

**Bi(OAc)₃/Chiral Phosphoric Acid Catalyzed Enantioselective
Allylation of Seven-Membered Cyclic Imines Dibenzo[*b,f*][1,4]
oxazepines**

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Supporting Information

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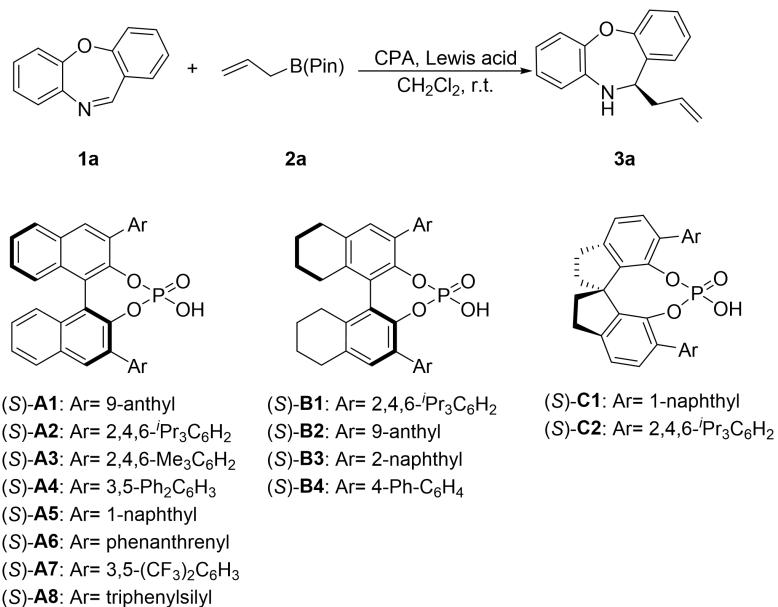
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1. General information

Chemicals reagents and solvents were purchased from commercial suppliers and used without further purification. ^1H NMR and ^{13}C NMR spectra were recorded on Brucker-400 (400 MHz for ^1H , 100MHz for ^{13}C)spectrometer, ^{19}F NMR were recorded on a Varian NMR 400 spectrometer. The chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard. The following abbreviations were used to designate chemical shift mutiplicities: s = singlet, d = doublet, t =triplet, q = quartet, m = multiplet. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m). HPLC analysis was performed using Chiralcel columns purchased. Mass spectra were obtained using electrospray ionization (ESI) mass spectrometer. ESI-MS studies on catalytic complex were conducted on Thermo LTQ XL. Seven-Membered Cyclic Imines (**1a-1r**) were prepared according to the reference.¹ Allylboronates (**2a-2d**) were obtained following the reported procedure.²

2. Optimization of reaction conditions

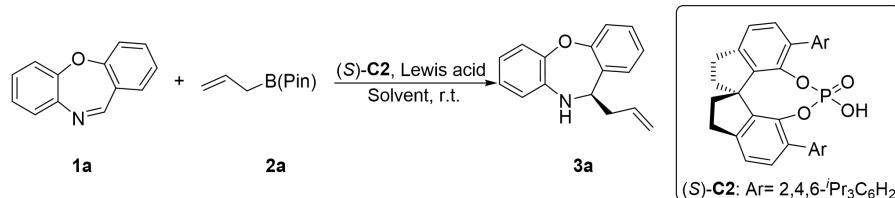
Table S1. Optimization of the catalysts



Entry ^a	CPA	Time (h)	Lewis acid	Yield (%) ^b	er (3a) ^c
1	A1	12	Bi(OAc) ₃	97	39:61
2	A2	12	Bi(OAc) ₃	98	23:77
3	A3	12	Bi(OAc) ₃	96	40:60
4	A4	12	Bi(OAc) ₃	98	39.5:60.5
5	A5	12	Bi(OAc) ₃	97	47.5:52.5
6	A6	12	Bi(OAc) ₃	98	45:55
7	A7	12	Bi(OAc) ₃	98	49:51
8	A8	12	Bi(OAc) ₃	99	0
9	B1	12	Bi(OAc) ₃	98	30:70
10	B2	12	Bi(OAc) ₃	96	14:86
11	B3	12	Bi(OAc) ₃	85	45.5:54.5
12	B4	12	Bi(OAc) ₃	98	45.5:54.5
13	C1	12	Bi(OAc) ₃	97	53.5:46.5
14	C2	12	Bi(OAc) ₃	98	93:7

^a The reaction was carried out with **1a** (0.1 mmol), **2a** (0.12 mmol), CPA (0.03 equiv), lewis acid (0.03 equiv) and solvent (1.0 mL) at rt. ^b Isolated yield. ^c Determined by HPLC analysis.

Table S2. Optimization of the solvents and lewis acids

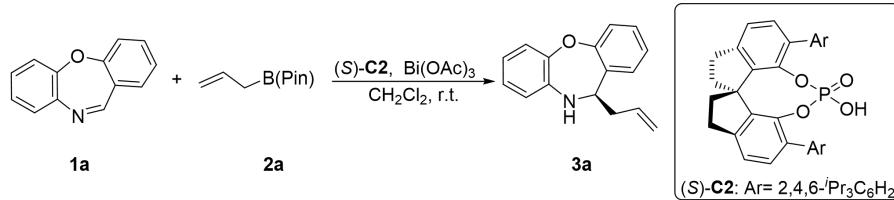


Entry ^a	Lewis acid	Time (h)	Solvent	Yield (%) ^b	er (3a) ^c
1	Bi(OAc) ₃	12	CH ₂ Cl ₂	98	93:7

2	Bi(OAc) ₃	12	Toluene	98	90.5:9.5
3	Bi(OAc) ₃	12	EA	98	92.5:7.5
4	Bi(OAc) ₃	12	MTBE	33	90:10
5	Bi(OAc) ₃	12	THF	55	58.5:41.5
6	Bi(OAc) ₃	12	DCE	97	89.5:10.5
7	Bi(OAc) ₃	12	1,4-Dioxane	96	70.5:29.5
8	Bi(OAc) ₃	12	Cyclohexane	84	58.5:41.5
9	BiCl ₃	12	CH ₂ Cl ₂	65	0
10	BiBr ₃	12	CH ₂ Cl ₂	46	0
11	Bi(OTf) ₃	12	CH ₂ Cl ₂	98	0
12	Bi(OH) ₃	12	CH ₂ Cl ₂	46	61.5:38.5
13	AgOAc	12	CH ₂ Cl ₂	98	56:44

^aThe reaction was carried out with **1a** (0.1 mmol), **2a** (0.12 mmol), CPA (0.03 equiv), lewis acid (0.03 equiv) and solvent (1.0 mL) at rt. ^bIsolated yield. ^cDetermined by HPLC analysis.

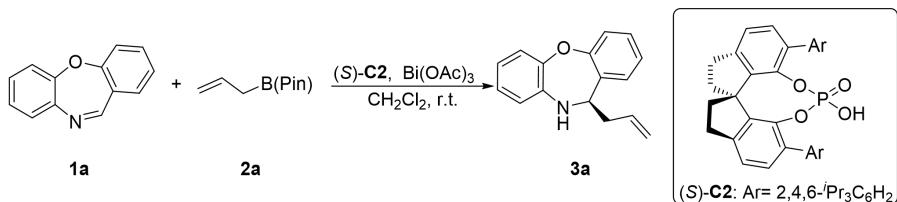
Table S3. Optimization of the additive, catalyst loading and solvent volume.



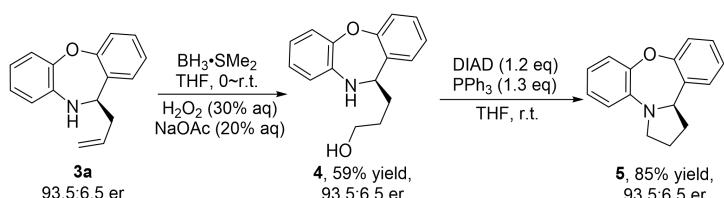
Entry ^a	Additive (20 mg)	Time (h)	Yield (%) ^b	er (3a) ^c
1	3 Å Ms	12	98	91:9
2	4 Å Ms	12	97	60:40
3	5 Å Ms	12	66	75.5:24.5
4	NaBARF	12	93	59.5:40.5
5	Ethylene glycol	12	82	72:28
6 ^d	-	12	98	83.5:16.5
7 ^e	-	12	97	90.5:9.5
8 ^f	-	12	98	90:10
9 ^g	-	12	98	95:5
10 ^h	-	12	98	95.5:4.5

^a The reaction was carried out with **1a** (0.1 mmol), **2a** (0.12 mmol), CPA (0.03 equiv), lewis acid (0.03 equiv) and CH₂Cl₂ (1.0 mL) at rt. ^b Isolated yield. ^c Determined by HPLC analysis. ^d 2 mol% catalyst loading. ^e 5 mol% catalyst loading. ^f CPA/lewis acid = 2:1. ^g CH₂Cl₂ = 2 mL. ^h CH₂Cl₂ = 3 mL.

3. General procedure for the synthesis of **3a**, **5**, **7**, **10** and **11**.

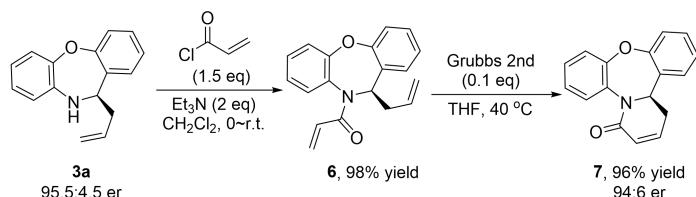


To an oven-dried reaction tube under nitrogen atmosphere, chiral phosphoric acid (S)-C2 (0.003 mmol, 2.2 mg), Bi(OAc)₃ (0.003 mmol, 1.2 mg) were dissolved in anhydrous CH₂Cl₂ (3 mL). Then the corresponding **1a** (0.1 mmol, 19.5 mg) and **2a** (0.12 mmol, 22.5 uL) were added. The mixture was stirred at rt for 12 h. The reaction mixture was purified directly by flash chromatography on silica gel PE/EA (20/1 to 15/1) to give the product **3a**.



To a stirred solution of compound **3a** (50.0 mg, 0.21 mmol, 87% *ee*) in dry THF (2.0 mL), BH₃·SMe₂ (0.5 M in THF, 50 uL, 0.63 mmol) was added at 0 °C. The mixture was warmed to room temperature and stirred for 5 h. H₂O₂ (30%, 1.1 mL) and NaOAc (20%, 1.4 mL) were added in order at 0 °C. And the resulting mixture was stirred for 3 h at room temperature. The aqueous layer was extracted with EtOAc (5 mL × 3), and the combined organic layers were dried over anhydrous Na₂SO₄. After filtered and evaporation, the crude mixture was purified by silica gel column chromatography PE/EA (2/1 to 1/1) to give compound **4** as colourless oil (30.0 mg, 59% yield, 93.5:6.5 er).

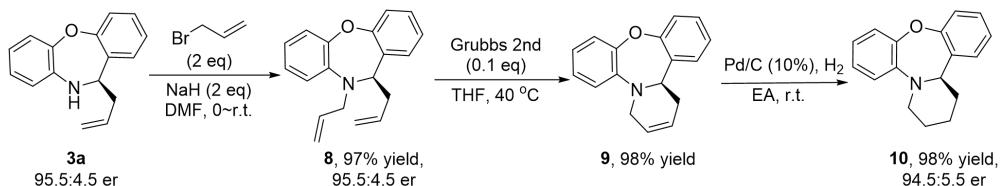
To a stirred solution of compound **4** (67.1 mg, 0.26 mmol) and Ph₃P (89.2 mg, 0.34 mmol) in DCM (2 mL) at 0 °C was added a solution of DIAD (63.1 mg, 0.31 mmol) in DCM (2 mL). The resulting mixture was warmed to room temperature slowly, and then stirred overnight. The reaction was quenched with EtOH (1 mL) and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography PE/EA (20/1 to 15/1) to afford compound **5** as colourless oil (57.0 mg, 85% yield, 93.5:6.5 er).



Acryloylchlorid (38.8 uL, 0.48 mmol, 91% *ee*) was dissolved in dry DCM (2 mL), compound **3a** (92.6 mg, 0.4 mmol) and triethylamine (66.7 uL, 0.48 mmol) was added. After 2 hours, 2 ml of H₂O was added to the reaction mixture. Organic layer was washed with water (2 × 10 mL) and the remained organic layer was dried over anhydrate Na₂SO₄, evaporated under reduced pressure to provide compound **6** as white solid (114.0 mg, 98% yield).

A mixture of compound **6** (45.0 mg, 0.15 mmol) and Grubbs 2nd (12.7 mg, 0.015 mmol) in THF (3.0 mL) was stirred at 40 °C for 0.5 h. After cooling to room temperature, the crude mixture was directly purified by silica gel column chromatography PE/EA (20/1 to 15/1) to give white solid **7** (38.0

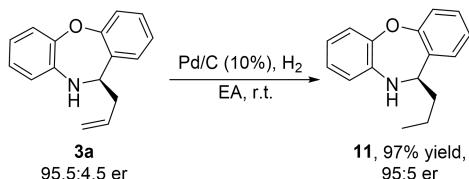
mg, 96% yield, 94:6 er).



To a stirred solution of compound **3a** (57.0 mg, 0.24 mmol, 91% *ee*) in DMF (2.0 mL), NaH (60% in oil, 19.2 mg, 0.48 mmol) was added at 0 °C. The resulting mixture was warmed to room temperature, after stirring for 30 min, allyl bromide (41.5 µL, 0.48 mmol) was added. The resulting mixture continued to stir for 5 h until disappearance of **3a** monitored by TLC. The crude mixture was directly purified by silica gel column chromatography PE/EA (20/1 to 15/1) to give compound **8** as colourless oil (64.6 mg, 97% yield, 95.5:4.5 er).

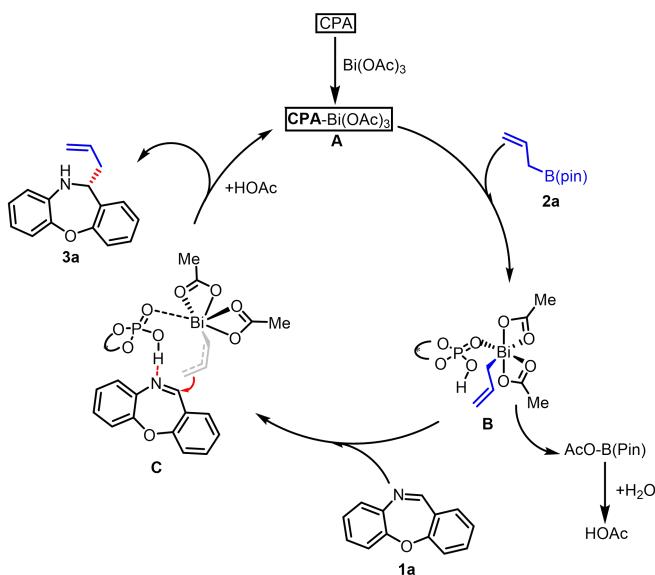
A mixture of compound **8** (37.5 mg, 0.135 mmol) and Grubbs 2nd (11.5 mg, 0.013 mmol) in THF (3.0 mL) was stirred at 40 °C for 0.5 h. After cooling to room temperature, the crude mixture was directly purified by silica gel column chromatography PE/EA (20/1 to 15/1) to give white solid **9** (33.0 mg, 98% yield).

The obtained compound **9** (33.0 mg, 0.132 mmol) was dissolved in EA (5 mL), then 10% Pd/C (5 mg) was added, the reaction was carried out overnight in hydrogen atmosphere, the Pd/C was suction filtered, and concentrated under reduced pressure, the crude mixture was directly purified by silica gel column chromatography PE/EA (20/1 to 15/1) to give compound **10** as colourless oil (32.5 mg, 98% yield, 94.5:5.5 er).



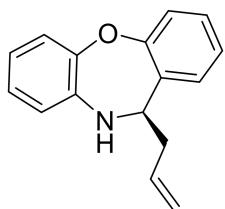
The compound **3a** (32.4 mg, 0.136 mmol, 91% *ee*) was dissolved in EA (5 mL), then 10% Pd/C (5 mg) was added, the reaction was carried out overnight in hydrogen atmosphere, the Pd/C was suction filtered, and concentrated under reduced pressure, the crude mixture was directly purified by silica gel column chromatography PE/EA (20/1 to 15/1) to give compound 11 as colourless oil (31.5 mg, 97% yield, 95:5 er).

4. Proposed Reaction Mechanism.



On the basis of the experiment results and our previous work,^{3a,b} plausible transition-state model was proposed. Firstly, one molecule of chiral phosphoric acids combined with Bi(OAc)₃ to form complex A, and the following allyl transferring from boron to bismuth atom by transmetalation process to form intermediate B, and a molecule of AcO-B(Pin) was lost. Then the seven-membered cyclic imines combined with intermediate B by H-bond interaction in C, and allyl bismuth attacked into C=N bond from *Re* face to form product 3a.

5. Analytical data

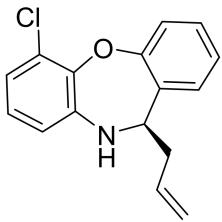


Compound 3a: (*R*)-11-allyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine colourless oil, 23.3 mg (98% of total yield), er = 95.5:4.5, $[\alpha]_D^{25} = -1.0$ (c = 0.40, CH₂Cl₂); HPLC condition: chiralpak ADH, 210 nm, 1 mL/min, hexane/i-PrOH = 19/1, t_{major} = 8.9 min, t_{minor} = 8.4 min.

¹H NMR (400 MHz, CDCl₃) δ 7.32 - 7.24 (m, 1H), 7.23 - 7.16 (m, 2H), 7.16 - 7.07 (m, 2H), 6.92 - 6.83 (m, 1H), 6.74 - 6.67 (m, 1H), 6.59 (dd, J = 7.9, 1.1 Hz, 1H), 6.05 - 5.67 (m, 1H), 5.33 - 5.05 (m, 2H), 4.67 (dd, J = 9.2, 5.5 Hz, 1H), 4.04 (s, 1H), 2.98 - 2.64 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 156.3, 143.1, 136.7, 134.1, 132.6, 127.9, 125.6, 123.4, 123.2, 120.7, 120.0, 118.00, 117.60, 117.5, 54.4, 37.8.

HRMS (ESI) calcd for C₁₆H₁₆NO (M+H)⁺: 238.1226, found: 238.1225.

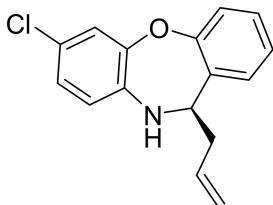


Compound 3b: (R)-11-allyl-6-chloro-10,11-dihydrodibenzo[b,f][1,4]oxazepine colourless oil, 26.4 mg (97% of total yield), er = 90.5:9.5, [α]_D²⁵ = -1.7, (c = 1.30, CH₂Cl₂); HPLC condition: chiralpak ADH, 210 nm, 1 mL/min, hexane/i-PrOH = 40/1, t_{major} = 9.9 min, t_{minor} = 9.6 min.

¹H NMR (400 MHz, CDCl₃) δ 7.38 - 7.19 (m, 2H), 7.11 - 6.97 (m, 2H), 6.88 (t, J = 7.6 Hz, 1H), 6.70 (t, J = 7.6 Hz, 1H), 6.56 (d, J = 7.9 Hz, 1H), 5.85 (td, J = 16.8, 8.5 Hz, 1H), 5.20 (m, 2H), 4.72 (dd, J = 8.8, 5.9 Hz, 1H), 3.59 (br, 1H), 2.93 - 2.67 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 153.0, 143.0, 137.7, 135.8, 134.7, 129.6, 126.5, 125.0, 124.9, 122.5, 119.0, 118.7, 118.3, 55.0, 38.5.

HRMS (ESI) calcd for C₁₆H₁₅ClNO (M+H)⁺: 272.0837, found: 272.0836 .

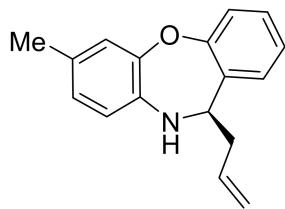


Compound 3c: (R)-11-allyl-7-chloro-10,11-dihydrodibenzo[b,f][1,4]oxazepine colourless oil, 24.0 mg (89% of total yield), er = 95.5:4.5; [α]_D²⁵ = -2.8, (c = 0.25, CH₂Cl₂); HPLC condition: chiralpak ADH, 210 nm, 1 mL/min, hexane/i-PrOH = 19/1, t_{major} = 11.3 min, t_{minor} = 9.9 min.

¹H NMR (400 MHz, CDCl₃) δ 7.44 - 7.37 (m, 1H), 7.32 - 7.21 (m, 4H), 6.95 (dd, J = 8.5, 2.4 Hz, 1H), 6.61 (d, J = 8.5 Hz, 1H), 6.05 - 5.88 (m, 1H), 5.37 - 5.28 (m, 2H), 4.74 (dd, J = 9.2, 5.6 Hz, 1H), 3.91 (br, 1H), 3.02 - 2.81 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 156.9, 144.2, 136.5, 134.8, 133.4, 129.1, 126.7, 124.6, 124.3, 122.8, 121.8, 121.0, 119.3, 118.7, 55.4, 38.7.

HRMS (ESI) calcd for C₁₆H₁₅ClNO (M+H)⁺: 272.0837, found: 272.0835.

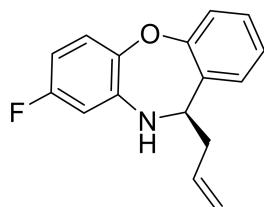


Compound 3d: (*R*)-11-allyl-7-methyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine colourless oil, 21.4 mg, (85% of total yield), er = 93.5:6.5; $[\alpha]_D^{25} = -1.8$, (c = 1.25, CH₂Cl₂); HPLC condition: chiralpak IC, 210 nm, 1 mL/min, hexane/i-PrOH = 19/1, t_{major} = 6.4 min, t_{minor} = 5.6 min.+

¹H NMR (400 MHz, CDCl₃) δ 7.36 - 7.27 (m, 1H), 7.23 (dd, *J* = 7.9, 0.9 Hz, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 8.1 Hz, 1H), 6.55 (dd, *J* = 8.1, 1.8 Hz, 1H), 6.45 (d, *J* = 1.4 Hz, 1H), 6.05 - 5.75 (m, 1H), 5.32 - 5.13 (m, 2H), 4.71 (dd, *J* = 9.2, 5.5 Hz, 1H), 3.83 (br, 1H), 2.98 - 2.64 (m, 2H), 2.25 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 157.5, 142.2, 137.3, 135.2, 134.0, 133.7, 128.9, 126.6, 124.2, 121.5, 120.9, 119.8, 119.0, 118.4, 55.4, 38.8, 20.6.

HRMS (ESI) calcd for C₁₇H₁₈NO (M+H)⁺: 252.1388, found: 252.1385.



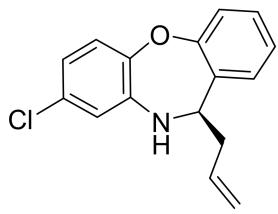
Compound 3e: (*R*)-11-allyl-8-fluoro-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine colourless oil, 20.0 mg (78% of total yield), er=94.5:5.5; $[\alpha]_D^{25} = 5.3$, (c = 1.20, CH₂Cl₂); HPLC condition: chiralpak ADH, 210 nm, 1 mL/min, hexane/i-PrOH = 19/1, t_{major} = 10.3 min, t_{minor} = 8.8 min.

¹H NMR (400 MHz, CDCl₃) δ 7.30 - 7.24 (m, 1H), 7.19 - 7.14 (m, 2H), 7.11 (td, *J* = 7.5, 1.1 Hz, 1H), 7.02 (dd, *J* = 8.8, 5.7 Hz, 1H), 6.36 - 6.29 (m, 1H), 6.24 (dd, *J* = 10.2, 2.9 Hz, 1H), 5.92 - 5.79 (m, 1H), 5.28 - 5.10 (m, 2H), 4.66 (dd, *J* = 9.2, 5.6 Hz, 1H), 4.01 (br, 1H), 2.96 - 2.63 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 159.61 (d, *J* = 240.1 Hz), 157.5, 140.1 (d, *J* = 2.4 Hz), 139.0 (d, *J* = 10.9 Hz), 134.9, 133.5, 129.2, 126.6, 124.6, 122.6 (d, *J* = 10.1 Hz), 120.9, 118.7, 104.8 (d, *J* = 23.1 Hz), 104.3 (d, *J* = 26.4 Hz), 54.9, 38.8.

¹⁹F NMR (376 MHz, CDCl₃) δ -119.4.

HRMS (ESI) calcd for C₁₆H₁₅FNO (M+H)⁺: 256.1132, found: 256.1130.

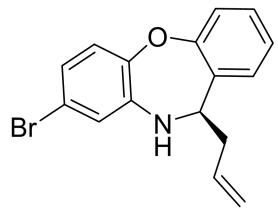


Compound 3f: (*R*)-11-allyl-8-chloro-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine colourless oil, 26.7 mg (98% of total yield), er=94.5:5.5, $[\alpha]_D^{25} = 5.5$, (c = 1.00, CH₂Cl₂); HPLC condition: chiralpak ADH, 210 nm, 1 mL/min, hexane/i-PrOH = 19/1, t_{major} = 13.6 min, t_{minor} = 10.5 min.

¹H NMR (400 MHz, CDCl₃) δ 7.55 - 7.48 (m, 1H), 7.44 - 7.33 (m, 3H), 7.25 (d, *J* = 8.5 Hz, 1H), 6.85 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.78 (d, *J* = 2.4 Hz, 1H), 6.23 - 5.98 (m, 1H), 5.57 - 5.36 (m, 2H), 4.95 - 4.72 (m, 1H), 4.31 (br, 1H), 3.23 - 2.80 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 157.1, 142.6, 138.9, 134.8, 133.4, 129.3, 129.2, 126.6, 124.6, 122.8, 121.0, 118.7, 118.4, 117.6, 55.2, 38.8.

HRMS (ESI) calcd for C₁₆H₁₅ClNO (M+H)⁺: 272.0837, found: 272.0835.

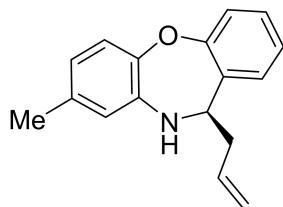


Compound 3g: (*R*)-11-allyl-8-bromo-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine colourless oil, 31.0 mg (98% of total yield), er=90:10; $[\alpha]_D^{25} = -2.5$, (c = 1.40, CH₂Cl₂); HPLC condition: chiralpak ADH, 210 nm, 1 mL/min, hexane/i-PrOH = 19/1, t_{major} = 15.1 min, t_{minor} = 11.7 min.

¹H NMR (400 MHz, CDCl₃) δ 7.31 - 7.21 (m, 1H), 7.20 - 7.05 (m, 3H), 6.95 (d, *J* = 8.5 Hz, 1H), 6.74 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.68 (d, *J* = 2.3 Hz, 1H), 5.93 - 5.73 (m, 1H), 5.25 - 5.11 (m, 2H), 4.63 (dd, *J* = 9.2, 5.5 Hz, 1H), 4.02 (br, 1H), 2.94 - 2.66 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 157.1, 143.1, 139.31, 134.8, 133.4, 129.2, 126.6, 124.6, 123.2, 121.4, 120.9, 120.5, 118.7, 116.8, 55.2, 38.8.

HRMS (ESI) calcd for C₁₆H₁₅BrNO (M+H)⁺: 316.0337, found: 316.0337.

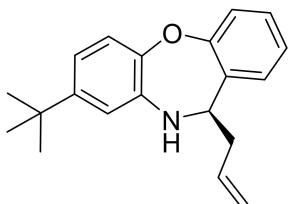


Compound 3h: (*R*)-11-allyl-8-methyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine colourless oil, 21.5 mg (82% of total yield), er=95:5; $[\alpha]_D^{25} = -21.6$, (c = 0.90, CH₂Cl₂); HPLC condition: chiralpak IC, 210 nm, 1 mL/min, hexane/i-PrOH = 19/1, t_{major} = 6.4 min, t_{minor} = 8.3 min.

¹H NMR (400 MHz, CDCl₃) δ 7.32 - 7.24 (m, 1H), 7.19 (d, *J* = 7.9 Hz, 2H), 7.11 (td, *J* = 7.5, 1.1 Hz, 1H), 6.97 (d, *J* = 1.3 Hz, 1H), 6.71 (dd, *J* = 8.0, 1.4 Hz, 1H), 6.52 (d, *J* = 8.0 Hz, 1H), 6.00 - 5.73 (m, 1H), 5.33 - 5.08 (m, 2H), 4.63 (dd, *J* = 9.1, 5.6 Hz, 1H), 3.80 (br, 1H), 2.96 - 2.66 (m, 2H), 2.27 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 157.2, 144.3, 135.2, 134.9, 133.5, 129.1, 128.8, 126.8, 124.9, 124.1, 122.1, 121.0, 119.0, 118.4, 55.8, 38.9, 20.3.

HRMS (ESI) calcd for C₁₇H₁₈NO (M+H)⁺: 252.1388, found: 252.1386.

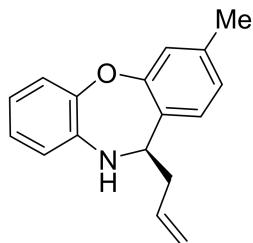


Compound 3i: (*R*)-11-allyl-8-(tert-butyl)-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine colourless oil, 25.4 mg (87% of total yield), er = 83:17, [α]_D²⁵ = -8.0, (c = 1.25, CH₂Cl₂); HPLC condition: chiralpak ADH, 210 nm, 1 mL/min, hexane/i-PrOH = 19/1, t_{major} = 6.0 min, t_{minor} = 9.5 min.

¹H NMR (400 MHz, CDCl₃) δ 7.19 - 7.13 (m, 1H), 7.08 (d, *J* = 7.1 Hz, 2H), 7.03 - 6.92 (m, 2H), 6.63 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.49 (d, *J* = 2.1 Hz, 1H), 6.04 - 5.63 (m, 1H), 5.38 - 4.82 (m, 2H), 4.60 (dd, *J* = 9.2, 5.4 Hz, 1H), 3.62 (br, 1H), 2.95 - 2.30 (m, 2H), 1.16 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 157.6, 147.4, 142.2, 136.8, 135.2, 133.6, 128.9, 126.6, 124.2, 121.2, 121.0, 118.5, 116.4, 115.8, 55.2, 38.8, 34.1, 31.4.

HRMS (ESI) calcd for C₂₀H₂₄NO (M+H)⁺: 294.1852, found: 294.1858.

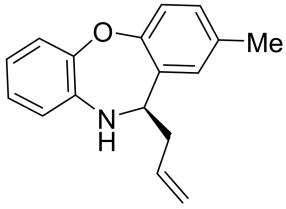


Compound 3j: (*R*)-11-allyl-3-methyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine colourless oil, 20.7 mg (82% of total yield), er = 94.5:5.5, [α]_D²⁵ = -1.2, (c = 0.90, CH₂Cl₂); HPLC condition: chiralpak ADH, 210 nm, 1 mL/min, hexane/i-PrOH = 19/1, t_{major} = 10.2 min, t_{minor} = 12.5 min.

¹H NMR (400 MHz, CDCl₃) δ 7.11 - 6.98 (m, 3H), 6.94 - 6.78 (m, 2H), 6.72 - 6.62 (m, 1H), 6.55 (dd, *J* = 7.9, 1.4 Hz, 1H), 5.96 - 5.75 (m, 1H), 5.26 - 5.04 (m, 2H), 4.61 (dd, *J* = 9.2, 5.5 Hz, 1H), 3.89 (br, 1H), 2.89 - 2.65 (m, 2H), 2.32 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 157.1, 144.3, 139.1, 137.5, 135.2, 130.5, 126.4, 126.0, 124.9, 124.4, 121.7, 121.5, 119.0, 118.7, 118.4, 55.2, 39.0, 21.0.

HRMS (ESI) calcd for C₁₇H₁₈NO (M+H)⁺: 252.1388, found: 252.1385.

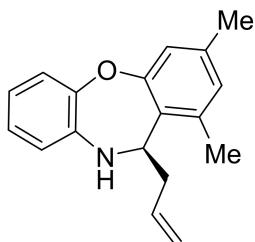


Compound 3k: (*R*)-11-allyl-2-methyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine colourless oil, 21.0 mg (84% of total yield), er = 91:9; $[\alpha]_D^{25} = 3.4$, (c = 1.05, CH₂Cl₂); HPLC condition: chiralpak ODH, 210 nm, 1 mL/min, hexane/i-PrOH = 19/1, t_{major} = 6.0 min, t_{minor} = 6.5 min.

¹H NMR (400 MHz, CDCl₃) δ 7.10 - 7.00 (m, 3H), 6.97 (s, 1H), 6.84 (td, *J* = 7.8, 1.5 Hz, 1H), 6.67 (td, *J* = 7.8, 1.5 Hz, 1H), 6.55 (dd, *J* = 7.9, 1.5 Hz, 1H), 5.98 - 5.70 (m, 1H), 5.30 - 5.04 (m, 2H), 4.60 (dd, *J* = 9.2, 5.5 Hz, 1H), 4.00 (br, 1H), 2.94 - 2.67 (m, 2H), 2.31 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 155.2, 144.3, 137.8, 135.2, 133.8, 133.2, 129.3, 127.2, 124.3, 121.7, 120.7, 119.0, 118.6, 118.4, 55.4, 38.8, 20.9.

HRMS (ESI) calcd for C₁₇H₁₈NO (M+H)⁺: 252.1388, found: 252.1385.

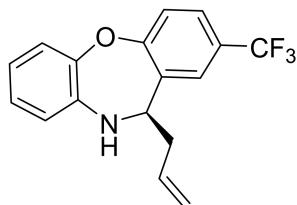


Compound 3l: (*R*)-11-allyl-1,3-dimethyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine colourless oil, 26.0 mg (98% of total yield), er = 90:10; $[\alpha]_D^{25} = -3.4$, (c = 1.20, CH₂Cl₂); HPLC condition: chiralpak ADH, 210 nm, 1 mL/min, hexane/i-PrOH = 19/1, t_{major} = 6.6 min, t_{minor} = 12.8 min.

¹H NMR (400 MHz, CDCl₃) δ 7.06 (dd, *J* = 7.9, 1.3 Hz, 1H), 6.88 - 6.80 (m, 2H), 6.75 (s, 1H), 6.64 (td, *J* = 7.9, 1.5 Hz, 1H), 6.53 (dd, *J* = 7.9, 1.4 Hz, 1H), 5.79 (ddt, *J* = 17.0, 10.1, 7.3 Hz, 1H), 5.16 - 4.92 (m, 2H), 4.36 (dd, *J* = 8.1, 7.0 Hz, 1H), 3.05 - 2.76 (m, 2H), 2.28 (d, *J* = 12.0 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 157.3, 143.3, 138.3, 137.4, 135.5, 135.1, 129.0, 127.1, 124.4, 121.6, 119.8, 118.4, 118.1, 117.6, 53.8, 40.5, 20.9, 19.9.

HRMS (ESI) calcd for C₁₈H₂₀NO (M+H)⁺: 266.1545, found: 266.1542.



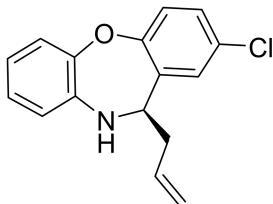
Compound 3m: (*R*)-11-allyl-2-(trifluoromethyl)-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine colourless oil, 29.3 mg (96% of total yield), er = 95.5:4.5; $[\alpha]_D^{25} = -3.4$, (c = 1.60, CH₂Cl₂); HPLC condition: chiralpak ADH, 210 nm, 1 mL/min, hexane/i-PrOH = 19/1, t_{major} = 7.9 min, t_{minor} = 8.5 min.

¹H NMR (400 MHz, CDCl₃) δ 7.52 (d, *J* = 8.3 Hz, 1H), 7.41 (s, 1H), 7.29 - 7.21 (m, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 6.92 - 6.83 (m, 1H), 6.72 (dd, *J* = 10.6, 4.7 Hz, 1H), 6.58 (d, *J* = 7.9 Hz, 1H), 5.84 (ddt, *J* = 17.4, 9.5, 7.1 Hz, 1H), 5.29 - 5.04 (m, 2H), 4.63 (dd, *J* = 8.7, 6.0 Hz, 1H), 3.99 (br, 1H), 2.86 - 2.63 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 159.5, 143.8, 137.1, 134.4, 134.0, 126.2 (dd, *J* = 7.6, 3.8 Hz), 126.1 (q, *J* = 32.7 Hz), 125.4, 124.8, 124.3 (q, *J* = 3.6 Hz), 122.7, 121.6 (d, *J* = 3.0 Hz), 119.7, 119.1, 55.7, 38.7.

¹⁹F NMR (376 MHz, CDCl₃) δ -64.3.

HRMS (ESI) calcd for C₁₇H₁₅F₃NO (M+H)⁺: 306.1106, found: 306.1096.

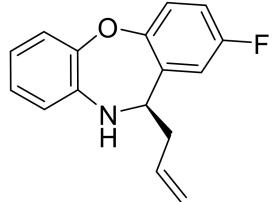


Compound 3n: (*R*)-11-allyl-2-chloro-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine colourless oil, 23.1 mg (85% of total yield), er = 95:5; [α]_D²⁵ = 9.4, (c = 1.18, CH₂Cl₂); HPLC condition: chiralpak ADH, 210 nm, 1 mL/min, hexane/i-PrOH = 19/1, t_{major} = 7.7 min, t_{minor} = 7.4 min.

¹H NMR (400 MHz, CDCl₃) δ 7.38 - 7.27 (m, 2H), 7.09 - 6.99 (m, 2H), 6.93 - 6.85 (m, 1H), 6.74 - 6.66 (m, 1H), 6.56 (dd, *J* = 8.0, 1.4 Hz, 1H), 5.93 - 5.79 (m, 1H), 5.30 - 5.10 (m, 2H), 4.72 (dd, *J* = 9.2, 5.6 Hz, 1H), 3.82 (br, 1H), 2.97 - 2.68 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 153.0, 143.0, 137.8, 135.9, 134.7, 129.6, 126.5, 125.1, 124.9, 124.8, 122.5, 118.9, 118.8, 118.2, 54.9, 38.5.

HRMS (ESI) calcd for C₁₆H₁₅ClNO (M+H)⁺: 272.0842, found: 272.0835.



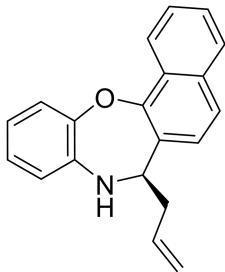
Compound 3o: (*R*)-11-allyl-2-fluoro-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine colourless oil, 20.1 mg (79% of total yield), er = 90.5:9.5; [α]_D²⁵ = -4.0 (c = 1.00, CH₂Cl₂); HPLC condition: chiralpak ADH, 210 nm, 1 mL/min, hexane/i-PrOH = 19/1, t_{major} = 8.6 min, t_{minor} = 9.3 min.

¹H NMR (400 MHz, CDCl₃) δ 7.15 - 7.04 (m, 2H), 6.94 - 6.85 (m, 2H), 6.80 (td, *J* = 8.4, 2.6 Hz, 1H), 6.70 (td, *J* = 8.0, 1.5 Hz, 1H), 6.57 (dd, *J* = 7.9, 1.5 Hz, 1H), 5.96 - 5.60 (m, 1H), 5.28 - 5.00 (m, 2H), 4.60 (dd, *J* = 9.2, 5.6 Hz, 1H), 3.99 (br, 1H), 2.97 - 2.55 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 162.4 (d, *J* = 247.0 Hz), 158.0 (d, *J* = 11.0 Hz), 143.8, 137.5, 134.8, 129.7, 127.6 (d, *J* = 9.6 Hz), 124.7, 121.7, 119.3, 118.8, 118.7, 110.9 (d, *J* = 21.0 Hz), 108.8 (d, *J* = 23.1 Hz), 55.1, 38.9.

¹⁹F NMR (376 MHz, CDCl₃) δ -112.9.

HRMS (ESI) calcd for C₁₆H₁₅FNO (M+H)⁺: 256.1138, found: 256.1133.

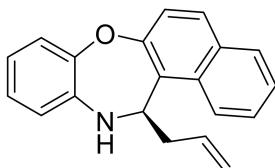


Compound 3p: (*R*)-7-allyl-7,8-dihydrobenzo[*b*]naphtho[2,1-*f*][1,4]oxazepine colourless oil, 24.5 mg (85% of total yield), er = 94.5:5.5; $[\alpha]_D^{25} = 27.4$, ($c = 1.20$, CH_2Cl_2); HPLC condition: chiralpak IC, 210 nm, 1 mL/min, hexane/i-PrOH = 19/1, $t_{\text{major}} = 12.8$ min, $t_{\text{minor}} = 6.3$ min.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.48 (d, $J = 8.4$ Hz, 1H), 7.82 (d, $J = 8.1$ Hz, 1H), 7.57 (dd, $J = 15.9$, 8.5 Hz, 2H), 7.49 (t, $J = 7.5$ Hz, 1H), 7.37 - 7.27 (m, 2H), 6.88 (t, $J = 7.6$ Hz, 1H), 6.74 (t, $J = 7.6$ Hz, 1H), 6.61 (d, $J = 7.9$ Hz, 1H), 6.02 - 5.75 (m, 1H), 5.32 - 5.10 (m, 2H), 4.79 (dd, $J = 8.8$, 5.7 Hz, 1H), 4.11 (br, 1H), 3.05 - 2.74 (m, 2H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 152.3, 144.3, 138.2, 135.2, 134.2, 128.5, 127.6, 127.4, 126.3, 124.7, 124.6, 123.8, 122.1, 121.8, 119.2, 119.0, 118.6, 56.0, 39.3.

HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{18}\text{NO} (\text{M}+\text{H})^+$: 288.1383, found: 288.1383.

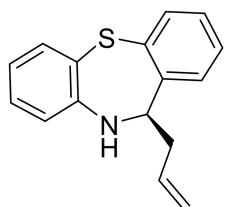


Compound 3q: (*R*)-12-allyl-12,13-dihydrobenzo[*b*]naphtho[2,3-*f*][1,4]oxazepine colourless oil, 27.9 mg (97% of total yield), er = 95:5; $[\alpha]_D^{25} = 93.2$, ($c = 1.45$, CH_2Cl_2); HPLC condition: chiralpak IC, 210 nm, 1 mL/min, hexane/i-PrOH = 19/1, $t_{\text{major}} = 9.3$ min, $t_{\text{minor}} = 18.9$ min.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.96 (d, $J = 8.6$ Hz, 1H), 7.83 (d, $J = 8.0$ Hz, 1H), 7.76 (d, $J = 8.8$ Hz, 1H), 7.58 - 7.49 (m, 1H), 7.46 - 7.33 (m, 2H), 7.16 (dd, $J = 8.0$, 1.4 Hz, 1H), 6.90 (td, $J = 7.7$, 1.4 Hz, 1H), 6.75 (td, $J = 7.7$, 1.5 Hz, 1H), 6.64 (dd, $J = 7.9$, 1.5 Hz, 1H), 6.04 - 5.60 (m, 1H), 5.28 - 4.86 (m, 3H), 3.14 - 2.97 (m, 1H), 2.93 - 2.79 (m, 1H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 154.3, 144.3, 137.2, 135.3, 131.0, 130.8, 129.4, 128.9, 126.8, 125.9, 124.5, 124.4, 122.2, 121.9, 121.4, 119.5, 119.2, 118.0, 53.3, 40.4.

HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{18}\text{NO} (\text{M}+\text{H})^+$: 288.1383, found: 288.1384.



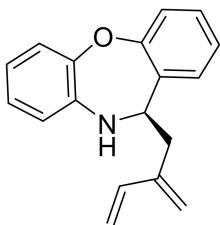
Compound 3r: (*R*)-11-allyl-10,11-dihydrodibenzo[*b,f*][1,4]thiazepine colourless oil, 17.5 mg (69% of total yield), er = 88.5:11.5, $[\alpha]_D^{25} = -21.6$, ($c = 0.90$, CH_2Cl_2); HPLC condition: chiralpak ADH, 210 nm, 1 mL/min, hexane/i-PrOH = 19/1, $t_{\text{major}} = 7.0$ min, t_{minor}

= 8.7 min.

¹H NMR (400 MHz, CDCl₃) δ 7.58 - 7.47 (m, 1H), 7.35 - 7.19 (m, 3H), 7.14 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.92 - 6.84 (m, 1H), 6.61 - 6.49 (m, 1H), 6.35 (dd, *J* = 8.1, 0.9 Hz, 1H), 6.01 - 5.86 (m, 2H), 5.35 - 5.15 (m, 2H), 3.80 (br, 1H), 2.91 - 2.74 (m, 1H), 2.73 - 2.56 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 146.6, 144.6, 136.3, 135.1, 132.0, 131.9, 128.7, 128.2, 128.1, 124.8, 118.5, 118.5, 117.8, 116.3, 53.9, 38.0.

HRMS (ESI) calcd for C₁₆H₁₆NS (M+H)⁺: 254.1003, found: 254.0097.

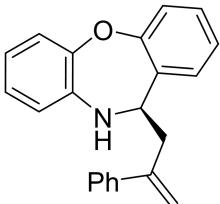


Compound 3s: (*R*)-11-(2-methylenebut-3-en-1-yl)-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine colourless oil, 20.5 mg (78% of total yield), er = 87:13, [α]_D²⁵ = -6.2, (c = 1.00, CH₂Cl₂); HPLC condition: chiralpak ADH, 210 nm, 1 mL/min, hexane/i-PrOH = 19/1, t_{major} = 9.2 min, t_{minor} = 6.9 min.

¹H NMR (400 MHz, CDCl₃) δ 7.39 - 6.91 (m, 10H), 6.75 (t, *J* = 7.5 Hz, 1H), 6.59 (t, *J* = 7.6 Hz, 1H), 6.42 (d, *J* = 7.9 Hz, 1H), 5.31 (s, 1H), 5.06 (s, 1H), 4.43 (dd, *J* = 9.3, 5.3 Hz, 1H), 3.34 - 3.04 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 157.2, 143.9, 142.9, 138.2, 137.3, 133.7, 124.4, 124.3, 121.8, 121.7, 121.1, 119.3, 119.2, 119.1, 118.8, 114.3, 55.2, 36.8.

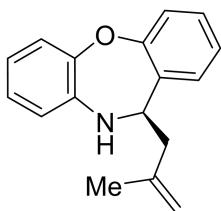
HRMS (ESI) calcd for C₁₈H₁₈NO (M+H)⁺: 264.1388, found: 264.1382.



Compound 3t: (*R*)-11-(2-phenylallyl)-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine colourless oil, 15.8 mg (50% of total yield), er = 92:8; [α]_D²⁵ = -4.5, (c = 0.40, CH₂Cl₂); HPLC condition: chiralpak ADH, 210 nm, 1 mL/min, hexane/i-PrOH = 19/1, t_{major} = 12.6 min, t_{minor} = 8.3 min.

¹H NMR (400 MHz, CDCl₃) δ 7.34 (d, *J* = 7.1 Hz, 2H), 7.30 - 7.13 (m, 4H), 7.09 (d, *J* = 7.8 Hz, 1H), 7.00 (t, *J* = 7.9 Hz, 3H), 6.75 (t, *J* = 7.5 Hz, 1H), 6.59 (t, *J* = 7.6 Hz, 1H), 6.42 (d, *J* = 7.9 Hz, 1H), 5.31 (s, 1H), 5.06 (s, 1H), 4.43 (dd, *J* = 9.3, 5.3 Hz, 1H), 3.41 - 3.03 (m, 2H).

HRMS (ESI) calcd for C₂₂H₂₀NO (M+H)⁺: 314.1539, found: 314.1541.

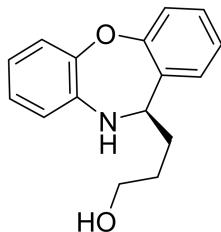


Compound 3u: (*R*)-11-(2-methylallyl)-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine colourless oil, 24.6 mg (98% of total yield), er = 77:23; $[\alpha]_D^{25} = -1.4$, (c = 1.15, CH₂Cl₂); HPLC condition: chiralpak ADH, 210 nm, 1 mL/min, hexane/i-PrOH = 19/1, t_{major} = 8.1 min, t_{minor} = 7.1 min.

¹H NMR (400 MHz, CDCl₃) δ 7.34 - 7.06 (m, 6H), 6.87 (t, *J* = 7.6 Hz, 1H), 6.70 (t, *J* = 7.6 Hz, 1H), 6.59 (d, *J* = 7.9 Hz, 1H), 5.03 - 4.79 (m, 3H), 2.93 - 2.56 (m, 2H), 1.83 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 157.5, 144.1, 142.2, 138.0, 134.0, 128.9, 126.1, 124.4, 124.3, 121.7, 121.0, 119.0, 118.5, 114.3, 52.5, 42.3, 22.1.

HRMS (ESI) calcd for C₁₇H₁₈NO (M+H)⁺: 252.1383, found: 252.1381.

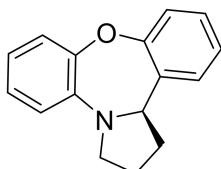


Compound 4: (*R*)-3-(10,11-dihydrodibenzo[*b,f*][1,4]oxazepin-11-yl)propan-1-ol colourless oil, 30.0 mg (59% of yield), er = 93.5:6.5, $[\alpha]_D^{25} = 5.4$, (c = 1.80, CH₂Cl₂); HPLC condition: chiralpak ADH, 210 nm, 1 mL/min, hexane/i-PrOH = 1/4, t_{major} = 9.4 min, t_{minor} = 8.9 min.

¹H NMR (400 MHz, CDCl₃) δ 7.32 - 7.03 (m, 5H), 6.94 - 6.83 (m, 1H), 6.76 - 6.65 (m, 1H), 6.61 (dd, *J* = 7.9, 1.1 Hz, 1H), 4.45 (t, *J* = 7.4 Hz, 1H), 3.71 (t, *J* = 6.4 Hz, 2H), 2.95 (s, 2H), 2.28 - 2.07 (m, 2H), 1.83 - 1.55 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 157.2, 144.0, 137.4, 134.0, 128.9, 127.2, 124.5, 124.3, 121.8, 121.1, 119.1, 118.8, 62.7, 57.2, 31.5, 30.0.

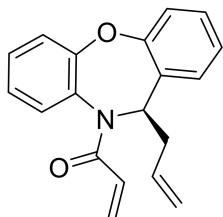
HRMS (ESI) calcd for C₁₆H₁₈NO₂ (M+H)⁺: 256.1332, found: 256.1332.



Compound 5: (*R*)-1,2,3,13b-tetrahydrodibenzo[*b,f*]pyrrolo[1,2-*d*][1,4]oxazepine colourless oil, 57.0 mg (85% of yield), er = 93.5:6.5, $[\alpha]_D^{25} = -76.5$, (c = 0.25, CH₂Cl₂); HPLC condition: chiralpak IC, 210 nm, 1 mL/min, hexane/i-PrOH = 40/1, t_{major} = 5.7 min, t_{minor} = 5.3 min.

¹H NMR (400 MHz, CDCl₃) δ 7.42 - 7.28 (m, 3H), 7.28 - 7.21 (m, 2H), 7.06 (td, *J* = 8.1, 1.5 Hz, 1H), 6.70 (dd, *J* = 10.9, 4.2 Hz, 1H), 6.60 (d, *J* = 7.9 Hz, 1H), 5.65 (t, *J* = 7.0 Hz, 1H), 3.62 - 3.51 (m, 1H), 3.45 (td, *J* = 8.4, 5.3 Hz, 1H), 2.58 - 2.46 (m, 1H), 2.41 (td, *J* = 12.4, 6.4 Hz, 1H), 2.32 - 2.09 (m, 2H).
¹³C NMR (101 MHz, CDCl₃) δ 158.3, 144.2, 139.8, 133.4, 129.0, 125.2, 124.6, 124.5, 121.2, 120.6, 116.7, 114.8, 57.6, 50.0, 29.2, 23.4.

HRMS (ESI) calcd for C₁₆H₁₆NO (M+H)⁺: 238.1226, found: 238.1229.

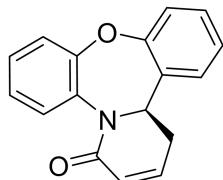


Compound 6: (*R*)-1-(11-allyldibenzo[*b,f*][1,4]oxazepin-10(11*H*)-yl)prop-2-en-1-one
white solid, 114.0 mg (98% of yield), er = 95.5:4.5, [α]_D²⁵ = -308.8, (c = 0.25, CH₂Cl₂); HPLC condition: chiralpak ADH, 210 nm, 1 mL/min, hexane/i-PrOH = 1/19, t_{major} = 12.5 min, t_{minor} = 17.7 min.

¹H NMR (400 MHz, CDCl₃) δ 7.32 - 7.00 (m, 7H), 6.94 (t, *J* = 7.2 Hz, 1H), 6.32 (dd, *J* = 16.7, 1.6 Hz, 1H), 6.19 – 6.02 (m, 2H), 5.79 - 5.64 (m, 1H), 5.50 (dd, *J* = 10.3, 1.5 Hz, 1H), 5.01 (d, *J* = 10.2 Hz, 1H), 4.90 (d, *J* = 17.2 Hz, 1H), 2.34 (dt, *J* = 15.2, 4.9 Hz, 1H), 2.21 - 2.05 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 165.4, 153.3, 153.1, 131.0, 130.4, 129.7, 129.5, 128.7, 128.4, 128.2, 123.9, 123.0, 121.6, 120.9, 117.8, 55.6, 41.0.

HRMS (ESI) calcd for C₁₉H₁₈NO₂ (M+H)⁺: 292.1332, found: 292.1338.

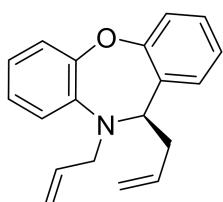


Compound 7: (*R*)-1,14b-dihydro-4*H*-dibenzo[*b,f*]pyrido[1,2-*d*][1,4]oxazepin-4-one
white solid, 38.0 mg (96% of yield), er = 94:6, [α]_D²⁵ = -52.0, (c = 0.65, CH₂Cl₂); HPLC condition: chiralpak ADH, 210 nm, 1 mL/min, hexane/i-PrOH = 3/2, t_{major} = 5.3 min, t_{minor} = 6.1 min.

¹H NMR (400 MHz, CDCl₃) δ 7.50 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.33 - 7.00 (m, 7H), 6.88 - 6.75 (m, 1H), 6.06 (dd, *J* = 9.9, 2.3 Hz, 1H), 5.47 (dd, *J* = 6.2, 2.6 Hz, 1H), 3.14 - 3.05 (m, 1H), 3.03 - 2.93 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 163.1, 156.1, 150.0, 138.7, 131.2, 130.0, 129.5, 129.0, 127.2, 126.4, 126.2, 123.5, 122.5, 121.2, 121.1, 56.7, 26.9.

HRMS (ESI) calcd for C₁₇H₁₄NO₂ (M+H)⁺: 264.1019, found: 264.1018.



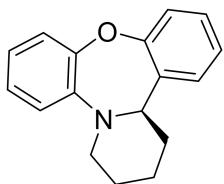
Compound 8: (*R*)-10,11-diallyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine

colourless oil, 64.6 mg (97% of yield), er = 95.5:4.5, $[\alpha]_D^{25} = -108.3$, ($c = 0.65$, CH_2Cl_2); HPLC condition: chiralpak ADH, 210 nm, 1 mL/min, hexane/i-PrOH = 1/200, $t_{\text{major}} = 8.9$ min, $t_{\text{minor}} = 8.6$ min.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.31 - 6.93 (m, 6H), 6.90 - 6.78 (m, 2H), 6.02 - 5.84 (m, 1H), 5.73 (ddt, $J = 17.2, 10.1, 7.1$ Hz, 1H), 5.30 - 5.10 (m, 2H), 5.06 - 4.93 (m, 2H), 4.02 (t, $J = 7.7$ Hz, 1H), 3.87 - 3.80 (m, 2H), 2.87 (t, $J = 7.2$ Hz, 2H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 156.7, 147.6, 138.8, 135.7, 135.2, 132.1, 129.3, 128.8, 124.2, 123.3, 122.0, 121.4, 120.7, 120.7, 116.8, 116.5, 64.6, 58.0, 38.8.

HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{20}\text{NO} (\text{M}+\text{H})^+$: 278.1539, found: 278.1544.

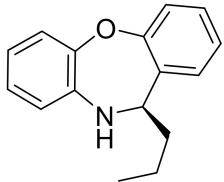


Compound 10: (*R*)-1,3,4,14b-tetrahydro-2*H*-dibenzo[*b,f*]pyrido[1,2-*d*][1,4]oxazepine colourless oil, 32.5 mg (98% of yield), er = 94.5:5.5, $[\alpha]_D^{25} = -347.2$, ($c = 0.50$, CH_2Cl_2); HPLC condition: chiralpak ADH, 210 nm, 1 mL/min, hexane/i-PrOH = 40/1, $t_{\text{major}} = 4.7$ min, $t_{\text{minor}} = 5.1$ min.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.33 - 7.00 (m, 7H), 6.87 (t, $J = 7.4$ Hz, 1H), 4.03 (d, $J = 10.1$ Hz, 1H), 3.71 - 3.36 (m, 1H), 3.23 - 2.87 (m, 1H), 2.08 - 1.58 (m, 6H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 155.5, 152.8, 143.0, 132.2, 128.6, 126.9, 124.3, 123.2, 120.7, 119.8, 119.5, 119.3, 64.2, 51.7, 36.3, 24.9, 24.2.

HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{18}\text{NO} (\text{M}+\text{H})^+$: 252.1388, found: 252.1386.



Compound 11: (*R*)-1,3,4,14b-tetrahydro-2*H*-dibenzo[*b,f*]pyrido[1,2-*d*][1,4]oxazepine colourless oil, 31.5 mg (97% of yield), er = 95:5, $[\alpha]_D^{25} = 22.2$, ($c = 0.65$, CH_2Cl_2); HPLC condition: chiralpak ADH, 210 nm, 1 mL/min, hexane/i-PrOH = 1/19, $t_{\text{major}} = 9.8$ min, $t_{\text{minor}} = 8.3$ min.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.32 - 7.07 (m, 5H), 6.89 (t, $J = 7.5$ Hz, 1H), 6.70 (t, $J = 7.5$ Hz, 1H), 6.59 (d, $J = 7.9$ Hz, 1H), 4.49 (t, $J = 7.3$ Hz, 1H), 3.90 (br, 1H), 2.20 - 1.95 (m, 2H), 1.63 - 1.35 (m, 2H), 1.01 (t, $J = 7.2$ Hz, 3H).

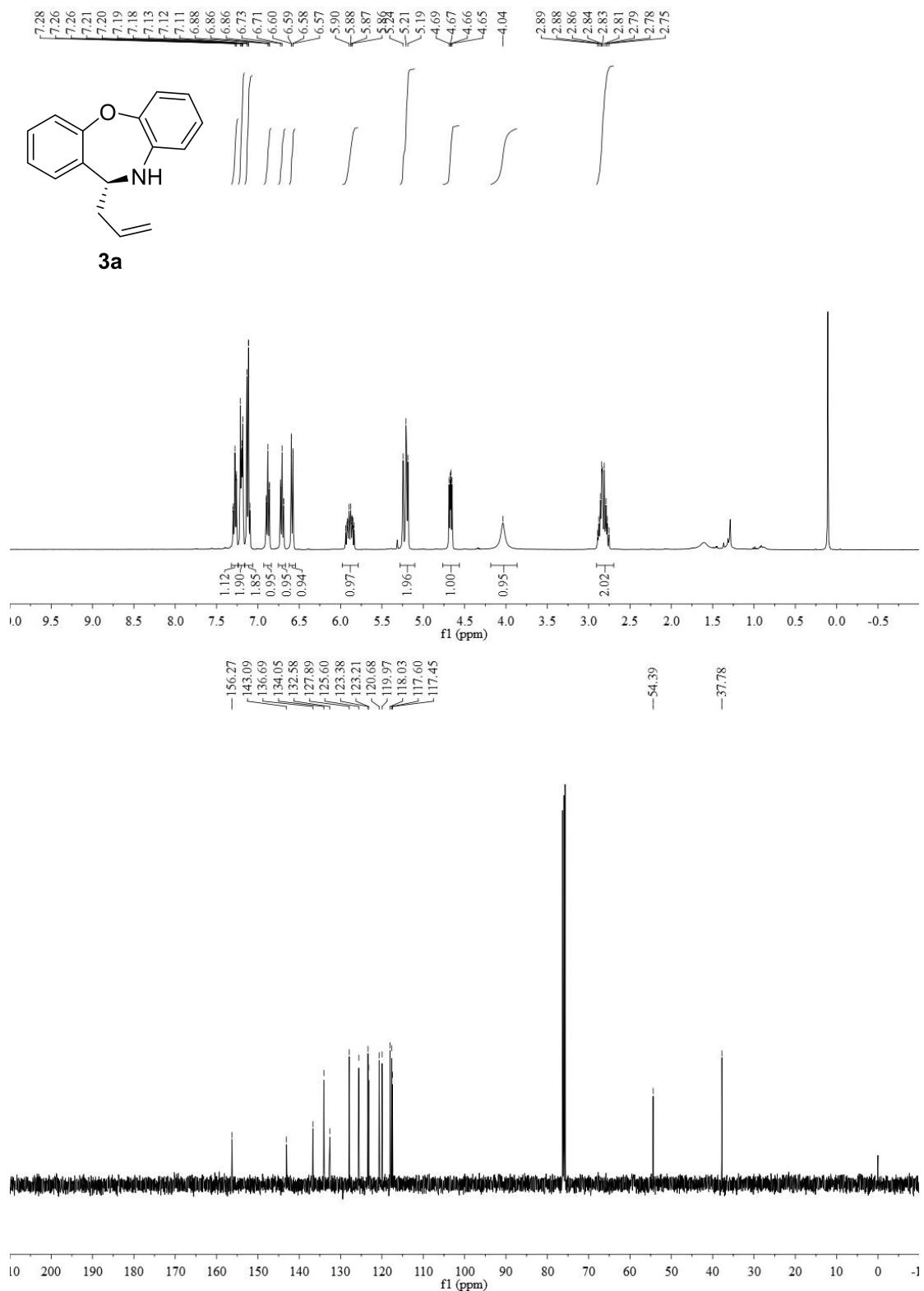
$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 157.3, 143.9, 137.7, 134.3, 128.7, 127.0, 124.4, 124.2, 121.7, 121.1, 118.8, 118.5, 56.8, 36.9, 20.1, 14.0.

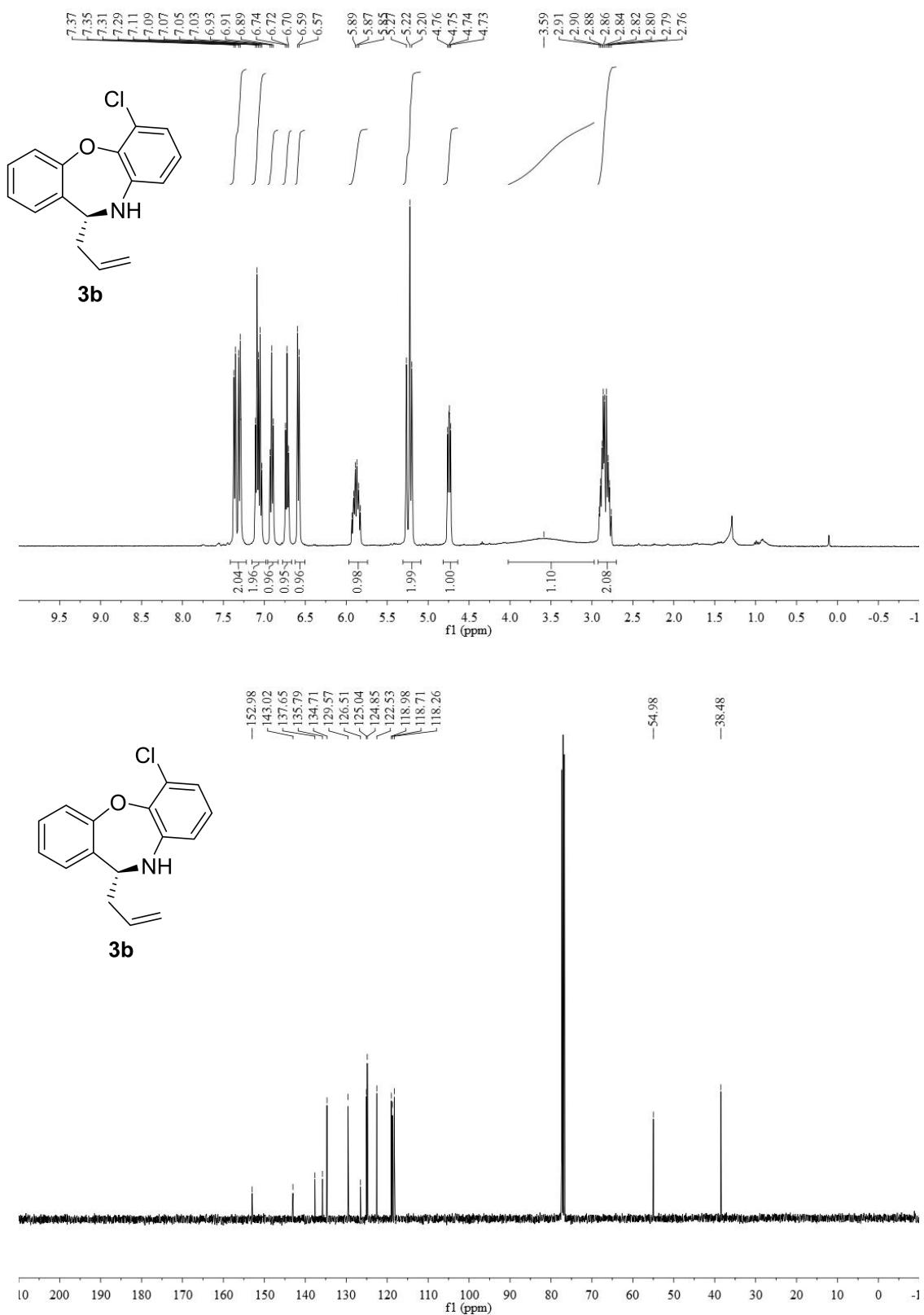
HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{18}\text{NO} (\text{M}+\text{H})^+$: 240.1388, found: 240.1387

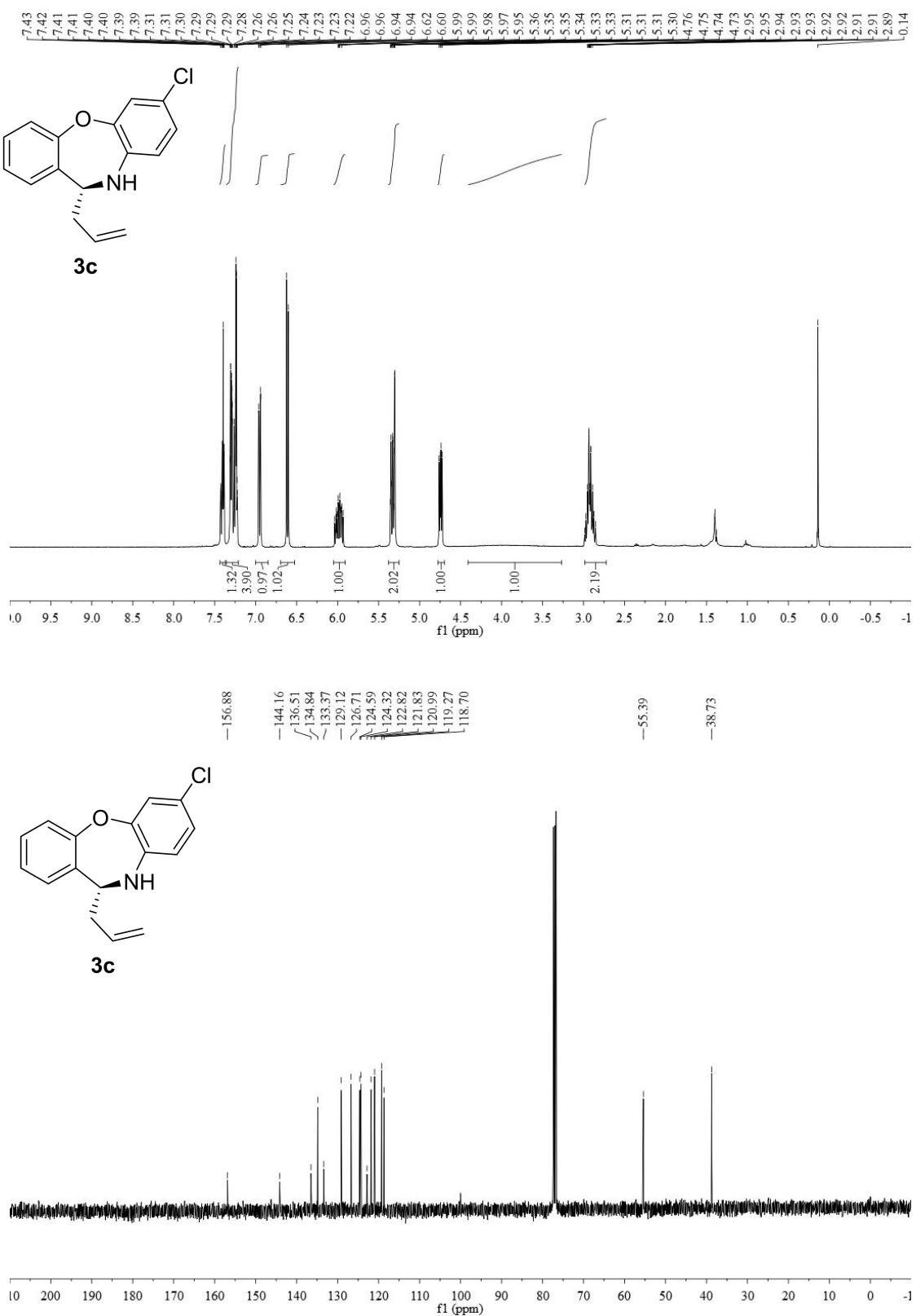
6. References

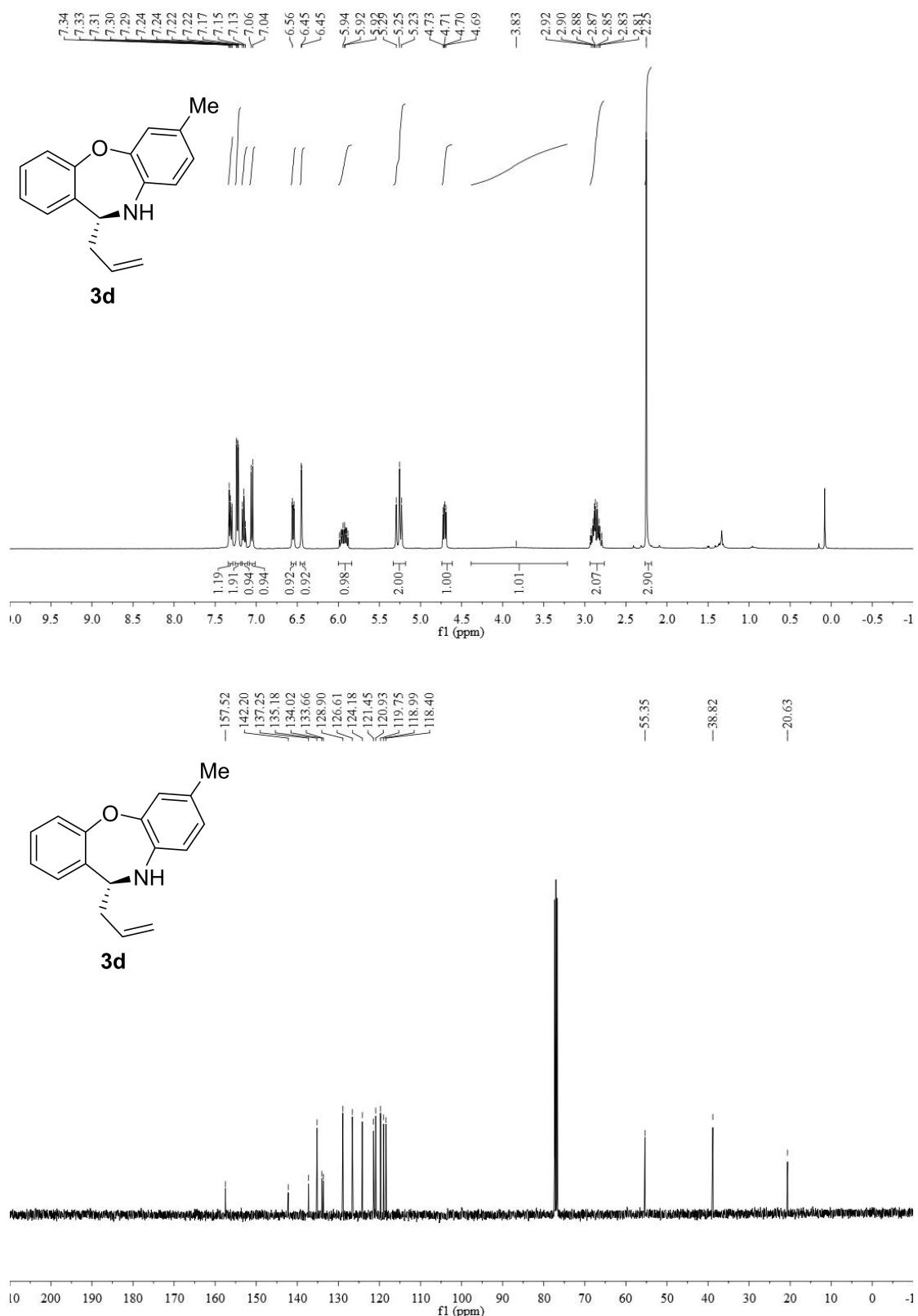
- 1 (a) Y. -Y. Ren, Y. -Q. Wang, S. Liu and K. Pan, *ChemCatChem*, 2014, **6**, 2985. (b) S. Debasmita, K. Tanpreet, S. Neetu, P. S. Udai and Anuj, S. *Asian J. Org. Chem.*, 2016, **5**, 82. (c) L. D. Munck, V. Sukowski, C. Vila, M. C. Muñoz, J. R. Pedro, *Org. Chem. Front.*, 2017, **4**, 1624.
- 2 (a) P. Zhang, I. A. Roundtree and J. P. Morken, *Org. Lett.*, 2012, **14**, 1416. (b) S. Niyomchon, D. Audisio, M. Luparia and N. Maulide, *Org. Lett.*, 2013, **15**, 2318. (c) N. Miralles, R. Alam, K. J. Szabó and E. Fernández. *Angew. Chem. Int. Ed.*, 2016, **55**, 4303.
- 3 (a) J. Wang, Q. X. Zhang, B. Y. Zhou, C. Yang, X. Li and J. -P. Cheng, *iScience*, 2019, **16**, 511. (b) Y. -L. Pan, H. -L. Zheng, J. Wang, C. Yang, X. Li and J. -P. Cheng, *ACS. Catal.*, 2020, **10**, 8069.

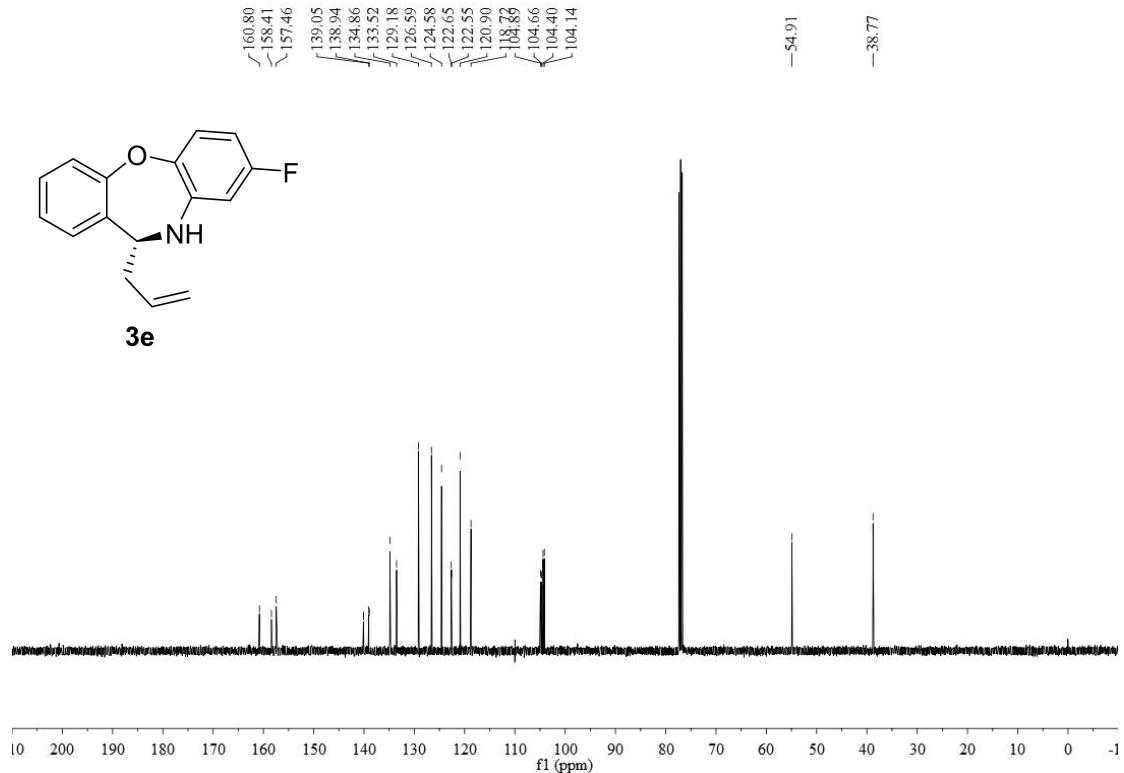
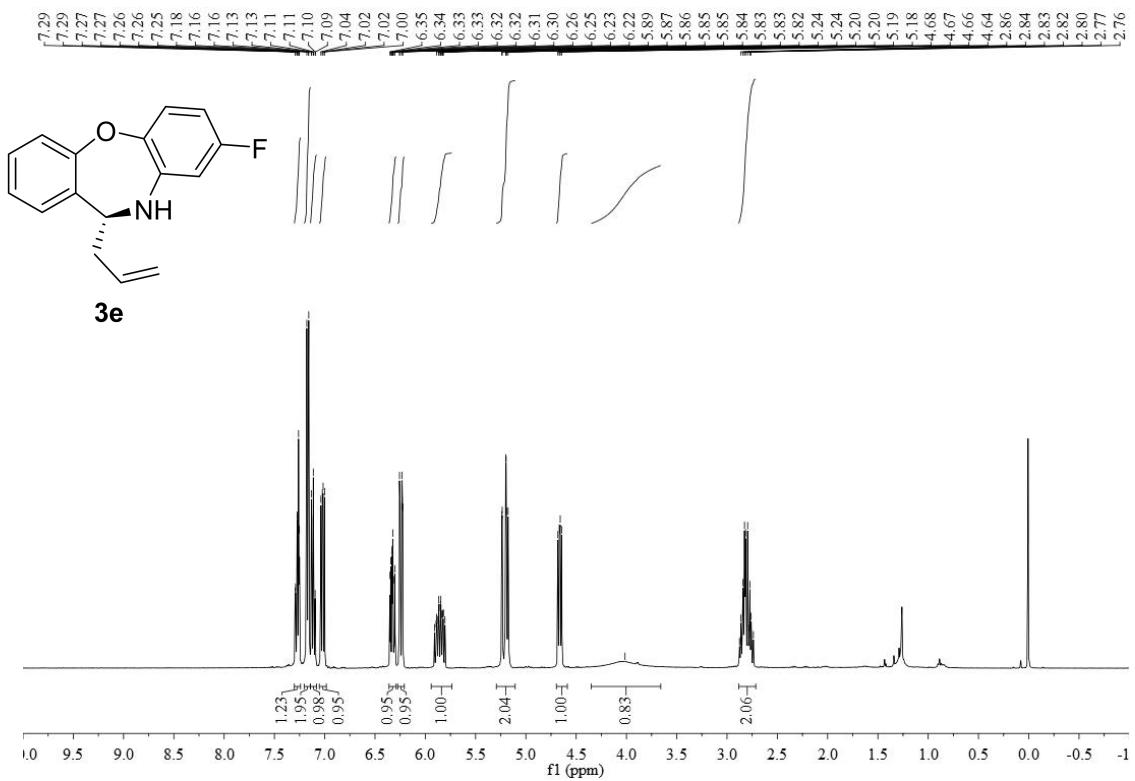
7. NMR and HPLC spectra

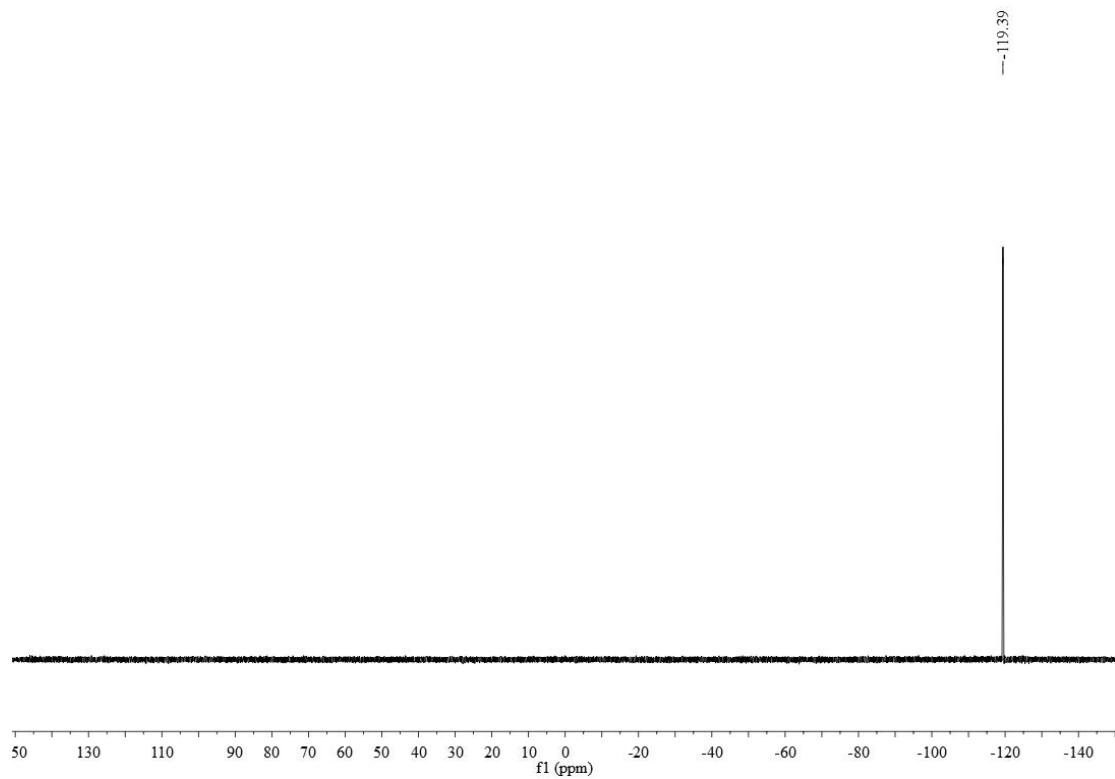


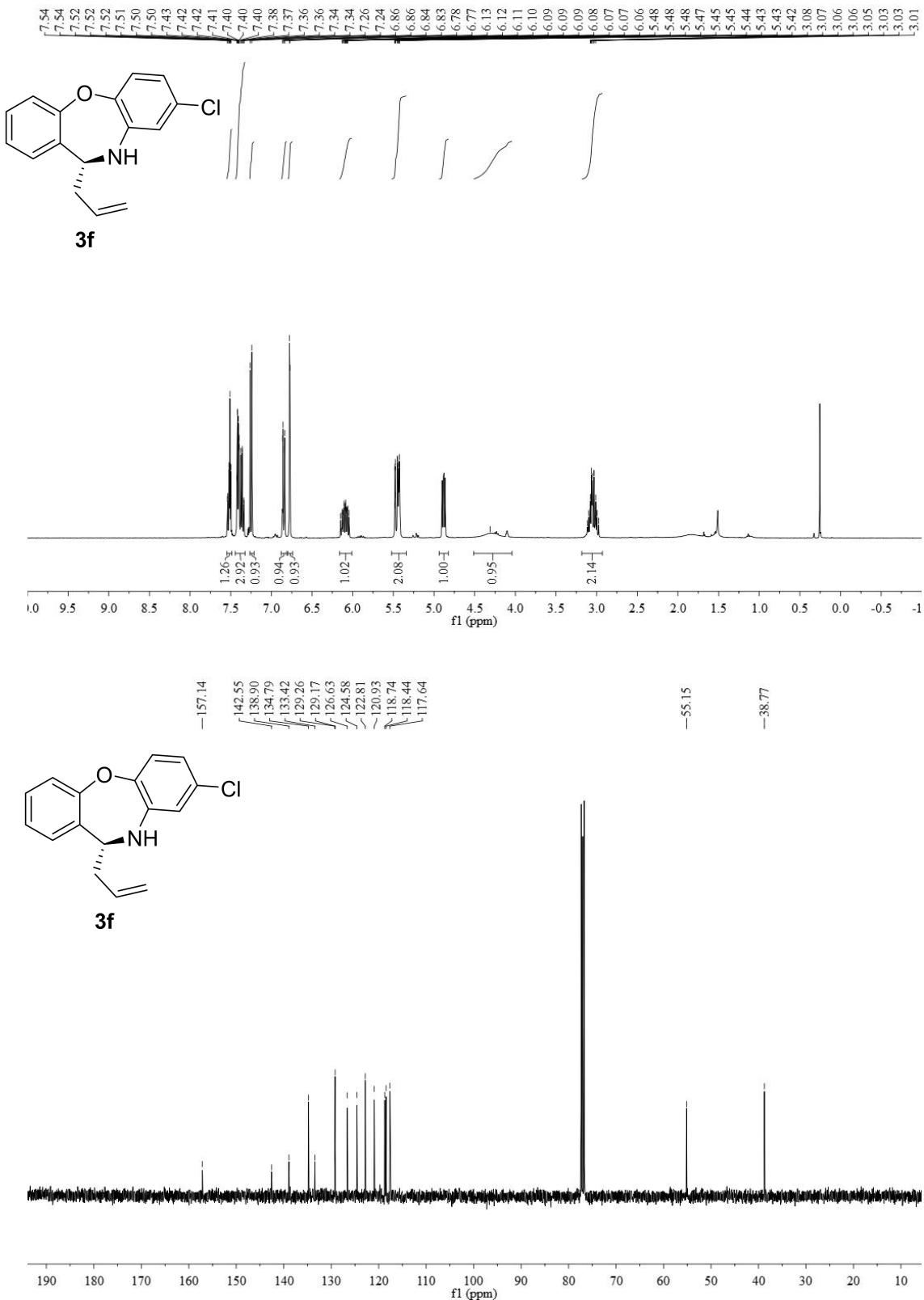


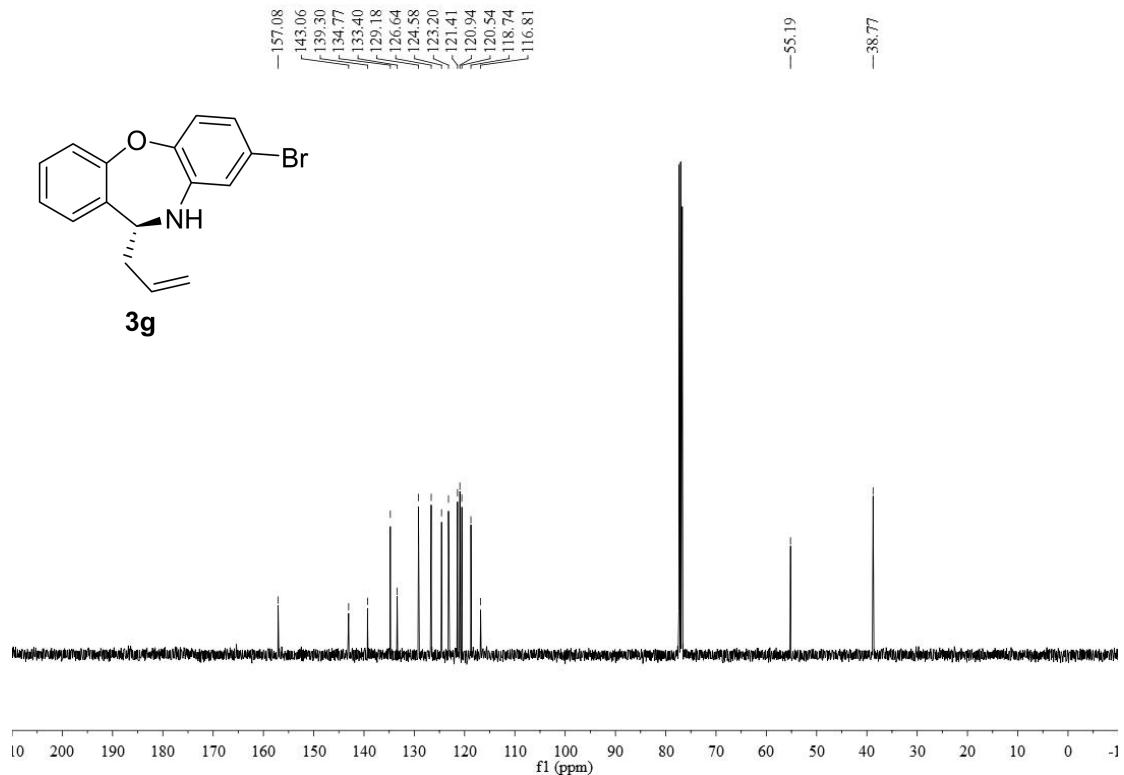
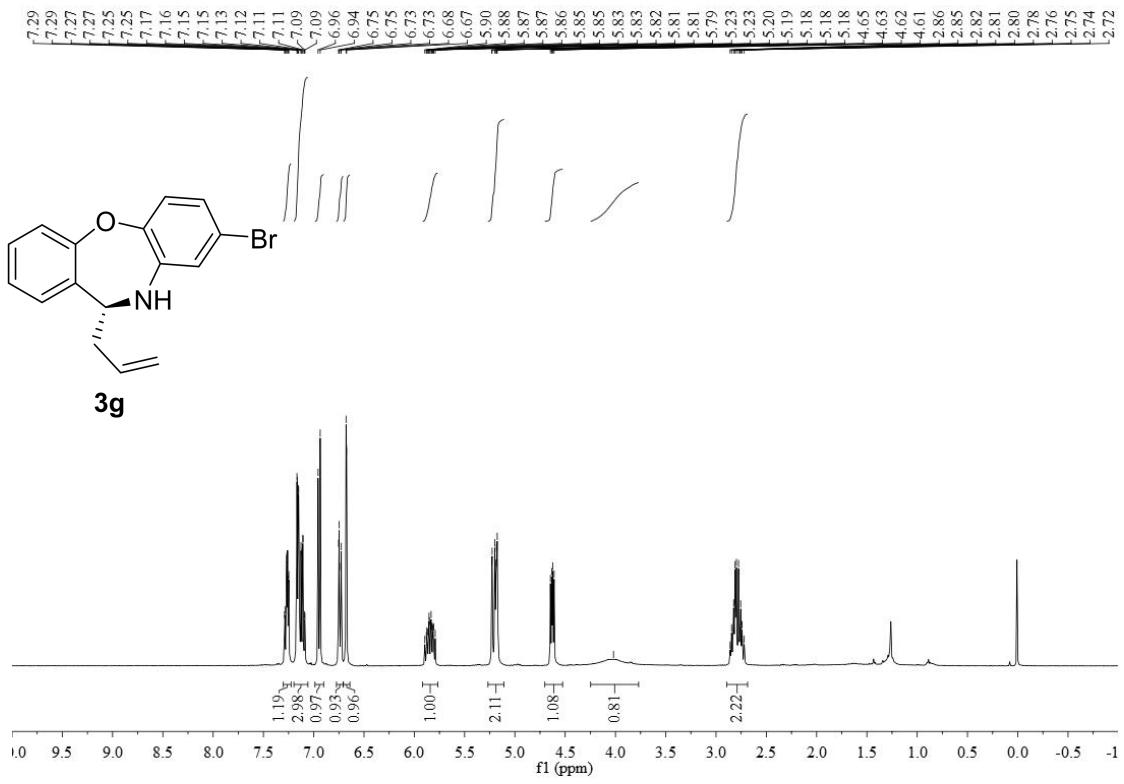


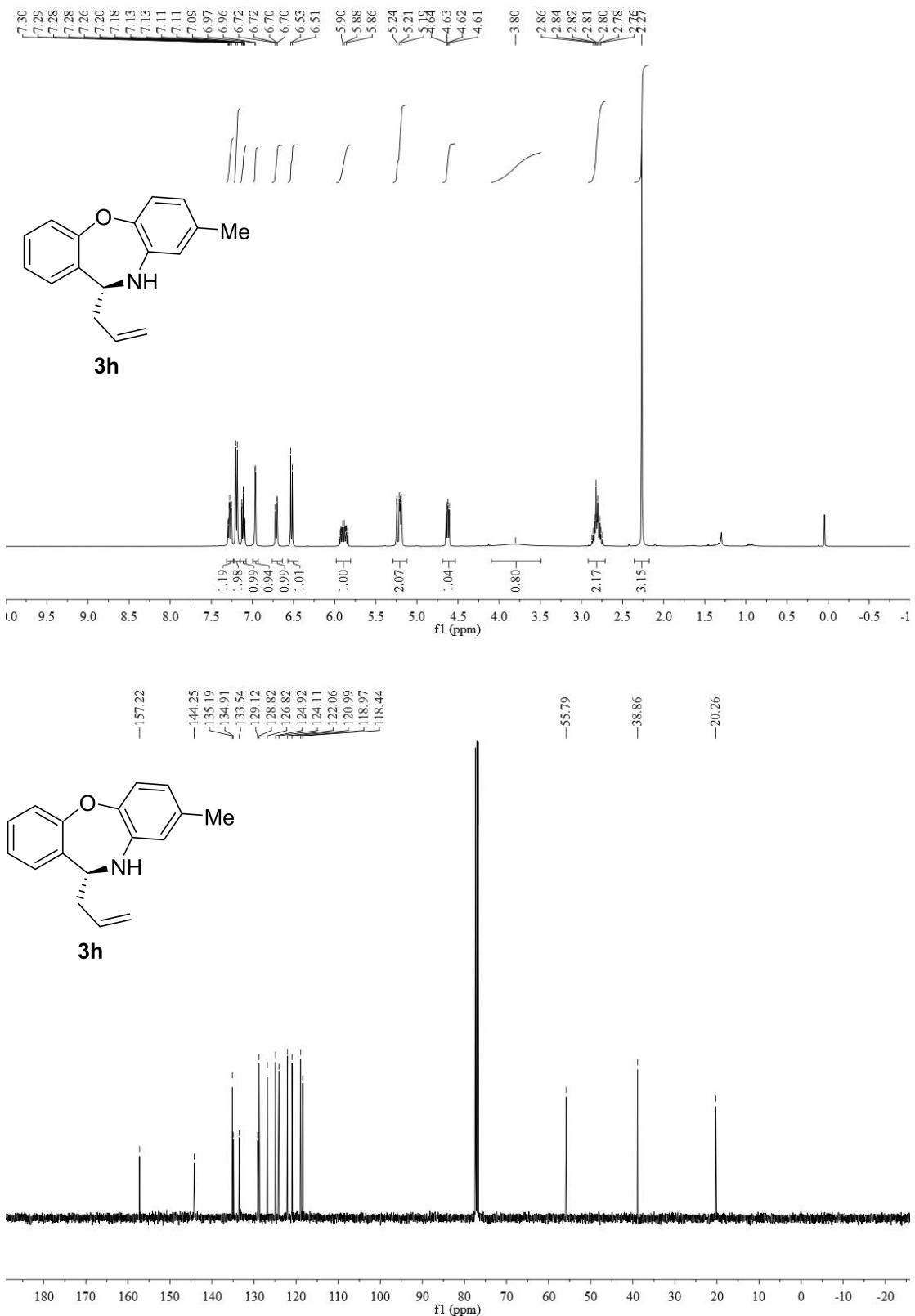


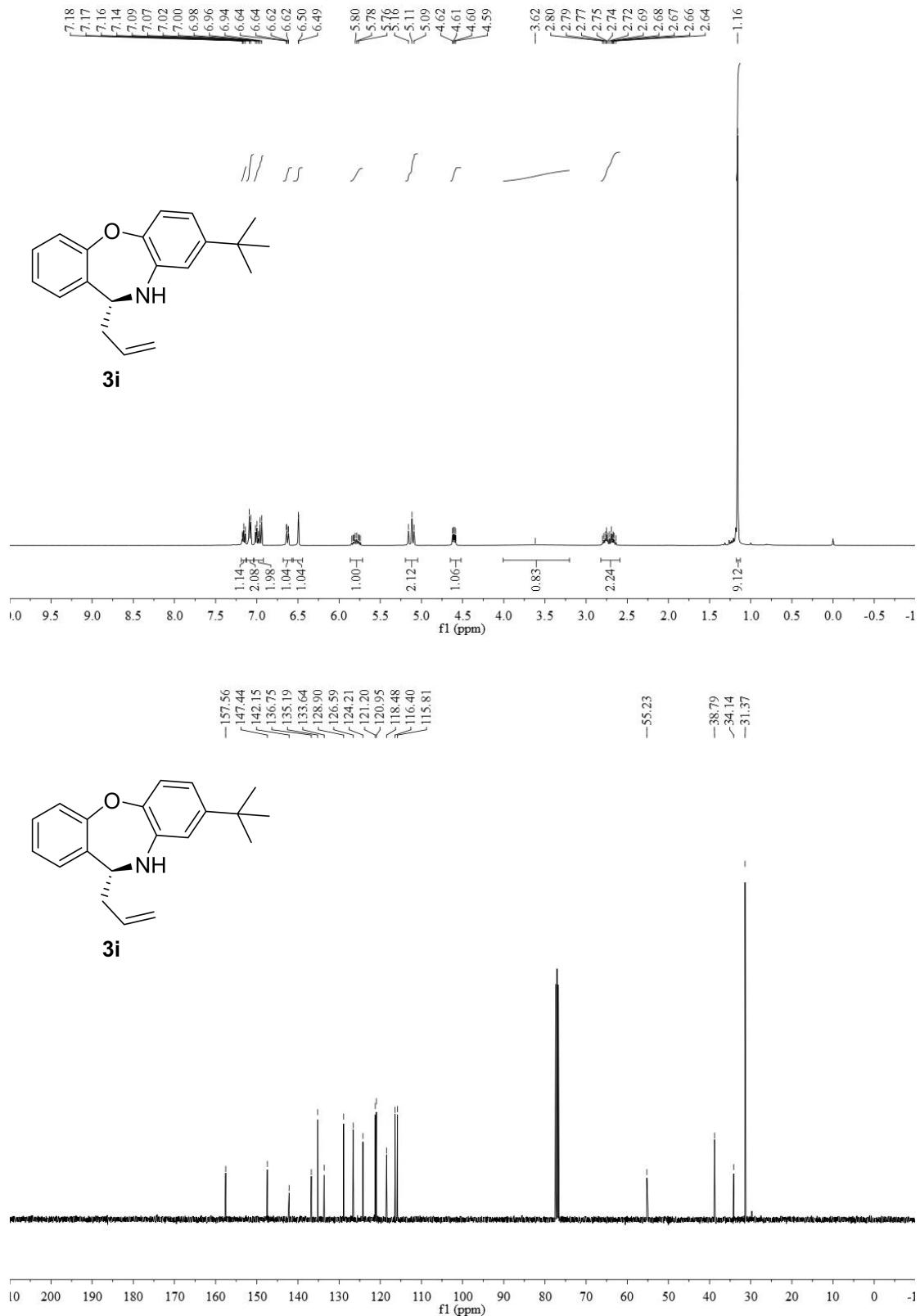


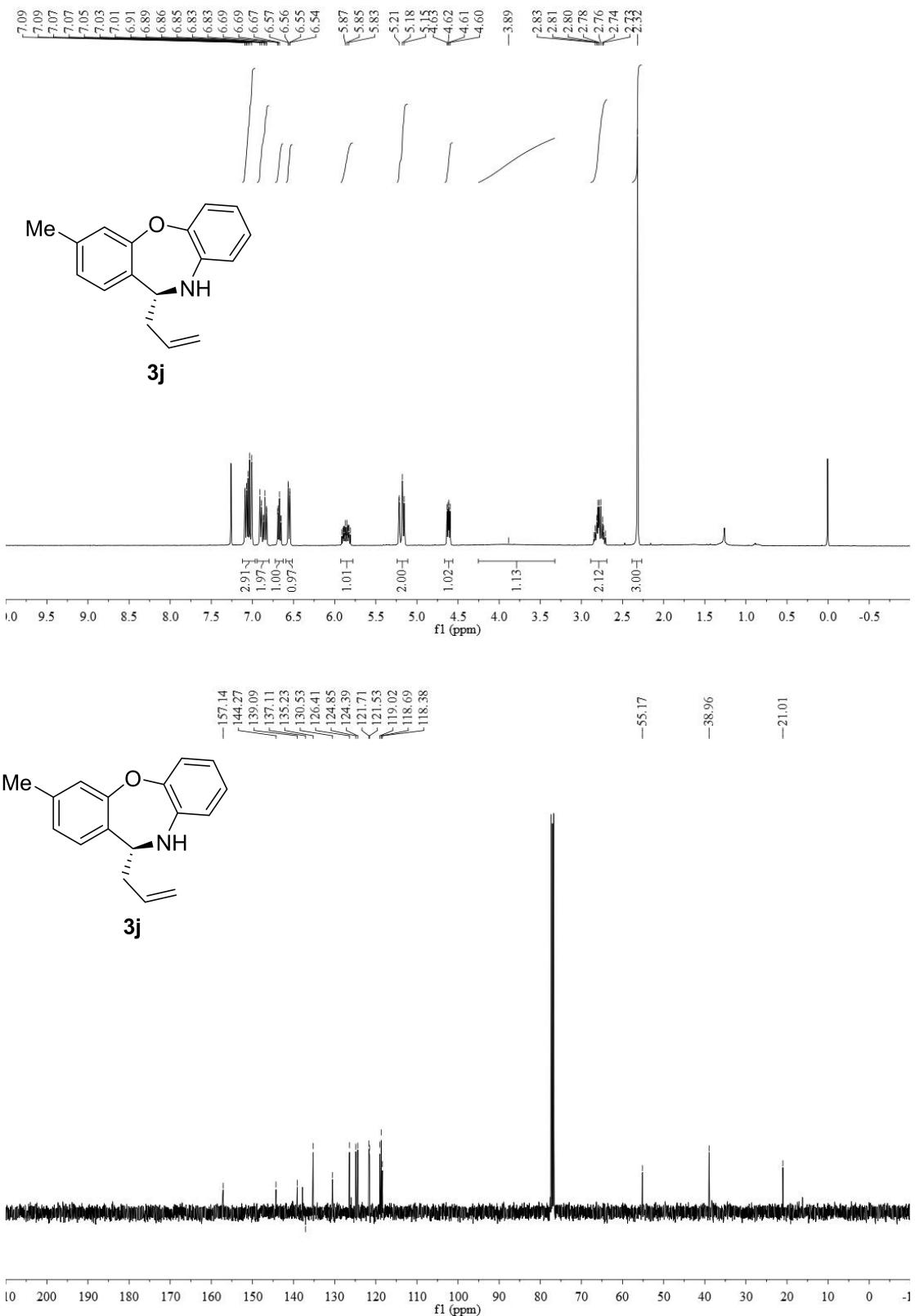


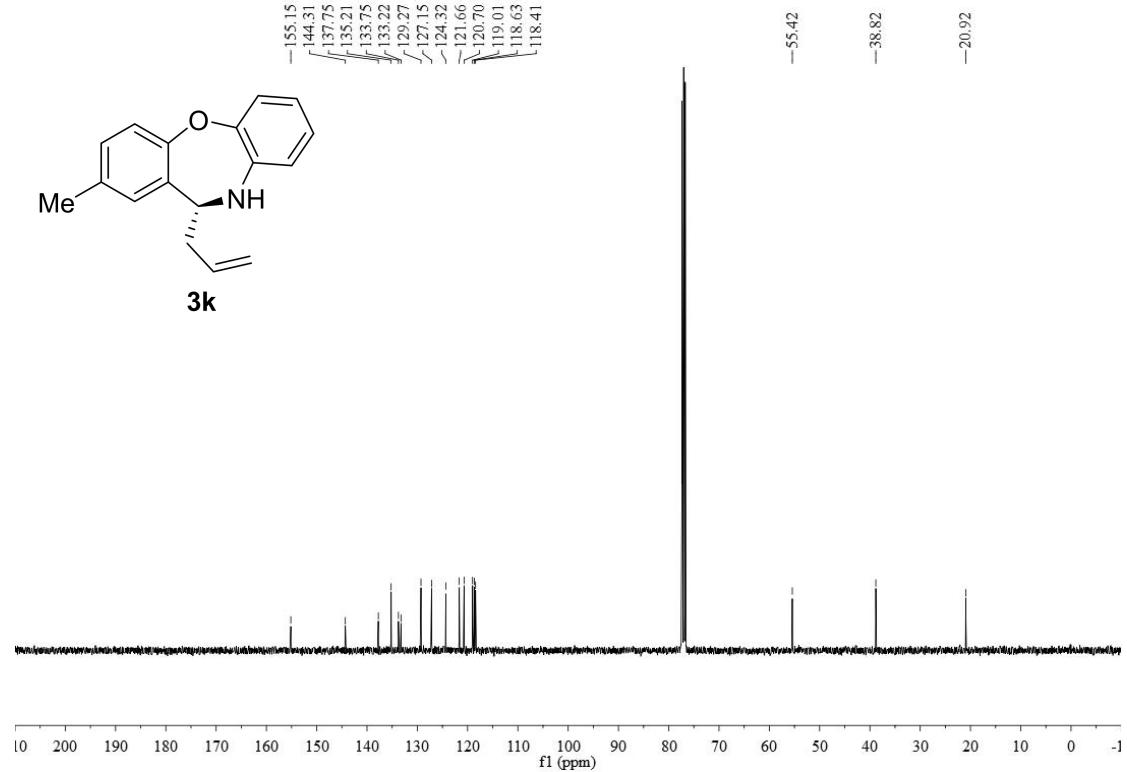
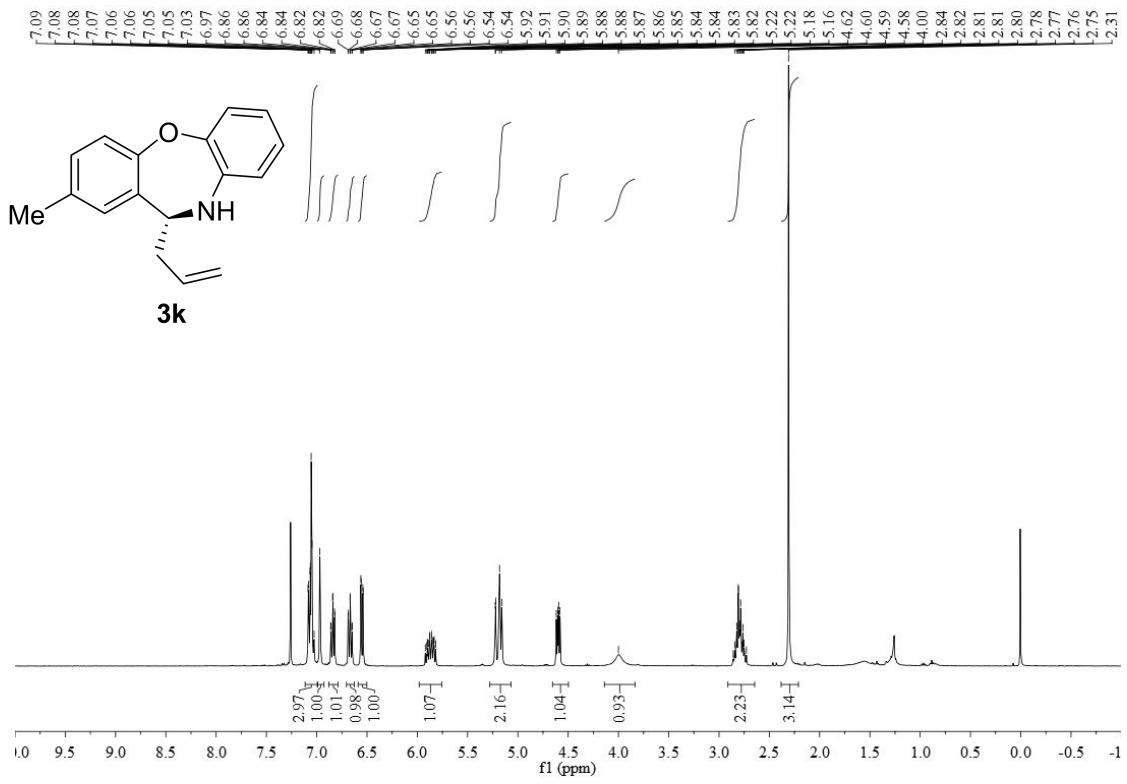


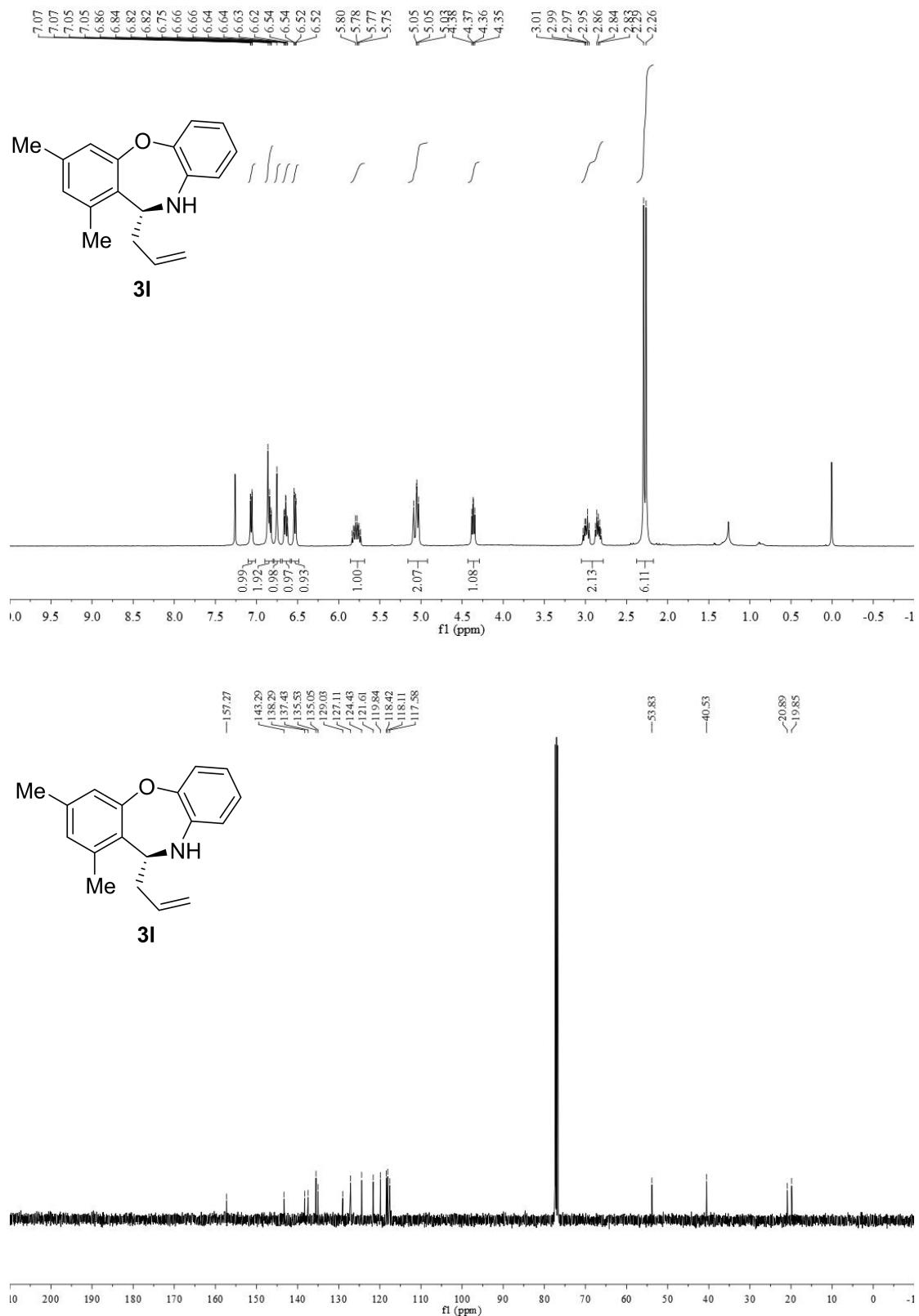


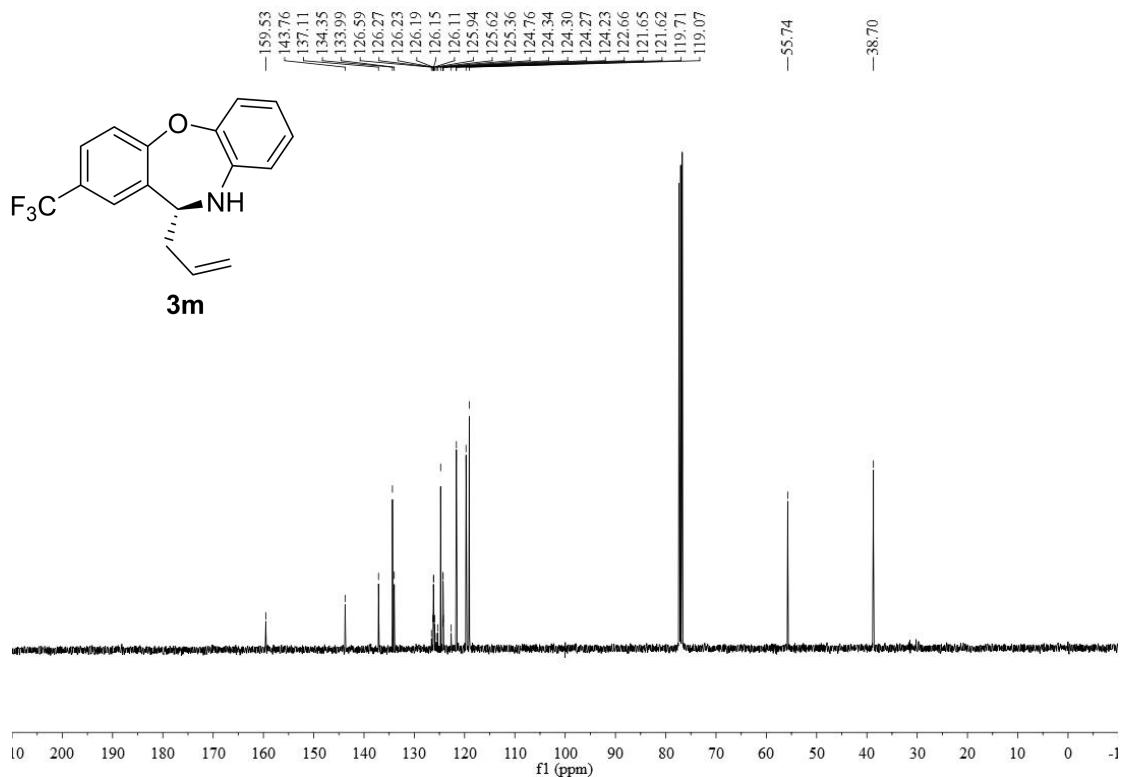
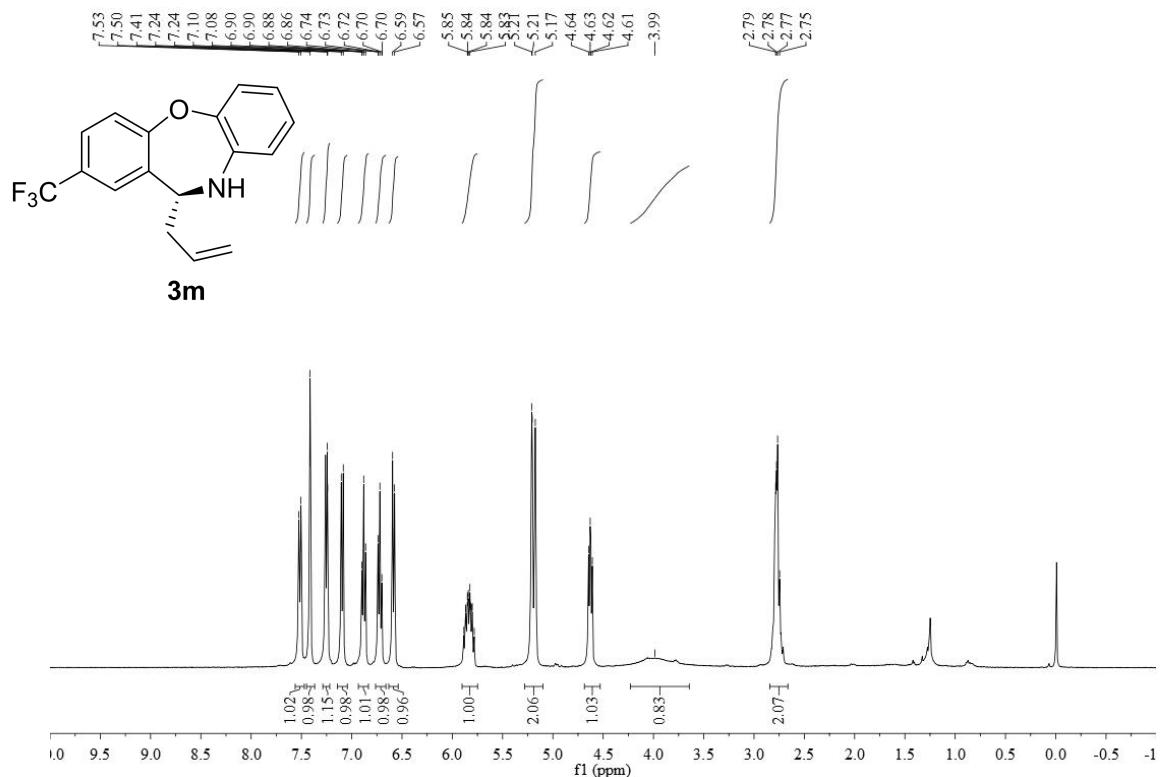


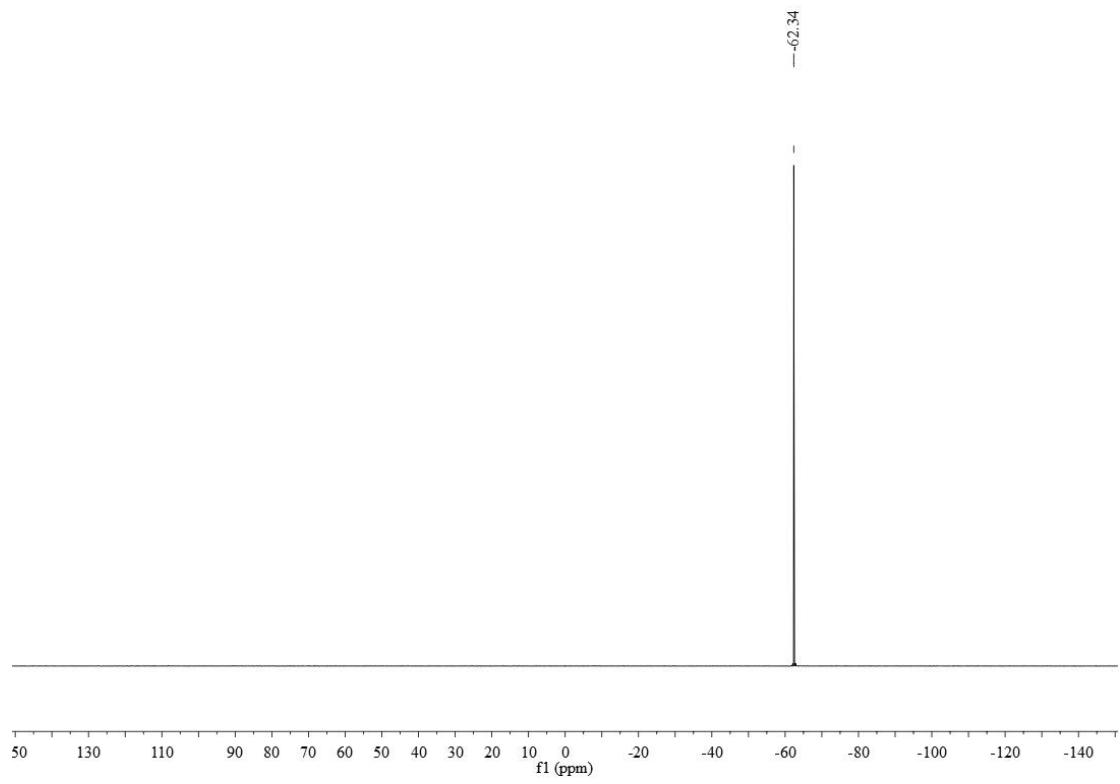


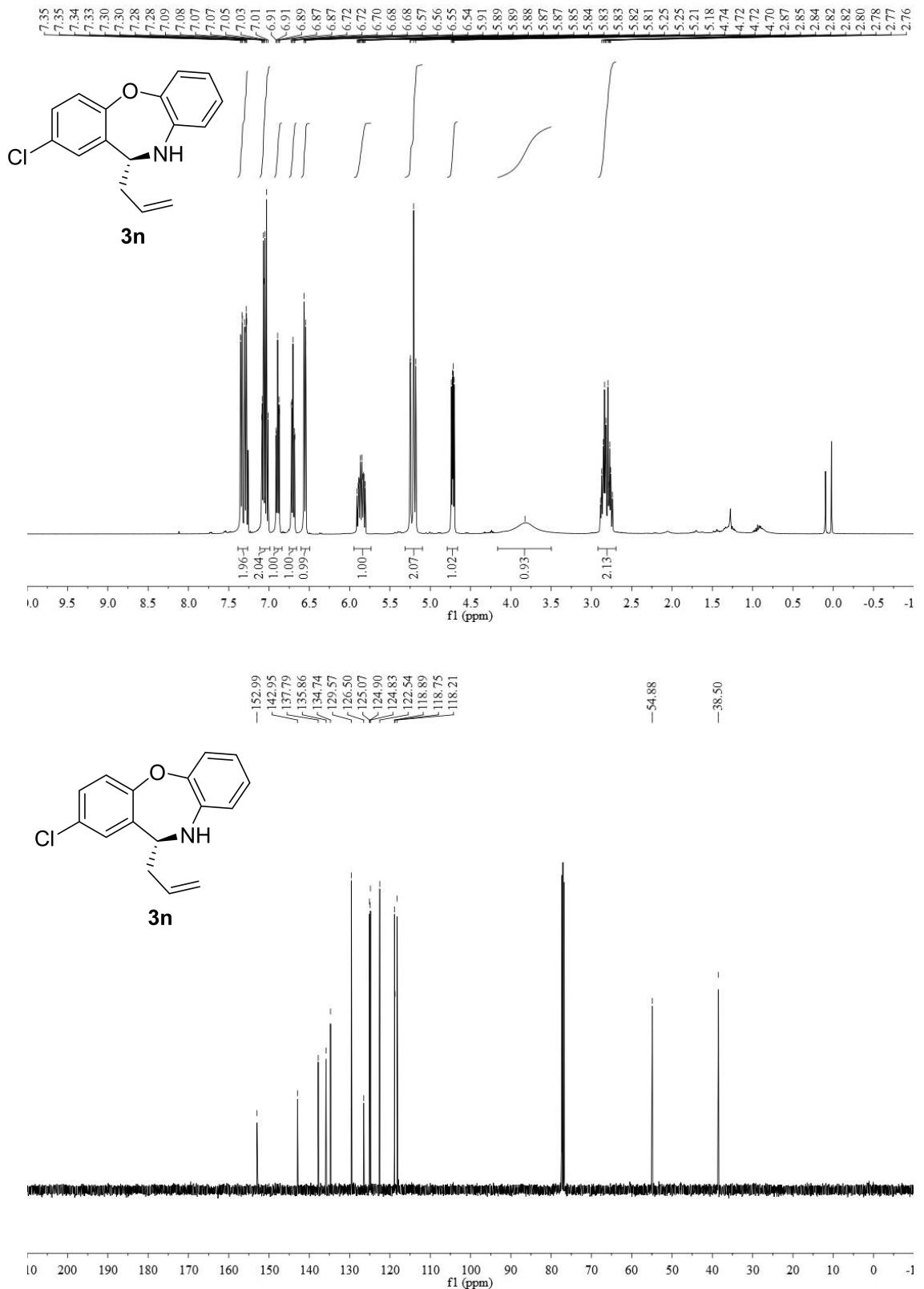


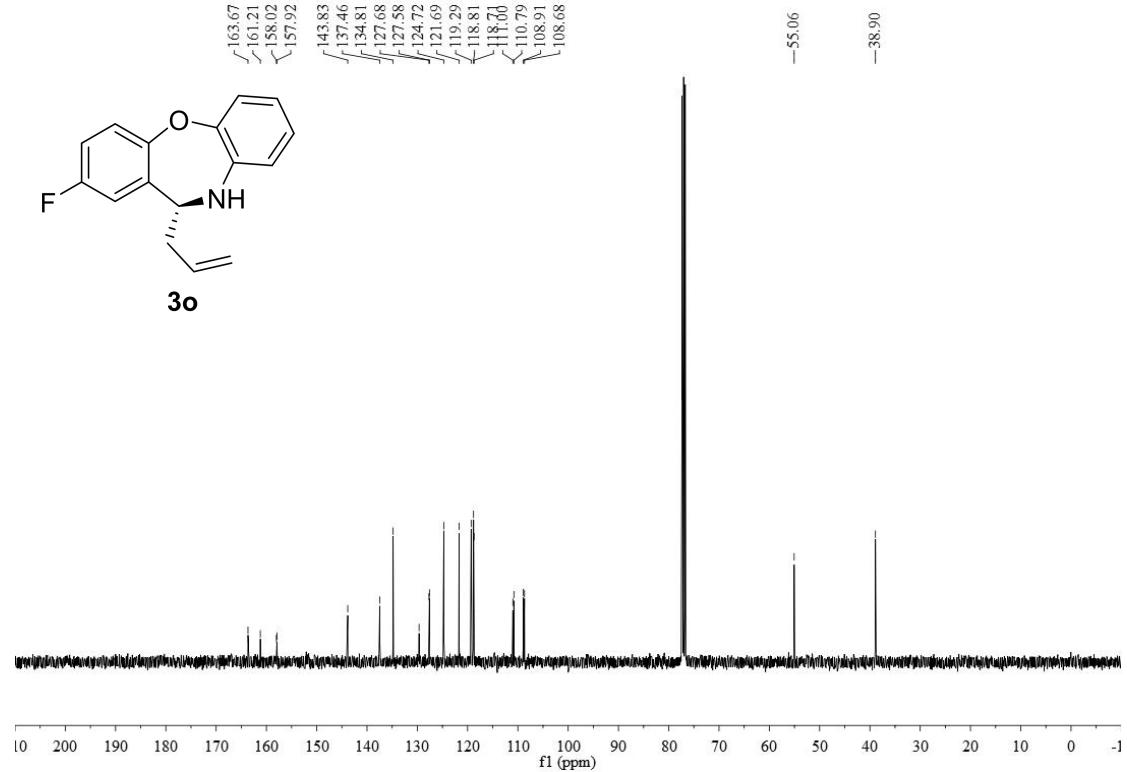
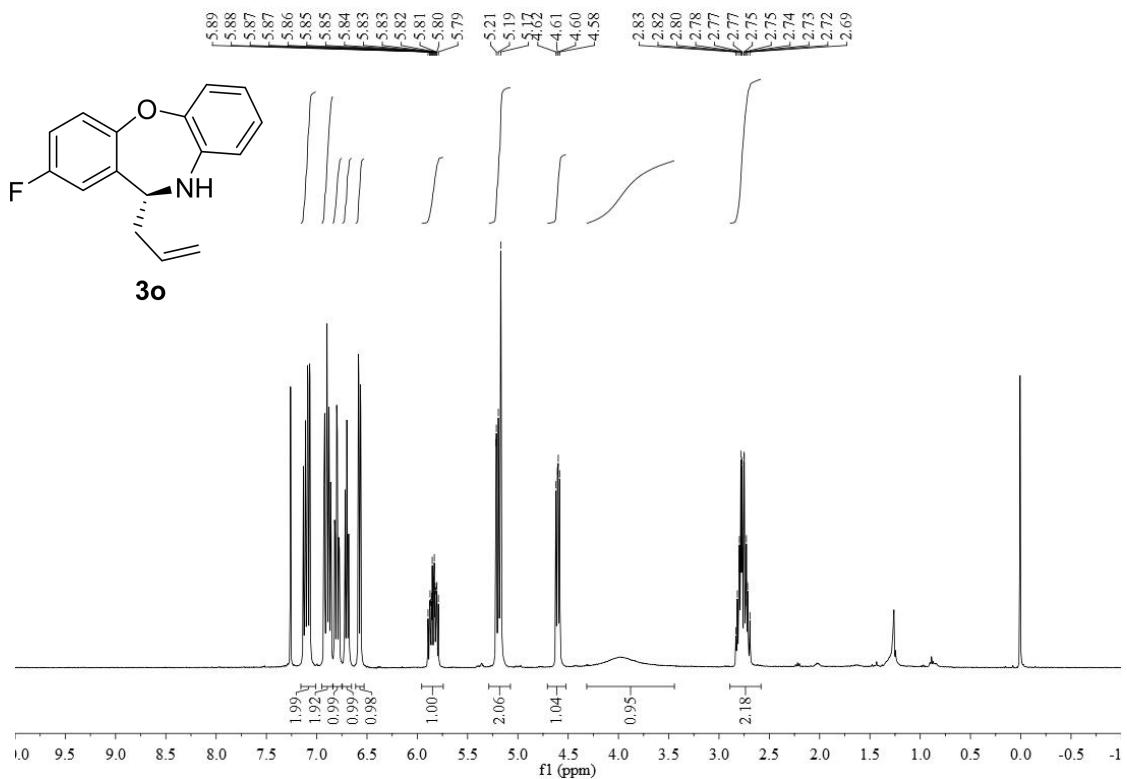


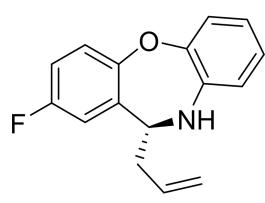




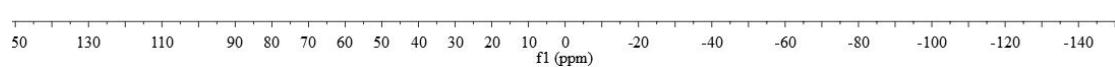


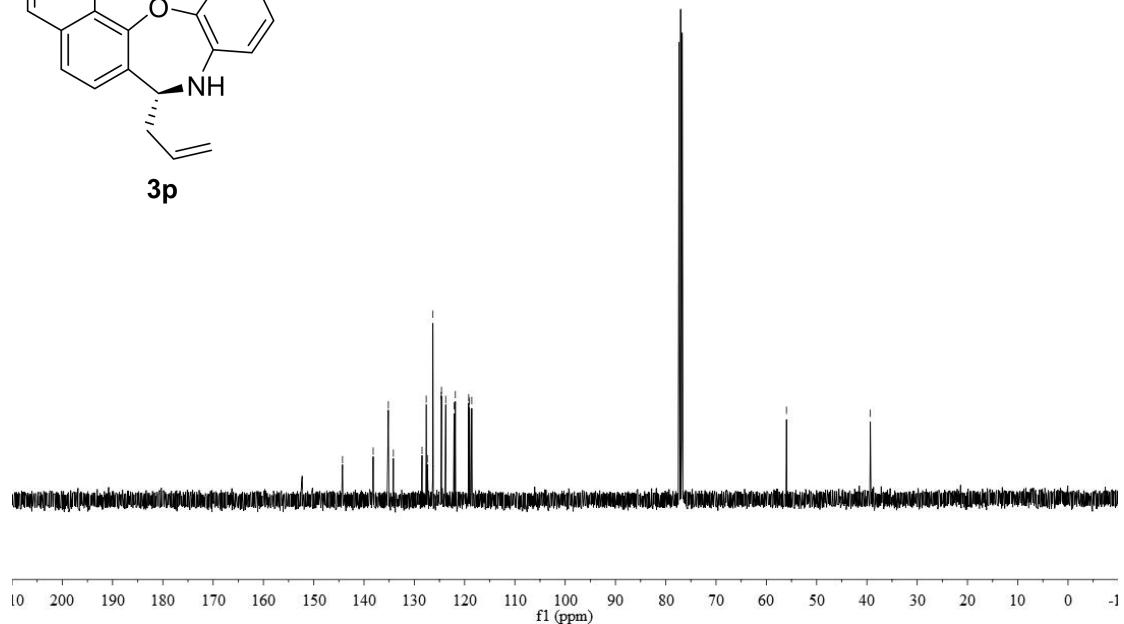
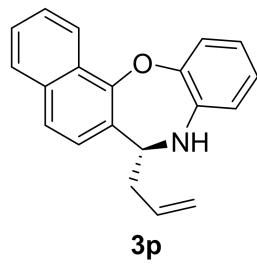
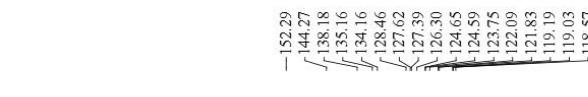
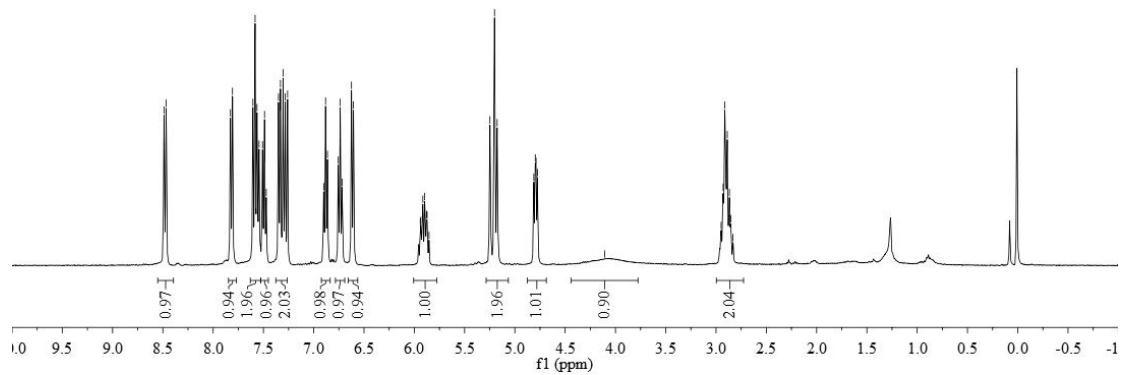
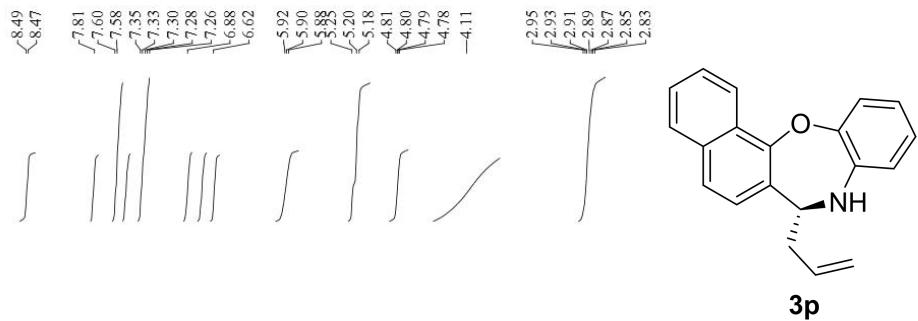


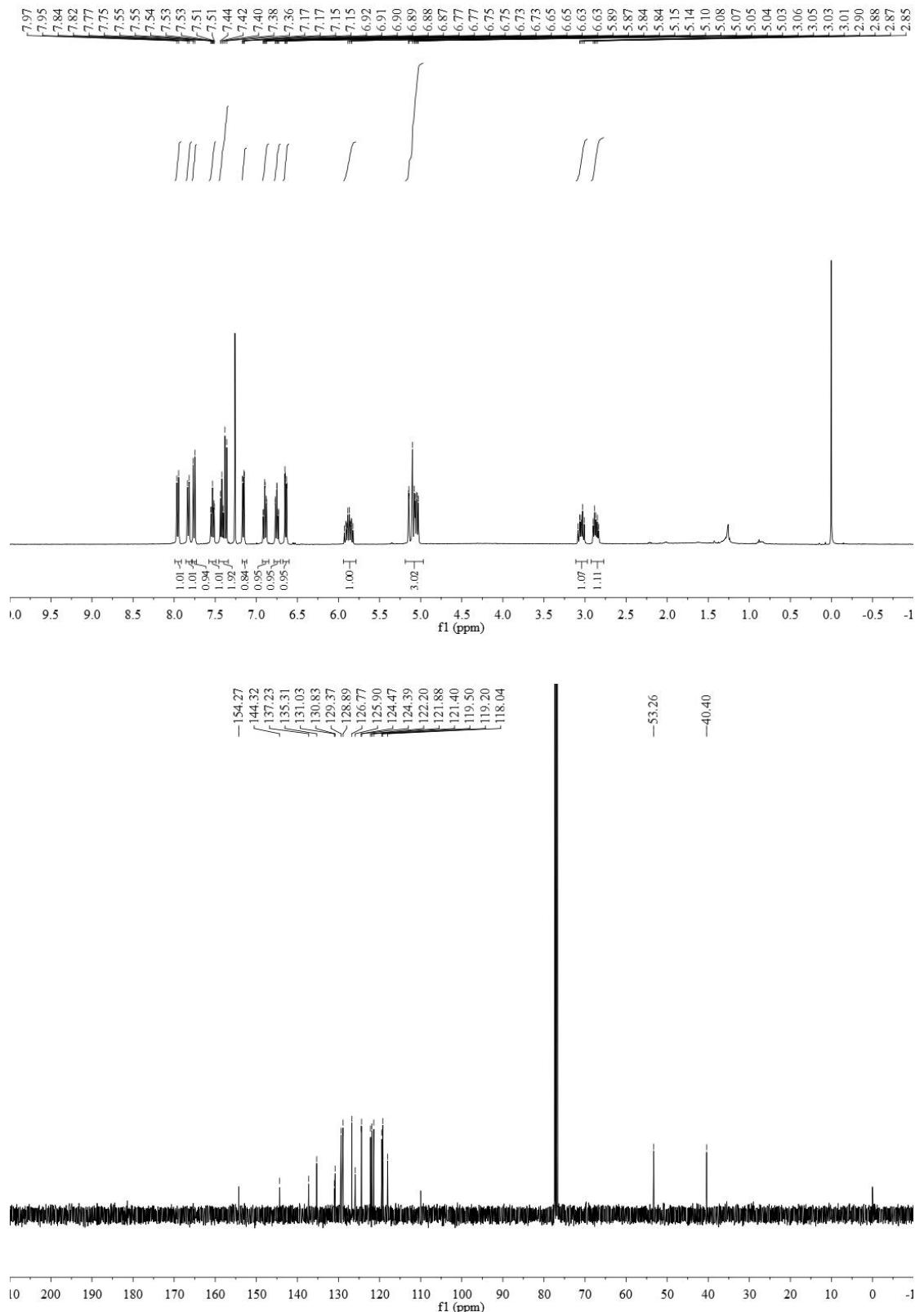


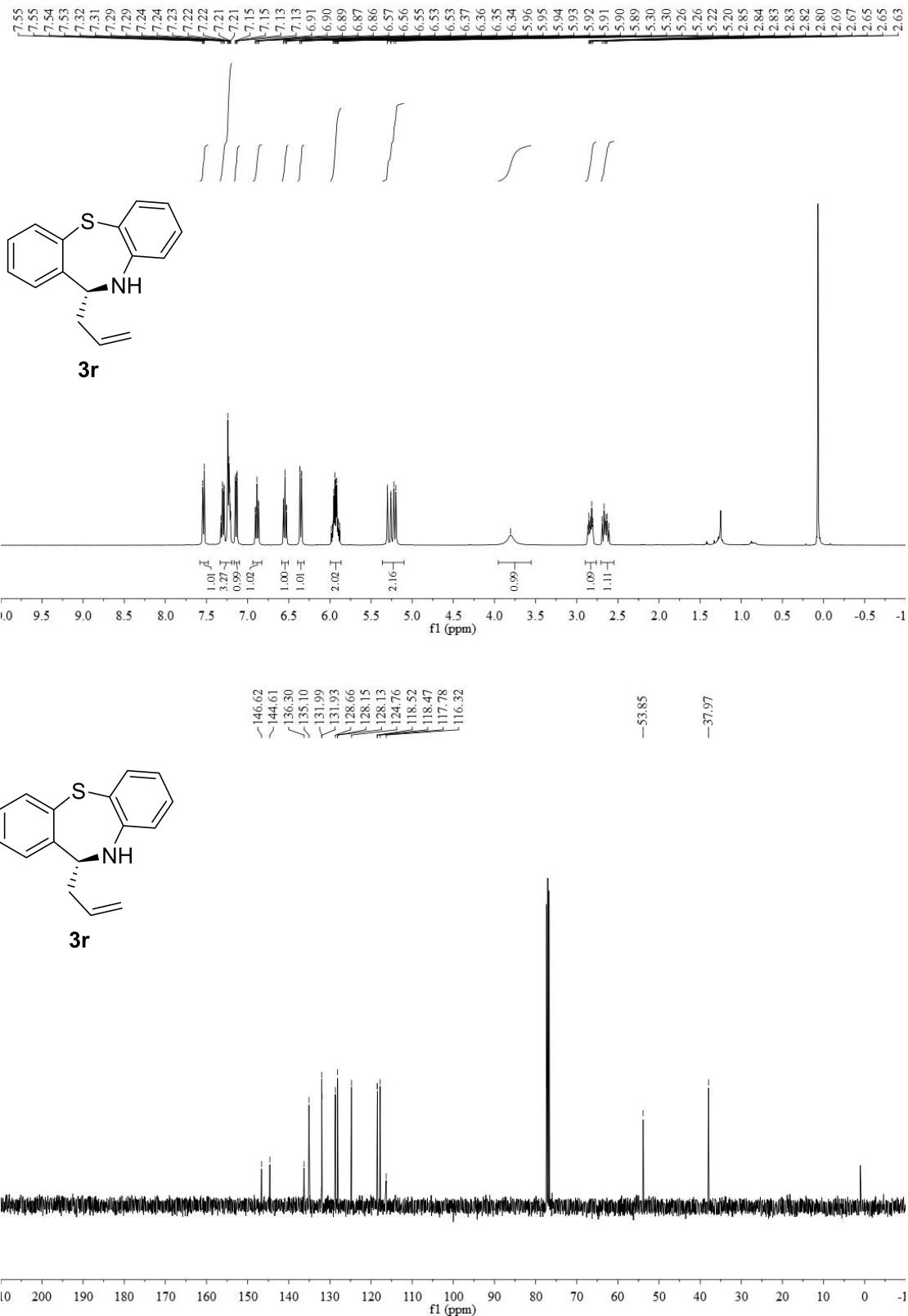


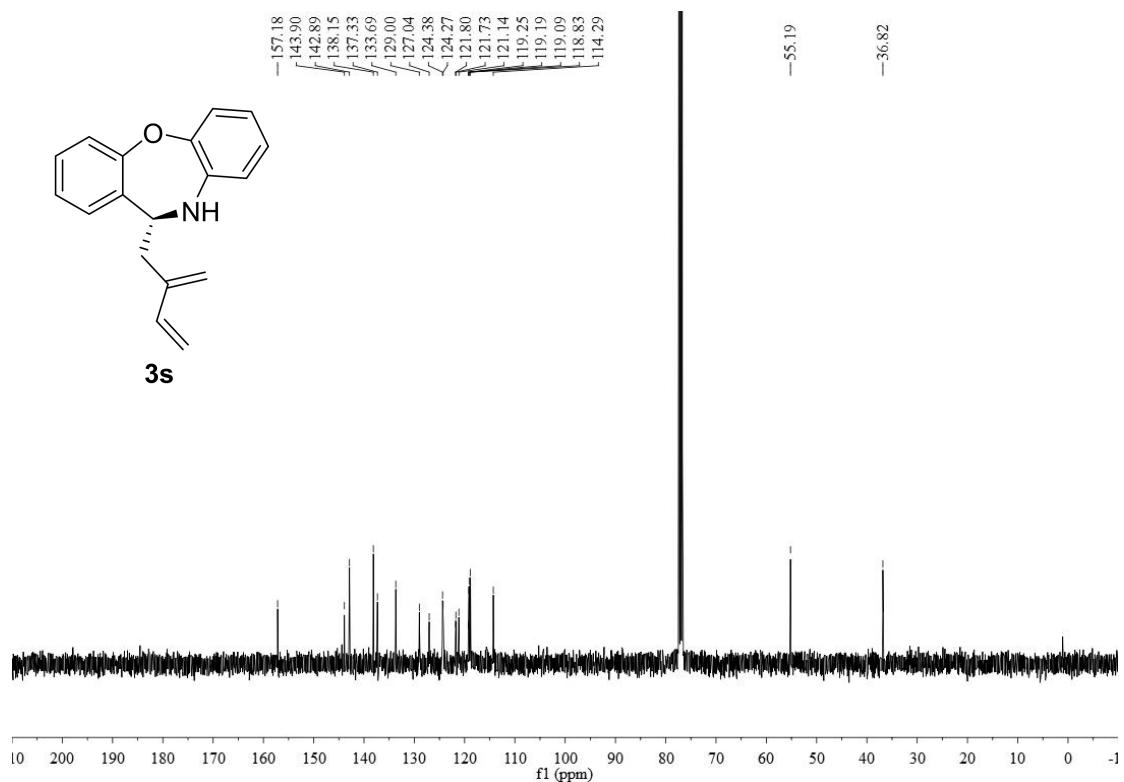
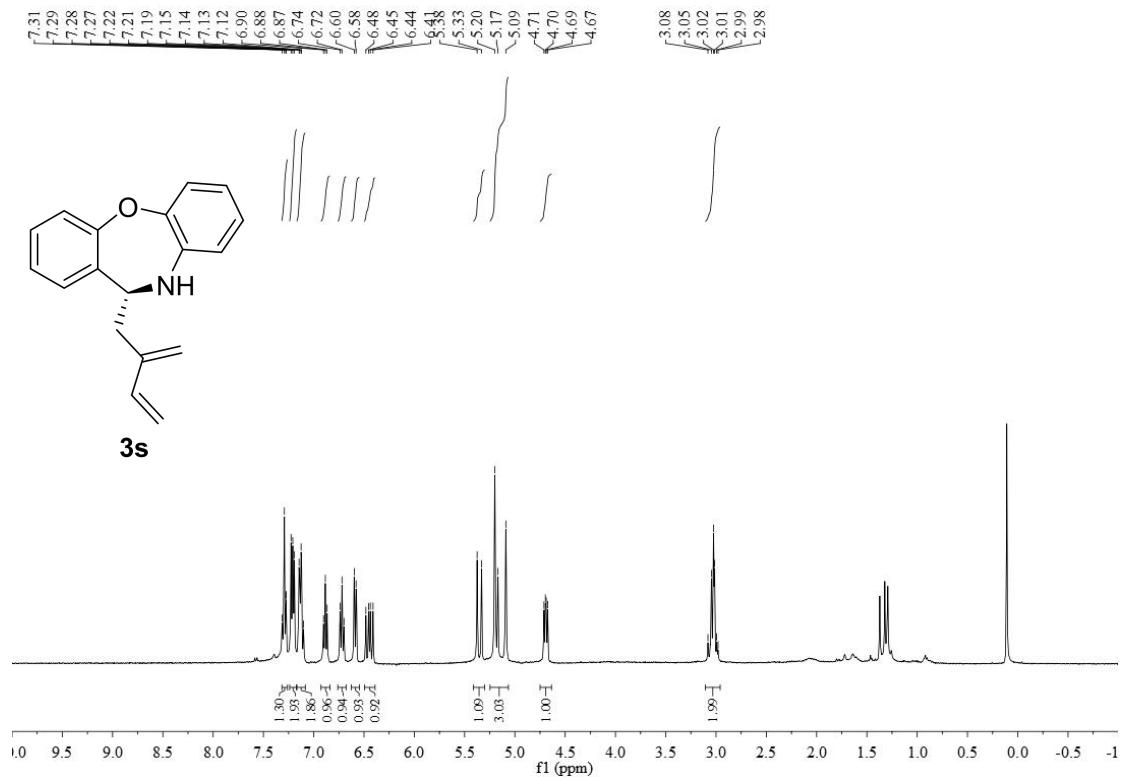
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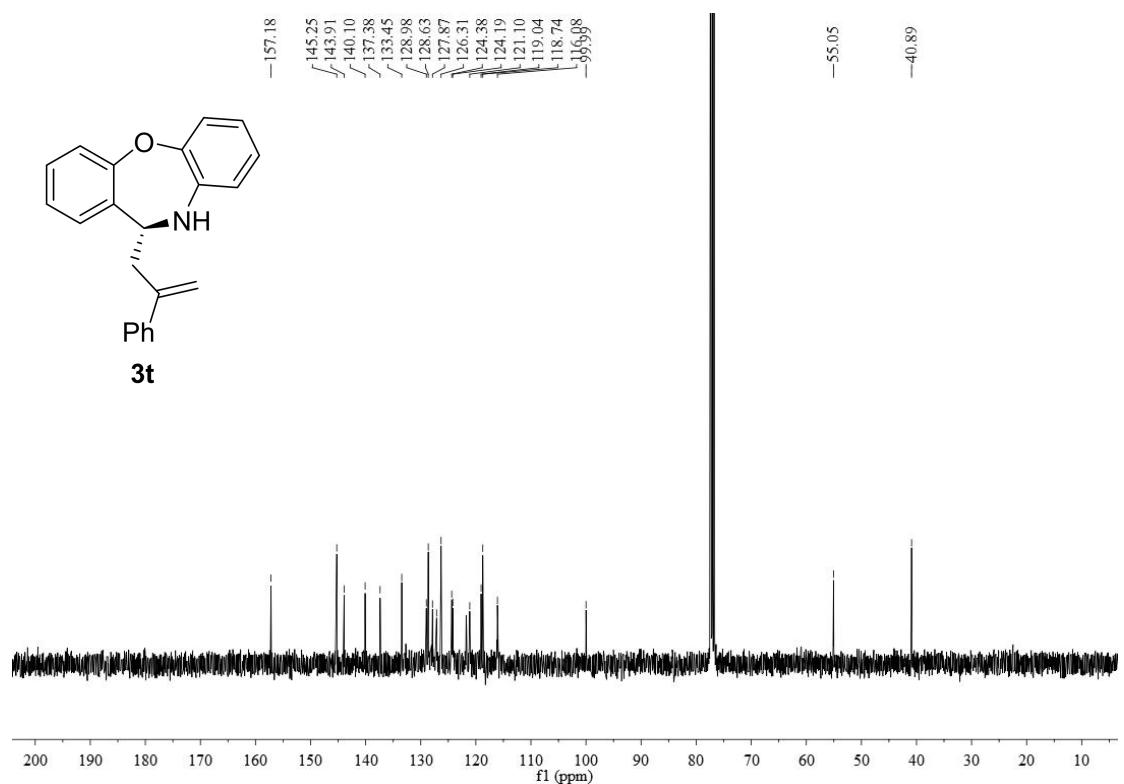
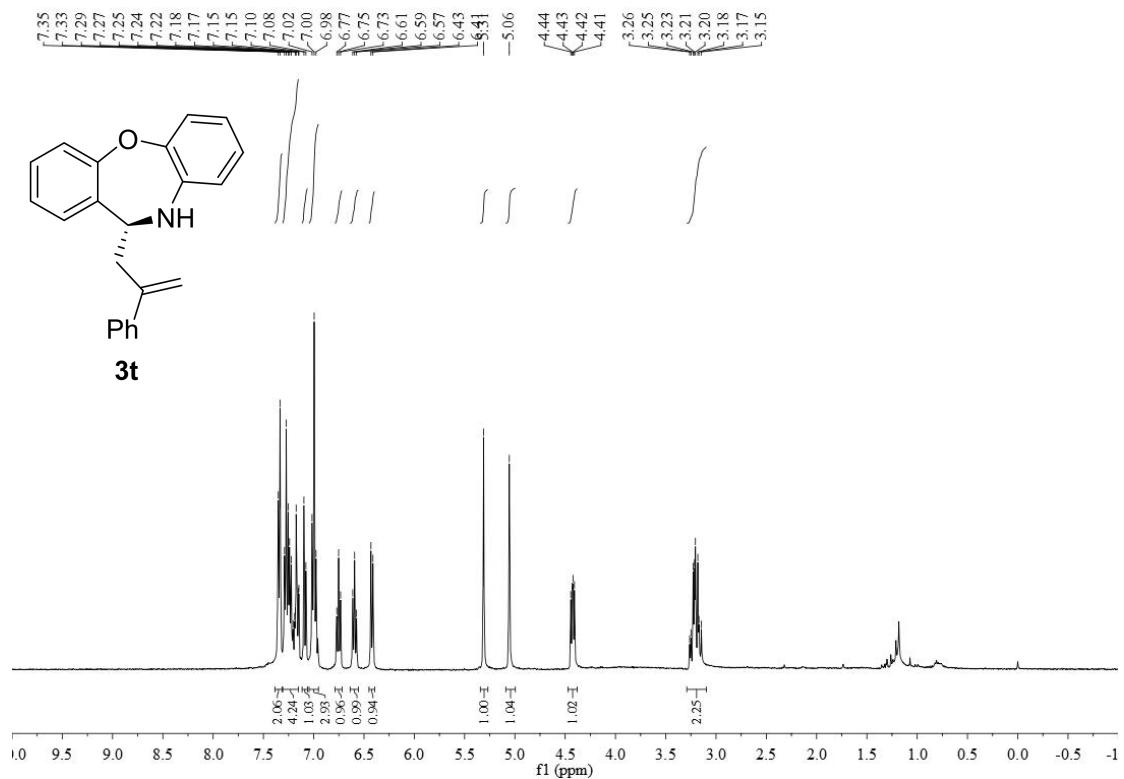


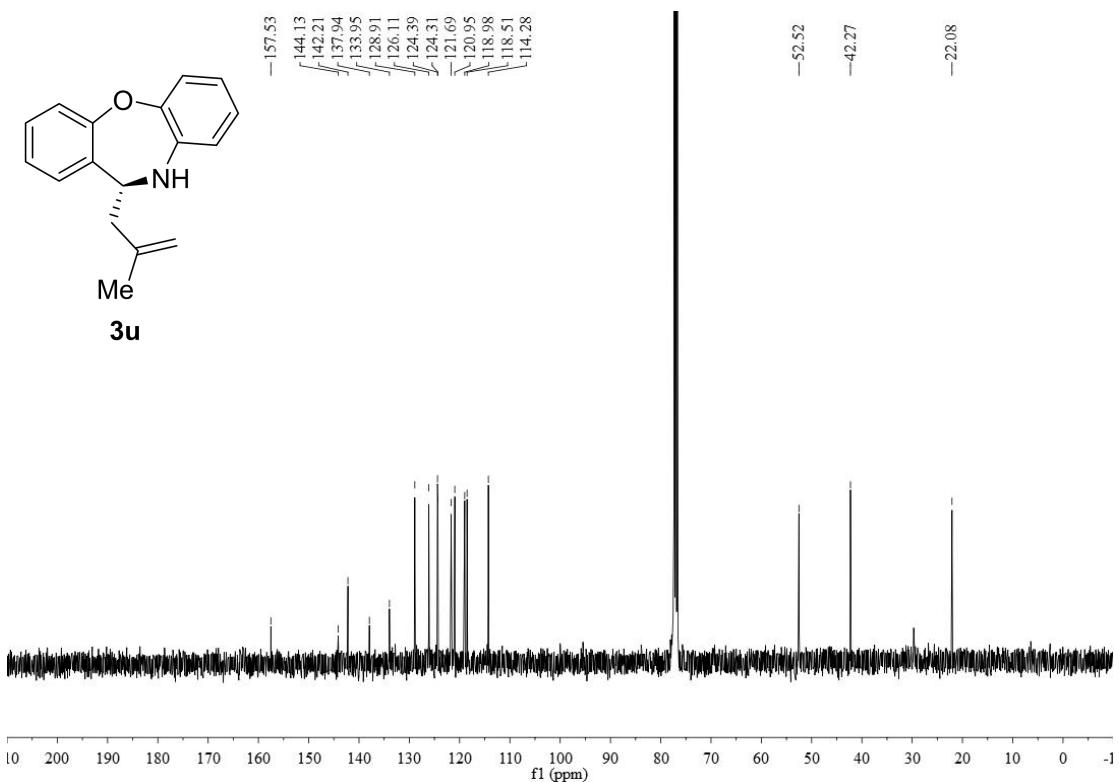
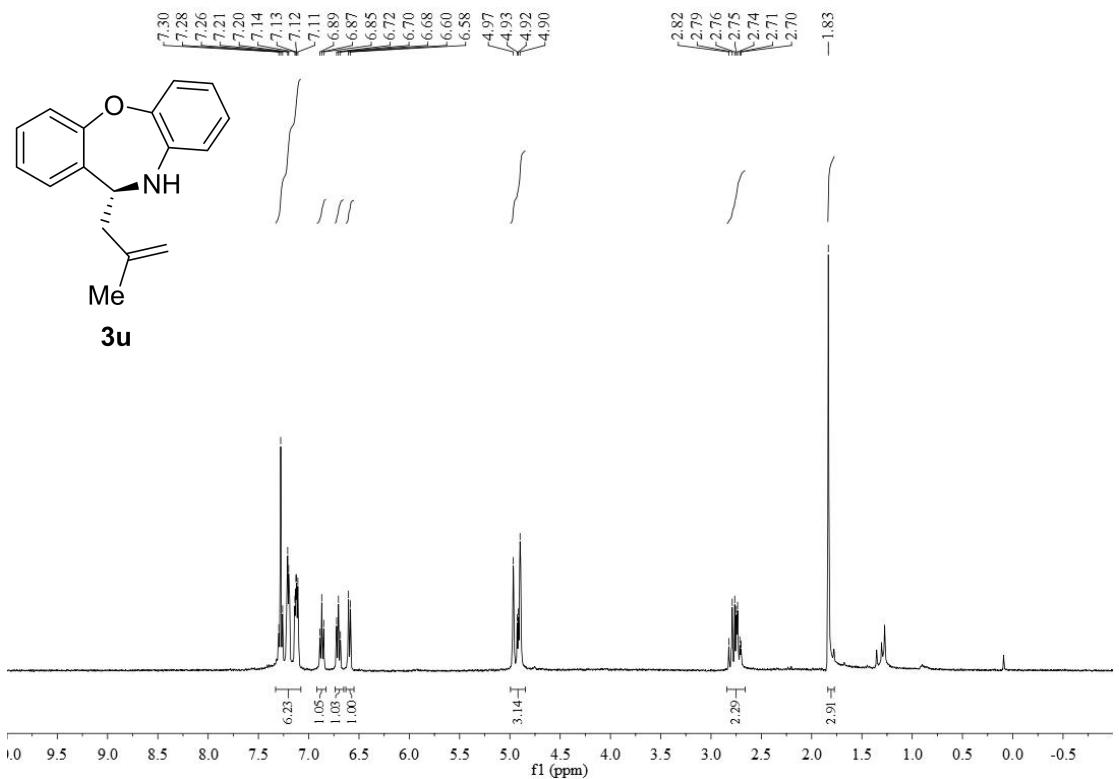


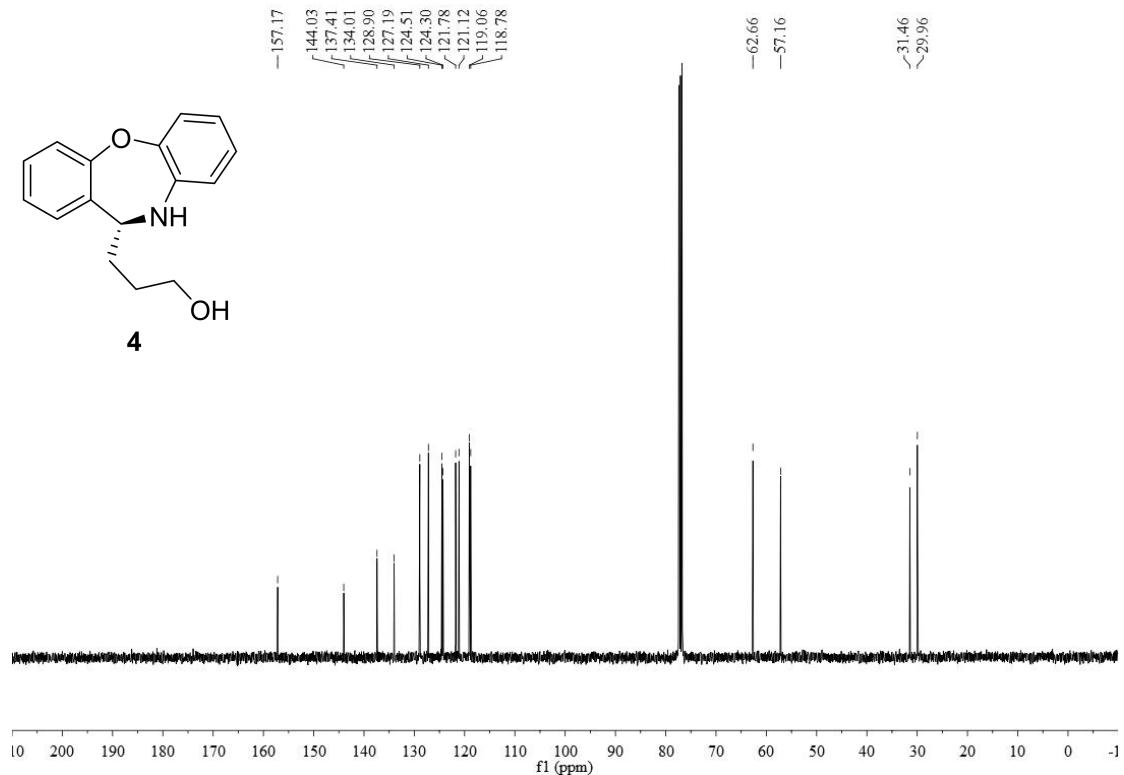
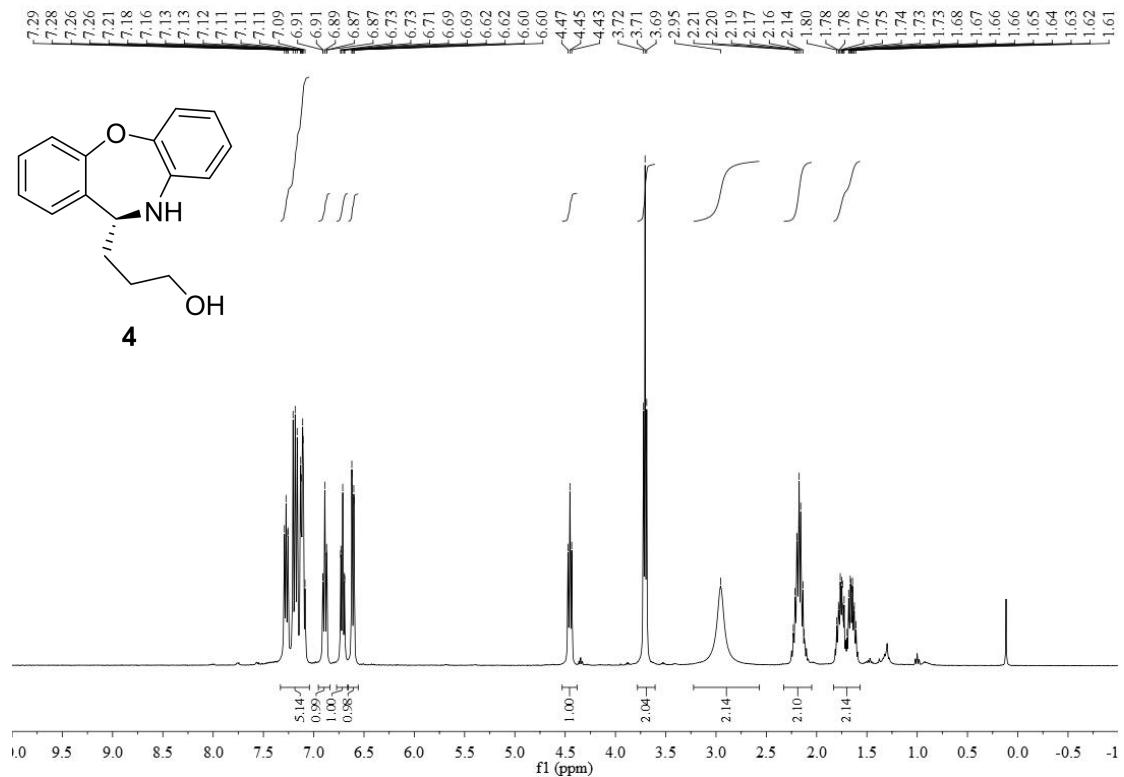


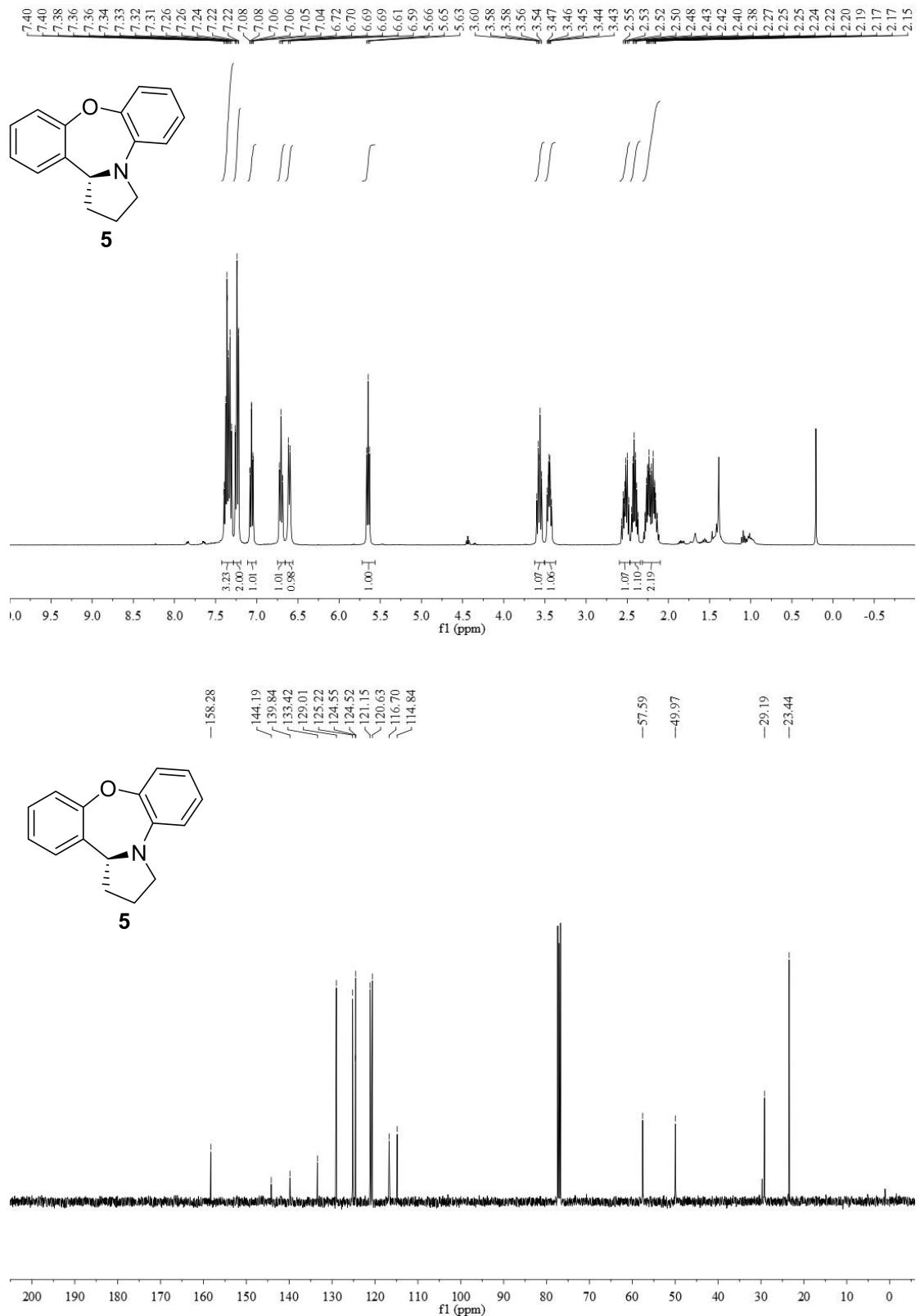


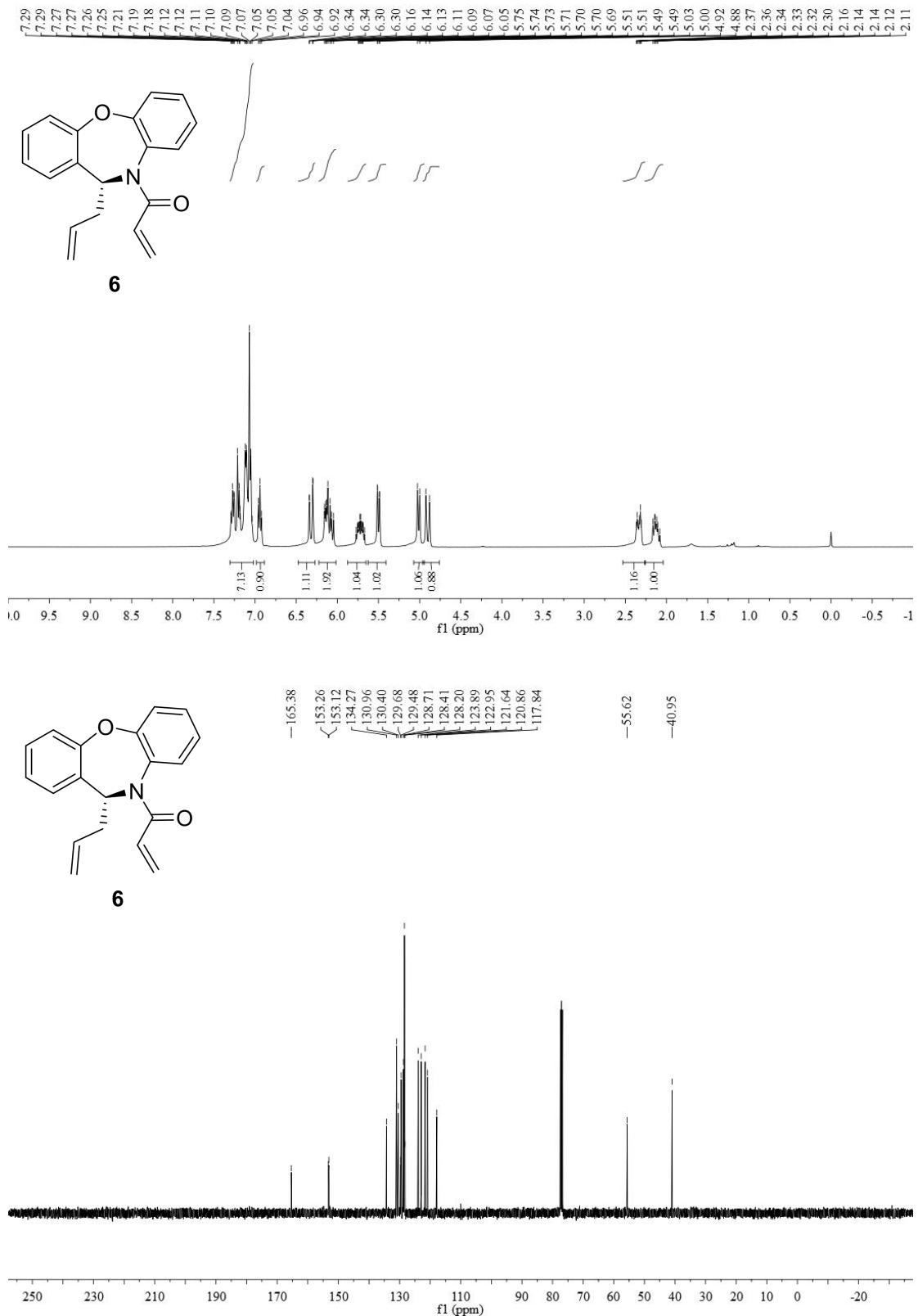


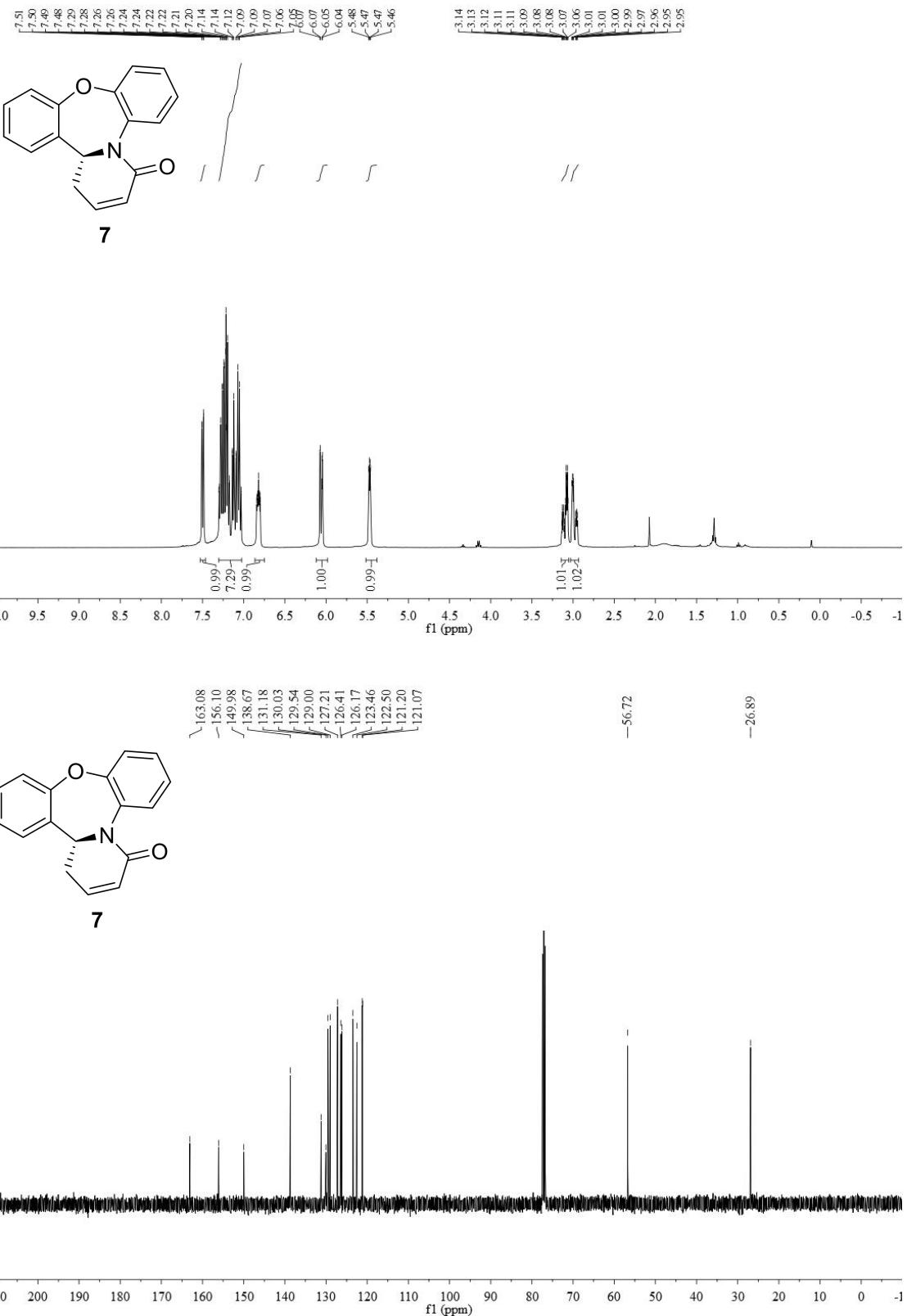


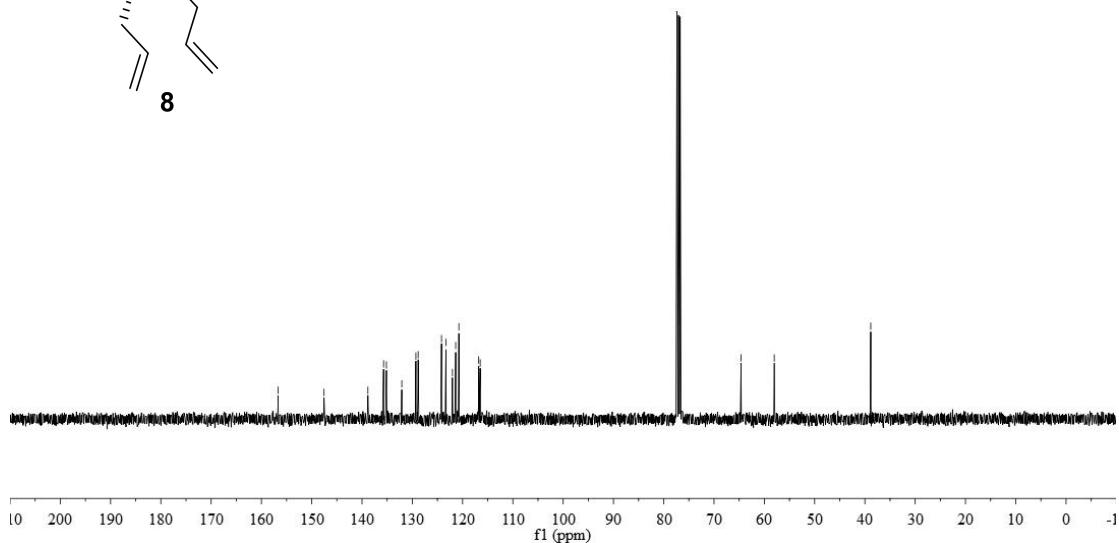
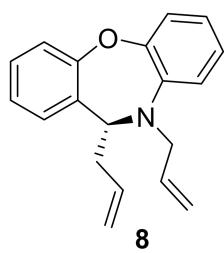
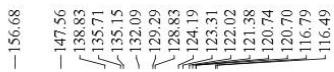
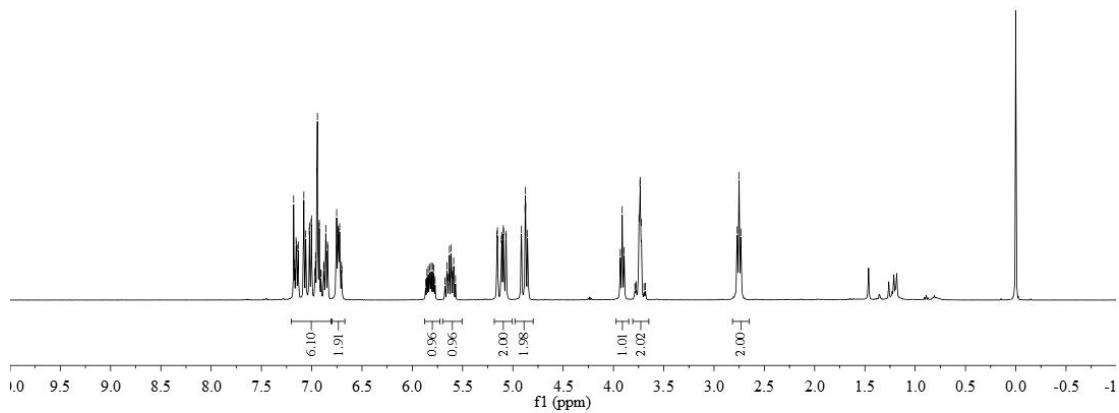
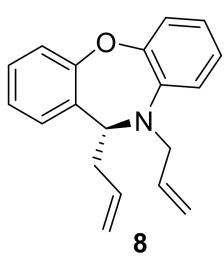
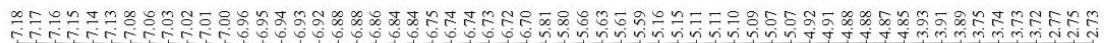


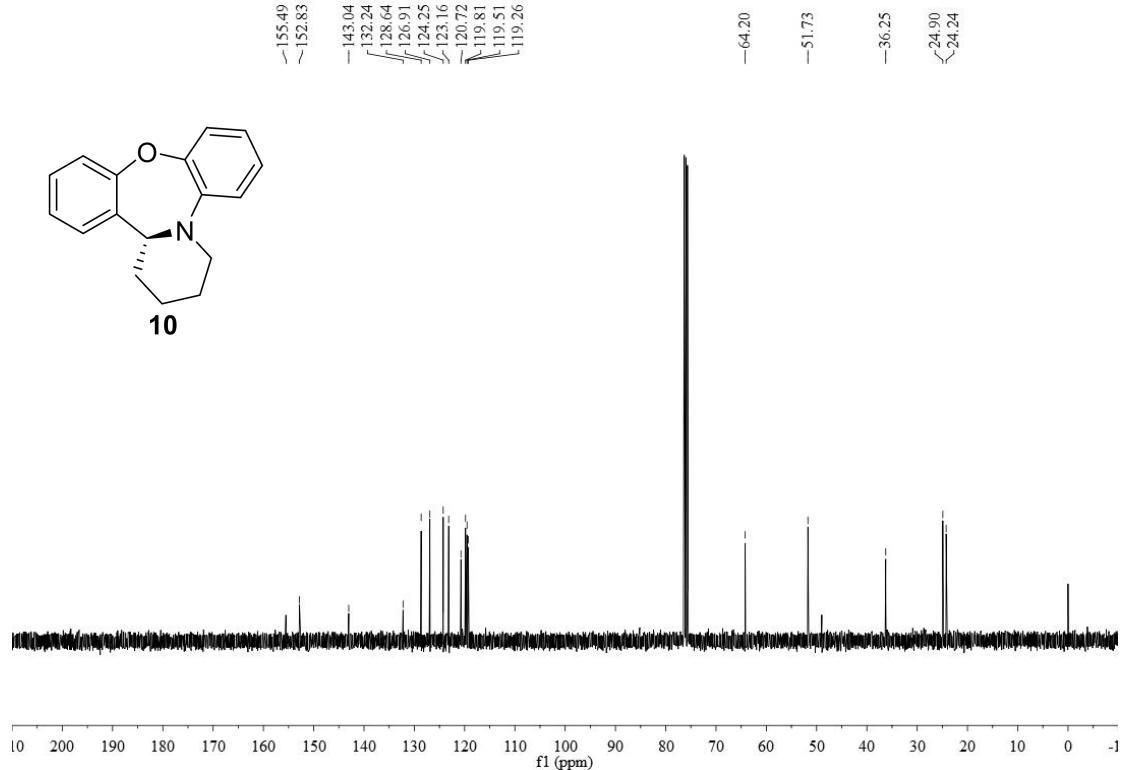
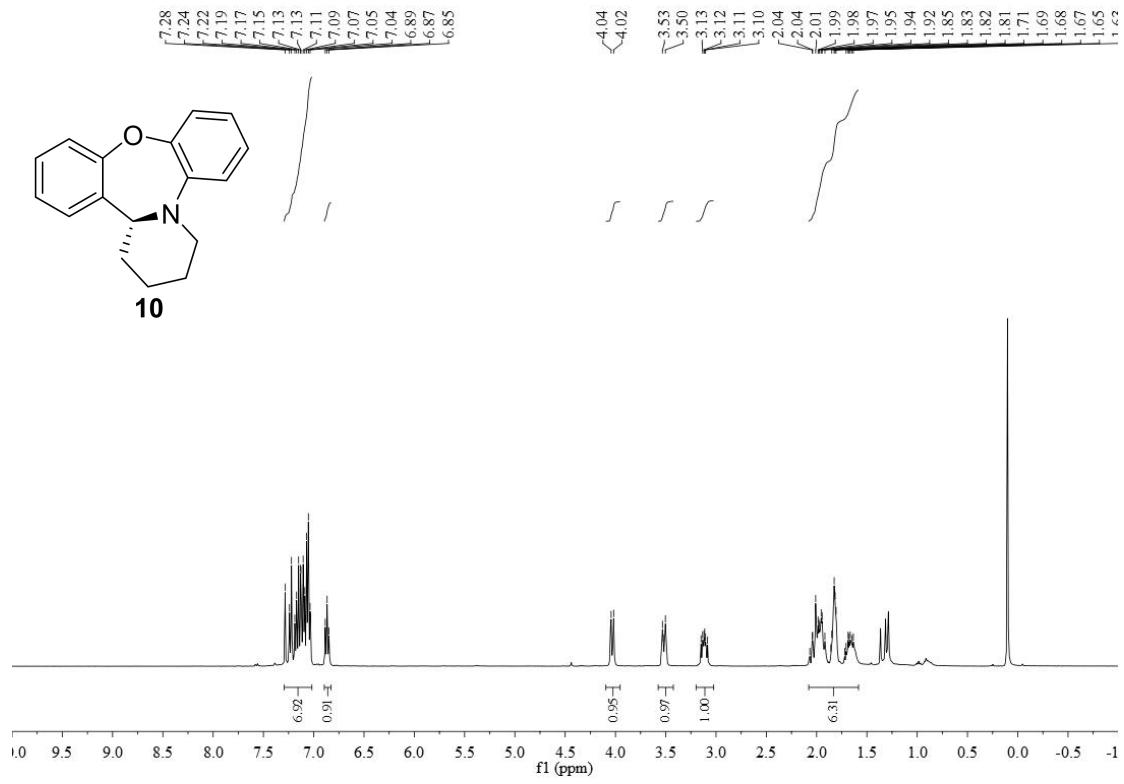


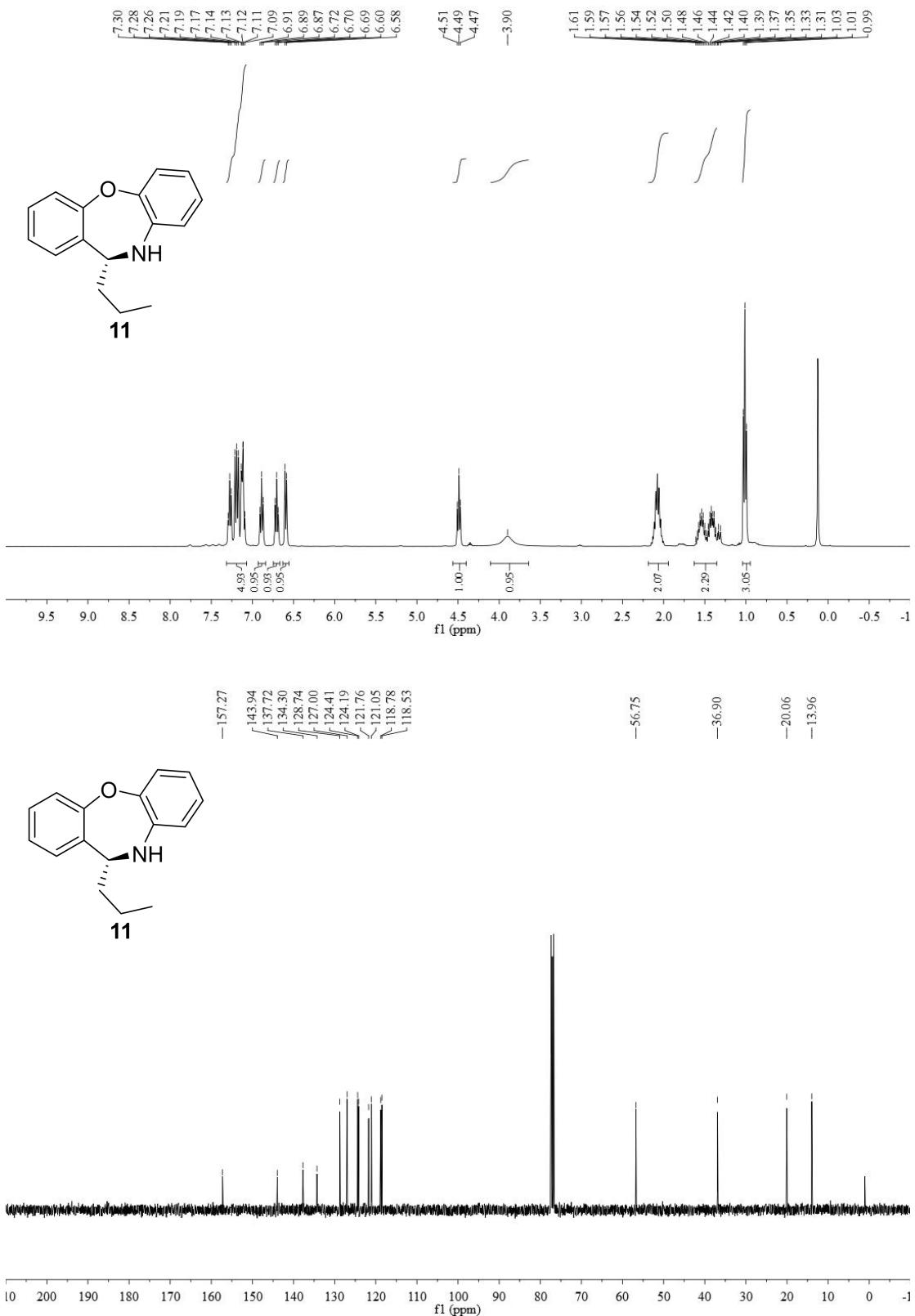


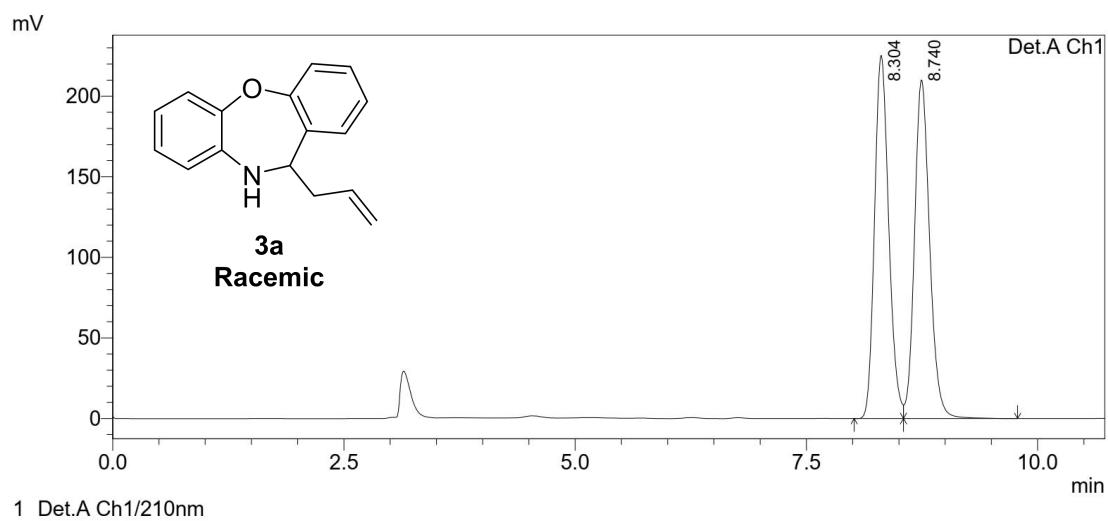








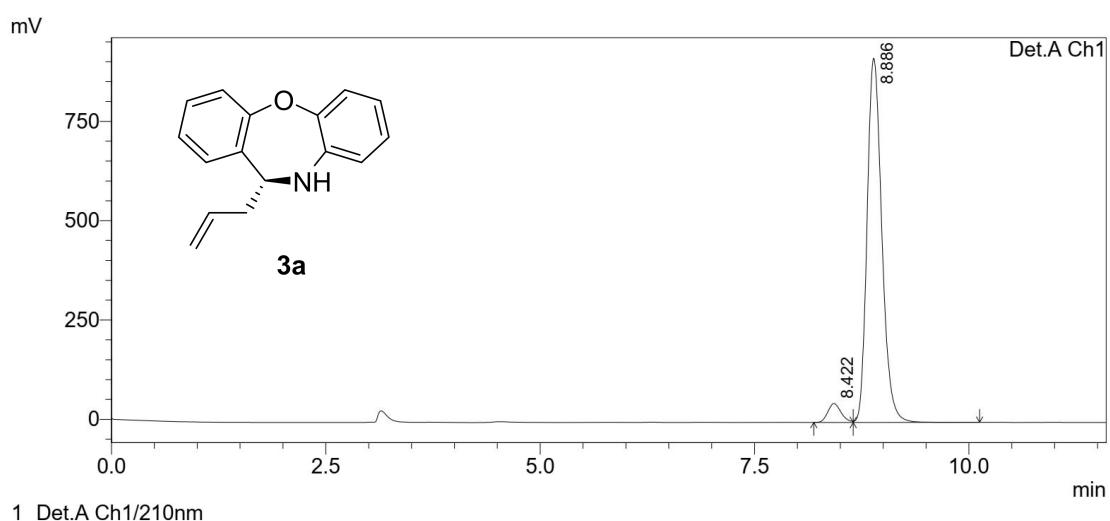




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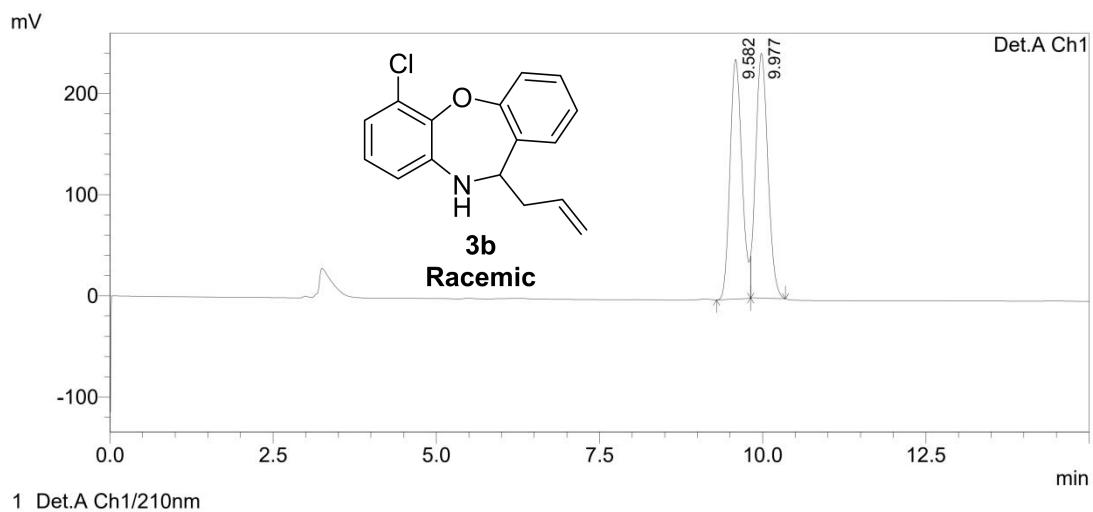
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.304	2408413	225413	50.144	51.754
2	8.740	2394579	210131	49.856	48.246
Total		4802992	435543	100.000	100.000



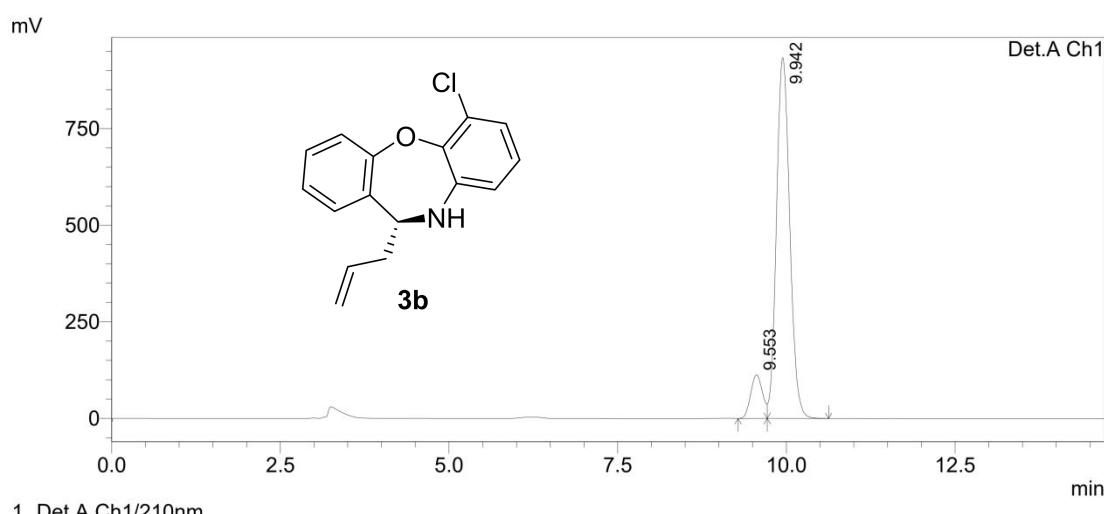
PeakTable

Detector A Ch1 210nm

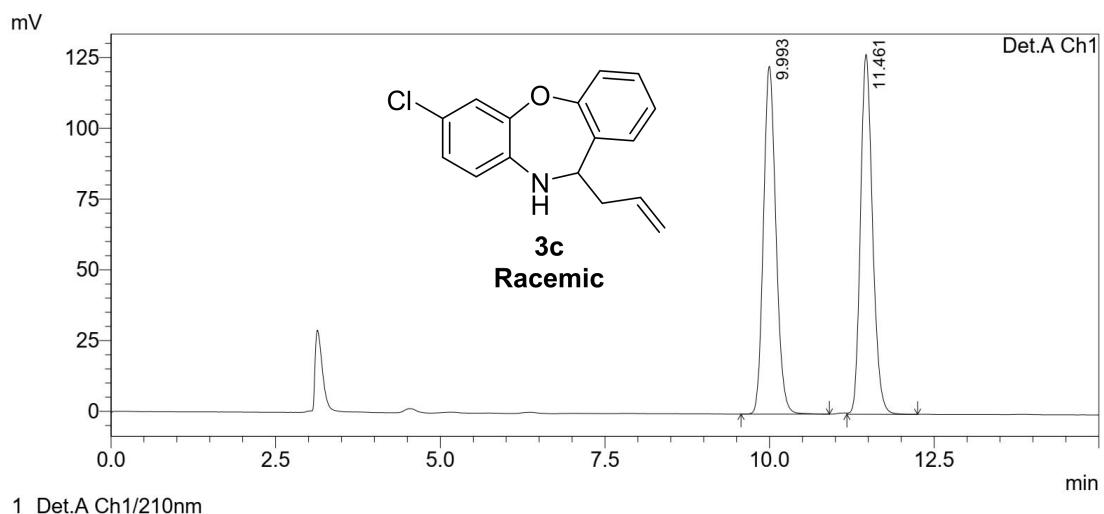
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.422	509823	47470	4.453	4.922
2	8.886	10938884	917054	95.547	95.078
Total		11448707	964524	100.000	100.000



PeakTable						
Detector A Ch1 210nm	Peak#	Ret. Time	Area	Height	Area %	Height %
	1	9.582	3050399	237160	49.281	49.491
	2	9.977	3139436	242040	50.719	50.509
	Total		6189834	479200	100.000	100.000



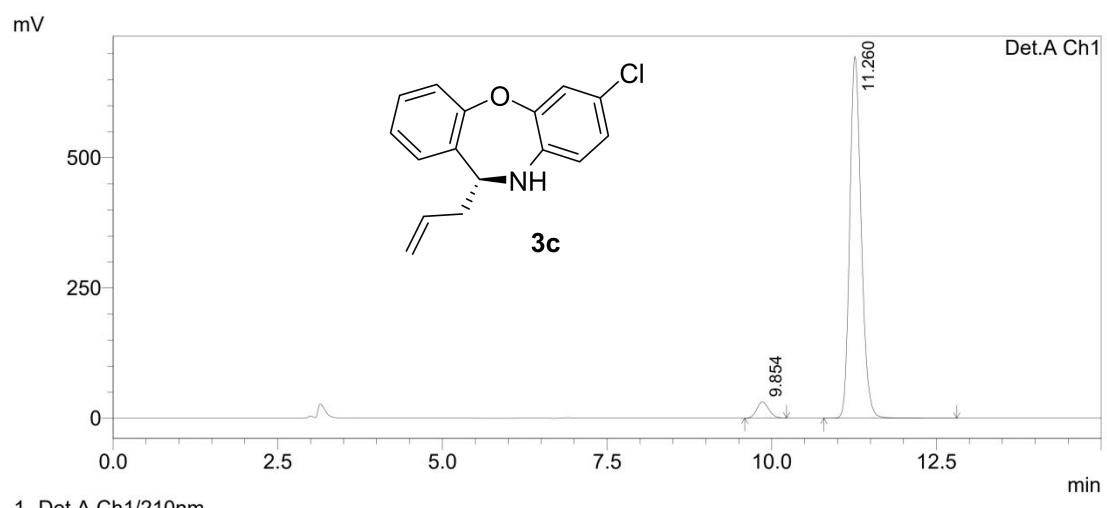
PeakTable						
Detector A Ch1 210nm	Peak#	Ret. Time	Area	Height	Area %	Height %
	1	9.553	1382968	112613	9.719	10.767
	2	9.942	12846082	933327	90.281	89.233
	Total		14229050	1045940	100.000	100.000



PeakTable

Detector A Ch1 210nm

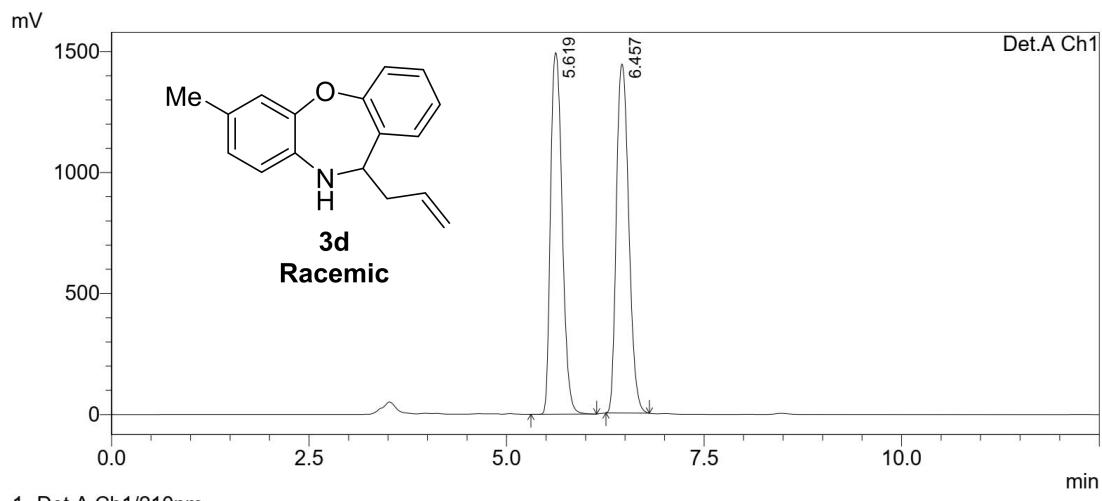
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.993	1619143	122876	49.999	49.136
2	11.461	1619211	127198	50.001	50.864
Total		3238354	250074	100.000	100.000



PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.854	395564	31390	4.498	4.324
2	11.260	8398991	694640	95.502	95.676
Total		8794555	726030	100.000	100.000

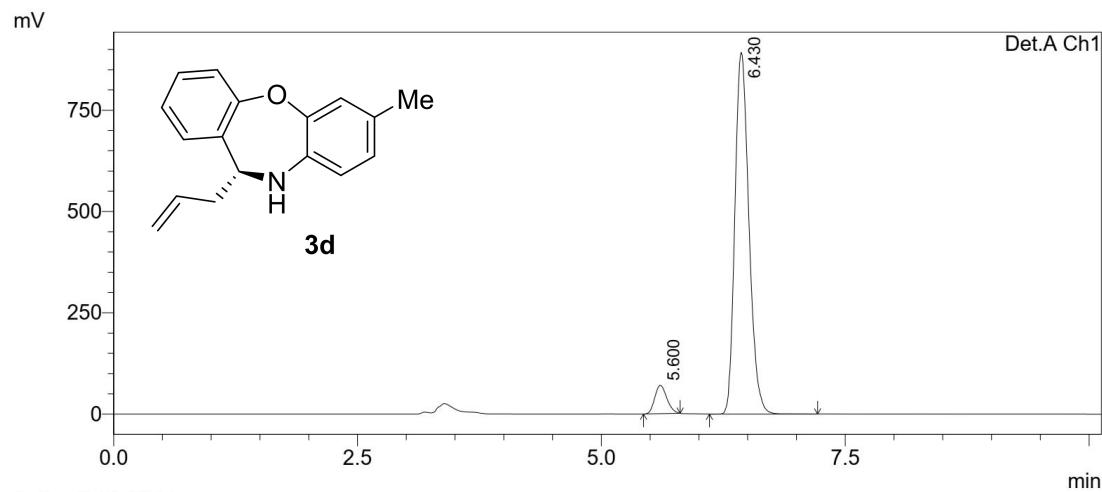


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.619	15262193	1493054	49.260	50.974
2	6.457	15720963	1435971	50.740	49.026
Total		30983156	2929025	100.000	100.000

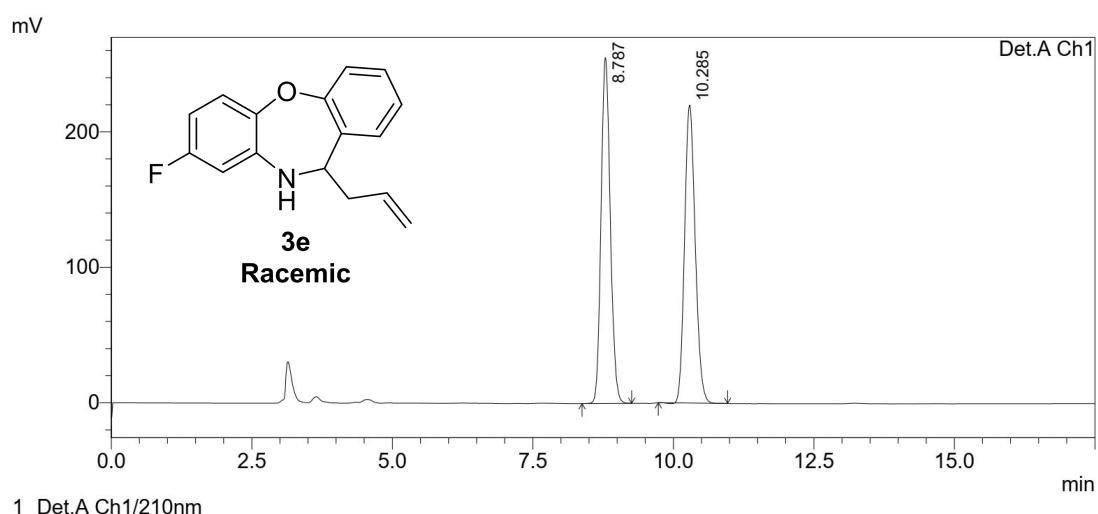


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

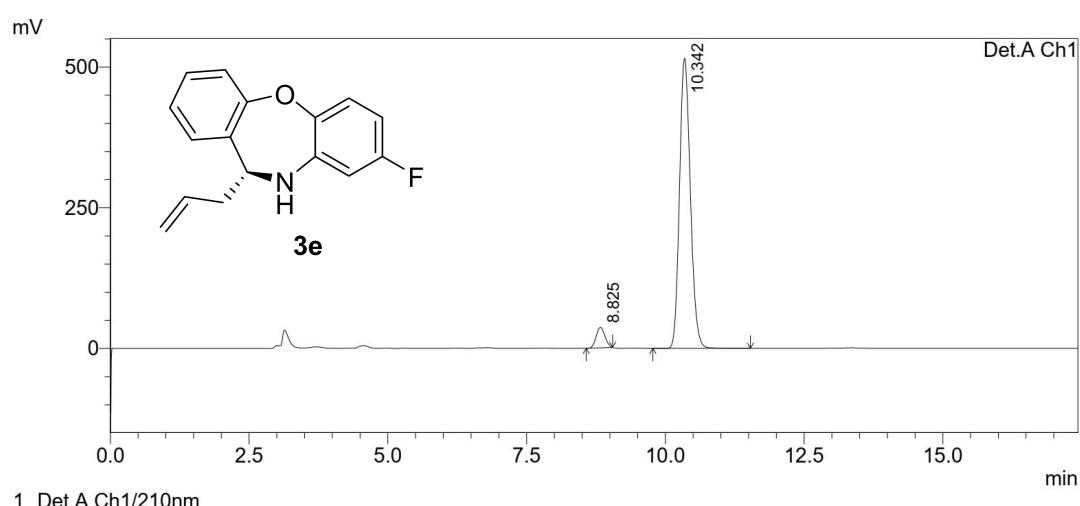
Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.600	603092	69923	6.327	7.262
2	6.430	8928452	892953	93.673	92.738
Total		9531544	962876	100.000	100.000



PeakTable

Detector A Ch1 210nm

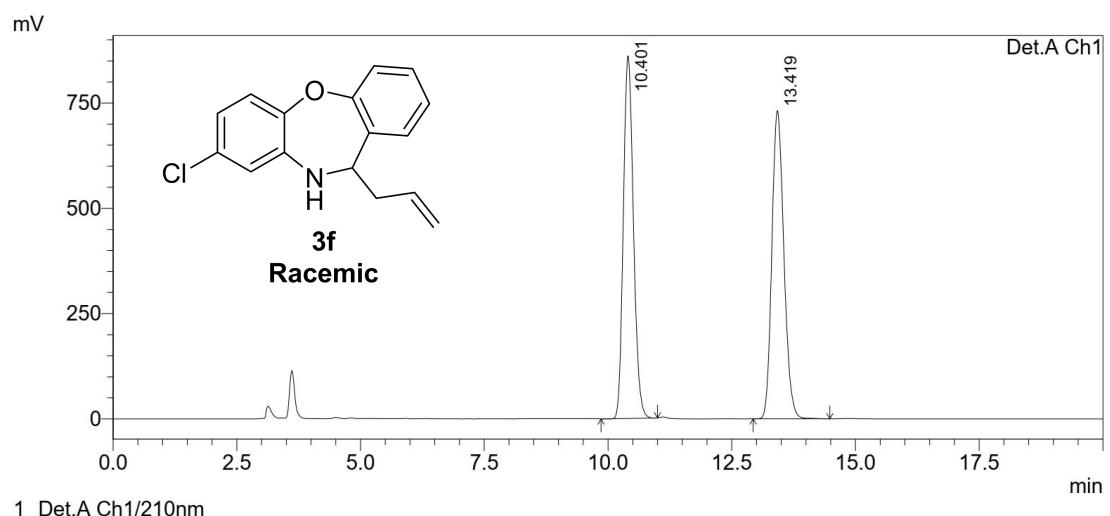
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.787	2915340	255488	50.148	53.736
2	10.285	2898086	219961	49.852	46.264
Total		5813426	475449	100.000	100.000



PeakTable

Detector A Ch1 210nm

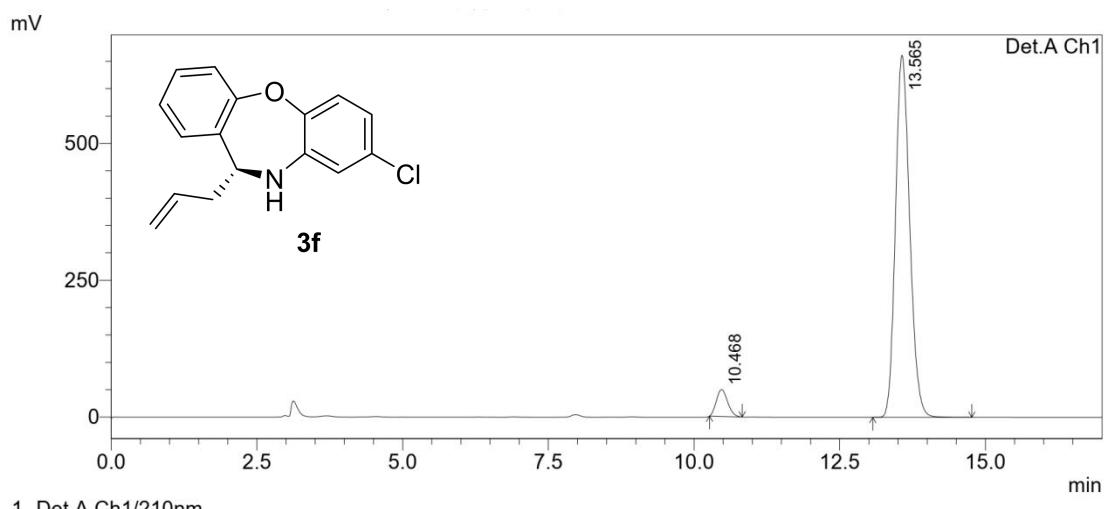
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.825	398882	36359	5.389	6.594
2	10.342	7002388	515028	94.611	93.406
Total		7401271	551387	100.000	100.000



PeakTable

Detector A Ch1 210nm

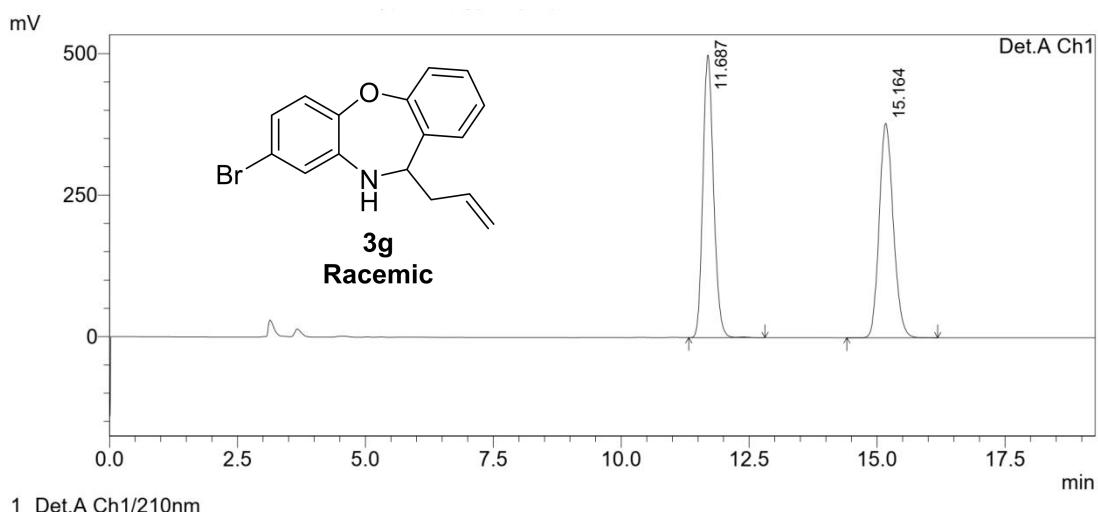
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.401	12224446	860855	49.696	54.062
2	13.419	12374079	731492	50.304	45.938
Total		24598525	1592347	100.000	100.000



PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.468	656125	49012	5.503	6.897
2	13.565	11266849	661613	94.497	93.103
Total		11922973	710625	100.000	100.000

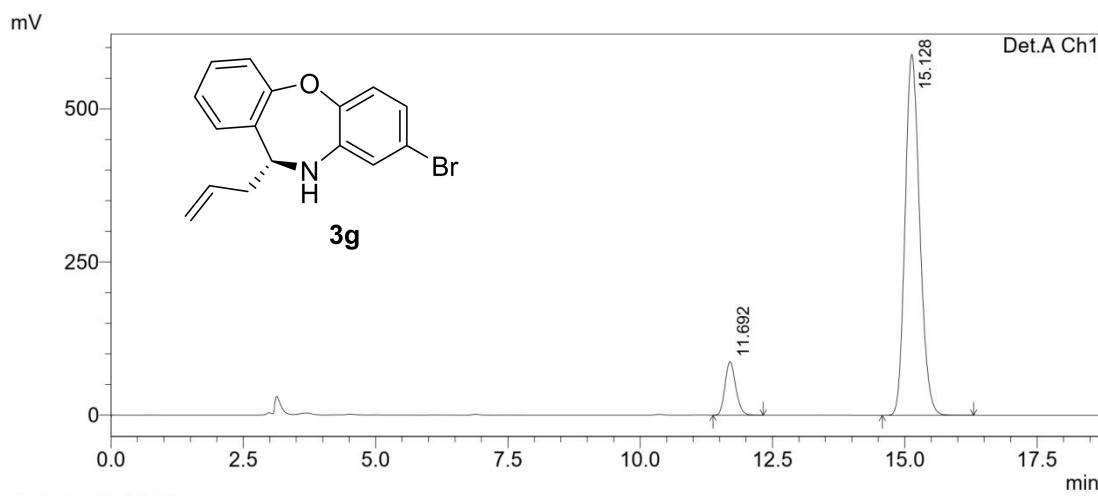


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.687	7260088	499556	49.930	56.867
2	15.164	7280358	378902	50.070	43.133
Total		14540446	878457	100.000	100.000

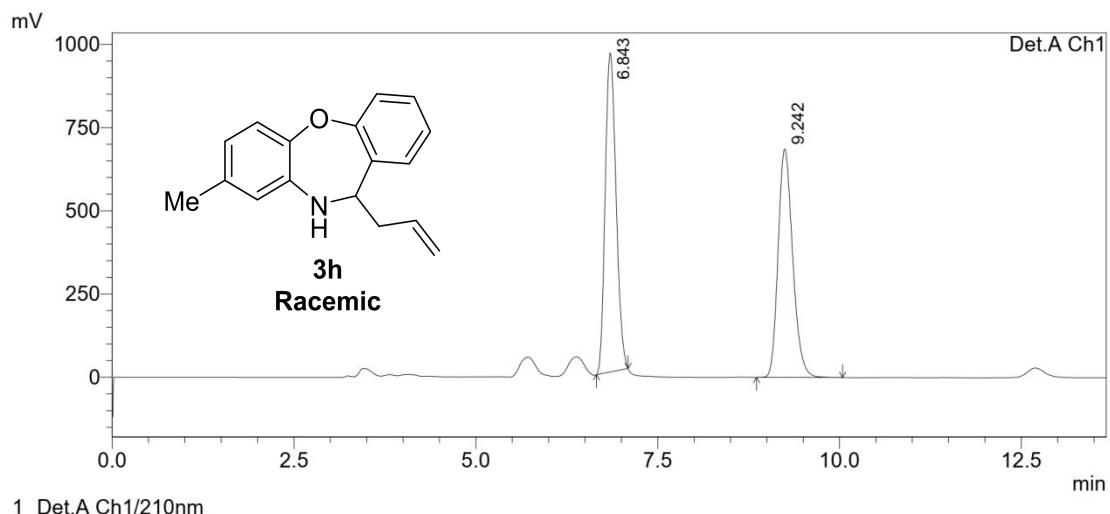


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

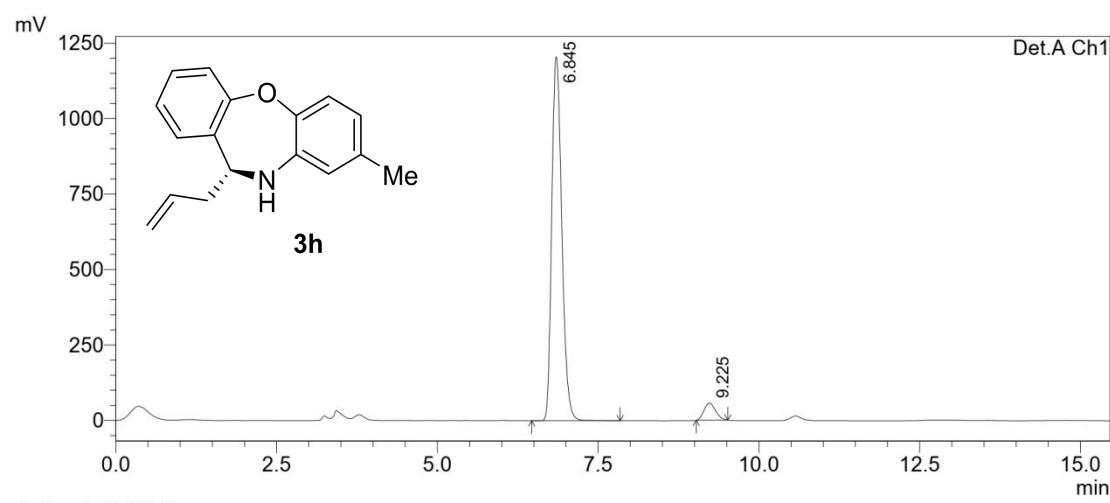
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.692	1235918	87557	9.833	12.934
2	15.128	11332608	589403	90.167	87.066
Total		12568526	676960	100.000	100.000



Detector A Ch1 210nm

PeakTable

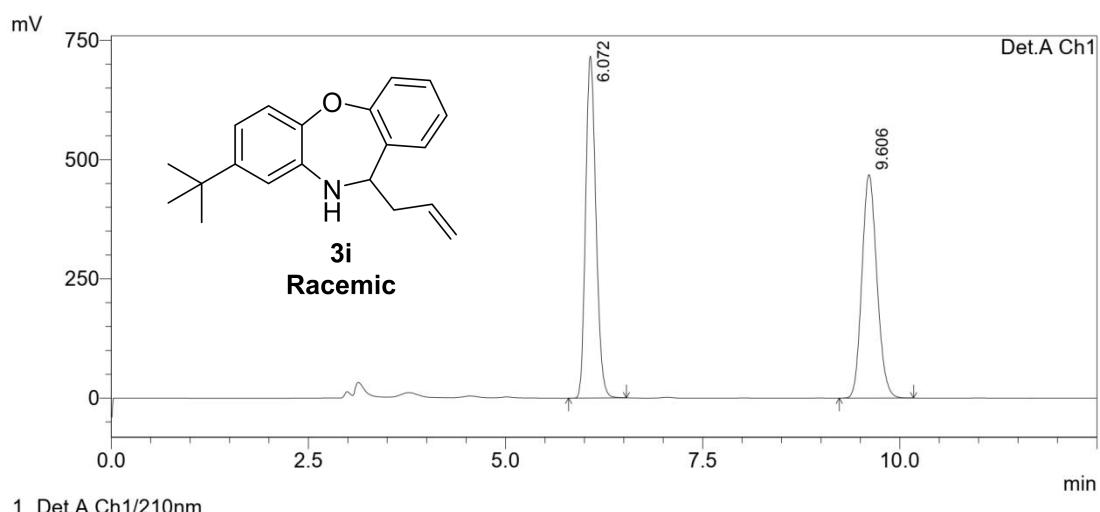
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.843	9942544	957866	50.912	58.290
2	9.242	9586170	685409	49.088	41.710
Total		19528714	1643275	100.000	100.000



Detector A Ch1 210nm

PeakTable

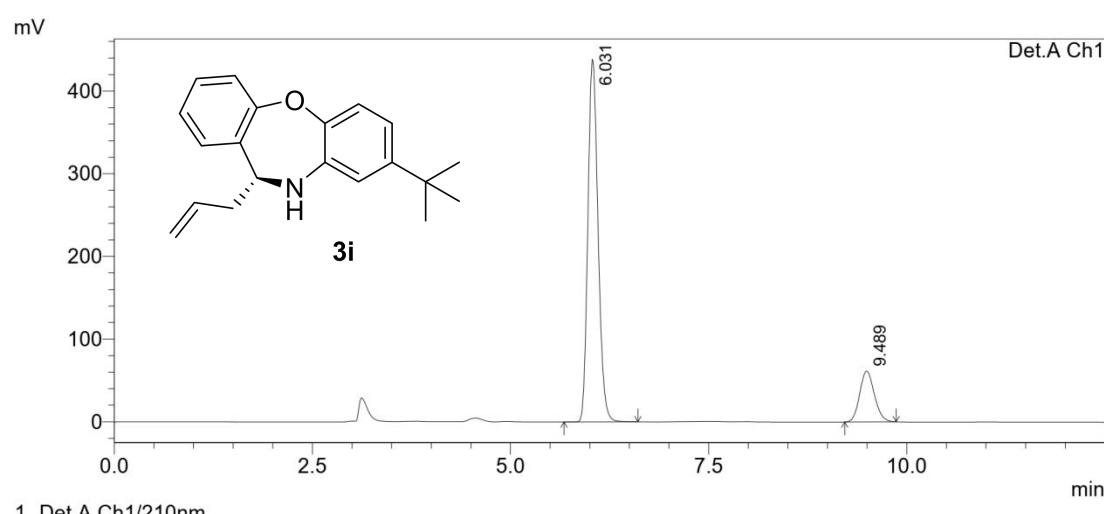
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.845	13074830	1205740	94.835	95.491
2	9.225	712163	56934	5.165	4.509
Total		13786993	1262674	100.000	100.000



PeakTable

Detector A Ch1 210nm

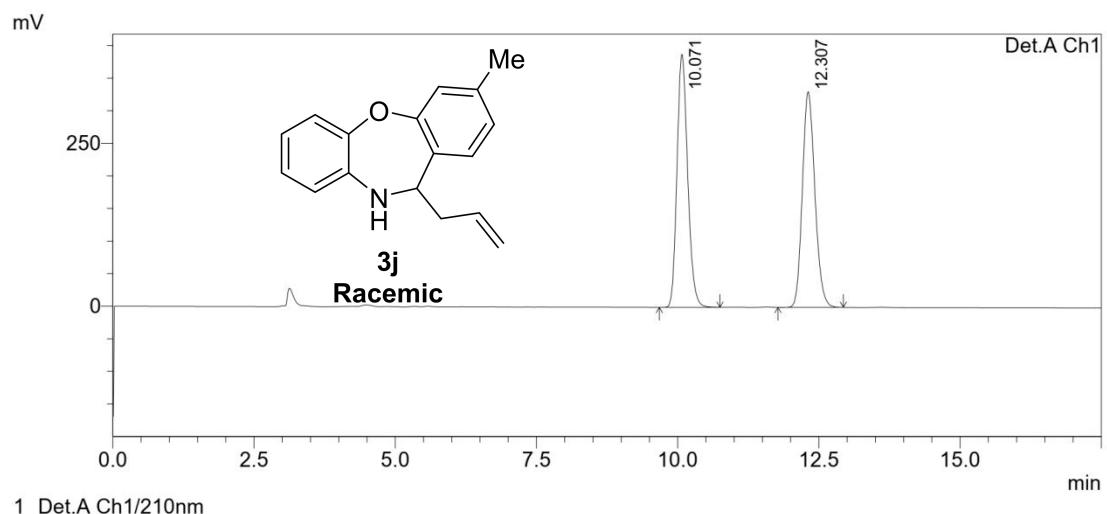
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.072	6520581	717229	51.237	60.483
2	9.606	6205802	468605	48.763	39.517
Total		12726383	1185834	100.000	100.000



PeakTable

Detector A Ch1 210nm

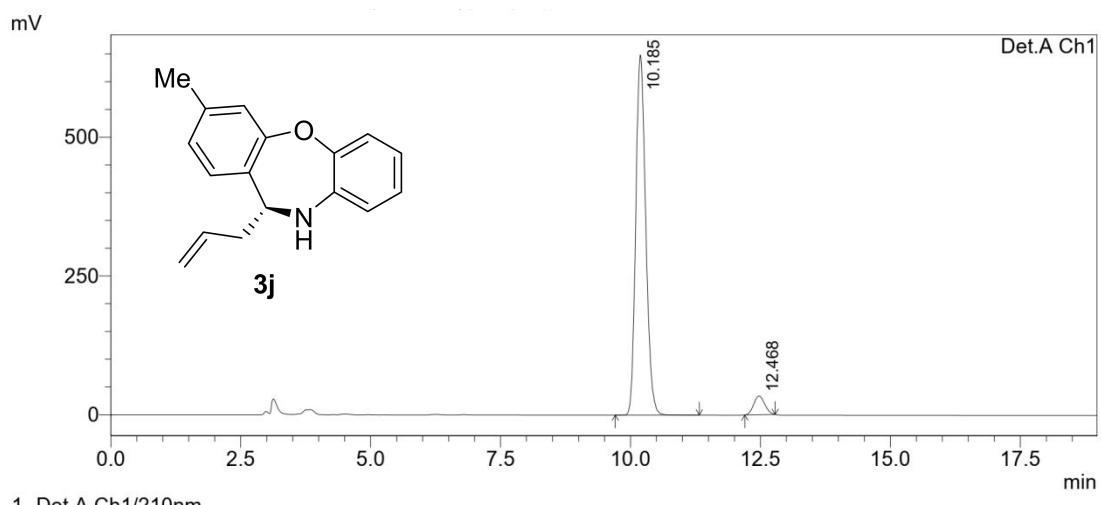
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.031	3909278	438842	83.174	87.722
2	9.489	790842	61421	16.826	12.278
Total		4700121	500263	100.000	100.000



PeakTable

Detector A Ch1 210nm

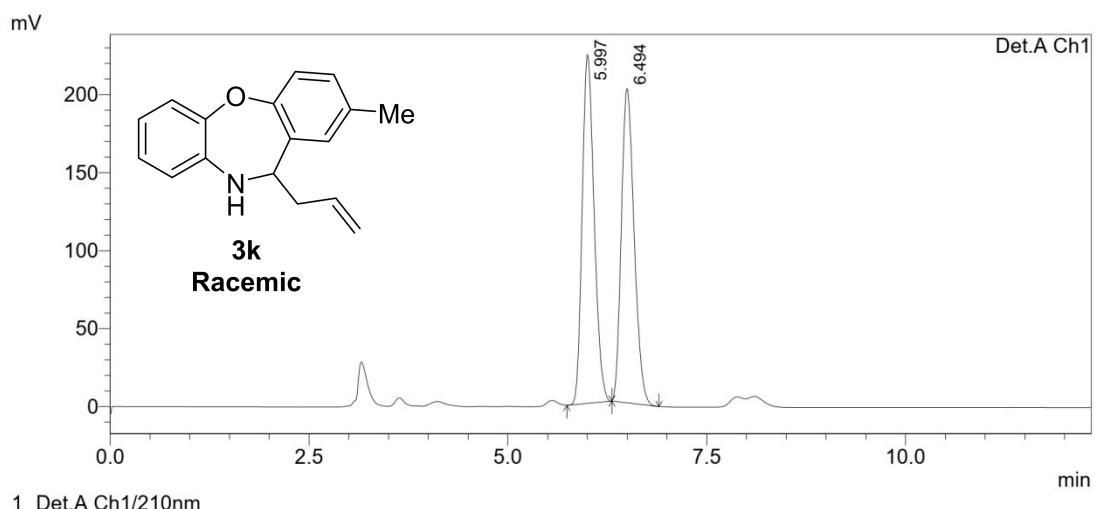
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.071	5101441	388380	49.988	53.999
2	12.307	5103961	330854	50.012	46.001
Total		10205403	719234	100.000	100.000



PeakTable

Detector A Ch1 210nm

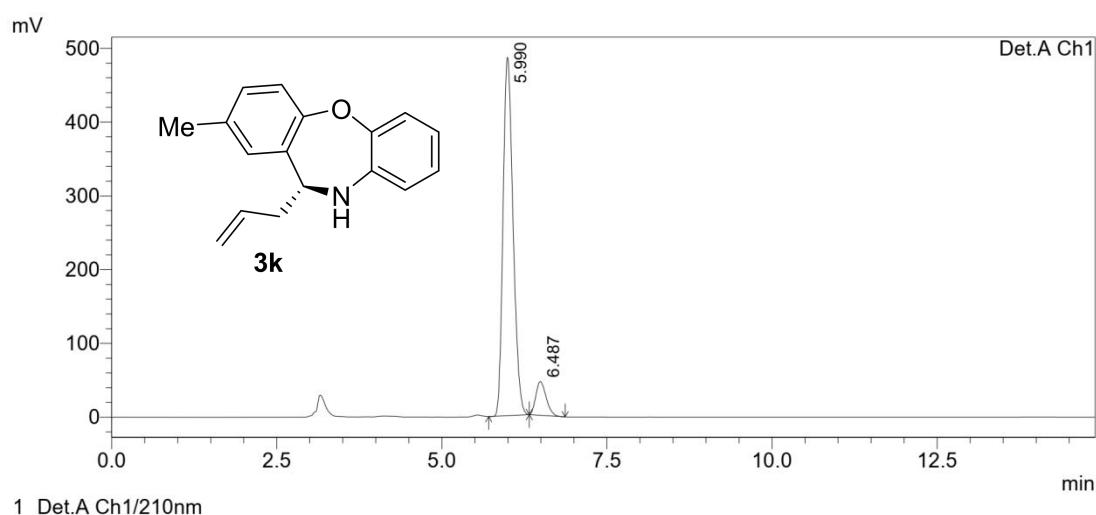
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.185	8676237	648887	94.577	95.065
2	12.468	497539	33681	5.423	4.935
Total		9173775	682568	100.000	100.000



PeakTable

Detector A Ch1 210nm

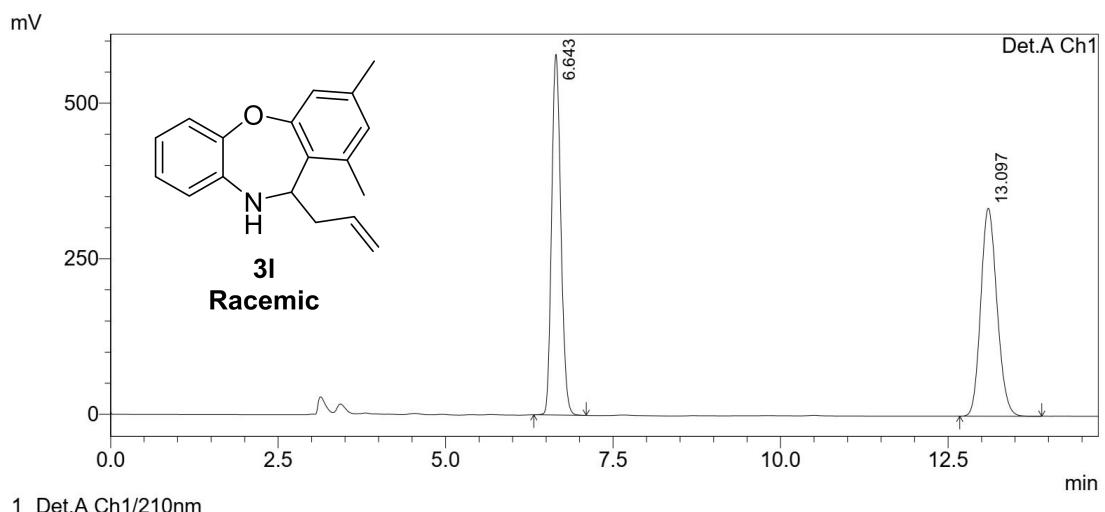
Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.997	2335831	223694	50.913	52.608
2	6.494	2252018	201517	49.087	47.392
Total		4587850	425211	100.000	100.000



PeakTable

Detector A Ch1 210nm

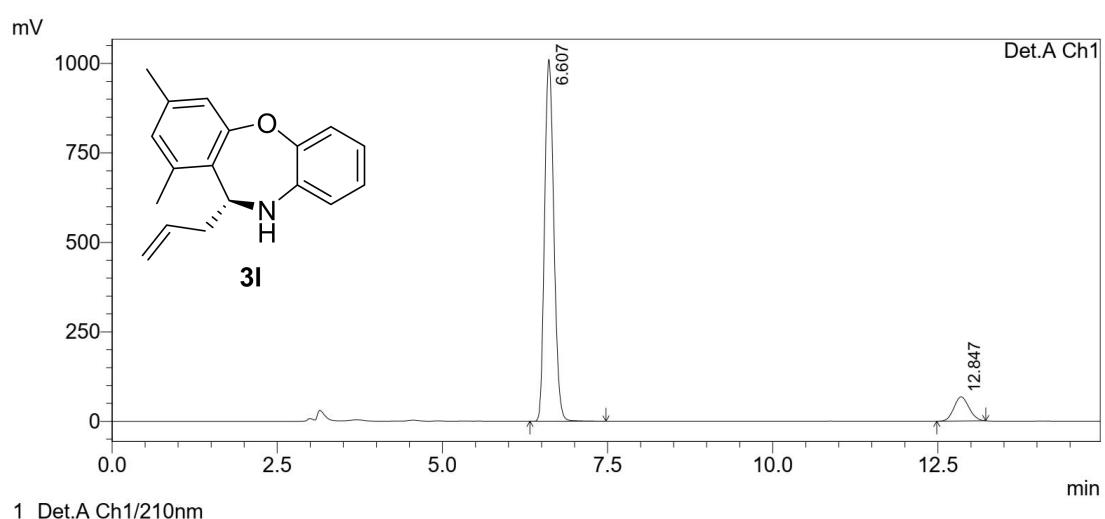
Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.990	5117390	485861	91.160	91.396
2	6.487	496218	45738	8.840	8.604
Total		5613608	531599	100.000	100.000



PeakTable

Detector A Ch1 210nm

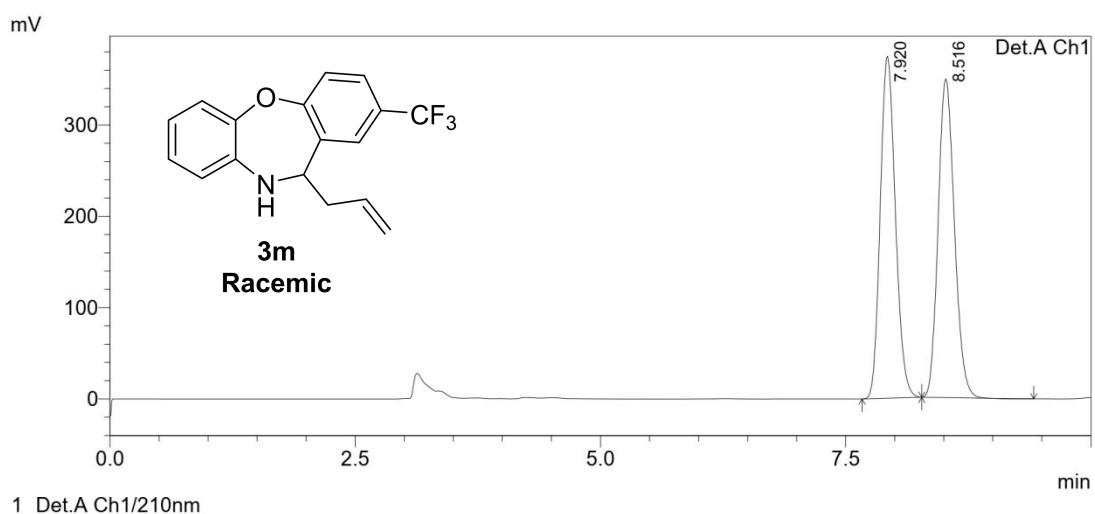
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.643	5520094	579661	49.502	63.422
2	13.097	5631263	334318	50.498	36.578
Total		11151357	913979	100.000	100.000



PeakTable

Detector A Ch1 210nm

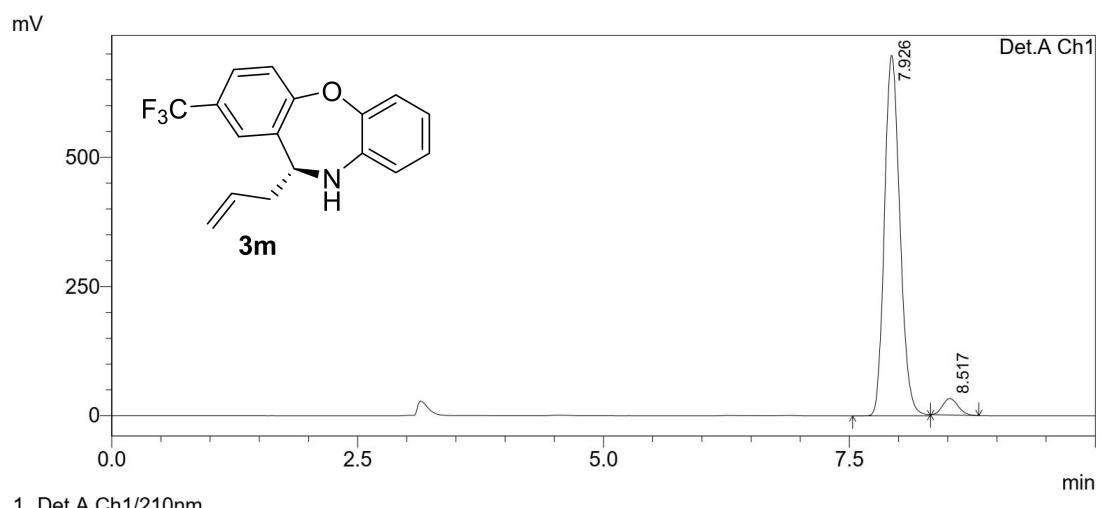
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.607	9856298	1011178	90.169	93.744
2	12.847	1074595	67480	9.831	6.256
Total		10930893	1078658	100.000	100.000



PeakTable

Detector A Ch1 210nm

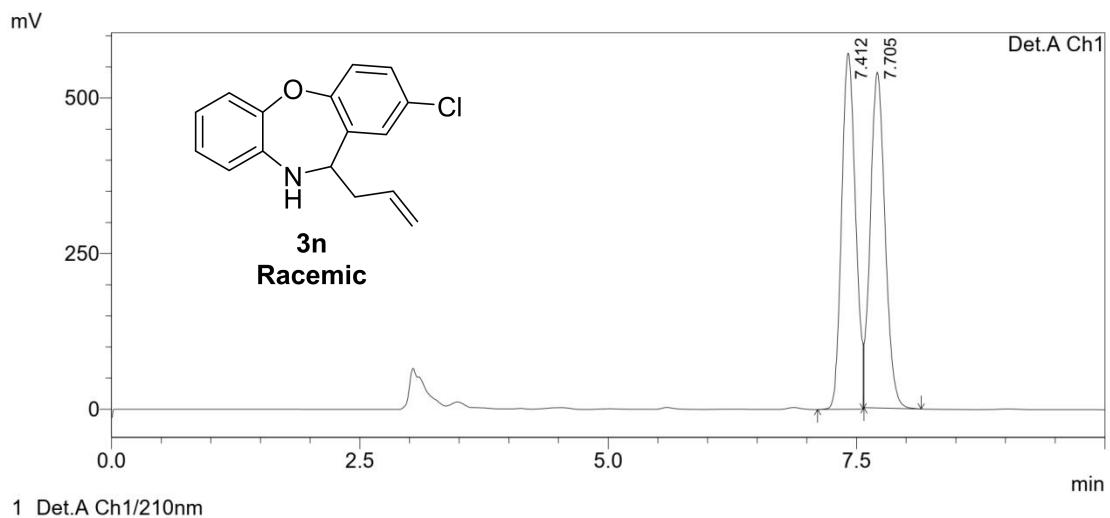
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.920	4027197	374582	50.017	51.795
2	8.516	4024483	348619	49.983	48.205
Total		8051681	723200	100.000	100.000



PeakTable

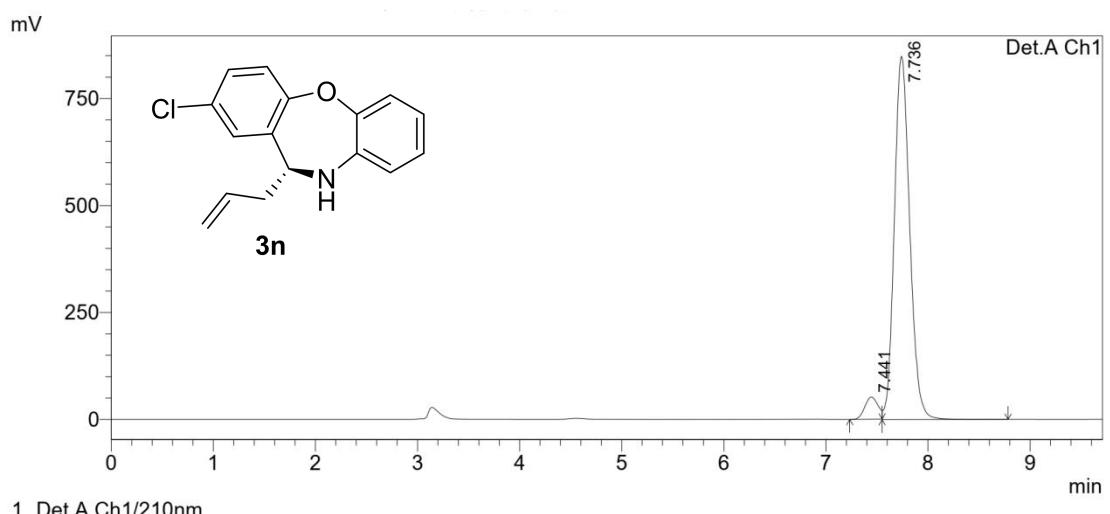
Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.926	7636598	697127	95.612	95.626
2	8.517	350473	31885	4.388	4.374
Total		7987072	729011	100.000	100.000



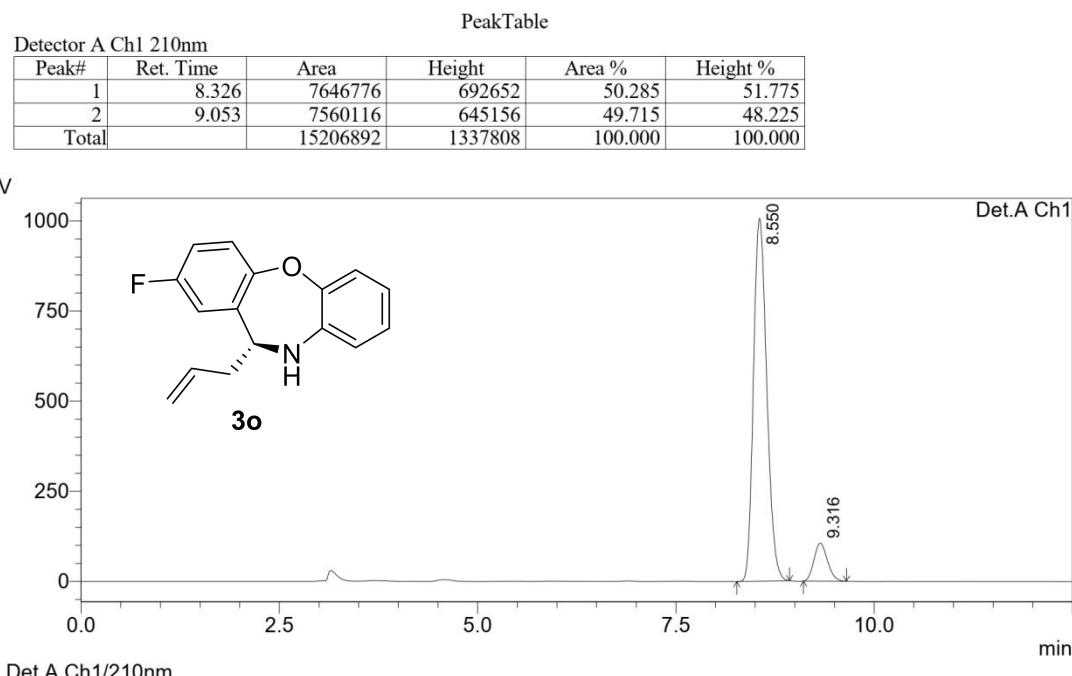
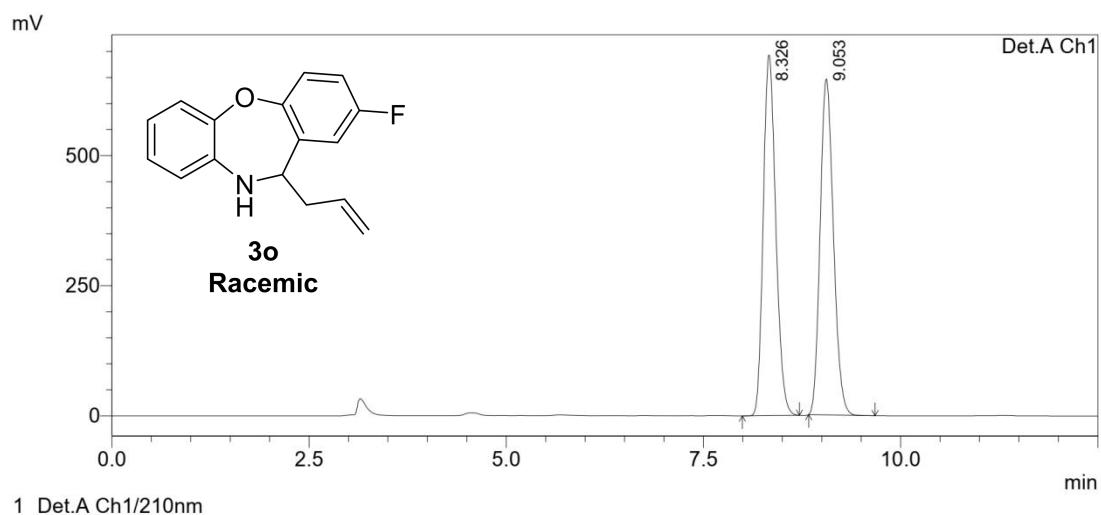
PeakTable

Detector A Ch1 210nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.412	5578607	572212	50.100	51.455
2	7.705	5556302	539854	49.900	48.545
Total		11134908	1112066	100.000	100.000



PeakTable

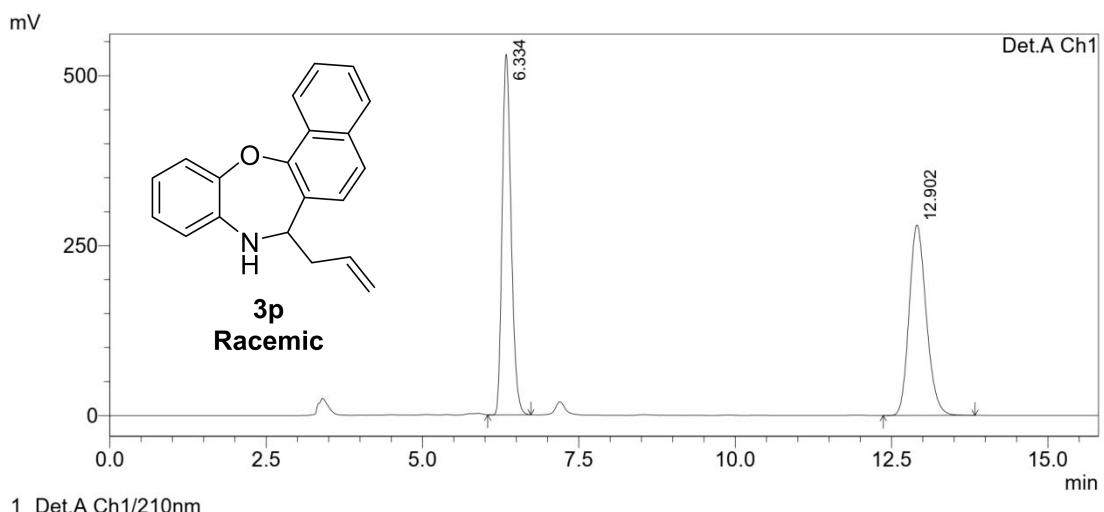
Detector A Ch1 210nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.441	466851	51699	4.978	5.740
2	7.736	8911365	848912	95.022	94.260
Total		9378217	900611	100.000	100.000



PeakTable

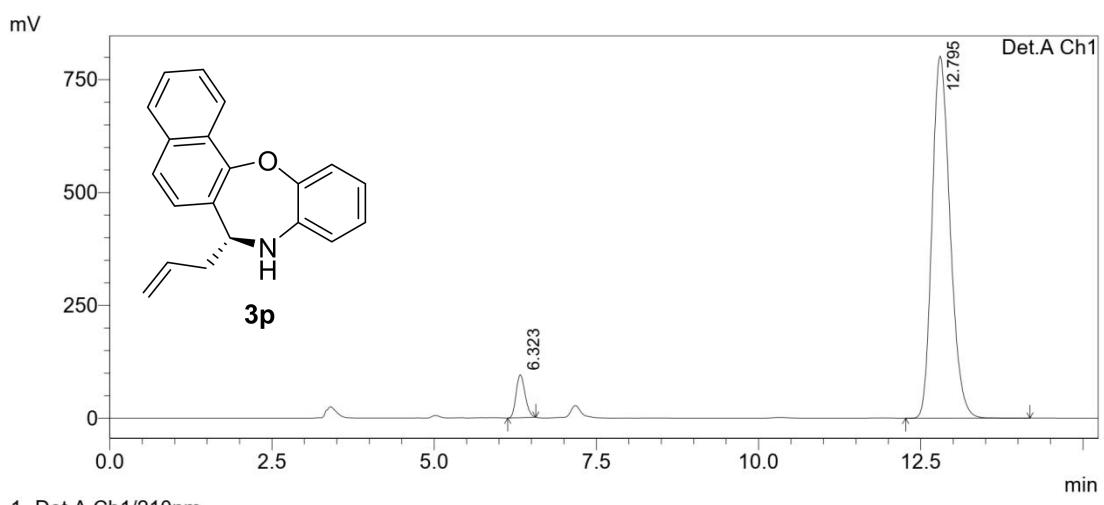
Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.550	11718840	1005940	90.408	90.511
2	9.316	1243267	105465	9.592	9.489
Total		12962108	1111405	100.000	100.000



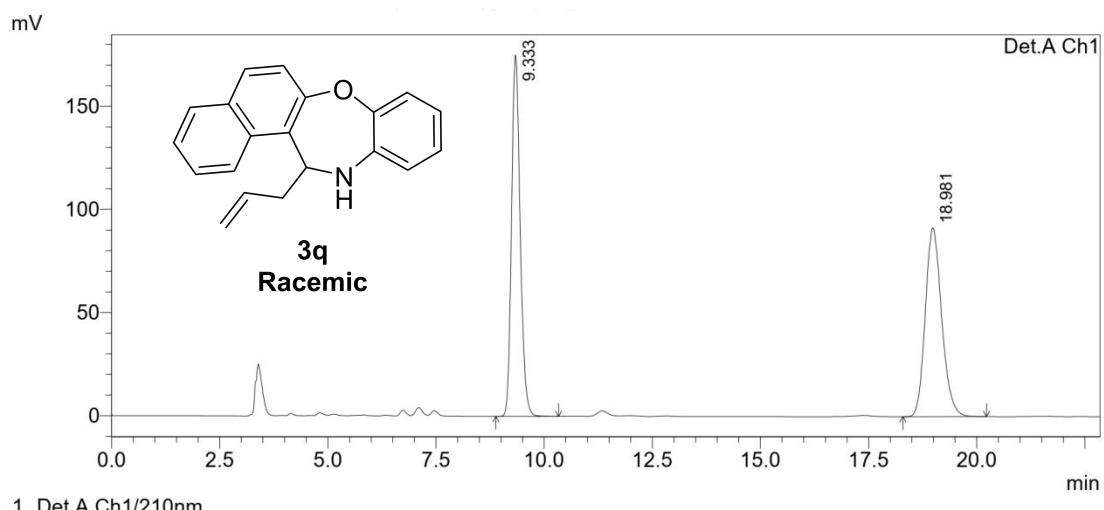
PeakTable

Detector A Ch1 210nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.334	5287354	530409	49.712	65.425
2	12.902	5348653	280307	50.288	34.575
Total		10636007	810716	100.000	100.000



PeakTable

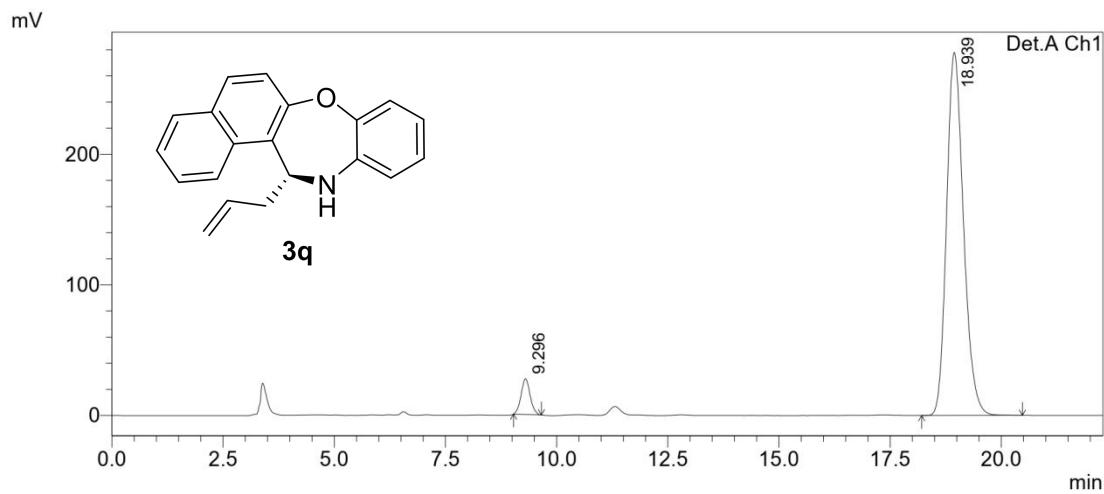
Detector A Ch1 210nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.323	919034	94777	5.587	10.572
2	12.795	15531808	801687	94.413	89.428
Total		16450841	896464	100.000	100.000



PeakTable

Detector A Ch1 210nm

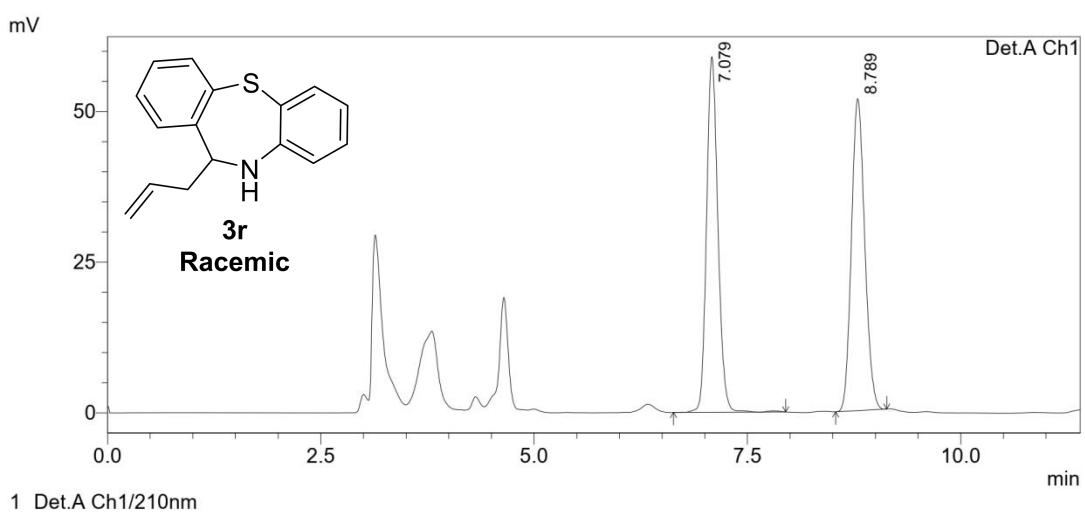
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.333	2434014	175168	50.198	65.672
2	18.981	2414819	91563	49.802	34.328
Total		4848833	266731	100.000	100.000



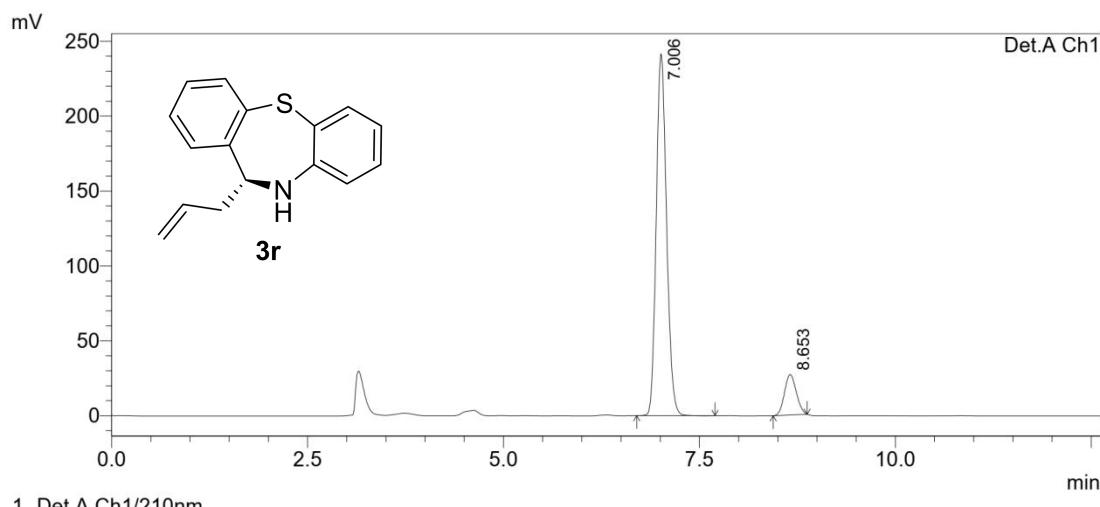
PeakTable

Detector A Ch1 210nm

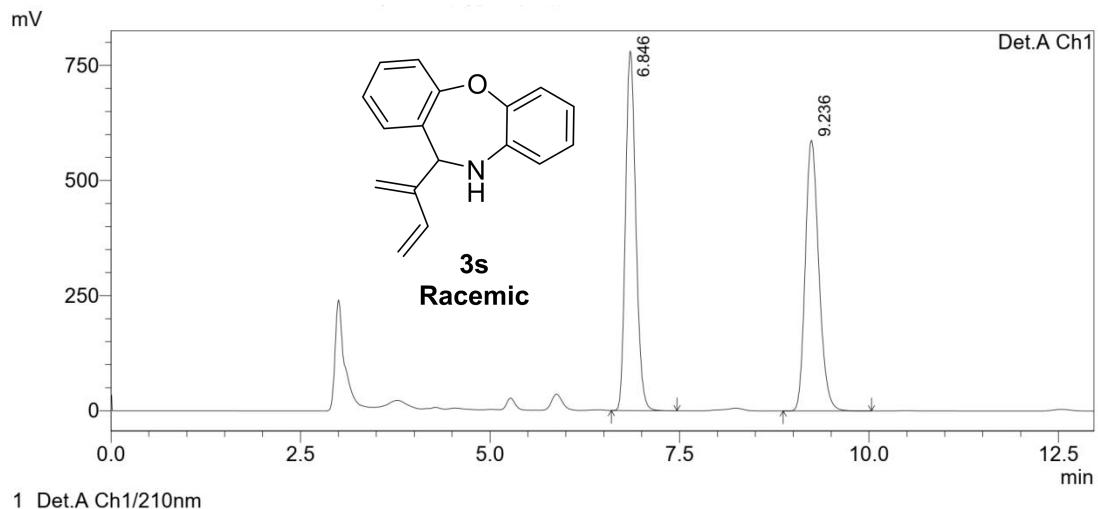
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.296	387622	27289	5.001	8.938
2	18.939	7363266	278040	94.999	91.062
Total		7750888	305329	100.000	100.000



PeakTable					
Detector A Ch1 210nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.079	546480	58695	49.277	53.202
2	8.789	562509	51630	50.723	46.798
Total		1108990	110325	100.000	100.000



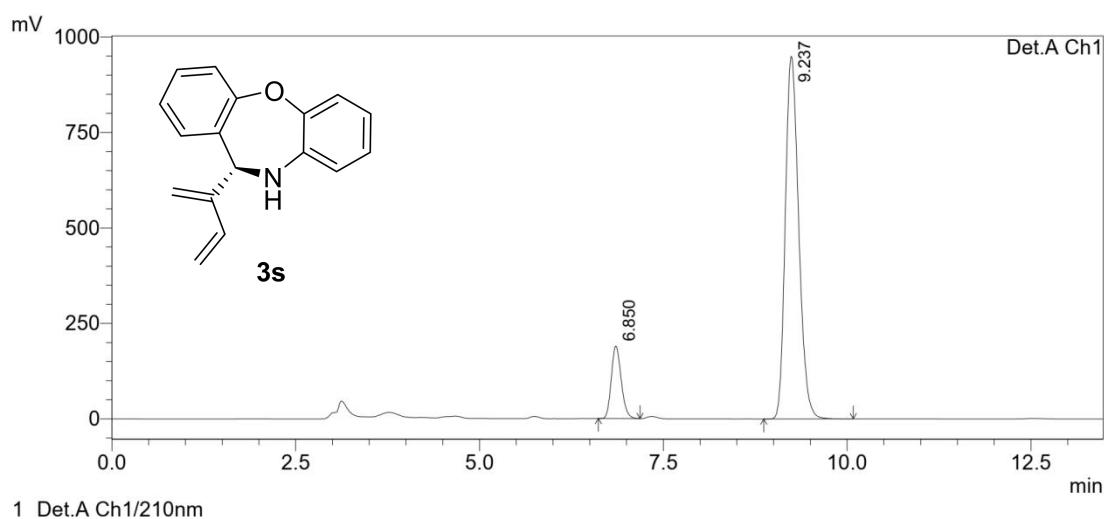
PeakTable					
Detector A Ch1 210nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.006	2207361	241495	88.636	89.941
2	8.653	282992	27009	11.364	10.059
Total		2490354	268504	100.000	100.000



PeakTable

Detector A Ch1 210nm

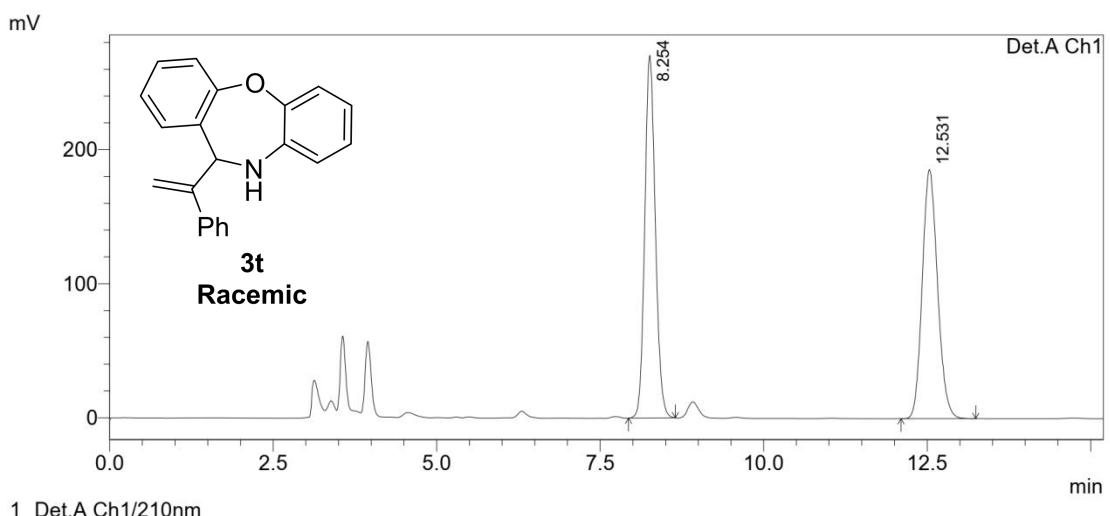
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.846	7383444	777320	50.237	57.045
2	9.236	7313645	585336	49.763	42.955
Total		14697089	1362656	100.000	100.000



PeakTable

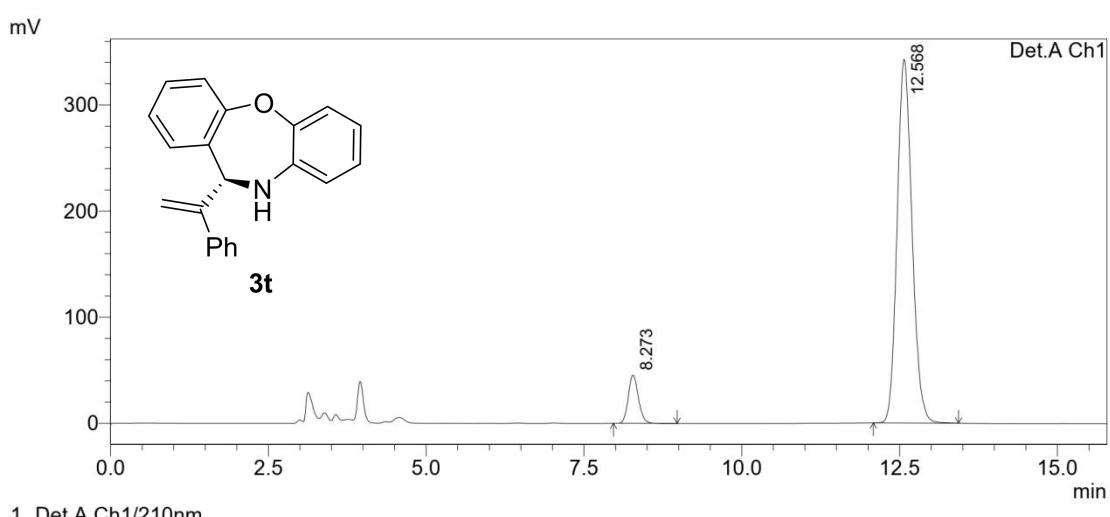
Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.850	1777131	188030	12.853	16.561
2	9.237	12049238	947371	87.147	83.439
Total		13826370	1135401	100.000	100.000



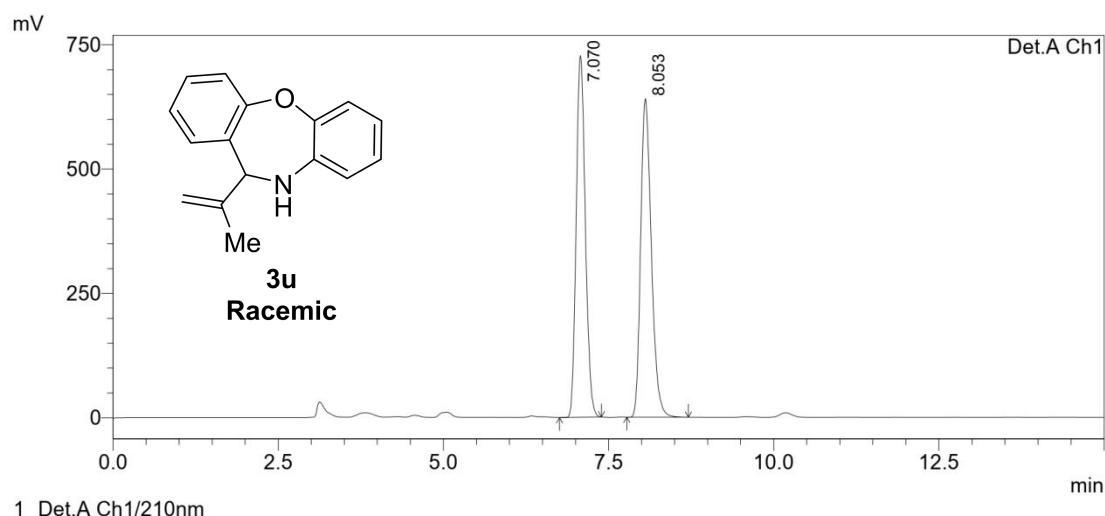
PeakTable

Detector A Ch1 210nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.254	3040336	270641	50.168	59.289
2	12.531	3019932	185840	49.832	40.711
Total		6060268	456482	100.000	100.000



PeakTable

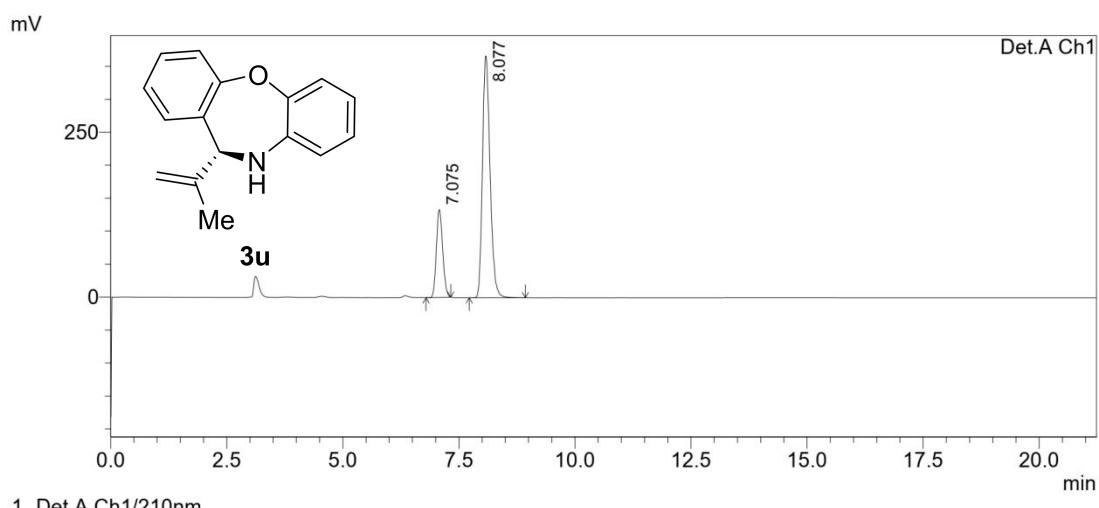
Detector A Ch1 210nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.273	503981	45431	8.206	11.703
2	12.568	5637315	342766	91.794	88.297
Total		6141296	388197	100.000	100.000



PeakTable

Detector A Ch1 210nm

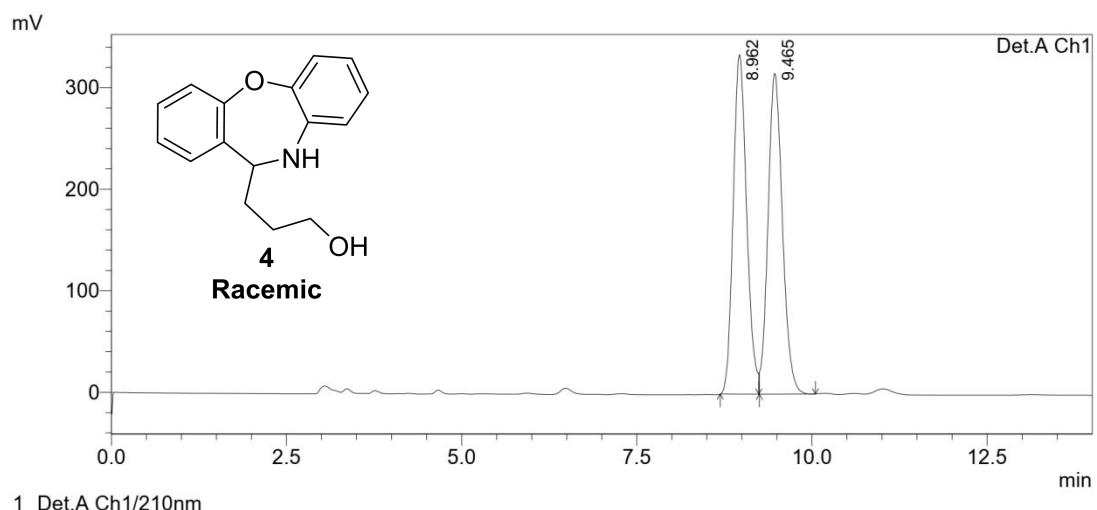
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.070	6985966	724454	49.243	53.152
2	8.053	7200876	638519	50.757	46.848
Total		14186843	1362973	100.000	100.000



PeakTable

Detector A Ch1 210nm

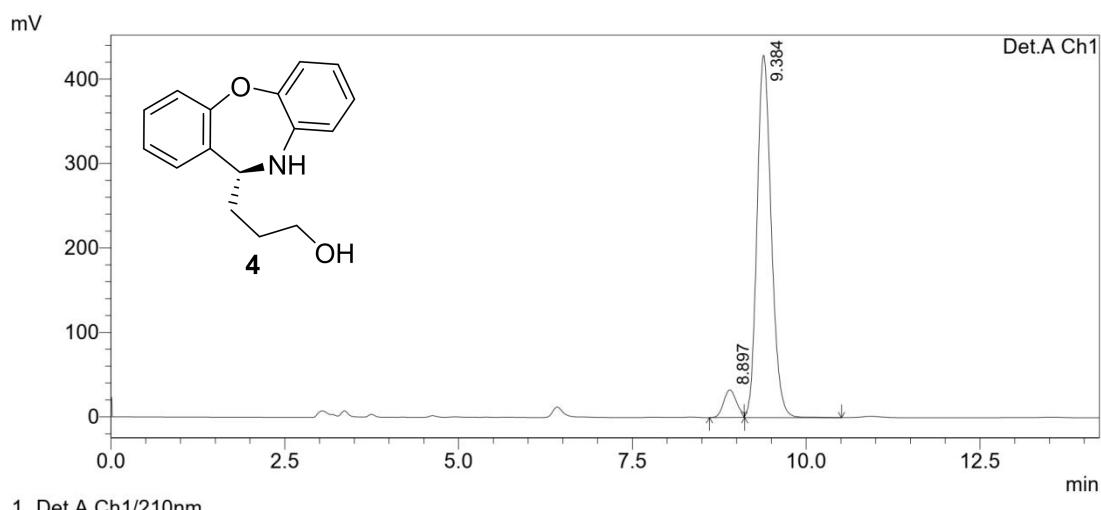
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.075	1258964	133160	23.176	26.622
2	8.077	4173200	367024	76.824	73.378
Total		5432163	500184	100.000	100.000



PeakTable

Detector A Ch1 210nm

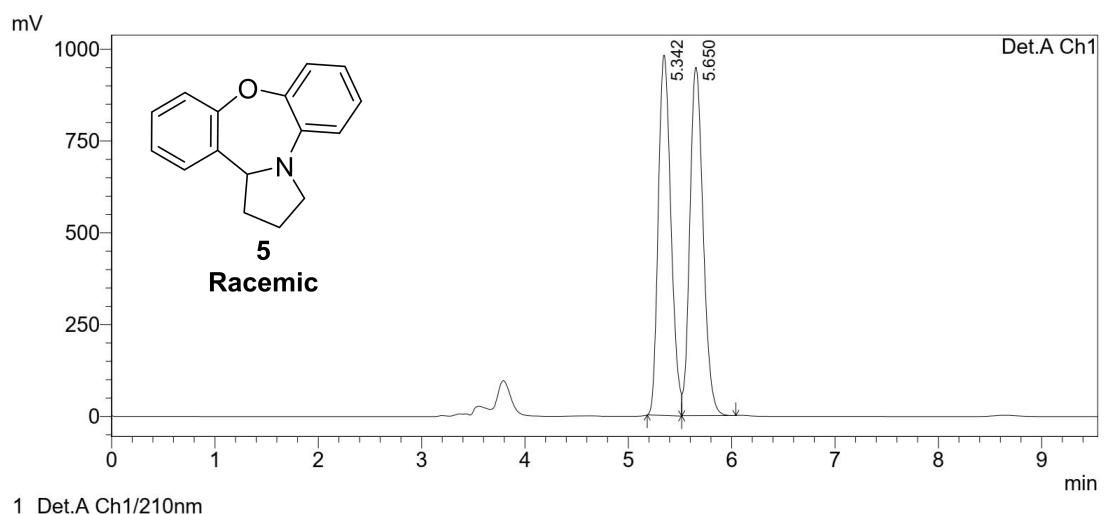
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.962	4460266	334344	49.693	51.421
2	9.465	4515409	315860	50.307	48.579
Total		8975675	650203	100.000	100.000



PeakTable

Detector A Ch1 210nm

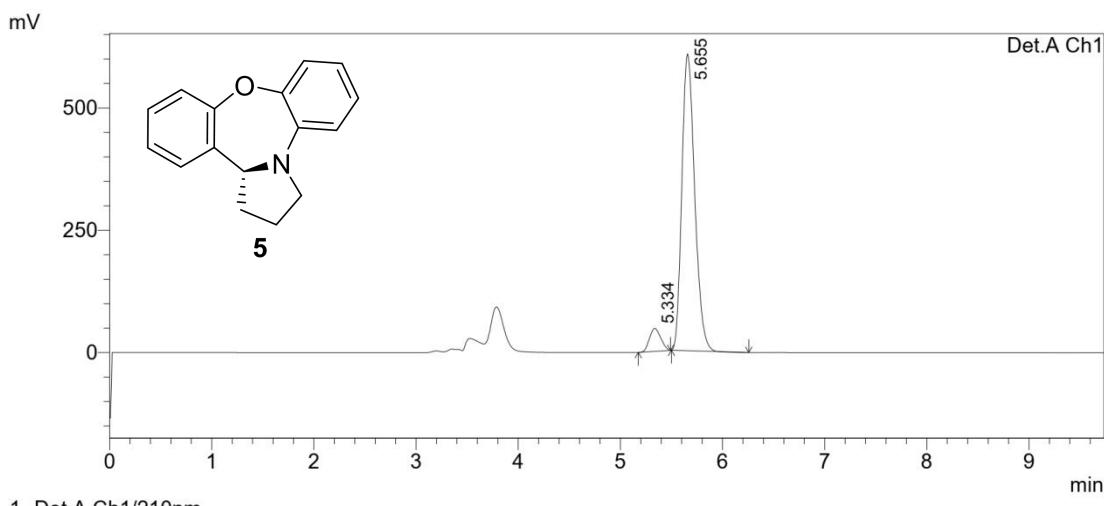
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.897	424693	32872	6.496	7.115
2	9.384	6112839	429118	93.504	92.885
Total		6537532	461990	100.000	100.000



PeakTable

Detector A Ch1 210nm

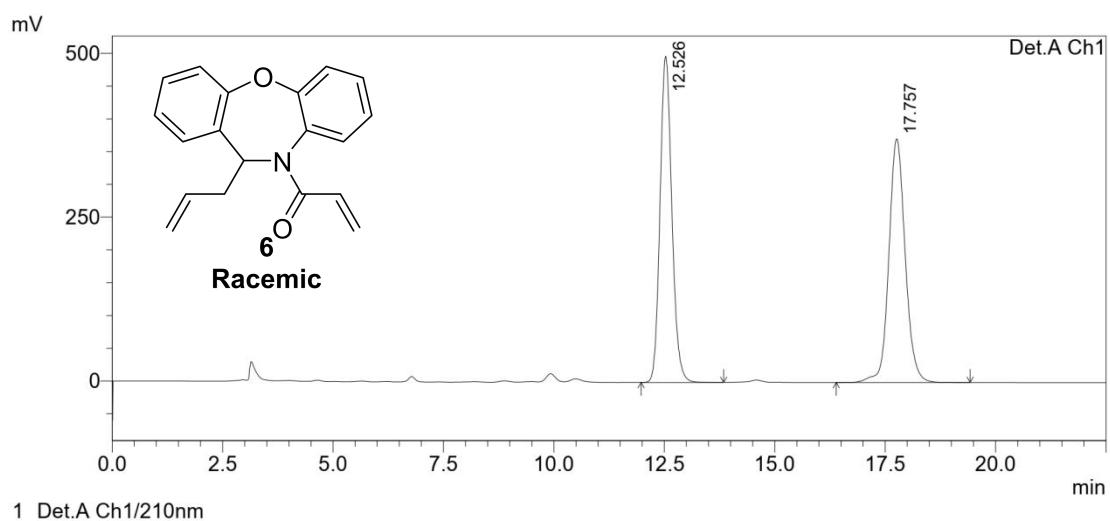
Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.342	8354752	980976	49.570	50.832
2	5.650	8499755	948849	50.430	49.168
Total		16854507	1929825	100.000	100.000



PeakTable

Detector A Ch1 210nm

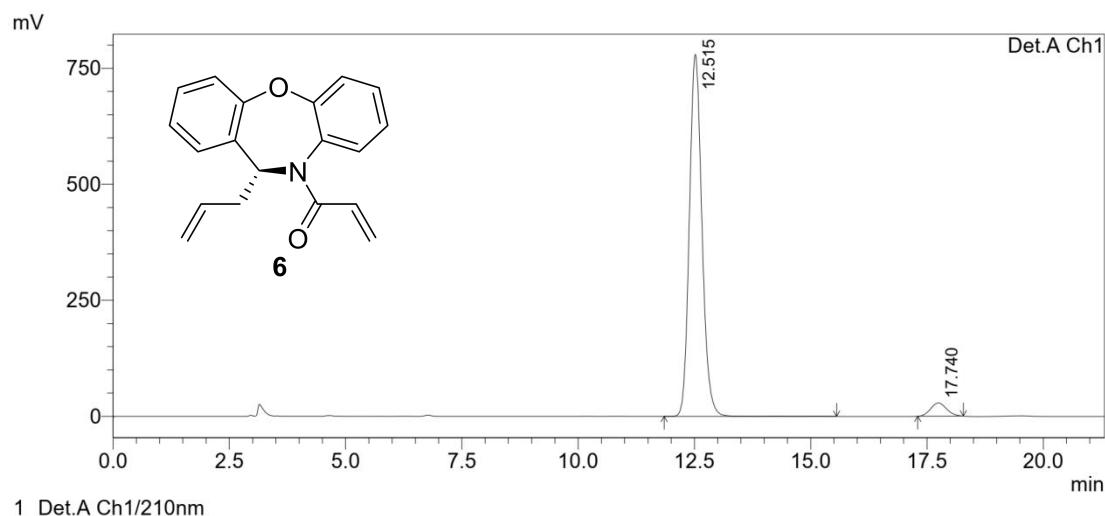
Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.334	361509	46912	6.397	7.177
2	5.655	5289947	606735	93.603	92.823
Total		5651456	653648	100.000	100.000



PeakTable

Detector A Ch1 210nm

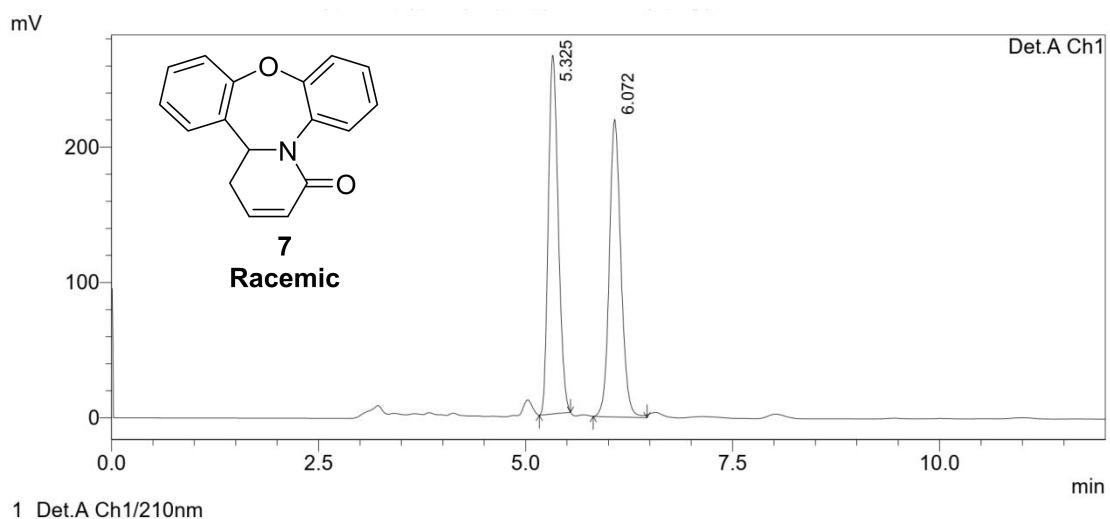
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.526	9287647	497537	49.238	57.239
2	17.757	9575015	371688	50.762	42.761
Total		18862662	869225	100.000	100.000



PeakTable

Detector A Ch1 210nm

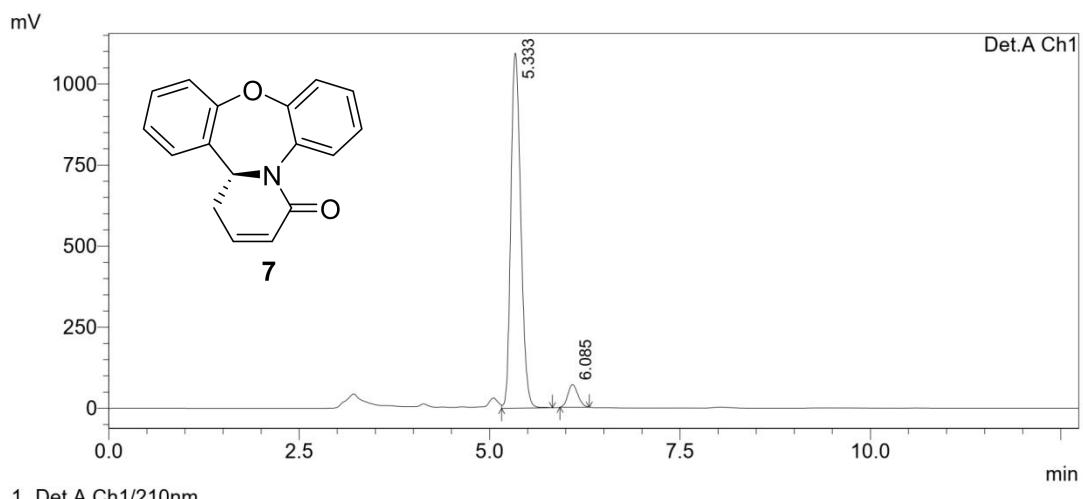
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.515	14687217	780249	95.609	96.495
2	17.740	674591	28343	4.391	3.505
Total		15361808	808592	100.000	100.000



PeakTable

Detector A Ch1 210nm

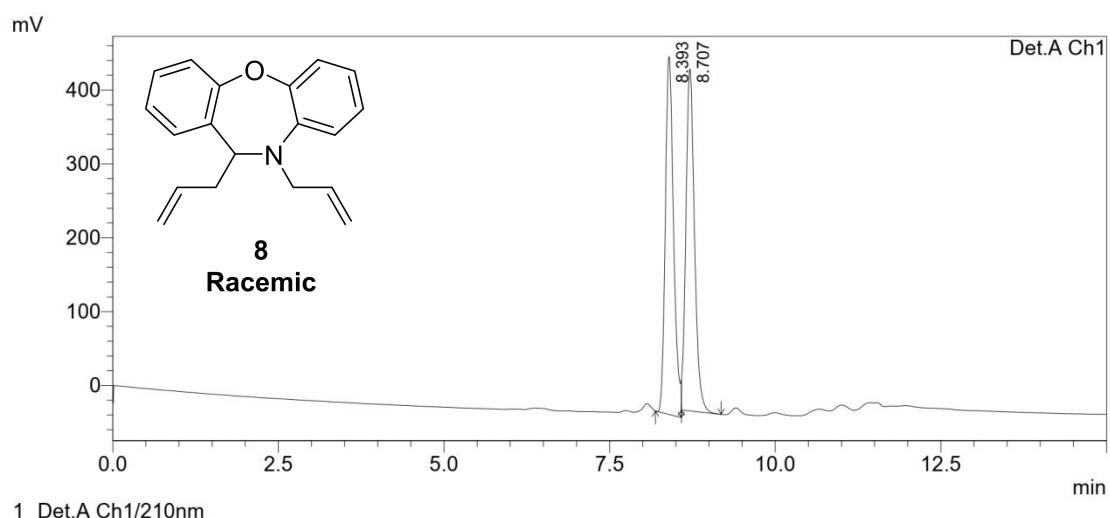
Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.325	2207401	264936	50.718	54.646
2	6.072	2144883	219889	49.282	45.354
Total		4352284	484824	100.000	100.000



PeakTable

Detector A Ch1 210nm

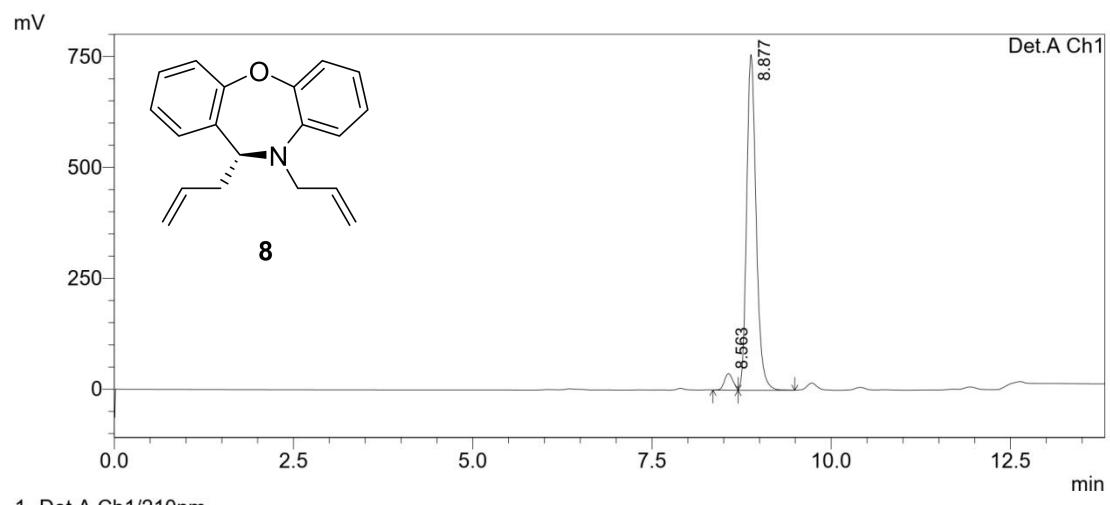
Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.333	9931311	1094267	93.968	94.009
2	6.085	637484	69735	6.032	5.991
Total		10568795	1164003	100.000	100.000



PeakTable

Detector A Ch1 210nm

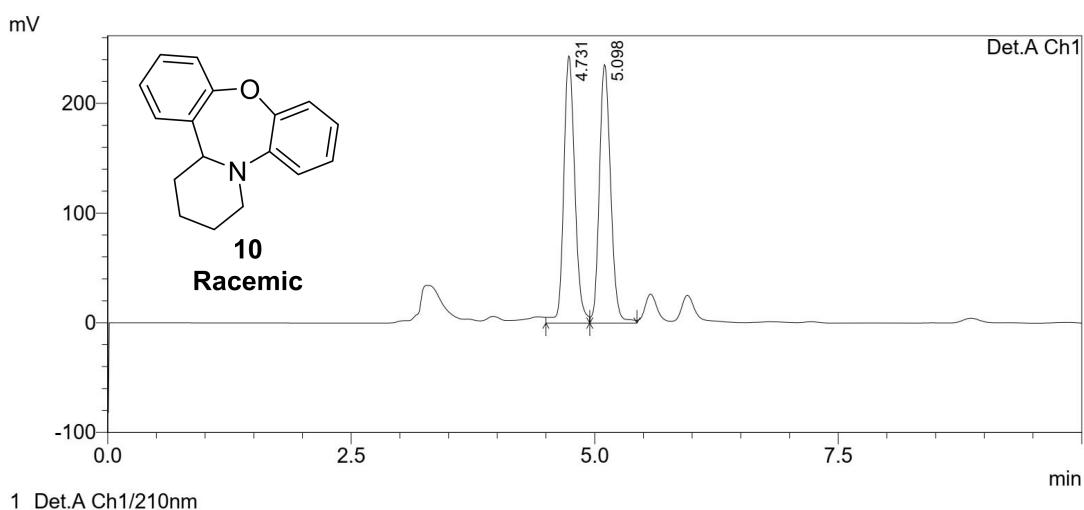
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.393	4220084	484274	50.357	51.118
2	8.707	4160221	463095	49.643	48.882
Total		8380306	947370	100.000	100.000



PeakTable

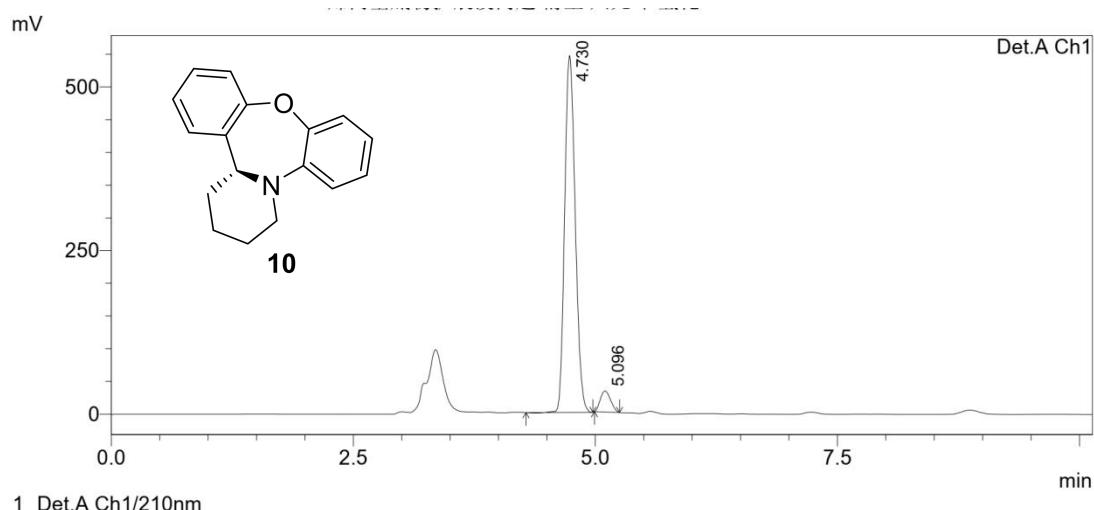
Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.563	314932	37466	4.311	4.714
2	8.877	6990628	757381	95.689	95.286
Total		7305560	794846	100.000	100.000



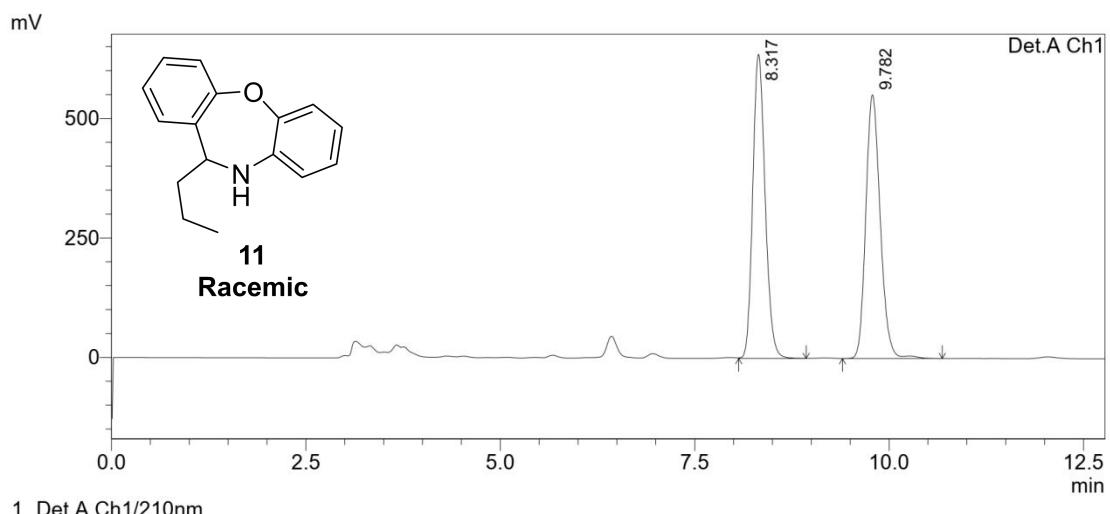
PeakTable

Detector A Ch1 210nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.731	1924542	243851	50.269	50.826
2	5.098	1903975	235925	49.731	49.174
Total		3828517	479776	100.000	100.000



PeakTable

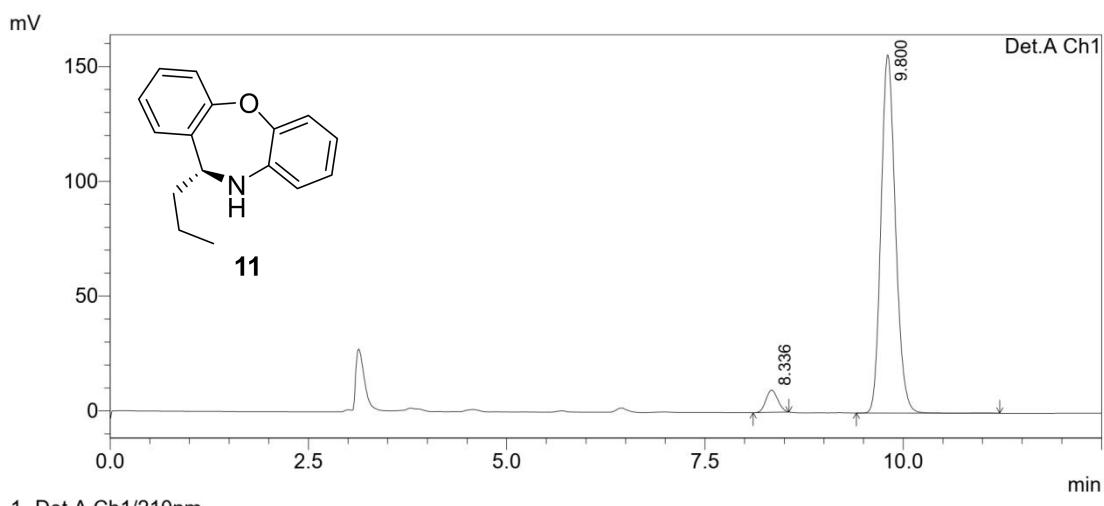
Detector A Ch1 210nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.730	4142392	545595	94.568	94.408
2	5.096	237929	32317	5.432	5.592
Total		4380321	577912	100.000	100.000



PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.317	7057649	636134	49.768	53.549
2	9.782	7123371	551814	50.232	46.451
Total		14181020	1187948	100.000	100.000



PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.336	101005	9713	4.850	5.861
2	9.800	1981749	156001	95.150	94.139
Total		2082754	165714	100.000	100.000