---Supporting information---

Concise Synthesis of Azilect via Cobalt-Catalyzed Enantioselective Hydrogenation in Bio-based Solvent

Soumyadeep Chakrabortty,[a] Felix J. de Zwart,[b] Demi D. Snabilié,[b] Ekambaram Balaraman,[c] Joost N. H. Reek,[b] Bas de Bruin,[b] Johannes G. de Vries*[a]

[a] Soumyadeep Chakrabortty, Ekambaram Balaraman, Johannes G. de Vries

Leibniz Institute for Catalysis e.V.

Albert-Einstein-Strasse 29a,18059 Rostock

Email: Johannes.deVries@catalysis.de

[b] Felix J. de Zwart, Demi D. Snabilié, Joost N. H. Reek, Bas de Bruin

Van't Hoff Institute for Molecular Sciences (HIMS), Science Park 904,

1098 XH Amsterdam, The Netherlands.

[c] Department of Chemistry, Indian Institute of Science Education and Research (IISER) Tirupati, Tirupati - 517507, Andhra Pradesh, India.

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1. General information

Chemical and solvents

All the reactions have been carried out using standard Schlenk techniques or under inert atmosphere in N_2 – filled glove box, unless noted otherwise. All the chemicals used were commercial grade and utilized without further purifications. All the chiral ligands have been purchased from Strem chemicals and directly used for further catalytic reactions. 2-Me THF was purchased from Merck (anhydrous and inhibitor free) and directly used for catalysis. All the other solvents were pre-dried with Solvent Purification System (SPS) from MBraun (MB SPS-800, with standard MBraun drying columns) as required. All the solvents were stored on activated 3 Å molecular sieves and degassed by sparging with argon before using in catalysis.

NMR spectroscopy

NMR spectra were recorded on Bruker Avance 300 (^{1}H: 300, ^{13}C: 75, ^{31}P: 121 MHz), Bruker Fourier 300 (^{1}H: 300, ^{13}C: 75, ^{31}P: 121 MHz) or Avance 400 (^{1}H: 400, ^{13}C: 100, ^{31}P: 161 MHz) instruments operating at the denoted spectrometer frequency given in megahertz (MHz) for the specified nucleus.

EPR spectroscopy

EPR measurements were performed in air-tight high-pressure tube (Wilmad 734-PV-7) in an atmosphere of purified argon. Frozen solution EPR spectra were recorded on a Bruker EMX-plus CW X-band spectrometer equipped with a Bruker ER 4112HV-CF100 helium cryostat.

High performance liquid chromatography (HPLC)

The chiral amides have been analyzed with chiral column in Agilent 1200 series HPLC. Method and column information have already been described in the HPLC traces.

Gas chromatography (GC)

The samples have been analyzed with Agilent HP6890 instrument with FID detector and a column. *HP5 (30 m x 250 mm x 0.25 μm)*: Front Injector Syringe Size 10 μL, Syringe 10 μL Agilent G4513-80203 , Injection Volume 1 μL, Front SS Inlet He, Mode Split Heater On 250 °C

Pressure On 0.60993 bar, Total Flow On 86.971 mL/min, Septum Purge Flow On 3 mL/min Pressure 0.60993 bar, Flow 1.6465 mL/min, Average Velocity 29.749 cm/sec Run Time 33.5 min

CP-Chirasil-Dex CB (25.955m x 320 μm x 0.25 μm): Flow 3 mL/min, Pressure 13.698 psi, Avg vel. 51.506 cm/sec, Initial 100 °C-hold 5 min, ramp (5 °C/min) 150 °C-hold 30 min, ramp (5 °C/min) 180 °C-hold 5°C, runtime 56 min

2. *Indanone derived carbocyclic enamide synthesis and analytical data*

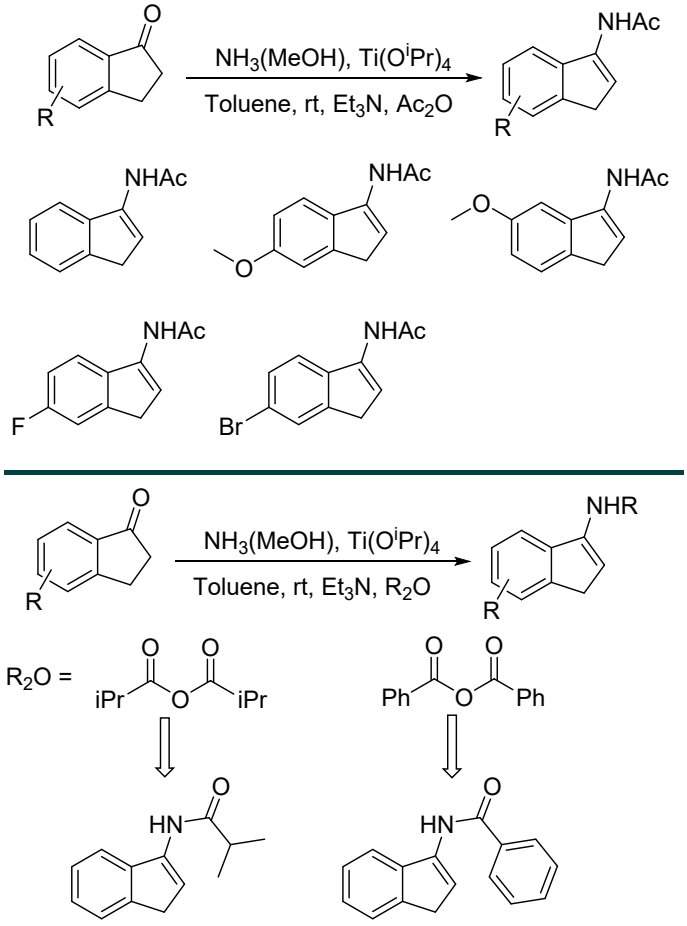


Figure S 1 General procedure for substrate synthesis

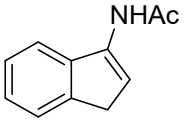
Indanone-enamide synthesis: Using the Ti-method (Ref. J. T. Reeves, Z. Tan, Z. S. Han, G. Li, Y. Zhang, Y. Xu, D. C. Reeves, N. C. Gonnella, S. Ma, H. Lee, B. Z. Lu and C. H. Senanayake, Angew. Chem. Int. Ed., 2012, 51, 1400-1404. ()

To a dry 50 mL Schlenk flask equipped with a magnetic stir bar was charged indanone derivative (1.17 mL, 10.0 mmol, 1 equiv.) and toluene (5 mL). The resultant solution was stirred and cooled in an

ice/water bath. To the cold stirring solution was added 7N NH_3 in MeOH (2.14 mL, 15.0 mmol, 1.5 equiv.) followed by dropwise addition of $Ti(Oi\text{-}Pr)_4$ (5.92 mL, 20.0 mmol, 2.0 equiv.) maintain the inert conditions. After 10 min, the ice/water cooling bath was removed, and the solution was stirred at rt for 18-24 h. The reaction mixture was then cooled in an ice/water bath (~5 °C) and treated with Et_3N (5.58 mL, 40.0 mmol, 4.0 equiv.) followed by Ac_2O (1.89 mL, 20.0 mmol, 2.0 equiv.). The cooling bath was then removed, and the solution was stirred at rt for 1-3 h. The reaction mixture was then treated with EDTE (4.51 mL, 21.0 mmol, 2.1 equiv.) at rt, and the solution was then heated at about 55 °C for 15 min The reaction mixture was allowed to cool to rt and was then poured into a separatory funnel containing a solution made from water (30 mL) and NH_4OH (10 mL) and also EtOAc (50 mL). Additional water and EtOAc were used to rinse all the flask contents into the separatory funnel. The mixture was shaken, and from the resultant two clear phases the lower aqueous phase was removed. The aqueous phase was extracted in dichloromethane or ethyl acetate. The combined organic extracts were dried ($MgSO_4$), filtered, and concentrated to give the crude product (as mostly dark solid). Purification by flash chromatography on SiO_2 (hexanes/EtOAc, 90:10 to 60:40) gave the corresponding enamides (1.31 g, 60-75% yield). The isopropyl and phenyl derivative can easily be synthesized upon using the corresponding anhydride derivatives.

Analytical data of the enamides:

- ***N-(1H-inden-3-yl)acetamide***



^{1}H NMR (300 MHz, CD_2Cl_2) δ; 7.70 (br, 1H), 7.50-7.48 (m, 1H), 7.38-7.23 (m, 2H), 6.83 (t, J = 2.47 Hz, 1H), 3.43 (dd, J = 2.44 Hz, 2H), 2.21 (s, 3H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ; 168.66, 142.90, 139.79, 125.94, 125.36, 124.19, 116.31, 115.27, 36.48, 23.93.

HRMS: m/z calculated for $C_{11}H_{11}NO$: 174.21 $[M+H]^+$; observed 174.31.

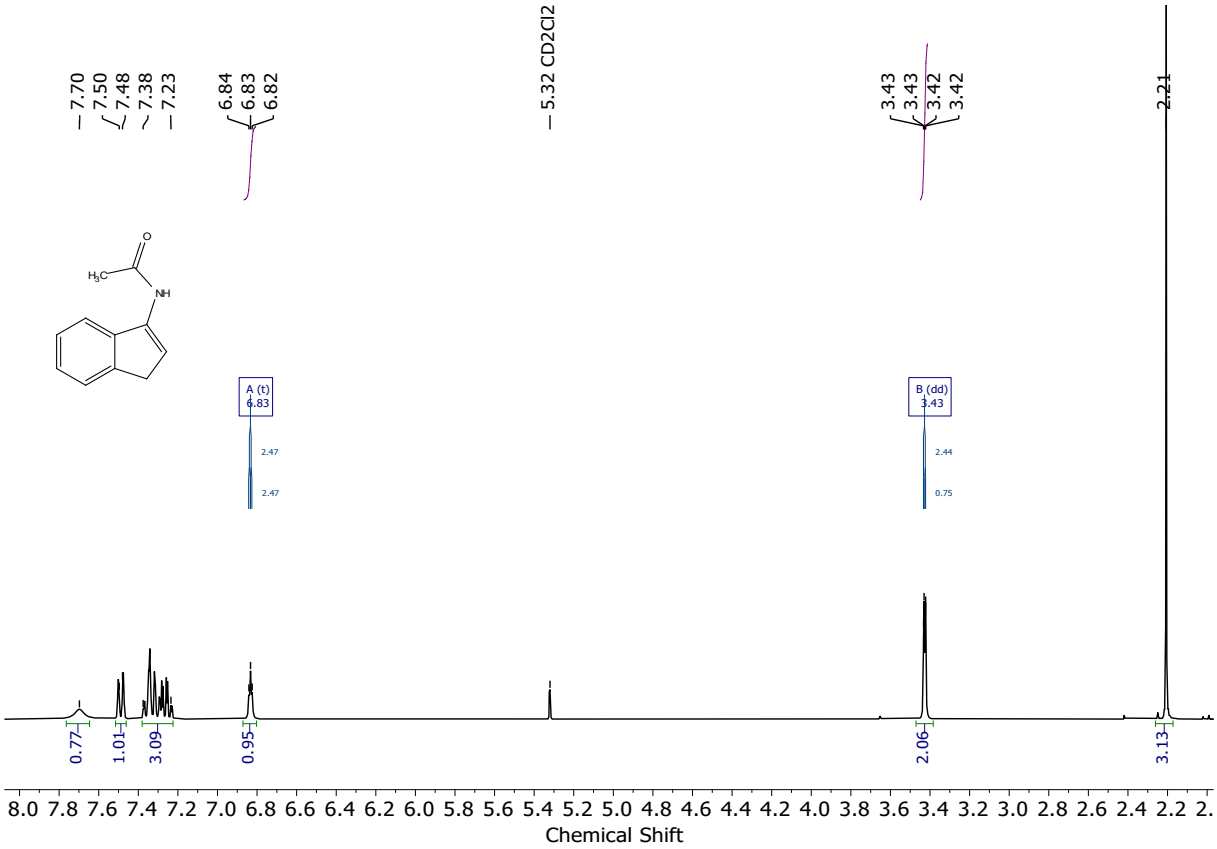


Figure S 2 ^{1}H NMR of 1a

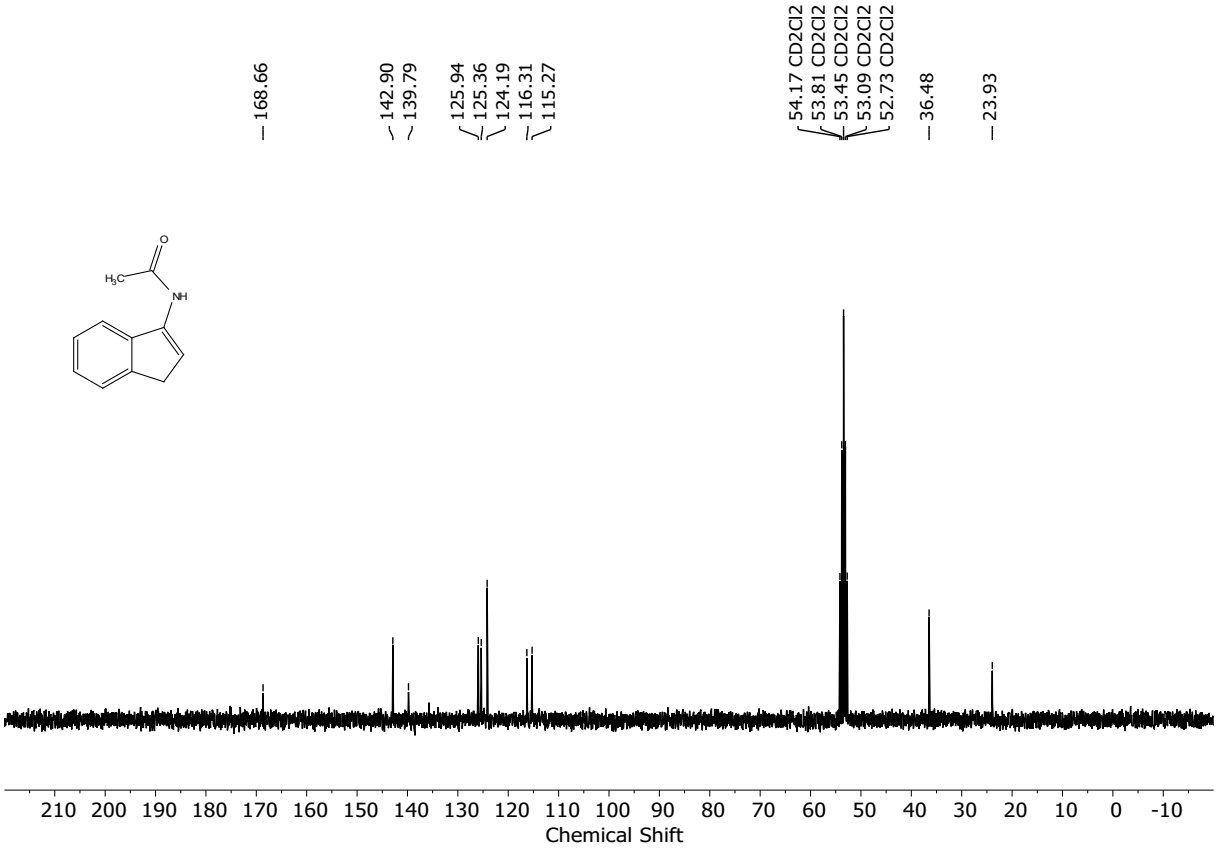
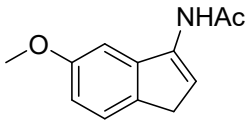


Figure S 3 ^{13}C NMR of 1a

- ***N-(5-methoxy-1H-inden-3-yl)acetamide***



^{1}H NMR (300 MHz, DMSO) δ; 9.69 (br, 1H), 7.45 (d, J = 2.40 Hz, 1H), 7.32 (dd, J = 8.23 Hz, 1H), 6.80-6.76 (m, 2H), 3.80 (s, 3H), 3.38 (s, 1H), 3.29-3.28 (m, 2H), 2.13 (s, 3H).

^{13}C NMR (75 MHz, DMSO) δ; 169.27, 158.88, 141.86, 137.04, 134.64, 124.73, 115.42, 111.67, 104.36, 55.78, 55.57, 35.60, 23.98, 23.33, 14.53.

HRMS: m/z calculated for $C_{12}H_{13}NO_2$: 204.29 $[M+H]^+$; observed 204.26

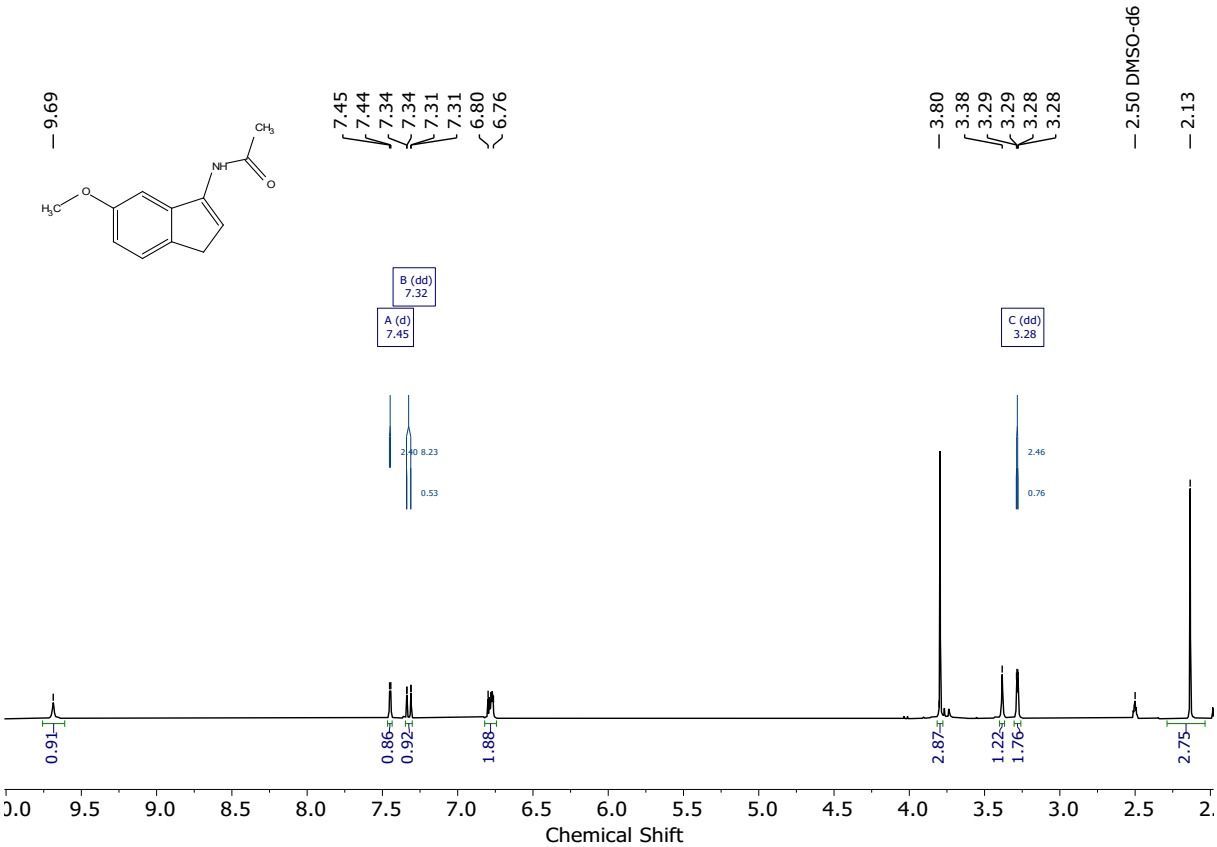


Figure S 4 ^{1}H NMR of 4a

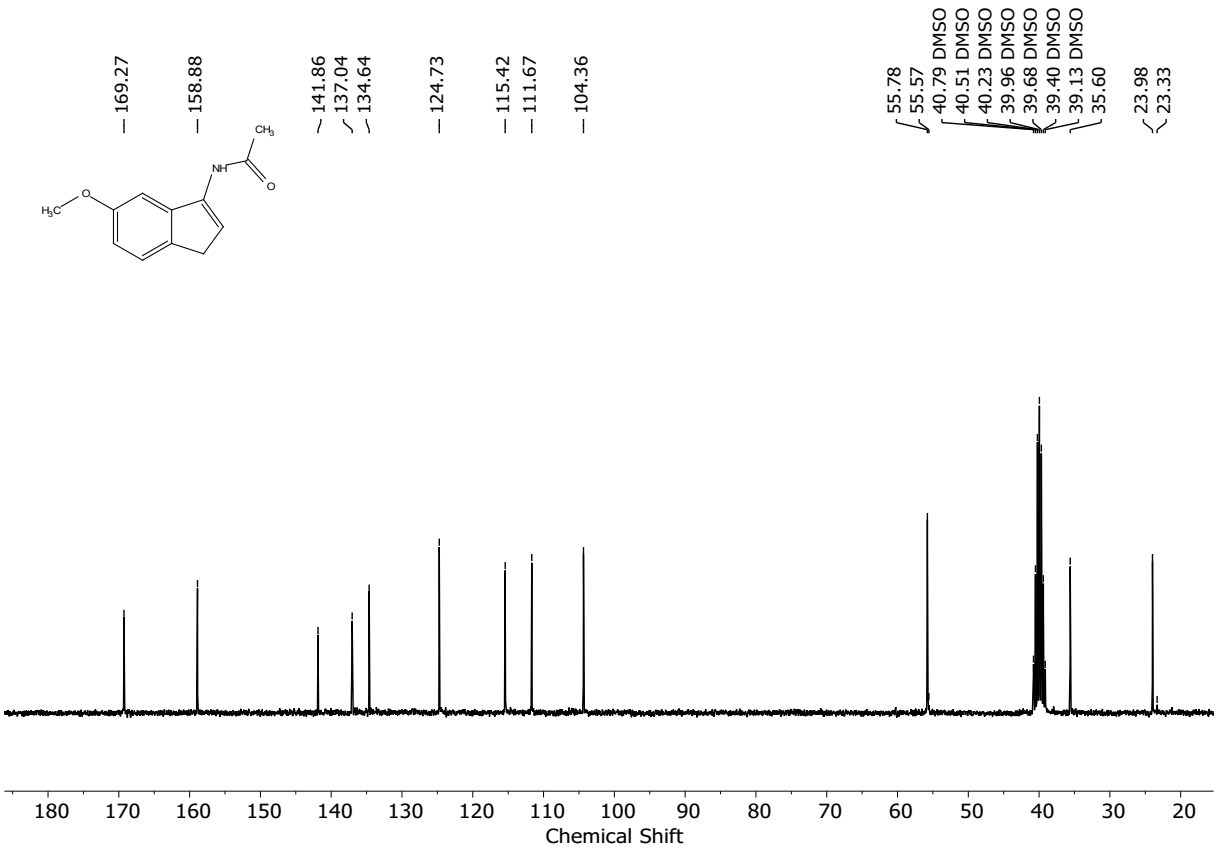
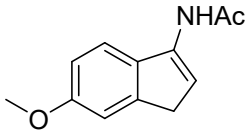


Figure S 5 ^{13}C NMR of 4a

- ***N-(6-methoxy-1H-inden-3-yl)acetamide***



^{1}H NMR (300 MHz, DMSO) δ; 9.68 (br, 1H), 7.66 (d, J= 8.43 Hz, 1H), 7.08 (s, 1H), 6.90 (dd, J = 8.41 Hz), 6.59 (m, 1H), 3.77 (s, 3H), 3.36 (m, 2H), 2.11 (s, 3H).

^{13}C NMR (75 MHz, DMSO) δ; 169.25, 158.33, 144.72, 136.76, 133.50, 119.12, 112.00, 111.92, 110.69, 55.70, 36.34, 23.95.

HRMS: m/z calculated for $C_{12}H_{13}NO_2$: 204.37 $[M+H]^+$; observed 204.31

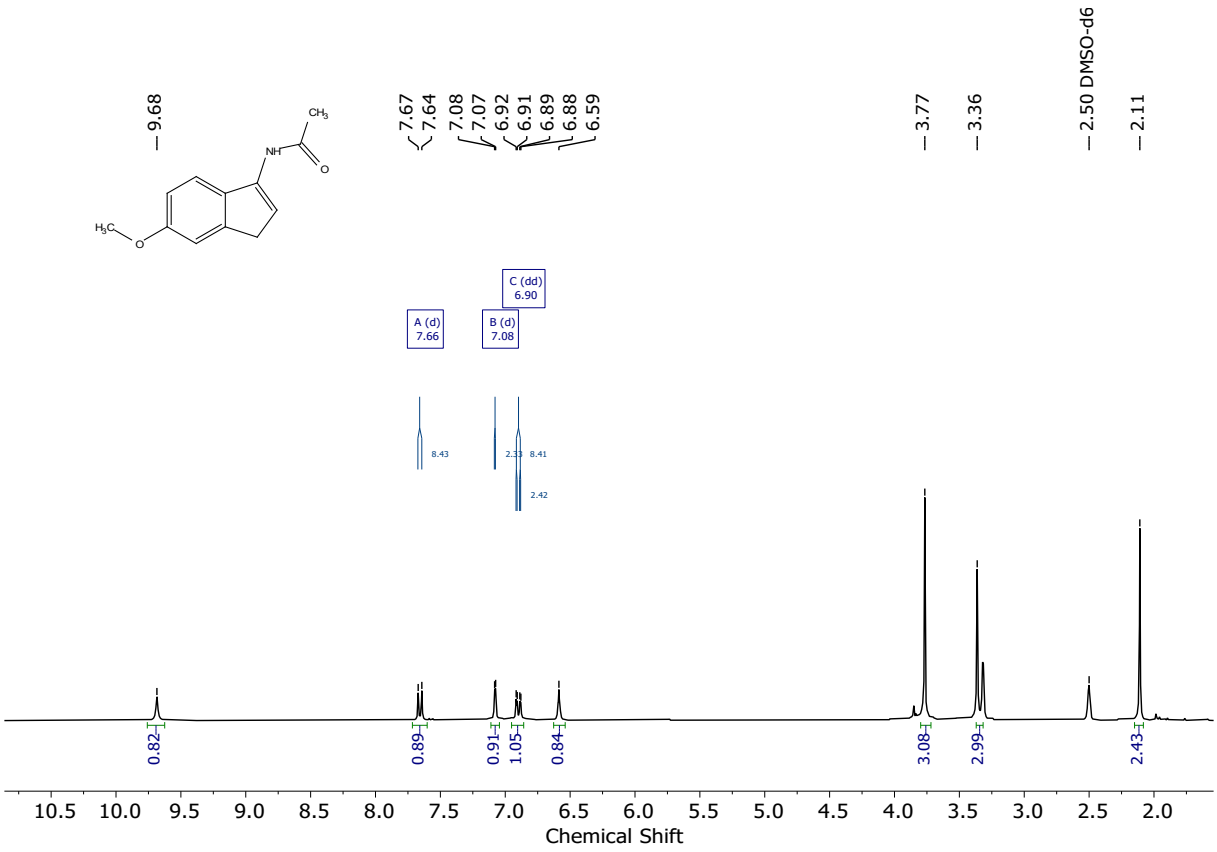


Figure S 6 ^{1}H NMR of 5a

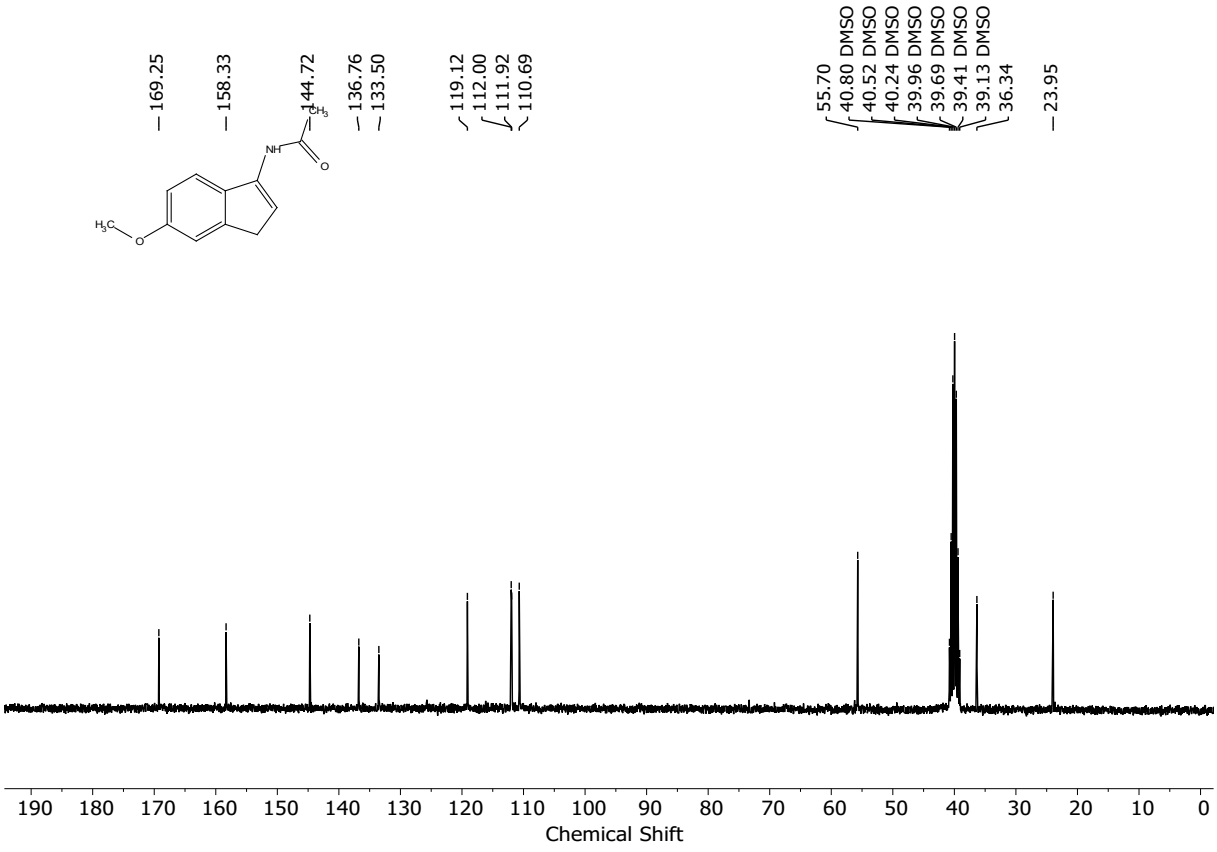
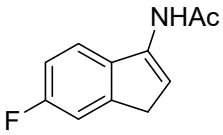


Figure S 7 ^{13}C NMR of 5a

- ***N-(6-fluoro-1H-inden-3-yl)acetamide***



^{1}H NMR (300 MHz, DMSO) δ; 9.77 (br, 1H), 7.76 (dd, J = 8.48 Hz, 1H), 7.31 (dd, J = 9.04 Hz, 1H), 7.16 (m, 1H), 6.73 (br, 1H), 3.37 (s, 3H), 2.12 (2H).

^{13}C NMR (75 MHz, DMSO) δ; 169.35, 163.03, 159.84, 145.40, 145.28, 136.84, 136.81, 136.43, 119.70, 119.59, 114.18, 114.13, 113.27, 112.97, 112.09, 111.79, 36.46, 36.43, 23.92.

HRMS: m/z calculated for $C_{10}H_{10}FNO$: 192.19 $[M+H]^+$; observed 192.25

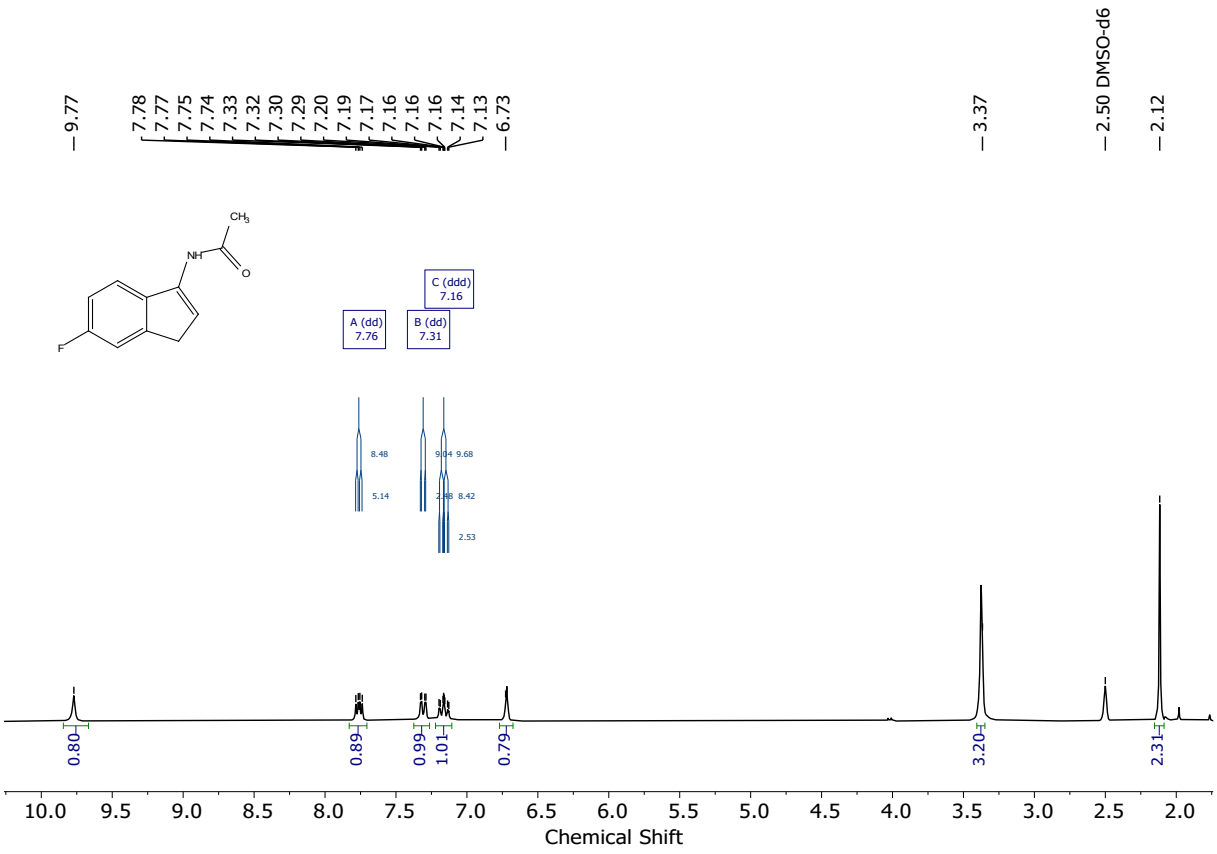


Figure S 8 ^{1}H NMR of 6a

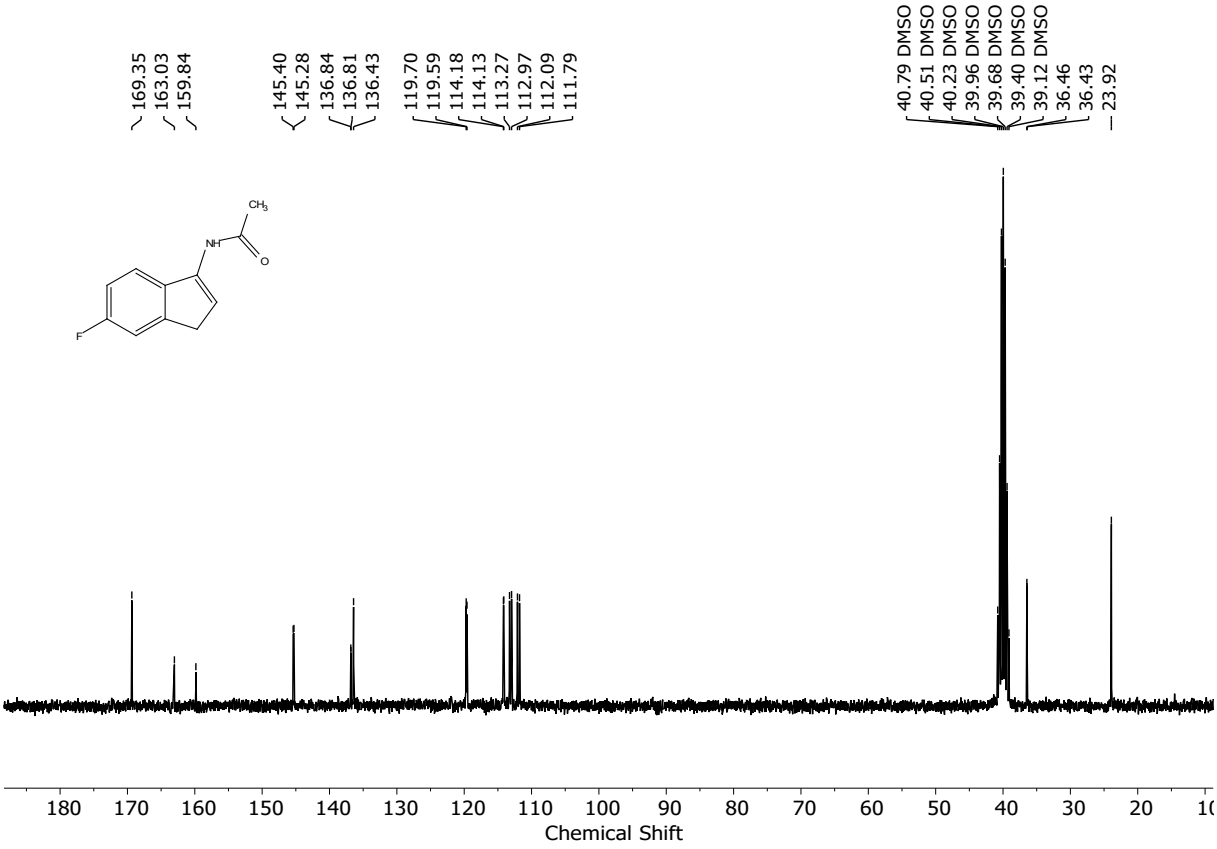
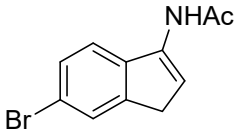


Figure S 9 ^{13}C NMR of 6a

- ***N-(6-bromo-1H-inden-3-yl)acetamide***



^{1}H NMR (300 MHz, DMSO) δ; 9.79 (br, 1H), 7.72 (d, J= 8.19 Hz, 1H), 7.64-7.63 (m, 1H), 7.54-7.50 (m, 1H), 3.38 (s, 3H), 2.12 (s, 2H).

^{13}C NMR (75 MHz, DMSO) δ; 169.37, 145.40, 139.79, 136.58, 129.16, 127.37, 120.45, 118.98, 115.01, 36.41, 23.91.

HRMS: m/z calculated for $C_{11}H_{10}BrNO$: 253.19 $[M+H]^+$; observed 253.36

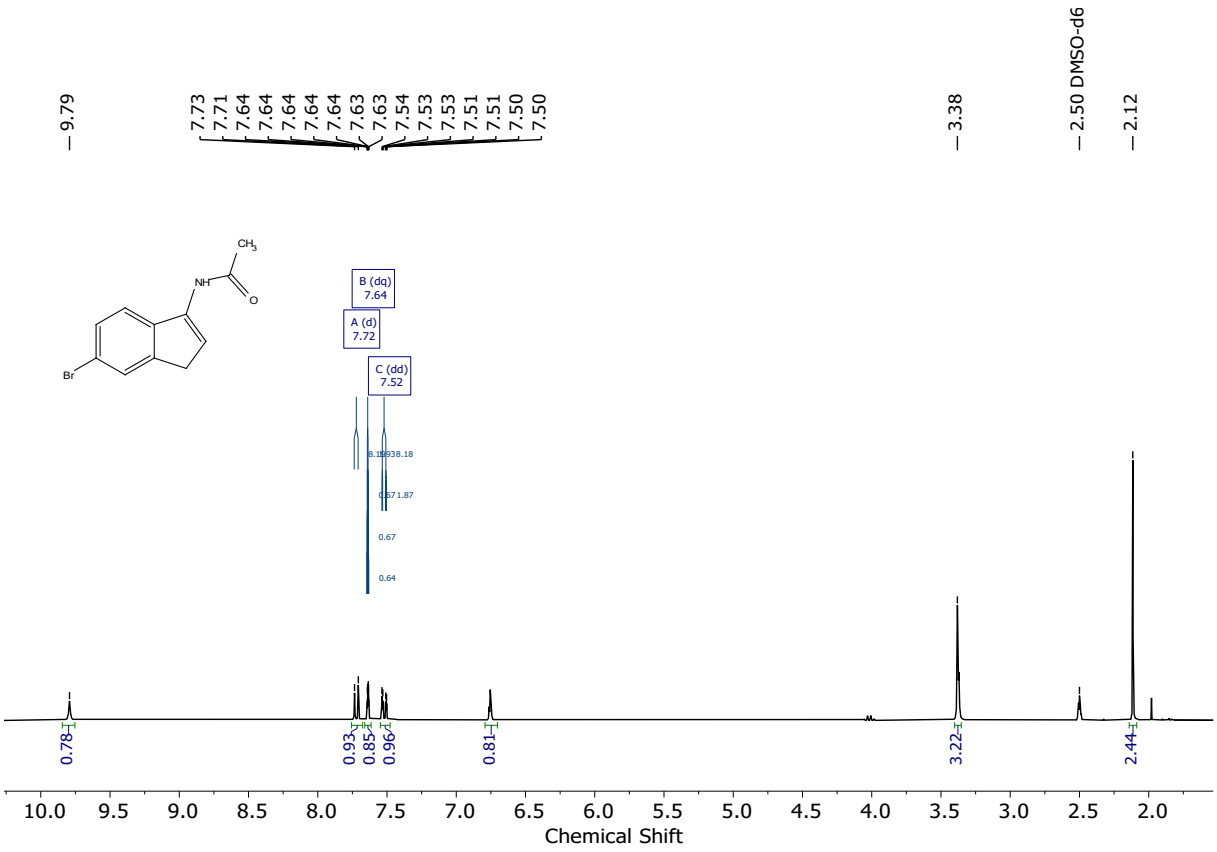


Figure S 10 ^{1}H NMR of 7a

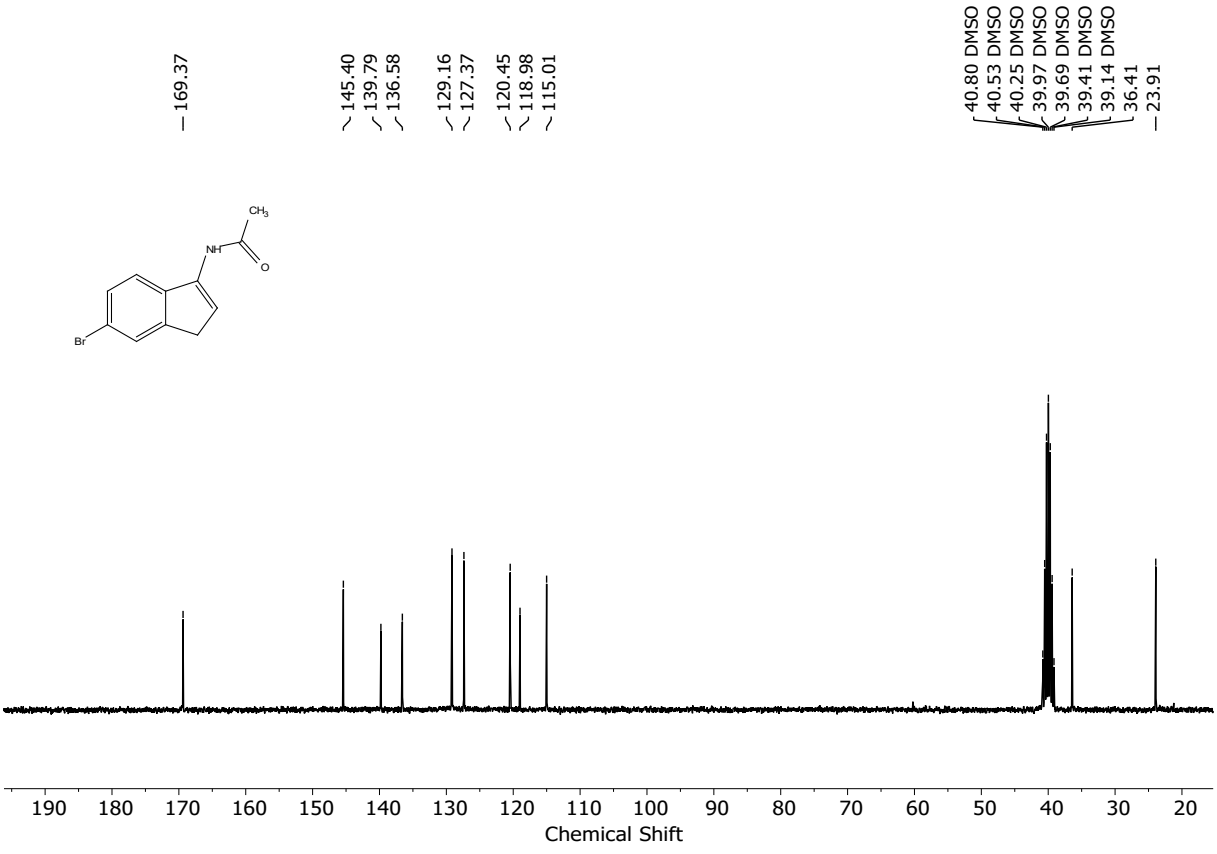
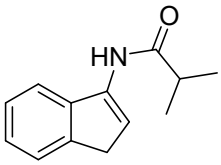


Figure S 11 ^{13}C NMR of 7a

- ***N-(1H-inden-3-yl)isobutyramide***



^{1}H NMR (300 MHz, CD_2Cl_2) δ; 7.54 (br, 1H), 7.51-7.48 (m, 1H), 7.33-7.30 (m, 2H), 7.29-7.23 (m, 1H), 6.85 (br, 1H), 3.43 (dd, J = 2.41 Hz, 2H), 1.25 (d, J= 6.87 Hz, 6H).

^{13}C NMR (75 MHz, CD2Cl2) δ; 175.48, 142.93, 139.85, 135.65, 125.91, 125.37, 124.21, 116.16, 115.17, 36.50, 36.18, 19.47.

HRMS: m/z calculated for $C_{13}H_{15}NO$: 202.36 $[M+H]^+$; observed 202.38

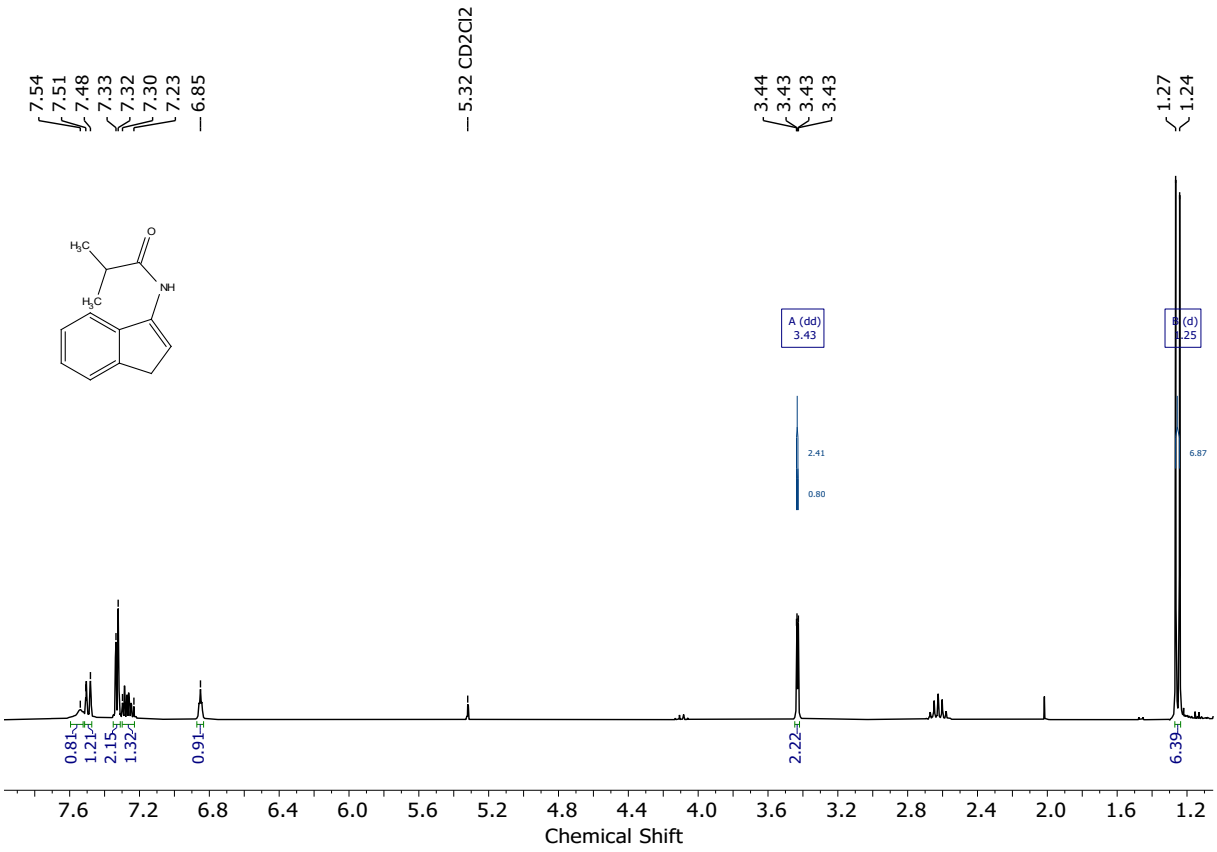


Figure S 12 ^{1}H NMR of 2a

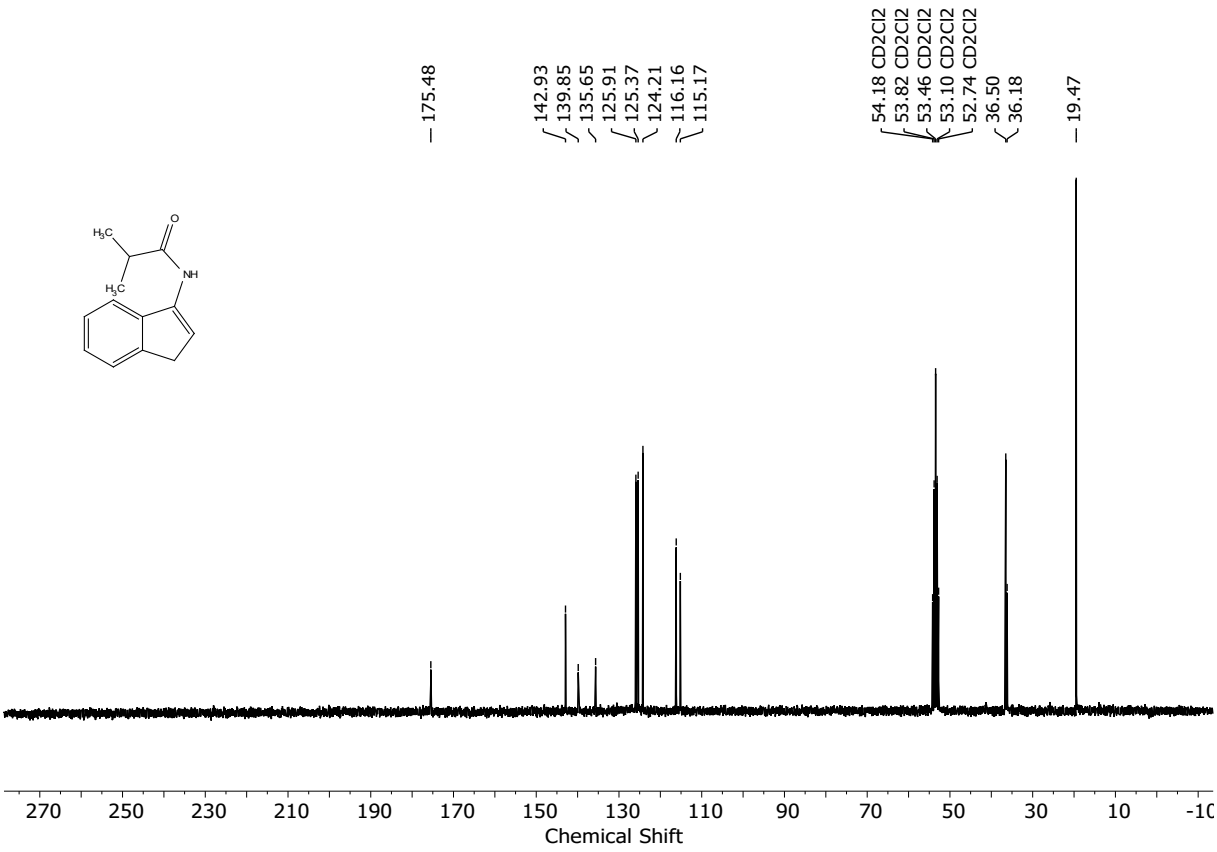
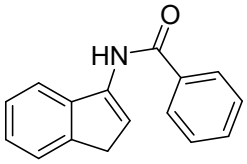


Figure S 13 ^{13}C NMR of 2a

- ***N-(1H-inden-3-yl)benzamide***



^{1}H NMR (300 MHz, CD_2Cl_2) δ; 8.04 (br, 1H), 7.93-7.90 (m, 2H), 7.63-7.51 (m, $H), 7.38-7.36 (m, 2H), 7.32-7.27 (m 1H), 7.00 (t, J = 2.42 Hz, 1H), 3.51 (dd, J = 2.47 Hz, 2H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ; 165.51, 142.96, 139.75, 135.60, 134.65, 131.89, 128.83, 126.99, 126.01, 125.54, 124.33, 116.09, 115.86, 36.64.

HRMS: m/z calculated for $C_{16}H_{13}NO$: 236.34 $[M+H]^+$; observed 236.39

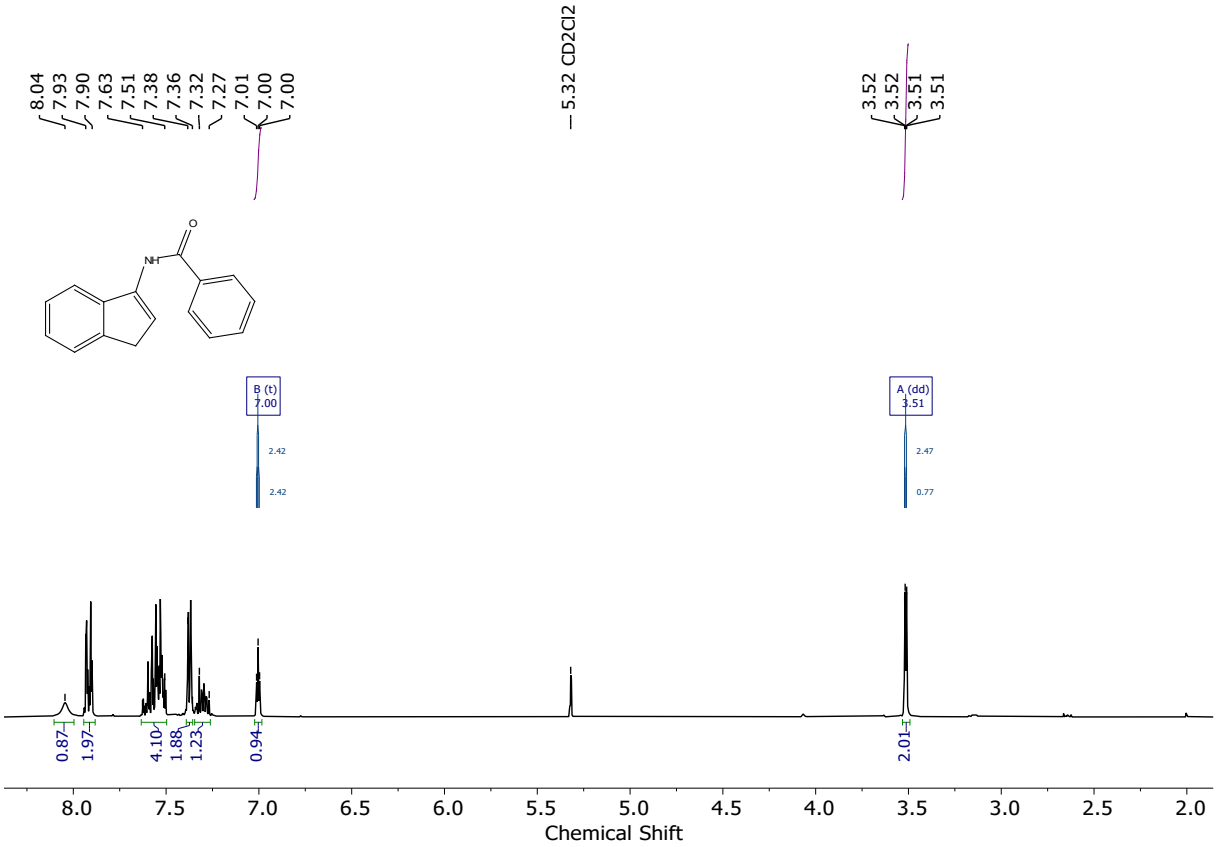


Figure S 14 ^{1}H NMR of 3a

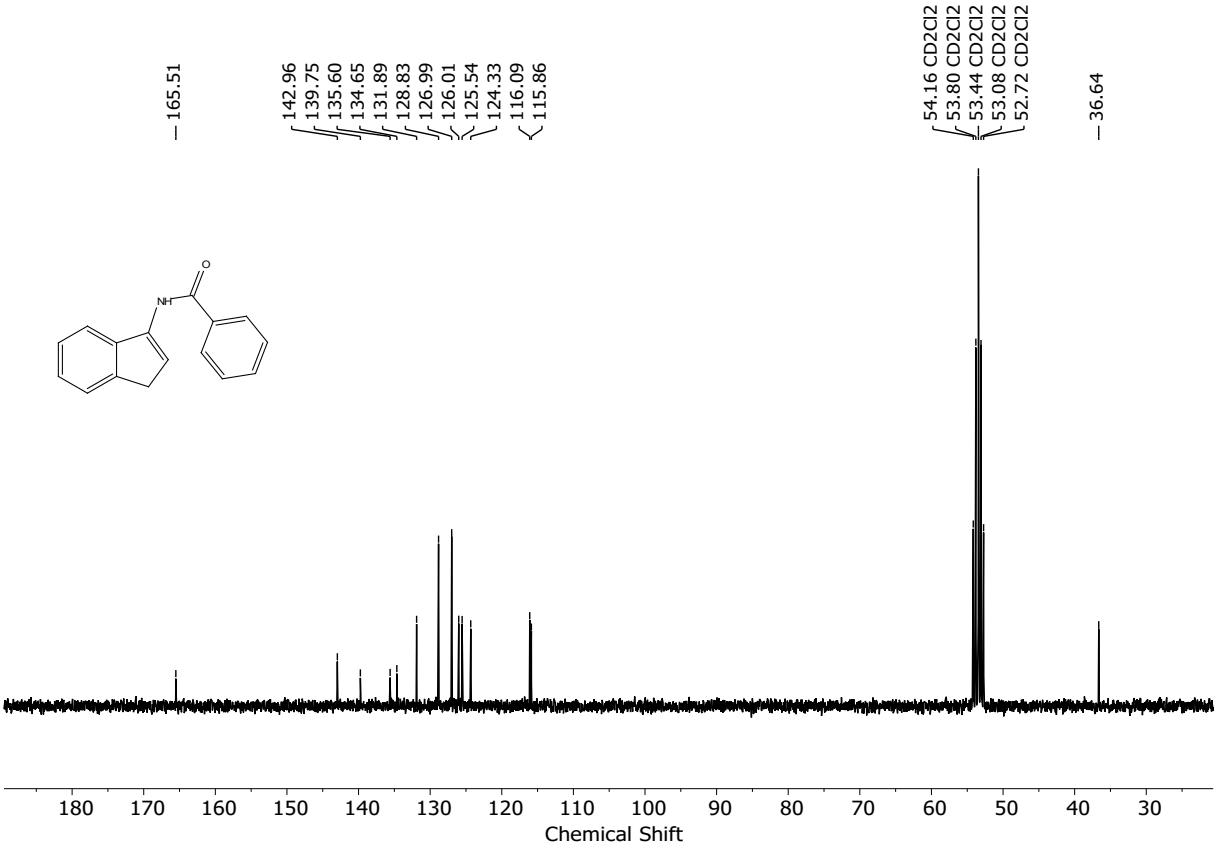


Figure S 15 ^{13}C NMR of 3a

3. Additional reaction optimization parameters

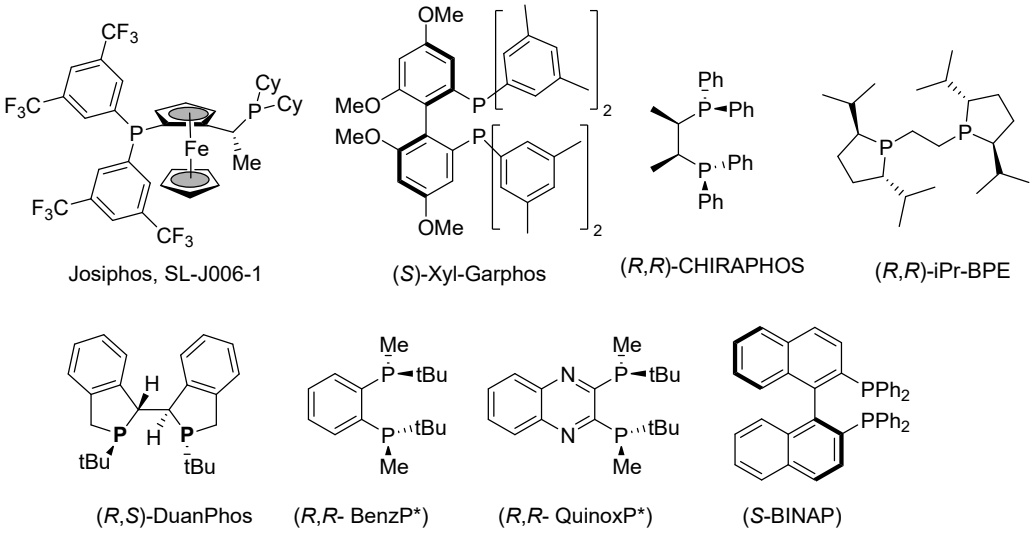
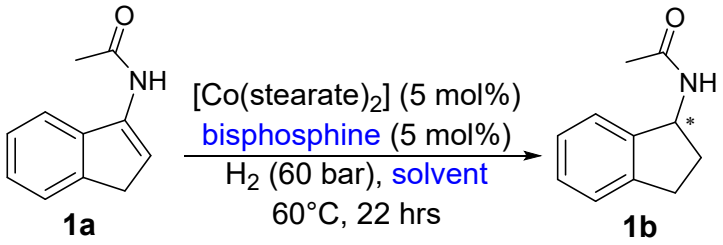


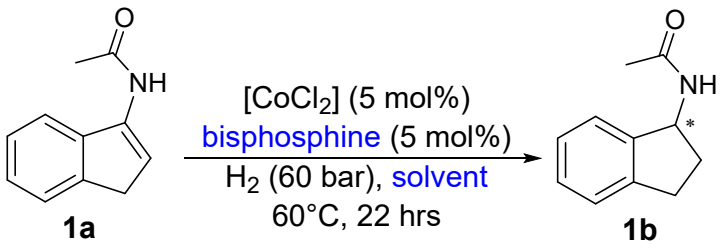
Figure S 16 Additional ligand screened in this work



Entry	Ligand	Solvent	Conversion	Enantiomeric excess
1	(*S*,*S*)-^{Ph}BPE	MeOH	-	
2	(*S*,*S*)-^{Ph}BPE	i-PrOH	>99%	52:47
3	(*S*,*S*)-^{Ph}BPE	tert-BuOH	75%	75:25
4	(*S*,*S*)-^{Ph}BPE	TFE	-	-
5	(*R*,*R*)-QunioxP*	MeOH	-	-
6	(*R*,*R*)-QunioxP*	i-PrOH	-	-
7	(*R*,*R*)-QunioxP*	tert-BuOH	-	-
8	(*R*,*R*)-QunioxP*	TFE	-	-

Reaction condition: [Co (stearate)$_2$] (5 mol%), Ligand (5 mol%), [substrate]= 0.1 mmol, solvent (2 mL) , H_2 (60 bar), temperature = 60°C, reaction time = 22 hrs. Conversion determined by GC and NMR analysis. Enantiomeric ratio was determined by chiral GC.

Table S 1 Optimization using [Co (stearate)$_2$]/bisphosphines

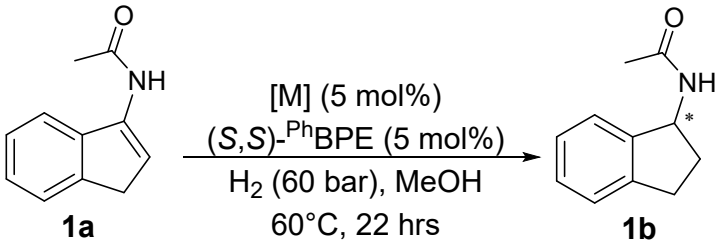


1a **1b**

Entry	Ligand	Solvent	Conversion	Enantiomeric excess
1	(*S*,*S*)-^{Ph}BPE	MeOH	70%	30:70
2	(*S*,*S*)-^{Ph}BPE	i-PrOH	-	-
3	(*S*,*S*)-^{Ph}BPE	tert-BuOH	-	-
4	(*S*,*S*)-^{Ph}BPE	TFE	-	-
5	(*S*,*S*)-^{Me}DuPhos	MeOH	-	-
6	(*S*,*S*)-^{Me}DuPhos	i-PrOH	-	-
7	(*S*,*S*)-^{Me}DuPhos	tert-BuOH	-	-
8	(*S*,*S*)-^{Me}DuPhos	TFE	-	-
9	(*R*,*R*)-QunioxP*	MeOH	-	-
10	(*R*,*R*)-QunioxP*	i-PrOH	-	-
11	(*R*,*R*)-QunioxP*	tert-BuOH	-	-
12	(*R*,*R*)-QunioxP*	TFE	-	-

Reaction condition: [$CoCl_2$] (5 mol%), Ligand (5 mol%), [substrate]= 0.1 mmol, solvent (2 mL) , H_2 (60 bar), temperature = 60°C, reaction time = 22 hrs. Conversion determined by GC and NMR analysis. Enantiomeric ratio was determined by chiral GC.

Table S 2 Optimization using [$CoCl_2$]/bisphosphines



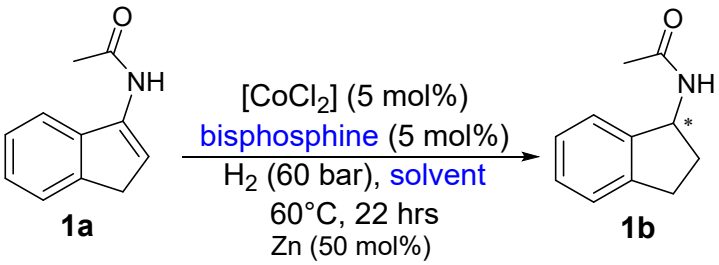
1a **1b**

Entry	Ligand	Solvent	Conversion	Enantiomeric excess
1	$NiCl_2$	MeOH	70%	30:70
2	$NiBr_2$	MeOH	-	-
3	$Ni(OTf)_2$	MeOH	-	-
4	$FeBr_2$	MeOH	-	-

5	$FeCl_2$	MeOH	-	-
6	$MnCl_2$	MeOH	-	-
7	$Mn(CO)_5Br$	MeOH	-	-

Reaction condition: [M] (5 mol%), (S,S)-^{Ph}BPE (5 mol%), [substrate]= 0.1 mmol, solvent (2 mL) , H_2 (60 bar), temperature = 60°C, reaction time = 22 hrs. Conversion determined by GC and NMR analysis. Enantiomeric ratio was determined by chiral GC.

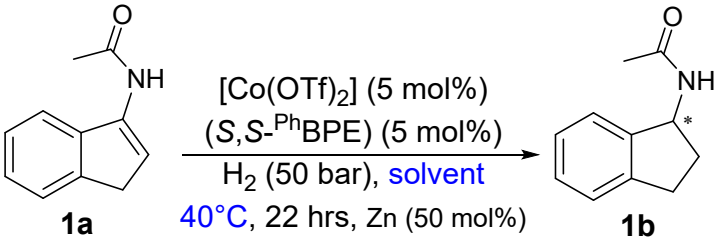
Table S 3 Optimization using other 1st row metals/bisphosphines



Entry	Ligand	Solvent	Conversion	Enantiomeric excess
1	(*S*,*S*)-^{Ph}BPE	MeOH	>99%	10:90
2	(*S*,*S*)-^{Ph}BPE	TFE	25%	8:92
3	(*S*,*S*)-^{Me}DuPhos	MeOH	60%	60:40
4	(*S*,*S*)-^{Me}DuPhos	TFE	-	-

Reaction condition: [$CoCl_2$] (5 mol%), Ligand (5 mol%), [substrate]= 0.1 mmol, solvent (2 mL) , H_2 (60 bar), temperature = 60°C, reaction time = 22 hrs. Conversion determined by GC and NMR analysis. Enantiomeric ratio was determined by chiral GC.

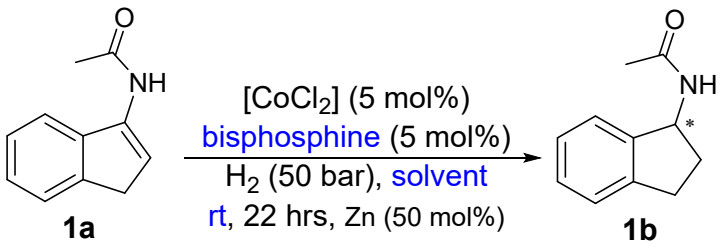
Table S 4 Optimization using Zn-additive



Entry	Solvent	Conversion	Enantiomeric excess
1	MeOH	90%	13:87
2	i-PrOH	40%	16:84
3	2-MeTHF	>99%	6:94
4	1-BuOH	90%	9:91

Reaction condition: $[Co(OTf)_2]$ (5 mol%), (S,S)-^{Ph}BPE (5 mol%), [substrate]= 0.1 mmol, solvent (2 mL) , H_2 (50 bar), temperature = 40°C, reaction time = 22 hrs. Conversion determined by GC and NMR analysis. Enantiomeric ratio was determined by chiral GC.

Table S 5 Optimization using other solvents and temparature

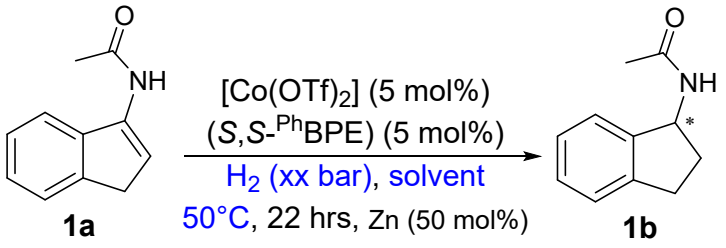


1a **1b**

Entry	Ligand	Solvent	Conversion	Enantiomeric excess
1	(*S*,*S*)-^{Ph}BPE	MeOH	40%	9:91
2	(*S*,*S*)-^{Ph}BPE	i-PrOH	20%	6:94
3	(*S*,*S*)-^{Ph}BPE	2-MeTHF	98%	8:92
4	(*S*,*S*)-^{Ph}BPE	1-BuOH	90%	7:93
5	(*R*,*R*)-^{iPr}BPE	MeOH	20%	n.d.
6	(*R*,*R*)-^{iPr}BPE	i-PrOH	-	-
7	(*R*,*R*)-^{iPr}BPE	2-MeTHF	70%	92:8
8	(*R*,*R*)-^{iPr}BPE	1-BuOH	50%	91:9

Reaction condition: [Co] (5 mol%), Ligand (5 mol%), [substrate]= 0.1 mmol, solvent (2 mL) , H_2 (50 bar), temperature = rt, reaction time = 22 hrs. Conversion determined by GC and NMR analysis. Enantiomeric ratio was determined by chiral GC.

Table S 6 Detailed solvent effect using $CoCl_2$ as metal precurosor



1a **1b**

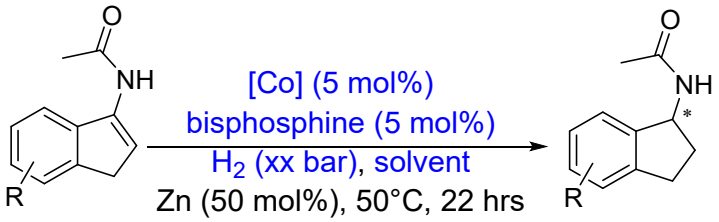
Entry	Solvent	H_2 (bar)	Conversion	Enantiomeric excess
1	MeOH	40 bar	>99%	10:90
2	2-MeTHF	40 bar	>99%	8:92
3	MeOH	30 bar	>99%	9:91

4	2-MeTHF	30 bar	>99%	9:91
5	MeOH	20 bar	>99%	9:91
6	2-MeTHF	20 bar	>99%	7:93
7	MeOH	10 bar	>99%	10:90
8	2-MeTHF	10 bar	>99%	6:94
9	MeOH	5 bar	80%	10:90
10	2-MeTHF	5 bar	>99%	6:94
11[a]	MeOH	10 bar	-	-
12[a]	2-MeTHF	10 bar	90%	6:94
13[b]	2-MeTHF	30 bar	30%	30:70

Reaction condition: $[Co(OTf)_2]$ (5 mol%), (S,S)-^{Ph}BPE (5 mol%), [substrate]= 0.1 mmol, solvent (2 mL) , H_2 (as desired), temperature = 50°C, reaction time = 22 hrs. Conversion determined by GC and NMR analysis. Enantiomeric ratio was determined by chiral GC. [a] at room temperature. [b]without Zn

Table S 7 Detailed solvent effect using $Co(OTf)_2$ as metal precurosor as different conditions

4. General procedure for asymmetric hydrogenation (AH)



SchemeS 1 General protocol for Co-catalyzed asymmetric hydrogenation of indanone derived enamides

All the hydrogenation experiments were performed in a stainless steel autoclave charged with an insert suitbale for up to 8 reaction vessels (4 mL) with teflon mini stirring bars. In a typical experiment, a reaction vessel is charged with [Co]-precursors (5 mol%) and ligand (5 mol%) and stirred for 10-15 mins in the appropiate solvent (2mL). Then the additive Zn (50 mol%) and desired substrates **Xa** (0.2 mmol) were added to the reaction vessel maintaining the inert atmosphere and the vessels were placed in the autoclave. The autoclave was purged two times with nitrogen and three times with hydrogen. Finally it was pressurized at the desired H_2 pressure at 50°C/60°C (as needed) for 22 h. After the required reaction time, the autoclave was depressurized and the reaction vessels were diluted with

EtOAc and filtered through a short pad of silica. The conversion was determined by GC, GC-MS and NMR measurement and the enantiomeric excess was measured by GC or HPLC using a chiral coloumn.

5. Synthesis of Co-^{Ph}BPE complexes

- **^{Ph}BPE-Co(II)-OTf$_2$** complex:

$$[Co(OTf)_2] + (S,S)^{Ph}BPE \xrightarrow[\text{rt, overnight}]{\text{THF}} [Co(S,S)^{Ph}BPE](OTf)_2$$

SchemeS 2 Co-complex synthesis

In a glove box, (*S*,*S*)-BPE (0.2 mmol, 101 mg) and anhydrous $Co(OTf)_2$ (0.2 mmol, 73 mg) was dissolved in dry THF with a stirring bar. The reaction mixture was stirred overnight (16 h) which was turned into light pink solution. The solvent was removed and the solid was washed with ether and dried in Schlenk which afforded light violet powder. Elemental analysis $C_{36}H_{36}CoF_6O_6P_2S_2$: Calculated (%) C: 50.07, H: 4.20 S: 7.42; Observed (%) C: 50.26 H: 4.78 S: 7.038.

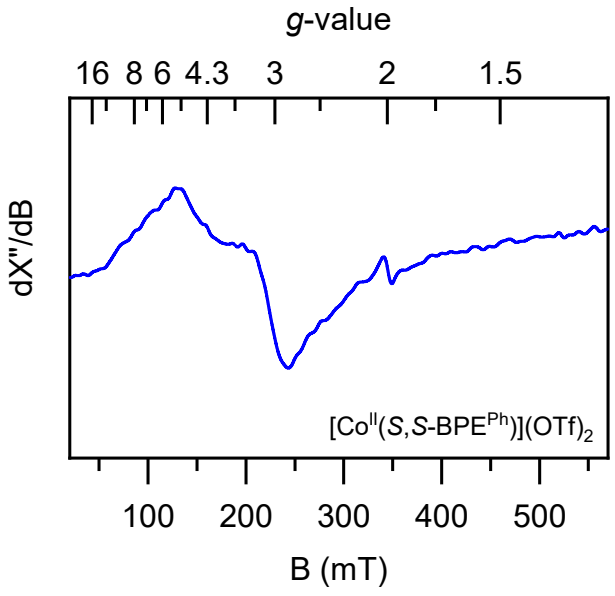
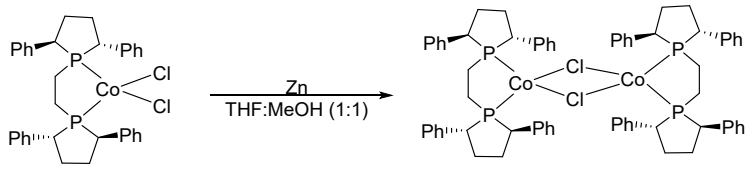


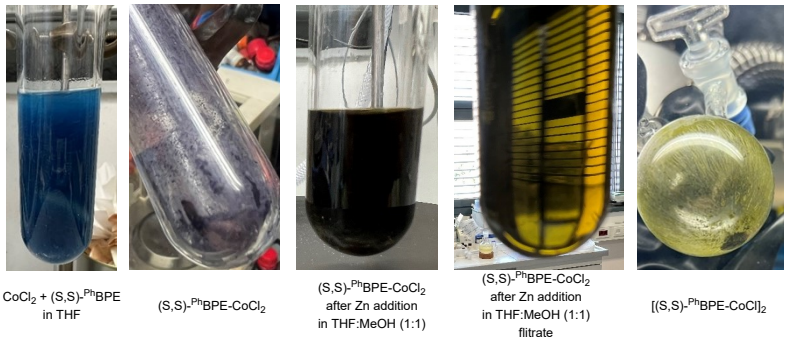
Figure S 17 Experimental X-band EPR spectrum of isolated [S,S-^{Ph}BPE)Co(OTf)$_2$]

- **[^{Ph}BPE-Co(I)-Cl]$_2$** dimer **Co(I)-1** synthesis:

The [^{Ph}BPE-Co(I)-Cl]$_2$ was synthesized according to the literature procedure via Zn-reduction. (Ref. M. R. Friedfeld, H. Zhong, R. T. Ruck, M. Shevlin, P. J. Chirik, Science 2018, 360, 888.)

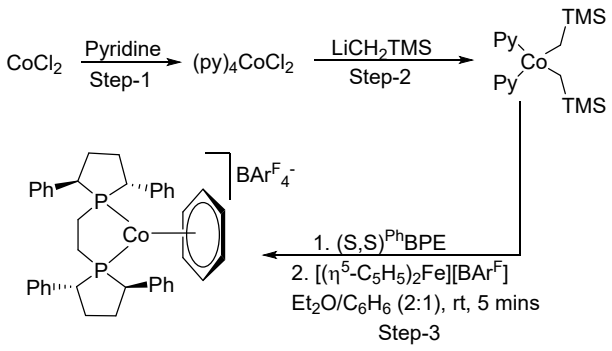


In a glove box, (S,S)-^{Ph}BPE$CoCl_2$ (0.125 mmol, 80 mg) and Zn dust <10 µm in size (0.6 mmol, 42 mg) was dissolved in dry THF and MeOH with a stirring bar. The reaction mixture was turned into a deep green solution and was stirred for 20 mins at room temperature. Then the solvent was removed and the solid was dissolved in THF and filtered under inert conditions and dried under the Schlenk line which afforded the desired [^{Ph}BPE-Co(I)-Cl]$_2$ as dark green solid. Elemental analysis $C_{68}H_{72}Cl_2Co_2P_4$: Calculated (%) C: 67.95, H: 6.04; Observed (%) C: 67.55, H: 6.26



- **[^{Ph}BPE-Co(benzene)]BArF**, **Co(I)-2** synthesis:

The cationic Co(I) complex was synthesized according to the reported procedure.



Step-1: (Ref. Zhu, D.; Janssen, F. F. B. J.; Budzelaar, P. H. M. (Py)2Co(CH2SiMe3)2. *Organometallics* **2010**, *29* (8), 1897-1908.)

(Py)$_4$CoCl$_2$: Anhydrous CoCl2 (1.36 g, 10.4 mmol) was transferred into a 100 mL Schlenk tube, and 15 mL of pyridine was added. The resulting suspension of initially blue solid in a pink solution was stirred

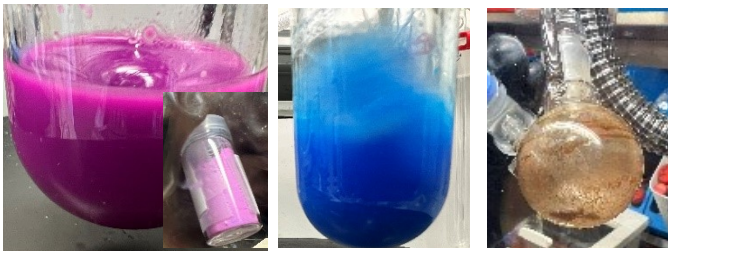
overnight at room temperature, during which the solid became pink. The solid was filtered off and dried in vacuo, giving 3.65 g (78%) of pink crude $(Py)_4CoCl_2$. Elemental analysis for $C_{20}H_{20}Cl_2CoN_4$: Calculated (%) C, 53.83; H, 4.52; N, 12.56; Cl, 15.89 ; Observed (%) C, 53.67; H, 4.85; N, 12.81; Cl, 16.10.

Step-2: (Ref. Zhu, D.; Janssen, F. F. B. J.; Budzelaar, P. H. M. *Organometallics* **2010**, *29* (8), 1897-1908.)

(Py)$_2$CoCH$_2$TMS: Synthesized as literature reported procedure. (Ref. Zhu, D.; Janssen, F. F. B. J.; Budzelaar, P. H. M. *Organometallics* **2010**, *29* (8), 1897-1908.)

[(R,R)-(PhBPE)Co(η^6-C$_6$H$_6$)][BArF$_4$]: **Co(I)-2** Synthesized according to literature procedure. (Ref. MacNeil, C. S.; Zhong, H.; Pabst, T. P.; Shevlin, M.; Chirik, P. J. *ACS. Catal.* **2022**, 4680-4687.)

In a glovebox, a 25 mL Schlenk was charged with $(py)_2Co(CH_2SiMe_3)_2$ (0.065 g, 0.17 mmol) as a dark green semisolid and dissolved in 2 mL of diethyl ether. In a separate flask, (R,R)-PhBPE (0.084 g, 0.17 mmol) was weighed and dissolved in diethyl ether. The $(py)_2Co(CH_2SiMe_3)_2$ solution was added dropwise to the (*R*,*R*)-PhBPE solution. Then the color of the mixture was changed to yellow. Finally, $[(\eta^5\text{-}C_5H_5)2Fe][BArF_4]$ (0.178 g, 0.17 mmol) was weighed out as a deep blue solid and dissolved in a mixture of diethyl ether and benzene (2:1) and added dropwise to the stirring ethereal solution of (*R*,*R*)- $(PhBPE)Co(CH_2SiMe_3)_2$ (formed in situ), the deep blue color instantly gave way to bright yellow. The reaction mixture was stirred for 15 minutes at ambient temperature. Volatiles were removed under reduced pressure and the residue was washed with pentane (x 2) to remove ferrocene and silane byproducts. The residue was dissolved in diethyl ether and filtered through cannula and dried under reduced pressure (88% yield) of [(*R*,*R*)-(^{Ph}BPE)Co(η^6-C$_6$H$_6$)][BArF$_4$] as bright yellow crystalline solid. Elemental analysis for $C_{72}H_{54}BCoF_{24}P_2$, : Calculated (%) C, 57.39; H, 3.61. Observed (%) C, 57.56; H, 3.48.



$(py)_4CoCl_2$ $(py)_4CoCl_2$ in pentane [(R,R)-^{Ph}BPECo(benzene)]$BAr^F{}_4^-$

- **^{Ph}BPE-Co(I)-OTf , Co(I)-3** complex:

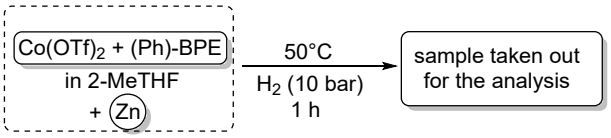
$$[Co(S,S)^{Ph}BPE](OTf)_2 \xrightarrow[\text{- Zn(OTf)}]{\text{Zn, THF:MeOH (1:1)}} [Co(S,S)^{Ph}BPE](OTf)$$

In a glove box, (S,S)-^{Ph}BPECoOTf$_2$ (0.115 mmol, 100 mg) and Zn dust <10 µm in size (0.15 mmol, 11 mg) was dissolved in dry THF and MeOH with a stirring bar. The reaction mixture was stirred for 1h mins at room temperature. Then the solvent was removed and the solid was dissolved in THF and filtered under inert conditions and dried under the Schlenk line which afforded the desired ^{Ph}BPE-Co(I)-OTf as light red solid. Elemental analysis $C_{35}H_{36}CoF_3O_2P_2S$: Calculated (%) C: 58.83, H: 5.08; Observed (%) C: 58.69, H: 5.26.

6. EPR experiments for mechanistic studies

In a prototypical measurement the sample have been prepared following different reaction set up in order to mimic the active catalytic conditions, which have been depicted as follows:

- **Experiment 1**:



SchemeS 3 Experiment-1

$[Co(OTf)_2]$ (3.6 mg) and (S,S)-^{Ph}BPE(5.4 mg) were stirred for 10-15 mins in 2-MeTHF (2mL) at room temparature follwed by the addition of Zn (5-6 mg). Then the vial was transferred into a autoclave and pressurized with 10 bar

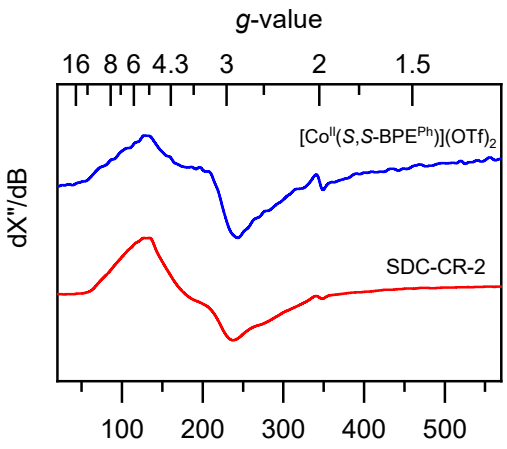
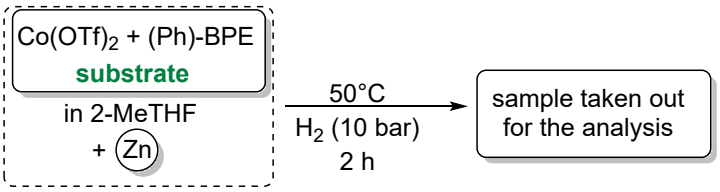


Figure S 18 Experimental X-band EPR spectrum

of H_2 and stirred the precatalyst for 1 h at 50°C. After that the reaction mixture was transferred into a EPR tube and immediately iced in liquid nitrogen and subjected to the EPR analysis.

- **Experiment 2**:



SchemeS 4 Experiment-2

$[Co(OTf)_2]$ (3.6 mg) and (S,S)-^{Ph}BPE(5.4 mg) were stirred for 10-15 mins in 2-MeTHF (2mL) at room temparature follwed by the addition of Zn (5-6 mg) and substrate 1a (0.2 mmol). Then the vial was transferred into a autoclave and pressurized with 10 bar of H_2 and stirred the precatalyst for 2 h at 50°C. After that the reaction mixture was transferred into a EPR tube and immediately iced in liquid nitrogen and subjected to the EPR analysis.

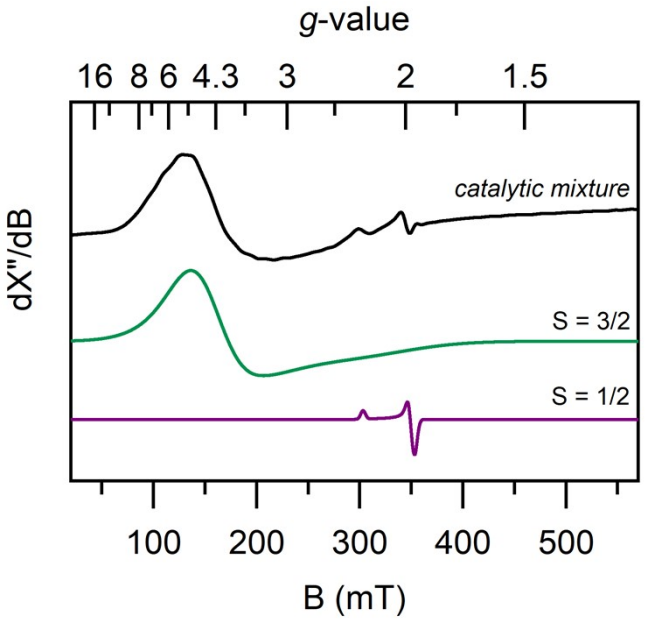
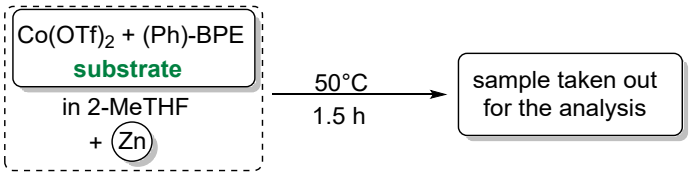


Figure S 19 Experimental X-band EPR spectrum

- **Eperiment 3**:



SchemeS 5 Experiment-3

$[Co(OTf)_2]$ (3.6 mg) and (S,S)-^{Ph}BPE(5.4 mg) were stirred for 10-15 mins in 2-MeTHF (2mL) at room temparature follwed by the addition of Zn (5-6 mg) and substrate 1a (0.2 mmol). The catalytic mixture was for 1.5 h at 50°C. After that the reaction

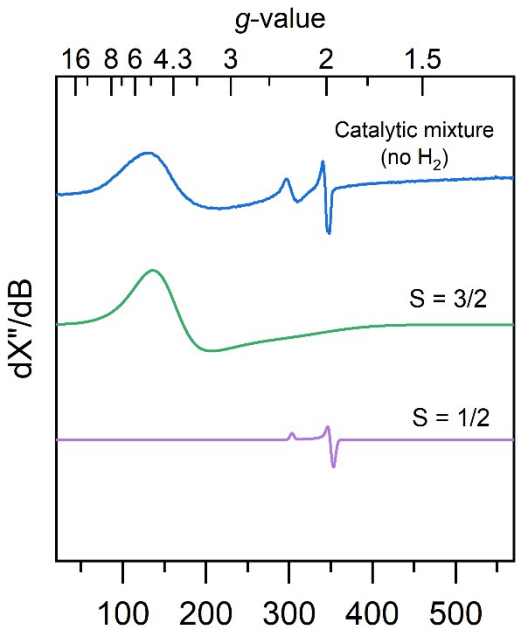


Figure S 20 Experimental X-band EPR spectrum

mixture was transferred into a EPR tube and immediately iced in liquid nitrogen and subjected to the EPR analysis.

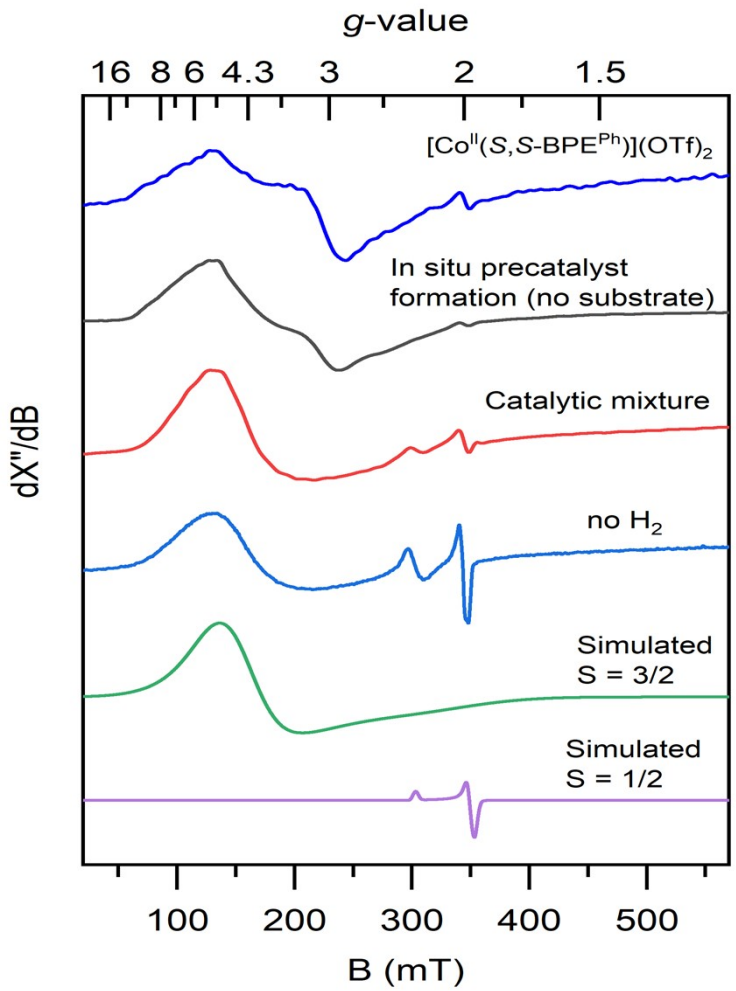
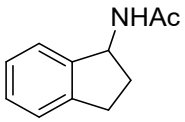


Figure S 21 Experimental X-band EPR spectrum comparison following catalytic conditions

7. Analytical data of the indanone-amides

- ***N-(2,3-dihydro-1H-inden-1-yl)acetamide***



^{1}H NMR (300 MHz, $CDCl_3$) δ; 7.31-7.20 (m, 4H), 5.64 (br, 1H), 5.52-5.44 (m, 1H), 3.03-2.81 (m, 2H), 2.66-2.55 (m, 1H), 2.03 (s, 3H), 1.89-1.76 (2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ; 167.89, 141.55, 141.22, 126.11, 124.87, 122.92, 122.10, 75.54, 75.11, 74.69, 52.86, 32.17, 28.31, 21.55.

HRMS: m/z calculated for $C_{11}H_{13}NO$: 176.26 $[M+H]^+$; observed 176.23

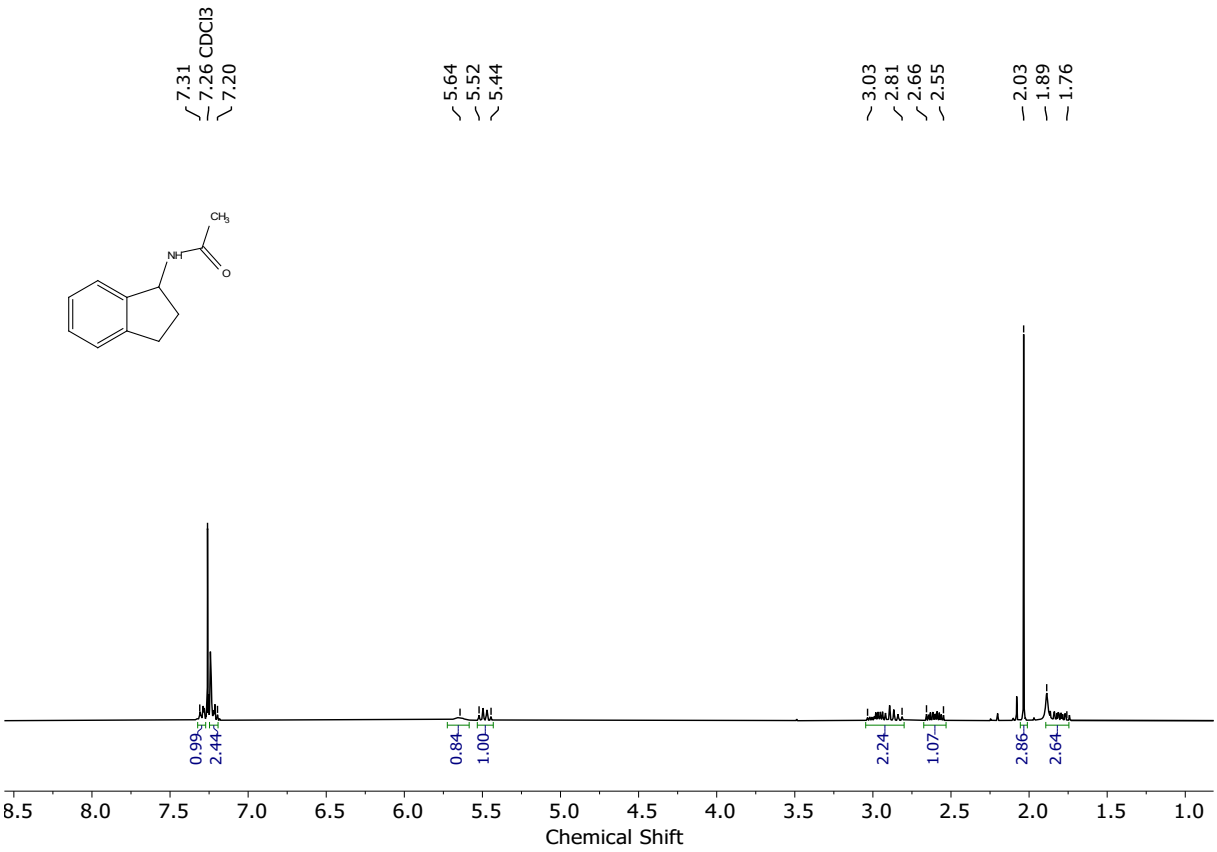


Figure S 22 ^{1}H NMR of1b

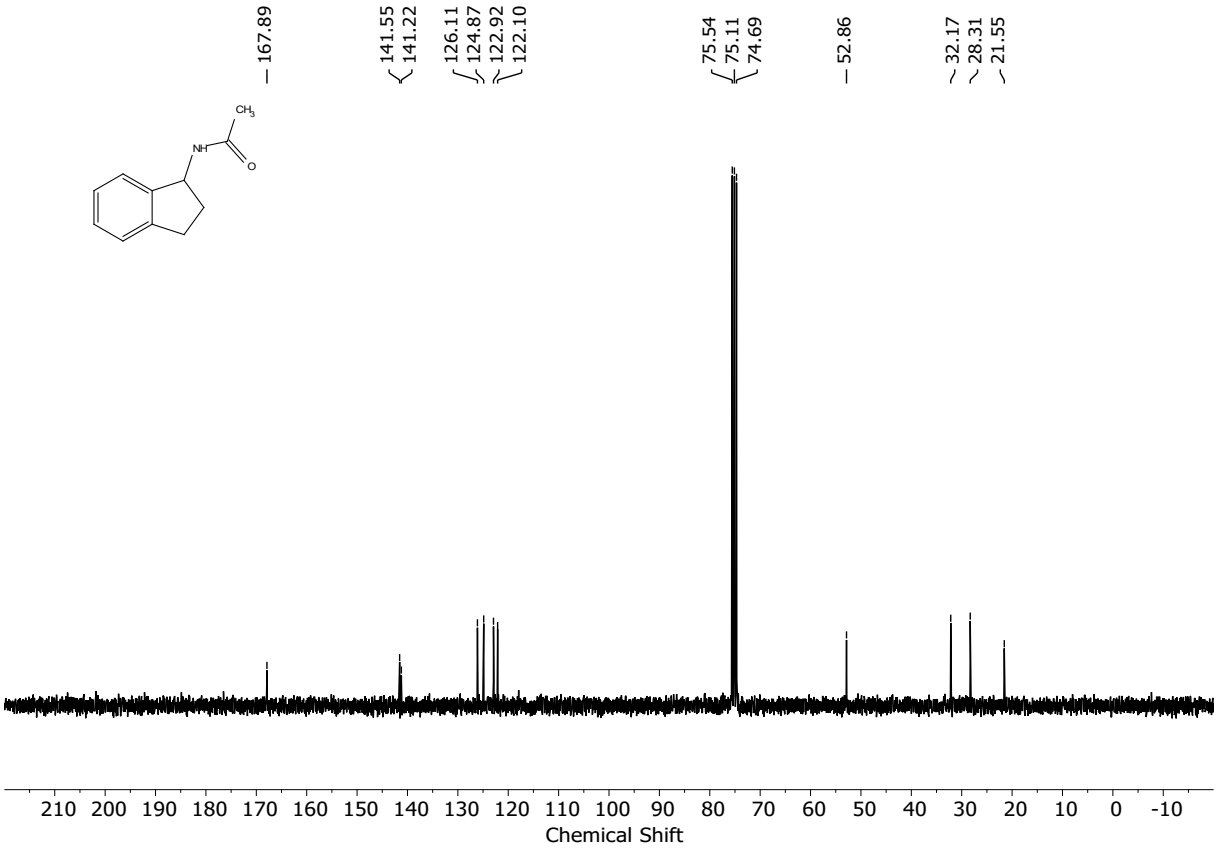
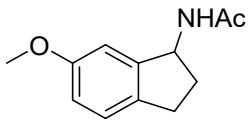


Figure S 23 ^{13}C NMR of1b

- ***N-(6-methoxy-2,3-dihydro-1H-inden-1-yl)acetamide***



^{1}H NMR (300 MHz, $CDCl_3$) δ; 7.11 (d, J = 8.09 HZ, 1H), 6.84-6.75 (m, 2H), 5.84 (br, 1H), 5.42 (q, J = 7.74 Hz, 1H), 3.77 (s, 3H), 2.94-2.71 (m, 2H), 2.62-2.51 (m, 1H), 2.01 (s, 3H), 1.85-1.73 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ; 169.86, 159.08, 144.60, 135.26, 125.37, 114.40, 108.96, 55.54, 54.87, 34.54, 29.37, 23.43.

HRMS: m/z calculated for $C_{12}H_{15}NO_2$: 206.34 $[M+H]^+$; observed 206.37

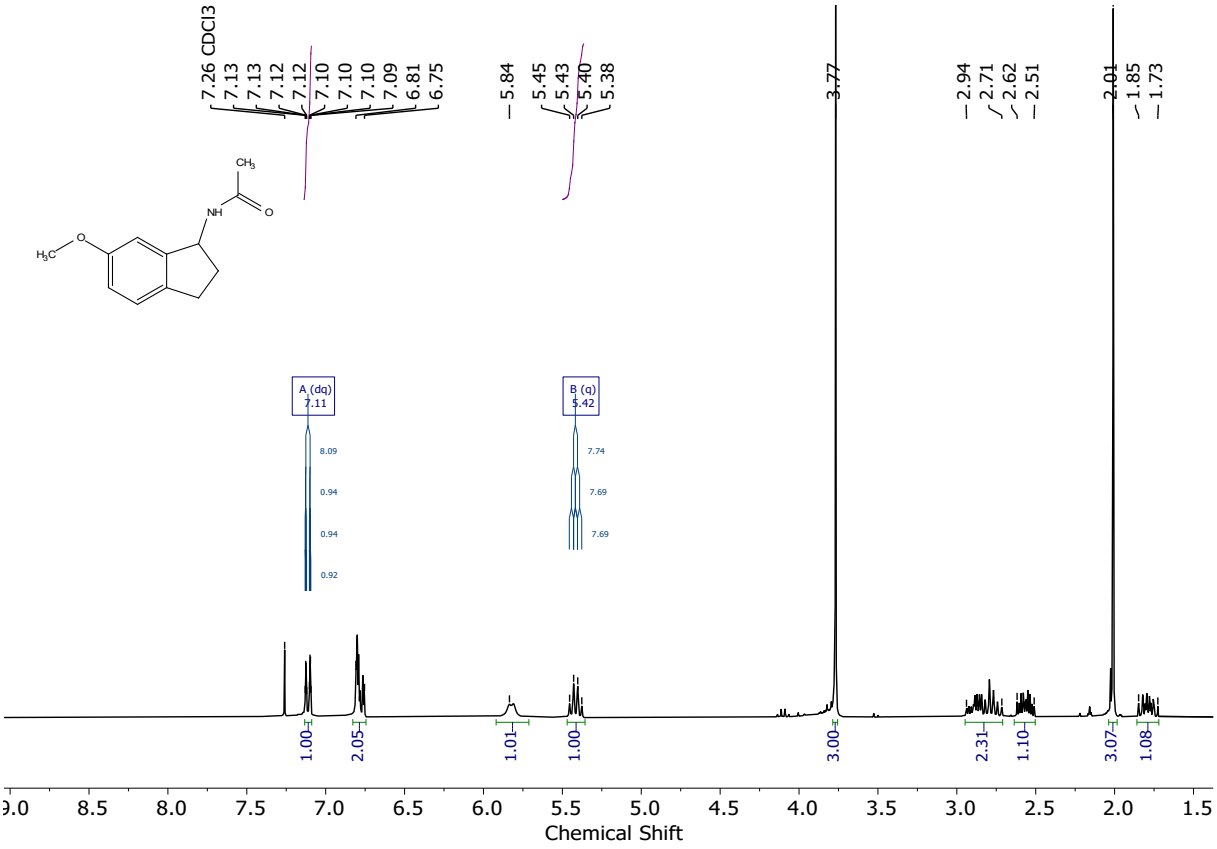


Figure S 24 ^{1}H NMR of 4b

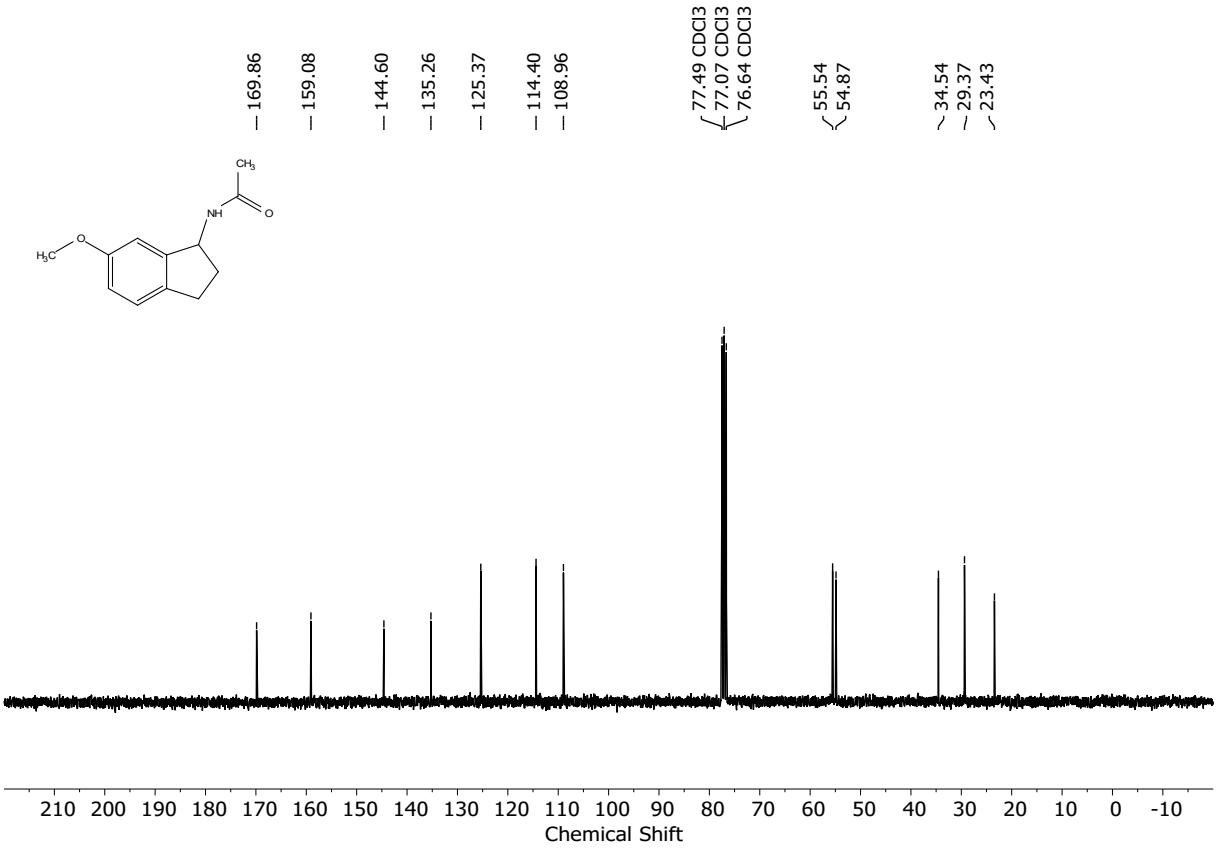
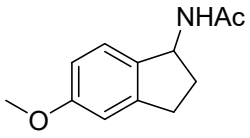


Figure S 25 ^{13}C NMR of 4b

- ***N-(5-methoxy-2,3-dihydro-1H-inden-1-yl)acetamide***



^{1}H NMR (300 MHz, $CDCl_3$) δ; 7.18 (d, J = 7.97 Hz), 6.77-6.72 (m, 2H), 5.75 (br, 1H), 5.38 (q, J = 7.50 Hz, 1H), 3.78 (s, 3H), 2.99-2.79 (m, 2H), 2.62-2.53 (m, 1H), 2.00 (s, 3H), 1.87-1.77 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ; 169.82, 160.01, 145.25, 135.20, 124.83, 112.93, 109.91, 55.46, 54.20, 34.36, 30.41, 23.45.

HRMS: m/z calculated for $C_{12}H_{15}NO_2$: 206.37 $[M+H]^+$; observed 206.31

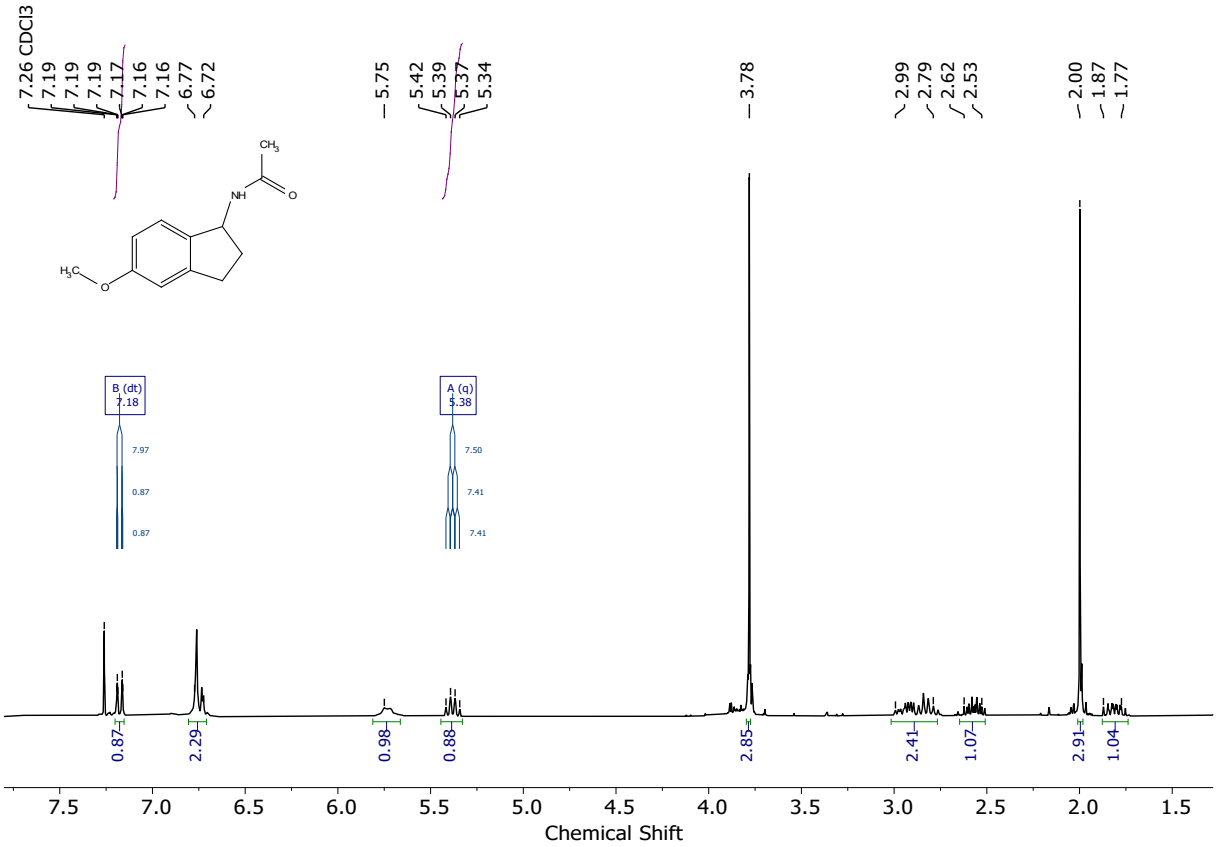


Figure S 26 ^{1}H NMR of 5b

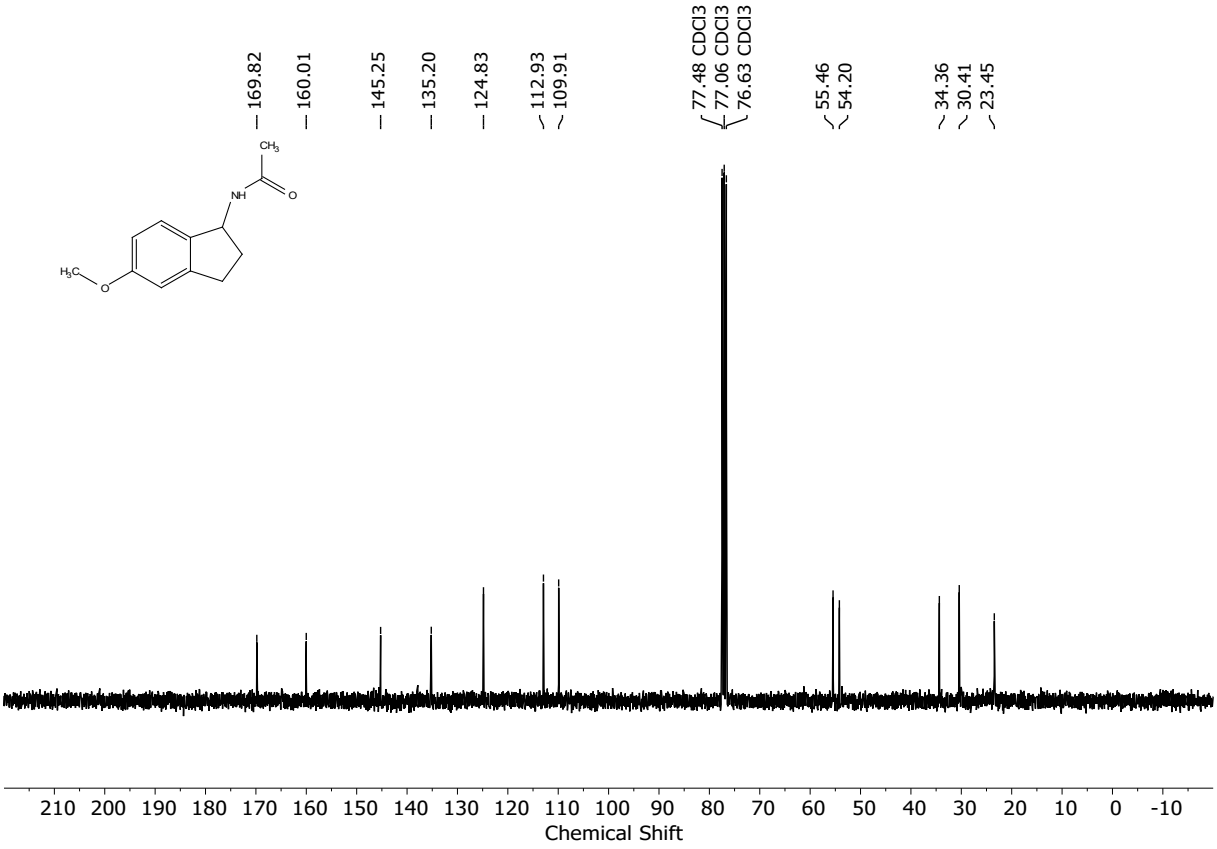
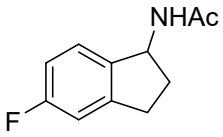


Figure S 27 ^{1}H NMR of 5b

- ***N-(5-fluoro-2,3-dihydro-1H-inden-1-yl)acetamide***



^{1}H NMR (300 MHz, $CDCl_3$) δ; 7.23-7.19 (m, 1H), 6.93-6.85 (m, 2H), 5.73 (br, 1H), 5.40 (q, J = 7.68 Hz, 1H), 3.00-2.78 (m, 2H), 2.64-2.53 (m, 1H), 2.01 (s, 3H), 1.89-1.76 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ; 169.87, 161.39, 145.77, 145.65, 138.74, 125.29, 125.17, 113.99, 113.69, 111.87, 111.58, 77.25, 54.03, 34.35, 30.25, 30.22, 23.40.

HRMS: m/z calculated for $C_{11}H_{12}FNO$: 194.36 $[M+H]^+$; observed 194.39

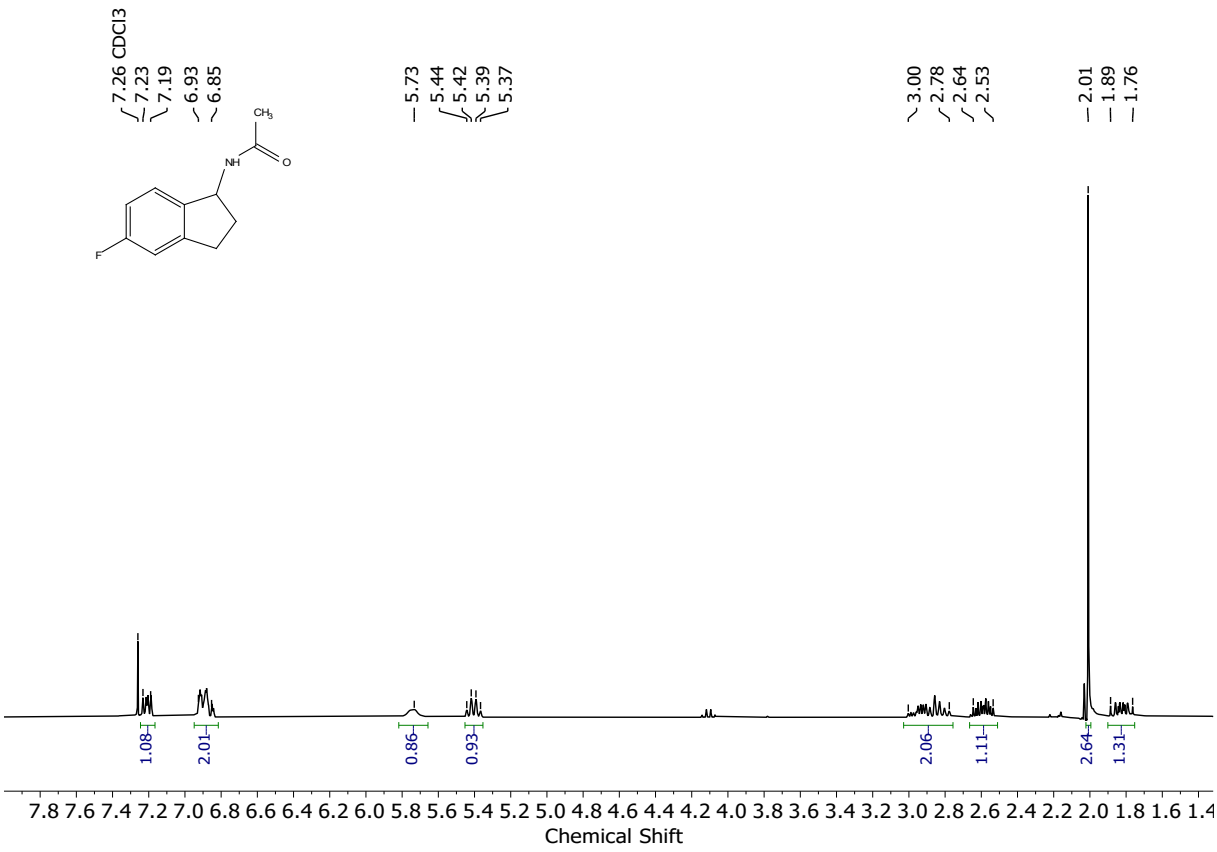


Figure S 28 ^{1}H NMR of 6b

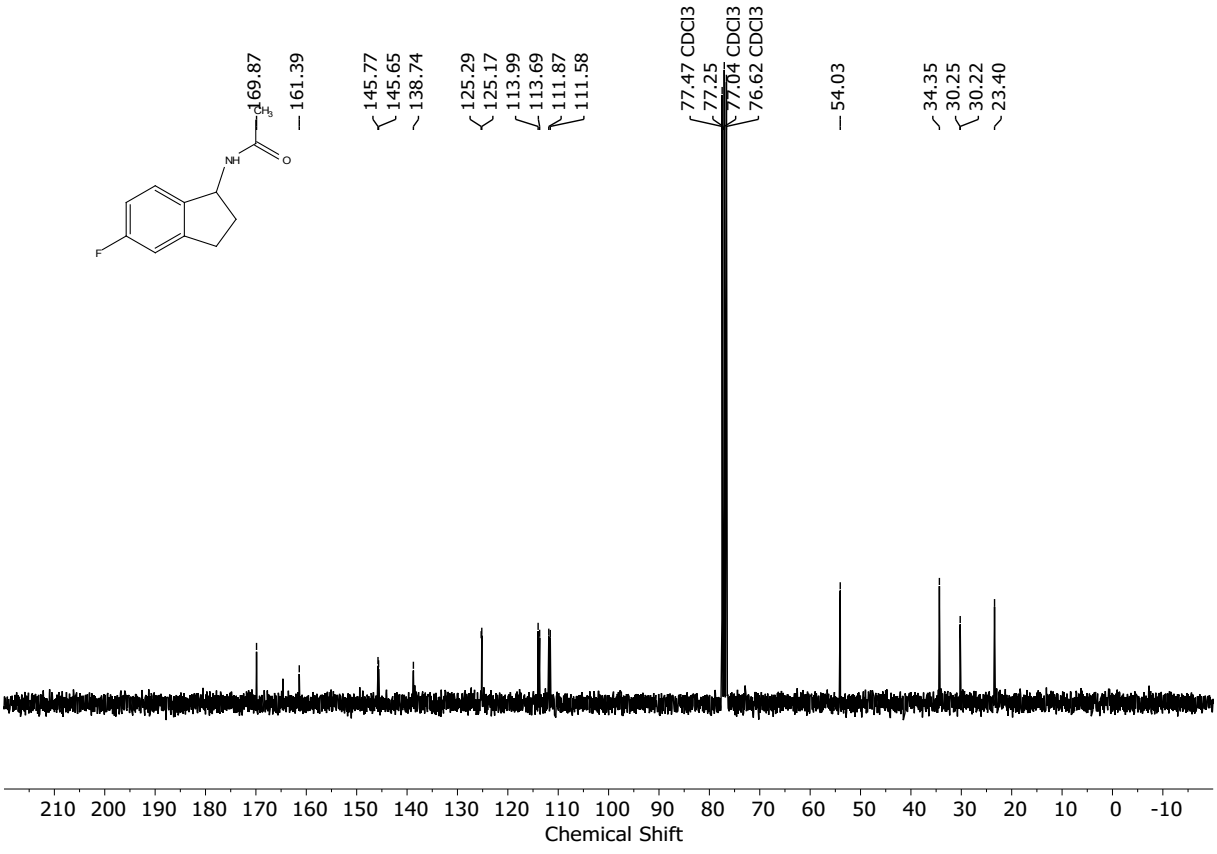


Figure S 29 ^{13}C NMR of 6b

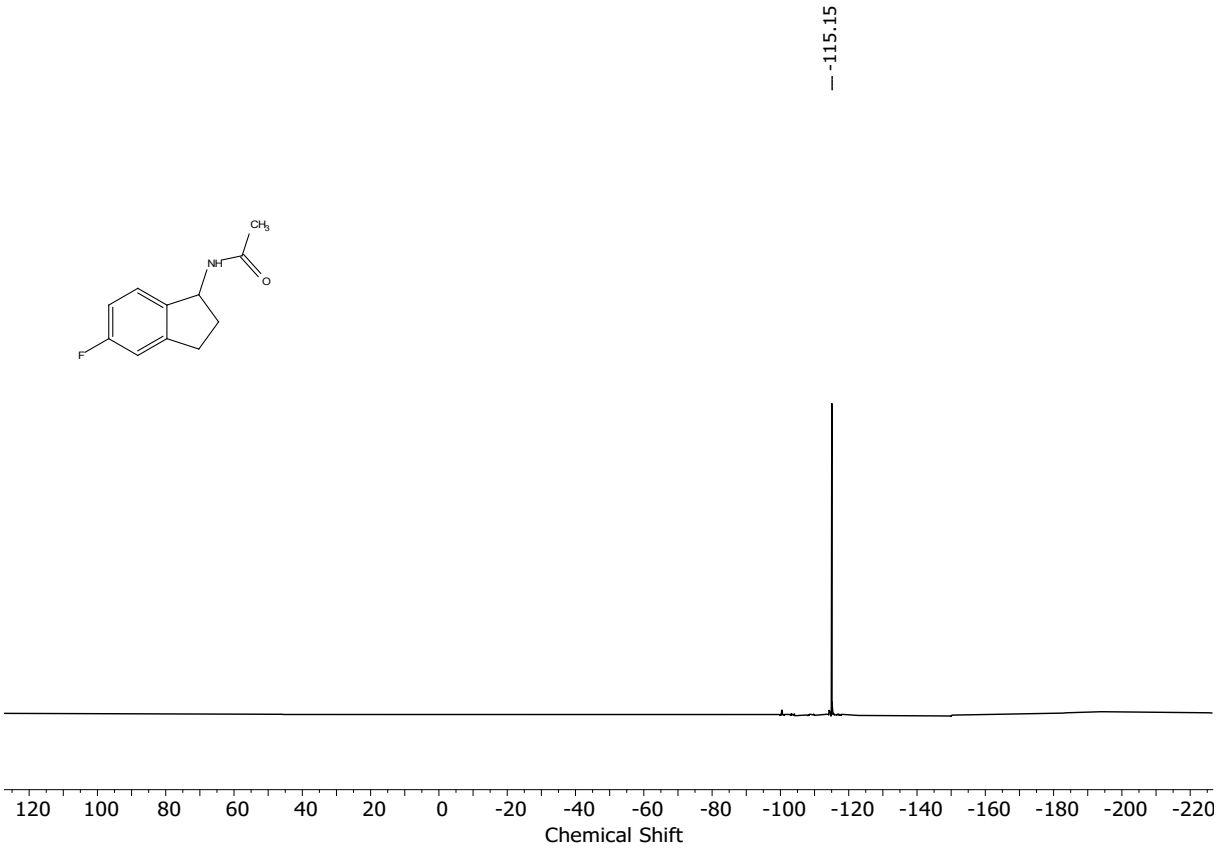
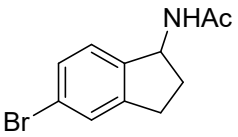


Figure S 30 ^{19}F NMR of 6b

- ***N-(5-bromo-2,3-dihydro-1H-inden-1-yl)acetamide***



^{1}H NMR (300 MHz, $CDCl_3$) δ; 7.37 (s, 1H), 7.34-7.30 (m, 1H), 7.14 (d, J = 8.00 Hz, 1H), 5.68 (br, 1H), 5.41 (1, J = 7.82 Hz, 1H), 3.00-2.79 (m, 2H), 2.63-2.52 (m, 1H), 2.02 (s, 3H), 1.86-1.73 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ; 169.85, 145.69, 142.29, 129.90, 128.00, 125.57, 121.91, 54.22, 34.06, 30.06, 23.42.

HRMS: m/z calculated for $C_{11}H_{12}BrNO$: 255.16 $[M+H]^+$; observed 255.18

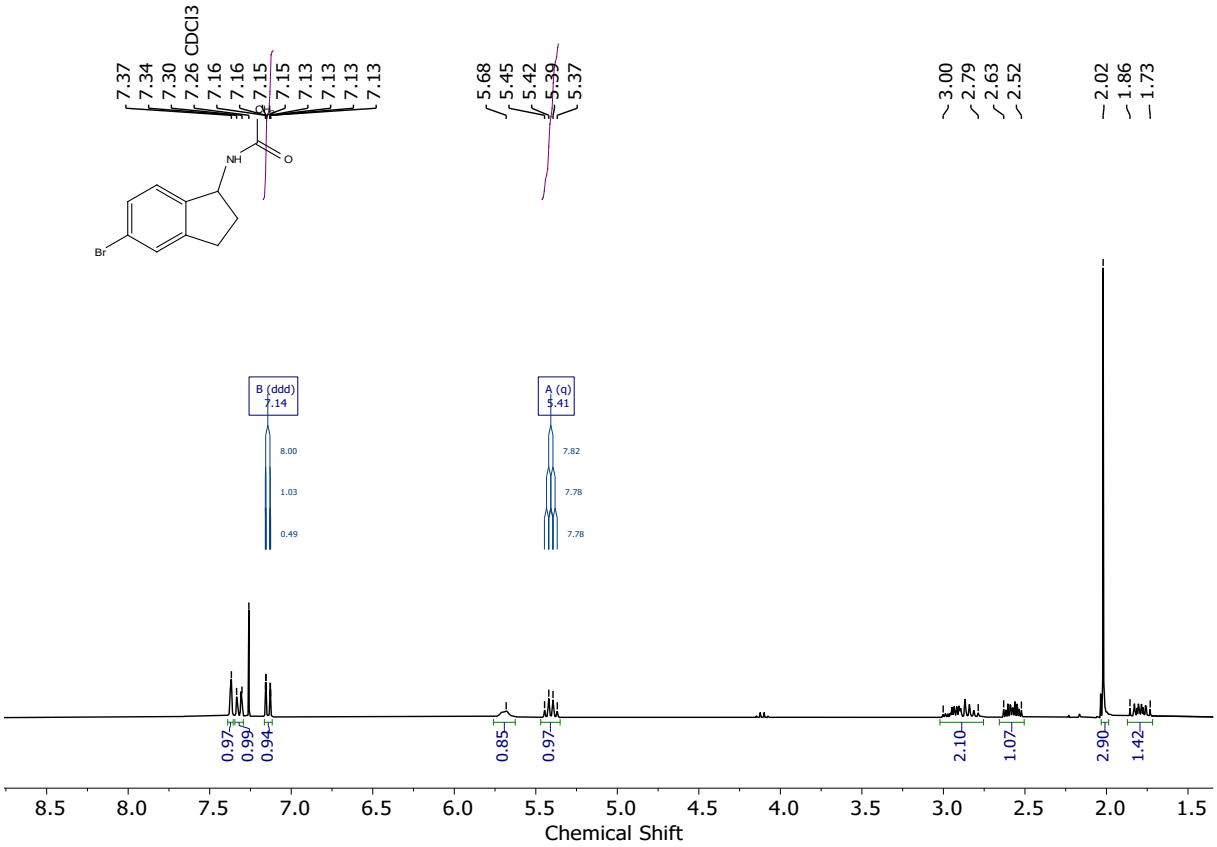


Figure S 31 ^{1}H NMR of 7b

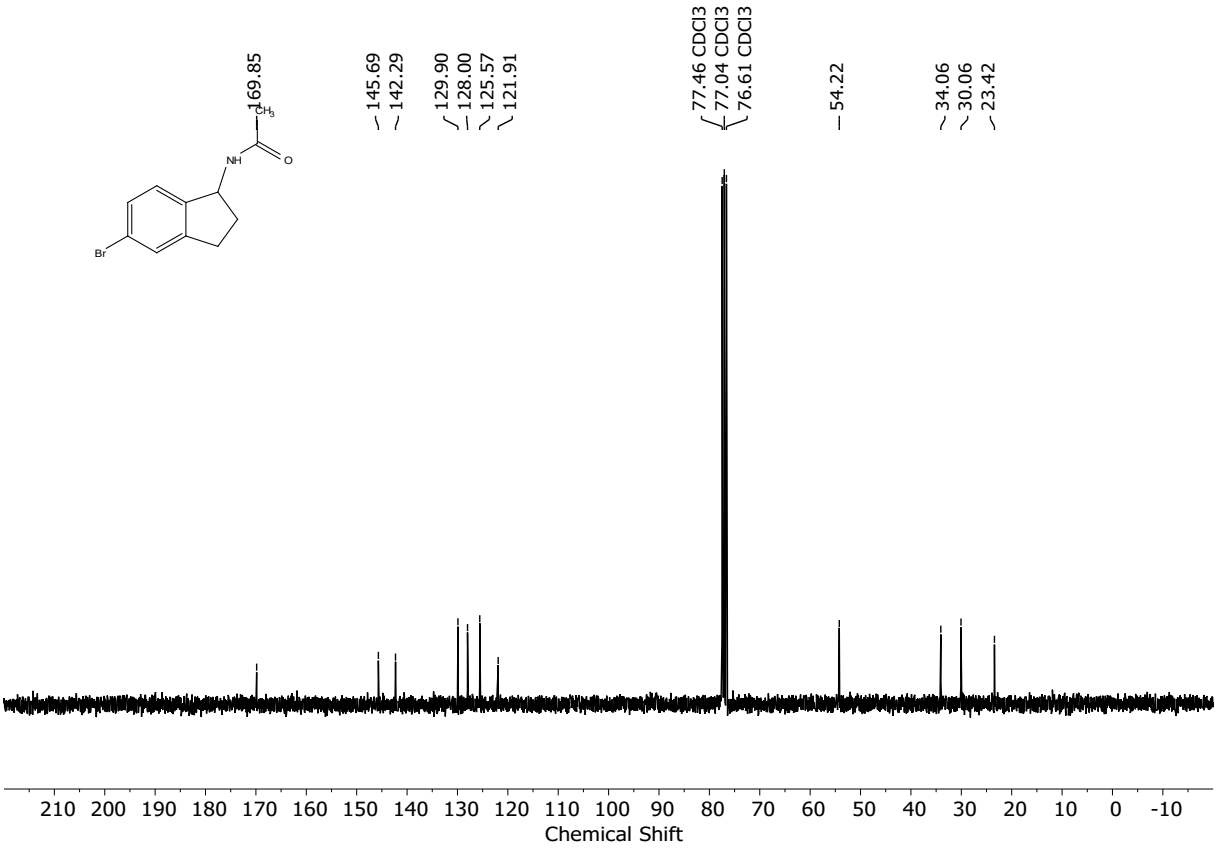
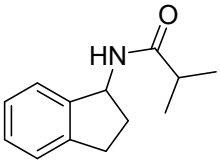


Figure S 32 ^{13}C NMR of 7b

- ***N-(2,3-dihydro-1H-inden-1-yl)isobutyramide***



^{1}H NMR (300 MHz, $CDCl_3$) δ; .25-7.19 (m, 3H), 5.65 (br, 1H), 5.49 (1, J = 7.888 Hz, 1H), 3.03- 2.81 (m, 2H), 2.65-2.55 (m, 1H), 2.42-2.33 (m, 1H), 1.83-1.72 (m, 1H), 1.21-1.17 (d, J = 11.92 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ; 176.77, 143.44, 127.93, 126.79, 124.82, 123.92, 54.38, 35.76, 34.16, 30.22, 19.81, 19.61.

HRMS: m/z calculated for $C_{13}H_{17}NO$:204.23 $[M+H]^+$; observed 204.29

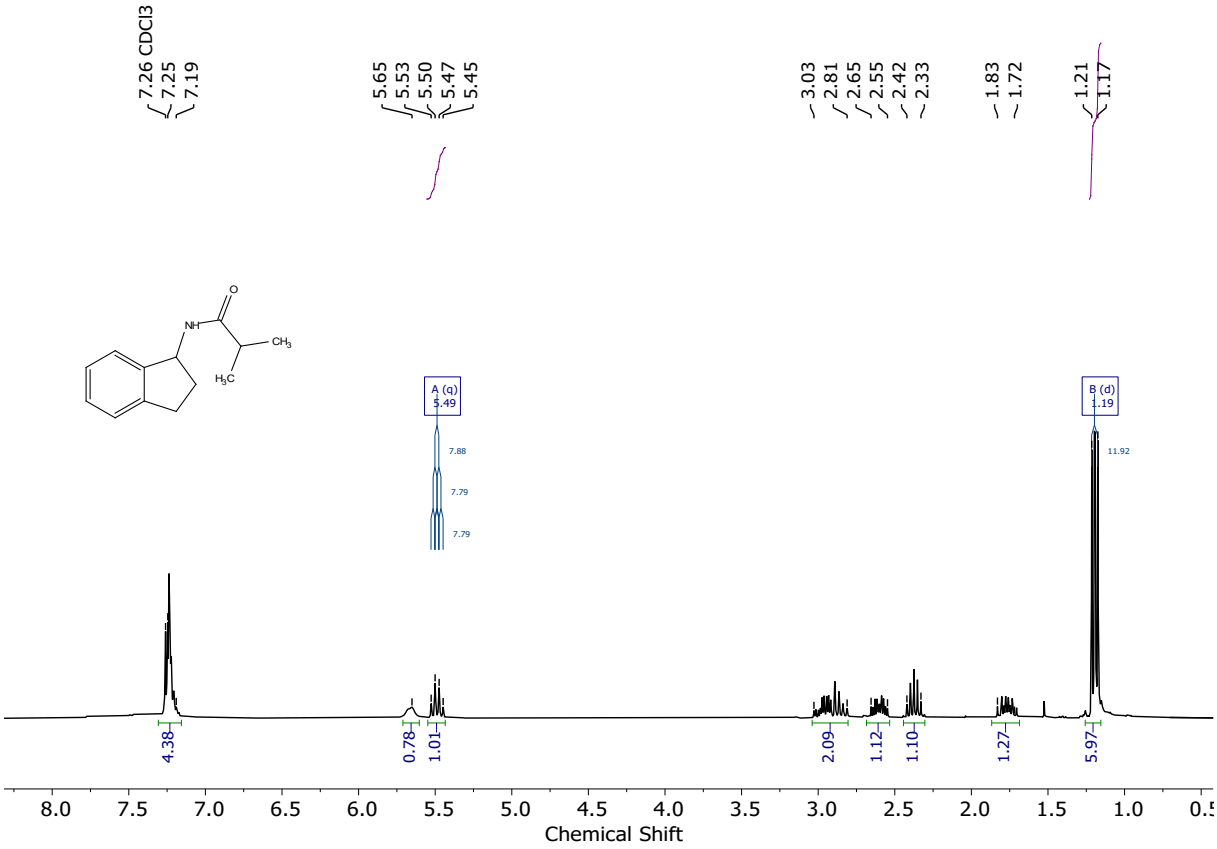


Figure S 33 ^{1}H NMR of 2b

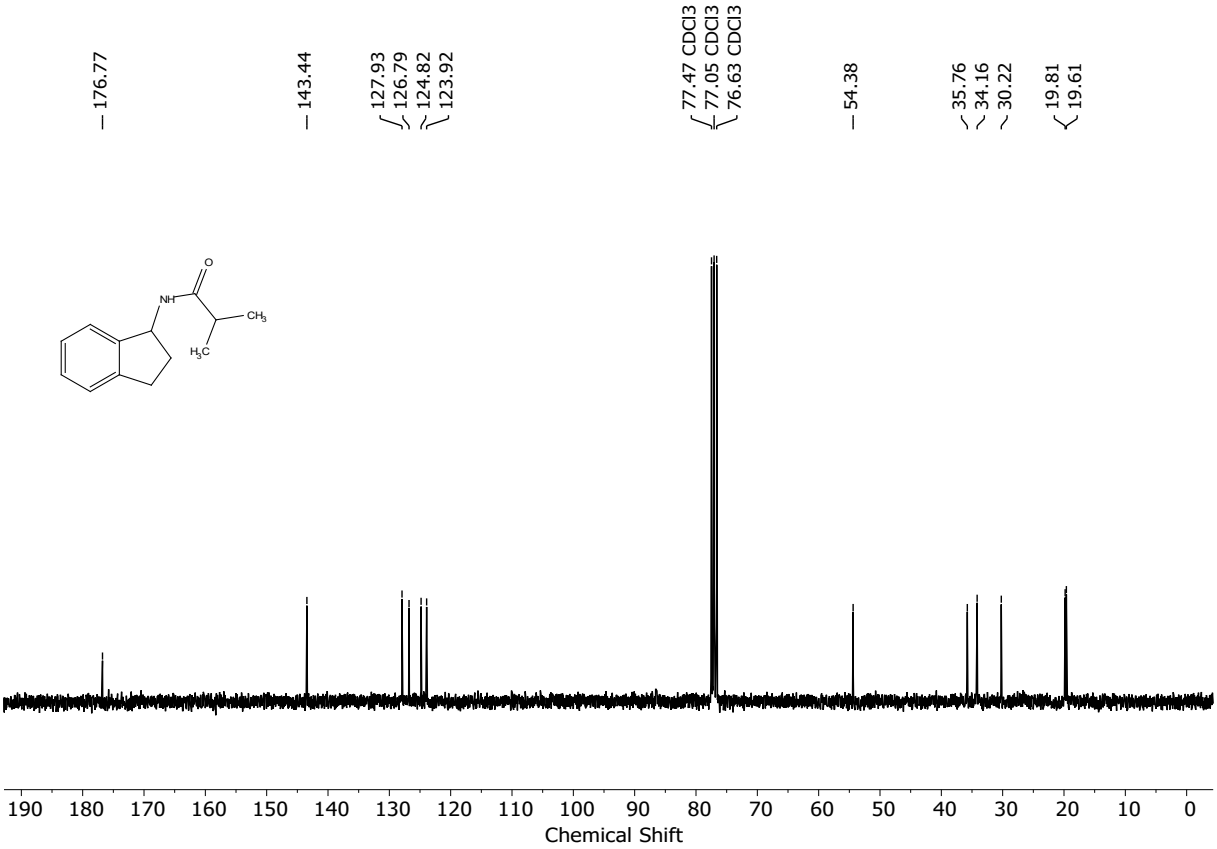
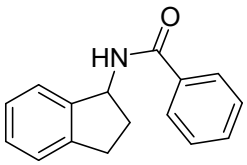


Figure S 34 ^{13}C NMR of 2b

- ***N-(2,3-dihydro-1H-inden-1-yl)benzamide***



^{1}H NMR (Xxx MHz, $CDCl_3$) δ; 7.82-7.77 (m, 2H), 7.54-7.35 (m, 4H), 7.29-7.20 (m, 3H), 6.36 (br, 1H), 5.71 (q, J=7.69 Hz, 1H), 3.09-2.88 (m, 2H), 2.77-2.66 (m, 1H), 1.99-1.87 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ; 167.24, 143.61, 143.15, 134.52, 131.55, 128.62, 128.13, 126.96, 126.89, 124.94, 124.14, 55.19, 34.23, 30.35.

HRMS: m/z calculated for $C_{16}H_{15}NO$:238.39 $[M+H]^+$; observed 238.41

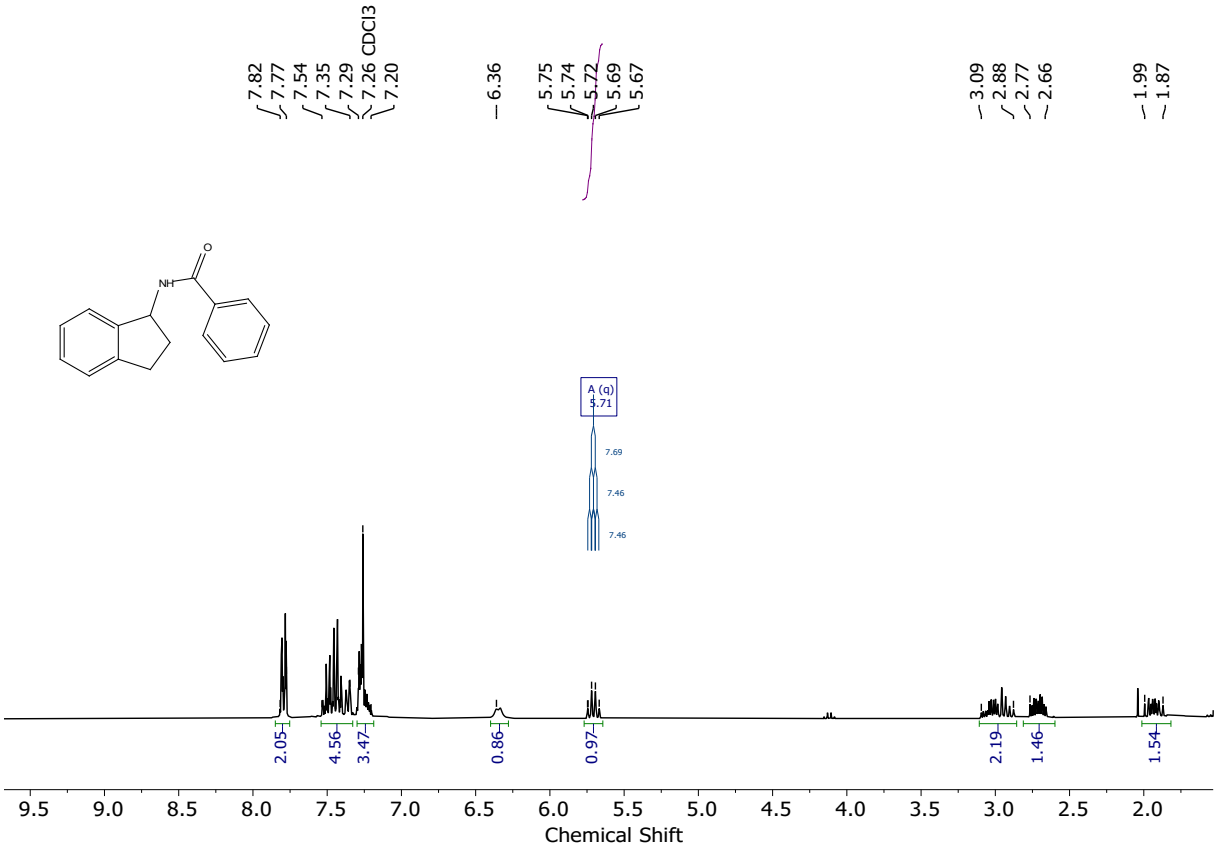


Figure S 35 ^{1}H NMR of 3b

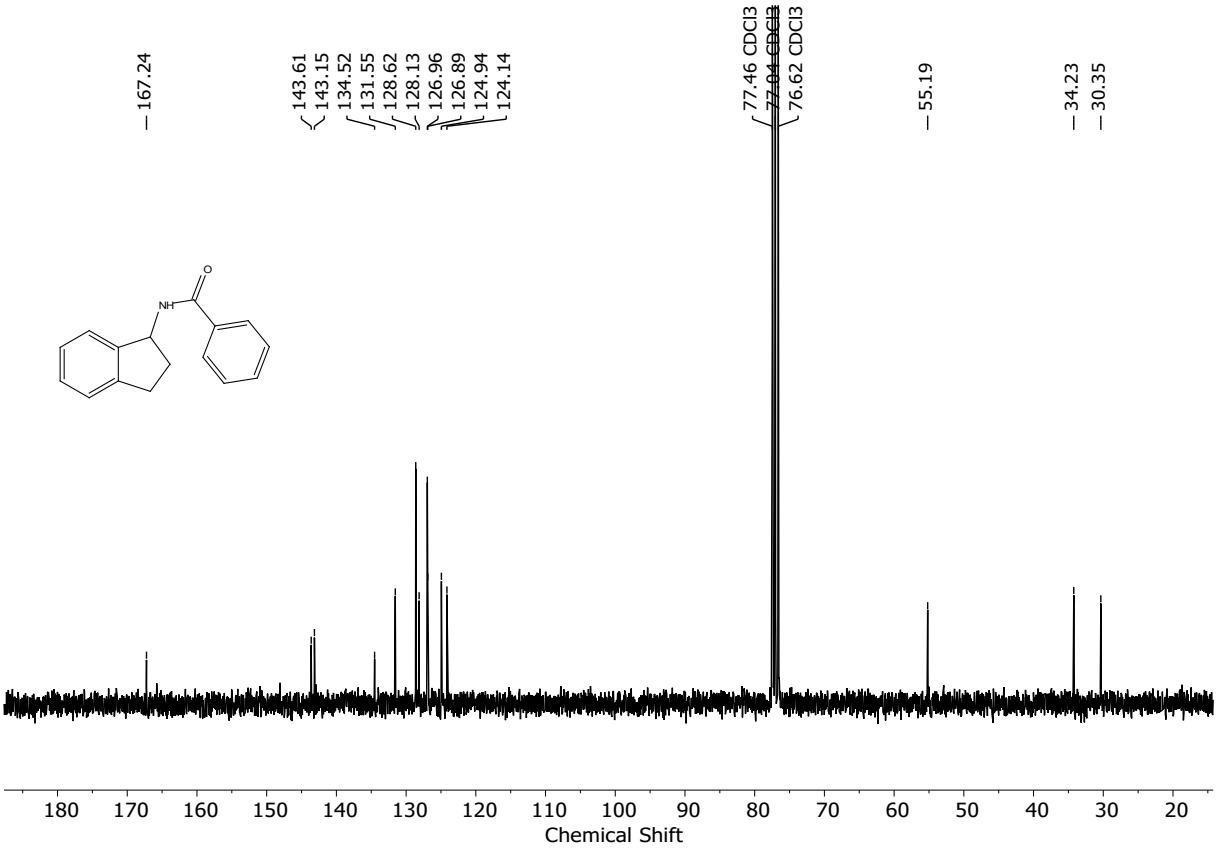
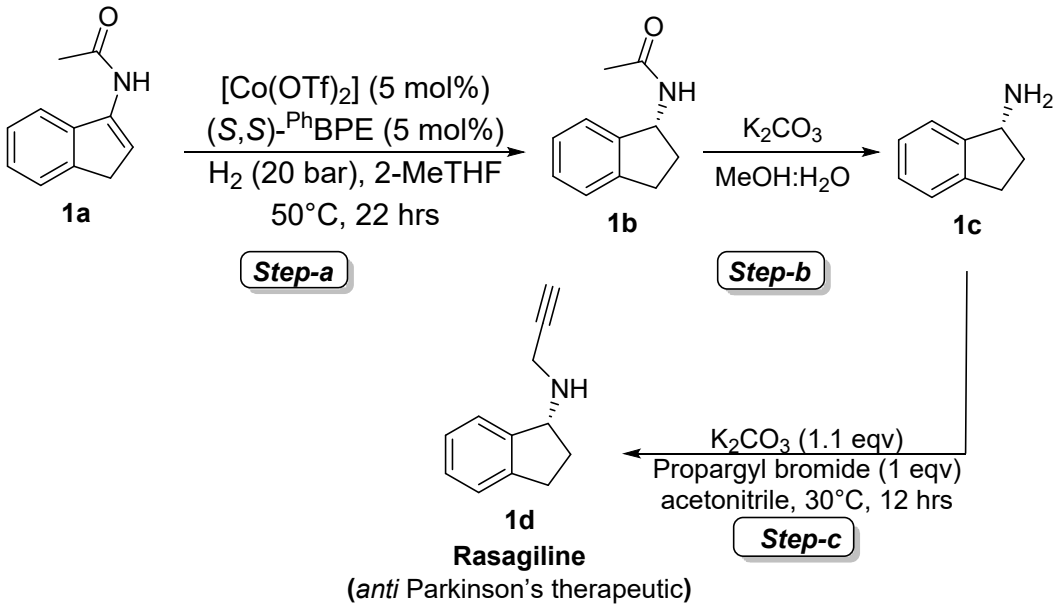


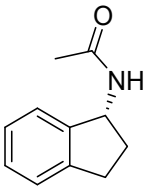
Figure S 3b

8. Synthetic protocol for Rasagiline synthesis



SchemeS 5 Azilect synthesis via C-catalyzed asymmetric hydrogenation

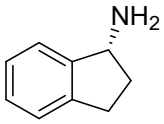
- *Step-a (Co-catalyzed asymmetric hydrogenation of 1a):*



1b

The hydrogenation experiments were performed in a stainless steel autoclave charged with an insert suitbale for up to 5 reaction vessels (7 mL) with teflon mini stirring bars. A reaction vessel is charged with [Co]-precursors (5 mol%) and ligand (5 mol%) and stirred for 10-15 mins in the 2-Me THF (5mL). Then the additive Zn (50 mol%) and desired substrates **1a** (1.0 mmol) were added to the reaction vessel maintaining the inert atmosphere and the vessels were placed in the autoclave. The autoclave was purged two times with nitrogen and three times with hydrogen. Finally it was pressurized at the 20 bar H_2 pressure at 50°C for 22 h. After the required reaction time, the autoclave was depressurized and the reaction vessels were diluted with EtOAc and filtered through a short pad of silica (96% isolated yield). The conversion was determined by GC, GC-MS and NMR measurement and the enantiomeric excess was measured by GC or HPLC using a chiral coloumn.

- *Step-b (deacylation of 1b)*



1c

Potassium carbonate, K_2CO_3 (3.0 mmol) was added to the MeOH/H_2O (1:1) solution of amide (1.5 mmol) and stirred for 25 hrs at 50°C. After that, the reaction mixture was concentrated in vacuum and extracted in solution of DCM and saturated sodium bicarbonate solution. The organic layer was separated and washed with brine and dried over $MgSO_4$ and concentrated to result the corresponding amine in 89% yield without the loss of optical purity (89% isolated yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ; 7.35-7.32 (m, 1H), 7.24-7.19 (m, 3H), 4.38-4.33 (m, 1H), 3.01-2.93 (m, 1H), 2.85-2.77 (m, 1H), 2.56-2.47 (m, 1H), 1.74-1.64 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ; 147.49, 143.12, 127.19, 126.50, 124.69, 123.32, 57.31, 37.40, 30.13.

$[\alpha]_D^{298} = \ -15.4°\ (c\ 1.5, methanol)$

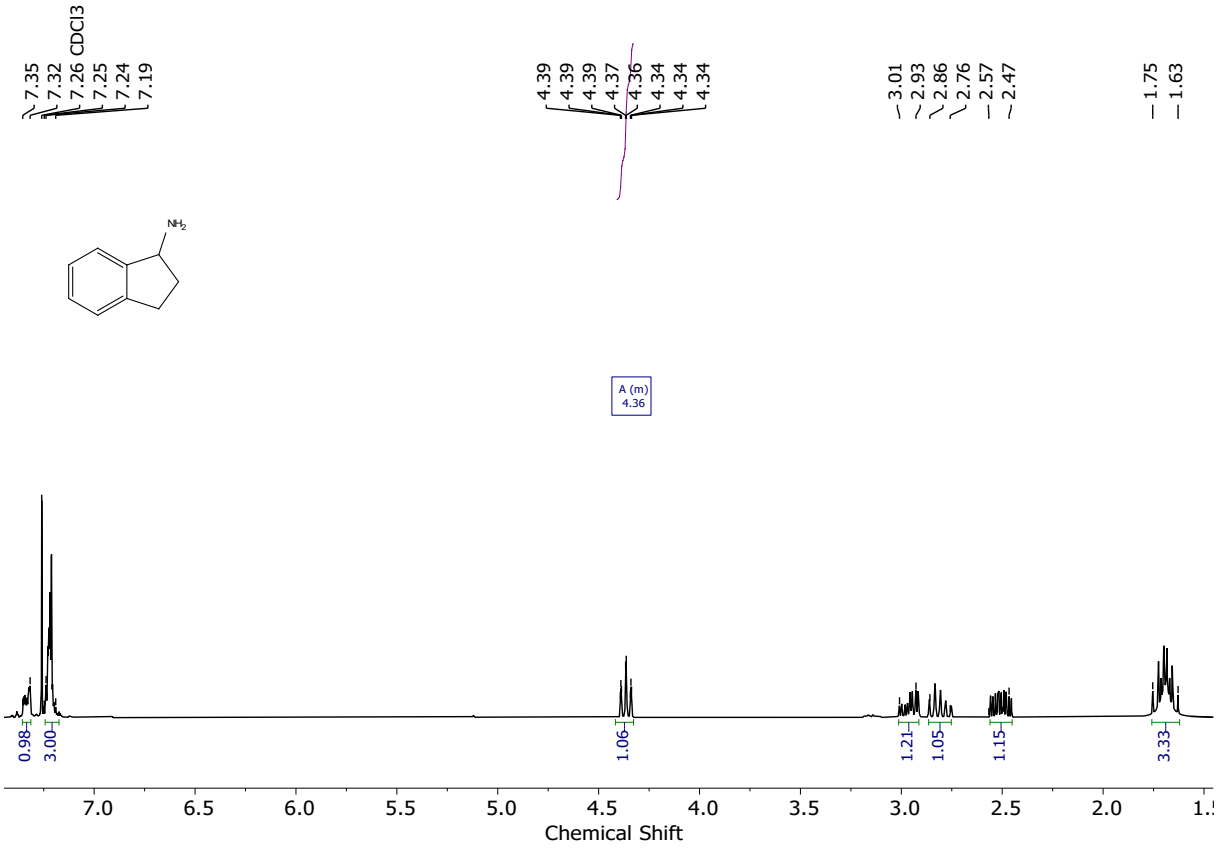


Figure S 36 ^{1}H NMR of 1c

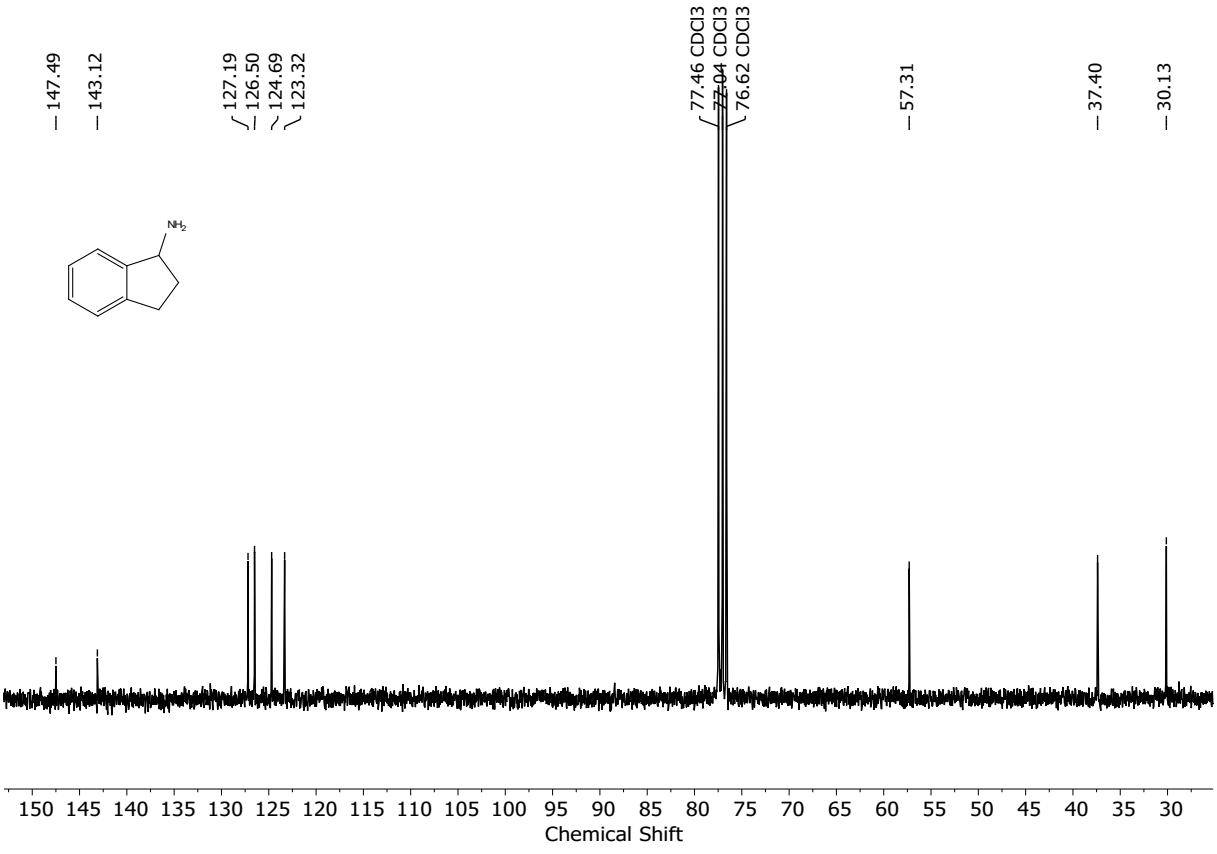
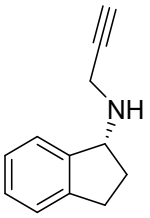


Figure S 37 ^{13}C NMR of 1c

- *Step-c (propargylation of 1c)*



1d

Potassium carbonate (1.1 eqv) was added to the solution of **1c** (1 eq.) in 10 mL in acetonitrile. Propargyl bromide (1.05 eq.) was added to the reaction mixture and stirred at 30°C for 12 h. The solid was filtered off and solvent was removed. The residue was further purified via flash column (EtOAc: Hexane , 30%) as yellow oil in 81% yield (98% ee).

^{1}H NMR (300 MHz, $CDCl_3$) δ; 7.37-7.33 (m, 1H), 7.26-7.18 (m, 3H), 4.38 (t, 1H, J= 6.7 Hz), 3.53 (dd, 2H, J=2.4 Hz), 3.10-3.00 (m, 1H), 2.88-2.78 (m, 1H), 2.46-2.34 (m, 1H), 2.26 (t, 1H, J= 2.45 Hz), 1.91-1.81 (m, 1H), 1.65 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ; 144.52, 143.84, 127.66, 126.28, 124.89, 124.21, 82.51, 71.43, 61.90, 36.19, 33.35, 30.48.

$[\alpha]_D^{298} = \ +17.9°\ (c\ 0.2, chloroform)$

HRMS: m/z calculated for $C_{12}H_{14}N$: 172.2490 $[M+H]^+$; observed 172.2468

HPLC: Cellulose-3

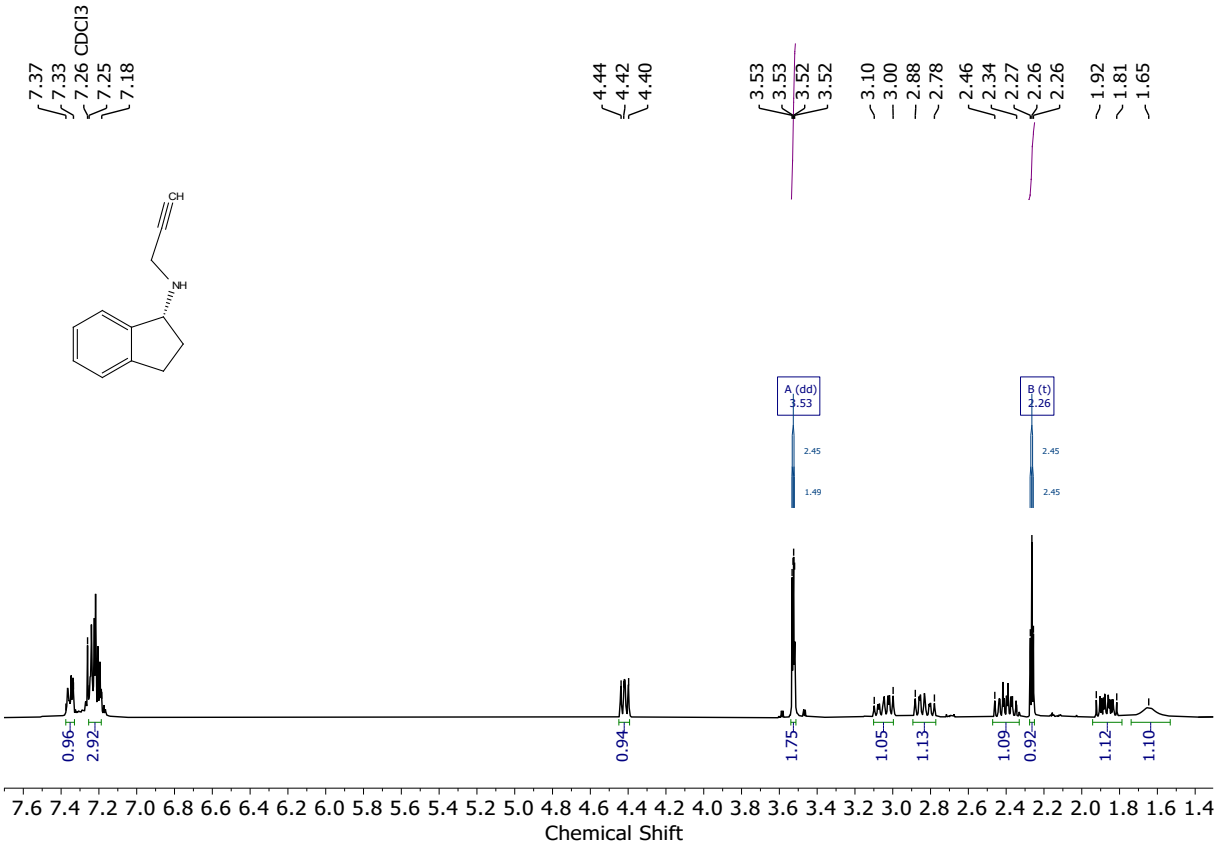


Figure S 38 ^{1}H NMR of 1d

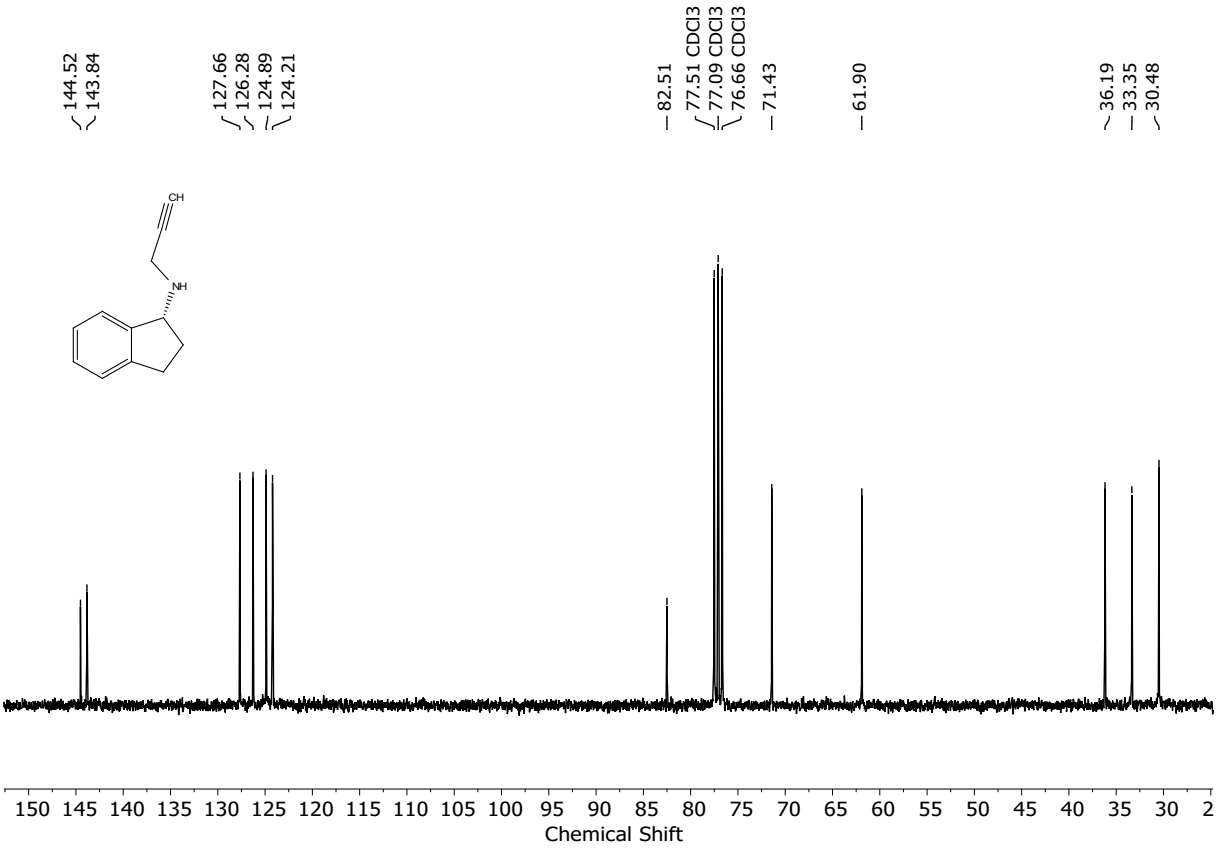
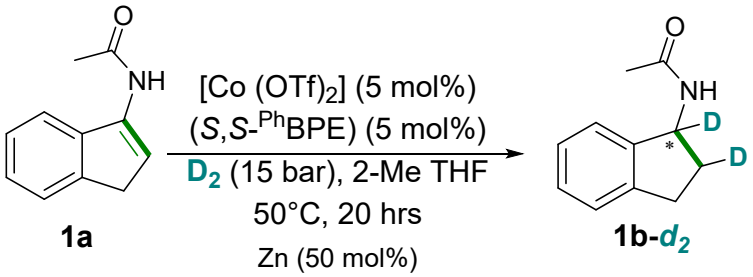


Figure S 39 ^{13}C NMR of 1d

9. Deuteration of 1a and analytical data



SchemeS 6 Asymmetric deuteration of 1a using Co/BPE precatalyst

Protocol for deuteration:

The deuteration experiment was performed in a stainless steel autoclave charged with an insert suitbale for up to 8 reaction vessels (4 mL) with teflon mini stirring bars. In the experiment, a reaction vessel is charged with [Co $(OTf)_2$]-precursor (5 mol%) and (*S*,*S*)-^{Ph}BPE (5 mol%) and stirred for 10-15 mins in 2-Me THF (2mL). Then the additive Zn (50 mol%) and desired substrates **1a** (0.5 mmol) were added to the reaction vessel maintaining the inert atmosphere and the vessels were placed in the autoclave. The autoclave was purged two times with nitrogen. Finally it was pressurized at the 15 bar of D_2 pressure at 50°C for 20 h. After that, the autoclave was depressurized and the reaction vessels were diluted with EtOAc and filtered through a short pad of silica. The conversion was determined by GC and GC-MS measurement. The *d*-incorporation was analysed via NMR analysis (95% isolated yield).

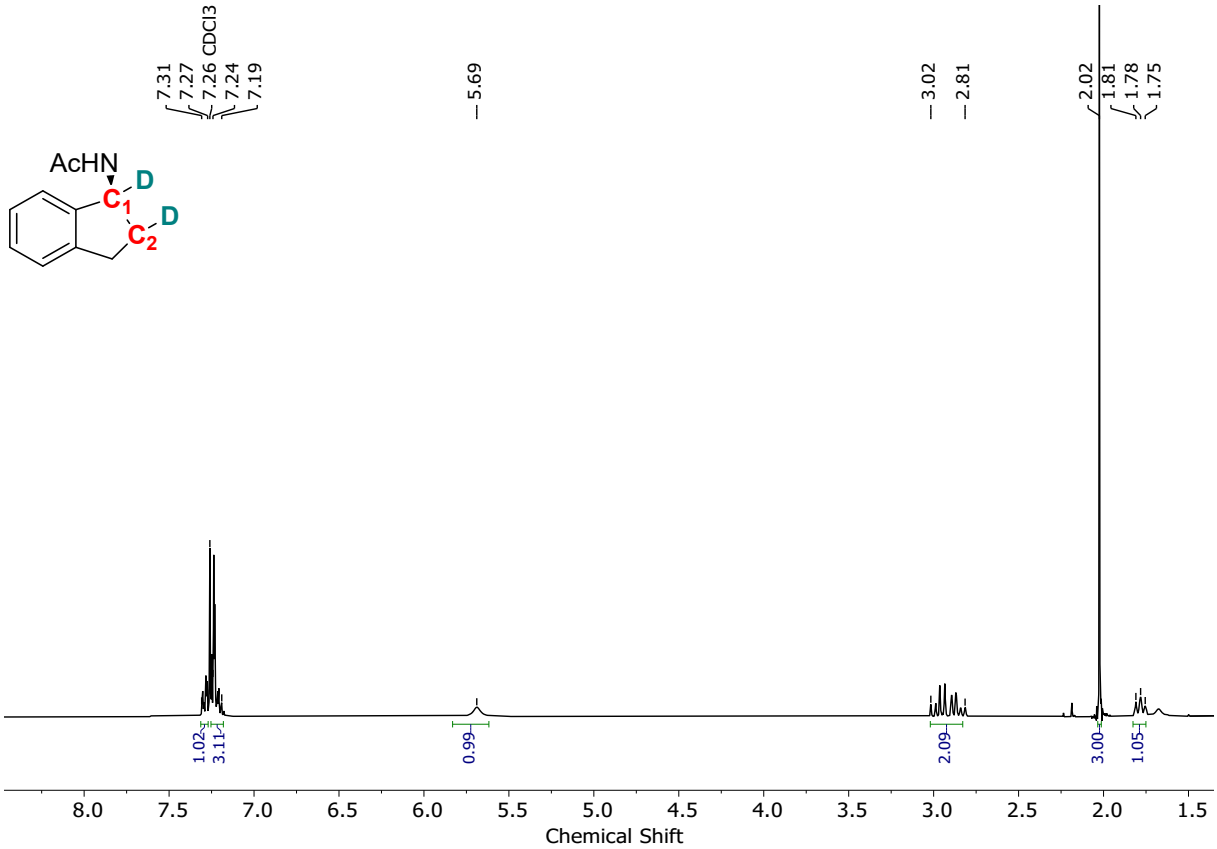


Figure S 40 ^{1}H NMR of 1b-d_2

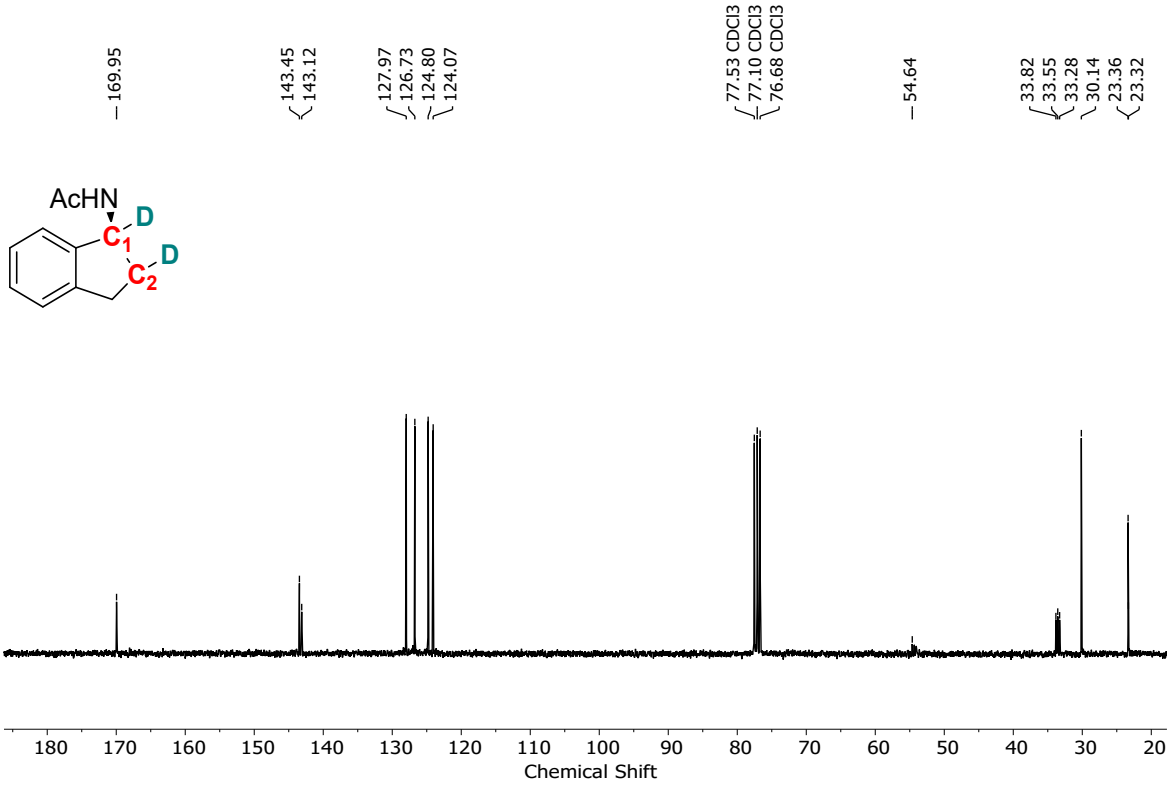


Figure S 41 ^{13}C NMR of 1b-d_2

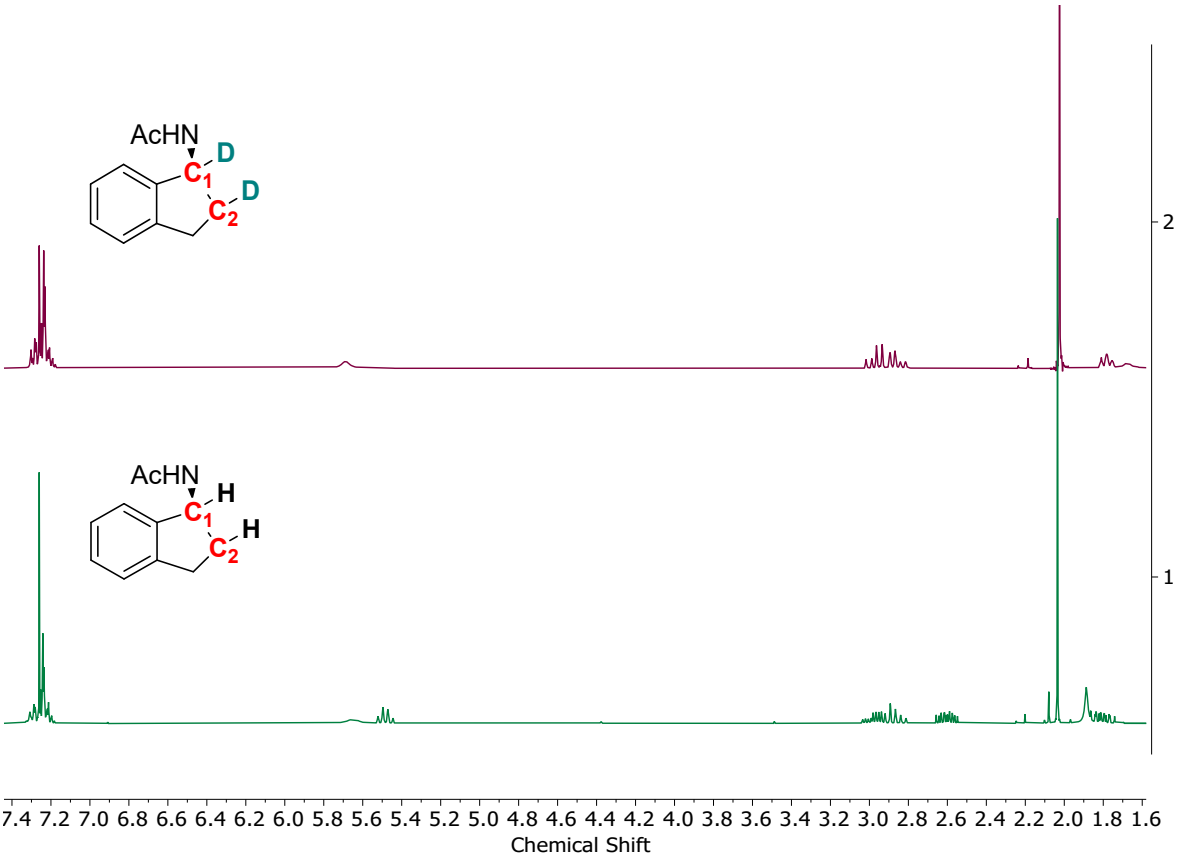


Figure S 42 ^{1}H NMR Hydrogen vs Deuteration experiments of 1a

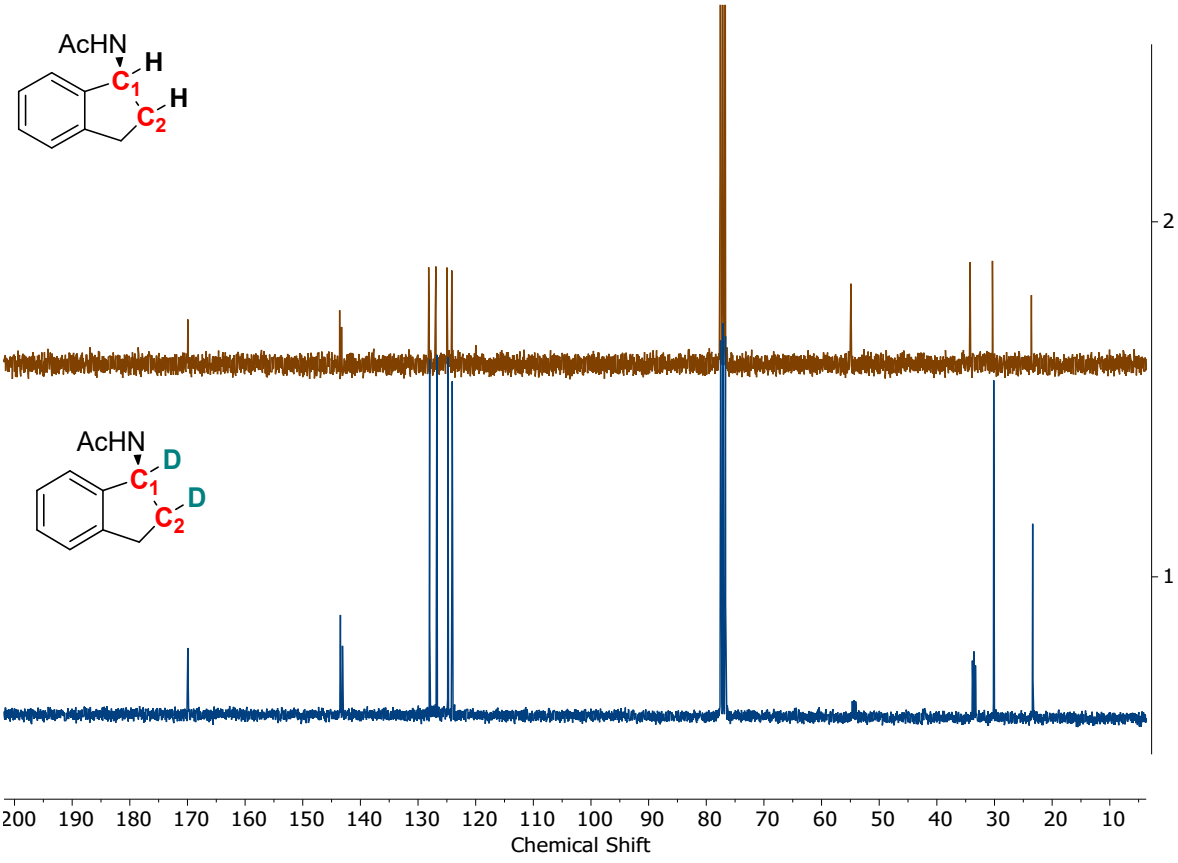


Figure S 43 ^{13}C NMR Hydrogen vs Deuteration experiments of 1a

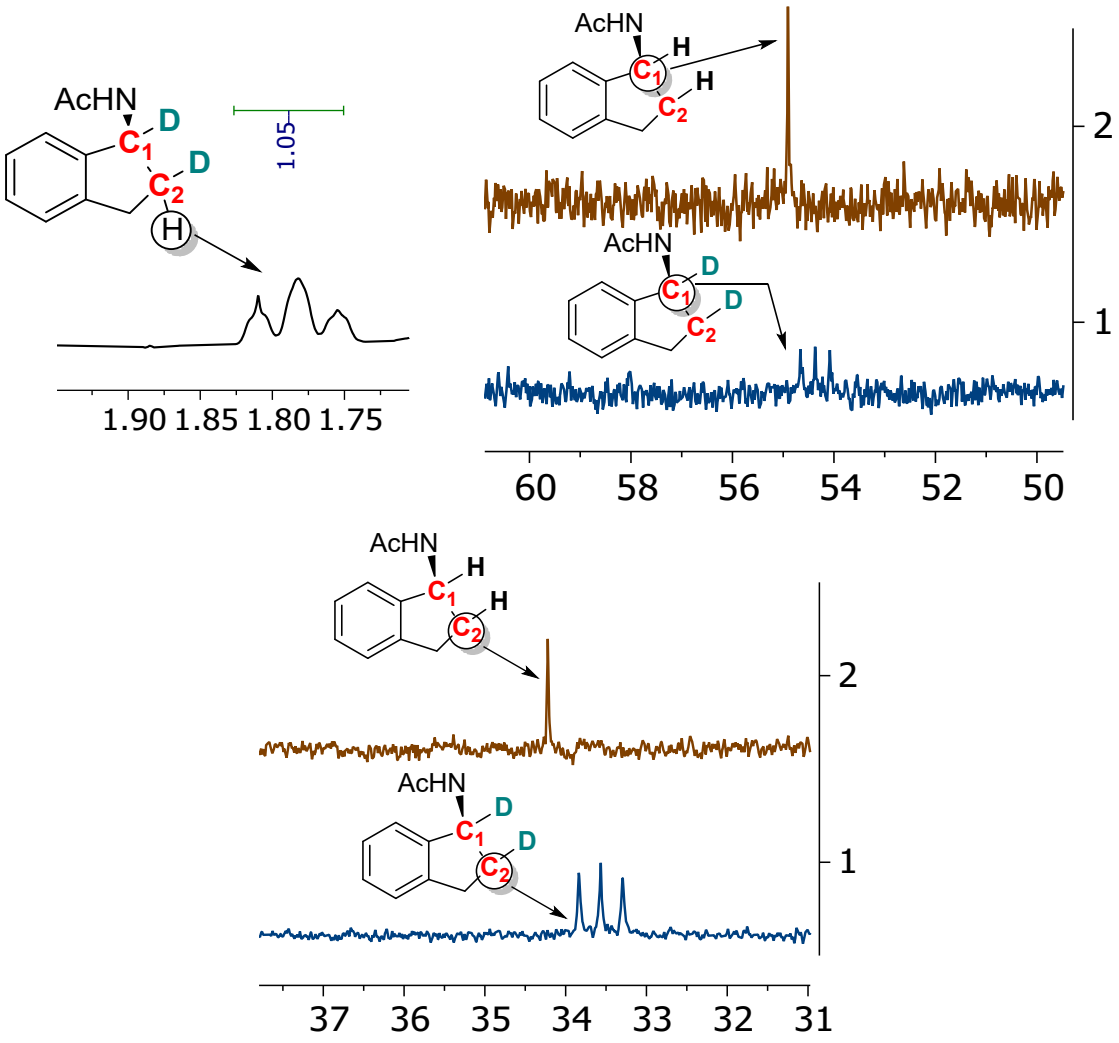


Figure S 44 ^{1}H NMR of 1b-d_2 (snapshot with characteristic peak region)

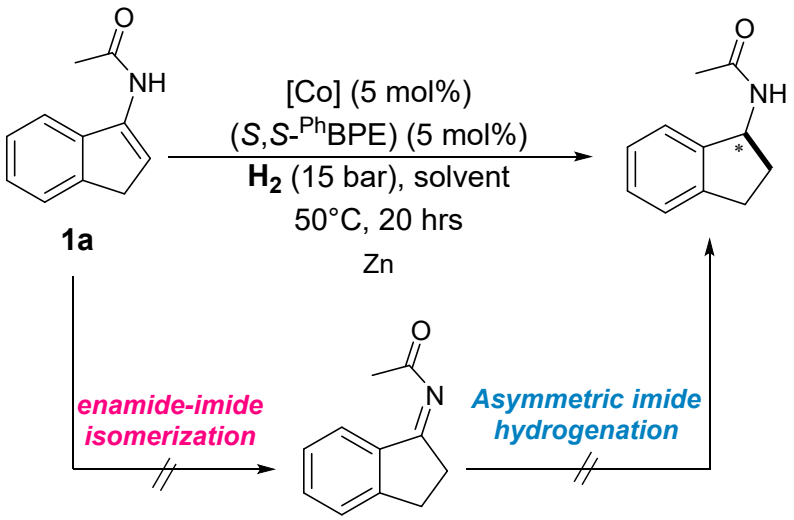
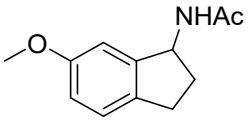


Figure S 45 Possible pathway of the hydrogenation of 1a

10. Chiral HPLC traces



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                                                Inj Volume : 0.2 µl
Acq. Method     : C:\CHEM32\1\METHODS\OD-H.M
Last changed    : 4/13/2023 12:39:49 PM by Analytik
Analysis Method : C:\CHEM32\1\METHODS\OD-H.M
Last changed    : 4/14/2023 9:58:52 AM by Analytik
                  (modified after loading)
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Additional Info : Peak(s) manually integrated
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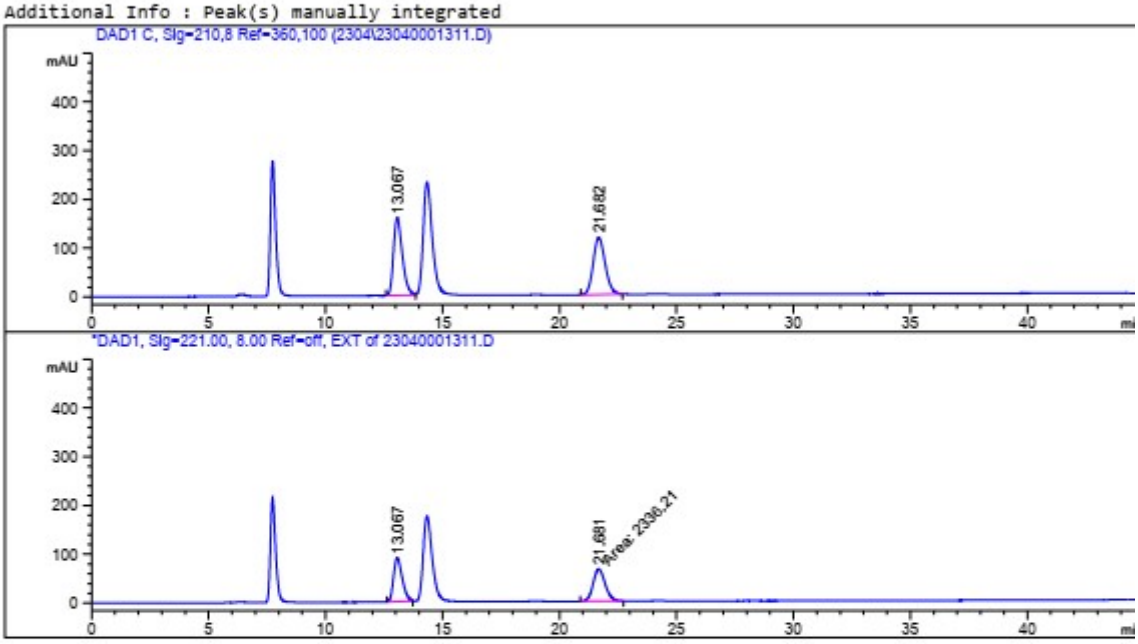


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Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

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   2  21.682 BB    0.5460 4165.86035  116.84090  49.8415

Totals :                  8358.21973  275.96278
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Figure S 46 HPLC trace of rac-4b

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                                               Inj Volume : 0.2 µl
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Analysis Method : C:\CHEM32\1\METHODS\OD-H.M
Last changed    : 4/14/2023 9:58:52 AM by Analytik
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Additional Info : Peak(s) manually integrated
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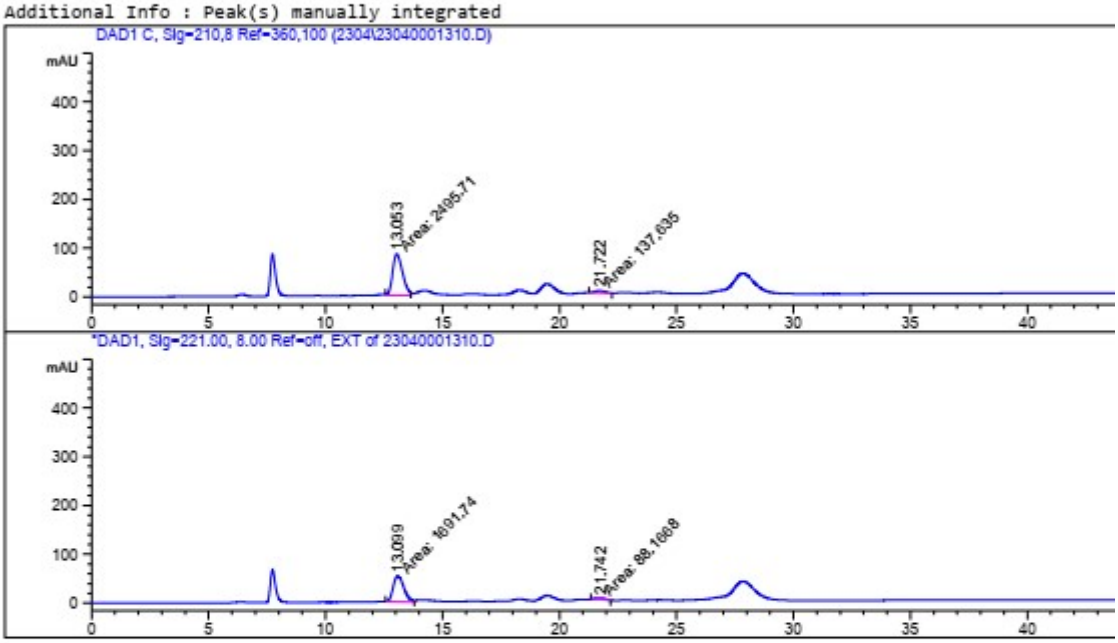


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Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
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----|-------|----|-------|----------|----------|--------|
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   2  21.722 MM    0.5046  137.63455    4.54607   5.2266

Totals :                  2633.34232   88.73314
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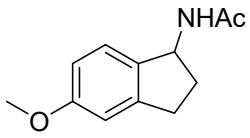
Figure S 47 HPLC trace of enantioenriched-4b

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Additional Info : Peak(s) manually integrated
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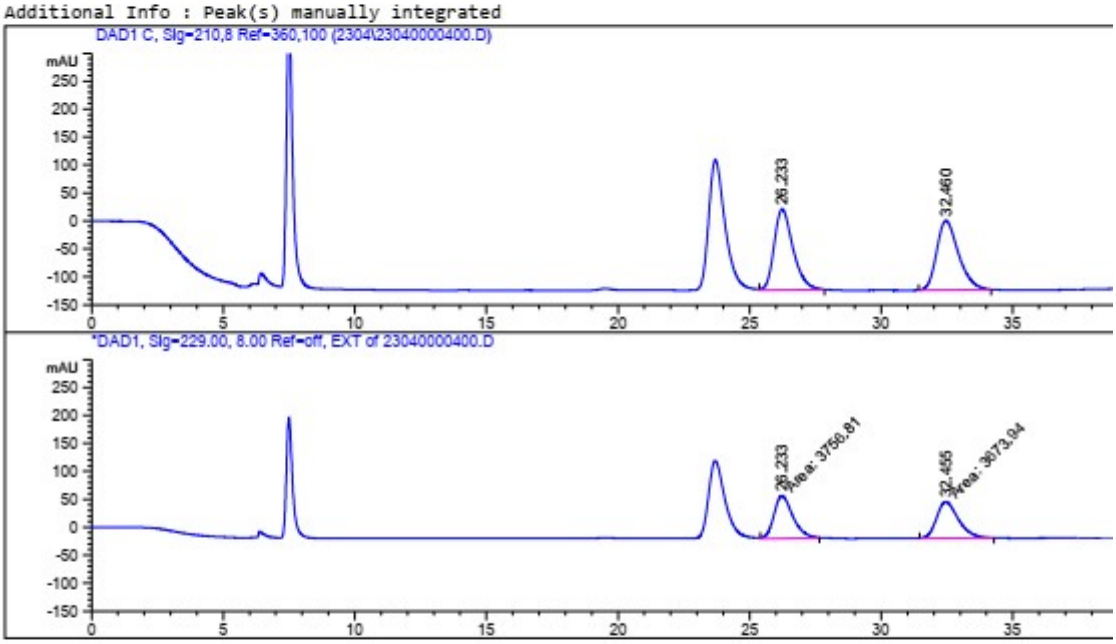


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Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

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  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
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   2  32.460 BB    0.8503 7176.14990  124.16216  49.9170

Totals :                  1.43762e4   268.56931
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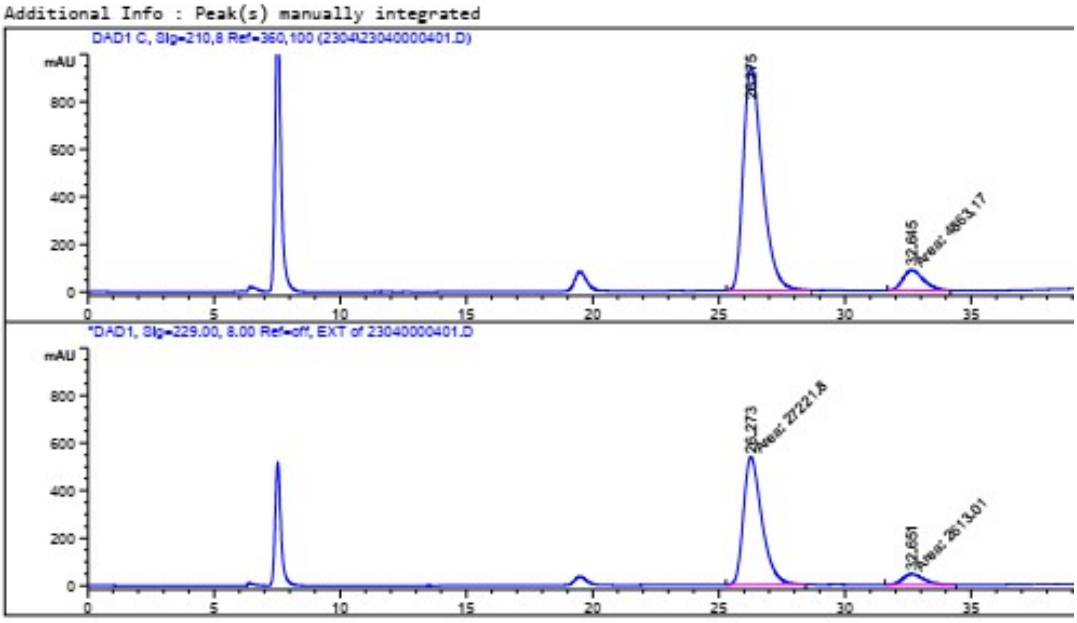
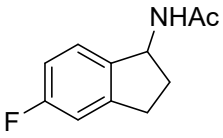
Figure S 48 HPLC trace of rac-5b

```
================================================================================
Acq. Operator   : Analytik                       Seq. Line :   2
Acq. Instrument : LC5                           Location : Vial 12
Injection Date  : 4/4/2023 10:44:41 AM               Inj :   1
                                               Inj Volume : 1.0 µl
Acq. Method     : C:\CHEM32\1\METHODS\OD-H0.3.M
Last changed    : 4/4/2023 9:57:57 AM by Analytik
Analysis Method : C:\CHEM32\1\METHODS\OD-H0.3.M
Last changed    : 4/4/2023 4:02:08 PM by Analytik
                  (modified after loading)
Method Info     : OD-H, Hept./EtOH 95:5,  0.3ml/min

Additional Info : Peak(s) manually integrated
```

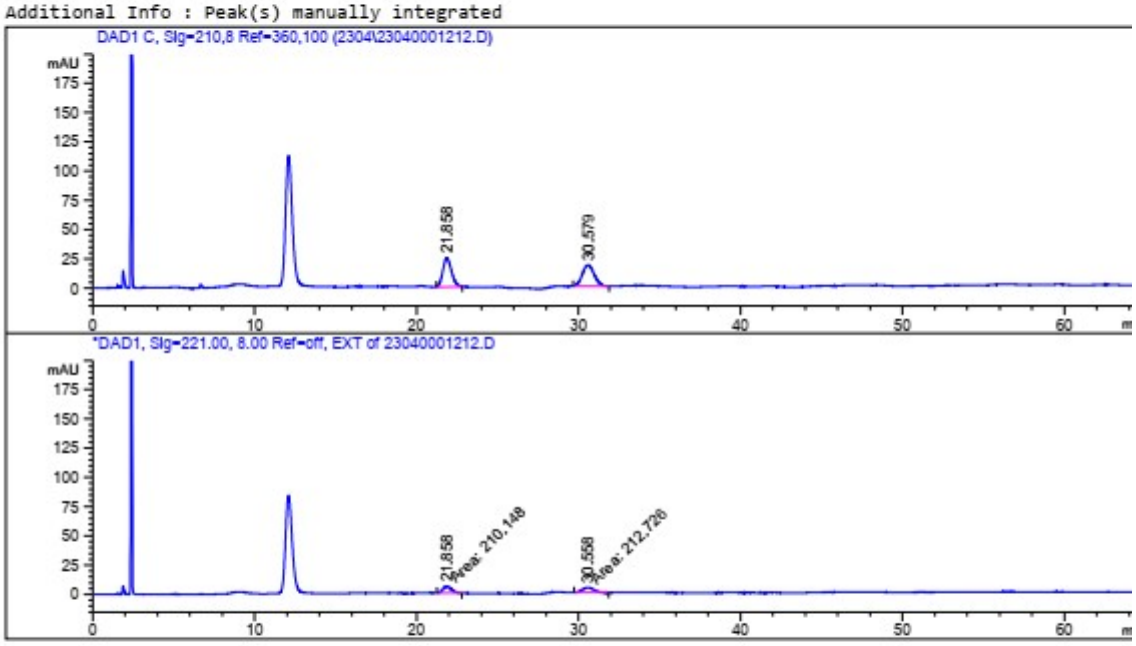



```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  26.275 BB    0.7996 4.91942e4   938.46130  91.0037
   2  32.645 MM    0.9475 4863.16650   85.54361   8.9963

Totals :                  5.40574e4  1024.00491
```

Figure S 49 HPLC trace of enantioenriched-5b



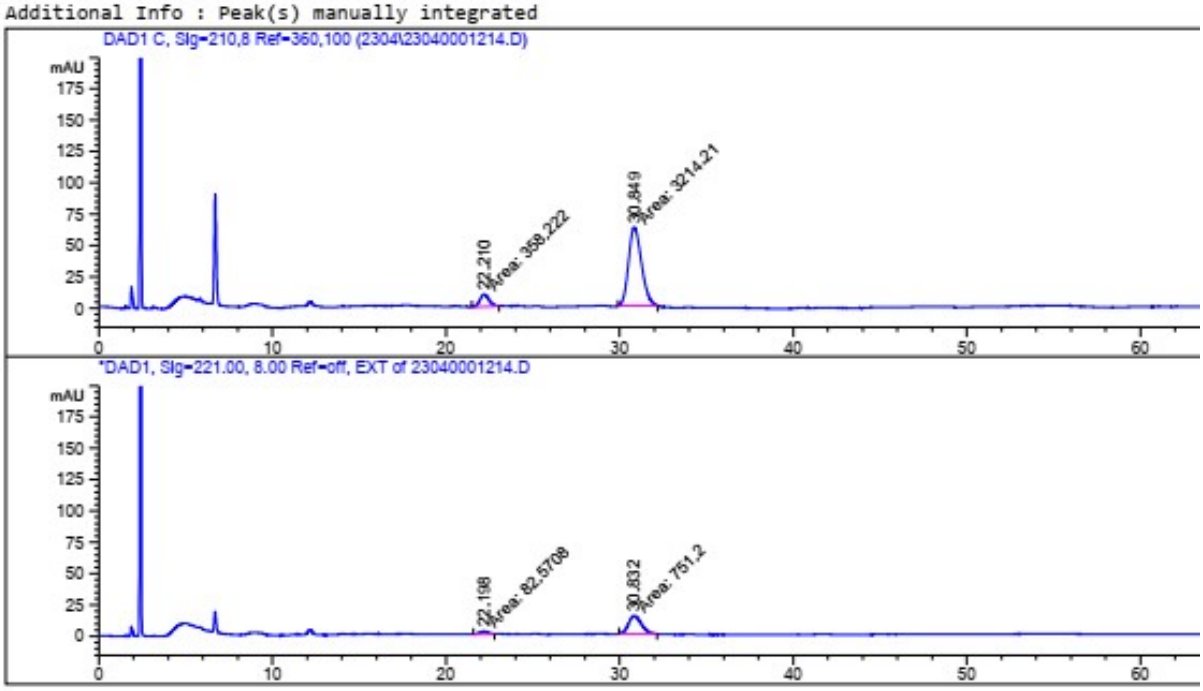

```
======================================================================
Acq. Operator   : Analytik                       Seq. Line :   6
Acq. Instrument : LC5                             Location : Vial 11
Injection Date  : 4/12/2023 8:28:59 PM                Inj :   1
                                                 Inj Volume : 1.0 µl

Acq. Method     : C:\CHEM32\1\METHODS\OJ-H.M
Last changed    : 4/12/2023 4:15:30 PM by Analytik
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\OJ-H.M
Last changed    : 4/13/2023 9:32:26 AM by Analytik
                  (modified after loading)
Method Info     : OJ-H, Hept./EtOH 98:2,  2ml/min

Additional Info : Peak(s) manually integrated
```




```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  21.858 BB    0.5439  917.46997   24.55559  49.8467
   2  30.579 BB    0.6184  923.11475   18.24245  50.1533

Totals :                  1840.58472   42.79804
```

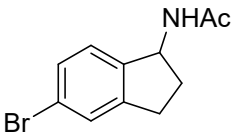
Figure S 50 HPLC trace of rac-6b

```
================================================================================
Acq. Operator   : Analytik                       Seq. Line :   8
Acq. Instrument : LC5                           Location : Vial 21
Injection Date  : 4/12/2023 10:41:07 PM             Inj :   1
                                               Inj Volume : 1.0 µl
Acq. Method     : C:\CHEM32\1\METHODS\OJ-H.M
Last changed    : 4/12/2023 4:15:30 PM by Analytik
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\OJ-H.M
Last changed    : 4/13/2023 9:32:26 AM by Analytik
                  (modified after loading)
Method Info     : OJ-H, Hept./EtOH 98:2,  2ml/min

Additional Info : Peak(s) manually integrated
```

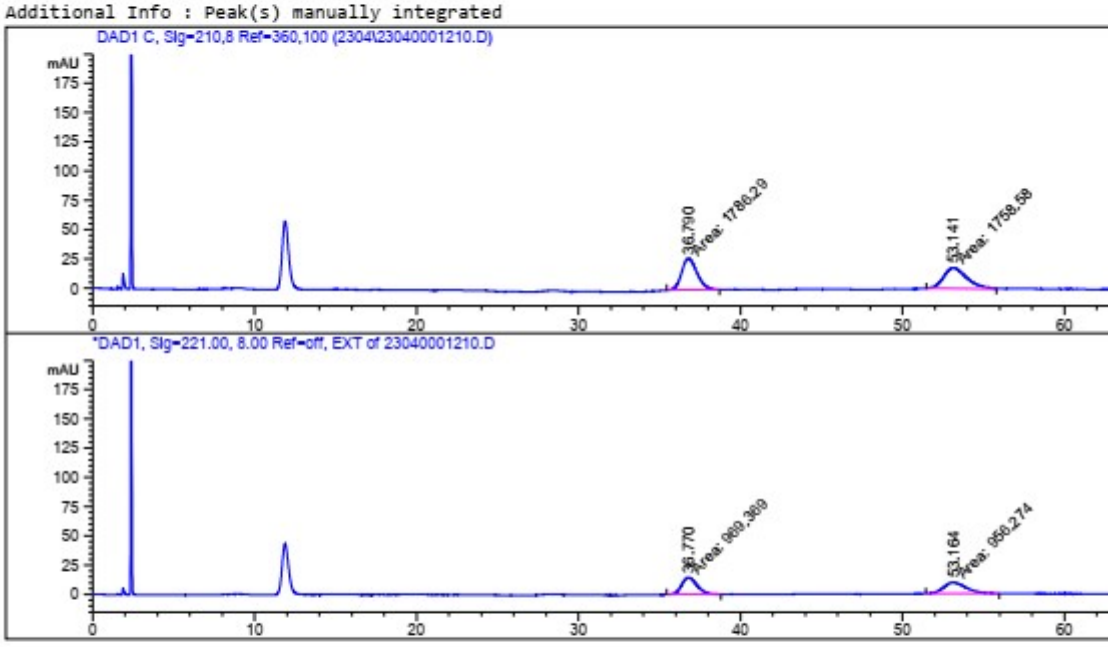



```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  22.210 MM    0.6124  358.22171    9.74888  10.0274
   2  30.849 MM    0.8601 3214.20923   62.28588  89.9726

Totals :                  3572.43094   72.03476
```

Figure S 51 HPLC trace of enantioenriched-6b



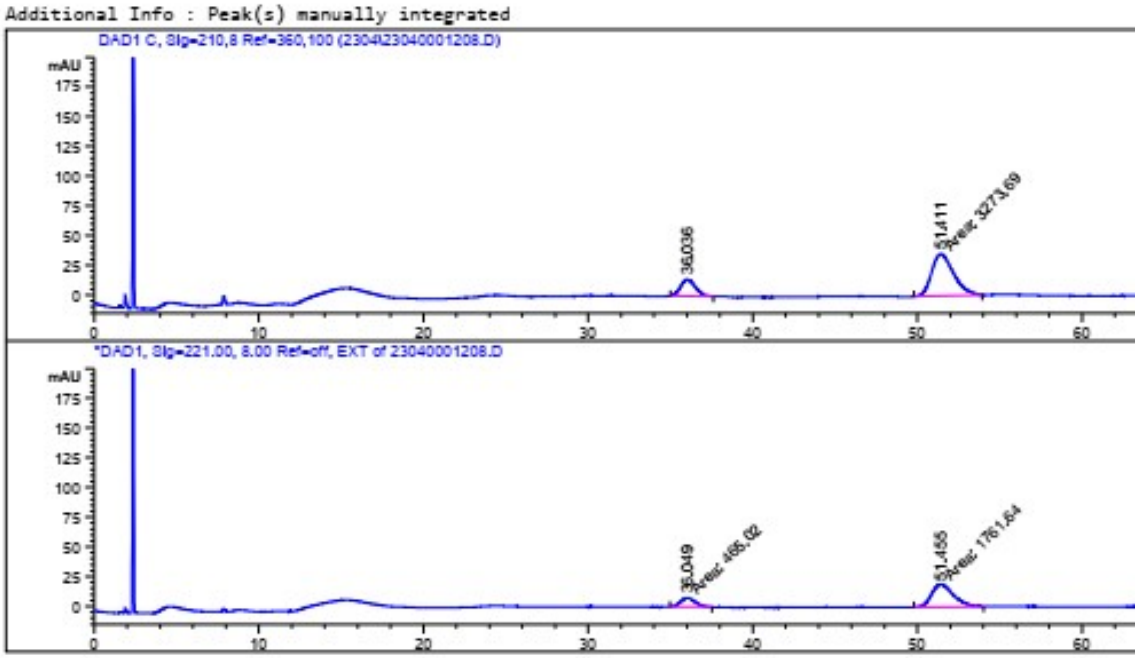

```
======================================================================
Acq. Operator   : Analytik                     Seq. Line :   4
Acq. Instrument : LC5                           Location : Vial 12
Injection Date  : 4/12/2023 6:16:50 PM              Inj :   1
                                               Inj Volume : 1.0 µl
Acq. Method     : C:\CHEM32\1\METHODS\OJ-H.M
Last changed    : 4/12/2023 4:15:30 PM by Analytik
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\OJ-H.M
Last changed    : 4/13/2023 9:32:26 AM by Analytik
                  (modified after loading)
Method Info     : OJ-H, Hept./EtOH 98:2,  2ml/min

Additional Info : Peak(s) manually integrated
```




```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  36.790 MM    1.1008 1786.29065   27.04559  50.3908
   2  53.141 MM    1.6715 1758.58386   17.53542  49.6092

Totals :                  3544.87451   44.58101
```

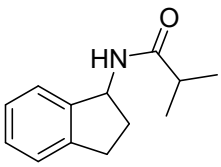
Figure S 52 HPLC trace of rac-7b

```
================================================================================
Acq. Operator   : Analytik                          Seq. Line :   2
Acq. Instrument : LC5                               Location : Vial 22
Injection Date  : 4/12/2023 4:04:40 PM                   Inj :   1
                                                   Inj Volume : 1.0 µl
Acq. Method     : C:\CHEM32\1\METHODS\OJ-H.M
Last changed    : 4/12/2023 4:15:30 PM by Analytik
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\OJ-H.M
Last changed    : 4/13/2023 9:32:26 AM by Analytik
                  (modified after loading)
Method Info     : OJ-H, Hept./EtOH 98:2,  2ml/min

Additional Info : Peak(s) manually integrated
```

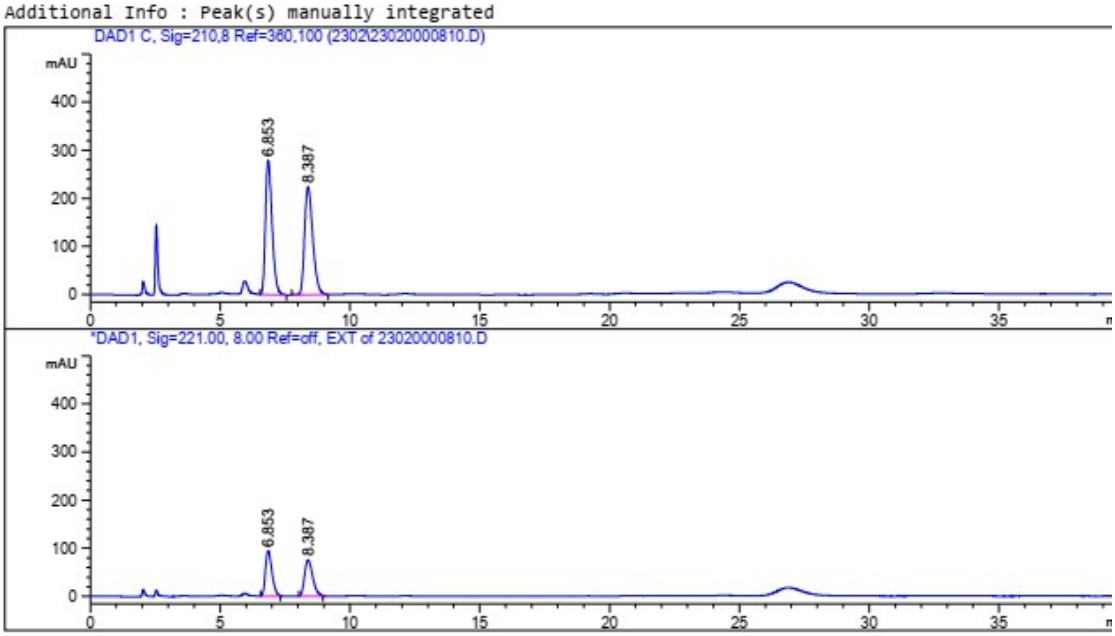



```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  36.036 BB    0.7318  870.04547   14.06362  20.9967
   2  51.411 MM    1.5516 3273.68555   35.16568  79.0033

Totals :                  4143.73102   49.22931
```

Figure S 53 HPLC trace of enantioenriched-7b



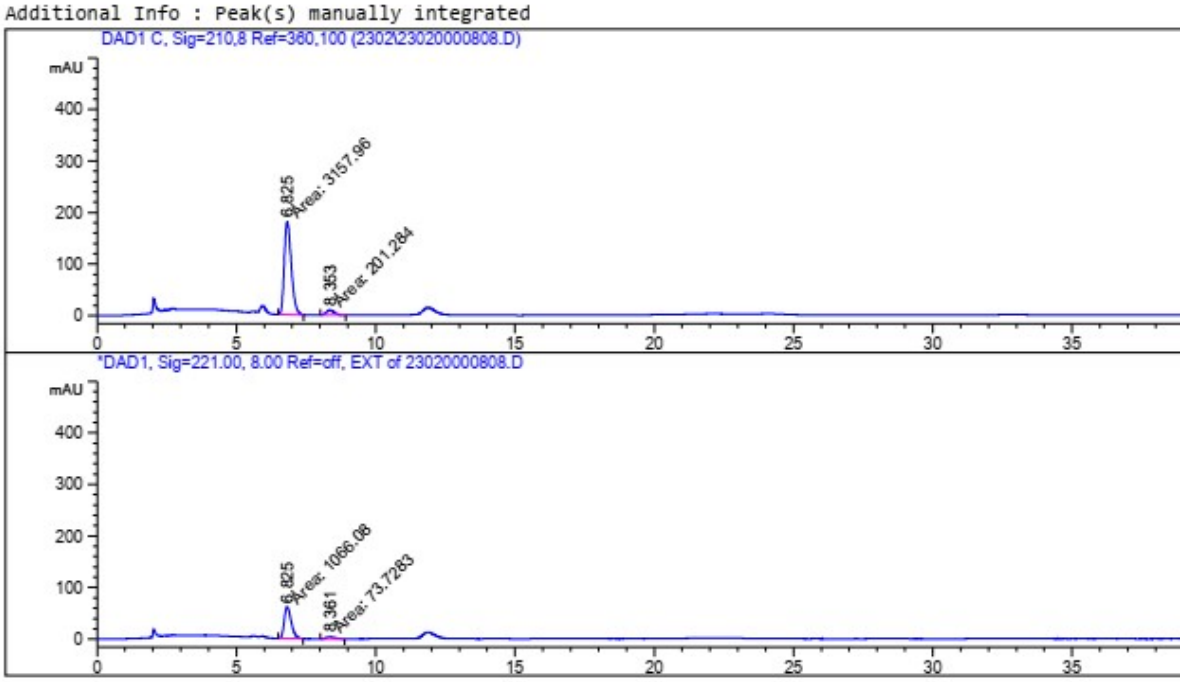

```
======================================================================
Acq. Operator   : Analytik                     Seq. Line :   5
Acq. Instrument : LC5                           Location : Vial 11
Injection Date  : 2/8/2023 8:25:14 PM               Inj :   1
                                               Inj Volume : 1.0 µl
Acq. Method     : C:\CHEM32\1\METHODS\AD-H.M
Last changed    : 2/8/2023 4:22:23 PM by Analytik
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\AD-H.M
Last changed    : 2/9/2023 2:31:19 PM by Analytik
                  (modified after loading)
Method Info     : AD-H, Hept./EtOH 95:5,  1ml/min

Additional Info : Peak(s) manually integrated
```




```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.853 BB    0.2751 4935.68701  278.06674  50.0328
   2   8.387 BB    0.3416 4929.20898  223.23030  49.9672

Totals :                  9864.89600  501.29704
```

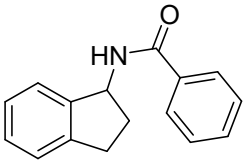
Figure S 54 HPLC trace of rac-2b

```
================================================================================
Acq. Operator   : Analytik                       Seq. Line :   4
Acq. Instrument : LC5                           Location : Vial 22
Injection Date  : 2/8/2023 7:03:06 PM               Inj :   1
                                               Inj Volume : 1.0 µl
Acq. Method     : C:\CHEM32\1\METHODS\AD-H.M
Last changed    : 2/8/2023 4:22:23 PM by Analytik
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\AD-H.M
Last changed    : 2/9/2023 2:31:19 PM by Analytik
                  (modified after loading)
Method Info     : AD-H, Hept./EtOH 95:5,  1ml/min

Additional Info : Peak(s) manually integrated
```

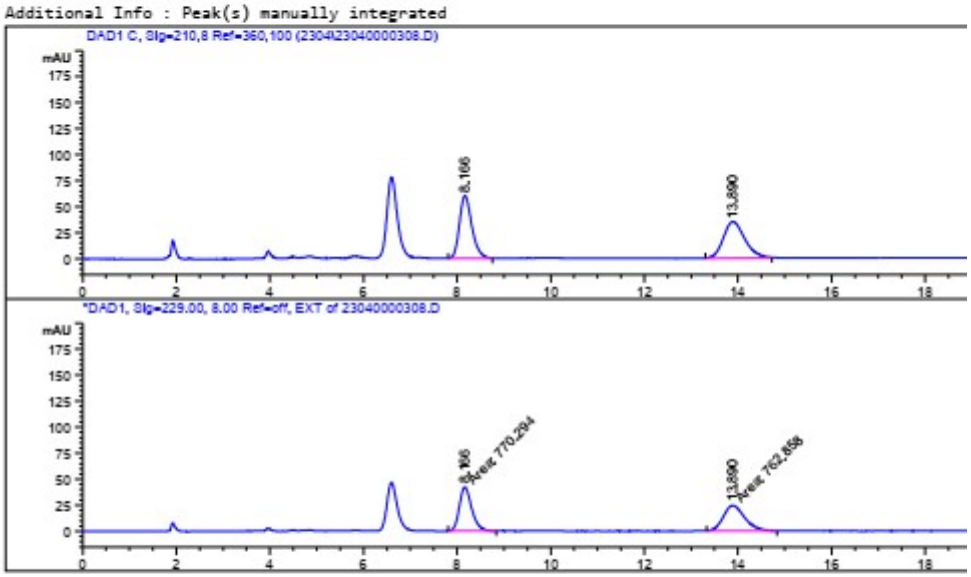



```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.825 MM    0.2916 3157.96143  180.48326  94.0081
   2   8.353 MM    0.3466  201.28401    9.67893   5.9919

Totals :                  3359.24544  190.16219
```

Figure S 55 HPLC trace of enantioenriched-2b



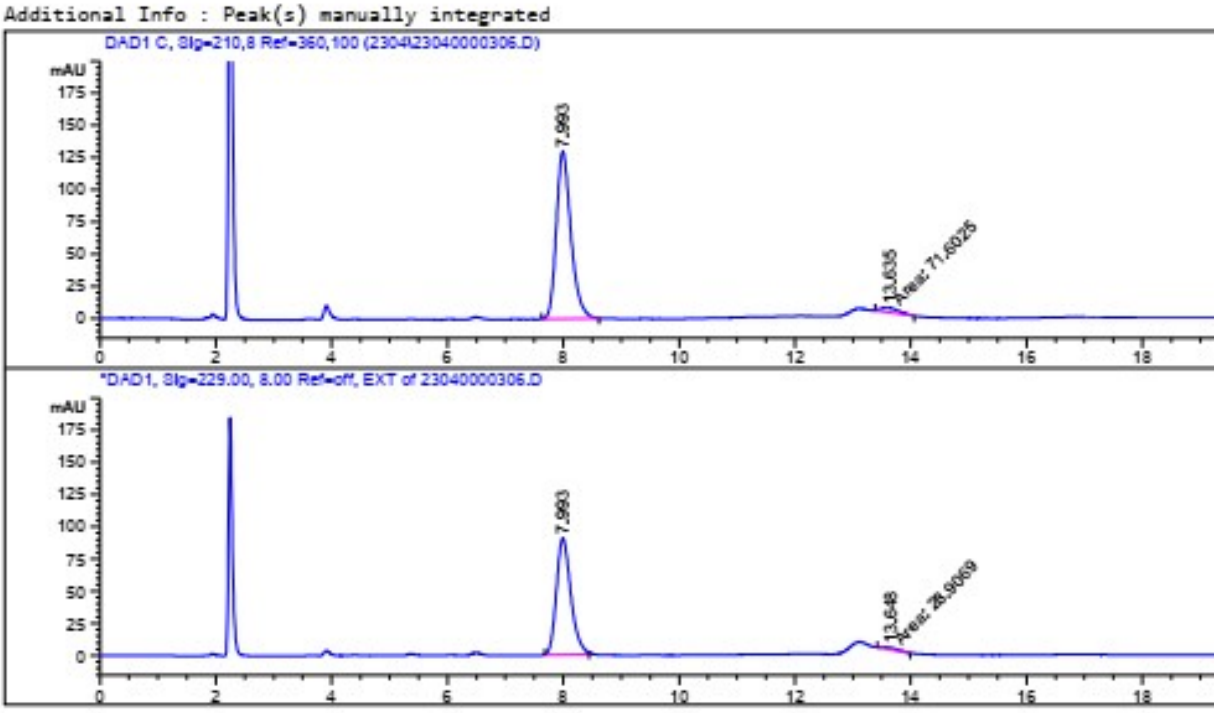

```
======================================================================
Acq. Operator   : Analytik                       Seq. Line :   8
Acq. Instrument : LC5                            Location : Vial 3
Injection Date  : 4/3/2023 4:32:08 PM                 Inj :   1
                                                 Inj Volume : 1.0 µl
Acq. Method     : C:\CHEM32\1\METHODS\OD-H.M
Last changed    : 4/3/2023 2:16:18 PM by Analytik
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\OD-H.M
Last changed    : 4/4/2023 9:19:16 AM by Analytik
                  (modified after loading)
Method Info     : OD-H, Hept./EtOH 95:5, 1ml/min

Additional Info : Peak(s) manually integrated
```




```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.166 BB    0.2785 1108.99890   60.31322  49.9537
   2  13.890 BB    0.4792 1111.05420   34.91668  50.0463

Totals :                  2220.05310   95.22990
```

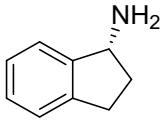
Figure S 56 HPLC trace of rac-3b

```
================================================================================
Acq. Operator   : Analytik                       Seq. Line :   7
Acq. Instrument : LC5                           Location : Vial 11
Injection Date  : 4/3/2023 3:00:01 PM               Inj :   1
                                                Inj Volume : 1.0 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 0.2 µl
Acq. Method     : C:\CHEM32\1\METHODS\OD-H.M
Last changed    : 4/3/2023 2:16:18 PM by Analytik
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\OD-H.M
Last changed    : 4/4/2023 9:19:16 AM by Analytik
                  (modified after loading)
Method Info     : OD-H, Hept./EtOH 95:5, 1ml/min

Additional Info : Peak(s) manually integrated
```

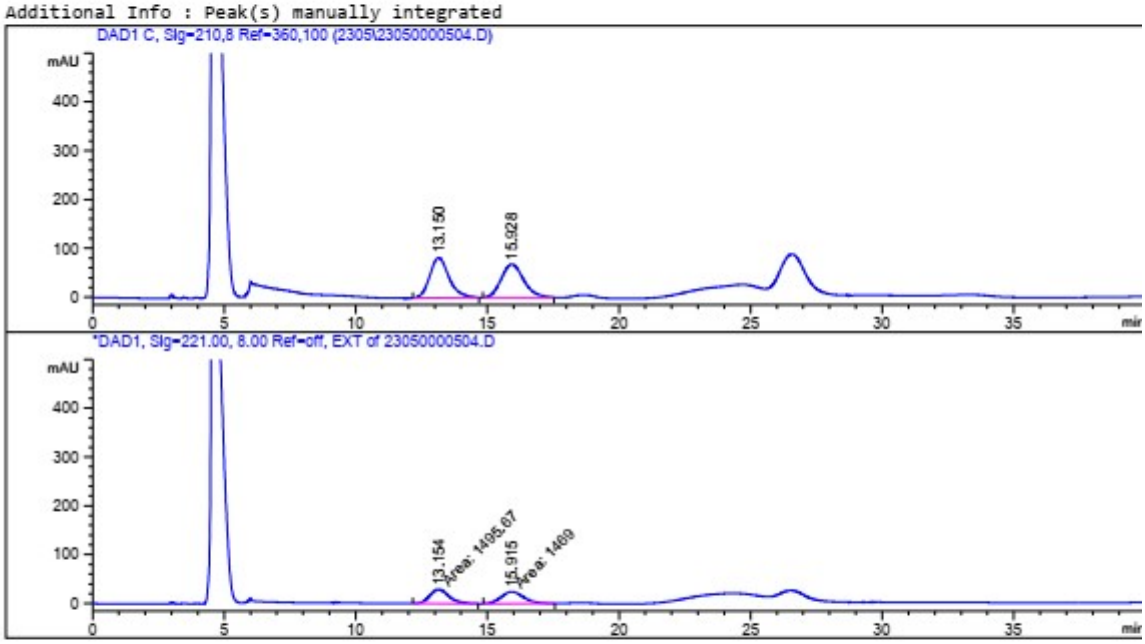



```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.993 BB    0.2649 2282.30176  129.97195  96.9581
   2  13.635 MM    0.3516   71.60250    3.39449   3.0419
```

Figure S 57 HPLC trace of enantioenriched-3b



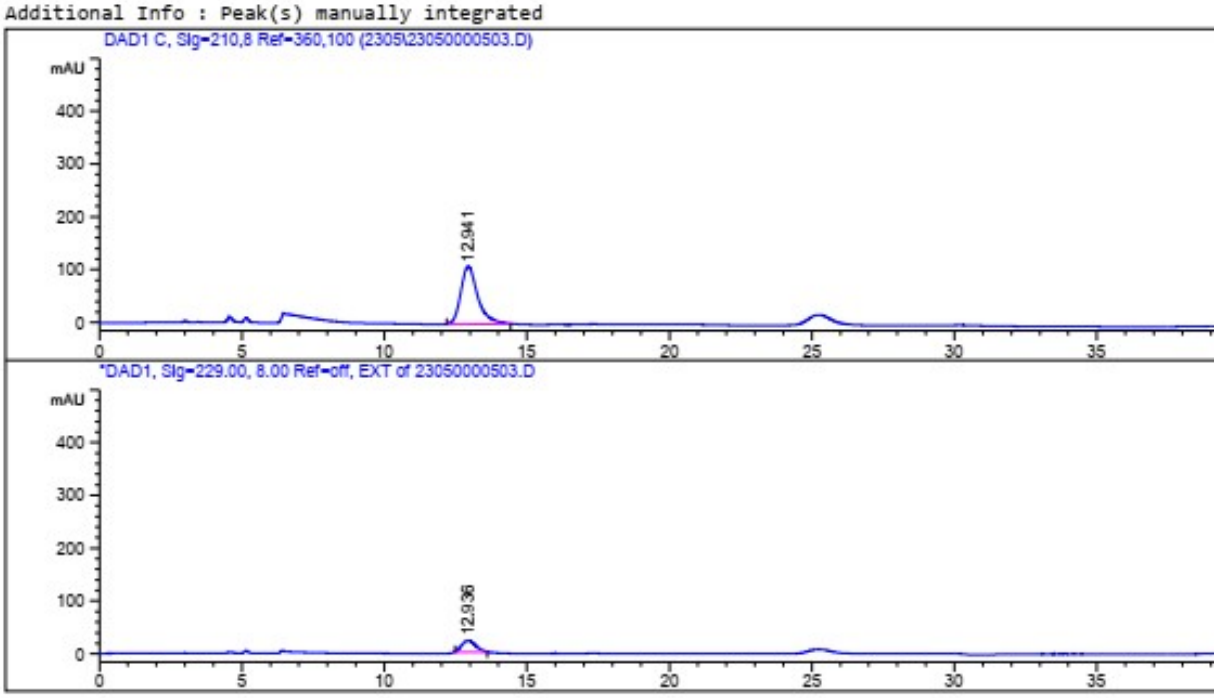

```
======================================================================
Acq. Operator   : Analytik                       Seq. Line :   5
Acq. Instrument : LC5                             Location : Vial 1
Injection Date  : 5/5/2023 1:53:33 PM                 Inj :   1
                                                 Inj Volume : 1.0 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 3.0 µl
Acq. Method     : C:\CHEM32\1\METHODS\CELLULOSE4.M
Last changed    : 5/5/2023 1:08:04 PM by Analytik
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\CELLULOSE4.M
Last changed    : 5/5/2023 3:30:17 PM by Analytik
                  (modified after loading)
Method Info     : AS-H , Hept./EtOH 90:10,  1ml/min

Additional Info : Peak(s) manually integrated
```




```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  13.150 BB    0.7584 4205.29346   82.53555  50.8551
   2  15.928 BB    0.7850 4063.86719   68.21700  49.1449
```

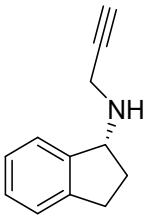
Figure S 58 HPLC trace of rac-1c

```
================================================================================
Acq. Operator   : Analytik                       Seq. Line :   4
Acq. Instrument : LC5                           Location : Vial 2
Injection Date  : 5/5/2023 1:07:28 PM               Inj :   1
                                               Inj Volume : 1.0 µl
Acq. Method     : C:\CHEM32\1\METHODS\CELLULOSE4.M
Last changed    : 5/5/2023 1:08:04 PM by Analytik
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\CELLULOSE4.M
Last changed    : 5/5/2023 3:30:17 PM by Analytik
                  (modified after loading)
Method Info     : AS-H , Hept./EtOH 90:10,  1ml/min

Additional Info : Peak(s) manually integrated
```

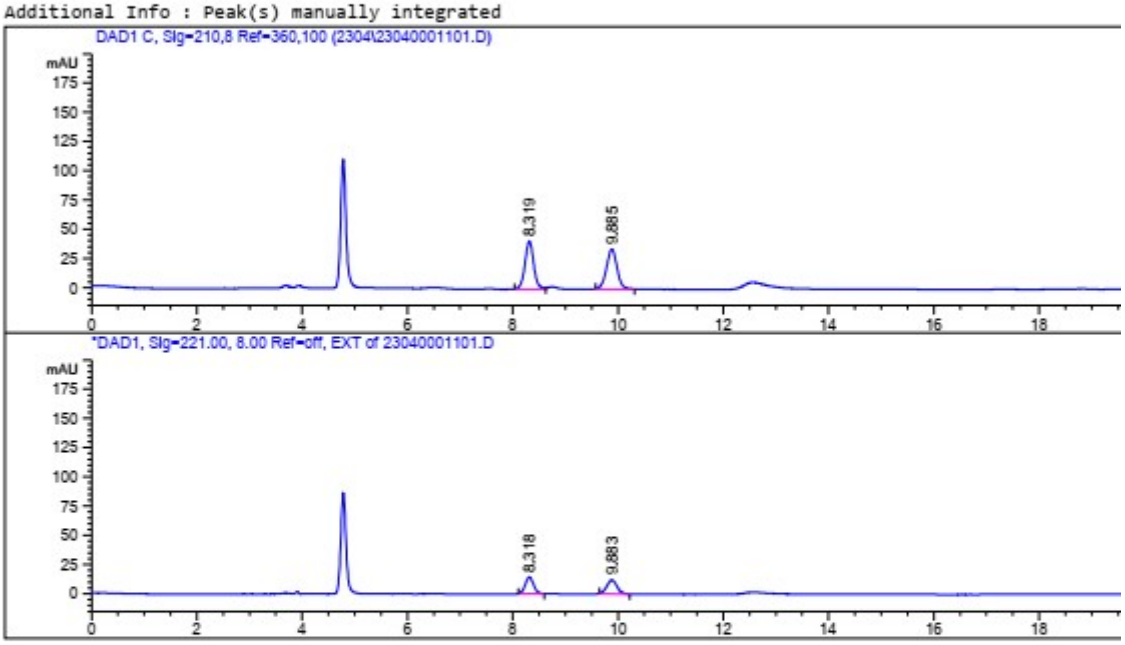



```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  12.941 BB    0.6236 4553.72607  109.39518 100.0000

Totals :                  4553.72607  109.39518
```

Figure S 59 HPLC trace of enantioenriched-1c



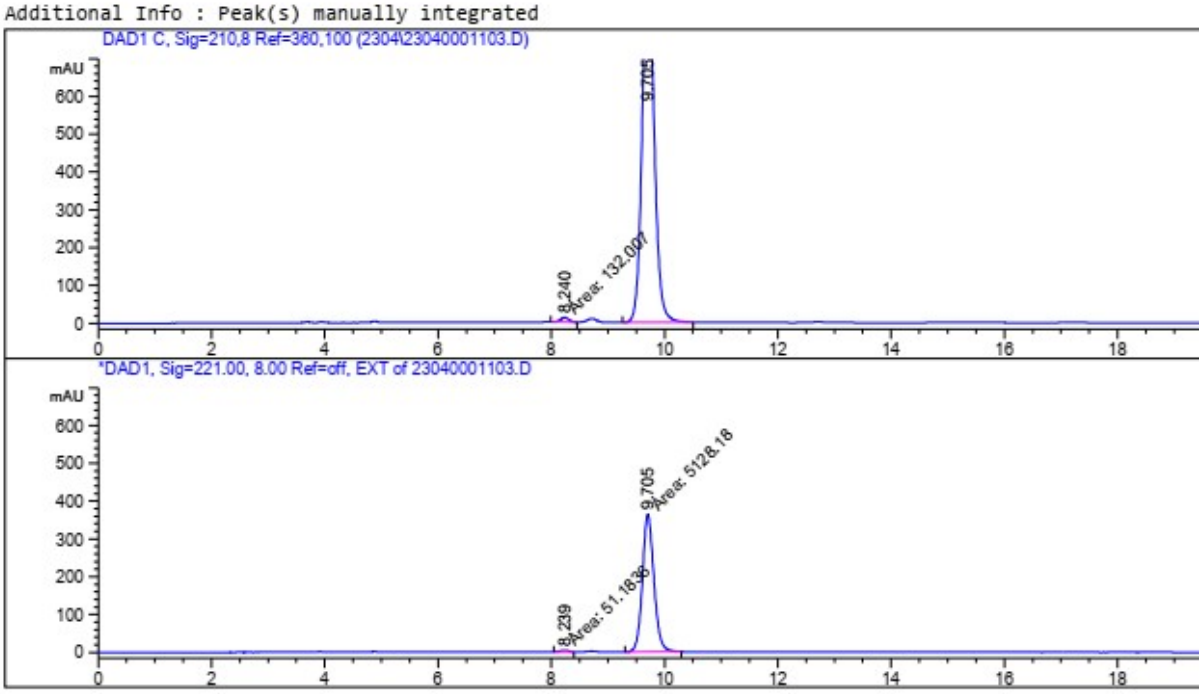

```
======================================================================
Acq. Operator   : Analytik                       Seq. Line :   2
Acq. Instrument : LC5                             Location : Vial 11
Injection Date  : 4/11/2023 12:31:11 PM               Inj :   1
                                                 Inj Volume : 0.2 µl
Acq. Method     : C:\CHEM32\1\METHODS\CELLULOSE3.M
Last changed    : 4/11/2023 12:27:12 PM by Analytik
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\CELLULOSE3.M
Last changed    : 4/11/2023 2:16:15 PM by Analytik
                  (modified after loading)
Method Info     : Cellulose 3 , Hept./EtOH 95:0,5, 0.5ml/min

Additional Info : Peak(s) manually integrated
```




```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.319 BB    0.1769  476.05875   41.16010  50.1582
   2   9.885 BB    0.2139  473.05508   34.09518  49.8418

Totals :                   949.11383   75.25528
```

Figure S 60 HPLC trace of rac-1d

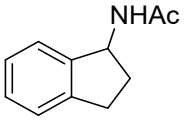
```
================================================================================
Acq. Operator   : Analytik                       Seq. Line :   4
Acq. Instrument : LC5                           Location : Vial 12
Injection Date  : 4/11/2023 1:23:16 PM              Inj :   1
                                                Inj Volume : 0.2 µl
Acq. Method     : C:\CHEM32\1\METHODS\CELLULOSE3.M
Last changed    : 4/11/2023 12:56:54 PM by Analytik
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\CELLULOSE3.M
Last changed    : 4/11/2023 2:18:24 PM by Analytik
                  (modified after loading)
Method Info     : Cellulose 3 , Hept./EtOH 95:0,5, 0.5ml/min

Additional Info : Peak(s) manually integrated
```



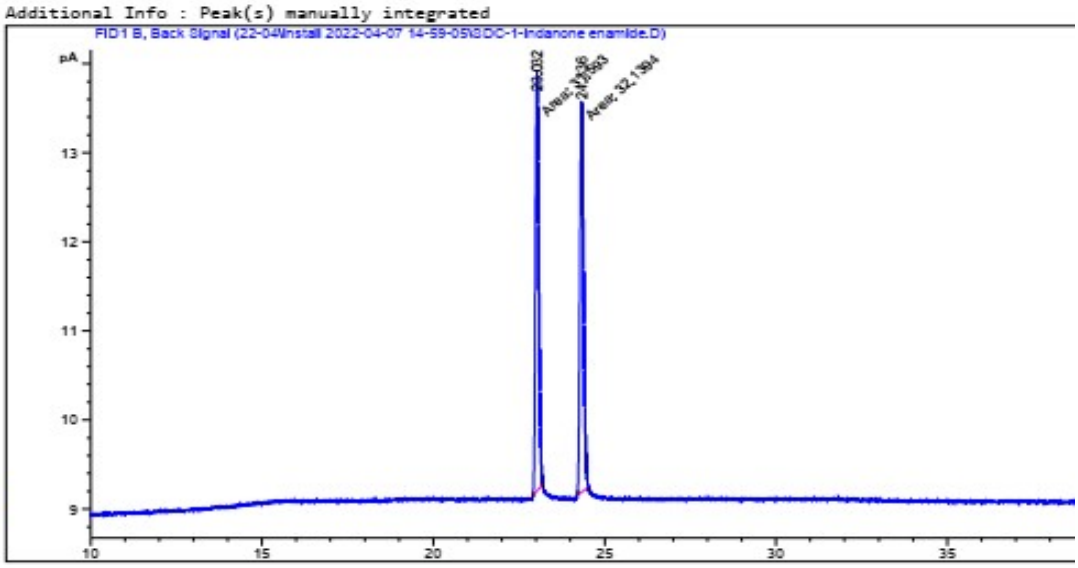

```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.240 MM    0.1749  132.00711   12.57682   0.9017
   2   9.705 BB    0.2168 1.45082e4  1014.97113  99.0983

Totals :                  1.46402e4  1027.54795
```

Figure S 61 HPLC trace of enantioenriched-1d

11. *Chiral GC traces*



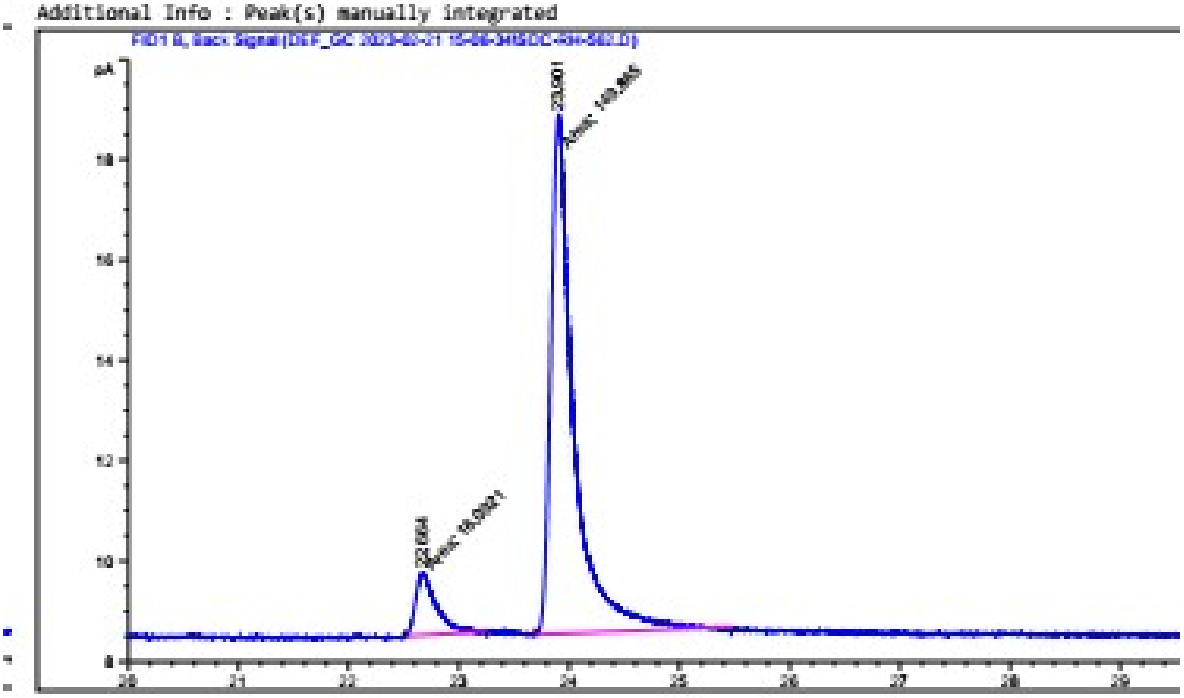

```
=====================================================================
Acq. Operator   : SYSTEM                        Seq. Line :   3
Sample Operator : SYSTEM
Acq. Instrument : GC 8890                        Location :   34  (F)
Injection Date  : 4/7/2022 4:58:50 PM                 Inj :   1
                                                Inj Volume : 1 µl
Acq. Method     : D:\ChemStation\1\Data\22-04\install 2022-04-07 14-59-05\alpha-enamide_FID-
                  m1.M
Last changed    : 4/7/2022 4:31:33 PM by SYSTEM
Analysis Method : D:\ChemStation\1\Data\22-04\install 2022-04-07 14-59-05\alpha-enamide_FID-
                  m1.M (Sequence Method)
Last changed    : 4/8/2022 8:33:37 AM by SYSTEM
                  (modified after loading)
Method Info     : alpha-enamide-AH

Sample Info     : SDC-1-indanone enamide

Additional Info : Peak(s) manually integrated
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 B, Back Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  23.032 MM T  0.1121   31.59302    4.69630 49.57137
   2  24.336 MM T  0.1225   32.13937    4.37179 50.42863

Totals :                    63.73240    9.06808
```

Figure S 62 Chiral GC trace of rac-1b

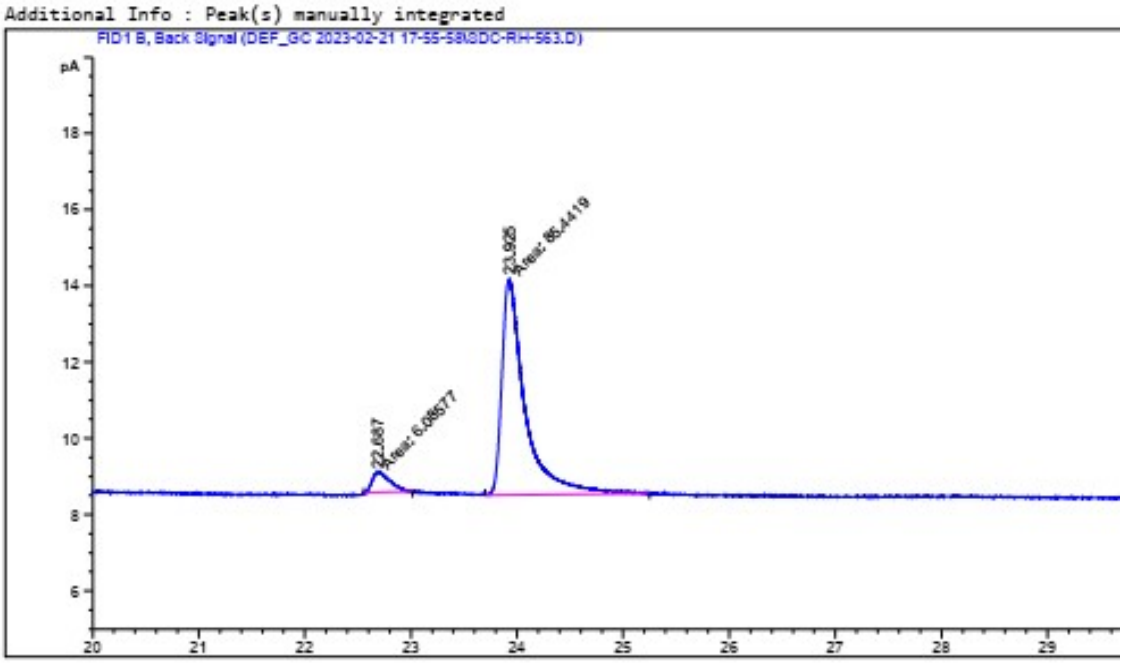
```
Acq. Operator   : SYSTEM                          Seq. Line :   1
Sample Operator : SYSTEM
Acq. Instrument : GC 8890                          Location :   1  (F)
Injection Date  : 2/21/2023 3:08:41 PM                Inj :   1
                                                  Inj Volume : 1 µl
Acq. Method     : D:\ChemStation\1\Data\DEF_GC 2023-02-21 15-06-34\alpha-enamide_FID-mi.M
Last changed    : 10/21/2022 10:09:04 AM by SYSTEM
Analysis Method : D:\ChemStation\1\Data\DEF_GC 2023-02-21 15-06-34\alpha-enamide_FID-mi.M (
                  Sequence Method)
Last changed    : 4/15/2023 4:37:13 PM by SYSTEM
                  (modified after loading)
Method Info     : alpha-enamide-AH

Sample Info     : SDC-RH-562

Additional Info : Peak(s) manually integrated
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 B, Back Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|-------|
   1  22.664 MM    0.2157   16.09285    1.24332  9.69653
   2  23.981 MM    0.2488  149.86482   10.37094 90.30347

Totals :                   165.95688   11.61426
```

Figure S 63 Chiral GC trace of enantioencihed-1b

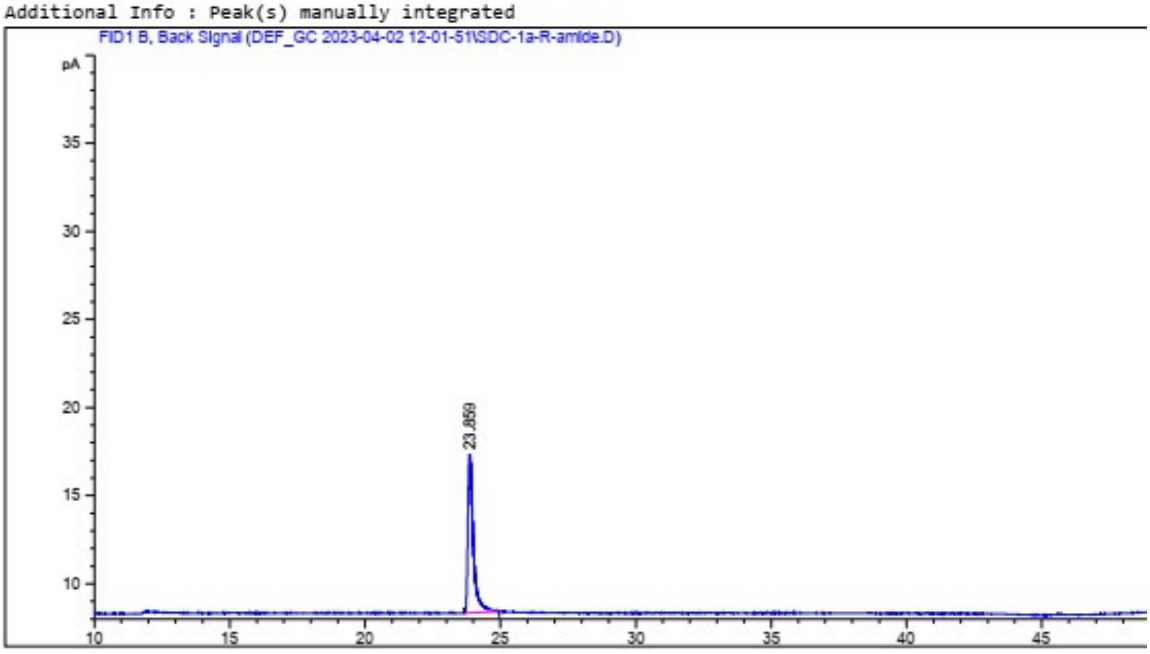
```
========================================================================
Acq. Operator   : SYSTEM                          Seq. Line :   1
Sample Operator : SYSTEM
Acq. Instrument : GC 8890                          Location :   2  (F)
Injection Date  : 2/21/2023 5:58:01 PM                 Inj :   1
                                                  Inj Volume : 1 µl
Acq. Method     : D:\ChemStation\1\Data\DEF_GC 2023-02-21 17-55-58\alpha-enamide_FID-m1.M
Last changed    : 10/21/2022 10:09:04 AM by SYSTEM
Analysis Method : D:\ChemStation\1\Data\DEF_GC 2023-02-21 17-55-58\alpha-enamide_FID-m1.M (
                  Sequence Method)
Last changed    : 4/15/2023 4:38:16 PM by SYSTEM
                  (modified after loading)
Method Info     : alpha-enamide-AH

Sample Info     : SDC-RH-563

Additional Info : Peak(s) manually integrated
```




```
========================================================================
                        Area Percent Report
========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 B, Back Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  22.687 MM    0.1903    6.08577 5.32949e-1  6.64910
   2  23.925 MM    0.2508   85.44192    5.67737 93.35090

Totals :                   91.52768    6.21032
```

Figure S 64 Chiral GC trace of enantioencihed-1b

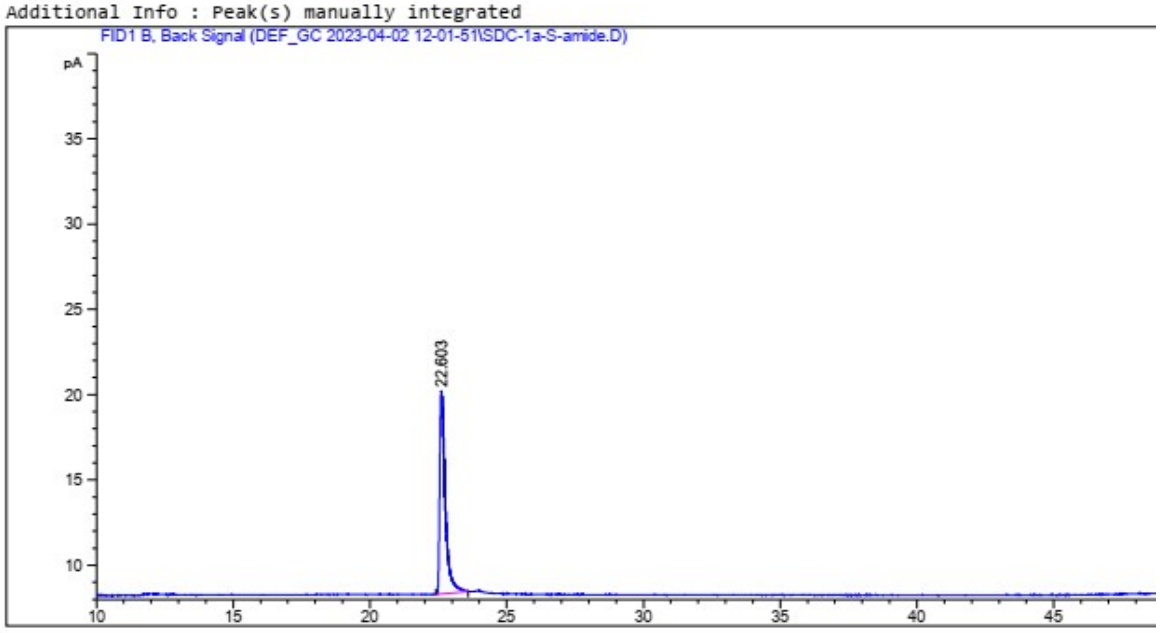
```
=====================================================================
Acq. Operator   : SYSTEM                        Seq. Line :   1
Sample Operator : SYSTEM
Acq. Instrument : GC 8890                        Location :   1  (F)
Injection Date  : 4/2/2023 12:04:03 PM                Inj :   1
                                                 Inj Volume : 1 µl
Acq. Method     : D:\ChemStation\1\Data\DEF_GC 2023-04-02 12-01-51\alpha-enamide_FID-m1.M
Last changed    : 10/21/2022 10:09:04 AM by SYSTEM
Analysis Method : D:\ChemStation\1\Data\DEF_GC 2023-04-02 12-01-51\alpha-enamide_FID-m1.M (
                  Sequence Method)
Last changed    : 4/2/2023 3:16:20 PM by SYSTEM
                  (modified after loading)
Method Info     : alpha-enamide-AH

Sample Info     : SDC-1a-R-amide

Additional Info : Peak(s) manually integrated
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 B, Back Signal


  Peak RetTime Type  Width     Area      Height     Area
    #   [min]        [min]   [pA*s]      [pA]         %
  ----|-------|----|-------|----------|----------|--------|
     1  23.859 BB    0.1987  127.26900    9.01262 1.000e2

  Totals :                   127.26900    9.01262
```

Figure S 65 Chiral GC trace of enantioencihed-1b (recrystallized)

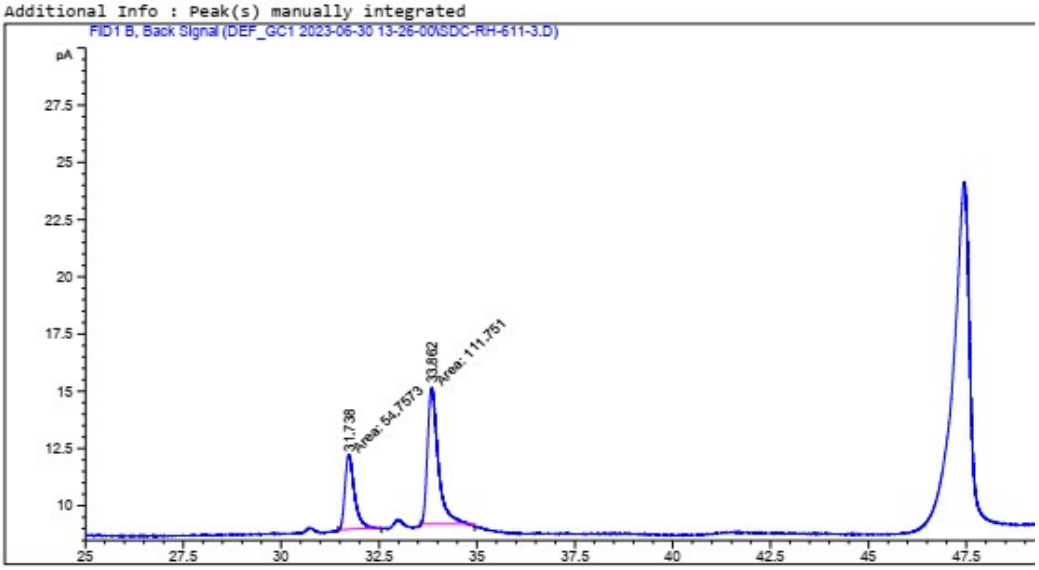
```
==========================================================================
Acq. Operator   : SYSTEM                          Seq. Line :   2
Sample Operator : SYSTEM
Acq. Instrument : GC 8890                          Location :   2  (F)
Injection Date  : 4/2/2023 1:02:59 PM                   Inj :   1
                                                  Inj Volume : 1 µl
Acq. Method     : D:\ChemStation\1\Data\DEF_GC 2023-04-02 12-01-51\alpha-enamide_FID-m1.M
Last changed    : 10/21/2022 10:09:04 AM by SYSTEM
Analysis Method : D:\ChemStation\1\Data\DEF_GC 2023-04-02 12-01-51\alpha-enamide_FID-m1.M (
                  Sequence Method)
Last changed    : 4/2/2023 3:19:01 PM by SYSTEM
                  (modified after loading)
Method Info     : alpha-enamide-AH

Sample Info     : SDC-1a-S-amide

Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 B, Back Signal


Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  22.603 BB    0.1928  168.32930   11.91964 1.000e2

Totals :                   168.32930   11.91964
```

Figure S 66 Chiral GC trace of enantioencihed-1b (recrystallized)

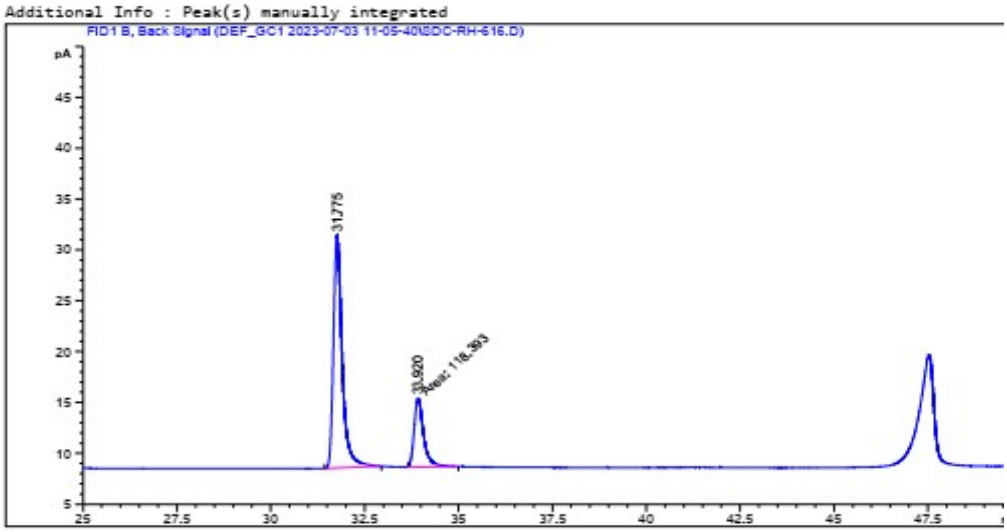
```
==========================================================================
Acq. Operator   : SYSTEM                        Seq. Line :   1
Sample Operator : SYSTEM
Acq. Instrument : GC 8890                        Location :   1  (F)
Injection Date  : 6/30/2023 1:28:56 PM               Inj :   1
                                                Inj Volume : 1 µl
Acq. Method     : D:\ChemStation\1\Data\DEF_GC1 2023-06-30 13-26-00\alpha-enamide_FID-m1-N2-a
                  .M
Last changed    : 6/30/2023 1:25:32 PM by SYSTEM
Analysis Method : D:\ChemStation\1\Data\DEF_GC1 2023-06-30 13-26-00\alpha-enamide_FID-m1-N2-a
                  .M (Sequence Method)
Last changed    : 7/3/2023 11:10:15 AM by SYSTEM
                  (modified after loading)
Method Info     : alpha-enamide-AH

Sample Info     : SDC-RH-611-3

Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                      Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

  Signal 1: FID1 B, Back Signal

  Peak RetTime Type  Width     Area      Height     Area
    #   [min]        [min]   [pA*s]      [pA]        %
  ----|-------|----|-------|----------|----------|--------|
     1  31.738 MM    0.2798   54.75732    3.26210 32.88563
     2  33.862 MM    0.3133  111.75101    5.94448 67.11437

  Totals :                   166.50834    9.20658


  ==========================================================================
                            *** End of Report ***
```

Figure S 67 Chiral GC trace of crude reaction using Co(I)-1 as precatalyst (as shown in Figure 7)

```
================================================================
Acq. Operator   : SYSTEM                       Seq. Line :   1
Sample Operator : SYSTEM
Acq. Instrument : GC 8890                       Location :   2  (F)
Injection Date  : 7/3/2023 11:07:44 AM              Inj :   1
                                                Inj Volume : 1 µl
Acq. Method     : D:\ChemStation\1\Data\DEF_GC1 2023-07-03 11-05-40\alpha-enamide_FID-m1-N2-a
                  .M
Last changed    : 6/30/2023 1:25:32 PM by SYSTEM
Analysis Method : D:\ChemStation\1\Data\DEF_GC1 2023-07-03 11-05-40\alpha-enamide_FID-m1-N2-a
                  .M (Sequence Method)
Last changed    : 7/3/2023 12:34:04 PM by SYSTEM
                  (modified after loading)
Method Info     : alpha-enamide-AH

Sample Info     : SDC-RH-616

Additional Info : Peak(s) manually integrated
```




```
================================================================
                      Area Percent Report
================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

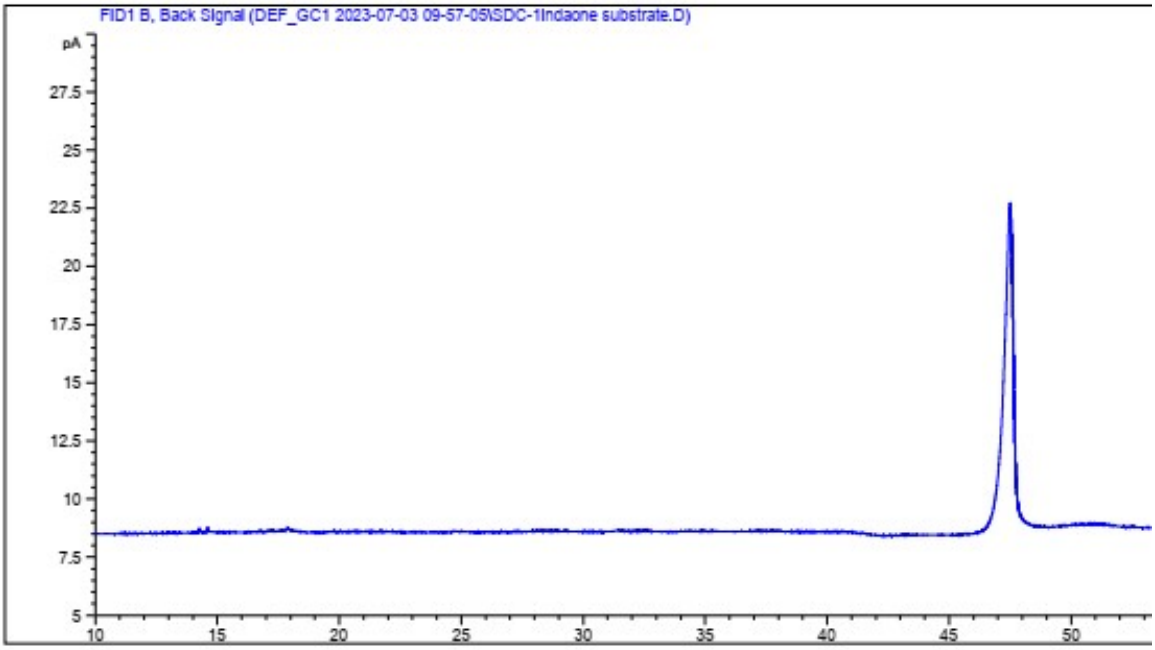
Signal 1: FID1 B, Back Signal

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	31.775	BB	0.1922	371.04453	22.88524	75.81038
2	33.920	NN	0.2919	118.39307	6.75964	24.18962
Totals :				489.43760	29.64488	

```
================================================================================
                            *** End of Report ***
```

*Figure S 68 Chiral GC trace of crude reaction using **Co(I)-2** as precatalyst (as shown in Figure 7)*

```
=====================================================================
Acq. Operator   : SYSTEM                        Seq. Line :   1
Sample Operator : SYSTEM
Acq. Instrument : GC 8890                        Location :   1  (F)
Injection Date  : 7/3/2023 9:59:53 AM                 Inj :   1
                                                Inj Volume : 1 µl
Acq. Method     : D:\ChemStation\1\Data\DEF_GC1 2023-07-03 09-57-05\alpha-enamide_FID-m1-N2-a
                  .M
Last changed    : 6/30/2023 1:25:32 PM by SYSTEM
Analysis Method : D:\ChemStation\1\Data\DEF_GC1 2023-07-03 09-57-05\alpha-enamide_FID-m1-N2-a
                  .M (Sequence Method)
Last changed    : 7/3/2023 11:07:18 AM by SYSTEM
                  (modified after loading)
Method Info     : alpha-enamide-AH

Sample Info     : SDC-1indaone substrate
```




```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 B, Back Signal
```

*Figure S 69 Chiral GC trace of substrate **1a***