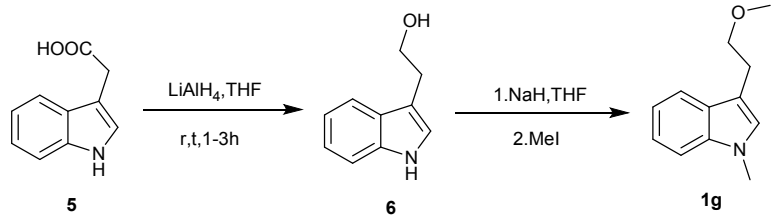
1. General remarks

Chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. Solvents were dried and purified according to the standard procedures before use. Reactions were monitored by TLC. Racemic products were obtained from corresponding substrates catalyzed by racemic catalyst at room temperature. Flash column chromatography was performed on silica gels (200-300 mesh). ^{1}H NMR and ^{13}C NMR (300 or 400 and 75 or 100 MHz, respectively) spectra were recorded on a Bruker 300 or 400 MHz NMR spectrometer in $CDCl_3$. ^{1}H NMR chemical shifts are reported in ppm (δ) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard ($CDCl_3$, δ 7.26 ppm, DMSO-d_6 at 2.50 ppm, Acetone-d_6 at 2.05 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, brs = broad singlet, d = doublet, t = triplet, td = triplet of doublets, q = quartet, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$, δ 77.0 ppm, DMSO-d_6 at 39.51 ppm, Acetone-d_6 at 206.45 ppm and 29.8 ppm). All enantiomeric ratios have been controlled by co-injections of the pure sample with the racemates. HRMS data were obtained on a Bruker Daltonics. Inc mass instrument (ESI). Chiralpak AD-H column was purchased from Daicel Chemical Industries (Hong Kong, China). Optical rotations were measured on a Perkin-Elmer 241 Polarimeter. Melting points were recorded on a Buchi Melting Point B-545.

2. Procedures and characterizations data of compounds.

2.1 Synthesis of indole 1g:



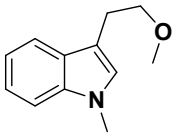
5 6 1g

To a solution of 2-(1H-indol-3-yl)acetic acid **5** (350 mg, 2 mmol) in 10 mL of THF was added $LiAlH_4$ (190 mg, 5 mmol) and the mixture was stirred for 1h. Then the solution was cooled in an ice bath. 50% NaOH aqueous solution (l mL) was introduced into the mixture and the mixture was stirred for 30 mins. Then water (10 mL) was added

into the solution. The residue was dissolved in EtOAc. The organic layer was washed with water and brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel chromatography (EtOAc/PE = 1/2) to give the pure product **6**.

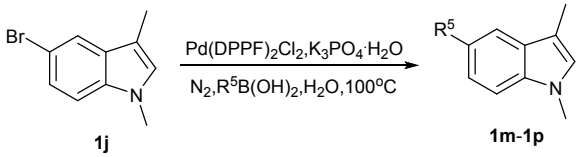
To a solution of 2-(1H-indol-3-yl)ethan-1-ol **6** (258 mg, 4 mmol) in THF (10 mL) at 0℃ was added NaH (200 mg, 5 mmol) and the reaction mixture was stirred at 0℃ for 30 mins. Then the mixture was added MeI (710 mg, 5 mmol) and stirred at r,t. for 1-3 h. The mixture was added CH_3CO_2H (1 mL) slowly. The residue was dissolved in EtOAc. The organic layer was washed with water and brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel chromatography (EtOAc/PE = 1/100) to give the pure product **1g** (238 mg, 1.26 mmol, 63% yield for two steps).

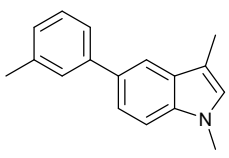
3-(2-methoxyethyl)-1-methyl-1H-indole (1g)

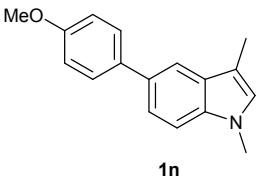


Yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.9 Hz, 1H), 7.35 (m, 2H), 7.27-7.18 (m, 1H), 7.00 (s, 1H), 3.85-3.74 (m, 5H), 3.51 (d, *J* = 1.4 Hz, 3H), 3.15 (t, *J* = 7.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.04, 128.07, 126.89, 121.59, 118.99, 118.79, 111.52, 109.29, 73.23, 58.70, 32.62, 25.71.

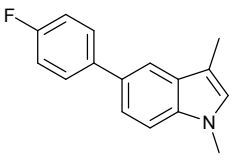
2.2 Synthesis of indoles 1m-1p:



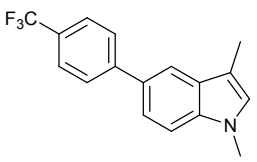

1m



1n



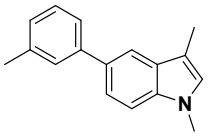
1o



1p

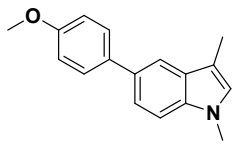
To a mixture of 5-Bromo-1,3-dimethyl-1H-indole (45 mg, 0.2 mmol), $R^5B(OH)_2$ (0.24 mmol) and H_2O (0.01 mL) in toluene (4 mL) was added $Pd(DPPF)_2Cl_2$ (15 mg, 0.02 mmol) and K_3PO_4 (51 mg, 0.24 mmol). Then the mixture was full of nitrogen gas and heated to 100 ℃ under N_2 for 10h. The solution was cooled to r.t.. The mixture was extracted with EtOAc. The organic layer was washed with water and brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel chromatography (EtOAc/PE = 1/100) to give the pure product (34-52% yield).

1,3-dimethyl-5-(m-tolyl)-1H-indole (1m)



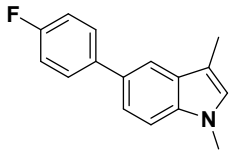
Yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 1.3 Hz, 1H), 7.60–7.48 (m, 3H), 7.43–7.32 (m, 2H), 7.19 (d, J = 7.4 Hz, 1H), 6.89 (s, 1H), 3.80 (s, 3H), 2.50 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.84, 138.18, 136.57, 132.28, 129.11, 128.58, 128.25, 127.20, 126.98, 124.56, 121.36, 117.55, 110.59, 109.24, 32.64, 21.66, 9.62. HRMS (ESI) Calcd. for $C_{17}H_{17}H^+$ $[M+H]^+$ 236.1439; Found: 236.1452.

5-(4-methoxyphenyl)-1,3-dimethyl-1H-indole (1n)



White solid, m.p: 128.1-129.3℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 1.1 Hz, 1H), 7.68 (d, J = 8.7 Hz, 2H), 7.51 (dd, J = 8.5, 1.5 Hz, 1H), 7.37 (d, J = 8.5 Hz, 1H), 7.07 (d, J = 8.7 Hz, 2H), 6.89 (s, 1H), 3.92 (s, 3H), 3.79 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.48, 136.35, 135.57, 131.89, 129.17, 128.38, 127.21, 121.13, 117.09, 114.17, 110.47, 109.27, 55.41, 32.60, 9.62. HRMS (ESI) Calcd. for $C_{17}H_{17}NOH^+$ $[M+H]^+$ 252.1388; Found: 252.1375.

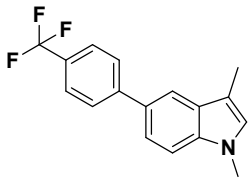
5-(4-fluorophenyl)-1,3-dimethyl-1H-indole (1o)



White solid, m.p: 71.2-72.3℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 2.2 Hz, 1H), 7.68 (m, 2H), 7.52-7.42 (m, 1H), 7.38 (d, J = 8.4 Hz, 1H), 7.24-7.09 (m, 2H), 6.91 (s, 1H), 3.80 (s, 3H), 2.43 (d, J = 3.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.19 (d, $^1\boldsymbol{J}_{C\text{-}F}$ = 245.5), 138.98, 136.54, 131.24, 129.15, 128.83 (d, $^3\boldsymbol{J}_{C\text{-}F}$ = 7.8), 127.41, 121.16, 117.45, 115.43 (d, $^2\boldsymbol{J}$

$_{C\text{-}F}$ = 21.3), 110.57, 109.38, 32.64, 9.61, HRMS (ESI) Calcd. for $C_{16}H_{14}NFH^+$ $[M+H]^+$ 240.1189; Found: 240.1178.

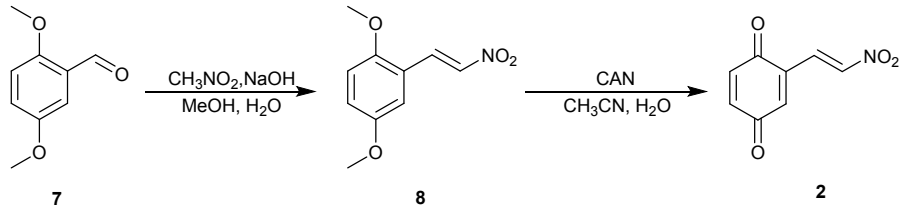
1,3-dimethyl-5-(4-(trifluoromethyl)phenyl)-1H-indole (1p)



White solid, m.p: 127.6-129.1 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93–7.78 (m, 3H), 7.73 (d, *J* = 8.1 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.40 (d, *J* = 8.5 Hz, 1H), 6.92 (s, 1H), 3.80 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.35, 136.97, 130.56, 129.20, 128.16 (q, $^2J_{C\text{-}F}$ = 32.1), 127.62, 127.48, 127.31 (q, $^1J_{C\text{-}F}$ = 268.2), 125.59, 125.55, 121.11, 117.87, 110.82, 109.56, 32.65, 9.56. HRMS (ESI) Calcd for $C_{17}H_{14}NF_3H^+$ $[M+H]^+$ 290.1157; Found: 290.1139.

2.3 Synthesis of 2-(2-Nitrovinyl)-1,4-benzoquinone 2

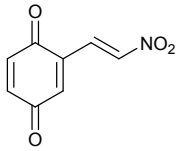
2-(2-Nitrovinyl)-1,4-benzoquinone **2** was prepared according to the literature procedure[1]:



A solution of 2,5-dimethoxybenzaldehyde **7** (4 g, 24.1 mmol) and CH_3NO_2 (1.4 mL, 26 mmol) in MeOH (24 mL) was cooled to 10 ℃ in an ice bath. A solution of NaOH (1 g, 25 mmol) in H_2O (8 mL) was added dropwise with stirring at a rate such that the temperature stayed under 15 ℃ for 5 mins. The reaction mixture was then poured into 5N HCl (60 mL) with stirring, and an orange precipitate formed. The precipitate was vacuum-filtered then dissolved with DCM and washed with water (30 mL × 3) and brine. The organic layer was separated and dried over $MgSO_4$. The mixture was subsequently filtered and the solvents were removed in vacuo to give the product 1,4-dimethoxy-2-(2-nitrovi-nyl)benzene (4.8 g, 23 mmol) which was used directly in the next step.

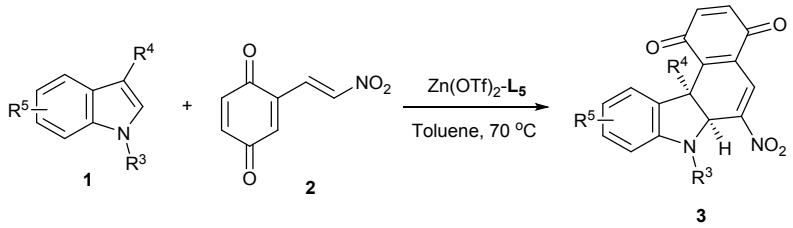
A solution of ceric ammonium nitrate (28 g, 51 mmol) in 3:1 H_2O/CH_3CN (48 mL) was poured into a solution of 1,4-dimethoxy-2-(2-nitrovinyl)benzene (4.8 g, 23

mmol) in CH_3CN (120 mL). The mixture was stirred for 5 min and then washed with brine (25 mL), and the brine layer was extracted with CH_3CN (25 mL × 2). The CH_3CN fractions were combined and concentrated under 28 ℃. The residue was dissolved with DCM (120 mL) and washed with water (50 mL), the water layer was extracted with DCM (50 mL). The organic layer was combined and washed with water (25 mL). Then the solution was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was crystallized from THF/heptane, giving the product 2-(2-nitrovinyl)-1,4-benzoquinone **2** as an orange needles (2 g, 11 mmol, 46% yield for two steps).

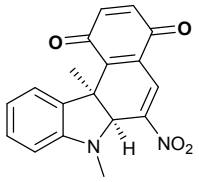


(*E*)-2-(2-nitrovinyl)cyclohexa-2,5-diene-1,4-dione (2): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 13.7 Hz, 1H), 7.64 (d, J = 13.7 Hz, 1H), 7.01 (m, 1H), 6.95–6.84 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.16, 184.86, 144.45, 137.96, 137.43, 136.80, 136.41, 130.23.

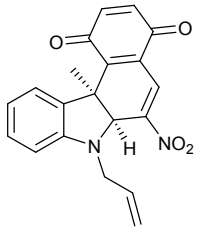
2.4 Asymmetric D-A reaction/oxidation of indoles 1 with 2-(2-Nitrovinyl)-1,4-benzoquinone 2:



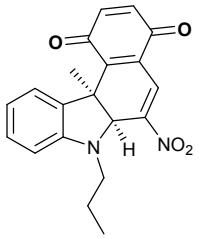
To a solution of $Zn(OTf)_2$ (3.6 mg, 0.01 mmol) in toluene (2 mL) at 25 ℃ was added L_5 (8.3 mg, 0.0167 mmol) and the reaction mixture was stirred for 2h at 25 ℃. Then indole **1** (0.1 mmol) was added and the mixture was stirred at 70 ℃ for 10 minutes. Then 2-(2-nitrovinyl)-1,4-benzoquinone **2** (39.7 mg, 0.22 mmol) was added and the mixture was stirred at 70 ℃ for indicated time. The reaction mixture was cooled to r.t. and purified by flash column chromatography (EtOAc/PE = 1/20) to give the product **3**.



(6aS,11bS)-7,11b-dimethyl-6-nitro-7,11b-dihydro-1H-benzo[c] carbazole-1,4(6aH)-dione (3a): black-blue solid, m.p: 159.1-161.2 ^{o}C, 99% yield (31.9 mg), 88% ee, HPLC condition: Chiralpak OD-H (*n*-hexane/isopropan-ol: 90/10, 1.0 mL/min, t_{major} = 11.037 min, t_{minor} = 18.735 min). $[\alpha]_D^{20}$ = +4.7 (c 0.01, acetonitrile). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.17 (t, *J* = 7.7 Hz, 1H), 6.90 (t, *J* = 7.5 Hz, 1H), 6.74 (m, 2H), 6.55 (d, *J* = 7.9 Hz, 1H), 4.41 (d, *J* = 1.0 Hz, 1H), 2.65 (s, 3H), 1.69 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.40, 183.31, 152.67, 148.57, 143.94, 139.02, 134.79, 131.84, 128.59, 128.45, 128.02, 124.84, 120.25, 107.46, 69.66, 50.85, 34.51, 22.13. HRMS (ESI) Calcd. for $C_{18}H_{14}N_2O_4Na^+$ $[M+Na]^+$ 345.0851; Found: 345.0870.

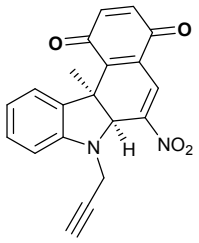


(6aS,11bS)-7-allyl-11b-methyl-6-nitro-7,11b-dihydro-1H-benzo [c]carbazole-1,4 (6aH)-dione (3b): black-blue solid, m.p: 142.0-143.9 ^{o}C, 34% yield (11.8 mg), 71% ee, HPLC condition: Chiralpak OD-H (*n*-hexane/ isopropanol: 70/30, 1.0 mL/min, t_{major} = 10.957 min, t_{minor} = 18.140 min). $[\alpha]_D^{20}$ = +3.5 (c 0.01, acetonitrile). ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 8.25 (d, *J* = 1.3 Hz, 1H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.14 (dd, *J* = 11.0, 4.4 Hz, 1H), 6.87 (t, *J* = 7.5 Hz, 1H), 6.75 (m, 2H), 6.54 (d, *J* = 7.9 Hz, 1H), 5.79 (m, 1H), 5.34–5.06 (m, 2H), 4.67 (d, *J* = 1.1 Hz, 1H), 3.68 (m, 2H), 1.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 185.49, 183.42, 151.58, 148.57, 143.83, 139.16, 134.80, 132.49, 131.89, 128.33, 128.15, 128.03, 124.88, 120.02, 118.40, 108.06, 67.61, 51.19, 49.63, 22.00. HRMS (ESI) Calcd. for $C_{20}H_{16}N_2O_4H^+$ $[M+H]^+$ 349.1188; Found: 349.1178.

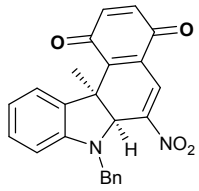


(6aS,11bS)-11b-methyl-6-nitro-7-propyl-7,11b-dihydro-1*H*-benzo[c]carbazole-1,4(6a*H*)-dione (3c): black-blue solid, m.p: 191.0-192.3 ^{o}C, 80% yield (28.2 mg), 37% ee, HPLC condition: Chiralpak AD-H (*n*-hexane/isopropanol: 70/30, 1.0 mL/min, t_{major} = 8.148min, t_{minor} = 13.841 min). $[\alpha]_D^{20}$ = +2.3 (c 0.01, acetonitrile). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 1.3 Hz, 1H), 7.79 (dd, *J* = 7.6, 0.7 Hz,1H), 7.16 (m, 1H), 6.86 (m, 1H), 6.76 (m, 2H), 6.50 (d, *J* = 7.9 Hz, 1H), 4.70 (d, *J* = 1.1 Hz, 1H), 3.18–3.00 (m, 1H), 2.87 (m, 1H), 1.72 (s, 3H), 1.66–1.46 (m, 2H), 0.86 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.53, 183.43, 151.72, 148.60, 143.94, 139.18, 134.77, 131.81, 128.37, 128.13, 127.85, 124.95, 119.50, 107.24, 67.04, 51.18, 48.41,

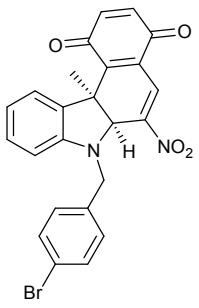
22.13, 17.84, 11.49. HRMS (ESI) Calcd. for $C_{20}H_{18}N_2O_4H^+$ $[M+H]^+$ 351.1345; Found: 351.1349.



(6aS,11bS)-11b-methyl-6-nitro-7-(prop-2-yn-1-yl)-7,11b-dihydro-1*H*-benzo[c]carbazole-1,4(6a*H*)-dione (3d): black solid, m.p: 184.5-186.3 °C, 62% yield (21.5 mg), 63% ee, HPLC condition: Chiralpak AD-H (*n*-hexane/isopropanol: 70/30, 1.0 mL/min, t_{major} = 13.196 min, t_{minor} = 11.355 min). $[\alpha]_D^{20}$ = +2.7 (c 0.01, acetonitrile). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, J = 1.3 Hz, 1H), 7.86 (dd, J = 7.7, 0.7 Hz, 1H), 7.23 (m, 1H), 6.98 (m, 1H), 6.77 (m, 2H), 6.69 (d, J = 7.9 Hz, 1H), 4.70 (d, J = 1.2 Hz, 1H), 4.04 (dd, J = 18.2, 2.3 Hz, 1H), 3.66 (dd, J = 18.2, 2.3 Hz, 1H), 2.20 (s, 1H), 1.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.40, 183.30, 150.19, 148.36, 143.90, 139.12, 134.84, 131.85, 129.01, 128.37, 128.20, 125.30, 121.21, 109.02, 73.40, 66.87, 51.06, 36.56, 22.13. HRMS (ESI) Calcd. for $C_{20}H_{14}N_2O_4Na^+$ $[M+Na]^+$ 369.0851; Found: 369.0852.

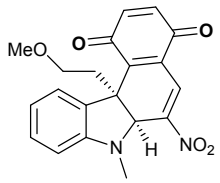


(6aS,11bS)-7-benzyl-11b-methyl-6-nitro-7,11b-dihydro-1H-benzo[c]car-bazole-1,4(6aH)-dione (3e): black-blue solid, m.p: 145.4-147.1 °C, 66% yield (26.3 mg), 56% ee, HPLC condition: Chiralpak AD-H (*n*-hexane/isopropanol: 70/30, 1.0 mL/min, t_{major} = 7.855 min, t_{minor} = 9.605 min). $[\alpha]_D^{20}$ = +2.8 (c 0.01, acetonitrile). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (d, J = 1.3 Hz, 1H), 7.84 (d, J = 7.6 Hz, 1H), 7.25 (dd, J = 5.0, 1.8 Hz, 3H), 7.20 –7.13 (m, 2H), 7.09 (t, J = 7.7 Hz, 1H), 6.90 (t, J = 7.5 Hz, 1H), 6.79 (m, 2H), 6.44 (d, J = 7.8 Hz, 1H), 4.79 (d, J = 1.2 Hz, 1H), 4.27 (q, J = 16.1 Hz, 2H), 1.73 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.43, 183.34, 152.46, 148.22, 144.07, 139.18, 137.74, 134.78, 131.82, 128.54, 128.40, 128.06, 127.99, 127.32, 126.99, 124.75, 120.15, 108.94, 107.67, 68.85, 52.08, 51.30, 21.88. HRMS (ESI) Calcd. for $C_{24}H_{18}N_2O_4H^+$ $[M+H]^+$ 399.1345; Found: 399.1331.

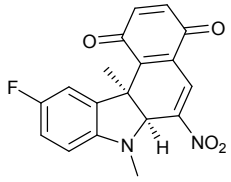


(6aS,11bS)-7-(4-bromobenzyl)-11b-methyl-6-nitro-7,11b-dihydro-1H-benzo[c] carbazole-1,4(6aH)-dione (3f): black-blue solid, m.p: 193,2-194.7 °C, 30% yield (14.3 mg), 51% ee, HPLC condition: Chiralpak AD-H (*n*-hexane/isopropanol: 70/30, 1.0

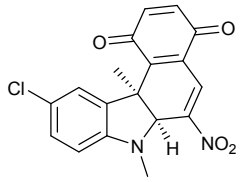
mL/min, t_{major} = 9.151min, t_{minor} =11.116 min). $[\alpha]_D^{20}$ = +1.4 (c 0.01, acetonitrile). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (d, *J* = 1.2 Hz, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.05 (m, 3H), 6.89 (t, *J* = 7.5 Hz, 1H), 6.78 (m, 2H), 6.37 (d, *J* = 7.9 Hz, 1H), 4.75 (s, 1H), 4.20 (s, 2H), 1.71 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.34, 183.27, 152.15, 148.14, 144.07, 139.18, 136.85, 134.81, 131.74, 131.64, 128.61, 128.43, 128.16, 128.00, 124.93, 121.07, 120.40, 107.65, 68.80, 51.56, 51.34, 21.97. HRMS (ESI) Calcd. for $C_{24}H_{17}N_2O_4BrH^+$ $[M+H]^+$ 477.0450 (^{79}Br), 479.0429 (^{81}Br); Found: 477.0424 (^{79}Br), 479.0561 (^{81}Br).



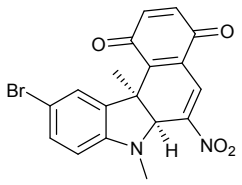
(6aS,11bS)-11b-(2-methoxyethyl)-7-methyl-6-nitro-7,11b-dihydro-1H-benzo[c] carbazole-1,4(6aH)-dione (3g): black-blue solid, m.p: 150.4-152.3 °C, 67% yield (24.5 mg), 31% ee, HPLC condition: Chiralpak AD-H (*n*-hexane/isopropanol: 70/30, 1.0 mL/min, t_{major} = 9.411min, t_{minor} = 7.910 min). $[\alpha]_D^{20}$ = +2.0 (c 0.01, acetonitrile). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (d, *J* = 1.5 Hz, 1H), 7.69 (d, *J* = 7.7 Hz, 1H), 7.16 (m, 1H), 6.86 (t, *J* = 7.6 Hz, 1H), 6.73 (m, 2H), 6.53 (d, *J* = 7.9 Hz, 1H), 4.65 (d, *J* = 1.3 Hz, 1H), 3.41 (m, 1H), 3.22–2.86 (m, 5H), 2.66 (s, 3H), 2.34–2.15 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.85, 183.42, 152.63, 150.69, 141.57, 138.98, 134.83, 128.47, 127.87, 122.30, 120.10, 107.25, 68.87, 58.04, 53.83, 38.15, 34.40. HRMS (ESI) Calcd. for $C_{20}H_{18}N_2O_5H^+$ $[M+H]^+$ 367.1294; Found: 367.1291.



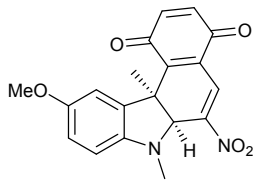
(6aS,11bS)-10-fluoro-7,11b-dimethyl-6-nitro-7,11b-dihydro-1H-benzo[c] carbazole-1,4(6aH)-dione (3h): black-blue solid, m.p: 191.0-192.3 °C, 79% yield (26.9 mg), 69% ee, HPLC condition: Chiralpak AD-H (*n*-hexane/isopropanol: 70/30, 1.0 mL/min, t_{major} = 9.827min, t_{minor} = 8.442 min). $[\alpha]_D^{20}$ = +3.8 (c 0.01, acetonitrile). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.31 (d, *J* = 1.3 Hz, 1H), 7.56 (dd, *J* = 8.9, 2.6 Hz, 1H), 6.90–6.84 (m, 1H), 6.79 (m, 2H), 6.46 (dd, *J* = 8.6, 4.3 Hz, 1H), 4.42 (d, *J* = 1.3 Hz, 1H), 2.65 (d, *J* = 10.5 Hz, 3H), 1.75–1.61 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 185.34, 183.22, 157.56(d, $^1J_{C\text{-}F}$ = 238.0), 149.03, 148.52, 143.36, 138.99, 135.00, 132.11, 130.45(d, $^3J_{C\text{-}F}$ = 8.6), 124.92, 115.67(d, $^2J_{C\text{-}F}$ = 25.6), 114.81(d, $^2J'_{C\text{-}F}$ = 23.4), 107.79(d, $^3J'_{C\text{-}F}$ = 8.2), 70.09, 50.83, 35.08, 22.11. HRMS (ESI) Calcd. for $C_{18}H_{13}N_2O_4FH^+$ $[M+H]^+$ 341.0938; Found: 341.0929.



(6aS,11bS)-10-chloro-7,11b-dimethyl-6-nitro-7,11b-dihydro-1H-benzo[c] carbazole-1,4(6aH)-dione (3i): black-blue solid, m.p: 196.3-198.5 °C, 73% yield (26.1 mg), 75% ee, HPLC condition: Chiralpak AD-H (*n*-hexane/isopropanol: 70/30, 1.0 mL/min, t_{major} = 10.948 min, t_{minor} = 9.200 min). $[\alpha]_D^{20}$ = +4.4 (c 0.01, acetonitrile). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, J = 0.9 Hz, 1H), 7.78 (d, J = 2.0 Hz, 1H), 7.12 (dd, J = 8.4, 2.0 Hz, 1H), 6.80 (m, 2H), 6.46 (d, J = 8.4 Hz, 1H), 4.45 (d, J = 0.9 Hz, 1H), 2.65 (s, 3H), 1.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.26, 183.18, 151.36, 148.26, 143.33, 139.04, 134.97, 132.06, 130.56, 128.42, 128.28, 125.01, 124.87, 108.32, 69.74, 50.92, 34.55, 22.11. HRMS (ESI) Calcd. for $C_{18}H_{13}N_2O_4ClH^+$ $[M+H]^+$ 357.0642 (^{35}Cl), 359.0613 (^{37}Cl); Found: 357.0625 (^{35}Cl), 359.0739 (^{37}Cl).

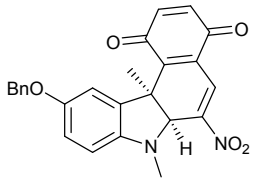


(6aS,11bS)-10-bromo-7,11b-dimethyl-6-nitro-7,11b-dihydro-1H-benzo[c]carbazo le-1,4(6aH)-dione (3j): black-blue solid, m.p: 200.3-202.1 °C, 63% yield (25.3 mg), 64% ee, HPLC condition: Chiralpak AD-H (*n*-hexane/isopropanol: 70/30, 1.0 mL/min, t_{major} = 11.339 min, t_{minor} = 9.493 min). $[\alpha]_D^{20}$ = +4.2 (c 0.01, acetonitrile). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.32 (d, J = 1.1 Hz, 1H), 7.92 (d, J = 1.9 Hz, 1H), 7.29–7.25 (m, 1H), 6.80 (m, 2H), 6.42 (d, J = 8.4 Hz, 1H), 4.44 (d, J = 1.0 Hz, 1H), 2.64 (s, 3H), 1.67 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.19, 183.14, 151.73, 148.16, 143.31, 139.02, 134.93, 131.99, 131.27, 131.02, 130.88, 124.97, 111.87, 108.85, 69.61, 50.87, 34.41, 22.07. HRMS (ESI) Calcd. for $C_{18}H_{13}BrN_2O_4H^+$ $[M+H]^+$ 401.0137 (^{79}Br), 403.0116 (^{81}Br); Found: 401.0134 (^{79}Br), 403.0272 (^{81}Br).

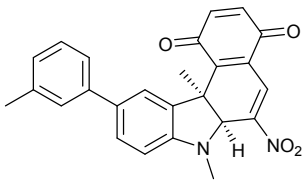


(6aS,11bS)-10-methoxy-7,11b-dimethyl-6-nitro-7,11b-dihydro-1H-benzo[c] carbazole-1,4(6aH)-dione (3k): black-blue solid, m.p: 145.3-147.1 °C, 99% yield (34.8 mg), 57% ee, HPLC condition: Chiralpak AD-H (*n*-hexane/isopropanol: 70/30, 1.0 mL/min, t_{major} = 11.664min, t_{minor} =18.881 min). $[\alpha]_D^{20}$ = +4.7 (c 0.01, acetonitrile). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.29 (d, J = 1.3 Hz, 1H), 7.44 (d, J = 2.5 Hz, 1H), 6.74 (m, 3H), 6.47 (d, J = 8.5 Hz, 1H), 4.32 (s, 1H), 3.83 (s, 3H), 2.61 (s, 3H), 1.66 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.46, 183.30, 154.41, 148.75, 147.21, 143.63, 138.97,

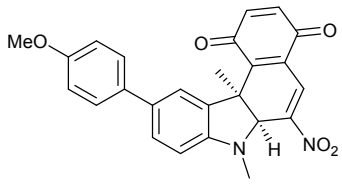
134.83, 131.90, 129.88, 124.80, 114.54, 113.56, 107.93, 70.22, 56.01, 50.89, 35.43, 22.09. HRMS (ESI) Calcd. for $C_{19}H_{16}N_2O_5H^+$ $[M+H]^+$ 353.1137; Found: 353.1130.



(6aS,11bS)-10-(benzyloxy)-7,11b-dimethyl-6-nitro-7,11b-dihydro-1H-benzo[c] carbazole-1,4(6aH)-dione (3l): black-blue solid, m.p: 204.1-205.8 °C, 29.1 mg, 68% yield (29.2 mg), 61% ee, HPLC condition: Chiralpak AD-H (*n*-hexane/isopropanol: 70/30, 1.0 mL/min, t_{major} = 13.195 min, t_{minor} = 18.861 min). $[\alpha]_D^{20}$ = +4.2 (c 0.01, acetonitrile). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 1.3 Hz, 1H), 7.55 (d, J = 2.5 Hz, 1H), 7.50 (d, J = 7.1 Hz, 2H), 7.42 (t, J = 7.3 Hz, 2H), 7.36 (d, J = 7.2 Hz, 1H), 6.80 (m, 3H), 6.49 (d, J = 8.5 Hz, 1H), 5.09 (s, 2H), 4.36 (d, J = 1.3 Hz, 1H), 2.64 (s, 3H), 1.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.48, 183.34, 153.61, 148.78, 147.46, 143.68, 139.01, 137.29, 134.87, 131.93, 129.88, 128.54, 127.92, 127.67, 124.85, 115.75, 114.90, 107.96, 71.07, 70.22, 50.95, 35.40, 22.17. HRMS (ESI) Calcd. for $C_{25}H_{20}N_2O_5H^+$ $[M+H]^+$ 429.1450; Found: 429.1440.

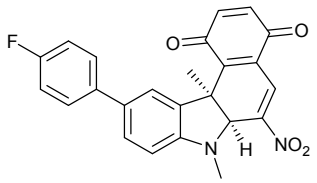


(6aS,11bS)-7,11b-dimethyl-6-nitro-10-(m-tolyl)-7,11b-dihydro-1H-benzo[c] carbazole-1,4(6aH)-dione (3m): black-blue solid, m.p: 115.3-116.8 °C, 90% yield (37.1 mg), 63% ee, HPLC condition: Chiralpak AD-H (*n*-hexane /isopropanol: 70/30, 1.0 mL/min, t_{major} = 10.376 min, t_{minor} = 15.988 min). $[\alpha]_D^{20}$ = +7.2 (c 0.01, acetonitrile). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.33 (d, J = 1.3 Hz, 1H), 8.06 (d, J = 1.6 Hz, 1H), 7.47–7.27 (m, 4H), 7.14 (d, J = 7.5 Hz, 1H), 6.76 (m, 2H), 6.60 (d, J = 8.2 Hz, 1H), 4.47 (d, J = 1.2 Hz, 1H), 2.69 (s, 3H), 2.45 (s, 3H), 1.74 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.40, 183.30, 152.15, 148.42, 143.83, 141.15, 139.05, 138.30, 134.78, 133.79, 131.84, 129.14, 128.66, 127.42, 127.34, 126.92, 124.96, 123.83, 107.55, 69.80, 50.93, 34.57, 22.17, 21.59. HRMS (ESI) Calcd. for $C_{25}H_{20}N_2O_4H^+$ $[M+H]^+$ 413.1501; Found: 413.1484.

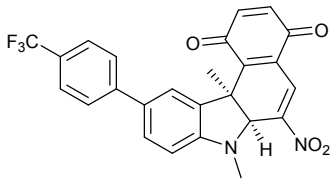


(6aS,11bS)-10-(4-methoxyphenyl)-7,11b-dimethyl-6-nitro-7,11b-dihydro-1H-benzo[c]carbazole-1,4(6aH)-dione (3n): black-blue solid, m.p: 203.2-204.8 °C, 63% yield (27.1 mg), 86% ee, HPLC condition: Chiralpak AD-

H (*n*-hexane/isopropanol: 70/30, 1.0 mL/min, t_{major} = 17.620 min, t_{minor} = 30.640 min). $[\alpha]_D^{20}$ = +8.5 (c 0.01, acetonitrile). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.32 (d, *J* = 1.2 Hz, 1H), 8.02 (d, *J* = 1.6 Hz, 1H), 7.54 (d, *J* = 8.7 Hz, 2H), 7.36 (dd, *J* = 8.1, 1.8 Hz, 1H), 6.98 (d, *J* = 8.7 Hz, 2H), 6.75 (m, 2H), 6.59 d, *J* = 8.2 Hz, 1H), 4.45 (d, *J* = 1.1 Hz, 1H), 3.86 (s, 3H), 2.68 (s, 3H), 1.72 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.44, 183.30, 158.64, 151.79, 148.45, 143.82, 139.06, 134.78, 133.85, 133.41, 131.84, 129.15, 127.68, 126.82, 126.51, 124.95, 114.19, 107.59, 69.82, 55.34, 50.92, 34.64, 22.17. HRMS (ESI) Calcd. for $C_{25}H_{20}N_2O_5H^+$ $[M+H]^+$ 429.1450; Found: 429.1444.

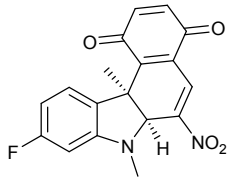


(6aS,11bS)-10-(4-fluorophenyl)-7,11b-dimethyl-6-nitro-7,11b-dihydro-1H-benzo[c]carbazole-1,4(6aH)-dione (3o): black-blue solid, m.p: 125.3-127.1 ^{o}C, 84% yield (34.9 mg), 64% ee, HPLC condition: Chiralpak AS-H (*n*-hexane /isopropanol: 50/50, 1.0 mL/min, t_{major} = 13.460 min, t_{minor} = 19.692 min). $[\alpha]_D^{20}$ = +7.1 (c 0.01, acetonitrile). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.33 (d, *J* = 1.2 Hz, 1H), 8.02 (d, *J* = 1.6 Hz, 1H), 7.56 (dd, *J* = 8.7, 5.4 Hz, 2H), 7.35 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.12 (t, *J* = 8.7 Hz, 2H), 6.76 (m, 2H), 6.60 (d, *J* = 8.2 Hz, 1H), 4.47 (d, *J* = 1.2 Hz, 1H), 2.69 (s, 3H), 1.73 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.45, 183.26, 162.03 (d, $^1J_{C\text{-}F}$ = 244.0 Hz), 152.16, 148.37, 143.70, 139.04, 137.32, 134.85, 132.65, 131.90, 129.31, 128.20, 128.09, 127.17, 126.79, 124.96, 115.55 (d, $^2J_{C\text{-}F}$ = 21.2 Hz), 107.60, 69.76, 50.90, 34.54, 22.14. HRMS (ESI) Calcd. for $C_{24}H_{17}FN_2O_4(CH_3OH)H^+$ $[M+(CH_3OH)+H]^+$ 449.1513; Found: 449.1498.

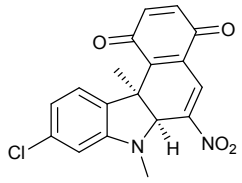


(6aS,11bS)-7,11b-dimethyl-6-nitro-10-(4-(trifluoro-methyl)phenyl)7,11b-dihydro-1H-benzo[c] carbazole-1,4(6aH)-dione (3p): black-blue solid, m.p: 212.1-213.0 ^{o}C, 78% yield (36.3 mg), 62% ee, HPLC condition: Chiralpak AD-H (*n*-hexane/isopropanol: 70/30, 1.0 mL/min, t_{major} = 9.460 min, t_{minor} =11.319 min). $[\alpha]_D^{20}$ = +5.8 (c 0.01, acetonitrile). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.35 (d, *J* = 0.9 Hz, 1H), 8.10 (d, *J* = 1.4 Hz, 1H), 7.81–7.63 (m, 4H), 7.45 (dd, *J* = 8.1, 1.6 Hz, 1H), 6.79 (m, 2H), 6.64 (d, *J* = 8.2 Hz, 1H), 4.53 (s, 1H), 2.72 (s, 3H), 1.76 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.43, 183.21, 152.83, 148.24, 144.61, 143.59, 139.05, 134.89, 131.96, 131.87, 129.52, 128.50 (q, $^2J_{C\text{-}F}$ = 32.3 Hz), 127.86, 127.61, 127.10,

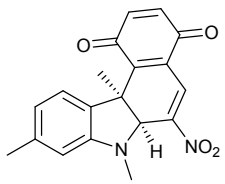
126.77, 125.72, 125.67, 125.02, 124.38 (q, $^{1}J_{C\text{-}F}$ = 270.1 Hz), 107.65, 69.68, 50.90, 34.35, 22.15. HRMS (ESI) Calcd. for $C_{25}H_{17}F_3N_2O_4(CH_3OH)H^+$ $[M+(CH_3OH)+H^+]^+$ 499.1481; Found: 499.1451.



(6aS,11bS)-9-fluoro-7,11b-dimethyl-6-nitro-7,11b-dihydro-1H-benzo[c]carbazole-1,4(6aH)-dione (3q): black-blue solid, m.p: 175.1-177.3 °C, 65% yield (22.1 mg), 66% ee, HPLC condition: Chiralpak AD-H (*n*-hexane/isopropanol: 70/30, 1.0 mL/min, t_{major} = 10.546 min, t_{minor} = 9.428 min). $[\alpha]_D^{20}$ = +3.7 (c 0.01, acetonitrile). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, J = 1.3 Hz, 1H), 7.71 (dd, J = 8.4, 5.6 Hz, 1H), 6.78 (m, 2H), 6.54 (td, J = 9.1, 2.3 Hz, 1H), 6.24 (dd, J = 9.7, 2.3 Hz, 1H), 4.49 (d, J = 1.2 Hz, 1H), 2.66 (d, J = 8.6 Hz, 3H), 1.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.44, 183.26, 163.72 (d, $^{1}J_{C\text{-}F}$ = 246.1 Hz), 154.28 (d, $^{3}J_{C\text{-}F}$ = 11.5 Hz), 148.06, 143.72, 139.02, 134.92, 131.80, 129.10 (d, $^{3}J'_{C\text{-}F}$ = 10.4 Hz), 125.13, 123.96, 106.27 (d, $^{2}J_{C\text{-}F}$ = 22.8 Hz), 95.61 (d, $^{2}J'_{C\text{-}F}$ = 27.2 Hz), 69.85, 50.46, 34.18, 22.25. HRMS (ESI) Calcd. for $C_{18}H_{13}N_2O_4FH^+$ $[M+H]^+$ 341.0938; Found: 341.0939.



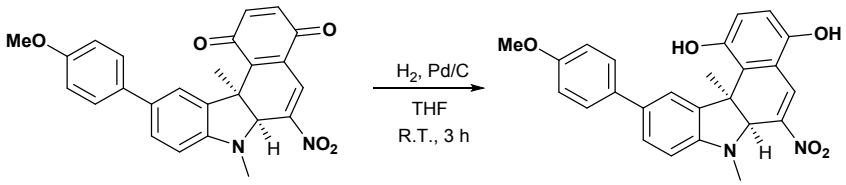
(6aS,11bS)-9-chloro-7,11b-dimethyl-6-nitro-7,11b-dihydro-1H-benzo[c]carbazole-1,4(6aH)-dione (3r): black-blue solid, m.p: 136.1-138.0 °C, 34% yield (12.1 mg), 55% ee, HPLC condition: Chiralpak AD-H (*n*-hexane/isopropanol: 70/30, 1.0 mL/min, t_{major} = 10.752 min, t_{minor} = 8.353 min). $[\alpha]_D^{20}$ = +3.8 (c 0.01, acetonitrile). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 1.3 Hz, 1H), 7.70 (d, J = 8.1 Hz, 1H), 6.97–6.67 (m, 3H), 6.51 (d, J = 1.8 Hz, 1H), 4.49 (d, J = 1.2 Hz, 1H), 2.65 (s, 3H), 1.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.36, 183.20, 153.71, 148.06, 143.59, 139.03, 134.95, 134.71, 131.95, 128.98, 127.26, 125.11, 119.96, 107.92, 69.66, 50.60, 34.17, 22.08. HRMS (ESI) Calcd for $C_{18}H_{13}N_2O_4ClH^+$ $[M+H]^+$ 357.0642 (^{35}Cl), 359.0613 (^{37}Cl); Found: 357.0653 (^{35}Cl), 359.0794 (^{37}Cl).



(6aS,11bS)-7,9,11b-trimethyl-6-nitro-7,11b-dihydro-1H-benzo [c]carbazole-1,4 (6aH)-dione (3s): black-blue solid, m.p: 135.1-137.0 °C, 36% yield (12.1 mg), 61% ee, HPLC condition: Chiralpak AD-H (*n*-hexane/isopropanol: 70/30, 1.0 mL/min, t_{major} = 8.230

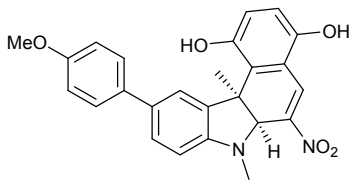
min, t_{minor} = 6.709 min). $[\alpha]_D^{20}$ = +4.2 (c 0.01, acetonitrile). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 1.3 Hz, 1H), 7.69 (d, J = 7.8 Hz, 1H), 6.88–6.65 (m, 3H), 6.40 (s, 1H), 4.41 (d, J = 1.3 Hz, 1H), 2.66 (s, 3H), 2.34 (s, 3H), 1.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.54, 183.44, 152.93, 148.65, 144.11, 139.07, 138.70, 134.79, 131.71, 127.77, 125.78, 124.91, 121.08, 108.45, 69.85, 50.58, 34.52, 22.30, 21.58. HRMS (ESI) Calcd. for $C_{19}H_{16}N_2O_4H^+$ $[M+H]^+$ 337.1188; Found: 337.1192.

2.5 Hydrogenation of 3n:



3n (86% ee) **4**, 91% yield 85% ee

To a solution of **3n** (34.4 mg, 0.08 mmol) in THF (4 mL) at r.t. was added Pd/C (5 mg, 10%) and the mixture was stirred for 1 h at r.t. under H_2. TLC was used to monitor this reaction. Then the mixture was subsequently filtered under the protection of N_2 and the solvent was removed in vacuo. The residue was purified by flash column chromatography (EtOAc/PE = 1/2) to give the pure product **4** (31.3 mg, 0.073 mmol, 91% yield, 85.4% ee).



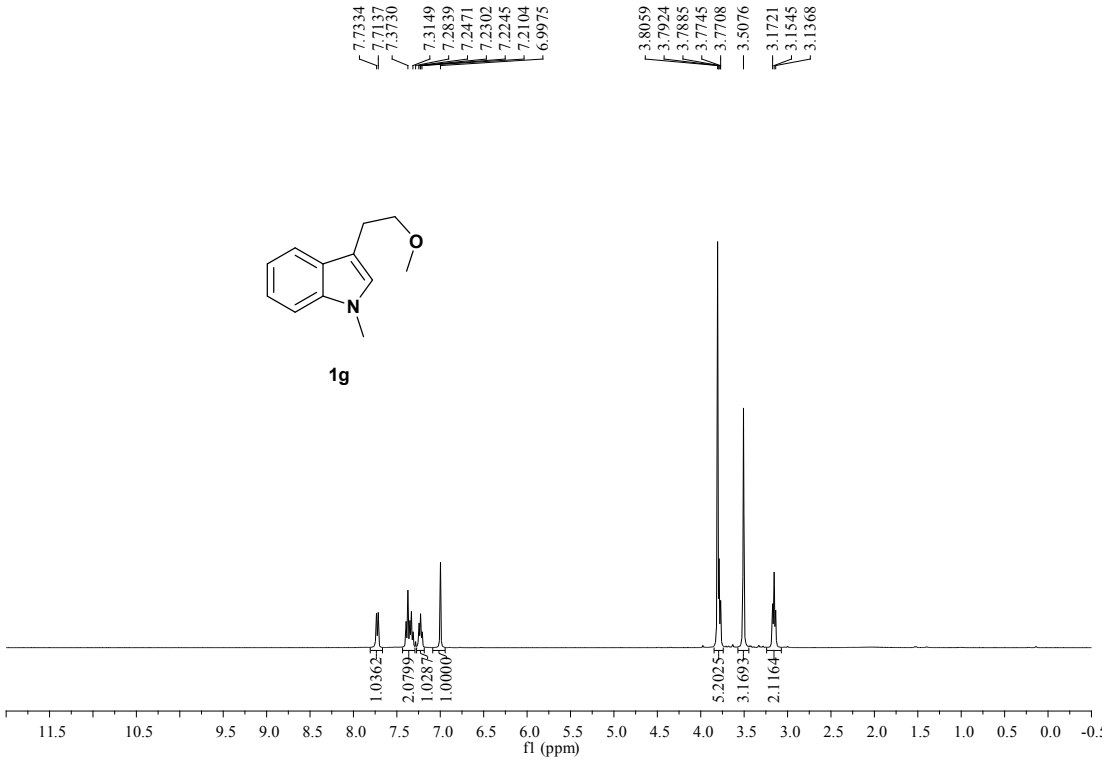
(6aS,11bS)-10-(4-methoxyphenyl)-7,11b-dimethyl-6-nitro-6a,11b-dihydro-7H-benzo[c]carbazole-1,4-diol (4): red solid, m.p: 252.3-254.1^{o}C, 91% yield, 85.4% ee, HPLC condition: Chiralpak IC-H (*n*-hexane/isopropanol: 80/20, 1.0 mL/min., t_{major} = 5.657 min., t_{minor} = 4.840 min.). $[\alpha]_D^{20}$ = +499 (c 0.1, acetonitrile). ^{1}H NMR (300 MHz, DMSO) δ10.06 (s, 1H), 9.33 (s, 1H), 8.52 (d, J = 1.6 Hz, 1H), 7.97 (d, J = 1.7 Hz, 1H), 7.52 (d, J = 8.7 Hz, 2H), 7.29 (dd, J = 8.1, 1.8 Hz, 1H), 7.00 (d, J = 8.7 Hz, 2H), 6.79 (d, J = 8.8 Hz, 1H), 6.70 (d, J = 8.8 Hz, 1H), 6.61 (d, J = 8.2 Hz, 1H), 4.30 (d, J = 1.6 Hz, 1H), 3.79 (s, 3H), 2.57 (s, 3H), 1.58 (s, 3H). ^{13}C NMR (75 MHz, DMSO) δ158.02, 151.68, 150.56, 147.96, 141.31, 133.93, 133.50, 130.77, 129.89, 127.17, 126.92, 125.27, 125.22, 123.48, 117.12, 115.14, 114.27,

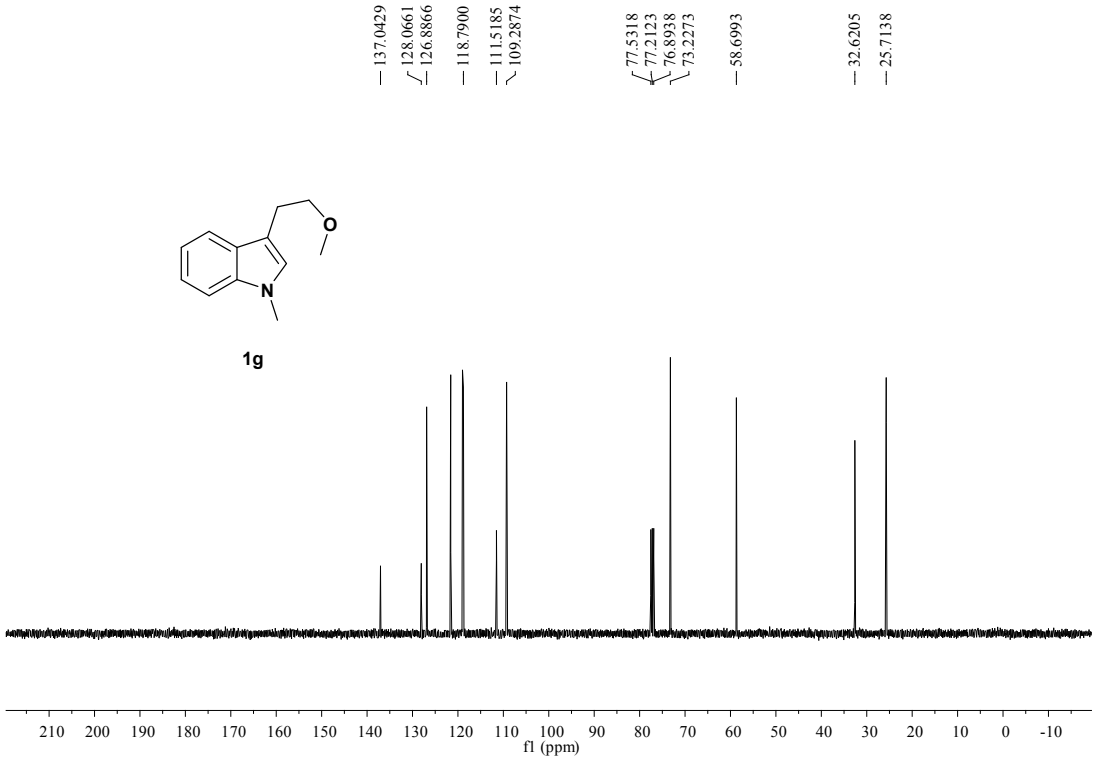
107.71, 70.45, 55.18, 49.56, 34.58, 20.93. HRMS (ESI) Calcd. for $C_{25}H_{22}N_2O_5H^+$ $[M+H]^+$ 431.1607; Found: 431.1596.

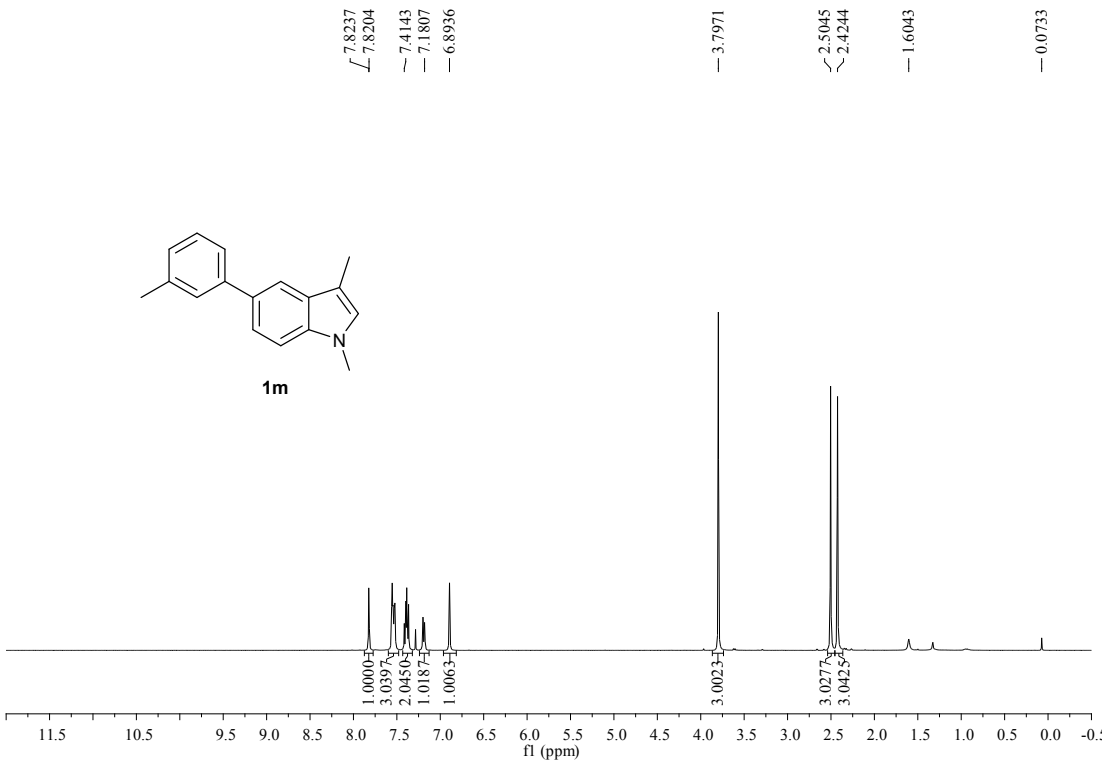
References:

1. W. E. Noland and B. L. Kedrowski, *J. Org. Chem.* **1999**, *64*, 596-603.

3. ^{1}H-NMR spectra and ^{13}C-NMR spectra:



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7.1807
6.8936
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2.5045
2.4244
1.6043
0.0733
1m
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2.0450
1.0187
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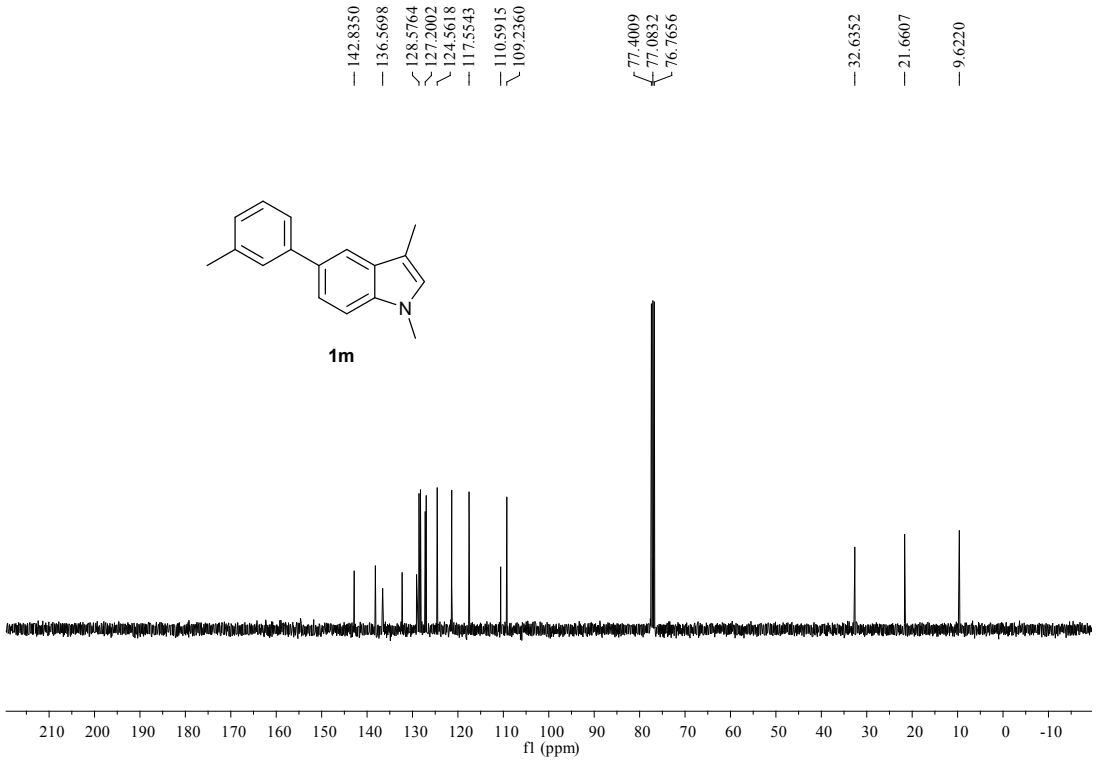
3.0023
3.0277
3.0425
fl (ppm)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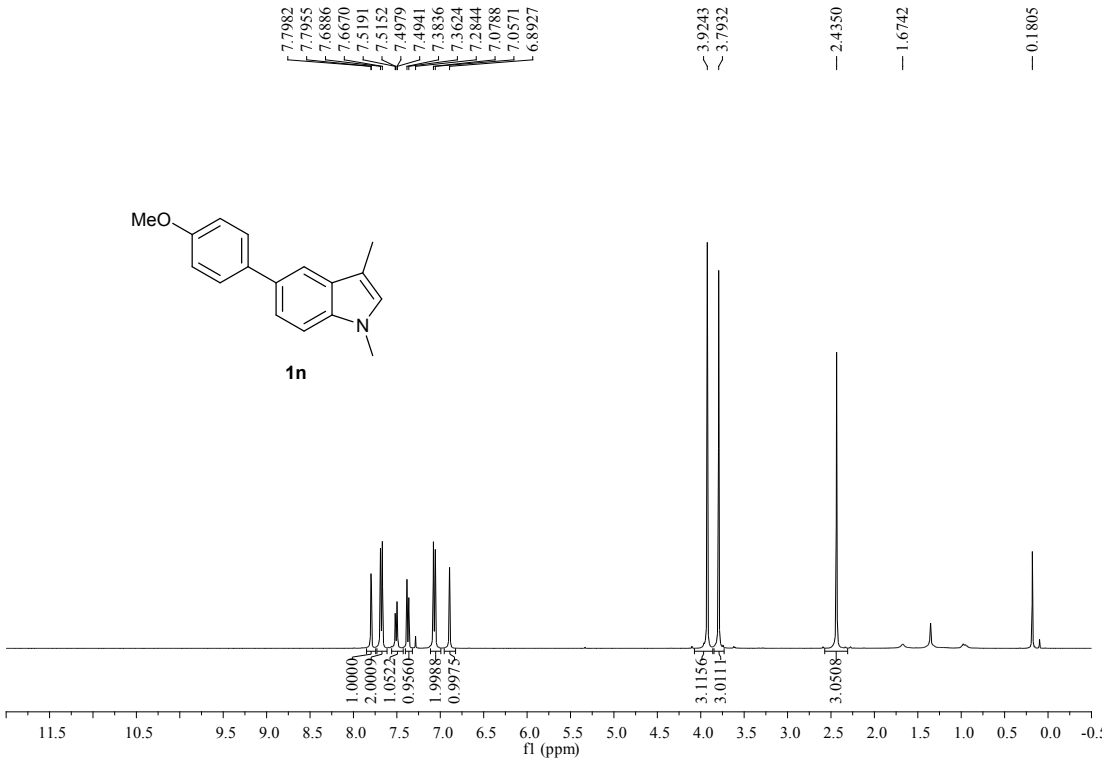
fl (ppm)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2.0009
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3.0114
3.0508
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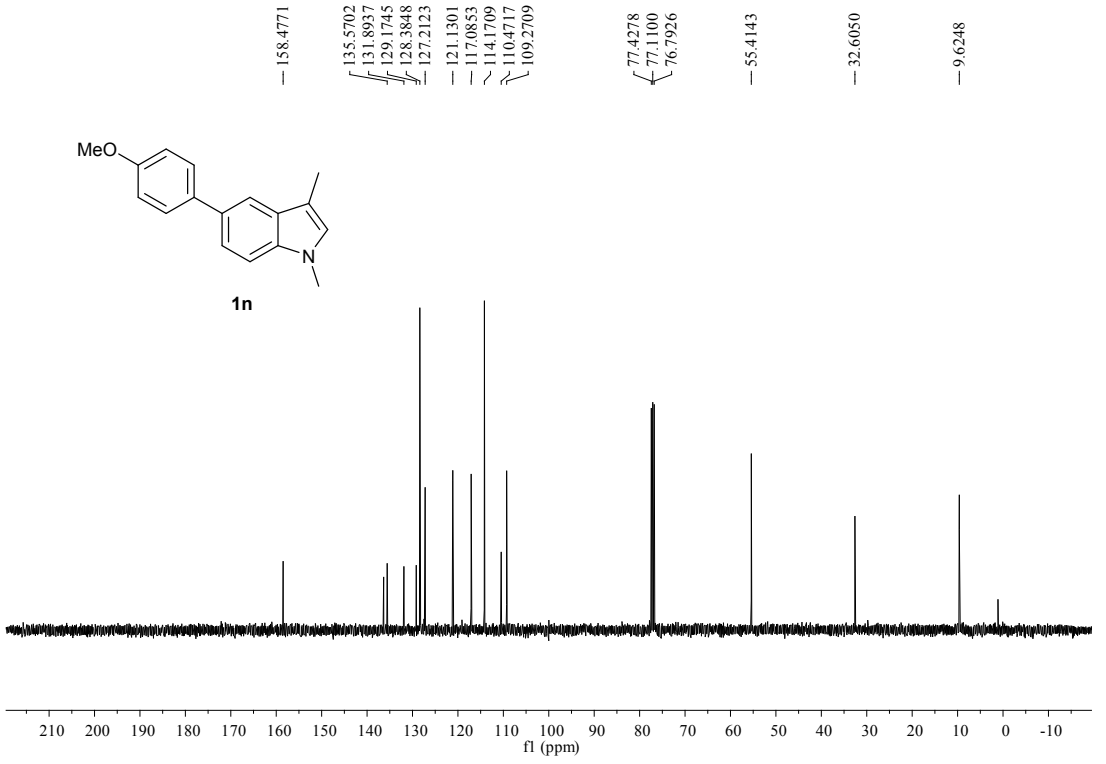
f1 (ppm)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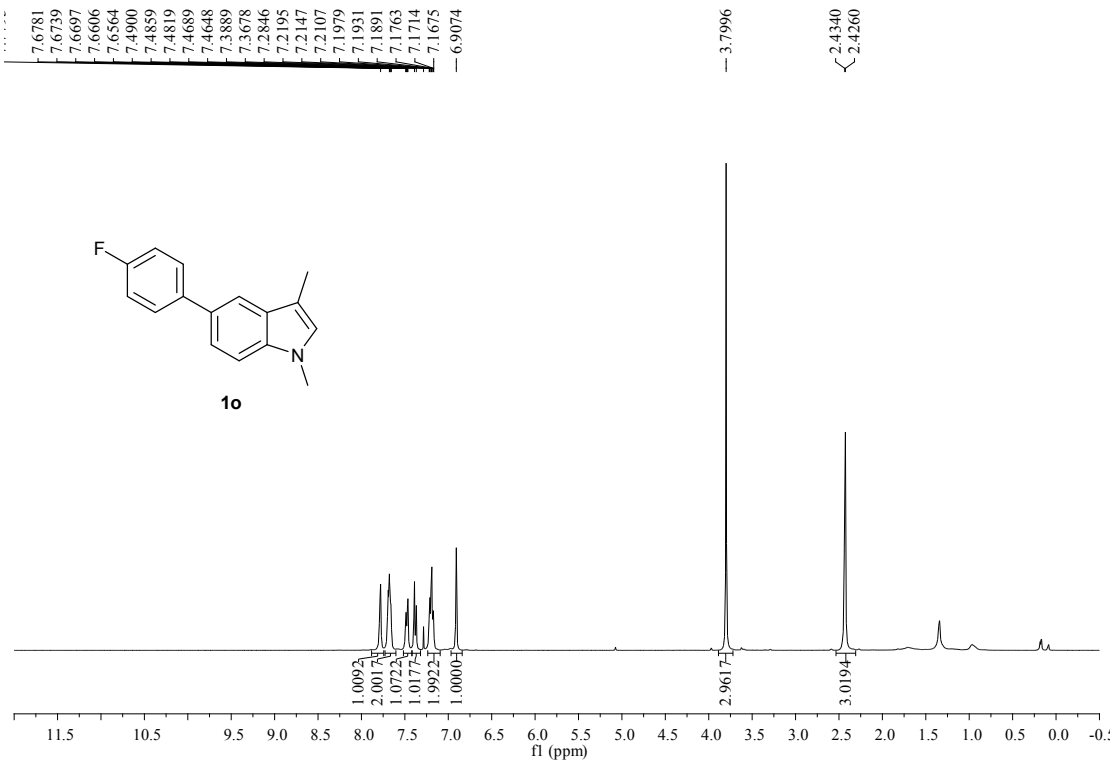
f1 (ppm)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7.2107
7.1979
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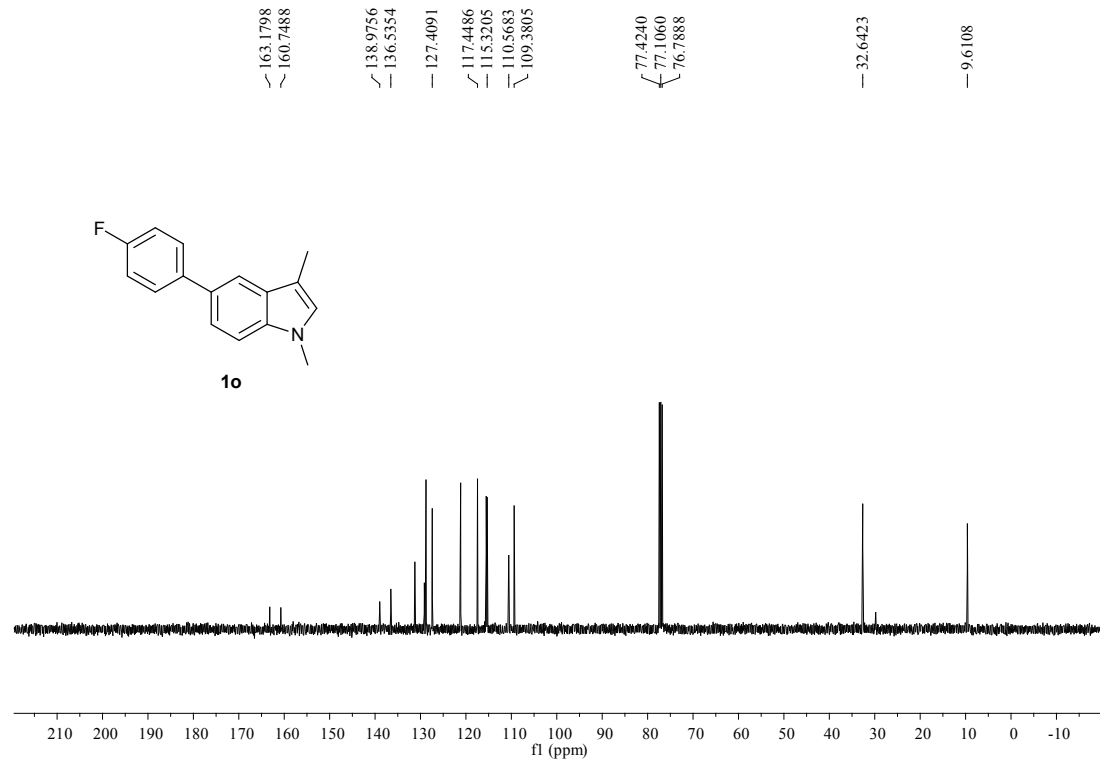
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77.1060
76.7888
32.6423
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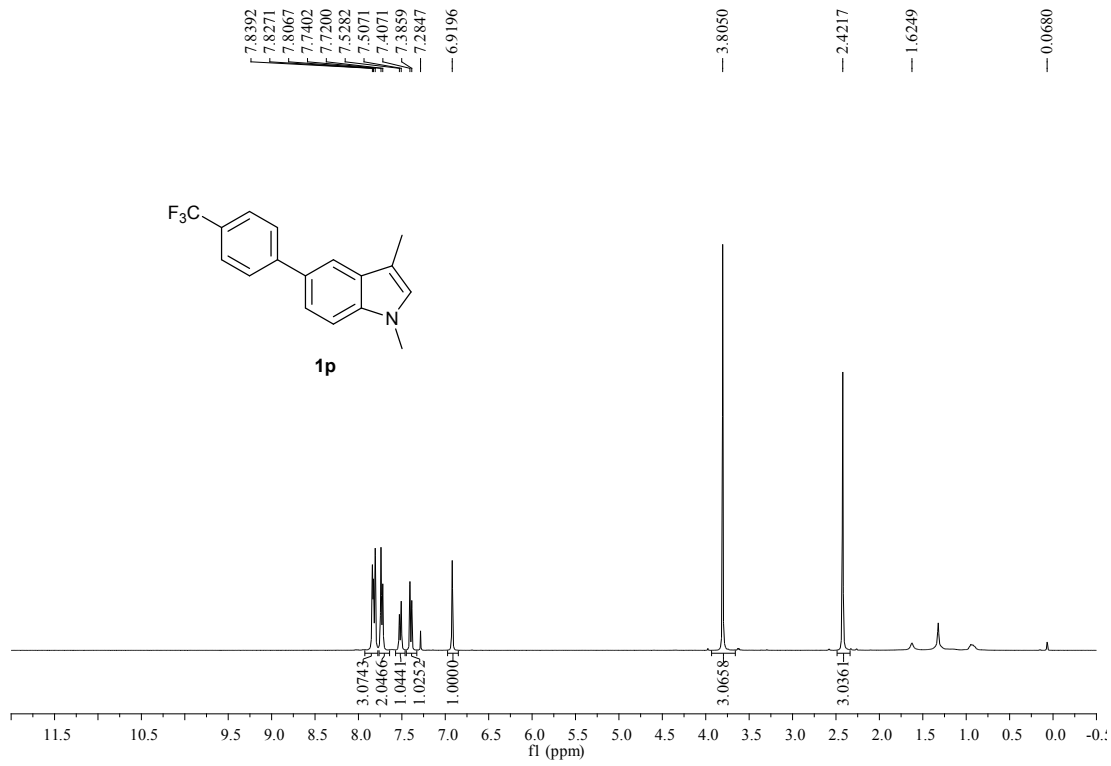
f1 (ppm)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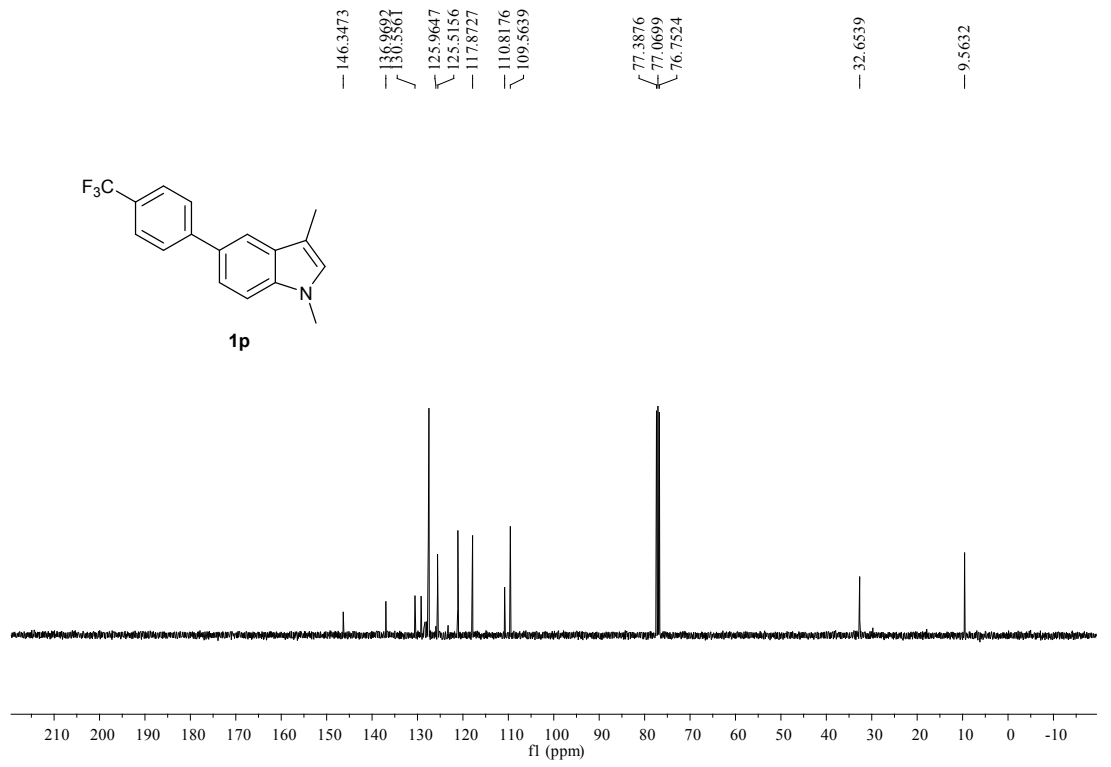
fl (ppm)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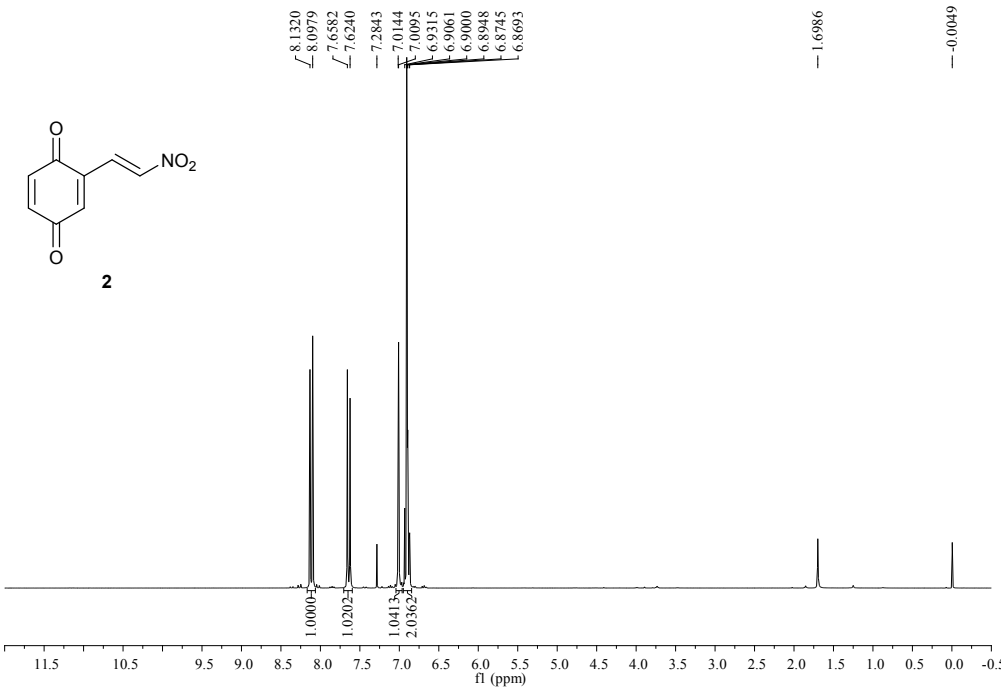
fl (ppm)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6.8693
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1.0413
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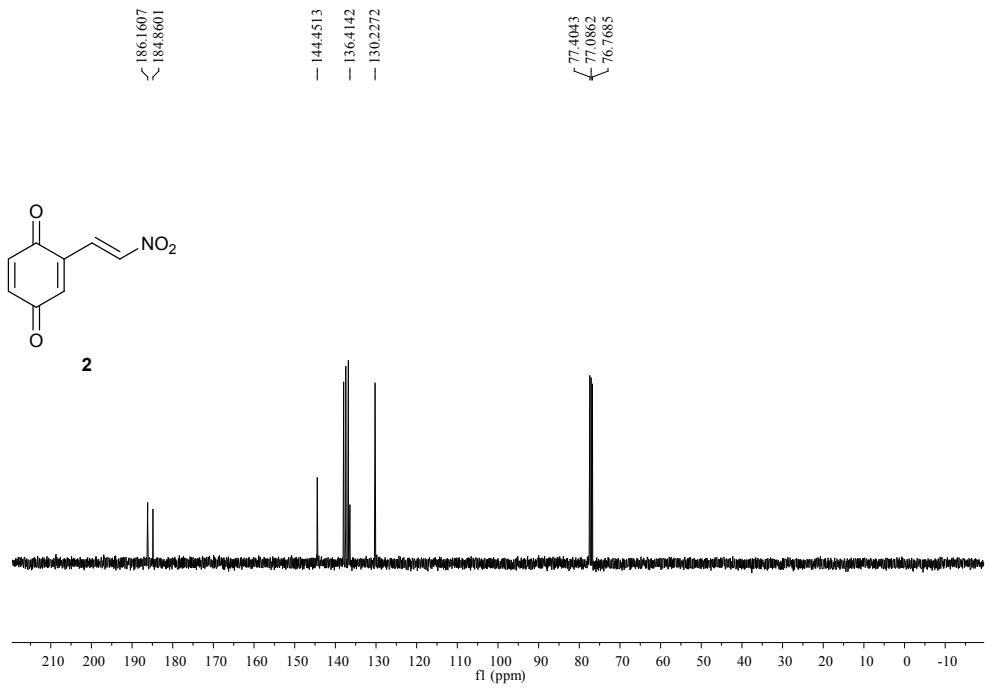
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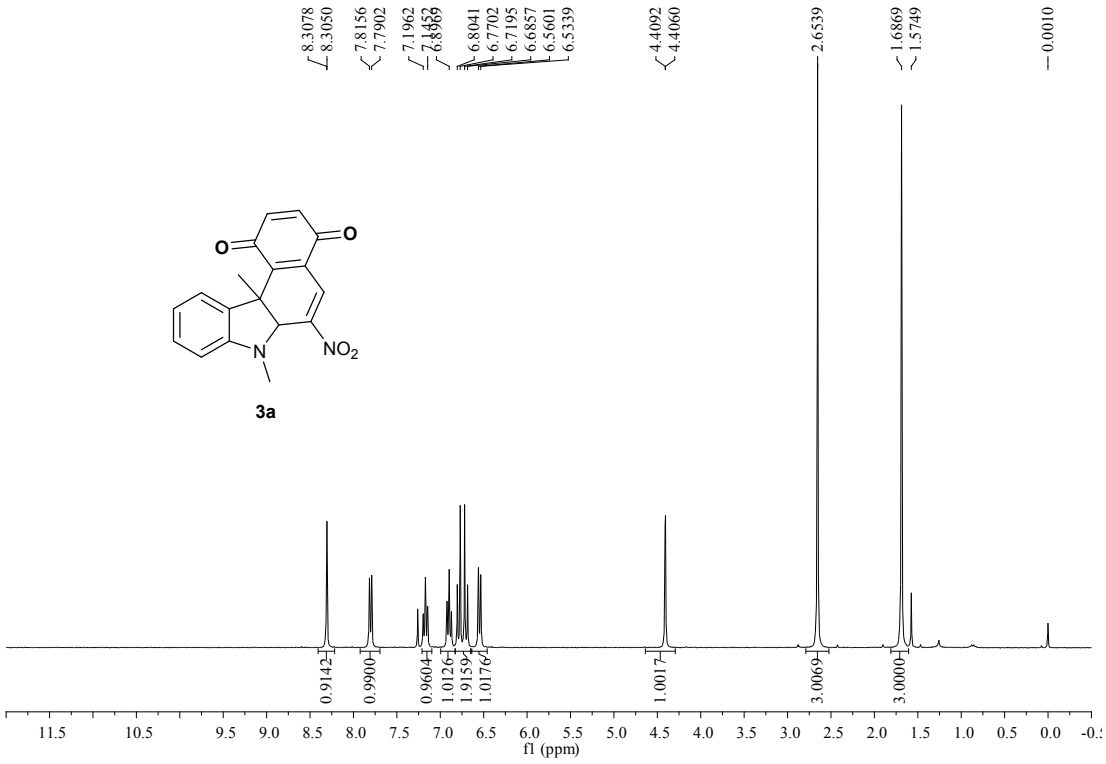
f1 (ppm)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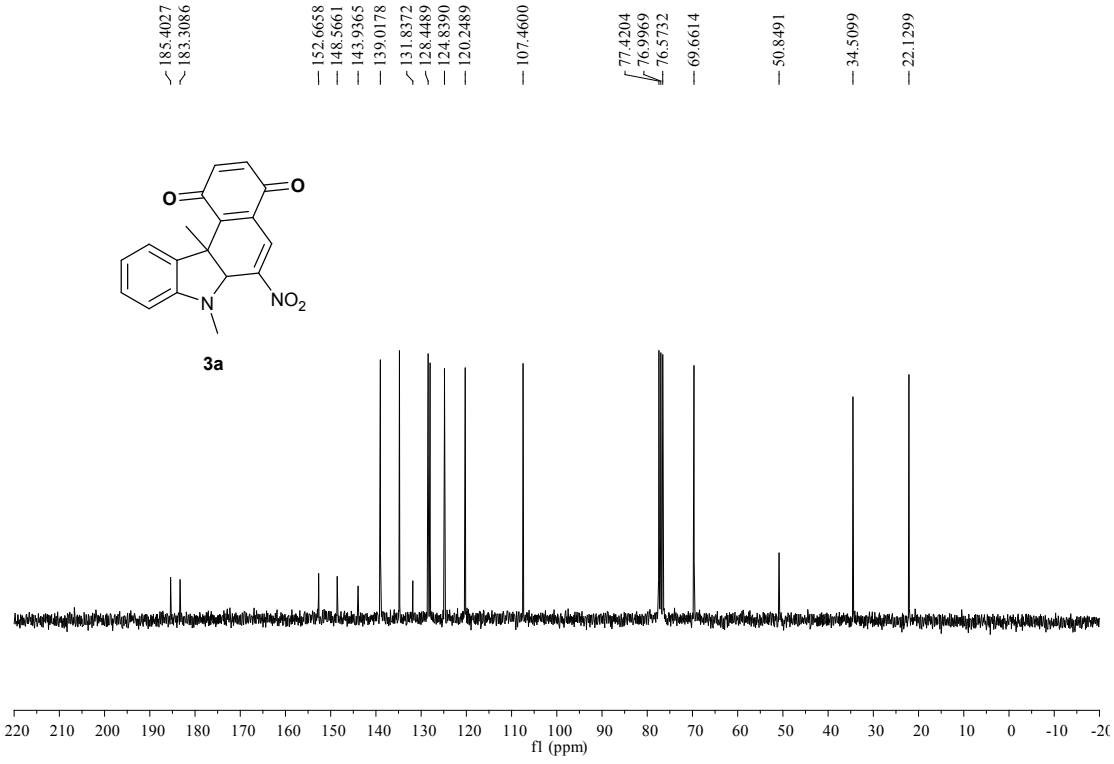
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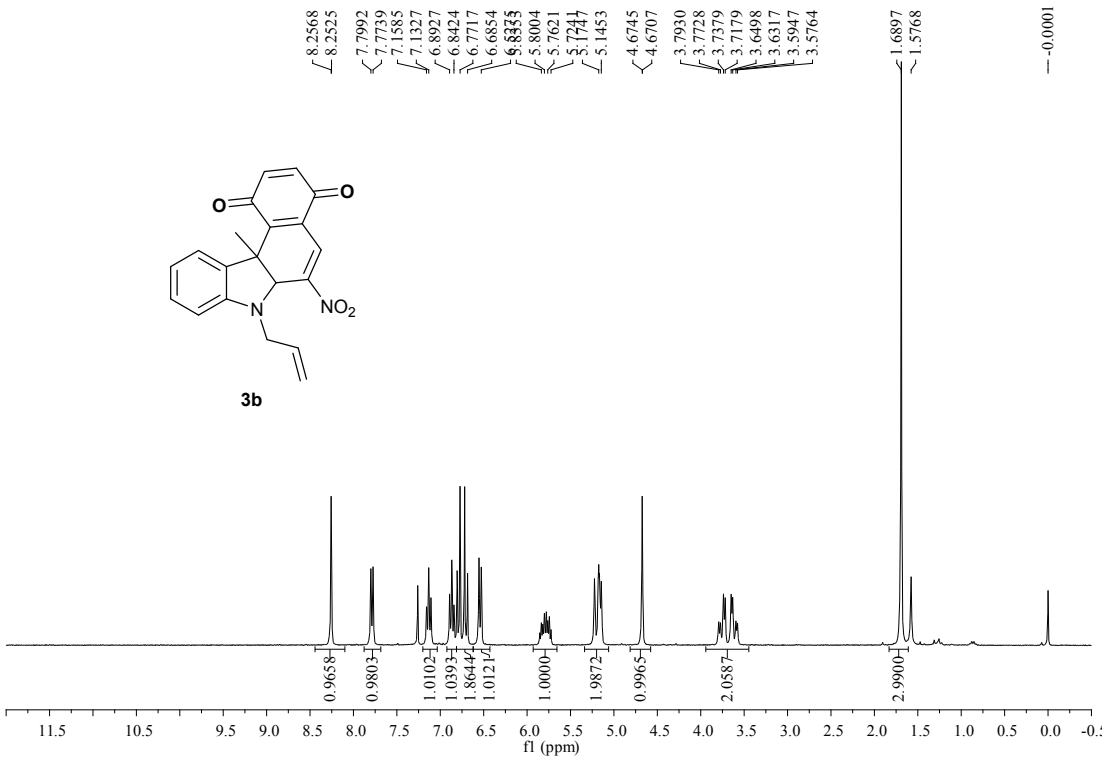
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5.1453
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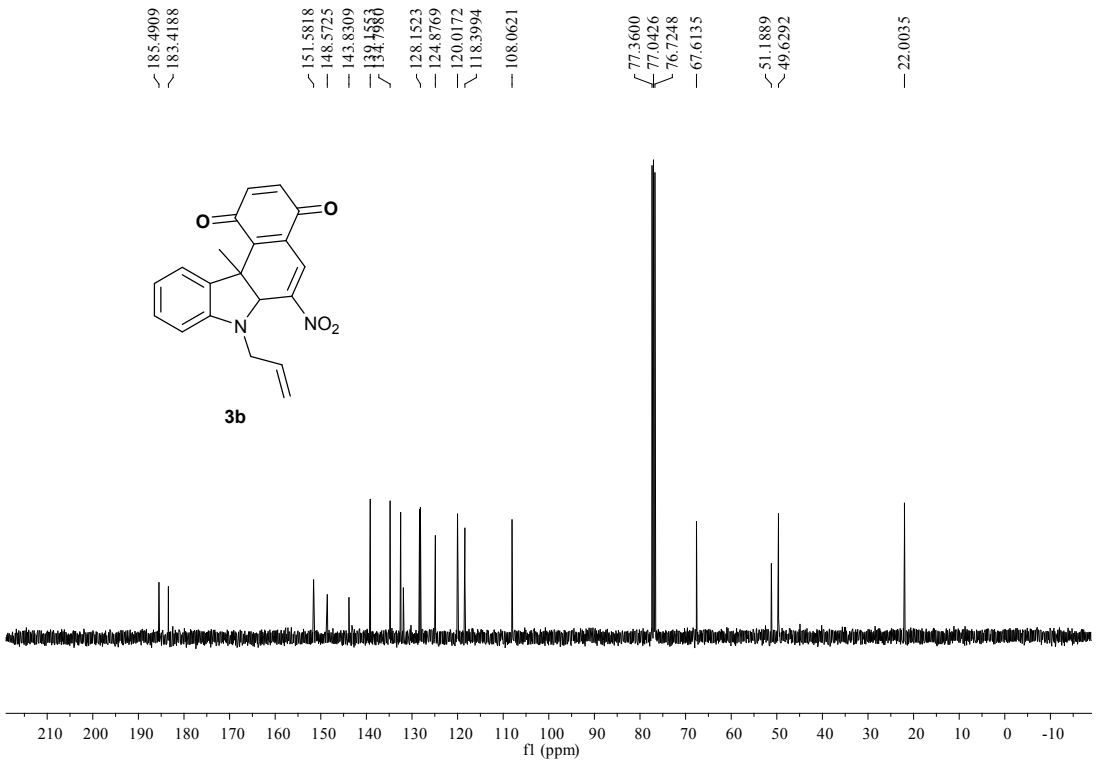
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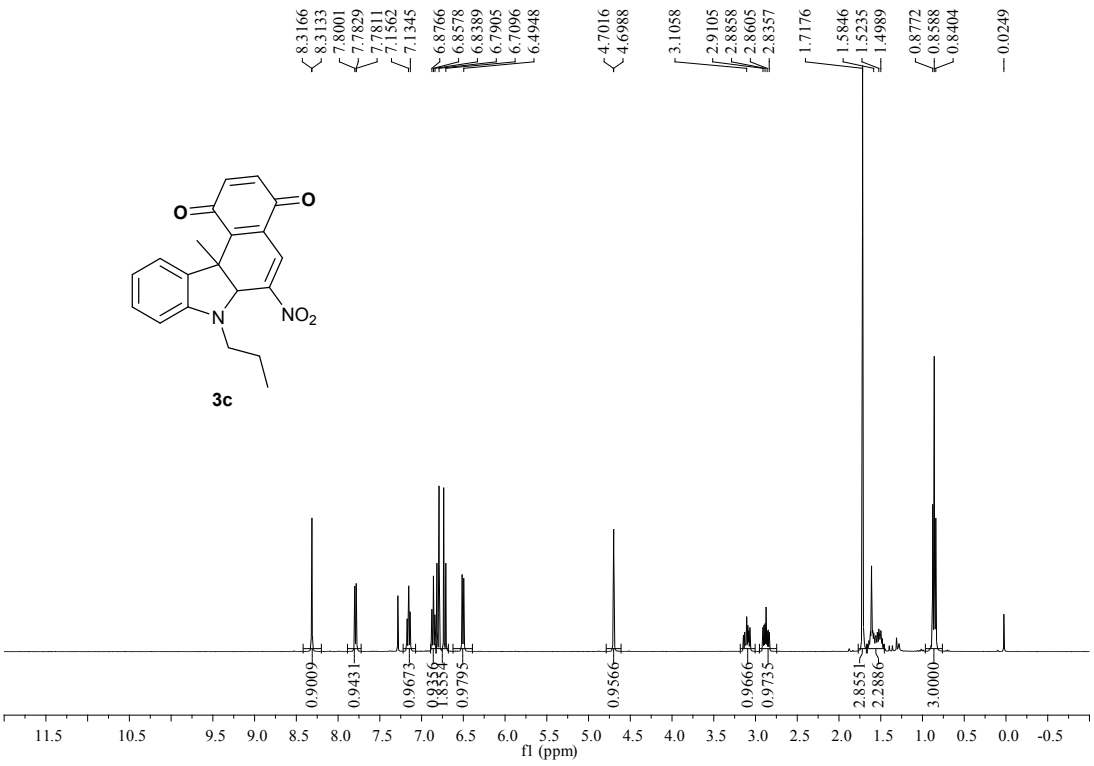
f1 (ppm)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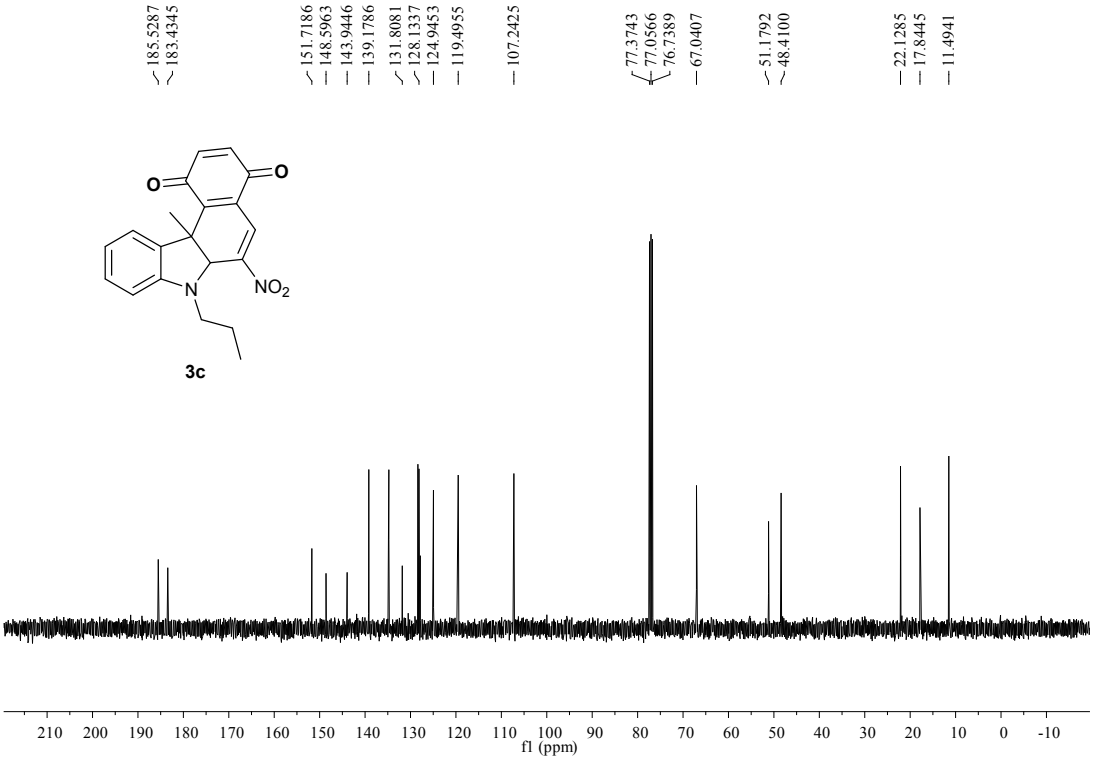
3.0000
f1 (ppm)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143.9446
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131.8081
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124.9453
119.4955
107.2425
77.3743
77.0566
76.7389
67.0407
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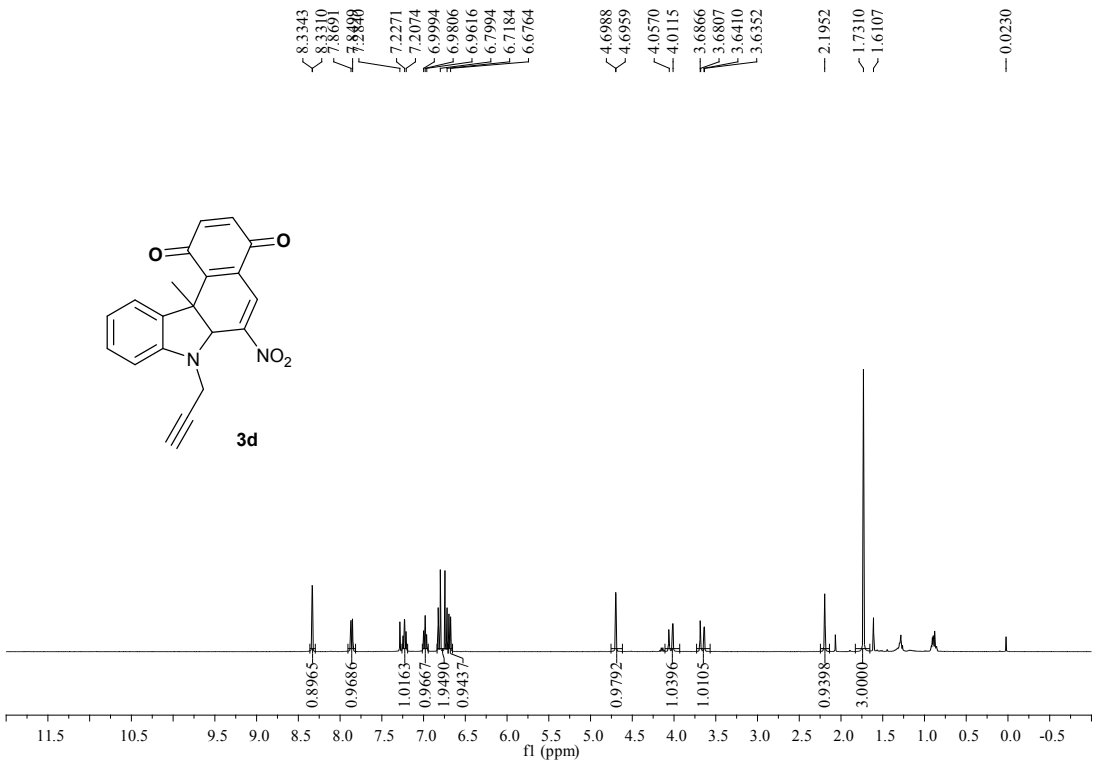
48.4100
22.1285
17.8445
11.4941
O
O
NO2
N
3c
f1 (ppm)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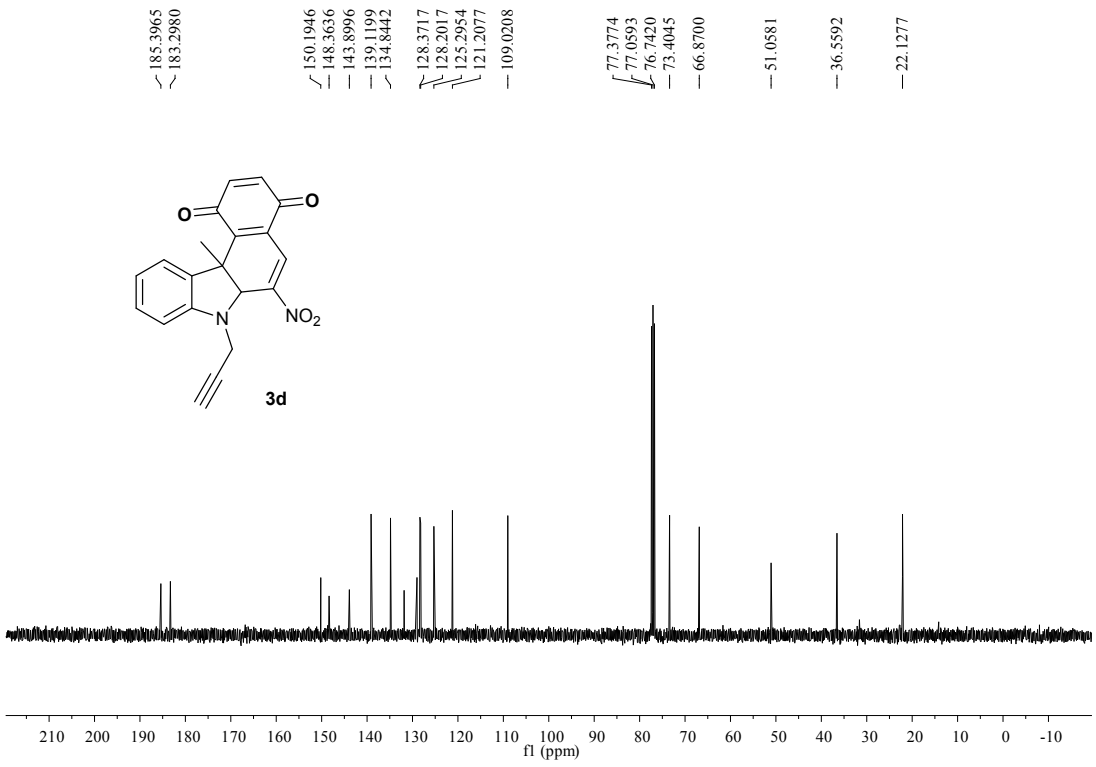
7.8440
7.2271
7.2074
6.9994
6.9806
6.9616
6.7994
6.7184
6.6764
4.6988
4.6959
4.0570
4.0115
3.6866
3.6807
3.6410
3.6352
2.1952
1.7310
1.6107
0.0230
O
O
N
NO2
3d
0.8965
0.9686
1.0163
0.9667
1.9490
0.9437
0.9792
1.0396
1.0105
0.9398
3.0000
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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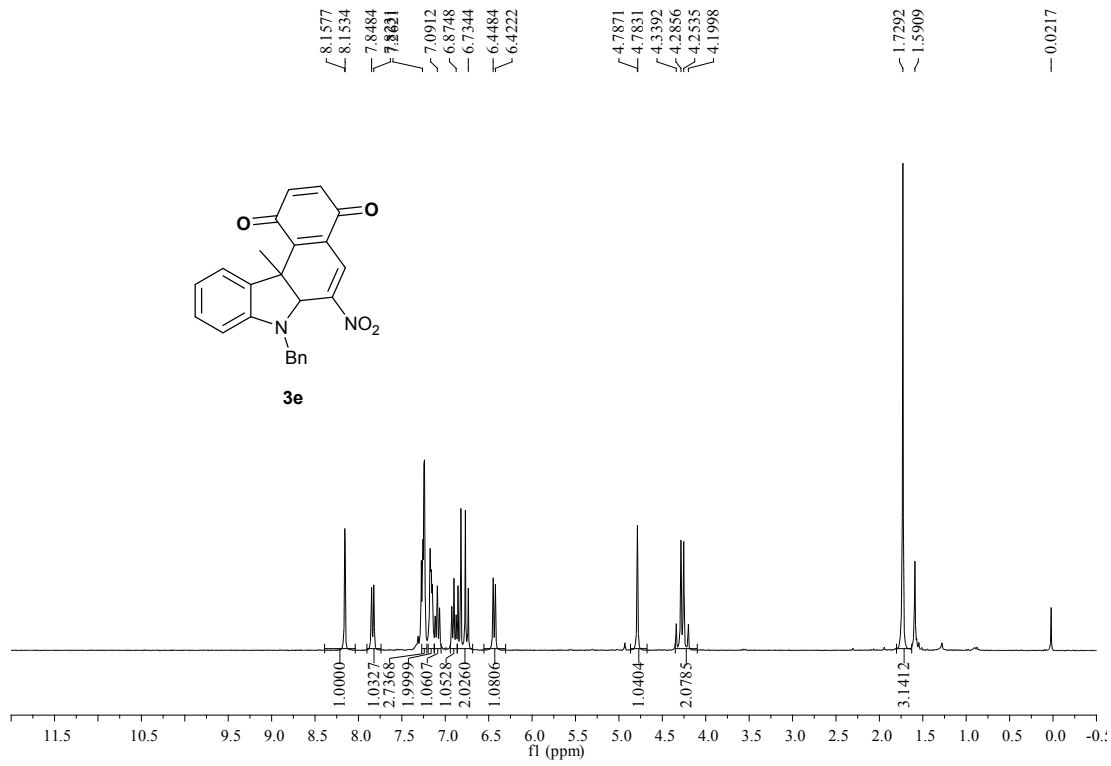
77.3774
77.0593
76.7420
73.4045
66.8700
51.0581
36.5592
22.1277
O
O
N
NO2
3d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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6.4484
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4.7871
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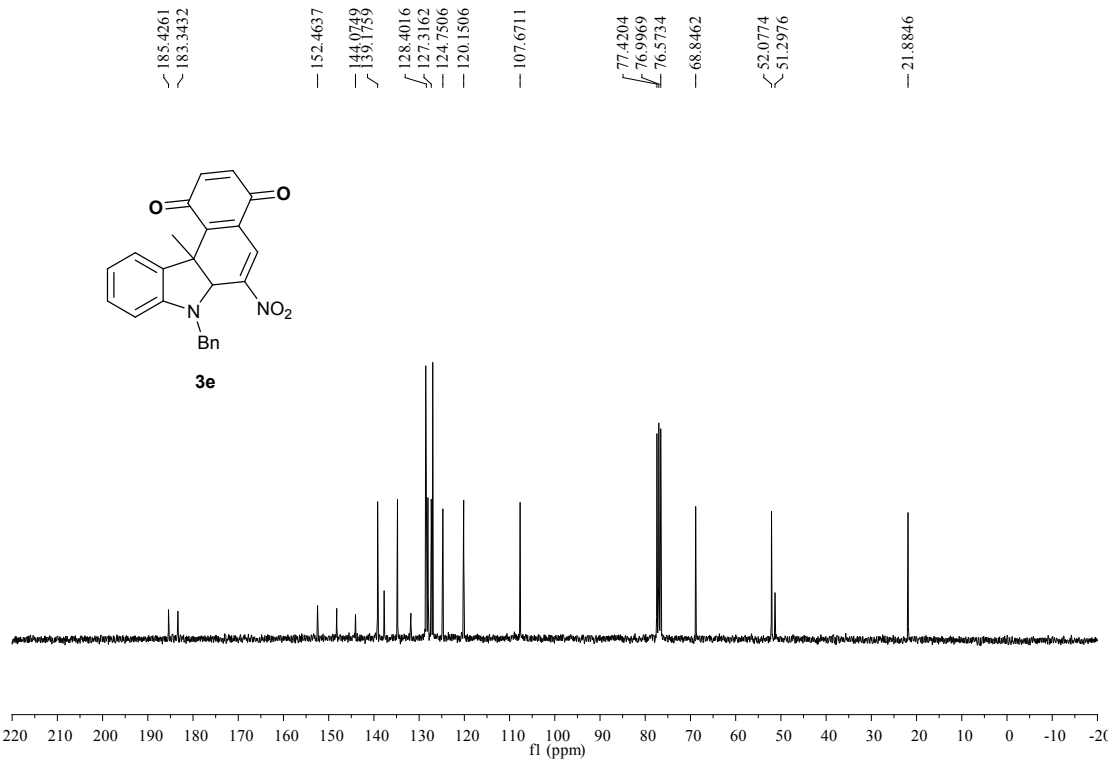
4.3392
4.2856
4.2535
4.1998
1.7292
1.5909
0.0217
O
O
N
Bn
NO2
3e
1.0000
1.0327
2.7368
1.9999
1.0607
1.0528
2.0260
1.0806
1.0404
2.0785
3.1412
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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127.3162
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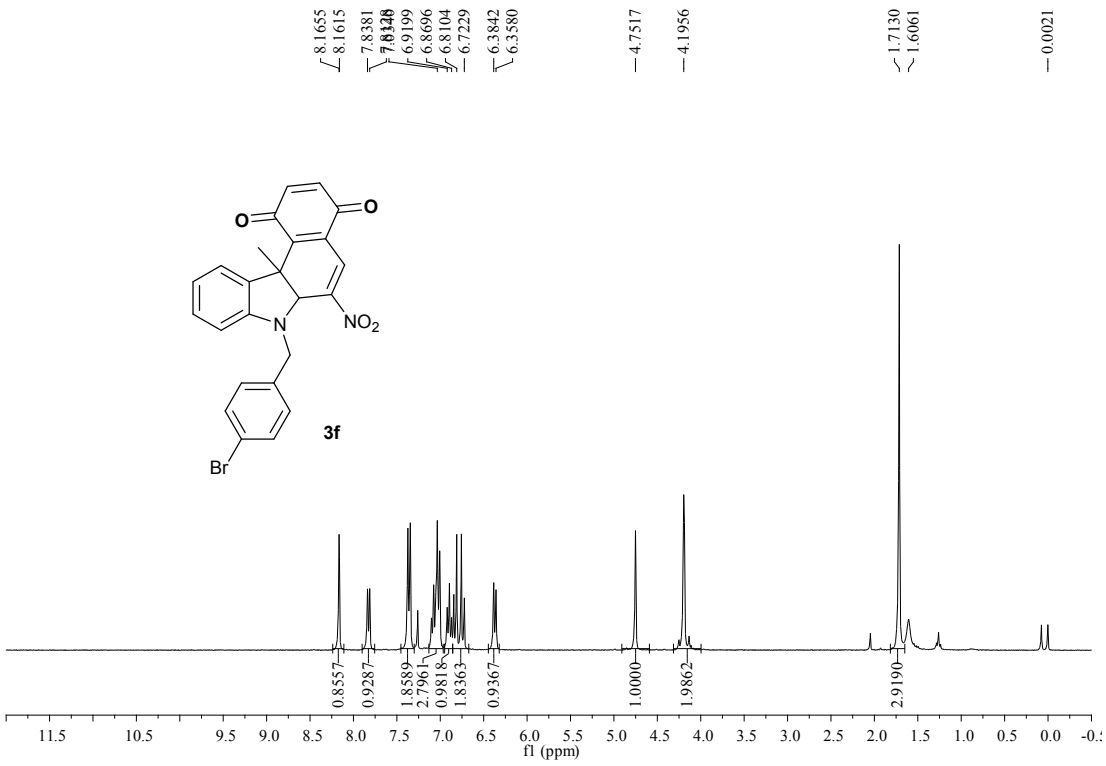
77.4204
76.9969
76.5734
68.8462
52.0774
51.2976
21.8846
O
O
N
Bn
NO2
3e
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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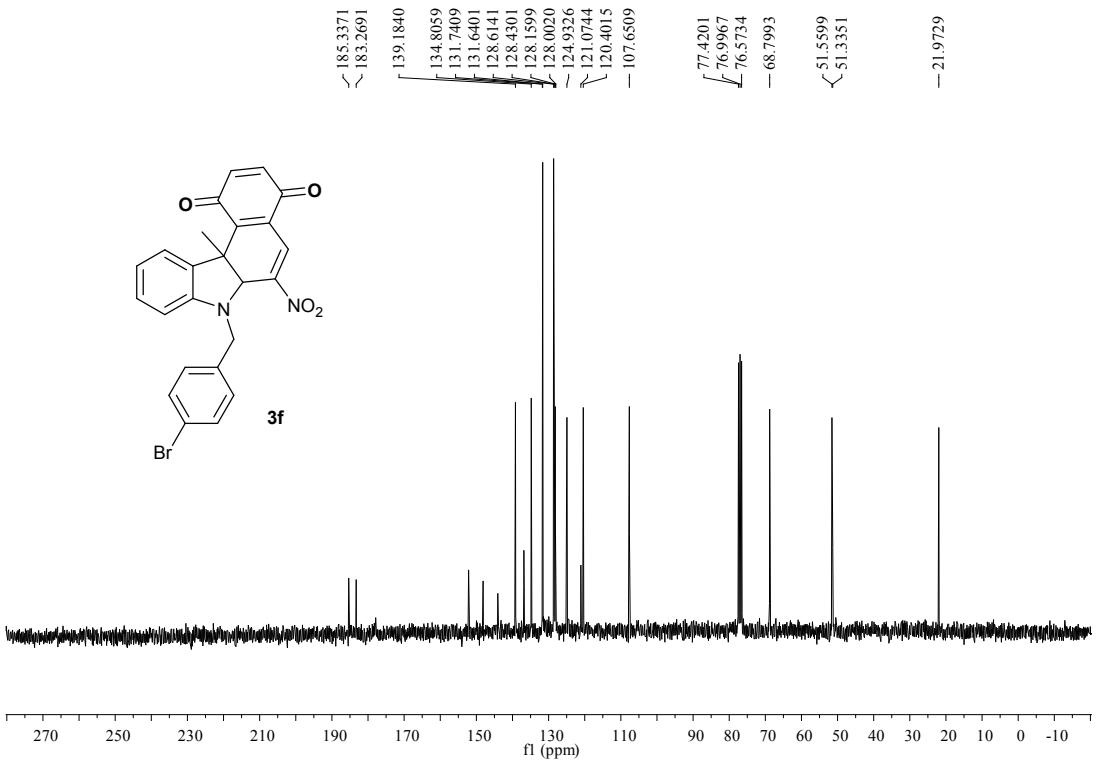
7.8381
6.9199
6.8696
6.8104
6.7229
6.3842
6.3580
4.7517
4.1956
1.7130
1.6061
0.0021
O
O
N
NO2
Br
3f
0.8557
0.9287
1.8589
2.7961
0.9818
1.8363
0.9367
1.0000
1.9862
2.9190
fl (ppm)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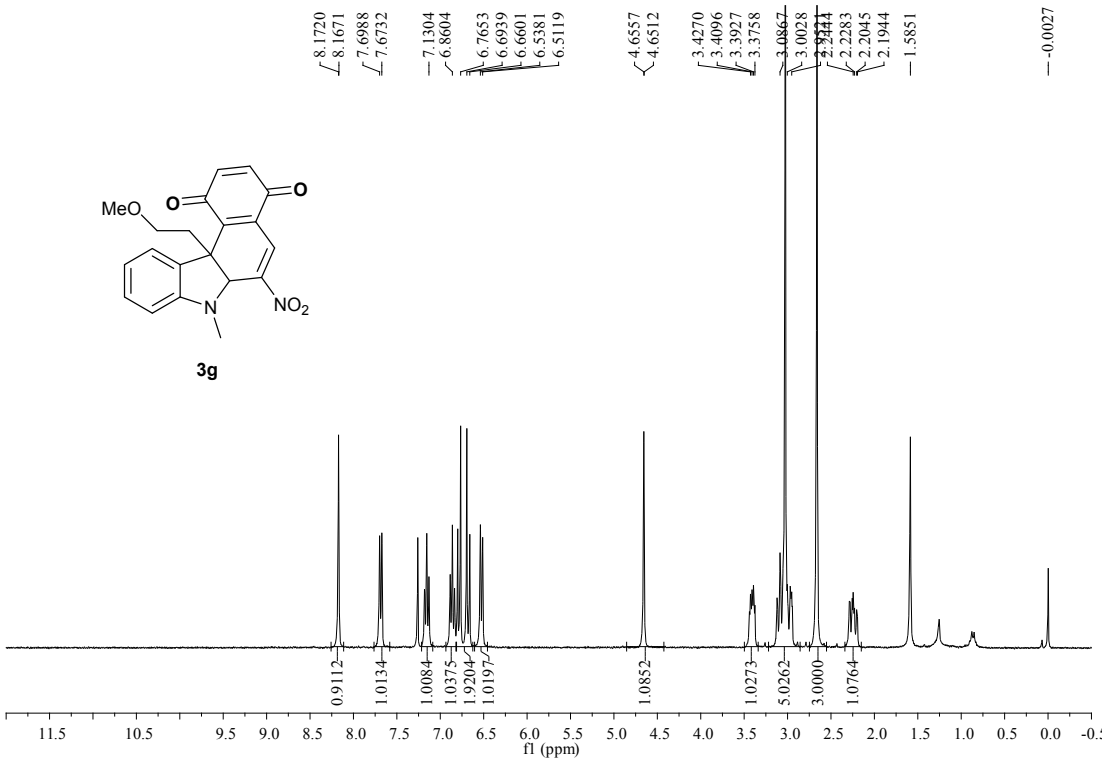
139.1840
134.8059
131.7409
131.6401
128.6141
128.4301
128.1599
128.0020
124.9326
121.0744
120.4015
107.6509
77.4201
76.9967
76.5734
68.7993
51.5599
51.3351
21.9729
O
O
N
NO2
Br
3f
fl (ppm)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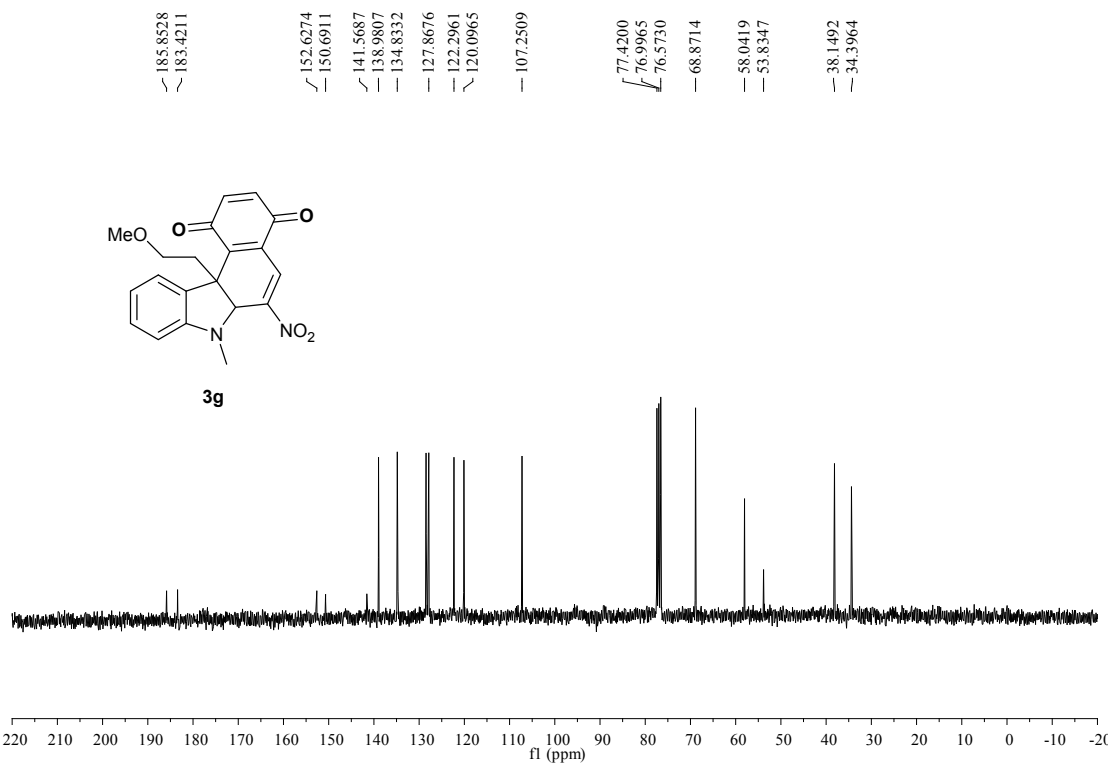
7.6988
7.6732
7.1304
6.8604
6.7653
6.6939
6.6601
6.5381
6.5119
4.6557
4.6512
3.4270
3.4096
3.3927
3.3758
3.0867
3.0028
2.2283
2.2045
2.1944
1.5851
-0.0027
MeO
O
O
N
NO2
3g
0.9112
1.0134
1.0084
1.0375
1.9204
1.0197
1.0852
1.0273
5.0262
3.0000
1.0764
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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141.5687
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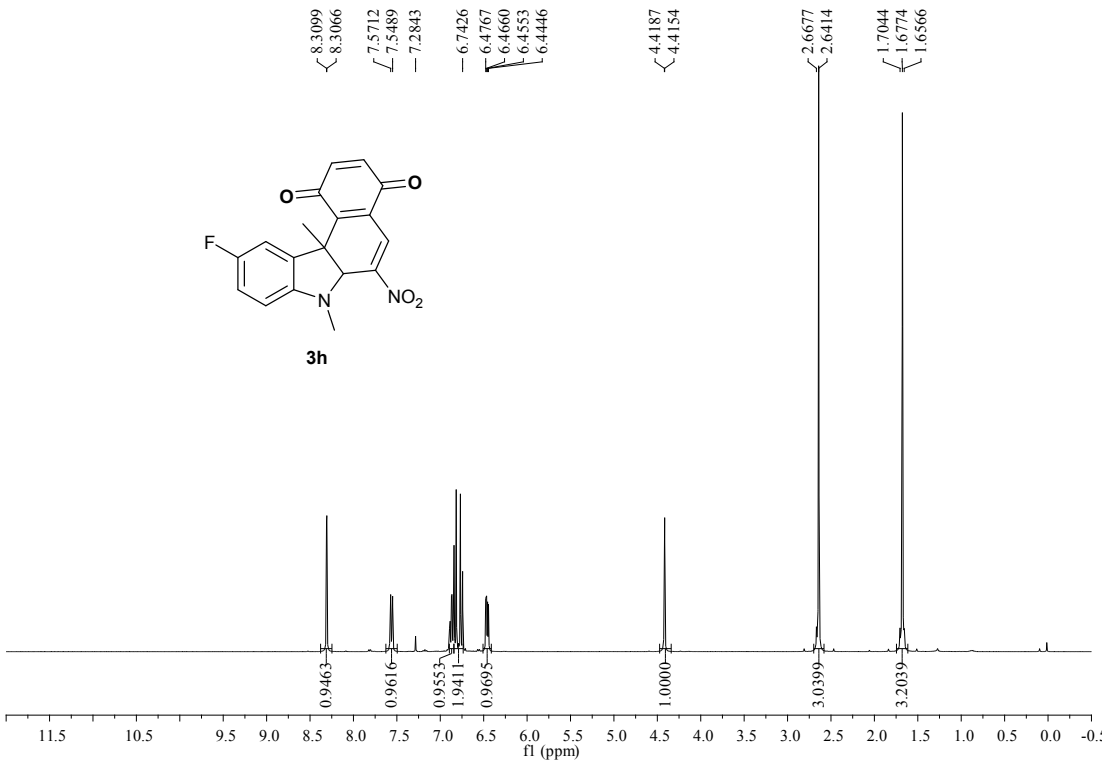
134.8332
127.8676
122.2961
120.0965
107.2509
77.4200
76.9965
76.5730
68.8714
58.0419
53.8347
38.1492
34.3964
MeO
O
O
N
NO2
3g
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.5489
7.2843
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6.4767
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6.4553
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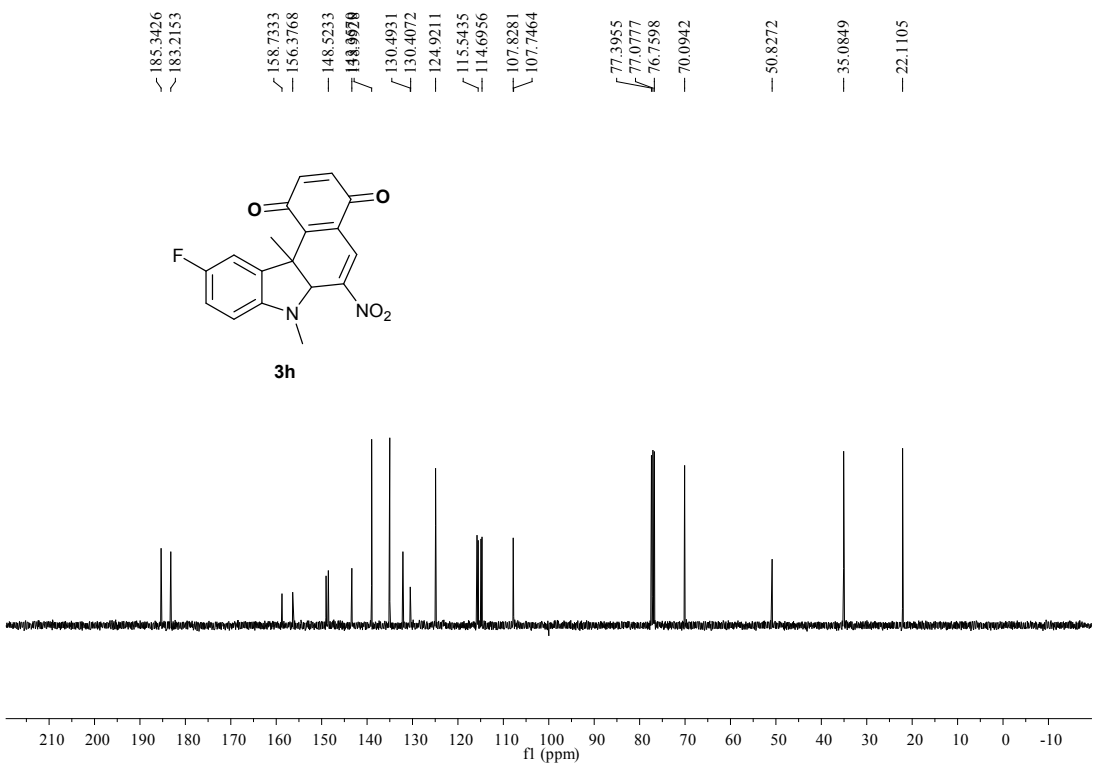
4.4187
4.4154
2.6677
2.6414
1.7044
1.6774
1.6566
O
O
F
N
NO2
0.9463
0.9616
0.9553
1.9411
0.9695
1.0000
3.0399
3.2039
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3h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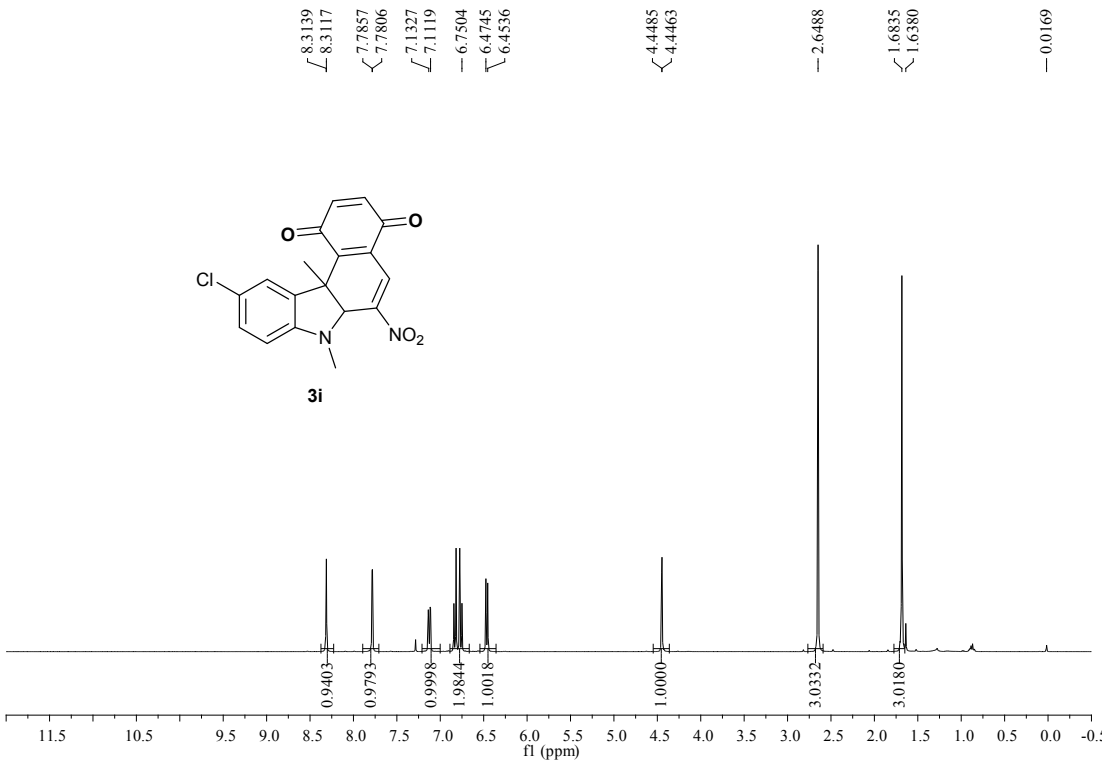
156.3768
148.5233
130.4931
130.4072
124.9211
115.5435
114.6956
107.8281
107.7464
77.3955
77.0777
76.7598
70.0942
50.8272
35.0849
22.1105
O
O
F
N
NO2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

3h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7.1327
7.1119
6.7504
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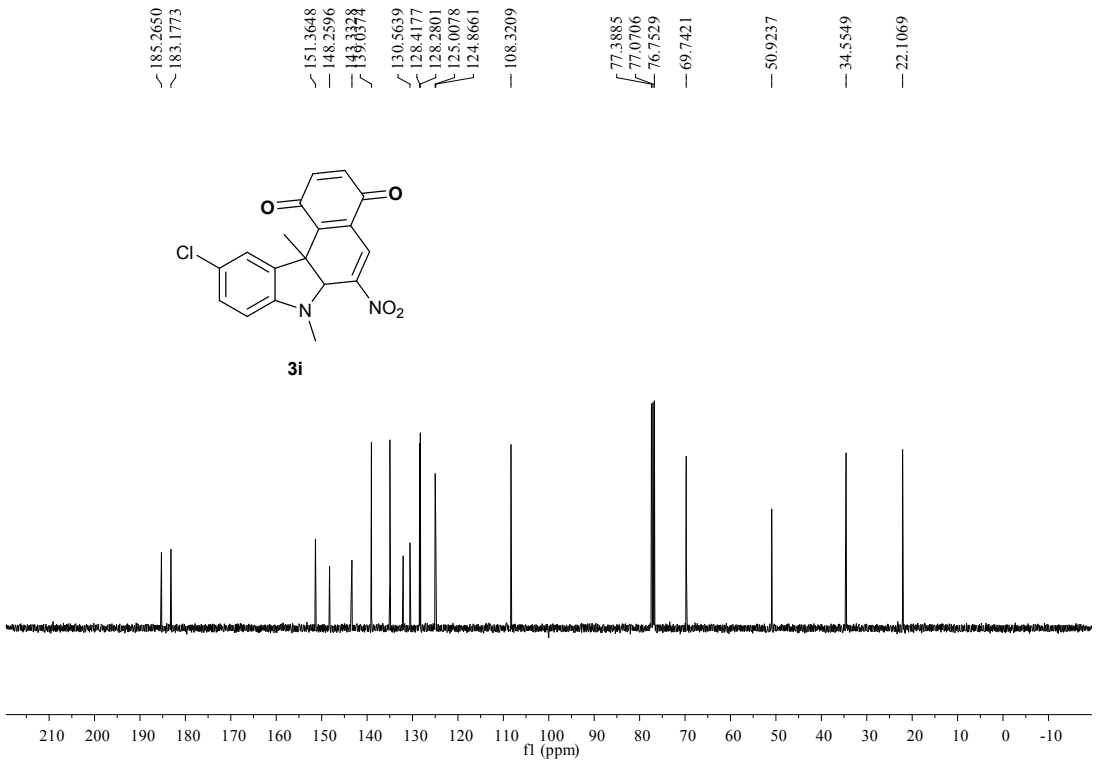
6.4536
4.4485
4.4463
2.6488
1.6835
1.6380
0.0169
O
O
Cl
N
NO2
0.9403
0.9793
0.9998
1.9844
1.0018
1.0000
3.0332
3.0180
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3i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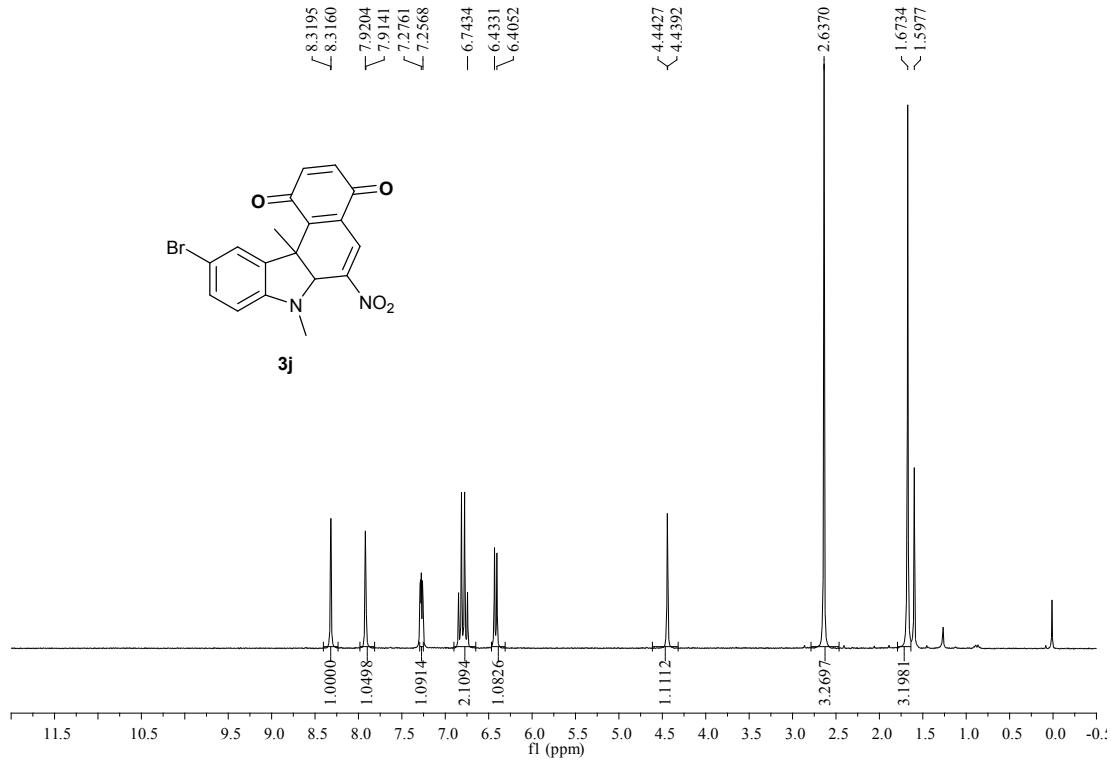
124.8661
108.3209
77.3885
77.0706
76.7529
69.7421
50.9237
34.5549
22.1069
O
O
Cl
N
NO2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

3i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6.7434
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6.4052
4.4427
4.4392
2.6370
1.6734
1.5977
O
O
Br
N
NO2
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1.0914
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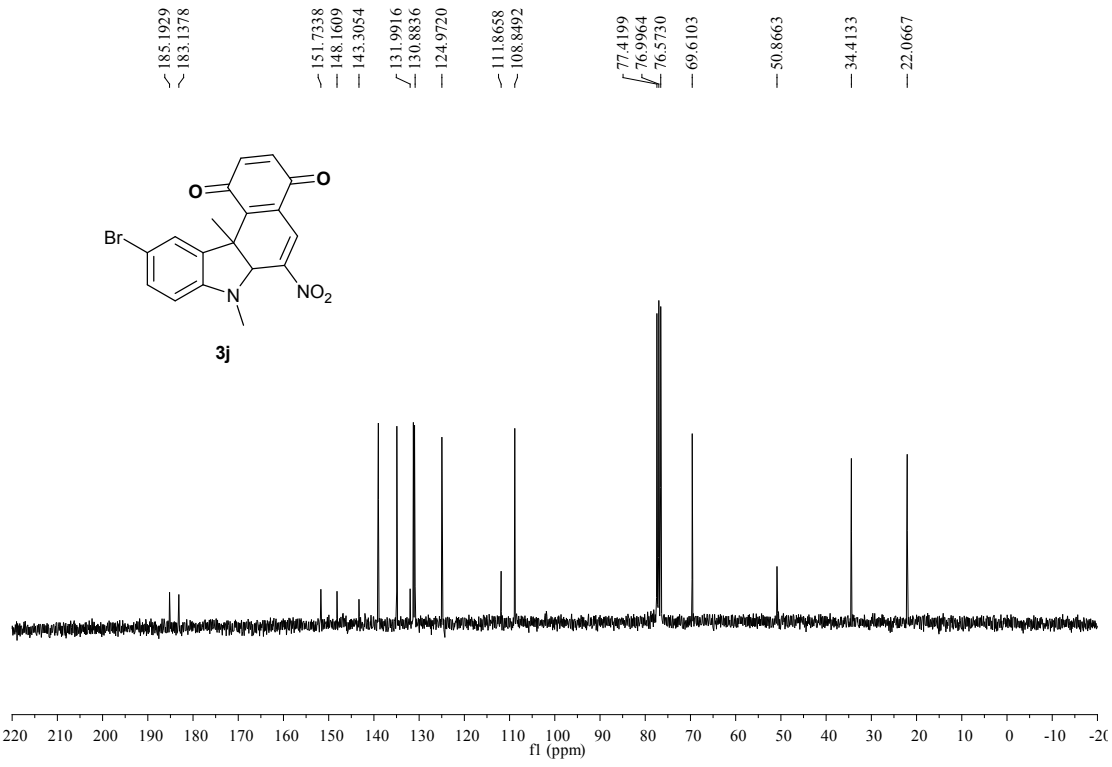
1.0826
1.1112
3.2697
3.1981
f1 (ppm)

3j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130.8836
124.9720
111.8658
108.8492
77.4199
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50.8663
34.4133
22.0667
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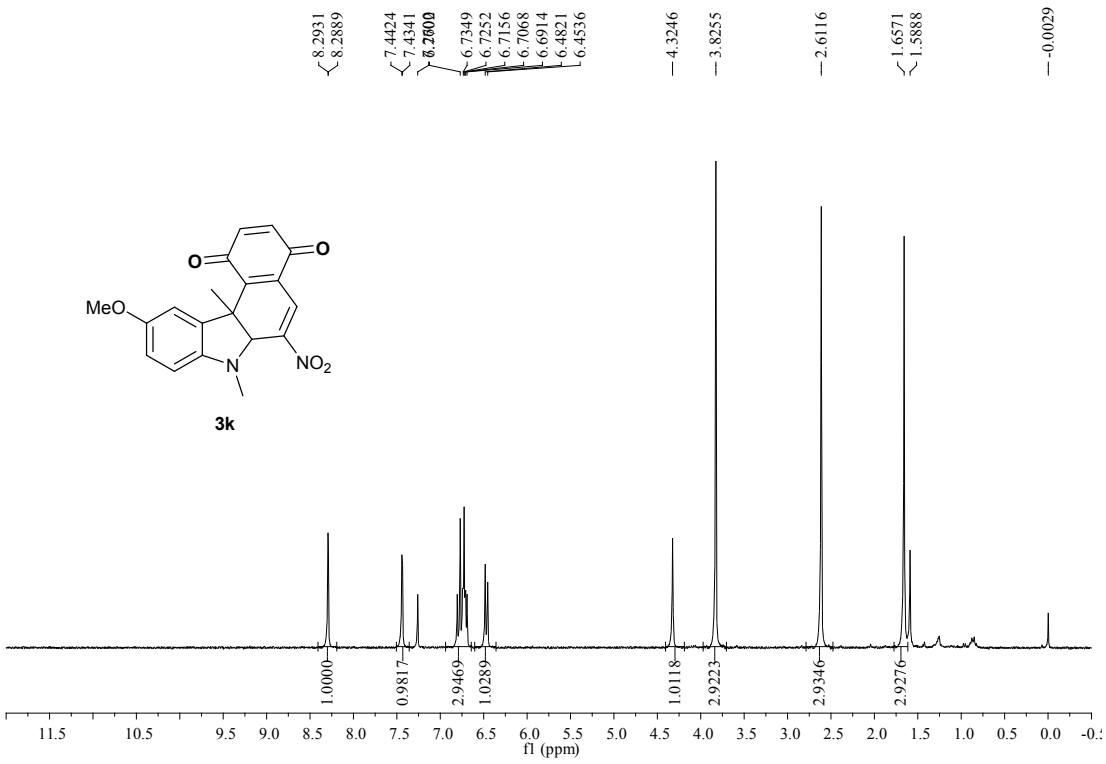
O
Br
N
NO2
f1 (ppm)

3j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7.4424
7.4341
6.7349
6.7252
6.7156
6.7068
6.6914
6.4821
6.4536
4.3246
3.8255
2.6116
1.6571
1.5888
-0.0029
O
O
MeO
N
NO2
3k
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2.9469
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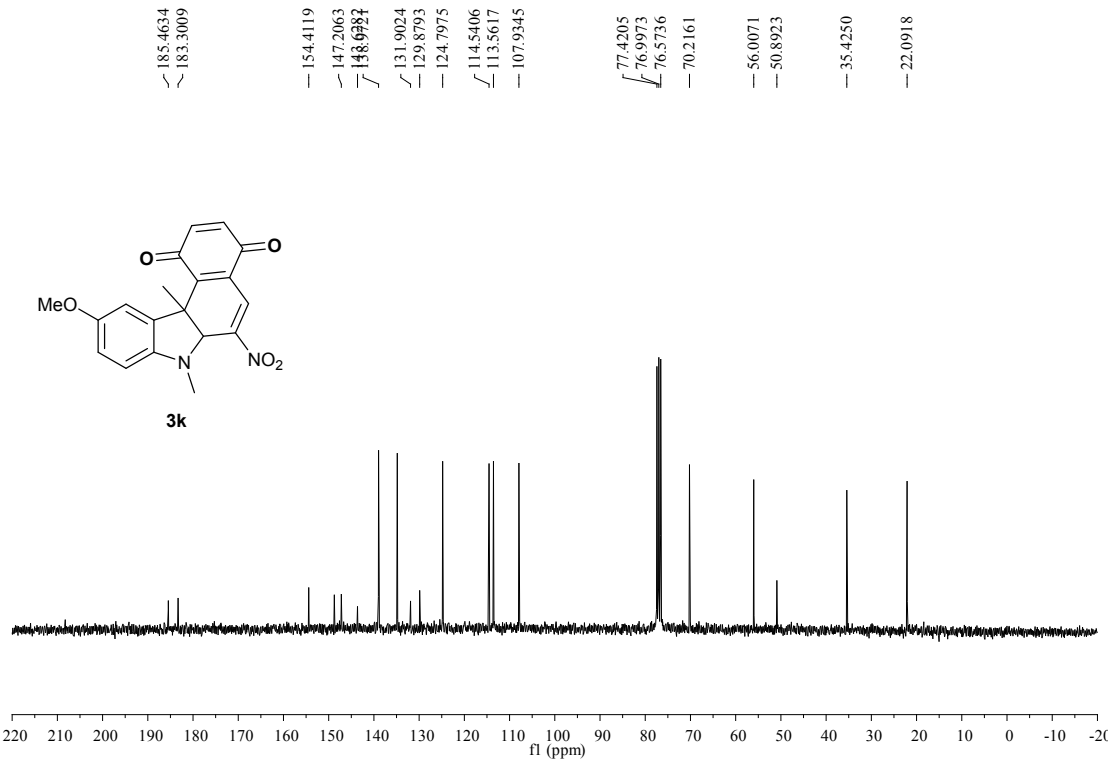
1.0118
2.9223
2.9346
2.9276
f1 (ppm)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76.5736
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50.8923
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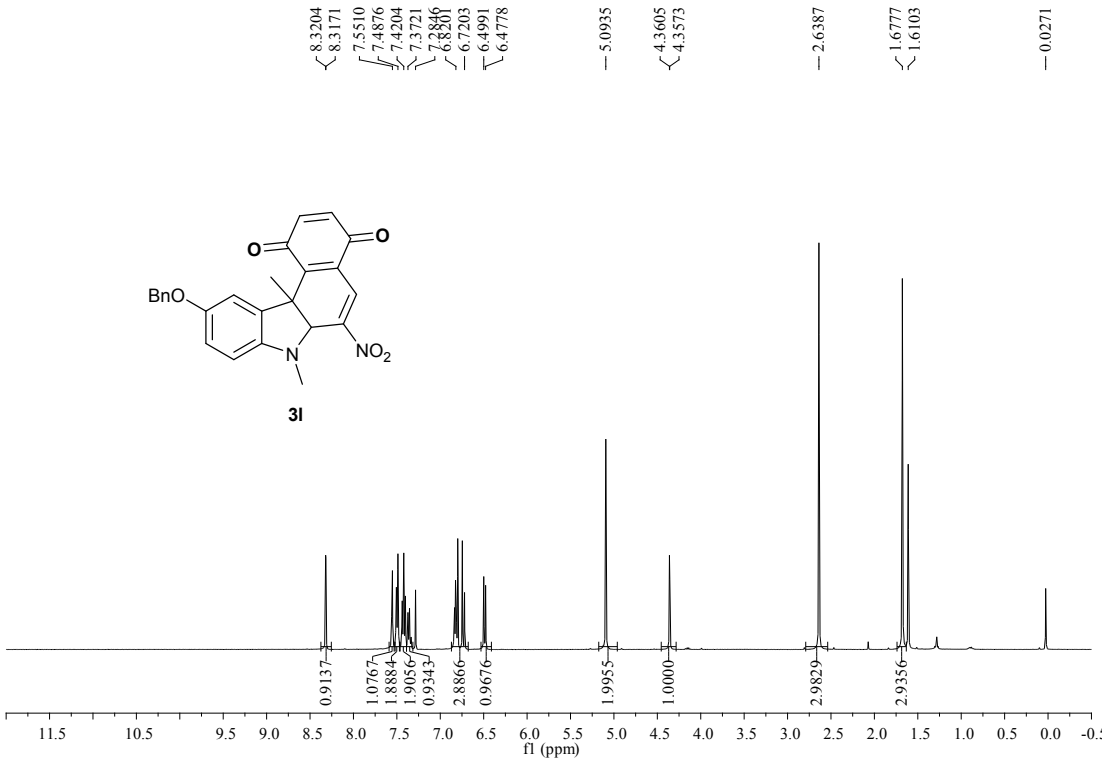
22.0918
O
O
MeO
N
NO2
3k
f1 (ppm)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7.2846
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6.7203
6.4991
6.4778
5.0935
4.3605
4.3573
2.6387
1.6777
1.6103
0.0271
O
O
BnO
N
NO2
3l
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1.9056
0.9343
2.8866
0.9676
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1.0000
2.9829
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11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
4.0
3.5
3.0
2.5
2.0
1.5
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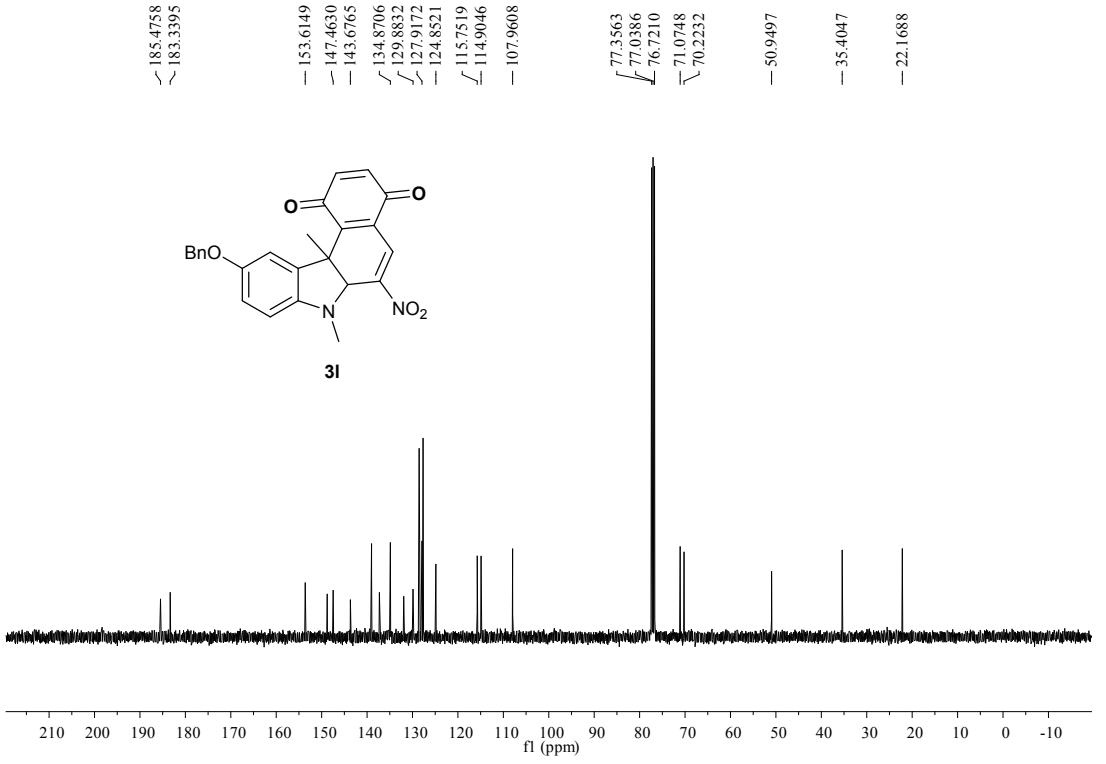
0.0
f1 (ppm)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107.9608
77.3563
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76.7210
71.0748
70.2232
50.9497
35.4047
22.1688
O
O
BnO
N
NO2
3l
210
200
190
180
170
160
150
140
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120
110
100
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80
70
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50
40
30
20
10
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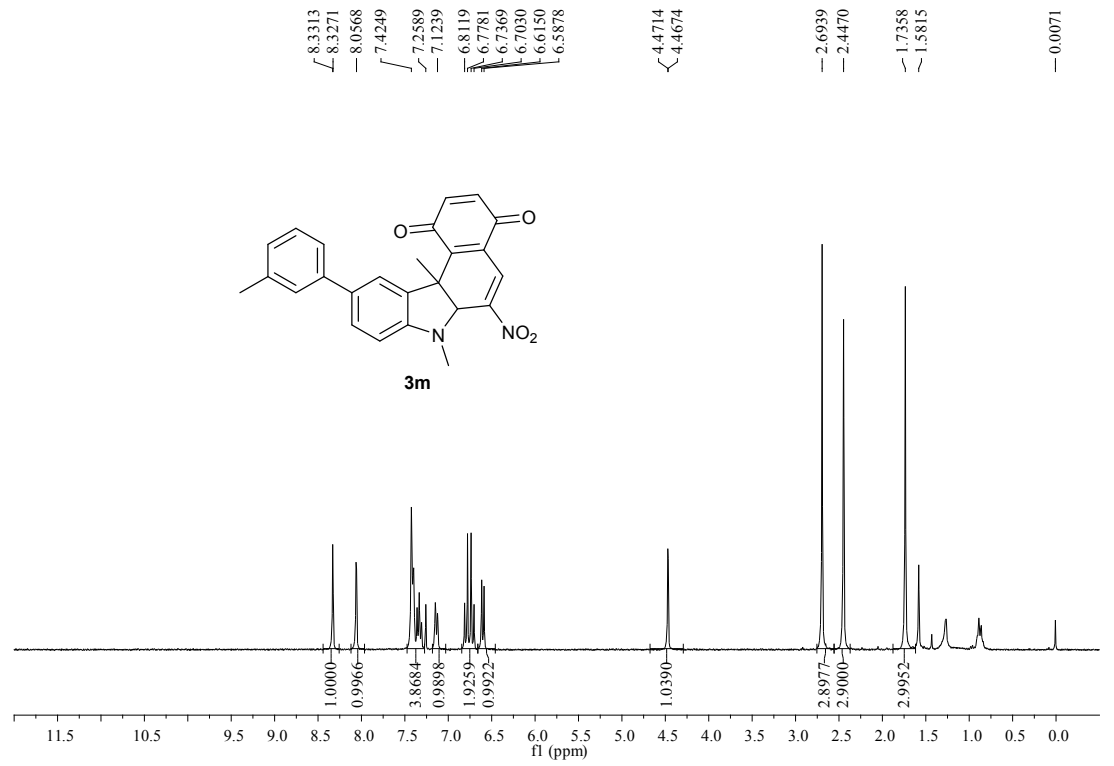
-10
f1 (ppm)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6.6150
6.5878
4.4714
4.4674
2.6939
2.4470
1.7358
1.5815
0.0071
O
O
N
NO2
3m
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1.9259
0.9922
1.0390
2.8977
2.9000
2.9952
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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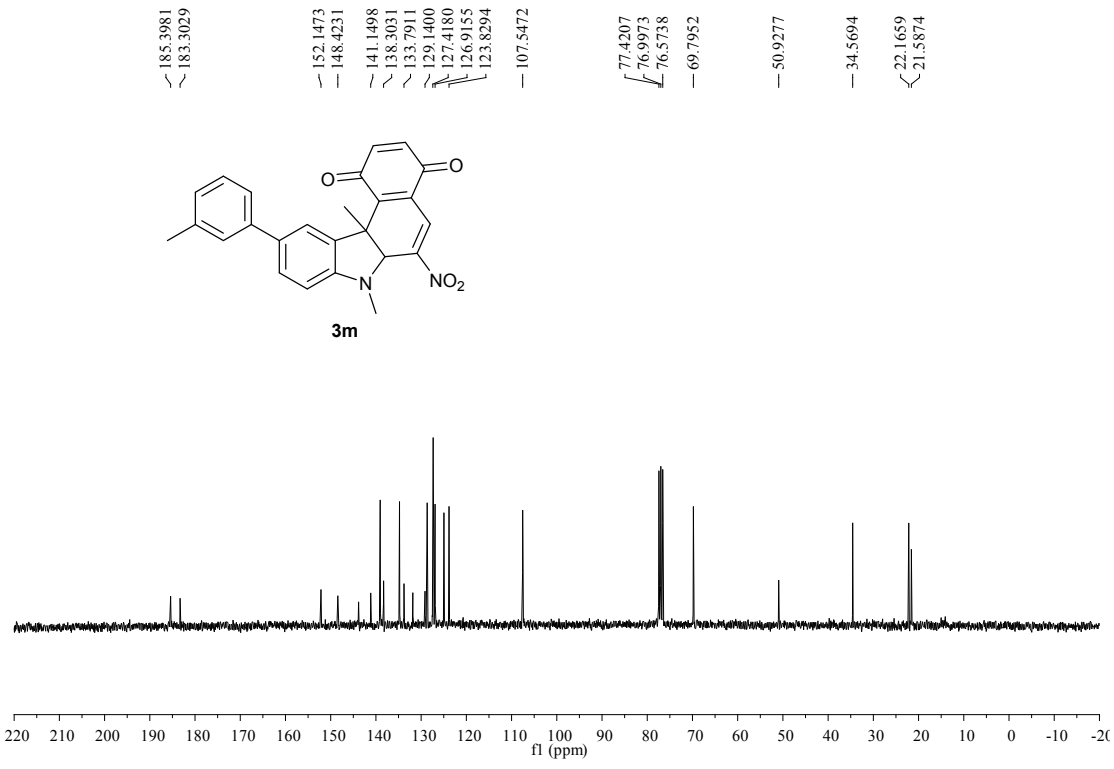
0.0
f1 (ppm)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133.7911
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127.4180
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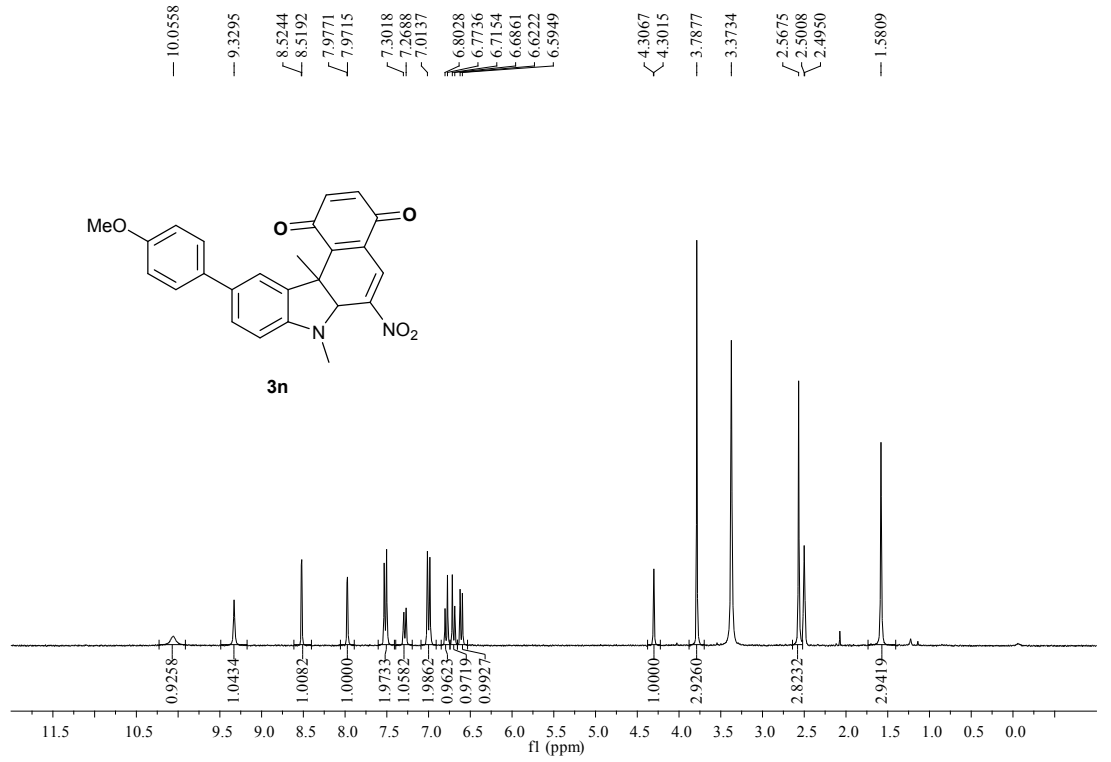
123.8294
107.5472
77.4207
76.9973
76.5738
69.7952
50.9277
34.5694
22.1659
21.5874
O
O
N
NO2
3m
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.9771
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6.7736
6.7154
6.6861
6.6222
6.5949
4.3067
4.3015
3.7877
3.3734
2.5675
2.5008
2.4950
1.5809
MeO
O
O
N
NO2
3n
0.9258
1.0434
1.0082
1.0000
1.9733
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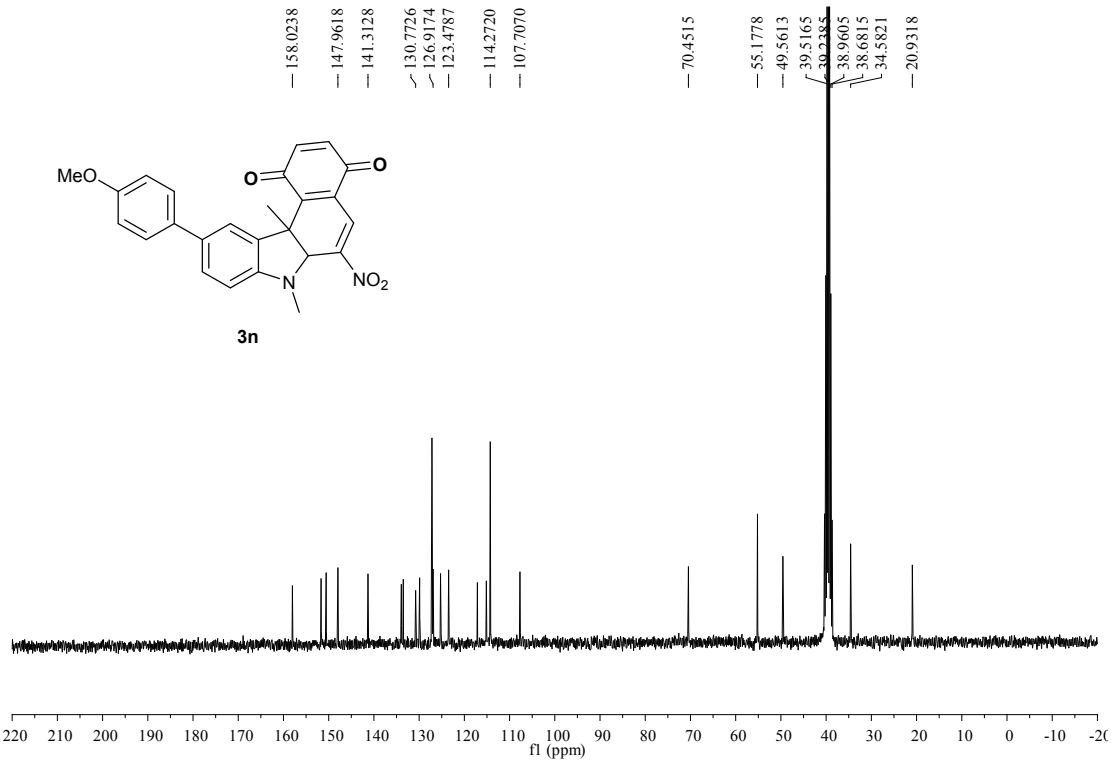
0.9623
0.9719
0.9927
1.0000
2.9260
2.8232
2.9419
f1 (ppm)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114.2720
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49.5613
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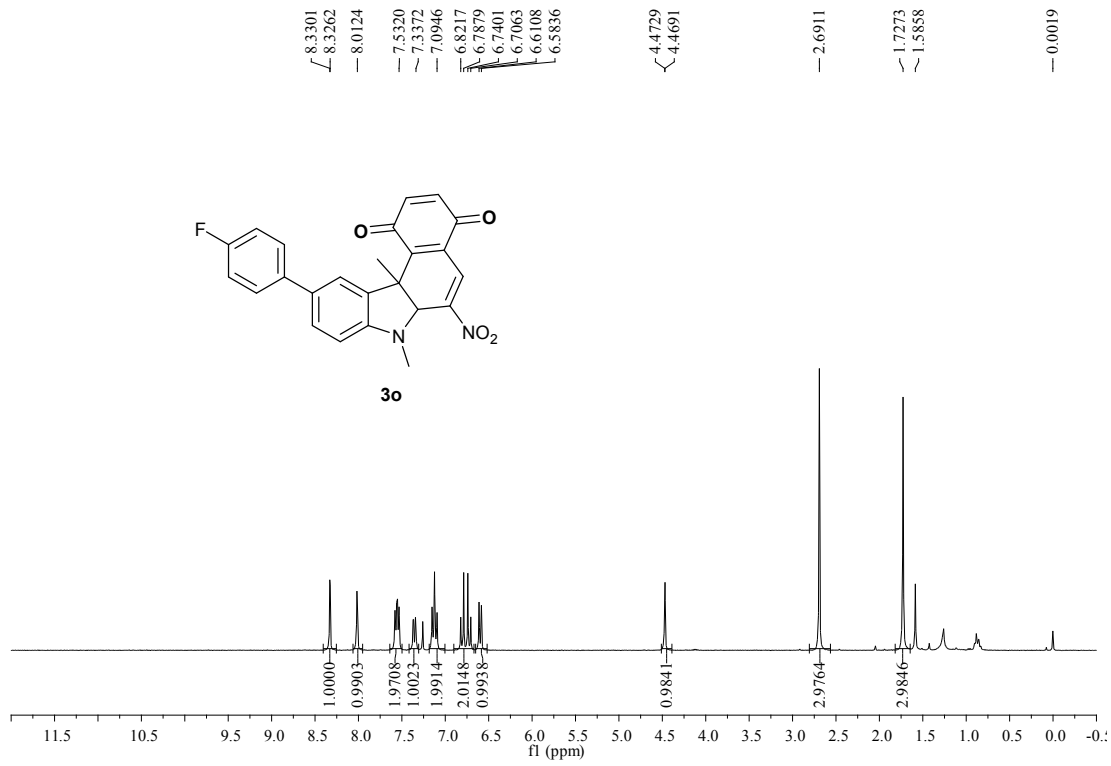
38.6815
34.5821
20.9318
MeO
O
O
N
NO2
3n
f1 (ppm)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6.6108
6.5836
4.4729
4.4691
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1.7273
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F
O
O
N
NO2
3o
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1.0023
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0.9938
0.9841
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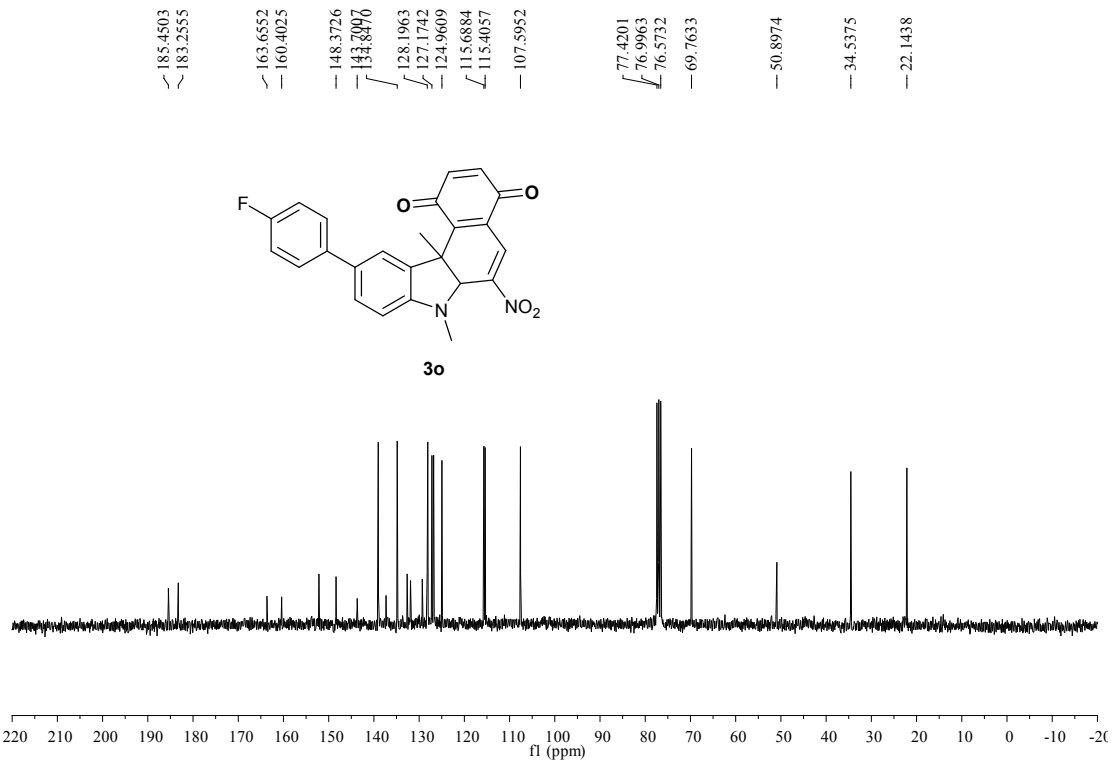
2.9846
f1 (ppm)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115.4057
107.5952
77.4201
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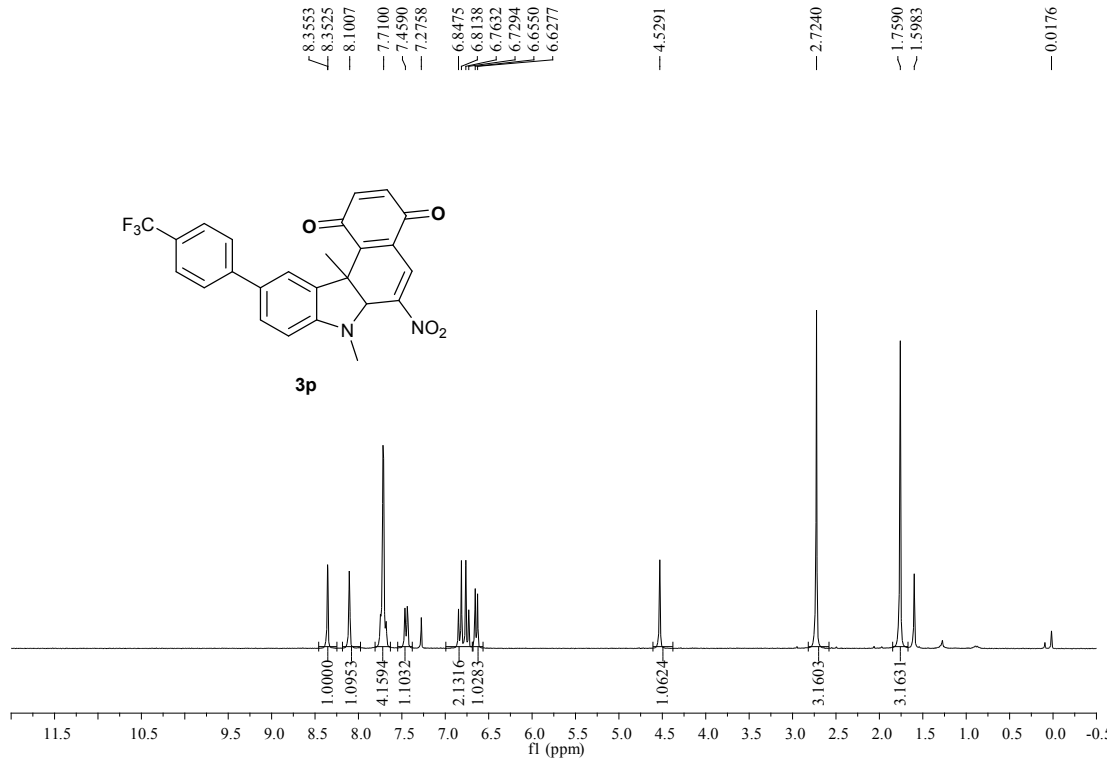
22.1438
F
O
O
N
NO2
3o
f1 (ppm)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6.6277
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2.7240
1.7590
1.5983
0.0176
F3C
O
O
N
NO2
3p
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1.0624
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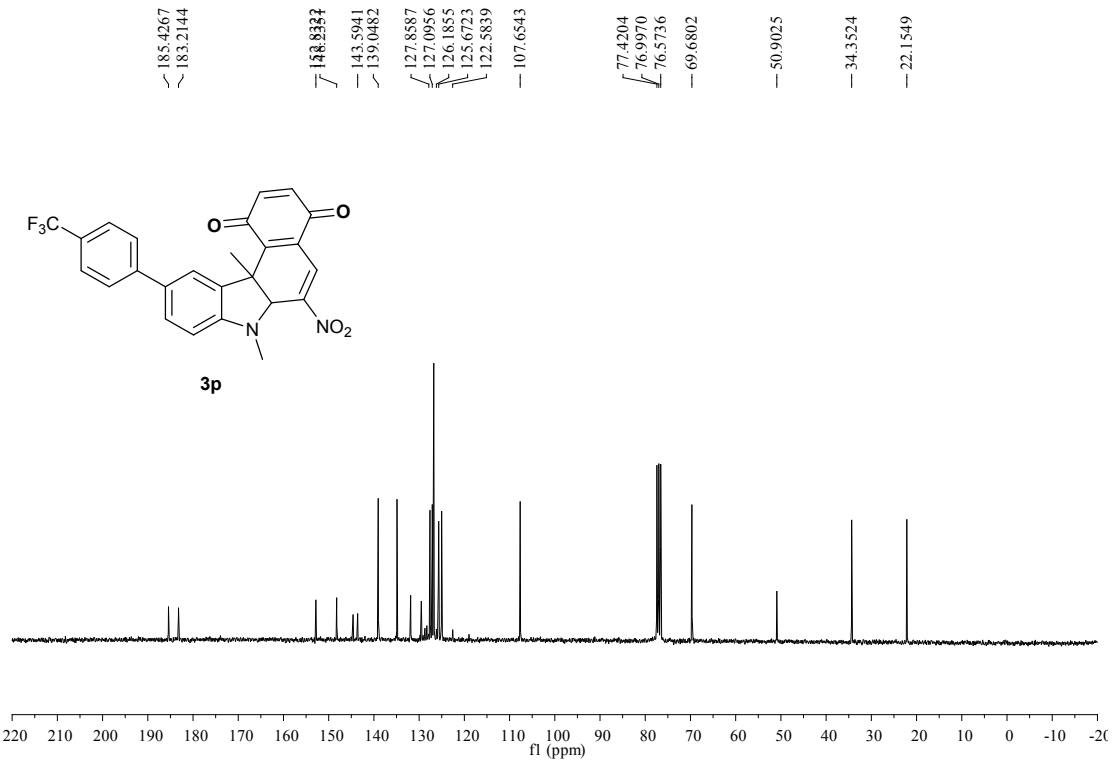
3.1631
fl (ppm)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125.6723
122.5839
107.6543
77.4204
76.9970
76.5736
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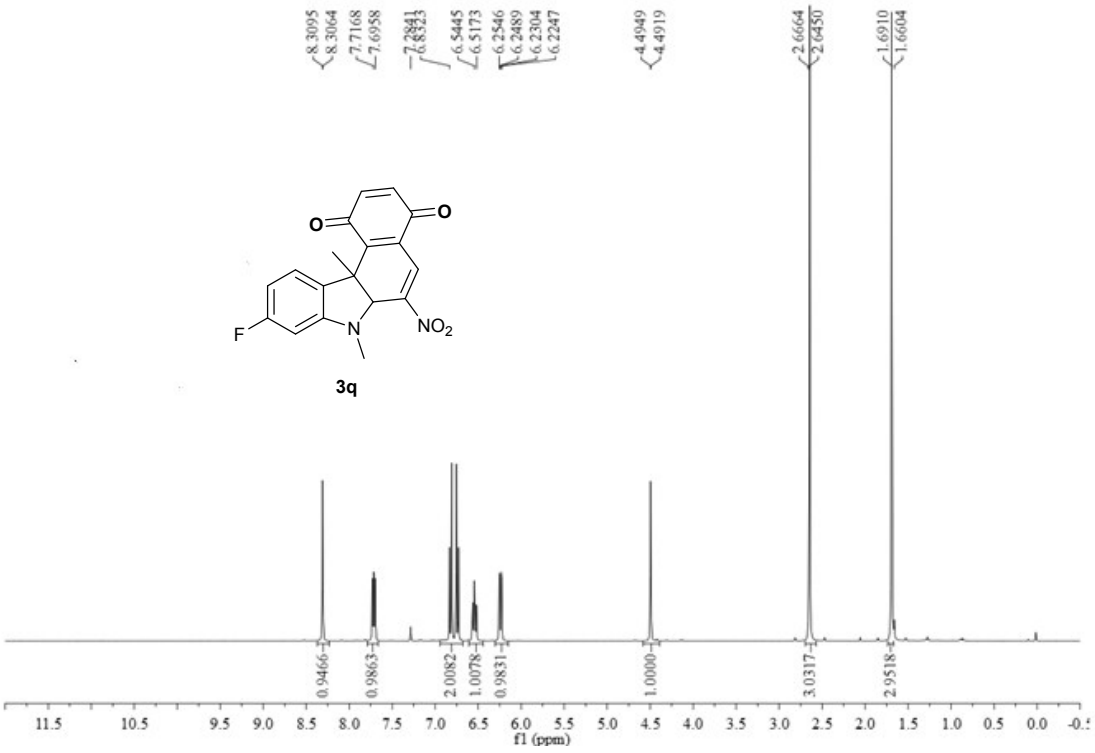
50.9025
34.3524
22.1549
F3C
O
O
N
NO2
3p
fl (ppm)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6.5445
6.5173
6.2546
6.2489
6.2304
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4.4949
4.4919
2.6664
2.6450
1.6910
1.6604
O
O
F
N
NO2
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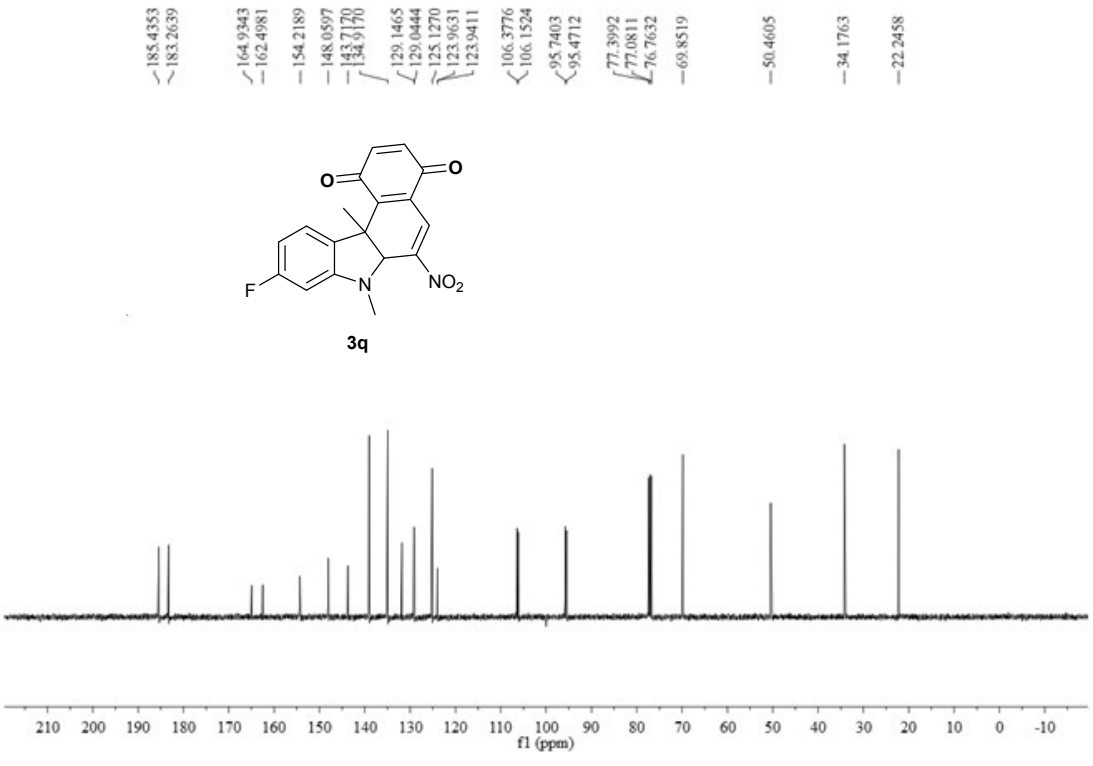
2.0082
1.0078
0.9831
1.0000
3.0317
2.9518
f1 (ppm)

3q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123.9631
123.9411
106.3776
106.1524
95.7403
95.4712
77.3992
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76.7632
69.8519
50.4605
34.1763
22.2458
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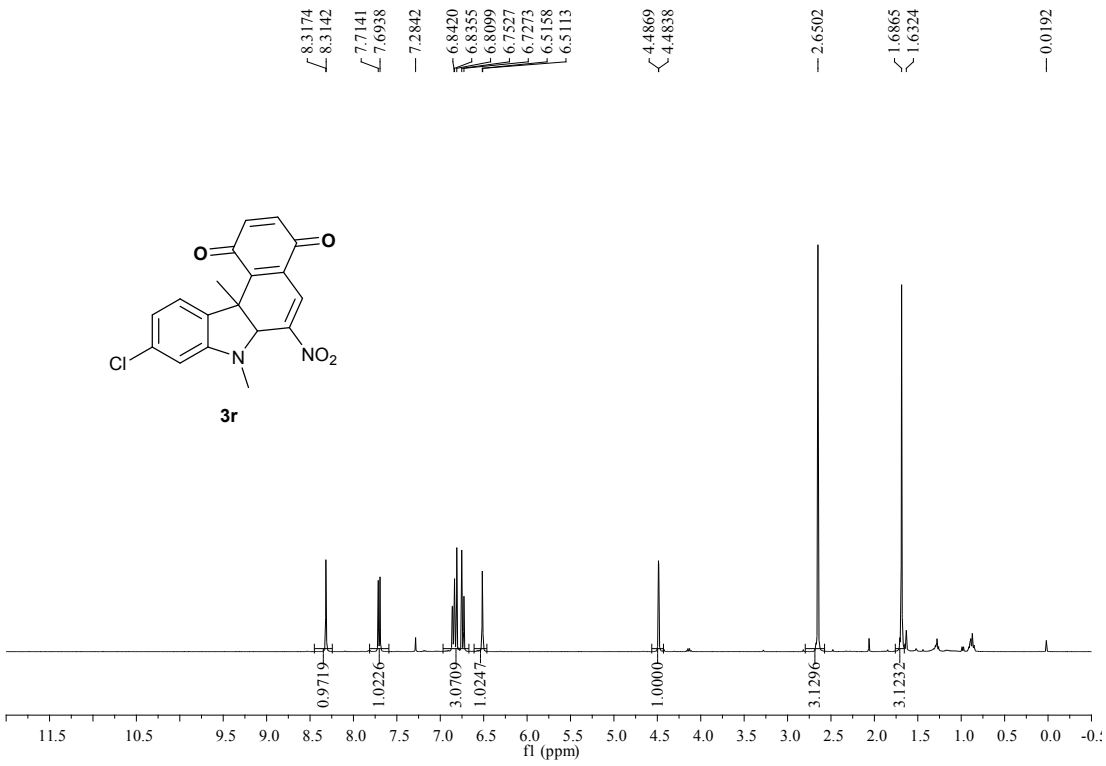
O
F
N
NO2
f1 (ppm)

3q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6.5113
4.4869
4.4838
2.6502
1.6865
1.6324
0.0192
O
O
Cl
N
NO2
3r
0.9719
1.0226
3.0709
1.0247
1.0000
3.1296
3.1232
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.5
2.0
1.5
1.0
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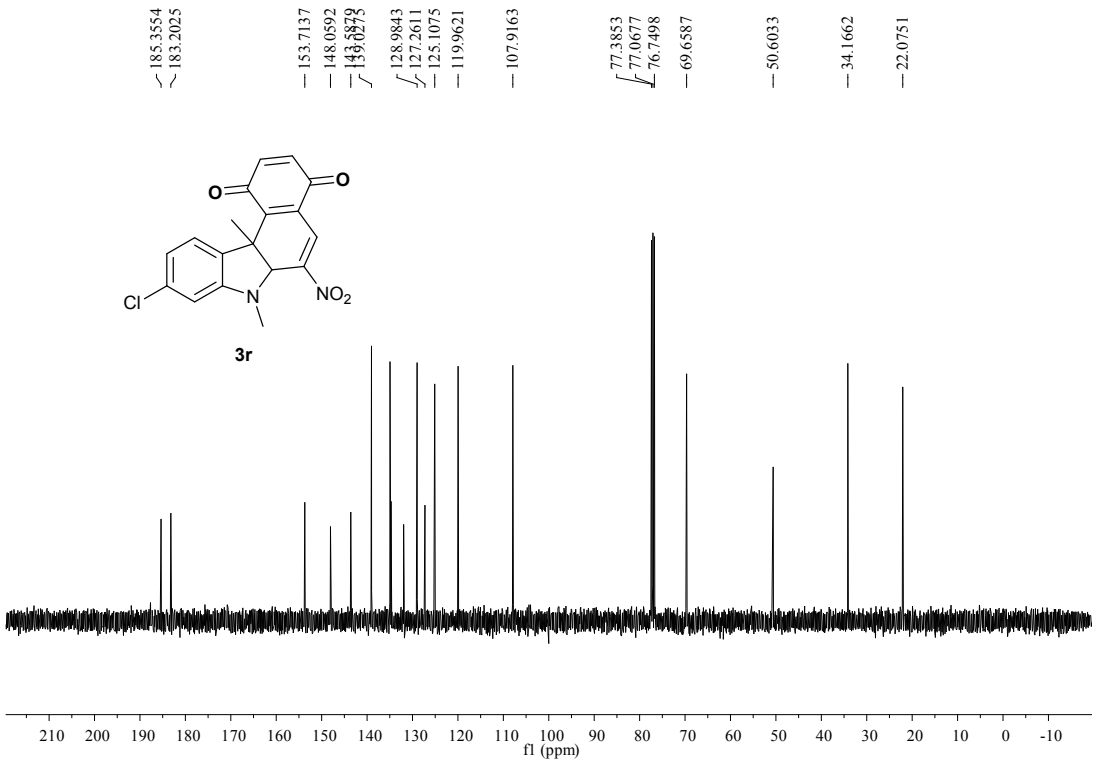
0.0
f1 (ppm)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77.0677
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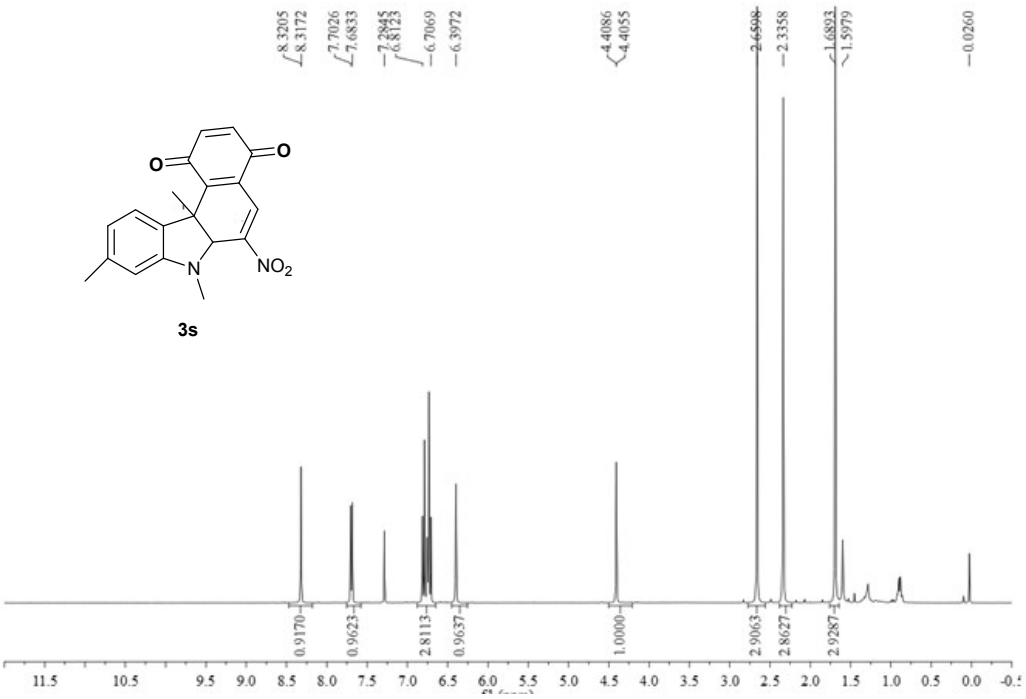
69.6587
50.6033
34.1662
22.0751
O
O
Cl
N
NO2
3r
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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6.7069
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4.4086
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2.3358
1.6893
1.5979
0.0260
O
O
N
NO2
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0.9623
2.8113
0.9637
1.0000
2.9063
2.8627
2.9287
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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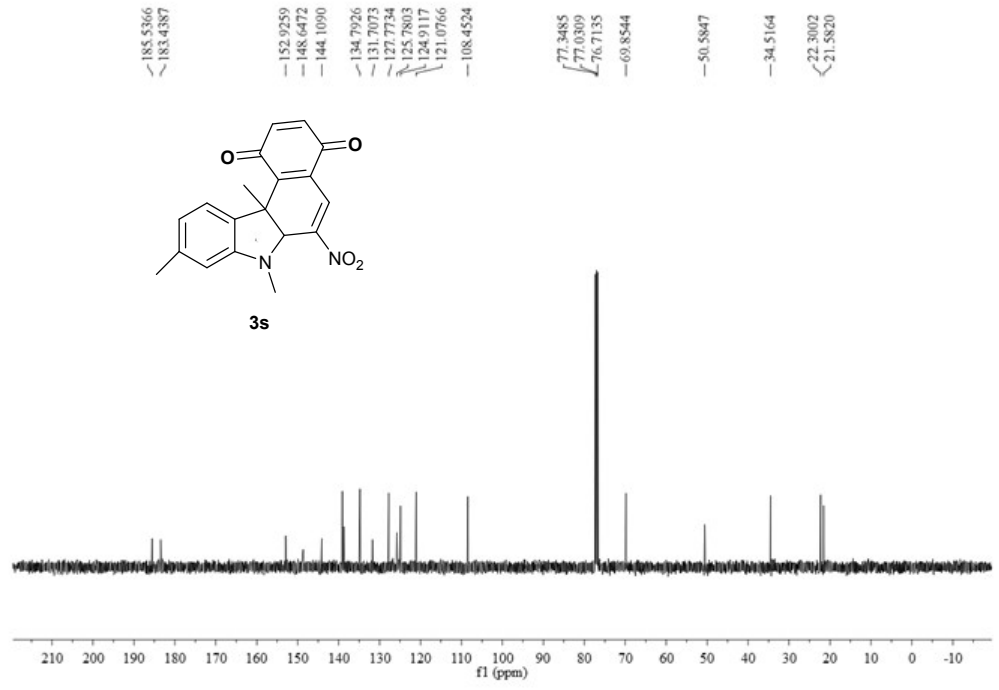
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

3s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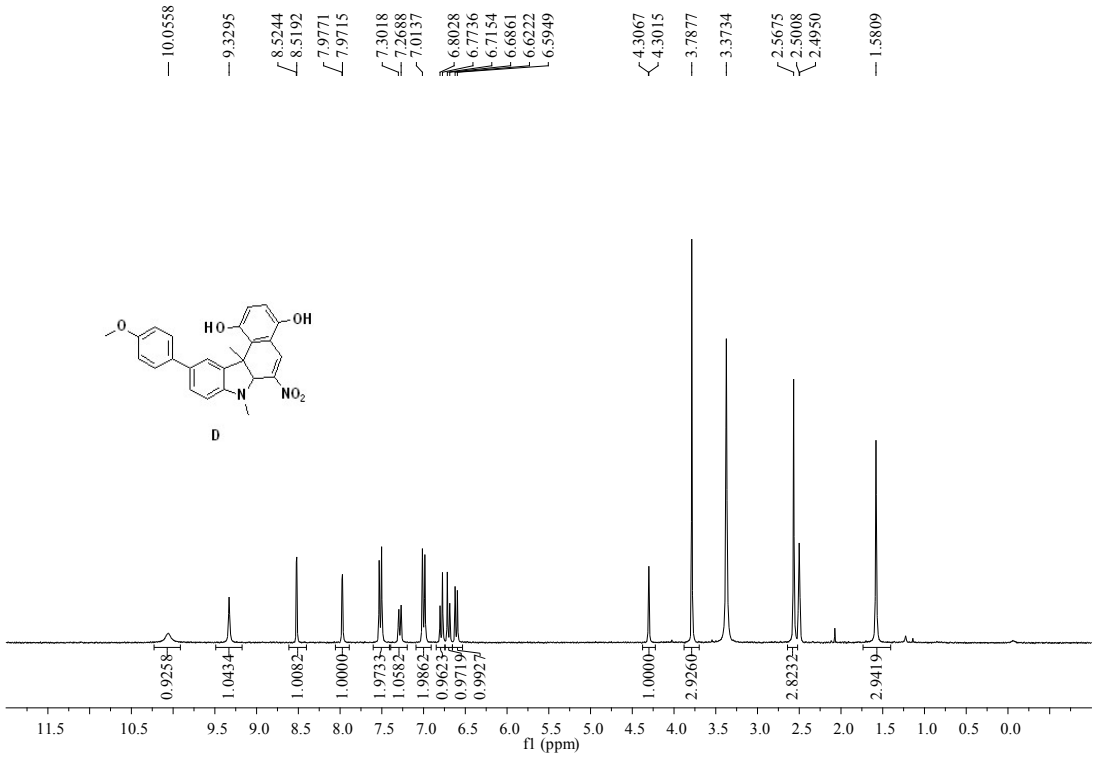
108.4524
77.3485
77.0309
76.7135
69.8544
50.5847
34.5164
22.3002
21.5820
O
O
N
NO2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

3s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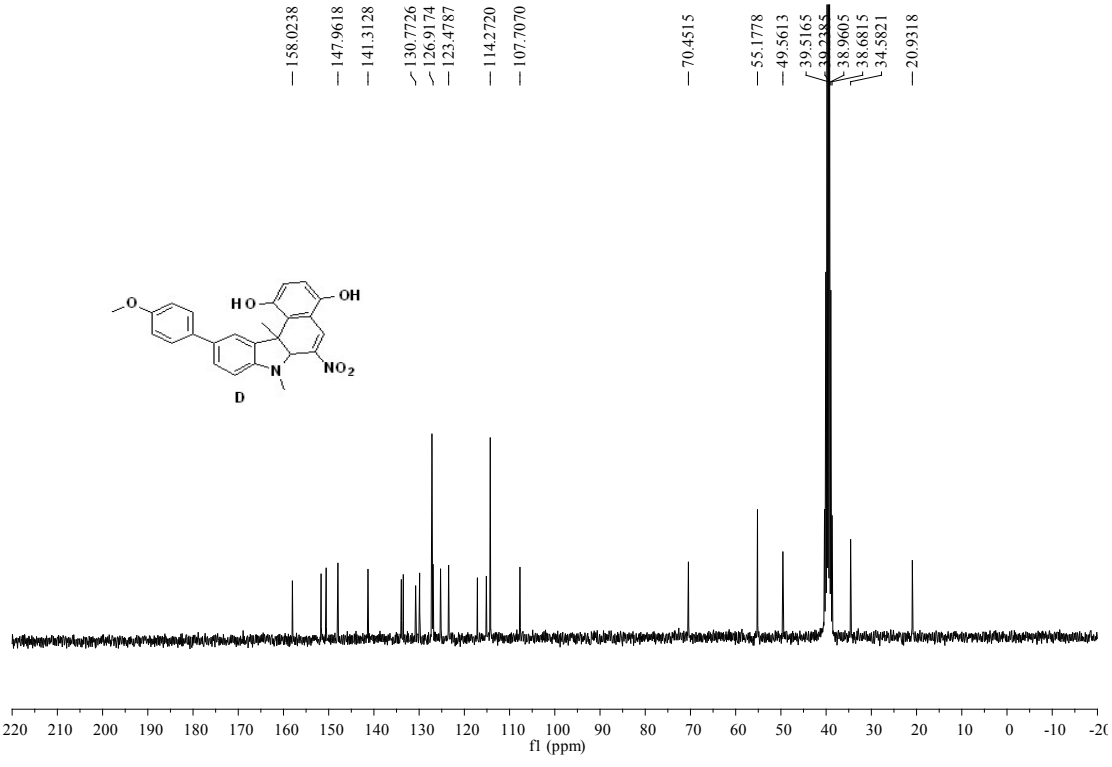
HO
OH
O
N
NO2
D
0.9258
1.0434
1.0082
1.0000
1.9733
1.0582
1.9862
0.9623
0.9719
0.9927
1.0000
2.9260
2.8232
2.9419
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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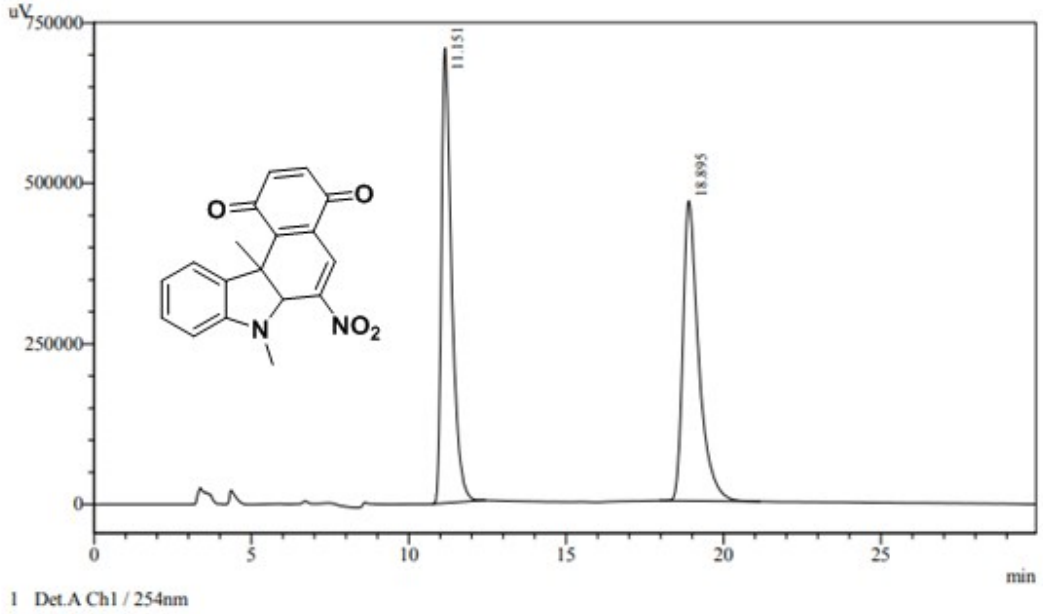
39.5165
38.9605
38.6815
34.5821
20.9318
HO
OH
O
N
NO2
D
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Chiral HPLC chromatograms:

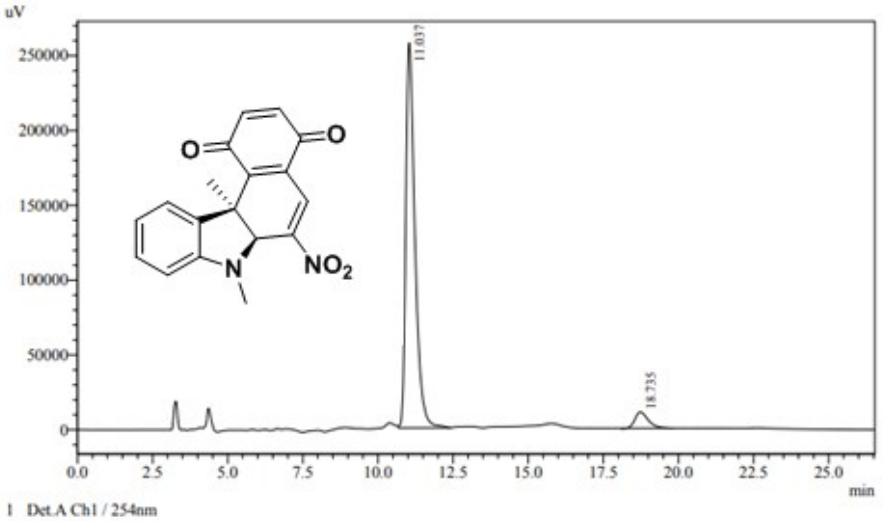
7,11b-dimethyl-6-nitro-7,11b-dihydro-1H-benzo[c]carbazole-1,4(6aH)-dione (**3a**)



1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.151	15866273	708309	49.391	60.253
2	18.895	16257293	467246	50.609	39.747
Total		32123566	1175555	100.000	100.000

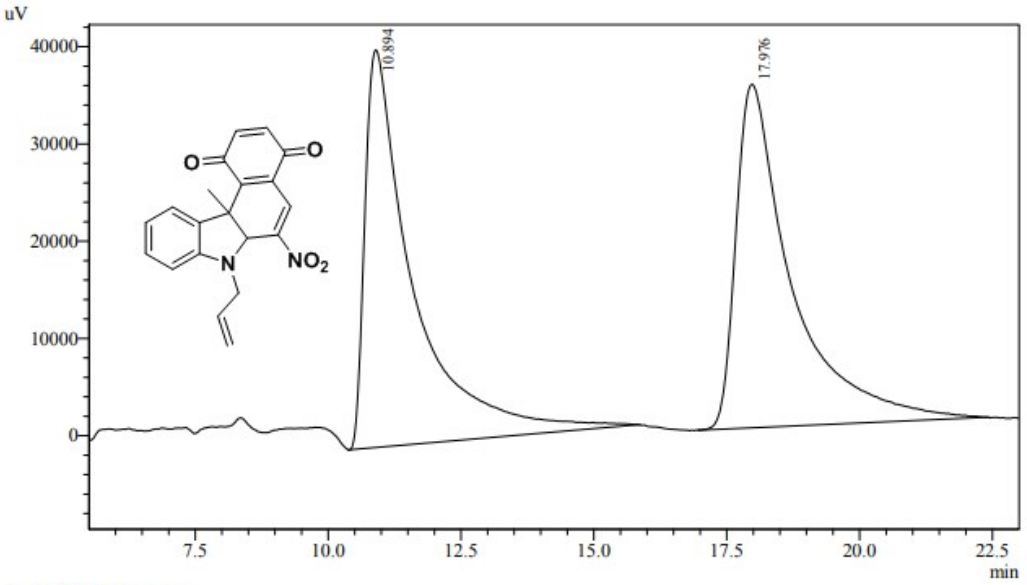


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.037	5441202	257151	94.020	95.881
2	18.735	346072	11047	5.980	4.119
Total		5787274	268198	100.000	100.000

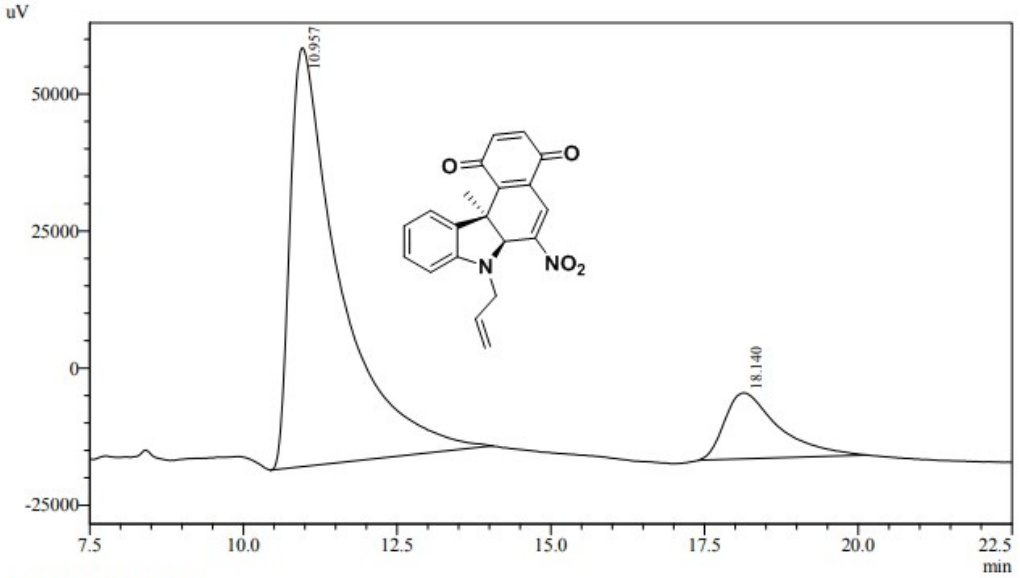
7-allyl-11b-methyl-6-nitro-7,11b-dihydro-1H-benzo[c]carbazole-1,4(6aH)-dione (**3b**)



1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.894	2588240	40881	50.106	53.651
2	17.976	2577324	35317	49.894	46.349
Total		5165564	76198	100.000	100.000

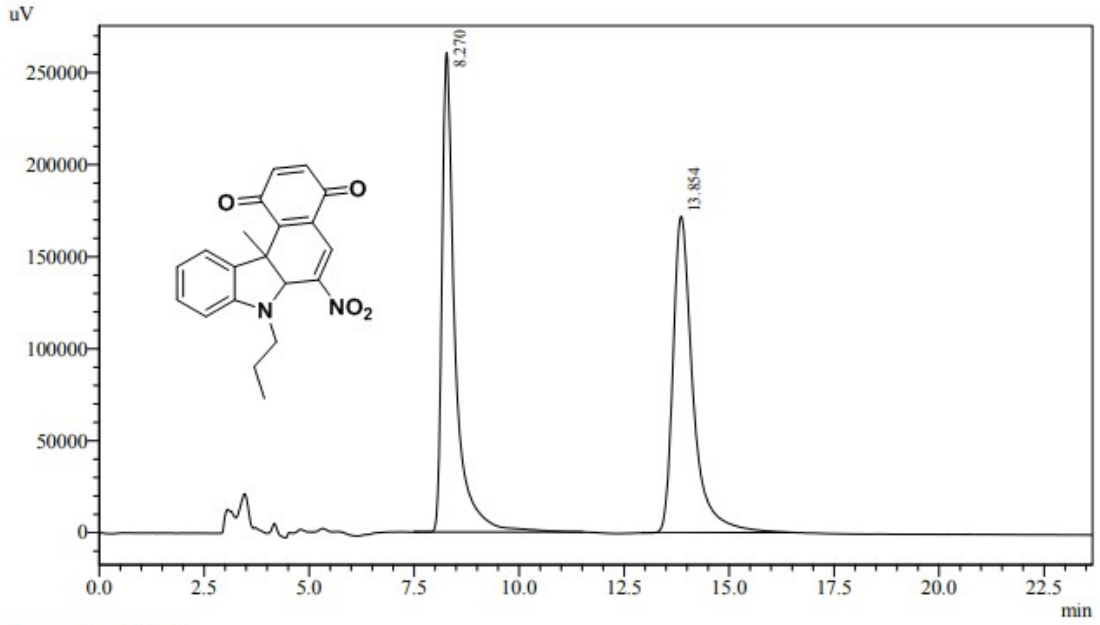


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

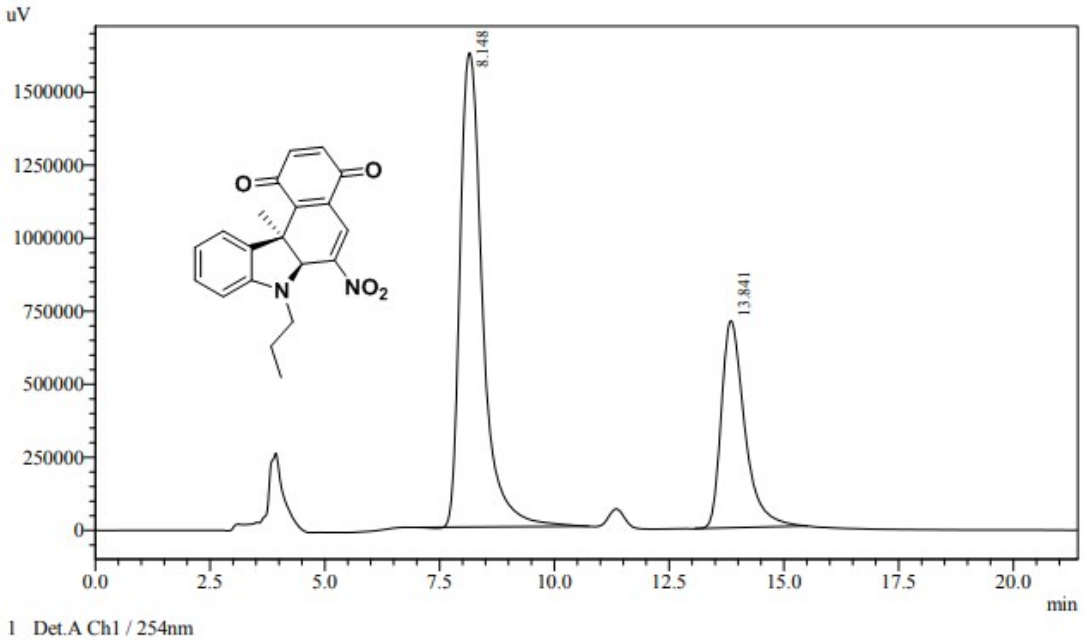
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.957	4312088	76381	85.449	86.397
2	18.140	734296	12026	14.551	13.603
Total		5046384	88407	100.000	100.000

11b-methyl-6-nitro-7-propyl-7,11b-dihydro-1H-benzo[c]carbazole-1,4(6aH)-dione (**3c**)



Detector A Ch1 254nm

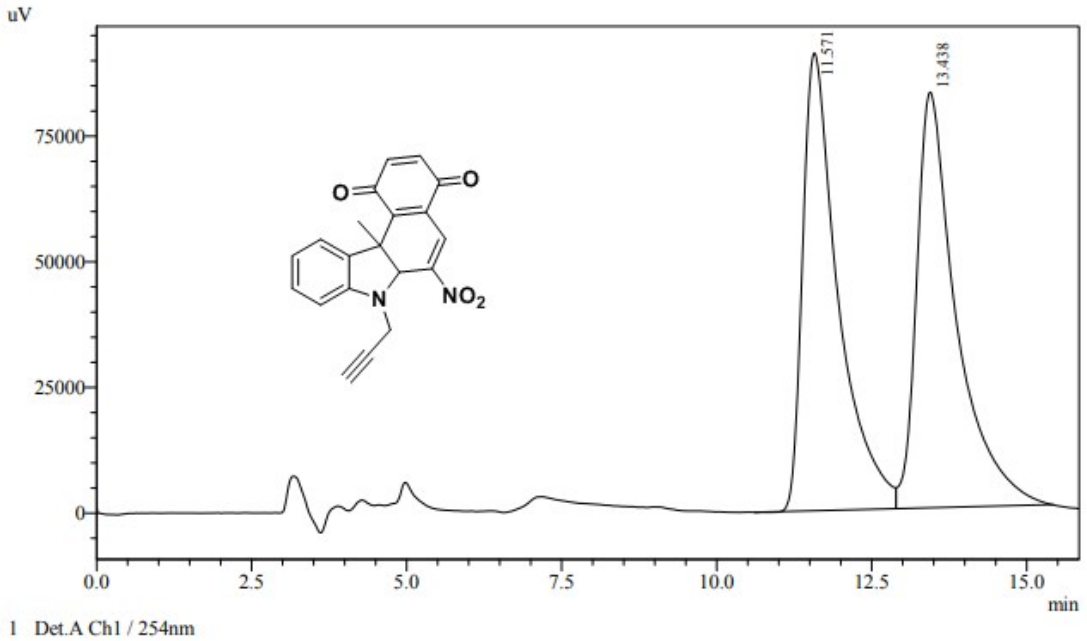
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.270	5652433	260380	49.893	60.221
2	13.854	5676650	171995	50.107	39.779
Total		11329083	432375	100.000	100.000



Detector A Ch1 254nm

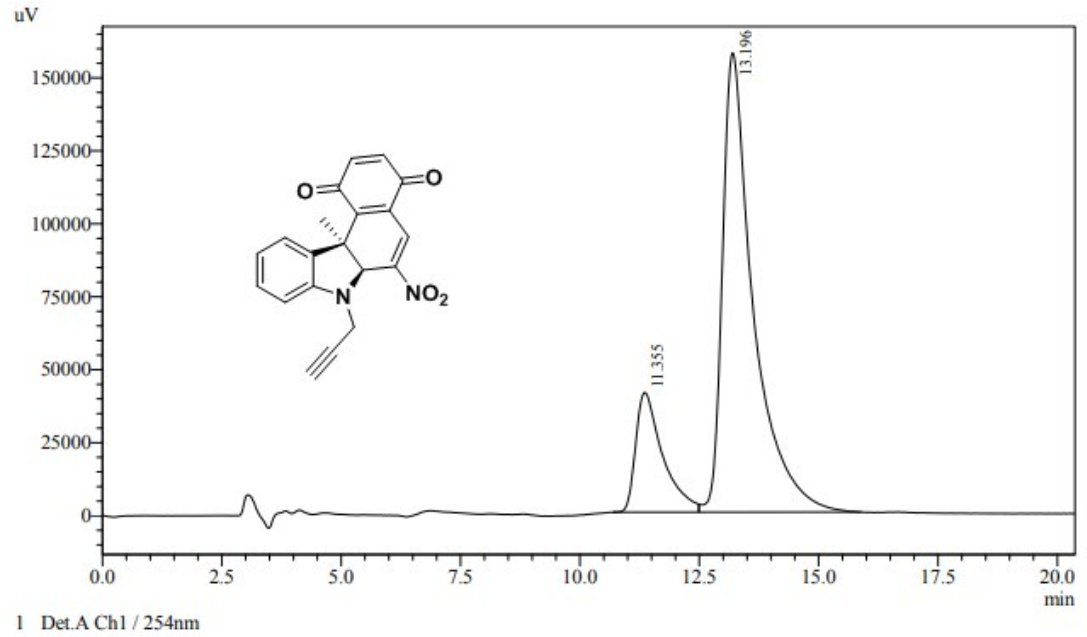
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.148	55354459	1622631	68.718	69.604
2	13.841	25198910	708608	31.282	30.396
Total		80553369	2331238	100.000	100.000

11b-methyl-6-nitro-7-(prop-2-yn-1-yl)-7,11b-dihydro-1H-benzo[c]carbazole-1,4(6aH)-dione (**3d**)



Detector A Ch1 254nm

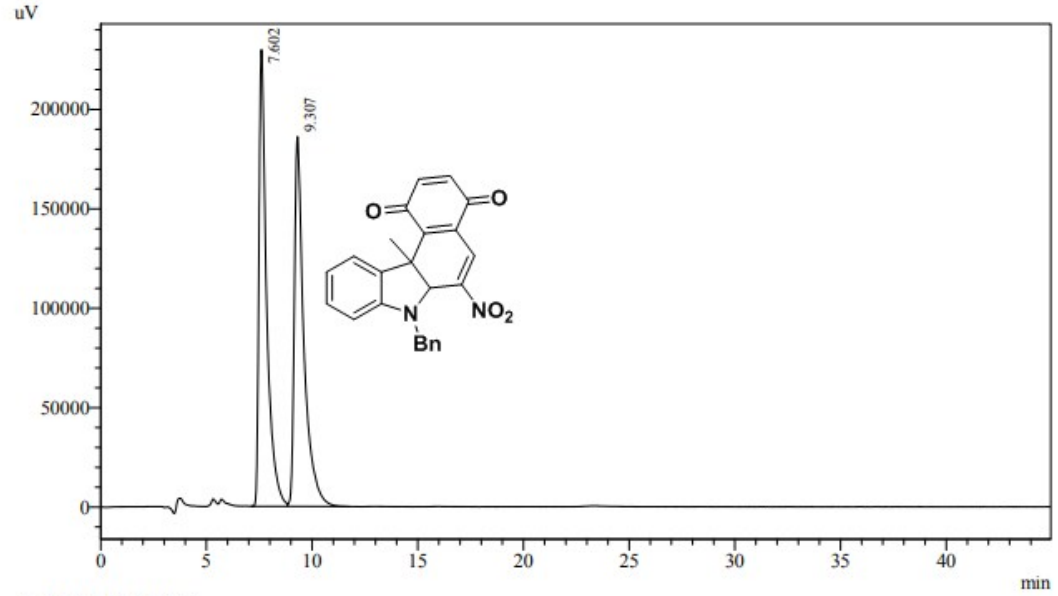
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.571	3620754	91046	49.568	52.410
2	13.438	3683817	82672	50.432	47.590
Total		7304571	173717	100.000	100.000



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.355	1610365	40965	18.544	20.665
2	13.196	7073472	157271	81.456	79.335
Total		8683837	198236	100.000	100.000

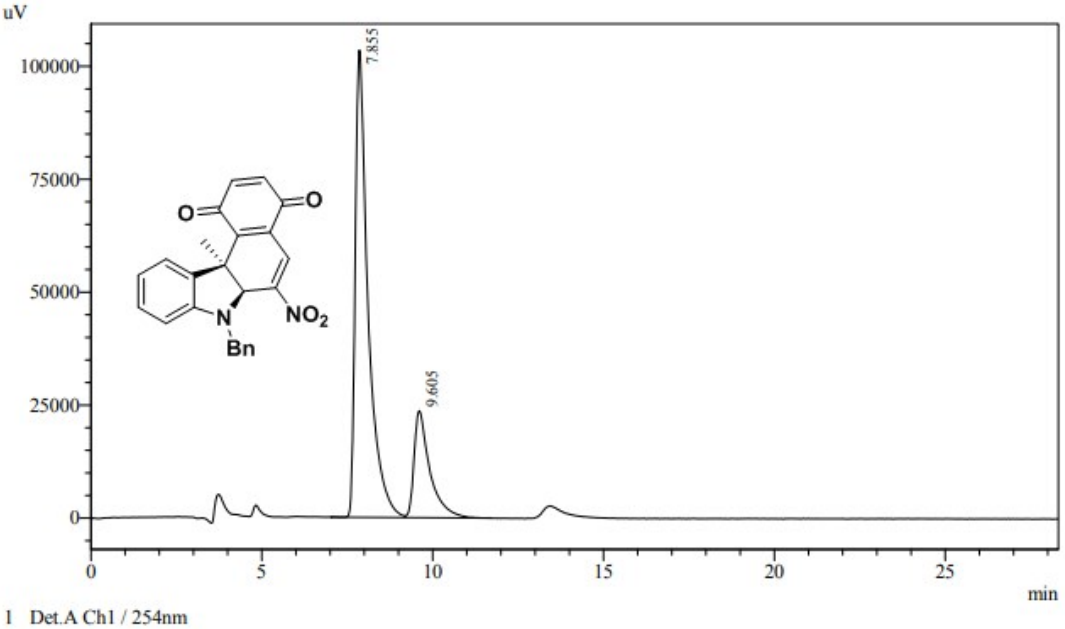
7-benzyl-11b-methyl-6-nitro-7,11b-dihydro-1H-benzo[c]car-bazole-1,4(6aH)-dione (**3e**)



1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.602	5809431	229613	49.880	55.253
2	9.307	5837406	185952	50.120	44.747
Total		11646837	415564	100.000	100.000

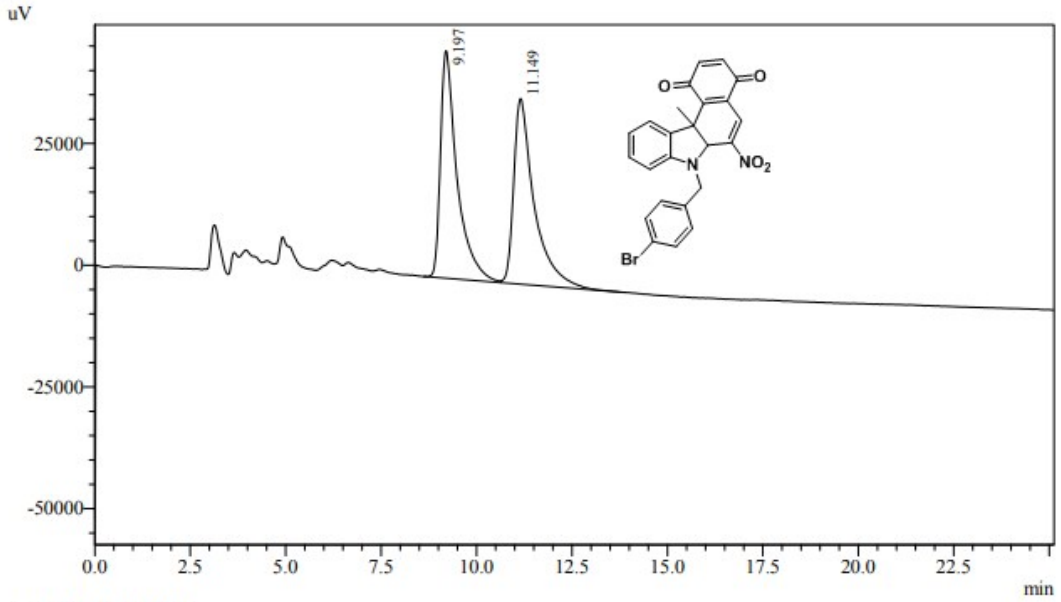


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.855	2694702	103388	78.091	81.371
2	9.605	756009	23669	21.909	18.629
Total		3450711	127057	100.000	100.000

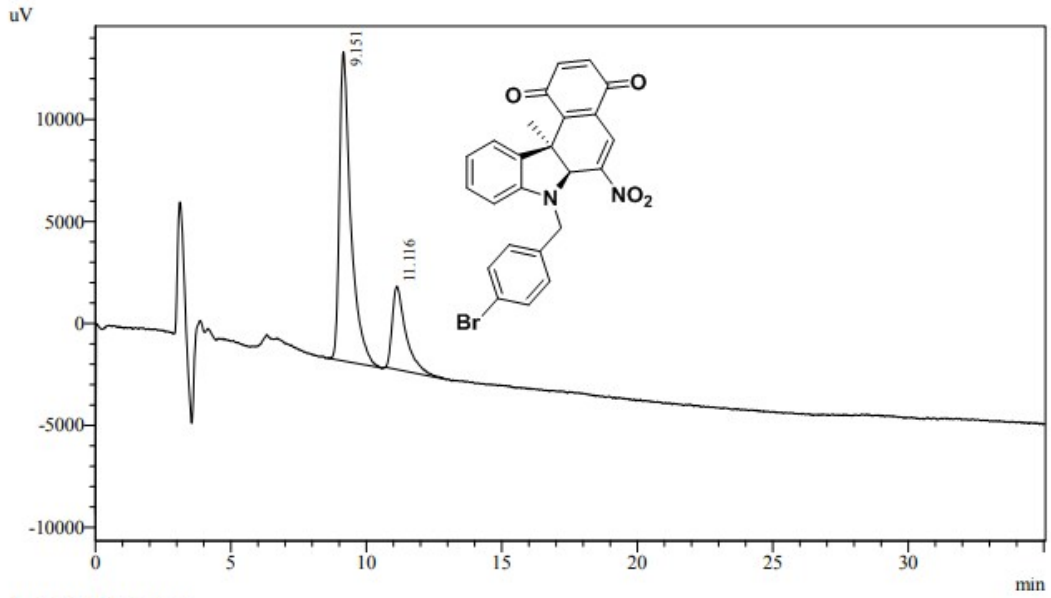
7-(4-bromobenzyl)-11b-methyl-6-nitro-7,11b-dihydro-1H-benzo[c]carbazole-1,4(6aH)-dione (**3f**)



1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.197	1404617	46702	49.764	55.066
2	11.149	1417939	38109	50.236	44.934
Total		2822557	84811	100.000	100.000

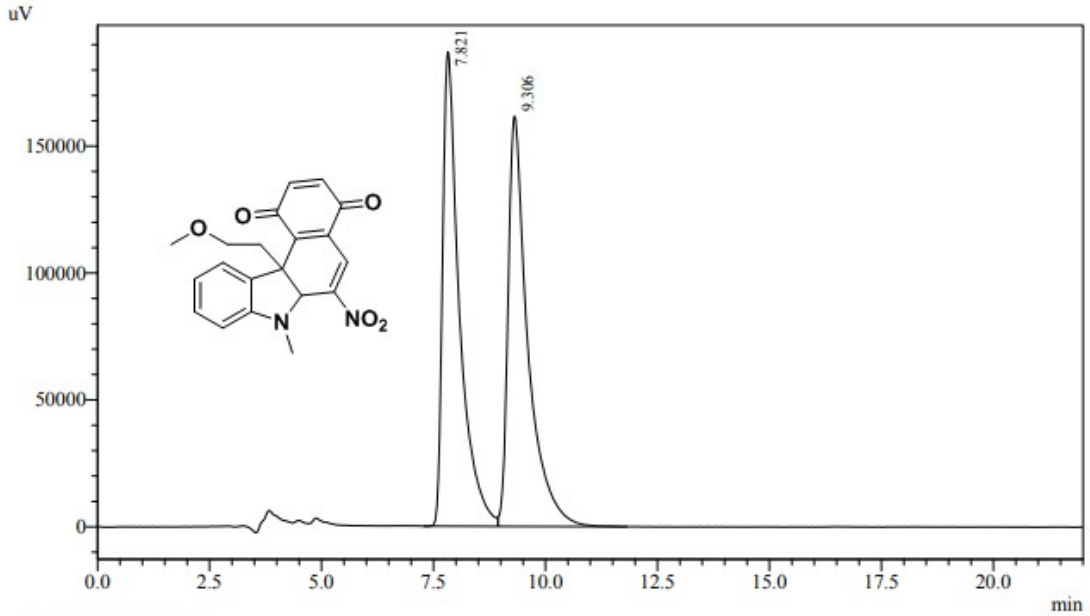


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.151	442319	15150	75.417	78.845
2	11.116	144176	4065	24.583	21.155
Total		586496	19215	100.000	100.000

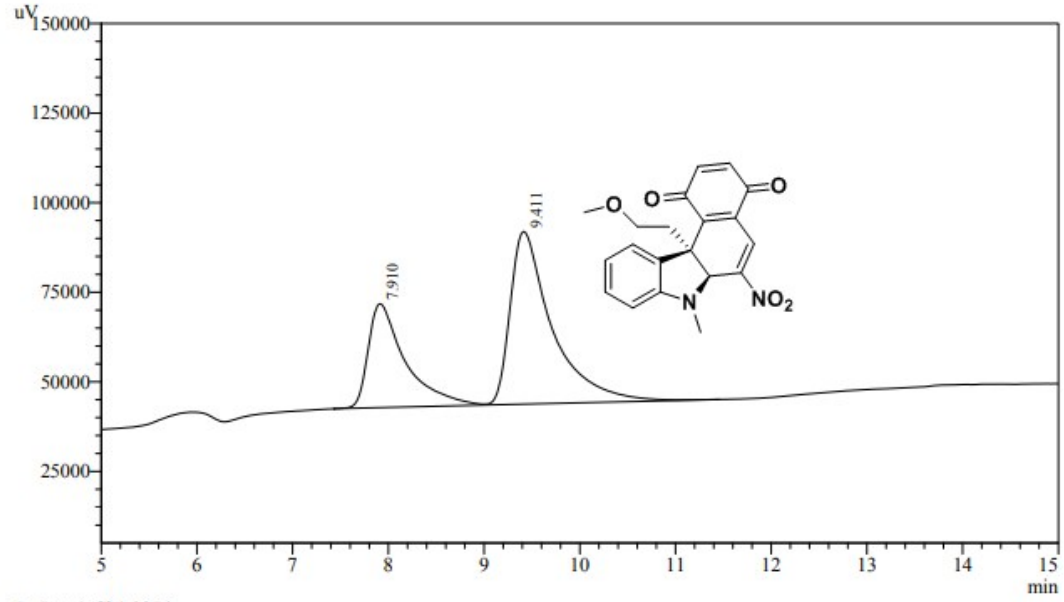
11b-(2-methoxyethyl)-7-methyl-6-nitro-7,11b-dihydro-1H-be-nzo[c]carbazole-1,4(6aH)-dione (**3g**)



1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.821	4895234	186887	49.725	53.619
2	9.306	4949324	161657	50.275	46.381
Total		9844557	348544	100.000	100.000

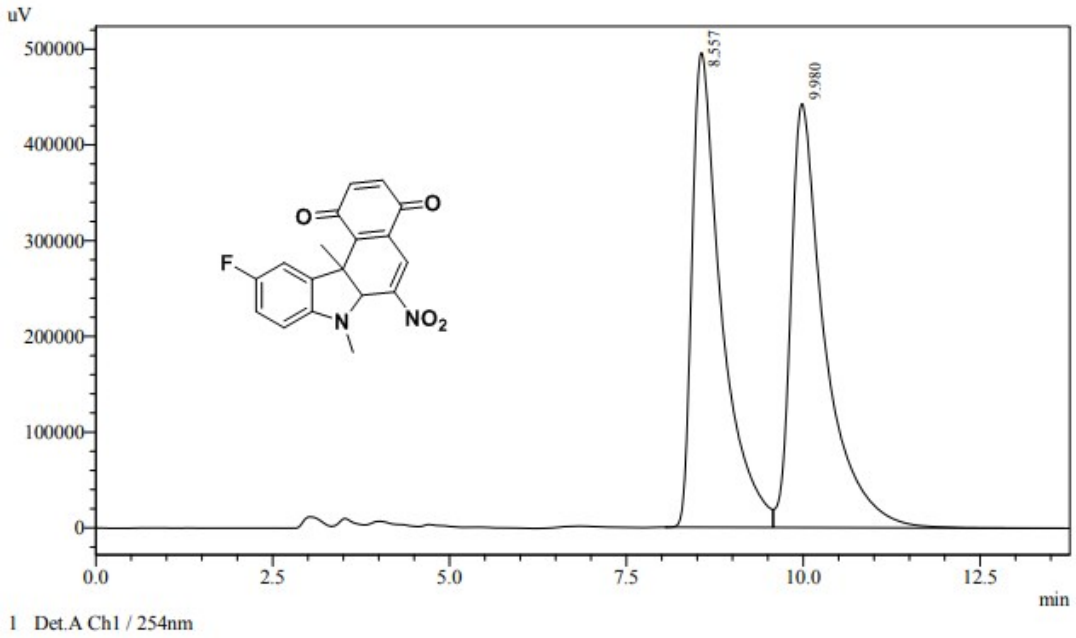


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

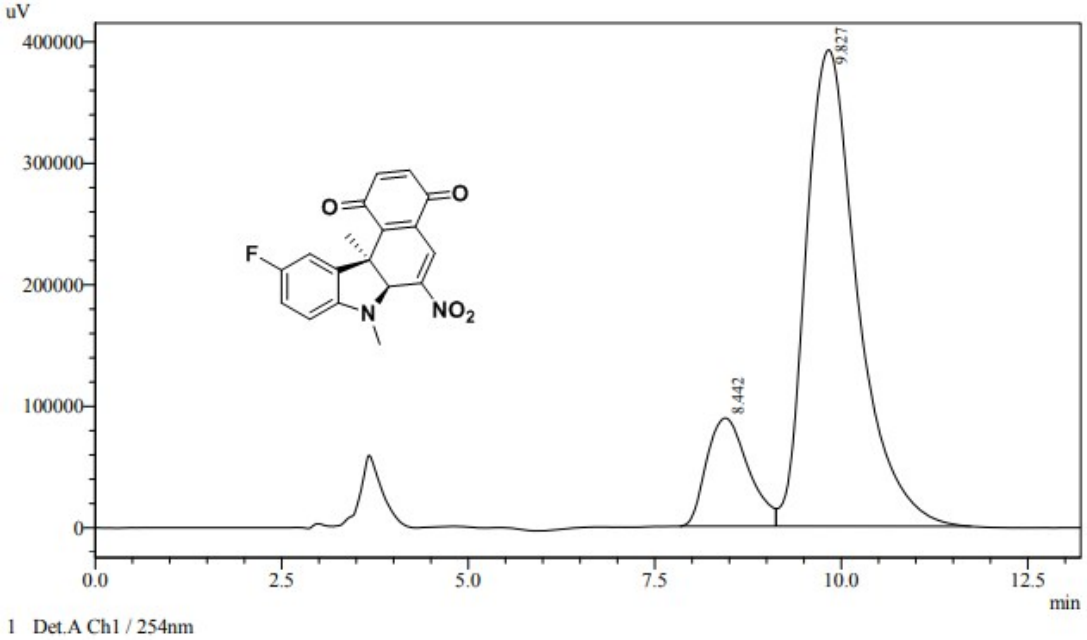
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.910	779054	28977	34.658	37.564
2	9.411	1468752	48163	65.342	62.436
Total		2247806	77139	100.000	100.000

10-fluoro-7,11b-dimethyl-6-nitro-7,11b-dihydro-1H-benzo[c]carbazole-1,4(6aH)-dione (**3h**)



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.557	14285197	495528	49.178	52.820
2	9.980	14762833	442610	50.822	47.180
Total		29048030	938138	100.000	100.000

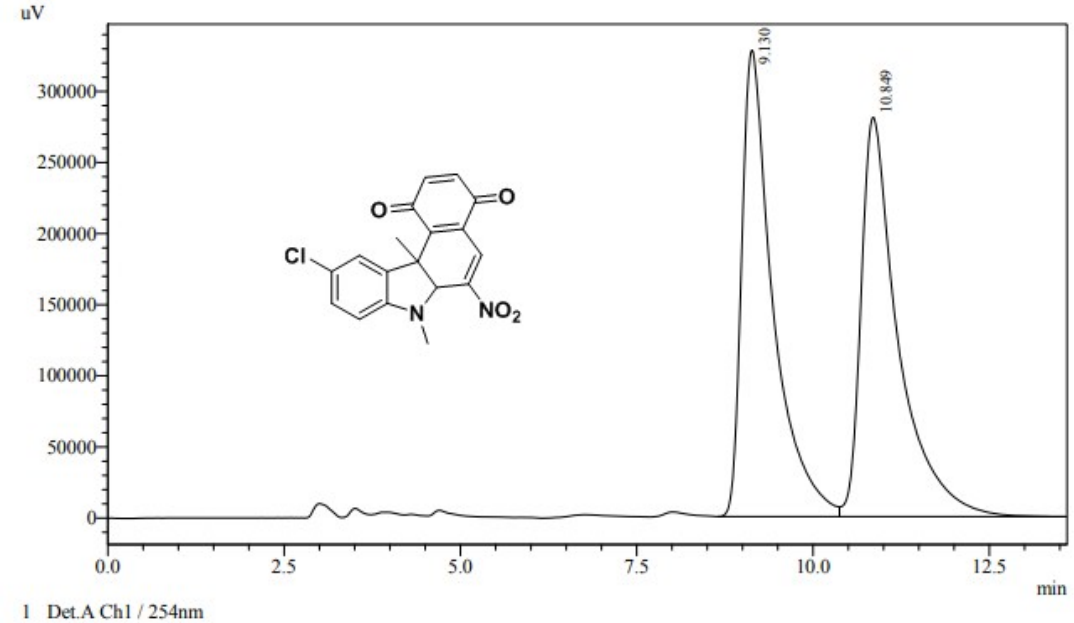


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.442	3461720	88955	15.515	18.491
2	9.827	18851053	392106	84.485	81.509
Total		22312773	481060	100.000	100.000

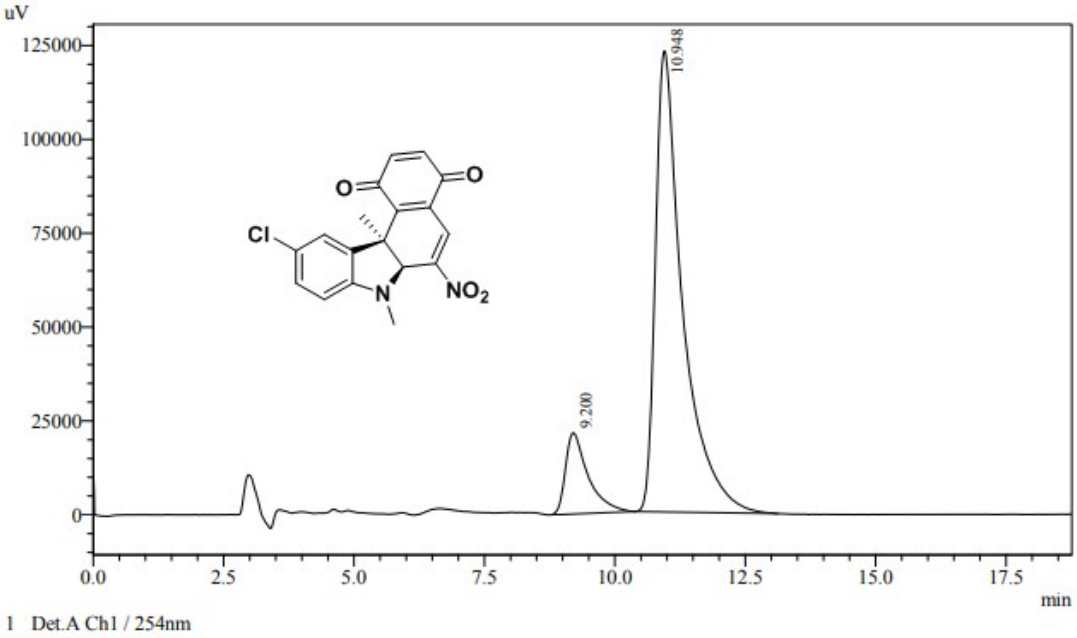
10-chloro-7,11b-dimethyl-6-nitro-7,11b-dihydro-1H-benzo[c]carbazole-1,4(6aH)-dione (**3i**)



1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

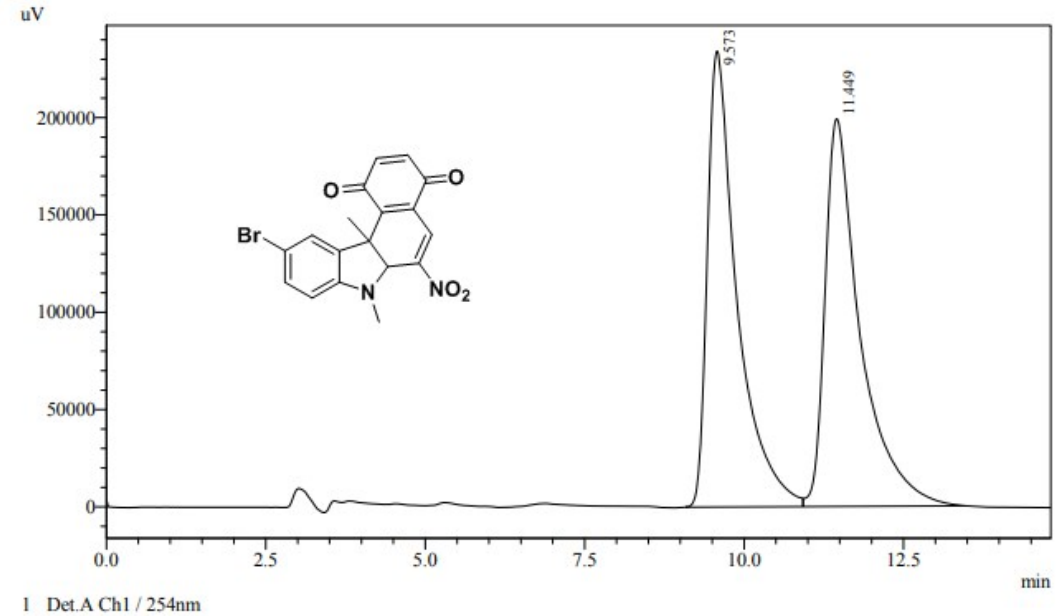
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.130	10122449	327942	49.624	53.877
2	10.849	10275920	280741	50.376	46.123
Total		20398368	608683	100.000	100.000



Detector A Ch1 254nm

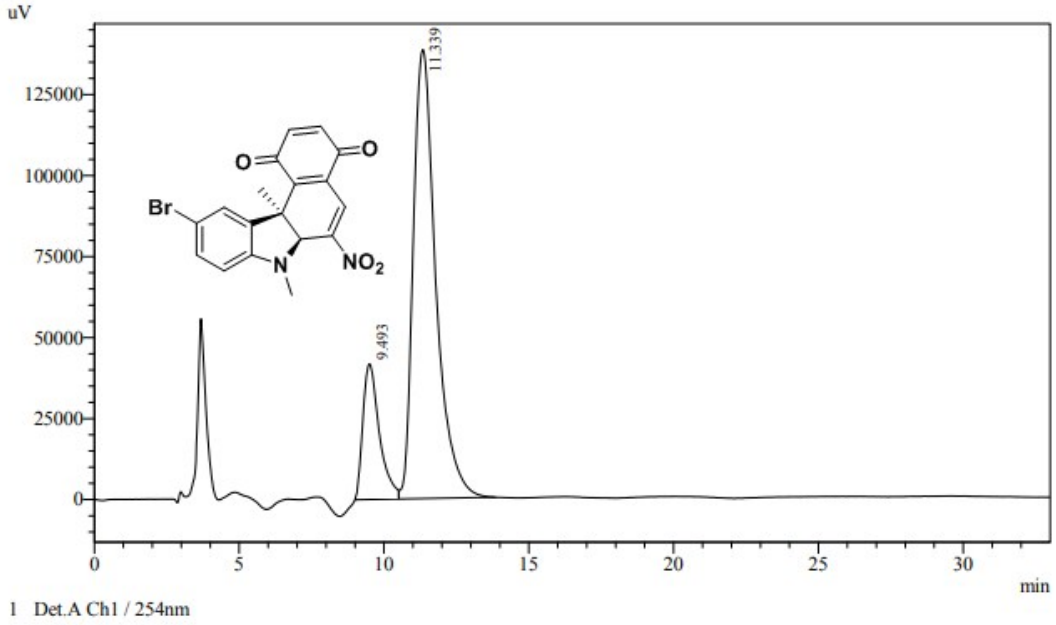
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.200	650023	21583	12.740	14.953
2	10.948	4452214	122762	87.260	85.047
Total		5102237	144345	100.000	100.000

10-bromo-7,11b-dimethyl-6-nitro-7,11b-dihydro-1H-benz-o[c]carbazole-1,4(6aH)-dione (**3j**)



Detector A Ch1 254nm

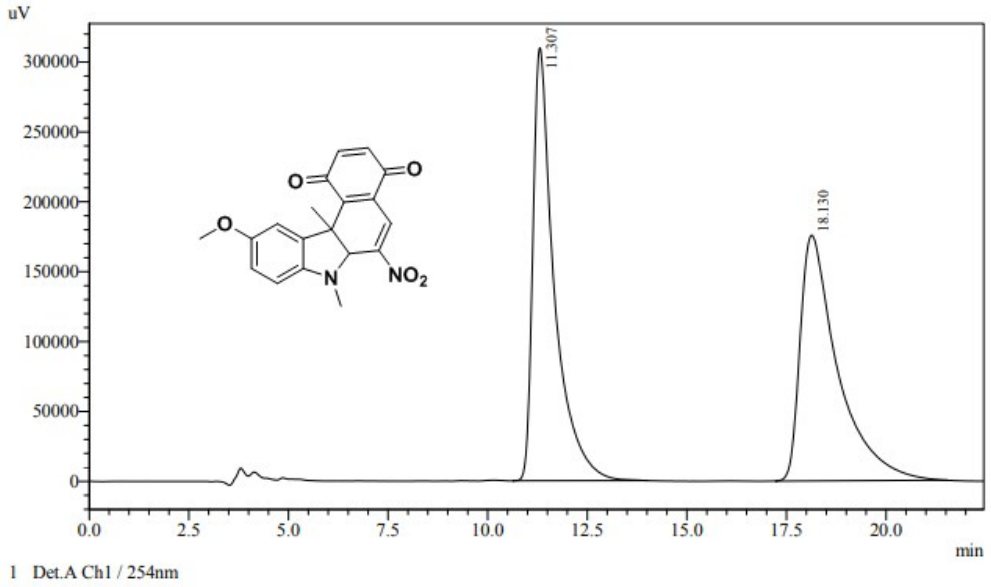
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.573	7612115	234248	49.942	54.047
2	11.449	7629855	199169	50.058	45.953
Total		15241971	433417	100.000	100.000



Detector A Ch1 254nm

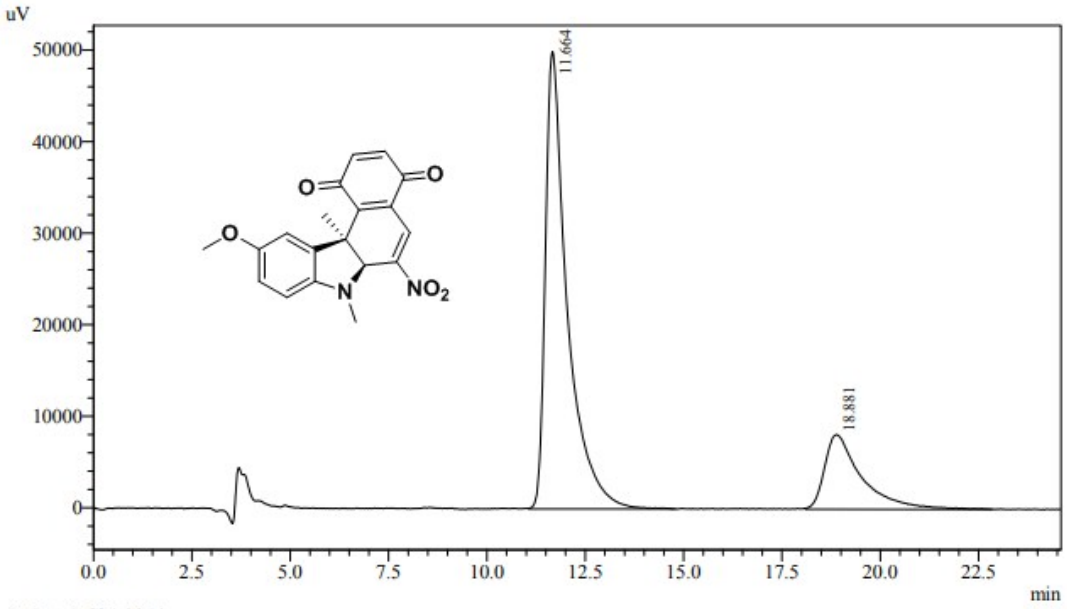
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.493	1657319	41845	18.134	23.197
2	11.339	7481962	138549	81.866	76.803
Total		9139281	180394	100.000	100.000

10-methoxy-7,11b-dimethyl-6-nitro-7,11b-dihydro-1H-benzo[c]carbazole-1,4(6aH)-dione (**3k**)



Detector A Ch1 254nm

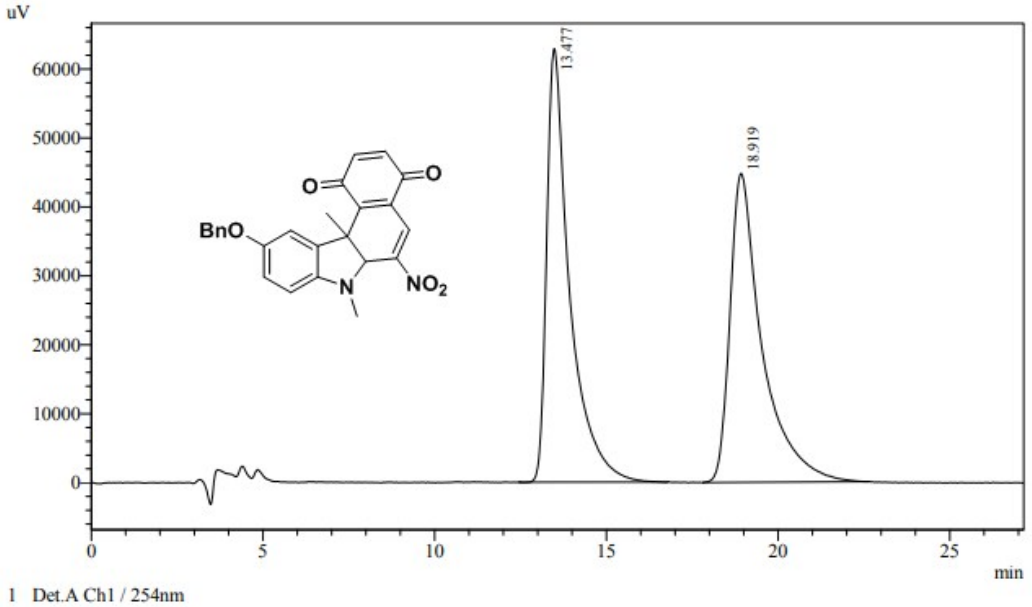
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.307	11580811	309655	50.188	63.793
2	18.130	11494076	175754	49.812	36.207
Total		23074887	485409	100.000	100.000



Detector A Ch1 254nm

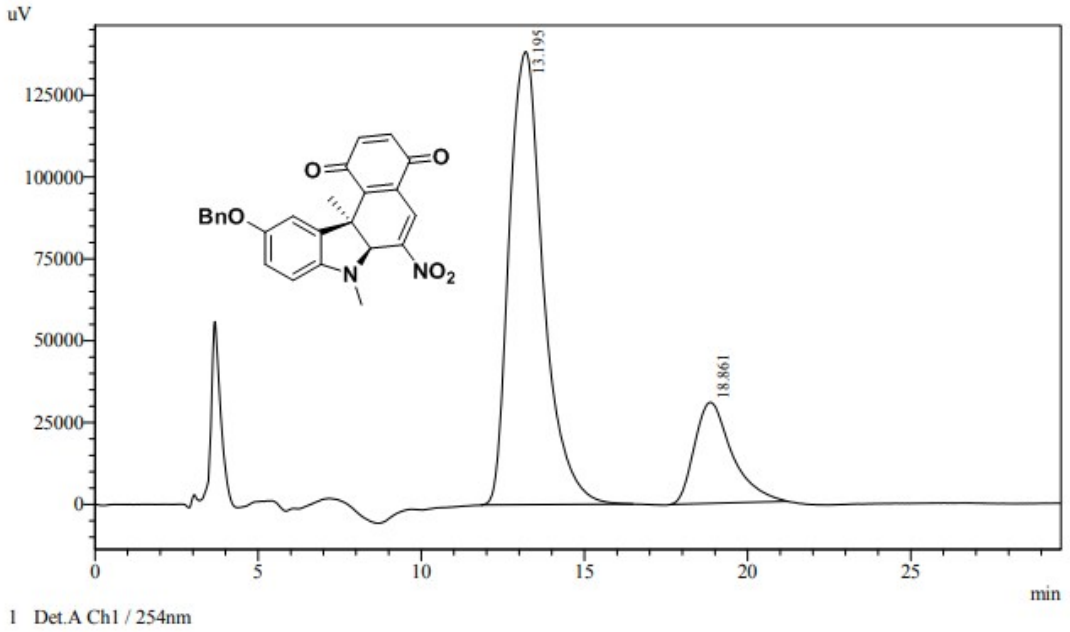
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.664	1931369	49949	78.429	85.959
2	18.881	531193	8159	21.571	14.041
Total		2462562	58108	100.000	100.000

10-(benzyloxy)-7,11b-dimethyl-6-nitro-7,11b-dihydro-1H-benzo[c]carbazole-1,4(6aH)-dione (**3l**)



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.477	2924468	62872	50.152	58.388
2	18.919	2906743	44808	49.848	41.612
Total		5831211	107680	100.000	100.000

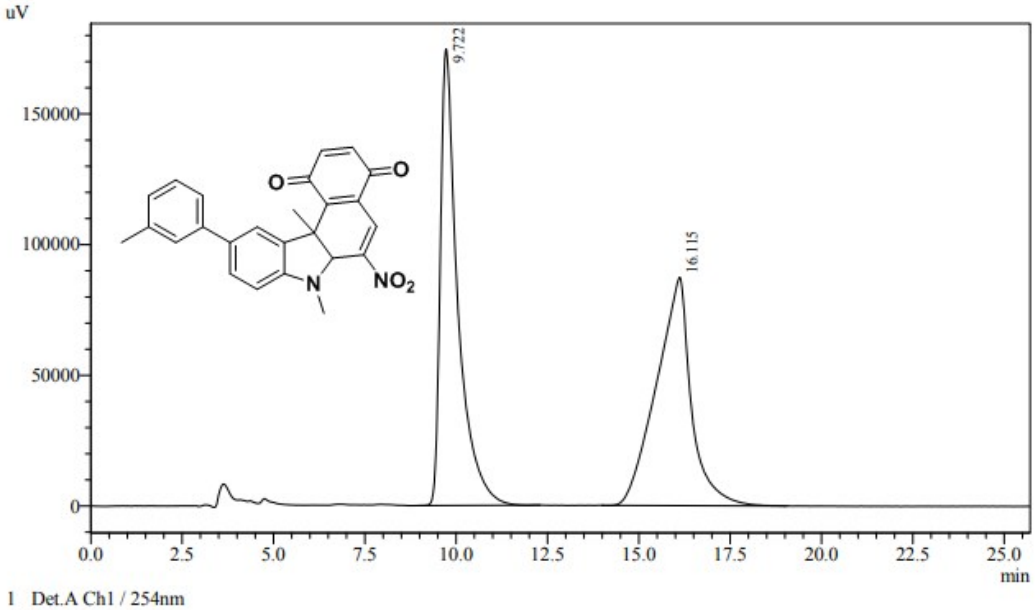


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.195	10087525	138391	80.330	81.768
2	18.861	2470037	30858	19.670	18.232
Total		12557562	169248	100.000	100.000

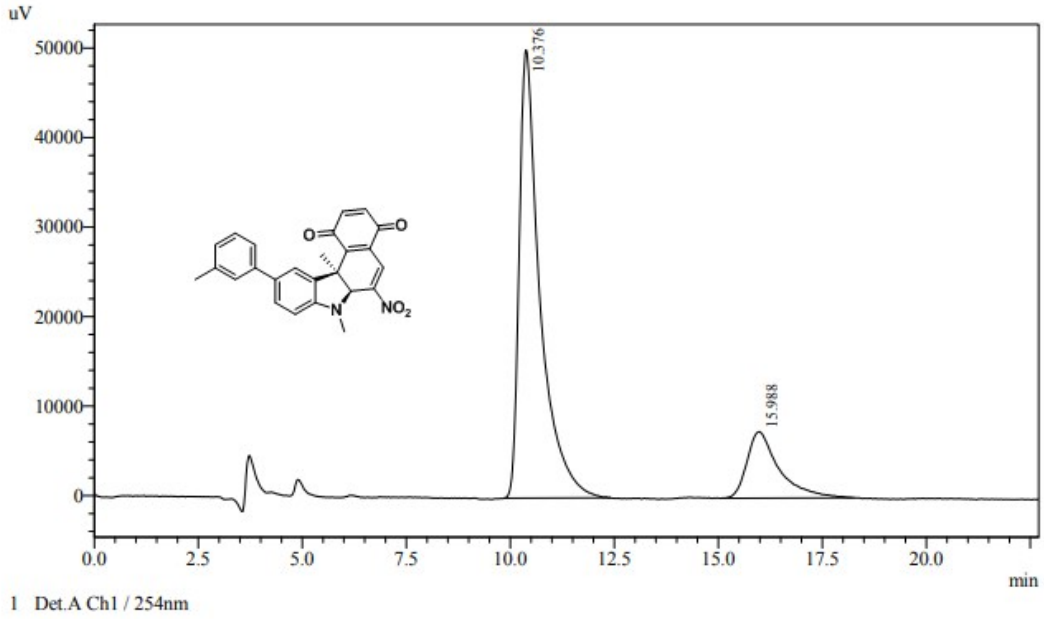
7,11b-dimethyl-6-nitro-10-(m-tolyl)-7,11b-dihydro-1H-ben-zo[c]carbazole-1,4(6aH)-dione (**3m**)



1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

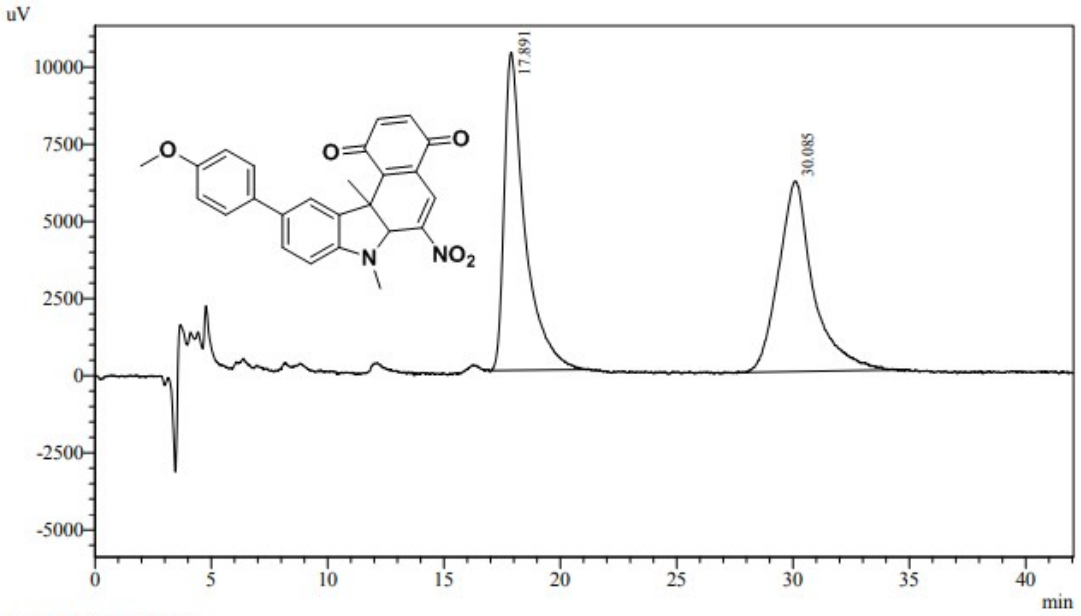
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.722	5817680	174636	50.097	66.663
2	16.115	5795178	87332	49.903	33.337
Total		11612858	261968	100.000	100.000



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.376	1742331	50042	81.452	87.074
2	15.988	396747	7429	18.548	12.926
Total		2139078	57471	100.000	100.000

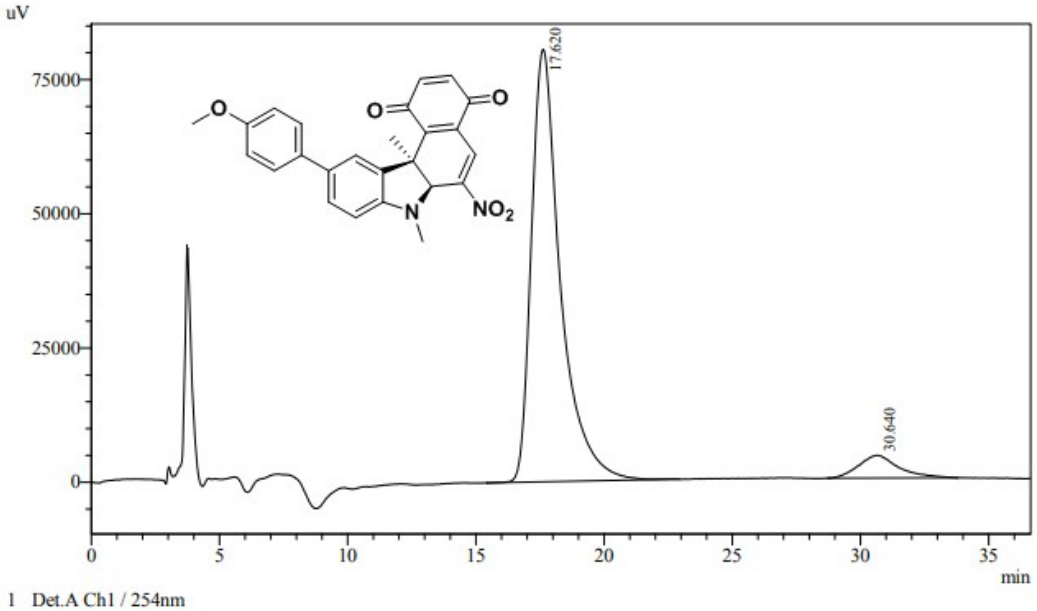
10-(4-methoxyphenyl)-7,11b-dimethyl-6-nitro-7,11b-dihy-dro-1H-benzo[c]carb-azole-1,4(6aH)-dione (**3n**)



1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.891	635625	10304	49.798	62.521
2	30.085	640770	6177	50.202	37.479
Total		1276396	16481	100.000	100.000

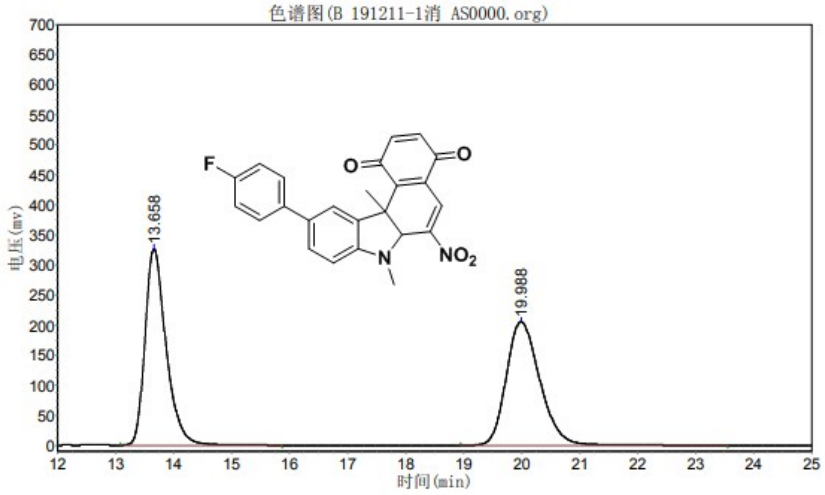


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

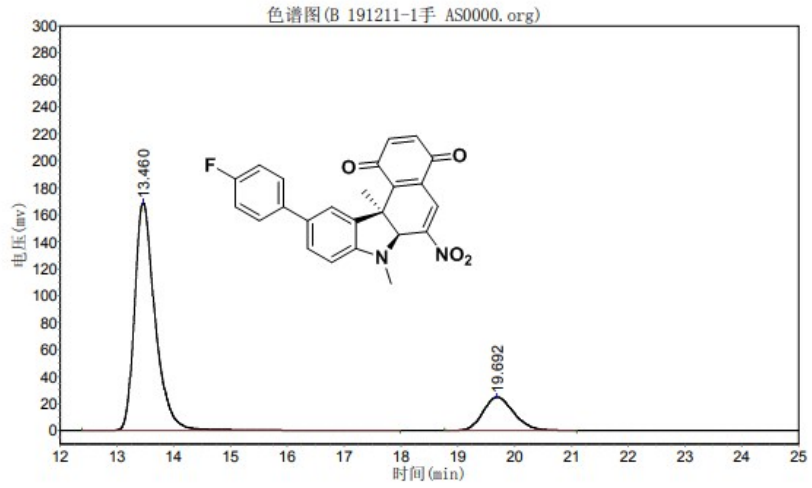
Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.620	6339612	80537	93.240	95.012
2	30.640	459609	4228	6.760	4.988
Total		6799221	84765	100.000	100.000

10-(4-fluorophenyl)-7,11b-dimethyl-6-nitro-7,11b-dihydro-1H-benzo[c]carbzole-1,4(6aH)-dione (**3o**)



分析结果表

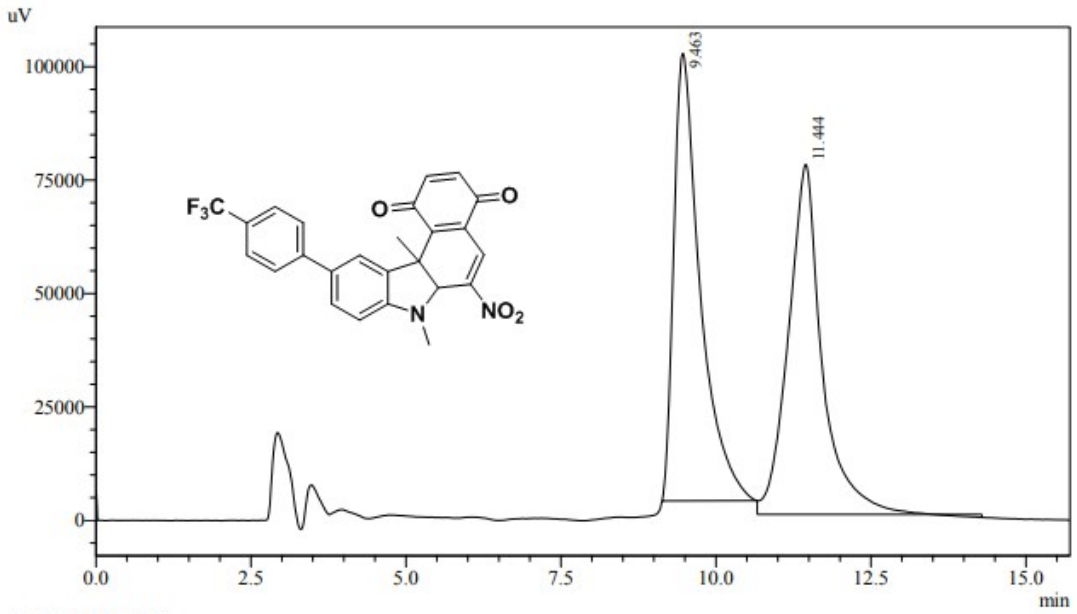
峰号	峰名	保留时间	峰高	峰面积	含量
1		13.658	326499.781	8225915.000	49.9052
2		19.988	205685.391	8257153.000	50.0948
总计			532185.172	16483068.000	100.0000



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		13.460	168782.953	4259817.500	82.1246
2		19.692	24644.600	927202.563	17.8754
总计			193427.553	5187020.063	100.0000

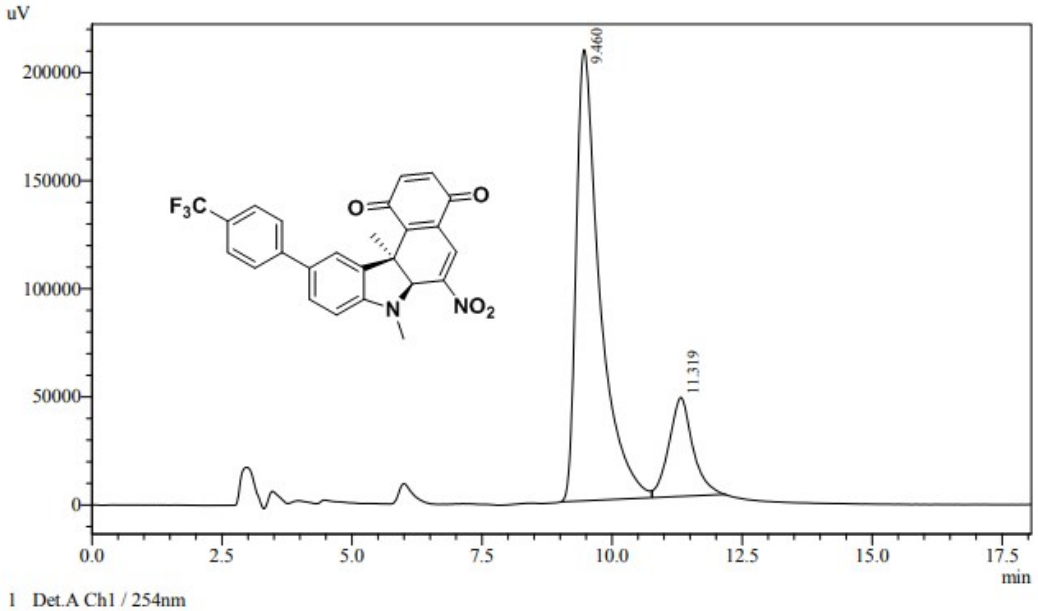
7,11b-dimethyl-6-nitro-10-(4-(trifluoromethyl)phenyl)7,11b-dihydro-1H-benzo-[c]carbazole-1,4(6aH)-dione (**3p**)



1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.463	2923044	98594	50.150	56.105
2	11.444	2905513	77136	49.850	43.895
Total		5828557	175730	100.000	100.000

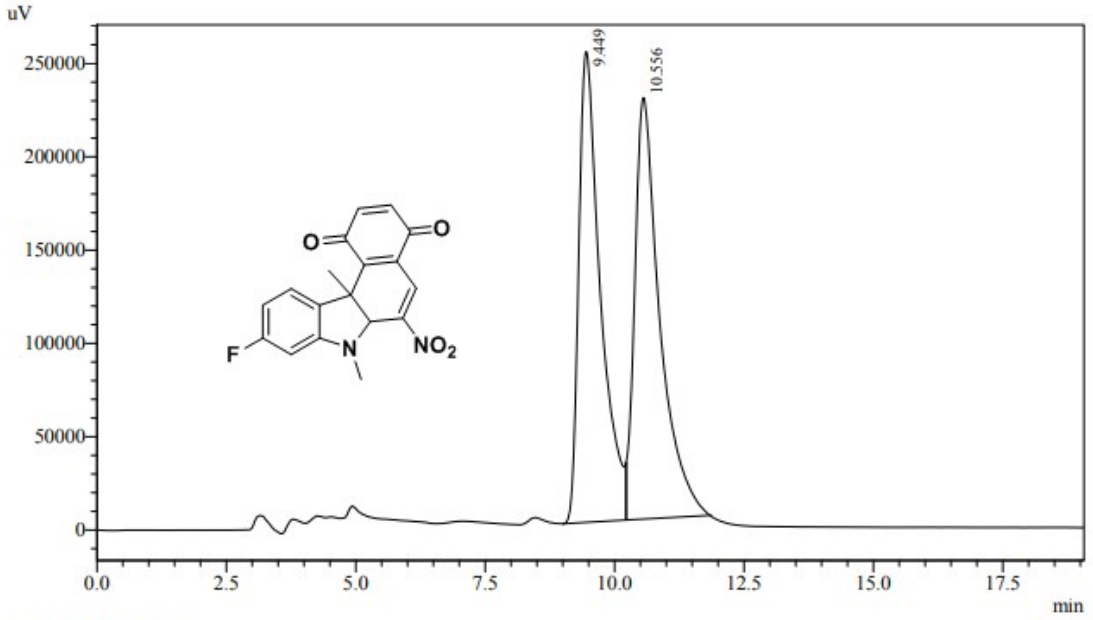


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

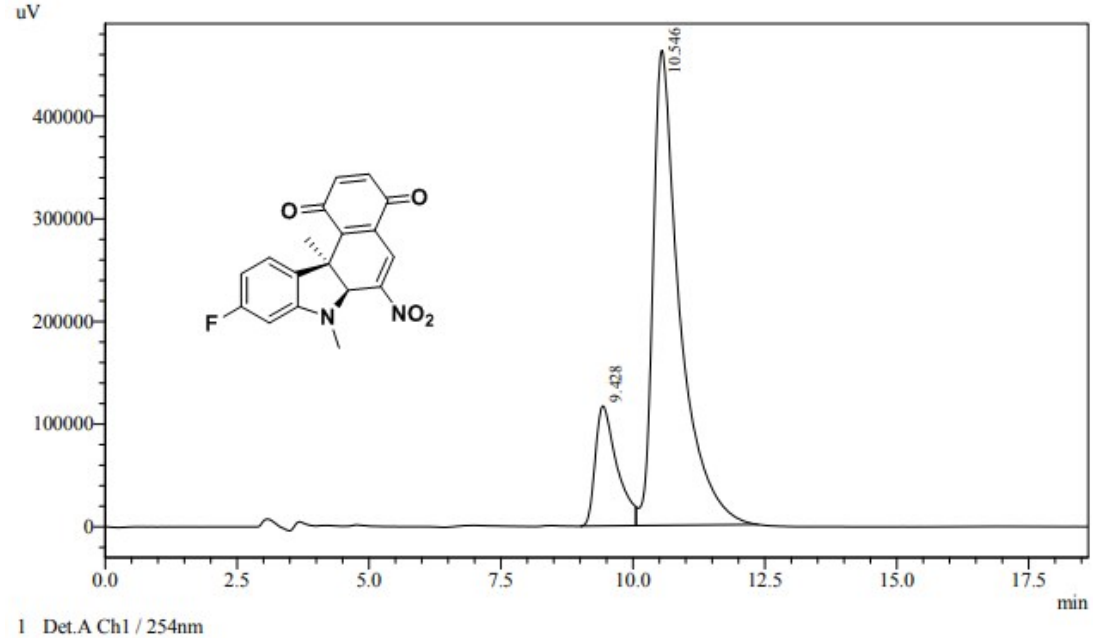
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.460	6589508	208622	81.808	82.021
2	11.319	1465322	45729	18.192	17.979
Total		8054830	254351	100.000	100.000

9-fluoro-7,11b-dimethyl-6-nitro-7,11b-dihydro-1H-benzo[c]carbazole-1,4(6aH)-dione (**3q**)



Detector A Ch1 254nm

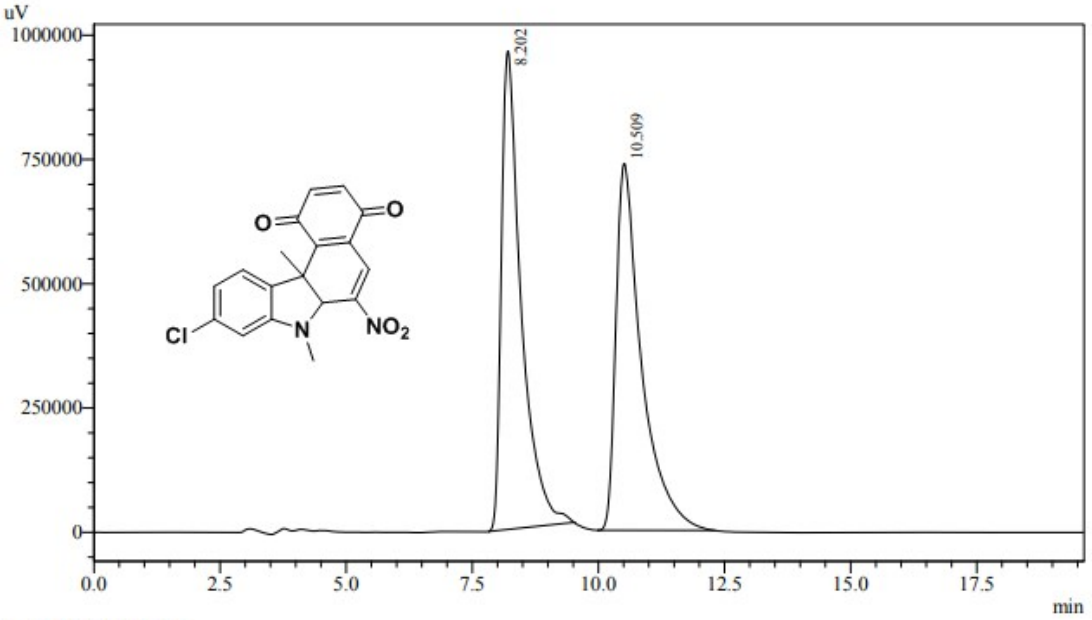
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.449	7383225	252216	49.251	52.754
2	10.556	7607748	225880	50.749	47.246
Total		14990972	478095	100.000	100.000



Detector A Ch1 254nm

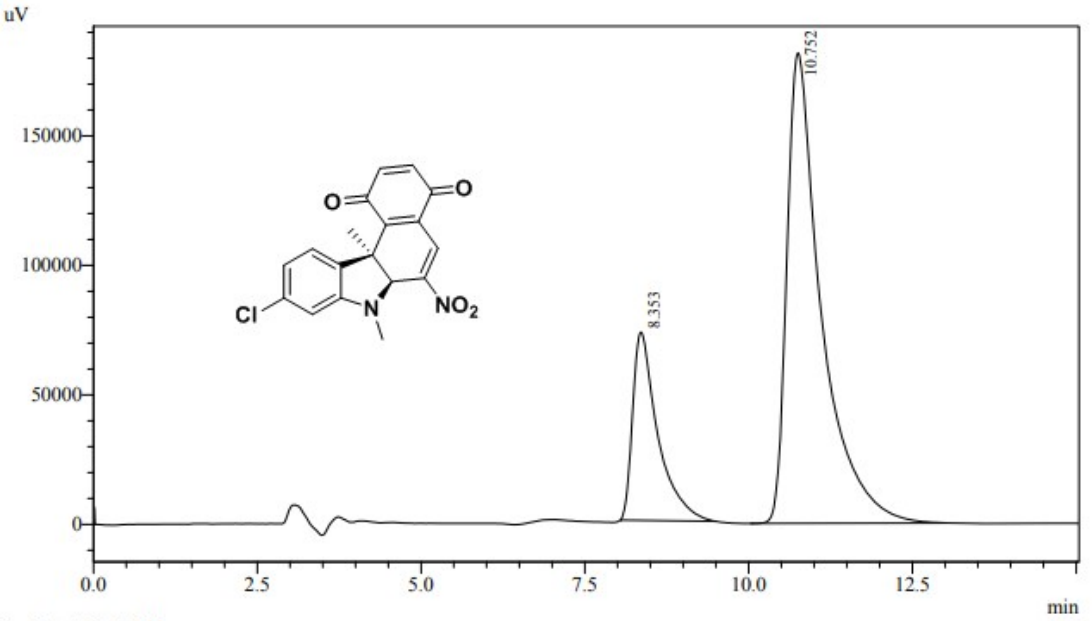
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.428	3330852	116864	16.903	20.161
2	10.546	16375320	462780	83.097	79.839
Total		19706171	579643	100.000	100.000

9-chloro-7,11b-dimethyl-6-nitro-7,11b-dihydro-1H-benzo[c]carbazole-1,4(6aH)-dione (**3r**)



Detector A Ch1 254nm

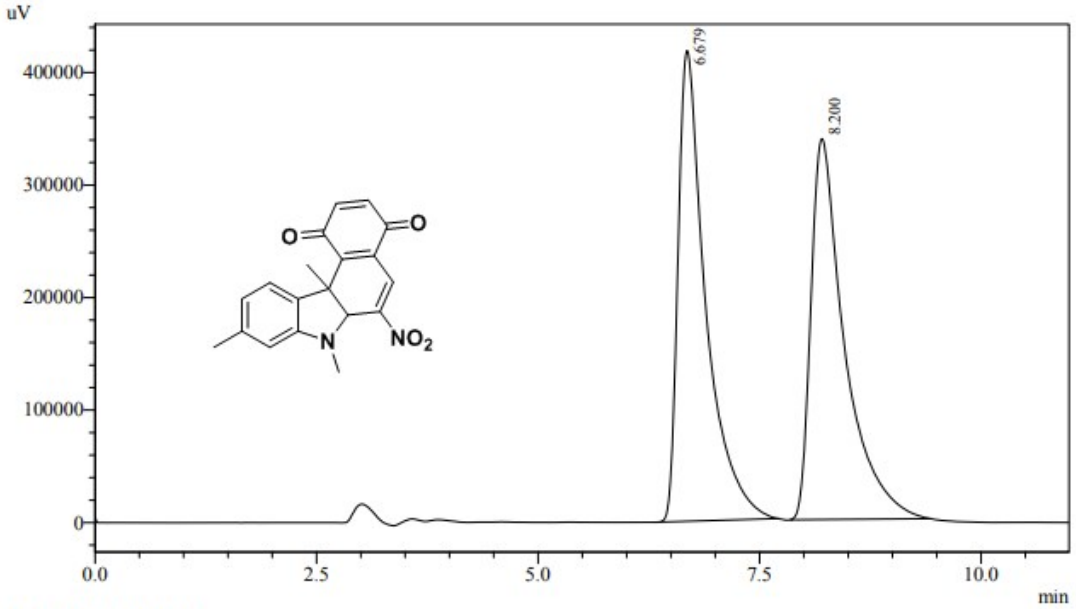
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.202	26341725	962118	50.260	56.589
2	10.509	26069668	738057	49.740	43.411
Total		52411393	1700175	100.000	100.000



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.353	1933202	72674	22.532	28.583
2	10.752	6646491	181578	77.468	71.417
Total		8579693	254252	100.000	100.000

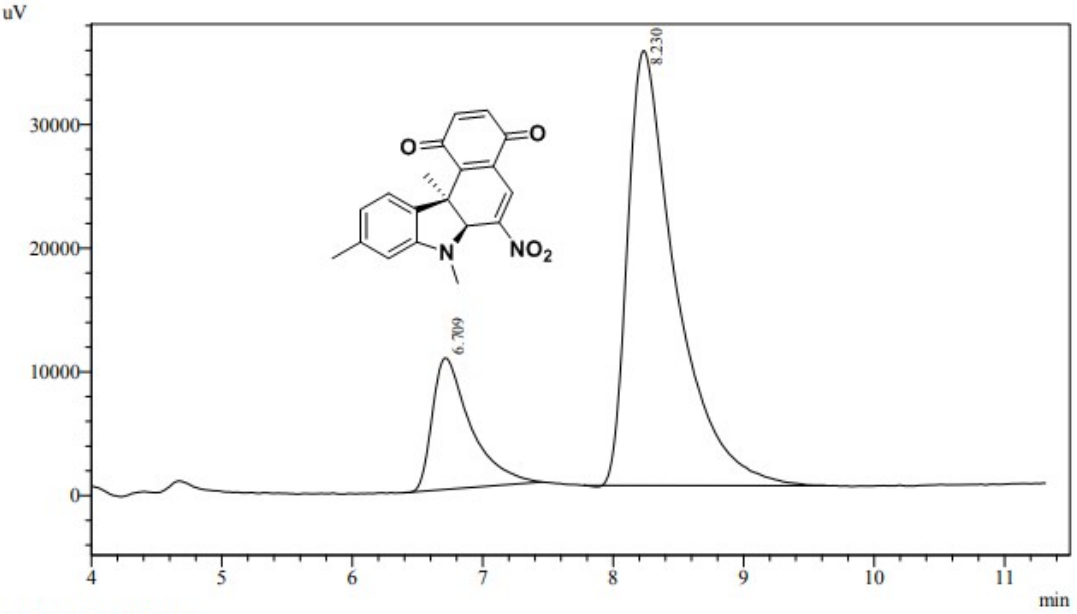
7,9,11b-trimethyl-6-nitro-7,11b-dihydro-1H-benzo[c]carbazole-1,4(6aH)-dione (**3s**)



1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.679	9103044	418241	50.472	55.283
2	8.200	8932742	338303	49.528	44.717
Total		18035786	756544	100.000	100.000

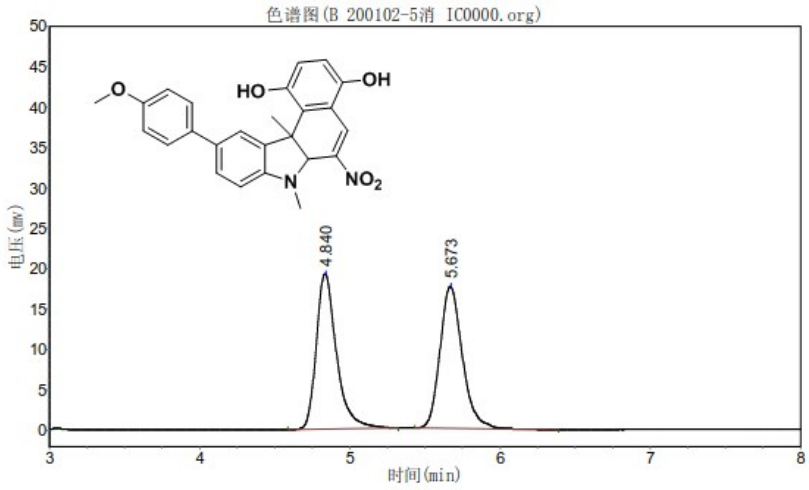


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

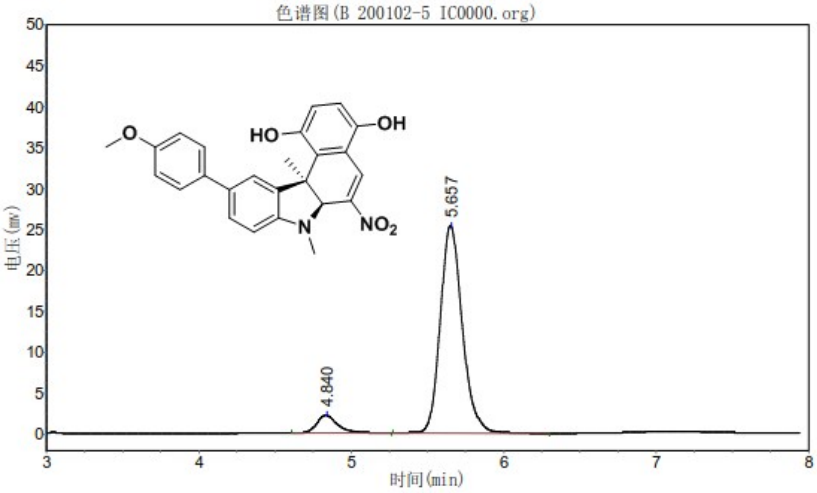
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.709	216509	10630	19.326	23.217
2	8.230	903801	35155	80.674	76.783
Total		1120311	45785	100.000	100.000

10-(4-methoxyphenyl)-7,11b-dimethyl-6-nitro-6a,11b-dihydro-7H-benzo[c] carbazole-1,4-diol (**4**)



分析结果表

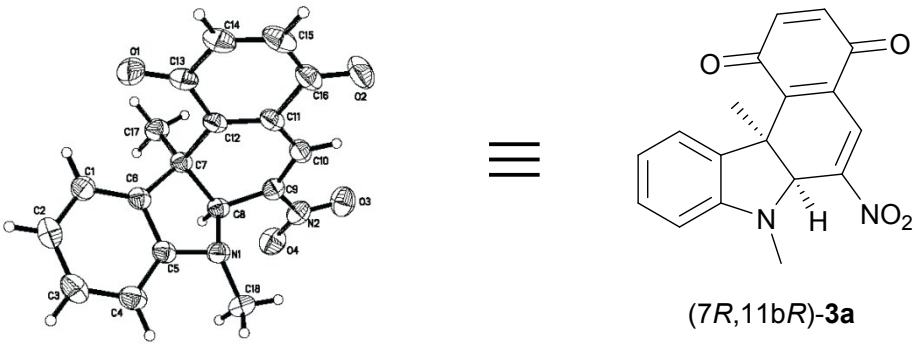
峰号	峰名	保留时间	峰高	峰面积	含量
1		4.840	19119.227	179243.406	49.6302
2		5.673	17515.322	181914.297	50.3698
总计			36634.549	361157.703	100.0000



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		4.840	2121.899	19954.449	7.2894
2		5.657	25287.219	253790.500	92.7106
总计			27409.117	273744.949	100.0000

Crystal data and structure of (7*R*, 11b*R*)-3a



(7*R*,11b*R*)-**3a**

Table 1 Crystal data and structure refinement for 20190366.

Identification code	20190366
Empirical formula	$C_{18}H_{14}N_2O_4$
Formula weight	322.31
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	8.8208(5)
b/Å	11.9769(12)
c/Å	14.7126(9)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1554.3(2)
Z	4
ρ_{calc}g/cm^3	1.377
μ/mm^{-1}	0.821
F(000)	672.0
Crystal size/mm^3	0.21 × 0.15 × 0.13
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.522 to 141.864
Index ranges	-6 ≤ h ≤ 10, -13 ≤ k ≤ 14, -17 ≤ l ≤ 17
Reflections collected	5902
Independent reflections	2927 [R_{int} = 0.0251, R_{sigma} = 0.0336]
Data/restraints/parameters	2927/0/219

Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0434, wR_2 = 0.1111
Final R indexes [all data]	R_1 = 0.0493, wR_2 = 0.1181
Largest diff. peak/hole / e $Å^{-3}$	0.13/-0.18
Flack parameter	-0.1(2)

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 20190366. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ}tensor.

Atom	*x*	*y*	*z*	U(eq)
C1	3616(3)	3537(3)	6803(2)	56.7(7)
C2	2777(4)	2567(3)	6692(3)	66.1(9)
C3	2337(4)	2218(3)	5836(3)	70.3(9)
C4	2729(4)	2820(3)	5069(2)	62.8(8)
C5	3575(3)	3791(3)	5177(2)	49.0(6)
C6	4018(3)	4148(2)	6041(2)	46.7(6)
C7	4857(3)	5258(2)	5944.1(19)	45.2(6)
C8	4276(3)	5610(2)	4983.4(19)	46.0(6)
C9	5362(3)	6345(3)	4490(2)	50.3(6)
C10	6853(3)	6258(3)	4586(2)	55.2(7)
C11	7461(3)	5515(3)	5274(2)	51.9(7)
C12	6580(3)	5075(2)	5930(2)	48.5(6)
C13	7317(4)	4495(3)	6707(2)	62.2(8)
C14	8943(4)	4219(3)	6625(3)	72.5(10)
C15	9785(4)	4622(4)	5968(3)	75.6(11)
C16	9147(4)	5355(3)	5278(3)	64.9(9)
C17	4456(4)	6144(3)	6661(2)	59.2(8)
C18	3272(4)	4547(3)	3638(2)	68.9(9)
N1	4065(3)	4533(2)	4513.1(16)	50.5(6)
N2	4743(4)	7175(2)	3859.0(19)	62.2(7)
O1	6638(3)	4271(3)	7401.8(18)	89.2(10)
O2	9936(3)	5836(3)	4718(2)	90.1(9)
O3	5616(4)	7719(2)	3395(2)	85.6(8)
O4	3359(3)	7288(2)	3843.0(18)	79.7(8)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 20190366. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	47.4(16)	65.9(19)	56.9(16)	1.3(15)	0.7(13)	3.3(14)
C2	58.8(18)	60.1(19)	79(2)	9.1(16)	11.8(18)	0.1(15)
C3	60.8(19)	55.4(18)	95(3)	-9.4(19)	12(2)	-9.2(16)
C4	55.1(17)	63.3(19)	70.2(19)	-17.4(17)	0.0(16)	-5.1(16)
C5	36.9(12)	53.6(15)	56.6(15)	-8.4(13)	1.3(11)	3.5(12)
C6	31.4(11)	53.8(14)	55.1(15)	-4.0(13)	0.9(12)	5.9(12)
C7	34.7(12)	52.7(15)	48.2(14)	-4.7(12)	-2.1(11)	3.8(11)
C8	36.1(12)	52.2(15)	49.9(14)	-6.2(12)	-2.9(11)	7.1(11)
C9	53.1(16)	48.3(14)	49.3(14)	-4.5(12)	0.1(12)	5.4(13)
C10	49.9(16)	56.3(16)	59.5(16)	-6.0(14)	7.2(13)	-6.8(14)
C11	37.9(13)	54.3(15)	63.4(17)	-10.2(14)	-0.9(13)	-1.6(12)
C12	36.3(13)	53.1(15)	56.3(15)	-10.1(13)	-4.9(13)	-0.2(12)
C13	45.8(16)	71(2)	70.0(19)	-1.9(17)	-15.0(16)	-1.4(16)
C14	45.5(17)	79(2)	93(2)	0(2)	-19.5(18)	3.4(17)
C15	36.3(15)	81(2)	109(3)	-12(2)	-10.8(19)	7.5(16)
C16	40.3(15)	70(2)	84(2)	-15.1(18)	6.0(16)	-3.0(15)
C17	55.1(16)	64.9(19)	57.4(16)	-14.2(15)	0.7(14)	3.5(15)
C18	74(2)	81(2)	51.6(17)	-10.0(16)	-10.0(16)	-8(2)
N1	43.8(12)	58.0(14)	49.6(12)	-8.4(11)	-2.0(10)	0.7(12)
N2	76.5(19)	54.6(14)	55.5(14)	-3.9(13)	0.5(14)	8.5(14)
O1	60.5(14)	138(3)	69.4(15)	26.2(17)	-12.5(13)	2.5(17)
O2	47.9(13)	114(2)	108(2)	0.5(19)	20.0(14)	-6.3(15)
O3	104(2)	72.0(16)	80.5(17)	19.3(14)	9.7(16)	-1.1(17)
O4	77.1(17)	85.8(18)	76.1(16)	9.9(15)	-9.0(14)	24.2(15)

Table 4 Bond Lengths for 20190366.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.387(5)	C9	N2	1.465(4)
C1	C6	1.384(4)	C10	C11	1.449(5)

C2	C3	1.383(6)	C11	C12	1.347(4)
C3	C4	1.383(5)	C11	C16	1.499(4)
C4	C5	1.391(4)	C12	C13	1.488(4)
C5	C6	1.397(4)	C13	C14	1.476(5)
C5	N1	1.389(4)	C13	O1	1.215(4)
C6	C7	1.529(4)	C14	C15	1.311(6)
C7	C8	1.561(4)	C15	C16	1.456(6)
C7	C12	1.536(4)	C16	O2	1.222(5)
C7	C17	1.537(4)	C18	N1	1.466(4)
C8	C9	1.490(4)	N2	O3	1.219(4)
C8	N1	1.475(4)	N2	O4	1.228(4)
C9	C10	1.327(4)			

Table 5 Bond Angles for 20190366.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom
C6	C1	C2	118.9(3)	C9	C10	C11
C3	C2	C1	120.6(3)	C10	C11	C16
C4	C3	C2	121.0(3)	C12	C11	C10
C3	C4	C5	118.5(3)	C12	C11	C16
C4	C5	C6	120.6(3)	C11	C12	C7
N1	C5	C4	128.4(3)	C11	C12	C13
N1	C5	C6	110.9(3)	C13	C12	C7
C1	C6	C5	120.3(3)	C14	C13	C12
C1	C6	C7	131.2(3)	O1	C13	C12
C5	C6	C7	108.4(3)	O1	C13	C14
C6	C7	C8	99.2(2)	C15	C14	C13
C6	C7	C12	110.9(2)	C14	C15	C16
C6	C7	C17	115.2(2)	C15	C16	C11
C12	C7	C8	110.5(2)	O2	C16	C11
C12	C7	C17	109.6(2)	O2	C16	C15
C17	C7	C8	111.1(2)	C5	N1	C8
C9	C8	C7	112.9(2)	C5	N1	C18

N1	C8	C7	103.3(2)	C18	N1	C8
N1	C8	C9	111.7(2)	O3	N2	C9
C10	C9	C8	122.6(3)	O3	N2	O4
C10	C9	N2	119.4(3)	O4	N2	C9
N2	C9	C8	118.0(3)			

Table 6 Torsion Angles for 20190366.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1	C2	C3	C4	0.5(6)	C8	C9	N2	O4	7.1(4)
C1	C6	C7	C8	-157.5(3)	C9	C8	N1	C5	156.6(2)
C1	C6	C7	C12	86.2(4)	C9	C8	N1	C18	-68.7(3)
C1	C6	C7	C17	-38.9(4)	C9	C10	C11	C12	-13.0(5)
C2	C1	C6	C5	0.3(4)	C9	C10	C11	C16	173.3(3)
C2	C1	C6	C7	176.7(3)	C10	C9	N2	O3	4.5(5)
C2	C3	C4	C5	-0.3(5)	C10	C9	N2	O4	-174.5(3)
C3	C4	C5	C6	0.1(5)	C10	C11	C12	C7	5.1(4)
C3	C4	C5	N1	-178.5(3)	C10	C11	C12	C13	-168.8(3)
C4	C5	C6	C1	-0.1(4)	C10	C11	C16	C15	179.4(3)
C4	C5	C6	C7	-177.3(3)	C10	C11	C16	O2	-0.3(5)
C4	C5	N1	C8	155.3(3)	C11	C12	C13	C14	-12.8(5)
C4	C5	N1	C18	21.0(5)	C11	C12	C13	O1	165.5(4)
C5	C6	C7	C8	19.2(3)	C12	C7	C8	C9	-36.3(3)
C5	C6	C7	C12	-97.0(3)	C12	C7	C8	N1	84.6(3)
C5	C6	C7	C17	137.8(3)	C12	C11	C16	C15	5.6(5)
C6	C1	C2	C3	-0.5(5)	C12	C11	C16	O2	-174.1(3)
C6	C5	N1	C8	-23.4(3)	C12	C13	C14	C15	11.1(6)
C6	C5	N1	C18	-157.7(3)	C13	C14	C15	C16	-0.8(6)
C6	C7	C8	C9	-152.8(2)	C14	C15	C16	C11	-7.7(6)
C6	C7	C8	N1	-32.0(2)	C14	C15	C16	O2	171.9(4)
C6	C7	C12	C11	128.9(3)	C16	C11	C12	C7	178.5(3)
C6	C7	C12	C13	-57.3(3)	C16	C11	C12	C13	4.6(4)
C7	C8	C9	C10	32.7(4)	C17	C7	C8	C9	85.6(3)
C7	C8	C9	N2	-148.8(3)	C17	C7	C8	N1	-153.6(2)
C7	C8	N1	C5	34.9(3)	C17	C7	C12	C11	-102.9(3)
C7	C8	N1	C18	169.6(2)	C17	C7	C12	C13	70.9(4)

C7	C12	C13	C14	173.2(3)	N1	C5	C6	C1	178.7(3)
C7	C12	C13	O1	-8.6(5)	N1	C5	C6	C7	1.5(3)
C8	C7	C12	C11	19.8(4)	N1	C8	C9	C10	-83.2(4)
C8	C7	C12	C13	-166.3(3)	N1	C8	C9	N2	95.2(3)
C8	C9	C10	C11	-7.6(5)	N2	C9	C10	C11	174.1(3)
C8	C9	N2	O3	-174.0(3)	O1	C13	C14	C15	-167.2(4)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 20190366.

Atom	*x*	*y*	*z*	U(eq)
H1	3905	3774	7380	68
H2	2508	2148	7199	79
H3	1767	1569	5775	84
H4	2435	2581	4494	75
H8	3297	5989	5042	55
H10	7501	6669	4217	66
H14	9381	3746	7052	87
H15	10808	4436	5943	91
H17A	4912	6843	6497	89
H17B	4831	5911	7243	89
H17C	3375	6230	6690	89
H18A	2234	4759	3730	103
H18B	3312	3817	3369	103
H18C	3752	5076	3240	103