Supporting Information

for

Asymmetric Diels–Alder Reaction of 3-Vinylindoles and Nitroolefins Promoted by Multiple Hydrogen Bonds

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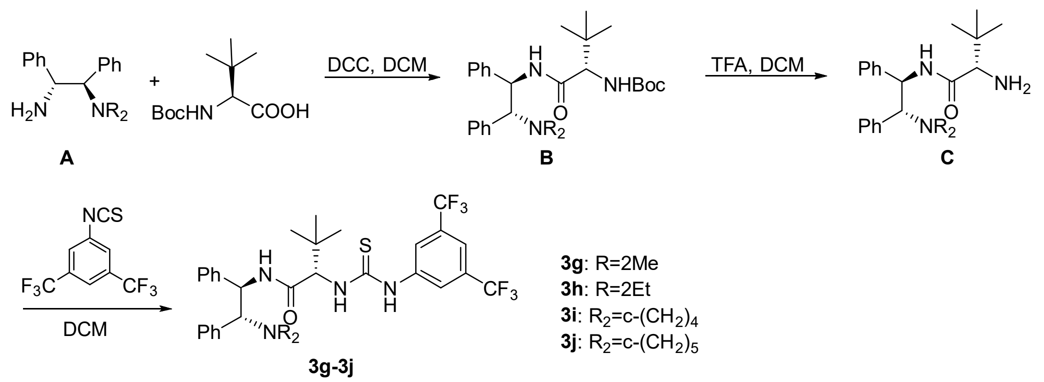
1. General data

Unless otherwise noted, commercial reagents were used as received.All reactions were monitored by TLC with silica gel coated plates. ^{1}H NMR (600 MHz) and^{13}C NMR (150 MHz) spectra were recorded on Bruker Avance 600 MHz spectrometer. Chemical shifts (δ) are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard. Proton gsignal multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad) or a combination of them. *J*-values are in Hz. Enantiomer ratios were determined by HPLC with chiral columns(Chiralpak AD-H, IC-H, IA-H, OD-H columns were purchased from Daicel Chemical Industries, LTD.). Optical rotations were determined at λ = 589 nm (sodium D line) by using a Perkin-Elmer-341 polarimeter.

2. Catalyst synthesis.

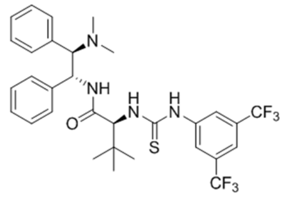


N,N'-dicyclohexylcarbodiimide (3.75 mmol, 1.25 eq.) was added to a solution of dry CH_2Cl_2 (10.0 mL) containing *N*-Boc-*L*-tert-Leucine (3.6 mmol, 1.2 eq.) at 0°C. The mixture was stirred for 30 minand then compound **A**[1] (3.0 mmol, 1.0 eq.**)** was added to the solution. The mixture was warmed to room temperature and stirred for additional 24 h. The solid formed was filtrated and washed with CH_2Cl_2 and the combined filtrate was concentrated and purified by flash chromatography on silica gel to afford the desired product **B** (88% - 95% yield).

Compound **B** (2.5 mmol, 1.0 eq.) was added to CH_2Cl_2 (5.0 mL) at 0°C, then a solution of CH_2Cl_2 (5.0 mL) containing trifluoroacetic acid (50.0 mmol, 20.0 eq.) was added dropwise. The mixture was warmed to room temperature and stirred for 12h. Aqueous $NaHCO_3$ was added to it until the pH to alkaline. The resulting mixture was then extracted with dichloromethane (30.0 mL x 3), and the organic extracts were combined, dried over Na_2SO_4, filtered, concentrated and purified by flash chromatography on silica gel to afford the desired product **C** (94% - 99% yield).

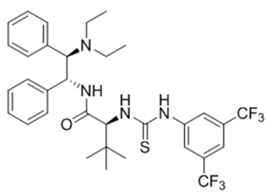
Compound **C** (2.0 mmol, 1.0 eq.) was dissolved in CH_2Cl_2 (10.0 mL) at room temperature and was treated with 3,5-bis(trifluoromethyl)phenyl isothiocyanate (2.4 mmol, 1.2 eq.). After stirring for 2 h, the reaction mixture was concentrated under reduced pressure and subjected to flash chromatographic separation to afford product **3g-3j** (94% - 98% yield) as a white solid.

(*S*)-2-(3-(3,5-bis(trifluoromethyl)phenyl)thioureido)-*N*-((1*R*,2*R*)-2-(dimethylamino)-1,2-diphenylethyl)-3,3-dimethylbutanamide (3g)



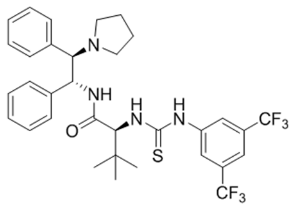
According to the general procedure, the title compound was obtained by silica-gel column chromatography (petroleum ether/ethyl acetate = 5:1); white solid; m.p. 123-124 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 9.10 (s, 1H), 8.07 (s, 2H), 7.94 (s, 2H), 7.62 (s, 1H), 7.23 – 7.17 (m, 3H), 7.12 – 7.00 (m, 5H), 6.94 (d, *J* = 3.5 Hz, 2H), 5.09 (s, 1H), 4.89 (d, *J* = 10.5 Hz, 1H), 3.74 (d, *J* = 10.3 Hz, 1H), 2.17 (s, 6H), 0.92 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ=182.03, 172.38, 140.64, 139.95, 132.02, 131.79, 131.57, 131.36, 129.56, 127.88, 127.80, 127.50, 126.97, 125.88, 124.07, 123.21, 122.26, 120.45, 117.85, 73.23, 66.26, 55.92, 40.44, 34.80, 27.22, 26.92; HRMS(ESI): calcd. for $C_{31}H_{35}F_6N_4OS$ $(M+H)^+$: 625.2430, found: 625.2437.

(*S*)-2-(3-(3,5-bis(trifluoromethyl)phenyl)thioureido)-*N*-((1*R*,2*R*)-2-(diethylamino)-1,2-diphenylethyl)-3,3-dimethylbutanamide (3h)



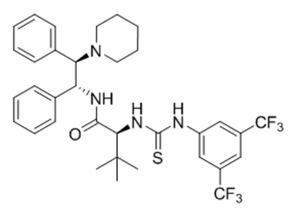
According to the general procedure, the title compound was obtained by silica-gel column chromatography (petroleum ether/ethyl acetate = 10:1);white solid; m.p.210-212 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.74 (s, 1H), 8.00 (s, 1H), 7.88 (s, 2H), 7.77 (s, 1H), 7.37 (s, 1H), 7.00 (s, 3H), 6.85 (s, 3H), 6.79 (s, 4H), 4.91 (d, *J* = 8.5 Hz, 1H), 4.65 (d, *J* = 10.8 Hz, 1H), 3.71 (d, *J* = 10.9 Hz, 1H), 2.53 (dd, *J* = 11.9, 6.5 Hz, 2H), 1.96 (dd, *J* = 11.8, 6.0 Hz, 2H), 1.00 (d, *J* = 6.2 Hz, 6H), 0.68 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 181.83, 172.09, 140.71, 140.45, 133.38, 131.60, 131.38, 129.43, 127.94, 127.90, 127.81, 127.30, 126.86, 124.11, 122.44, 122.30, 117.40, 68.41, 66.28, 56.04, 42.90, 34.69, 27.34, 14.13; HRMS(ESI): calcd. for $C_{33}H_{39}F_6N_4OS$ $(M+H)^+$: 653.2743, found: 653.2746.

(*S*)-2-(3-(3,5-bis(trifluoromethyl)phenyl)thioureido)-*N*-((1*R*,2*R*)-1,2-diphenyl-2-(pyrrolidin-1-yl)ethyl)-3,3-dimethylbutanamide (3i)



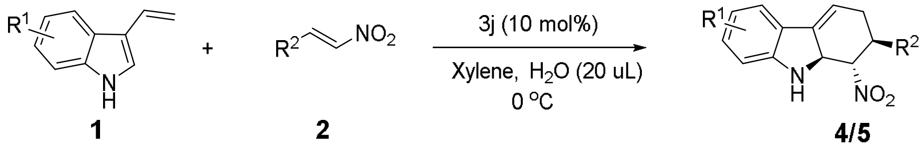
According to the general procedure, the title compound was obtained by silica-gel column chromatography (petroleum ether/ethyl acetate = 5:1); white solid; m.p.101-102 °C; ^{1}H NMR (600 MHz, DMSO-d6) δ = 10.45 (s, 1H), 8.60 (d, *J* = 7.0 Hz, 1H), 8.39 (s, 2H), 8.10 (d, *J* = 8.9 Hz, 1H), 7.74 (s, 1H), 7.24 (d, *J* = 7.6 Hz, 2H), 7.15 (t, *J* = 7.4 Hz, 2H), 7.10 (t, *J* = 8.5 Hz, 5H), 7.03 (t, *J* = 7.3 Hz, 1H), 5.36 (t, *J* = 7.3 Hz, 1H), 5.00 (d, *J* = 7.4 Hz, 1H), 4.03 (dd, *J* = 19.7, 8.2 Hz, 1H), 2.41 (s, 2H), 2.34 (s, 2H), 1.53 (s, 4H), 0.89 (s, 9H); ^{13}C NMR (151 MHz, DMSO-d6) δ = 181.18, 169.55, 142.50, 141.72, 136.80, 131.02, 130.80, 130.59, 129.69, 128.37, 127.91, 127.18, 126.82, 126.43, 124.62, 122.81, 121.99, 121.00, 116.57, 69.95, 64.56, 55.25, 49.26, 35.46, 27.09, 23.01; HRMS(ESI): calcd. for $C_{33}H_{37}F_6N_4OS$ $(M+H)^+$: 651.2587, found:651.2580.

(*S*)-2-(3-(3,5-bis(trifluoromethyl)phenyl)thioureido)-*N*-((1*R*,2*R*)-1,2-diphenyl-2-(piperidin-1-yl)ethyl)-3,3-dimethylbutanamide (3j)



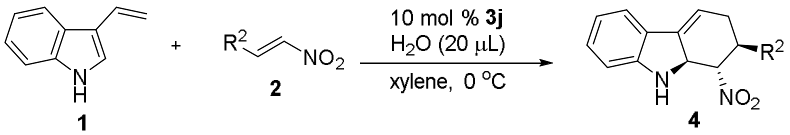
According to the general procedure, the title compound was obtained by silica-gel column chromatography (petroleum ether/ethyl acetate = 5:1); white solid; m.p.165-166 °C; ^{1}H NMR (600 MHz, DMSO-d6) δ = 10.45 (s, 1H), 8.59 (d, *J* = 7.8 Hz, 1H), 8.34 (s, 2H), 8.15 (d, *J* = 9.4 Hz, 1H), 7.72 (s, 1H), 7.27 (d, *J* = 7.5 Hz, 2H), 7.18 (t, *J* = 7.4 Hz, 2H), 7.09 (dt, *J* = 22.7, 7.4 Hz, 5H), 6.99 (t, *J* = 7.3 Hz, 1H), 5.50 (dd, *J* = 11.2, 8.3 Hz, 1H), 5.06 (d, *J* = 9.4 Hz, 1H), 3.88 (d, *J* = 11.5 Hz, 1H), 2.34 (s, 2H), 2.17 (s, 2H), 1.51 (d, *J* = 3.2 Hz, 2H), 1.45 (d, *J* = 3.4 Hz, 2H), 1.12 (s, 2H), 0.90 (s, 9H); ^{13}C NMR (151 MHz, DMSO-d6) δ = 181.28, 169.29, 142.52, 141.76, 134.73, 131.00, 130.78, 130.56, 130.34, 129.68, 128.64, 127.99, 127.81, 127.20, 126.82, 126.41, 124.60, 122.79, 122.25, 120.98, 116.54, 73.38, 64.66, 52.72, 50.09, 35.65, 27.09, 26.23, 24.82; HRMS(ESI): calcd. for $C_{34}H_{39}F_6N_4OS$ $(M+H)^+$: 665.2743, found: 665.2747.

3. General procedure for the asymmetric reaction.



A dry tube was charged with **1**[2] (0.2 mmol), **2**[3][4] (0.1 mmol) and **3j** (0.01 mmol). After the addition of xylene (1.0 mL) and H_2O (20 μL), the mixture was effectively stirred at 0 ºC and monitored by TLC. Upon the complete consumption ofnitroolefins **2**, the mixture was concentrated in vacuo and purified by flash chromatography on silica gel to afford thetarget compound **4/5**. The analytic data of compounds **4** and **5** were listed below.

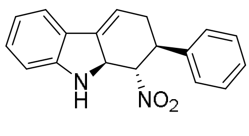
Table S1. Substrate scope of nitroolefins.[a]



entry	**4**	R^2	time (h)	yield (%)[b]	ee (%)[c]
1	**4s**	4-FC_6H_5	48	61	91
2	**4t**	4-BrC_6H_5	48	60	92
3	**4u**	4-$NO_2C_6H_5$	48	69	90
4	**4v**	4-$C_6H_5C_6H_5$	72	63	91
5	**4w**	4-MeC_6H_5	48	48	90
6	**4x**	4-$^tBuC_6H_5$	72	62	86
7	**4y**	3-FC_6H_5	48	51	89
8	**4z**	3-ClC_6H_5	48	57	83
9	**4aa**	2-FC_6H_5	48	54	88
10	**4ab**	2-ClC_6H_5	48	62	87
11	**4ac**	2-$NO_2C_6H_5$	72	65	86
12	**4ad**	2,6-2ClC_6H_5	60	19	90

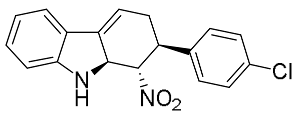
[a]Reaction conditions: **1** (0.20 mmol), **2** (0.10 mmol), **3j** (0.01 mmol), xylene (1.0 mL). [b] Isolated yield. [c]Determined by chiral HPLC.

(1*S*,2*S*,9a*S*)-1-nitro-2-phenyl-2,3,9,9a-tetrahydro-1*H*-carbazole (4a)



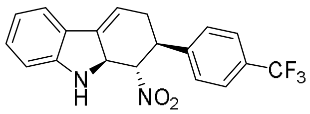
According to the general procedure, the title compound was obtained by silica-gel column chromatography (petroleum ether/ethyl acetate = 30:1); yellow solid (18.4 mg, 63% yield); m.p. 132-133 °C; $[\alpha]_D^{20}$ = + 86.25 (c = 0.24, CH_2Cl_2); ^1H NMR (600 MHz, $CDCl_3$) δ = 7.28 – 7.17 (m, 6H), 7.11 – 6.96 (m, 1H), 6.82 – 6.69 (m, 1H), 6.65 (d, *J* = 7.9 Hz, 1H), 5.86 (q, *J* = 3.5 Hz, 1H), 4.98 (dd, *J* = 8.3, 4.0 Hz, 1H), 4.87 (dd, *J* = 11.6, 9.4 Hz, 1H), 4.07 (d, *J* = 3.8 Hz, 1H), 3.55 (td, *J* = 11.0, 7.1 Hz, 1H), 2.83 (ddt, *J* = 19.4, 6.9, 3.4 Hz, 1H), 2.65 – 2.50 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 152.03, 138.99, 136.51, 129.74, 129.02, 127.90, 127.51, 126.34, 120.78, 120.26, 114.71, 111.34, 92.15, 64.37, 44.31, 35.44; HPLC: Chiralpak IC-H (hexane/*i*-PrOH = 70/30, flow rate 1 mL/min, λ = 254 nm), t_R (minor) =11.758 min,t_R (major) = 8.660 min, 91% ee; HRMS(ESI): calcd. for $C_{18}H_{17}N_2O_2(M+H)^+$: 293.1285, found: 293.1283.

(1*S*,2*S*,9a*S*)-2-(4-chlorophenyl)-1-nitro-2,3,9,9a-tetrahydro-1*H*-carbazole (4b)



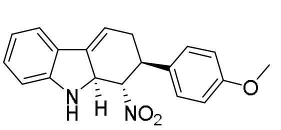
According to the general procedure, the title compound was obtained by silica-gel column chromatography (petroleum ether/ethyl acetate = 30:1); yellow solid (21.5 mg, 66% yield); m.p.117-118 °C; $[\alpha]_D^{20}$ = + 57.91 (c = 0.43 , CH_2Cl_2); ^1H NMR (600 MHz, $CDCl_3$) δ = 7.36 – 7.27 (m, 3H), 7.18 (d, *J* = 8.3 Hz, 2H), 7.12 (t, *J* = 7.7 Hz, 1H), 6.82 (t, *J* = 7.5 Hz, 1H), 6.71 (d, *J* = 7.9 Hz, 1H), 5.91 (d, *J* = 3.3 Hz, 1H), 5.09 – 4.98 (m, 1H), 4.88 (dd, *J*= 11.5, 9.4 Hz, 1H), 4.14 (d, *J* = 4.1 Hz, 1H), 3.60 (dd, *J* = 18.2, 11.0 Hz, 1H), 2.94 – 2.81 (m, 1H), 2.66 – 2.51 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 151.98, 137.47, 136.59, 133.77, 129.84, 129.25, 128.89, 126.22, 120.82, 120.35, 114.38, 111.40, 91.94, 64.25, 43.72, 35.32; HPLC: Chiralpak IC-H (hexane/*i*-PrOH = 70/30, flow rate 1 mL/min, λ = 254 nm), t_R (minor) = 10.575 min, t_R (major) = 7.304 min, 92% ee; HRMS(ESI): calcd. for $C_{18}H_{16}ClN_2O_2$ $(M+H)^+$: 327.0895, found: 327.0899.

(1*S*,2*S*,9a*S*)-1-nitro-2-(4-(trifluoromethyl)phenyl)-2,3,9,9a-tetrahydro-1*H*-carbazole (4c)



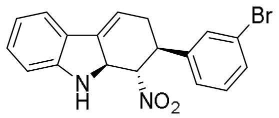
According to the general procedure, the title compound was obtained by silica-gel column chromatography (petroleum ether/ethyl acetate = 30:1); yellow solid (24.5 mg, 68% yield); m.p.72-73 °C; $[\alpha]_D^{20}$ = + 43.27 (c = 0.49, CH_2Cl_2);^1H NMR (600 MHz, $CDCl_3$) δ=7.59 (d, *J* = 8.1 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.32 (s, 1H), 7.12 (d, *J* = 15.3 Hz, 1H), 6.83 (t, *J* = 7.4 Hz, 1H), 6.72 (d, *J* = 7.9 Hz, 1H), 5.91 (q, *J* = 3.6 Hz, 1H), 5.08 – 4.99 (m, 1H), 4.94 (dd, *J* = 11.6, 9.3 Hz, 1H), 4.18 (s, 1H), 3.70 (td, *J* = 10.9, 7.2 Hz, 1H), 2.89 (ddt, *J* = 19.3, 6.9, 3.4 Hz, 1H), 2.67 – 2.54 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 151.97, 143.15, 136.72, 130.36, 130.14, 129.92, 127.97, 126.15, 126.04, 124.83, 123.03, 120.86, 120.40, 114.16, 111.43, 91.66, 64.21, 44.02, 35.23; HPLC: Chiralpak IC-H (hexane/*i*-PrOH = 70/30, flow rate 1 mL/min, λ = 254 nm), t_R (minor) = 7.991 min,t_R (major) = 5.821 min,90%ee; HRMS(ESI): calcd. for $C_{19}H_{16}F_3N_2O_2$ $(M+H)^+$: 361.1158, found: 361.1159.

(1*S*,2*S*,9a*S*)-2-(4-methoxyphenyl)-1-nitro-2,3,9,9a-tetrahydro-1*H*-carbazole (4d)



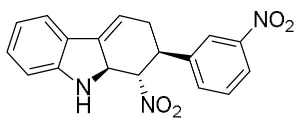
According to the general procedure, the title compound was obtained by silica-gel column chromatography (petroleum ether/ethyl acetate = 30:1); yellow solid (16.7 mg, 52% yield); m.p.192-193 °C; $[\alpha]_D^{20}$ = + 63.61 (c = 0.34, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.31 (d, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 8.6 Hz, 2H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 8.6 Hz, 2H), 6.82 (t, *J* = 7.5 Hz, 1H), 6.71 (d, *J* = 7.9 Hz, 1H), 5.92 (q, *J* = 3.4 Hz, 1H), 5.05 (dt, *J* = 12.7, 4.2 Hz, 1H), 4.88 (dd, *J* = 11.5, 9.4 Hz, 1H), 4.13 (d, *J* = 4.8 Hz, 1H), 3.80 (d, *J* = 19.3 Hz, 3H), 3.57 (td, *J* = 11.0, 7.1 Hz, 1H), 2.87 (ddt, *J* = 19.4, 6.8, 3.4 Hz, 1H), 2.68 – 2.55 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 159.19, 152.02, 136.43, 130.77, 129.70, 128.57, 126.37, 120.76, 120.25, 114.83, 114.42, 111.33, 92.42, 64.37, 55.25, 43.65, 35.49; HPLC: Chiralpak IC-H (hexane/*i*-PrOH = 70/30, flow rate 1 mL/min, λ = 254 nm), t_R (minor) = 15.701 min, t_R (major) = 10.999 min, 91% ee; HRMS(ESI): calcd. for $C_{19}H_{19}N_2O_3$ $(M+H)^+$: 323.1390, found: 323.1391.

(1*S*,2*S*,9a*S*)-2-(3-bromophenyl)-1-nitro-2,3,9,9a-tetrahydro-1*H*-carbazole (4e)



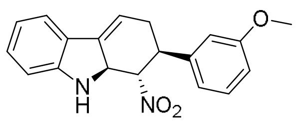
According to the general procedure, the title compound was obtained by silica-gel column chromatography (petroleum ether/ethyl acetate = 30:1); yellow solid (19.6 mg, 53% yield); m.p.145-146 °C; $[\alpha]_D^{20}$ = +53.76 (c = 0.39, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ=7.41 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 7.3 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 2H), 7.12 (t, *J* = 7.4 Hz, 1H), 6.82 (t, *J* = 7.4 Hz, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 5.91 (d, *J* = 3.0 Hz, 1H), 5.02 (d, *J* = 3.8 Hz, 1H), 4.89 (t, *J* = 10.4 Hz, 1H), 4.15 (s, 1H), 3.59 (dd, *J* = 18.2, 10.7 Hz, 1H), 2.94 – 2.79 (m, 1H), 2.66 – 2.53 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ=151.94, 141.39, 136.64, 131.11, 130.80, 130.58, 129.85, 126.17, 126.05, 122.96, 120.83, 120.33, 114.22, 111.36, 91.75, 64.22, 43.85, 35.28; HPLC: Chiralpak IC-H (hexane/*i*-PrOH = 70/30, flow rate 1 mL/min, λ = 254 nm), t_R (minor) = 9.787 min, t_R (major) = 7.616 min, 91% ee; HRMS(ESI): calcd. for $C_{18}H_{16}BrN_2O_2$ $(M+H)^+$: 371.0390, found: 371.0391.

(1*S*,2*S*,9a*S*)-1-nitro-2-(3-nitrophenyl)-2,3,9,9a-tetrahydro-1*H*-carbazole (4f)



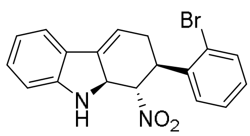
According to the general procedure, the title compound was obtained by silica-gel column chromatography (petroleum ether/ethyl acetate = 20:1); yellow solid (21.9 mg, 65% yield); m.p. 89-90 °C; $[\alpha]_D^{20}$ = + 48.62 (c = 0.44, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.14 (d, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 1H), 7.13 (t, *J* = 7.7 Hz, 1H), 6.83 (t, *J* = 7.5 Hz, 1H), 6.72 (d, *J* = 7.9 Hz, 1H), 5.91 (q, J = 3.5 Hz, 1H), 5.12 – 5.00 (m, 1H), 4.95 (dd, J = 11.5, 9.4 Hz, 1H), 4.19 (d, J = 4.8 Hz, 1H), 3.75 (td, J = 10.9, 7.2 Hz, 1H), 2.93 (ddt, J = 19.2, 6.9, 3.4 Hz, 1H), 2.73 – 2.53 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ=151.98, 148.65, 141.24, 136.83, 133.66, 130.11, 129.99, 126.06, 123.06, 122.73, 120.91, 120.44, 113.82, 111.45, 91.56, 64.07, 43.93, 35.18; HPLC: Chiralpak IC-H (hexane/*i*-PrOH = 70/30, flow rate 1 mL/min, λ = 254 nm), t_R (minor) = 16.643 min, t_R (major) = 20.932 min, 89% ee; HRMS(ESI): calcd. for $C_{18}H_{16}N_3O_4$ $(M+H)^+$: 338.1135, found: 338.1135.

(1*S*,2*S*,9a*S*)-2-(3-methoxyphenyl)-1-nitro-2,3,9,9a-tetrahydro-1*H*-carbazole (4g)



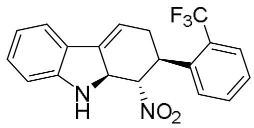
According to the general procedure, the title compound was obtained by silica-gel column chromatography (petroleum ether/ethyl acetate = 30:1); yellow solid (17.7 mg, 55% yield); m.p. 134-135 °C; $[\alpha]_D^{20}$ = + 63.92 (c = 0.32, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.31 (d, J = 7.5 Hz, 1H), 7.24 (t, J = 7.9 Hz, 1H), 7.11 (t, J = 7.7 Hz, 1H), 6.80 (ddd, J = 13.4, 12.8, 5.4 Hz, 4H), 6.71 (d, J = 7.9 Hz, 1H), 5.92 (q, J = 3.5 Hz, 1H), 5.03 (dt, J = 8.3, 4.3 Hz, 1H), 4.92 (dd, J = 11.6, 9.3 Hz, 1H), 4.14 (d, J = 4.9 Hz, 1H), 3.78 (s, 3H), 3.59 (td, J = 10.9, 7.1 Hz, 1H), 2.94 – 2.82 (m, 1H), 2.73 – 2.49 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 159.97, 152.01, 140.59, 136.45, 130.05, 129.73, 126.34, 120.78, 120.26, 119.66, 114.70, 113.63, 113.02, 111.35, 92.04, 64.36, 55.23, 44.24, 35.35; HPLC: Chiralpak IC-H (hexane/*i*-PrOH = 70/30, flow rate 1 mL/min, λ = 254 nm), t_R (minor) = 13.536 min, t_R (major) = 10.451 min, 91% ee; HRMS(ESI): calcd. for $C_{19}H_{19}N_2O_3$$(M+H)^+$: 323.1390, found: 323.1386.

(1*S*,2*S*,9a*S*)-2-(2-bromophenyl)-1-nitro-2,3,9,9a-tetrahydro-1*H*-carbazole (4h)



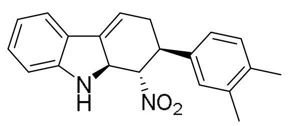
According to the general procedure, the title compound was obtained by silica-gel column chromatography (petroleum ether/ethyl acetate = 30:1); yellow solid (22.2 mg, 60% yield); m.p. 85-86 °C; $[\alpha]_D^{20}$ = + 33.56 (c = 0.44, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.56 (d, J = 8.1 Hz, 1H), 7.32 (d, J = 7.4 Hz, 3H), 7.12 (t, J = 8.0 Hz, 2H), 6.82 (t, J = 7.5 Hz, 1H), 6.73 (dd, J = 7.8, 3.2 Hz, 1H), 5.91 (d, J = 2.4 Hz, 1H), 5.06 (s, 2H), 4.33 (s, 1H), 4.18 (d, J = 3.6 Hz, 1H), 2.98 (d, J = 15.0 Hz, 1H), 2.37 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 151.93, 138.56, 136.52, 132.40, 129.12, 127.41, 124.78, 122.82, 120.82, 120.32, 114.49, 111.72, 111.36, 100.07, 90.61, 64.31, 42.34, 34.29; HPLC: Chiralpak IC-H (hexane/*i*-PrOH = 70/30, flow rate 1 mL/min, λ = 254 nm), t_R (minor) = 8.997 min,t_R (major) = 7.872 min,87% ee; HRMS(ESI): calcd. for $C_{18}H_{16}BrN_2O_2$ $(M+H)^+$: 371.0390, found: 371.0386.

(1*S*,2*S*,9a*S*)-1-nitro-2-(2-(trifluoromethyl)phenyl)-2,3,9,9a-tetrahydro-1*H*-carbazole (4i)



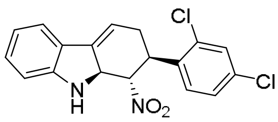
According to the general procedure, the title compound was obtained by silica-gel column chromatography (petroleum ether/ethyl acetate = 30:1); yellow solid (25.2 mg, 70% yield); m.p. 68-70 ^{o}C; $[\alpha]_D^{20}$ = + 6.13 (c = 0.51, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.65 (d, *J* = 7.9 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 7.7 Hz, 1H), 6.82 (t, *J* = 7.5 Hz, 1H), 6.72 (d, *J* = 7.9 Hz, 1H), 5.89 (d, *J* = 2.5 Hz, 1H), 5.08 (d, *J* = 7.3 Hz, 2H), 4.19 (d, *J* = 2.8 Hz, 1H), 4.10 (td, *J* = 10.4, 6.8 Hz, 1H), 2.97 (ddd, *J* = 22.6, 6.6, 3.1 Hz, 1H), 2.55 – 2.40 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 151.99, 138.33, 136.61, 132.56, 129.84, 129.30, 129.10, 127.65, 126.26, 125.07, 123.26, 120.85, 120.37, 114.28, 111.41, 90.95, 64.14, 39.54, 36.34; HPLC: Chiralpak IC-H (hexane/*i*-PrOH = 70/30, flow rate 1 mL/min, λ = 254 nm), t_R (minor) = 11.290 min, t_R (major) = 10.662 min, 86% ee; HRMS(ESI): calcd. for $C_{19}H_{16}F_3N_2O_2$ $(M+H)^+$: 361.1158, found: 361.1155.

(1*S*,2*S*,9a*S*)-2-(3,4-dimethylphenyl)-1-nitro-2,3,9,9a-tetrahydro-1*H*-carbazole (4j)



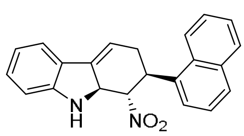
According to the general procedure, the title compound was obtained by silica-gel column chromatography (petroleum ether/ethyl acetate = 30:1); yellow solid (19.8 mg, 62% yield); m.p. 153-155 ^{o}C; $[\alpha]_D^{20}$ = +62.44 (c = 0.39, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.31 (d, *J* = 7.5 Hz, 1H), 7.09 (dd, *J* = 16.2, 7.8 Hz, 2H), 7.03 – 6.93 (m, 2H), 6.81 (t, *J* = 7.5 Hz, 1H), 6.70 (d, *J* = 7.9 Hz, 1H), 5.97 – 5.86 (m, 1H), 5.03 (td, *J* = 8.2, 4.1 Hz, 1H), 4.90 (dd, *J* = 11.5, 9.4 Hz, 1H), 4.13 (d, *J* = 4.5 Hz, 1H), 3.54 (td, *J* = 11.0, 7.2 Hz, 1H), 2.85 (ddt, *J* = 19.4, 6.8, 3.3 Hz, 1H), 2.69 – 2.54 (m, 1H), 2.23 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 152.06, 137.14, 136.40, 136.33, 136.21, 130.21, 129.67, 128.86, 126.42, 124.69, 120.75, 120.21, 114.92, 111.32, 92.27, 64.43, 43.93, 35.53, 19.81, 19.38; HPLC: Chiralpak IC-H (hexane/*i*-PrOH = 70/30, flow rate 1 mL/min, λ = 254 nm), t_R (minor) =9.973 min, t_R (major) = 6.797 min, 91% ee; HRMS(ESI): calcd. for $C_{20}H_{21}N_2O_2$ $(M+H)^+$: 321.1598, found: 321.1602.

(1*S*,2*S*,9a*S*)-2-(2,4-dichlorophenyl)-1-nitro-2,3,9,9a-tetrahydro-1*H*-carbazole (4k)



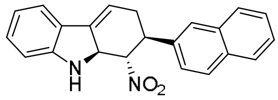
According to the general procedure, the title compound was obtained by silica-gel column chromatography (petroleum ether/ethyl acetate = 30:1); yellow solid (20.5 mg, 57% yield); m.p. 86-87 °C; $[\alpha]_D^{20}$ = +10.39 (c = 0.41, CH_2Cl_2); ^{1}H NMR (600 MHz, DMSO-d6) δ = 7.77 (s, 1H), 7.62 (d, *J* = 2.2 Hz, 1H), 7.45 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.34 (d, *J* = 7.4 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.69 (t, *J* = 7.4 Hz, 1H), 6.64 (d, *J* = 7.9 Hz, 1H), 6.40 (d, *J* = 4.5 Hz, 1H), 5.94 (d, *J* = 3.0 Hz, 1H), 5.41 (dd, *J* = 11.5, 9.3 Hz, 1H), 4.97 – 4.84 (m, 1H), 4.16 (s, 1H), 2.79 (ddt, *J* = 18.6, 6.5, 3.2 Hz, 1H), 2.42 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 151.93, 136.68, 135.32, 134.71, 134.08, 130.20, 129.89, 129.68, 127.96, 126.19, 120.84, 120.35, 114.06, 111.38, 90.15, 64.24, 53.40, 33.71; HPLC: Chiralpak IC-H (hexane/*i*-PrOH = 90/10, flow rate 1 mL/min, λ = 254 nm), t_R(minor) = 13.178 min,t_R (major) = 10.616 min, 90% ee; HRMS(ESI): calcd. for $C_{18}H_{15}Cl_2N_2O_2$ $(M+H)^+$: 361.0505, found: 361.0501.

(1*S*,2*S*,9a*S*)-2-(naphthalen-1-yl)-1-nitro-2,3,9,9a-tetrahydro-1*H*-carbazole (4l)



According to the general procedure, the title compound was obtained by silica-gel column chromatography (petroleum ether/ethyl acetate = 30:1); yellow solid (23.6 mg, 69% yield); m.p. 91-92 °C; $[\alpha]_D^{20}$ = +61.65 (c = 0.47, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.16 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.47 (dt, *J* = 15.0, 7.7 Hz, 3H), 7.34 (s, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.83 (t, *J* = 7.4 Hz, 1H), 6.73 (d, *J* = 7.8 Hz, 1H), 5.94 (s, 1H), 5.26 (t, *J* = 10.3 Hz, 1H), 5.15 (s, 1H), 4.67 (dd, *J* = 18.0, 10.6 Hz, 1H), 4.19 (s, 1H), 3.15 – 3.00 (m, 1H), 2.62 – 2.48 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 152.01, 136.58, 135.80, 134.12, 131.60, 129.81, 129.14, 128.10, 126.58, 126.37, 125.89, 125.63, 122.94, 122.27, 120.84, 120.30, 115.01, 111.37, 91.24, 65.02, 37.77, 35.83; HPLC: Chiralpak IC-H (hexane/*i*-PrOH = 70/30, flow rate 1 mL/min, λ = 254 nm), t_R (minor) = 12.116 min, t_R (major) = 9.068 min, 91% ee; HRMS(ESI): calcd. for $C_{22}H_{19}N_2O_2$ $(M+H)^+$: 343.1441, found: 343.1441.

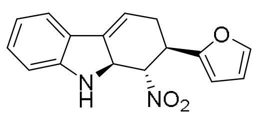
(1*S*,2*S*,9a*S*)-2-(naphthalen-2-yl)-1-nitro-2,3,9,9a-tetrahydro-1*H*-carbazole (4m)



According to the general procedure, the title compound was obtained by silica-gel column chromatography (petroleum ether/ethyl acetate = 30:1); yellow solid (21.2 mg, 62% yield); m.p. 177-178 °C; $[\alpha]_D^{20}$ = + 63.44 (c = 0.42, CH_2Cl_2);

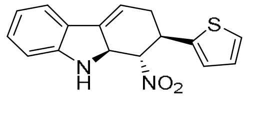
^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.83 (d, *J* = 8.5 Hz, 1H), 7.82 – 7.75 (m, 2H), 7.68 (s, 1H), 7.51 – 7.42 (m, 2H), 7.38 (d, *J* = 8.5 Hz, 1H), 7.34 (d, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 7.7 Hz, 1H), 6.83 (t, *J* = 7.5 Hz, 1H), 6.72 (d, *J* = 7.9 Hz, 1H), 5.95 (d, *J* = 3.4 Hz, 1H), 5.10 (td, *J* = 8.1, 4.1 Hz, 1H), 5.04 (dd, *J* = 11.2, 9.5 Hz, 1H), 4.16 (d, *J* = 4.7 Hz, 1H), 3.79 (td, *J* = 10.8, 7.3 Hz, 1H), 3.00 – 2.89 (m, 1H), 2.74 (ddd, *J* = 15.0, 9.9, 4.2 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 152.05, 136.58, 136.33, 133.47, 132.95, 129.78, 128.98, 127.81, 127.71, 127.06, 126.39, 126.35, 126.15, 124.66, 120.82, 120.29, 114.68, 111.37, 92.09, 64.35, 44.44, 35.37; HPLC: Chiralpak IC-H (hexane/*i*-PrOH = 70/30, flow rate 1 mL/min, λ = 254 nm), t_R (minor) = 14.594 min, t_R (major) = 9.430 min, 92% ee; HRMS(ESI): calcd. for $C_{22}H_{19}N_2O_2(M+H)^+$: 343.1441, found: 343.1438.

(1*S*,2*R*,9a*S*)-2-(furan-2-yl)-1-nitro-2,3,9,9a-tetrahydro-1*H*-carbazole (4n)



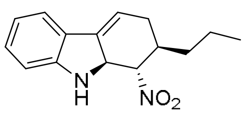
According to the general procedure, the title compound was obtained by silica-gel column chromatography (petroleum ether/ethyl acetate = 30:1); yellow solid (13.8 mg, 49% yield); m.p. 99-100 °C; $[\alpha]_D^{20}$ = + 29.71 (c = 0.28, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.36 (s, 1H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.81 (t, *J* = 7.4 Hz, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 6.29 (s, 1H), 6.18 (s, 1H), 5.90 (d, *J* = 2.7 Hz, 1H), 5.01 (d, *J* = 3.6 Hz, 1H), 4.85 (t, *J* = 10.5 Hz, 1H), 4.15 (s, 1H), 3.77 (dd, *J* = 19.9, 9.0 Hz, 1H), 2.96 – 2.67 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 151.93, 151.53, 142.53, 136.33, 129.77, 126.22, 120.78, 120.26, 113.92, 111.32, 110.32, 107.51, 90.71, 63.76, 37.52, 31.59; HPLC: Chiralpak IC-H (hexane/*i*-PrOH = 70/30, flow rate 1 mL/min, λ = 254 nm), t_R (minor) = 12.280 min, t_R (major) = 8.595 min, 90% ee; HRMS(ESI): calcd. for $C_{16}H_{15}N_2O_3$ $(M+H)^+$: 283.1077, found: 283.1077.

(1*S*,2*R*,9a*S*)-1-nitro-2-(thiophen-2-yl)-2,3,9,9a-tetrahydro-1*H*-carbazole (4o)



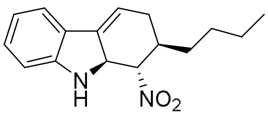
According to the general procedure, the title compound was obtained by silica-gel column chromatography (petroleum ether/ethyl acetate = 30:1); yellow solid (17.9 mg, 60% yield); m.p. 54-55 °C; $[\alpha]_D^{20}$ = + 112.64 (c = 0.36, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.31 (d, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 4.8 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.96 – 6.90 (m, 2H), 6.82 (t, *J* = 7.5 Hz, 1H), 6.71 (d, *J* = 7.9 Hz, 1H), 5.91 (q, *J* = 3.3 Hz, 1H), 5.09 – 4.98 (m, 1H), 4.81 (dd, *J* = 11.1, 9.7 Hz, 1H), 4.13 (d, *J* = 4.6 Hz, 1H), 4.02 – 3.91 (m, 1H), 3.08 – 2.95 (m, 1H), 2.84 – 2.70 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 151.98, 141.64, 136.54, 129.83, 127.03, 126.20, 125.99, 124.71, 120.81, 120.32, 114.15, 111.38, 93.30, 64.17, 39.45, 36.06; HPLC: Chiralpak IC-H (hexane/*i*-PrOH = 70/30, flow rate 1 mL/min, λ = 254 nm), t_R (minor) = 12.159 min, t_R (major) = 9.188 min, 92% ee; HRMS(ESI): calcd. for $C_{16}H_{15}N_2O_2S$ $(M+H)^+$: 299.0849, found: 299.0847.

(1*S*,2*R*,9a*S*)-1-nitro-2-propyl-2,3,9,9a-tetrahydro-1H-carbazole (4p)



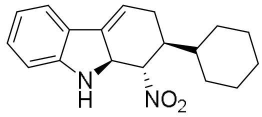
According to the general procedure, the title compound was obtained by silica-gel column chromatography (petroleum ether/ethyl acetate = 50:1); yellow solid (14.7 mg, 57% yield); m.p. 85-87 °C; $[\alpha]_D^{20}$ = + 7.14 (c = 0.42, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.25 (dd, *J* = 12.6, 8.9 Hz, 1H), 7.08 (dd, *J* = 11.1, 4.1 Hz, 1H), 6.78 (td, *J* = 7.5, 0.6 Hz, 1H), 6.68 (d, *J* = 7.9 Hz, 1H), 5.83 (q, *J* = 3.7 Hz, 1H), 4.91 (dt, *J* = 7.7, 3.5 Hz, 1H), 4.41 (dd, *J* = 11.2, 9.5 Hz, 1H), 2.70 (ddt, *J* = 19.0, 6.9, 3.5 Hz, 1H), 2.46 – 2.33 (m, 1H), 2.21 – 2.09 (m, 1H), 1.52 – 1.20 (m, 5H), 0.91 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 151.91, 136.34, 129.55, 126.41, 120.65, 120.10, 114.44, 111.26, 93.13, 64.01, 36.58, 34.22, 31.87, 19.01, 13.92; HPLC: Chiralpak IC-H (hexane/*i*-PrOH = 80/20, flow rate 1 mL/min, λ = 254 nm), t_R (minor) = 7.746 min, t_R (major) = 6.239 min, 89% ee; HRMS(ESI): calcd. for $C_{15}H_{19}N_2O_2$ $(M+H)^+$: 259.1441, found: 259.1448.

(1*S*,2*R*,9a*S*)-2-butyl-1-nitro-2,3,9,9a-tetrahydro-1*H*-carbazole (4q)



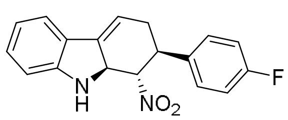
According to the general procedure, the title compound was obtained by silica-gel column chromatography (petroleum ether/ethyl acetate = 50:1); yellow solid (12.0 mg, 44% yield); m.p. 80-82 °C; $[\alpha]_D^{20}$ = + 85.83 (c = 0.24, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.29 – 7.24 (m, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.78 (t, *J* = 7.2 Hz, 1H), 6.68 (d, *J* = 7.9 Hz, 1H), 5.83 (q, *J* = 3.7 Hz, 1H), 4.97 – 4.86 (m, 1H), 4.41 (dd, *J* = 11.3, 9.4 Hz, 1H), 4.10 (d, *J* = 4.7 Hz, 1H), 2.71 (ddt, *J* = 19.0, 6.9, 3.5 Hz, 1H), 2.40 (qd, *J* = 9.9, 3.1 Hz, 1H), 2.22 – 2.12 (m, 1H), 1.46 – 1.38 (m, 2H), 1.32 (ddd, *J* = 24.1, 13.4, 7.2 Hz, 4H), 0.92 – 0.85 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 151.91, 136.32, 129.55, 126.41, 120.65, 120.11, 114.47, 111.26, 93.14, 64.02, 36.73, 31.91, 31.70, 27.90, 22.57, 13.86; HPLC: Chiralpak IC-H (hexane/*i*-PrOH = 80/20, flow rate 1 mL/min, λ = 254 nm), t_R (minor) = 7.833 min, t_R (major) = 6.121 min, 88% ee; HRMS(ESI): calcd. for $C_{16}H_{21}N_2O_2$ $(M+H)^+$: 273.1598, found: 273.1593.

(1*S*,2*S*,9a*S*)-2-cyclohexyl-1-nitro-2,3,9,9a-tetrahydro-1*H*-carbazole (4r)



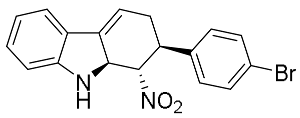
According to the general procedure, the title compound was obtained by silica-gel column chromatography (petroleum ether/ethyl acetate = 50:1); yellow solid (16.7 mg, 56% yield); m.p. 113-114 °C; $[\alpha]_D^{20}$ = + 67.77 (c = 0.33, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.26 (d, *J* = 8.3 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.78 (t, *J* = 7.4 Hz, 1H), 6.68 (d, *J* = 7.9 Hz, 1H), 5.86 (q, *J* = 3.6 Hz, 1H), 4.97 – 4.88 (m, 1H), 4.65 – 4.55 (m, 1H), 4.10 (d, *J* = 4.8 Hz, 1H), 2.48 (ddt, *J* = 17.8, 6.9, 3.4 Hz, 1H), 2.41 (ddd, *J* = 10.1, 9.0, 3.1 Hz, 1H), 2.35 (ddd, *J* = 17.8, 8.8, 4.4 Hz, 1H), 1.81 – 1.74 (m, 2H), 1.69 (dd, *J* = 22.3, 12.8 Hz, 2H), 1.51 (d, *J* = 11.3 Hz, 1H), 1.38 (td, *J* = 11.7, 2.9 Hz, 1H), 1.26 (dd, *J* = 20.4, 7.8 Hz, 2H), 1.21 – 1.16 (m, 1H), 1.15 – 1.04 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 151.92, 136.16, 129.52, 126.36, 120.63, 120.07, 114.67, 111.24, 90.82, 64.41, 41.56, 38.34, 30.86, 26.72, 26.63, 26.44, 26.21, 25.81; HPLC: Chiralpak IC-H (hexane/*i*-PrOH = 80/20, flow rate 1 mL/min, λ = 254 nm), t_R (minor) =8.390min, t_R (major) = 6.087min, 90% ee; HRMS(ESI): calcd. for $C_{18}H_{23}N_2O_2$ $(M+H)^+$: 299.1754, found: 299.1757.

(1*S*,2*S*,9a*S*)-2-(4-fluorophenyl)-1-nitro-2,3,9,9a-tetrahydro-1*H*-carbazole (4s)



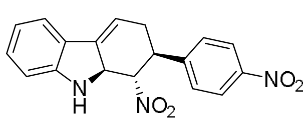
According to the general procedure, the title compound was obtained by silica-gel column chromatography (petroleum ether/ethyl acetate = 30:1); yellow solid (18.9 mg, 61% yield); m.p.134-135°C; $[\alpha]_D^{20}$ = + 91.57 (c = 0.38, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.32 (t, J = 8.8 Hz, 1H), 7.25 – 7.19 (m, 2H), 7.11 (t, J = 7.7 Hz, 1H), 7.06 – 6.98 (m, 2H), 6.85 (dt, J = 14.9, 6.9 Hz, 1H), 6.70 (t, J = 9.5 Hz, 1H), 6.00 – 5.78 (m, 1H), 5.04 (tt, J = 8.3, 4.0 Hz, 1H), 4.94 – 4.81 (m, 1H), 4.14 (d, J = 4.8 Hz, 1H), 3.61 (td, J = 11.0, 7.1 Hz, 1H), 2.87 (ddt, J = 19.4, 6.9, 3.4 Hz, 1H), 2.67 – 2.52 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 163.10, 161.47, 152.00, 136.53, 134.63, 129.81, 129.12, 126.27, 120.81, 120.33, 116.05, 115.90, 114.52, 111.40, 92.17, 64.29, 43.64, 35.46; HPLC: Chiralpak IC-H (hexane/*i*-PrOH = 70/30, flow rate 1 mL/min, λ = 254 nm), t_R (minor) = 9.997 min, t_R (major) = 7.144 min,91% ee; HRMS(ESI): calcd. for$C_{18}H_{16}FN_2O_2$ $(M+H)^+$: 311.1190, found: 311.1191.

(1*S*,2*S*,9a*S*)-2-(4-bromophenyl)-1-nitro-2,3,9,9a-tetrahydro-1*H*-carbazole (4t)



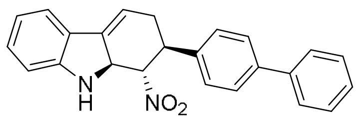
According to the general procedure, the title compound was obtained by silica-gel column chromatography (petroleum ether/ethyl acetate = 30:1); yellow solid (22.2 mg, 60% yield); m.p. 183-185 °C; $[\alpha]_D^{20}$ = + 46.19 (c = 0.45, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.45 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 7.5 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 3H), 6.82 (t, *J* = 7.5 Hz, 1H), 6.70 (d, *J* = 7.9 Hz, 1H), 5.90 (d, *J* = 3.1 Hz, 1H), 5.08 – 4.97 (m, 1H), 4.94 – 4.82 (m, 1H), 4.15 (d, *J* = 4.7 Hz, 1H), 3.58 (dd, *J* = 18.2, 10.9 Hz, 1H), 2.94 – 2.80 (m, 1H), 2.66 – 2.49 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 151.98, 138.00, 136.59, 132.21, 129.85, 129.24, 126.22, 121.84, 120.83, 120.35, 114.38, 111.41, 91.85, 64.24, 43.78, 35.27; HPLC: Chiralpak IC-H (hexane/*i*-PrOH = 70/30, flow rate 1 mL/min, λ = 254 nm), t_R (minor) = 11.108 min, t_R (major) = 7.565 min, 92% ee; HRMS(ESI): calcd. for $C_{18}H_{16}BrN_2O_2$ $(M+H)^+$: 371.0390, found: 371.0388.

(1*S*,2*S*,9a*S*)-1-nitro-2-(4-nitrophenyl)-2,3,9,9a-tetrahydro-1*H*-carbazole (4u)



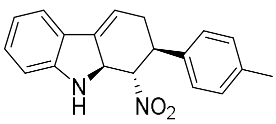
According to the general procedure, the title compound was obtained by silica-gel column chromatography (petroleum ether/ethyl acetate = 20:1); yellow solid (23.3 mg, 69% yield); m.p. 112-113 °C; $[\alpha]_D^{20}$ = + 24.03 (c = 0.47, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.19 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 8.6 Hz, 2H), 7.32 (d, *J* = 7.5 Hz, 1H), 7.13 (t, *J* = 7.7 Hz, 1H), 6.83 (t, *J* = 7.5 Hz, 1H), 6.72 (d, *J* = 7.9 Hz, 1H), 5.91 (q, *J* = 3.5 Hz, 1H), 5.04 (td, *J* = 8.4, 4.2 Hz, 1H), 4.94 (dd, *J* = 11.5, 9.3 Hz, 1H), 4.21 (d, *J* = 4.7 Hz, 1H), 3.75 (td, *J* = 10.9, 7.3 Hz, 1H), 2.91 (ddt, *J* = 19.2, 6.9, 3.3 Hz, 1H), 2.68 – 2.54 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 151.95, 147.64, 146.54, 136.89, 130.03, 128.57, 126.02, 124.31, 120.91, 120.47, 113.74, 111.47, 91.48, 64.05, 43.97, 35.05; HPLC: Chiralpak IC-H (hexane/*i*-PrOH = 70/30, flow rate 1 mL/min, λ = 254 nm), t_R (minor) = 19.984 min,t_R (major) = 14.175 min,90% ee; HRMS(ESI): calcd. for $C_{18}H_{16}N_3O_4$ $(M+H)^+$: 338.1135, found: 338.1135.

(1*S*,2*S*,9a*S*)-2-([1,1'-biphenyl]-4-yl)-1-nitro-2,3,9,9a-tetrahydro-1*H*-carbazol (4v)



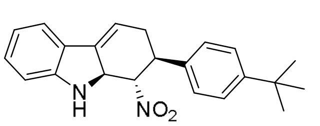
According to the general procedure, the title compound was obtained by silica-gel column chromatography (petroleum ether/ethyl acetate = 30:1); yellow solid (23.2, 63% yield); m.p. 157-159 °C; $[\alpha]_D^{20}$ = + 17.60 (c = 0.47, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.55 (dd, *J* = 7.7, 3.1 Hz, 4H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.37 – 7.30 (m, 4H), 7.12 (t, J = 7.6 Hz, 1H), 6.83 (t, J = 7.4 Hz, 1H), 6.73 (d, J = 7.9 Hz, 1H), 5.95 (q, J = 3.4 Hz, 1H), 5.07 (td, J = 8.3, 4.1 Hz, 1H), 4.97 (dd, J = 11.5, 9.4 Hz, 1H), 4.16 (d, J = 4.9 Hz, 1H), 3.67 (td, J = 11.0, 7.1 Hz, 1H), 2.98 – 2.85 (m, 1H), 2.75 – 2.60 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 152.02, 140.85, 140.54, 137.94, 136.53, 129.77, 128.77, 127.93, 127.74, 127.39, 127.07, 126.33, 120.80, 120.29, 114.71, 111.36, 92.11, 64.39, 43.98, 35.45; HPLC: Chiralpak IC-H (hexane/*i*-PrOH = 70/30, flow rate 1 mL/min, λ = 254 nm), t_R (minor) = 13.952 min, t_R (major) = 9.513 min, 91% ee; HRMS(ESI): calcd. for $C_{24}H_{21}N_2O_2$ $(M+H)^+$: 369.1598, found: 369.1596.

(1*S*,2*S*,9a*S*)-1-nitro-2-(*p*-tolyl)-2,3,9,9a-tetrahydro-1*H*-carbazole (4w)



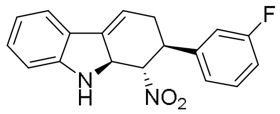
According to the general procedure, the title compound was obtained by silica-gel column chromatography (petroleum ether/ethyl acetate = 30:1); yellow solid (14.7 mg, 48% yield); m.p. 136-137 °C; $[\alpha]_D^{20}$ = + 75.92 (c = 0.32, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.31 (d, J = 7.5 Hz, 1H), 7.13 (s, 4H), 7.11 (t, J = 7.7 Hz, 1H), 6.82 (d, J = 7.4 Hz, 1H), 6.71 (d, J = 7.9 Hz, 1H), 5.92 (q, J = 3.5 Hz, 1H), 5.04 (tt, J = 8.3, 4.0 Hz, 1H), 4.90 (dd, J = 11.6, 9.4 Hz, 1H), 4.13 (d, J = 4.9 Hz, 1H), 3.58 (td, J = 11.0, 7.1 Hz, 1H), 2.86 (ddt, J = 19.5, 6.9, 3.4 Hz, 1H), 2.68 – 2.56 (m, 1H), 2.31 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 152.03, 137.60, 136.43, 135.86, 129.69, 127.37, 126.38, 122.21, 120.76, 120.24, 114.83, 111.33, 92.28, 64.38, 43.98, 35.46, 21.06; HPLC: Chiralpak IC-H (hexane/*i*-PrOH = 70/30, flow rate 1 mL/min, λ = 254 nm), t_R (minor) =11.406 min, t_R (major) = 7.673 min,90% ee; HRMS(ESI): calcd. for $C_{19}H_{19}N_2O_2$ $(M+H)^+$: 307.1441, found: 307.1439.

(1*S*,2*S*,9a*S*)-2-(4-(tert-butyl)phenyl)-1-nitro-2,3,9,9a-tetrahydro-1*H*-carbazole (4x)



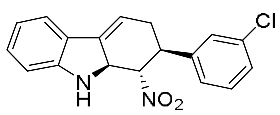
According to the general procedure, the title compound was obtained by silica-gel column chromatography (petroleum ether/ethyl acetate = 30:1); yellow solid (21.6 mg, 62% yield); m.p. 190-192 °C; $[\alpha]_D^{20}$ = + 51.21 (c = 0.41, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.32 (dd, J = 14.8, 7.9 Hz, 3H), 7.16 (d, J = 8.3 Hz, 2H), 7.10 (t, J = 7.7 Hz, 1H), 6.81 (t, J = 7.5 Hz, 1H), 6.70 (d, J = 7.9 Hz, 1H), 5.92 (q, J = 3.5 Hz, 1H), 5.09 – 4.98 (m, 1H), 4.95 – 4.87 (m, 1H), 4.13 (d, J = 5.0 Hz, 1H), 3.59 (td, J = 11.0, 7.1 Hz, 1H), 2.86 (ddt, J = 19.5, 6.9, 3.4 Hz, 1H), 2.71 – 2.46 (m, 1H), 1.29 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 152.03, 150.74, 136.40, 135.79, 129.69, 127.14, 126.40, 125.90, 120.76, 120.25, 114.93, 111.33, 92.18, 64.46, 43.81, 35.48, 34.51, 31.29; HPLC: Chiralpak IC-H (hexane/*i*-PrOH = 70/30, flow rate 1 mL/min, λ = 254 nm), t_R (minor) = 9.430 min, t_R (major) = 6.258 min,86% ee; HRMS(ESI): calcd. for $C_{22}H_{25}N_2O_2$ $(M+H)^+$: 349.1911, found: 349.1913.

(1S,2S,9aS)-2-(3-fluorophenyl)-1-nitro-2,3,9,9a-tetrahydro-1H-carbazole (4y)



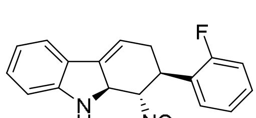
According to the general procedure, the title compound was obtained by silica-gel column chromatography (petroleum ether/ethyl acetate = 30:1); yellow solid (15.8 mg, 51% yield); m.p. 122-123 °C; $[\alpha]_D^{20}$ = + 70.89 (c = 0.32, CH_2Cl_2); ^1H NMR (600 MHz, $CDCl_3$) δ = 7.30 (dd, *J* = 16.8, 7.5 Hz, 2H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 7.4 Hz, 1H), 6.97 (t, *J* = 8.2 Hz, 2H), 6.82 (t, *J* = 7.4 Hz, 1H), 6.72 (d, *J* = 7.8 Hz, 1H), 5.92 (d, *J* = 2.8 Hz, 1H), 5.03 (d, *J* = 3.5 Hz, 1H), 4.90 (t, *J* = 10.4 Hz, 1H), 4.15 (s, 1H), 3.63 (dd, *J* = 18.4, 10.5 Hz, 1H), 2.95 – 2.86 (m, 1H), 2.67 – 2.55 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 163.83, 162.19, 151.98, 141.53, 136.62, 130.57, 129.84, 126.19, 123.15, 120.82, 120.33, 115.00, 114.86, 114.70, 114.55, 114.27, 111.37, 91.88, 64.23, 43.94, 35.21; HPLC: Chiralpak IC-H (hexane/*i*-PrOH = 70/30, flow rate 1 mL/min, λ = 254 nm), t_R (minor) = 9.307 min, t_R (major) = 7.045 min, 89% ee; HRMS(ESI): calcd. for $C_{18}H_{16}FN_2O_2$ $(M+H)^+$: 311.1190, found: 311.1187.

(1*S*,2*S*,9a*S*)-2-(3-chlorophenyl)-1-nitro-2,3,9,9a-tetrahydro-1*H*-carbazole (4z)



According to the general procedure, the title compound was obtained by silica-gel column chromatography (petroleum ether/ethyl acetate = 30:1); yellow solid (18.6 mg, 57% yield); m.p. 71-72 °C; $[\alpha]_D^{20}$ = + 55.14 (c = 0.37, CH_2Cl_2); ^1H NMR (600 MHz, $CDCl_3$) δ = 7.20 (t, *J* = 19.3 Hz, 4H), 7.05 (dd, *J* = 15.1, 6.9 Hz, 2H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.65 (d, *J* = 7.8 Hz, 1H), 5.84 (d, *J* = 2.7 Hz, 1H), 4.96 (s, 1H), 4.83 (t, *J* = 10.4 Hz, 1H), 4.08 (s, 1H), 3.53 (dd, *J* = 18.4, 10.6 Hz, 1H), 2.88 – 2.76 (m, 1H), 2.60 – 2.46 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 151.98, 141.09, 136.61, 134.80, 130.32, 129.85, 128.18, 127.89, 126.19, 125.61, 120.83, 120.34, 114.28, 111.38, 91.75, 64.23, 43.90, 35.25; HPLC: Chiralpak IC-H (hexane/*i*-PrOH = 70/30, flow rate 1 mL/min, λ = 254 nm), t_R (minor) = 9.438 min, t_R (major) = 7.265 min, 83% ee; HRMS(ESI): calcd. for $C_{18}H_{16}ClN_2O_2$ $(M+H)^+$: 327.0895, found: 327.0896.

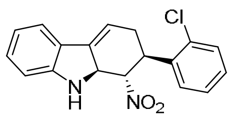
(1*S*,2*S*,9a*S*)-2-(2-fluorophenyl)-1-nitro-2,3,9,9a-tetrahydro-1*H*-carbazole (4aa)



According to the general procedure, the title compound was obtained by silica-gel column chromatography (petroleum ether/ethyl acetate = 30:1); yellow solid (16.7 mg, 54% yield); m.p. 125-126 °C; $[\alpha]_D^{20}$ = + 41.32(c = 0.33, CH_2Cl_2); ^1H NMR (600 MHz, $CDCl_3$) δ = 7.32 (d, *J* = 7.5 Hz, 1H), 7.29 – 7.26 (m, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.11

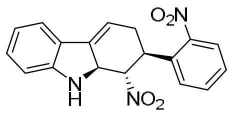
(q, J = 7.2 Hz, 2H), 7.06 (dd, J = 10.3, 8.8 Hz, 1H), 6.82 (t, J = 7.4 Hz, 1H), 6.72 (d, J = 7.9 Hz, 1H), 5.92 (q, J = 3.5 Hz, 1H), 5.16 – 5.07 (m, 1H), 5.08 – 5.00 (m, 1H), 4.17 (d, J = 4.7 Hz, 1H), 3.84 (td, J = 10.9, 7.5 Hz, 1H), 2.88 (ddt, J = 19.2, 6.9, 3.3 Hz, 1H), 2.77 – 2.65 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 161.83, 160.20, 151.90, 136.44, 129.77, 129.62, 126.34, 124.67, 120.80, 120.28, 116.29, 116.15, 114.43, 111.34, 90.34, 64.20, 39.37, 33.67; HPLC: Chiralpak IC-H (hexane/*i*-PrOH = 80/20, flow rate 1 mL/min, λ = 254 nm), t_R (minor) = 12.729 min, t_R (major) = 8.502 min, 88% ee; HRMS(ESI): calcd. for $C_{18}H_{16}FN_2O_2$ $(M+H)^+$: 311.1190, found: 311.1190.

(1*S*,2*S*,9a*S*)-2-(2-chlorophenyl)-1-nitro-2,3,9,9a-tetrahydro-1*H*-carbazole (4ab)



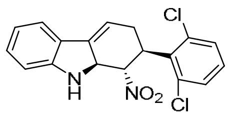
According to the general procedure, the title compound was obtained by silica-gel column chromatography (petroleum ether/ethyl acetate = 30:1); yellow solid (20.2 mg, 62% yield); m.p. 78-79 °C; $[\alpha]_D^{20}$ = + 33.28 (c = 0.40, CH_2Cl_2); ^{1}H NMR (600 MHz, DMSO-d6) δ = 7.66 (s, 1H), 7.41 (d, J = 8.1 Hz, 1H), 7.31 (t, J = 7.0 Hz, 3H), 7.25 (t, J = 7.4 Hz, 1H), 7.01 (t, J = 7.6 Hz, 1H), 6.66 (t, J = 7.4 Hz, 1H), 6.61 (d, J = 7.9 Hz, 1H), 6.35 (d, J = 4.5 Hz, 1H), 5.91 (d, J = 2.7 Hz, 1H), 5.35 (dd, J = 11.5, 9.3 Hz, 1H), 4.87 (dt, J = 8.3, 4.0 Hz, 1H), 4.16 (s, 1H), 2.76 (ddt, J = 18.7, 6.5, 3.1 Hz, 1H), 2.39 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 151.97, 136.56, 133.98, 130.41, 129.79, 128.87, 127.60, 126.31, 120.81, 120.28, 114.44, 111.35, 90.25, 64.37, 40.07, 33.43; HPLC: Chiralpak IC-H (hexane/*i*-PrOH = 80/20, flow rate 1 mL/min, λ = 254 nm), t_R (minor) = 10.776 min, t_R(major) = 9.264 min,87% ee; HRMS(ESI): calcd. for $C_{18}H_{16}ClN_2O_2$ $(M+H)^+$: 327.0895, found: 327.0895.

(1*S*,2*S*,9a*S*)-1-nitro-2-(2-nitrophenyl)-2,3,9,9a-tetrahydro-1*H*-carbazole (4ac)



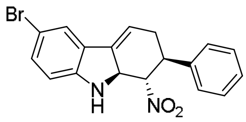
According to the general procedure, the title compound was obtained by silica-gel column chromatography (petroleum ether/ethyl acetate = 20:1); yellow solid (21.9 mg, 65% yield); m.p. 193-194 °C; $[\alpha]_D^{20}$ = + 52.04 (c = 0.44, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.84 (d, J = 8.2 Hz, 1H), 7.61 (t, J = 7.6 Hz, 1H), 7.50 (d, J = 7.4 Hz, 1H), 7.42 (t, J = 7.8 Hz, 1H), 7.32 (d, J = 7.5 Hz, 1H), 7.12 (t, J = 7.6 Hz, 1H), 6.83 (t, J = 7.5 Hz, 1H), 6.72 (d, J = 7.9 Hz, 1H), 5.93 (q, J = 3.6 Hz, 1H), 5.05 (dd, J = 11.4, 9.4 Hz, 1H), 5.00 – 4.91 (m, 1H), 4.30 (dd, J = 18.0, 10.6 Hz, 1H), 4.18 (d, J = 2.9 Hz, 1H), 3.19 (ddt, J = 19.1, 6.8, 3.3 Hz, 1H), 2.67 – 2.46 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 151.84, 150.38, 136.62, 133.93, 133.35, 129.89, 128.54, 128.18, 126.14, 124.98, 120.87, 120.39, 114.19, 111.33, 90.70, 64.25, 38.60, 34.83; HPLC: Chiralpak AS-H (hexane/*i*-PrOH = 70/30, flow rate 1 mL/min, λ = 254 nm), t_R (minor) = 21.202 min, t_R (major) = 13.668 min, 86% ee; HRMS(ESI): calcd. for $C_{18}H_{16}N_3O_4$ $(M+H)^+$: 338.1135, found: 338.1138.

(1*S*,2*S*,9a*S*)-2-(2,6-dichlorophenyl)-1-nitro-2,3,9,9a-tetrahydro-1*H*-carbazole (4ad)



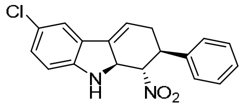
According to the general procedure, the title compound was obtained by silica-gel column chromatography (petroleum ether/ethyl acetate = 30:1); yellow solid (6.8 mg, 19% yield); m.p. 112-114 °C; $[\alpha]_D^{20}$ = + 109.28 (c = 0.14, CH_2Cl_2); ^1H NMR (600 MHz, DMSO-d6) δ = 7.51 (ddd, *J* = 12.1, 8.1, 1.1 Hz, 2H), 7.39 – 7.32 (m, 2H), 7.09 – 7.04 (m, 1H), 6.70 (t, *J* = 7.4 Hz, 1H), 6.64 (d, *J* = 7.9 Hz, 1H), 6.47 (d, *J* = 4.8 Hz, 1H), 6.02 (q, *J* = 3.6 Hz, 1H), 5.54 (dd, *J* = 12.0, 9.1 Hz, 1H), 4.97 – 4.89 (m, 1H), 4.61 (dt, *J* = 11.9, 9.1 Hz, 1H), 2.95 – 2.86 (m, 1H), 2.86 – 2.78 (m, 1H); ^{13}C NMR (151 MHz, DMSO-d6) δ = 153.47, 137.23, 136.43, 134.47, 133.47, 131.09, 130.80, 129.98, 129.68, 126.26, 119.21, 114.04, 111.23, 88.55, 67.49, 64.04, 30.15, 25.60; HPLC: Chiralpak IC-H (hexane/*i*-PrOH = 70/30, flow rate 1 mL/min, λ = 254 nm), t_R (minor) = 7.263 min, t_R (major) = 6.458 min, 90% ee; HRMS(ESI): calcd. for $C_{18}H_{15}Cl_2N_2O_2$ $(M+H)^+$: 361.0505, found: 361.0503.

(1*S*,2*S*,9a*S*)-6-bromo-1-nitro-2-phenyl-2,3,9,9a-tetrahydro-1*H*-carbazole (5a)



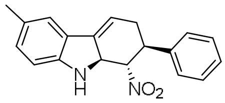
According to the general procedure, the title compound was obtained by silica-gel column chromatography (petroleum ether/ethyl acetate = 30:1); yellow solid (22.6 mg, 61% yield); m.p. 76-77 °C; $[\alpha]_D^{20}$ = + 55.47 (c = 0.46, CH_2Cl_2); ^1H NMR (600 MHz, $CDCl_3$) δ = 7.40 (s, 1H), 7.33 (t, *J* = 7.4 Hz, 2H), 7.27 (t, *J* = 7.3 Hz, 1H), 7.24 (d, *J* = 7.4 Hz, 2H), 7.19 (d, *J* = 8.3 Hz, 1H), 6.57 (d, *J* = 8.3 Hz, 1H), 5.93 (s, 1H), 5.05 (d, *J* = 3.9 Hz, 1H), 4.97 – 4.84 (m, 1H), 4.16 (d, *J* = 4.7 Hz, 1H), 3.60 (dd, *J* = 18.2, 10.9 Hz, 1H), 2.89 (d, *J* = 19.7 Hz, 1H), 2.73 – 2.53 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 150.94, 138.67, 135.31, 132.23, 129.06, 128.47, 128.01, 127.48, 123.77, 116.33, 112.62, 112.27, 91.80, 64.60, 44.16, 35.36; HPLC: Chiralpak IC-H (hexane/*i*-PrOH = 70/30, flow rate 1 mL/min, λ = 254 nm), t_R (minor) = 10.029min, t_R (major) = 7.827min, 93% ee; HRMS(ESI): calcd. for $C_{18}H_{16}BrN_2O_2$ $(M+H)^+$: 371.0390, found: 371.0389.

(1*S*,2*S*,9a*S*)-6-chloro-1-nitro-2-phenyl-2,3,9,9a-tetrahydro-1*H*-carbazole (5b)



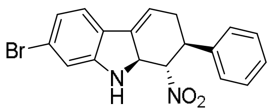
According to the general procedure, the title compound was obtained by silica-gel column chromatography (petroleum ether/ethyl acetate = 30:1); yellow solid (17.3 mg, 53% yield); m.p. 141-142 °C; $[\alpha]_D^{20}$ = + 109.48 (c = 0.37, CH_2Cl_2); ^1H NMR (600 MHz, $CDCl_3$) δ = 7.34 (t, *J* = 7.2 Hz, 2H), 7.30 – 7.23 (m, 4H), 7.06 (d, *J* = 8.3 Hz, 1H), 6.62 (d, *J* = 8.4 Hz, 1H), 5.94 (d, *J* = 3.1 Hz, 1H), 5.17 – 5.00 (m, 1H), 4.92 (t, *J* = 10.5 Hz, 1H), 4.15 (d, *J* = 3.7 Hz, 1H), 3.61 (dd, *J* = 18.2, 10.9 Hz, 1H), 2.97 – 2.80 (m, 1H), 2.70 – 2.58 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 150.49, 138.68, 135.48, 129.41, 129.06, 128.00, 127.97, 127.48, 125.25, 120.87, 116.24, 112.12, 91.84, 64.69, 44.18, 35.36;HPLC: Chiralpak IC-H (hexane/*i*-PrOH = 80/20, flow rate 1 mL/min, λ = 254 nm), t_R (minor) = 16.673 min; t_R (major) = 11.328 min; 90% ee; HRMS(ESI): calcd. for $C_{18}H_{16}ClN_2O_2$ $(M+H)^+$: 327.0895, found: 327.0894.

(1*S*,2*S*,9a*S*)-6-methyl-1-nitro-2-phenyl-2,3,9,9a-tetrahydro-1*H*-carbazole (5c)



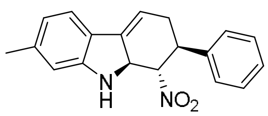
According to the general procedure, the title compound was obtained by silica-gel column chromatography (petroleum ether/ethyl acetate = 30:1); yellow solid (12.5 mg, 41% yield); m.p. 81-82 °C; $[\alpha]_D^{20}$ = + 100.33 (c = 0.35, CH_2Cl_2); ^1H NMR (600 MHz, $CDCl_3$) δ = 7.32 (t, *J* = 7.4 Hz, 2H), 7.26 (dd, *J* = 16.6, 7.5 Hz, 3H), 7.13 (s, 1H), 6.93 (d, *J* = 7.9 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 5.89 (d, *J* = 3.5 Hz, 1H), 5.02 (dd, *J* = 8.7, 3.9 Hz, 1H), 4.96 – 4.86 (m, 1H), 4.03 (s, 1H), 3.61 (td, *J* = 11.0, 7.3 Hz, 1H), 2.98 – 2.78 (m, 1H), 2.69 – 2.57 (m, 1H), 2.28 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 149.83, 139.03, 136.67, 130.39, 129.72, 128.99, 127.87, 127.51, 126.49, 121.21, 114.31, 111.26, 92.23, 64.58, 44.35, 35.44, 20.82; HPLC: Chiralpak IC-H (hexane/*i*-PrOH = 80/20, flow rate 1 mL/min, λ = 254 nm), t_R (minor) = 15.020min, t_R (major) = 11.434 min, 84% ee; HRMS(ESI): calcd. for $C_{19}H_{19}N_2O_2$ $(M+H)^+$: 307.1441, found: 307.1443.

(1*S*,2*S*,9a*S*)-7-bromo-1-nitro-2-phenyl-2,3,9,9a-tetrahydro-1*H*-carbazole (5d)



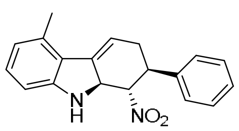
According to the general procedure, the title compound was obtained by silica-gel column chromatography (petroleum ether/ethyl acetate = 30:1); yellow solid (14.1 mg, 38% yield); m.p. 152-153°C; $[\alpha]_D^{20}$ = + 44.2 (c = 0.28, CH_2Cl_2); ^1H NMR (600 MHz, $CDCl_3$) δ = 7.33 (t, *J* = 7.4 Hz, 2H), 7.27 (t,*J* = 7.4 Hz, 1H), 7.25 – 7.22 (m, 2H), 7.14 (d, *J* = 8.0 Hz, 1H), 6.92 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.83 (d, *J* = 1.3 Hz, 1H), 5.93 (q, *J* = 3.6 Hz, 1H), 5.05 (td, *J* = 8.2, 4.0 Hz, 1H), 4.90 (dd, *J* = 11.6, 9.3 Hz, 1H), 4.21 (d, *J* = 4.4 Hz, 1H), 3.59 (td, J = 11.0, 7.1 Hz, 1H), 2.87 (ddt, J = 19.6, 7.0, 3.4 Hz, 1H), 2.71 – 2.55 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ=153.14, 138.72, 135.29, 129.06, 127.99, 127.49, 125.43, 123.20, 123.17, 121.77, 115.62, 114.31, 91.82, 64.50, 44.15, 35.39; HPLC: Chiralpak IC-H (hexane/*i*-PrOH = 70/30, flow rate 1 mL/min, λ = 254 nm), t_R (minor) = 19.205 min, t_R (major) = 11.322 min, 88% ee; HRMS(ESI): calcd. for $C_{18}H_{16}BrN_2O_2$ $(M+H)^+$: 371.0390, found: 371.0386.

(1*S*,2*S*,9a*S*)-7-methyl-1-nitro-2-phenyl-2,3,9,9a-tetrahydro-1*H*-carbazole (5e)



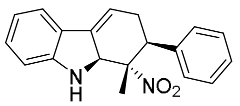
According to the general procedure, the title compound was obtained by silica-gel column chromatography (petroleum ether/ethyl acetate = 30:1); yellow solid (9.2 mg, 30% yield); m.p. 129-131 °C; $[\alpha]_D^{20}$ = + 66.67 (c = 0.19, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.24 (t, J = 7.4 Hz, 2H), 7.18 (d, J = 7.3 Hz, 1H), 7.15 (dd, J = 7.4, 6.2 Hz, 2H), 7.11 (d, J = 7.6 Hz, 1H), 6.55 (d, J = 7.6 Hz, 1H), 6.44 (s, 1H), 5.75 (q, J = 3.6 Hz, 1H), 4.92 (dt, J = 7.6, 3.4 Hz, 1H), 4.82 (dd, J = 11.6, 9.3 Hz, 1H), 3.88 (ddd, J = 10.0, 6.8, 3.5 Hz, 1H), 3.50 (td, J = 11.0, 7.1 Hz, 1H), 2.77 (ddt, J = 19.3, 6.9, 3.3 Hz, 1H), 2.60 – 2.43 (m, 1H), 2.20 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 152.33, 140.15, 139.12, 136.39, 128.99, 127.85, 127.52, 123.79, 121.20, 120.49, 113.54, 112.02, 92.25, 64.55, 44.35, 35.42, 21.75; HPLC: Chiralpak IC-H (hexane/*i*-PrOH = 70/30, flow rate 1 mL/min, λ = 254 nm), t_R (minor) = 12.801 min, t_R (major) = 8.488 min,78% ee; HRMS(ESI): calcd. for $C_{19}H_{19}N_2O_2$ $(M+H)^+$: 307.1441, found: 307.1443.

(1*S*,2*S*,9a*S*)-5-methyl-1-nitro-2-phenyl-2,3,9,9a-tetrahydro-1*H*-carbazole (5f)



According to the general procedure, the title compound was obtained by silica-gel column chromatography (petroleum ether/ethyl acetate = 30:1); yellow solid (8.9 mg, 29% yield); m.p. 130-132 °C; $[\alpha]_D^{20}$ = + 49.44 (c = 0.18, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.26 (t, J = 7.4 Hz, 2H), 7.22 – 7.15 (m, 3H), 6.92 (t, J = 7.7 Hz, 1H), 6.54 (d, J = 7.6 Hz, 1H), 6.48 (d, J = 7.8 Hz, 1H), 5.87 (q, J = 3.6 Hz, 1H), 5.00 – 4.91 (m, 1H), 4.87 (dd, J = 11.6, 9.3 Hz, 1H), 4.04 (dd, J = 14.3, 7.1 Hz, 1H), 3.54 (td, J = 10.9, 7.1 Hz, 1H), 2.87 (ddt, J = 19.4, 6.9, 3.4 Hz, 1H), 2.65 – 2.49 (m, 1H), 2.37 – 2.27 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 152.44, 139.09, 137.02, 134.37, 129.01, 127.88, 127.32, 124.38, 122.30, 117.12, 108.73, 92.32, 64.46, 43.99, 35.77, 20.07; HPLC: Chiralpak IC-H (hexane/*i*-PrOH = 70/30, flow rate 1 mL/min, λ = 254 nm), t_R (minor) = 11.646 min, t_R (major) = 9.142min, 86% ee; HRMS(ESI): calcd. for $C_{19}H_{19}N_2O_2$ $(M+H)^+$: 307.1441, found: 307.1437.

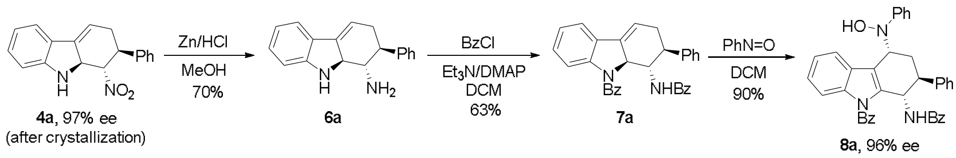
(1*S*,2*S*,9a*S*)-1-methyl-1-nitro-2-phenyl-2,3,9,9a-tetrahydro-1*H*-carbazole (5g)



According to the general procedure, the title compound was obtained by silica-gel column chromatography (petroleum ether/ethyl acetate = 30:1); yellow solid (4.9 mg, 16% yield); m.p. 80-89 °C; $[\alpha]_D^{20}$ = + 122.81 (c = 0.10, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.33 – 7.26 (m, 4H), 7.23 – 7.20 (m, 2H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.80 (d, *J* = 15.0 Hz, 1H), 6.69 (d, *J* = 7.9 Hz, 1H), 5.95 (q, *J* = 3.6 Hz, 1H), 5.46 – 5.33 (m, 1H), 3.90 (d, *J* = 5.0 Hz, 1H), 3.78 (dd, *J* = 10.2, 7.5 Hz, 1H), 2.80 (ddd, *J* = 11.3, 7.5, 3.9 Hz, 2H), 1.62 – 1.44 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 152.37, 137.46, 137.02, 129.65, 128.79, 128.60, 128.19, 126.27, 120.72, 120.00, 114.03, 111.41, 93.89, 68.33, 48.12, 32.46, 10.91; HPLC: Chiralpak IC-H (hexane/*i*-PrOH = 70/30, flow rate 1 mL/min, λ = 254 nm), t_R (minor) =6.782 min; t_R (major) = 5.984 min; 93% ee; HRMS(ESI): calcd. for $C_{19}H_{19}N_2O_2$ $(M+H)^+$: 307.1441, found: 307.1440.

4. Product transformation

1) Preparation of 8a from 4a

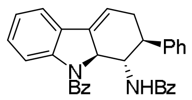


A suspension of the product **4a** (2.69 mmol, 1.0 eq.) in methanol (45.0 mL) was carefully treated with concentrated HCl (53.8 mmol, 20.0 eq.) at 0 °C. After 2 min, zinc dust (107.6 mmol, 40.0 eq.) was slowly added to the suspension. The suspension was stirred at 0 °C for 10 min and warmed to 25 °C for 1 h. The mixture was filtered through celite, eluting with EtOAc, adding aqueous $NaHCO_3$ solution to the filtrate to adjust the pH to alkaline. The mixture was extracted with EtOAc (30.0 mL x 3), and the organic extracts were combined, dried over Na_2SO_4, filtered, concentrated and purified by flash chromatography (petroleum ether/ethyl acetate = 2:1) on silica gel to afford the desired product **6a** (493.3 mg, 70% yield).

Benzoyl chloride (2.2 mmol, 2.2 eq.) and DMAP (0.1mmol,0.1eq.) were added to CH_2Cl_2 (10.0 mL), then a solution of CH_2Cl_2 (10.0 mL) containing compound **6a** (1.0mmol,1.0eq.) and triethylamine (2.2 mmol, 2.2 eq.) was added dropwise to the solution. The mixture was stirred for 2h at room temperature and monitored by TLC. Upon completion, the reaction mixture was concentrated under reduced pressure and subjected to flash chromatographic separation (ethyl acetate/petroleum ether = 1:10) to afford product **7a** (296.1 mg, 63% yield) as a white solid.

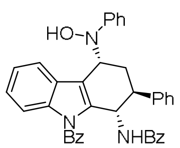
The compound **7a** (0.8 mmol, 1.0 eq.) and nitrosobenzene (0.8 mmol, 1.0 eq.) were dissolved in CH_2Cl_2 (15.0 mL) at room temperature. After stirring for 1h, the reaction mixture was concentrated under reduced pressure and subjected to flash chromatographic separation (ethyl acetate/petroleum ether= 1:10) to afford product **8a** (415.4 mg, 90% yield) as a white solid.

***N*-((1*S*,2*S*,9a*S*)-9-benzoyl-2-phenyl-2,3,9,9a-tetrahydro-1*H*-carbazol-1-yl)benzamide（7a）**



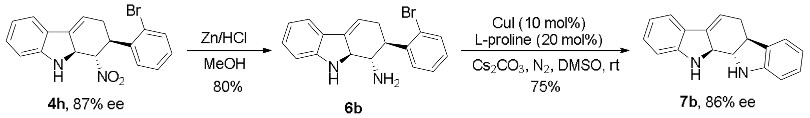
white solid (63% yield); m.p. 255-257 °C; $[\alpha]_D^{20}$ = + 3.20 (c = 0.375, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.55 (d, *J* = 5.3 Hz, 2H), 7.50 (t, *J* = 7.3 Hz, 1H), 7.42 (d, *J* = 7.1 Hz, 3H), 7.30 (s, 4H), 7.26 (dd, *J* = 13.2, 4.5 Hz, 2H), 7.22 (d, *J* = 7.1 Hz, 1H), 7.15 (dt, *J* = 22.6, 7.1 Hz, 3H), 6.94 (t, *J* = 7.4 Hz, 1H), 6.82 (t, *J* = 7.8 Hz, 1H), 6.55 (d, *J* = 9.8 Hz, 1H), 6.11 (s, 1H), 5.89 (d, *J* = 8.3 Hz, 1H), 5.64 – 5.46 (m, 1H), 4.90 (q, *J* = 10.4 Hz, 1H), 3.32 (dd, *J* = 18.3, 9.2 Hz, 1H), 3.00 (dd, *J* = 19.4, 4.1 Hz, 1H), 2.70 (dd, *J* = 12.4, 7.1 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 173.82, 167.66, 144.64, 142.50, 136.82, 135.87, 135.31, 131.48, 130.61, 128.94, 128.63, 128.56, 128.51, 128.14, 128.07, 126.77, 126.58, 123.46, 120.69, 116.16, 114.45, 64.33, 55.87, 46.79, 36.12; HRMS(ESI): calcd. for $C_{32}H_{27}N_2O_2$ $(M+H)^+$: 471.2067, found: 471.2060.

***N*-((1*S*,2*S*,4*R*)-9-benzoyl-4-(hydroxy(phenyl)amino)-2-phenyl-2,3,4,9-tetrahydro-1*H*-carbazol-1-yl)benzamide（8a）**



white solid (90% yield); m.p. 155-156 °C; $[\alpha]_D^{20}$ = - 48.74 (c = 0.595, CH_2Cl_2); ^{1}H NMR (600 MHz, DMSO-d6) δ = 8.78 (d, *J* = 7.6 Hz, 1H), 8.46 (s, 1H), 7.77 – 7.65 (m, 4H), 7.53 (dd, *J* = 12.3, 5.3 Hz, 4H), 7.41 (t, *J* = 7.3 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.28 – 7.17 (m, 9H), 7.12 (t, *J* = 7.4 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.88 (t, *J* = 7.1 Hz, 1H), 6.81 (d, *J* = 8.2 Hz, 1H), 5.55 (t, *J* = 6.6 Hz, 1H), 4.97 (t, *J* = 5.1 Hz, 1H), 3.76 (s, 1H), 2.44 (dd, *J* = 9.5, 4.8 Hz, 1H), 2.25 – 2.14 (m, 1H); ^{13}C NMR (151 MHz, DMSO-d6) δ = 169.66, 166.07, 152.92, 143.26, 137.92, 137.38, 135.05, 134.89, 133.95, 131.28, 130.02, 129.35, 129.04, 128.52, 128.33, 128.01, 127.71, 126.73, 123.88, 122.32, 121.40, 121.02, 119.52, 116.86, 113.27, 60.23, 58.16, 48.83, 44.66, 28.80, 21.23, 14.56; HPLC: Chiralpak As-H (hexane/*i*-PrOH = 70/30, flow rate 1 mL/min, λ = 254 nm), t_R (minor) = 12.374 min, t_R (major) = 22.941 min, 96% ee; HRMS(ESI): calcd. for $C_{38}H_{32}N_3O_3$ $(M+H)^+$: 578.2438, found: 578.2430.

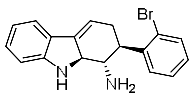
2) Preparation of 7b from 4h



A suspension of the product **4h** (2.3 mmol, 1.0 eq.) in methanol (30.0 mL) was carefully treated with concentrated HCl (46 mmol, 20.0 eq.) at 0 °C. After 2 min, zinc dust (92 mmol, 40.0 eq.) was slowly added to the suspension. The suspension was stirred at 0 °C for 10 min and warmed to 25 °C for 4 h. The mixture was filtered through celite, eluting with EtOAc, adding aqueous $NaHCO_3$ solution to the filtrate to adjust the pH to alkaline. The mixture was extracted with EtOAc (30.0 mL x 3), and the organic extracts were combined, dried over Na_2SO_4, filtered, concentrated and purified by flash chromatography (petroleum ether/ethyl acetate = 2:1) on silica gel to afford the desired product **6b** (625.6 mg, 80% yield).

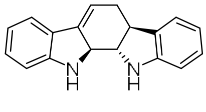
A dry tube was charged with compound **6b** (0.3 mmol, 1.0 eq.), CuI (0.03 mmol, 0.1 eq.), *L*-proline (0.06 mmol, 0.2 eq.) and Cs_2CO_3 (0.6 mmol, 2.0 eq.) at N_2. After addition of DMSO (3.0 mL), the reaction mixture was effectively stirred at room temperature and monitored by TLC. After completion of the reaction, the system was diluted with an appropriate amount of ethyl acetate and washed twice with water to remove DMSO. The organic extract was dried over Na_2SO_4, filtered, concentrated and purified by flash chromatography (petroleum ether/ethyl acetate = 10:1) on silica gel to afford the desired product **7b** (58.5 mg, 75% yield).

(1*S*,2*S*,9a*S*)-2-(2-bromophenyl)-2,3,9,9a-tetrahydro-1*H*-carbazol-1-amine（6b）



white solid (80% yield); m.p. 121-122 °C; $[\alpha]_D^{20}$ = + 47.86 (c = 0.46, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.60 (d, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.29 (d, *J* = 7.5 Hz, 2H), 7.09 (ddd, *J* = 20.5, 11.6, 4.5 Hz, 2H), 6.76 (t, *J* = 7.4 Hz, 1H), 6.72 (d, *J* = 7.8 Hz, 1H), 5.98 – 5.72 (m, 1H), 4.28 (s, 1H), 3.57 (dd, *J* = 17.1, 10.0 Hz, 1H), 3.24 (t, *J* = 9.7 Hz, 1H), 2.78 (d, *J* = 18.6 Hz, 1H), 2.43 – 2.21 (m, 1H), 1.43 (s, 2H), 1.26 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 152.90, 142.13, 138.19, 133.31, 129.06, 128.33, 128.13, 127.70, 127.65, 126.28, 120.60, 119.48, 114.34, 110.92, 67.75, 56.33, 46.05, 34.73; HRMS(ESI): calcd. for $C_{18}H_{18}BrN_2$ $(M+H)^+$: 341.0648, found: 341.0648.

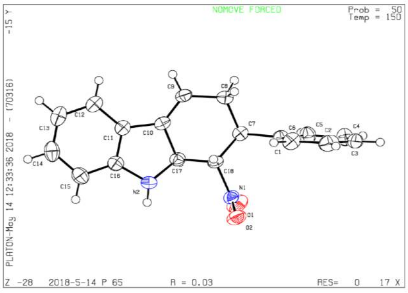
(4b*S*,11a*S*,11b*S*)-4b,5,11,11a,11b,12-hexahydroindolo[2,3-a]carbazole（7b）

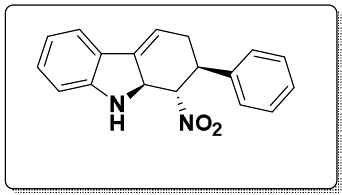


white solid (75% yield); m.p. 174-175 °C; $[\alpha]_D^{20}$ = + 3.04 (c = 0.30, CH_2Cl_2); ^{1}H NMR (600 MHz, DMSO-d6) δ = 7.28 (d, *J* = 6.9 Hz, 1H), 7.07 (d, *J* = 6.4 Hz, 1H), 7.04 – 6.92 (m, 2H), 6.75 – 6.57 (m, 4H), 6.07 (s, 1H), 5.94 (d, *J* = 26.1 Hz, 2H), 4.41 (s, 1H), 3.20 (t, J = 10.5 Hz, 1H), 2.97 – 2.81 (m, 2H), 2.45 – 2.32 (m, 1H); ^{13}C NMR (151 MHz, DMSO-d6) δ = 154.22, 152.80, 140.18, 131.83, 129.31, 127.47, 122.70, 120.85, 118.44, 118.38, 115.54, 110.91, 110.16, 69.82, 67.09, 43.50, 28.75; HPLC: Chiralpak IA-H (hexane/*i*-PrOH = 70/30, flow rate 1 mL/min, λ = 254 nm), t_R (minor) = 6.931 min, t_R (major) = 10.468 min, 86% ee; HRMS(ESI): calcd. for $C_{18}H_{17}N_2$ $(M+H)^+$: 261.1386, found: 261.1386.

5. Determination of absolute configurations of 4a and 8a

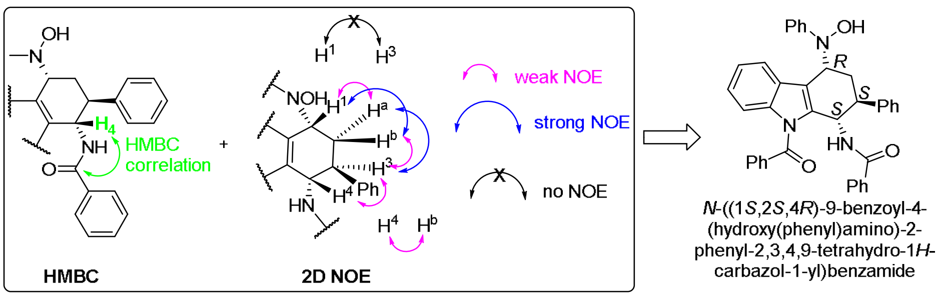
1) X-ray crystal analysis data of 4a



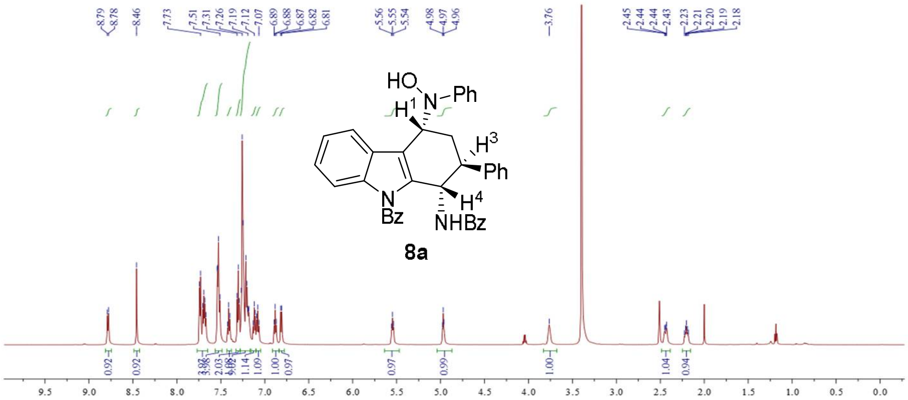


Empirical formula	$C_{18}H_6N_2O_2$
Formula weight	292.33
Temperature	150 K
Wavelength	1.54184
Crystal system, space group	hexagonal, P 65
a, Á	10.86074(5)
b, Á	10.86074(5)
c, Á	21.89996(14)
α, °	90
β, °	90
γ, °	120
V, A^3	2237.14(3)
Z, Calculated density	6, 1.302 g/cm^3

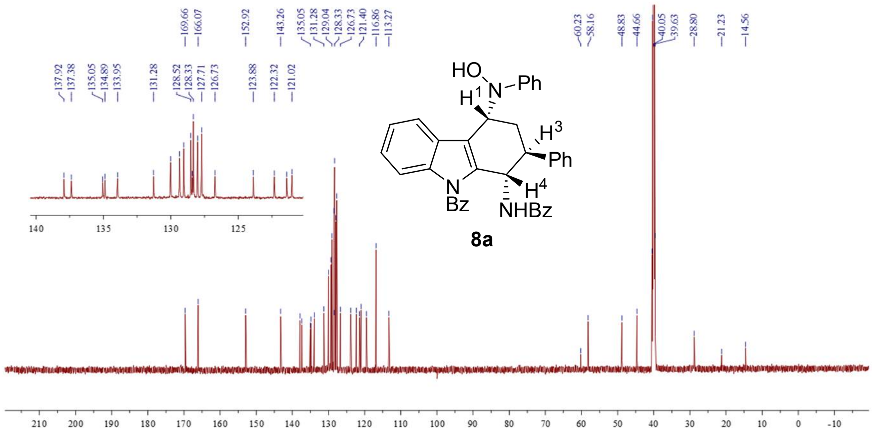
2) Determining the absolute configuration of 8a by 2D NMR



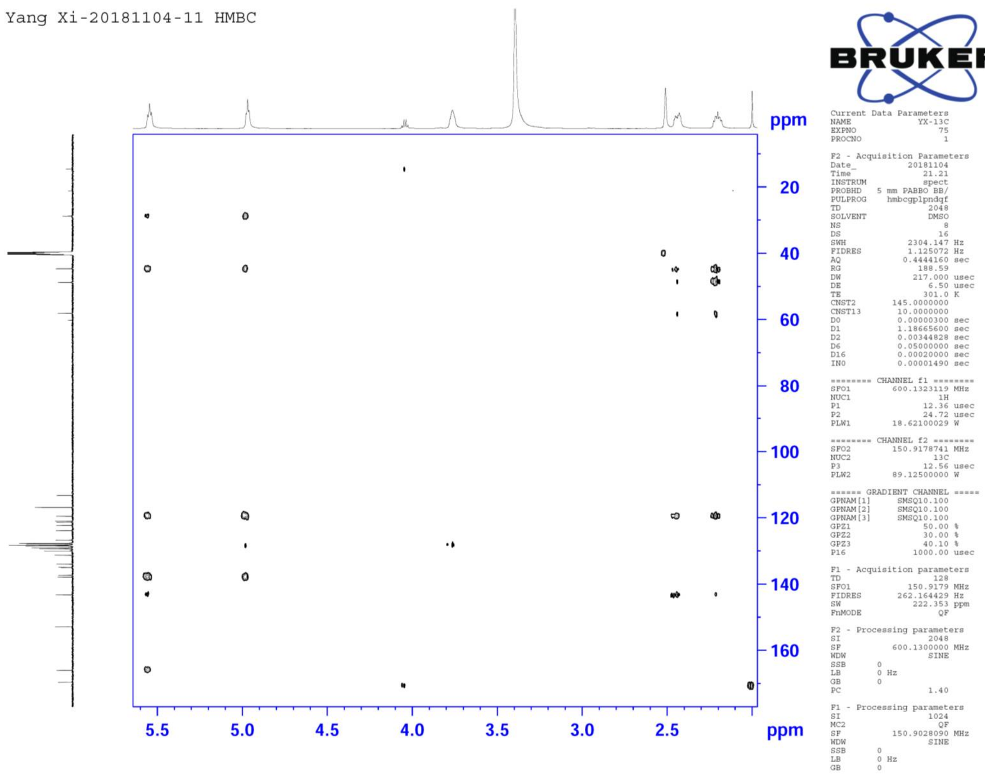
^{1}H NMR of 8a



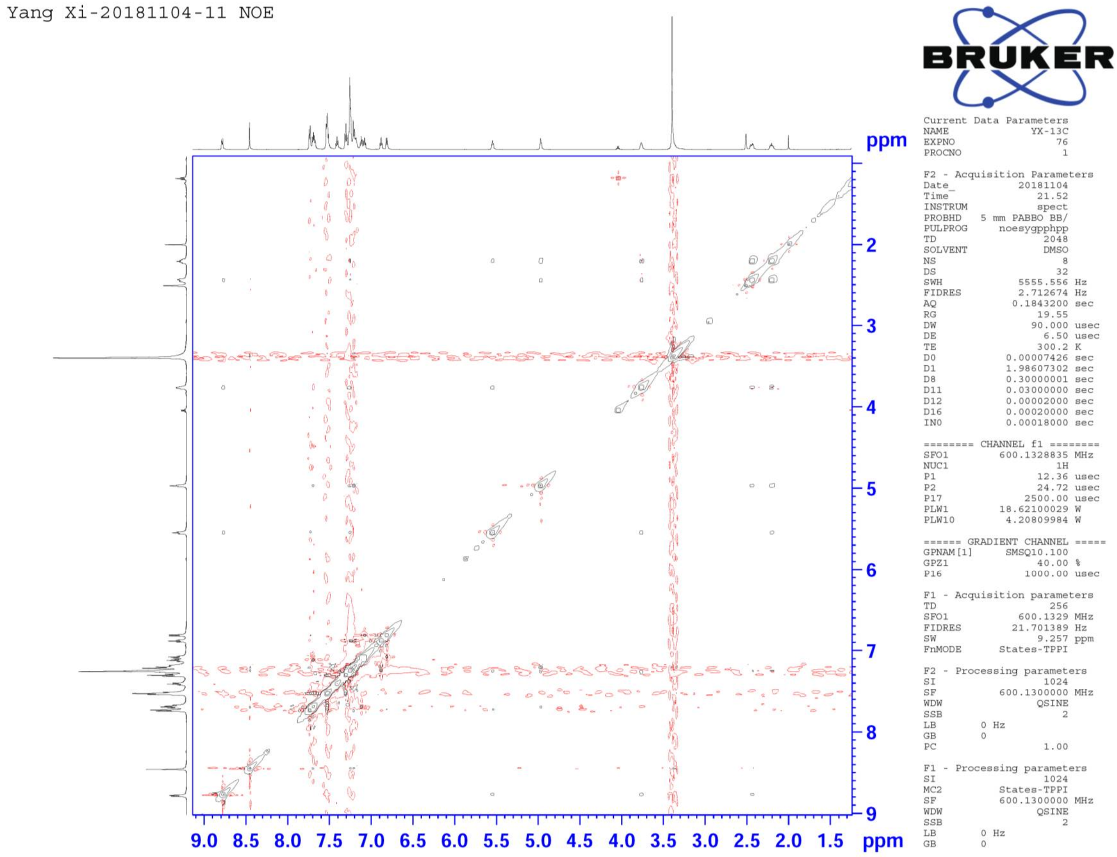
^{13}C NMR of 8a



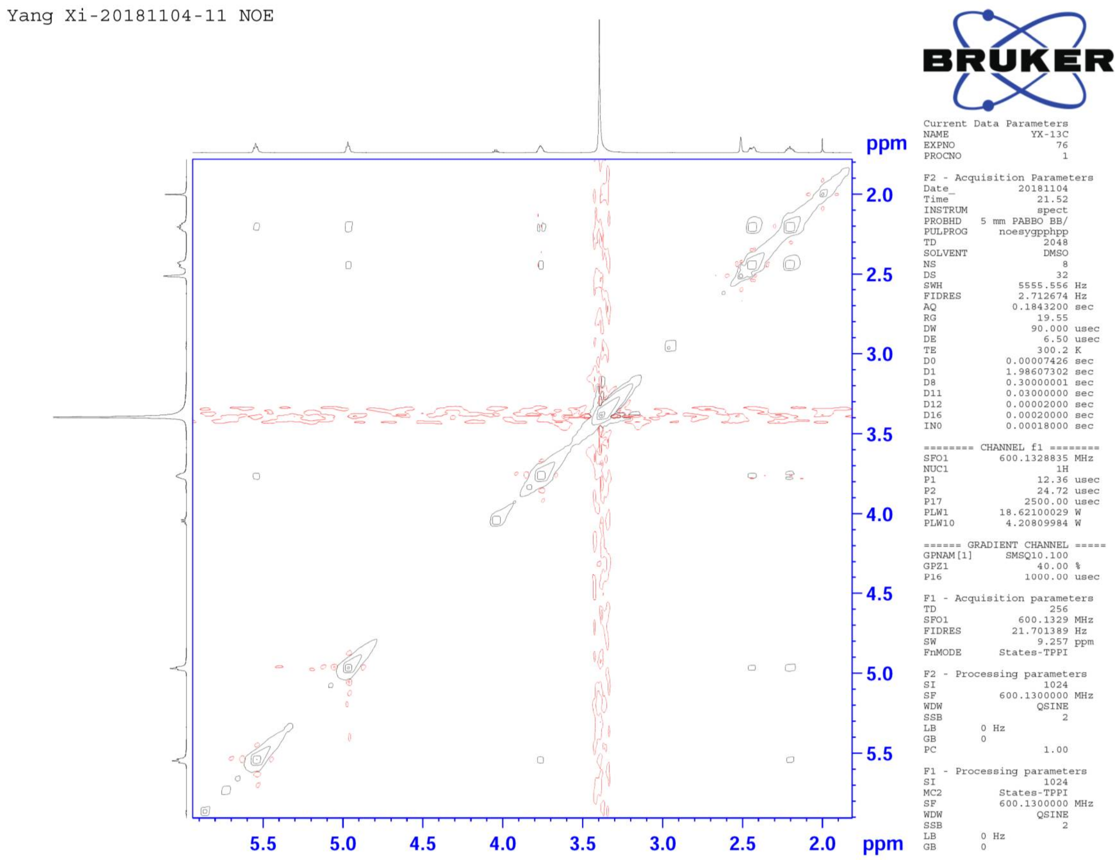
HMBC of 8a



NOE of 8a (full)



NOE of 8a (expand)



6. Transition states study

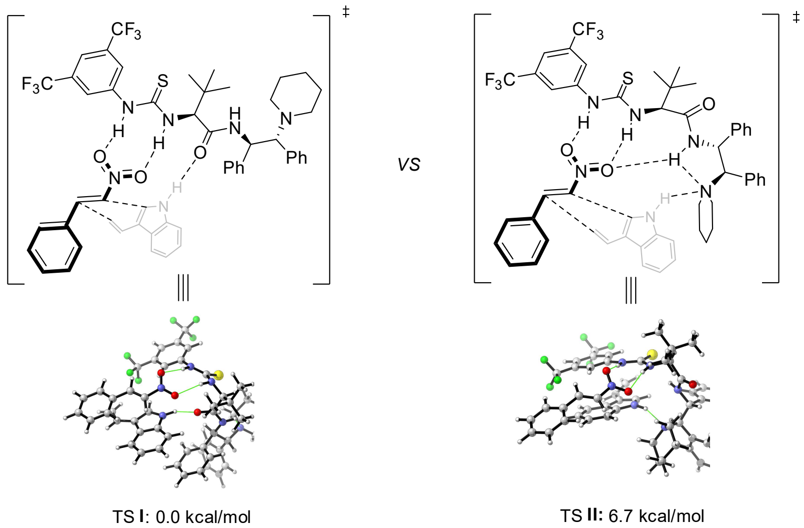
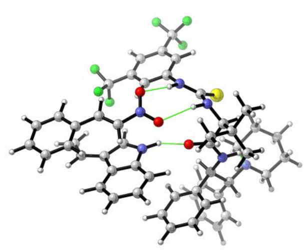


Figure S1. Two optimal transition states by DFT calculation.

Computational method:

All calculations were carried out with the GAUSSIAN 09 packages.[5] The recently developed M06-2x functional,[6] together with the standard 6-31G(d) basis set, were used for optimizing the geometry. All the optimized structures were confirmed by frequency calculations to be minima states using the same level of theory. To take solvent effects into account, solution-phase single-point calculations were performed on the gas-phase geometries.[7] The solution-phase single point energy calculations were done using M06-2x method at a larger basis set 6-31++G(d,p). Solvent effect was accounted for using self-consistent reaction field (SCRF) method, using SMD model and UAKS radii.[8] Xylene-mixture was used as the solvent. Solution-phase single-point energies corrected by the gas-phase Gibbs free energy corrections were used to describe all the reaction energetics. All of these energies correspond to the reference state of 1 mol/L, 298 K. Structures were generated using GaussView5.0.8 and CYL view.

Computational data for TS I:



Zero-point correction= 0.996211 (Hartree/Particle)

Thermal correction to Energy= 1.059387

Thermal correction to Enthalpy= 1.060331

Thermal correction to Gibbs Free Energy= 0.892527

E(sov) = -3564.38604027 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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3	6	0	2.730928	-0.461825	-2.612005
4	6	0	3.363410	0.759176	-2.444911
5	6	0	2.734631	1.813026	-1.753827
6	6	0	1.472869	1.657150	-1.199612
7	6	0	-0.579097	-1.297829	-1.365505
8	6	0	0.519092	-1.747876	-2.059332
9	1	0	3.232527	-1.271666	-3.135091
10	1	0	4.358672	0.908719	-2.851778
11	1	0	3.242556	2.769862	-1.667774
12	1	0	0.973219	2.470753	-0.678479
13	1	0	-1.503037	-1.820058	-1.157314
14	6	0	0.719542	-3.080099	-2.621151
15	6	0	0.088027	-4.182836	-2.208441
16	1	0	1.455251	-3.160006	-3.421084
17	1	0	0.271541	-5.145945	-2.671915
18	1	0	-0.608550	-4.157709	-1.372515
19	7	0	-0.386847	-0.014796	-0.918567
20	1	0	-1.147639	0.589953	-0.575655
21	6	0	5.624731	6.226450	-0.233821
22	6	0	4.743595	5.382404	0.425628
23	6	0	4.938939	3.993934	0.390840
24	6	0	6.036020	3.469869	-0.306501

25	6	0	6.911480	4.318967	-0.973256
26	6	0	6.707130	5.695766	-0.937167
27	1	0	5.473577	7.300360	-0.197392
28	1	0	3.914063	5.800962	0.988519
29	1	0	6.183354	2.393790	-0.336603
30	1	0	7.754224	3.905623	-1.517643
31	1	0	7.394233	6.359669	-1.452498
32	6	0	4.024198	3.057535	1.035586
33	6	0	2.763395	3.330442	1.393205
34	7	0	1.943966	2.276439	1.924173
35	8	0	2.477979	1.265644	2.371333
36	8	0	0.732046	2.438159	1.889926
37	1	0	4.381323	2.039965	1.183071
38	1	0	2.205601	4.240576	1.223800
39	6	0	-3.782661	0.749736	-1.019597
40	6	0	-4.204204	0.185552	0.359862
41	7	0	-2.706741	1.744057	-0.923446
42	6	0	-5.113623	-1.020361	0.180274
43	6	0	-5.012379	1.169781	-1.817552
44	7	0	-3.056936	-0.133498	1.194916
45	6	0	-2.951563	0.357278	2.462950
46	8	0	-3.666675	1.250088	2.893851
47	6	0	-1.849736	-0.339852	3.284829
48	6	0	-2.782730	2.839465	0.050090
49	6	0	-3.395071	4.147446	-0.468270
50	6	0	-2.732300	4.579823	-1.775586
51	6	0	-2.827011	3.444881	-2.795884
52	6	0	-2.175332	2.184190	-2.219001
53	6	0	-5.980932	2.029524	-1.289682
54	6	0	-7.061354	2.443742	-2.061418

55	6	0	-7.197582	1.994924	-3.374034
56	6	0	-6.253059	1.120886	-3.902530
57	6	0	-5.172807	0.710186	-3.124457
58	6	0	-4.597230	-2.253582	-0.224150
59	6	0	-5.434224	-3.350719	-0.400052
60	6	0	-6.803238	-3.226595	-0.177166
61	6	0	-7.326947	-2.002419	0.227186
62	6	0	-6.485277	-0.908326	0.406228
63	7	0	-0.624180	-0.387718	2.503899
64	6	0	-1.598318	0.229321	4.702327
65	6	0	-0.075487	-1.500970	1.957360
66	7	0	1.221207	-1.295676	1.603124
67	16	0	-0.949600	-2.929220	1.751041
68	6	0	2.157353	-2.042690	0.875753
69	6	0	3.322756	-1.341549	0.537932
70	6	0	4.327832	-1.954831	-0.186154
71	6	0	4.200487	-3.274655	-0.606725
72	6	0	3.041546	-3.959587	-0.265209
73	6	0	2.024437	-3.376229	0.483486
74	6	0	2.904301	-5.376785	-0.749184
75	9	0	1.755440	-5.943790	-0.368898
76	9	0	3.906025	-6.144562	-0.288148
77	9	0	2.965602	-5.439512	-2.090333
78	6	0	5.561038	-1.188459	-0.562103
79	9	0	5.770502	-1.198284	-1.887837
80	9	0	6.661145	-1.704764	0.003085
81	9	0	5.493199	0.104424	-0.180167
82	6	0	-0.479700	-0.601224	5.347425
83	6	0	-1.177176	1.703027	4.664230
84	6	0	-2.872200	0.068053	5.542867

85	1	0	-3.330458	-0.089695	-1.572867
86	1	0	-4.756700	0.947995	0.914274
87	1	0	-2.533410	-0.985943	1.000015
88	1	0	-2.174042	-1.382172	3.395537
89	1	0	-3.300874	2.498397	0.949679
90	1	0	-1.745281	3.053412	0.356895
91	1	0	-3.276641	4.916150	0.304101
92	1	0	-4.469296	4.024875	-0.639896
93	1	0	-3.194702	5.493935	-2.162472
94	1	0	-1.672486	4.809338	-1.588859
95	1	0	-2.313250	3.712672	-3.726228
96	1	0	-3.877841	3.254261	-3.043392
97	1	0	-2.240448	1.343320	-2.919052
98	1	0	-1.102646	2.394013	-2.083080
99	1	0	-5.893648	2.384999	-0.265469
100	1	0	-7.801140	3.115799	-1.636783
101	1	0	-8.041396	2.317397	-3.976106
102	1	0	-6.357348	0.753075	-4.918734
103	1	0	-4.439723	0.021026	-3.538112
104	1	0	-3.527935	-2.377000	-0.387435
105	1	0	-5.014848	-4.303349	-0.708557
106	1	0	-7.457711	-4.081926	-0.314134
107	1	0	-8.392281	-1.897641	0.408557
108	1	0	-6.896725	0.046266	0.723639
109	1	0	-0.109792	0.488714	2.433009
110	1	0	1.591745	-0.390240	1.883175
111	1	0	3.410799	-0.292747	0.804032
112	1	0	4.979685	-3.754449	-1.191412
113	1	0	1.134752	-3.938292	0.727674
114	1	0	-0.346235	-0.294223	6.390198

115	1	0	-0.721531	-1.670525	5.335120
116	1	0	0.476929	-0.465354	4.831990
117	1	0	-1.031219	2.067890	5.687090
118	1	0	-1.940256	2.317721	4.181258
119	1	0	-0.226106	1.837959	4.135642
120	1	0	-3.192022	-0.980655	5.566581
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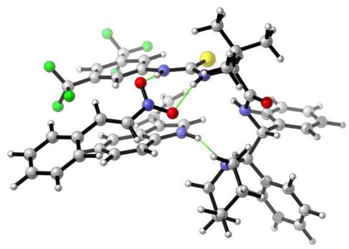
122	1	0	-2.669345	0.376402	6.574399

Computational data for TS II:



Zero-point correction= 0.997353 (Hartree/Particle)

Thermal correction to Energy= 1.060018

Thermal correction to Enthalpy= 1.060962

Thermal correction to Gibbs Free Energy= 0.894267

E(sov) = -3564.39848436 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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2	6	0	-2.690753	-2.926309	-0.675989
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4	6	0	-2.614437	-5.016344	0.505988
5	6	0	-1.485167	-4.574823	1.229412
6	6	0	-0.938598	-3.321578	1.019287

7	6	0	-2.167941	-0.820771	-1.273944
8	6	0	-3.068911	-1.833225	-1.534855
9	1	0	-4.078634	-4.561643	-1.003910
10	1	0	-3.008988	-6.010848	0.693084
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12	1	0	-0.052570	-2.976778	1.541791
13	1	0	-2.097243	0.163236	-1.719117
14	6	0	-4.207225	-1.828146	-2.446925
15	6	0	-4.530178	-0.865922	-3.315589
16	1	0	-4.856565	-2.701664	-2.373342
17	1	0	-5.415940	-0.951160	-3.936272
18	1	0	-3.934684	0.034826	-3.429669
19	7	0	-1.276674	-1.216440	-0.313052
20	1	0	-0.457900	-0.719575	0.026785
21	6	0	-6.869667	-3.558908	0.148870
22	6	0	-5.848085	-2.885208	0.804146
23	6	0	-5.643674	-1.517071	0.570401
24	6	0	-6.485544	-0.843752	-0.324582
25	6	0	-7.508708	-1.520021	-0.977872
26	6	0	-7.702043	-2.878319	-0.741535
27	1	0	-7.021291	-4.617737	0.334368
28	1	0	-5.202463	-3.423341	1.491574
29	1	0	-6.309473	0.208823	-0.527607
30	1	0	-8.148012	-0.988678	-1.675522
31	1	0	-8.501362	-3.409520	-1.249188
32	6	0	-4.579923	-0.755971	1.212705
33	6	0	-3.583002	-1.254322	1.958280
34	7	0	-2.611973	-0.344027	2.500335
35	8	0	-2.835979	0.868258	2.457154
36	8	0	-1.596893	-0.812767	2.990702

37	1	0	-4.595345	0.321379	1.063940
38	1	0	-3.338800	-2.289400	2.157612
39	6	0	4.513800	-1.317031	-0.897129
40	6	0	3.083528	-1.318081	-0.307908
41	7	0	5.241830	-0.107290	-0.490284
42	6	0	2.471364	-2.703438	-0.386854
43	6	0	4.519846	-1.607172	-2.390093
44	7	0	3.177027	-0.816251	1.055463
45	6	0	2.056424	-0.494535	1.724468
46	8	0	0.934660	-0.799125	1.319879
47	6	0	2.197447	0.305375	3.030304
48	6	0	6.680009	-0.216143	-0.731291
49	6	0	7.424423	0.918766	-0.032776
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51	6	0	5.381569	2.333683	-0.323129
52	6	0	4.713843	1.152674	-1.022156
53	6	0	5.385441	-2.581702	-2.890775
54	6	0	5.451698	-2.852369	-4.254594
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59	6	0	2.314116	-4.984364	0.402726
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62	6	0	1.549073	-3.002460	-1.388832
63	7	0	1.021152	1.161776	3.102275
64	6	0	2.332441	-0.573815	4.298778
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67	16	0	2.108492	2.789422	1.262127
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74	6	0	-0.689491	6.649644	-0.631139
75	9	0	-0.273993	7.256218	0.488158
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85	1	0	5.042827	-2.144562	-0.404451
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88	1	0	3.078992	0.949735	2.962355
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121	1	0	3.362702	-2.263840	3.365755
122	1	0	3.738347	-2.018985	5.079419

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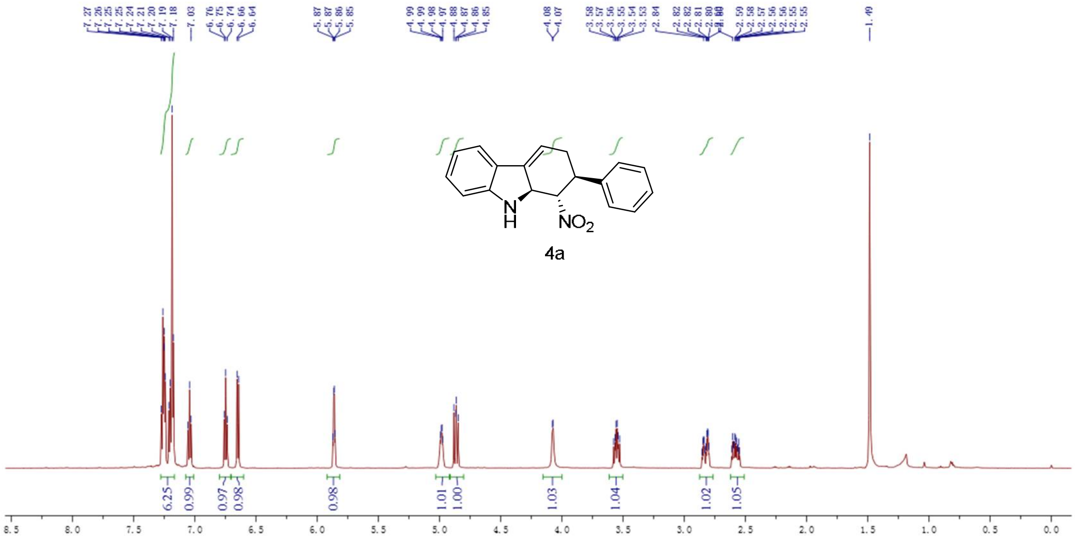
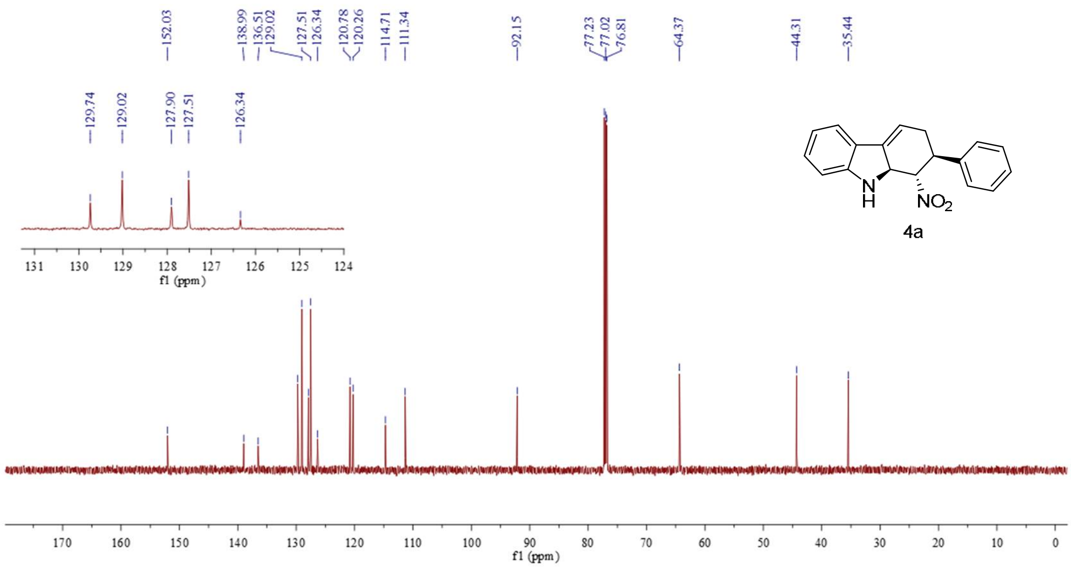
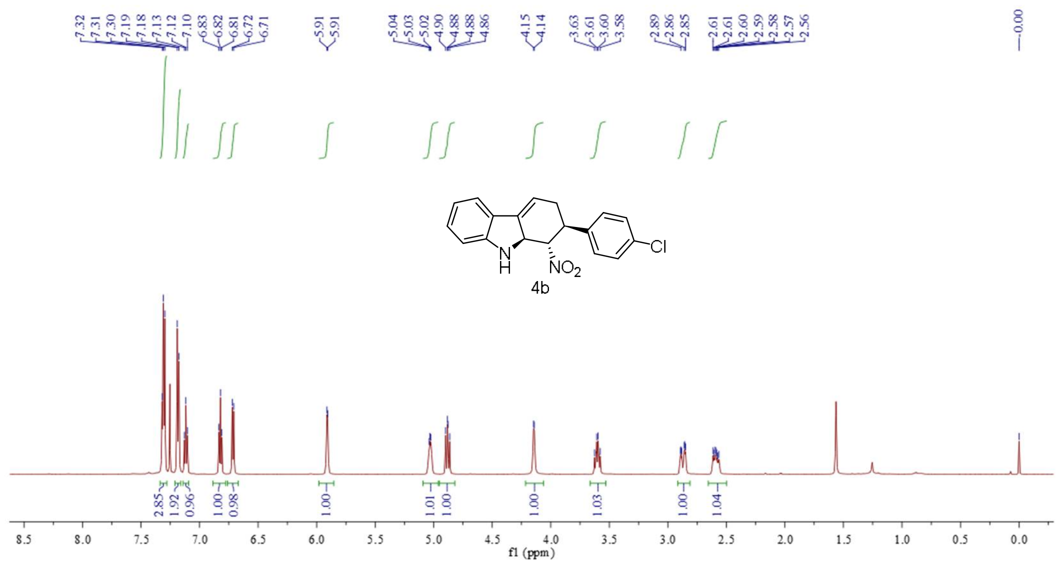
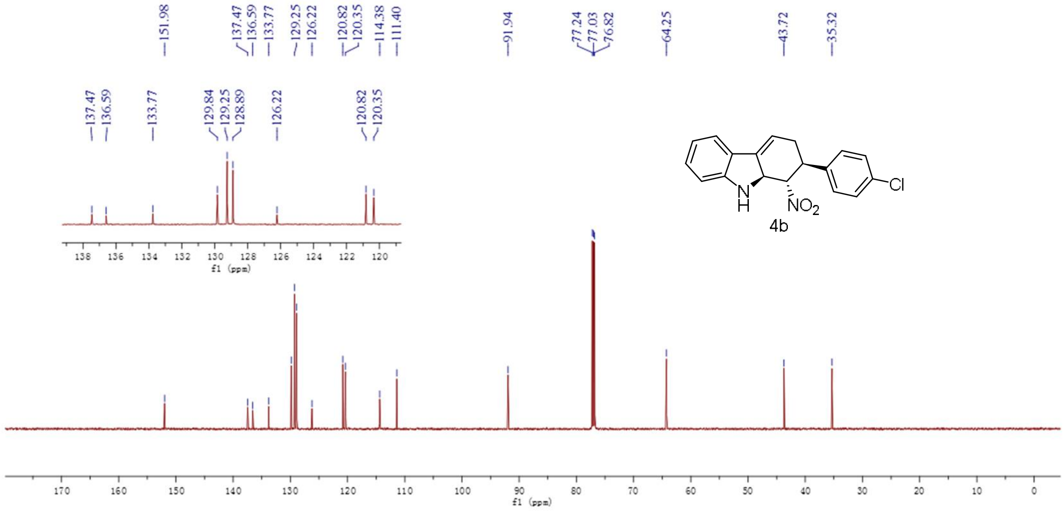
8. The spectrums of [1]H NMR, [13]C NMR and HPLC.





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76.82
64.25
43.72
35.32
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120.35
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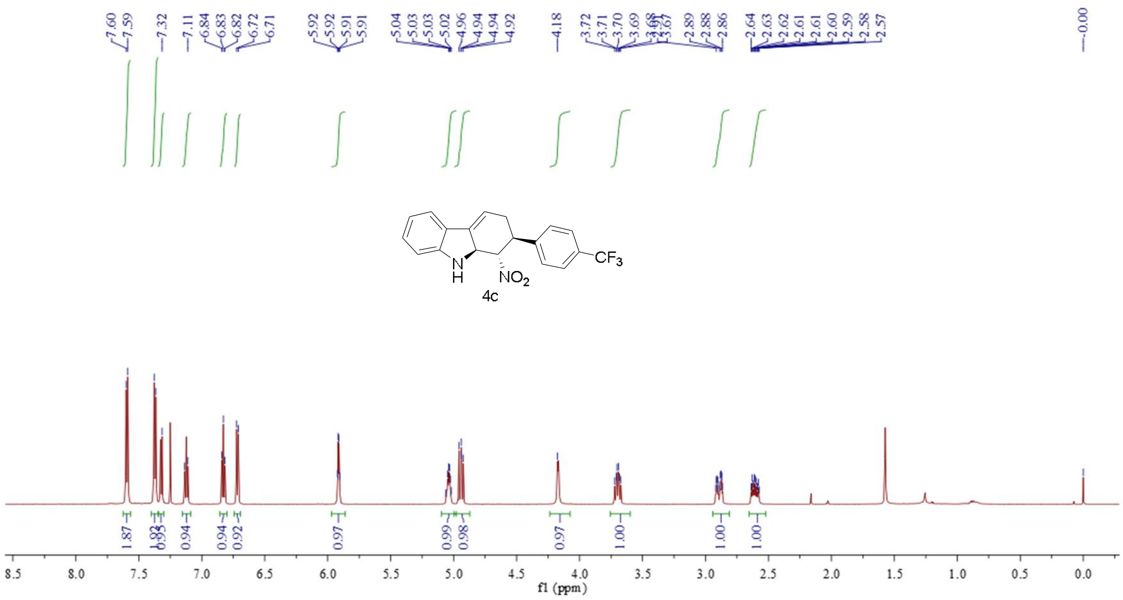
NO2
4b
f1 (ppm)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4.94
4.92
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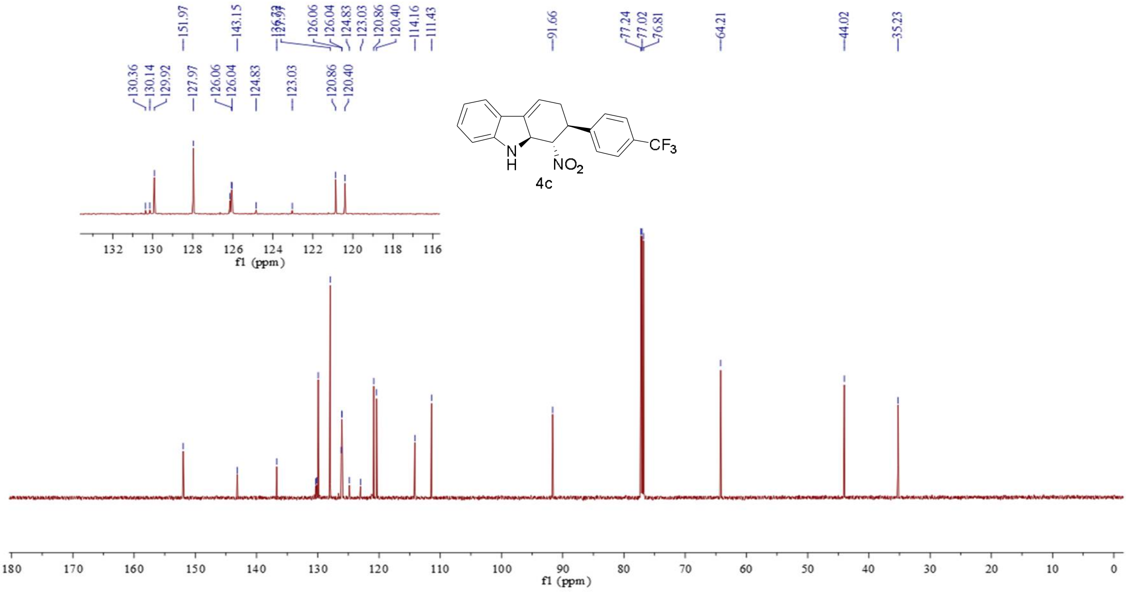
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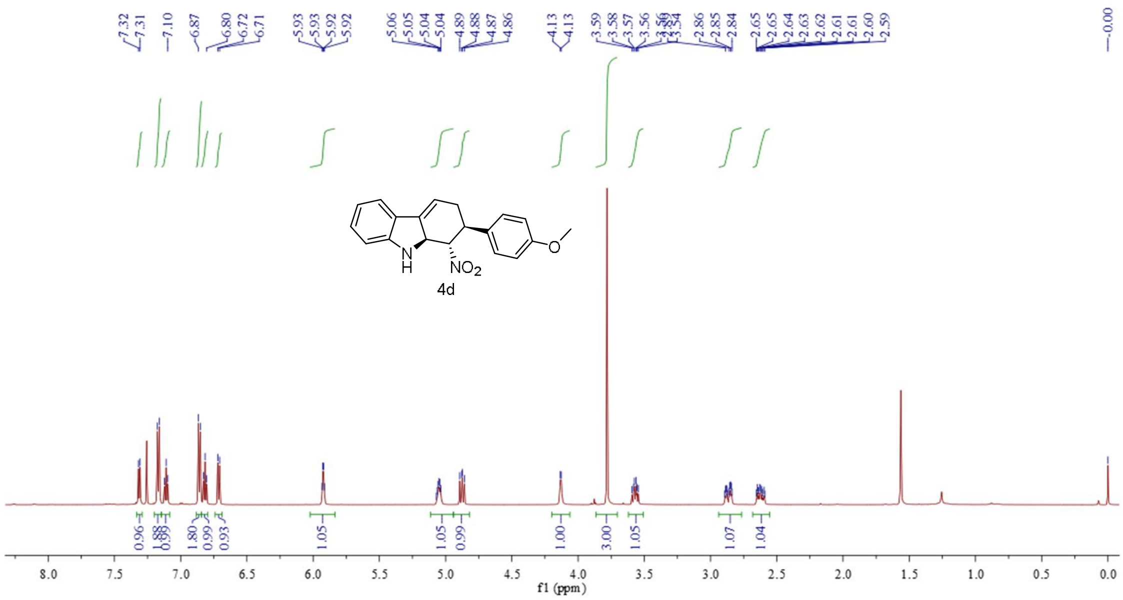

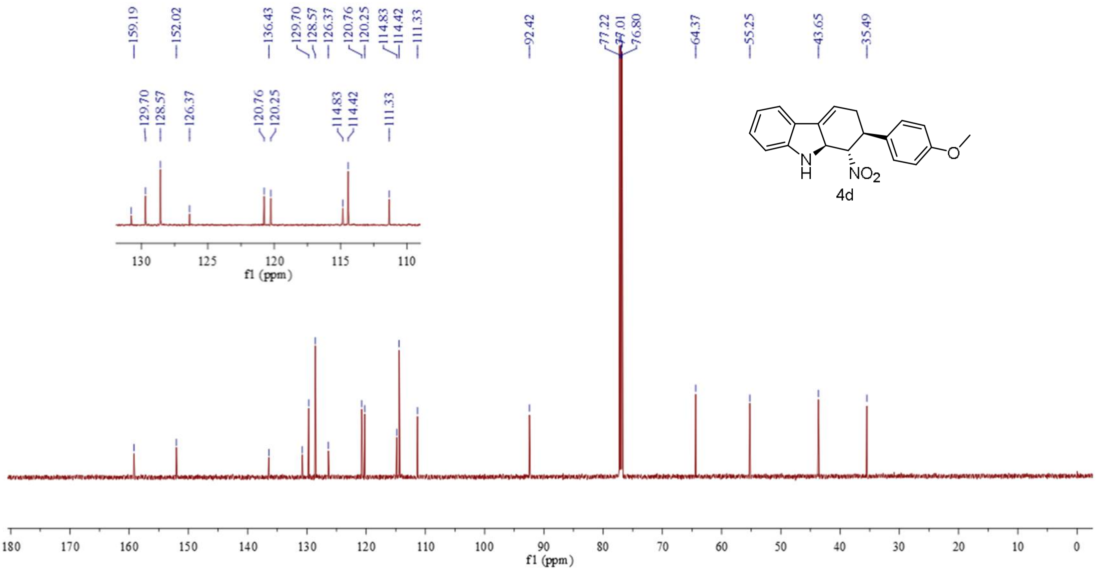

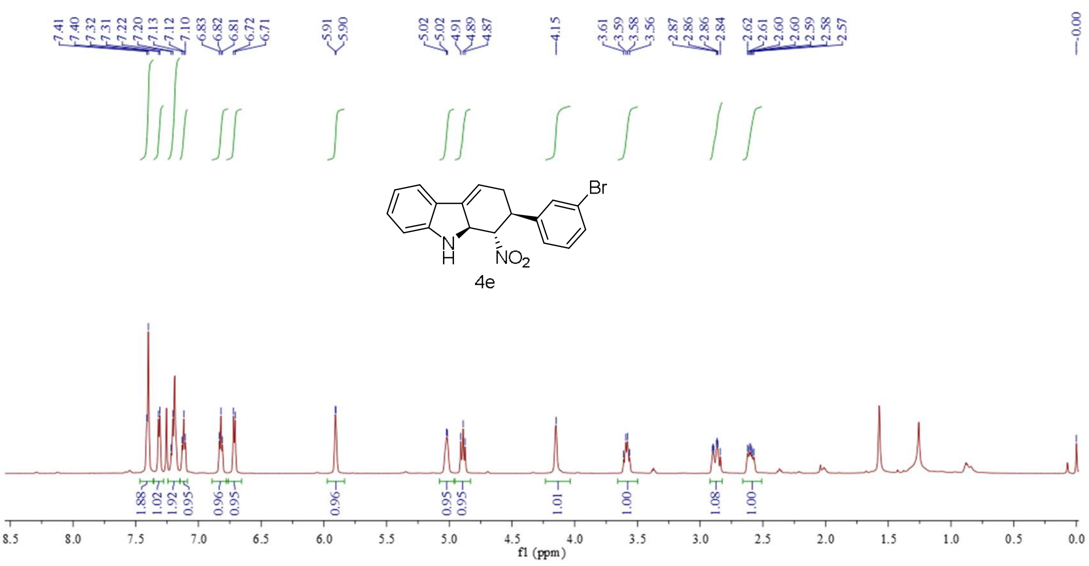

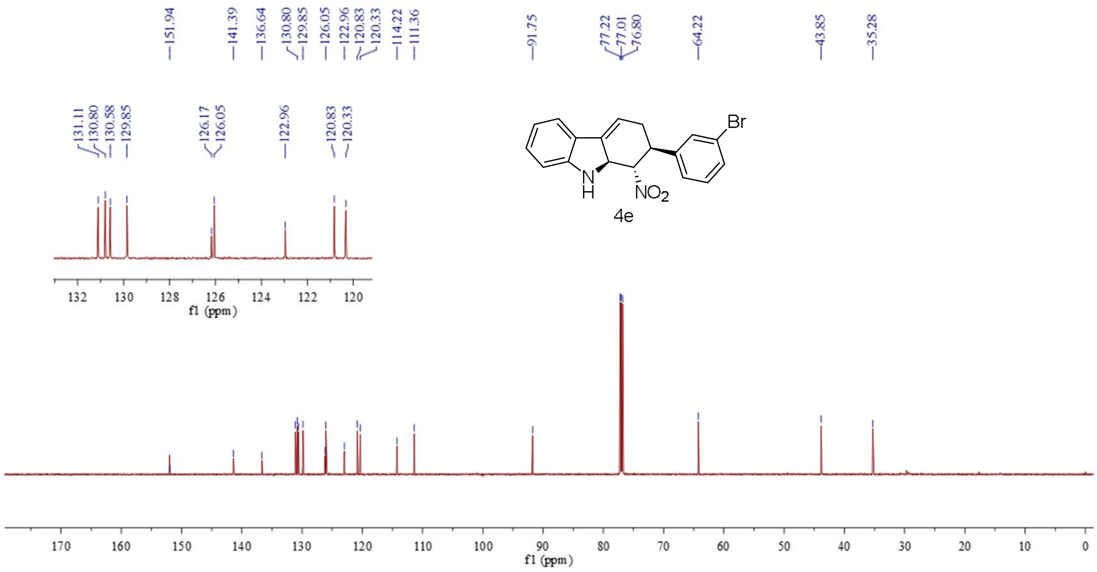
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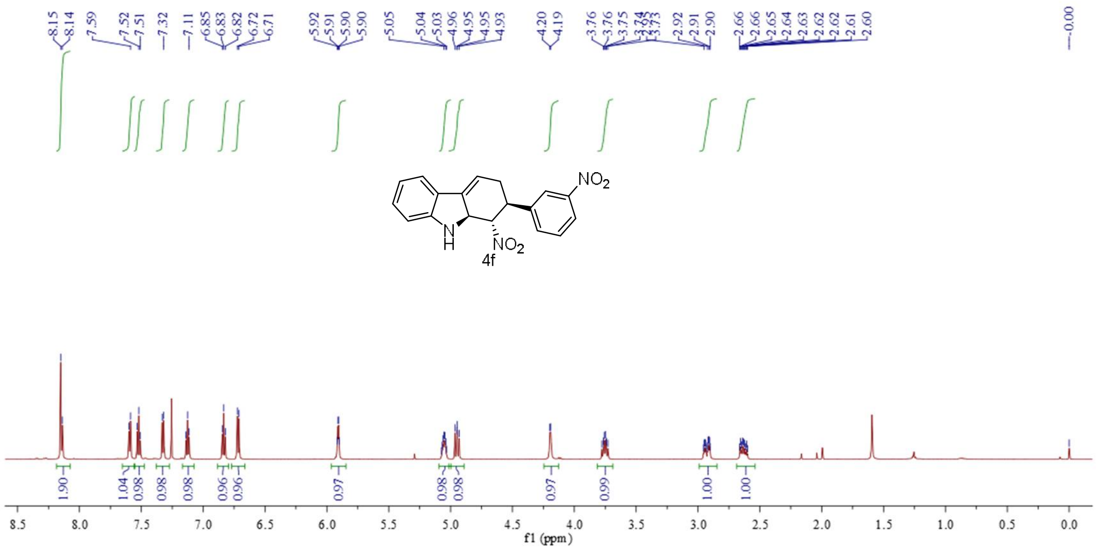
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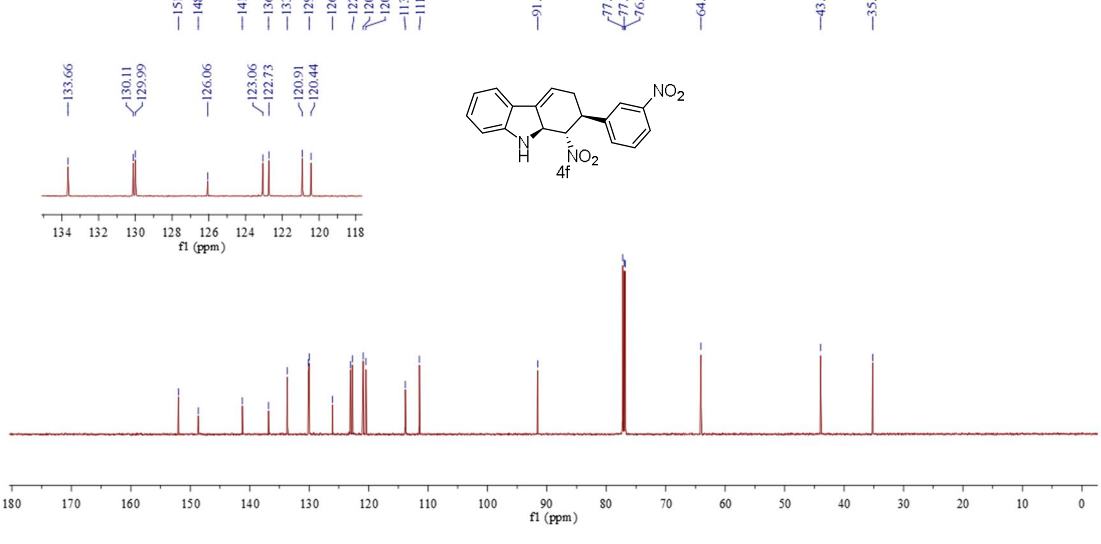
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NO_2
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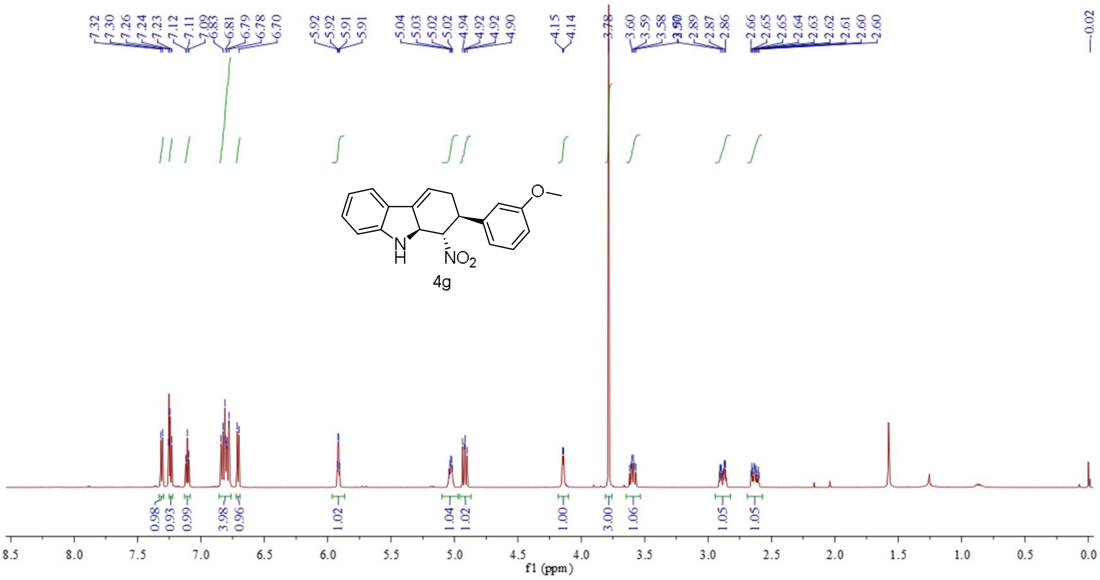
f1 (ppm)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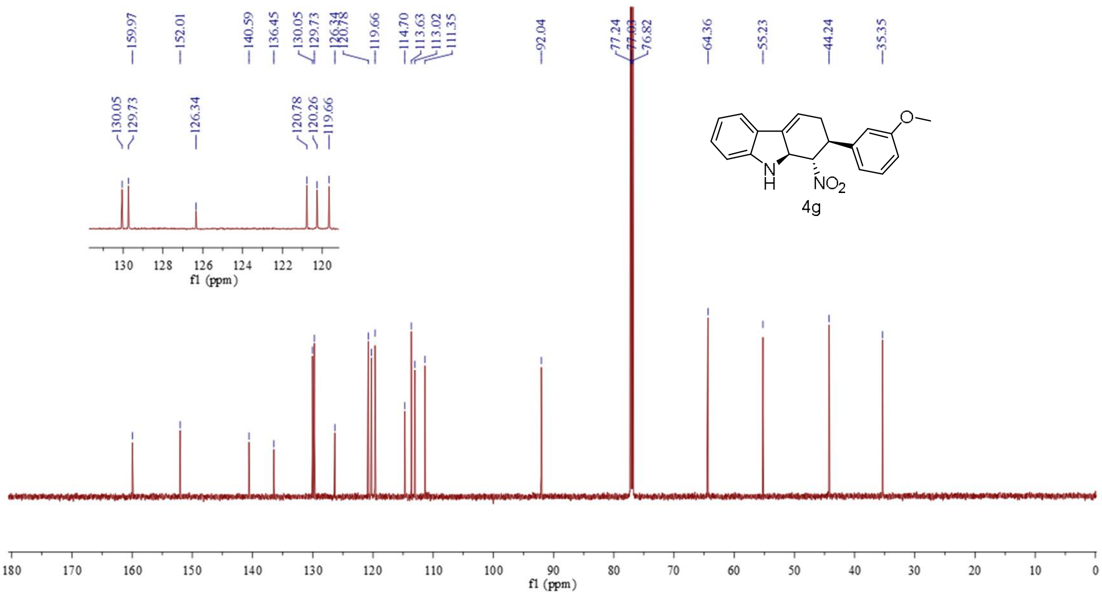
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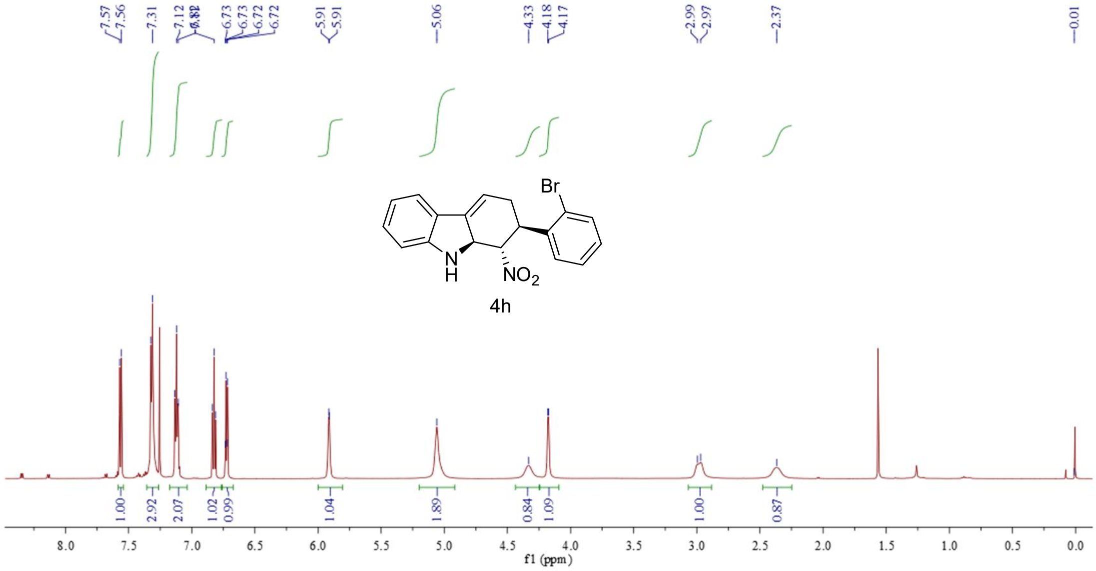
f1 (ppm)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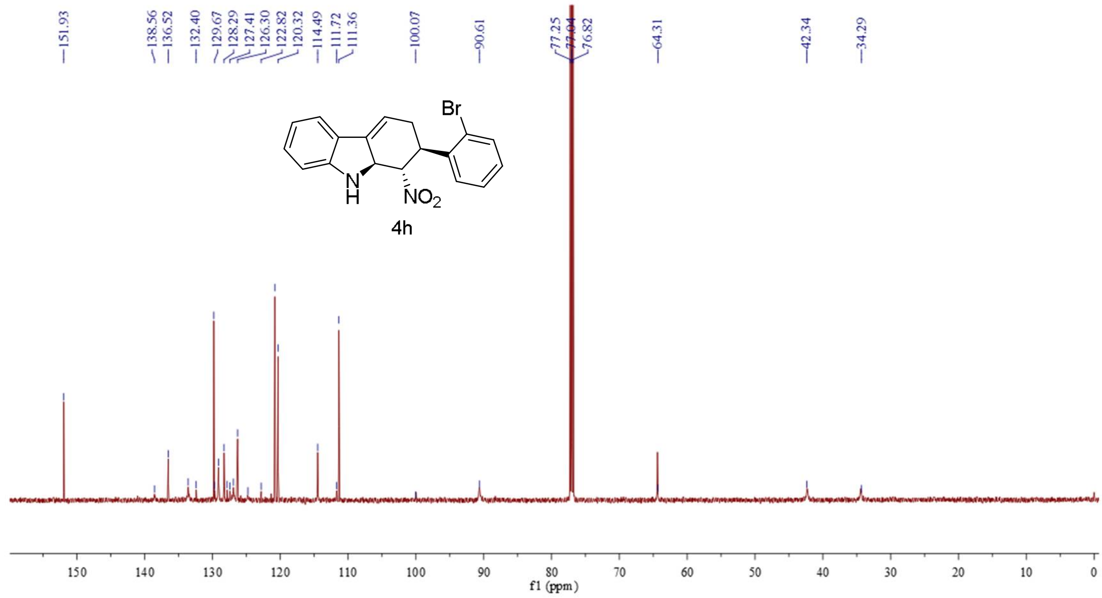
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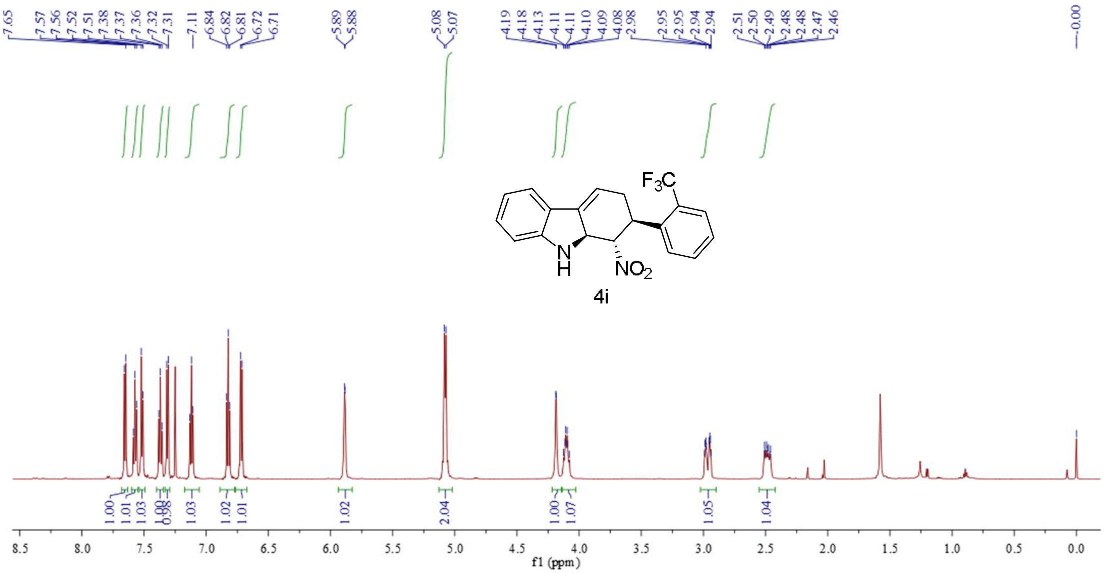
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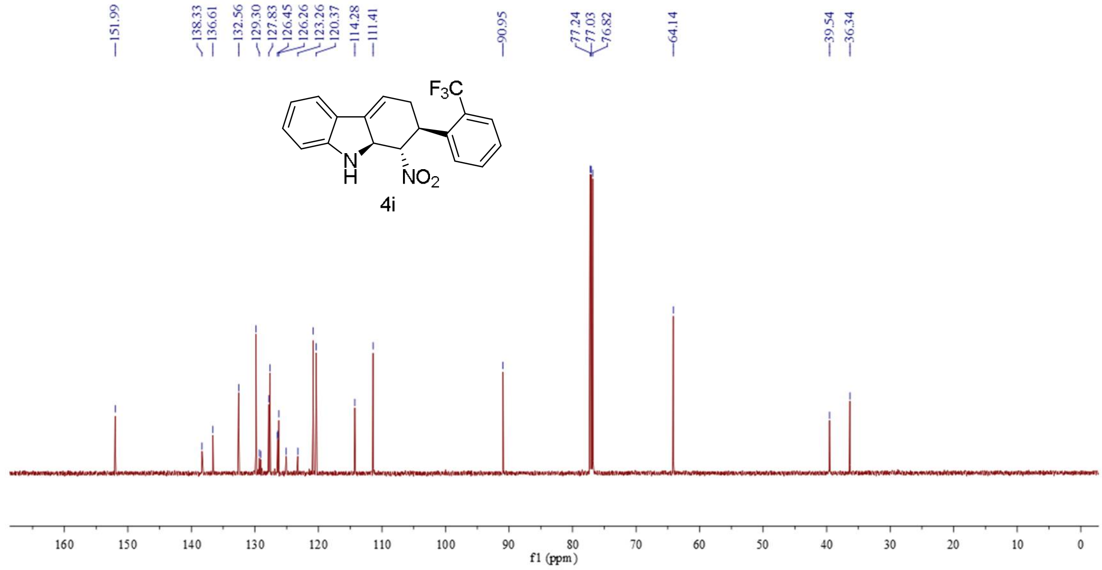
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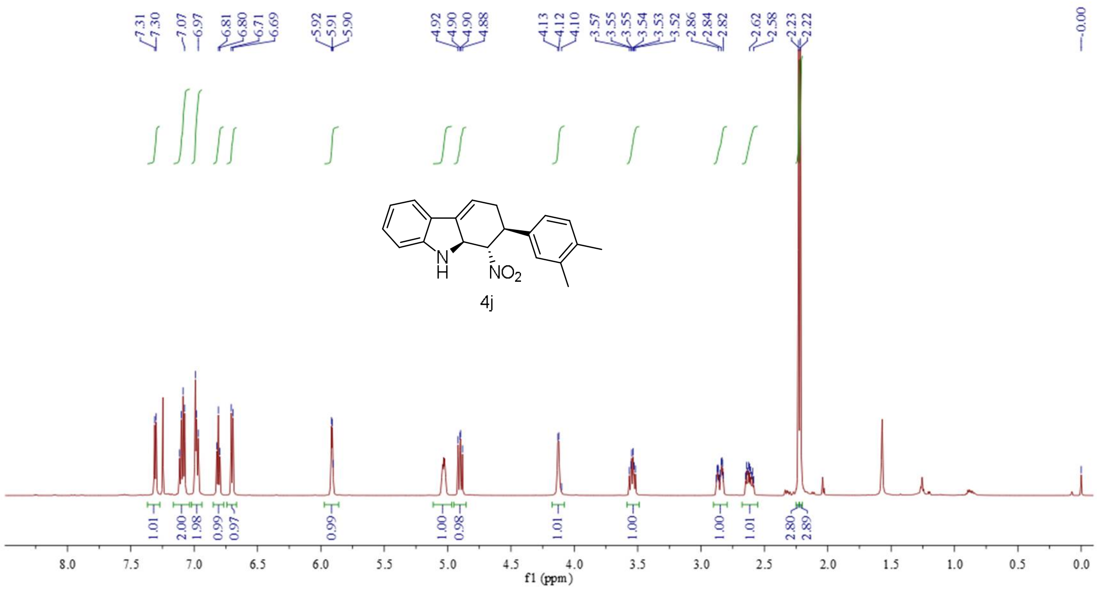

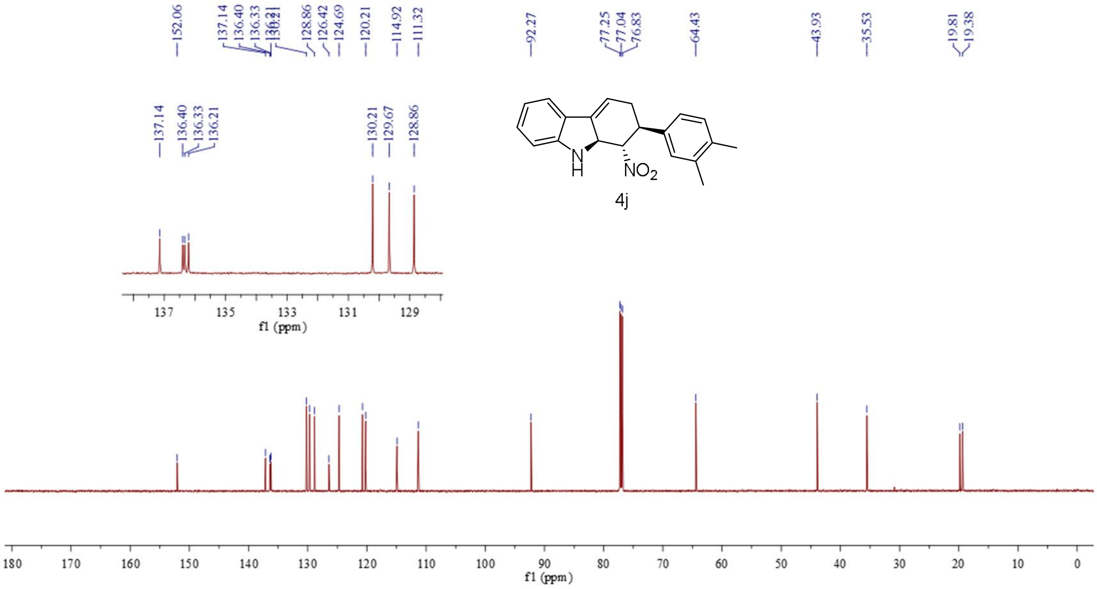

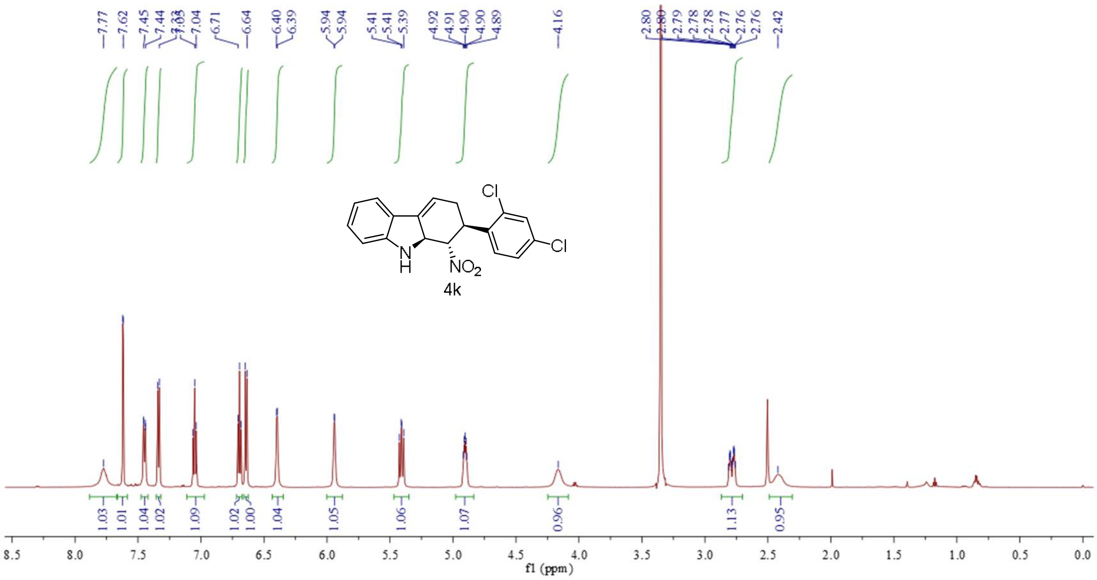

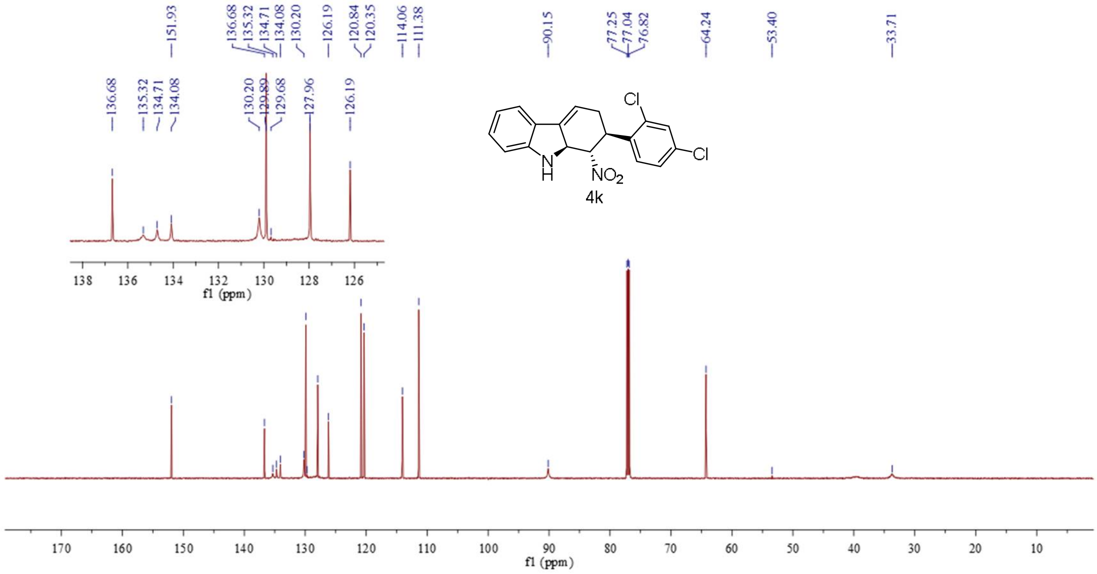
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NO_2
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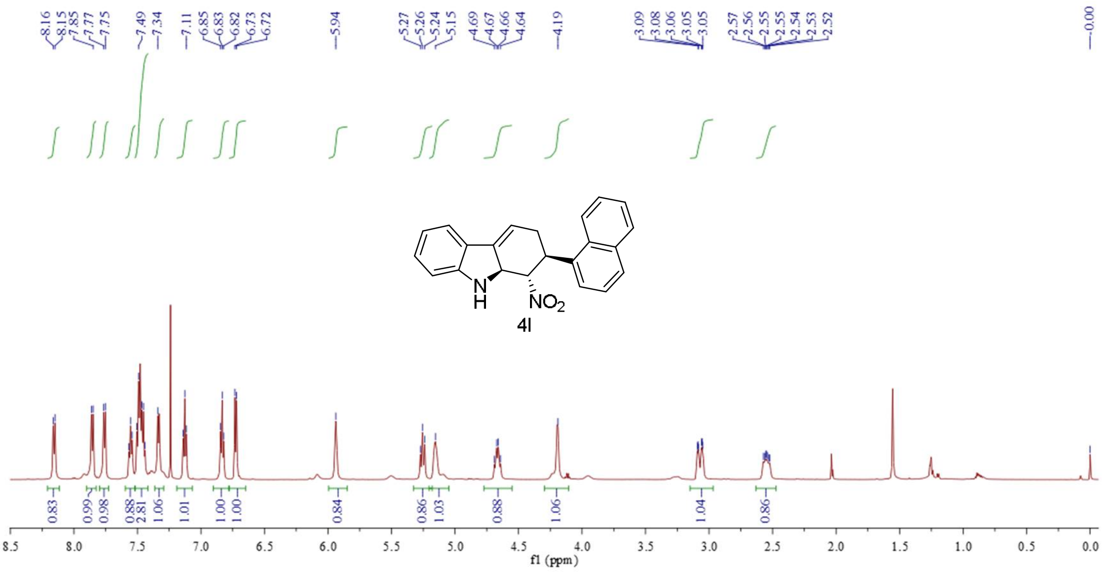
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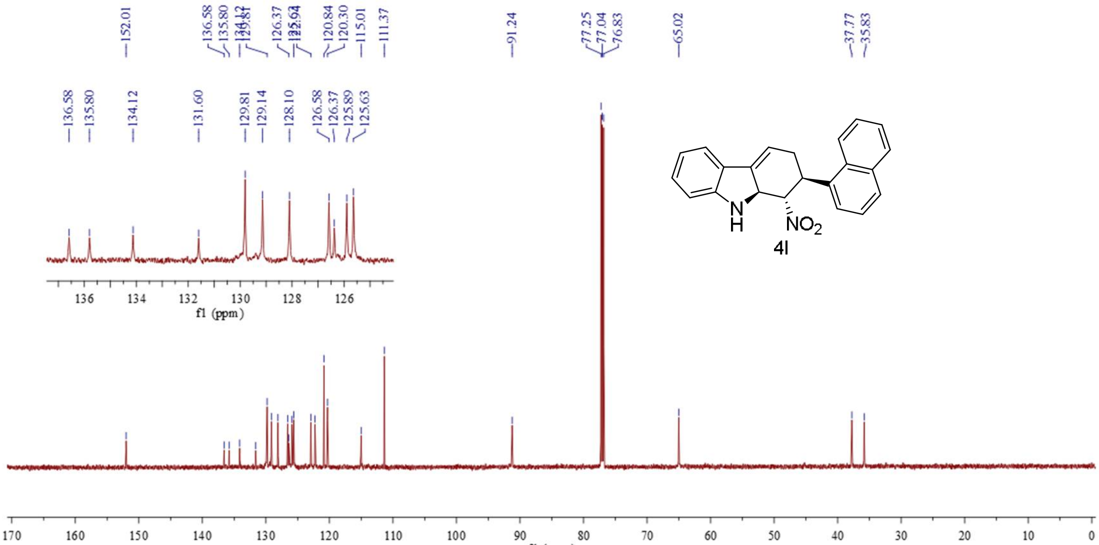
4.67
4.66
4.64
4.19
3.09
3.08
3.06
3.05
3.05
2.57
2.56
2.55
2.55
2.54
2.53
2.52
0.00
N
H
NO_2
4l
0.83
0.99
0.98
0.88
2.81
1.06
1.01
1.00
1.00
0.84
0.86
1.03
0.88
1.06
1.04
0.86
f1 (ppm)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125.63
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120.30
115.01
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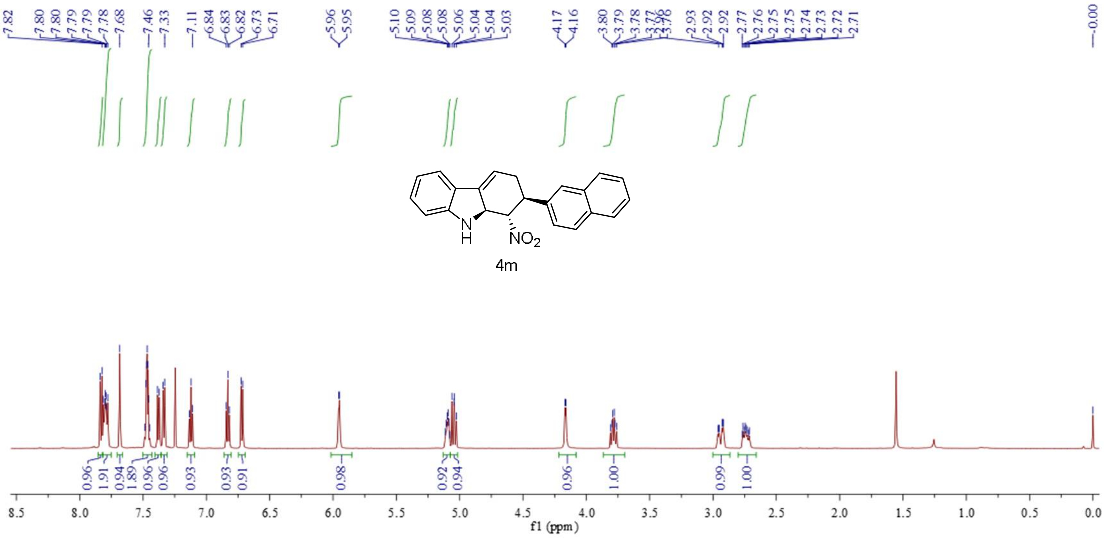
77.04
76.83
65.02
37.77
35.83
N
H
NO_2
4l
f1 (ppm)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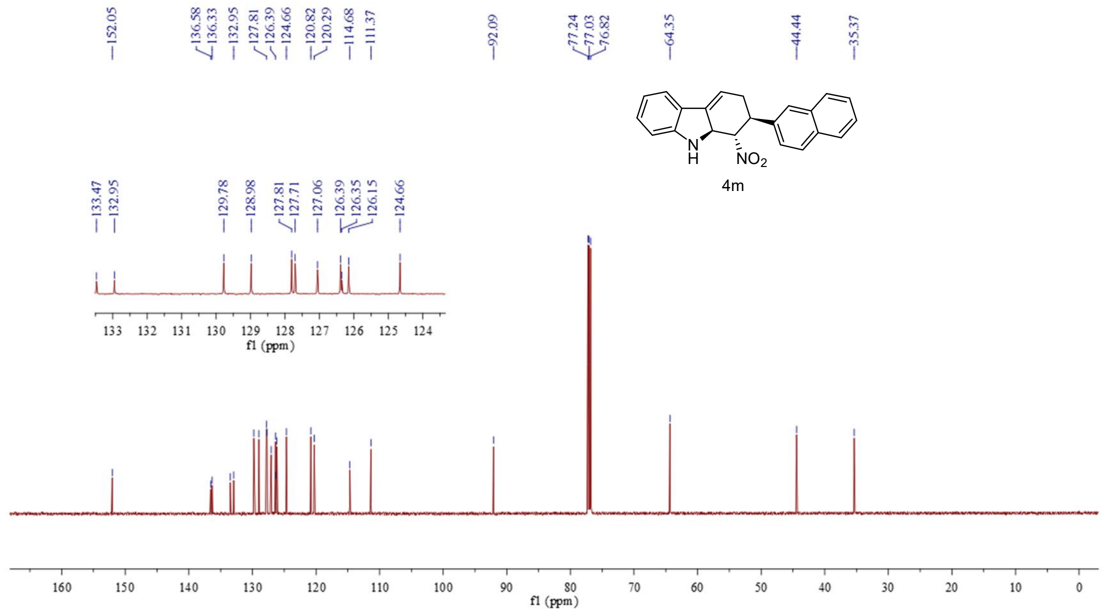
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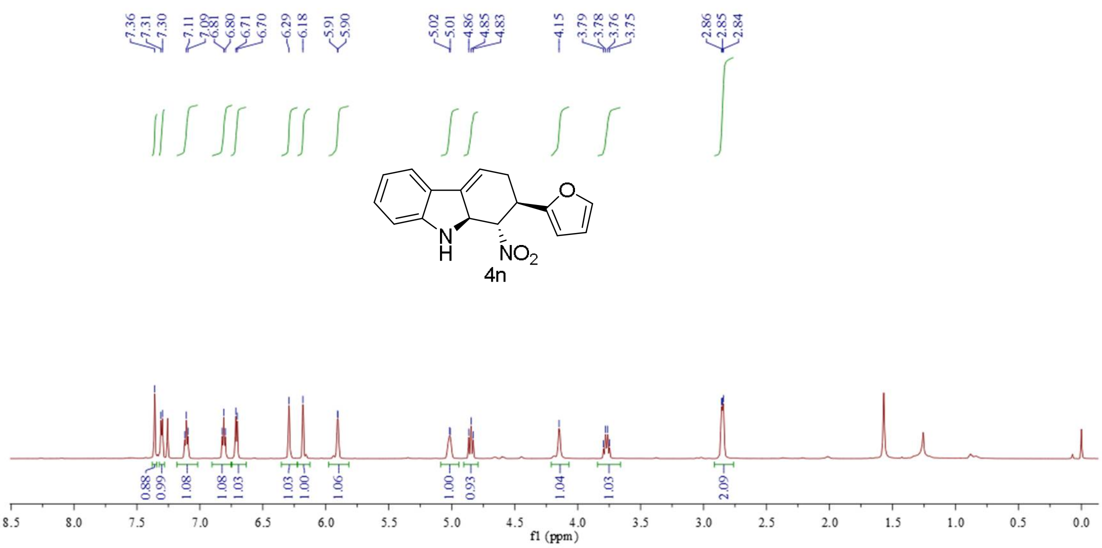
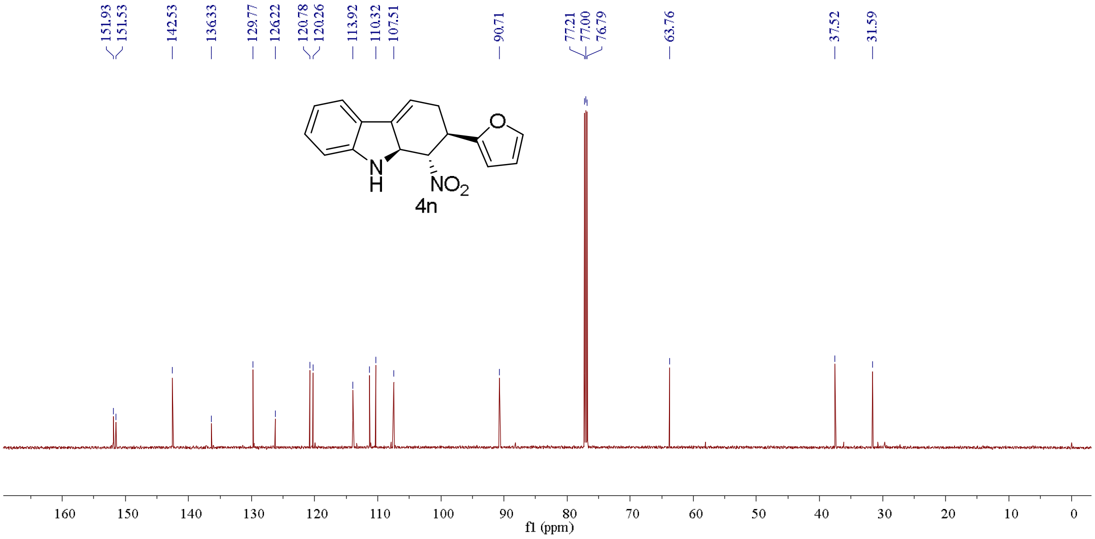

4n
f1 (ppm)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110.32
107.51
90.71
77.21
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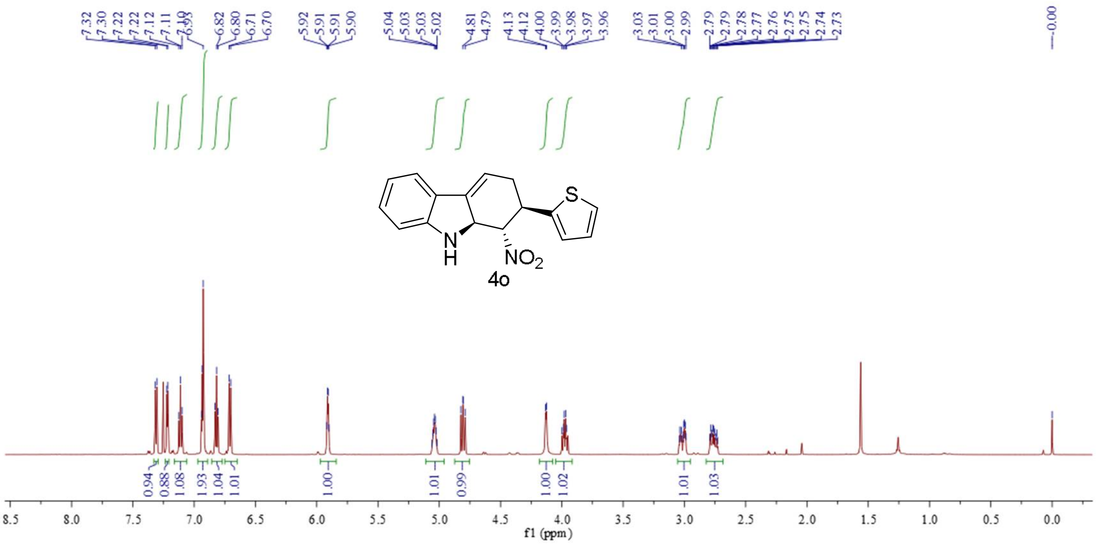
63.76
37.52
31.59
NO2
4n
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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6.80
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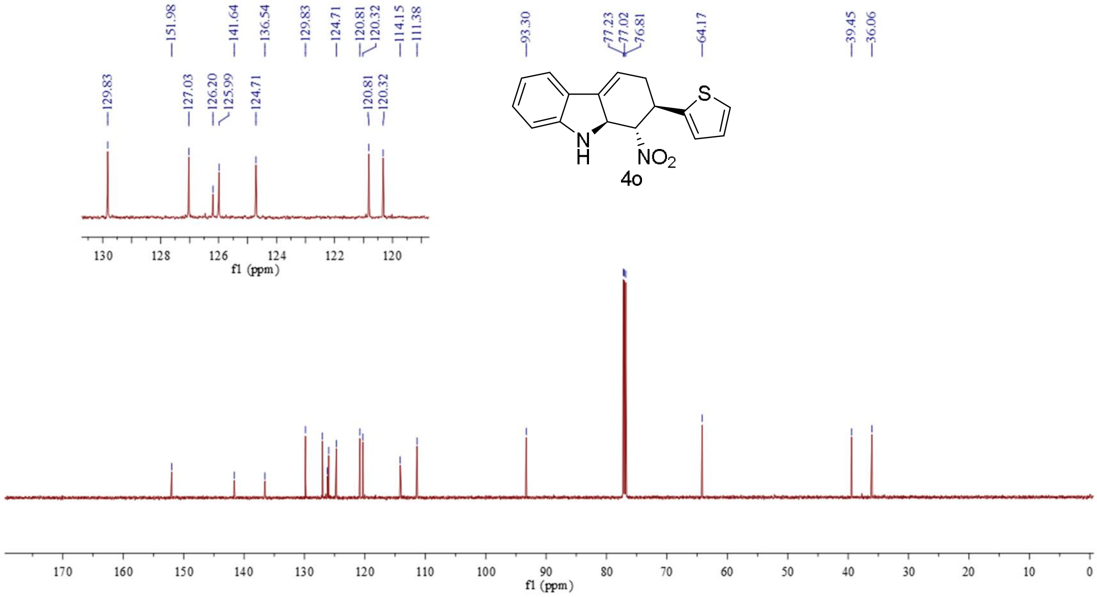
5.92
5.91
5.91
5.90
5.04
5.03
5.03
5.02
4.81
4.79
4.13
4.12
4.00
3.99
3.98
3.97
3.96
3.03
3.01
3.00
2.99
2.79
2.79
2.78
2.77
2.76
2.75
2.75
2.74
2.73
0.00
S
NO2
4o
0.94
0.88
1.08
1.93
1.04
1.01
1.00
1.01
0.99
1.00
1.02
1.01
1.03
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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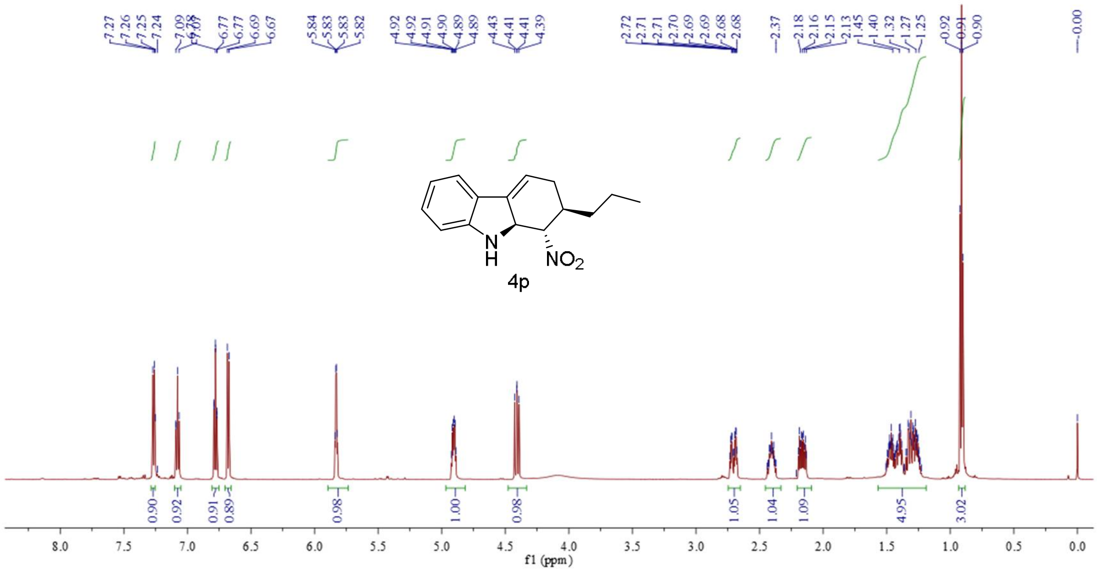
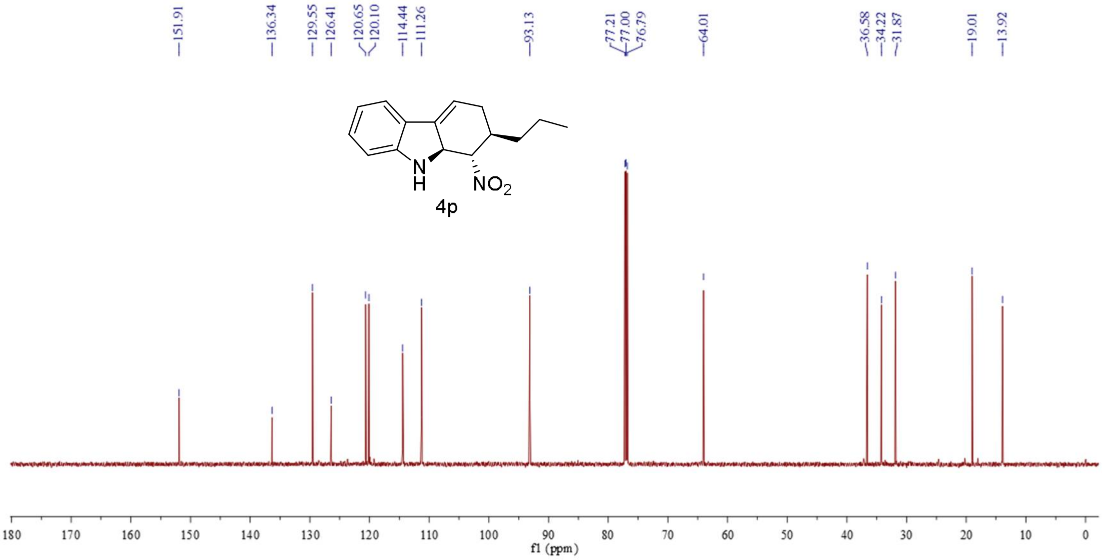
77.02
76.81
64.17
39.45
36.06
129.83
127.03
126.20
125.99
124.71
120.81
120.32
130 128 126 124 122 120
f1 (ppm)
S
NO2
4o
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


4p
f1 (ppm)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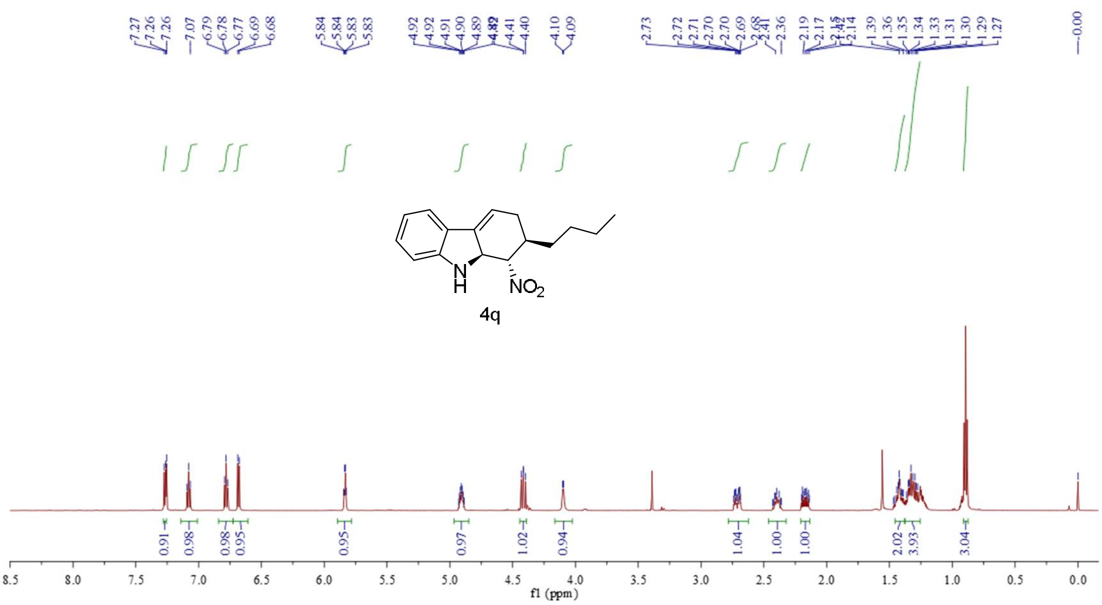
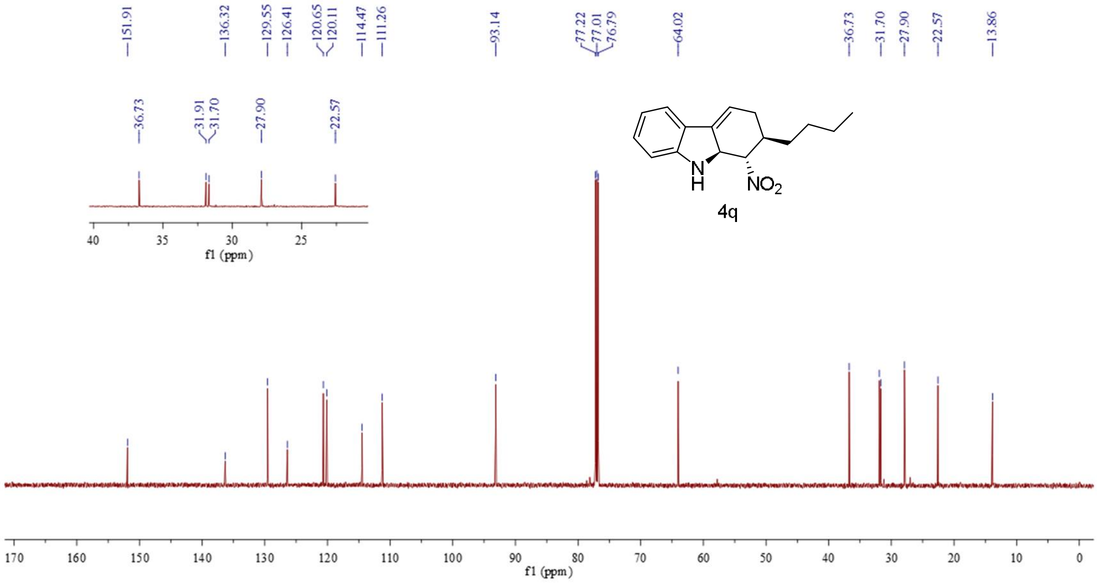
f1 (ppm)


4q
f1 (ppm)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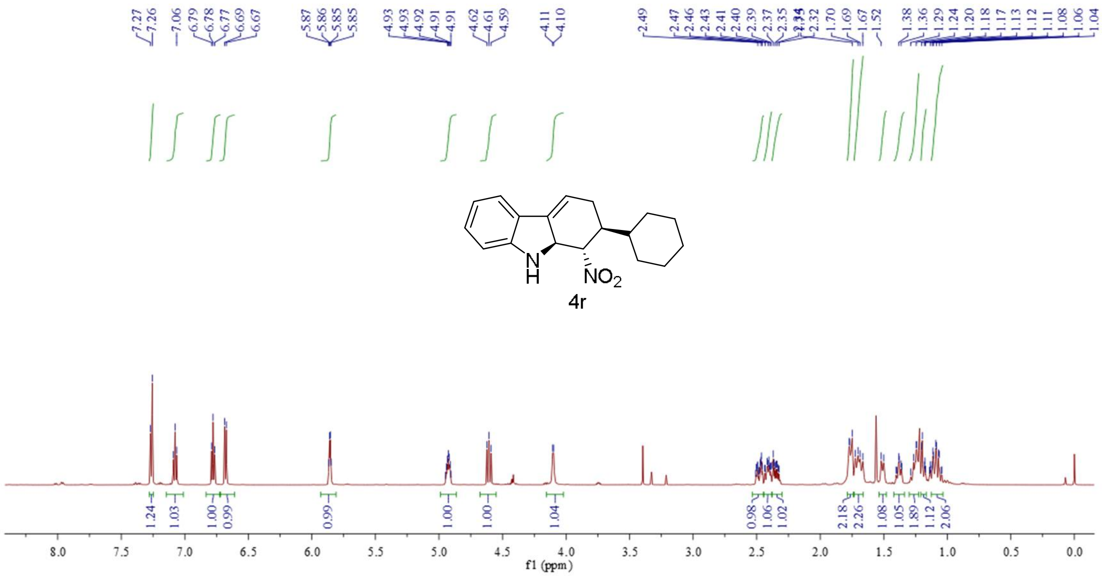
77.22
77.01
76.79
64.02
36.73
31.70
27.90
22.57
13.86
36.73
31.91
31.70
27.90
22.57
f1 (ppm)
NO2
H
N
4q
f1 (ppm)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5.85
4.93
4.93
4.92
4.91
4.91
4.62
4.61
4.59
4.11
4.10
2.49
2.47
2.46
2.43
2.41
2.40
2.39
2.37
2.35
2.34
2.32
1.70
1.69
1.67
1.52
1.38
1.36
1.29
1.24
1.20
1.18
1.17
1.13
1.12
1.11
1.08
1.06
1.04
N
H
NO2
4r
1.24
1.03
1.00
0.99
0.99
1.00
1.00
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1.02
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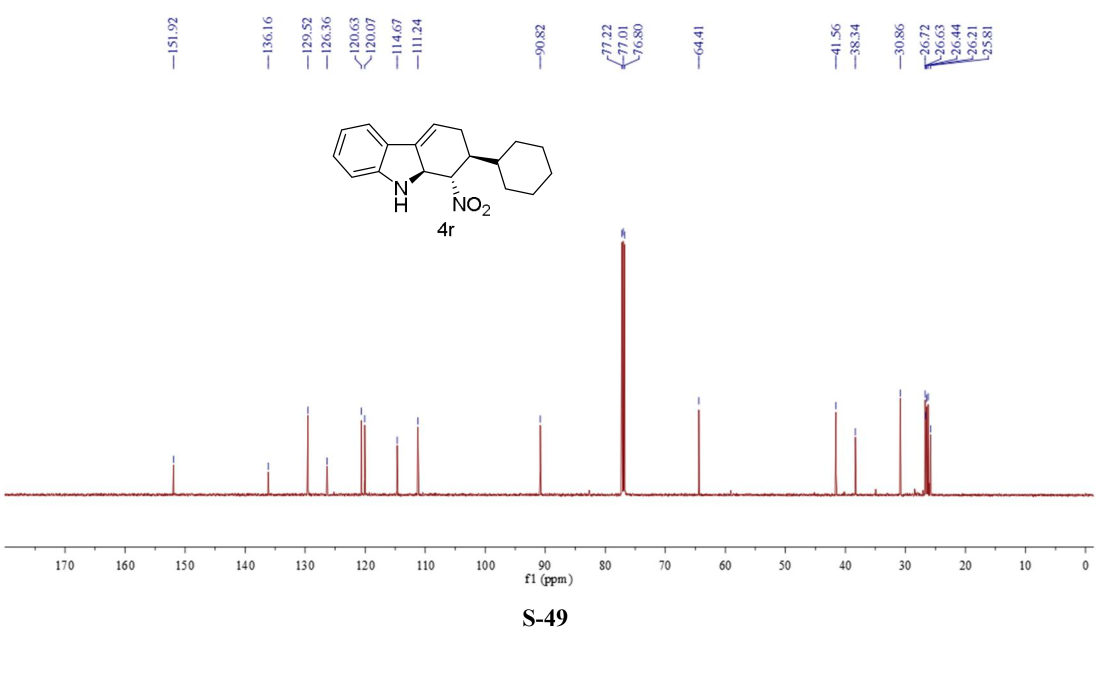
1.89
1.12
2.06
f1 (ppm)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64.41
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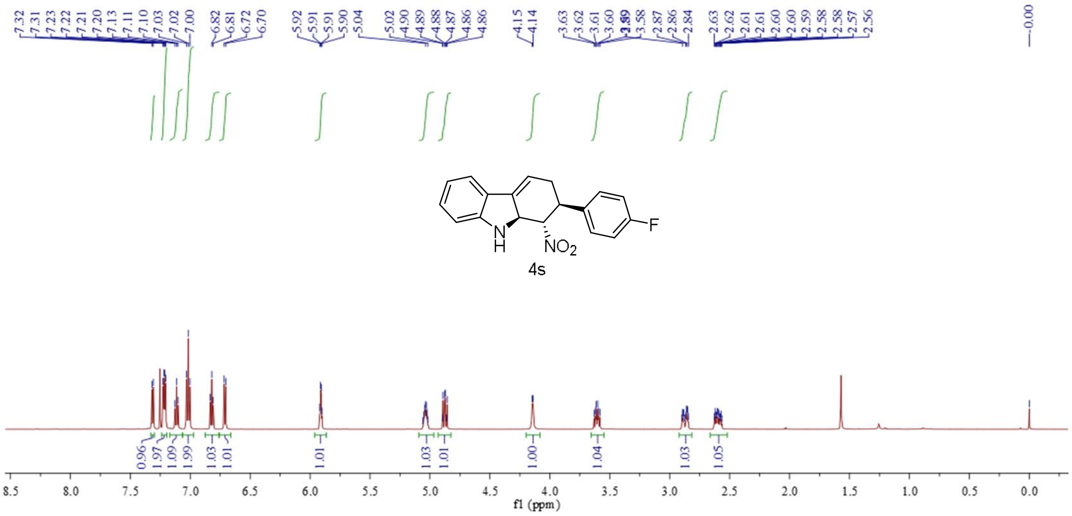
25.81
N
H
NO2
4r
f1 (ppm)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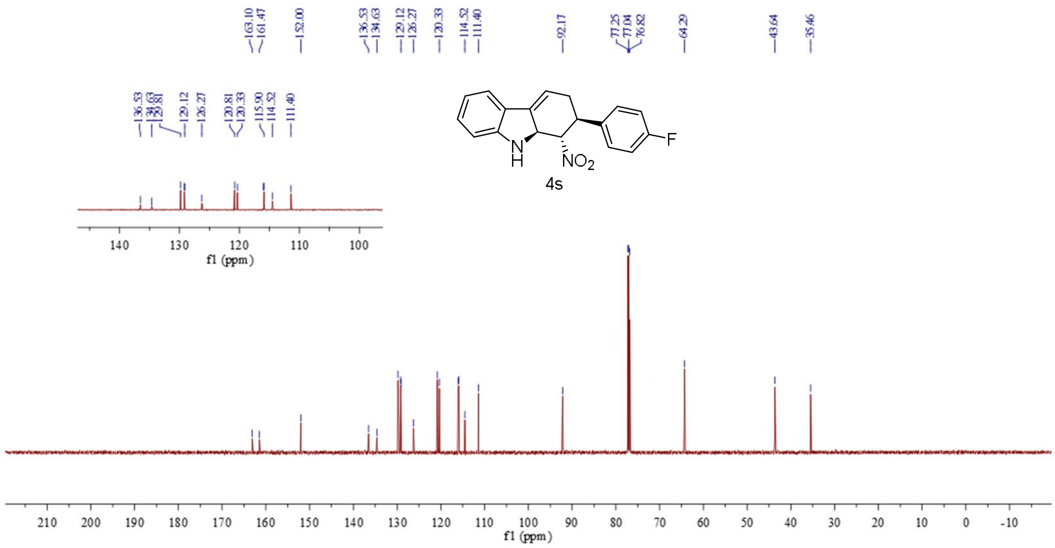
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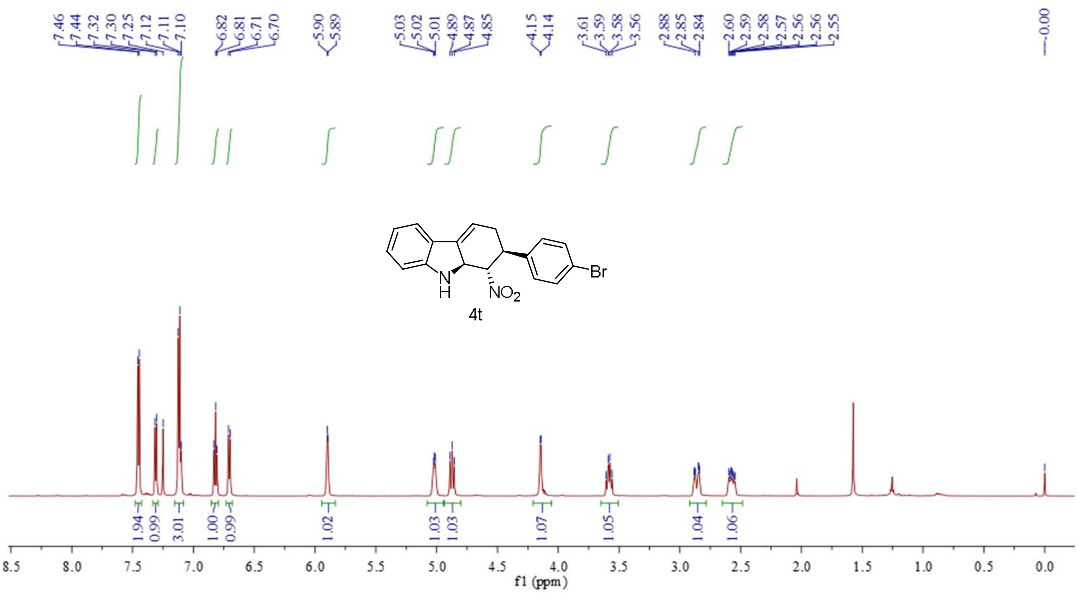
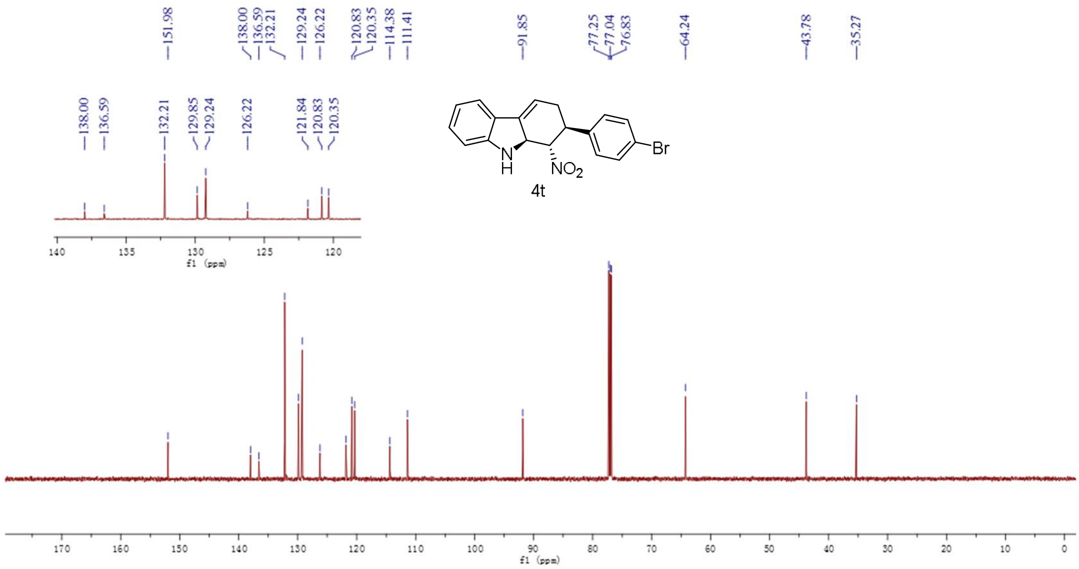

4t
f1 (ppm)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76.83
64.24
43.78
35.27
138.00
136.59
132.21
129.85
129.24
126.22
121.84
120.83
120.35
Br
N
H
NO2
4t
140 135 130 125 120
f1 (ppm)
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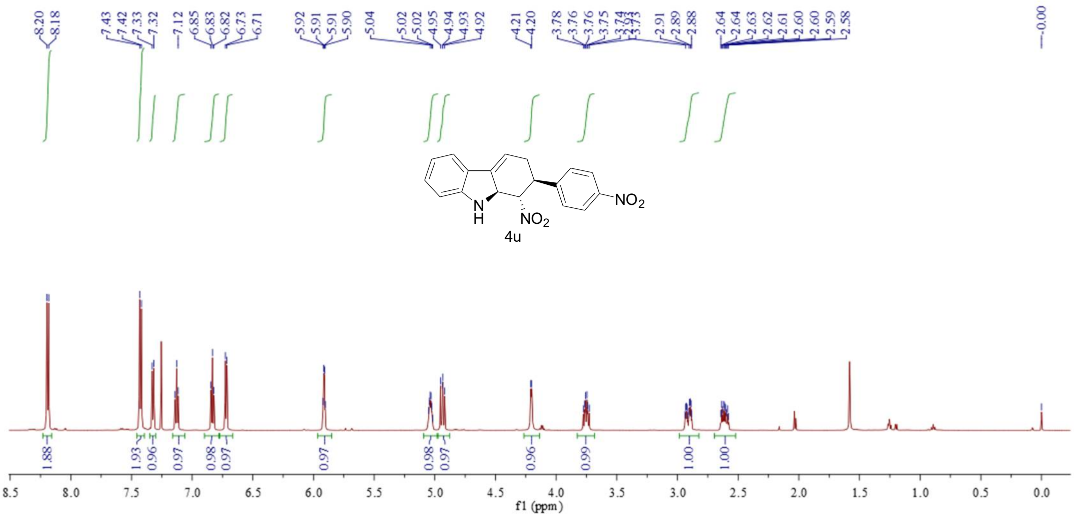
f1 (ppm)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5.91
5.91
5.90
5.04
5.02
5.02
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4.92
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2.64
2.63
2.62
2.61
2.60
2.60
2.59
2.58
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NO2
N
H
NO2
4u
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1.93
0.96
0.97
0.98
0.97
0.97
0.98
0.97
0.96
0.99
1.00
1.00
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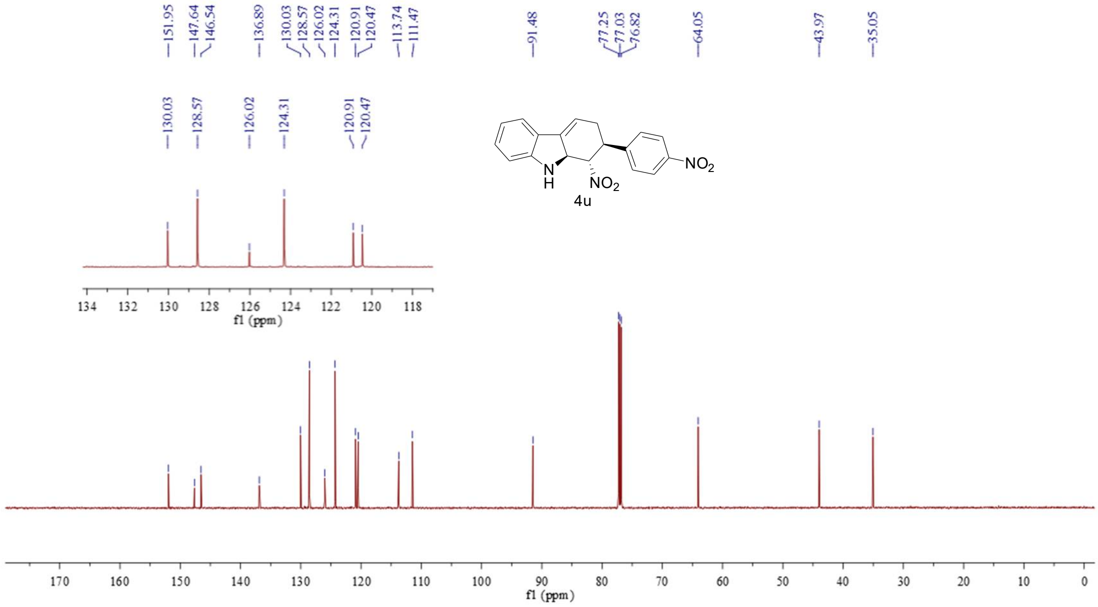
f1 (ppm)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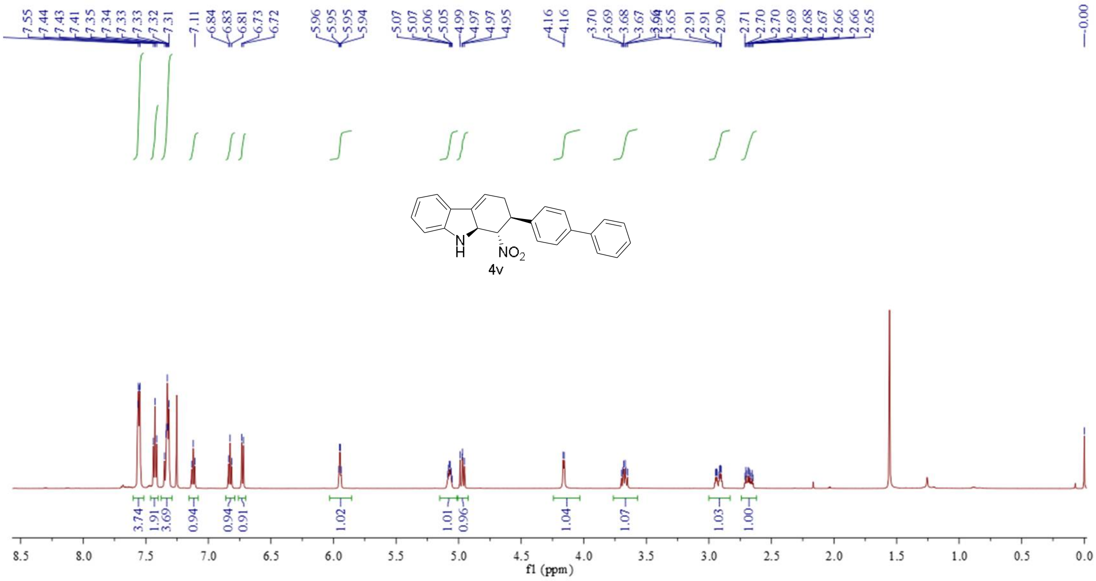
77.03
76.82
64.05
43.97
35.05
130.03
128.57
126.02
124.31
120.91
120.47
NO2
N
H
NO2
4u
134 132 130 128 126 124 122 120 118
f1 (ppm)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



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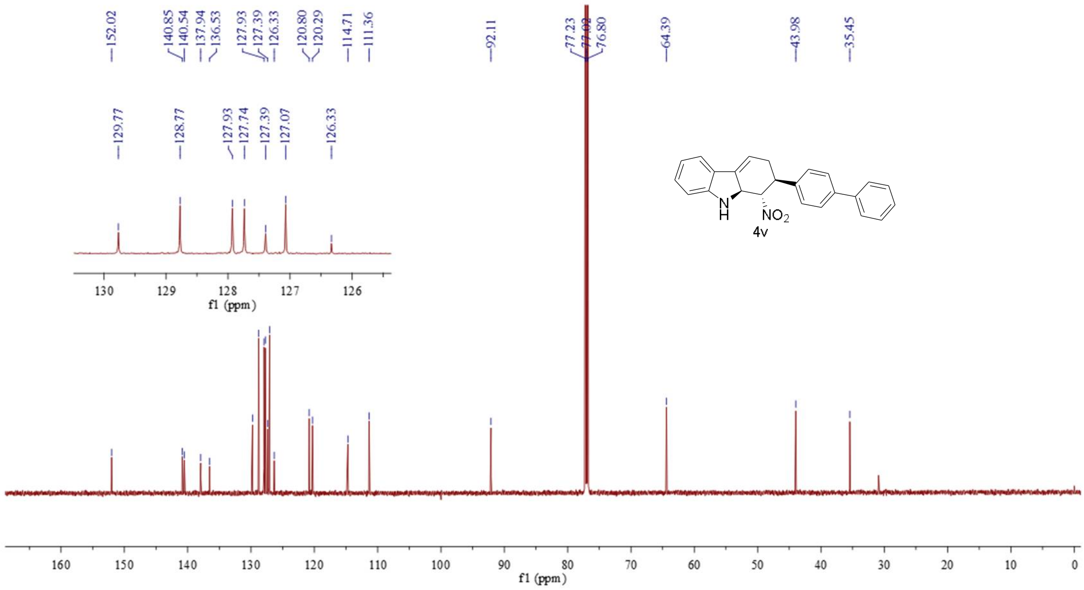

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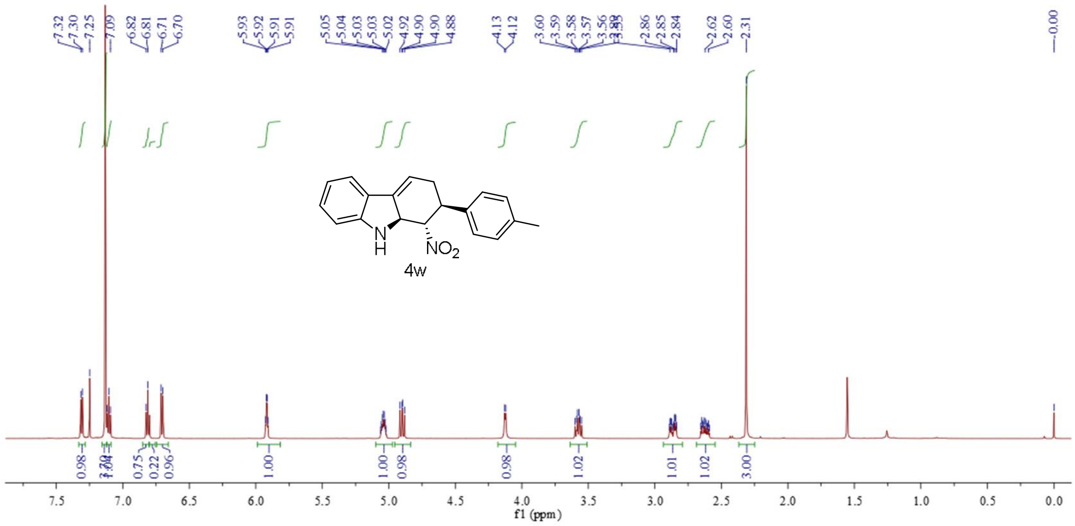

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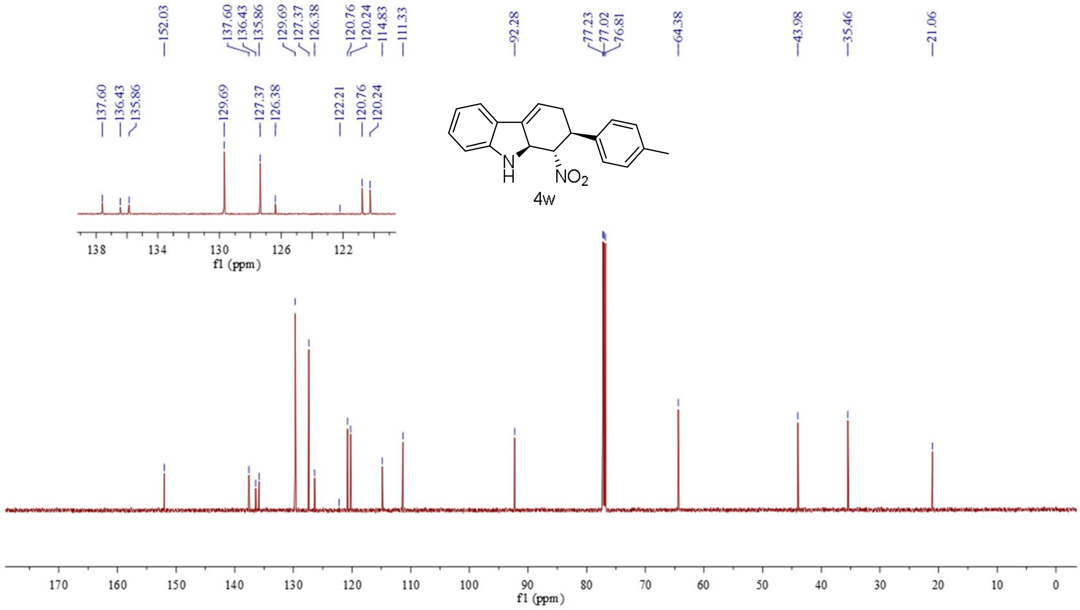
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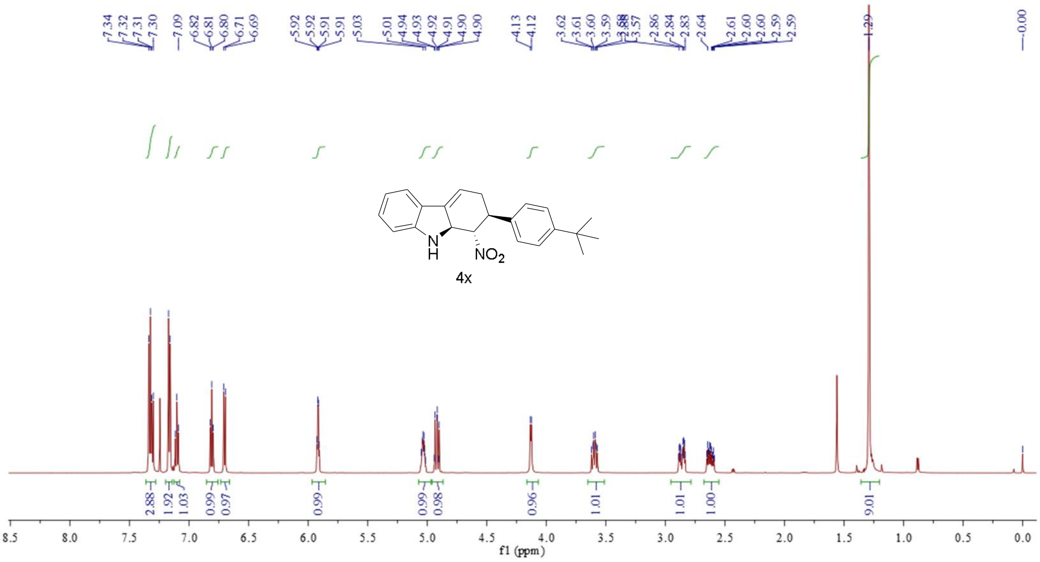
35.46
21.06
122.21
4w
f1 (ppm)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5.91
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2.88
1.92
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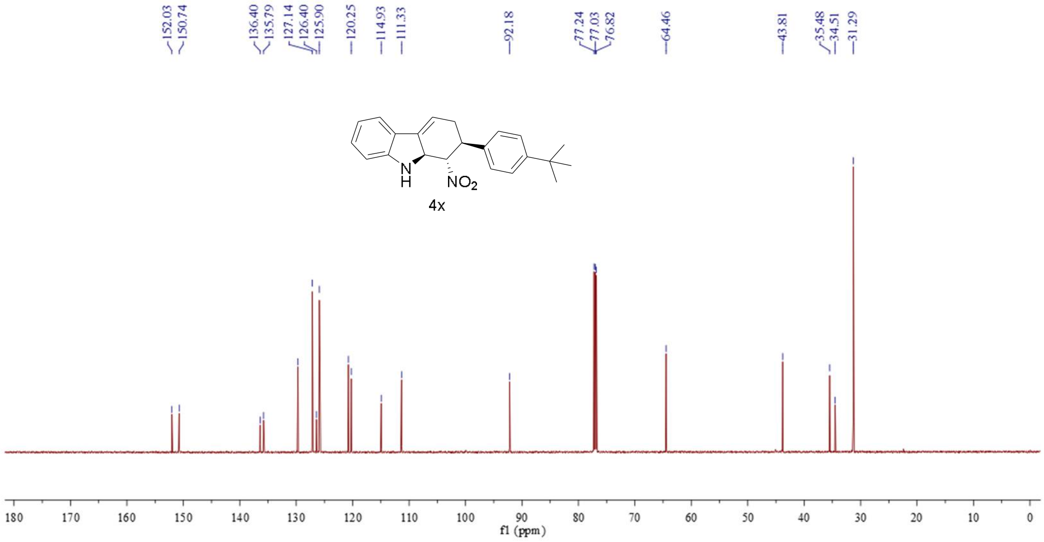
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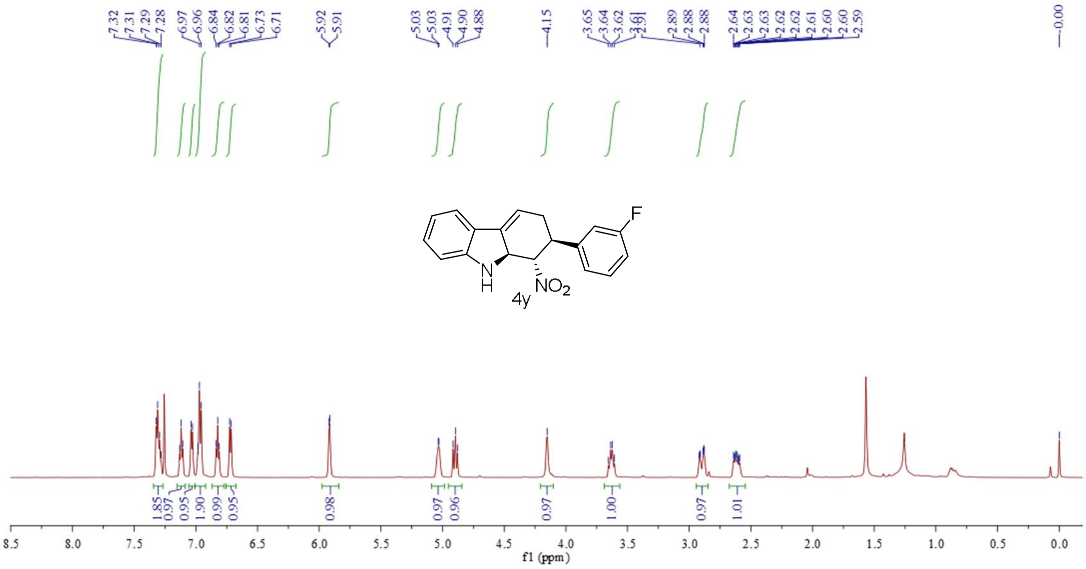
4x
f1 (ppm)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5.91
5.03
5.03
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2.63
2.63
2.62
2.62
2.61
2.60
2.60
2.59
0.00
F
N
H
NO2
4y
1.85
0.97
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0.95
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0.97
0.96
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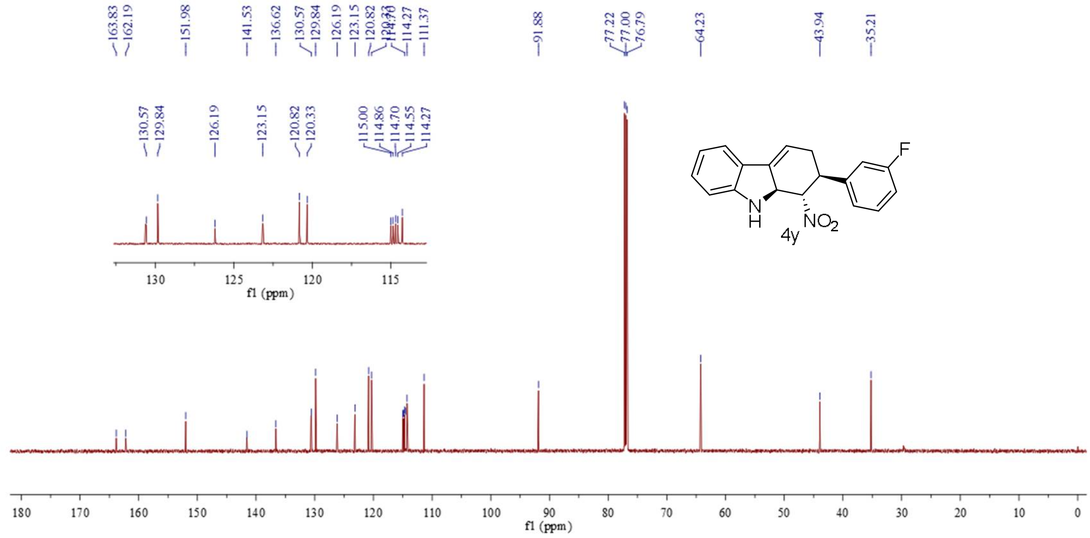
1.01
f1 (ppm)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129.84
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123.15
120.82
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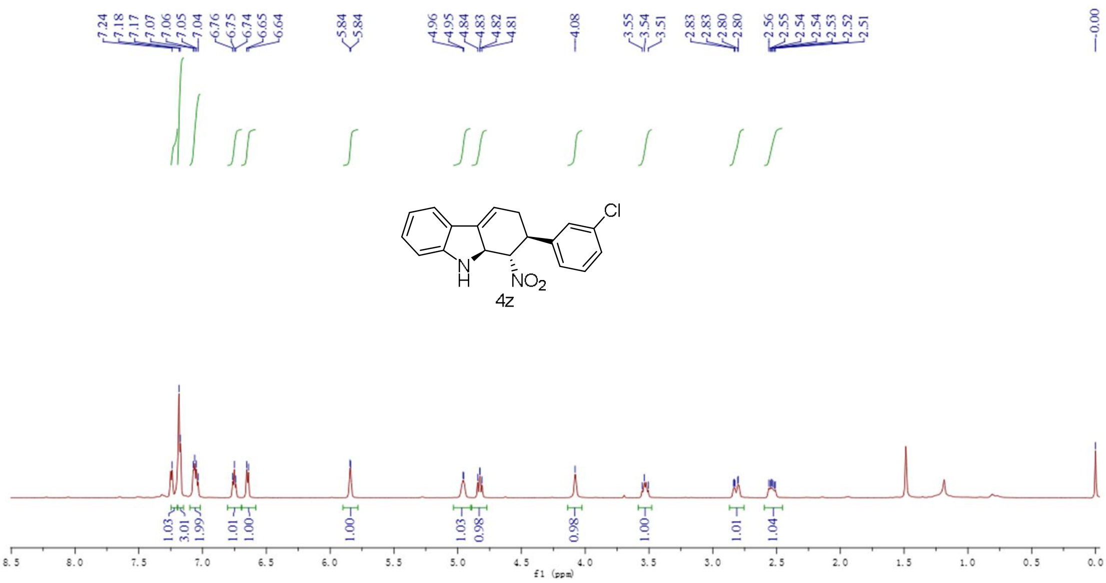
NO2
4y
f1 (ppm)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Cl
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H
NO2
4z
1.03
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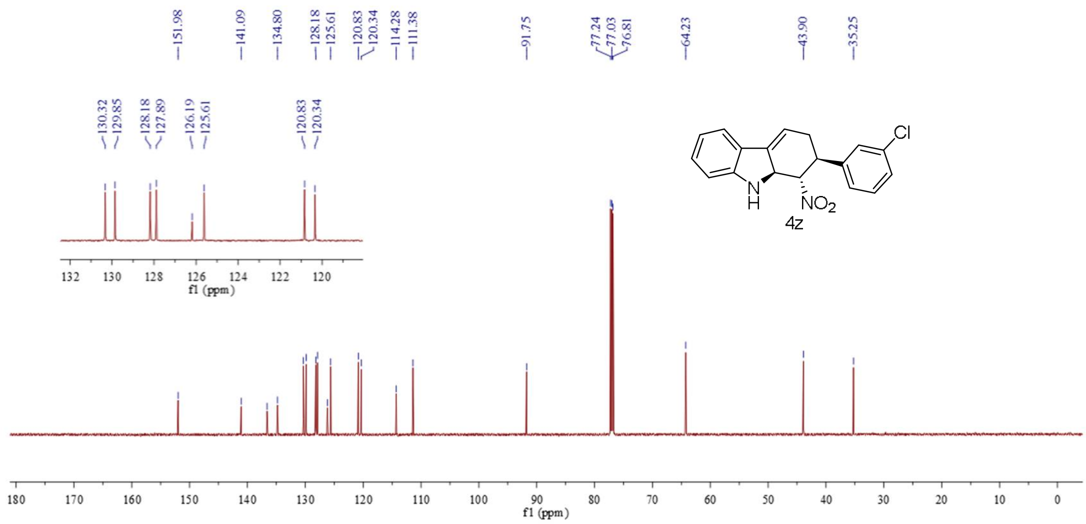
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130.32
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Cl
N
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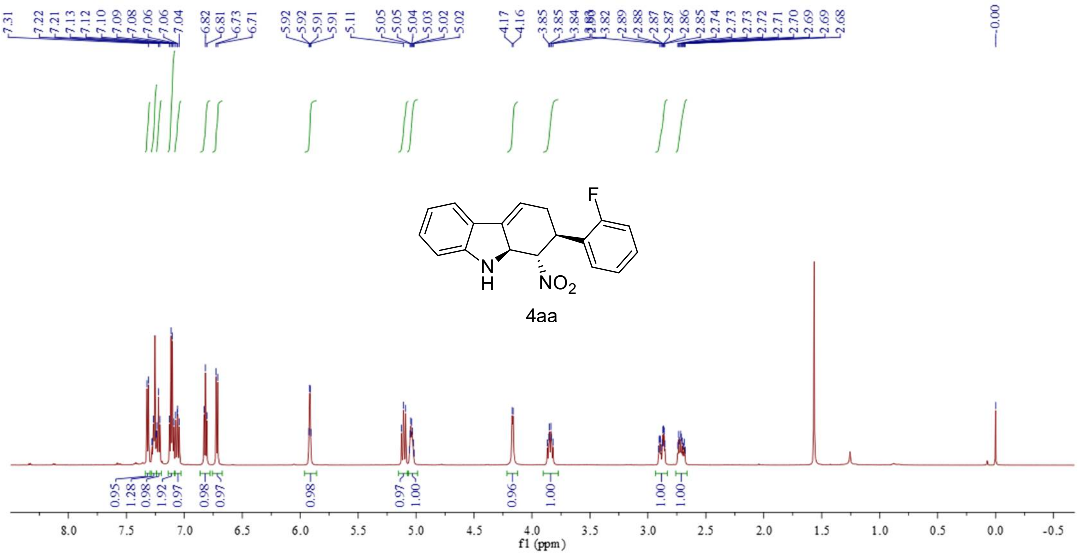
NO_2
4z
f1 (ppm)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F
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H
NO_2
4aa
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1.00
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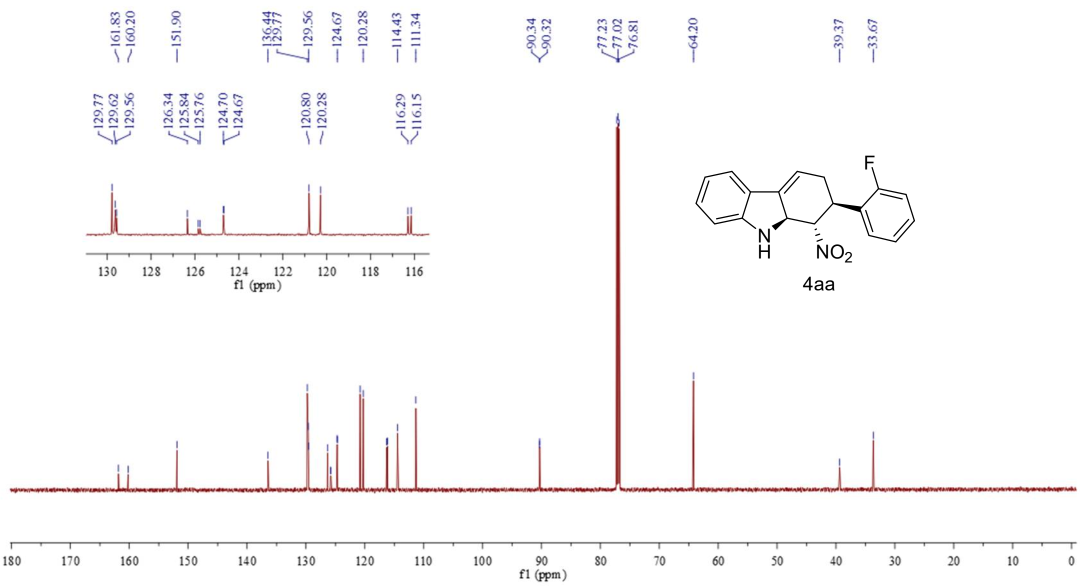
1.00
f1 (ppm)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77.02
76.81
64.20
39.37
33.67
129.77
129.62
129.56
126.34
125.84
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120.80
120.28
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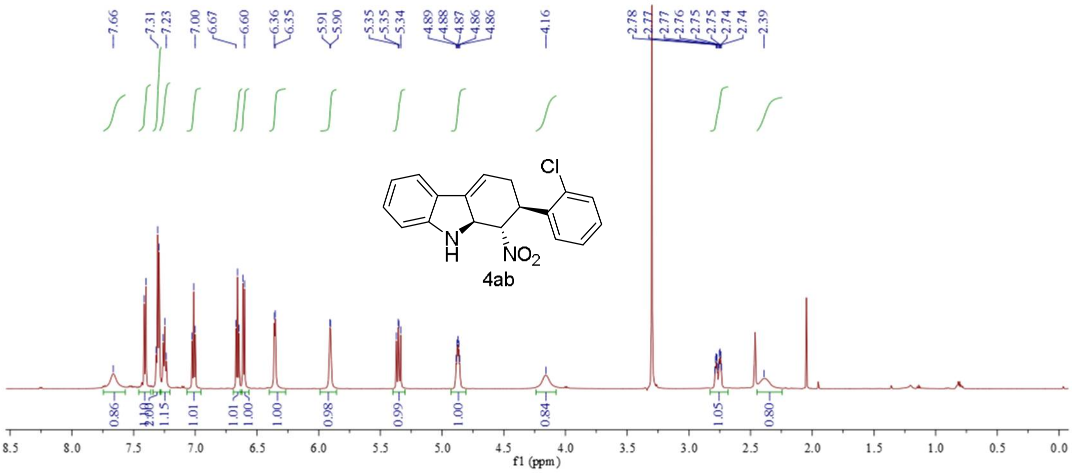
N
H
NO_2
4aa
f1 (ppm)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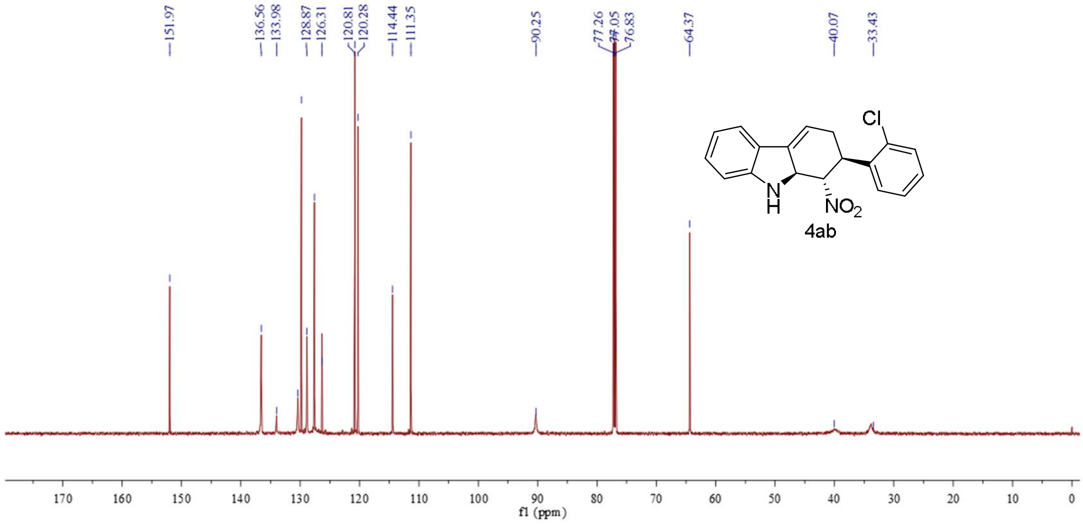
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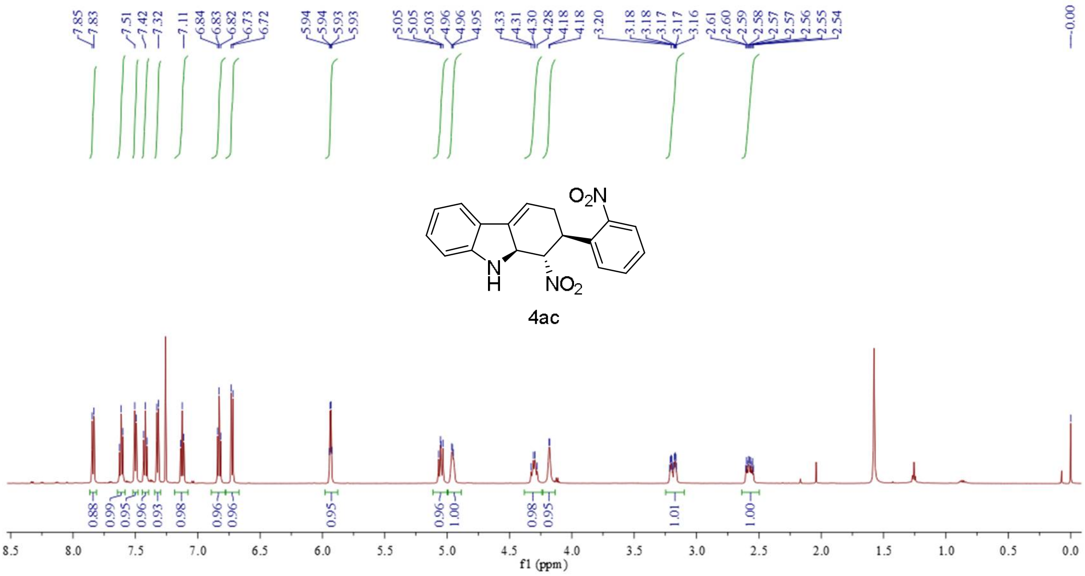
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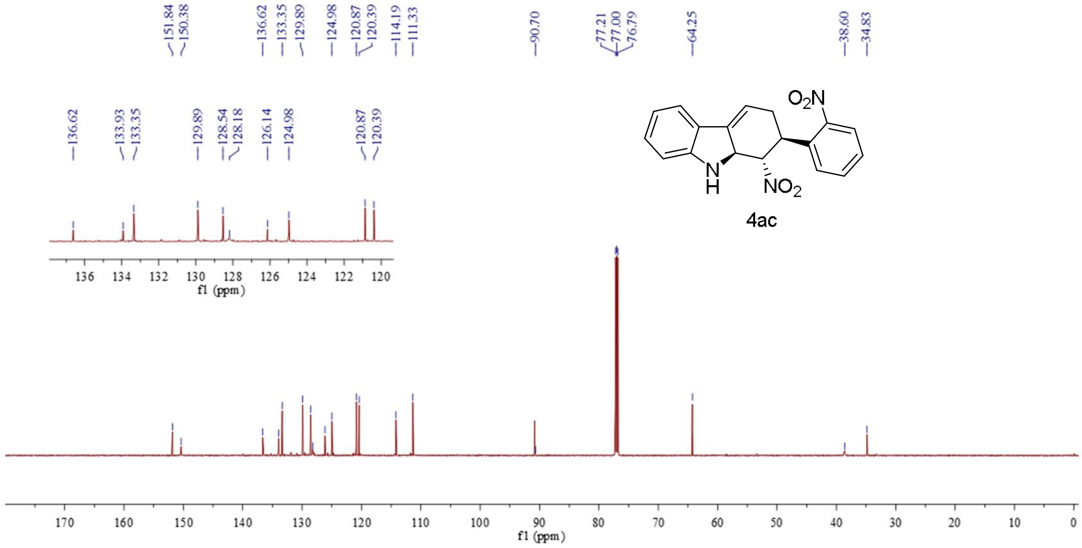
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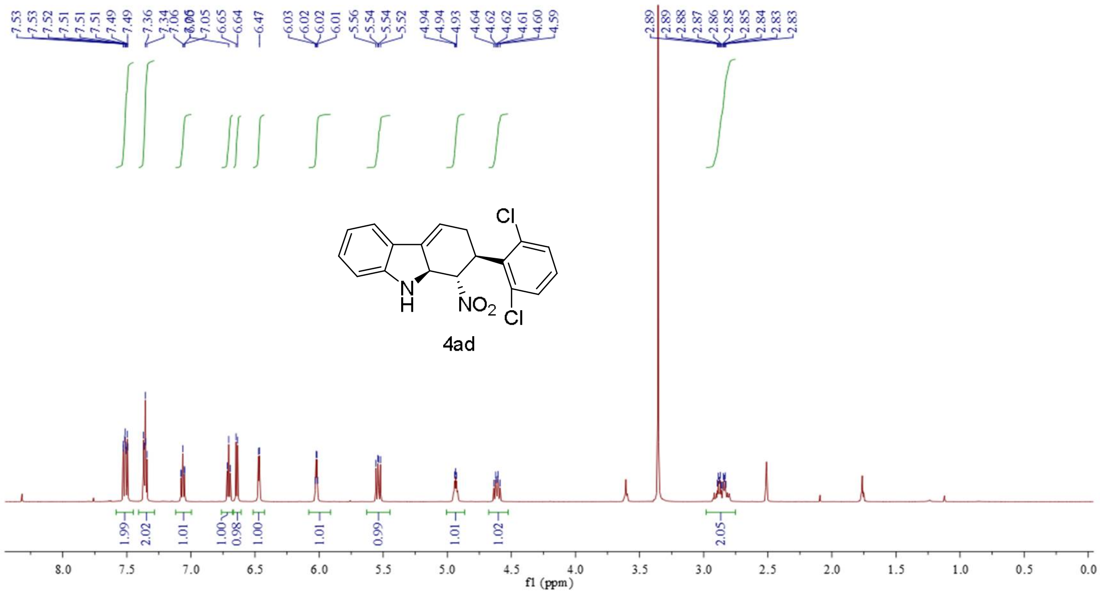
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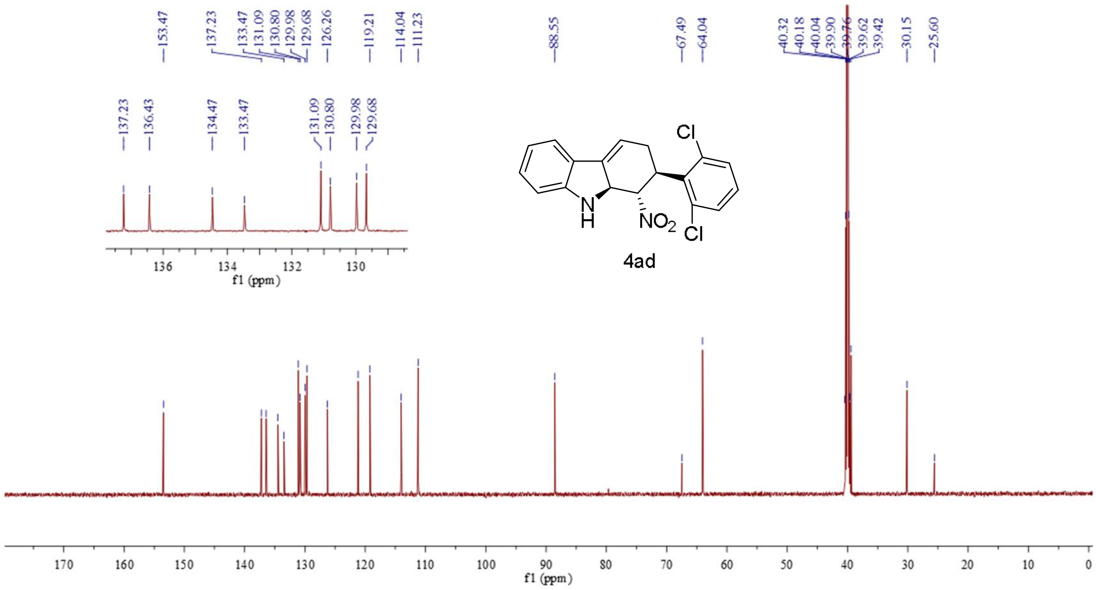
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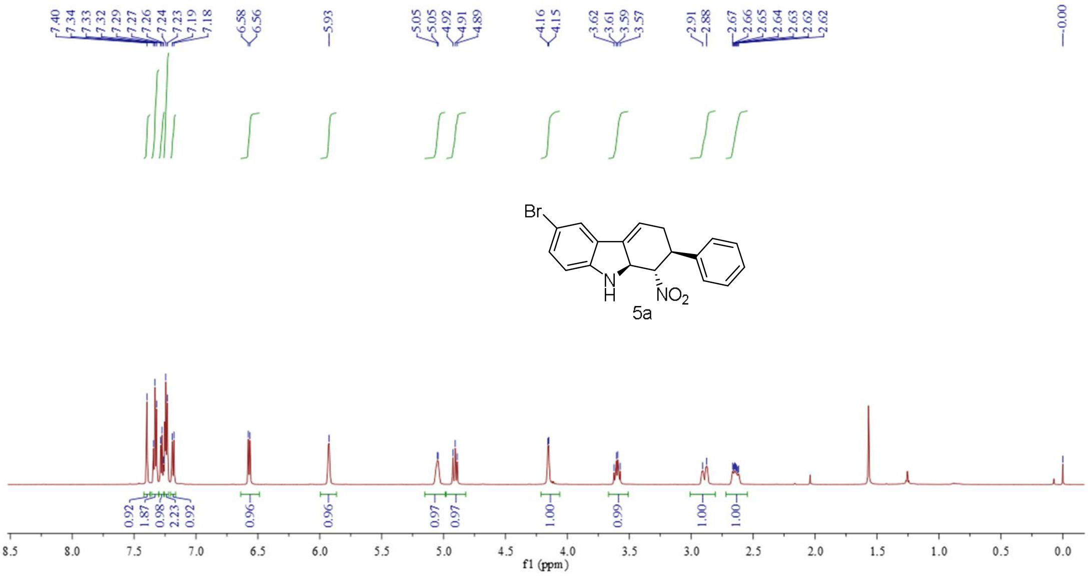
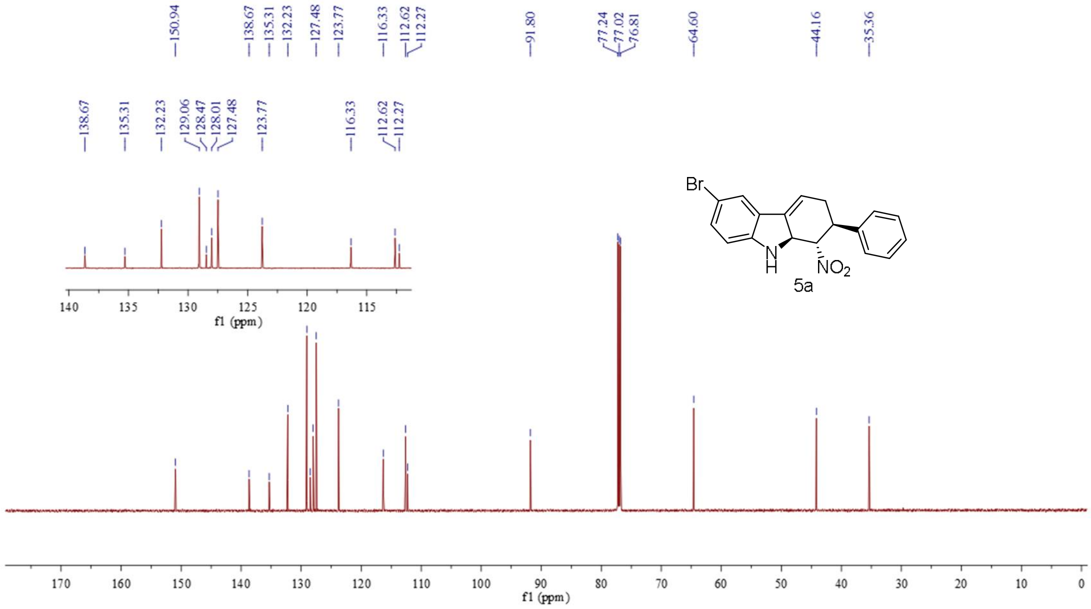
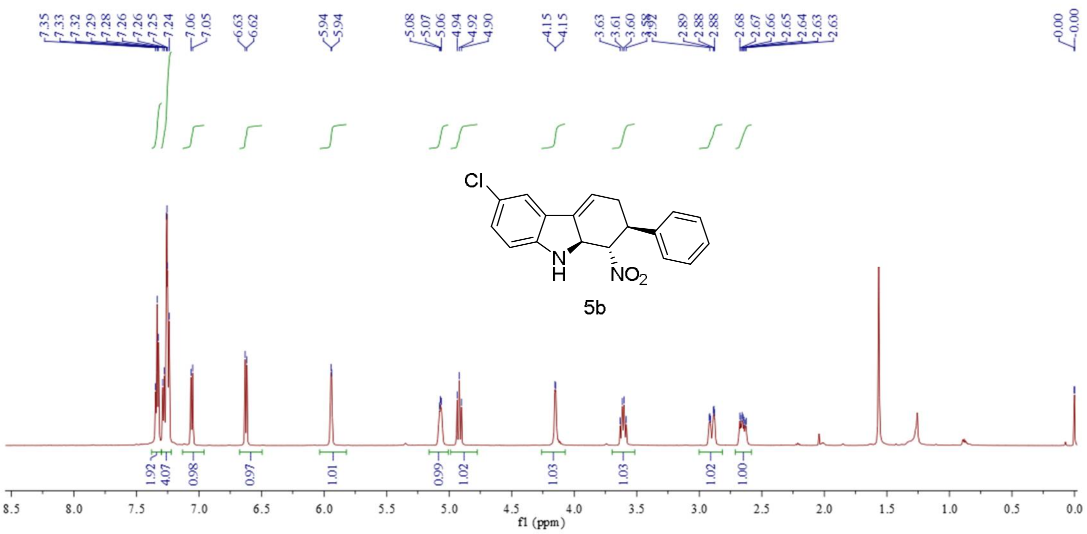
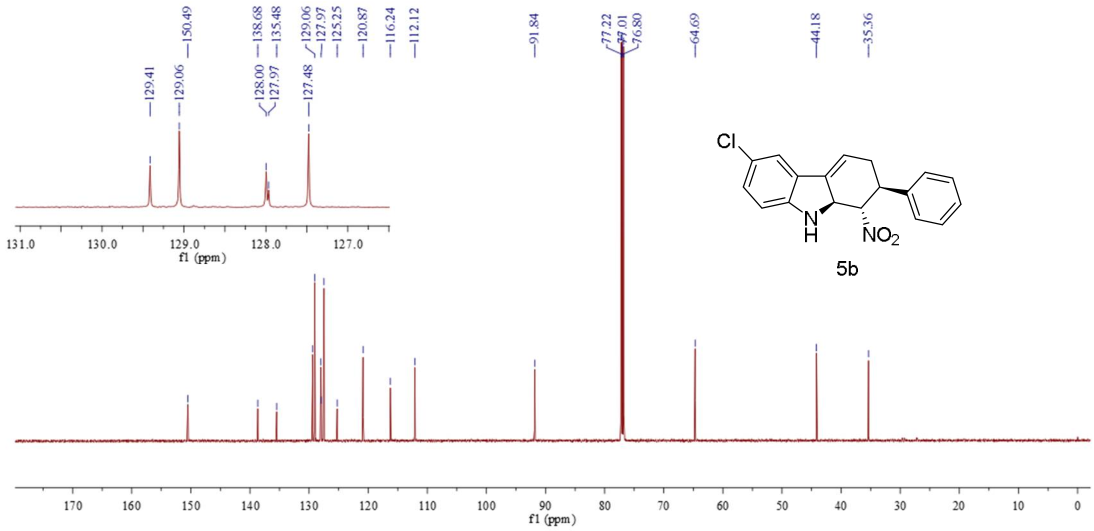
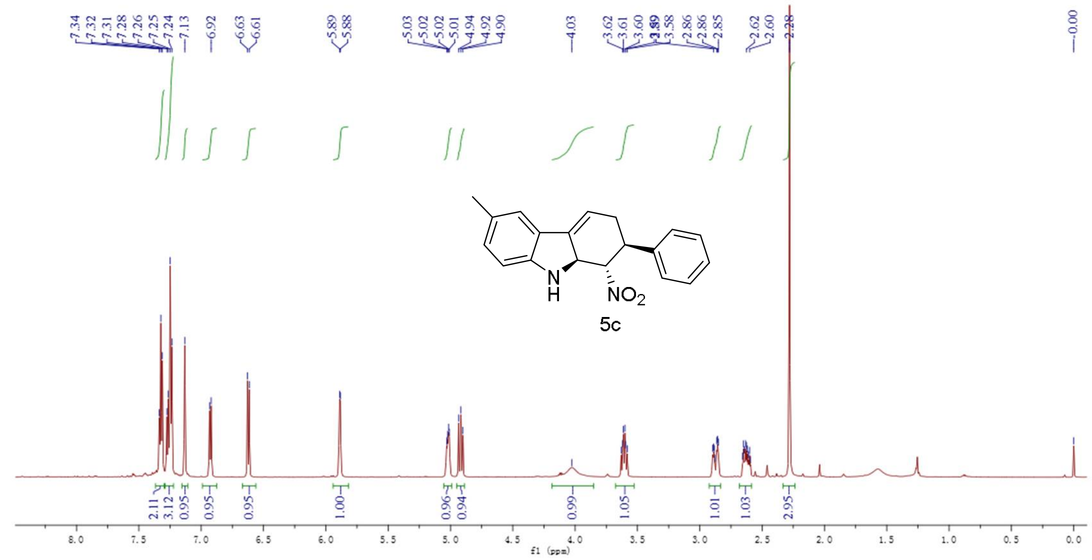

7.40 7.34 7.33 7.32 7.29 7.27 7.26 7.24 7.23 7.19 7.18
6.58 6.56
5.93
5.05 5.05 4.92 4.91 4.89
4.16 4.15
3.62 3.61 3.59 3.57
2.91 2.88
2.67 2.66 2.65 2.64 2.63 2.62 2.62
0.00
Br
N
H
NO_2
5a
0.92 1.87 0.98 2.23 0.92
0.96
0.96
0.97 0.97
1.00
0.99
1.00 1.00
f1 (ppm)


150.94
138.67 135.31 132.23 127.48 123.77
116.33 112.62 112.27
91.80
77.24 77.02 76.81
64.60
44.16
35.36
138.67 135.31 132.23 129.06 128.47 128.01 127.48 123.77 116.33 112.62 112.27
f1 (ppm)
Br
N
H
NO_2
5a
f1 (ppm)


7.35 7.33 7.32 7.29 7.28 7.26 7.26 7.25 7.24
7.06 7.05
6.63 6.62
5.94 5.94
5.08 5.07 5.06 4.94 4.92 4.90
4.15 4.15
3.63 3.61 3.60 3.58 3.57
2.89 2.88 2.88
2.68 2.67 2.66 2.65 2.64 2.63 2.63
0.00 -0.00
Cl
N
H
NO_2
5b
1.92 4.07
0.98
0.97
1.01
0.99 1.02
1.03
1.03
1.02 1.00
f1 (ppm)


5b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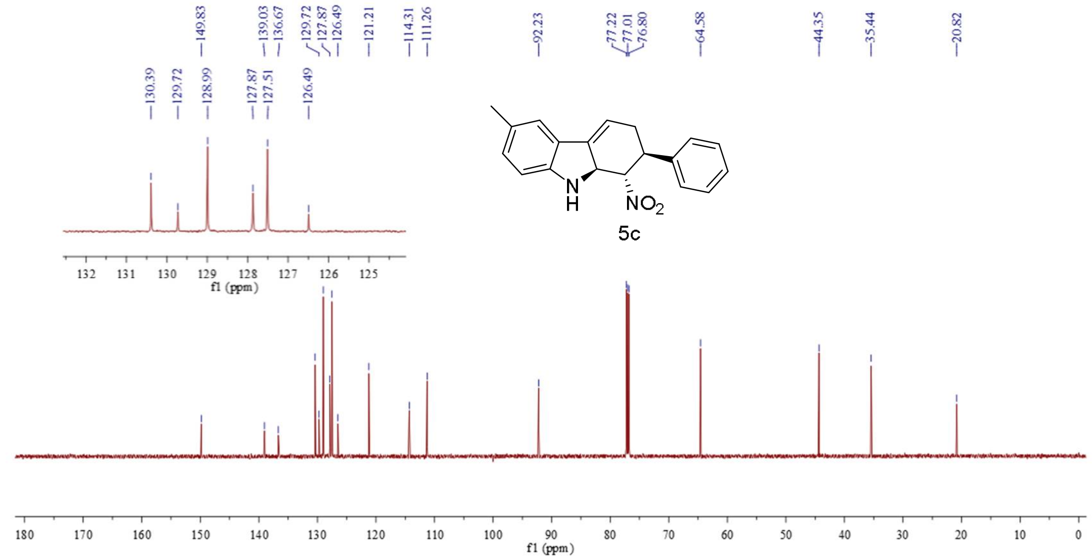
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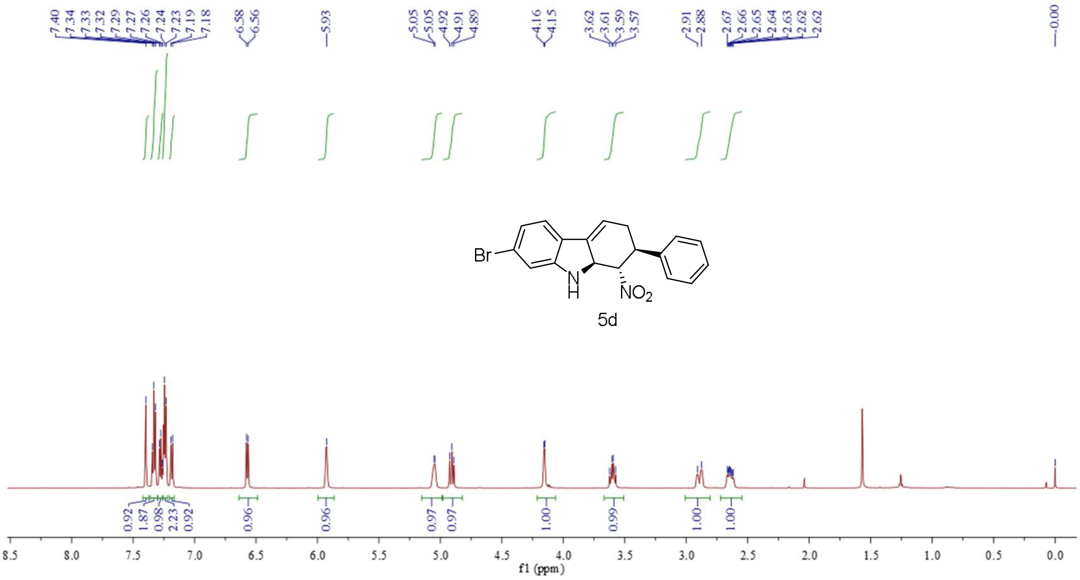
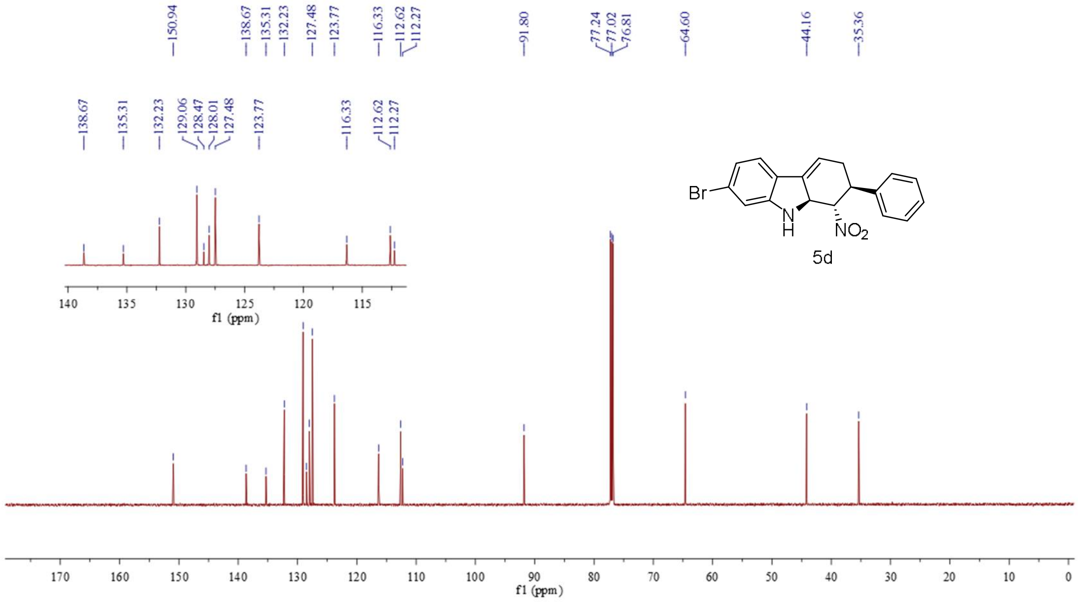
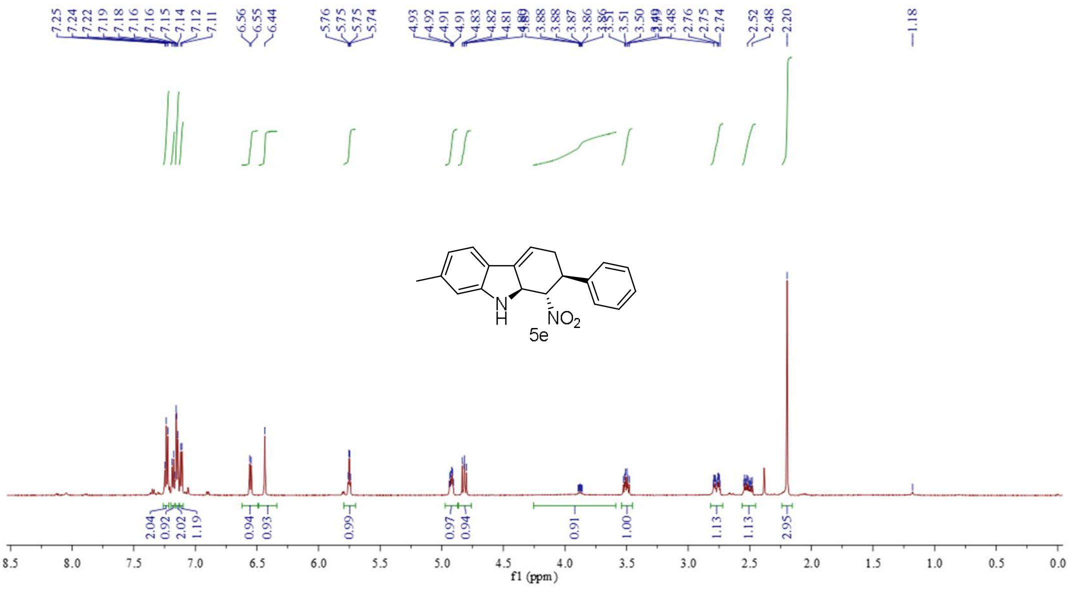
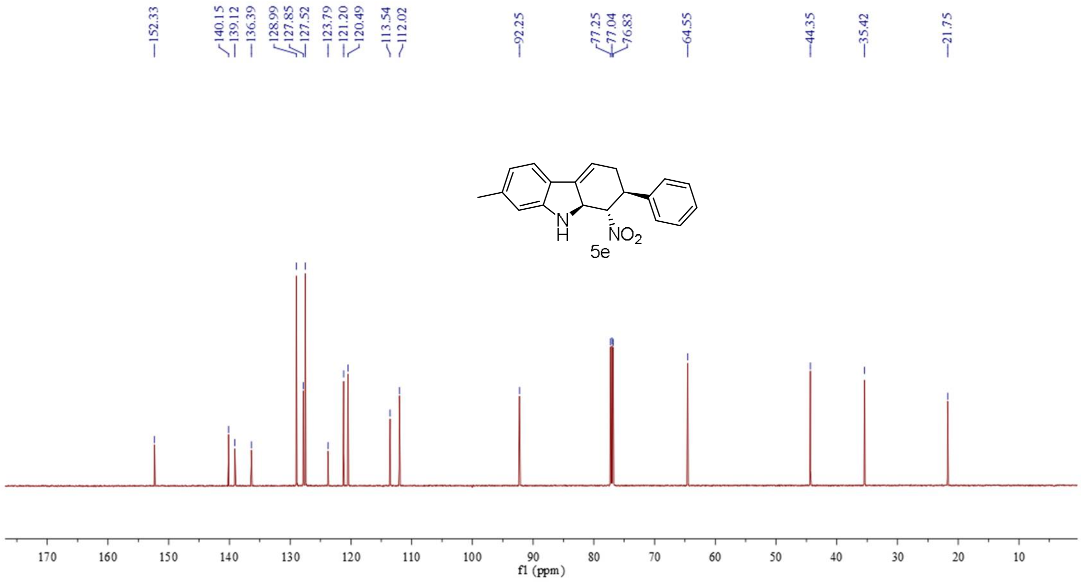

5d
f1 (ppm)


5d
f1 (ppm)


5e
f1 (ppm)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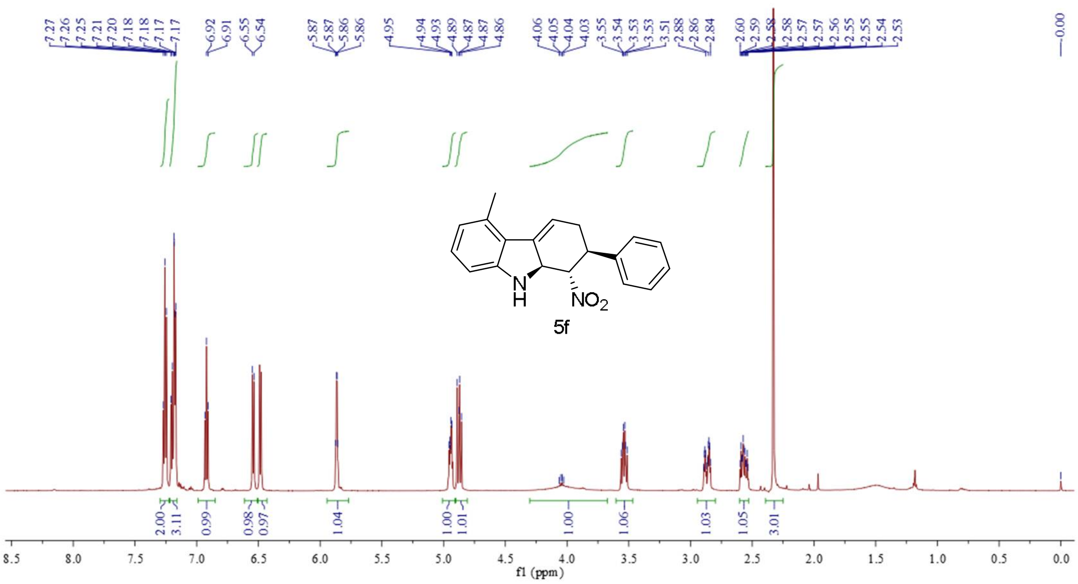
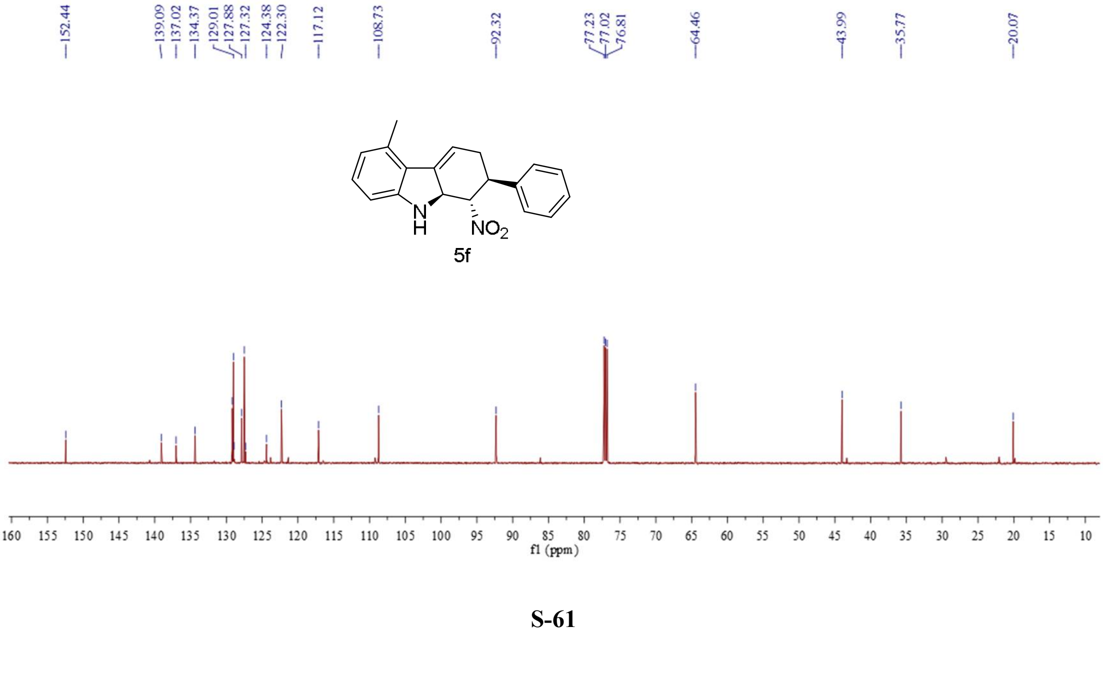
140.15
139.12
136.39
128.99
127.85
127.52
123.79
121.20
120.49
113.54
112.02
92.25
77.25
77.04
76.83
64.55
44.35
35.42
21.75
NO2
5e
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.27
7.26
7.25
7.21
7.20
7.18
7.18
7.17
7.17
6.92
6.91
6.55
6.54
5.87
5.87
5.86
5.86
4.95
4.94
4.93
4.89
4.87
4.87
4.86
4.06
4.05
4.04
4.03
3.55
3.54
3.53
3.53
3.51
2.88
2.86
2.84
2.60
2.59
2.58
2.58
2.57
2.56
2.55
2.55
2.54
2.53
0.00
NO2
5f
2.00
3.11
0.99
0.98
0.97
1.04
1.00
1.01
1.00
1.06
1.03
1.05
3.01
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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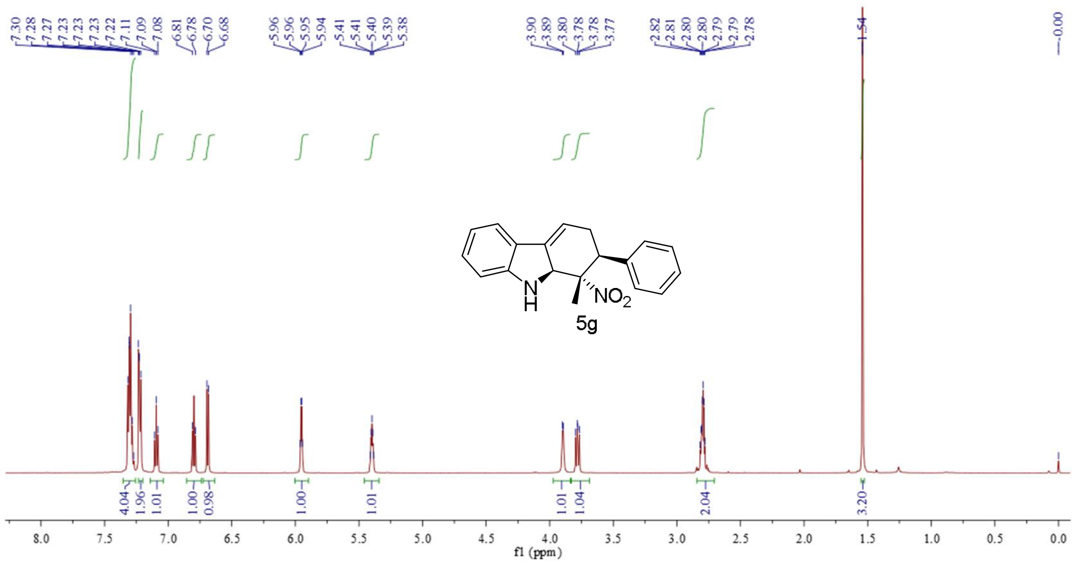
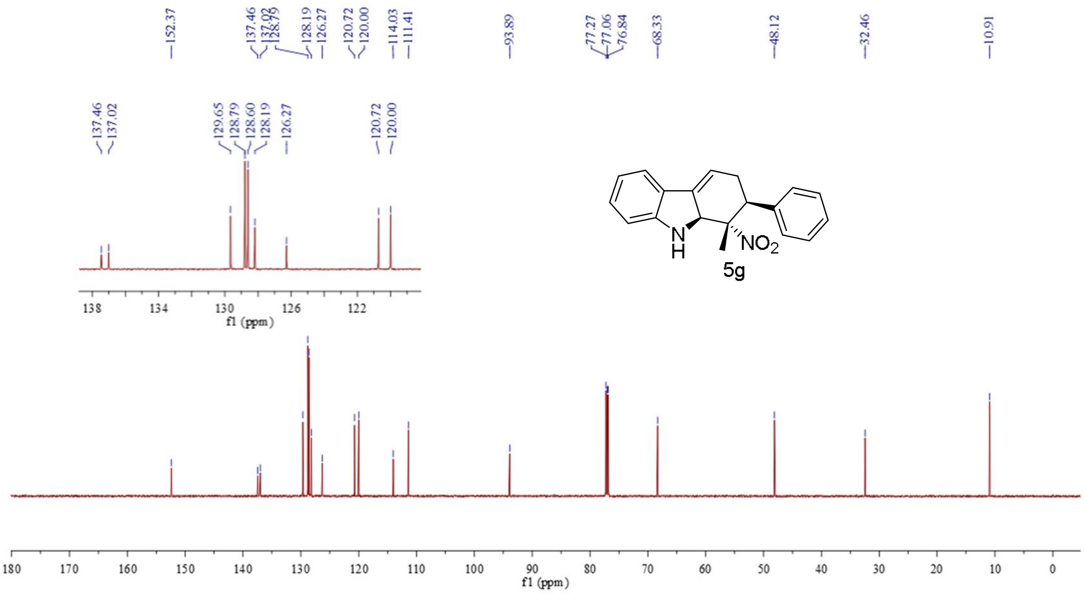
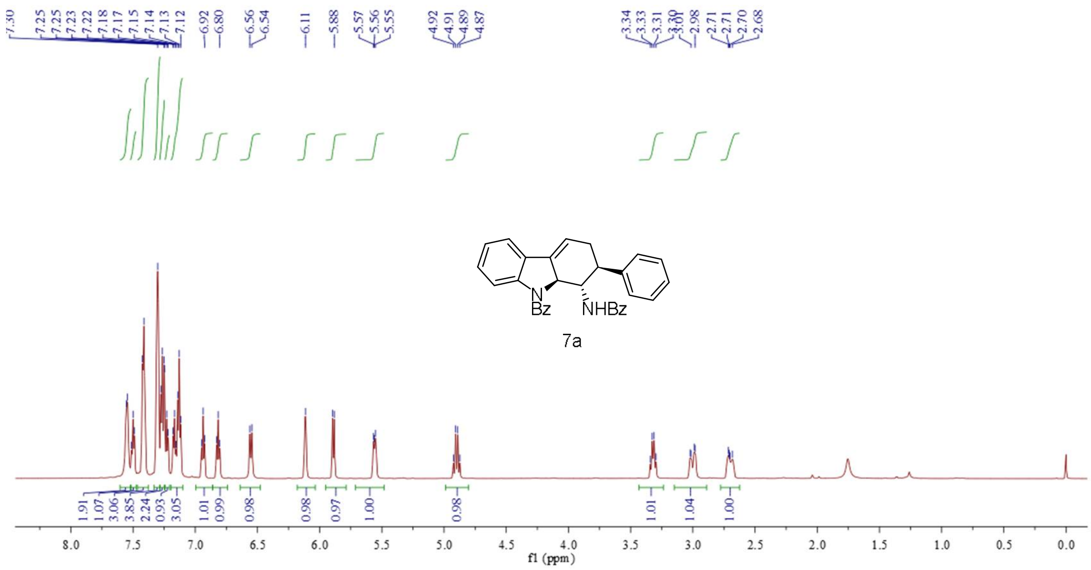
137.02
134.37
129.01
127.88
127.32
124.38
122.30
117.12
108.73
92.32
77.23
77.02
76.81
64.46
43.99
35.77
20.07
NO2
5f
160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
f1 (ppm)



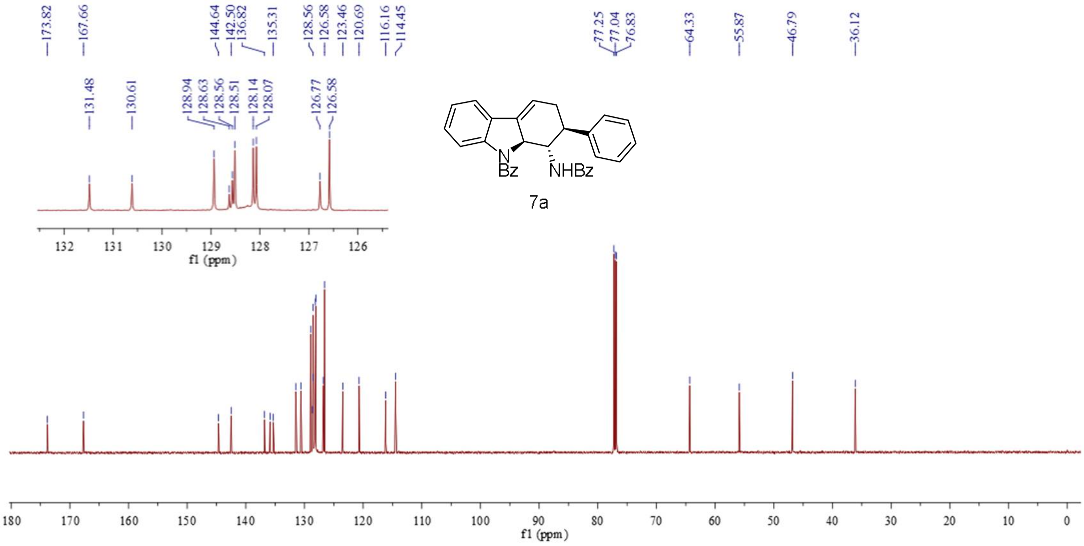
7.30 7.28 7.27 7.23 7.23 7.23 7.22 7.11 7.09 7.08 6.81 6.78 6.70 6.68
5.96 5.96 5.95 5.94 5.41 5.41 5.40 5.39 5.38
3.90 3.89 3.80 3.78 3.78 3.77
2.82 2.81 2.80 2.80 2.79 2.79 2.78
1.54
0.00
H
NO2
5g
4.04 1.96 1.01 1.00 0.98 1.00 1.01 1.01 1.04 2.04 3.20
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



152.37
137.46 137.02 128.79 128.19 126.27 120.72 120.00 114.03 111.41
93.89
77.27 77.06 76.84 68.33
48.12
32.46
10.91
137.46 137.02 129.65 128.79 128.60 128.19 126.27 120.72 120.00
138 134 130 126 122
f1 (ppm)
H
NO2
5g
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



7.30 7.25 7.25 7.23 7.22 7.18 7.17 7.15 7.14 7.13 7.12 6.92 6.80 6.56 6.54
6.11 5.88 5.57 5.56 5.55
4.92 4.91 4.89 4.87
3.34 3.33 3.31 3.00 3.01 2.98 2.71 2.71 2.70 2.68
Bz
NHBz
7a
1.91 1.07 3.06 3.85 2.24 0.93 3.05 1.01 0.99 0.98 0.98 0.97 1.00 0.98 1.01 1.04 1.00
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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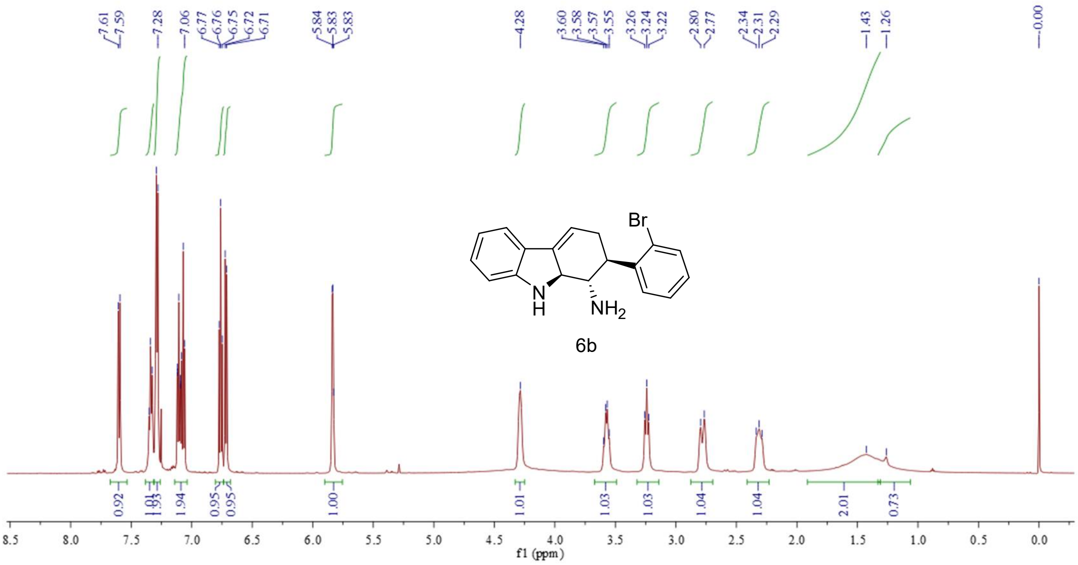
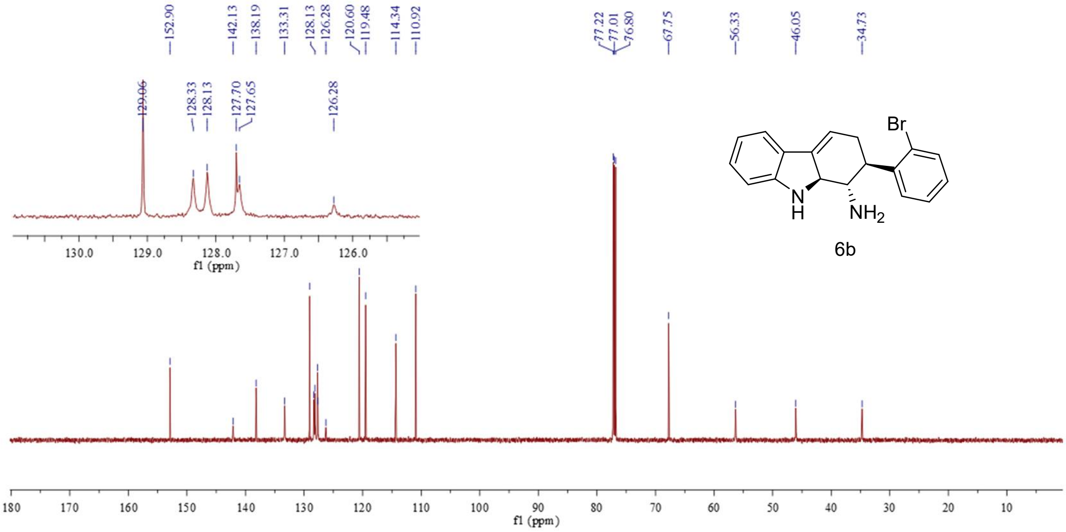
167.66
144.64
142.50
136.82
135.31
128.56
126.58
123.46
120.69
116.16
114.45
131.48
130.61
128.94
128.63
128.56
128.51
128.14
128.07
126.77
126.58
77.25
77.04
76.83
64.33
55.87
46.79
36.12
N
Bz
NHBz
7a
f1 (ppm)
f1 (ppm)


7.61
7.59
7.28
7.06
6.77
6.76
6.75
6.72
6.71
5.84
5.83
5.83
4.28
3.60
3.58
3.57
3.55
3.26
3.24
3.22
2.80
2.77
2.34
2.31
2.29
1.43
1.26
0.00
Br
N
H
NH_2
6b
0.92
1.01
1.93
1.94
0.95
0.95
1.00
1.01
1.03
1.03
1.04
1.04
2.01
0.73
f1 (ppm)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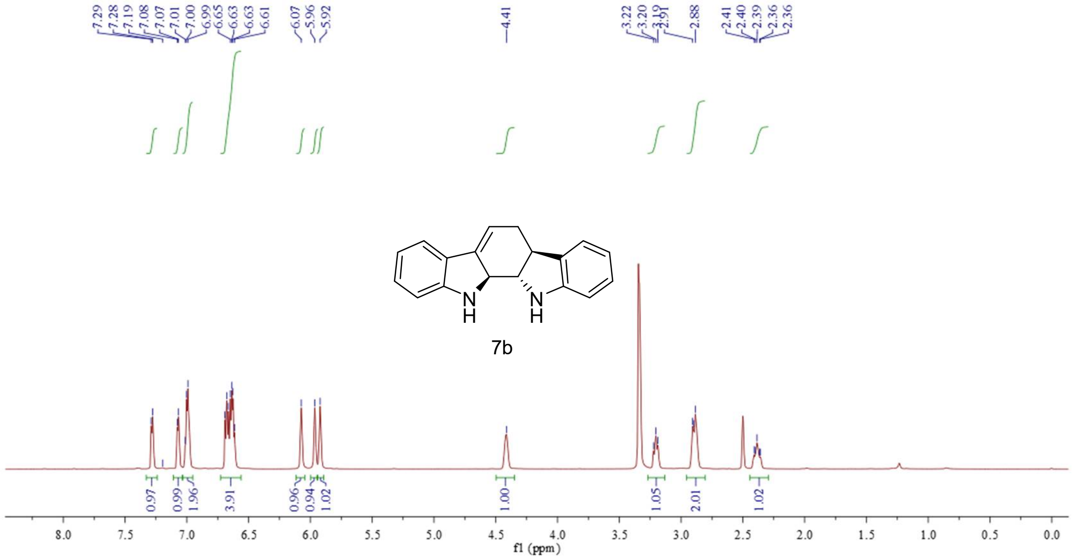
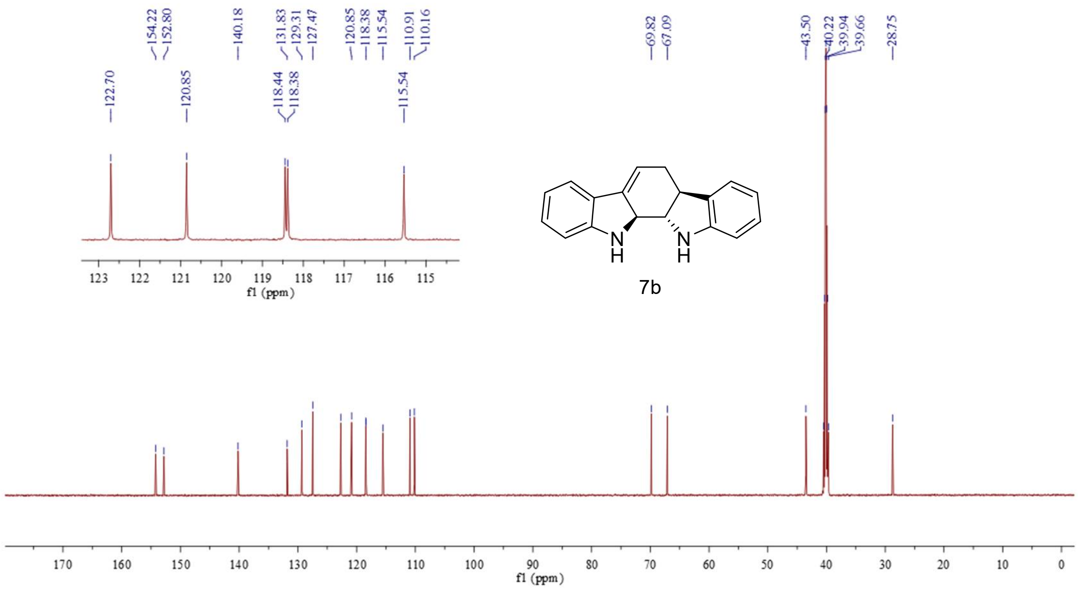
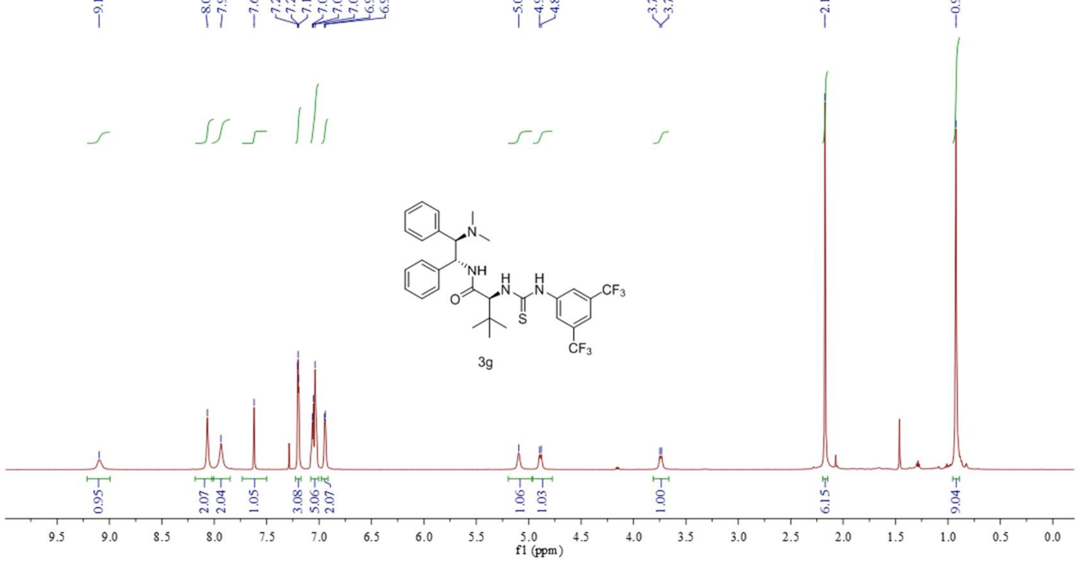
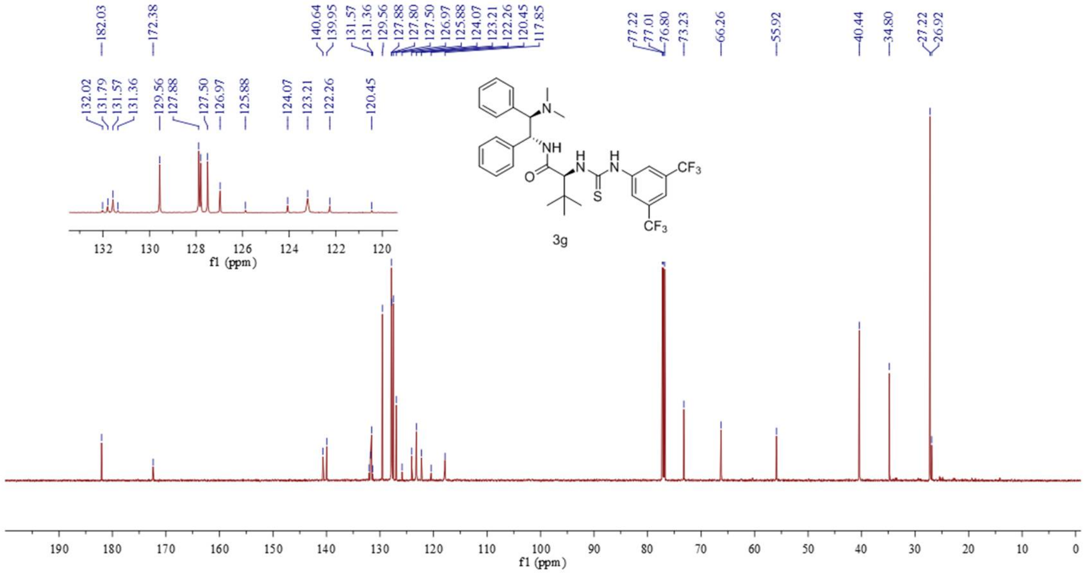
142.13
138.19
133.31
128.13
126.28
120.60
119.48
114.34
110.92
77.22
77.01
76.80
67.75
56.33
46.05
34.73
129.06
128.33
128.13
127.70
127.65
126.28
Br
N
H
NH_2
6b
f1 (ppm)
f1 (ppm)


7b
f1 (ppm)


7b
f1 (ppm)


3g
f1 (ppm)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129.56
127.88
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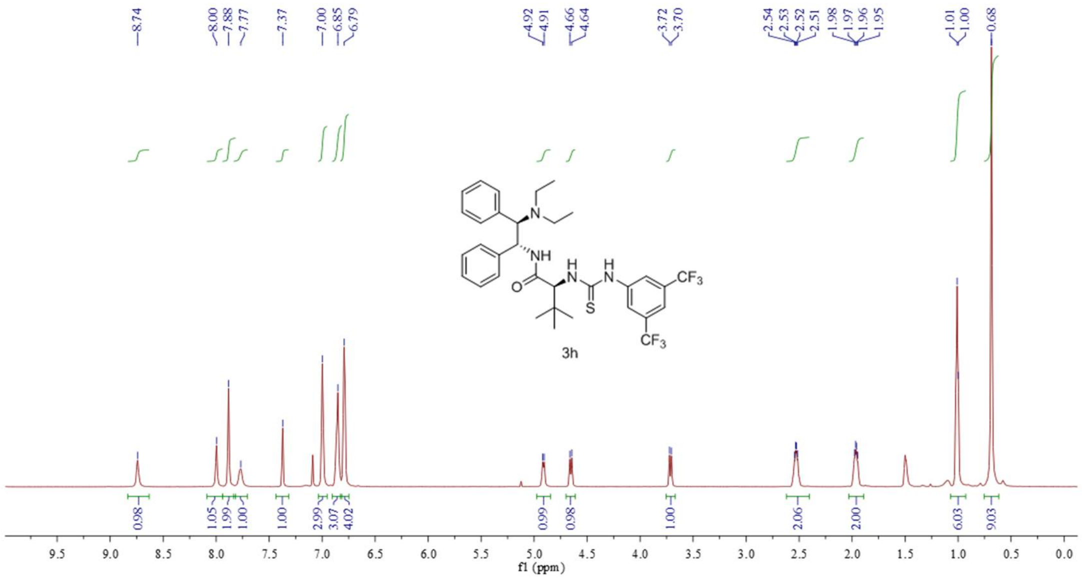
127.50
126.97
125.88
124.07
123.21
122.26
120.45
117.85
77.22
77.01
76.80
73.23
66.26
55.92
40.44
34.80
27.22
26.92
132.02
131.79
131.57
131.36
129.56
127.88
127.50
126.97
125.88
124.07
123.21
122.26
120.45
132 130 128 126 124 122 120
f1 (ppm)
N
NH
H
N
H
N
O
S
CF3
CF3
3g
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.37
7.00
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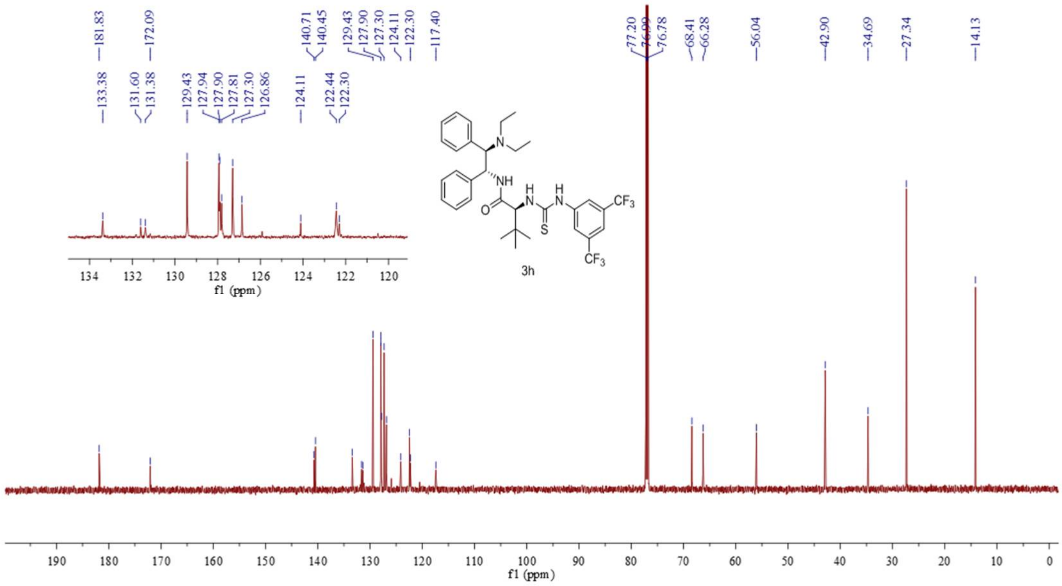
6.79
4.92
4.91
4.66
4.64
3.72
3.70
2.54
2.53
2.52
2.51
1.98
1.97
1.96
1.95
1.01
1.00
0.68
N
NH
H
N
H
N
O
S
CF3
CF3
3h
0.98
1.05
1.99
1.00
1.00
2.99
3.07
4.02
0.99
0.98
1.00
2.06
2.00
6.03
9.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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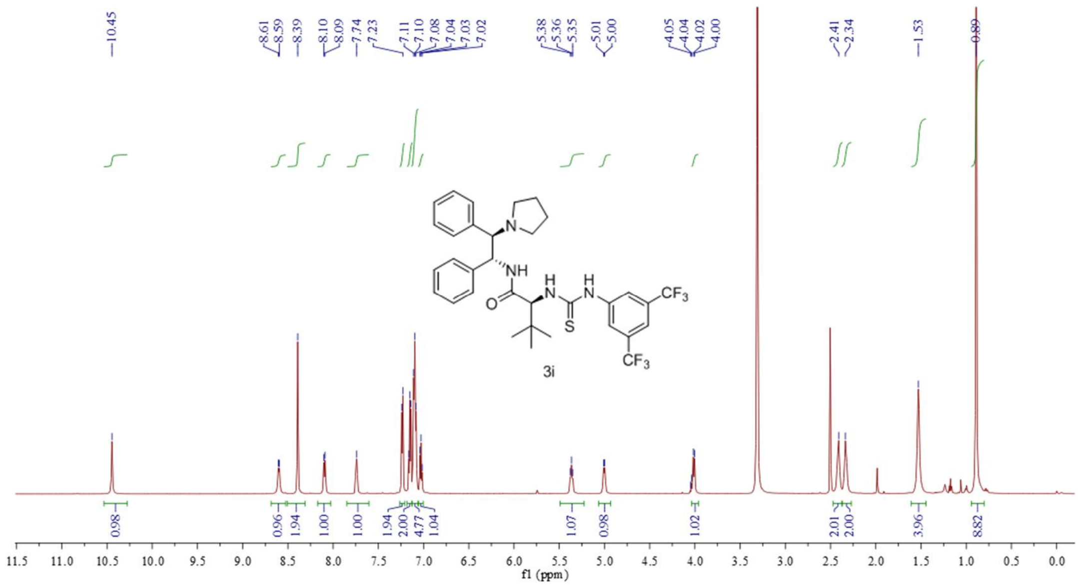
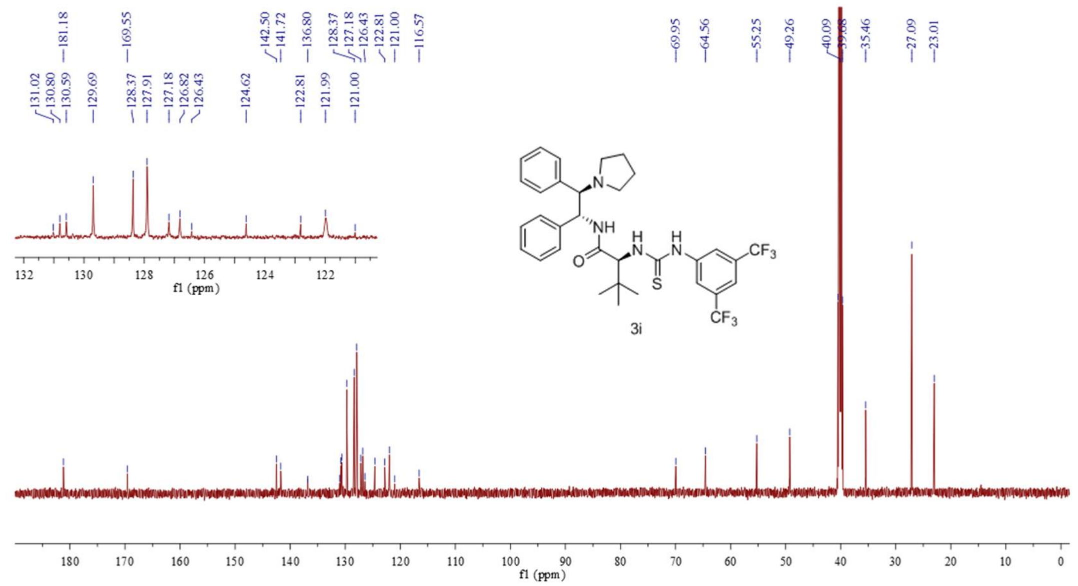
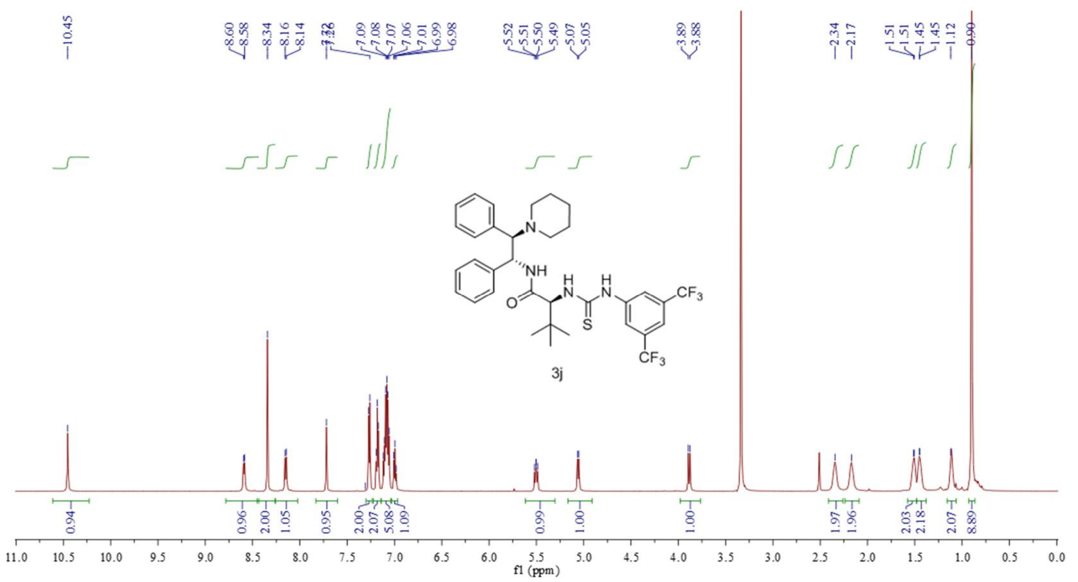
127.90
127.30
124.11
122.30
117.40
77.20
76.78
68.41
66.28
56.04
42.90
34.69
27.34
14.13
133.38
131.60
131.38
129.43
127.94
127.90
127.81
127.30
126.86
124.11
122.44
122.30
134 132 130 128 126 124 122 120
f1 (ppm)
N
NH
H
N
H
N
O
S
CF3
CF3
3h
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



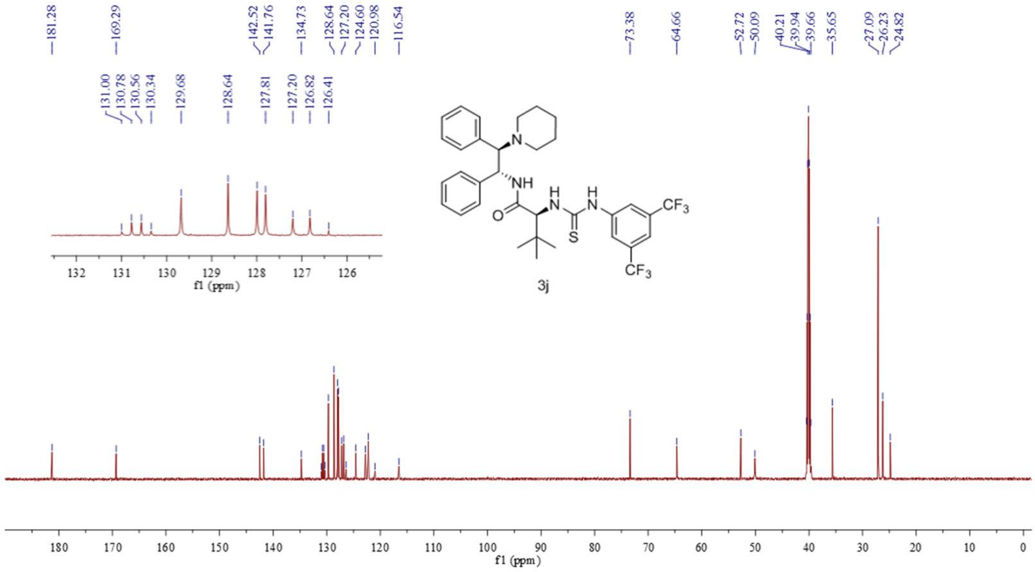
3i
f1 (ppm)



3i
f1 (ppm)



3j
f1 (ppm)


181.28
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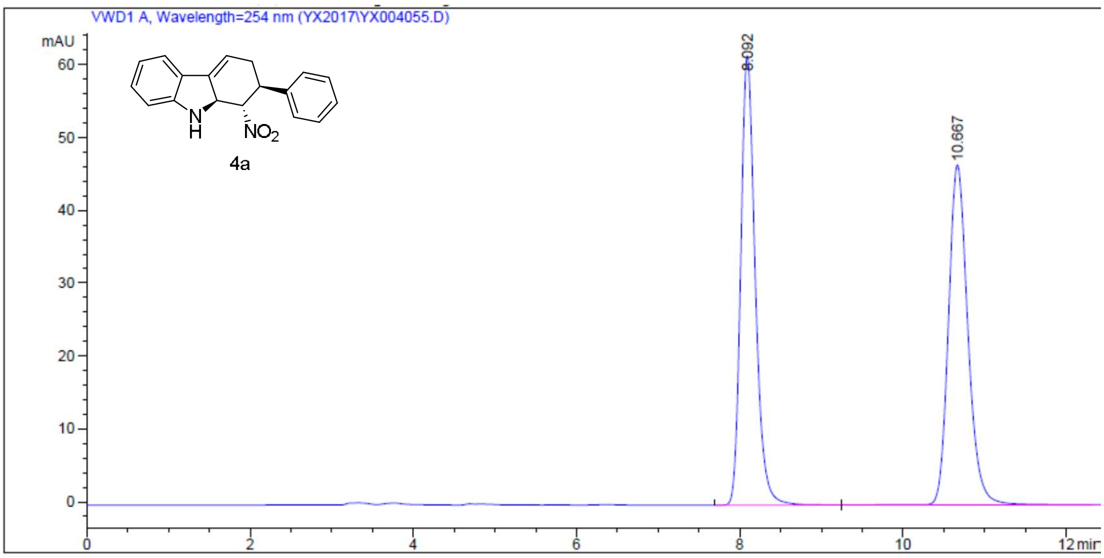
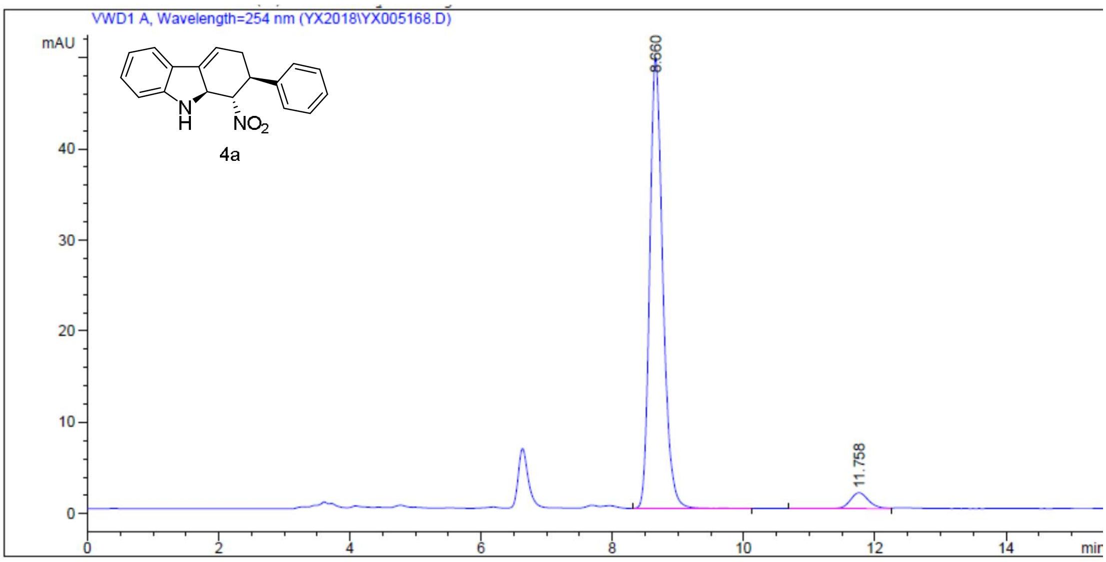
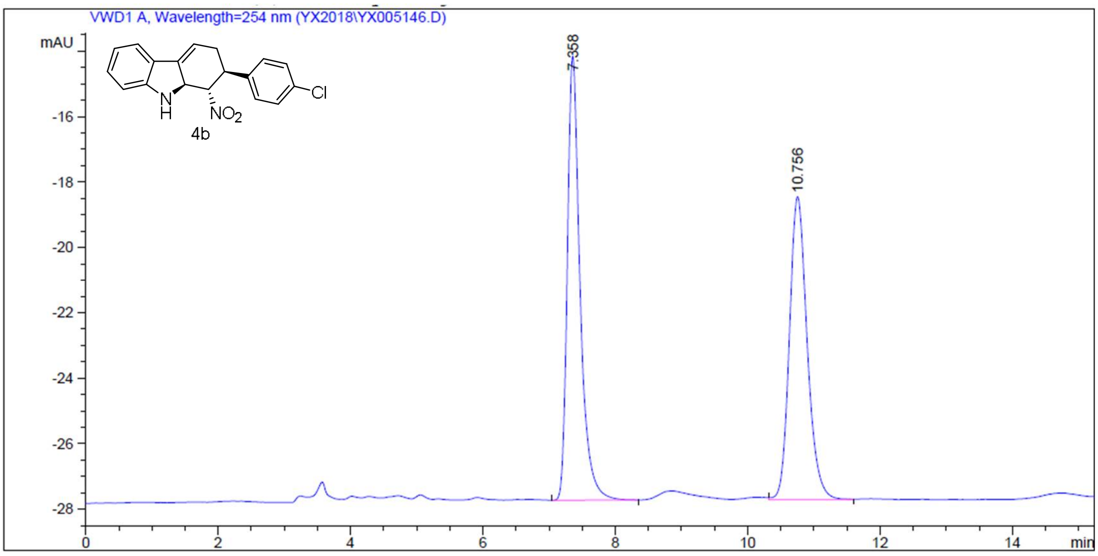
128.64
127.20
124.60
120.98
116.54
73.38
64.66
52.72
50.09
40.21
39.94
39.66
35.65
27.09
26.23
24.82
131.00
130.78
130.56
130.34
129.68
128.64
127.81
127.20
126.82
126.41
NH
N
H
H
O
S
CF_3
CF_3
3j
f1 (ppm)
f1 (ppm)



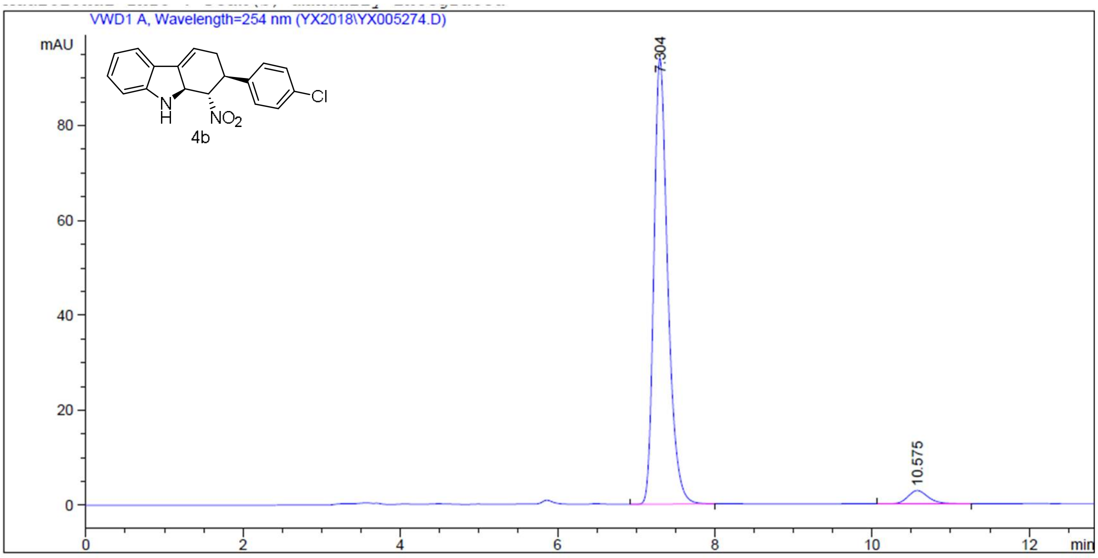
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.092	BB	0.1908	760.20544	61.50956	49.6959
2	10.667	BBA	0.2568	769.51019	46.57536	50.3041



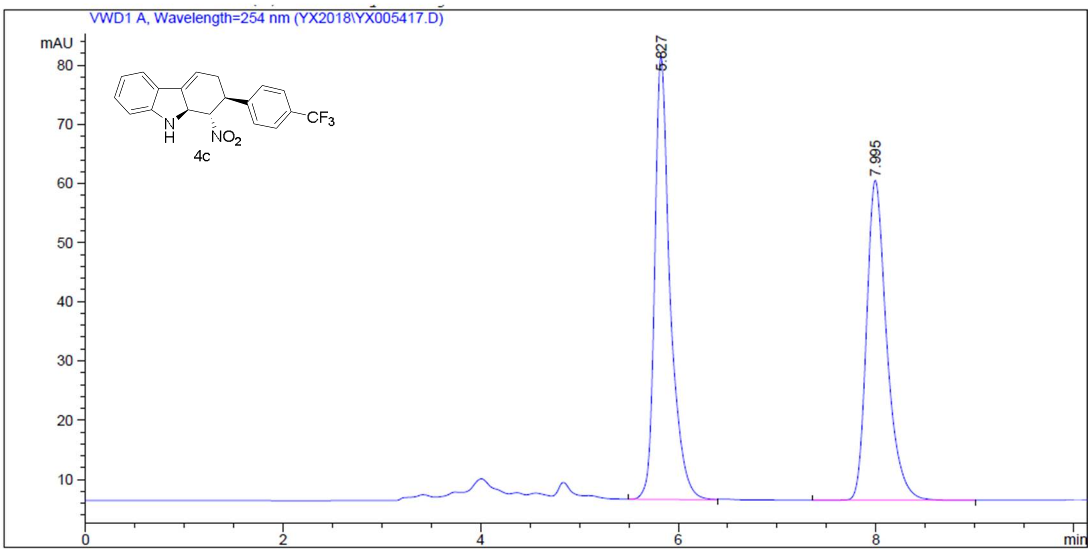
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.660	BB	0.2150	686.68774	49.27265	95.3491
2	11.758	BV	0.2955	33.49493	1.73237	4.6509



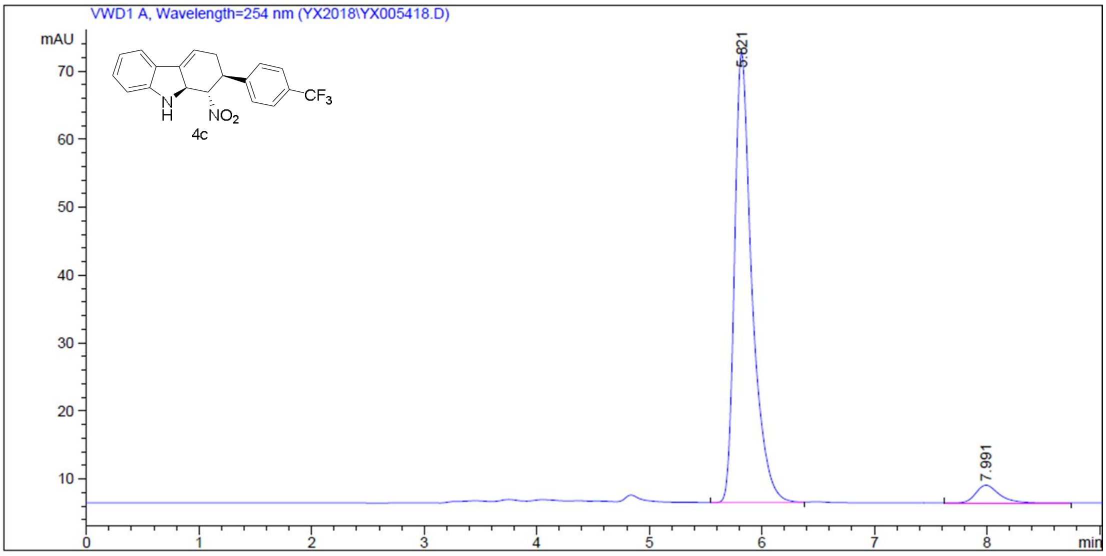
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.358	BB	0.2028	181.03471	13.52236	51.1639
2	10.756	VV	0.2877	172.79803	9.25405	48.8361



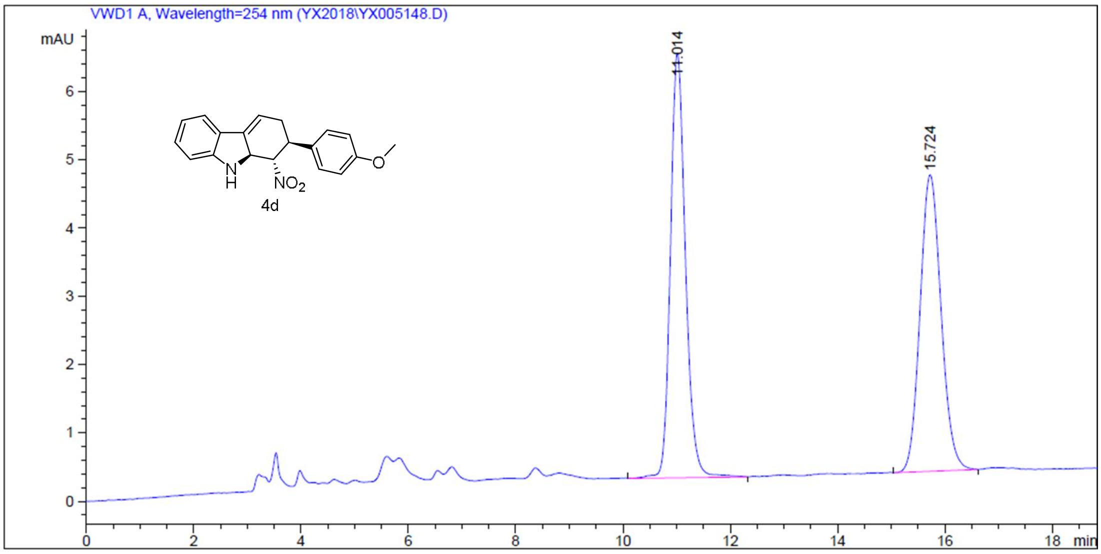
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.304	BV	0.1902	1152.98181	93.66585	95.9079
2	10.575	BB	0.2767	49.19442	2.77473	4.0921



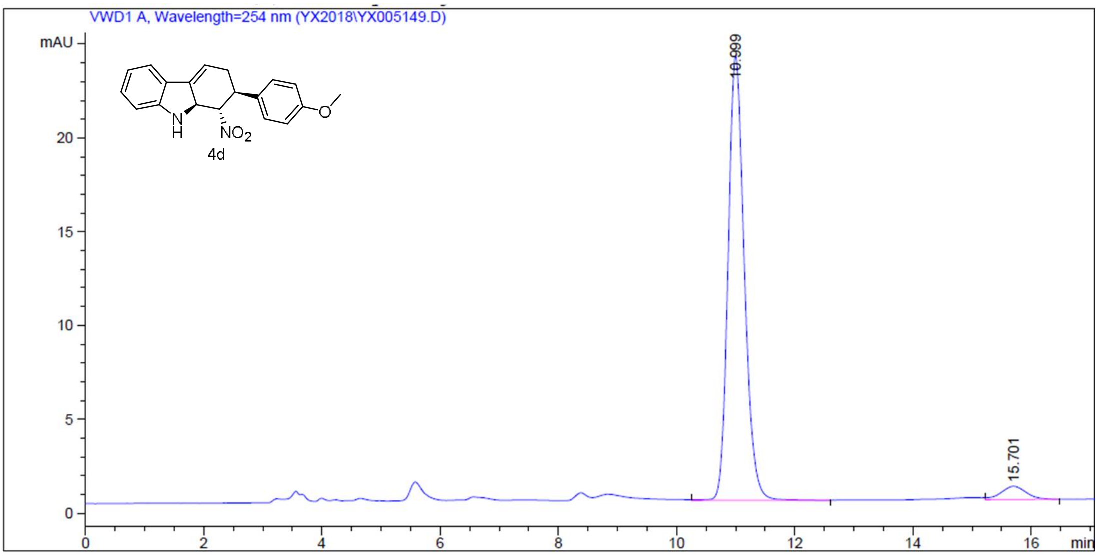
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.827	BV	0.1623	811.42889	74.32701	51.4154
2	7.995	BV	0.2123	766.75275	53.99635	48.5846



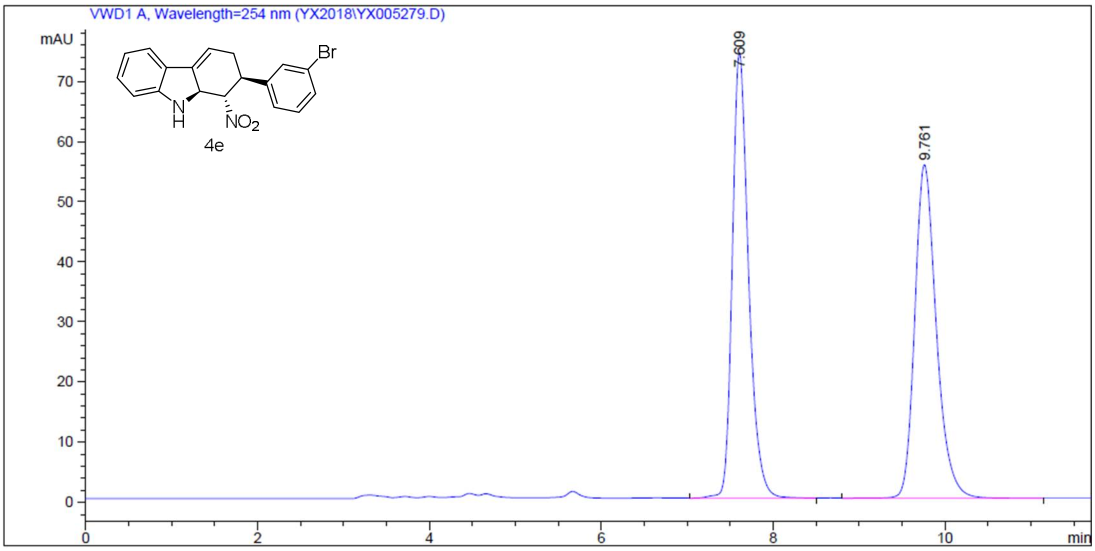
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.821	BV	0.1611	713.54327	65.98581	94.9697
2	7.991	BBA	0.2215	37.79490	2.60718	5.0303



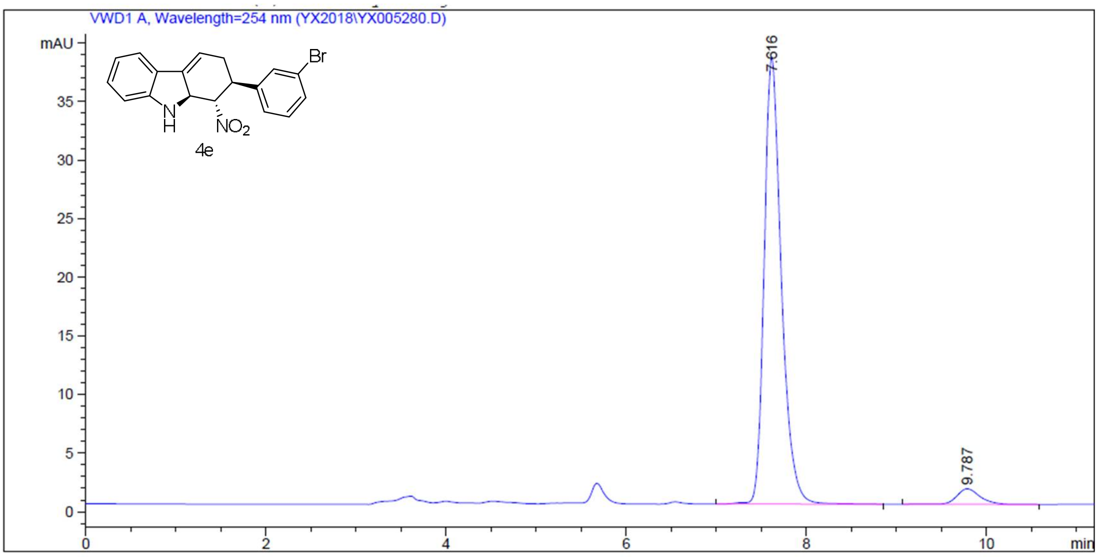
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.014	BB	0.3029	120.98040	6.21371	50.5893
2	15.724	BB	0.4225	118.16186	4.34020	49.4107



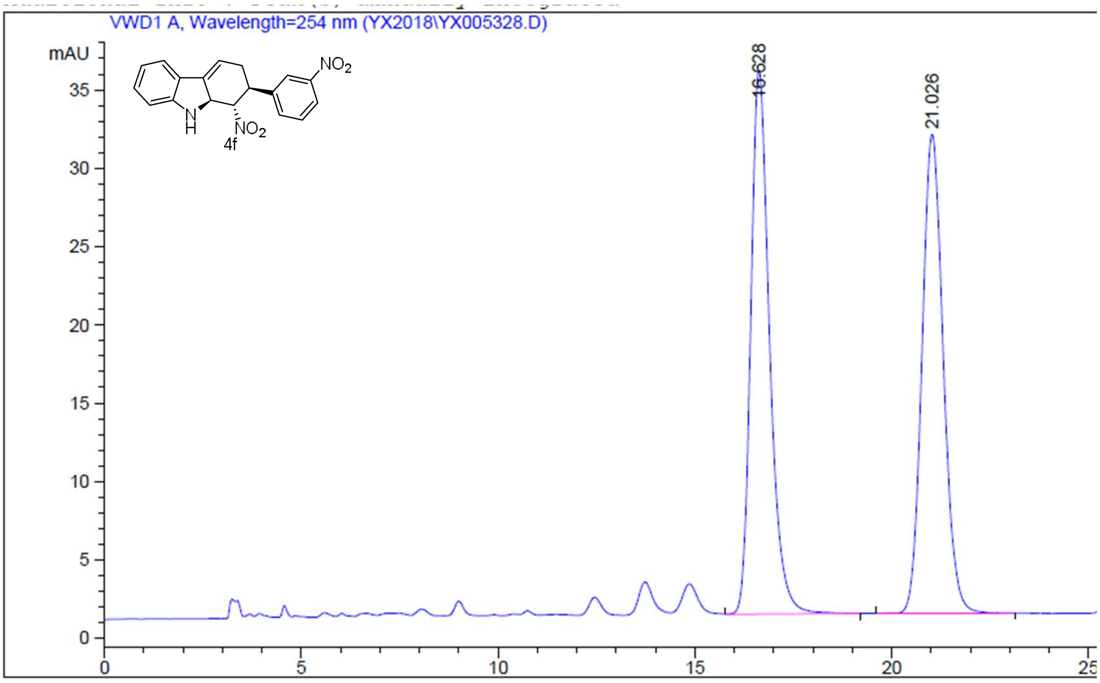
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.999	VB	0.2930	452.44354	23.66241	95.6565
2	15.701	VB	0.4291	20.54402	7.01375e-1	4.3435



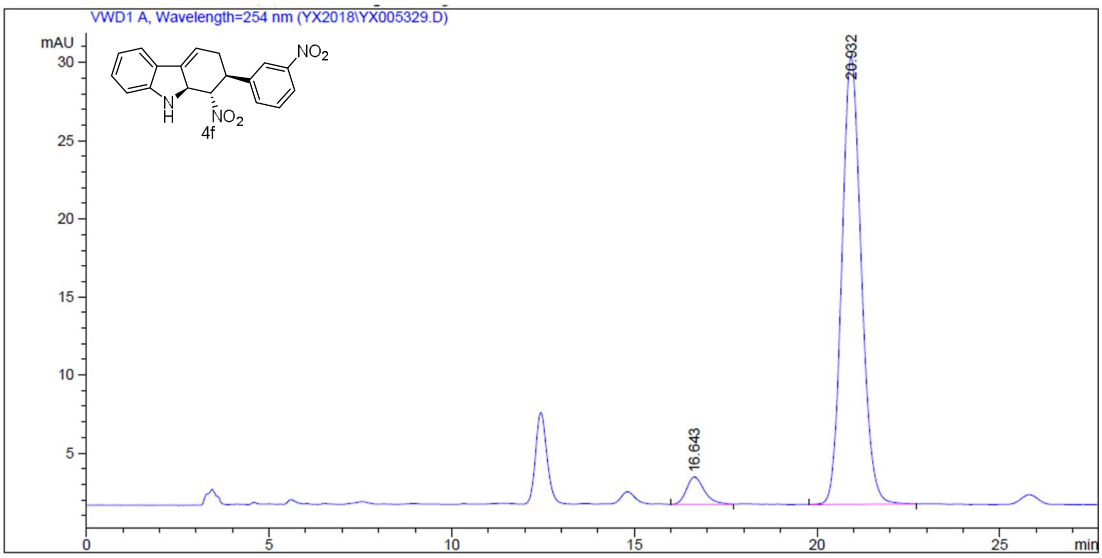
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.609	VV	0.2006	974.21692	73.81171	50.1036
2	9.761	BB	0.2683	970.18945	55.42501	49.8964



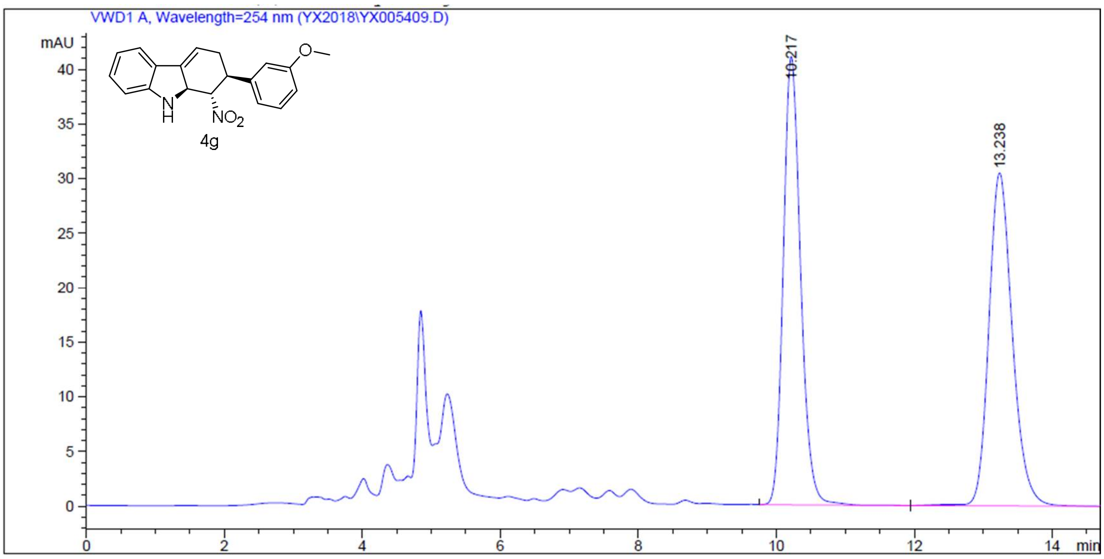
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.616	BB	0.2018	505.64780	38.02026	95.5526
2	9.787	BB	0.2724	23.53493	1.31806	4.4474



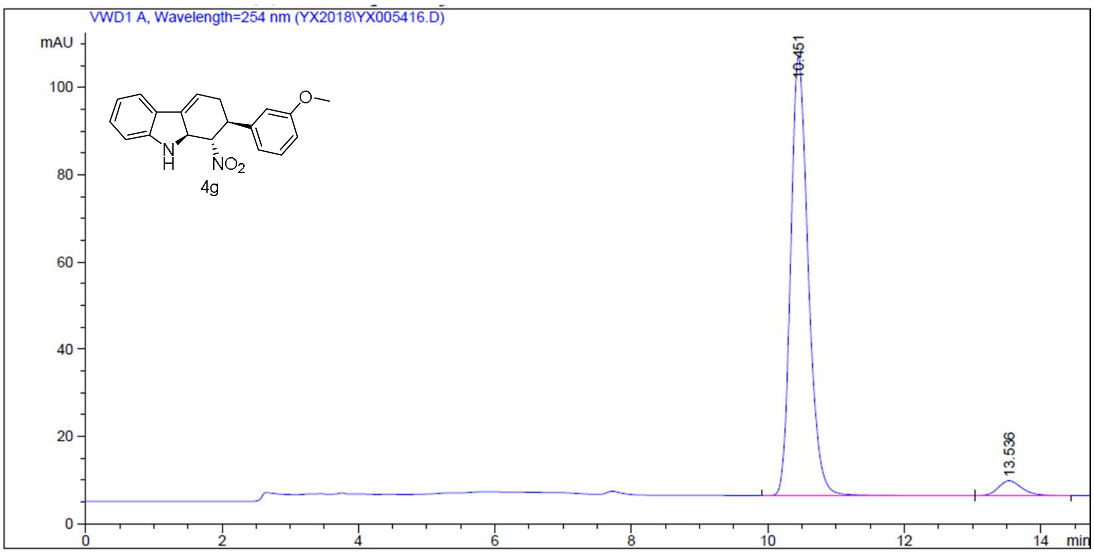
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.628	VB	0.5098	1152.29053	34.69603	50.1616
2	21.026	BB	0.5768	1144.86475	30.56254	49.8384



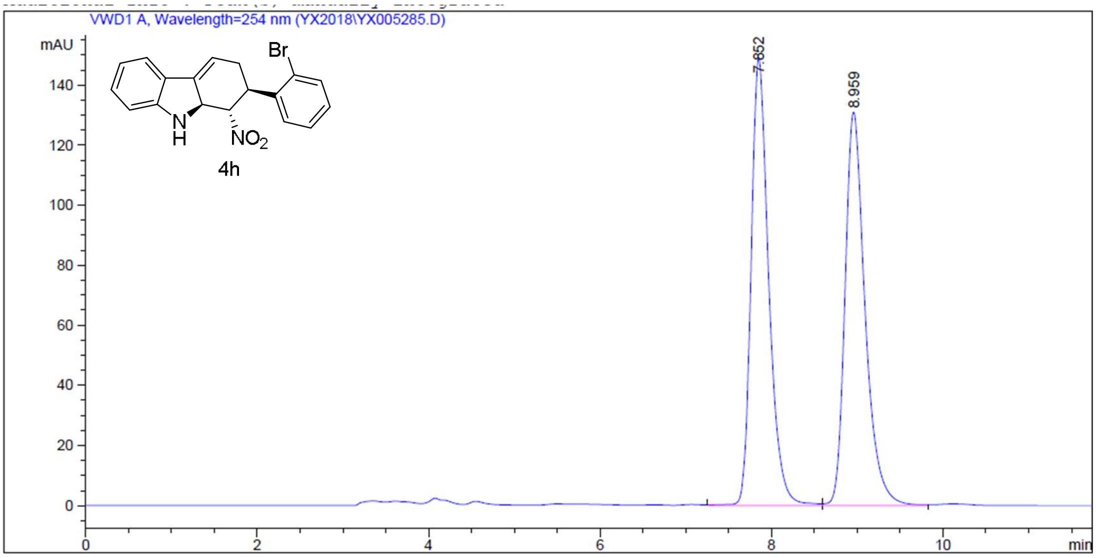
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.643	BV	0.5086	60.30756	1.76802	5.3845
2	20.932	VB	0.5769	1059.70483	28.66201	94.6155



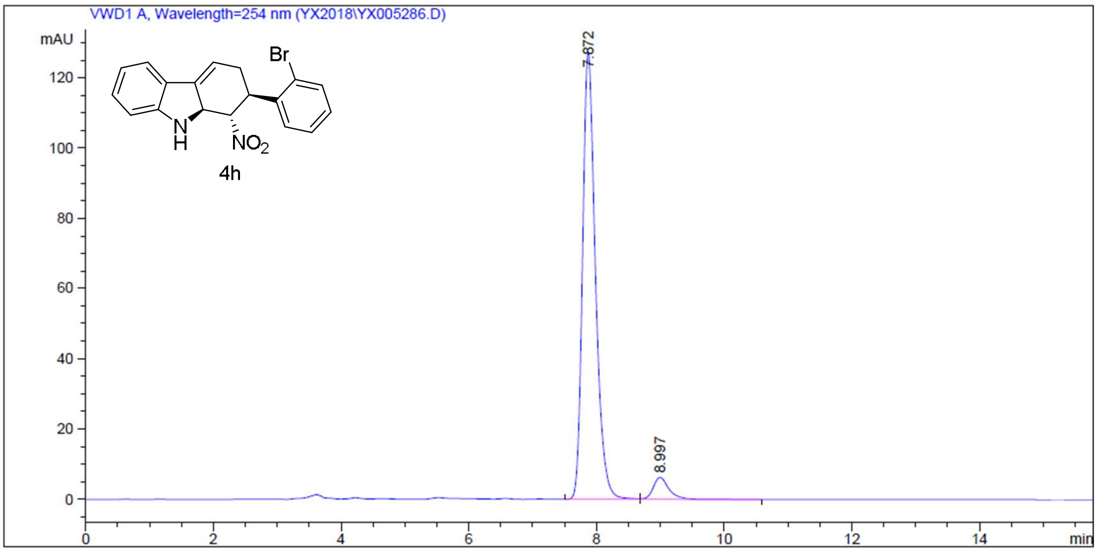
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.217	VB	0.2677	715.39313	40.98610	49.8549
2	13.238	BBA	0.3629	719.55743	30.46993	50.1451



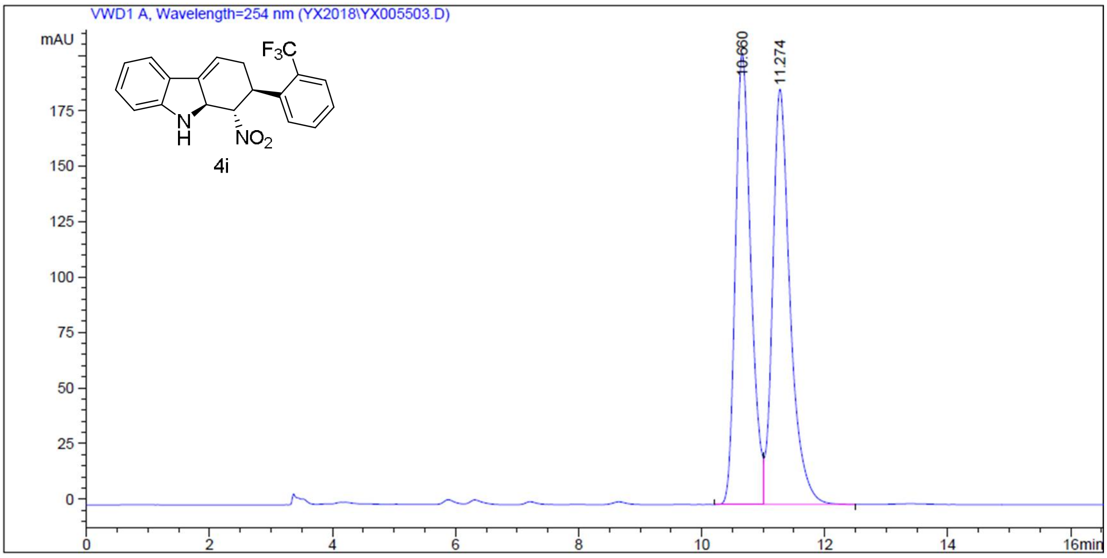
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.451	BB	0.2724	1796.66650	100.59808	95.7177
2	13.536	BBA	0.3649	80.38038	3.37909	4.2823



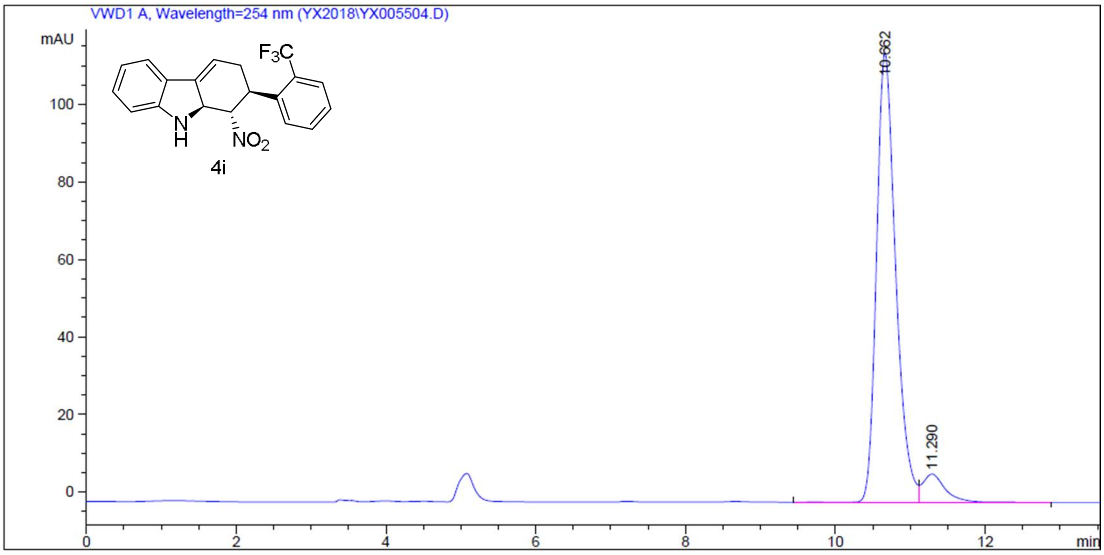
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.852	VV	0.2192	2123.76733	148.55760	49.9840
2	8.959	VV	0.2420	2125.12573	130.75835	50.0160



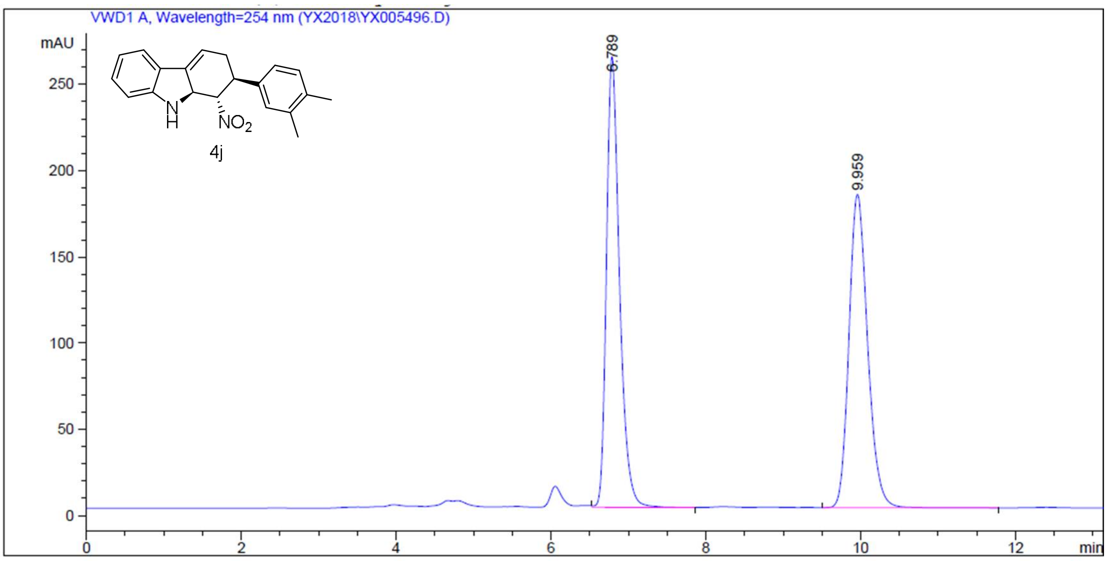
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.872	BV	0.2158	1776.49353	126.84616	94.2536
2	8.997	VB	0.2609	108.30882	6.23492	5.7464



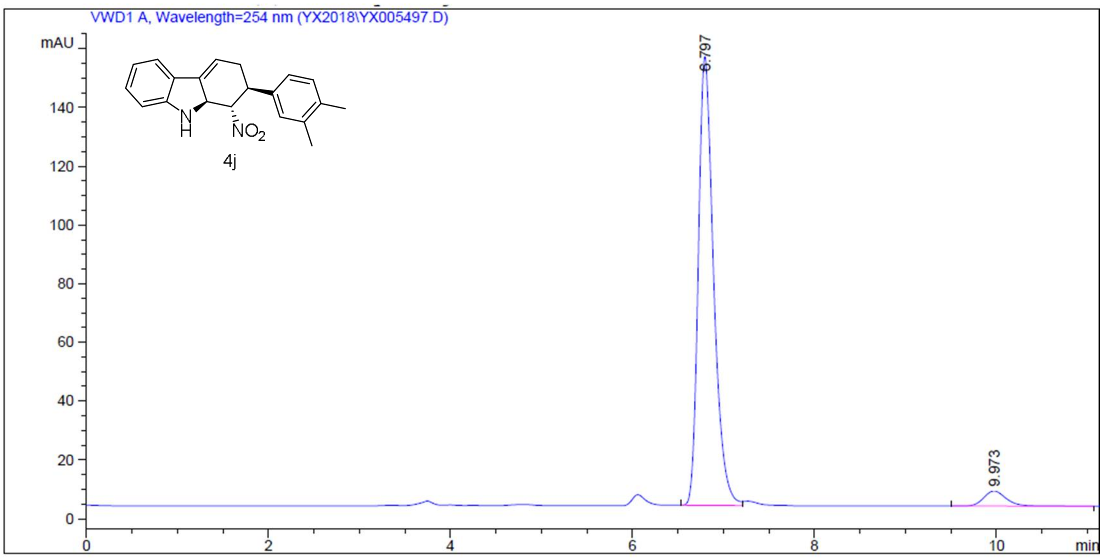
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.660	VV	0.2687	3562.73828	203.09692	49.0241
2	11.274	VB	0.3009	3704.57520	187.09879	50.9759



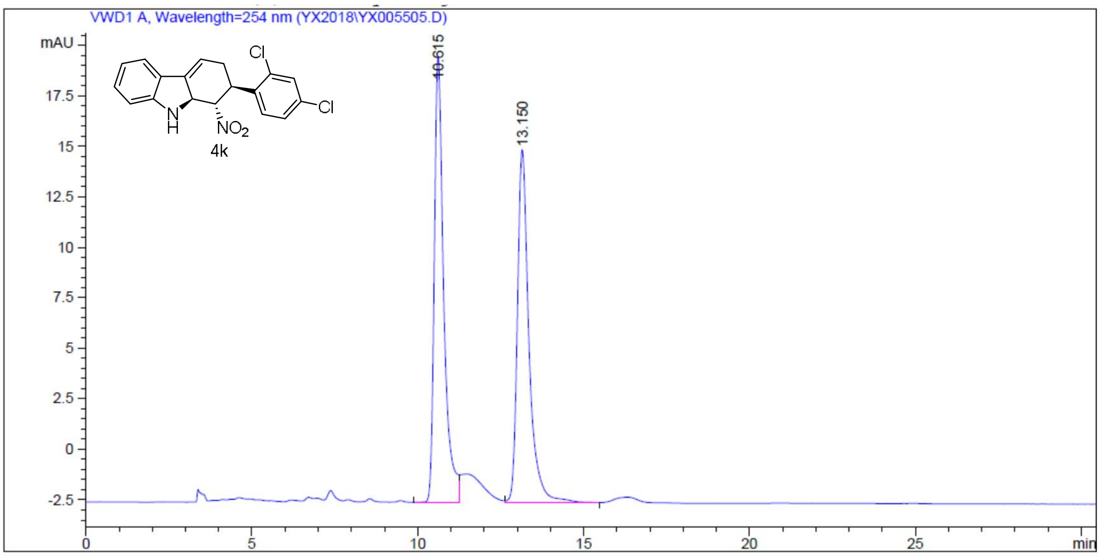
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.662	BV	0.2716	2058.40112	115.73526	93.2269
2	11.290	VB	0.3043	149.54674	7.26273	6.7731



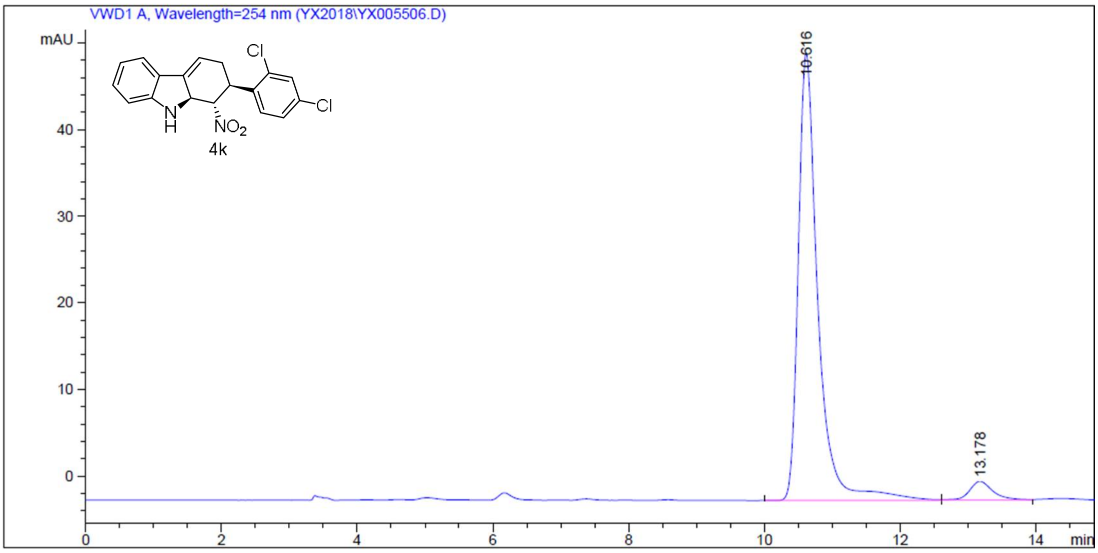
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.789	VB	0.1775	3055.32568	260.72147	50.1614
2	9.959	BB	0.2535	3035.66846	181.37799	49.8386



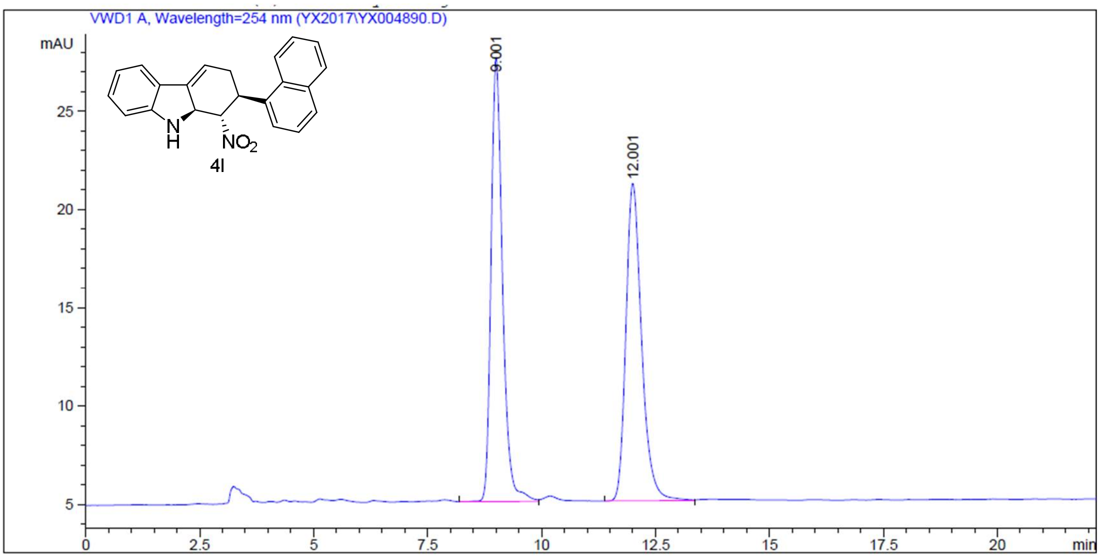
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.797	BV	0.1773	1780.77185	152.18086	95.3463
2	9.973	BBA	0.2623	86.91679	5.11525	4.6537



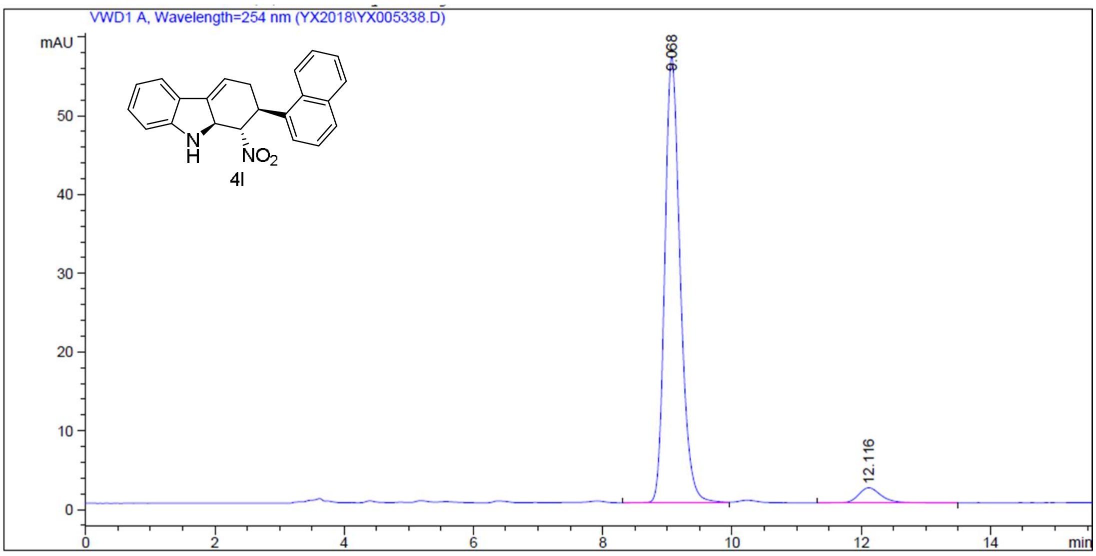
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.615	BV	0.2957	438.06461	22.06342	50.9184
2	13.150	VB	0.3581	422.26239	17.44628	49.0816



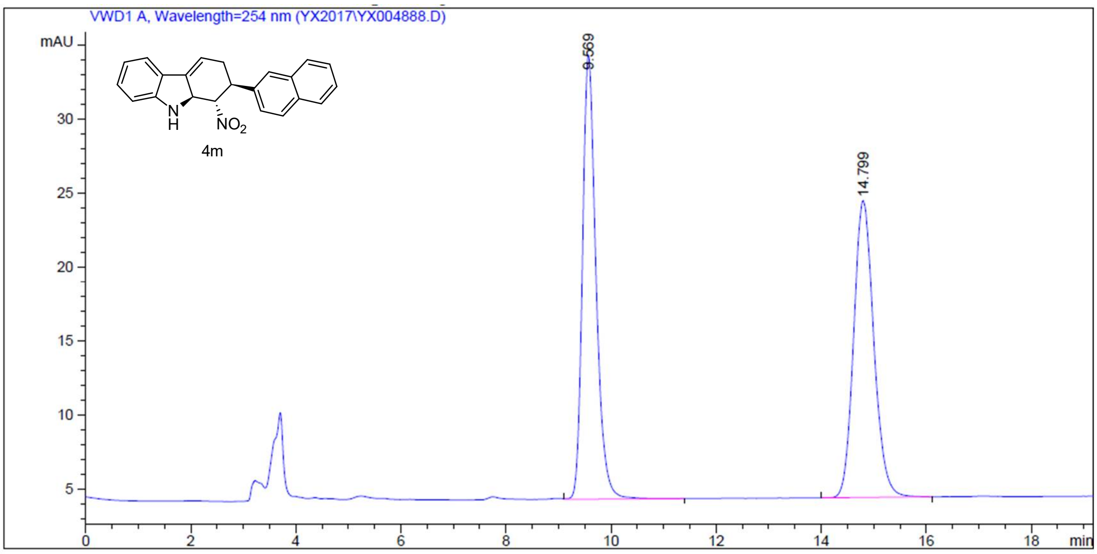
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.616	BV	0.2984	1035.40869	51.55610	95.1677
2	13.178	VV	0.3653	52.57425	2.16175	4.8323



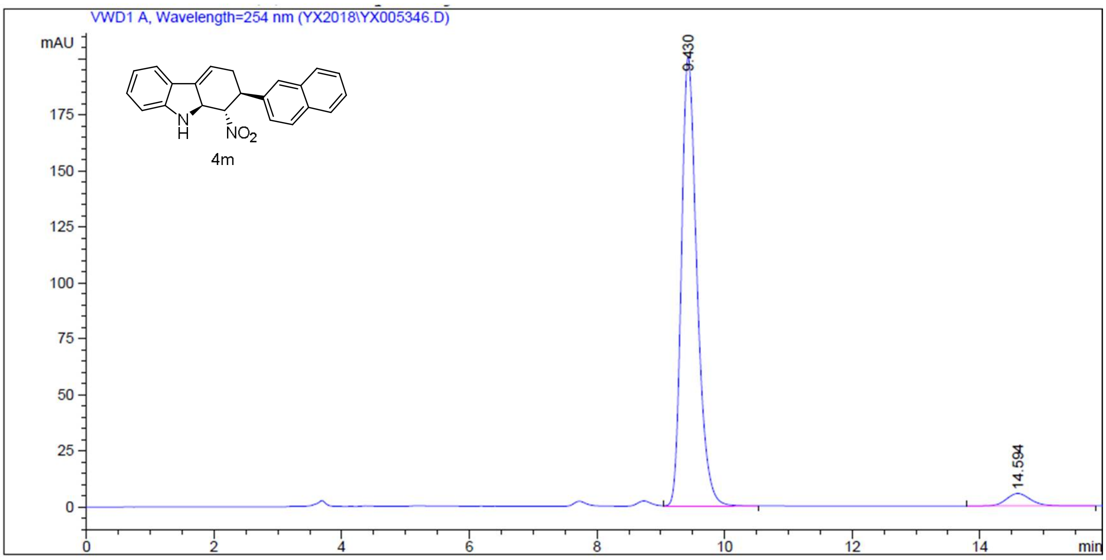
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.001	BV	0.2680	394.59518	22.56902	50.4949
2	12.001	BV	0.3670	386.86005	16.13859	49.5051



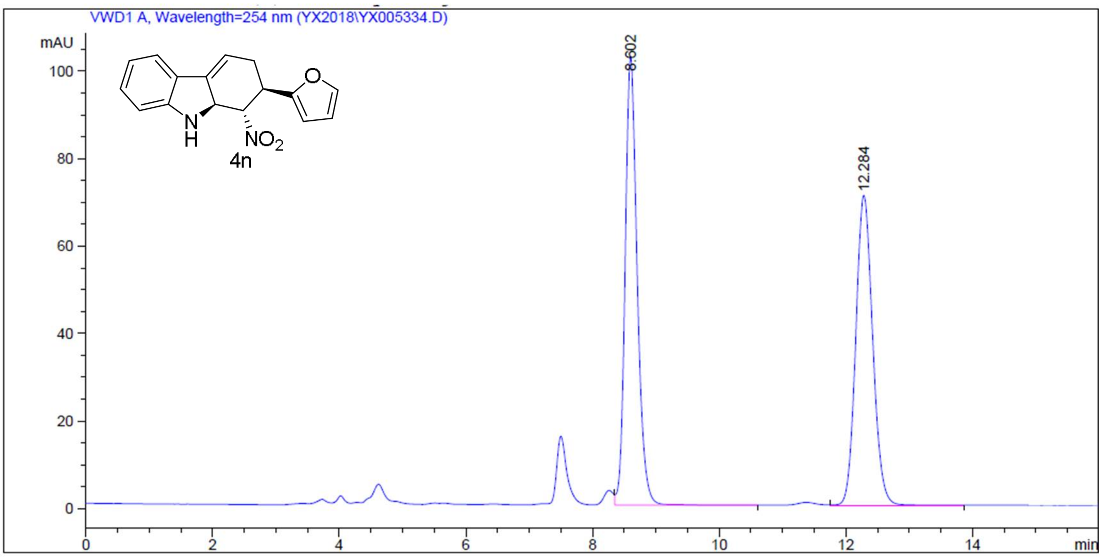
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.068	BV	0.2522	940.27649	56.55170	95.3335
2	12.116	BB	0.3688	46.02589	1.90782	4.6665



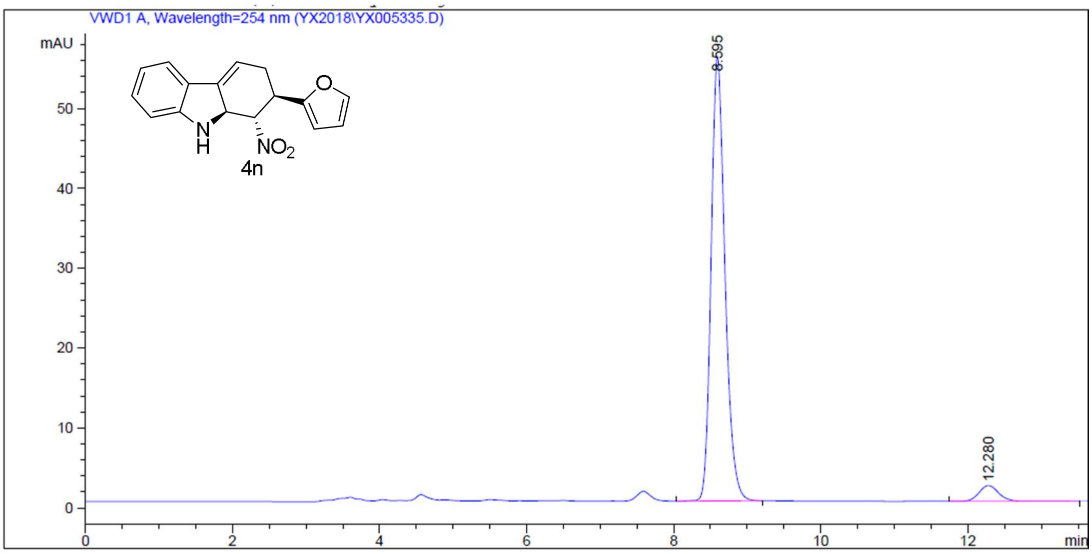
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.569	VB	0.2732	535.80511	29.89490	50.1377
2	14.799	BB	0.4097	532.86151	20.01254	49.8623



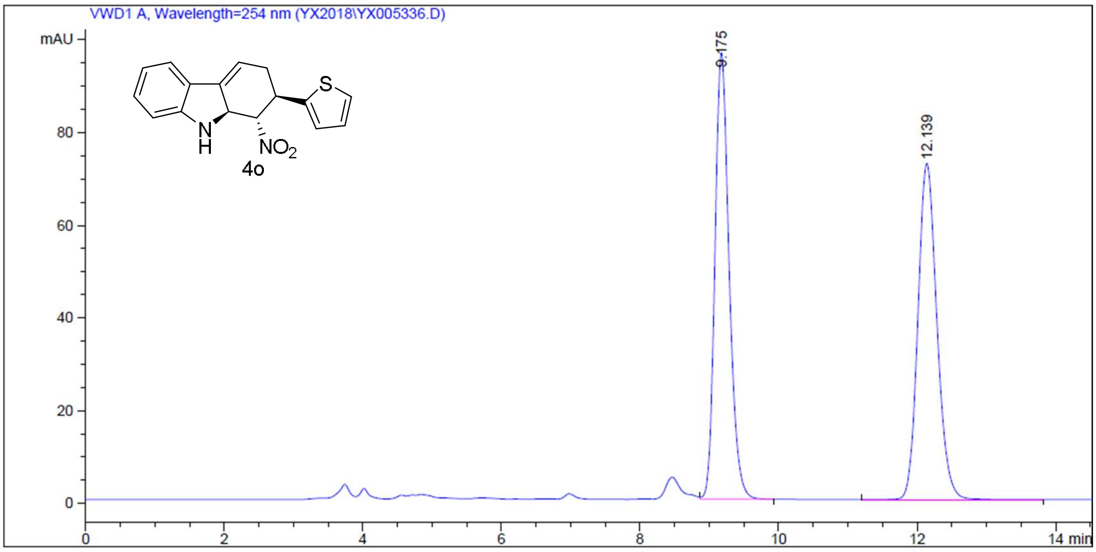
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.430	VV	0.2562	3401.98755	200.53830	95.9449
2	14.594	BB	0.4019	143.78503	5.53792	4.0551



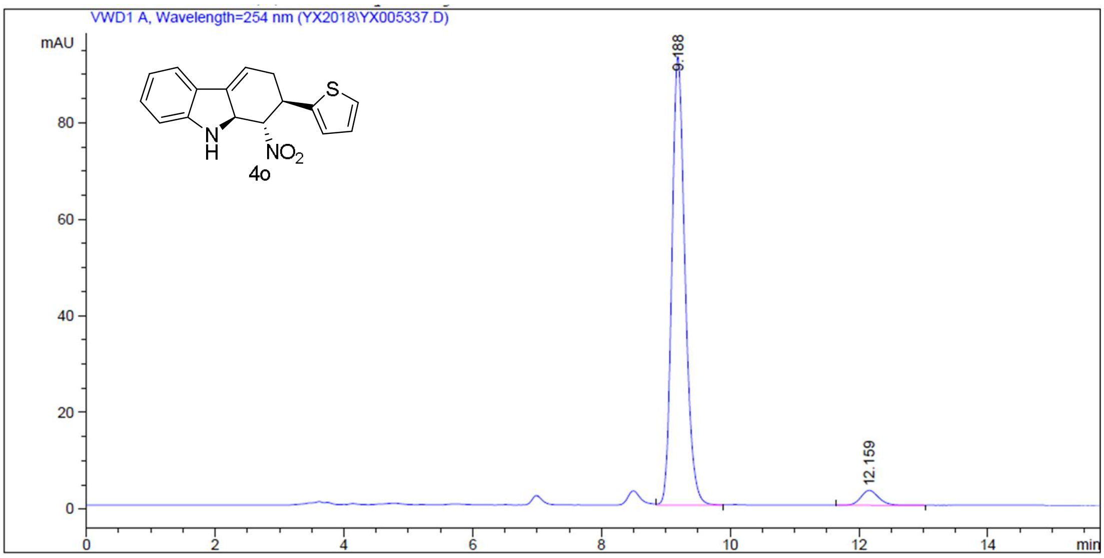
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.602	VB	0.2010	1352.57092	102.20098	50.7988
2	12.284	VB	0.2859	1310.03308	70.74937	49.2012



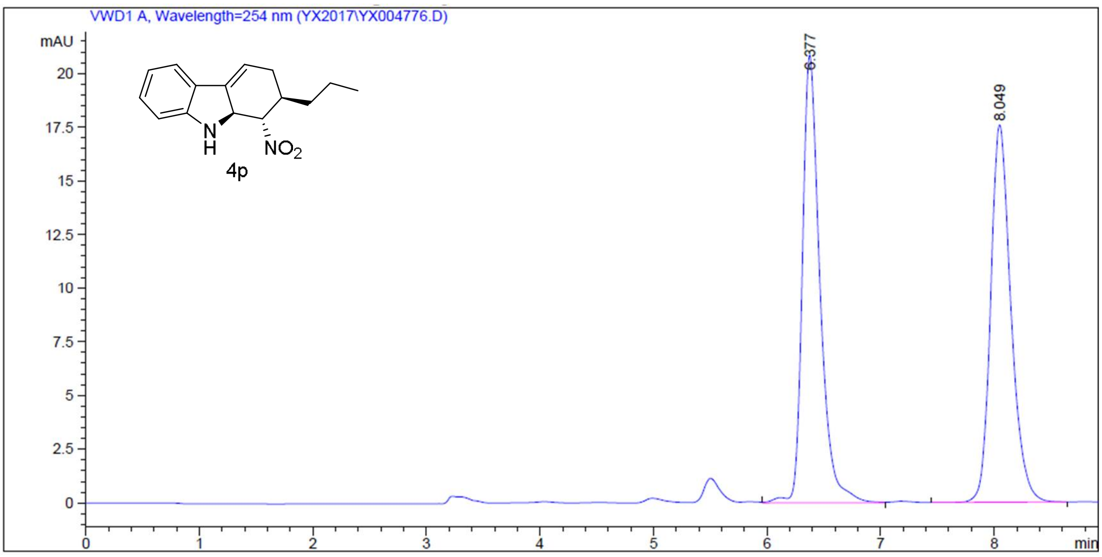
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.595	BB	0.1998	728.60950	55.48958	95.1492
2	12.280	BBA	0.2899	37.14520	1.96997	4.8508



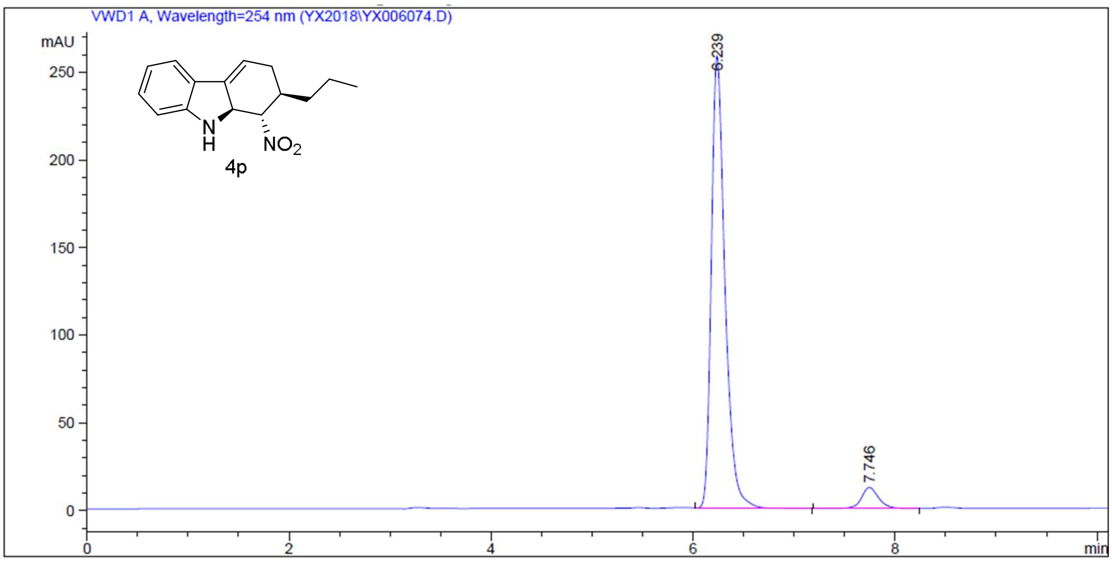
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.175	VV	0.2188	1372.12085	96.19083	49.8757
2	12.139	BB	0.2977	1378.96204	72.46756	50.1243



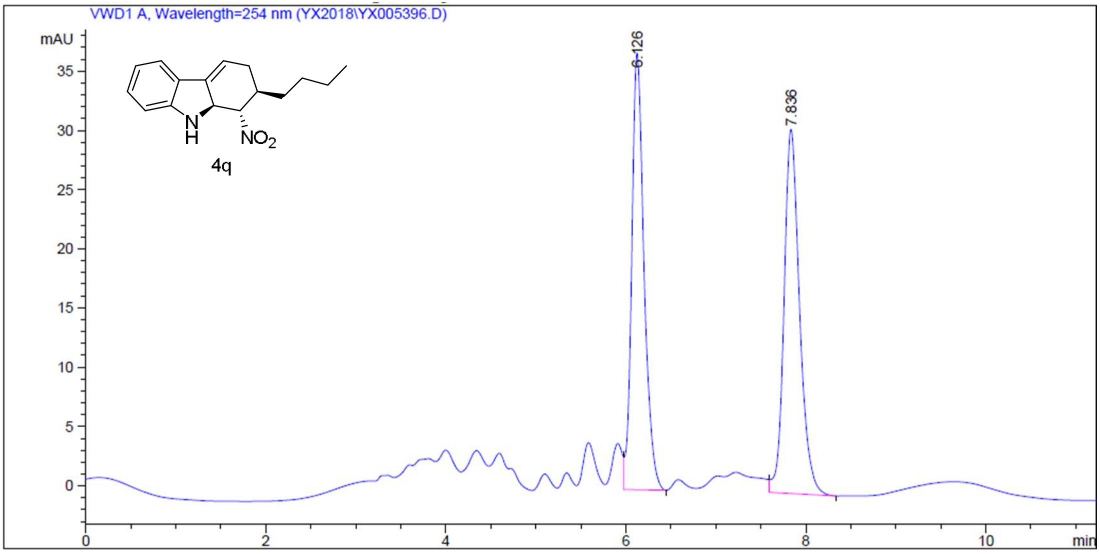
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.188	VV	0.2185	1319.05713	92.67544	95.7700
2	12.159	BB	0.2985	58.26005	3.05107	4.2300



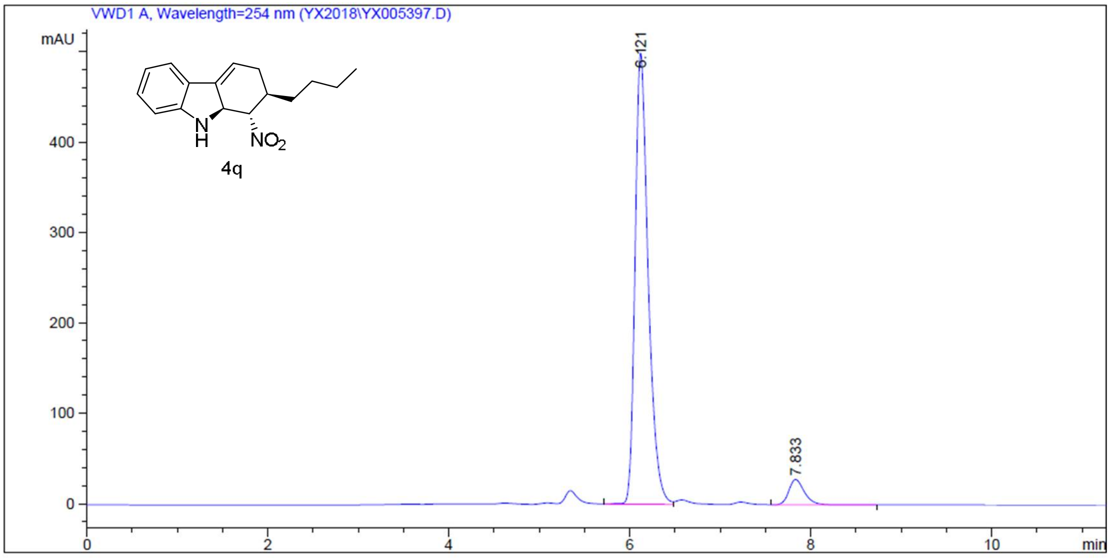
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.377	VV	0.1668	224.50836	20.78570	50.6706
2	8.049	BB	0.1920	218.56548	17.54077	49.3294



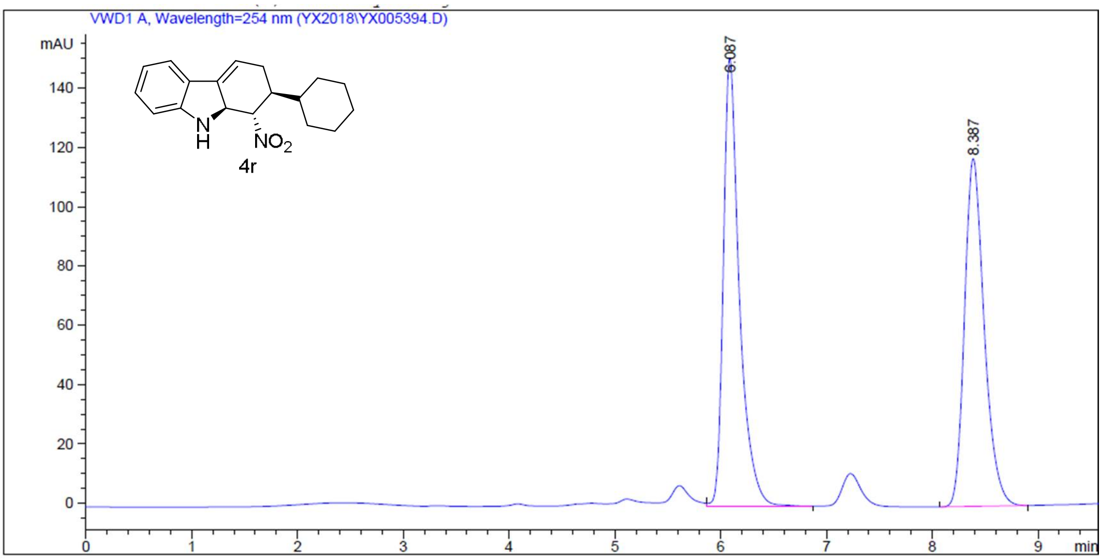
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.239	VB	0.1389	2416.81787	256.78766	94.5172
2	7.746	BB	0.1776	140.19652	11.95525	5.4828



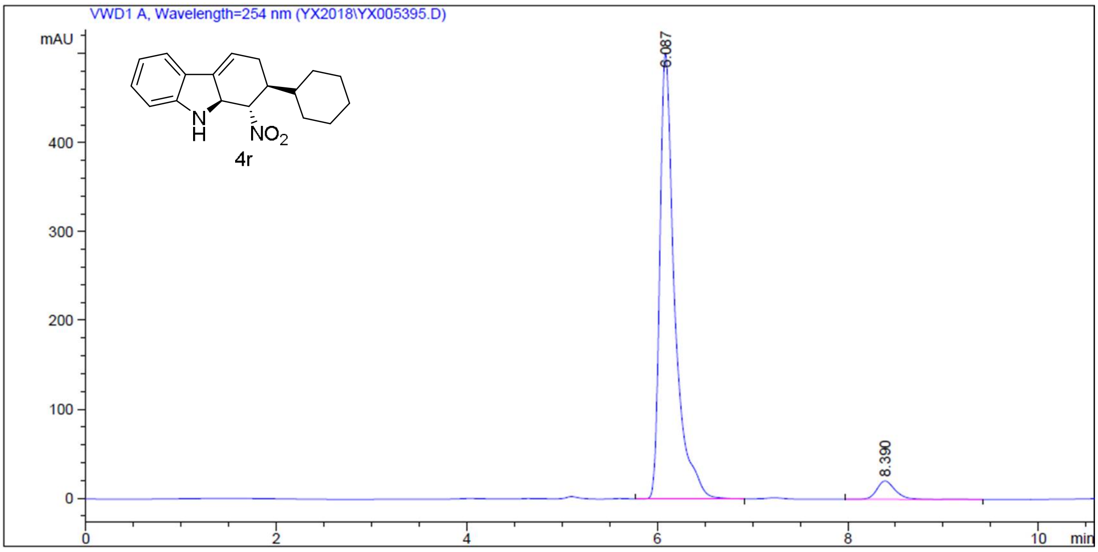
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.126	VB	0.1462	350.29214	36.73932	48.7520
2	7.836	VB	0.1808	368.22577	30.67670	51.2480



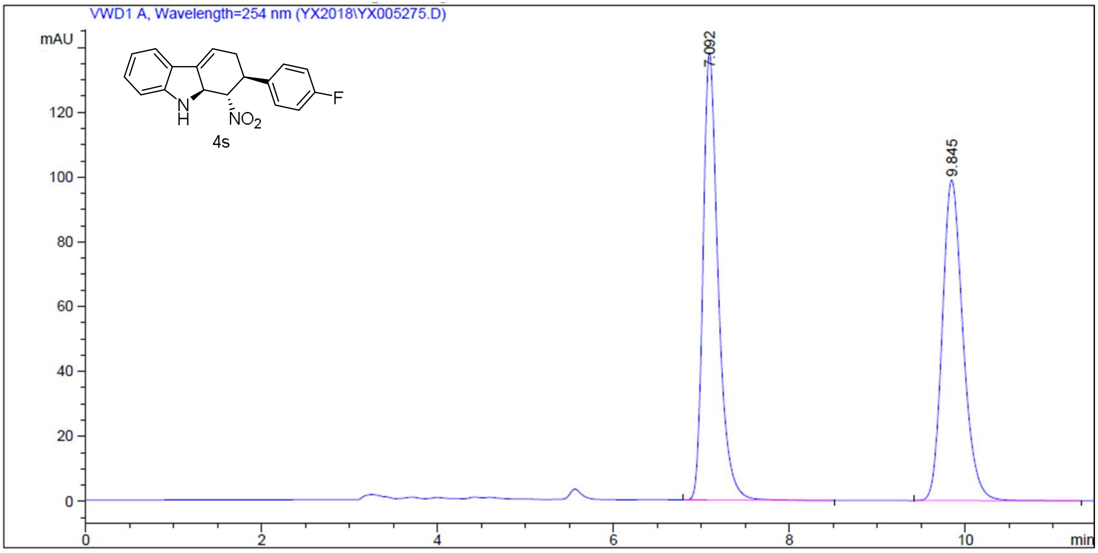
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.121	BV	0.1531	5025.46533	496.30371	93.7525
2	7.833	BB	0.1808	334.88907	27.89371	6.2475



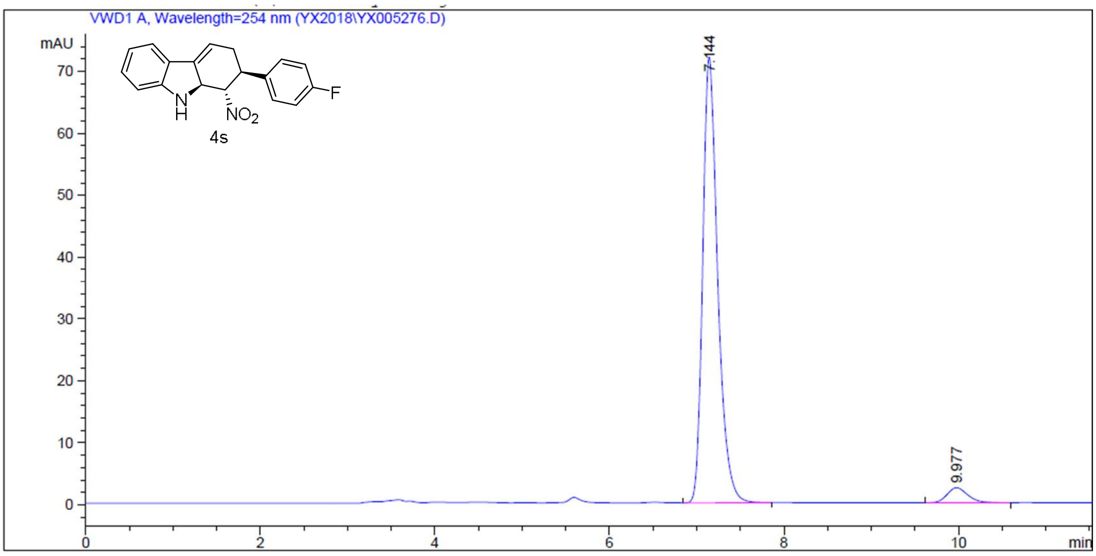
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.087	VB	0.1580	1589.80847	150.68513	51.1211
2	8.387	BB	0.1984	1520.07678	116.84438	48.8789



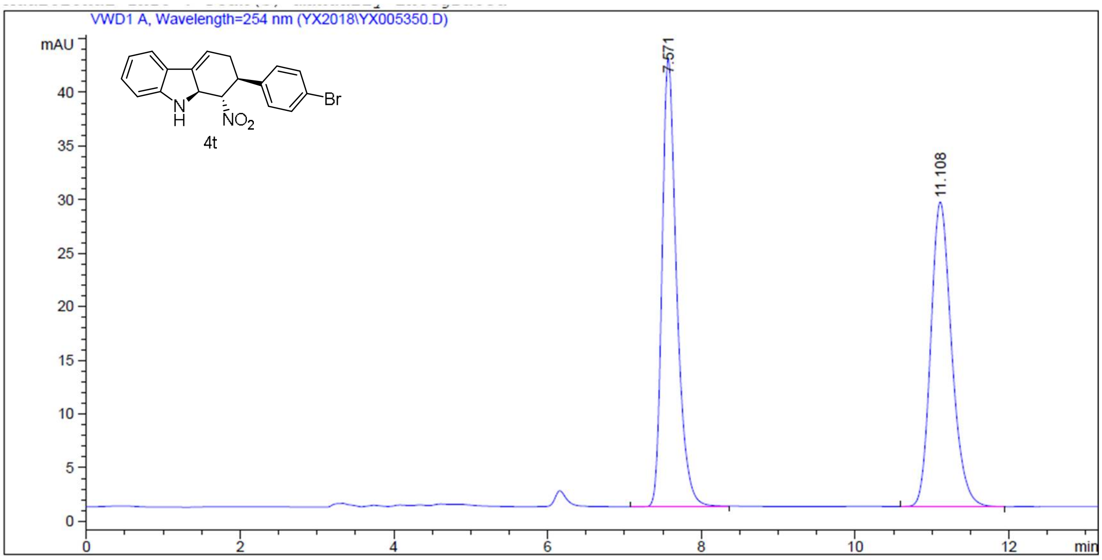
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.087	VV	0.1620	5447.03760	500.31613	95.1859
2	8.390	BB	0.2024	275.49011	20.63382	4.8141



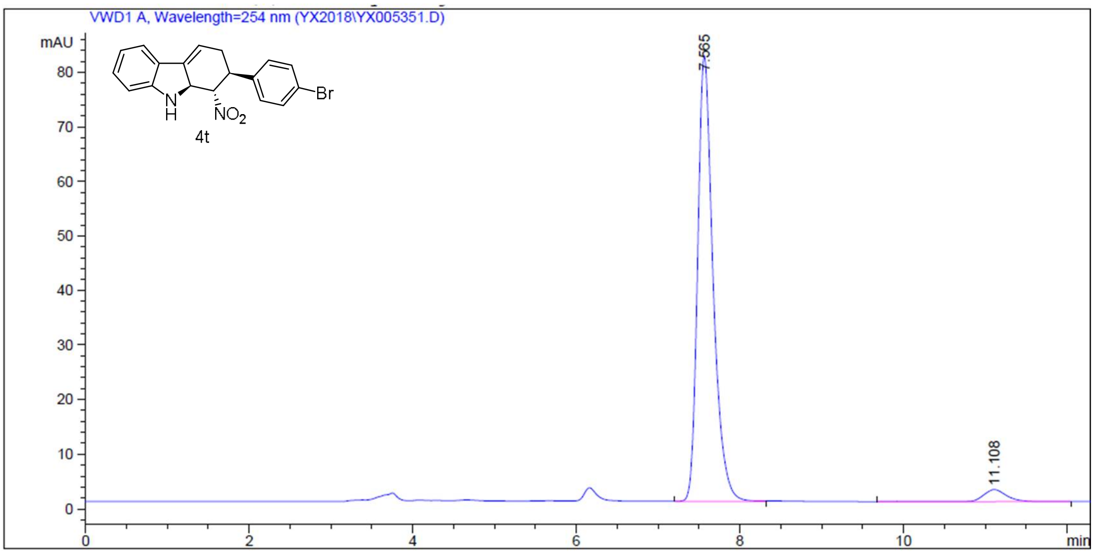
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.092	BB	0.1806	1648.42505	137.51622	50.5661
2	9.845	BBA	0.2487	1611.51367	98.69177	49.4339



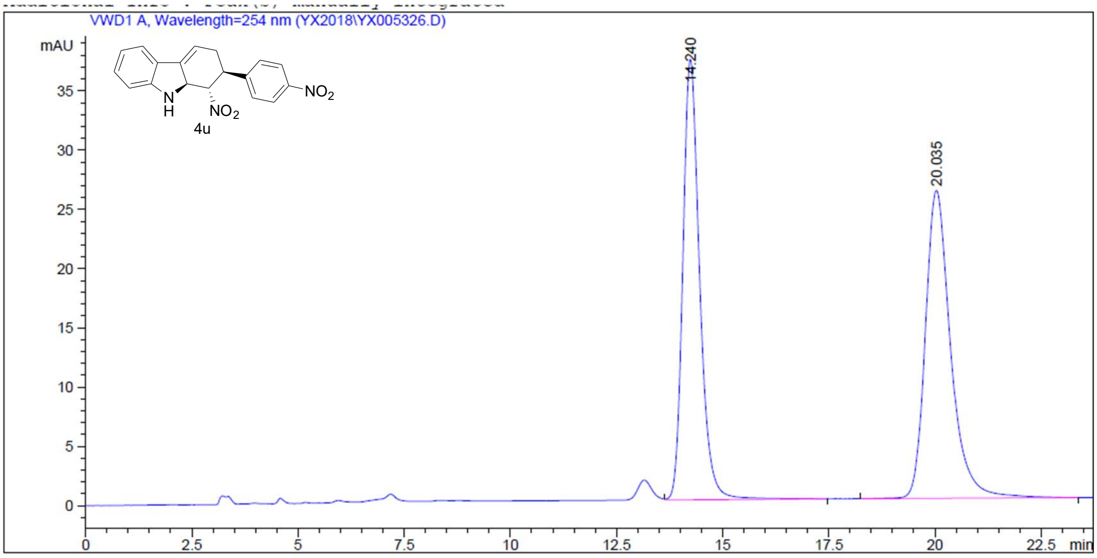
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.144	BV	0.1865	859.29773	71.67496	95.5835
2	9.977	BB	0.2498	39.70409	2.41793	4.4165



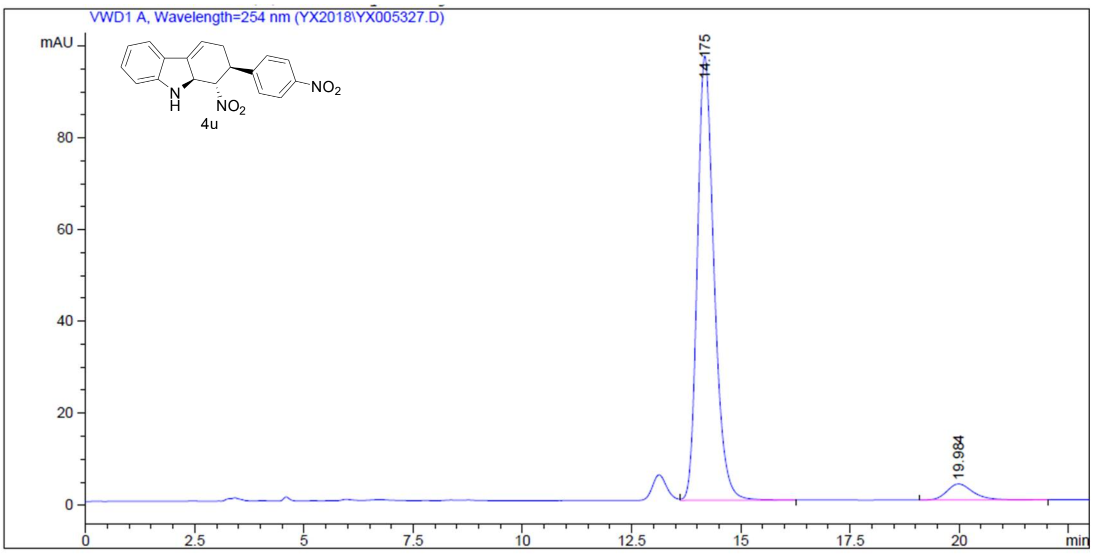
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.571	BV	0.2014	552.28070	41.63106	50.7018
2	11.108	VB	0.2907	536.99127	28.37760	49.2982



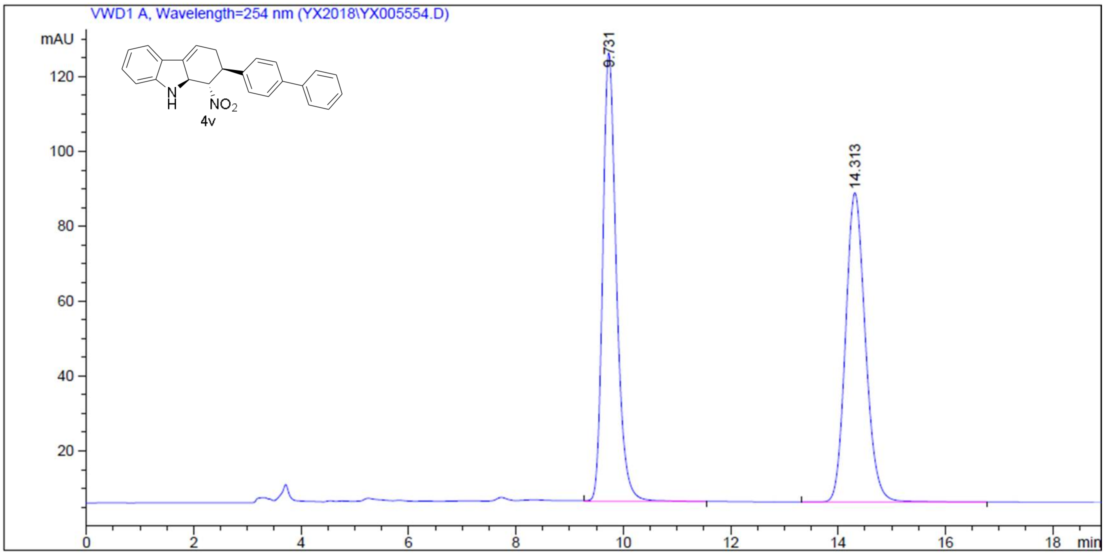
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.565	VV	0.1998	1069.65564	81.47628	96.0519
2	11.108	BB	0.3033	43.96646	2.19796	3.9481



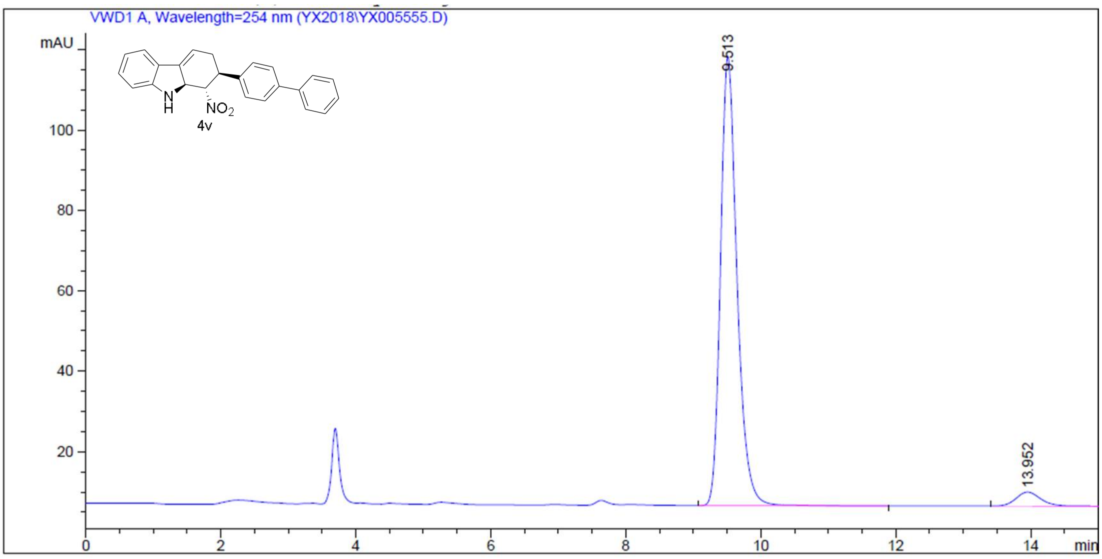
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.240	VB	0.4201	1022.48273	37.15171	48.7341
2	20.035	BB	0.6225	1075.60339	25.99386	51.2659



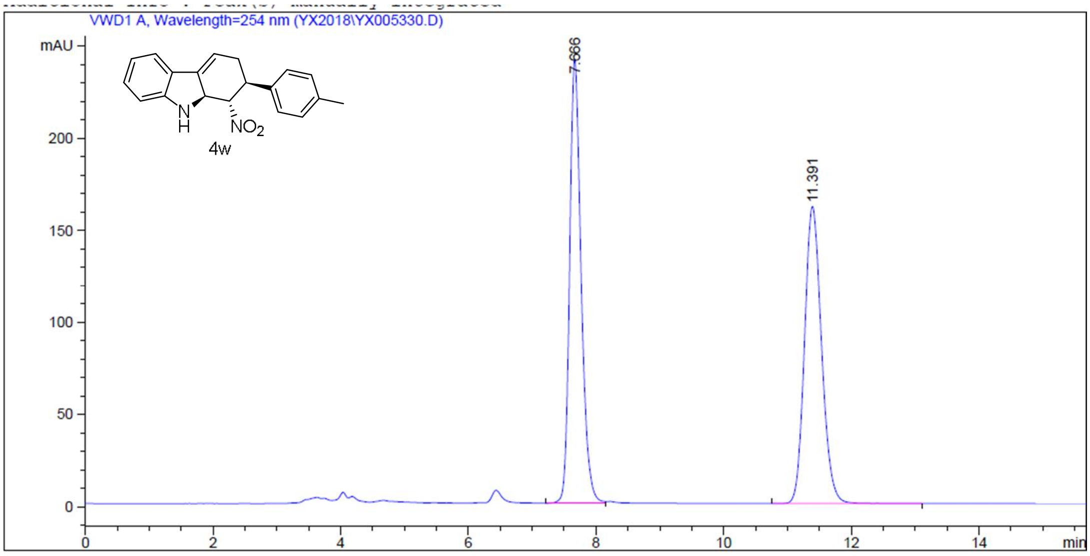
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.175	VB	0.4098	2576.53101	96.72379	94.7086
2	19.984	BB	0.6235	143.95029	3.47157	5.2914



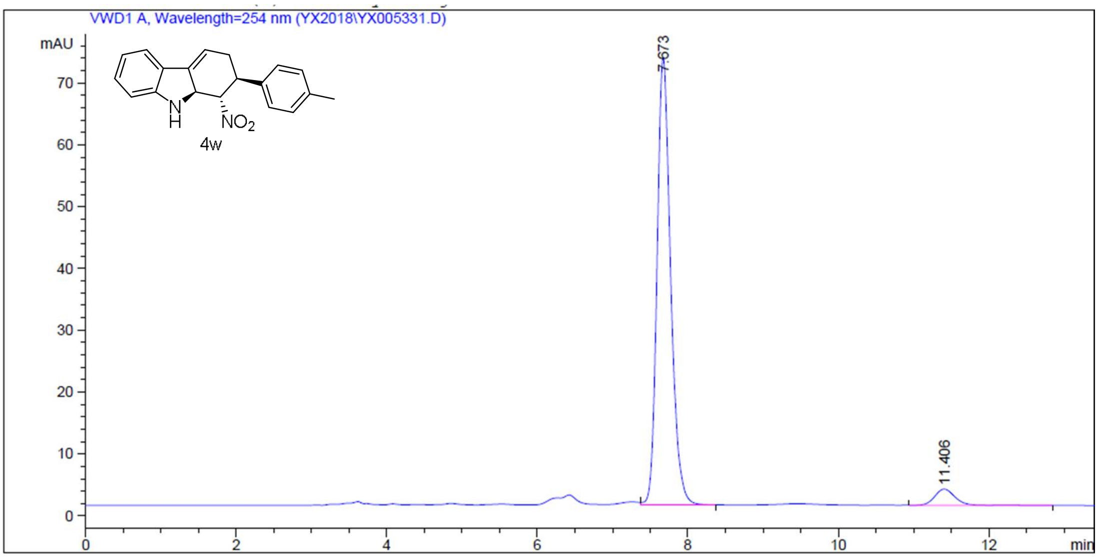
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.731	VB	0.2708	2118.35596	119.56272	50.1420
2	14.313	BV	0.3969	2106.36157	82.48332	49.8580



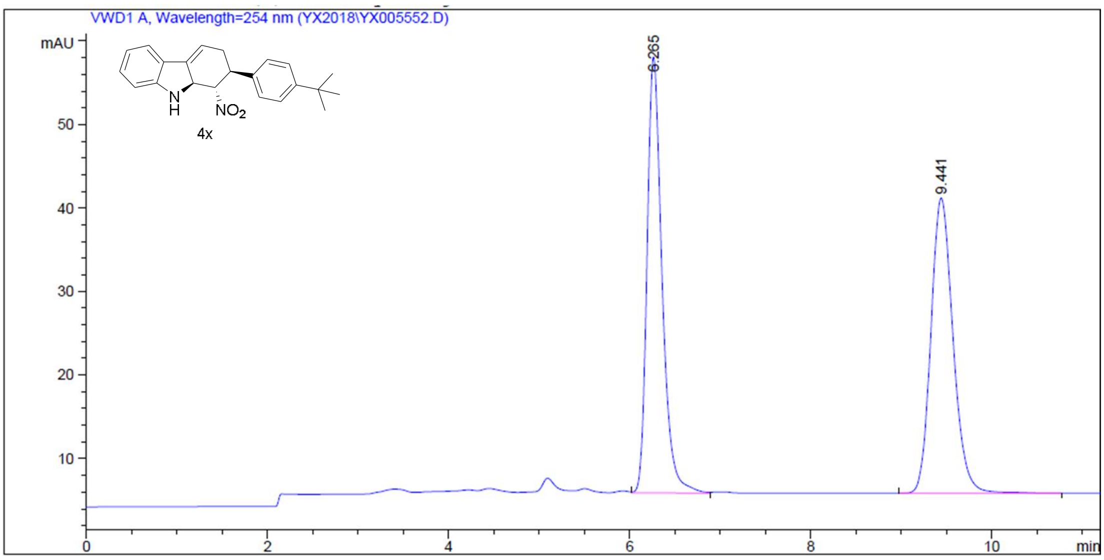
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.513	BB	0.2565	1893.27917	111.41103	95.6271
2	13.952	VBA	0.3858	86.57780	3.45243	4.3729



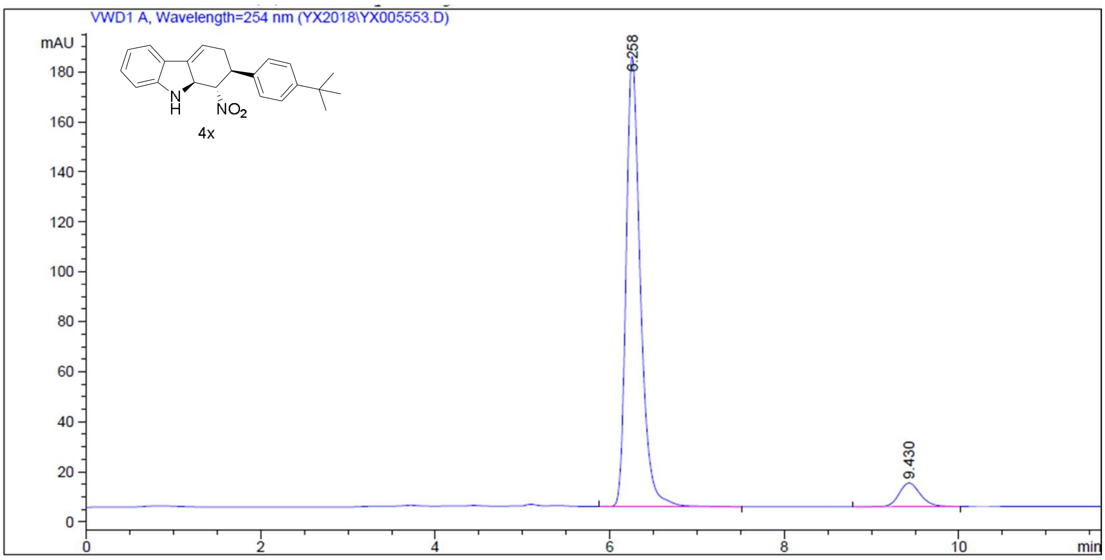
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.666	BV	0.1932	3017.78564	240.15654	50.2819
2	11.391	BV	0.2859	2983.94580	161.16211	49.7181



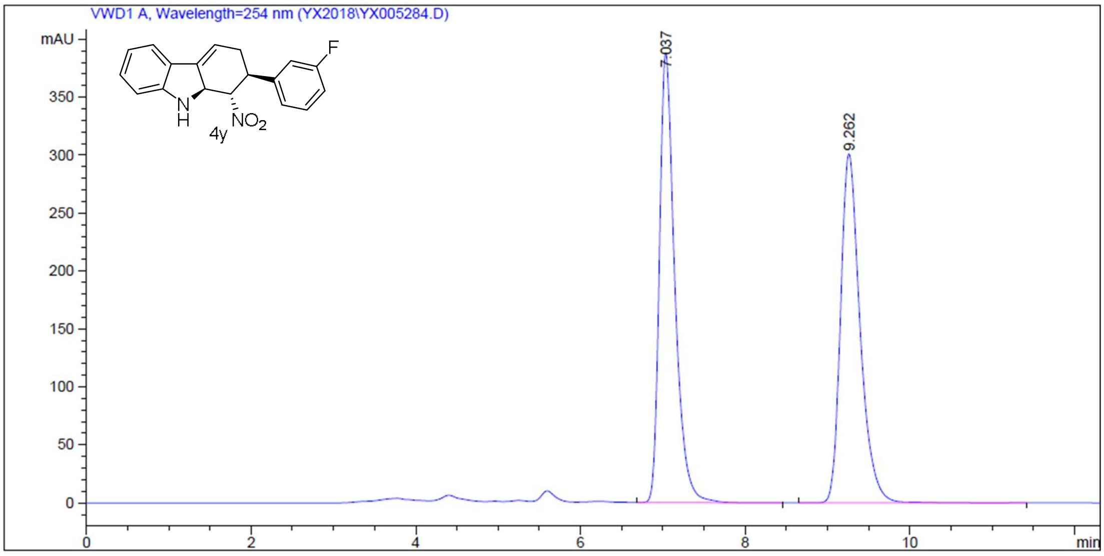
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.673	VB	0.1932	906.40607	72.14899	94.8247
2	11.406	VB	0.2901	49.46930	2.62038	5.1753



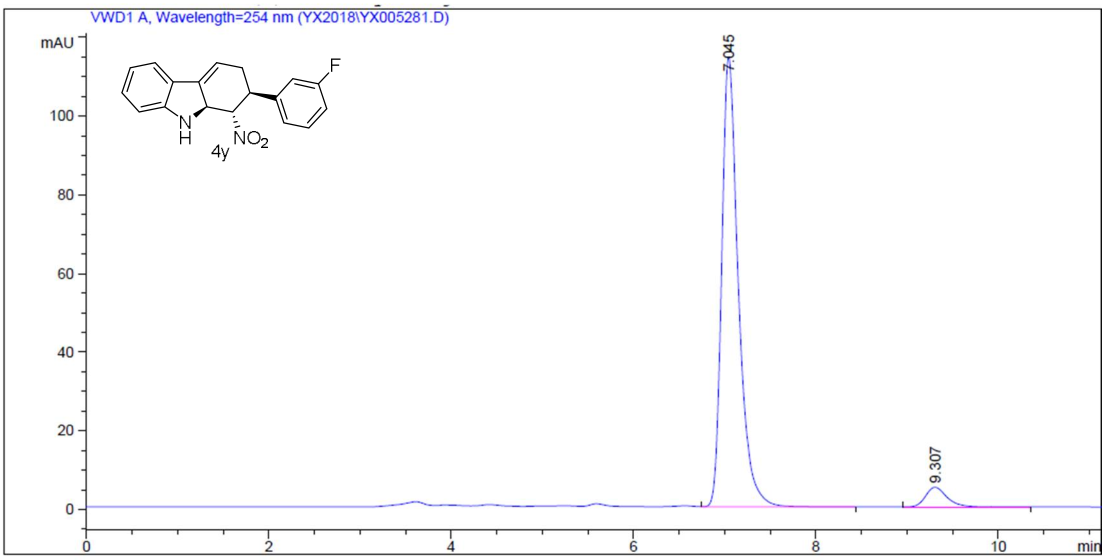
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.265	VV	0.1748	597.99072	52.06849	49.9610
2	9.441	BB	0.2620	598.92395	35.29411	50.0390



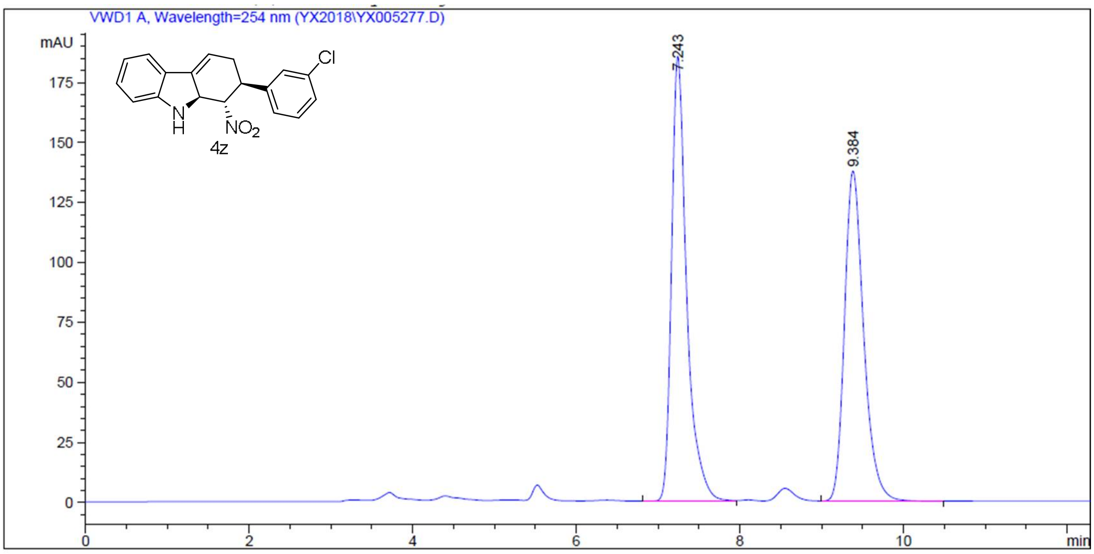
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.258	BB	0.1735	2040.70081	179.33725	92.7802
2	9.430	BV	0.2614	158.80017	9.38623	7.2198



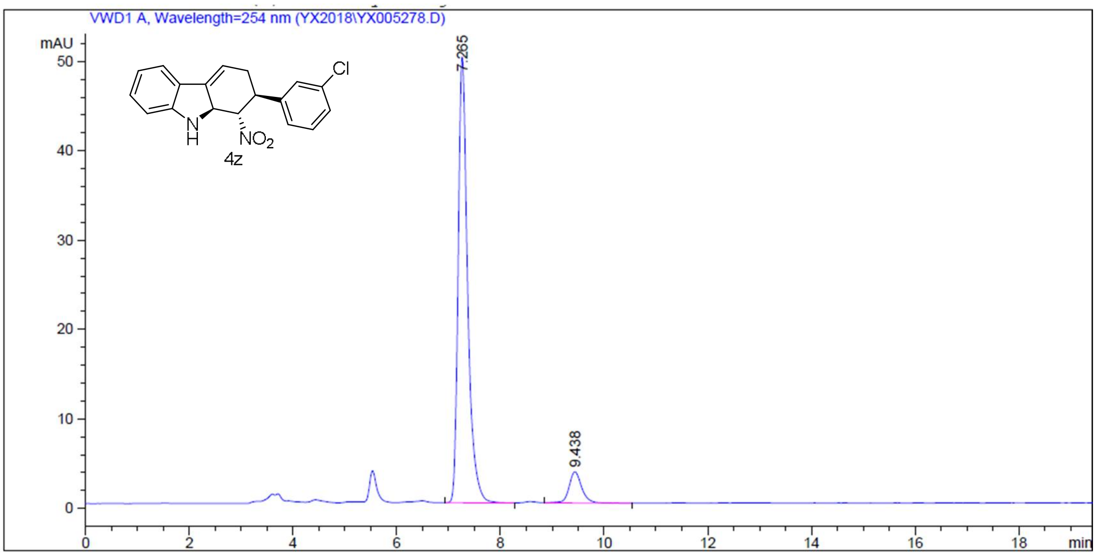
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.037	BB	0.1918	5011.87500	387.17892	50.3390
2	9.262	BB	0.2502	4944.37988	300.44217	49.6610



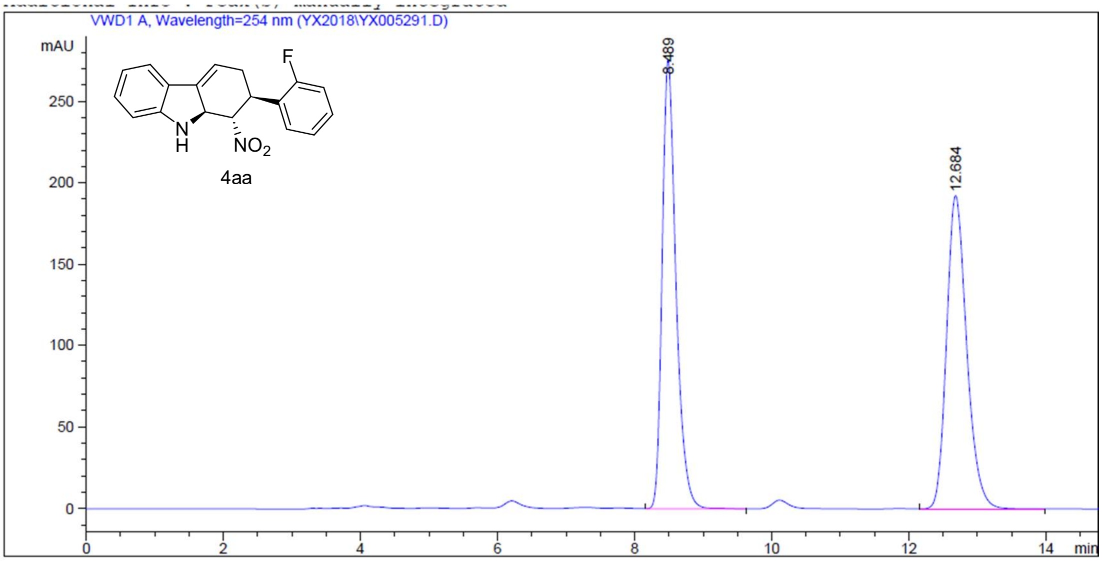
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.045	VB	0.1950	1447.99634	113.86707	94.6481
2	9.307	BB	0.2493	81.87668	5.00009	5.3519



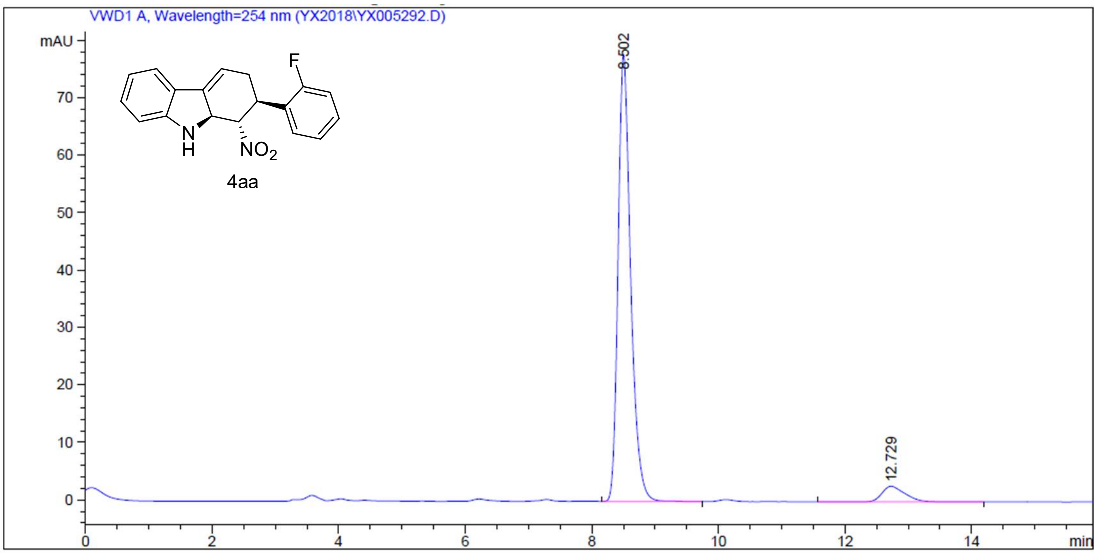
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.243	BV	0.1971	2381.98511	184.61162	51.5634
2	9.384	BV	0.2483	2237.54565	137.33449	48.4366



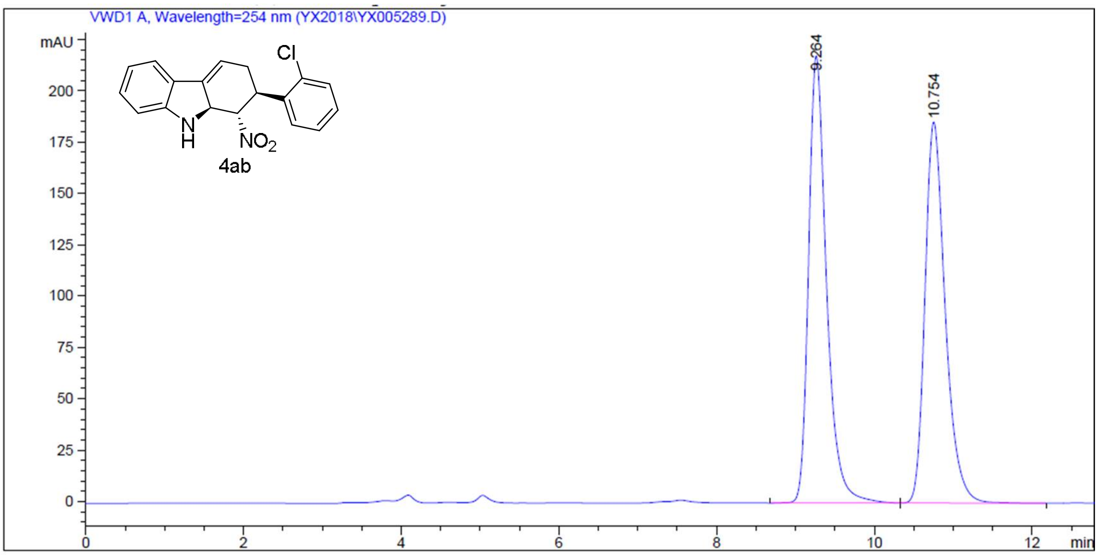
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.265	VB	0.1947	631.24097	49.70780	91.3869
2	9.438	VB	0.2573	59.49350	3.48763	8.6131



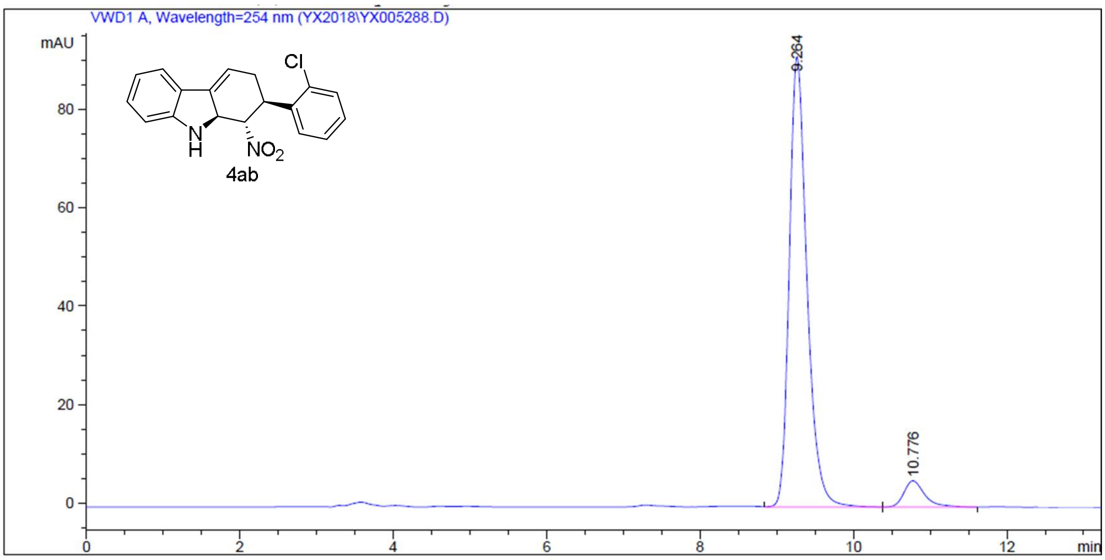
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.489	BB	0.2159	3850.89111	274.84183	49.5144
2	12.684	VV	0.3141	3926.42798	192.17195	50.4856



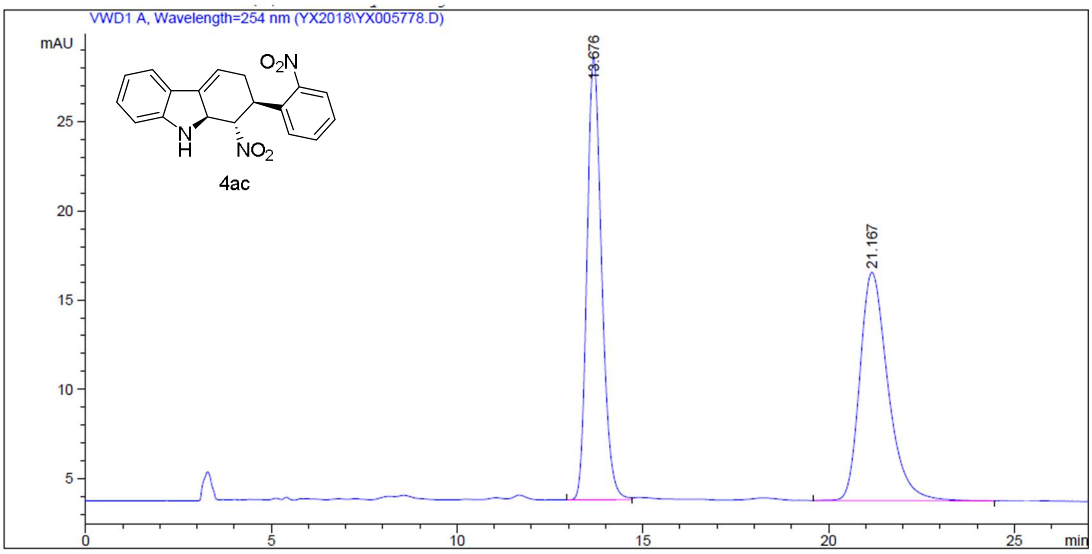
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.502	VV	0.2088	1077.44446	77.49831	94.0149
2	12.729	BB	0.3711	68.59143	2.70910	5.9851



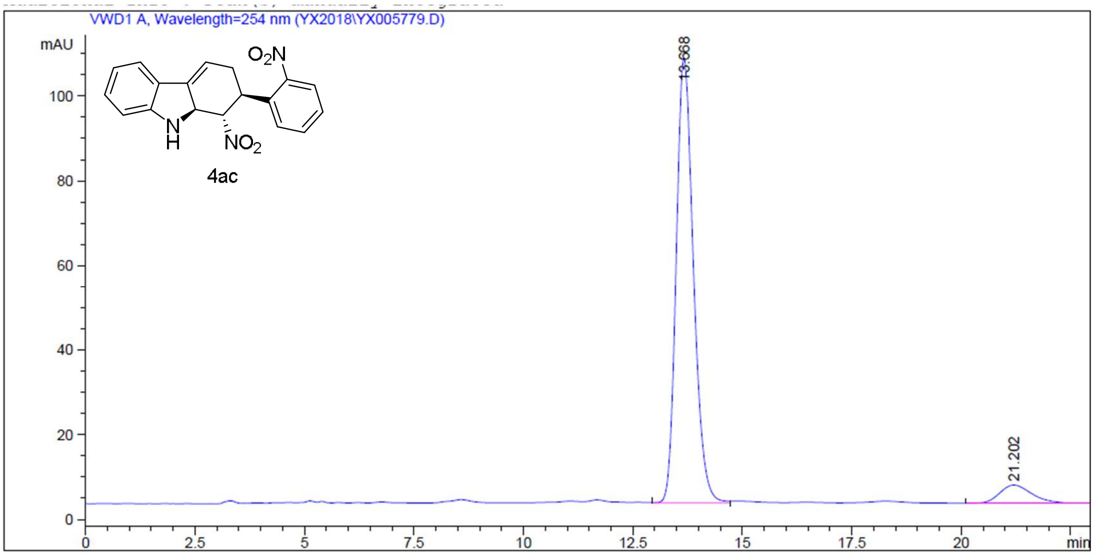
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.264	BB	0.2371	3436.93164	217.12454	50.9541
2	10.754	BB	0.2784	3308.22339	185.05940	49.0459



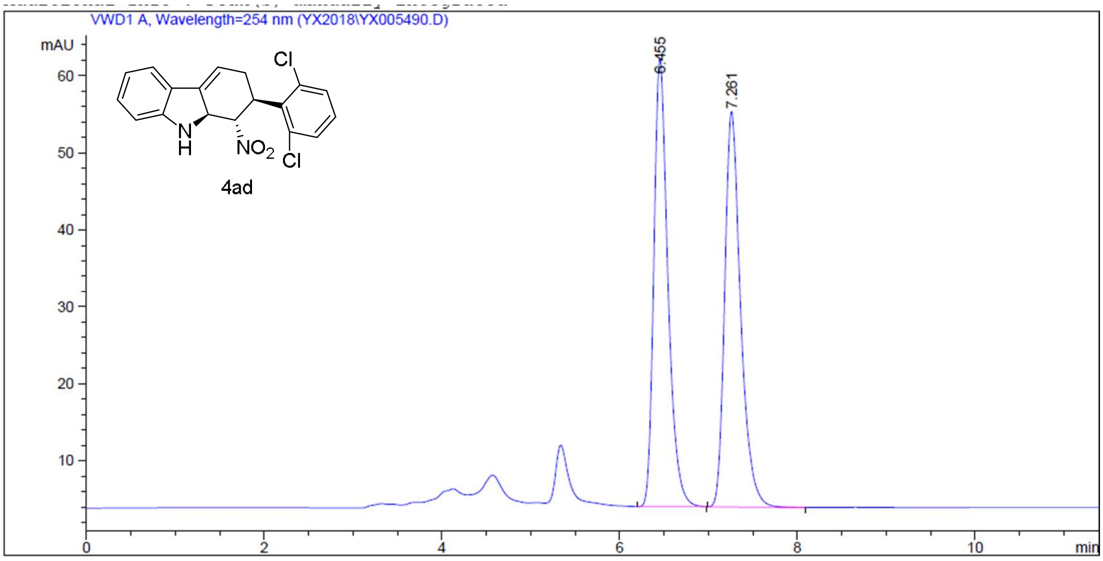
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.264	VB	0.2449	1459.29480	91.22594	93.5984
2	10.776	BB	0.2897	99.80772	5.29839	6.4016



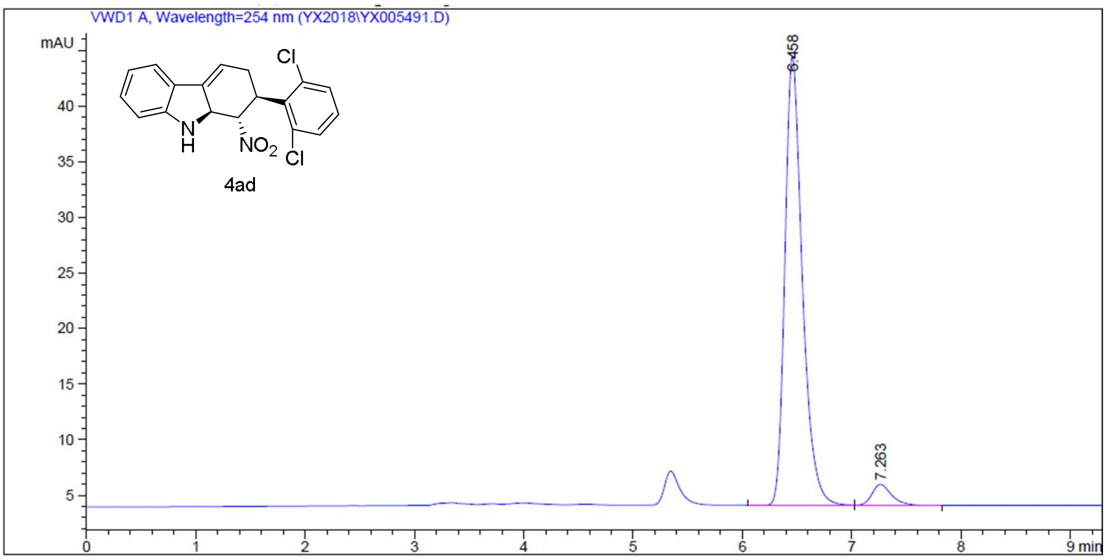
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.676	BV	0.4194	681.29645	24.80646	50.3482
2	21.167	BB	0.8051	671.87286	12.78992	49.6518



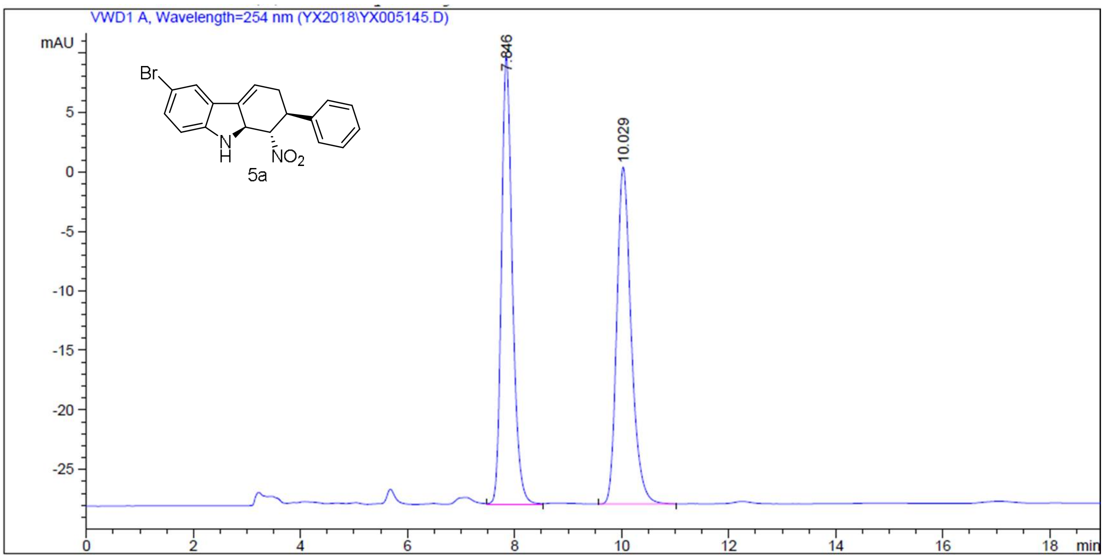
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.668	BV	0.4239	2869.64575	104.92857	92.8210
2	21.202	BBA	0.8057	221.94572	4.30242	7.1790



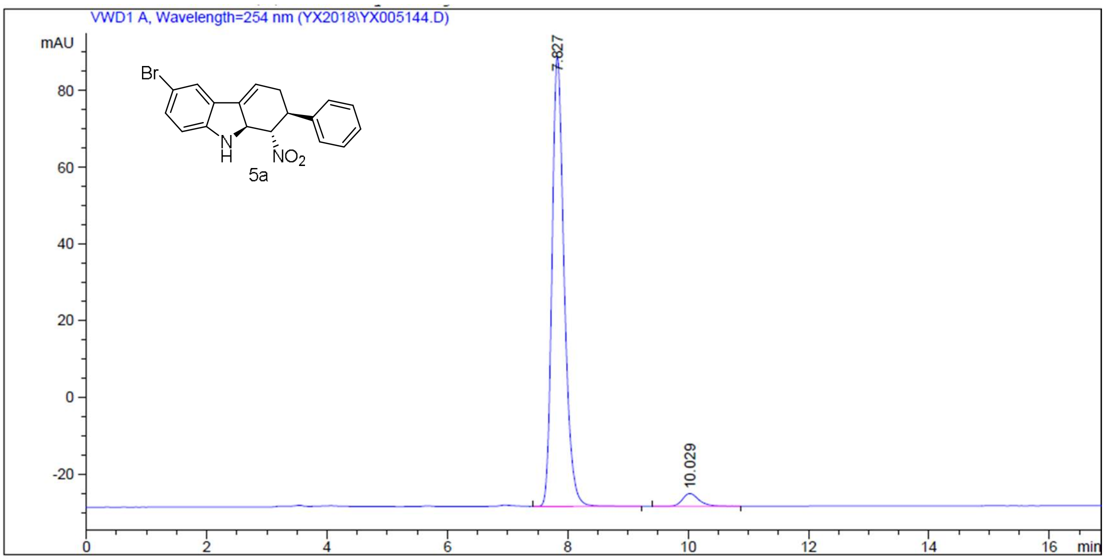
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.455	BB	0.1696	640.26984	57.98511	50.0045
2	7.261	BB	0.1926	640.15344	51.14673	49.9955



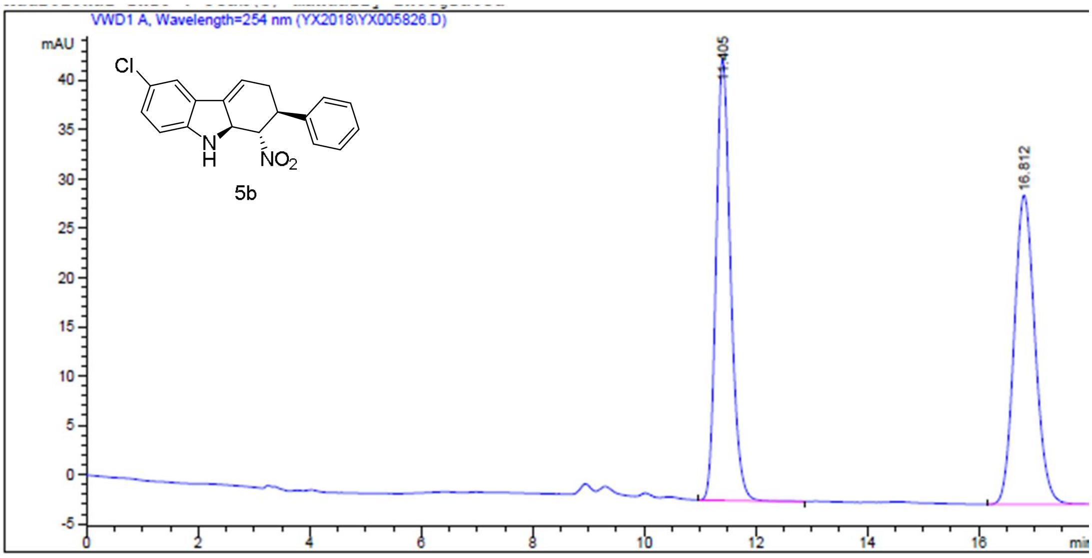
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.458	BV	0.1703	446.99359	40.25139	94.9695
2	7.263	VB	0.1933	23.67720	1.88316	5.0305



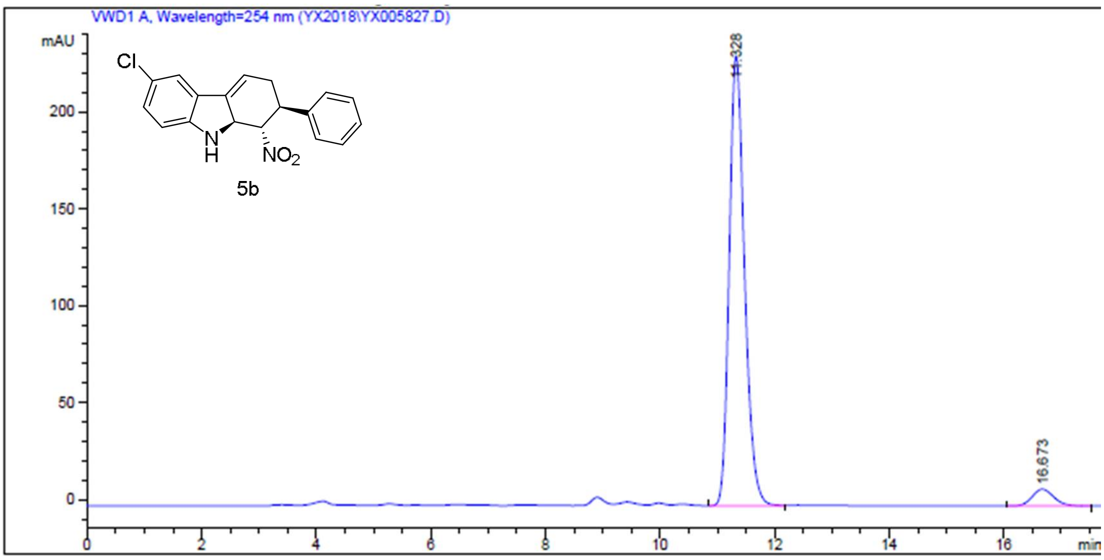
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.846	VV	0.2183	533.16028	37.49148	50.1289
2	10.029	BB	0.2830	530.41931	28.26546	49.8711



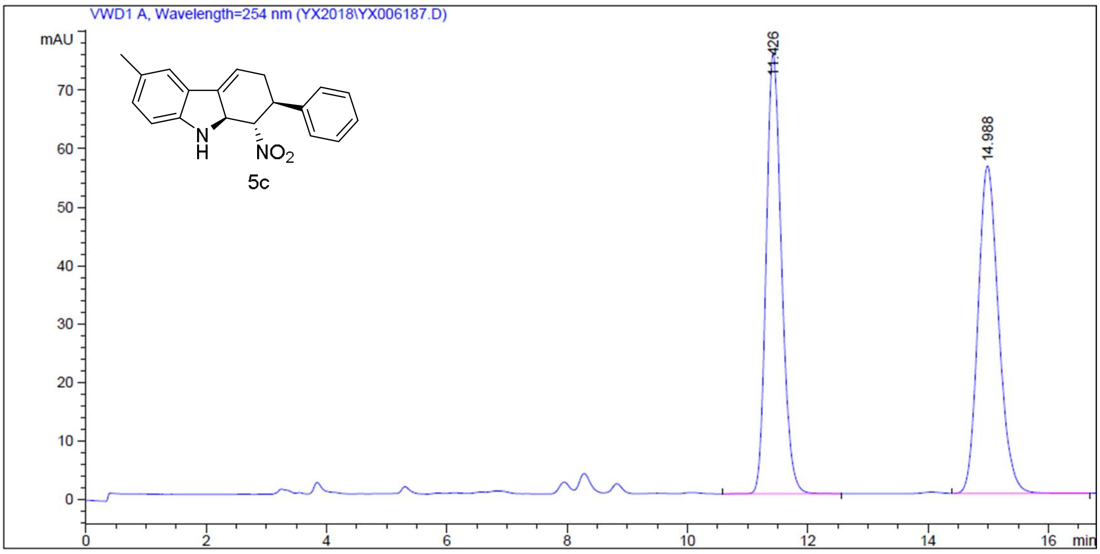
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.827	VB	0.2163	1642.26294	116.87894	96.3455
2	10.029	BB	0.2838	62.29224	3.30742	3.6545



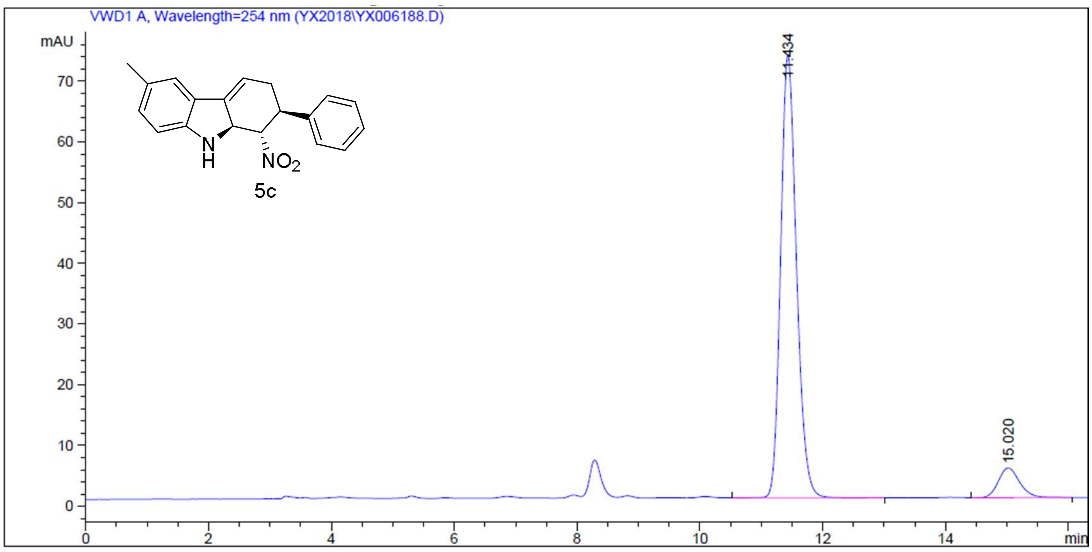
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.405	BV	0.2758	812.12134	44.75503	49.9446
2	16.812	BBA	0.4077	813.92273	31.35397	50.0554



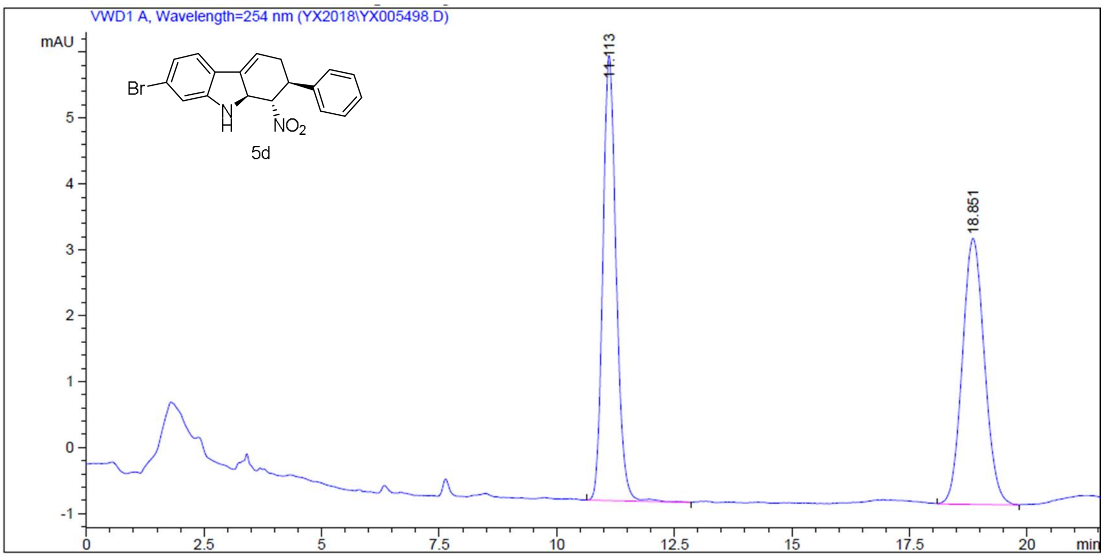
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.328	BV	0.2804	4296.08252	231.67859	95.0467
2	16.673	VB	0.4076	223.88710	8.62644	4.9533



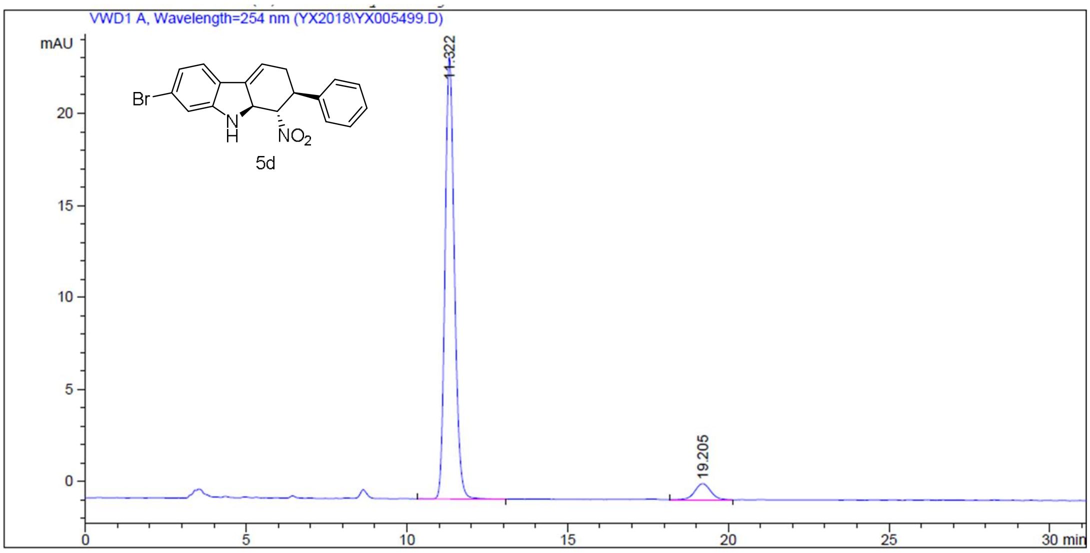
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.426	BB	0.2708	1332.21167	75.19160	49.9892
2	14.988	VB	0.3711	1332.78723	55.94923	50.0108



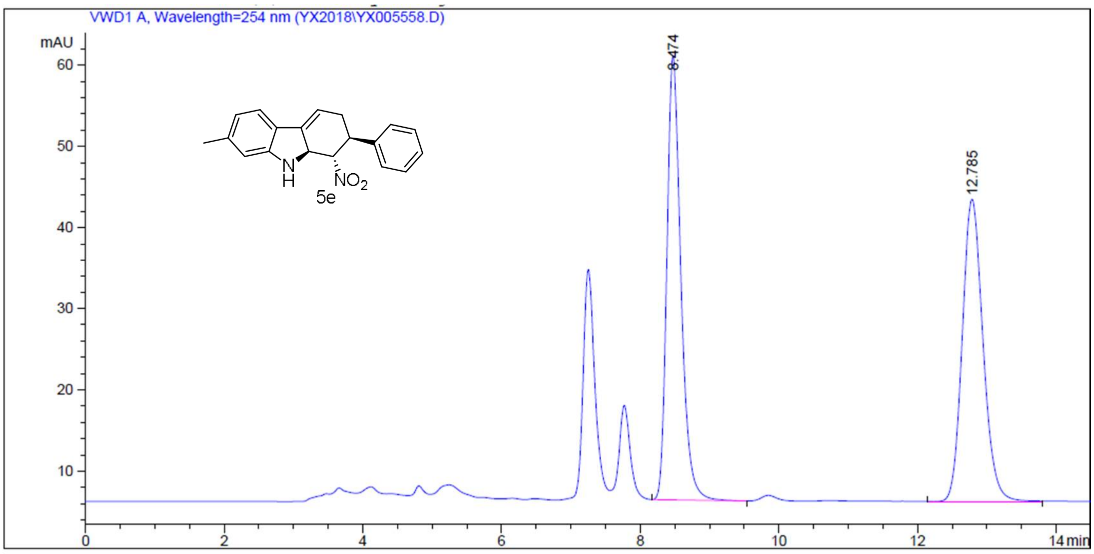
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.434	VB	0.2792	1306.89563	72.84361	91.7821
2	15.020	VB	0.3669	117.01516	4.88308	8.2179



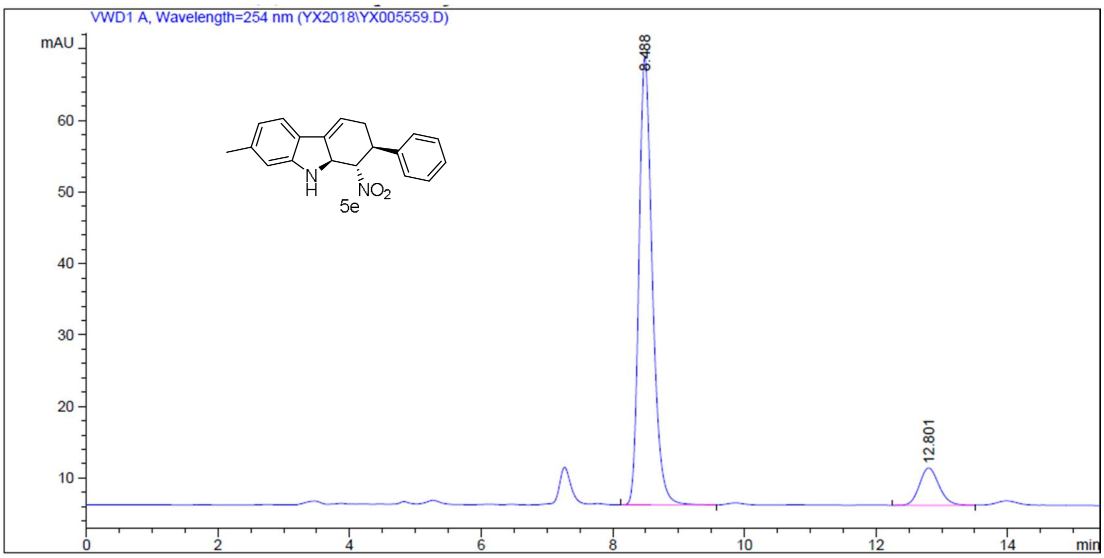
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.113	BB	0.3060	133.14662	6.74521	50.2809
2	18.851	VB	0.5087	131.65898	4.03568	49.7191



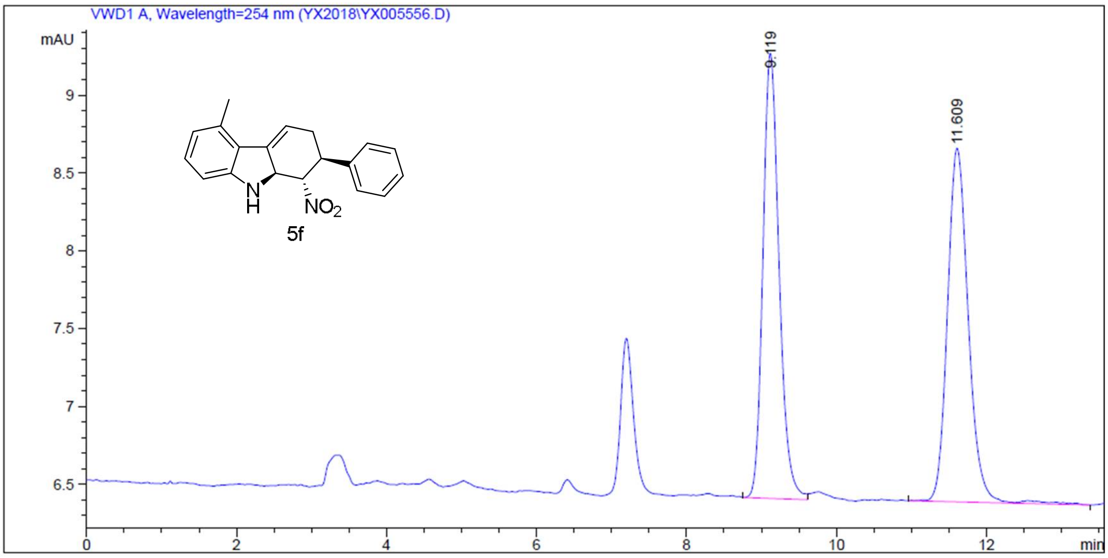
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.322	VB	0.3128	487.69174	23.99629	94.2064
2	19.205	BB	0.5289	29.99257	8.73139e-1	5.7936



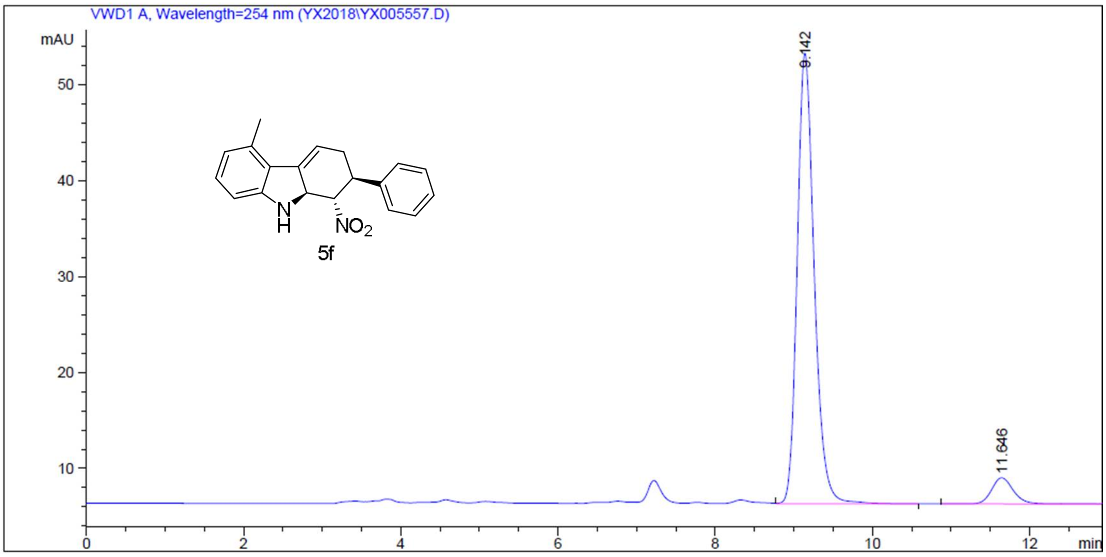
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.474	BB	0.2160	764.84943	54.54768	49.7762
2	12.785	BV	0.3179	771.72784	37.17810	50.2238



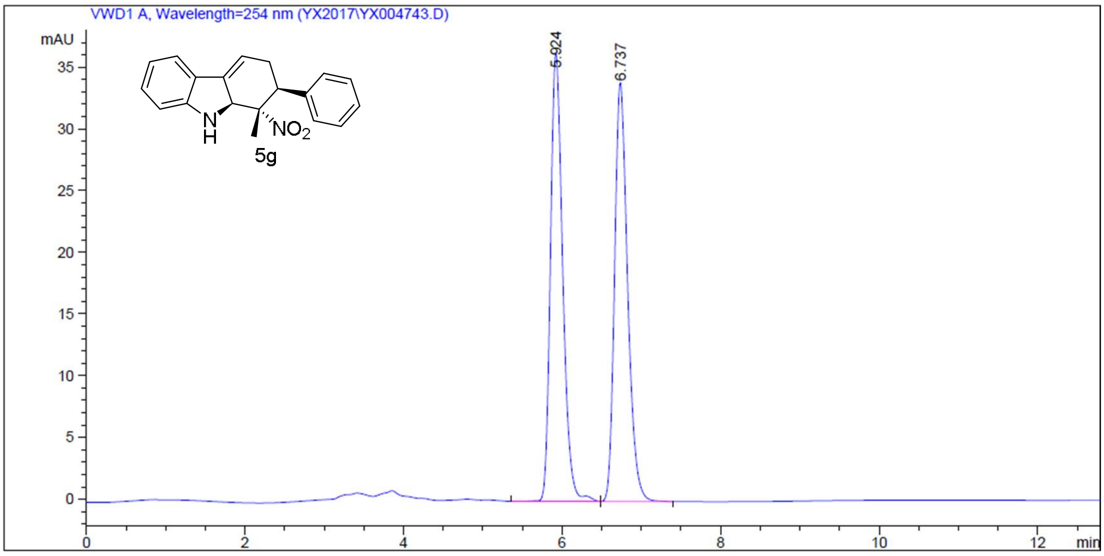
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.488	BV	0.2180	888.08527	62.56037	89.1513
2	12.801	BV	0.3176	108.07005	5.21172	10.8487



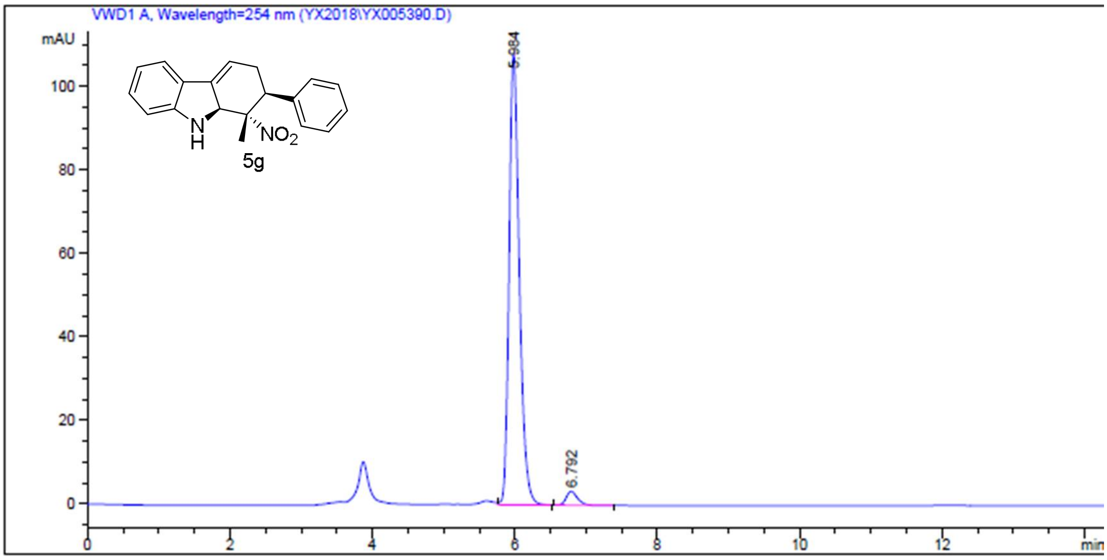
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.119	BV	0.2331	42.78351	2.85453	49.3054
2	11.609	BB	0.2962	43.98903	2.26785	50.6946



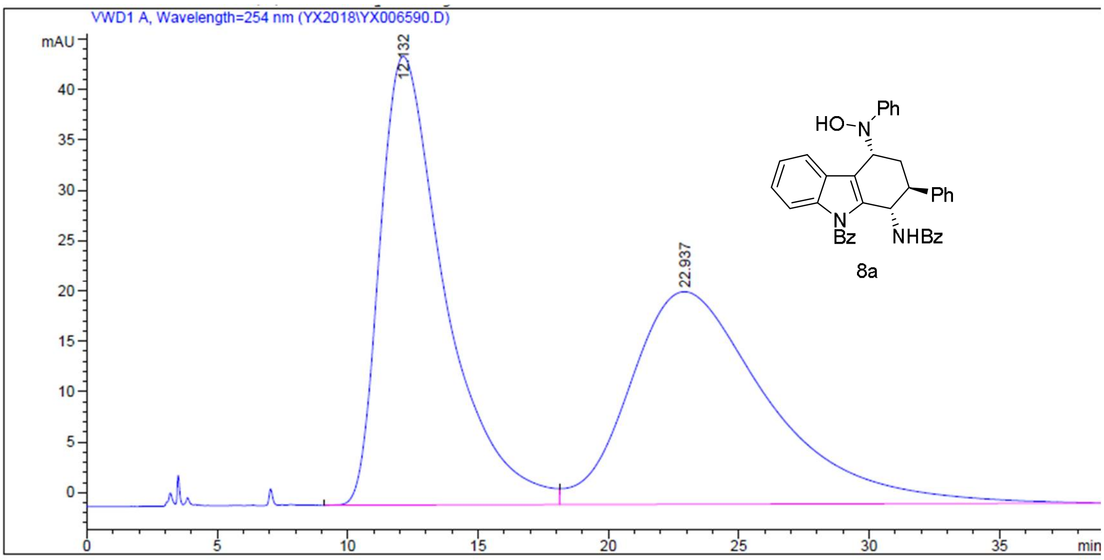
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.142	VB	0.2339	705.68335	46.86735	93.1278
2	11.646	BBA	0.2940	52.07436	2.71053	6.8722



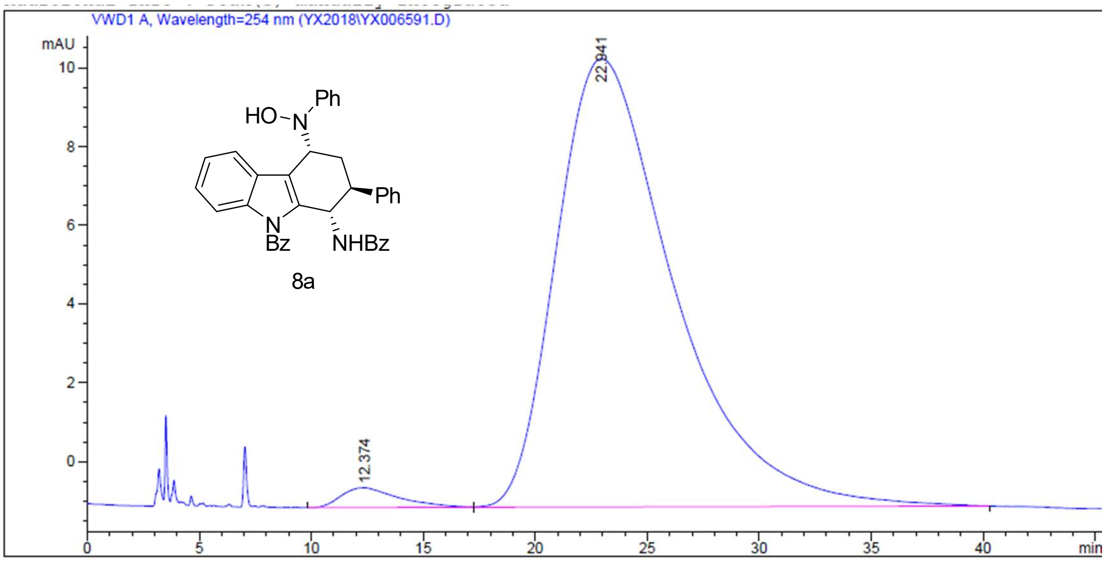
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.924	BB	0.1665	389.30106	36.13264	50.1468
2	6.737	BV	0.1803	387.02151	33.77393	49.8532



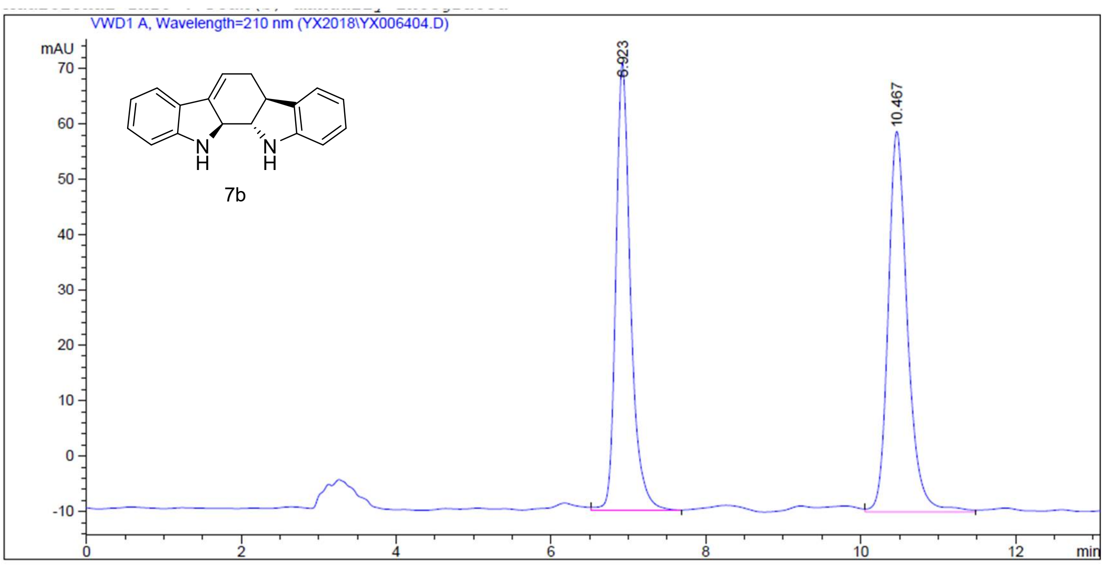
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.984	VB	0.1518	1076.57446	107.47665	96.7333
2	6.792	BB	0.1639	36.35611	3.28950	3.2667



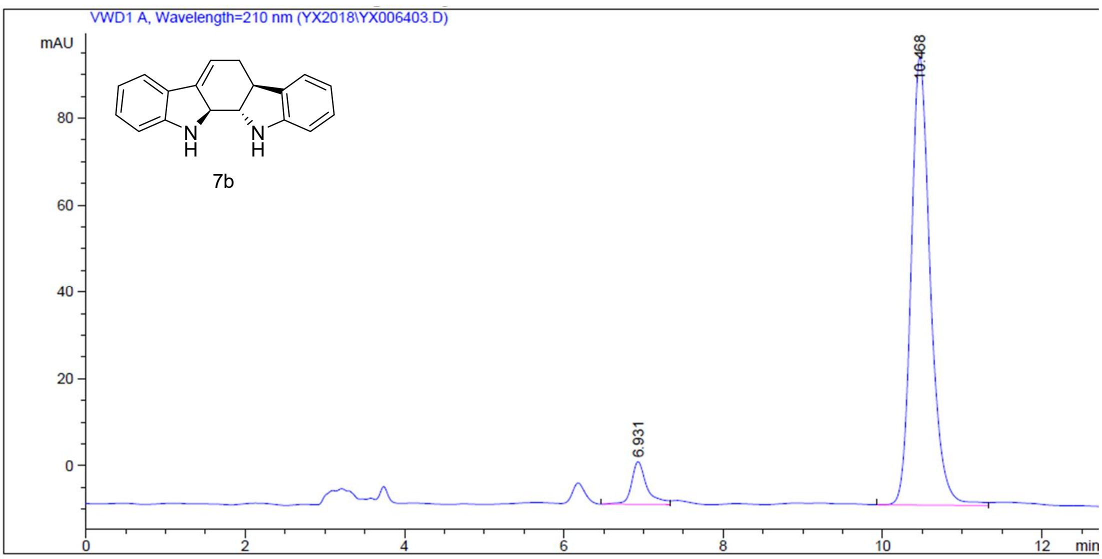
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.132	BV	2.6124	7745.98145	44.51629	49.7804
2	22.937	VBA	4.5998	7814.30859	21.04555	50.2196



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.374	BV	2.0948	89.63381	5.03399e-1	2.1068
2	22.941	VB	4.3013	4164.96484	11.37392	97.8932



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.923	VB	0.2008	1066.07410	80.65153	47.1140
2	10.467	VV	0.2617	1196.68127	68.60285	52.8860



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.931	BV	0.2037	131.68634	9.78059	7.0623
2	10.468	BV	0.2544	1732.94470	103.04939	92.9377