Electronic Supplementary Material (ESI) for ChemComm.


# Sequential Organo and Metal Catalyzed Reaction Between 3-Pyrrolyloxindoles and Linear Nitroenynes: Access to Cyclic Aza-Spirooxindoles

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**1. General Information:**

Chemicals and solvents were purchased from commercial suppliers and used as received. $^{1}H$ NMR spectra were recorded on 400 MHz, 500 MHz and 600 MHz spectrometer. $^{13}C$ NMR spectra were recorded on 100 MHz, 125 MHz and 150 MHz. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton ($CDCl_3$: δ 7.260), carbon ($CDCl_3$: δ 77.16). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), brs (broad singlet). Coupling constants were reported in Hertz (Hz). Using ESI mode HRMS spectra were recorded. Enantiomeric ratios were determined by HPLC analysis performed on Chiral Columns using a Daicel Chiralpak ID Column, Daicel Chiralpak IE Column, Daicel Chiralpak IF Column, and Daicel Chiralpak ADH Column. For visualizing the products UV light and $I_2$ were used. DCM was distilled over $CaH_2$ under argon and stored over 4A° molecular sieves. Silica gel (230-400 mesh size) was used for the flash column chromatography. Reactions were monitored by TLC on silica gel 60 F254 (0.25 mm).

**2. General procedure for the synthesis of 3-pyrrolyloxindoles:**

3-pyrrolyloxindoles were prepared according to reported procedure. [1]

**3. General procedure for the synthesis of nitrolefines:**

Nitrolefines were prepared according to reported procedures. [2]

**4. General procedure for the synthesis of catalyst:**

The catalyst (**I, II, III, IV, V, VI** and **VII**) was prepared according to reported procedures. [3]

## 5. Reaction condition optimization:

## (a) Catalyst optimization:

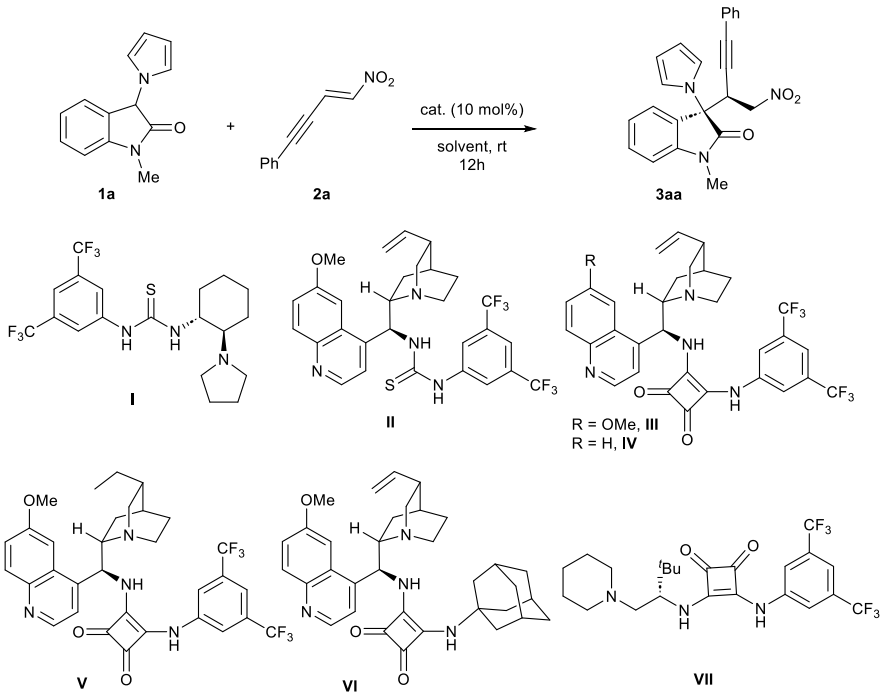



**Table 1**. Catalyst optimization of the Michael addition

| Entry[a] | Catalyst | Solvent | Yield (%)[b] | dr[c] | *ee*[d] |
|---|---|---|---|---|---|
| **1** | I | toluene | 86 | 1.2:1 | 50 |
| **2** | II | toluene | 88 | 1.1:1 | 62 |
| **3** | III | toluene | 85 | 1.1:1 | 80 |
| **4** | IV | toluene | 92 | 1.4:1 | 85 |
| **5** | V | toluene | 88 | 1.3:1 | 82 |
| **6** | VI | toluene | 84 | 0.6:1 | 53 |
| **7** | **VII** | **toluene** | **88** | **2.8:1** | **90** |

[a] Unless otherwise mentioned, reactions were carried out with 0.1 mmol of **1a** with 0.1 mmol of **2a** in 1 mL solvent using 10 mol% catalyst at room temperature for 12 hours. [b] Isolated combined yield after silica gel column chromatography. [c] Determined by $^1$H NMR. [d] Determined by chiral HPLC.

**(b) Screening of different solvent and catalyst loading optimization:**

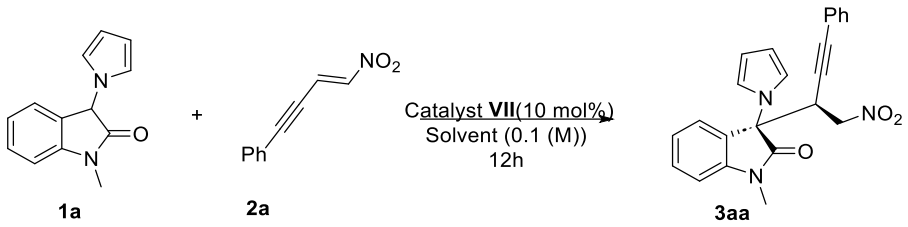



**Table 2**. Solvent optimization of the Michael addition

| Entry[a] | Solvent | Yield (%)[b] | dr[c] | *ee*[d] |
|---|---|---|---|---|
| **1.** | Toluene | 88 | 2.8:1 | 90 |
| **2.** | $PhCF_3$ | 90 | 5.0:1 | 97 |
| **3.** | **$CH_2Cl_2$** | **96** | **5.2:1** | **97** |
| **4.** | $CHCl_3$ | 92 | 5.1:1 | 97 |
| **5.** | $Et_2O$ | 94 | 4.5:1 | 94 |
| **6.** | Xylene | 86 | 3.6:1 | 93 |
| **7.** | Mesilylene | 80 | 3.7:1 | 93 |

[a] Unless otherwise mentioned, reactions were carried out with 0.1 mmol of **1a** with 0.1 mmol of **2a** in 1 mL solvent using 10 mol% catalyst at room temperature for 12 hours. [b] Isolated combined yield after silica gel column chromatography. [c] Determined by $^1$H NMR. [d] Determined by chiral HPLC.

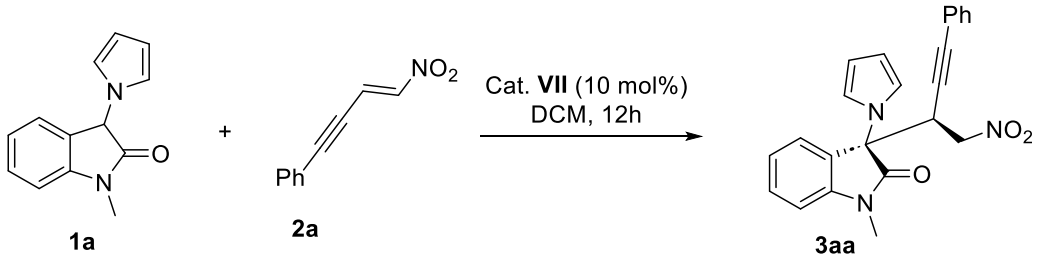



**Table 3**. Concentration optimization of the Michael addition

| Entry[a] | Conc. | Yield (%)[b] | dr[c] | *ee*[d] |
|---|---|---|---|---|
| **1.** | **0.05 (M)** | **95** | **6:1** | **97** |

| | | | | |
|---|---|---|---|---|
| **2.** | 0.1 (M) | 96 | 5.2:1 | 97 |
| **3.** | 0.25 (M) | 95 | 5.:1 | 97 |

[a] Unless otherwise mentioned, reactions were carried out with 0.1 mmol of **1a** with 0.1 mmol of **2a** using 10 mol% catalyst at room temperature for 12 hours. [b] Isolated combined yield after silica gel column chromatography. [c] Determined by $^1$H NMR. [d] Determined by chiral HPLC.

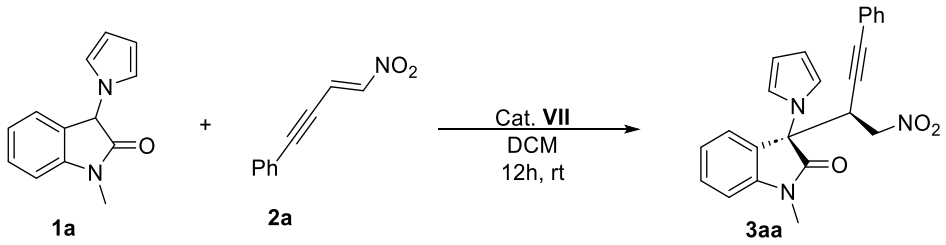



**Table 4**. Catalyst loading optimization of the Michael addition

| **Entry[a]** | **Catalyst (mol%)** | **Yield (%)[b]** | **dr[c]** | ***ee*[d]** |
|---|---|---|---|---|
| **1.** | **2** | **95** | **6:1** | **97** |
| **2.** | 5 | 95 | 6:1 | 97 |
| **3.** | 10 | 95 | 6:1 | 97 |
| **4.** | 20 | 95 | 6:1 | 96 |

[a] Unless otherwise mentioned, reactions were carried out with 0.1 mmol of **1a** with 0.1 mmol of **2a** in 2 mL solvent using 10 mol% catalyst at room temperature for 12 hours. [b] Isolated combined yield after silica gel column chromatography. [c] Determined by $^1$H NMR. [d] Determined by chiral HPLC.

## (C) Optimization studies for the metal catalyzed cyclization

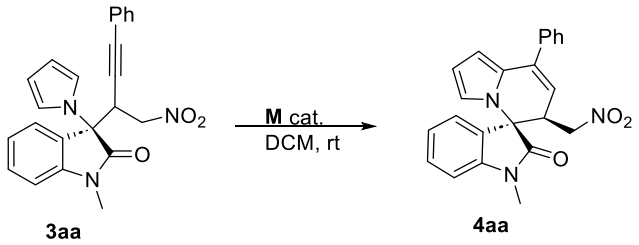
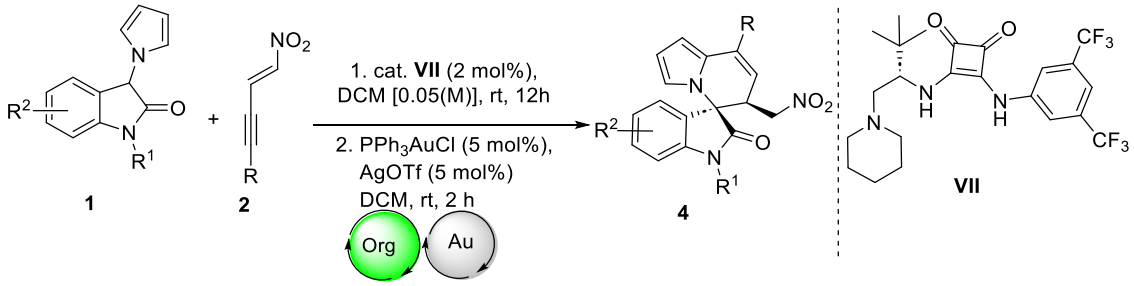



**Table 5.** Optimization studies for the metal catalyzed cyclization[a]

| Entry | **catalyst** | **Time (h)** | **Yield[b]** | **dr[c]** | ***ee*[d]** |
|---|---|---|---|---|---|
| **1.** | $Ag_2O$ | 24 | - | - | - |
| **2.** | $AgNO_3$ | 24 | - | - | - |
| **3.** | $Ag_2CO_3$ | 24 | - | - | - |
| **4.** | $AgBF_4$ | 24 | - | - | - |
| **5.** | AgOTf | 24 | - | - | - |
| **6.** | $AgNTf_2$ | 24 | - | - | - |
| **7.** | $PPh_3AuCl$ | 24 | - | - | - |
| **8.** | $PPh_3AuCl$/AgOTf | 1 | 98 | >20:1 | 97 |
| **9.** | $PPh_3AuCl/AgNTf_2$ | 4 | 82 | >20:1 | 97 |
| 10.[e] | **$PPh_3AuCl$/AgOTf** | **2** | **98** | **>20:1** | **97** |

[a] Reaction conditions: 0.10 mmol of 3a, 10 mol% of catalyst, DCM 2 mL, rt. [b] Yield of isolated 4a after flash chromatography. [c] Determined by 1HNMR after flash chromatography. [d] Determined by HPLC analysis on a chiral stationary phase. [e]5 mol% of catalyst was used.

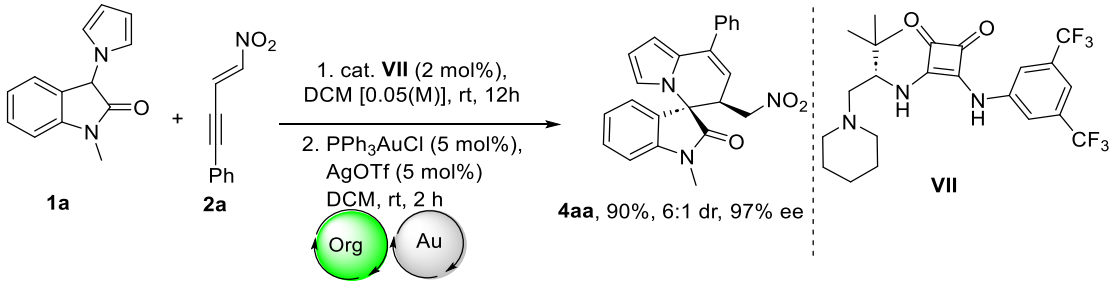
## 6. General procedure for the synthesis of compound 4:




In an oven dried 5 mL round bottom flask, 3-pyrrole oxindole **1** (0.1 mmol), nitroenyne **2** (0.1 mmol) and 2 mol% of catalyst (**VII**) were taken. Then 2 mL of $CH_2Cl_2$ was added to the reaction mixture and stirred at rt for 16 h. Progress of the reaction was monitored by TLC. After the completion of reaction, reaction mixture was passed through a short silica gel eluting with hexane/ethyl acetate (90/10) to afford the intermediate. Then the intermediate was then treated with 5 mol% $PPh_3AuCl$ and 5 mol% AgOTf catalyst in 1 ml $CH_2Cl_2$ at rt and the reaction was monitored by TLC (2 h). After complete consumption of the intermediate, the

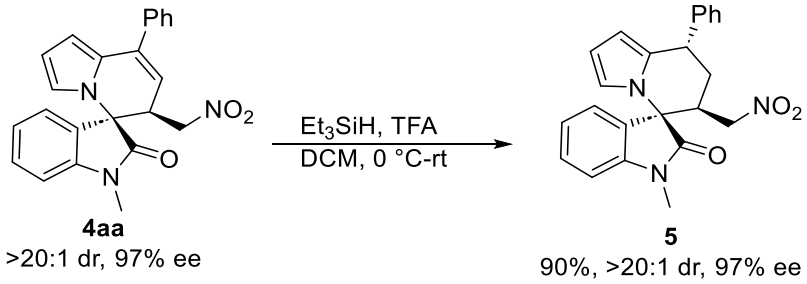
reaction mixture was subjected to directly in flash chromatography eluting with hexane/ethyl acetate (90/10) to afford the product **4**.

**7. Scale up reaction:**




In an oven dried 50 mL round bottom flask, 3-pyrrole oxindole **1a** (1 mmol), nitro enyne **2a** (1 mmol) and 2 mol% of catalyst (**VII**) were taken. Then 20 mL of $CH_2Cl_2$ was added to the reaction mixture and stirred at rt for 16 h. Progress of the reaction was monitored by TLC. After the completion of reaction, reaction mixture was passed through a short silica gel eluting with hexane/ethyl acetate (90/10) to afford the intermediate. Then the intermediate was treated with 5 mol% $PPh_3AuCl$ and 5 mol% AgOTf catalyst in 10 ml $CH_2Cl_2$ at rt and the reaction was monitored by TLC (2 h). After complete consumption of the intermediate, the reaction mixture was subjected to directly in flash chromatography eluting with hexane/ethyl acetate (90/10) to afford the product **4** (346.5mg, 90% yield, white solid).

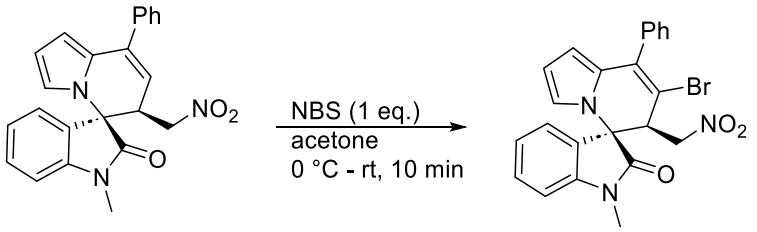
**8. General procedure for the synthesis of compound 5**[4]




Triethylsilane (0.6 mmol, 68 mg) was added to a solution of **4aa** (0.1 mmol, 38.5 mg) and trifluoroacetic acid (1 mmol, 80 µL) in $CH_2Cl_2$ (2 mL) at 0 °C and slowly allowed to warm to room temperature and the progress of the reaction was monitored by TLC using hexane and ethyl acetate as an eluent. The reaction mixture was quenched with saturated $K_2CO_3$ and extracted with $CH_2Cl_2$ (2 x 10 mL). The combined organic layer was washed with brine, drying ($Na_2SO_4$), and evaporation of the solvent gave a residue that was purified on flash

chromatography eluting with hexane/ethyl acetate (90/10) to give the product **5** (34.8 mg, 90% yield, white sticky solid).

### 9. General procedure for the synthesis of compound 6[5]

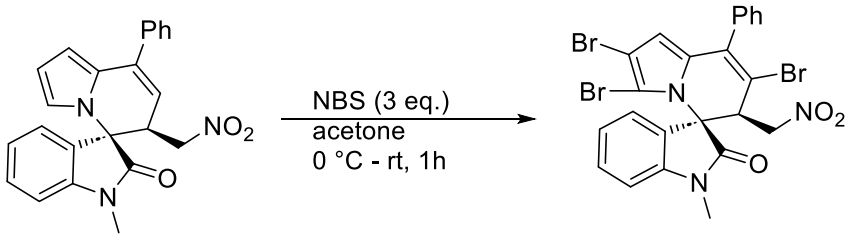



**4aa**
>20:1 dr, 97% ee

**6**
94%, >20:1 dr, 97% ee

Under air atmosphere in a 5ml round bottom flask, **4aa** (38.5 mg, 0.1 mmol) in acetone (1.0 mL) was taken and NBS (17.7 mg, 0.1 mmol) was added slowly at 0 °C. Then it was stirred at rt for 10 min. At the end of the reaction, the solvent was removed in vacuo. The residue was purified by flash chromatography eluting with hexane/ethyl acetate (95/5) to give the product **4** (43.6 mg, 94% yield, white solid).

### 10. General procedure for the synthesis of compound 7[5]




**4aa**
>20:1 dr, 97% ee

**7**
58%, >20:1 dr, 97% ee

Under air atmosphere, **4aa** (67.2 mg, 0.1 mmol) and NBS (53.1 mg, 0.3 mmol) in acetone (1.0 mL) was stirred under room temperature for 5 min. At the end of the reaction, the solvent was removed in vacuo. The residue was purified by flash chromatography eluting with hexane/ethyl acetate (95/5) to give the product **4** (36.0 mg, 58% yield, white solid).

## 11. General procedure for the synthesis of compound 8[6]


**4pa**, >20:1 dr, 96% ee

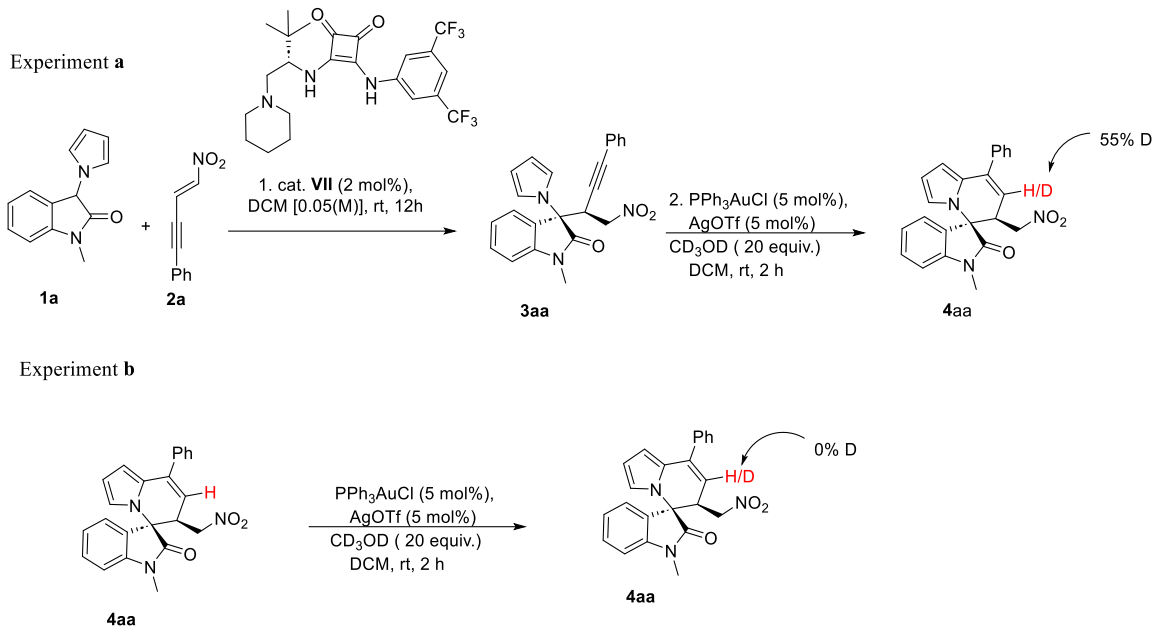
**8**
64%, >20:1 dr, 96% ee

To a round bottom flask 10 ml **4pa** (0.1 mmol), $Pd(OAc)_2$ (5 mol%), $PCy_3$ (5 mol%), 4-methoxy phenyl boronic acid and $Na_2CO_3$ (0.2 mmol) were added under nitrogen atomosphere. Then 0.5 ml DMF was added to the reaction mixture and the reaction mixture was stirred at room temperature for overnight. Next $H_2O$ was added to the mixture and the mixture was extracted with ethyl acetate. Then the combined organic layers were again washed with $H_2O$ twice and the organic layer was dried over $Na_2SO_4$ and concentrated in vacuo and the crude product was purified by flash chromatography eluting with hexane/ethyl acetate (85/15) to give the product **4** (31.4 mg, 64% yield, white sticky solid).

## 12. Control experiments:

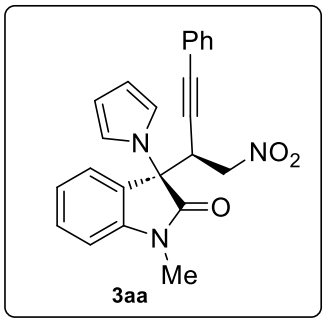
Here we have performed D-exchange experiment with $d^4$-MeOH. In experiment **a**, the Michael adduct **3aa** was treated with $PPh_3AuCl$/ AgOTf (5 mol%) and 20 equivalent $d^4$-MeOH and after 2 hours the final product **4aa** was isolated. We found that the olefinic proton of the 6-membered ring was deuterated by 55% and also the protons of pyrrole ring were deuterated to some extent.

After that we put a reaction with the product **4aa** under the same condition (experiment **b**) and found that no deuteration of the olefinic proton of the 6-membered ring was observed and again the pyrrole ring proton was deuterated to some extent.




## 13. Characterisation of the products:

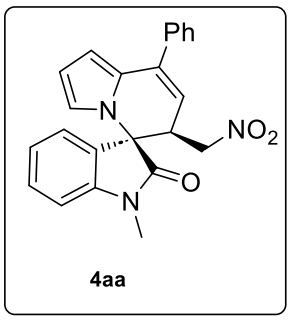
### (R)-1-methyl-3-((S)-1-nitro-4-phenylbut-3-yn-2-yl)-3-(1H-pyrrol-1-yl)indolin-2-one (3aa)




White solid (36.5 mg, combined yield: 95%); $R_f$ = 0.50 in 1:9 ethyl acetate/hexane; **Crude diastereomeric ratio**: 6:1; **$^1$H NMR (600 MHz, Chloroform-*d*)** δ 7.52 (td, *J* = 7.8, 1.2 Hz, 1H), 7.47 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.28 – 7.23 (m, 2H), 7.20 (dd, *J* = 8.4, 7.0 Hz, 2H), 7.08 – 7.01 (m, 4H), 6.98 (d, *J* = 7.9 Hz, 1H), 6.25 (t, *J* = 2.2 Hz, 2H), 4.75 – 4.66 (m, 2H), 4.46 (dd, *J* = 11.8, 2.3 Hz, 1H), 3.21 (s, 3H). **$^{13}$C NMR (151 MHz, CDCl$_3$)** δ 172.46, 144.88, 131.82, 131.28, 128.95, 128.34, 126.19, 124.30, 123.21, 121.58, 119.34, 110.36, 109.37, 86.13, 81.61, 74.72, 66.67, 39.50, 26.78.

**ESI HRMS**: calcd. for $C_{23}H_{19}N_3O_3$ $[M+H]^+$ 386.1499, found 386.1505.
**HPLC Analysis**: *ee* = 97%, Chiralpak ID Column, n-Hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 220 nm ($t_{major}$ = 18.3 min, $t_{minor}$ = 24.6 min).

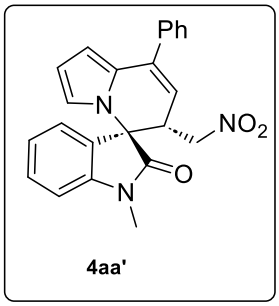
### (3R,6'S)-1-methyl-6'-(nitromethyl)-8'-phenyl-6'H-spiro[indoline-3,5'-indolizin]-2-one (4aa)




White solid (35.8 mg, combined yield: 93%); $R_f$ = 0.42 in 1:9 ethyl acetate/hexane; **Crude diastereomeric ratio**: 6:1; **$^1$H NMR (400 MHz, Chloroform-*d*)** δ 7.63 – 7.53 (m, 2H), 7.48 – 7.35 (m, 4H), 7.30 (d, *J* = 7.5 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 6.44 – 6.36 (m, 1H), 6.28 (dd, *J* = 3.8, 1.6 Hz, 1H), 6.16 (t, *J* = 3.3 Hz, 1H), 5.65 (d, *J* = 5.3 Hz, 1H), 4.82 (dd, *J* = 13.7, 5.7 Hz, 1H), 4.43 (dd, *J* = 13.7, 8.5 Hz, 1H), 3.76 (dt, *J* = 8.5, 5.5 Hz, 1H), 3.30 (s, 3H). **$^{13}$C NMR (126 MHz, CDCl$_3$)** δ 172.76, 142.42, 138.10, 136.64,

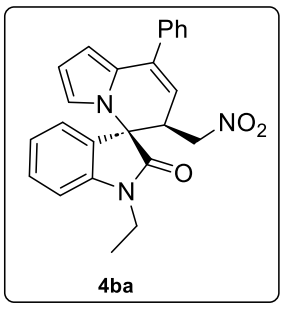
130.65, 129.23, 128.63, 128.58, 128.27, 128.04, 124.61, 123.87, 120.88, 113.04, 111.51, 110.20, 109.10, 74.69, 63.76, 41.58, 26.81.
**ESI HRMS**: calcd. for $C_{23}H_{19}N_3O_3$ $[M+H]^+$ 386.1499, found 386.1506.
**HPLC Analysis**: *ee* = 97%, Chiralpak ID Column, n-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm ($t_{major}$ = 15.5 min, $t_{minor}$ = 17.5 min).

**(3R,6'R)-1-methyl-6'-(nitromethyl)-8'-phenyl-6'H-spiro[indoline-3,5'-indolizin]-2-one (4aa′)**



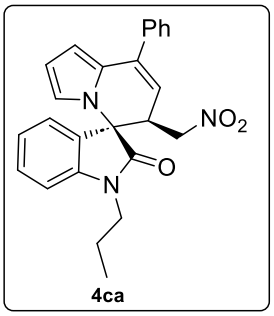

**$^1$H NMR (600 MHz, Chloroform-*d*)** δ 7.61 – 7.57 (m, 2H), 7.47 – 7.40 (m, 3H), 7.36 (td, *J* = 7.8, 1.2 Hz, 1H), 7.16 (dd, *J* = 7.5, 1.3 Hz, 1H), 6.99 (td, *J* = 7.6, 0.9 Hz, 1H), 6.95 (d, *J* = 7.9 Hz, 1H), 6.44 (dd, *J* = 3.0, 1.5 Hz, 1H), 6.28 (dd, *J* = 3.7, 1.4 Hz, 1H), 6.15 (t, *J* = 3.3 Hz, 1H), 5.58 (d, *J* = 2.8 Hz, 1H), 4.23 (ddd, *J* = 9.8, 4.8, 2.8 Hz, 1H), 4.14 (dd, *J* = 12.8, 4.8 Hz, 1H), 4.07 (dd, *J* = 12.8, 9.7 Hz, 1H), 3.37 (s, 3H). **$^{13}$C NMR (151 MHz, $CDCl_3$)** δ 173.64, 141.84, 138.00, 135.98, 130.74, 129.39, 128.67, 128.59, 128.15, 125.57, 124.77, 123.93, 120.44, 113.53, 111.08, 110.35, 109.44, 75.07, 64.99, 41.95, 27.08.
**ESI HRMS**: calcd. for $C_{23}H_{19}N_3O_3$ $[M+H]^+$ 386.1499, found 386.1506.

**(3R,6'S)-1-ethyl-6'-(nitromethyl)-8'-phenyl-6'H-spiro[indoline-3,5'-indolizin]-2-one (4ba)**




White solid (35.9 mg, combined yield: 90%); $R_f$ = 0.44 in 1:9 ethyl acetate/hexane; **Crude diastereomeric ratio**: 3.6:1; **$^1$H NMR (400 MHz, Chloroform-*d*)** δ 7.62 – 7.53 (m, 2H), 7.48 – 7.35 (m, 4H), 7.31 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.04 (td, *J* = 7.6, 1.0 Hz, 1H), 6.95 (d, *J* = 7.8 Hz, 1H), 6.39 (dd, *J* = 2.9, 1.5 Hz, 1H), 6.28 (dd, *J* = 3.7, 1.5 Hz, 1H), 6.15 (dd, *J* = 3.7, 2.8 Hz, 1H), 5.64 (d, *J* = 5.2 Hz, 1H), 4.81 (dd, *J* = 13.8, 6.0 Hz, 1H), 4.41 (dd, *J* = 13.8, 8.0 Hz, 1H), 3.88 (dd, *J* = 14.2, 7.2 Hz, 1H), 3.79 (dtd, *J* = 12.5, 7.1, 6.3, 3.5 Hz, 2H), 1.34 (t, *J* = 7.2 Hz, 3H). **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 172.36, 141.49, 138.07, 136.57, 130.58, 129.17, 128.61, 128.56, 128.27, 128.23, 124.78, 123.65, 120.78, 113.00, 111.41, 110.17, 109.21, 74.37, 63.54, 41.50, 35.38, 12.74.
**ESI HRMS**: calcd. for $C_{24}H_{21}N_3O_3$ $[M+H]^+$ 400.1656, found 400.1676.
**HPLC Analysis**: *ee* = 97%, Chiralpak IE Column, n-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm ($t_{major}$ = 12.5 min, $t_{minor}$ = 16.7 min).

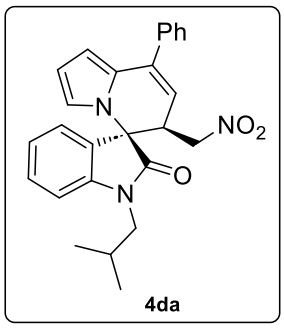
**(3R,6'S)-6'-(nitromethyl)-8'-phenyl-1-propyl-6'H-spiro[indoline-3,5'-indolizin]-2-one (4ca)**




White solid (37.9 mg, combined yield: 92%); $R_f$ = 0.46 in 1:9 ethyl acetate/hexane; **Crude diastereomeric ratio**: 3.4:1; **$^1$H NMR (600 MHz, Chloroform-*d*)** δ 7.62 – 7.54 (m, 2H), 7.48 – 7.39 (m, 3H), 7.37 (td, *J* = 7.8, 1.3 Hz, 1H), 7.31 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.03 (td, *J* = 7.6, 0.9 Hz, 1H), 6.94 (d, *J* = 7.9 Hz, 1H), 6.39 (dd, *J* = 2.9, 1.5 Hz, 1H), 6.28 (dd, *J* = 3.7, 1.5 Hz, 1H), 6.16 (t, *J* = 3.3 Hz, 1H), 5.65 (d, *J* = 5.2 Hz, 1H), 4.81 (dd, *J* = 13.7, 5.8 Hz, 1H), 4.42 (dd, *J* = 13.7, 8.3 Hz, 1H), 3.78 (dtd, *J* = 14.2, 7.2, 4.6 Hz, 2H), 3.71 (dt, *J* = 14.2, 7.4 Hz, 1H), 1.78 (h, *J* = 7.3 Hz, 2H), 1.01 (t, *J* = 7.4 Hz, 3H).**$^{13}$C NMR (151 MHz, $CDCl_3$)** δ 172.72, 141.97, 138.13, 136.62, 130.58, 129.26, 128.64, 128.58,

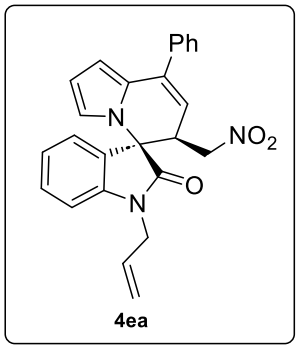
128.28, 128.18, 124.79, 123.65, 120.82, 113.08, 111.49, 110.22, 109.39, 74.63, 63.63, 42.23, 41.61, 20.86, 11.56.
**ESI HRMS**: calcd. for $C_{25}H_{23}N_3O_3$ $[M+H]^+$ 414.1812, found 414.1836.
**HPLC Analysis**: *ee* = 97%, Chiralpak IE Column, n-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm ($t_{major}$ = 11.0 min, $t_{minor}$ = 15.3 min).

**(3R,6'S)-1-isobutyl-6'-(nitromethyl)-8'-phenyl-6'H-spiro[indoline-3,5'-indolizin]-2-one (4da)**



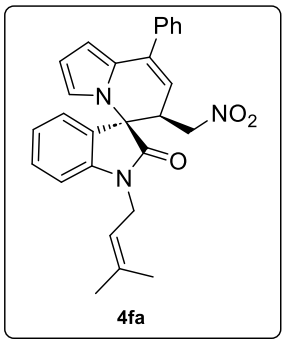

White solid (38.4 mg, combined yield: 90%); $R_f$ = 0.47 in 1:9 ethyl acetate/hexane; **Crude diastereomeric ratio**: 3.4:1; **$^1$H NMR (500 MHz, Chloroform-*d*)** δ 7.62 – 7.53 (m, 2H), 7.47 – 7.39 (m, 3H), 7.36 (td, *J* = 7.8, 1.3 Hz, 1H), 7.31 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.03 (td, *J* = 7.6, 0.9 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 6.40 (dd, *J* = 2.8, 1.5 Hz, 1H), 6.29 (dd, *J* = 3.7, 1.5 Hz, 1H), 6.16 (t, *J* = 3.3 Hz, 1H), 5.66 (d, *J* = 5.2 Hz, 1H), 4.81 (dd, *J* = 13.5, 5.6 Hz, 1H), 4.44 (dd, *J* = 13.5, 8.6 Hz, 1H), 3.77 (dt, *J* = 8.6, 5.4 Hz, 1H), 3.66 – 3.51 (m, 2H), 2.21 (tt, *J* = 14.3, 7.1 Hz, 1H), 1.01 (t, *J* = 6.6 Hz, 6H).
**$^{13}$C NMR (151 MHz, $CDCl_3$)** δ 172.97, 142.31, 138.12, 136.63, 130.54, 129.27, 128.64, 128.59, 128.29, 128.05, 124.77, 123.64, 120.82, 113.12, 111.53, 110.23, 109.65, 74.81, 63.63, 48.15, 41.67, 27.16, 20.42.
**ESI HRMS**: calcd. for $C_{26}H_{25}N_3O_3$ $[M+H]^+$ 428.1969, found 428.1966.
**HPLC Analysis**: *ee* = 97%, Chiralpak IE Column, n-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm ($t_{major}$ = 9.1 min, $t_{minor}$ = 12.3 min).

**(3R,6'S)-1-allyl-6'-(nitromethyl)-8'-phenyl-6'H-spiro[indoline-3,5'-indolizin]-2-one (4ea)**




White solid (38.6 mg, combined yield: 94%); $R_f$ = 0.45 in 1:9 ethyl acetate/hexane; **Crude diastereomeric ratio**: 6:1; **$^1$H NMR (600 MHz, Chloroform-*d*)** δ 7.60 – 7.54 (m, 2H), 7.45 – 7.39 (m, 3H), 7.38 – 7.30 (m, 2H), 7.05 (td, *J* = 7.6, 1.0 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 6.39 (dd, *J* = 2.9, 1.5 Hz, 1H), 6.29 (dd, *J* = 3.7, 1.5 Hz, 1H), 6.18 – 6.15 (m, 1H), 5.88 (ddt, *J* = 16.2, 10.6, 5.4 Hz, 1H), 5.65 (d, *J* = 5.1 Hz, 1H), 5.31 (d, *J* = 1.6 Hz, 1H), 5.29 (dq, *J* = 7.4, 1.3 Hz, 1H), 4.80 (dd, *J* = 13.7, 5.8 Hz, 1H), 4.47 – 4.34 (m, 3H), 3.82 (dt, *J* = 8.3, 5.5 Hz, 1H). **$^{13}$C NMR (151 MHz, $CDCl_3$)** δ 172.50, 141.68, 138.10, 136.64, 130.78, 130.58, 129.31, 128.65, 128.60, 128.28, 127.99, 124.72, 123.86, 120.81, 118.58, 113.03, 111.55, 110.31, 110.01, 74.55, 63.67, 42.87, 41.70.
**ESI HRMS**: calcd. for $C_{25}H_{21}N_3O_3$ $[M+H]^+$ 412.1656, found 412.1663.
**HPLC Analysis**: *ee* = 98%, Chiralpak ID Column, n-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm ($t_{major}$ = 12.3 min, $t_{minor}$ = 14.8 min).

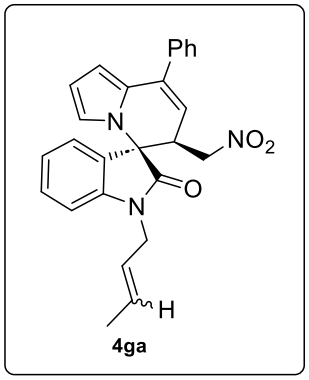
**(3R,6'S)-1-(3-methylbut-2-en-1-yl)-6'-(nitromethyl)-8'-phenyl-6'H-spiro[indoline-3,5'-indolizin]-2-one (4fa)**



4fa

White solid (39.0 mg, combined yield: 89%); $R_f$ = 0.47 in 1:9 ethyl acetate/hexane; **Crude diastereomeric ratio**: 6:1; **$^1$H NMR (400 MHz, Chloroform-*d*)** δ 7.60 – 7.55 (m, 2H), 7.47 – 7.40 (m, 3H), 7.38 – 7.29 (m, 2H), 7.04 (td, *J* = 7.6, 1.0 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 6.39 (dd, *J* = 2.9, 1.5 Hz, 1H), 6.28 (dd, *J* = 3.6, 1.5 Hz, 1H), 6.16 (dd, *J* = 3.7, 2.9 Hz, 1H), 5.64 (d, *J* = 5.2 Hz, 1H), 5.20 (ddt, *J* = 6.7, 5.0, 1.4 Hz, 1H), 4.79 (dd, *J* = 13.7, 5.6 Hz, 1H), 4.48 – 4.39 (m, 2H), 4.32 (dd, *J* = 15.5, 6.8 Hz, 1H), 3.79 (dt, *J* = 8.5, 5.4 Hz, 1H), 1.85 (s, 3H), 1.77 (s, 3H).
**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 172.24, 141.85, 138.11, 138.03, 136.54, 130.54, 129.22, 128.62, 128.56, 128.27, 128.12, 124.63, 123.67, 120.82, 117.56, 113.06, 111.43, 110.15, 109.79, 74.60, 63.67, 41.60, 38.69, 25.83, 18.42.
**ESI HRMS**: calcd. for $C_{27}H_{25}N_3O_3$ $[M+H]^+$ 440.1969, found 440.1976.
**HPLC Analysis**: *ee* = 98%, Chiralpak IE Column, n-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm ($t_{major}$ = 10.5 min, $t_{minor}$ = 14.5 min).

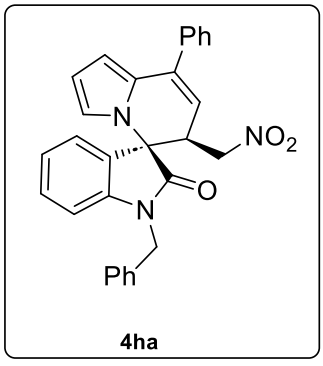
**(3R,6'S)-1-((E)-but-2-en-1-yl)-6'-(nitromethyl)-8'-phenyl-6'H-spiro[indoline-3,5'-indolizin]-2-one (4ga)**



4ga

White solid (37.4 mg, combined yield: 88%); $R_f$ = 0.47 in 1:9 ethyl acetate/hexane; **Crude diastereomeric ratio**: 5:1; **$^1$H NMR (500 MHz, Chloroform-*d*)** δ 7.57 (d, *J* = 7.1 Hz, 3H), 7.43 (q, *J* = 6.7 Hz, 4H), 7.38 – 7.28 (m, 3H), 7.04 (q, *J* = 7.6, 6.3 Hz, 1H), 6.93 (dd, *J* = 17.6, 7.9 Hz, 1H), 6.39 (d, *J* = 6.7 Hz, 1H), 6.28 (d, *J* = 3.7 Hz, 1H), 6.16 (d, *J* = 4.3 Hz, 1H), 5.86 – 5.74 (m, 1H), 5.65 (d, *J* = 4.9 Hz, 1H), 5.51 (dd, *J* = 14.6, 7.1 Hz, 1H), 4.79 (dt, *J* = 10.3, 5.3 Hz, 1H), 4.50 – 4.21 (m, 4H), 3.80 (dt, *J* = 8.9, 5.3 Hz, 1H), 1.86 (d, *J* = 7.0 Hz, 1H), 1.73 (d, *J* = 6.6 Hz, 3H).
**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 172.35, 141.79, 138.09, 136.57, 130.52, 129.63, 129.23, 128.62, 128.57, 128.26, 128.03, 124.63, 123.70, 123.59, 120.82, 113.04, 111.46, 110.19, 110.00, 74.53, 63.59, 42.34, 41.61, 17.87.
**ESI HRMS**: calcd. for $C_{26}H_{23}N_3O_3$ $[M+H]^+$ 426.1812, found 426.1830.
**HPLC Analysis**: *ee* = >99%, Chiralpak ID Column, n-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm ($t_{major}$ = 11.6 min, $t_{minor}$ = 20.0 min).

**(3R,6'S)-1-benzyl-6'-(nitromethyl)-8'-phenyl-6'H-spiro[indoline-3,5'-indolizin]-2-one (4ha)**

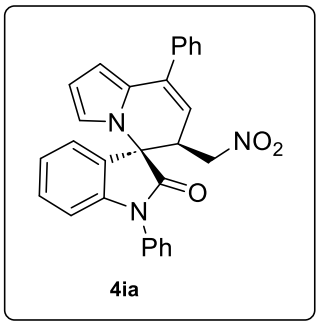


4ha

White solid (40.5 mg, combined yield: 88%); $R_f$ = 0.48 in 1:9 ethyl acetate/hexane; **Crude diastereomeric ratio**: 6:1; **$^1$H NMR (500 MHz, Chloroform-*d*)** δ 7.58 (d, *J* = 7.0 Hz, 2H), 7.43 (q, *J* = 7.2, 6.6 Hz, 3H), 7.31 (ddd, *J* = 32.3, 16.3, 9.0 Hz, 7H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 7.9 Hz, 1H), 6.44 – 6.37 (m, 1H), 6.30 (d, *J* = 3.7 Hz, 1H), 6.18 (t, *J* = 3.3 Hz, 1H), 5.66 (d, *J* = 5.1 Hz, 1H), 4.97 (s, 2H), 4.78 (dd, *J* = 13.7, 5.6 Hz, 1H), 4.44 (dd, *J* = 13.7, 8.5 Hz, 1H), 3.85 (dt, *J* = 8.6, 5.4 Hz, 1H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 172.89, 141.75, 138.10, 136.60, 135.18, 130.62, 129.39, 129.21,

128.65, 128.60, 128.29, 128.24, 127.96, 127.52, 124.76, 123.95, 120.80, 113.10, 111.60, 110.37, 110.18, 74.63, 63.75, 44.45, 41.80.
**ESI HRMS**: calcd. for $C_{29}H_{23}N_3O_3$ $[M+H]^+$ 462.1812, found 462.1831.
**HPLC Analysis**: *ee* = 98%, Chiralpak ID Column, n-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm ($t_{major}$ = 16.1 min, $t_{minor}$ = 21.4 min).

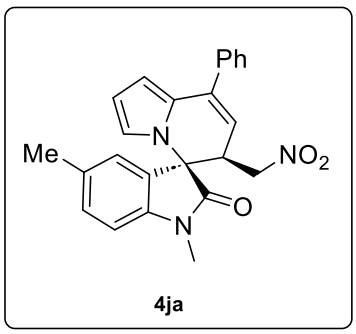
**(3R,6'S)-6'-(nitromethyl)-1,8'-diphenyl-6'H-spiro[indoline-3,5'-indolizin]-2-one (4ia)**



4ia

White solid (39.3 mg, combined yield: 88%); $R_f$ = 0.44 in 1:9 ethyl acetate/hexane; **Crude diastereomeric ratio**: 3.5:1; **$^1$H NMR (500 MHz, Chloroform-*d*)** δ 7.58 (p, *J* = 9.1, 7.5 Hz, 4H), 7.50 – 7.36 (m, 7H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 6.53 (s, 1H), 6.31 (d, *J* = 3.7 Hz, 1H), 6.20 (d, *J* = 3.4 Hz, 1H), 5.66 (d, *J* = 5.2 Hz, 1H), 4.90 (dd, *J* = 14.0, 6.3 Hz, 1H), 4.48 (dd, *J* = 14.0, 7.5 Hz, 1H), 3.96 (q, *J* = 6.4 Hz, 1H). **$^{13}$C NMR (126 MHz, CDCl$_3$)** δ 172.25, 142.56, 138.04, 136.66, 133.52, 130.57, 130.00, 129.28, 128.90, 128.63, 128.59, 128.25, 127.75, 126.69, 124.87, 124.29, 120.94, 112.86, 111.61, 110.44, 110.40, 74.28, 63.76, 41.90.
**ESI HRMS**: calcd. for $C_{28}H_{21}N_3O_3$ $[M+H]^+$ 448.1656, found 448.1673.
**HPLC Analysis**: *ee* = 95%, Chiralpak IE Column, n-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm ($t_{major}$ = 20.5 min, $t_{minor}$ = 25.7 min).

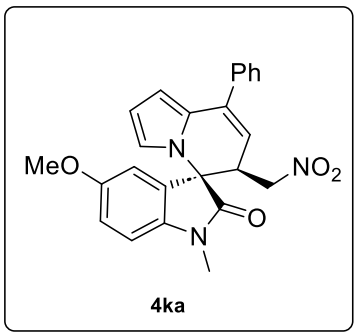
**(3R,6'S)-1,5-dimethyl-6'-(nitromethyl)-8'-phenyl-6'H-spiro[indoline-3,5'-indolizin]-2-one (4ja)**



4ja

White solid (36.7 mg, combined yield: 92%); $R_f$ = 0.46 in 1:9 ethyl acetate/hexane; **Crude diastereomeric ratio**: 4.6:1; **$^1$H NMR (400 MHz, Chloroform-*d*)** δ 7.60 – 7.54 (m, 2H), 7.47 – 7.39 (m, 3H), 7.19 (ddd, *J* = 7.9, 1.7, 0.8 Hz, 1H), 7.12 (d, *J* = 1.7 Hz, 1H), 6.83 (d, *J* = 7.9 Hz, 1H), 6.38 (dd, *J* = 2.8, 1.5 Hz, 1H), 6.28 (dd, *J* = 3.7, 1.5 Hz, 1H), 6.16 (dd, *J* = 3.7, 2.9 Hz, 1H), 5.63 (d, *J* = 5.0 Hz, 1H), 4.75 (dd, *J* = 13.5, 5.5 Hz, 1H), 4.43 (dd, *J* = 13.5, 8.8 Hz, 1H), 3.78 (dt, *J* = 8.8, 5.3 Hz, 1H), 3.27 (s, 3H), 2.28 (s, 3H). **$^{13}$C NMR (101 MHz, CDCl$_3$)** δ 172.59, 140.12, 138.20, 136.46, 133.67, 130.96, 129.35, 128.63, 128.52, 128.27, 127.92, 125.30, 120.84, 113.12, 111.34, 110.12, 108.88, 74.76, 63.82, 41.63, 26.80, 21.36.
**ESI HRMS**: calcd. for $C_{24}H_{21}N_3O_3$ $[M+H]^+$ 400.1656, found 400.1656.
**HPLC Analysis**: *ee* = 96%, Chiralpak IE Column, n-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm ($t_{major}$ = 15.9 min, $t_{minor}$ = 19.8 min).

**(3R,6'S)-5-methoxy-1-methyl-6'-(nitromethyl)-8'-phenyl-6'H-spiro[indoline-3,5'-indolizin]-2-one (4ka)**



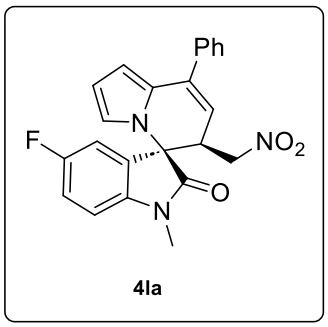
4ka

White solid (38.1 mg, combined yield: 92%); $R_f$ = 0.34 in 1:9 ethyl acetate/hexane; **Crude diastereomeric ratio**: 4.1:1; **$^1$H NMR (500 MHz, Chloroform-*d*)** δ 7.60 – 7.51 (m, 2H), 7.47 – 7.37 (m, 3H), 6.95 – 6.87 (m, 2H), 6.84 (d, *J* = 8.5 Hz, 1H), 6.41 (dd, *J* = 2.9, 1.5 Hz, 1H), 6.28 (dd, *J* = 3.7, 1.5 Hz, 1H), 6.16 (t, *J* = 3.3 Hz, 1H), 5.64 (d, *J* = 5.2 Hz, 1H), 4.83 (dd, *J* = 13.7, 5.6 Hz, 1H), 4.43 (dd, *J* = 13.6, 8.6 Hz, 1H), 3.75 (dt, *J* = 8.6, 5.4 Hz, 1H), 3.71 (s, 3H), 3.27 (s, 3H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 172.40, 156.66, 138.10, 136.60, 135.59, 129.16, 129.15, 128.63, 128.55, 128.22, 120.95, 114.89, 113.00, 111.85, 111.52, 110.23, 109.60, 74.71, 64.00, 55.86, 41.51, 26.87.

**ESI HRMS**: calcd. for $C_{24}H_{21}N_3O_4$ $[M+H]^+$ 416.1605, found 416.1594.

**HPLC Analysis**: *ee* = 98%, Chiralpak IE Column, n-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm ($t_{major}$ = 21.0 min, $t_{minor}$ = 27.2 min).

**(3R,6'S)-5-fluoro-1-methyl-6'-(nitromethyl)-8'-phenyl-6'H-spiro[indoline-3,5'-indolizin]-2-one (4la)**



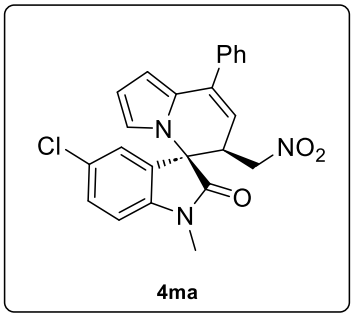
4la

White solid (36.2 mg, combined yield: 90%); $R_f$ = 0.41 in 1:9 ethyl acetate/hexane; **Crude diastereomeric ratio**: 4.9:1; **$^1$H NMR (400 MHz, Chloroform-*d*)** δ 7.61 – 7.53 (m, 2H), 7.50 – 7.41 (m, 3H), 7.08 (td, *J* = 8.7, 2.6 Hz, 1H), 7.02 (dd, *J* = 7.7, 2.6 Hz, 1H), 6.88 (dd, *J* = 8.5, 4.0 Hz, 1H), 6.44 (dd, *J* = 2.9, 1.5 Hz, 1H), 6.31 (dd, *J* = 3.7, 1.5 Hz, 1H), 6.19 (dd, *J* = 3.7, 2.9 Hz, 1H), 5.67 (d, *J* = 5.7 Hz, 1H), 4.96 (dd, *J* = 13.9, 6.1 Hz, 1H), 4.42 (dd, *J* = 14.0, 8.0 Hz, 1H), 3.68 (dt, *J* = 8.0, 5.9 Hz, 1H), 3.32 (s, 3H). **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 172.72, 160.64, 158.22, 137.99 (d, $J_{C-F}$ = 3.03 Hz), 137.80 (d, $J_{C-F}$ = 87.87 Hz), 129.75 (d, $J_{C-F}$ = 8.08 Hz), 128.78, 128.76, 128.74, 128.22, 121.04, 117.00 (d, $J_{C-F}$ = 23.23 Hz), 113.03 (d, $J_{C-F}$ = 25.25 Hz), 112.60, 111.91, 110.50, 109.89 (d, $J_{C-F}$ = 8.08 Hz), 74.39, 63.80 (d, $J_{C-F}$ = 2.02 Hz), 41.12, 27.06. **$^{19}$F NMR (377 MHz, $CDCl_3$)** δ -117.78.

**ESI HRMS**: calcd. for $C_{23}H_{18}FN_3O_3$ $[M+H]^+$ 404.1405, found 404.1428.

**HPLC Analysis**: *ee* = 96%, Chiralpak IE Column, n-Hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 220 nm ($t_{major}$ = 21.6 min, $t_{minor}$ = 29.8 min).

**(3R,6'S)-5-chloro-1-methyl-6'-(nitromethyl)-8'-phenyl-6'H-spiro[indoline-3,5'-indolizin]-2-one (4ma)**

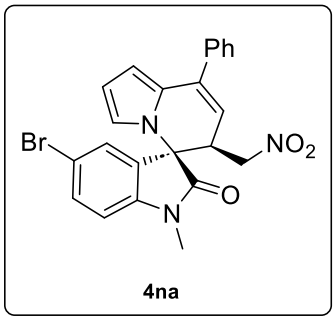


4ma

White solid (38.9 mg, combined yield: 93%); $R_f$ = 0.43 in 1:9 ethyl acetate/hexane; **Crude diastereomeric ratio**: 4.6:1; **$^1$H NMR (500 MHz, Chloroform-*d*)** δ 7.62 – 7.52 (m, 2H), 7.51 – 7.40 (m, 3H), 7.36 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.24 (d, *J* = 2.1 Hz, 1H), 6.88 (d, *J* = 8.3 Hz, 1H), 6.43 (dd, *J* = 2.9, 1.4 Hz, 1H), 6.30 (dd, *J* = 3.7, 1.4 Hz, 1H), 6.19 (t, *J* = 3.3 Hz, 1H), 5.67 (d, *J* = 5.7 Hz, 1H), 4.94 (dd, *J* = 14.0, 6.1 Hz, 1H), 4.42 (dd, *J* = 13.9, 7.9 Hz, 1H), 3.69 (dt, *J* = 7.8, 5.9 Hz, 1H), 3.31 (s, 3H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 172.59, 140.63, 137.84, 136.96, 130.50,

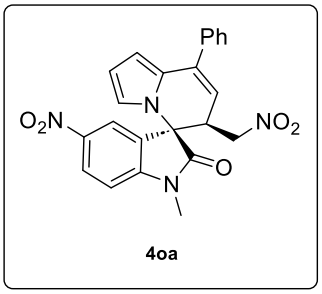
129.81, 129.17, 128.86, 128.77, 128.75, 128.24, 125.08, 121.02, 112.60, 111.93, 110.56, 110.15, 74.31, 63.65, 41.15, 27.04.
**ESI HRMS**: calcd. for $C_{23}H_{18}ClN_3O_3$ $[M+H]^+$ 420.1109, found 420.1105.
**HPLC Analysis**: *ee* = 97%, Chiralpak IE Column, n-Hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 220 nm ($t_{major}$ = 20.4 min, $t_{minor}$ = 26.3 min).

**(3R,6'S)-5-bromo-1-methyl-6'-(nitromethyl)-8'-phenyl-6'H-spiro[indoline-3,5'-indolizin]-2-one (4na)**



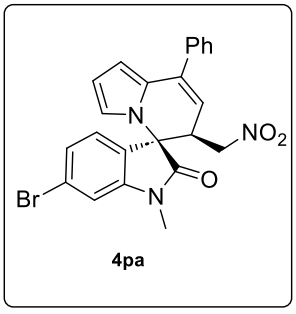

White solid (43.6 mg, combined yield: 94%); $R_f$ = 0.48 in 1:9 ethyl acetate/hexane; **Crude diastereomeric ratio**: 4.5:1; **$^1$H NMR (500 MHz, Chloroform-*d*)** δ 7.59 – 7.53 (m, 2H), 7.53 – 7.49 (m, 1H), 7.48 – 7.40 (m, 3H), 7.38 (d, *J* = 1.9 Hz, 1H), 6.83 (d, *J* = 8.3 Hz, 1H), 6.46 – 6.37 (m, 1H), 6.30 (dd, *J* = 3.5, 1.7 Hz, 1H), 6.19 (d, *J* = 3.3 Hz, 1H), 5.66 (d, *J* = 5.7 Hz, 1H), 4.93 (dd, *J* = 14.0, 6.1 Hz, 1H), 4.42 (dd, *J* = 14.0, 7.9 Hz, 1H), 3.74 – 3.64 (m, 1H), 3.31 (s, 3H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 172.47, 141.14, 137.85, 136.95, 133.42, 130.13, 128.89, 128.74, 128.23, 127.79, 121.01, 116.39, 112.60, 111.92, 110.62, 110.57, 74.27, 63.59, 41.17, 27.00.
**ESI HRMS**: calcd. for $C_{23}H_{18}BrN_3O_3$ $[M+H]^+$ 464.0604, found 464.0611.
**HPLC Analysis**: *ee* = 96%, Chiralpak IE Column, n-Hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 220 nm ($t_{major}$ = 21.3 min, $t_{minor}$ = 27.1 min).

**(3R,6'S)-1-methyl-5-nitro-6'-(nitromethyl)-8'-phenyl-6'H-spiro[indoline-3,5'-indolizin]-2-one (4oa)**




White solid (37.8 mg, combined yield: 88%); $R_f$ = 0.28 in 1:9 ethyl acetate/hexane; **Crude diastereomeric ratio**: 4.6:1; **$^1$H NMR (500 MHz, Chloroform-*d*)** δ 8.37 – 8.31 (m, 1H), 8.17 – 8.10 (m, 1H), 7.63 – 7.54 (m, 2H), 7.51 – 7.41 (m, 3H), 7.05 (dd, *J* = 8.7, 1.2 Hz, 1H), 6.44 (dt, *J* = 2.8, 1.4 Hz, 1H), 6.36 – 6.29 (m, 1H), 6.24 – 6.15 (m, 1H), 5.73 – 5.65 (m, 1H), 5.08 – 4.99 (m, 1H), 4.43 (ddd, *J* = 14.5, 6.7, 1.2 Hz, 1H), 3.70 (q, *J* = 6.5, 6.0 Hz, 1H), 3.40 (s, 3H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 173.42, 147.32, 143.97, 137.50, 129.08, 128.92, 128.84, 128.16, 127.28, 121.06, 120.33, 112.51, 112.17, 111.07, 109.00, 73.64, 63.23, 40.94, 27.40.
**ESI HRMS**: calcd. for $C_{23}H_{18}N_4O_5$ $[M+H]^+$ 431.1350, found 431.1373.
**HPLC Analysis**: *ee* = 94%, Chiralpak ADH Column, n-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm ($t_{major}$ = 26.9 min, $t_{minor}$ = 35.7 min).

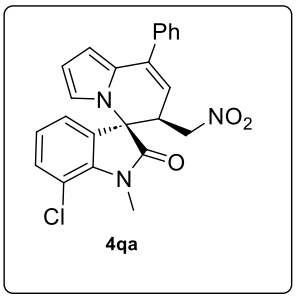
**(3R,6'S)-6-bromo-1-methyl-6'-(nitromethyl)-8'-phenyl-6'H-spiro[indoline-3,5'-indolizin]-2-one (4pa)**




White solid (42.6 mg, combined yield: 92%); $R_f$ = 0.48 in 1:9 ethyl acetate/hexane; **Crude diastereomeric ratio**: 4.7:1; **$^1$H NMR (400 MHz, Chloroform-*d*)** δ 7.55 (dd, *J* = 7.1, 2.6 Hz, 2H), 7.48 – 7.40 (m, 3H), 7.19 – 7.07 (m, 3H), 6.40 (dd, *J* = 2.9, 1.5 Hz, 1H), 6.29 (dd, *J* = 3.7, 1.5 Hz, 1H), 6.17 (dd, *J* = 3.7, 2.8 Hz, 1H), 5.65 (d, *J* = 5.5 Hz, 1H), 4.88 (dd, *J* = 13.9, 6.0 Hz, 1H), 4.41 (dd, *J* = 13.9, 8.1 Hz, 1H), 3.70 (dt, *J* = 8.0, 5.8 Hz, 1H), 3.30 (s, 3H). **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 172.73, 143.51, 137.83, 136.83, 128.92, 128.74, 128.71, 128.20, 127.00, 126.64, 125.83, 124.39, 120.90, 112.73, 112.67,

111.83, 110.49, 74.32, 63.44, 41.23, 26.99. **ESI HRMS**: calcd. for $C_{23}H_{18}BrN_3O_3$ $[M+H]^+$ 464.0604, found 464.0610.
**HPLC Analysis**: *ee* = 96%, Chiralpak IE Column, n-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm ($t_{major}$ = 12.1 min, $t_{minor}$ = 15.1 min).

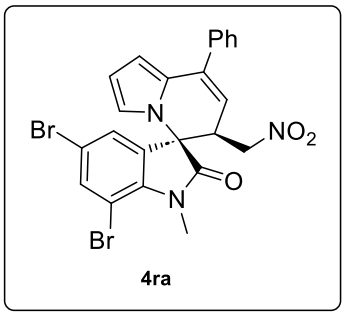
**(3R,6'S)-7-chloro-1-methyl-6'-(nitromethyl)-8'-phenyl-6'H-spiro[indoline-3,5'-indolizin]-2-one (4qa)**



4qa

White solid (38.5 mg, combined yield: 92%); $R_f$ = 0.43 in 1:9 ethyl acetate/hexane; **Crude diastereomeric ratio**: 5:1; **$^1$H NMR (500 MHz, Chloroform-*d*)** δ 7.61 – 7.51 (m, 2H), 7.48 – 7.39 (m, 3H), 7.34 – 7.28 (m, 1H), 7.21 – 7.15 (m, 1H), 6.95 (t, *J* = 7.9 Hz, 1H), 6.40 (dd, *J* = 2.9, 1.5 Hz, 1H), 6.30 (dd, *J* = 3.7, 1.5 Hz, 1H), 6.18 (t, *J* = 3.3 Hz, 1H), 5.62 (d, *J* = 5.4 Hz, 1H), 4.83 (dd, *J* = 13.9, 6.0 Hz, 1H), 4.41 (dd, *J* = 13.9, 8.0 Hz, 1H), 3.72 (dt, *J* = 8.0, 5.7 Hz, 1H), 3.67 (s, 3H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 173.22, 138.22, 137.87, 136.74, 132.86, 130.76, 128.98, 128.71, 128.69, 128.22, 124.59, 123.07, 120.98, 116.47, 112.59, 111.81, 110.51, 74.43, 63.21, 41.65, 30.33.
**ESI HRMS**: calcd. for $C_{23}H_{18}ClN_3O_3$ $[M+H]^+$ 420.1109, found 420.1093.
**HPLC Analysis**: *ee* = 96%, Chiralpak ID Column, n-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm ($t_{major}$ = 10.7 min, $t_{minor}$ = 12.3 min).

**(3R,6'S)-5,7-dibromo-1-methyl-6'-(nitromethyl)-8'-phenyl-6'H-spiro[indoline-3,5'-indolizin]-2-one (4ra)**

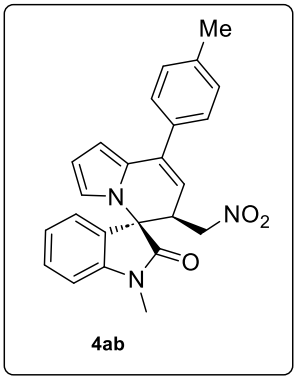


4ra

White solid (48.8 mg, combined yield: 90%); $R_f$ = 0.60 in 1:9 ethyl acetate/hexane; **Crude diastereomeric ratio**: 4.6:1; **$^1$H NMR (500 MHz, Chloroform-*d*)** δ 7.64 (q, *J* = 1.7 Hz, 1H), 7.53 (dt, *J* = 6.7, 1.9 Hz, 2H), 7.44 (d, *J* = 6.6 Hz, 3H), 7.29 (d, *J* = 2.2 Hz, 1H), 6.44 – 6.38 (m, 1H), 6.33 – 6.27 (m, 1H), 6.20 (d, *J* = 3.0 Hz, 1H), 5.62 (d, *J* = 5.8 Hz, 1H), 4.91 (dd, *J* = 14.2, 6.4 Hz, 1H), 4.39 (dd, *J* = 14.2, 7.4 Hz, 1H), 3.67 (s, 3H), 3.65 (d, *J* = 7.2 Hz, 1H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 173.17, 138.73, 138.02, 137.71, 137.05, 132.63, 128.84, 128.78, 128.19, 126.79, 121.12, 116.56, 112.24, 112.23, 110.91, 103.75, 74.10, 63.09, 41.43, 30.60.
**ESI HRMS**: calcd. for $C_{23}H_{17}Br_2N_3O_3$ $[M+H]^+$ 543.9689, found 543.9706.
**HPLC Analysis**: *ee* = 90%, Chiralpak IE Column, n-Hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 220 nm ($t_{major}$ = 12.6 min, $t_{minor}$ = 16.5 min).

**(3R,6'S)-1-methyl-6'-(nitromethyl)-8'-(p-tolyl)-6'H-spiro[indoline-3,5'-indolizin]-2-one (4ab)**

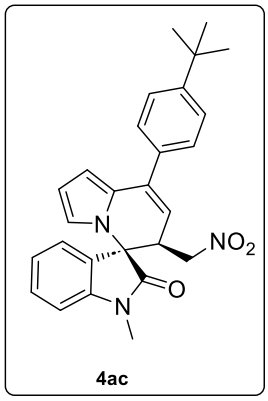
White solid (35.9 mg, combined yield: 90%); $R_f$ = 0.46 in 1:9 ethyl acetate/hexane; **Crude diastereomeric ratio**: 4.6:1; **$^1$H NMR (500 MHz, Chloroform-*d*)** δ 7.47 (d, *J* = 8.0 Hz, 2H), 7.37 (td, *J* = 7.8, 1.3 Hz, 1H), 7.32 – 7.20 (m, 3H), 7.06 – 6.98 (m, 1H), 6.93 (d, *J* = 7.9 Hz, 1H), 6.40 (dd, *J* = 2.8, 1.5 Hz, 1H), 6.29 (dd, *J* = 3.7, 1.5 Hz, 1H), 6.15 (t, *J* = 3.3 Hz, 1H), 5.62 (d, *J* = 5.4 Hz, 1H), 4.84 (dd, *J* = 13.7, 5.8 Hz, 1H), 4.41 (dd, *J* = 13.7, 8.4 Hz, 1H), 3.73 (dt, *J* = 8.3, 5.5 Hz, 1H), 3.30 (s, 3H), 2.41 (s, 3H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 172.81, 142.28, 138.47, 136.47, 135.15, 130.55, 129.30, 129.19, 128.10, 124.58, 123.79, 120.80, 112.48, 111.41, 110.09, 109.07, 74.64, 63.69, 41.43, 26.80,



4ab

21.38. **ESI HRMS**: calcd. for $C_{24}H_{21}N_3O_3$ $[M+H]^+$ 400.1656, found 400.1656.
**HPLC Analysis**: *ee* = 98%, Chiralpak IE Column, n-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm ($t_{major}$ = 16.8 min, $t_{minor}$ = 20.5 min).

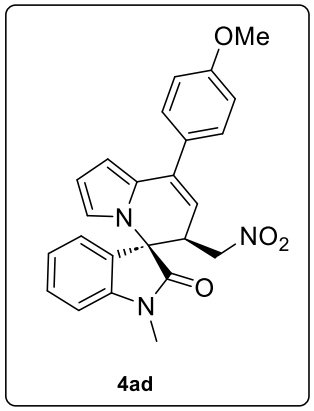
**(3R,6'S)-8'-(4-(tert-butyl)phenyl)-1-methyl-6'-(nitromethyl)-6'H-spiro[indoline-3,5'-indolizin]-2-one (4ac)**



4ac

White solid (38.8 mg, combined yield: 88%); $R_f$ = 0.48 in 1:9 ethyl acetate/hexane; **Crude diastereomeric ratio**: 5:1; **$^1$H NMR (500 MHz, Chloroform-*d*)** δ 7.56 – 7.49 (m, 2H), 7.49 – 7.42 (m, 2H), 7.37 (td, *J* = 7.8, 1.2 Hz, 1H), 7.29 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.05 – 7.00 (m, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 6.41 (dd, *J* = 2.9, 1.5 Hz, 1H), 6.33 (dd, *J* = 3.7, 1.5 Hz, 1H), 6.16 (t, *J* = 3.3 Hz, 1H), 5.65 (d, *J* = 5.4 Hz, 1H), 4.86 (dd, *J* = 13.7, 5.8 Hz, 1H), 4.41 (dd, *J* = 13.7, 8.4 Hz, 1H), 3.73 (dt, *J* = 8.3, 5.6 Hz, 1H), 3.30 (s, 3H), 1.37 (s, 9H).
**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 172.89, 151.73, 142.28, 136.47, 135.13, 130.55, 129.18, 128.20, 127.92, 125.56, 124.65, 123.81, 120.82, 112.57, 111.54, 110.12, 109.06, 74.69, 63.74, 41.48, 34.82, 31.50, 26.83.
**ESI HRMS**: calcd. for $C_{27}H_{27}N_3O_3$ $[M+H]^+$ 442.2125, found 442.2120.
**HPLC Analysis**: *ee* = 93%, Chiralpak IF Column, n-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm ($t_{major}$ = 9.2 min, $t_{minor}$ = 10.1 min).

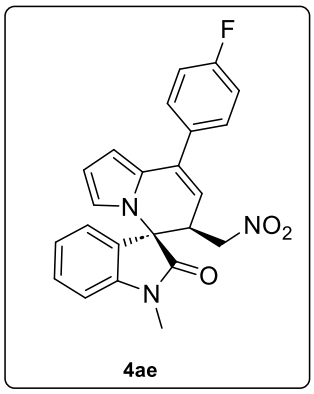
**(3R,6'S)-8'-(4-methoxyphenyl)-1-methyl-6'-(nitromethyl)-6'H-spiro[indoline-3,5'-indolizin]-2-one (4ad)**



4ad

White solid (36.9 mg, combined yield: 89%); $R_f$ = 0.40 in 1:9 ethyl acetate/hexane; **Crude diastereomeric ratio**: 4.1:1; **$^1$H NMR (400 MHz, Chloroform-*d*)** δ 7.54 – 7.47 (m, 2H), 7.38 (td, *J* = 7.6, 1.3 Hz, 1H), 7.33 – 7.26 (m, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 7.00 – 6.89 (m, 3H), 6.44 – 6.32 (m, 1H), 6.28 (dd, *J* = 3.8, 1.6 Hz, 1H), 6.15 (t, *J* = 3.3 Hz, 1H), 5.59 (d, *J* = 5.4 Hz, 1H), 4.82 (dd, *J* = 13.6, 5.7 Hz, 1H), 4.41 (dd, *J* = 13.6, 8.5 Hz, 1H), 3.86 (s, 3H), 3.72 (dt, *J* = 8.5, 5.6 Hz, 1H), 3.30 (s, 3H).
**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 172.83, 160.05, 142.36, 136.11, 130.58, 130.54, 129.40, 129.35, 128.12, 124.62, 123.82, 120.79, 114.04, 112.03, 111.40, 110.09, 109.06, 74.77, 63.74, 55.51, 41.53, 26.80.
**ESI HRMS**: calcd. for $C_{24}H_{21}N_3O_4$ $[M+H]^+$ 416.1605, found 416.1599.
**HPLC Analysis**: *ee* = 98%, Chiralpak IE Column, n-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm ($t_{major}$ = 25.0 min, $t_{minor}$ = 30.4 min).

**(3R,6'S)-8'-(4-fluorophenyl)-1-methyl-6'-(nitromethyl)-6'H-spiro[indoline-3,5'-indolizin]-2-one (4ae)**



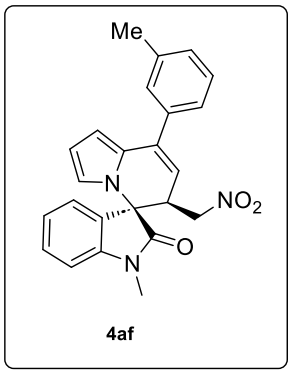

White solid (35.4 mg, combined yield: 88%); $R_f$ = 0.42 in 1:9 ethyl acetate/hexane; **Crude diastereomeric ratio**: 7:1; **$^1$H NMR (500 MHz, Chloroform-*d*)** δ 7.59 – 7.48 (m, 2H), 7.40 (td, *J* = 7.7, 1.2 Hz, 1H), 7.29 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.17 – 7.03 (m, 3H), 6.95 (d, *J* = 7.8 Hz, 1H), 6.38 (dd, *J* = 2.9, 1.5 Hz, 1H), 6.24 (dd, *J* = 3.7, 1.5 Hz, 1H), 6.15 (t, *J* = 3.3 Hz, 1H), 5.60 (d, *J* = 5.0 Hz, 1H), 4.74 (dd, *J* = 13.5, 5.5 Hz, 1H), 4.42 (dd, *J* = 13.5, 8.8 Hz, 1H), 3.78 (dt, *J* = 8.8, 5.3 Hz, 1H), 3.29 (s, 3H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 172.56, 164.03 (248.22 Hz), 142.56, 135.55, 134.10 (3.78 Hz), 130.77, 129.94 (7.56 Hz), 129.20, 127.76, 124.55, 123.93, 120.97, 115.63 (21.42 Hz), 113.05, 111.40, 110.23, 109.15, 74.68, 63.72, 41.63, 26.77.

**$^{19}$F NMR (471 MHz, $CDCl_3$)** δ -113.45.

**ESI HRMS**: calcd. for $C_{23}H_{18}FN_3O_3$ $[M+H]^+$ 404.1405, found 404.1397.

**HPLC Analysis**: *ee* = 99%, Chiralpak IE Column, n-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm ($t_{major}$ = 14.6 min, $t_{minor}$ = 18.7 min).

**(3R,6'S)-1-methyl-6'-(nitromethyl)-8'-(m-tolyl)-6'H-spiro[indoline-3,5'-indolizin]-2-one (4af)**

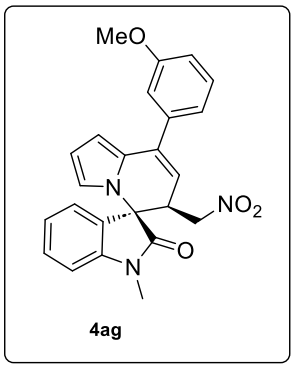



White solid (36.7 mg, combined yield: 92%); $R_f$ = 0.46 in 1:9 ethyl acetate/hexane; **Crude diastereomeric ratio**: 4.7:1; **$^1$H NMR (400 MHz, Chloroform-*d*)** δ 7.42 – 7.28 (m, 5H), 7.25 – 7.20 (m, 1H), 7.05 (td, *J* = 7.6, 1.0 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 6.39 (dd, *J* = 2.9, 1.5 Hz, 1H), 6.29 (dd, *J* = 3.7, 1.5 Hz, 1H), 6.15 (dd, *J* = 3.7, 2.9 Hz, 1H), 5.64 (d, *J* = 5.3 Hz, 1H), 4.82 (dd, *J* = 13.7, 5.7 Hz, 1H), 4.42 (dd, *J* = 13.7, 8.5 Hz, 1H), 3.75 (dt, *J* = 8.5, 5.5 Hz, 1H), 3.30 (s, 3H), 2.42 (s, 3H). **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 172.82, 142.42, 138.33, 138.06, 136.72, 130.63, 129.35, 129.33, 128.90, 128.52, 128.10, 125.38, 124.65, 123.88, 120.83, 112.86, 111.53, 110.17, 109.09, 74.72, 63.78, 41.59, 26.81, 21.60.

**ESI HRMS**: calcd. for $C_{24}H_{21}N_3O_3$ $[M+H]^+$ 400.1656, found 400.1656.

**HPLC Analysis**: *ee* = 99%, Chiralpak ID Column, n-Hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm ($t_{major}$ = 17.0 min, $t_{minor}$ = 19.9 min).

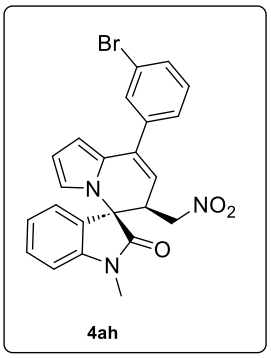
**(3R,6'S)-8'-(3-methoxyphenyl)-1-methyl-6'-(nitromethyl)-6'H-spiro[indoline-3,5'-indolizin]-2-one (4ag)**




White solid (39.0 mg, combined yield: 94%); $R_f$ = 0.39 in 1:9 ethyl acetate/hexane; **Crude diastereomeric ratio**: 4.2:1; **$^1$H NMR (500 MHz, Chloroform-*d*)** δ 7.42 – 7.27 (m, 3H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.11 (t, *J* = 2.1 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.99 – 6.89 (m, 2H), 6.42 – 6.35 (m, 1H), 6.34 – 6.29 (m, 1H), 6.15 (t, *J* = 3.3 Hz, 1H), 5.66 (d, *J* = 5.2 Hz, 1H), 4.80 (dd, *J* = 13.7, 5.7 Hz, 1H), 4.41 (dd, *J* = 13.7, 8.4 Hz, 1H), 3.85 (s, 3H), 3.76 (dt, *J* = 8.4, 5.5 Hz, 1H), 3.29 (s, 3H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 172.74, 159.83, 142.46, 139.51, 136.47, 130.66, 129.65, 129.15, 128.04, 124.62, 123.89, 120.90, 120.76, 114.17, 113.88, 113.09, 111.54, 110.23, 109.09, 74.65, 63.74,

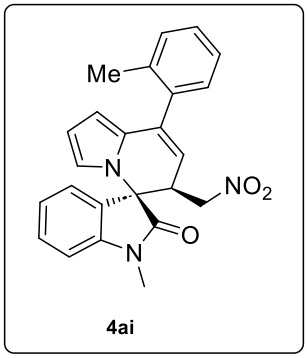
55.52, 41.60, 26.79. **ESI HRMS**: calcd. for $C_{24}H_{21}N_3O_4$ $[M+H]^+$ 416.1605, found 416.1602. **HPLC Analysis**: *ee* = 98%, Chiralpak IE Column, n-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm ($t_{major}$ = 20.4 min, $t_{minor}$ = 29.2 min).

**(3R,6'S)-8'-(3-bromophenyl)-1-methyl-6'-(nitromethyl)-6'H-spiro[indoline-3,5'-indolizin]-2-one (4ah)**



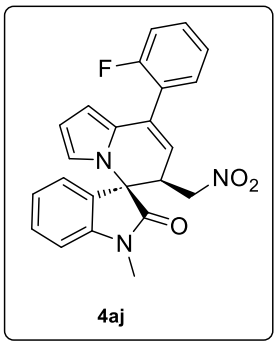

White solid (43.1 mg, combined yield: 93%); $R_f$ = 0.49 in 1:9 ethyl acetate/hexane; **Crude diastereomeric ratio**: 4.7:1; **$^1$H NMR (500 MHz, Chloroform-*d*)** δ 7.72 (s, 1H), 7.51 (dd, *J* = 22.9, 7.9 Hz, 2H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.30 (t, *J* = 8.1 Hz, 2H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.9 Hz, 1H), 6.42 – 6.33 (m, 1H), 6.26 (d, *J* = 3.7 Hz, 1H), 6.16 (t, *J* = 3.3 Hz, 1H), 5.64 (d, *J* = 5.0 Hz, 1H), 4.72 (dd, *J* = 13.7, 5.5 Hz, 1H), 4.41 (dd, *J* = 13.6, 8.7 Hz, 1H), 3.81 (dt, *J* = 9.8, 5.2 Hz, 1H), 3.28 (s, 3H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 172.48, 142.65, 140.15, 135.28, 131.60, 131.14, 130.85, 130.20, 128.86, 127.65, 126.96, 124.57, 124.01, 122.69, 121.10, 113.87, 111.49, 110.36, 109.18, 74.56, 63.70, 41.71, 26.78.
**ESI HRMS**: calcd. for $C_{23}H_{18}BrN_3O_3$ $[M+H]^+$ 464.0604, found 464.0582.
**HPLC Analysis**: *ee* = 98%, Chiralpak IE Column, n-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm ($t_{major}$ = 13.8 min, $t_{minor}$ = 19.1 min).

**(3R,6'S)-1-methyl-6'-(nitromethyl)-8'-(o-tolyl)-6'H-spiro[indoline-3,5'-indolizin]-2-one (4ai)**



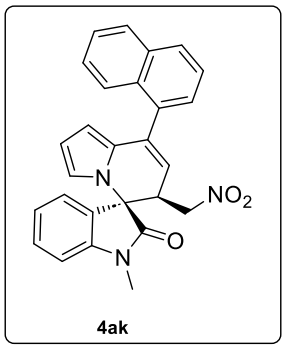

White solid (36.7 mg, combined yield: 92%); $R_f$ = 0.47 in 1:9 ethyl acetate/hexane; **Crude diastereomeric ratio**: 4.7:1; $^1$H NMR (500 MHz, Chloroform-*d*) δ 7.50 – 7.40 (m, 2H), 7.33 – 7.21 (m, 4H), 7.16 (t, *J* = 7.6 Hz, 1H), 6.95 (d, *J* = 7.9 Hz, 1H), 6.29 – 6.22 (m, 1H), 6.08 (t, *J* = 3.4 Hz, 1H), 5.90 (d, *J* = 3.6 Hz, 1H), 5.44 (d, *J* = 4.1 Hz, 1H), 4.56 (dd, *J* = 13.4, 5.6 Hz, 1H), 4.46 (dd, *J* = 13.4, 8.7 Hz, 1H), 3.94 (dt, *J* = 9.3, 4.8 Hz, 1H), 3.26 (s, 3H), 2.39 (s, 3H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 172.48, 143.17, 137.61, 136.81, 135.67, 130.98, 130.55, 130.43, 129.68, 128.13, 127.76, 125.68, 124.69, 124.07, 120.46, 113.91, 111.05, 110.49, 109.09, 74.88, 64.09, 42.18, 26.66, 20.11.
**ESI HRMS**: calcd. for $C_{24}H_{21}N_3O_3$ $[M+H]^+$ 400.1656, found 400.1651.
**HPLC Analysis**: *ee* = 98%, Chiralpak IE Column, n-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm ($t_{major}$ = 10.8 min, $t_{minor}$ = 15.6 min).

**(3R,6'S)-8'-(2-fluorophenyl)-1-methyl-6'-(nitromethyl)-6'H-spiro[indoline-3,5'-indolizin]-2-one (4aj)**



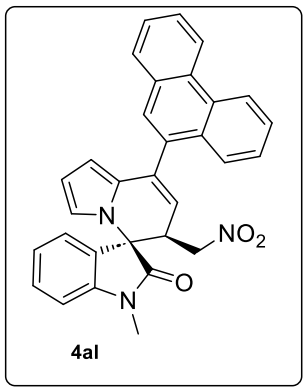

White solid (36.2 mg, combined yield: 90%); $R_f$ = 0.43 in 1:9 ethyl acetate/hexane; **Crude diastereomeric ratio**: 4.9:1; **$^1$H NMR (500 MHz, Chloroform-*d*)** δ 7.52 – 7.42 (m, 2H), 7.41 – 7.34 (m, 2H), 7.23 – 7.12 (m, 2H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 6.37 (dd, *J* = 2.9, 1.5 Hz, 1H), 6.11 (dd, *J* = 8.8, 3.4 Hz, 2H), 5.67 (d, *J* = 5.2 Hz, 1H), 4.85 (dd, *J* = 13.9, 5.9 Hz, 1H), 4.45 (dd, *J* = 13.9, 8.1 Hz, 1H), 3.79 (dt, *J* = 8.2, 5.7 Hz, 1H), 3.30 (s, 3H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 172.66, 161.14 (248.22 Hz), 142.20, 131.18 (2.52 Hz), 130.67, 130.51, 129.97 (7.56 Hz), 128.99, 128.02, 125.44 (15.12 Hz), 124.52 (1.26 Hz), 124.12 (3.78 Hz), 123.81, 120.75, 116.05 (22.68 Hz), 115.41 (2.52 Hz), 110.95, 110.31, 108.95, 74.33, 63.72, 41.50, 26.67.
**$^{19}$F NMR (471 MHz, $CDCl_3$)** δ -114.03.
**ESI HRMS**: calcd. for $C_{23}H_{18}FN_3O_3$ $[M+H]^+$ 404.1405, found 404.1395.
**HPLC Analysis**: *ee* = 98%, Chiralpak ID Column, n-Hexane/*i*-PrOH = 95/15, flow rate 1.0 mL/min, λ = 254 nm ($t_{major}$ = 29.8 min, $t_{minor}$ = 27.0 min).

**(3R,6'S)-1-methyl-8'-(naphthalen-1-yl)-6'-(nitromethyl)-6'H-spiro[indoline-3,5'-indolizin]-2-one (4ak)**




White solid (40.0 mg, combined yield: 92%); $R_f$ = 0.46 in 1:9 ethyl acetate/hexane; **Crude diastereomeric ratio**: 5.2:1; **$^1$H NMR (400 MHz, Chloroform-*d*)** δ 8.34 (d, *J* = 7.4 Hz, 1H), 7.88 (dt, *J* = 6.9, 3.6 Hz, 2H), 7.72 – 7.42 (m, 6H), 7.21 (t, *J* = 7.7 Hz, 1H), 6.97 (d, *J* = 7.8 Hz, 1H), 6.27 (s, 1H), 6.12 – 5.98 (m, 1H), 5.84 (d, *J* = 22.1 Hz, 1H), 5.63 (d, *J* = 3.7 Hz, 1H), 4.51 (q, *J* = 8.1, 7.5 Hz, 2H), 4.11 (td, *J* = 7.8, 7.2, 3.7 Hz, 1H), 3.29 (s, 3H). **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 172.37, 143.57, 135.98, 134.73, 133.81, 132.56, 131.44, 131.18, 128.61, 128.03, 127.36, 126.81, 126.55, 126.39, 126.13, 125.24, 124.86, 124.23, 120.37, 115.15, 111.46, 110.54, 109.14, 74.84, 64.20, 42.70, 26.69.
**ESI HRMS**: calcd. for $C_{27}H_{21}N_3O_3$ $[M+H]^+$ 436.1656, found 436.1660.
**HPLC Analysis**: *ee* = >99%, Chiralpak IE Column, n-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm ($t_{major}$ = 14.0 min, $t_{minor}$ = 24.2 min).

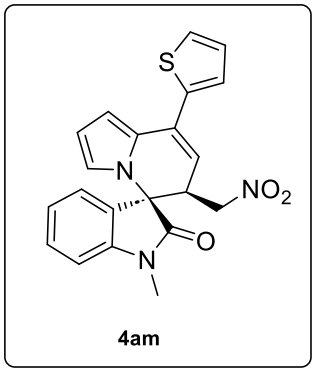
**(3R,6'S)-1-methyl-6'-(nitromethyl)-8'-(phenanthren-9-yl)-6'H-spiro[indoline-3,5'-indolizin]-2-one (4al)**




White solid (44.6 mg, combined yield: 92%); $R_f$ = 0.47 in 1:9 ethyl acetate/hexane; **Crude diastereomeric ratio**: 6.5:1; **$^1$H NMR (500 MHz, Chloroform-*d*)** δ 8.73 (d, *J* = 8.3 Hz, 2H), 8.45 (d, *J* = 8.0 Hz, 1H), 7.92 (q, *J* = 7.4 Hz, 1H), 7.80 (d, *J* = 3.4 Hz, 1H), 7.74 – 7.41 (m, 6H), 7.25 (q, *J* = 7.9, 6.0 Hz, 1H), 6.98 (dd, *J* = 7.9, 3.4 Hz, 1H), 6.27 (d, *J* = 12.1 Hz, 1H), 6.09 – 5.99 (m, 1H), 5.93 – 5.81 (m, 1H), 5.71 (dd, *J* = 7.7, 3.9 Hz, 1H), 4.62 – 4.38 (m, 2H), 4.18 (tt, *J* = 5.8, 3.4 Hz, 1H), 3.29 (s, 3H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 172.30, 143.78, 134.87, 134.83, 131.59, 131.44, 131.30, 130.66, 130.53, 128.82, 127.87, 127.36, 127.16, 126.99, 126.84, 124.91, 124.34, 122.75, 122.63, 120.33, 115.22, 111.42, 110.61, 109.16, 74.81, 64.23, 42.90, 26.67.
**ESI HRMS**: calcd. for $C_{31}H_{23}N_3O_3$ $[M+H]^+$ 486.1812, found 486.1804.

**HPLC Analysis**: *ee* = 99%, Chiralpak ADH Column, n-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm ($t_{major}$ = 11.6 min, $t_{minor}$ = 18.2 min).

**(3R,6'S)-1-methyl-6'-(nitromethyl)-8'-(thiophen-2-yl)-6'H-spiro[indoline-3,5'-indolizin]-2-one (4am)**



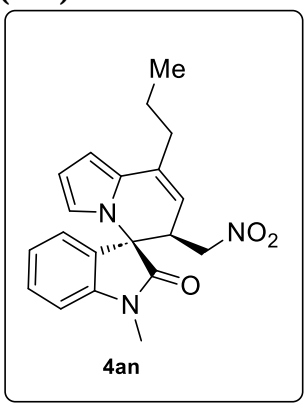
4am

White solid (34.4 mg, combined yield: 88%); $R_f$ = 0.47 in 1:9 ethyl acetate/hexane; **Crude diastereomeric ratio**: 4.6:1; $^1$H NMR (500 MHz, Chloroform-*d*) δ 7.44 – 7.29 (m, 3H), 7.28 – 7.23 (m, 1H), 7.12 (dd, *J* = 5.1, 3.6 Hz, 1H), 7.04 (td, *J* = 7.6, 1.0 Hz, 1H), 6.93 (d, *J* = 7.9 Hz, 1H), 6.59 (dd, *J* = 3.7, 1.5 Hz, 1H), 6.41 (dd, *J* = 2.9, 1.5 Hz, 1H), 6.19 (dd, *J* = 3.8, 2.9 Hz, 1H), 5.82 (d, *J* = 5.5 Hz, 1H), 4.81 (dd, *J* = 14.0, 5.8 Hz, 1H), 4.39 (dd, *J* = 13.9, 8.1 Hz, 1H), 3.77 (dt, *J* = 8.1, 5.6 Hz, 1H), 3.29 (s, 3H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 172.62, 142.38, 139.84, 130.69, 129.77, 128.15, 127.83, 127.59, 126.18, 125.50, 124.65, 123.92, 121.21, 112.78, 111.70, 110.20, 109.12, 74.24, 63.53, 41.56, 26.83.

**ESI HRMS**: calcd. for $C_{21}H_{17}N_3O_3S$ $[M+H]^+$ 392.1063, found 392.1058.

**HPLC Analysis**: *ee* = 94%, Chiralpak IE Column, n-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm ($t_{major}$ = 20.7 min, $t_{minor}$ = 25.0 min).

**(3R,6'S)-1-methyl-6'-(nitromethyl)-8'-propyl-6'H-spiro[indoline-3,5'-indolizin]-2-one (4an)**



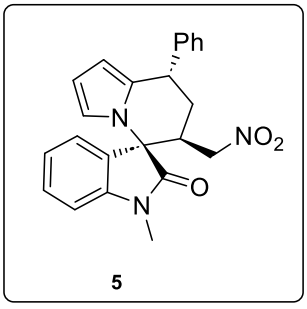
4an

White solid (30.8 mg, combined yield: 88%); $R_f$ = 0.48 in 1:9 ethyl acetate/hexane; **Crude diastereomeric ratio**: 4.4:1; **$^1$H NMR (500 MHz, Chloroform-*d*)** δ 7.38 (td, *J* = 7.7, 1.3 Hz, 1H), 7.24 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.05 (td, *J* = 7.6, 1.0 Hz, 1H), 6.91 (d, *J* = 7.9 Hz, 1H), 6.35 (dd, *J* = 3.7, 1.6 Hz, 1H), 6.26 (dd, *J* = 2.9, 1.5 Hz, 1H), 6.13 (t, *J* = 3.3 Hz, 1H), 5.36 (dt, *J* = 4.8, 1.3 Hz, 1H), 4.67 (dd, *J* = 13.7, 5.8 Hz, 1H), 4.33 (dd, *J* = 13.7, 8.3 Hz, 1H), 3.69 – 3.61 (m, 1H), 3.26 (s, 3H), 2.52 – 2.39 (m, 2H), 1.76 – 1.67 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 172.85, 142.50, 134.72, 130.56, 130.44, 128.30, 124.45, 123.77, 120.18, 111.01, 110.18, 108.99, 108.28, 74.85, 64.00, 41.47, 34.45, 26.71, 22.11, 14.18.

**ESI HRMS**: calcd. for $C_{20}H_{21}N_3O_3$ $[M+H]^+$ 352.1656, found 352.1647.

**HPLC Analysis**: *ee* = 97%, Chiralpak ID Column, n-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm ($t_{major}$ = 13.3 min, $t_{minor}$ = 11.4 min).

**(3R,6'S,8'R)-1-methyl-6'-(nitromethyl)-8'-phenyl-7',8'-dihydro-6'H-spiro[indoline-3,5'-indolizin]-2-one (5)**

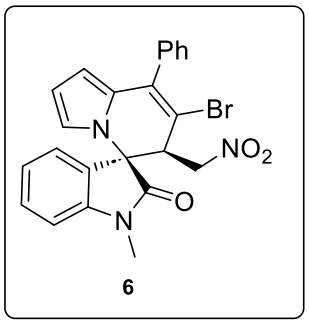


5

White sticky olid (34.8 mg, yield: 90%); $R_f$ = 0.38 in 1:9 ethyl acetate/hexane; **Diastereomeric ratio**: >20:1; **$^1$H NMR (500 MHz, Chloroform-*d*)** δ 7.48 (dd, *J* = 15.4, 7.6 Hz, 3H), 7.41 (d, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.28 (t, *J* = 7.4 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 7.9 Hz, 1H), 6.04 (t, *J* = 3.3 Hz, 1H), 5.97 – 5.89 (m, 1H), 5.59 (dd, *J* = 3.4, 1.8 Hz, 1H), 4.21 (ddd, *J* = 22.5, 12.6, 7.7 Hz, 2H), 3.95 (dd, *J* = 12.8, 4.1 Hz, 1H), 3.44 (ddt, *J* = 13.0, 9.5, 3.5 Hz, 1H), 3.25 (s, 3H), 2.94 (q, *J* = 12.7 Hz, 1H), 2.06 (ddd, *J* = 13.2, 5.8, 2.9 Hz, 1H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 173.14,

144.18, 143.68, 134.46, 131.35, 128.70, 127.22, 127.18, 124.73, 124.51, 117.07, 110.15, 109.01, 107.84, 75.92, 64.01, 42.20, 41.55, 30.17, 26.64.
**ESI HRMS**: calcd. for $C_{23}H_{21}N_3O_3$ $[M+H]^+$ 388.1656, found 388.1661.
**HPLC Analysis**: *ee* = 97%, Chiralpak IE Column, n-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm ($t_{major}$ = 13.6 min, $t_{minor}$ = 16.4 min).

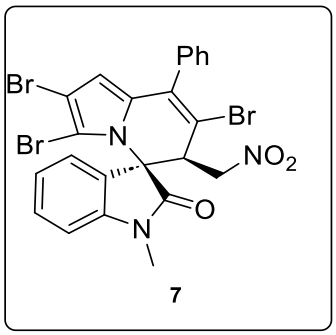
**(3R,6'S)-7'-bromo-1-methyl-6'-(nitromethyl)-8'-phenyl-6'H-spiro[indoline-3,5'-indolizin]-2-one (6)**



6

White solid (43.6 mg, yield: 94%); $R_f$ = 0.48 in 1:9 ethyl acetate/hexane; **Diastereomeric ratio**: >20:1; **$^1$H NMR (500 MHz, Chloroform-*d*)** δ 7.47 (q, *J* = 7.2, 6.7 Hz, 5H), 7.39 (td, *J* = 7.8, 1.2 Hz, 1H), 7.36 – 7.31 (m, 1H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 7.9 Hz, 1H), 6.48 (dd, *J* = 3.0, 1.5 Hz, 1H), 6.08 (t, *J* = 3.3 Hz, 1H), 5.92 (dd, *J* = 3.7, 1.5 Hz, 1H), 5.31 (dd, *J* = 15.6, 8.2 Hz, 1H), 4.53 (dd, *J* = 15.6, 3.2 Hz, 1H), 3.96 (dd, *J* = 8.2, 3.2 Hz, 1H), 3.33 (s, 3H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 172.62, 141.53, 136.82, 135.86, 130.60, 129.82, 129.42, 128.85, 128.81, 128.49, 123.97, 123.78, 121.78, 112.53, 110.98, 109.47, 108.23, 71.43, 63.87, 50.61, 27.03.
**ESI HRMS**: calcd. for $C_{23}H_{18}BrN_3O_3$ $[M+H]^+$ 466.0584, found 466.0573.
**HPLC Analysis**: *ee* = 97%, Chiralpak IE Column, n-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm ($t_{major}$ = 9.6 min, $t_{minor}$ = 13.6 min).

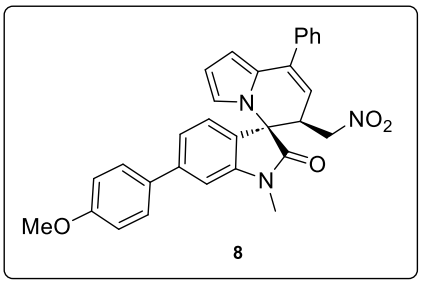
**(3R,6'S)-3',7'-dibromo-1-methyl-6'-(nitromethyl)-8'-phenyl-6'H-spiro[indoline-3,5'-indolizin]-2-one (7)**



7

White solid (36.0 mg, yield: 58%); $R_f$ = 0.52 in 1:9 ethyl acetate/hexane; **Diastereomeric ratio**: >20:1; **$^1$H NMR (600 MHz, Chloroform-*d*)** 1H NMR (600 MHz, Chloroform-d) δ 7.51 – 7.45 (m, 3H), 7.43 (td, J = 7.8, 1.3 Hz, 1H), 7.39 (d, J = 6.4 Hz, 1H), 7.21 (dd, J = 7.4, 1.3 Hz, 1H), 7.10 – 7.06 (m, 1H), 7.00 (d, J = 7.8 Hz, 1H), 6.11 (d, J = 3.9 Hz, 1H), 5.86 (d, J = 3.9 Hz, 1H), 5.59 (dd, J = 15.5, 8.0 Hz, 1H), 4.54 (dd, J = 15.5, 3.0 Hz, 1H), 3.90 (dd, J = 8.1, 3.0 Hz, 1H), 3.32 (s, 3H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 171.81, 141.83, 136.22, 135.66, 132.32, 130.84, 128.97, 128.61, 127.69, 123.88, 123.50, 115.08, 113.20, 109.55, 108.32, 103.99, 71.84, 64.08, 51.00, 27.24.
**ESI HRMS**: calcd. for $C_{23}H_{16}Br_3N_3O_3$ $[M+H]^+$ 621.8795, found 621.8795.
**HPLC Analysis**: *ee* = 97%, Chiralpak IE Column, n-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm ($t_{major}$ = 10.7 min, $t_{minor}$ = 16.7 min).

**(3R,6'S)-6-(4-methoxyphenyl)-1-methyl-6'-(nitromethyl)-8'-phenyl-6'H-spiro[indoline-3,5'-indolizin]-2-one (8)**



8

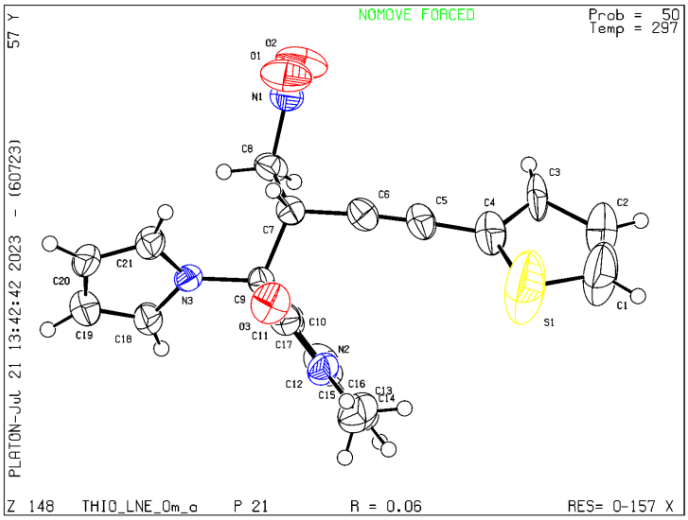
White sticky solid (31.4 mg, yield: 64%); $R_f$ = 0.38 in 1:9 ethyl acetate/hexane; **Diastereomeric ratio**: >20:1; **$^1$H NMR (500 MHz, Chloroform-*d*)** δ 7.61 – 7.56 (m, 2H), 7.50 (d, *J* = 8.3 Hz, 2H), 7.43 (t, *J* = 7.3 Hz, 3H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.21 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.07 (d, *J* = 1.5 Hz, 1H), 6.99 (d, *J* = 8.3 Hz, 2H), 6.44 (dd, *J* = 2.9, 1.4 Hz, 1H), 6.30 (dd, *J* = 3.5, 1.5 Hz, 1H), 6.17 (t, *J* = 3.3 Hz, 1H), 5.68 (d, *J* = 5.2 Hz, 1H), 4.85 (dd, *J* = 13.6, 5.6 Hz, 1H), 4.45 (dd, *J* = 13.6, 8.6 Hz, 1H), 3.86 (s, 3H), 3.80 (dt, *J* = 8.9, 5.5 Hz, 1H), 3.35 (s, 3H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 173.01, 159.96, 143.92, 142.99, 138.15, 136.67, 132.92, 129.30, 128.66, 128.60, 128.41, 128.30, 126.19, 124.82, 122.30, 120.92, 114.59, 113.13, 111.55, 110.25, 107.57, 74.73, 63.74, 55.55, 41.68, 26.88.
**ESI HRMS**: calcd. for $C_{30}H_{25}N_3O_4$ $[M+H]^+$ 492.1918, found 492.1914.
**HPLC Analysis**: *ee* = 96%, Chiralpak IE Column, n-Hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm ($t_{major}$ = 42.8 min, $t_{minor}$ = 50.2 min).

## 14. Single crystal X-ray diffraction analysis:

### (a) Single crystal X-ray diffraction analysis of 3am:

| | |
|---|---|
| CCDC No. | 2283728 |
| Empirical formula | $C_{21}H_{17}N_3O_3S$ |
| Formula weight | 391.43 |
| Crystal habit, colour | Block / colourless |
| Temperature, T | 297 K |
| Wavelength, λ (Å) | 0.71073 |
| Crystal system | monoclinic |
| Space group | 'P 21' |
| Unit cell dimensions | a = 6.4614(4) Å |
| | b = 10.7877(7) Å |
| | c = 14.3616(9) Å |
| | α = 90°, β = 101.675°, γ = 90° |
| Volume, V (Å$^3$) | 980.35(11) |
| Z | 2 |
| Calculated density, g·cm$^{-3}$ | 1.326 |
| F (000) | 408.0 |
| Refinement method | 'SHELXL−2019/1' |
| Goodness−of−fit on $F^2$ | 1.073 |
| Theta(max) | 24.985 |
| Data completeness | 1.89/1.00 |
| R(reflections) | 0.0609 (2877) |
| wR2(reflections) | 0.1715 (3441) |

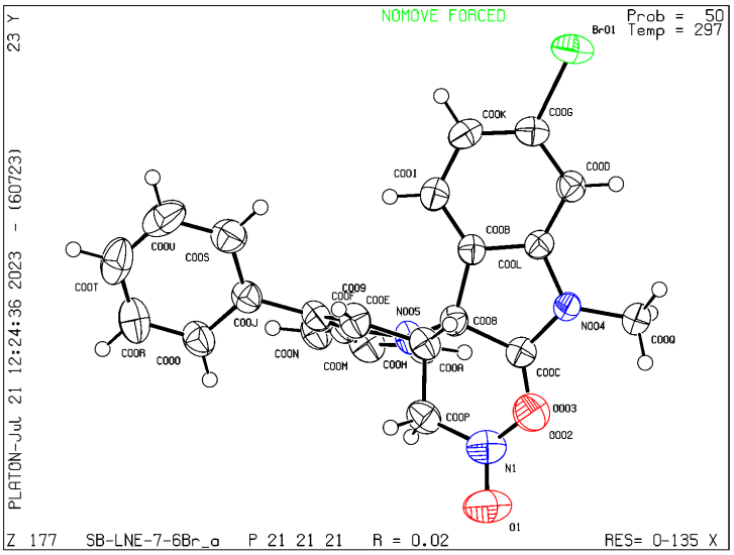



**ORTEP diagram of 3am**

**(b) Single crystal X-ray diffraction analysis of 4pa:**

| | |
|---|---|
| CCDC No. | 2283724 |
| Empirical formula | $C_{23}H_{18}BrN_3O_3$ |
| Formula weight | 464.31 |
| Crystal habit, colour | Block / colourless |
| Temperature, T | 297 K |
| Wavelength, λ (Å) | 0.71073 |
| Crystal system | Orthorhombic |
| Space group | 'P 21' |
| Unit cell dimensions | a = 10.1820(6) Å |
| | b = 10.2729(6) Å |
| | c = 19.3413(12) Å |
| | α = 90°, β = 90°, γ = 90° |
| Volume, V (Å$^3$) | 2023.1(2) |
| Z | 4 |
| Calculated density, g·cm$^{-3}$ | 1.524 |
| F (000) | 944.0 |
| Refinement method | 'SHELXL–2019/1' |
| Goodness–of–fit on $F^2$ | 1.013 |
| Theta(max) | 24.996 |

| | |
|---|---|
| Data completeness | 1.73/0.99 |
| R(reflections) | 0.0228 (3323) |
| wR2(reflections) | 0.0604 (3531) |

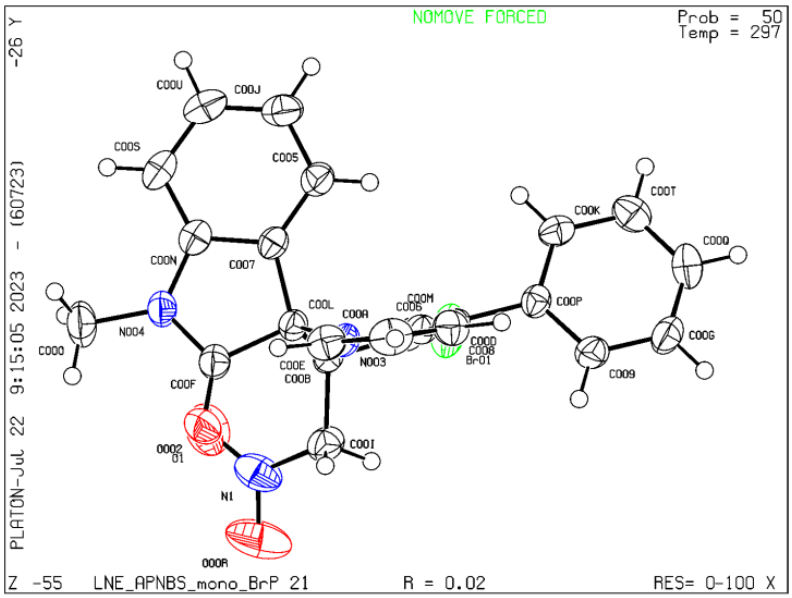



**ORTEP diagram of 4pa**

**(c) Single crystal X-ray diffraction analysis of 6:**

| | |
|---|---|
| CCDC No. | 2283725 |
| Empirical formula | $C_{23}H_{18}BrN_3O_3$ |
| Formula weight | 464.31 |
| Crystal habit, colour | Block / colourless |
| Temperature, T | 297 K |
| Wavelength, λ (Å) | 0.71073 |
| Crystal system | monoclinic |
| Space group | 'P 21' |
| Unit cell dimensions | a = 7.7574(7) Å |
| | b = 13.9180(14) Å |
| | c = 9.8197(9) Å |
| | α = 90°, β = 107.102°, γ = 90° |
| Volume, V ($Å^3$) | 1013.33(17) |
| Z | 2 |
| Calculated density, $g·cm^{-3}$ | 1.522 |

| | |
|---|---|
| F (000) | 472.0 |
| Refinement method | 'SHELXL−2019/1' |
| Goodness−of−fit on $F^2$ | 0.709 |
| Theta(max) | 24.493 |
| Data completeness | 1.83/0.96 |
| R(reflections) | 0.0234 (3025) |
| wR2(reflections) | 0.0570 (3224) |




**ORTEP diagram of 6**

## 15. Computational details:

### Computational Details for the Michael Step:

The topology of electron density was analyzed within the realm of quantum theory of atoms in molecules (QTAIM) [1]. To understand the nature of intramolecular interactions within the molecule AIM analysis was performed using Multiwfn program code. [2] For obtaining a better insight about the nature of non-covalent interactions in both the major and minor products, non-covalent interaction (NCI) index analysis [3,4] was done. For visualization of such NCI surfaces we have used visual molecular dynamics (VMD) software [5] based on the files exported from Multiwfn program code. [2]

### Results and Discussion

To investigate the reason behind the formation of the major product, the electron density for both the isomers were analyzed. It is evident form figure 1 that the major isomer (**3aa**) contains more intramolecular non-covalent interactions compared to the minor one (**3aa'**). Atoms in molecules analysis reveals the formation of C-H $\pi$ interaction in the major product which has also been confirmed by the presence of attractive zone in the NCI plots. From the coloured NCI plots, we can confirm the presence of non-covalent interactions. The light bluish green colour denotes attractive interactions, the green region tells us the C-H $\pi$ interactions and the bluish green region H-bonding interactions. The presence of significant intramolecular non-covalent interactions makes the *Re*-face product more stable, whereas, no such interactions were observed for the *Si*-face product.

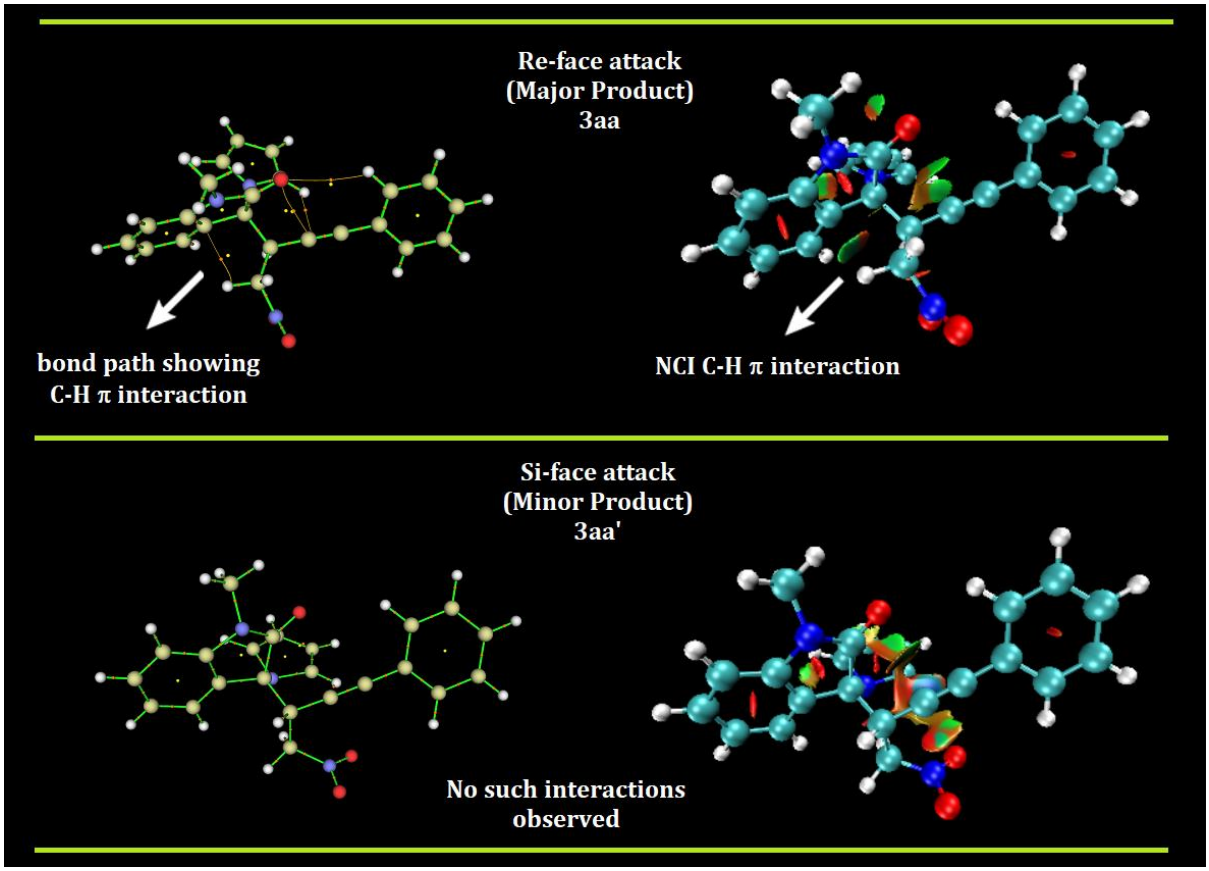



**Figure 1.** Non-covalent interactions (NCI) plots

## References


1. R. W. F. Bader, Atoms in Molecules: A Quantum Theory, Oxford Univ. Press, Oxford, 1990.
2. T. Lu, F. Chen, *J. Comput. Chem.* 2012, **33**, 580.
3. E. R. Johnson, S. Keinan, P. Mori-Sánchez, J. Contreras-García, A. J.Cohen, W. Yang, J. Am. Chem. Soc. 2010, 132, 6498.
4. J. Contreras-García, E. R. Johnson, S. Keinan, R. Chaudret, J.-P. Piquemal, D. N. Beratan, W. Yang, J. Chem. Theory Comput. 2011, 7, 625.
5. W. Humphrey, A. Dalke, K. Schulten, J. Mol. Graph. 1996, 14, 33.


## Computational Details for the Hydroarylation Step:

All the structures were fully optimized without any symmetry constraint using M06-1X/def2-TZVP level.[1] Harmonic vibrational frequency calculations were performed at the same level to understand the nature of stationary points. Intermediates were characterized as true minima with all real values of the Hessian matrix while transition states were characterized with one imaginary value. All calculations were performed at gas phase and at ambient

condition (298K and 1 atm). Energies are zero-point and thermal corrected. All these calculations were performed using Gaussian16 suite of program.[2]

## Results and Discussion

Figure 1 shows the energy profile diagram for the Au catalyzed formation of Aza-Spirooxindoles. Both endo and exo-cyclization process were considered. Binding of $[Au]^+$ to the C≡C triple bond of **3aa** to generate intermediate **A** is found to exergonic by 6.7 kcal/mol. Intermediate **A** then converts to **C** or **E** through two different pathways. Formation of **C** involves endo cyclization which involves a barrier of 17.2 kcal/mol. Similarly, formation of **E** involving exo-cyclization has a higher barrier of 21.8 kcal/mol. As a consequence, construction of the endo product **4aa** is more likely compared to exo product **F**.

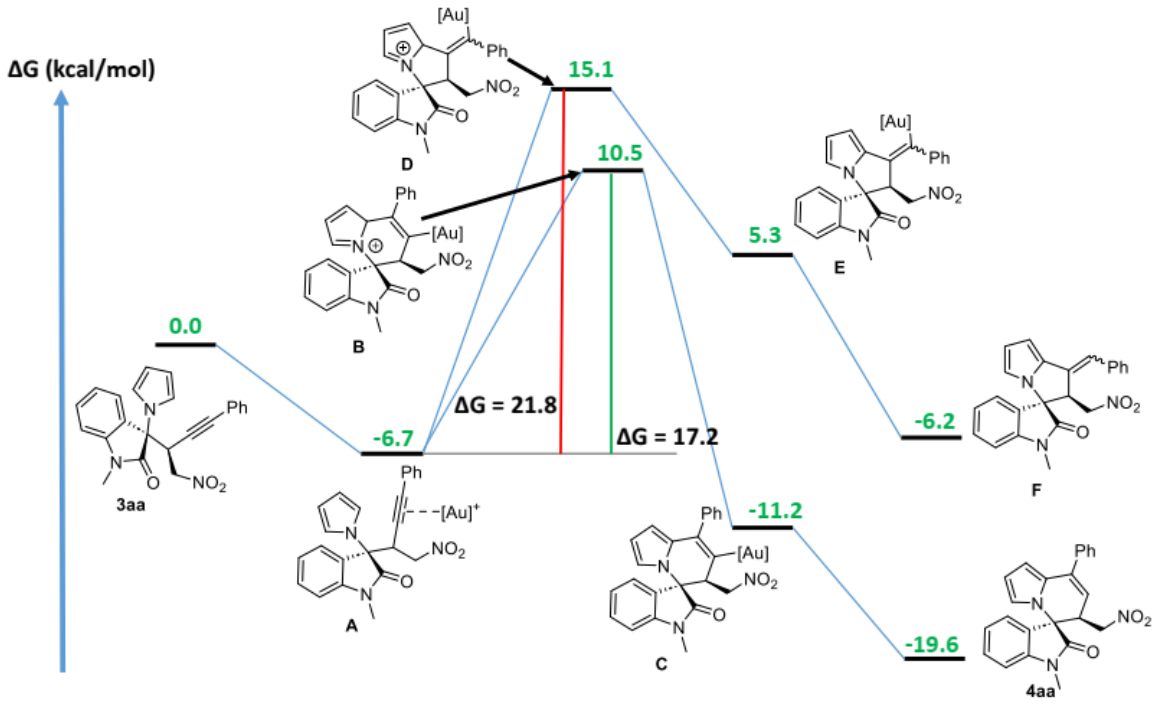


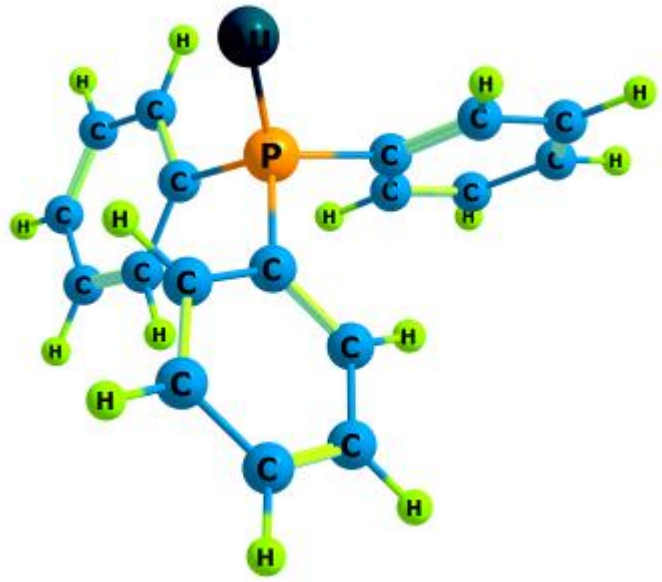

**Figure 2**. Energy ($\Delta G_{298}$, kcal/mol) profile diagram for the formation of Aza-Spirooxindoles.

## References

1. Zhao, Y; Truhlar, D. G. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functional. *Theor Chem Acc*. 2008, **120**, 215-241.

2. Frisch M J, Trucks G W, Schlegel H B, Scuseria G E, Robb M A, Cheeseman J R, Scalmani G, Barone V, Petersson G A, Nakatsuji H, Li X, Caricato M, Marenich A V, Bloino J, Janesko B G, Gomperts R, Mennucci B, Hratchian H P, Ortiz J V, Izmaylov A F, Sonnenberg J L, Williams−Young D, Ding F, Lipparini F, Egidi F, Goings J, Peng B, Petrone A, Henderson T, Ranasinghe D, Zakrzewski V G, Gao J, Rega N, Zheng G, Liang W, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Throssell K, Montgomery Jr J A, Peralta J E, Ogliaro F, Bearpark M J, Heyd J J, Brothers E N, Kudin K N, Staroverov V N, Keith T A, Kobayashi R, Normand J, Raghavachari K, Rendell A P, Burant J C, Iyengar S S, Tomasi J, Cossi M, Millam J M, Klene M, Adamo C, Cammi R, Ochterski J W, Martin R L, Morokuma K, Farkas O, Foresman J B, Fox D J. Gaussian 16, Revision A.03, Gaussian, Inc., Wallingford CT, 2016.

**Cartesian Coordinates of the Optimised Geometries:**



**[PPh$_3$Au]$^+$**

| | | | |
|---|---|---|---|
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| 6 | -2.016881000 | -0.888185000 | 1.678137000 |
| 6 | -1.219173000 | -2.525736000 | 0.063187000 |
| 6 | -2.890772000 | -1.848428000 | 2.208608000 |
| 1 | -2.010259000 | 0.113372000 | 2.121286000 |

| | | | |
|---|---|---|---|
| 6 | -2.087270000 | -3.476617000 | 0.599496000 |
| 1 | -0.576789000 | -2.818970000 | -0.771044000 |
| 6 | -2.925656000 | -3.137099000 | 1.673075000 |
| 1 | -3.544463000 | -1.585513000 | 3.044019000 |
| 1 | -2.118320000 | -4.487879000 | 0.186768000 |
| 1 | -3.606778000 | -3.886009000 | 2.088375000 |
| 6 | -0.471677000 | 1.651309000 | 0.606818000 |
| 6 | -1.578134000 | 2.318377000 | 0.063288000 |
| 6 | 0.239211000 | 2.190926000 | 1.677909000 |
| 6 | -1.967717000 | 3.545584000 | 0.599578000 |
| 1 | -2.153349000 | 1.908507000 | -0.770807000 |
| 6 | -0.155584000 | 3.427817000 | 2.208358000 |
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| 1 | 3.144732000 | -2.275165000 | 3.045849000 |
| 1 | 5.168450000 | -1.180115000 | 2.089358000 |
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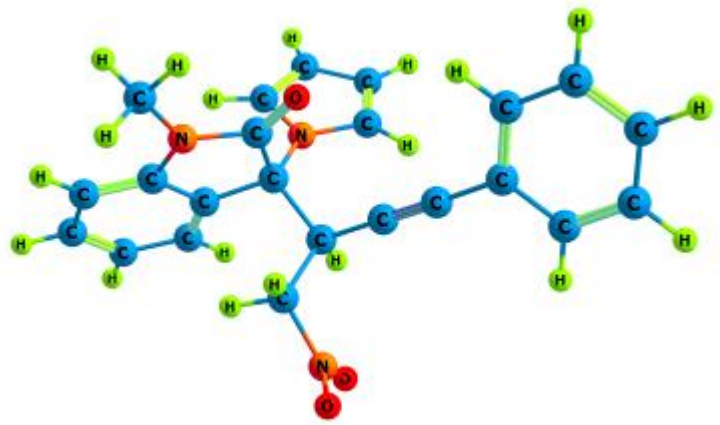

**3**

| | | | |
|---|---|---|---|
| 6 | -1.604193000 | 0.018918000 | 1.152032000 |
| 6 | -0.408311000 | 0.317016000 | 0.504692000 |
| 6 | -0.160098000 | 1.613596000 | -0.038972000 |
| 6 | -1.107987000 | 2.615103000 | 0.086143000 |
| 6 | -2.317946000 | 2.319009000 | 0.737968000 |
| 6 | -2.556821000 | 1.044997000 | 1.257907000 |
| 1 | -1.797487000 | -0.966260000 | 1.565473000 |
| 1 | -0.919211000 | 3.615241000 | -0.307274000 |
| 1 | -3.072882000 | 3.097234000 | 0.841138000 |
| 1 | -3.502991000 | 0.837160000 | 1.761584000 |
| 6 | 1.215017000 | 1.649194000 | -0.689259000 |
| 7 | 0.709954000 | -0.519886000 | 0.252980000 |
| 6 | 1.763101000 | 0.189717000 | -0.398883000 |
| 8 | 2.828196000 | -0.296436000 | -0.664230000 |
| 7 | 2.080421000 | 2.625751000 | -0.012530000 |
| 6 | 3.196641000 | 3.299437000 | -0.546340000 |
| 6 | 1.950146000 | 2.982249000 | 1.348701000 |
| 6 | 3.738560000 | 4.083521000 | 0.463807000 |
| 1 | 3.526605000 | 3.179874000 | -1.561706000 |
| 6 | 2.961149000 | 3.884645000 | 1.647017000 |
| 1 | 1.174824000 | 2.587287000 | 1.977233000 |
| 1 | 4.591128000 | 4.727344000 | 0.380732000 |

| | | | |
|---|---|---|---|
| 1 | 3.138669000 | 4.354760000 | 2.593294000 |
| 6 | 1.115890000 | 1.903005000 | -2.229946000 |
| 1 | 0.903884000 | 3.008565000 | -2.371828000 |
| 6 | -0.048704000 | 1.100556000 | -2.856210000 |
| 1 | 0.211996000 | 0.019098000 | -2.946239000 |
| 1 | -0.968928000 | 1.148948000 | -2.226773000 |
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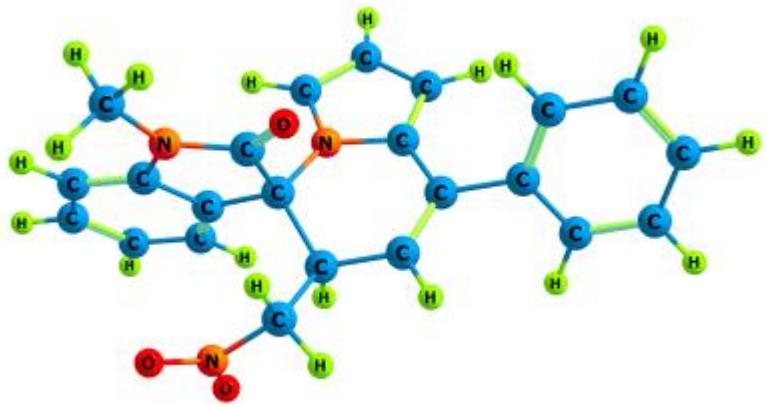

**4**

| | | | |
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| 6 | -3.025619000 | 0.690043000 | 0.510230000 |
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| 6 | -2.605087000 | 0.375736000 | -1.868865000 |
| 6 | -3.973544000 | 0.604627000 | -2.095287000 |
| 6 | -4.840494000 | 0.866660000 | -1.032230000 |
| 1 | -5.063360000 | 1.119536000 | 1.113563000 |
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| | | | |
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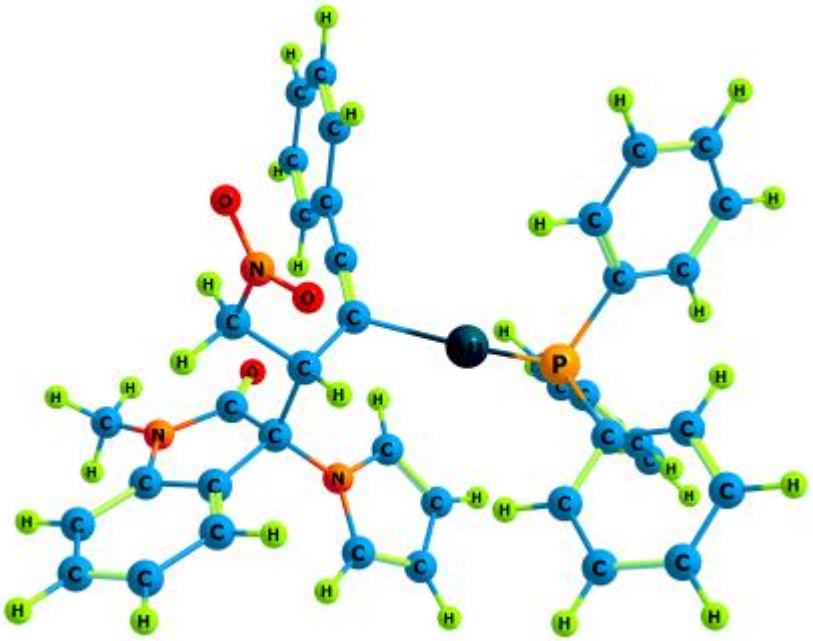

**A**

| | | | |
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| 1 | 5.154226000 | -4.241305000 | -2.136838000 |
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| 6 | 2.793755000 | -0.875593000 | 0.304135000 |
| 7 | 4.898729000 | -0.293783000 | 1.334781000 |
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| 8 | 3.063063000 | 0.920226000 | 2.059780000 |
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| 6 | 0.731714000 | -1.016448000 | 1.793544000 |
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| 6 | -0.081095000 | -2.030811000 | 2.298746000 |

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| 1 | -0.938847000 | -1.904355000 | 2.932218000 |
| 1 | 0.041134000 | -4.243167000 | 2.078504000 |
| 6 | 2.152645000 | -0.071550000 | -0.884806000 |
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| 6 | 1.147592000 | 0.899800000 | -0.422507000 |
| 6 | 1.213254000 | 2.139496000 | -0.133469000 |
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| 6 | 1.677463000 | 3.836072000 | 1.538988000 |
| 6 | 1.021813000 | 4.499195000 | -0.740999000 |
| 6 | 1.753964000 | 5.178861000 | 1.894715000 |
| 1 | 1.920465000 | 3.047932000 | 2.251329000 |
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| 1 | 0.754851000 | 4.226784000 | -1.757732000 |
| 6 | 1.466426000 | 6.185571000 | 0.953620000 |
| 1 | 2.041772000 | 5.457172000 | 2.906076000 |
| 1 | 0.895994000 | 6.620129000 | -1.085324000 |
| 1 | 1.527384000 | 7.230274000 | 1.240503000 |
| 7 | 2.754606000 | 0.973479000 | -3.092610000 |
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| 1 | 5.455562000 | 1.144429000 | 2.785319000 |
| 1 | 6.341448000 | -0.407634000 | 2.904349000 |

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| 6 | -4.050318000 | -1.469898000 | 2.027664000 |
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| 6 | -4.533582000 | -1.522782000 | 3.342918000 |
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| 6 | -3.164603000 | 0.390588000 | 3.928094000 |
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| 6 | -2.872896000 | -1.988714000 | -0.857863000 |
| 6 | -1.932480000 | -3.015502000 | -0.750620000 |
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| 6 | -2.210771000 | -4.264987000 | -1.314843000 |
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| 1 | -4.822001000 | -1.392634000 | -1.625616000 |
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| 6 | -4.930500000 | 1.039628000 | -0.433884000 |
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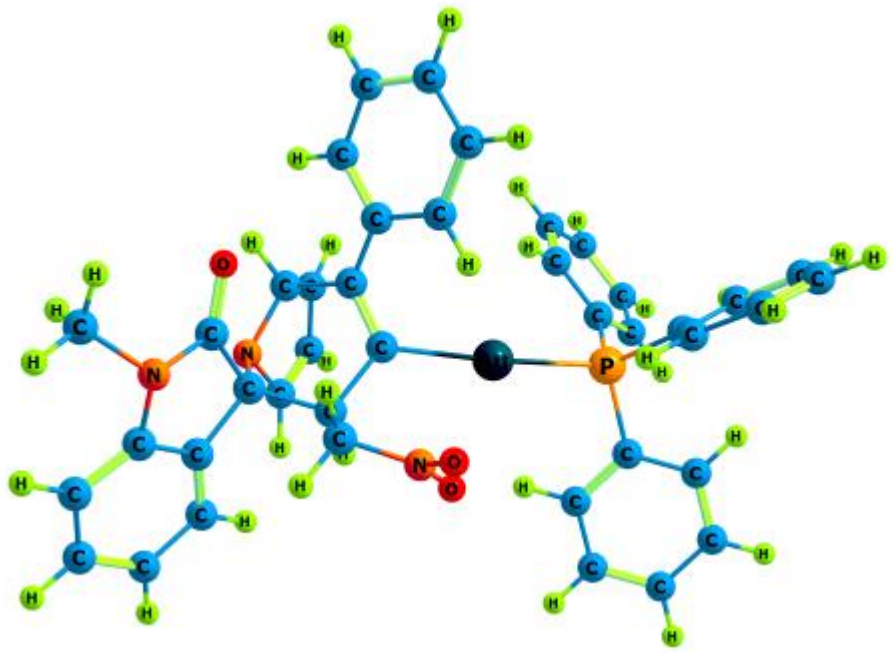

**B**

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| 6 | 5.945630200 | -0.968387280 | -0.272372310 |
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| 6 | 4.671140210 | -2.993146680 | -0.115137750 |
| 6 | 5.812874900 | -3.717356610 | -0.514328050 |
| 6 | 7.045336710 | -3.053586330 | -0.712935500 |
| 1 | 8.041035730 | -1.131971150 | -0.730846560 |
| 1 | 3.738747780 | -3.490542450 | 0.052626230 |
| 1 | 5.744267010 | -4.770866070 | -0.673168060 |
| 1 | 7.915861560 | -3.612086260 | -0.965409360 |
| 6 | 3.727359870 | -0.692493230 | 0.594558850 |
| 7 | 5.737690780 | 0.504675980 | -0.249058910 |

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|---|---|---|---|
| 6 | 4.519000080 | 0.632087510 | 0.582945150 |
| 8 | 4.200008890 | 1.666630630 | 1.222104730 |
| 7 | 3.357871230 | -0.941830080 | 1.965837260 |
| 6 | 2.534707940 | 0.189840340 | 2.504070800 |
| 6 | 2.545749640 | -2.139255650 | 2.127693920 |
| 6 | 1.658233410 | -0.498102080 | 3.400547340 |
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| 6 | 1.647839440 | -1.880399890 | 3.134822530 |
| 1 | 2.634533980 | -3.055005990 | 1.572870740 |
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| 1 | 1.028302350 | -2.610388450 | 3.619932890 |
| 6 | 2.419918940 | -0.766052680 | -0.260497800 |
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| 6 | 2.765698770 | -0.243077890 | -1.659185380 |
| 1 | 3.092102430 | 0.777613610 | -1.596041080 |
| 1 | 3.550021400 | -0.838377080 | -2.078003690 |
| 6 | 1.294026330 | 0.085343960 | 0.393844320 |
| 6 | 1.638916240 | 0.866927340 | 1.431579600 |
| 6 | 1.240624180 | 2.163156690 | 1.571986140 |
| 6 | 1.614406970 | 2.886611450 | 2.716420790 |
| 6 | 0.469511380 | 2.790030080 | 0.581480500 |
| 6 | 1.247184480 | 4.231139790 | 2.863663020 |
| 1 | 2.191216890 | 2.413454870 | 3.481875190 |
| 6 | 0.096055730 | 4.137380430 | 0.730357040 |
| 1 | 0.166035150 | 2.244736380 | -0.284344830 |
| 6 | 0.491548740 | 4.858614490 | 1.863044470 |
| 1 | 1.539511840 | 4.782359830 | 3.737422360 |
| 1 | -0.486082940 | 4.621410390 | -0.031523200 |
| 1 | 0.217987630 | 5.886534280 | 1.969606170 |
| 7 | 1.566477530 | -0.339364070 | -2.512003460 |

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| 8 | 0.746744310 | -1.190909990 | -2.307127090 |
| 6 | 6.890917310 | 1.258366770 | 0.285258780 |
| 1 | 7.755760130 | 1.074873010 | -0.326444960 |
| 1 | 6.661166460 | 2.305375240 | 0.271836470 |
| 1 | 7.096957330 | 0.950228900 | 1.287400570 |
| 15 | -3.120518440 | -0.277282950 | -0.475284660 |
| 6 | -3.772102680 | -0.333792190 | 1.222144920 |
| 6 | -4.895285160 | -1.098717810 | 1.550010250 |
| 6 | -3.119792670 | 0.416032070 | 2.206727170 |
| 6 | -5.359097180 | -1.120832430 | 2.875733460 |
| 1 | -5.395902420 | -1.662401110 | 0.791682420 |
| 6 | -3.577202600 | 0.399891840 | 3.528169170 |
| 1 | -2.266015140 | 1.004512660 | 1.944318890 |
| 6 | -4.697618440 | -0.371603960 | 3.864652370 |
| 1 | -6.216671340 | -1.709207830 | 3.132190740 |
| 1 | -3.071796690 | 0.977138560 | 4.278144440 |
| 1 | -5.049985830 | -0.385635650 | 4.873197270 |
| 6 | -3.472251860 | -1.810772710 | -1.391881390 |
| 6 | -2.551196470 | -2.866107320 | -1.409573560 |
| 6 | -4.680648780 | -1.926238200 | -2.097176850 |
| 6 | -2.828793130 | -4.026315320 | -2.147579980 |
| 1 | -1.637382260 | -2.784196270 | -0.864031560 |
| 6 | -4.961885690 | -3.086497040 | -2.826418230 |
| 1 | -5.387154240 | -1.122013750 | -2.074743740 |
| 6 | -4.033831410 | -4.136345970 | -2.858589210 |
| 1 | -2.121507790 | -4.830479140 | -2.170725030 |
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| 6 | -3.970673320 | 1.068473390 | -1.380715490 |

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| 6 | -5.293677170 | 1.355195600 | -1.000430020 |
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| 1 | -2.365446080 | 1.616414300 | -2.715587490 |
| 6 | -6.046209480 | 2.310510900 | -1.688005570 |
| 1 | -5.735356610 | 0.832134190 | -0.179426110 |
| 6 | -5.482657900 | 3.002856340 | -2.756994980 |
| 1 | -3.718986150 | 3.303673880 | -3.940309700 |
| 1 | -7.053512000 | 2.505286330 | -1.394154540 |
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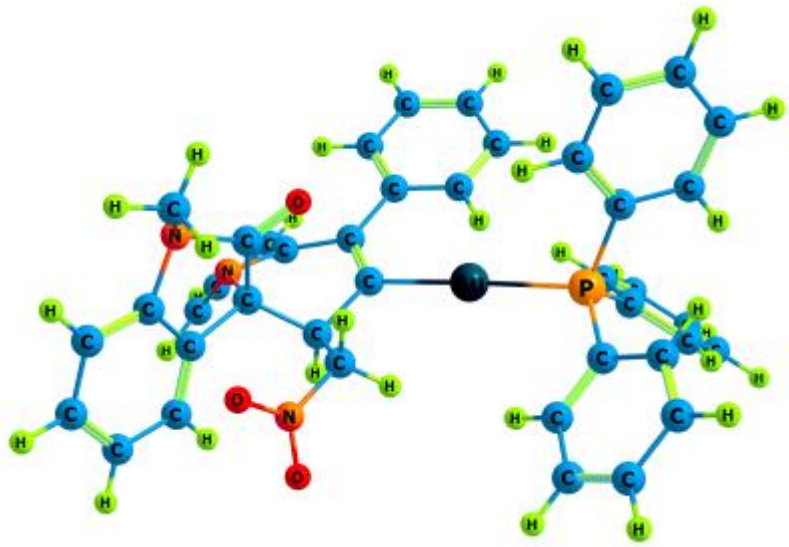

**C**

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| 6 | 4.873260220 | -0.226406950 | 0.493508160 |
| 6 | 5.357475740 | -0.733101490 | 1.702958070 |
| 6 | 6.520769360 | -1.530667880 | 1.661402380 |
| 6 | 7.165621630 | -1.789803840 | 0.424182540 |
| 1 | 7.116884270 | -1.465288520 | -1.708139650 |
| 1 | 4.863457650 | -0.528614460 | 2.636666850 |

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| 1 | 8.054791380 | -2.386097280 | 0.398180810 |
| 6 | 3.637289110 | 0.628318480 | 0.230182260 |
| 7 | 4.785805600 | 0.106296080 | -1.862740270 |
| 6 | 3.471401620 | 0.432704640 | -1.274938600 |
| 8 | 2.398399600 | 0.524471650 | -1.916419510 |
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| 6 | 4.674053050 | 2.534034740 | 1.673547470 |
| 6 | 2.905976550 | 4.031680460 | 1.270072760 |
| 6 | 4.210273660 | 3.822254240 | 2.025271650 |
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| 1 | 4.671721720 | 4.510987600 | 2.699090300 |
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| 6 | 1.300873230 | 2.292469080 | 0.289885560 |
| 6 | 0.166314940 | 3.198456570 | -0.200198410 |
| 6 | 0.452919850 | 4.525541200 | -0.540506070 |
| 6 | -1.140521350 | 2.700612650 | -0.305392860 |
| 6 | -0.573814540 | 5.378827390 | -0.957671950 |
| 1 | 1.461620300 | 4.885079190 | -0.483330510 |
| 6 | -2.176177010 | 3.557177680 | -0.705886980 |
| 1 | -1.345062780 | 1.673168540 | -0.076333220 |
| 6 | -1.891677780 | 4.901109130 | -1.021930550 |
| 1 | -0.350798260 | 6.393961470 | -1.225906070 |

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| 7 | 3.232882790 | -2.179465690 | 1.042251490 |
| 8 | 4.128119410 | -2.378982560 | 0.274412750 |
| 8 | 3.250826180 | -2.667083540 | 2.129472040 |
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| 6 | -5.045274890 | -0.981641630 | 1.841017620 |
| 6 | -3.871400570 | 1.119786820 | 1.529085280 |
| 6 | -5.910931050 | -0.361457550 | 2.755147670 |
| 1 | -5.161926920 | -2.019490750 | 1.609128360 |
| 6 | -4.733374580 | 1.739098850 | 2.438163510 |
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| 1 | -0.758198240 | -4.911364770 | 2.239713360 |

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| 6 | -2.781088390 | -0.752549140 | -2.763085780 |
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| 1 | -2.759152850 | -0.572583010 | -4.907614760 |
| 1 | -6.648636880 | -0.637405440 | -3.104192030 |
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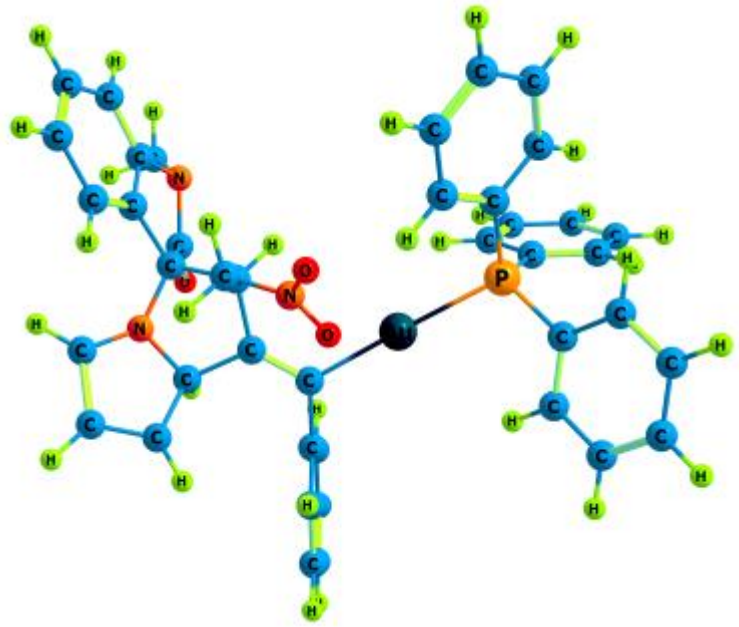

**D**

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| 6 | -4.864337900 | -0.183633450 | 0.257070180 |

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| 6 | -7.255778890 | -1.524416470 | -0.057877070 |
| 1 | -7.038427230 | -2.094013650 | 2.019411480 |
| 1 | -4.995887220 | 0.400546160 | -1.761376680 |
| 1 | -7.162260320 | -0.785167130 | -2.085169270 |
| 1 | -8.183933510 | -2.036123490 | -0.195946220 |
| 6 | -3.571371510 | 0.496477720 | 0.684804030 |
| 7 | -4.603739460 | -0.703187890 | 2.559646450 |
| 6 | -3.742879510 | 0.446190620 | 2.207652840 |
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| 6 | -1.734836320 | 3.230989350 | -0.766580540 |
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| 1 | -0.810220120 | 3.514613490 | -1.220931960 |
| 1 | -3.205821550 | 4.555307250 | -1.680114600 |
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| 6 | -2.460512600 | -0.515635710 | -1.343613910 |
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| 6 | 0.162615090 | 0.706336370 | 0.364134780 |
| 7 | -1.221779220 | -1.084260250 | -1.881675140 |
| 8 | -1.264662430 | -1.860974350 | -2.792231840 |
| 8 | -0.169389710 | -0.768642430 | -1.410849390 |
| 6 | -5.419110020 | -0.460038870 | 3.758626680 |
| 1 | -6.043322560 | -1.308451450 | 3.946739490 |
| 1 | -4.775378680 | -0.297050560 | 4.598555810 |

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| 6 | 2.482677680 | -3.878958120 | 2.075962890 |
| 6 | 3.598239910 | -4.691828240 | 2.318023220 |
| 6 | 1.680193580 | -3.454681480 | 3.142931150 |
| 6 | 3.913505650 | -5.077454060 | 3.627264490 |
| 1 | 4.210083790 | -5.018288770 | 1.503147520 |
| 6 | 1.994512050 | -3.841258850 | 4.452840740 |
| 1 | 0.827892400 | -2.836188690 | 2.957565420 |
| 6 | 3.111909990 | -4.651589120 | 4.694647320 |
| 1 | 4.766595710 | -5.697447980 | 3.812078130 |
| 1 | 1.381101740 | -3.517789320 | 5.268210530 |
| 1 | 3.352967420 | -4.945400760 | 5.694569240 |
| 6 | 3.610858370 | -3.272480490 | -0.608491730 |
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| 6 | 5.487215700 | -1.960954190 | -1.417632010 |
| 1 | 3.934897800 | -1.204560680 | -0.144156430 |
| 6 | 5.277926950 | -4.296353300 | -2.046748470 |
| 1 | 3.564832370 | -5.320853390 | -1.254710900 |
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| 1 | 5.650960510 | -5.150395700 | -2.573148930 |
| 1 | 6.874770080 | -3.005248180 | -2.675927630 |
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| 6 | 0.029285010 | -4.254273440 | -1.334133020 |
| 6 | 1.052453980 | -5.954861510 | 0.063476130 |
| 6 | -0.821299910 | -5.224700390 | -1.885767490 |
| 1 | -0.038090220 | -3.237240810 | -1.658347380 |
| 6 | 0.203266650 | -6.922932330 | -0.487642050 |

| | | | |
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| 1 | 1.768408450 | -6.235282410 | 0.808287190 |
| 6 | -0.734499090 | -6.558569700 | -1.462020780 |
| 1 | -1.537569330 | -4.947560170 | -2.630714560 |
| 1 | 0.271136890 | -7.940615510 | -0.164002190 |
| 1 | -1.384616990 | -7.298363560 | -1.882198850 |
| 79 | 1.036307220 | -1.221616240 | 0.398616540 |
| 1 | -2.076221160 | -1.128037900 | 0.669440410 |
| 6 | 1.050462670 | 1.938700080 | 0.632067770 |
| 6 | 1.258606760 | 2.357934330 | 1.952601610 |
| 6 | 1.647649050 | 2.637776220 | -0.427421980 |
| 6 | 2.057901900 | 3.474508050 | 2.216485360 |
| 1 | 0.803459150 | 1.823210490 | 2.760913600 |
| 6 | 2.452319880 | 3.756390470 | -0.162330250 |
| 1 | 1.489934180 | 2.317594430 | -1.435316900 |
| 6 | 2.654018410 | 4.175912710 | 1.160734120 |
| 1 | 2.213386450 | 3.793267780 | 3.225789960 |
| 1 | 2.910829950 | 4.288377120 | -0.967770340 |
| 1 | 3.264678930 | 5.031769070 | 1.363305300 |
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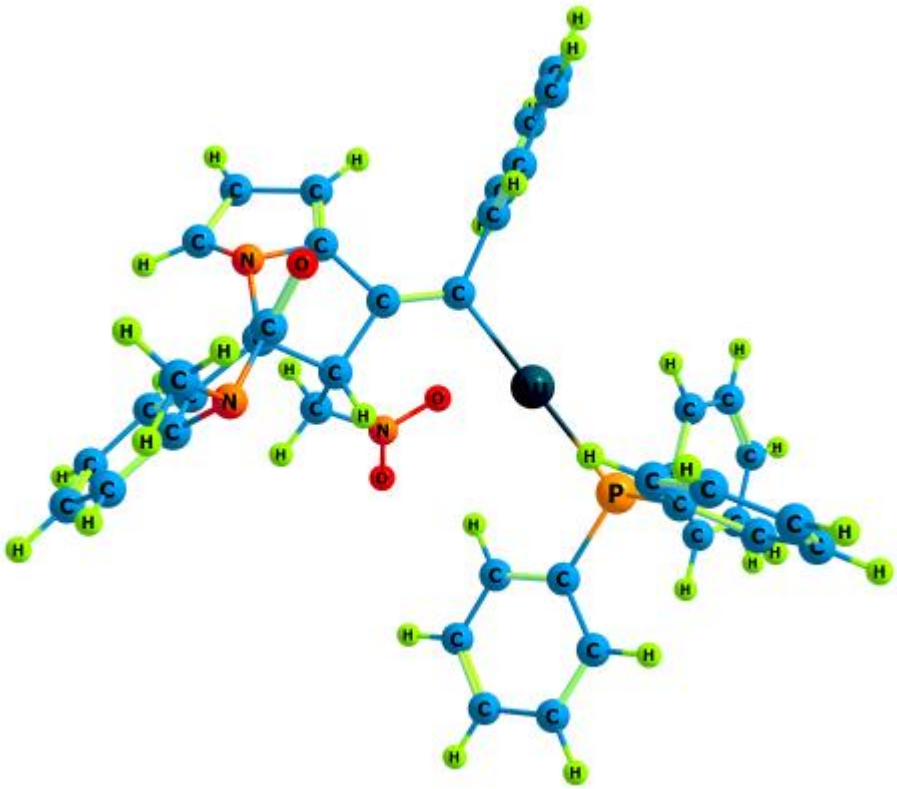

**E**

| | | | |
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| 6 | -5.397773310 | -0.858253810 | 1.373099570 |
| 6 | -4.874946910 | -0.139242910 | 0.313067210 |
| 6 | -5.483925410 | -0.045006770 | -0.883606990 |
| 6 | -6.674109000 | -0.755289090 | -1.087579200 |
| 6 | -7.235164060 | -1.503532580 | -0.021784980 |
| 1 | -7.015561060 | -2.078380220 | 2.049559920 |
| 1 | -5.061626530 | 0.551685720 | -1.667692360 |
| 1 | -7.153586920 | -0.731216780 | -2.047147640 |
| 1 | -8.147216900 | -2.039128820 | -0.177519430 |
| 6 | -3.565318720 | 0.512552960 | 0.700551510 |
| 7 | -4.553573860 | -0.761379620 | 2.578293860 |
| 6 | -3.632120970 | 0.352115070 | 2.221916110 |
| 8 | -3.024498420 | 1.073858210 | 3.024231790 |
| 7 | -3.402244990 | 1.975767130 | 0.366250110 |
| 6 | -2.000994020 | 2.110770500 | 0.003799040 |

| | | | |
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| 6 | -1.726206400 | 3.261684850 | -0.585217760 |
| 6 | -3.066828390 | 3.700845080 | -1.141624160 |
| 1 | -0.805995970 | 3.755940620 | -0.702379350 |
| 1 | -3.206201810 | 4.575724300 | -1.736602370 |
| 6 | -2.311284420 | -0.205052870 | 0.124211100 |
| 6 | -2.499369590 | -0.521490190 | -1.379267360 |
| 1 | -3.305482520 | -1.212073210 | -1.509560020 |
| 1 | -2.717762550 | 0.383083590 | -1.905360330 |
| 6 | -1.197320030 | 0.857290310 | 0.221853510 |
| 6 | 0.139368920 | 0.720183550 | 0.358087160 |
| 7 | -1.259045770 | -1.109505290 | -1.889099040 |
| 8 | -1.289290990 | -1.890441820 | -2.794704180 |
| 8 | -0.211306810 | -0.797467420 | -1.400294670 |
| 6 | -5.374096700 | -0.502256910 | 3.772944380 |
| 1 | -6.037569250 | -1.329359420 | 3.935927770 |
| 1 | -4.742929470 | -0.382648620 | 4.626858590 |
| 1 | -5.945786170 | 0.388223020 | 3.619257180 |
| 15 | 2.079838990 | -3.362853070 | 0.383303580 |
| 6 | 2.484807770 | -3.867393150 | 2.089503290 |
| 6 | 3.602735330 | -4.695111800 | 2.323750390 |
| 6 | 1.685858220 | -3.451493520 | 3.149425180 |
| 6 | 3.915069950 | -5.081239730 | 3.639482850 |
| 1 | 4.211111270 | -5.035042300 | 1.510150190 |
| 6 | 2.001164950 | -3.841923140 | 4.460763440 |
| 1 | 0.826936740 | -2.837393930 | 2.963609210 |
| 6 | 3.114960310 | -4.654189230 | 4.706201350 |
| 1 | 4.760213950 | -5.707413230 | 3.823435890 |
| 1 | 1.385487160 | -3.524196220 | 5.274530160 |
| 1 | 3.352224450 | -4.955098420 | 5.707403850 |

| | | | |
|---|---|---|---|
| 6 | 3.608654380 | -3.272807630 | -0.597455580 |
| 6 | 4.316415920 | -2.063287920 | -0.665480910 |
| 6 | 4.096149880 | -4.394439050 | -1.295128830 |
| 6 | 5.489961520 | -1.964655630 | -1.416528530 |
| 1 | 3.945011200 | -1.218977220 | -0.134180500 |
| 6 | 5.272454010 | -4.301155530 | -2.047694740 |
| 1 | 3.559505730 | -5.326277690 | -1.247078500 |
| 6 | 5.966259490 | -3.086300740 | -2.106354920 |
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| 1 | 5.637642830 | -5.159713850 | -2.576908570 |
| 1 | 6.865646590 | -3.013966390 | -2.678113650 |
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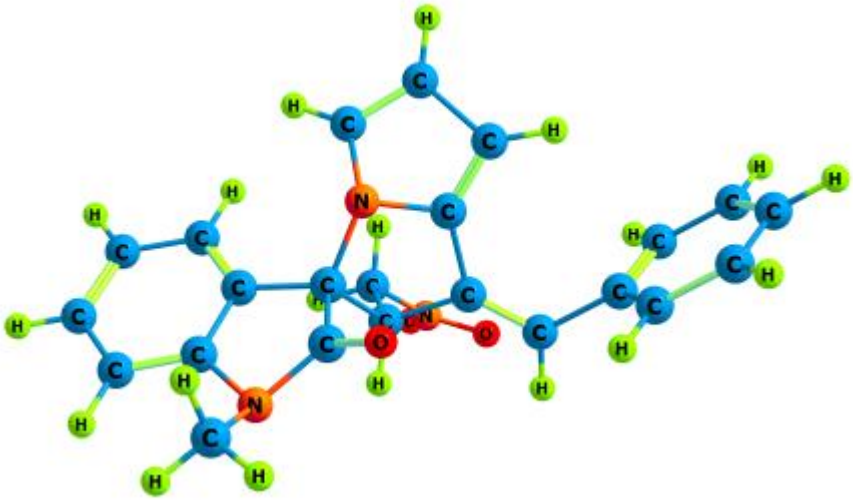
| 6 | 1.050062660 | -5.944782760 | 0.071632520 |
| 6 | -0.816887790 | -5.208914920 | -1.880213920 |
| 1 | -0.038237070 | -3.226521860 | -1.645144040 |
| 6 | 0.202337940 | -6.913995330 | -0.486824050 |
| 1 | 1.759148260 | -6.234423920 | 0.813078400 |
| 6 | -0.734183830 | -6.547172260 | -1.465425310 |
| 1 | -1.536700490 | -4.928591360 | -2.626895040 |
| 1 | 0.263343820 | -7.937023840 | -0.167243680 |
| 1 | -1.385735790 | -7.284804610 | -1.890048240 |
| 79 | 1.048934490 | -1.193554370 | 0.370006430 |
| 1 | -2.112471070 | -1.131697440 | 0.636959520 |
| 6 | 1.036229180 | 1.941887800 | 0.658053080 |
| 6 | 1.251232350 | 2.367268690 | 1.969354580 |
| 6 | 1.639392890 | 2.636602550 | -0.409806250 |
| 6 | 2.052651870 | 3.479532740 | 2.222507300 |
| 1 | 0.786820270 | 1.829616420 | 2.776368020 |
| 6 | 2.442275680 | 3.751258600 | -0.160386530 |

| | | | |
|---|---|---|---|
| 1 | 1.472683110 | 2.305046460 | -1.415340260 |
| 6 | 2.644397070 | 4.168505550 | 1.161135960 |
| 1 | 2.206132010 | 3.800086150 | 3.233070900 |
| 1 | 2.893220080 | 4.280121240 | -0.970714080 |
| 1 | 3.255425200 | 5.020301230 | 1.357543940 |
| 1 | -5.007831410 | 2.596927250 | -1.095113610 |



**F**

| | | | |
|---|---|---|---|
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| 6 | -5.091209300 | -1.186273000 | 1.448540190 |
| 6 | -4.919476430 | -0.179690830 | 0.511393290 |
| 6 | -5.877691970 | 0.156607330 | -0.376171150 |
| 6 | -7.092200230 | -0.559615400 | -0.353876850 |
| 6 | -7.289980550 | -1.598621460 | 0.586749900 |
| 1 | -6.407757190 | -2.695211820 | 2.229115490 |
| 1 | -5.719583560 | 0.947117540 | -1.080054900 |
| 1 | -7.866827010 | -0.316258960 | -1.050295440 |
| 1 | -8.212369190 | -2.141011290 | 0.598844370 |
| 6 | -3.543724310 | 0.448788100 | 0.696641670 |
| 7 | -3.909825080 | -1.328909230 | 2.336859450 |
| 6 | -3.191085350 | -0.055733600 | 2.098486030 |

| | | | |
|---|---|---|---|
| 8 | -2.427360430 | 0.520541470 | 2.915605890 |
| 7 | -3.491464470 | 1.946538330 | 0.636810700 |
| 6 | -2.124676600 | 2.211674480 | 0.229290100 |
| 6 | -4.180183690 | 2.904499430 | -0.240413180 |
| 6 | -1.895023670 | 3.493874220 | -0.002211000 |
| 6 | -3.310996370 | 3.975202910 | -0.412046500 |
| 1 | -0.975367350 | 4.039179230 | 0.029219850 |
| 1 | -3.567042910 | 4.947067530 | -0.779075040 |
| 6 | -2.446008580 | -0.050060750 | -0.266662630 |
| 6 | -2.876265070 | 0.059473550 | -1.740991380 |
| 1 | -3.713255280 | -0.583463680 | -1.916836740 |
| 1 | -3.151400510 | 1.070417280 | -1.957832580 |
| 6 | -1.312304550 | 0.958518640 | 0.007216350 |
| 6 | 0.031395730 | 0.784948630 | -0.005973110 |
| 7 | -1.760101900 | -0.341382710 | -2.610421620 |
| 8 | -1.981270420 | -0.840943000 | -3.675134520 |
| 8 | -0.630996590 | -0.168140170 | -2.253496110 |
| 6 | -4.284823160 | -1.530180410 | 3.744045080 |
| 1 | -4.834367660 | -2.443652960 | 3.839929850 |
| 1 | -3.400842560 | -1.580779870 | 4.344286560 |
| 1 | -4.892978550 | -0.712431760 | 4.071905690 |
| 1 | -2.185324230 | -1.069000540 | -0.069180730 |
| 6 | 0.959120650 | 1.975995440 | 0.298477780 |
| 6 | 1.403525780 | 2.800623110 | -0.744939310 |
| 6 | 1.357531730 | 2.237529940 | 1.615712680 |
| 6 | 2.239735090 | 3.891021420 | -0.469540480 |
| 1 | 1.103507030 | 2.597063780 | -1.750998470 |
| 6 | 2.190885640 | 3.329719710 | 1.891507580 |
| 1 | 1.024820090 | 1.603576590 | 2.411020960 |
| 6 | 2.631227970 | 4.157012940 | 0.849358080 |

| | | | |
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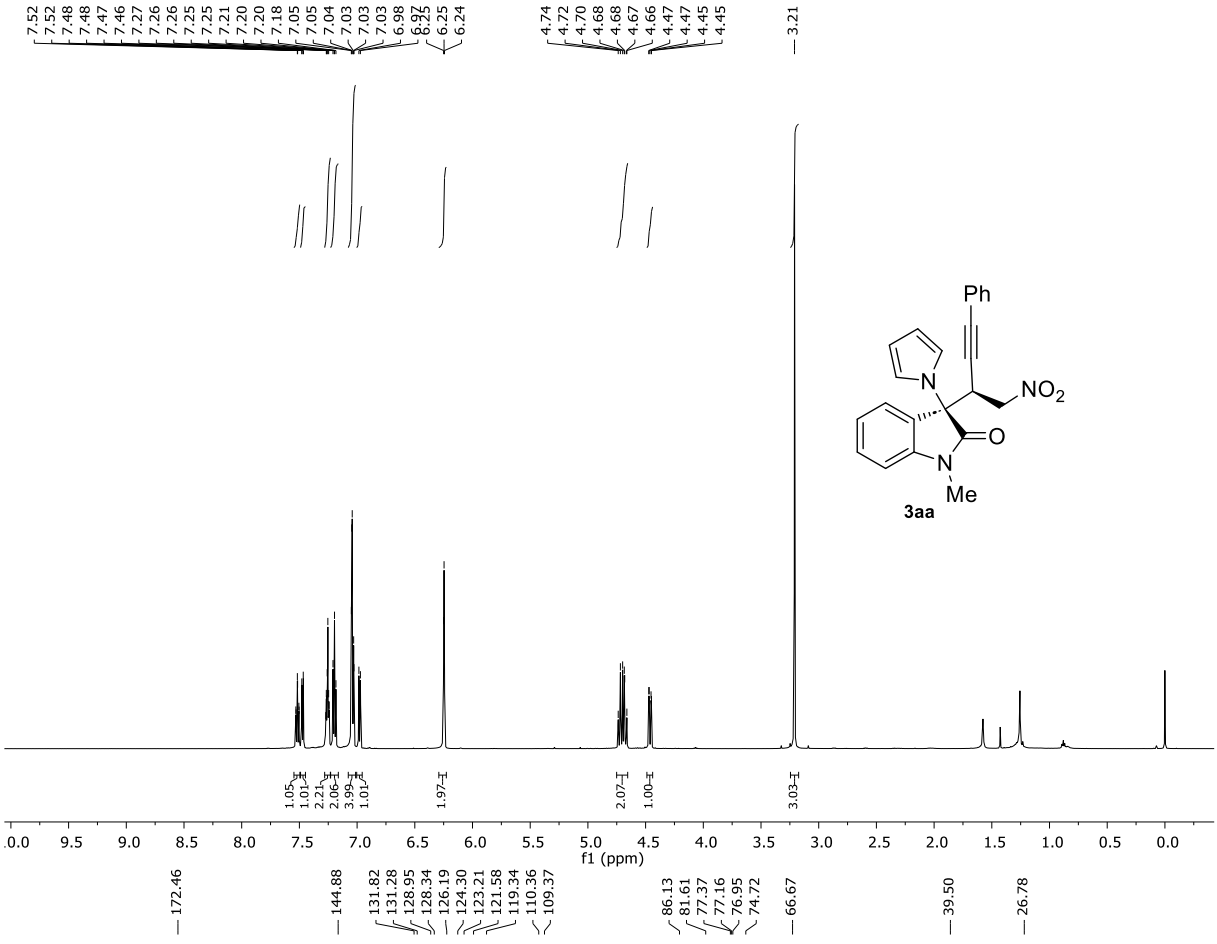
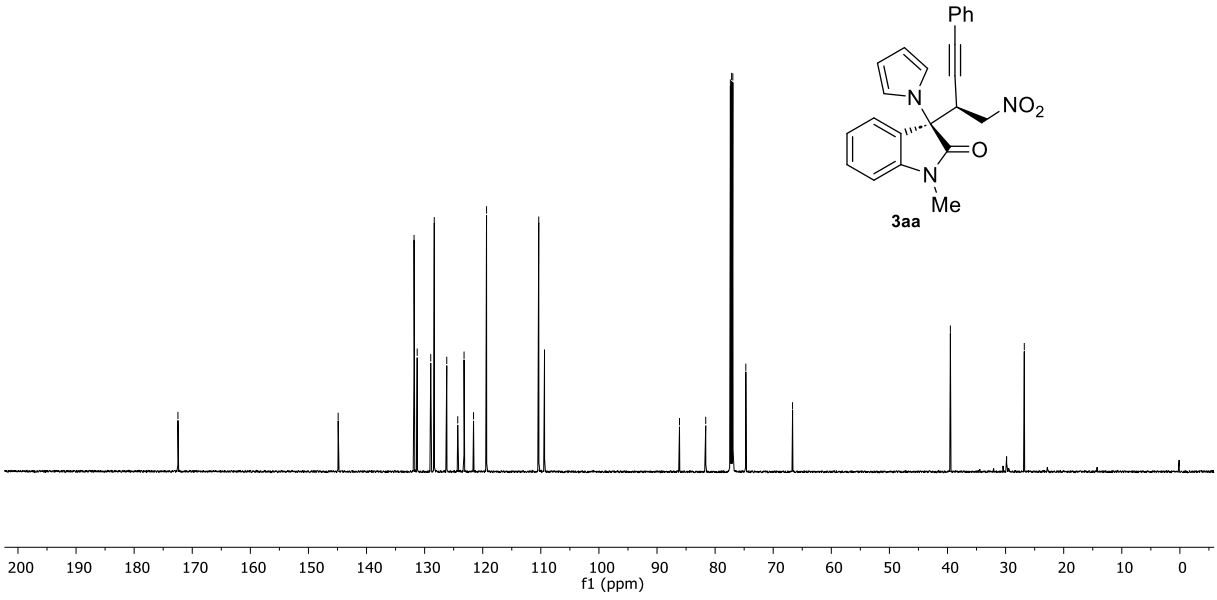
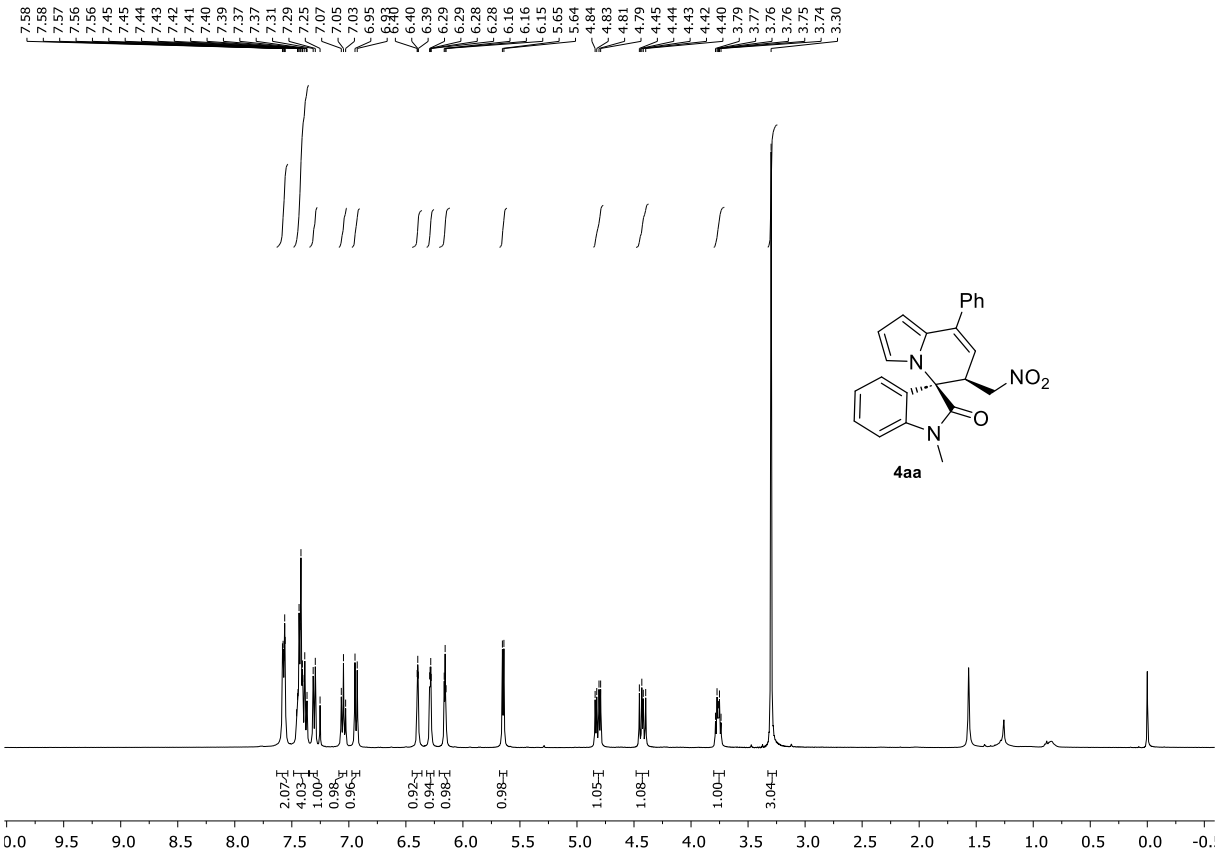
| 1 | 2.578961520 | 4.520216260 | -1.265893190 |
| 1 | 2.491361780 | 3.532514570 | 2.897762640 |
| 1 | 3.266560850 | 4.991542990 | 1.060852560 |
| 1 | -5.165764300 | 2.807269630 | -0.646005730 |
| 1 | 0.446154480 | -0.177395570 | -0.224707990 |

## 16. NMR spectra of the products:

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7.58
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7.56
7.56
7.45
7.45
7.44
7.43
7.42
7.41
7.40
7.39
7.37
7.37
7.31
7.29
7.25
7.07
7.05
7.03
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6.40
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6.28
6.28
6.16
6.16
6.15
5.65
5.64
4.84
4.83
4.81
4.79
4.45
4.44
4.43
4.42
4.40
3.79
3.77
3.76
3.76
3.75
3.74
3.30
Ph
N
NO2
O
N
4aa
2.07
4.03
1.00
0.98
0.96
0.92
0.94
0.98
0.98
1.05
1.08
1.00
3.04
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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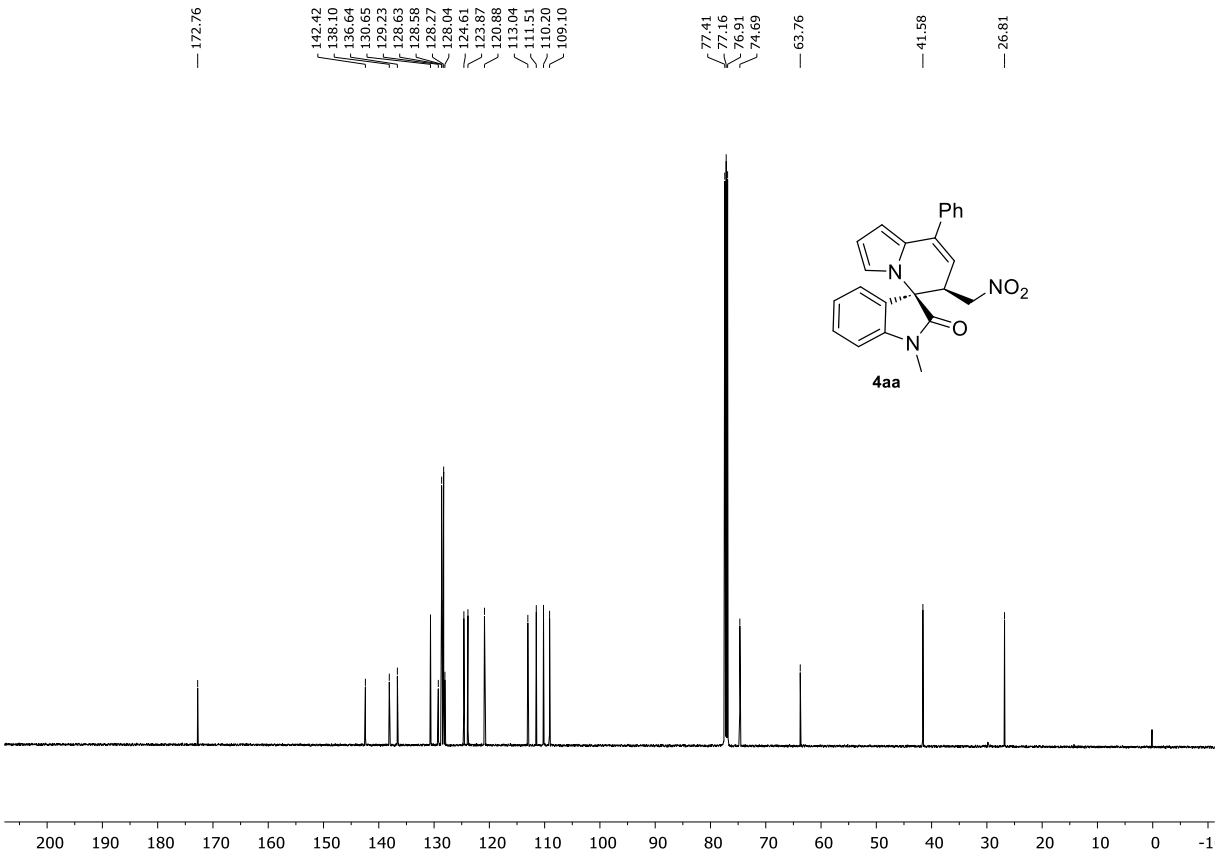
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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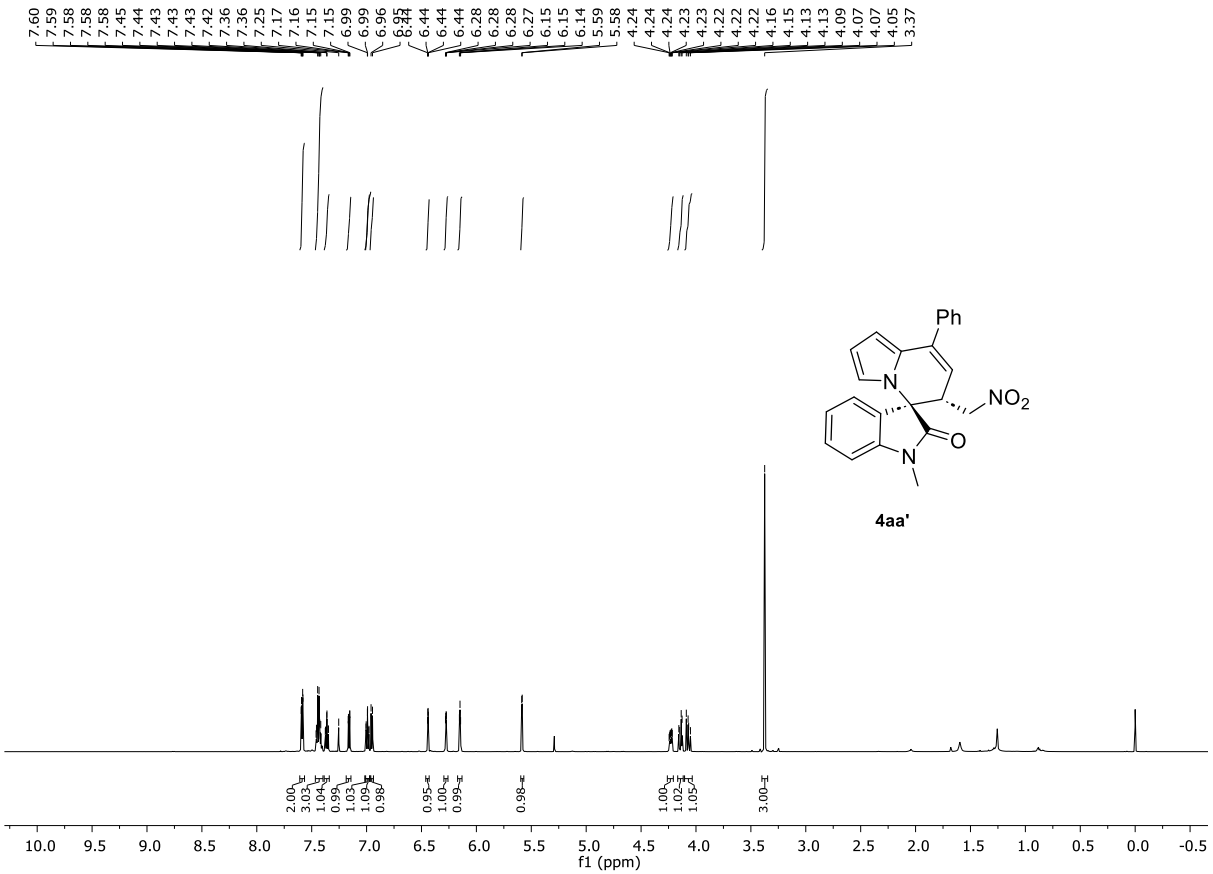
142.42
138.10
136.64
130.65
129.23
128.63
128.58
128.27
128.04
124.61
123.87
120.88
113.04
111.51
110.20
109.10
77.41
77.16
76.91
74.69
63.76
41.58
26.81
Ph
N
NO2
O
N
4aa
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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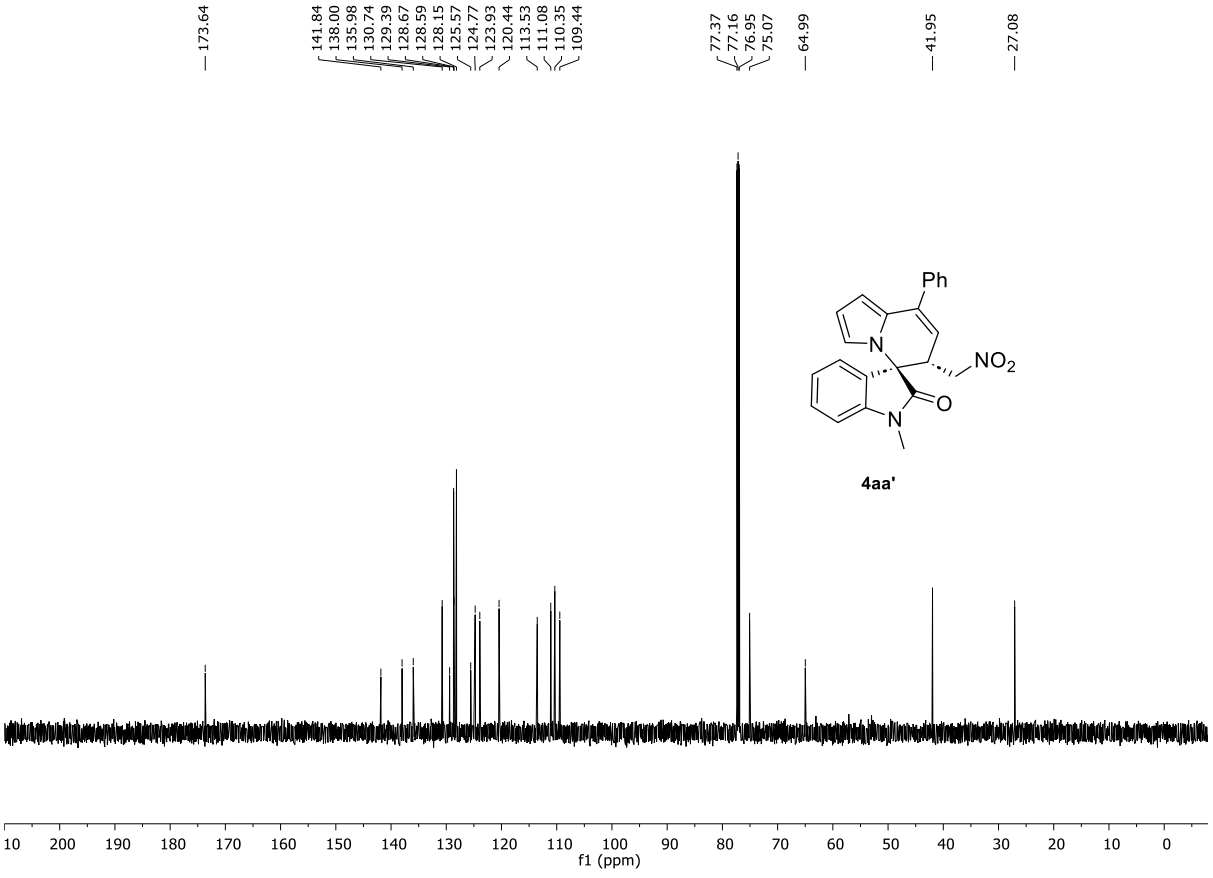
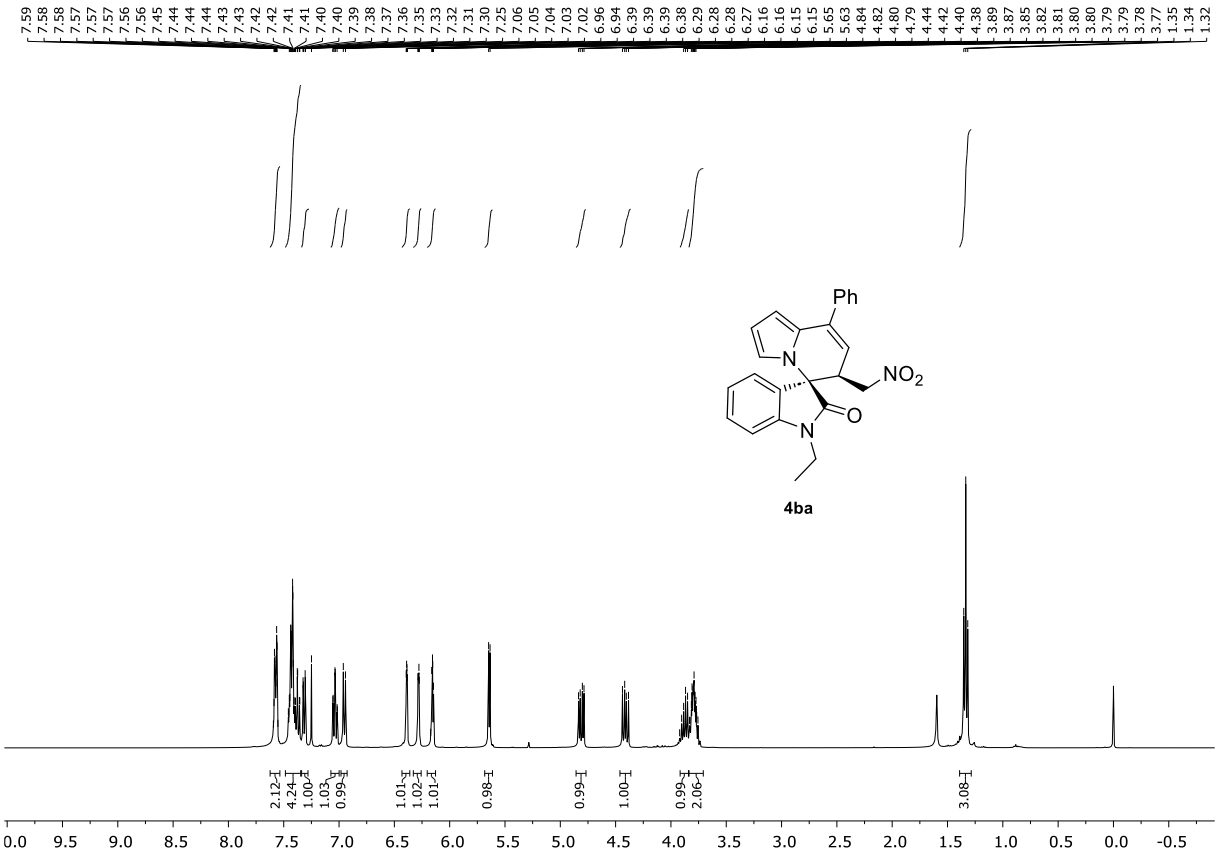
Ph
N
NO2
O
N
4aa'
2.00 3.03 1.04 0.99 1.03 1.09 0.98 0.95 1.00 0.99 0.98 1.00 1.02 1.05 3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


173.64
141.84 138.00 135.98 130.74 129.39 128.67 128.59 128.15 125.57 124.77 123.93 120.44 113.53 111.08 110.35 109.44
77.37 77.16 76.95 75.07
64.99
41.95
27.08
Ph
N
NO2
O
N
4aa'
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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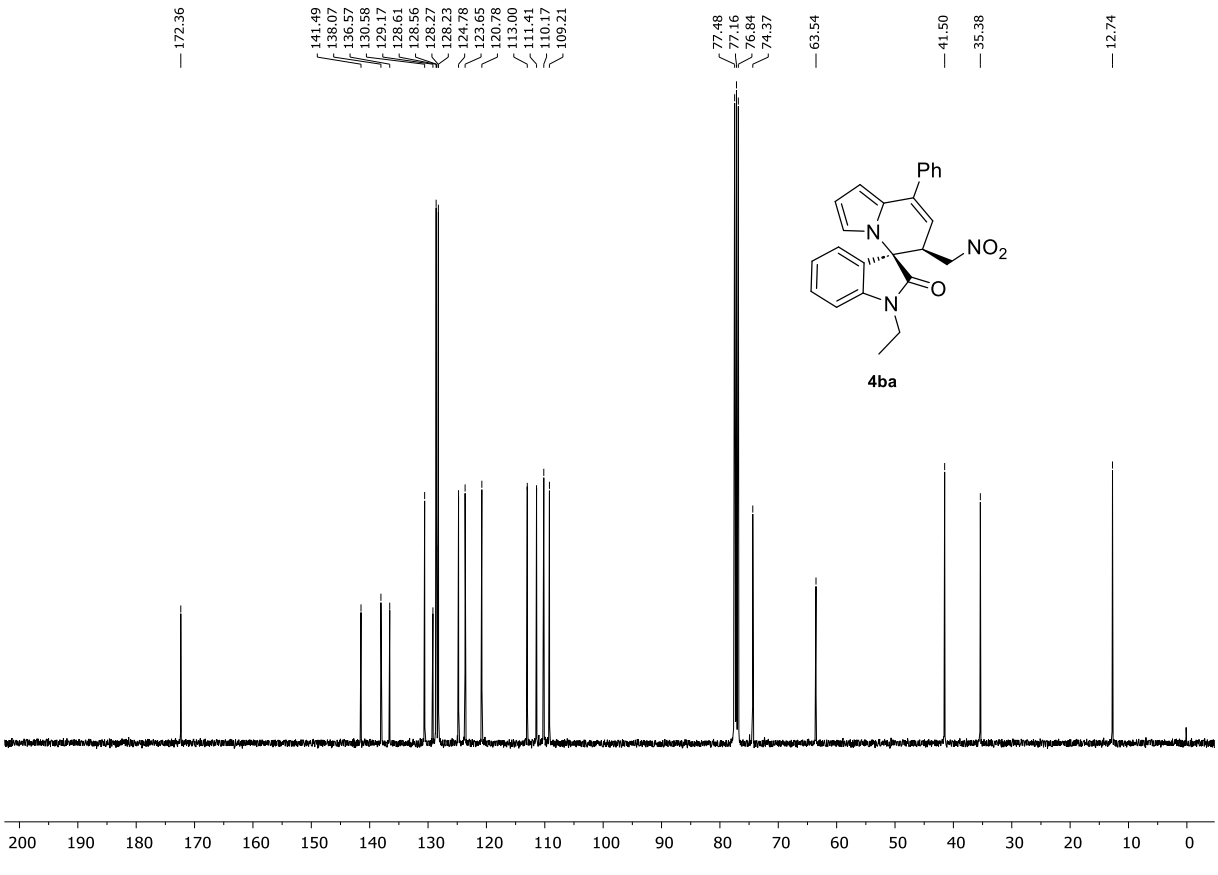
Ph
N
NO2
O
N
4ba
2.12 4.24 1.00 1.03 0.99 1.01 1.02 1.01 0.98 0.99 1.00 0.99 2.06 3.08
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5


172.36
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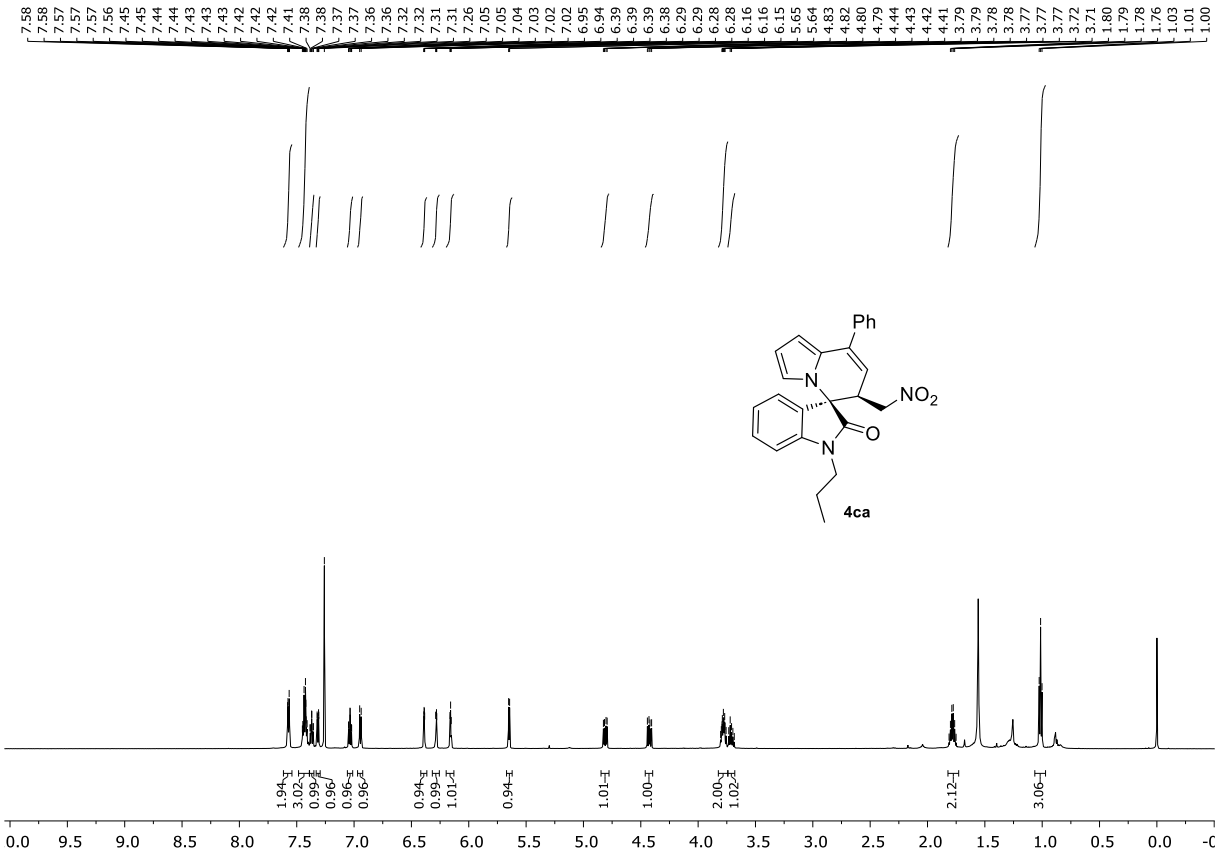
77.48 77.16 76.84 74.37
63.54
41.50
35.38
12.74
Ph
N
NO2
O
N
4ba
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


Ph
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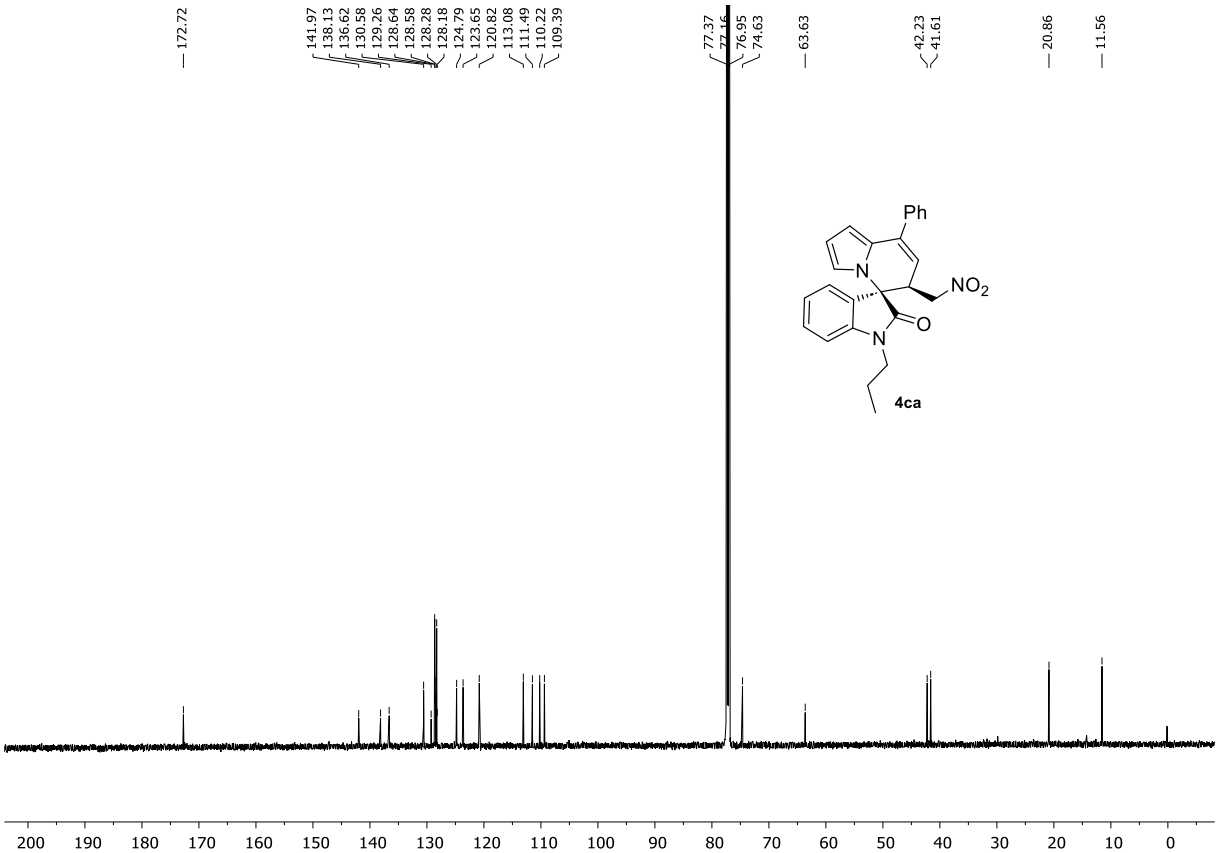
O
N
4ca


Ph
NO2
O
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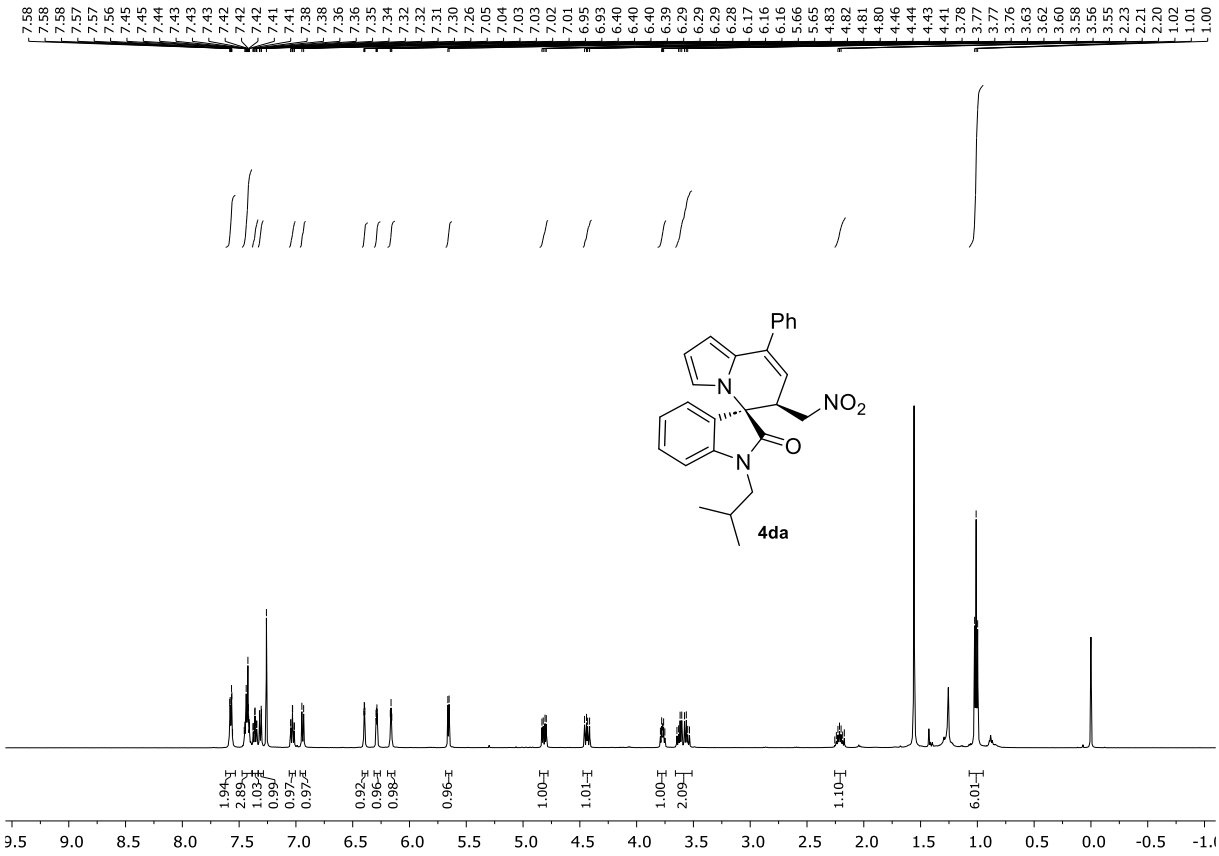
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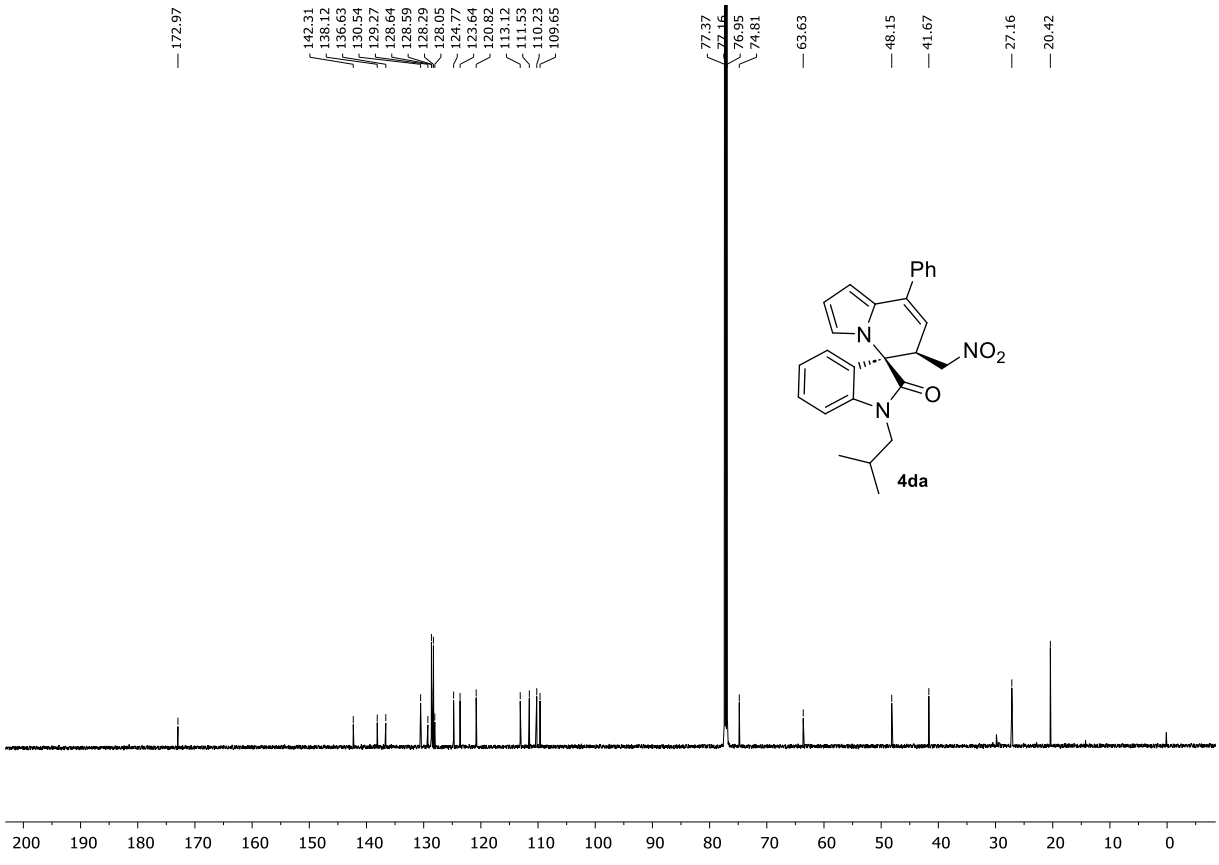
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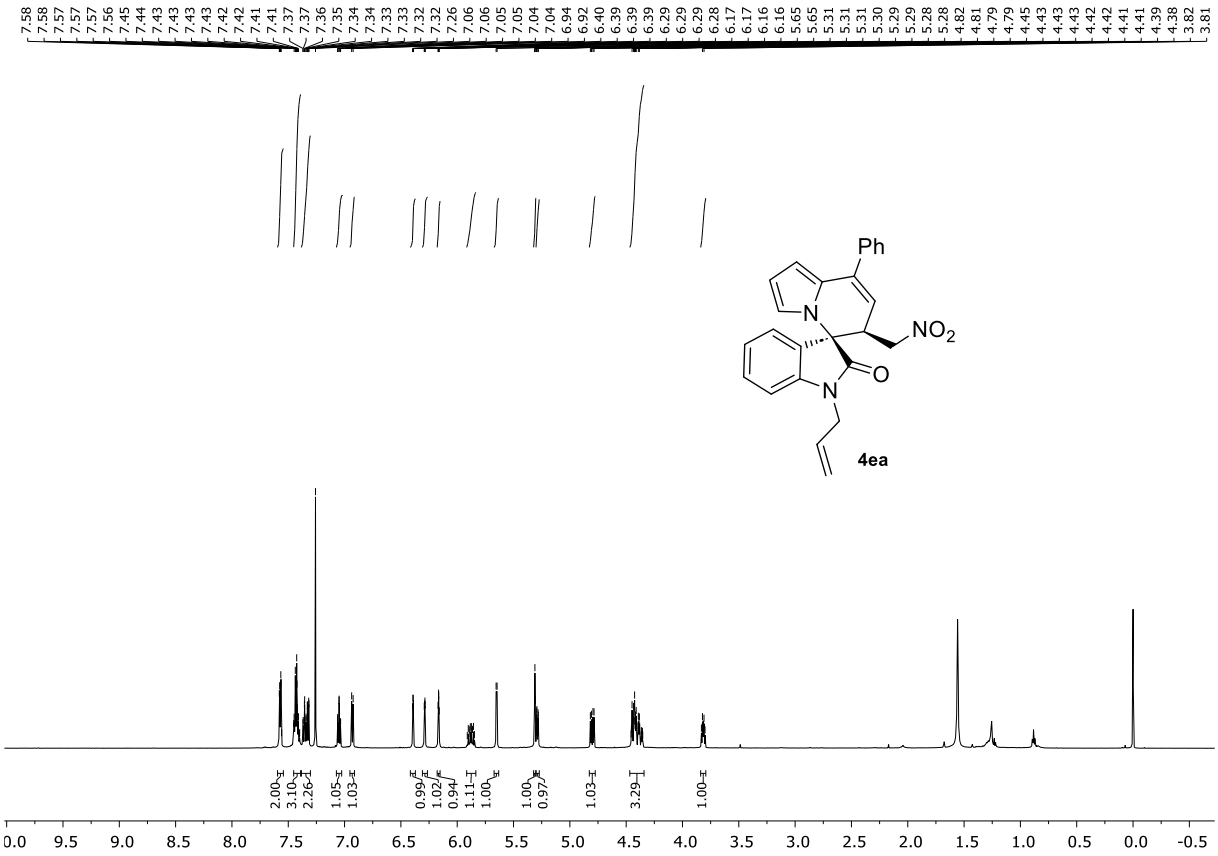
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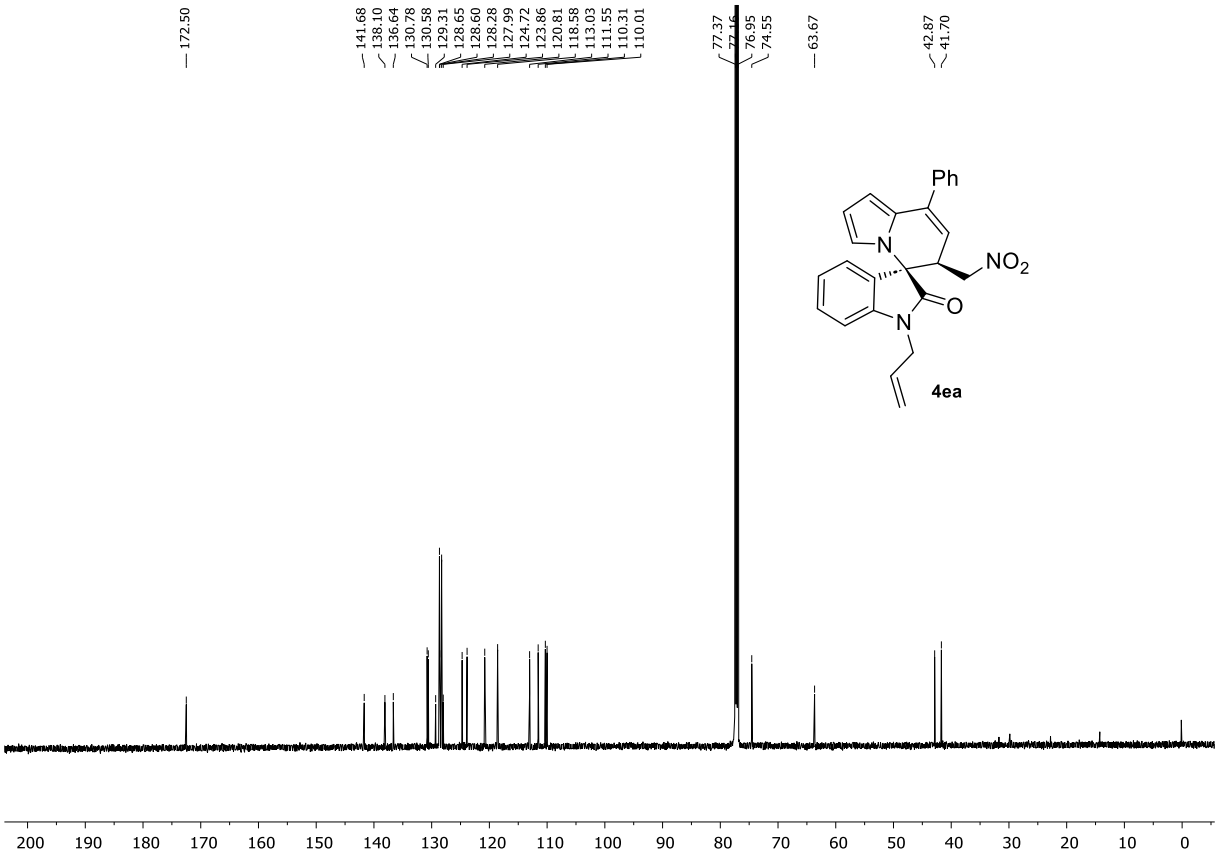
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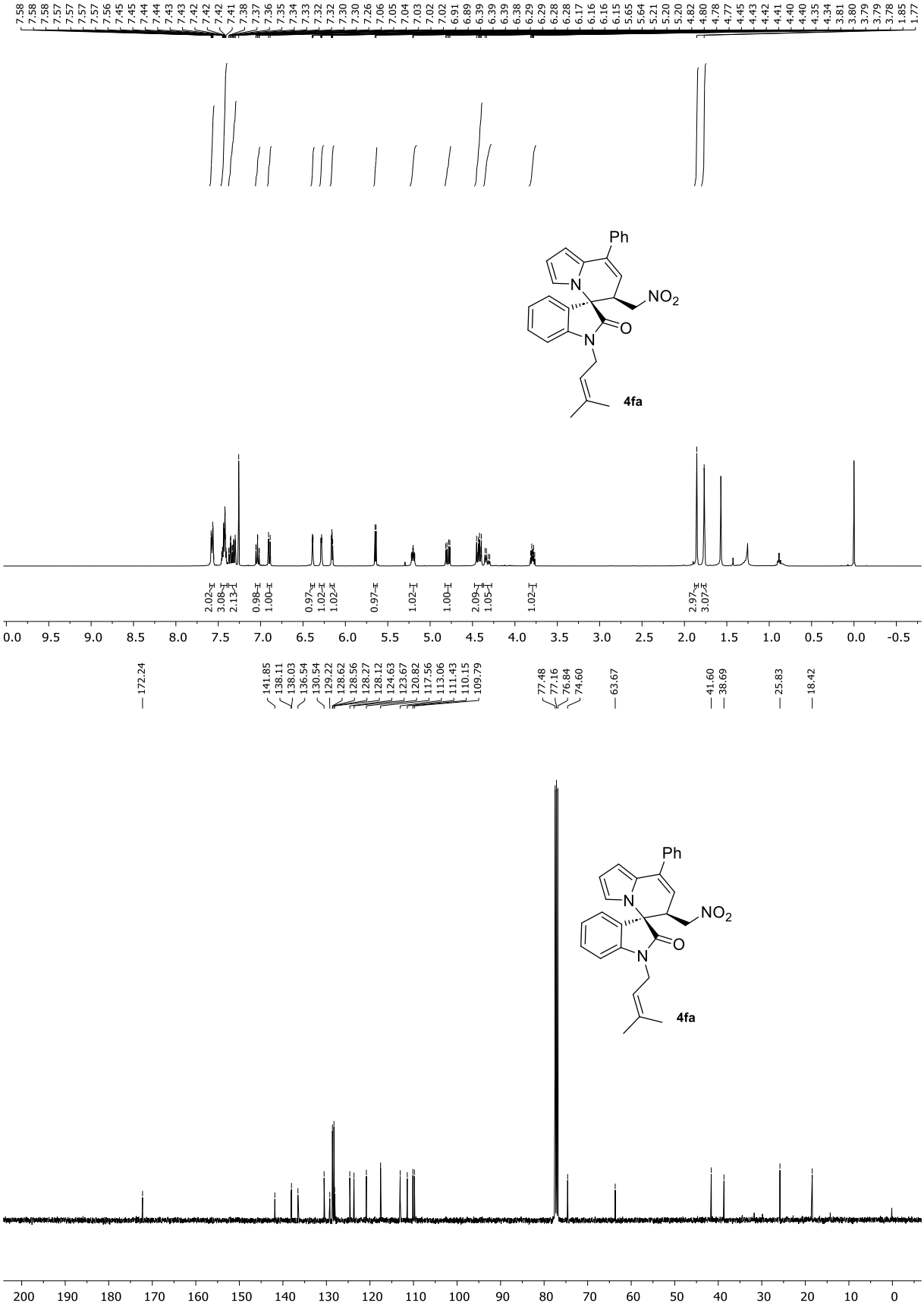
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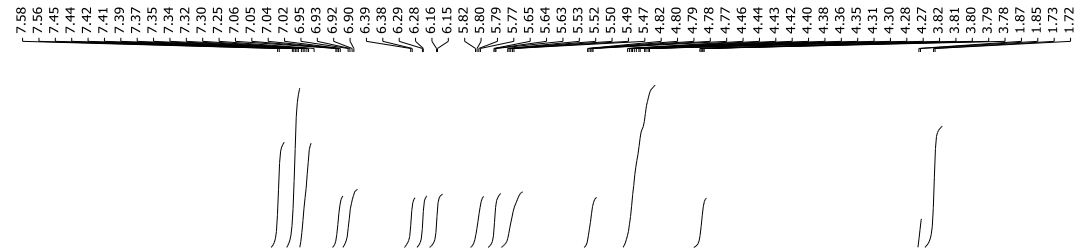

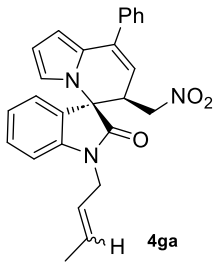


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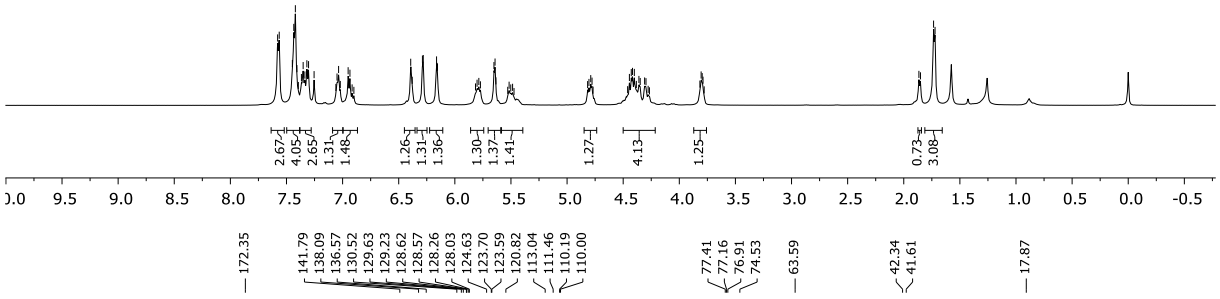

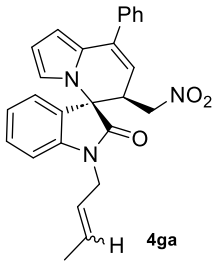


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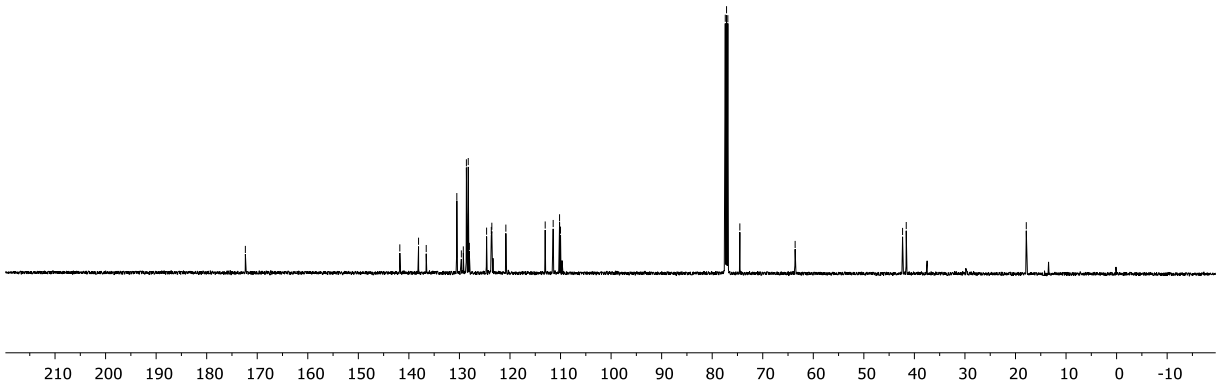

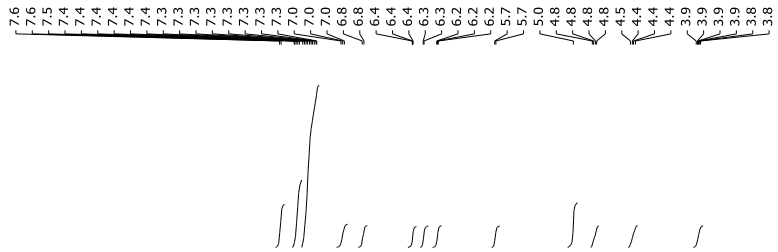

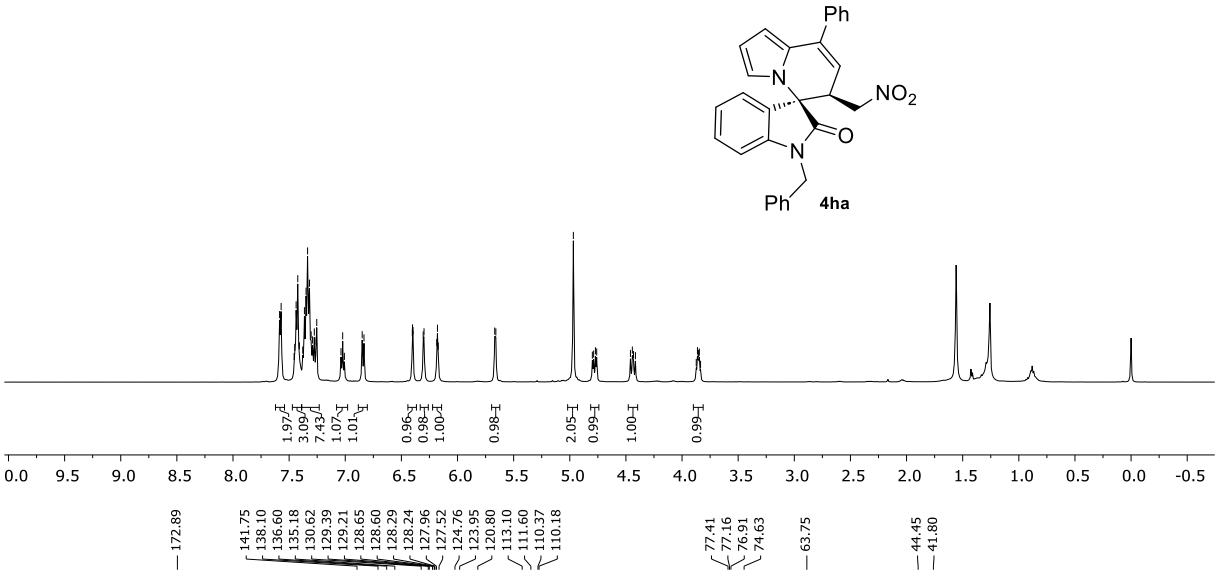
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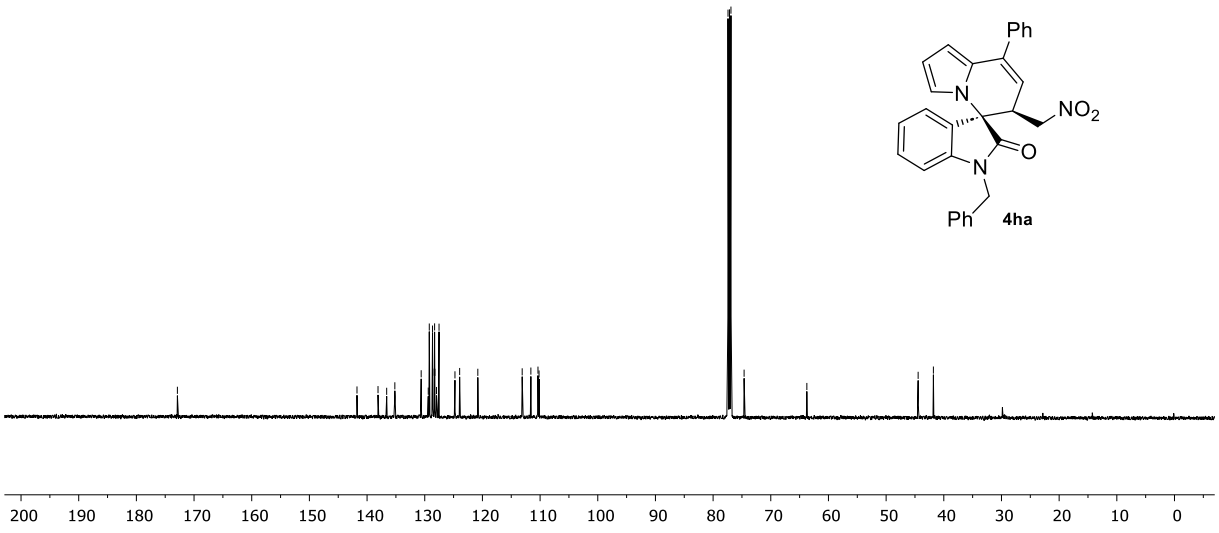
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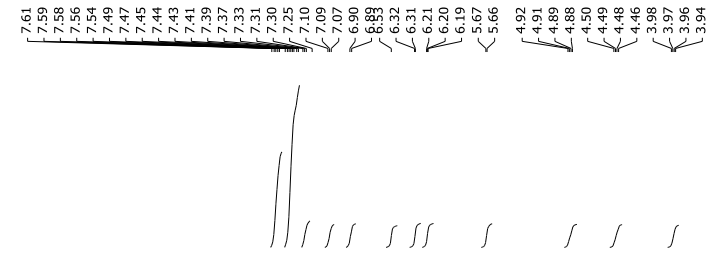
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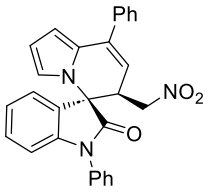
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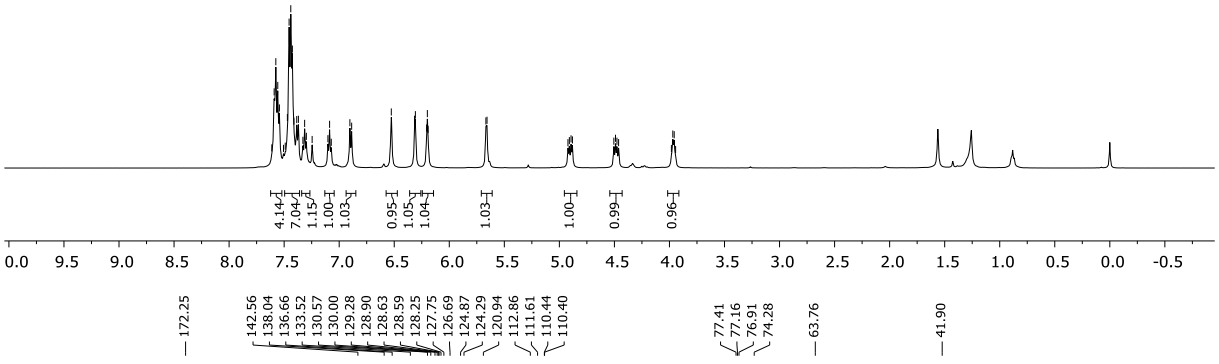
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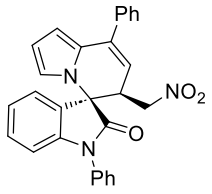
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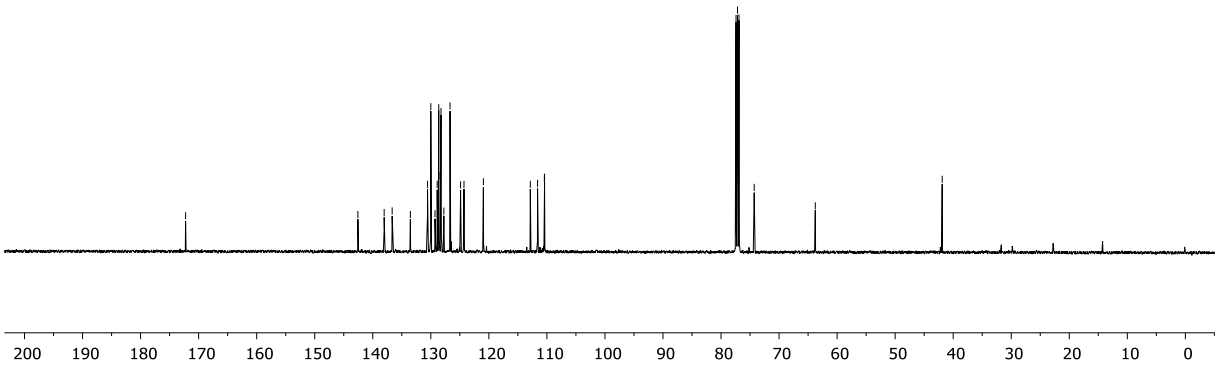
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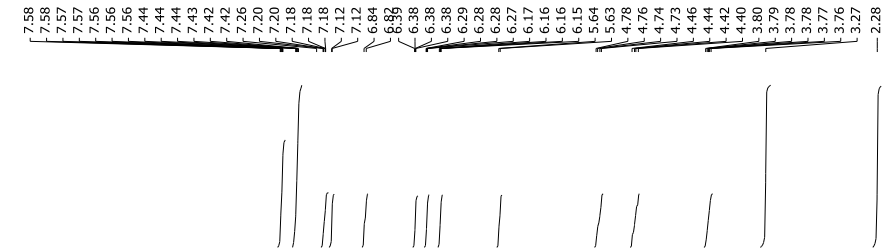
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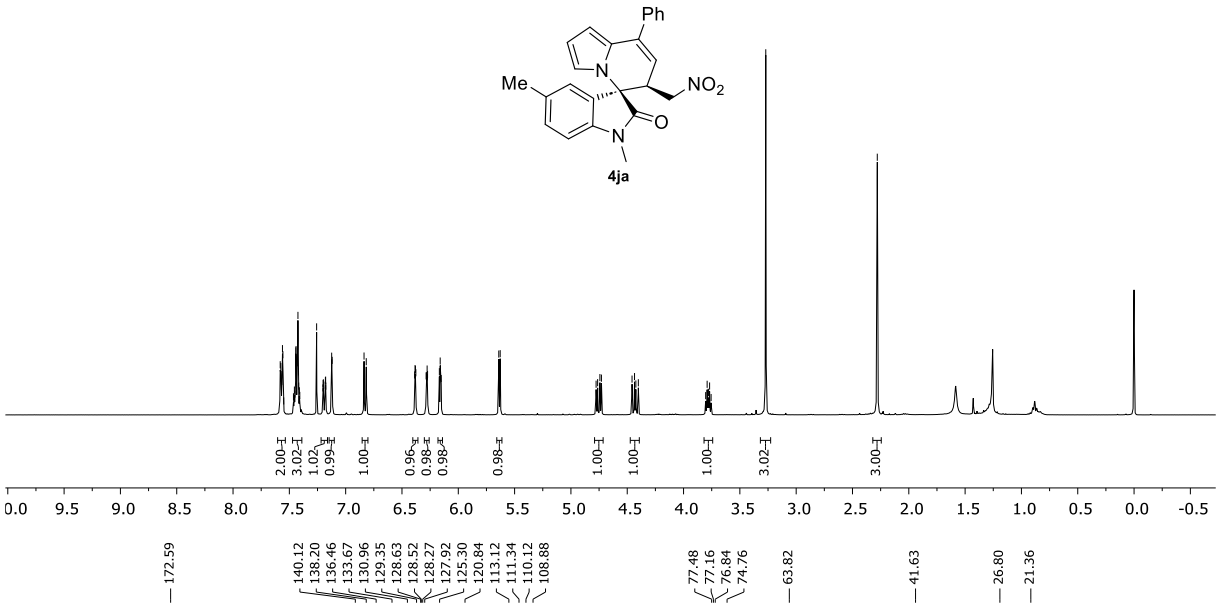
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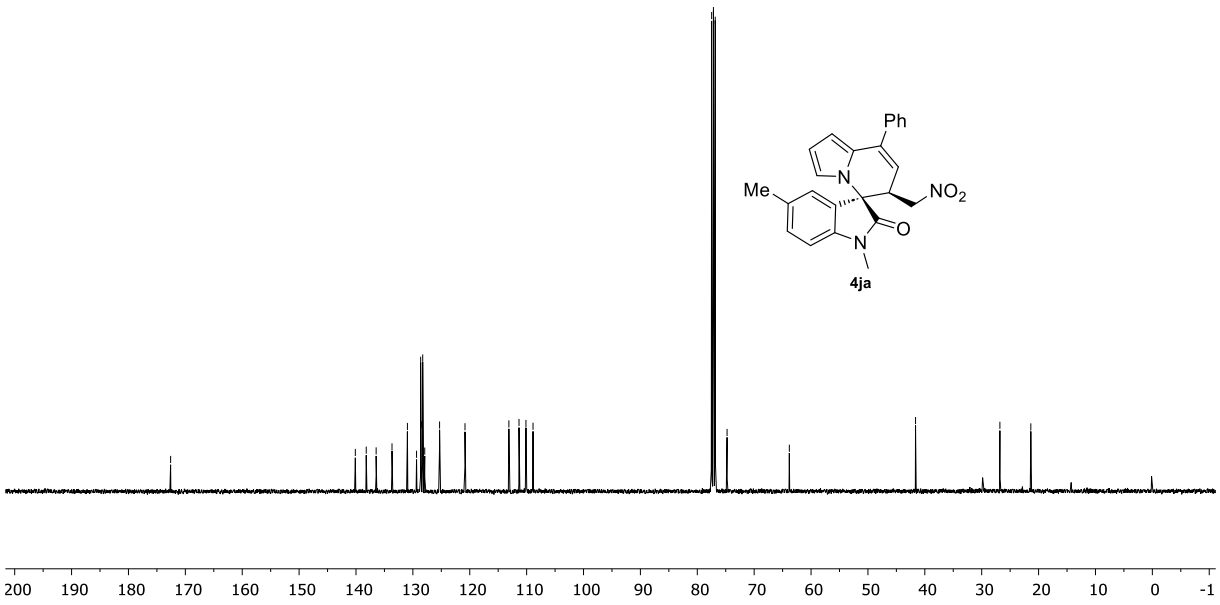
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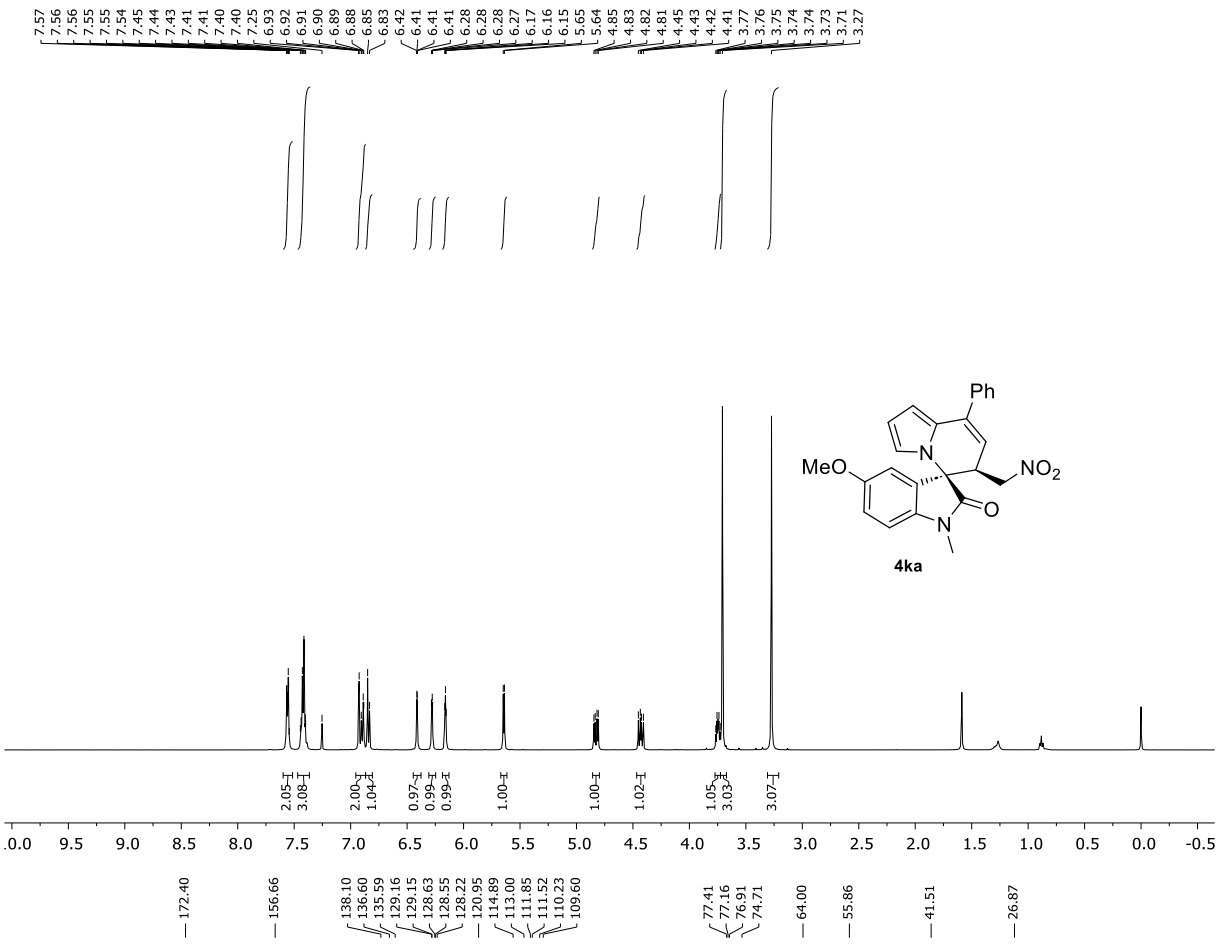
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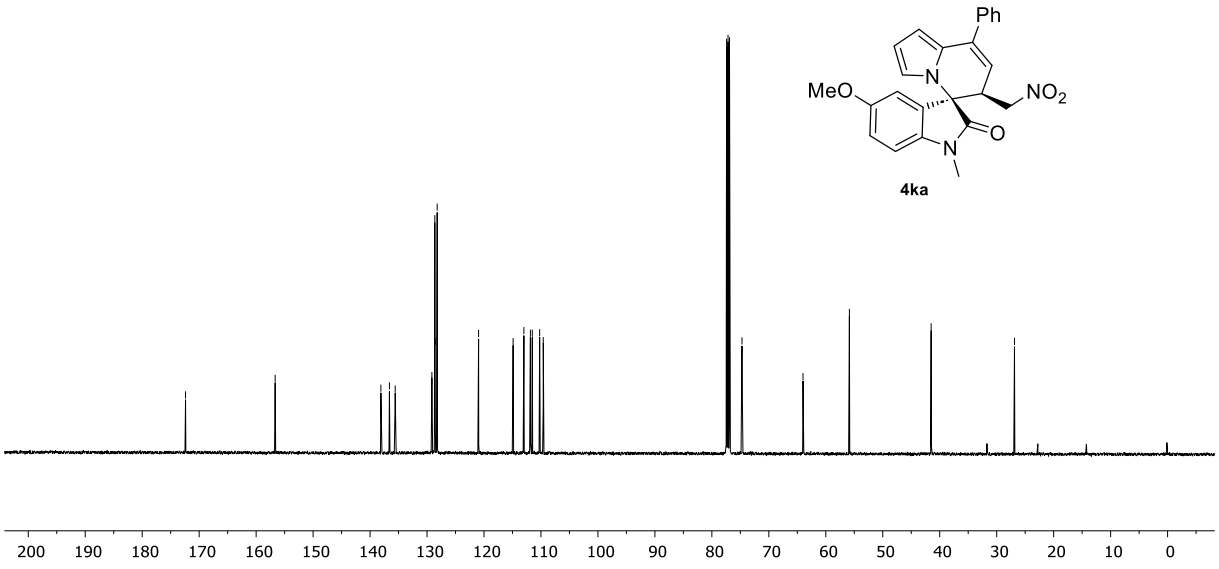
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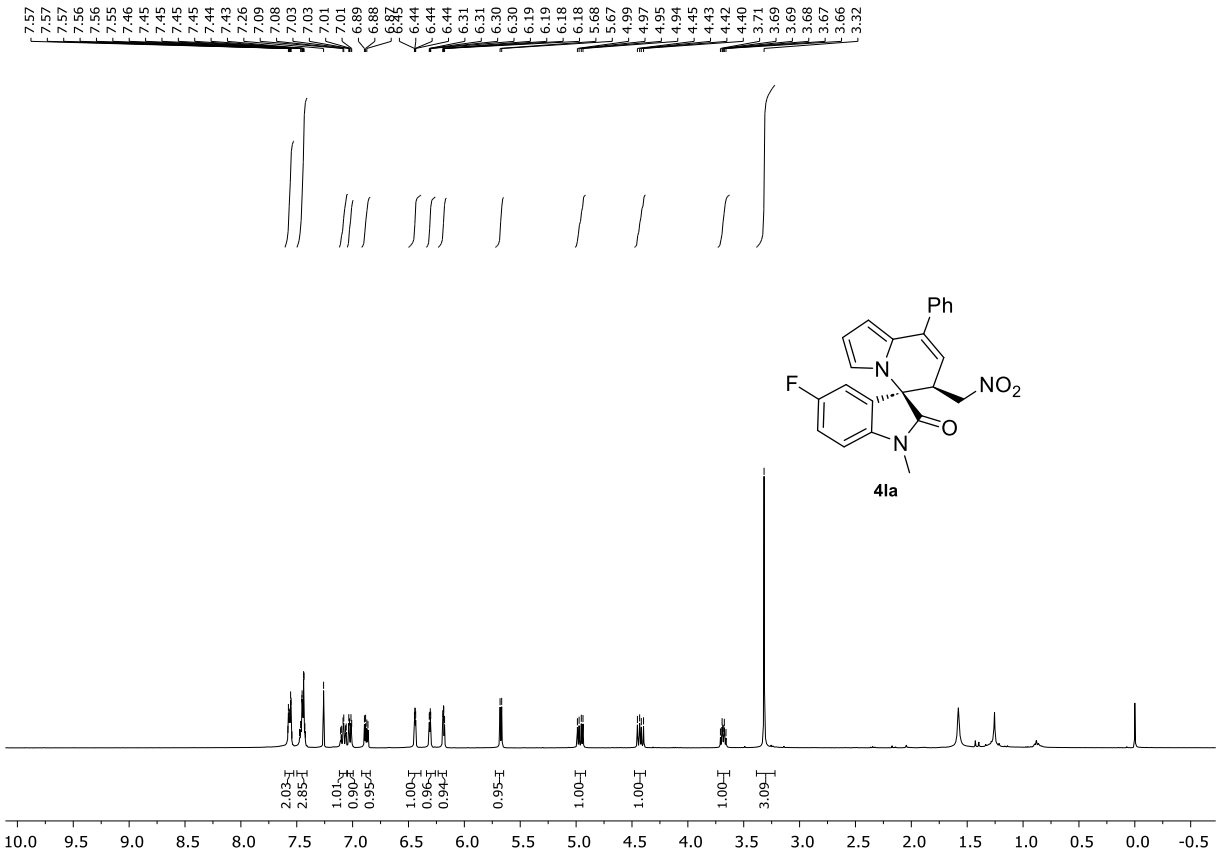
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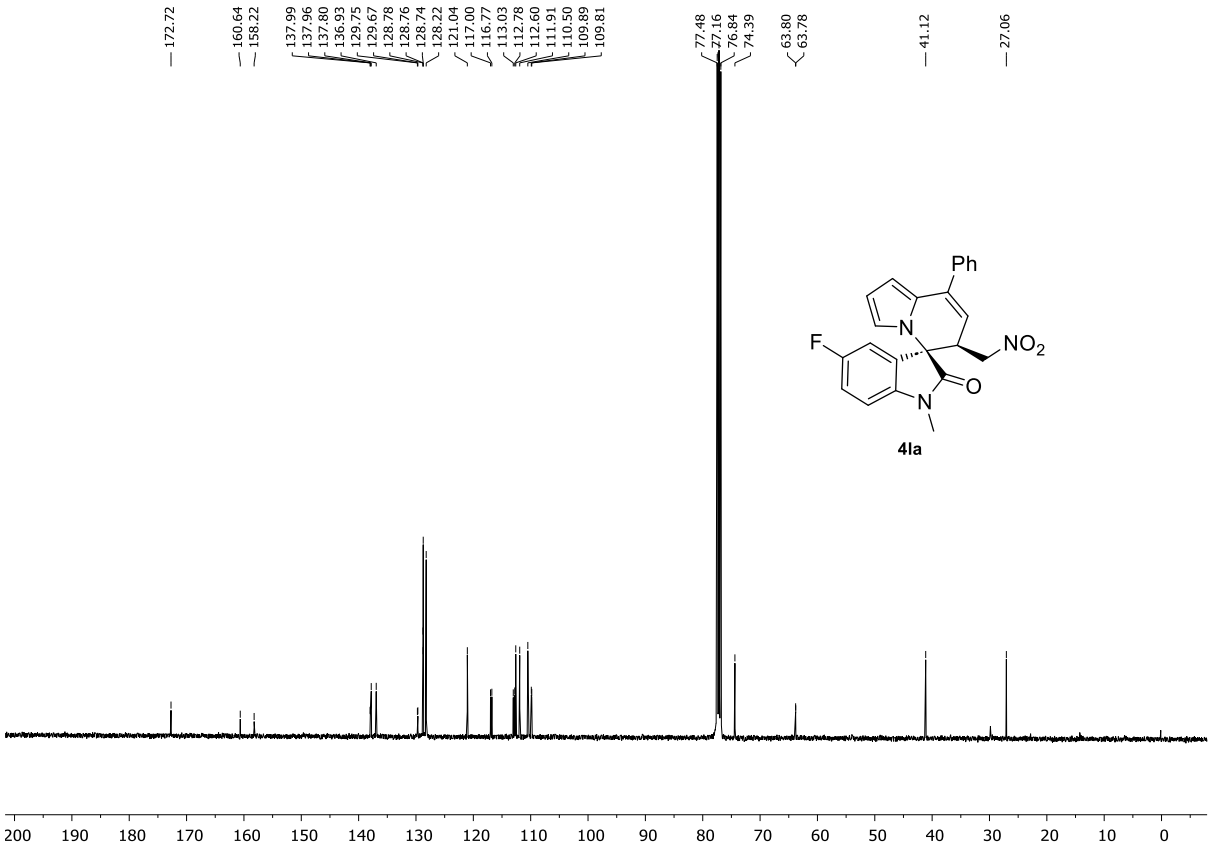
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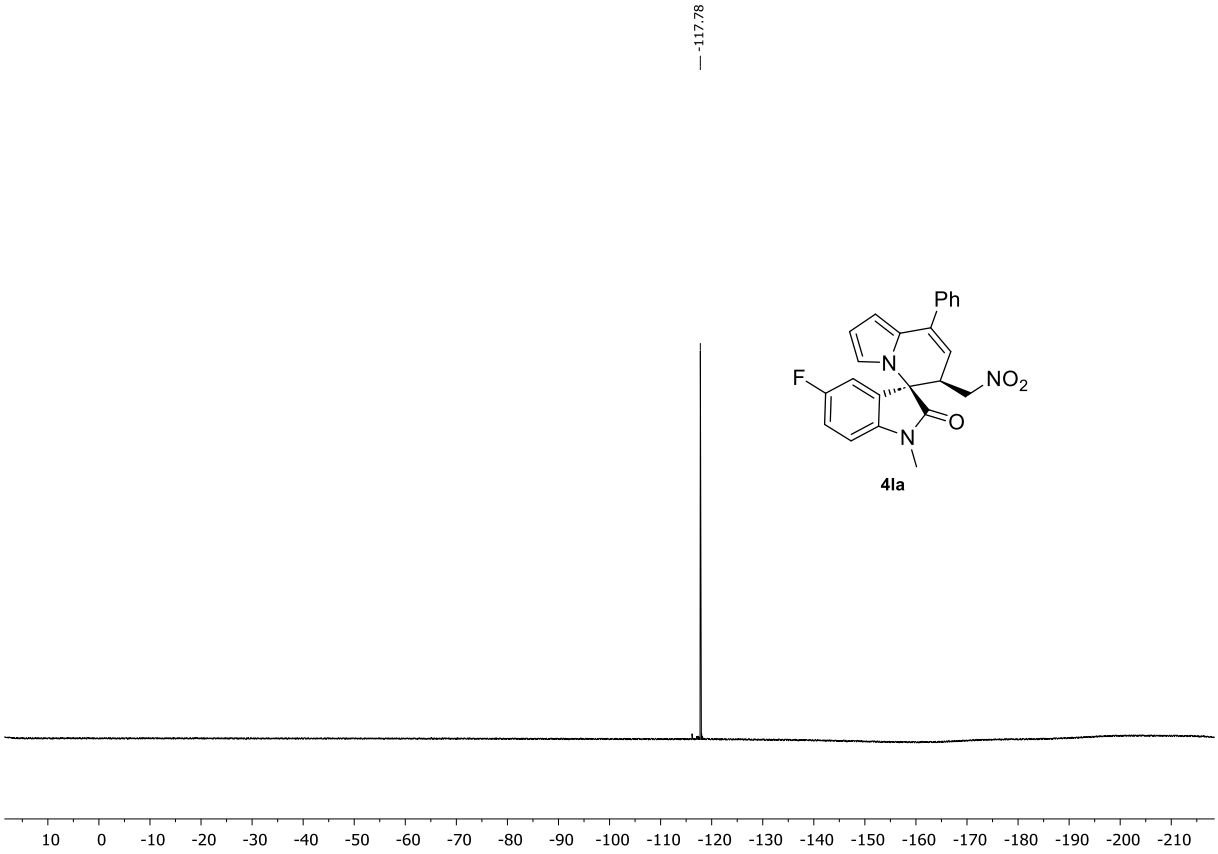
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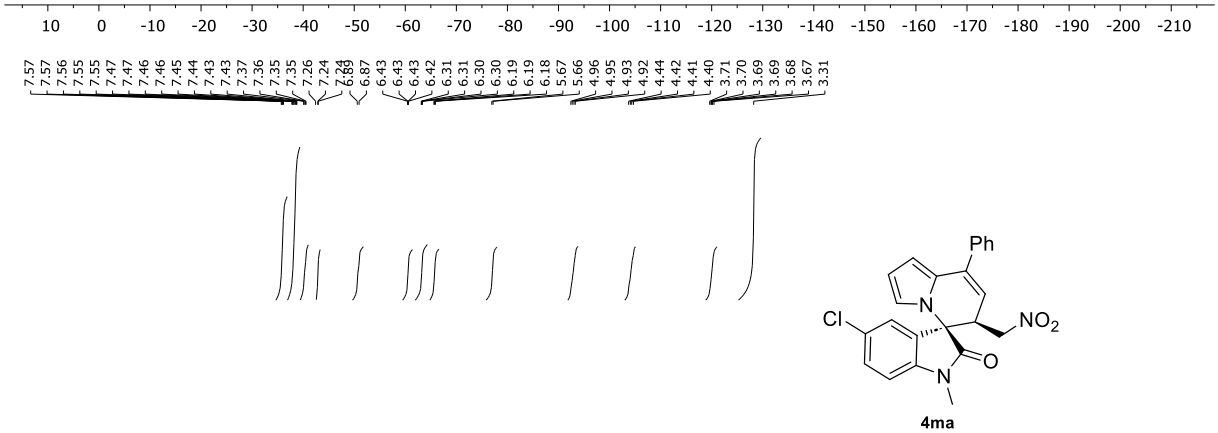
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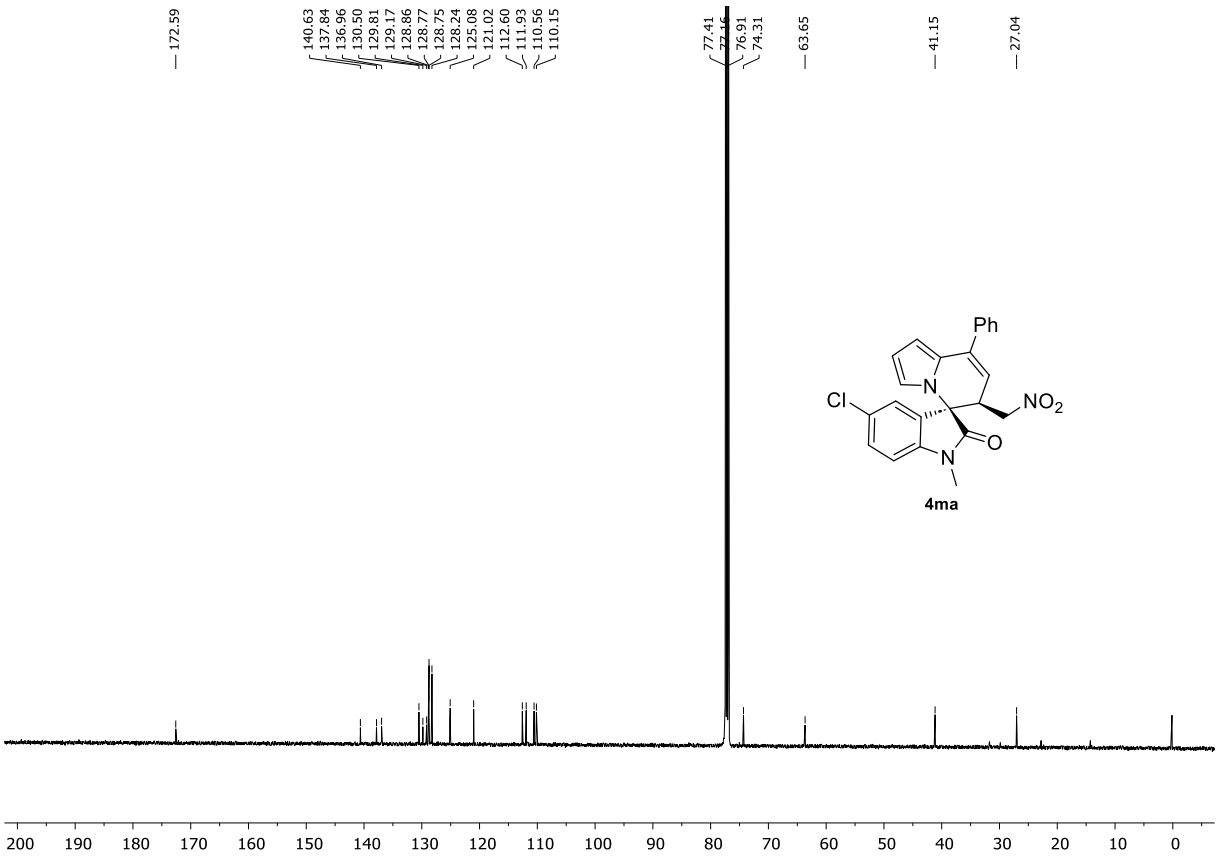
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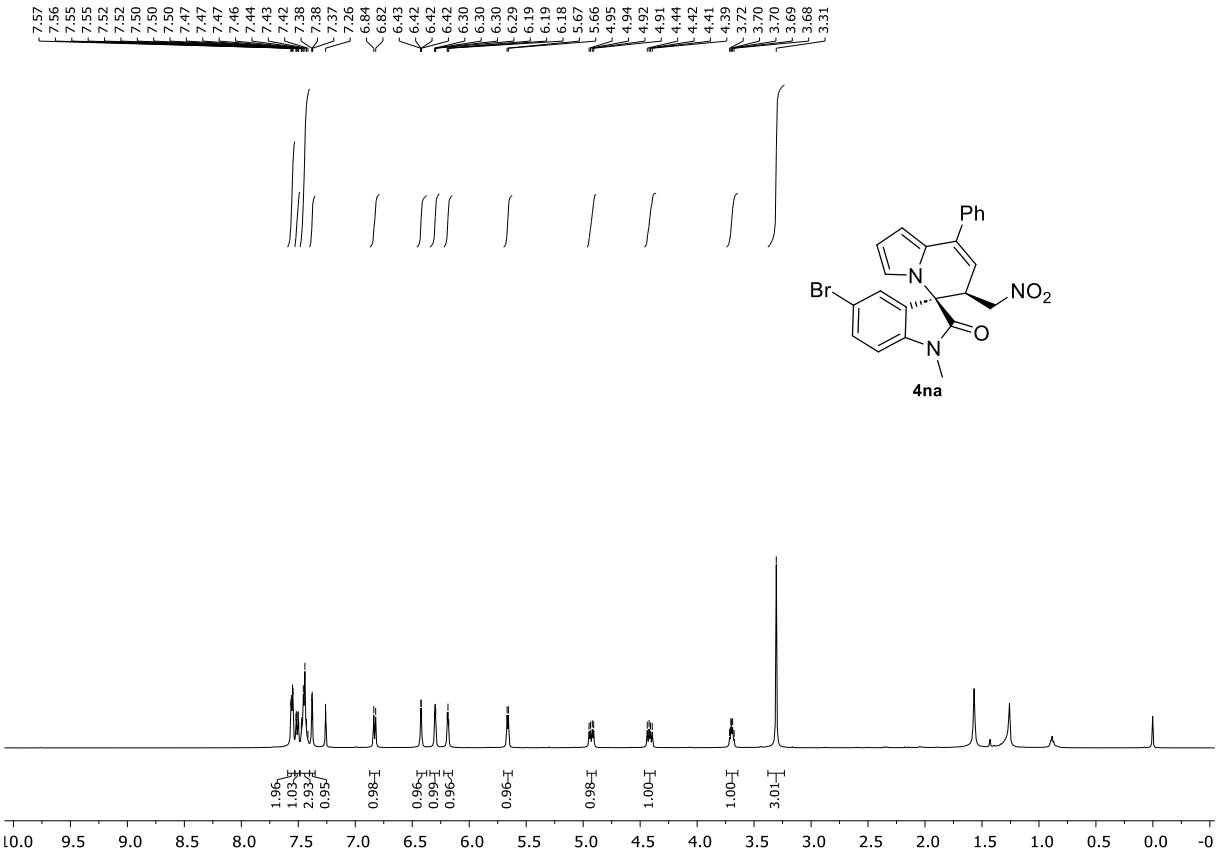
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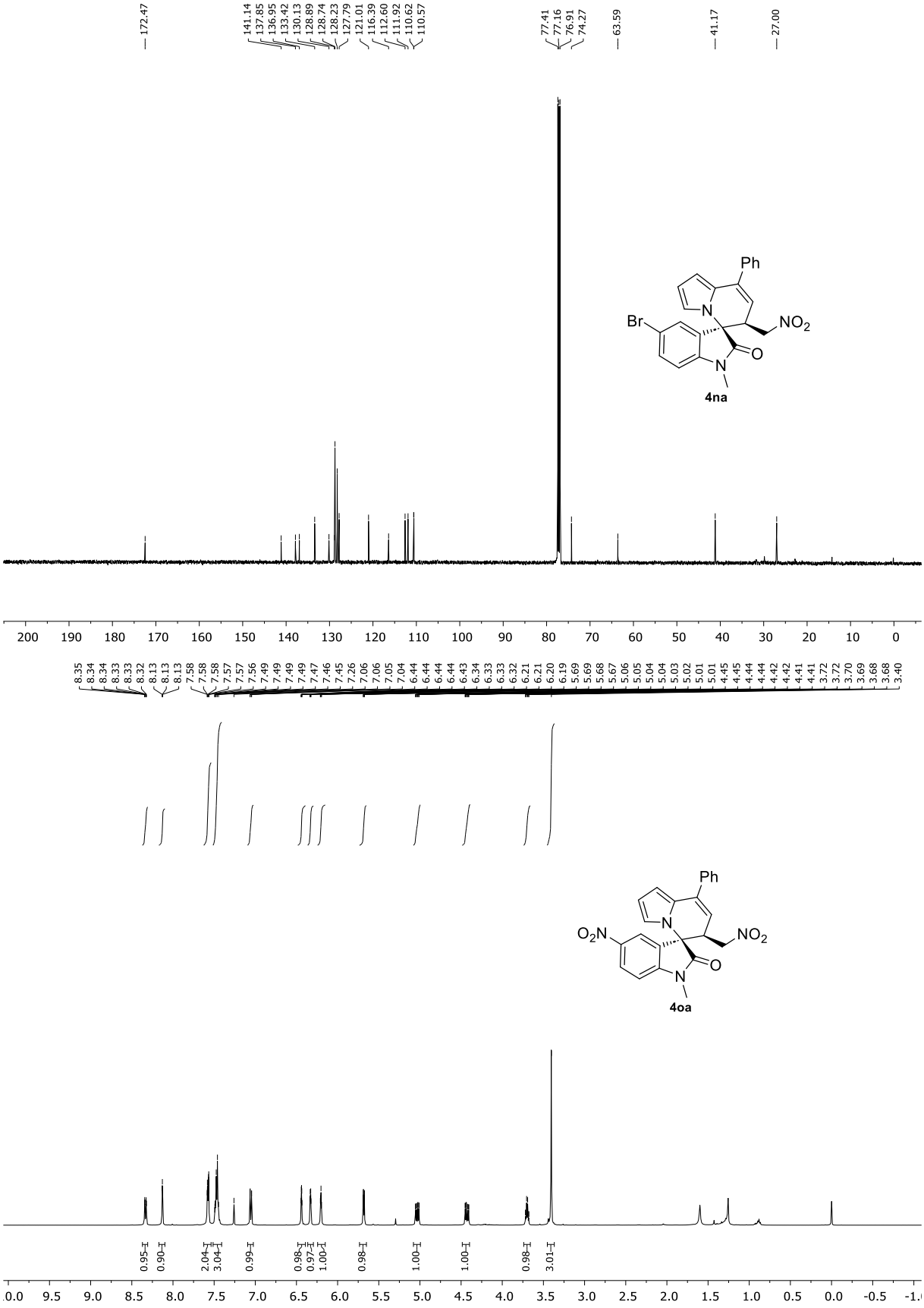
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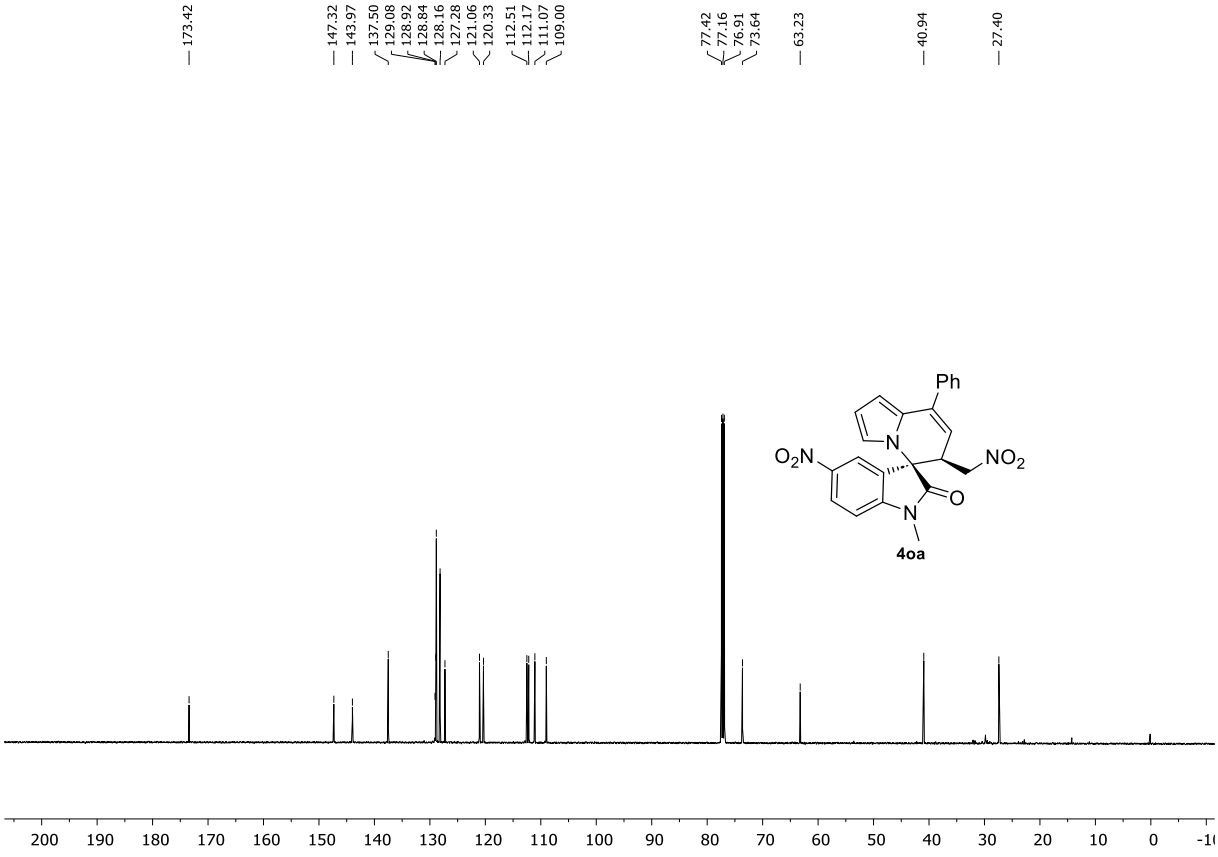
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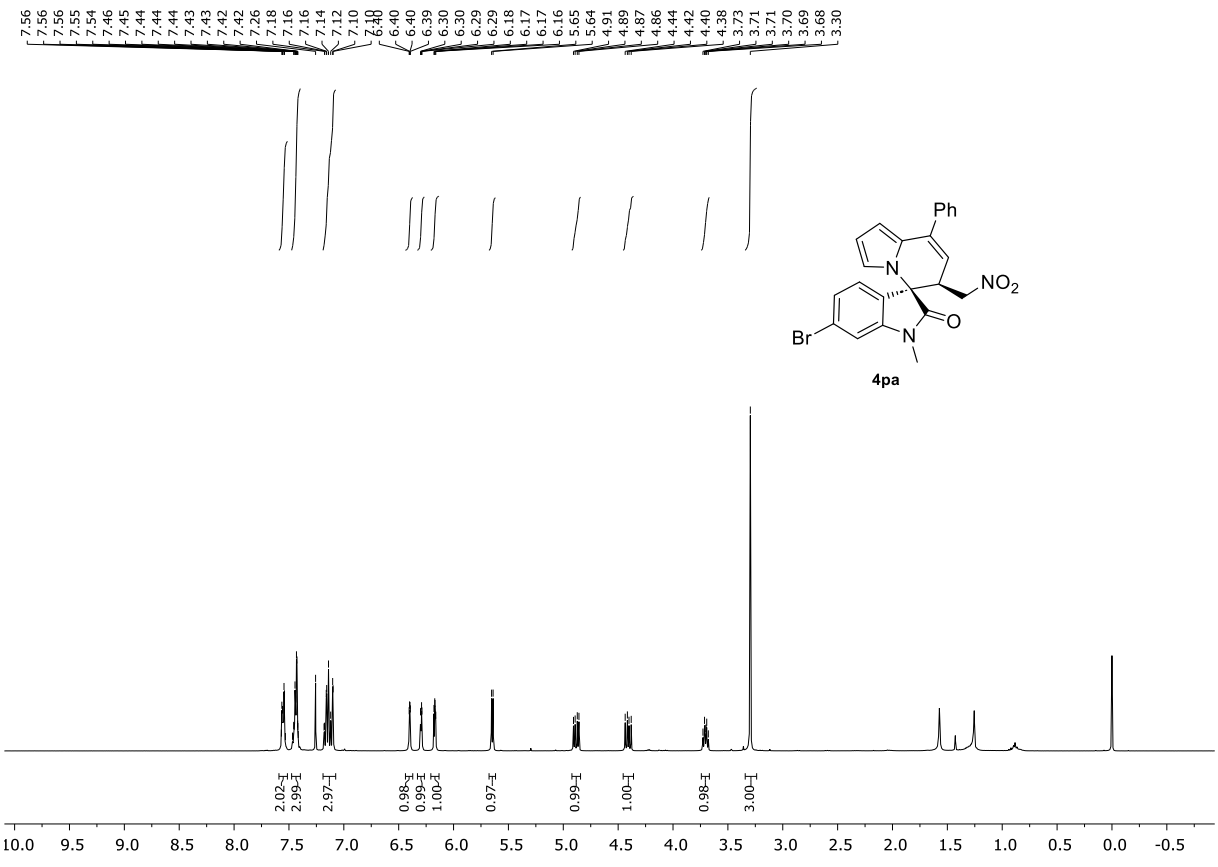
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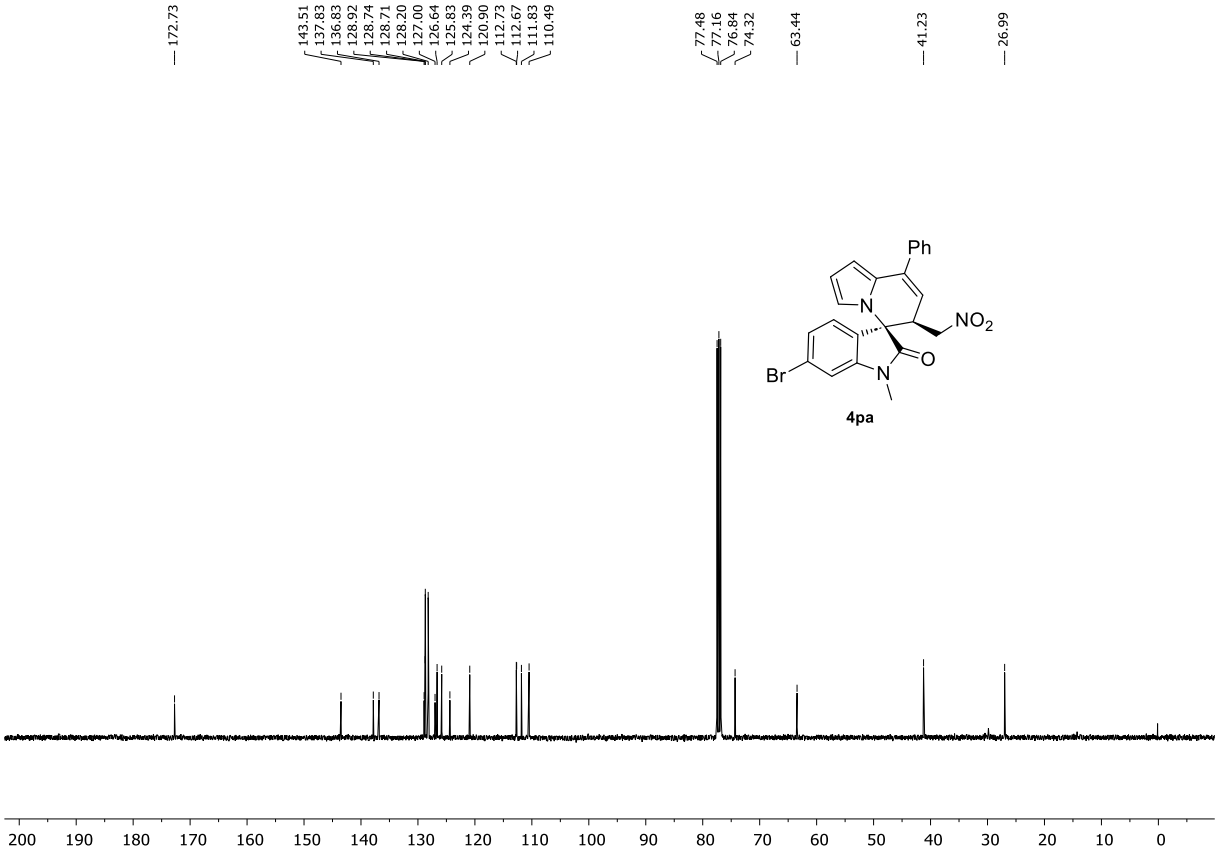
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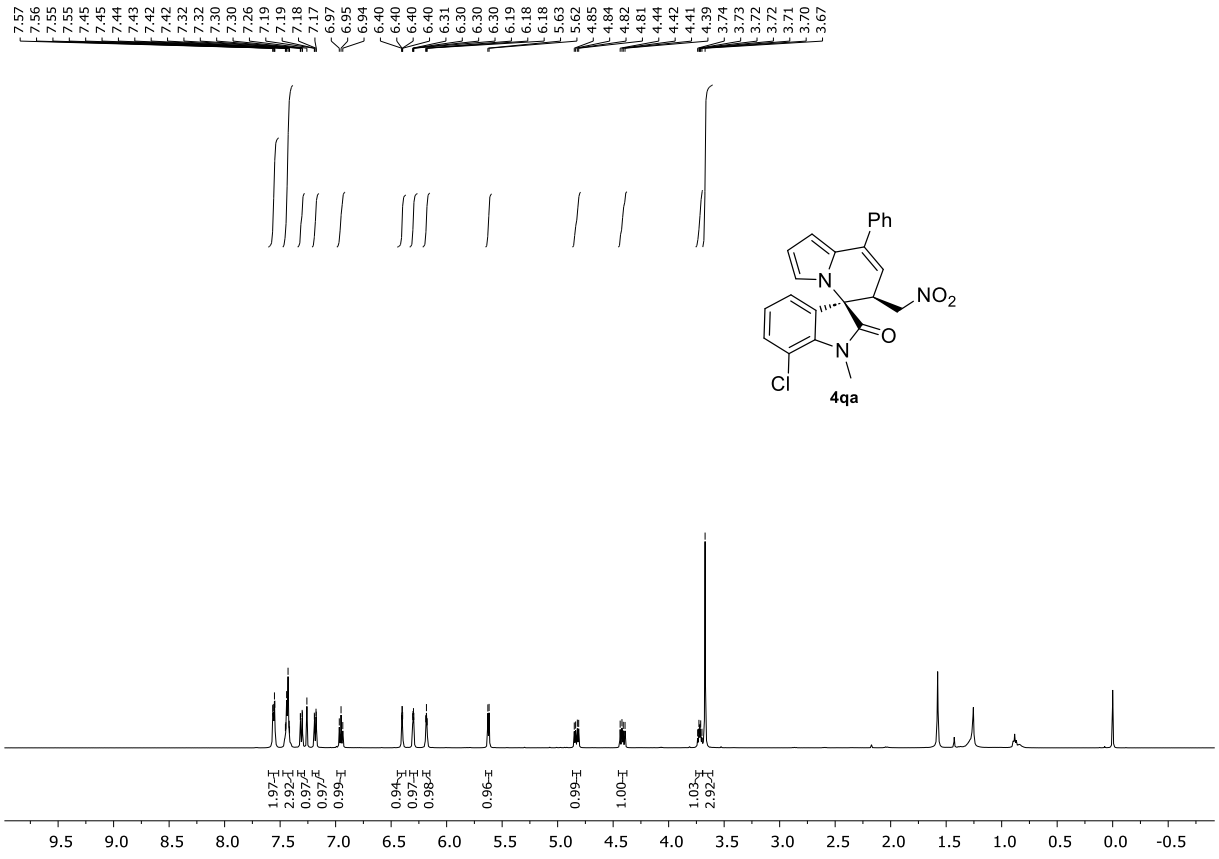
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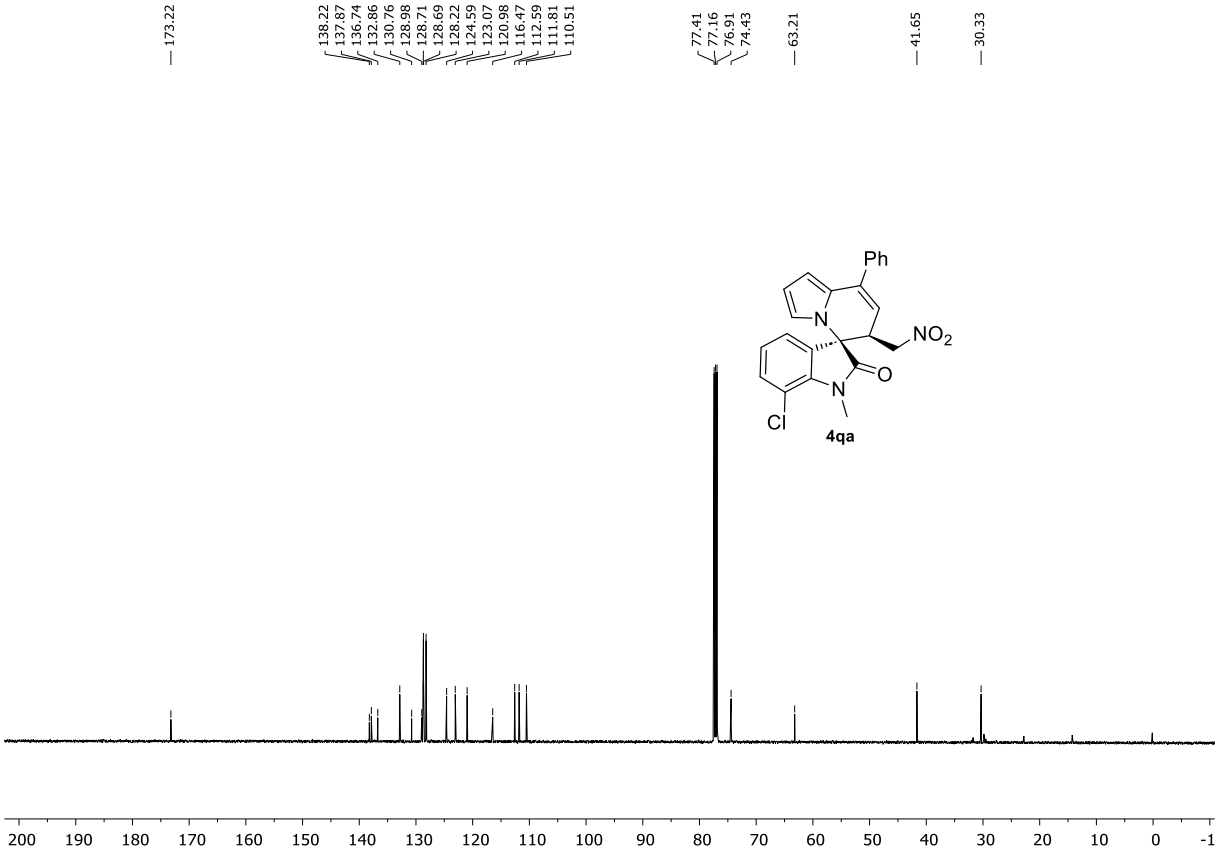
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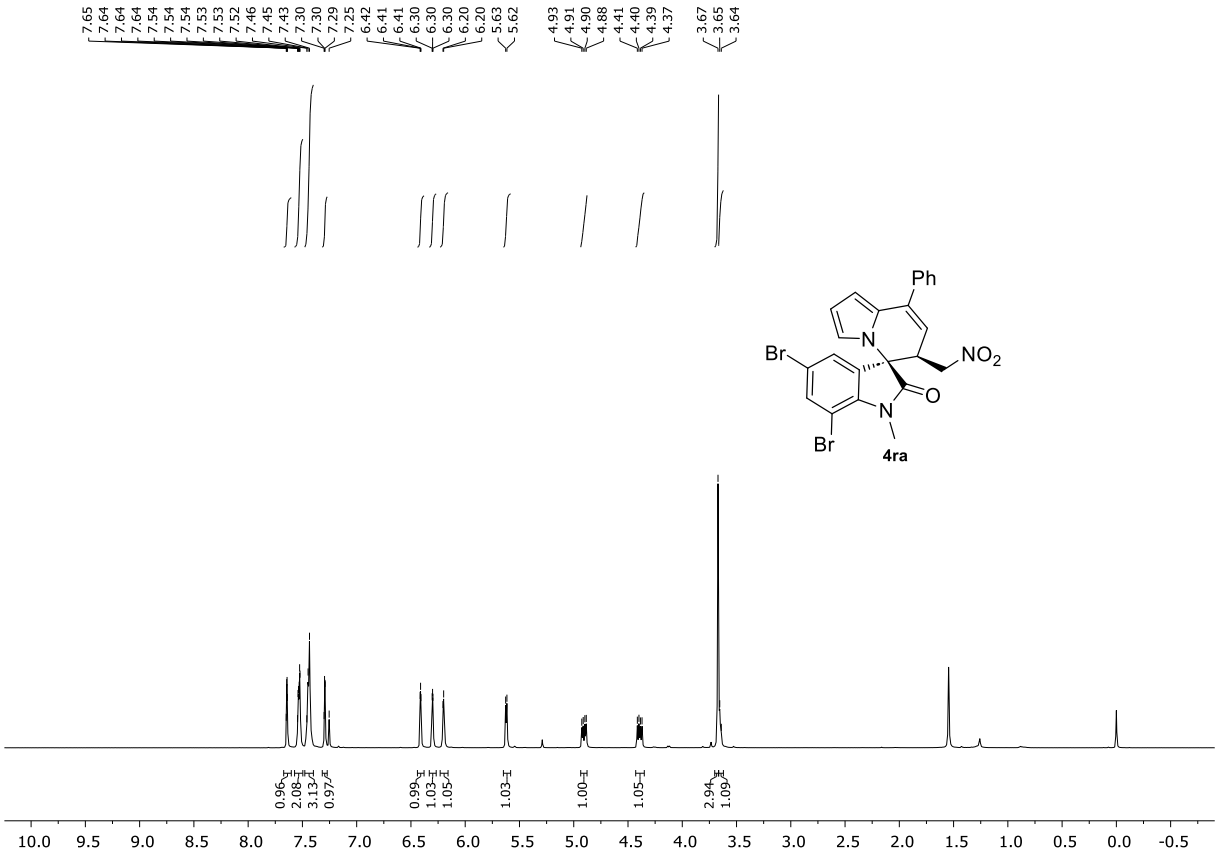
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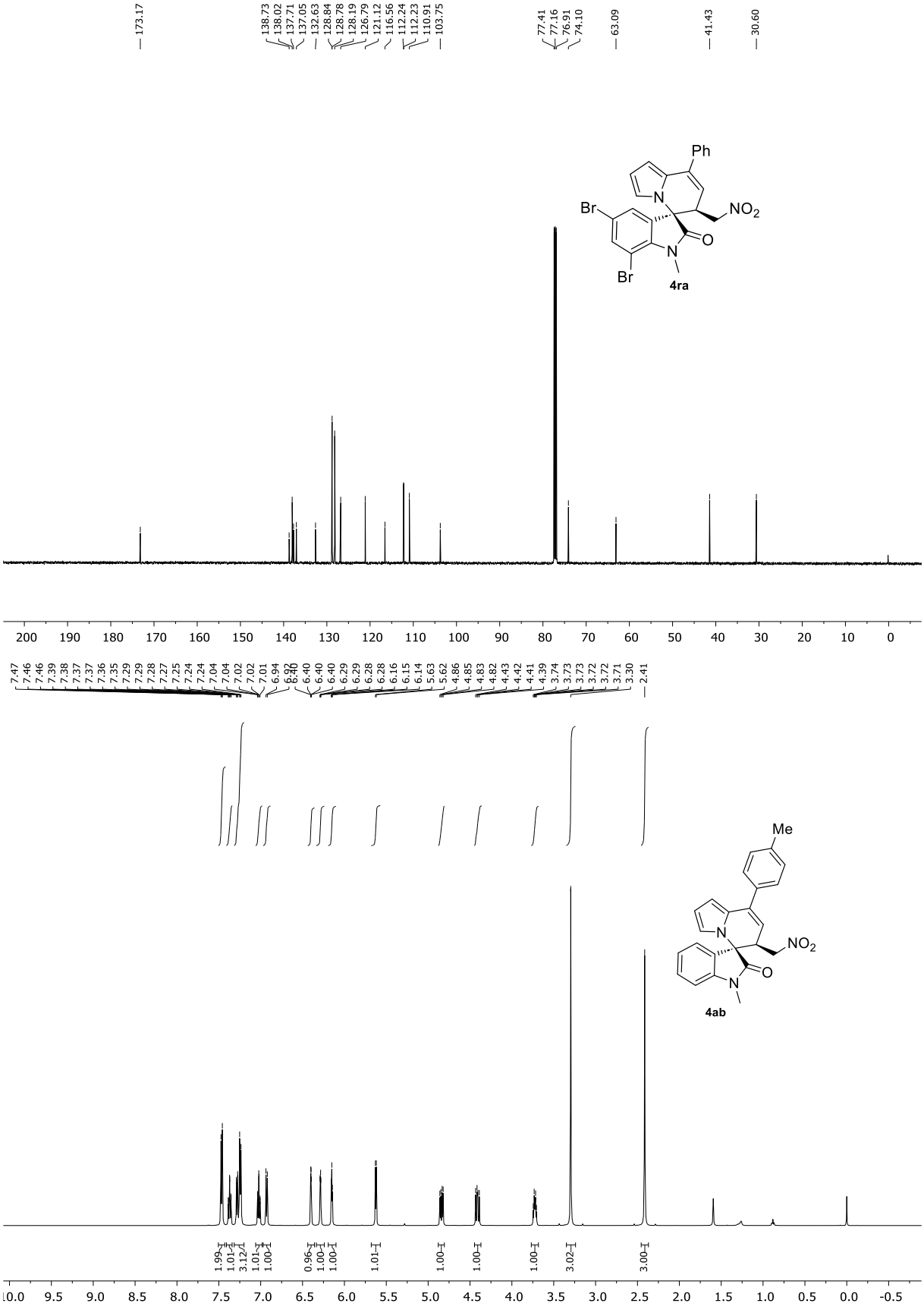
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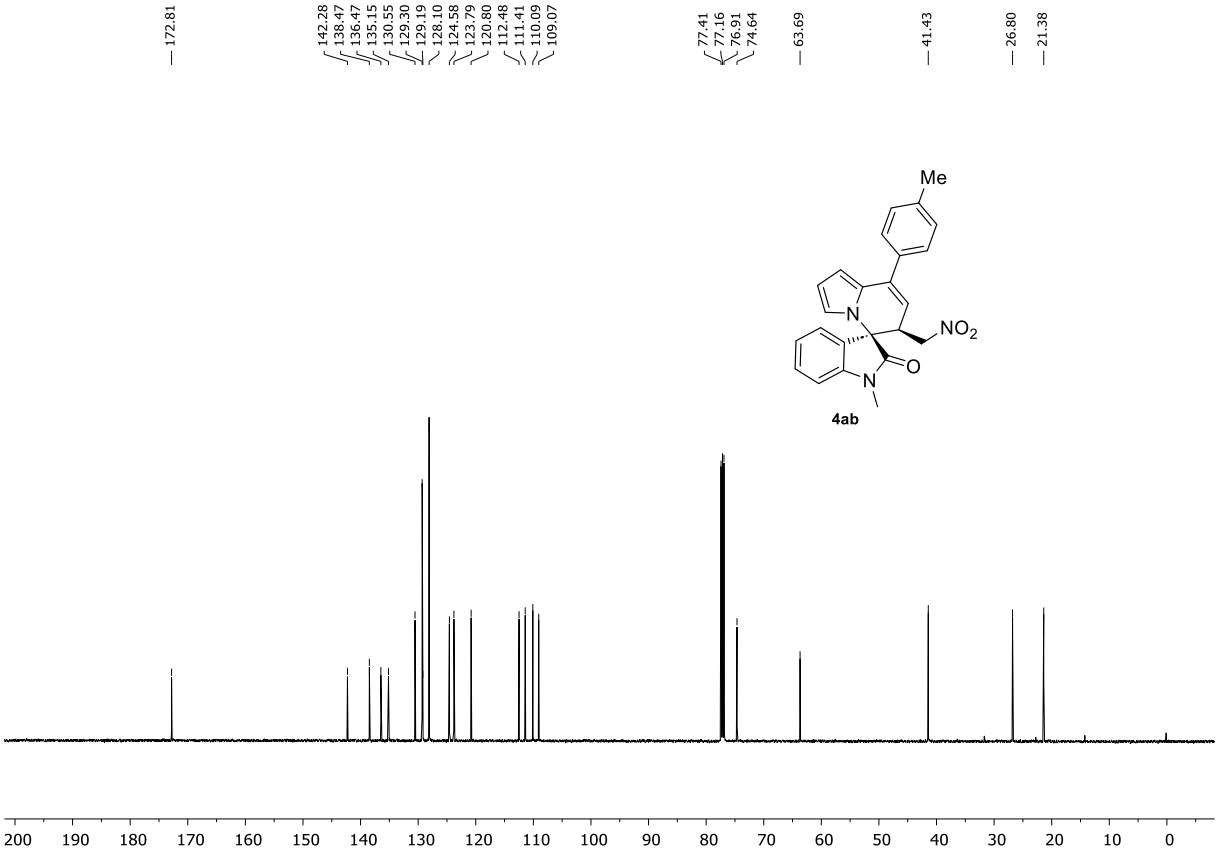
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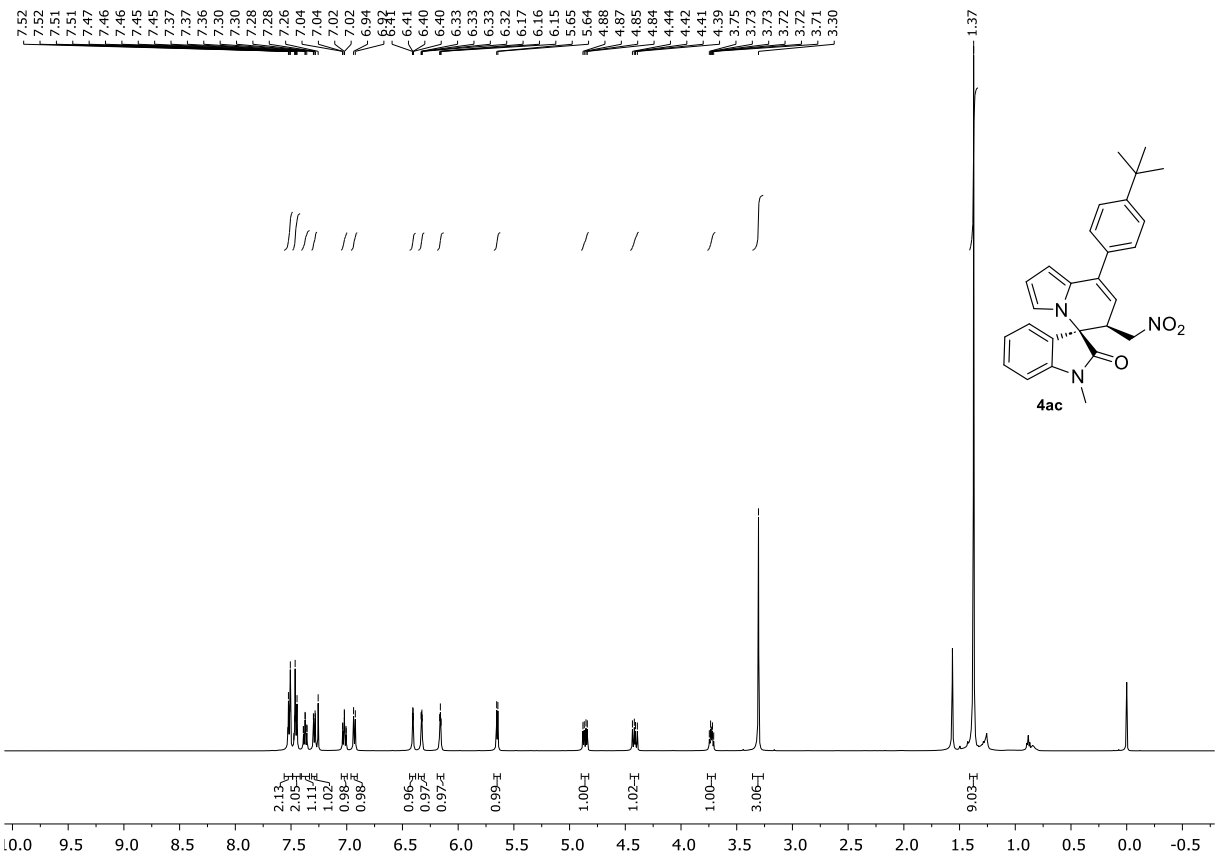
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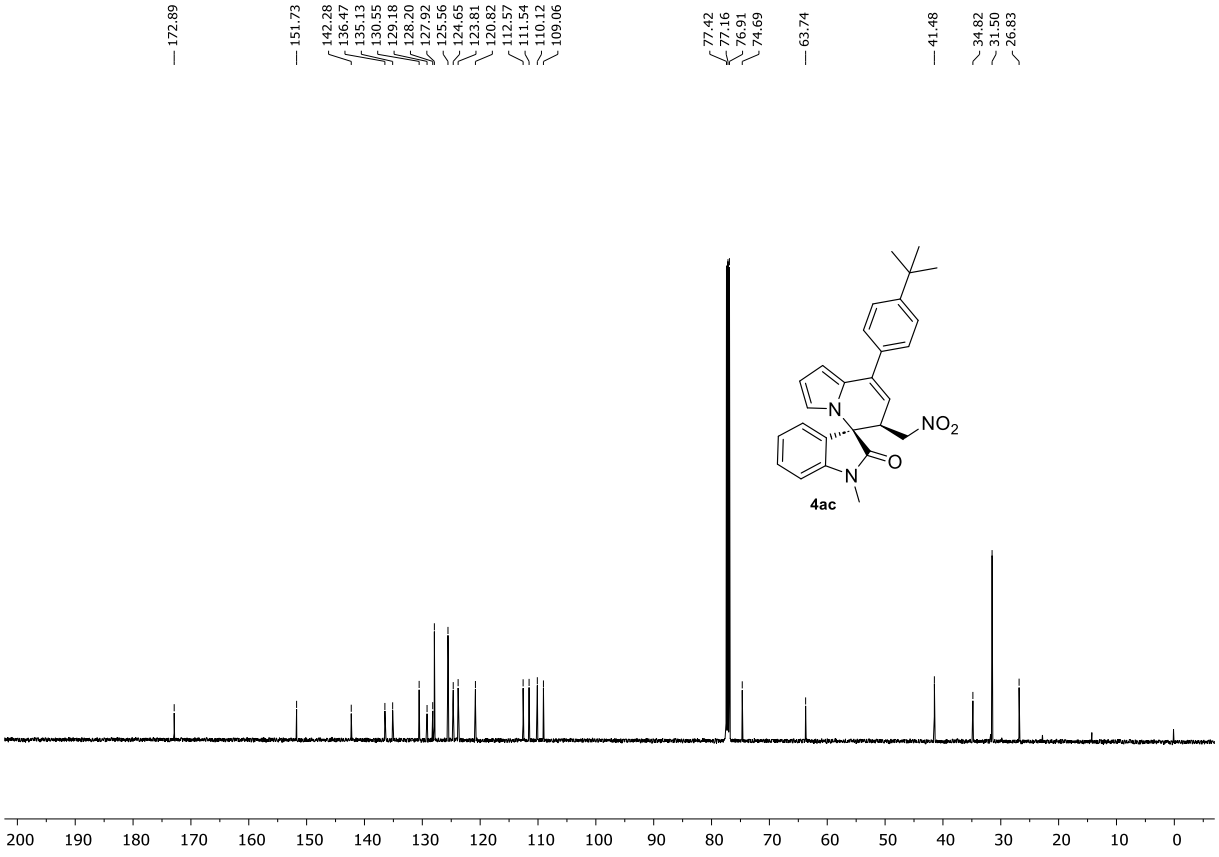
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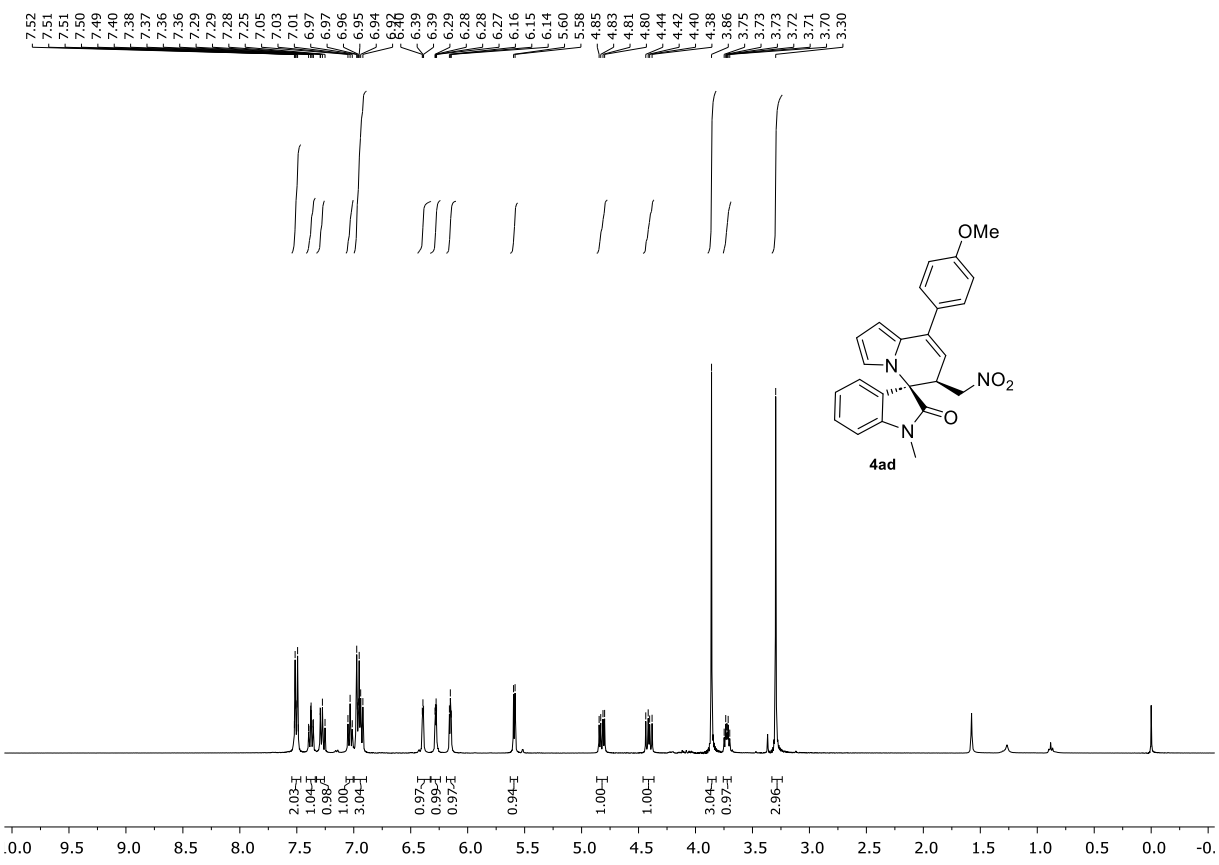
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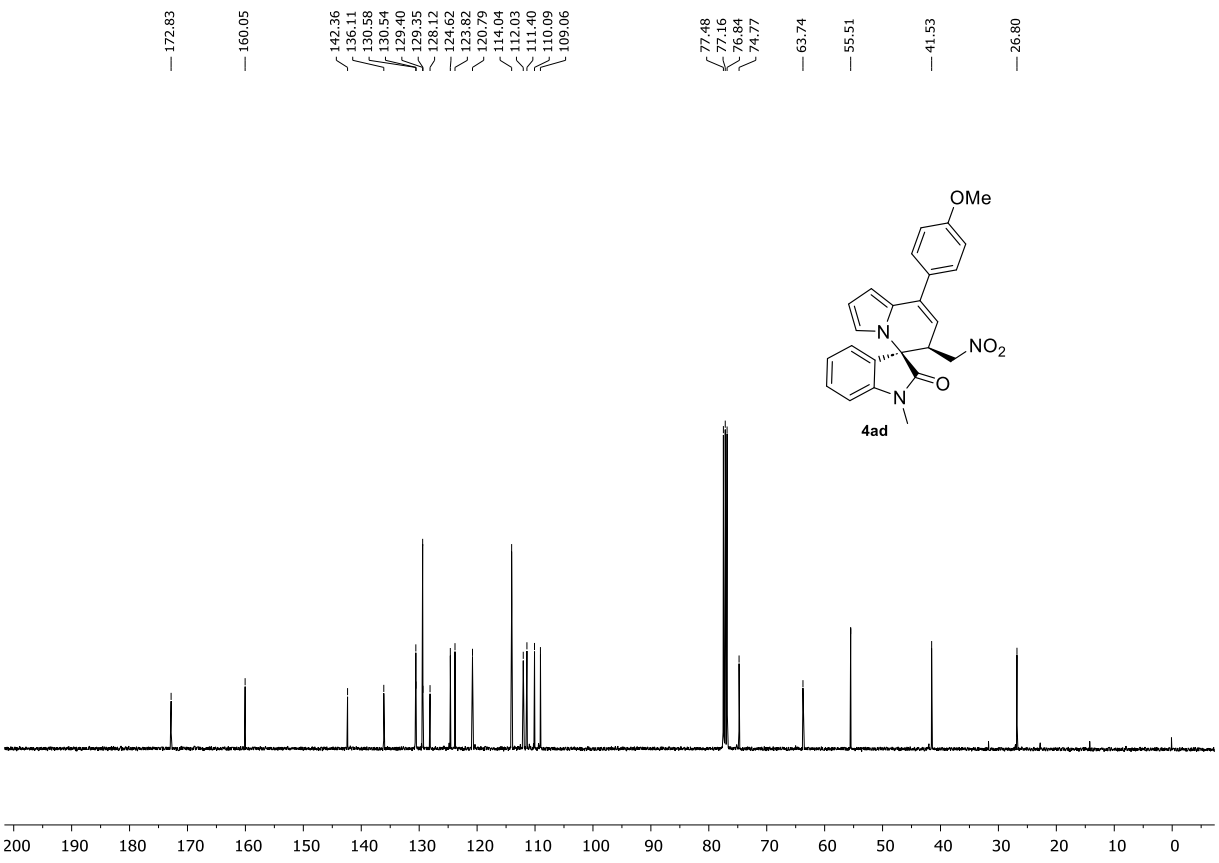
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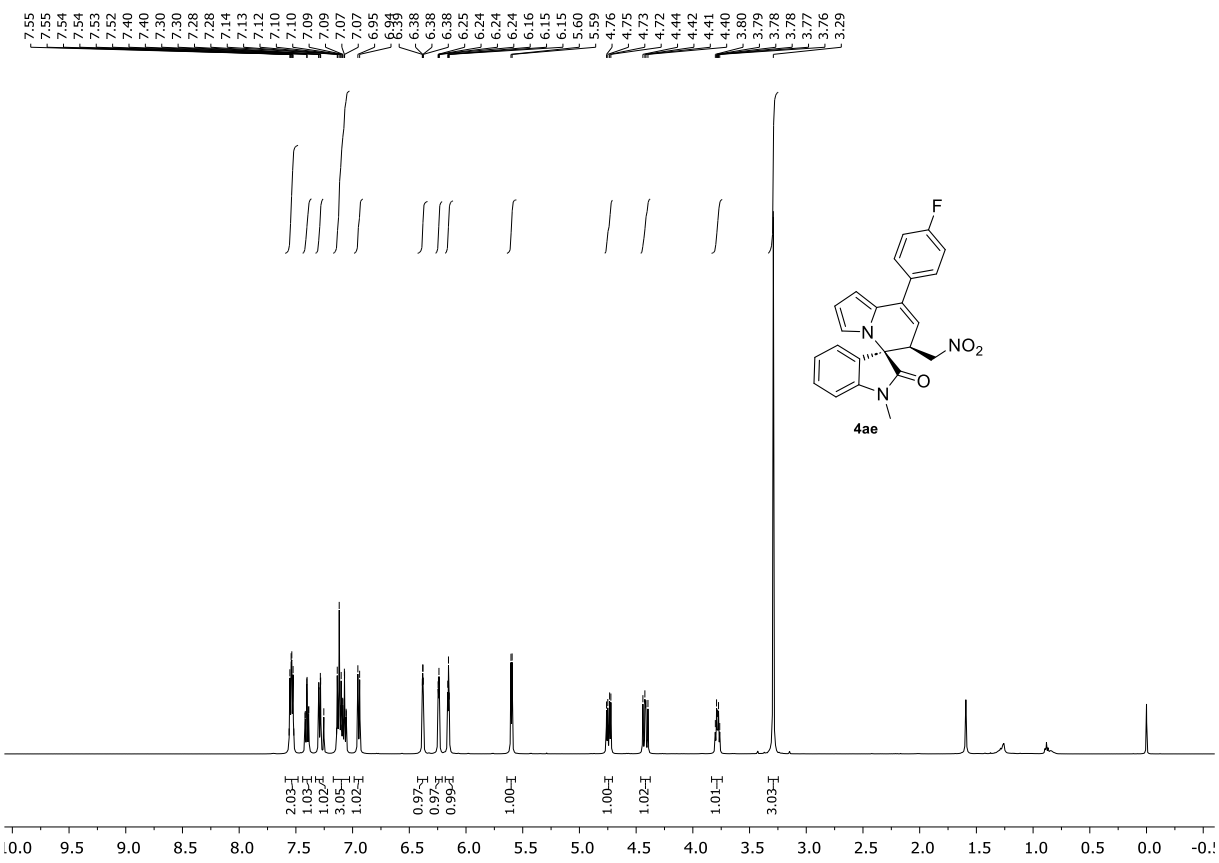
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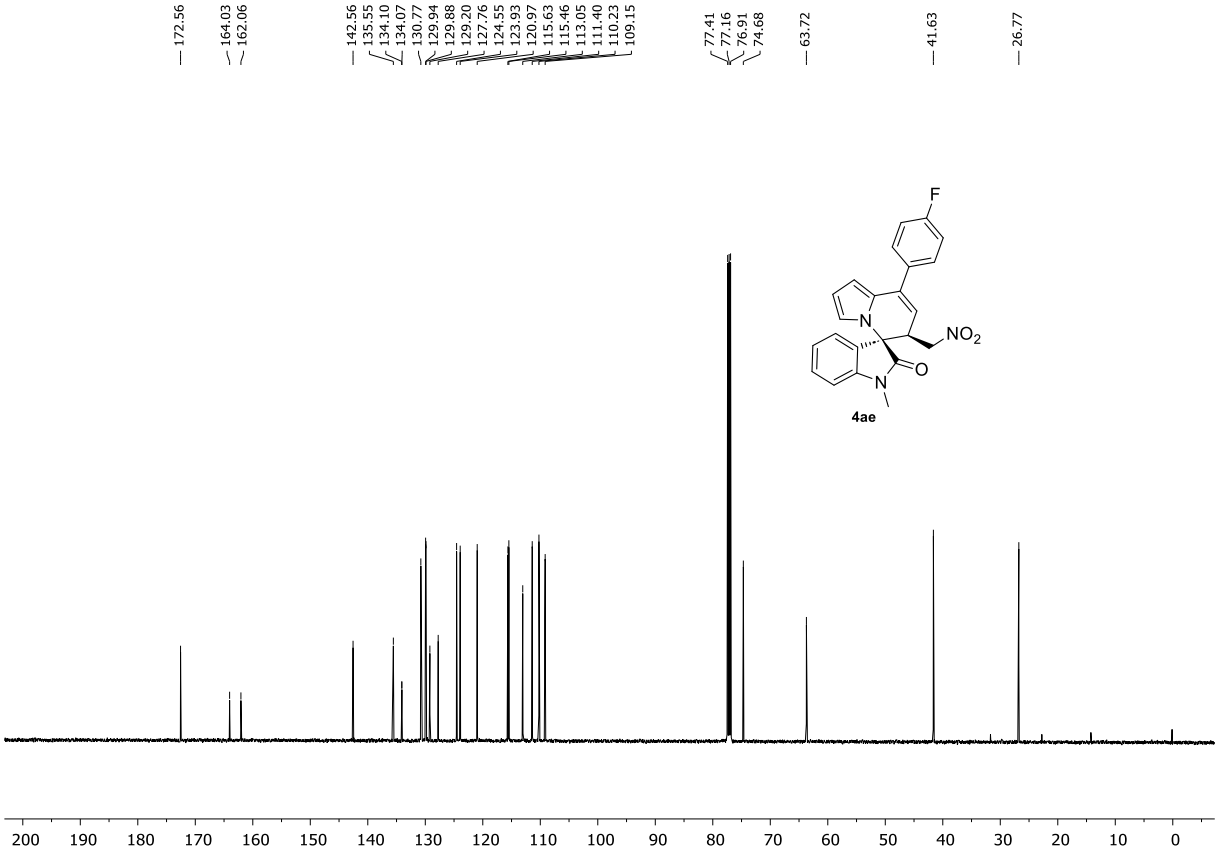
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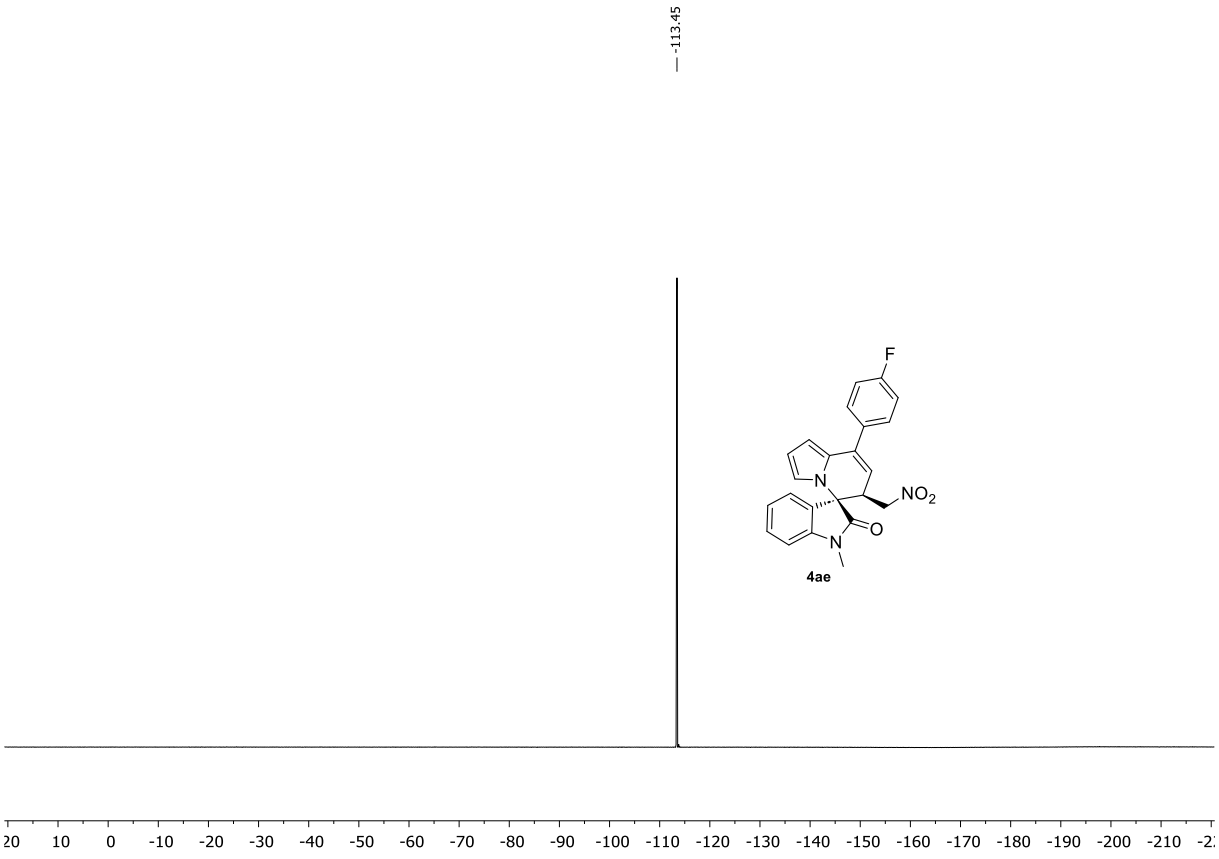
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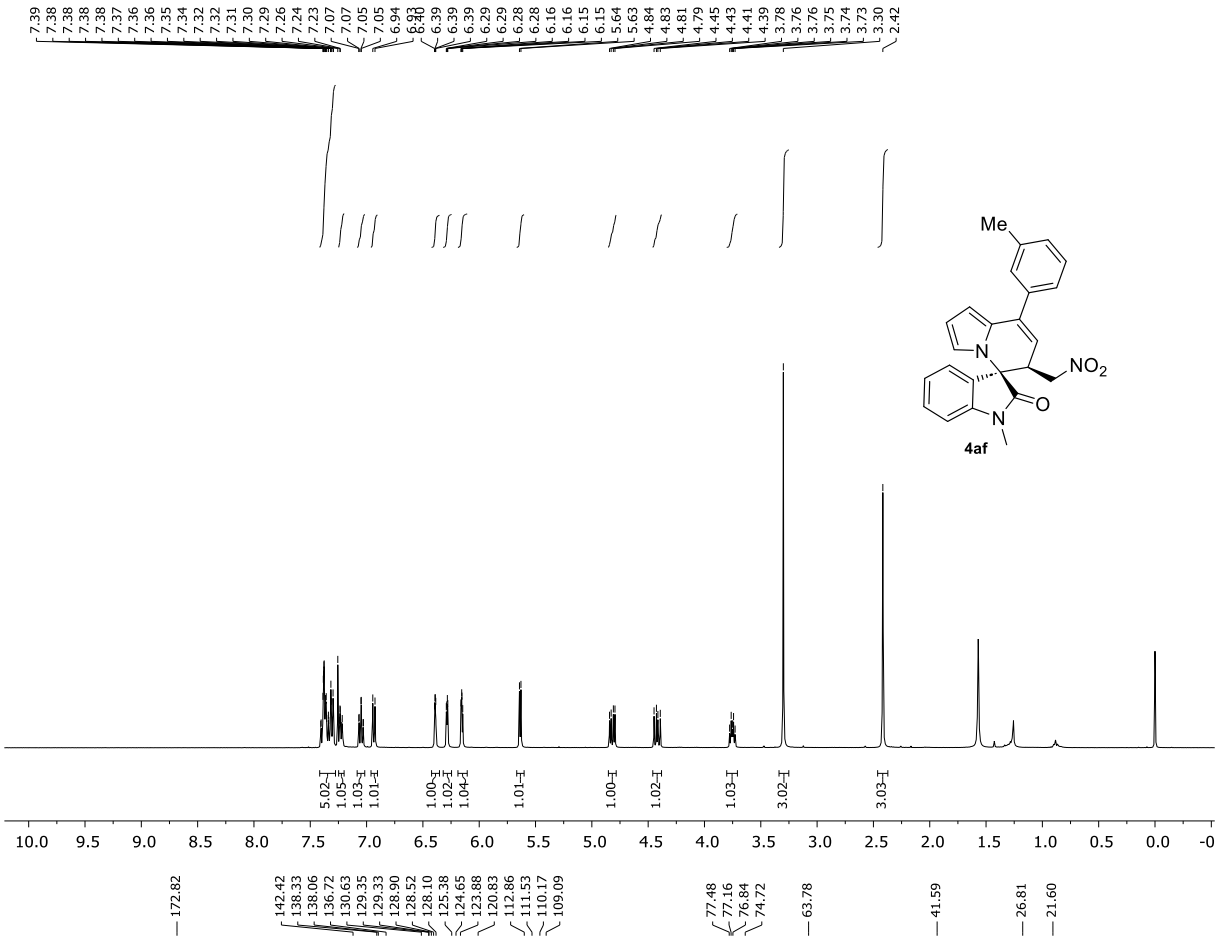
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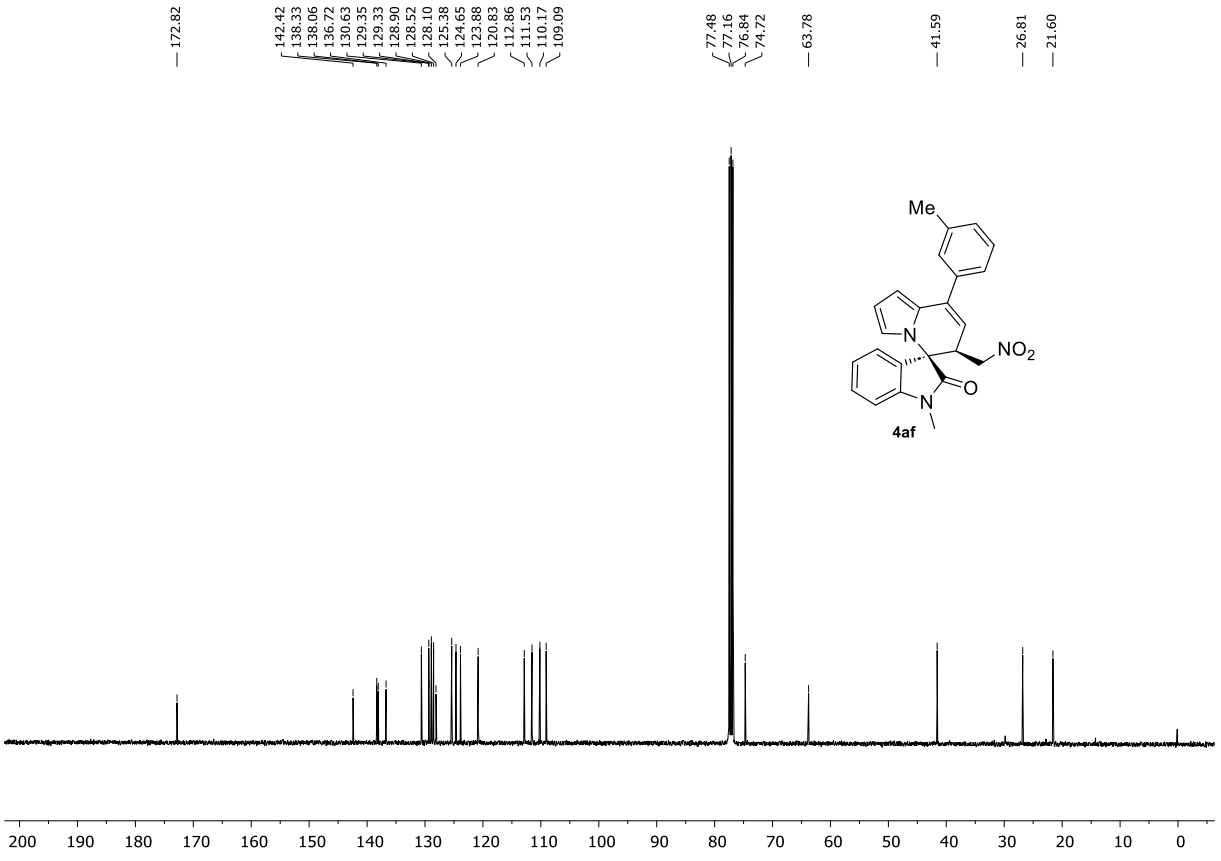
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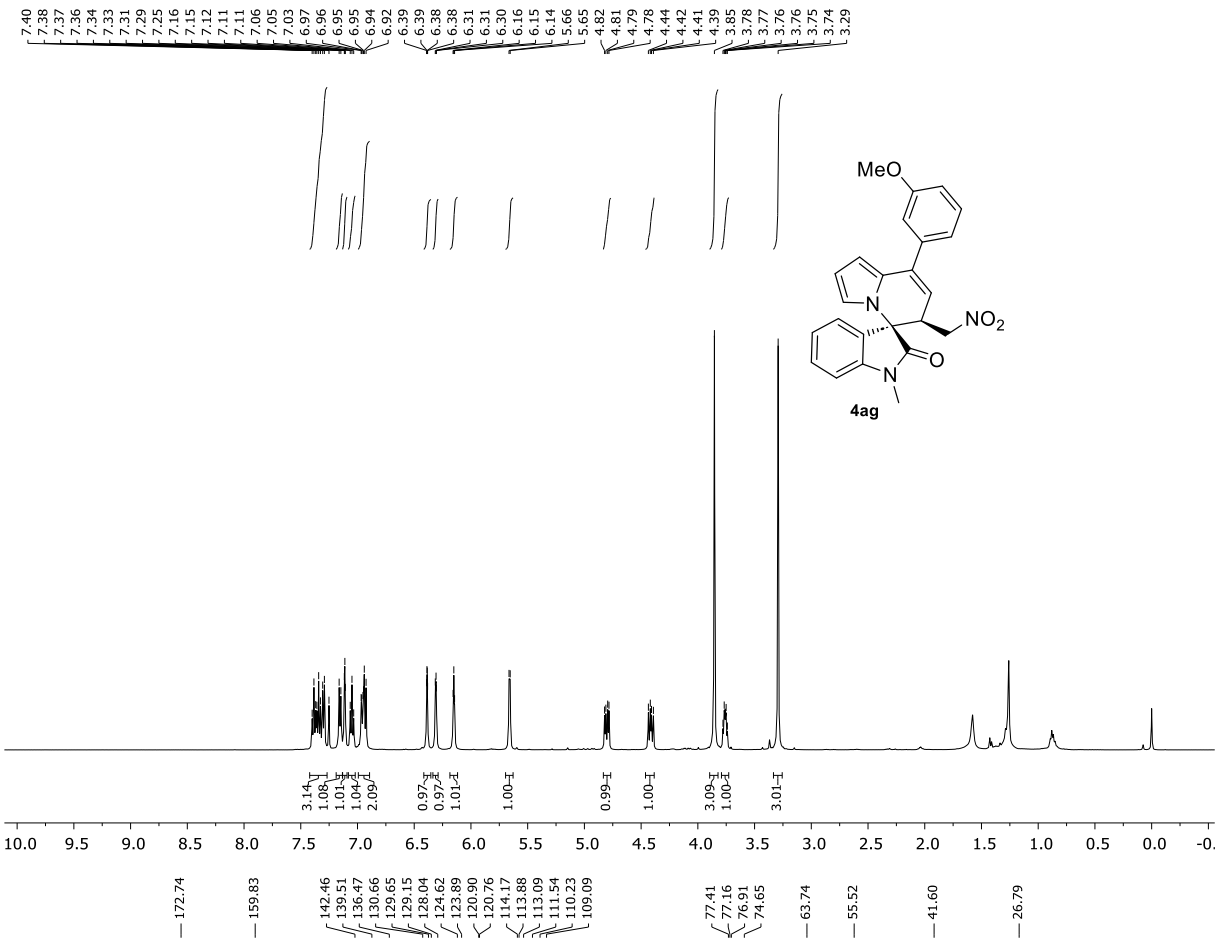
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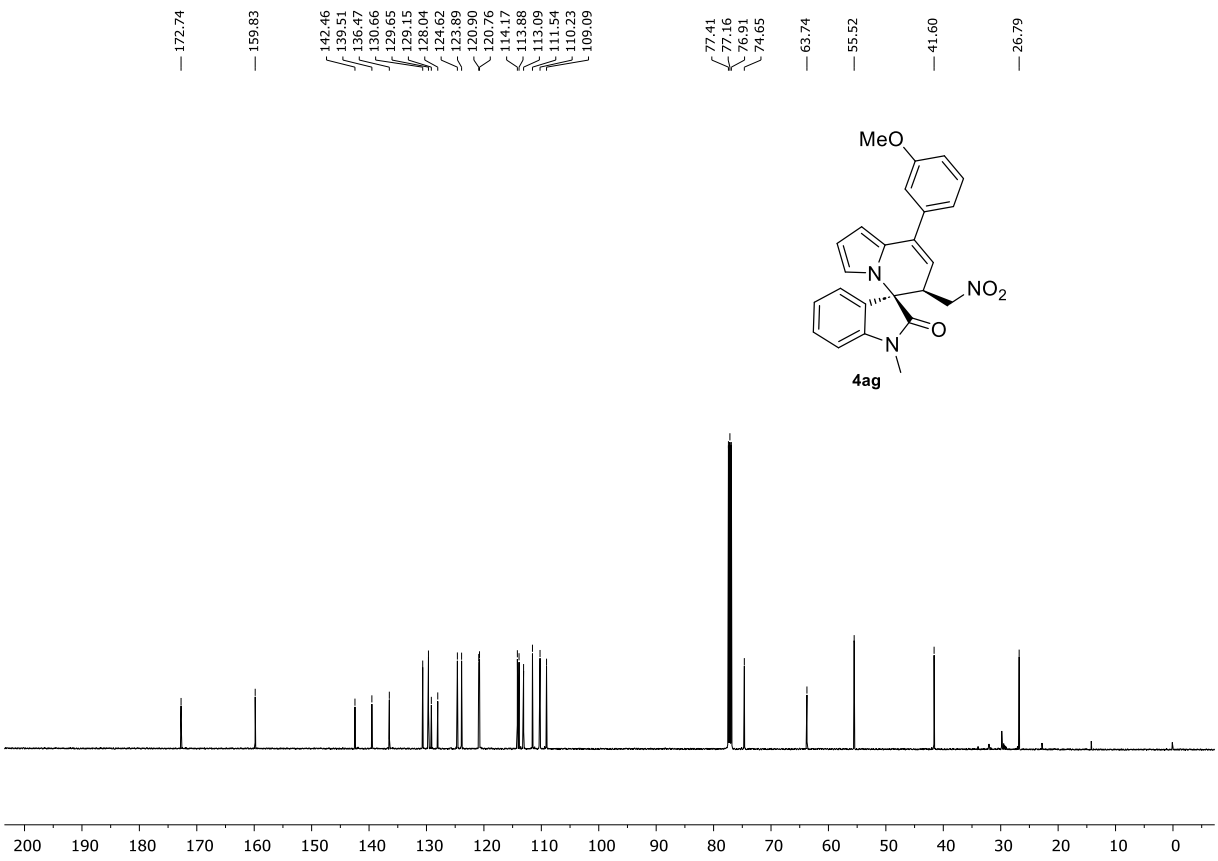
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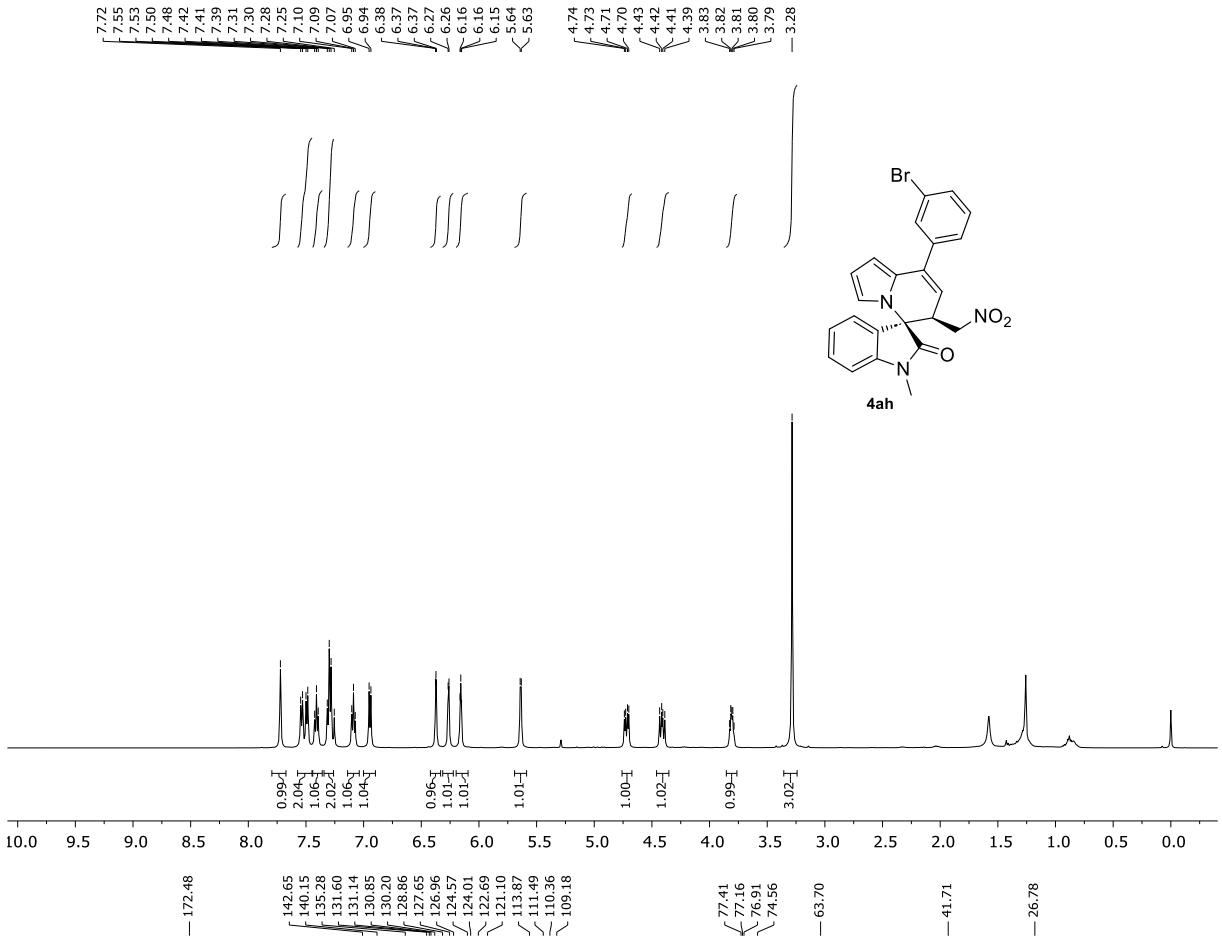
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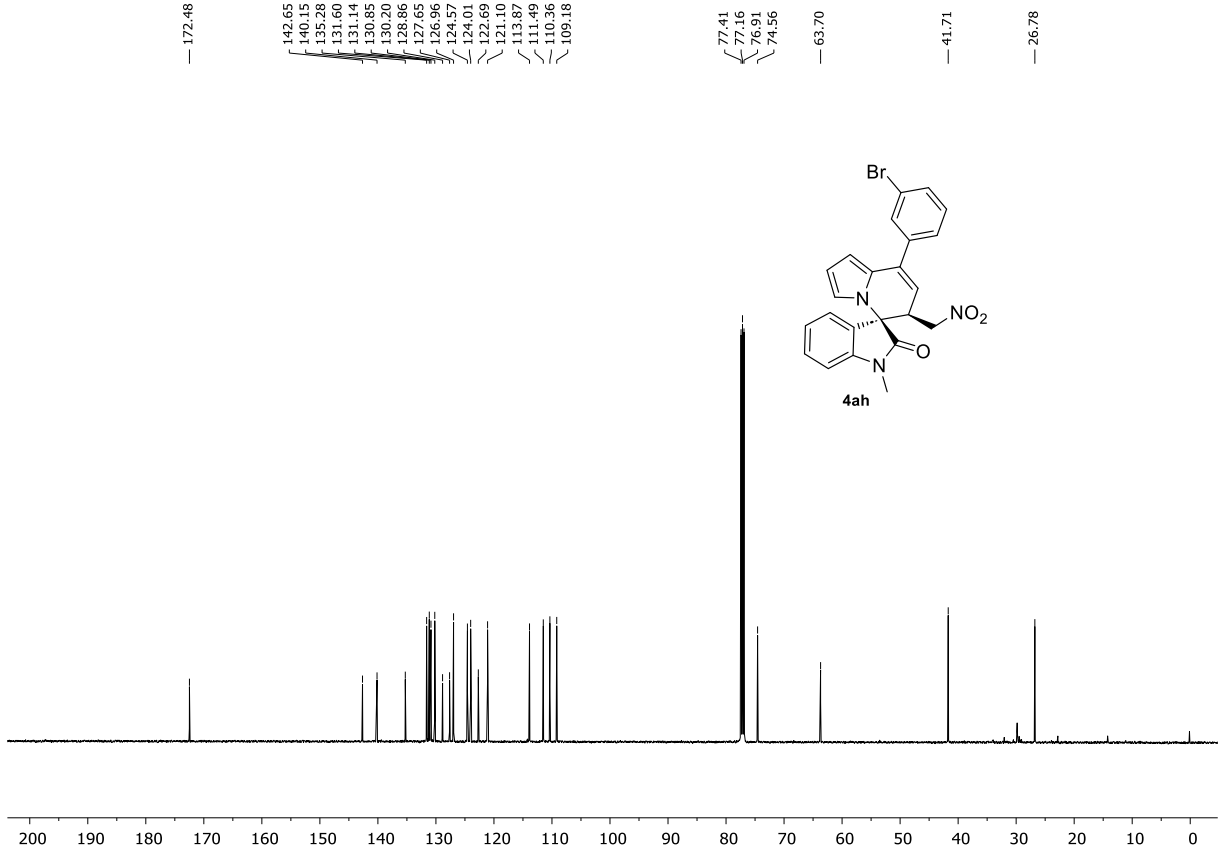
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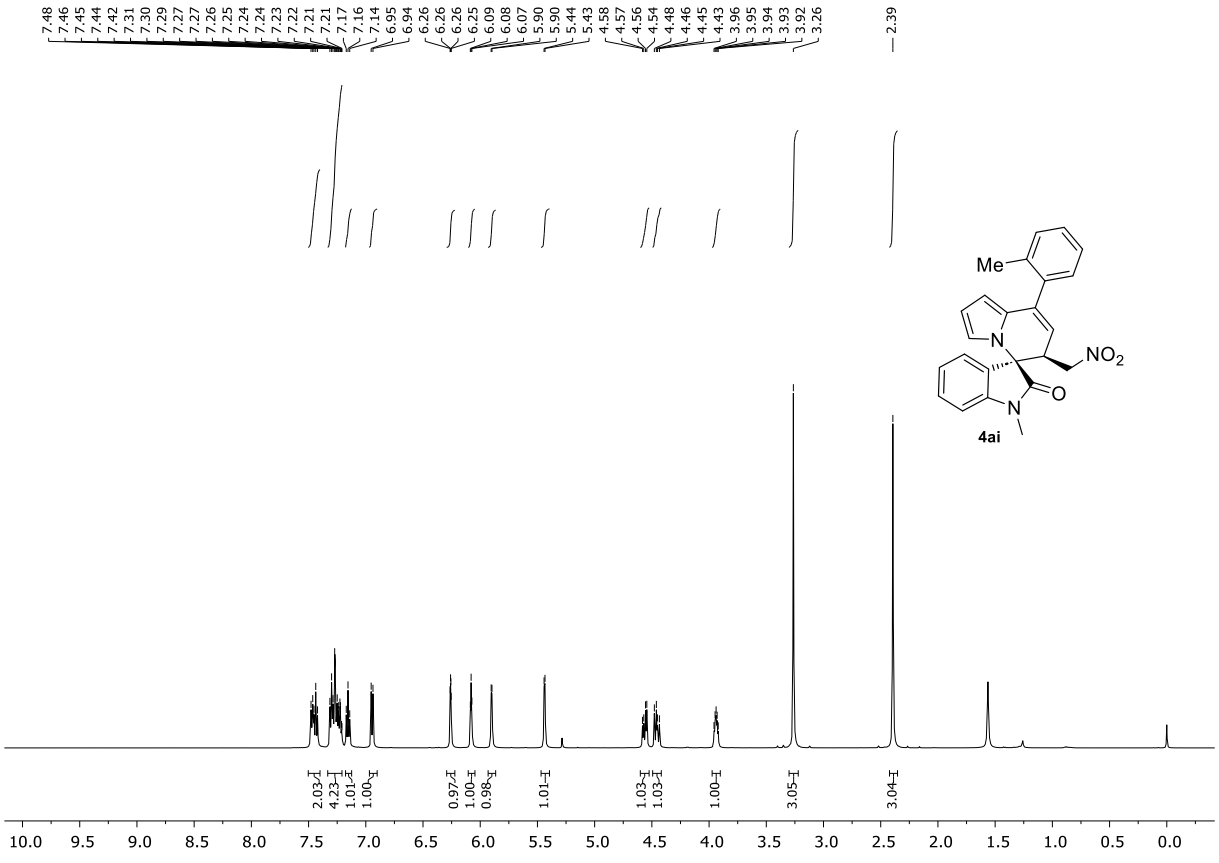
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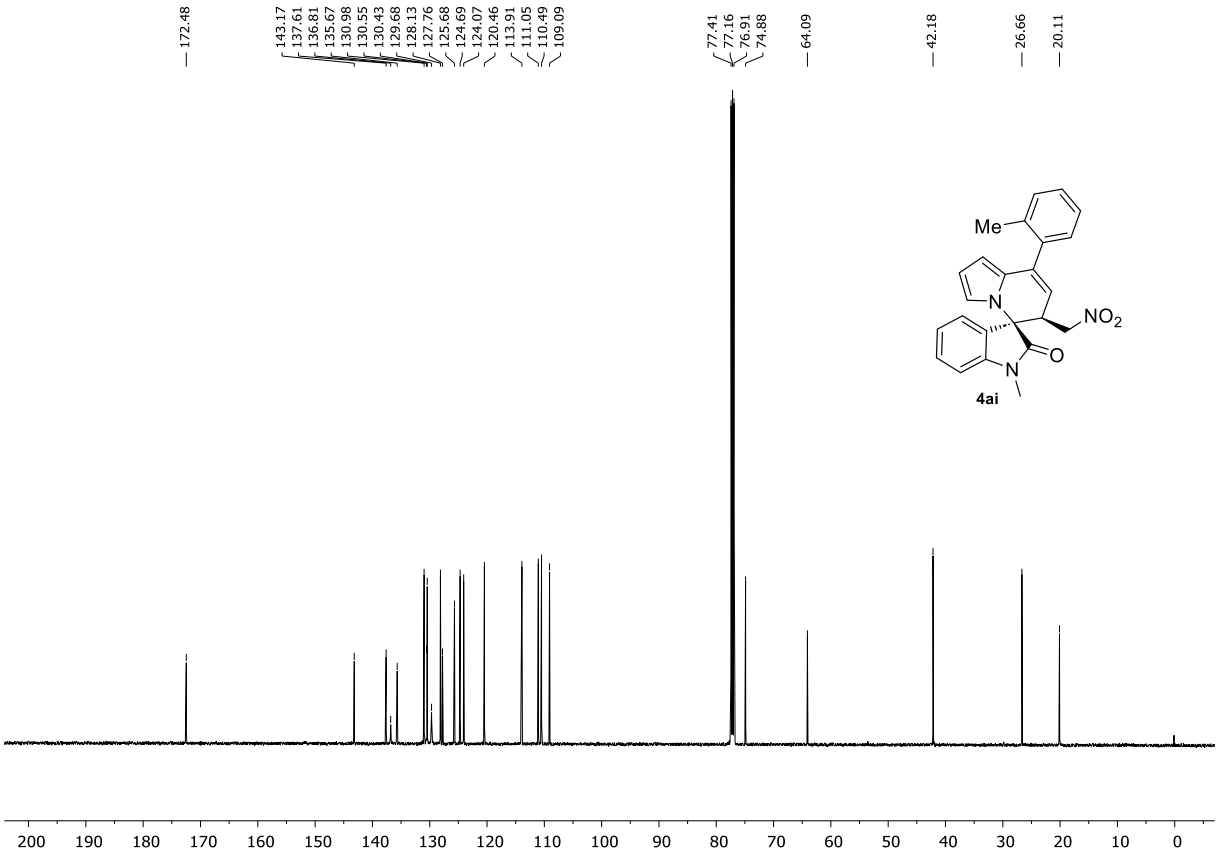
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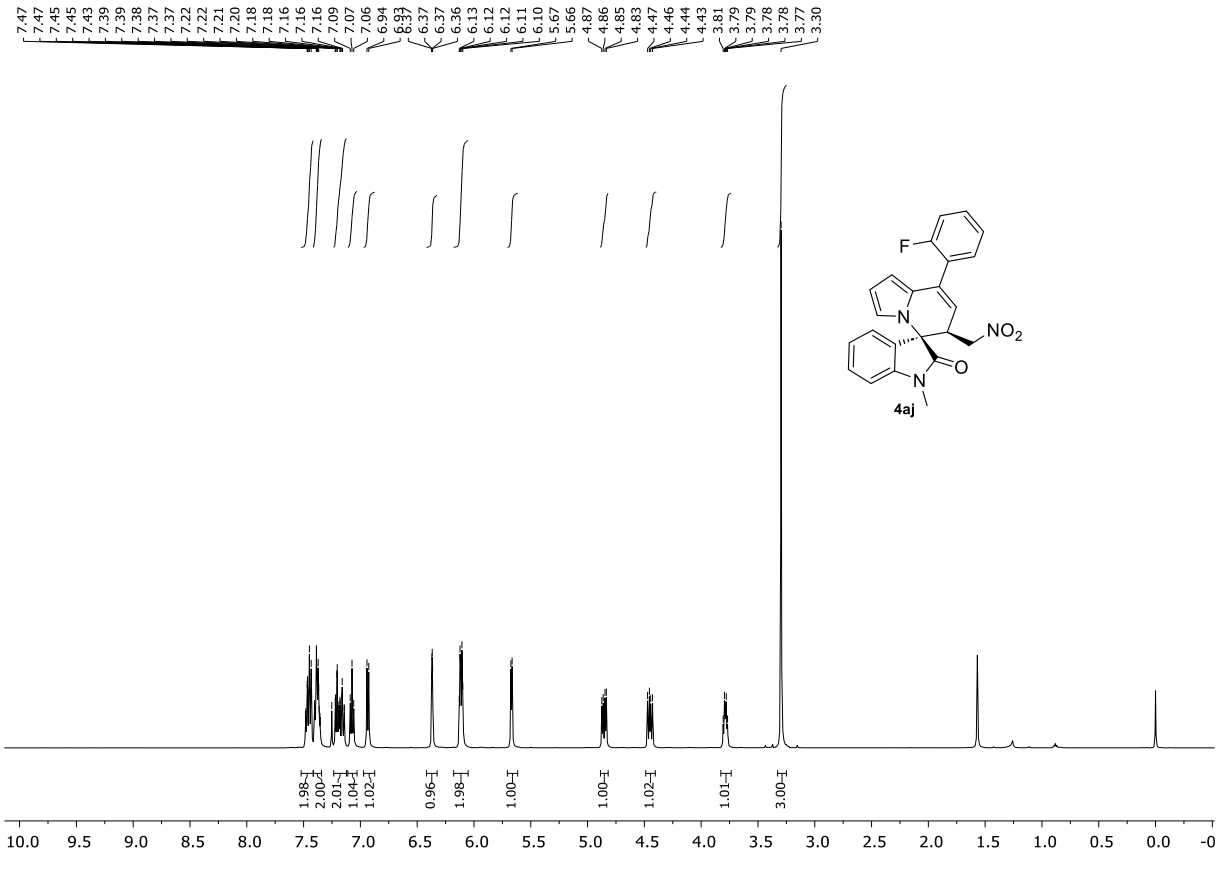
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3.77
3.30
F
N
NO2
O
N
4aj
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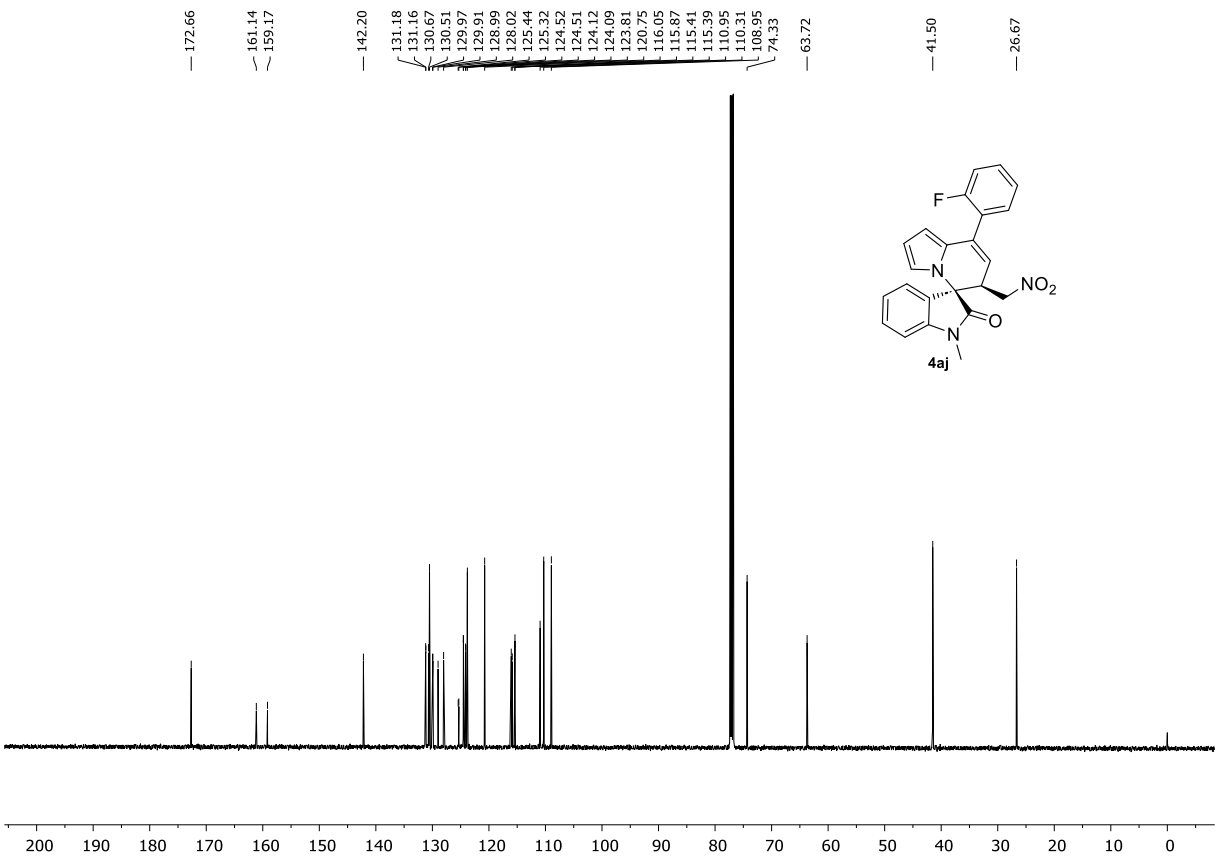
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NO2
O
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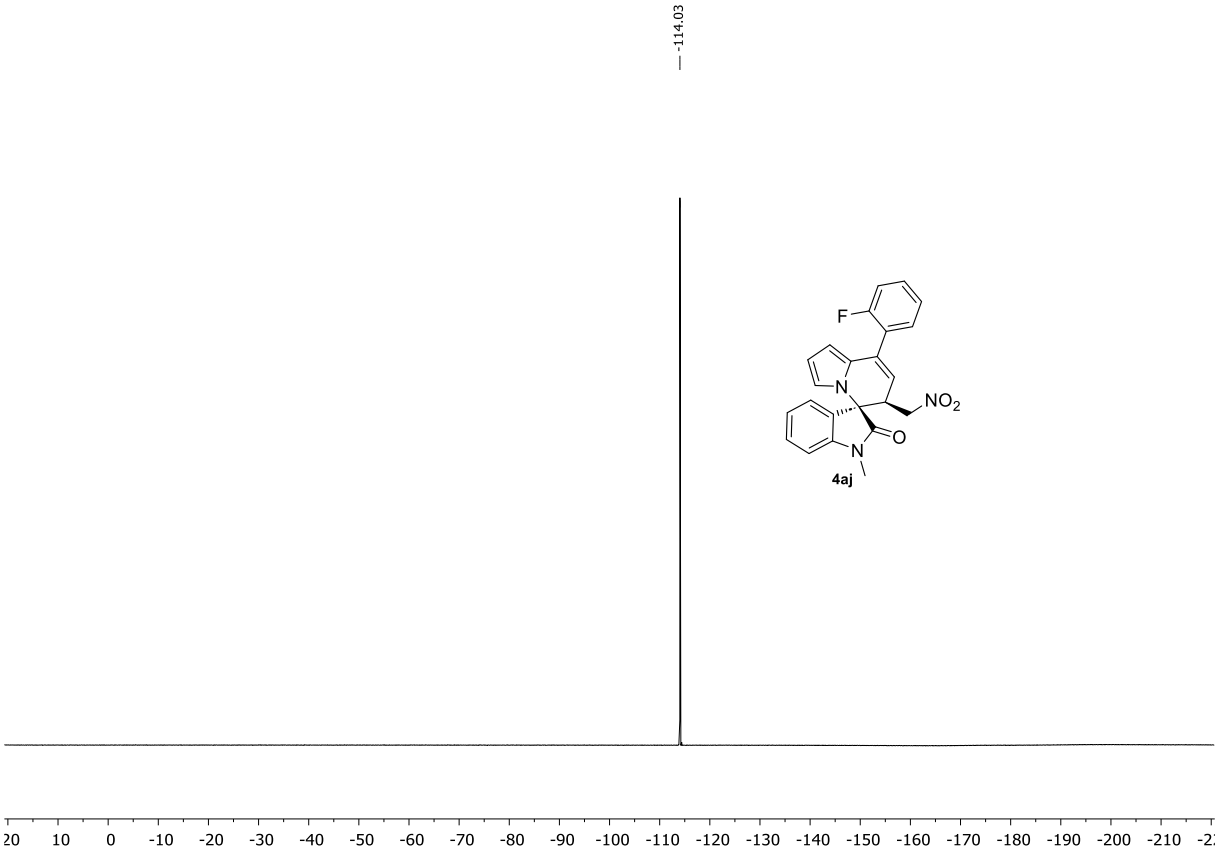
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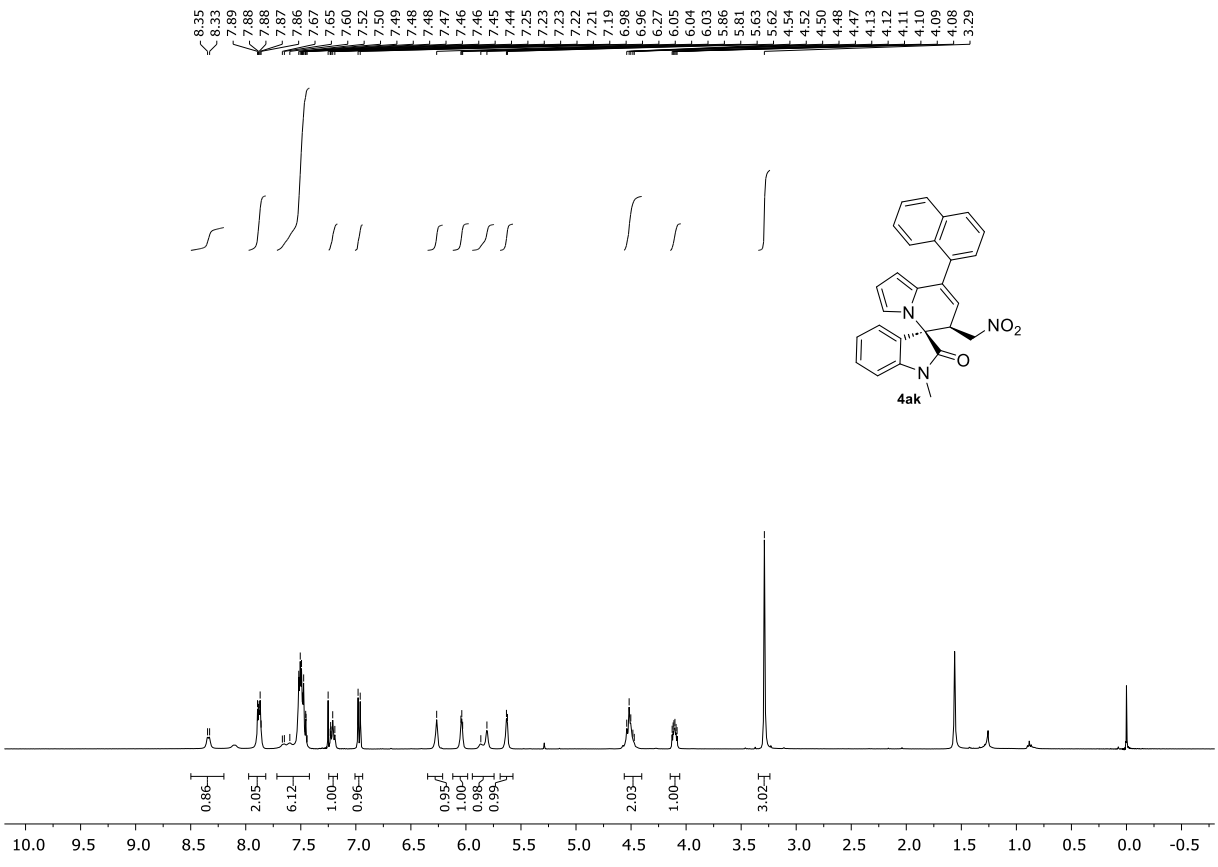
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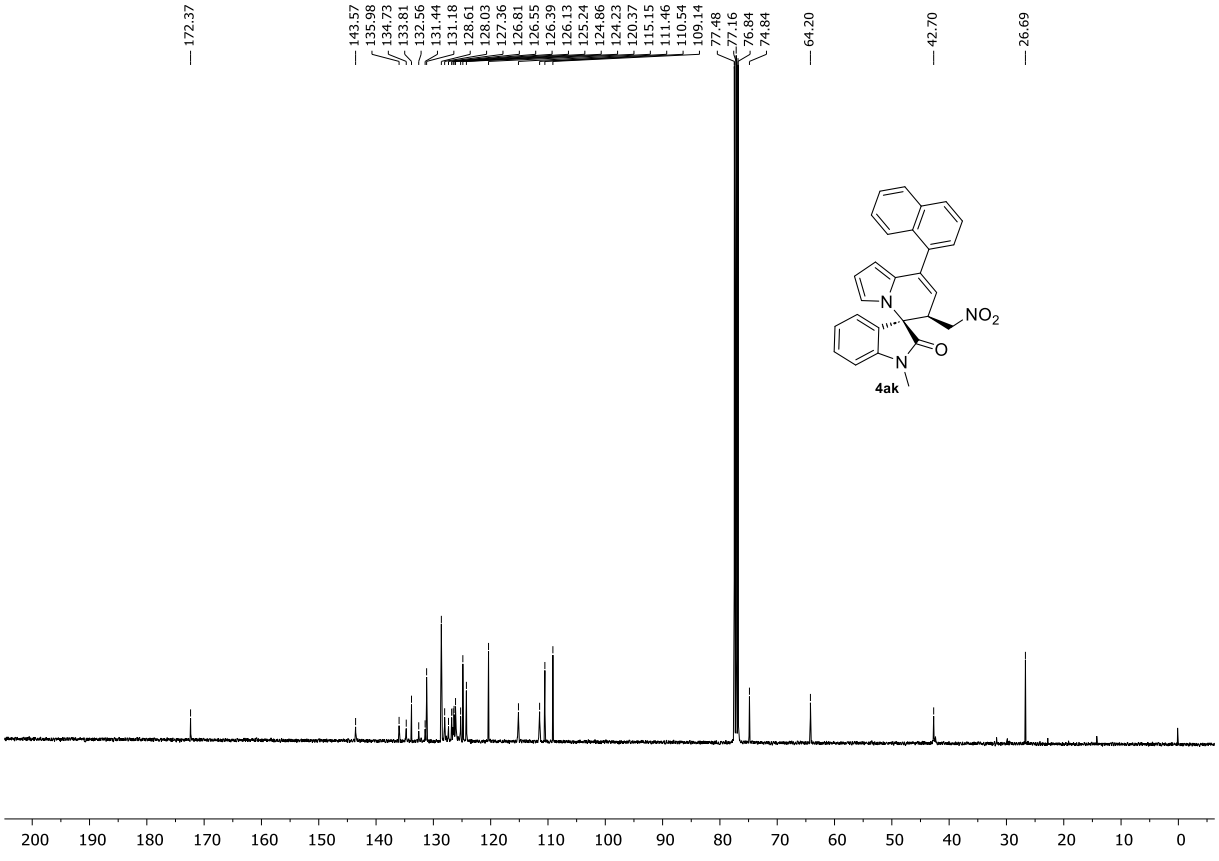
N
NO2
O
N
4ak
0.86 2.05 6.12 1.00 0.96 0.95 1.00 0.98 0.99 2.03 1.00 3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5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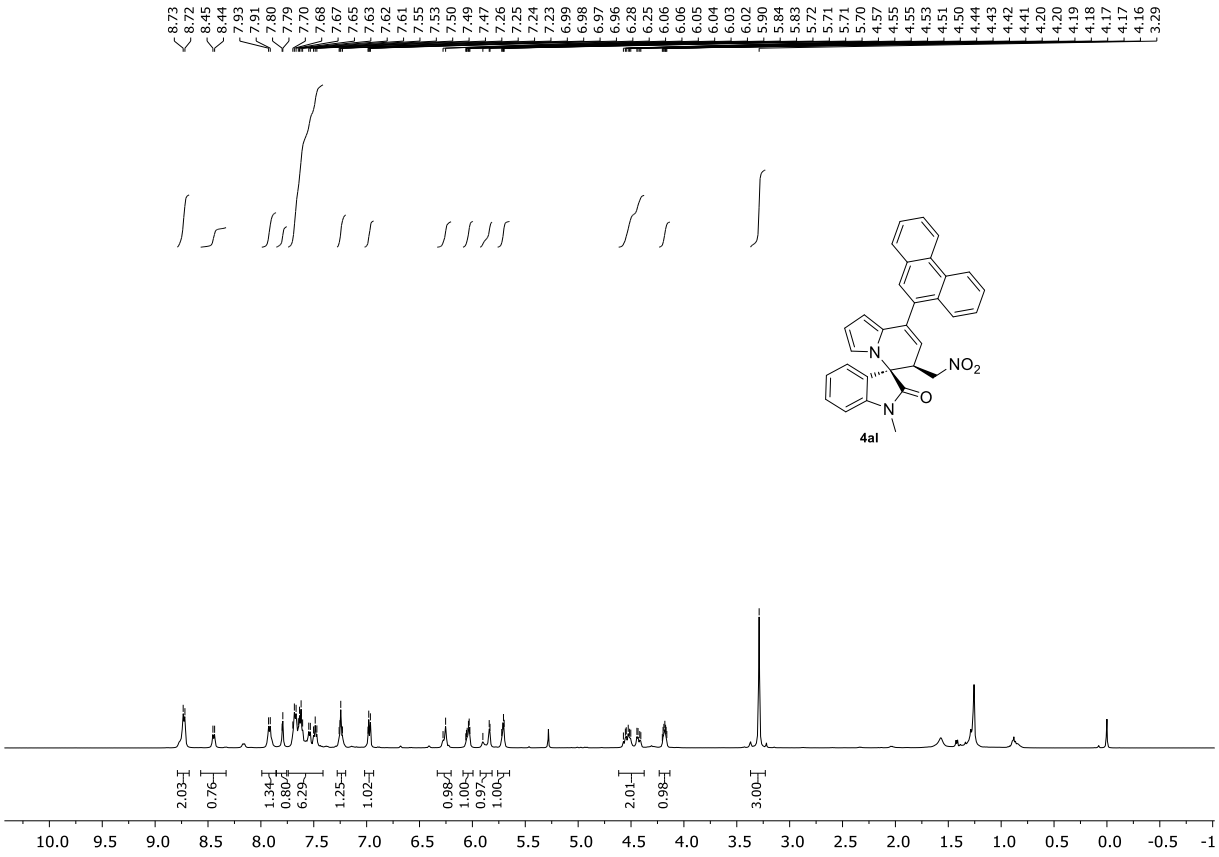
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4.16
3.29
NO2
O
N
4al


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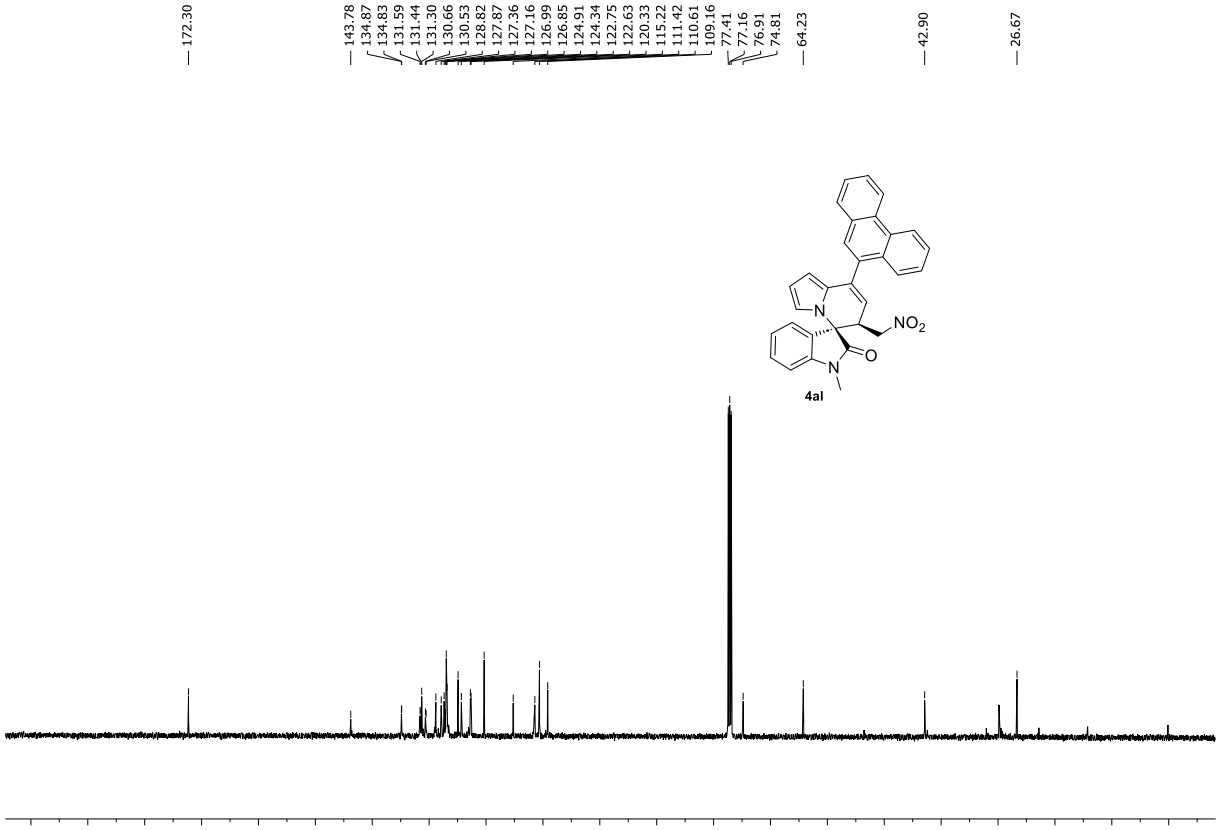
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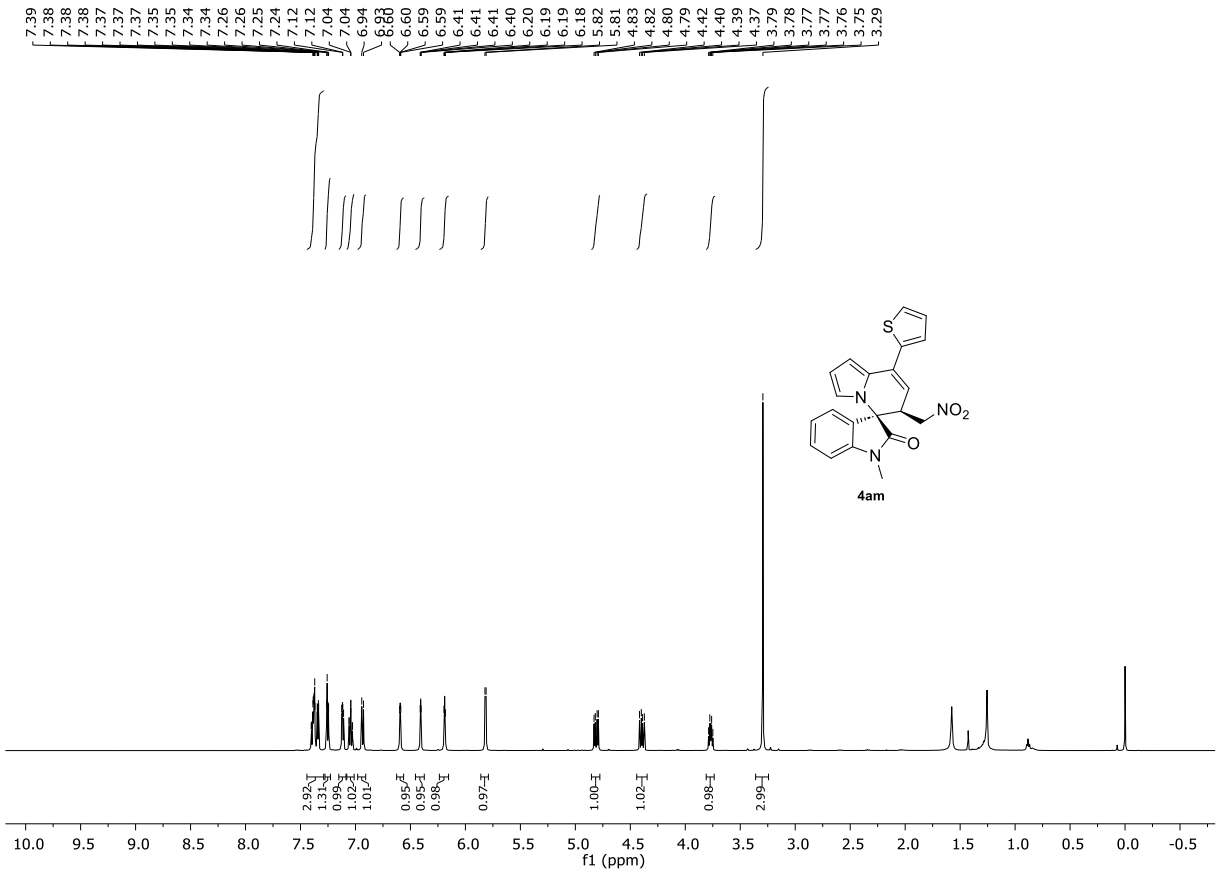
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6.19
6.18
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4.40
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4.37
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3.78
3.77
3.77
3.76
3.75
3.29
S
NO2
O
N
4am
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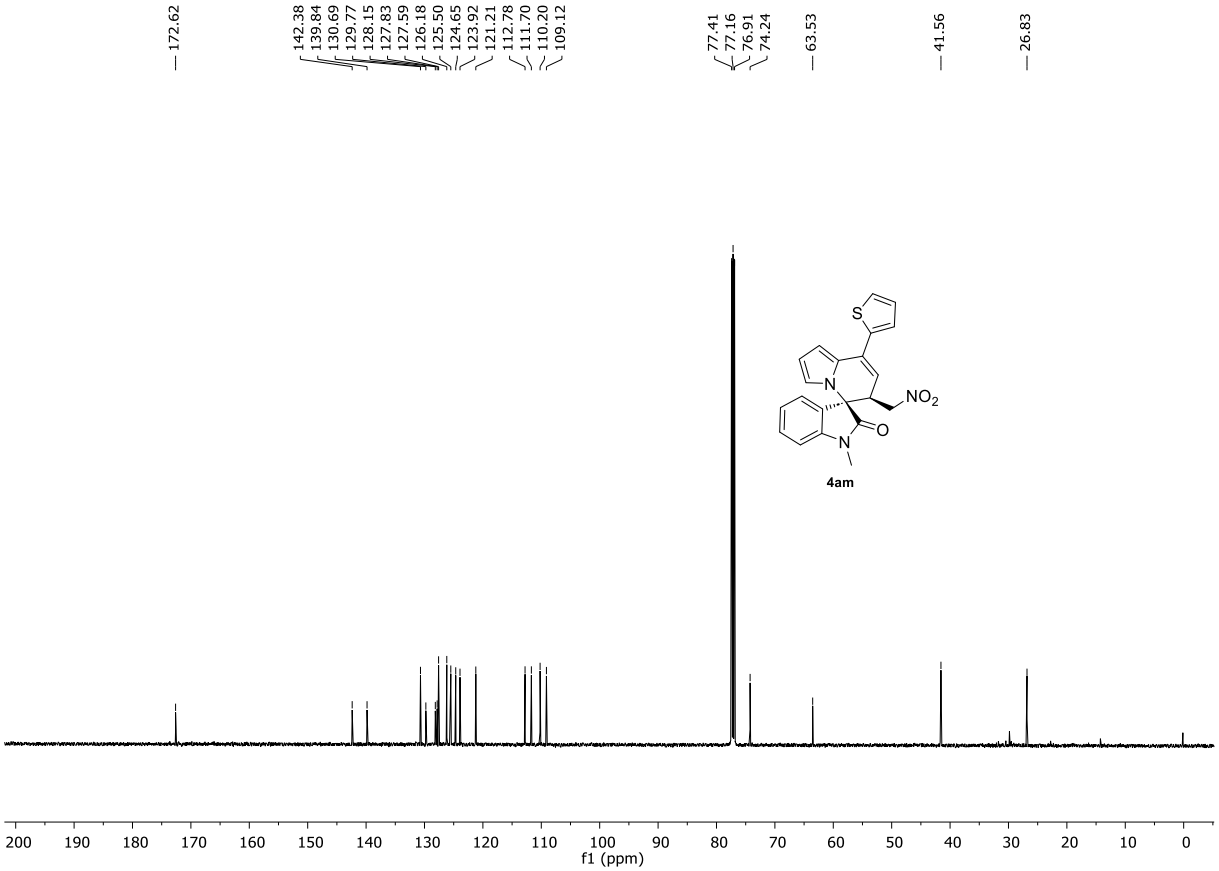
f1 (ppm)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76.91
74.24
63.53
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S
N
NO2
O
N
4am
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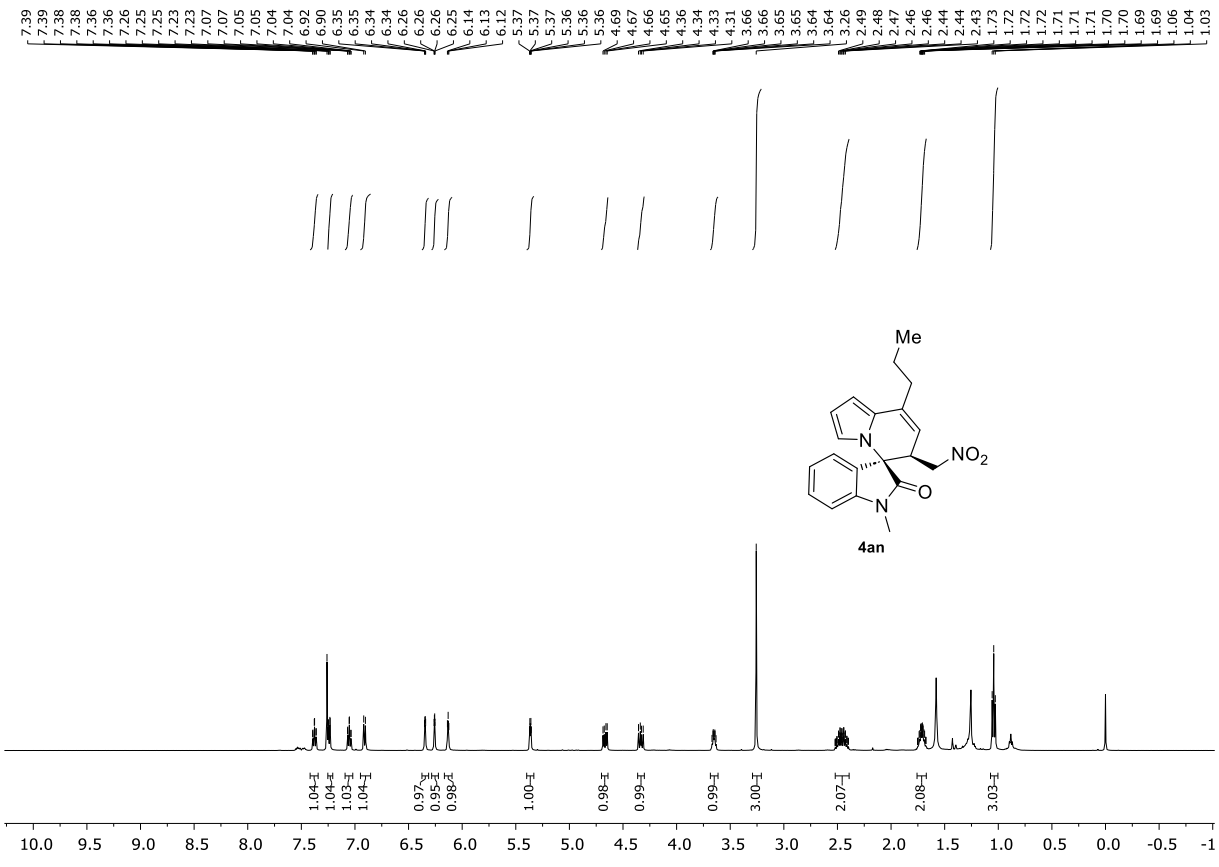
f1 (ppm)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7.04
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NO2
O
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4an
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1.04
1.03
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0.99
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2.08
3.03
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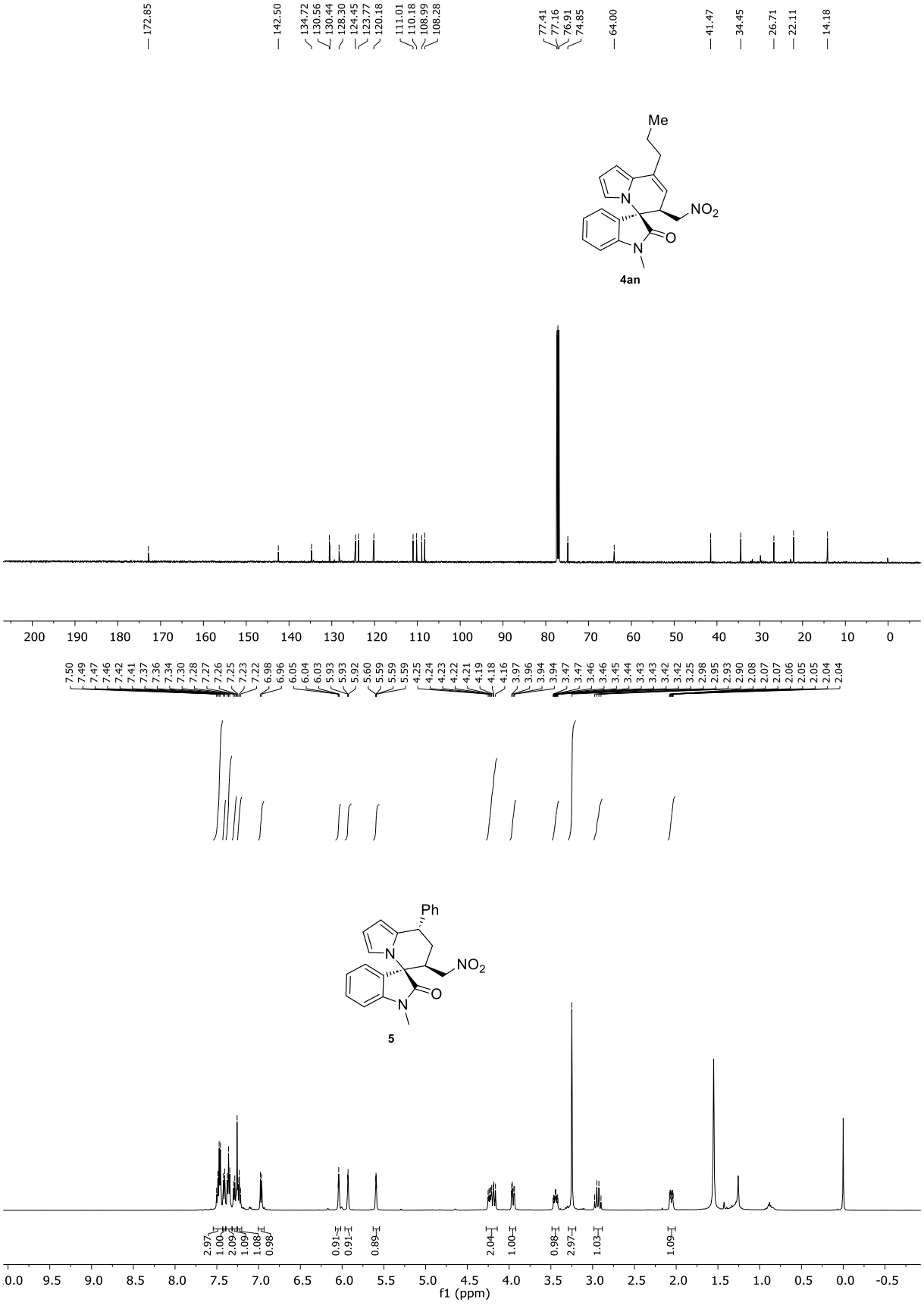
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2.04
2.04
Ph
NO2
O
N
5
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1.00
2.09
1.09
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0.91
0.89
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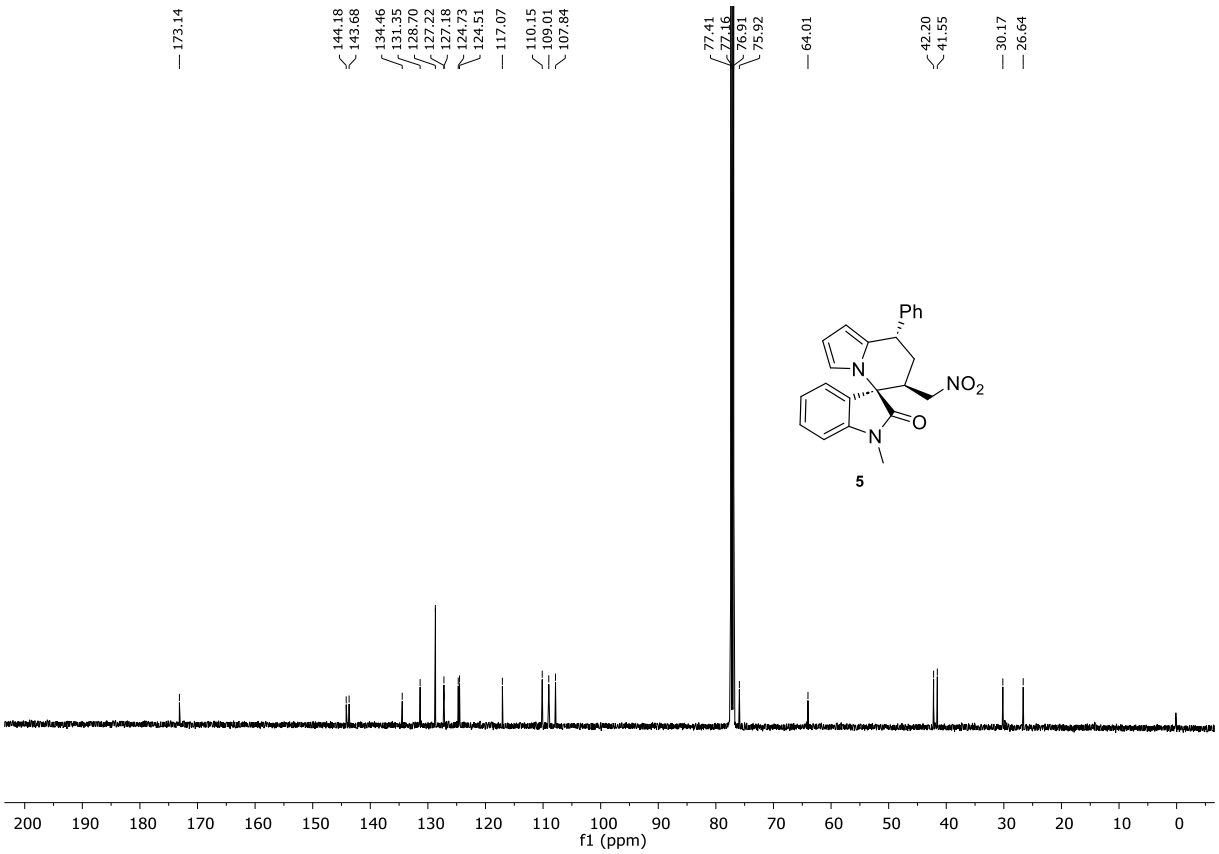
1.00
0.98
2.97
1.03
1.09
f1 (ppm)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77.16
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30.17
26.64
Ph
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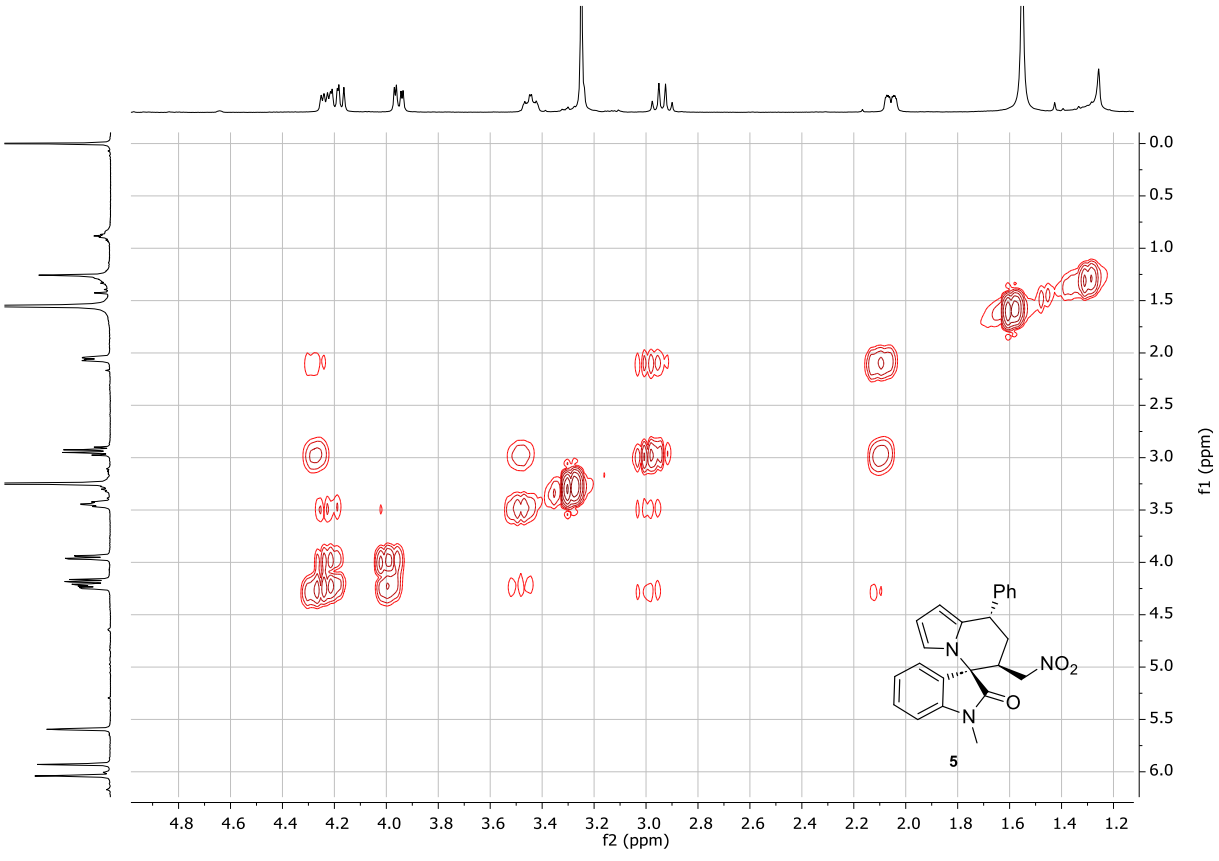
NO2
O
N
5
f1 (ppm)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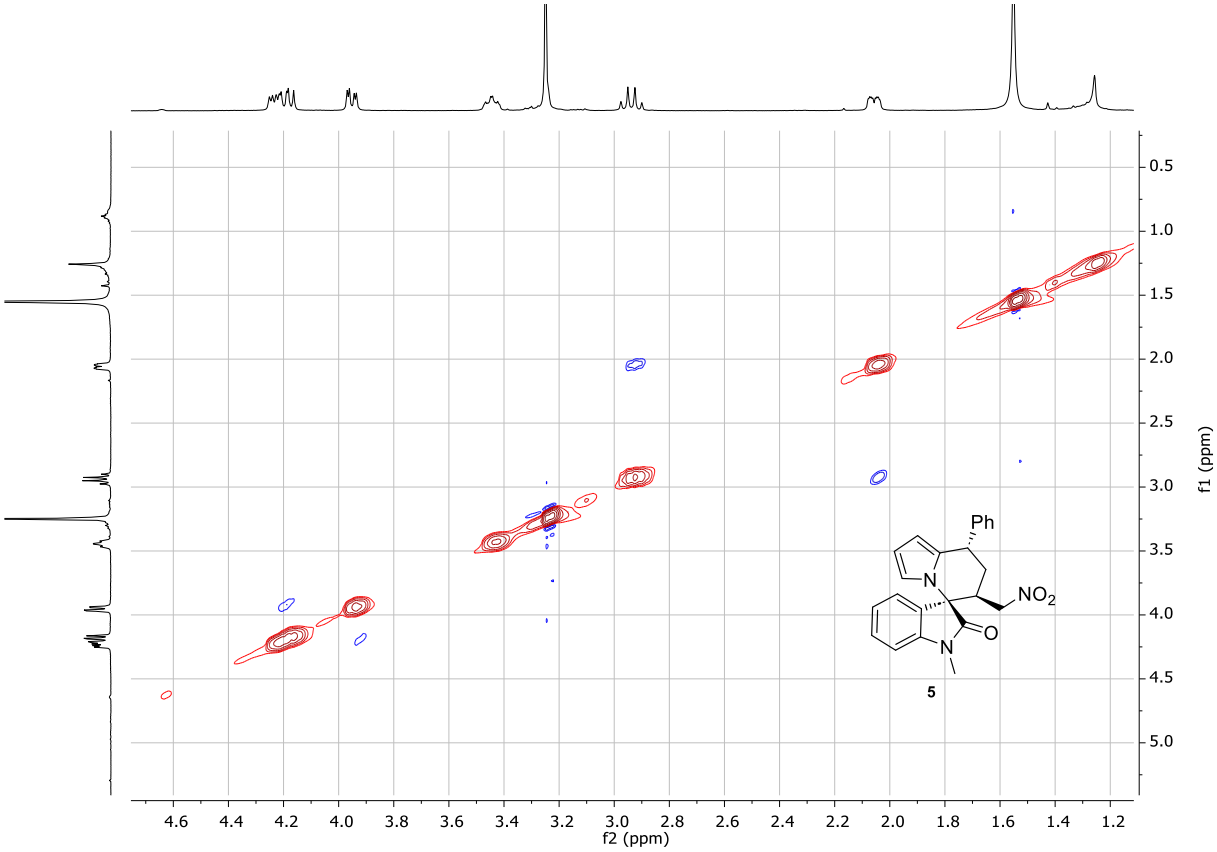
f2 (ppm)
f1 (ppm)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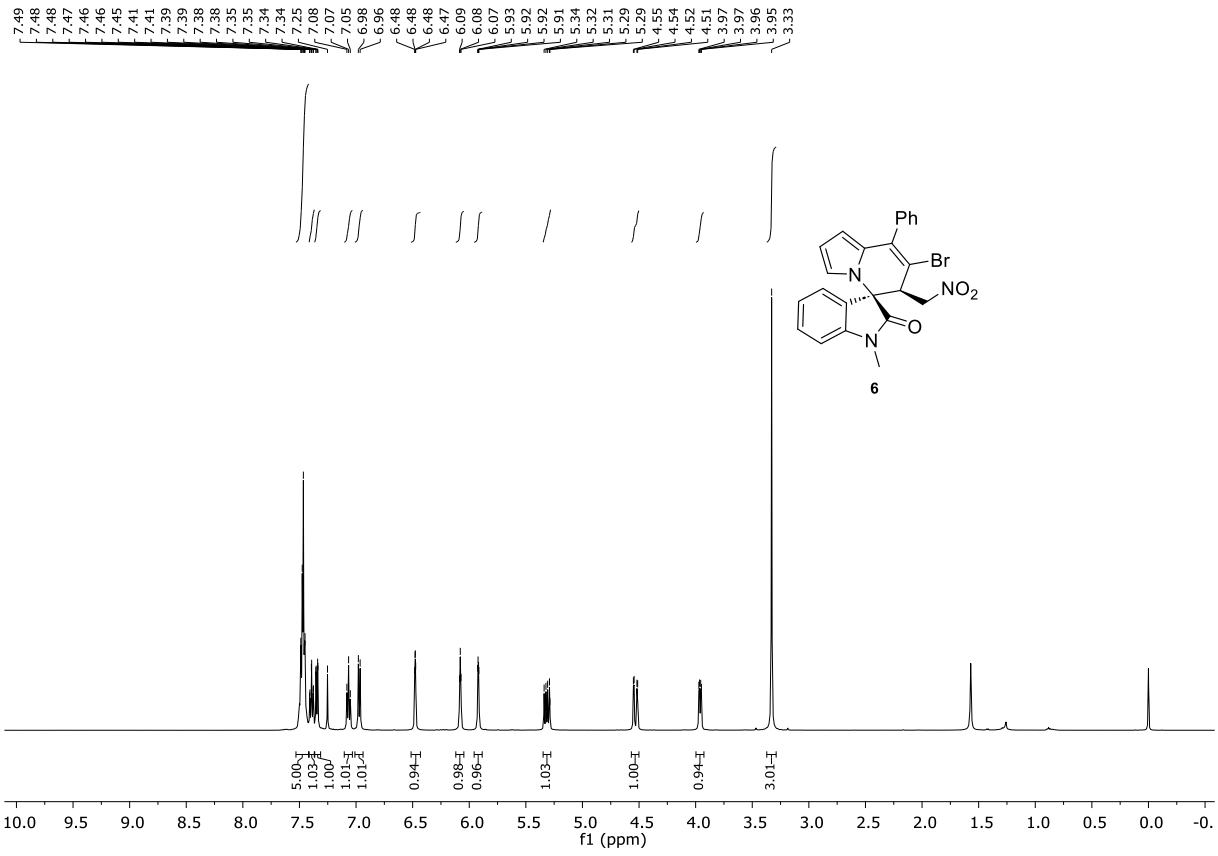
f2 (ppm)
f1 (ppm)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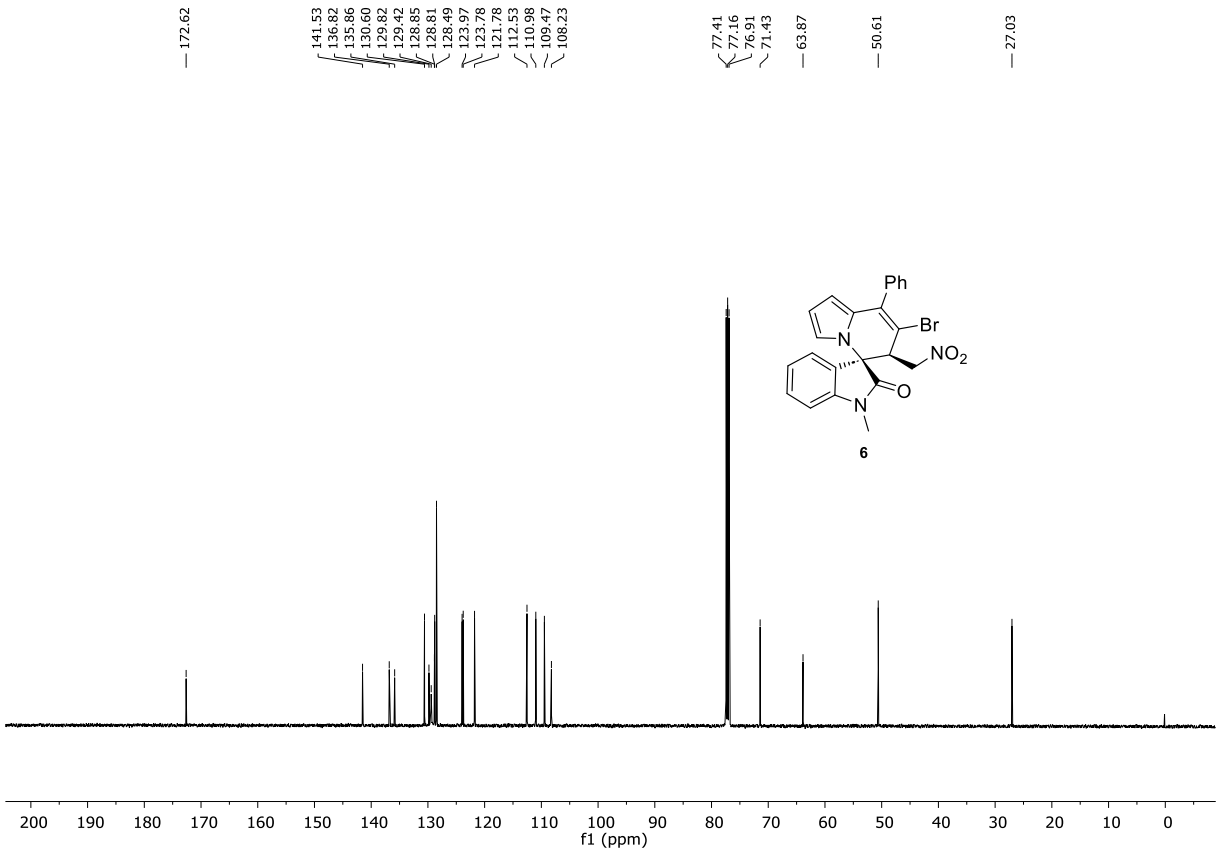
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Br
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NO2
O
N
6
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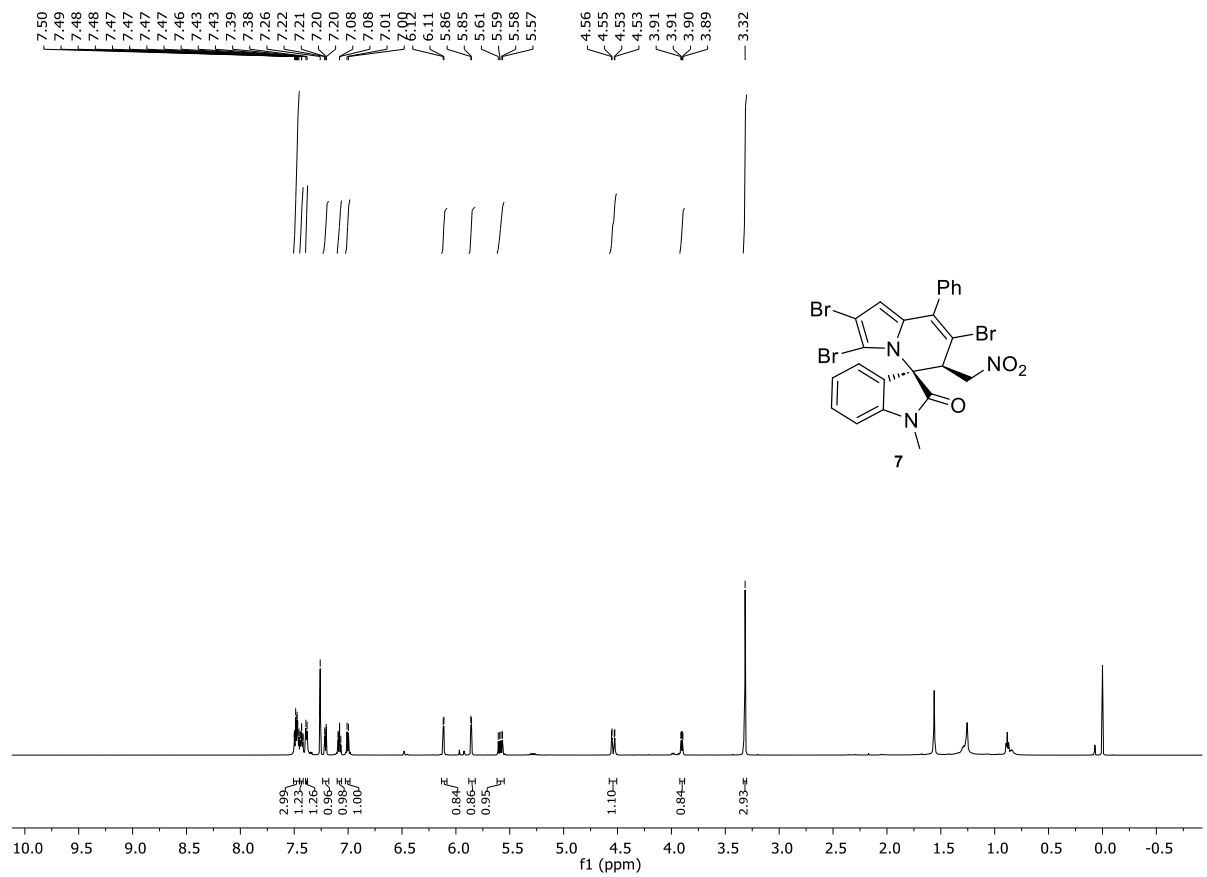
f1 (ppm)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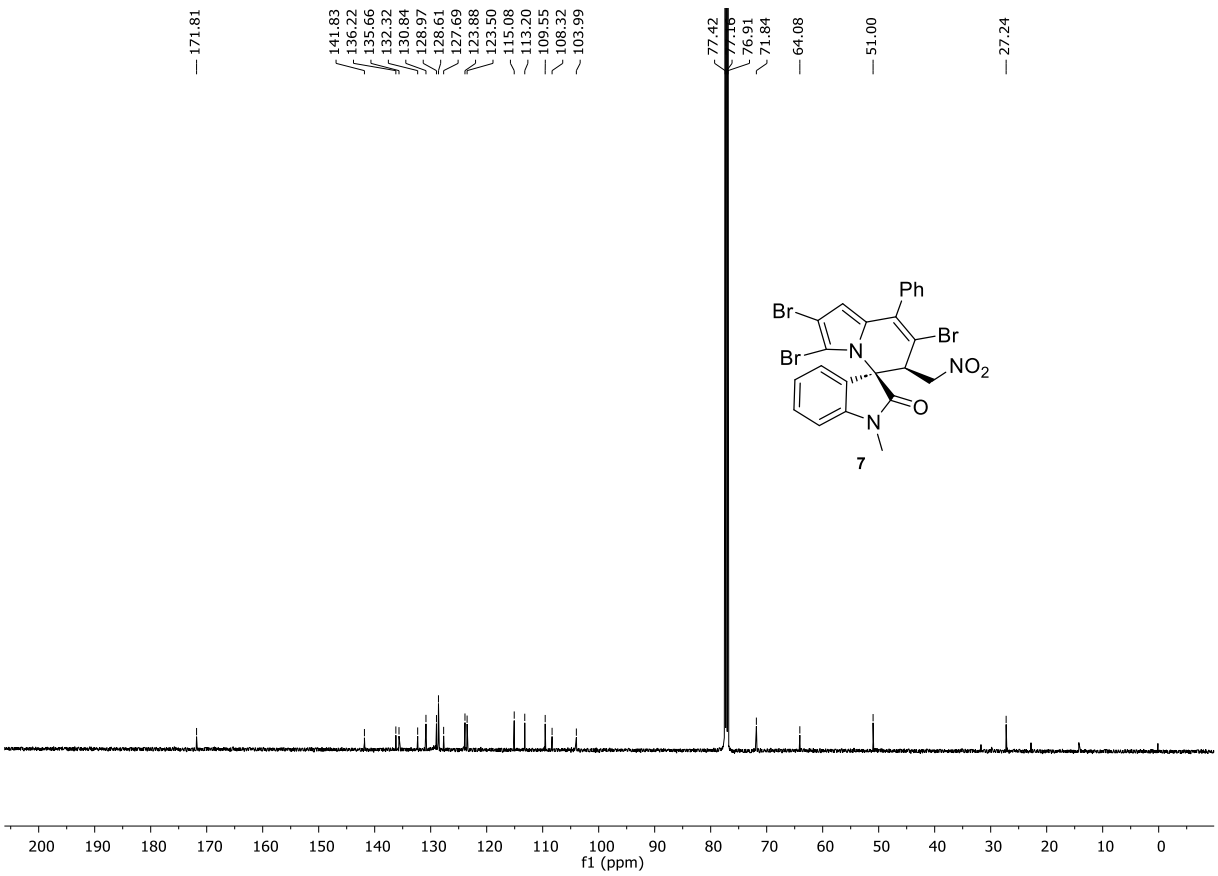
0.95
1.10
0.84
2.93
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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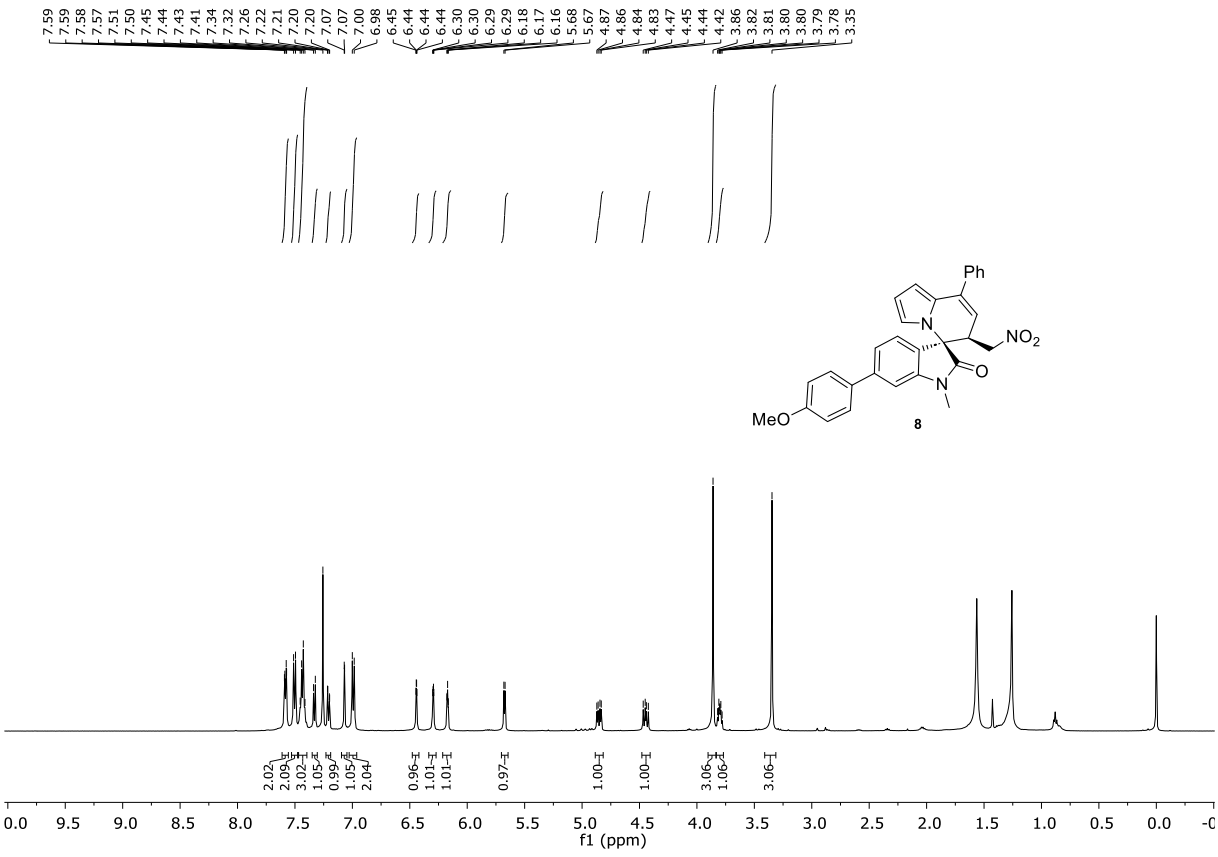
Ph
Br
Br
Br
N
NO2
O
N
7
f1 (ppm)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3.78
3.35
Ph
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NO2
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MeO
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3.02
1.05
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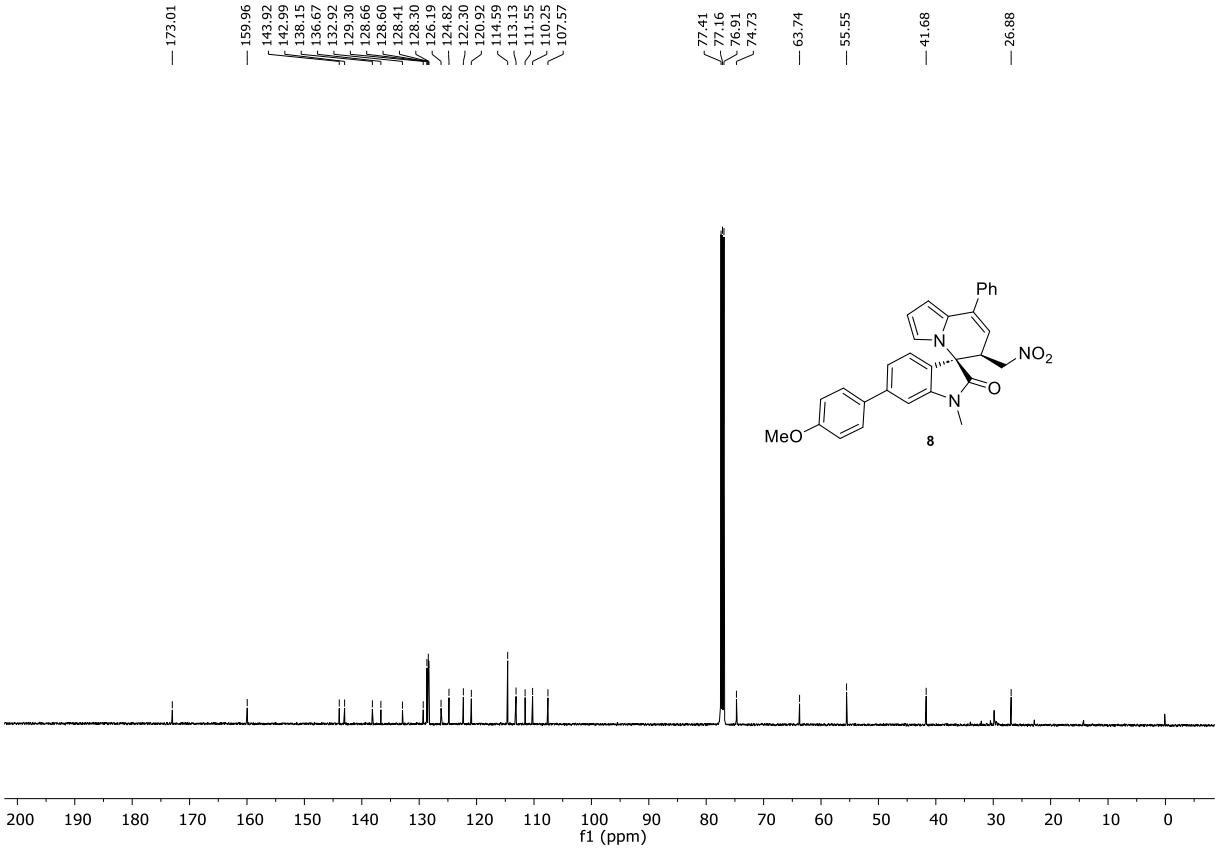
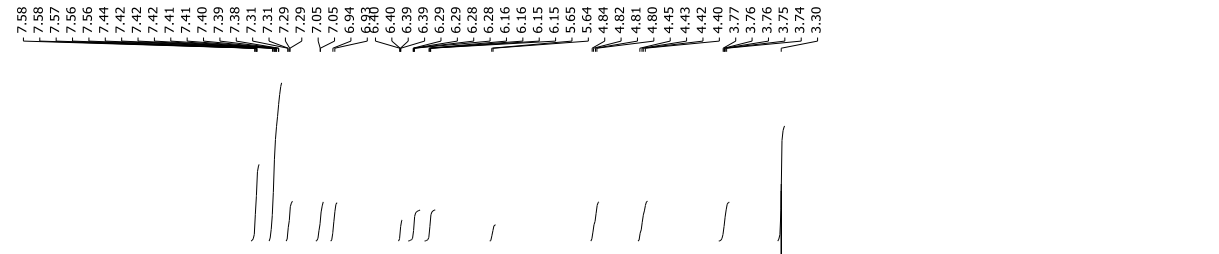
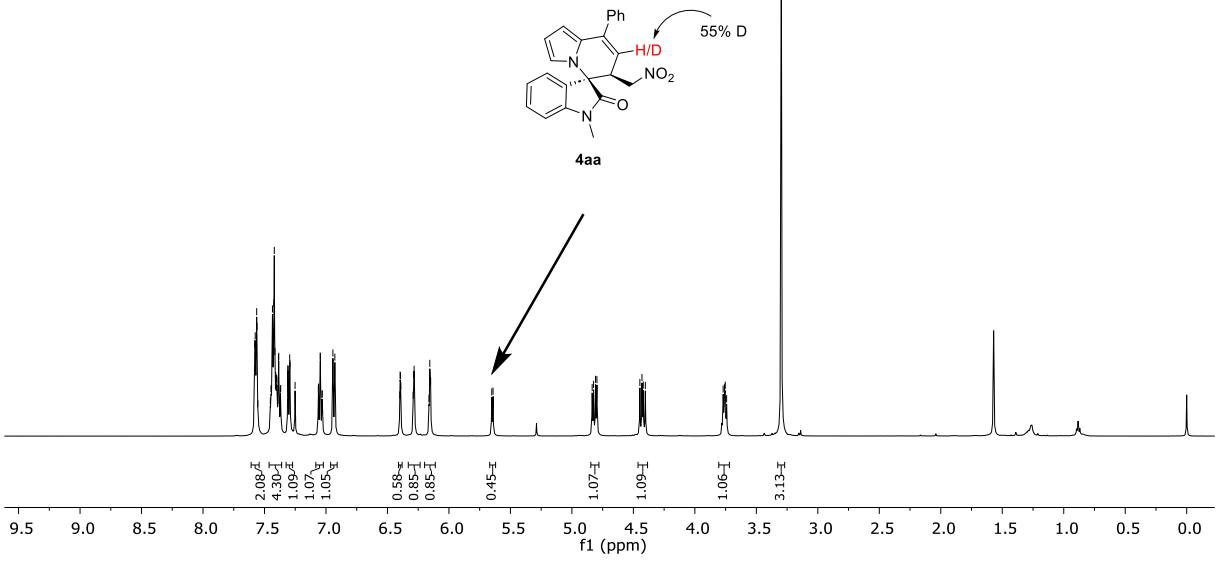
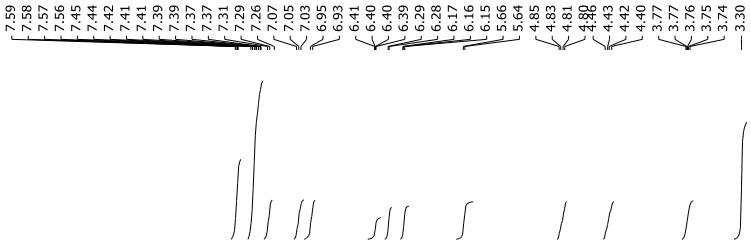
f1 (ppm)



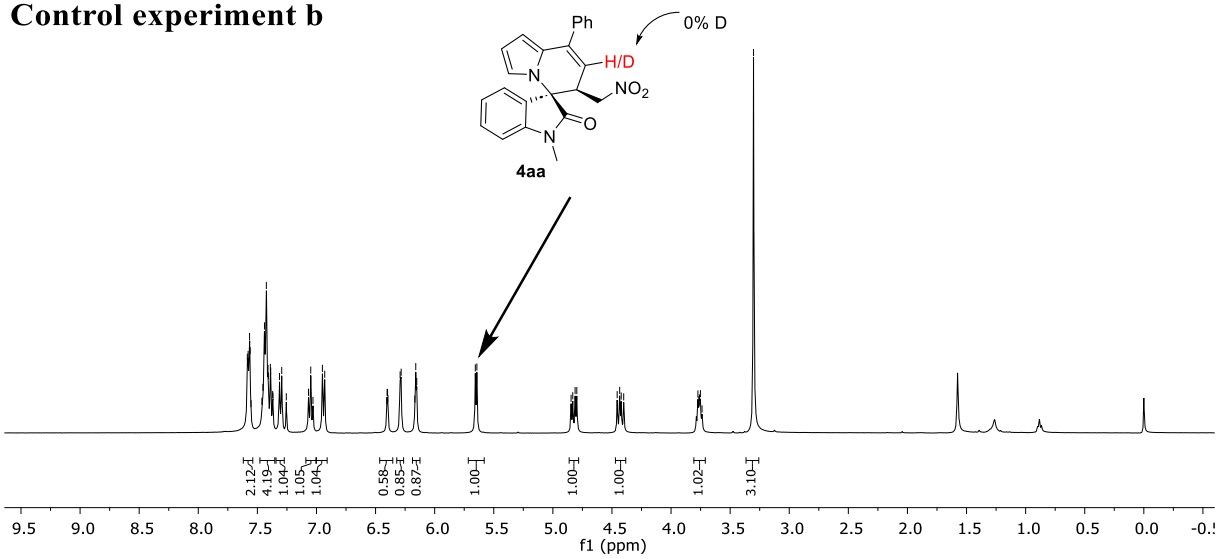




## Control experiment a

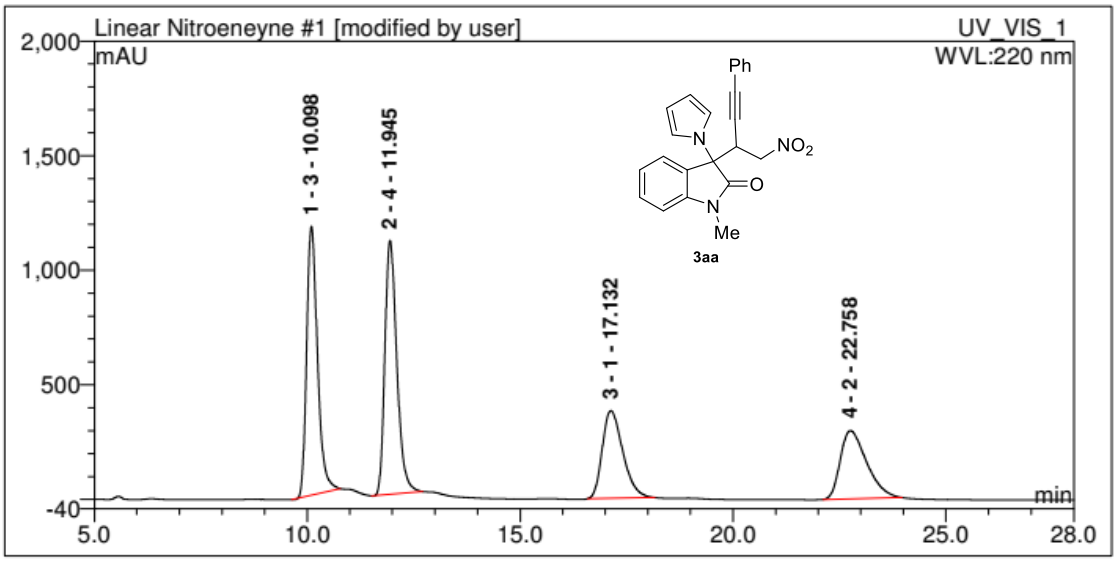




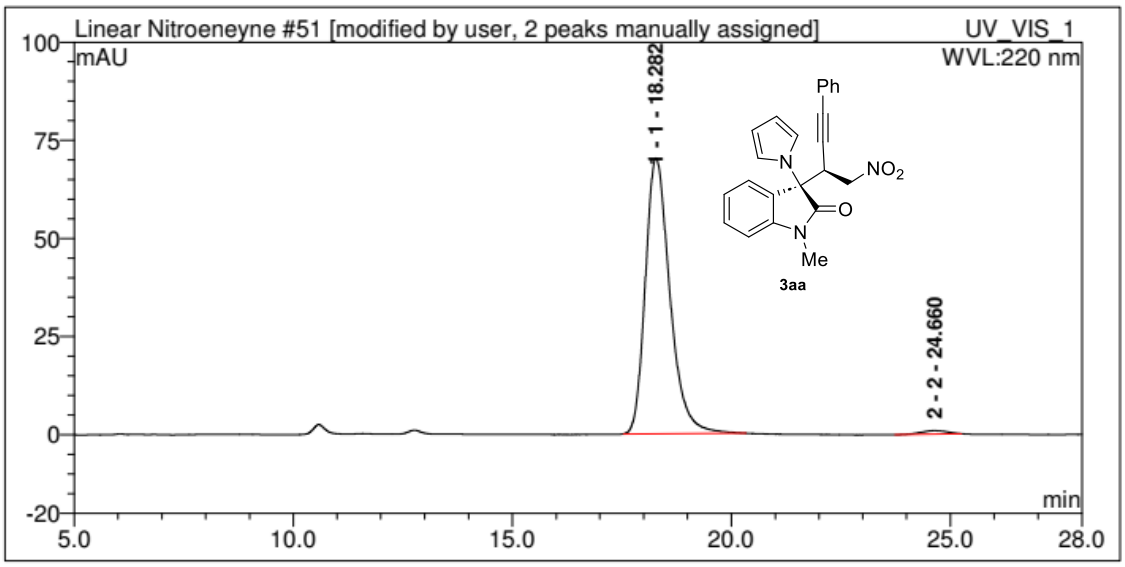

**Control experiment b**



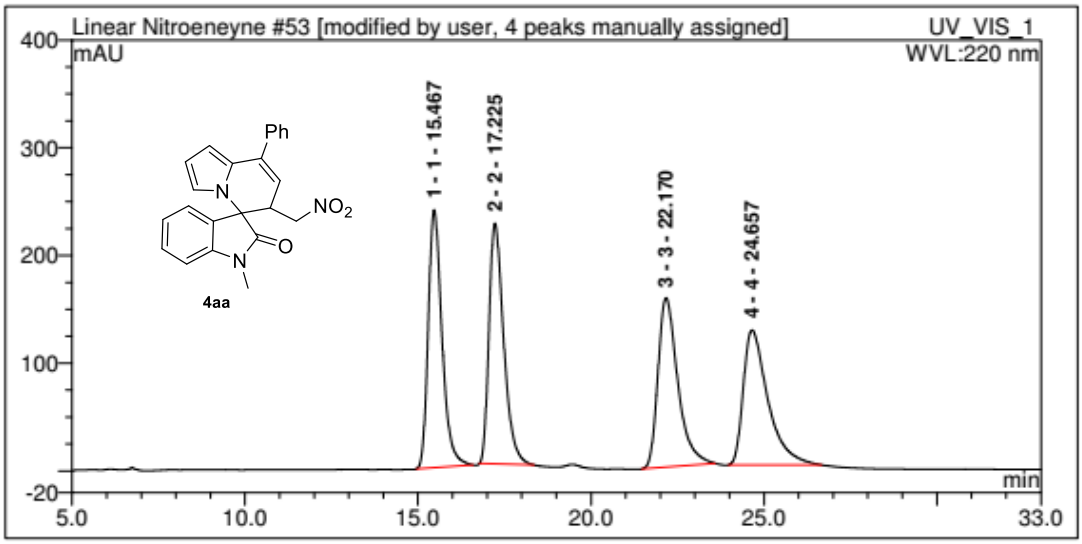
## 17. HPLC chromatogram of the products:



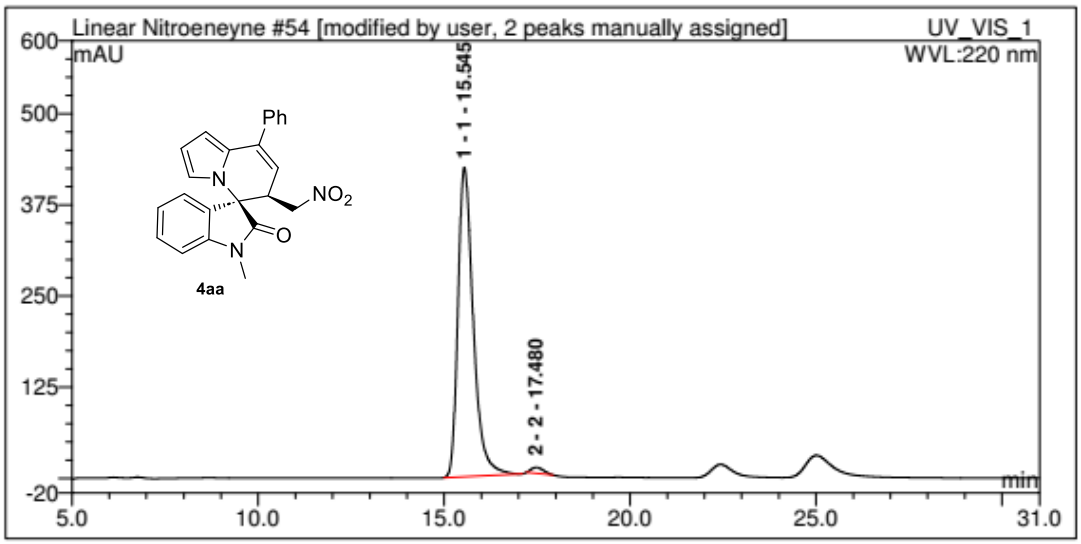

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 3 | 10.10 | 344.8536 | 30.4078974 | 1173.906 | n.a. |
| 2 | 4 | 11.95 | 361.204 | 31.84960864 | 1108.19 | n.a. |
| 3 | 1 | 17.13 | 214.4226 | 18.90698065 | 382.8223 | n.a. |
| 4 | 2 | 22.76 | 213.612 | 18.83551331 | 297.619 | n.a. |



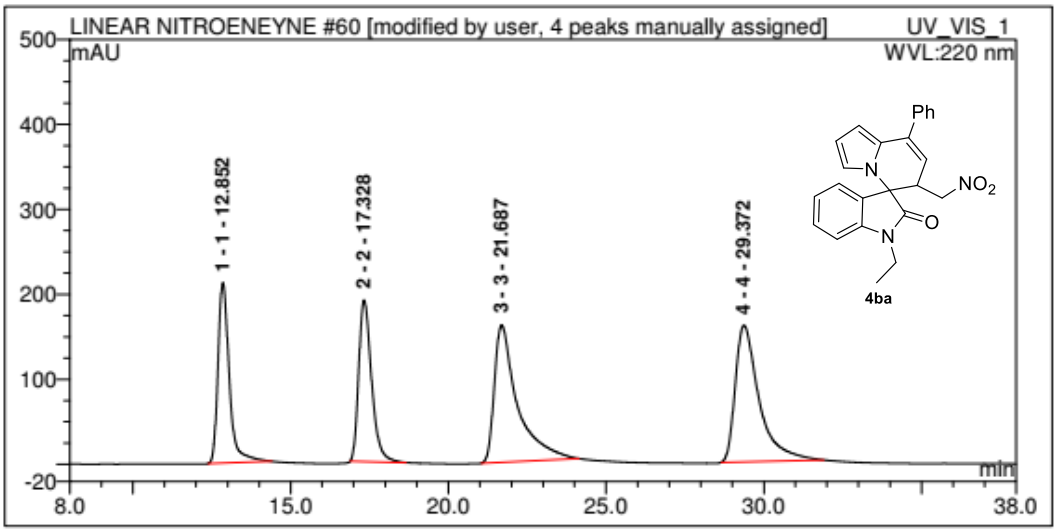

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 18.28 | 45.70046 | 98.64582791 | 70.28438 | n.a. |
| 2 | 2 | 24.66 | 0.627 | 1.35417209 | 0.890 | n.a. |



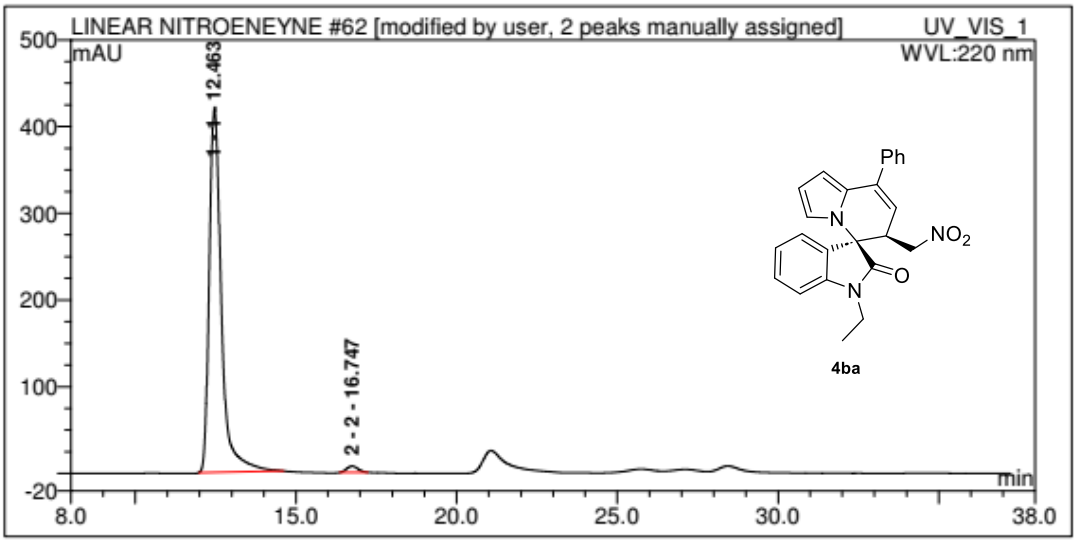

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 15.47 | 110.5138 | 25.80394602 | 239.2405 | n.a. |
| 2 | 2 | 17.23 | 109.8557 | 25.65029197 | 223.4079 | n.a. |
| 3 | 3 | 22.17 | 104.4018 | 24.37686502 | 157.086 | n.a. |
| 4 | 4 | 24.66 | 103.511 | 24.16889699 | 125.252 | n.a. |



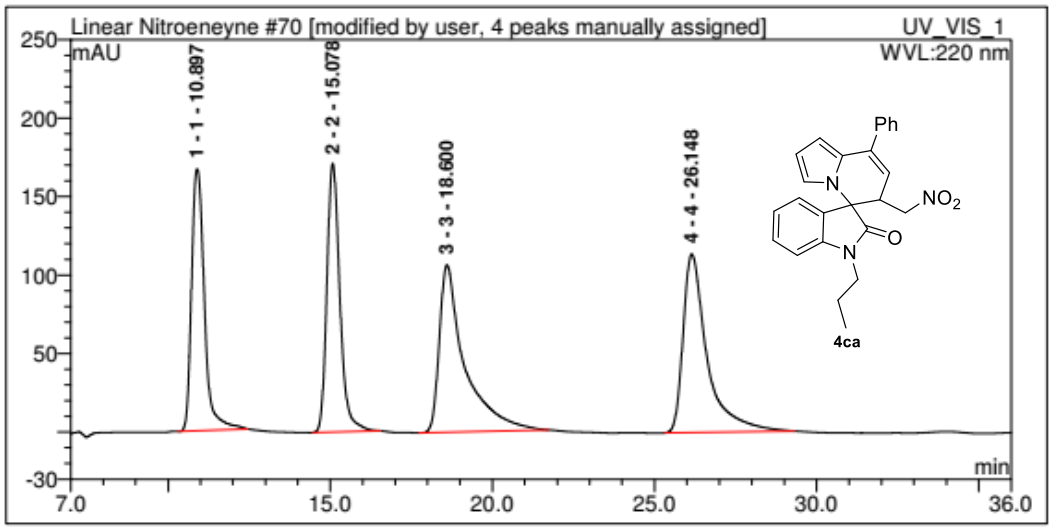

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 15.55 | 202.187 | 98.47334732 | 424.3441 | n.a. |
| 2 | 2 | 17.48 | 3.135 | 1.526652679 | 8.119 | n.a. |



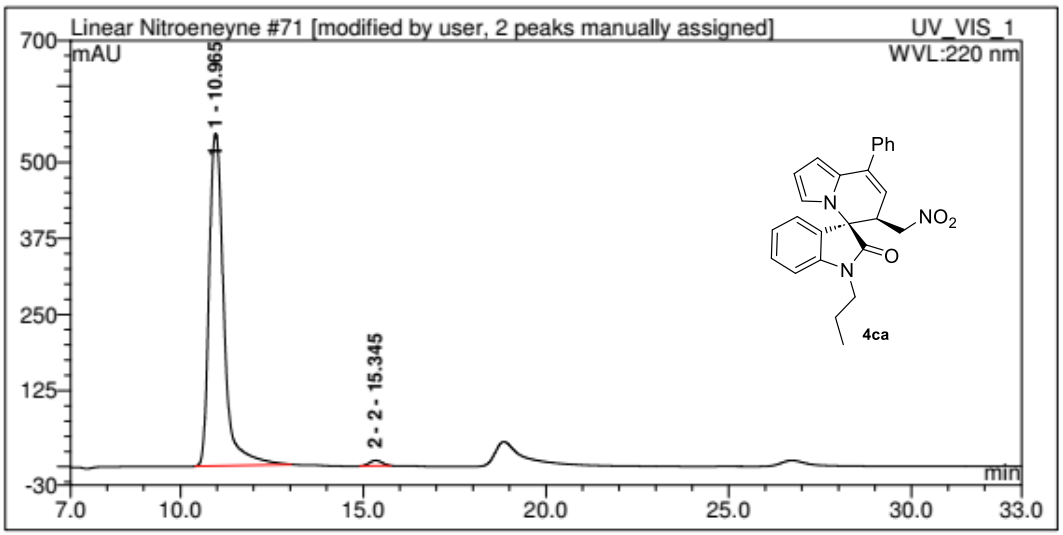

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 12.85 | 88.2105 | 19.31917069 | 212.4018 | n.a. |
| 2 | 2 | 17.33 | 90.06438 | 19.72519406 | 190.2734 | n.a. |
| 3 | 3 | 21.69 | 137.2872 | 30.06755643 | 161.5053 | n.a. |
| 4 | 4 | 29.37 | 141.034 | 30.88807882 | 160.593 | n.a. |



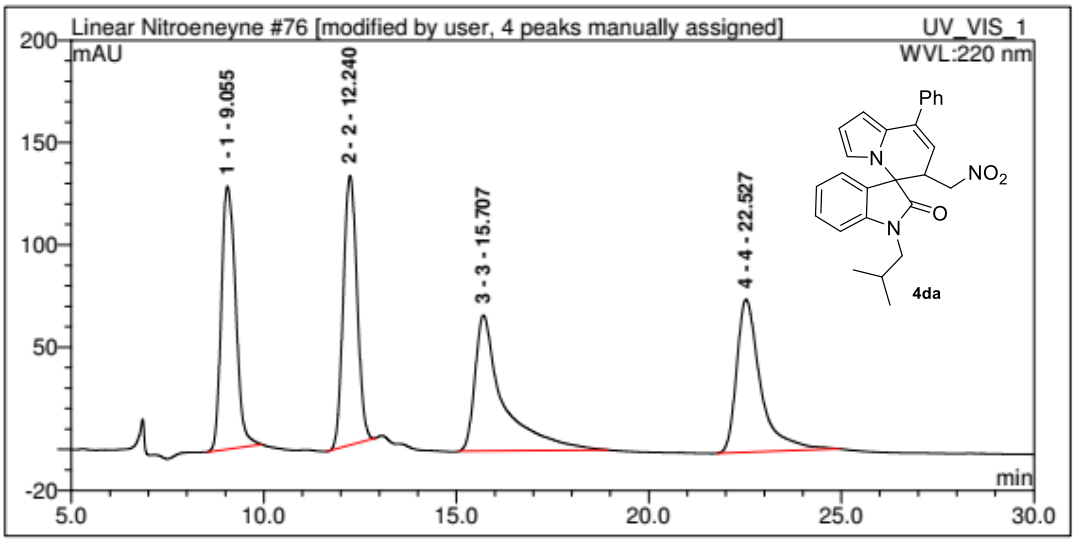

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 12.46 | 184.2835 | 98.41775302 | 418.6137 | n.a. |
| 2 | 2 | 16.75 | 2.963 | 1.582246976 | 7.242 | n.a. |



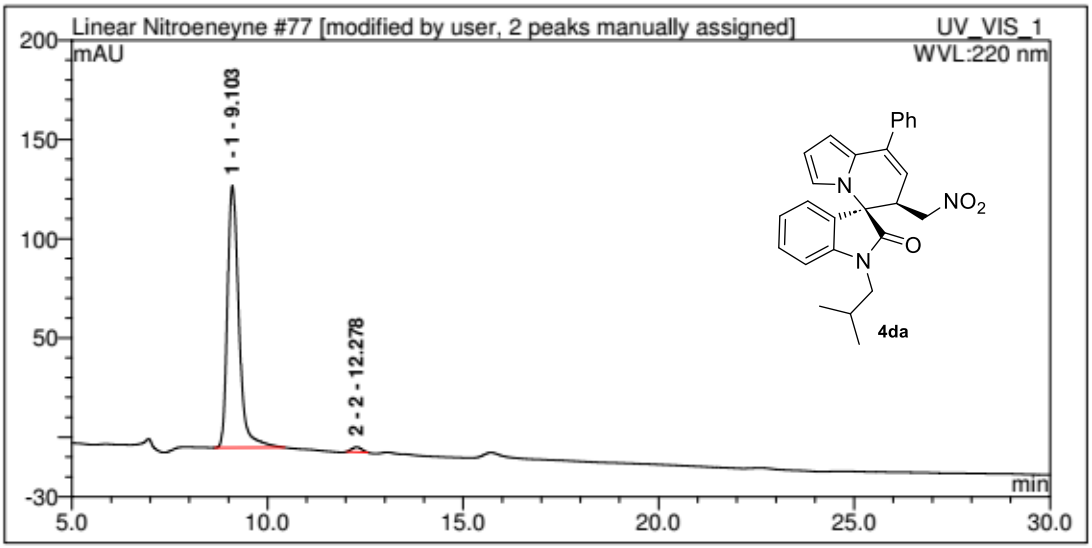

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 10.90 | 76.55668 | 21.83859404 | 166.8177 | n.a. |
| 2 | 2 | 15.08 | 79.48459 | 22.67381017 | 171.1378 | n.a. |
| 3 | 3 | 18.60 | 96.60364 | 27.55719712 | 106.5947 | n.a. |
| 4 | 4 | 26.15 | 97.912 | 27.93039867 | 113.718 | n.a. |



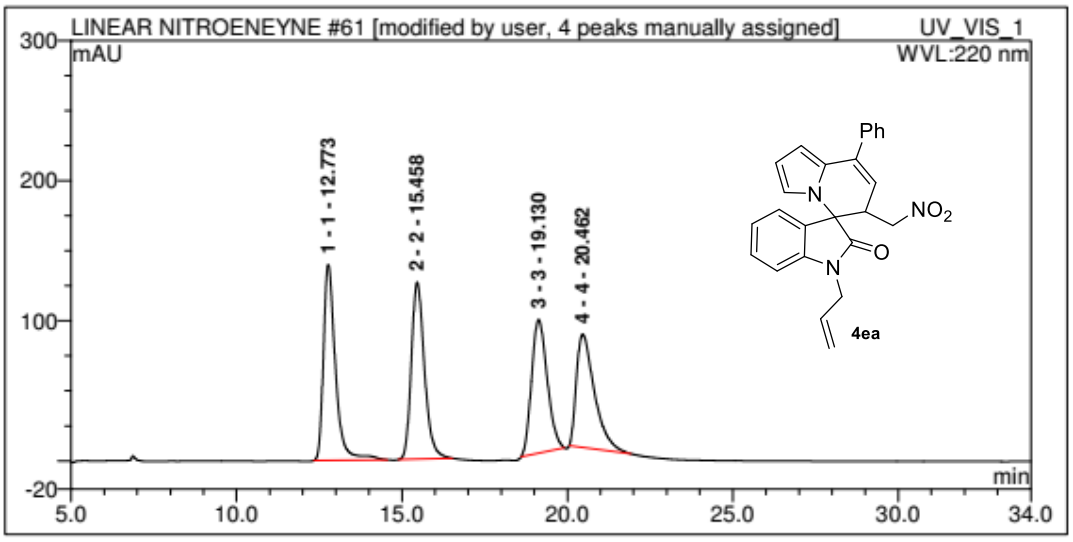

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 10.97 | 255.1452 | 98.62507634 | 546.2892 | n.a. |
| 2 | 2 | 15.35 | 3.557 | 1.374923663 | 8.876 | n.a. |



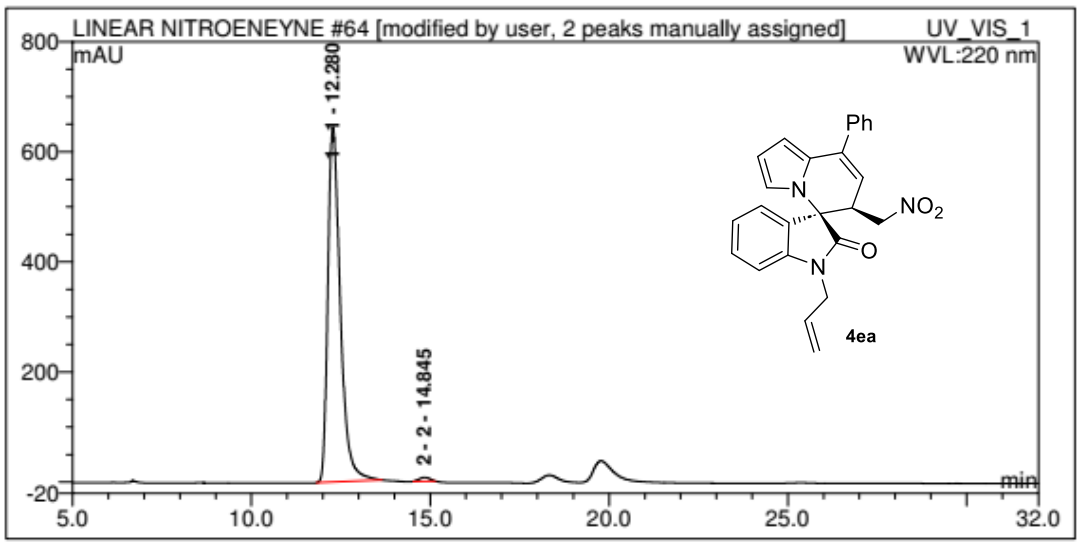

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 9.06 | 55.34963 | 25.14588475 | 128.5657 | n.a. |
| 2 | 2 | 12.24 | 54.4723 | 24.74730615 | 131.7994 | n.a. |
| 3 | 3 | 15.71 | 56.32928 | 25.59095268 | 66.33989 | n.a. |
| 4 | 4 | 22.53 | 53.963 | 24.51585642 | 74.621 | n.a. |



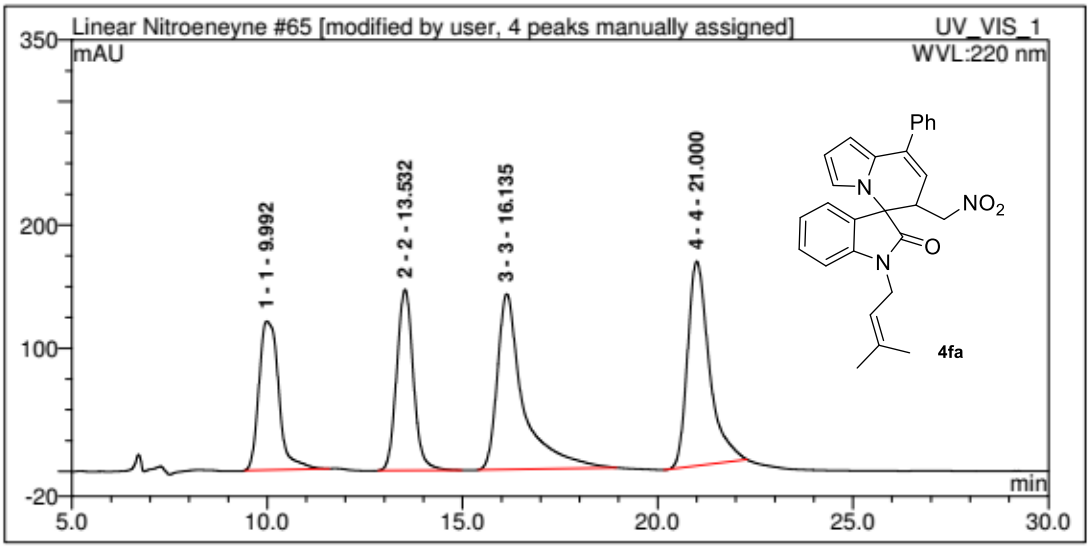

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 9.10 | 44.95319 | 98.43160871 | 131.9212 | n.a. |
| 2 | 2 | 12.28 | 0.716 | 1.568391295 | 2.476 | n.a. |



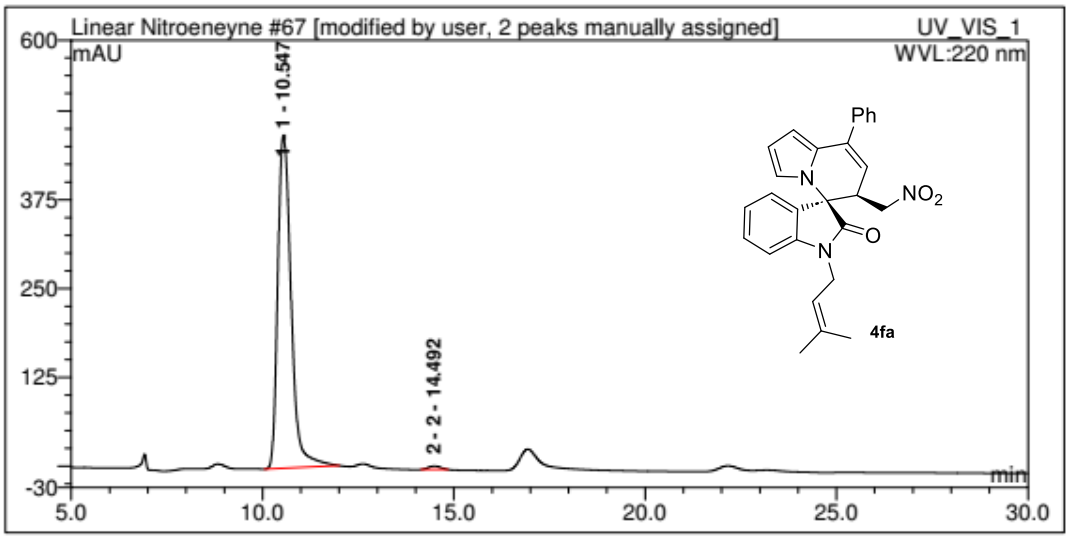

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 12.77 | 58.88817 | 26.72647388 | 139.5453 | n.a. |
| 2 | 2 | 15.46 | 58.1058 | 26.37139336 | 126.2739 | n.a. |
| 3 | 3 | 19.13 | 52.24124 | 23.70975631 | 95.29495 | n.a. |
| 4 | 4 | 20.46 | 51.101 | 23.19237646 | 80.796 | n.a. |



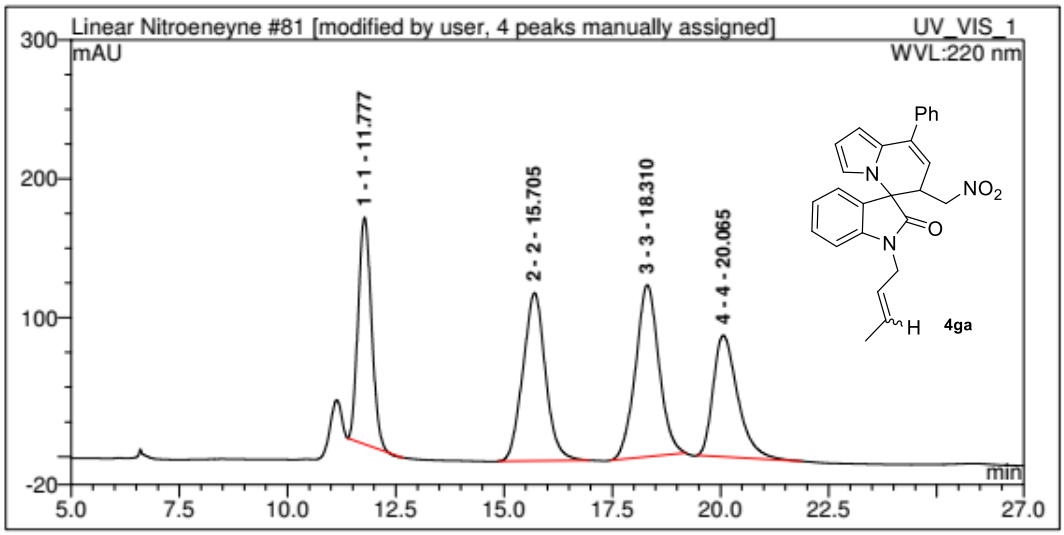

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 12.28 | 260.1647 | 99.09785028 | 644.9742 | n.a. |
| 2 | 2 | 14.85 | 2.368 | 0.9021497204 | 6.970 | n.a. |



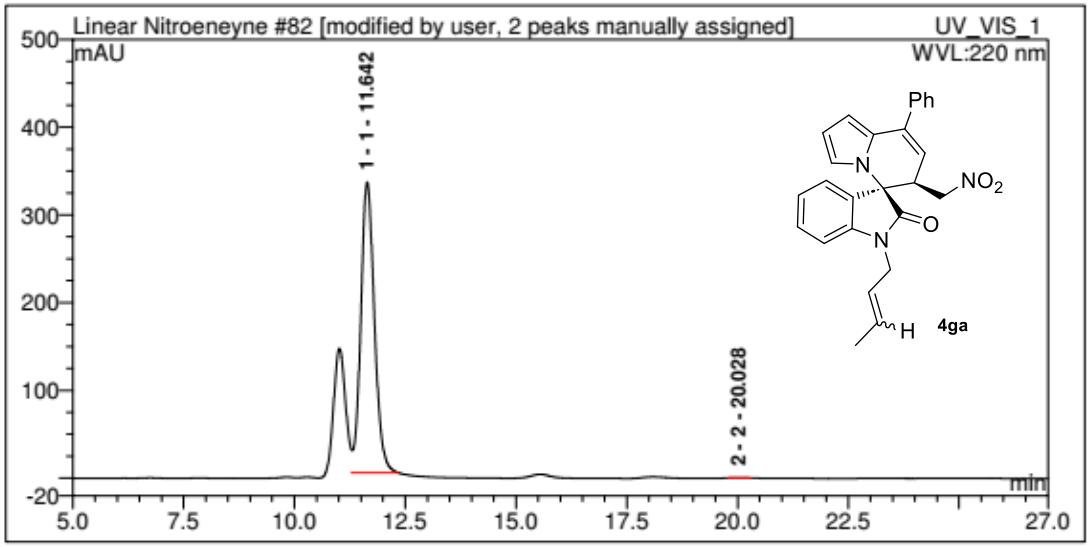

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 9.99 | 71.05701 | 19.68143583 | 120.7695 | n.a. |
| 2 | 2 | 13.53 | 72.80242 | 20.1648811 | 146.9265 | n.a. |
| 3 | 3 | 16.14 | 109.5843 | 30.35274939 | 142.3328 | n.a. |
| 4 | 4 | 21.00 | 107.592 | 29.80093368 | 165.957 | n.a. |



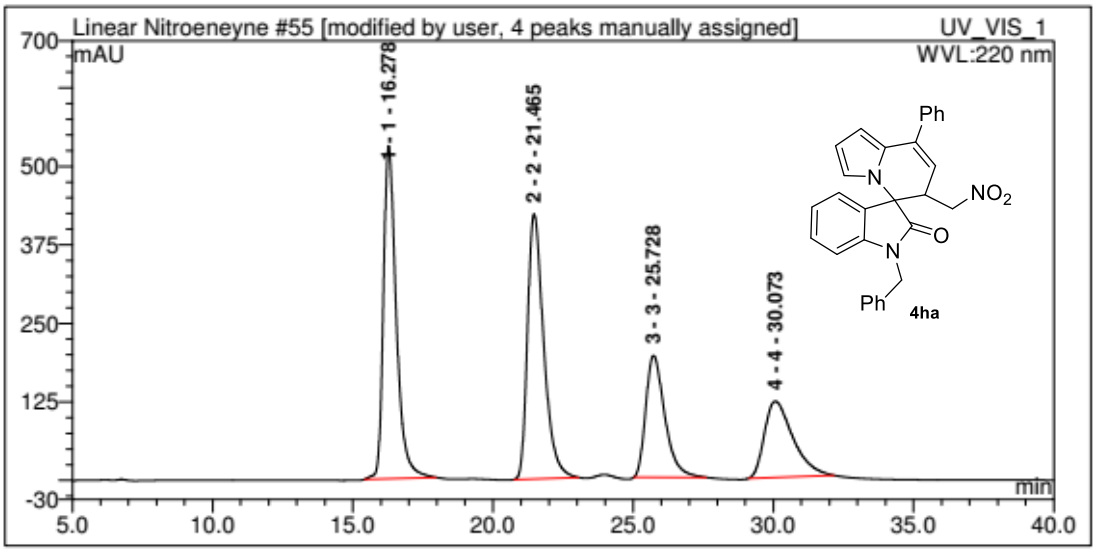

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 10.55 | 190.3708 | 99.05922541 | 468.3376 | n.a. |
| 2 | 2 | 14.49 | 1.808 | 0.9407745852 | 4.950 | n.a. |



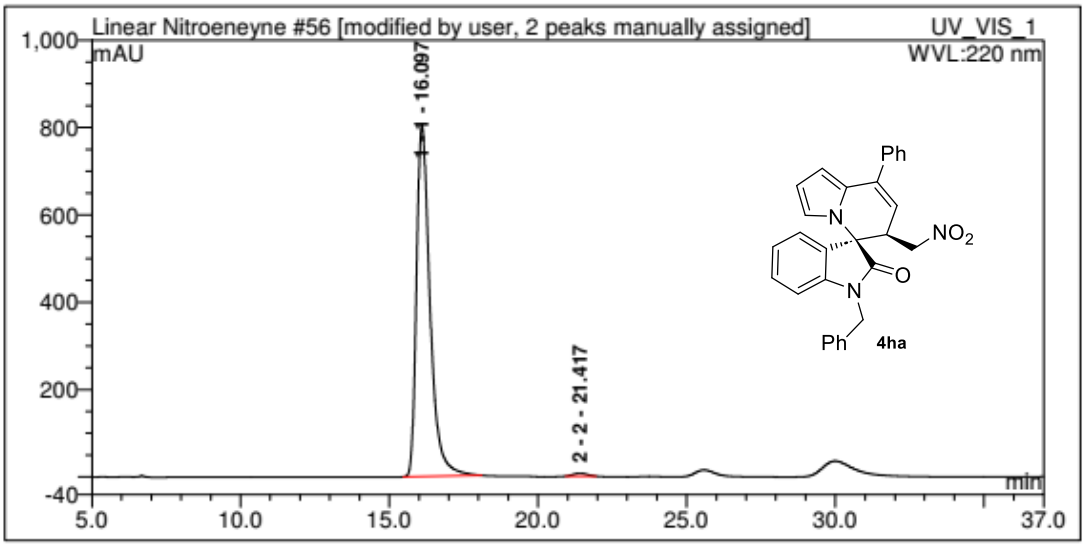

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 11.78 | 58.35706 | 21.88091392 | 163.097 | n.a. |
| 2 | 2 | 15.71 | 73.33481 | 27.49680116 | 120.9273 | n.a. |
| 3 | 3 | 18.31 | 77.39743 | 29.02007735 | 123.5987 | n.a. |
| 4 | 4 | 20.07 | 57.614 | 21.60220757 | 87.518 | n.a. |



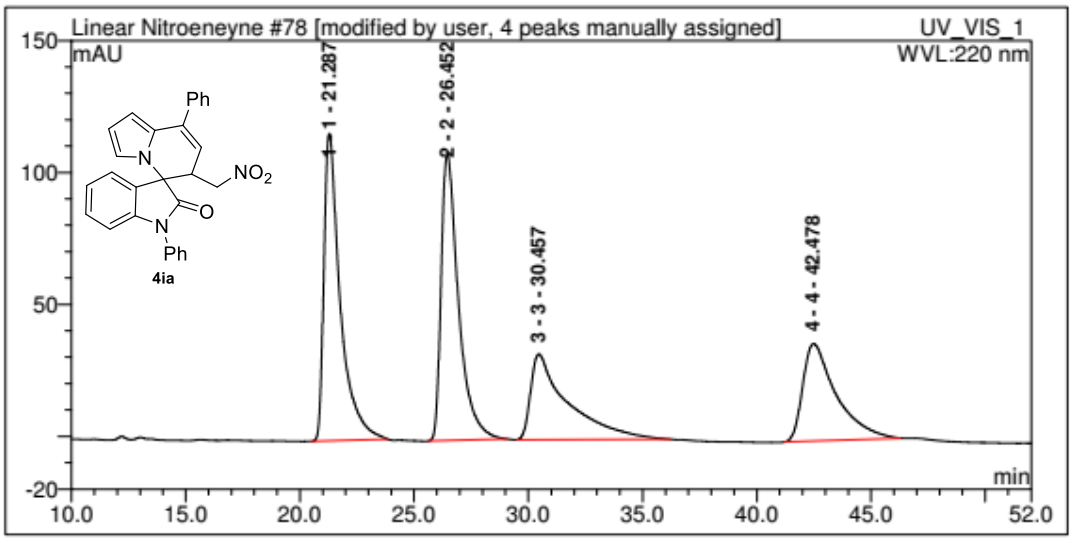

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 11.64 | 118.0836 | 99.89023535 | 331.3802 | n.a. |
| 2 | 2 | 20.03 | 0.130 | 0.1097646478 | 0.399 | n.a. |



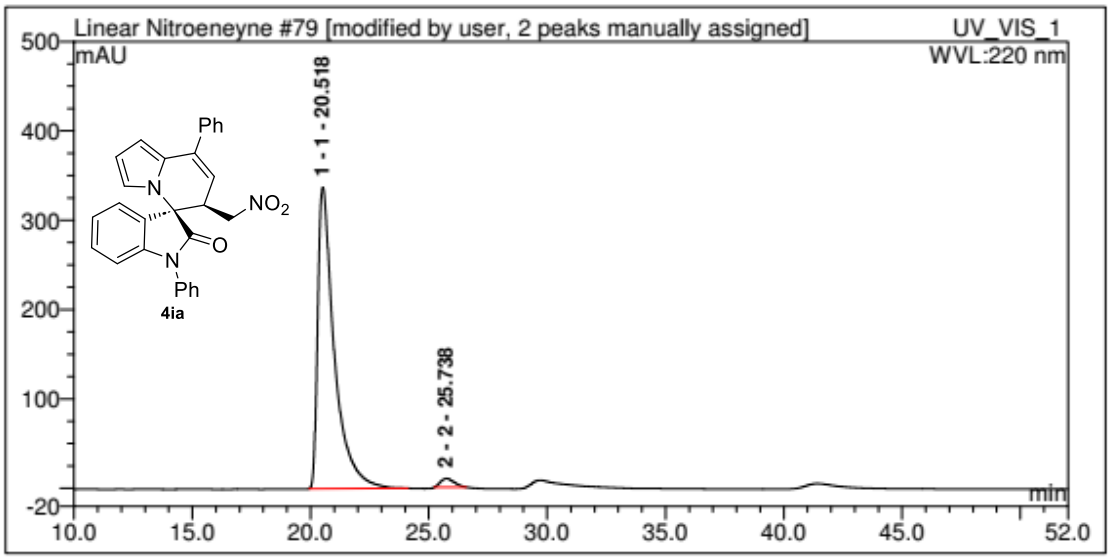

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 16.28 | 281.8699 | 32.74247056 | 529.8356 | n.a. |
| 2 | 2 | 21.47 | 281.9697 | 32.75406185 | 421.9169 | n.a. |
| 3 | 3 | 25.73 | 153.5265 | 17.83389682 | 193.7904 | n.a. |
| 4 | 4 | 30.07 | 143.503 | 16.66957077 | 121.462 | n.a. |



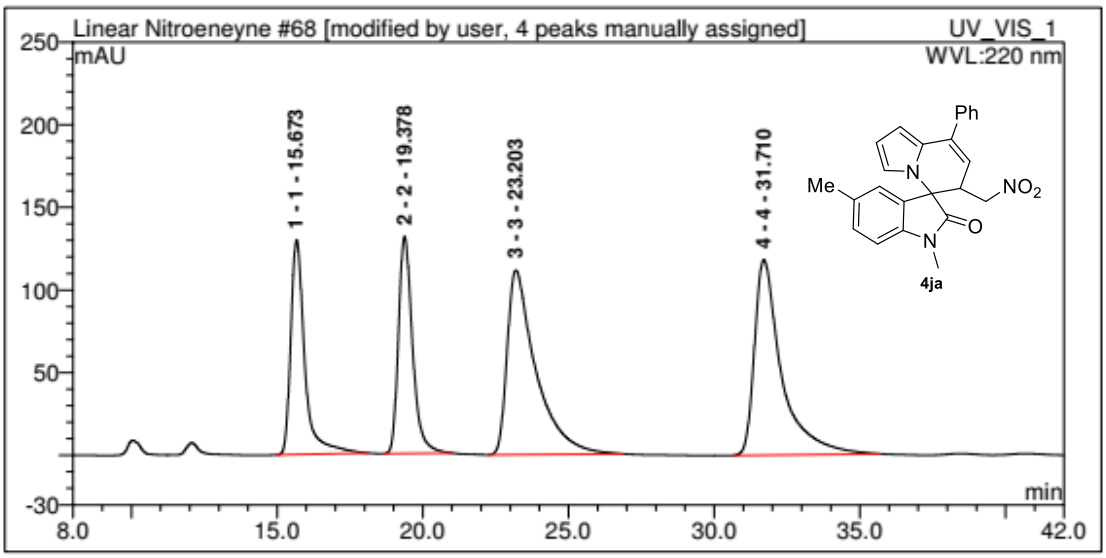

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 16.10 | 424.7522 | 99.18963003 | 805.2604 | n.a. |
| 2 | 2 | 21.42 | 3.470 | 0.8103699714 | 6.399 | n.a. |



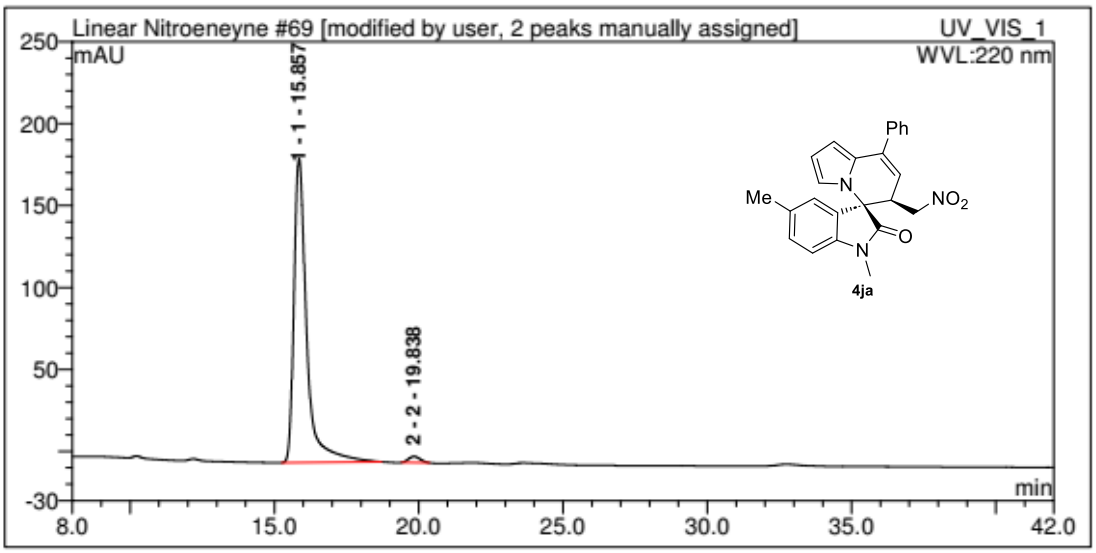

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 21.29 | 96.50378 | 30.54261996 | 116.5649 | n.a. |
| 2 | 2 | 26.45 | 95.98213 | 30.37752366 | 109.0498 | n.a. |
| 3 | 3 | 30.46 | 60.98269 | 19.3005013 | 32.46497 | n.a. |
| 4 | 4 | 42.48 | 62.496 | 19.77935508 | 36.891 | n.a. |



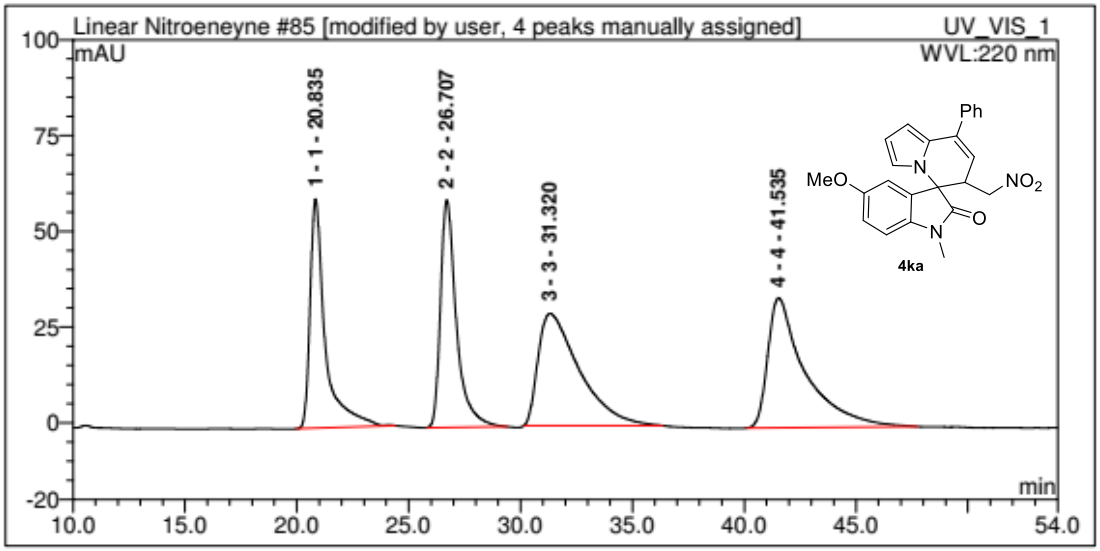

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 20.52 | 274.0895 | 97.65380256 | 337.261 | n.a. |
| 2 | 2 | 25.74 | 6.585 | 2.346197445 | 9.772 | n.a. |



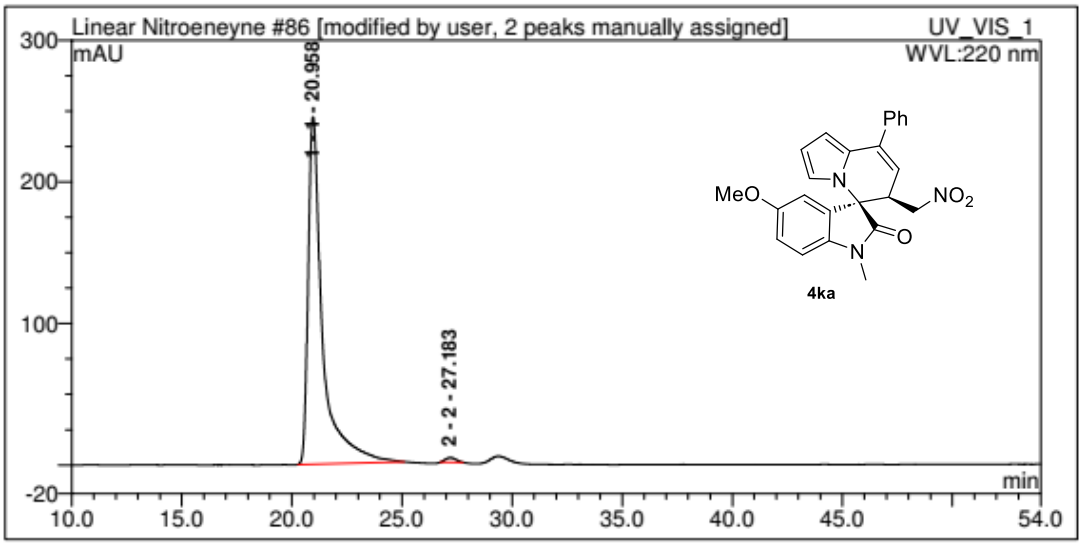

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 15.67 | 72.79872 | 18.15147292 | 129.8653 | n.a. |
| 2 | 2 | 19.38 | 73.71794 | 18.38066849 | 131.3991 | n.a. |
| 3 | 3 | 23.20 | 127.2017 | 31.71620191 | 111.5524 | n.a. |
| 4 | 4 | 31.71 | 127.344 | 31.75165668 | 118.218 | n.a. |



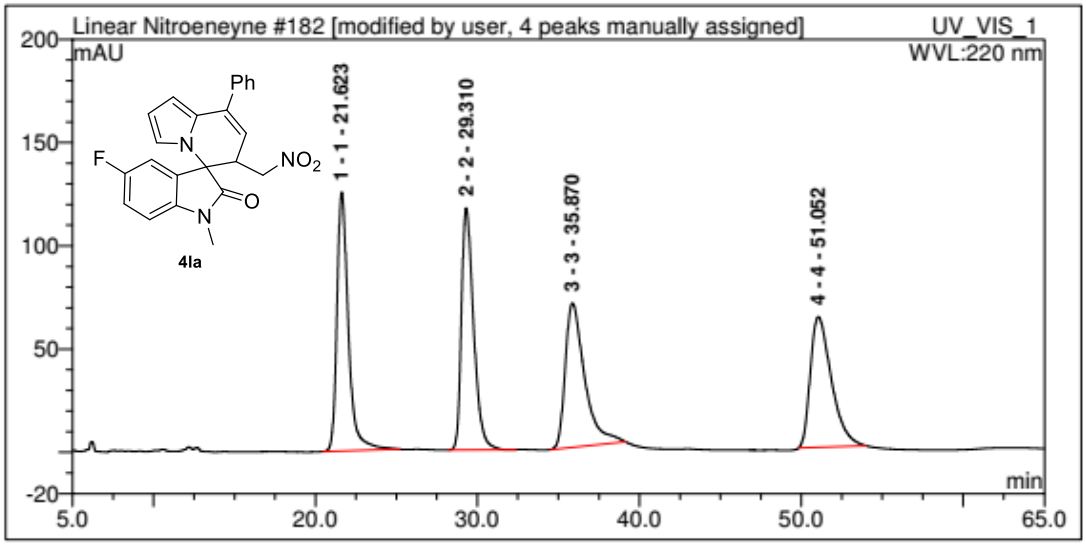

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 15.86 | 95.24545 | 98.19730285 | 185.4162 | n.a. |
| 2 | 2 | 19.84 | 1.749 | 1.802697149 | 3.764 | n.a. |



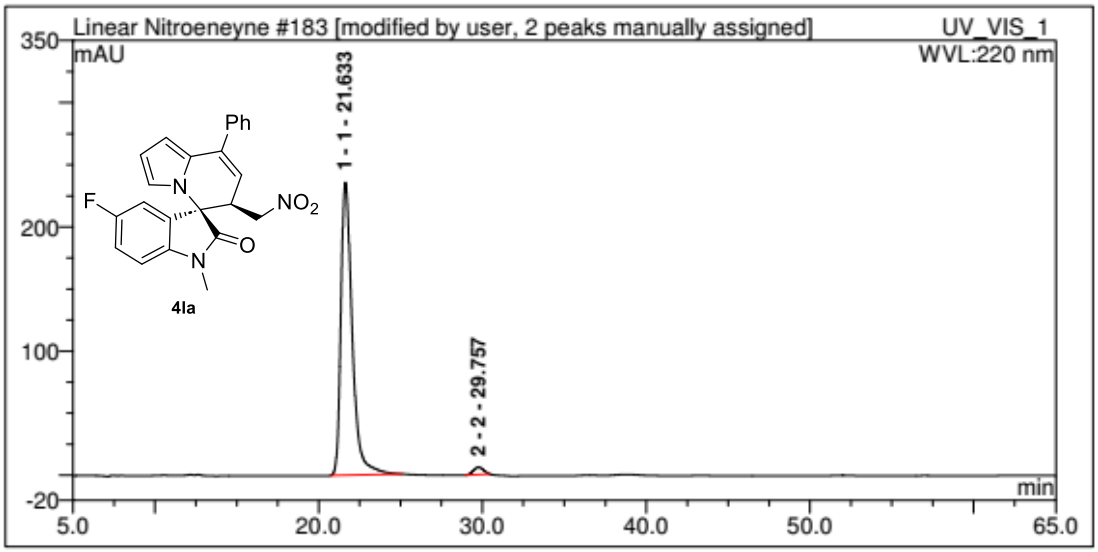

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 20.84 | 47.01138 | 20.99571226 | 59.83843 | n.a. |
| 2 | 2 | 26.71 | 48.98895 | 21.87891244 | 59.44914 | n.a. |
| 3 | 3 | 31.32 | 62.5145 | 27.91954624 | 29.24162 | n.a. |
| 4 | 4 | 41.54 | 65.395 | 29.20582906 | 33.898 | n.a. |



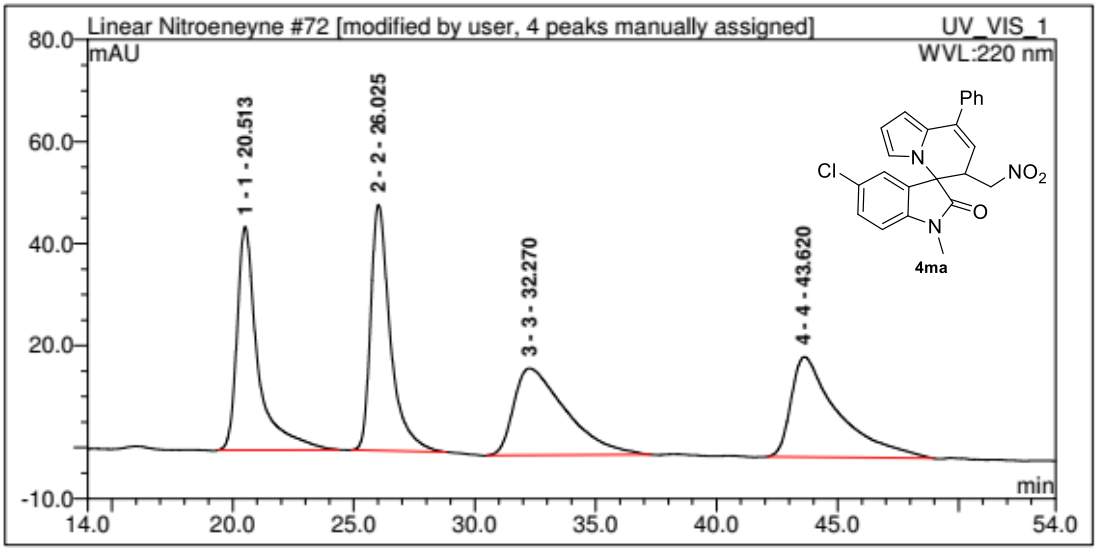

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 20.96 | 185.9435 | 99.04328219 | 245.2224 | n.a. |
| 2 | 2 | 27.18 | 1.796 | 0.9567178101 | 3.212 | n.a. |



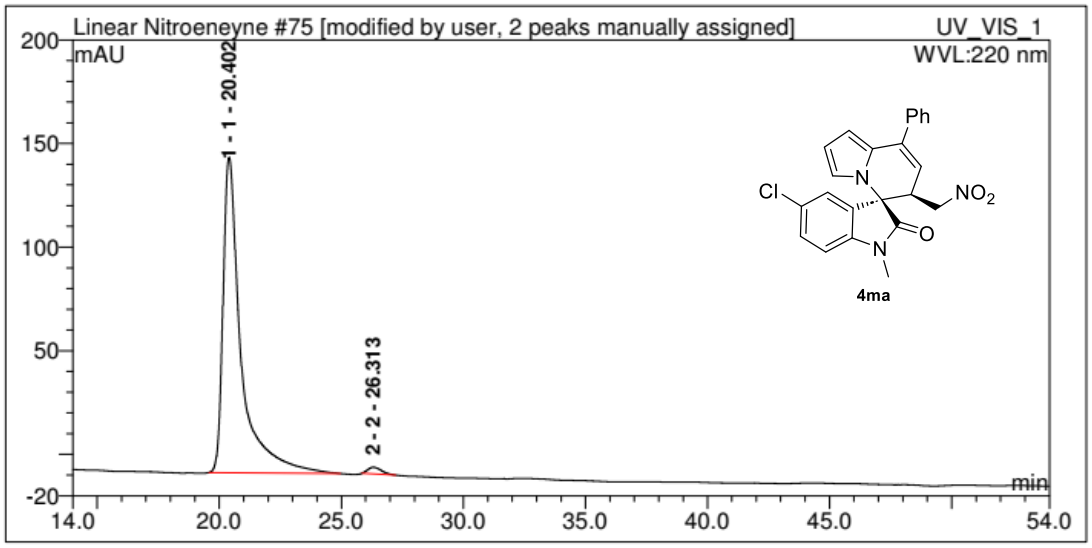

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 21.62 | 102.7232 | 25.83925223 | 125.4266 | n.a. |
| 2 | 2 | 29.31 | 101.9075 | 25.63405801 | 117.1148 | n.a. |
| 3 | 3 | 35.87 | 97.42272 | 24.50595616 | 69.89257 | n.a. |
| 4 | 4 | 51.05 | 95.494 | 24.0207336 | 63.302 | n.a. |



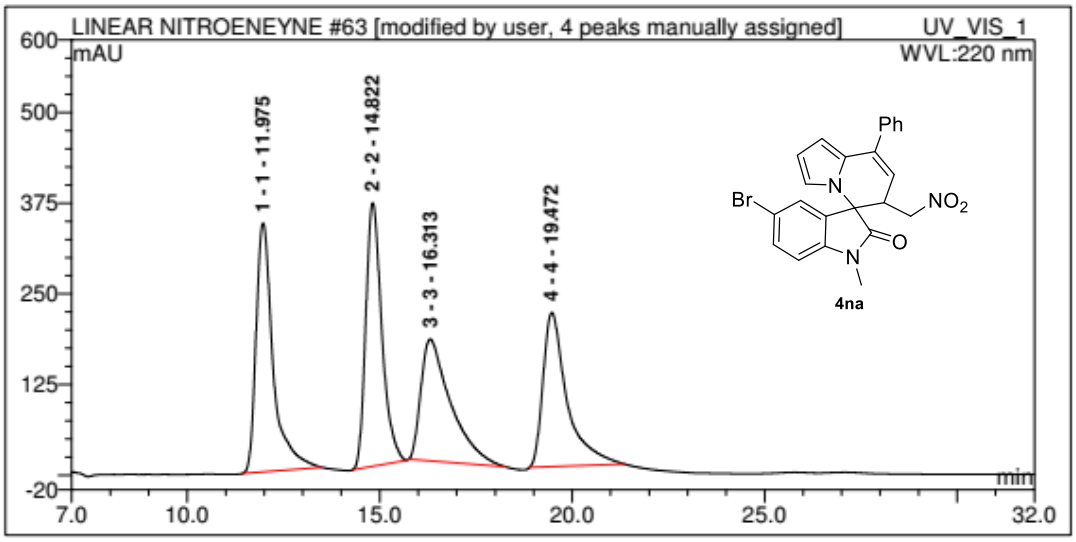

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 21.63 | 189.2473 | 97.79230648 | 235.7749 | n.a. |
| 2 | 2 | 29.76 | 4.272 | 2.20769352 | 5.892 | n.a. |



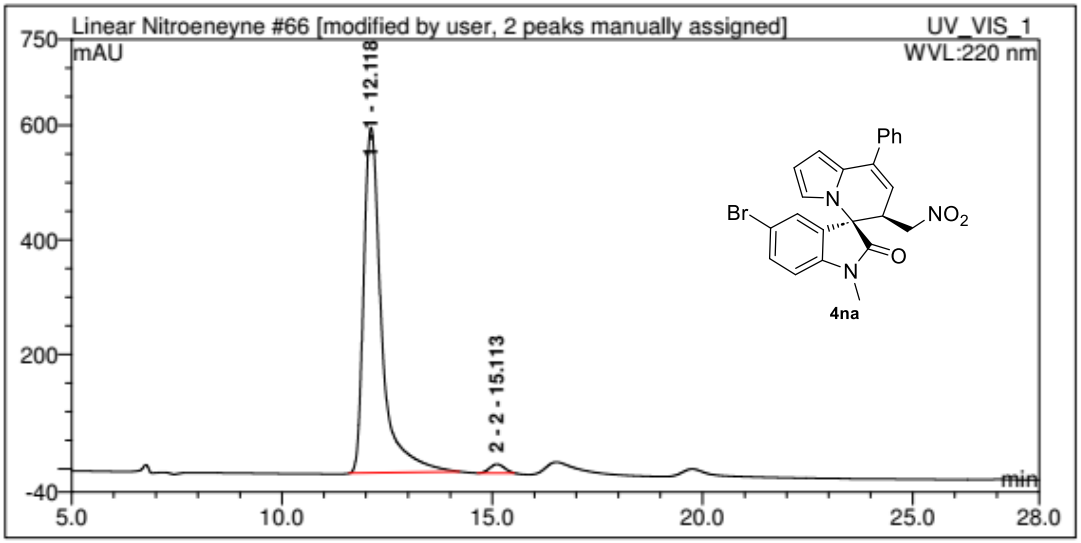

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 20.51 | 44.08013 | 24.98365495 | 43.87088 | n.a. |
| 2 | 2 | 26.03 | 45.55953 | 25.82214523 | 48.22815 | n.a. |
| 3 | 3 | 32.27 | 42.50508 | 24.09094872 | 17.0349 | n.a. |
| 4 | 4 | 43.62 | 44.291 | 25.1032511 | 19.647 | n.a. |



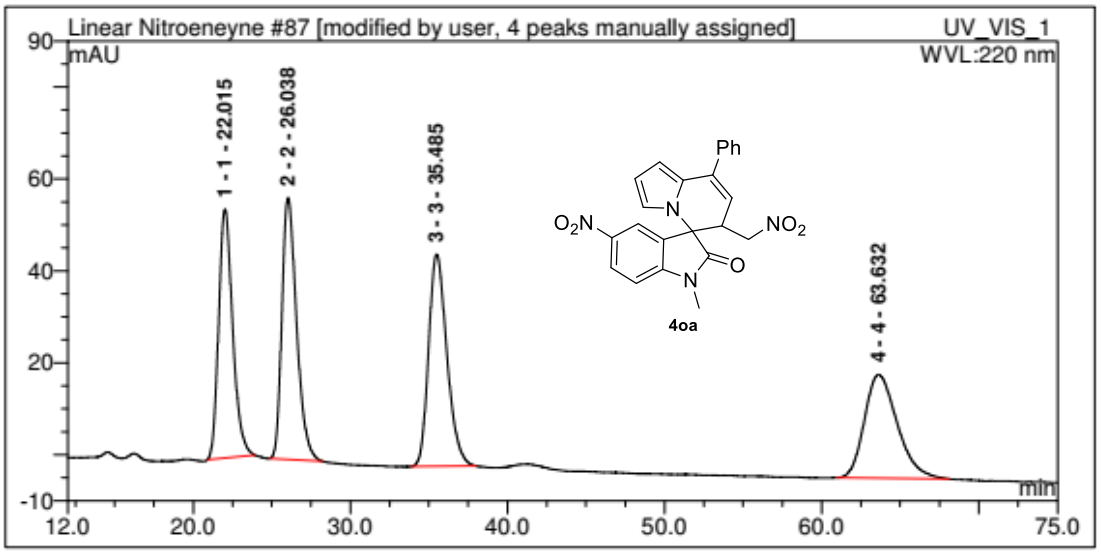

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 20.40 | 129.9812 | 98.41879614 | 152.0008 | n.a. |
| 2 | 2 | 26.31 | 2.088 | 1.581203861 | 3.226 | n.a. |



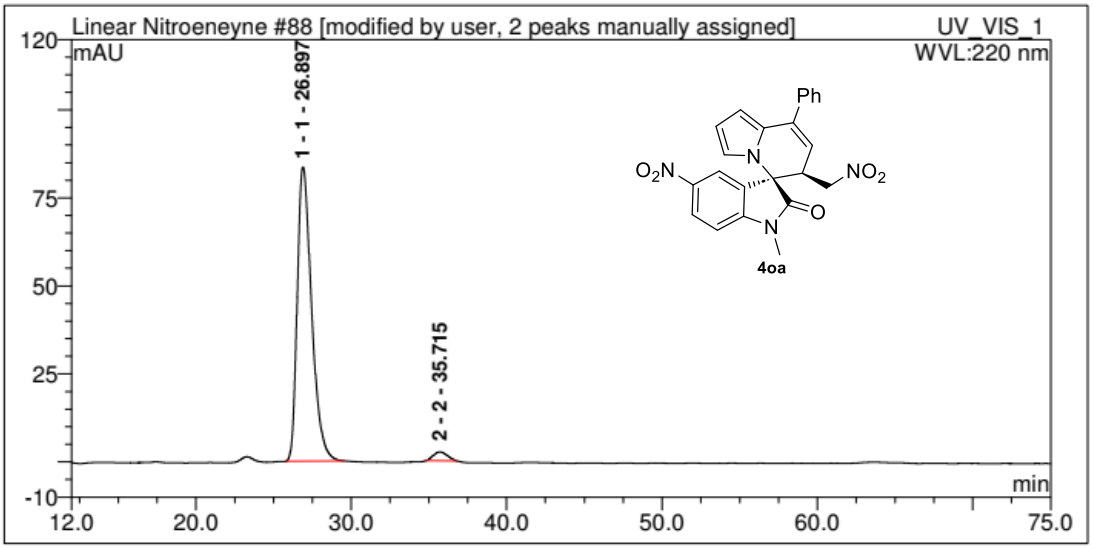

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 11.98 | 176.0715 | 26.87119408 | 342.8737 | n.a. |
| 2 | 2 | 14.82 | 175.3069 | 26.75450863 | 363.1266 | n.a. |
| 3 | 3 | 16.31 | 150.4376 | 22.95906723 | 167.9146 | n.a. |
| 4 | 4 | 19.47 | 153.427 | 23.41523007 | 212.339 | n.a. |



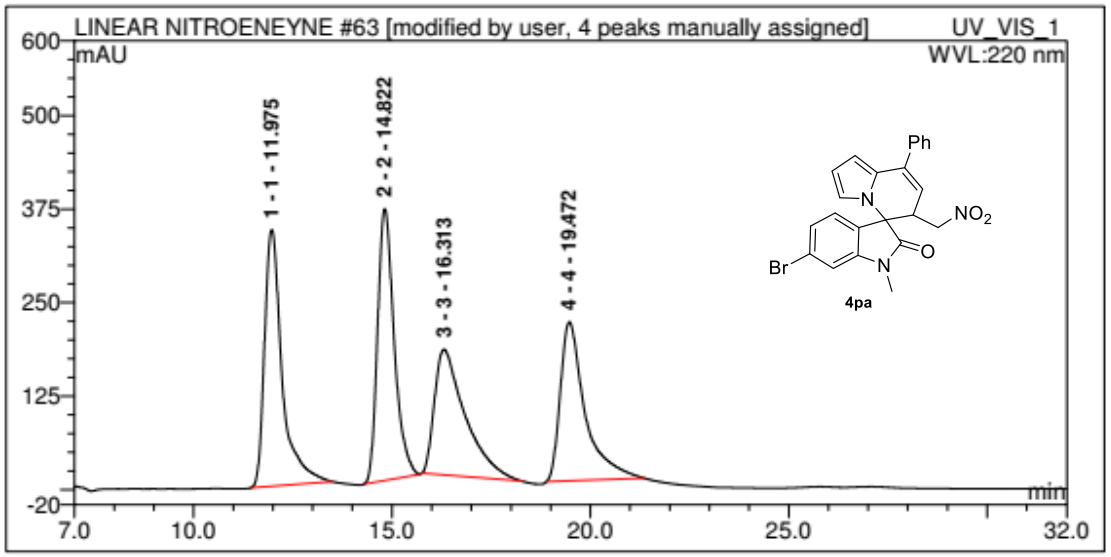

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 12.12 | 298.6228 | 97.95286369 | 603.2291 | n.a. |
| 2 | 2 | 15.11 | 6.241 | 2.047136311 | 15.512 | n.a. |



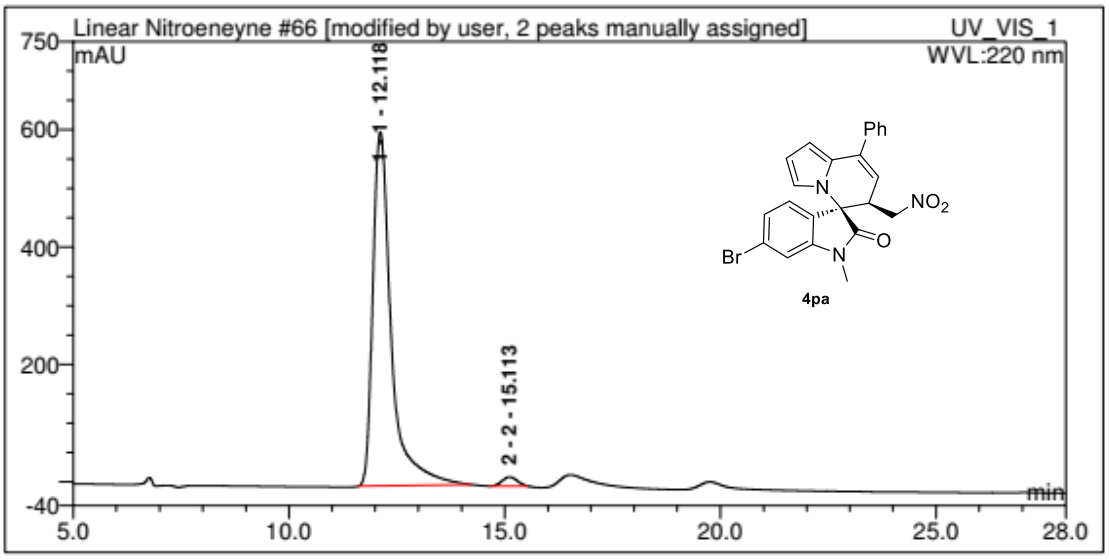

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 22.02 | 55.86434 | 23.81937654 | 54.11244 | n.a. |
| 2 | 2 | 26.04 | 61.61097 | 26.26961746 | 56.94071 | n.a. |
| 3 | 3 | 35.49 | 62.40984 | 26.61023915 | 46.11386 | n.a. |
| 4 | 4 | 63.63 | 54.648 | 23.30076685 | 22.495 | n.a. |



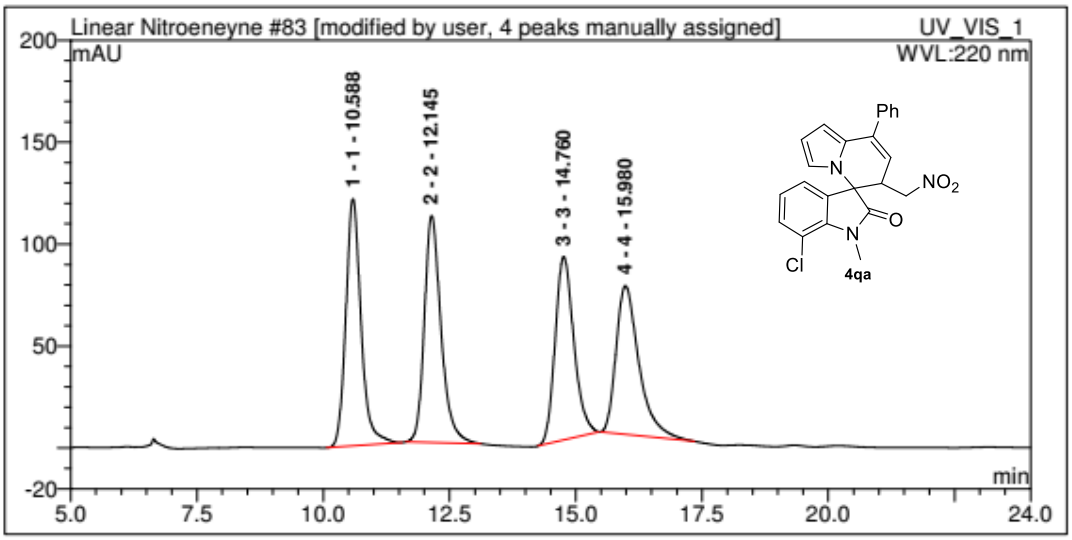

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 26.90 | 89.31907 | 97.13738248 | 83.55332 | n.a. |
| 2 | 2 | 35.72 | 2.632 | 2.862617524 | 2.517 | n.a. |



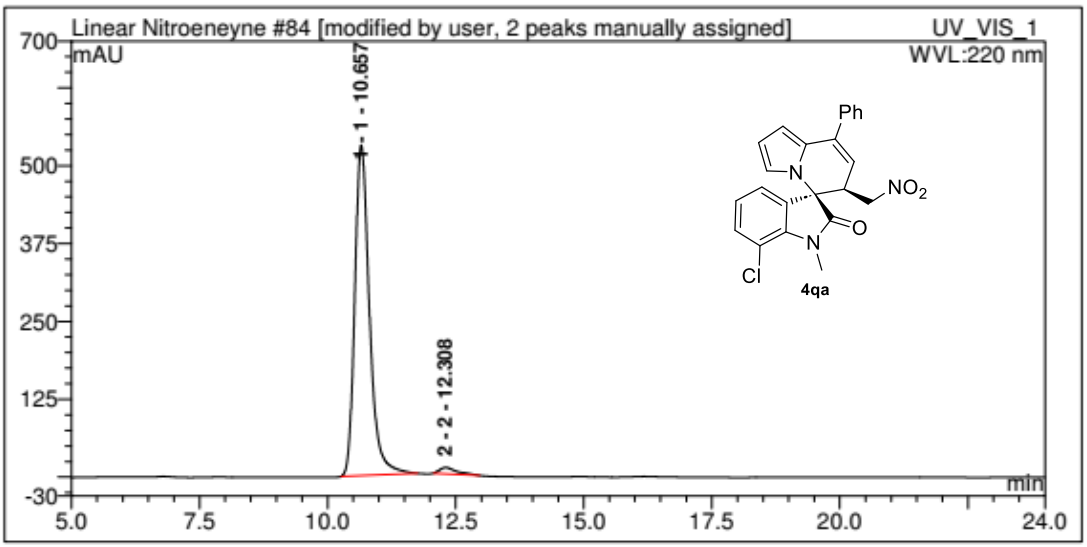

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 11.98 | 176.0715 | 26.87119408 | 342.8737 | n.a. |
| 2 | 2 | 14.82 | 175.3069 | 26.75450863 | 363.1266 | n.a. |
| 3 | 3 | 16.31 | 150.4376 | 22.95906723 | 167.9146 | n.a. |
| 4 | 4 | 19.47 | 153.427 | 23.41523007 | 212.339 | n.a. |



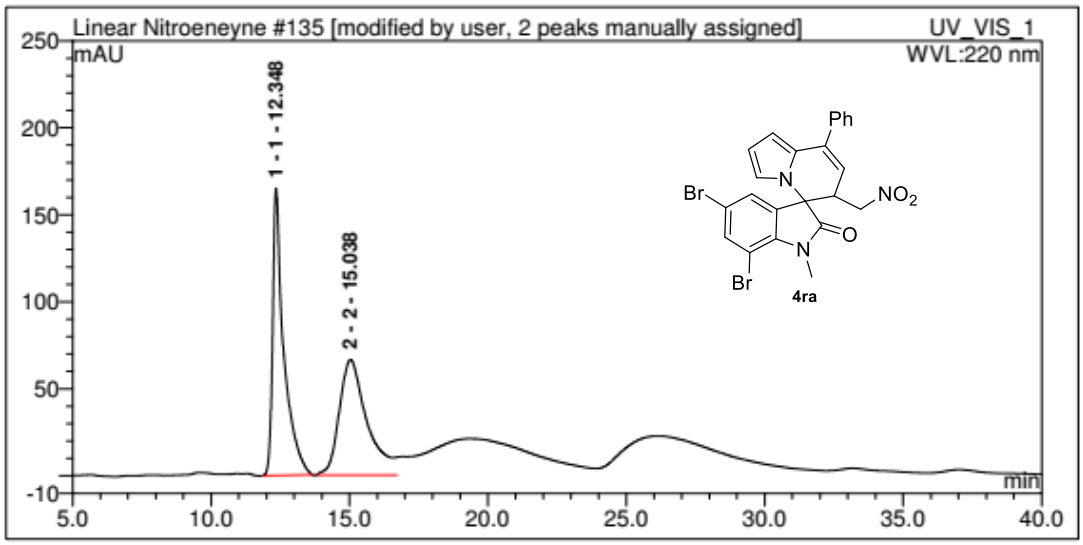

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 12.12 | 298.6228 | 97.95286369 | 603.2291 | n.a. |
| 2 | 2 | 15.11 | 6.241 | 2.047136311 | 15.512 | n.a. |



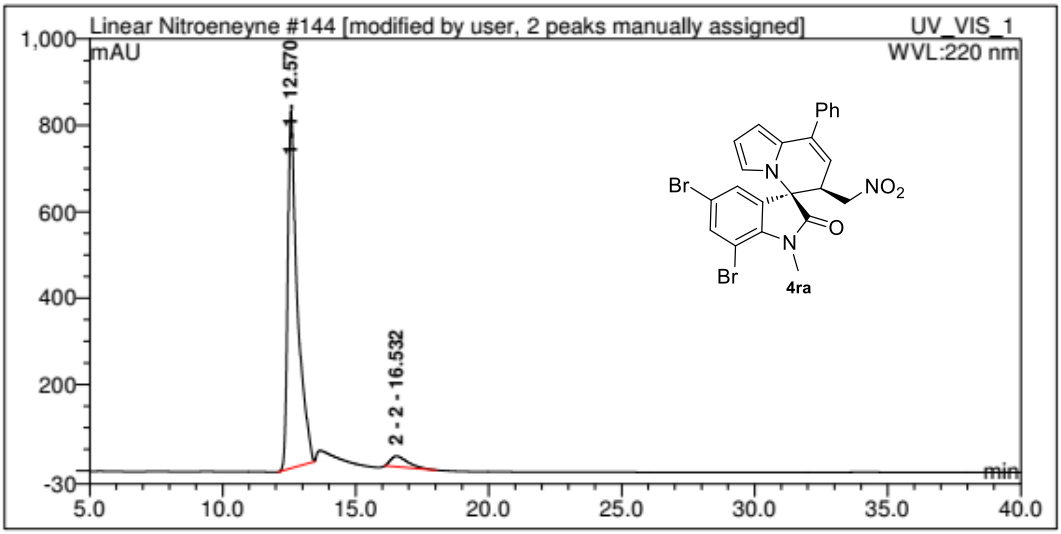

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 10.59 | 42.31732 | 26.10567616 | 121.1736 | n.a. |
| 2 | 2 | 12.15 | 42.67447 | 26.32600067 | 111.1148 | n.a. |
| 3 | 3 | 14.76 | 38.66691 | 23.85372938 | 90.02571 | n.a. |
| 4 | 4 | 15.98 | 38.441 | 23.71459379 | 72.916 | n.a. |



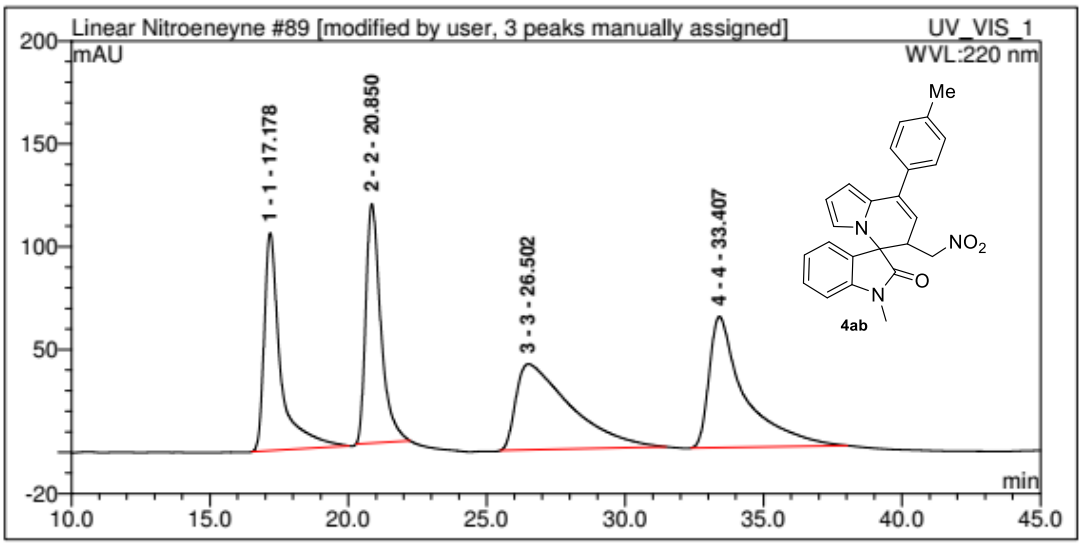

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 10.66 | 176.1829 | 97.81690987 | 530.9543 | n.a. |
| 2 | 2 | 12.31 | 3.932 | 2.183090126 | 10.021 | n.a. |



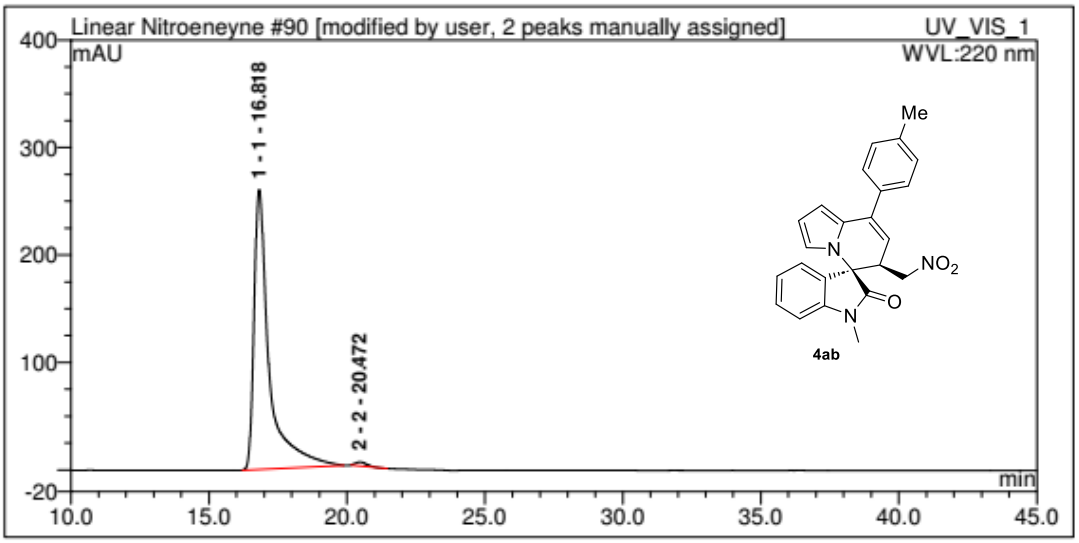

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 12.35 | 76.42049 | 49.70160044 | 164.968 | n.a. |
| 2 | 2 | 15.04 | 77.338 | 50.29839956 | 66.262 | n.a. |



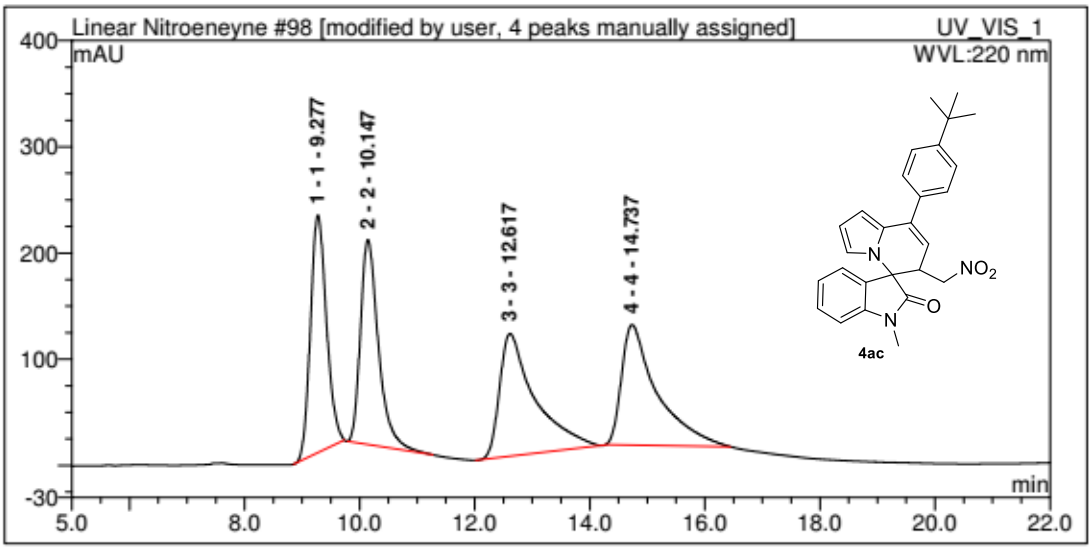

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 12.57 | 349.3217 | 95.02161987 | 827.2137 | n.a. |
| 2 | 2 | 16.53 | 18.302 | 4.978380134 | 24.300 | n.a. |



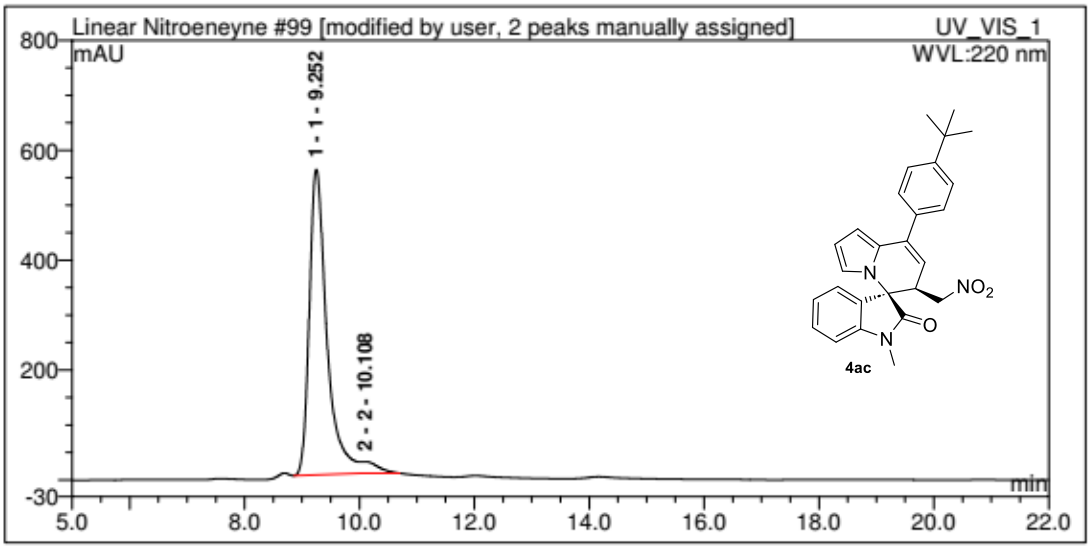

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 17.18 | 72.85568 | 21.71594095 | 105.7782 | n.a. |
| 2 | 2 | 20.85 | 73.23062 | 21.82770066 | 116.3425 | n.a. |
| 3 | 3 | 26.50 | 94.83294 | 28.26665776 | 41.6863 | n.a. |
| 4 | 4 | 33.41 | 94.575 | 28.18970062 | 63.673 | n.a. |



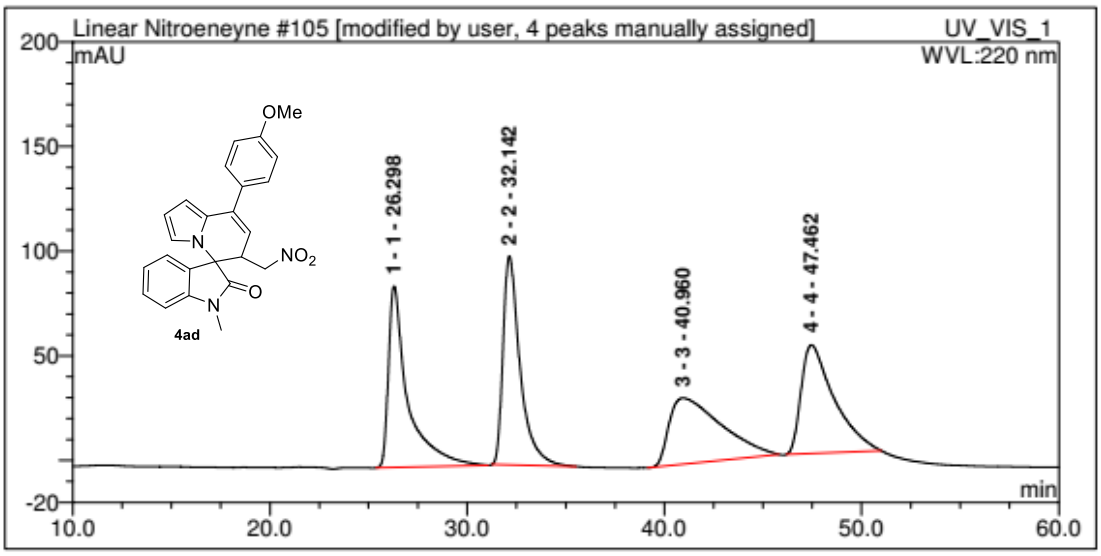

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 16.82 | 166.4706 | 99.00003695 | 260.2522 | n.a. |
| 2 | 2 | 20.47 | 1.681 | 0.9999630475 | 3.594 | n.a. |



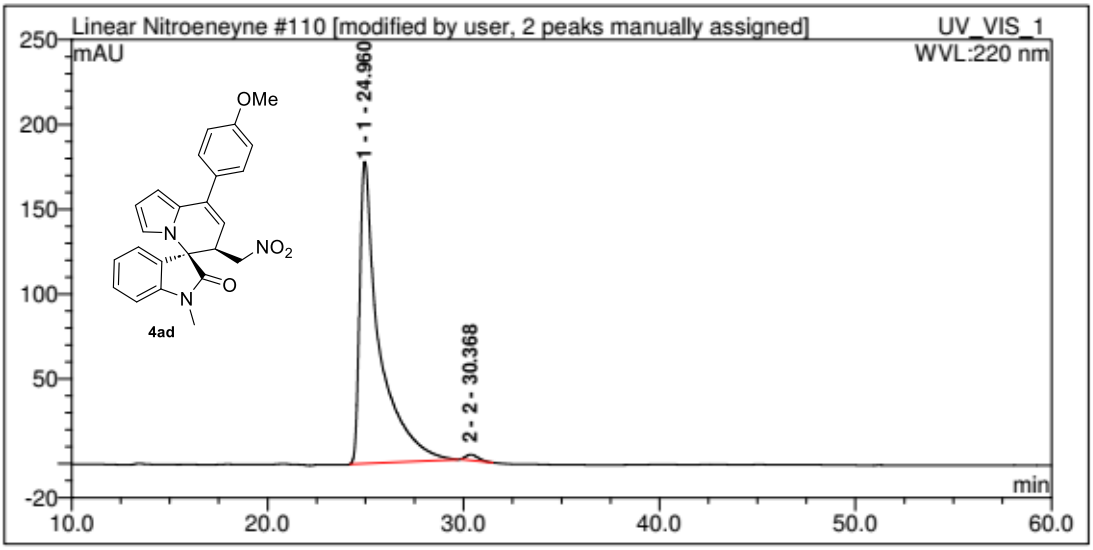

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 9.28 | 72.06837 | 23.65491113 | 223.7512 | n.a. |
| 2 | 2 | 10.15 | 70.10619 | 23.01086768 | 193.1048 | n.a. |
| 3 | 3 | 12.62 | 81.68529 | 26.81145906 | 115.4634 | n.a. |
| 4 | 4 | 14.74 | 80.806 | 26.52276213 | 113.274 | n.a. |



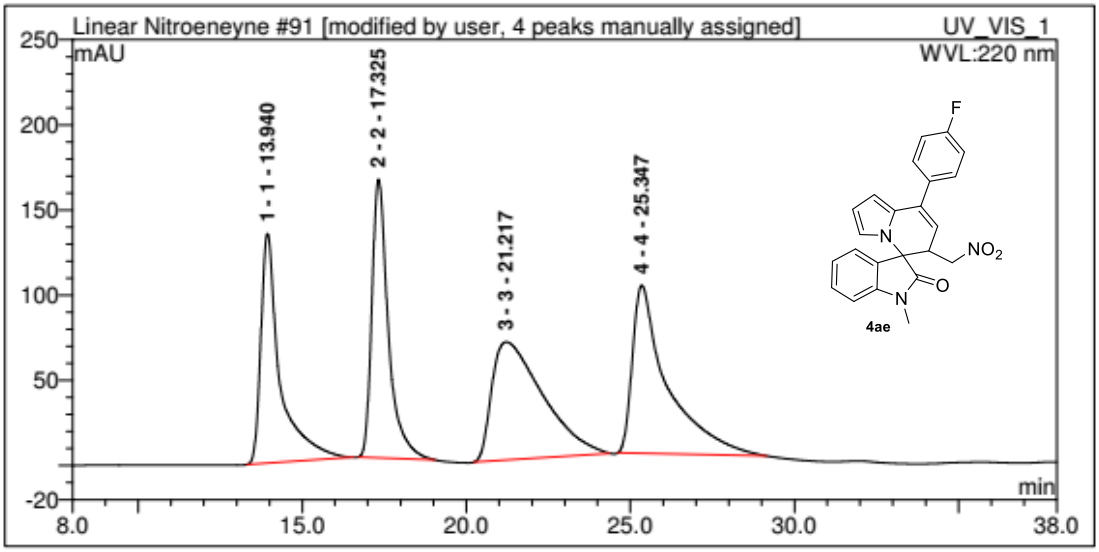

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 9.25 | 195.3936 | 96.47992369 | 556.1837 | n.a. |
| 2 | 2 | 10.11 | 7.129 | 3.520076312 | 20.921 | n.a. |



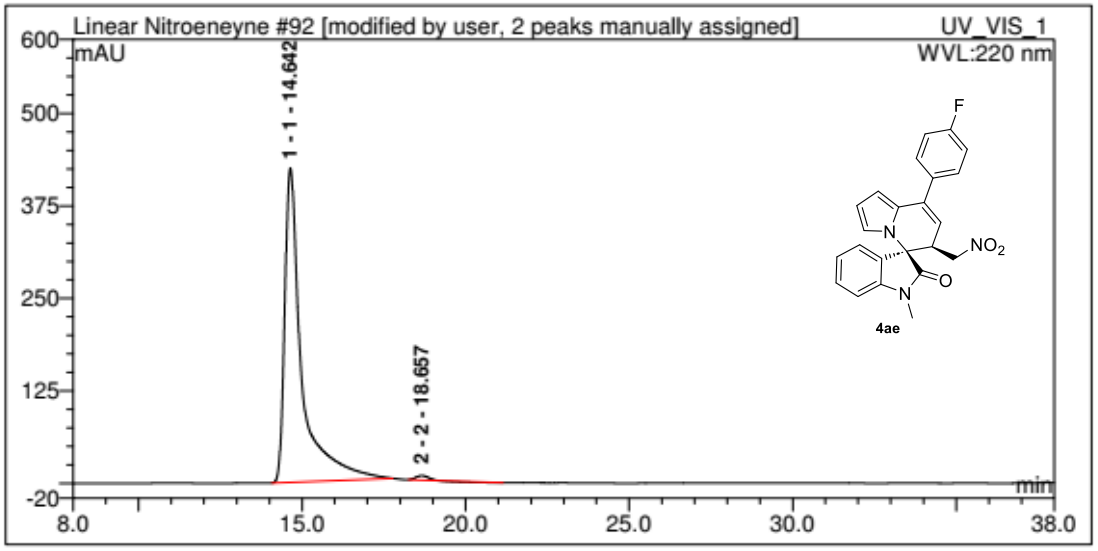

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 26.30 | 97.99659 | 24.84705438 | 86.5246 | n.a. |
| 2 | 2 | 32.14 | 100.2776 | 25.42539689 | 99.68244 | n.a. |
| 3 | 3 | 40.96 | 95.61681 | 24.24366106 | 31.60831 | n.a. |
| 4 | 4 | 47.46 | 100.508 | 25.48388767 | 51.843 | n.a. |



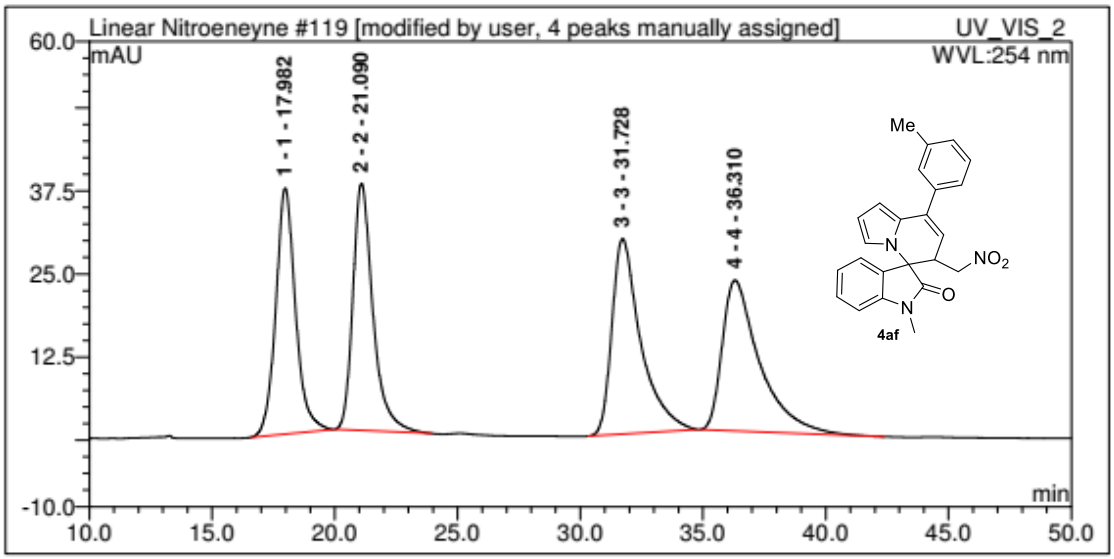

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 24.96 | 207.6059 | 98.83240363 | 178.0077 | n.a. |
| 2 | 2 | 30.37 | 2.453 | 1.167596369 | 3.338 | n.a. |



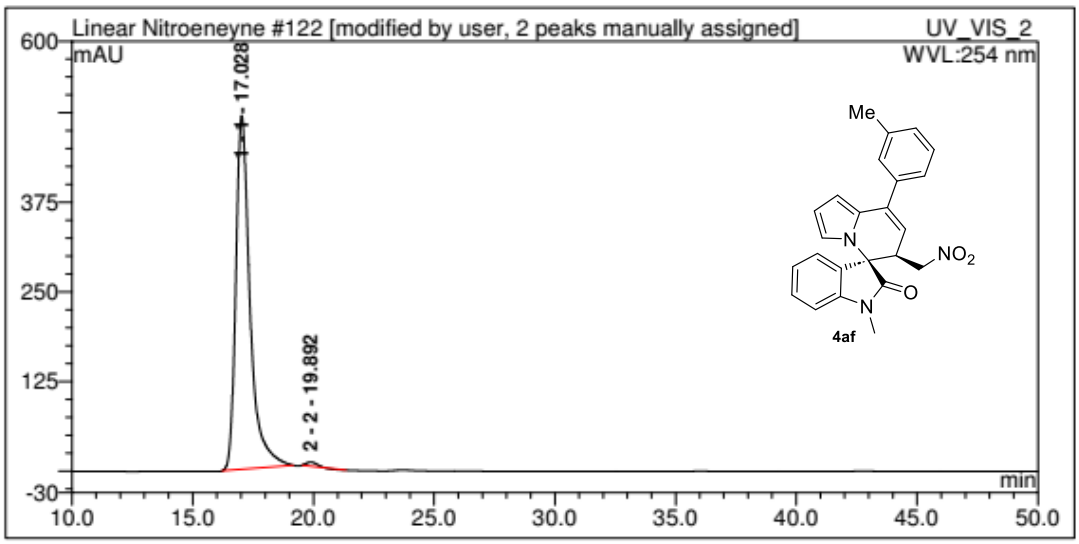

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 13.94 | 91.02473 | 21.06938869 | 134.75 | n.a. |
| 2 | 2 | 17.33 | 95.05638 | 22.00258994 | 163.546 | n.a. |
| 3 | 3 | 21.22 | 124.1485 | 28.73650012 | 69.28347 | n.a. |
| 4 | 4 | 25.35 | 121.794 | 28.19152126 | 98.684 | n.a. |



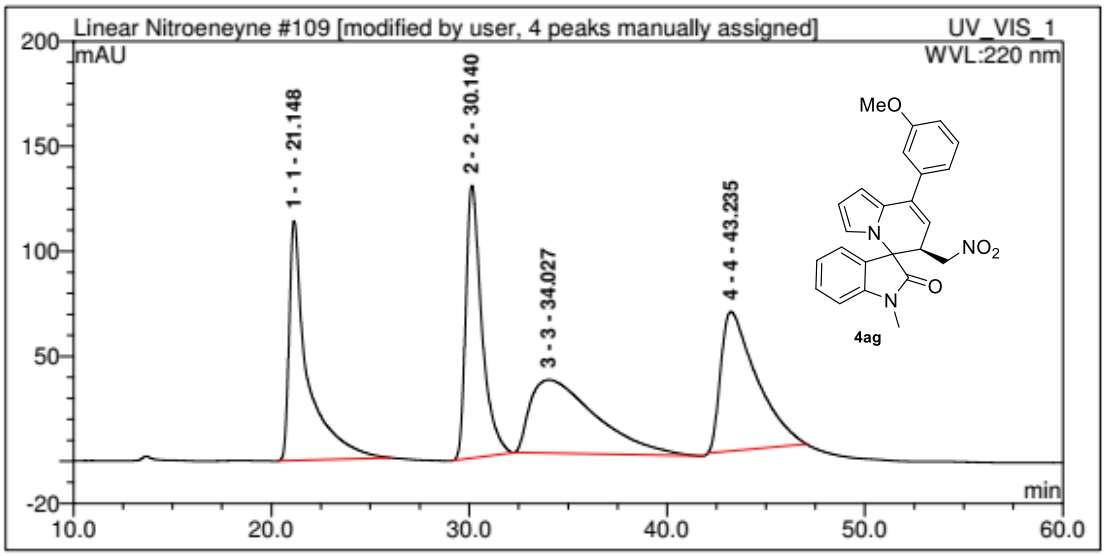

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 14.64 | 257.0852 | 99.46822376 | 424.7064 | n.a. |
| 2 | 2 | 18.66 | 1.374 | 0.5317762407 | 5.958 | n.a. |



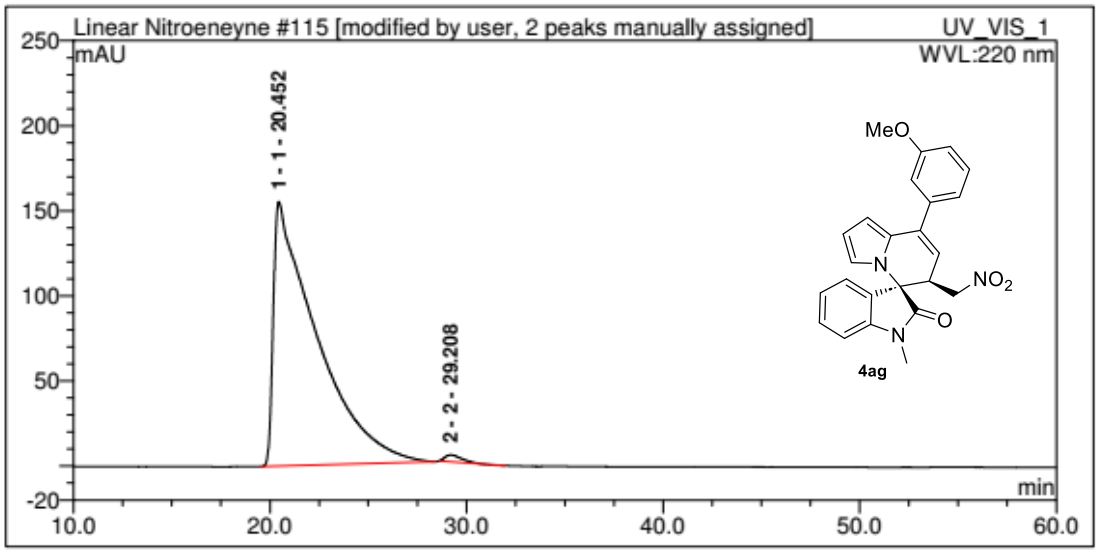

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 17.98 | 34.47031 | 23.0343234 | 36.97254 | n.a. |
| 2 | 2 | 21.09 | 35.20669 | 23.52639675 | 37.16396 | n.a. |
| 3 | 3 | 31.73 | 39.94887 | 26.69529934 | 29.38218 | n.a. |
| 4 | 4 | 36.31 | 40.022 | 26.74398052 | 22.664 | n.a. |



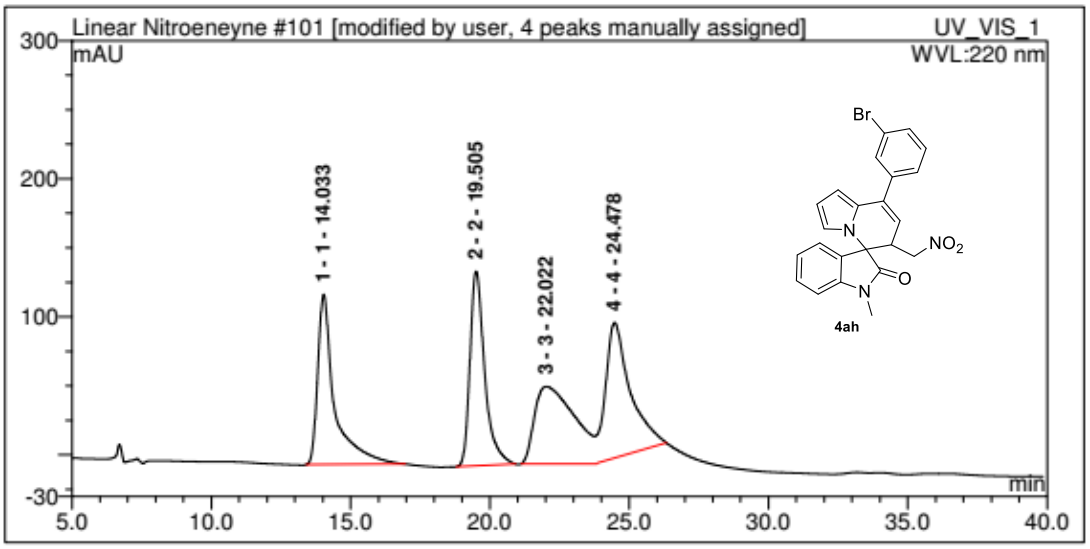

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 17.03 | 337.2778 | 99.29668588 | 494.2215 | n.a. |
| 2 | 2 | 19.89 | 2.389 | 0.7033141161 | 5.680 | n.a. |



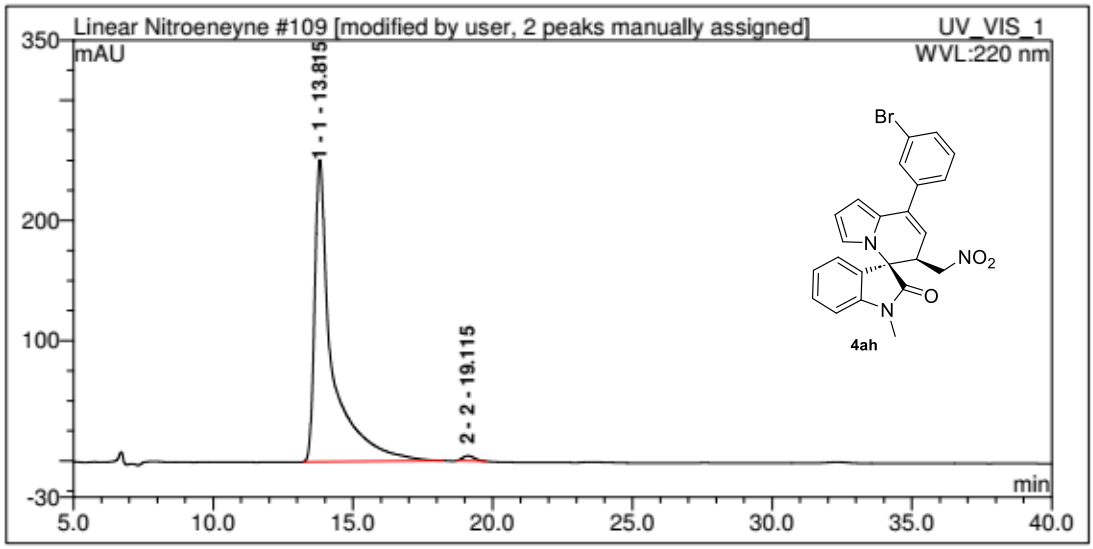

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 21.15 | 122.5227 | 23.65351767 | 114.0782 | n.a. |
| 2 | 2 | 30.14 | 121.6555 | 23.48609302 | 129.7767 | n.a. |
| 3 | 3 | 34.03 | 134.266 | 25.92060656 | 34.82883 | n.a. |
| 4 | 4 | 43.24 | 139.545 | 26.93978275 | 66.389 | n.a. |



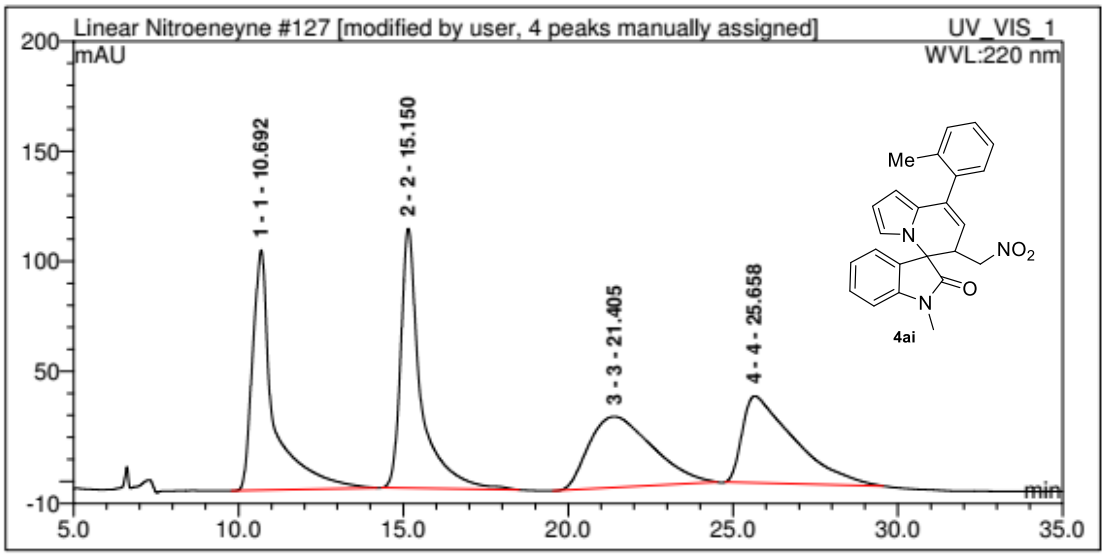

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 20.45 | 395.2186 | 99.03937068 | 155.4563 | n.a. |
| 2 | 2 | 29.21 | 3.833 | 0.9606293221 | 4.001 | n.a. |



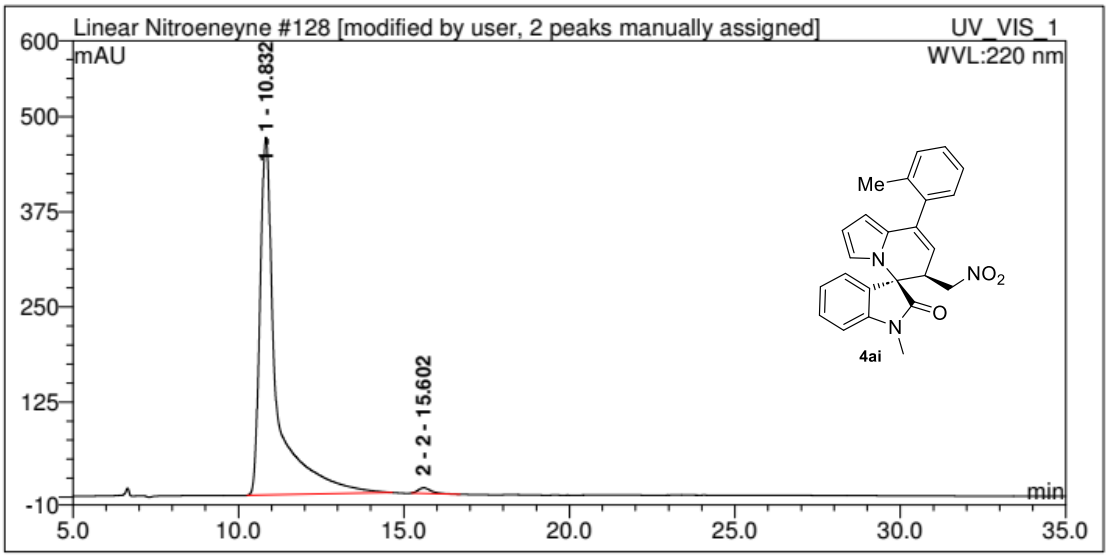

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 14.03 | 86.37656 | 23.4329592 | 123.206 | n.a. |
| 2 | 2 | 19.51 | 86.33151 | 23.42073799 | 140.8372 | n.a. |
| 3 | 3 | 22.02 | 95.68573 | 25.95843084 | 56.07839 | n.a. |
| 4 | 4 | 24.48 | 100.218 | 27.18787197 | 98.095 | n.a. |



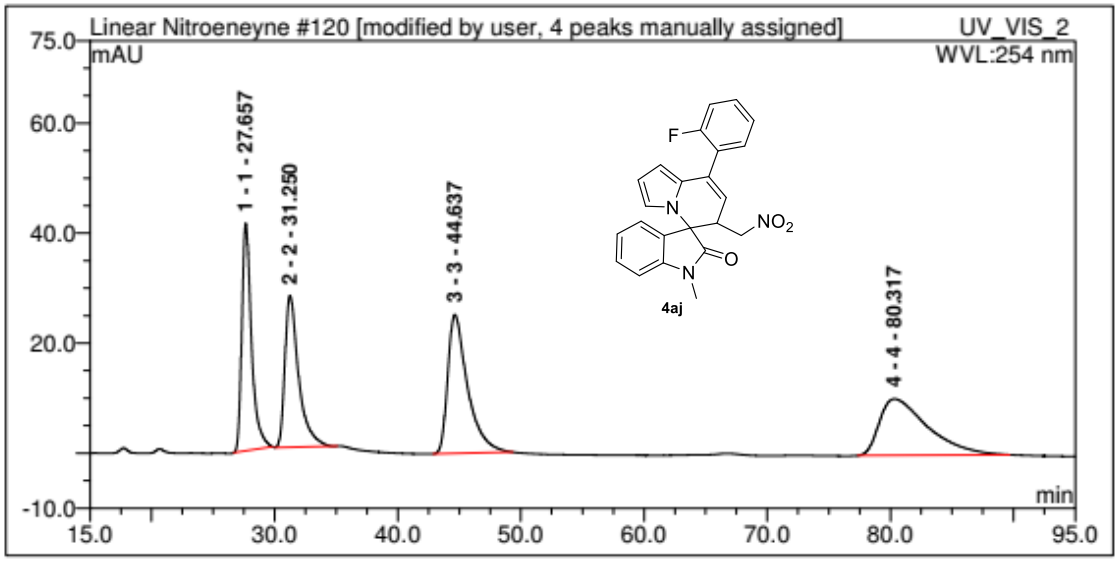

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 13.82 | 180.8305 | 98.88402924 | 251.3282 | n.a. |
| 2 | 2 | 19.12 | 2.041 | 1.115970755 | 4.263 | n.a. |



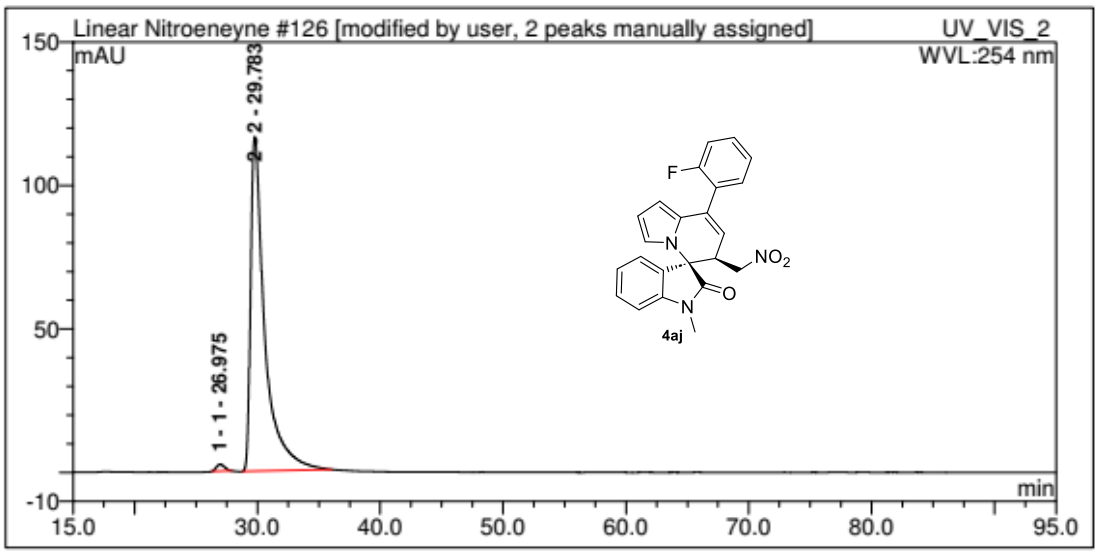

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 10.69 | 80.64702 | 26.23785463 | 109.1841 | n.a. |
| 2 | 2 | 15.15 | 82.87578 | 26.96296171 | 117.9236 | n.a. |
| 3 | 3 | 21.41 | 71.69442 | 23.3251981 | 32.24304 | n.a. |
| 4 | 4 | 25.66 | 72.152 | 23.47398557 | 39.450 | n.a. |



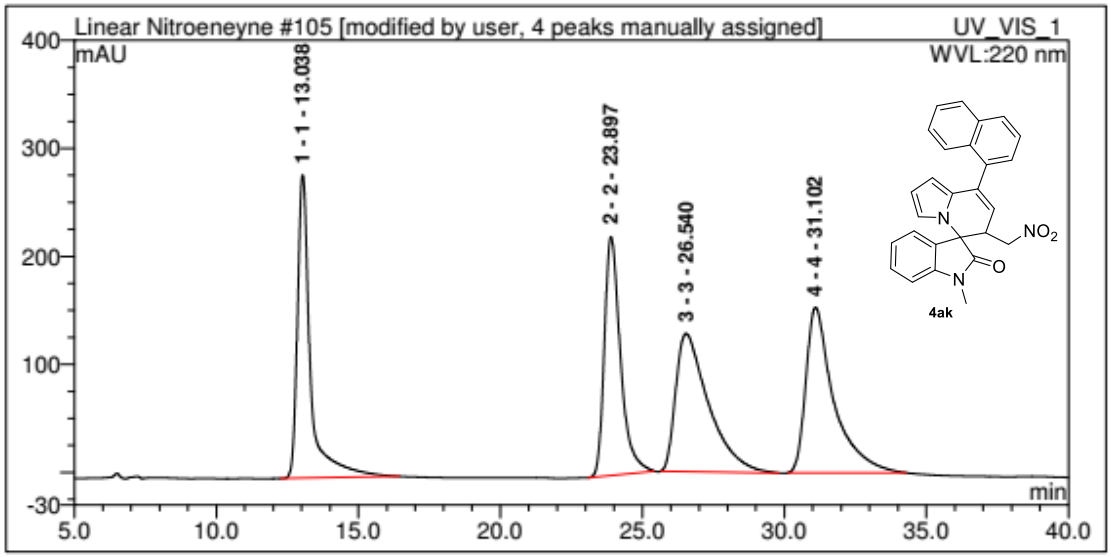

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 10.83 | 273.0894 | 98.84038848 | 470.2737 | n.a. |
| 2 | 2 | 15.60 | 3.204 | 1.159611517 | 7.159 | n.a. |



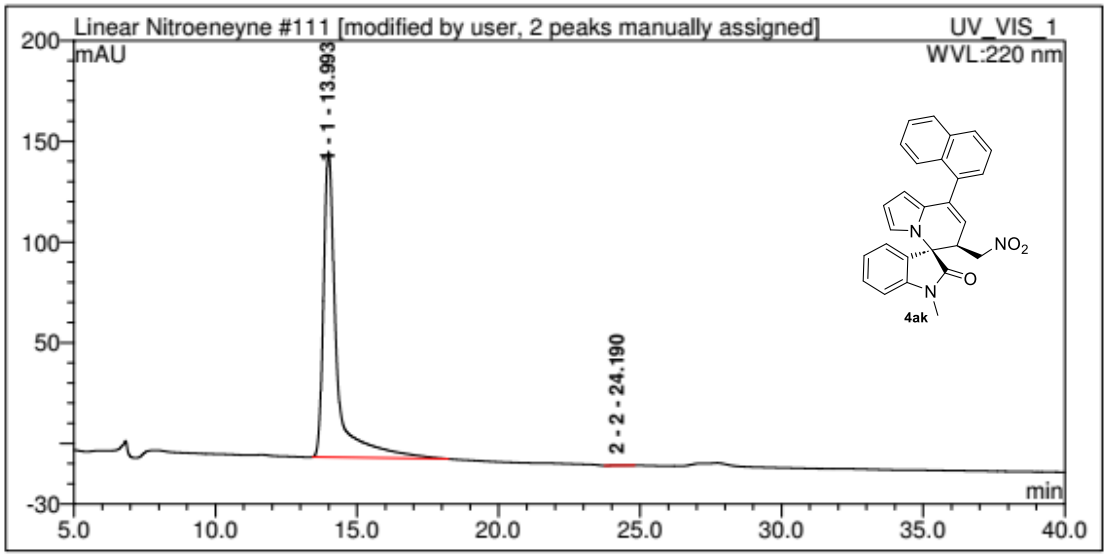

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 27.66 | 37.77693 | 22.56884703 | 41.30786 | n.a. |
| 2 | 2 | 31.25 | 35.76482 | 21.36676004 | 27.60082 | n.a. |
| 3 | 3 | 44.64 | 47.34505 | 28.28507138 | 25.27216 | n.a. |
| 4 | 4 | 80.32 | 46.499 | 27.77932155 | 10.265 | n.a. |



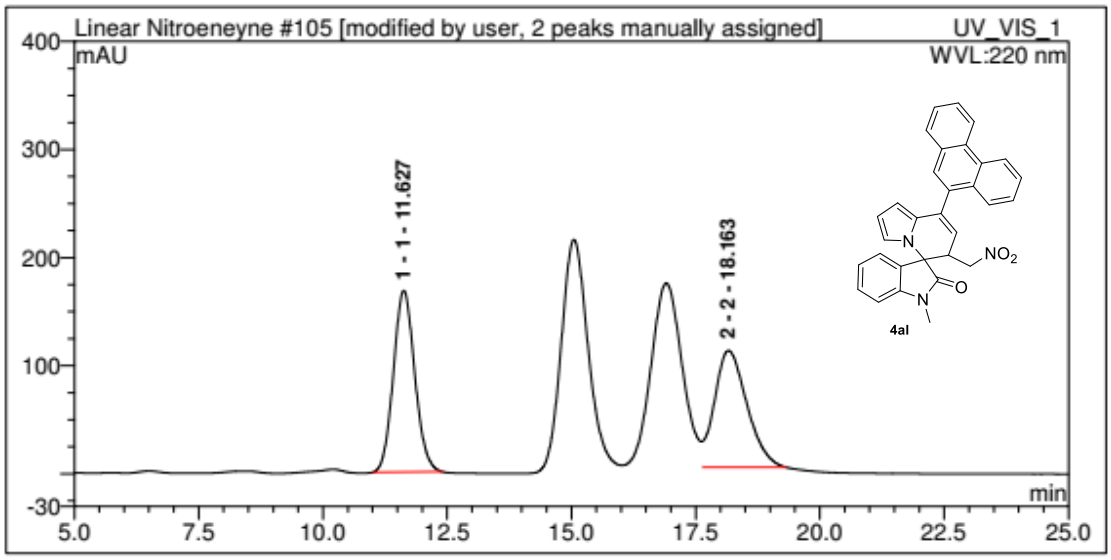

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 26.98 | 1.803607 | 1.148290989 | 2.39367 | n.a. |
| 2 | 2 | 29.78 | 155.265 | 98.85170901 | 116.372 | n.a. |



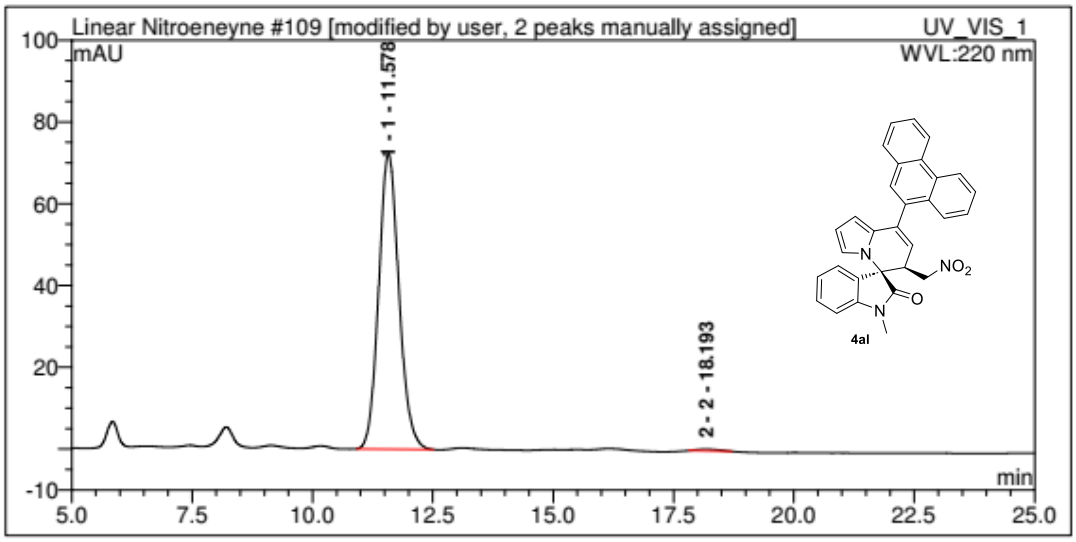

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 13.04 | 149.3131 | 23.31142635 | 280.812 | n.a. |
| 2 | 2 | 23.90 | 145.093 | 22.65256165 | 221.0347 | n.a. |
| 3 | 3 | 26.54 | 171.3676 | 26.75466855 | 127.8178 | n.a. |
| 4 | 4 | 31.10 | 174.741 | 27.28134345 | 153.090 | n.a. |



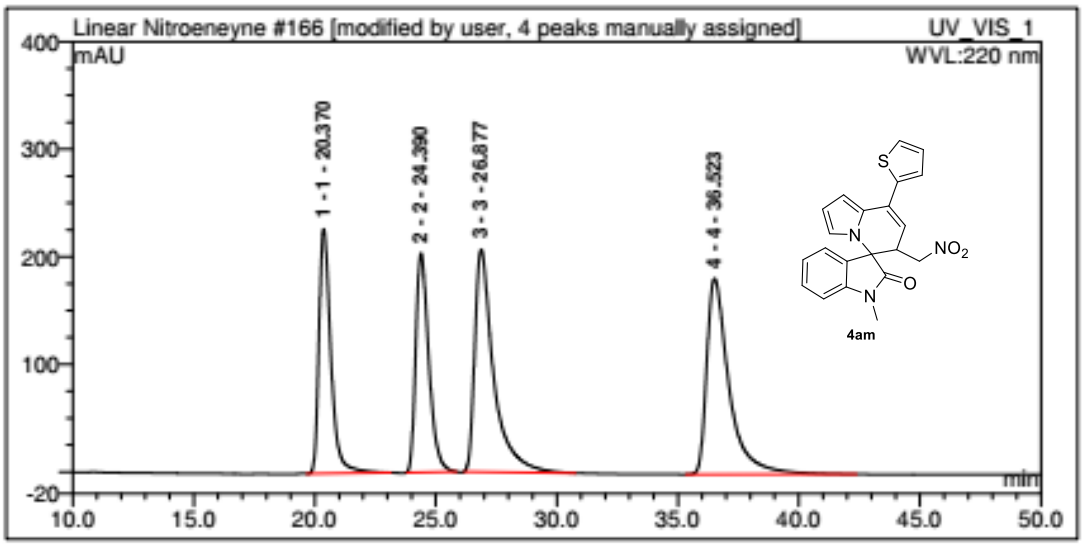

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 13.99 | 82.43032 | 99.89353836 | 151.7436 | n.a. |
| 2 | 2 | 24.19 | 0.088 | 0.1064616372 | 0.177 | n.a. |



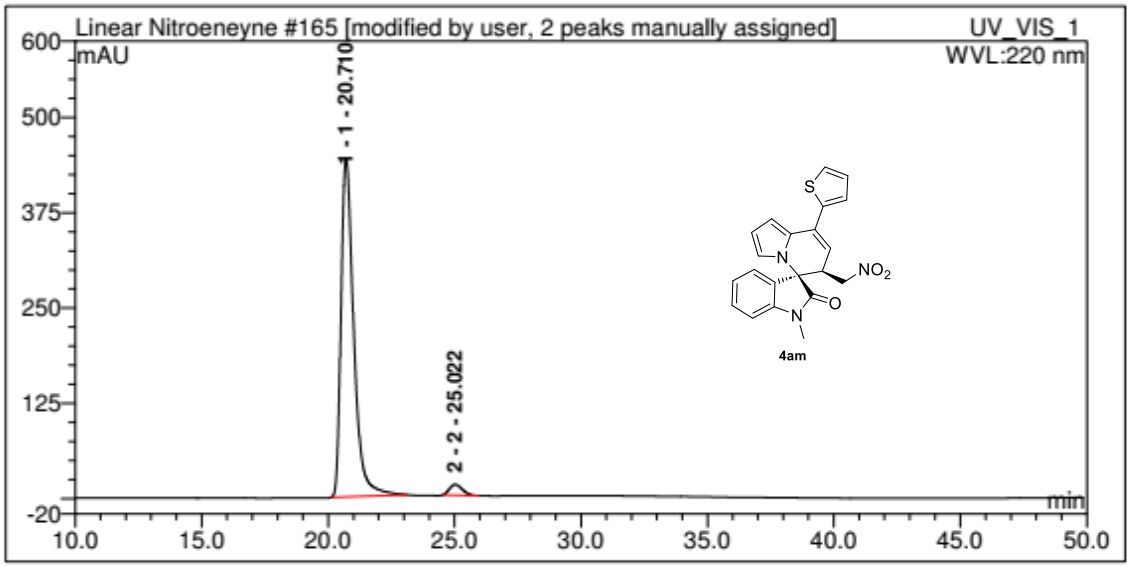

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 11.63 | 83.72116 | 50.59471179 | 167.8439 | n.a. |
| 2 | 2 | 18.16 | 81.753 | 49.40528821 | 108.030 | n.a. |



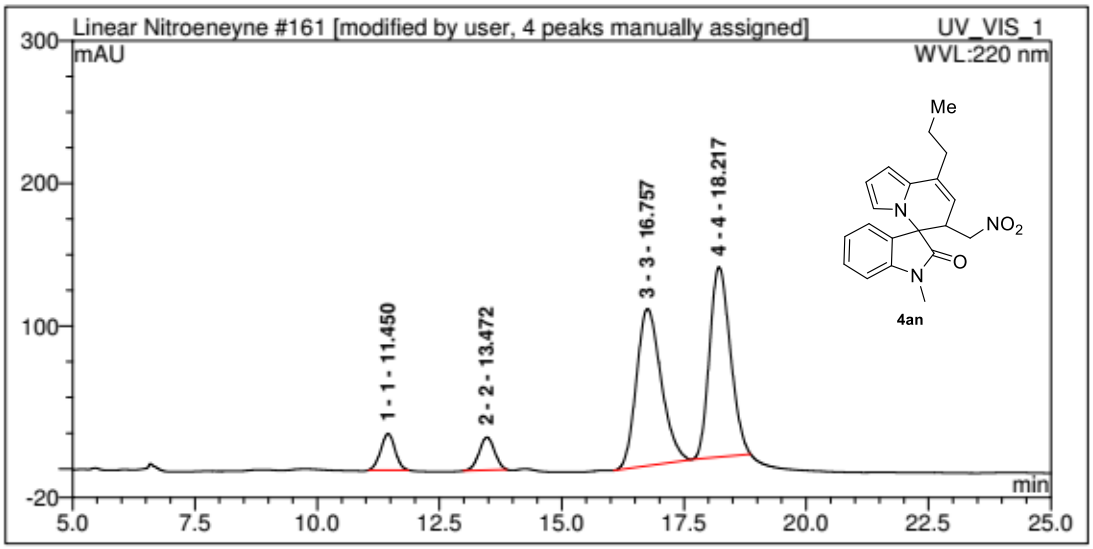

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 11.58 | 35.29133 | 99.36445804 | 72.37832 | n.a. |
| 2 | 2 | 18.19 | 0.226 | 0.635541956 | 0.416 | n.a. |



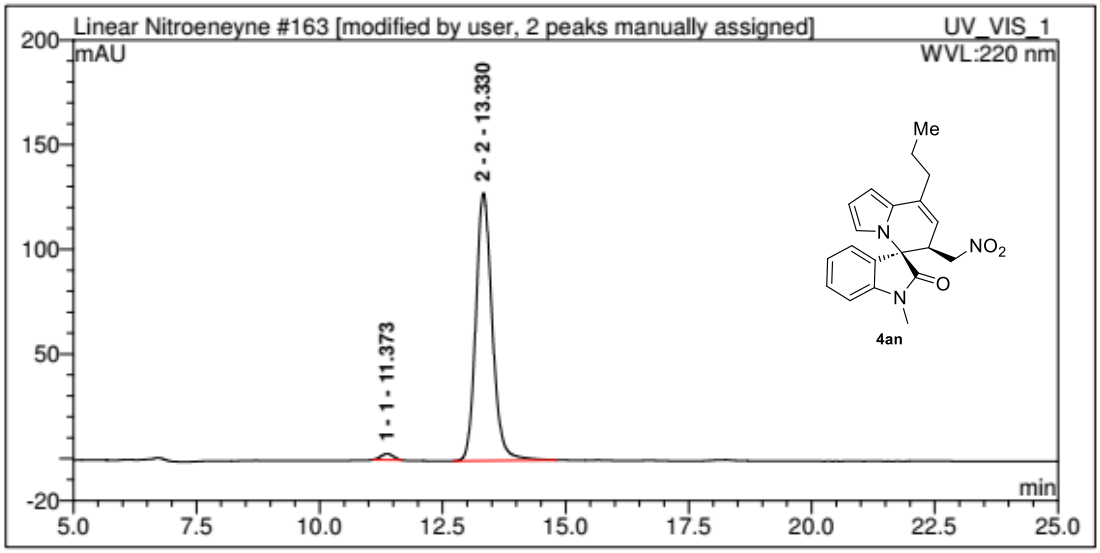

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 20.37 | 129.7294 | 20.30254513 | 227.319 | n.a. |
| 2 | 2 | 24.39 | 127.4208 | 19.94125618 | 203.7274 | n.a. |
| 3 | 3 | 26.88 | 187.1408 | 29.28737268 | 206.7762 | n.a. |
| 4 | 4 | 36.52 | 194.690 | 30.468826 | 181.736 | n.a. |



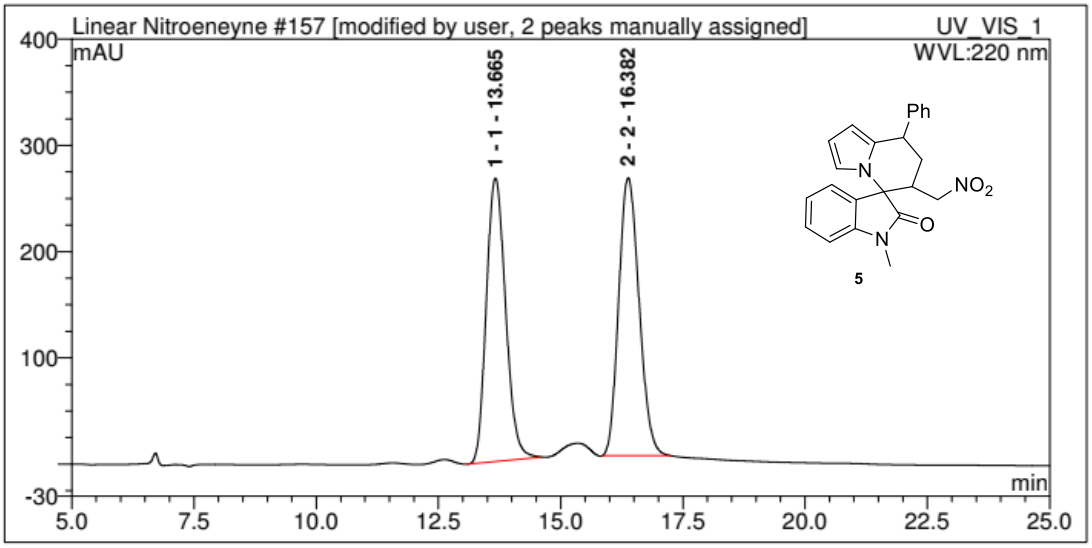

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 20.71 | 257.8376 | 96.9655193 | 442.844 | n.a. |
| 2 | 2 | 25.02 | 8.069 | 3.034480703 | 13.859 | n.a. |



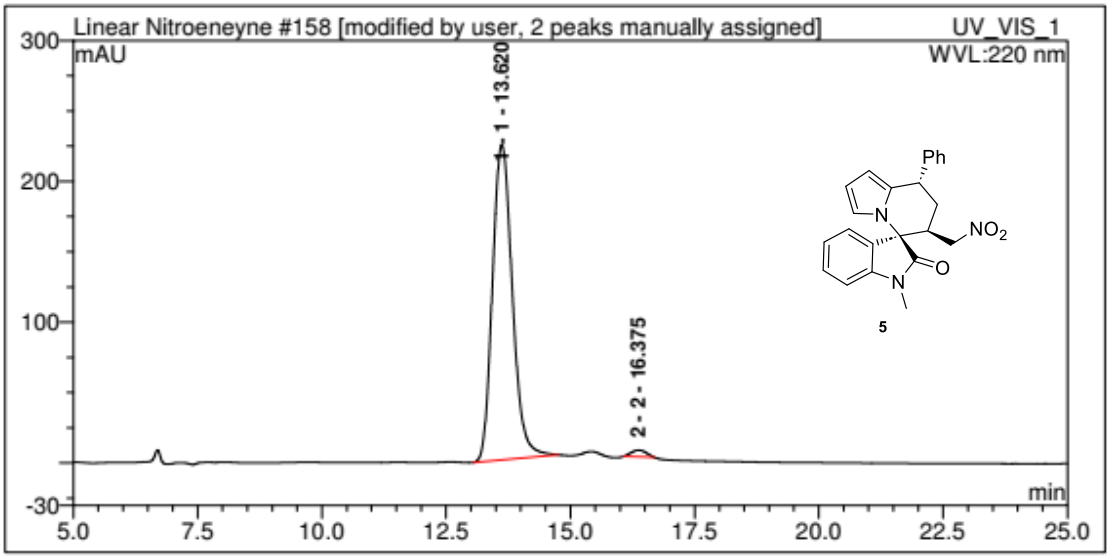

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 11.45 | 8.693197 | 5.905570606 | 25.63347 | n.a. |
| 2 | 2 | 13.47 | 8.447142 | 5.738417644 | 23.01245 | n.a. |
| 3 | 3 | 16.76 | 64.48395 | 43.80603974 | 109.9136 | n.a. |
| 4 | 4 | 18.22 | 65.579 | 44.54997201 | 133.172 | n.a. |



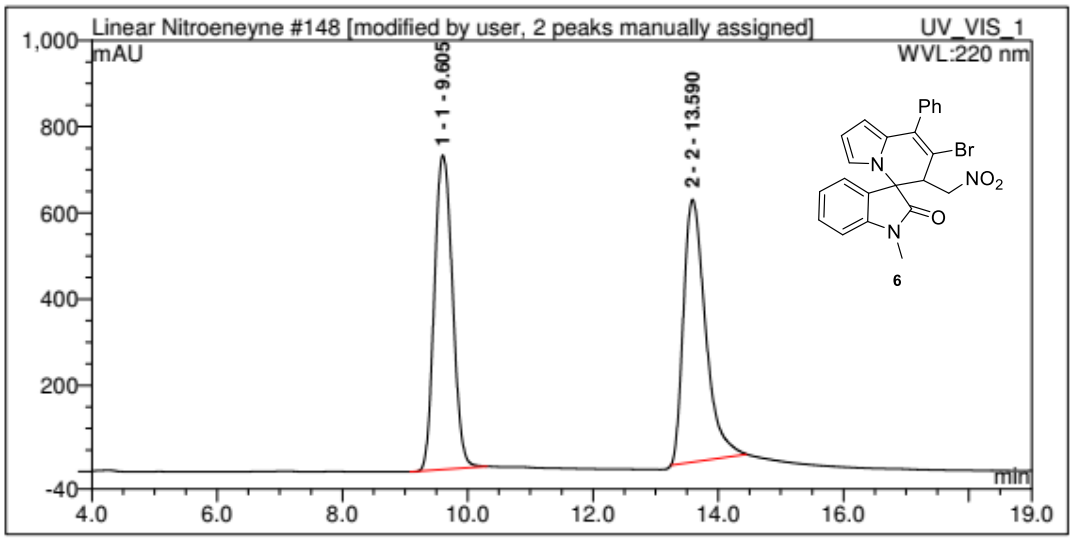

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 11.37 | 0.847816 | 1.691490292 | 2.90056 | n.a. |
| 2 | 2 | 13.33 | 49.275 | 98.30850971 | 127.908 | n.a. |



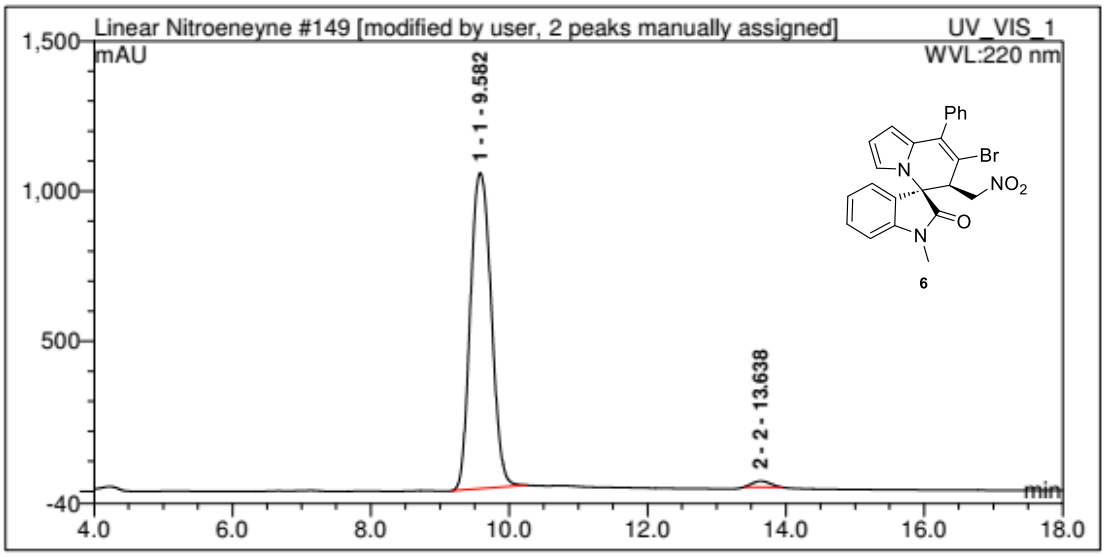

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 13.67 | 121.8001 | 49.07719311 | 266.5414 | n.a. |
| 2 | 2 | 16.38 | 126.381 | 50.92280689 | 261.550 | n.a. |



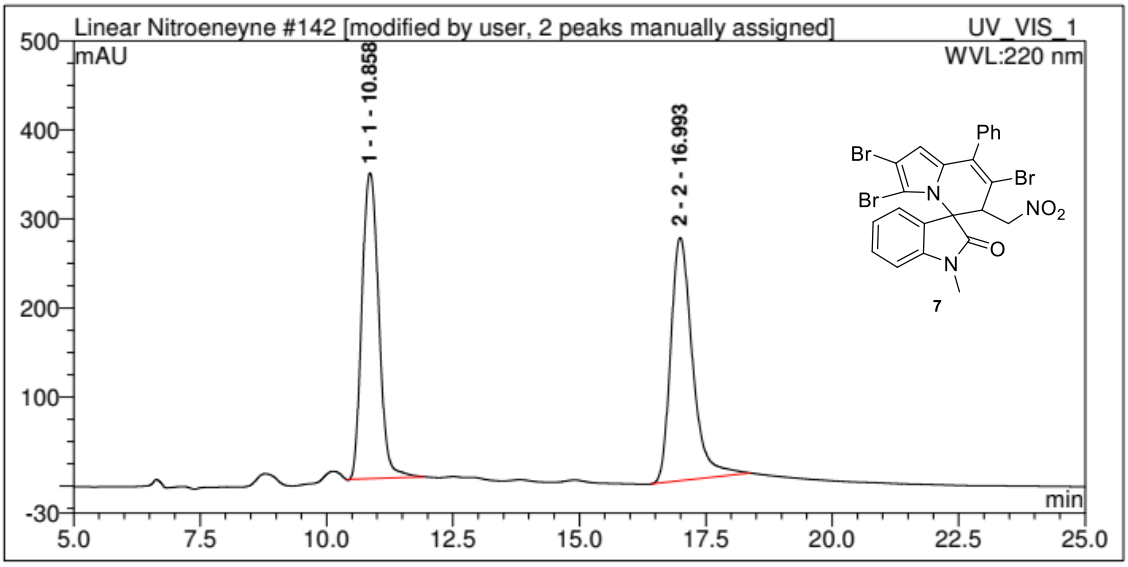

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 13.62 | 103.788 | 98.42711412 | 223.996 | n.a. |
| 2 | 2 | 16.38 | 1.659 | 1.572885879 | 4.706 | n.a. |



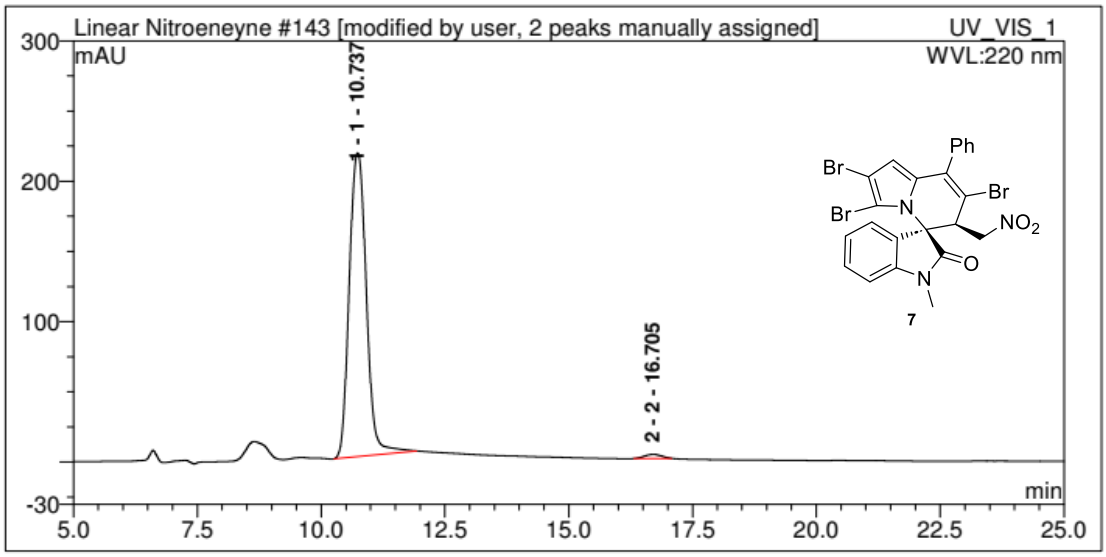

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 9.61 | 243.9732 | 49.64919474 | 728.6481 | n.a. |
| 2 | 2 | 13.59 | 247.421 | 50.35080526 | 608.854 | n.a. |



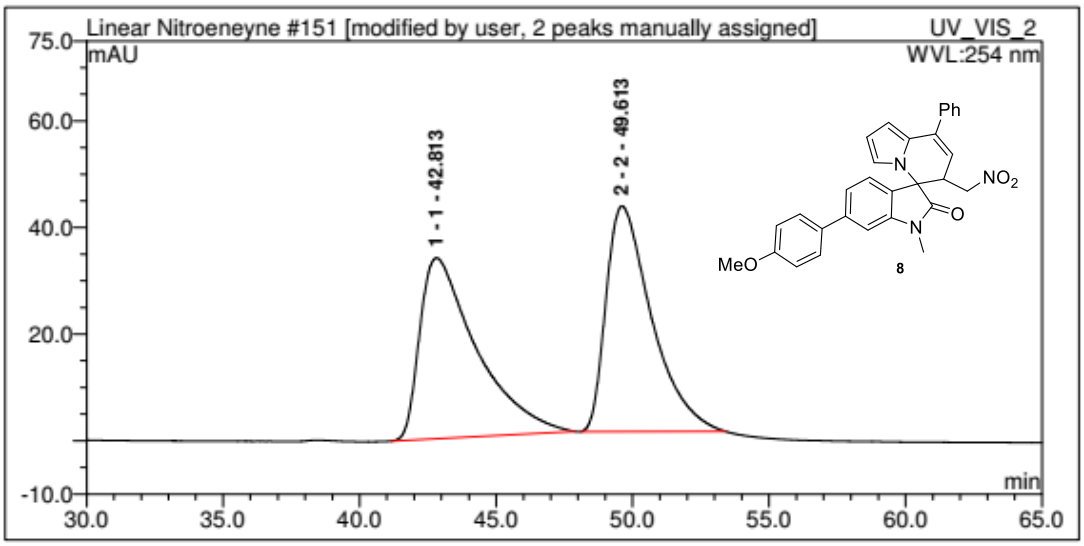

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 9.58 | 366.6111 | 98.42180387 | 1052.617 | n.a. |
| 2 | 2 | 13.64 | 5.879 | 1.578196135 | 19.796 | n.a. |



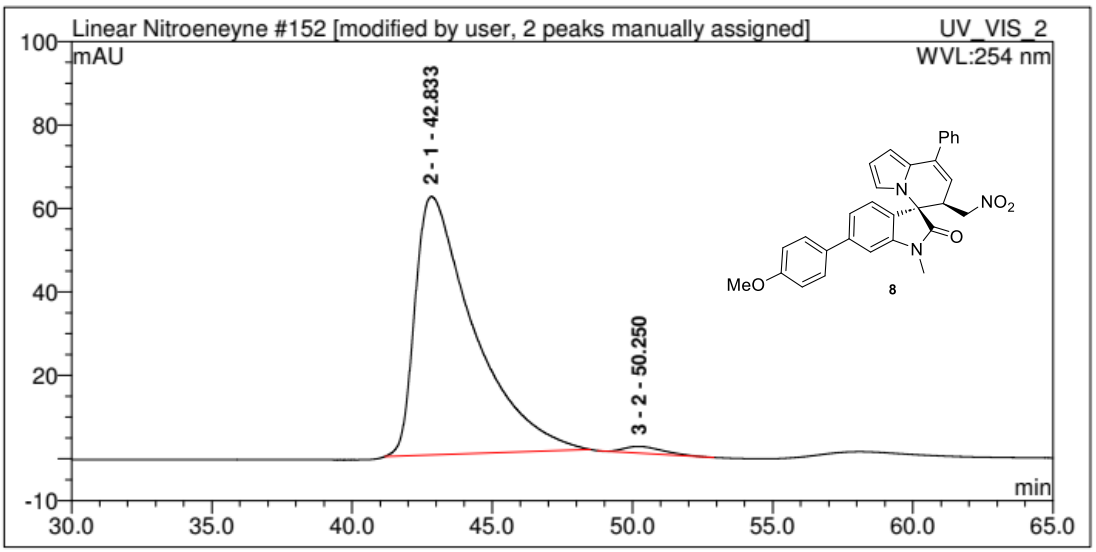

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 10.86 | 132.3884 | 49.36322094 | 343.1548 | n.a. |
| 2 | 2 | 16.99 | 135.804 | 50.63677906 | 273.008 | n.a. |




| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 10.74 | 86.34113 | 98.70191575 | 216.3848 | n.a. |
| 2 | 2 | 16.71 | 1.136 | 1.298084254 | 2.892 | n.a. |




| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 42.81 | 81.47118 | 49.85774262 | 33.90765 | n.a. |
| 2 | 2 | 49.61 | 81.936 | 50.14225738 | 42.297 | n.a. |




| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 2 | 1 | 42.83 | 150.778 | 98.31856337 | 61.91388 | n.a. |
| 3 | 2 | 50.25 | 2.579 | 1.681407181 | 1.590 | n.a. |

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