Electronic Supporting Information

The polyhedral nature of selenium-catalysed reactions: Se(IV) instead of Se(VI) species make the difference in the *on water* selenium-mediated oxidation of arylamines

Damiano Tanini,* Camilla Dalia and Antonella Capperucci

Dipartimento di Chimica "Ugo Schiff", Università di Firenze, Via della Lastruccia 3-13, 50019 Sesto Fiorentino, Italy. Email: damiano.tanini@unifi.it

Abstract: Selenium-catalysed oxidations are highly sought after in organic synthesis and in biology. Herein, we report our studies on the *on water* selenium mediated oxidation of anilines. In the presence of diphenyl diselenide or benzeneseleninic acid, anilines react with hydrogen peroxide providing direct and selective access to nitroarenes. Instead, the use of selenium dioxide or sodium selenite led to azoxyarenes. Careful mechanistic analysis and ^{77}Se NMR studies revealed that only Se(IV) species, such as benzeneperoxyseleninic acid, are the active oxidants involved in the catalytic cycle operating in water and leading to nitroarenes. While other selenium-catalysed oxidations occurring in organic solvents have been recently demonstrated to proceed through Se(VI) key intermediates, the *on water* oxidation of anilines to nitroarenes, do not. These findings shed new light on the multifaceted nature of organoselenium-catalysed transformations and open new directions to exploit selenium-based-catalysis.

Table of Contents

1. General Experimental

All commercial materials were purchased from various commercial sources and used as received, without further purification. Flash column chromatography purifications were performed with Silica gel 60 (230-400 mesh). Thin layer chromatography was performed with TLC plates Silica gel 60 F_{254}, which was visualised under UV light, or by staining with an ethanolic acid solution of *p*-anisaldehyde followed by heating. Mass spectra were recorded by Electrospray Ionization (ESI) using a Thermo LCQ-Fleet instrument. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$, D_2O or CD_3OD using Mercury 400, Bruker 400 Ultrashield, and Varian Gemini 200 spectrometers operating at 400 MHz and 200 MHz (for ^{1}H), 100 MHz and 50 MHz (for ^{13}C). ^{77}Se NMR spectra were recorded using Bruker 400 Ultrashield spectrometer, operating at 76 MHz. NMR signals were referenced to nondeuterated residual solvent signals ($CDCl_3$: 7.26 ppm for ^{1}H, 77.0 ppm for ^{13}C; CD_3OD: 3.31 ppm for ^{1}H, 49.0 ppm for ^{13}C). Diphenyl diselenide $(PhSe)_2$ was used as an external reference for ^{77}Se NMR (δ = 461 ppm). Chemical shifts (δ) are given in parts per million (ppm), and coupling constants (J) are given in Hertz (Hz), rounded to the nearest 0.1 Hz. ^{1}H NMR data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, ap d = apparent doublet, m = multiplet, dd = doublet of doublet, bs = broad singlet, bd = broad doublet, ecc.), coupling constant (J) or line separation (ls), and assignment.

Naming of Compounds. Compound names are those generated by ChemBioDraw 15.0 software (PerkinElmer), following IUPAC nomenclature.

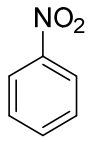
2. Synthesis and characterisation of compounds

2.1. Selenium-mediated *on water* synthesis of nitroarenes 1

***General Procedure*: Selenium-mediated *on water* oxidation of arylamines to nitroarenes**

Diphenyl diselenide or benzeneseleninic acid **4** (0.4 mmol, 0.2 equiv.) and arylamine (2.0 mmol, 1.0 equiv.) were treated with 30% hydrogen peroxide (2 mL, 20 mmol, 10.0 equiv.) and the mixture was stirred at room temperature for 3 h. Afterwards, the aqueous reaction mixture was extracted with EtOAc (3 x 5 mL). The combined organic phases were washed with brine (10 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by flash chromatography to yield nitroarenes **1**.

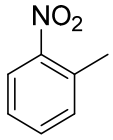
Synthesis of nitrobenzene 1a



1a

Following the general procedure, aniline (280 mg, 3 mmol) gave, after purification by flash column chromatography (petroleum ether/EtOAc 15:1), nitrobenzene **1a** (328 mg, 90%) as a pale yellowish oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.59 (2H, ap t, ls = 7.8 Hz), 7.74 (1H, ap t, ls = 7.4 Hz), 8.26 (2H, ap d, ls = 8.0 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 124.1 (CH), 129.9 (CH), 135.2 (CH), 148.8 (C). **MS** (ESI, positive) $[M+Na]^+$ 146.2. Spectroscopic data matched those previously reported in the literature.[1]

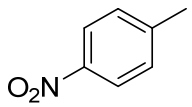
Synthesis of 1-methyl-2-nitrobenzene 1b



1b

Following the general procedure, *o*-toluidine (107 mg, 1 mmol) gave, after purification by flash column chromatography (petroleum ether/EtOAc 15:1), 1-methyl-2-nitrobenzene **1b** (119 mg, 87%) as a yellowish oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 2.61 (3H, s), 7.32-7.36 (2H, m), 7.50 (1H, ap.t, J = 7.5 Hz), 7.97 (1H, d, J = 7.5 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 20.4 (CH_3), 124.6 (CH), 126.8 (CH), 132.7 (CH), 132.9 (CH), 133.5 (C), 149.3 (C). **MS** (ESI, positive) $[M+Na]^+$ 160.0. Spectroscopic data matched those previously reported in the literature.[2]

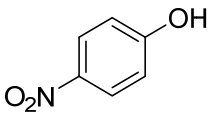
Synthesis of 1-methyl-4-nitrobenzene 1c



1c

Following the general procedure, *p*-toluidine (321 mg, 3 mmol) gave, after purification by flash column chromatography (petroleum ether/EtOAc 15:1), 1-methyl-4-nitrobenzene **1c** (385 mg, 94%) as a yellowish solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 2.46 (3H, s), 7.31 (2H, d, J = 8.2 Hz), 8.10 (2H, d, J = 8.2 Hz). **^{13}C NMR** (100 MHz, CDCl3) δ (ppm): 21.6 (CH_3), 123.5 (CH), 129.8 (CH), 146.0 (C), 146.1 (C) **MS** (ESI, positive) $[M+Na]^+$ 160.2. Spectroscopic data matched those previously reported in the literature.[1]

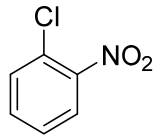
Synthesis of 4-nitrophenol 1d



1d

Following the general procedure, 4-aminophenol (218 mg, 2 mmol) gave, after purification by flash column chromatography (petroleum ether/EtOAc 3:2), 4-nitrophenol **1d** (150 mg, 54%) as a pale yellow solid. **^{1}H NMR** (200 MHz, CD_3OD) δ (ppm): 6.89 (2H, d, J = 9.3 Hz), 8.12 (2H, d, J = 9.3 Hz). **^{13}C NMR** (50 MHz, CD_3OD) δ (ppm): 115.1(CH), 125.6 (CH), 140.3 (C), 163.7 (C). **MS** (ESI, positive) $[M+H]^+$ 140.0. Spectroscopic data matched those previously reported in the literature.[3]

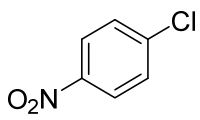
Synthesis of 1-chloro-2-nitrobenzene 1e



1e

Following the general procedure, 2-chloroaniline (381 mg, 3 mmol) gave, after purification by flash column chromatography (petroleum ether/EtOAc 10:1), 1-chloro-2-nitrobenzene **1e** (357 mg, 76%) as a yellowish solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.44-7.48 (1H, m), 7.54-7.61 (2H, m), 7.9 (dd, J = 1.1, 8.1 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 126.2 (CH), 127.7 (C), 128.2 (CH), 132.5 (CH), 133.8 (CH), 141.2. **MS** (ESI, positive) $[M+Na]^+$ 180.1. Spectroscopic data matched those previously reported in the literature.[1]

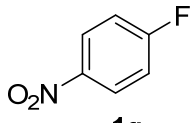
Synthesis of 1-chloro-4-nitrobenzene 1f



1f

Following the general procedure, 4-chloroaniline (64 mg, 0.5 mmol) gave, after purification by flash column chromatography (petroleum ether/EtOAc 15:1), 1-chloro-4-nitrobenzene **1f** (64 mg, 81%) as a yellowish solid.[§] **^{1}H NMR** (200 MHz, $CDCl_3$) δ (ppm): 7.53 (2H, d, J = 8.8 Hz), 8.19 (2H, d, J = 8.8 Hz). **^{13}C NMR** (50 MHz, $CDCl_3$) δ (ppm): 124.9 (CH), 129.6 (CH), 141.4 (C), 146.0 (C). **MS** (ESI, positive) $[M+Na]^+$ 179.8. Spectroscopic data matched those previously reported in the literature.[4]

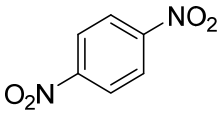
Synthesis of 1-fluoro-4-nitrobenzene 1g



1g

Following the general procedure, 4-fluoroaniline (224 mg, 2 mmol) gave, after purification by flash column chromatography (petroleum ether/EtOAc 15:1), 1-fluoro-4-nitrobenzene **1g** (182 mg, 64%) as a yellowish oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.21 (2H, dd, J = 78.90 Hz), 8.26-8.29 (2H, n). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 117.0 (d, $J_{C\text{-}F}$ = 23.6 Hz), 126.90 (d, $^{3}J_{C\text{-}N}$ = 10.2 Hz), 166.9 (d, $^{1}J_{C\text{-}F}$ = 257.9 Hz), 144.4. **MS** (ESI, positive) $[M+Na]^+$ 164.0. Spectroscopic data matched those previously reported in the literature.[2]

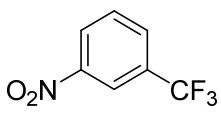
Synthesis of 1,4-dinitrobenzene 1h



1h

Following the general procedure, 4-nitroaniline (276 mg, 2 mmol) gave, after purification by flash column chromatography (petroleum ether/EtOAc 3:1), 1,4-dinitrobenzene **1h** (245 mg, 73%) as a yellowish solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 8.43 (4H, s). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 124.9 (CH), 149.9 (C). **MS** (ESI, positive) $[M+Na]^+$ 191.0. Spectroscopic data matched those previously reported in the literature.[1]

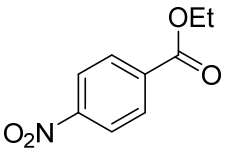
Synthesis of 1-nitro-3-(trifluoromethyl)benzene 1i



1i

Following the general procedure, 3-(trifluoromethyl)aniline (162 mg, 1.0 mmol) gave, after purification by flash column chromatography (petroleum ether/EtOAc 20:1), 1-nitro-3-(trifluoromethyl)benzene **1i** (127 mg, 66%) as a yellowish oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.73 (1H, t, J = 8.0 Hz), 7.97 (1H, d, J = 8.0 Hz), 8.42 (1H, d, J = 8.0 Hz), 8.48 (1H, s). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 120.7 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 122.8 (q, $^{1}J_{C\text{-}F}$ = 271.9 Hz), 126.4 (q, $^{4}J_{C\text{-}F}$ = 1.2 Hz), 130.3, 131.2 (q, $^{3}J_{C\text{-}F}$ = 3.4 Hz), 132.3 (q, $^{2}J_{C\text{-}F}$ = 34.1 Hz), 148.3. **MS** (ESI, positive) $[M+H]^+$ 192.0. Spectroscopic data matched those previously reported in the literature.[1]

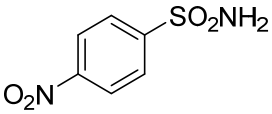
Synthesis of ethyl 4-nitrobenzoate 1j



1j

Following the general procedure, ethyl 4-aminobenzoate (benzocaine, 495 mg, 3 mmol) gave, after purification by flash column chromatography (petroleum ether/EtOAc 12:1), ethyl 4-nitrobenzoate **1j** (560 mg, 96%) as a yellowish solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 1.43 (3H, t, J = 7.1 Hz), 4.44 (2H, q, J = 7.1 Hz), 7.93 (2H, d, J = 8.5 Hz), 8.30 (2H, d, J = 8.5 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 14.9 (CH_3), 62.5 (CH_2), 121.0 (CH), 131.6 (CH), 136.2 (C), 165.1 (C), 165.9 (C). **MS** (ESI, positive) $[M+Na]^+$ 218.0. Spectroscopic data matched those previously reported in the literature.[5]

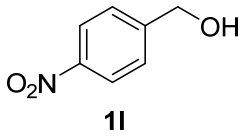
Synthesis of 4-nitrobenzenesulfonamide 1k



1k

Following the general procedure, 4-aminobenzenesulfonamide (sulfanilamide, 344 mg, 2 mmol) gave, after purification by flash column chromatography (petroleum ether/EtOAc 3:2), 4-nitrobenzenesulfonamide **1k** (356 mg, 88%) as a pale yellow solid. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ (ppm): 7.79 (2H, bs, NH_2), 80.09-8.12 (2H, m), 8.44-8.47 (2H, m). **^{13}C NMR** (100 MHz, DMSO-*d6*) δ (ppm): 124.9 (CH), 127.7 (CH), 149.6 (C), 149.8 (C). **MS** (ESI, positive) $[M+H]^+$ 203.0. Spectroscopic data matched those previously reported in the literature.[6]

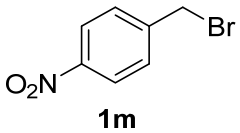
Synthesis of (4-nitrophenyl)methanol 1l



1l

Following the general procedure, (4-aminophenyl)methanol (369 mg, 3 mmol) gave, after purification by flash column chromatography (petroleum ether/EtOAc 2:1), (4-nitrophenyl)methanol **1l** (445 mg, 97%) as a pale yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 2.12 (1H, bs, OH), 4.83 (2H, s, CH_2O), 7.52 (2H, d, J = 8.5), 8.20 (2H, d, J = 8.5). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 64.0 (CH_2), 123.7 (CH), 127.0 (CH), 147.3 (C), 148.2 (C). **MS** (ESI, positive) $[M+Na]^+$ 176.0. Spectroscopic data matched those previously reported in the literature.[3]

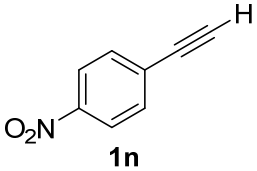
Synthesis of 1-(bromomethyl)-4-nitrobenzene 1m



1m

Following the general procedure, 4-(bromomethyl)aniline (372 mg, 2 mmol) gave, after purification by flash column chromatography (petroleum ether/EtOAc 15:1), 1-(bromomethyl)-4-nitrobenzene **1m** (367 mg, 85%) as a yellowish solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 4.52 (2H, s), 7.56 (2H, d, J = 8.4 Hz), 8.21 (2H, d, J = 8.4 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 31.6 (CH_2), 124.7 (CH), 130.5 (CH), 145.4 (C), 148.3 (C). Spectroscopic data matched those previously reported in the literature.[7]

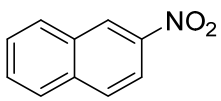
Synthesis of 1-ethynyl-4-nitrobenzene 1n



1n

Following the general procedure, 4-ethynylaniline (59 mg, 0.5 mmol) gave, after purification by flash column chromatography (petroleum ether/EtOAc 9:1), 1-ethynyl-4-nitrobenzene **1n** (46 mg, 62%) as a yellowish solid.[§] **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 3.35 (1H, s), 7.64 (2H, d, J = 8.8 Hz), 8.20 (2H, d, J = 8.8 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 82.2 (C), 82.9 (CH), 124.2 (CH), 129.2 (C), 133.6 (CH), 148.2 (C). **MS** (ESI, positive) $[M+Na]^+$ 170.0. Spectroscopic data matched those previously reported in the literature.[8]

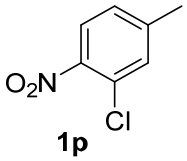
Synthesis of 2-nitronaphthalene 1o



1o

Following the general procedure, naphthalen-2-amine (72 mg, 0.5 mmol) gave, after purification by flash column chromatography (petroleum ether/EtOAc 15:1), 2-nitronaphthalene **1o** (55 mg, 64%) as a yellowish solid.[§] **^{1}H NMR** (200 MHz, $CDCl_3$) δ (ppm): 7.61-7.74 (2H, m), 7.93-8.10 (3H, m), 8.25 (1H, dd, *J* = 2.3, 9.0 Hz), 8.81 (1H, d, J = 2.3 Hz). **^{13}C NMR** (50 MHz, $CDCl_3$) δ (ppm): 119.5, 124.9, 127.9, 129.9, 130.0, 130.1, 130.2, 132.4, 136.3. **MS** (ESI, positive) $[M+Na]^+$ 196.0. Spectroscopic data matched those previously reported in the literature.[9]

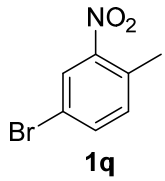
Synthesis of 2-chloro-4-methyl-1-nitrobenzene 1p



1p

Following the general procedure, 2-chloro-4-methylaniline (284 mg, 2 mmol) gave, after purification by flash column chromatography (petroleum ether/EtOAc 15:1), 2-chloro-4-methyl-1-nitrobenzene **1p** (266 mg, 78%) as a yellowish solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 2.42 (3H, s), 7.19 (1H, d, *J* = 8.3 Hz), 7.35 (1H, s), 7.81 (1H, d, *J* = 8.3 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 21.8 (CH_3), 126.4 (CH), 127.7 (C), 128.8 (CH), 132. 9 (CH), 145.5 (C), 146.2 (C). Spectroscopic data matched those previously reported in the literature.[1]

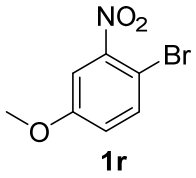
Synthesis of 4-bromo-1-methyl-2-nitrobenzene 1q



1q

Following the general procedure, 5-bromo-2-methylaniline (186 mg, 1 mmol) gave, after purification by flash column chromatography (petroleum ether/EtOAc 15:1), 4-bromo-1-methyl-2-nitrobenzene **1q** (152 mg, 70%) as a dark yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 2.42 (3H, s), 7.19 (2H, d, *J* = 8.4 Hz), 7.35 (1H, s), 7.81 (2H, d, *J* = 8.4 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 21.8 (CH_3), 126.4 (CH), 127.7 (C), 128.8 (CH), 132.9 (CH), 145.5 (C), 146.2 (C). **MS** (ESI, positive) $[M+H]^+$ 216.0.

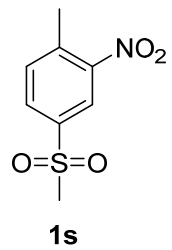
Synthesis of 1-bromo-4-methoxy-2-nitrobenzene 1r



1r

Following the general procedure, 2-bromo-5-methoxyaniline (100 mg, 0.5 mmol) gave, after purification by flash column chromatography (petroleum ether/EtOAc 8:1), 1-bromo-4-methoxy-2-nitrobenzene **1r** (85 mg, 72%) as an orange solid.[§] **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 3.85 (3H, s), 6.99 (1H, dd, *J* = 2.6, 8.9 Hz), 7.36 (1H, d, *J* = 2.6 Hz), 7.59 (1H, d, *J* = 8.9 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 55.7 (CH_3), 105.2 (C), 111.4 (CH), 120.6 (CH), 136.1 (CH), 150.9 (C), 159.8 (C).

Synthesis of 1-methyl-4-(methylsulfonyl)-2-nitrobenzene 1s

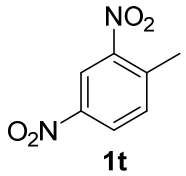


1s

Following the general procedure, 2-methyl-5-(methylsulfonyl)aniline (93 mg, 0.5 mmol) gave, after purification by flash column chromatography (petroleum ether/EtOAc 2:1), 1-methyl-4-(methylsulfonyl)-2-nitrobenzene **1s** (59 mg, 55%) as a pale yellow solid.[§] **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 2.70 (3H, s), 3.10 (3H, s), 7.59 (1H, d, *J* = 8.0 Hz), 8.05 (1H, dd, *J* = 1.6, 8.0 Hz), 8.51 (1H, d, *J* = 1.6 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 21.2 (CH_3), 45.0 (CH_3), 124.7 (CH), 131.7 (CH), 134.8 (CH), 140.3 (C), 140.6 (C), 150.0 (C).

Synthesis of 1-methyl-2,4-dinitrobenzene 1t

a) Following the general procedure, 2-methyl-5-nitroaniline (304 mg, 2 mmol) gave, after purification by flash column chromatography (petroleum ether/EtOAc 3:2), 1-methyl-2,4-dinitrobenzene **1t** (248 mg, 68%) as a yellow solid.



1t

b) Following the general procedure, 4-methyl-3-nitroaniline (304 mg, 2 mmol) gave, after purification by flash column chromatography (petroleum ether/EtOAc 3:2), 1-methyl-2,4-dinitrobenzene **1t** (327 mg, 90%) as a yellow solid.

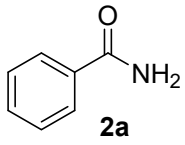
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.74 (3H, s), 7.58 (1H, d, J = 8.5 Hz), 8.36 (1H, dd, J = 2.3, 8.5 Hz), 8.84 (1H, d, J = 2.3 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 20.8 (CH_3), 120.2 (CH), 127.0 (CH), 134.0 (CH), 140.7 (C), 146.7 (C), 149.2 (C). **MS** (ESI, positive) $[M+Na]^+$ 205.0. Spectroscopic data matched those previously reported in the literature.[2]

2.2. Selenium-mediated *on water* synthesis of benzamides 2

***General Procedure*: Selenium-mediated *on water* oxidation of benzylamines to benzamides 2**

Diphenyl diselenide or benzeneseleninic acid **4** (0.4 mmol, 0.2 equiv.) and a suitable benzylamine (2.0 mmol, 1.0 equiv.) were treated with 30% hydrogen peroxide (2 mL, 20 mmol, 10.0 equiv.) and the mixture was stirred at 90°C for 2 h. Afterwards, the aqueous reaction mixture was extracted with EtOAc (3 x 5 mL). The combined organic phases were washed with brine (10 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by flash chromatography to yield benzamides **2**.

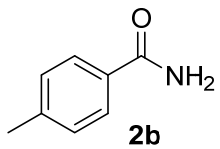
Synthesis of benzamide 2a



2a

Following the general procedure, benzylamine (214 mg, 2 mmol) gave, after purification by flash column chromatography (petroleum ether/EtOAc 2:1), benzamide **2a** as a white solid (111 mg, 46%). **^{1}H NMR** (200 MHz, $CDCl_3$) δ (ppm): 6.25 (2H, bs, NH_2), 7.39-7.57 (3H, m), 7.79-7.84 (2H, m). **^{13}C NMR** (50 MHz, $CDCl_3$) δ (ppm): 127.3 (CH), 128.6 (CH), 131.9 (CH), 133.4 (C), 169.6 (C). **MS** (ESI, positive) $[M+Na]^+$ 143.8. Spectroscopic data matched those previously reported in the literature.[10]

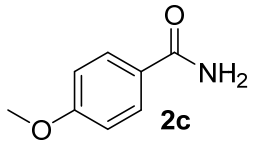
Synthesis of 4-methylbenzamide (*p*-toluamide) 2b



2b

Following the general procedure, 4-methylbenzylamine (242 mg, 2 mmol) gave, after purification by flash column chromatography (petroleum ether/EtOAc 2:1), *p*-toluamide **2b** as a white solid (85 mg, 32%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 2.40 (3H, s), 5.93 (1H, bs), 6.10 (1H, bs), 7.25 (2H, d, J = 8.0 Hz), 7.71 (2H, d, J = 8.0 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 21.5 (CH_3), 127.4 (CH), 129.3 (CH), 130.4 (C), 142.5 (C), 169.4 (C). **MS** (ESI, positive) $[M+H]^+$ 136.2. Spectroscopic data matched those previously reported in the literature.[10]

Synthesis of 4-methoxybenzamide (anisamide) 2c



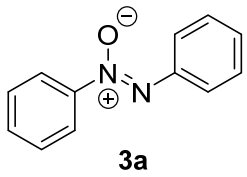
Following the general procedure, 4-methoxybenzylamine (274 mg, 2 mmol) gave, after purification by flash column chromatography (petroleum ether/EtOAc 1:1), 4-methoxybenzamide **2c** as a white solid (110 mg, 37%). **^{1}H NMR** (200 MHz, $CDCl_3$) δ (ppm): 3.87 (3H, s), 5.84 (2H, bs), 6.91 (2H, d, J = 8.5 Hz), 7.79 (2H, d, J = 8.5 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 55.4 (CH_3), 113.9 (CH), 125.0 (C), 129.4 (CH), 162.8 (C), 169.6 (C). **MS** (ESI, positive) $[M+H]^+$ 152.1. Spectroscopic data matched those previously reported in the literature.[10]

2.3. Selenium-mediated *on water* synthesis of azoxyarenes 3

***General Procedure*: Selenium-mediated *on water* oxidation of arylamines to azoxyarenes 3**

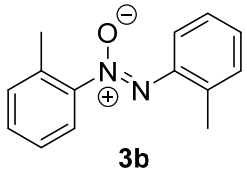
Selenium dioxide or sodium selenite (0.4 mmol, 0.2 equiv.) and arylamine (2.0 mmol, 1.0 equiv.) were treated with 30% hydrogen peroxide (2 mL, 20 mmol, 10.0 equiv.) and the mixture was stirred at room temperature for 3 h. Afterwards, the aqueous reaction mixture was extracted with EtOAc (3 x 5 mL). The combined organic phases were washed with brine (10 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by flash chromatography to yield azoxyarenes **3**.

Synthesis of 1,2-diphenyldiazene 1-oxide 3a



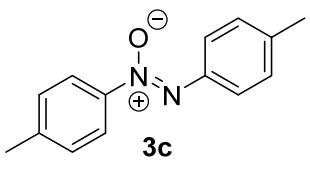
Following the general procedure, aniline (187 mg, 2 mmol) gave, after purification by flash column chromatography (petroleum ether/EtOAc 9:1), 1,2-diphenyldiazene 1-oxide **3a** (170 mg, 86%) as a yellowish oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.40 (1H, ap t, J = 7.4 Hz), 7.48-7.58 (5H, m), 8.19 (2H, ap.d, J = 7.8 Hz), 8.33 (2H, ap.d, J = 7.5 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 122.3, 125.5, 128.7, 128.8, 129.6, 131.6, 144.0, 148.3. **MS** (ESI, positive) $[M+Na]^+$ 221.0.

Synthesis of 1,2-di-*o*-tolyldiazene 1-oxide 3b



Following the general procedure, *o*-toluidine (216 mg, 2 mmol) gave, after purification by flash column chromatography (petroleum ether/EtOAc 20:1), 1,2-di-*o*-tolyldiazene 1-oxide **3b** as a yellowish glassy solid (185 mg, 82%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 2.38 (3H, s), 2.53 (3H, s), 7.25-7.29 (1H, m), 7.31-7.34 (4H, m), 7.38-7.41 (1H, m), 7.67-7.69 (1H, m), 8.03 (1H, ap.d, J = 7.9 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 18.3 (CH_3), 18.4 (CH_3), 121.5 (CH), 123.6 (CH). 126.0 (CH), 126.6 (CH), 128.6 (CH), 130.0 (CH), 130.8 (CH), 131.2 (C), 131.8 (CH), 134.1 (C), 142.8 (C), 149.4 (C). **MS** (ESI, positive) $[M+Na]^+$ 249.2.

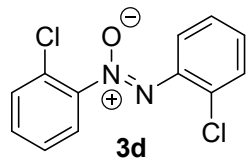
Synthesis of 1,2-di-*p*-tolyldiazene 1-oxide 3c



Following the general procedure, *p*-toluidine (216 mg, 2 mmol) gave, after purification by flash column chromatography (petroleum ether/EtOAc 20:1), 1,2-di-*p*-tolyldiazene 1-oxide **3c** as a yellowish glassy solid (199 mg, 86%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 2.41 (3H, s), 2.44 (3H, s), 7.48 (4H, ap.d, J = 8.3 Hz), 8.12 (2H, d, J = 8.3 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ

(ppm): 21.3 (CH_3), 21.6 (CH_3), 122.1 (CH), 125.7 (CH). 129.2 (CH_3), 129.3 (CH), 140.0 (C), 141.8 (C), 141.9 (C), 146.2 (C). **MS** (ESI, positive) $[M+Na]^+$ 249.0.

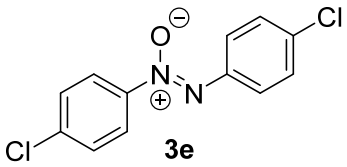
Synthesis of 1,2-bis(2-chlorophenyl)diazene 1-oxide 3d



3d

Following the general procedure, 2-chloroaniline (256 mg, 2 mmol) gave, after purification by flash column chromatography (petroleum ether/EtOAc 12:1), 1,2-bis(2-chlorophenyl)diazene 1-oxide **3d** as a pale yellowish glassy solid (201 mg, 75%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.29-7.33 (1H, m), 7.37-7.41 (1H, m), 7.42-7.48 (2H, m), 7.52-7.57 (2H, m), 7.76 (1H, dd, J = 1.9, 7.4 Hz), 8.01 (1H, dd, J = 1.7, 8.0 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 123.4 (CH), 125.2 (CH), 126.8 (C), 127.0 (CH). 127.6 (CH), 129.6 (CH), 129.8 (C), 130.3 (CH), 131.1 (CH), 132.2 (CH), 140.9 (C), 148.3 (C). **MS** (ESI, positive) $[M+H]^+$ 267.0.

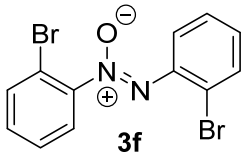
Synthesis of 1,2-bis(4-chlorophenyl)diazene 1-oxide 3e



3e

Following the general procedure, 4-chloroaniline (64 mg, 0.5 mmol) gave, after purification by flash column chromatography (petroleum ether/EtOAc 8:1), 1,2-bis(4-chlorophenyl)diazene 1-oxide **3e** as a pale yellowish glassy solid (56 mg, 83%).[§] **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.45 (2H, ap.d, J = 8.90 Hz), 7.48 (2H, ap.d, J = 8.9 Hz), 8.16 (2H, ap.d, J = 8.9 Hz), 8.25 (2H, ap.d, J = 8.9 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 123.7 (CH), 127.1 (CH), 128.9 (CH), 129.0 (CH), 135.2 (C), 138.1 (C), 142.2 (C), 146.5 (C). **MS** (ESI, positive) $[M+Na]^+$ 289.1. Spectroscopic data matched those previously reported in the literature.[11]

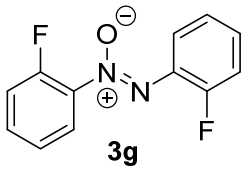
Synthesis of 1,2-bis(2-bromophenyl)diazene 1-oxide 3f



3f

Following the general procedure, 2-bromoaniline (86 mg, 0.5 mmol) gave, after purification by flash column chromatography (petroleum ether/EtOAc 20:1), 1,2-bis(2-bromophenyl)diazene 1-oxide **3f** as a dark glassy solid (67 mg, 75%).[§] **^{1}H NMR** (200 MHz, $CDCl_3$) δ (ppm): 7.23 (1H, td, J = 1.6, 7.7 Hz), 7.33 – 7.52 (3H, m), 7.69-7.78 (3H, m), 7.97 (1H, dd, J = 1.6, 8.1 Hz). **^{13}C NMR** (50 MHz, $CDCl_3$) δ (ppm): 115.0 (C), 119.3 (C), 123.4 (CH), 128.2 (CH). 129.7 (CH), 131.2 (CH), 133.4 (CH), 134.1 (CH), 142.2 (C), 165.4 (C). **MS** (ESI, positive) $[M+Na]^+$ 376.8.

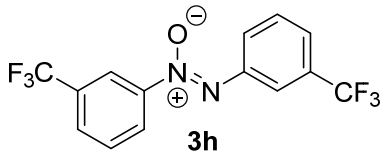
Synthesis of 1,2-bis(2-fluorophenyl)diazene 1-oxide 3g



3g

Following the general procedure, 2-fluoroaniline (112 mg, 1 mmol) gave, after purification by flash column chromatography (petroleum ether/EtOAc 25:1), 1,2-bis(2-fluorophenyl)diazene 1-oxide **3g** as a yellowish solid (74 mg, 62%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.24-7.35 (4H, m), 7.39-7.43 (1H, m), 7.53-7.57 (1H, m), 7.95-7.99 (1H, m), 8.30-8.34 (1H, m). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 116.9 (d, $^2J_{C\text{-}F}$ = 20.1 Hz), 118.34 (d, $^2J_{C\text{-}F}$ = 20.2 Hz), 124.6 (d, $^3J_{C\text{-}F}$ = 3.8 Hz), 124.7, 125.0 (d, $^3J_{C\text{-}F}$ = 4.2 Hz), 126.2 (d, $^4J_{C\text{-}F}$ = 1.0 Hz), 131.2 (d, $^3J_{C\text{-}F}$ = 8.3 Hz), 133.1 (d, $^3J_{C\text{-}F}$ = 8.0 Hz), 155.4 (d, $^1J_{C\text{-}F}$ = 259.0 Hz), 157.0 (d, $^1J_{C\text{-}F}$ = 255.8 Hz). Carbon atoms attached to nitrogen not detected. **MS** (ESI, positive) $[M+Na]^+$ 257.2.

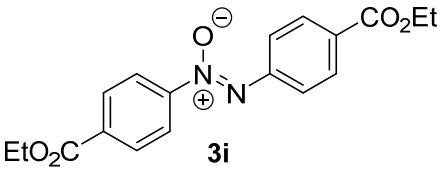
Synthesis of 1,2-bis(3-(trifluoromethyl)phenyl)diazene 1-oxide 3h



3h

Following the general procedure, 3-(trifluoromethyl)aniline (164 mg, 1 mmol) gave, after purification by flash column chromatography (petroleum ether/EtOAc 8:1), 1,2-bis(3-(trifluoromethyl)phenyl)diazene 1-oxide **3h** as a yellowish solid (119 mg, 71%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.62-7.72 (3H, m), 7.87 (1H, d, J = 7.8 Hz), 8.38 (1H, d, J = 7.8 Hz), 8.48 (1H, s), 8.54 (1H, d, J = 8.3 Hz), 8.63 (1H, s). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 119.8 (q, $^{3}J_{C\text{-}F}$ = 4.0 Hz), 122.7 (q, $^{3}J_{C\text{-}F}$ = 4.0 Hz), 123.3 (q, $^{1}J_{C\text{-}F}$ = 272.7 Hz), 123.7 (q, $^{1}J_{C\text{-}F}$ = 272.5 Hz), 125.6 (q, $^{4}J_{C\text{-}F}$ = 0.7 Hz), 126.5 (q, $^{3}J_{C\text{-}F}$ = 3.7 Hz), 128.6, 128.7 (q, $^{3}J_{C\text{-}F}$ = 3.6 Hz), 129.4, 129.8, 131.3 (q, $^{2}J_{C\text{-}F}$ = 32.8 Hz), 131.7 (q, $^{2}J_{C\text{-}F}$ = 33.6 Hz), 143.7, 148.2 (q, $^{4}J_{C\text{-}F}$ = 1.7 Hz), 155.1. **MS** (ESI, positive) $[M+H]^+$ 355.0.

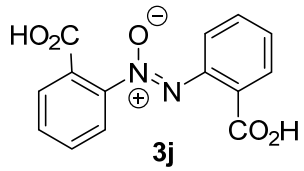
Synthesis of 1,2-bis(4-(ethoxycarbonyl)phenyl)diazene 1-oxide 3i



3i

Following the general procedure, ethyl 4-aminobenzoate (benzocaine, 332 mg, 2 mmol) gave, after purification by flash column chromatography (petroleum ether/EtOAc 8:1), 1,2-bis(4-(ethoxycarbonyl)phenyl)diazene 1-oxide **3i** as a glassy brownish solid (223 mg, 66%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 1.47 (3H, t, J = 7.1 Hz), 1.48 (3H, t, J = 7.1 Hz), 4.46 (2H, q, J = 7.1 Hz), 4.48 (2H, q, J = 7.1 Hz), 8.19-8.26 (6H, m), 8.43 (2H, d, J = 8.8 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 14.8 (CH_3), 14.9 (CH_3), 61.9 (CH_2), 62.2 (CH_2), 123.1 (CH), 125.9 (CH), 130.8 (CH), 130.9 (CH), 131.7 (C), 134.3 (C), 147.6 (C), 151.5 (C), 165.9 (C), 166.4 (C). **MS** (ESI, positive) $[M+H]^+$ 365.0.

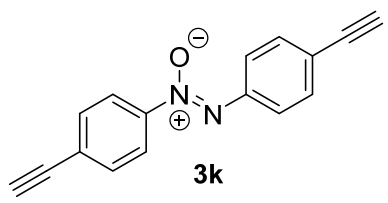
Synthesis of 1,2-bis(2-carboxyphenyl)diazene 1-oxide 3j



3j

Following the general procedure, anthranilic acid (136 mg, 1 mmol) gave, after purification by flash column chromatography ($CHCl_3$/CH_3OH 6:1), 1,2-bis(2-carboxyphenyl)diazene 1-oxide **3j** as a glassy brownish solid (92 mg, 64%). **^{1}H NMR** (200 MHz, CD_3OD) δ (ppm): 7.30–7.35 (1H, m), 7.43 (1H, td, J = 1.3, 7.6 Hz), 7.62-7.76 (3H, m), 7.91-7.98 (2H, m), 8.04 (1H, dd, J = 1.5, 7.8 Hz). **^{13}C NMR** (50 MHz, CD_3OD) δ (ppm): 121.9 (CH), 123.7 (CH), 126.2 (C), 126.9 (CH), 129.6 (C), 130.0 (CH), 130.2 (CH), 130.4 (CH), 132.1 (CH), 132.6 (CH), 133.6 (C), 144.7 (C), 166.5 (C), 168.9 (C).

Synthesis of 1,2-bis(4-ethynylphenyl)diazene 1-oxide 3k



3k

Following the general procedure (reaction time 1.5 h instead of 3 h; longer reaction times led to side products arising from oxidation of alkyne functions), 4-ethynylaniline (59 mg, 0.5 mmol) gave, after purification by flash column chromatography (petroleum ether/EtOAc 9:1), (*Z*)-1,2-bis(4-ethynylphenyl)diazene 1-oxide **3k** as a brownish solid (39 mg, 63%).[§] **^{1}H NMR** (200 MHz, $CDCl_3$) δ (ppm): 3.21 (1H, s), 3.27 (1H, s), 7.57-7.65 (4H, m), 8.16 (2H, ap d, J = 8.5 Hz), 8.28 (2H, ap d, J = 8.9 Hz). **^{13}C NMR** (50 MHz, $CDCl_3$) δ (ppm): 79.2, 80.5, 82.8, 120.7, 122.4, 123.0, 125.6, 132.5, 132.6, 153.1. **MS** (ESI, positive) $[M+Na]^+$ 269.2.

2.4. Preparation of peroxybenzeneseleninic acid 5

Benzeneseleninic acid **4** (100 mg, 0.53 mmol) was trated with 0.6 mL of 30% hydrogen peroxide at -5 °C. After stirring at -5 °C for 1.5 h, the white precipitate formed was filtered, washed with a small amount of cold hydrogen peroxide solution and dried by suction, while shielded from light by aluminium foil. peroxybenzeneseleninic acid **5** (white solid recovered, mp 53 ºC with decomposition)[12] was freshly used in the further experiment.

2.5. Preparation of benzeneselenonic acid 7 and related ^{77}Se NMR spectra [13]

Benzeneselenenyl chloride (200 mg, 1.0 mmol) was dissolved in chloroform (10 mL), cooled to 0 ºC and treated with 30% hydrogen peroxide (540 µL, 5.2 mmol). The reaction was stirred at room temperature for 2 h. After this time, the pale yellow solution formed was concentrated under reduced pressure to afford benzeneselenonic acid **7** as a pale yellowish glassy solid (179 mg, 84%). All spectroscopic data matched those previously reported in the literature.[12,13] ^{77}Se NMR ($CDCl_3$) δ = 1027.7 ppm; ^{77}Se NMR (D_2O) δ = 1024.9 ppm (Figure S1 and S2).

Benzeneselenonic **7** was also formed upon treatment of benzeneseleninic acid **4** or (diphenyl diselenide) with a large excess hydrogen peroxide. This has been also highlighted by the ^{77}Se NMR spectrum of the aqueous phase recovered after the oxidation of aniline (Figure S2).

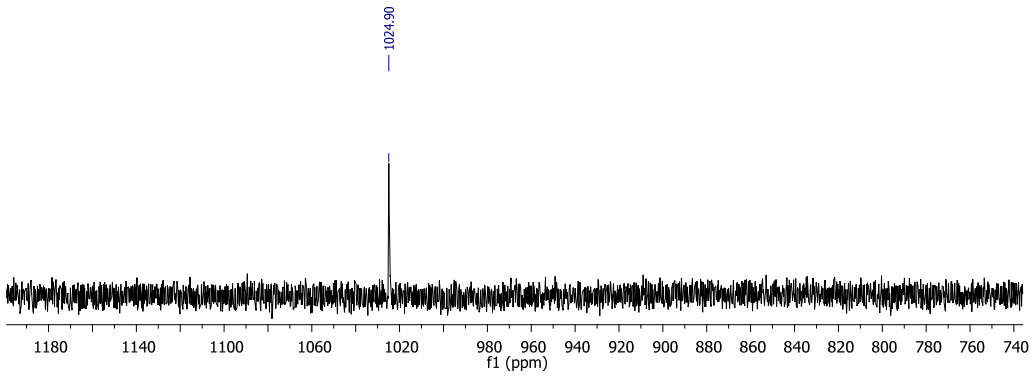


Figure S1. ^{77}Se NMR spectrum (D_2O, 76 MHz) of benzeneselenonic acid **7**, prepared according to literature.[13,14]

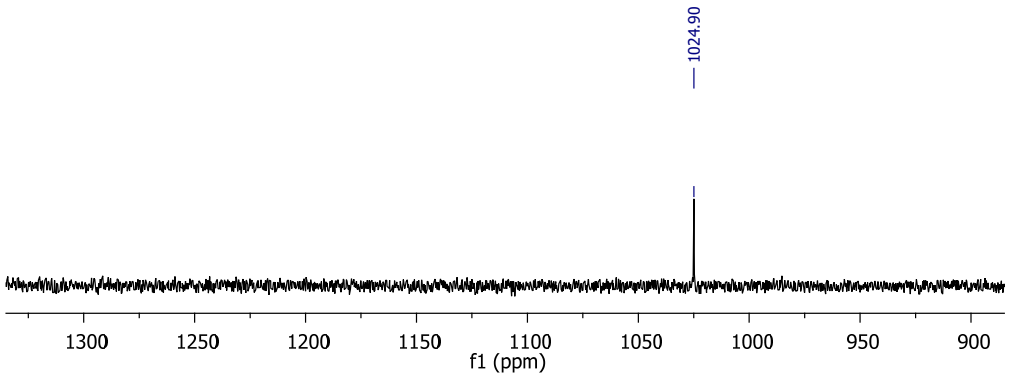


Figure S2. ^{77}Se NMR spectrum (D_2O, 76 MHz) of the aqueous phase recovered after the diphenyl diselenide-promoted oxidation of aniline. The chemical shift is identical to that of an authentic sample of benzeneselenonic acid **7**, prepared according to literature.

2.6. Preparation of selenonium salt 6 and related ^{77}Se NMR spectra

Method 1. Benzeneseleninic acid **4** (100 mg, 0.53 mmol) was suspended in 2 mL of acetonitrile and treated with 30% hydroxen peroxide (28 µL, 0.27 mmol) and stirred at room temperature for 0.5 h. After an additional 0.5 h at 75 ºC, the solution was cooled to room temperature and the solvent was removed under reduce pressure to afford **6** as colourless solid (70 mg, 68%). Spectroscopic data matched those previously reported in the literature.[14]

Method 2. Diphenyl diselenide (100 mg, 0.32 mmol) was solubilised in 2 mL of acetonitrile and treated with 30% hydroxen peroxide (133 µL, 1.28 mmol) and stirred at room temperature for 2 h. Afterwards, the mixture was heated at 75 °C and stirred at this temperature for 1 h. Then, the solution was cooled to room temperature and the solvent was removed under reduce pressure to afford 5 as colourless solid (76 mg, 63%). Spectroscopic data matched those previously reported in the literature (Figure S3).[14]

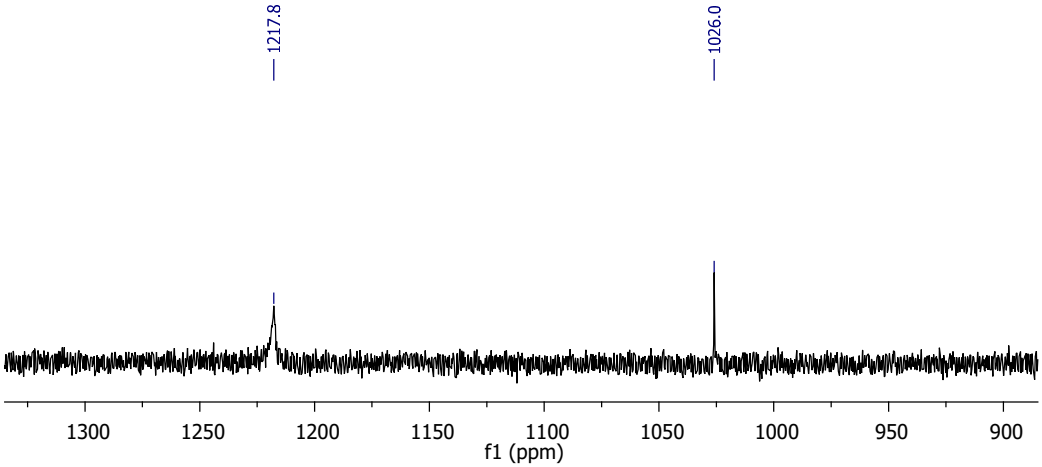


Figure S3. ^{77}Se NMR spectrum ($CDCl_3$, 76 MHz) of selenonium salt **6**

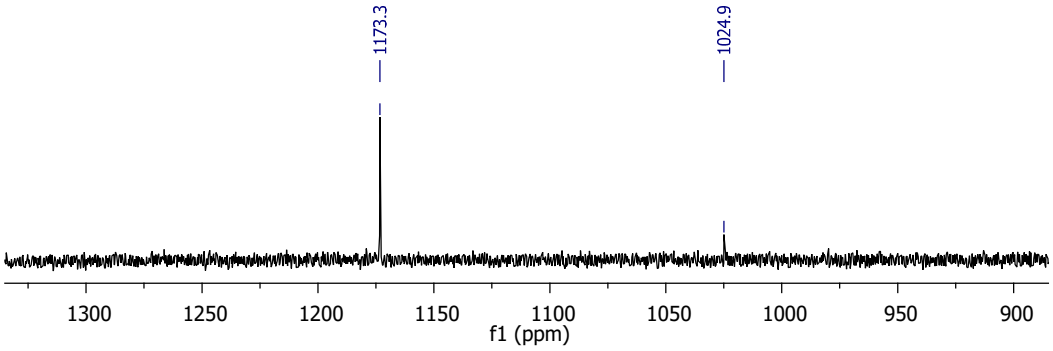


Figure S4. ^{77}Se NMR spectrum (D_2O, 76 MHz) recorded solubilizing selenonium salt **5** in D_2O. Benzeneseleninic acid **4** and benzeneselenonic acid **7** are formed.

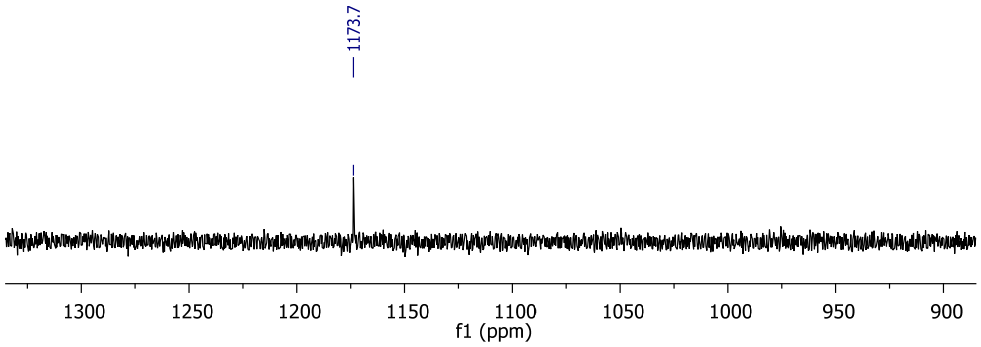
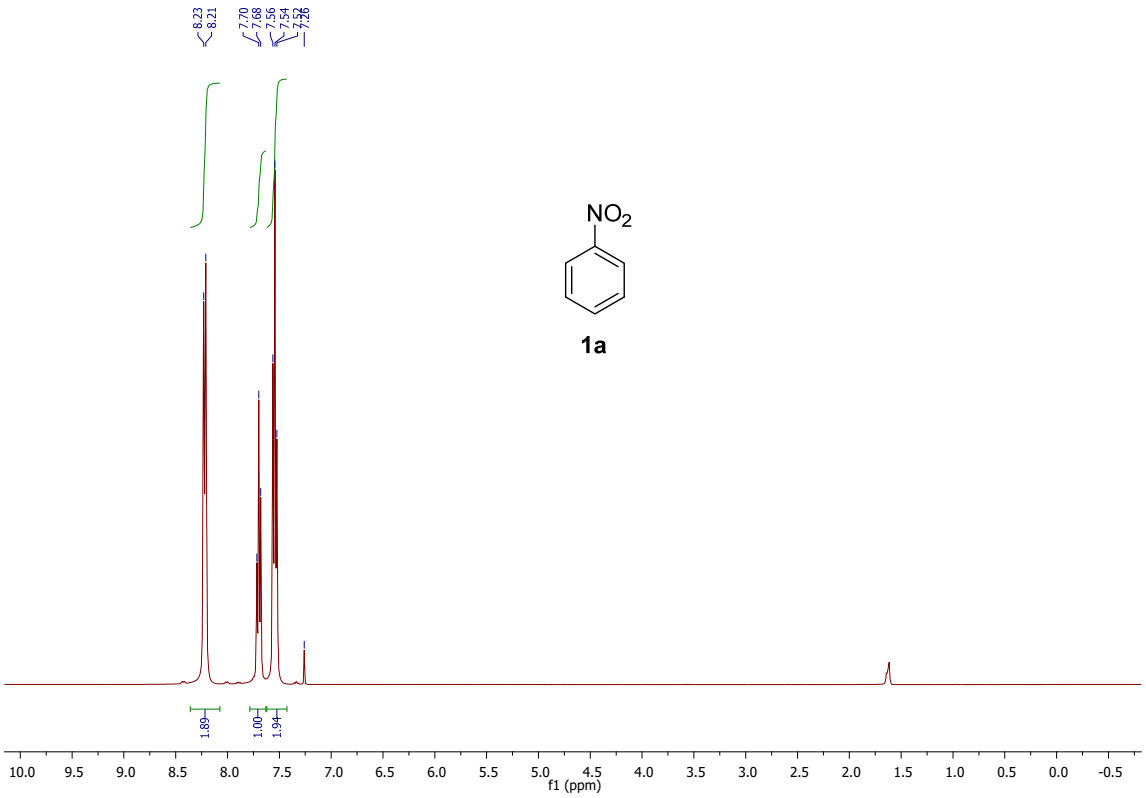
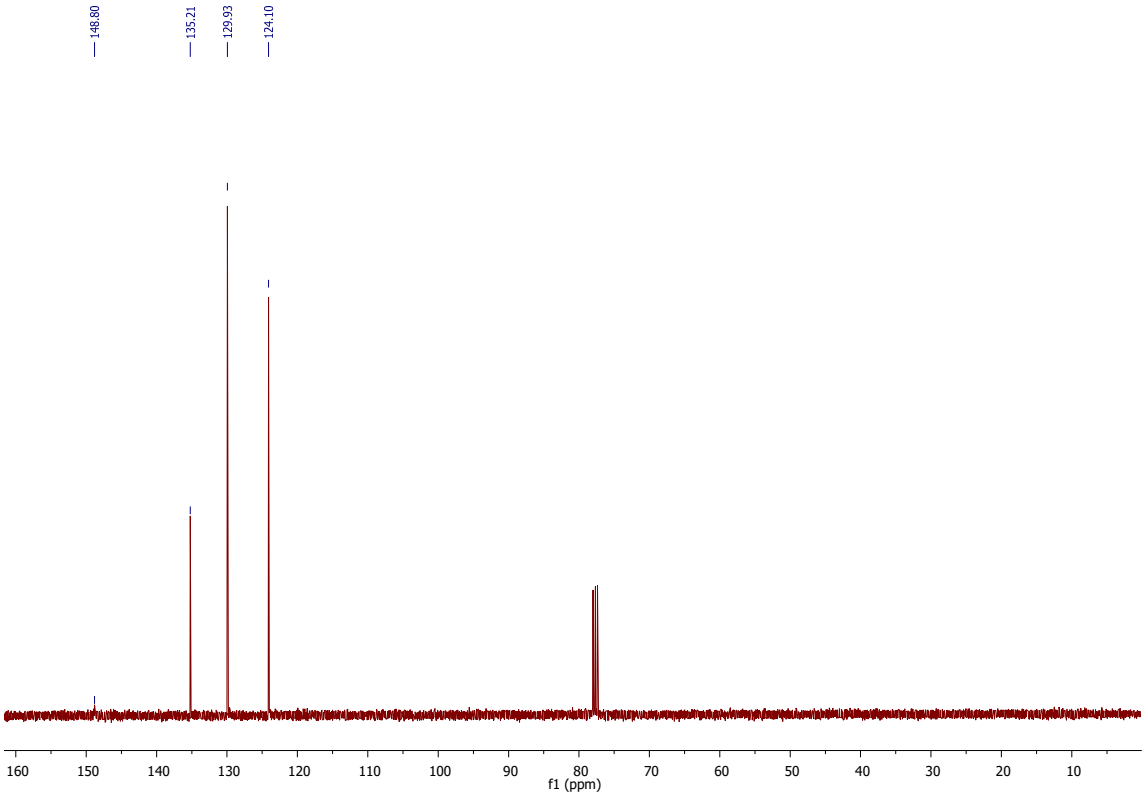


Figure S5. ^{77}Se NMR spectrum ($CDCl_3$, 76 MHz) of benzeneseleninic acid **4**.

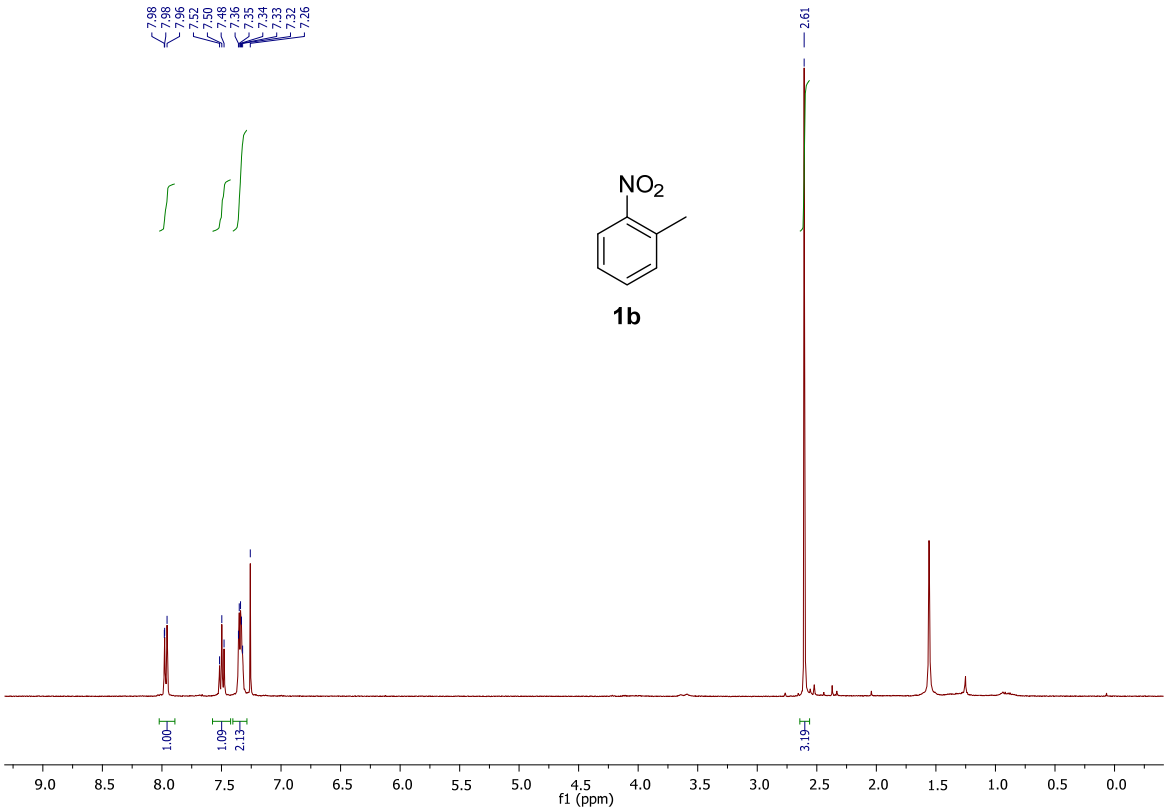
3. Copies of NMR Spectra[§§]



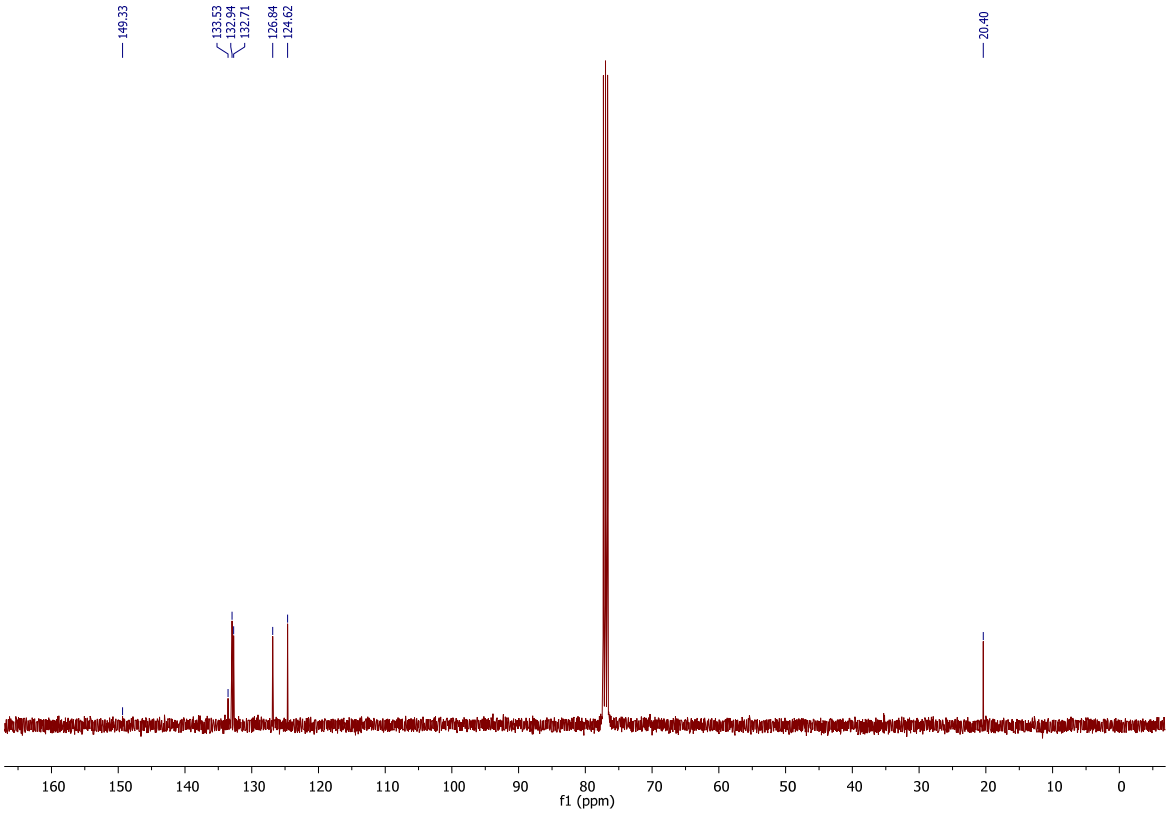
^{1}H NMR spectrum of compound **1a** ($CDCl_3$, 400 MHz)



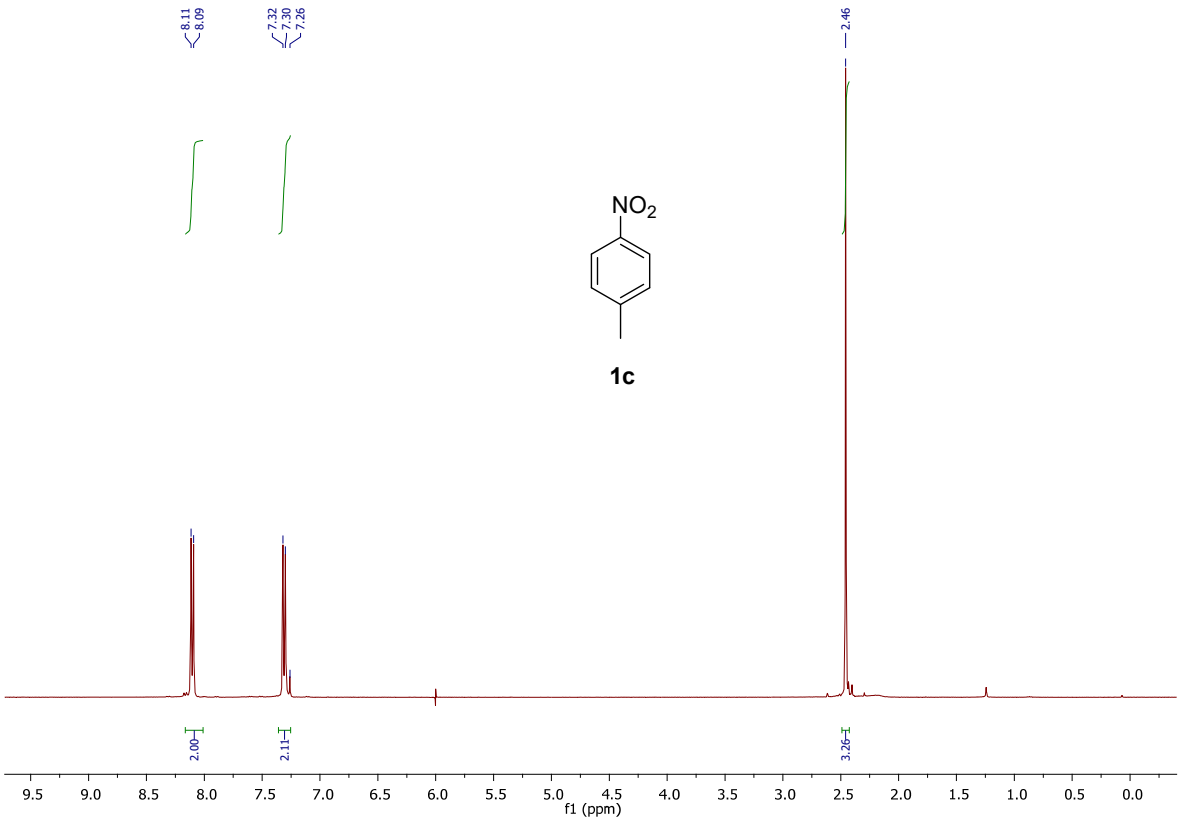
^{13}C NMR spectrum of compound **1a** ($CDCl_3$, 100 MHz)



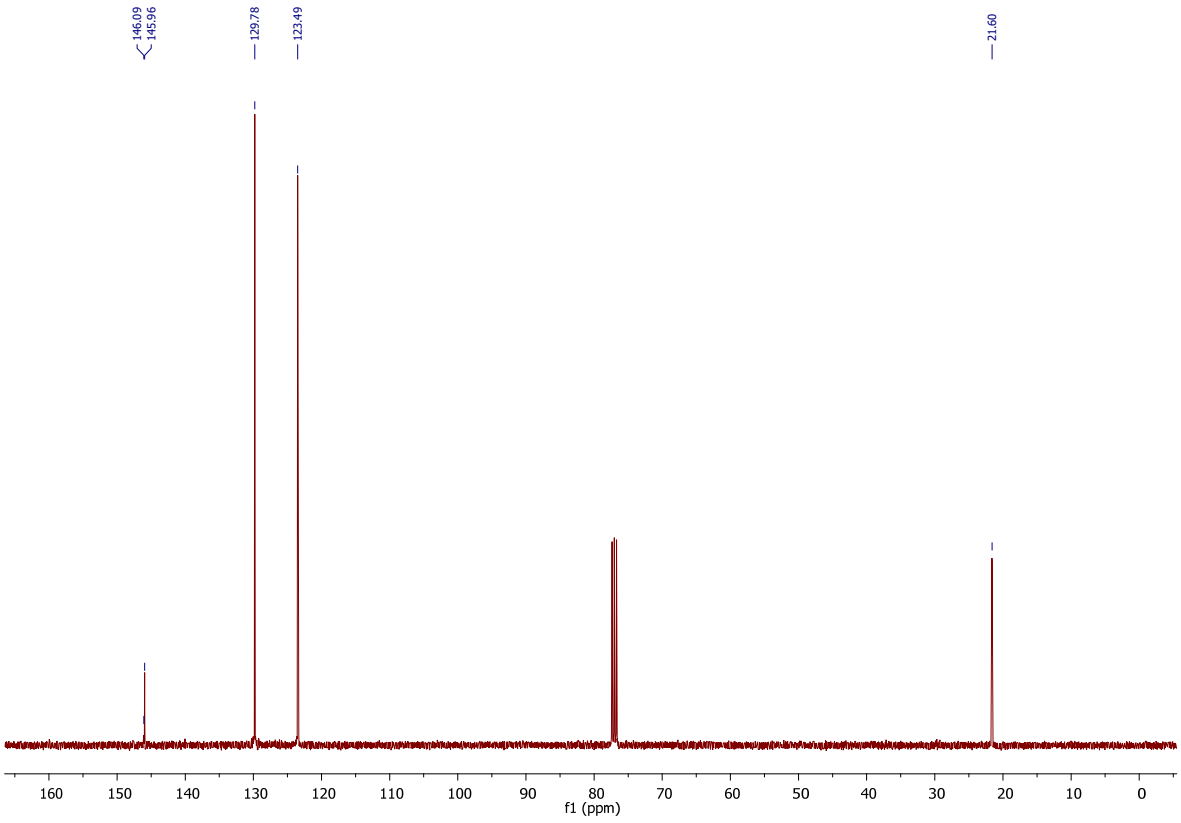
^{1}H NMR spectrum of compound **1b** ($CDCl_3$, 400 MHz)



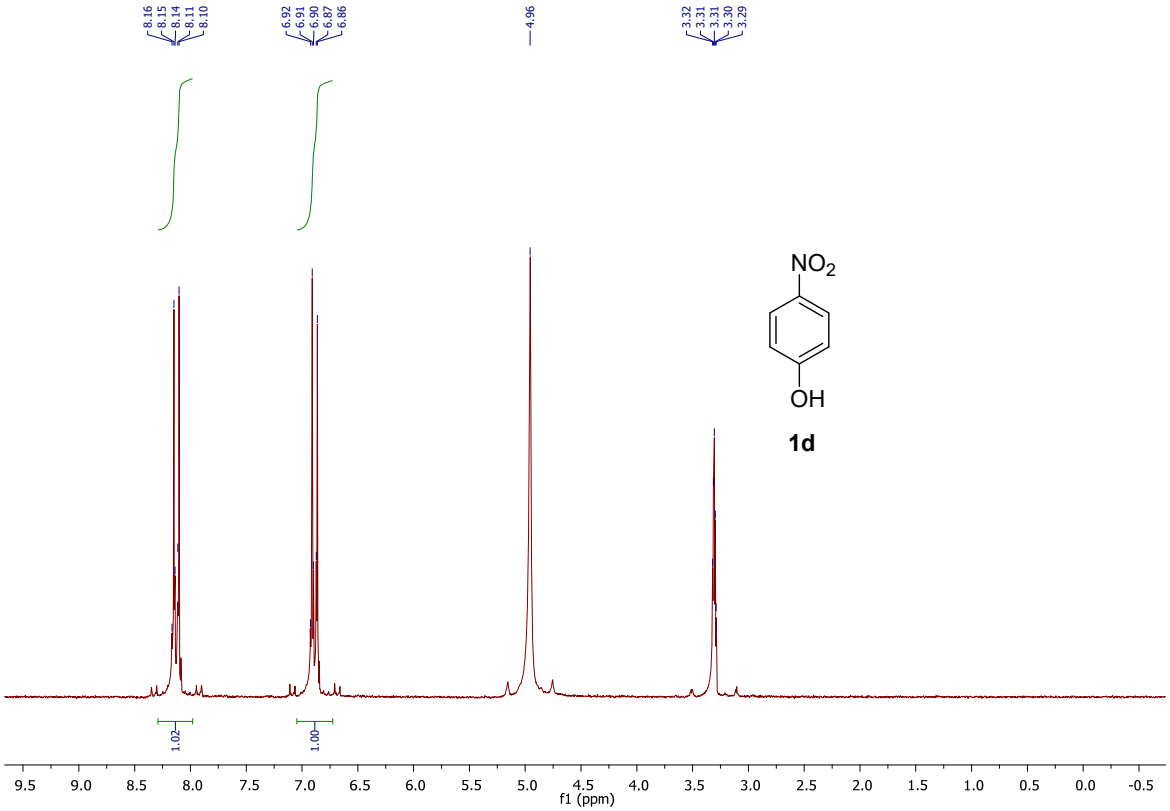
^{13}C NMR spectrum of compound **1b** ($CDCl_3$, 100 MHz)



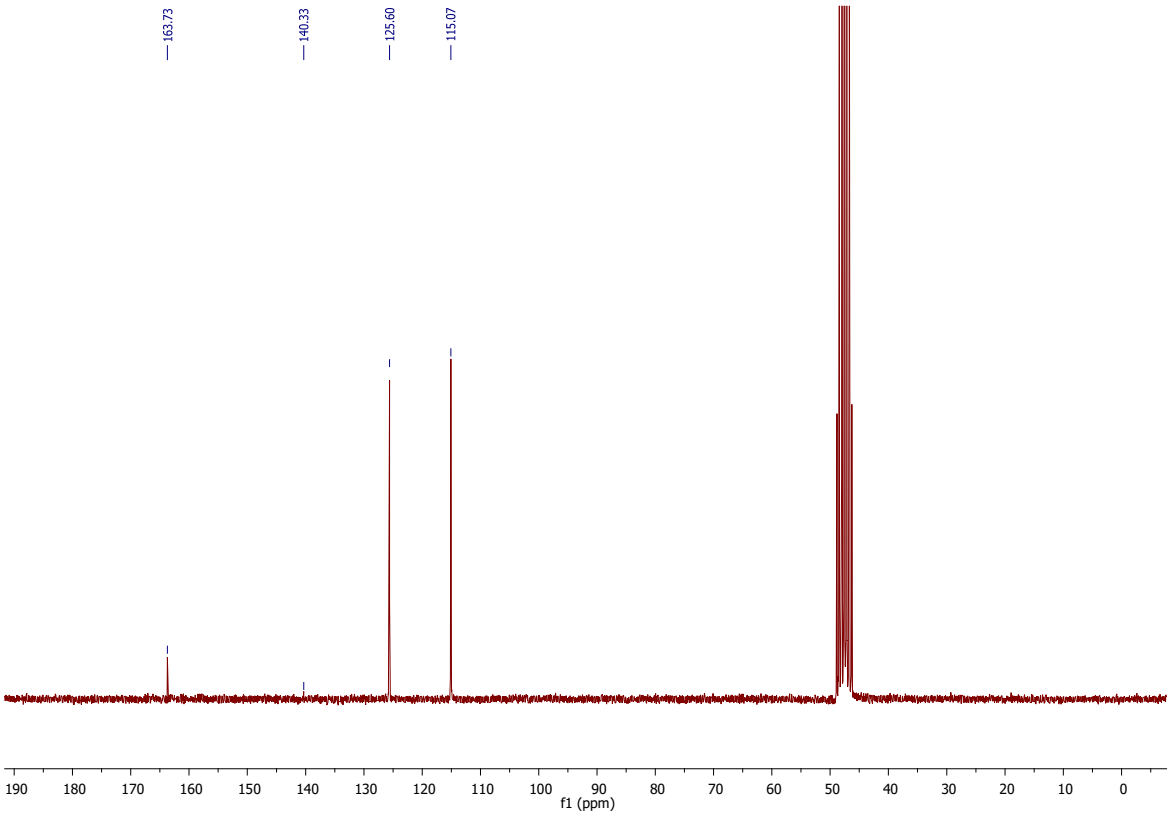
^{1}H NMR spectrum of compound **1c** ($CDCl_3$, 400 MHz)



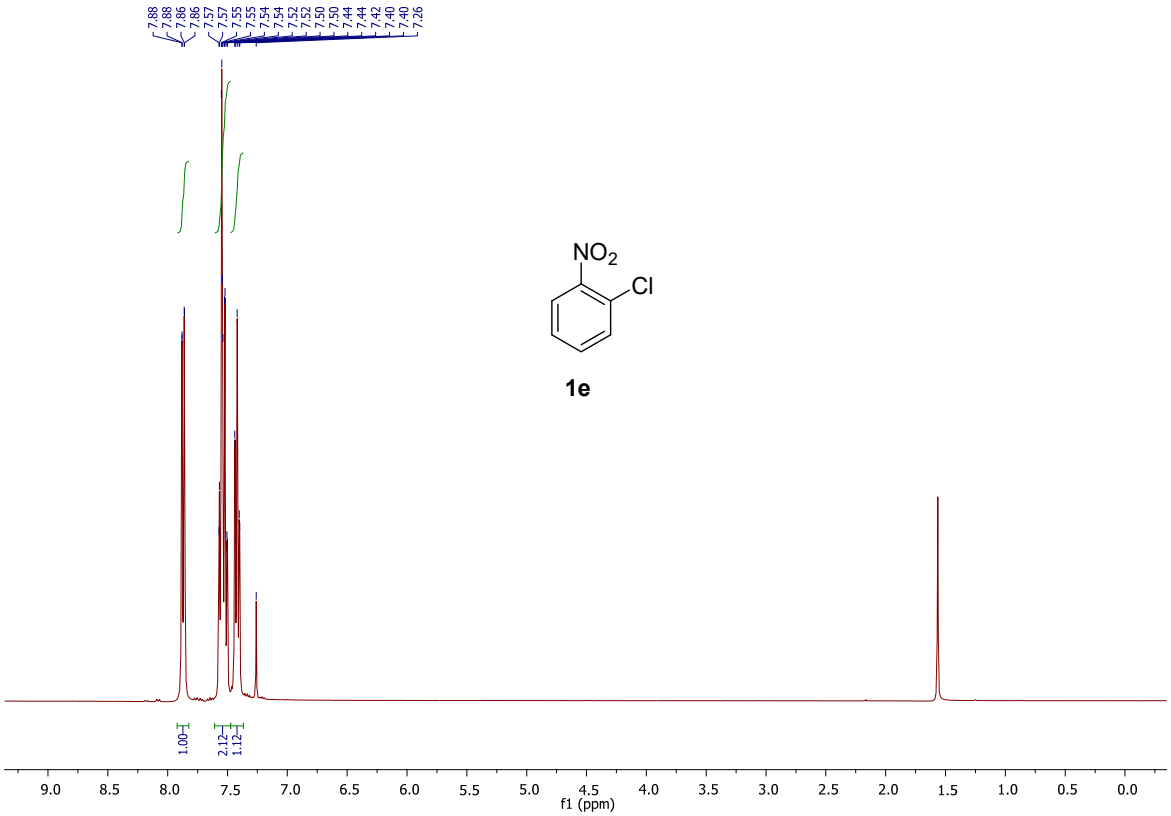
^{13}C NMR spectrum of compound **1c** ($CDCl_3$, 100 MHz)



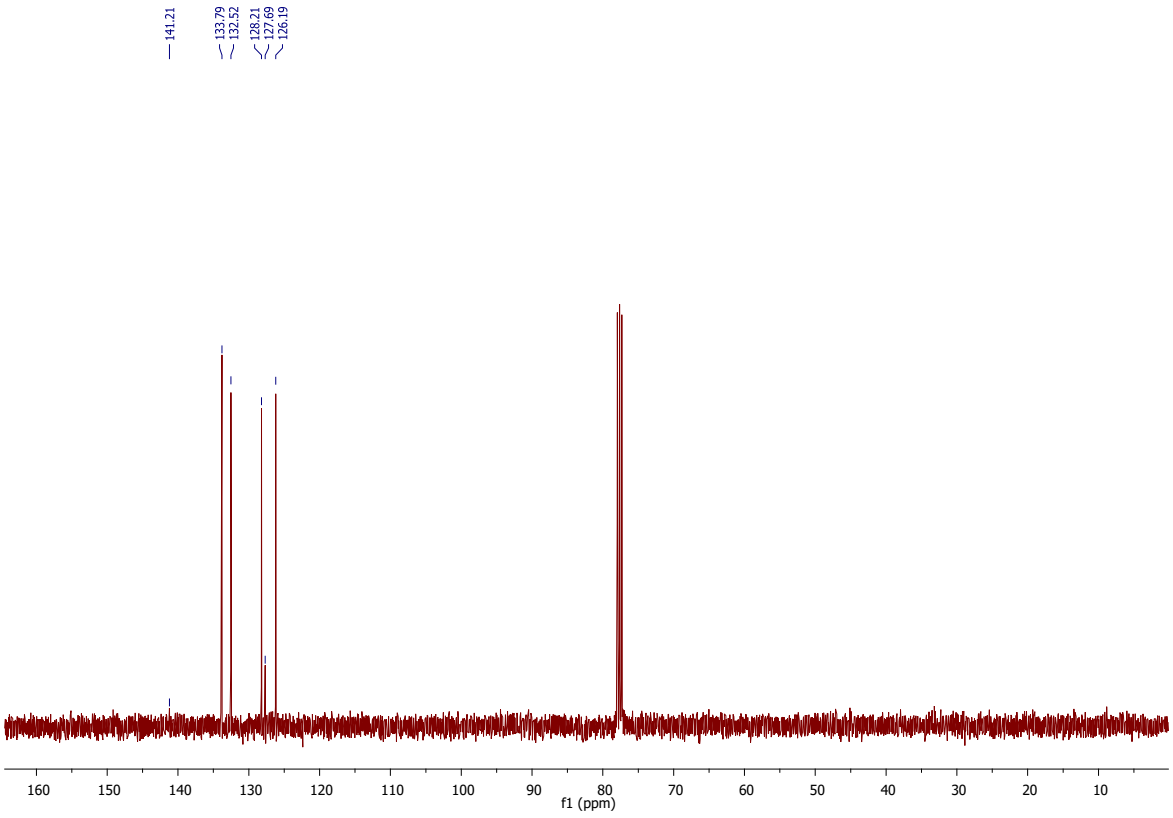
^{1}H NMR spectrum of compound **1d** (CD_3OD, 200 MHz)



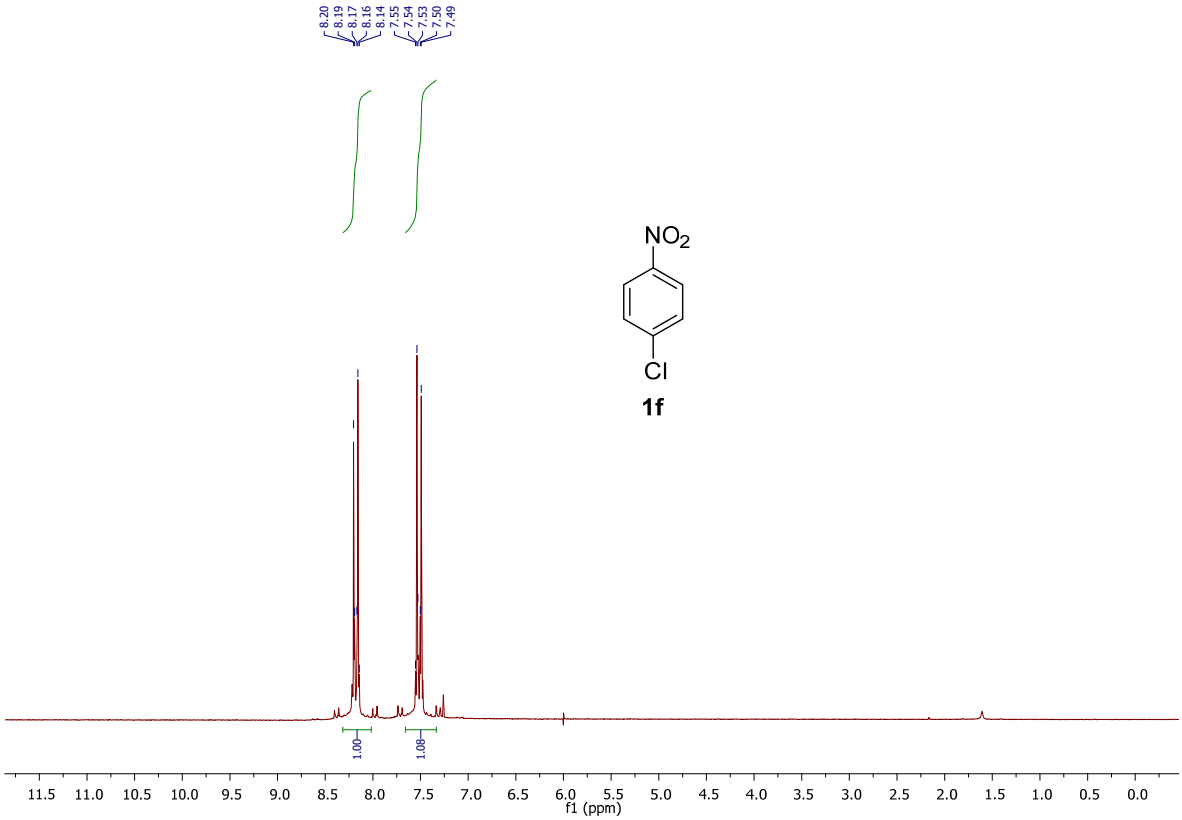
^{13}C NMR spectrum of compound **1d** (CD_3OD, 50 MHz)



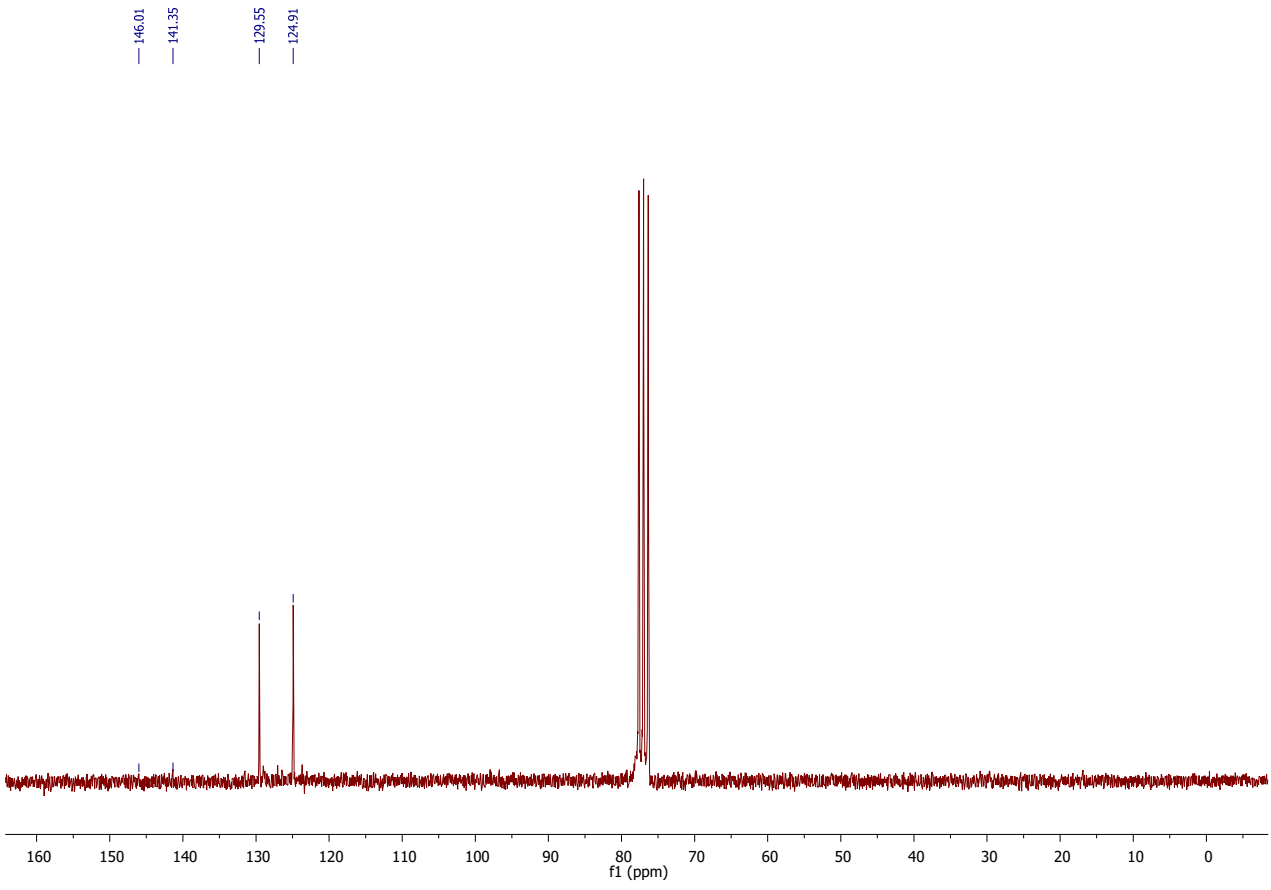
^{1}H NMR spectrum of compound **1e** ($CDCl_3$, 400 MHz)



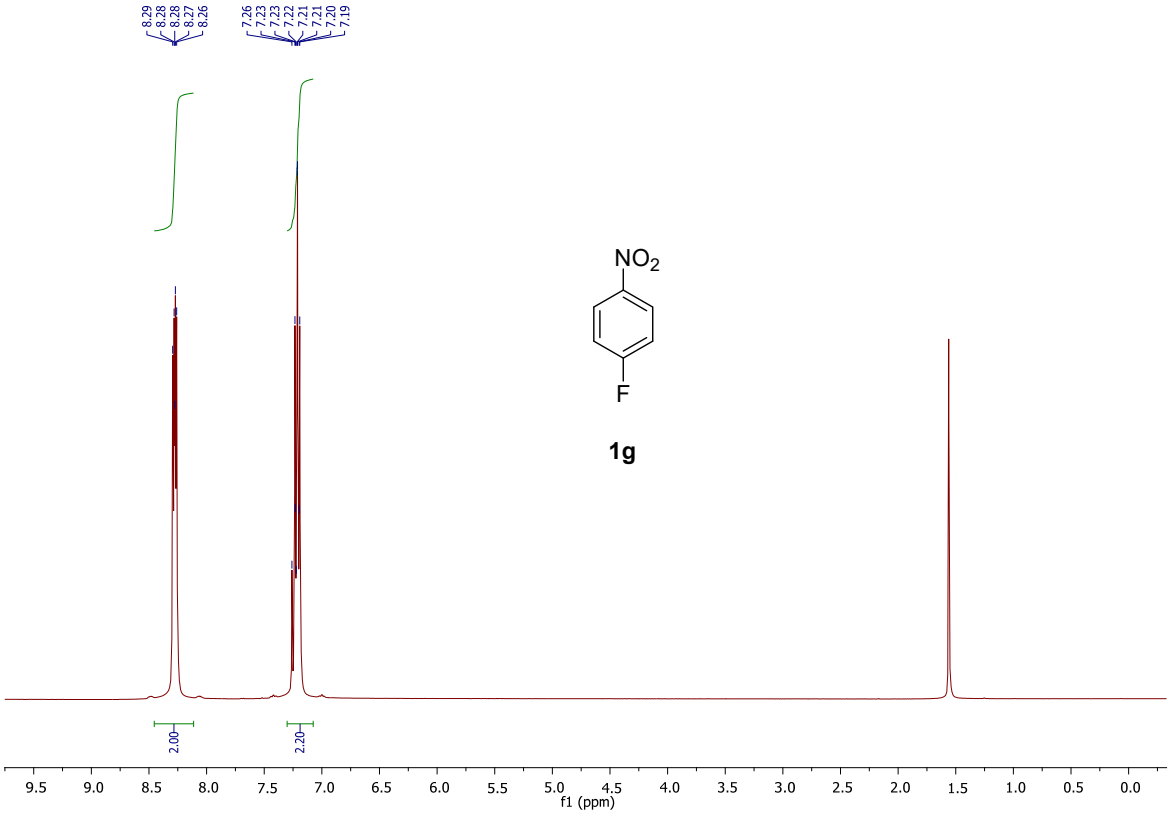
^{13}C NMR spectrum of compound **1e** ($CDCl_3$, 100 MHz)



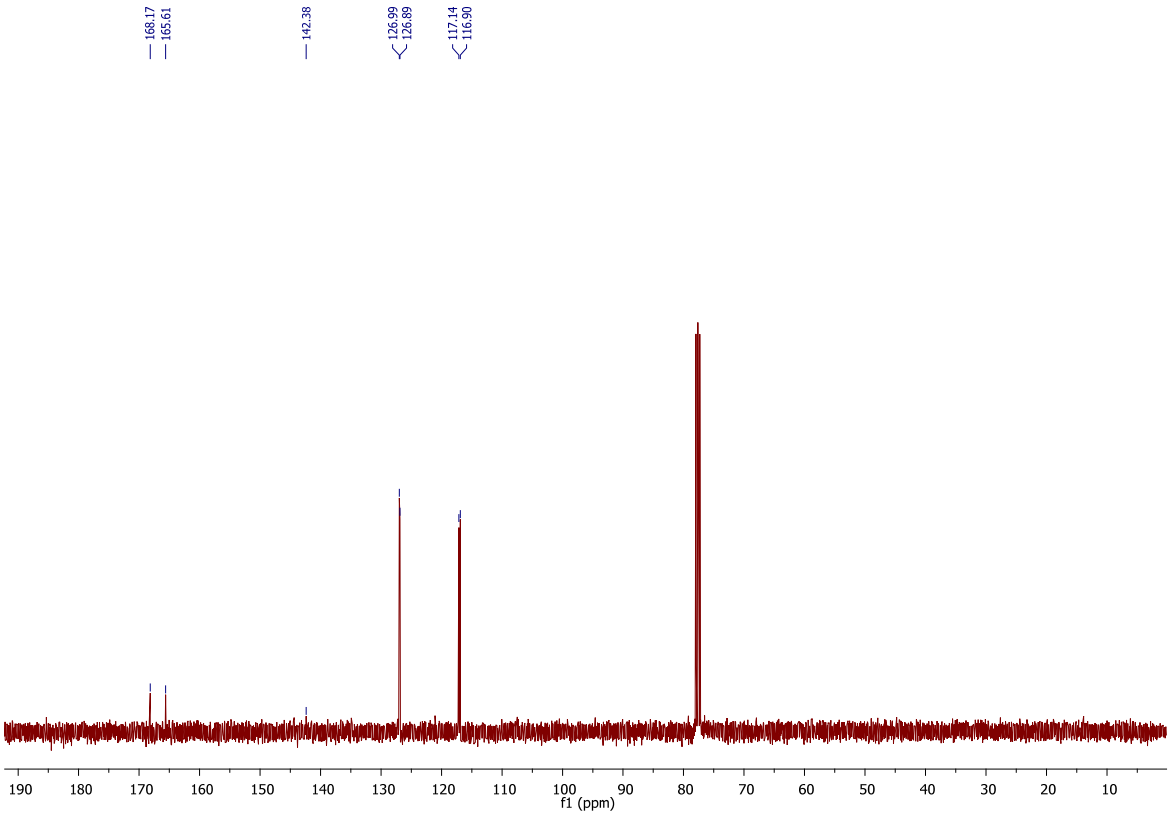
^{1}H NMR spectrum of compound **1f**. ($CDCl_3$, 200 MHz)



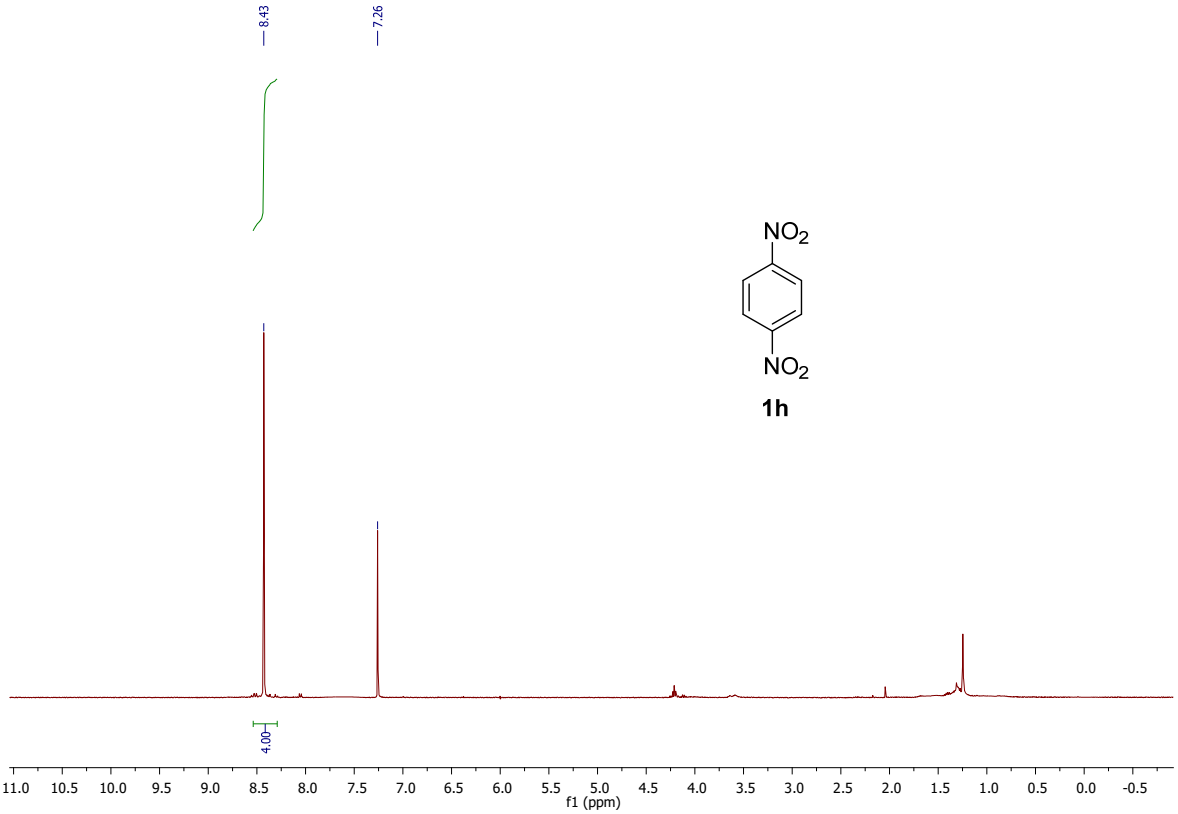
^{13}C NMR spectrum of compound **1f** ($CDCl_3$, 50 MHz)



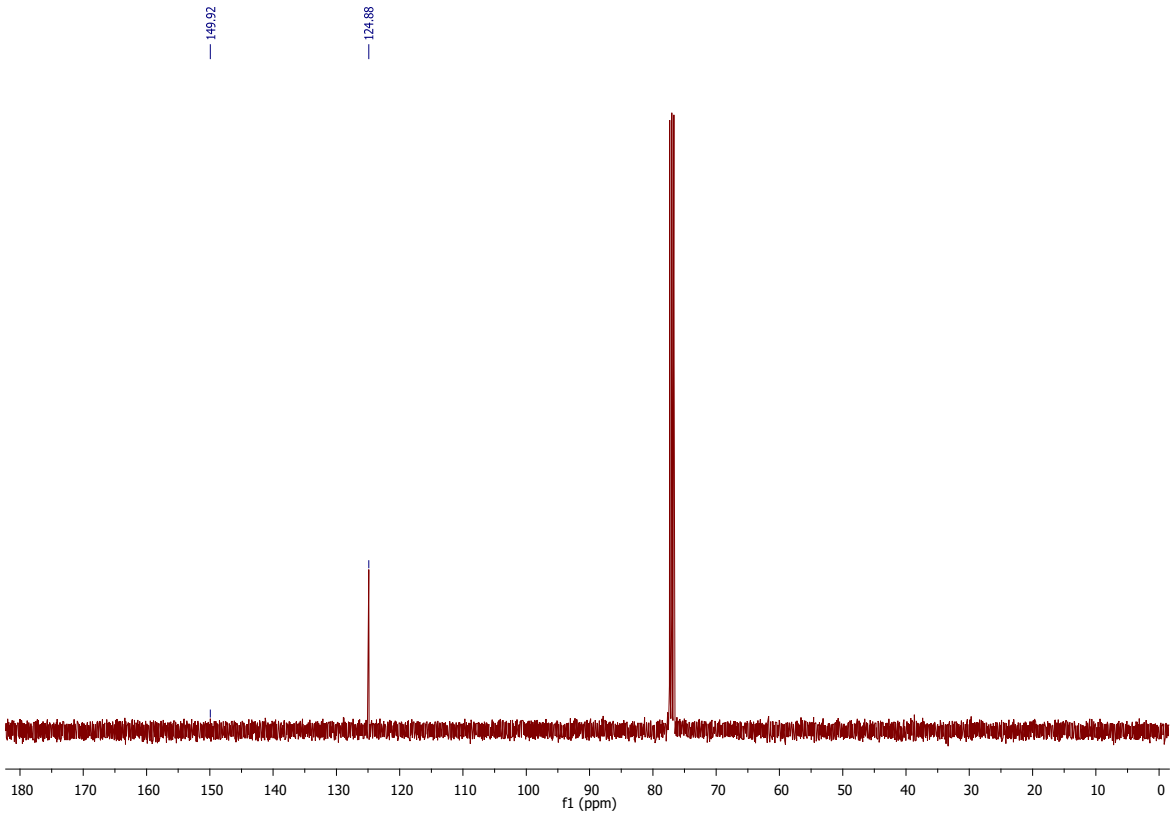
^{1}H NMR spectrum of compound **1g** ($CDCl_3$, 400 MHz)



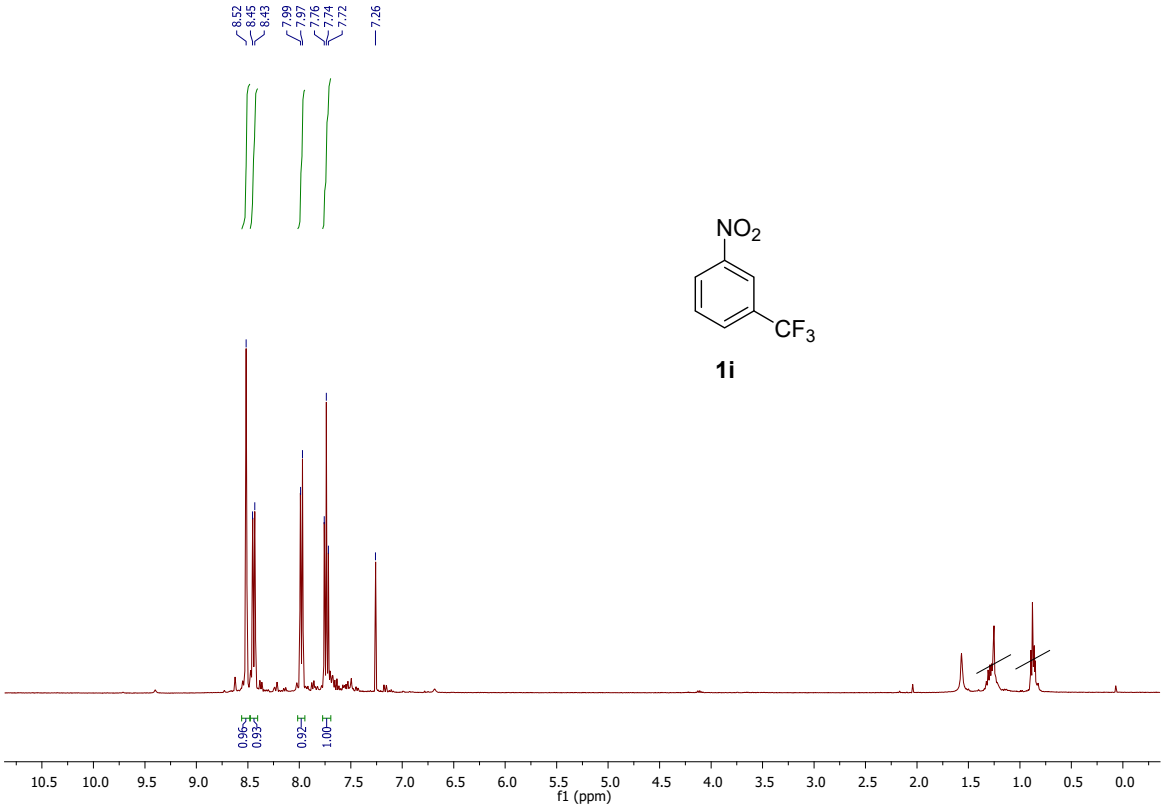
^{13}C NMR spectrum of compound **1g** ($CDCl_3$, 100 MHz)



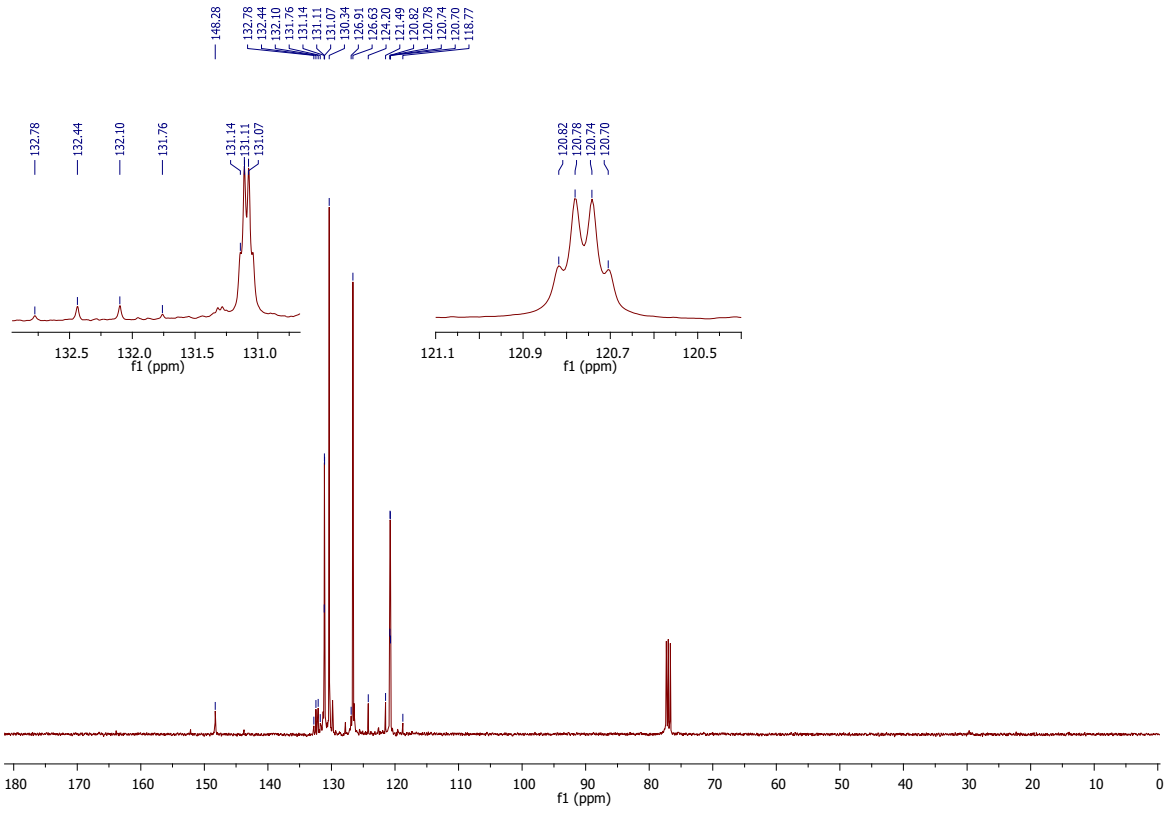
^{1}H NMR spectrum of compound **1h** ($CDCl_3$, 400 MHz)



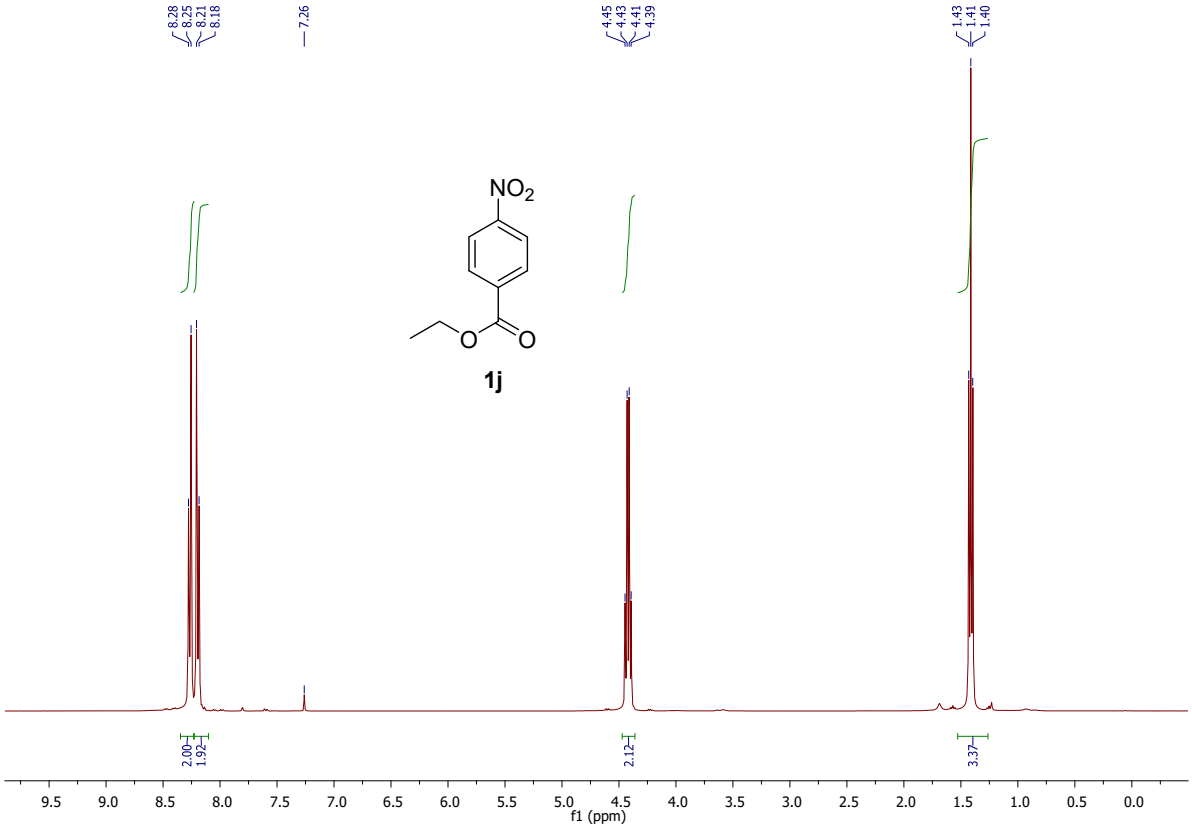
^{13}C NMR spectrum of compound **1h** ($CDCl_3$, 100 MHz)



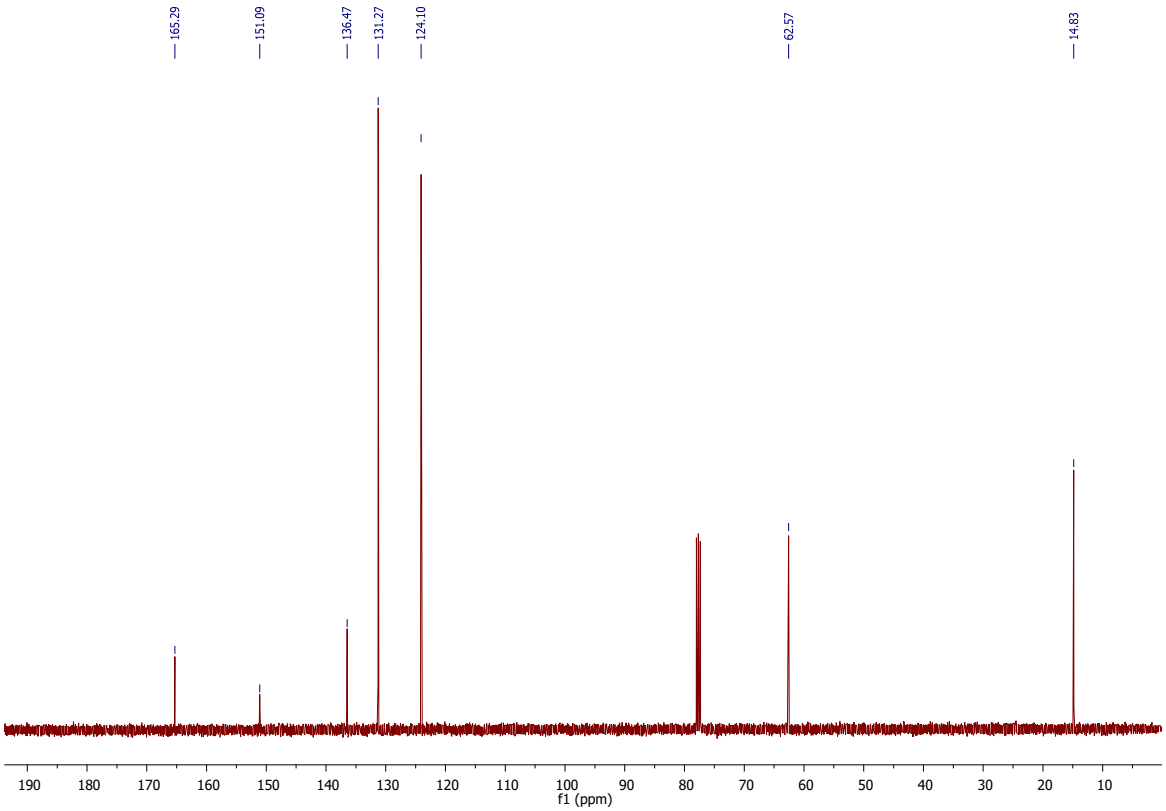
^{1}H NMR spectrum of compound **1i** ($CDCl_3$, 400 MHz) – *Reaction conducted on a 1.0 mmol scale*



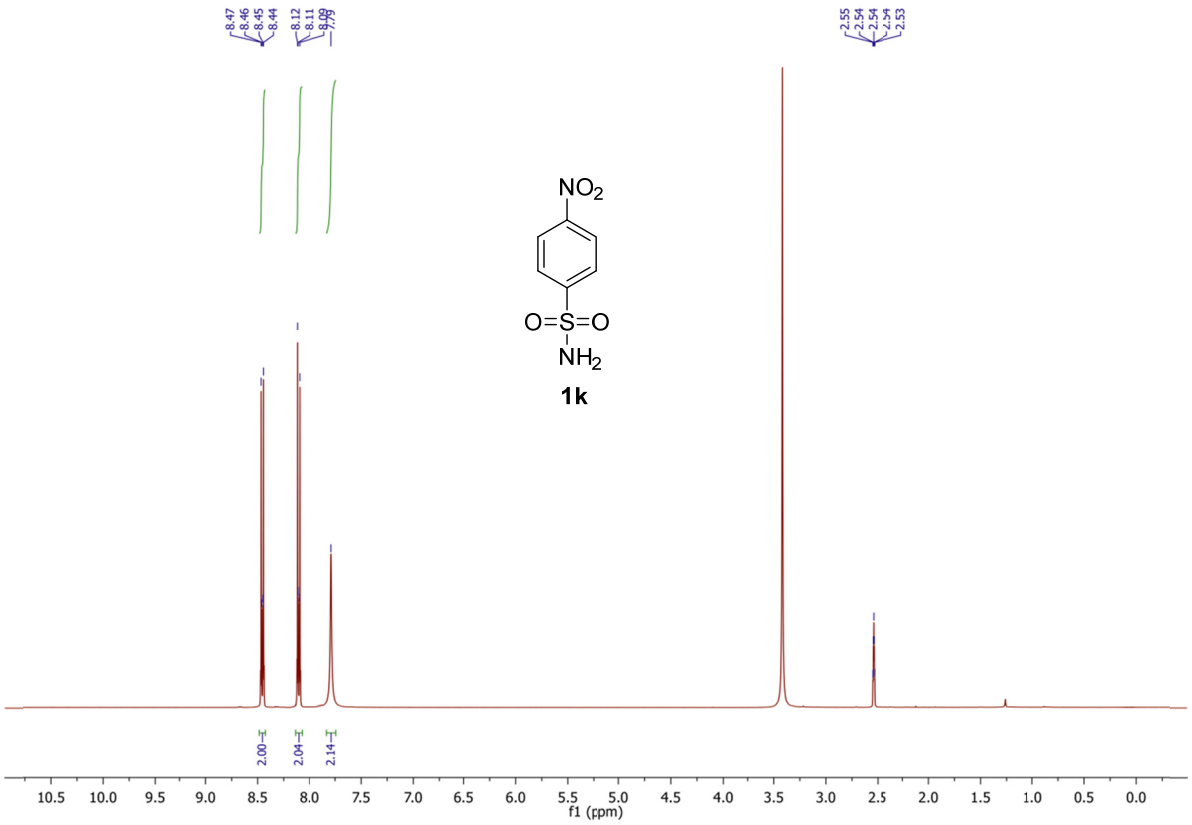
^{13}C NMR spectrum of compound **1i** ($CDCl_3$, 100 MHz) – *Reaction conducted on a 1.0 mmol scale*



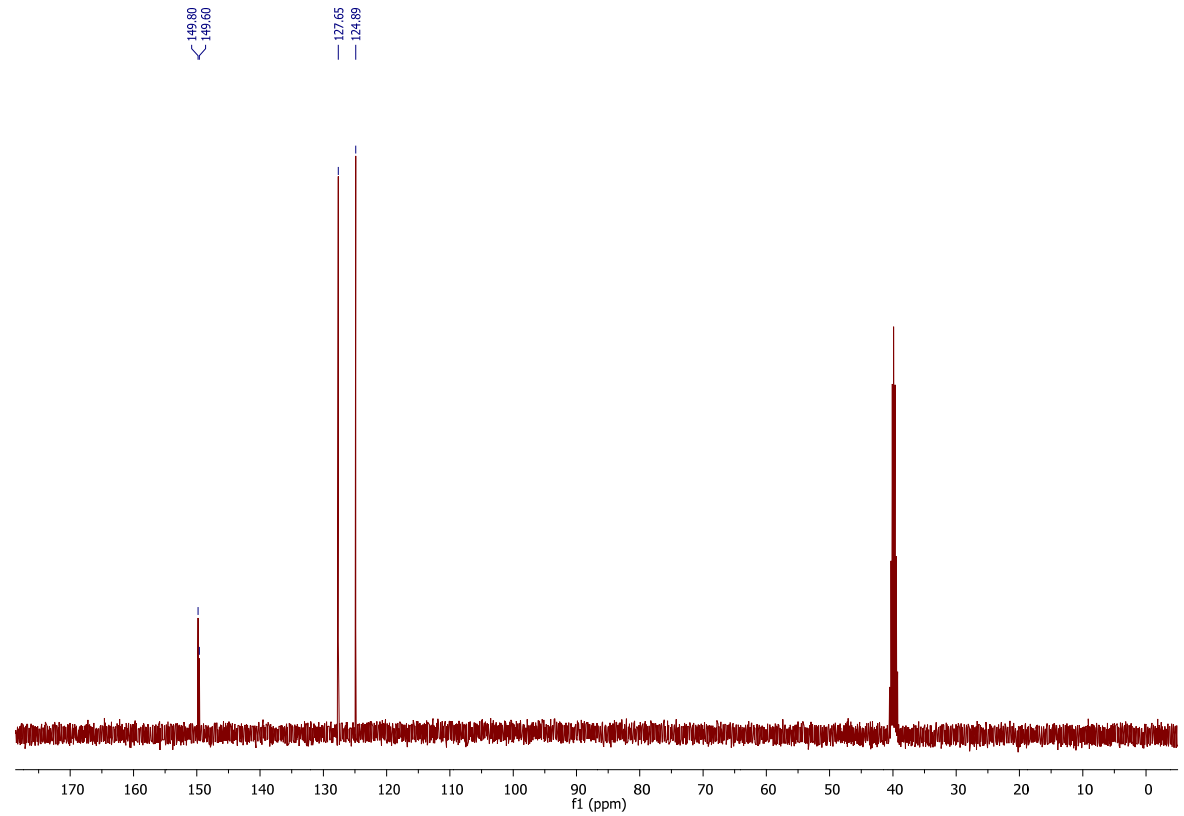
^{1}H NMR spectrum of compound **1j** ($CDCl_3$, 400 MHz)



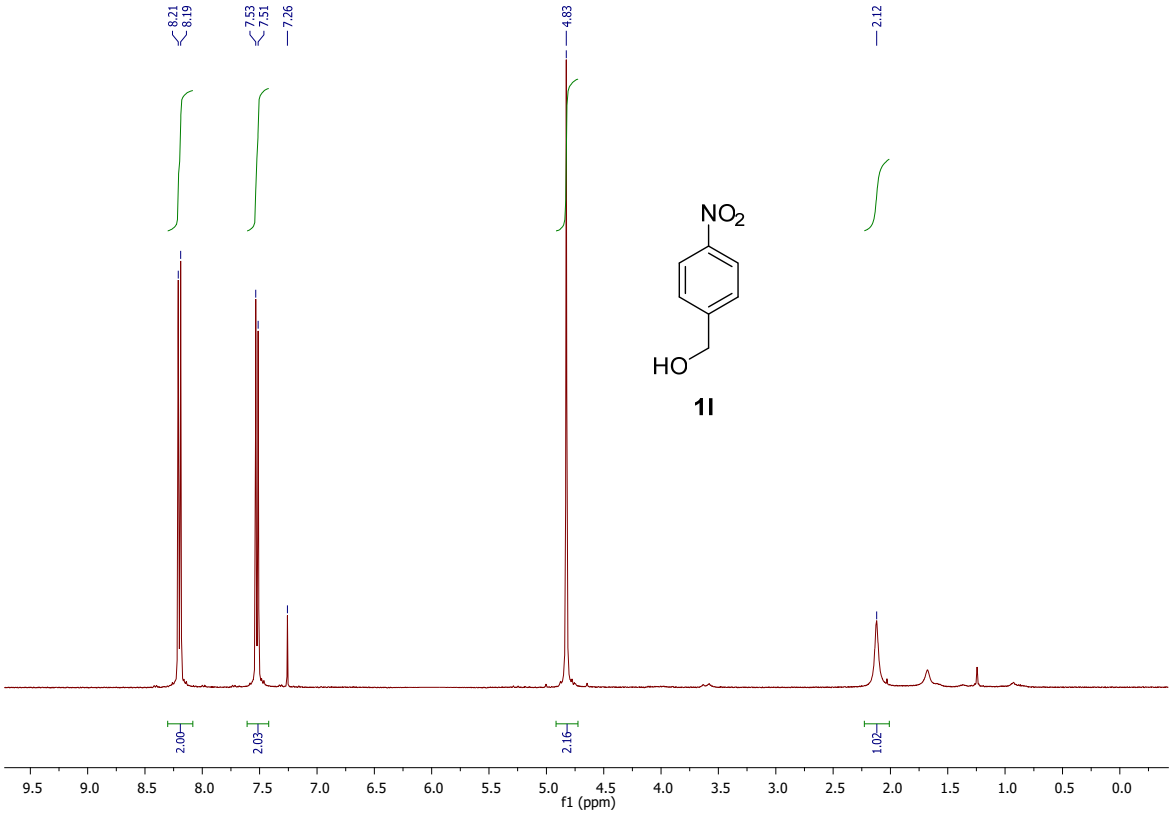
^{13}C NMR spectrum of compound **1j** ($CDCl_3$, 100 MHz)



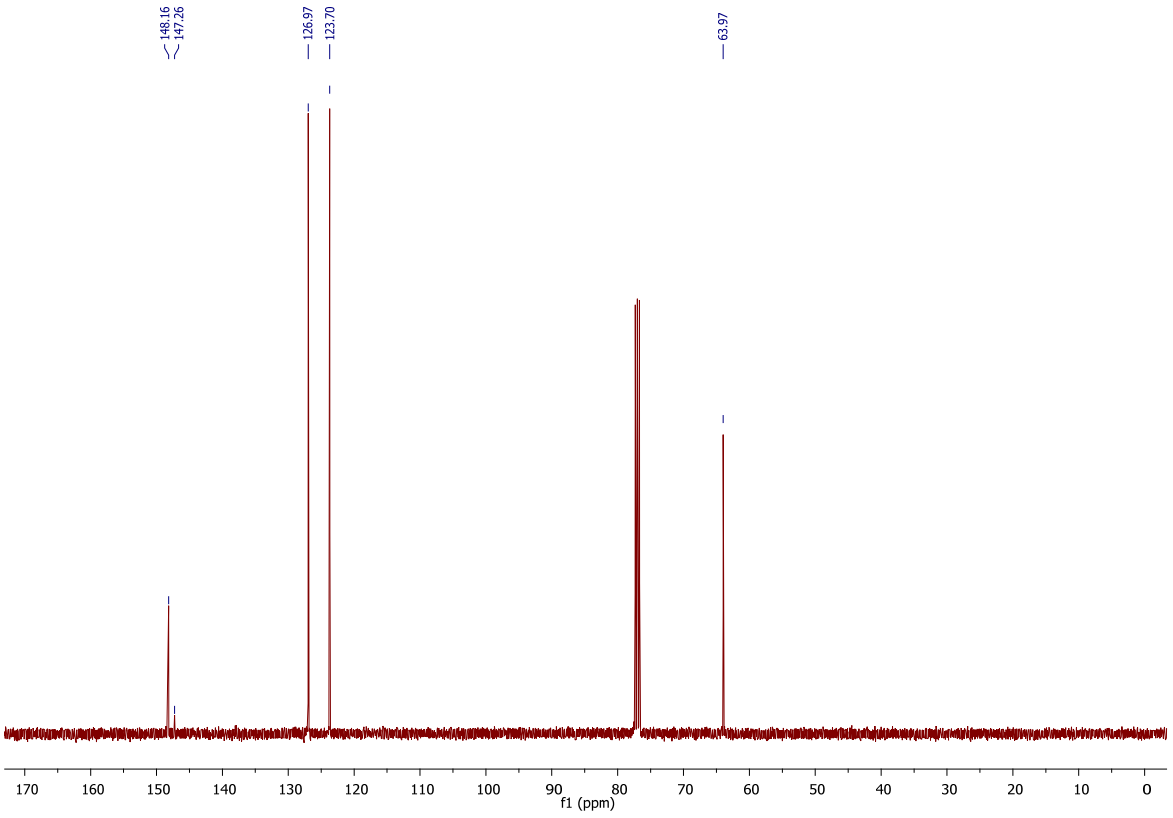
^{1}H NMR spectrum of compound **1k** (DMSO-d_6, 400 MHz)



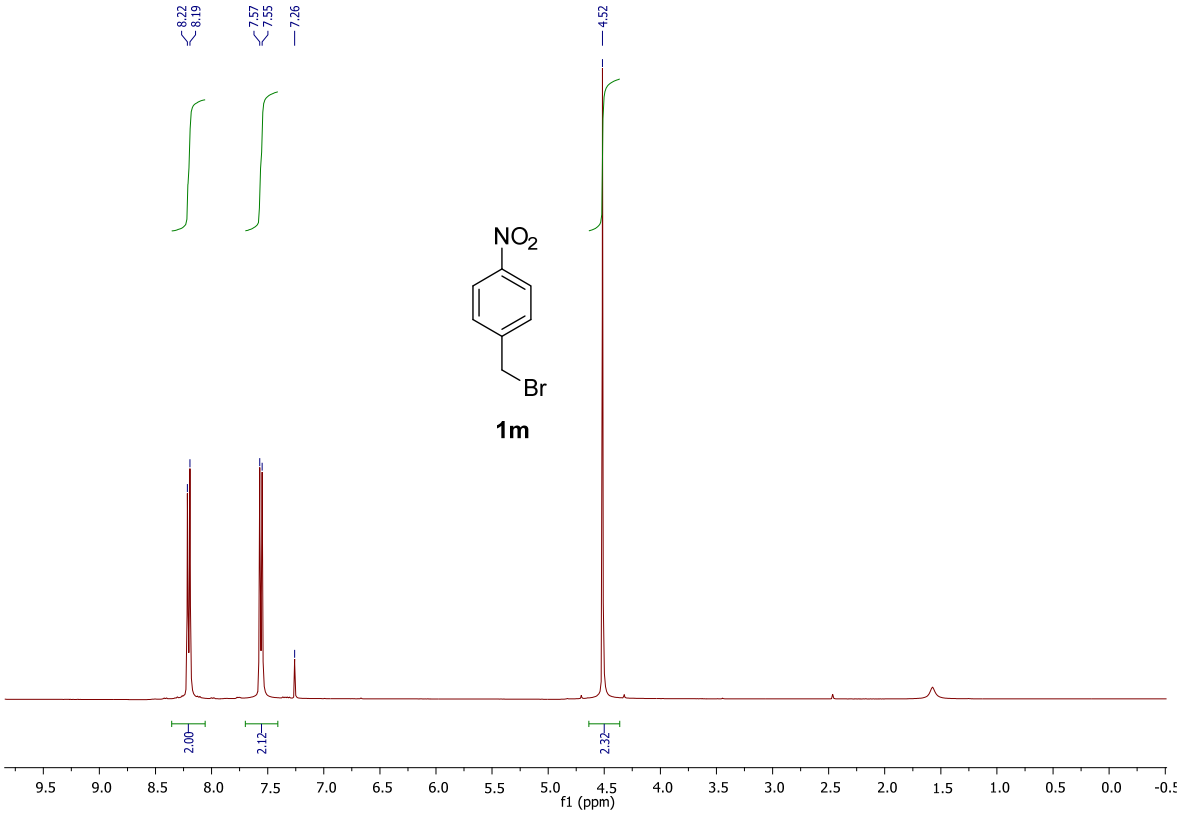
^{13}C NMR spectrum of compound **1k** (DMSO-d_6, 100 MHz)



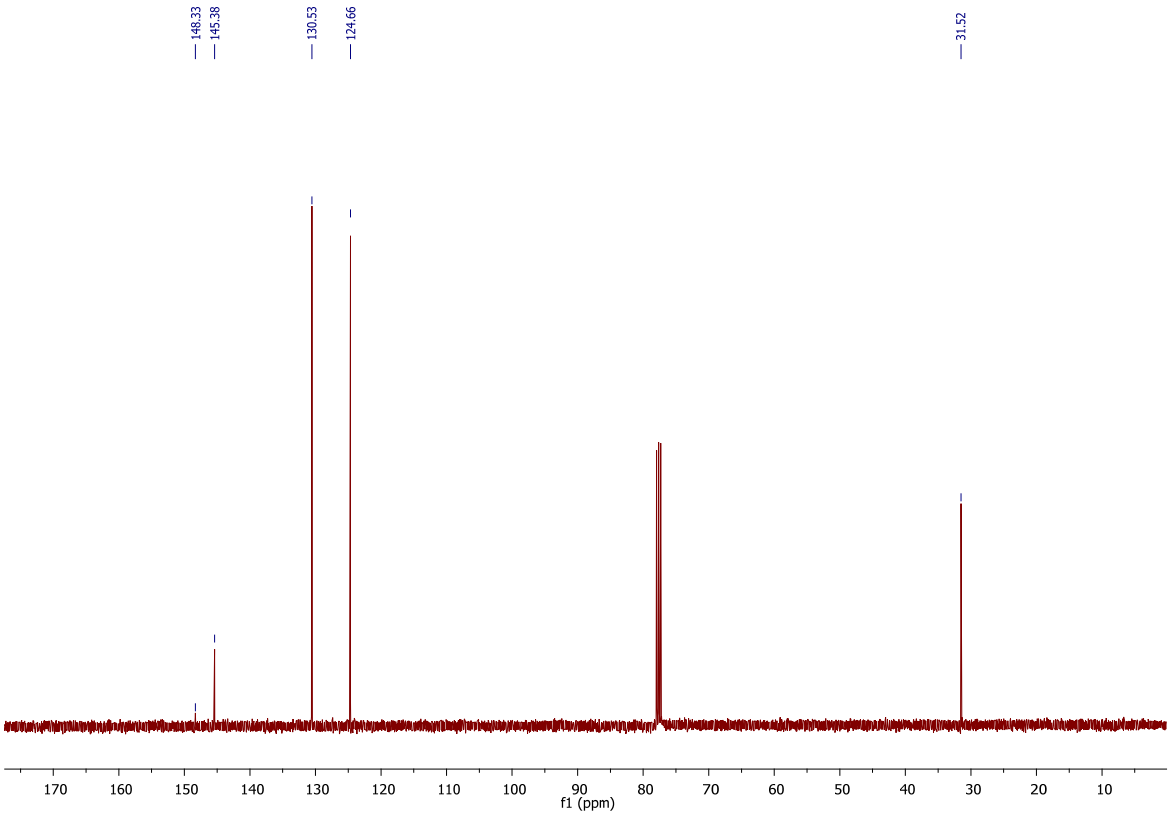
^{1}H NMR spectrum of compound **1l**. ($CDCl_3$, 400 MHz)



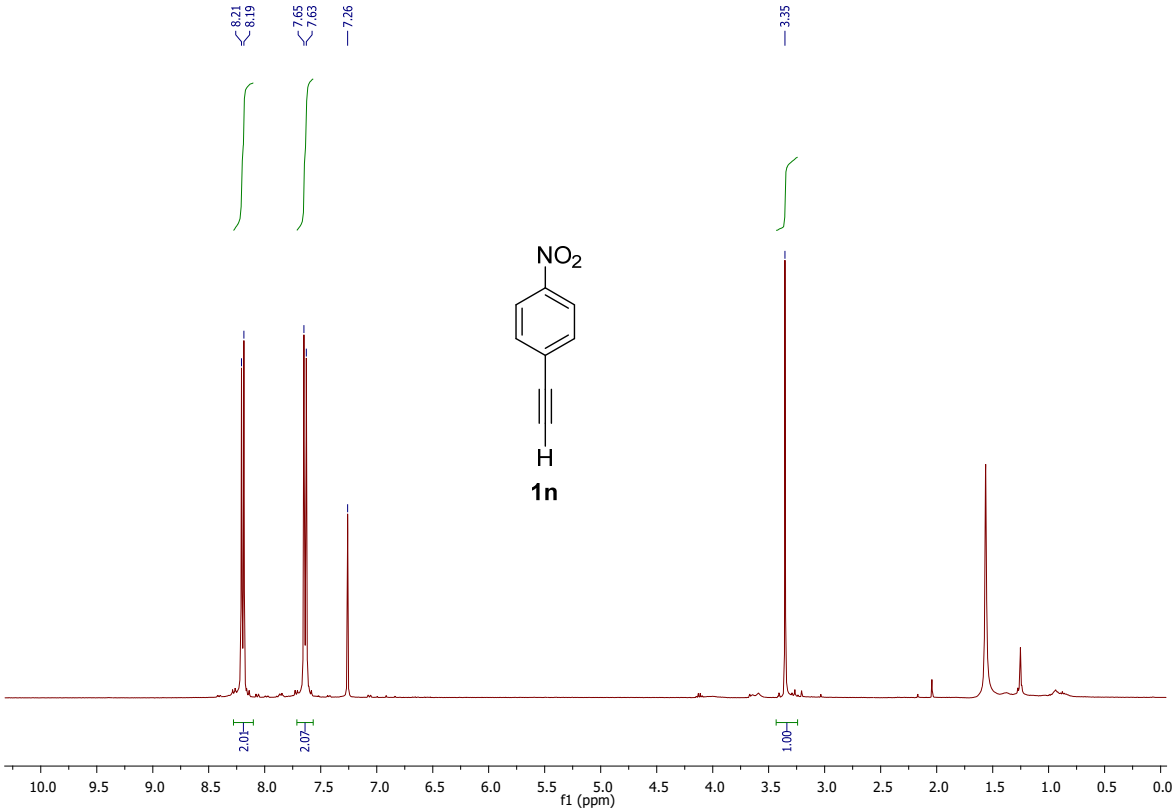
^{13}C NMR spectrum of compound **1l** ($CDCl_3$, 100 MHz)



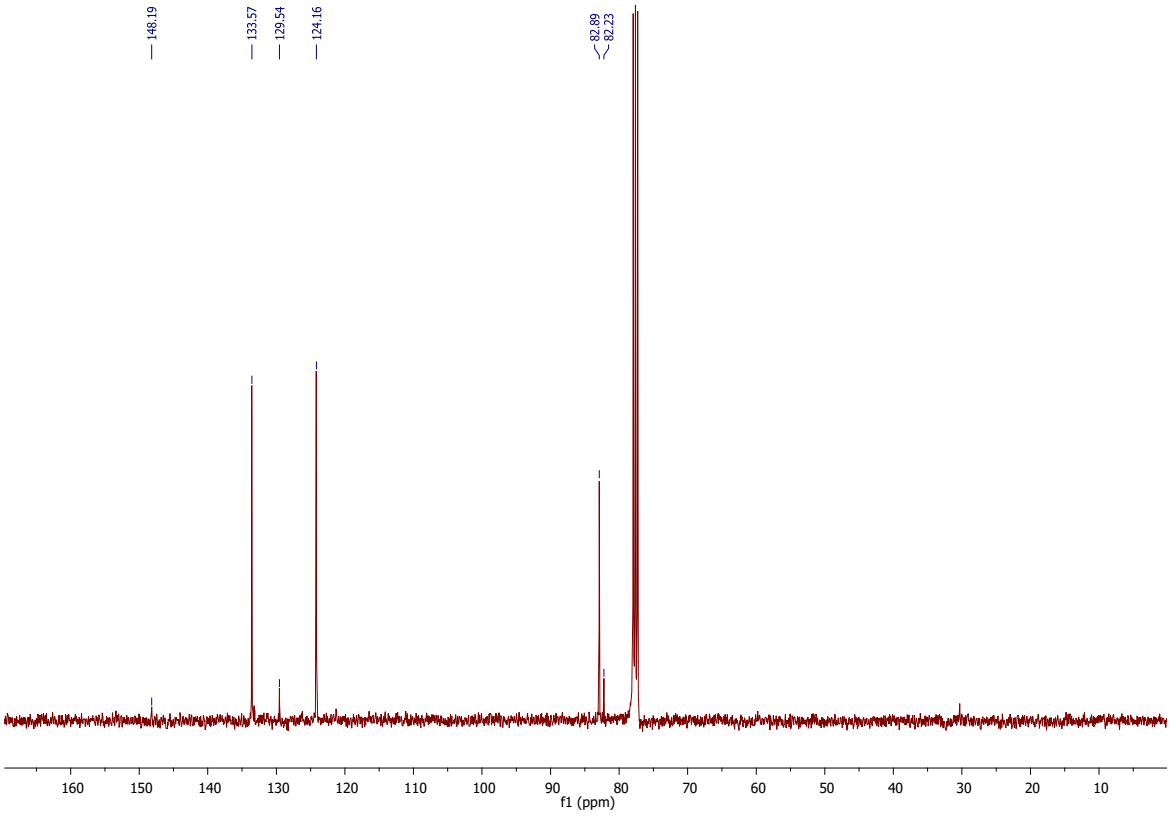
^{1}H NMR spectrum of compound **1m** ($CDCl_3$, 400 MHz)



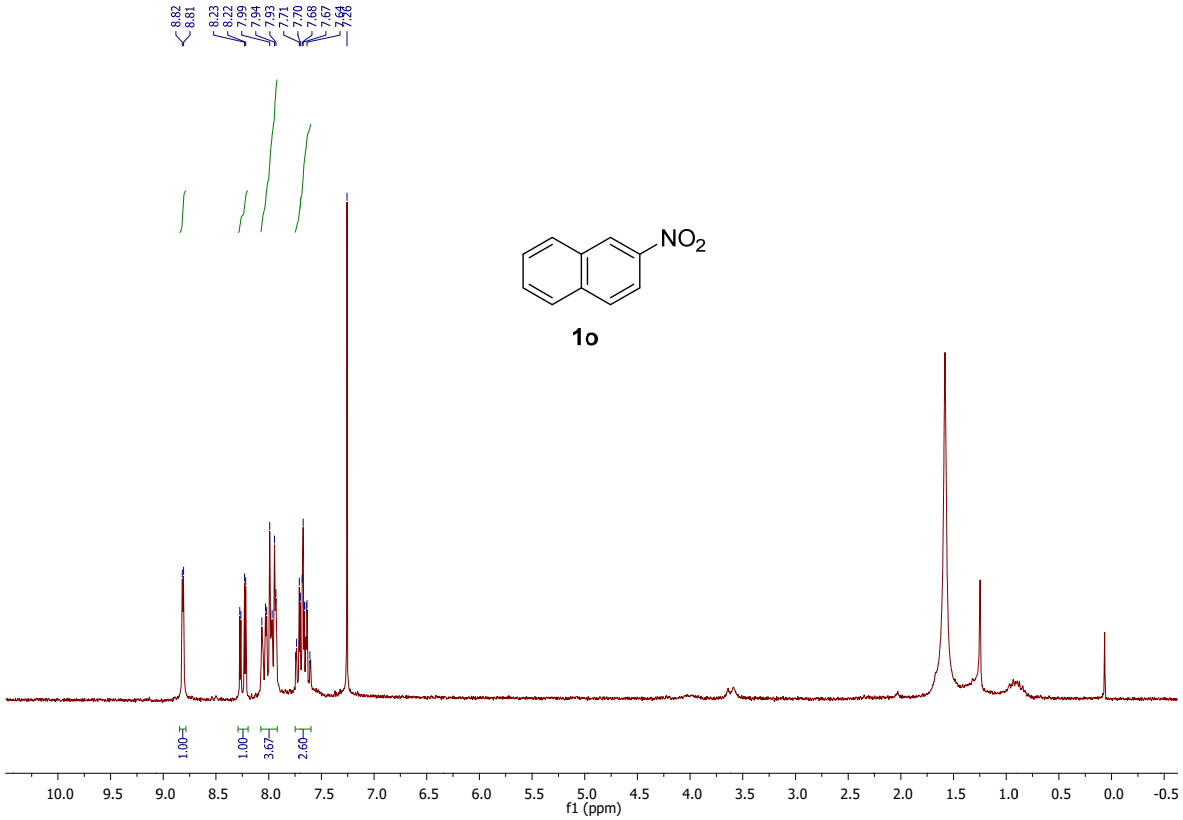
^{13}C NMR spectrum of compound **1m** ($CDCl_3$, 100 MHz)



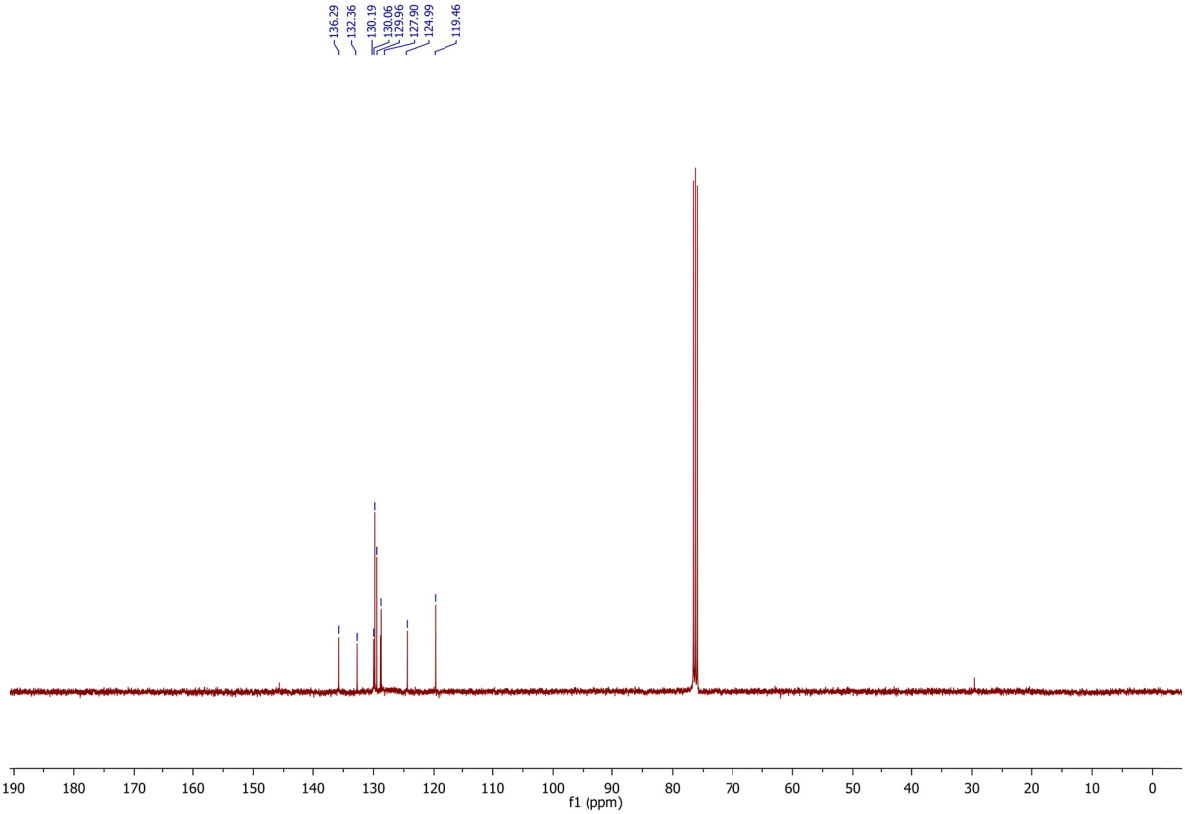
^{1}H NMR spectrum of compound **1n** ($CDCl_3$, 400 MHz)



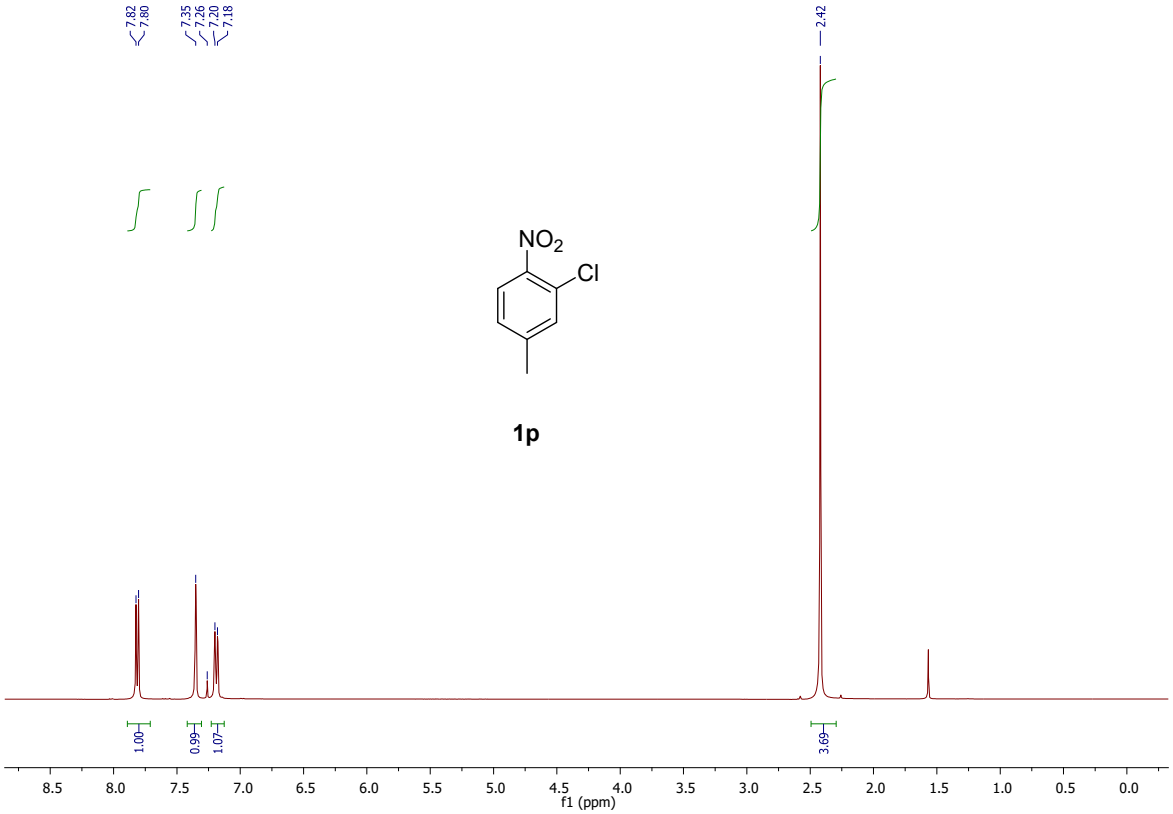
^{13}C NMR spectrum of compound **1n** ($CDCl_3$, 100 MHz)



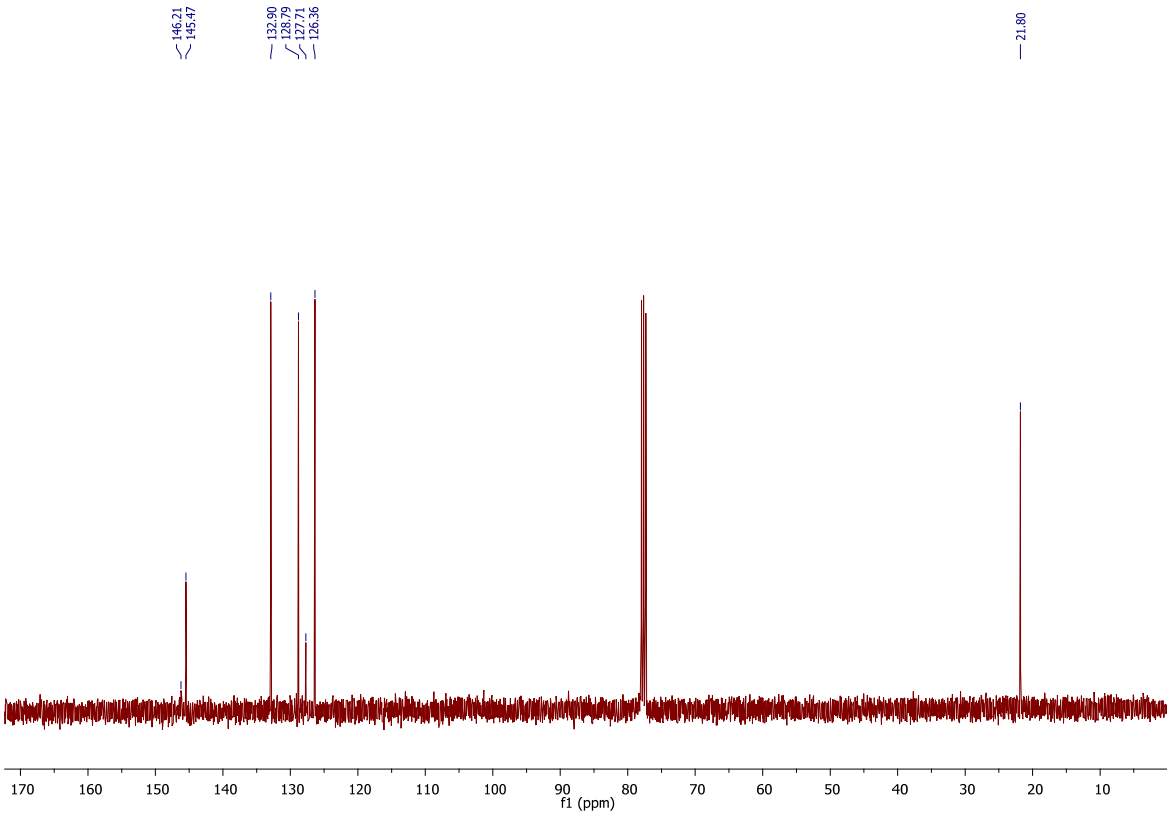
^{1}H NMR spectrum of compound **1o** ($CDCl_3$, 200 MHz)



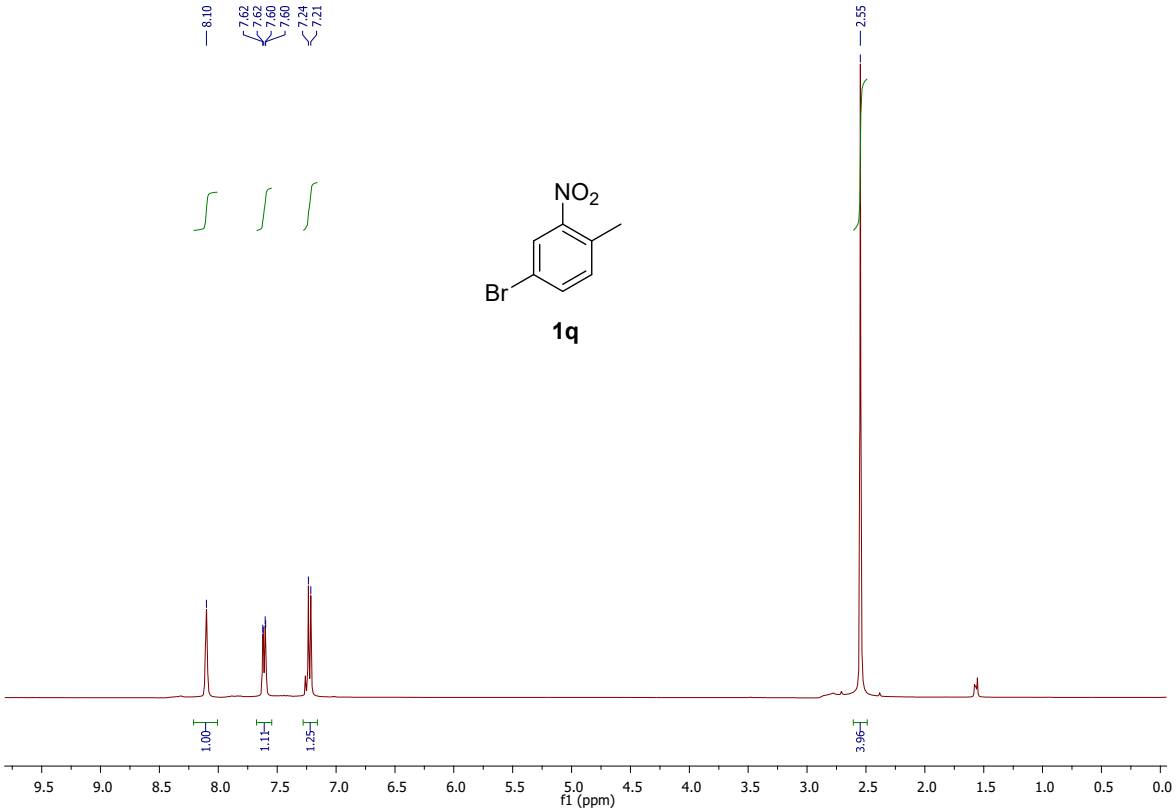
^{13}C NMR spectrum of compound **1o** ($CDCl_3$, 50 MHz)



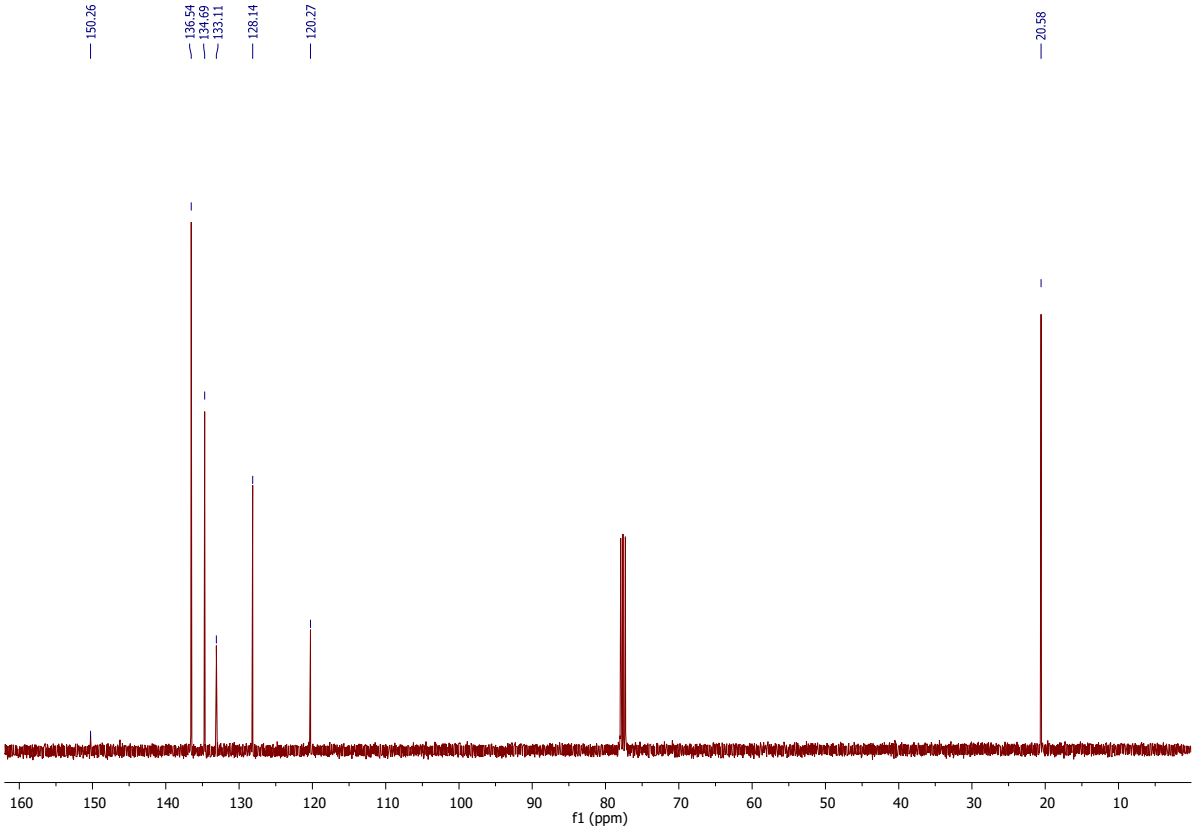
^{1}H NMR spectrum of compound **1p**. ($CDCl_3$, 400 MHz)



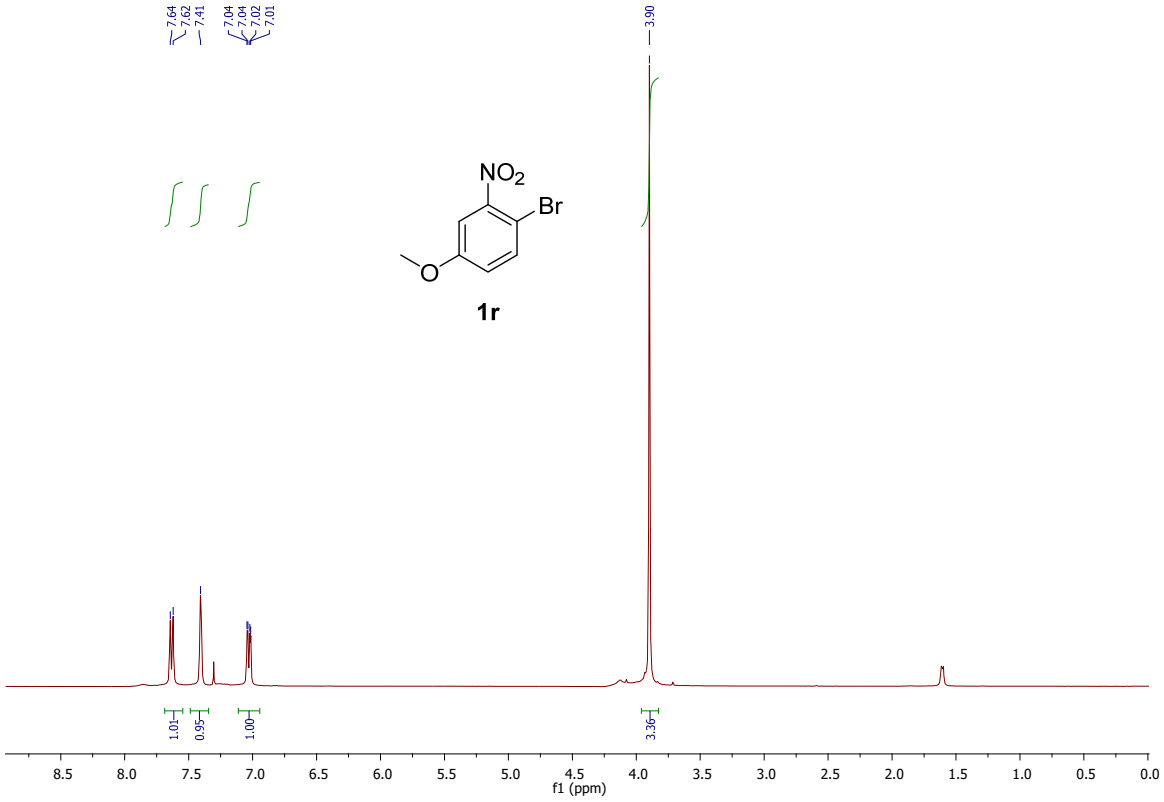
^{13}C NMR spectrum of compound **1p**. ($CDCl_3$, 100 MHz)



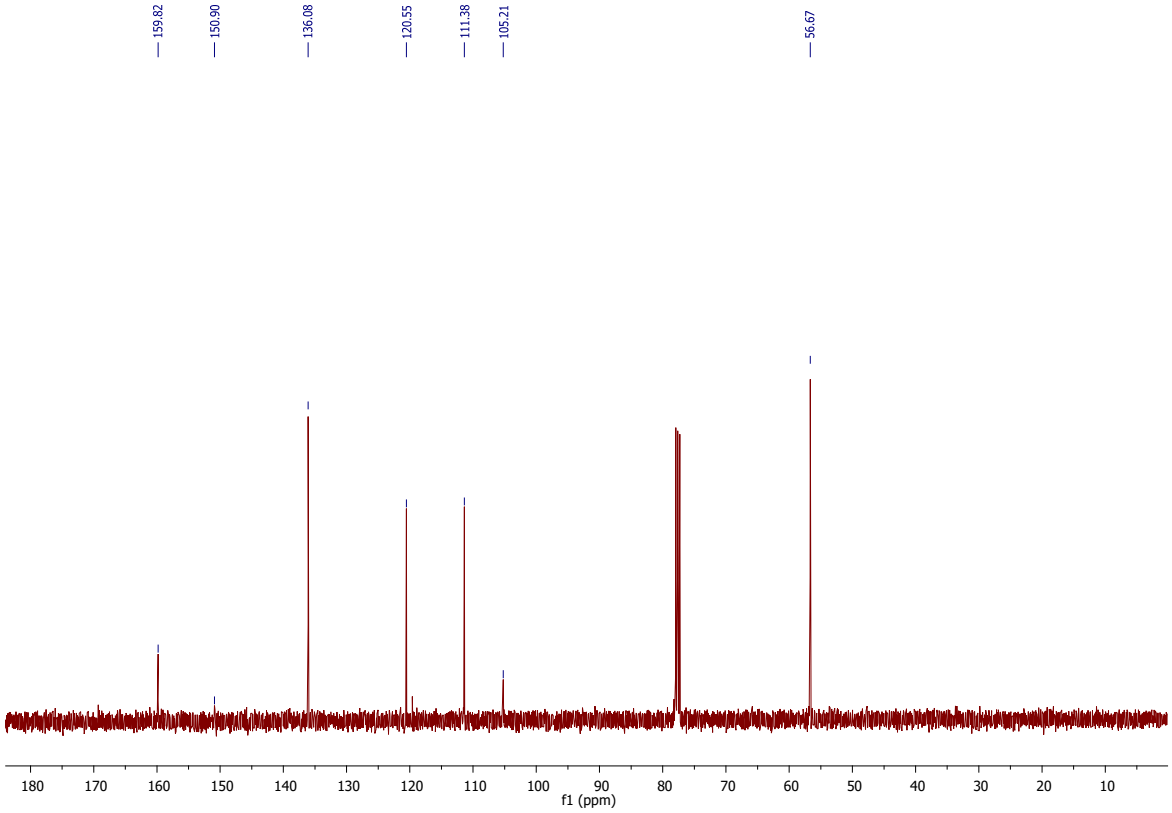
^{1}H NMR spectrum of compound **1q** ($CDCl_3$, 400 MHz)



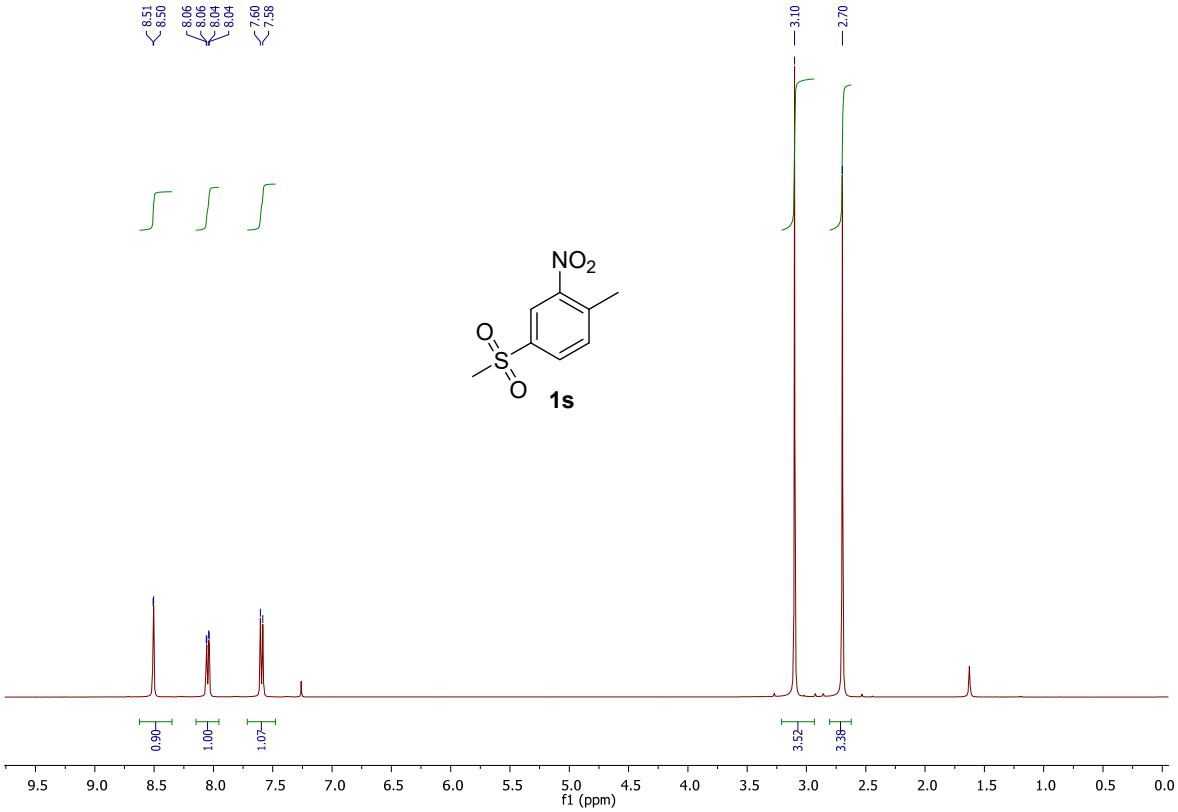
^{13}C NMR spectrum of compound **1q** ($CDCl_3$, 100 MHz)



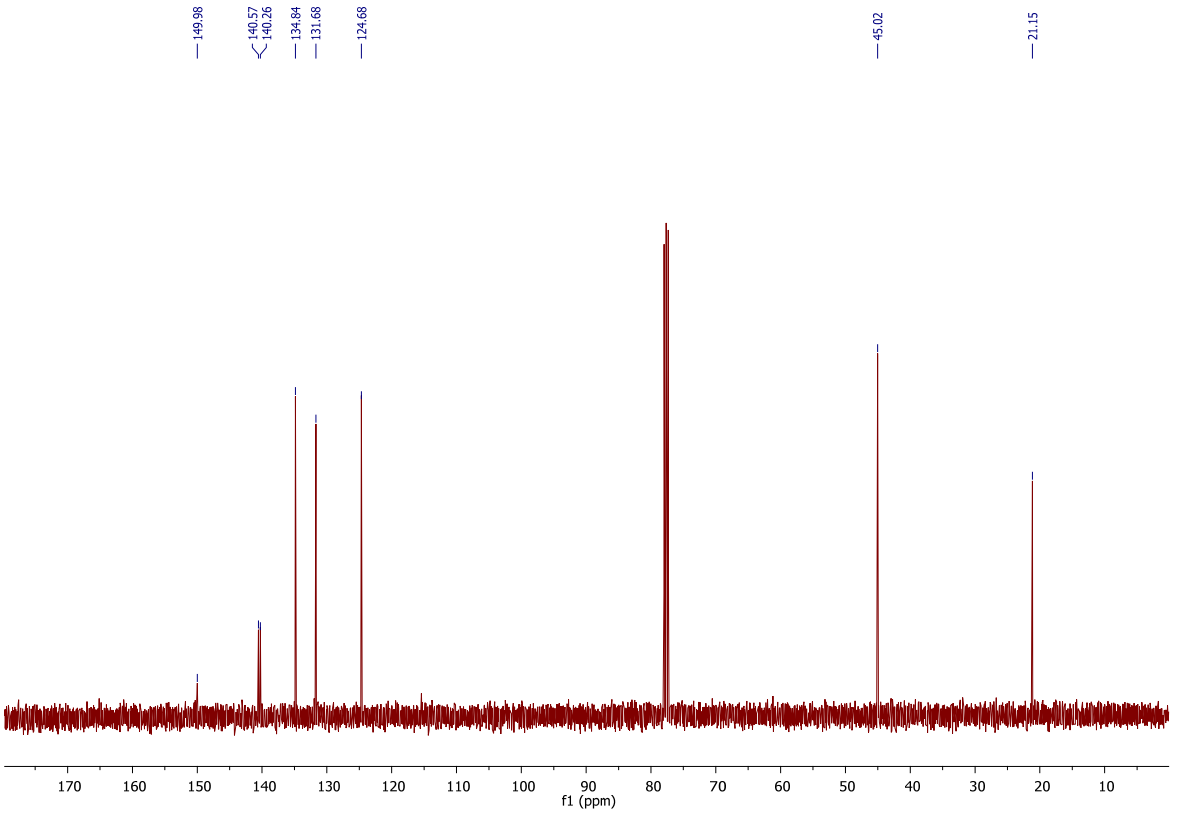
^{1}H NMR spectrum of compound **1r** ($CDCl_3$, 400 MHz)



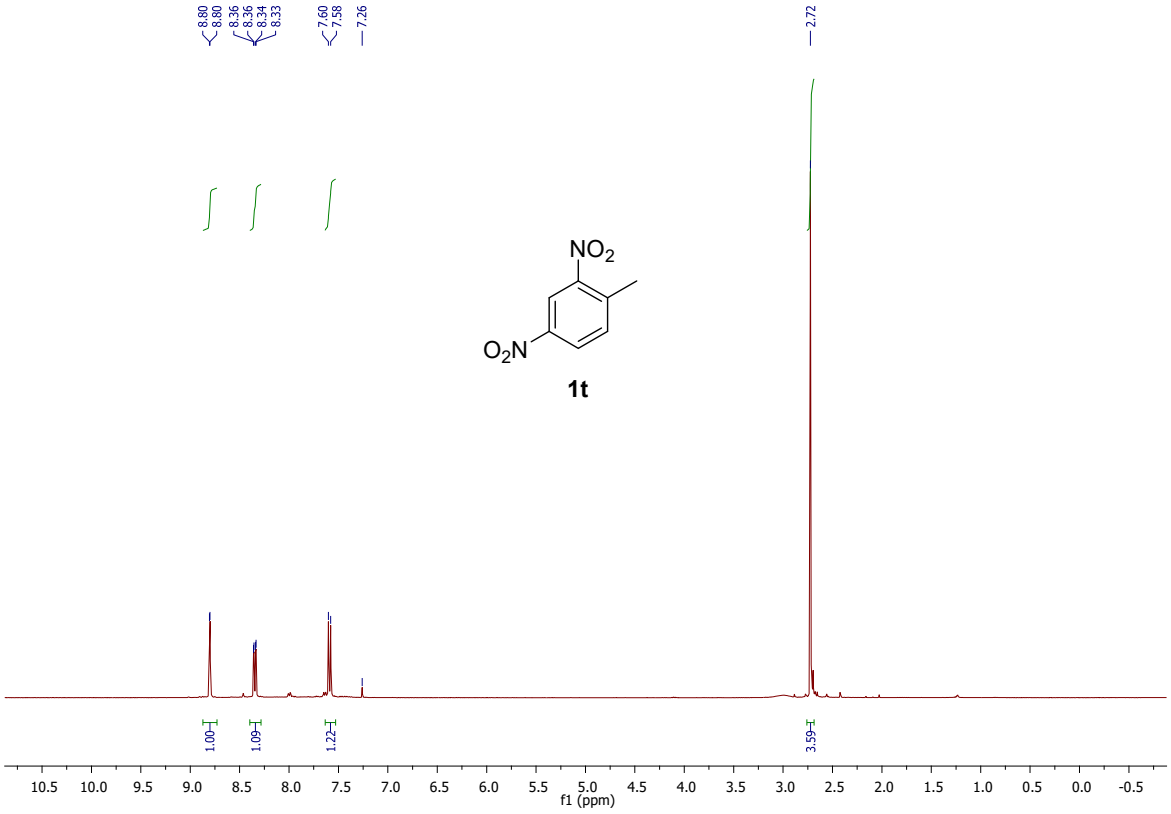
^{13}C NMR spectrum of compound **1r** ($CDCl_3$, 100 MHz)



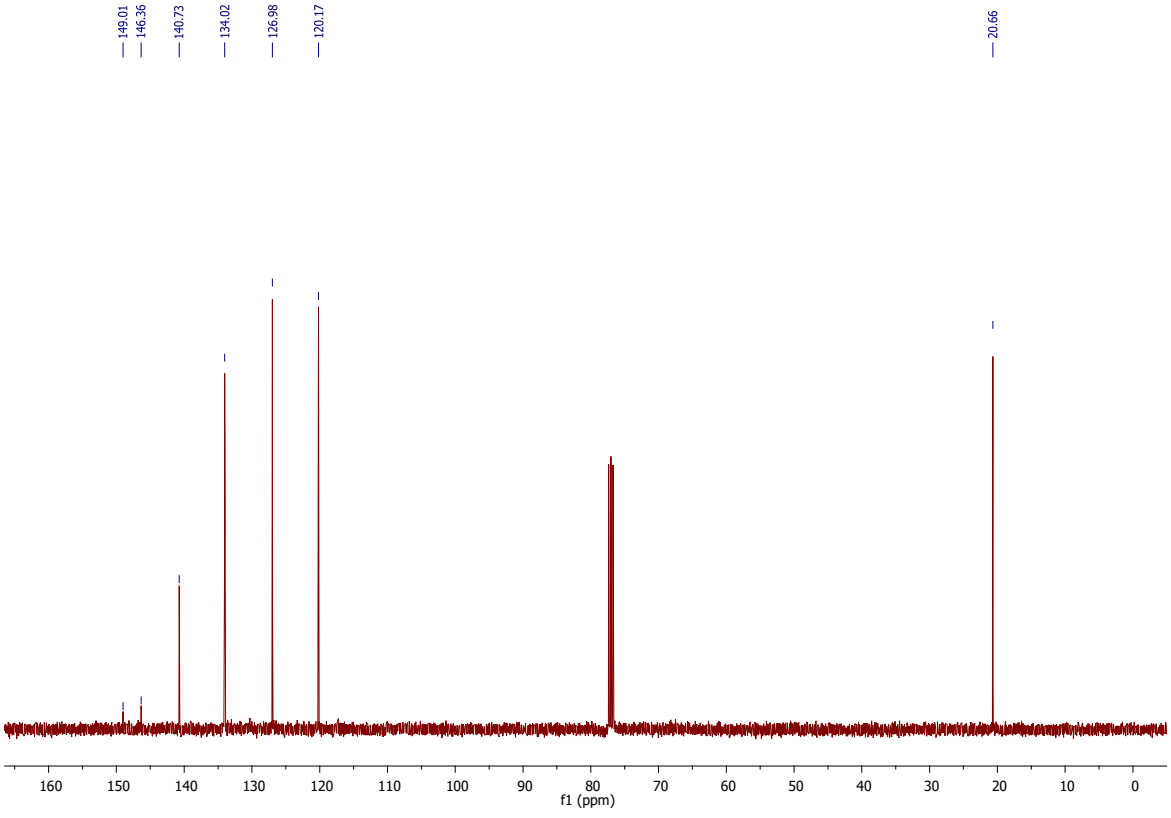
^{1}H NMR spectrum of compound **1s** ($CDCl_3$, 400 MHz)



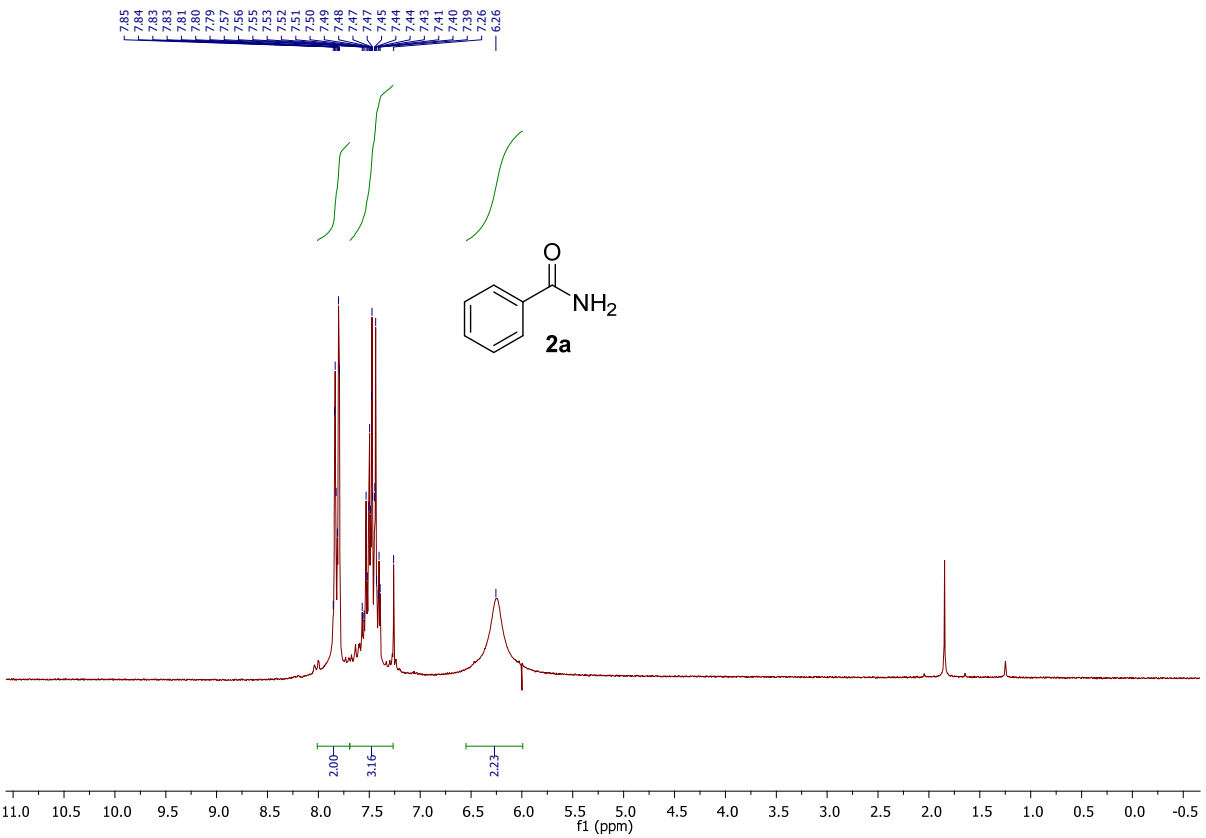
^{13}C NMR spectrum of compound **1s** ($CDCl_3$, 100 MHz)



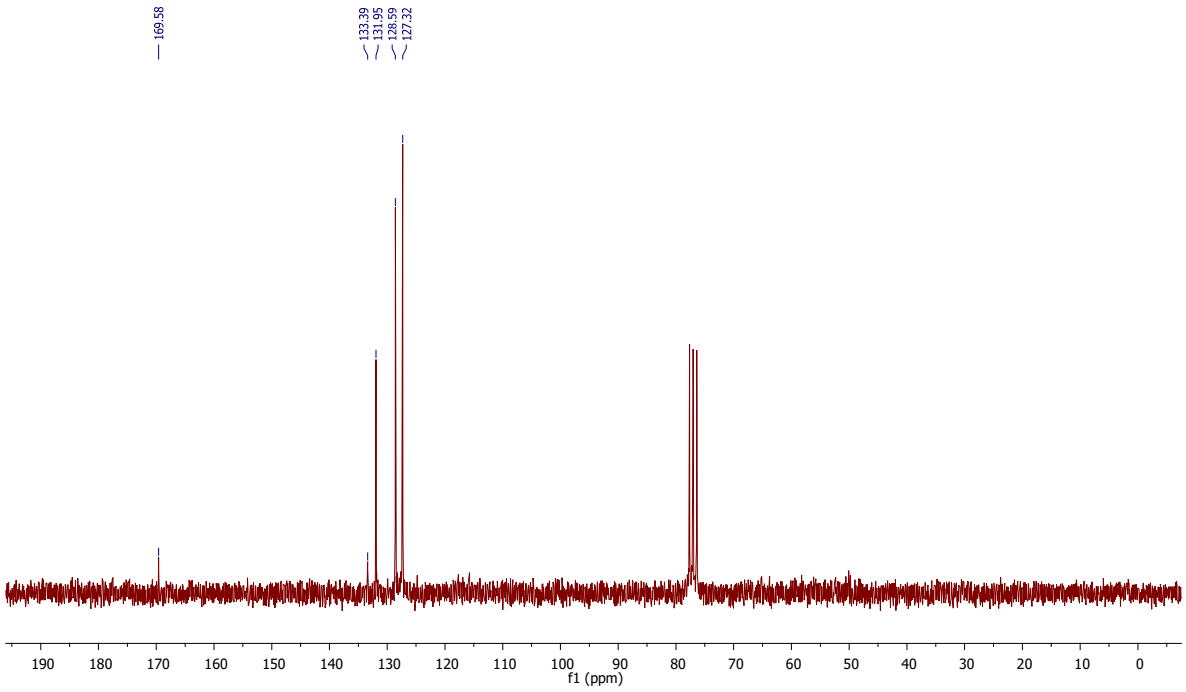
^{1}H NMR spectrum of compound **1t** ($CDCl_3$, 400 MHz)



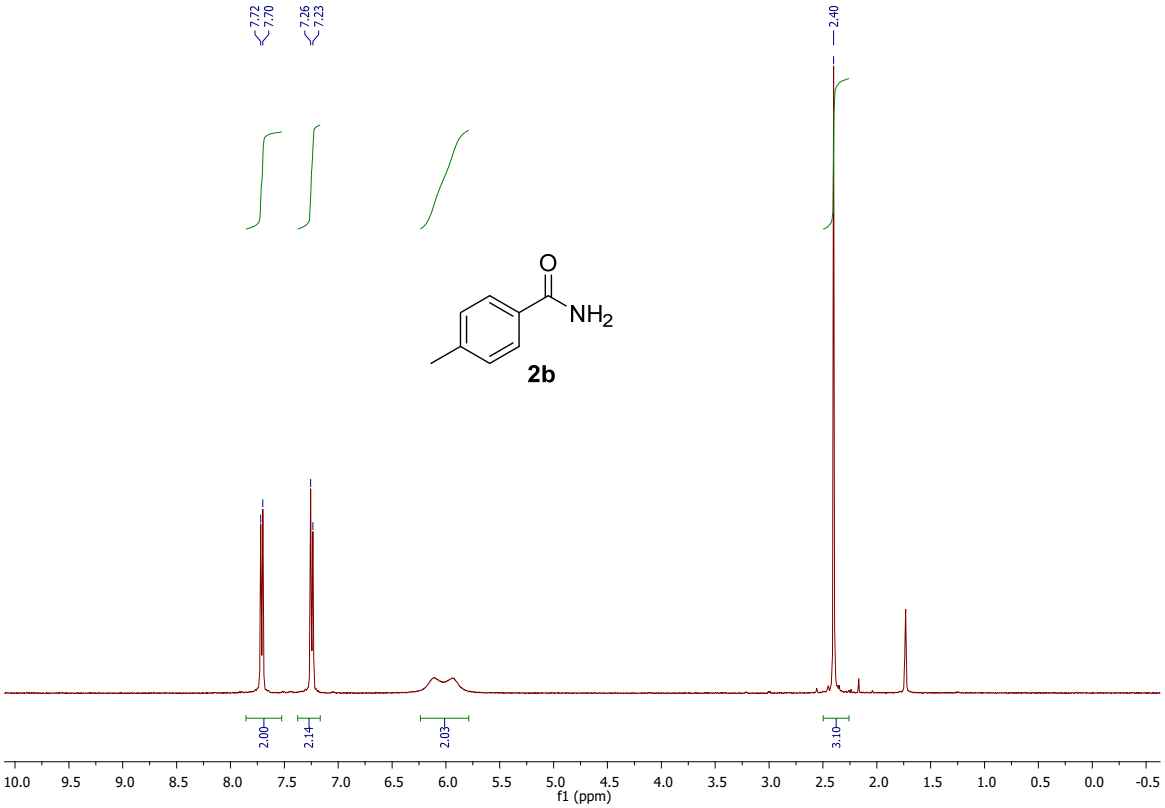
^{13}C NMR spectrum of compound **1t** ($CDCl_3$, 100 MHz)



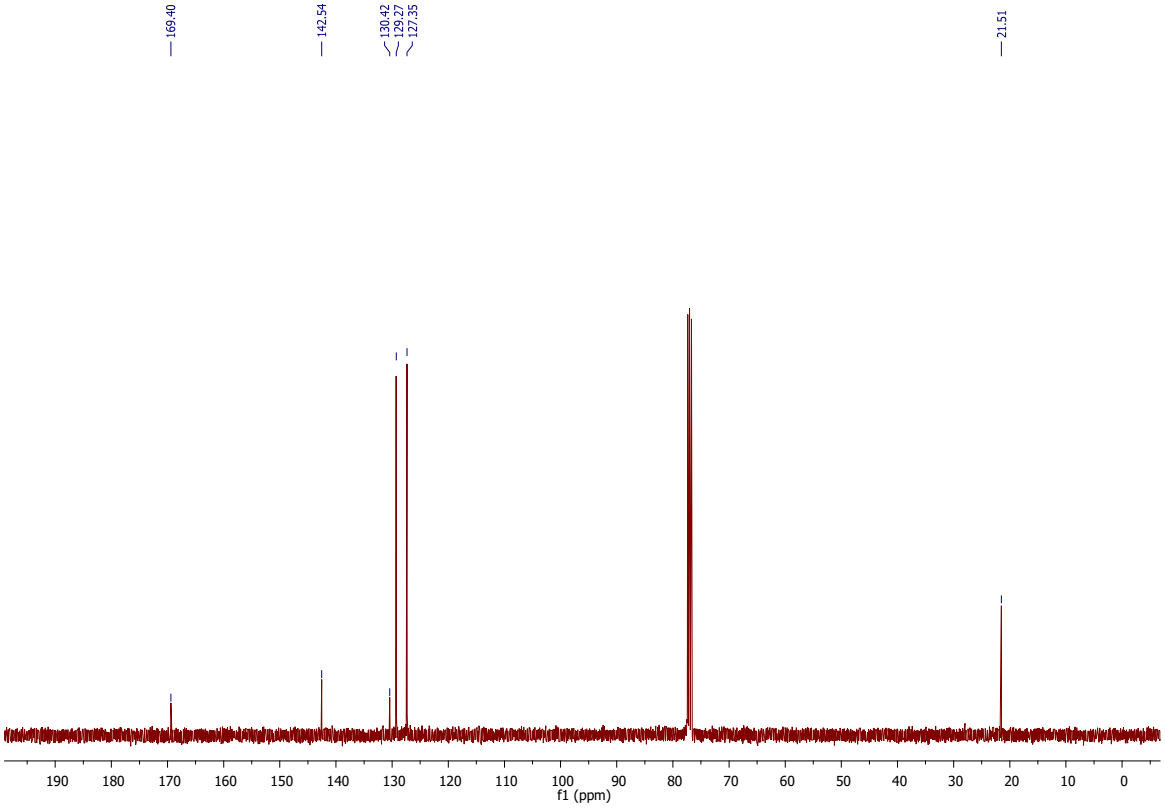
^{1}H NMR spectrum of compound **2a** ($CDCl_3$, 200 MHz) – *Reaction conducted on a 2.0 mmol scale*



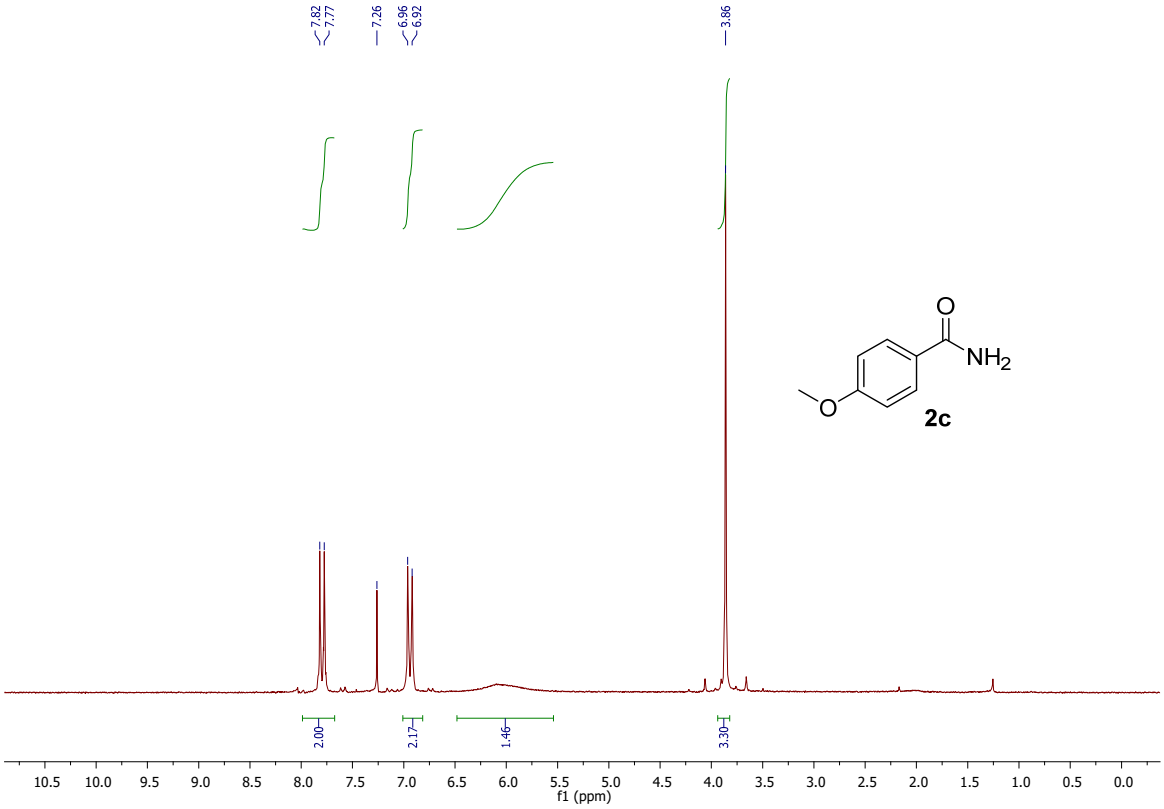
^{13}C NMR spectrum of compound **2a** ($CDCl_3$, 50 MHz) – *Reaction conducted on a 2.0 mmol scale*



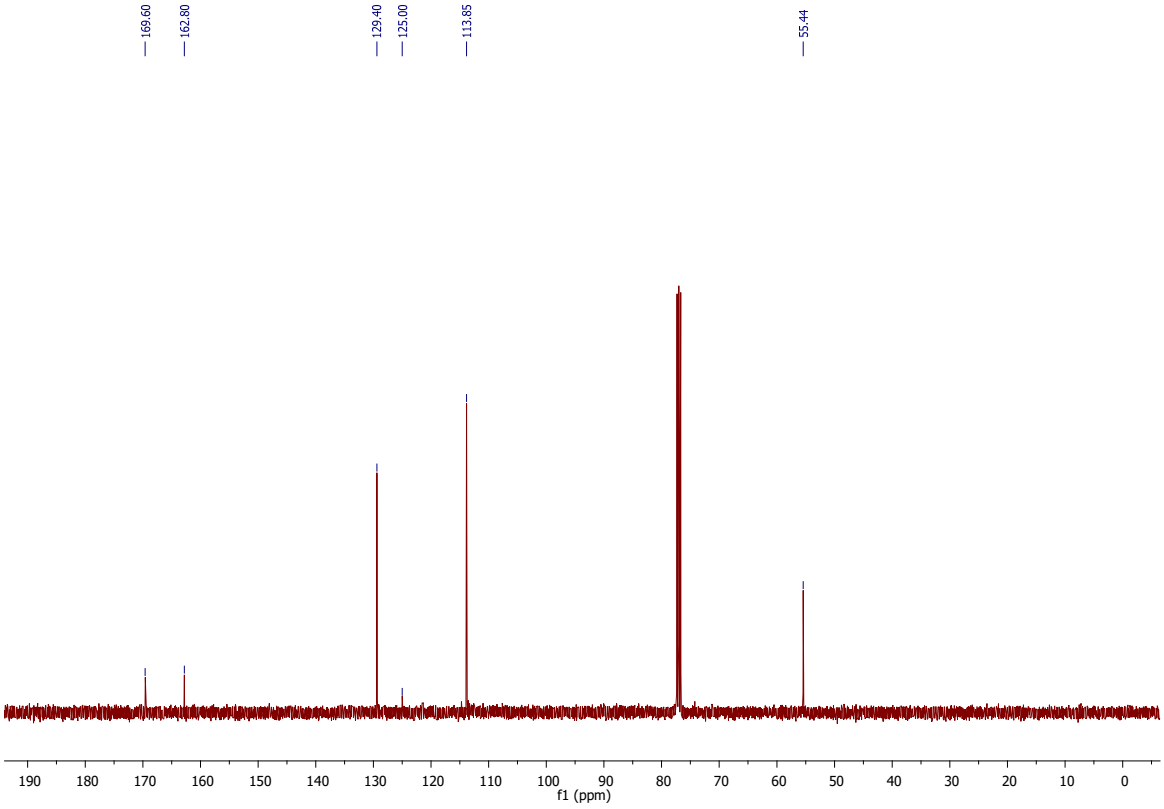
^{1}H NMR spectrum of compound **2b** ($CDCl_3$, 400 MHz) – *Reaction conducted on a 2.0 mmol scale*



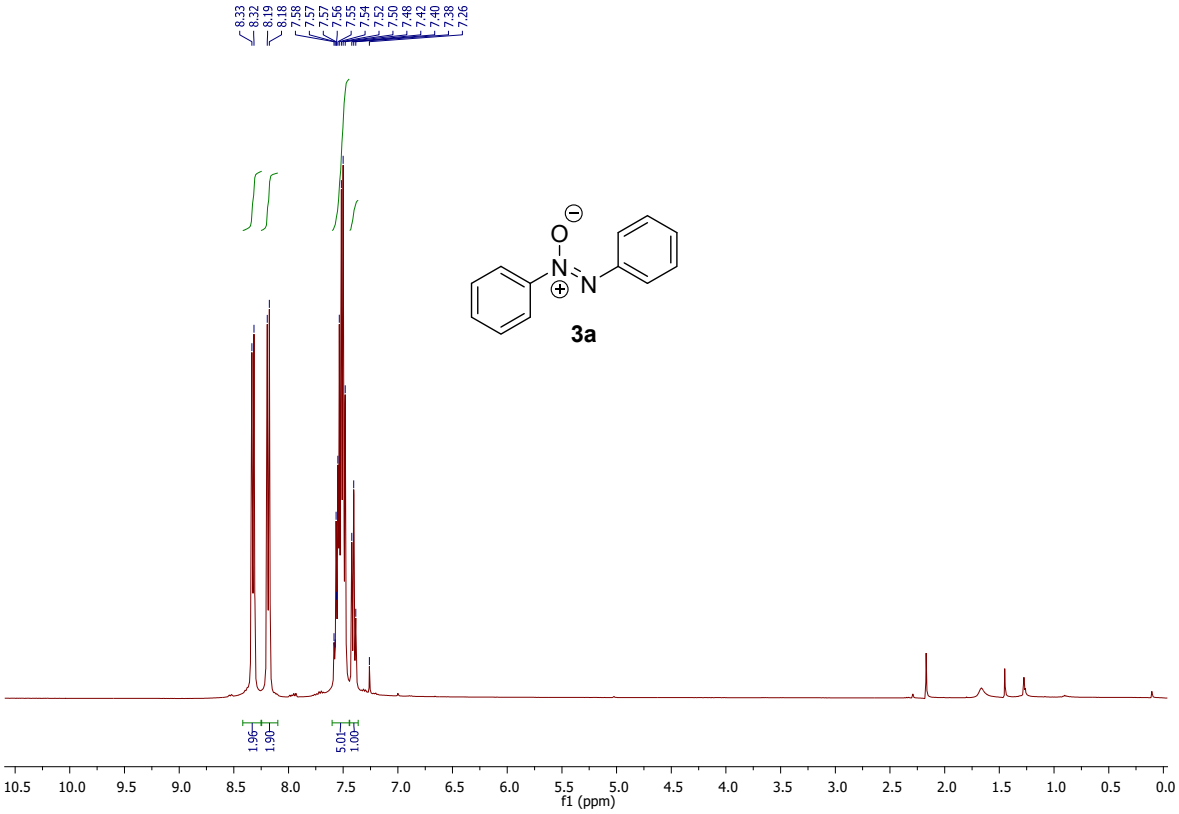
^{13}C NMR spectrum of compound **2b** ($CDCl_3$, 100 MHz) – *Reaction conducted on a 2.0 mmol scale*



^{1}H NMR spectrum of compound **2c** ($CDCl_3$, 200 MHz) – *Reaction conducted on a 2.0 mmol scale*

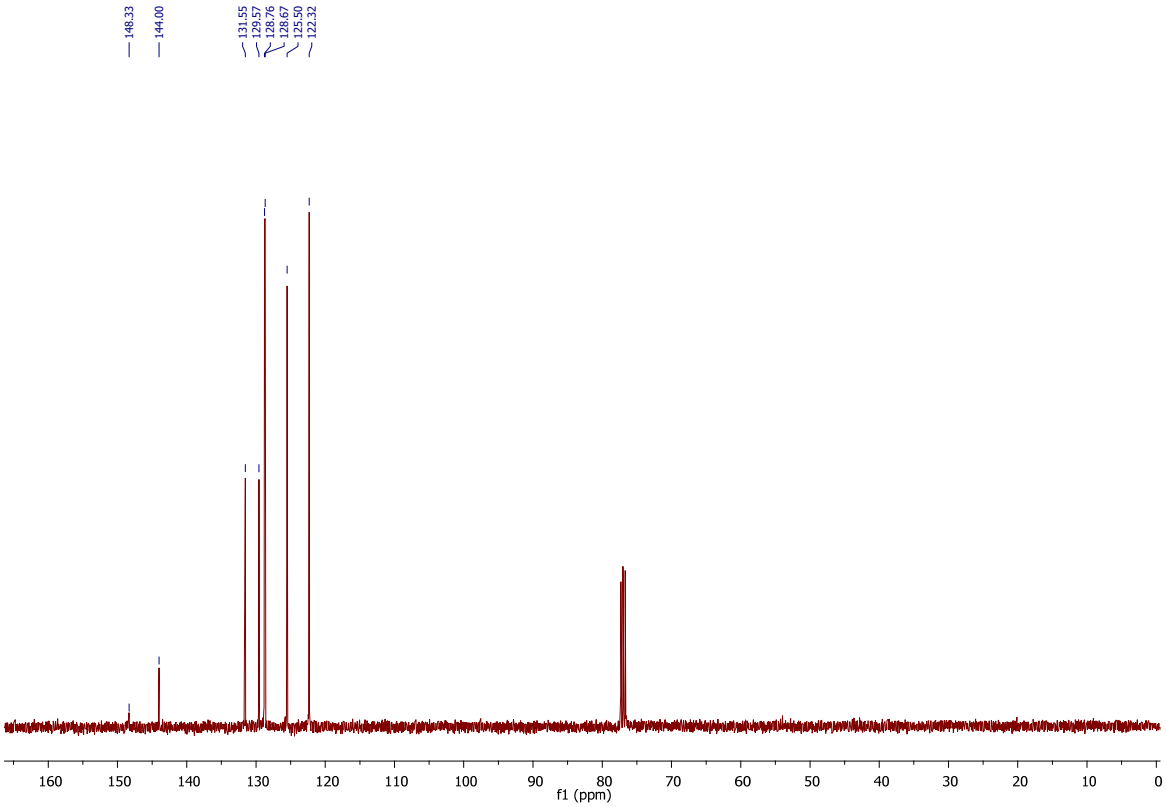


^{13}C NMR spectrum of compound **2c** ($CDCl_3$, 100 MHz) – *Reaction conducted on a 2.0 mmol scale*

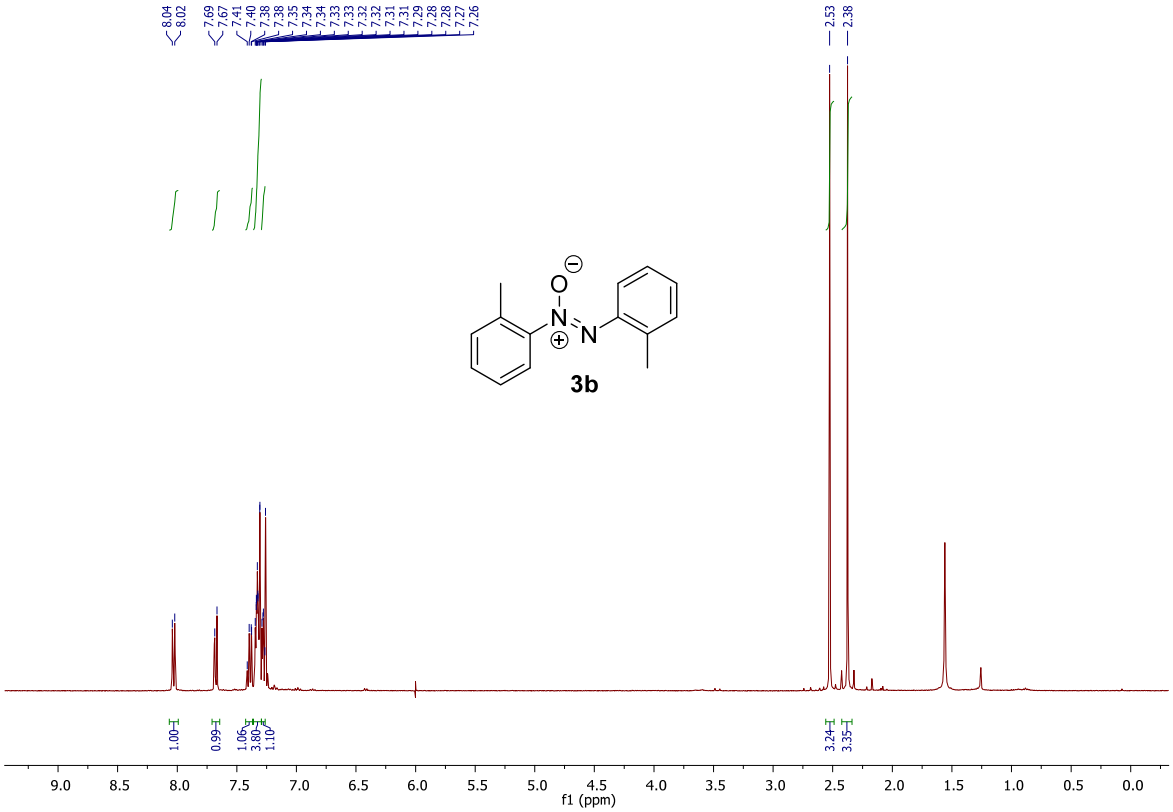


3a

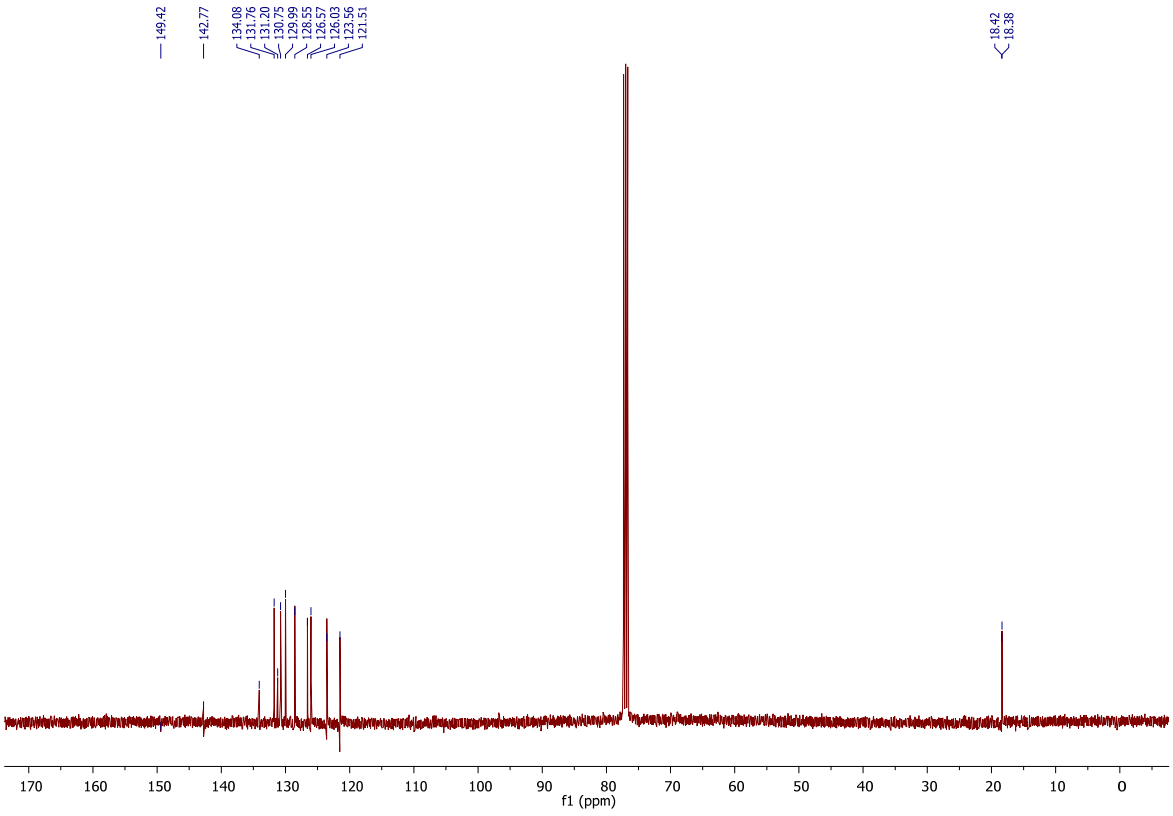
^{1}H NMR spectrum of compound **3a** ($CDCl_3$, 400 MHz) – *Reaction conducted on a 2.0 mmol scale*



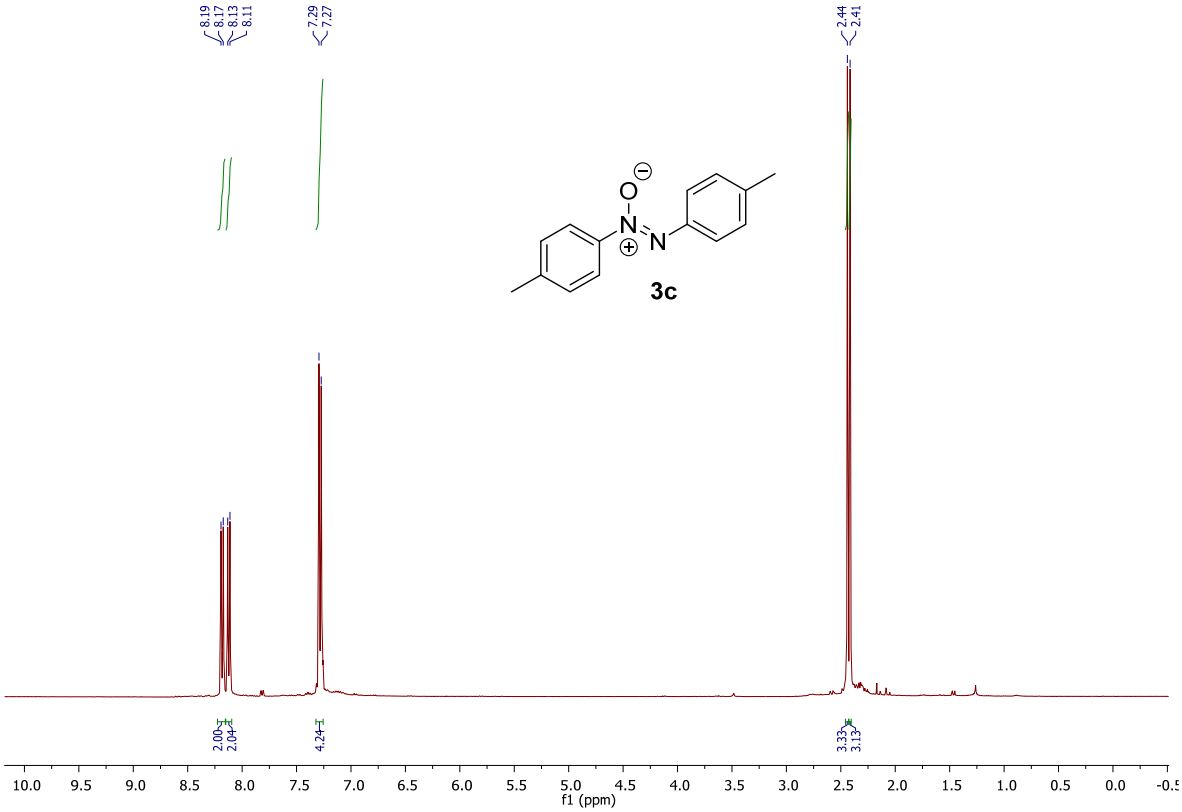
^{13}C NMR spectrum of compound **3a** ($CDCl_3$, 100 MHz) – *Reaction conducted on a 2.0 mmol scale*



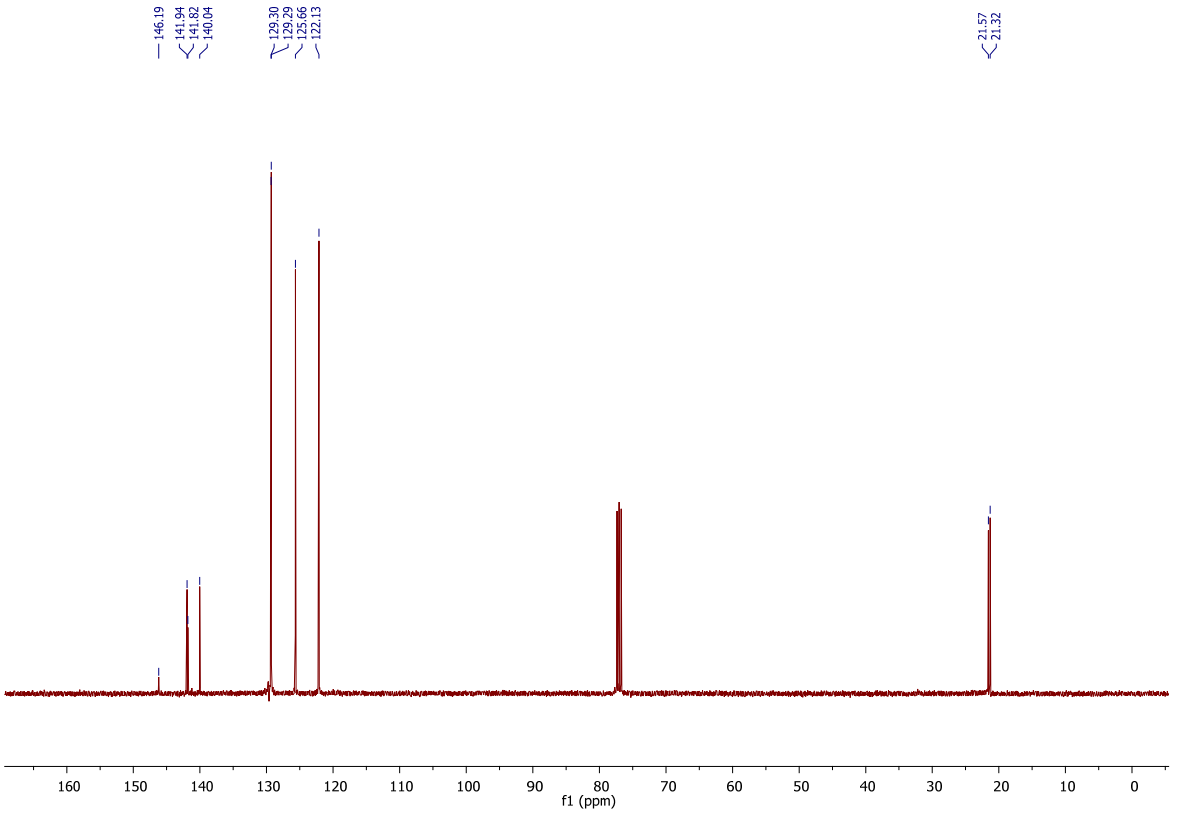
^{1}H NMR spectrum of compound **3b** ($CDCl_3$, 400 MHz)



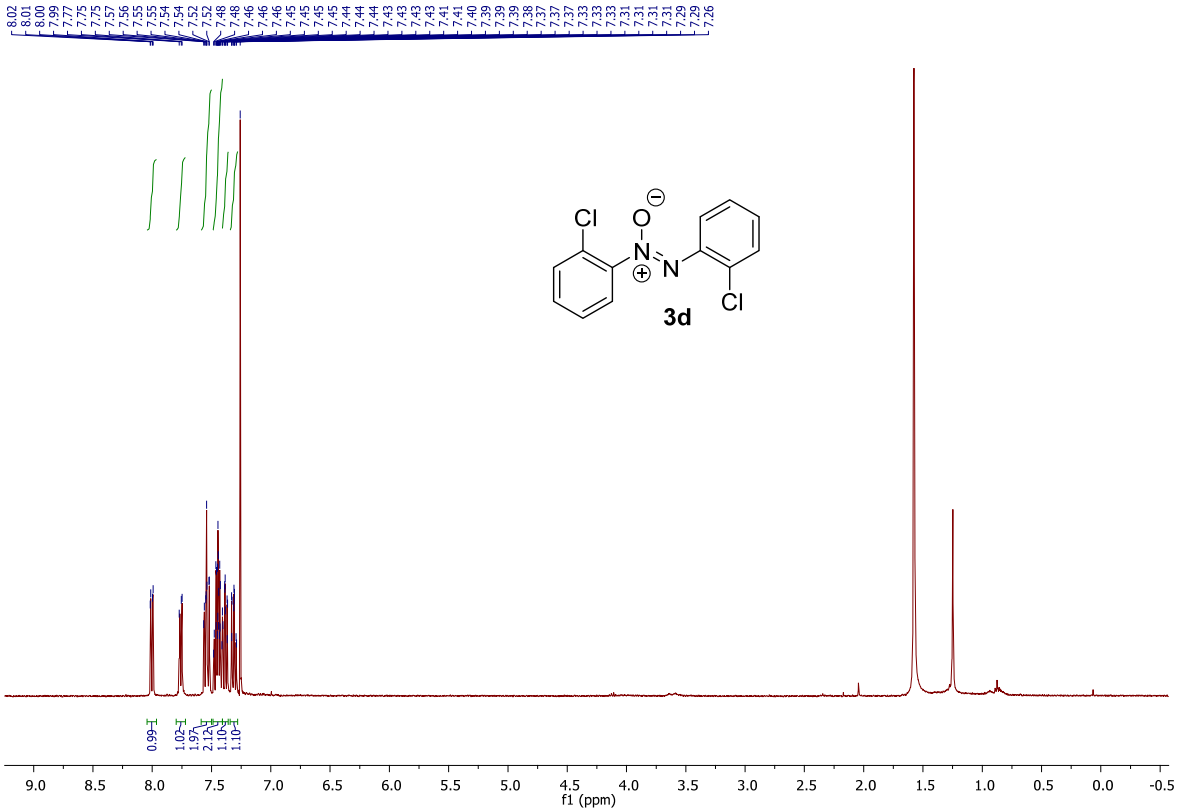
^{13}C NMR spectrum of compound **3b** ($CDCl_3$, 100 MHz)



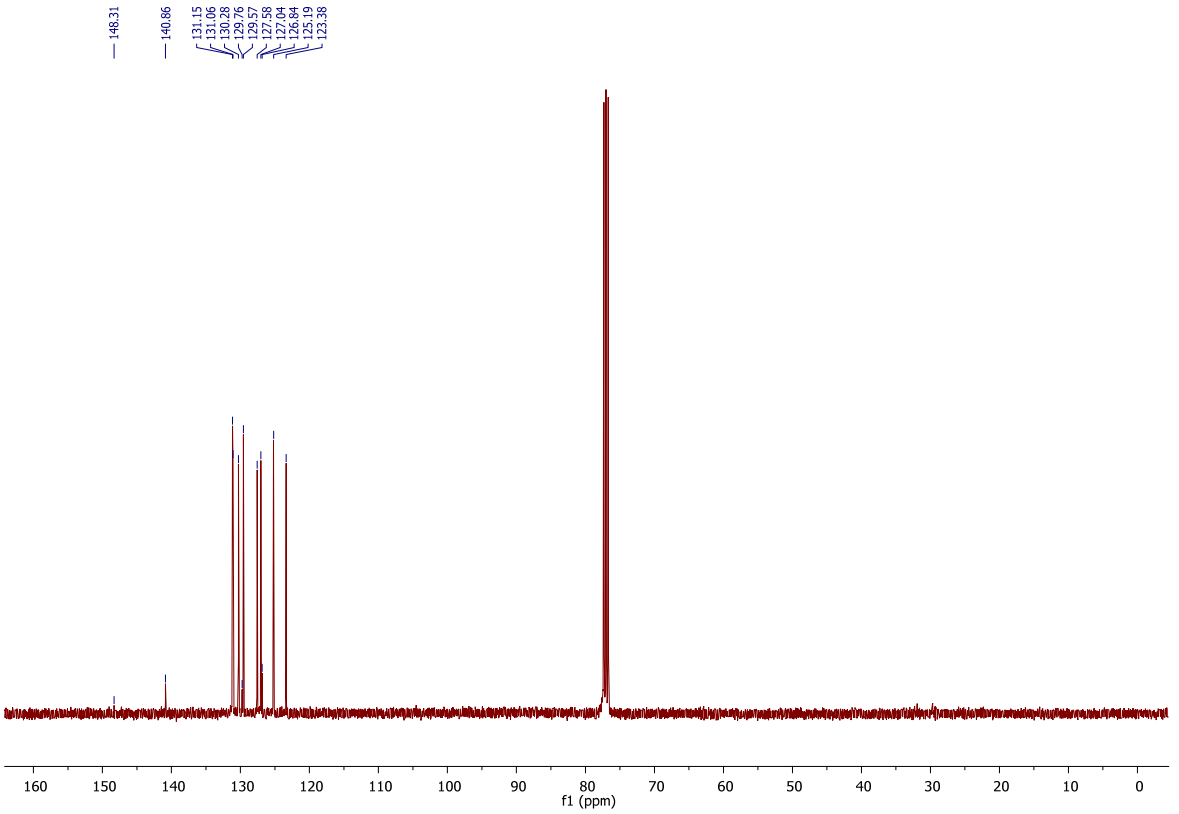
^{1}H NMR spectrum of compound **3c** ($CDCl_3$, 400 MHz)



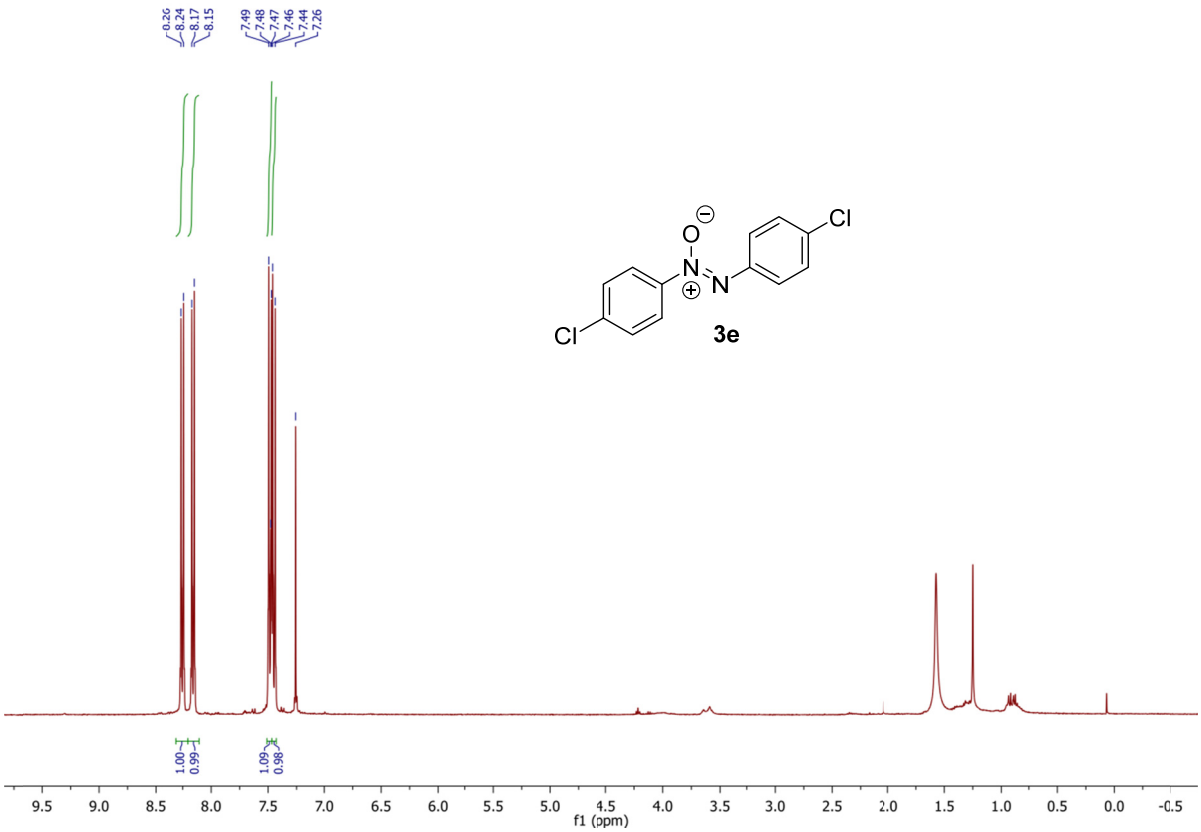
^{13}C NMR spectrum of compound **3c** ($CDCl_3$, 100 MHz)



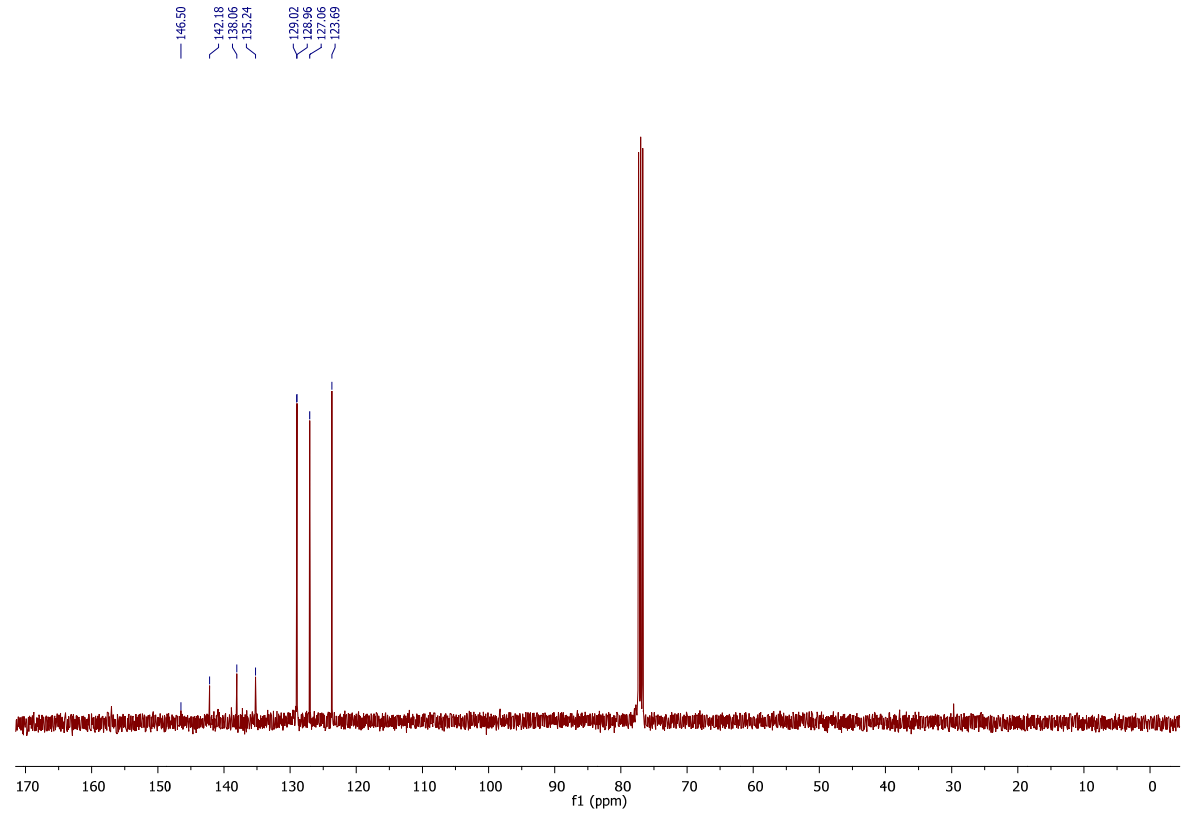
^{1}H NMR spectrum of compound **3d** ($CDCl_3$, 400 MHz)



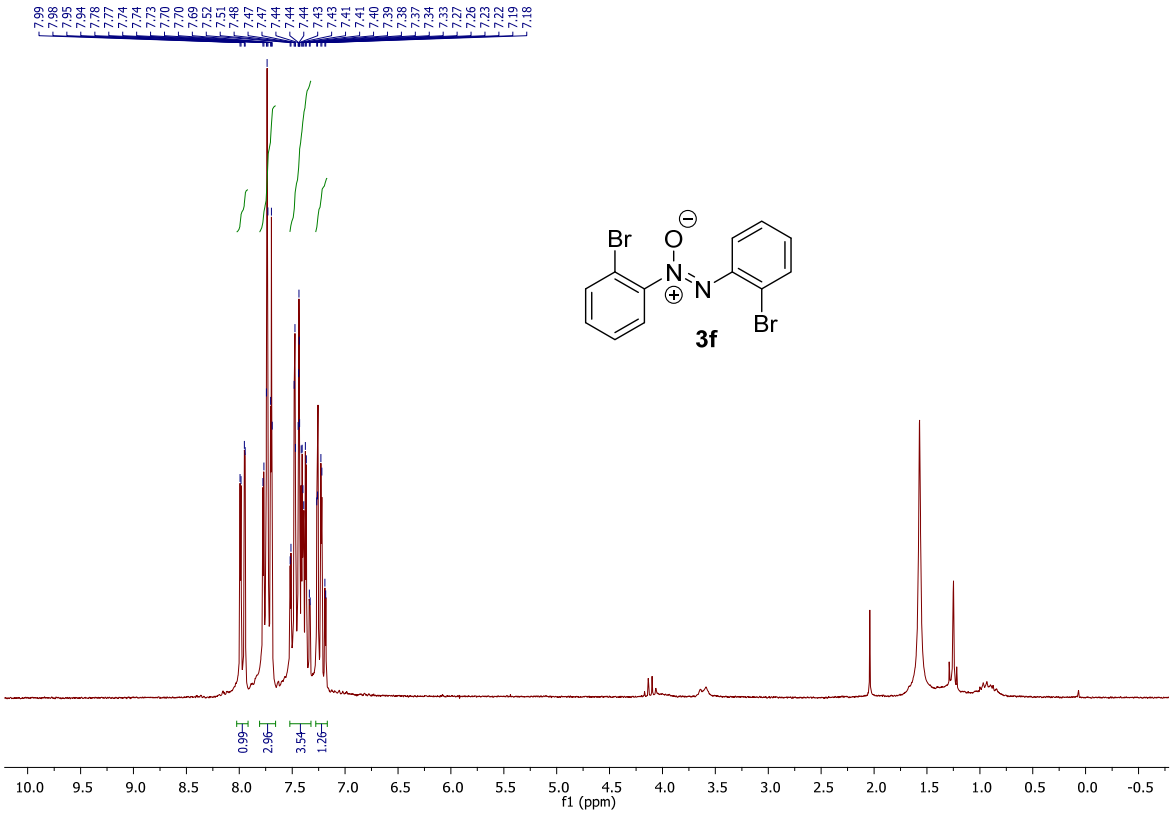
^{13}C NMR spectrum of compound **3d** ($CDCl_3$, 100 MHz)



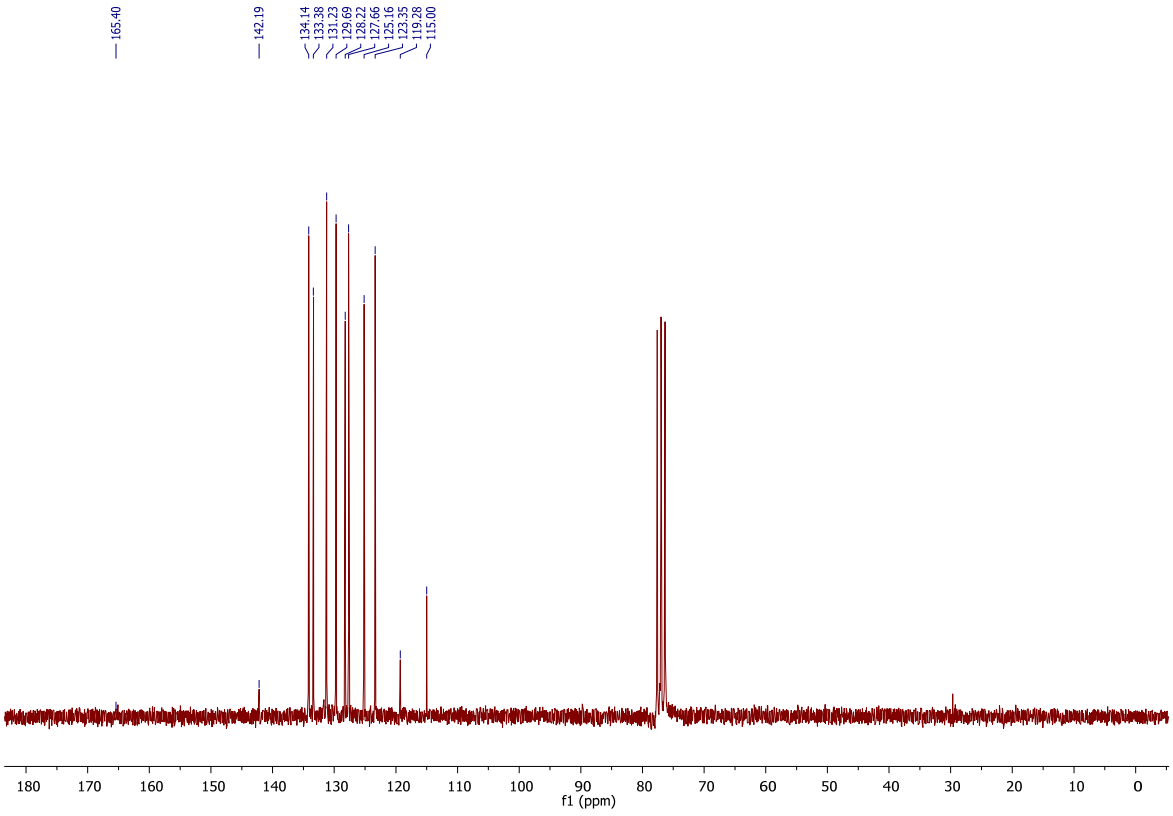
^{1}H NMR spectrum of compound **3e** ($CDCl_3$, 400 MHz)



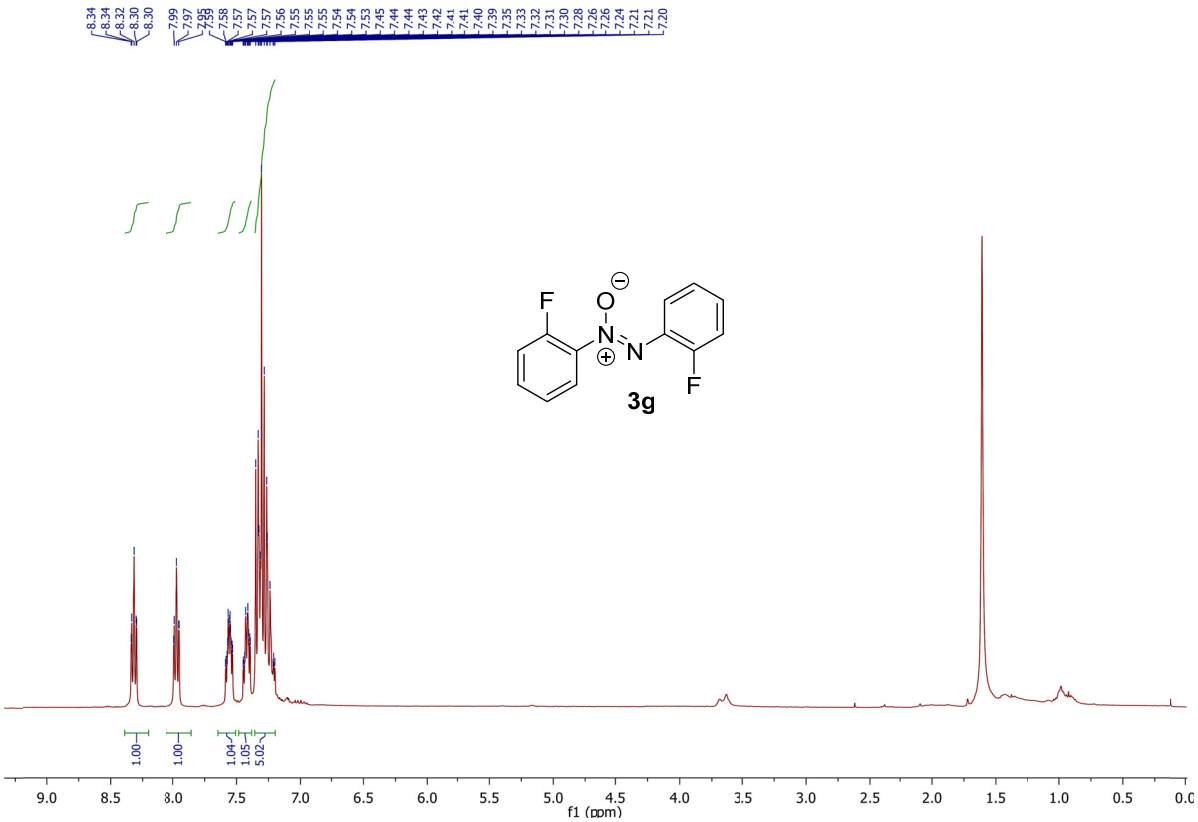
^{13}C NMR spectrum of compound **3e** ($CDCl_3$, 100 MHz)



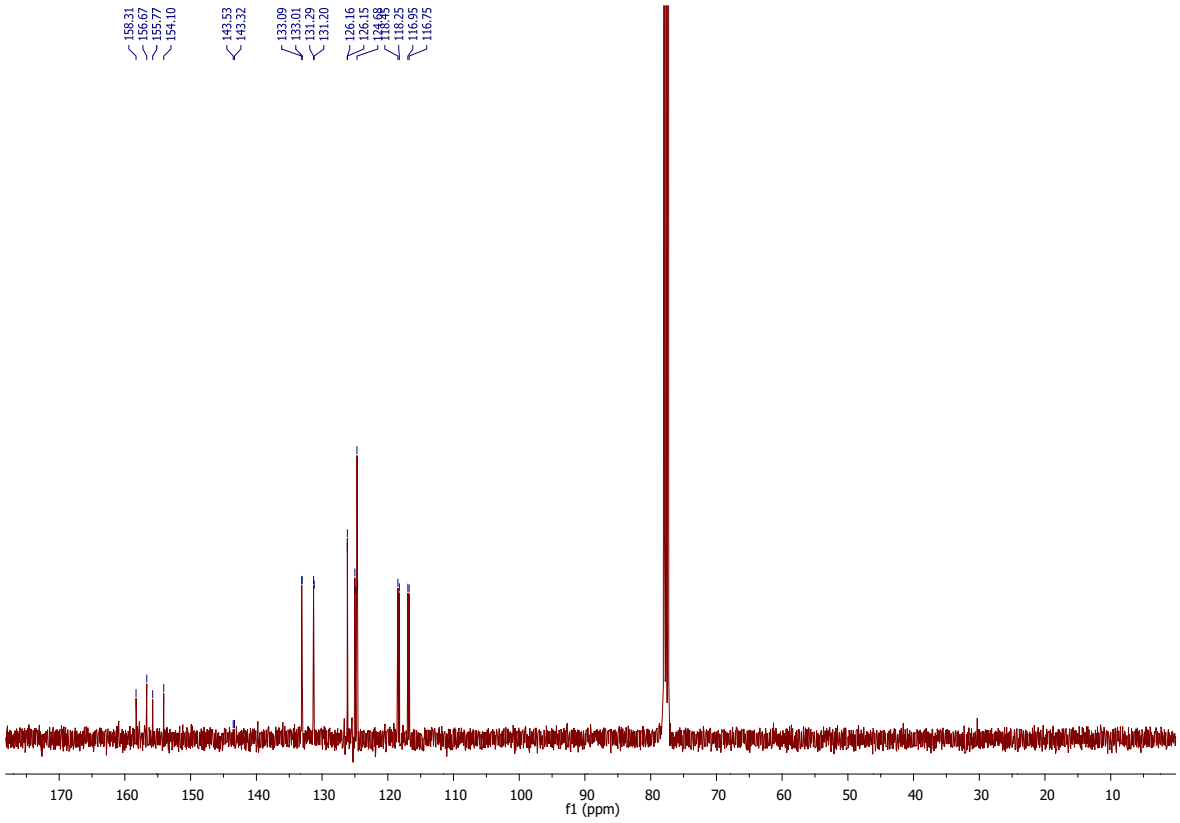
^{1}H NMR spectrum of compound **3f** ($CDCl_3$, 200 MHz)



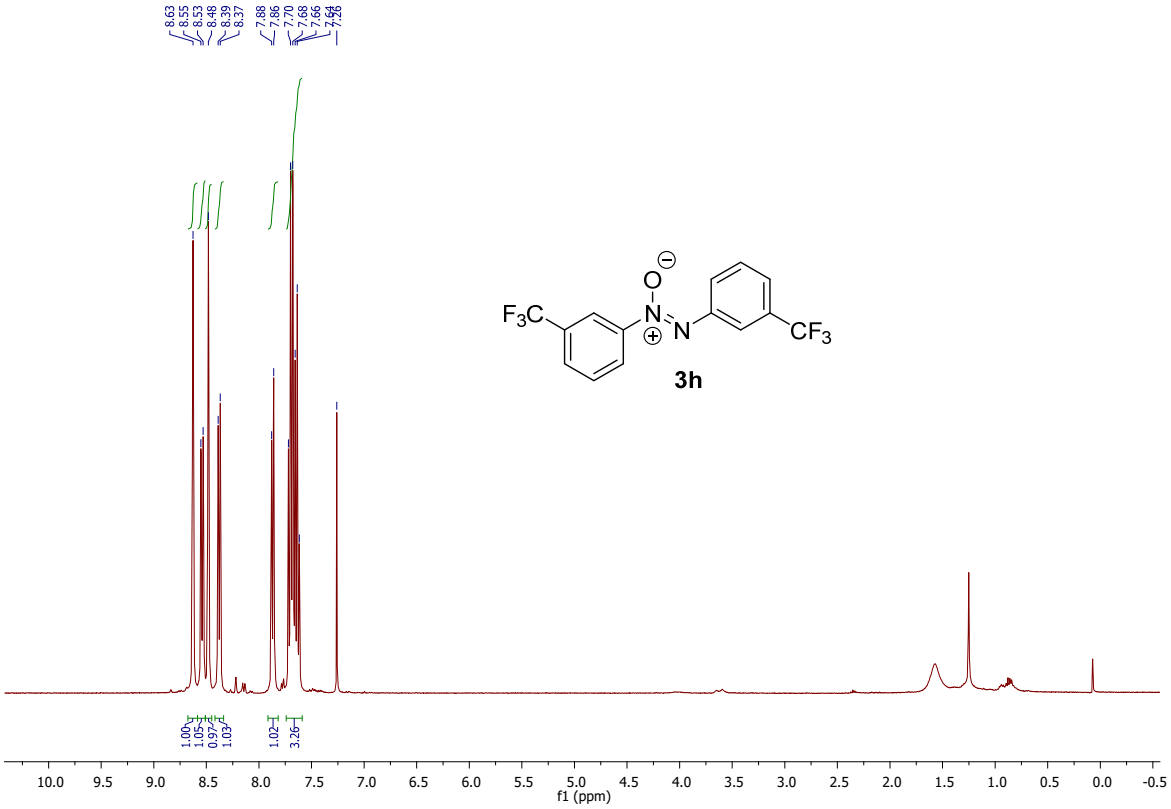
^{13}C NMR spectrum of compound **3f** ($CDCl_3$, 50 MHz)



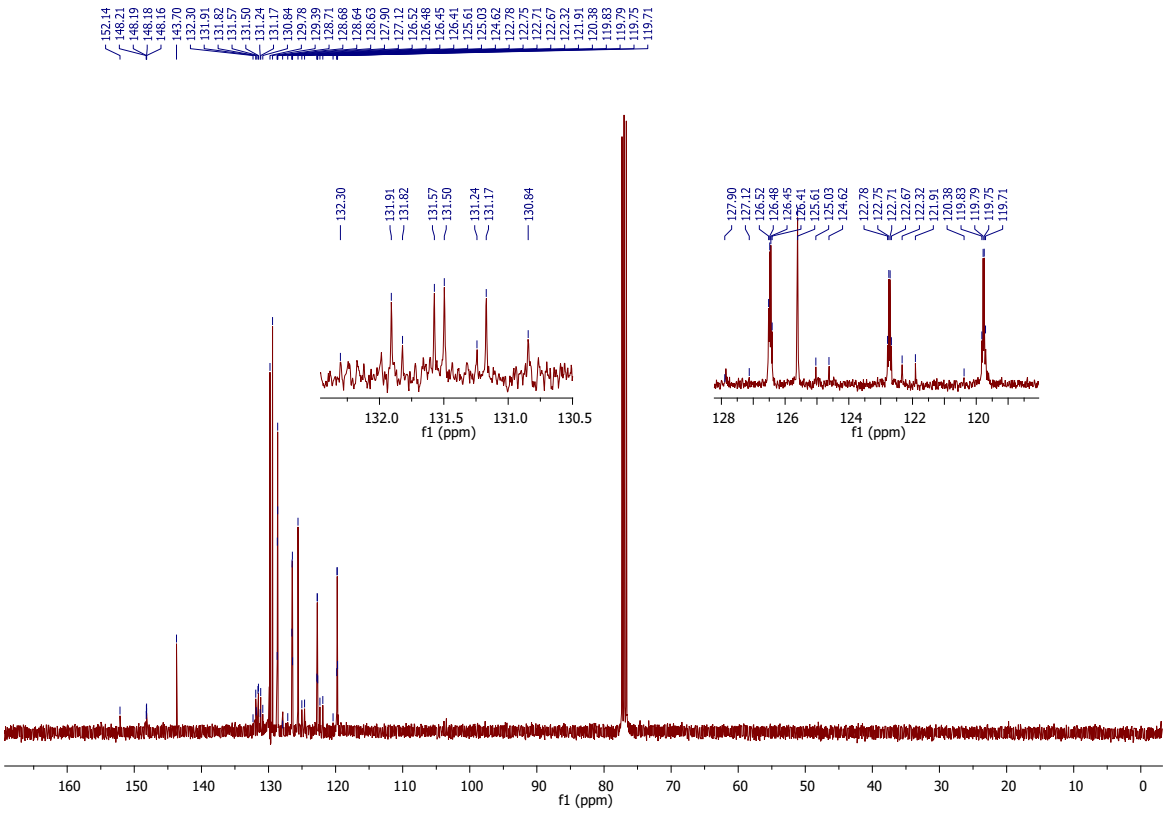
^{1}H NMR spectrum of compound **3g** ($CDCl_3$, 400 MHz)



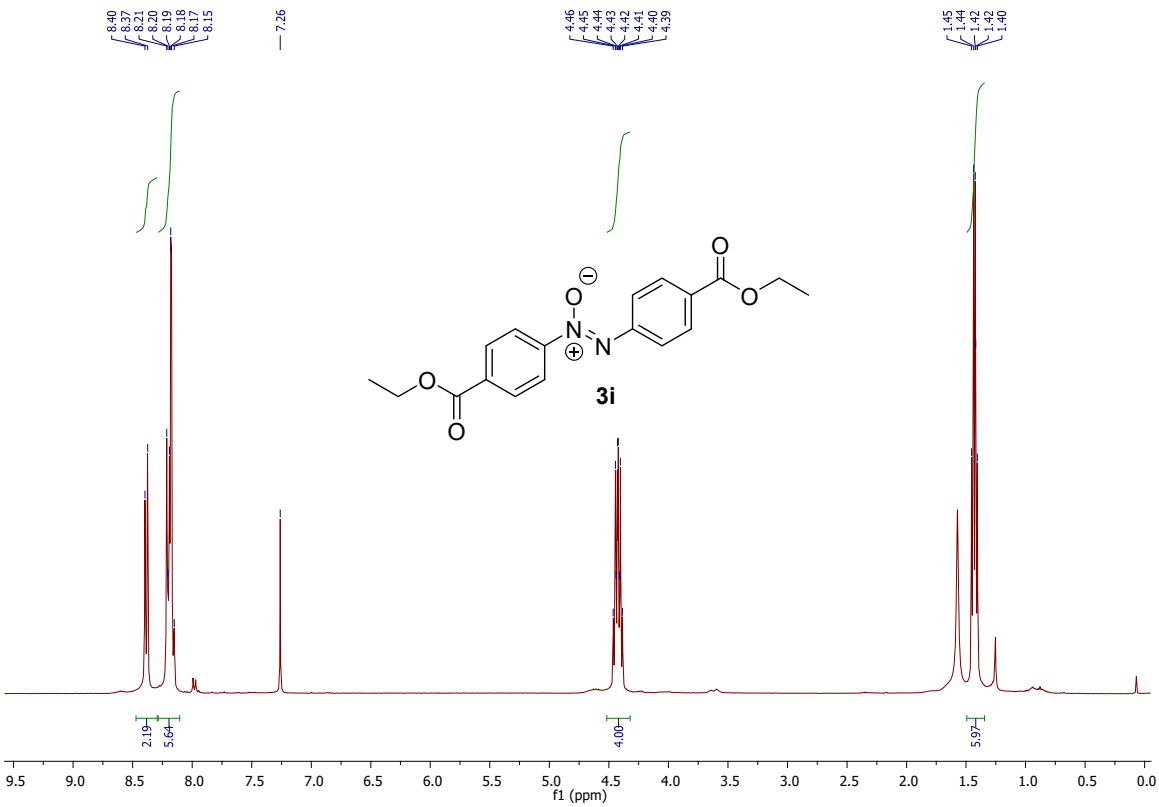
^{13}C NMR spectrum of compound **3g** ($CDCl_3$, 100 MHz)



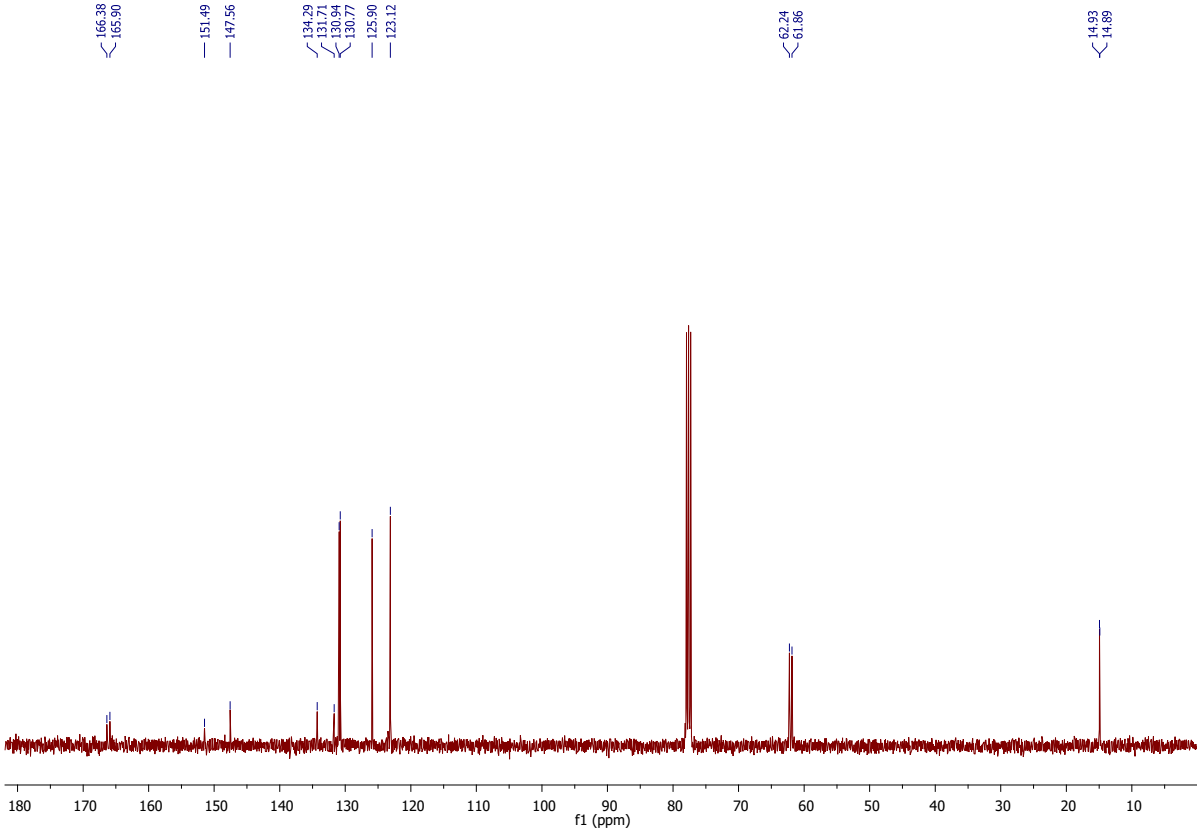
^{1}H NMR spectrum of compound **3h** ($CDCl_3$, 400 MHz) – *Reaction conducted on a 1.0 mmol scale*



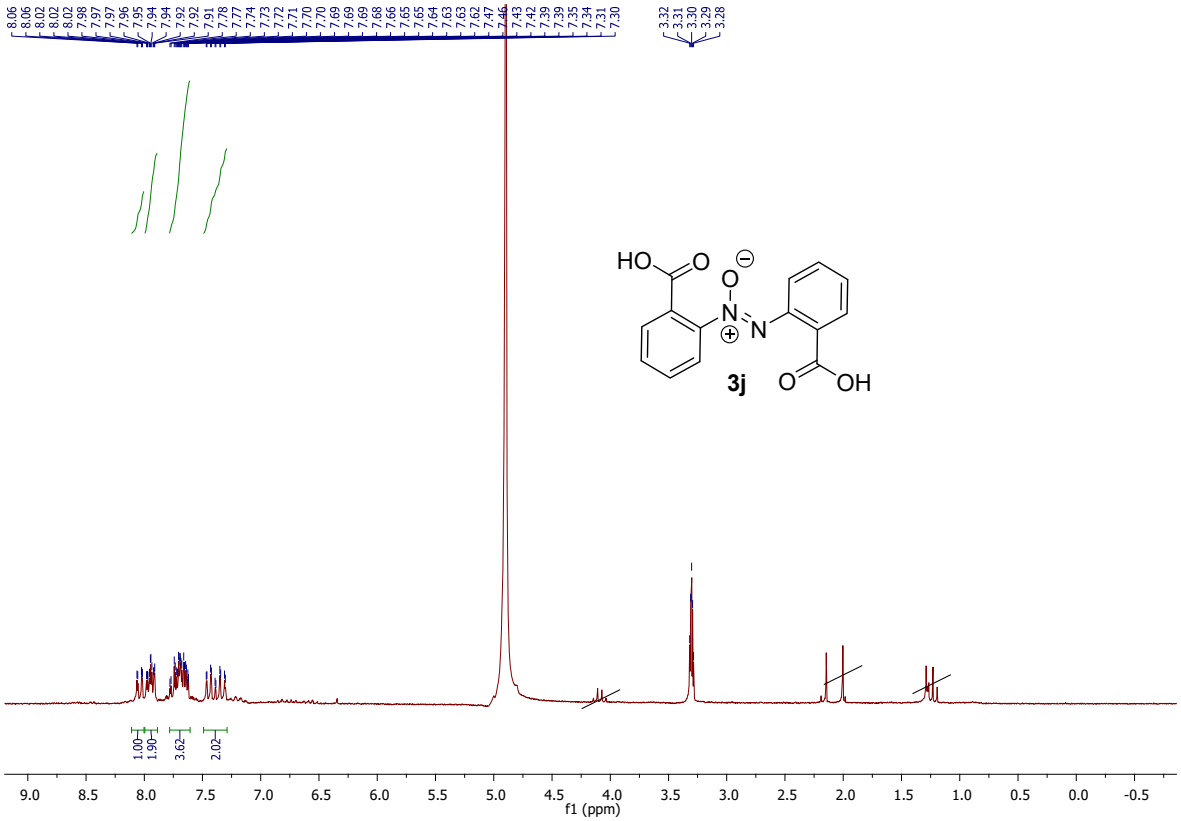
^{13}C NMR spectrum of compound **3h** ($CDCl_3$, 100 MHz) – *Reaction conducted on a 1.0 mmol scale*



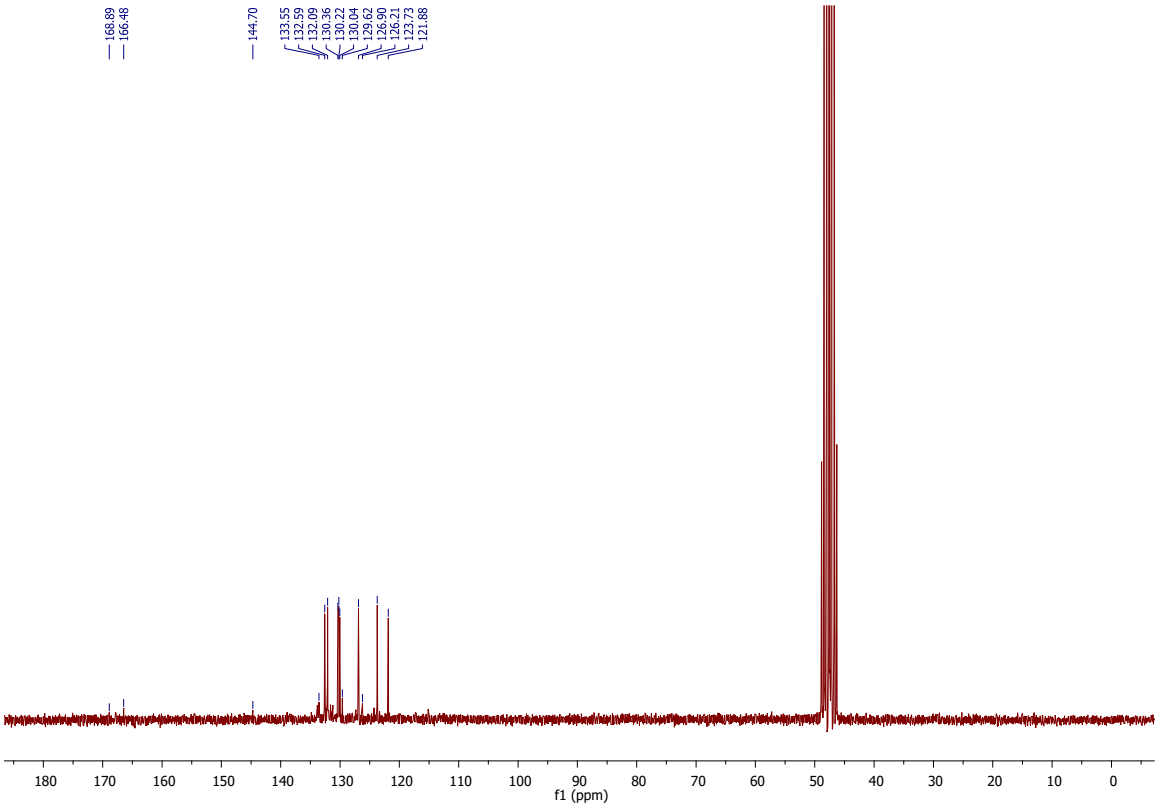
^{1}H NMR spectrum of compound **3i** ($CDCl_3$, 400 MHz)



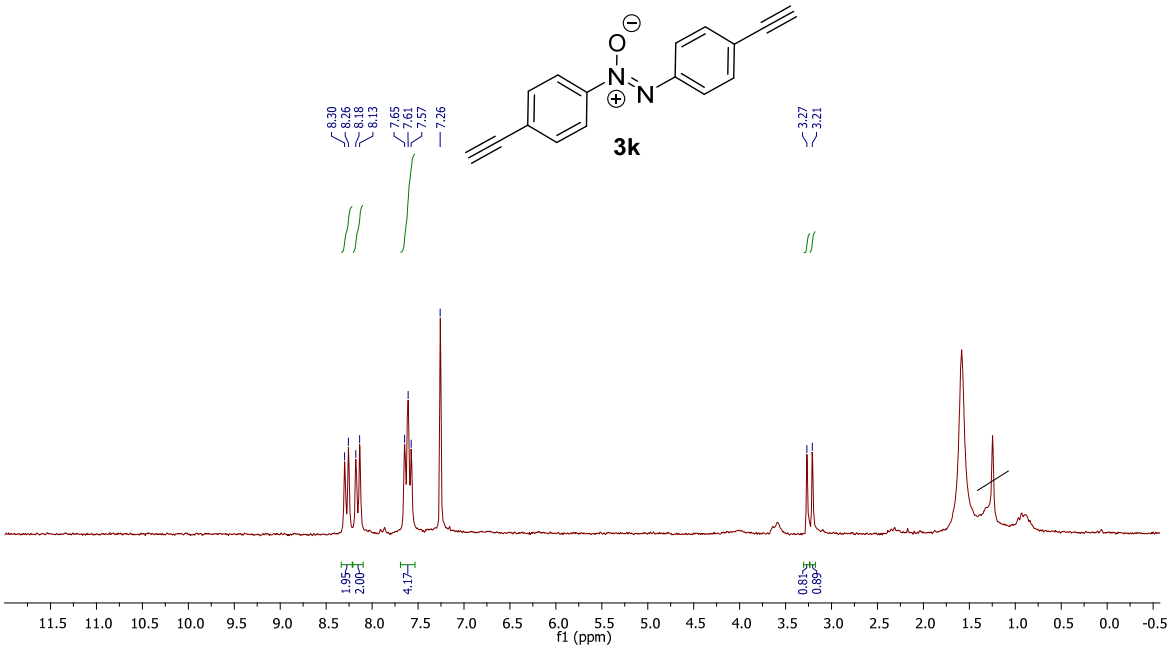
^{13}C NMR spectrum of compound **3i** ($CDCl_3$, 100 MHz)



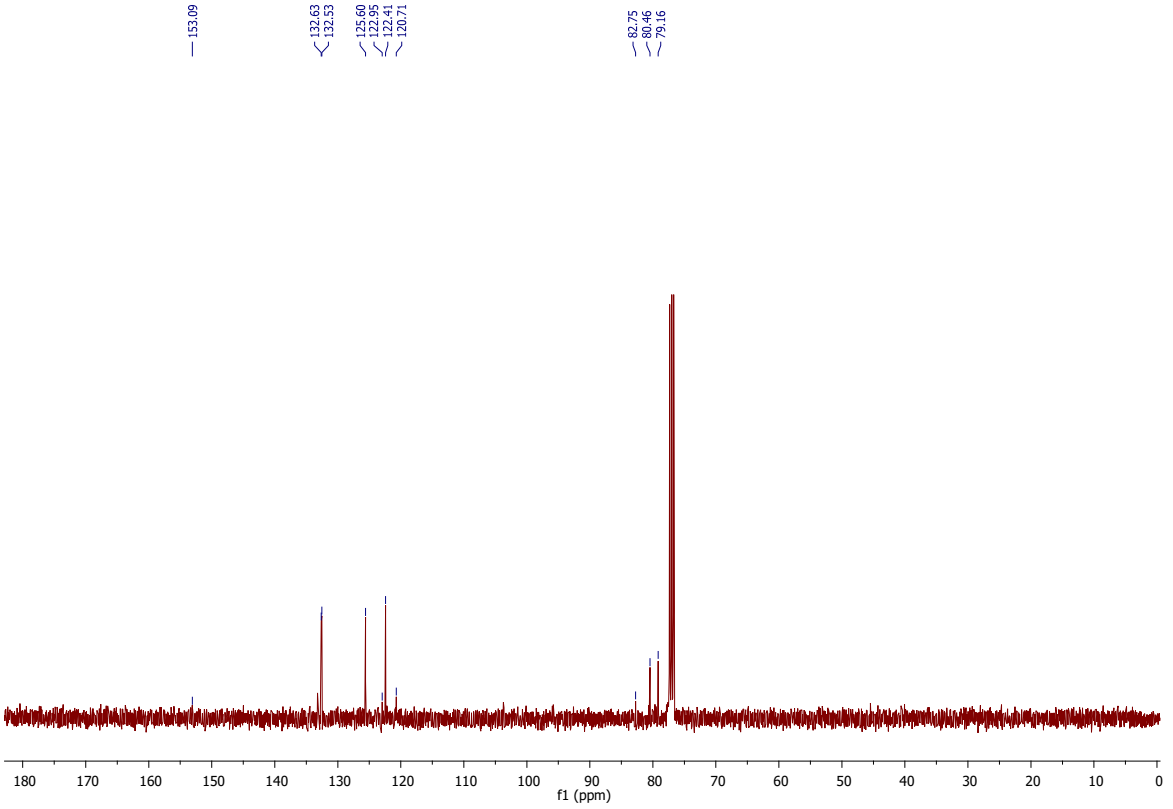
^{1}H NMR spectrum of compound **3j** (CD_3OD, 200 MHz)



^{13}C NMR spectrum of compound **3j** (CD_3OD, 50 MHz)

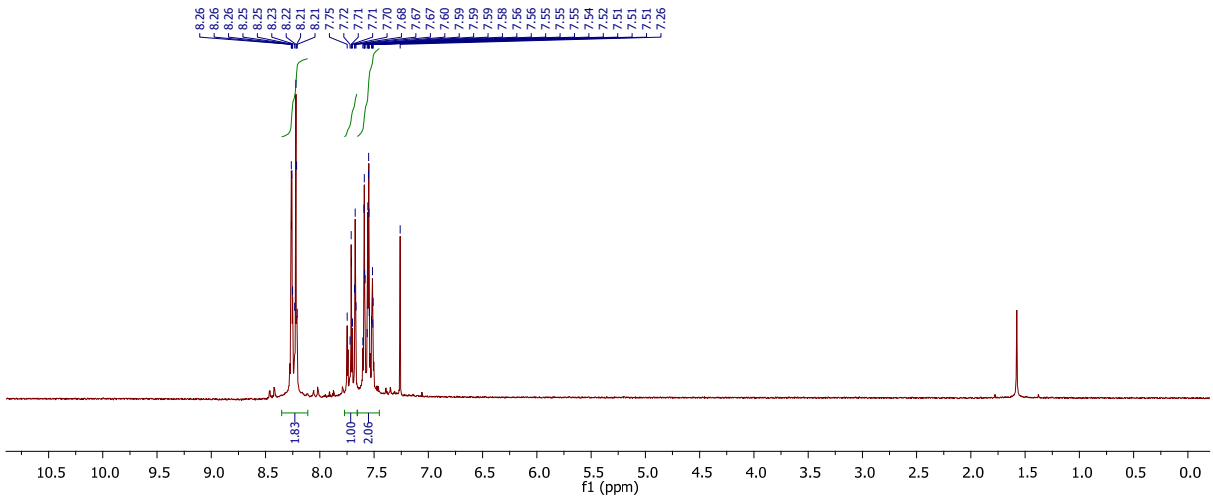


^{1}H NMR spectrum of compound **3k** ($CDCl_3$, 200 MHz)

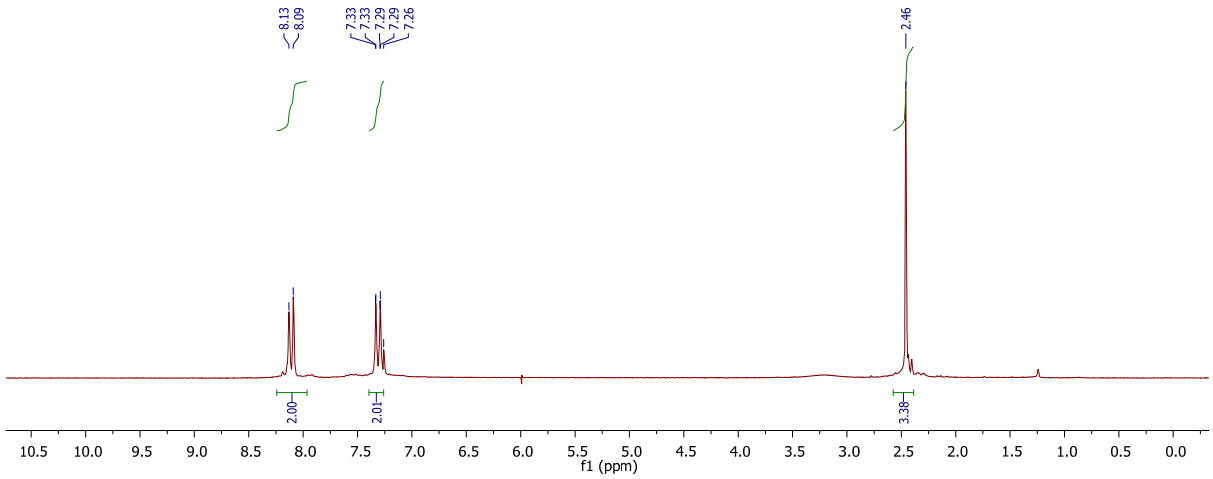


^{13}C NMR spectrum of compound **3k** ($CDCl_3$, 50 MHz)

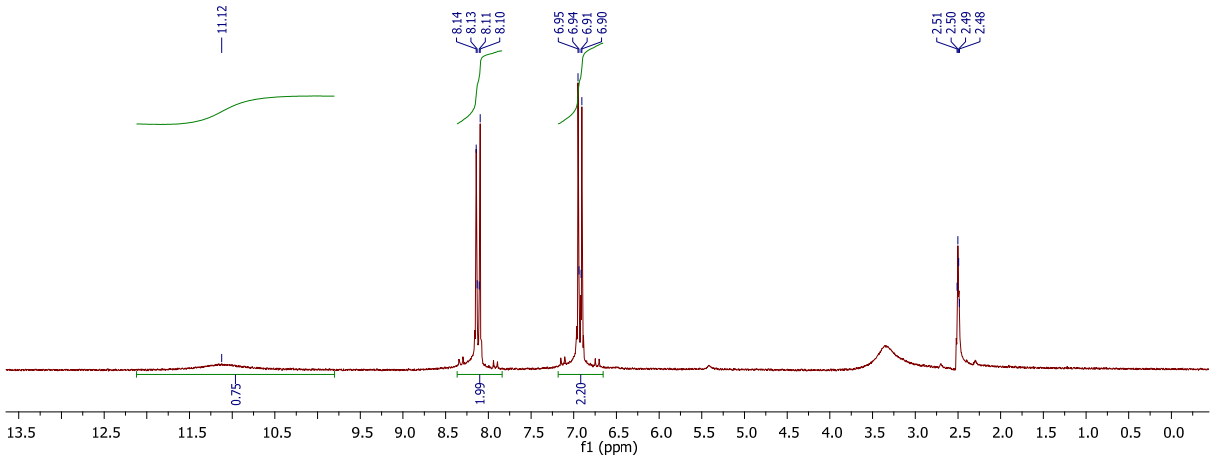
4. ^{1}H NMR Spectra conducted on products arising from scaled-up reactions



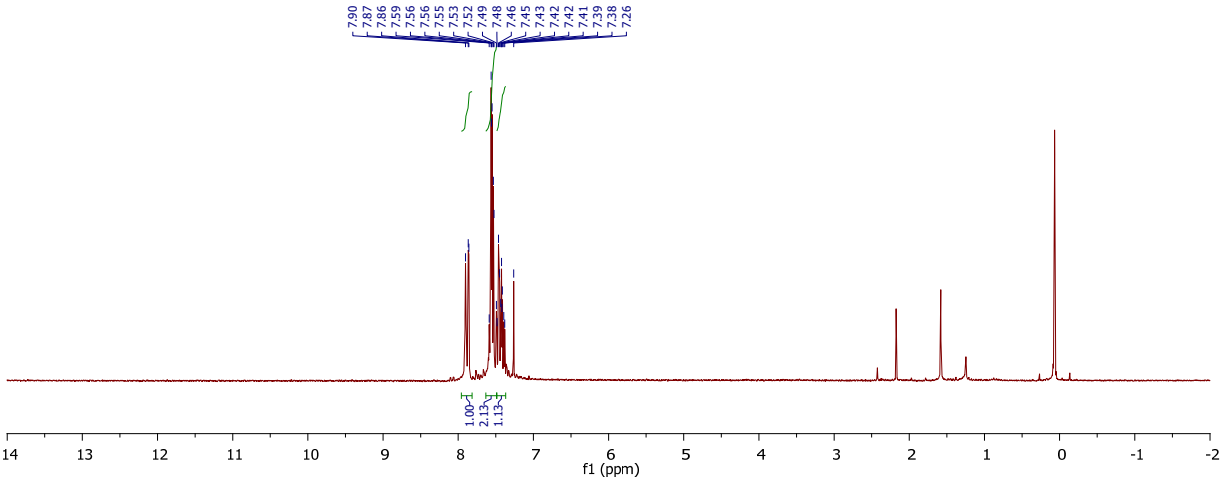
^{1}H NMR spectrum of compound **1a** ($CDCl_3$, 200 MHz) – *Reaction conducted on a 3.0 mmol scale*



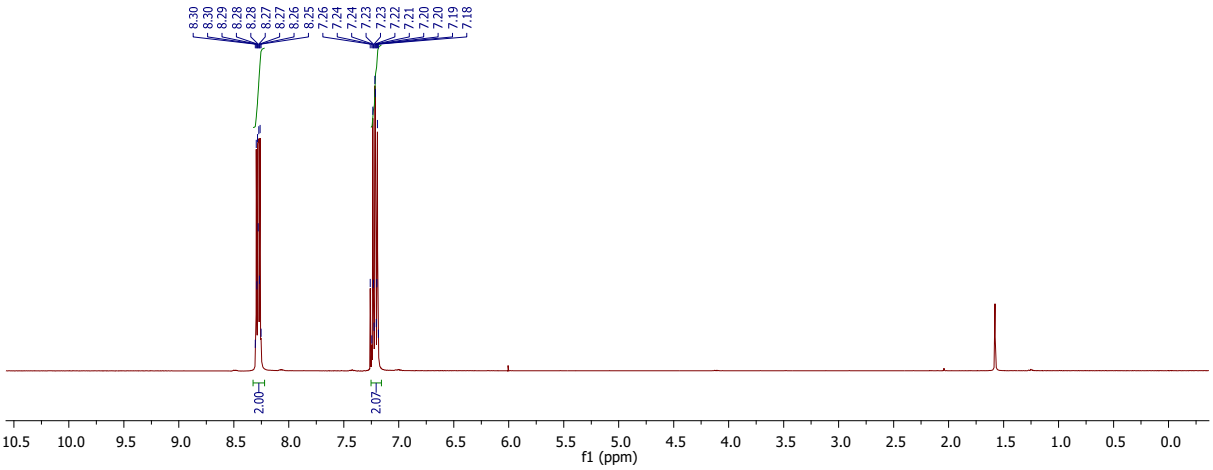
^{1}H NMR spectrum of compound **1c** ($CDCl_3$, 200 MHz) – *Reaction conducted on a 3.0 mmol scale*



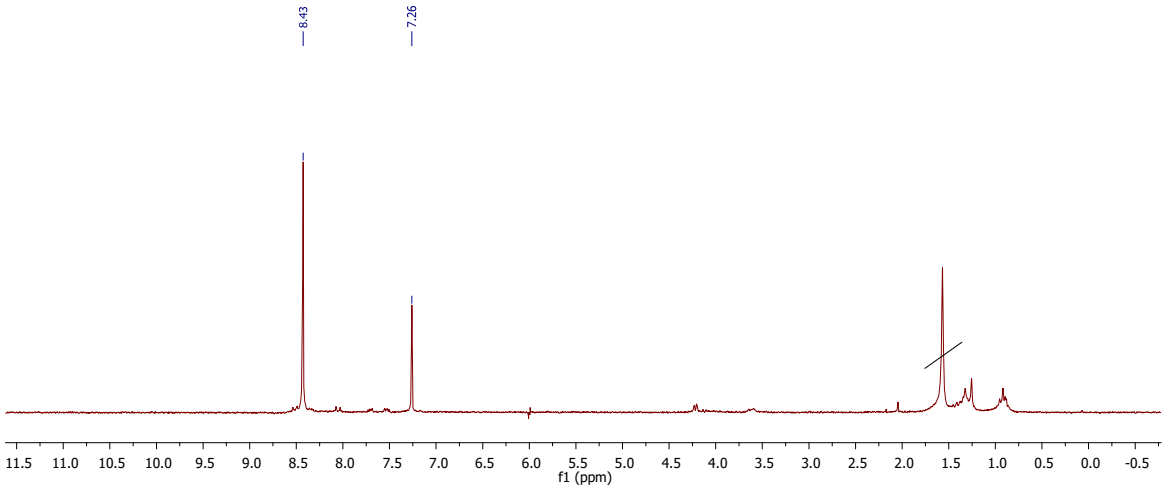
^{1}H NMR spectrum of compound **1d** (DMSO-d_6, 200 MHz) – *Reaction conducted on a 2.0 mmol scale*



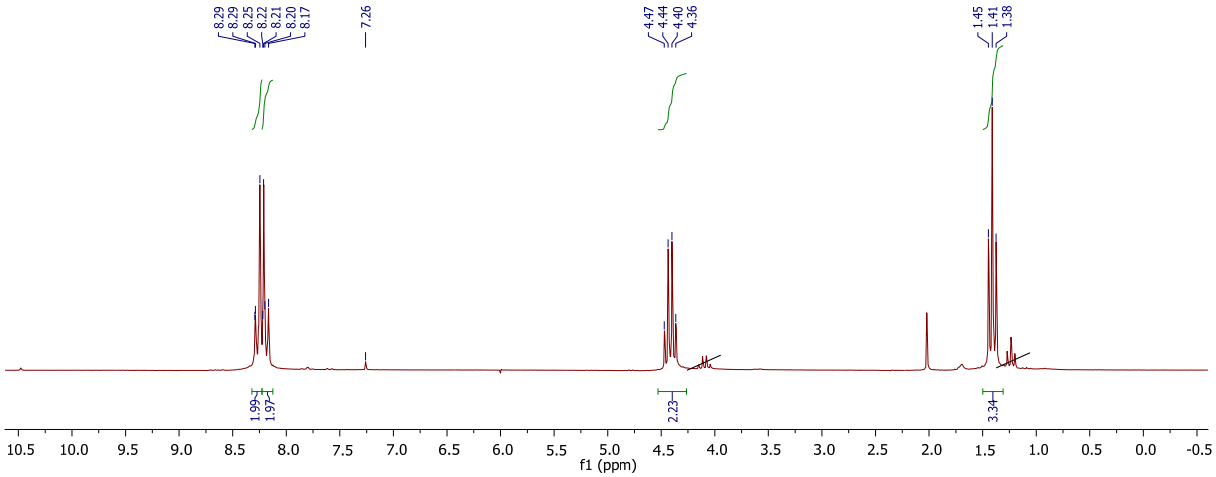
^{1}H NMR spectrum of compound **1e** ($CDCl_3$, 200 MHz) – *Reaction conducted on a 3.0 mmol scale*



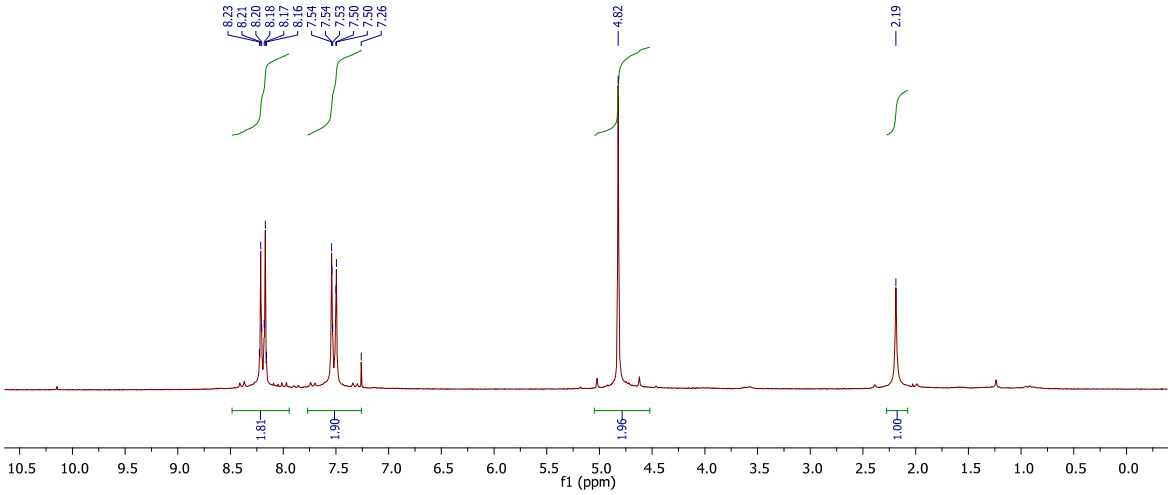
^{1}H NMR spectrum of compound **1g** ($CDCl_3$, 400 MHz) – *Reaction conducted on a 2.0 mmol scale*



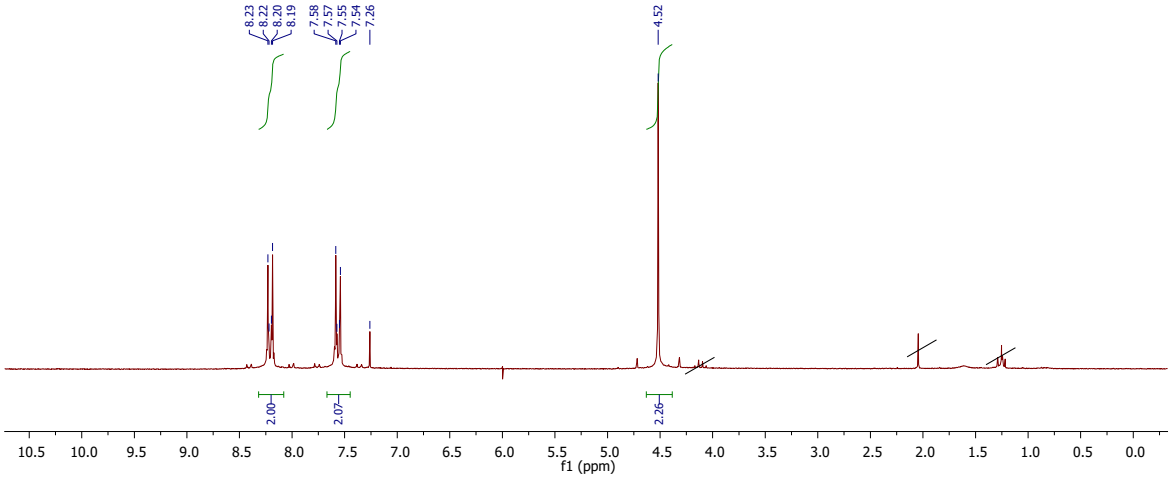
^{1}H NMR spectrum of compound **1h** ($CDCl_3$, 200 MHz) – *Reaction conducted on a 2.0 mmol scale*



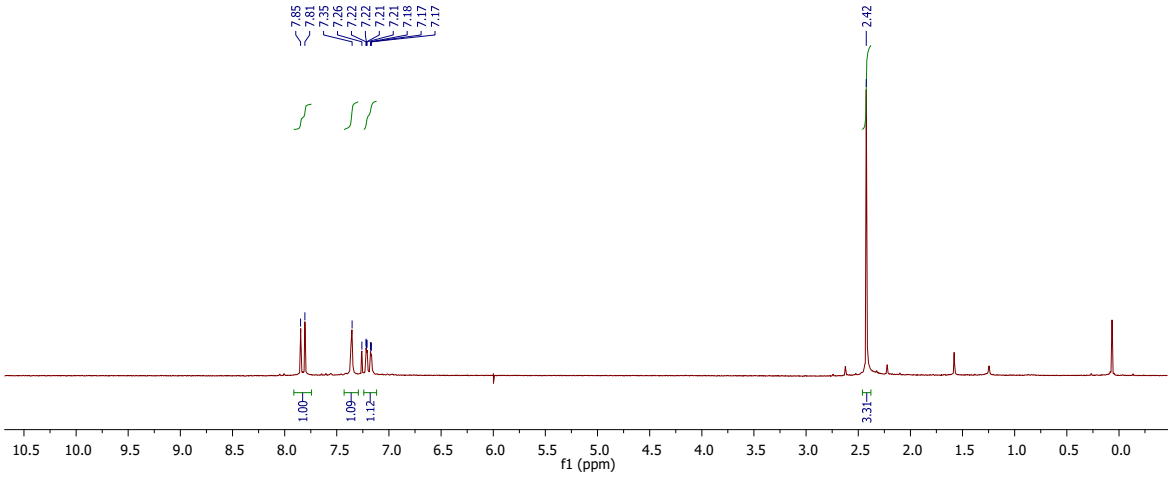
^{1}H NMR spectrum of compound **1j** ($CDCl_3$, 200 MHz) – *Reaction conducted on a 3.0 mmol scale*



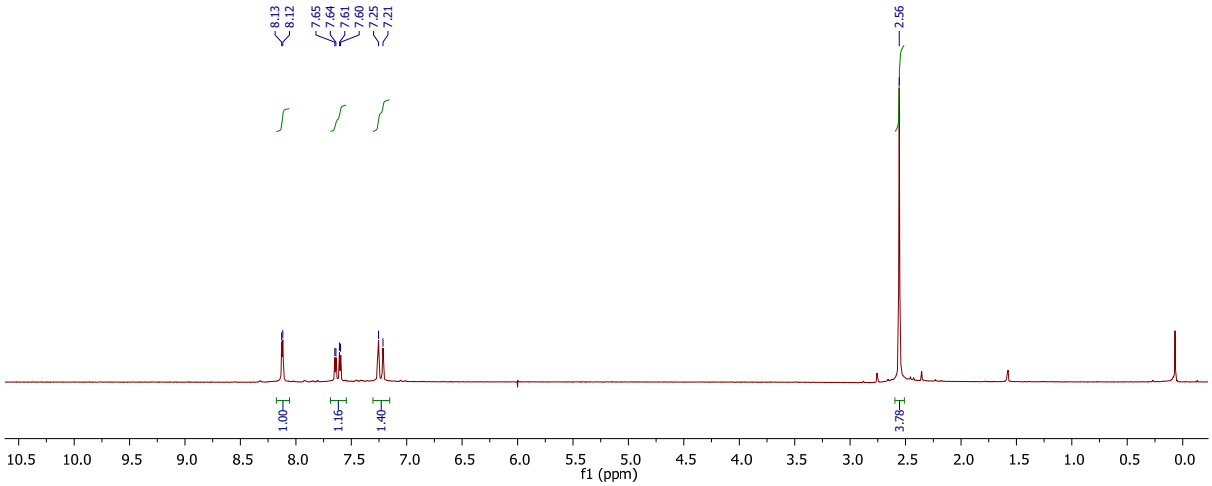
^{1}H NMR spectrum of compound **1l** ($CDCl_3$, 200 MHz) – *Reaction conducted on a 3.0 mmol scale*



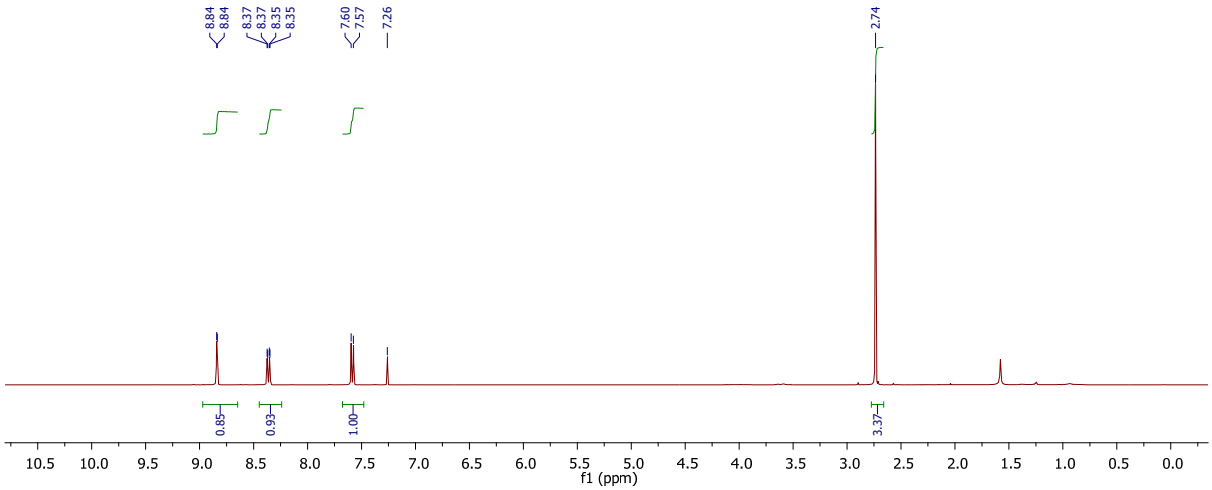
^{1}H NMR spectrum of compound **1m** ($CDCl_3$, 200 MHz) – *Reaction conducted on a 2.0 mmol scale*



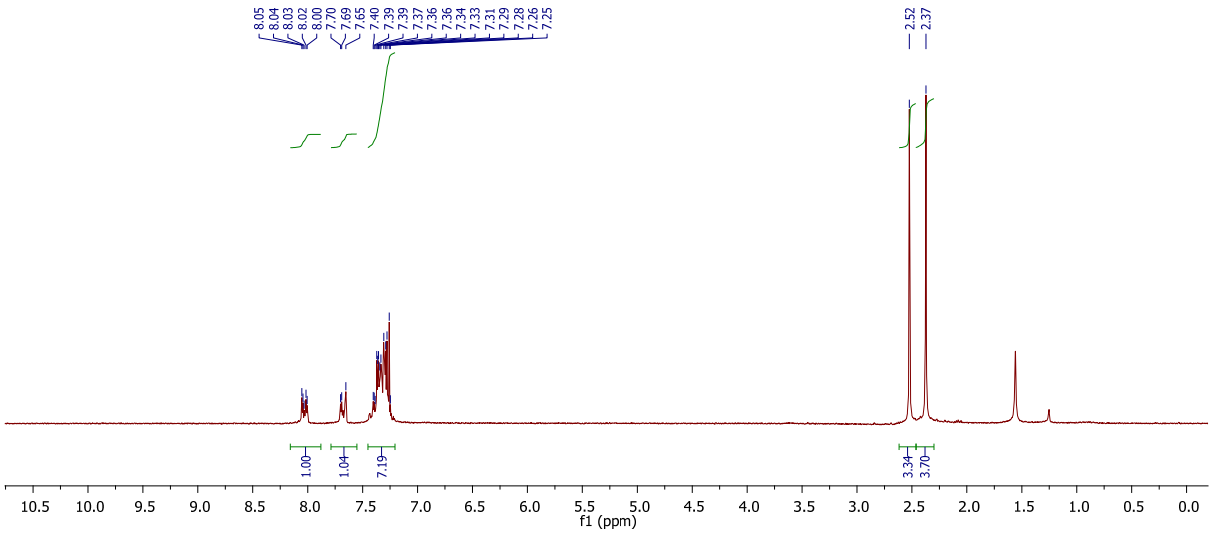
^{1}H NMR spectrum of compound **1p** ($CDCl_3$, 200 MHz) – *Reaction conducted on a 2.0 mmol scale*



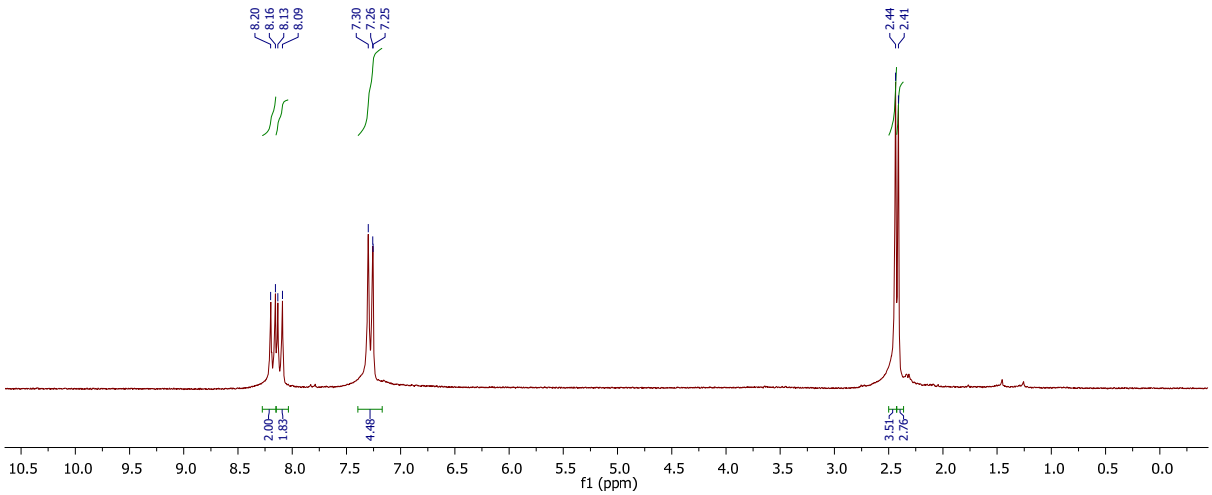
^{1}H NMR spectrum of compound **1q** ($CDCl_3$, 200 MHz) – *Reaction conducted on a 1.0 mmol scale*



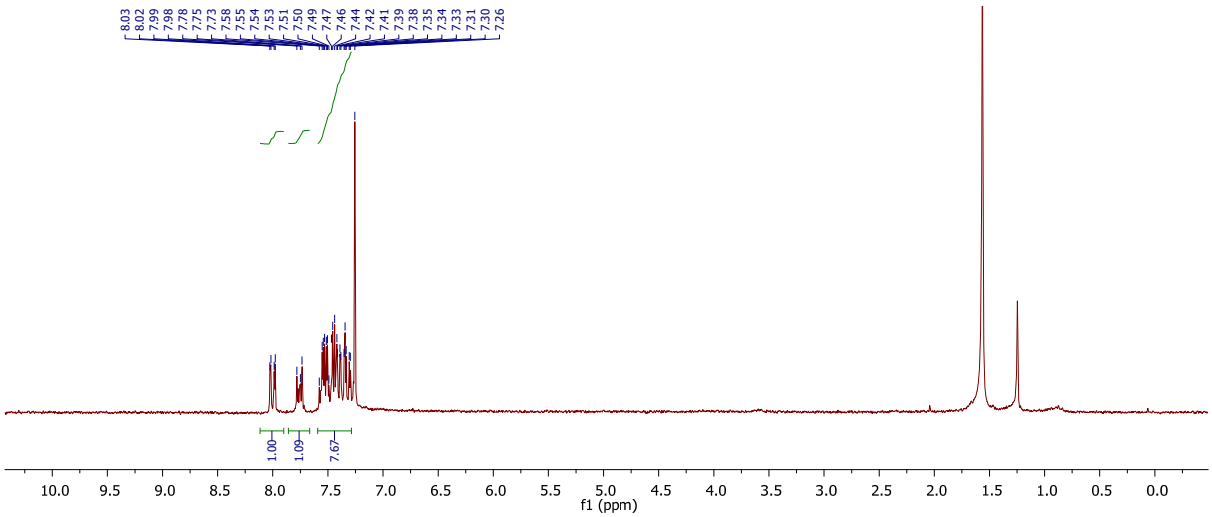
^{1}H NMR spectrum of compound **1t** ($CDCl_3$, 400 MHz) – *Reaction conducted on a 2.0 mmol scale*



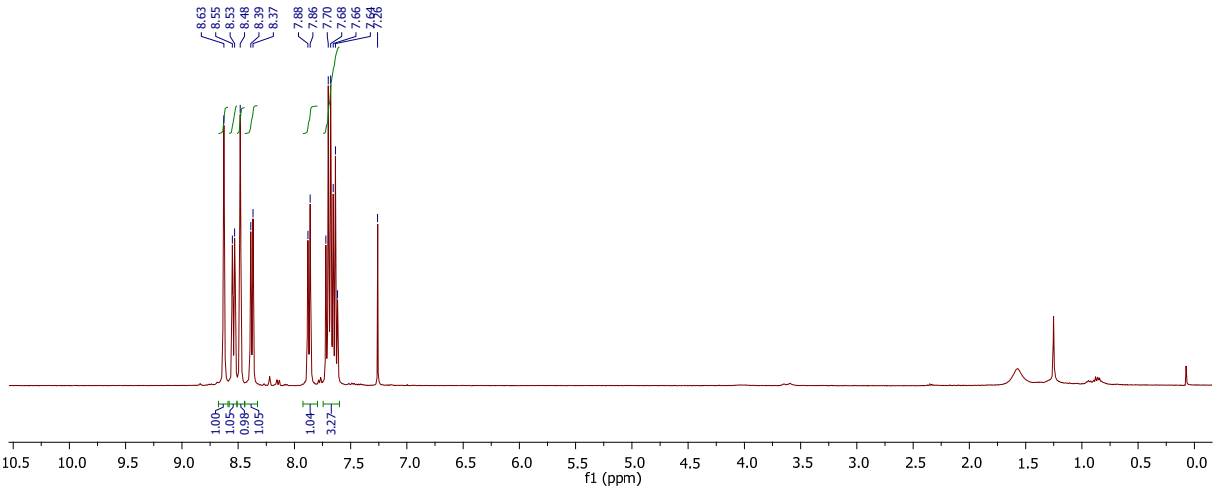
^{1}H NMR spectrum of compound **3b** ($CDCl_3$, 200 MHz) – *Reaction conducted on a 2.0 mmol scale*



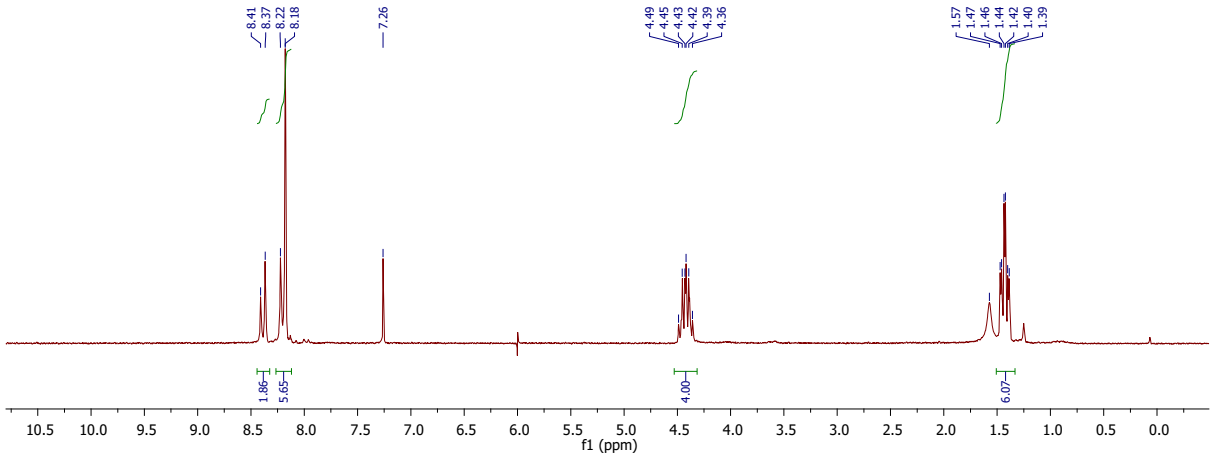
^{1}H NMR spectrum of compound **3c** ($CDCl_3$, 200 MHz) – *Reaction conducted on a 2.0 mmol scale*



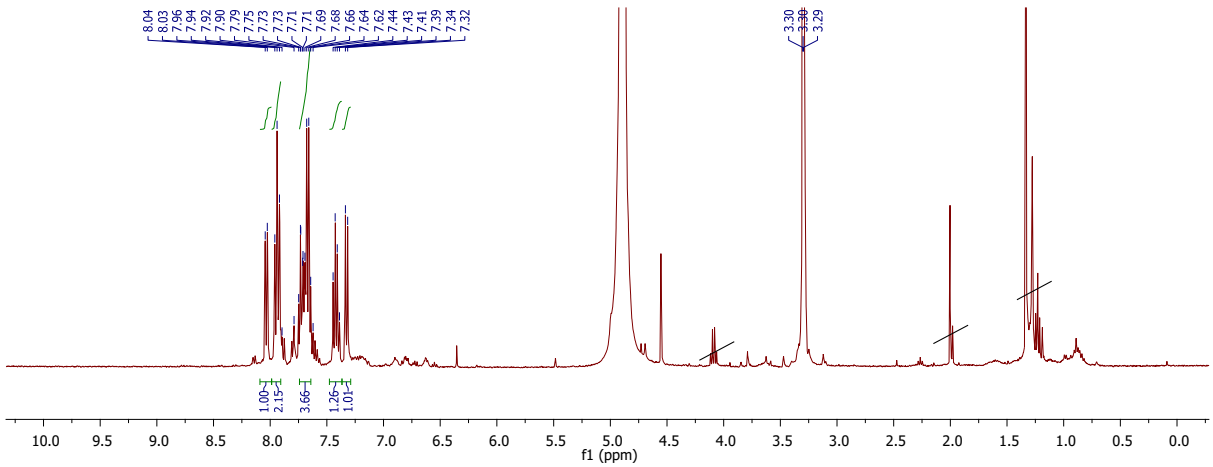
^{1}H NMR spectrum of compound **3d** ($CDCl_3$, 200 MHz) – *Reaction conducted on a 2.0 mmol scale*



^{1}H NMR spectrum of compound **3h** ($CDCl_3$, 400 MHz) – *Reaction conducted on a 1.0 mmol scale*



^{1}H NMR spectrum of compound **3i** ($CDCl_3$, 200 MHz) – *Reaction conducted on a 2.0 mmol scale*



^{1}H NMR spectrum of compound **3j** (CD_3OD, 400 MHz) – *Reaction conducted on a 1.0 mmol scale*

Notes and References

[§] Low mass of starting material may affect the accuracies of the reaction yield.

[§§] Where not differently specified, NMR spectra refer to samples arising from reactions conducted on 0.5 mmol scale. Scale-up experiments were performed on 2.0 or 3.0 mmol scale during the revision of the manuscript. Control ^{1}H NMR spectra of products arising from these scale-up reactions are also reported in the Section 4 of this Supplementary Information.

[1] S. Gupta, A. Ansari and K. V. Sashidhara, *Tetrahedron Lett*. 2019, **60**, 151076.

[2] G. Aridoss and K. K. Laali, *J. Org. Chem*. 2011, **76**, 8088.

[3] V. V. Patil and G. S. Shankarling, *J. Org. Chem*. 2015, **80**, 7876.

[4] J. Liu, J. Li, J. Ren and B.-B. Zeng, *Tetrahedron Lett*. 2014, **55**, 1581.

[5] X.-F. Wu and C. Darcel, *Eur. J. Org. Chem*. 2009, 1144.

[6] A. Perjéssy, E. Kolehmainen, W. M. F. Fabian, M. Ludwig, K. Laihia, J. Kulhánek and Z. Šusteková, *Sulfur Lett.* 2002, **25**, 71.

[7] A. Mirjafari, I. Mohammadpoor-Baltork, M. Moghadam, S. Tangestaninejad, V. Mirkhani and A. R. Khosropour, *Tetrahedron Lett*. 2010, **51**, 3274.

[8] S. Rondeau-Gagné, C. Curutchet, F. Grenier, G. D. Scholes and J.-F. Morin, *Tetrahedron,* 2010, **66**, 4230.

[9] B. P. Fors and S. L. Buchwald, *J. Am. Chem. Soc*. 2009, **131**, 12898.

[10] K. S. Gayen, T. Sengupta, Y. Saima, A. Das, D. K. Maiti and A. Mitra, *Green Chem*., 2012,**14**, 1589.

[11] G. B. Priewisch, E. Irran and K. Rück-Braun, *Synthesis,* 2008, **12**, 1889.

[12] L. Syper and J. Młochowski, *Tetrahedron*, 1987, **43**, 207.

[13] D. Wei, M. Han and L. Yu *Sci. Rep*. 2017, **7**, 6376.

[14] K. N. Sands, E. M. Rengifo, G. N. George, I. J. Pickering, B. S. Gelfand and T. G. Back, *Angew. Chem. Int. Ed.* 2020, **59**, 4283.