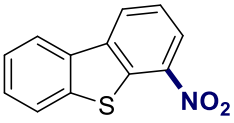


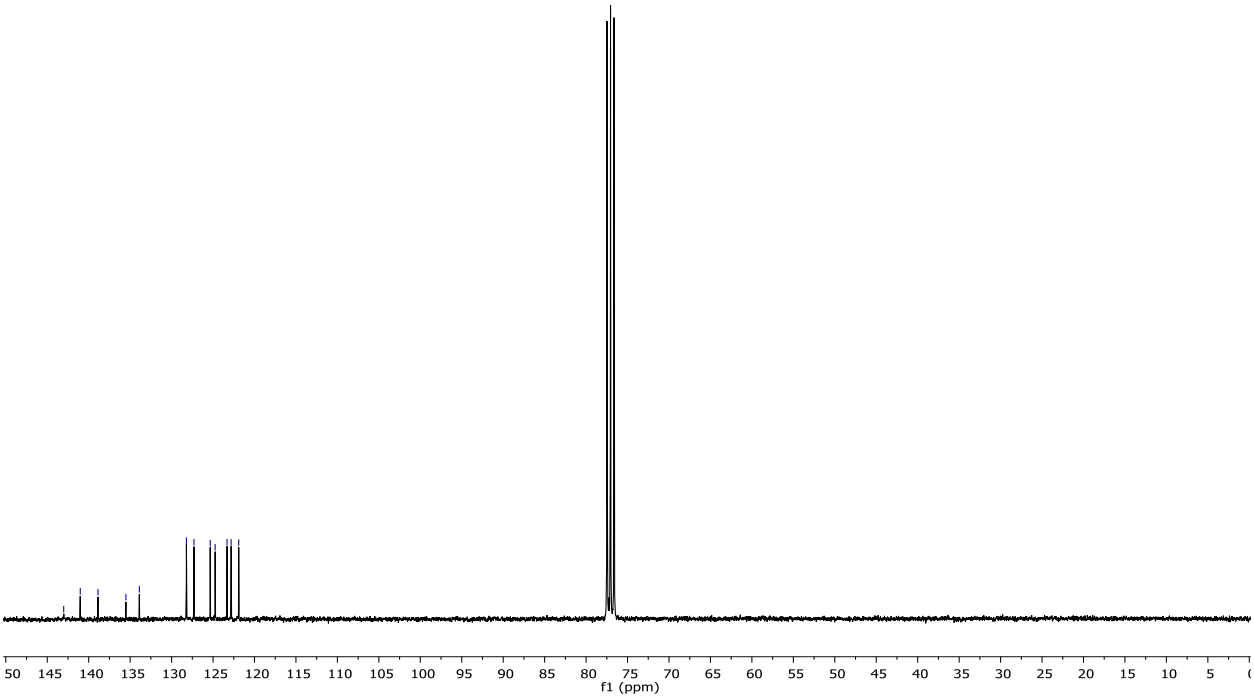




^{13}C-NMR (75 MHz, $CDCl_3$) **(2an)**







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