Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Deoxygenation of Heterocyclic *N*-oxides Employing Iodide and Formic Acid as a Sustainable Reductant

Alicia Elvira Cruz-Jiménez,[a] Paola Alejandra Argumedo-Castrejón,[a] Jeferson B. Mateus-Ruiz,[a] Victor A. Lucas-Rosales,[b] Octavio Adrián Valle-González,[a] J. Oscar C. Jimenez-Halla[b] and Jesús Armando Luján-Montelongo*[a]

[a] Departamento de Química, Centro de Investigación y de Estudios Avanzados (Cinvestav) Av. Instituto Politécnico Nacional 2508 San Pedro Zacatenco, 07360 Ciudad de México (México). jalujanm@cinvestav.mx

[b] Departamento de Química, División de Ciencias Naturales y Exactas, Sede Noria Alta, Universidad de Guanajuato, Noria Alta s/n, C.P. 36050, Guanajuato, Gto, México

Supporting Information

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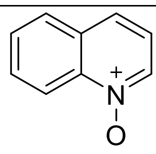
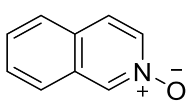
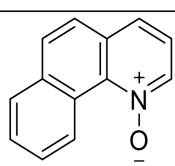
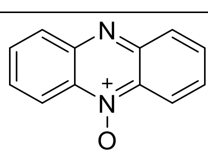
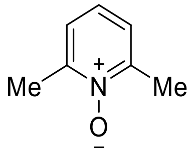
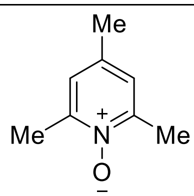
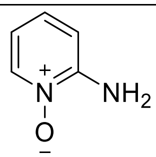
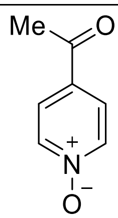
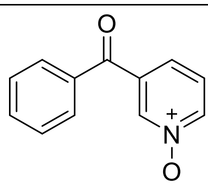
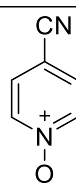
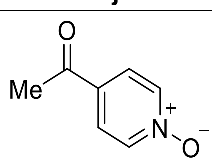
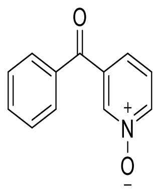
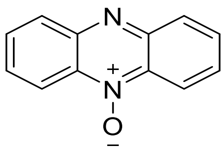
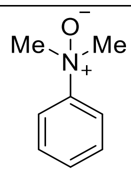
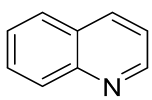
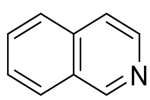
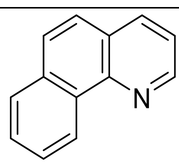
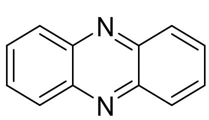
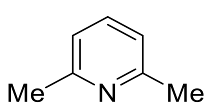
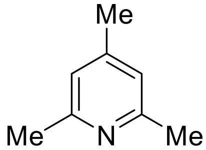
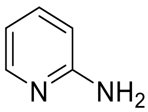
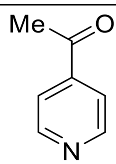
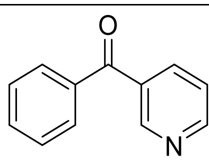
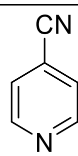
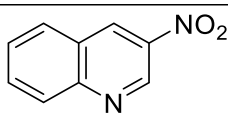
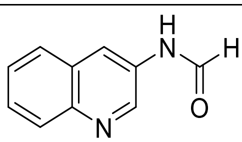
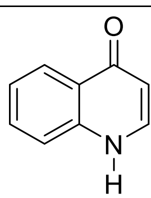
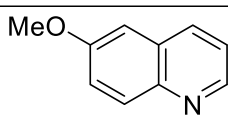
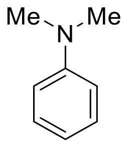
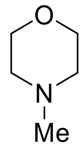
5. **General procedure for heterocycle *N*-oxides reduction (2a-o)**
6. **NMR Spectra**
7. **Computational details**

Compound	Experimental and spectroscopy data	^{1}H NMR	^{13}C NMR
 **1a**	**S6**	**S13**	**S13**
 **1b**	**S7**	**S14**	**S14**
 **1c**	**S7**	**S15**	**S15**
 **1d**	**S7**	**S16**	**S16**

 **1e**	**S7**	**S17**	**S17**
 **1f**	**S7**	**S18**	**S18**
 **1g**	**S8**	**S19**	**S19**
 **1h**	**S8**	**S20**	**S20**
 **1i**	**S8**	**S21**	**S21**
 **1j**	**S8**	**S22**	**S22**
 **1k**	**S8**	**S23**	**S23**

 **1l**	**S9**	**S24**	**S24**
 **1m**	**S9**	**S25**	**S25**
 **1n**	**S9**	**S26**	**S26**
 **2a**	**S9**	**S27**	**S27**
 **2b**	**S10**	**S28**	**S28**
 **2c**	**S10**	**S29**	**S29**
 **2d**	**S10**	**S30**	**S30**
 **2e**	**S10**	**S31**	**S31**

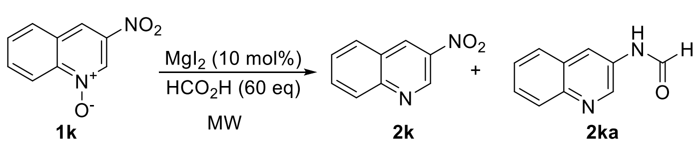
 **2f**	**S10**	**S32**	**S32**
 **2g**	**S10**	**S33**	**S33**
 **2h**	**S11**	**S34**	**S34**
 **2i**	**S11**	**S35**	**S35**
 **2j**	**S11**	**S36**	**S36**
 **2k**	**S11**	**S37**	**S37**
 **2ka**	**S11**	**S38**	**S38**
 **2la**	**S12**	**S39**	**S39**
 **2m**	**S12**	**S40**	**S40**

 2n	**S12**	**S41**	**S41**
 2o	**S12**	**S42**	**S42**

1. General experimental conditions

All reagents and solvents were of reagent or analytical grade and used without further purification unless otherwise stated. Qualitative thin layer chromatography (TLC) analyses and preparative runs were performed using glass or aluminum baked silica gel (F_{254}). TLC plates were visualized by exposition to UV light (254 nm), iodine and/or phosphomolybdic acid solution (20%). Purifications were performed by flash column chromatography on 230-400 mesh silica gel. ^{1}H and ^{13}C NMR were acquired using Bruker Advance III HD 400 and JEOL ECA 500 spectrometers. Chemical shifts of both ^{1}H and ^{13}C are reported in parts per million (ppm) on the δ scale, referenced with respect to residual solvent at 7.26 ($CDCl_3$) and 2.50 ppm (DMSO-d_6) or from internal standard tetramethylsilane (TMS) at 0.00 ppm for ^{1}H-NMR and 77.16 ppm ($CDCl_3$) and 39.5 ppm (DMSO-d_6) for ^{13}C-NMR. Data were reported as follows: chemical shift, multiplicity (*s* = singlet, *d* = doublet, *dd* = doublet of doublets, *t* = triplet, *m* = multiplet), coupling constants (Hz) and integration. ^{13}C NMR data were collected with complete proton decoupling. Infrared spectra were recorded on a Varian FT-IR 600IR spectrometer equipped with an ATR sampling accessory and IR Spectrum GX. Mass spectra were acquired on an Agilent G1969A ESI-TOF. Melting points were measured on an MelTemp II.

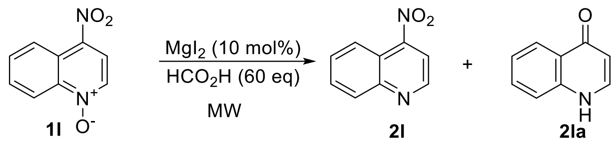
2 Optimizing deoxygenation conditions for NO_2-substituted *N*-oxide 1k



Entry	Temp (°C)	Time (h)	Conversion (%)	Ratio 2k : 2ka
1	140	3	100	0 : 100 (59)[a]
2	100	1	10	96 : 4
3	90	10	33	100 : 0
4	100	10	72	58 (47)[a] : 14

[a] isolated yield (%)

3 Exploration of the deoxygenation conditions for 1l

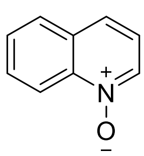


Entry	Temp (°C)	Time (h)	Yield[a] 2la
1	140	3	27
2	140	0.5	4
3	90	10	15
4	80	4	-[b]
5	70	4	-[b]
6	50	4	-[b]
7	60	4	-[b]

[a] Determined by ^{1}H-NMR using an internal standard (mesitylene).
[b] Starting material recovered.

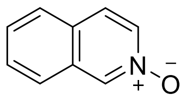
4 General procedure for the syntheses of *N*-oxides (1a-o)

To a cold solution (0°C) of the *N*-heterocycle **(2)** in DCM (0.3 M), *m*-CPBA (1.2 eq) was added portionwise with stirring. The mixture was allowed to warm (rt) and stirred for *ca.* 12 h until starting material was consumed (TLC). The mixture was cooled (0 °C), and a saturated solution of $NaHCO_3$ was added until pH=8. The biphasic mixture was transferred to a separating funnel, the organic layer was separated, and the aqueous was extracted with ethyl acetate (x4). The combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated to afford crude *N*-oxide **(1)**. Pure **1** was obtained through SiO_2 chromatography using mixtures of hexanes:EtOAc and EtOAc:MeOH as eluents.

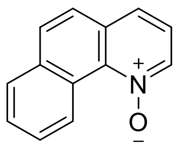


Quinoline 1-oxide (1a) was prepared from **2a** (3 g, 23.23 mmol) following the general procedure. **1a** was purified through SiO_2 column chromatography using hexanes:EtOAc (9:1 to 1:1 V/V) and EtOAc:MeOH (9:1 V/V). Pure **1a** was obtained as a yellow wax with a yield of 92% (3.1 g, 21.36 mmol). The ^{1}H NMR and ^{13}C NMR spectra matched the data reported in the literature.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 8.8 Hz, 1H), 8.56 (d, *J* = 6.0 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.78 (t, *J* = 8.5 Hz, 2H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.38 – 7.25 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 135.8, 130.6, 128.9, 128.2, 126.3, 121.1, 119.8. mp 50-52 °C.

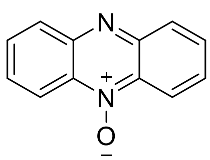
[1] E. M. Gayakwad, K. P. Patel and G. S. Shankarling, *ChemistrySelect*, 2018, **3**, 11219-11222.



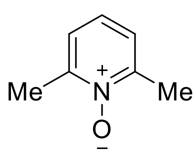
Isoquinoline 2-oxide (1b) was prepared from **2b** (303 mg, 2.35 mmol) following the general procedure. **1b** was purified through SiO_2 column chromatography using a solvent system of hexanes:EtOAc (9:1 to 1:1 V/V) and EtOAc:MeOH (9:1 V/V). Pure **1b** was obtained as a yellow solid with a yield of 74% (251 mg, 1.73 mmol). The ^1H NMR and ^{13}C NMR spectra matched the data reported in the literature.[2] ^1H NMR (400 MHz, $CDCl_3$) δ 8.80 (s, 1H), 8.16 (dd, *J* = 7.1, 1.8 Hz, 1H), 7.82 – 7.80 (m, 1H), 7.77 – 7.75 (m, 1H), 7.70 (d, *J* = 7.2 Hz, 1H), 7.65 – 7.60 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 136.5, 129.7, 129.6, 129.4, 129.1, 126.8, 125.3, 124.5 ppm.



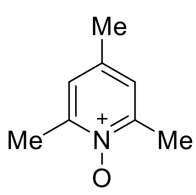
Benzo[*h*]quinoline 1-oxide (2c) was prepared from **1c** (500 mg, 2.79 mmol) following the general procedure. **2c** was purified through SiO_2 column chromatography using a solvent system of hexanes:EtOAc (9:1 to 1:1 V/V) and EtOAc:MeOH (9:1 V/V). Pure **2c** was obtained as a yellow solid with a yield of 80% (438 mg, 2.24 mmol). The ^1H NMR and ^{13}C NMR spectra matched the data reported in the literature.[3] ^1H NMR (400 MHz, $CDCl_3$) δ 10.87 - 10.84 (m, 1H), 8.75 (d, *J* = 6.2 Hz, 1H), 7.97 – 7.93 (m, 1H), 7.89 (d, *J* = 8.9 Hz, 1H), 7.84 – 7.77 (m, 3H), 7.68 (d, *J* = 8.8 Hz, 1H), 7.45 (dd, J = 8.0, 6.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6, 134.3, 131.4, 130.9, 129.3, 128.6, 128.3, 128.0, 126.6, 126.2, 125.1, 121.4 ppm.



Phenazine 5-oxide (1d) was prepared from **2d** (500 mg, 2.77 mmol) following the general procedure. **2j** was purified through SiO_2 column chromatography using a solvent system of hexanes:EtOAc (9:1 to 1:1 V/V) and EtOAc:MeOH (9:1 V/V). Pure **2d** was obtained as an orange solid with a yield of 75% (406 mg, 2.07 mmol). The ^1H NMR and ^{13}C NMR spectra matched the data reported in the literature.[4] ^1H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 8.5 Hz, 1H), 8.23 (d, *J* = 8.7 Hz, 1H), 7.85 (t, *J* = 7.60 Hz, 1H) 7.79 – 7.75 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7, 135.0, 131.5, 130.6, 130.3, 119.3 ppm.

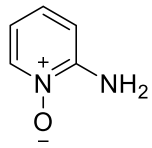


2,6-dimethylpyridine 1-oxide (1e) was prepared from **2e** (519 mg, 4.84 mmol) following the general procedure. **1e** was purified through SiO_2 column chromatography using a solvent system of hexanes:EtOAc (9:1 to 1:1 V/V) and EtOAc:MeOH (9:1 V/V). Pure **1e** was obtained as a yellow solid with a yield of 77% (461 mg, 3.74 mmol). The ^1H NMR and ^{13}C NMR spectra matched the data reported in the literature.[5] ^1H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, *J* = 7.6 Hz, 2H), 7.09 (dd, *J* = 8.7, 6.6 Hz, 1H), 2.54 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 124.8, 124.0, 18.3 ppm.

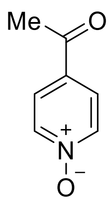


2,4,6-trimethylpyridine 1-oxide (1f) was prepared from **2f** (500 mg, 4.13 mmol) following the general procedure. **1f** was purified through SiO_2 column chromatography using a solvent system of hexanes:EtOAc (9:1 to 1:1 V/V) and EtOAc:MeOH (9:1 V/V). Pure **1f** was obtained as a yellow solid with a yield of 90% (508 mg, 3.70 mmol). The ^1H NMR and ^{13}C NMR spectra matched the data reported in the literature.[6] ^1H NMR (400 MHz, $CDCl_3$) δ 6.97 (s, 1H), 2.51 (s, 6H), 2.28 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 135.8, 124.7, 20.1 18.1 ppm.

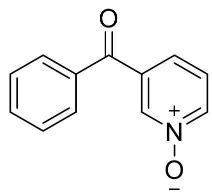
[2] Y. Ding, W. Zhao, W. Song, Z. Zhang and B. Ma, *Green Chem.,* 2011, **13**, 1486–1489.
[3] C. Sen and S. C. Ghosh, *Adv. Synth. Catal.,* 2018, **360**, 905–910.
[4] J. Sheng, R. He, J. Xue, C. Wu, J. Qiao and C. Chen, *Org. Lett*., 2018, **20**, 4458–4461.
[5] Y. Ding, W. Zhao, W. Song, Z. Zhang and B. Ma, *Green Chem.,* 2011, **13**, 1486.
[6] G. Li, S. Yang, B. Lv, Q. Han, X. Ma, K. Sun, Z. Wang, F. Zhao and H. Wu, *Org. Biomol. Chem.,* 2015, **13**, 11184-11188.



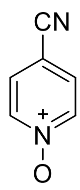
2-aminopyridine 1-oxide (1g) was prepared from **2g** (500 mg, 5.31 mmol) following the general procedure. **1g** was purified through SiO_2 column chromatography using a solvent system of hexanes:EtOAc (9:1 to 1:1 V/V) and EtOAc:MeOH (9:1 V/V). Pure **1g** was obtained as a brown solid with a yield of 85% (497 mg, 4.51 mmol. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 6.6, 1.4 Hz, 1H), 7.13 (ddd, *J* = 8.6, 7.4, 1.5 Hz, 1H), 6.82 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.61 (td, *J* = 7.0, 1.8 Hz, 1H), 6.11 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 137.7, 128.5, 113.3, 109.9. IR (ATR) ν_{max} (cm^{-1}) 3253, 3143, 2994, 1642, 1506, 1192, 782, 737. ESI calculated for $C_5H_6N_2O$ $(M+H)^+$ 111.1; found 111.1.



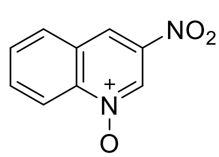
4-acetylpyridine 1-oxide (1h) was prepared from **2h** (1 g, 8.25 mmol) following the general procedure. **1h** was purified through SiO_2 column chromatography using a solvent system of hexanes:EtOAc (2:1 to 1:1 V/V) and EtOAc:MeOH (9:1 V/V). Pure **1h** was obtained as a white solid with a yield of 91% (1.03 g, 7.51 mmol). The ^{1}H NMR and ^{13}C NMR spectra matched the data reported in the literature.[7] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 6.7 Hz, 2H), 7.82 (d, *J* = 6.6 Hz, 2H), 2.61 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7, 139.7, 132.5, 125.2, 26.4 ppm. mp 128-130 °C.



3-benzoylpyridine 1-oxide (1i) was prepared from **2i** (1 g, 5.46 mmol) following the general procedure. **1i** was purified through SiO_2 column chromatography using a solvent system of hexanes:EtOAc (9:1 to 1:1 V/V) and EtOAc:MeOH (9:1 V/V). Pure **1i** was obtained as a brown oil with a yield of 87% (954 mg, 4.79 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.40 (d, *J* = 6.5 Hz, 1H), 7.80 (d, *J* = 6.9 Hz, 2H), 7.69 – 7.64 (m, 2H), 7.53 (t, *J* = 7.8 Hz, 2H), 7.47 (t, *J* = 7.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 141.5, 139.9, 136.3, 135.3, 133.6, 129.7, 128.6, 126.2, 125.8, 121.0 ppm. IR (ATR) ν_{max} (cm^{-1}) 3377, 3065, 1661, 1595, 1427, 1283, 1218, 1013, 850, 710 cm^{-1}. ESI calculated for $C_{12}H_9NO_2$ $(M+H)^+$ 200.2; found 200.1. mp 156-158 °C.



4-cyanopyridine 1-oxide (1j) was prepared from **2j** (500 mg, 4.80 mmol) following the general procedure. **1j** was purified through SiO_2 column chromatography using a solvent system of hexanes:EtOAc (9:1 to 1:1 V/V) and EtOAc:MeOH (9:1 V/V). Pure **1j** was obtained as a white solid with a yield of 94% (545 mg, 4.54 mmol). The ^{1}H NMR and ^{13}C NMR spectra matched the data reported in the literature.[8] ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.41 – 8.38 (m, 2H), 7.94 – 7.91 (m, 2H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ 140.1, 129.8, 116.7, 106.4 ppm.

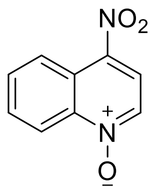


3-nitroquinoline 1-oxide (1k) According to literature,[9] quinoline *N*-oxide **1a** (402 mg, 2.77 mmol, 1 eq) was dissolved in CH_3CN (1M) and *tert*-butyl nitrite (3.5 eq) was added, the mixture was stirred at 100 ºC for 24 h. The mixture was cooled at room room temperature and poured into brine. EtOAc was added, and the biphasic mixture was transferred to a separating funnel, the organic layer was separated, and the aqueous layer was extracted with EtOAc (4 times). **1k** was purified through SiO_2 column chromatography using a solvent system of hexanes:EtOAc (9:1 to 1:1 V:V) and EtOAc:MeOH (9:1 V:V). Pure **1k** was obtained as a bright yellow powder with a yield of 47 % (250 mg, 131 mmol). The ^{1}H NMR and ^{13}C NMR spectra matched the data reported in the literature.[9] ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.26 (d, *J* = 1.9 Hz, 1H), 8.80 (d, *J* = 8.8 Hz, 1H), 8.60 (s, 1H), 8.11 (d, *J* = 8.2 Hz, 1H), 7.99 (ddd, *J* = 8.6, 7.0, 1.4 Hz, 1H), 7.86 – 7.82 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 142.1, 134.0, 131.0, 130.8, 130.1, 127.8, 120.9, 120.6 ppm.

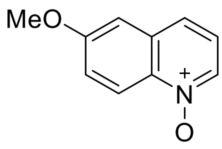
[7] F. Napoly, R. Kieffer, L. Jean-Gérard, C. Goux-Henry, M. Draye and B. Andrioletti, *Tetrahedron Lett.,* 2015, **56**, 2517-2520.

[8] V. A. Rassadin, D. P. Zimin, G. Z. Raskil'dina, A. Y. Ivanov, V. P. Boyarskiy, S. S. Zlotskii and V. Y. Kukushkin, *Green Chem.,* 2016, **18**, 6630-6636.

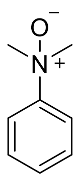
[9] J. Zhao, P. Lia, C. Xia and F. Li, *RSC Adv.,* 2015, **5**, 32835-32838.



4-nitroquinoline 1-oxide (1l) To a mixture of **1a** (541 mg, 3.73 mmol) and H_2SO_4 (0.44 mL, 8.20 mmol) was heated to 65 °C. HNO_3 65% (034 mL, 8.20 mmol) was added dropwise. The mixture was stirred for 6 hours at 65 °C. Reaction was cooled and poured into ice. Cold Na_2CO_3 saturated solution was added until reaching pH 9. The biphasic mixture was transferred to a separating funnel, and the aqueous layer was extracted with ethyl acetate (x4). The combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated to afford crude **1l**. **1l** was purified through SiO_2 column chromatography using a solvent system of hexanes:EtOAc (9:1 to 1:1 V/V) and EtOAc:MeOH (9:1 V/V). Pure **1l** was obtained as a yellow solidwith a yield of 72% (509 mg, 2.68 mmol). The ^1H NMR and ^{13}C NMR spectra matched the data reported in the literature.[10] ^1H NMR (400 MHz, $CDCl_3$) δ 8.87 – 8.77 (m, 2H), 8.51 (d, J = 6.8 Hz, 1H), 8.20 (d, J = 6.8 Hz, 1H), 7.90 – 7.88 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.2, 132.1, 131.6, 124.9, 120.5, 119.3 ppm.



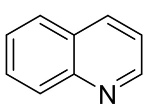
6-methoxyquinoline 1-oxide (1m) was prepared from **2m** (500 mg, 3.14 mmol) following the general procedure. **2m** was purified through SiO_2 column chromatography using a solvent system of hexanes:EtOAc (9:1 to 1:1 V/V) and EtOAc:MeOH (9:1 V/V). Pure **1m** was obtained as a white solid with a yield of 76% (416 mg, 2.40 mmol). The ^1H NMR and ^{13}C NMR spectra matched the data reported in the literature.[11] ^1H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, J = 9.6 Hz, 1H), 8.40 (d, J = 6.0 Hz, 1H), 7.63 (d, J = 8.5 Hz, 1H), 7.39 (dd, J = 9.6, 2.7 Hz, 1H), 7.25 (dd, J = 8.7, 6.3 Hz, 1H), 7.11 (d, J = 2.7 Hz, 1H), 3.95 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 134.0, 132.1, 125.1, 122.9, 121.6, 105.9, 55.9 ppm.



***N*,*N*-dimethylaniline *N*-oxide (1n)** was prepared from **2n** (500 mg, 4.13 mmol) following the general procedure. **1n** was purified through SiO_2 column chromatography using a solvent system of hexanes:EtOAc (9:1 to 1:1 V/V) and EtOAc:MeOH (9:1 V/V). Pure **1n** was obtained as an orange solid with a yield of 95% (537 mg, 3.91 mmol). The ^1H NMR and ^{13}C NMR spectra matched the data reported in the literature.[12] ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.3 Hz, 2H), 7.48 - 7.37 (m, 3H), 3.58 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 129.3, 129.1, 120.0, 63.3 ppm.

5 General procedure for heterocycle *N*-oxides reduction (2a-o)

In a microwave vial, the corresponding *N*-oxide (**1**), MgI_2 (10 %mol) and formic acid (60 eq) were added. The vial was sealed, and the mixture was heated in the microwave reactor at 140°C for 3 hours. The solution was then cooled at 0°C, and a saturated solution of $NaHCO_3$ was added until reaching pH 8. The biphasic mixture was transferred to a separating funnel, and the aqueous layer was extracted with DCM (x4).[13] The combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated to afford crude *N*-heterocycle (**2**).



Quinoline (2a) was prepared following the general procedure from **1a** (100 mg, 6.89 mmol). **2a** was purified through SiO_2 column chromatography using a solvent system of hexanes:EtOAc (5:1 to 2:1 V/V). Pure **2a** was obtained as a light brown oil with a yield of 91% (81 mg, 0.63 mmol). The ^1H NMR and ^{13}C NMR spectra matched the data reported in the literature.[14] ^1H NMR (400 MHz, $CDCl_3$) δ 8.92 (dd, J = 4.3, 1.8 Hz, 1H), 8.16 – 8.11 (m, 1H), 7.81 (d, J = 8.2 Hz, 1H), 7.72 (dd, J = 8.5, 6.8 Hz, 1H), 7.54 (t, J = 7.5 Hz, 1H), 7.39 (dd, J =

[10] L. H. Heitman, A. Goblyos, A. M. Zweemer, R. Bakker, T. Mulder-Krieger, J. P. van Veldhoven, H. de Vries, J.Brussee and A. P. IJzerman, *J. Med. Chem.,* 2009, **52**, 926-931.

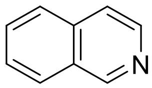
[11] P. Li, J. Zhao, C. Xia, F. Li, *Org. Chem. Front.,* 2015, **2**, 1313-1317.

[12] C. Liu, Y. Zou, H. Song, Y.-Y Jiang, H.-G. Hu, *Eur. J. Org. Chem.,* 2017, **2017**, 5916-5920.

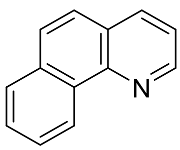
[13] For a more sustainable alternative, the use of dichloromethane can be avoided, and other extraction solvents such as ethyl acetate can be employed.

[14] W. Zhou, D. Chen, F. Sun, J. Qian, M. He, Q. Chen, *Tetrahedron Lett.,* 2018, **59**, 949–953.

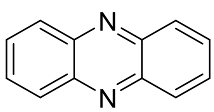
8.2, 4.1 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 148.3, 136.1, 129.5, 129.4, 128.3, 127.8, 126.6, 121.1 ppm.



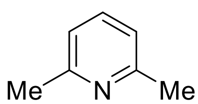
Isoquinoline (2b) was prepared following the general procedure from **1b** (100 mg, 6.89 mmol). **2b** was purified through SiO_2 column chromatography using a solvent system of hexanes:EtOAc (9:1 to 2:1 V/V). Pure **2b** was obtained as a light brown oil with a yield of 73% (65 mg, 0.50 mmol). The ^{1}H NMR and ^{13}C NMR spectra matched the data reported in the literature.[15] ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.27 (s, 1H), 8.53 (d, *J* = 5.8 Hz, 1H), 7.97 (d, *J* = 8.3 Hz, 1H), 7.83 (d, *J* = 8.3 Hz, 1H), 7.72 – 7.60 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 143.1, 135.9, 130.5, 128.8, 127.8, 127.4, 126.6, 120.6 ppm.



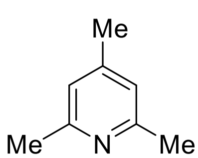
Benzo[*h*]quinoline (2c) was prepared following the general procedure from **1c** (100 mg, 6.89 mmol). **2c** was purified through SiO_2 column chromatography using a solvent system of hexanes:EtOAc (9:1 to 1:1 V/V) and EtOAc:MeOH (9:1 V/V). Pure **2c** was obtained as a light brown oil with a yield of 78% (78 mg, 0.43 mmol). The ^{1}H NMR and ^{13}C NMR spectra matched the data reported in the literature.[16] ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 (d, *J* = 6.2 Hz, 1H), 9.00 (dd, *J* = 4.4, 1.8 Hz, 2H), 8.16 (dd, *J* = 8.0, 1.8 Hz, 2H), 7.91 (d, *J* = 7.7 Hz, 1H), 7.81 (d, *J* = 8.8 Hz, 2H), 7.77 – 7.66 (m, 4H), 7.52 (dd, *J* = 8.0, 4.4 Hz, 2H) ppm.^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 146.7, 136.0, 133.7, 131.6, 128.3, 127.9, 127.9, 127.2, 126.5, 125.4, 124.4, 121.9 ppm.



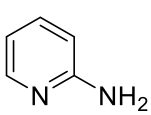
Phenazine (2d) was prepared following the general procedure from **1d** (102 mg, 0.51 mmol). **2d** was purified through SiO_2 column chromatography using a solvent system of hexanes:EtOAc (4:6 V:V). Pure **2d** was obtained as yellow crystal with a yield of 90% (91 mg, 0.50 mmol). The ^{1}H NMR and ^{13}C NMR spectra matched the data reported in the literature. The ^{1}H NMR and ^{13}C NMR spectra matched the data reported in the literature.[17] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 – 8.25 (m, 4H), 7.86 (dd, *J* = 6.9, 3.5 Hz, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 130.6, 129.8 ppm.



2,6-dimethylpyridine (2e) was prepared following the general procedure from **1e** (100 mg, 0.82 mmol) for 5 h. **2e** was purified through SiO_2 column chromatography using a solvent system of hexanes:EtOAc (1:1 V:V). Pure **2e** was obtained as a colorless oil with a yield of 95% (83 mg, 0.77 mmol). The ^{1}H NMR and ^{13}C NMR spectra matched the data reported in the literature.[18] ^{1}H NMR (400 MHz, $CDCl_3$ δ 7.45 (t, *J* = 7.7 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 2H), 2.52 (s, 6H) ppm.^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 136.6, 120.2, 24.6 ppm.



2,4,6-trimethylpyridine (2f) was prepared following the general procedure from **1f** (112 mg, 0.82 mmol) for 6 h. **2f** was purified through SiO_2 column chromatography using a solvent system of hexanes:EtOAc (1:1 V:V). Pure **2f** was obtained as colorless oil with a yield of 92% (91 mg, 0.75 mmol). The ^{1}H NMR and ^{13}C NMR spectra matched the data reported in the literature.[19] ^{1}H NMR (400 MHz, $CDCl_3$ δ 6.78 (s, 2H), 2.47 (s, 6H), 2.26 (s, 3H) ppm.^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 147.6, 120.3, 24.4, 20.9 ppm.



2-aminopyridine (2g) was prepared following the general procedure from **1g** (105 mg, 0.95 mmol). **2g** was purified through SiO_2 column chromatography using a solvent system of hexanes:EtOAc (2:1 V:V). Pure **2g** was obtained as yellow solid with a yield of 97% (87 mg, 0.92 mmol). The ^{1}H NMR and ^{13}C NMR spectra matched the data

[15] B. Sahoo, A. Surkus, M. Pohl, J. Radnik, M. Schneider, S. Bachmann, M. Scalone, K. Junge and M. Beller, *Angew. Chem. Int. Ed*., 2017, **56**, 11242–11247.

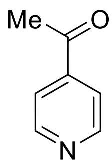
[16] A. Iosub and S. Stahl, *Org. Lett*., 2015, **17**, 4404–4407.

[17] Y. Xiao, X. Wu, H. Wang, S. Sun, J.-T. Yu and J. Cheng, *Org. Lett.,* 2019, **21**, 2565-2568.

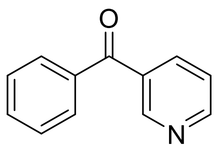
[18] M. Zheng, P. Chen, W. Wua and H. Jiang, *Chem. Commun.,* 2016, **52**, 84-87.

[19] Z. Song, X. Huang, W. Yi and W. Zhang, *Org. Lett.,* 2016, **18**, 5640-5643.

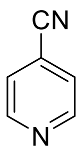
reported in the literature.[20] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 5.1, 1.9 Hz, 1H), 7.42 (ddd, *J* = 8.8, 7.2, 1.9 Hz, 1H), 6.64 (dd, *J* = 7.2, 5.1 Hz, 1H), 6.50 (d, *J* = 8.3 Hz, 1H), 4.42 (bs, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 148.2, 137.9, 114.1, 108.7 ppm.



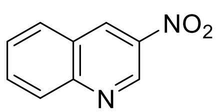
1-(pyridin-4-yl)ethan-1-one (2h) was prepared following the general procedure from **1h** (100 mg, 0.73 mmol). **2h** was purified through SiO_2 column chromatography using a solvent system of hexanes:EtOAc (2:1 V:V). Pure **2h** was obtained as yellow liquid with a yield of 93% (83 mg, 0.68 mmol). The ^{1}H NMR and ^{13}C NMR spectra matched the data reported in the literature.[21] ^{1}H NMR (400 MHz, $CDCl_3$) (400 MHz, CDCl3) δ 8.83 – 8.82 (m, 2H), 7.75 – 7.73 (m, 2H), 2.64 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 151.1, 142.8, 121.3, 26.8 ppm.



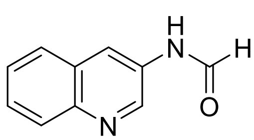
Phenyl(pyridin-3-yl)methanone (2i) was prepared following the general procedure from **1i** (105 mg, 0.53 mmol). **2i** was purified through SiO_2 column chromatography using a solvent system of hexanes:EtOAc (9:1 to 1:1 V:V) and EtOAc:MeOH (9:1 V:V). Pure **2i** was obtained as yellow liquid with a yield of 92% (89 mg, 0.48 mmol). The ^{1}H NMR and ^{13}C NMR spectra matched the data reported in the literature.[22] ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (d, *J* = 2.2 Hz, 1H), 8.81 (dd, *J* = 4.9, 1.8 Hz, 1H), 8.13 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.84 – 7.81 (m, 2H), 7.67 – 7.62 (m, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.46 (dd, *J* = 7.9, 4.9 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.0, 153.0, 151.1, 137.3, 136.9, 133.3, 130.2, 128.8, 123.5 ppm.



4-Cyanopyridine (2j) was prepared following the general procedure from **1j** (121 mg, 1.01 mmol). **2j** was purified through SiO_2 column chromatography using a solvent system of hexanes:EtOAc (8:2 V:V). Pure **2j** was obtained as yellow solid with a yield of 87% (91 mg, 0.87 mmol). The ^{1}H NMR and ^{13}C NMR spectra matched the data reported in the literature.[23] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 – 8.82 (m, 2H), 7.55 – 7.54 (m, 2H) ppm.^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 125.3, 120.5, 116.5 ppm.



3-nitroquinoline (2k) was prepared following the general procedure from **1k** (52 mg, 0.27 mmol), at 100 °C for 10 h. **2k** was purified through SiO_2 column chromatography using a hexanes:EtOAc (5:1 to 2:1 V:V) solvent system. Pure **2k** was obtained as yellow solid with a yield of 52% (25 mg, 0.14 mmol). The ^{1}H NMR and ^{13}C NMR spectra matched the data reported in the literature.[9] ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.65 (d, *J* = 2.6 Hz, 1H), 9.04 (d, *J* = 2.6 Hz, 1H), 8.24 (d, *J* = 8.5 Hz, 1H), 8.05 (d, *J* = 8.2 Hz, 1H), 7.96 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.75 (t, *J* = 7.5 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) 150.2, 144.2, 141.1, 133.5, 132.4, 130.0, 129.9, 128.9, 126.1 ppm.



***N*-(quinolin-3-yl)formamide (2ka)** was prepared following the general procedure from **1k** (96 mg, 0.50 mmol). **2ka** was purified through SiO_2 column chromatography using a solvent system of hexanes:EtOAc (8:2 V:V). Pure **2ka** was obtained as light brown solid with a yield of 59% (51 mg, 0.30 mmol). The ^{1}H NMR and ^{13}C NMR spectra matched the data reported in the literature.[24] ^{1}H NMR (400 MHz, $CDCl_3$, *mixture of rotamers trans/cis, 80/20*) δ 9.51 - 9.44 (m, 1H), 8.84 (d, J = 6.5 Hz, 1.8H), 8.80 (s, 0.2H), 8.51 (s, 1H), 8.08 (d, *J* = 8.6 Hz, 0.20H), 8.03 (d, *J* = 8.5 Hz, 0.80H), 7.85 (s, 0.2H), 7.82 – 7.77 (m, 1H), 7.69 – 7.61 (m, 1H), 7.57 -7.51 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, *mixture to rotamers*) δ 162.4, 160.1, 145.9, 145.2, 144.0, 143.9, 131.4, 131.1, 129.3, 129.0, 128.7, 128.3, 128.3, 128.0, 127.8, 127.8, 127.3, 127.2, 142.2, 122.2 ppm

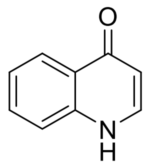
[20] M. K. Elmkaddem, C. Fischmeister, C. M. Thomas, J. L. Renaud, *Chem. Commun.,* 2010, **46**, 925-927.

[21] B. Sahoo, A.-E. Surkus, M.-M. Pohl, J. Radnik, M. Schneider, S. Bachmann, M. Scalone, K. Junge and M. Beller, *Angew. Chem. Int. Ed.,* 2017, **56**, 11242–11247.

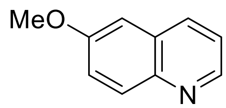
[22] M. Cai, J. Peng, W. Hao and G. Ding, *Green Chem.,* 2011, **13**, 190-196.

[23] X. Jiang, J.-M. Wang, Y. Zhang, Z. Chen, Y.-M. Zhu and S.-J. Ji, *Tetrahedron*, 2015, **71**, 4883-4887.

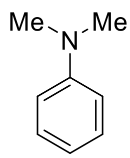
[24] F. Cuccu, F. Basoccu, C. Fattuoni, A. Porcheddu, *Molecules*, 2022, **27**, 5450.



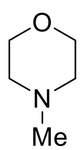
Quinolin-4(1*H*)-one (2la) was synthesized according to the general procedure using 4-nitroquinoline *N*-oxide (**1l**, 100 mg, 0.52 mmol) with the modification of using a sodium carbonate solution instead of a sodium bicarbonate solution in the neutralization step. **2la** was purified through SiO_2 column chromatography using a hexanes:EtOAc (8:2 V:V) solvent system. Pure **2la** was obtained as light brown solid with a yield of 27%. The ^1H NMR and ^{13}C NMR spectra matched the data reported in the literature.[25] ^1H NMR (400 MHz, DMSO-d_6) δ 11.87 (bs, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 7.3 Hz, 1H), 7.69 – 7.61 (m, 1H), 7.54 (d, *J* = 8.3 Hz, 1H), 7.33 (t, *J* = 7.7 Hz, 1H), 6.08 (d, *J* = 7.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, DMSO d_6) δ 177.6, 140.2, 139.9, 132.1, 125.9, 125.2, 123.6, 118.6, 108.9 ppm.



6-methoxyquinoline (2m) was prepared following the general procedure from **1m** (103 mg, 0.58 mmol) for 5 h. **2m** was purified through SiO_2 column chromatography using a hexanes:EtOAc (5:1 to 2:1 V:V) solvent system. Pure **2m** was obtained as magenta liquid with a yield of 90% (84 mg, 0.53 mmol). The ^1H NMR and ^{13}C NMR spectra matched the data reported in the literature.[26] ^1H NMR (400 MHz, $CDCl_3$) δ 8.76 – 8.75 (m, 1H), 8.01 (t, *J* = 8.0 Hz, 2H), 7.38 – 7.30 (m, 2H), 7.04 (s, 1H), 3.91 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 148.0, 144.5, 134.8, 130.9, 129.4, 122.3, 121.4, 105.2, 55.6 ppm.



***N*,*N*-dimethylaniline (2n)** was prepared following the general procedure from **1n** (108 mg, 0.79 mmol). **2n** was purified through SiO_2 column chromatography using a solvent system of hexanes:EtOAc (5:1 to 2:1 V:V). Pure **2n** was obtained as light brown oil with a yield of 80% (76 mg, 0.63 mmol). The ^1H NMR and ^{13}C NMR spectra matched the data reported in the literature.[27] ^1H NMR (400 MHz, $CDCl_3$) δ 7.26 -7.22 (m, 2H), 6.75 - 6.70 (m, 3H), 2.93 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 129.2, 116.7, 112.7, 40.7 ppm.



4-methylmorpholine (2o) was prepared following the general procedure from 4-methylmorpholine *N*-oxide (109 mg, 0.93 mmol). **2n** was purified through SiO_2 column chromatography using a solvent system of hexanes:EtOAc (5:1 to 2:1 V:V), Pure **2o** was obtained as a light yellow oil with a yield of 86% (81 mg, 0.80 mmol). The ^1H NMR and ^{13}C NMR spectra matched the data reported in the literature.[28] ^1H NMR (400 MHz, $CDCl_3$) δ 3.71 (t, *J* = 4.7 Hz, 4H), 2.42 – 2.39 (m, 4H), 2.28 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 66.8, 55.3, 46.3 ppm.

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[25] F. Wang, L. Jin, L. Kong and X. Li. *Org. Lett.,* 2017, **19**, 1812–1815.
[26] Q. Wang, H. Chai and Z. Yu. *Organometallics*, 2018, **37**, 584-591.
[27] H. Li, T. P. Gonçalves, Q. Zhao, D. Gong, Z. Lai, Z. Wang, J. Zheng and K. W. Huang. *Chem. Commun.,* 2018, **54**, 11395-11398.
[28] X. Ge, C. Luo, C. Qian, Z. Yua and X. Chen. *RSC Adv.,* 2014, **4**, 43195-43203.

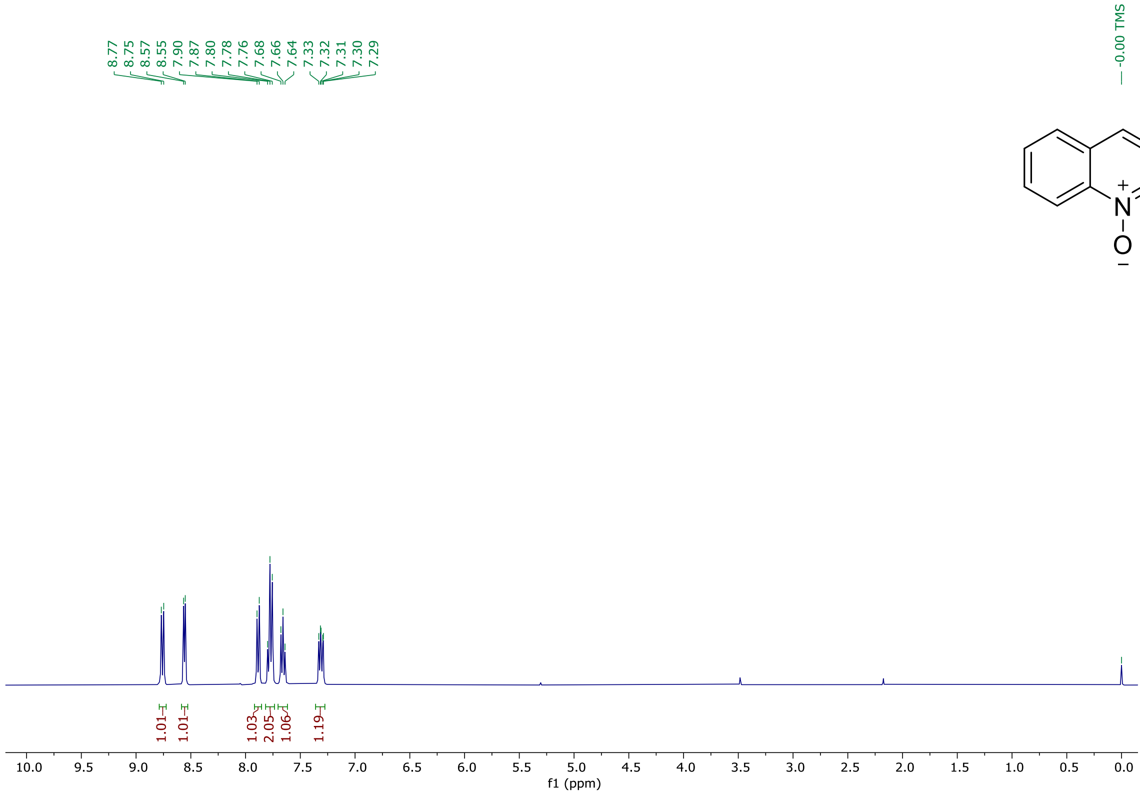


Figure 1. ^{1}H NMR spectra of compound **1a**

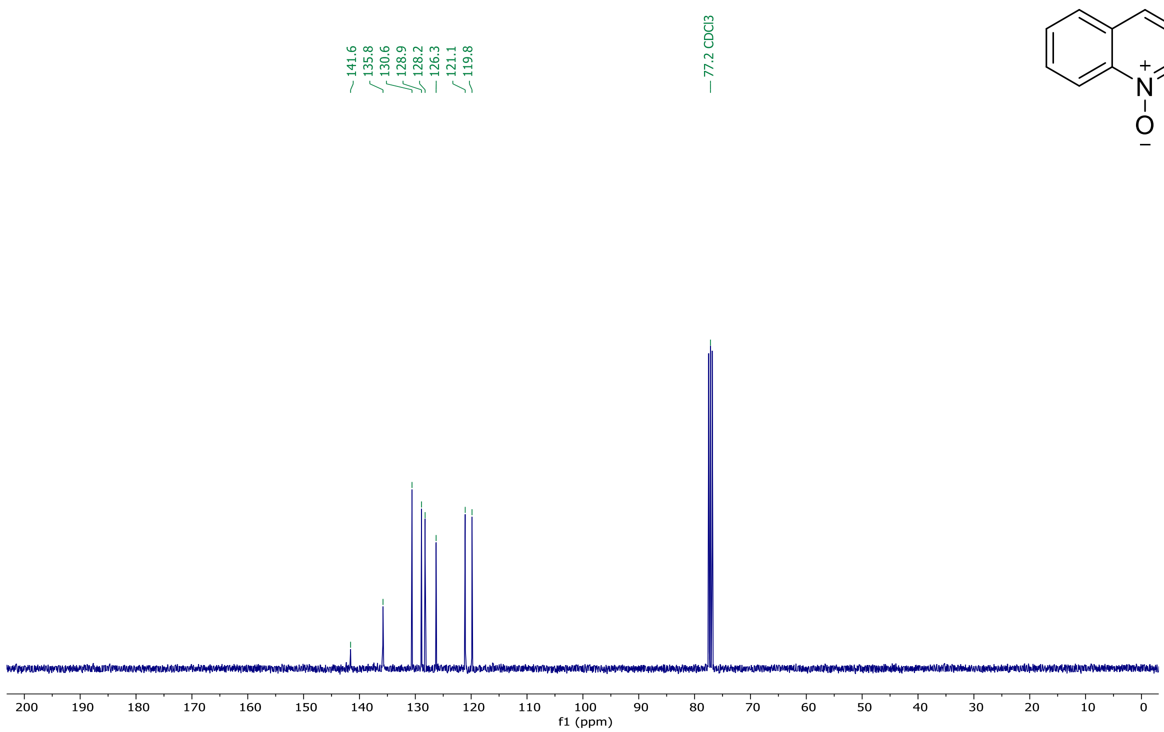


Figure 2. ^{13}C NMR spectra of compound **1a**

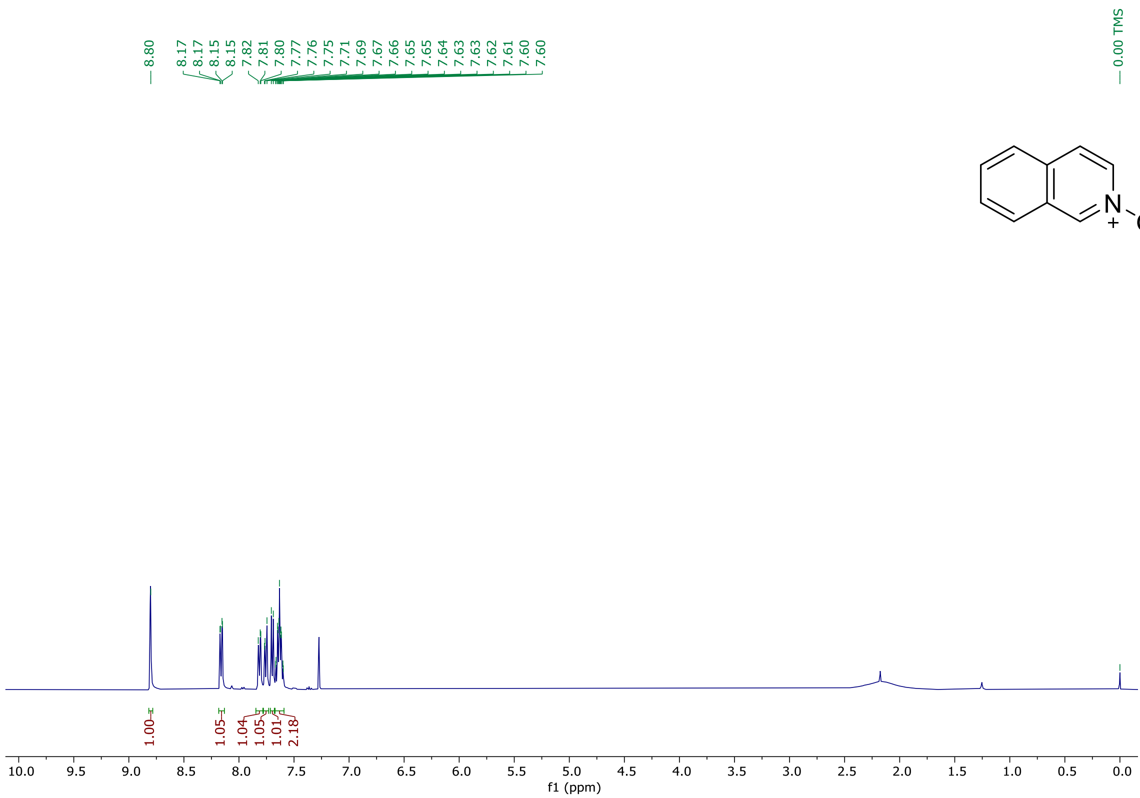


Figure 3. ^{1}H NMR spectra of compound **1b**

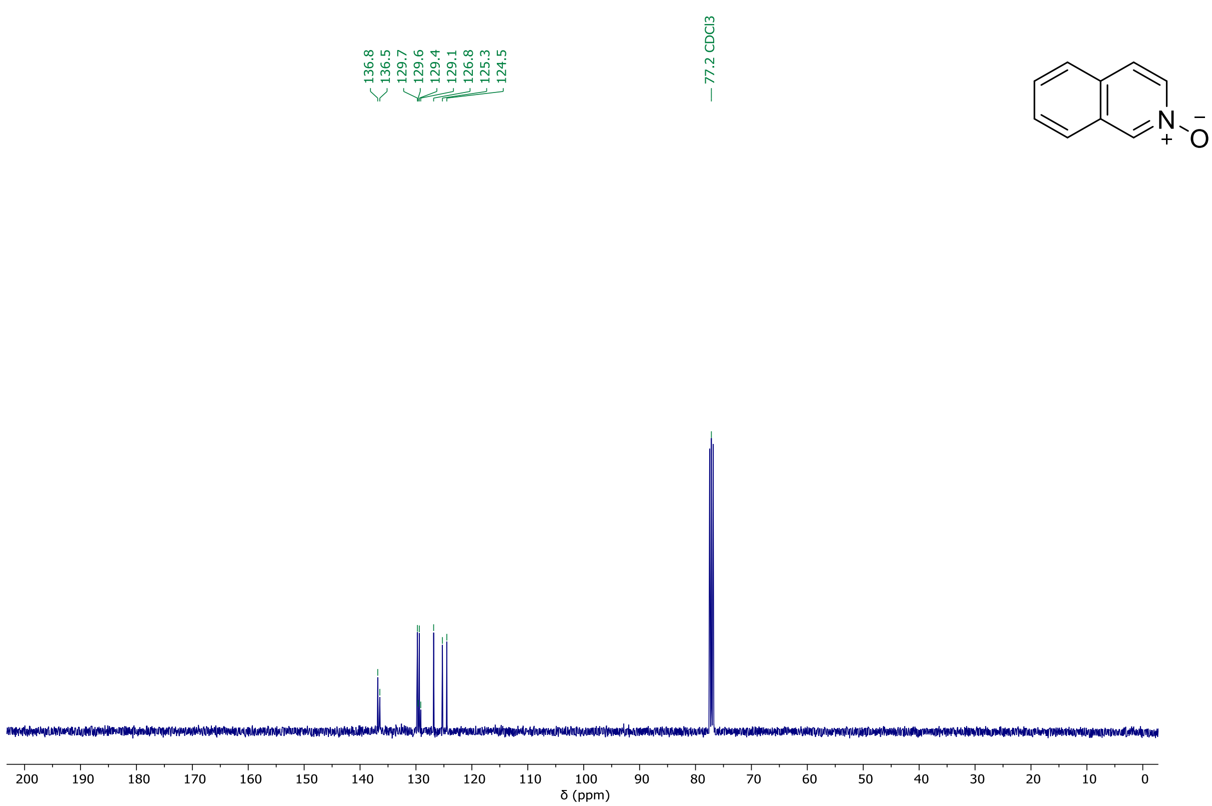


Figure 4. ^{13}C NMR spectra of compound **1b**

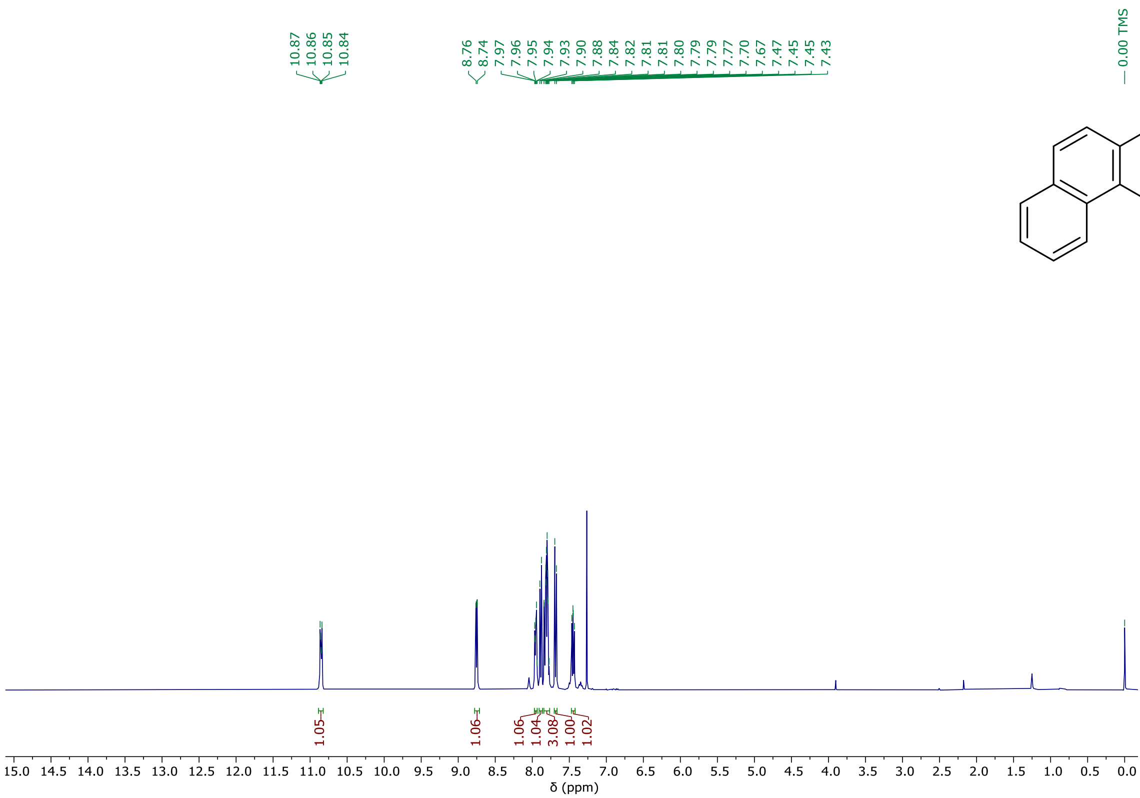


Figure 5. ^{1}H NMR spectra of compound **1c**

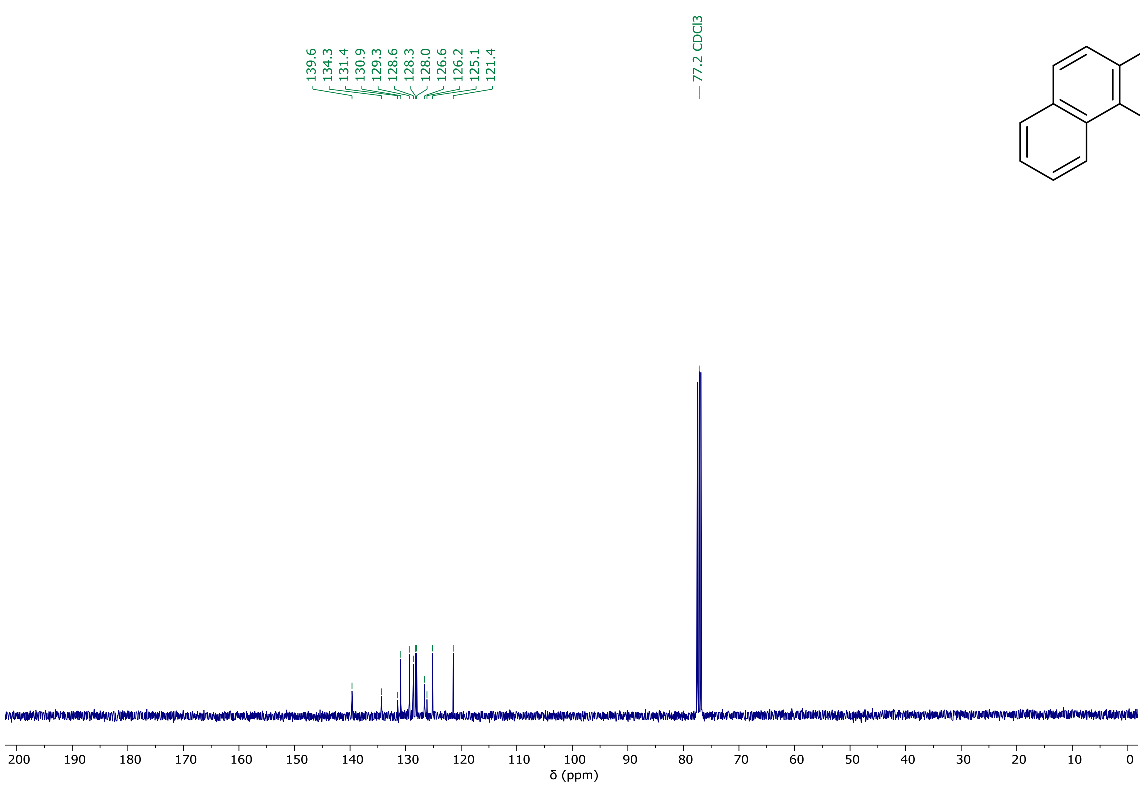


Figure 6. ^{13}C NMR spectra of compound **1c**

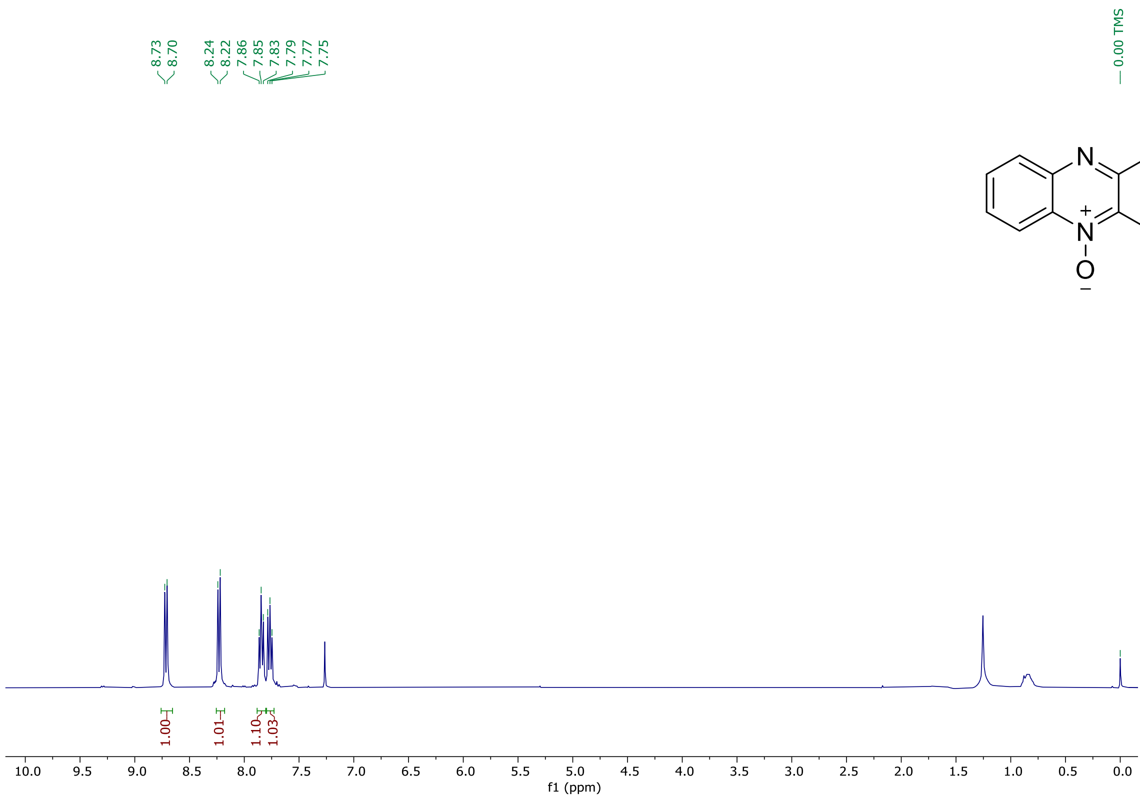


Figure 7. ^{1}H NMR spectra of compound **1d**

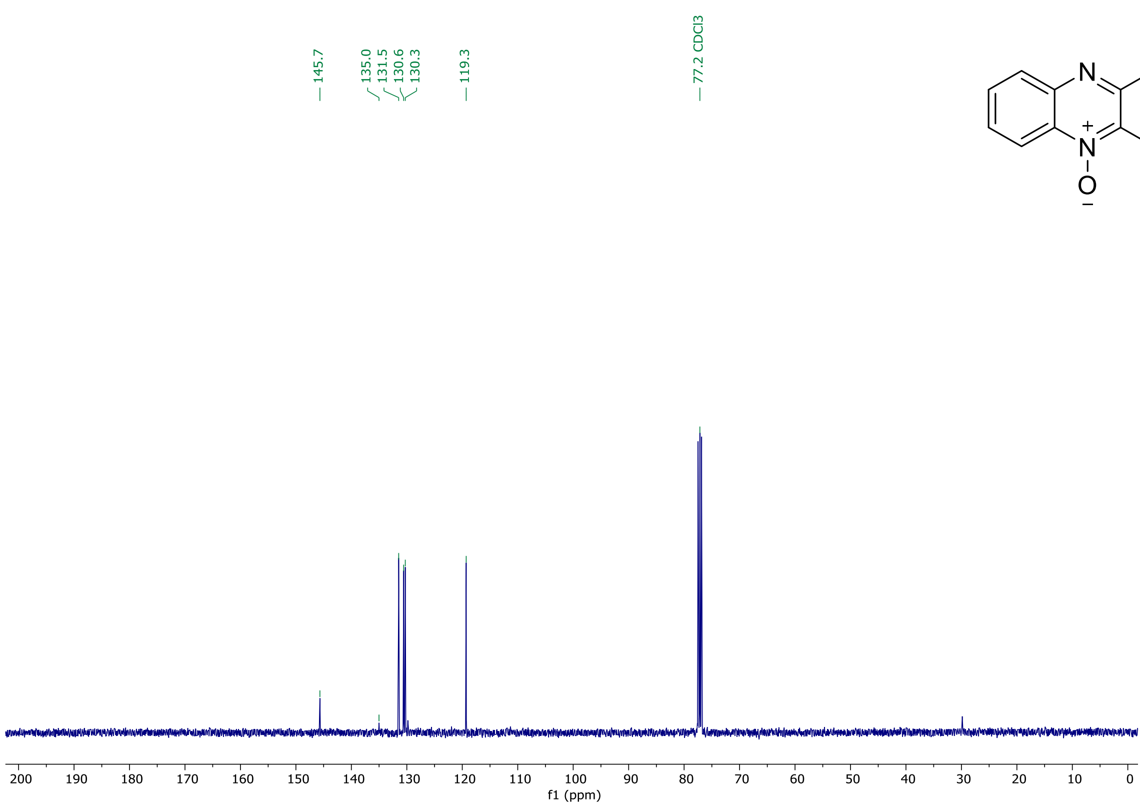


Figure 8. ^{13}C NMR spectra of compound **1d**

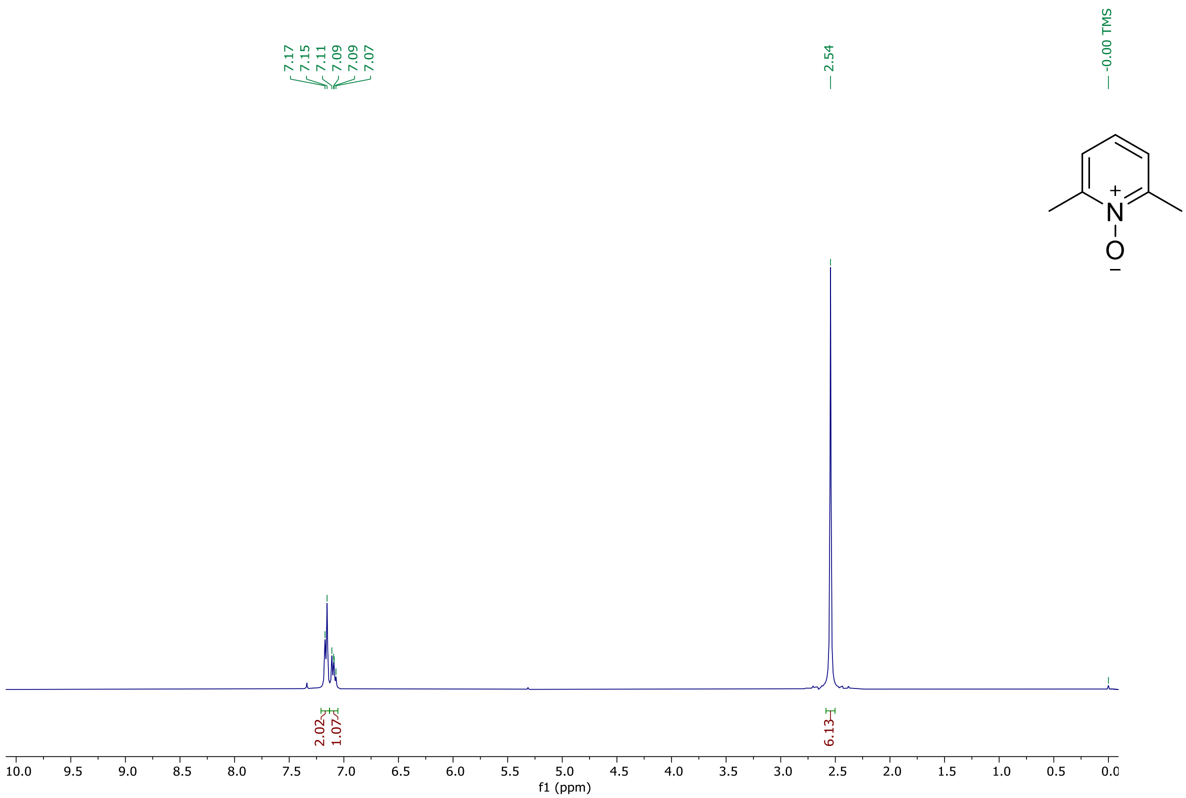


Figure 9. ^{1}H NMR spectra of compound **1e**

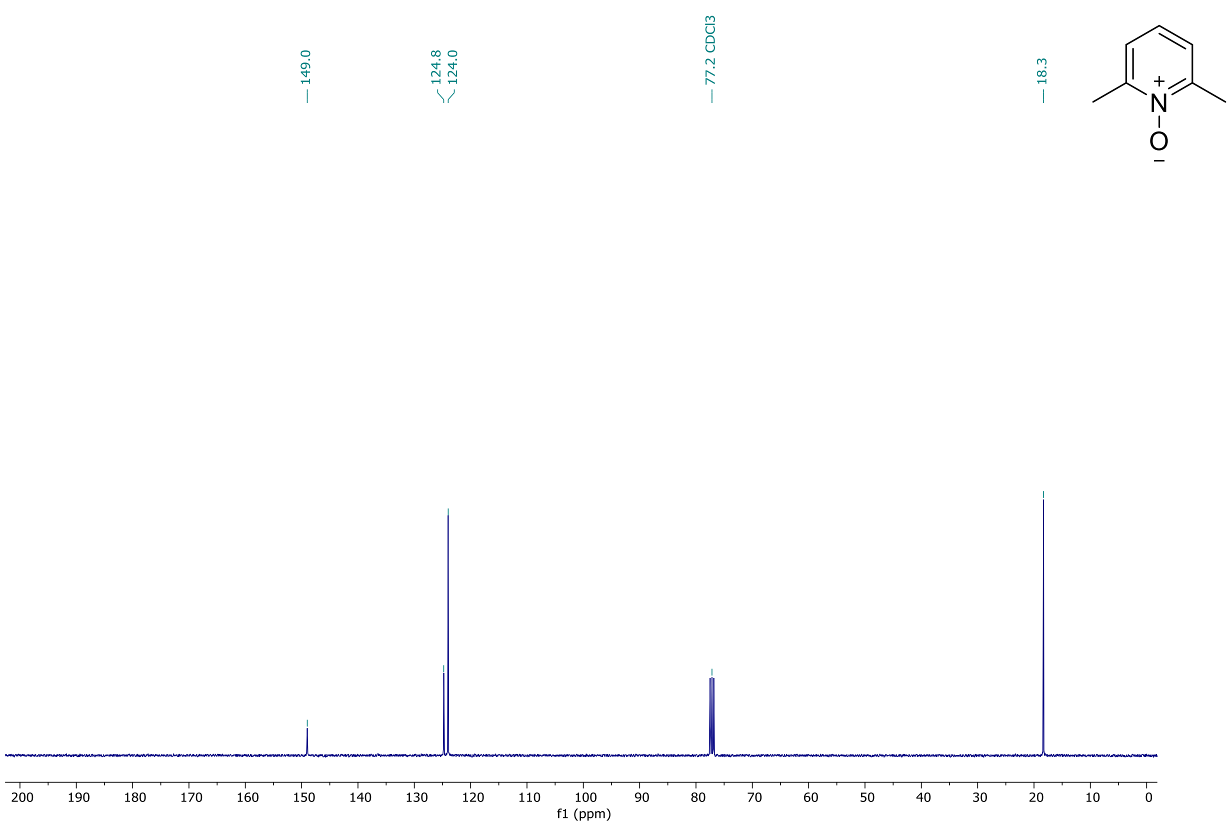


Figure 10. ^{13}C NMR spectra of compound **1e**

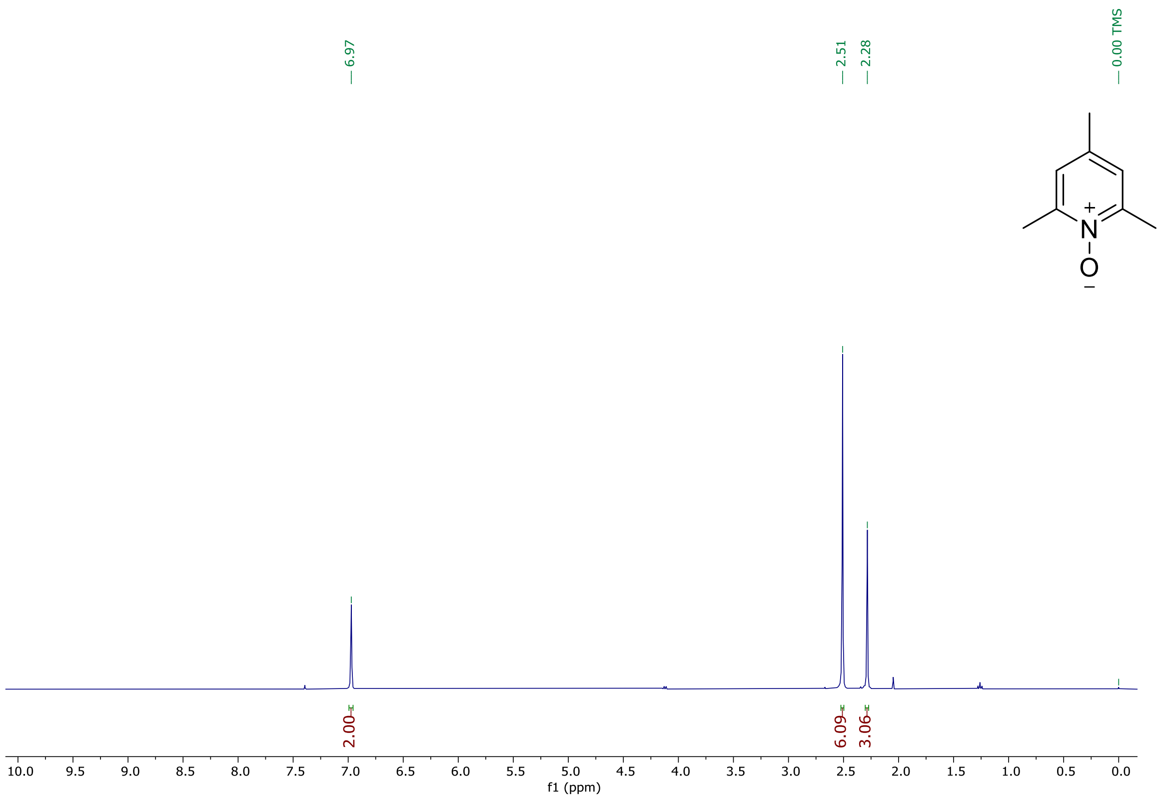


Figure 11. ^{1}H NMR spectra of compound **1f**

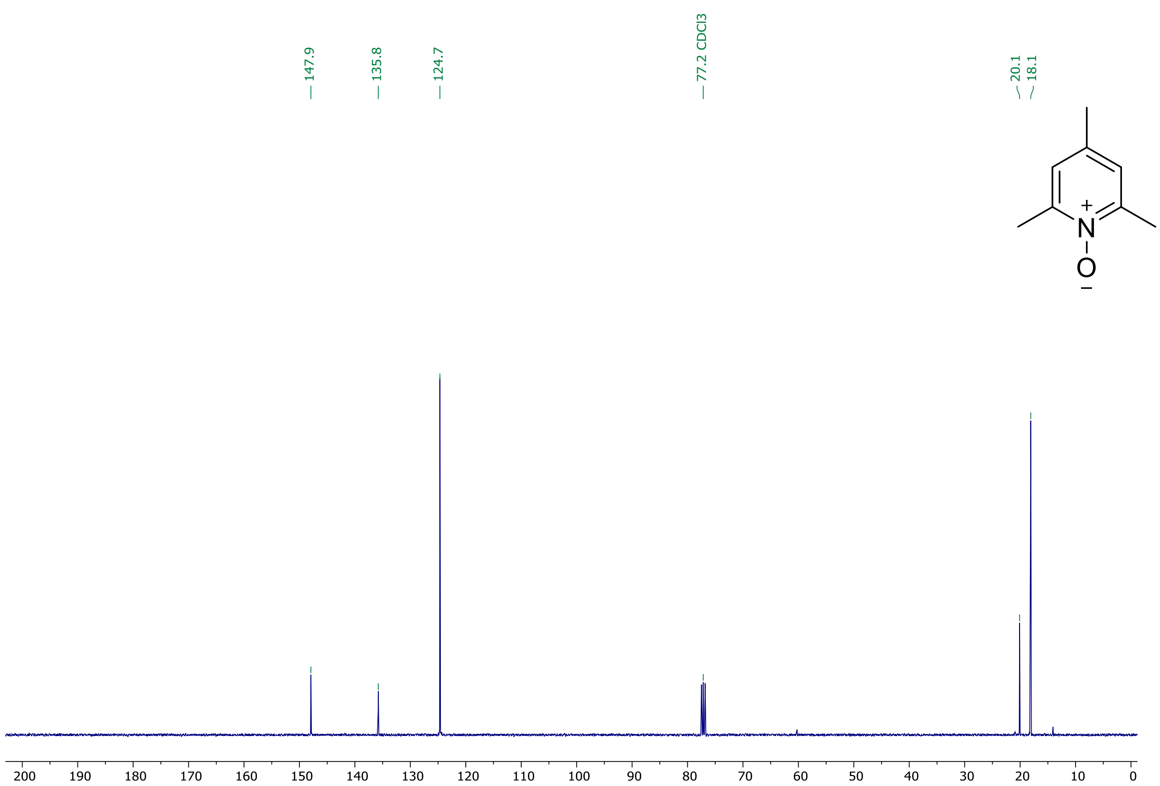


Figure 12. ^{13}C NMR spectra of compound **1f**

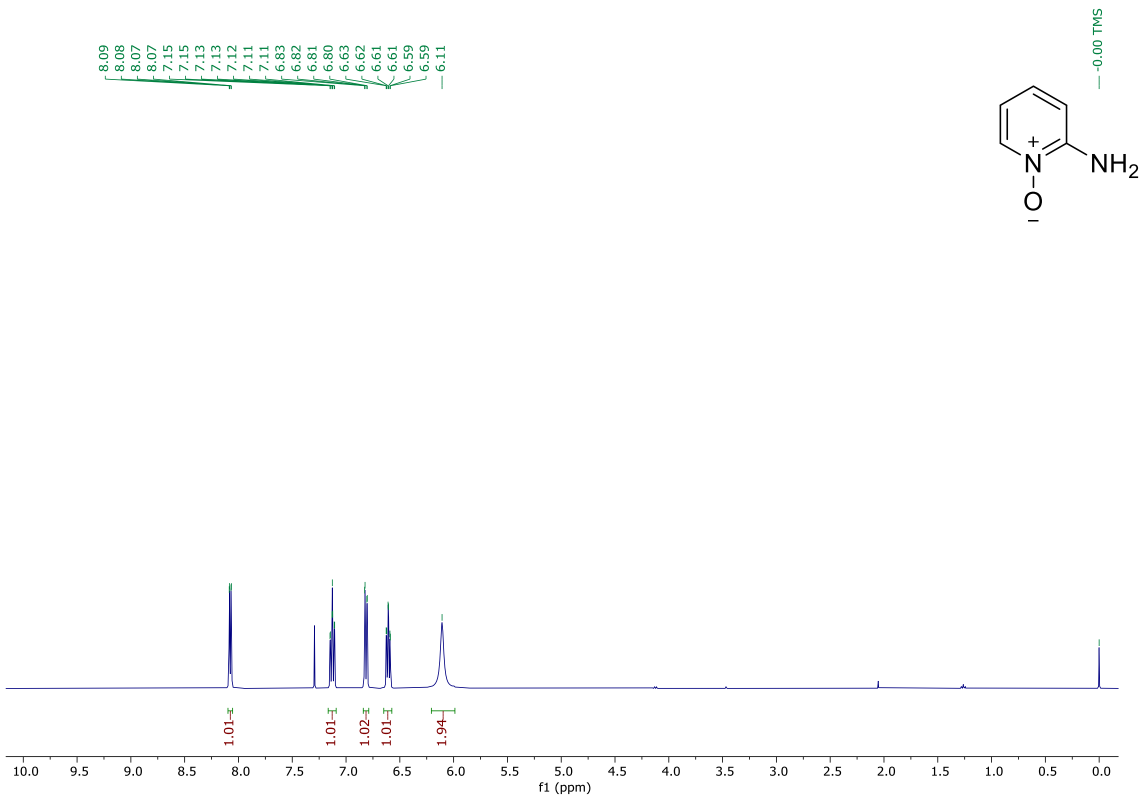


Figure 13. ^{1}H NMR spectra of compound **1g**

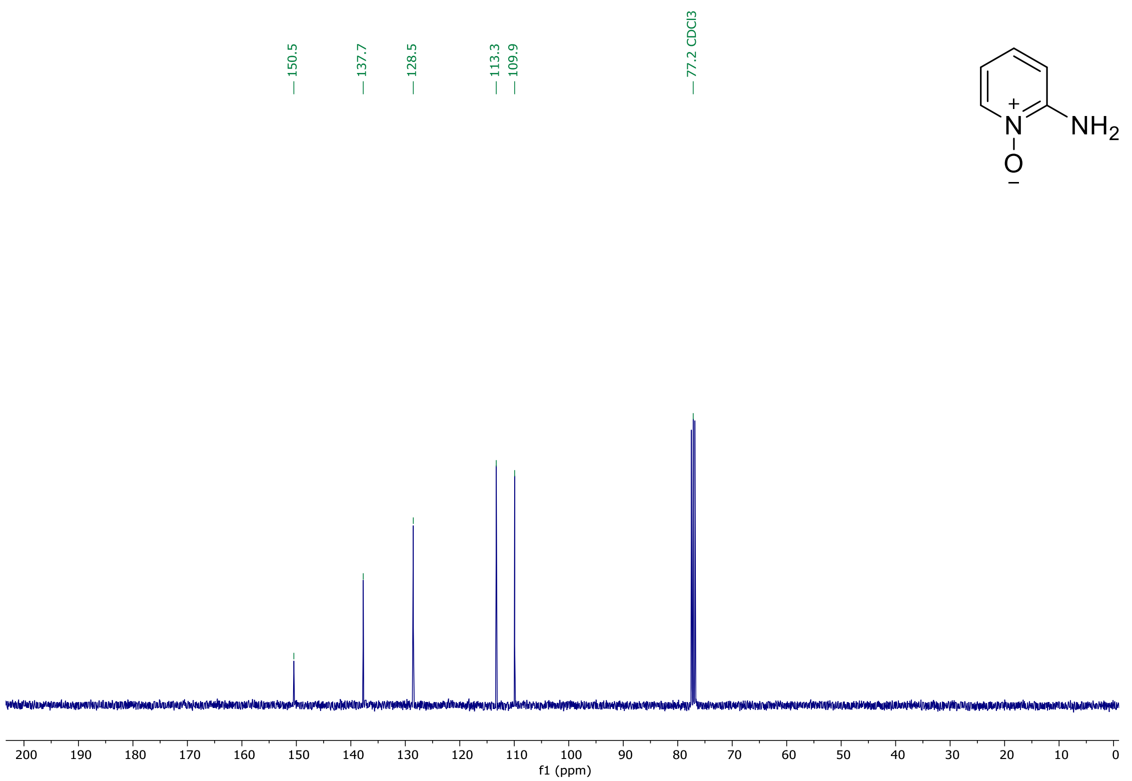


Figure 14. ^{13}C NMR spectra of compound **1g**

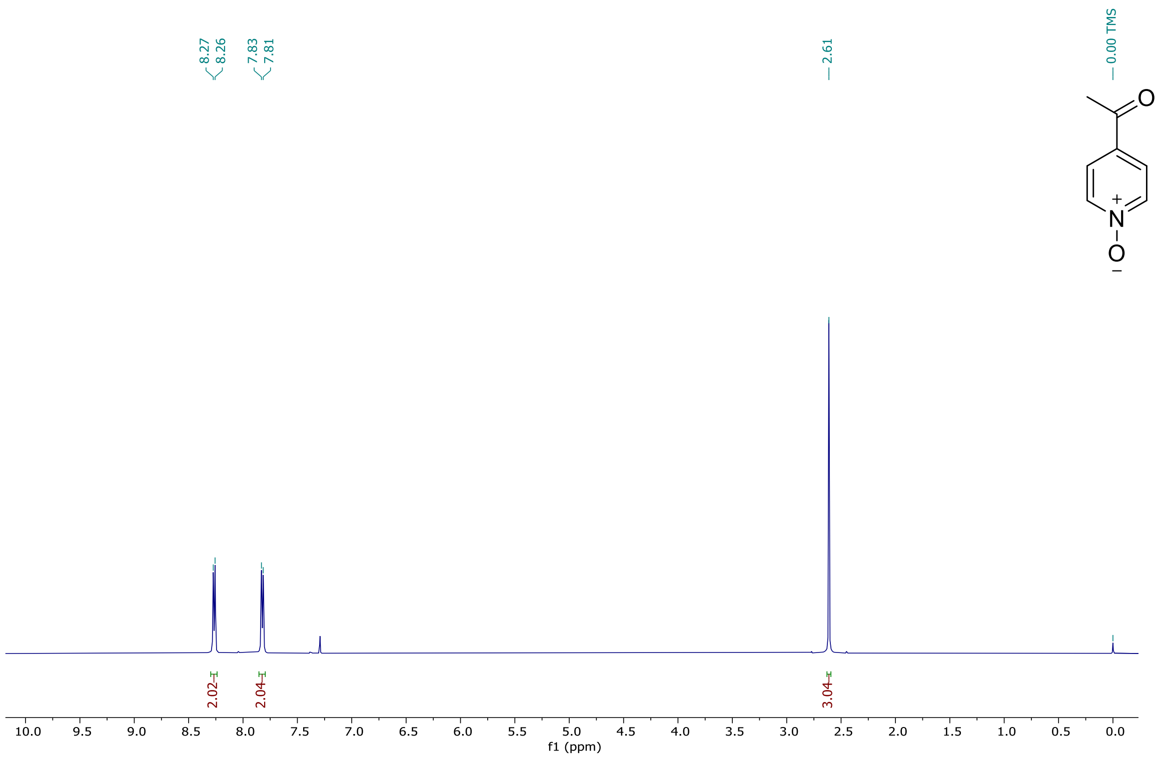


Figure 15. ^{1}H NMR spectra of compound **1h**

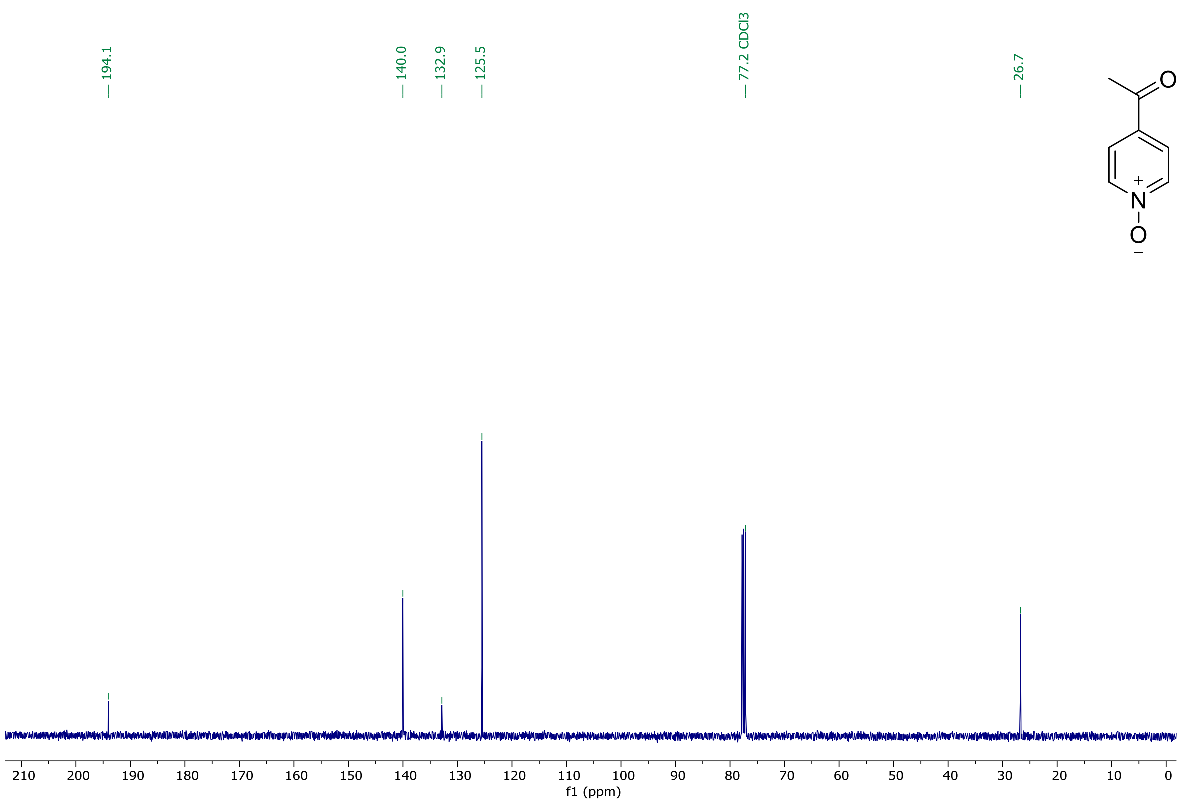


Figure 16. ^{13}C NMR spectra of compound **1h**

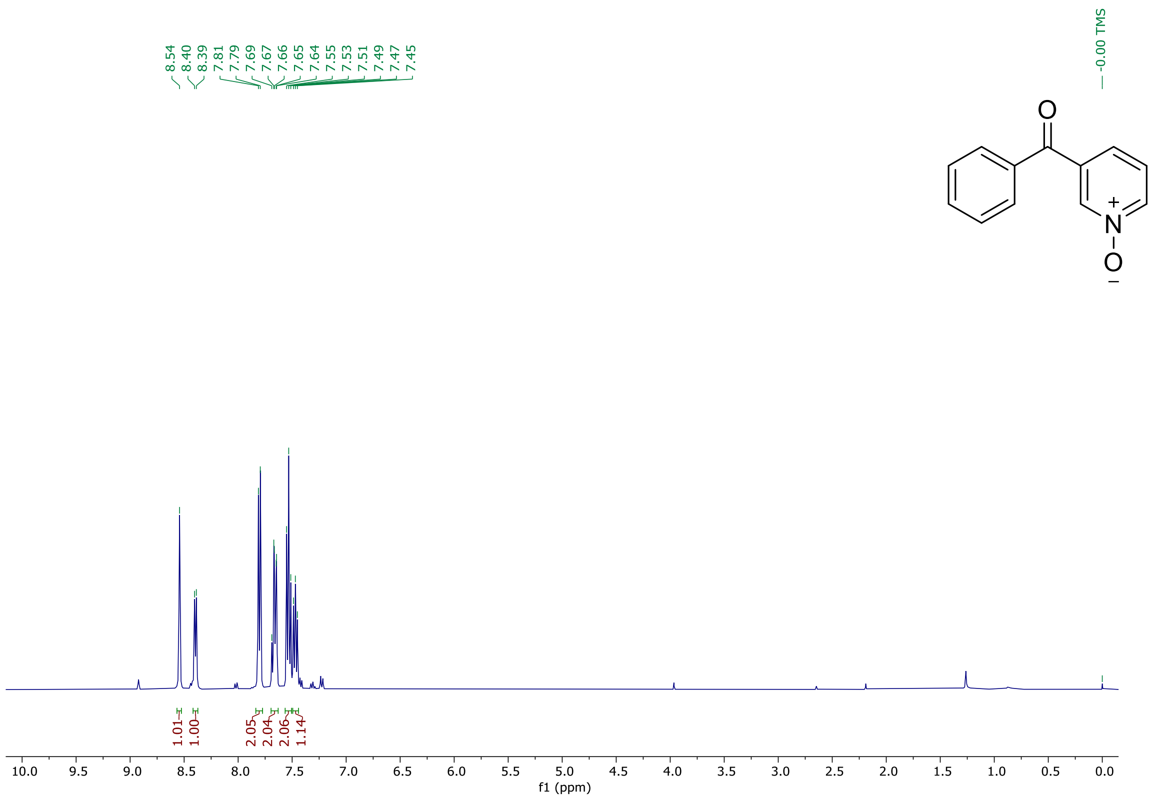


Figure 17. ^{1}H NMR spectra of compound **1i**

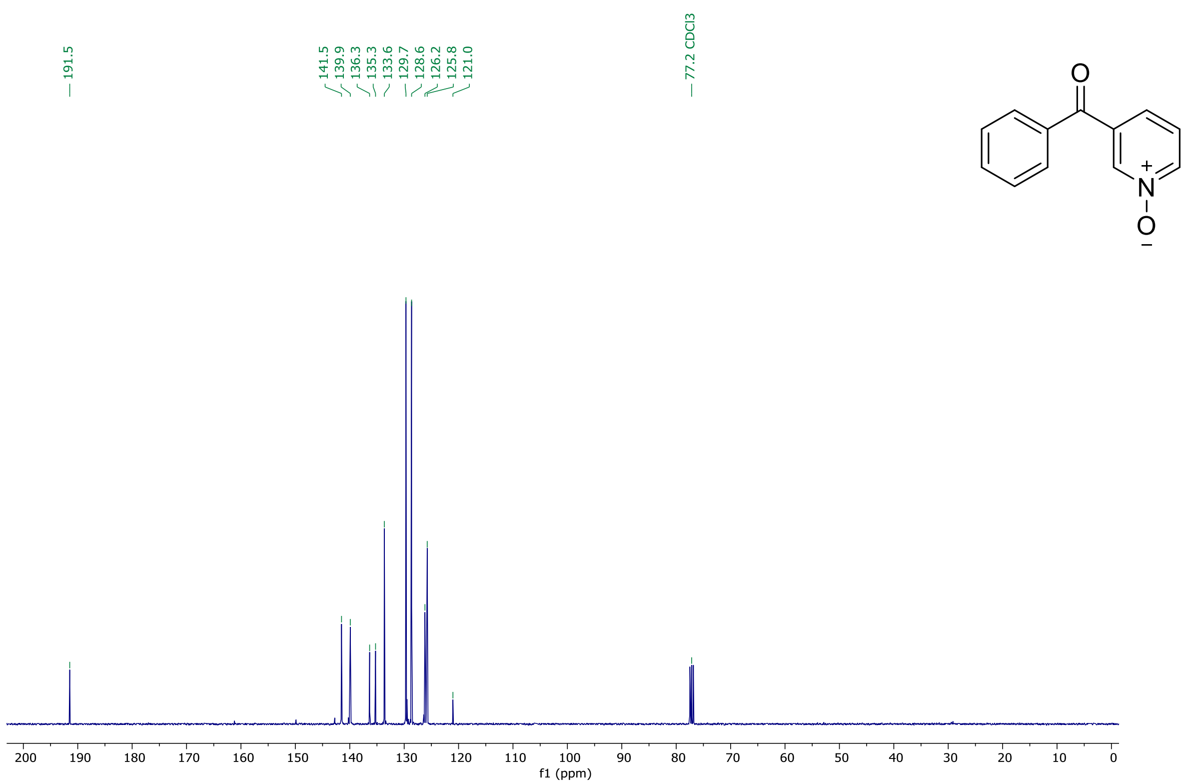


Figure 7. ^{13}C NMR spectra of compound **1i**

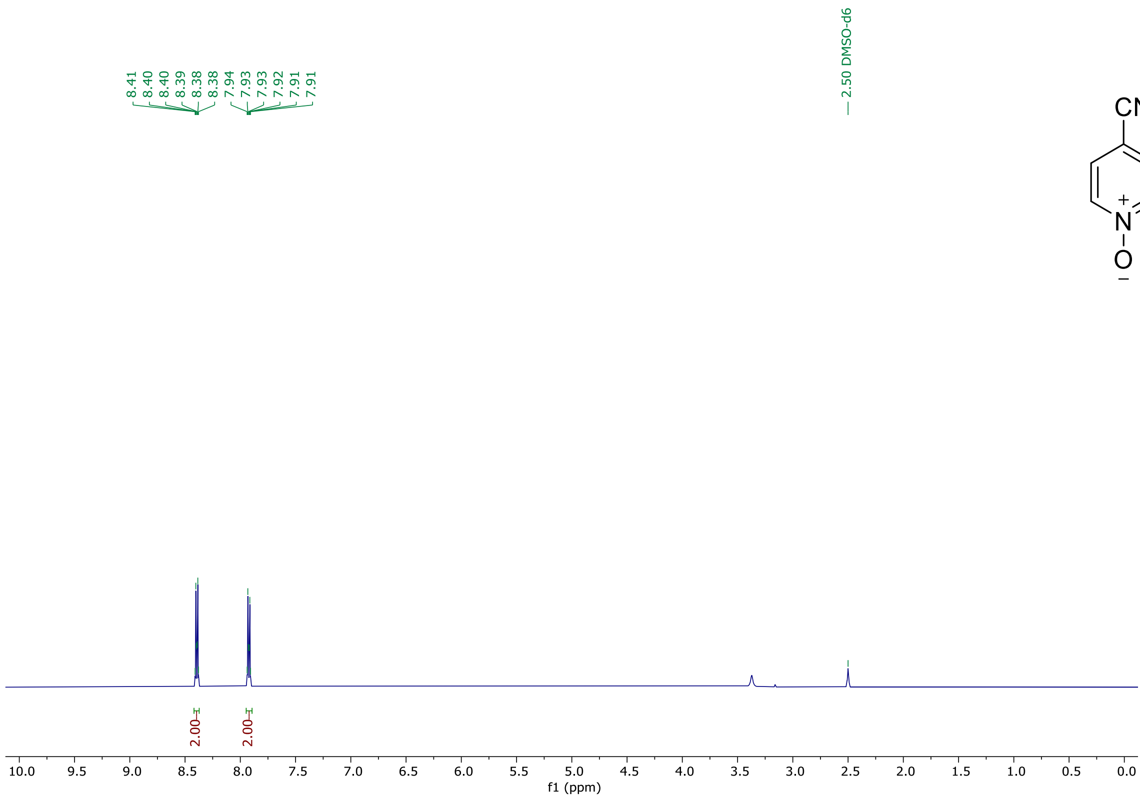


Figure 19. ^{1}H NMR spectra of compound **1j**

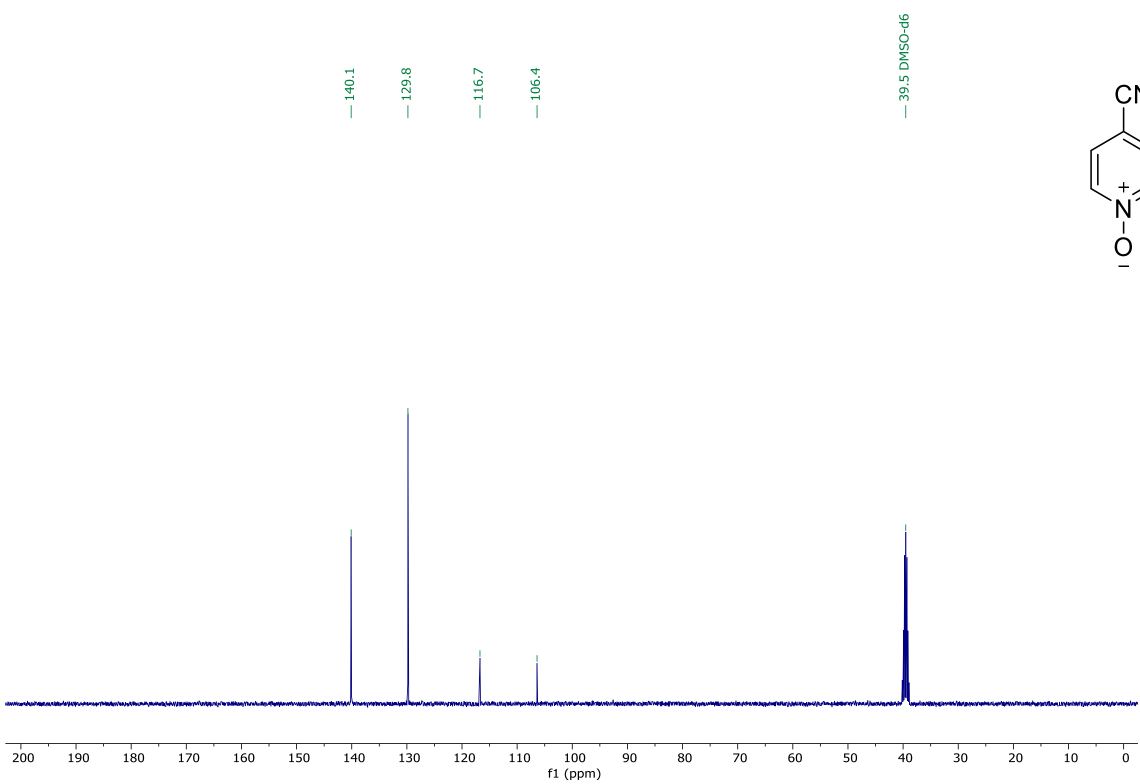


Figure 20. ^{13}C NMR spectra of compound **1j**

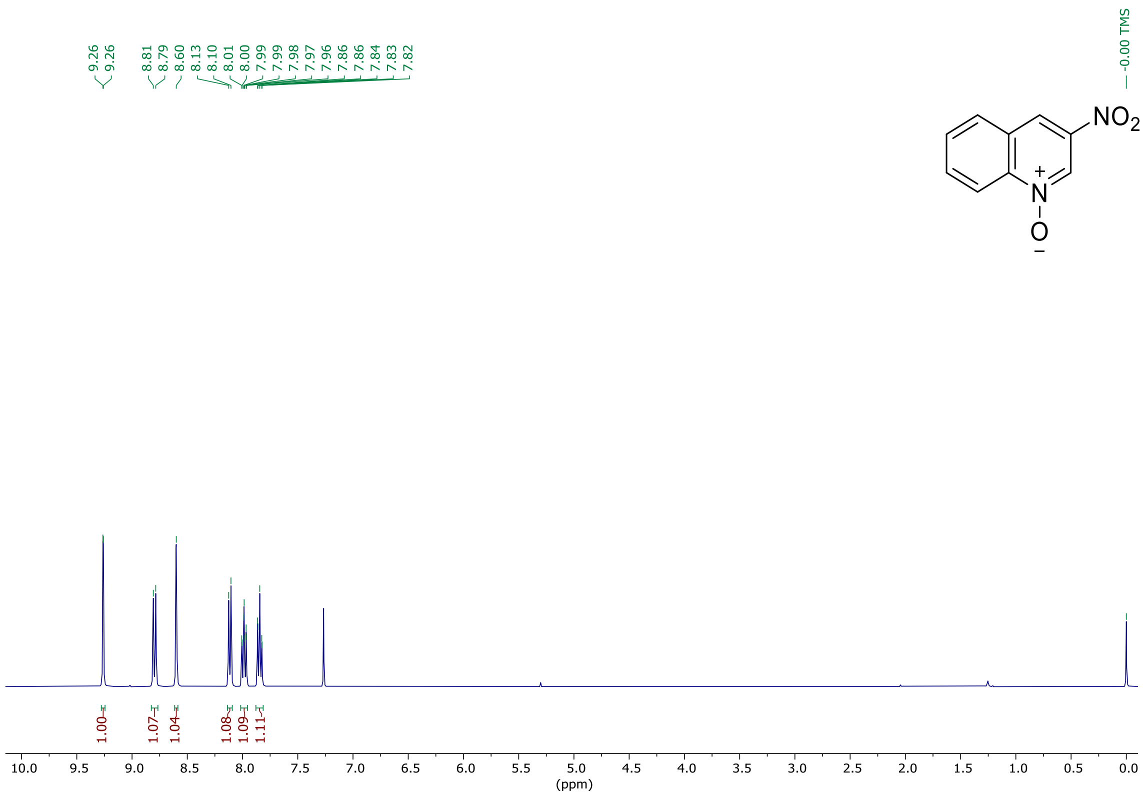


Figure 21. ^{1}H NMR spectra of compound **1k**

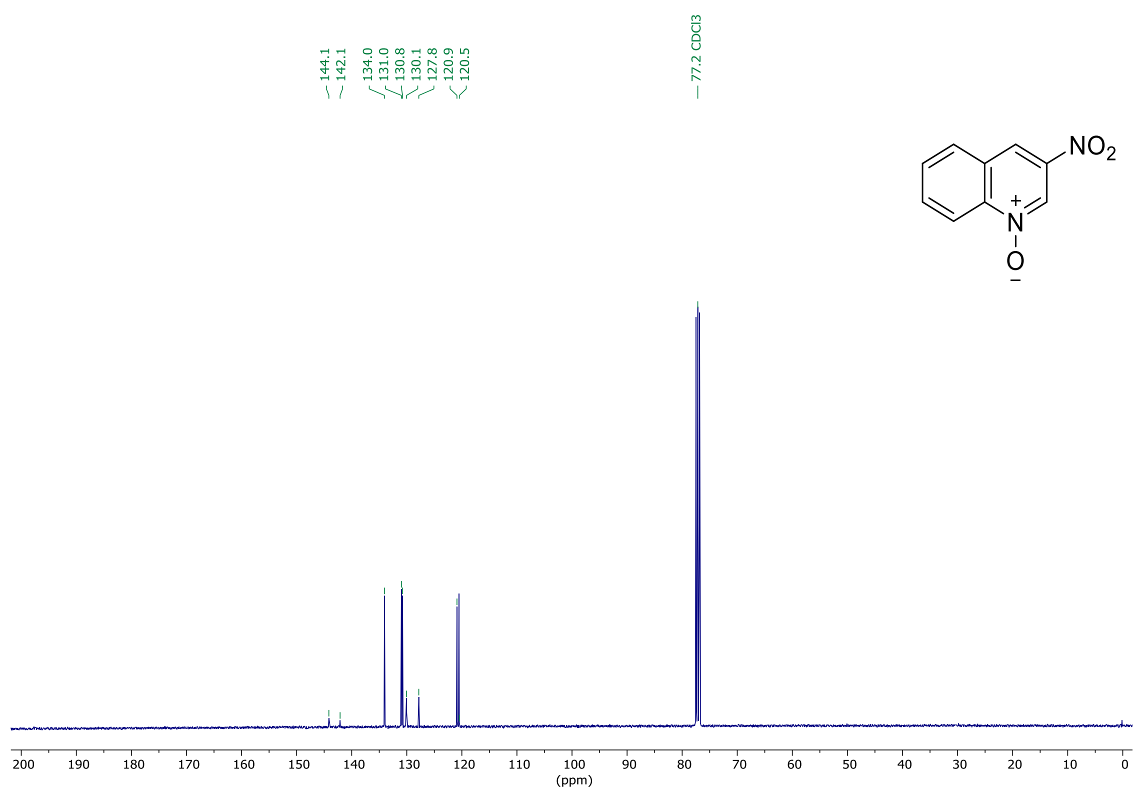


Figure 22. ^{13}C NMR spectra of compound **1k**

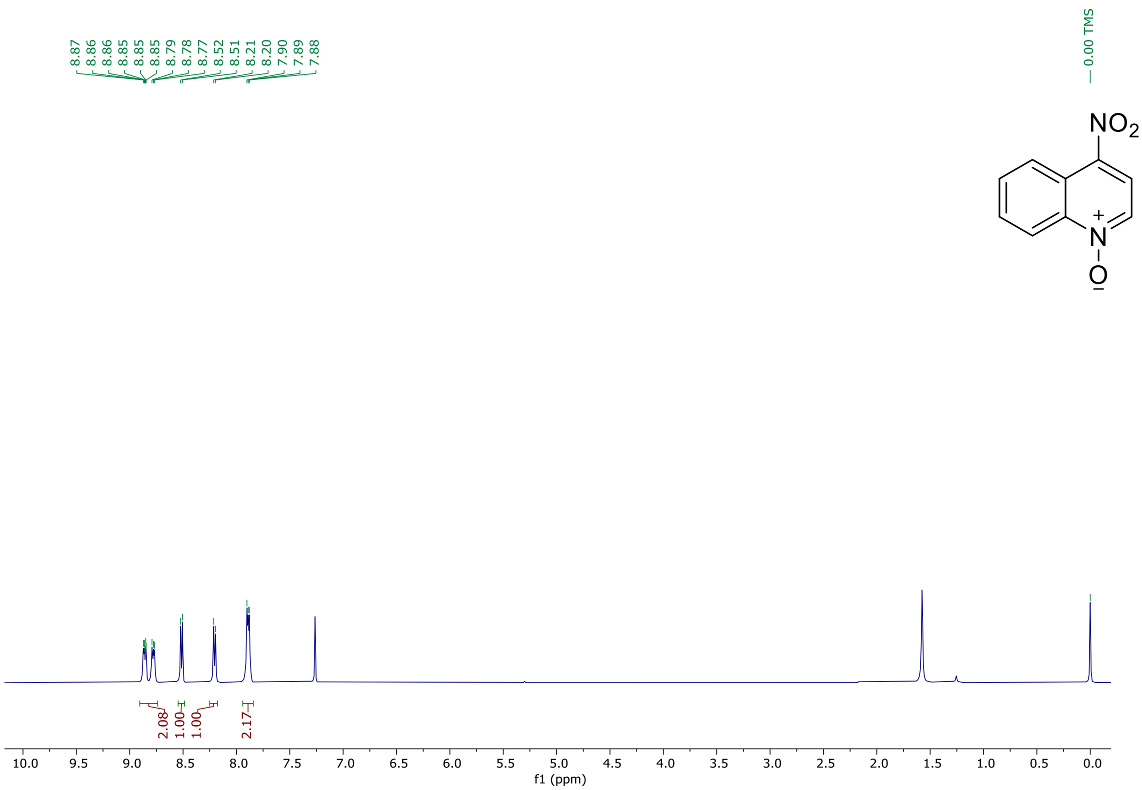


Figure 23. ^{1}H NMR spectra of compound **2l**

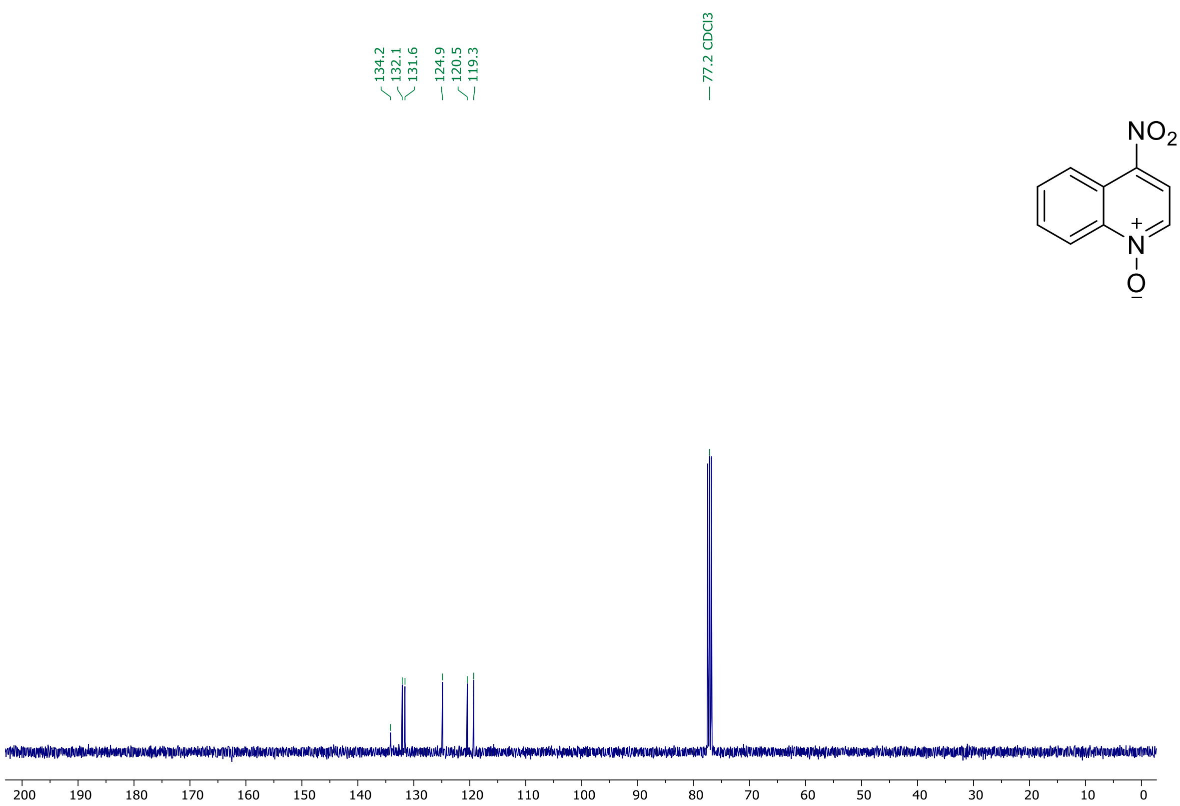


Figure 24. ^{13}C NMR spectra of compound **1l**

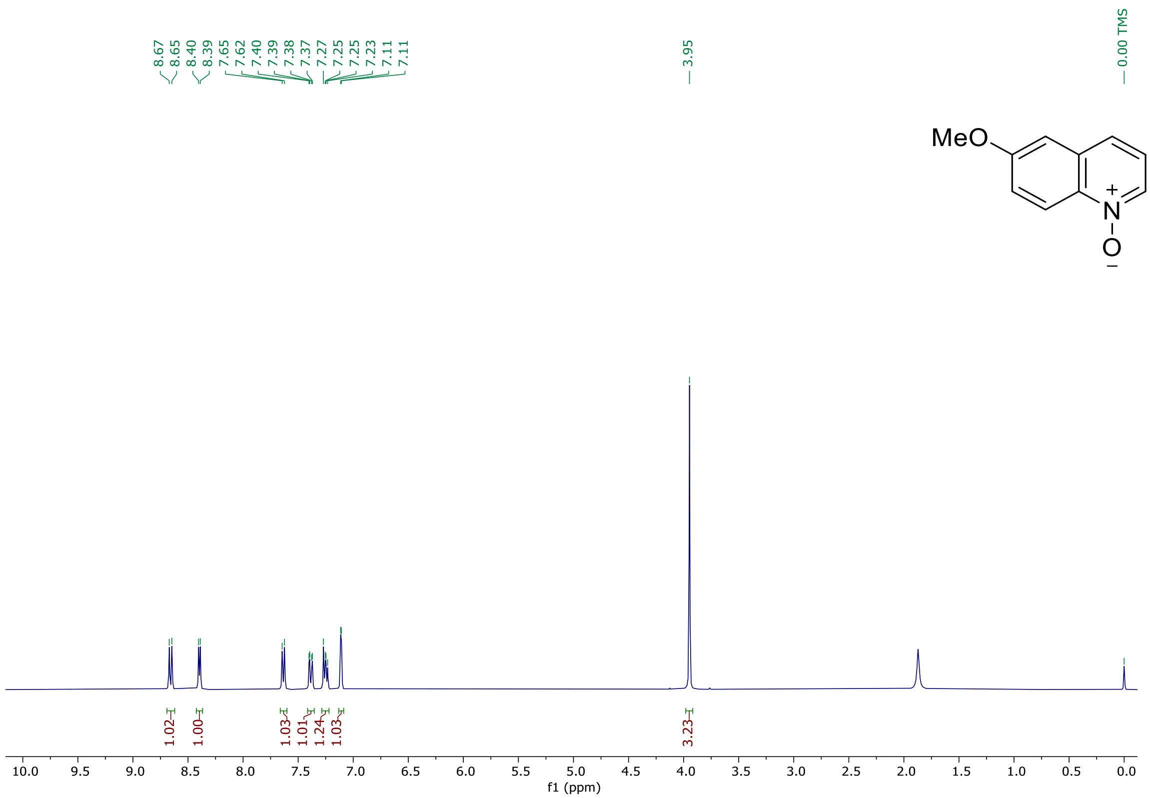


Figure 25. ^{1}H NMR spectra of compound **1m**

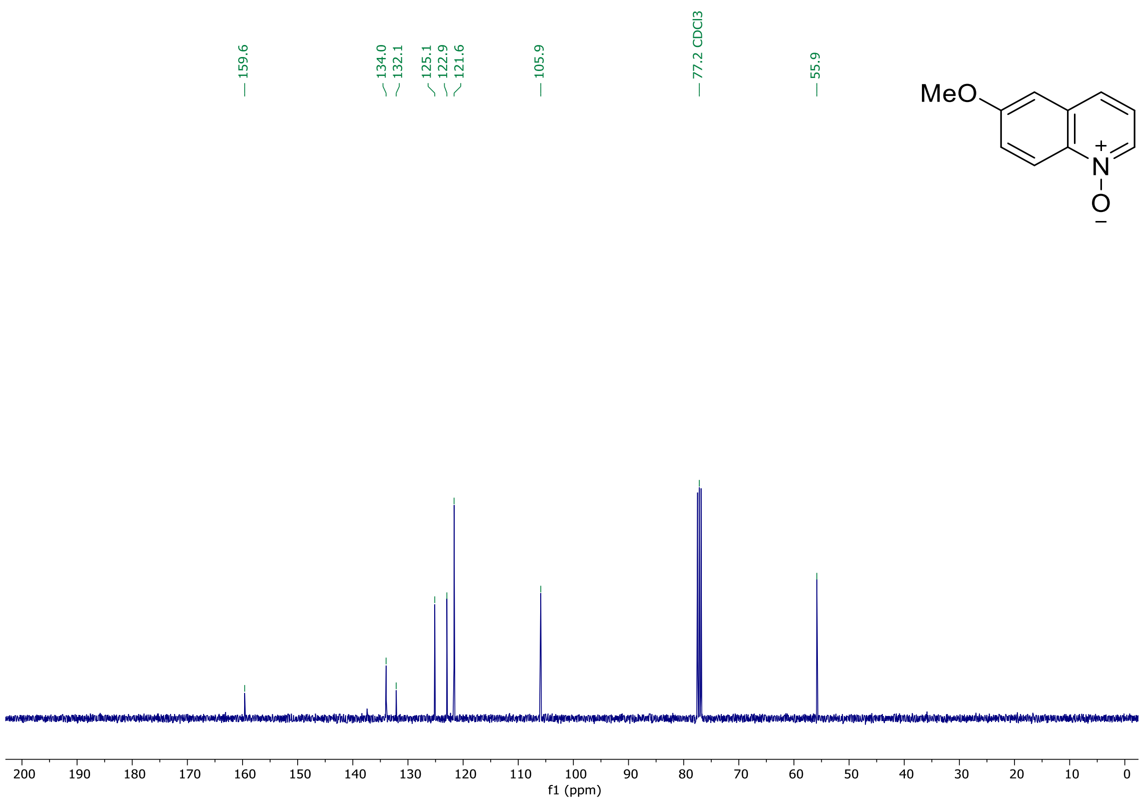


Figure 26. ^{13}C NMR spectra of compound **1m**

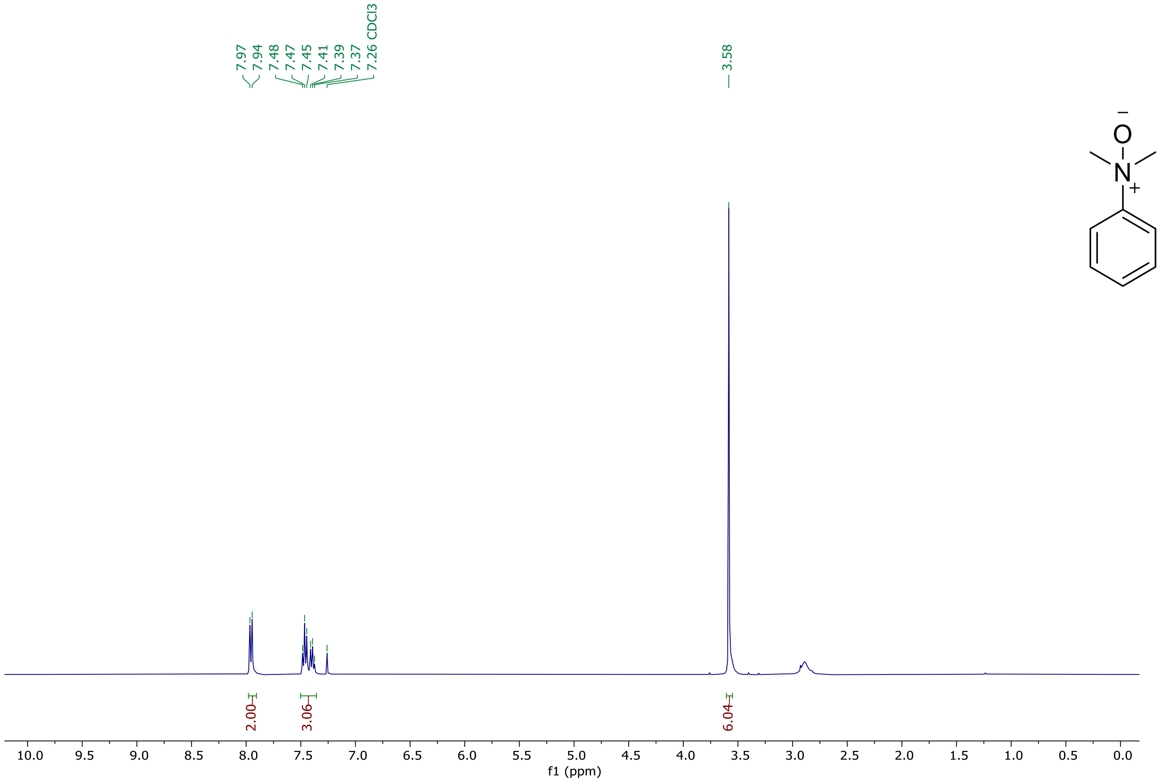


Figure 27. ^{1}H NMR spectra of compound **1n**

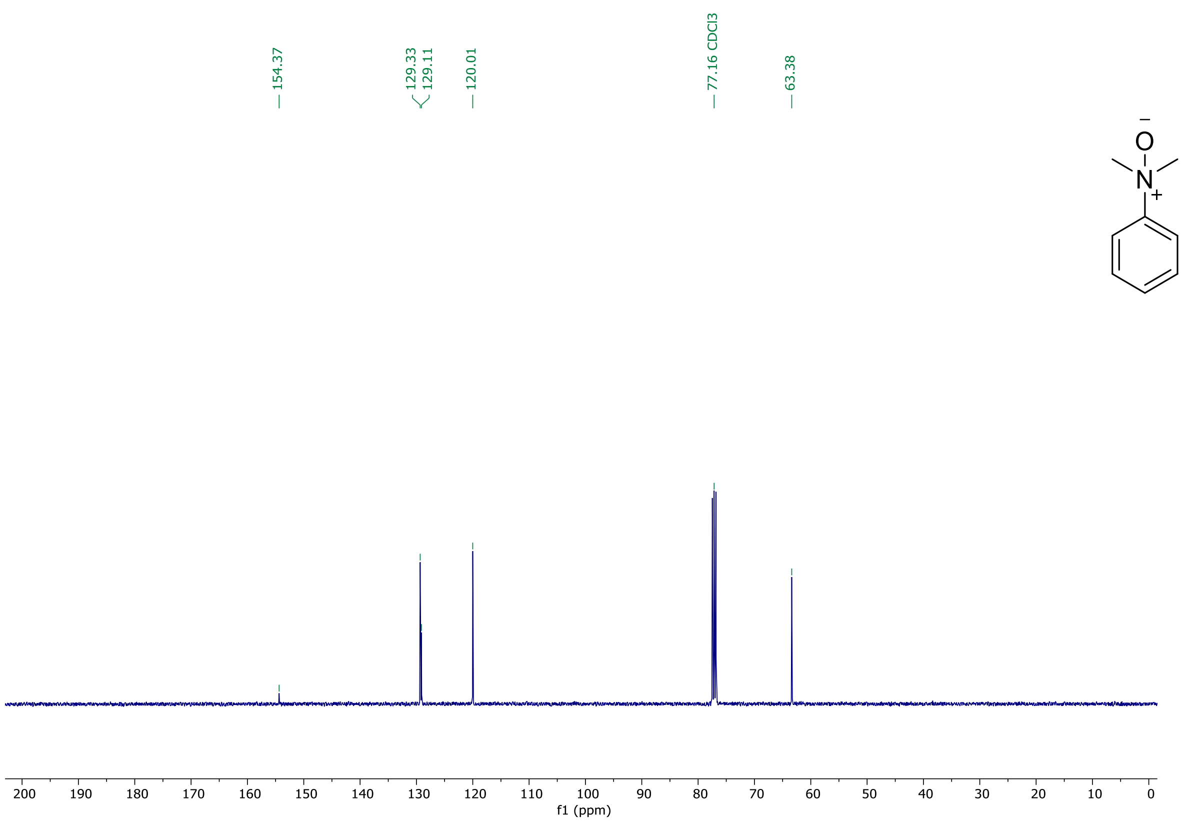


Figure 28. ^{13}C NMR spectra of compound **1n**

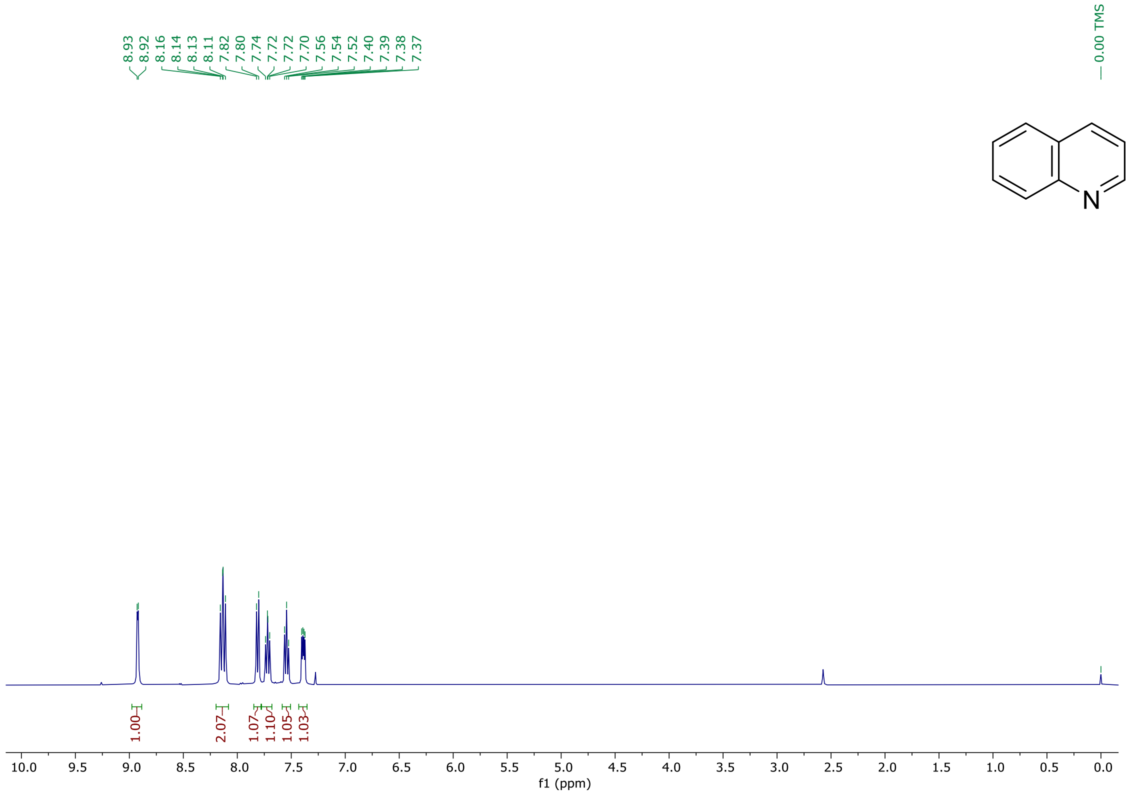


Figure 29. ^{1}H NMR spectra of compound **2a**

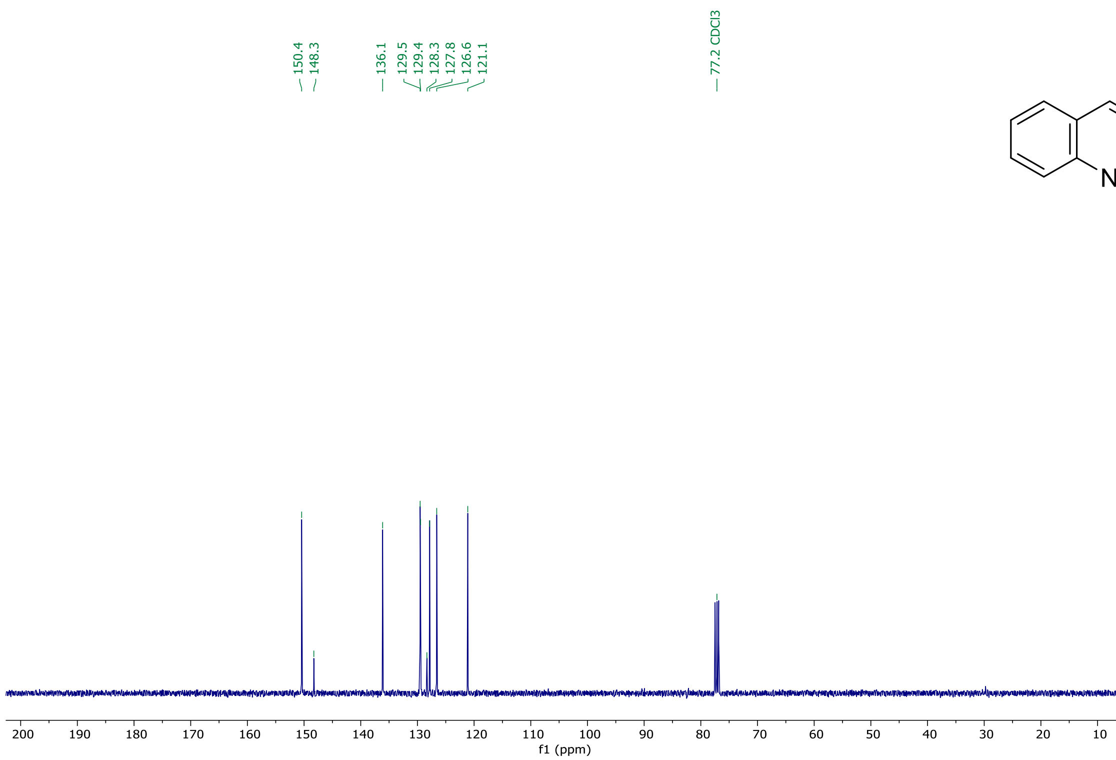


Figure 30. ^{13}C NMR spectra of compound **2a**

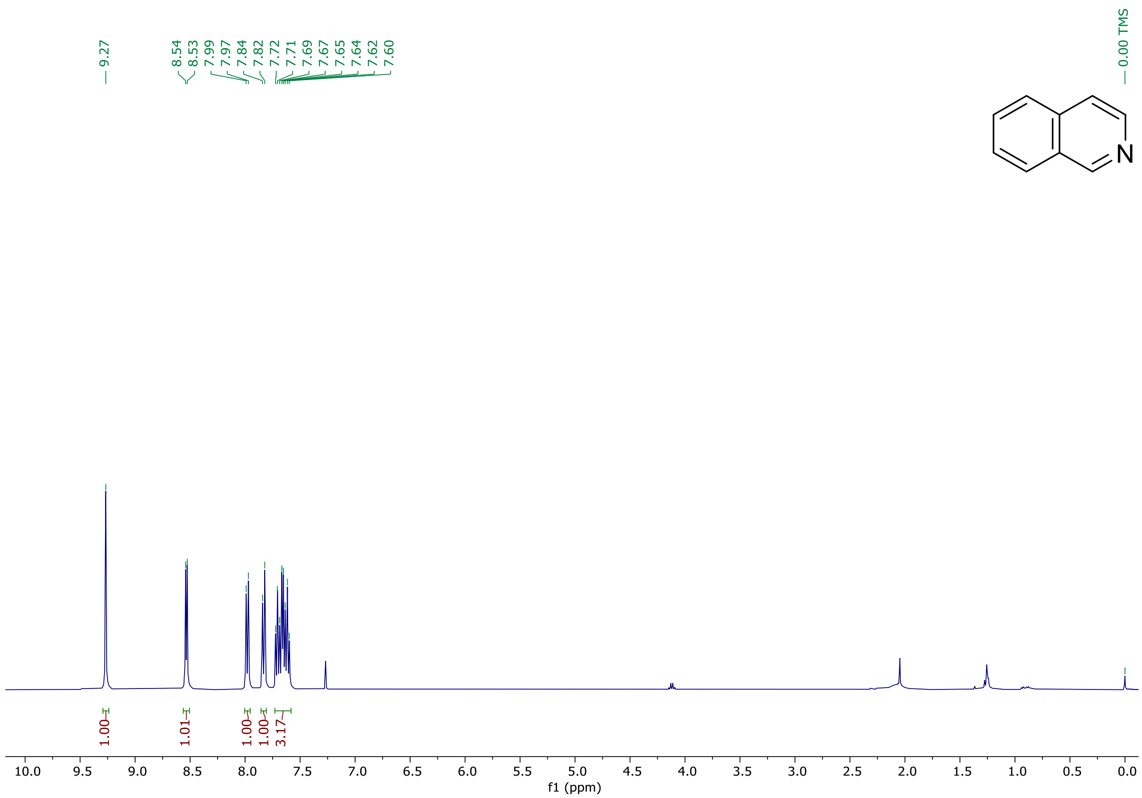


Figure 31. ^{1}H NMR spectra of compound **2b**

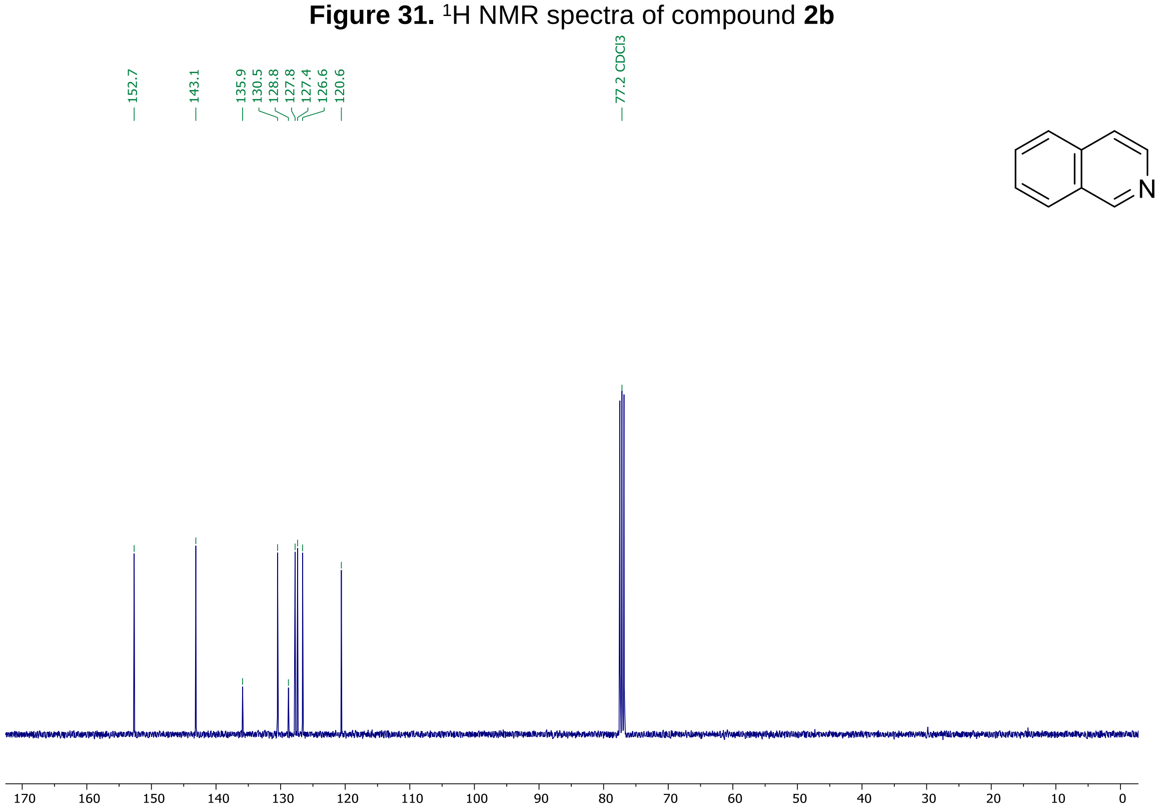


Figure 32. ^{13}C NMR spectra of compound **2b**

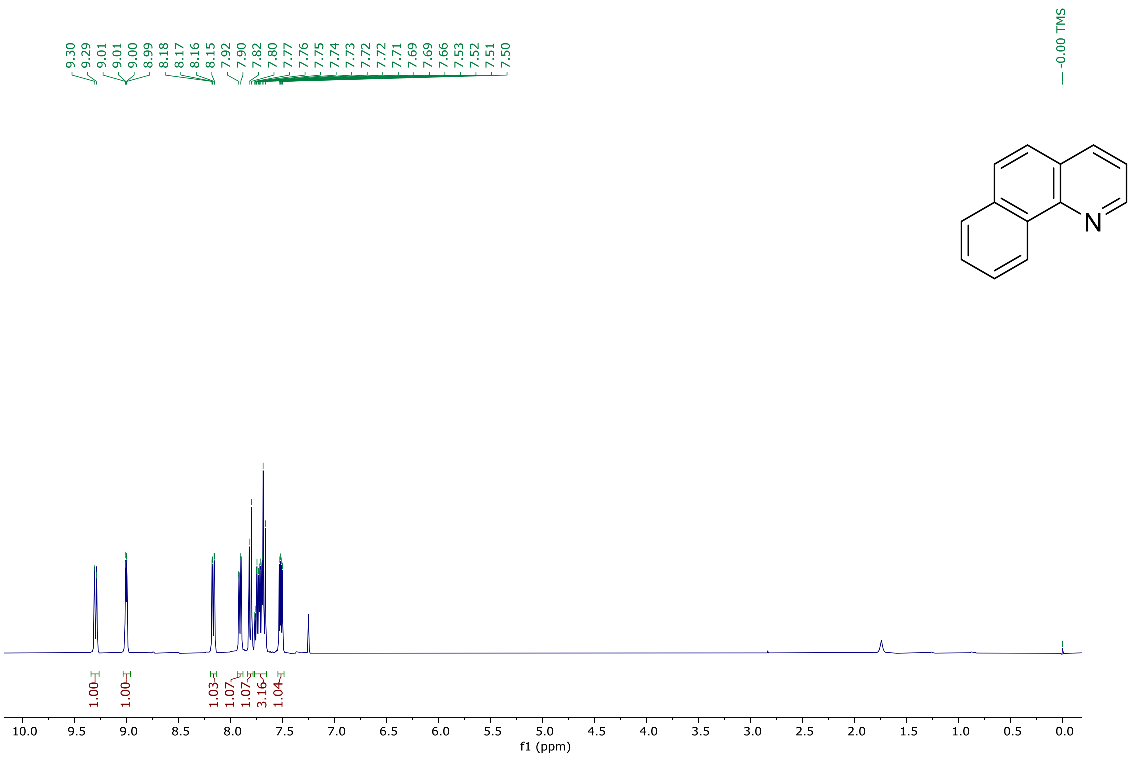


Figure 33. ^{1}H NMR spectra of compound **2c**

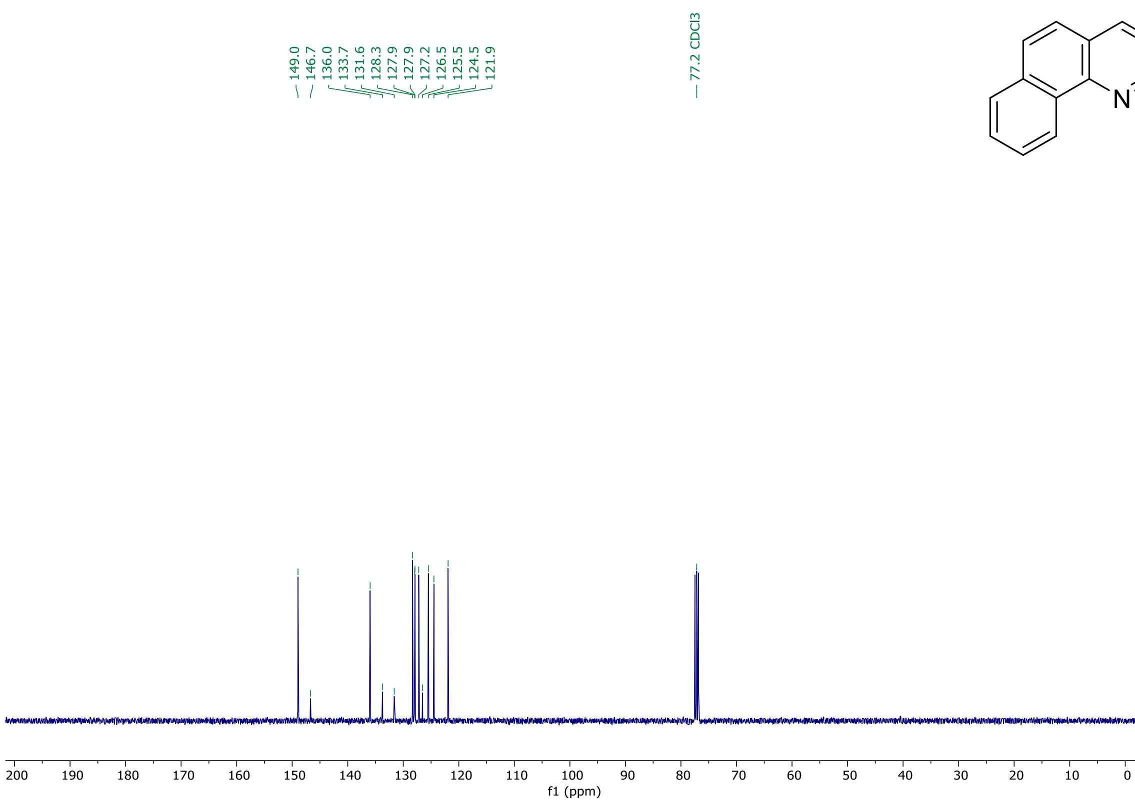


Figure 34. ^{13}C NMR spectra of compound **2c**

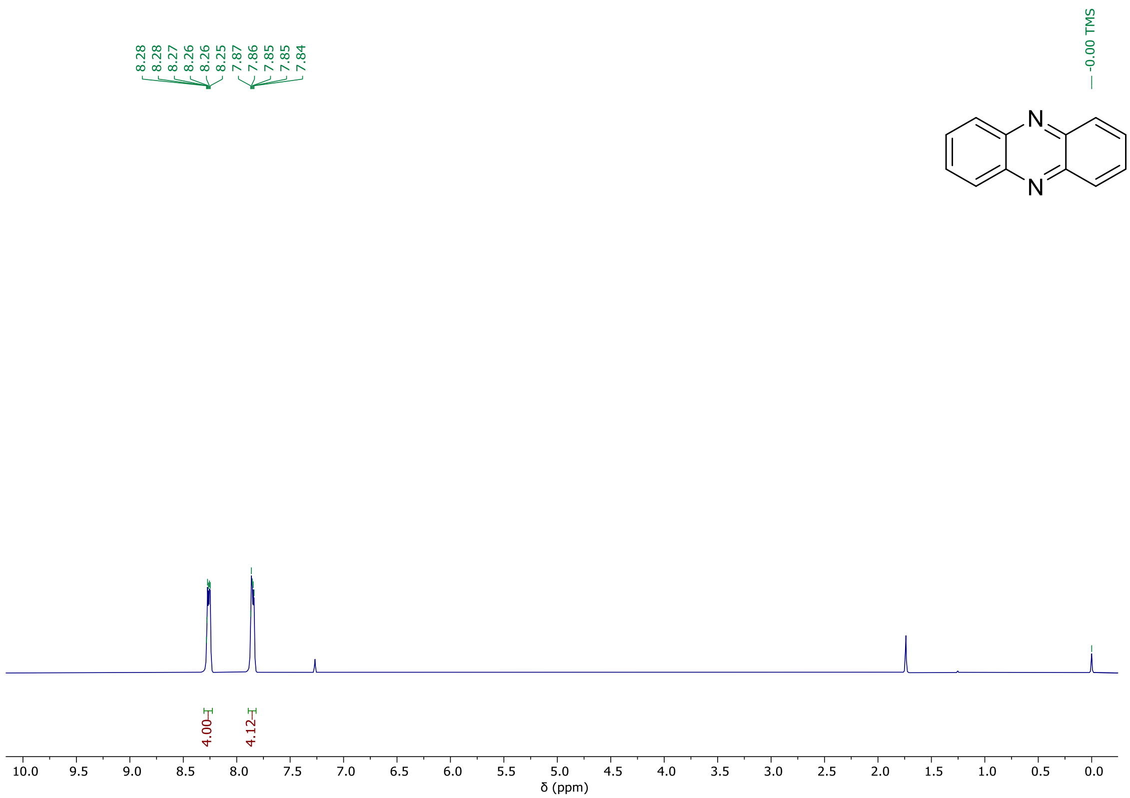


Figure 35. ^{1}H NMR spectra of compound **2d**

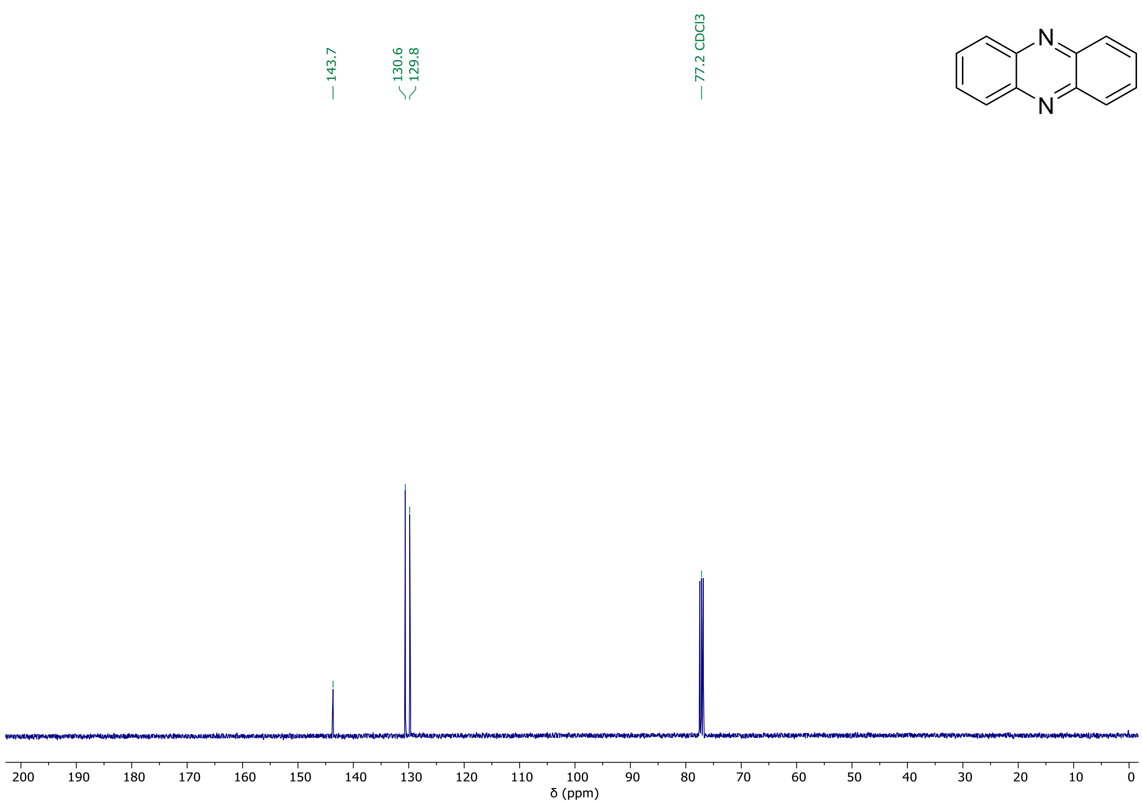


Figure 36. ^{13}C NMR spectra of compound **2d**

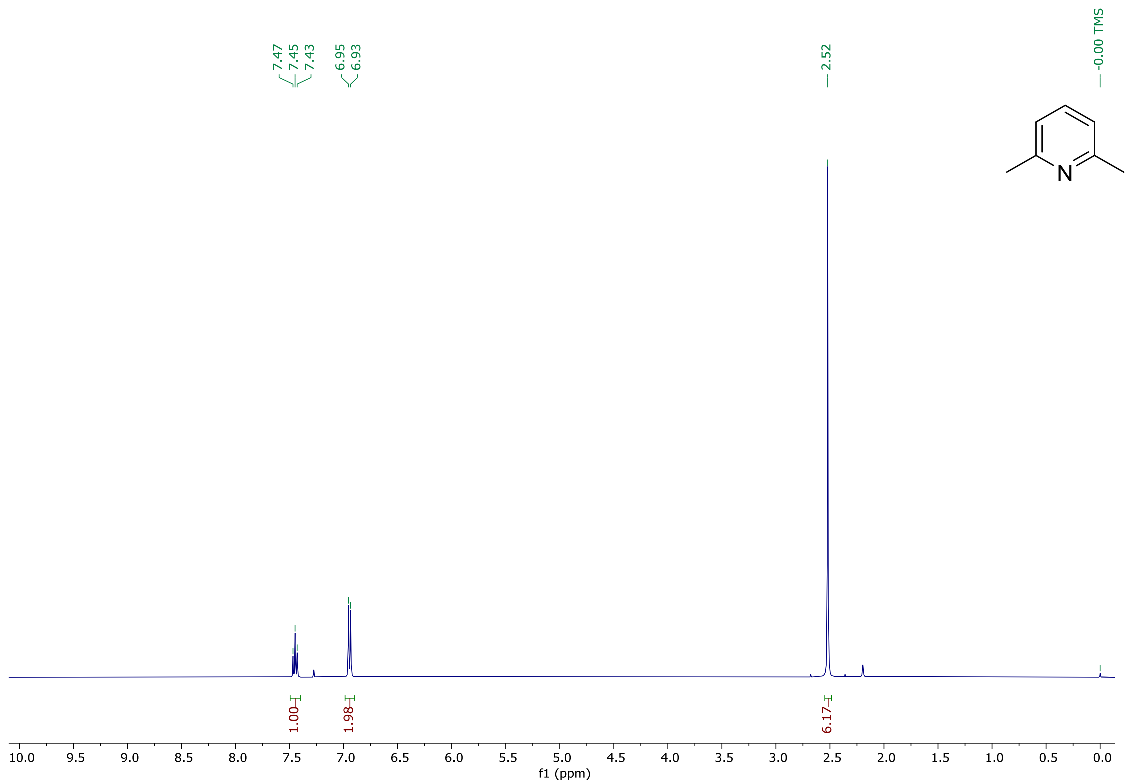


Figure 37. ^{1}H NMR spectra of compound **2e**

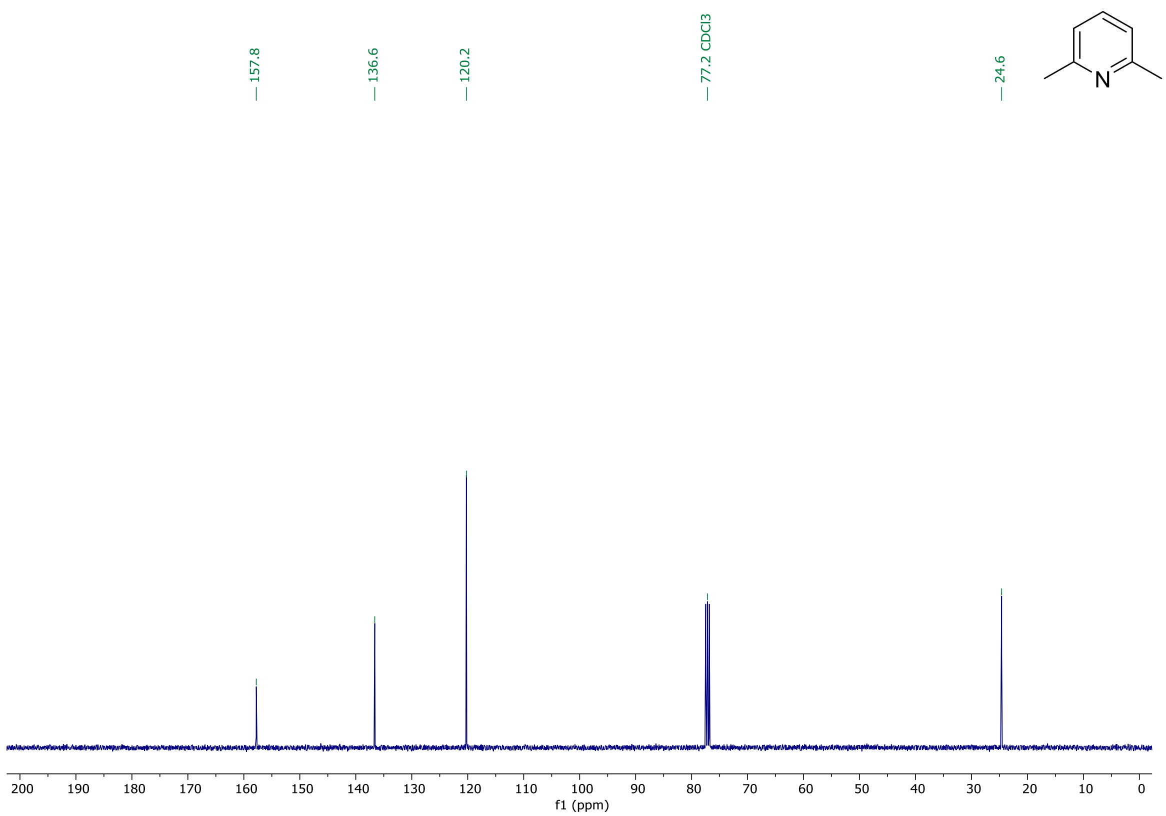


Figure 38. ^{13}C NMR spectra of compound **2e**

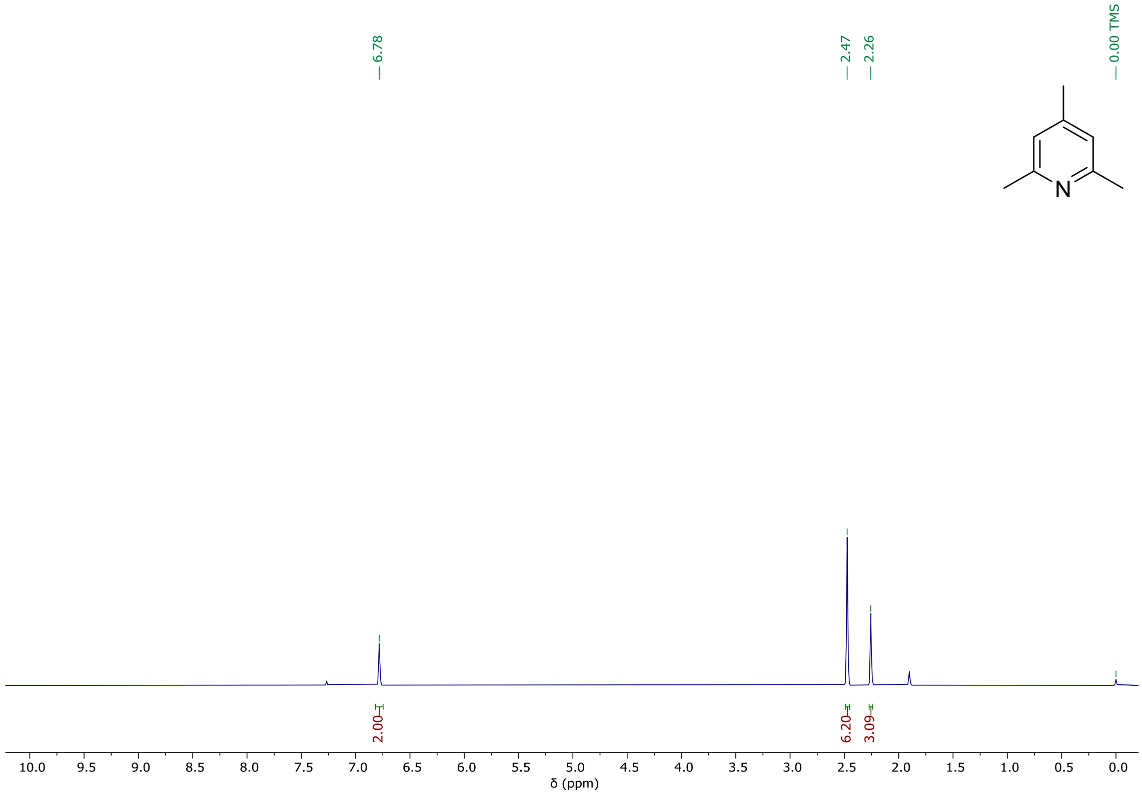


Figure 39. ^{1}H NMR spectra of compound **2f**

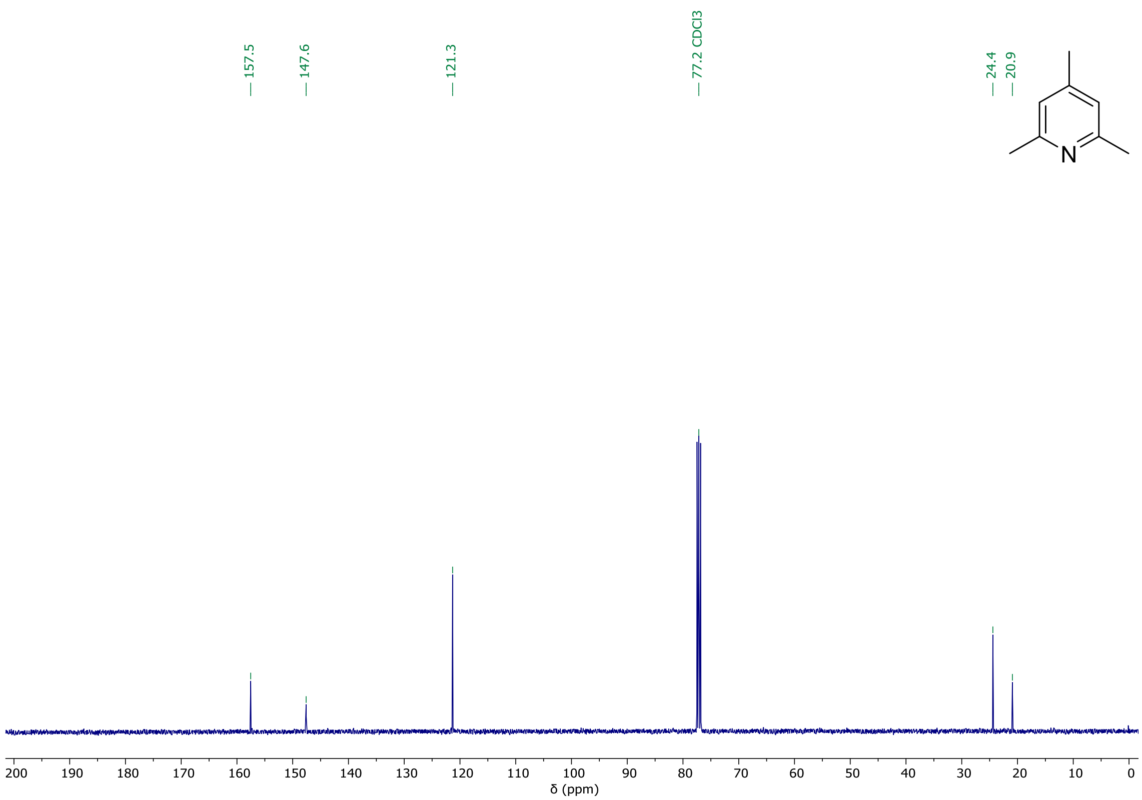


Figure 40. ^{13}C NMR spectra of compound **2f**

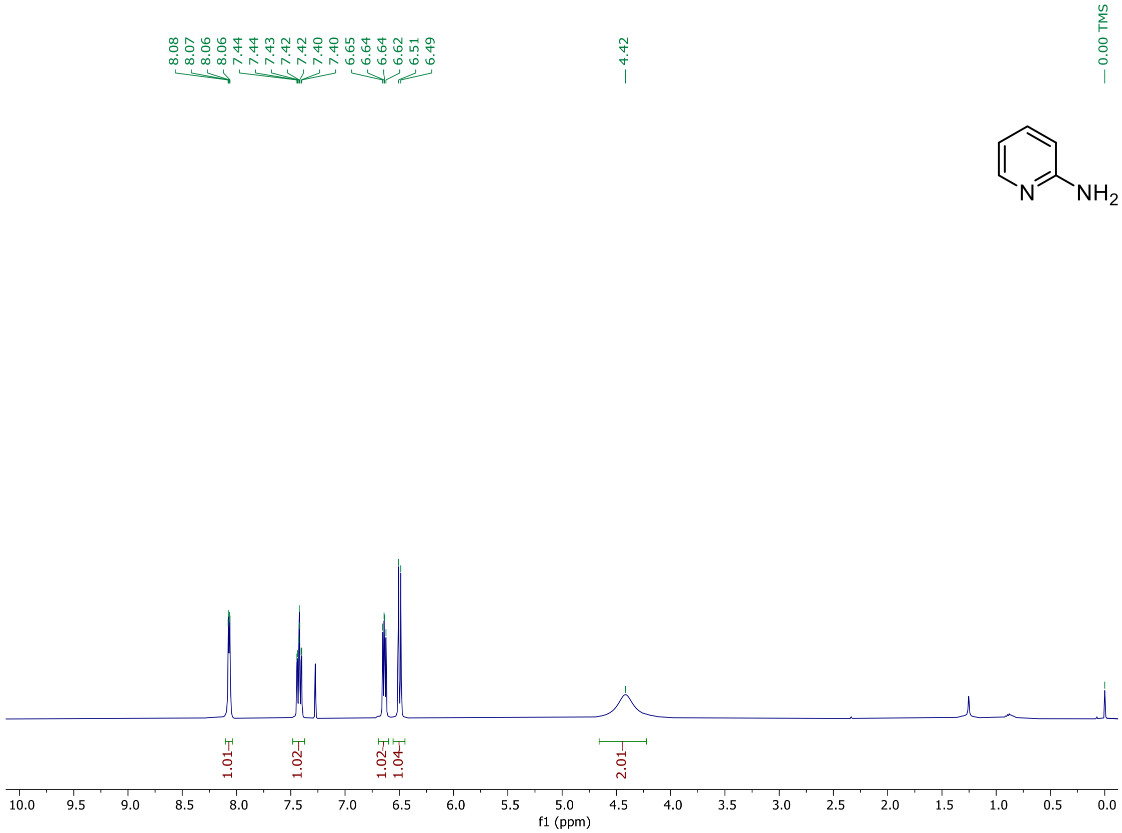


Figure 41. ^{1}H NMR spectra of compound **2g**

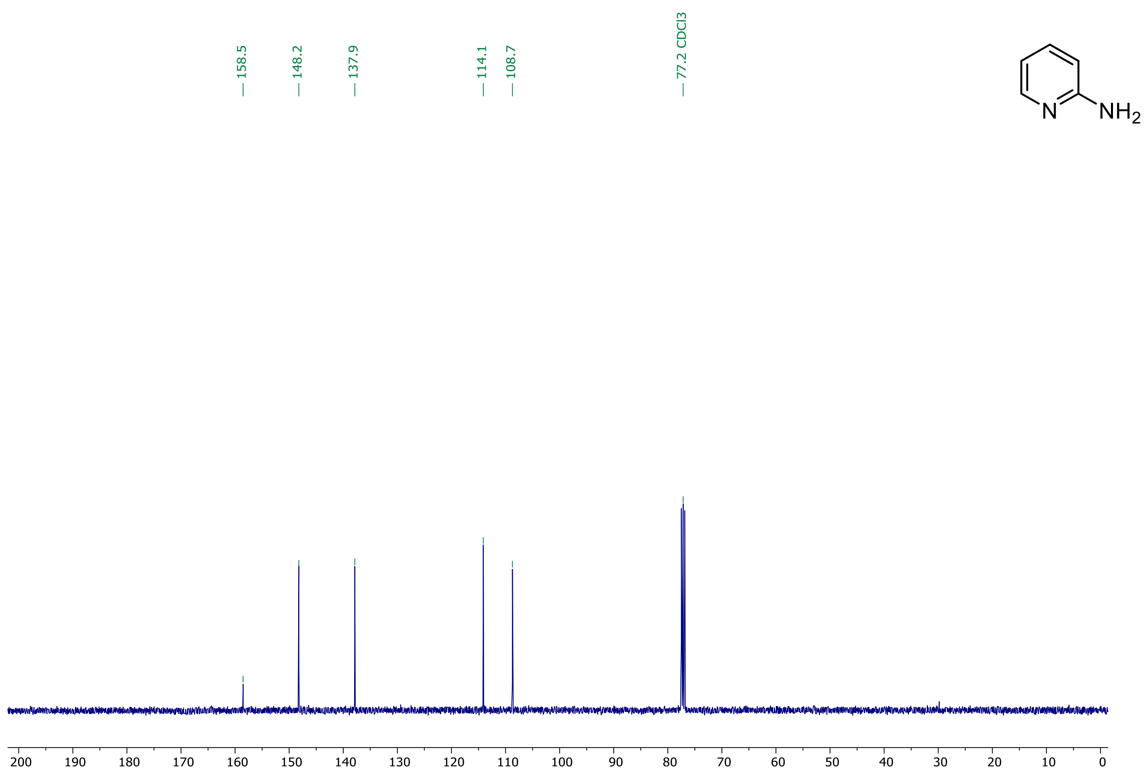


Figure 42. ^{13}C NMR spectra of compound **2g**

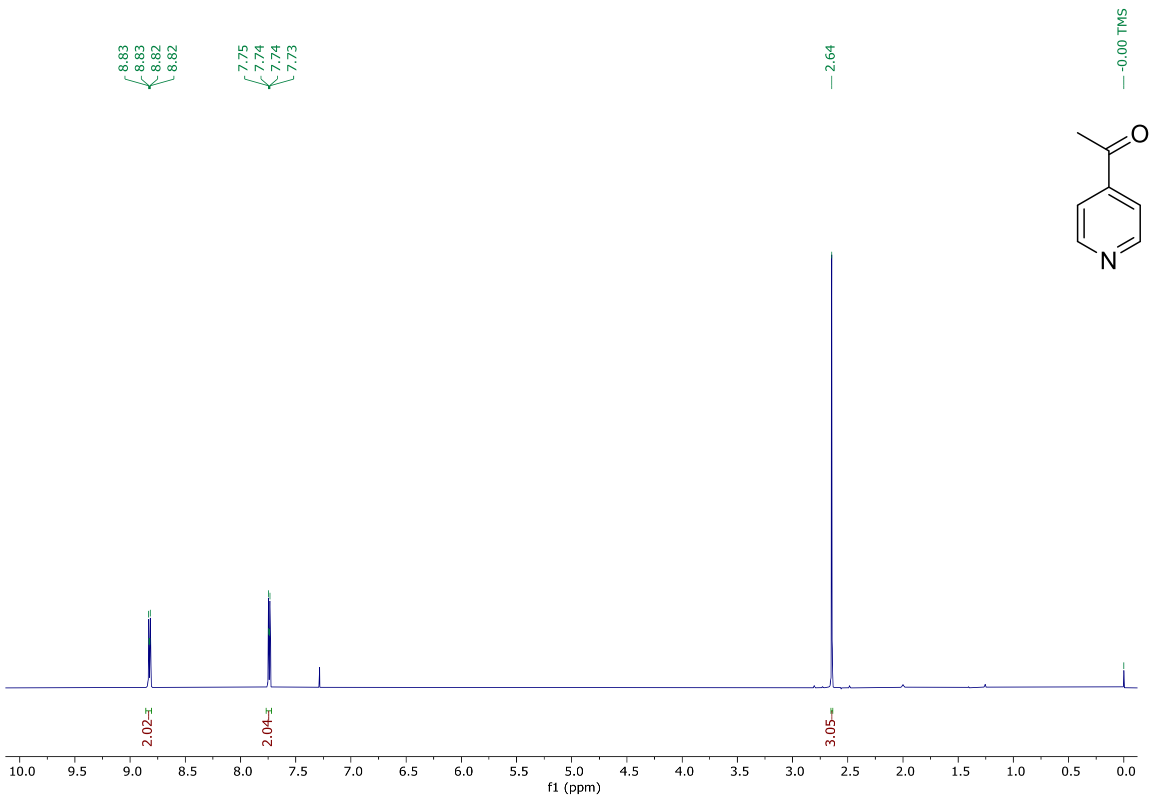


Figure 43. ^{1}H NMR spectra of compound **2h**

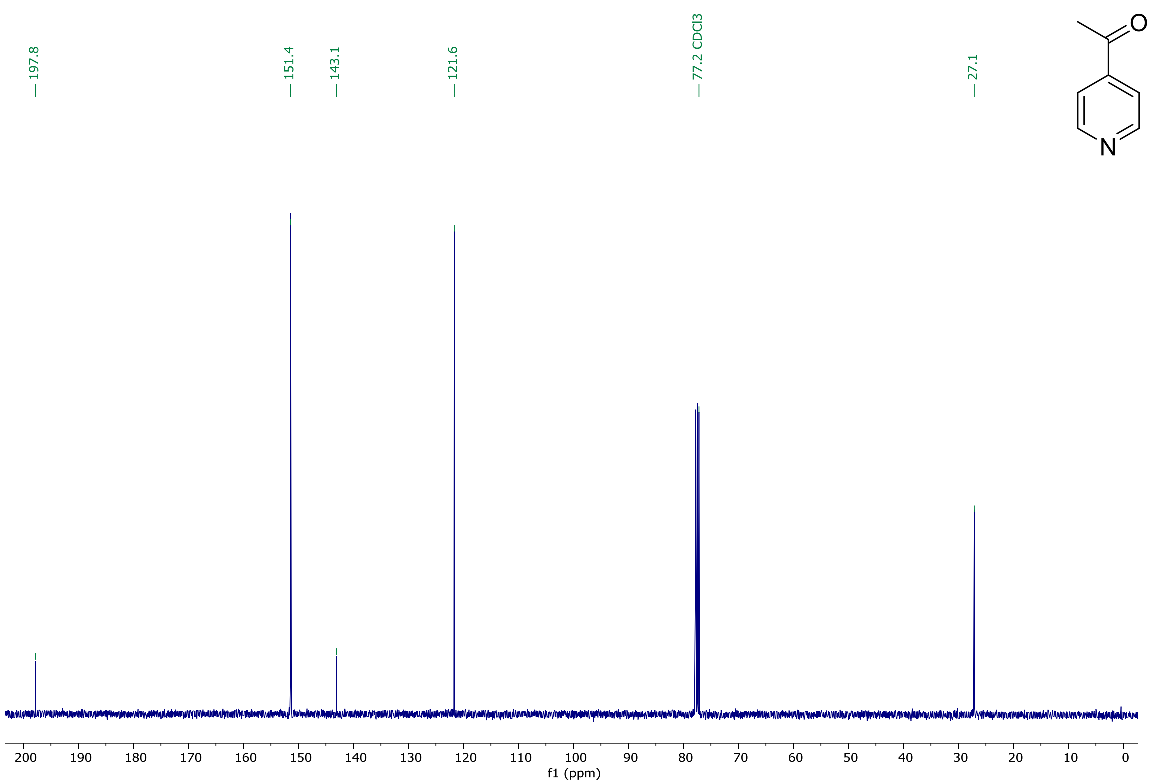


Figure 44. ^{13}C NMR spectra of compound **2h**

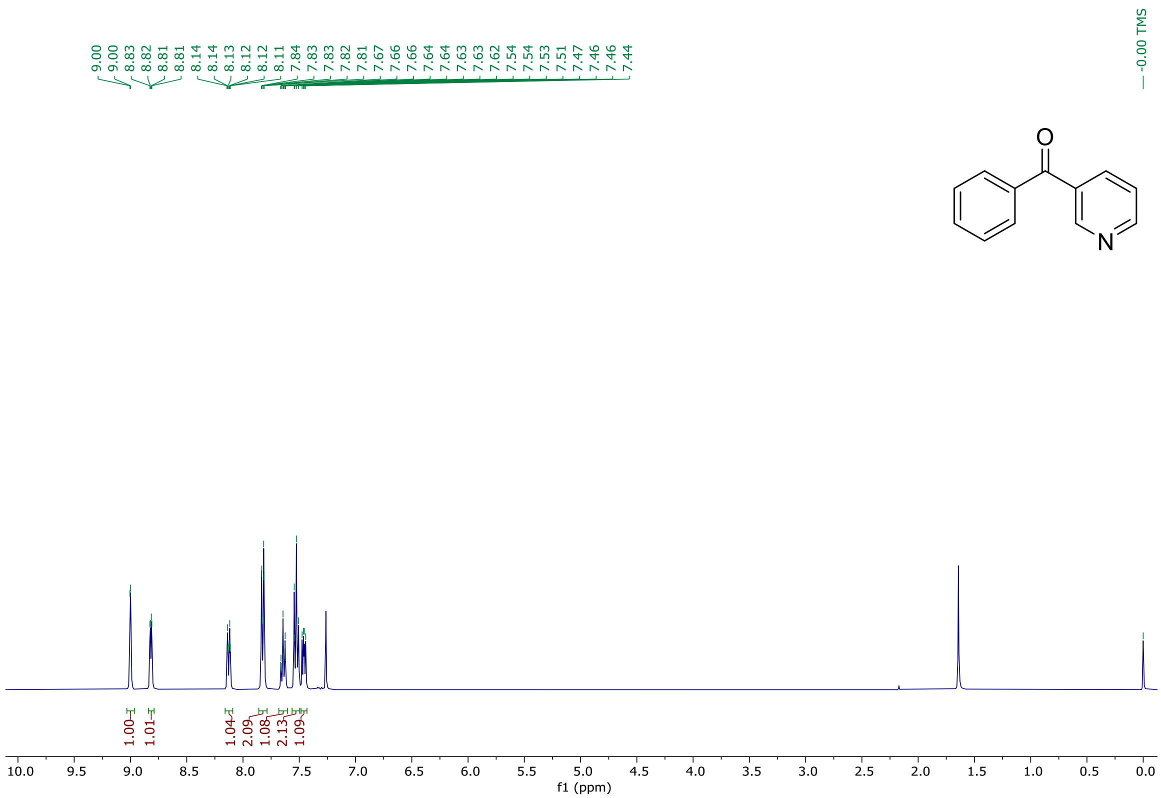


Figure 45. ^{1}H NMR spectra of compound **2i**

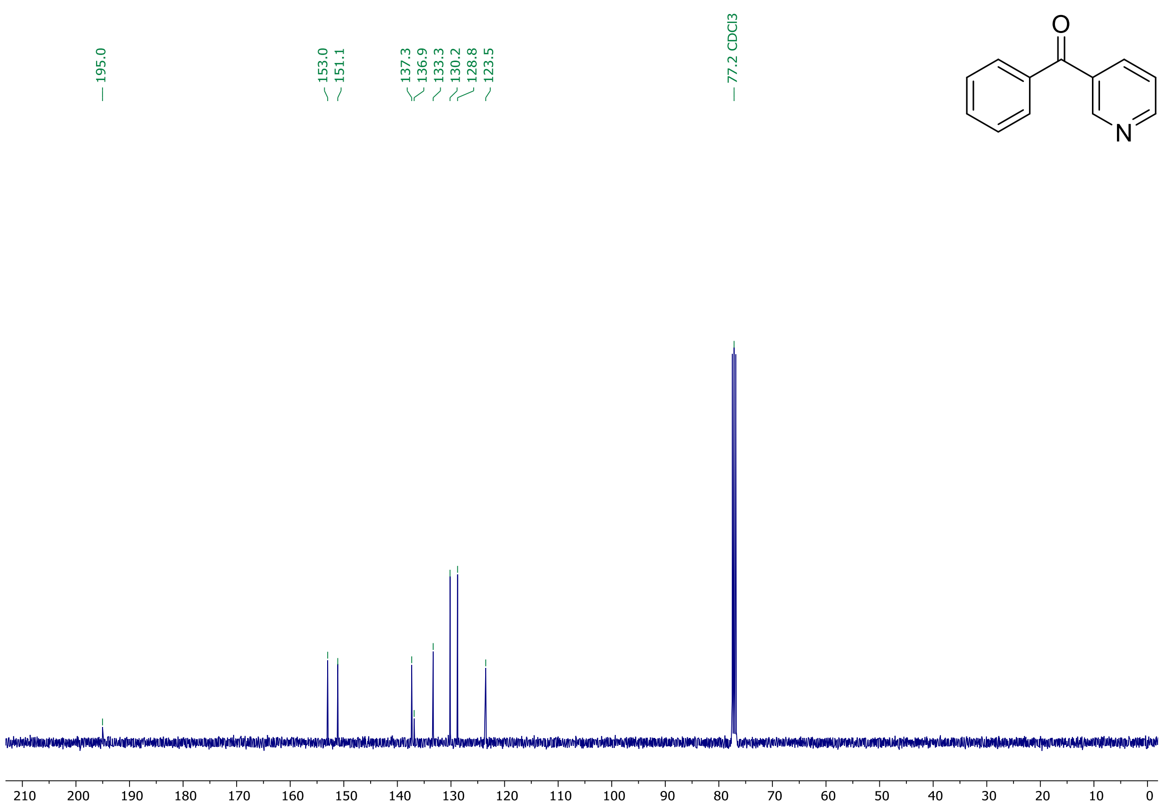


Figure 46. ^{13}C NMR spectra of compound **2i**

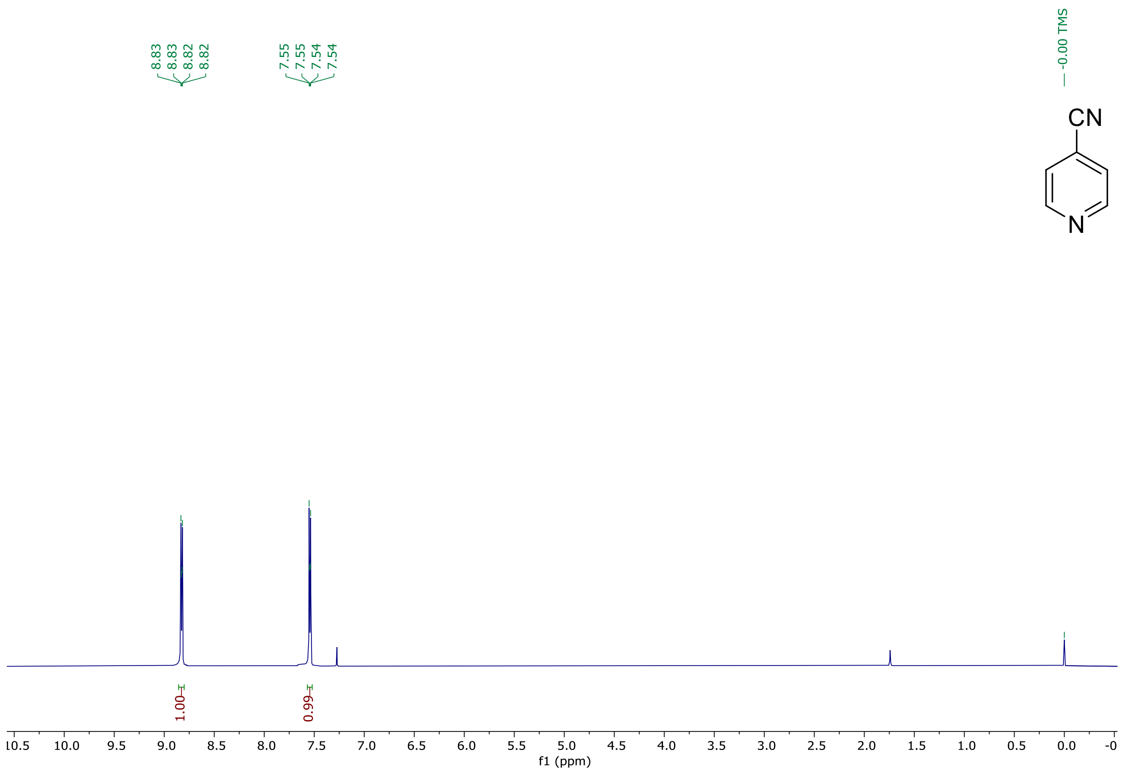


Figure 47. ^{1}H NMR spectra of compound **2j**

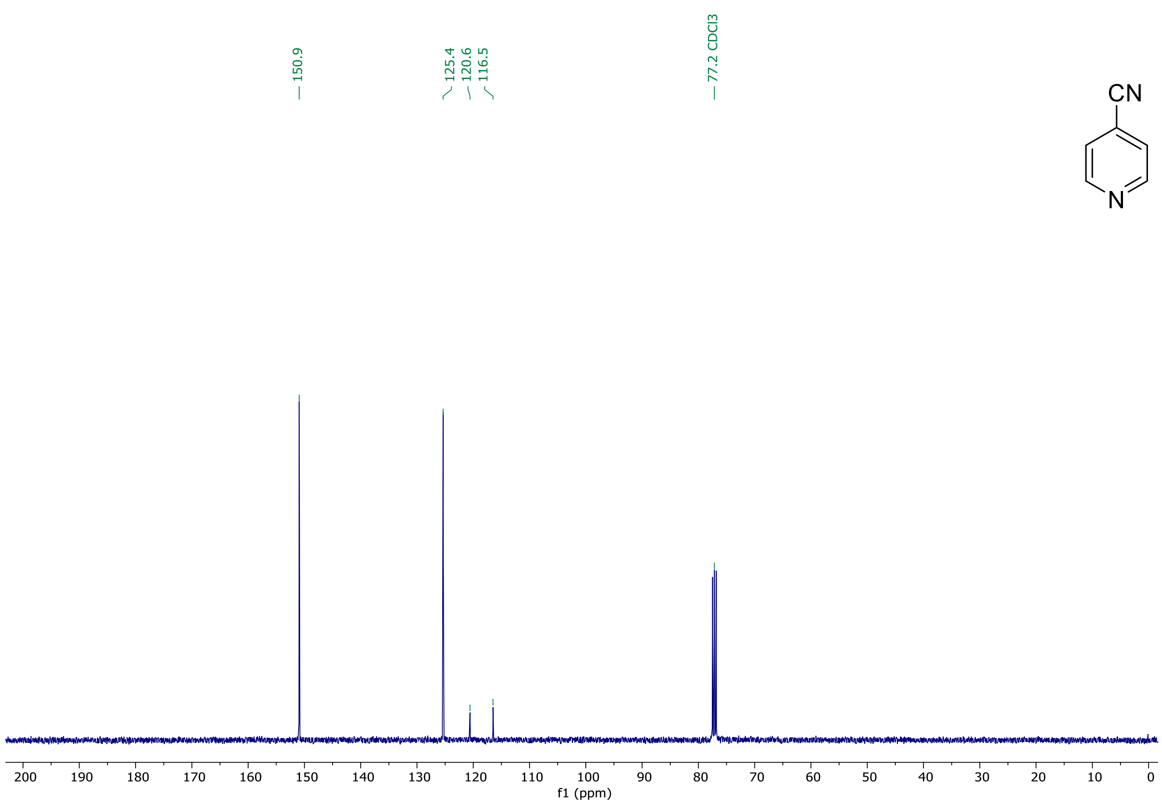


Figure 48. ^{13}C NMR spectra of compound **2j**

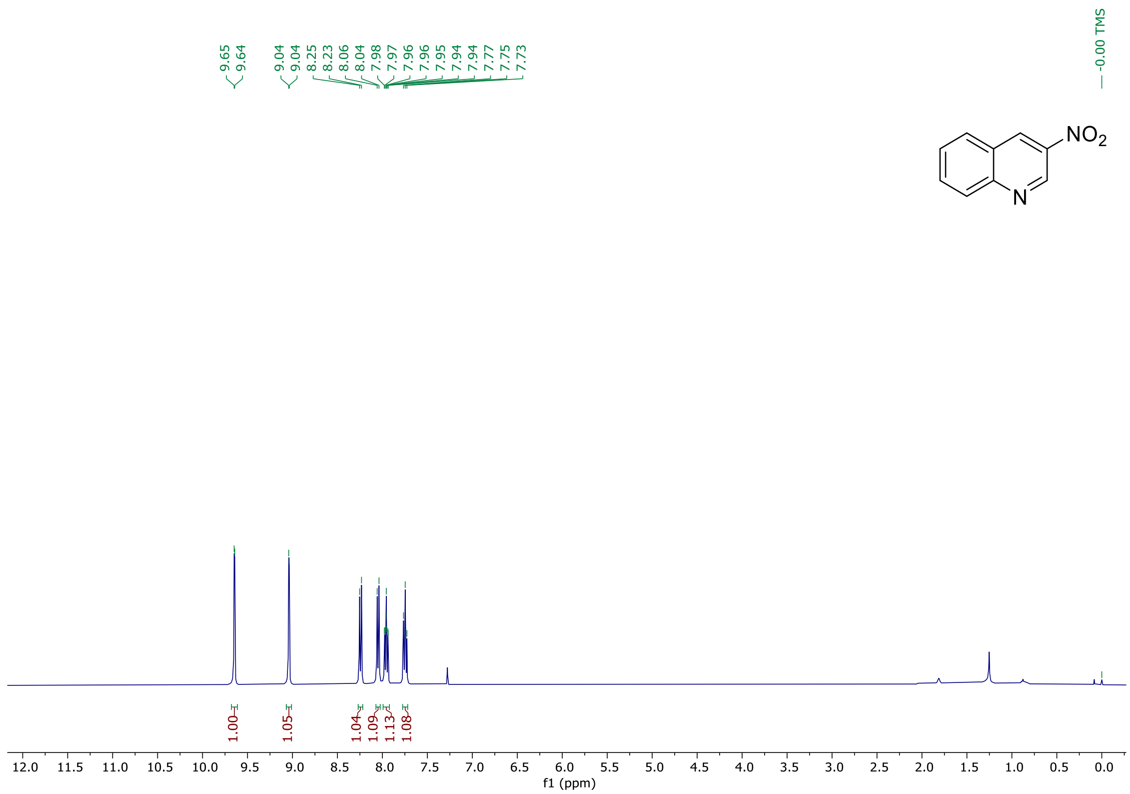


Figure 49. ^{1}H NMR spectra of compound **2k**

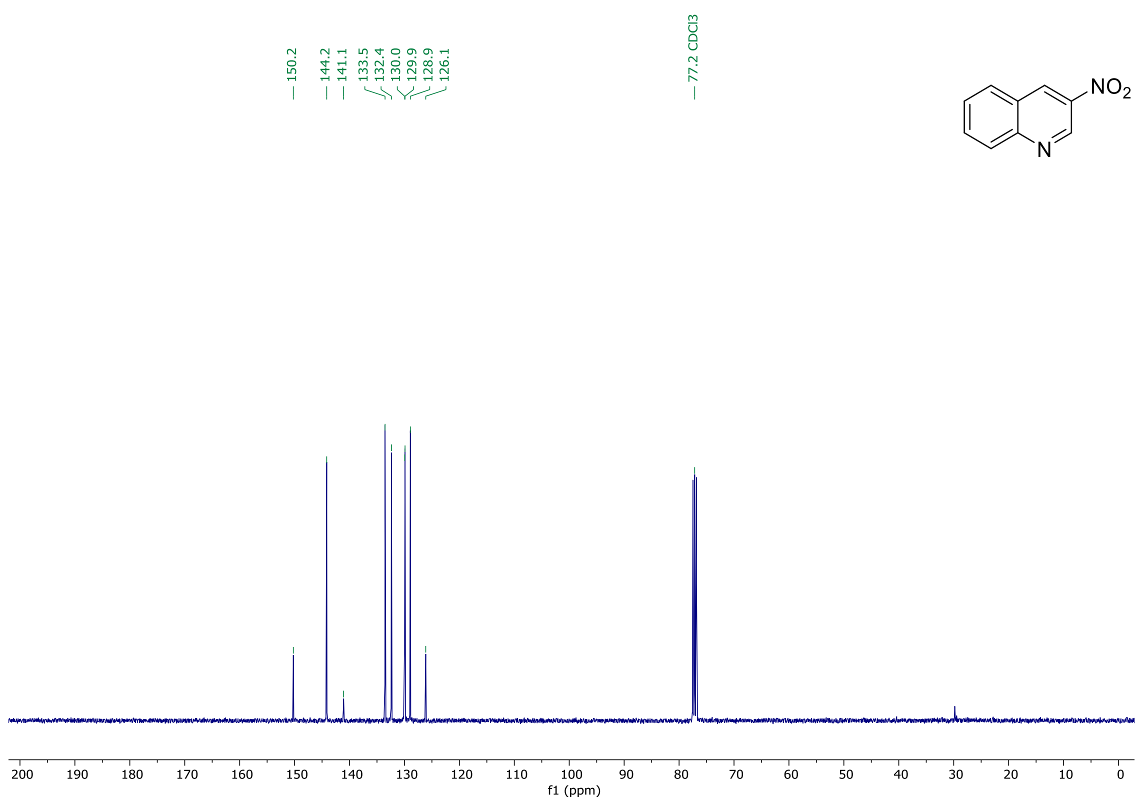


Figure 50. ^{13}C NMR spectra of compound **2k**

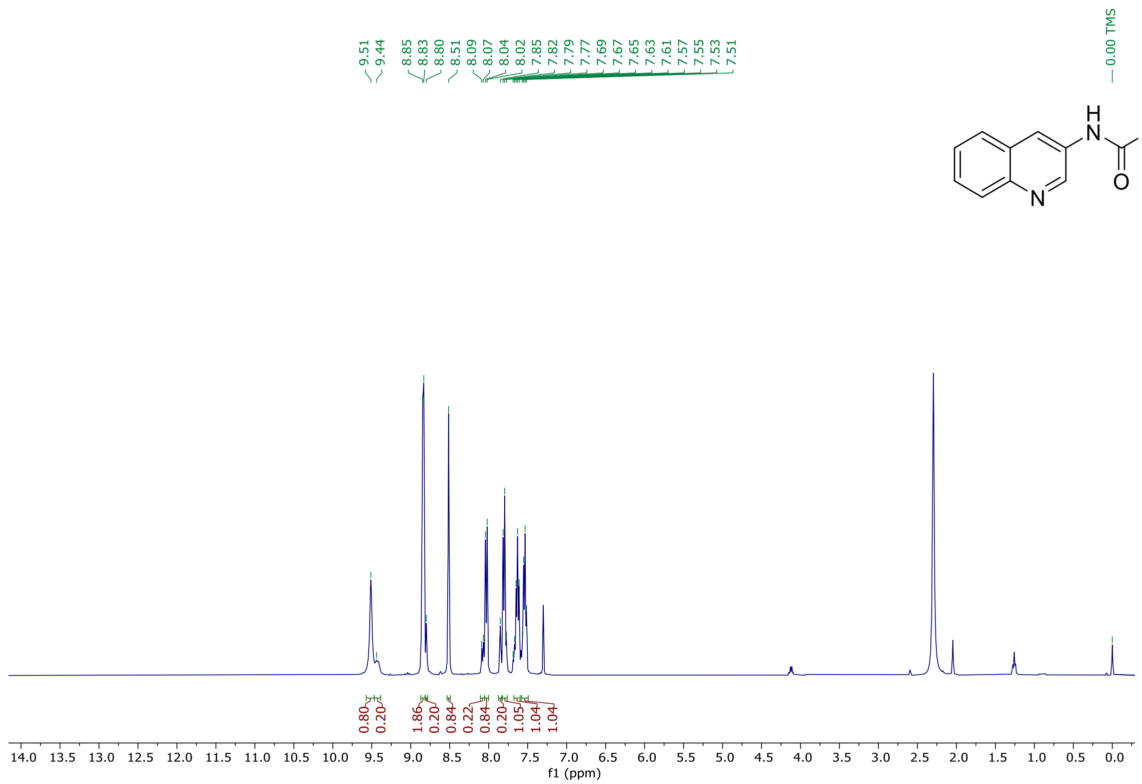


Figure 51. ^{1}H NMR spectra of compound **2ka**

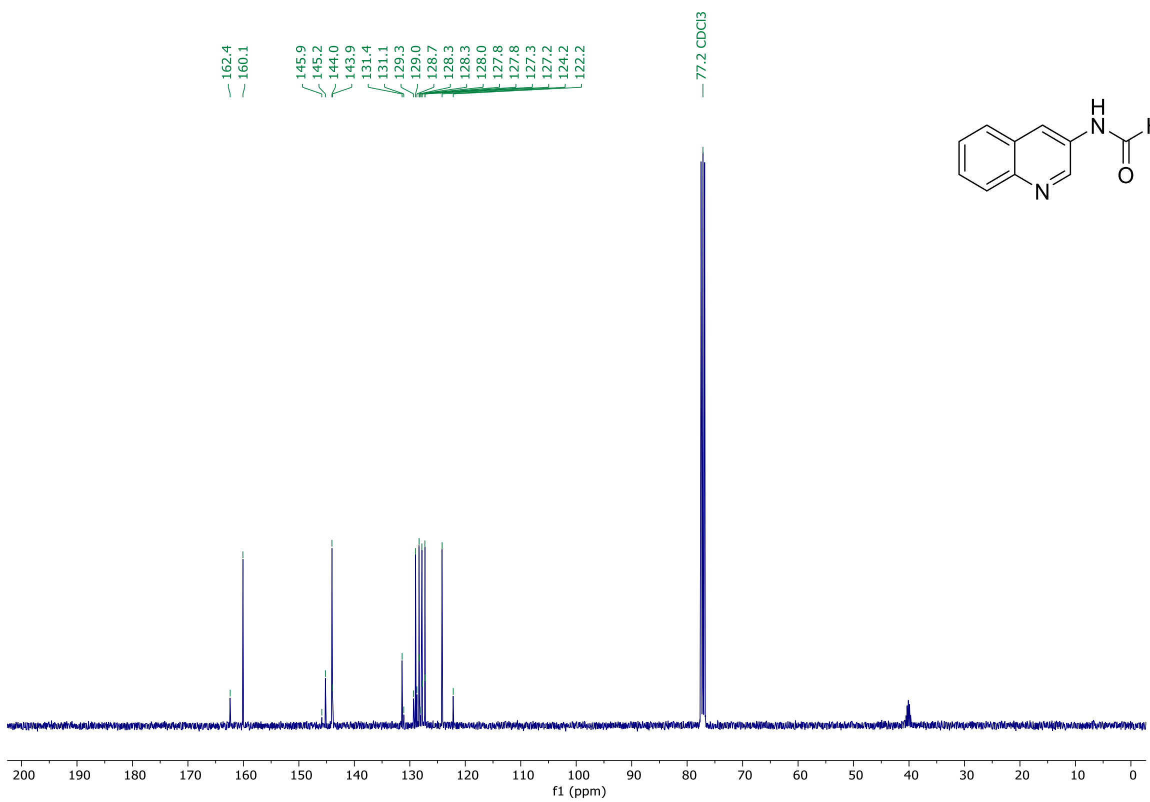


Figure 52. ^{13}C NMR spectra of compound **2ka**

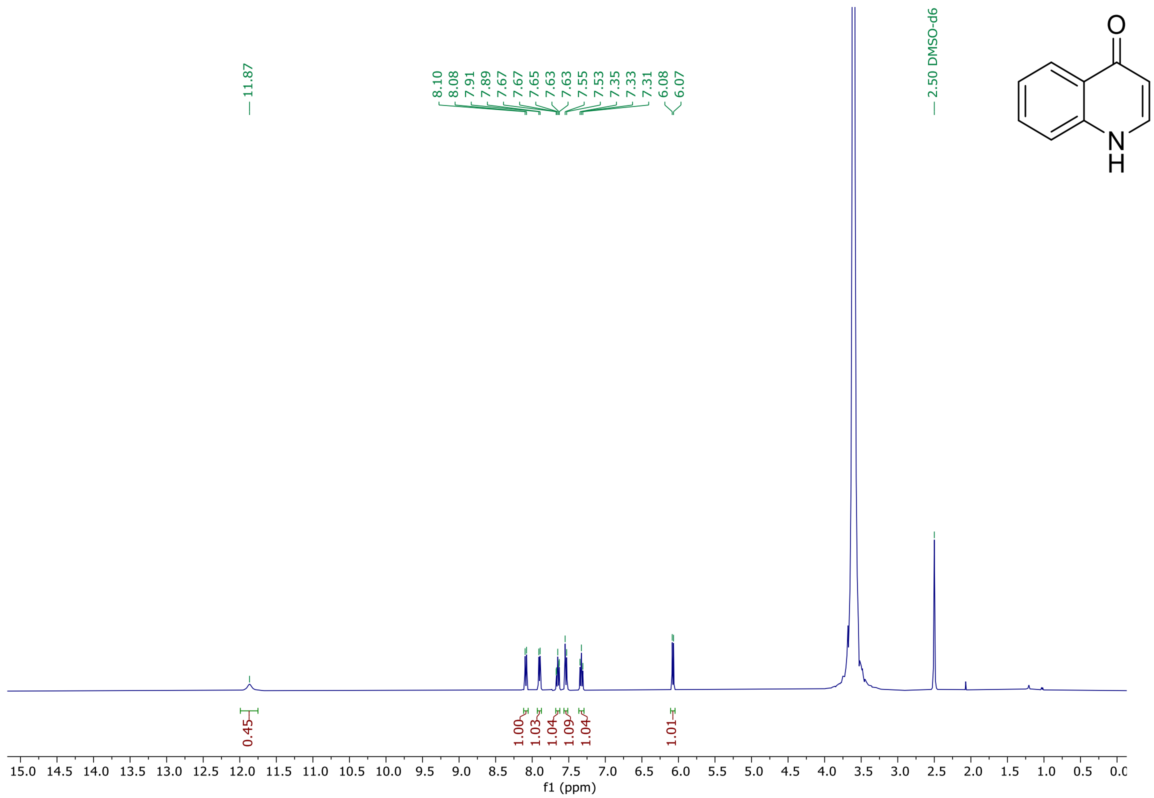


Figure 53. ^{1}H NMR spectra of compound **2la**

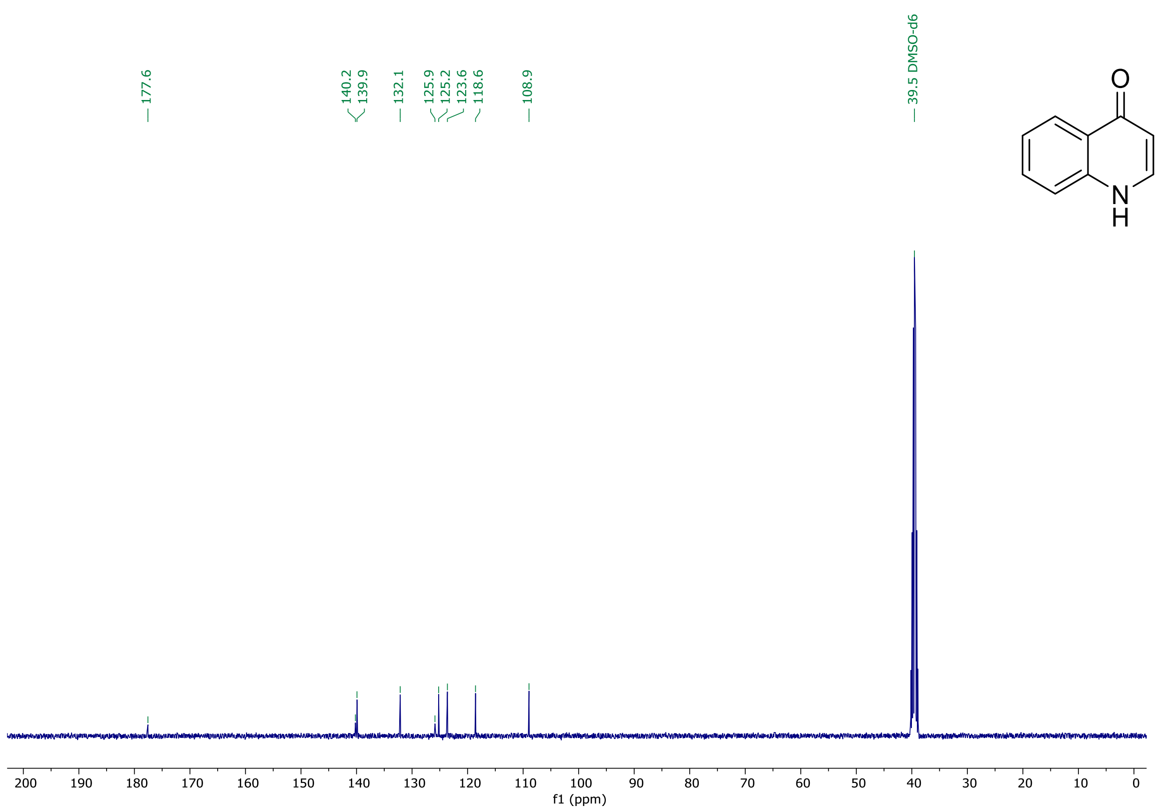


Figure 54. ^{13}C NMR spectra of compound **2la**

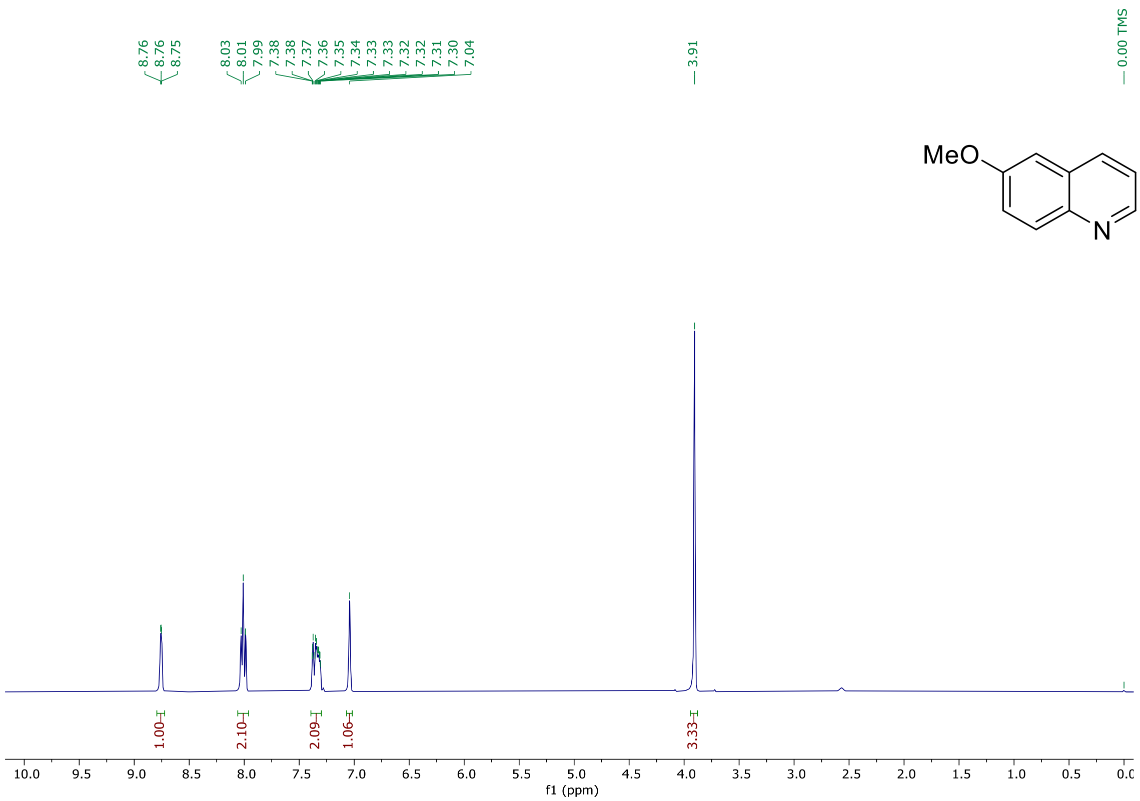


Figure 55. ^{1}H NMR spectra of compound **2m**

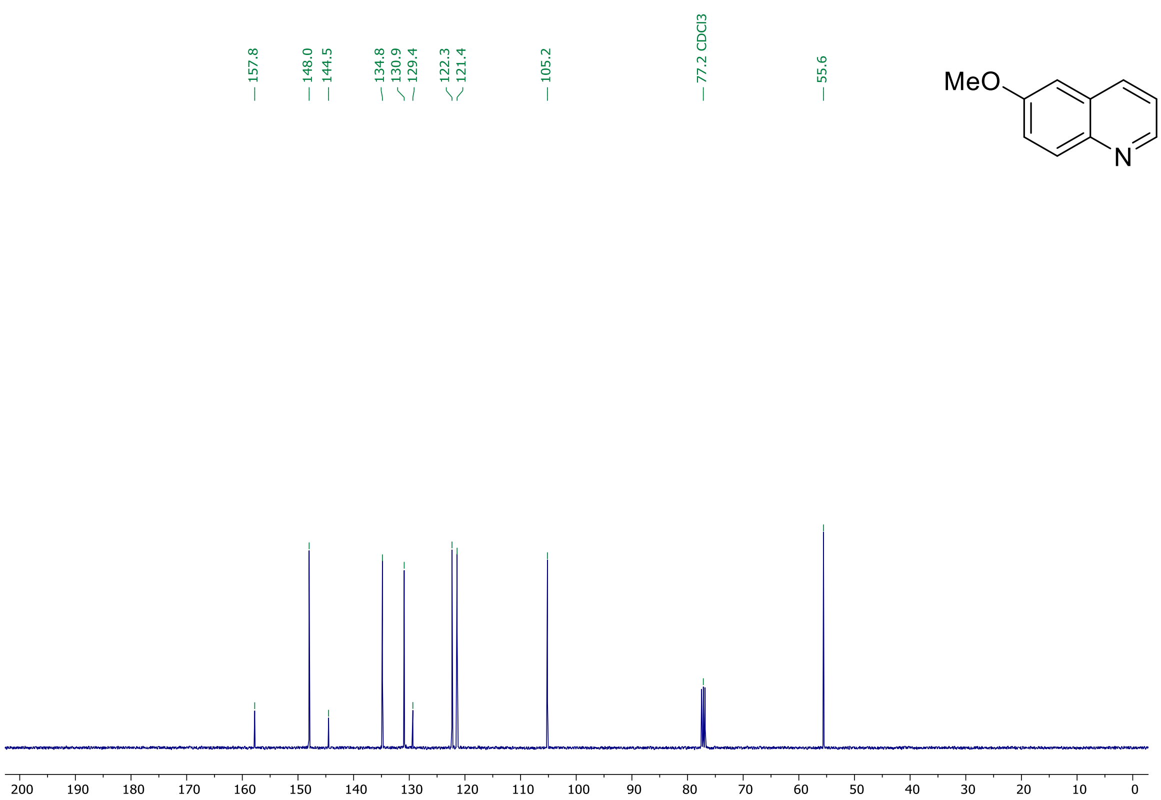


Figure 56. ^{13}C NMR spectra of compound **2m**

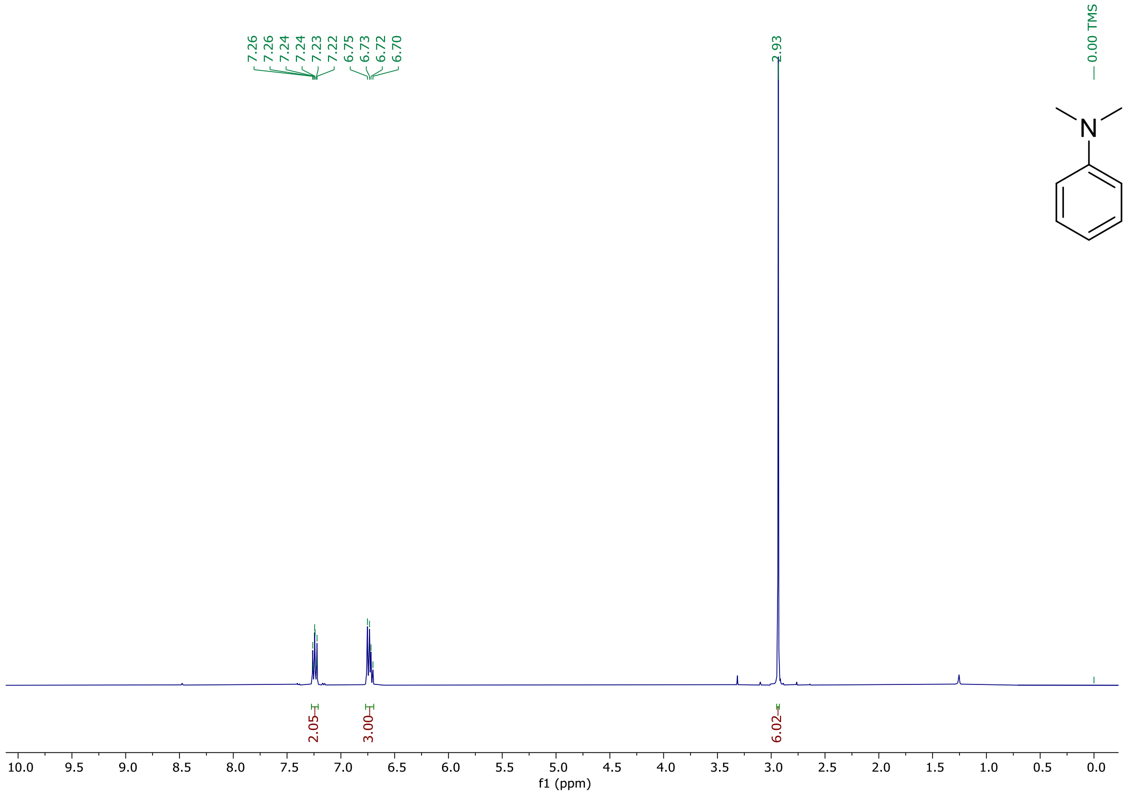


Figure 57. ^{1}H NMR spectra of compound **2n**

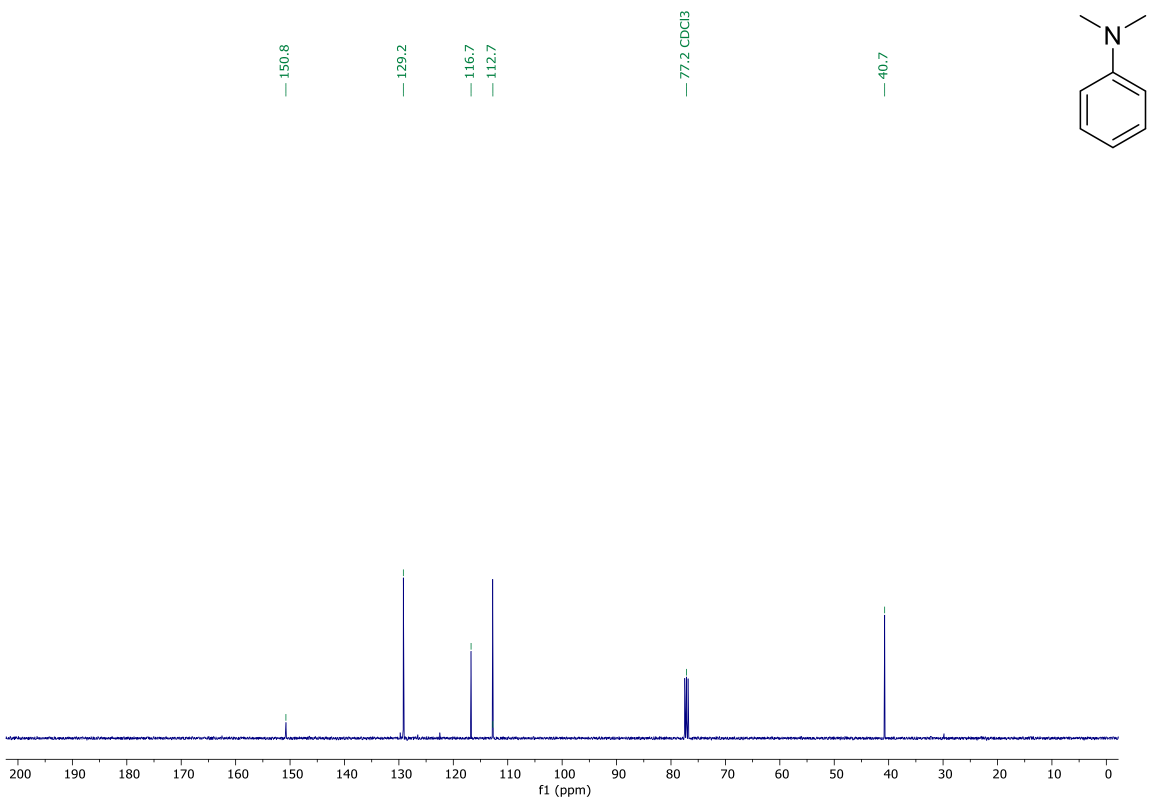


Figure 58. ^{13}C NMR spectra of compound **2n**

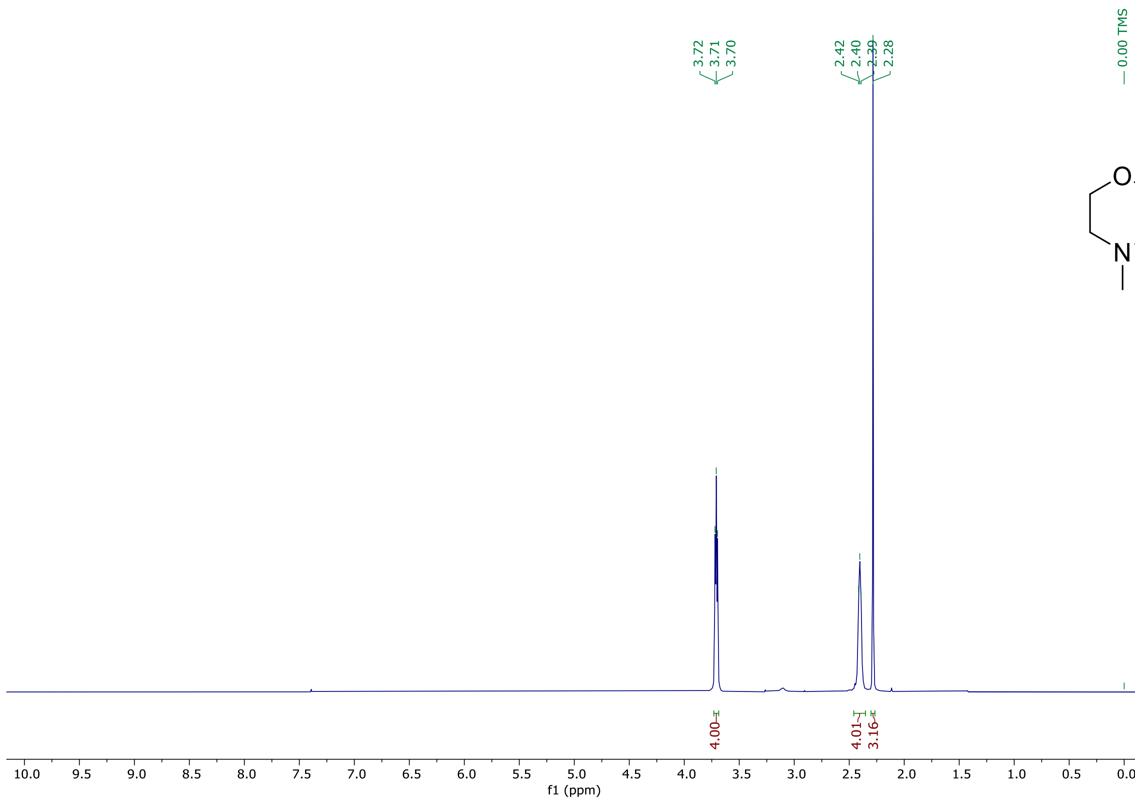


Figure 59. ^{1}H NMR spectra of compound **2o**

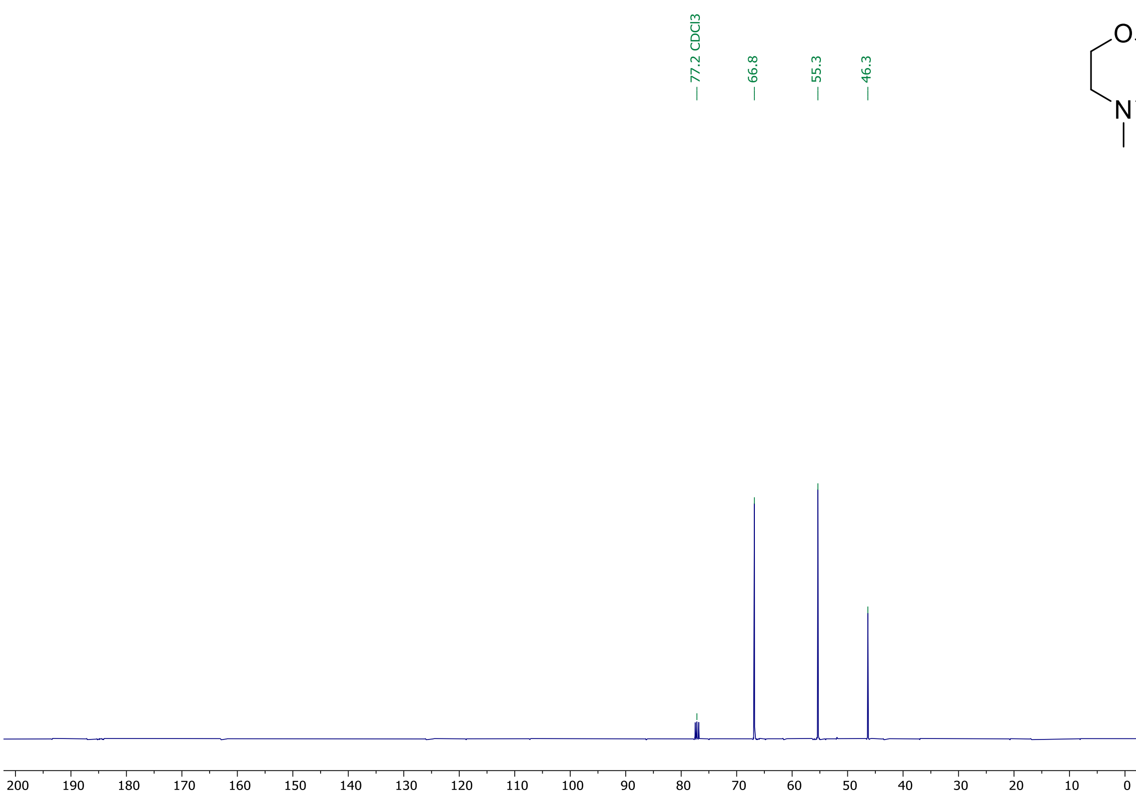


Figure 60. ^{13}C NMR spectra of compound **2o**

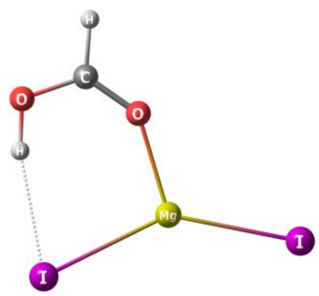
7 Computational details

All electronic structure calculations were performed using the Gaussian 09 rev D.01 package.[29] Gas-phase geometry optimizations were calculated with no symmetry restrictions using the long-range hybrid functional ωB97X-D[30] and Ahlrichs' def2-SVP basis set[31] for all atoms (H, C, N, O, Mg, and I). Harmonic frequency calculations were performed to discern between a local minimum (zero negative eigenvalues of the Hessian matrix) or a transition state (one negative eigenvalue of the Hessian matrix). Thermal correction of Gibbs free energy from thermochemistry analysis considering an ideal gas at 298.15 K and 1.00 atm was calculated for each species. Also, implicit solvation effect was considered by performing single-point calculations over the optimized geometries at the same level of theory implementing the PCM model via the SMD parameters according to Truhlar's model[32] with formic acid (ε = 51.1). Finally, electronic energies were corrected via single-point calculations over the optimized geometries using the larger Ahlrichs' def2-TZVPP basis set. Gibbs free energy and implicit solvation corrections were added to the improved electronic energies. Hence, the final reported relative Gibbs free energies are considered in formic acid phase, calculated at the (SMD:HCO_2H)ωB97X-D/def2-TZVPP//ωB97X-D/def2-SVP level.

Table S1. Cartesian coordinates (x y z) of the optimized geometries (at ωB97X-D/def2-SVP level) involved in the explicit solvation of MgI_2 and the *N*-oxide deoxygenation profiles.

A-1

SCF energy = -985.307149164 a.u.



8	-2.651262	2.375566	0.002379
1	-2.652677	1.378328	0.003252
6	-1.451547	2.841415	-0.000660
1	-1.413724	3.943855	-0.002533
8	-0.419389	2.177421	-0.001623
53	-2.111881	-1.013973	-0.000089
53	2.765461	-0.153641	0.000252
12	0.225095	0.257412	-0.000951

A-2

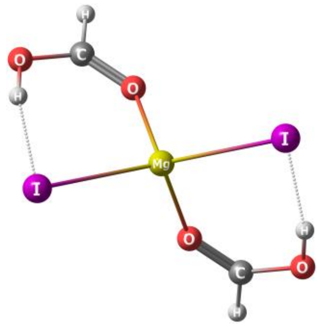
[29] M. J. Frisch, G. W. Trucks, H. B. G. E. Schlegel, M. A. Scuseria, J. R. Robb, G. Cheeseman, V. Scalmani, B. Barone, G. A. Mennucci, H. Petersson, M. Nakatsuji, X. Caricato, H. P. Li, A. F. Hratchian, J. Izmaylov, G. Bloino, J. L. Zheng, M. Sonnenberg, M. Hada, K. Ehara, R. Toyota, J. Fukuda, M. Hasegawa, T. Ishida, Y. Nakajima, O. Honda, H. Kitao, T. Nakai, J. A. Vreven, Jr., J. E. Montgomery, F. Peralta, M. Ogliaro, J. J. Bearpark, E. Heyd, K. N. Brothers, V. N. Kudin, T. Staroverov, R. Keith, J. Kobayashi, K. Normand, A. Raghavachari, J. C. Rendell, S. S. Burant, J. Iyengar, M. Tomasi, N. Cossi, J. M. Rega, M. Millam, J. E. Klene, J. B. Knox, V. Cross, C. Bakken, J. Adamo, R. Jaramillo, R. E. Gomperts, O. Stratmann, A. J. Yazyev, R. Austin, C. Cammi, J. W. Pomelli, R. L. Ochterski, K. Martin, V. G. Morokuma, G. A. Zakrzewski, P. Voth, J. J. Salvador, S. Dannenberg, A. D. Dapprich, O. Daniels, J. B. Farkas, J. V. Foresman, J. Ortiz, Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, **2013**.

[30] a) A. D. Becke, *J. Chem. Phys.* 1997, **107**, 8554; b) Q. Wu and W. Yang, *J. Chem. Phys.* 2002, **116**, 515; c) S. Grimme, *J. Comput. Chem.* **2006**, *27*, 1787–1799; d) J. Da Chai and M. Head-Gordon, *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615–6620.

[31] a) A. Schäfer H. Horn and R. Ahlrichs, *J. Chem. Phys.* 1992, **97**, 2571–2577; b) A. Schäfer, C. Huber and R. Ahlrichs, *J. Chem. Phys.* 1994, **100**, 5829–5835; c) F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.* 2005, **7**, 3297–3305; d) F. Weigend, *Phys. Chem. Chem. Phys.* 2006, **8**, 1057–1065.

[32] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* 2009, **113**, 6378–6396.

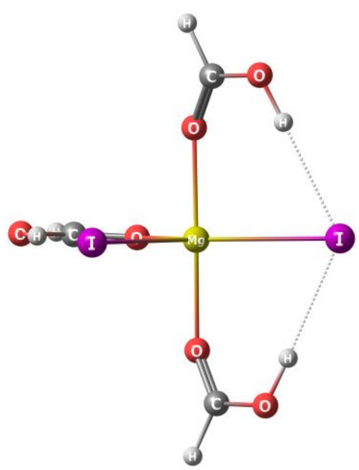
SCF energy = -1174.91642603 a.u.



8	2.812260	1.518939	-1.837083
1	2.810563	0.809292	-1.133189
6	1.635857	2.014433	-2.009889
1	1.610975	2.803973	-2.780382
8	0.616931	1.686053	-1.413722
53	2.341824	-0.820621	0.609669
53	-2.342256	-0.819267	-0.610734
12	0.000098	0.357336	-0.000010
8	-2.810937	1.515758	1.841024
1	-2.809816	0.807494	1.135762
6	-1.634769	2.012040	2.012437
1	-1.609136	2.800861	2.783664
8	-0.616679	1.684945	1.414209

A-3

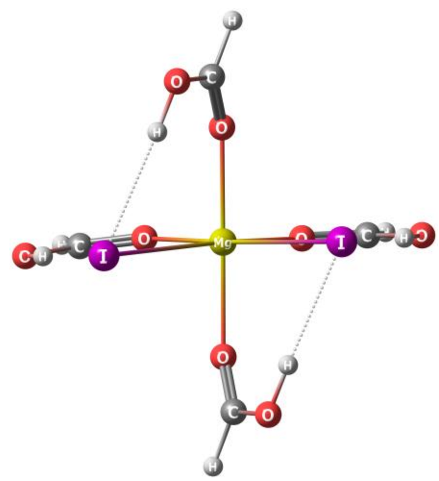
SCF energy = -1364.51067485 a.u.



8	1.280416	3.096603	-0.493275
1	1.702920	2.204606	-0.574249
6	0.315055	3.069966	0.367976
1	-0.134786	4.065193	0.527406
8	-0.090189	2.086113	0.965407
53	2.629039	-0.037532	0.010390
53	-1.927902	0.058534	-1.351388
12	-0.105583	0.004507	0.727316
8	1.146646	-3.090782	-0.617720
1	1.597181	-2.210981	-0.676002
6	0.198903	-3.063836	0.262816
1	-0.276164	-4.050697	0.399556
8	-0.166542	-2.088972	0.899564
8	-3.454295	-0.078237	1.716844
1	-3.090532	-0.042592	0.785963
6	-2.514882	-0.061104	2.602082
1	-2.905275	-0.094981	3.634219
8	-1.313668	-0.013217	2.385548

A-4

SCF energy = -1554.10954779 a.u.

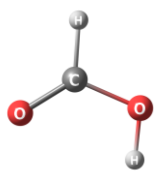


8	0.859607	-0.717817	-3.049378
1	1.204275	-0.987261	-2.154085
6	0.233443	0.408843	-2.990336
1	-0.125589	0.743847	-3.979608
8	0.034351	1.078363	-1.988243
53	2.144705	-1.173207	0.081424
53	-2.149468	-1.146981	-0.227194
12	-0.000906	0.915605	0.089107
8	-0.869928	-1.159030	2.941668
1	-1.216280	-1.287683	2.016495
6	-0.242769	-0.036857	3.052955
1	0.118422	0.144228	4.080656
8	-0.045196	0.775600	2.162714
8	3.607146	1.871166	0.276442

1	3.281781	0.928586	0.207639
6	2.616336	2.701851	0.278827
1	2.949621	3.752542	0.359181
8	1.433257	2.421721	0.201806
8	-3.576777	1.922930	-0.192703
1	-3.256278	0.976682	-0.211960
6	-2.594375	2.737666	0.015394
1	-2.923571	3.792112	0.052379
8	-1.423073	2.438398	0.165795

Formic acid (HCO_2H)

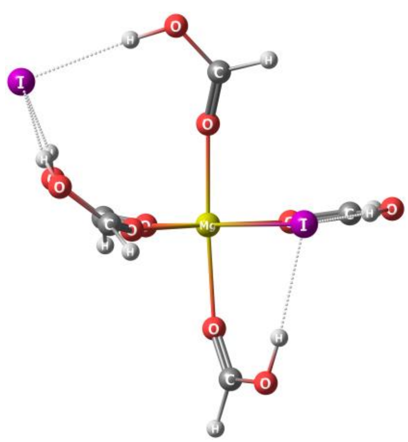
SCF energy = -189.558956169 a.u.



8	1.108844	-0.091160	-0.000004
1	1.040034	-1.058580	0.000002
6	-0.131225	0.397363	0.000017
1	-0.098813	1.505730	-0.000035
8	-1.128078	-0.262755	-0.000005

I-1

SCF energy = -1743.69552391 a.u.

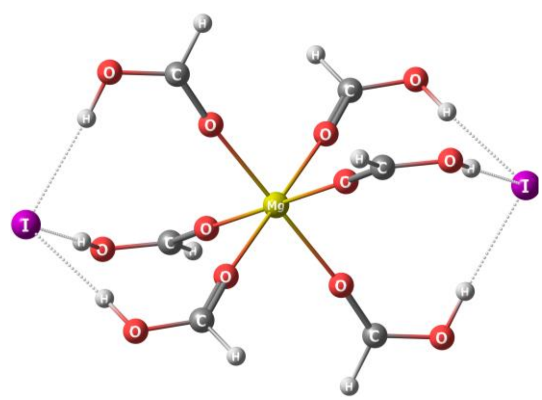


8	1.659599	-1.716044	-2.217021
1	2.353941	-1.265989	-1.645796
6	0.510208	-1.151495	-2.086615
1	-0.294049	-1.681322	-2.630153
8	0.295367	-0.136429	-1.443164
53	3.862637	-0.422079	0.000298
53	-2.798103	-1.426490	-0.015808
12	-0.694822	0.898868	0.008783
8	-3.579690	0.815381	2.404551
1	-3.414390	0.106668	1.719792
6	-2.735015	1.786959	2.285216
1	-2.907048	2.586258	3.028755
8	-1.835685	1.868530	1.467203
8	2.877252	2.802457	0.005027
1	3.026431	1.808349	0.003762
6	1.637780	3.147928	0.018411
1	1.513167	4.246934	0.021416
8	0.671781	2.406596	0.028015
8	-3.593552	0.875201	-2.373295
1	-3.426130	0.152165	-1.704123
6	-2.734847	1.834040	-2.250943
1	-2.906089	2.646041	-2.980768
8	-1.823850	1.892115	-1.443922
8	1.650731	-1.760463	2.182822
1	2.344311	-1.298171	1.620499
6	0.501459	-1.192267	2.069152
1	-0.300727	-1.732537	2.605401
8	0.284377	-0.163798	1.448096

I-2

SCF energy = -1933.27557152 a.u.

PG = D_{3d}

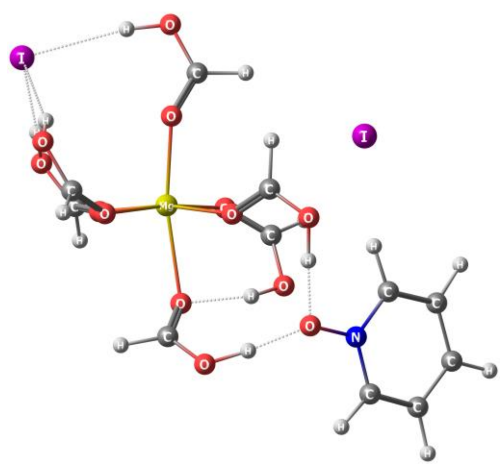


8	0.000000	2.903089	3.062414
1	0.000000	2.019480	3.542224
6	0.000000	2.758548	1.781129
1	0.000000	3.731572	1.252983
8	0.000000	1.701678	1.179579
53	0.000000	0.000000	4.783548
53	0.000000	0.000000	-4.783548

12	0.000000	0.000000	0.000000
8	0.000000	-2.903089	-3.062414
1	0.000000	-2.019480	-3.542224
6	0.000000	-2.758548	-1.781129
1	0.000000	-3.731572	-1.252983
8	0.000000	-1.701678	-1.179579
8	-2.514149	-1.451544	3.062414
1	-1.748921	-1.009740	3.542224
6	-2.388972	-1.379274	1.781129
1	-3.231636	-1.865786	1.252983
8	-1.473696	-0.850839	1.179579
8	-2.514149	1.451544	-3.062414
1	-1.748921	1.009740	-3.542224
6	-2.388972	1.379274	-1.781129
1	-3.231636	1.865786	-1.252983
8	-1.473696	0.850839	-1.179579
8	2.514149	-1.451544	3.062414
1	1.748921	-1.009740	3.542224
6	2.388972	-1.379274	1.781129
1	3.231636	-1.865786	1.252983
8	1.473696	-0.850839	1.179579
8	2.514149	1.451544	-3.062414
1	1.748921	1.009740	-3.542224
6	2.388972	1.379274	-1.781129
1	3.231636	1.865786	-1.252983
8	1.473696	0.850839	-1.179579

I-3

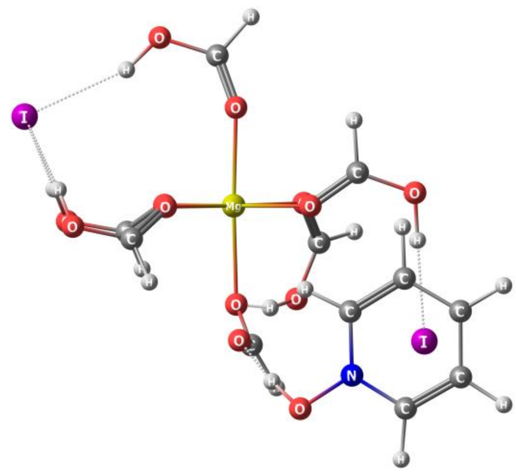
SCF energy = -2256.40535183 a.u.



8	0.359715	2.906037	2.649503
1	0.513772	2.095920	3.262858
6	-0.327910	2.645914	1.599690
1	-0.330013	3.464982	0.859232
8	-0.950811	1.607072	1.389431
53	0.407156	-3.717172	2.533964
53	-0.619981	-0.828778	-4.754513
12	-0.491865	0.066938	-0.162536
8	-0.084892	-3.350284	-2.487438
1	-0.163310	-2.680086	-3.224205
6	0.026546	-2.743554	-1.353863
1	0.052724	-3.413798	-0.471729
8	0.107357	-1.524654	-1.248909
8	-1.696718	-0.424959	3.020064
1	-1.311042	0.364319	2.566825
6	-1.968819	-1.323026	2.110944
1	-2.422457	-2.238576	2.516248
8	-1.792066	-1.147145	0.915431
8	-3.397307	-0.016906	-3.053017
1	-2.542686	-0.258984	-3.532513
6	-3.185536	0.425714	-1.864503
1	-4.123051	0.695803	-1.342984
8	-2.097195	0.562840	-1.331265
8	2.667669	-0.573707	2.633720
1	2.145839	0.083144	3.185979
6	2.028378	-0.803004	1.533616
1	2.452914	-1.621875	0.932071
8	1.068178	-0.133953	1.169823
8	1.519700	1.248465	-3.216099
1	0.821901	0.562534	-3.456534
6	1.432725	1.766933	-2.045389
1	2.184035	2.564699	-1.894231
8	0.649087	1.476760	-1.153113
8	1.080550	0.947154	4.069331
7	0.467418	0.313116	5.042574
6	-0.093490	1.030546	6.042685
6	0.401517	-1.032519	5.027811
6	-0.754043	0.393646	7.075707
1	0.029759	2.109549	5.958005
6	-0.246867	-1.709915	6.047344
1	0.834486	-1.562374	4.170164
6	-0.835445	-1.000083	7.086953
1	-1.198323	0.998171	7.866874
1	-0.287946	-2.798088	5.971498
1	-1.353690	-1.518394	7.895119

I-4

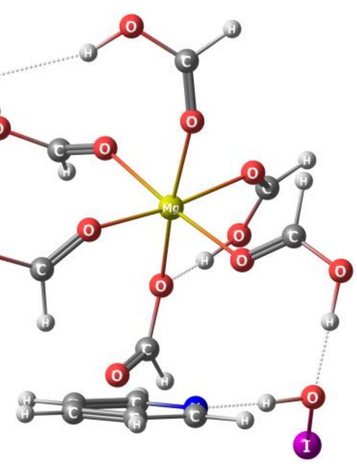
SCF energy = -2256.40960789 a.u.



8	-0.530296	0.744003	-1.972839
1	-1.587929	1.587944	-2.291716
6	-0.813528	-0.464684	-1.845323
1	-1.786420	-0.828596	-2.232205
8	-0.055835	-1.320639	-1.311711
53	-3.693695	-0.590018	0.423042
53	5.914006	-1.028677	-0.840492
12	1.245808	-1.058510	0.311300
8	4.624846	-1.535538	2.239528
1	4.781049	-1.360327	1.263781
6	3.424824	-1.334605	2.657875
1	3.340587	-1.496575	3.749071
8	2.453799	-1.000630	2.000728
8	-1.036736	-3.514147	-0.354335
1	-0.694366	-2.722355	-0.875907
6	-0.703045	-3.366883	0.884283
1	-1.173999	-4.107096	1.554344
8	0.071368	-2.523289	1.316324
8	3.836529	-3.444670	-1.965642
1	4.480688	-2.754075	-1.615855
6	2.689148	-3.353996	-1.387006
1	1.953665	-4.077501	-1.787487
8	2.407679	-2.578928	-0.489196
8	-1.634688	0.444986	2.766082
1	-2.282473	0.202436	2.006790
6	-0.409298	0.396304	2.379856
1	0.314104	0.461648	3.215183
8	-0.033759	0.303153	1.219109
8	3.730157	1.202809	-2.185409
1	4.434429	0.653059	-1.730221
6	2.578805	0.999296	-1.637515
1	1.738877	1.485912	-2.164608
8	2.401280	0.330106	-0.633304
8	-2.399600	2.262974	-2.421386
7	-2.844790	2.608646	-1.216259
6	-4.163987	2.839553	-1.103193
6	-2.006388	2.710326	-0.167976
6	-4.691817	3.256092	0.103728
1	-4.737289	2.667729	-2.012407
6	-2.497641	3.119213	1.059046
1	-0.968698	2.432995	-0.353814
6	-3.850681	3.406889	1.202245
1	-5.764302	3.432809	0.176469
1	-1.809488	3.191796	1.900207
1	-4.250896	3.721059	2.166819

I-5

SCF energy = -2256.41557215 a.u.

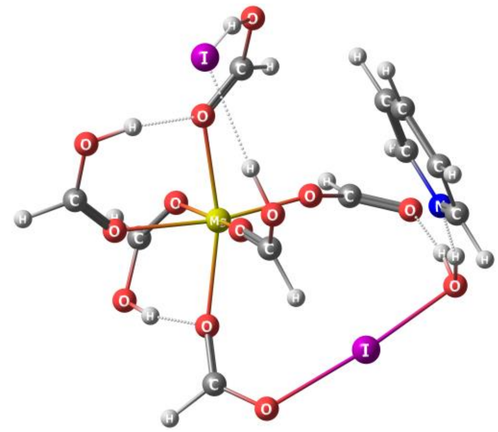


8	-0.883400	-0.291431	-2.524579
1	-3.619821	1.112900	0.429841
6	-0.798000	-1.490577	-2.344103
1	-1.393572	-2.191315	-2.978437
8	-0.055107	-2.083677	-1.469225
53	-4.510668	-0.893765	-0.775070
53	5.075089	0.864309	0.286789
12	0.773956	-1.443241	0.317216
8	3.714371	-0.809057	2.877904
1	3.919906	-0.367248	2.000405
6	2.496173	-1.194143	3.030497
1	2.328620	-1.622189	4.037336
8	1.587807	-1.122316	2.221233

8	-0.170378	-4.499498	-0.832426
1	-0.145708	-3.539803	-1.228019
6	0.056807	-4.428143	0.432353
1	-0.012442	-5.403571	0.949453
8	0.327837	-3.407569	1.053925
8	4.422632	-1.856643	-1.615337
1	4.643766	-1.088092	-1.003177
6	3.319157	-2.433977	-1.283271
1	3.035310	-3.237306	-1.989580
8	2.638714	-2.161312	-0.309233
8	-2.654811	-0.715442	2.637888
1	-3.239523	-0.337312	1.886767
6	-1.466925	-0.980984	2.225624
1	-0.804787	-1.387348	3.011238
8	-1.063368	-0.813284	1.080573
8	2.394545	2.020154	-1.446109
1	3.142292	1.863205	-0.800386
6	1.449655	1.158106	-1.249063
1	0.671589	1.141659	-2.031659
8	1.402868	0.400653	-0.293386
8	-4.100456	0.283960	0.799307
7	-2.842682	2.419906	-0.047012
6	-3.100754	3.588789	0.543414
6	-1.903176	2.356143	-0.995384
6	-2.424932	4.758762	0.214108
1	-3.880233	3.582946	1.310752
6	-1.182213	3.480814	-1.392187
1	-1.722151	1.377258	-1.452591
6	-1.444979	4.700730	-0.775082
1	-2.663548	5.693190	0.723854
1	-0.425051	3.397750	-2.173167
1	-0.892407	5.598006	-1.061994

I-6

SCF energy = -2256.43074278 a.u.



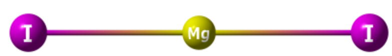
8	-3.403728	-0.310188	-2.201583
1	-1.807713	3.112453	0.791991
6	-3.077091	-1.482359	-1.926787
1	-3.362767	-2.242294	-2.685237
8	-2.484719	-1.888401	-0.893753
53	-3.131849	1.324880	-0.627351
53	4.264330	-0.153196	-0.409178
12	-0.726645	-1.609750	0.295120
8	2.741916	-0.712019	2.465606
1	3.296006	-0.660654	1.612794
6	1.580394	-1.214489	2.243840
1	0.889182	-1.130514	3.099868
8	1.225249	-1.741243	1.193567
8	-2.883164	-4.258359	0.142770
1	-2.752775	-3.425108	-0.401544
6	-2.170337	-4.162332	1.217843
1	-2.297773	-5.020428	1.901767
8	-1.422970	-3.236103	1.489320
8	2.253199	-3.153069	-0.924328
1	2.167681	-2.421281	-0.265849
6	1.102382	-3.580084	-1.321723
1	1.194066	-4.401368	-2.055025
8	0.009137	-3.168337	-0.967758
8	-2.549698	1.060373	2.874393
1	-2.663497	2.159906	1.792468
6	-2.037784	-0.036849	2.630478
1	-2.300946	-0.888646	3.302548
8	-1.224280	-0.288753	1.693523
8	1.584742	1.183541	-1.948963
1	2.342779	0.718145	-1.469437
6	0.434076	0.668371	-1.691549
1	-0.394691	1.209102	-2.184764

8	0.234539	-0.310866	-0.990138
8	-2.753733	2.758050	0.967916
7	-0.235297	3.340254	0.533904
6	0.353714	4.202205	-0.297472
6	0.524382	2.510820	1.257476
6	1.735558	4.268308	-0.446701
1	-0.308307	4.858511	-0.869562
6	1.911816	2.511406	1.177340
1	-0.013260	1.806372	1.897956
6	2.528632	3.402256	0.302070
1	2.176255	4.976921	-1.149151
1	2.500186	1.808707	1.767323
1	3.615015	3.397277	0.193354

MgI_2

SCF energy = -795.698373407 a.u.

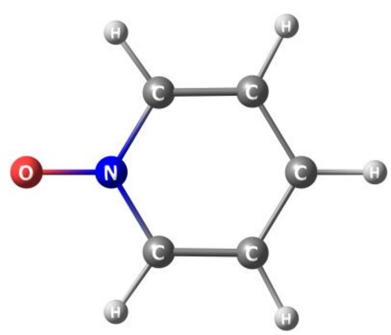
PG = C_{V}



53	0.000000	0.000000	2.547522
53	0.000000	0.000000	-2.547630
12	0.000000	0.000000	0.000476

Pyridine *N*-oxide (C_5H_5NO)

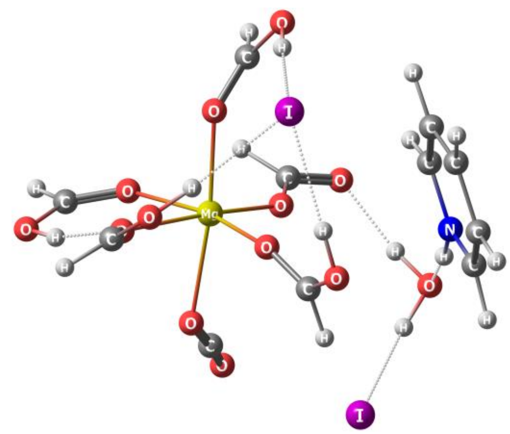
SCF energy = -323.097599412 a.u.



8	-2.242627	0.000000	-0.000003
7	-0.989937	0.000000	-0.000002
6	-0.287147	-1.176463	0.000000
6	-0.287147	1.176463	-0.000001
6	1.095387	-1.192072	0.000001
1	-0.921218	-2.061738	-0.000001
6	1.095387	1.192072	0.000002
1	-0.921218	2.061738	-0.000002
6	1.817364	0.000000	0.000003
1	1.601158	-2.159018	0.000002
1	1.601158	2.159018	0.000003
1	2.907633	0.000000	0.000005

P-A

SCF energy = -2256.47423215 a.u.

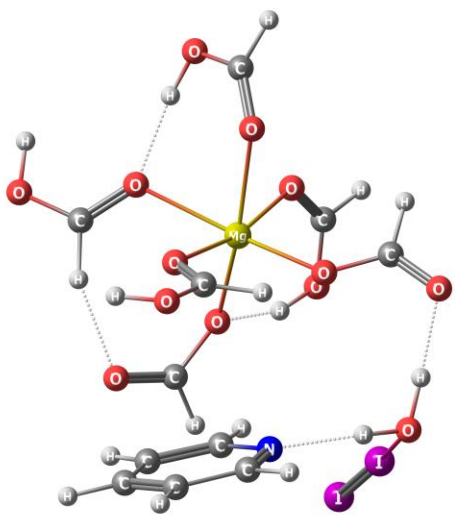


8	3.950889	2.180294	-0.017860
1	2.383560	-2.177704	1.680953
6	2.896307	2.079890	-0.459753
53	3.514641	-1.075106	-1.464027
8	1.799734	2.126782	-0.878598
1	3.875329	-1.199604	1.130418
53	-4.024607	-0.978397	-0.518693
12	-0.043982	1.674244	0.305614
8	-3.140590	0.142724	2.514070
1	-3.452067	-0.155950	1.600766
6	-2.205184	1.023824	2.419614
1	-1.801525	1.326619	3.404143
8	-1.787973	1.497607	1.374943
8	-0.128583	5.165727	-0.423720
1	-0.479562	4.372876	-0.903556
6	0.325865	4.776166	0.727792
1	0.700382	5.609221	1.347700
8	0.353417	3.621006	1.114267
8	-2.748012	1.641206	-2.253602
1	-2.807736	0.972974	-1.511273
6	-1.924794	2.610456	-2.132244
1	-1.990101	3.316934	-2.978519
8	-1.128514	2.813000	-1.215009
8	2.340834	0.355508	3.434141
1	3.293638	-0.785003	2.538336
6	1.612419	1.094761	2.779043

1	1.336906	2.090010	3.210036
8	1.118855	0.831477	1.633993
8	-1.043381	-1.699329	-2.038749
1	-1.949786	-1.518750	-1.661299
6	-0.191070	-0.833791	-1.594416
1	0.864411	-1.017803	-1.886311
8	-0.518425	0.114581	-0.886008
8	3.614172	-1.551377	2.005791
7	1.352748	-2.573647	1.470423
6	1.136921	-3.366012	0.415319
6	0.362757	-2.149468	2.262007
6	-0.149017	-3.791579	0.116798
1	2.012965	-3.607997	-0.190657
6	-0.946320	-2.527649	2.009742
1	0.666390	-1.493190	3.080291
6	-1.204148	-3.358731	0.919107
1	-0.321043	-4.424190	-0.753453
1	-1.755224	-2.164455	2.643797
1	-2.231621	-3.644554	0.685150

P-B

SCF energy = -2256.42130705 a.u.

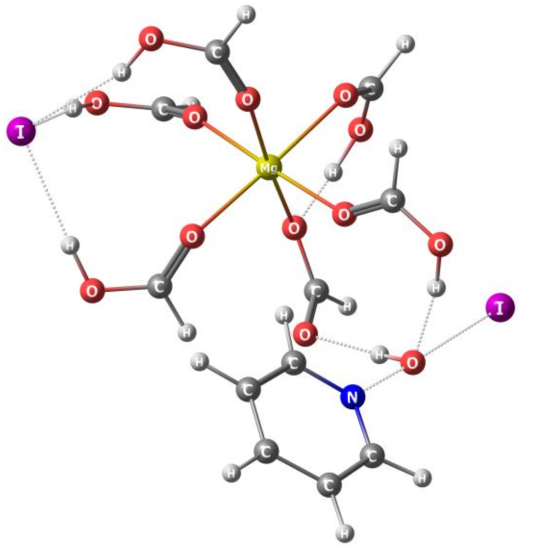


8	0.483647	-0.179583	-2.824932
1	-3.548262	1.121400	0.661742
6	-0.268260	-1.058604	-2.424256
1	-1.155139	-1.362507	-3.024784
8	-0.121878	-1.705637	-1.319486
53	-4.077248	-1.310530	-0.837312
53	-3.972594	-3.105333	-2.958598
12	0.699150	-1.303518	0.502802
8	3.646493	-2.587872	1.953993
1	3.402951	-2.418421	1.014925
6	2.808260	-1.947249	2.720816
1	3.043922	-2.064633	3.793188
8	1.870515	-1.282124	2.331179
8	-0.968537	-3.986632	-0.581627
1	-0.797169	-3.062087	-0.984542
6	-0.195936	-4.182012	0.421272
1	-0.311455	-5.182194	0.876848
8	0.616421	-3.377959	0.877071
8	4.170289	-1.294887	-2.047757
1	4.747613	-1.819011	-1.469477
6	2.992476	-1.160811	-1.500056
1	2.255152	-0.592724	-2.108839
8	2.712263	-1.636340	-0.406435
8	-2.666809	-0.885701	2.875495
1	-3.569257	-0.035518	1.729472
6	-1.581894	-1.280210	2.469155
1	-1.085535	-2.126435	3.009407
8	-0.935096	-0.814043	1.472493
8	0.743577	2.892997	0.774198
1	1.490098	3.022222	0.167495
6	0.485873	1.613032	0.858541
1	-0.399150	1.369207	1.468857
8	1.161826	0.762574	0.306245
8	-4.079622	0.357056	0.975053
7	-2.500762	2.388669	-0.230374
6	-2.485784	3.717476	-0.131040
6	-1.792357	1.814508	-1.204567
6	-1.761432	4.530351	-1.000466
1	-3.079124	4.152672	0.678884
6	-1.032901	2.537262	-2.122875
1	-1.838252	0.722358	-1.247137
6	-1.021485	3.925973	-2.015489
1	-1.781886	5.614828	-0.880326
1	-0.465065	1.996844	-2.882553
1	-0.444600	4.533175	-2.717401

TS-1

SCF energy = -2256.35439912 a.u.

ν = -508.7979 cm^{-1}

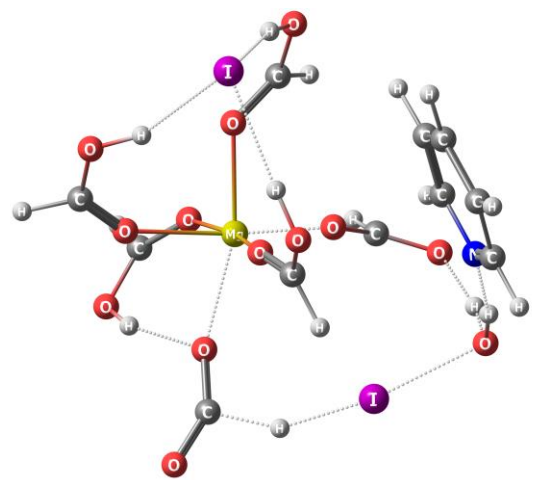


8	-1.560797	0.385828	-1.756627
1	-2.981978	0.711682	-0.844339
6	-1.352260	-0.820469	-1.890360
1	-2.021163	-1.427541	-2.536599
8	-0.394249	-1.464438	-1.333465
53	-4.569210	-1.348072	-0.302119
53	5.083203	0.753987	-0.211307
12	0.606203	-0.964562	0.421727
8	3.781756	-0.365575	2.700000
1	3.957537	-0.086358	1.752998
6	2.556265	-0.647453	2.976542
1	2.428208	-0.901634	4.045652
8	1.604254	-0.647745	2.216208
8	-0.593112	-3.919223	-0.714742
1	-0.530718	-2.980045	-1.114227
6	-0.375209	-3.853483	0.554125
1	-0.539067	-4.813574	1.076094
8	-0.010523	-2.857660	1.166964
8	4.067995	-2.111682	-1.707556
1	4.424670	-1.294130	-1.242872
6	2.895836	-2.421497	-1.269847
1	2.458861	-3.289170	-1.799154
8	2.306727	-1.849064	-0.369415
8	-2.950537	0.313057	2.361109
1	-3.289716	0.519029	1.440832
6	-1.746958	-0.138410	2.281971
1	-1.351976	-0.522572	3.239301
8	-1.080731	-0.132090	1.258270
8	2.406608	1.943768	-1.881585
1	3.203178	1.706281	-1.315500
6	1.326121	1.439230	-1.390556
1	0.436309	1.566177	-2.035449
8	1.250390	0.871826	-0.309706
8	-3.603403	1.074537	-0.152007
7	-2.911040	2.615897	-0.104021
6	-3.776084	3.620794	-0.160581
6	-1.606718	2.767661	0.100557
6	-3.320838	4.924658	-0.009317
1	-4.820087	3.348919	-0.331190
6	-1.088877	4.048590	0.257539
1	-1.008624	1.852271	0.121828
6	-1.957931	5.137390	0.201997
1	-4.026799	5.754348	-0.058128
1	-0.018762	4.179992	0.423068
1	-1.573747	6.151898	0.324709

TS-2A

SCF energy = -2256.38541107 a.u.

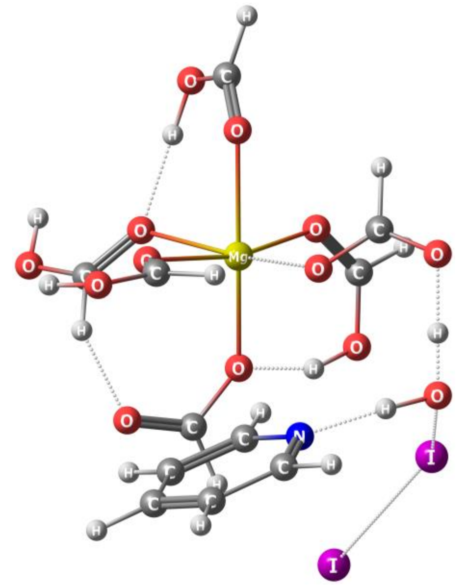
ν = -298.9292 cm^{-1}



8	-3.444580	-2.109885	-2.769872
1	-2.093458	3.261395	0.616261
6	-2.936183	-1.712276	-1.784698
1	-3.290764	-0.358124	-1.679571
8	-2.244595	-2.017727	-0.826232
53	-3.280633	1.144798	-0.644035
53	4.165115	-0.096896	-0.488888
12	-0.502611	-1.519827	0.485947
8	2.873717	-0.362957	2.596399
1	3.371636	-0.377014	1.721209
6	1.715540	-0.918568	2.461180

1	1.072812	-0.805487	3.352732
8	1.341049	-1.510588	1.461244
8	-2.303381	-4.526352	0.284328
1	-2.211491	-3.767890	-0.337575
6	-1.786970	-4.197454	1.430808
1	-1.906443	-4.989650	2.190709
8	-1.227692	-3.146066	1.678107
8	2.546128	-3.090400	-1.055322
1	2.642584	-2.178722	-0.674666
6	1.357044	-3.585460	-1.082136
1	1.348340	-4.584838	-1.554550
8	0.325433	-3.085418	-0.665609
8	-2.545052	1.215106	2.845034
1	-2.824209	2.352368	1.689673
6	-2.041450	0.108418	2.653948
1	-2.321542	-0.721456	3.348185
8	-1.210799	-0.188598	1.740697
8	1.486795	1.305075	-1.973774
1	2.274091	0.855499	-1.535573
6	0.370063	0.767523	-1.625668
1	-0.506585	1.294988	-2.044375
8	0.250601	-0.219746	-0.917447
8	-2.993960	2.882410	0.855129
7	-0.430991	3.508027	0.313253
6	0.194060	4.358404	-0.503208
6	0.301022	2.693197	1.080365
6	1.581261	4.428004	-0.594857
1	-0.442474	5.007131	-1.112278
6	1.692226	2.696023	1.059153
1	-0.259805	1.995963	1.709372
6	2.344765	3.576291	0.199929
1	2.049530	5.129400	-1.286750
1	2.255869	2.005549	1.687062
1	3.435048	3.580376	0.140586

TS-2B
SCF energy = -2256.36054589 a.u.
ν = -58.4461cm^{-1}
Approximated



8	-0.759637	-0.286236	2.676592
1	1.131963	3.006445	-1.237024
6	-0.048311	-0.754711	1.789981
1	1.027659	-0.982646	1.956522
8	-0.477544	-1.030229	0.602403
53	2.402041	0.764861	-1.439810
53	3.358902	-2.564069	1.003338
12	-2.150926	-0.510678	-0.396932
8	-5.008991	-2.355592	-1.242498
1	-4.376515	-2.434233	-0.490723
6	-4.836478	-1.203694	-1.823915
1	-5.546348	-1.041207	-2.653966
8	-4.006522	-0.373221	-1.508963
8	0.374698	-2.570963	-1.277610
1	0.266585	-1.970207	-0.461842
6	-0.694035	-2.634842	-1.970292
1	-0.610826	-3.310153	-2.840811
8	-1.751032	-2.036142	-1.751057
8	-3.711085	-2.941648	2.773925
1	-4.284900	-3.508243	2.233201
6	-3.106684	-2.065303	2.021826
1	-2.399117	-1.397548	2.558077
8	-3.294510	-1.982063	0.813131
8	-0.584291	1.911145	-3.346889
1	0.544524	2.278471	-2.652315
6	-1.408541	1.235661	-2.710387
1	-2.265738	0.815541	-3.282915
8	-1.362858	0.988324	-1.474649
8	-3.218738	2.936001	1.832272

1	-3.616315	2.418840	2.551722
6	-2.820316	2.114819	0.895178
1	-2.307952	2.619708	0.059897
8	-3.000477	0.914653	0.937597
8	1.433958	2.540164	-2.099742
7	0.735455	3.520722	0.244716
6	0.951095	4.746924	0.724365
6	0.345602	2.555708	1.084136
6	0.778124	5.061606	2.069201
1	1.279992	5.501669	0.004609
6	0.157438	2.771577	2.445766
1	0.184347	1.571114	0.636416
6	0.377887	4.053492	2.944454
1	0.964639	6.077348	2.420819
1	-0.143732	1.931358	3.075541
1	0.246232	4.263909	4.008011