Supporting Information

Stereoselective construction of 5-6-5 aza-tricyclic scaffolds *via* catalytic asymmetric aza-Piancatelli/Diels-Alder reactions

Lishu Wang,[a,c] Han Wang,[a,c] Xukun Nie,[a] Jun Li,*[b] Yurong Tang,[a] and Yunfei Cai*[a]

[a] School of Chemistry and Chemical Engineering, Chongqing University, Chongqing, 400044, China. E-mail: yf.cai@cqu.edu.cn.

[b] Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, Institute of Advanced Fluorine-Containing Materials, Zhejiang Normal University, 688 YingbinRoad, 321004 Jinhua, China. E-mail: jun_li@zjnu.edu.cn

[c] L. Wang and H. Wang contributed equally to this work.

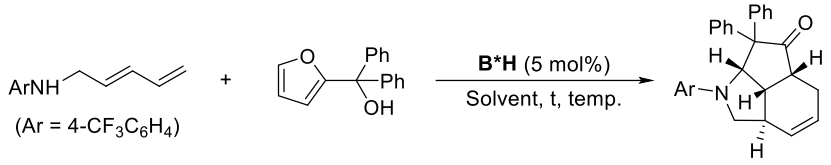
Contents

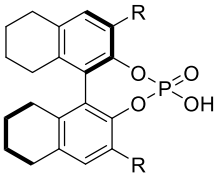
1. General information

All reactions were carried out using oven-dried glassware and magnetic stirring under an inert atmosphere (argon). All chemical were obtained from commercial supplier and were used without further purification unless otherwise stated. All solvents were dried and distilled under argon prior to use. Solvents for chromatography were of technical grade and distilled prior to use. Analytical thin layer chromatography was carried out using silica gel GF254, visualized under UV light (at 254 nm). Analytical thin layer chromatography was carried out using silica gel GF254. ^{1}H NMR (TMS as internal reference), $^{13}C\{^{1}H\}$ NMR and ^{19}F NMR spectra were recorded on Bruker 400 (400, 101, 377 MHz). ^{19}F NMR data of compounds **3**-**10**, **15**, **16, 18, 22**-**31, 33**-**38**, **41**-**44** and **2a**-**2i**, **2m**, **2n**, **2q**, **2r** were collected at 377 MHz with complete proton decoupling. Chemical shifts were referenced relative to internal reference or residual solvent. Data for ^{1}H NMR and ^{19}F NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet, br = broad), integration, coupling constant (Hz). ^{13}C spectra were reported as chemical shifts in ppm and multiplicity where appropriate. Optical rotations were measured with a Rudolph Auto II polarimeter and reported as follows: $[\alpha]_D^T$ (*c*: g/100 mL, in $CHCl_3$, λ = 589 nm). Melting points were measured using a melting point apparatus in open glass capillaries. High resolution mass spectra (HRMS) of **3**-**10**, **12**-**19**, **21**-**31**, **33**-**38**, **41**-**44**, and **2a**-**2s** were acquired on an LTQ Orbitrap Elite mass spectrometer with ESI mode. The X-ray was measured on Agilent Supernova. In reactions where low temperatures were necessary a cryostatic temperature regulator was used. Enantiomeric excesses (ee) were determined by high performance liquid chromatography (HPLC). Structural assignments for compounds **4**, **33**, **42**, **43** and **44** were made with additional information from NOESY experiments.

2. Optimization of the reaction conditions

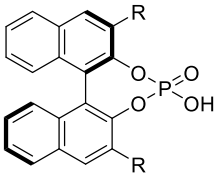
Table S1. Extra optimization of the reaction conditions[a]





A1: R = 2,6-Me_2-4-^{t}Bu-C_6H_2
A2: 2,6-Et_2-4-^{t}BuC_6H_2

A3: 4-^{t}BuC_6H_4
A4: 2,6-Me_2-4-(1-admantyl)-C_6H_2
A5: R = 2,4,6-$Me_3C_6H_2$
A6: R = 2,4,6-^{i}Pr$_3C_6H_2$
A8: R = $SiPh_3$
A9: R = 4-PhC_6H_4
A10: R = 2-naphthyl
A11: R = 9-phenanthrenyl
A12: R = 9-anthryl

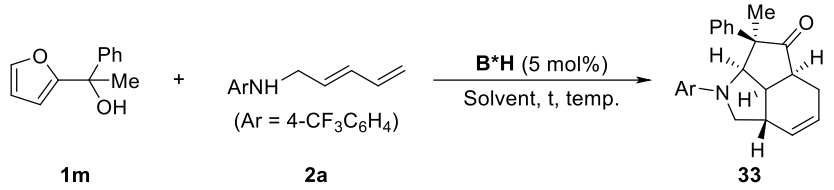


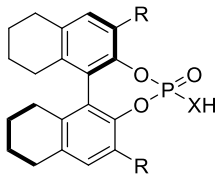
A7: R = 4-^{t}Bu-2,6-$Me_2C_6H_2$

entry[a]	B*H	solvent	temp. (°C)	time (h)	yield[b] (%)	ee[c] (%)
1	**A1**	PhF	70	24	93	93
2	**A2**	PhF	70	24	85	89
3	**A3**	PhF	70	24	79	65
4	**A4**	PhF	70	24	70	85
5	**A5**	PhF	70	24	78	72
6	**A6**	PhF	70	24	80	80
7	**A7**	PhF	70	24	85	88
8	**A8**	PhF	70	24	trace	-
9	**A9**	PhF	70	24	80	40
10	**A10**	PhF	70	24	75	30
11	**A11**	PhF	70	24	83	57
12	**A12**	PhF	70	24	81	59
13	**A1**	PhCl	70	24	75	84
14	**A1**	PhMe	70	24	60[d]	92
15[e]	**A1**	PhMe	70	24	86	92
16	**A1**	$CHCl_3$	70	24	90	86
17	**A1**	EtOAc	70	24	43	85
18	**A1**	1,4-dioxane	70	24	trace	-
19	**A1**	PhF	80	24	90	90
20[f]	**A1**	PhF	40	24	37	93
21[g]	**A1**	PhF	70	48	48	81
22[h]	**A1**	PhF	70	48	trace	-

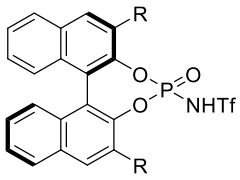
[a]Reaction conditions: (1) **1a** (0.05 mmol), **2a** (0.05 mmol), **B*H** (5 mol%), in solvent (0.5 mL) at the indicated temperature under argon. [b]Yields were determined by ^{1}H NMR analysis of the crude product using trimethyl benzene-1,3,5-tricarboxylate as an internal standard. [c]The ee values were determined by chiral HPLC. [d]25% of arylamine **1a** was recovered, with full decomposition of 2-furylcarbinol **2a** observed. [e]1.5 equivalent of **2a** was used. [f]The cyclopentenone intermediate **3'** was also obtained in 30% yield with 93% ee. [g]The catalyst loading was 3 mol%. [h]The catalyst loading was 1 mol%.

Table S2. Extra optimization of the reaction conditions[a]





A1: X = O, R = 2,6-Me_2-4-^{t}BuC_6H_2
A13: X = NTf, R = 2,4,6-^{i}$Pr_3C_6H_2$
A14: X = NTf, R = 2,6-^{i}Pr_2-4-AdC_6H_2
A15: X = NTf, R = 2,6-^{i}$Pr_2C_6H_3$
A16: X = NTf, R = 4-biphenl
A17: X = NTf, R = 9-anthracenyl

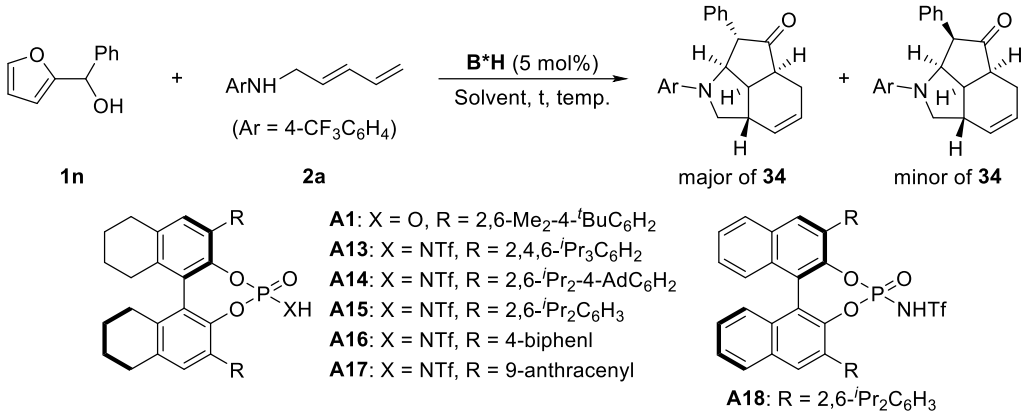


A18: R = 2,6-^{i}$Pr_2C_6H_3$

entry	**B*H**	solvent	temp. (°C)	time (h)	yield[b] (%)	ee[c] (%)
1	**A1**	PhF	70	48	trace	-
2	**A13**	$CHCl_3$	20	48	43	77
3	**A14**	$CHCl_3$	20	48	42	83
4	**A15**	$CHCl_3$	20	48	45	86
5	**A16**	$CHCl_3$	20	48	41	21
6	**A17**	$CHCl_3$	20	48	40	17
7	**A18**	$CHCl_3$	20	48	36	70
8	**A15**	1,4-dioxane	20	48	30	86
9	**A15**	PhF	20	48	34	72
10	**A15**	THF	20	48	34	79
11	**A15**	EtOAc	20	48	35	82
12	**A15**	$CHCl_3$	20	96	46	86
13	**A15**	$CHCl_3$	10	96	44	86
14	**A15**	$CHCl_3$	30	24	66	78
15	**A15**	$CHCl_3$	50	24	70	77

[a]Reaction conditions: (1) **1a** (0.05 mmol), **2a** (0.075 mmol), **B*H** (5 mol%), in solvent (0.5 mL) at the indicated temperature under argon. [b]Yields were determined by ^{1}H NMR analysis of the crude product using trimethyl benzene-1,3,5-tricarboxylate as an internal standard. [c]The ee values were determined by chiral HPLC.

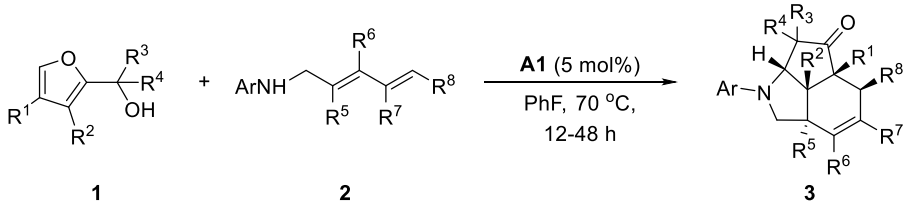
Table S3. Extra optimization of the reaction conditions[a]



entry	B*H	solvent	temp. (°C)	time (h)	yield[b] (%)	ee[c] (%)	major/minor[d]
1	**A1**	PhF	70	24	40	–70	4/1
2	**A13**	$CHCl_3$	20	48	51	79	4/1
3	**A14**	$CHCl_3$	20	48	48	76	4/1
4	**A15**	$CHCl_3$	20	48	50	88	4/1
5	**A16**	$CHCl_3$	20	48	41	7	4/1
6	**A17**	$CHCl_3$	20	48	40	19	4/1
7	**A18**	$CHCl_3$	20	48	36	70	4/1
8	**A15**	1,4-dioxane	20	48	47	84	4/1
9	**A15**	PhF	20	48	46	82	4/1
10	**A15**	THF	20	48	39	71	4/1
11	**A15**	EtOAc	20	48	37	65	4/1
13	**A15**	$CHCl_3$	10	96	48	88	4/1
15	**A15**	$CHCl_3$	30	48	52	86	4/1

[a]Reaction conditions: (1) **1a** (0.05 mmol), **2a** (0.05 mmol), **B*H** (5 mol%), in solvent (0.5 mL) at the indicated temperature under argon. [b]Yields were determined by ^{1}H NMR analysis of the crude product using trimethyl benzene-1,3,5-tricarboxylate as an internal standard. [c]The ee values were determined by chiral HPLC. [d]The major/minor values were determined by ^{1}H NMR analysis of the crude product.

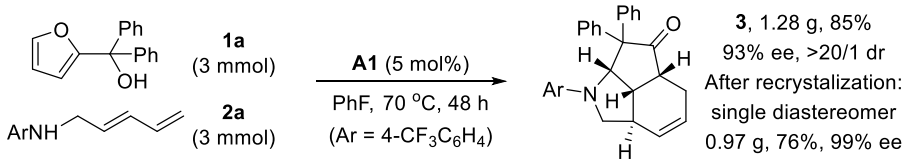
3. General procedure



1 2 3

A dry reaction tube equipped with a stir bar was charged with **A1** (5 mol%, 3.4 mg) or **A15** (5 mol%, 4.0 mg). It was capped with a rubber septum, evacuated and backfilled with N_2 three times. Then, PhF (1.0 mL) or $CHCl_3$ (1.0 mL) and aniline derivative **2** (0.1 mmol, 1 equiv.) were added and stirred at rt, and 2-furylcarbinol **1** (0.1 mmol, 1.0 equiv.) was added. The reaction mixture was stirred at 70 °C or 20 °C for 12–48 h. Upon completion (monitored by TLC), the solvent was removed in vacuo and the crude product was purified by by column chromatography on silica gel using gradients of petroleum ether/ethyl acetate to give the desired products. The enantiomeric excess (ee) was determined by high-perfomance liquid chromatography (HPLC) with Chiralcel AD-H, Chiralcel IA or FLM Chiral INB. The major/minor values were determined by ^{1}H NMR analysis of the crude product.

4. Scale-up of the reaction



A dry flask equipped with a stir bar was charged with **A1** (101.6 mg, 0.15 mmol, 5 mol%). It was capped with a rubber septum, evacuated and backfilled with N_2 three times. Then, PhF (60 mL) and (*E*)-*N*-(penta-2,4-dien-1-yl)-4-(trifluoromethyl)aniline **2a** (681.7 mg, 3 mmol, 1.0 equiv.) were added and stirred at rt, and furan-2-yldiphenylmethanol **1a** (750.9 mg, 3 mmol, 1.0 equiv.) was added. The reaction mixture was stirred at 70 °C for 48 h. The solvent was removed in vacuo, and the residue was purified by column chromatography on silica gel from petroleum ether/ethyl acetate to afford product **3** (1.28 g, 85% yield, 93% ee). After recrystallization from petroleum ether/DCM, product **3** (0.97 g, 76% yield, 99% ee) was afforded.

5. Determination of the absolute configuration and X-ray structure

5.1. Structure report for substrate 19

A Single crystal of **19** suitable for X-ray crystallography was obtained by crystallization via evaporation from its dichloromethane/petroleum ether solution. The absolute configurations of C8, C13, C14 are *S* and C12 is *R*.

Crystallographic data have been deposited in the Cambridge Crystallographic Data Centre database (CCDC) and the deposition number CCDC is 2364690. Copies of the data can be obtained free of charge from the CCDC at www.ccdc.cam.ac.uk.

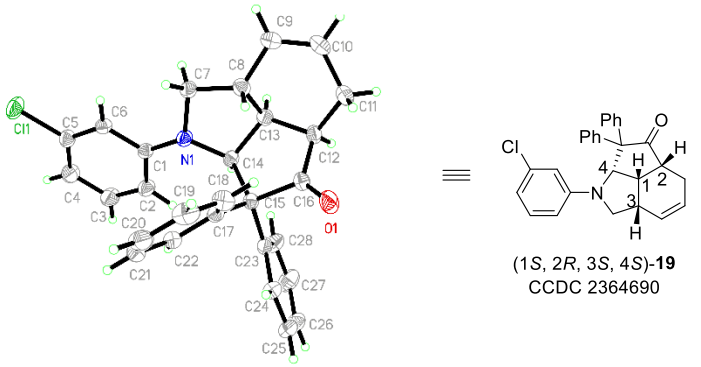


Table S2 Crystal data and structure refinement for 19

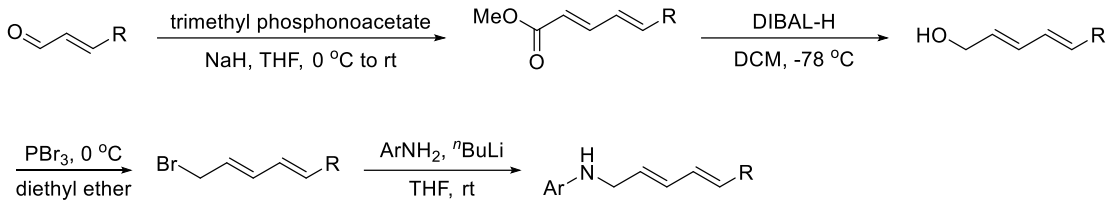
Bond precision:	C–C = 0.0044 A		Wavelength = 1.54178
Cell:	a = 10.2452(4)	b = 14.4399(7)	c = 14.5364(4)
	alpha = 90	beta = 90	gamma = 90
Temperature:	293 K		
	Calculated		Reported
Volume	2150.51 (15)		2150.51 (15)
Space group	P 21 21 21		P 21 21 21
Hall group	P 2ac 2ab		P 2ac 2ab
Moiety formula	C28 H24 Cl N O		C28 H24 Cl N O
Sum formula	C28 H24 Cl N O		C28 H24 Cl N O
Mr	425.93		425.93
Dx, g cm^{-3}	1.316		1.316
Z	4		4
Mu (mm^{-1})	1.721		1.721
F000	896.0		896.0
F000’	899.70		
h,k,lmax	12, 17, 17		12, 15, 17
Nref	3814 [2179]		3120
Tmin, Tmax			0.690, 1.000
Tmin’			

Correction method = # Reported T Limits: Tmin=0.690 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness = 1.43/0.82	Theta (max) = 66.720
R (reflections)= 0.0453 (2814)	wR2(reflections) = 0.1306 (3120)
S = 0.980	Npar = 280

6. Preparation and characteriof the starting materials

6.1 Sythesis of *N*-Pentadienylanilines (2a–2s)[1]



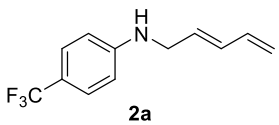
To a 500 mL round bottom flask containing NaH (7.2 g, 30 mmol, 60% mineral dispersion, 1.5 equiv.) and anhydrous THF (40 mL) at 0 ºC, was added trimethyl phosphonoacetate (4.9 mL, 30 mmol, 1.5 equiv.) dropwise via an addition funnel. The reaction mixture was naturally warmed to rt, followed by a dropwise addition of acetophenone (20 mmol, 1.0 equiv.). The reaction mixture was stirred for 6 h, quench the reaction mixture with water. The organic layer was collected, and the aqueous layer was extracted with ethyl acetate (3×30 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 10/1) to afford the corresponding α,β-unsaturated ester as a yellow oil.

To a stirred solution of the α,β-unsaturated ester (1.0 equiv.) in anhydrous DCM (0.2 M) at −78 °C under N_2 was added DIBAL-H (1.0 M in hexanes, 2.2 equiv.) dropwise. The reaction was stirred at −78 °C for 1.5 h, and quenched with 10% aq NaOH (equal volume). The resultant mixture was allowed to warm to rt and stirred for 1 h. The layers were separated and the aqueous layer extracted with DCM (2 × equal volume). The combined organics were washed with brine (equal volume), dried over $MgSO_4$, filtered, and concentrated in vacuo to leave the pure allylic alcohols.

To a stirred solution of the allylic alcohol (1.0 equiv.) in anhydrous Et_2O (0.33 M) at 0 °C under N_2 in the dark was added PBr_3 (0.4 equiv.). The reaction was stirred until completion, as monitored by TLC analysis (typically 0.25–1 h), and poured into sat aq $NaHCO_3$ (equal volume). The layers were separated and the aqueous layer extracted with Et_2O (2 × equal volume). The combined organics were washed with sat aq $Na_2S_2O_3$ and brine (1/1, equal volume), dried over $MgSO_4$, filtered and concentrated in vacuo to leave the pure allylic bromides.

In a 100 mL round-bottomed flask were placed the allylic bromides (10.0 mmol), ^{n}BuLi (11.0 mL, 11.0 mmol), and THF (10 mL). Aniline (3.44 g, 10.0 mmol) was added to the solution and the mixture was stirred under rt for 12 h. The solution was filtered and concentrated under reduced pressure by an aspirator and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 50/1) as eluent to give **2**.

(*E*)-*N*-(penta-2,4-dien-1-yl)-4-(trifluoromethyl)aniline (2a)

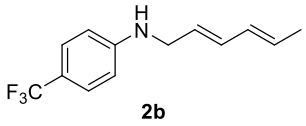


2a

The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 50/1) giving the product **2a** as a yellow oil in 43% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.5 Hz, 2H), 6.57 (d, *J* = 8.5 Hz, 2H), 6.40 – 6.17 (m, 2H), 5.74 (dt, *J* = 14.9, 5.7 Hz, 1H), 5.23 – 5.14 (m, 1H), 5.12 – 5.03 (m, 1H), 4.09

(s, 1H), 3.86 – 3.73 (m, 2H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 149.4, 135.1, 131.8, 128.9, 125.5 (q, *J* = 3.7 Hz), 122.7 (q, *J* = 270.2 Hz), 117.7 (q, *J* = 32.6 Hz), 116.4, 111.0, 44.0. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –62.8 (s). **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{13}F_3N$ 228.0995; Found 228.0996.

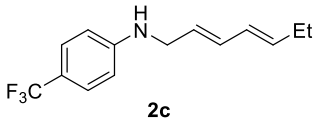
***N*-((2*E*,4*E*)-hexa-2,4-dien-1-yl)-4-(trifluoromethyl)aniline (2b)**



2b

The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 30/1) giving the product **2b** as a yellow oil in 70% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (s, 2H), 6.59 (d, *J* = 8.3 Hz, 2H), 6.28 – 6.16 (m, 1H), 6.05 (ddq, *J* = 14.0, 10.5, 1.8 Hz, 1H), 5.65 (ddt, *J* = 26.9, 15.2, 6.3 Hz, 2H), 4.05 (s, 1H), 3.80 (d, *J* = 5.9 Hz, 2H), 1.76 (d, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 150.5, 132.6, 130.6, 130.0, 126.6 (q, *J* = 3.7 Hz), 126.4, 123.7 (q, *J* = 270.3 Hz), 118.7 (q, *J* = 32.6 Hz), 112.0, 45.3, 18.1. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –61.0. **HRMS (ESI)** *m/z*: $[M + NH_4]^+$ Calcd for $C_{13}H_{18}F_3N_2$ 259.1416; Found 259.1444.

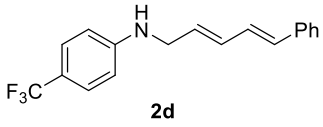
***N*-((2*E*,4*E*)-hepta-2,4-dien-1-yl)-4-(trifluoromethyl)aniline (2c)**



2c

The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 30/1) giving the product **2c** as a yellow oil in 40% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.4 Hz, 2H), 6.60 (d, *J* = 8.4 Hz, 2H), 6.29 – 6.17 (m, 1H), 6.10 – 5.98 (m, 1H), 5.69 (ddt, *J* = 35.7, 15.2, 6.2 Hz, 2H), 4.08 (s, 1H), 3.81 (dd, *J* = 6.0, 1.4 Hz, 2H), 2.15 – 2.05 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 150.5, 137.0, 132.8, 128.3, 126.7, 126.6 (q, *J* = 3.8 Hz), 123.7 (q, *J* = 270.3 Hz), 118.7 (q, *J* = 32.6 Hz), 112.0, 45.3, 25.6, 13.4. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –61.0. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{17}F_3N$ 256.1308; Found 256.1292.

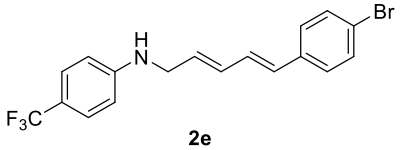
***N*-((2*E*,4*E*)-5-phenylpenta-2,4-dien-1-yl)-4-(trifluoromethyl)aniline (2d)**



2d

The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 50/1) giving the product **2d** as a yellow solid in 65% yield. mp = 100 – 102 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.36 (m, 4H), 7.30 (dd, *J* = 8.5, 6.7 Hz, 2H), 7.21 (d, *J* = 6.9 Hz, 1H), 6.77 (dd, *J* = 15.6, 10.5 Hz, 1H), 6.62 (d, *J* = 8.4 Hz, 2H), 6.52 (d, *J* = 15.7 Hz, 1H), 6.46 – 6.35 (m, 1H), 5.87 (dt, *J* = 15.2, 5.8 Hz, 1H), 4.14 (s, 1H), 3.92 – 3.85 (m, 2H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 150.4, 137.1, 132.7, 132.4, 129.9, 128.7, 128.0, 127.7, 126.6 (q, *J* = 3.9 Hz), 126.4, 119.2 (q, *J* = 32.5 Hz), 112.1, 111.8, 45.4. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –61.0 (s). **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{16}F_3N$ 304.1308; Found 304.1310.

***N*-((2*E*,4*E*)-5-(4-bromophenyl)penta-2,4-dien-1-yl)-4-(trifluoromethyl)aniline (2e)**

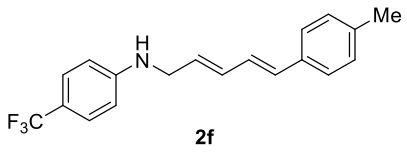


2e

The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 50/1) giving the product **2e** as a yellow solid in 55% yield. mp = 124 – 125 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 8.4, 6.3 Hz, 4H), 7.25 (d, *J* = 12.3 Hz, 2H), 6.76 (dd, *J* = 15.6, 10.5 Hz,

1H), 6.63 (d, *J* = 8.4 Hz, 2H), 6.50 – 6.35 (m, 2H), 5.90 (dt, *J* = 15.2, 5.7 Hz, 1H), 4.19 (s, 1H), 3.91 (d, *J* = 5.7 Hz, 2H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 150.3, 136.0, 132.0, 131.8, 131.3, 130.7, 128.7, 127.8, 126.6 (q, *J* = 3.8 Hz), 123.6 (q, *J* = 322.5 Hz), 121.4, 118.9 (q, *J* = 33.0 Hz), 112.1, 45.3. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –61.0 (s). **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{16}BrF_3N$ 382.0413; Found 382.0416.

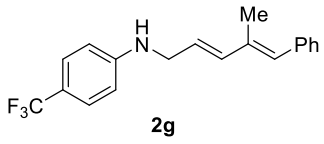
***N*-((2*E*,4*E*)-5-(p-tolyl)penta-2,4-dien-1-yl)-4-(trifluoromethyl)aniline (2f)**



2f

The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 50/1) giving the product **2f** as a yellow solid in 58% yield. mp = 121 – 123 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.73 (dd, *J* = 15.6, 10.5 Hz, 1H), 6.62 (d, *J* = 8.5 Hz, 2H), 6.50 (d, *J* = 15.6 Hz, 1H), 6.44 – 6.36 (m, 1H), 5.84 (dt, *J* = 15.2, 5.8 Hz, 1H), 4.15 (s, 1H), 3.89 (d, *J* = 5.8 Hz, 2H), 2.33 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 150.4, 137.6, 134.3, 132.7, 132.6, 129.4, 129.2, 127.0, 126.6 (q, *J* = 3.8 Hz), 126.3, 123.8, 118.8 (q, *J* = 32.8 Hz), 112.1, 45.4, 21.2. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –61.0 (s). **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{19}F_3N$ 318.1464; Found 318.1470.

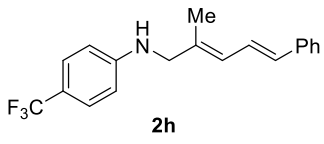
***N*-((2*E*,4*E*)-4-methyl-5-phenylpenta-2,4-dien-1-yl)-4-(trifluoromethyl)aniline (2g)**



2g

The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 30/1) giving the product **2g** as a yellow solid in 68% yield. mp = 110 – 112 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.6 Hz, 2H), 7.36 – 7.31 (m, 2H), 7.30 – 7.26 (m, 2H), 7.24 – 7.20 (m, 1H), 6.64 (d, *J* = 8.6 Hz, 2H), 6.47 (d, *J* = 26.7 Hz, 2H), 5.84 (dt, *J* = 15.6, 5.9 Hz, 1H), 4.53 – 4.00 (m, 1H), 3.92 (d, *J* = 7.5 Hz, 2H), 2.00 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 150.5, 137.6, 137.4, 134.9, 131.6, 129.2, 128.2, 126.7 (q, *J* = 7.8, 4.1 Hz), 125.0, 119.1, 113.3, 112.0, 111.7, 45.7, 14.0. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –61.0 (s). **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{19}F_3N$ 318.1464; Found 318.1469.

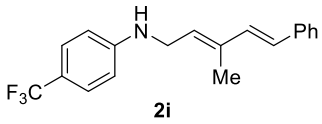
***N*-((2*E*,4*E*)-2-methyl-5-phenylpenta-2,4-dien-1-yl)-4-(trifluoromethyl)aniline (2h)**



2h

The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 10/1) giving the product **2h** was a yellow solid in 77% yield. mp = 108 – 110 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.37 (m, 4H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.24 – 7.18 (m, 1H), 7.01 (dd, *J* = 15.5, 11.0 Hz, 1H), 6.61 (d, *J* = 8.5 Hz, 2H), 6.51 (d, *J* = 15.5 Hz, 1H), 6.26 – 6.18 (m, 1H), 4.26 (s, 1H), 3.81 (s, 2H), 1.90 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 149.6, 136.5, 134.2, 131.1, 127.6, 126.4, 125.6 (q, *J* = 3.8 Hz), 125.3, 124.8, 123.5, 122.7, 118.0, 110.9, 50.1, 14.3. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –61.0 (s). **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{19}F_3N$ 318.1464; Found 318.1471.

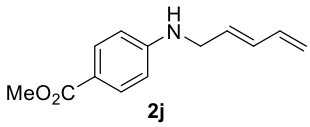
***N*-((2*E*,4*E*)-3-methyl-5-phenylpenta-2,4-dien-1-yl)-4-(trifluoromethyl)aniline (2i)**



2i

The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 10/1) giving the product **2i** was a brown solid in 77% yield. mp = 90 – 92 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 8.3, 1.6 Hz, 4H), 7.32 (dd, *J* = 8.5, 6.8 Hz, 2H), 7.25 – 7.20 (m, 1H), 6.81 (d, *J* = 16.1 Hz, 1H), 6.65 – 6.54 (m, 3H), 5.71 (t, *J* = 6.6 Hz, 1H), 4.07 (s, 1H), 3.95 (d, *J* = 6.7 Hz, 2H), 1.97 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 150.5, 137.3, 136.9, 132.6, 128.7, 128.7, 127.9, 127.5, 126.6 (q, *J* = 3.9 Hz), 126.4, 123.6, 118.8 (q, *J* = 32.7 Hz), 112.0, 41.7, 12.8. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –61.0 (s). **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{19}F_3N$ 318.1464; Found 318.1466.

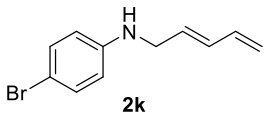
methyl (*E*)-4-(penta-2,4-dien-1-ylamino)benzoate (2j)



2j

The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 10/1) giving the product **2j** as a yellow oil in 65% yield. mp = 85 – 87 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 – 7.82 (m, 2H), 6.59 – 6.53 (m, 2H), 6.40 – 6.21(m, 2H), 5.78 (dt, *J* = 14.8, 5.7 Hz, 1H), 5.16 (dd, *J* = 43.9, 1.9 Hz, 1H), 5.13(dt, *J* = 41.7, 0.9 Hz, 1H), 3.86 (dd, *J* = 5.7, 1.5 Hz, 2H), 3.85 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 167.3, 151.7, 136.1, 132.9, 131.6, 129.8, 118.6, 117.6, 111.7, 51.5, 45.0. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{16}NO_2$ 218.1176; Found 218.1183.

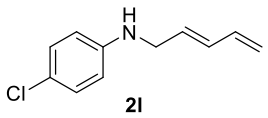
(*E*)-4-bromo-*N*-(penta-2,4-dien-1-yl)aniline (2k)



2k

The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 30/1) giving the product **2k** as a yellow oil in 60% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.18 (m, 2H), 6.50 – 6.44 (m, 2H), 6.40 – 6.18 (m, 2H), 5.76 (dt, *J* = 14.8, 5.8 Hz, 1H), 5.18 (d, *J* = 15.9 Hz, 1H), 5.07 (d, *J* = 9.2 Hz, 1H), 3.75 (dd, *J* = 5.8, 1.6 Hz, 2H), 3.45 (s, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 147.0, 136.2, 132.6, 131.9, 130.5, 117.3, 114.6, 109.1, 45.6. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{13}BrN$ 238.0226; Found 238.0229.

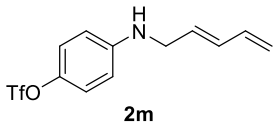
(*E*)-4-chloro-*N*-(penta-2,4-dien-1-yl)aniline (2l)



2l

The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 30/1) giving the product **2l** as a yellow oil in 68% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.13 – 7.08 (m, 2H), 6.53 – 6.49 (m, 2H), 6.40 – 6.19 (m, 2H), 5.76 (dt, *J* = 14.9, 5.7 Hz, 1H), 5.14 (dd, *J* = 17.4, 1.4 Hz, 1H), 5.11 (dt, *J* = 38.9, 1.1 Hz, 1H), 3.75 (dd, *J* = 5.8, 1.6 Hz, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 146.6, 136.3, 132.6, 130.6, 129.1, 122.1, 117.3, 114.1, 45.7. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{12}ClN$ 194.0731; Found 194.0737.

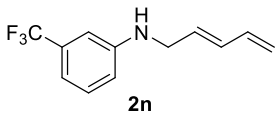
(*E*)-4-(penta-2,4-dien-1-ylamino)phenyl trifluoromethanesulfonate (2m)



2m

The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 20/1) giving the product **2m** as a yellow oil in 57% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.09 – 6.99 (m, 2H), 6.59 – 6.52 (m, 2H), 6.40 – 6.21 (m, 2H), 5.76 (dt, *J* = 14.8, 5.7 Hz, 1H), 5.16 (dd, *J* = 45.3, 1.9 Hz, 1H), 5.13 (d, *J* = 38.5 Hz, 1H). 3.99 (s, 1H), 3.79 (d, *J* = 5.9 Hz, 2H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 147.8, 140.9, 136.1, 132.8, 130.0, 122.1, 118.8 (q, *J* = 321.0 Hz), 117.5, 113.1, 45.6. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –72.8. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{13}F_3NO_3S$ 308.0563; Found 308.0566.

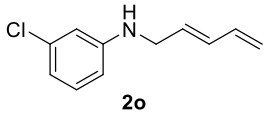
(*E*)-*N*-(penta-2,4-dien-1-yl)-3-(trifluoromethyl)aniline (2n)



2n

The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 30/1) giving the product **2n** as a yellow oil in 59% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 (t, *J* = 7.9 Hz, 1H), 6.96 – 6.90 (m, 1H), 6.79 (d, *J* = 2.2 Hz, 1H), 6.72 (dd, *J* = 8.2, 2.4 Hz, 1H), 6.43 – 6.19 (m, 2H), 5.77 (dt, *J* = 14.7, 5.8 Hz, 1H), 5.22 – 5.05 (m, 2H), 3.98 (s, 1H), 3.91 (s, 1H), 3.81 (dd, *J* = 5.8, 1.6 Hz, 2H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 147.1, 135.1, 131.8, 130.4 (q, *J* = 31.7 Hz), 129.0, 128.6, 124.7 (q, *J* = 272.4 Hz), 116.4, 114.8 (d, *J* = 1.4 Hz), 112.9 (q, *J* = 4.0 Hz), 108.1 (q, *J* = 4.0 Hz), 44.4. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –62.8 (s). **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{13}F_3N$ 228.0995; Found 228.0995.

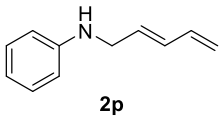
(*E*)-3-chloro-*N*-(penta-2,4-dien-1-yl)aniline (2o)



2o

The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 30/1) giving the product **2o** as a yellow oil in 55% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.04 (t, *J* = 8.1 Hz, 1H), 6.58 – 6.53 (m, 1H), 6.56 (t, *J* = 2.2 Hz, 1H), 6.44 (dd, *J* = 8.2, 2.3 Hz, 1H), 6.39 – 6.17 (m, 2H), 5.75 (dt, *J* = 14.9, 5.8 Hz, 1H), 5.18 (dd, *J* = 16.6, 1.5 Hz, 1H), 5.07 (dd, *J* = 10.1, 1.7 Hz, 1H), 3.74 (m, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 149.2, 136.3, 135.0, 132.7, 130.4, 130.2, 117.4, 117.4, 112.6, 111.3, 45.4. **HRMS (ESI)** *m/z*: $[M + NH_4]^+$ Calcd for $C_{11}H_{16}ClN_2$ 211.0996; Found 211.0984.

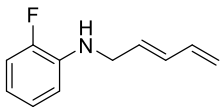
(*E*)-*N*-(penta-2,4-dien-1-yl)aniline (2p)



2p

The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 50/1) giving the product **2p** as a yellow oil in 44% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 – 7.13 (m, 2H), 6.70 (dd, *J* = 7.9, 6.7 Hz, 1H), 6.63 – 6.58 (m, 2H), 6.40 – 6.21 (m, 2H), 5.80 (dt, *J* = 14.7, 5.8 Hz, 1H), 5.17 (dd, *J* = 16.5, 1.9 Hz, 1H), 5.10 – 5.01 (m, 1H), 3.79 (dd, *J* = 5.8, 1.6 Hz, 2H), 3.74 (s, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 147.0, 135.4, 131.3, 130.1, 128.2, 116.6, 116.0, 112.0, 44.6.

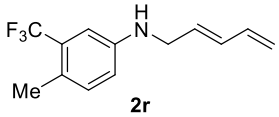
(*E*)-2-fluoro-*N*-(penta-2,4-dien-1-yl)aniline (2q)



2q

The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 50/1) giving the product **2q** as a yellow oil in 64% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.97 (m, 2.5 Hz, 2H), 6.72 – 6.59 (m, 2H), 6.41 – 6.24 (m, 2H), 5.81 (dt, *J* = 14.5, 5.7 Hz, 1H), 5.23 – 5.06 (m, 2H), 4.04 (s, 1H), 3.84 (d, *J* = 5.8 Hz, 2H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) 150.4 (d, *J* = 238.3 Hz), 136.5, 136.3, 132.5, 130.6, 124.6 (d, *J* = 3.5 Hz), 117.3, 116.8 (d, *J* = 6.9 Hz), 114.3 (d, *J* = 18.5 Hz), 112.3 (d, *J* = 3.3 Hz), 45.2. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –136.6 (s). **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{13}FN$ 178.1027; Found 178.1035.

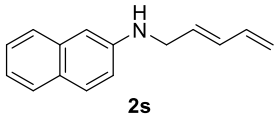
(*E*)-4-methyl-*N*-(penta-2,4-dien-1-yl)-3-(trifluoromethyl)aniline (2r)



2r

The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 30/1) giving the product **2r** as a yellow oil in 77% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.04 (d, *J* = 8.3 Hz, 1H), 6.84 (d, *J* = 2.6 Hz, 1H), 6.63 (dd, *J* = 8.4, 2.6 Hz, 1H), 6.42 – 6.17 (m, 2H), 5.77 (dt, *J* = 14.8, 5.8 Hz, 1H), 5.18 (d, *J* = 15.7 Hz, 1H), 5.07 (d, *J* = 9.0 Hz, 1H), 3.78 (d, *J* = 5.9 Hz, 2H), 3.56 (s, 1H), 2.33 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 144.8, 135.2, 131.6 (d, *J* = 6.2 Hz), 129.4, 128.2 (q, *J* = 29.4 Hz), 123.6, 122.3, 119.6, 116.2, 114.6, 109.4 (q, *J* = 5.8 Hz), 44.6, 17.2 (q, *J* = 2.1 Hz) **^{19}F NMR** (377 MHz, $CDCl_3$) δ –61.8. **HRMS (ESI)** *m/z*: $[M + NH_4]^+$ Calcd for $C_{13}H_{18}F_3N_2$ 259.1416; Found 259.1444.

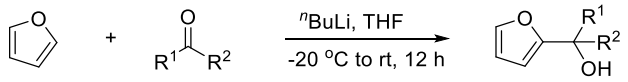
(*E*)-*N*-(penta-2,4-dien-1-yl)naphthalen-2-amine (2s)



2s

The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 30/1) giving the product **2s** as a brown oil in 40% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.1 Hz, 1H), 7.58 (dd, *J* = 8.6, 2.2 Hz, 2H), 7.36 – 7.29 (m, 1H), 7.17 (t, *J* = 7.7 Hz, 1H), 6.81 – 6.74 (m, 2H), 6.39 – 6.18 (m, 2H), 5.78 (dt, *J* = 14.6, 5.8 Hz, 1H), 5.23 – 5.11 (m, 1H), 5.08 – 5.01 (m, 1H), 3.80 (m, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 145.7, 136.5, 135.3, 132.6, 130.9, 129.1, 127.8, 127.7, 126.5, 126.1, 122.2, 118.1, 117.3, 104.9, 45.7. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –61.8. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{16}N$ 210.1278; Found 210.1273.

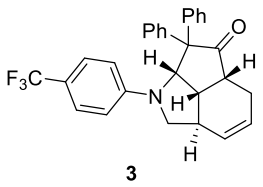
6.2 Sythesis of 2-Furylcarbinols.



The 2-furylcarbinols were prepared according to literature procedure,[2] and the spectral data (^{1}H NMR, ^{13}C{^{1}H} NMR, ^{19}F NMR) matched those previously reported in the literature.

7. Characterization data for the products

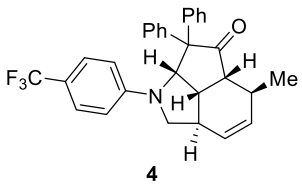
(2a*S*,2a^1*S*,4a*R*,7a*S*)-3,3-diphenyl-2-(4-(trifluoromethyl)phenyl)-1,2,2a,2a^1,3,4a,5,7a-octahydro-4*H*-cyclopenta[*cd*]isoindol-4-one (3)



3

According to **GP** starting from furan-2-yldiphenylmethanol (0.05 mmol) and (*E*)-*N*-(penta-2,4-dien-1-yl)-4-(trifluoromethyl)aniline (0.05 mmol) over the course of 24 h, the product **3** was isolated as white solid after silica gel column chromatography (petroleum ether/ethyl acetate 50/1–30/1), 21.1 mg (92% yield, 93% ee). The dr value was determined by crude ^{1}H NMR analysis. The ee value was determined by HPLC analysis (FLM Chiral INB, hexane/^{i}PrOH = 90/10, flow rate = 1.0 mL/min, l = 254 nm), t_r (major) = 8.1 min, t_r (minor) = 7.2 min; $[\alpha]_D^{20}$ = –355.13 (c = 0.11, in $CHCl_3$); mp = 224 – 226 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 – 7.42 (m, 2H), 7.39 (td, *J* = 6.9, 5.8, 1.4 Hz, 2H), 7.36 – 7.31 (m, 1H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.10 – 7.02 (m, 3H), 7.01 – 6.92 (m, 2H), 6.39 (d, *J* = 8.5 Hz, 2H), 6.07 (dt, *J* = 9.8, 2.9 Hz, 1H), 5.85 – 5.73 (m, 1H), 5.25 (d, *J* = 7.2 Hz, 1H), 3.47 – 3.35 (m, 1H), 3.09 – 2.97 (m, 2H), 2.73 – 2.61 (m, 2H), 2.58 – 2.40 (m, 2H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 216.0, 150.2, 141.7, 139.8, 130.6, 129.0, 128.2, 128.1, 127.6, 127.3, 126.7, 126.1, 126.0 (q, *J* = 3.8 Hz), 123.7 (q, *J* = 270.3 Hz), 118.0 (q, *J* = 32.7 Hz), 112.3, 68.4, 67.6, 51.9, 46.7, 42.8, 39.6, 22.6. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –60.9. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{29}H_{25}F_3NO$ 460.1882; Found 460.1888.

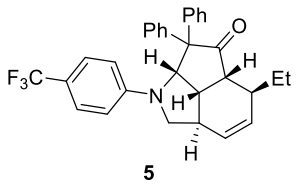
(2a*S*,2a^1*S*,4a*R*,7a*S*)-4a-methyl-3,3-diphenyl-2-(4-(trifluoromethyl)phenyl)-1,2,2a,2a^1,3,4a,5,7a-octahydro-4*H*-cyclopenta[*cd*]isoindol-4-one (4)



4

According to **GP** starting from furan-2-yldiphenylmethanol (0.05 mmol) and *N*-((2*E*,4*E*)-hexa-2,4-dien-1-yl)-4-(trifluoromethyl)aniline (0.05 mmol) over the course of 24 h, the product **4** was isolated as white solid after silica gel column chromatography (petroleum ether/ethyl acetate 50/1–30/1), 22.5 mg (95% yield, 92% ee). The dr value was determined by crude ^{1}H NMR analysis. The ee value was determined by HPLC analysis (Chiralcel ADH, hexane/^{i}PrOH = 95/5, flow rate = 1.0 mL/min, l = 254 nm), t_r (major) = 7.5 min, t_r (minor) = 6.8 min; $[\alpha]_D^{20}$ = –259.03 (c = 0.20, in $CHCl_3$); mp = 245 – 247 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.32 (m, 5H), 7.31 – 7.28 (m, 2H), 7.08 (m, 3H), 7.01 – 6.95 (m, 2H), 6.36 (d, *J* = 8.6 Hz, 2H), 6.04 (dt, *J* = 9.4, 3.1 Hz, 1H), 5.63 (dt, *J* = 9.4, 2.6 Hz, 1H), 5.17 (d, *J* = 6.9 Hz, 1H), 3.36 (dd, *J* = 8.1, 6.9 Hz, 1H), 3.03 (dd, *J* = 11.8, 8.1 Hz, 1H), 2.78 (m, 1H), 2.67 – 2.56 (m, 2H), 2.46 (m, 1H), 1.28 (d, *J* = 7.4 Hz, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 216.8, 150.3, 142.4, 139.5, 135.4, 130.7, 128.9, 128.1, 127.5, 127.4, 126.7, 126.1 (q, *J* = 3.8 Hz), 125.8, 123.7 (q, *J* = 270.4 Hz), 118.4 (q, *J* = 32.7 Hz), 112.3, 69.3, 68.0, 51.8, 51.6, 47.1, 39.7, 29.8, 22.6. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –60.9 (s). **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{30}H_{27}F_3NO$ 474.2040; Found 474.2041.

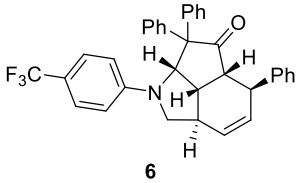
(2a*S*,2a1*S*,5*S*,7a*S*)-5-ethyl-3,3-diphenyl-2-(4-(trifluoromethyl)phenyl)-1,2,2a,2a1,3,4a,5,7a-octahydro-4H-cyclopenta[cd]isoindol-4-one (5)



5

According to **GP** starting from furan-2-yldiphenylmethanol (0.05 mmol) and *N*-((2*E*,4*E*)-hepta-2,4-dien-1-yl)-4-(trifluoromethyl)aniline (0.05 mmol) over the course of 24 h, the product **5** was isolated as yellow solid after after silica gel column chromatography (petroleum ether/ethyl acetate 10/1–5/1), 20.7 mg (85% yield, 87% ee). The dr value was determined by crude ^{1}H NMR analysis. The ee value was determined by HPLC analysis (Chiralcel IA, hexane/^{i}PrOH = 90/10, flow rate = 1.0 mL/min, l = 254 nm), t_r (major) = 6,1 min, t_r (minor) = 4.5 min; $[\alpha]_D^{20}$ = +26.44 (c = 0.02, in $CHCl_3$); mp = 261 – 263 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 4.3 Hz, 4H), 7.32 (m, 3H), 7.08 (m, 3H), 6.98 (m, 2H), 6.37 (d, *J* = 8.5 Hz, 2H), 6.08 (dt, *J* = 9.5, 3.0 Hz, 1H), 5.69 (dt, *J* = 9.6, 2.5 Hz, 1H), 5.20 (d, *J* = 7.0 Hz, 1H), 3.40 – 3.32 (m, 1H), 3.03 (dd, *J* = 11.6, 8.1 Hz, 1H), 2.75 – 2.63 (m, 2H), 2.58 (m, 1H), 2.50 (m, 1H), 1.63 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 216.8, 150.3, 142.3, 139.8, 133.6, 130.6, 128.9, 128.1, 127.5, 127.4, 126.7, 126.2, 126.1 (q, *J* = 3.7 Hz), 123.7 (q, *J* = 536.7 Hz), 118.0, 112.2, 69.1, 67.9, 51.8, 49.3, 47.3, 39.9, 35.8, 28.9, 11.0. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –60.9 (s). **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{31}H_{29}F_3NO$ 488.2196; Found 488.2197.

(2a*S*,2a^1*S*,5*S*,7a*S*)-3,3,5-triphenyl-2-(4-(trifluoromethyl)phenyl)-1,2,2a,2a^1,3,4a,5,7a-octahydro-4*H*-cyclopenta[*cd*]isoindol-4-one (6)

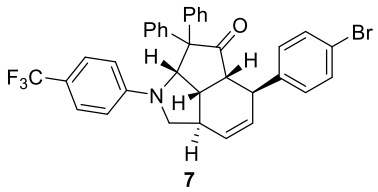


6

According to **GP** starting from furan-2-yldiphenylmethanol (0.05 mmol) and *N*-((2*E*,4*E*)-5-phenylpenta-2,4-dien-1-yl)-4-(trifluoromethyl)aniline (0.05 mmol) over the course of 24 h, the product **6** was isolated as yellow solid after after silica gel column chromatography (petroleum ether/ethyl acetate 10/1–5/1), 23.6 mg (88% yield, 96% ee). The dr value was determined by crude ^{1}H NMR analysis. The ee value was determined by HPLC analysis (Chiralcel ADH, hexane/^{i}PrOH = 95/5, flow rate = 1.0 mL/min, l = 254 nm), t_r (major) = 7.5 min, t_r (minor) = 6.8 min; $[\alpha]_D^{20}$ = –78.75 (c = 0.12, in $CHCl_3$); mp = 255 – 57 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.26 (m, 11H), 7.22 (dd, J = 6.5, 2.4 Hz, 1H), 7.07 (q, J = 3.3 Hz, 3H), 7.01 (dd, J = 6.6, 3.2 Hz, 2H), 6.40 (d, J = 8.5 Hz, 2H), 6.21 (dt, J = 9.7, 3.0 Hz, 1H), 5.84 (dt, J = 9.6, 2.6 Hz, 1H), 5.25 (d, J = 7.2 Hz, 1H), 4.01 (m, 1H), 3.42 (t, J = 7.5 Hz, 1H), 3.10 (dd, J = 11.8, 8.1 Hz, 1H), 2.96 (dd, J = 6.9, 2.7 Hz, 1H), 2.80 (m, 1H), 2.65 (m, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 215.1, 150.2, 146.0, 141.6, 140.0, 133.0, 130.5, 129.0, 129.0, 128.1, 127.8, 127.6, 127.4, 126.7, 126.6, 126.1 (q, *J* = 270.1 Hz), 126.1, 123.7 (q, *J* = 3.2 Hz), 118.2, 112.3 (q, *J* = 32.7 Hz), 68.3, 67.5, 52.9, 51.8, 46.0, 40.4, 39.4. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –61.9. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{35}H_{29}F_3NO$ 536.2196; Found 536.2190.

(2a*S*,2a^1*S*,5*S*,7a*S*)-5-(4-bromophenyl)-3,3-diphenyl-2-(4-(trifluoromethyl)phenyl)-1,2,2a,2a^1,3,4a,5,7a-octahydro-4*H*-cyclopenta[*cd*]isoindol-4-one (7)

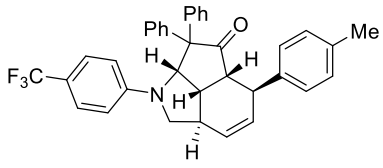
According to **GP** starting from furan-2-yldiphenylmethanol (0.05 mmol) and *N*-((2*E*,4*E*)-5-(4-bromophenyl)penta-2,4-dien-1-yl)-4-(trifluoromethyl)aniline (0.05 mmol) over the course of 24 h, the product **7** was isolated as yellow solid after silica



7

gel column chromatography (petroleum ether/ethyl acetate 10/1–5/1), 26.1 mg (85% yield, 95% ee). The dr value was determined by crude ^{1}H NMR analysis. The ee value was determined by HPLC analysis (FLM Chiral INB, hexane/^{i}PrOH = 90/10, flow rate = 1.0 mL/min, l = 254 nm), t_r (major) = 8.8 min, t_r (minor) = 11.1 min; $[\alpha]_D^{20}$ = +45.00 (c = 0.07, in $CHCl_3$); mp = 164 – 172 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.40 (m, 2H), 7.37 – 7.29 (m, 7H), 7.18 – 7.14 (m, 2H), 7.10 – 7.07 (m, 3H), 7.01 – 6.98 (m, 2H), 6.43 – 6.37 (m, 2H), 6.24 (dt, *J* = 9.6, 3.1 Hz, 1H), 5.80 (dt, *J* = 9.6, 2.6 Hz, 1H), 5.24 (d, *J* = 7.2 Hz, 1H), 3.96 (q, *J* = 2.7 Hz, 1H), 3.43 (dd, *J* = 8.1, 6.8 Hz, 1H), 3.10 (dd, *J* = 11.8, 8.1 Hz, 1H), 2.88 (m, 1H), 2.77 (m, *J* = 11.8, 7.0 Hz, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 215.0, 150.1, 144.9, 141.5, 139.8, 132.2, 132.0, 130.5, 129.6, 129.0, 128.0, 127.6, 127.4, 126.8, 126.8, 126.1 (q, *J* = 4.0 Hz), 123.6 (q, *J* = 270.2 Hz), 120.5, 118.2 (q, *J* = 32.5 Hz), 112.3, 68.3, 67.5, 52.8, 51.8, 45.8, 39.8, 39.3. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –61.0 (s). **HRMS (ESI)** *m/z*: $[M + NH_4]^+$ Calcd for $C_{35}H_{31}BrF_3NO$ 638.1566; Found 638.1546.

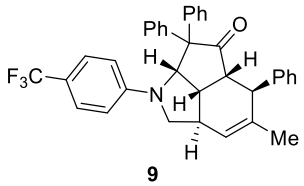
(2a*S*,2a^1*S*,5*S*,7a*S*)-3,3-diphenyl-5-(*p*-tolyl)-2-(4-(trifluoromethyl)phenyl)-1,2,2a,2a^1,3,4a,5,7a-octahydro-4*H*-cyclopenta[*cd*]isoindol-4-one (8)



8

According to **GP** starting from furan-2-yldiphenylmethanol and (0.05 mmol) *N*-((2*E*,4*E*)-5-(*p*-tolyl)penta-2,4-dien-1-yl)-4-(trifluoromethyl)aniline (0.05 mmol) over the course of 24 h, the product **8** was isolated as yellow solid after silica gel column chromatography (petroleum ether/ethyl acetate 10/1–5/1), 24.7mg (90% yield, 96% ee). The dr value was determined by crude ^{1}H NMR analysis. The ee value was determined by HPLC analysis (Chiralcel IA, hexane/^{i}PrOH = 98/2, flow rate = 1.0 mL/min, l = 254 nm), t_r (major) = 8.9 min, t_r (minor) = 6.7 min; $[\alpha]_D^{20}$ = –7.13 (c = 0.08, in $CHCl_3$); mp = 200 – 203 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 7H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 7.08 (m, 3H), 7.01 (m, 2H), 6.40 (d, *J* = 8.6 Hz, 2H), 6.20 (dt, *J* = 9.6, 3.0 Hz, 1H), 5.83 (dt, *J* = 9.6, 2.6 Hz, 1H), 5.24 (d, *J* = 7.1 Hz, 1H), 3.98 (m, 1H), 3.42 (dd, *J* = 8.1, 6.8 Hz, 1H), 3.09 (dd, *J* = 11.8, 8.1 Hz, 1H), 2.93 (dd, *J* = 6.9, 2.7 Hz, 1H), 2.79 (m, 1H), 2.64 (m, 1H), 2.31 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 215.1, 150.2, 143.1, 141.6, 140.0, 136.2, 133.2, 130.5, 129.6, 129.0, 128.1, 127.7, 127.5, 127.4, 126.7, 126.1 (q, *J* = 3.8 Hz), 125.9, 118.5 (q, *J* = 32.7 Hz), 112.3, 68.3, 67.5, 53.0, 51.8, 46.0, 40.0, 39.4, 21.0. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –60.9 (s). **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{36}H_{31}F_3NO$ 550.2352; Found 550.2351.

(2a*S*,2a^1*S*,5*R*,7a*S*)-6-methyl-3,3,5-triphenyl-2-(4-(trifluoromethyl)phenyl)-1,2,2a,2a^1,3,4a,5,7a-octahydro-4*H*-cyclopenta[*cd*]isoindol-4-one (9)

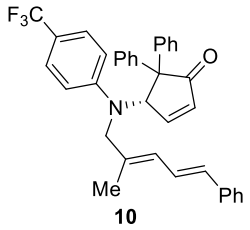


9

According to **GP** starting from furan-2-yldiphenylmethanol (0.05 mmol) and *N*-((2*E*,4*E*)-4-methyl-5-phenylpenta-2,4-dien-1-yl)-4-(trifluoromethyl)aniline (0.05 mmol) over the course of 24 h, the product **9** was isolated as yellow solid after silica gel column chromatography (petroleum ether/ethyl

acetate 10/1–5/1), 23.4mg (85% yield, 94% ee). The dr value was determined by crude ^{1}H NMR analysis. The ee value was determined by HPLC analysis (Chiralcel IA, hexane/^{i}PrOH = 90/10, flow rate = 1.0 mL/min, l = 254 nm), t_r (major) = 6.7 min, t_r (minor) = 4.9 min; $[\alpha]_D^{20}$ = +189.79 (c = 0.04, in $CHCl_3$); mp = 269 – 271 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.25 (m, 7H), 7.20 – 7.10 (m, 4H), 7.10 – 7.04 (m, 3H), 7.01 (dd, *J* = 6.7, 3.1 Hz, 2H), 6.40 (d, *J* = 8.4 Hz, 2H), 6.20 (dt, *J* = 9.7, 3.1 Hz, 1H), 5.83 (dt, *J* = 9.6, 2.7 Hz, 1H), 5.24 (d, *J* = 7.2 Hz, 1H), 3.97 (m, 1H), 3.42 (t, *J* = 7.5 Hz, 1H), 3.09 (dd, *J* = 11.8, 8.1 Hz, 1H), 2.93 (dd, *J* = 6.9, 2.7 Hz, 1H), 2.79 (m, 1H), 2.69 – 2.58 (m, 1H), 2.31 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 213.4, 150.2, 145.2, 141.5, 140.6, 138.2, 130.4, 129.8, 128.9, 128.9, 128.1, 127.9, 127.5, 127.3, 126.6, 126.5, 126.0 (q, *J* = 3.9 Hz), 120.9, 118.3 (q, *J* = 32.3 Hz), 112.2, 67.7, 67.1, 53.0, 52.2, 45.2, 44.3, 40.1, 22.3. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –60.9 (s). **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{36}H_{30}F_3NONa$ 572.2172; Found 572.2171.

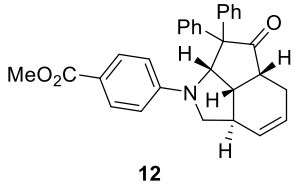
(*S*)-4-(argio((2*E*,4*E*)-2-methyl-5-phenylpenta-2,4-dien-1-yl)amino)-5,5-diphenylcyclopent-2-en-1-one (10)



10

According to **GP** starting from furan-2-yldiphenylmethanol (0.05 mmol) and methyl *N*-((2*E*,4*E*)-2-methyl-5-phenylpenta-2,4-dien-1-yl)-4-(trifluoromethyl)aniline (0.05 mmol) over the course of 48 h, the product **10** was isolated as white solid after silica gel column chromatography (petroleum ether/ethyl acetate 20/1–10/1), 22.0 mg (80% yield, 94% ee). The dr value was determined by crude ^{1}H NMR analysis. The ee value was determined by HPLC analysis (Chiralcel IA, hexane/^{i}PrOH = 90/10, flow rate = 1.0 mL/min, l = 254 nm), t_r (major) = 6.7 min, t_r (minor) = 5.3 min; $[\alpha]_D^{20}$ = +5.95 (c = 0.06 in $CHCl_3$); mp = 132 – 134 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 5.9, 2.4 Hz, 1H), 7.40 – 7.32 (m, 5H), 7.29 (td, *J* = 7.9, 4.7 Hz, 5H), 7.23 – 7.16 (m, 5H), 7.06 – 7.01 (m, 2H), 6.95 (dd, *J* = 15.5, 11.0 Hz, 1H), 6.52 (dd, *J* = 5.9, 2.2 Hz, 1H), 6.44 – 6.35 (m, 3H), 6.05 (d, *J* = 2.7 Hz, 1H), 5.96 – 5.89 (m, 1H), 2.96 (d, *J* = 19.7 Hz, 1H), 2.52 (d, *J* = 19.7 Hz, 1H), 1.62 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 207.4, 161.0, 150.4, 142.1, 137.4, 137.1, 134.4, 133.8, 132.1, 130.9, 129.0, 128.6, 128.0, 127.5, 127.5, 127.4, 127.3, 126.5 (q, *J* = 3.8 Hz), 126.2, 124.4, 124.2, 123.5, 118.5 (q, *J* = 32.5 Hz), 112.4, 71.4, 66.3, 53.3, 15.0. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -61.0 (s). **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{36}H_{31}F_3NO$ 550.2353; Found 550.2350.

methyl 4-((2a*S*,2a^1*S*,4a*R*,7a*S*)-4-oxo-3,3-diphenyl-1,2a,2a^1,3,4,4a,5,7a-octahydro-2*H*-cyclopenta[*cd*]isoindol-2-yl)benzoate (12)

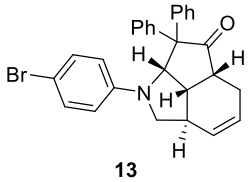


12

According to **GP** starting from furan-2-yldiphenylmethanol (0.05 mmol) and methyl (*E*)-4-(penta-2,4-dien-1-ylamino)benzoate (0.05 mmol) over the course of 48 h, the product **12** was isolated as white solid after silica gel column chromatography (petroleum ether/ethyl acetate 20/1–10/1), 21.4 mg (95% yield, >20/1 dr, 83% ee). The dr value was determined by crude ^{1}H NMR analysis. The ee value was determined by HPLC analysis (FLM Chiral INB, hexane/^{i}PrOH = 70/30, flow rate = 1.0 mL/min, l = 254 nm), t_r (major) = 11.0 min, t_r

(minor) = 8.7 min; $[\alpha]_D^{20}$ = –540.00 (c = 0.03 in $CHCl_3$); mp = 231 – 233 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 – 7.70 (m, 2H), 7.48 – 7.42 (m, 2H), 7.39 (m, 2H), 7.35 – 7.31 (m, 1H), 7.07 – 7.02 (m, 3H), 6.99 – 6.94 (m, 2H), 6.38 – 6.32 (m, 2H), 6.07 (dt, *J* = 9.6, 2.9 Hz, 1H), 5.78 (m, 1H), 5.30 (d, *J* = 7.3 Hz, 1H), 3.81 (s, 3H), 3.42 (dd, *J* = 8.3, 6.8 Hz, 1H), 3.10 – 3.00 (m, 2H), 2.73 – 2.63 (m, 2H), 2.58 – 2.42 (m, 2H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 216.0, 167.3, 151.3, 141.6, 139.8, 130.9, 130.6, 129.0, 128.2, 128.1, 127.6, 127.3, 126.6, 126.1, 117.9, 112.1, 68.2, 67.6, 51.8, 51.5, 46.7, 42.8, 39.6, 22.6. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{30}H_{28}NO_3$ 450.2064; Found 450.2068.

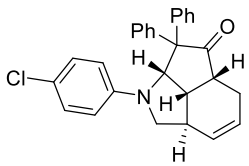
(2a*S*,2a^1*S*,4a*R*,7a*S*)-2-(4-bromophenyl)-3,3-diphenyl-1,2,2a,2a^1,3,4a,5,7a-octahydro-4*H*-cyclopenta[*cd*]isoindol-4-one (13)



13

According to **GP** starting from furan-2-yldiphenylmethanol (0.05 mmol) and (*E*)-4-bromo-*N*-(penta-2,4-dien-1-yl)aniline (0.05 mmol) over the course of 48 h, the product **13** was isolated as yellow solid after silica gel column chromatography (petroleum ether/ethyl acetate 10/1–5/1), 19.8 mg (84% yield, 84% ee). The dr value was determined by crude ^{1}H NMR analysis. The ee value was determined by HPLC analysis (FLM Chiral INB, hexane/^{i}PrOH = 90/10, flow rate = 1.0 mL/min, l = 254 nm), t_r (major) = 8.4 min, t_r (minor) = 7.7 min; $[\alpha]_D^{20}$ = –123.39 (c = 0.07, in $CHCl_3$); mp = 231–233 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 2H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.35 – 7.20 (m, 1H), 7.12 (d, *J* = 8.7 Hz, 2H), 7.09 – 7.03 (m, 3H), 6.96 (dd, *J* = 6.7, 3.1 Hz, 2H), 6.24 (d, *J* = 8.7 Hz, 2H), 6.06 (dt, *J* = 9.5, 2.9 Hz, 1H), 5.77 (td, *J* = 6.0, 2.8 Hz, 1H), 5.14 (d, *J* = 7.3 Hz, 1H), 3.36 (t, *J* = 7.2 Hz, 1H), 3.05 – 2.93 (m, 2H), 2.71 – 2.59 (m, 2H), 2.54 – 2.40 (m, 2H), **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 216.2, 147.1, 141.8, 139.9, 131.3, 130.7, 128.9, 128.3, 128.0, 127.5, 127.2, 126.5, 126.3, 114.3, 108.6, 68.5, 67.7, 52.0, 46.8, 42.8, 39.7, 22.5. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{28}H_{25}BrNO$ 470.1114; Found 470.1111.

(2a*S*,2a^1*S*,4a*R*,7a*S*)-2-(4-chlorophenyl)-3,3-diphenyl-1,2,2a,2a^1,3,4a,5,7a-octahydro-4*H*-cyclopenta[*cd*]isoindol-4-one (14)

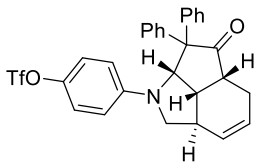


14

According to **GP** starting from furan-2-yldiphenylmethanol (0.05 mmol) and (*E*)-4-chloro-*N*-(penta-2,4-dien-1-yl)aniline (0.05 mmol) over the course of 48 h, the product **14** was isolated as white solid after silica gel column chromatography (petroleum ether/ethyl acetate 50/1–30/1), 17.3 mg (81% yield, 78% ee). The dr value was determined by crude ^{1}H NMR analysis. The ee value was determined by HPLC analysis (FLM Chiral INB, hexane/^{i}PrOH = 90/10, flow rate = 1.0 mL/min, l = 254 nm), t_r (major) = 8.3 min, t_r (minor) = 7.4 min; $[\alpha]_D^{20}$ = –222.86 (c = 0.02, in $CHCl_3$); mp = 222 – 228 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.42 (m, 2H), 7.41 – 7.35 (m, 2H), 7.35 – 7.30 (m, 1H), 7.10 – 7.03 (m, 3H), 7.02 – 6.92 (m, 4H), 6.34 – 6.25 (m, 2H), 6.06 (dt, *J* = 9.6, 3.0 Hz, 1H), 5.77 (ddd, *J* = 9.2, 5.7, 2.7 Hz, 1H), 5.15 (d, *J* = 7.4 Hz, 1H), 3.37 (t, *J* = 6.6 Hz, 1H), 3.05 – 2.93 (m, 2H), 2.72 – 2.60 (m, 2H), 2.54 – 2.39 (m, 2H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 216.2, 146.7, 141.7, 140.0, 130.7, 128.9, 128.5, 128.3, 128.0, 127.5, 127.2, 126.5, 126.3, 121.4, 113.7, 68.5, 67.7, 52.0, 46.7,

42.8, 39.8, 22.5. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{28}H_{25}ClNO$ 426.1619; Found 426.1616.

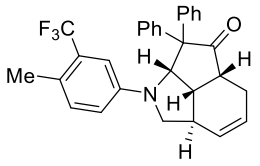
4-((2a*S*,2a^1*S*,4a*R*,7a*S*)-4-oxo-3,3-diphenyl-1,2a,2a^1,3,4,4a,5,7a-octahydro-2*H*-cyclopenta[*cd*]isoindol-2-yl)phenyl trifluoromethanesulfonate (15)



15

According to **GP** starting from furan-2-yldiphenylmethanol (0.05 mmol) and (*E*)-4-(penta-2,4-dien-1-ylamino)phenyl trifluoromethanesulfonate (0.05 mmol) over the course of 24 h, the product **15** was isolated as yellow solid after silica gel column chromatography (petroleum ether/ethyl acetate 30/1–20/1), 24.0 mg (89% yield, 89% ee). The dr value was determined by crude ^{1}H NMR analysis. The ee value was determined by HPLC analysis (Chiralcel ADH, hexane/^{i}PrOH = 90/10, flow rate = 1.0 mL/min, l = 254 nm), t_r (major) = 8.4 min, t_r (minor) = 6.1 min; $[\alpha]_D^{20}$ = –326.72 (c = 0.22, in $CHCl_3$); mp = 142 – 144 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.43 (m, 2H), 7.41 – 7.36 (m, 2H), 7.35 – 7.31 (m, 1H), 7.09 – 7.02 (m, 3H), 6.99 – 6.89 (m, 4H), 6.36 – 6.30 (m, 2H), 6.07 (dt, *J* = 9.6, 3.0 Hz, 1H), 5.81 – 5.74 (m, 1H), 5.21 (d, *J* = 7.3 Hz, 1H), 3.39 (dd, *J* = 7.9, 6.7 Hz, 1H), 3.06 – 2.95 (m, 2H), 2.73 – 2.62 (m, 2H), 2.57 – 2.39 (m, 2H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 215.8, 147.6, 141.4, 140.4, 139.9, 130.6, 129.0, 128.2, 128.1, 127.6, 127.2, 126.6, 126.0, 121.5, 118.8 (d, *J* = 321.0 Hz), 113.1, 68.2, 67.6, 52.0, 46.7, 42.8, 39.8, 22.5. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –72.8. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{29}H_{25}F_3NO_4S$ 540.1451; Found 540.1458.

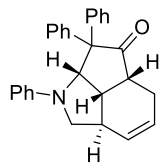
(2a*S*,2a^1*S*,4a*R*,7a*S*)-2-(4-methyl-3-(trifluoromethyl)phenyl)-3,3-diphenyl-1,2,2a,2a^1,3,4a,5,7a-octahydro-4*H*-cyclopenta[*cd*]isoindol-4-one (16)



16

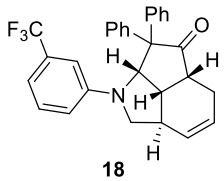
According to **GP** starting from furan-2-yldiphenylmethanol (0.05 mmol) and and (*E*)-4-methyl-*N*-(penta-2,4-dien-1-yl)-3-(trifluoromethyl)aniline (0.05 mmol) over the course of 48 h, the product **16** was isolated as white solid after silica gel column chromatography (petroleum ether/ethyl acetate 30/1–20/1), 19.9 mg (84% yield, 88% ee). The dr value was determined by crude ^{1}H NMR analysis. The ee value was determined by HPLC analysis (FLM Chiral INB, hexane/^{i}PrOH = 95/5, flow rate = 1.0 mL/min, l = 254 nm), t_r (major) = 7.9 min, t_r (minor) = 7.4 min; $[\alpha]_D^{20}$ = –300.06 (c = 0.05, in $CHCl_3$); mp = 212 – 218 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.46 (m, 2H), 7.44 – 7.37 (m, 2H), 7.36 – 7.29 (m, 1H), 7.11 – 7.00 (m, 3H), 6.97 – 6.88 (m, 3H), 6.64 (d, *J* = 2.7 Hz, 1H), 6.41 (dd, *J* = 8.4, 2.7 Hz, 1H), 6.08 (dt, *J* = 9.7, 2.9 Hz, 1H), 5.83 – 5.73 (m, 1H), 5.18 (d, *J* = 7.4 Hz, 1H), 3.45 (dd, *J* = 7.9, 6.5 Hz, 1H), 3.06 – 2.95 (m, 2H), 2.73 – 2.59 (m, 2H), 2.56 – 2.39 (m, 2H), 2.27 (q, *J* = 2.0 Hz, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 216.2, 145.9, 141.3, 140.0, 132.2, 130.8, 128.9, 128.6 (d, *J* = 29.5 Hz), 128.3, 128.1, 127.5, 127.1, 126.5, 126.2, 124.7 (d, *J* = 276.3 Hz), 123.6, 115.2, 110.1 (d, *J* = 6.0 Hz), 68.3, 67.5, 51.9, 46.6, 42.8, 39.8, 22.5, 18.1. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –61.8. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{30}H_{27}F_3NO$ 474.2039; Found 474.2039.

(2a*S*,2a^1*S*,4a*R*,7a*S*)-2,3,3-triphenyl-1,2,2a,2a^1,3,4a,5,7a-octahydro-4*H*-cyclopenta[*cd*]isoindol-4-one (17)


17

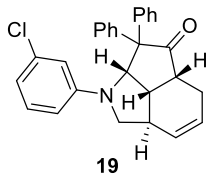
According to **GP** starting from furan-2-yldiphenylmethanol (0.05 mmol) and (*E*)-*N*-(penta-2,4-dien-1-yl)aniline (0.05 mmol) over the course of 72 h, the product **17** was isolated as white solid after silica gel column chromatography (petroleum ether/ethyl acetate 50/1–30/1), 8.8 mg (45% yield, 89% ee). The dr value was determined by crude ^{1}H NMR analysis. The ee value was determined by HPLC analysis (Chiralcel IA, hexane/^{i}PrOH = 95/5, flow rate = 1.0 mL/min, l = 254 nm), t_r (major) = 8.2 min, t_r (minor) = 6.1 min; $[\alpha]_D^{20}$ = –319.21 (c = 0.05, in $CHCl_3$); mp = 250 – 252 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.43 (m, 2H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.34 – 7.29 (m, 1H), 7.09 – 7.03 (m, 5H), 7.00 (dd, *J* = 7.0, 3.0 Hz, 2H), 6.61 (t, *J* = 7.3 Hz, 1H), 6.38 (d, *J* = 8.1 Hz, 2H), 6.07 (dt, *J* = 9.6, 2.9 Hz, 1H), 5.76 (ddt, *J* = 8.5, 5.4, 2.6 Hz, 1H), 5.21 (d, *J* = 7.3 Hz, 1H), 3.39 (dd, *J* = 7.9, 6.6 Hz, 1H), 3.05 – 2.97 (m, 2H), 2.71 – 2.58 (m, 2H), 2.54 – 2.39 (m, 2H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 216.6, 148.1, 142.1, 140.2, 130.8, 128.8, 128.7, 128.3, 127.9, 127.3, 127.1, 126.5, 126.4, 116.6, 112.8, 68.6, 67.8, 51.9, 46.8, 42.9, 39.7, 29.7, 22.6. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{28}H_{26}NO$ 392.2009; Found 392.2017.

(2a*S*,2a^1*S*,4a*R*,7a*S*)-3,3-diphenyl-2-(3-(trifluoromethyl)phenyl)-1,2,2a,2a^1,3,4a,5,7a-octahydro-4*H*-cyclopenta[*cd*]isoindol-4-one (18)


18

According to **GP** starting from furan-2-yldiphenylmethanol (0.05 mmol) and (*E*)-*N*-(penta-2,4-dien-1-yl)-3-(trifluoromethyl)aniline (0.05 mmol) over the course of 24 h, the product **18** was isolated as white solid after silica gel column chromatography (petroleum ether/ethyl acetate 50/1–30/1), 20.4 mg (89% yield, 90% ee). The dr value was determined by crude ^{1}H NMR analysis. The ee value was determined by HPLC analysis (FLM Chiral INB, hexane/^{i}PrOH = 90/10, flow rate = 1.0 mL/min, l = 254 nm), t_r (major) = 7.4 min, t_r (minor) = 6.8 min; $[\alpha]_D^{20}$ = –68.85 (c = 0.02, in $CHCl_3$); mp = 178 – 186 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.47 (m, 2H), 7.43 – 7.38 (m, 2H), 7.37 – 7.32 (m, 1H), 7.12 (t, *J* = 8.0 Hz, 1H), 7.07 – 7.01 (m, 3H), 6.96 – 6.90 (m, 2H), 6.83 (d, *J* = 7.6 Hz, 1H), 6.60 (t, *J* = 2.2 Hz, 1H), 6.52 (dd, *J* = 8.3, 2.6 Hz, 1H), 6.09 (dt, *J* = 9.6, 3.1 Hz, 1H), 5.79 (ddt, *J* = 8.3, 5.4, 2.5 Hz, 1H), 5.23 (d, *J* = 7.4 Hz, 1H), 3.46 (dd, *J* = 7.9, 6.6 Hz, 1H), 3.08 – 2.97 (m, 2H), 2.73 – 2.61 (m, 2H), 2.58 – 2.38 (m, 2H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 216.0, 150.2, 141.7, 139.8, 130.6, 129.0, 128.2, 128.1, 128.0, 127.6, 127.3, 126.7, 126.4, 126.1, 126.0 (q, *J* = 4.0 Hz), 123.7 (q, *J* = 270.6 Hz), 118.1 (q, *J* = 32.5 Hz), 112.3, 68.4, 67.6, 51.9, 46.7, 42.8, 39.6, 22.6. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –62.9. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{29}H_{25}F_3NO$ 460.1883; Found 460.1883.

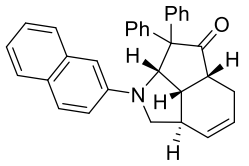
(2a*S*,2a^1*S*,4a*R*,7a*S*)-2-(3-chlorophenyl)-3,3-diphenyl-1,2,2a,2a^1,3,4a,5,7a-octahydro-4*H*-cyclopenta[*cd*]isoindol-4-one (19)


19

According to **GP** starting from furan-2-yldiphenylmethanol (0.05 mmol) and (*E*)-3-chloro-*N*-(penta-2,4-dien-1-yl)aniline (0.05 mmol) over the course of 48 h, the product **19** was isolated as yellow solid after silica gel column chromatography (petroleum ether/ethyl acetate 50/1–30/1), 17.5 mg (82% yield, 85% ee). The dr value was

determined by crude ^{1}H NMR analysis. The ee value was determined by HPLC analysis (Chiralcel ADH, hexane/^{i}PrOH = 90/10, flow rate = 1.0 mL/min, l = 254 nm), t_r (major) = 7.0 min, t_r (minor) = 5.2 min; $[\alpha]_D^{20}$ = –453.4 (c = 0.05, in $CHCl_3$); mp = 201 – 208 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 – 7.43 (m, 2H), 7.42 – 7.36 (m, 2H), 7.35 – 7.30 (m, 1H), 7.07 (dt, *J* = 6.2, 2.7 Hz, 3H), 7.01 – 6.89 (m, 3H), 6.57 (dd, *J* = 7.8, 1.9 Hz, 1H), 6.35 (t, *J* = 2.2 Hz, 1H), 6.24 (dd, *J* = 8.3, 2.4 Hz, 1H), 6.07 (dt, *J* = 9.6, 3.0 Hz, 1H), 5.77 (ddt, *J* = 8.5, 5.4, 2.6 Hz, 1H), 5.18 (d, *J* = 7.3 Hz, 1H), 3.37 (dd, *J* = 8.0, 6.7 Hz, 1H), 3.08 – 2.95 (m, 2H), 2.72 – 2.59 (m, 2H), 2.55 – 2.39 (m, 2H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 216.1, 149.1, 141.6, 139.9, 134.5, 130.7, 129.5, 128.9, 128.3, 128.0, 127.5, 127.2, 126.6, 126.2, 116.5, 112.6, 111.2, 68.3, 67.6, 51.9, 46.7, 42.8, 39.7, 22.5. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{28}H_{25}ClNO$ 426.1619; Found 426.1615.

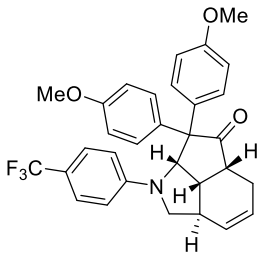
(2a*S*,2a^1*S*,4a*R*,7a*S*)-2-(naphthalen-2-yl)-3,3-diphenyl-1,2,2a,2a^1,3,4a,5,7a-octahydro-4*H*-cyclopenta[*cd*]isoindol-4-one (21)



21

According to **GP** starting from furan-2-yldiphenylmethanol (0.05 mmol) and and (*E*)-*N*-(penta-2,4-dien-1-yl)naphthalen-2-amine (0.05 mmol) over the course of 48 h, the product **21** was isolated as white solid after silica gel column chromatography (petroleum ether/ethyl acetate 30/1–20/1), 16.6 mg (75% yield, 80% ee). The dr value was determined by crude ^{1}H NMR analysis. The ee value was determined by HPLC analysis (Chiralcel ADH, hexane/^{i}PrOH = 90/10, flow rate = 1.0 mL/min, l = 254 nm), t_r (major) = 9.3 min, t_r (minor) = 7.0 min; $[\alpha]_D^{20}$ = +52.39 (c = 0.03, in $CHCl_3$); mp = 212 – 218 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.1 Hz, 1H), 7.54 (d, *J* = 9.0 Hz, 1H), 7.51 – 7.46 (m, 2H), 7.45 – 7.39 (m, 3H), 7.38 – 7.34 (m, 1H), 7.29 (ddd, *J* = 8.2, 6.7, 1.3 Hz, 1H), 7.14 (ddd, *J* = 8.1, 6.7, 1.2 Hz, 1H), 7.02 (qq, *J* = 5.1, 2.9, 2.2 Hz, 5H), 6.77 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.59 (d, *J* = 2.5 Hz, 1H), 6.11 (dt, *J* = 9.6, 3.0 Hz, 1H), 5.79 (ddt, *J* = 8.4, 5.4, 2.6 Hz, 1H), 5.32 (d, *J* = 7.3 Hz, 1H), 3.52 (dd, *J* = 7.9, 6.6 Hz, 1H), 3.14 (dd, *J* = 11.8, 7.9 Hz, 1H), 3.04 (ddd, *J* = 10.2, 7.0, 2.9 Hz, 1H), 2.72 – 2.63 (m, 2H), 2.59 – 2.43 (m, 2H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 216.9, 146.0, 142.3, 140.0, 134.6, 130.8, 128.9, 128.4, 128.4, 127.9, 127.4, 127.4, 127.2, 126.7, 126.7, 126.5, 126.1, 126.0, 121.8, 116.1, 106.6, 69.1, 67.9, 52.1, 47.0, 43.0, 39.7, 22.7. **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{32}H_{28}NO$ 442.2166; Found 442.2165.

(2a*S*,2a^1*S*,4a*R*,7a*S*)-3,3-bis(4-methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)-1,2,2a,2a^1,3,4a,5,7a-octahydro-4*H*-cyclopenta[*cd*]isoindol-4-one (22)

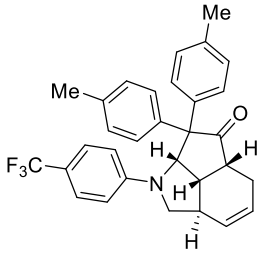


22

According to **GP** starting from furan-2-ylbis(4-methoxyphenyl)methanol (0.05 mmol) and (*E*)-*N*-(penta-2,4-dien-1-yl)-4-(trifluoromethyl)aniline (0.05 mmol) over the course of 48 h, the product **22** was isolated as yellow solid after silica gel column chromatography (petroleum ether/ethyl acetate 40/1–30/1), 23.1 mg (89% yield, 86% ee). The dr value was determined by crude ^{1}H NMR analysis. The ee value was determined by HPLC analysis (FLM Chiral INB, hexane/^{i}PrOH = 70/30, flow rate = 1.0 mL/min, l = 254 nm), t_r (major) = 10.3 min, t_r (minor) = 7.7 min; $[\alpha]_D^{20}$ = –83.91 (c = 0.25, in $CHCl_3$); mp = 231 – 234 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m,

3H), 7.05 – 6.97 (m, 2H), 6.91 (t, *J* = 2.2 Hz, 1H), 6.85 (dd, *J* = 8.1, 2.4 Hz, 1H), 6.63 (dd, *J* = 8.0, 2.2 Hz, 2H), 6.49 (t, *J* = 2.1 Hz, 1H), 6.42 (d, *J* = 8.6 Hz, 2H), 6.06 (dt, *J* = 9.7, 2.9 Hz, 1H), 5.78 (ddt, *J* = 8.4, 5.4, 2.6 Hz, 1H), 5.21 (d, *J* = 7.1 Hz, 1H), 3.75 (s, 3H), 3.42 – 3.37 (m, 1H), 3.35 (s, 3H), 3.10 – 2.98 (m, 2H), 2.70 – 2.59 (m, 2H), 2.50 (ddd, *J* = 18.9, 10.3, 5.8 Hz, 2H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 216.6, 158.8, 157.9, 150.3, 133.8, 132.0, 131.7, 129.3, 128.1, 126.1, 126.0 (q, *J* = 3.8 Hz), 123.7 (q, *J* = 270.3 Hz), 118.0 (q, *J* = 32.7 Hz), 114.3, 112.7, 112.2, 68.6, 66.2, 55.3, 55.1, 51.8, 46.6, 42.6, 39.6, 22.6. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –60.8. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{31}H_{29}F_3NO_3$ 520.2094; Found 520.2093.

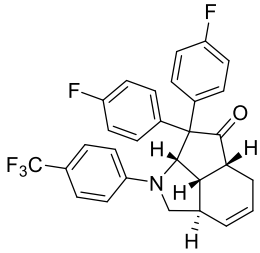
(2a*S*,2a^{1}*S*,4a*R*,7a*S*)-3,3-di-*p*-tolyl-2-(4-(trifluoromethyl)phenyl)-1,2,2a,2a^{1},3,4a,5,7a-octahydro-4*H*-cyclopenta[*cd*]isoindol-4-one (23)



23

According to **GP** starting from furan-2-yldi-*p*-tolylmethanol (0.05 mmol) and (*E*)-*N*-(penta-2,4-dien-1-yl)-4-(trifluoromethyl)aniline (0.05 mmol) over the course of 24 h, the product **23** was isolated as yellow solid after silica gel column chromatography (petroleum ether/ethyl acetate 40/1–30/1), 19.0 mg (78% yield, 95% ee). The dr value was determined by crude ^{1}H NMR analysis. The ee value was determined by HPLC analysis (FLM Chiral INB, hexane/^{i}PrOH = 90/10, flow rate = 1.0 mL/min, l = 254 nm), t_r (major) = 7.2 min, t_r (minor) = 5.8 min; $[\alpha]_D^{20}$ = –187.79 (c = 0.45, in $CHCl_3$); mp = 207 – 209 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 8.5 Hz, 4H), 7.18 (d, *J* = 8.1 Hz, 2H), 6.89 – 6.80 (m, 4H), 6.40 (d, *J* = 8.5 Hz, 2H), 6.06 (dt, *J* = 9.7, 2.9 Hz, 1H), 5.77 (ddt, *J* = 8.7, 5.4, 2.6 Hz, 1H), 5.19 (d, *J* = 7.2 Hz, 1H), 3.41 (dd, *J* = 8.1, 6.7 Hz, 1H), 3.06 – 2.96 (m, 2H), 2.70 – 2.58 (m, 2H), 2.55 – 2.41 (m, 2H), 2.36 (s, 3H), 2.18 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 216.4, 150.4, 138.9, 137.3, 136.9, 136.1, 130.4, 129.6, 128.1, 128.0, 128.0, 126.1, 125.9 (q, *J* = 3.9 Hz), 123.7, 117.9 (q, *J* = 32.4 Hz), 112.2, 68.7, 67.0, 51.9, 46.7, 42.7, 39.6, 22.6, 20.9, 20.9. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –60.9. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{31}H_{29}F_3NO$ 488.2196; Found 488.2191.

(2a*S*,2a^{1}*S*,4a*R*,7a*S*)-3,3-bis(4-fluorophenyl)-2-(4-(trifluoromethyl)phenyl)-1,2,2a,2a^{1},3,4a,5,7a-octahydro-4*H*-cyclopenta[*cd*]isoindol-4-one (24)

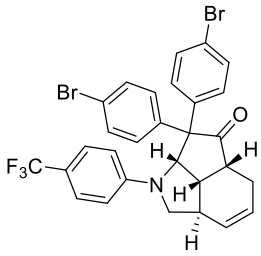


24

According to **GP** starting from bis(4-fluorophenyl)(furan-2-yl)methanol (0.05 mmol) and (*E*)-*N*-(penta-2,4-dien-1-yl)-4-(trifluoromethyl)aniline (0.05 mmol) over the course of 24 h, the product **24** was isolated as yellow solid after silica gel column chromatography (petroleum ether/ethyl acetate 10/1–5/1), 19.8 mg (80% yield, 90% ee). The dr value was determined by crude ^{1}H NMR analysis. The ee value was determined by HPLC analysis (FLM Chiral INB, hexane/^{i}PrOH = 90/10, flow rate = 1.0 mL/min, l = 254 nm), t_r (major) = 9.2 min, t_r (minor) = 8.2 min; $[\alpha]_D^{20}$ = –295.25 (c = 0.28, in $CHCl_3$); mp = 269 – 271 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.35 (m, 2H), 7.31 (d, *J* = 8.6 Hz, 2H), 7.13 – 7.04 (m, 2H), 6.97 – 6.88 (m, 2H), 6.81 – 6.71 (m, 2H), 6.38 (d, *J* = 8.6 Hz, 2H), 6.07 (dt, *J* = 9.7, 3.0 Hz, 1H), 5.83 – 5.73 (m, 1H), 5.15 (d, *J* = 7.3 Hz, 1H), 3.43

(dd, *J* = 8.1, 6.8 Hz, 1H), 3.09 – 2.96 (m, 2H), 2.73 – 2.60 (m, 2H), 2.54 – 2.38 (m, 2H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 215.8, 162.6 (d, *J* = 72.5 Hz), 160.2 (d, *J* = 70.7 Hz), 150.1, 137.3 (d, *J* = 3.4 Hz), 135.5 (d, *J* = 3.6 Hz), 132.2 (d, *J* = 8.0 Hz), 129.7 (d, *J* = 8.0 Hz), 128.1, 126.1 (q, *J* = 3.9 Hz), 125.9, 123.6 (q, *J* = 270.4 Hz), 118.5 (q, *J* = 32.6 Hz), 115.9 (d, *J* = 21.3 Hz), 114.2 (d, *J* = 21.2 Hz), 112.2, 68.5, 66.4, 51.9, 46.6, 42.7, 39.7, 22.5. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -61.0, -114.4, -115.5. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{29}H_{23}F_5NO$ 496.1694; Found 496.1700.

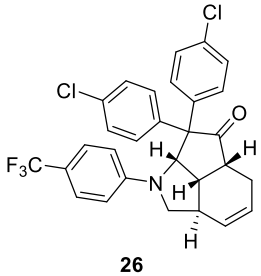
(2a*S*,2a^{1}*S*,4a*R*,7a*S*)-3,3-bis(4-bromophenyl)-2-(4-(trifluoromethyl)phenyl)-1,2,2a,2a^{1},3,4a,5,7a-octahydro-4*H*-cyclopenta[*cd*]isoindol-4-one (25)



25

According to **GP** starting from bis(4-bromophenyl)(furan-2-yl)methanol (0.05 mmol) and (*E*)-*N*-(penta-2,4-dien-1-yl)-4-(trifluoromethyl)aniline (0.05 mmol) over the course of 48 h, the product **25** was isolated 3ab yellow solid after silica gel column chromatography (petroleum ether/ethyl acetate 40/1–30/1), 25.9 mg (84% yield, 90% ee). The dr value was determined by crude ^{1}H NMR analysis. The ee value was determined by HPLC analysis (FLM Chiral INB, hexane/^{i}PrOH = 90/10, flow rate = 1.0 mL/min, l = 254 nm), t_r (major) = 10.8 min, t_r (minor) = 9.2 min; $[\alpha]_D^{20}$ = –41.49 (c = 0.17, in $CHCl_3$); mp = 189 – 203 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 – 7.47 (m, 2H), 7.33 (d, *J* = 8.6 Hz, 2H), 7.27 – 7.24 (m, 2H), 7.23 – 7.18 (m, 2H), 6.88 – 6.80 (m, 2H), 6.38 (d, *J* = 8.6 Hz, 2H), 6.06 (dt, *J* = 9.7, 3.0 Hz, 1H), 5.83 – 5.74 (m, 1H), 5.14 (d, *J* = 7.3 Hz, 1H), 3.42 (dd, *J* = 8.1, 6.8 Hz, 1H), 3.09 – 2.96 (m, 2H), 2.71 – 2.60 (m, 2H), 2.56 – 2.36 (m, 2H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 215.4, 150.1, 140.5, 138.6, 132.2, 130.6, 129.7, 128.1, 126.2 (q, *J* = 3.8 Hz), 125.9, 122.1, 121.2, 118.7 (q, *J* = 32.4 Hz), 112.3, 68.6, 66.9, 52.0, 46.7, 42.9, 39.7, 22.6. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –61.0. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{29}H_{23}Br_2F_3NO$ 618.0073; Found 618.0068.

(2a*S*,2a^{1}*S*,4a*R*,7a*S*)-3,3-bis(4-chlorophenyl)-2-(4-(trifluoromethyl)phenyl)-1,2,2a,2a^{1},3,4a,5,7a-octahydro-4*H*-cyclopenta[*cd*]isoindol-4-one (26)

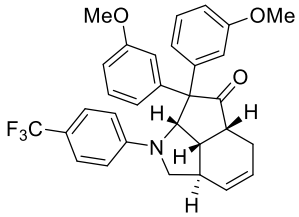


26

According to **GP** starting from bis(4-chlorophenyl)(furan-2-yl)methanol (0.05 mmol) and (*E*)-*N*-(penta-2,4-dien-1-yl)-4-(trifluoromethyl)aniline (0.05 mmol) over the course of 48 h, the product **26** was isolated as yellow solid after silica gel column chromatography (petroleum ether/ethyl acetate 40/1–30/1), 20.1 mg (76% yield, 91% ee). The dr value was determined by crude ^{1}H NMR analysis. The ee value was determined by HPLC analysis (FLM Chiral INB, hexane/^{i}PrOH = 90/10, flow rate = 1.0 mL/min, l = 254 nm), t_r (major) = 9.9 min, t_r (minor) = 8.6 min; $[\alpha]_D^{20}$ = –172.77 (c = 0.25, in $CHCl_3$); mp = 200 – 202 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.30 (m, 6H), 7.10 – 7.02 (m, 2H), 6.94 – 6.86 (m, 2H), 6.38 (d, *J* = 8.6 Hz, 2H), 6.06 (dt, *J* = 9.5, 2.9 Hz, 1H), 5.79 (ddt, *J* = 9.5, 5.4, 2.6 Hz, 1H), 5.14 (d, *J* = 7.3 Hz, 1H), 3.42 (dd, *J* = 8.1, 6.8 Hz, 1H), 3.09 – 2.96 (m, 2H), 2.71 – 2.61 (m, 2H), 2.56 – 2.36 (m, 2H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 215.5, 150.1, 140.0, 138.2, 133.9, 132.9, 131.8, 129.4, 129.2, 128.1, 127.7,

126.2 (q, *J* = 3.8 Hz), 125.9, 123.5, 118.6 (q, *J* = 32.7 Hz), 112.3, 68.6, 66.7, 52.0, 46.7, 42.8, 39.7, 22.6. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –61.0. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{29}H_{23}Cl_2F_3NO$ 530.1074; Found 530.1069.

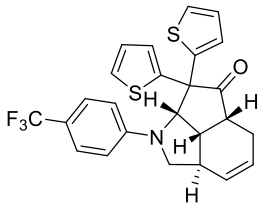
(2a*S*,2a^1*S*,4a*R*,7a*S*)-3,3-bis(3-methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)-1,2,2a,2a^1,3,4a,5,7a-octahydro-4*H*-cyclopenta[*cd*]isoindol-4-one (27)



27

According to **GP** starting from furan-2-ylbis(3-methoxyphenyl)methanol (0.05 mmol) and (*E*)-*N*-(penta-2,4-dien-1-yl)-4-(trifluoromethyl)aniline (0.05 mmol) over the course of 48 h, the product **27** was isolated as yellow solid after silica gel column chromatography (petroleum ether/ethyl acetate 50/1–40/1), 21.6 mg (83% yield, 84% ee). The dr value was determined by crude ^{1}H NMR analysis. The ee value was determined by HPLC analysis (Chiralcel ADH, hexane/^{i}PrOH = 90/10, flow rate = 1.0 mL/min, l = 254 nm), t_r (major) = 9.4 min, t_r (minor) = 15.6 min; $[\alpha]_D^{20}$ = –136.36 (c = 0.07, in $CHCl_3$); mp = 157 – 159 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 6.95 – 6.83 (m, 4H), 6.64 – 6.55 (m, 2H), 6.39 (d, *J* = 8.6 Hz, 2H), 6.06 (dt, *J* = 9.5, 2.9 Hz, 1H), 5.77 (ddt, *J* = 8.5, 5.5, 2.6 Hz, 1H), 5.14 (d, *J* = 7.3 Hz, 1H), 3.82 (s, 3H), 3.67 (s, 3H), 3.43 (dd, *J* = 8.1, 6.7 Hz, 1H), 3.10 – 2.95 (m, 2H), 2.72 – 2.56 (m, 2H), 2.47 (m, *J* = 15.7, 10.3, 4.3 Hz, 2H). **^{13}C{^{1}H} NMR** (101 MHz, $CHCl_3$) δ 216.0, 159.9, 158.6, 150.3, 143.6, 141.0, 129.8, 128.2, 128.0, 126.3, 126.2, 126.1 (q, *J* = 3.8 Hz), 122.8, 120.2, 118.0 (q, *J* = 32.6 Hz), 116.7, 114.9, 112.8, 112.3, 112.2, 68.9, 67.6, 55.3, 54.9, 51.8, 46.9, 42.9, 39.5, 22.7. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –60.9. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{31}H_{29}F_3NO_3$ 520.2094; Found 520.2100.

(2a*S*,2a^1*S*,4a*R*,7a*S*)-3,3-di(thiophen-2-yl)-2-(4-(trifluoromethyl)phenyl)-1,2,2a,2a^1,3,4a,5,7a-octahydro-4*H*-cyclopenta[*cd*]isoindol-4-one (28)

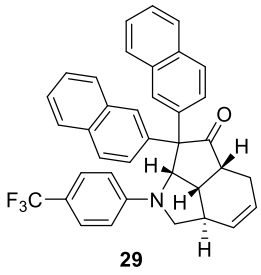


28

According to **GP** starting from furan-2-yldi(thiophen-2-yl)methanol (0.05 mmol) and (*E*)-*N*-(penta-2,4-dien-1-yl)-4-(trifluoromethyl)aniline (0.05 mmol) over the course of 48 h, the product **28** was isolated as yellow solid after silica gel column chromatography (petroleum ether/ethyl acetate 20/1–10/1), 17.5 mg (74% yield, 88% ee). The dr value was determined by crude ^{1}H NMR analysis. The ee value was determined by HPLC analysis (Chiralcel IA, hexane/^{i}PrOH = 98/2, flow rate = 1.0 mL/min, l = 254 nm), t_r (major) = 16.7 min, t_r (minor) = 10.7 min; $[\alpha]_D^{20}$ = –114.37 (c = 0.12, in $CHCl_3$); mp = 128 – 130 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) *d*) δ 7.39 – 7.33 (m, 3H), 7.16 (dd, *J* = 5.0, 1.4 Hz, 1H), 7.06 (dd, *J* = 5.2, 3.7 Hz, 1H), 7.00 (dd, *J* = 3.7, 1.3 Hz, 1H), 6.83 – 6.74 (m, 2H), 6.61 (d, *J* = 8.5 Hz, 2H), 6.08 (dt, *J* = 9.5, 3.0 Hz, 1H), 5.77 (dtd, *J* = 11.4, 5.7, 3.0 Hz, 1H), 4.97 (d, *J* = 7.1 Hz, 1H), 3.65 (dd, *J* = 8.0, 6.6 Hz, 1H), 3.21 – 3.13 (m, 2H), 2.69 – 2.60 (m, 2H), 2.56 – 2.40 (m, 2H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 212.9, 150.1, 146.2, 140.9, 129.0, 128.3, 127.5, 127.1, 126.7, 126.2 (q, *J* = 3.8 Hz), 125.8, 125.6, 125.6, 123.6, 118.8 (q, *J* = 32.7 Hz), 112.6, 72.2, 61.2, 51.7, 46.4, 42.5, 39.4, 22.8. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –61.0. **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{25}H_{21}F_3NOS_2$

472.1011; Found 472.1020.

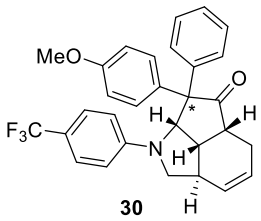
(2a*S*,2a^1*S*,4a*R*,7a*R*)-3,3-di(naphthalen-2-yl)-2-(4-(trifluoromethyl)phenyl)-1,2,2a,2a^1,3,4a,5,7a-octahydro-4*H*-cyclopenta[*cd*]isoindol-4-one (29)



29

According to **GP** starting from furan-2-yldi(naphthalen-2-yl)methanol (0.05 mmol) and (*E*)-*N*-(penta-2,4-dien-1-yl)-4-(trifluoromethyl)aniline (0.05 mmol) over the course of 48 h, the product **29** was isolated as white solid after silica gel column chromatography (petroleum ether/ethyl acetate 30/1–20/1), 21.8 mg (78% yield, 89% ee). The dr value was determined by crude ^{1}H NMR analysis. The ee value was determined by HPLC analysis (FLM Chiral INB, hexane/^{i}PrOH = 90/10, flow rate = 1.0 mL/min, l = 254 nm), t_r (major) = 14.0 min, t_r (minor) = 9.6 min; $[\alpha]_D^{20}$ = +31.94 (c = 0.07, in $CHCl_3$); mp = 246 – 249 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 2.1 Hz, 1H), 7.82 (dd, *J* = 12.3, 6.9 Hz, 3H), 7.71 – 7.62 (m, 2H), 7.60 (d, *J* = 1.8 Hz, 1H), 7.55 – 7.47 (m, 3H), 7.43 – 7.34 (m, 3H), 7.26 (s, 1H), 7.07 (dd, *J* = 8.7, 2.0 Hz, 1H), 6.44 (d, *J* = 8.4 Hz, 2H), 6.08 (dt, *J* = 9.5, 3.0 Hz, 1H), 5.81 (m, 1H), 5.50 (d, *J* = 7.0 Hz, 1H), 3.34 (t, *J* = 7.4 Hz, 1H), 3.17 (dd, *J* = 9.8, 6.7 Hz, 1H), 3.03 (dd, *J* = 11.6, 8.1 Hz, 1H), 2.82 – 2.63 (m, 3H), 2.52 (m, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 215.9, 150.4, 139.2, 137.6, 133.2, 132.6, 132.5, 132.0, 129.4, 128.9, 128.8, 128.3, 128.2, 128.1, 127.6, 127.3, 127.0, 126.8, 126.7, 126.6, 126.2, 126.1, 126.1, 126.0, 125.7, 118.2 (q, *J* = 32.4 Hz), 112.4, 68.8, 67.8, 52.1, 47.0, 42.9, 39.8, 22.7. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –61.0. **HRMS (ESI)** *m/z*: $[M + NH_4]^+$ Calcd for $C_{37}H_{32}F_3N_2O$ 577.2461; Found 577.2483.

(2a*S*,2a^1*S*,3*S*,4a*R*,7a*S*)-3-(4-methoxyphenyl)-3-phenyl-2-(4-(trifluoromethyl)phenyl)-1,2,2a,2a^1,3,4a,5,7a-octahydro-4*H*-cyclopenta[*cd*]isoindol-4-one (30)

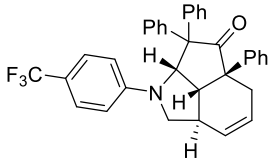


30

According to **GP** starting from furan-2-yl(4-methoxyphenyl)(phenyl)methanol (0.05 mmol) and (*E*)-*N*-(penta-2,4-dien-1-yl)-4-(trifluoromethyl)aniline (0.05 mmol) over the course of 24 h, the product **30** was isolated as yellow solid after silica gel column chromatography (petroleum ether/ethyl acetate 10/1–5/1), 20.8 mg (85% yield, major/minor = 1.6/1 dr, 90% ee, 94% ee). The dr value was determined by crude ^{1}H NMR analysis. The ee value was determined by HPLC analysis (Chiralcel ADH, hexane/^{i}PrOH = 90/5, flow rate = 1.0 mL/min, l = 254 nm), t_r (major) = 26.8 min, 29.2 min, t_r (minor) = 13.8 min, 16.5 min; $[\alpha]_D^{20}$ = –291.10 (c = 0.37, in $CHCl_3$); mp = 212 – 215 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 1H), 7.39 – 7.33 (m, 2H), 7.28 (dd, *J* = 8.7, 4.2 Hz, 2H), 7.04 (q, *J* = 3.8 Hz, 2H), 6.96 (dd, *J* = 6.8, 3.0 Hz, 1H), 6.94 – 6.85 (m, 2H), 6.64 – 6.56 (m, 1H), 6.39 (dd, *J* = 8.8, 3.7 Hz, 2H), 6.07 (dt, *J* = 9.6, 2.9 Hz, 1H), 5.78 (ddt, *J* = 8.6, 5.4, 2.6 Hz, 1H), 5.19 (d, *J* = 7.2 Hz, 1H), 3.83 (s, 2H), 3.68 (s, 1H), 3.42 (ddd, *J* = 8.1, 6.7, 1.6 Hz, 1H), 3.03 (m, *J* = 11.5, 7.8 Hz, 2H), 2.75 – 2.59 (m, 2H), 2.57 – 2.38 (m, 2H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 216.0, 158.9, 150.2, 140.1, 133.4, 131.7, 129.4, 128.1, 128.1, 127.5, 127.2, 126.2, 125.9 (q, *J* = 3.8 Hz), 118.1 (q, *J* = 32.8 Hz), 114.3, 112.2, 68.3, 66.8, 55.3, 51.9, 46.6, 42.6, 39.6, 22.5. **^{19}F NMR** (377

MHz, $CDCl_3$) δ –60.9, -60.9. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{30}H_{27}F_3NO_2$ 490.1988; Found 490.1993.

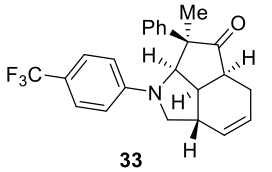
(2a*S*,2a^1*S*,4a*R*,7a*R*)-3,3,4a-triphenyl-2-(4-(trifluoromethyl)phenyl)-1,2,2a,2a^1,3,4a,5,7a-octahydro-4*H*-cyclopenta[*cd*]isoindol-4-one (31)



31

According to **GP** starting from diphenyl(3-phenylfuran-2-yl)methanol (0.05 mmol) and (*E*)-*N*-(penta-2,4-dien-1-yl)-4-(trifluoromethyl)aniline (0.05 mmol) over the course of 48 h, the product **31** was isolated as yellow solid after silica gel column chromatography (petroleum ether/ethyl acetate 10/1–5/1), 21.4 mg (80% yield, 88% ee). The dr value was determined by crude ^{1}H NMR analysis. The ee value was determined by HPLC analysis (Chiralcel ADH, hexane/^{i}PrOH = 90/5, flow rate = 1.0 mL/min, l = 254 nm), t_r (major) = 4.5 min, t_r (minor) = 5.3 min; $[\alpha]_D^{20}$ = –177.21 (c = 0.10, in $CHCl_3$); mp = 252 – 255 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (s, 2H), 7.23 – 7.14 (m, 5H), 7.10 – 6.98 (m, 8H), 6.95 (d, *J* = 7.1 Hz, 2H), 6.41 (d, *J* = 8.5 Hz, 2H), 6.13 (dt, *J* = 9.4, 3.1 Hz, 1H), 5.85 (ddt, *J* = 9.1, 5.8, 2.7 Hz, 1H), 5.31 (d, *J* = 6.9 Hz, 1H), 3.30 – 3.20 (m, 2H), 3.15 (dt, *J* = 13.1, 6.9 Hz, 2H), 2.85 (ddt, *J* = 15.8, 11.7, 5.6 Hz, 1H), 2.46 (dd, *J* = 18.4, 6.1 Hz, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 217.5, 150.1, 142.6, 142.5, 141.5, 130.5, 128.8, 128.6, 128.3, 128.2, 128.0, 127.4, 127.2, 126.6, 126.5, 126.3 (q, *J* = 4.0 Hz), 126.1, 123.7, 117.9 (q, *J* = 32.7 Hz), 112.0, 68.0, 67.2, 56.3, 52.3, 51.6, 39.4, 36.2. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –60.9. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{35}H_{29}F_3NO$ 536.2196; Found 536.2196.

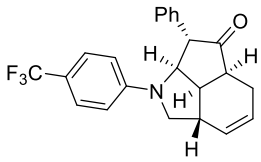
(2a*R*,2a^1*R*,3*R*,4a*S*,7a*S*)-3-methyl-3-phenyl-2-(4-(trifluoromethyl)phenyl)-1,2,2a,2a^1,3,4a,5,7a-octahydro-4*H*-cyclopenta[*cd*]isoindol-4-one (33)



33

According to **GP** starting from 1-(furan-2-yl)-1-phenylethan-1-ol (0.05 mmol) and (*E*)-*N*-(penta-2,4-dien-1-yl)-4-(trifluoromethyl)aniline (0.05 mmol) over the course of 12 h, the product **33** was isolated as white solid after silica gel column chromatography (petroleum ether/ethyl acetate 10/1–5/1), 8.9 mg (45% yield, 86% ee). The dr value was determined by crude ^{1}H NMR analysis. The ee value was determined by HPLC analysis (Chiralcel ADH, hexane/^{i}PrOH = 70/30, flow rate = 1.0 mL/min, l = 254 nm), t_r (major) = 6.5 min, t_r (minor) = 5.3 min; $[\alpha]_D^{20}$ = +179.08 (c = 0.14, in $CHCl_3$); mp = 186 – 188 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 (s, 2H), 7.15 – 7.04 (m, 5H), 6.40 (d, *J* = 8.5 Hz, 2H), 6.09 (dt, *J* = 9.4, 3.1 Hz, 1H), 5.80 (ddt, *J* = 8.8, 5.4, 2.5 Hz, 1H), 4.12 (d, *J* = 7.0 Hz, 1H), 3.51 (dd, *J* = 8.2, 6.5 Hz, 1H), 3.17 (ddd, *J* = 10.0, 6.8, 2.9 Hz, 1H), 3.04 (dd, *J* = 11.6, 8.2 Hz, 1H), 2.67 (dp, *J* = 18.9, 2.9 Hz, 1H), 2.61 – 2.44 (m, 3H), 1.79 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 220.4, 149.9, 138.7, 128.5, 128.2, 127.6, 126.8, 126.1, 126.0 (q, *J* = 3.7 Hz), 123.7 (q, *J* = 270.1 Hz), 118.0 (q, *J* = 32.7 Hz), 111.7, 70.8, 58.1, 51.6, 46.8, 42.2, 39.4, 26.4, 22.6. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –60.9. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{23}F_3NO$ 398.1727; Found 398.1728.

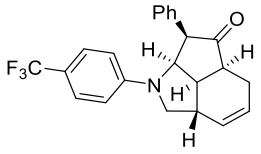
(2a*R*,2a^1*R*,3*S*,4a*S*,7a*S*)-3-phenyl-2-(4-(trifluoromethyl)phenyl)-1,2,2a,2a^1,3,4a,5,7a-octahydro-4*H*-cyclopenta[*cd*]isoindol-4-one (34)



34

According to **GP** starting from furan-2-yl(phenyl)methanol (0.05 mmol) and (*E*)-*N*-(penta-2,4-dien-1-yl)-4-(trifluoromethyl)aniline (0.05 mmol) over the course of 12 h, the product **34** was isolated as white solid after silica gel column chromatography (petroleum ether/ethyl acetate 10/1–5/1), 10.0 mg (52% yield, major/minor = 4/1, 89% ee). The dr value was determined by crude ^{1}H NMR analysis. The ee value was determined by HPLC analysis (Chiralcel ADH, hexane/^{i}PrOH = 90/10, flow rate = 1.0 mL/min, l = 254 nm), t_r (major) = 12.1 min, t_r (minor) = 14.7 min; $[\alpha]_D^{20}$ = +172.10 (c = 0.05, in $CHCl_3$); mp = 186 – 188 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 8.1, 6.4 Hz, 2H), 7.36 – 7.31 (m, 1H), 7.27 (d, *J* = 8.6 Hz, 2H), 7.24 – 7.19 (m, 2H), 6.27 (d, *J* = 8.5 Hz, 2H), 6.14 (dt, *J* = 9.8, 3.1 Hz, 1H), 5.82 (m, 1H), 4.33 (dd, *J* = 7.3, 4.9 Hz, 1H), 3.82 (dd, *J* = 8.3, 6.5 Hz, 1H), 3.30 (d, *J* = 4.8 Hz, 1H), 3.24 (dd, *J* = 11.9, 8.3 Hz, 1H), 3.02 (m, 1H), 2.69 – 2.50 (m, 3H), 2.44 – 2.32 (m, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 216.0, 149.5, 138.8, 129.3, 128.6, 127.9, 127.6, 126.5 (q, *J* = 3.8 Hz), 126.0, 118.7, 118.1, 111.6, 66.9, 62.5, 51.5, 47.3, 45.5, 40.0, 22.9. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –60.9. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{21}F_3NO$ 384.1170; Found 384.1571.

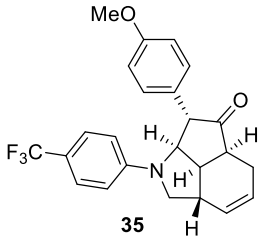
(2a*R*,2a^1*R*,3*R*,4a*S*,7a*S*)-3-phenyl-2-(4-(trifluoromethyl)phenyl)-1,2,2a,2a^1,3,4a,5,7a-octahydro-4*H*-cyclopenta[*cd*]isoindol-4-one (stereoisomer of 34)



stereoisomer of **34**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.26 (m, 5H), 7.18 – 7.12 (m, 2H), 6.36 (d, *J* = 8.6 Hz, 2H), 5.98 – 5.83 (m, 2H), 4.72 (dd, *J* = 8.6, 4.7 Hz, 1H), 3.83 (dd, *J* = 9.7, 8.3 Hz, 1H), 3.67 – 3.54 (m, 1H), 3.23 – 3.14 (m, 2H), 3.13 – 2.96 (m, 2H), 2.63 (ddd, *J* = 17.0, 5.8, 2.6 Hz, 1H), 2.25 (m, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 216.1, 149.0, 138.8, 129.3, 129.2, 127.8, 127.6, 127.5, 126.3 (q, *J* = 3.8 Hz), 118.9, 113.4, 67.0, 61.5, 54.4, 44.3, 40.4, 34.5, 22.7. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –61.1.

(2a*R*,2a^1*R*,3*S*,4a*S*,7a*S*)-3-(4-methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)-1,2,2a,2a^1,3,4a,5,7a-octahydro-4*H*-cyclopenta[*cd*]isoindol-4-one (35)

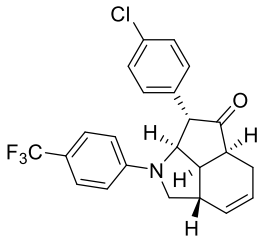


35

According to **GP** starting from furan-2-yl(4-methoxyphenyl)methanol (0.05 mmol) and (*E*)-*N*-(penta-2,4-dien-1-yl)-4-(trifluoromethyl)aniline (0.05 mmol) over the course of 12 h, the product **35** was isolated as white solid after silica gel column chromatography (petroleum ether/ethyl acetate 10/1–5/1), 11.4 mg (55% yield, major/minor = 4/1, 82% ee). The dr value was determined by crude ^{1}H NMR analysis. The ee value was determined by HPLC analysis (Chiralcel IA, hexane/^{i}PrOH = 70/30, flow rate = 1.0 mL/min, l = 254 nm), t_r (major) = 8.5 min, t_r (minor) = 9.5 min; $[\alpha]_D^{20}$ = +137.63 (c = 0.03, in $CHCl_3$); mp = 175 – 177 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.5 Hz, 2H), 7.15 – 7.10 (m, 2H), 6.96 – 6.90 (m, 2H), 6.29 (d, *J* = 8.5 Hz, 2H), 6.14 (d, *J* = 9.6 Hz, 1H), 5.81 (ddt, *J* = 9.6, 5.5, 2.8 Hz, 1H), 4.28 (dd, *J* = 7.4, 4.9 Hz, 1H), 3.84 (s, 3H), 3.83 – 3.77 (m, 1H), 3.28 – 3.19 (m, 2H), 2.99 (ddd, *J* = 10.2, 7.2,

3.3 Hz, 1H), 2.67 – 2.50 (m, 3H). 2.37 (s, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 216.5, 159.0, 149.6, 130.9, 129.0, 128.6, 126.5 (q, *J* = 4.0 Hz), 126.0, 123.7 (q, *J* = 270.6 Hz), 117.8 (q, *J* = 32.6 Hz), 114.7, 112.0, 111.7, 67.0, 61.6, 55.3, 51.5, 47.2, 45.3, 39.9, 22.9. δ 126.51, 125.07, 117.96. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –60.9. **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{24}H_{22}F_3NO_2Na$ 436.1495; Found 436.1499.

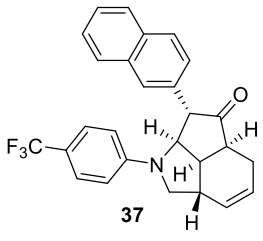
(2a*R*,2a^1*R*,3*S*,4a*S*,7a*S*)-3-(4-chlorophenyl)-2-(4-(trifluoromethyl)phenyl)-1,2,2a,2a^1,3,4a,5,7a-octahydro-4*H*-cyclopenta[*cd*]isoindol-4-one (36)



36

According to **GP** starting from (4-chlorophenyl)(furan-2-yl)methanol (0.05 mmol) and (*E*)-*N*-(penta-2,4-dien-1-yl)-4-(trifluoromethyl)aniline (0.05 mmol) over the course of 12 h, the product **36** was isolated as white solid after silica gel column chromatography (petroleum ether/ethyl acetate 10/1–5/1), 11.1 mg (53% yield, major/minor = 4/1, 83% ee). The dr value was determined by crude ^{1}H NMR analysis. The ee value was determined by HPLC analysis (Chiralcel ADH, hexane/^{i}PrOH = 90/10, flow rate = 1.0 mL/min, l = 254 nm), t_r (major) = 14.4 min, t_r (minor) = 12.7 min; $[\alpha]_D^{20}$ = +126.00 (c = 0.02, in $CHCl_3$); mp = 201 – 202 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.34 (m, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.19 – 7.12 (m, 2H), 6.26 (d, *J* = 8.5 Hz, 2H), 6.19 – 6.10 (m, 1H), 5.82 (ddt, *J* = 9.5, 5.5, 2.8 Hz, 1H), 4.29 (dd, *J* = 7.3, 4.9 Hz, 1H), 3.83 (dd, *J* = 8.3, 6.5 Hz, 1H), 3.28 (d, *J* = 5.0 Hz, 1H), 3.24 (dd, *J* = 11.9, 8.2 Hz, 1H), 2.99 (ddd, *J* = 10.6, 7.4, 3.7 Hz, 1H), 2.69 – 2.62 (m, 1H), 2.62 – 2.51 (m, 2H), 2.43 – 2.30 (m, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 215.6, 149.4, 137.2, 133.6, 129.5, 129.2, 128.5, 126.6 (q, *J* = 3.9 Hz), 126.0, 118.5, 118.1, 111.6, 66.7, 61.8, 51.5, 47.3, 45.4, 39.9, 22.9. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -61.0. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{20}ClF_3NO$ 418.1180; Found 418.1178.

(2a*R*,2a^1*R*,3*S*,4a*S*,7a*S*)-3-(naphthalen-2-yl)-2-(4-(trifluoromethyl)phenyl)-1,2,2a,2a^1,3,4a,5,7a-octahydro-4*H*-cyclopenta[*cd*]isoindol-4-one (37)

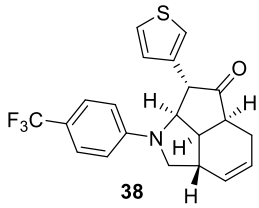


37

According to **GP** starting from furan-2-yl(naphthalen-2-yl)methanol (0.05 mmol) and (*E*)-*N*-(penta-2,4-dien-1-yl)-4-(trifluoromethyl)aniline (0.05 mmol) over the course of 12 h, the product **37** was isolated as white solid after silica gel column chromatography (petroleum ether/ethyl acetate 10/1–5/1), 8.9 mg (41% yield, major/minor = 3/1, 87% ee). The dr value was determined by crude ^{1}H NMR analysis. The ee value was determined by HPLC analysis (Chiralcel IA, hexane/^{i}PrOH = 70/30, flow rate = 1.0 mL/min, l = 254 nm), t_r (major) = 10.7 min, t_r (minor) = 9.4 min; $[\alpha]_D^{20}$ = –118.66 (c = 0.07, in $CHCl_3$); mp = 211 – 213 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 – 7.85 (m, 2H), 7.83 – 7.79 (m, 1H), 7.69 (d, *J* = 1.9 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.32 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.23 (s, 2H), 6.28 (d, *J* = 8.5 Hz, 2H), 6.16 (dt, *J* = 9.7, 3.1 Hz, 1H), 5.83 (ddt, *J* = 8.5, 5.5, 2.8 Hz, 1H), 4.46 (dd, *J* = 7.4, 4.8 Hz, 1H), 3.85 (dd, *J* = 8.3, 6.5 Hz, 1H), 3.47 (d, *J* = 4.8 Hz, 1H), 3.26 (dd, *J* = 11.9, 8.3 Hz, 1H), 3.11 (ddd, *J* = 10.2, 7.2, 3.1 Hz, 1H), 2.74 – 2.53 (m, 3H), 2.42 (d, *J* = 7.7 Hz, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 215.9, 149.5, 136.1, 133.6, 132.6, 129.3, 128.6, 127.8, 126.8, 126.6, 126.5 (q, *J* = 3.8 Hz), 126.3,

126.2, 126.0, 125.8, 123.4, 117.9 (q, *J* = 32.8 Hz), 111.7, 66.8, 62.5, 51.5, 47.4, 45.6, 40.0, 22.9. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –60.9. **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{27}H_{22}F_3NONa$ 456.1546; Found 456.1599.

(2a*R*,2a^1*R*,3*S*,4a*S*,7a*S*)-3-(thiophen-3-yl)-2-(4-(trifluoromethyl)phenyl)-1,2,2a,2a^1,3,4a,5,7a-octahydro-4*H*-cyclopenta[*cd*]isoindol-4-one (38)

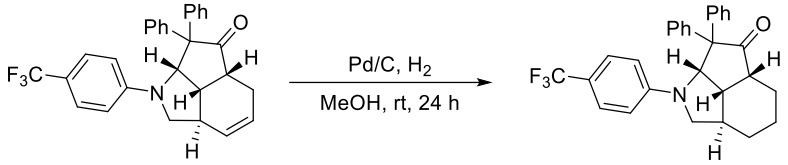


38

According to **GP** starting from furan-2-yl(thiophen-3-yl)methanol (0.05 mmol) and (*E*)-*N*-(penta-2,4-dien-1-yl)-4-(trifluoromethyl)aniline (0.05 mmol) over the course of 12 h, the product **38** was isolated as white solid after silica gel column chromatography (petroleum ether/ethyl acetate 5/1–3/1), 8.0 mg (54% yield, major/minor = 3/1, 76% ee). The dr value was determined by crude ^{1}H NMR analysis. The ee value was determined by HPLC analysis (Chiralcel IA, hexane/^{i}PrOH = 90/10, flow rate = 1.0 mL/min, l = 254 nm), t_r (major) = 7.0 min, t_r (minor) = 9.4 min; $[\alpha]_D^{20}$ = –207.75 (c = 0.01, in $CHCl_3$); mp = 165 – 167 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 5.0, 2.9 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 3.0 Hz, 1H), 7.00 (d, *J* = 5.0 Hz, 1H), 6.35 (d, *J* = 8.4 Hz, 2H), 6.12 (dd, *J* = 9.6, 3.1 Hz, 1H), 5.83 – 5.78 (m, 1H), 4.29 (dd, *J* = 7.4, 4.6 Hz, 1H), 3.80 (dd, *J* = 8.3, 6.4 Hz, 1H), 3.46 (d, *J* = 4.7 Hz, 1H), 3.22 (dd, *J* = 11.9, 8.3 Hz, 1H), 3.01 (ddd, *J* = 10.1, 7.1, 3.0 Hz, 1H), 2.66 – 2.48 (m, 3H), 2.37 – 2.30 (m, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 215.2, 149.6, 138.0, 128.6, 127.2, 126.6, 126.5 (q, *J* = 3.8 Hz), 125.9, 123.8, 122.0, 118.0 (q, *J* = 32.1 Hz), 111.6, 66.3, 57.3, 51.5, 47.2, 44.6, 39.9, 22.7. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –60.9. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{19}F_3NOS$ 390.1134; Found 390.1171.

8. Synthetic transformations

8.1. Synthesis of (2a*S*,2a^1*S*,4a*R*,7a*S*)-2-argio-3,3-diphenyldecahydro-4*H*-cyclopenta[*cd*]isoindol-4-one (41)[3]

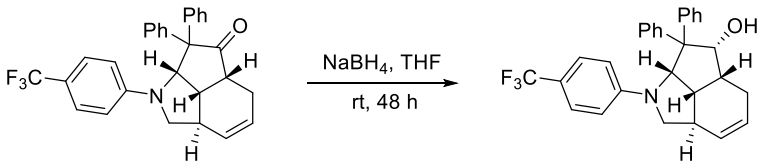


3, 99% ee — **41**, 92% yeild, 99% ee

At rt, a flask was charged with a solution of the compound **3** (46.0g, 0.1 mmol, 1.0 equiv., 99% ee) in MeOH (4 mL), Pd/C (10.0 mg) was added in one portion to the above solution. The flask was evacuated and refilled with H_2 with a ballon. The reaction mixture was stirred under H_2 atmosphere for 24 h. Then the reaction mixture was filtered through a pad of celite. The filtrate was concentrated in vacuo and the residue was subjected to column chromatography on silica gel (petroleum ether/ethyl acetate 10/1–5/1) to give the product **41** as a white solid (42.5 mg, 92% yield, 99% ee). The dr value was determined by ^{1}H NMR analysis. The ee value was determined by HPLC analysis (Chiralcel ADH, hexane/^{i}PrOH = 95/5, flow rate = 1.0 mL/min, l = 254 nm), t_r (major) = 7.4 min, t_r (minor) = 6.8 min; $[\alpha]_D^{20}$ = –156.47 (c = 0.58, in $CHCl_3$); mp = 203 – 205 °C.

(2a*S*,2a^1*S*,4a*R*,7a*S*)-2-argio-3,3-diphenyldecahydro-4*H*-cyclopenta[*cd*]isoindol-4-one (41): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.27 (m, 7H), 7.11 – 6.99 (m, 5H), 6.37 (d, *J* = 8.6 Hz, 2H), 5.18 (d, *J* = 7.2 Hz, 1H), 3.16 (dd, *J* = 8.2, 6.5 Hz, 1H), 2.97 (td, *J* = 6.5, 2.4 Hz, 1H), 2.88 (dd, *J* = 11.5, 8.2 Hz, 1H), 2.47 (dt, *J* = 13.0, 6.7 Hz, 1H), 2.22 (m, 1H), 1.94 (dt, *J* = 11.8, 3.8 Hz, 1H), 1.84 (m, 2H), 1.67 (m, 1H), 1.58 – 1.40 (m, 2H), 1.27 (dd, *J* = 11.7, 4.0 Hz, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 214.1, 150.3, 142.6, 140.7, 130.4, 128.8, 128.1, 127.4, 127.3, 126.5, 126.0 (q, *J* = 3.8 Hz), 123.7 (q, *J* = 270.1 Hz), 117.8 (q, *J* = 32.6 Hz), 112.1, 68.5, 67.5, 53.5, 46.8, 45.1, 42.1, 25.4, 23.2, 20.9. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –60.9. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{29}H_{27}F_3NO$ 462.2039; Found 462.2089.

8.2. Synthesis of (2a*S*,2a^1*S*,4*S*,4a*R*,7a*S*)-2-argio-3,3-diphenyl-2,2a,2a^1,3,4,4a,5,7a-octahydro-1*H*-cyclopenta[*cd*]isoindol-4-ol (42)[4]



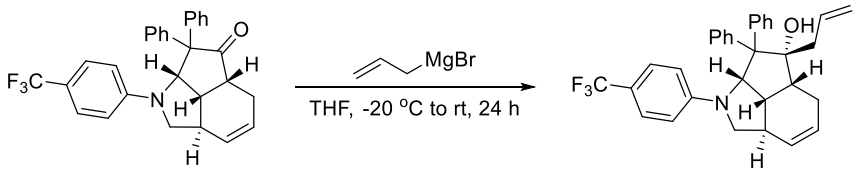
3, 99% ee — **42**, 80% yeild, 99% ee, >20/1 dr

At rt, to a flask charged with a solution of the compound **3** (46.0g, 0.1 mmol, 1.0 equiv., 99% ee) in MeOH (4 mL) was added $NaBH_4$ (12.4 mg) in one portion. The resultant reaction mixture was stirred at rt for 48 h. After completion of the reaction, methanol was removed under reduced pressure and the residue was purified by silica gel flash chromatography (petroleum ether/ethyl acetate 5/1–3/1) to give the product **42** as a

white solid (40.0 mg, 80% yield, 99% ee). The dr value was determined by ^{1}H NMR analysis. The ee value was determined by HPLC analysis (Chiralcel ADH, hexane/^{i}PrOH = 90/10, flow rate = 1.0 mL/min, l = 254 nm), t_r (major) = 9.5 min, t_r (minor) = 6.2 min; $[\alpha]_D^{20}$ = –210.32 (c = 0.68, in $CHCl_3$); mp = 235 – 237 °C.

(2a*S*,2a^1*S*,4*S*,4a*R*,7a*S*)-2-argio-3,3-diphenyl-2,2a,2a^1,3,4,4a,5,7a-octahydro-1*H*-cyclopenta[*cd*]isoindol-4-ol (42): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.25 (m, 10H), 7.20 – 7.10 (m, 3H), 6.50 (d, *J* = 8.6 Hz, 2H), 6.10 (dt, *J* = 9.9, 3.0 Hz, 1H), 5.83 (m, 1H), 4.79 (dd, *J* = 6.7, 2.0 Hz, 1H), 4.40 (d, *J* = 6.9 Hz, 1H), 3.76 (t, *J* = 7.2 Hz, 1H), 3.39 – 3.27 (m, 1H), 3.03 (dd, *J* = 12.4, 7.7 Hz, 1H), 2.93 (m, 1H), 2.66 (m, 1H), 2.51 – 2.40 (m, 1H), 2.36 (m, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 150.5, 149.8, 143.0, 130.9, 129.3, 128.5, 128.4, 128.1, 126.5, 126.4, 126.4, 126.1 (q, *J* = 3.7 Hz), 112.6, 86.1, 75.8, 64.6, 53.3, 52.7, 37.9, 36.9, 23.7. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -60.9. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{29}H_{27}F_3NO$ 462.2039; found 462.2089.

8.3. synthesis of (2a*S*,2a^1*S*,4*S*,4a*R*,7a*S*)-4-allyl-2-argio-3,3-diphenyl-2,2a,2a^1,3,4,4a,5,7a-octahydro-1*H*-cyclopenta[*cd*]isoindol-4-ol (43)[4]



3, 99% ee

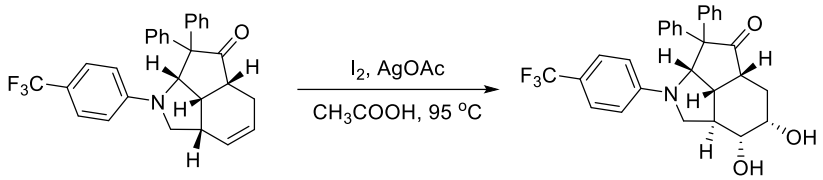
43, 85% yeild
99% ee, >20/1 dr

At –20 °C, a solution of allylmagnesium bromide (0.30 mL, 0.30 mmol, 1.0 M in ether) was slowly added to a solution of compound **3** (46.0g, 0.1 mmol, 1.0 equiv., 99% ee) in THF (1 mL). The reaction was allowed to warm up to rt and was stirred at the same temperature for 24 h. Upon completion, a saturated aqueous solution of NH_4Cl (1 mL) was added. The layers were separated, and the aqueous layer was extracted with ethyl acetate (5 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated. The residue was subjected to column chromatography on silica gel (petroleum ether/ethyl acetate 5/1–3/1) to give the product **43** as a white solid (45.6 mg, 91% yield, 99% ee). The dr value was determined by ^{1}H NMR analysis. The ee value was determined by HPLC analysis (Chiralcel IA, hexane/^{i}PrOH = 98/2, flow rate = 1.0 mL/min, l = 254 nm), t_r (major) = 7.2 min, t_r (minor) = 5.9 min; $[\alpha]_D^{20}$ = –111.5 (c = 0.47, in $CHCl_3$), mp = 179 – 181 °C.

(2a*S*,2a^1*S*,4*S*,4a*R*,7a*S*)-4-allyl-2-argio-3,3-diphenyl-2,2a,2a^1,3,4,4a,5,7a-octahydro-1*H*-cyclopenta[*cd*]isoindol-4-ol (43): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 – 7.62 (m, 2H), 7.42 (d, *J* = 7.8 Hz, 2H), 7.35 (m, 2H), 7.24 (d, *J* = 16.3 Hz, 5H), 6.33 (d, *J* = 8.5 Hz, 2H), 6.08 (dt, *J* = 9.7, 2.8 Hz, 1H), 5.96 – 5.85 (m, 1H), 5.79 (m, 1H), 5.09 – 4.97 (m, 2H), 4.33 (d, *J* = 7.5 Hz, 1H), 3.80 (t, *J* = 7.3 Hz, 1H), 3.62 – 3.52 (m, 1H), 3.01 (dd, *J* = 12.1, 7.9 Hz, 2H), 2.87 (dd, *J* = 14.3, 8.3 Hz, 1H), 2.61 (m, 1H), 2.40 (m, 2H), 2.19 (dd, *J* = 14.3, 6.4 Hz, 1H), 1.17 (s, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 150.5, 148.9, 141.3, 134.9, 130.8, 130.4, 129.6, 128.3 (q, *J* = 180.0 Hz), 128.0, 127.8, 126.8, 126.4, 126.3, 126.0 (q, *J* = 3.7 Hz), 118.0 (q, *J* = 32.6 Hz), 117.8, 112.9, 89.5, 81.4, 69.4, 53.2, 52.7, 46.0, 42.5, 37.7, 25.7. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –60.9.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{32}H_{31}F_3NO$ 502.2352; Found 570.2309.

8.4. Synthesis of (2a*S*,2a^1*S*,4a*R*,7a*S*)-2-argio-6,7-dihydroxy-3,3-diphenyldecahydro-4*H*-cyclopenta[*cd*]isoindol-4-one (44)[5]



3, 99% ee

44, 70% yeild
99% ee, >20/1 dr

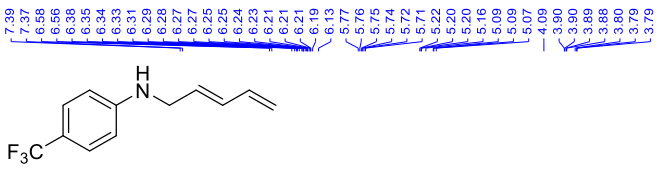
A dry reaction tube equipped with a stir bar was charged with **3** (46.0g, 0.1 mmol, 1.0 equiv.) was dissolved in 0.5 mL of glacial acetic acid. After addition of silver acetate (33.4 mg, 0.2 mmol, 2.0 equiv.), finely powdered iodine (27.9 mg, 0.11 mmol, 1.0 equiv.) was added in small portions to the vigorously stirred reaction mixture for 0.5 h at rt. When all of the iodine had been consumed, 46 μL of aqueous glacial acetic acid (0.0438 mole of water, prepared by dilution of 2.0 mL of water up to 50 mL with glacial acetic acid was added. The reaction mixture was then heated at 95 °C for 3 h with vigorous stirring. At the end of this time it was cooled, treated with excess sodium chloride, and filtered free from insoluble salts. The filtrate was treated with potassium hydroxide in methanol (1 M, 5 mL) and stirred at rt for 24 h. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated. The residue was subjected to column chromatography on silica gel (petroleum ether/ethyl acetate 1/3–1/5) to give the product **44** as a white solid (34.5 mg, 91% yield, 99% ee). The dr value was determined by ^{1}H NMR analysis. The ee value was determined by HPLC analysis (Chiralcel ADH, hexane/^{i}PrOH = 90/10, flow rate = 1.0 mL/min, l = 254 nm), t_r (major) = 29.890 min, t_r (minor) = 25.455 min; $[\alpha]_D^{20}$ = –144.24 (c = 0.61, in $CHCl_3$); mp = 225 – 227 °C.

(2a*S*,2a^1*S*,4a*R*,7a*S*)-2-argio-6,7-dihydroxy-3,3-diphenyldecahydro-4*H*-cyclopenta[*cd*]isoindol-4-one (44): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 4H), 7.32 (m, 3H), 7.07 (m, 5H), 6.40 (d, *J* = 8.5 Hz, 2H), 5.26 (d, *J* = 7.1 Hz, 1H), 4.18 (m, 1H), 3.73 (d, *J* = 10.7 Hz, 1H), 3.36 (dd, *J* = 8.3, 6.4 Hz, 1H), 3.10 (dd, *J* = 11.3, 8.3 Hz, 1H), 2.93 – 2.86 (m, 1H), 2.69 – 2.45 (m, 4H), 2.28 (s, 1H), 2.00 (ddd, *J* = 15.7, 7.1, 3.9 Hz, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 213.9, 150.0, 141.8, 140.2, 130.4, 129.0, 128.0, 127.6, 127.4, 126.7, 126.0 (q, *J* = 3.8 Hz), 123.7 (q, *J* = 270.4 Hz) 118.1 (q, *J* = 34.5 Hz), 112.1, 72.1, 69.1, 68.2, 67.6, 51.5, 45.7, 42.9, 41.7, 29.0. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –60.9 (s). **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{35}H_{31}F_3NO_3$ 570.2251; Found 570.2264.

9. References

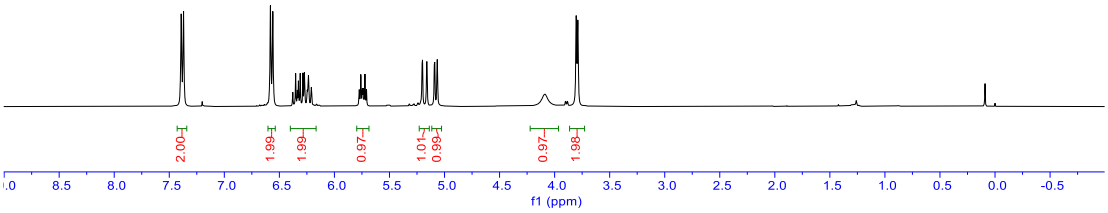
1. West H., Daniels S., Slawin M. An Isothiourea-Catalyzed Asymmetric [2,3]-Rearrangement of Allylic Ammonium Ylides. *J. Am. Chem. Soc.* **2014**, *136*, 4476−4479.
2. Zhao, C., Li, F., Wang, J. N-Heterocyclic Carbene Catalyzed Dynamic Kinetic Resolution of Pyranones. *Angew. Chem., Int. Ed.* **2016**, *55*, 1820−1824
3. Wang, X. Z., Zhu, Y. F., Li, X. N. Kinetics of *o*-Chloronitrobenzene Hydrogenation on Palladium/Carbon *Catalyst. Adv. Mater.* **2011**, *239*, 161−167.
4. Wang, S., Guillot, R., Carpentier, J. F., Sarazin, Y., Bour, C., Gandon, V., Lebœuf, D. Synthesis of Bridged Tetrahydrobenzo-[*b*]azepines and Derivatives through an Aza-Piancatelli Cyclization/Michael Addition Sequence. *Angew. Chem., Int. Ed.* **2020**, *59*, 1134−1138.
5. Woodward, R. B., Brutcher, F. V. *Cis*-Hydroxylation of a Synthetic Steroid Intermediate with Iodine, Silver Acetate and Wet Acetic Acid. *J. Am. Chem. Soc.* **1958**, *80*, 209−211.

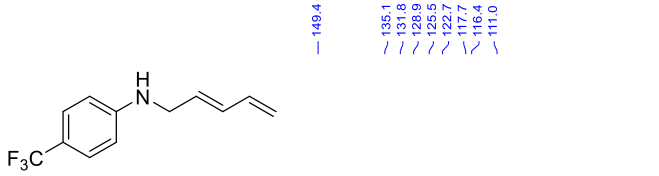
10. NMR spectra of the starting materials and products



2a

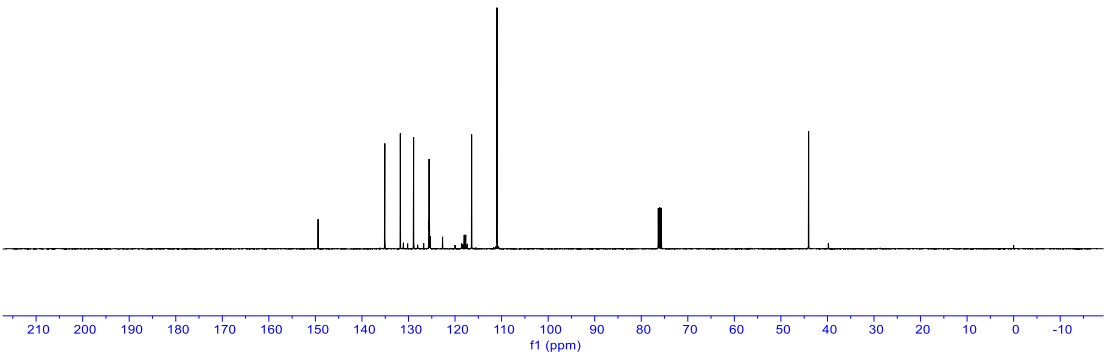
^{1}H (400 MHz, $CDCl_3$)

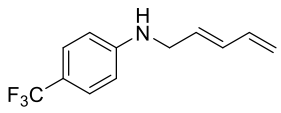




2a

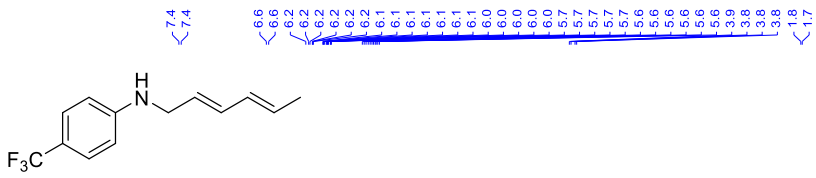
^{13}C (101 MHz, $CDCl_3$)





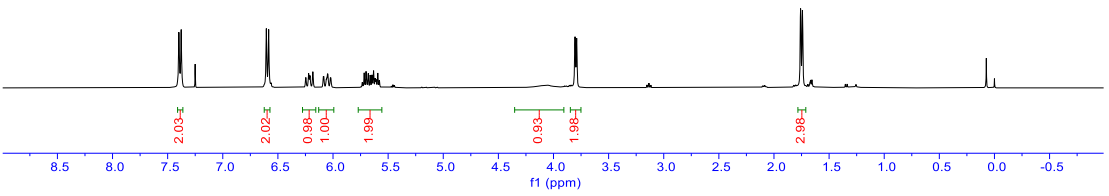
2a

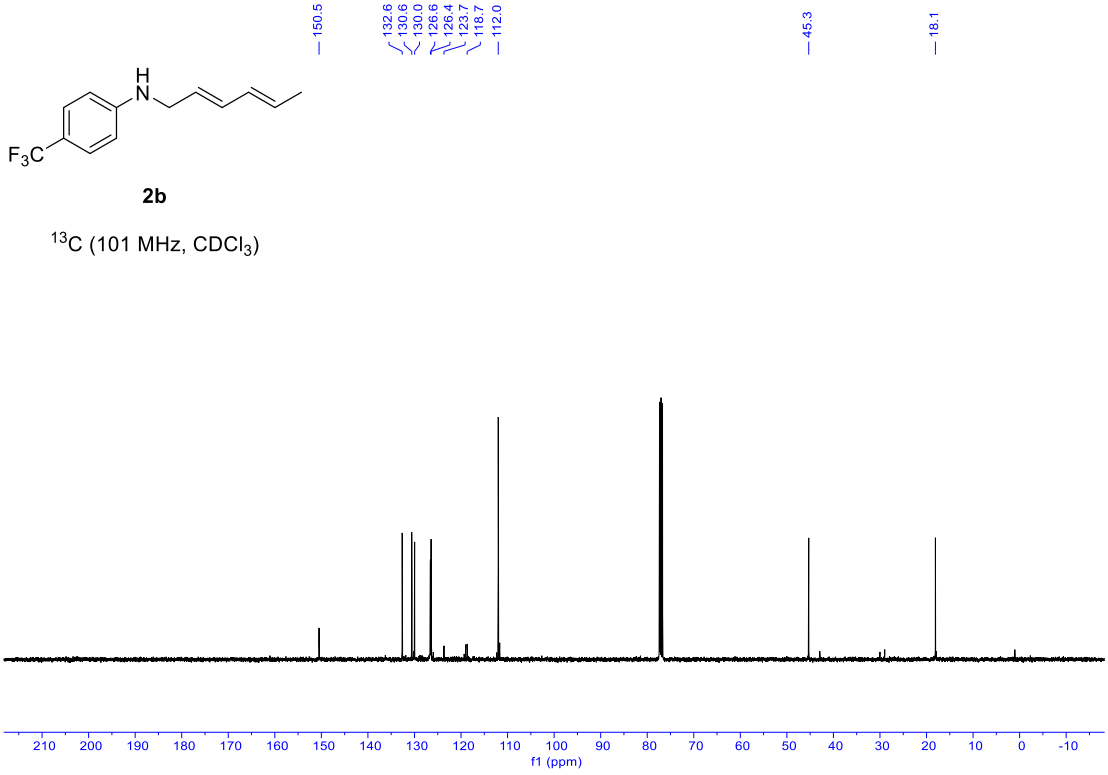
^{19}F (377 MHz, $CDCl_3$)



2b

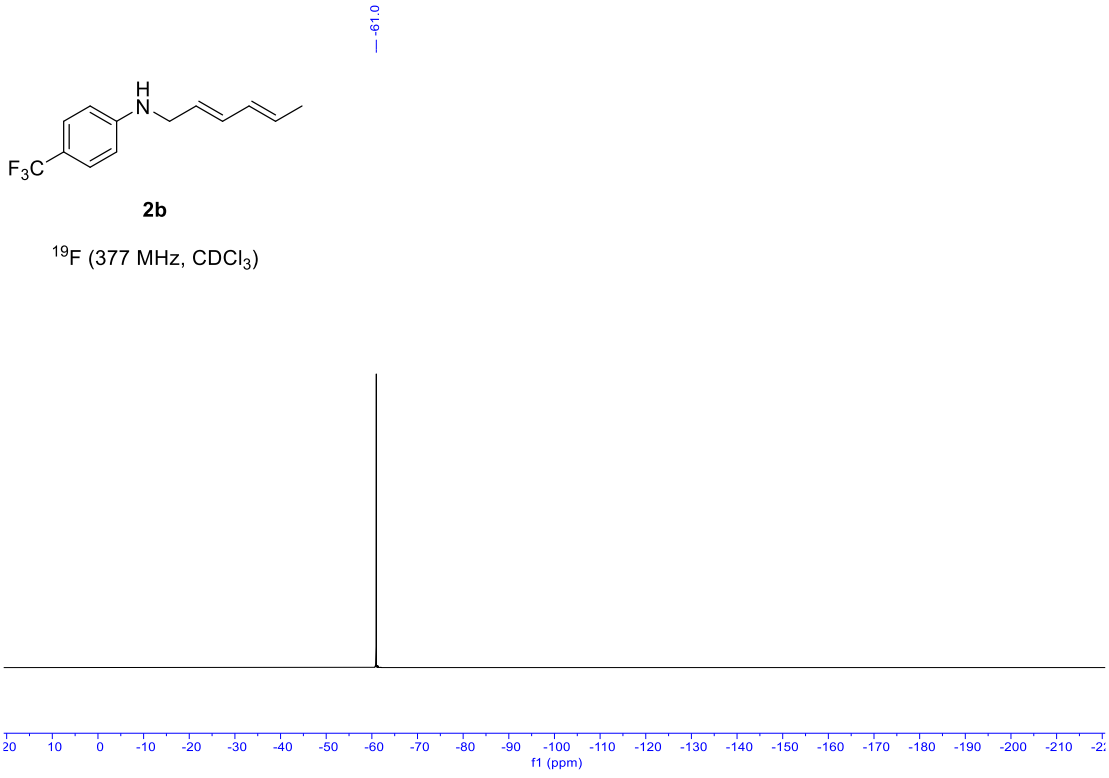
^{1}H (400 MHz, $CDCl_3$)





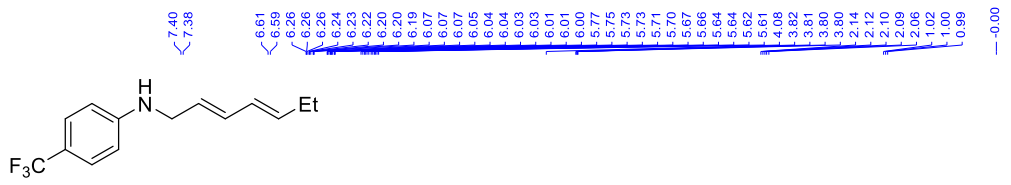
2b

^{13}C (101 MHz, $CDCl_3$)



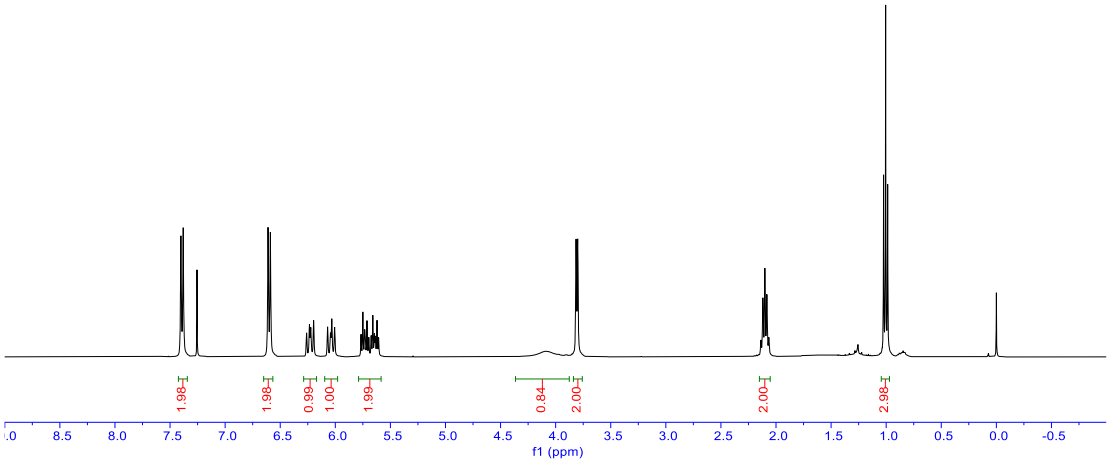
2b

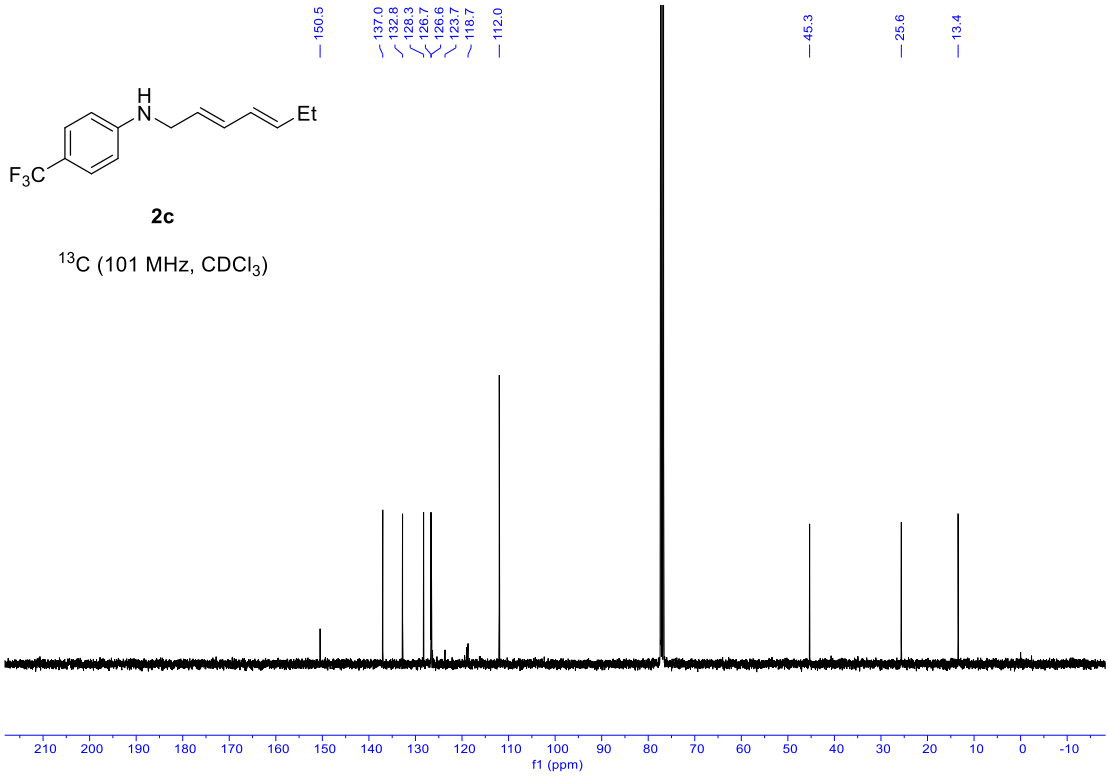
^{19}F (377 MHz, $CDCl_3$)



2c

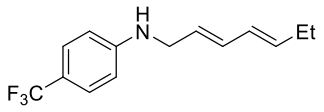
^{13}C (101 MHz, $CDCl_3$)





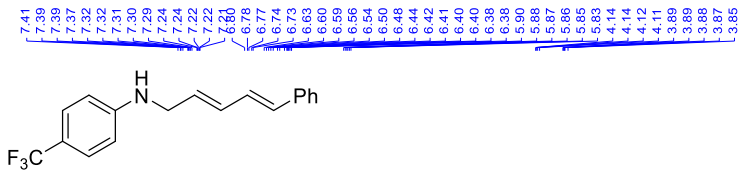
2c

^{13}C (101 MHz, $CDCl_3$)



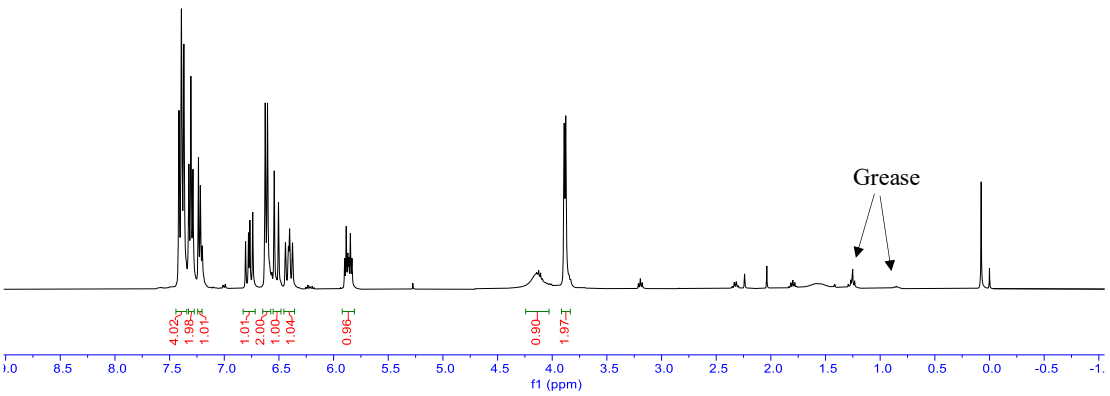
2c

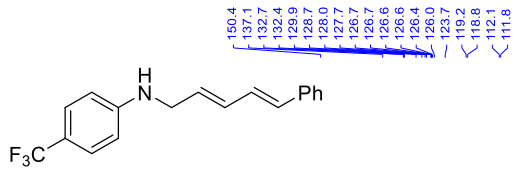
^{19}F (377 MHz, $CDCl_3$)



2d

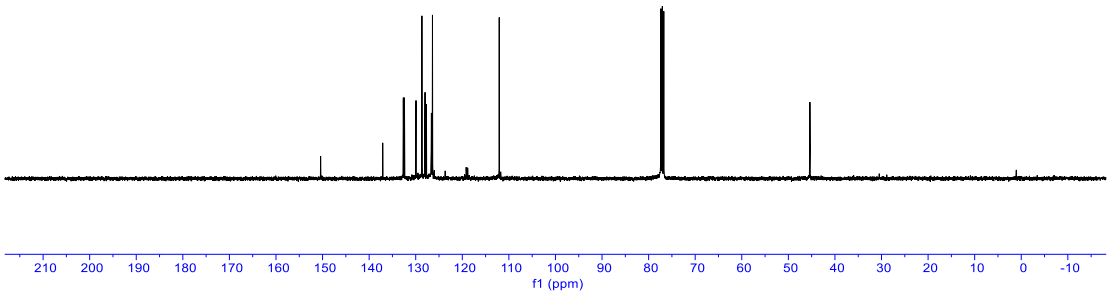
^{1}H (400 MHz, $CDCl_3$)

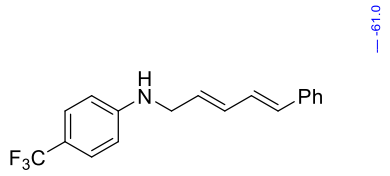




2d

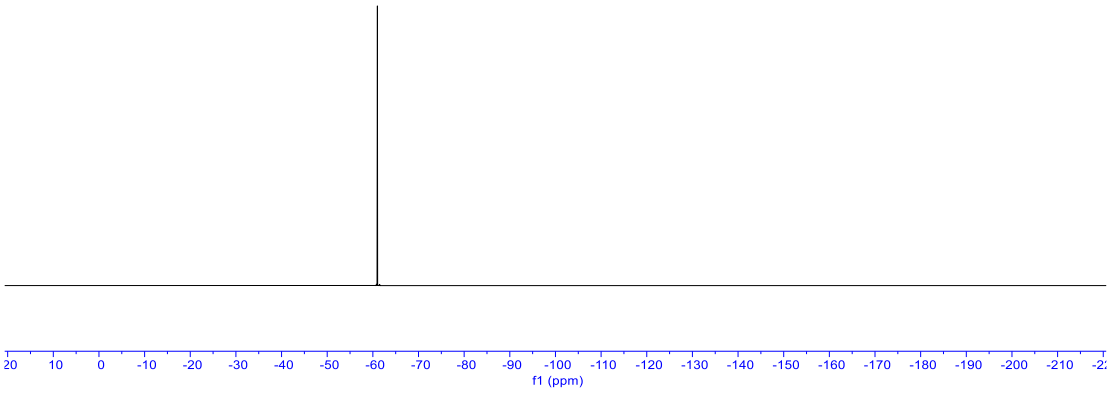
^{13}C (101 MHz, $CDCl_3$)

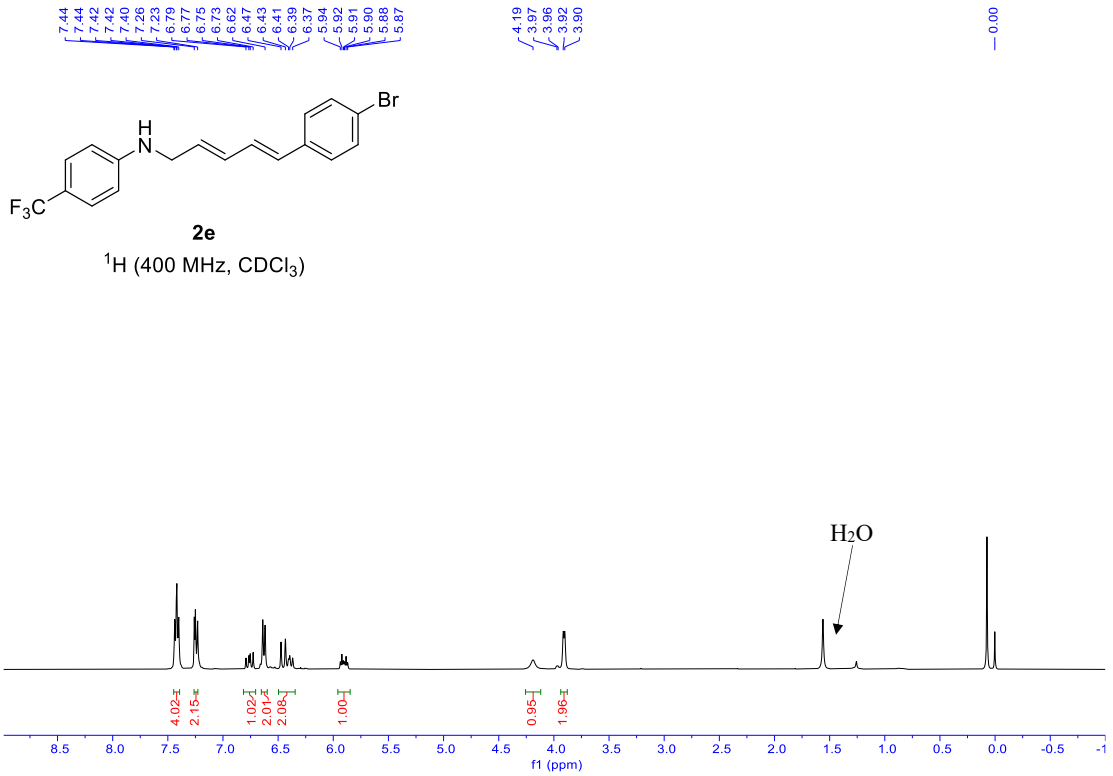




2d

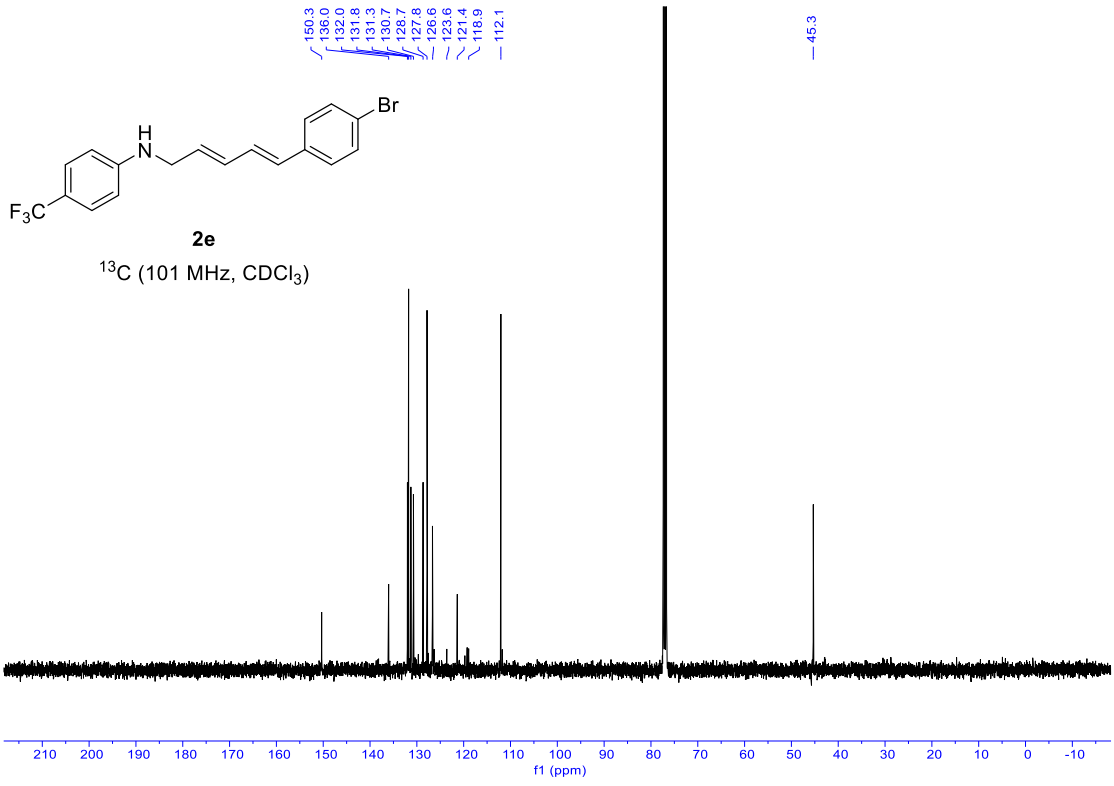
^{19}F (377 MHz, $CDCl_3$)





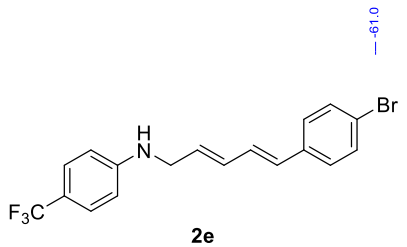
2e

^{1}H (400 MHz, $CDCl_3$)



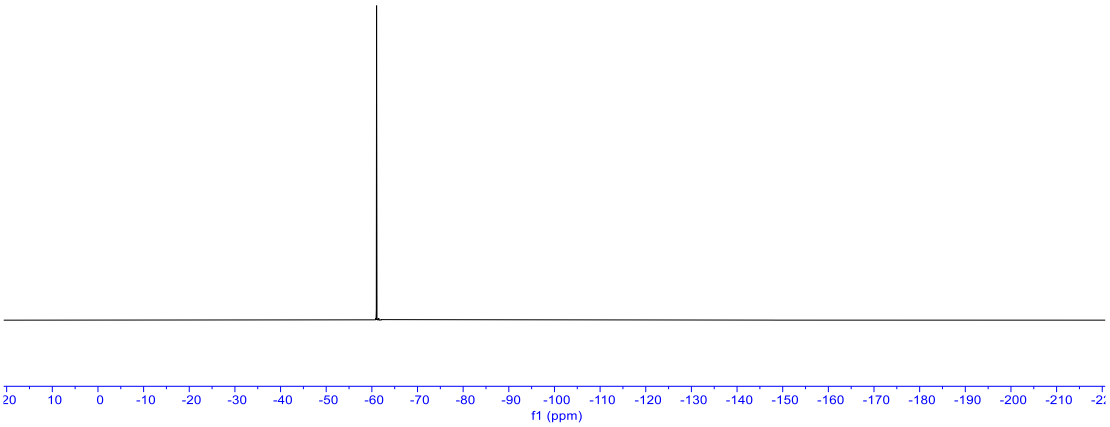
2e

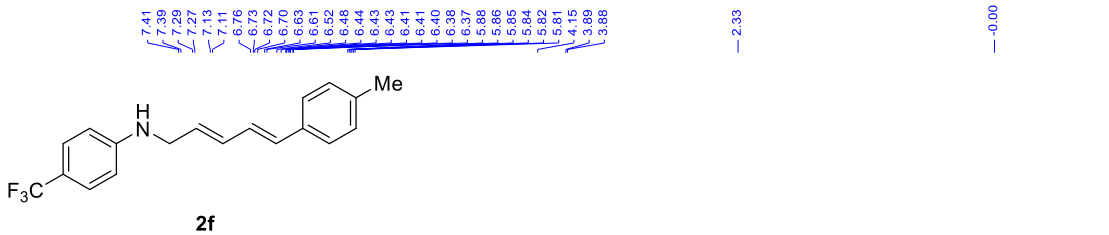
^{13}C (101 MHz, $CDCl_3$)



2e

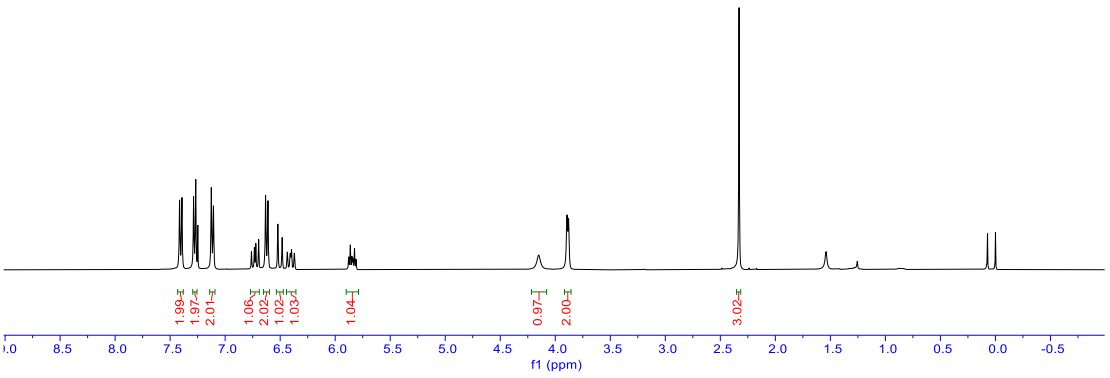
^{19}F (377 MHz, $CDCl_3$)

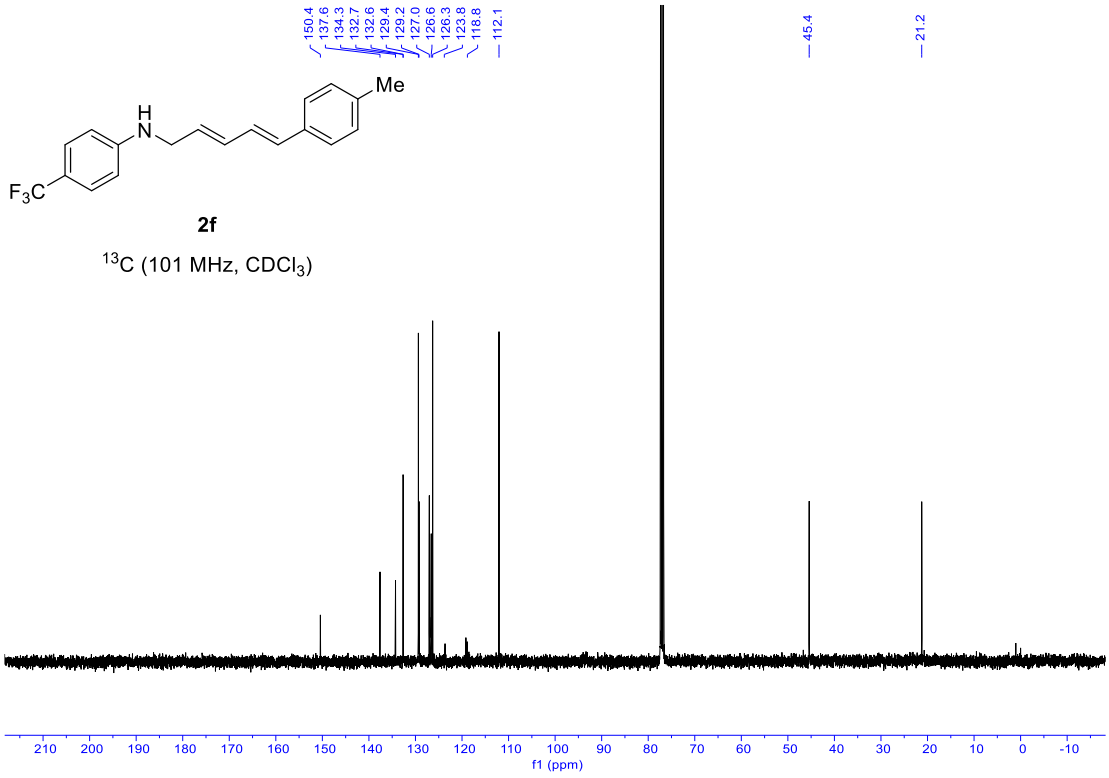




2f

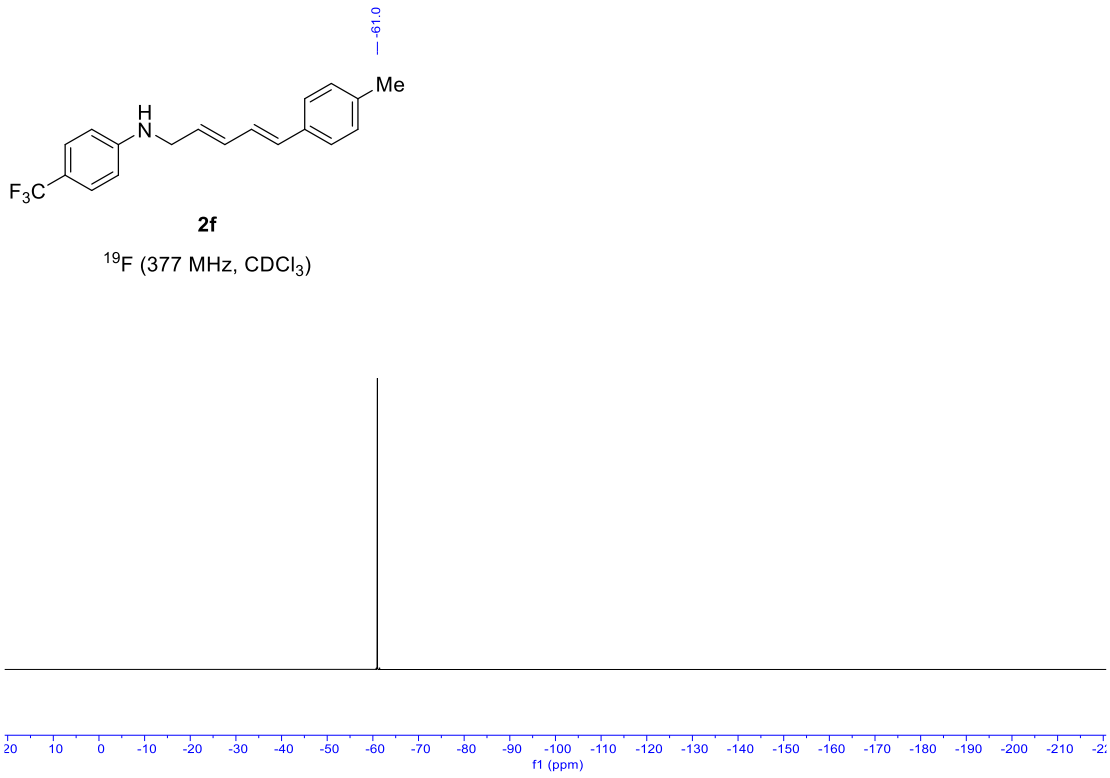
^{1}H (400 MHz, $CDCl_3$)





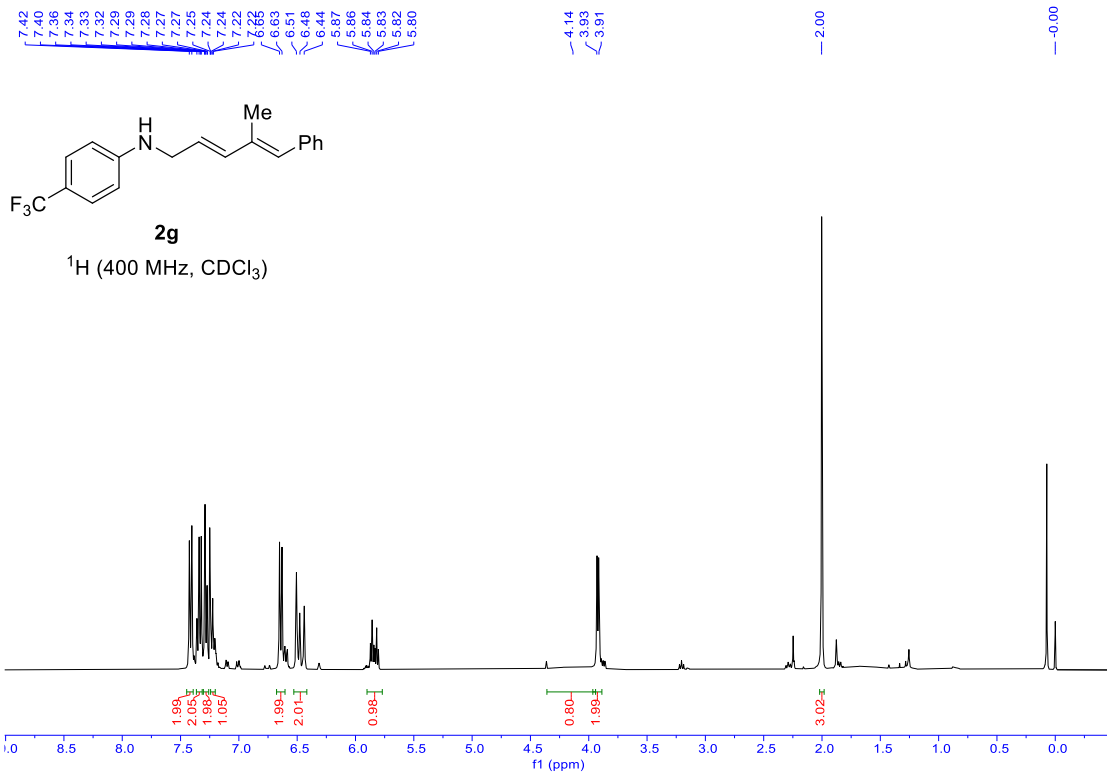
2f

^{13}C (101 MHz, $CDCl_3$)



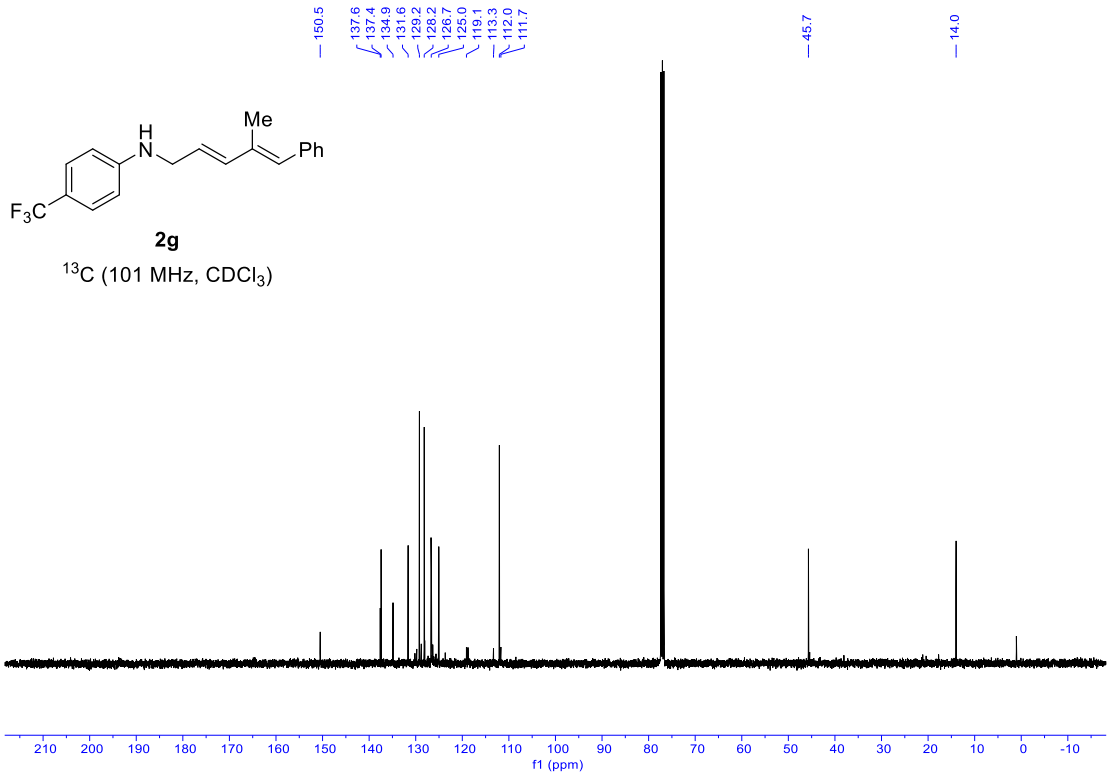
2f

^{19}F (377 MHz, $CDCl_3$)



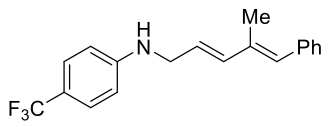
2g

^{1}H (400 MHz, $CDCl_3$)



2g

^{13}C (101 MHz, $CDCl_3$)

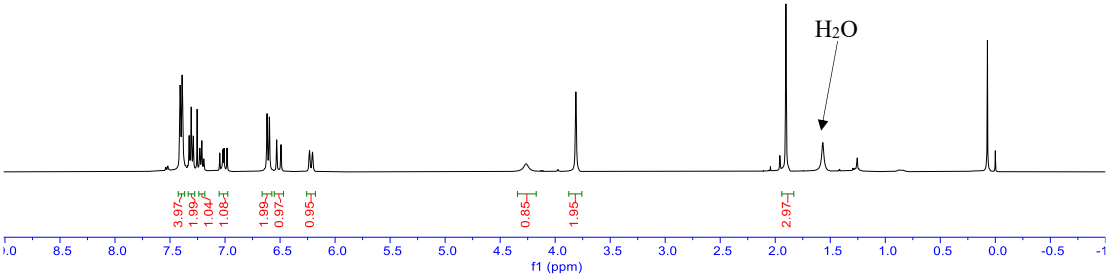


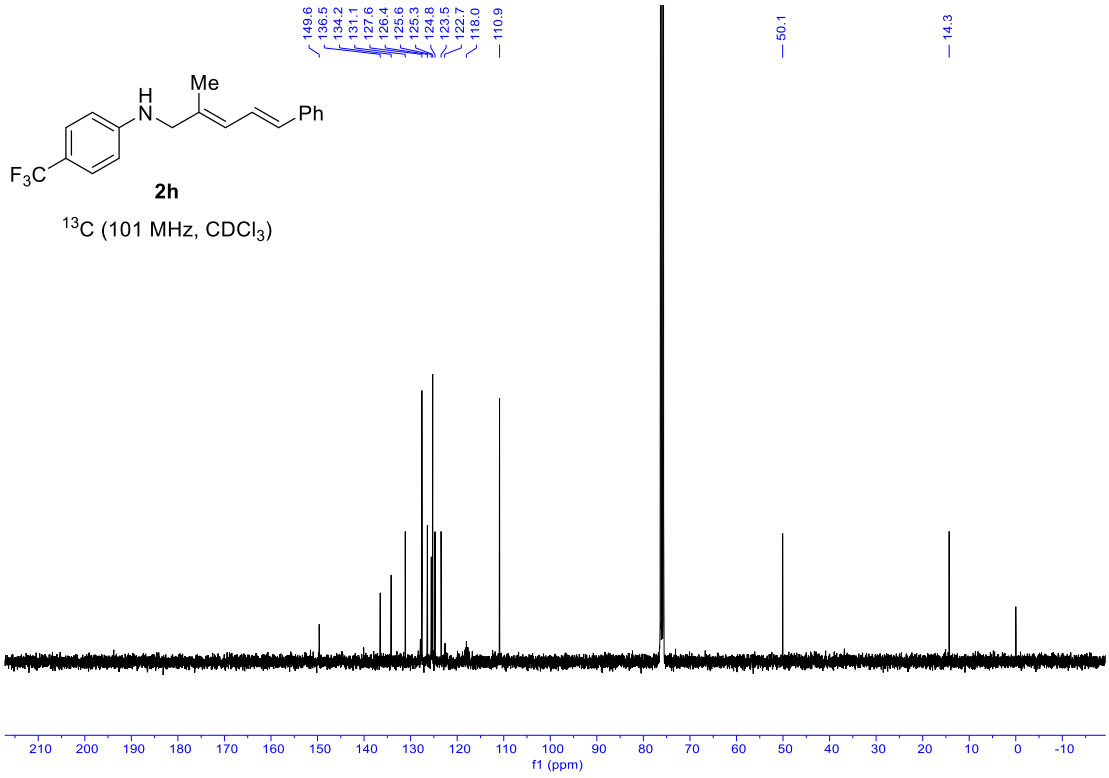
2g

^{19}F (377 MHz, $CDCl_3$)

2h

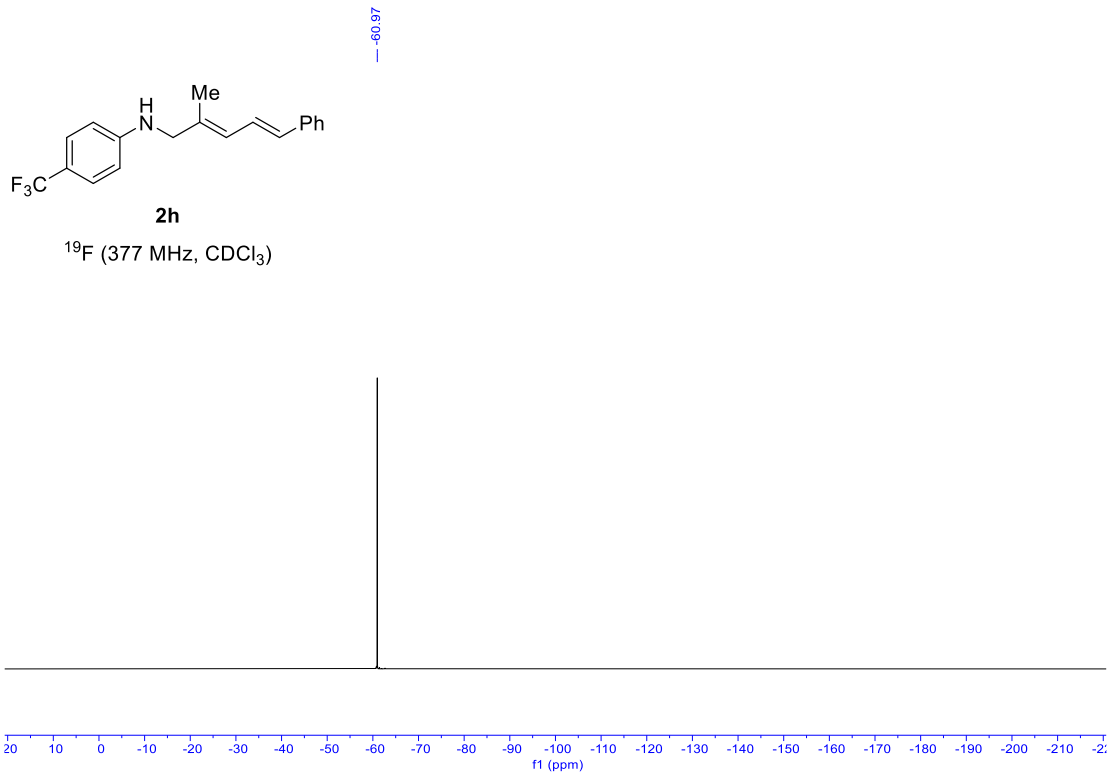
^{1}H (400 MHz, $CDCl_3$)





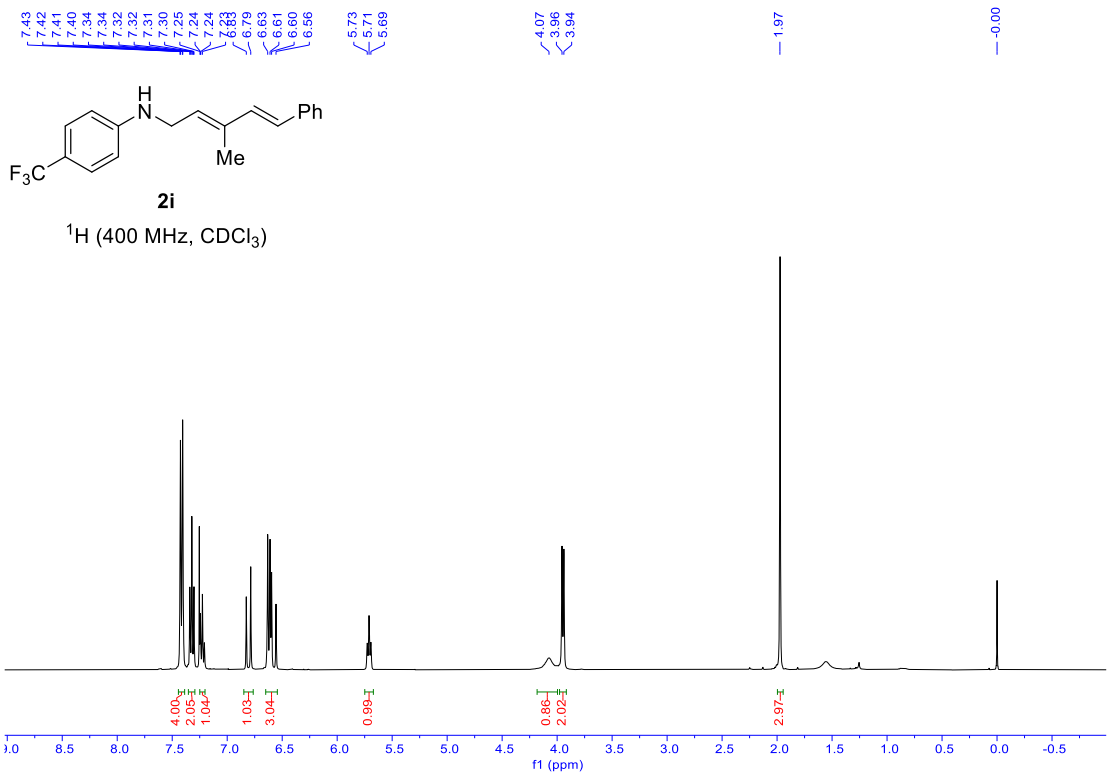
2h

^{13}C (101 MHz, $CDCl_3$)



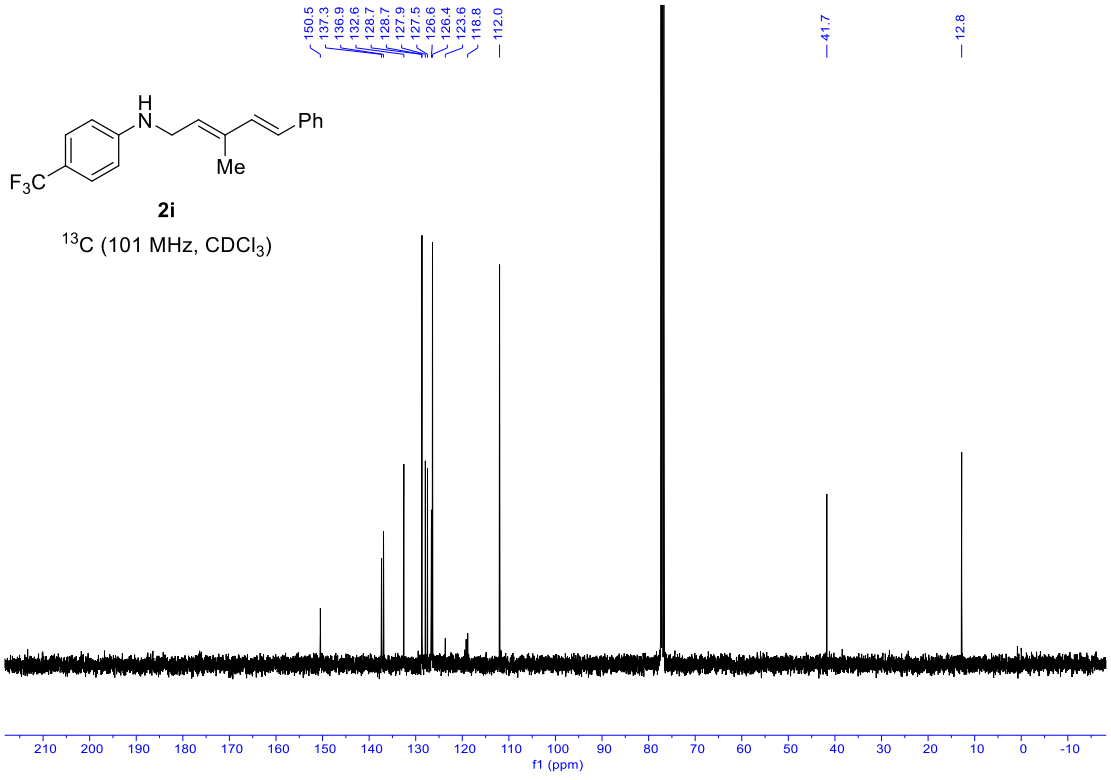
2h

^{19}F (377 MHz, $CDCl_3$)



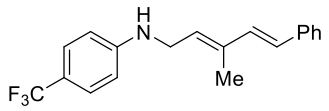
2i

^{1}H (400 MHz, $CDCl_3$)



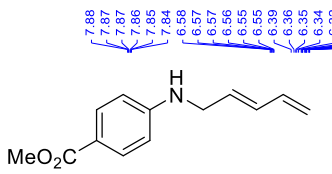
2i

^{13}C (101 MHz, $CDCl_3$)



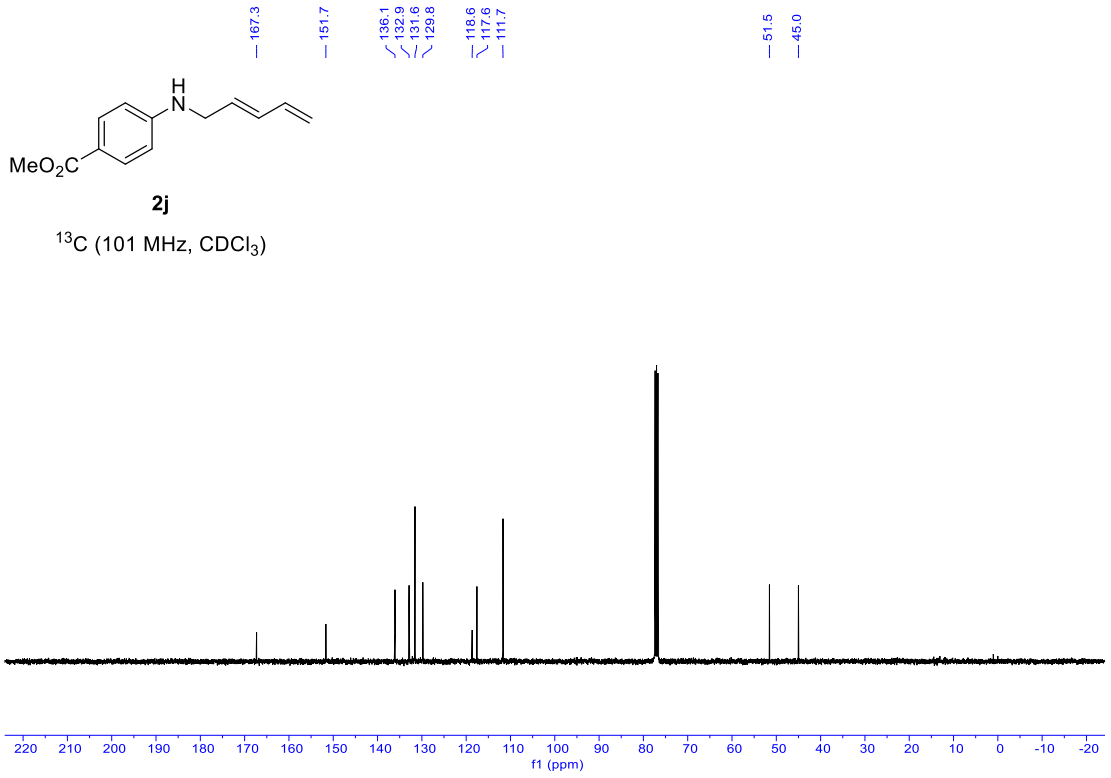
2i

^{19}F (377 MHz, $CDCl_3$)



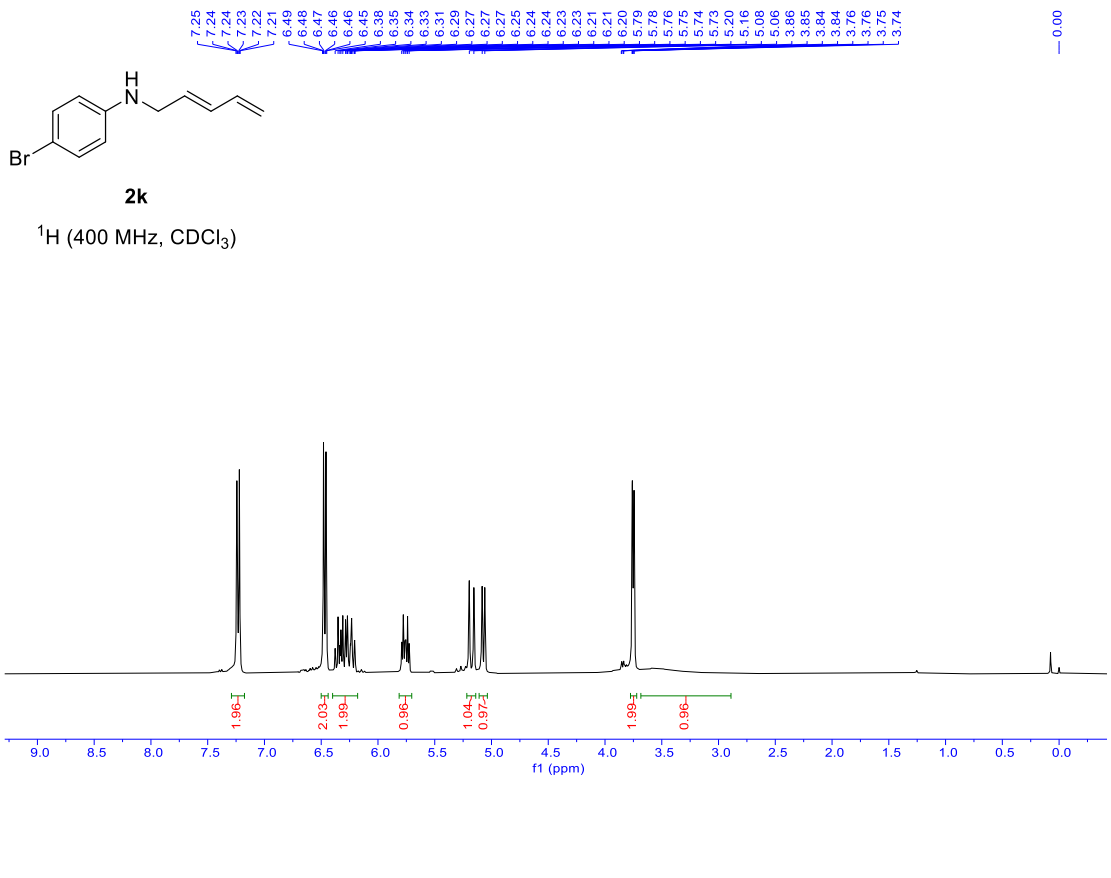
2j

^{1}H (400 MHz, $CDCl_3$)



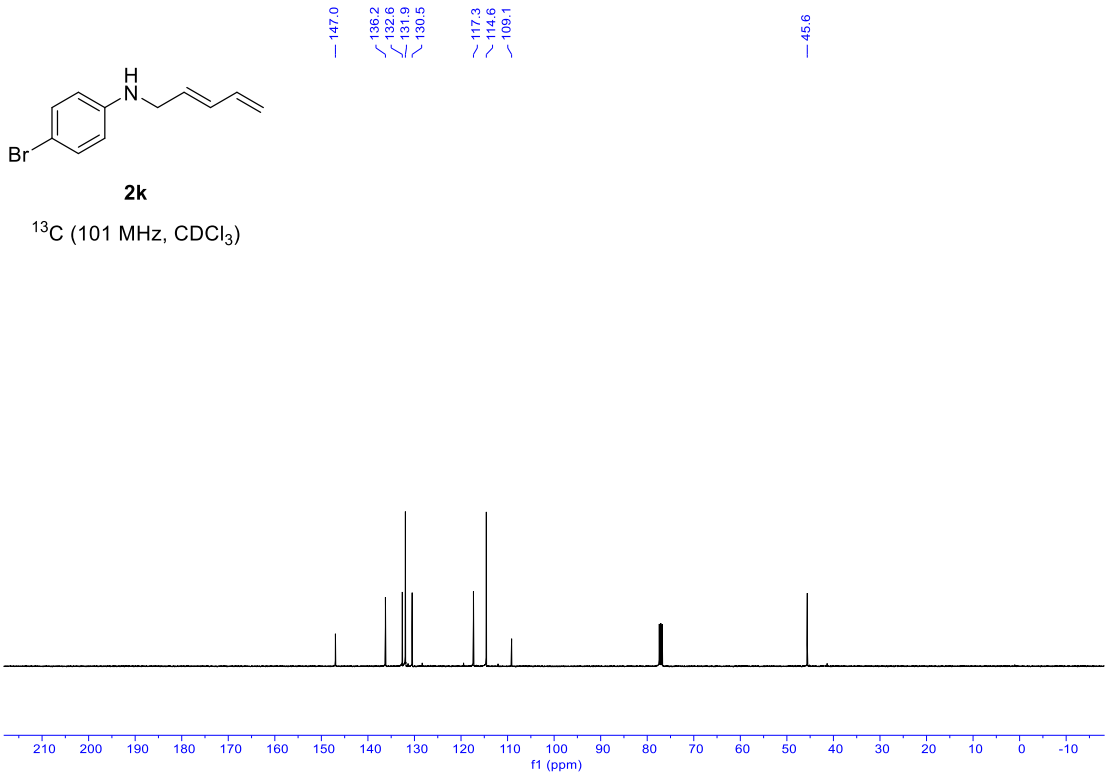
2j

^{13}C (101 MHz, $CDCl_3$)



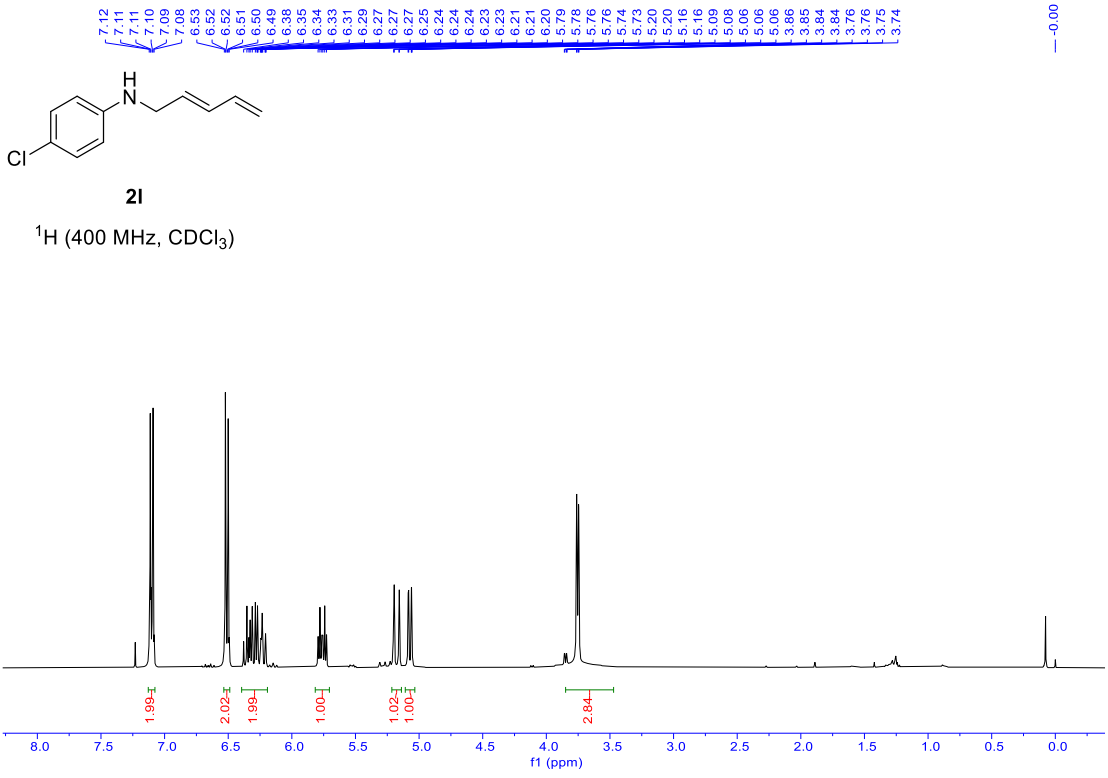
2k

^{1}H (400 MHz, $CDCl_3$)



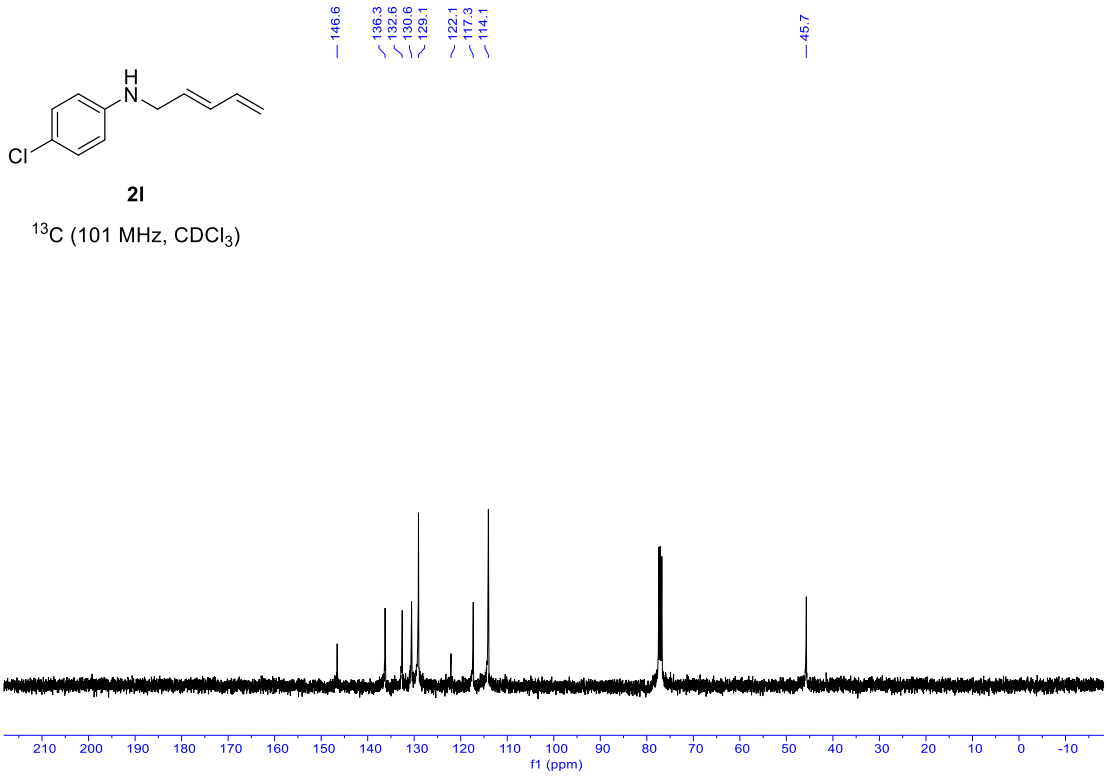
2k

^{13}C (101 MHz, $CDCl_3$)



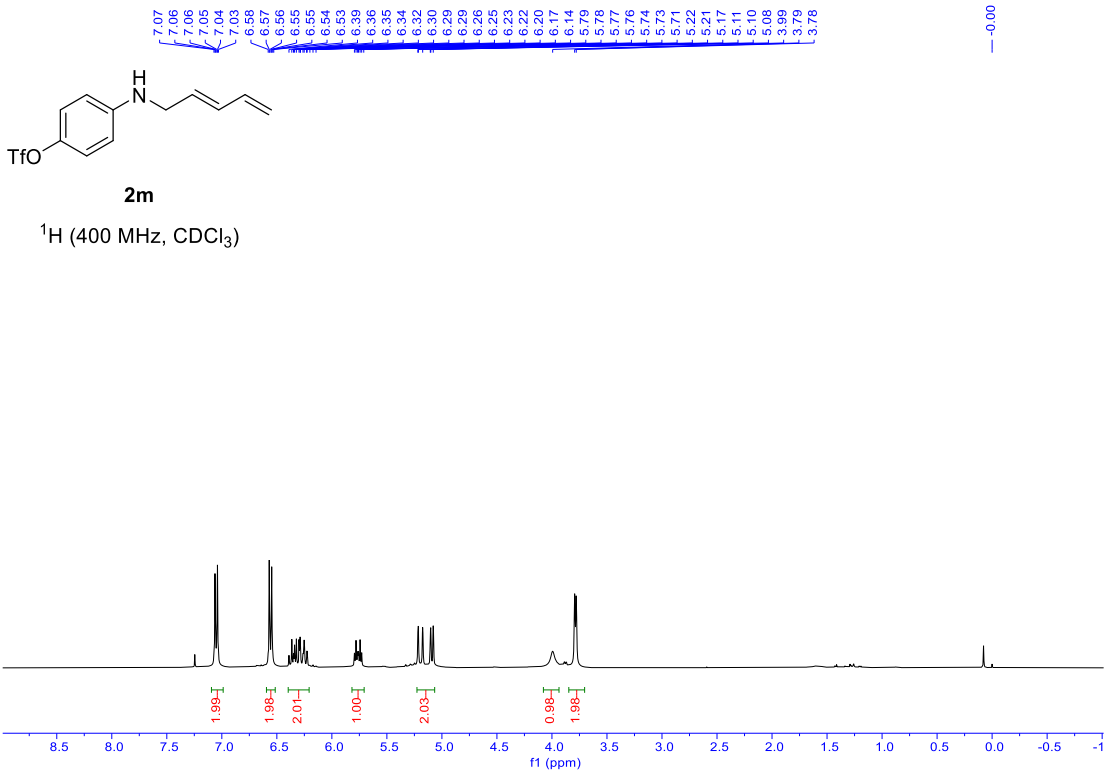
2l

^{1}H (400 MHz, $CDCl_3$)



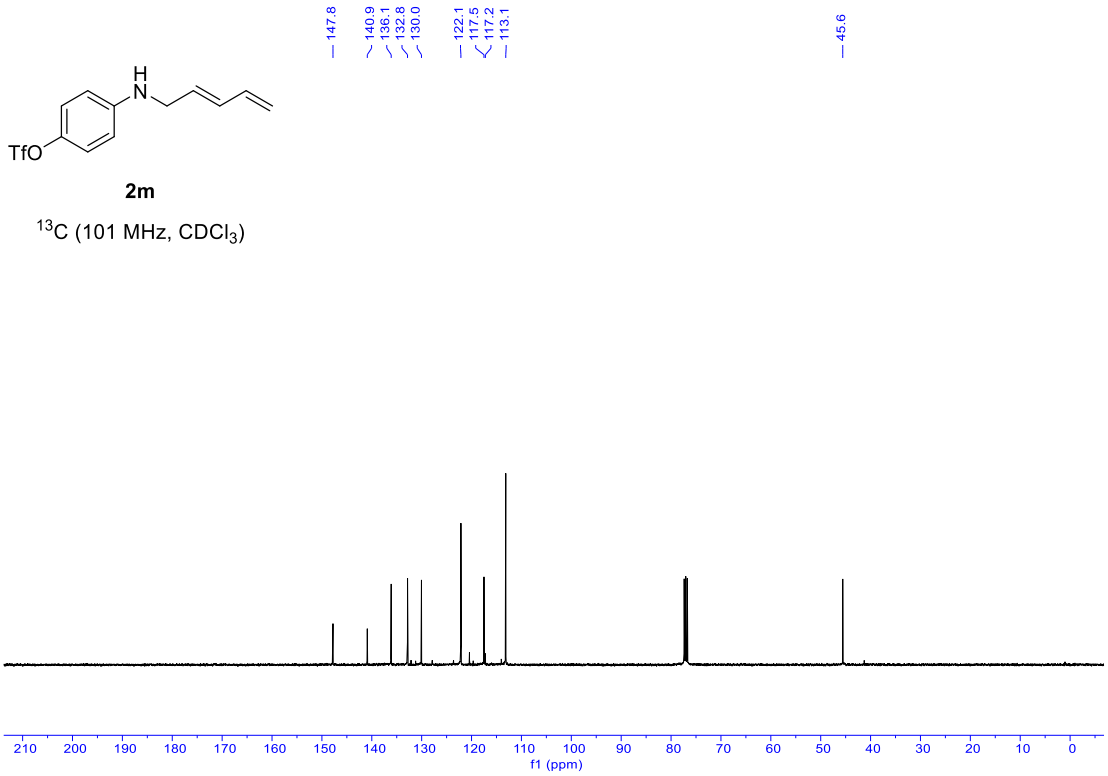
2l

^{13}C (101 MHz, $CDCl_3$)



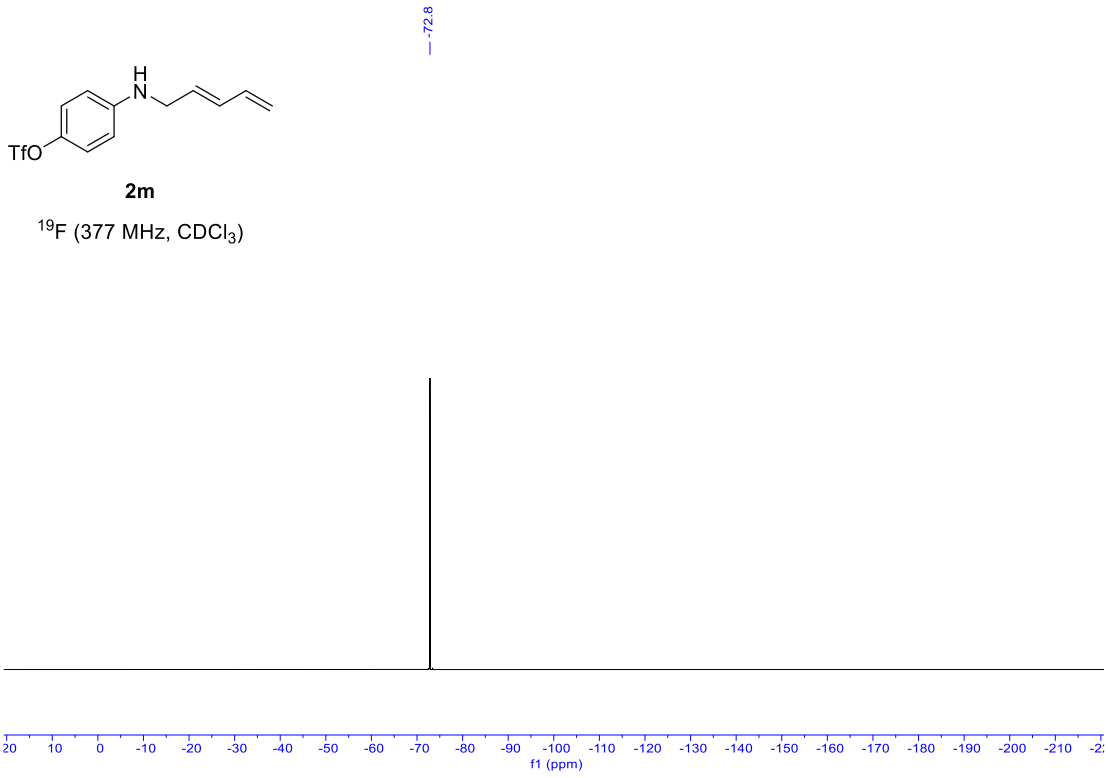
2m

^{1}H (400 MHz, $CDCl_3$)



2m

^{13}C (101 MHz, $CDCl_3$)

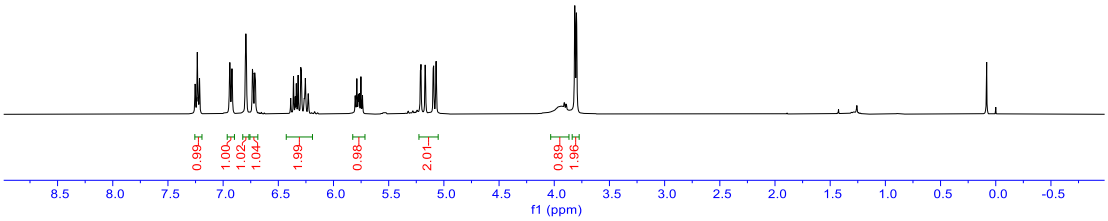


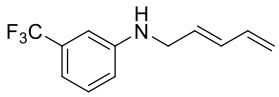
2m

^{19}F (377 MHz, $CDCl_3$)

2n

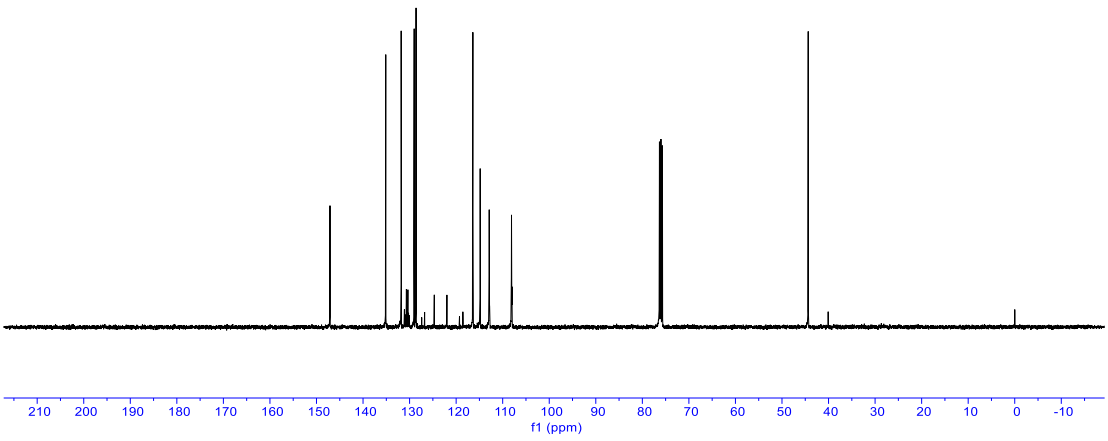
^{1}H (400 MHz, $CDCl_3$)

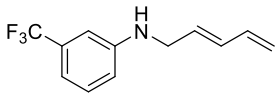




2n

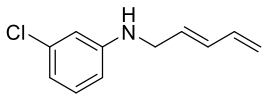
^{13}C (101 MHz, $CDCl_3$)





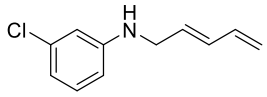
2n

^{19}F (377 MHz, $CDCl_3$)



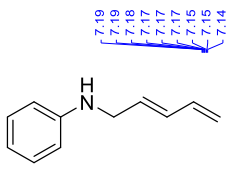
2o

^{1}H (400 MHz, $CDCl_3$)



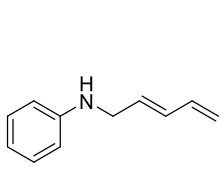
2o

^{13}C (101 MHz, $CDCl_3$)



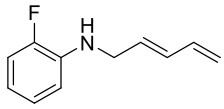
2p

^{1}H (400 MHz, $CDCl_3$)



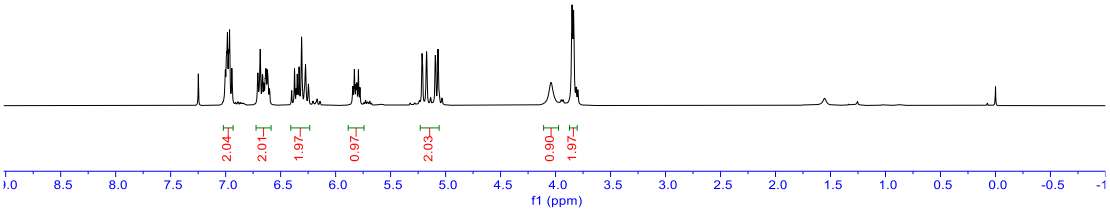
2p

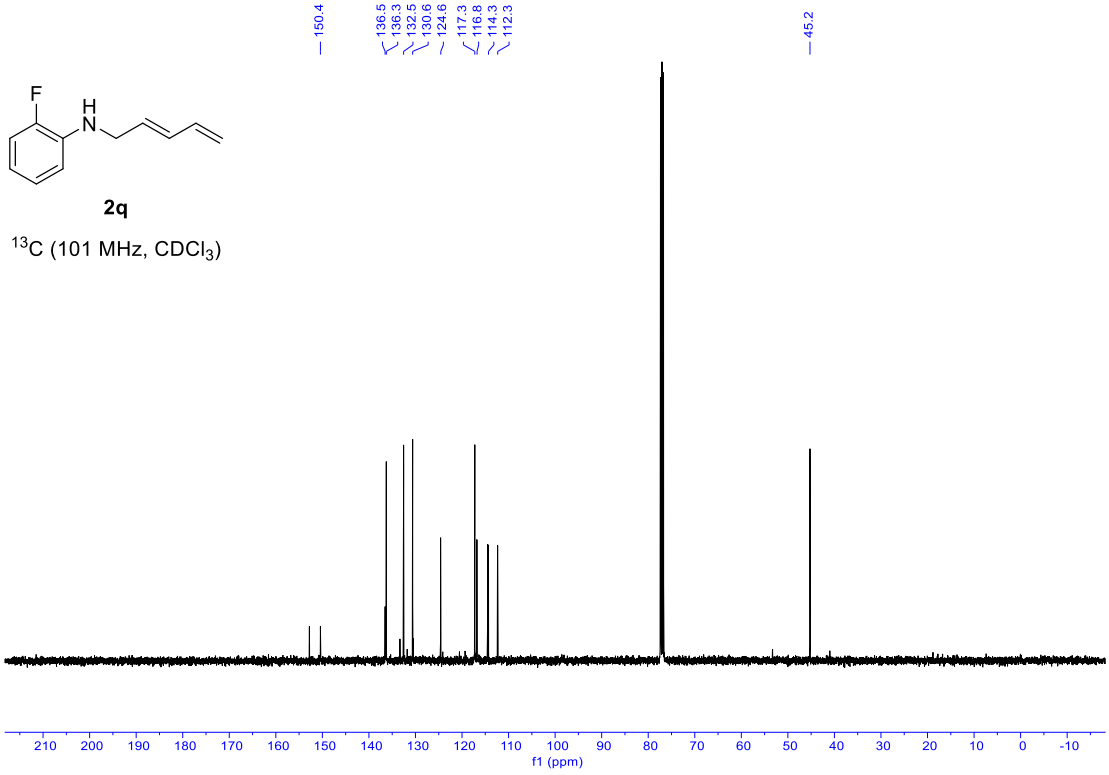
^{13}C (101 MHz, $CDCl_3$)



2q

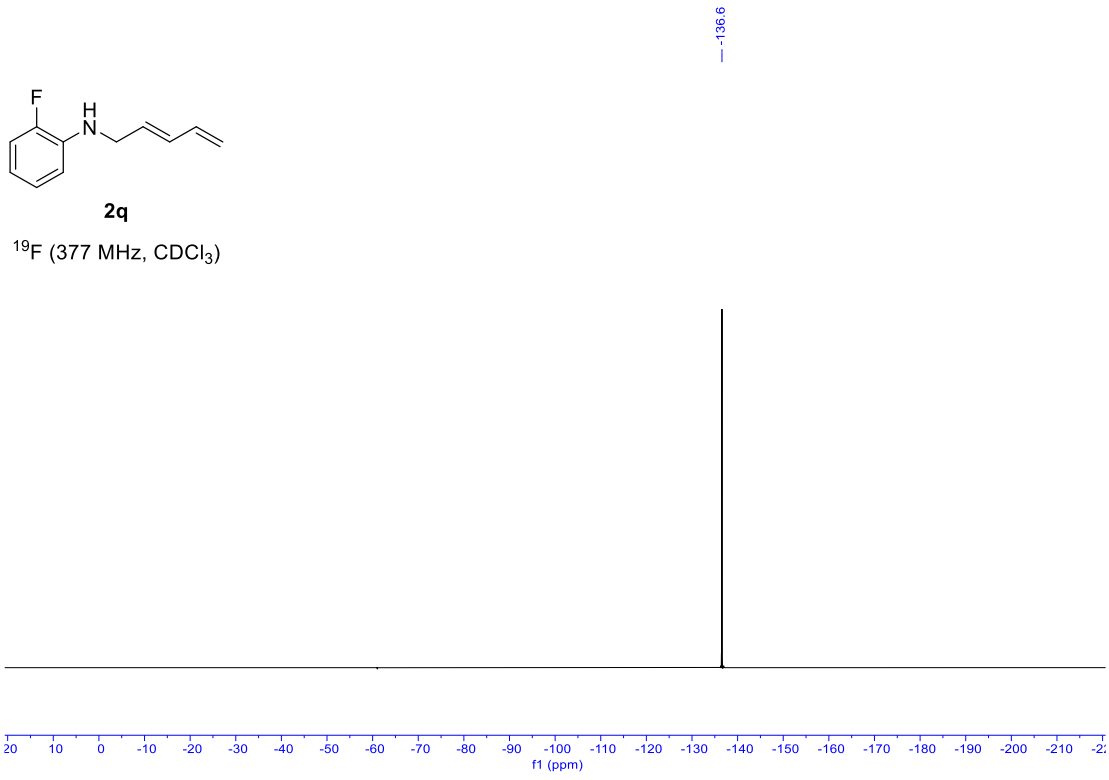
^{1}H (400 MHz, $CDCl_3$)





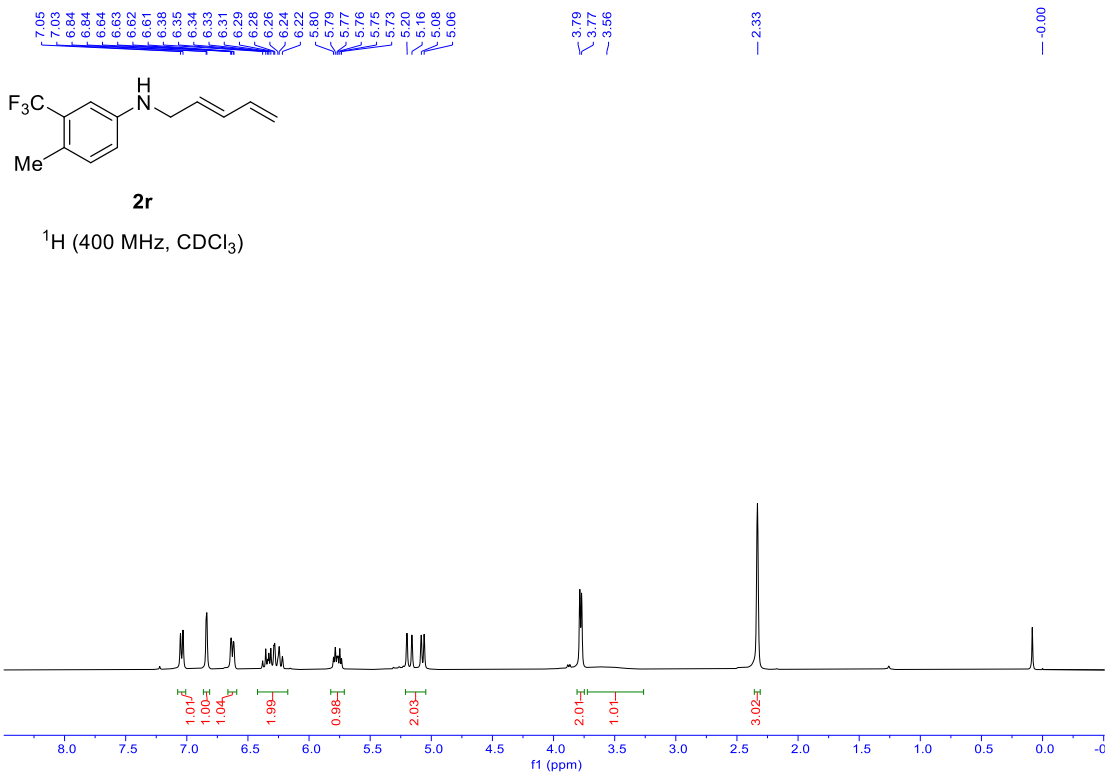
2q

^{13}C (101 MHz, $CDCl_3$)



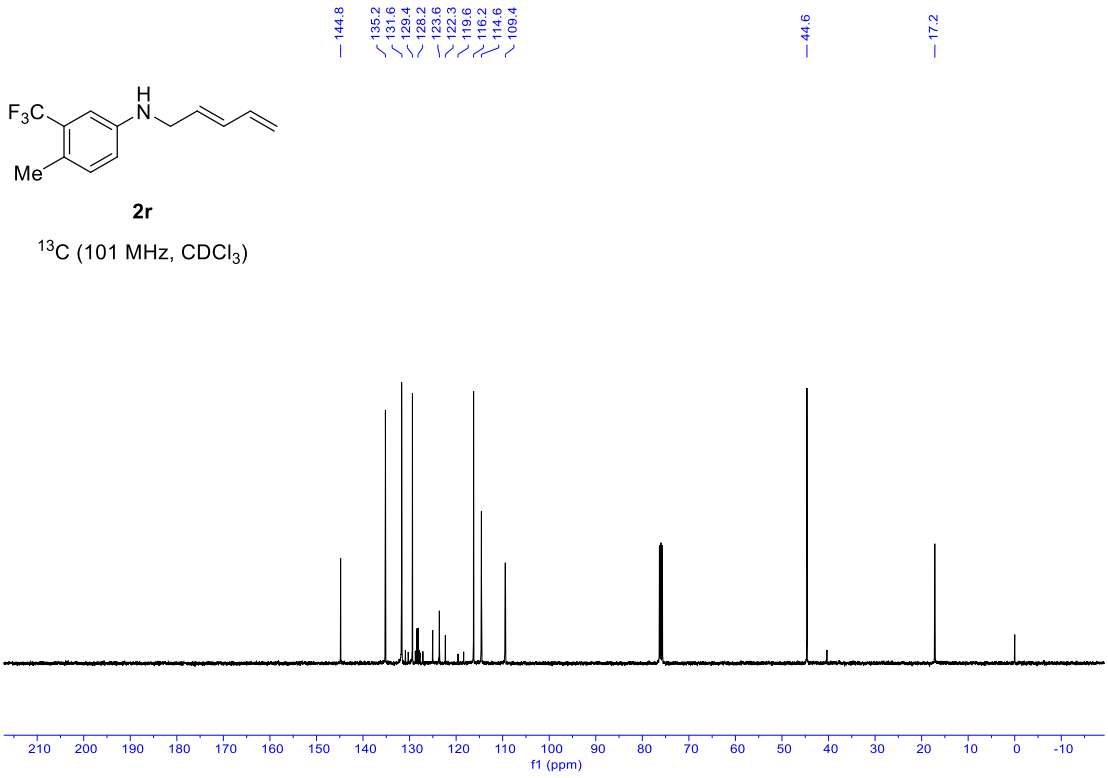
2q

^{19}F (377 MHz, $CDCl_3$)



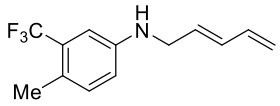
2r

^{1}H (400 MHz, $CDCl_3$)



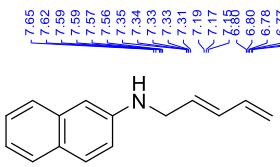
2r

^{13}C (101 MHz, $CDCl_3$)



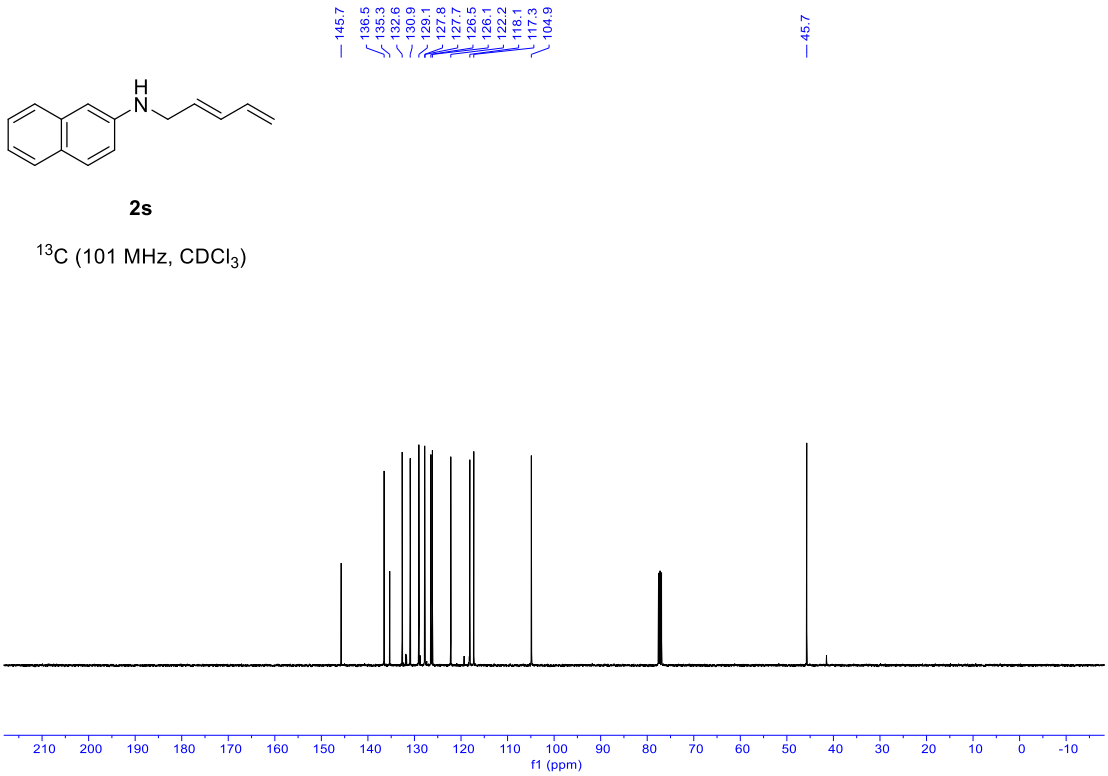
2r

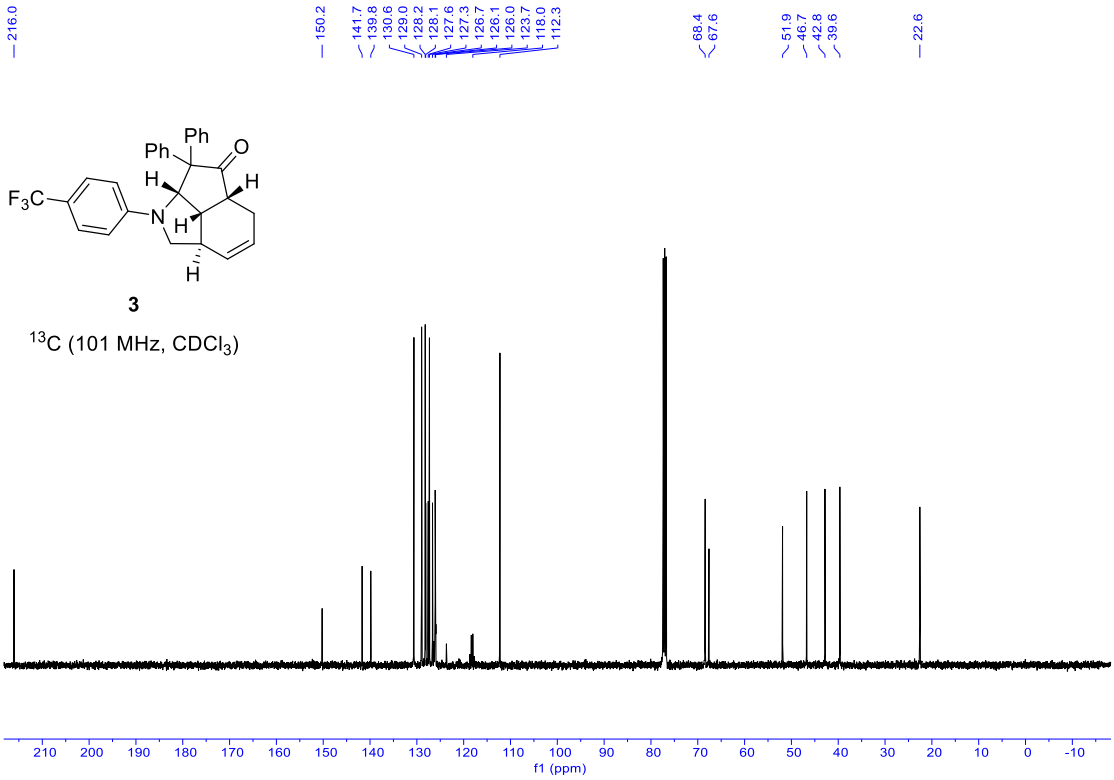
^{19}F (377 MHz, $CDCl_3$)



2s

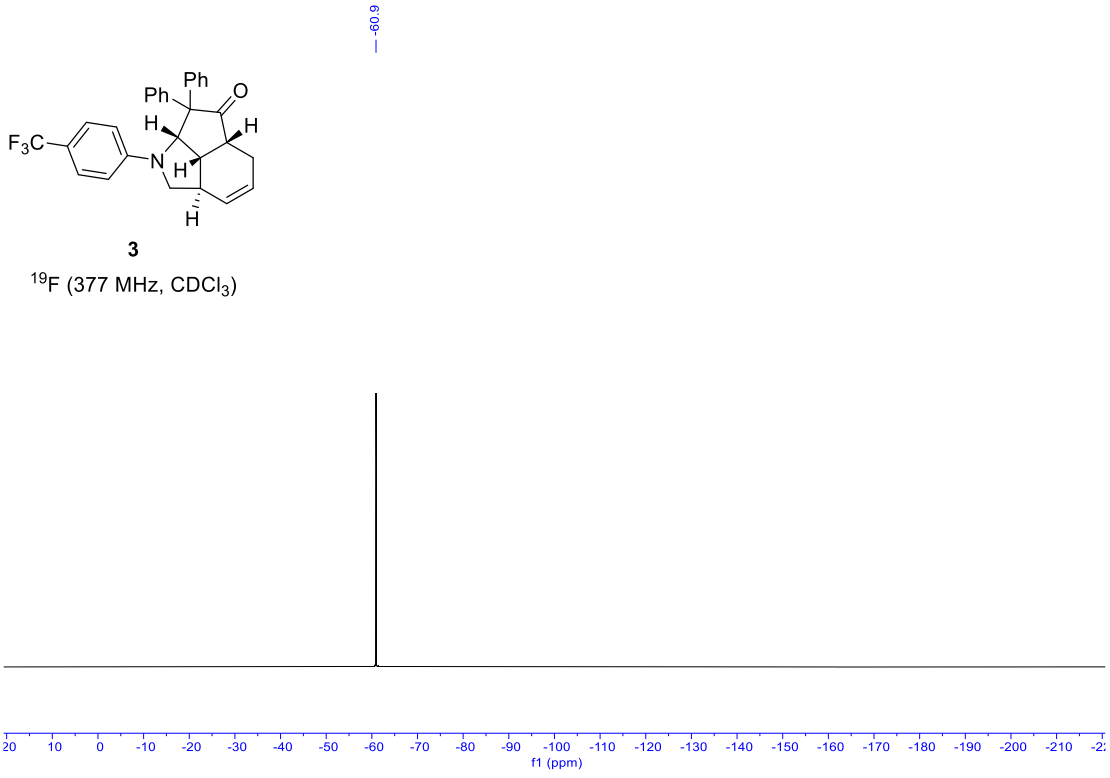
^{1}H (400 MHz, $CDCl_3$)


145.7
136.5
135.3
132.6
130.9
129.1
127.8
127.7
126.5
126.1
122.2
118.1
117.3
104.9
45.7
H
N
2s
13C (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
7.46 7.45 7.45 7.44 7.44 7.41 7.41 7.39 7.38 7.37 7.37 7.35 7.35 7.34 7.33 7.32 7.31 7.31 7.30 7.27 7.07 7.07 7.06 7.06 7.05 6.98 6.98 6.97 6.97 6.96 6.40 6.38 6.09 6.08 6.08 6.07 6.06 6.05 5.80 5.80 5.79 5.77 5.76 5.26 5.24 3.42 3.40 3.40 3.39 3.06 3.05 3.04 3.03 3.02 3.01 2.71 2.69 2.67 2.67 2.66 2.65 2.64 2.62 2.54 2.54 2.52 2.51 2.50 2.49 2.47 0.00
Ph
Ph
O
H
H
F3C
N
H
H
3
1H (400 MHz, CDCl3)
H2O
Grease
1.99 2.00 0.98 1.98 2.99 1.99 2.01 0.99 0.98 0.99 1.00 2.01 2.01 2.00
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)



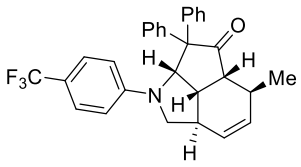
3

^{13}C (101 MHz, $CDCl_3$)



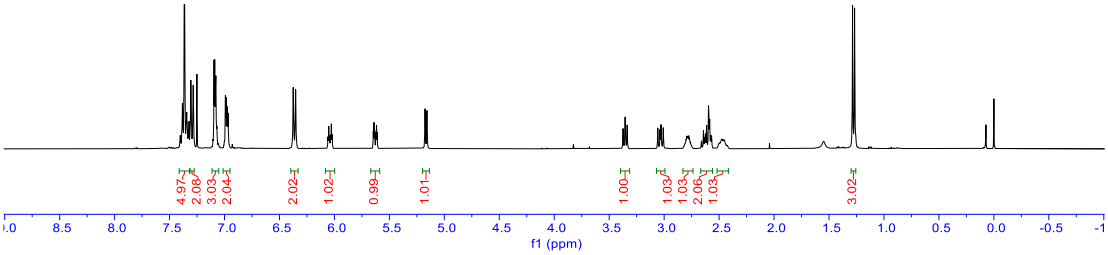
3

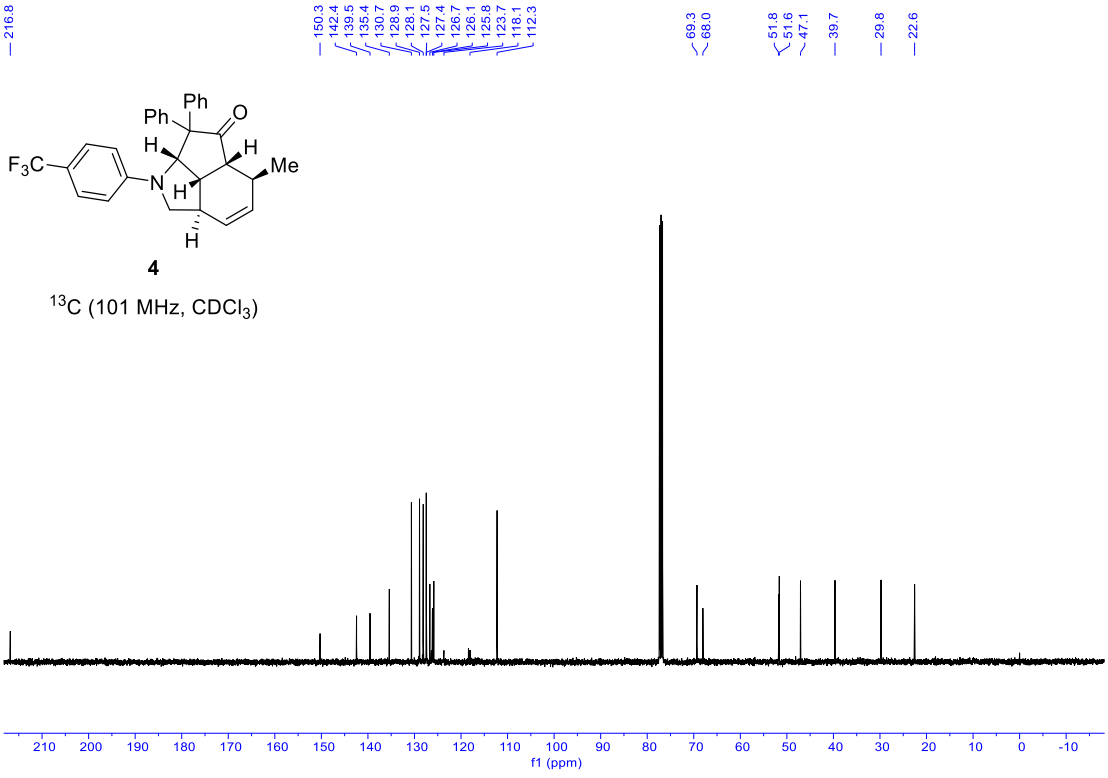
^{19}F (377 MHz, $CDCl_3$)



4

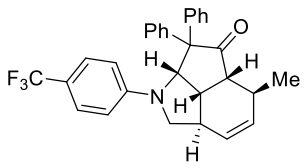
^{1}H (400 MHz, $CDCl_3$)





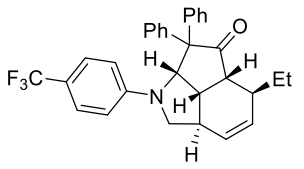
4

^{13}C (101 MHz, $CDCl_3$)



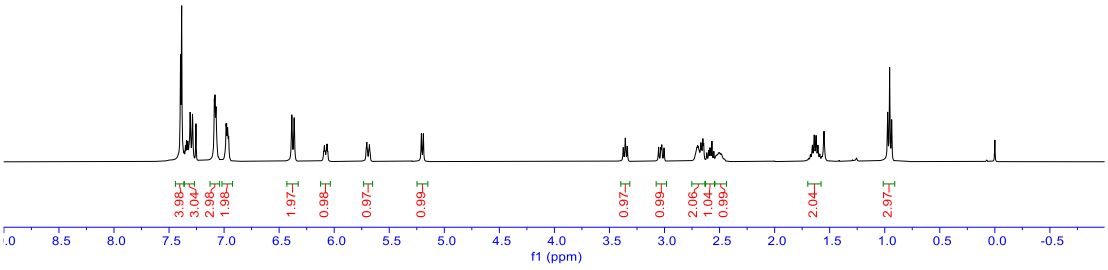
4

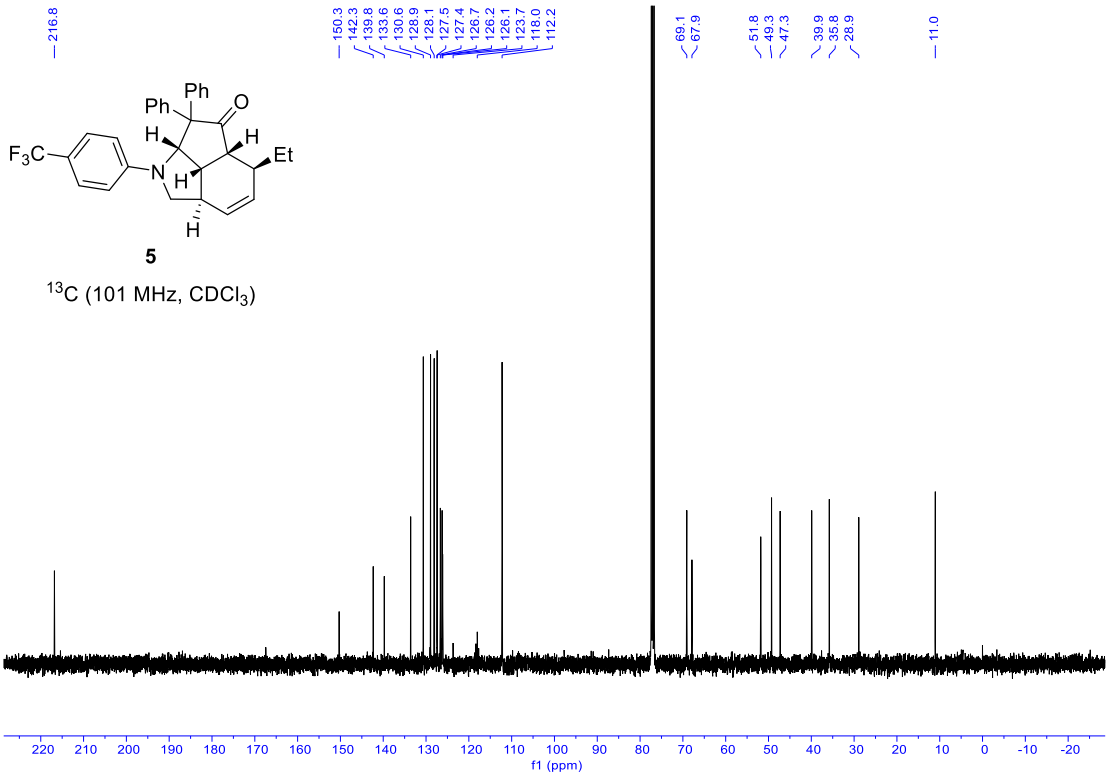
^{19}F (377 MHz, $CDCl_3$)



5

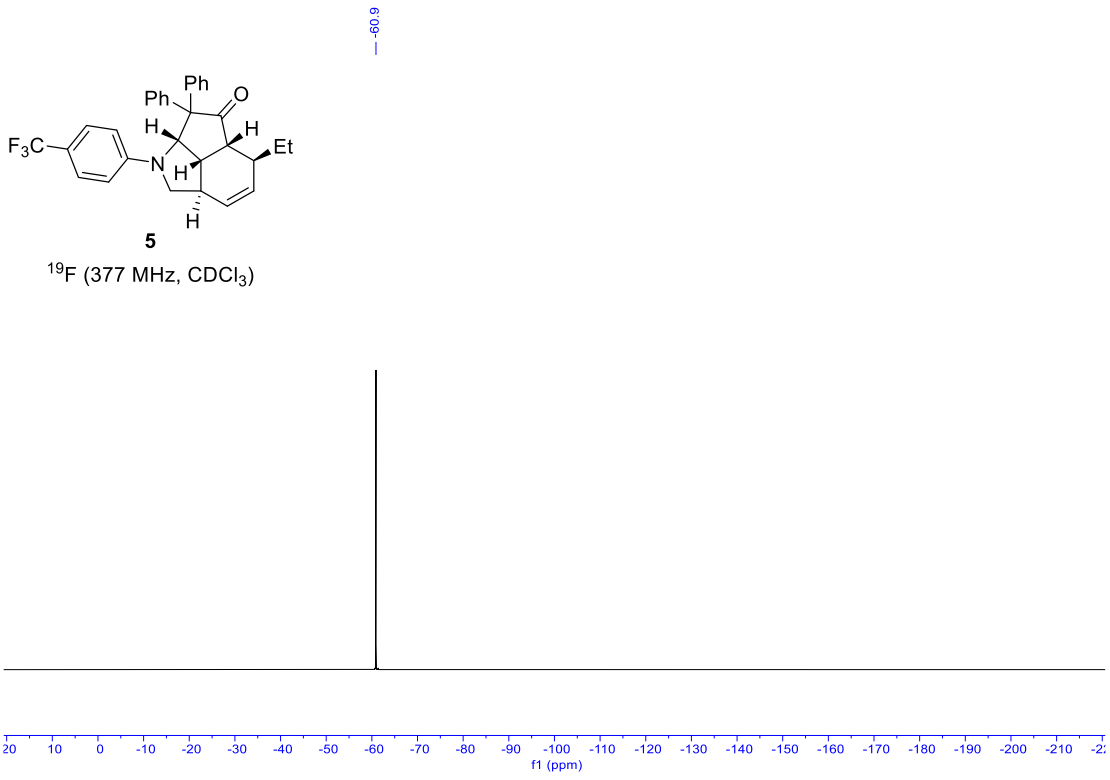
^{1}H (400 MHz, $CDCl_3$)





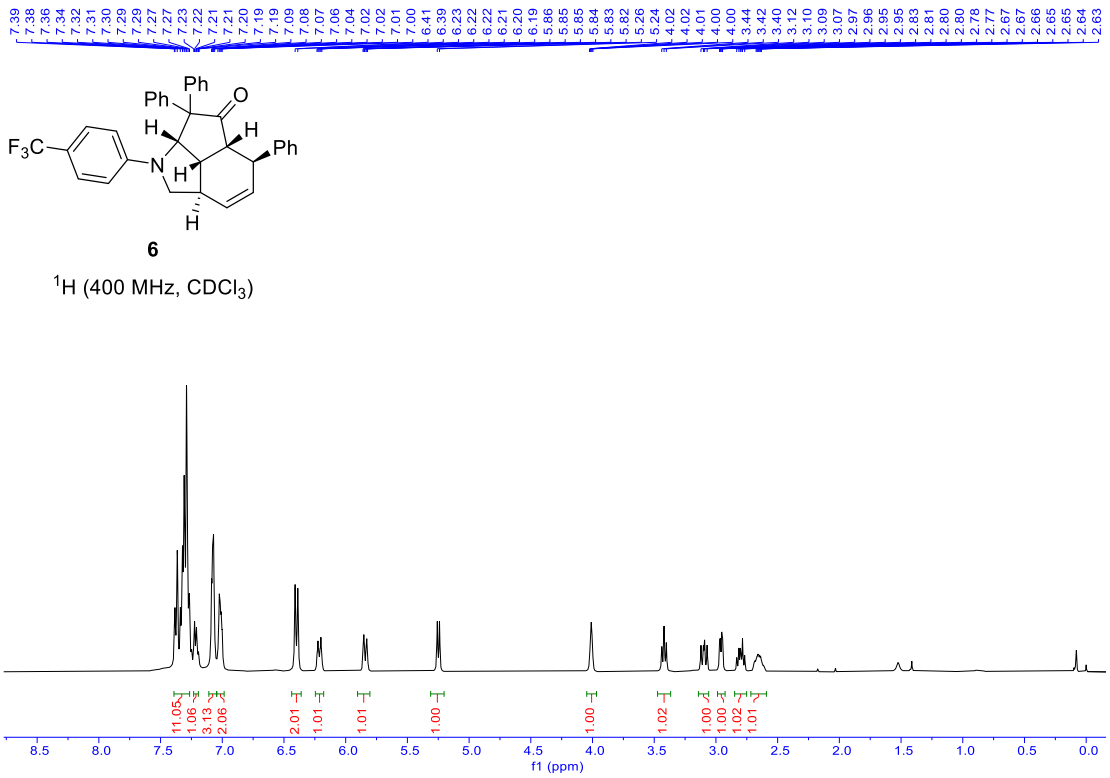
5

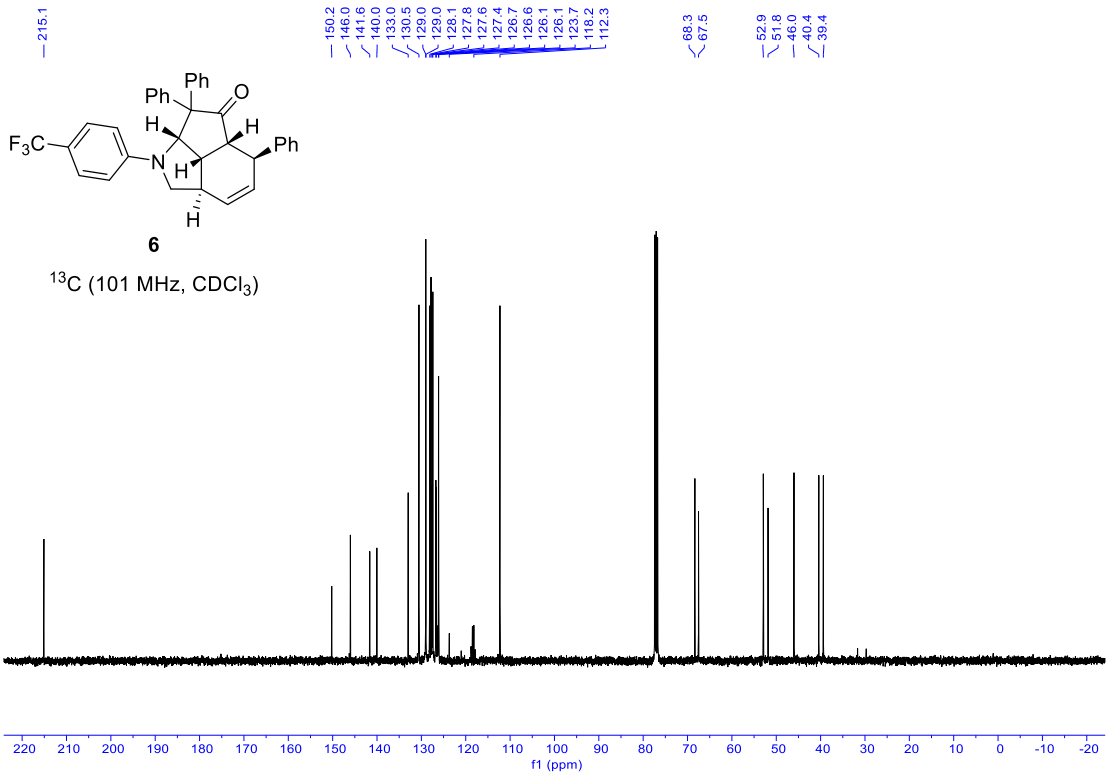
^{13}C (101 MHz, $CDCl_3$)

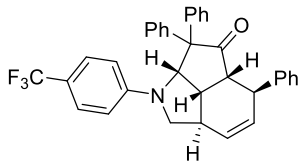


5

^{19}F (377 MHz, $CDCl_3$)

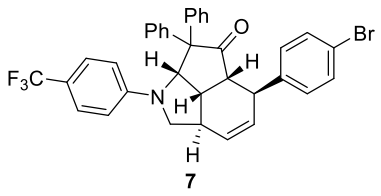

7.39 7.38 7.36 7.34 7.32 7.31 7.30 7.29 7.29 7.27 7.27 7.23 7.22 7.21 7.21 7.20 7.19 7.19 7.09 7.08 7.07 7.06 7.04 7.02 7.02 7.01 7.00 6.41 6.39 6.23 6.22 6.22 6.21 6.20 6.19 5.86 5.85 5.85 5.84 5.83 5.82 5.26 5.24 4.02 4.02 4.01 4.00 4.00 3.44 3.42 3.40 3.12 3.10 3.09 3.07 2.97 2.96 2.95 2.95 2.83 2.81 2.80 2.80 2.78 2.77 2.67 2.67 2.66 2.65 2.65 2.64 2.63
Ph
Ph
O
H
H
H
Ph
F3C
N
H
H
6
1H (400 MHz, CDCl3)
11.05
1.06
3.13
2.06
2.01
1.01
1.01
1.00
1.00
1.02
1.00
1.00
1.02
1.01
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)


215.1
150.2
146.0
141.6
140.0
133.0
130.5
129.0
129.0
128.1
127.8
127.6
127.4
126.7
126.6
126.1
126.1
123.7
118.2
112.3
68.3
67.5
52.9
51.8
46.0
40.4
39.4
Ph
Ph
O
H
H
H
Ph
F3C
N
H
H
6
13C (101 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)



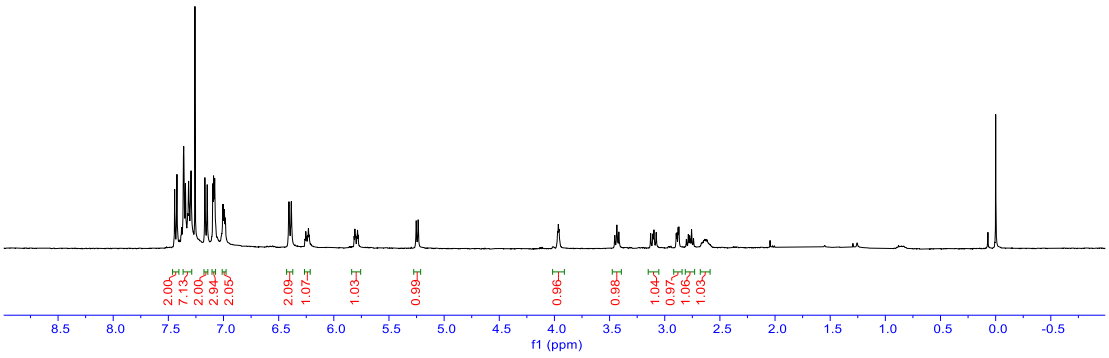
6

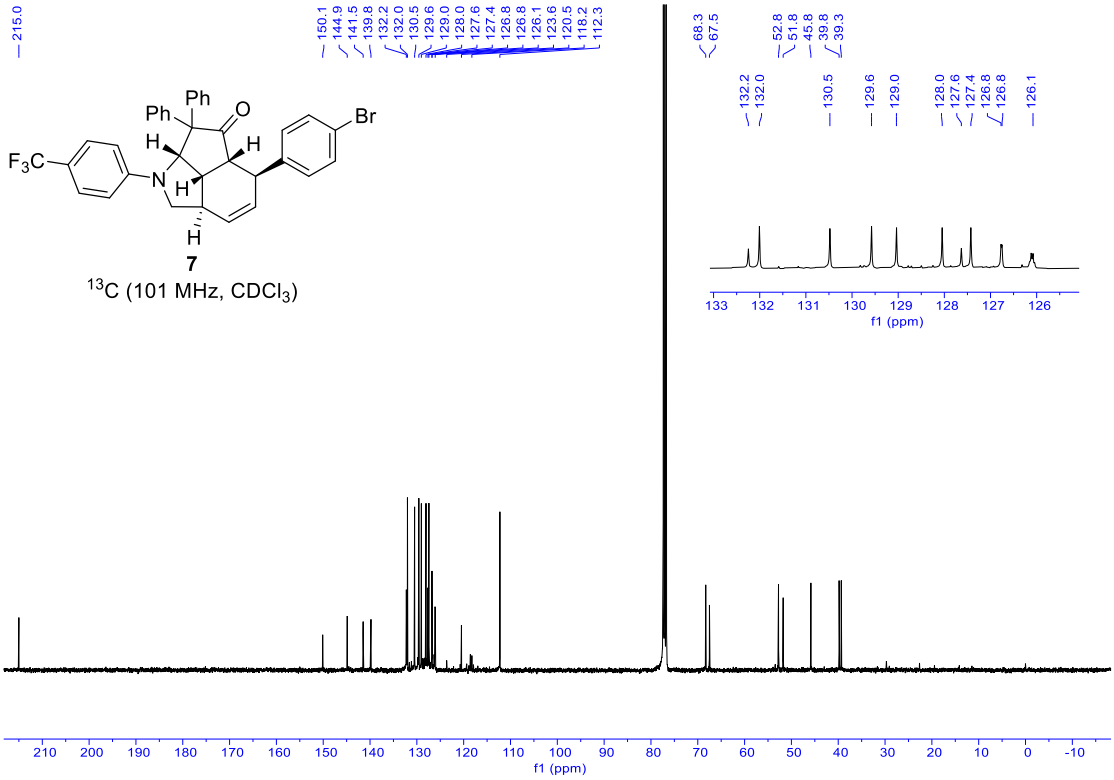
^{19}F (377 MHz, $CDCl_3$)

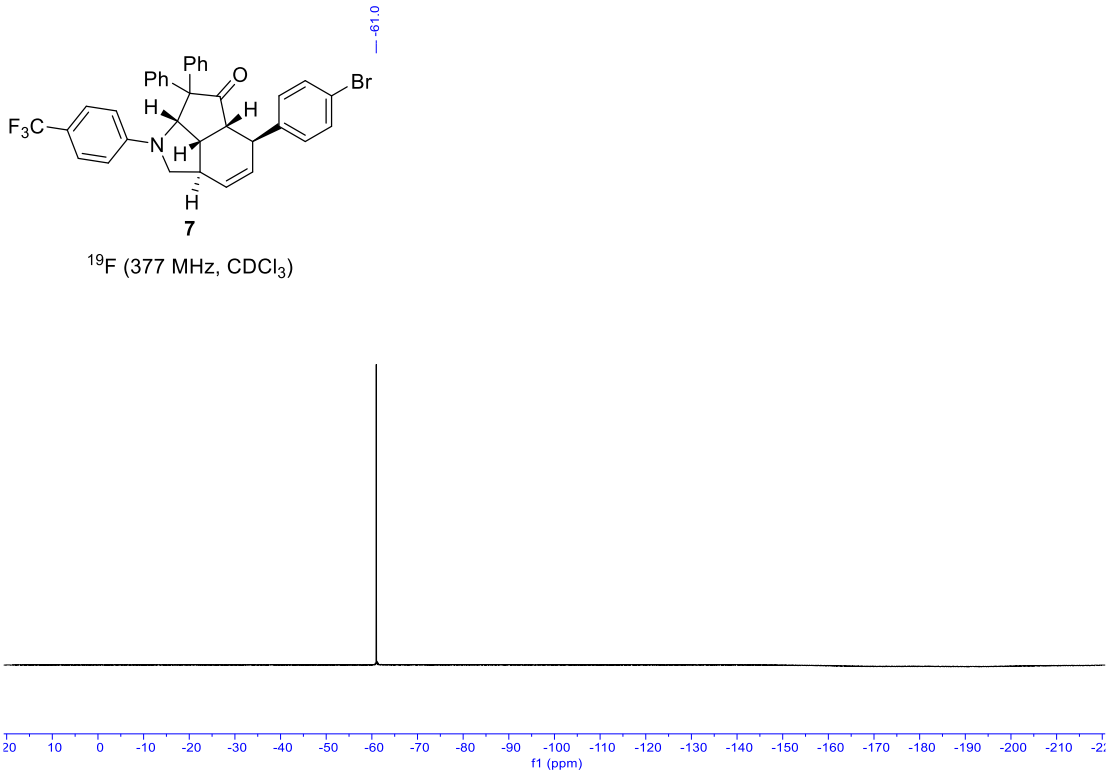


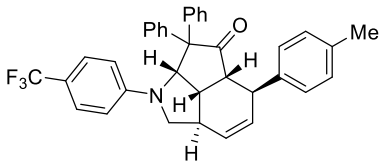
7

^{1}H (400 MHz, $CDCl_3$)



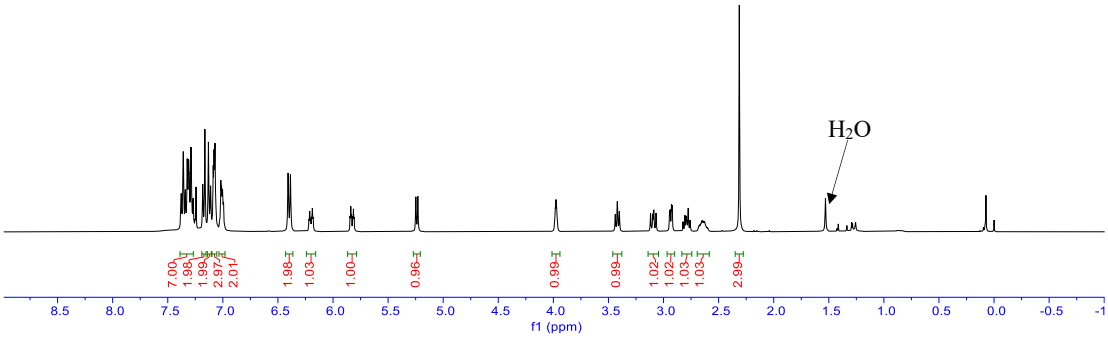

215.0
150.1
144.9
141.5
139.8
132.2
132.0
130.5
129.6
129.0
128.0
127.6
127.4
126.8
126.8
126.1
123.6
120.5
118.2
112.3
68.3
67.5
52.8
51.8
45.8
39.8
39.3
132.2
132.0
130.5
129.6
129.0
128.0
127.6
127.4
126.8
126.8
126.1
Ph
Ph
O
H
H
N
H
H
F3C
Br
7
13C (101 MHz, CDCl3)
f1 (ppm)
f1 (ppm)

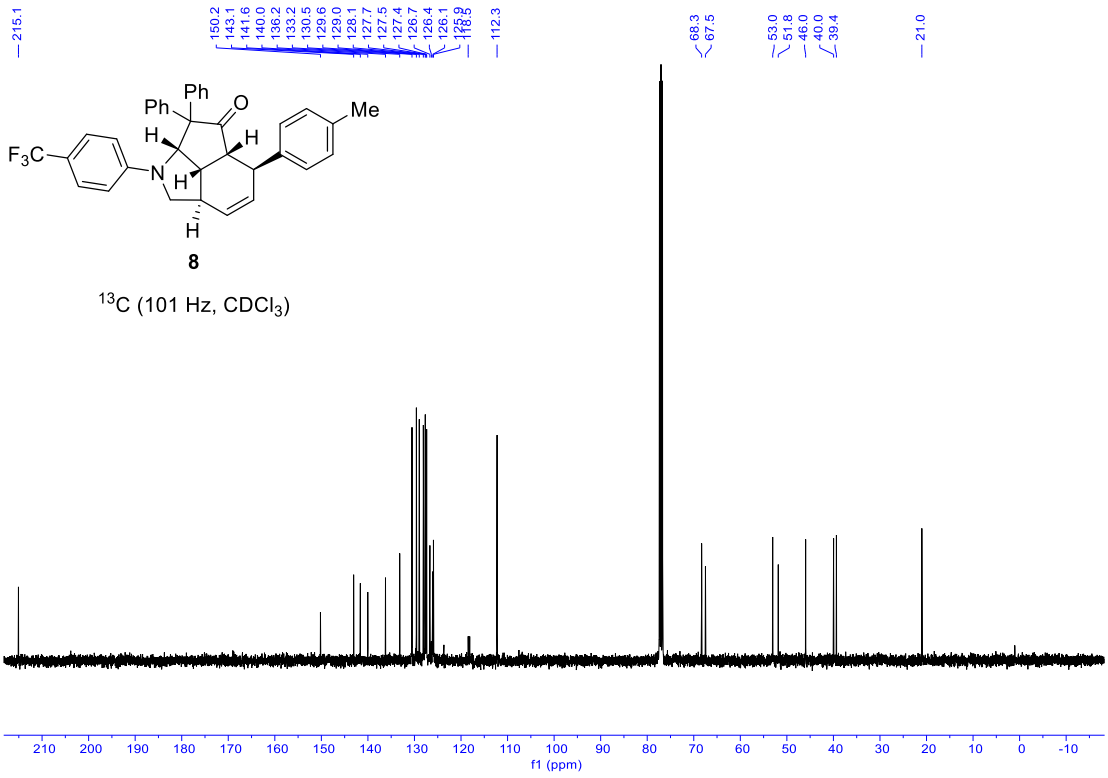

-61.0
Ph
Ph
O
H
H
N
H
H
F3C
Br
7
19F (377 MHz, CDCl3)
f1 (ppm)



8

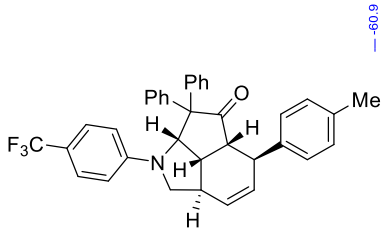
^{1}H (400 Hz, $CDCl_3$)





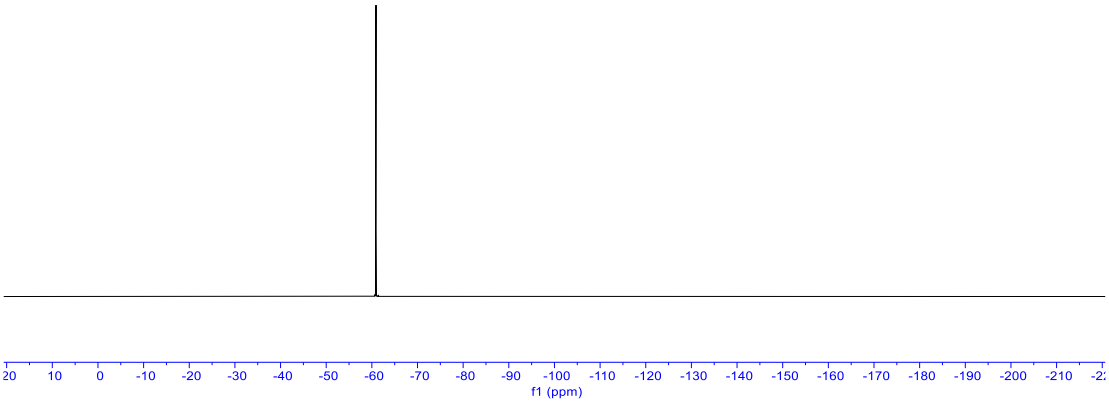
8

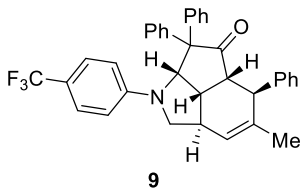
^{13}C (101 Hz, $CDCl_3$)



8

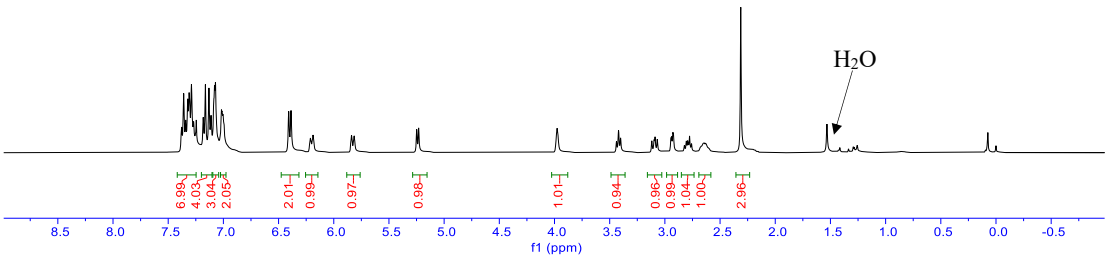
^{19}F (377 Hz, $CDCl_3$)

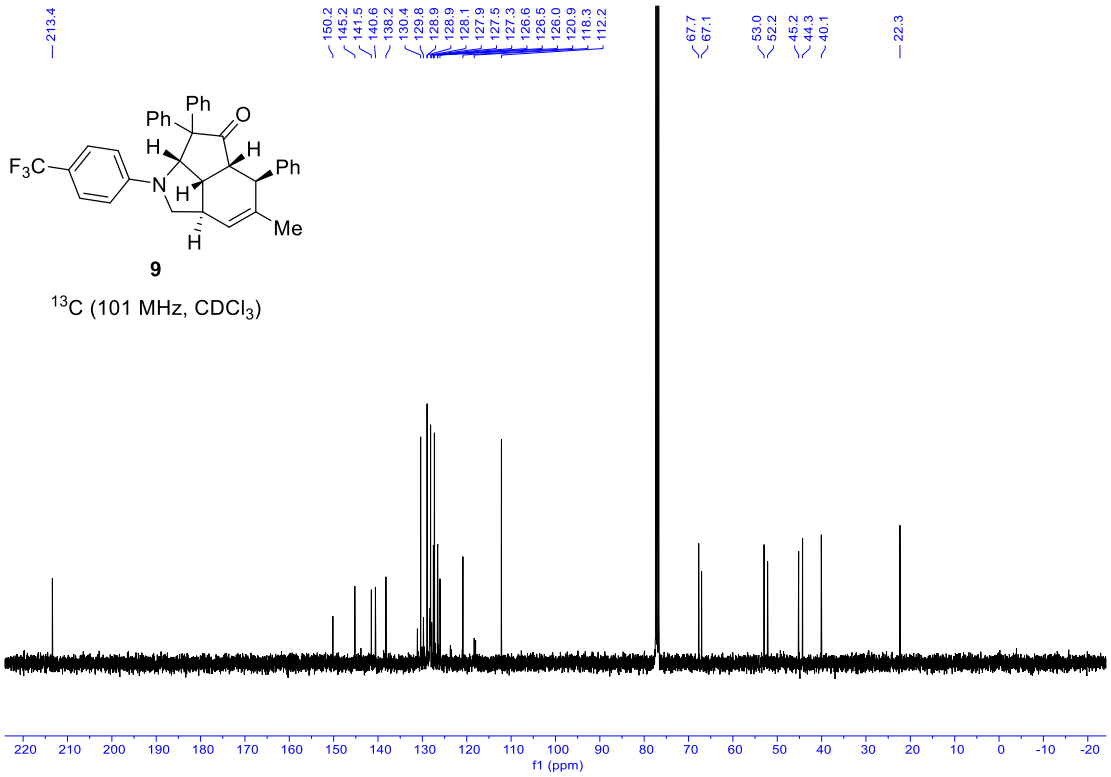




9

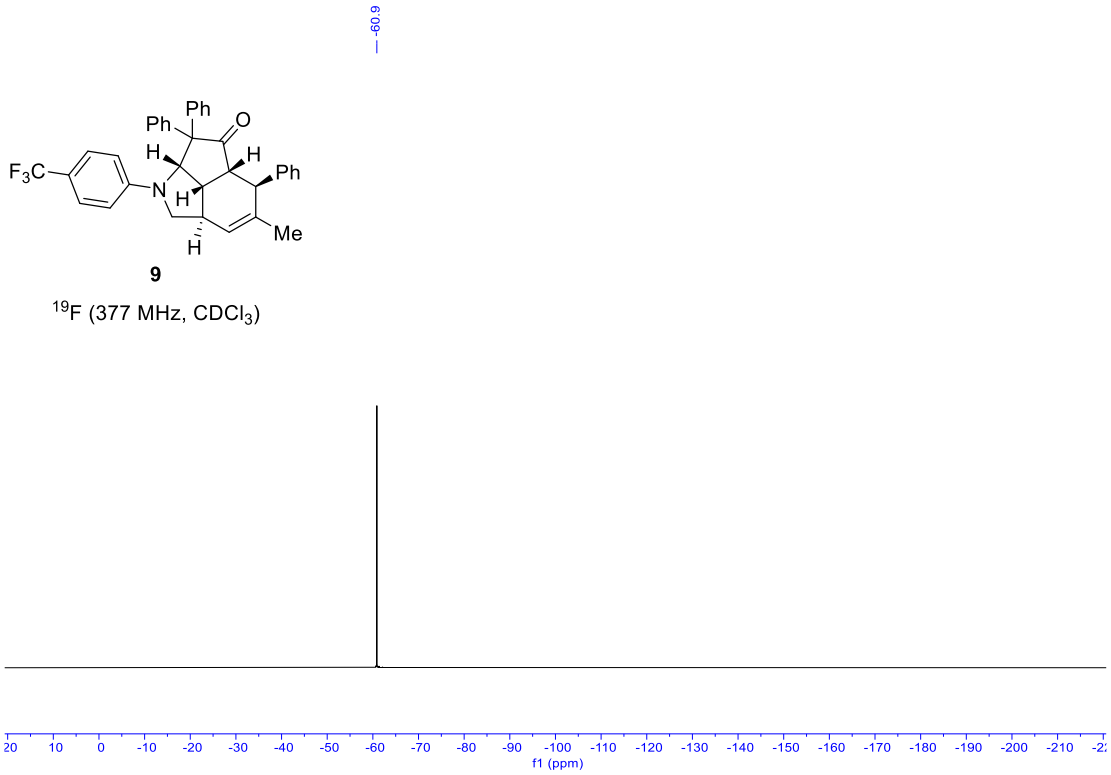
^{1}H (400 MHz, $CDCl_3$)





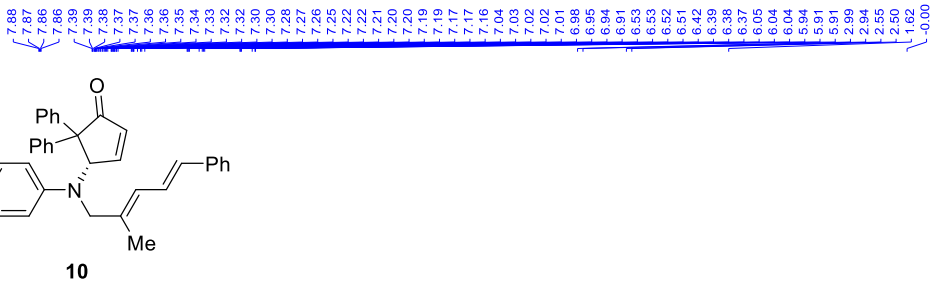
9

^{13}C (101 MHz, $CDCl_3$)



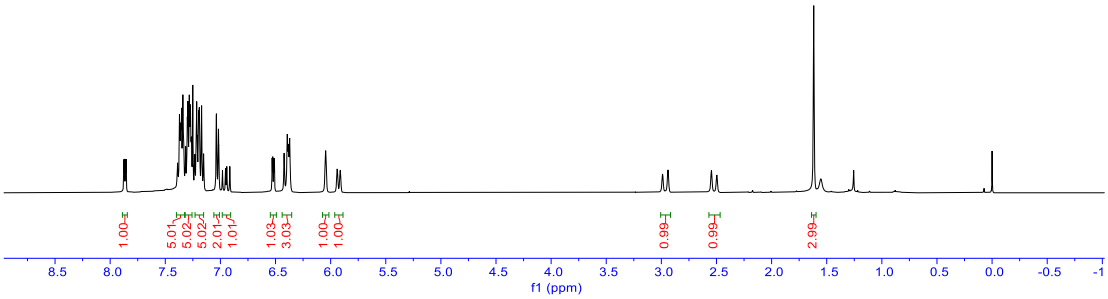
9

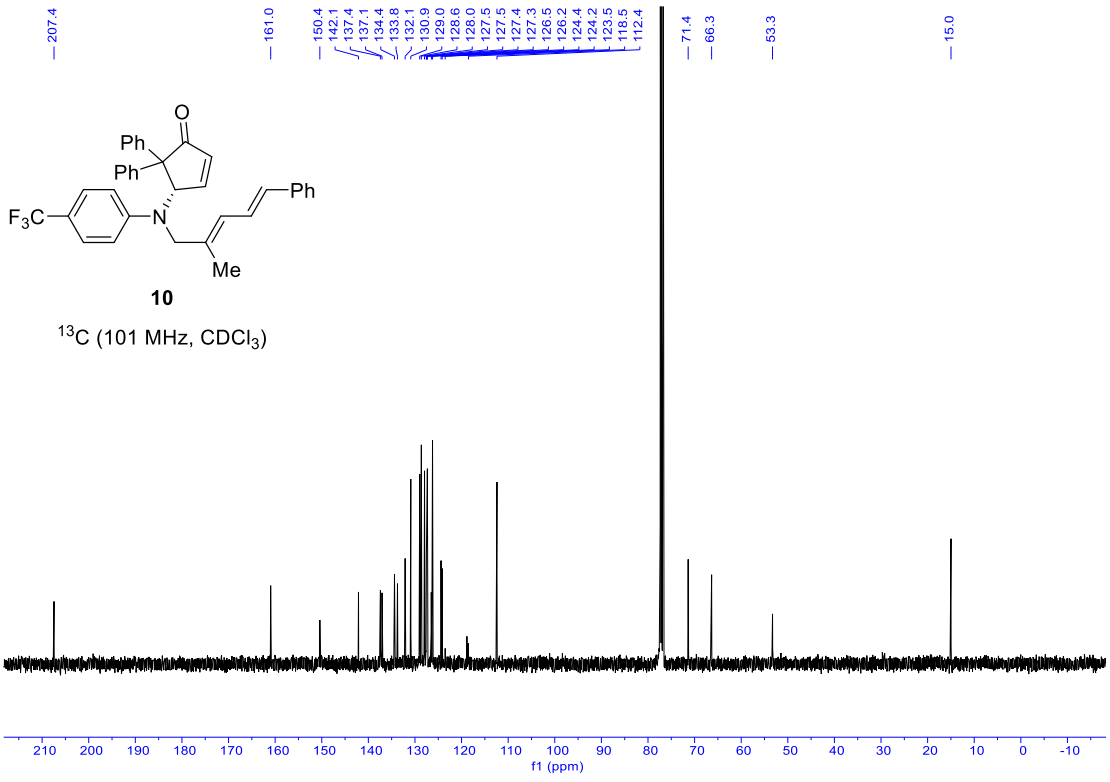
^{19}F (377 MHz, $CDCl_3$)



10

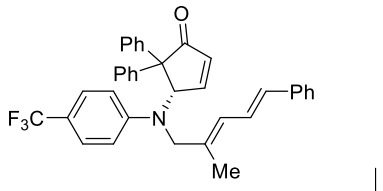
^{1}H (400 MHz, $CDCl_3$)





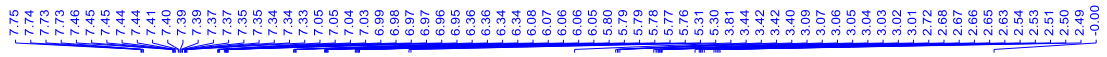
10

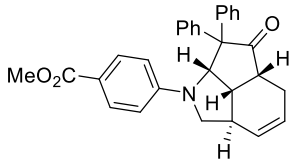
^{13}C (101 MHz, $CDCl_3$)



10

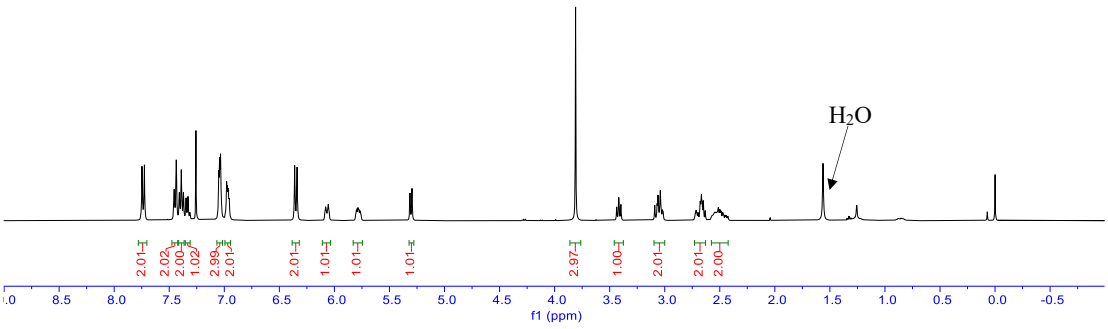
^{19}F (377 MHz, $CDCl_3$)

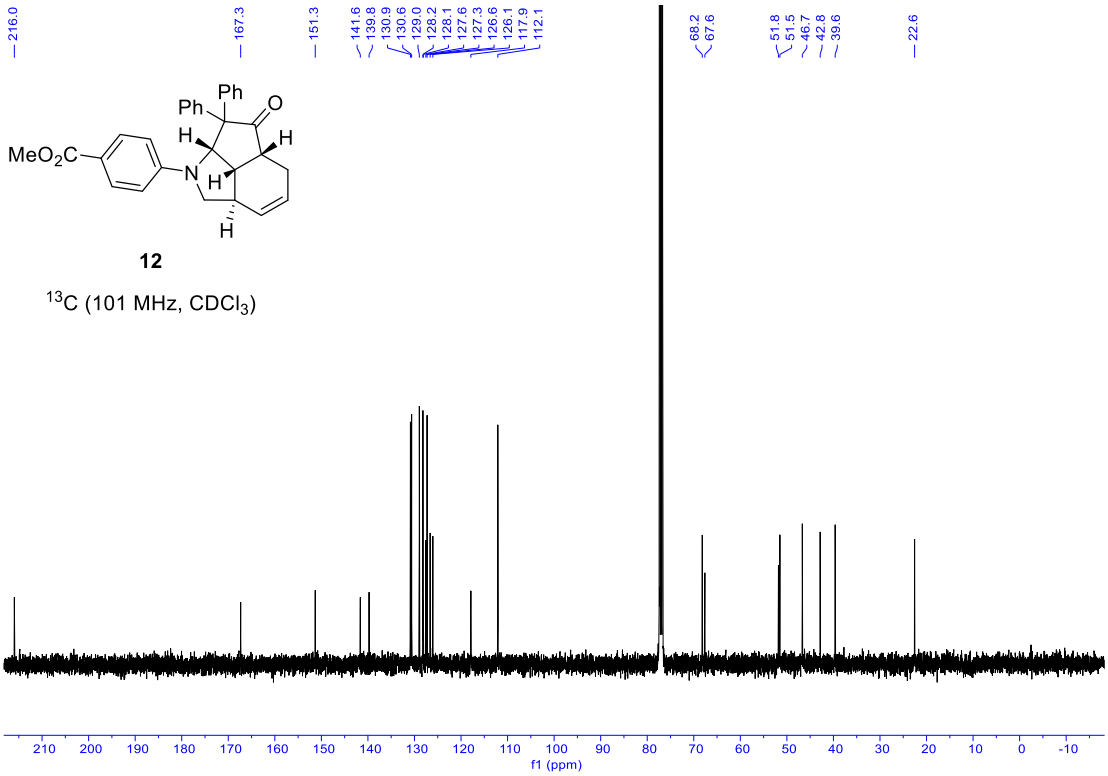




12

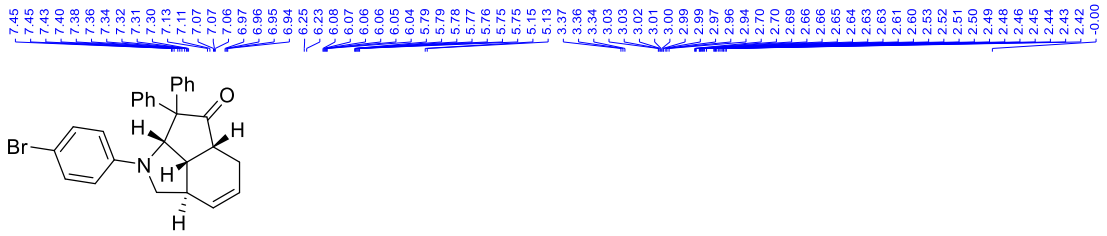
^{1}H (400 MHz, $CDCl_3$)





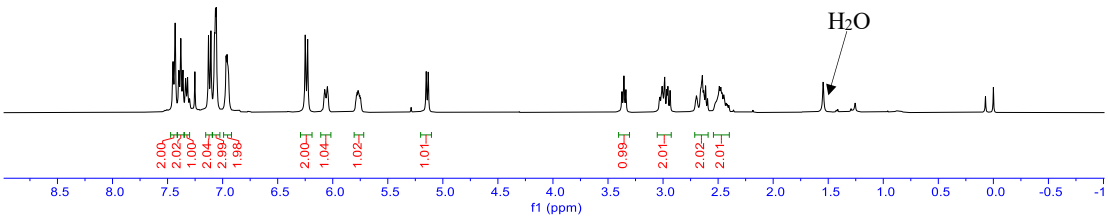
12

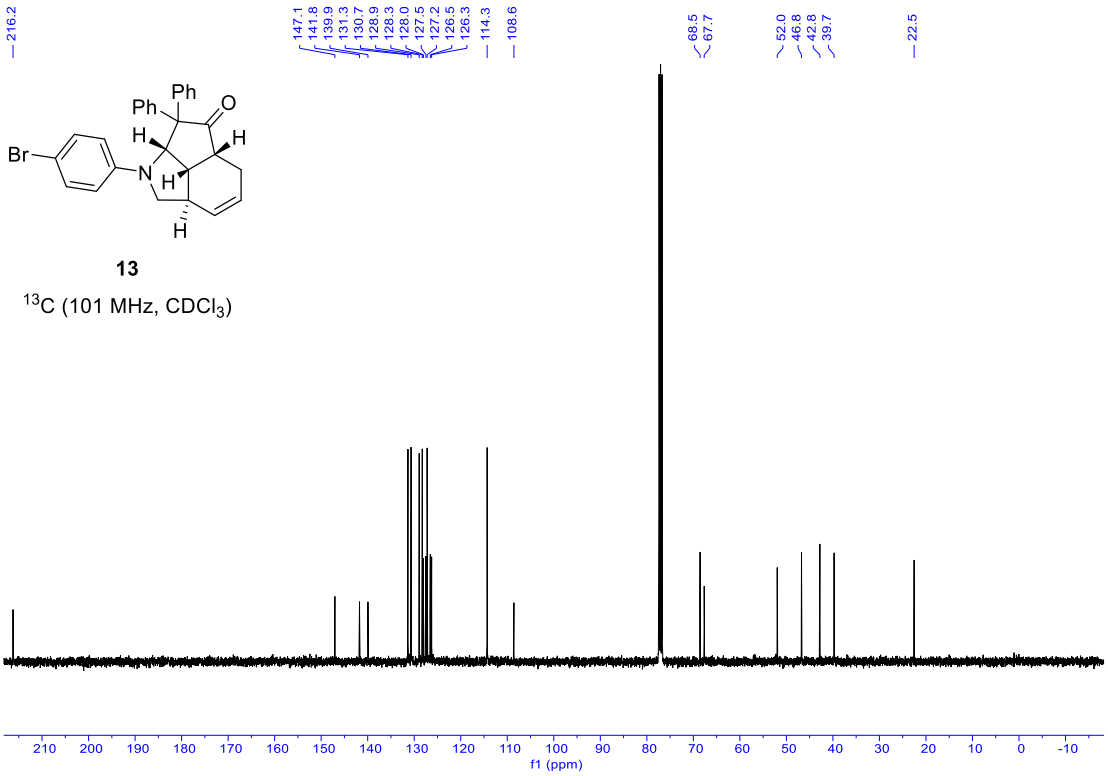
^{13}C (101 MHz, $CDCl_3$)



13

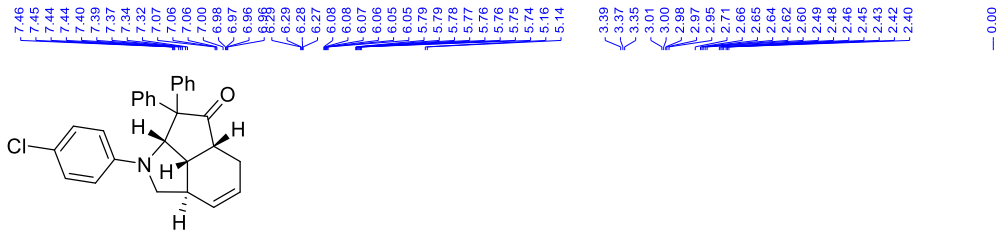
^{1}H (400 MHz, $CDCl_3$)





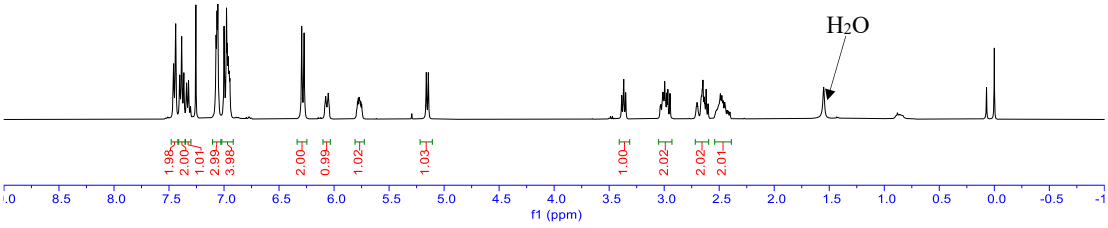
13

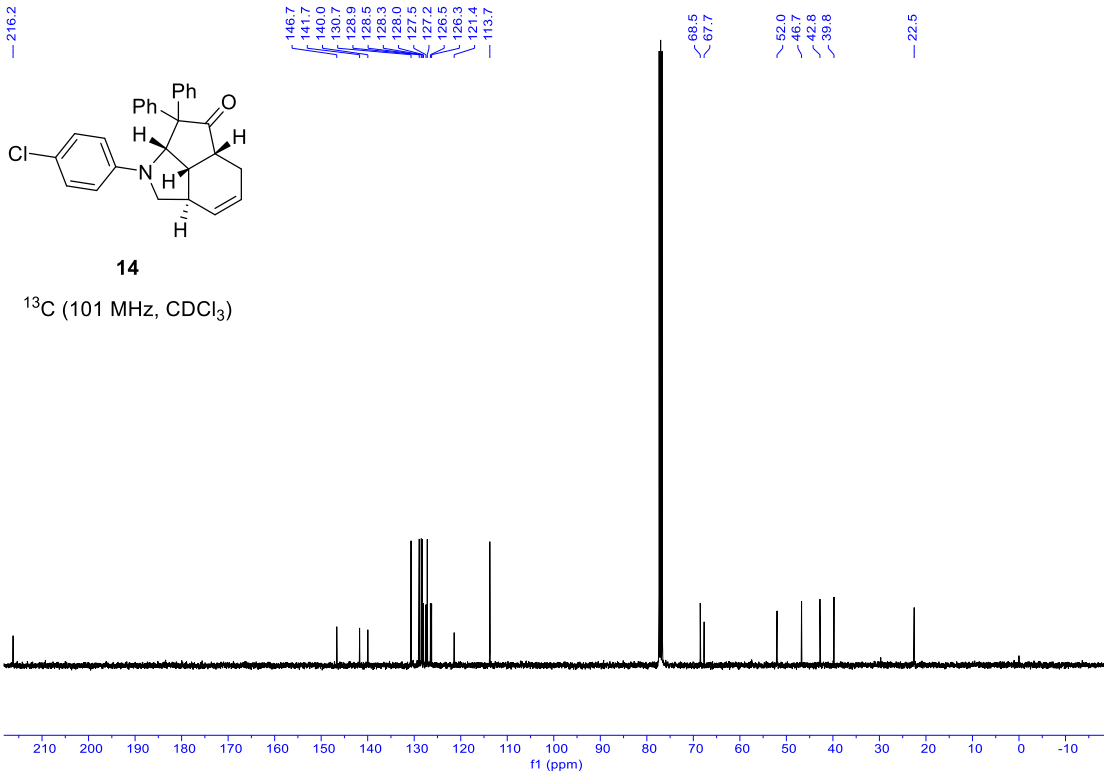
^{13}C (101 MHz, $CDCl_3$)



14

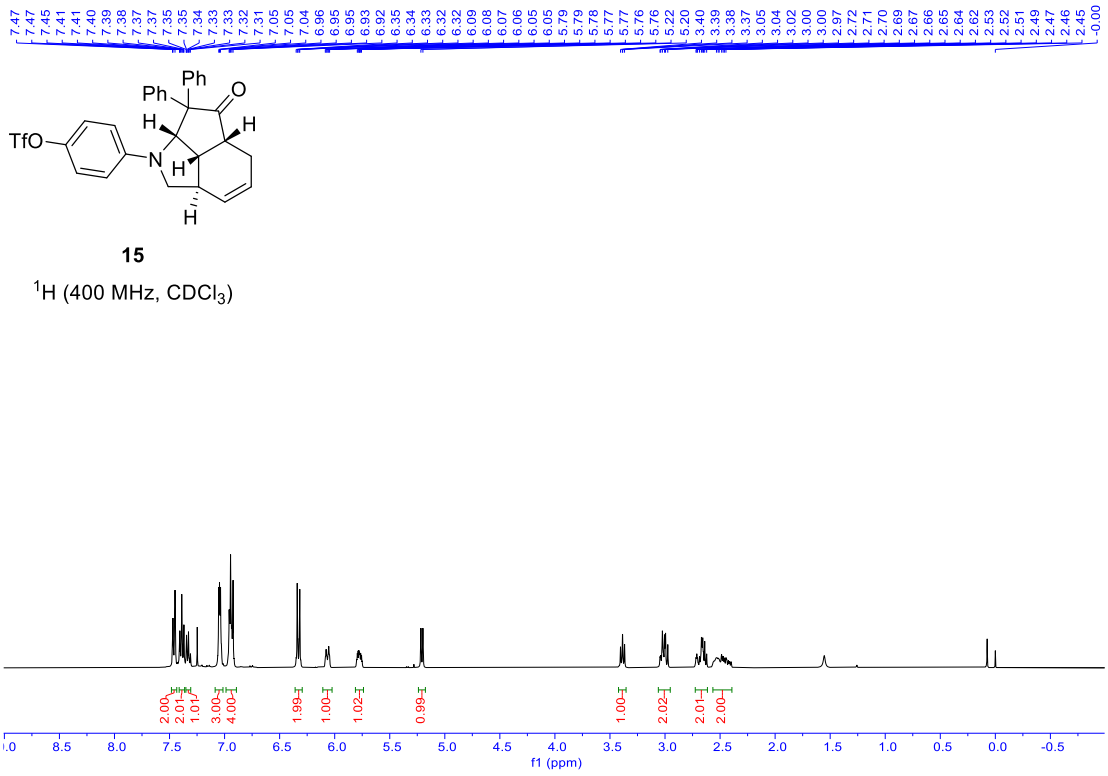
^{1}H (400 MHz, $CDCl_3$)





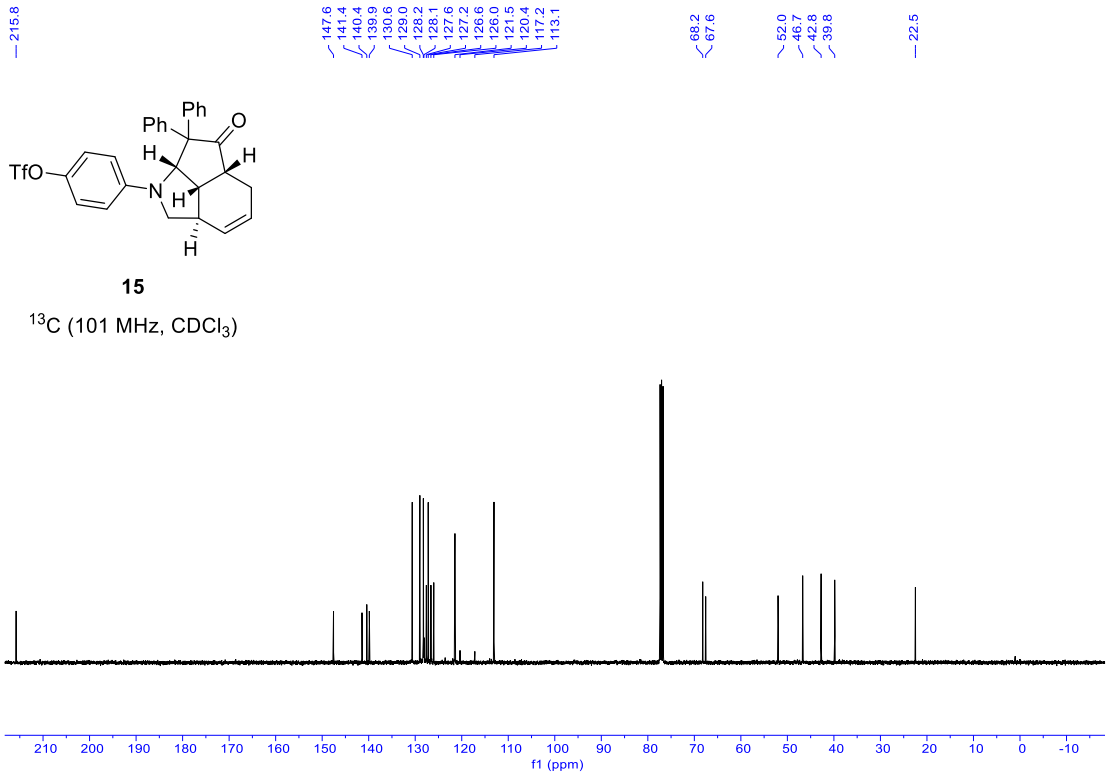
14

^{13}C (101 MHz, $CDCl_3$)



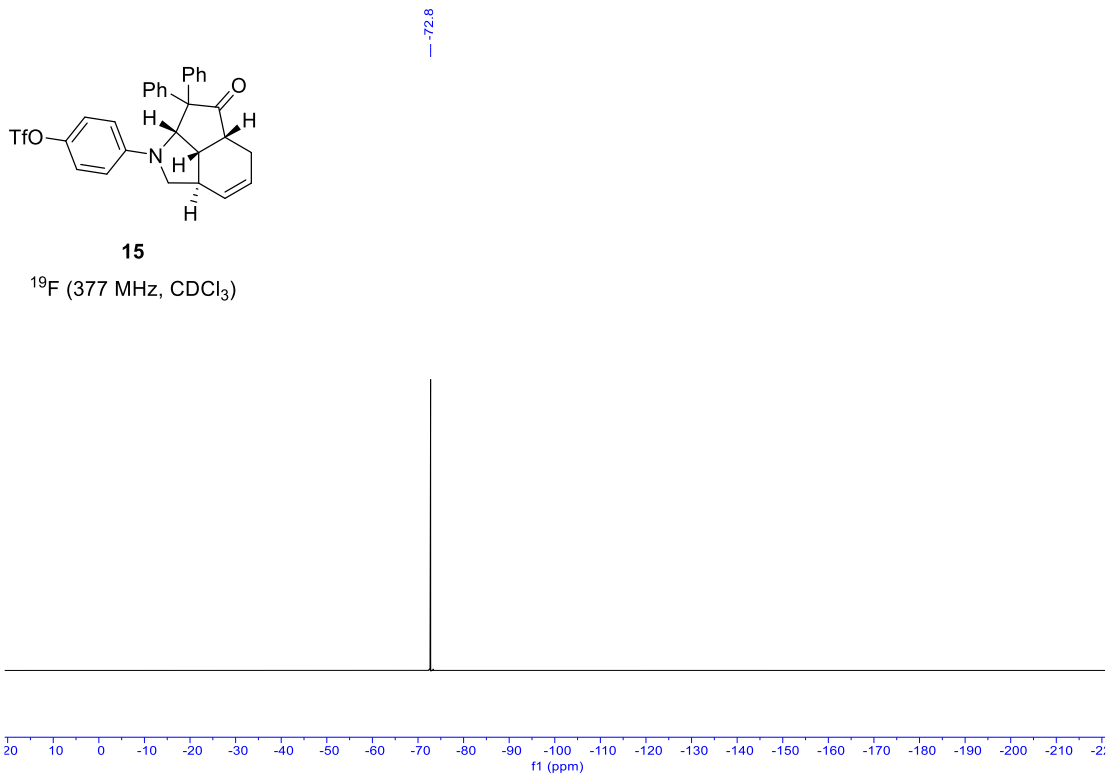
15

^{1}H (400 MHz, $CDCl_3$)



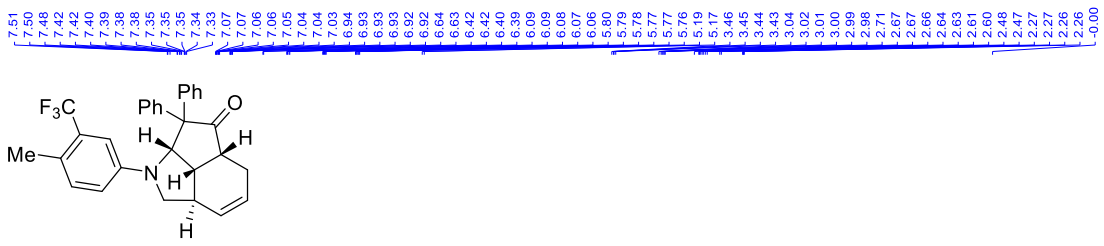
15

^{13}C (101 MHz, $CDCl_3$)



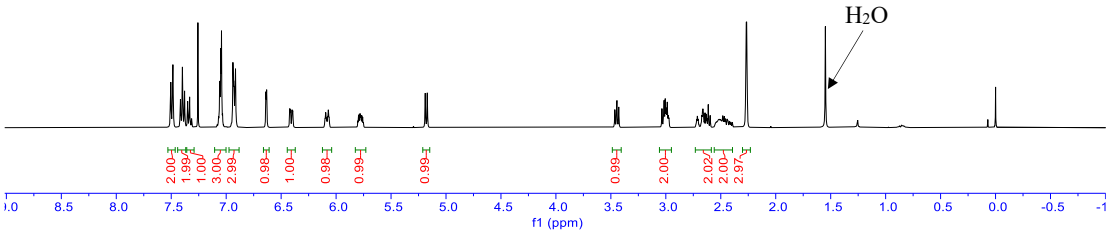
15

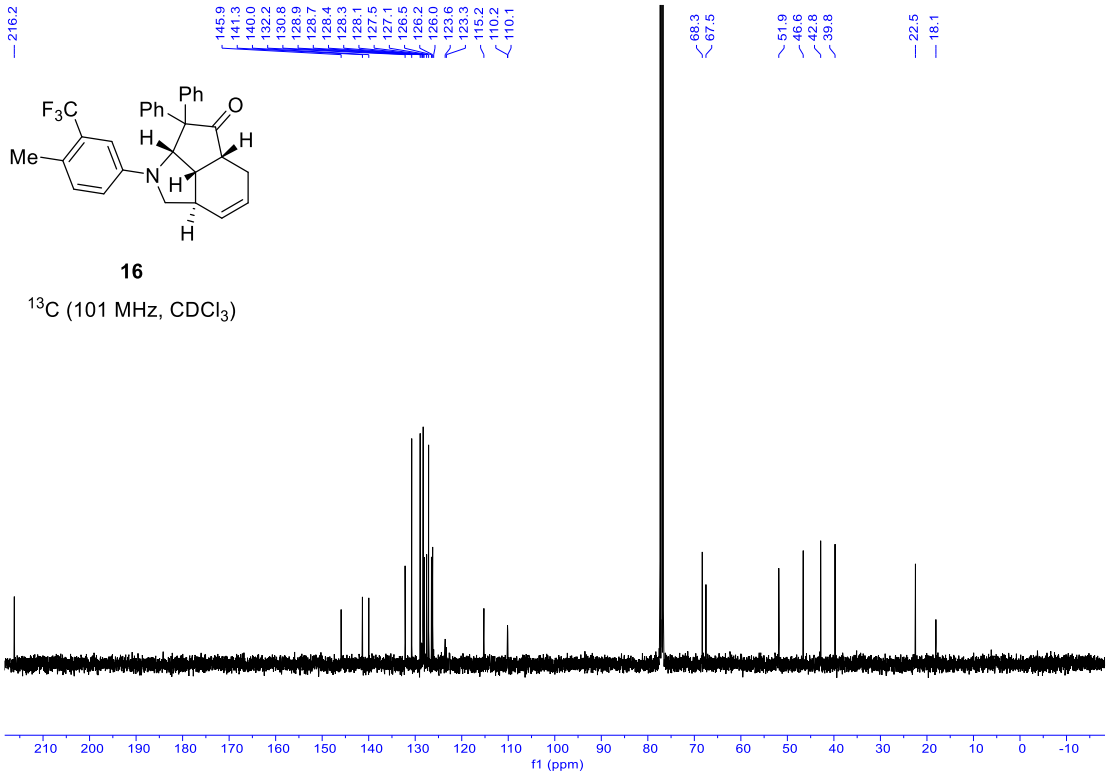
^{19}F (377 MHz, $CDCl_3$)



16

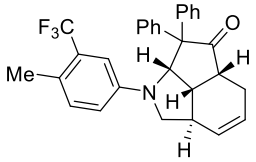
^{1}H (400 MHz, $CDCl_3$)





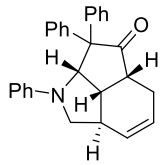
16

^{13}C (101 MHz, $CDCl_3$)



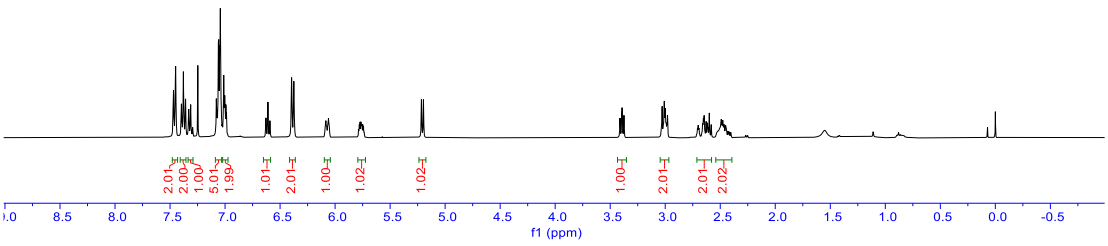
16

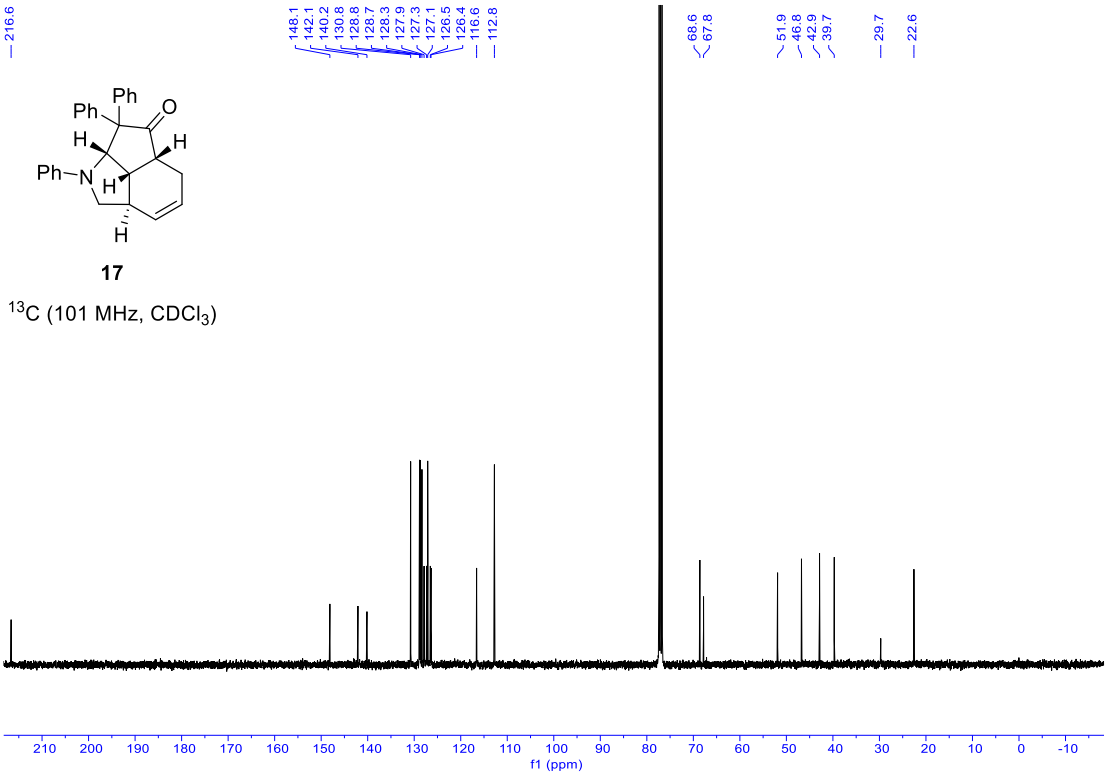
^{19}F (377 MHz, $CDCl_3$)



17

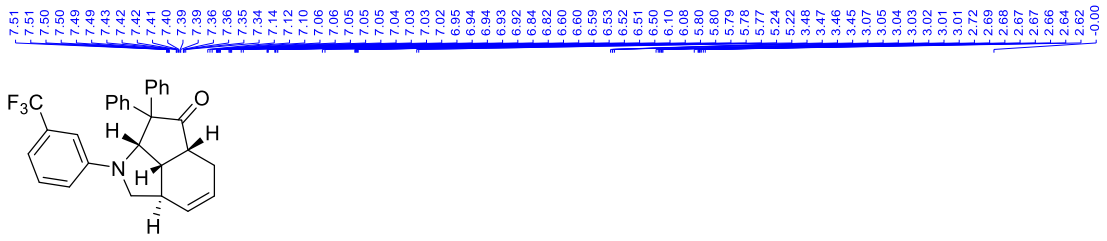
^{1}H (400 MHz, $CDCl_3$)





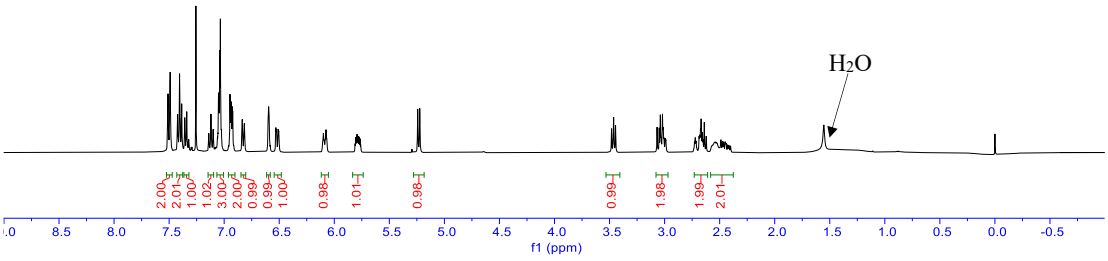
17

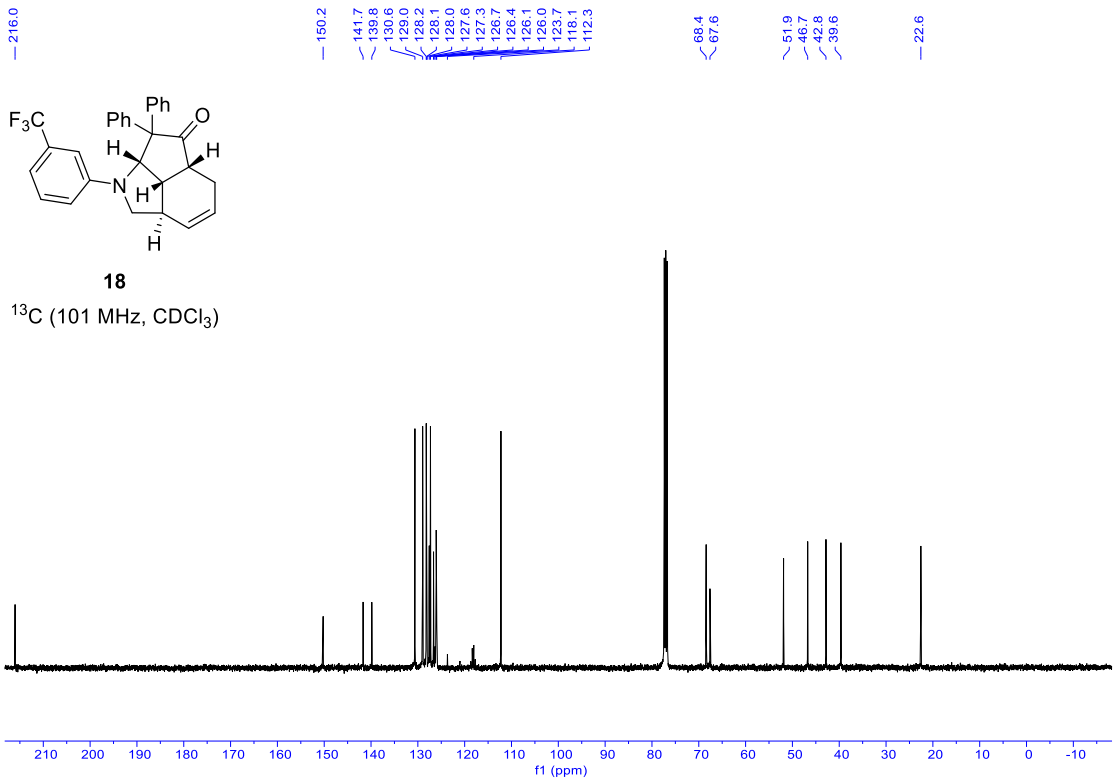
^{13}C (101 MHz, $CDCl_3$)



18

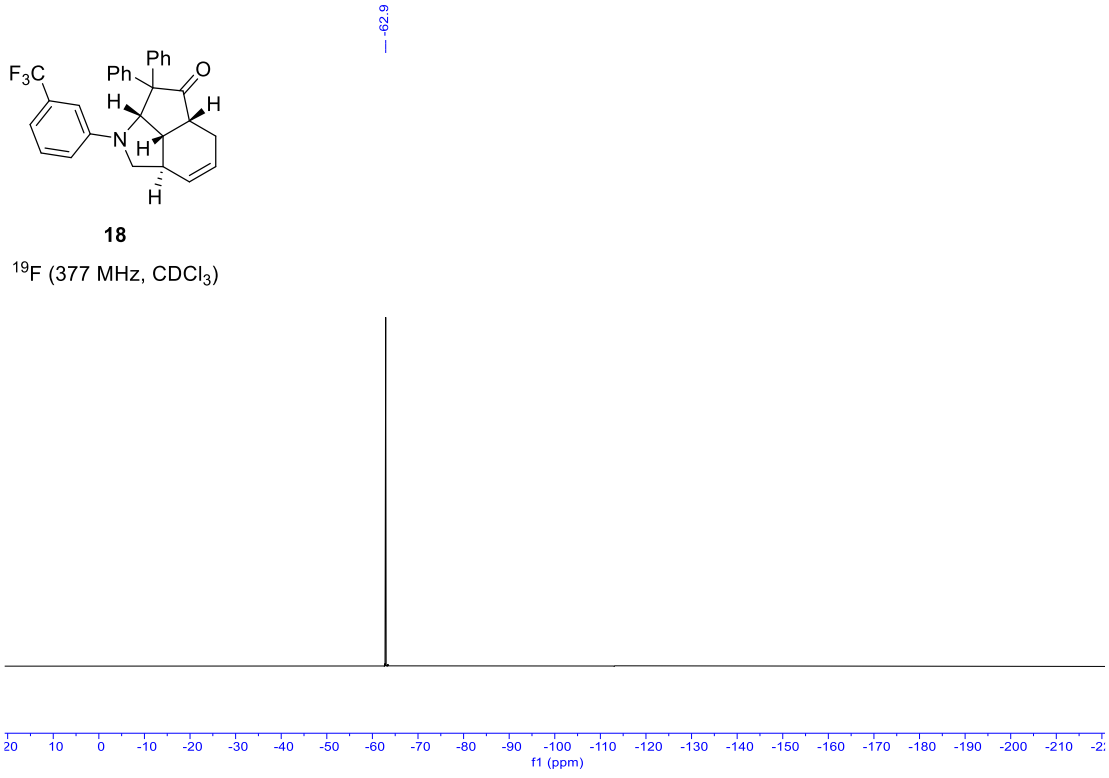
^{1}H (400 MHz, $CDCl_3$)





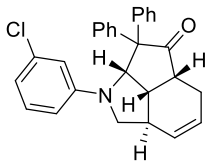
18

^{13}C (101 MHz, $CDCl_3$)



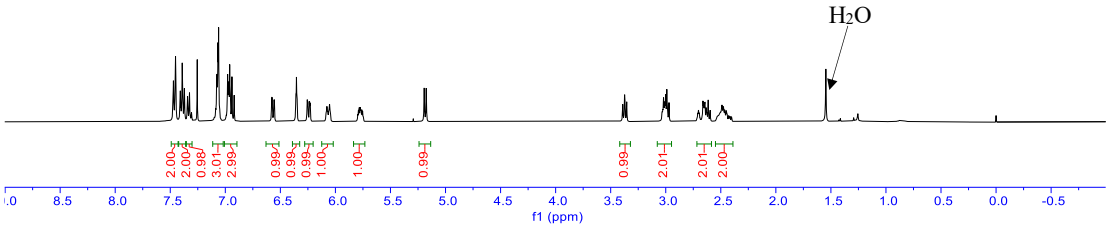
18

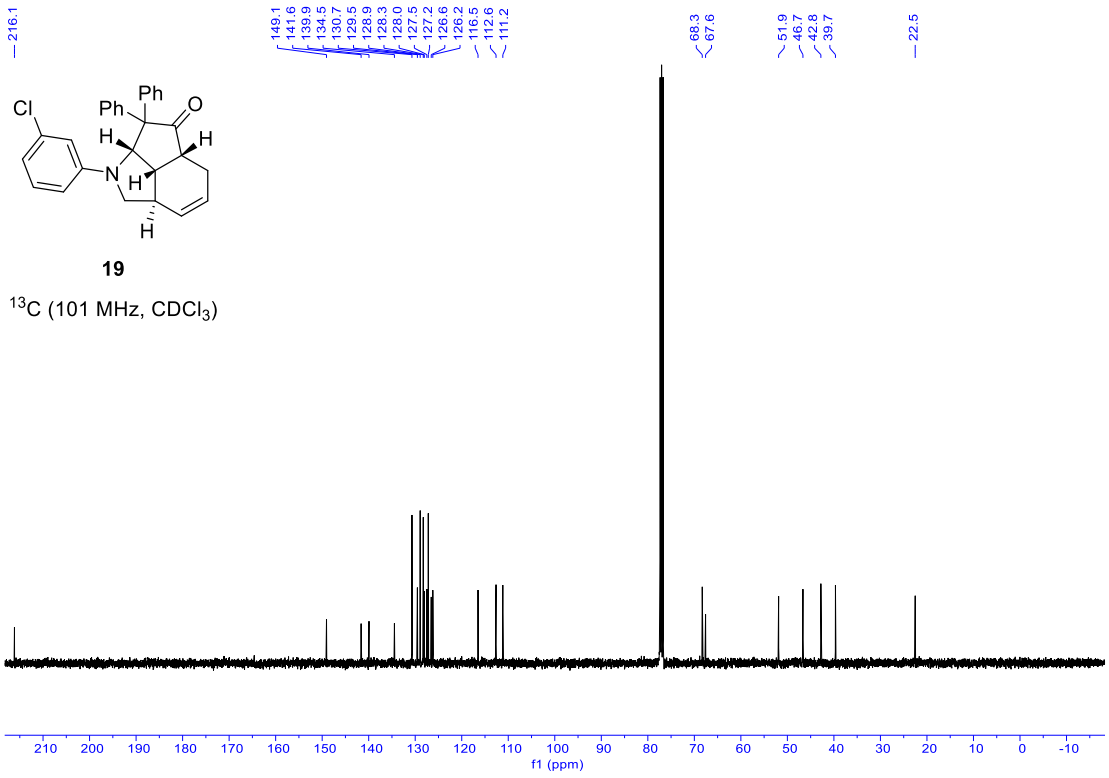
^{19}F (377 MHz, $CDCl_3$)



19

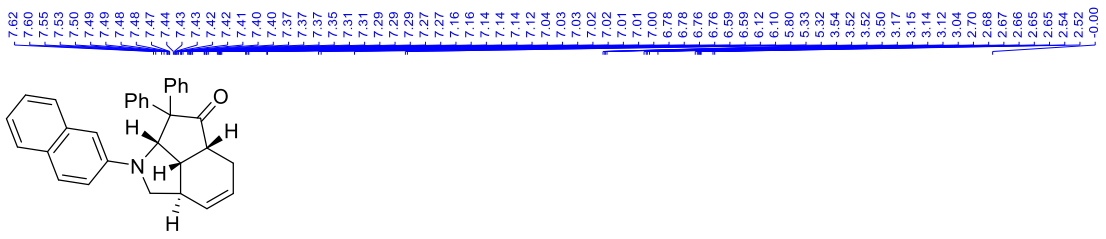
^{1}H (400 MHz, $CDCl_3$)





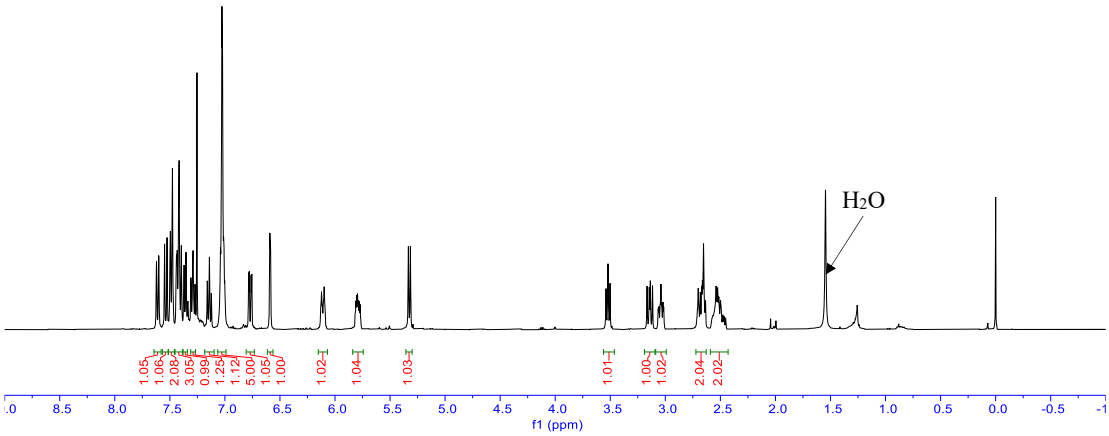
19

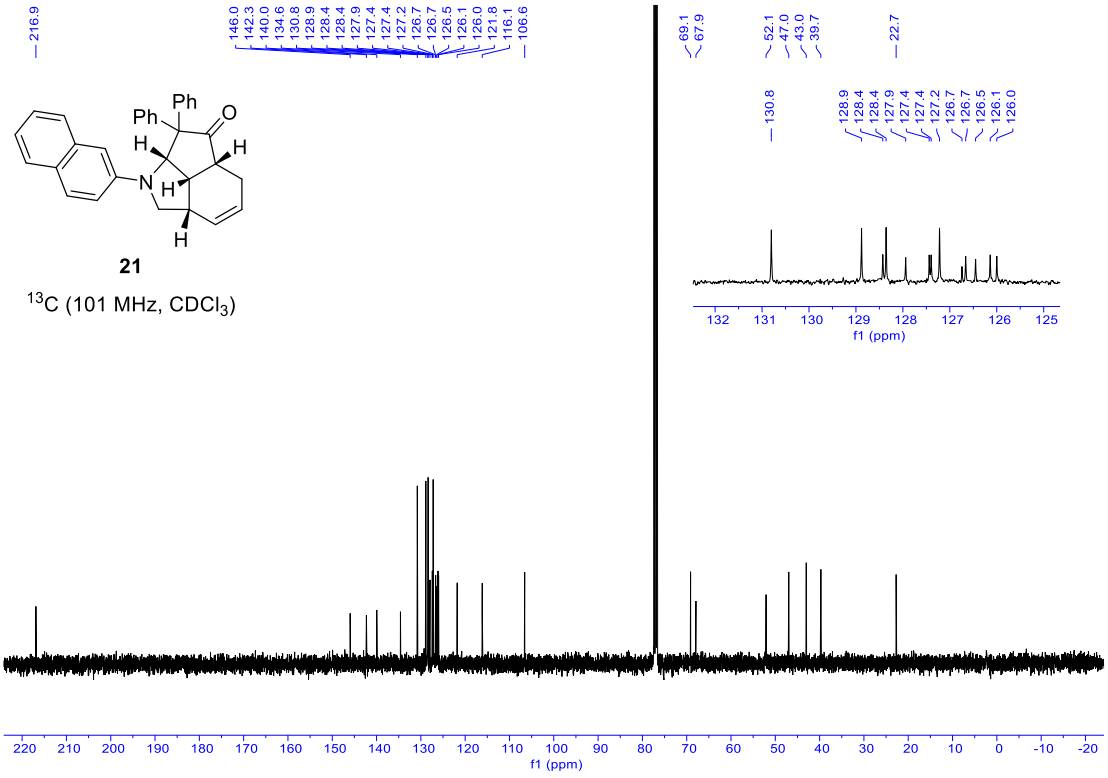
^{13}C (101 MHz, $CDCl_3$)



21

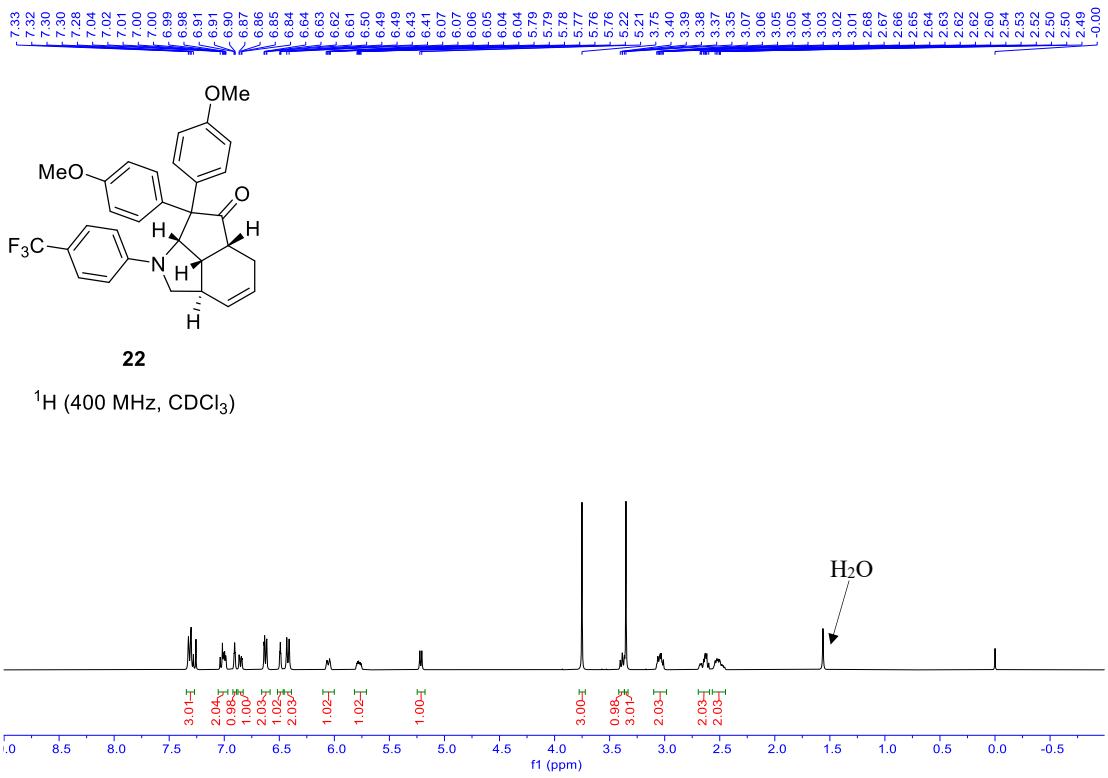
^{1}H (400 MHz, $CDCl_3$)

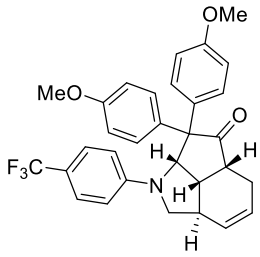




21

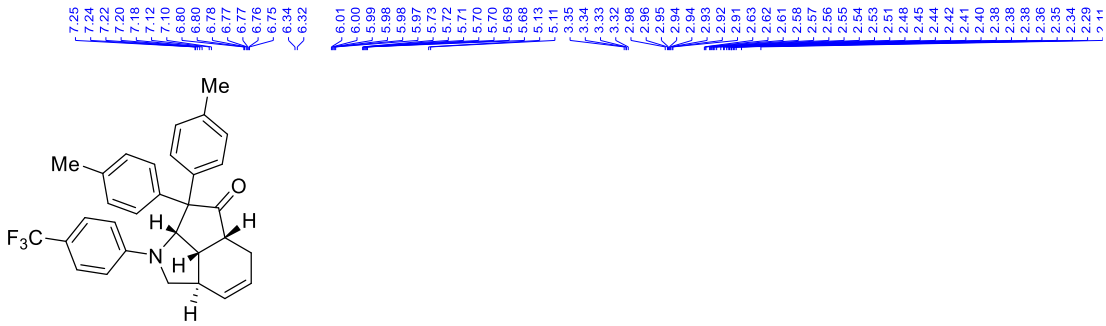
^{13}C (101 MHz, $CDCl_3$)


OMe
MeO
O
H
H
F3C
N
H
H
22
1H (400 MHz, CDCl3)
H2O
f1 (ppm)
OMe
MeO
O
H
H
F3C
N
H
H
22
13C (101 MHz, CDCl3)
f1 (ppm)



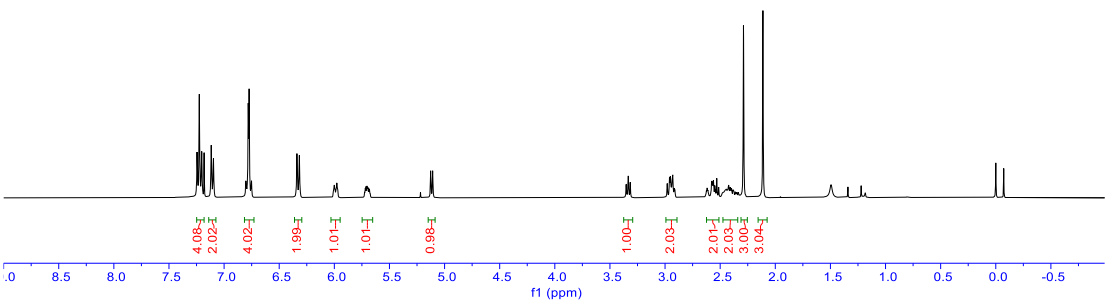
22

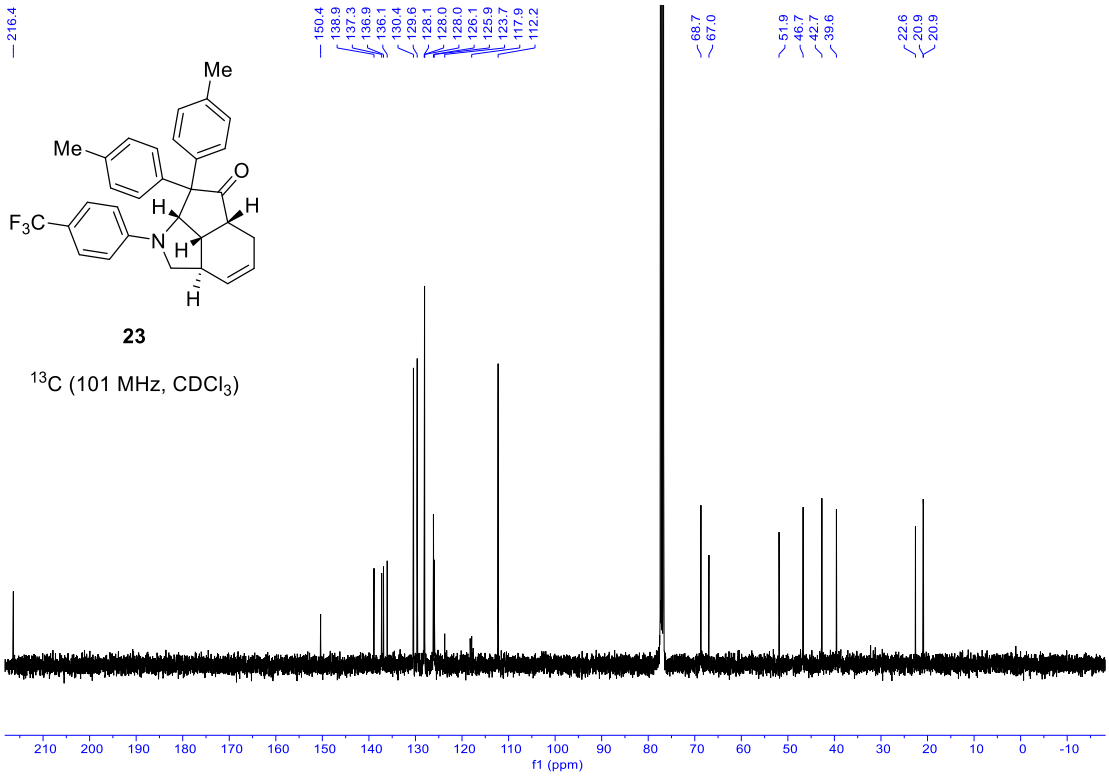
^{19}F (377 MHz, $CDCl_3$)



23

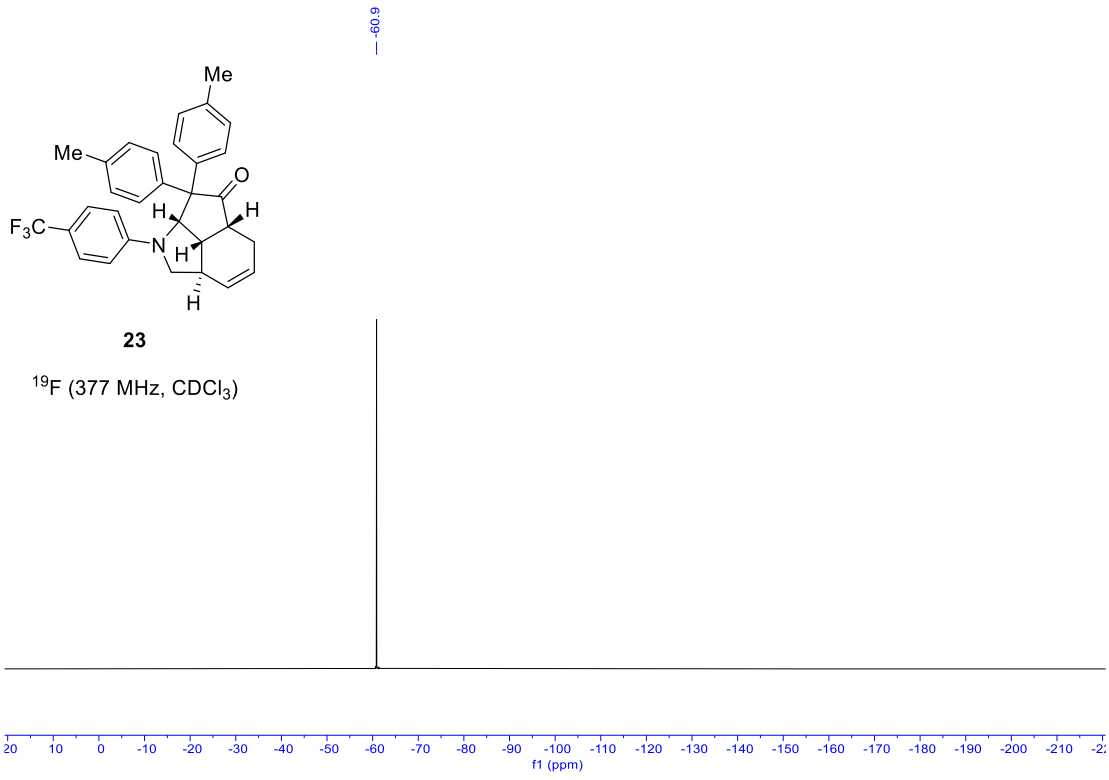
^{1}H (400 MHz, $CDCl_3$)





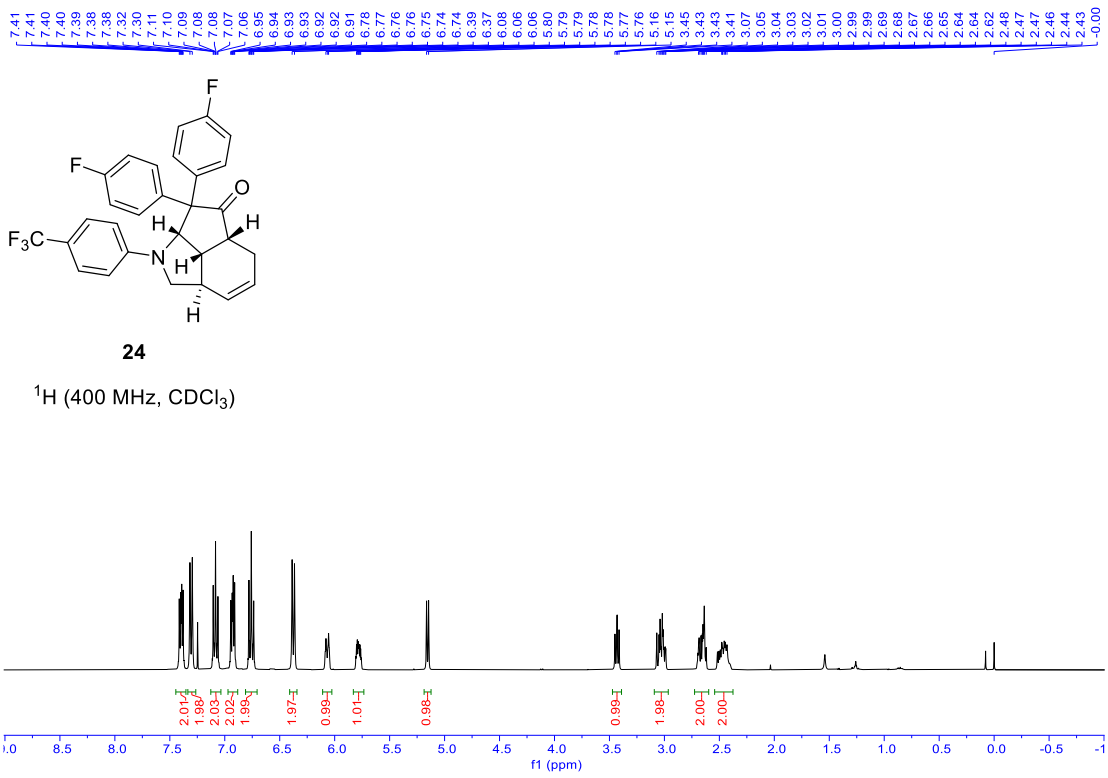
23

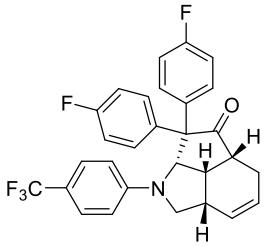
^{13}C (101 MHz, $CDCl_3$)



23

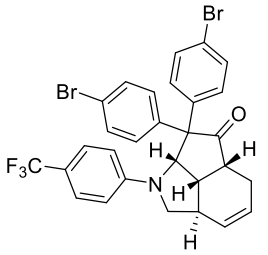
^{19}F (377 MHz, $CDCl_3$)


F
F
O
H
H
F3C
N
H
H
24
1H (400 MHz, CDCl3)
f1 (ppm)
13C (101 MHz, CDCl3)
f1 (ppm)



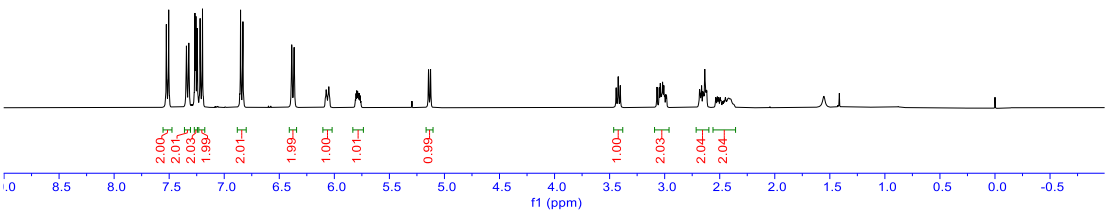
24

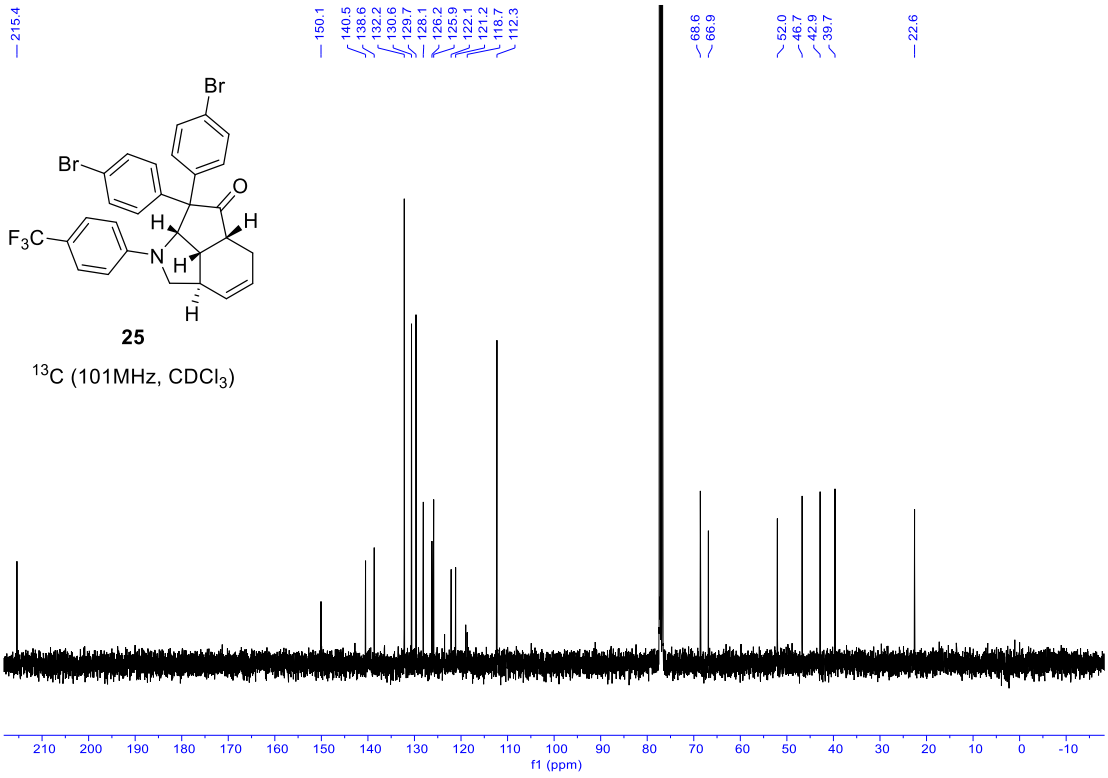
^{19}F (377 MHz, $CDCl_3$)



25

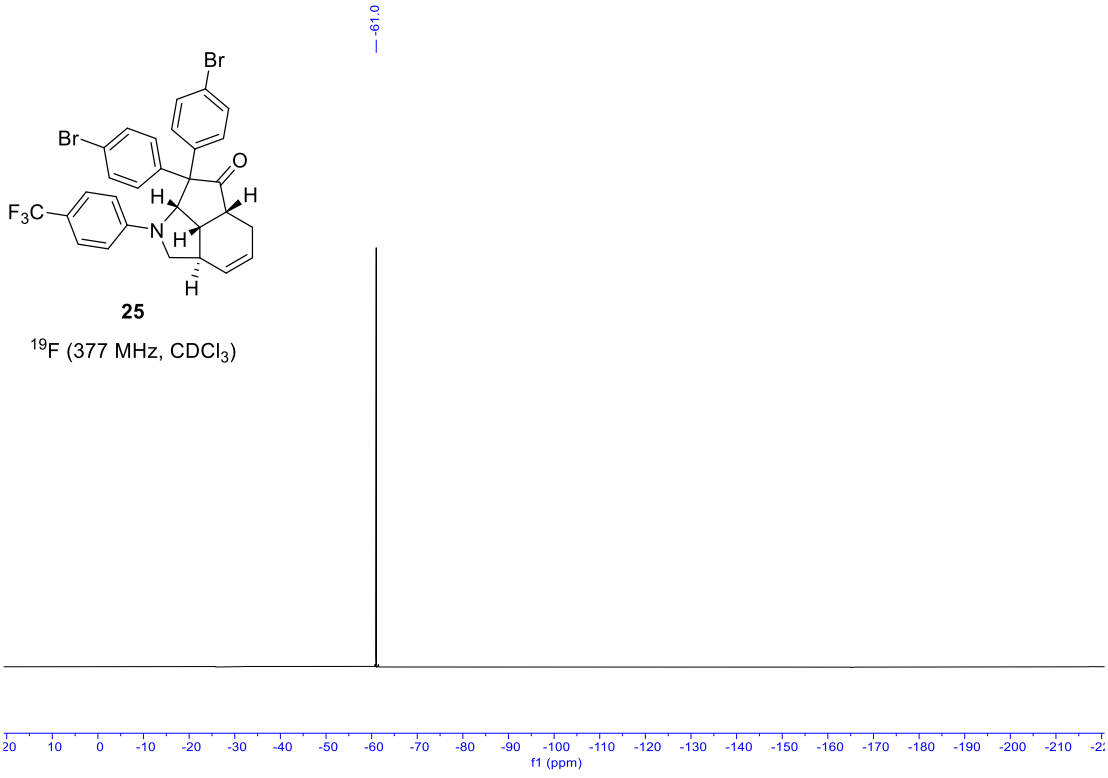
^{1}H (400 MHz, $CDCl_3$)





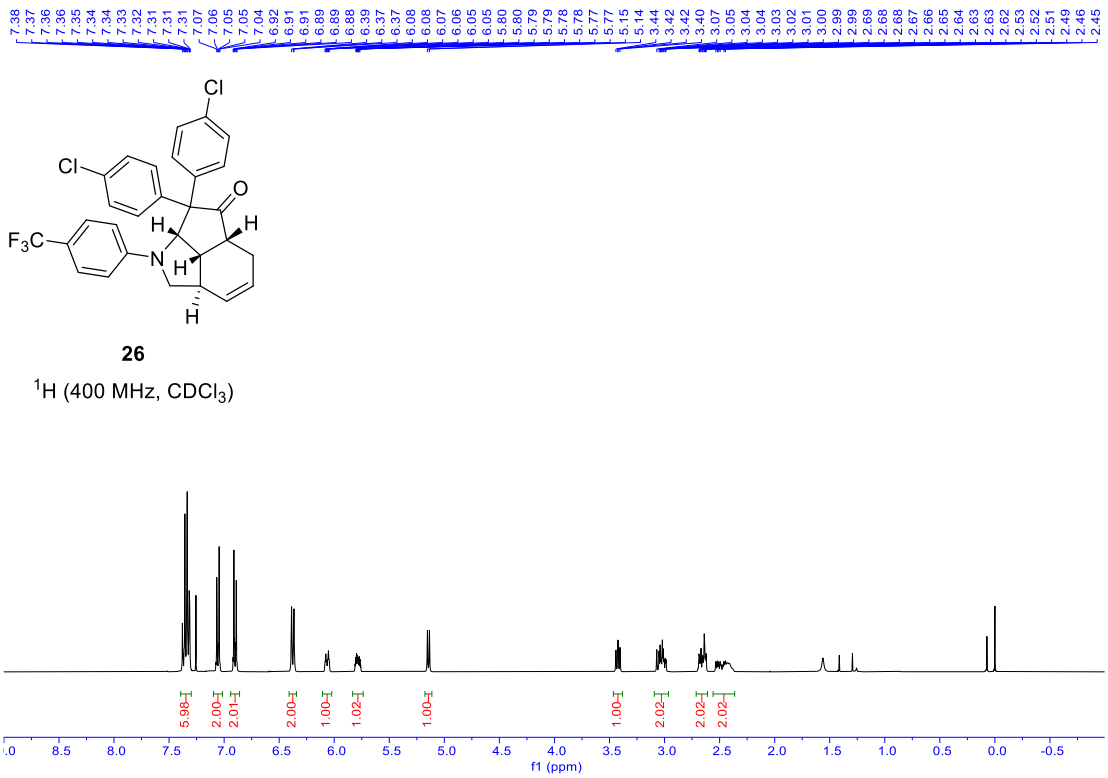
25

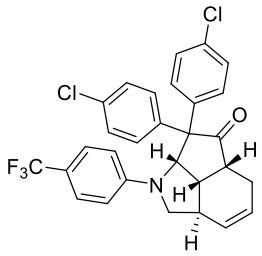
^{13}C (101MHz, $CDCl_3$)



25

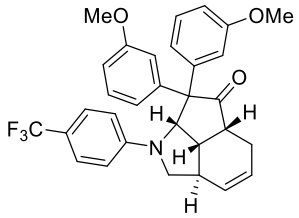
^{19}F (377 MHz, $CDCl_3$)


Cl
Cl
O
H
H
F3C
N
H
H
26
1H (400 MHz, CDCl3)
5.98
2.00
2.01
2.00
1.00
1.02
1.00
1.00
2.02
2.02
2.02
f1 (ppm)
215.5
150.1
140.0
138.2
133.9
132.9
131.8
129.4
129.2
128.1
127.7
126.2
125.9
123.5
118.6
112.3
68.6
66.7
52.0
46.7
42.8
39.7
22.6
Cl
Cl
O
H
H
H
F3C
N
H
26
13C (101 MHz, CDCl3)
f1 (ppm)



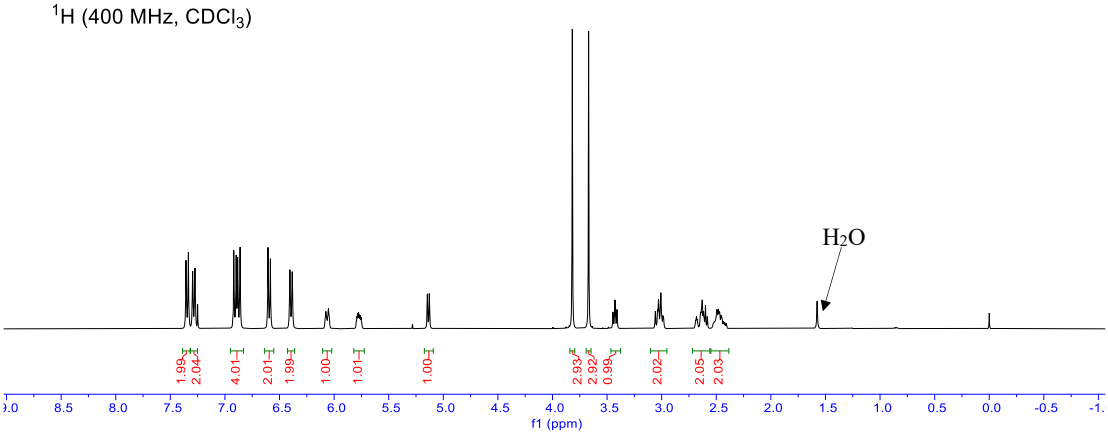
26

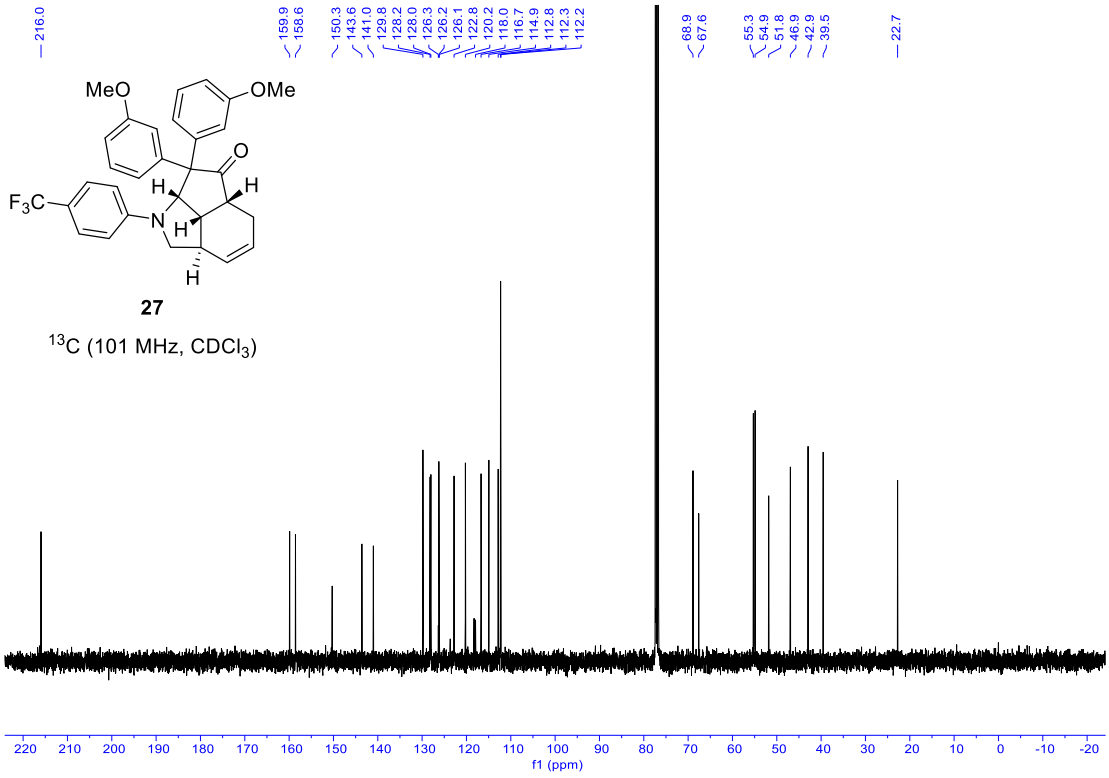
^{19}F (377 MHz, $CDCl_3$)



27

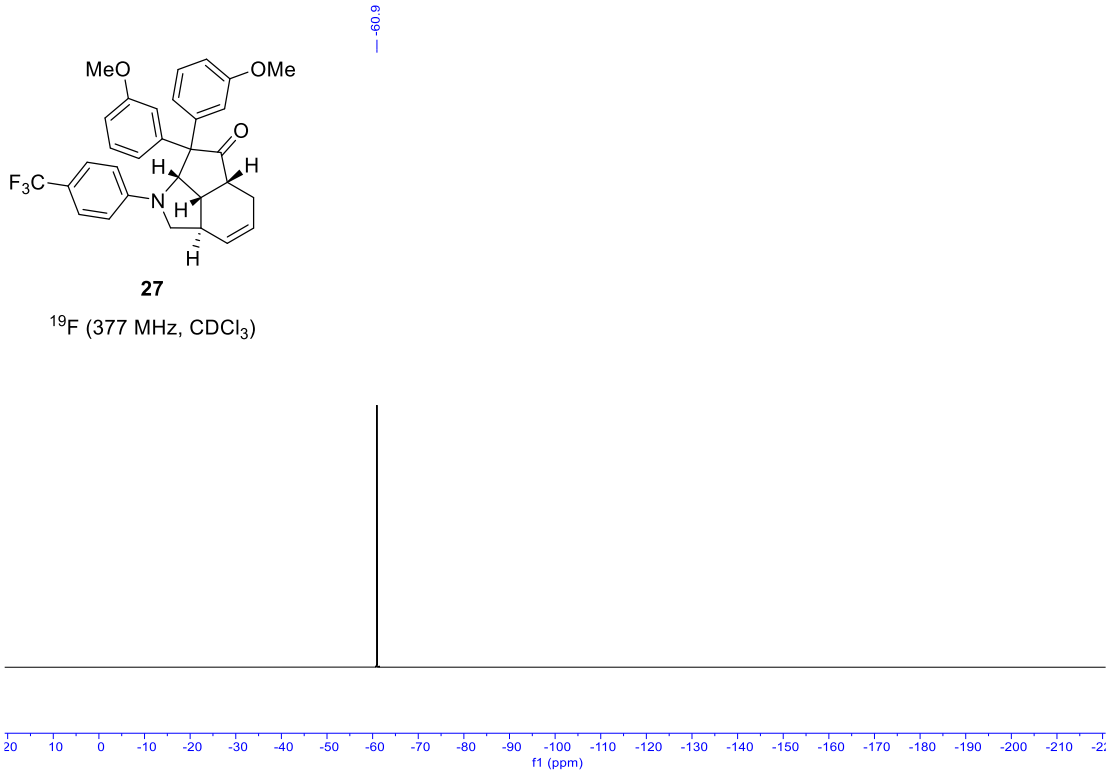
^{1}H (400 MHz, $CDCl_3$)





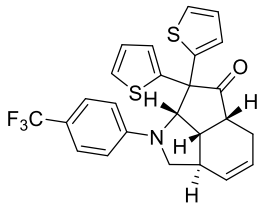
27

^{13}C (101 MHz, $CDCl_3$)



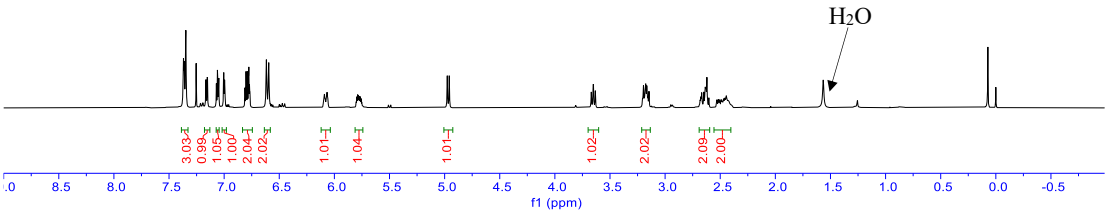
27

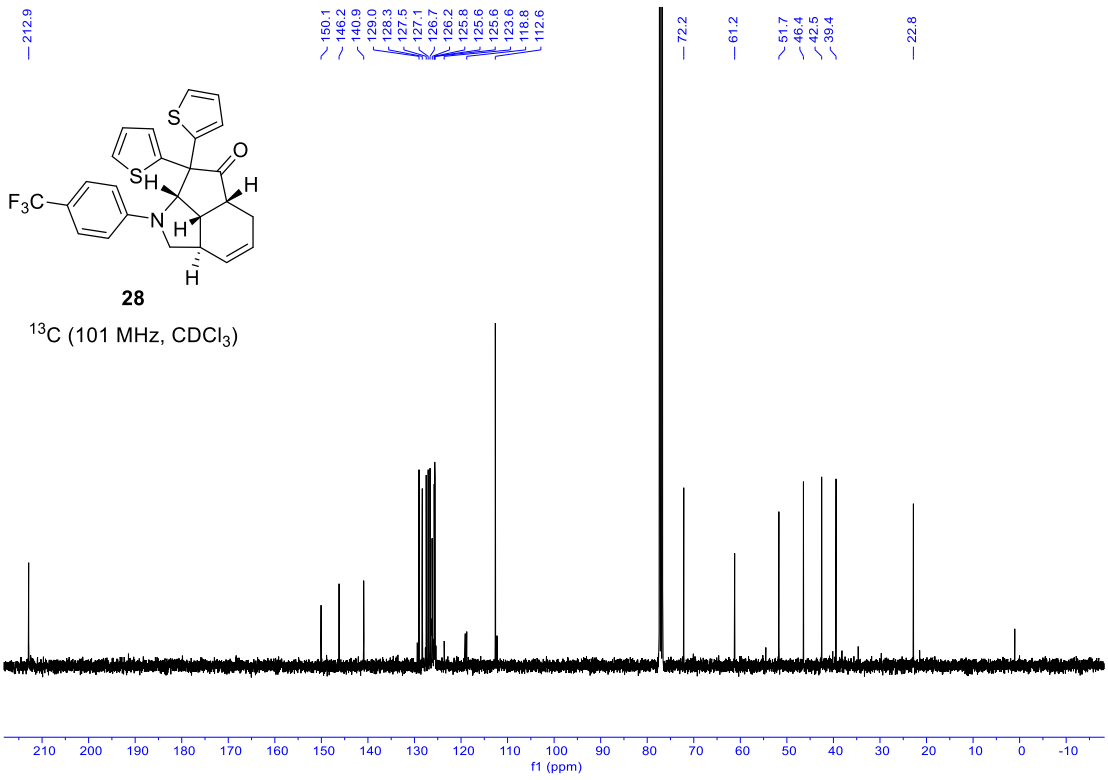
^{19}F (377 MHz, $CDCl_3$)



28

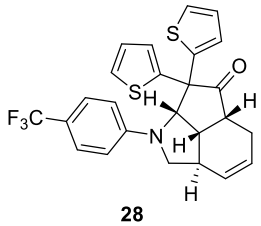
^{1}H (400 MHz, $CDCl_3$)





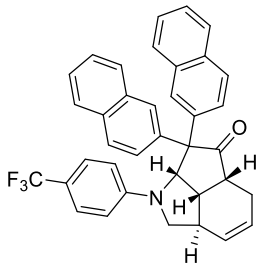
28

^{13}C (101 MHz, $CDCl_3$)



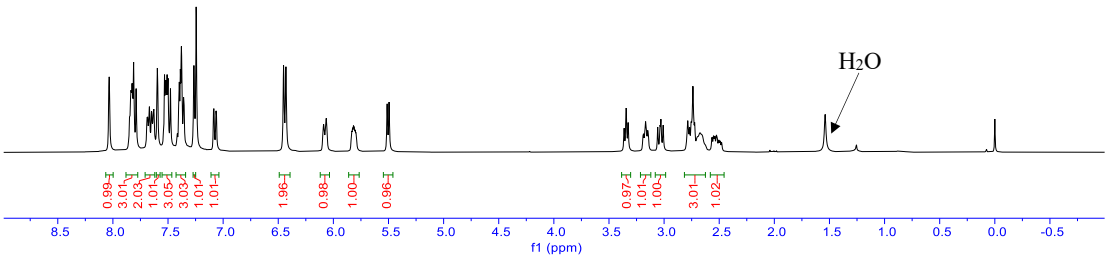
28

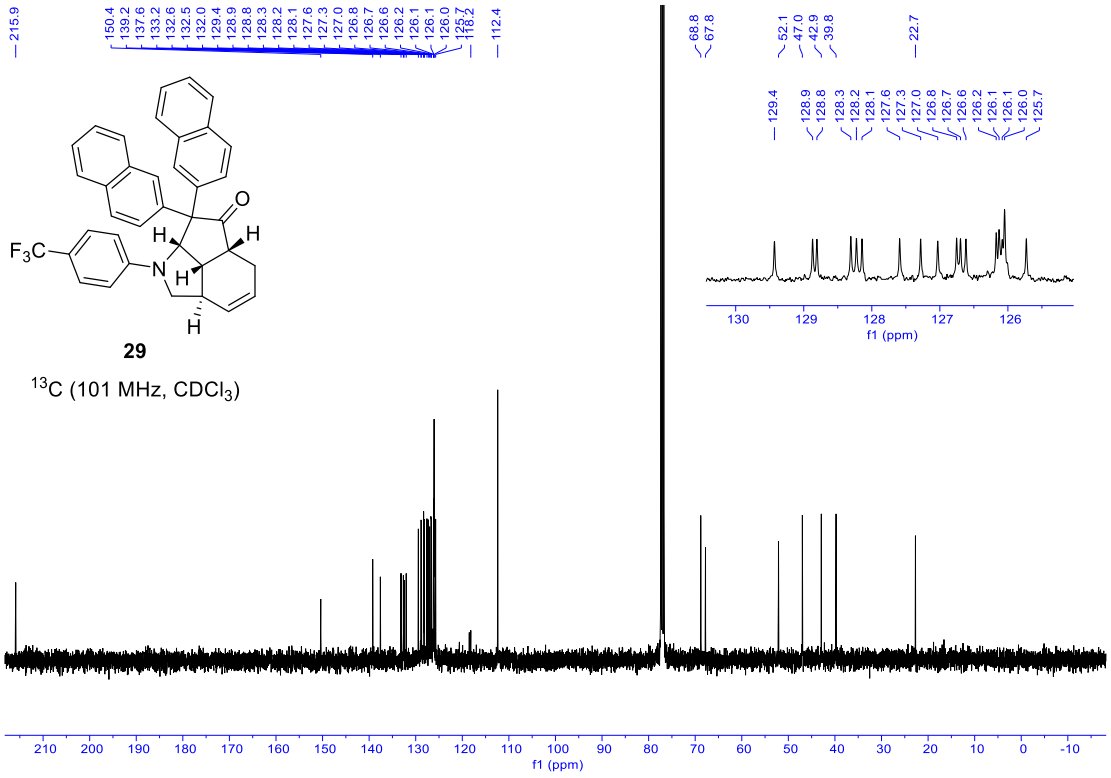
^{19}F (377 MHz, $CDCl_3$)



29

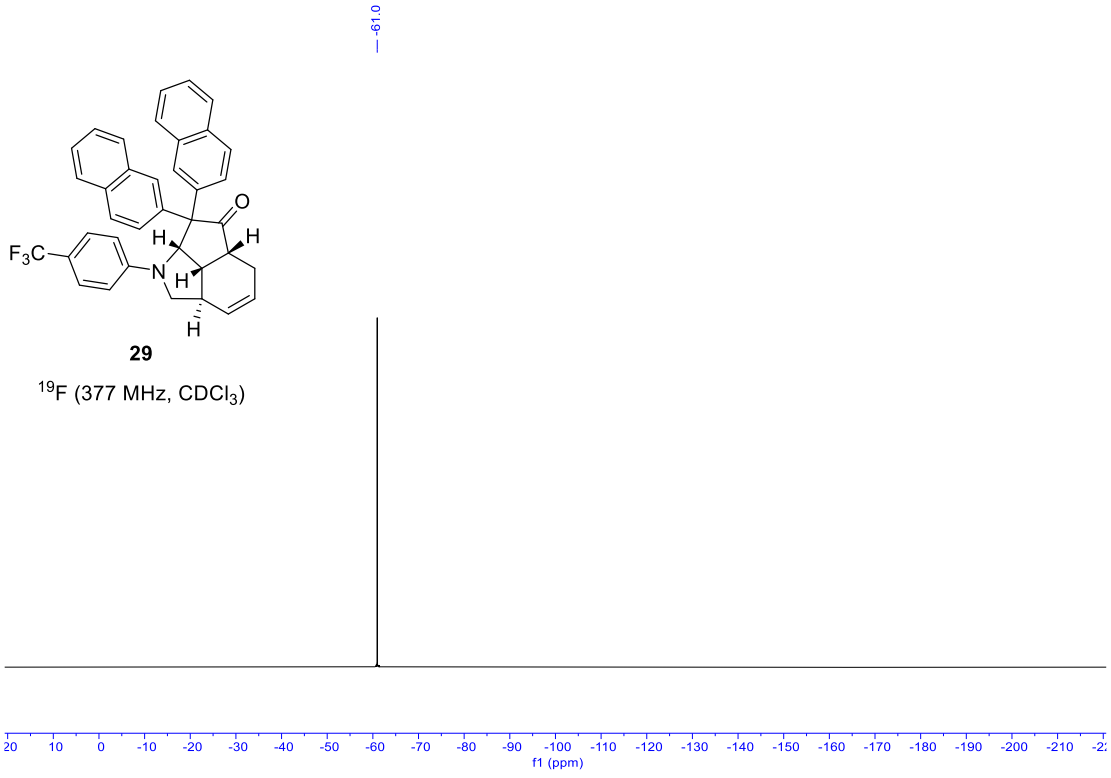
^{1}H (400 MHz, $CDCl_3$)





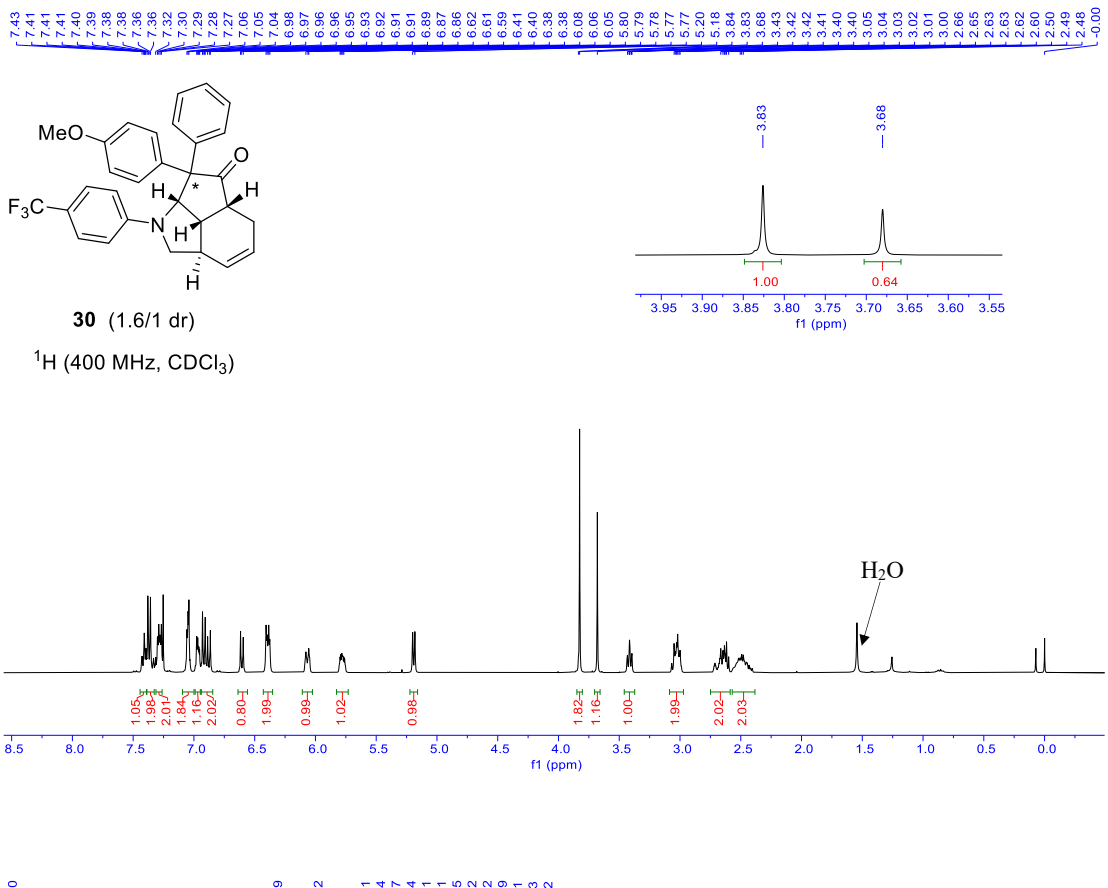
29

^{13}C (101 MHz, $CDCl_3$)



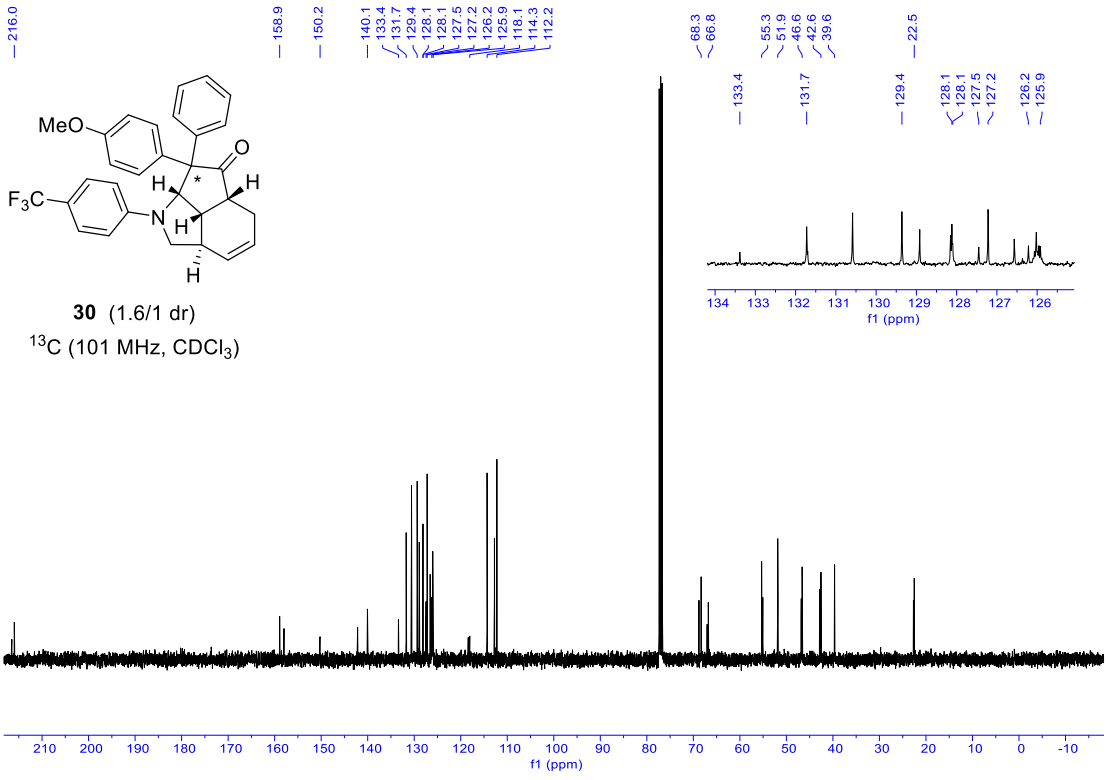
29

^{19}F (377 MHz, $CDCl_3$)



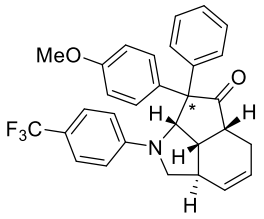
30 (1.6/1 dr)

^{1}H (400 MHz, $CDCl_3$)



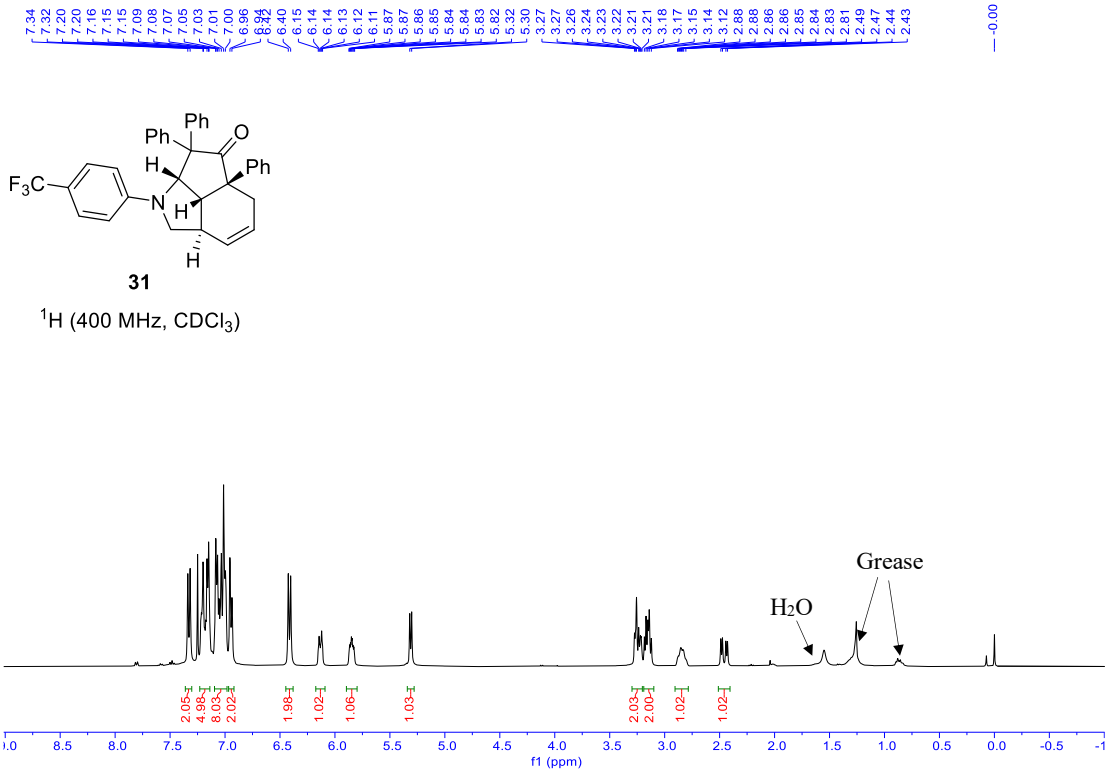
30 (1.6/1 dr)

^{13}C (101 MHz, $CDCl_3$)



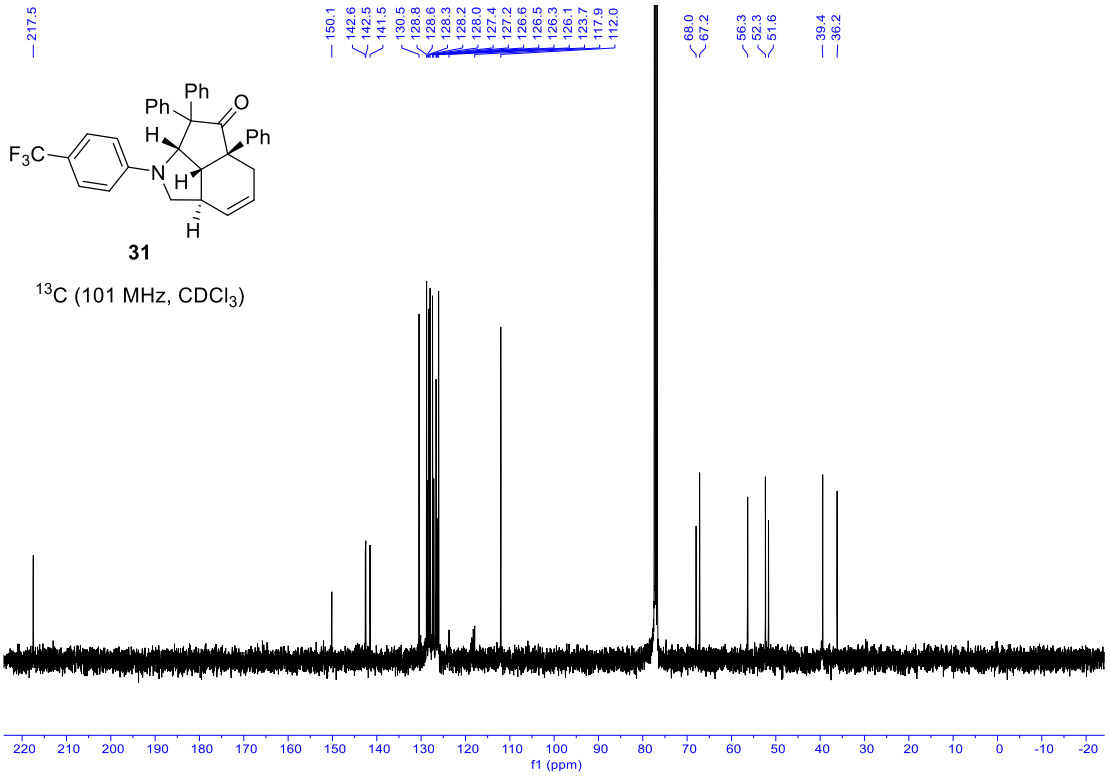
30 (1.6/1 dr)

^{19}F (377 MHz, $CDCl_3$)



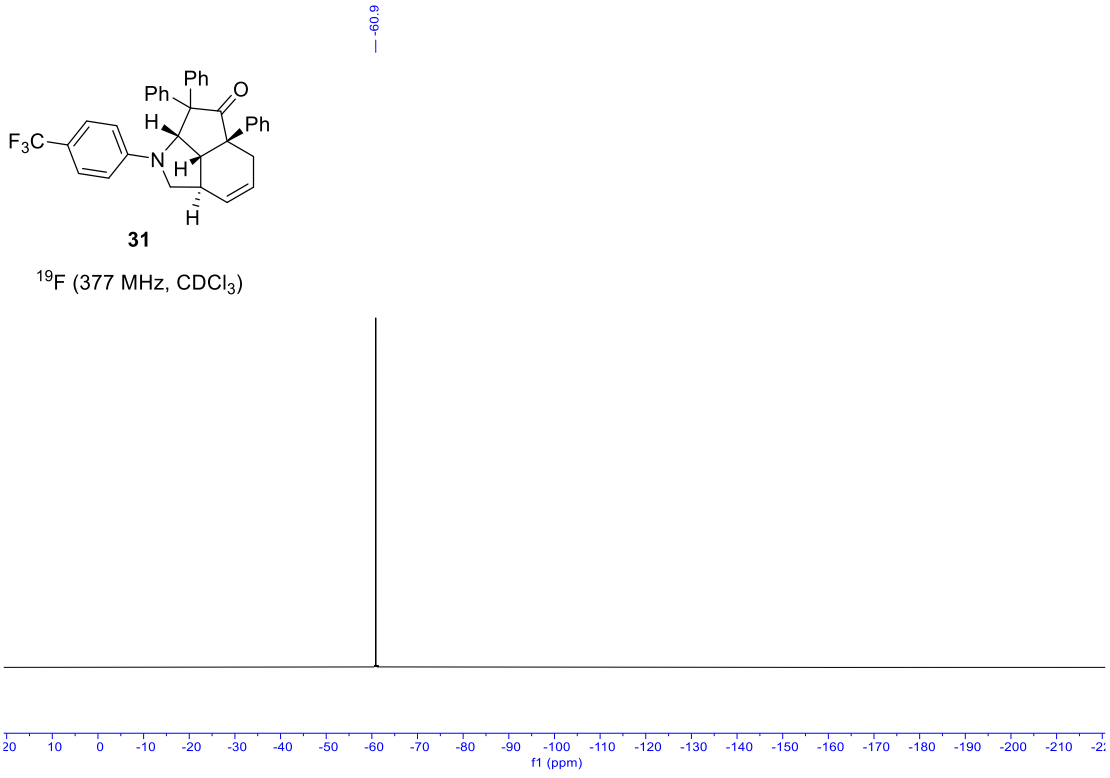
31

^{1}H (400 MHz, $CDCl_3$)



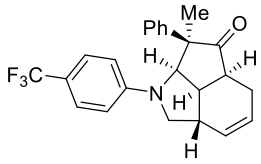
31

^{13}C (101 MHz, $CDCl_3$)



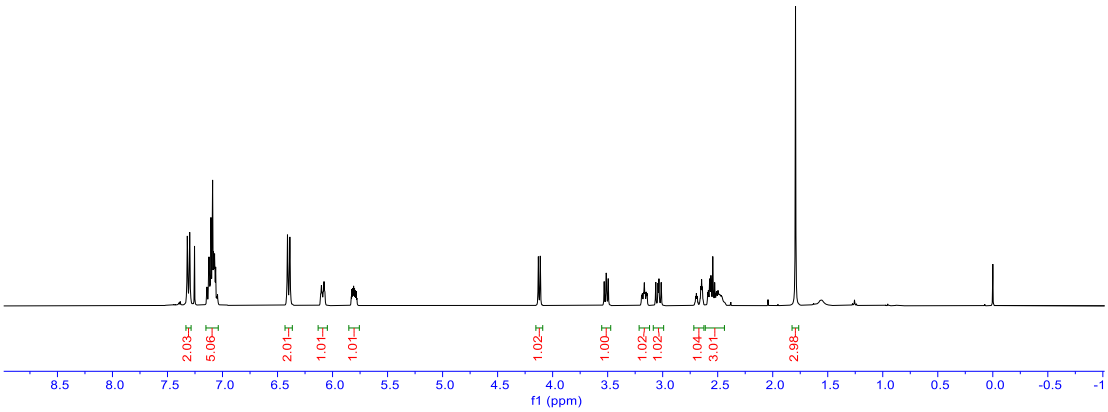
31

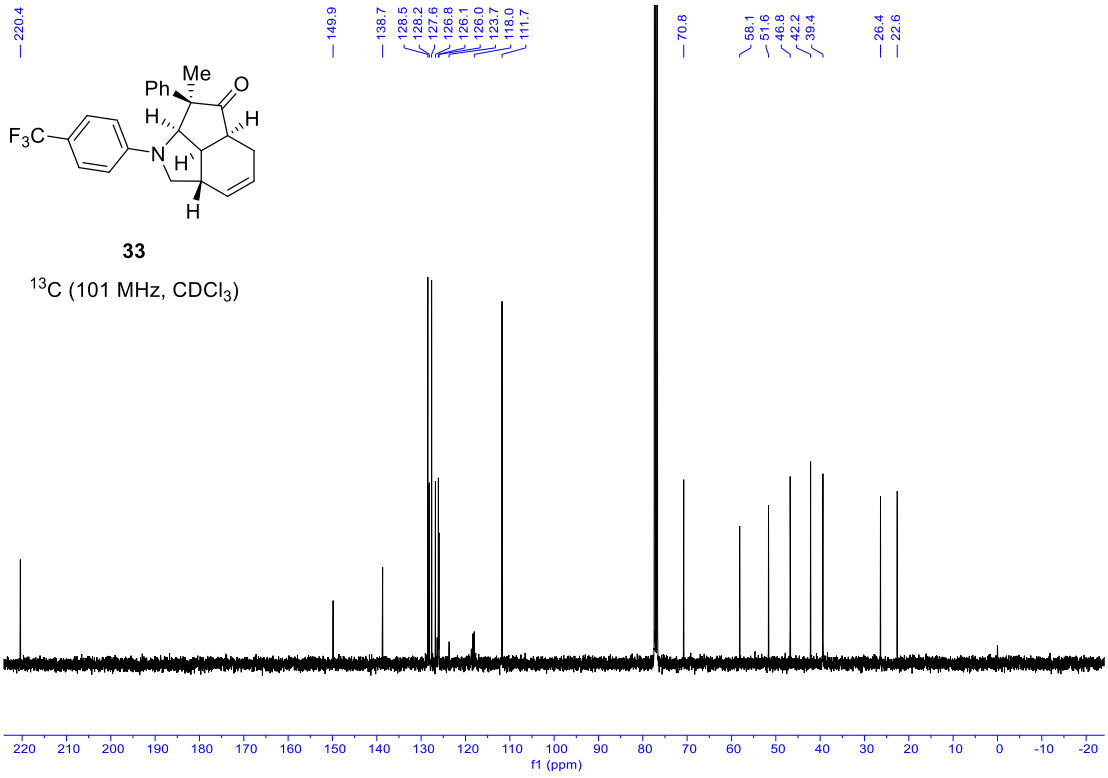
^{19}F (377 MHz, $CDCl_3$)



33

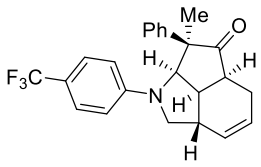
^{1}H (400 MHz, $CDCl_3$)





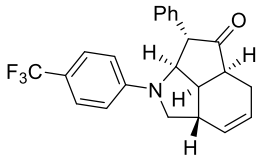
33

^{13}C (101 MHz, $CDCl_3$)



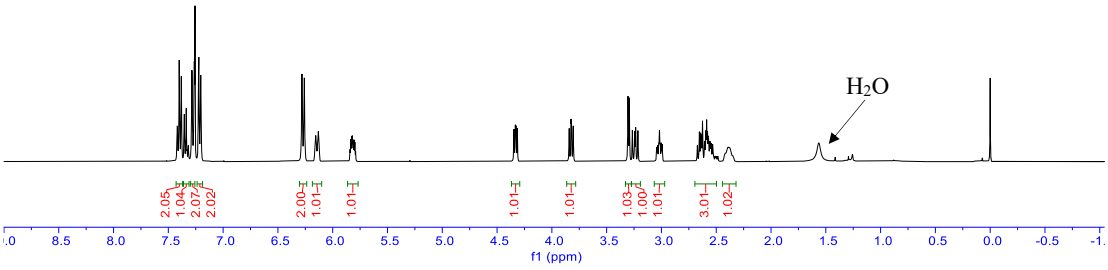
33

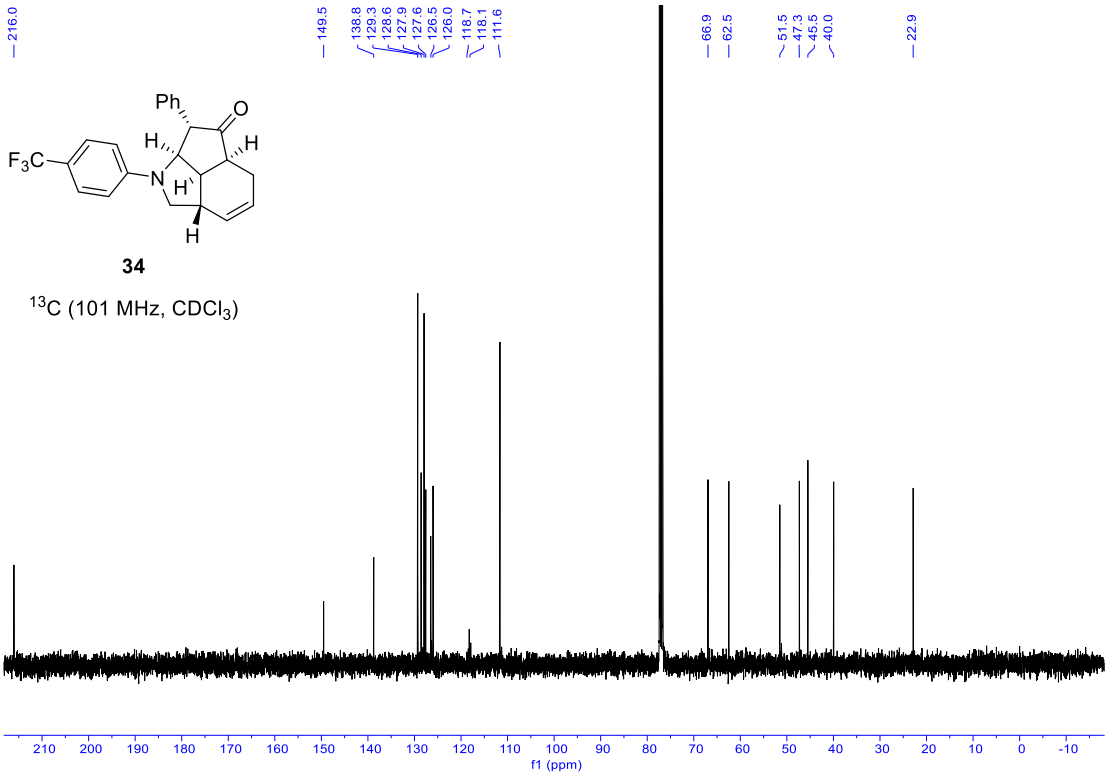
^{19}F (377 MHz, $CDCl_3$)



34

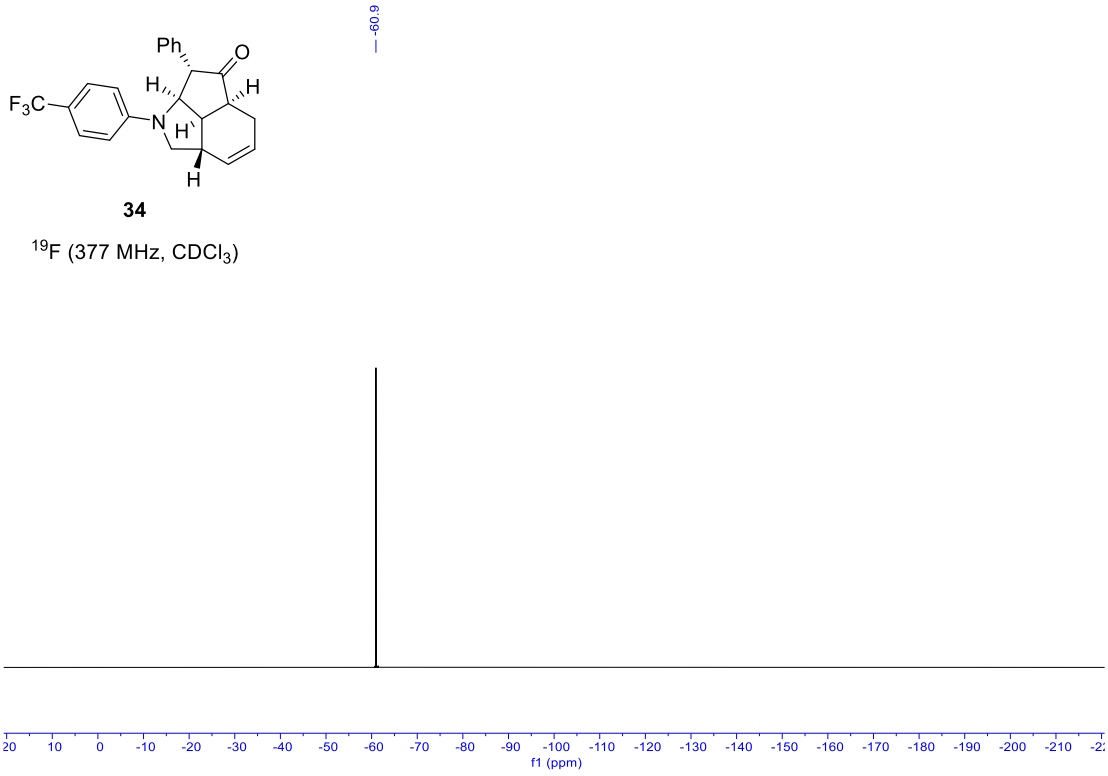
^{1}H (400 MHz, $CDCl_3$)





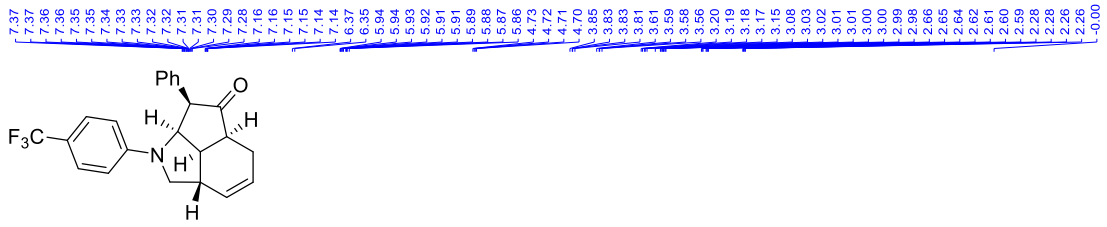
34

^{13}C (101 MHz, $CDCl_3$)



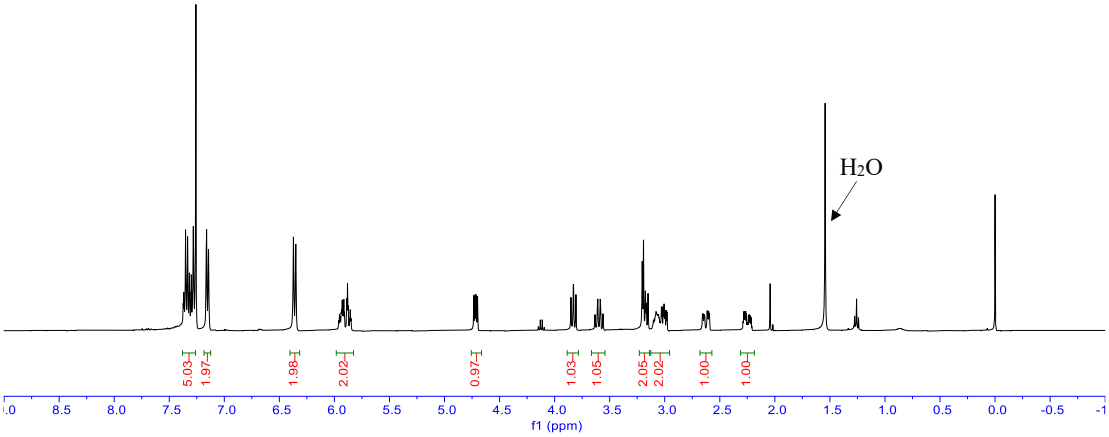
34

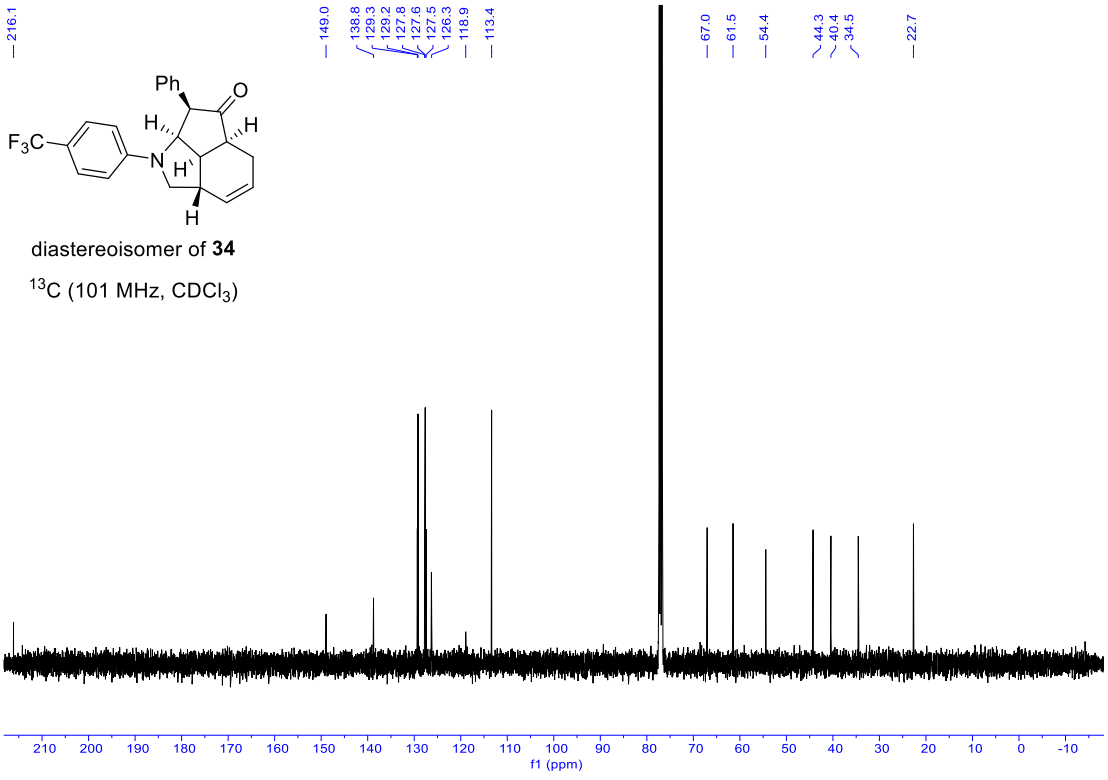
^{19}F (377 MHz, $CDCl_3$)



diastereoisomer of **34**

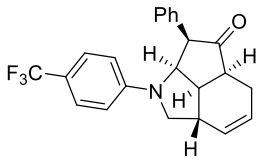
^{1}H (400 MHz, $CDCl_3$)





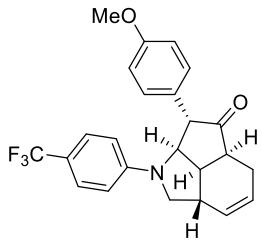
diastereoisomer of **34**

^{13}C (101 MHz, $CDCl_3$)



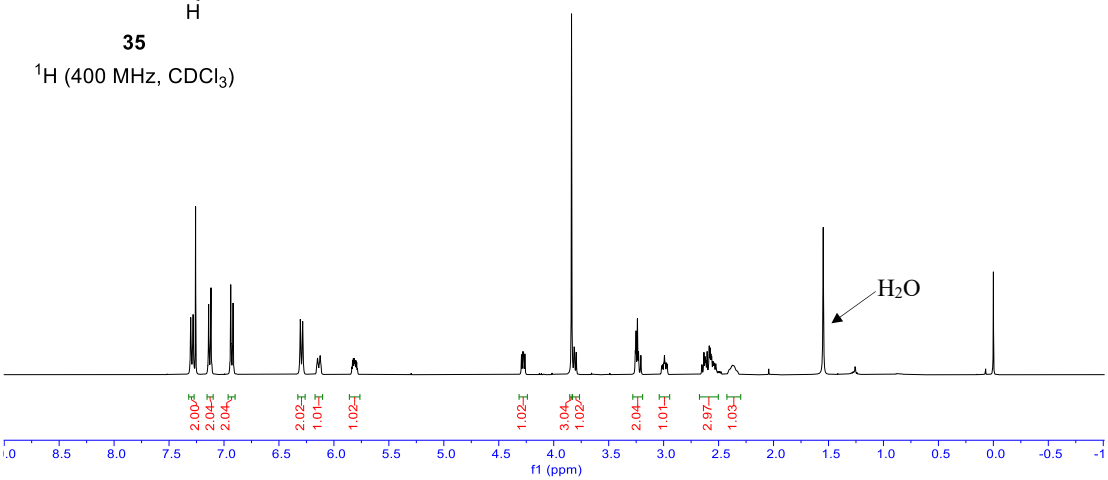
diastereoisomer of **34**

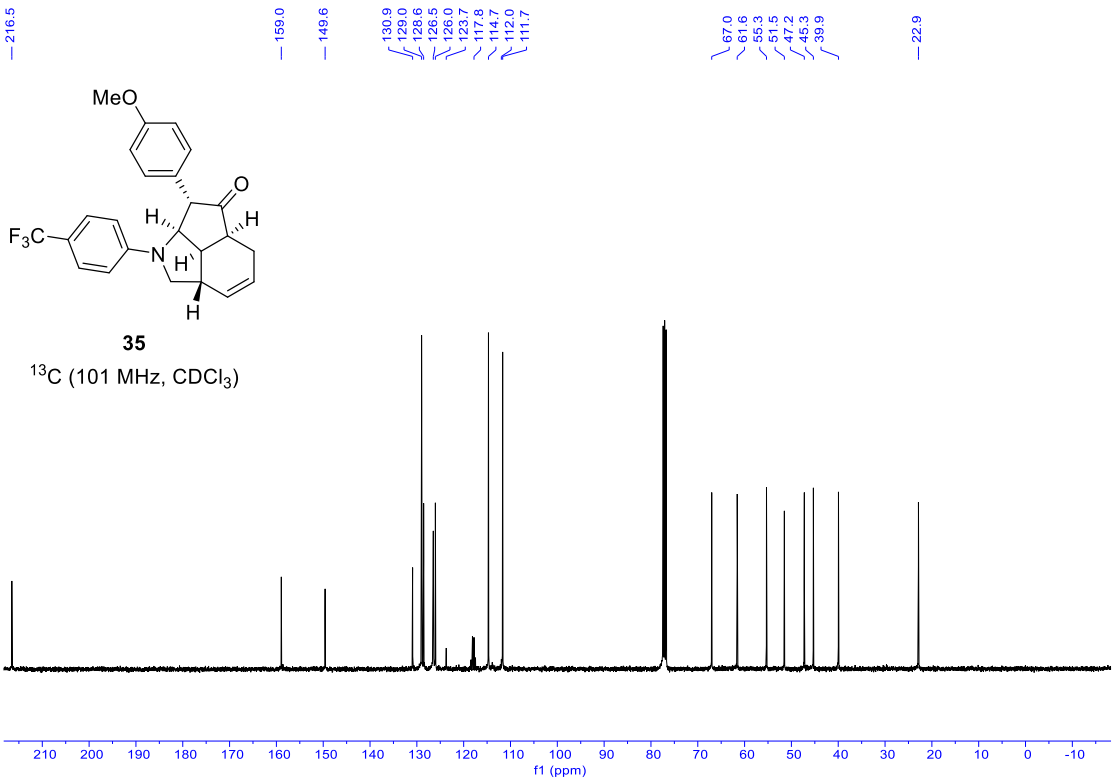
^{19}F (377 MHz, $CDCl_3$)



35

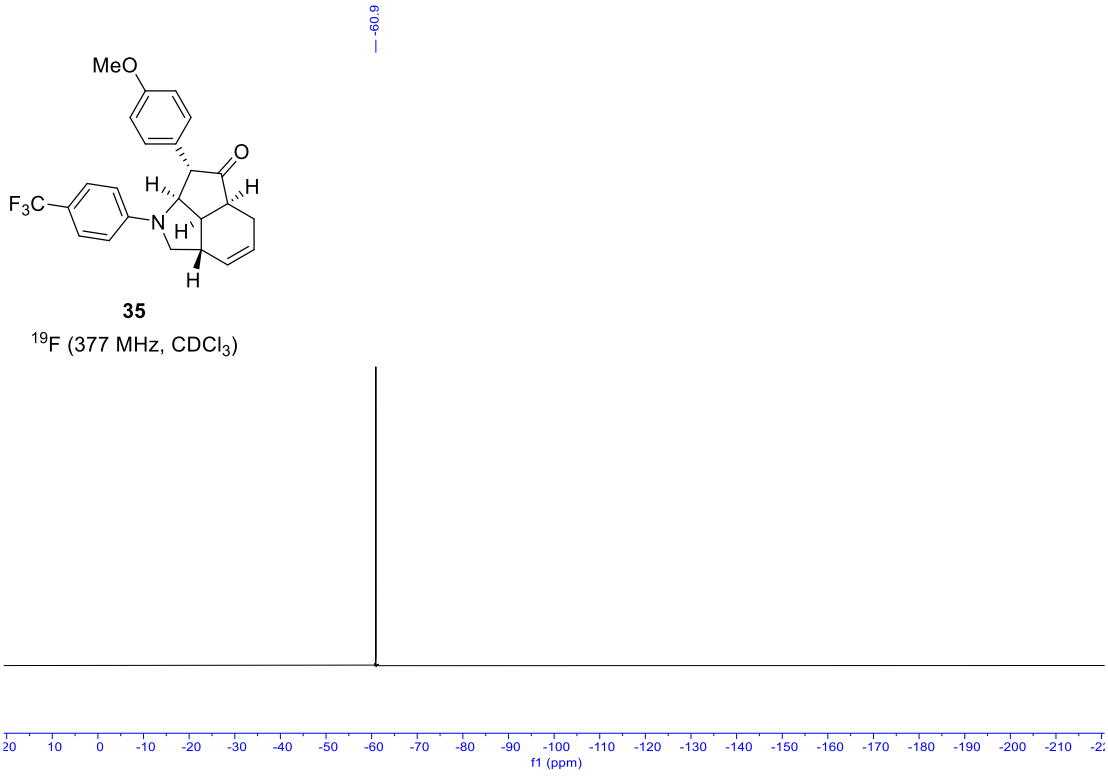
^{1}H (400 MHz, $CDCl_3$)





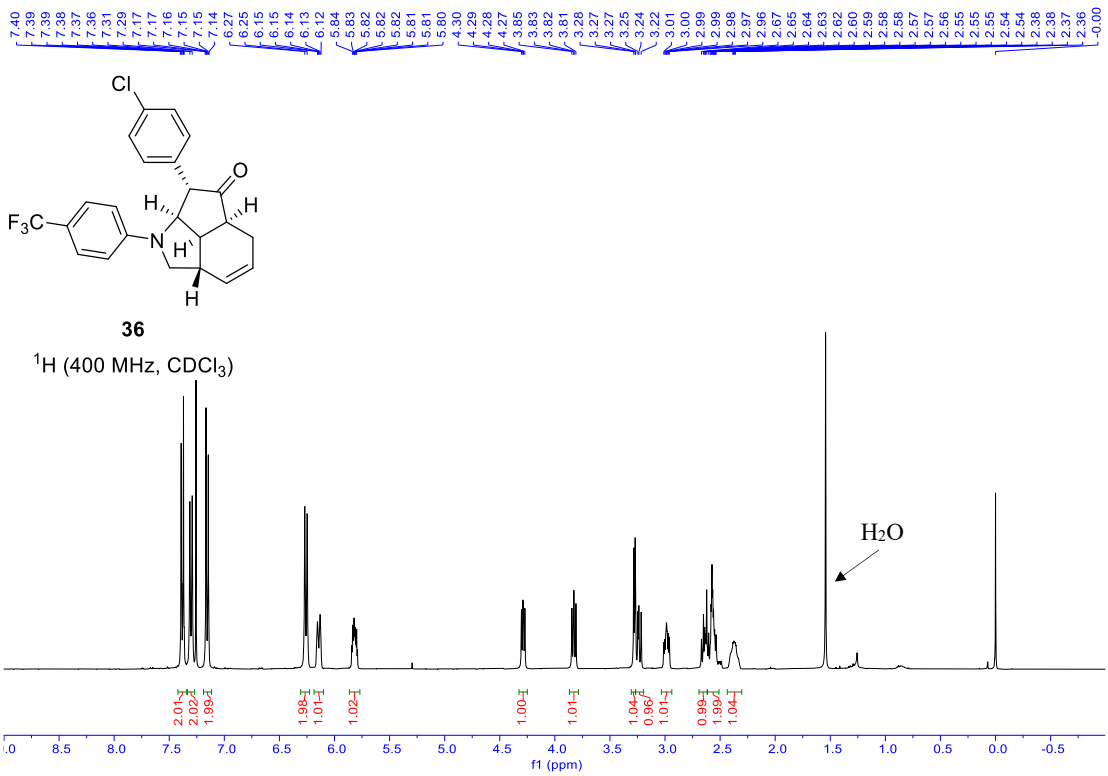
35

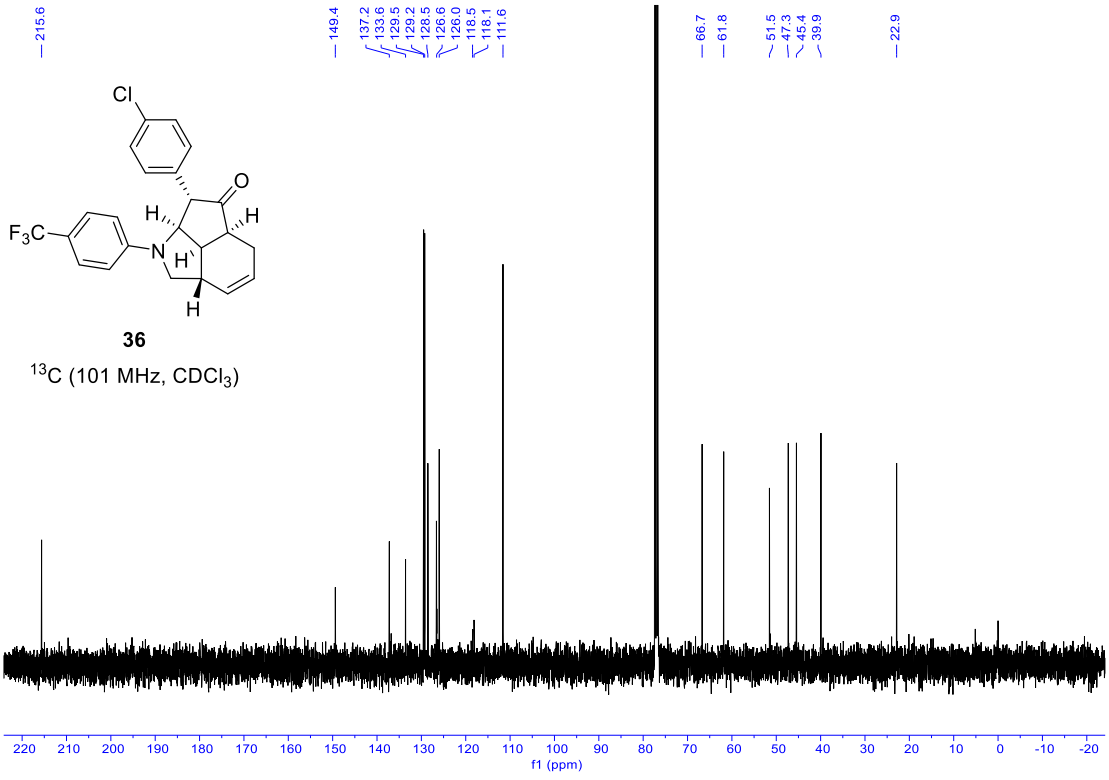
^{13}C (101 MHz, $CDCl_3$)

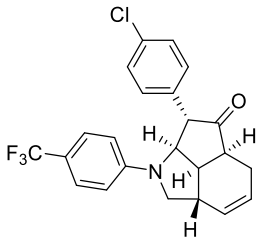


35

^{19}F (377 MHz, $CDCl_3$)

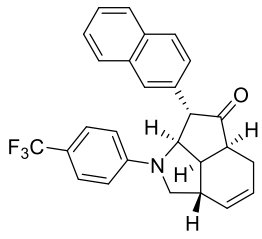

Cl
O
H
H
F3C
N
H
H
36
1H (400 MHz, CDCl3)
H2O
f1 (ppm)


Cl
O
H
H
F3C
N
H
H
36
13C (101 MHz, CDCl3)
f1 (ppm)



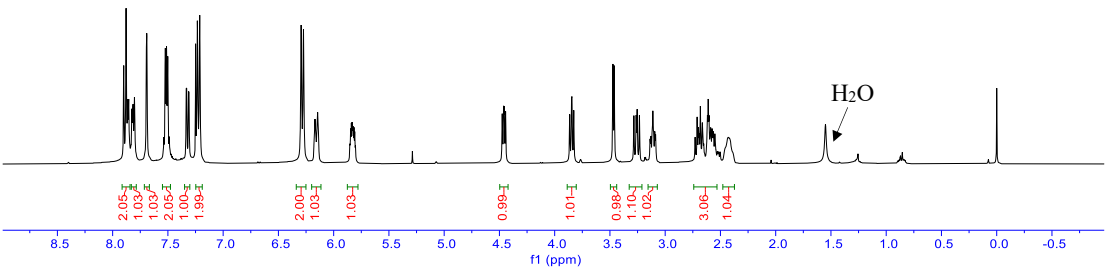
36

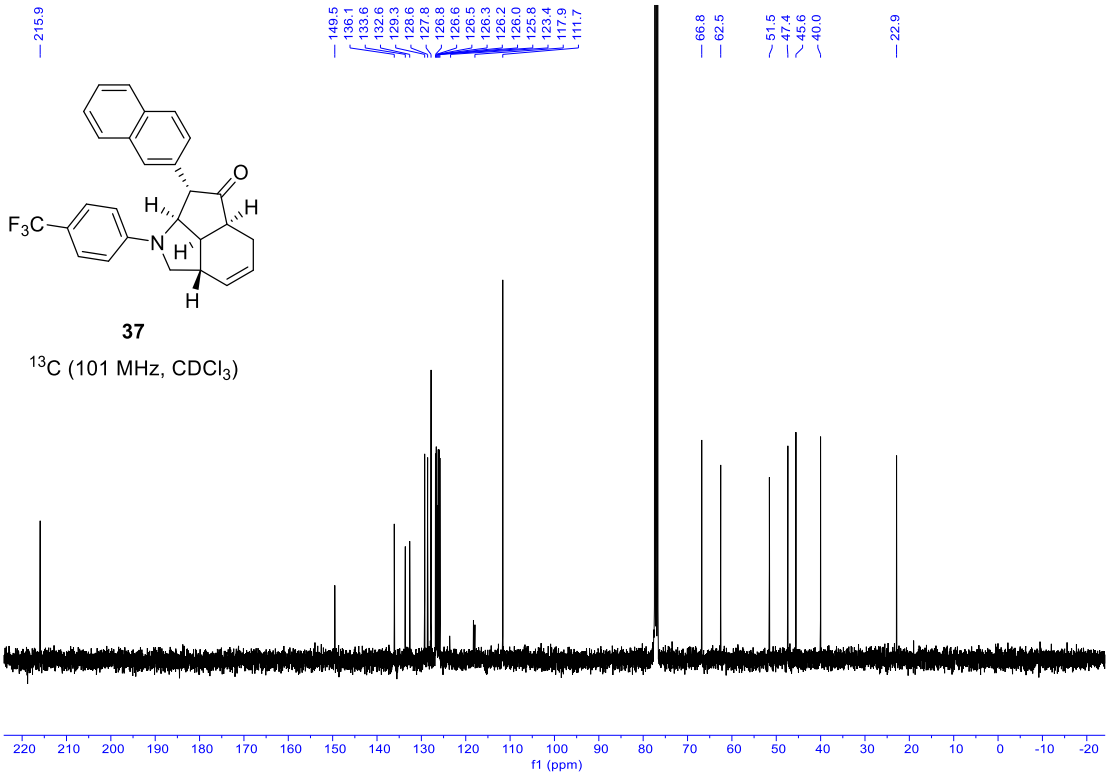
^{19}F (377 MHz, $CDCl_3$)



37

^{1}H (400 MHz, $CDCl_3$)



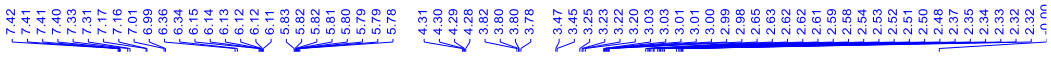


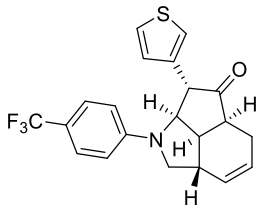
37

^{13}C (101 MHz, $CDCl_3$)

37

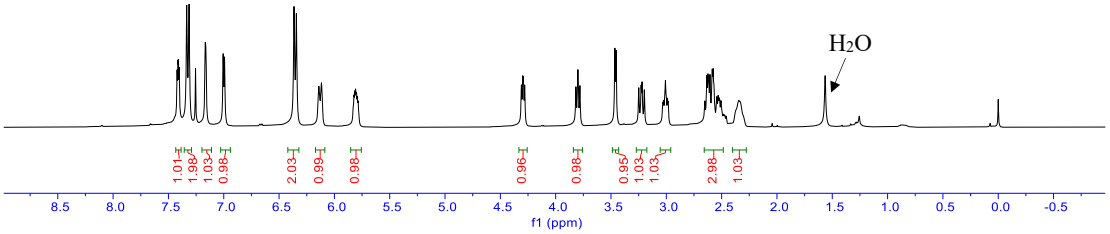
^{19}F (377 MHz, $CDCl_3$)

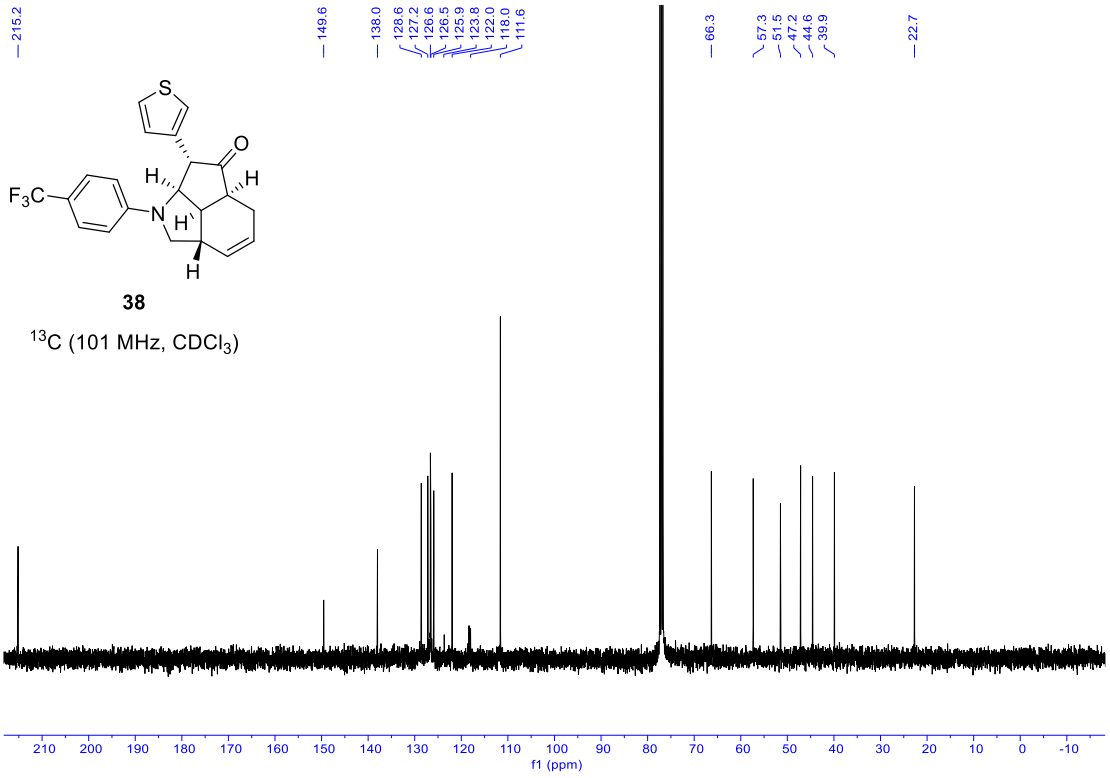




38

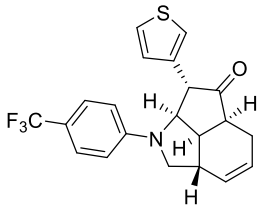
^{1}H (400 MHz, $CDCl_3$)





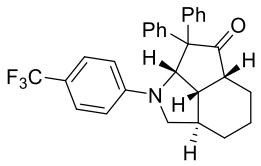
38

^{13}C (101 MHz, $CDCl_3$)



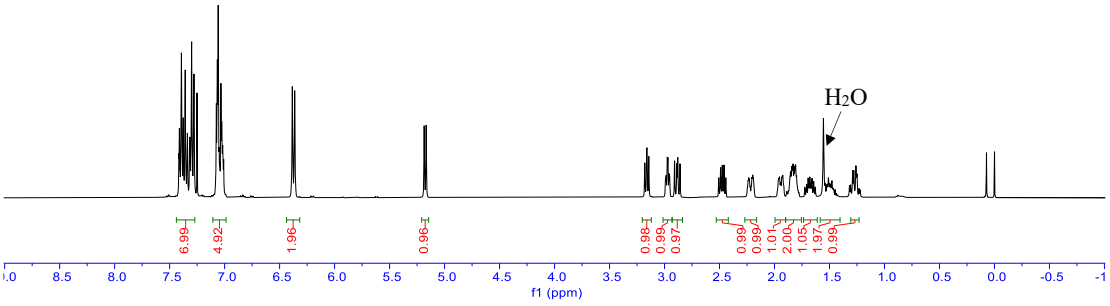
38

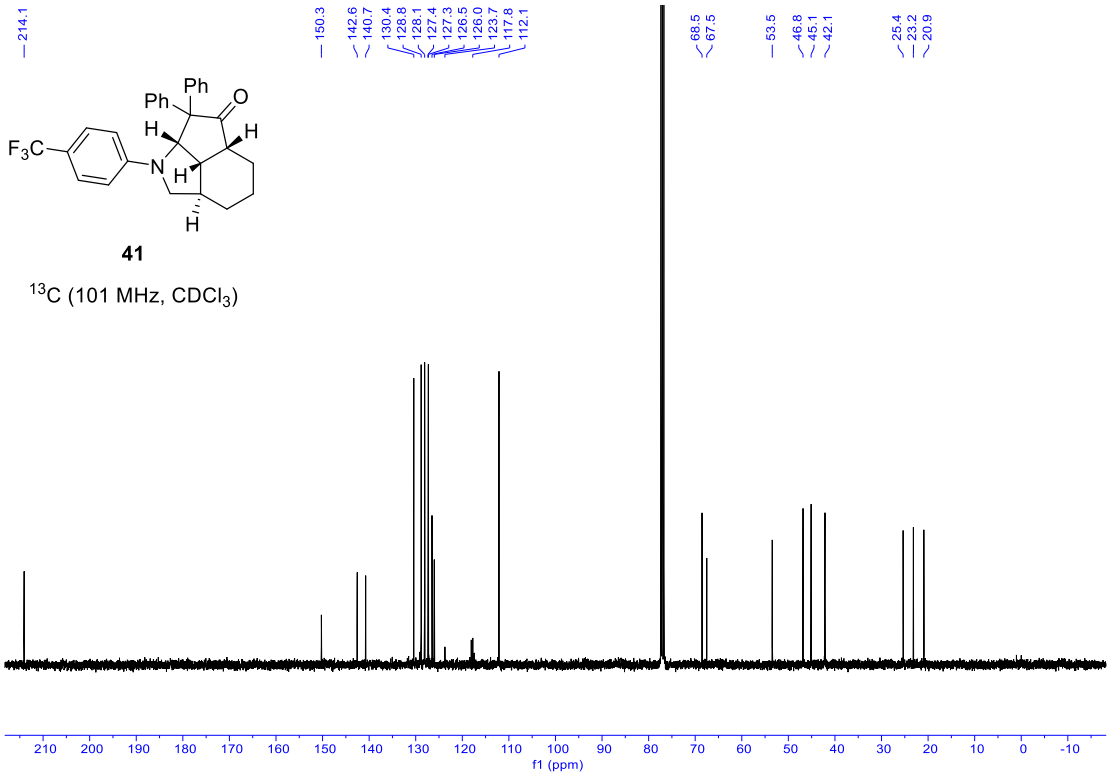
^{19}F (377 MHz, $CDCl_3$)



41

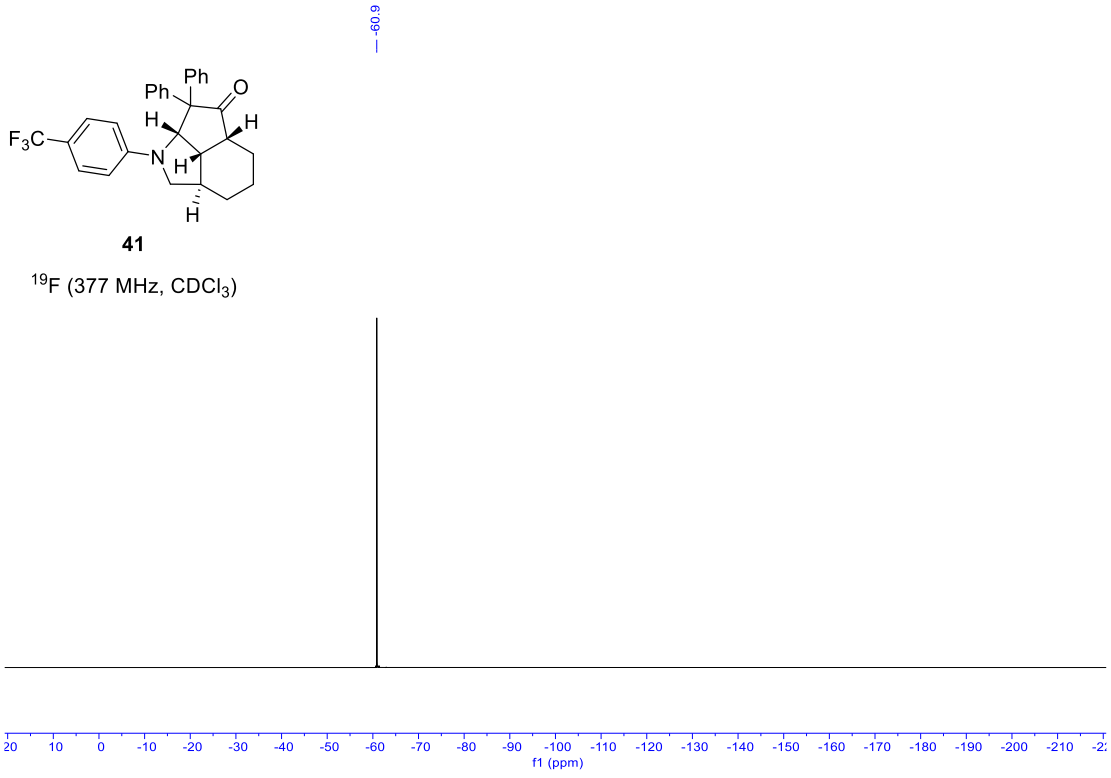
^{1}H (400 MHz, $CDCl_3$)





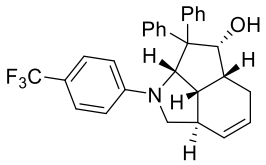
41

^{13}C (101 MHz, $CDCl_3$)



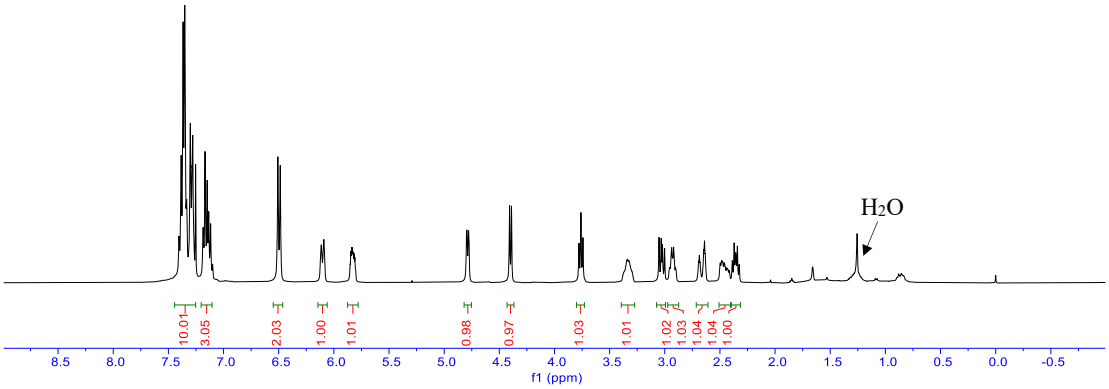
41

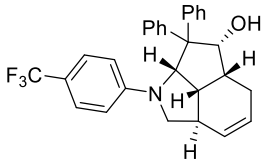
^{19}F (377 MHz, $CDCl_3$)



42

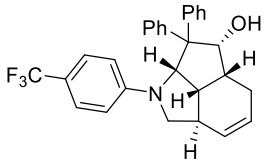
^{1}H (400 MHz, $CDCl_3$)





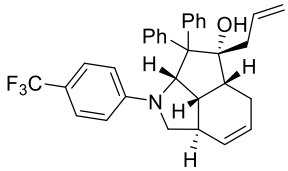
42

^{13}C (101 MHz, $CDCl_3$)



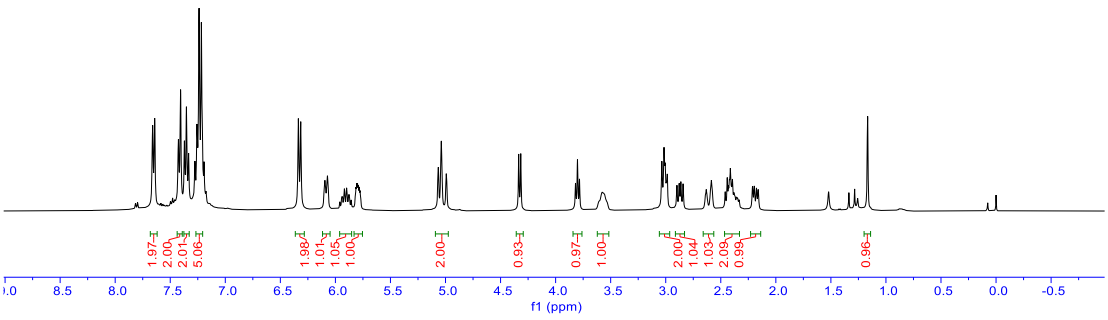
42

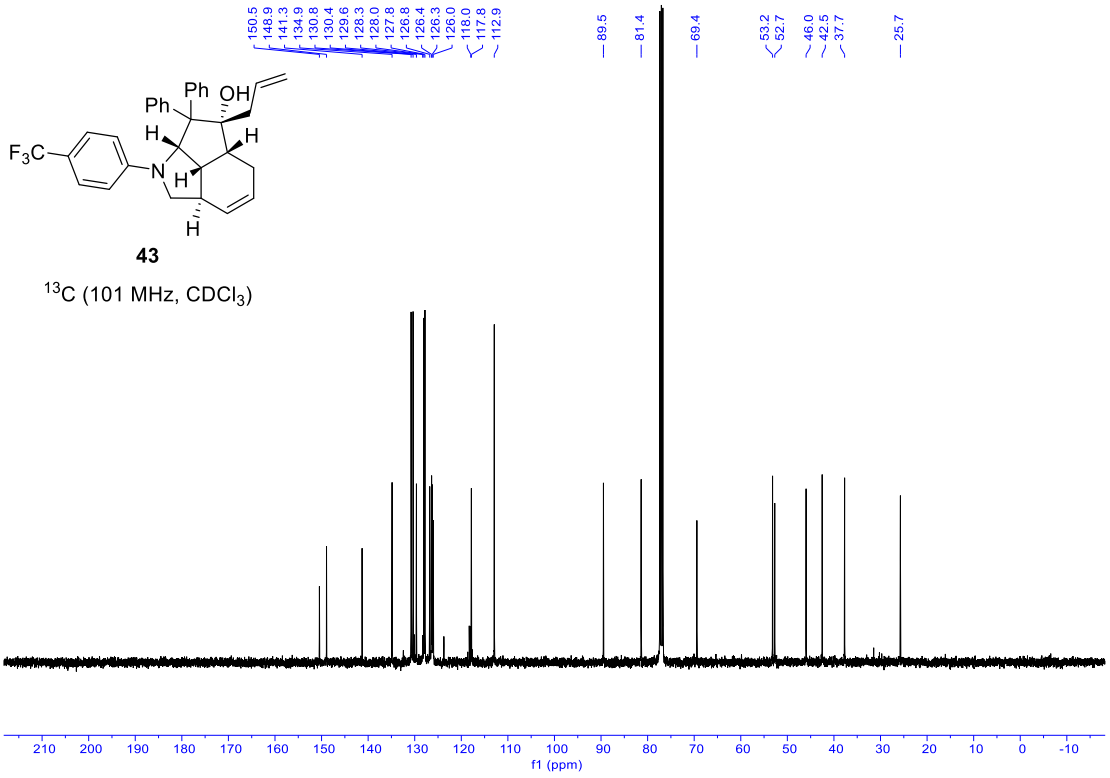
^{19}F (377 MHz, $CDCl_3$)



43

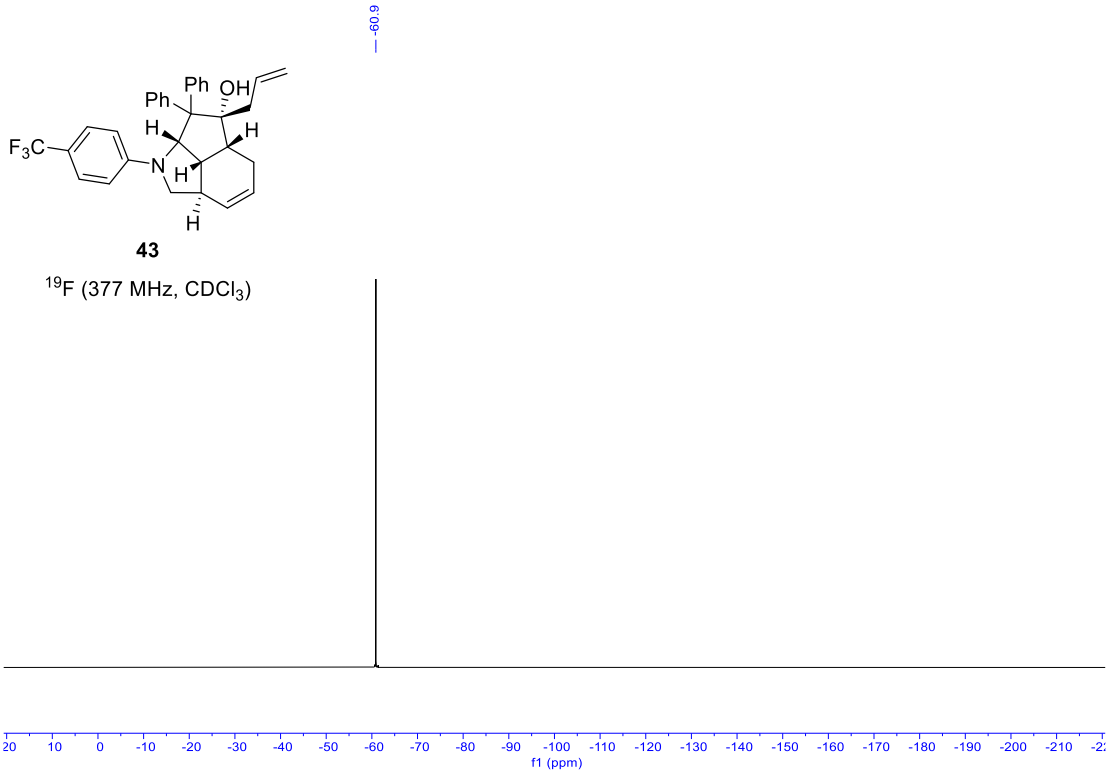
^{1}H (400 MHz, $CDCl_3$)





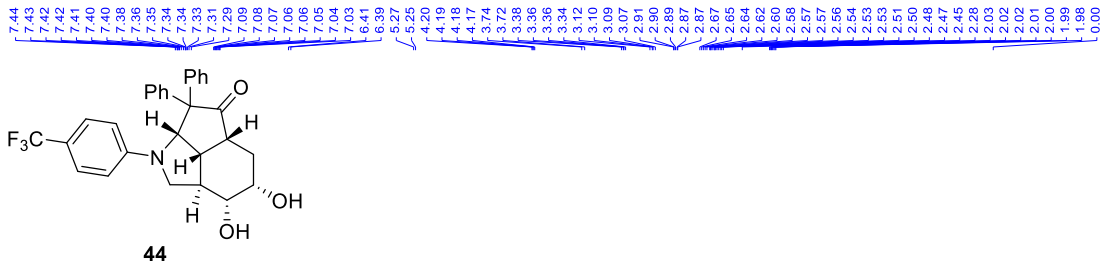
43

^{13}C (101 MHz, $CDCl_3$)



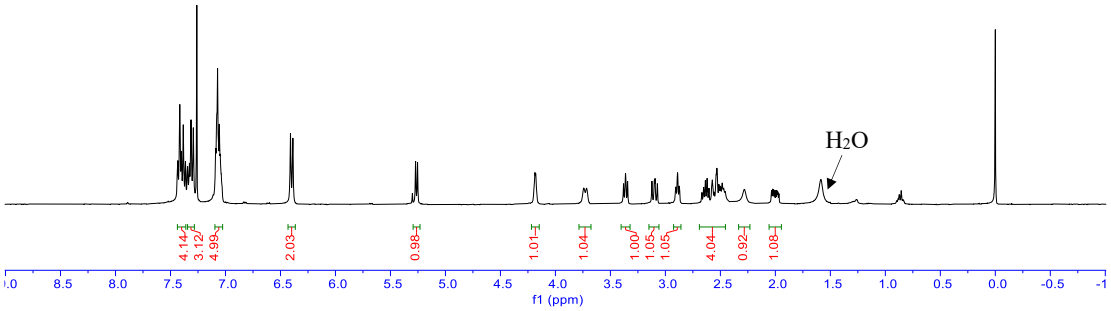
43

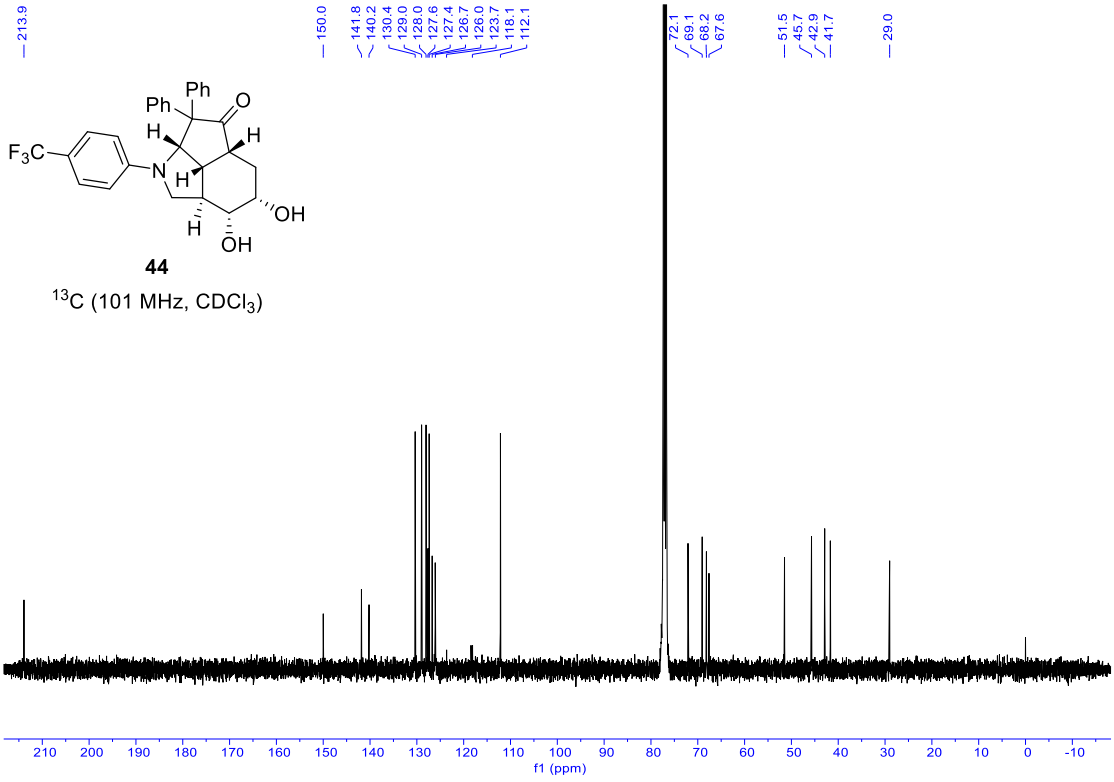
^{19}F (377 MHz, $CDCl_3$)



44

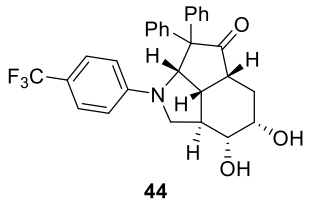
^{1}H (400 MHz, $CDCl_3$)





44

^{13}C (101 MHz, $CDCl_3$)



44

^{19}F (377 MHz, $CDCl_3$)

11. NOESY spectras

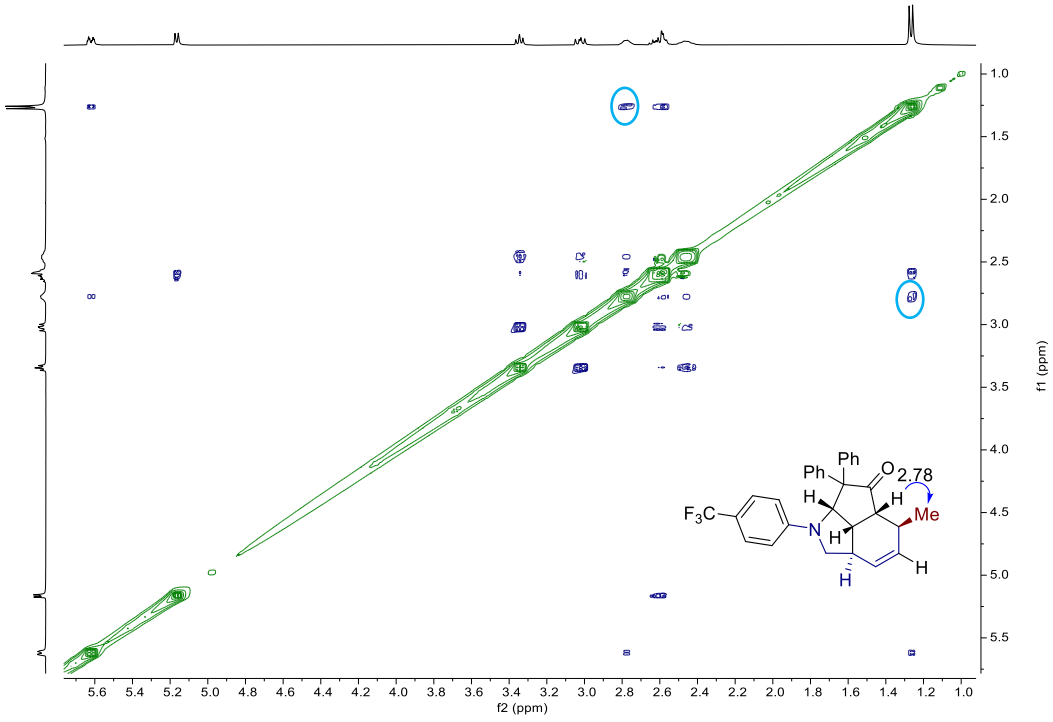


Figure S1. NOESY spectra of **4**

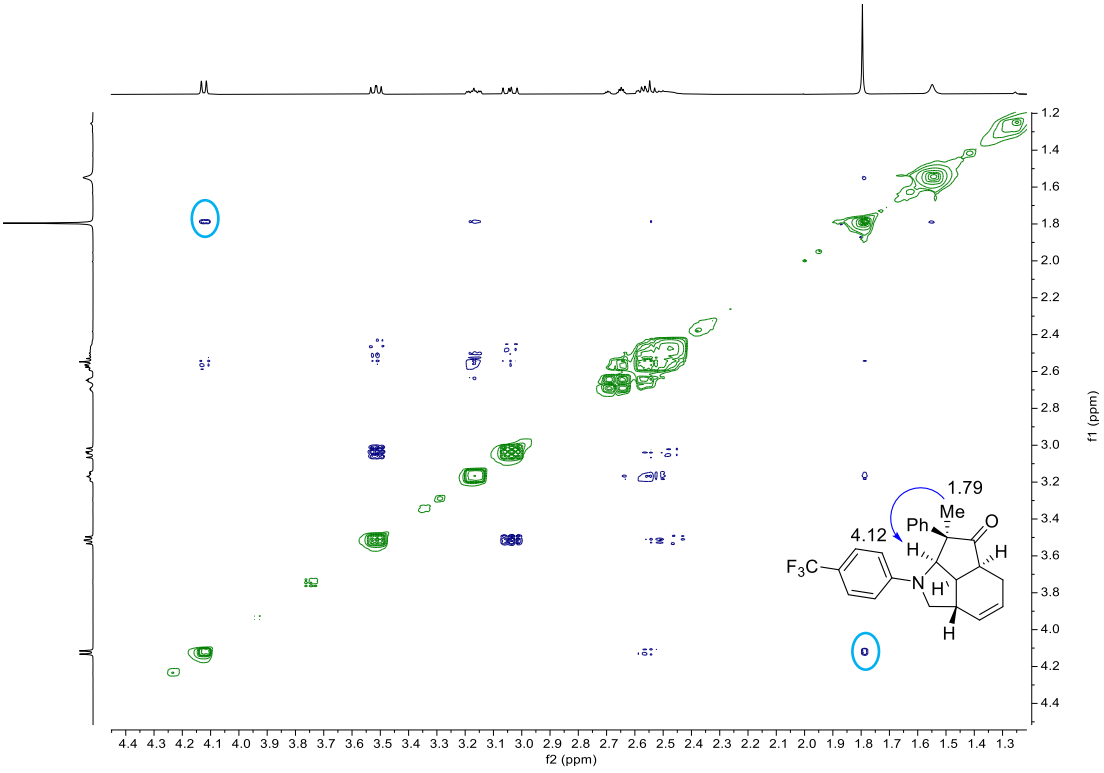


Figure S2. NOESY spectra of **33**

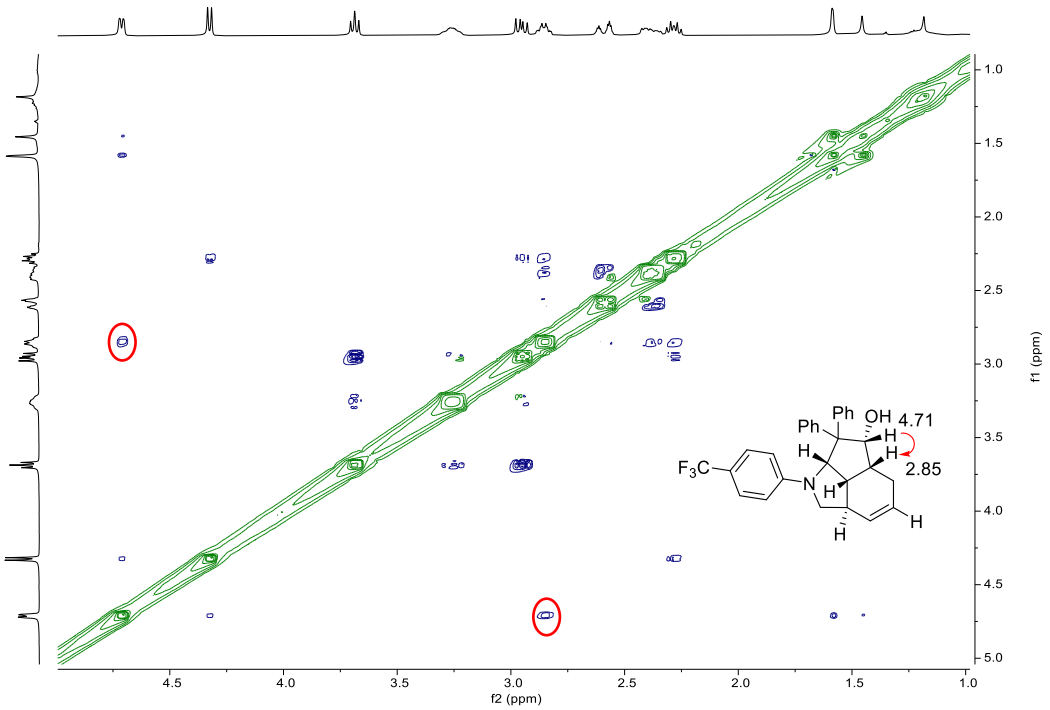


Figure S3. NOESY spectra of **42**

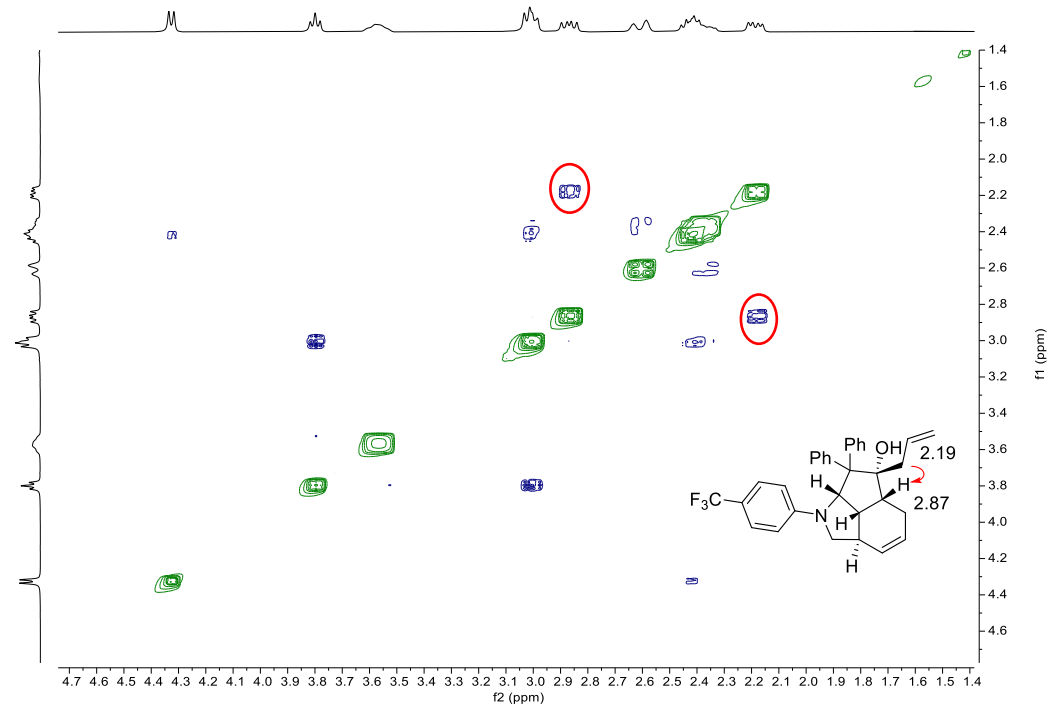


Figure S4. NOESY spectra of **43**

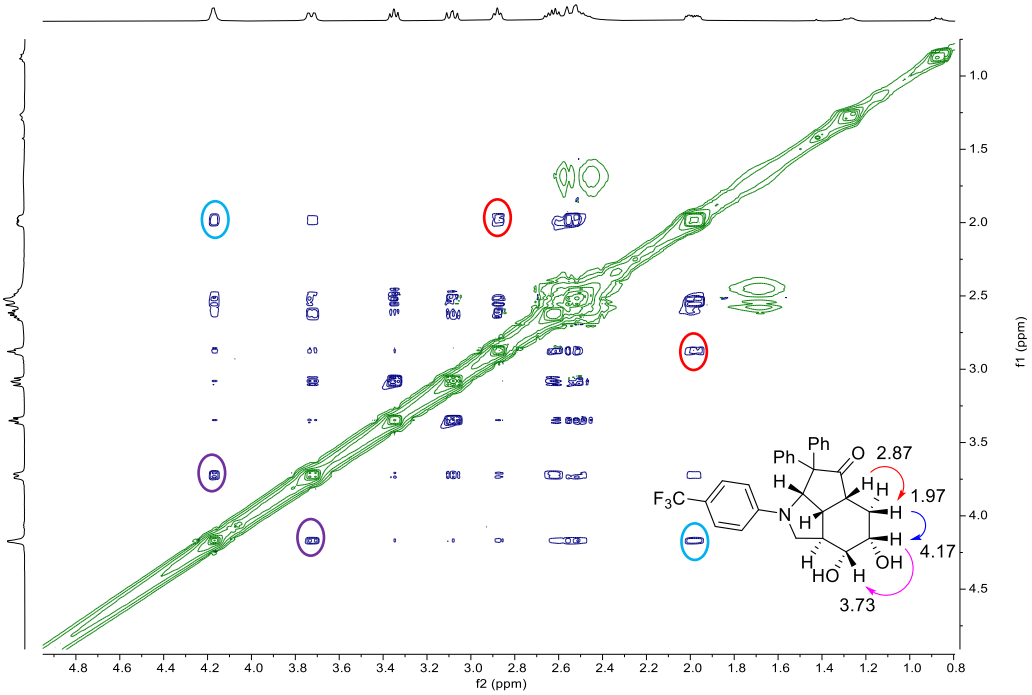
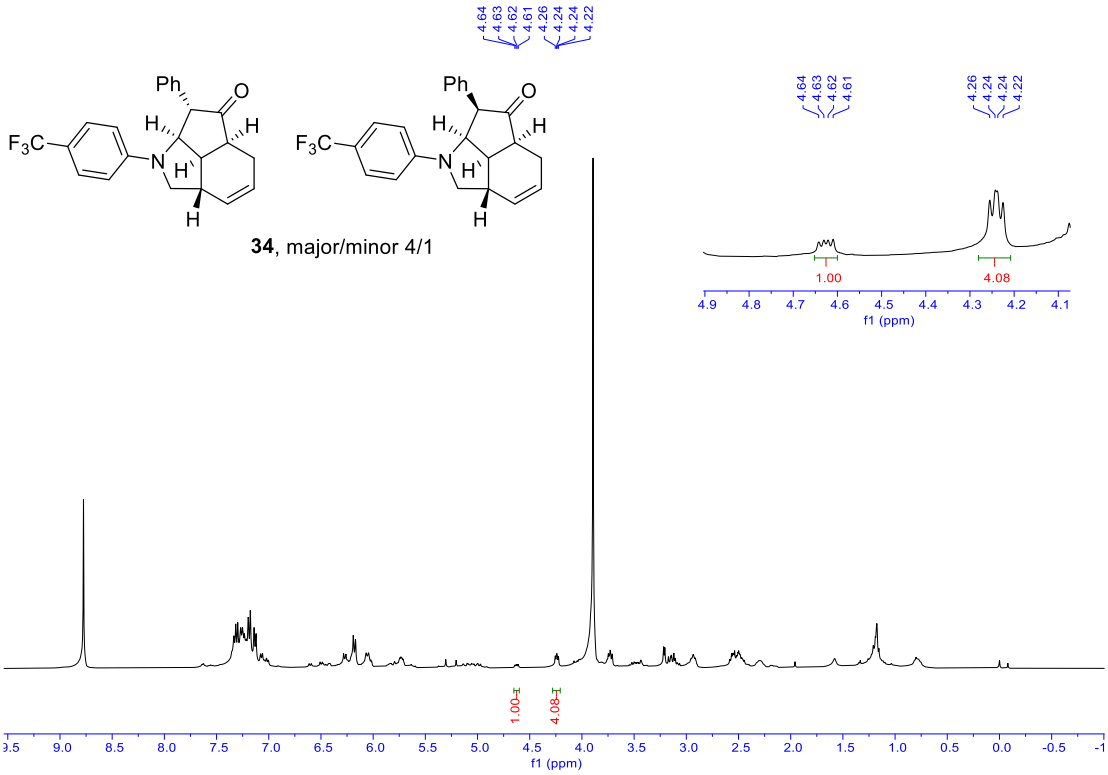
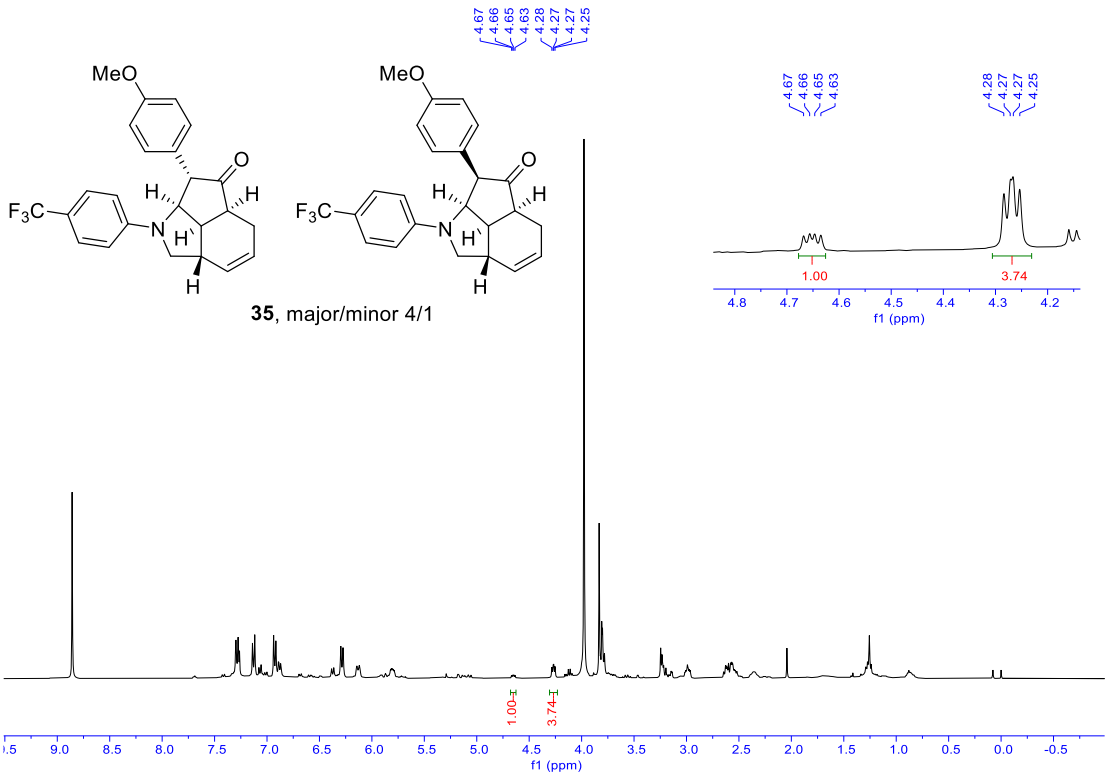
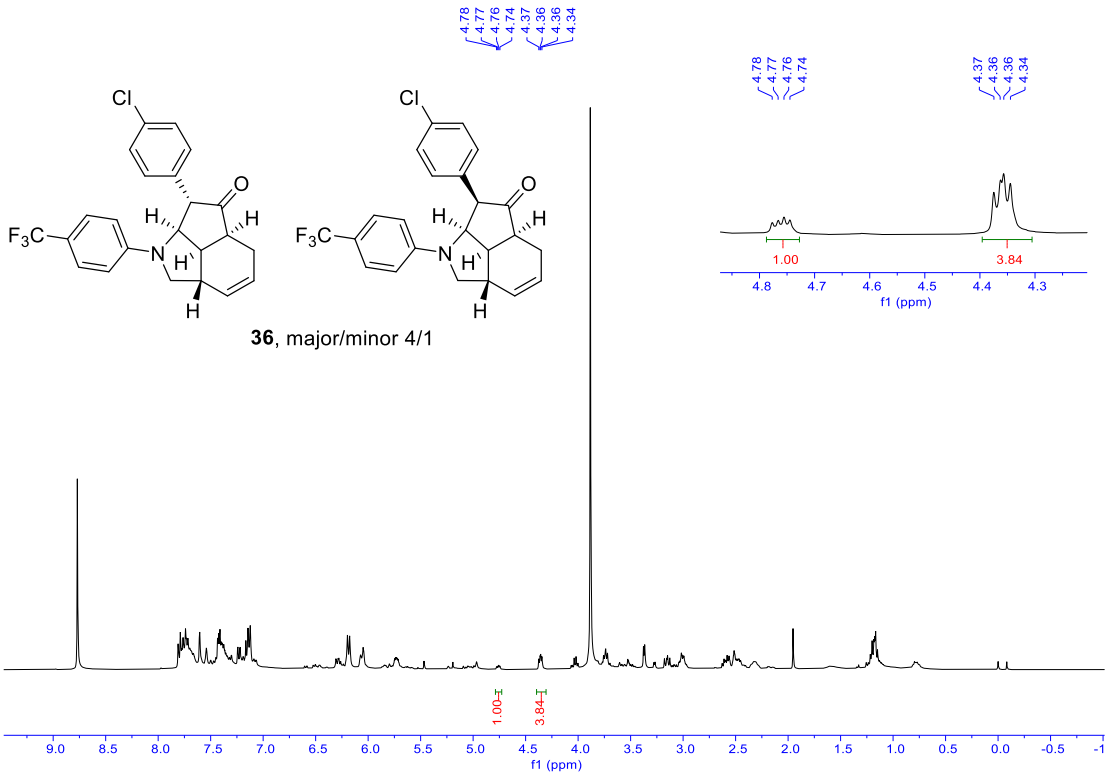


Figure S5. NOESY spectra of **44**

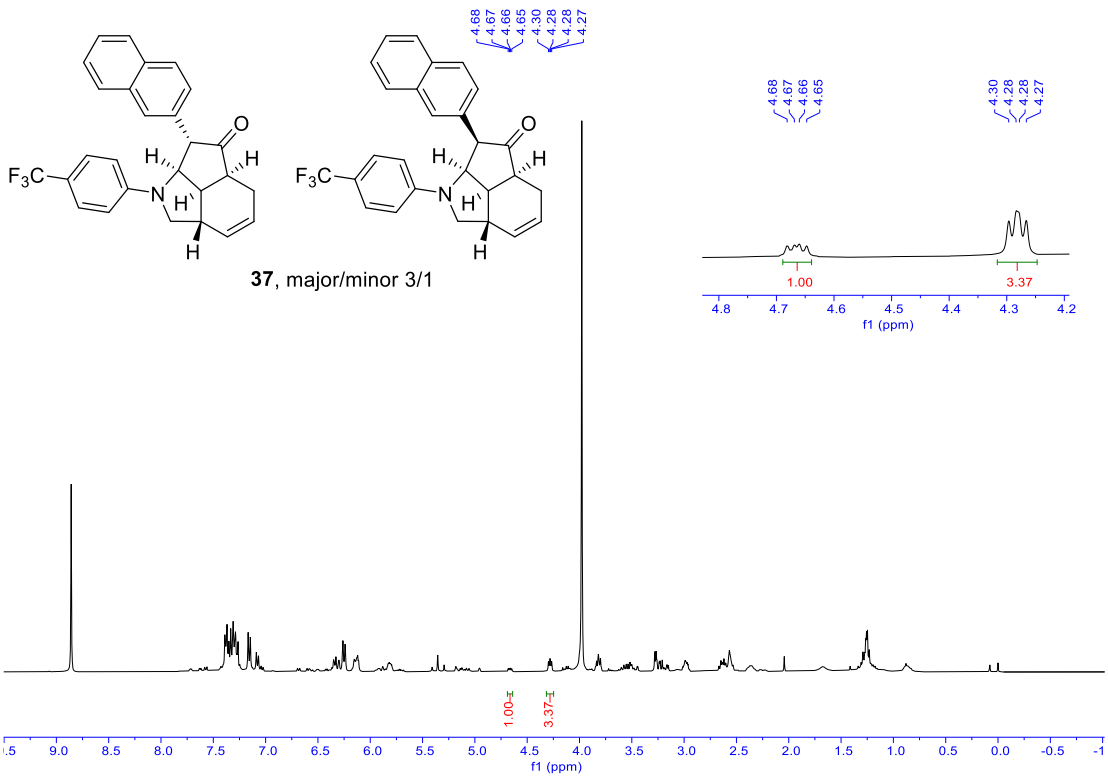
12. Crude ^{1}H NMR spectra for the determination of dr ratio and yield



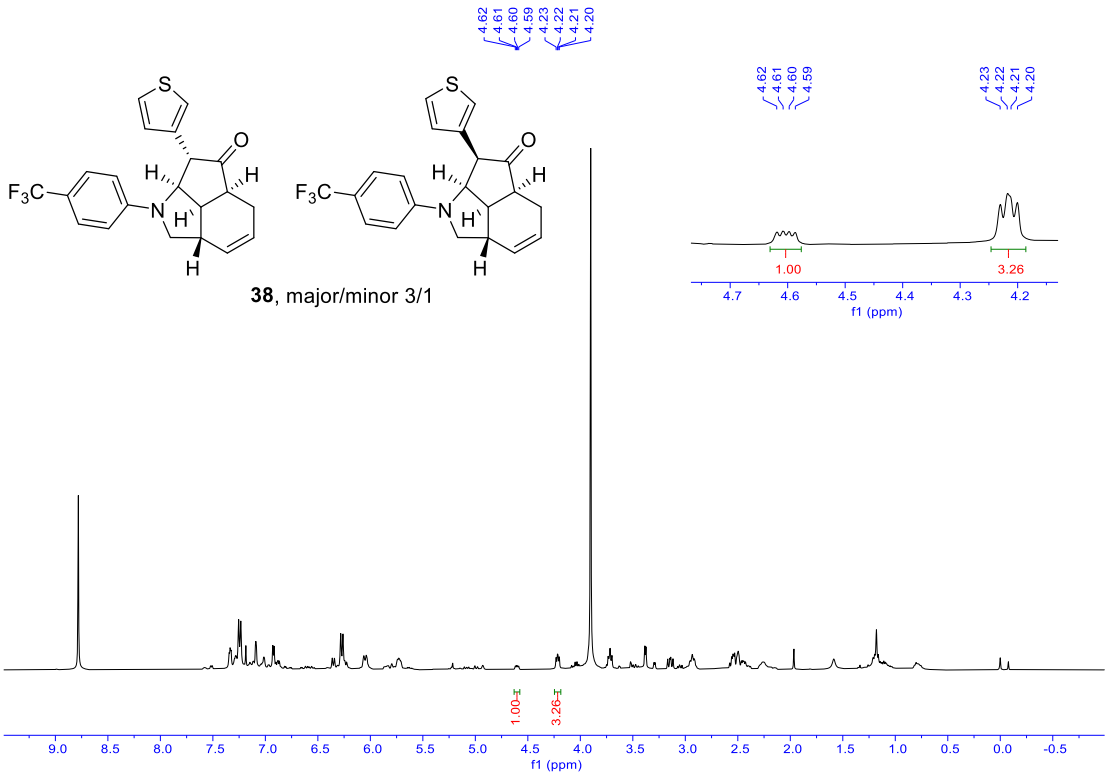




36, major/minor 4/1

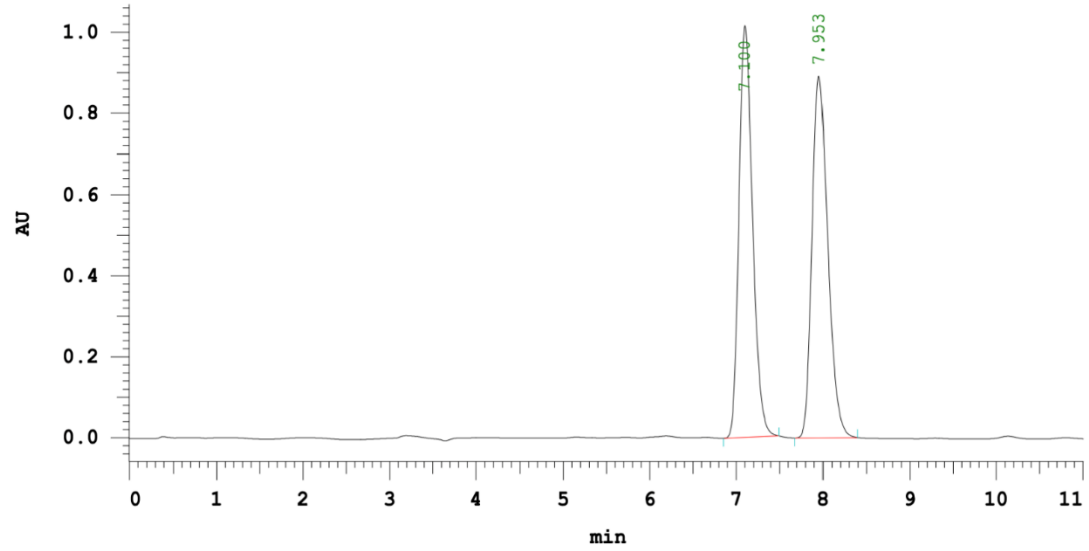


37, major/minor 3/1


4.62
4.61
4.60
4.59
4.23
4.22
4.21
4.20
S
O
H
N
H
F3C
38, major/minor 3/1
1.00
3.26
f1 (ppm)

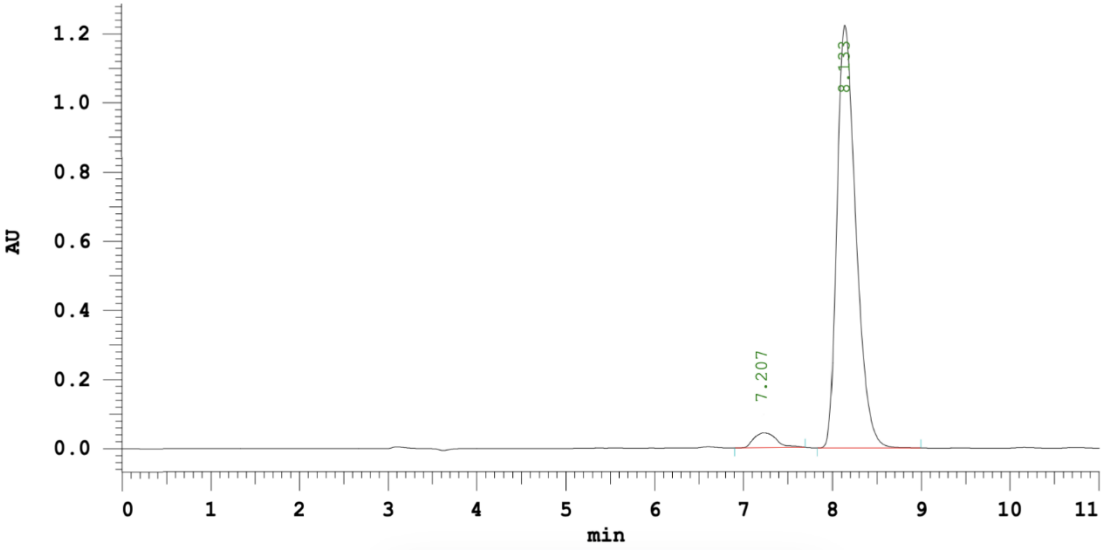
13. HPLC chromatograms of all products

HPLC Chromatogram of Racemic 3



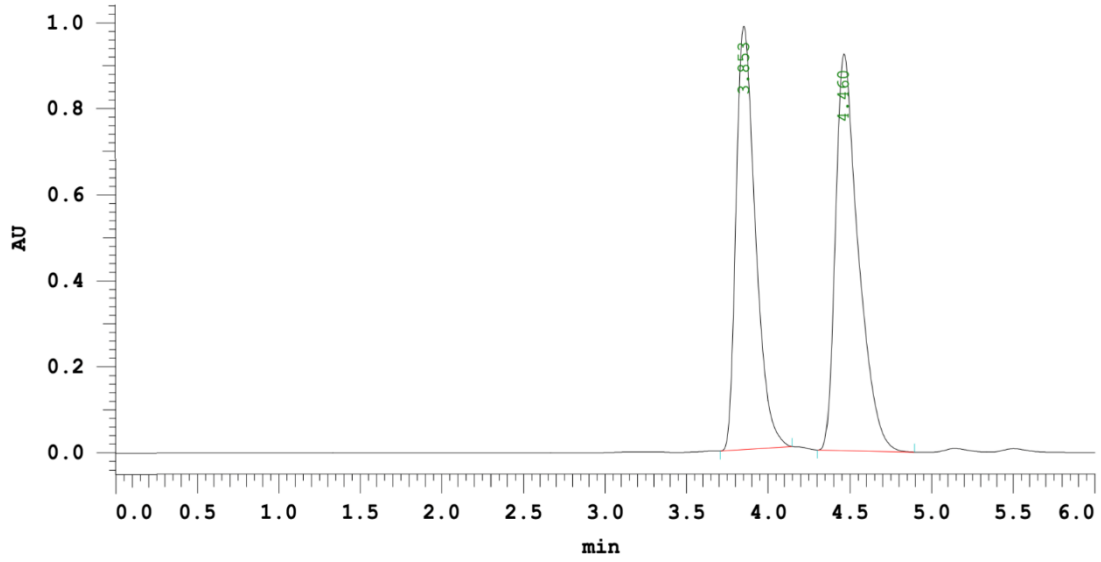
	Retention Time	Area	% Area
1	7.100	5528567	50.079
2	7.953	5511066	49.921

HPLC Chromatogram of Chiral 3



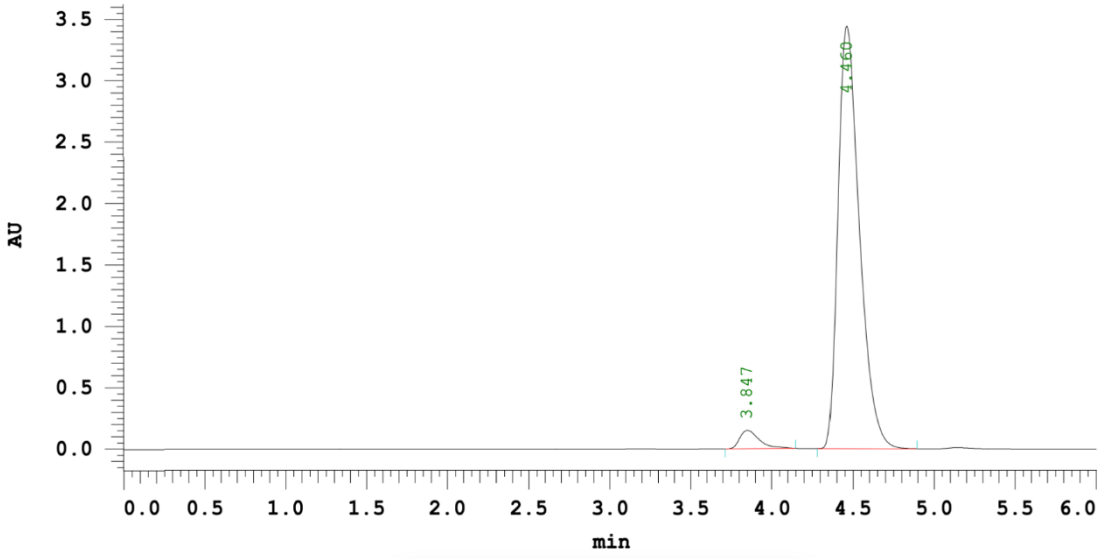
	Retention Time	Area	% Area
1	7.207	328944	3.528
2	8.133	8996124	96.472

HPLC Chromatogram of Racemic 4



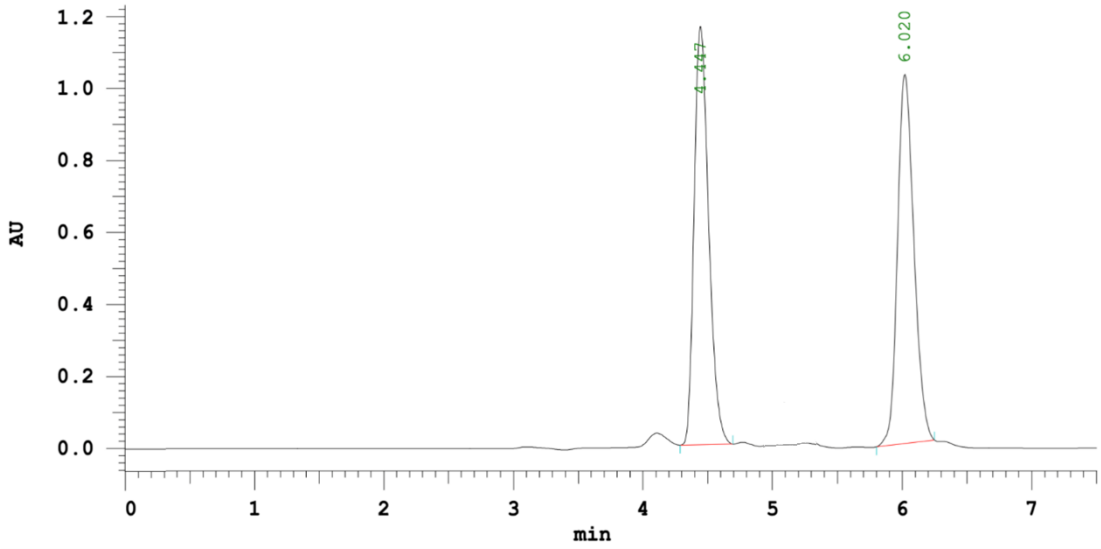
	Retention Time	Area	% Area
1	3.853	4273464	50.290
2	4.460	4225808	50.720

HPLC Chromatogram of Chiral 4



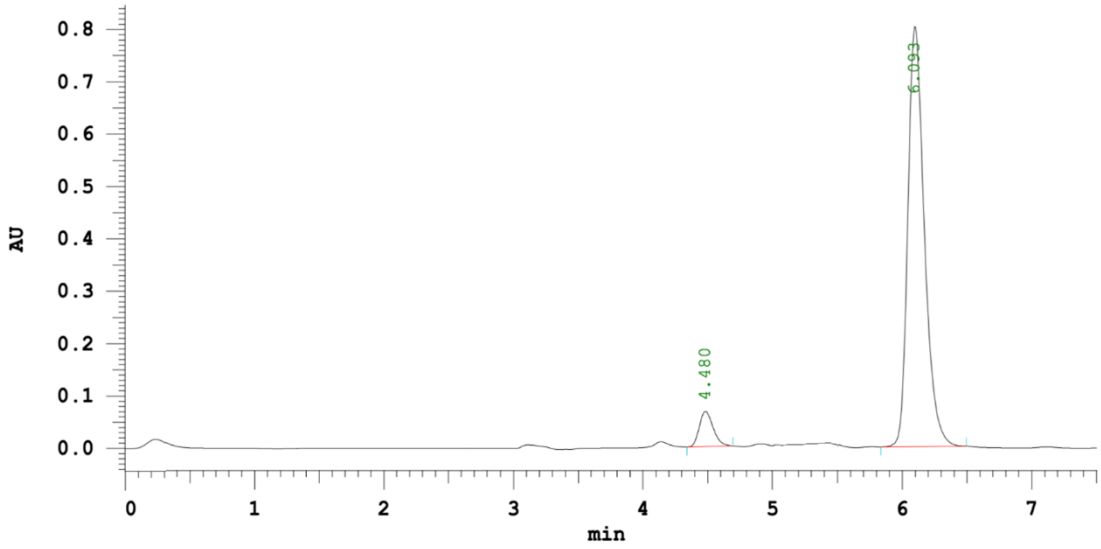
	Retention Time	Area	% Area
1	3.847	628877	3.842
2	4.460	15739889	96.158

HPLC Chromatogram of Racemic 5



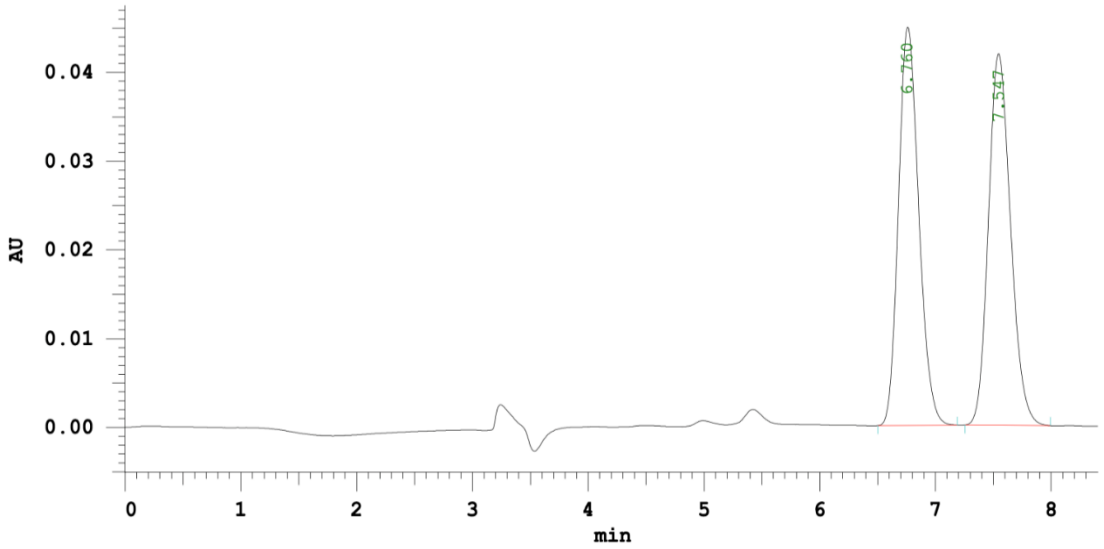
	Retention Time	Area	% Area
1	4.447	4529360	50.126
2	6.020	4506519	49.874

HPLC Chromatogram of Chiral 5



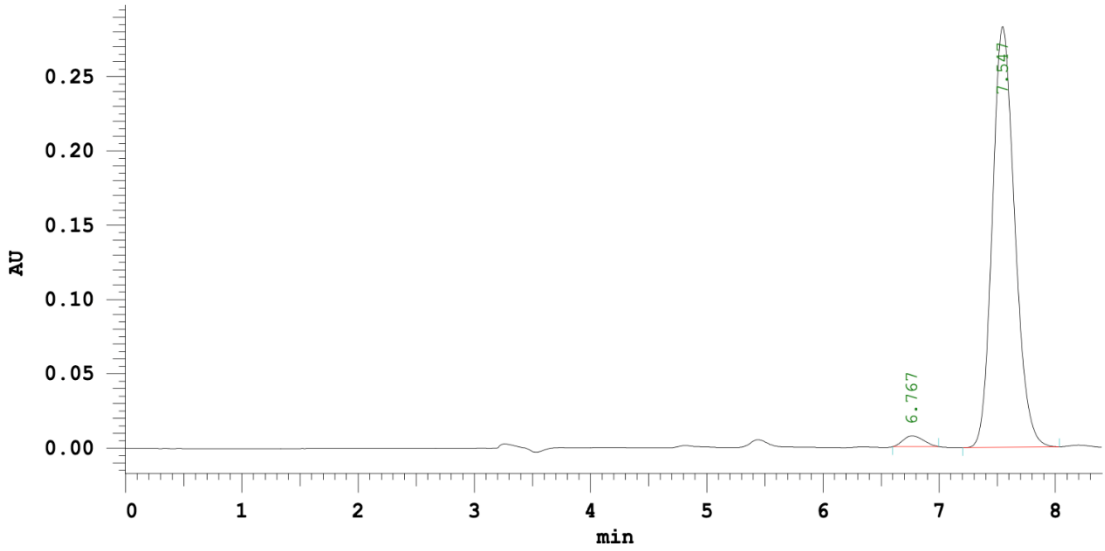
	Retention Time	Area	% Area
1	4.480	249129	6. 553
2	6.093	3552631	93.447

HPLC Chromatogram of Racemic 6



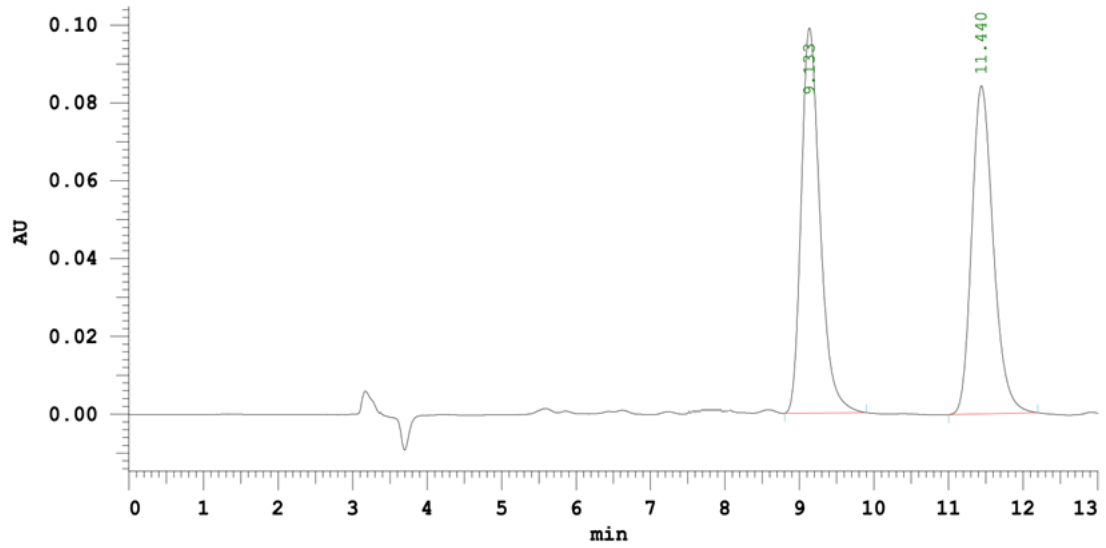
	Retention Time	Area	% Area
1	6.760	272637	49.442
2	7.547	278786	50.558

HPLC Chromatogram of Chiral 6



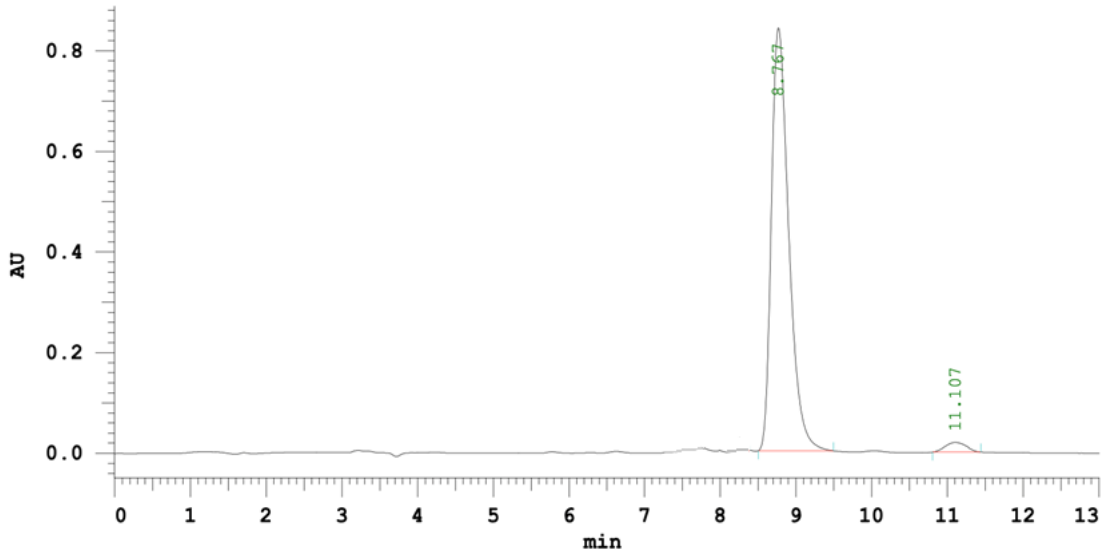
	Retention Time	Area	% Area
1	6.767	43150	2.223
2	7.547	1897829	97.777

HPLC Chromatogram of Racemic 7



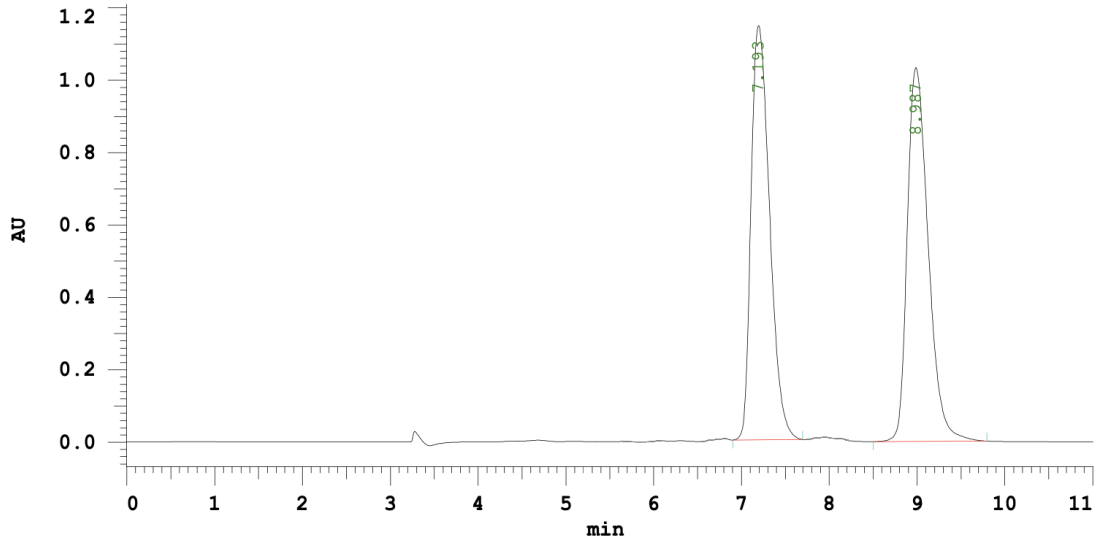
	Retention Time	Area	% Area
1	9.133	867069	50.471
2	11.440	850872	49.529

HPLC Chromatogram of Chiral 7



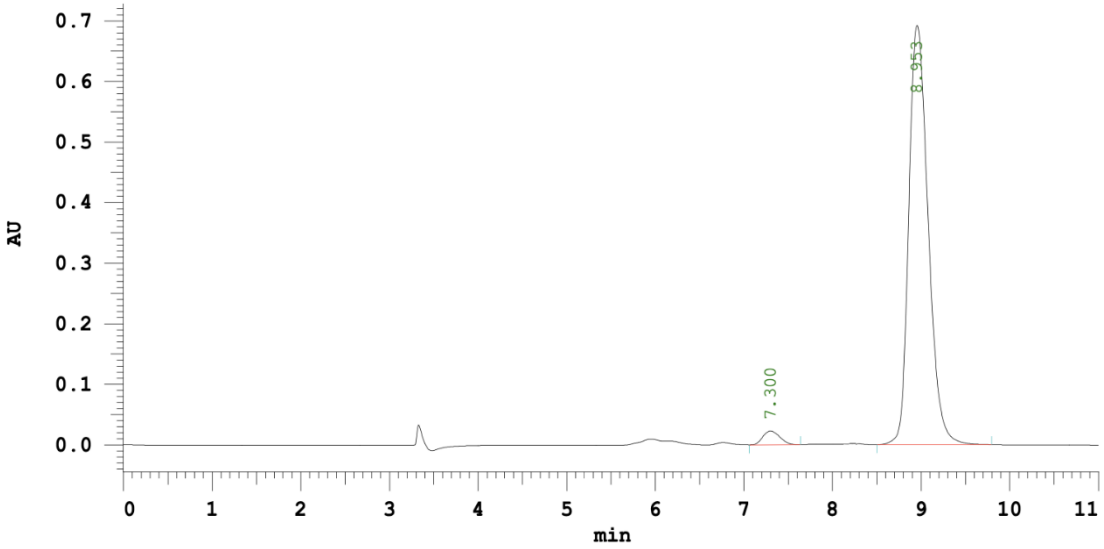
	Retention Time	Area	% Area
1	8.767	6695280	97.325
2	11.107	184012	2.675

HPLC Chromatogram of Racemic 8



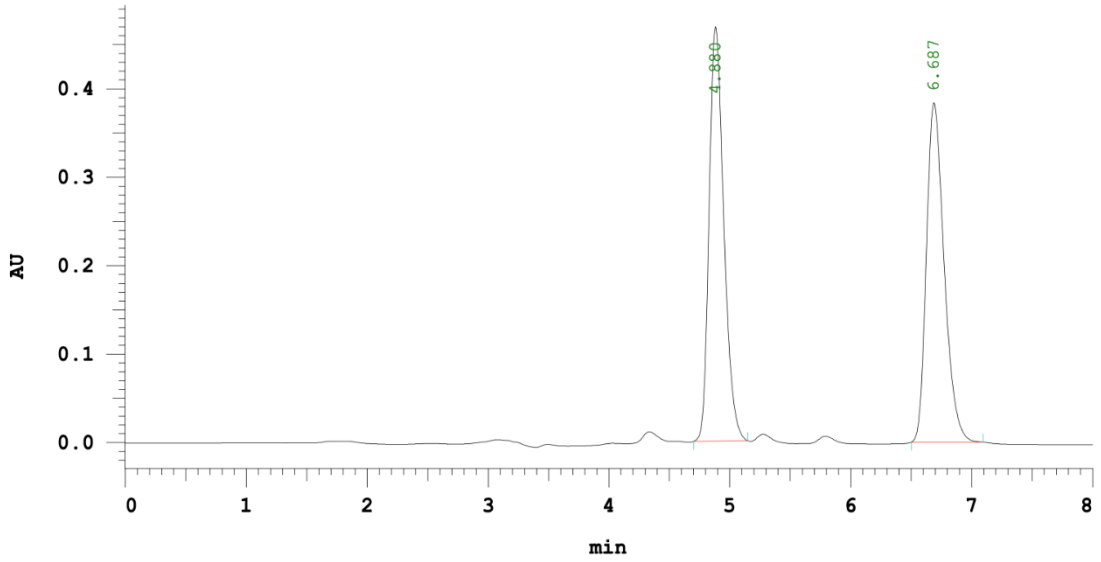
	Retention Time	Area	% Area
1	7.300	150917	2.800
2	8.953	5239559	97.200

HPLC Chromatogram of Chiral 8



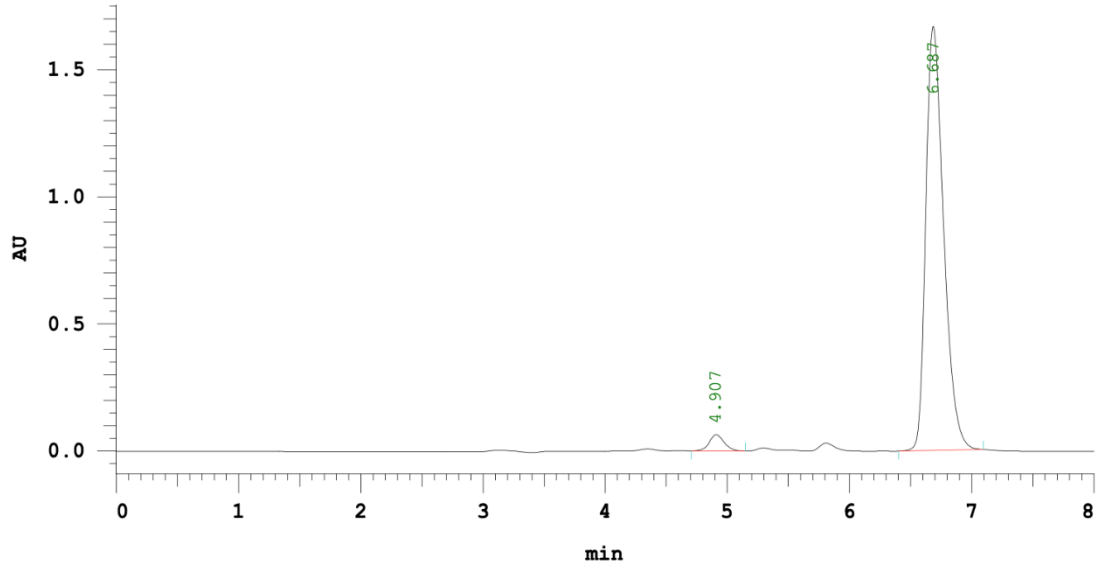
	Retention Time	Area	% Area
1	6.680	17026	1.806
2	8.940	925546	98. 194

HPLC Chromatogram of Racemic 9



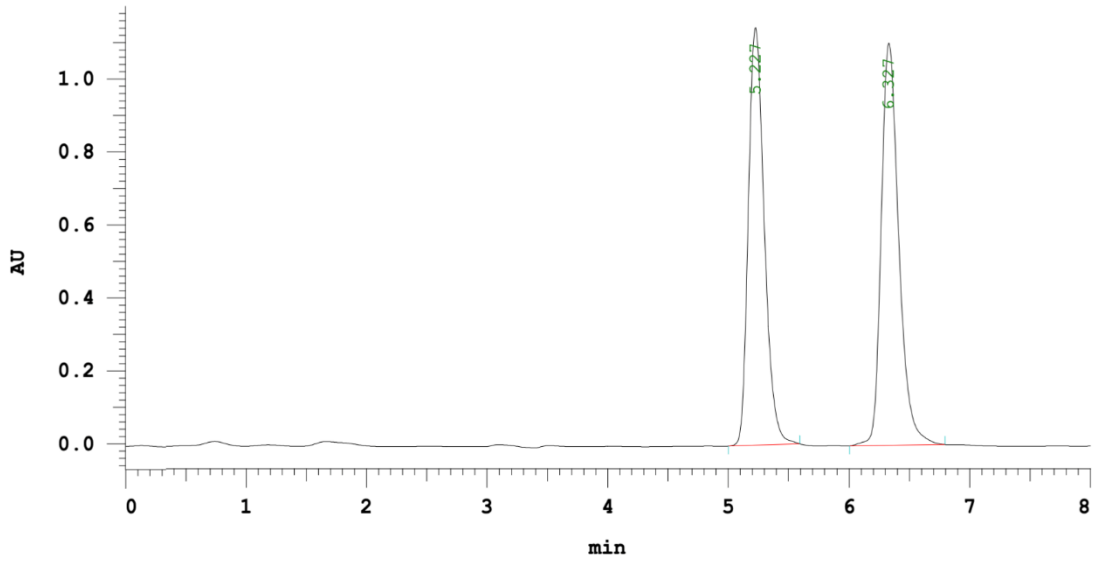
	Retention Time	Area	% Area
1	4.880	1989493	50.371
2	6.687	1960171	49.629

HPLC Chromatogram of Chiral 9



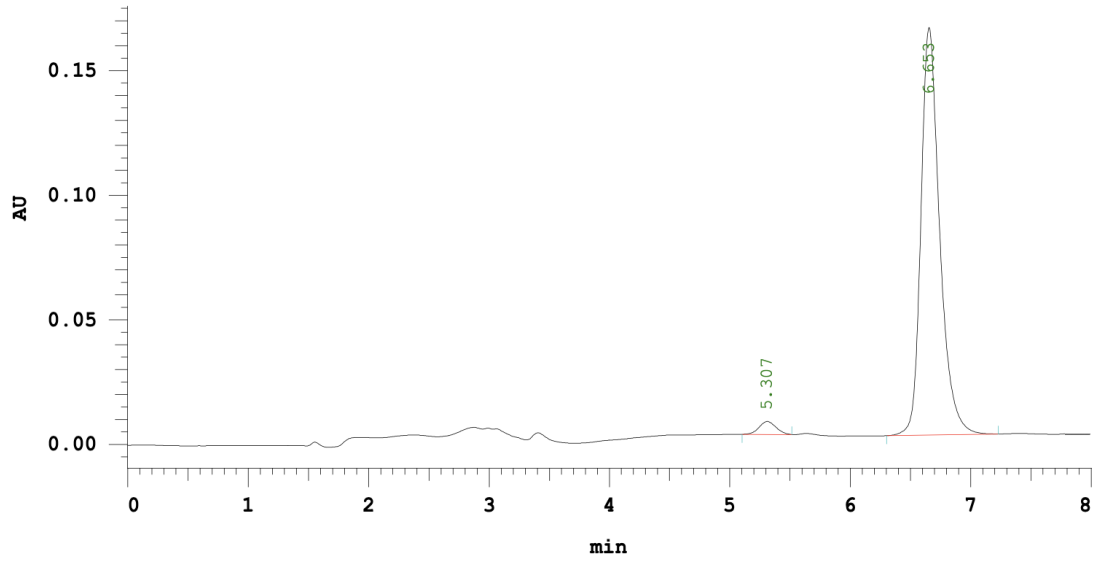
	Retention Time	Area	% Area
1	4.907	277155	3.163
2	6.687	8483876	96.837

HPLC Chromatogram of Racemic 10



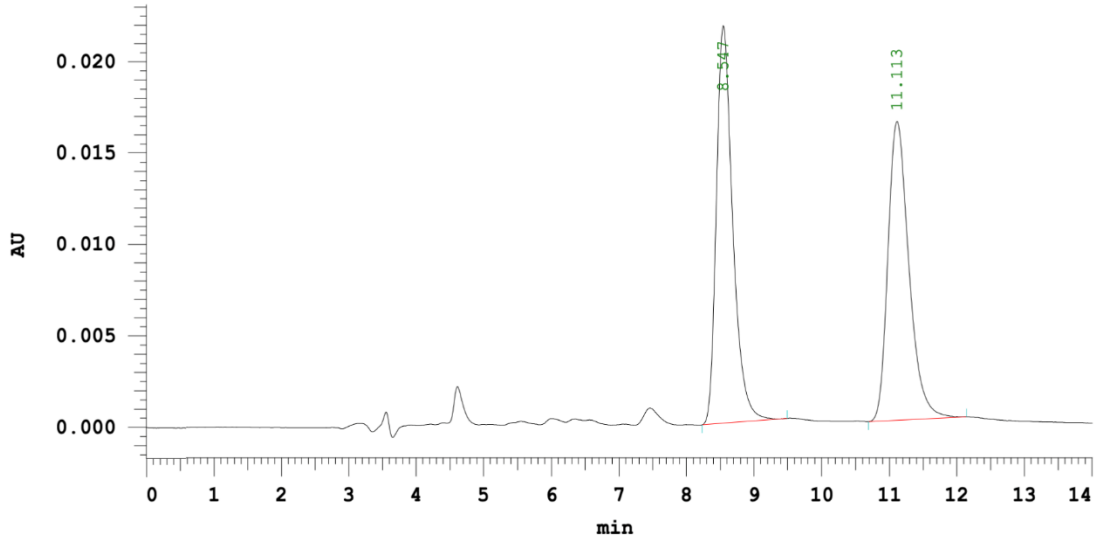
	Retention Time	Area	% Area
1	5.227	5279843	49.443
2	6.327	5398767	50.557

HPLC Chromatogram of Chiral 10



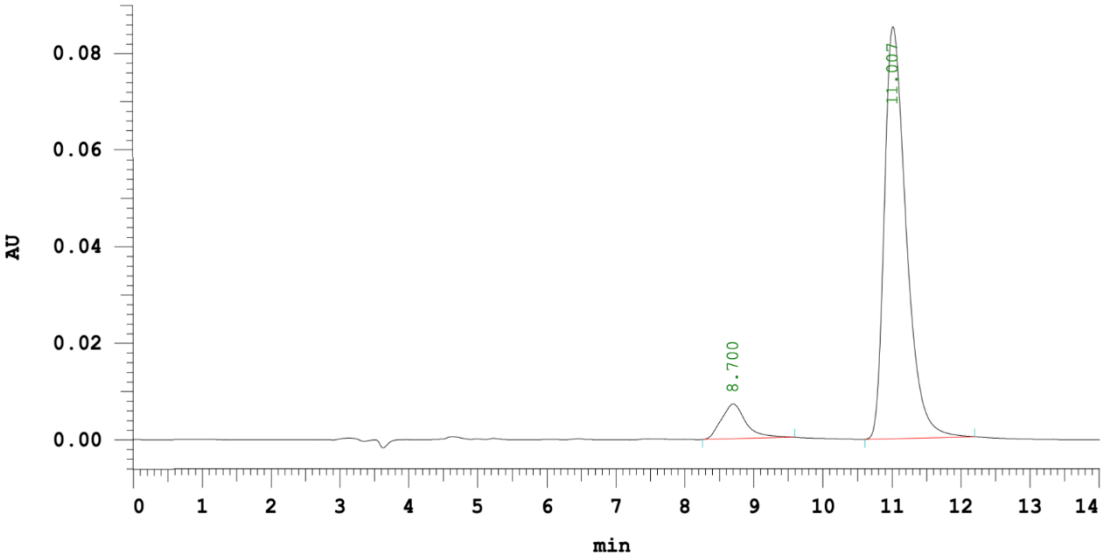
	Retention Time	Area	% Area
1	5.307	25790	2.820
2	6.653	888650	97.180

HPLC Chromatogram of Racemic 12



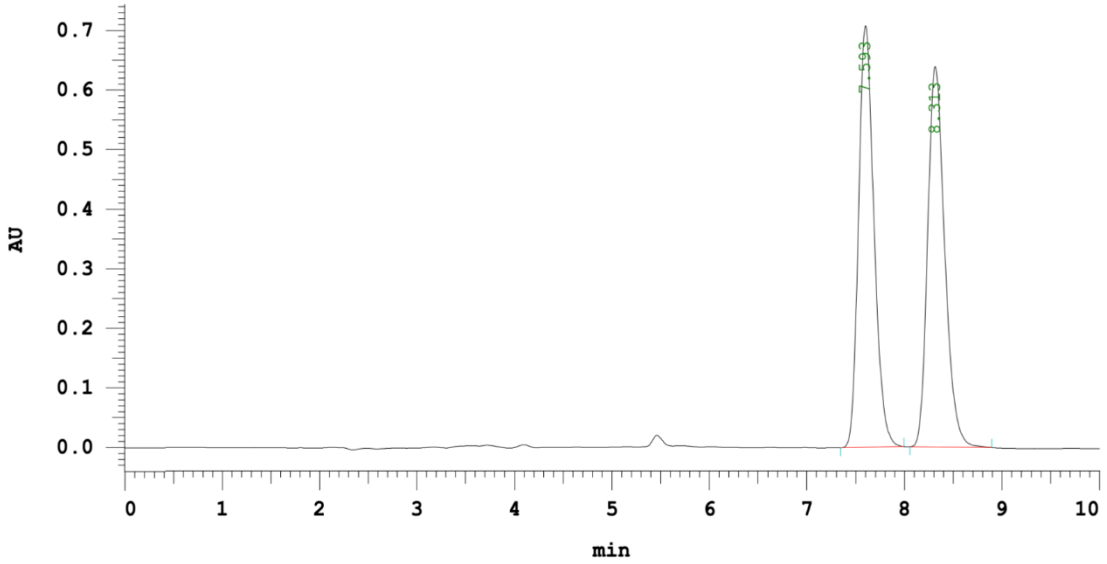
	Retention Time	Area	% Area
1	8.547	177237	50.136
2	11.113	176277	49.864

HPLC Chromatogram of Chiral 12



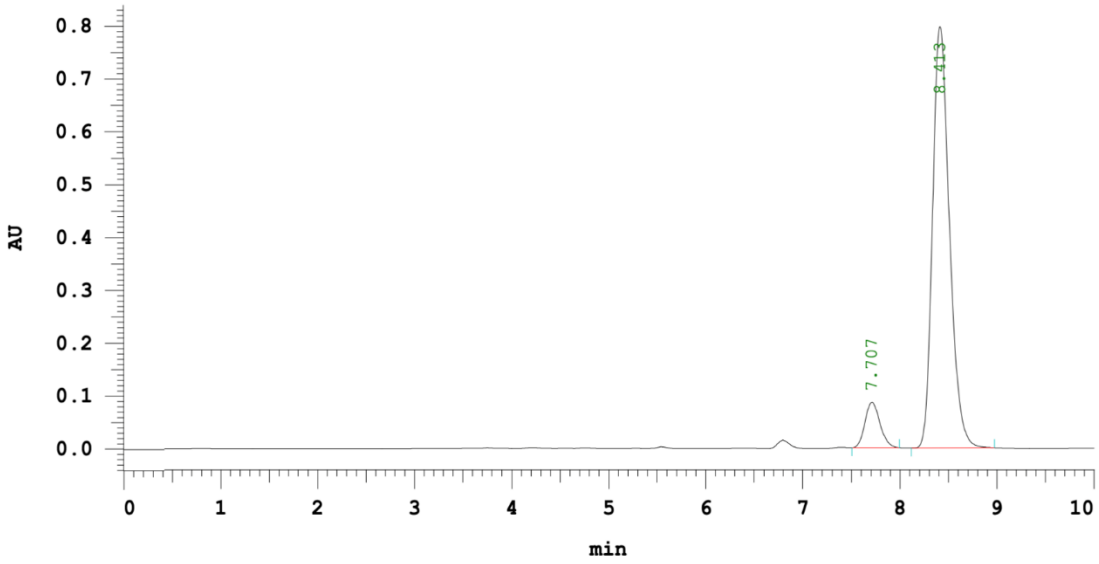
	Retention Time	Area	% Area
1	8.700	89430	8.670
2	11.007	942099	91.330

HPLC Chromatogram of Racemic 13



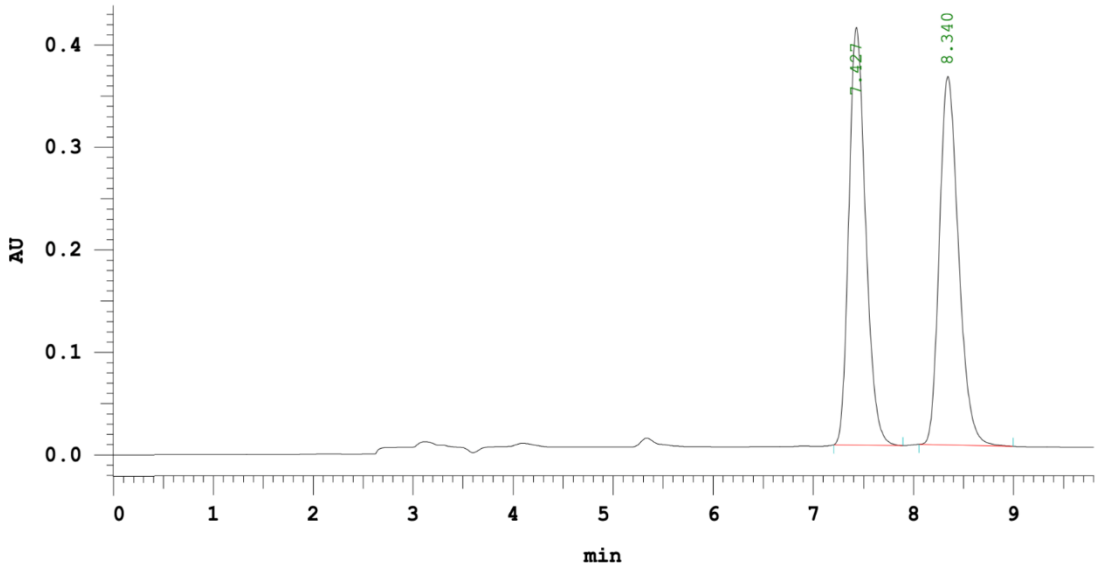
	Retention Time	Area	% Area
1	7.593	3889278	49.891
2	8.313	3906246	50.109

HPLC Chromatogram of Chiral 13



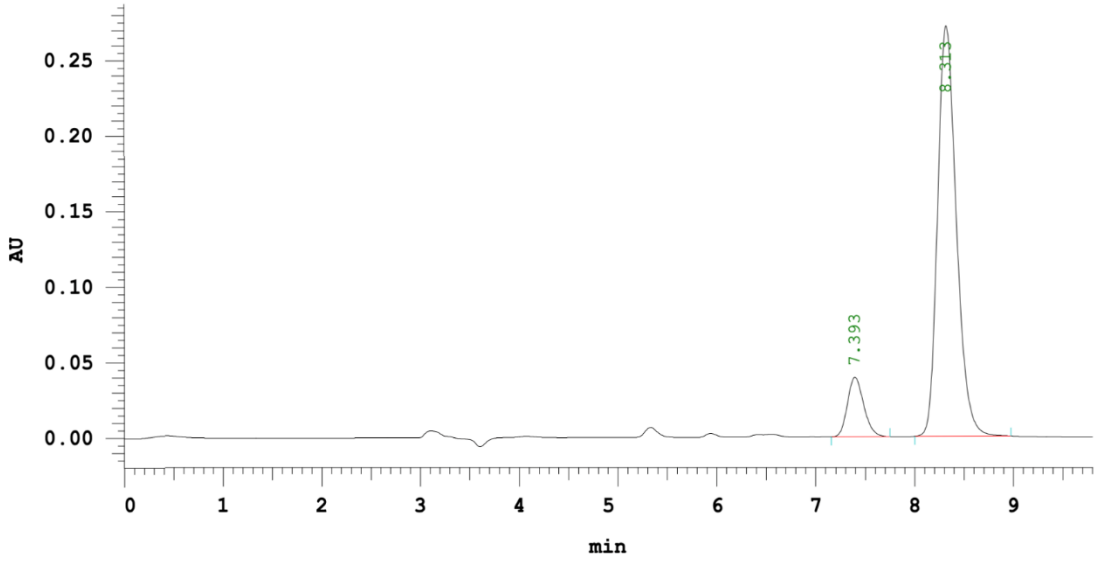
	Retention Time	Area	% Area
1	7.707	425183	8.095
2	8.413	4827463	91. 905

HPLC Chromatogram of Racemic 14



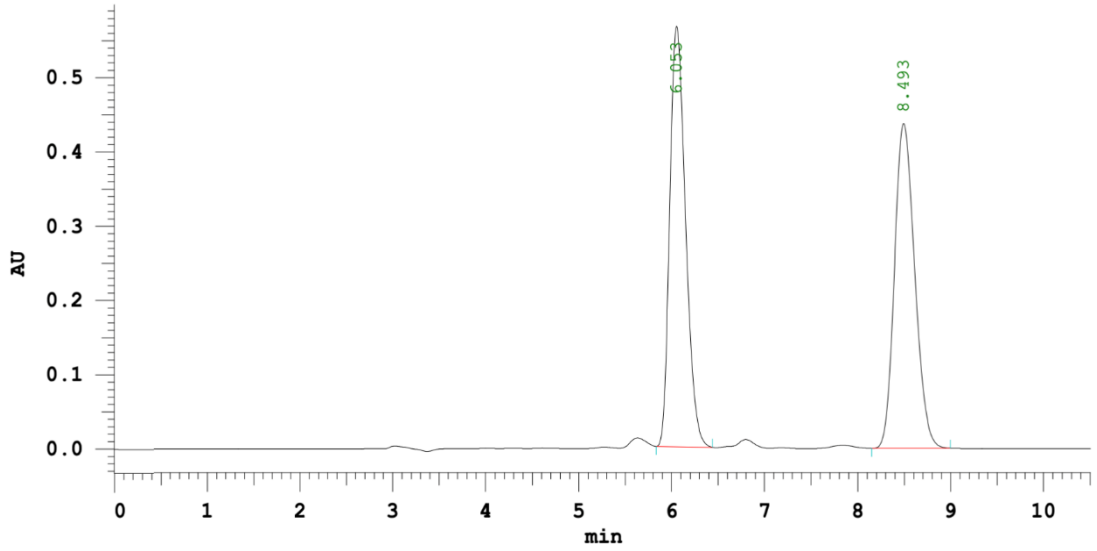
	Retention Time	Area	% Area
1	7.427	2370274	49.761
2	8.340	2393068	50.239

HPLC Chromatogram of Chiral 14



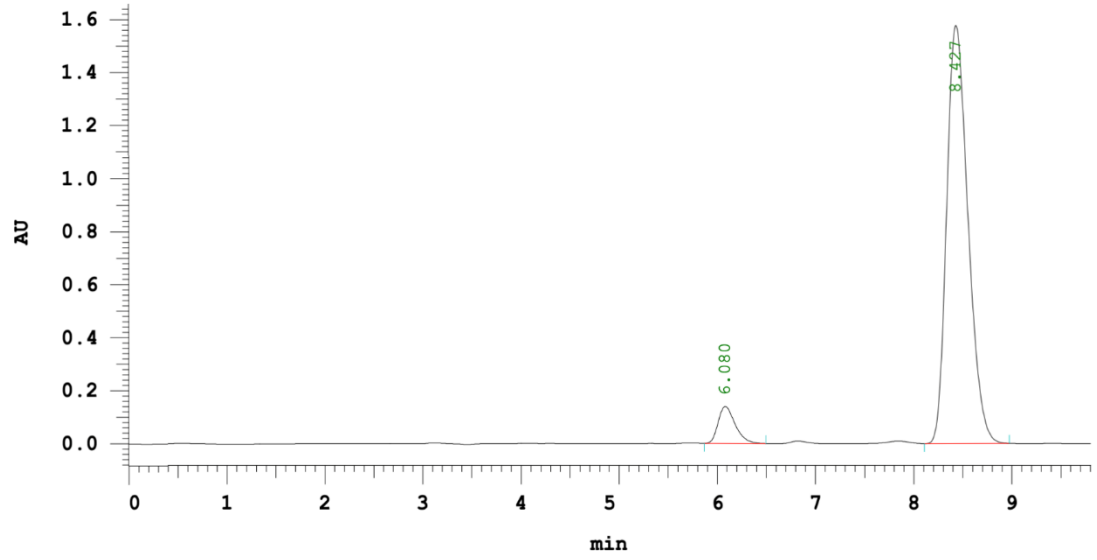
	Retention Time	Area	% Area
1	7.393	226116	11.172
2	8.313	1797767	88.828

HPLC Chromatogram of Racemic 15



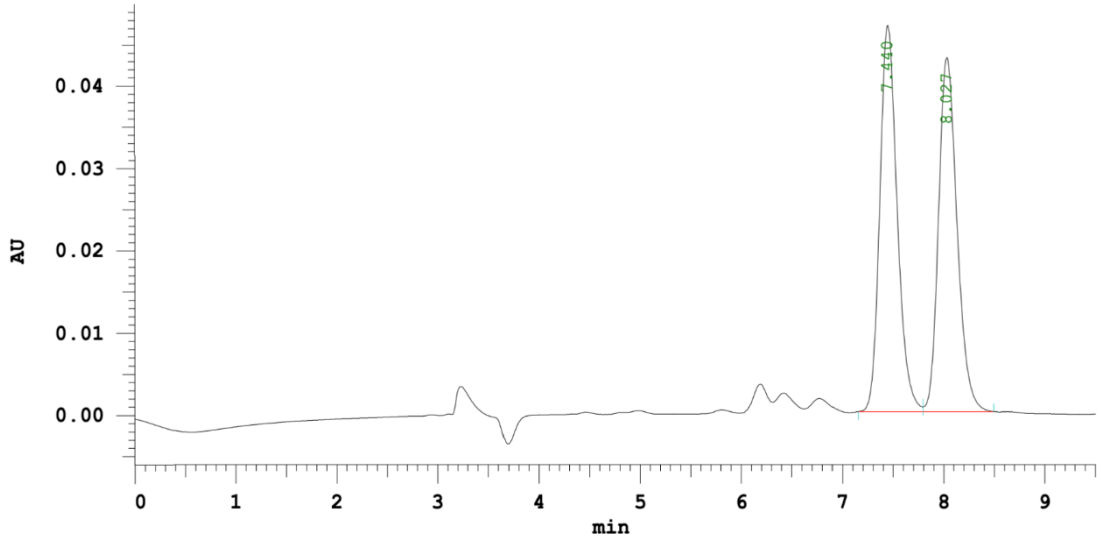
	Retention Time	Area	% Area
1	6.053	3330913	50.141
2	8.493	3312212	49.859

HPLC Chromatogram of Chiral 15



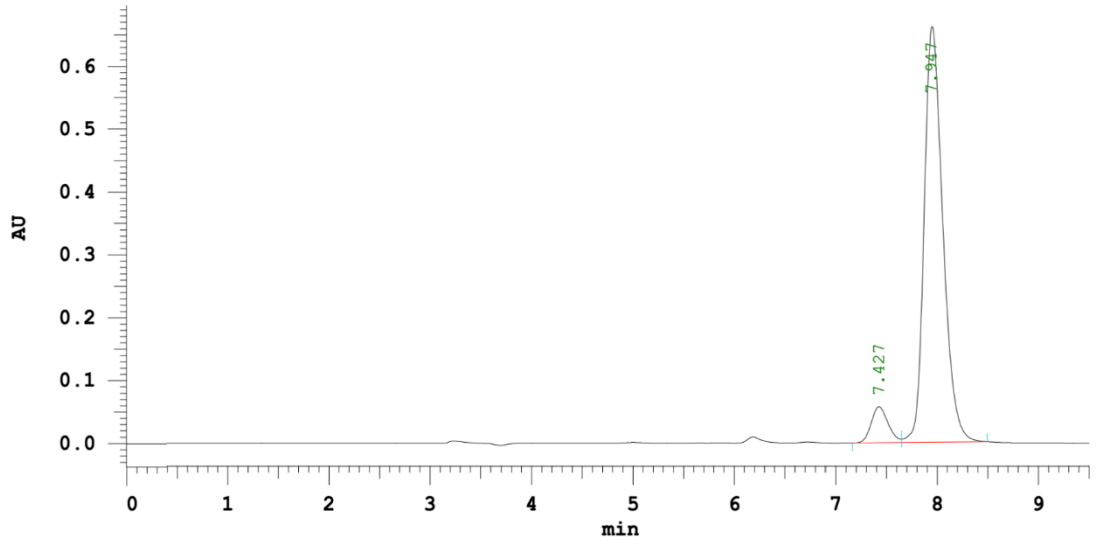
	Retention Time	Area	% Area
1	6.080	686904	5. 456
2	8.427	11903298	94.544

HPLC Chromatogram of Racemic 16



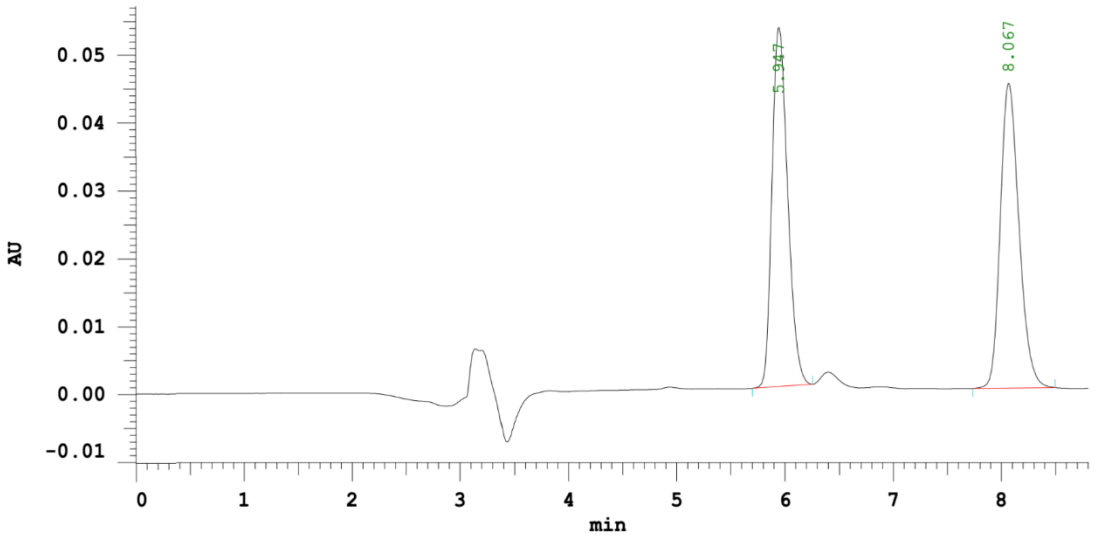
	Retention Time	Area	% Area
1	7.440	271652	50.401
2	8.027	267329	49.599

HPLC Chromatogram of Chiral 16



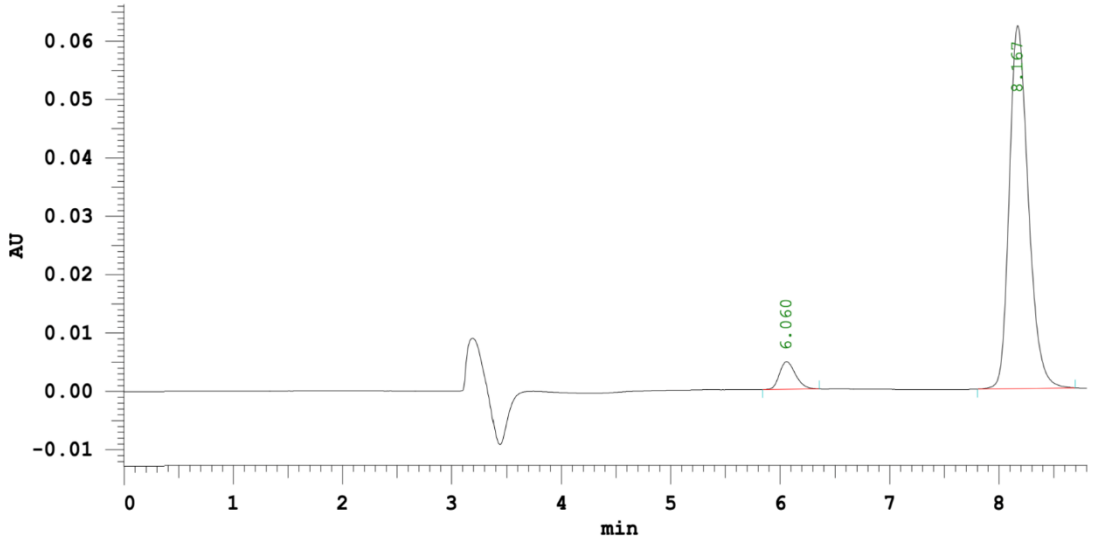
	Retention Time	Area	% Area
1	7.427	259332	5. 819
2	7.947	4197344	94.181

HPLC Chromatogram of Racemic 17



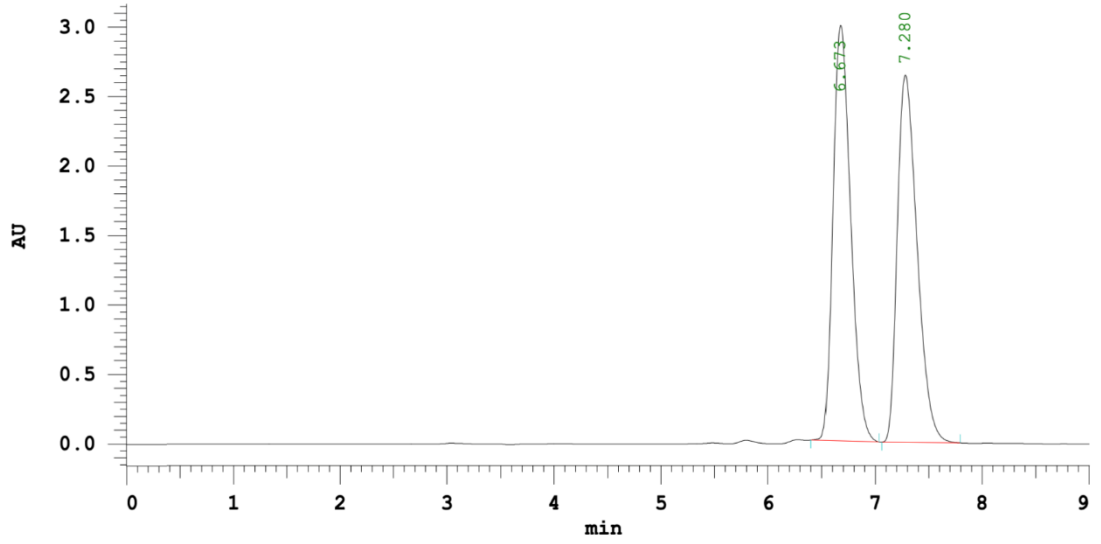
	Retention Time	Area	% Area
1	5.947	267223	49.769
2	8.067	269699	50.231

HPLC Chromatogram of Chiral 17



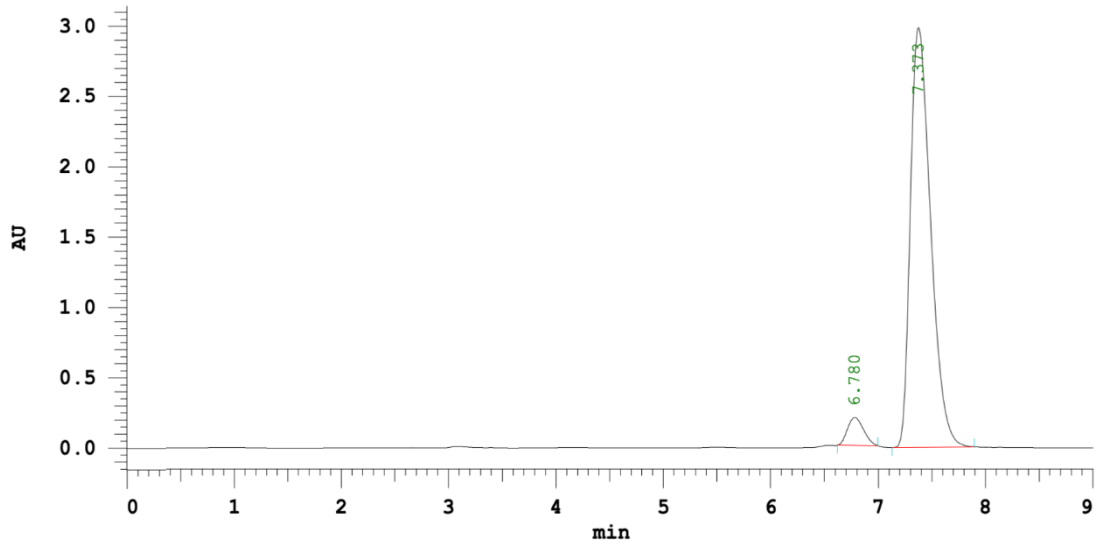
	Retention Time	Area	% Area
1	6.060	21040	5. 273
2	8.167	378012	94.727

HPLC Chromatogram of Racemic 18



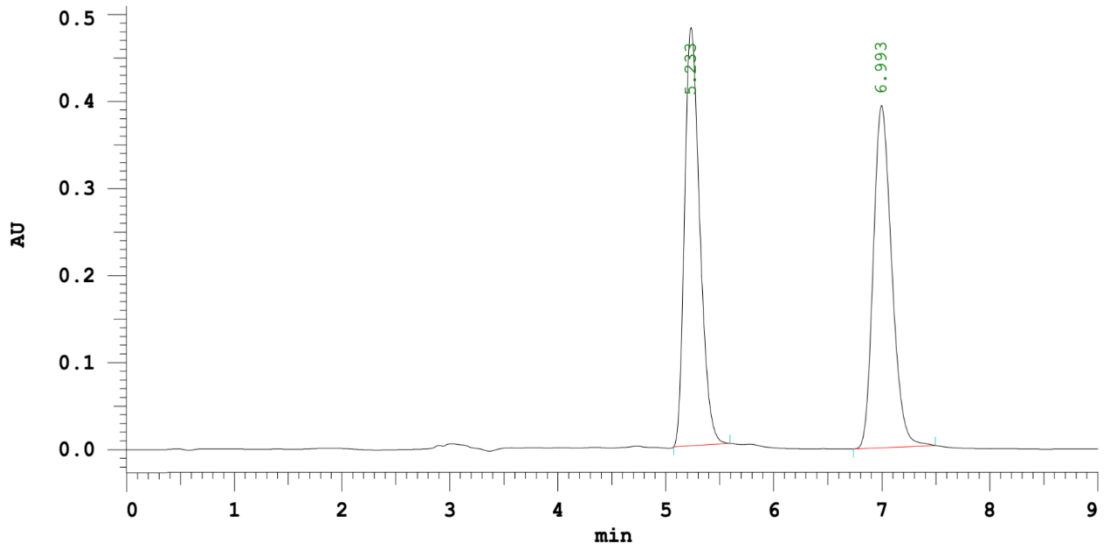
	Retention Time	Area	% Area
1	6.673	17003119	50.025
2	7.280	16986279	49.975

HPLC Chromatogram of Chiral 18



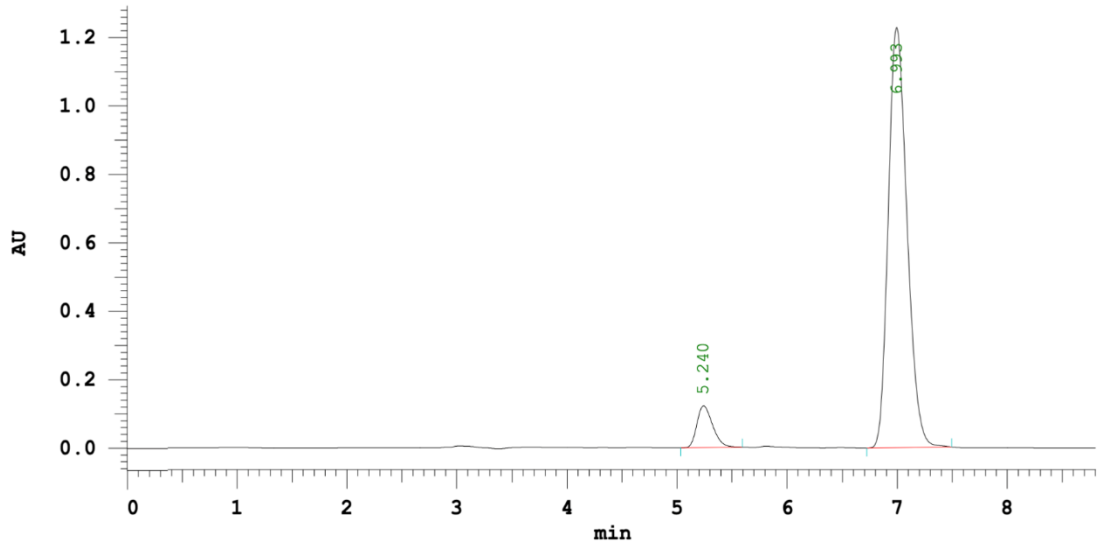
	Retention Time	Area	% Area
1	6.780	1036574	5. 024
2	7.373	19595211	94. 976

HPLC Chromatogram of Racemic 19



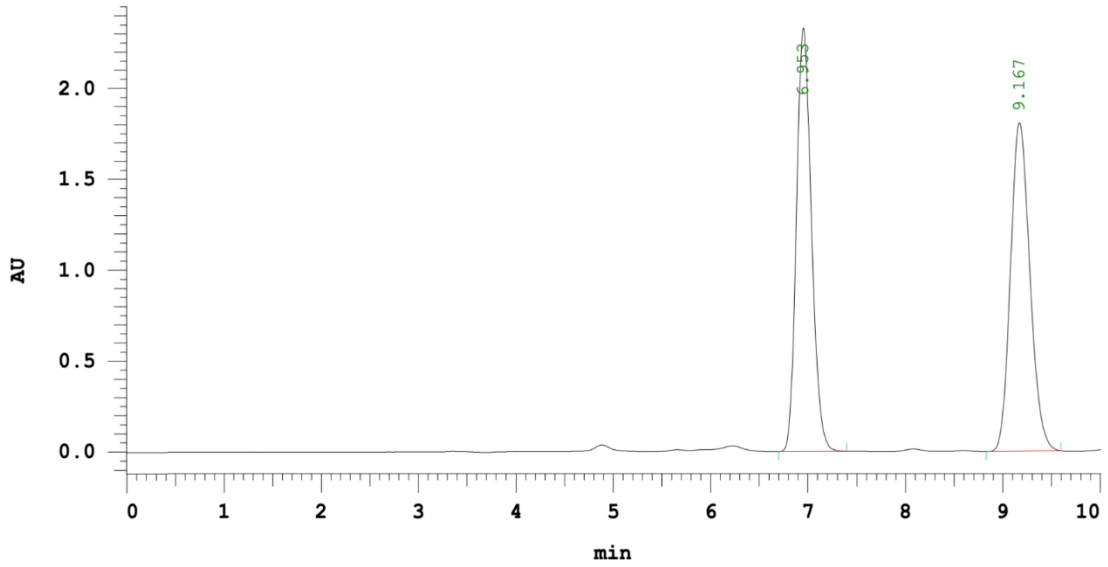
	Retention Time	Area	% Area
1	5.233	2343866	50.002
2	6.993	2343685	49.998

HPLC Chromatogram of Chiral 19



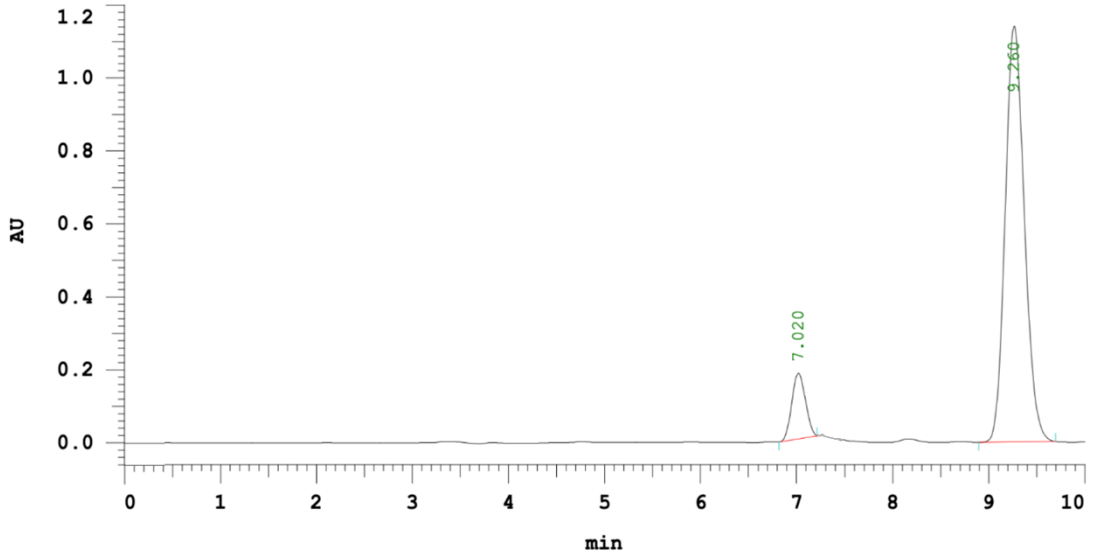
	Retention Time	Area	% Area
1	5.240	606800	7.697
2	6.993	7276446	92.303

HPLC Chromatogram of Racemic 21



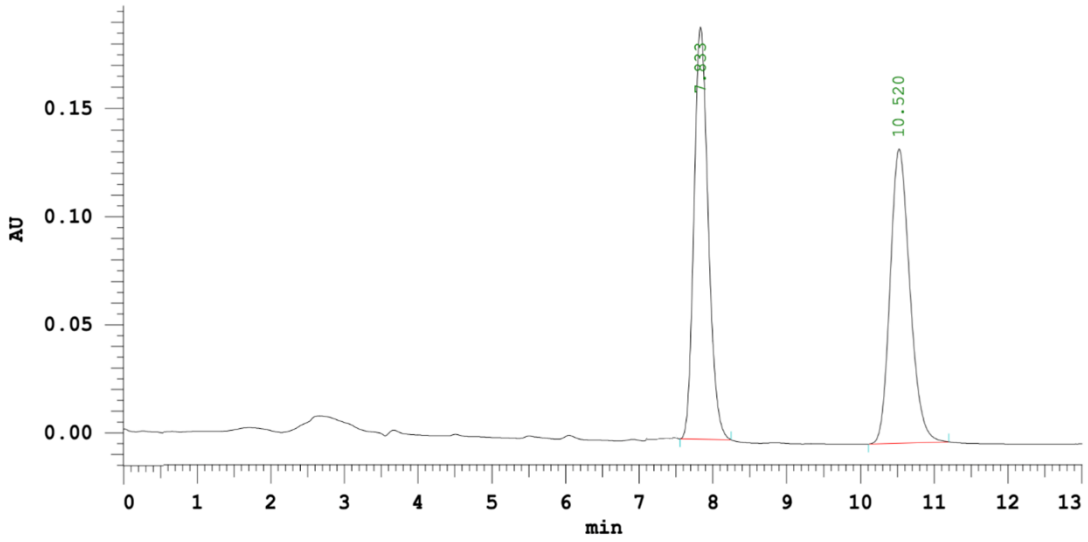
	Retention Time	Area	% Area
1	6.953	12483568	49.917
2	9.167	12524840	50.083

HPLC Chromatogram of Chiral 21



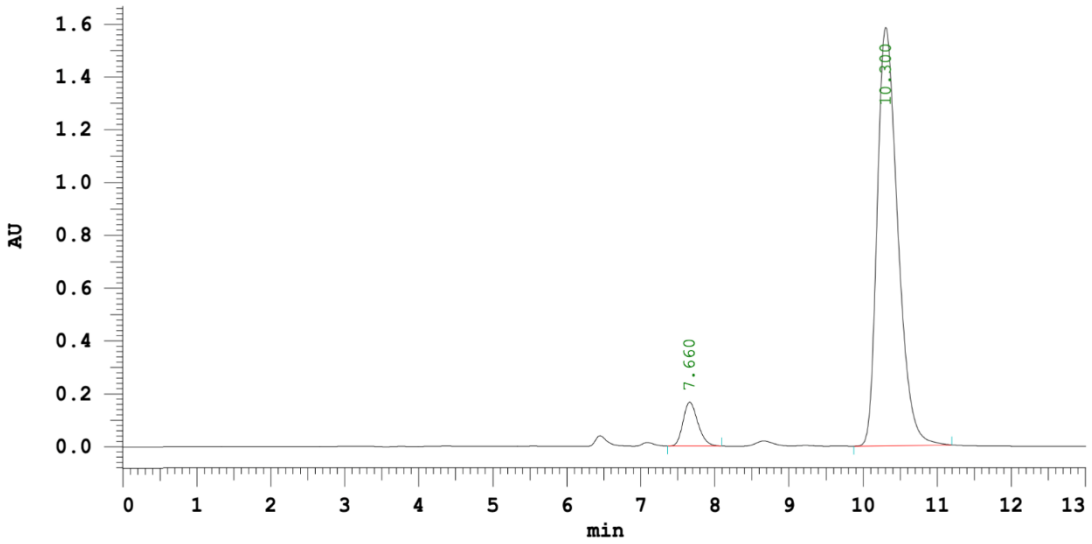
	Retention Time	Area	% Area
1	7.020	887280	10.076
2	9.260	7918981	89.924

HPLC Chromatogram of Racemic 22



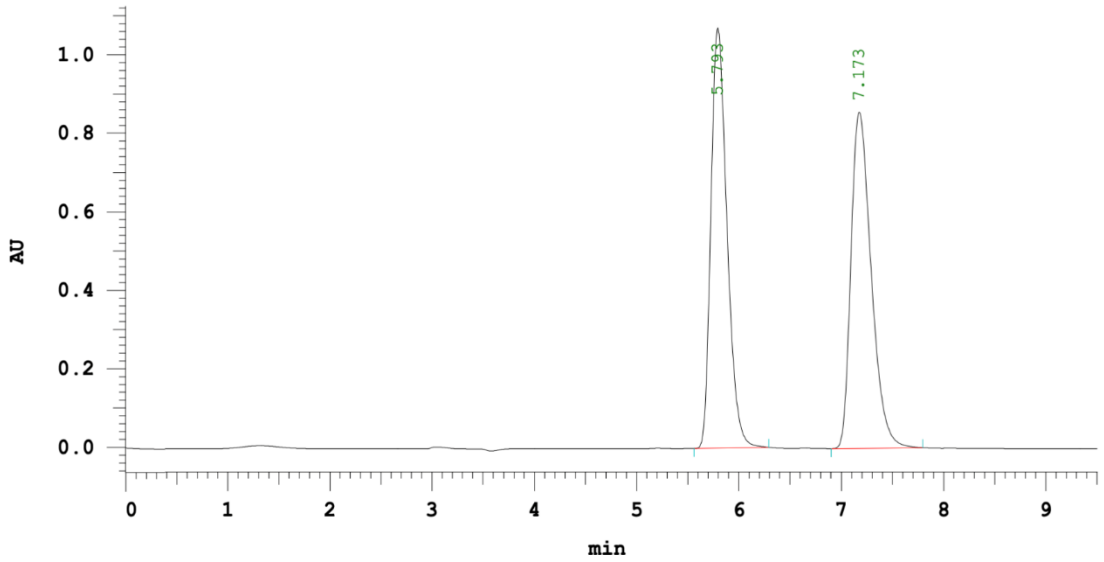
	Retention Time	Area	% Area
1	7.833	1288066	50.411
2	10.520	1267039	49.589

HPLC Chromatogram of Chiral 22



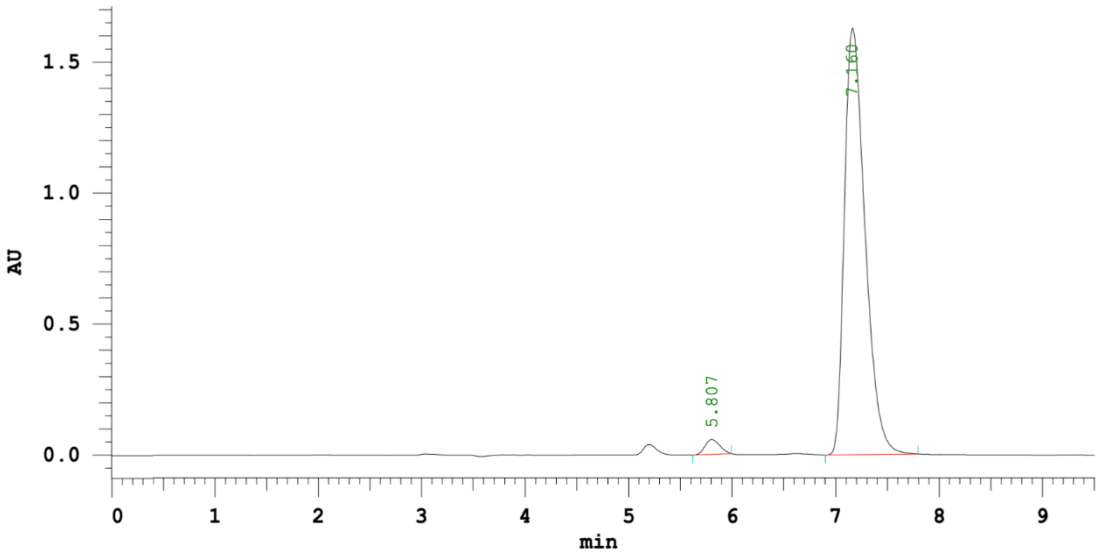
	Retention Time	Area	% Area
1	7.660	1154027	7.017
2	10.300	15292696	92.983

HPLC Chromatogram of Racemic 23



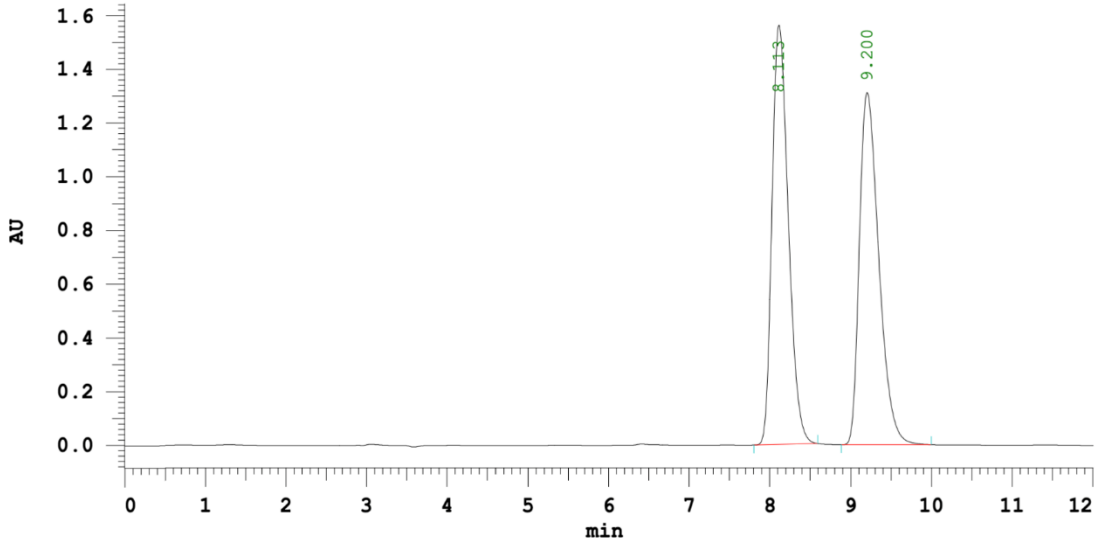
	Retention Time	Area	% Area
1	5.793	5884696	50.021
2	7.173	5879720	49.979

HPLC Chromatogram of Chiral 23



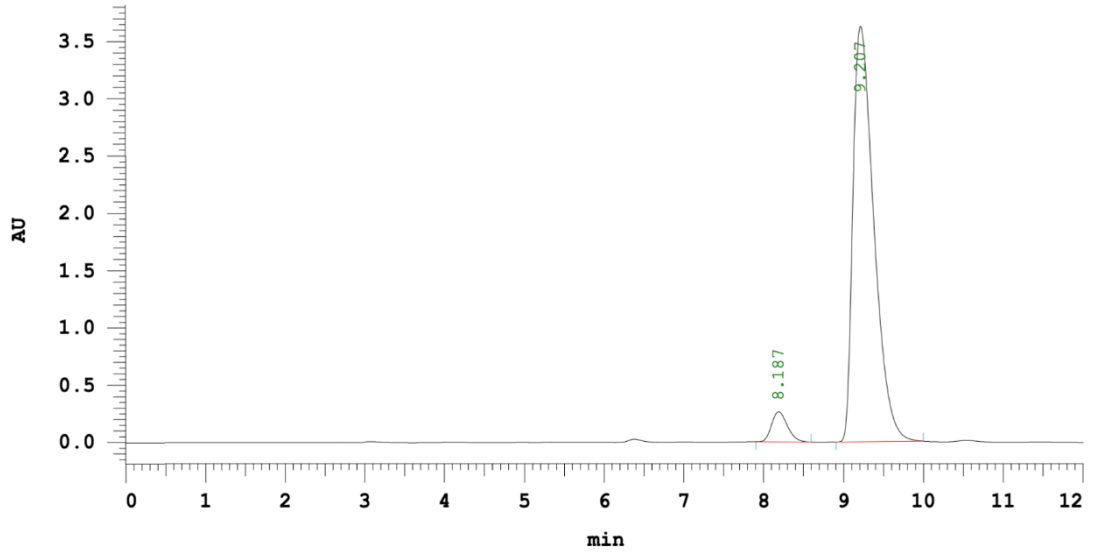
	Retention Time	Area	% Area
1	5.807	279528	2. 424
2	7.160	11251983	97.576

HPLC Chromatogram of Racemic 24



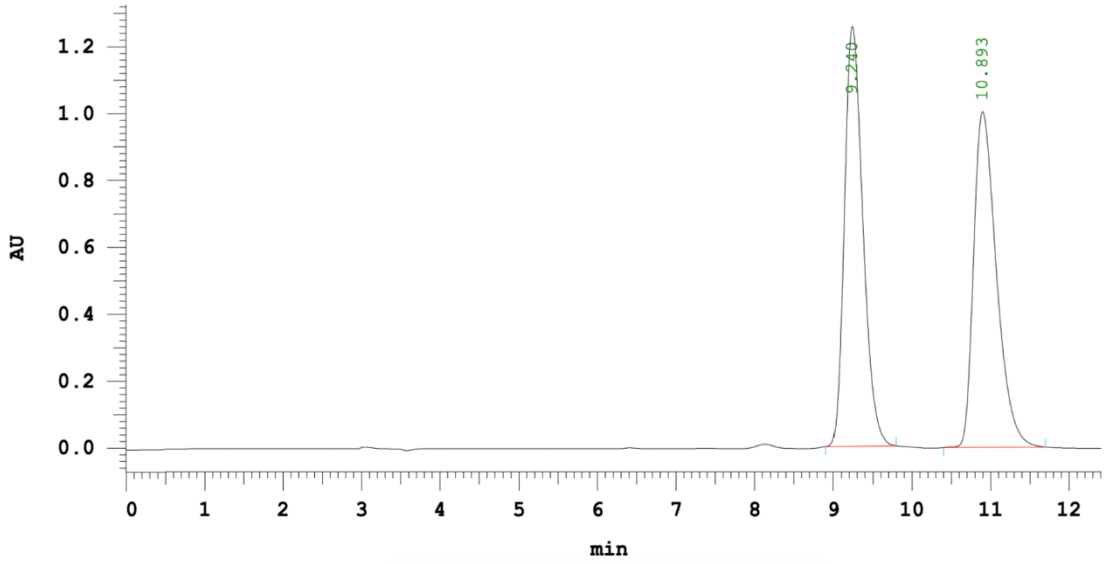
	Retention Time	Area	% Area
1	8.113	10954414	49.906
2	9.200	10995898	50.094

HPLC Chromatogram of Chiral 24



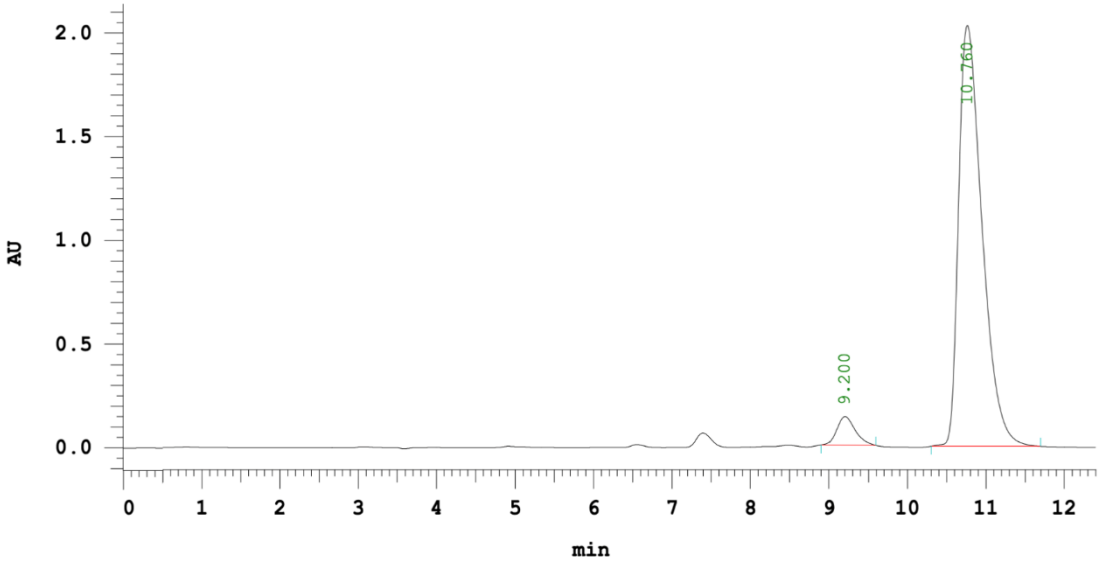
	Retention Time	Area	% Area
1	8.187	1809473	5.186
2	9.207	33083558	94.814

HPLC Chromatogram of Racemic 25



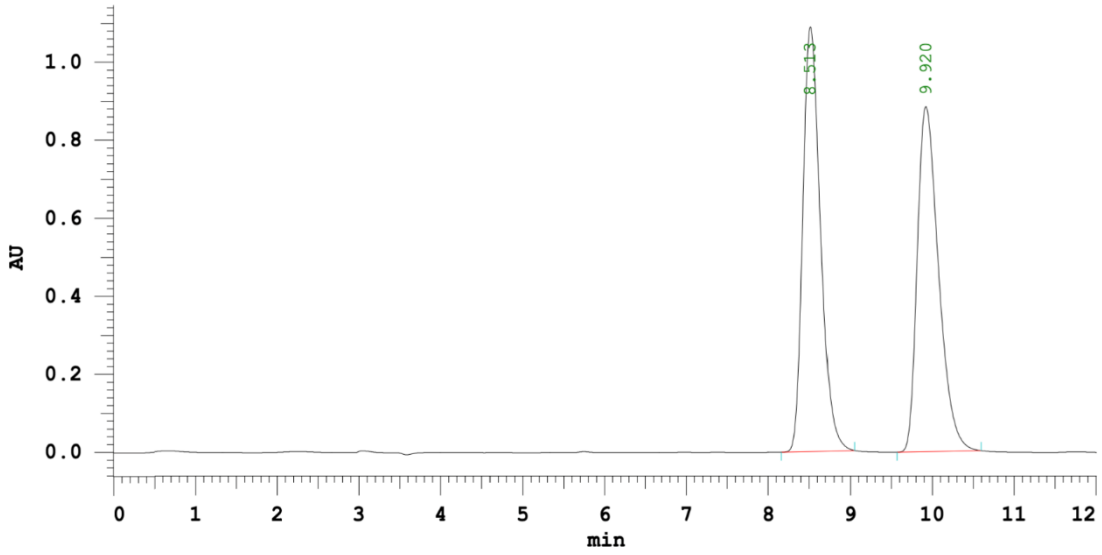
	Retention Time	Area	% Area
1	9.240	10187733	50.110
2	10.893	10142913	49.890

HPLC Chromatogram of Chiral 25



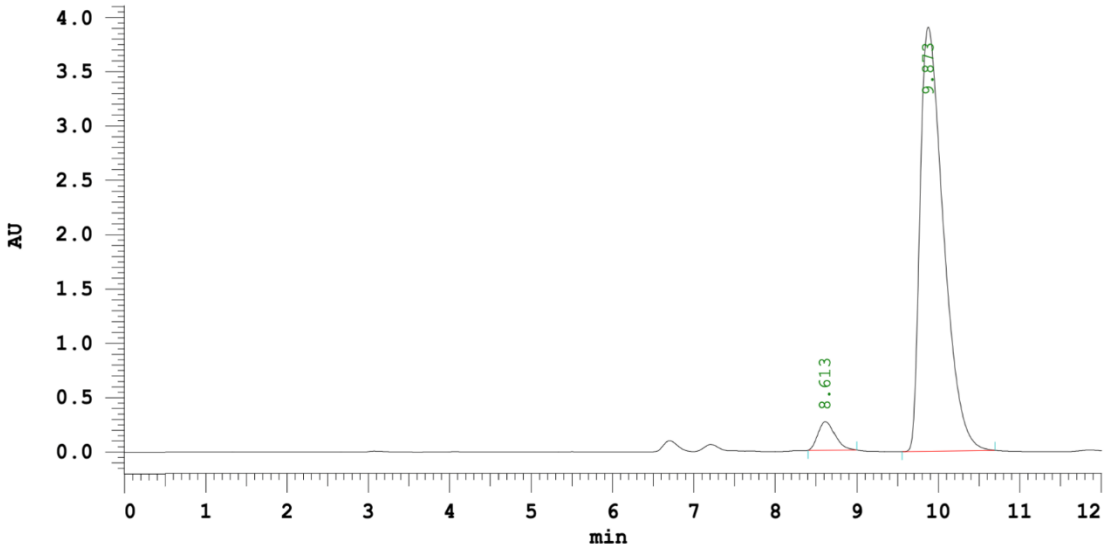
	Retention Time	Area	% Area
1	9.200	1113578	5.011
2	10.760	21108426	94. 989

HPLC Chromatogram of Racemic 26



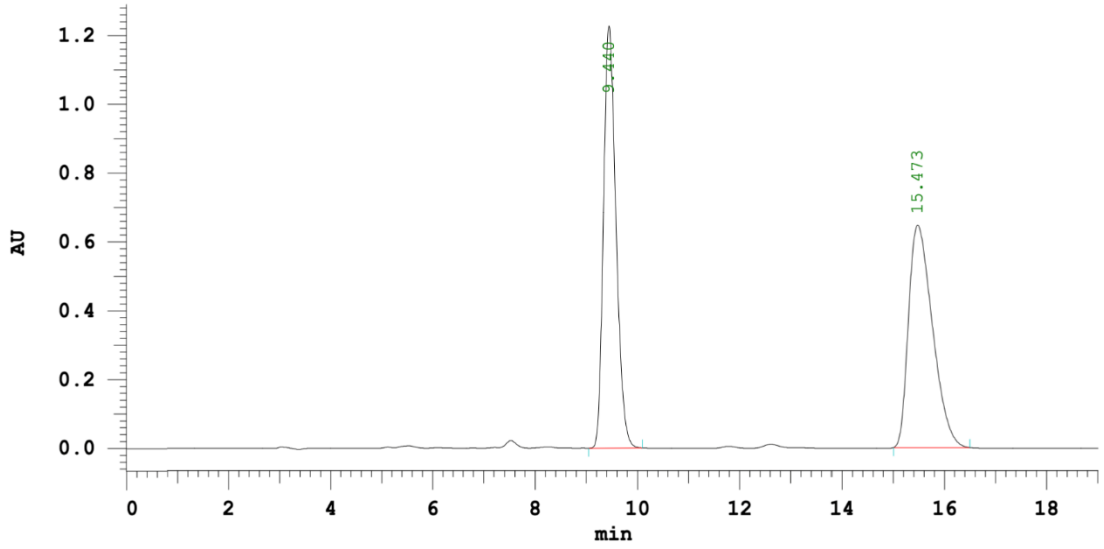
	Retention Time	Area	% Area
1	8.513	8107823	50.258
2	9.920	8024488	49.742

HPLC Chromatogram of Chiral 26



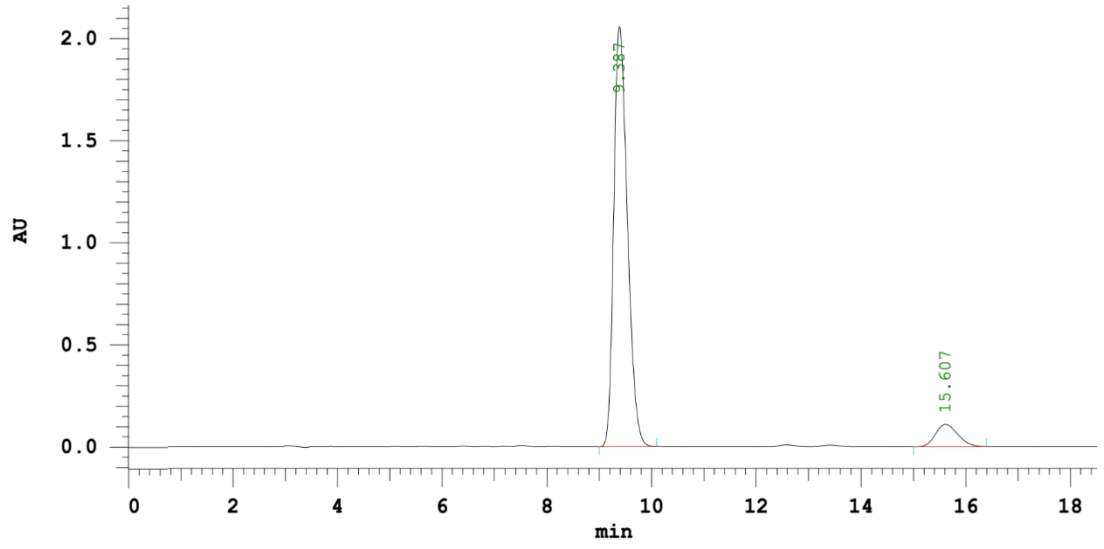
	Retention Time	Area	% Area
1	8.613	1876400	4.587
2	9.873	39031185	95.413

HPLC Chromatogram of Racemic 27



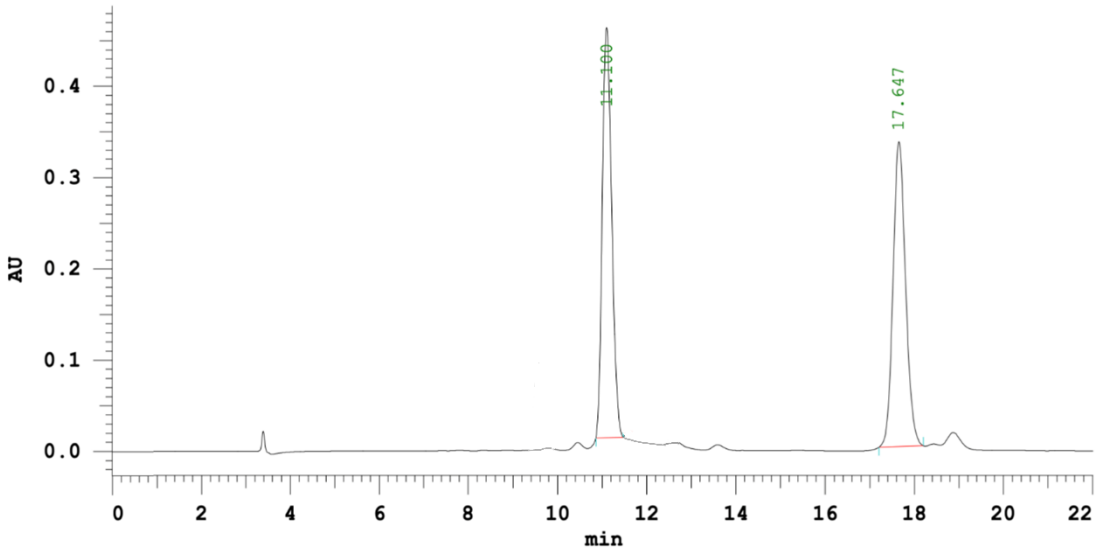
	Retention Time	Area	% Area
1	9.440	10513198	49.964
2	15.473	10528376	50.036

HPLC Chromatogram of Chiral 27



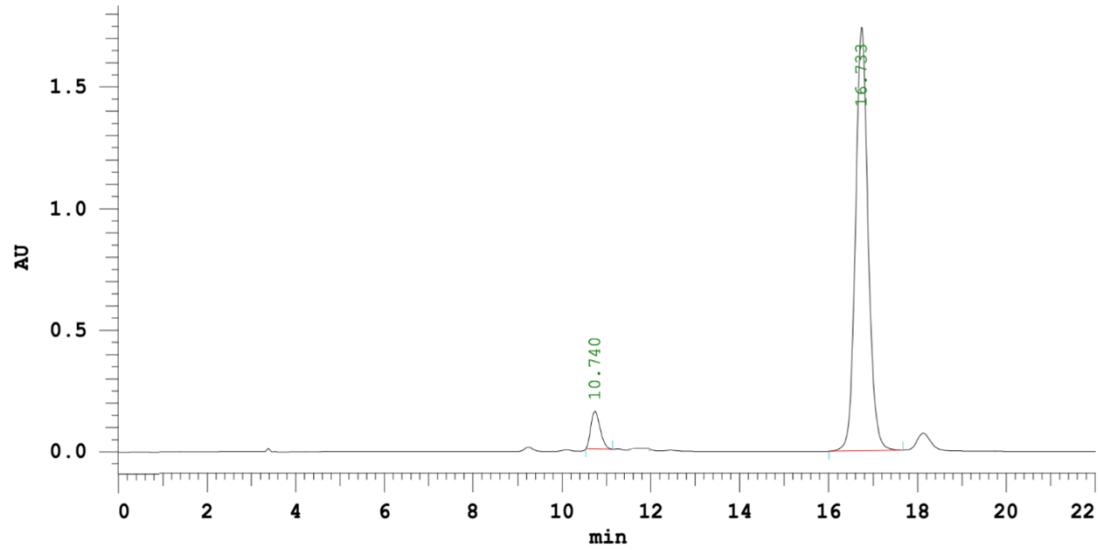
	Retention Time	Area	% Area
1	9.387	18628454	91.930
2	15.607	1635225	8.070

HPLC Chromatogram of Racemic 28



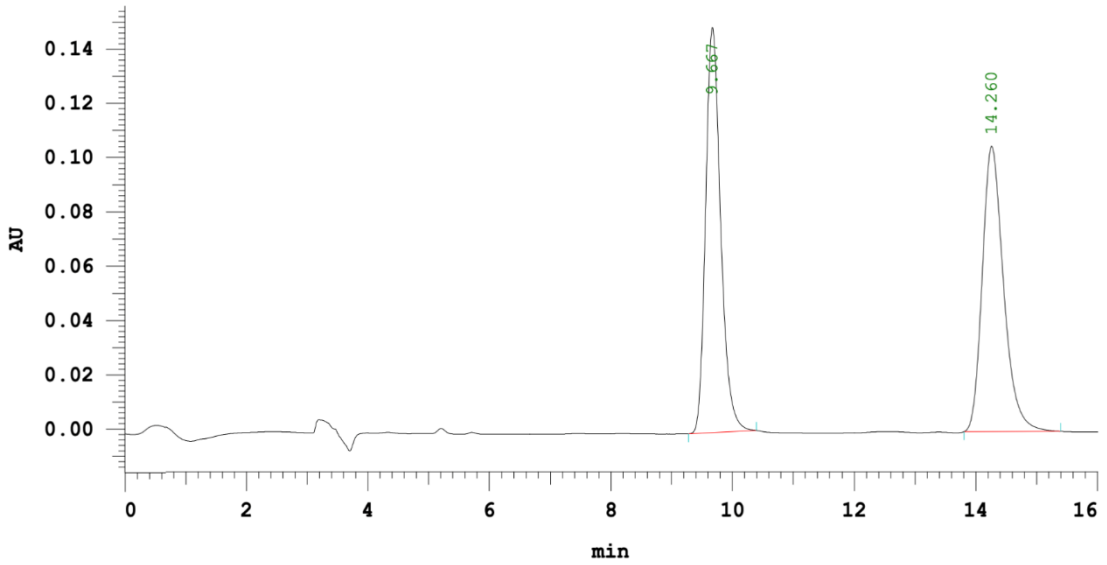
	Retention Time	Area	% Area
1	11.100	3295615	50.301
2	17.647	3256134	49.699

HPLC Chromatogram of Chiral 28



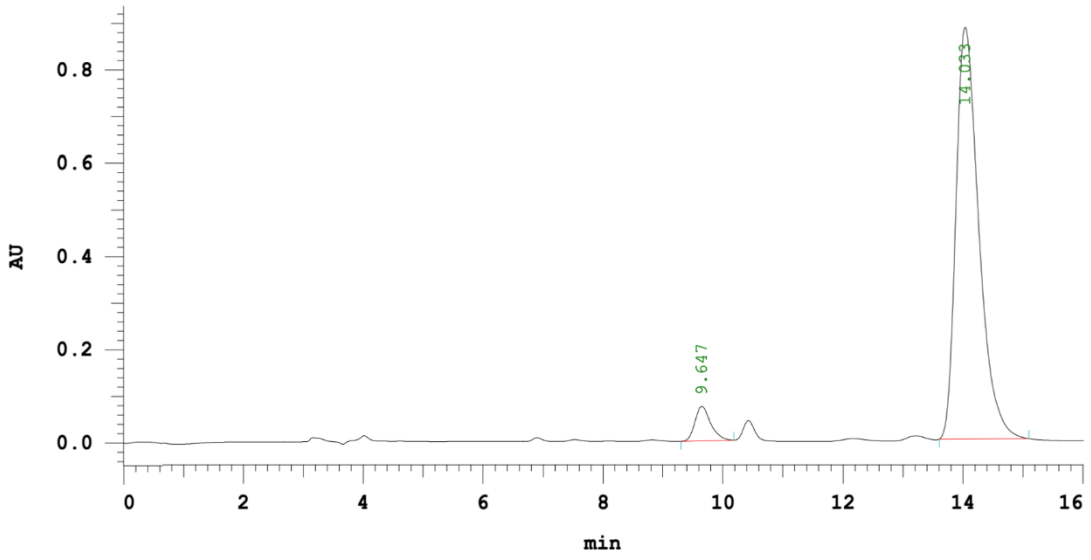
	Retention Time	Area	% Area
1	10.740	1124875	6. 127
2	16.733	17235008	93.873

HPLC Chromatogram of Racemic 29



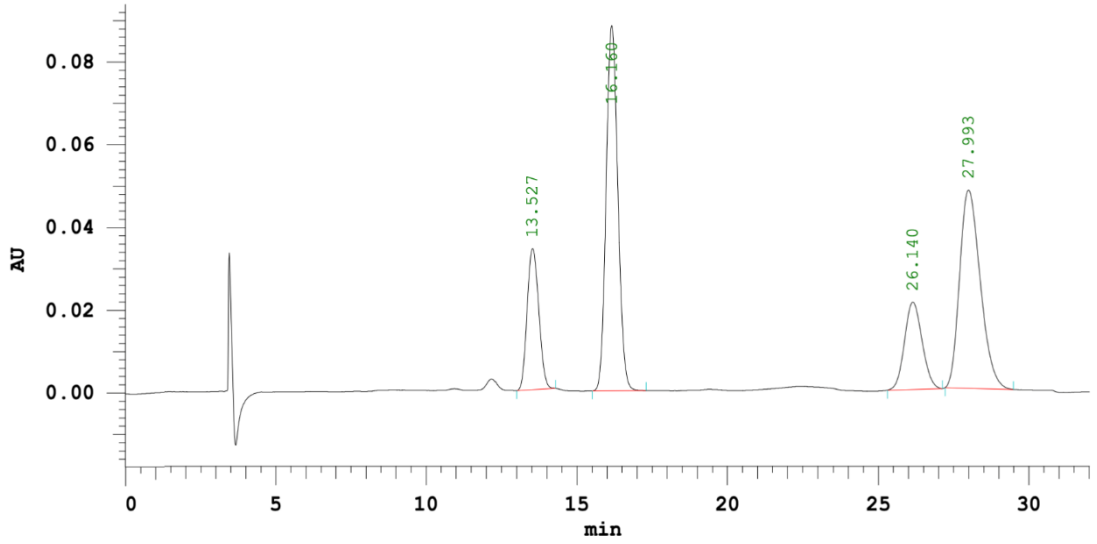
	Retention Time	Area	% Area
1	9.667	1292949	50.020
2	14.260	1291914	49.980

HPLC Chromatogram of Chiral 29



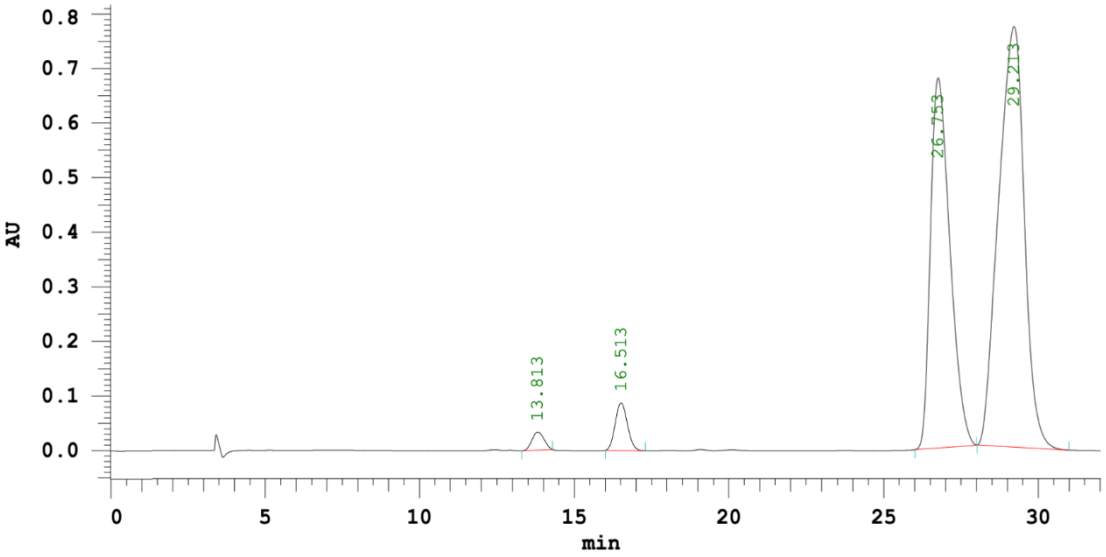
	Retention Time	Area	% Area
1	9.647	673189	5.426
2	14.033	11732421	94.574

HPLC Chromatogram of Racemic 30



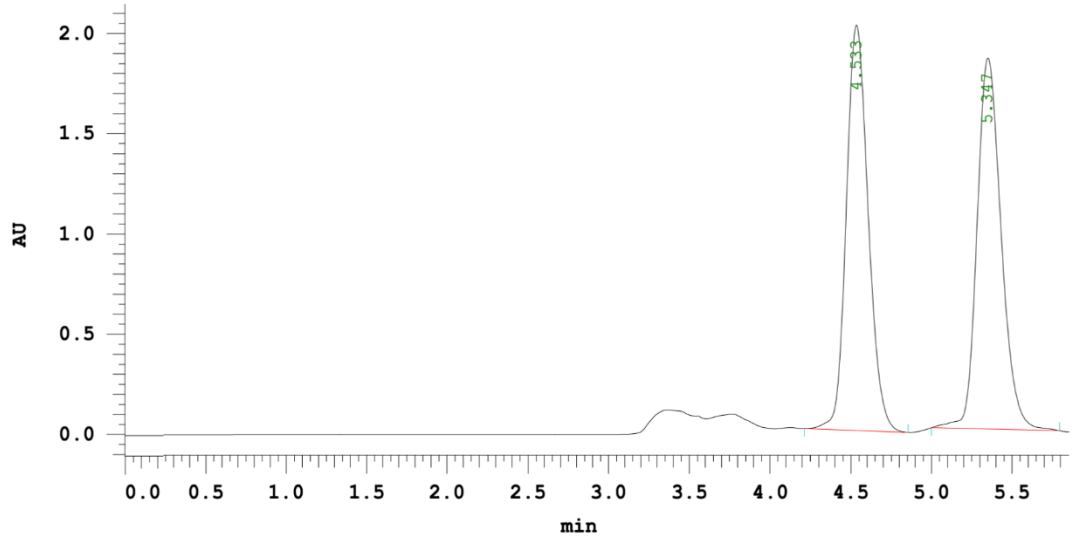
	Retention Time	Area	% Area
1	13.527	455309	14.168
2	16.160	1187314	36.947
3	26.140	426455	13. 270
4	27.993	1144498	35.614

HPLC Chromatogram of Chiral 30



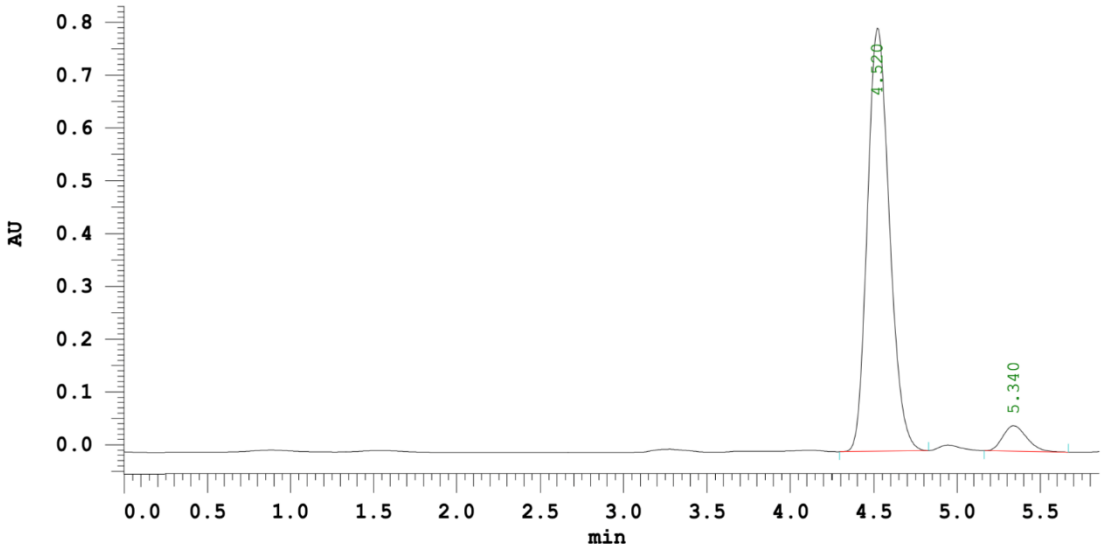
	Retention Time	Area	% Area
1	13.813	439039	1.133
2	16.513	1187609	3.066
3	26.753	14856526	38.351
4	29.213	22255119	57.450

HPLC Chromatogram of Racemic 31



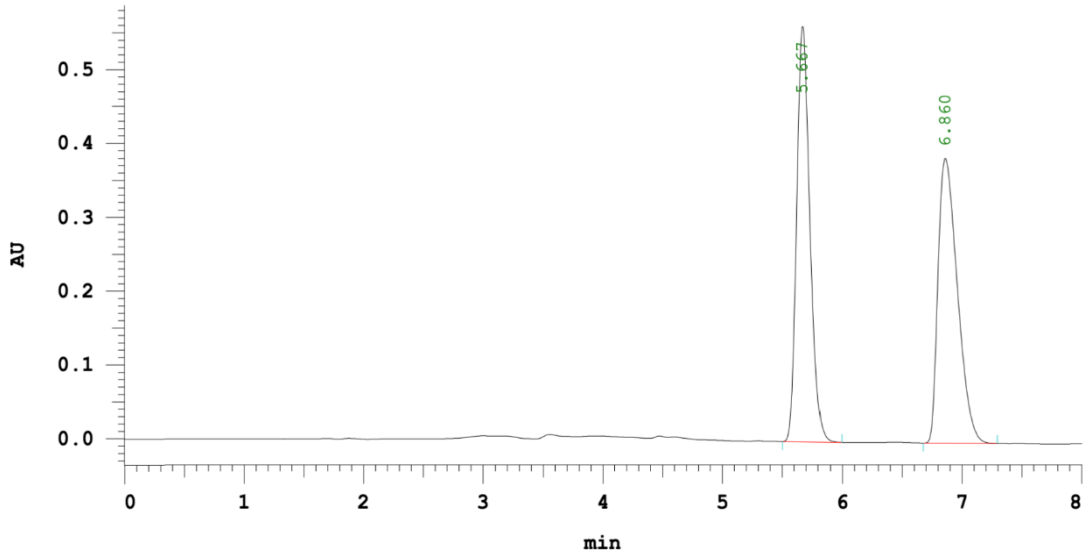
	Retention Time	Area	% Area
1	4.533	9428300	50.357
2	5.347	9294677	49.643

HPLC Chromatogram of Chiral 31



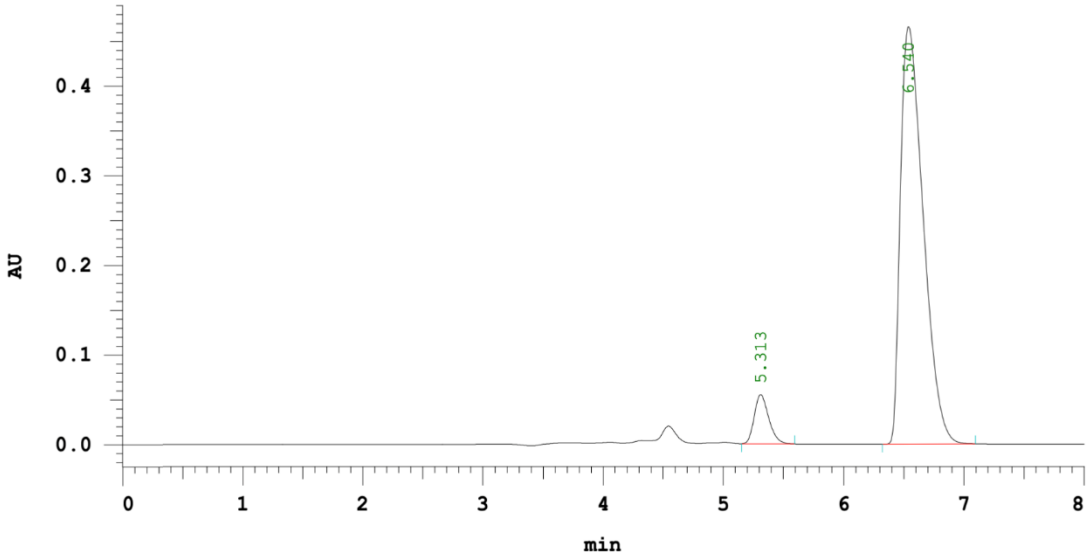
	Retention Time	Area	% Area
1	4.520	3702821	93.901
2	5.340	240509	6.099

HPLC Chromatogram of Racemic 33



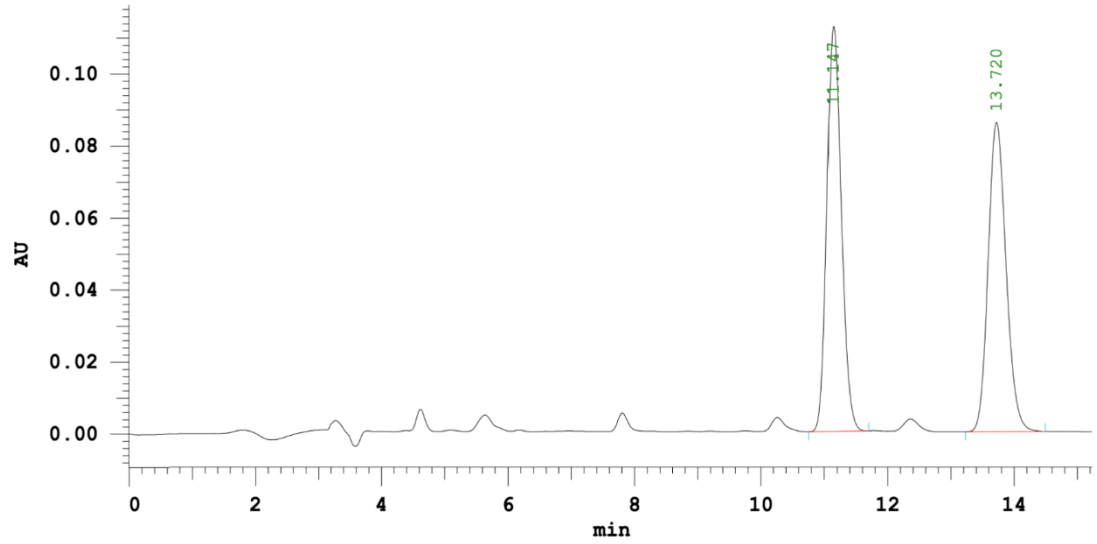
	Retention Time	Area	% Area
1	5.667	2153049	49.845
2	6.860	2166474	50.155

HPLC Chromatogram of Chiral 33



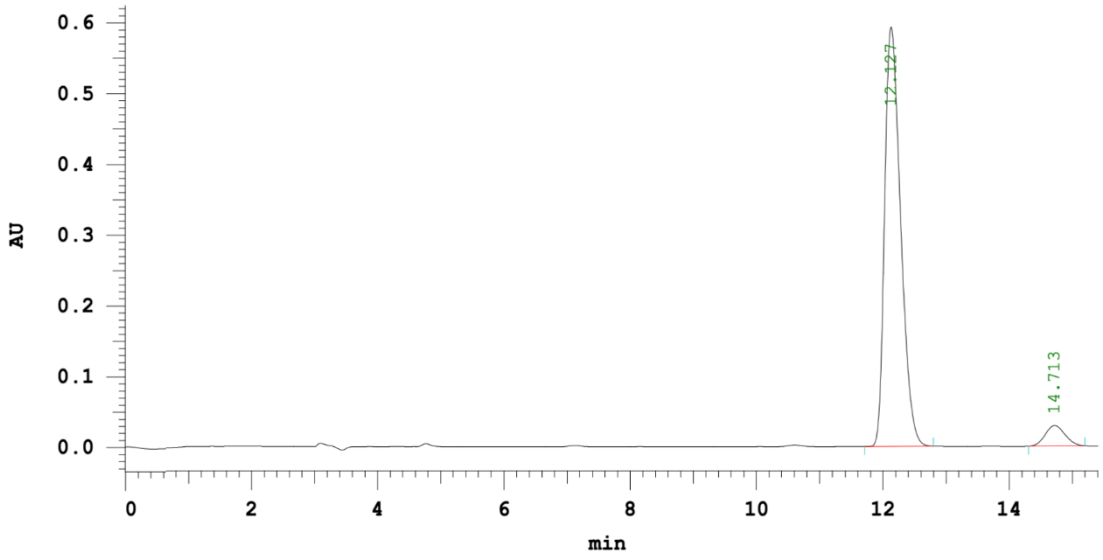
	Retention Time	Area	% Area
1	5.313	231401	7.014
2	6.540	3067569	92.986

HPLC Chromatogram of Racemic 34



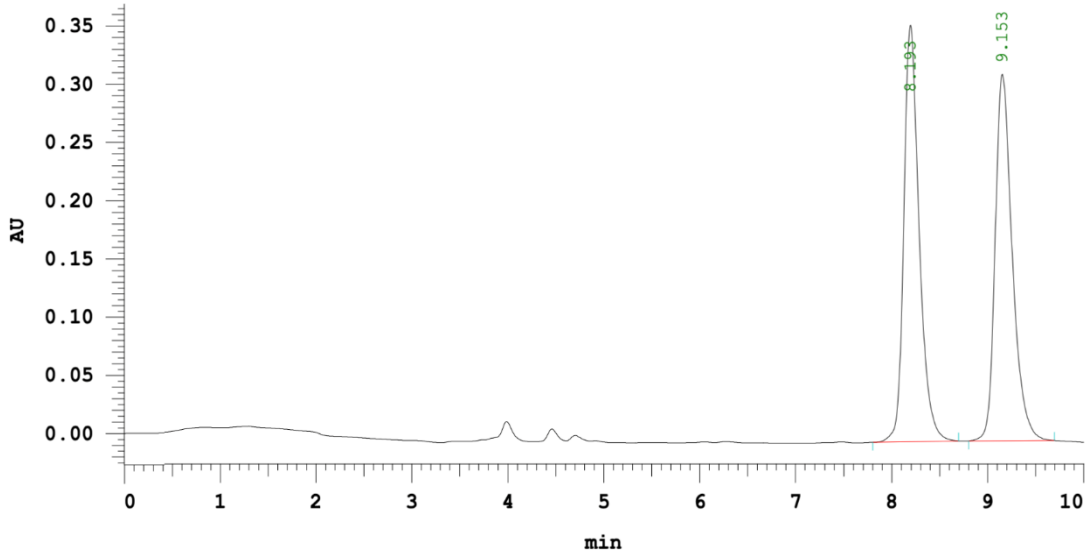
	Retention Time	Area	% Area
1	11.147	880306	50.935
2	13.720	847978	49.065

HPLC Chromatogram of Chiral 34



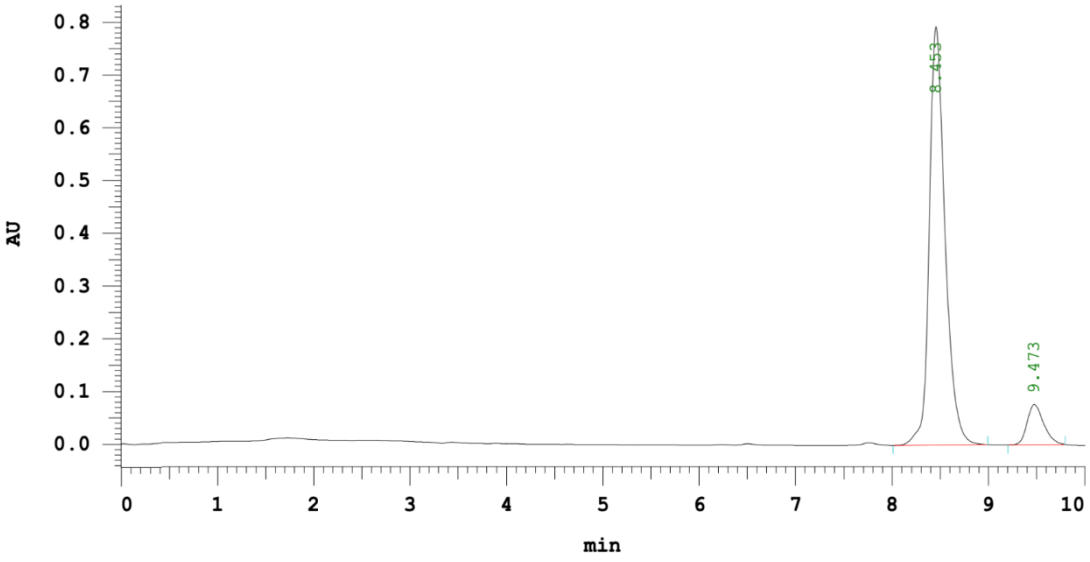
	Retention Time	Area	% Area
1	12.127	5222572	94.294
2	14.713	316058	5.706

HPLC Chromatogram of Racemic 35



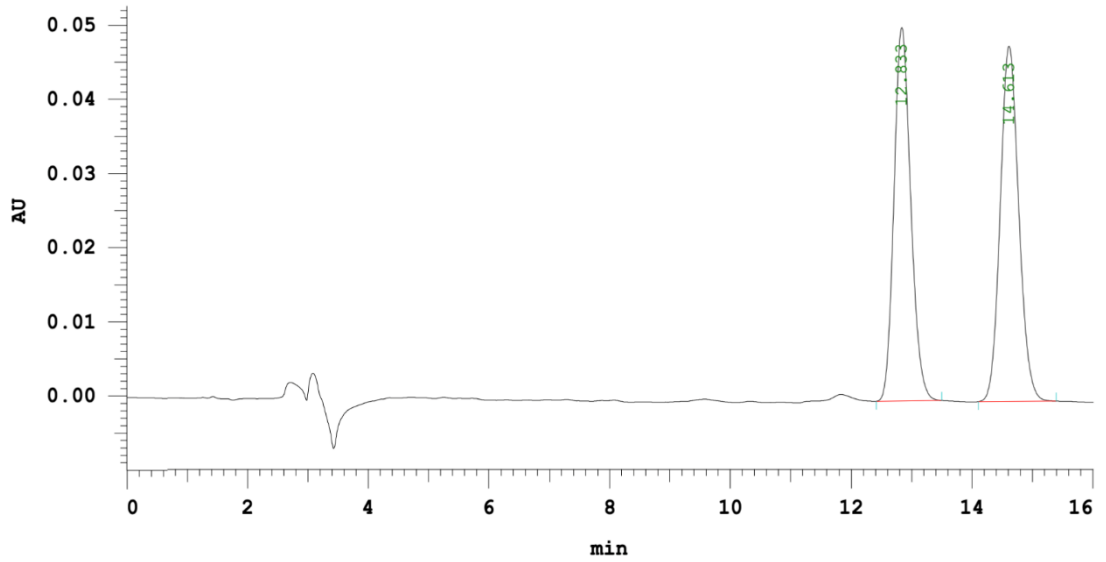
	Retention Time	Area	% Area
1	8.193	1992057	50.456
2	9.153	1956072	49.544

HPLC Chromatogram of Chiral 35



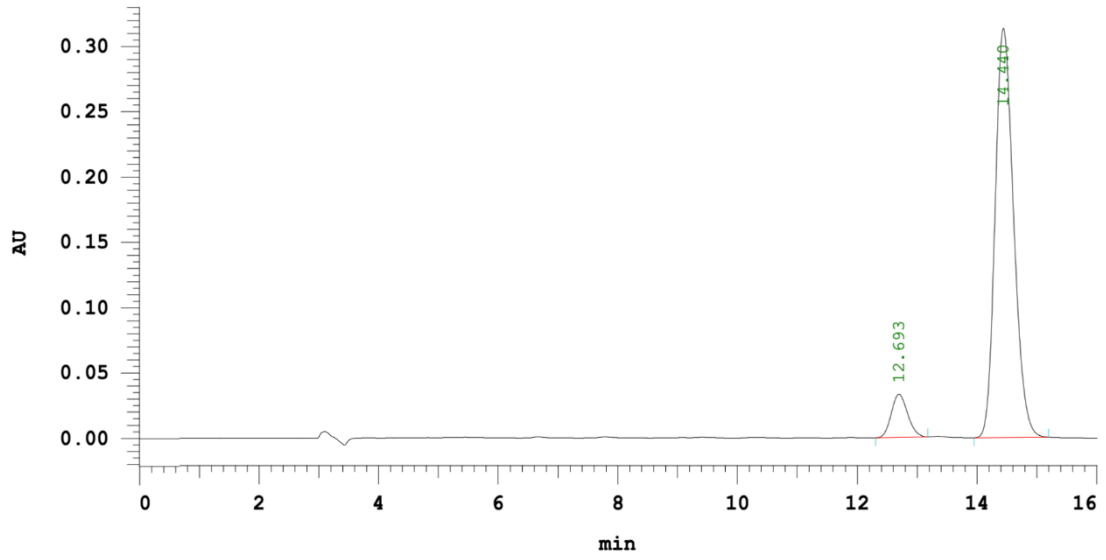
	Retention Time	Area	% Area
1	8.453	4521035	90.775
2	9.473	459424	9.225

HPLC Chromatogram of Racemic 36



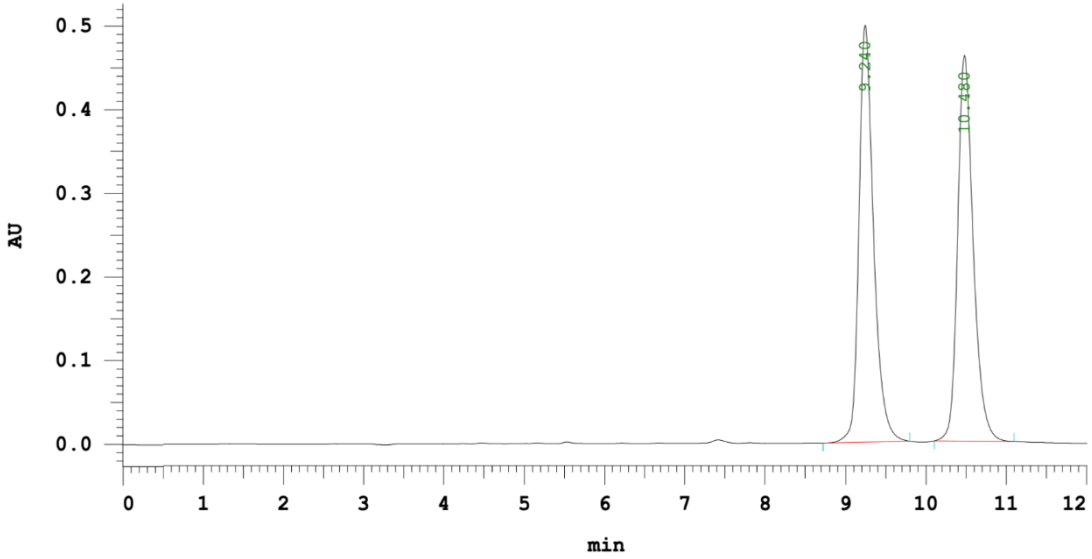
	Retention Time	Area	% Area
1	12.833	505864	49.701
2	14.613	511945	50.299

HPLC Chromatogram of Chiral 36



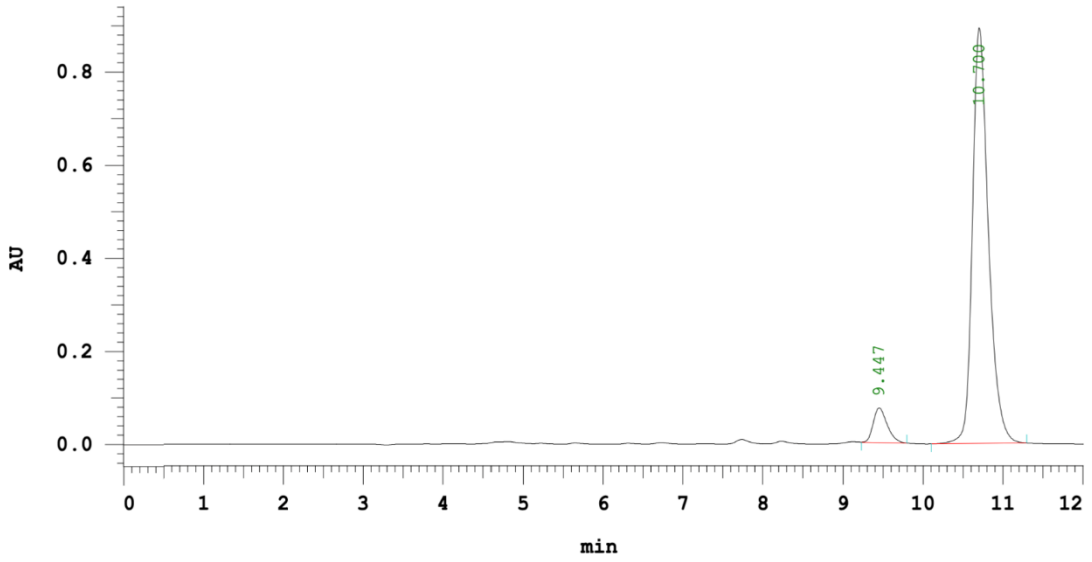
	Retention Time	Area	% Area
1	12.693	311752	8.466
2	14.440	3370521	91.534

HPLC Chromatogram of Racemic 37



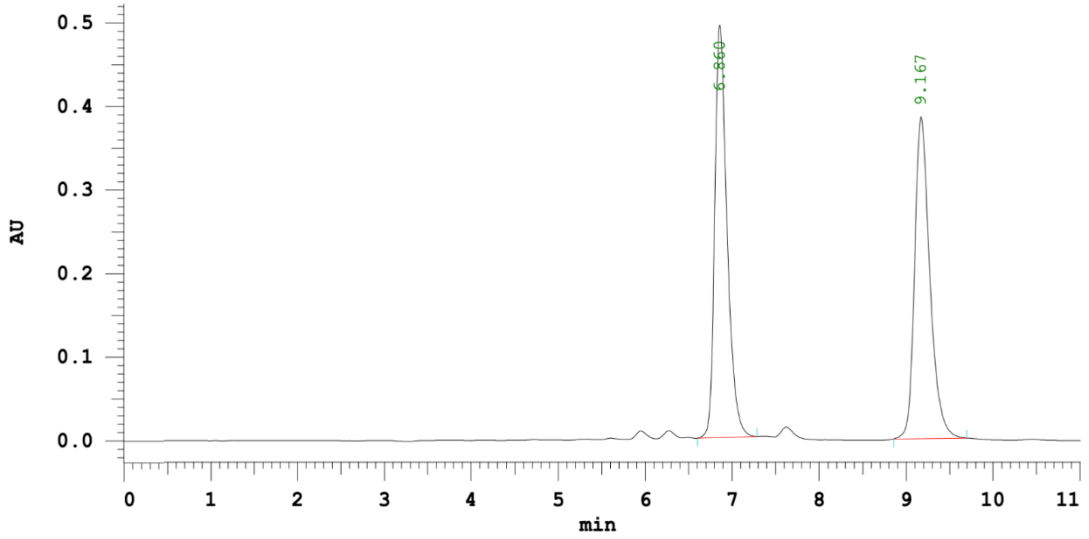
	Retention Time	Area	% Area
1	9.240	3174060	50.457
2	10.480	3116507	49.543

HPLC Chromatogram of Chiral 37



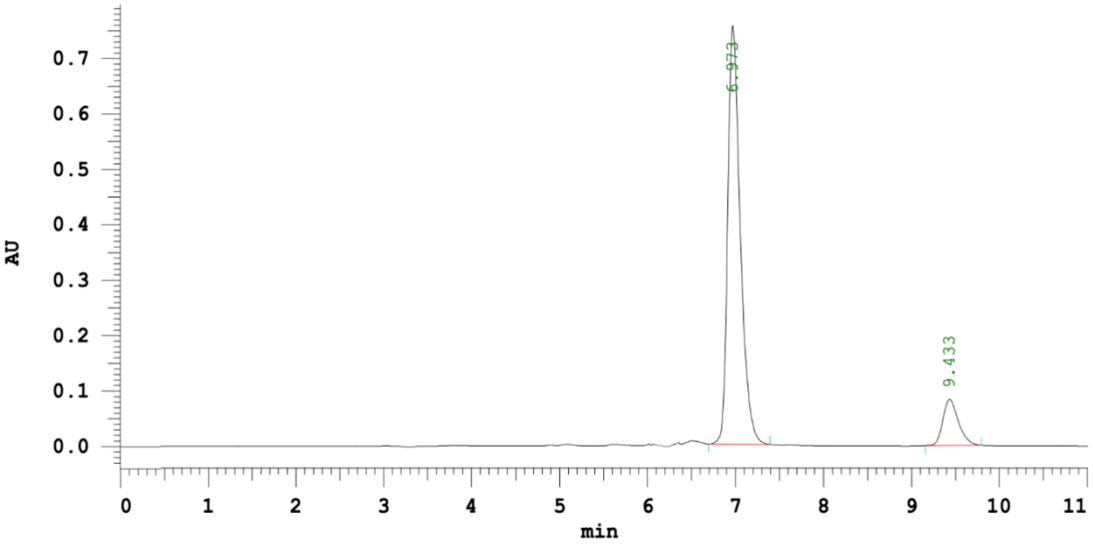
	Retention Time	Area	% Area
1	9.447	448804	6.699
2	10.700	6251109	93.301

HPLC Chromatogram of Racemic 38



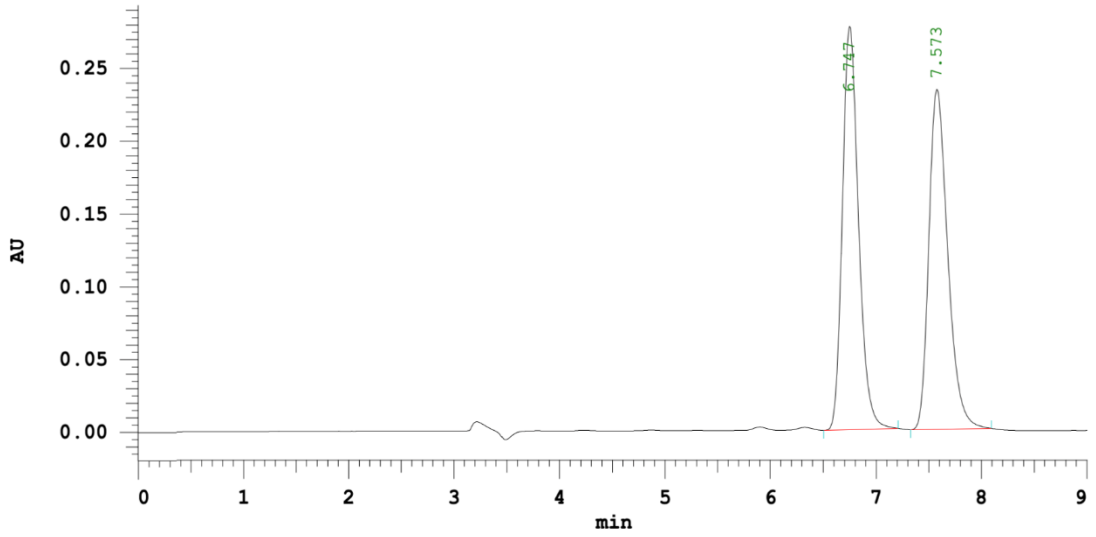
	Retention Time	Area	% Area
1	6.860	2426862	50.684
2	9.167	2361339	49.316

HPLC Chromatogram of Chiral 38



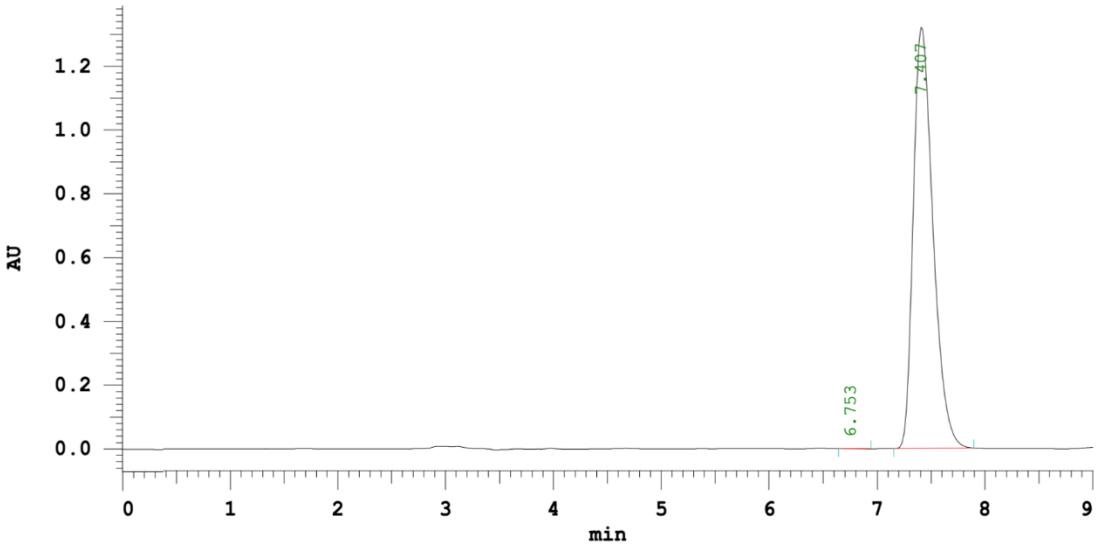
	Retention Time	Area	% Area
1	6.973	3748036	87.975
2	9.433	512304	12.025

HPLC Chromatogram of Racemic 41



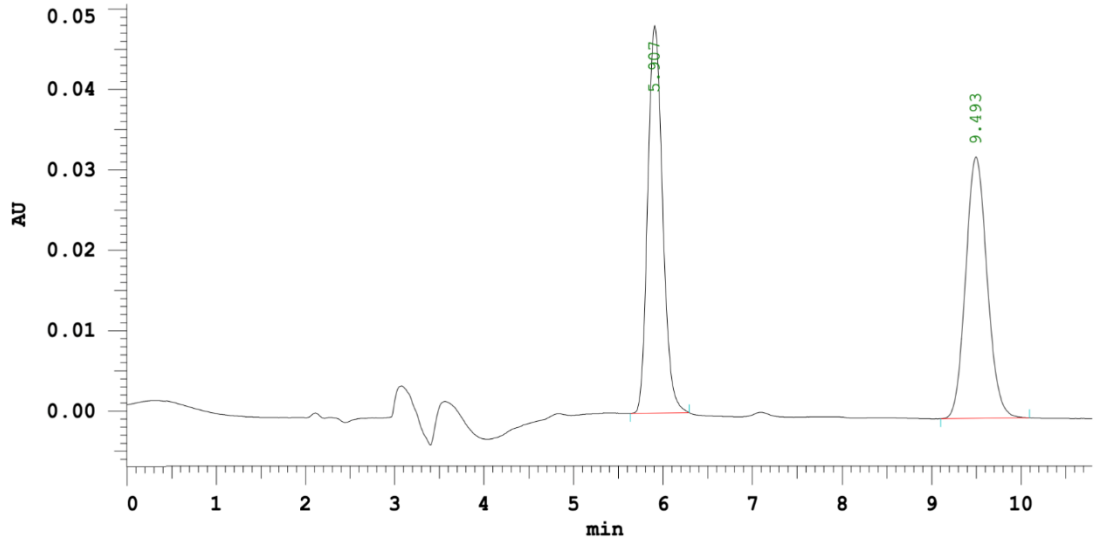
	Retention Time	Area	% Area
1	6.747	1471435	50.162
2	7.573	1461911	49.838

HPLC Chromatogram of Chiral 41



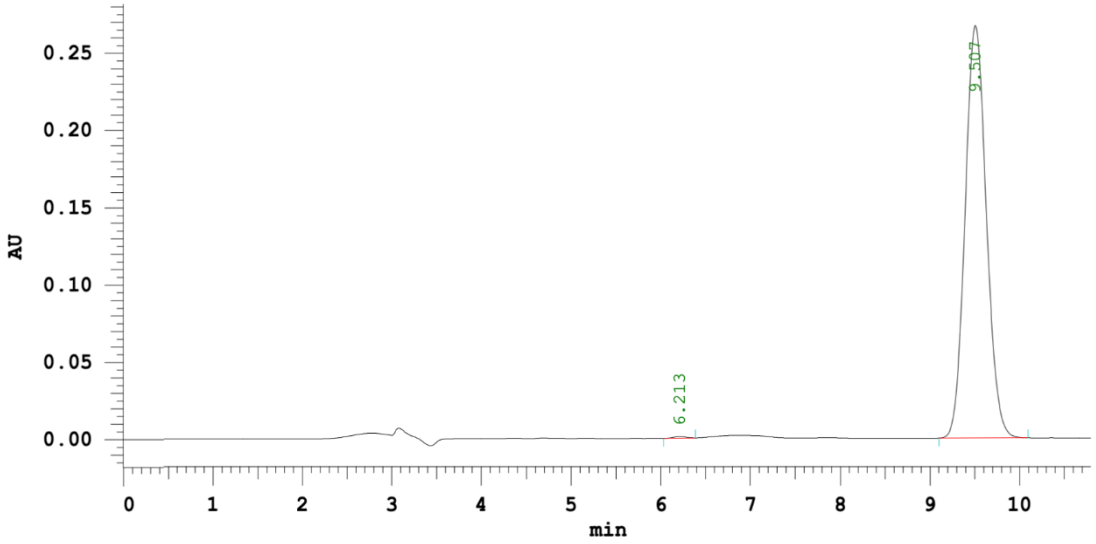
	Retention Time	Area	% Area
1	6.753	3941	0.047
2	7.407	8427523	99.953

HPLC Chromatogram of Racemic 42



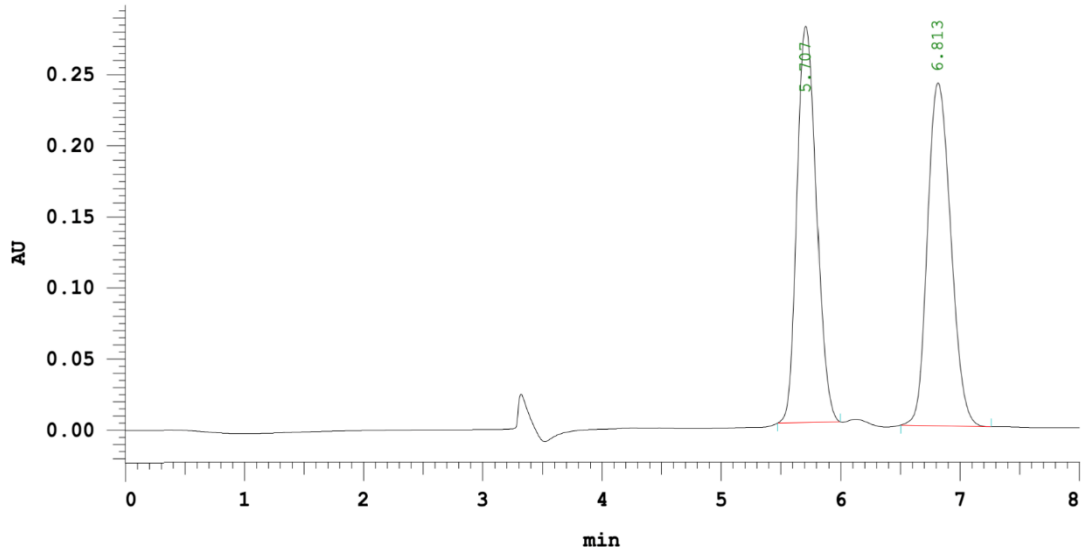
	Retention Time	Area	% Area
1	5.907	280366	50.698
2	9.493	272651	49.302

HPLC Chromatogram of Chiral 42



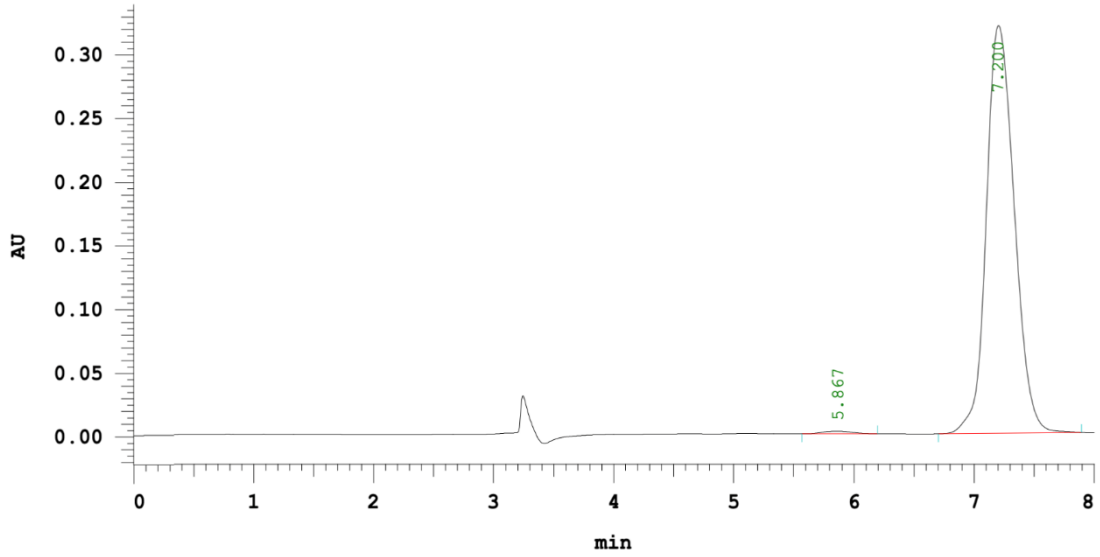
	Retention Time	Area	% Area
1	6.213	4496	0.204
2	9.507	2202726	99.796

HPLC Chromatogram of Racemic 43



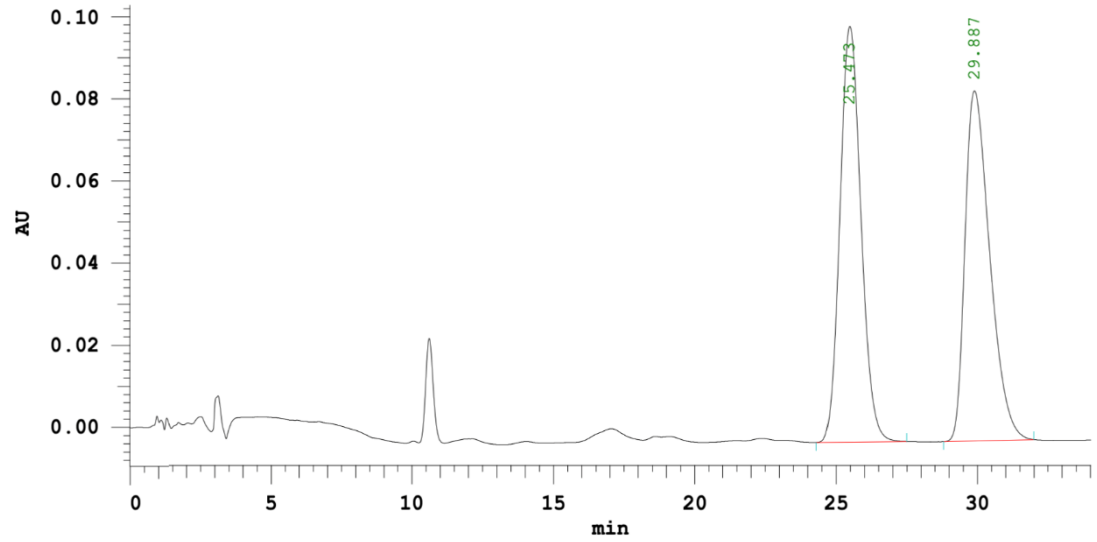
	Retention Time	Area	% Area
1	5.707	1576344	50.551
2	6.813	1541955	49.449

HPLC Chromatogram of Chiral 43



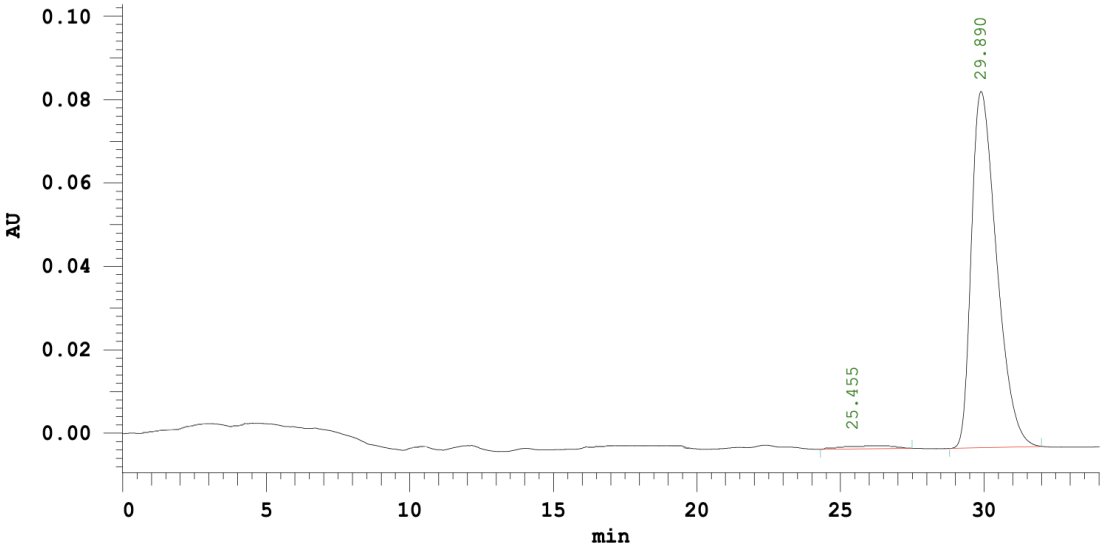
	Retention Time	Area	% Area
1	5.867	16508	0.630
2	7.200	2604110	99.370

HPLC Chromatogram of Racemic 44



	Retention Time	Area	% Area
1	25.473	2602182	50.043
2	29.887	2597736	49.957

HPLC Chromatogram of Chiral 44



	Retention Time	Area	% Area
1	25.455	2601995	0.689
2	29.890	18052	99.311