Supporting information

Enantiodivergent Rh^{III}-Catalyzed Synthesis of Imidazo[1,5-a]indole

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Table of contents

1. General comments…….. S2

2. Analytical methods …….S2

3. General procedure for the synthesis of substituted *N*-(pivaloyloxy)-1H-indole-1-carboxamide……S3

4. Optimization……... S7

5. General procedure for the synthesis of racemic compounds …… S9

6. General procedure for the enantioselective synthesis of Imidazo[1,5-a]indole (*R*-isomer)…… S9

7. General procedure for the enantioselective synthesis of Imidazo[1,5-a]indole (*S*-isomer)…… S10

8. Properties of synthesized compounds…….S10

9. Synthetic application……...S42

10. Control experiments……..S46

11. Plausible mechanism and stereochemical outcome……..S49

12. Spectral data……..S50

13. Crystal data for compound **(*S*)-3h** and **(*R*)-3h**…….....S97

14. References…….S99

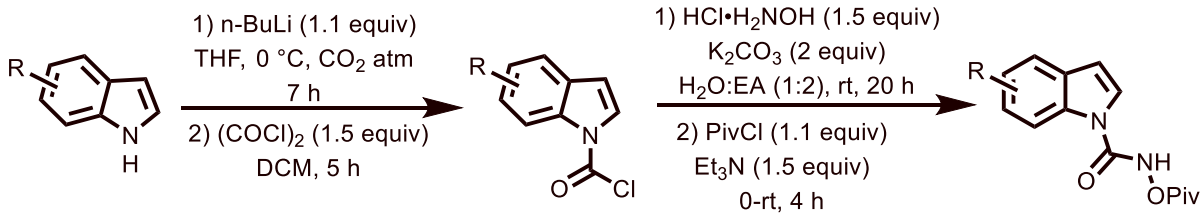
1. General comments:

All reactions were performed under an atmosphere of air with magnetic stirring, unless otherwise indicated. Solvents such as acetonitrile (CH_3CN), acetone, tetrahydrofuran (THF), diethyl ether, and other solvents were purchased from commercial sources and used as received. Column chromatography was performed using Rankem Silica gel (100-200 mesh), and the solvent system used, unless otherwise specified, was ethyl acetate-hexane with various percentages of polarity depending on the nature of the substrate. All chemicals and acids were purchased from either Sigma-Aldrich or Spectrochem and, unless otherwise noted, were used as received.

2. Analytical Methods:

Analytical thin-layer chromatography was performed with commercial aluminium sheets coated with silica gel (Merck (Supelco), Kieselgel 60 F254). Compounds were visualized by UV-light at 254 nm. NMR data were recorded on Bruker (400 and 500 MHz) spectrometers. ^{1}H, ^{13}C, ^{19}F spectra were referenced to signals of deuteron solvents and residual protonated solvents, respectively. Infrared spectra were recorded on a Thermo Nicolet iS10 FT and Jasco ATR-IR spectrometer. HRMS were recorded by the electrospray ionization (ESI) method on a Q-TOF Micro with lock spray source. The crystal data were collected and integrated using a Bruker AXS kappa Apex2 CCD diffractometer, with graphite monochromated Mo-Kα radiation. The enantiomeric ratio (er) of the products was determined by high-performance liquid chromatography (HPLC) with a chiral stationary phase in comparison with the authenticated racemate. All the chiral stationary phases, including IG, IC, IA, IB, ID, were purchased from Daicel Chiral Technologies. Optical rotations recorded on the Labindia polarimeter were reported as follows: $[\alpha]_D^T$ (c (g/100 mL), in $CHCl_3$).

3. General procedure for the synthesis of substituted *N*-(pivaloyloxy)-1H-indole-1-carboxamide.



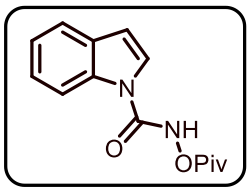
The synthesis of 1H-indole-1-carboxylic acid[1]: In a dry reaction flask, indole (2 g, 17 mmol) in THF (20 mL) was taken. A solution of *n*-BuLi (12 mL, 1.6 M in hexane, 1.1 equiv) was added at 0 °C under a nitrogen atmosphere. After stirring at 0 °C for 2 h, the flask is freed of nitrogen by alternately evacuating and repressurizing with CO_2 gas using a balloon. The mixture was stirred for 5 h under the CO_2 pressure, then quenched carefully by adding cold aqueous HCl solution (2 M) to adjust the pH to 2. The organic phase was extracted with ethyl acetate and dried over anhydrous Na_2SO_4. The obtained compound was recrystallized by using hexane as a white solid (2.2 g, 80% yield), which could be used directly in the next step without further purification.

The synthesis of *N*-hydroxy-1H-indole-1-carboxamide: In a nitrogen-filled flask, the mixture of 1H-indole-1-carboxylic acid (1g, 6.2 mmol, 1.0 equiv), oxalyl chloride (1.1 mL, 12.4 mmol, 2 equiv), and a few drops of DMF (ca. 0.1 equiv) in dichloromethane (20 mL) was stirred for 5 h at room temperature. After evaporating under vacuum, the obtained residue was treated with $NH_2OH{\cdot}HCl$ (0.650 g, 9.3 mmol, 1.5 equiv) and K_2CO_3 (1.75 g, 12.4 mmol, 2.0 equiv) followed by EtOAc/water (50 mL, 2:1) were added. After reaction, the reaction mixture was extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4. The solvent was removed in vacuo, and the obtained crude was taken next step without further purification.

Synthesis of *N*-(pivaloyloxy)-1H-indole-1-carboxamide: The obtained crude *N*-hydroxy-1H-indole-1-carboxamide were taken in a reaction flask, and THF (20 mL) and triethylamine (1.5 equiv) were added. Subsequently, pivaloyl chloride (1.1 equiv) was added at 0 °C with constant stirring at room temperature for 4 h. After consuming the starting material, the reaction mixture was quenched with ice-cold water, followed by extraction with ethyl acetate. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resultant crude product was purified by column chromatography to obtain the corresponding compounds.

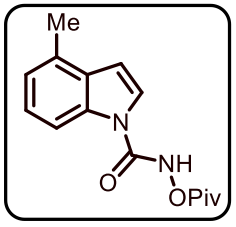
N-(pivaloyloxy)-1H-indole-1-carboxamide (1a)

Yield: 45% (three steps yield); colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.90 (br, 1H), 8.06 (d, J = 8.5 Hz, 1H), 7.49 (d, J = 7.5 Hz, 1H), 7.38 (d, J = 3.5 Hz, 1H), 7.27-7.23 (m, 1H), 7.19-7.15 (m, 1H), 6.55 (d, J = 3.7 Hz, 1H), 1.29 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 177.8, 152.4, 135.1, 130.1, 124.9, 123.5, 123.3, 121.2, 114.9, 109.1, 38.4, 27.0.



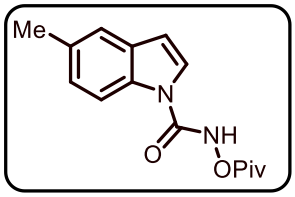
4-methyl-N-(pivaloyloxy)-1H-indole-1-carboxamide (1b)

Yield: 52% (three steps yield); colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.90 (br, 1H), 7.87 (d, J = 8.5 Hz, 1H), 7.37 (d, J = 3.7 Hz, 1H), 7.15 (d, J = 8.4 Hz, 1H), 6.97 (d, J = 7.2 Hz, 1H), 6.56 (s, 1H), 2.42 (s, 3H), 1.29 (s, 9H).. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 177.7, 152.4, 134.8, 130.7, 129.8, 124.9, 123.7, 122.9, 112.3, 107.4, 38.4, 27.0, 18.4.



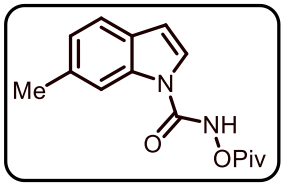
5-methyl-N-(pivaloyloxy)-1H-indole-1-carboxamide (1c)

Yield: 49% (three steps yield); colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.86 (s, 1H), 7.91 (d, J = 8.5 Hz, 1H), 7.35 (d, J = 3.7 Hz, 1H), 7.27 (s, 1H), 7.06 (dd, J = 8.5, 1.6 Hz, 1H), 6.48 (d, J = 3.7 Hz, 1H), 2.35 (s, 3H), 1.29 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 177.7, 152.4, 133.2, 132.8, 130.4, 126.2, 123.5, 121.1, 114.4, 108.8, 38.4, 27.0, 21.2.



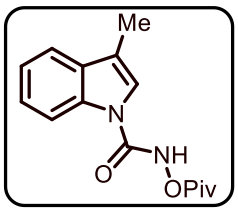
6-methyl-N-(pivaloyloxy)-1H-indole-1-carboxamide (1d)

Yield: 58% (three steps yield); colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.84 (br, 1H), 7.89 (s, 1H), 7.35 (d, J = 8.1 Hz, 1H), 7.29 (d, J = 3.7 Hz, 1H), 7.00 (d, J = 7.8 Hz, 1H), 6.50 (d, J = 3.7 Hz, 1H), 2.39 (s, 3H), 1.29 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 177.8, 152.5, 135.5, 135.1, 127.8, 124.8, 122.8, 120.7, 115.1, 109.0, 38.4, 27.0, 21.8.



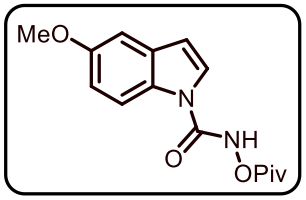
3-methyl-N-(pivaloyloxy)-1H-indole-1-carboxamide (1e)

Yield: 48% (three steps yield); yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.85 (br, 1H), 8.05 (d, J = 8.2 Hz, 1H), 7.43-7.38 (m, 1H), 7.27-7.23 (m, 1H), 7.21-7.20 (m, 1H), 7.12 (s, 1H), 2.15 (s, 3H), 1.29 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 177.9, 152.4, 135.5, 131.0, 124.9, 123.0, 120.2, 119.2, 118.5, 115.0, 38.4, 27.0, 9.6.



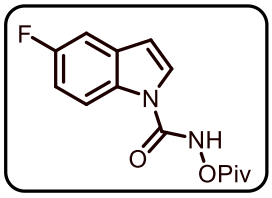
5-methoxy-N-(pivaloyloxy)-1H-indole-1-carboxamide (1f)

Yield: 53% (three steps yield); colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.89 (s, 1H), 7.93 (d, J = 9.2 Hz, 1H), 7.34 (d, J = 3.7 Hz, 1H), 6.93, J = 2.2 Hz, 1H), 6.85 (dd, J = 8.9, 2.8 Hz, 1H), 6.46 (d, J = 3.7 Hz, 1H), 3.75 (s, 3H), 1.28 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 177.8, 156.2, 152.3, 131.0, 129.8, 124.0, 115.6, 113.6, 108.9, 103.8, 55.6, 38.4, 27.0.



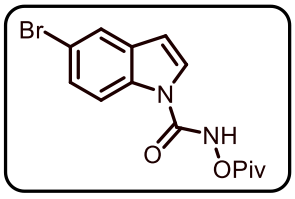
5-fluoro-N-(pivaloyloxy)-1H-indole-1-carboxamide (1g)

Yield: 42% (three steps yield); colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.93 (br, 1H), 8.03-8.00 (m, 1H), 7.39 (d, J = 3.7 Hz, 1H), 7.13-7.10 (m, 1H), 6.99-6.93 (m, 1H), 6.49-6.48 (m, 1H), 1.28 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 177.8, 159.5 (d, J = 239.8 Hz), 152.1, 131.6, 130.9 (d, J = 10.7 Hz), 124.8, 115.9 (d, J = 9.2 Hz), 112.7 (d, J = 25.3 Hz), 108.8 (d, J = 4.0 Hz), 106.6 (d, J = 23.9 Hz), 38.4, 26.8. ^{19}F NMR (375 MHz, $CDCl_3$, 24˚C): δ –119.95.



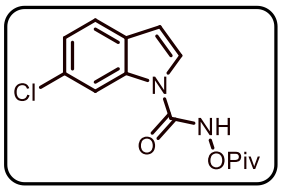
5-bromo-N-(pivaloyloxy)-1H-indole-1-carboxamide (1h)

Yield: 38% (three steps yield); colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.96 (s, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.58 (s, 1H), 7.35-7.31 (m, 2H), 6.45 (d, J = 3.5 Hz, 1H), 1.28 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 177.8, 152.0, 133.9, 131.6, 127.7, 124.4, 123.8, 116.6, 116.3, 108.3, 38.5, 26.5.



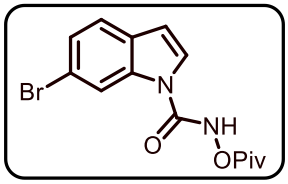
6-chloro-N-(pivaloyloxy)-1H-indole-1-carboxamide (1j)

Yield: 39% (three steps yield); colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$, 24 °C): δ 8.92 (s, 1H), 8.11 (s, 1H), 7.35-7.31 (m, 2H), 7.12 (d, J = 8.5 Hz, 1H), 6.48 (s, 1H), 1.29 (s, 9H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 24 °C): δ 177.7, 152.0, 135.6, 130.9, 128.4, 123.9, 123.7, 121.8, 115.3, 108.8, 38.5, 26.9.



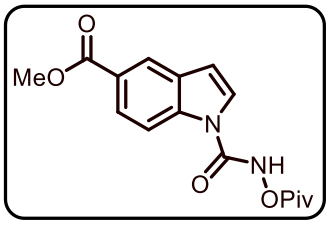
6-bromo-N-(pivaloyloxy)-1H-indole-1-carboxamide (1k)

Yield: 41% (three steps yield); colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.90 (br, 1H), 8.28 (s, 1H), 7.33-7.26 (m, 3H), 6.50 (d, J = 3.7 Hz, 1H), 1.30 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 177.8, 152.0, 135.9, 128.7, 126.6, 123.7, 122.2, 118.6, 118.1, 108.9, 38.5, 27.0.



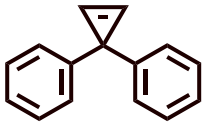
methyl 1-((pivaloyloxy)carbamoyl)-1H-indole-5-carboxylate (1l)

Yield: 29% (three steps yield); colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$, 24 °C): δ 9.01 (s, 1H), 8.20 (s, 1H), 8.10 (d, J = 8.7 Hz, 1H), 7.93 (dd, J = 8.7, 1.8 Hz, 1H), 7.44 (d, J = 3.7 Hz, 1H), 6.63 (d, J = 3.7 Hz, 1H), 3.86 (s, 3H), 1.3 (s, 9H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 24 °C): δ 177.7, 167.3, 152.0, 137.8, 129.7, 126.1, 125.2, 124.7, 123.5, 114.6, 109.4, 52.1, 38.5, 27.0.



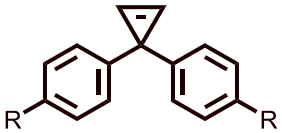
Synthesis of cyclopropenes:

The following cyclopropenes were prepared from the corresponding ketones following the literature procedure.[2,3]

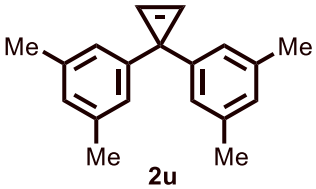


2a

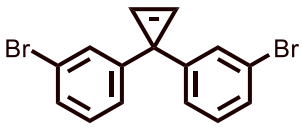
2o (*p*-Me)
2p (*m*-Me)
2q (*o*-Me)



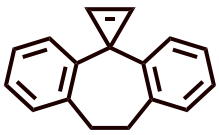
2r (R = F)
2s (R = Cl)
2t (R = Br



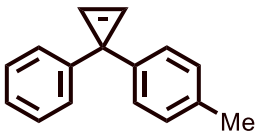
2u



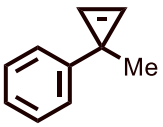
2v



3w



2x

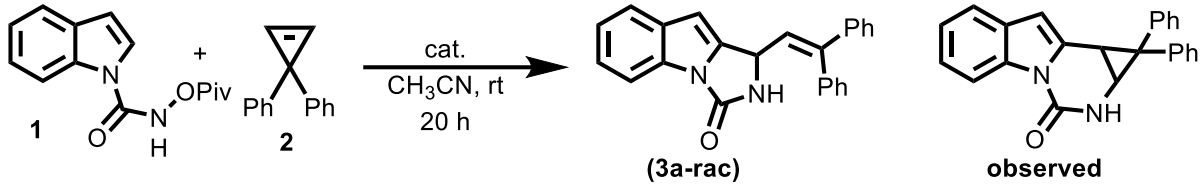


3y

The chiral catalysts **Rh1-Rh6** were prepared from the corresponding *R*-BINOL according to a literature procedure.[4-7]

4. Optimization:

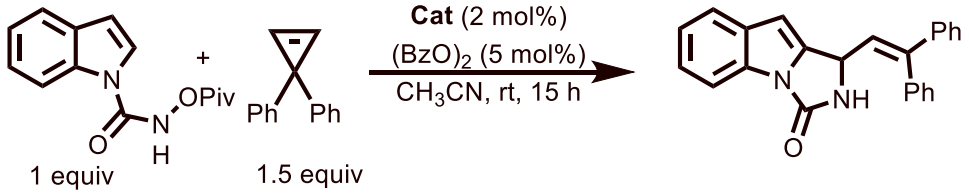
Screened catalyst for the synthesis of 3a-rac.

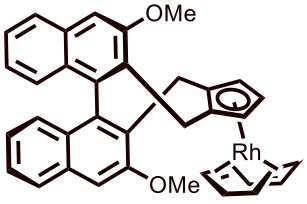


entry	Cat (2 mol%)	3a-rac	6-member
1[a]	$[Cp^*RhCl_2]_2$	-	observed
2[b]	[Cp*RhCOD]	-	observed
3[b]	*rac*-**Rh2**	observed	-

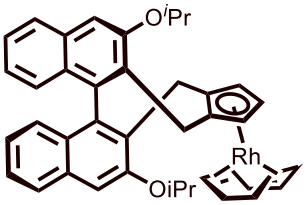
[a] CH_3CO_2Na (20 mol%), [b] (BzO)2 (5 mol%)

Screening of chiral Rh-complexes in Rh-catalyzed C-H bond functionalization.

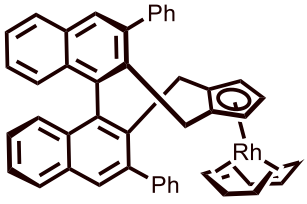




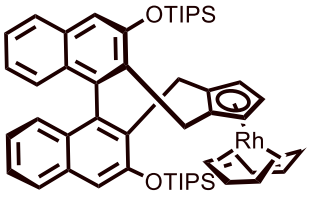
Rh1 (75%, 35:65 er)



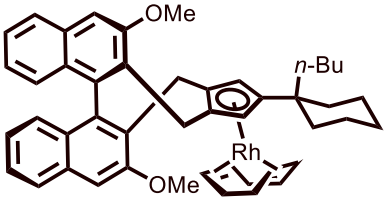
Rh2 (68%, 34:66 er)



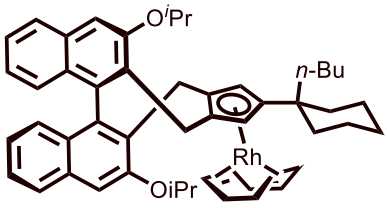
Rh3 (75%, 45:55 er)



Rh4 (68%, 20:80 er)

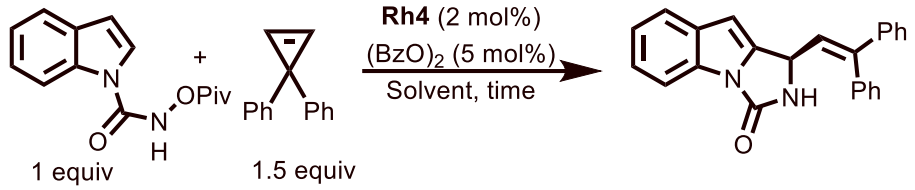


Rh5 (57%, 90:10 er)



Rh6 (65%, 73:27 er)

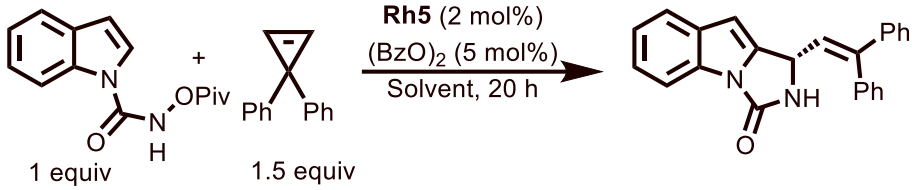
Solvent screening for the synthesis of *R*-isomer:



entry	solvent	temp °C	time h	yield (%)[a]	(er)[b]
1	MeOH	rt	20	68	25:75
2	DCM	rt	20	35	15:85
3	1,4-dioxane	rt	30	57	13:87
4	EA	rt	30	75	13:87
5	EA	0	30	35	8:92
6	EA	10	30	78	13:87
7	MTBE	rt	30	52	10:90
8	Et_2O	rt	30	47	9:91
9[c]	**Et_2O**	**rt**	**20**	**80**	**8:92**
10[c]	EA: Et_2O	rt	30	80	10:90
11[c]	EA: Et_2O	10	30	70	9:91
12[c]	EA: Et_2O	20	30	80	9:91

[a] Isolated yield, [b] The enantiomeric ratio (er) were determined by HPLC analysis on a chiral stationary phase, [c] **Rh4** (4 mol%).

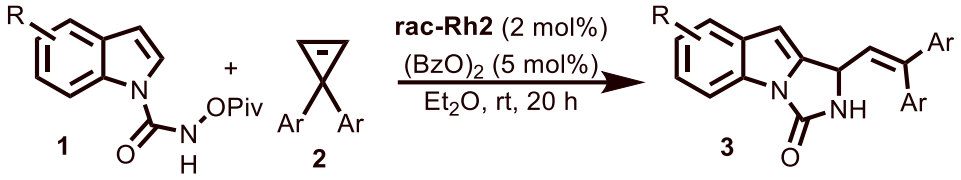
Solvent screening for the synthesis of *S*-isomer:



entry	solvent	yield (%)[a]	(er)[b]
1	**Et_2O**	**80**	**96:4**
2	EA	54	96:4
3	1,4-dioxane	57	96:4
4	THF	80	96:4
5	Acetone	72	96:4
6	MeOH	57	88:12
7[c]	Et_2O	80	96:4
8[d]	Et_2O	80	96:4
9	DCM	55	95:5
10	MTBE	70	96:4

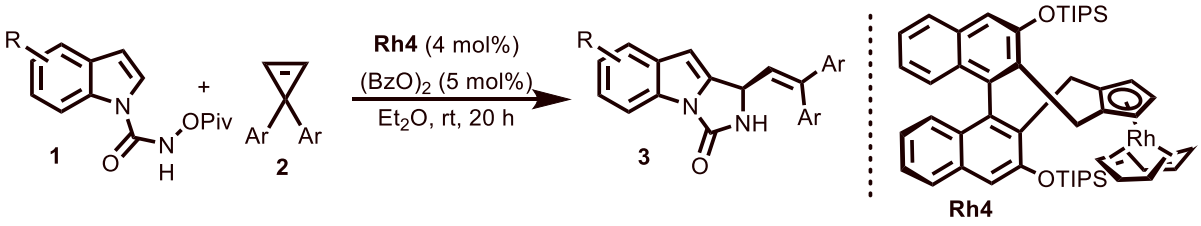
[a] Isolated yield, [b] The enantiomeric ratio (er) were determined by HPLC analysis on a chiral stationary phase, [c] **Rh6** (2 mol%), [d] 20 °C.

5. General procedure for the synthesis of racemic compounds 3



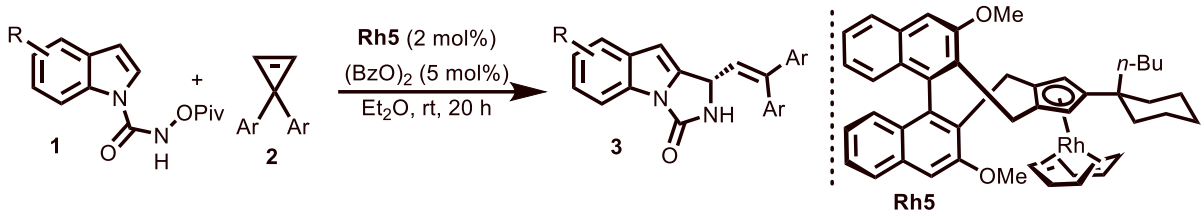
In a reaction tube, (*rac*)-**Rh2** (0.0007 mmol, 2 mol%), $(BzO)_2$ (0.002 mmol, 5 mol%), and *N*-(pivaloyloxy)-1H-indole-1-carboxamide **1a** (10 mg, 0.04 mmol, 1 equiv) were added. The mixture was dissolved in diethyl ether (1.0 mL), and the reaction mixture was stirred at room temperature for 5 min. Then, the solution of cyclopropene **2a** (15 mg, 0.0.057 mmol, 1.5 equiv) in diethyl ether (0.5 mL) was added to the reaction tube. After 20 h, the obtained reaction mixture was purified by column chromatography using hexane/ethyl acetate as an eluent to afford product **3** in racemic form.

6. General procedure for the enantioselective synthesis of *R*-isomer of Imidazo[1,5-a]indole.



In a reaction tube, (*R*)-**Rh4** (2.8 mg, 0.003 mmol, 4 mol%), $(BzO)_2$ (1.1 mg, 0.0038 mmol, 5 mol%), and *N*-(pivaloyloxy)-1H-indole-1-carboxamide **1a** (20 mg, 0.076 mmol, 1 equiv) were added. The mixture was dissolved in diethyl ether (1.0 mL), and the reaction mixture was stirred at room temperature for 5 min. Then, the solution of cyclopropene **2a** (25 mg, 0.115 mmol, 1.5 equiv) in diethyl ether (0.5 mL) was added to the reaction tube and stirred at room temperature for 20 h. The reaction was monitored by TLC. After the complete consumption of the starting material, the obtained reaction mixture was purified by column chromatography using hexane/ethyl acetate as an eluent to afford products **3**. All the substrates were synthesized from 20 mg of *N*-(pivaloyloxy)-1H-indole-1-carboxamide.

7. General procedure for the enantioselective synthesis of *S*-isomer of Imidazo[1,5-a]indole.

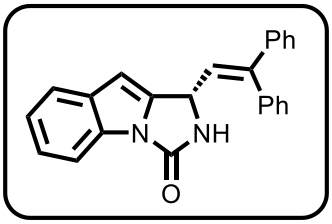


In a reaction tube, (*R*)-**Rh5** (1.8 mg, 0.002 mmol, 2 mol%), $(BzO)_2$ (1.3 mg, 0.0057 mmol, 5 mol%), and *N*-(pivaloyloxy)-1H-indole-1-carboxamide **1a** (30 mg, 0.11 mmol, 1 equiv) were added. The mixture was dissolved in diethyl ether (1.0 mL), and the reaction mixture was stirred at room temperature for 5 min. Then, the solution of cyclopropene **2a** (35 mg, 0.17 mmol, 1.5 equiv) in diethyl ether (0.5 mL) was added to the reaction tube and stirred at room temperature for 20 h. The reaction was monitored by TLC. After complete consumption of the starting material, the obtained reaction mixture was purified by column chromatography using hexane/ethyl acetate as an eluent to afford products **3a**. All the substrates were synthesized from 30 mg of *N*-(pivaloyloxy)-1H-indole-1-carboxamide.

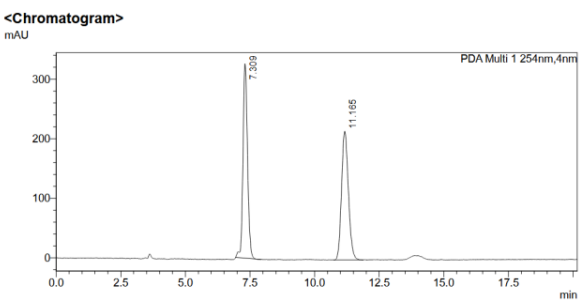
8. Properties of synthesized compounds:

(*S*)-1-(2,2-diphenylvinyl)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3a)

Yield: 80% (32 mg); brown colour solid; TLC: (25% EtOAc in hexanes, R_f): 0.3; $[\alpha]_D^{20}$ +247.1 (c 0.1, $CHCl_3$); IR (ATR): ν(cm^{-1}) =3683, 3019, 1742, 1522, 1422, 1214, 747; ^1H NMR (500 MHz, $CDCl_3$, 24 °C): δ 7.91 (d, J = 8.0 Hz, 1H, ArH), 7.50 (d, J = 8.0 Hz, 1H, ArH), 7.41-7.38 (m, 2H, ArH), 7.36-7.33 (m, 1H, ArH), 7.26-7.24 (m, 2H, ArH), 7.22-7.21 (m, 4H, ArH), 7.19-7.15 (m, 3H, ArH), 6.35 (s, 1H, ArH), 5.92 (d, J = 9.4 Hz, 1H, =CH), 5.66 (s, 1H, NH), 5.27 (d, J = 9.4 Hz, 1H, CH). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 24 °C): δ 153.1 (C=O), 146.9 (CAr), 140.6 (CAr), 140.3 (CAr), 138.2 (CAr), 133.5 (CAr), 130.5 (CAr), 129.7 (C–HAr), 128.7 (C–HAr), 128.39 (C–HAr), 128.33 (C–HAr), 128.2 (C–HAr), 127.6 (C–HAr), 124.1 (=CH), 123.2 (C–HAr), 122.7 (C–HAr), 121.0 (C–HAr), 112.6 (C–HAr), 98.2 (C–HAr), 52.0 (C–H). HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{19}N_2O$ 351.1492; Found 351.1494.

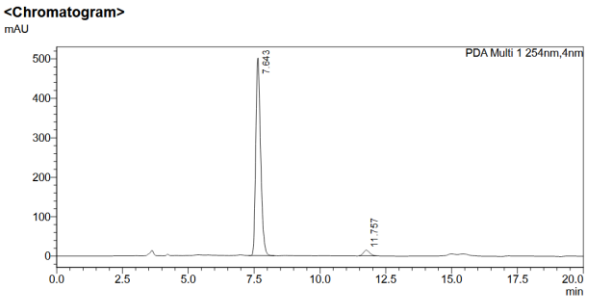


The enantiomeric ratio (96:4) was determined by Daicel Chiralpak IB (35 ºC), Hexane/IPA = 85/15, 1.0 mL/min, λ = 254 nm, tR (major) = 7.64 min, tR (minor) = 11.75 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	7.309	3984011	49.991	60.171
2	11.165	3985421	50.009	39.829
Total		7969431	100.000	100.000

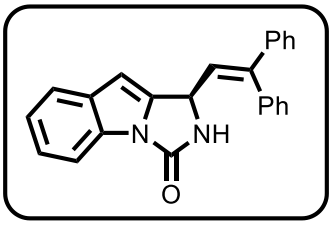


<Peak Table>
PDA Ch1 254nm

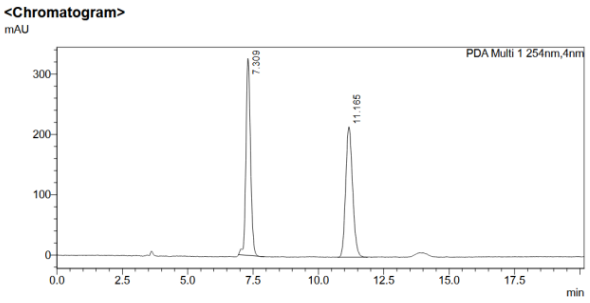
Peak#	Ret. Time	Area	Area%	Height%
1	7.643	6433238	96.294	97.185
2	11.757	247603	3.706	2.815
Total		6680841	100.000	100.000

(*R*)-1-(2,2-diphenylvinyl)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3a)

Yield: 80% (22 mg); brown colour solid, $[\alpha]_D^{20}$ –233.3 (c 0.1, $CHCl_3$).

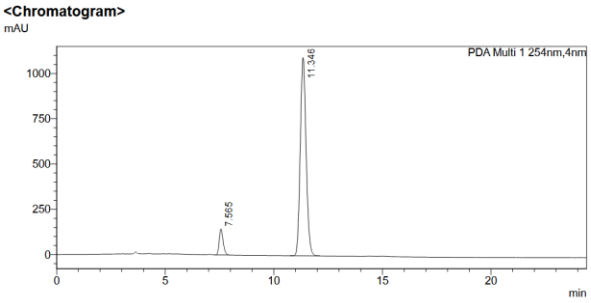


The enantiomeric ratio (8:92) was determined by Daicel Chiralpak IB (35 °C), Hexane/IPA = 85/15, 1.0 mL/min, λ = 254 nm, tR (minor) = 7.56 min, tR (major) = 11.34 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	7.309	3984011	49.991	60.171
2	11.165	3985421	50.009	39.829
Total		7969431	100.000	100.000

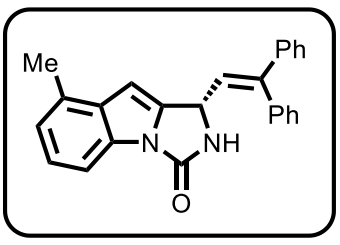


<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	7.565	1801673	8.084	11.593
2	11.346	20485917	91.916	88.407
Total		22287590	100.000	100.000

(*S*)-1-(2,2-diphenylvinyl)-8-methyl-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3b)

Yield: 66% (26 mg); brown colour solid; TLC: (25% EtOAc in hexanes, R_f): 0.3; $[\alpha]_D^{20}$ +245.9

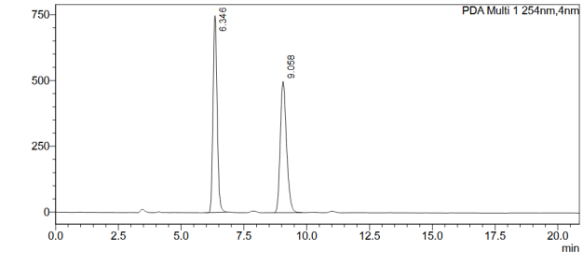


(c 0.1, $CHCl_3$); IR (ATR): ν(cm^{-1}) = 3683, 3458, 3257, 3020, 2925, 1733, 1422, 1214, 754; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): *δ* 7.86 (d, *J* = 8.1 Hz, 1H), 7.53-7.49 (m, 2H), 7.47-7.43 (m, 1H), 7.39-7.37 (m, 2H), 7.31-7.28 (m, 5H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 7.3 1H), 6.47 (s, 1H), 6.02 (d, *J* = 9.4 Hz, 1H), 5.99 (s, 1H), 5.37 (d, *J* = 9.4 Hz, 1H), 2.57 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): *δ* 152.9, 146.9, 140.6, 139.7, 138.2, 133.2, 130.4, 130.2, 129.7, 128.7, 128.38, 128.32, 128.2,

127.6, 124.2, 123.3, 123.0, 110.1, 96.7, 52.0, 18.7. HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{21}N_2O$ 365.1648; Found 365.1654.

The enantiomeric ratio (97:3) was determined by Daicel Chiralpak IB (35 ºC), Hexane/IPA = 85/15, 1.0 mL/min, λ = 254 nm, tR (major) = 6.80 min, tR (minor) = 9.41 min.

<Chromatogram>

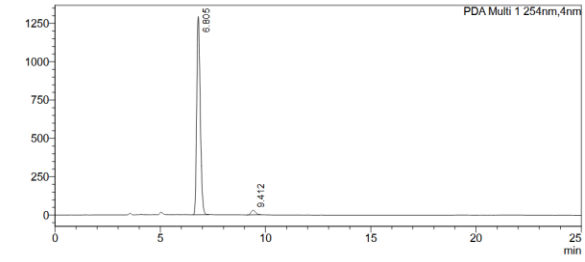


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	6.346	8566320	49.671	59.978
2	9.058	8679638	50.329	40.022
Total		17245958	100.000	100.000

<Chromatogram>



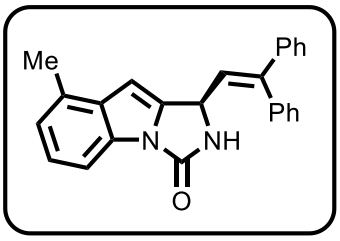
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	6.805	15150067	97.098	97.791
2	9.412	452833	2.902	2.209
Total		15602900	100.000	100.000

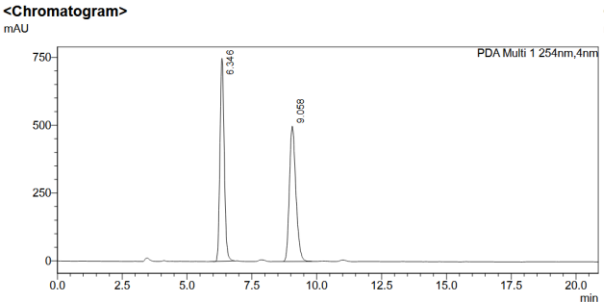
(*R*)-1-(2,2-diphenylvinyl)-8-methyl-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3b)

Yield: 65% (17 mg); brown colour solid, $[\alpha]_D^{20}$ –158.8 (c 0.1, $CHCl_3$).



The enantiomeric ratio (15:85) was determined by Daicel Chiralpak IB (35 ºC), Hexane/IPA = 85/15, 1.0 mL/min, λ = 254 nm, tR (minor) = 6.34 min, tR (major) = 9.02 min.

<Chromatogram>

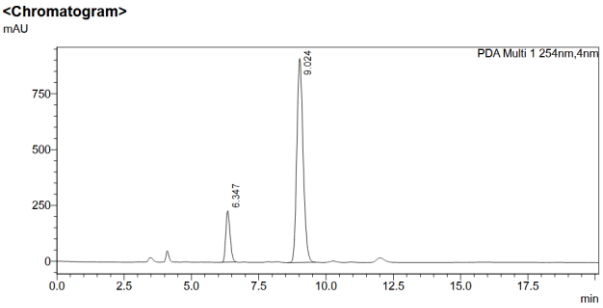


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	6.346	8566320	49.671	59.978
2	9.058	8679638	50.329	40.022
Total		17245958	100.000	100.000

<Chromatogram>



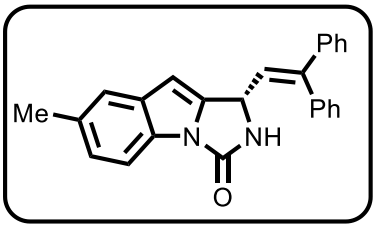
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	6.347	2550064	14.607	20.138
2	9.024	14907925	85.393	79.862
Total		17457989	100.000	100.000

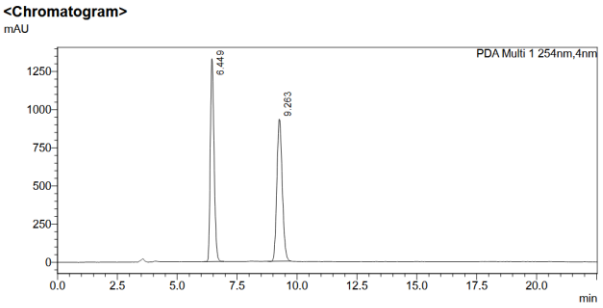
(*S*)-1-(2,2-diphenylvinyl)-7-methyl-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3c)

Yield: 60% (24 mg); brown colour solid; TLC: (25% EtOAc in hexanes, R_f): 0.3; $[\alpha]_D^{20}$ +158.4



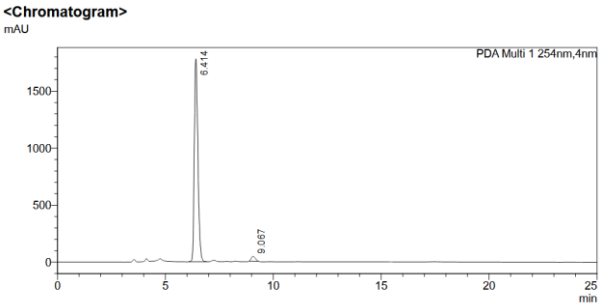
(c 0.1, $CHCl_3$); IR (ATR): ν(cm^{-1}) = 3602, 3441, 3018, 2892, 1720, 1403, 1230, 768; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.77 (d, J = 8.4 Hz, 1H), 7.40-7.30 (m, 3H), 7.27-7.23 (m, 3H), 7.21-7.51 (m, 5H), 7.02 (dd, J = 9.6, 1.3 Hz, 1H), 6.25-6.24 (m,1H), 5.94 (s, 1H), 5.90 (d, J = 9.4 Hz, 1H), 5.23 (d, J = 9.4 Hz, 1H), 2.36 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 153.0, 146.8, 140.6, 140.4, 138.3, 133.7, 132.2 x 2, 129.7, 128.7, 128.3, 128.29, 128.22, 127.6, 124.7, 124.2, 120.8, 112.1, 97.9, 52.0, 21.6. HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{21}N_2O$ 365.1648; Found 365.1650.

The enantiomeric ratio (97:3) was determined by Daicel Chiralpak IB (35 ºC), Hexane/IPA = 85/15, 1.0 mL/min, λ = 254 nm, tR (major) = 6.41 min, tR (minor) = 9.06 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	6.449	14552917	49.923	58.830
2	9.263	14597812	50.077	41.170
Total		29150729	100.000	100.000

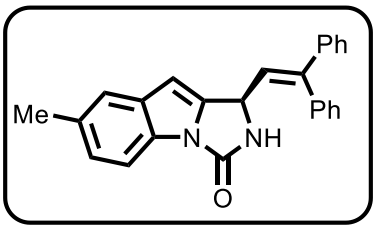


<Peak Table>
PDA Ch1 254nm

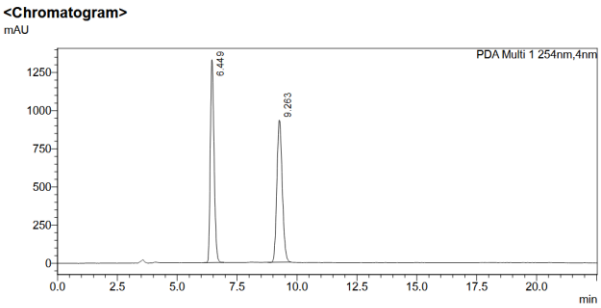
Peak#	Ret. Time	Area	Area%	Height%
1	6.414	20643988	97.325	97.647
2	9.067	567503	2.675	2.353
Total		21211491	100.000	100.000

(*R*)-1-(2,2-diphenylvinyl)-7-methyl-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3c)

Yield: 69% (18 mg); brown colour solid, $[\alpha]_D^{20}$ –128.8 (c 0.1, $CHCl_3$).

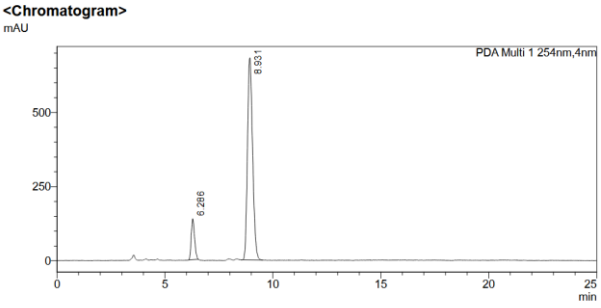


The enantiomeric ratio (12:88) was determined by Daicel Chiralpak IB (35 ºC), Hexane/IPA = 85/15, 1.0 mL/min, λ = 254 nm, tR (minor) = 6.28 min, tR (major) = 8.93 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	6.449	14552917	49.923	58.830
2	9.263	14597812	50.077	41.170
Total		29150729	100.000	100.000

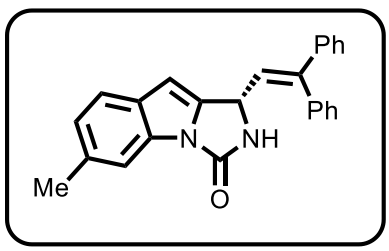


<Peak Table>
PDA Ch1 254nm

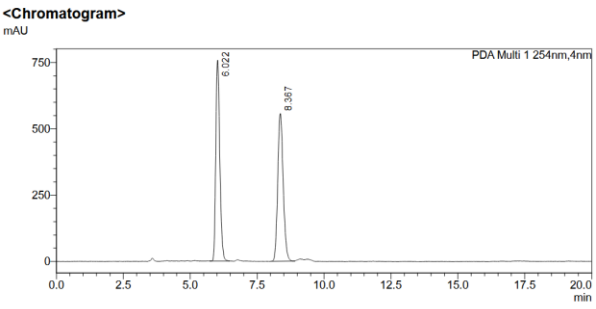
Peak#	Ret. Time	Area	Area%	Height%
1	6.286	1472779	11.570	16.843
2	8.931	11256834	88.430	83.157
Total		12729614	100.000	100.000

(*S*)-1-(2,2-diphenylvinyl)-6-methyl-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3d)

Yield: 77% (31 mg); brown colour solid; TLC: (25% EtOAc in hexanes, R_f): 0.3; $[\alpha]_D^{20}$ +187.6 (c 0.1, $CHCl_3$); IR (ATR): ν(cm^{-1}) = 3683, 3458, 3020, 1735, 1447, 1394, 1215, 753; ^{1}H NMR (500 MHz, DMSO-d_6, 24 °C): δ 8.63 (s, 1H), 7.66 (s, 1H), 7.54-7.51 (m, 2H), 7.48-7.43 (m, 2H), 7.38-7.36 (m, 2H), 7.34-7.29 (m, 3H), 7.25-7.23 (m, 2H), 7.03 (dd, J = 8.1, 1.0 Hz, 1H), 6.47 (d, J = 1.0 Hz, 1H), 6.05 (d, J = 9.4 Hz, 1H), 5.11 (d, J = 9.4 Hz, 1H), 2.42 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6, 24 °C): δ 152.7, 145.1, 140.8, 140.4, 138.4, 132.5, 131.4, 130.5, 130.0, 129.1, 128.8, 128.5, 128.4, 127.6, 125.5, 124.1, 121.1, 112.1, 97.5, 51.9, 21.7. HRMS (ESI/Q-TOF) m/z: [M + H]$^+$ Calcd for $C_{25}H_{21}N_2O$ 365.1648; Found 365.1651.

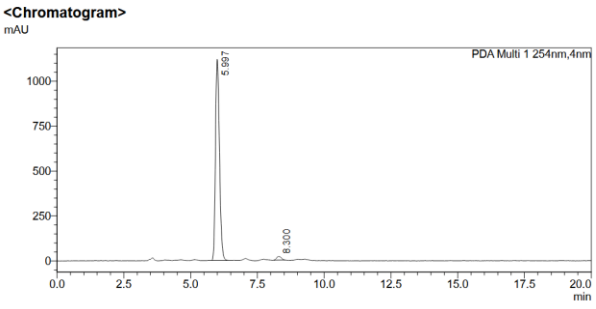


The enantiomeric ratio (98:2) was determined by Daicel Chiralpak IB (35 ºC), Hexane/IPA = 85/15, 1.0 mL/min, λ = 254 nm, tR (major) = 5.99 min, tR (minor) = 8.30 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	6.022	7881628	49.918	57.624
2	8.367	7907637	50.082	42.376
Total		15789265	100.000	100.000

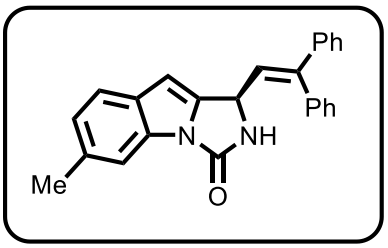


<Peak Table>
PDA Ch1 254nm

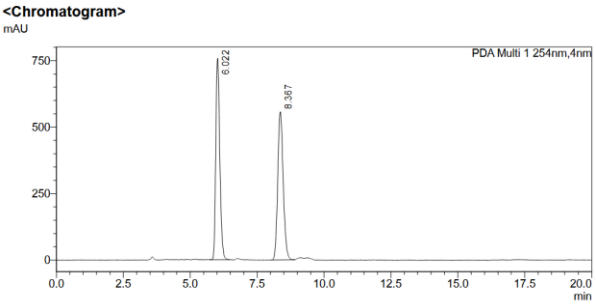
Peak#	Ret. Time	Area	Area%	Height%
1	5.997	11634096	97.899	98.190
2	8.300	249722	2.101	1.810
Total		11883819	100.000	100.000

(*R*)-1-(2,2-diphenylvinyl)-6-methyl-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3d)

Yield: 80% (22 mg); brown colour solid, $[\alpha]_D^{20}$ –226.8 (c 0.1, $CHCl_3$).

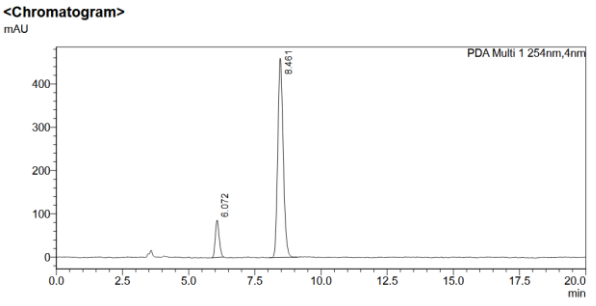


The enantiomeric ratio (12:88) was determined by Daicel Chiralpak IB (35 °C), Hexane/IPA = 85/15, 1.0 mL/min, λ = 254 nm, tR (minor) = 6.07 min, tR (major) = 8.46 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	6.022	7881628	49.918	57.624
2	8.367	7907637	50.082	42.376
Total		15789265	100.000	100.000

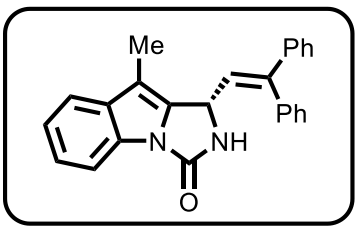


<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	6.072	879602	11.807	15.793
2	8.461	6570092	88.193	84.207
Total		7449694	100.000	100.000

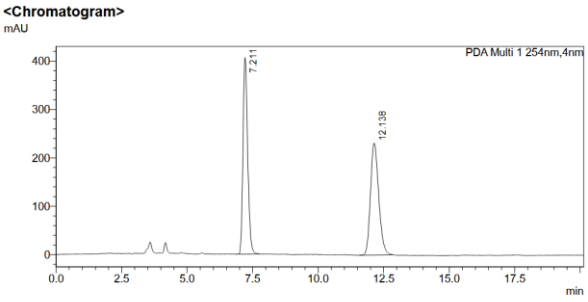
(*S*)-1-(2,2-diphenylvinyl)-9-methyl-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3e)

Yield: 80% (32 mg); brown colour solid; TLC: (25% EtOAc in hexanes, R_f): 0.3; $[\alpha]_D^{20}$ –30.3



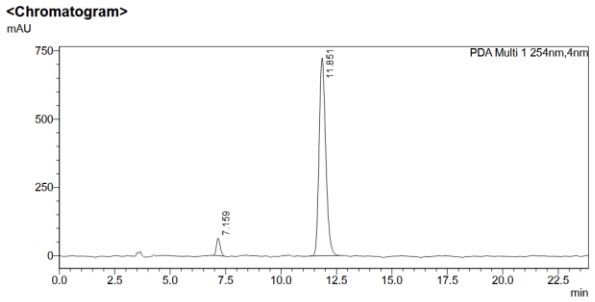
(c 0.1, $CHCl_3$); IR (ATR): ν(cm^{-1}) = 3098, 2982, 1758, 1493, 1353, 1273, 618; ^{1}H NMR (500 MHz, DMSO-d_6, 24 °C): δ 8.62 (s, 1H), 7.78 (d, J = 7.9 Hz, 1H), 7.55-7.52 (m, 3H), 7.46-7.43 (m, 1H), 7.39-7.37 (m, 2H), 7.34-7.29 (m, 3H), 7.26-7.18 (m, 4H), 6.01 (d, J = 9.9 Hz, 1H), 5.13 (d, J = 9.9 Hz, 1H), 2.14 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6, 24 °C): δ 152.7, 145.7, 141.0, 138.6, 136.4x2, 134.2, 129.9, 129.2, 128.9, 128.5, 128.4, 127.6, 124.5, 123.1, 122.1, 119.5, 111.9, 106.0, 51.6, 8.2. HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{21}N_2O$ 365.1648; Found 365.1649.

The enantiomeric ratio (95:5) was determined by Daicel Chiralpak IB (35 °C), Hexane/IPA = 85/15, 1.0 mL/min, λ = 254 nm, tR (major) = 11.85 min, tR (minor) = 7.15 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	7.211	5061357	50.064	63.733
2	12.138	5048395	49.936	36.267
Total		10109751	100.000	100.000

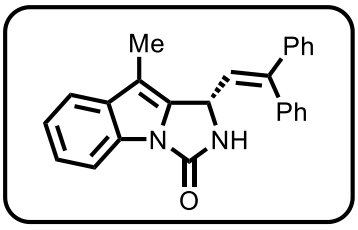


<Peak Table>
PDA Ch1 254nm

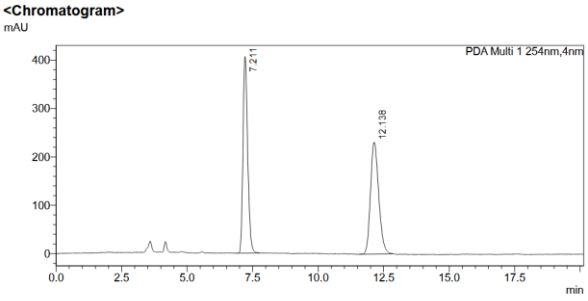
Peak#	Ret. Time	Area	Area%	Height%
1	7.159	761055	4.806	8.149
2	11.851	15074419	95.194	91.851
Total		15835474	100.000	100.000

(*S*)-1-(2,2-diphenylvinyl)-9-methyl-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3e)

Yield: 60% (17 mg); brown colour solid, $[\alpha]_D^{20}$ –15.5 (c 0.1, $CHCl_3$).

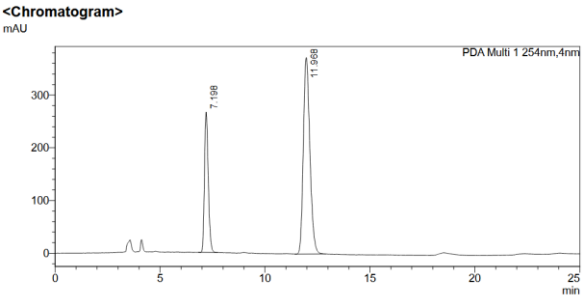


The enantiomeric ratio (30:70) was determined by Daicel Chiralpak IB (35 ºC), Hexane/IPA = 85/15, 1.0 mL/min, λ = 254 nm, tR (minor) = 7.19 min, tR (major) = 11.96 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	7.211	5061357	50.064	63.733
2	12.138	5048395	49.936	36.267
Total		10109751	100.000	100.000

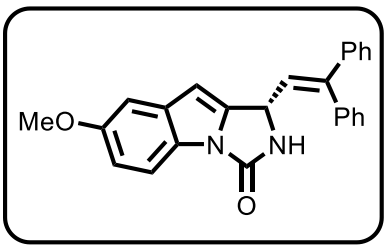


<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	7.198	3356407	29.335	41.701
2	11.968	8085272	70.665	58.299
Total		11441679	100.000	100.000

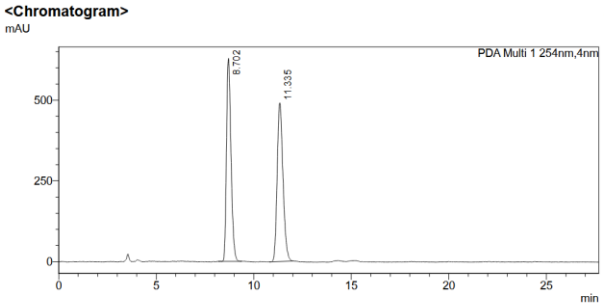
(*S*)-1-(2,2-diphenylvinyl)-7-methoxy-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3f)

Yield: 64% (25 mg); brown colour solid; TLC: (25% EtOAc in hexanes, R_f): 0.2; $[\alpha]_D^{20}$ +102.0



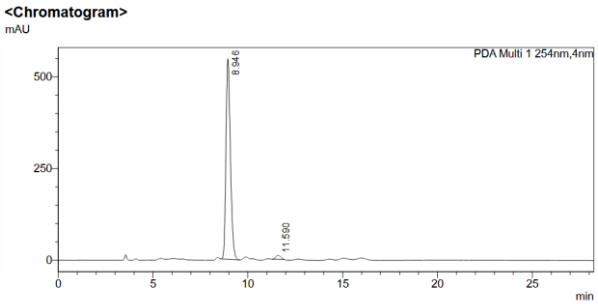
(c 0.1, $CHCl_3$); IR (ATR): ν(cm^{-1}) = 3683, 3459, 3019, 2925, 1735, 1585, 1214, 749; ^1H NMR (500 MHz, $CDCl_3$, 24 °C): *δ*. 7.77 (d, *J* = 9.0 Hz, 1H), 7.39-7.36 (m, 2H), 7.34-7.31 (m, 1H), 7.25-7.24 (m, 2H), 7.19-7.16 (m, 5H), 6.95 (s, 1H), 6.83 (d, *J* = 8.7 Hz, 1H), 6.25 (s, 1H), 5.90 (d, *J* = 9.4 Hz, 1H), 5.22 (d, *J* = 9.4 Hz, 1H), 3.76 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): *δ* 156.0, 152.8, 146.9, 141.2, 140.6, 138.3, 134.3, 129.6, 128.7, 128.3, 128.29, 128.21, 127.5, 125.5, 124.1, 113.1, 112.3, 103.7, 98.0, 55.7, 52.0. HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{21}N_2O_2$ 381.1598; Found 381.1601.

The enantiomeric ratio (98:2) was determined by Daicel Chiralpak IB (35 ºC), Hexane/IPA = 85/15, 1.0 mL/min, λ = 254 nm, tR (major) = 8.94 min, tR (minor) = 11.59 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	8.702	10119853	49.891	56.128
2	11.335	10163953	50.109	43.872
Total		20283806	100.000	100.000

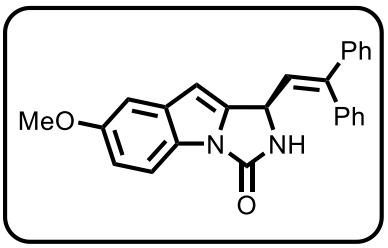


<Peak Table>
PDA Ch1 254nm

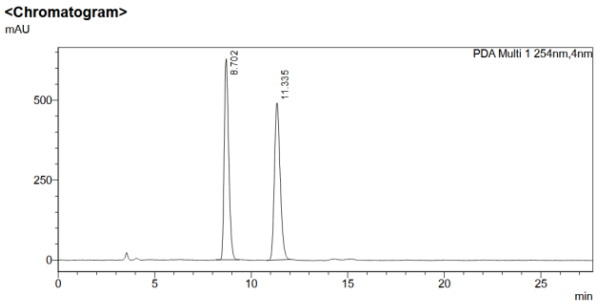
Peak#	Ret. Time	Area	Area%	Height%
1	8.946	8906125	97.803	98.025
2	11.590	200052	2.197	1.975
Total		9106177	100.000	100.000

(*R*)-1-(2,2-diphenylvinyl)-7-methoxy-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3f)

Yield: 69% (18 mg); brown colour solid, $[\alpha]_D^{20}$ –212.5 (c 0.1, $CHCl_3$).

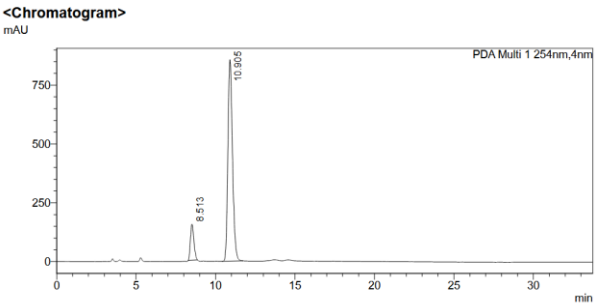


The enantiomeric ratio (12:88) was determined by Daicel Chiralpak IB (35 ºC), Hexane/IPA = 85/15, 1.0 mL/min, λ = 254 nm, tR (minor) = 8.51 min, tR (major) = 10.90 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	8.702	10119853	49.891	56.128
2	11.335	10163953	50.109	43.872
Total		20283806	100.000	100.000

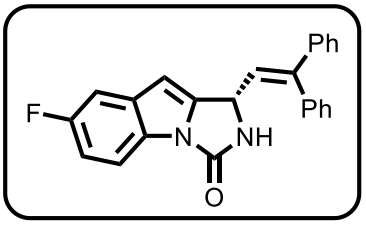


<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	8.513	2324181	11.930	15.222
2	10.905	17157745	88.070	84.778
Total		19481926	100.000	100.000

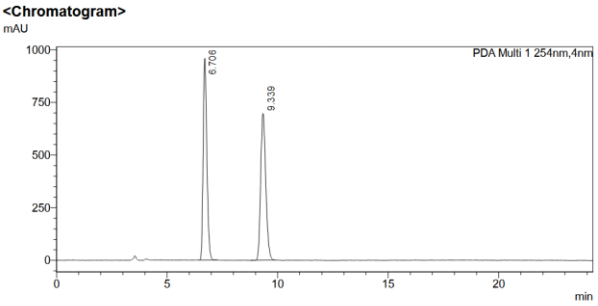
(*S*)-1-(2,2-diphenylvinyl)-7-fluoro-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3g)

Yield: 76% (30 mg); brown colour solid; TLC: (25% EtOAc in hexanes, R_f): 0.4; $[\alpha]_D^{20}$ +140.8 (c 0.1, $CHCl_3$); IR (ATR): ν(cm^{-1}) = 3682, 3456, 3249, 3059, 3021, 2926, 1735, 1587, 1475, 1215, 750; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.84-7.81 (m, 1H), 7.42-7.32 (m, 3H), 7.25-7.19 (m, 5H), 7.19-7.18 (m, 1H), 7.18-7.13 (m, 2H), 6.97-6.92 (m, 1H), 6.31 (s, 1H), 5.91 (d, J = 9.4 Hz, 1H), 5.72 (s, 1H),



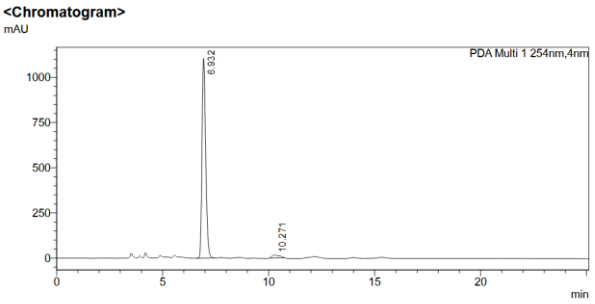
5.26 (d, J = 9.4 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 160.4, 158.1, 152.6, 147.3, 142.0, 140.5, 138.2, 134.2 (d, J = 9.8 Hz), 129.6, 128.8, 128.4, 128.3, 127.6, 127.0, 123.6, 113.3 (d, J = 9.3 Hz), 111.3 (d, J = 26.0 Hz), 106.4 (d, J = 24.0 Hz), 98.1 (d, J = 3.6 Hz), 52.0. ^{19}F NMR (375 MHz, $CDCl_3$, 24°C): δ –120.12. HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{18}FN_2O$ 369.1398; Found 369.1399.

The enantiomeric ratio (97:3) was determined by Daicel Chiralpak IB (35 ºC), Hexane/IPA = 85/15, 1.0 mL/min, λ = 254 nm, tR (major) = 6.93 min, tR (minor) = 10.27 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	6.706	11168423	49.936	57.899
2	9.339	11197198	50.064	42.101
Total		22365621	100.000	100.000

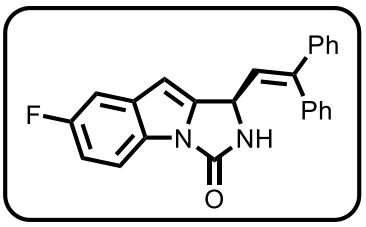


<Peak Table>
PDA Ch1 254nm

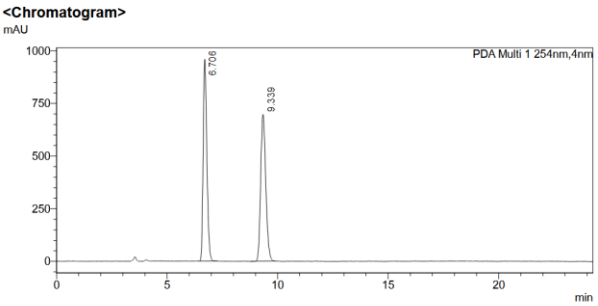
Peak#	Ret. Time	Area	Area%	Height%
1	6.932	13416124	97.040	98.460
2	10.271	409288	2.960	1.540
Total		13825412	100.000	100.000

(*R*)-1-(2,2-diphenylvinyl)-7-fluoro-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3g)

Yield: 73% (19 mg); brown colour solid, $[\alpha]_D^{20}$ –166.4 (c 0.1, $CHCl_3$).

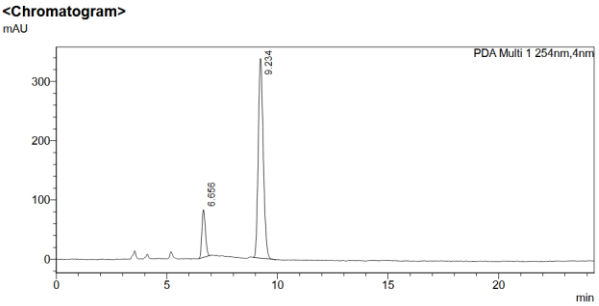


The enantiomeric ratio (15:85) was determined by Daicel Chiralpak IB (35 ºC), Hexane/IPA = 85/15, 1.0 mL/min, λ = 254 nm, tR (minor) = 6.65 min, tR (major) = 9.23 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	6.706	11168423	49.936	57.899
2	9.339	11197198	50.064	42.101
Total		22365621	100.000	100.000

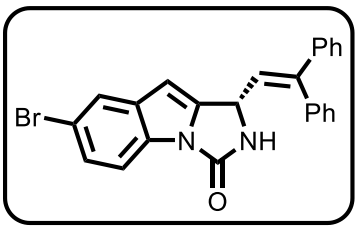


<Peak Table>
PDA Ch1 254nm

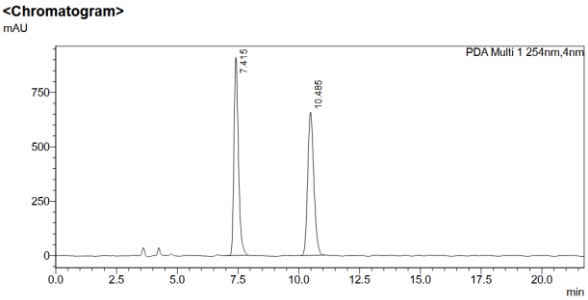
Peak#	Ret. Time	Area	Area%	Height%
1	6.656	897415	14.439	19.294
2	9.234	5317872	85.561	80.706
Total		6215287	100.000	100.000

(*S*)-7-bromo-1-(2,2-diphenylvinyl)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3h)

Yield: 78% (30 mg); brown colour solid; TLC: (25% EtOAc in hexanes, R_f): 0.4; $[\alpha]_D^{20}$ +196.7 (c 0.1, $CHCl_3$); IR (ATR): ν(cm^{-1}) = 3671, 3450, 3049, 2828, 1730, 1166, 701; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.74 (d, J = 8.4 Hz, 1H), 7.62 (d, J = 1.6 Hz, 1H), 7.41-7.37 (m, 2H), 7.35-7.33 (m, 1H), 7.30-7.37 (m, 1H), 7.25-7.15 (m, 7H), 6.26 (s, 1H), 6.07 (s, 1H), 5.90 (d, J = 9.4 Hz, 1H), 5.25 (d, J = 9.4 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 152.5, 147.4, 141.5, 140.4, 138.1, 135.0, 129.6, 129.1, 128.8, 128.45, 128.42, 128.3, 127.6, 126.2, 123.6, 123.4, 115.9, 113.8, 97.5, 52.0. HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{18}BrN_2O$ 429.0597; Found 429.0606.

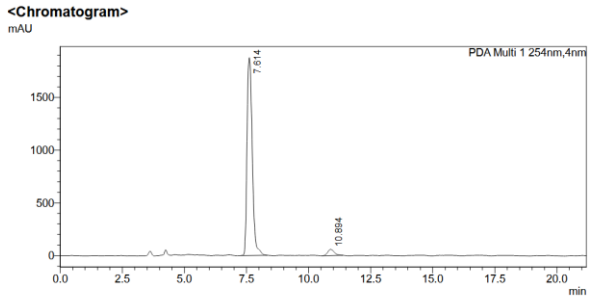


The enantiomeric ratio (96:4) was determined by Daicel Chiralpak IB (35 ºC), Hexane/IPA = 85/15, 1.0 mL/min, λ = 254 nm, tR (major) = 7.61 min, tR (minor) = 10.89 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	7.415	11594550	50.103	58.043
2	10.485	11546992	49.897	41.957
Total		23141543	100.000	100.000

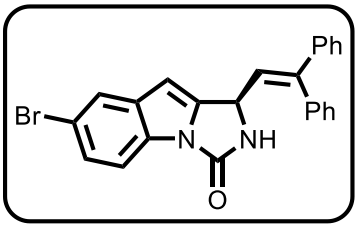


<Peak Table>
PDA Ch1 254nm

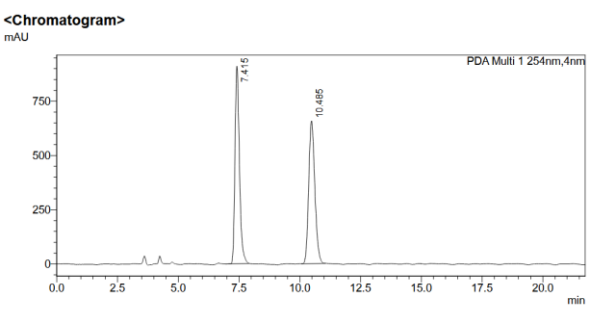
Peak#	Ret. Time	Area	Area%	Height%
1	7.614	27578205	96.307	96.963
2	10.894	1057645	3.693	3.037
Total		28635850	100.000	100.000

(*R*)-7-bromo-1-(2,2-diphenylvinyl)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3h)

Yield: 80% (20 mg); brown colour solid, $[\alpha]_D^{20}$ –177.3 (c 0.1, $CHCl_3$).

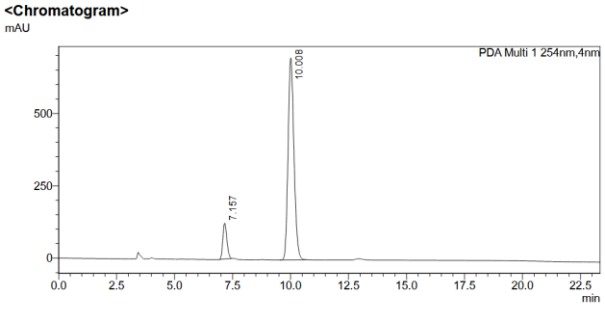


The enantiomeric ratio (11:89) was determined by Daicel Chiralpak IB (35 ºC), Hexane/IPA = 85/15, 1.0 mL/min, λ = 254 nm, tR (minor) = 7.15 min, tR (major) = 10.00 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	7.415	11594550	50.103	58.043
2	10.485	11546992	49.897	41.957
Total		23141543	100.000	100.000

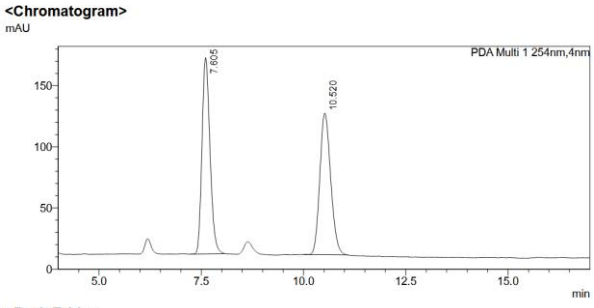


<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	7.157	1510926	10.932	15.108
2	10.008	12310055	89.068	84.892
Total		13820982	100.000	100.000

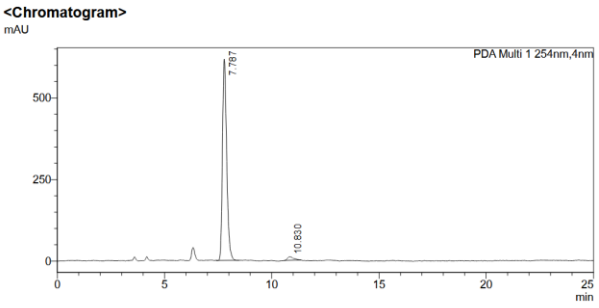
(*S*)-1-(2,2-diphenylvinyl)-7-iodo-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3i)

Yield: 81% (30 mg); brown colour solid; TLC: (25% EtOAc in hexanes, R_f): 0.4; $[\alpha]_D^{20}$ +113.6 (c 0.1, $CHCl_3$); IR (ATR): ν(cm^{-1}) = 3684, 3455, 3019, 1739, 1445, 1215, 929; ^{1}H NMR (400 MHz, DMSO-d_6, 24 °C): δ 8.77 (s, 1H), 7.99 (d, J = 1.4 Hz, 1H), 7.65 (d, J = 8.4 Hz, 1H), 7.55-7.50 (m, 3H), 7.47-7.42 (m, 1H), 7.37-7.29 (m, 5H), 7.24-7.22 (m, 2H), 6.5 (s, 1H), 6.07 (d, J = 9.6 Hz, 1H), 5.15 (d, J = 9.6 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, 24 °C): δ 152.2, 145.5, 142.1, 140.8, 138.4, 136.1, 131.2, 130.0, 129.9, 129.3, 129.2, 128.9, 128.57, 128.52, 127.6, 125.0, 114.2, 96.8, 86.6, 51.9. HRMS (ESI/Q-TOF) m/z: [M + H]$^+$ Calcd for $C_{24}H_{18}IN_2O$ 477.0458; Found 477.0455. The enantiomeric ratio (97:3) was determined by Daicel Chiralpak IB (35 ºC), Hexane/IPA = 85/15, 1.0 mL/min, λ = 254 nm, tR (major) = 7.78 min, tR (minor) = 10.83 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	7.605	2169914	50.279	58.091
2	10.520	2145807	49.721	41.909
Total		4315721	100.000	100.000

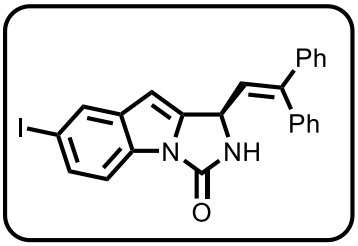


<Peak Table>
PDA Ch1 254nm

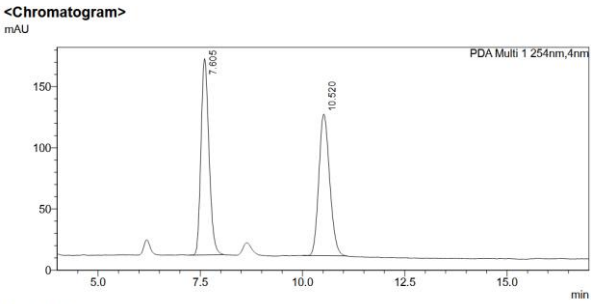
Peak#	Ret. Time	Area	Area%	Height%
1	7.787	8436830	97.432	98.240
2	10.830	222375	2.568	1.760
Total		8659204	100.000	100.000

(*R*)-1-(2,2-diphenylvinyl)-7-iodo-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3i)

Yield: 66% (16 mg); brown colour solid, $[\alpha]_D^{20}$ –118.0 (c 0.1, $CHCl_3$).

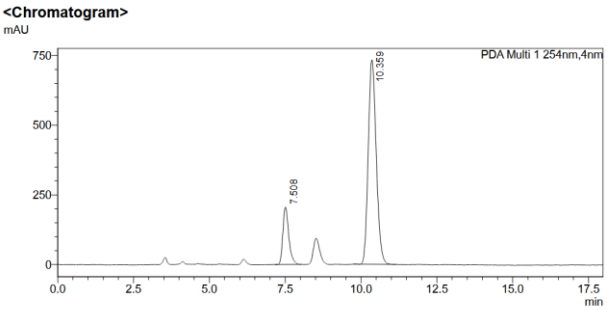


The enantiomeric ratio (86:14) was determined by Daicel Chiralpak IG (35 °C), Hexane/IPA = 85/15, 1.0 mL/min, λ = 254 nm, tR (major) = 14.04 min, tR (minor) = 16.94 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	7.605	2169914	50.279	58.091
2	10.520	2145807	49.721	41.909
Total		4315721	100.000	100.000

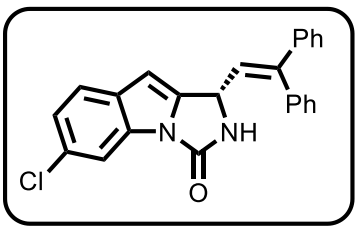


<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	7.508	2795327	17.230	21.960
2	10.359	13427915	82.770	78.040
Total		16223243	100.000	100.000

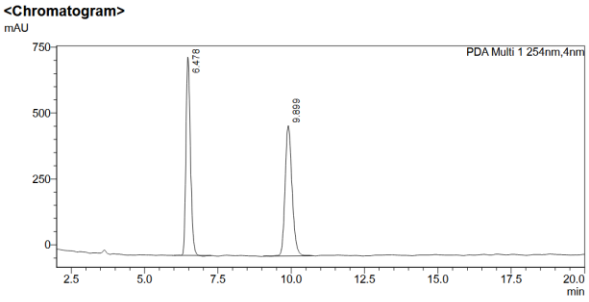
(*S*)-6-chloro-1-(2,2-diphenylvinyl)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3j)

Yield: 84% (33 mg); brown colour solid; TLC: (25% EtOAc in hexanes, R_f): 0.4; $[\alpha]_D^{20}$ +287.6



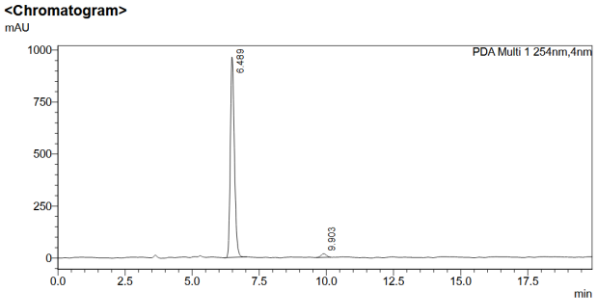
(c 0.1, $CHCl_3$); IR (ATR): ν(cm^{-1}) = 3682, 3454, 3244, 3020, 1736, 1459, 1215, 755; ^{1}H NMR (400 MHz, DMSO-d_6, 24 °C): δ 8.79 (s, 1H), 7.79 (d, J = 1.9 Hz, 1H), 7.60 (d, J = 8.4 Hz, 1H), 7.53-7.49 (m, 2H), 7.46-7.42 (m, 1H), 7.37-7.35 (m, 2H), 7.32-7.28 (m, 3H), 7.24-7.20 (m, 3H), 6.55 (s, 1H), 6.07 (d, J = 9.5 Hz, 1H), 5.14 (d, J = 9.5 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6, 24 °C): δ 156.9, 150.3, 146.7, 145.5, 143.1, 137.2, 135.1, 134.7, 133.9, 133.6, 133.3, 133.2, 132.4x3, 129.7, 127.6, 127.5, 116.4, 102.4, 56.8. HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{18}ClN_2O$ 385.1102; Found 385.1103.

The enantiomeric ratio (97:3) was determined by Daicel Chiralpak IB (35 °C), Hexane/IPA = 85/15, 1.0 mL/min, λ = 254 nm, tR (major) = 6.48 min, tR (minor) = 9.90 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	6.478	8014475	49.471	60.341
2	9.899	8186018	50.529	39.659
Total		16200493	100.000	100.000

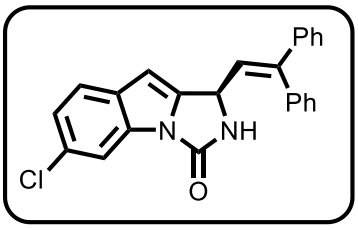


<Peak Table>
PDA Ch1 254nm

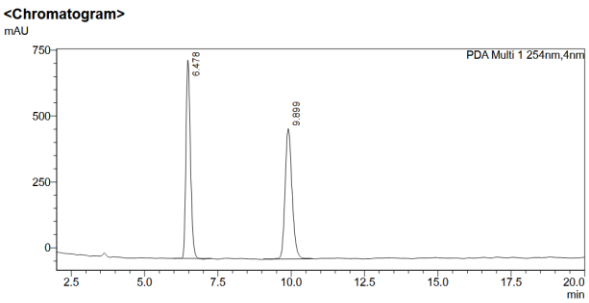
Peak#	Ret. Time	Area	Area%	Height%
1	6.489	10196227	97.630	98.245
2	9.903	247560	2.370	1.755
Total		10443787	100.000	100.000

(*R*)-6-chloro-1-(2,2-diphenylvinyl)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3j)

Yield: 76% (20 mg); brown colour solid, $[\alpha]_D^{20}$ –193.2 (c 0.1, $CHCl_3$).

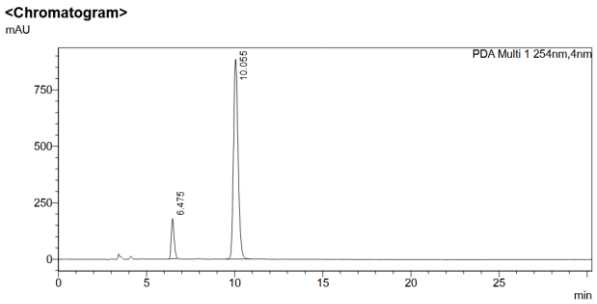


The enantiomeric ratio (11:89) was determined by Daicel Chiralpak IB (35 ºC), Hexane/IPA = 85/15, 1.0 mL/min, λ = 254 nm, tR (minor) = 6.47 min, tR (major) = 10.05 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	6.478	8014475	49.471	60.341
2	9.899	8186018	50.529	39.659
Total		16200493	100.000	100.000

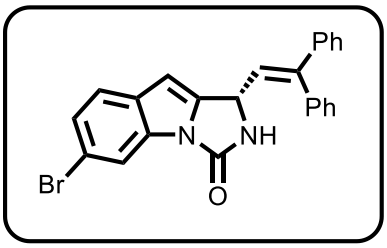


<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	6.475	2006999	11.141	16.778
2	10.055	16007210	88.859	83.222
Total		18014209	100.000	100.000

(*S*)-6-bromo-1-(2,2-diphenylvinyl)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3k)

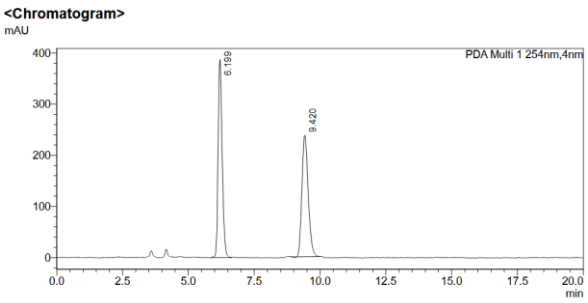
Yield: 66% (26 mg); brown colour solid; TLC: (25% EtOAc in hexanes, R_f): 0.4; $[\alpha]_D^{20}$ +274.4



(c 0.1, $CHCl_3$); IR (ATR): ν(cm^{-1}) = 3683, 3456, 3019, 1737, 1464, 1215, 753; ^{1}H NMR (500 MHz, DMSO-d_6, 24 °C): δ 8.8 (s, 1H), 7.93 (d, J = 1.6 Hz, 1H), 7.58 (d, J = 7.5 Hz, 1H), 7.54-7.51 (m, 2H), 7.47-7.43 (m, 1H), 7.38-7.30 (m, 6H), 7.25-7.23 (m, 2H), 6.58 (d, J = 0.9 Hz, 1H), 6.09 (d, J = 9.5 Hz, 1H), 5.14 (d, J = 9.5 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6, 24 °C): δ 152.1, 145.5, 141.9, 140.7, 138.4, 132.7, 130.7, 130.0, 129.2, 128.9, 128.58, 128.54, 127.6, 125.4, 124.9,

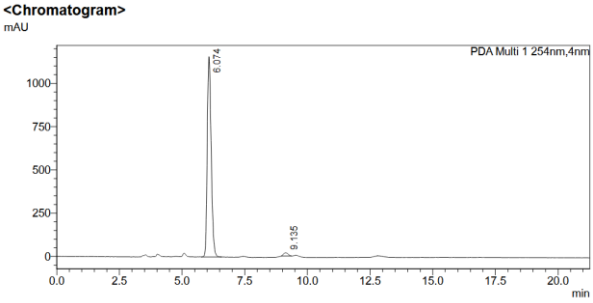
123.3, 115.5, 114.5, 97.7, 52.1. HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{18}BrN_2O$ 429.0597; Found 429.0588.

The enantiomeric ratio (98:2) was determined by Daicel Chiralpak IB (35 ºC), Hexane/IPA = 85/15, 1.0 mL/min, λ = 254 nm, tR (major) = 6.07 min, tR (minor) = 9.13 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	6.199	4158930	51.335	61.961
2	9.420	3942625	48.665	38.039
Total		8101555	100.000	100.000

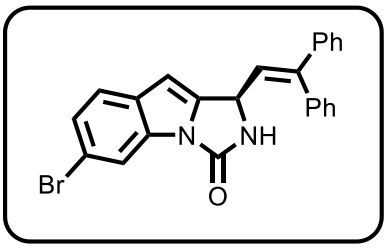


<Peak Table>
PDA Ch1 254nm

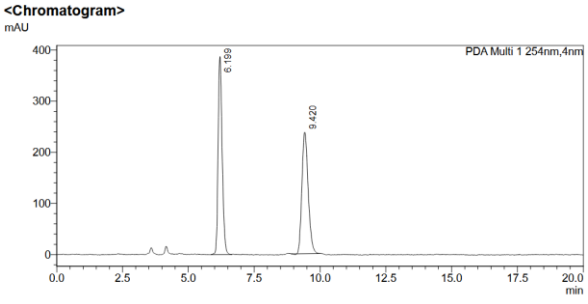
Peak#	Ret. Time	Area	Area%	Height%
1	6.074	12587839	98.170	98.411
2	9.135	234624	1.830	1.589
Total		12822463	100.000	100.000

(*R*)-6-bromo-1-(2,2-diphenylvinyl)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3k)

Yield: 71% (18 mg); brown colour solid, $[\alpha]_D^{20}$ –183.2 (c 0.1, $CHCl_3$).

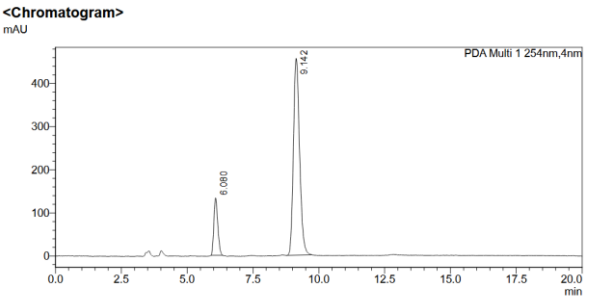


The enantiomeric ratio (16:84) was determined by Daicel Chiralpak IB (35 ºC), Hexane/IPA = 85/15, 1.0 mL/min, λ = 254 nm, tR (minor) = 6.08 min, tR (major) = 9.14 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	6.199	4158930	51.335	61.961
2	9.420	3942625	48.665	38.039
Total		8101555	100.000	100.000

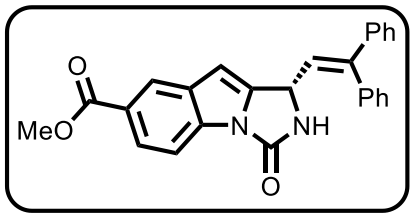


<Peak Table>
PDA Ch1 254nm

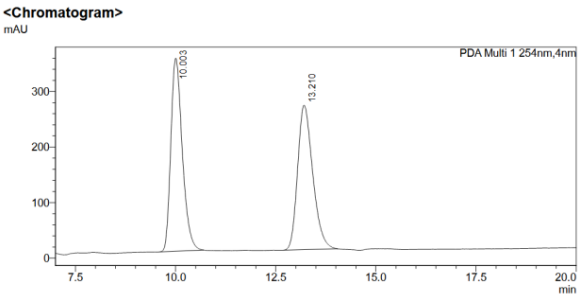
Peak#	Ret. Time	Area	Area%	Height%
1	6.080	1374737	15.594	22.572
2	9.142	7440829	84.406	77.428
Total		8815566	100.000	100.000

Methyl (*S*)-1-(2,2-diphenylvinyl)-3-oxo-2,3-dihydro-1H-imidazo[1,5-a]indole-7-carboxylate (3l)

Yield: 79% (30 mg); brown colour solid; TLC: (30% EtOAc in hexanes, R_f): 0.3; $[\alpha]_D^{20}$ +208.0 (c 0.1, $CHCl_3$); IR (ATR): ν(cm^{-1}) = 3683, 3457, 3019, 1747, 1713, 1438, 1214, 744; ^{1}H NMR (500 MHz, DMSO-d_6, 24 °C): δ 8.86 (s, 1H), 8.29 (s, 1H), 7.92-7.87 (m, 2H), 7.54-7.51 (m, 2H), 7.47-7.44 (m, 1H), 7.38-7.37 (m, 2H), 7.34-7.29 (m, 3H), 7.25-7.23 (m, 2H), 6.70 (s, 1H), 6.11 (d, J = 9.5 Hz, 1H), 5.18 (d, J = 9.5 Hz, 1H), 3.86 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6, 24 °C): δ 167.1, 152.1, 145.6, 142.6, 140.7, 138.3, 133.5, 132.6, 130.0, 129.2, 128.9, 128.58, 128.54, 127.7, 124.9, 124.0, 123.9, 123.6, 112.0, 98.4, 52.4, 52.1. HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{21}N_2O_3$ 409.1547; Found 409.1550.

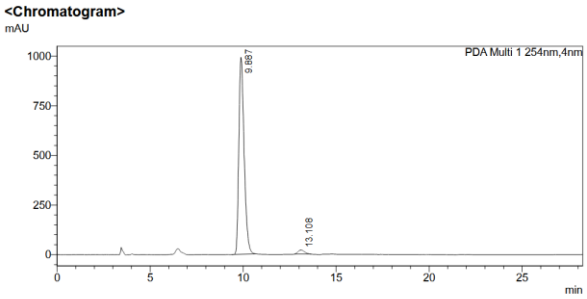


The enantiomeric ratio (97:3) was determined by Daicel Chiralpak IB (35 ºC), Hexane/IPA = 85/15, 1.0 mL/min, λ = 254 nm, tR (major) = 9.88 min, tR (minor) = 13.10 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	10.003	6914653	50.285	57.227
2	13.210	6836225	49.715	42.773
Total		13750878	100.000	100.000

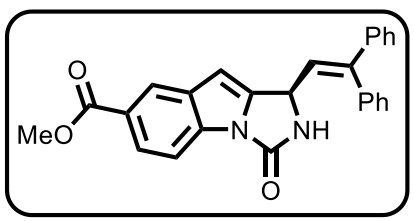


<Peak Table>
PDA Ch1 254nm

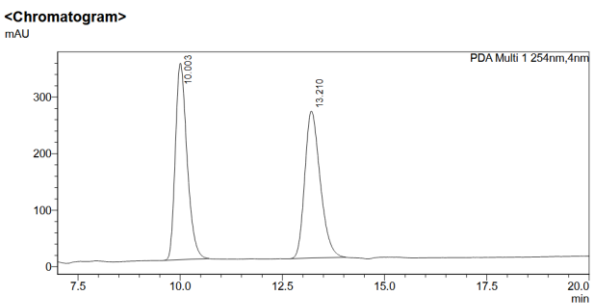
Peak#	Ret. Time	Area	Area%	Height%
1	9.887	19686199	97.502	97.953
2	13.108	504300	2.498	2.047
Total		20190499	100.000	100.000

Methyl (*R*)-1-(2,2-diphenylvinyl)-3-oxo-2,3-dihydro-1H-imidazo[1,5-a]indole-7-carboxylate (3l)

Yield: 75% (19 mg); brown colour solid, $[\alpha]_D^{20}$ –147.2 (c 0.1, $CHCl_3$).

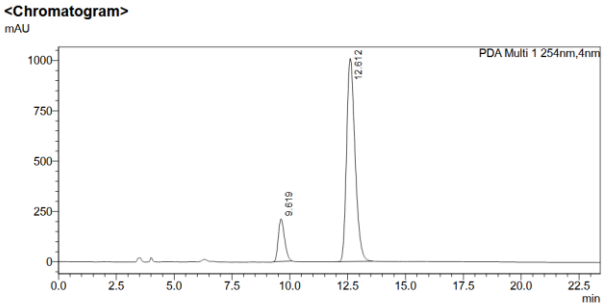


The enantiomeric ratio (14:86) was determined by Daicel Chiralpak IB (35 ºC), Hexane/IPA = 85/15, 1.0 mL/min, λ = 254 nm, tR (minor) = 9.61 min, tR (major) = 12.61 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	10.003	6914653	50.285	57.227
2	13.210	6836225	49.715	42.773
Total		13750878	100.000	100.000

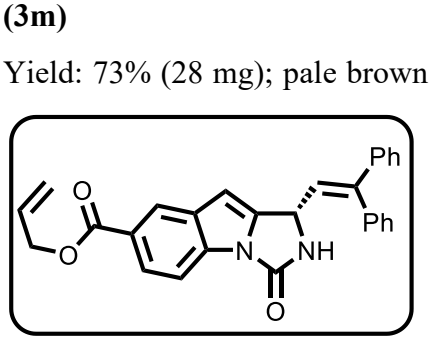


<Peak Table>
PDA Ch1 254nm

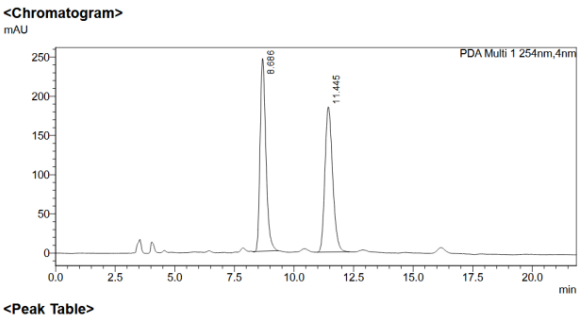
Peak#	Ret. Time	Area	Area%	Height%
1	9.619	4004706	13.507	17.332
2	12.612	25644957	86.493	82.668
Total		29649663	100.000	100.000

Allyl (*S*)-1-(2,2-diphenylvinyl)-3-oxo-2,3-dihydro-1H-imidazo[1,5-a]indole-7-carboxylate (3m)

Yield: 73% (28 mg); pale brown colour solid; TLC: (30% EtOAc in hexanes, R_f): 0.3; $[\alpha]_D^{20}$ +208.0 (c 0.1, $CHCl_3$); IR (ATR): ν(cm^{-1}) = 3683, 3457, 3019, 1751, 1710, 1523, 1422, 1214, 745; ^{1}H NMR (500 MHz, $CDCl_3$, 24 °C): δ 8.29 (s, 1H), 7.97-7.92 (m, 2H), 7.42-7.39 (m, 2H), 7.36-7.33 (m, 1H), 7.27-7.25 (m, 2H), 7.23-7.21 (m, 3H), 7.19-7.17 (m, 2H), 6.42 (s, 1H), 6.04-5.96 (m, 1H), 5.95-5.93 (m, 2H), 5.38-5.34 (m, 1H), 5.30 (d, J = 9.5 Hz, 1H), 5.24-5.21 (m, 1H), 4.79-4.77 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 166.7, 152.2, 147.5, 141.3, 140.4, 138.1, 133.1, 133.0, 132.4, 129.6, 128.8, 128.48, 128.42, 128.3, 127.5, 124.75, 124.72, 123.6, 123.4, 118.1, 112.2, 98.9, 65.5, 52.1. HRMS (ESI/Q-TOF) m/z: [M + H]$^+$ Calcd for $C_{28}H_{23}N_2O_3$ 435.1703; Found 435.1712.

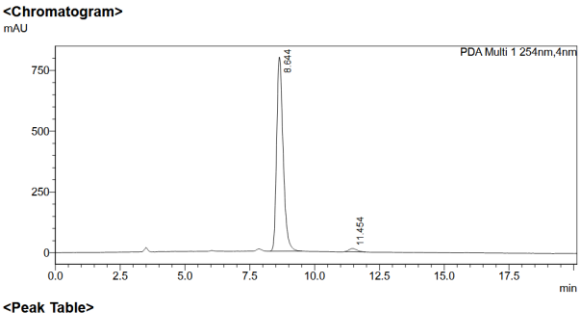


The enantiomeric ratio (98:2) was determined by Daicel Chiralpak IB (35 ºC), Hexane/IPA = 85/15, 1.0 mL/min, λ = 254 nm, tR (major) = 8.64 min, tR (minor) = 11.45 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	8.686	4172624	49.933	57.031
2	11.445	4183877	50.067	42.969
Total		8356502	100.000	100.000

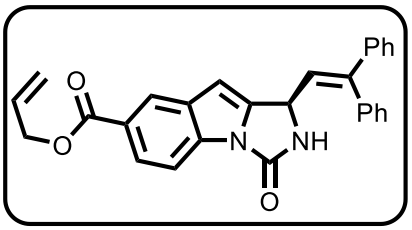


<Peak Table>
PDA Ch1 254nm

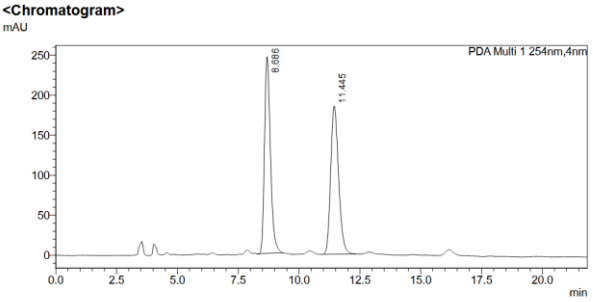
Peak#	Ret. Time	Area	Area%	Height%
1	8.644	13904196	98.053	98.396
2	11.454	276077	1.947	1.604
Total		14180273	100.000	100.000

Allyl (*R*)-1-(2,2-diphenylvinyl)-3-oxo-2,3-dihydro-1H-imidazo[1,5-a]indole-7-carboxylate (3m)

Yield: 76% (19 mg); pale brown colour solid, $[\alpha]_D^{20}$ –152.8 (c 0.1, $CHCl_3$).

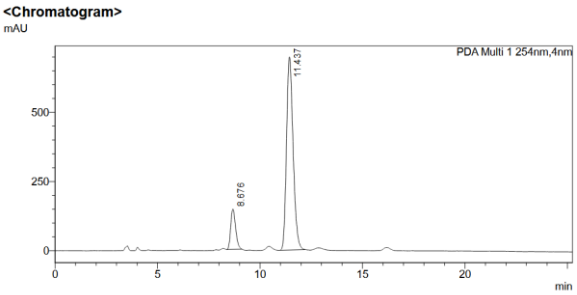


The enantiomeric ratio (14:86) was determined by Daicel Chiralpak IB (35 ºC), Hexane/IPA = 85/15, 1.0 mL/min, λ = 254 nm, tR (minor) = 8.67 min, tR (major) = 11.43 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	8.686	4172624	49.933	57.031
2	11.445	4183877	50.067	42.969
Total		8356502	100.000	100.000

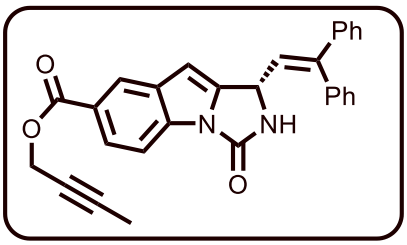


<Peak Table>
PDA Ch1 254nm

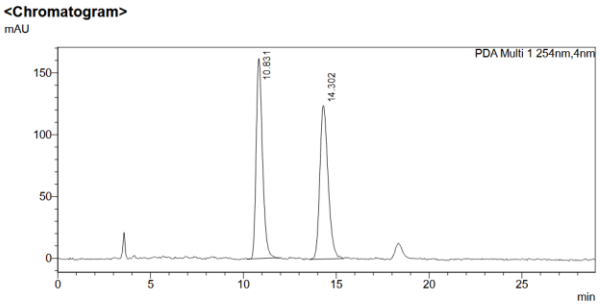
Peak#	Ret. Time	Area	Area%	Height%
1	8.676	2422998	13.463	17.263
2	11.437	15574165	86.537	82.737
Total		17997162	100.000	100.000

But-2-yn-1-yl (*S*)-1-(2,2-diphenylvinyl)-3-oxo-2,3-dihydro-1H-imidazo[1,5-a]indole-7-carboxylate (3n)

Yield: 75% (29 mg); pale brown colour solid; TLC: (30% EtOAc in hexanes, R_f): 0.3; $[\alpha]_D^{20}$ +180.0 (c 0.1, $CHCl_3$); IR (ATR): ν(cm^{-1}) = 3019, 1743, 1737, 1409, 1294, 1250, 1216, 1147, 761; ^1H NMR (500 MHz, $CDCl_3$, 24 °C): δ 8.39 (s, 1H), 8.07-8.02 (m, 2H), 7.52-7.49 (m, 2H), 7.47-7.44 (m, 1H), 7.36-7.31 (m, 5H), 7.29-7.27 (m, 2H), 6.52 (s, 1H), 6.04 (d, J = 9.4 Hz, 1H), 5.91 (s, 1H), 5.40 (d. J = 9.4 Hz, 1H), 4.94 (q, J = 2.3 Hz, 2H), 1.91 (t, J = 2.3 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 166.4, 152.1, 147.5, 141.3, 140.3, 138.1, 133.17, 133.11, 129.6, 128.8, 128.48, 128.42, 128.3, 127.5, 124.8, 124.2, 123.8, 123.4, 112.2, 98.9, 83.2, 73.4, 53.2, 52.1, 3.7. HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{22}N_2O_3Na$ 469.1523; Found 469.1541.

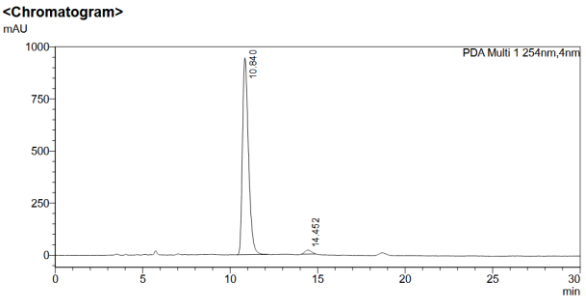


The enantiomeric ratio (98:2) was determined by Daicel Chiralpak IB (35 ºC), Hexane/IPA = 85/15, 1.0 mL/min, λ = 254 nm, tR (major) = 10.84 min, tR (minor) = 14.45 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	10.831	3826044	49.883	56.525
2	14.302	3843950	50.117	43.475
Total		7669994	100.000	100.000

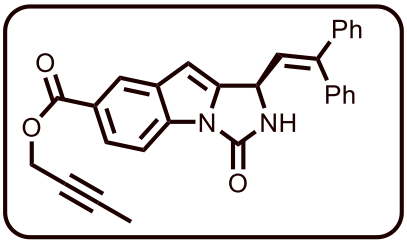


<Peak Table>
PDA Ch1 254nm

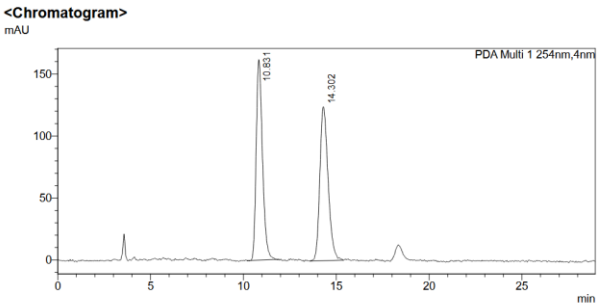
Peak#	Ret. Time	Area	Area%	Height%
1	10.840	22586829	97.827	98.029
2	14.452	501802	2.173	1.971
Total		23088631	100.000	100.000

But-2-yn-1-yl (*R*)-1-(2,2-diphenylvinyl)-3-oxo-2,3-dihydro-1H-imidazo[1,5-a]indole-7-carboxylate (3n)

Yield: 76% (19 mg); pale brown colour solid, $[\alpha]_D^{20}$ –35.5 (c 0.1, $CHCl_3$).

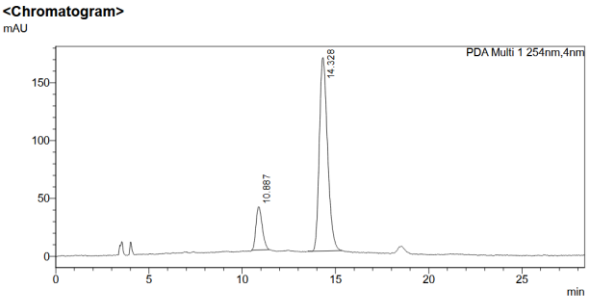


The enantiomeric ratio (15:85) was determined by Daicel Chiralpak IB (35 °C), Hexane/IPA = 85/15, 1.0 mL/min, λ = 254 nm, tR (minor) = 10.88 min, tR (major) = 14.32 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	10.831	3826044	49.883	56.525
2	14.302	3843950	50.117	43.475
Total		7669994	100.000	100.000

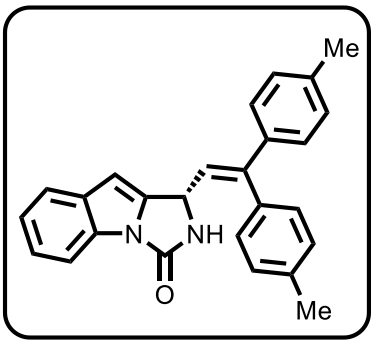


<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	10.887	874674	14.580	18.329
2	14.328	5124337	85.420	81.671
Total		5999010	100.000	100.000

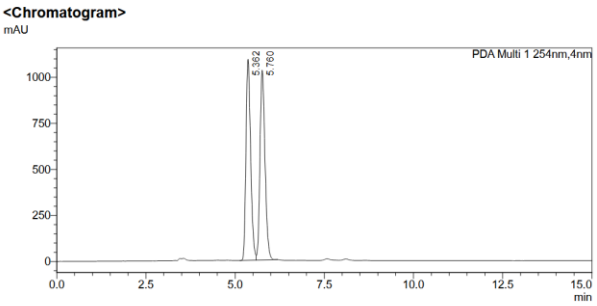
(*S*)-1-(2,2-di-*p*-tolylvinyl)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3o)

Yield: 76% (33 mg); brown colour solid; TLC: (25% EtOAc in hexanes, R_f): 0.3; $[\alpha]_D^{20}$ +225.3



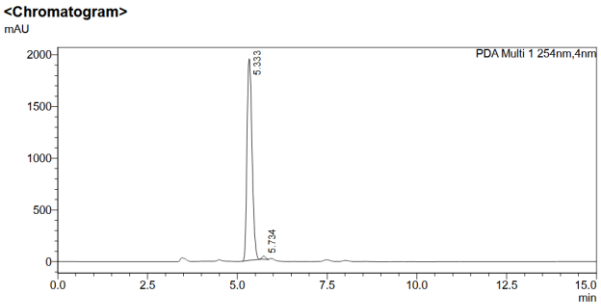
(c 0.1, $CHCl_3$); IR (ATR): ν(cm^{-1}) = 3683, 3459, 3019, 2925, 1739, 1214, 929, 743; ^{1}H NMR (500 MHz, $CDCl_3$, 24 °C): δ 7.90 (d, J = 7.8 Hz, 1H), 7.49 (d, J = 7.8 Hz, 1H), 7.22-7.12 (m, 6H), 7.06 (d, J = 7.6 Hz, 2H), 7.00 (d, J = 7.6 Hz, 2H), 6.32 (s, 1H), 5.87 (s, 1H), 5.83 (d, J = 9.4 Hz, 1H), 5.26 (d, J = 9.4 Hz, 1H), 2.32 (s, 3H), 2.24 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 24 °C): δ 152.9, 146.9, 140.6, 138.2, 138.0x2, 135.4, 133.5, 130.5, 129.6, 129.4, 129.0, 127.5, 123.2, 122.9, 122.6, 120.9, 112.6, 98.1, 52.1, 21.2, 21.1. HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{23}N_2O$ 379.1805; Found 379.1807.

The enantiomeric ratio (99:1) was determined by Daicel Chiralpak IB (35 ºC), Hexane/IPA = 85/15, 1.0 mL/min, λ = 254 nm, tR (major) = 5.33 min, tR (minor) = 5.73 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	5.362	9979206	49.751	51.473
2	5.760	10078967	50.249	48.527
Total		20058174	100.000	100.000

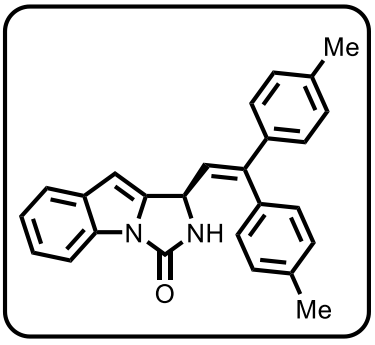


<Peak Table>
PDA Ch1 254nm

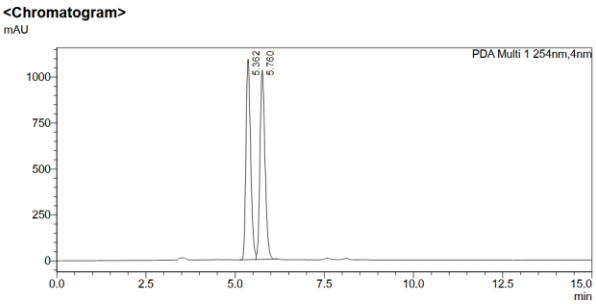
Peak#	Ret. Time	Area	Area%	Height%
1	5.333	19219213	98.916	98.463
2	5.734	210562	1.084	1.537
Total		19429775	100.000	100.000

(*R*)-1-(2,2-di-*p*-tolylvinyl)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3o)

Yield: 23% (75 mg); brown colour solid, $[\alpha]_D^{20}$ –155.6 (c 0.1, $CHCl_3$).

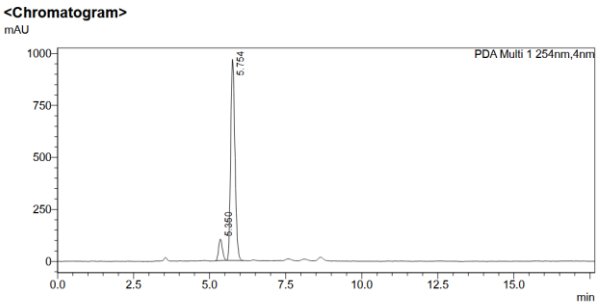


The enantiomeric ratio (9:91) was determined by Daicel Chiralpak IB (35 ºC), Hexane/IPA = 85/15, 1.0 mL/min, λ = 254 nm, tR (minor) = 5.53 min, tR (major) = 5.75 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	5.362	9979206	49.751	51.473
2	5.760	10078967	50.249	48.527
Total		20058174	100.000	100.000

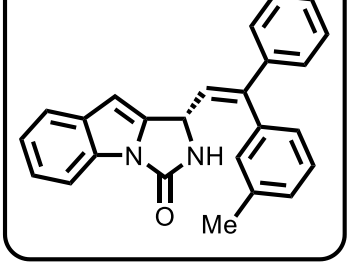


<Peak Table>
PDA Ch1 254nm

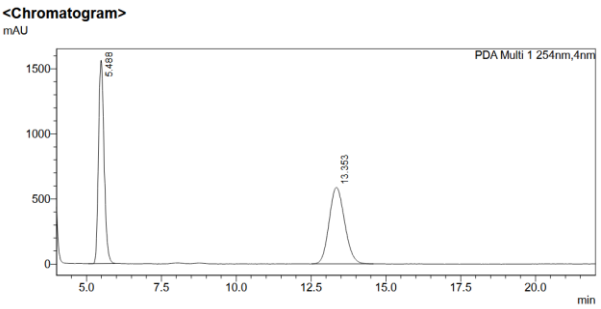
Peak#	Ret. Time	Area	Area%	Height%
1	5.350	890717	8.580	9.634
2	5.754	9490988	91.420	90.366
Total		10381705	100.000	100.000

(*S*)-1-(2,2-di-*m*-tolylvinyl)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3p)

Yield: 74% (32 mg); brown colour solid; TLC: (25% EtOAc in hexanes, R_f): 0.4; $[\alpha]_D^{20}$ +53.2 (c 0.1, $CHCl_3$); IR (ATR): ν(cm^{-1}) = 3680, 3455, 3258, 2923, 2855, 1733, 1451, 1215, 1198, 786; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.90 (d, J = 7.6 Hz, 1H), 7.49 (d, J = 7.5 Hz, 1H), 7.28-7.24 (m, 1H), 7.21-7.12 (m, 3H), 7.10-7.05 (m, 3H), 7.01-7.00 (m, 2H), 6.95-6.93 (m, 1H), 6.32 (s, 1H), 6.14 (br, 1H), 5.87 (d, J = 9.4 Hz, 1H), 5.24 (d, J = 9.4 Hz, 1H), 2.32 (s, 3H), 2.20 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 153.0, 147.2, 140.7, 140.5, 138.4, 138.3, 137.9, 133.5, 130.5, 130.2, 129.0, 128.9, 128.5, 128.2, 128.1, 126.7, 124.9, 123.8, 123.2, 122.6, 121.0, 112.6, 98.1, 52.1, 21.5, 21.4. HRMS (ESI/Q-TOF) m/z: [M + H]$^+$ Calcd for $C_{26}H_{23}N_2O$ 379.1805; Found 379.1812.

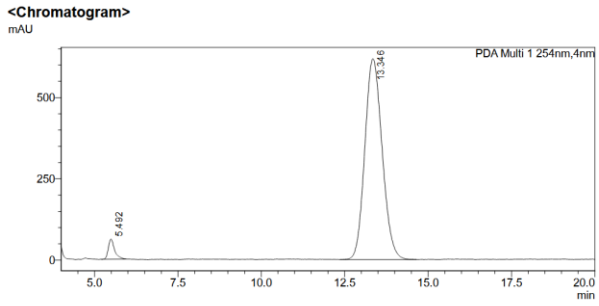


The enantiomeric ratio (96:4) was determined by Daicel Chiralpak IG (35 ºC), Hexane/IPA = 50/50, 1.0 mL/min, λ = 254 nm, tR (major) = 13.34 min, tR (minor) = 5.49 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	5.488	20300574	48.983	72.652
2	13.353	21143743	51.017	27.348
Total		41444317	100.000	100.000

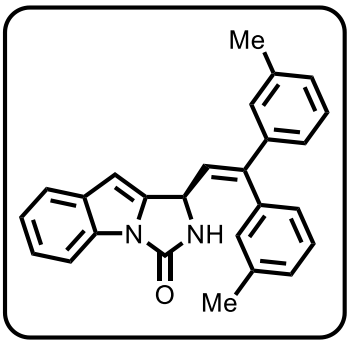


<Peak Table>
PDA Ch1 254nm

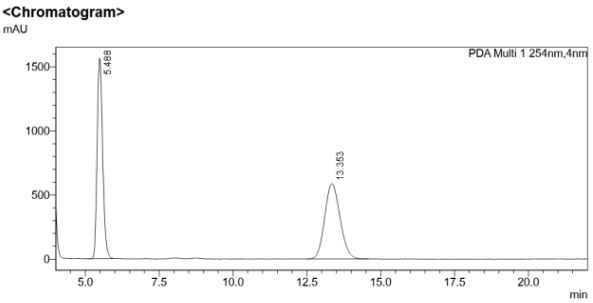
Peak#	Ret. Time	Area	Area%	Height%
1	5.492	816007	3.522	9.149
2	13.346	22350949	96.478	90.851
Total		23166956	100.000	100.000

(*R*)-1-(2,2-di-*m*-tolylvinyl)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3p)

Yield: 46% (14 mg); brown colour solid, $[\alpha]_D^{20}$ –192.0 (c 0.1, $CHCl_3$).

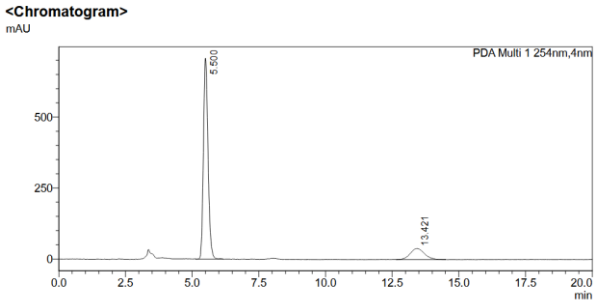


The enantiomeric ratio (14:86) was determined by Daicel Chiralpak IG (35 °C), Hexane/IPA = 50/50, 1.0 mL/min, λ = 254 nm, tR (minor) = 13.42 min, tR (major) = 5.50 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	5.488	20300574	48.983	72.652
2	13.353	21143743	51.017	27.348
Total		41444317	100.000	100.000

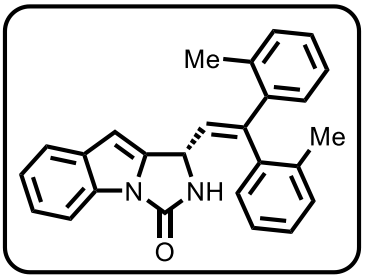


<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	5.500	8512452	85.805	94.804
2	13.421	1408250	14.195	5.196
Total		9920702	100.000	100.000

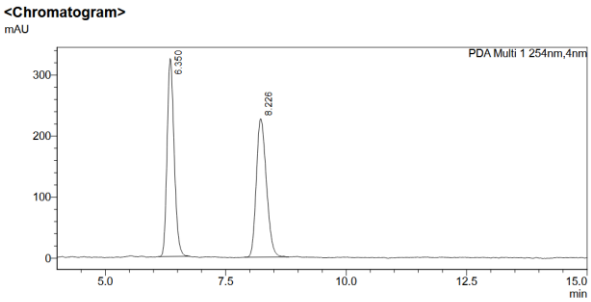
(*S*)-1-(2,2-di-*o*-tolylvinyl)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3q)

Yield: 82% (36 mg); brown colour solid; TLC: (25% EtOAc in hexanes, R_f): 0.4; $[\alpha]_D^{20}$ +89.3



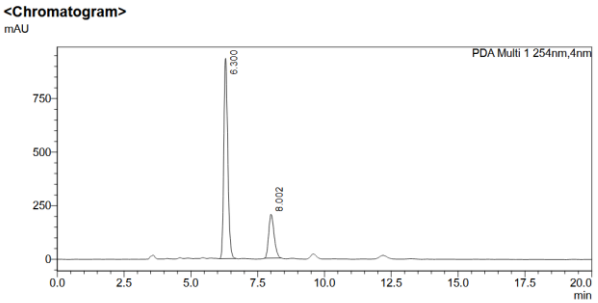
(c 0.1, $CHCl_3$); IR (ATR): ν(cm^{-1}) = 3682, 3458, 3247, 3018, 2925, 2855, 1735, 1215, 747; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.90 (d, J = 7.5 Hz, 1H), 7.50 (d, J = 7.5 Hz, 1H), 7.24-7.19 (m, 4H), 7.17-7.14 (m, 2H), 7.09-7.08 (m, 2H), 7.04-6.98 (m, 2H), 6.32 (s, 1H), 5.78 (s, 1H), 5.65 (d, J = 9.5 Hz, 1H), 5.21 (d, J = 9.5 Hz, 1H), 2.24 (s, 3H), 2.12 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 152.8, 146.4, 140.1, 140.0, 138.3, 136.1, 135.4, 133.4, 131.1, 130.9, 130.5, 130.3, 129.6, 128.4, 128.2, 127.7, 125.9, 125.7, 123.2, 122.7, 121.0, 112.6, 98.0, 52.1, 21.0, 20.1. HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{23}N_2O$ 379.1805; Found 379.1806.

The enantiomeric ratio (76:24) was determined by Daicel Chiralpak IB (35 °C), Hexane/IPA = 85/15, 1.0 mL/min, λ = 254 nm, tR (major) = 6.30 min, tR (minor) = 8.00 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	6.350	3321176	50.117	58.848
2	8.226	3305620	49.883	41.152
Total		6626795	100.000	100.000

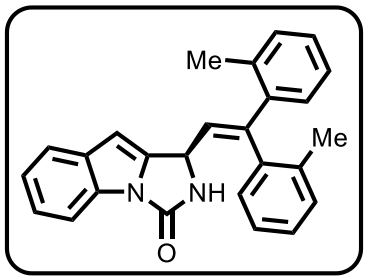


<Peak Table>
PDA Ch1 254nm

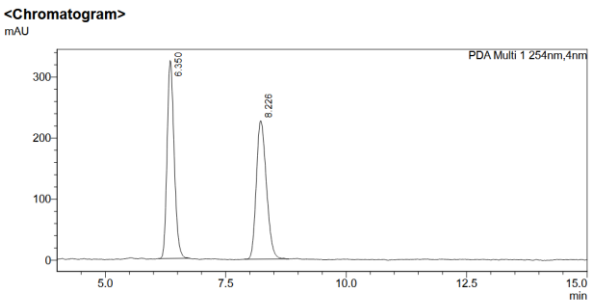
Peak#	Ret. Time	Area	Area%	Height%
1	6.300	9630236	76.760	82.000
2	8.002	2915748	23.240	18.000
Total		12545984	100.000	100.000

(*R*)-1-(2,2-di-*o*-tolylvinyl)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3q)

Yield: 68% (20 mg); brown colour solid, $[\alpha]_D^{20}$ –19.5 (c 0.1, $CHCl_3$).

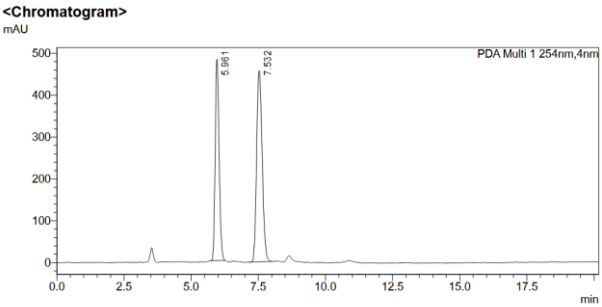


The enantiomeric ratio (43:57) was determined by Daicel Chiralpak IB (35 ºC), Hexane/IPA = 85/15, 1.0 mL/min, λ = 254 nm, tR (minor) = 5.96 min, tR (major) = 7.53 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	6.350	3321176	50.117	58.848
2	8.226	3305620	49.883	41.152
Total		6626795	100.000	100.000

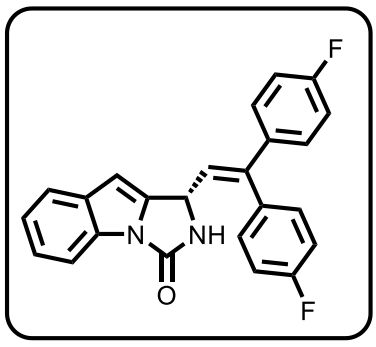


<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	5.961	4843345	42.455	51.308
2	7.532	6564891	57.545	48.692
Total		11408236	100.000	100.000

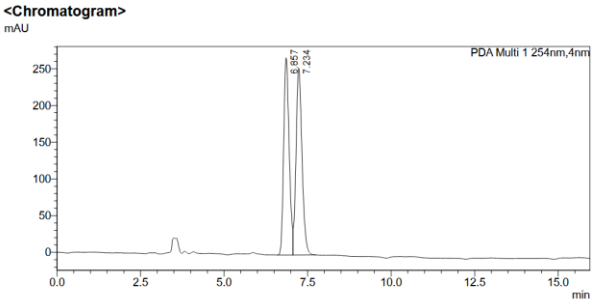
(*S*)-1-(2,2-bis(4-fluorophenyl)vinyl)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3r)

Yield: 50% (22 mg); sandal colour solid; TLC: (25% EtOAc in hexanes, R_f): 0.4; $[\alpha]_D^{20}$ +248.3 (c 0.1, $CHCl_3$); IR (ATR): ν(cm^{-1}) = 3683, 3458, 3019, 1743, 1603, 1214, 748; ^1H NMR (500 MHz, $CDCl_3$, 24 °C): δ 7.89 (d, J = 8.0 Hz, 1H), 7.49 (d, J = 7.8 Hz, 1H), 7.24-7.20 (m, 3H), 7.18-7.15 (m, 1H), 7.13-7.07 (m, 4H), 6.89 (t, J = 8.2 Hz, 2H), 6.32 (s, 1H), 6.29 (s, 1H), 5.85 (d, J = 9.5 Hz, 1H), 5.21 (d, J = 9.5 Hz, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 24 °C): δ 162.8



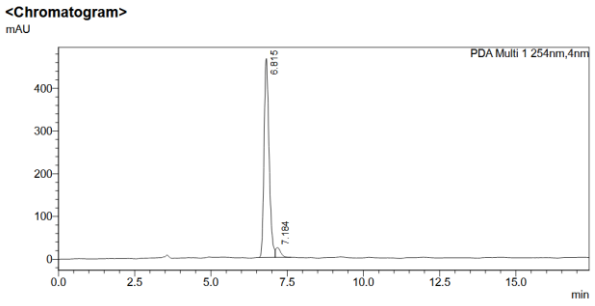
(d, J = 248.8 Hz), 162.6 (d, J = 248.8 Hz), 153.1, 144.9, 140.0, 136.6 (d, J = 3.4 Hz), 133.9 (d, J = 3.4 Hz), 133.4, 131.4 (d, J = 8.4 Hz), 130.5, 129.3 (d, J = 8.4 Hz), 124.3, 123.4, 122.8, 121.0, 115.9 (d, J = 21.7 Hz), 115.4 (d, J = 21.7 Hz), 112.5, 98.3, 51.9. ^{19}F NMR (470 MHz, $CDCl_3$, 24˚C): δ –112.80, –113.17. HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{17}F_2N_2O$ 387.1303; Found 387.1305.

The enantiomeric ratio (95:5) was determined by Daicel Chiralpak IB (35 ºC), Hexane/IPA = 85/15, 1.0 mL/min, λ = 254 nm, tR (major) = 6.81 min, tR (minor) = 7.18 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	6.857	3075564	49.288	51.334
2	7.234	3164378	50.712	48.666
Total		6239942	100.000	100.000

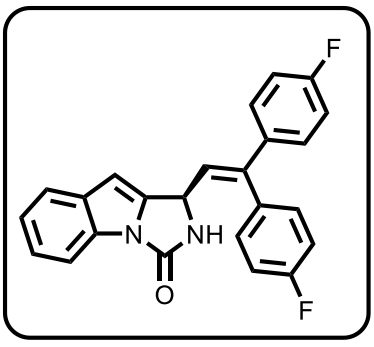


<Peak Table>
PDA Ch1 254nm

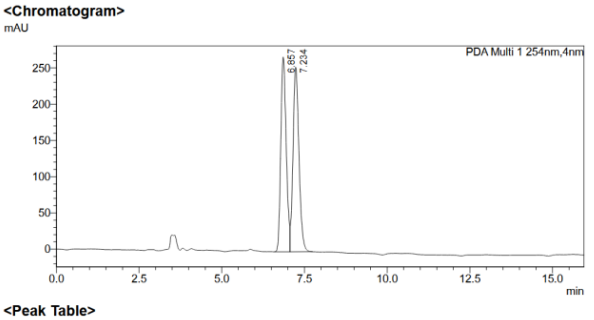
Peak#	Ret. Time	Area	Area%	Height%
1	6.815	5339400	95.369	95.335
2	7.184	259300	4.631	4.665
Total		5598700	100.000	100.000

(*R*)-1-(2,2-bis(4-fluorophenyl)vinyl)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3r)

Yield: 72% (21 mg); sandal colour solid, $[\alpha]_D^{20}$ –208.8 (c 0.1, $CHCl_3$).

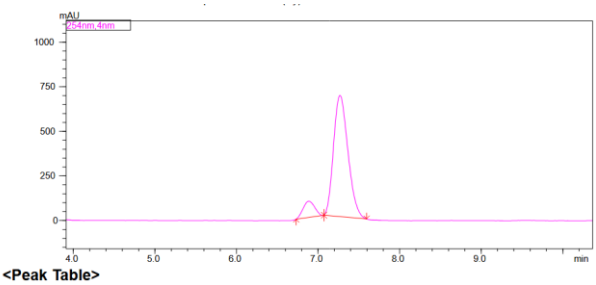


The enantiomeric ratio (10:90) was determined by Daicel Chiralpak IB (35 ºC), Hexane/IPA = 85/15, 1.0 mL/min, λ = 254 nm, tR (minor) = 6.88 min, tR (major) = 7.26 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	6.857	3075564	49.288	51.334
2	7.234	3164378	50.712	48.666
Total		6239942	100.000	100.000

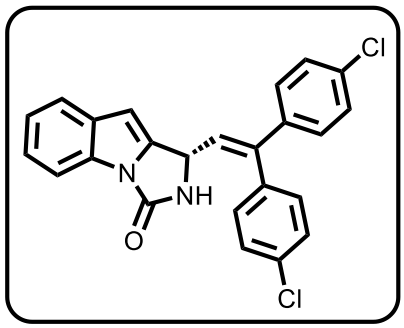


<Peak Table>
PDA Ch1 254nm

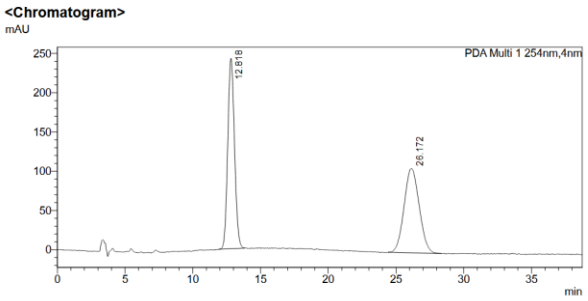
Peak#	Ret. Time	Area	Area%	Height%
1	6.887	890152	9.649	11.718
2	7.268	8335294	90.351	88.282
Total		9225446	100.000	100.000

(*S*)-1-(2,2-bis(4-chlorophenyl)vinyl)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3s)

Yield: 47% (23 mg); sandal colour solid; TLC: (25% EtOAc in hexanes, R_f): 0.4; $[\alpha]_D^{20}$ + 208.8 (c 0.1, $CHCl_3$); IR (ATR): ν(cm^{-1}) = 3657, 3455, 3242, 3020, 1737, 1452, 1214, 1092, 747; ^1H NMR (500 MHz, $CDCl_3$, 24 °C): δ 7.90 (d, J = 8.0 Hz, 1H), 7.50 (d, J = 7.7 Hz, 1H), 7.40-7.37 (m, 2H), 7.25-7.21 (m, 1H), 7.20-7.16 (m, 5H), 7.09-7.06 (m, 2H), 6.34-6.33 (m, 1H), 6.07 (s, 1H), 5.91 (d, J = 9.4 Hz, 1H), 5.22 (d, J = 9.4 Hz, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 24 °C): δ 152.9, 144.6, 139.6, 138.6, 136.1, 134.6, 134.5, 133.4, 131.0, 130.5, 129.2, 128.8, 128.6, 125.0, 123.5, 122.8, 121.0, 112.6, 98.4, 51.8. HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{17}Cl_2N_2O$ 419.0721; Found 419.0717.

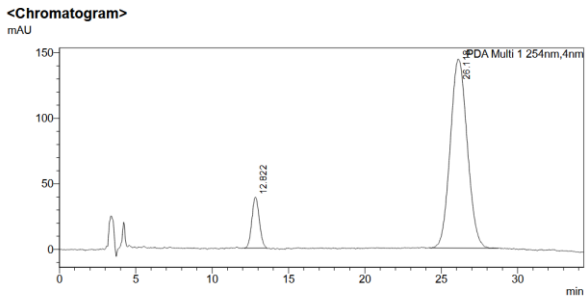


The enantiomeric ratio (90:10) was determined by Daicel Chiralpak IG (35 ºC), Hexane/IPA = 55/45, 1.0 mL/min, λ = 254 nm, tR (major) = 26.11 min, tR (minor) = 12.82 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	12.818	8362934	50.092	69.338
2	26.172	8332344	49.908	30.662
Total		16695278	100.000	100.000

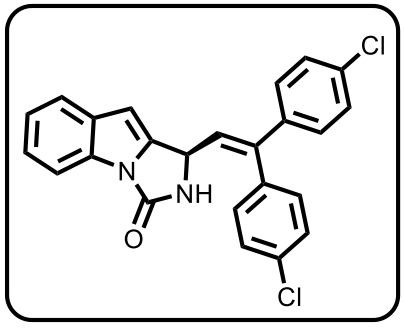


<Peak Table>
PDA Ch1 254nm

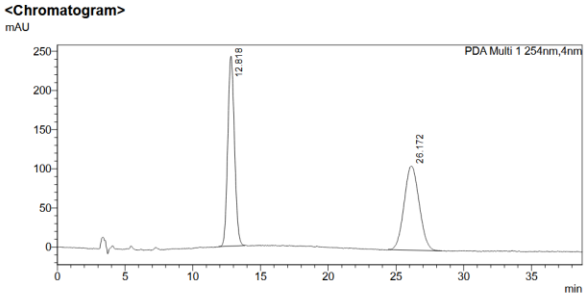
Peak#	Ret. Time	Area	Area%	Height%
1	12.822	1318047	10.560	21.243
2	26.118	11162898	89.440	78.757
Total		12480945	100.000	100.000

(*R*)-1-(2,2-bis(4-chlorophenyl)vinyl)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3s)

Yield: 62% (20 mg); sandal colour solid, $[\alpha]_D^{20}$ –214.1 (c 0.1, $CHCl_3$).

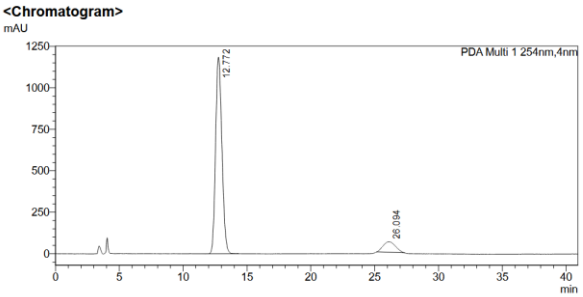


The enantiomeric ratio (10:90) was determined by Daicel Chiralpak IG (35 ºC), Hexane/IPA = 55/45, 1.0 mL/min, λ = 254 nm, tR (minor) = 12.77 min, tR (major) = 26.09 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	12.818	8362934	50.092	69.338
2	26.172	8332344	49.908	30.662
Total		16695278	100.000	100.000

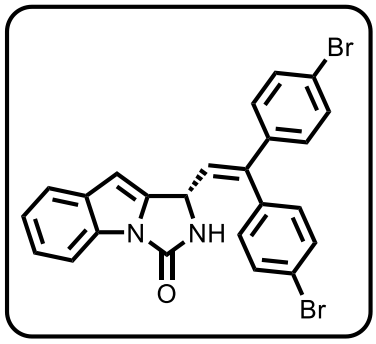


<Peak Table>
PDA Ch1 254nm

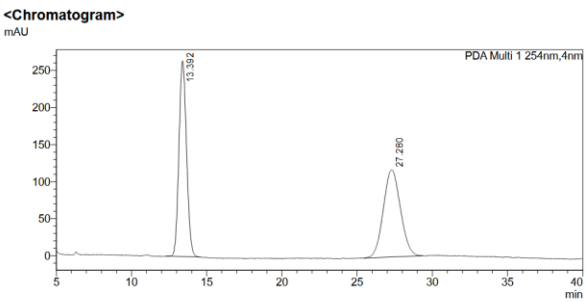
Peak#	Ret. Time	Area	Area%	Height%
1	12.772	40897232	90.535	94.890
2	26.094	4275843	9.465	5.110
Total		45173074	100.000	100.000

(*S*)-1-(2,2-bis(4-bromophenyl)vinyl)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3t)

Yield: 50% (29 mg); pale brown colour solid; TLC: (25% EtOAc in hexanes, R_f): 0.3; $[\alpha]_D^{20}$ +184.3 (c 0.1, $CHCl_3$); IR (ATR): ν(cm^{-1}) = 3680, 3451, 3022, 1732, 1452, 1014, 930; ^{1}H NMR (400 MHz, DMSO-d_6, 24 °C): δ 8.67 (s, 1H), 7.83 (d, J = 7.9 Hz, 1H), 7.61-7.57 (m, 3H), 7.40-7.38 (m, 4H), 7.28-7.20 (m, 4H), 6.55 (s, 1H), 6.16 (d, J = 9.5 Hz, 1H), 5.12 (d, J = 9.5 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, 24 °C): δ 152.6, 142.8, 140.8, 139.3, 136.8, 133.6, 133.5, 133.3, 131.9, 130.2, 129.4, 129.3, 128.9, 126.7, 123.1, 122.6, 121.5, 112.0, 97.8, 51.8. HRMS (ESI/Q-TOF) m/z: [M + H]$^+$ Calcd for $C_{24}H_{17}Br_2N_2O$ 506.9702; Found 506.9712.

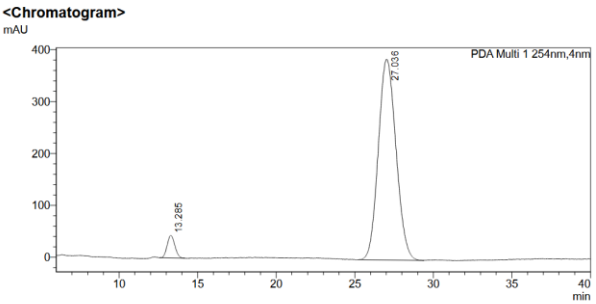


The enantiomeric ratio (95:5) was determined by Daicel Chiralpak IG (35 ºC), Hexane/IPA = 60/40, 1.0 mL/min, λ = 254 nm, tR (major) = 27.03 min, tR (minor) = 13.28 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	13.392	9275715	49.948	69.175
2	27.280	9294903	50.052	30.825
Total		18570618	100.000	100.000

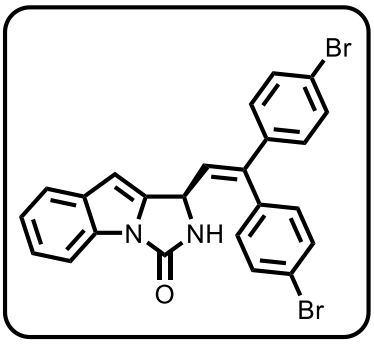


<Peak Table>
PDA Ch1 254nm

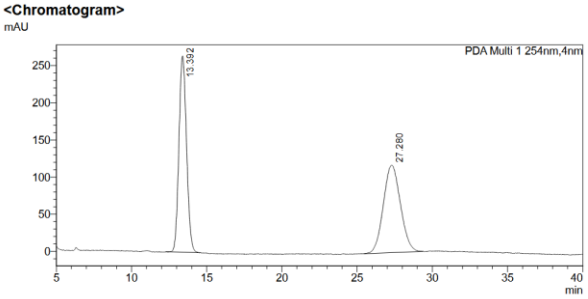
Peak#	Ret. Time	Area	Area%	Height%
1	13.285	1461489	4.593	10.070
2	27.036	30357063	95.407	89.930
Total		31818552	100.000	100.000

(*R*)-1-(2,2-bis(4-bromophenyl)vinyl)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3t)

Yield: 70% (70 mg); pale brown colour solid, $[\alpha]_D^{20}$ –122.4 (c 0.1, $CHCl_3$).

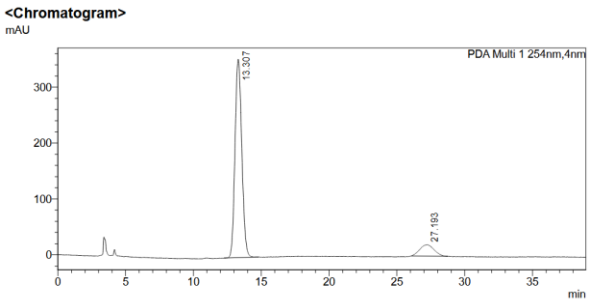


The enantiomeric ratio (11:89) was determined by Daicel Chiralpak IG (35 °C), Hexane/IPA = 60/40, 1.0 mL/min, λ = 254 nm, tR (minor) = 27.19 min, tR (major) = 13.30 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	13.392	9275715	49.948	69.175
2	27.280	9294903	50.052	30.825
Total		18570618	100.000	100.000

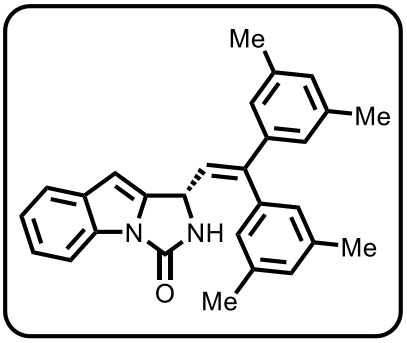


<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	13.307	12364014	89.241	94.595
2	27.193	1490655	10.759	5.405
Total		13854669	100.000	100.000

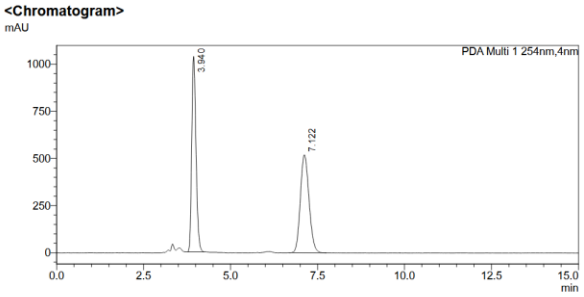
(*S*)-1-(2,2-bis(3,5-dimethylphenyl)vinyl)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3u)

Yield: 50% (24 mg); brown colour solid; TLC: (25% EtOAc in hexanes, R_f): 0.4; $[\alpha]_D^{20}$ +112.4



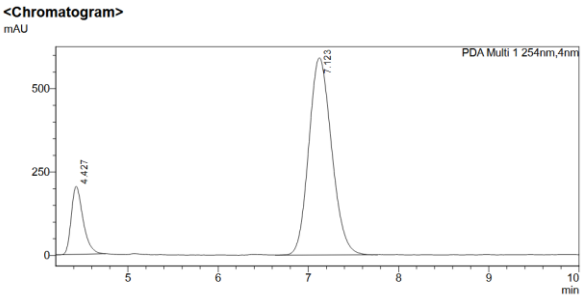
(c 0.1, $CHCl_3$); IR (ATR): ν(cm^{-1}) = 3683, 3459, 3018, 2925, 1737, 1599, 1214, 745, 665; ^{1}H NMR (500 MHz, $CDCl_3$, 24 °C): δ 7.90 (d, J = 7.9 Hz, 1H), 7.50 (d, J = 7.9 Hz, 1H), 7.22-7.19 (m, 1H), 7.16-7.14 (m, 1H), 6.95 (s, 1H), 6.84 (s, 3H), 6.79 (s, 2H), 6.33 (s, 1H), 5.85-5.83 (m, 2H), 5.25 (d, J = 9.4 Hz, 1H), 2.29 (s, 6H), 2.17 (s, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 24 °C): δ 152.9, 147.6, 140.8, 140.7, 138.3, 138.2, 137.8, 133.5, 130.5, 129.9, 129.7, 127.3, 125.4, 123.5, 123.1, 122.6, 120.9, 112.6, 98.0, 52.1, 21.4, 21.2. HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd for $C_{28}H_{27}N_2O$ 407.2118; Found 407.2122.

The enantiomeric ratio (85:15) was determined by Daicel Chiralpak IG (35 °C), Hexane/IPA = 65/35, 1.0 mL/min, λ = 254 nm, tR (major) = 7.12 min, tR (minor) = 4.42 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	3.940	8847971	49.584	66.661
2	7.122	8996439	50.416	33.339
Total		17844410	100.000	100.000

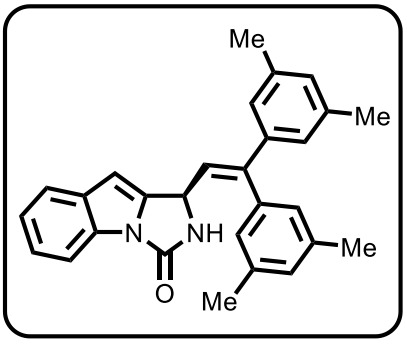


<Peak Table>
PDA Ch1 254nm

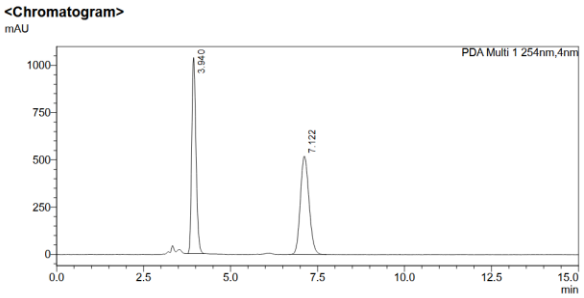
Peak#	Ret. Time	Area	Area%	Height%
1	4.427	1856514	15.155	25.689
2	7.123	10393896	84.845	74.311
Total		12250410	100.000	100.000

(*R*)-1-(2,2-bis(3,5-dimethylphenyl)vinyl)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3u)

Yield: 41% (17 mg); brown colour solid, $[\alpha]_D^{20}$ –76.4 (c 0.1, $CHCl_3$).

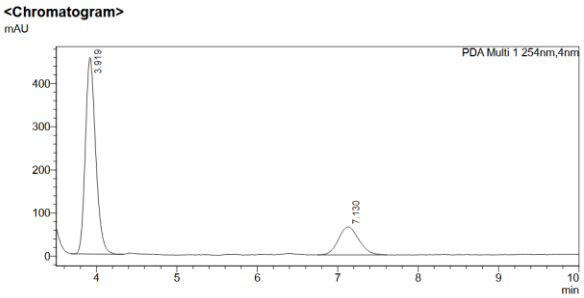


The enantiomeric ratio (22:78) was determined by Daicel Chiralpak IG (35 ºC), Hexane/IPA = 65/35, 1.0 mL/min, λ = 254 nm, tR (minor) = 7.13 min, tR (major) = 3.91 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	3.940	8847971	49.584	66.661
2	7.122	8996439	50.416	33.339
Total		17844410	100.000	100.000

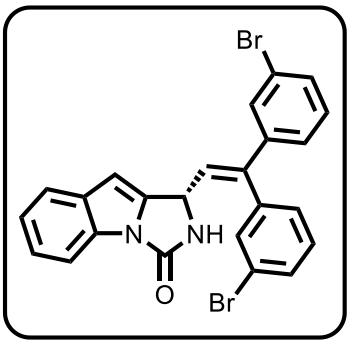


<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	3.919	4063485	78.020	87.566
2	7.130	1144781	21.980	12.434
Total		5208266	100.000	100.000

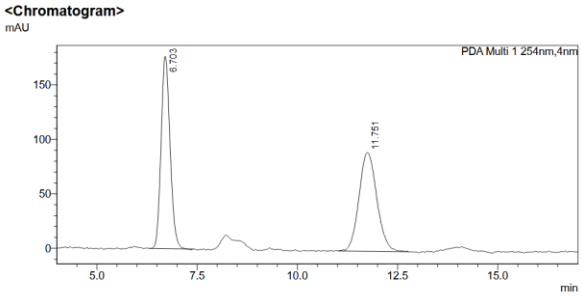
(*S*)-1-(2,2-bis(3-bromophenyl)vinyl)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3v)

Yield: 44% (27 mg); brown colour solid; TLC: (25% EtOAc in hexanes, R_f): 0.3; $[\alpha]_D^{20}$ +136.8



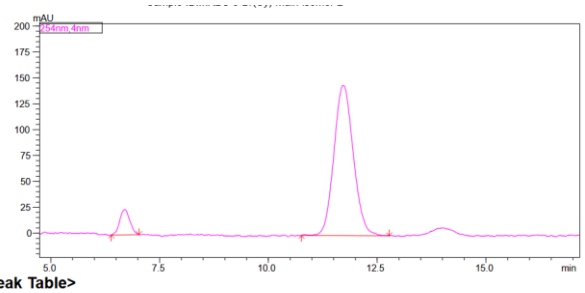
(c 0.1, $CHCl_3$); IR (ATR): ν(cm^{-1}) = 3683, 3459, 3019, 2925, 1723, 1631, 1214, 744; ^{1}H NMR (500 MHz, DMSO-d_6, 24 °C): δ 8.65 (s, 1H), 7.83 (d, J = 8.3 Hz,1H), 7.68 (d, J = 8.3 Hz, 1H), 7.61 (d, J = 8.3 Hz, 1H), 7.58 (s, 1H), 7.52-7.49 (m, 2H), 7.44 (s, 1H), 7.41 (d, J = 7.5 Hz, 1H), 7.32-7.25 (m, 2H), 7.22-7.19 (m 2H), 6.55 (s, 1H), 6.25 (d, J = 9.6 Hz, 1H), 5.09 (d, J = 9.6 Hz, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, DMSO-d_6, 24 °C): δ 153.4, 143.5, 143.0, 141.5, 141.0, 134.5, 133.2, 132.5, 132.3, 132.2, 132.0, 131.0, 130.8, 130.1, 128.7, 127.6, 124.0, 123.47, 123.45, 123.3, 122.4, 112.9, 98.6, 52.5. HRMS (ESI/Q-TOF) m/z: [M + H]$^+$ Calcd for $C_{24}H_{17}Br_2N_2O$ 506.9702; Found 506.9659.

The enantiomeric ratio (92:8) was determined by Daicel Chiralpak IG (35 °C), Hexane/IPA = 50/50, 1.0 mL/min, λ = 254 nm, tR (major) = 11.72 min, tR (minor) = 6.70 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	6.703	2768388	49.592	66.066
2	11.751	2813911	50.408	33.934
Total		5582299	100.000	100.000

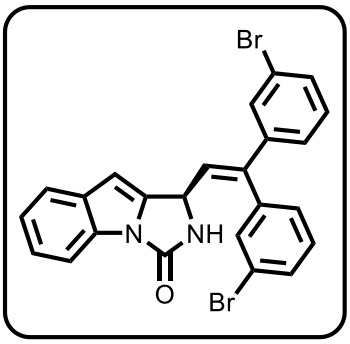


<Peak Table>
PDA Ch1 254nm

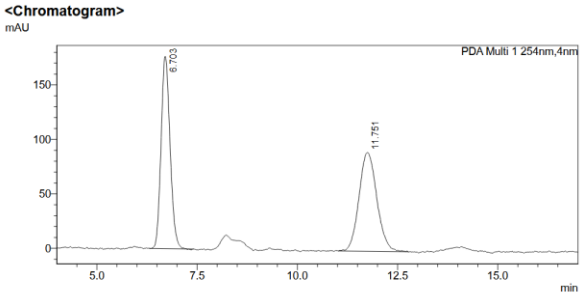
Peak#	Ret. Time	Area	Area%	Height%
1	6.702	394396	8.034	14.491
2	11.720	4514707	91.966	85.509
Total		4909104	100.000	100.000

(*R*)-1-(2,2-bis(3-bromophenyl)vinyl)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3v)

Yield: 48% (18 mg); pale brown colour solid, $[\alpha]_D^{20}$ –72.4 (c 0.1, $CHCl_3$).

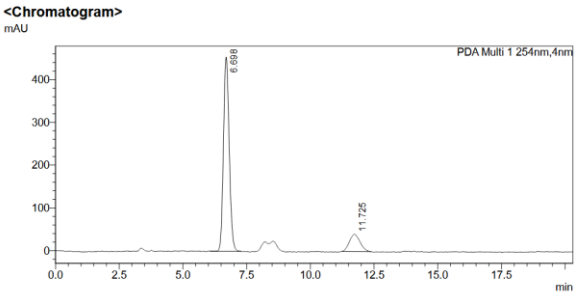


The enantiomeric ratio (14:86) was determined by Daicel Chiralpak IG (35 °C), Hexane/IPA = 50/50, 1.0 mL/min, λ = 254 nm, tR (minor) = 11.72 min, tR (major) = 6.69 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	6.703	2768388	49.592	66.066
2	11.751	2813911	50.408	33.934
Total		5582299	100.000	100.000

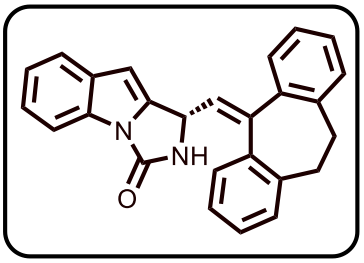


<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	6.698	7130504	85.959	91.774
2	11.725	1164781	14.041	8.226
Total		8295285	100.000	100.000

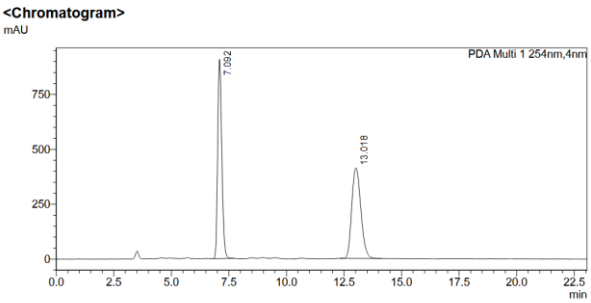
(*S*)-1-((10,11-dihydro-5H-dibenzo[a,d][7]annulen-5-ylidene)methyl)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3w)

Yield: 85% (37 mg); brown colour solid; TLC: (25% EtOAc in hexanes, R_f): 0.4; $[\alpha]_D^{20}$ +



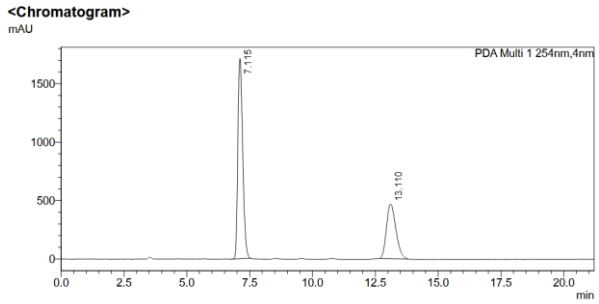
31.1 (c 0.1, $CHCl_3$); IR (ATR): ν(cm^{-1}) = 3684, 3459, 3261, 3019, 2925, 1736, 1453, 1215, 749; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.92-7.88 (m, 1H), 7.58-7.56 (m, 0.6 H, 7.44-7.42 (m, 0.5 H), 7.21-7.15 (m, 7H), 7.11-6.98 (m, 3H), 6.53 (s, 0.5 H), 6.30 (s, 0.3 H), 6.08 (s, 0.4 H), 5.76-5.71 (m, 1.4 H), 5.32-5.24 (m, 1H), 3.44-3.27 (m, 2H), 2.97-2.78 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 153.3, 152.8, 148.9, 148.1, 140.3, 139.4, 139.2, 138.3, 137.2, 133.5, 130.6, 130.3, 128.6, 128.4, 128.3, 128.0, 127.3, 126.4, 126.3, 126.1, 123.3, 123.2, 122.7, 122.6, 121.0, 112.6, 98.1, 97.9, 51.9, 51.6, 33.6, 31.1. HRMS (ESI/Q-TOF) m/z: [M + H]$^+$ Calcd for $C_{26}H_{21}N_2O$ 377.1648; Found 377.1654.

The enantiomeric ratio (65:35) was determined by Daicel Chiralpak IB (35 ºC), Hexane/IPA = 85/15, 1.0 mL/min, λ = 254 nm, tR (major) = 7.11 min, tR (minor) = 13.11 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	7.092	11310885	49.967	68.757
2	13.018	11325881	50.033	31.243
Total		22636766	100.000	100.000

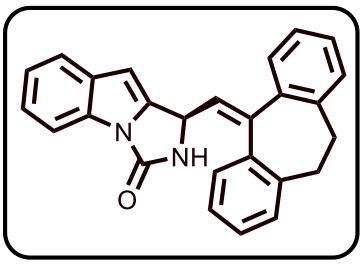


<Peak Table>
PDA Ch1 254nm

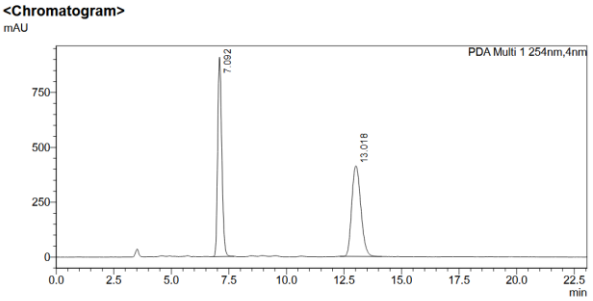
Peak#	Ret. Time	Area	Area%	Height%
1	7.115	23052592	65.485	78.546
2	13.110	12150449	34.515	21.454
Total		35203041	100.000	100.000

(*R*)-1-((10,11-dihydro-5H-dibenzo[a,d][7]annulen-5-ylidene)methyl)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3w)

Yield: 68% (20 mg); brown colour solid, $[\alpha]_D^{20}$ –67.6 (c 0.1, $CHCl_3$).

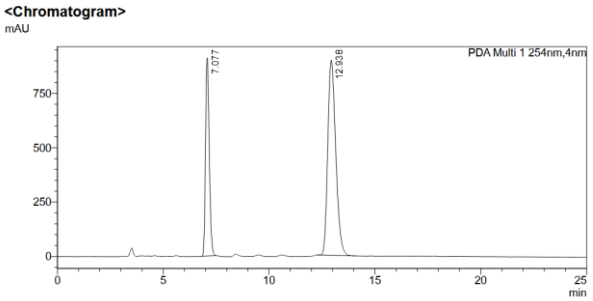


The enantiomeric ratio (33:67) was determined by Daicel Chiralpak IB (35 ºC), Hexane/IPA = 85/15, 1.0 mL/min, λ = 254 nm, tR (minor) = 7.07 min, tR (major) = 12.93 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	7.092	11310885	49.967	68.757
2	13.018	11325881	50.033	31.243
Total		22636766	100.000	100.000

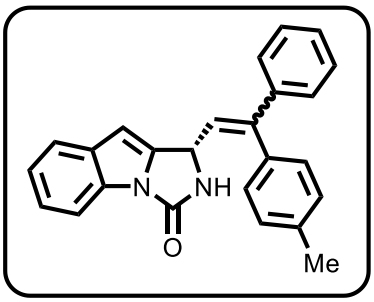


<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	7.077	11205628	32.260	50.389
2	12.938	23529496	67.740	49.611
Total		34735124	100.000	100.000

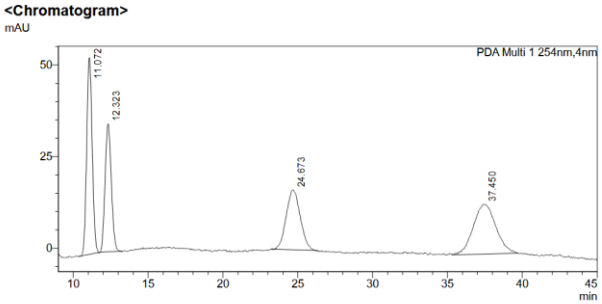
(*S*)-1-(2-phenyl-2-(*p*-tolyl)vinyl)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3x)

Yield: 78% (33 mg); brown colour semisolid; TLC: (25% EtOAc in hexanes, R_f): 0.4; $[\alpha]_D^{20}$ +194.7 (c 0.1, $CHCl_3$); IR (ATR): ν(cm^{-1}) = 3681, 3452, 3261, 3019, 2925, 1738, 1453, 1215, 744; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.90 (d, J = 7.9 Hz, 1H), 7.48 (d, J = 7.9 Hz, 1H), 7.39-7.31 (m, 2H), 7.25-7.23 (m, 1H), 7.19-7.14 (m, 6H), 7.06-6.98 (m, 2H), 6.31 (s, 1H), 6.17-6.13 (br, 1H), 5.86 (d, J = 9.4 Hz, 1H), 5.24 (m, 1H), 2.31 (s, 1.59 H), 2.23 (s, 1.43 H).



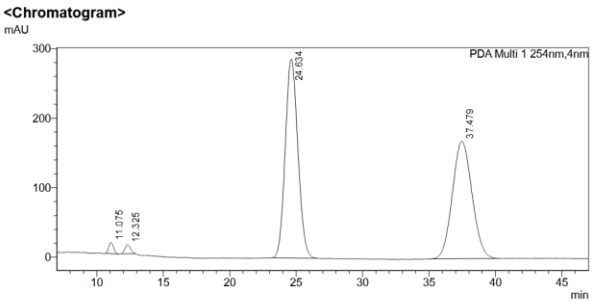
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 153.0, 147.0, 146.8, 140.8, 140.5, 138.4, 138.3, 138.1, 137.8, 135.3, 133.5, 130.5, 129.7, 129.6, 129.4, 129.0, 128.7, 128.3, 128.2, 128.1, 127.6, 127.5, 123.9, 123.2, 123.1, 122.6, 121.0, 112.6, 98.1, 52.1, 21.2, 21.1. HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{21}N_2O$ 365.1648; Found 365.1650.

The enantiomeric ratio (98:2) was determined by Daicel Chiralpak IG (35 ºC), Hexane/IPA = 60/40, 1.0 mL/min, λ = 254 nm, tR (major) = 24.63, 37.47 min, tR (minor) = 11.07, 12.32 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	11.072	1375058	28.168	45.269
2	12.323	1014171	20.775	29.445
3	24.673	1064550	21.807	13.788
4	37.450	1427920	29.250	11.497
Total		4881700	100.000	100.000

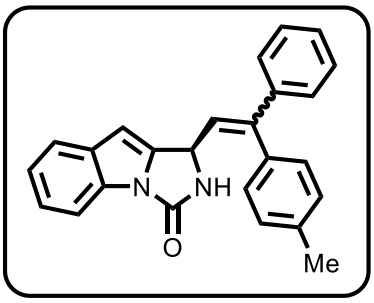


<Peak Table>
PDA Ch1 254nm

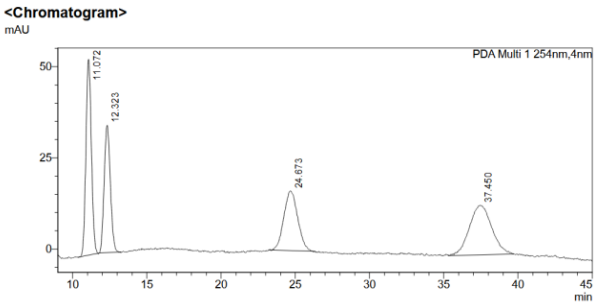
Peak#	Ret. Time	Area	Area%	Height%
1	11.075	398719	1.076	3.294
2	12.325	364051	0.982	2.597
3	24.634	18901868	51.002	59.163
4	37.479	17396699	46.940	34.946
Total		37061337	100.000	100.000

(*R*)-1-(2-phenyl-2-(*p*-tolyl)vinyl)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3x)

Yield: 78% (22 mg); brown colour semisolid, $[\alpha]_D^{20}$ –186.9 (c 0.1, $CHCl_3$).

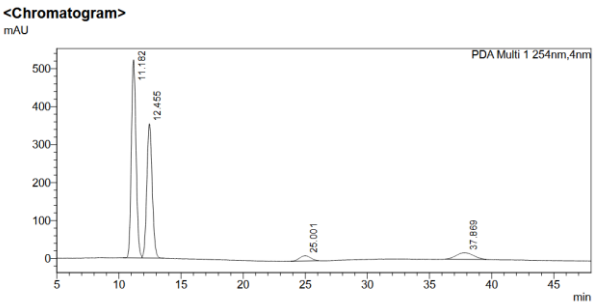


The enantiomeric ratio (13.5:86.5) was determined by Daicel Chiralpak IG (35 ºC), Hexane/IPA = 60/40, 1.0 mL/min, λ = 254 nm, tR (minor) = 25.00, 37.86 min, tR (major) = 11.18, 12.45 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	11.072	1375058	28.168	45.269
2	12.323	1014171	20.775	29.445
3	24.673	1064550	21.807	13.788
4	37.450	1427920	29.250	11.497
Total		4881700	100.000	100.000

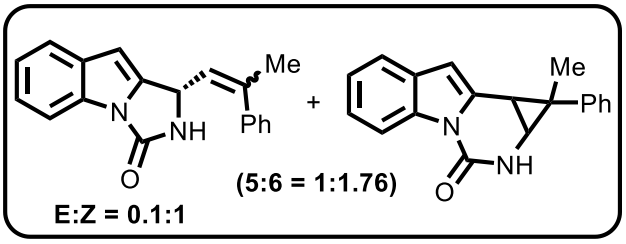


<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	11.182	13720550	50.996	57.558
2	12.455	10688224	39.726	39.013
3	25.001	859300	3.194	1.534
4	37.869	1637120	6.085	1.894
Total		26905194	100.000	100.000

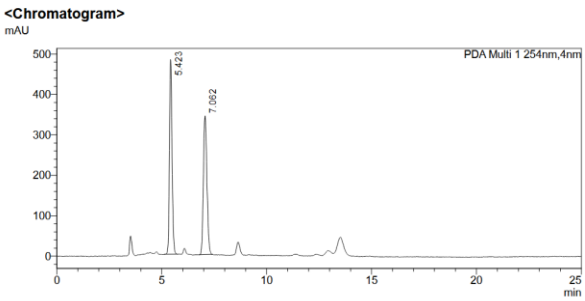
(*S*)-1-(2-phenylprop-1-en-1-yl)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3y)

Yield: 80% (27 mg); ^{1}H NMR (500 MHz, DMSO-d_6, 24 °C): δ 8.55 (s, 2.7 H), 8.28 (d, J = 8.2 Hz, 1.6 H),7.78 (d, J = 8.2 Hz, 1H), 7.57 (d, J = 8.2 Hz, 1.3 H), 7.51 (d, J = 7.5 Hz, 2H), 7.45-7.39 (m, 4.5 H), 7.36-7.32 (m, 8.7 H), 7.23-7.15 (m, 8H), 6.70 (s, 1.6 H), 6.45 (s,



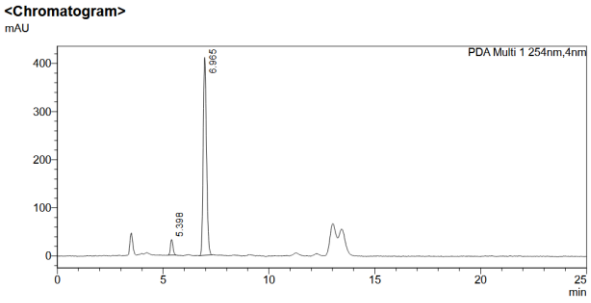
1H), 5.80-5.78 (m, 0.1H), 5.75-5.72 (m, 0.1H), 5.43 (d, J = 9.2 Hz, 1H), 5.07 (d, J = 9.2 Hz, 1H) 3.44-3.42 (m, 2.1 H), 2.94 (d, J = 8.6 Hz, 1.7 H), 2.26 (s, 0.3 H), 2.08 (s, 3H), 1.06 (s, 5.2 H). $^{13}C\{^{1}H\}$ NMR (125 MHz, DMSO-d_6, 24 °C): δ. 152.6, 149.3, 144.1, 141.9, 141.7, 140.2, 134.8, 133.6, 130.1, 129.5, 129.05, 129.01, 128.2, 128.1, 126.8, 126.7, 126.0, 124.2, 123.5, 123.0, 122.9, 122.5, 121.5, 120.1, 115.6, 112.0, 106.0, 51.6, 27.5, 25.5, 21.2, 13.7.

The enantiomeric ratio (94:6) was determined by Daicel Chiralpak IB (35 ºC), Hexane/IPA = 85/15, 1.0 mL/min, λ = 254 nm, tR (major) = 6.96, 37.47 min, tR (minor) = 5.39, 12.32 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	5.423	4128303	50.508	58.394
2	7.062	4045225	49.492	41.606
Total		8173528	100.000	100.000

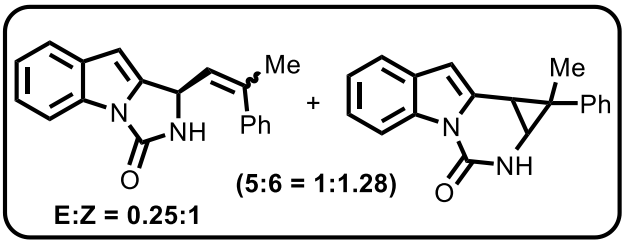


<Peak Table>
PDA Ch1 254nm

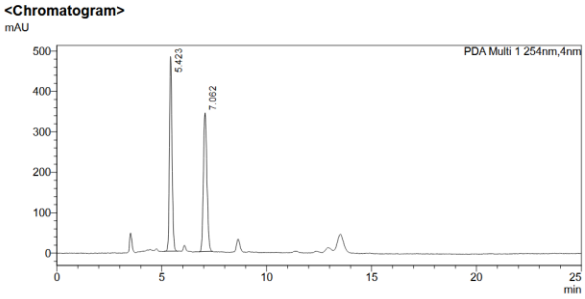
Peak#	Ret. Time	Area	Area%	Height%
1	5.398	270835	5.702	7.320
2	6.965	4479274	94.298	92.680
Total		4750109	100.000	100.000

(*R*)-1-(2-phenylprop-1-en-1-yl)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3y)

Yield: 82% (19 mg)

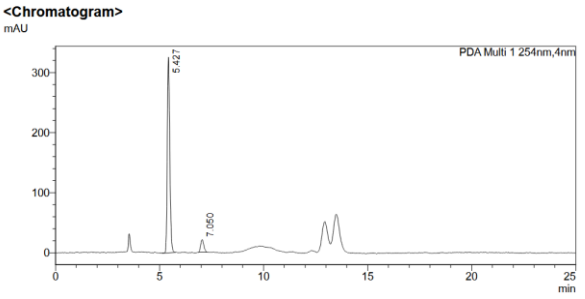


The enantiomeric ratio (8:92) was determined by Daicel Chiralpak IB (35 ºC), Hexane/IPA = 85/15, 1.0 mL/min, λ = 254 nm, tR (minor) = 7.05, 37.86 min, tR (major) = 5.42, 12.45 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	5.423	4128303	50.508	58.394
2	7.062	4045225	49.492	41.606
Total		8173528	100.000	100.000

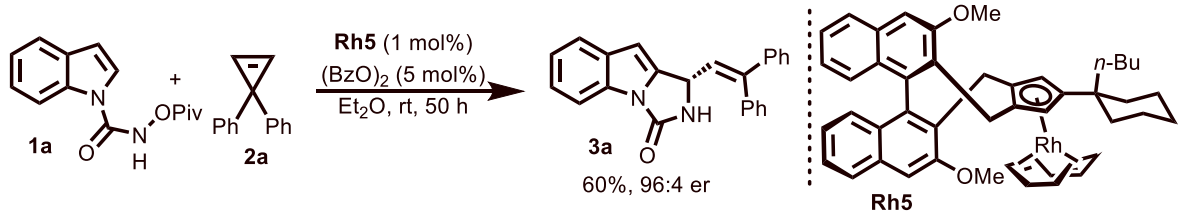


<Peak Table>
PDA Ch1 254nm

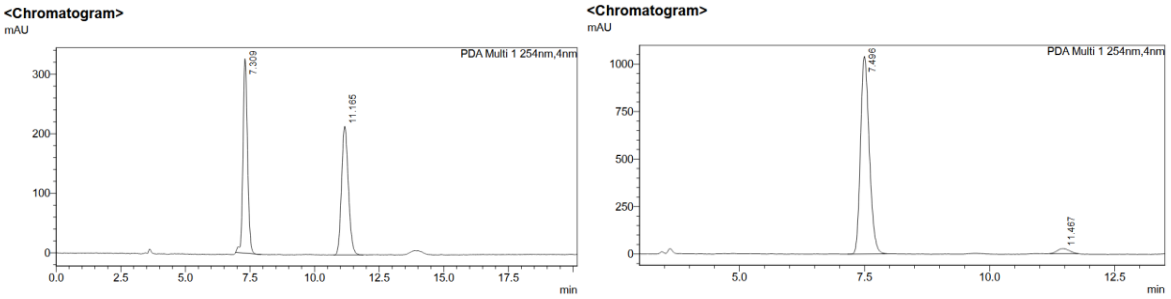
Peak#	Ret. Time	Area	Area%	Height%
1	5.427	2722963	92.501	93.940
2	7.050	220747	7.499	6.060
Total		2943709	100.000	100.000

9. Synthetic application:

1 mmol scale reaction



In a reaction tube, (*R*)-**Rh5** (0.01 mmol, 1 mol%), $(BzO)_2$ (0.05 mmol, 5 mol%), and *N*-(pivaloyloxy)-1H-indole-1-carboxamide **1a** (260 mg, 1 mmol, 1 equiv) were added. The mixture was dissolved in diethyl ether (8.0 mL), and the reaction mixture was stirred at room temperature for 5 min. Then, the solution of cyclopropene **2a** (290 mg, 1.5 mmol, 1.5 equiv) in diethyl ether (2 mL) was added to the reaction tube and stirred at room temperature for 50 h. The reaction was monitored by TLC. After 50 h, the obtained reaction mixture was purified by column chromatography using hexane/ethyl acetate as an eluent to afford products **3a** in 60% yield (210 mg).



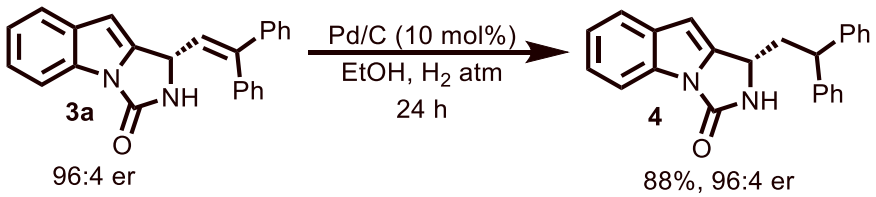
<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	7.309	3984011	49.991	60.171
2	11.165	3985421	50.009	39.829
Total		7969431	100.000	100.000

<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	7.496	12746115	96.533	97.463
2	11.467	457816	3.467	2.537
Total		13203931	100.000	100.000

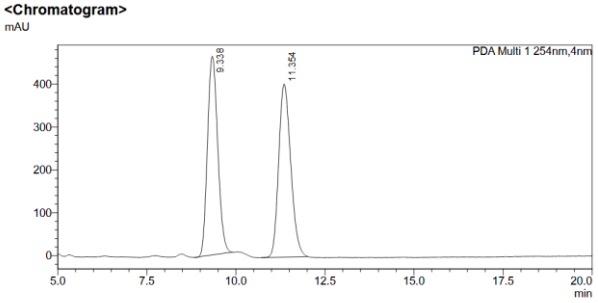
Hydrogenation of 3a



In a dry reaction tube, compound **3a** (30 mg, 0.16 mmol) was taken, followed by ethanol (3 mL) and Pd/C (10 mol%, 10 mg) were added. The reaction mixture was stirred under hydrogen atmosphere (H_2, 10 bar) at room temperature. After 20 h, the reaction mixture was filtered through the short pad of Celite and washed with ethanol. The filtrate was concentrated under

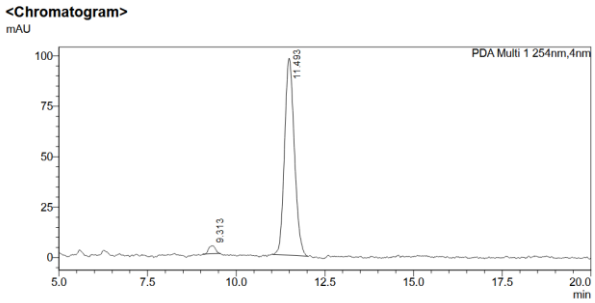
reduced pressure to obtain the crude. The crude product was purified by flash column chromatography with EtOAc/hexane as an eluent to afford the desired product **4**. Yield: 88% (24 mg): colourless semisolid; $[\alpha]_D^{20}$ –20.0 (c 0.1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.91 (d, J = 8.1 Hz, 1H), 7.50 (d, J = 7.4 Hz, 1H), 7.25-7.20 (m, 9H), 7.18-7.12 (m, 3H), 6.28 (s, 1H), 6.25 (s, 1H), 4.53-4.50 (m, 1H), 4.24-4.20 (m, 1H), 2.58-2.52 (m, 1H), 2.46-2.39 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 153.2, 143.2, 143.1, 141.1, 133.3, 130.2, 128.9 (one carbon signal is merging), 127.79, 127.76, 126.9, 126.8, 123.2, 122.6, 120.9, 112.5, 97.5, 51.8, 48.2, 41.7. HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{21}N_2O$ 353.1648; Found 353.1652.

The enantiomeric ratio (96:4) was determined by Daicel Chiralpak IB (35 °C), Hexane/IPA = 85/15, 1.0 mL/min, λ = 254 nm, tR (major) = 11.49 min, tR (minor) = 9.31 min.



<Peak Table>
PDA Ch1 254nm

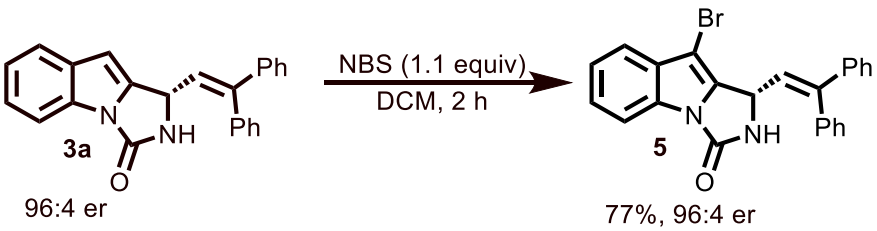
Peak#	Ret. Time	Area	Area%	Height%
1	9.338	9286438	49.394	53.436
2	11.354	9514130	50.606	46.564
Total		18800568	100.000	100.000



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	9.313	51435	2.664	3.945
2	11.493	1879398	97.336	96.055
Total		1930833	100.000	100.000

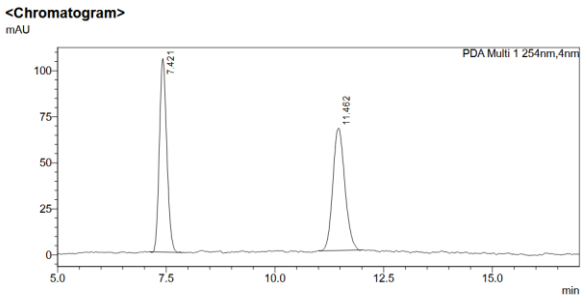
Bromination of 3a:



In a dry reaction tube, compound **3a** was taken (20 mg, 0.057 mmol, 1 equiv) and dissolved in dichloromethane (3 mL). *N*-Bromosuccinimide (11 mg, 0.068 mmol, 1 equiv) was added under an argon atmosphere. After complete conversion of the starting material, the reaction mixture was purified in column chromatography using ethyl acetate/hexane to get the corresponding brominated product **5**. Yield: 79% (19 mg): pale yellow solid; $[\alpha]_D^{20}$ +90.0 (c 0.1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.89-7.87 (m, 1H), 7.47-7.45 (m, 1H), 7.41-7.37 (m, 2H),

7.34-7.23 (m, 3H), 7.29-7.23 (m, 2H), 7.20-7.19 (m, 5H), 6.00 (s, 1H), 5.86 (d, J = 9.6 Hz, 1H), 5.25 (d, J = 9.6 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 152.2, 148.6, 140.6, 138.3, 136.7, 132.2, 130.0, 129.8, 128.7, 128.4, 128.3, 128.2, 127.6, 124.4, 123.2, 121.5, 119.4, 112.7, 87.8, 52.1. HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{18}BrN_2O$ 429.0597; Found 429.0597.

The enantiomeric ratio (96:4) was determined by Daicel Chiralpak IB (35 ºC), Hexane/IPA = 85/15, 1.0 mL/min, λ = 254 nm, tR (major) = 7.31 min, tR (minor) = 11.53 min.



<Peak Table>
PDA Ch1 254nm

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1	7.421	1245734	49.335	61.140
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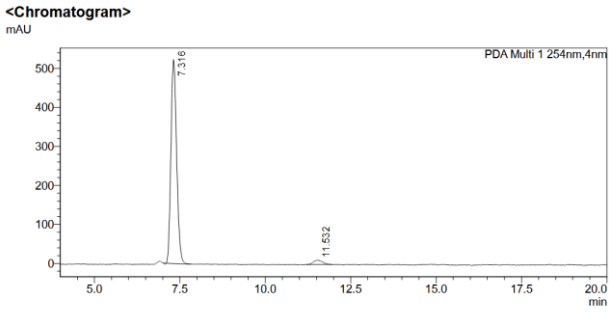
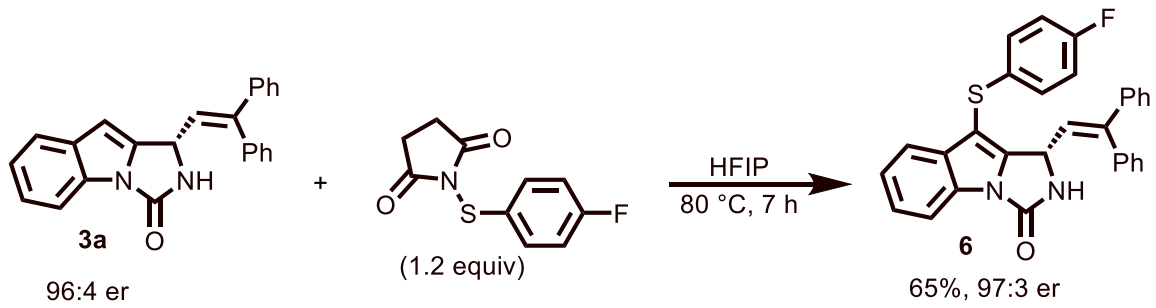
3	27.151	1748	0.069	0.236
Total		2525034	100.000	100.000



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	7.316	6073902	96.694	97.918
2	11.532	207682	3.306	2.082
Total		6281584	100.000	100.000

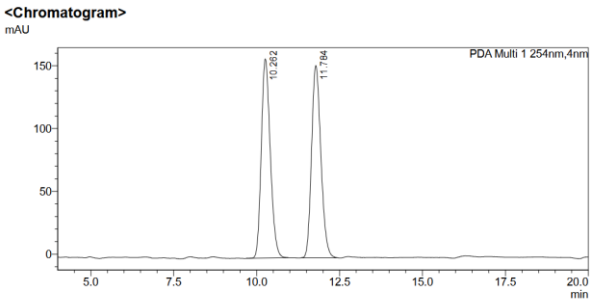
Arylthiolation of 3a:



In a dry reaction flask, compound **3a** (25 mg, 0.071 mmol, 1 equiv) and 1-((4-fluorophenyl)thio)pyrrolidine-2,5-dione (20 mg, 0.085, 1.2 equiv) were taken. The compound was dissolved in HFIP (2 mL) under an argon atmosphere. The reaction mixture was stirred at 80 °C for 7 h. After completion of the starting materials, the reaction mixture was concentrated under reduced pressure using a rotavapor. The crude product was purified by column chromatography using EtOAc/hexane as an eluent to afford compound **6** in 65% yield (23 mg) as a pale-yellow solid; $[\alpha]_D^{26}$ +12.4 (c 0.35, $CHCl_3$); ^1H NMR (500 MHz, DMSO-d_6, 24 °C): δ 8.97 (s, 1H), 7.90 (d, J = 8.1 Hz, 1H), 7.49 (d, J = 8.1 Hz, 1H), 7.39-7.32 (m, 6H), 7.28-7.19 (m, 4H), 7.15-7.12 (m, 2H), 7.03-7.00 (m, 2H), 6.96-6.95 (m, 2H), 5.99 (d, J = 10.0 Hz, 1H),

5.24 (d, J = 10.0 Hz, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, DMSO-d_6, 24 °C): δ 160.9 (d, J = 242.4 Hz), 152.2, 146.4, 146.2, 140.9, 138.5, 134.3, 133.1 (d, J = 2.8 Hz), 130.5, 130.0, 128.9, 128.6, 128.5 (d, J = 8.2 Hz), 128.4, 128.3, 127.6, 124.2, 123.4, 123.1, 119.4, 116.5 (d, J = 22.2 Hz), 112.6, 97.2, 52.3. ^{19}F NMR (470 MHz, $CDCl_3$, 24°C): δ –117.54. HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd for $C_{30}H_{22}FN_2OS$ 477.1437; Found 477.1450.

The enantiomeric ratio (97:3) was determined by Daicel Chiralpak IB (35 ºC), Hexane/IPA = 90/10, 1.0 mL/min, λ = 254 nm, tR (major) = 10.19 min, tR (minor) = 11.65 min.



<Peak Table>
PDA Ch1 254nm

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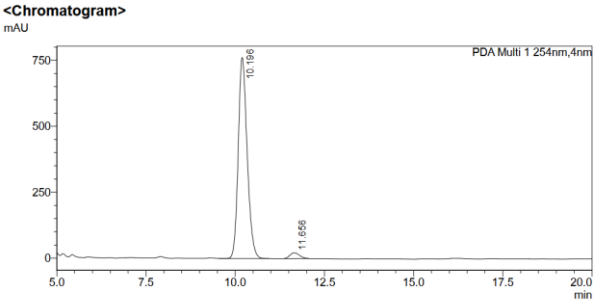
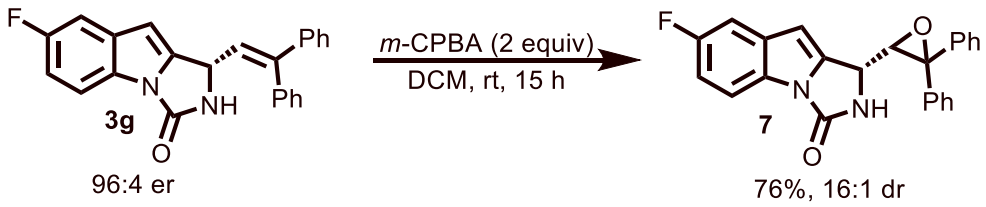
1	10.262	2980612	49.862	50.854
2	11.784	2997159	50.138	49.146
Total		5977771	100.000	100.000



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
1	10.196	13248179	96.983	97.178
2	11.656	412074	3.017	2.822
Total		13660253	100.000	100.000

Epoxidation of 3g:

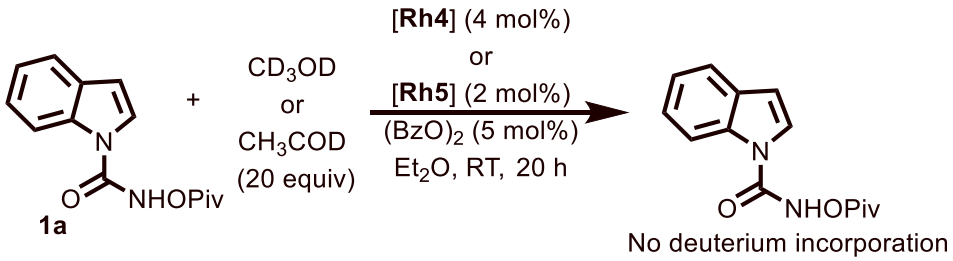


In a dry reaction flask, compound **3g** (20 mg, 0.052 mmol, 1 equiv) was taken. The compound was dissolved in dry DCM (2 mL) under an argon atmosphere, followed by meta-chloroperoxybenzoic acid (*m*-CPBA) (18 mg, 0.1 mmol, 2 equiv) was added with constant stirring. Once all the starting material has converted into the product, monitored by TLC, the reaction mixture is diluted with DCM (2 mL) and then washed with a saturated solution of $NaHCO_3$. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography using EtOAc/hexane as an eluent to afford compound **7** in 76% yield (16 mg) as a colourless solid. ^1H NMR (500 MHz, $CDCl_3$, 24 °C): δ 7.85-7.82 (m, 1H), 7.51-7.49 (m, 2H), 7.41-7.38 (m, 2H), 7.33-7.31 (m, 1H), 7.26 (m, 5H), 7.18-7.15 (m, 1H), 6.99-6.95 (m, 1H), 6.31 (s, 1H), 5.79 (s, 1H), 4.18 (d, J = 8.7 Hz, 1H), 3.54 (d, J = 8.7 Hz, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 24 °C): δ 160.2, 158.3,

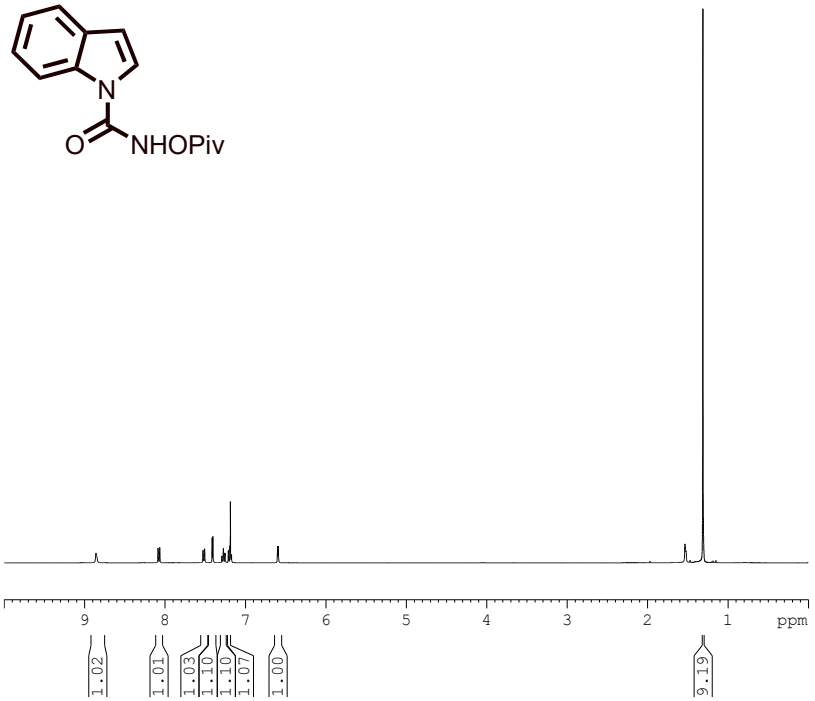
152.0, 138.8, 137.5, 136.3, 133.8 (d, J = 10.1 Hz), 128.8, 128.6, 128.5, 127.5, 127.3, 127.1, 113.4 (d, J = 9.9 Hz), 111.96 (d, J = 25.9 Hz), 106.5 (d, J = 23.5 Hz), 98.9 (d, J = 4.1 Hz), 67.0, 66.1, 53.1. ^{19}F NMR (470 MHz, CDCl3, 24˚C): δ –119.71. HRMS (ESI/Q-TOF) m/z: [M + H]+ Calcd for $C_{24}H_{18}FN_2O_2$ 385.1347; Found 385.1362.

10. Control experiments:

Deuterium exchange experiment:



In a reaction tube, **Rh4** or **Rh5** (4 mol% or 2 mol%), $(BzO)_2$ (5 mol%), and *N*-(pivaloyloxy)-1H-indole-1-carboxamide **1a** (30 mg, 0.11 mmol, 1 equiv) were taken. The reaction mixture was dissolved in diethyl ether (1.0 mL), and the reaction mixture was stirred at room temperature. Followed by CD_3OD or CH_3COD (20 equiv) was added, the reaction mixture was stirred at room temperature for 20 h. Evaporation of solvent followed by purification through column chromatography using hexane/ethyl acetate as an eluent gave the product. ^{1}H NMR analysis of the isolated compound revealed that no deuterium incorporation was observed at the indole second position in both reaction conditions.

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EXPNO                      9
PROCNO

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TD                  2685
SOLVENT             CDCl
NS                     1
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SWH                8196.72
FIDRES             0.61037
AQ                1.638338
RG                      10
DW                   61.00
DE                    13.8
TE                   299.
D1                0.5000000
TD0
SFO1            400.132470
NUC1                    1
P0                    2.6
P1                    8.0
PLW1            26.1499996

F2 - Processing parame
SI                   6553
SF              400.130038
WDW                     E
SSB
LB                    0.3
GB
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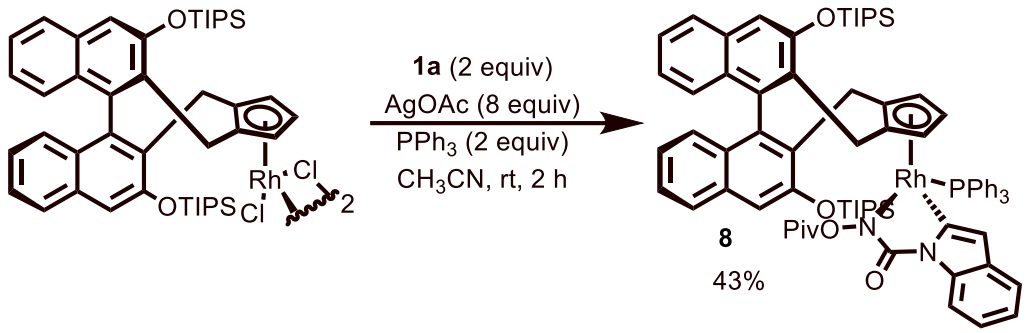
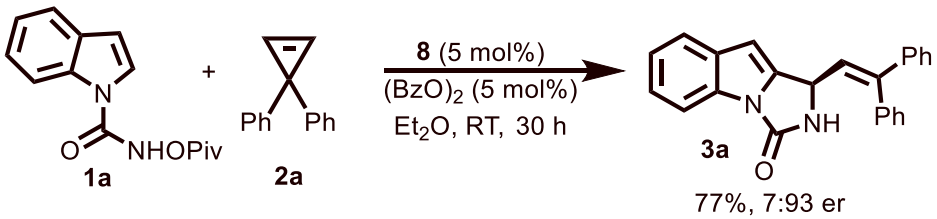
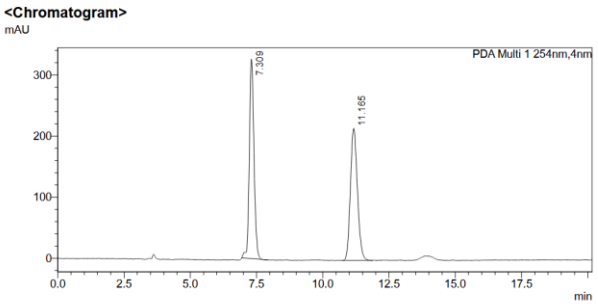
Isolation of complex 8:



In a dry reaction tube, **Rh4-Cl** (20 mg, 0.011 mmol, 1 equiv), **1a** (6 mg, 0.023 mmol, 2 equiv), and AgOAc (16 mg, 0.093 mmol, 8 equiv) were taken, followed by acetonitrile (3 mL) was added under N_2 atmosphere with continuous stirring at room temperature. After stirring at room temperature for 40 min, PPh_3 (6 mg, 0.023 mmol, 2 equiv) was added and stirred further for 1 h. The reaction mixture was filtered through a PTFE syringe and washed with 10 mL of acetonitrile. The filtrate was concentrated under reduced pressure. The crude was purified by column chromatography using (ethyl acetate/ hexane) to obtain the **8** as a yellow solid, 43% yield (14 mg). ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.03 (d, J = 7.9 Hz, 1H, ArH), 7.69 (d, J = 7.9 Hz, 1H, ArH), 7.63 (d, J = 7.9 Hz, 1H, ArH), 7.38-7.34 (m, 7H, ArH), 7.28-7.22 (m, 4H, ArH), 7.12-7.08 (m, 6H, ArH), 6.98-6.92 (m, 4H, ArH), 6.84-6.71 (m, 5H, ArH), 6.06 (s, 1H, ArH), 5.42 (s, 1H, CpC–H), 5.06 (s, 1H, CpH), 4.14-4.06 (m, 2H, CpH&CH_2–H), 3.88 (d, J = 13.6 Hz, 1H, CH_2–H), 3.10 (t, J = 2.3 Hz, 1H, CH_2–H), 2.81 (t, J = 16.0 Hz, 1H, CH_2–H), 1.39-1.33 (m, 2H), 1.12-1.07 (m, 19 H), 0.81-0.79 (m, 2H), 0.73-0.69 (m, 19H), 0.38 (s, 9H, –$(CH_3)_3$); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 24 °C): δ 176.1 (C=O), 158.7 (C=O), 152.3, 151.5, 137.8, 137.3, 136.7, 134.0, 133.5, 132.4, 130.0, 129.3, 128.9, 128.1, 127.8, 127.7, 127.6, 126.7, 126.5, 126.1, 125.9, 125.3, 124.1, 123.6, 119.1, 118.2, 116.8, 115.4, 113.5, 112.8, 112.7, 112.3, 107.7, 99.62, 99.60, 91.4, 91.3, 37.7, 31.9, 31.6, 29.6, 29.4, 29.3, 29.2, 27.5, 26.7, 26.0, 25.6, 24.7, 22.6, 18.25, 18.22, 17.9, 17.8, 14.1, 13.2, 12.5. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 35.2 (d, J = 147.5 Hz). HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd for $C_{77}H_{89}N_2O_5PRhSi_2$ 1311.5097; Found 1311.5083.



In a reaction tube, **8** (0.0019 mmol, 5 mol%), $(BzO)_2$ (0.0019 mmol, 5 mol%), and *N*-(pivaloyloxy)-1H-indole-1-carboxamide **1a** (10 mg, 0.03 mmol, 1 equiv) were added. The mixture was dissolved in diethyl ether (1.0 mL), and the reaction mixture was stirred at room temperature for 5 min. Then, the solution of cyclopropene **2a** (12 mg, 0.057 mmol, 1.5 equiv) in diethyl ether (0.5 mL) was added to the reaction tube and stirred at room temperature for 20 h. The reaction was monitored by TLC. After complete consumption of the starting material, the obtained reaction mixture was purified by column chromatography using hexane/ethyl acetate as an eluent to afford products **3a** in 77% yield (11 mg).



<Peak Table>
PDA Ch1 254nm

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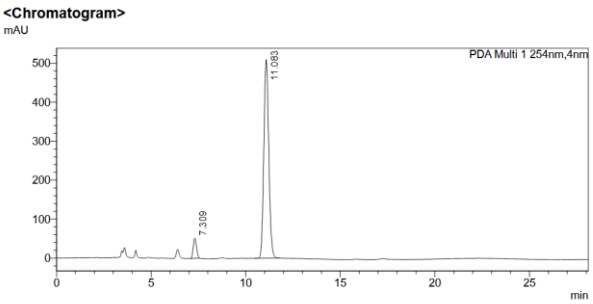
Total		7969431	100.000	100.000



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height%
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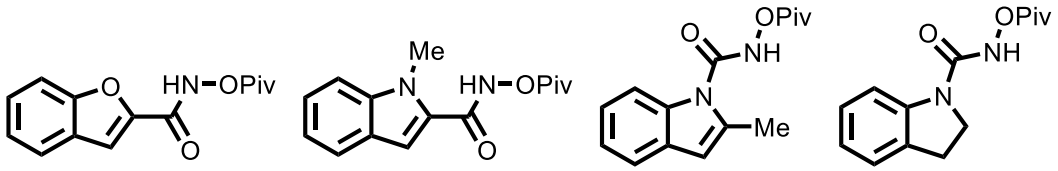
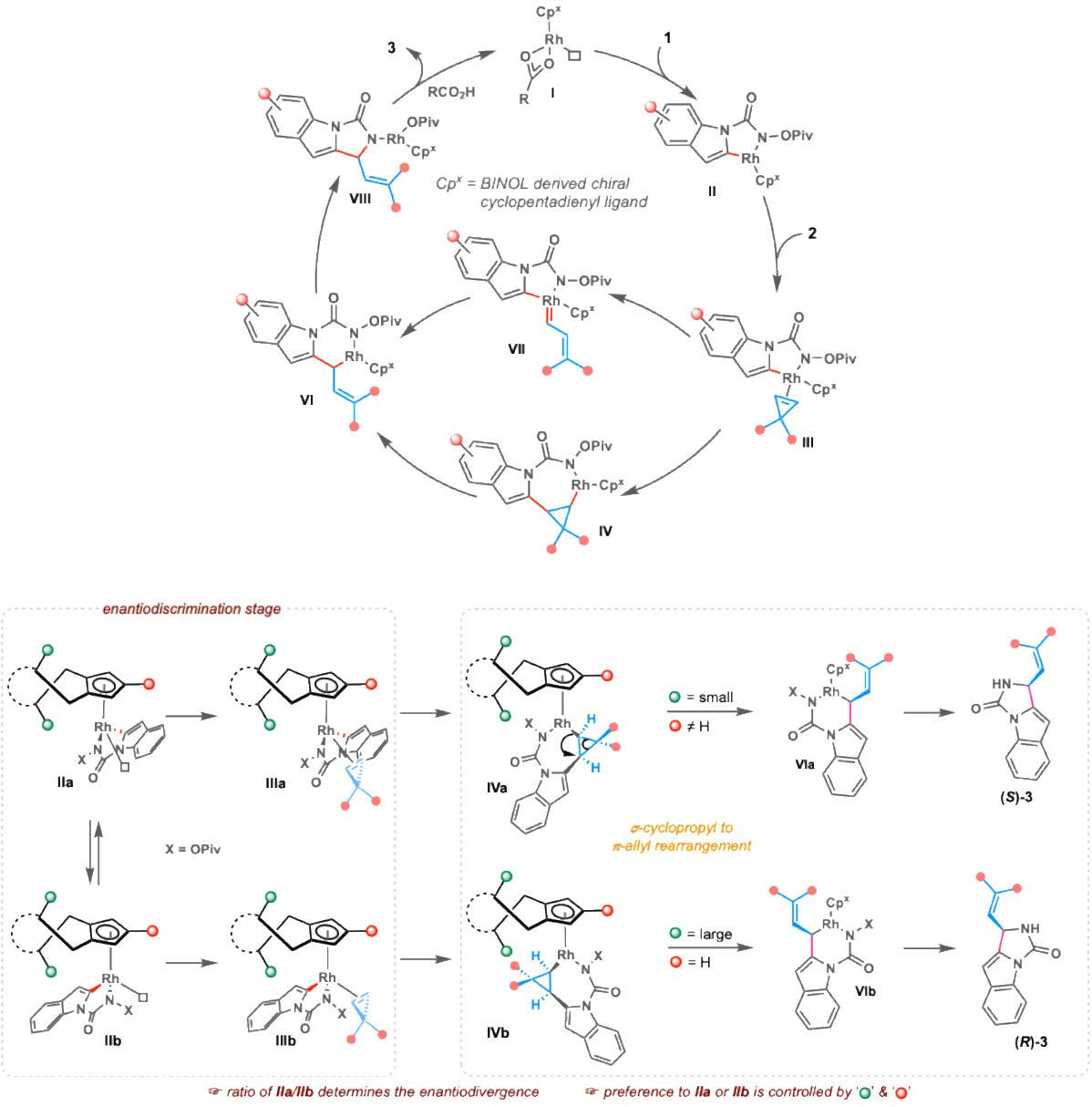
Unsuccessful substrates



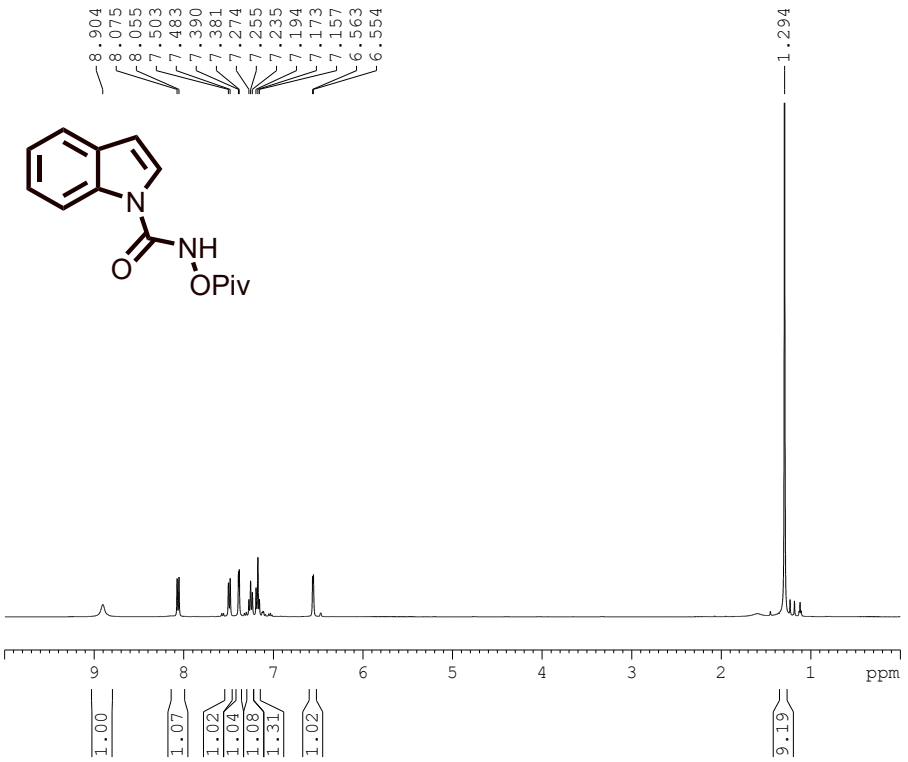
11. Plausible mechanism and stereochemical outcome:



Reversal of chirality is originated from the preferential formation of either **IIa** over **IIb** or **IIIa** over **IIIb**, since both faces of cyclopropenes are identical. Based on our observation, it is clear that preferential formation of **IIa** over **IIb** is controlled by the presence of substituent on the cyclopentadienyl ligand. When no addition substituent is present in cyclopentadienyl ligand, as in **Rh4**-cat., the catalyst favours **IIb** and afford the **(*R*)-3** as major enantiomer. On the other, presence of substituent in cyclopentadienyl ligand, as in **Rh5**-cat., the catalyst favours the formation of **IIa** and affords the **(*S*)-3** as major enantiomer.

12. Spectral data

N-(pivaloyloxy)-1H-indole-1-carboxamide (1a)

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PROCNO

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TD                   6553
SOLVENT              CDCl
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SWH                8196.72
FIDRES             0.25014
AQ                3.997696
RG                      10
DW                   61.00
DE                    13.8
TE                   300.
D1              1.0000000
TD0
SFO1           400.132470
NUC1                    1
P0                    2.6
P1                    8.0
PLW1           26.1499996

F2 - Processing parame
SI                   6553
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SSB
LB                    0.3
GB
PC                    1.0
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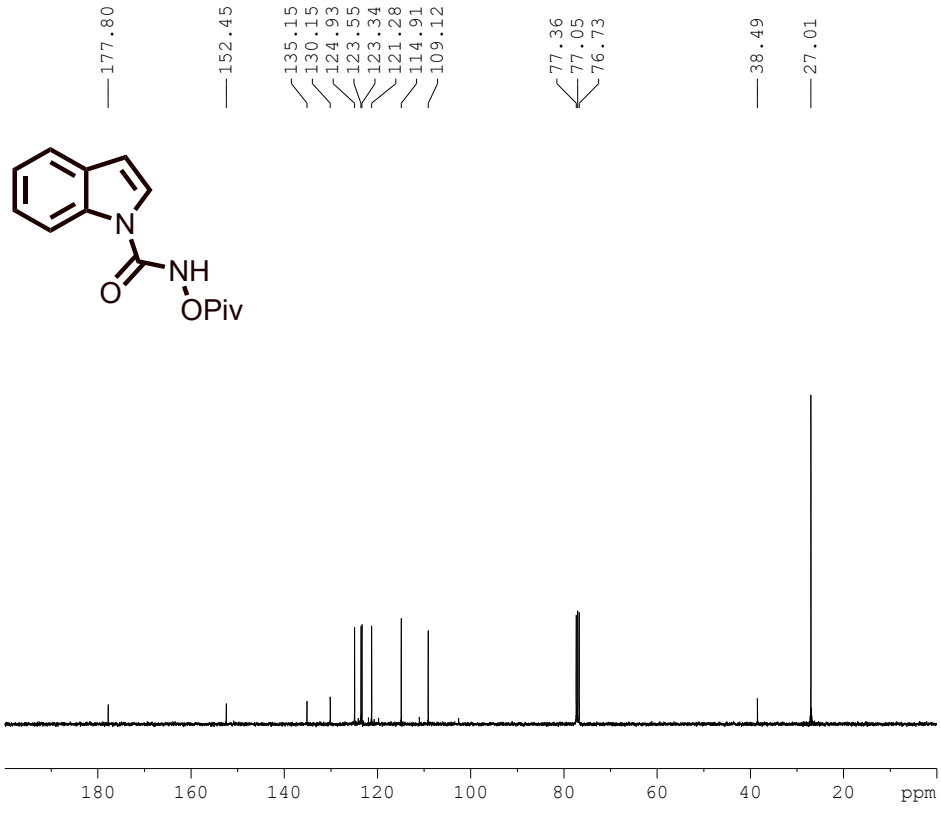
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1a

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Current Data Parameter
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PROCNO

F2 - Processing parame
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SF            100.612768
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SSB
LB                    1.0
GB
PC                    1.4
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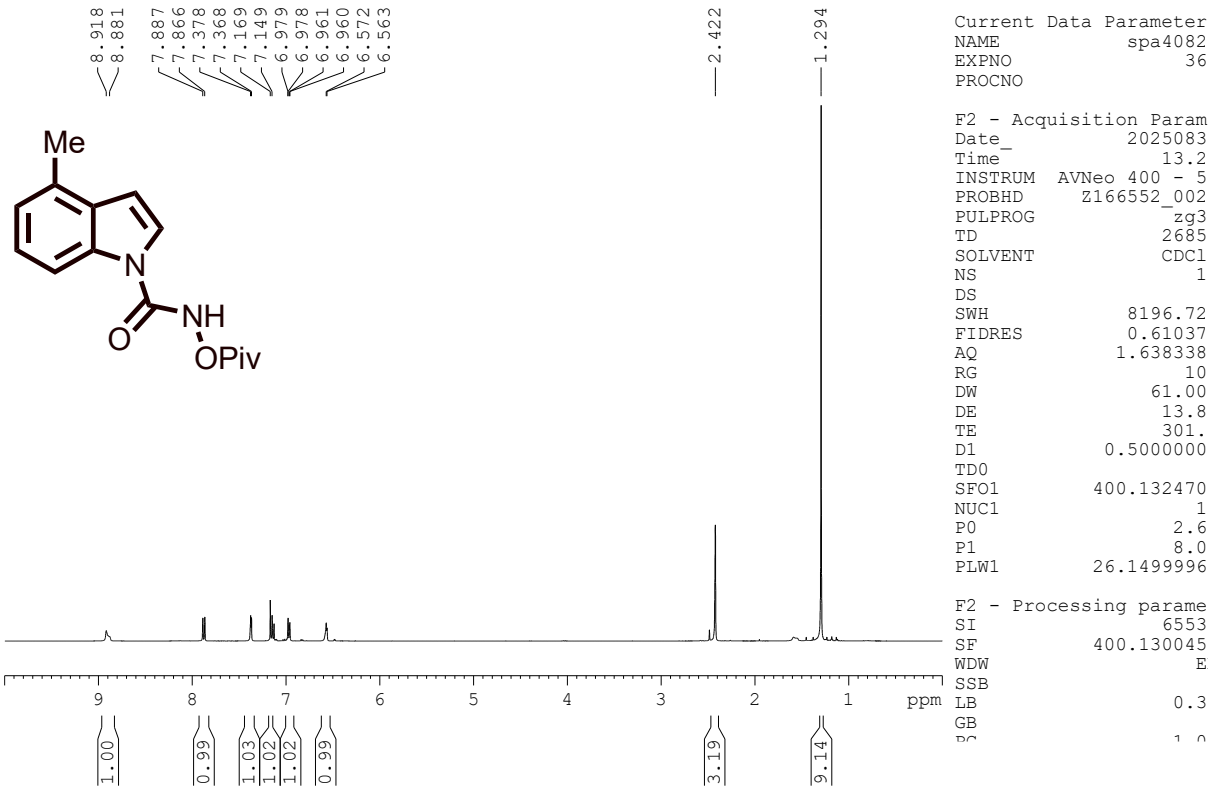
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 1a

4-methyl-N-(pivaloyloxy)-1H-indole-1-carboxamide (1b)

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EXPNO                  36
PROCNO

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PULPROG              zg3
TD                  2685
SOLVENT             CDCl
NS                     1
DS
SWH             8196.72
FIDRES          0.61037
AQ             1.638338
RG                   10
DW                61.00
DE                 13.8
TE                 301.
D1            0.5000000
TD0
SFO1          400.132470
NUC1                   1
P0                   2.6
P1                   8.0
PLW1          26.1499996

F2 - Processing parame
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SSB
LB                   0.3
GB
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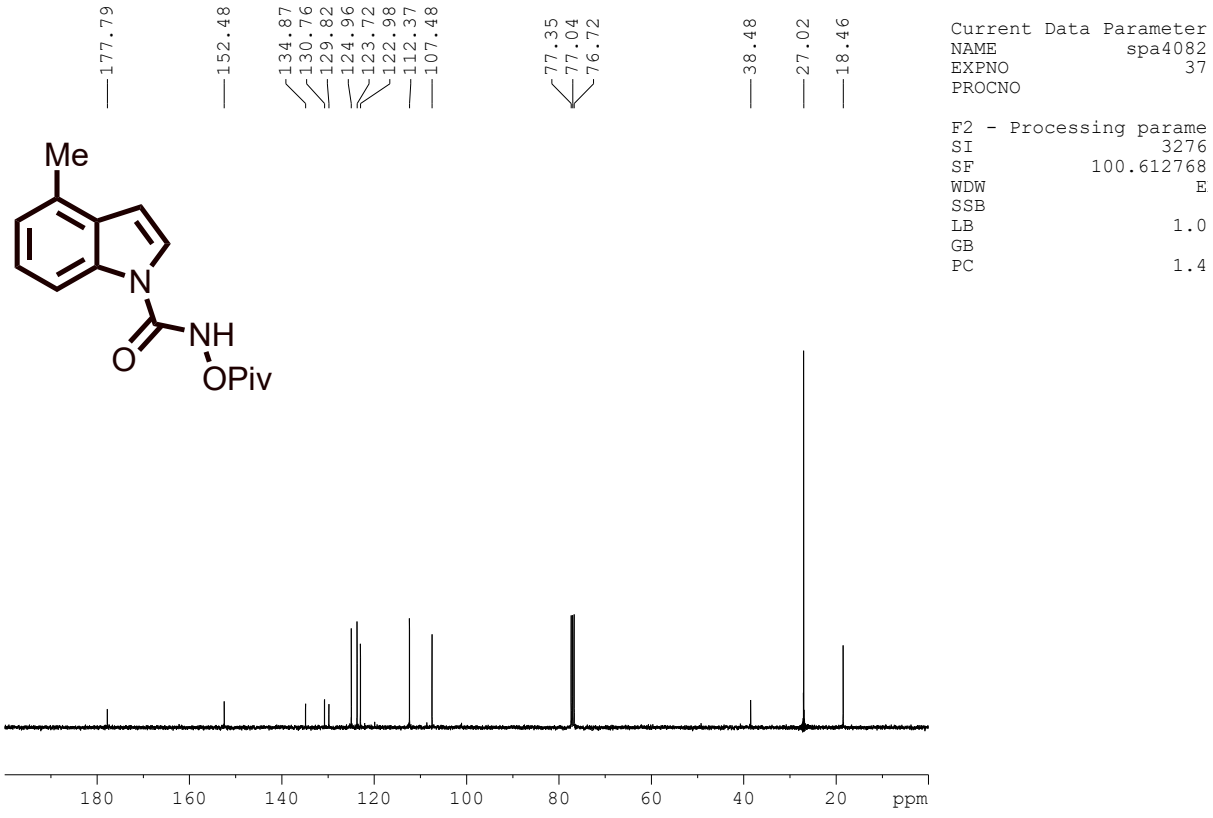
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1b

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Current Data Parameter
NAME              spa4082
EXPNO                  37
PROCNO

F2 - Processing parame
SI                  3276
SF            100.612768
WDW                    E
SSB
LB                   1.0
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PC                   1.4
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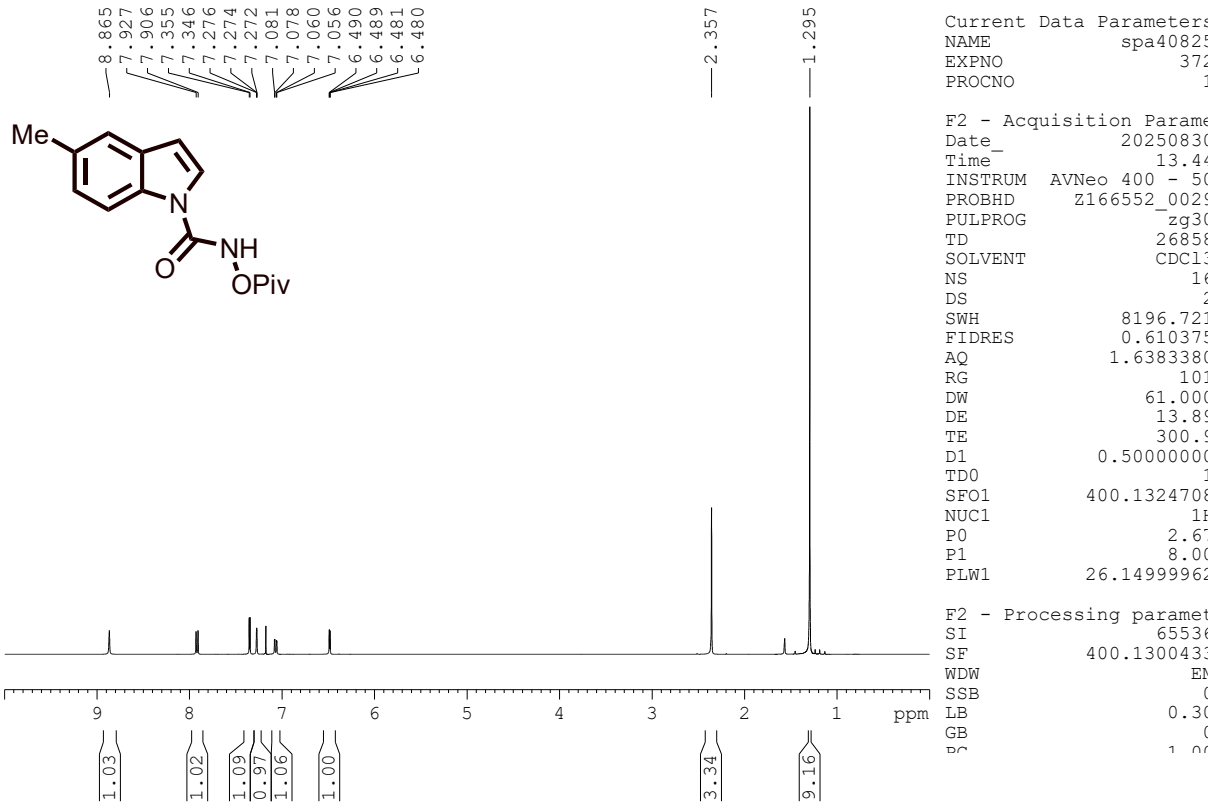
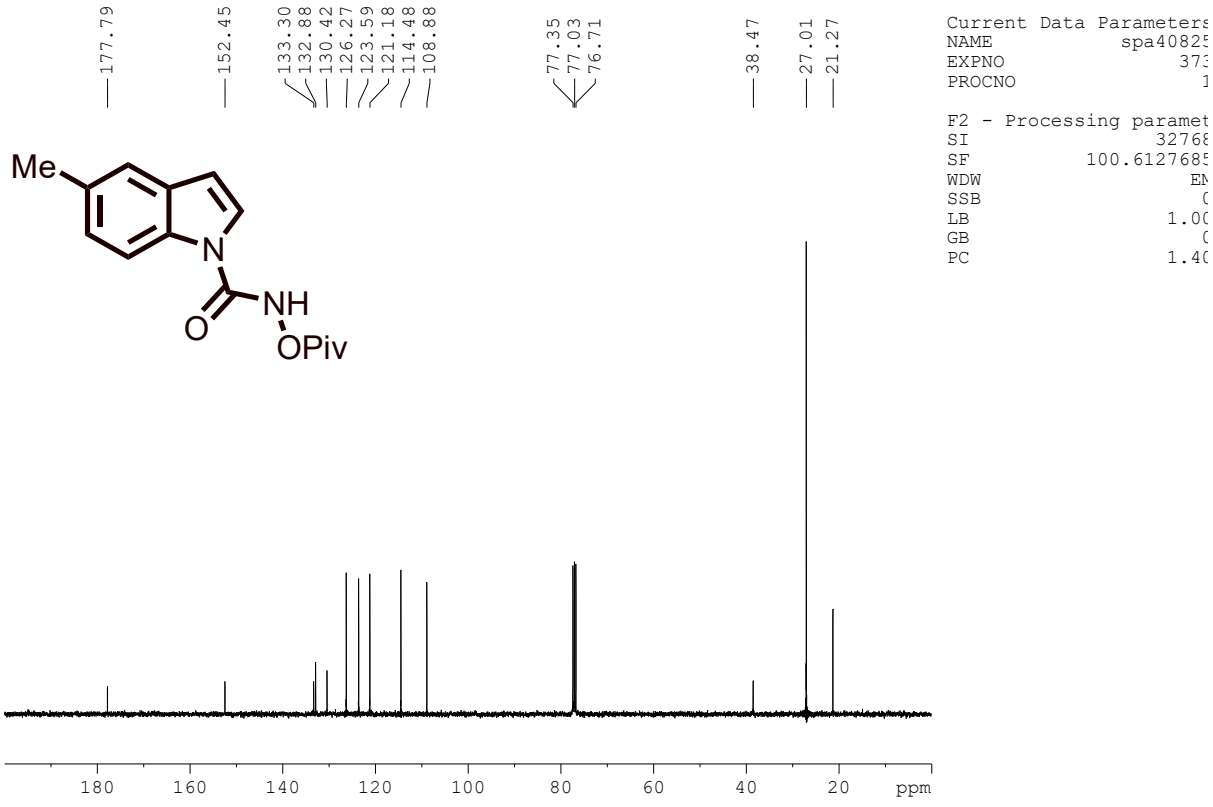
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 1b

5-methyl-N-(pivaloyloxy)-1H-indole-1-carboxamide (1c)

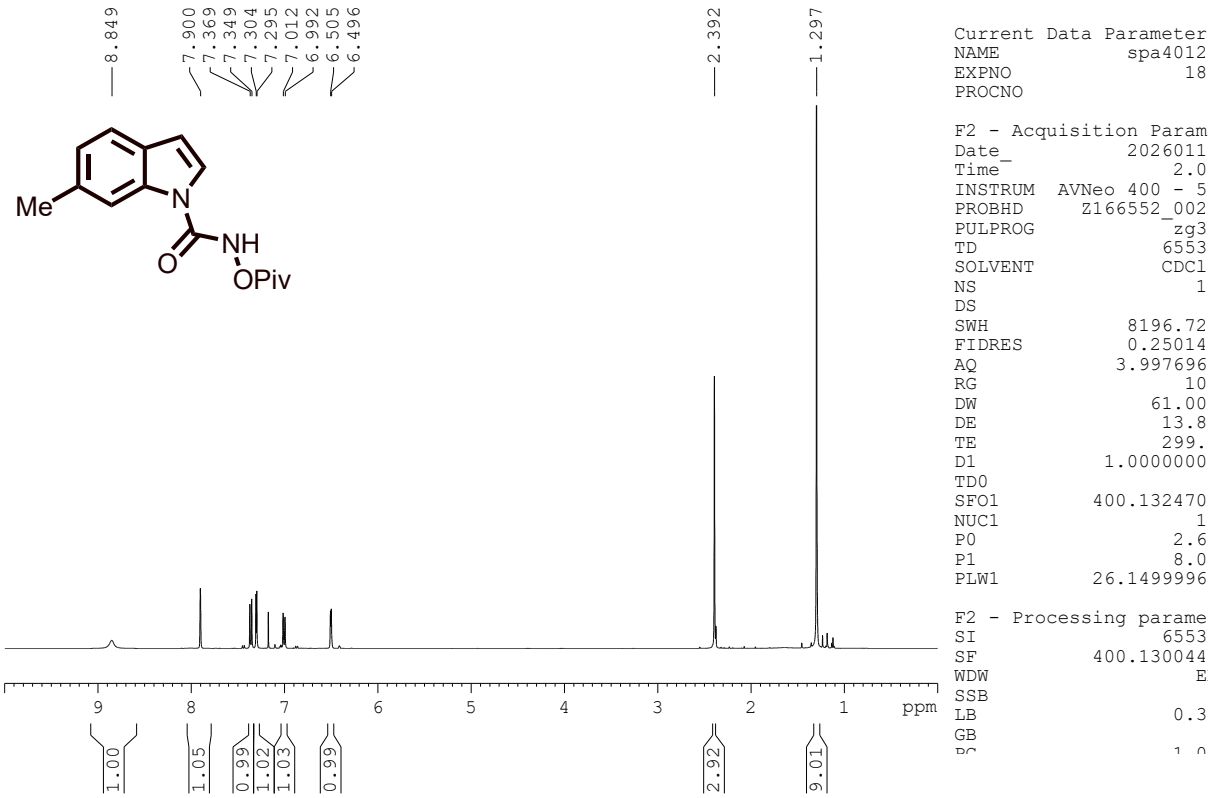


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1c



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 1c

6-methyl-N-(pivaloyloxy)-1H-indole-1-carboxamide (1d)



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NAME spa4012
EXPNO 18
PROCNO

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Time 2.0
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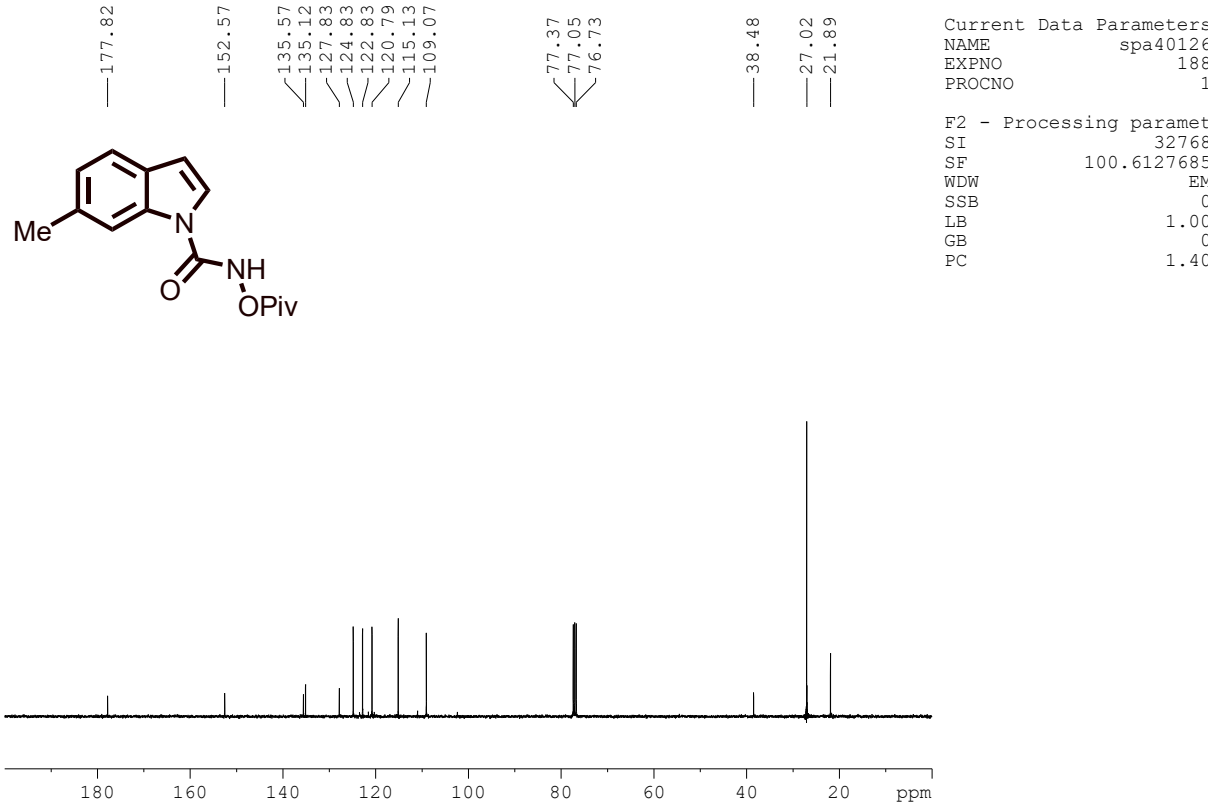
PROBHD Z166552_002
PULPROG zg3
TD 6553
SOLVENT CDCl
NS 1
DS
SWH 8196.72
FIDRES 0.25014
AQ 3.997696
RG 10
DW 61.00
DE 13.8
TE 299.
D1 1.0000000
TD0
SFO1 400.132470
NUC1 1
P0 2.6
P1 8.0
PLW1 26.1499996

F2 - Processing parame
SI 6553
SF 400.130044
WDW E
SSB
LB 0.3
GB

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1d

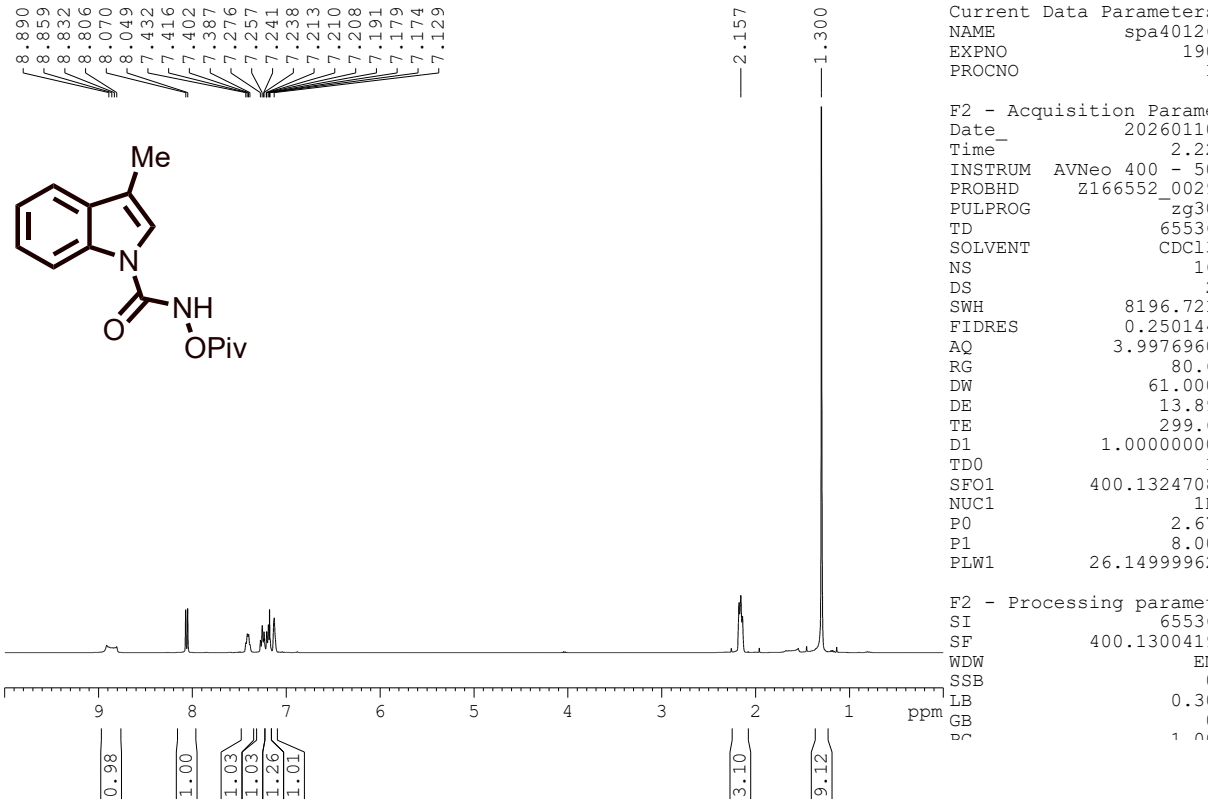


Current Data Parameters
NAME spa40126
EXPNO 188
PROCNO 1

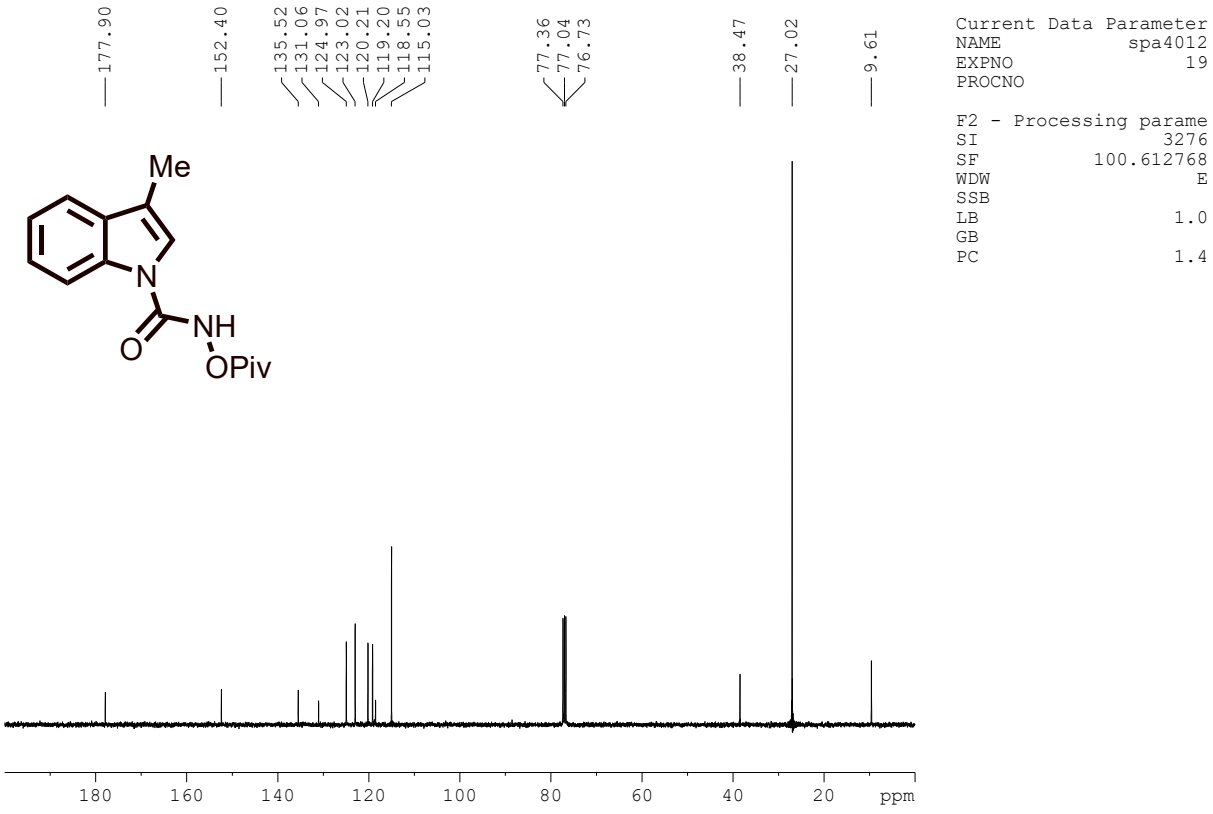
F2 - Processing paramet
SI 32768
SF 100.6127685
WDW EM
SSB 0
LB 1.00
GB 0
PC 1.40

^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 1d

3-methyl-N-(pivaloyloxy)-1H-indole-1-carboxamide (1e)

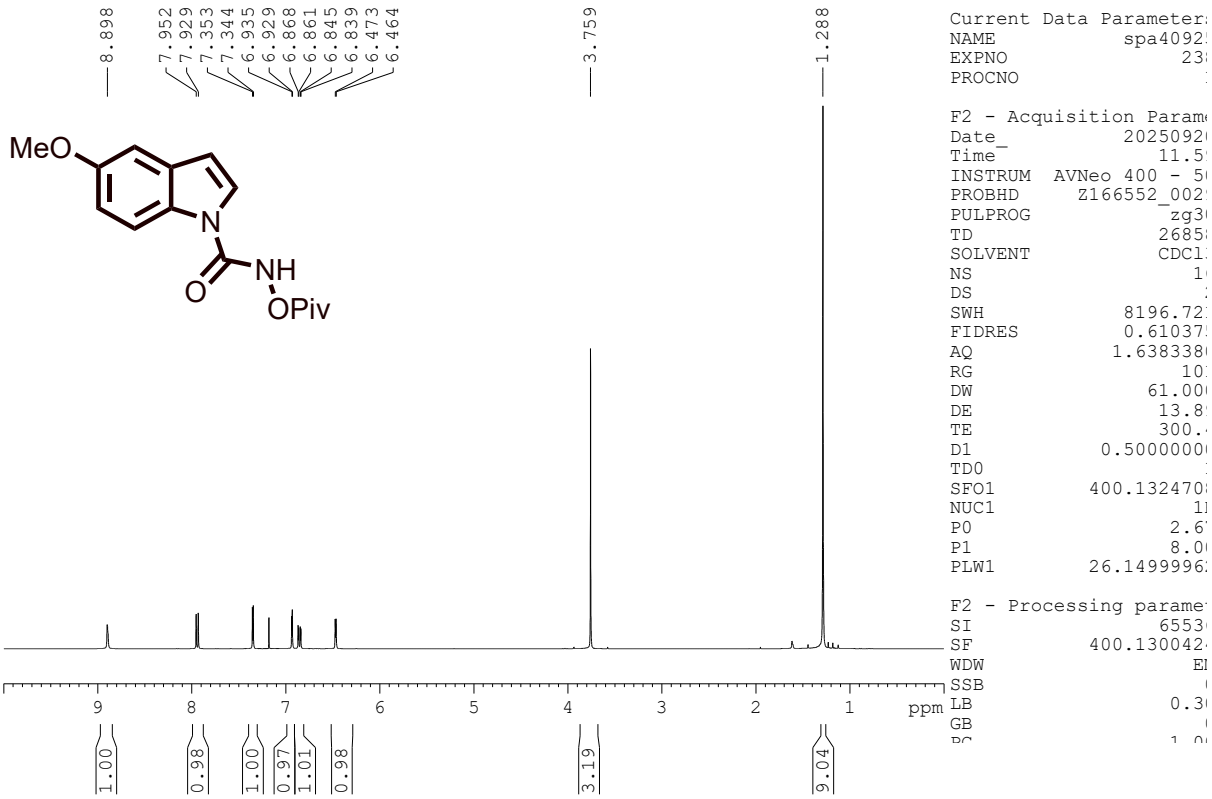


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1e

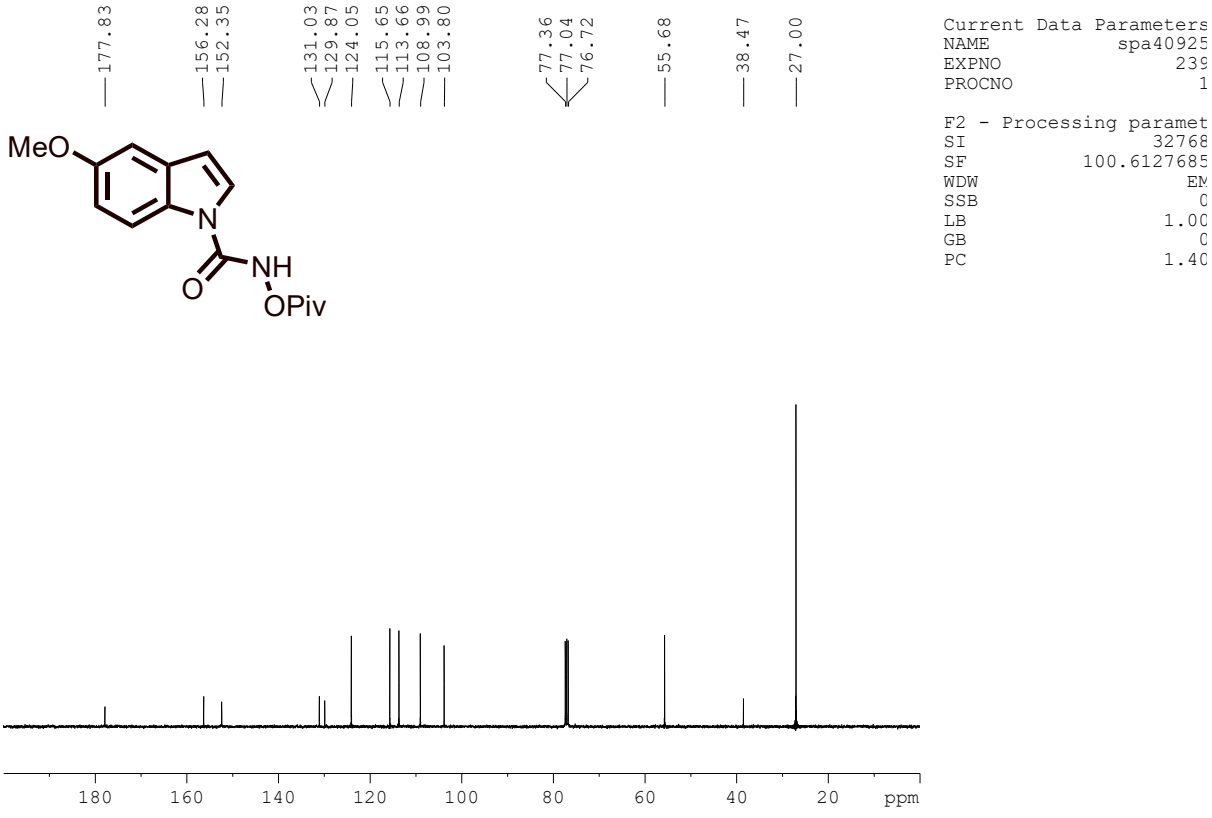


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 1e

5-methoxy-N-(pivaloyloxy)-1H-indole-1-carboxamide (1f)

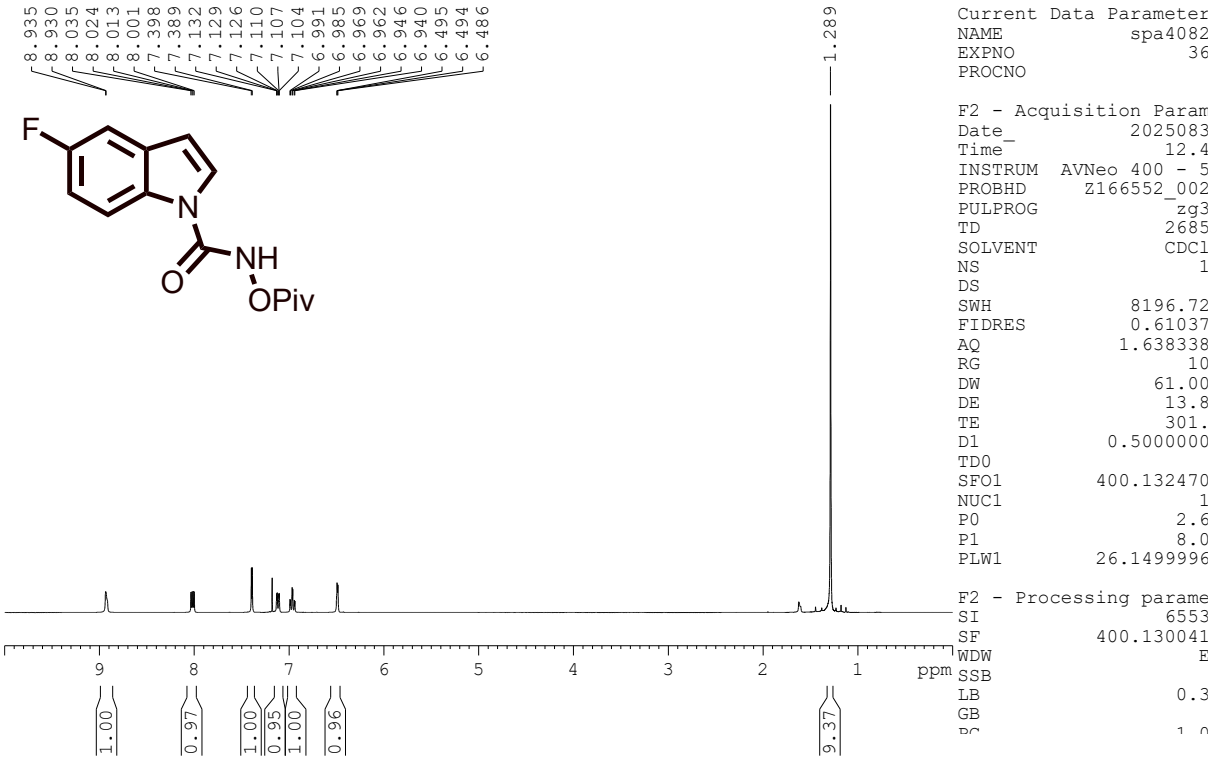


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1f

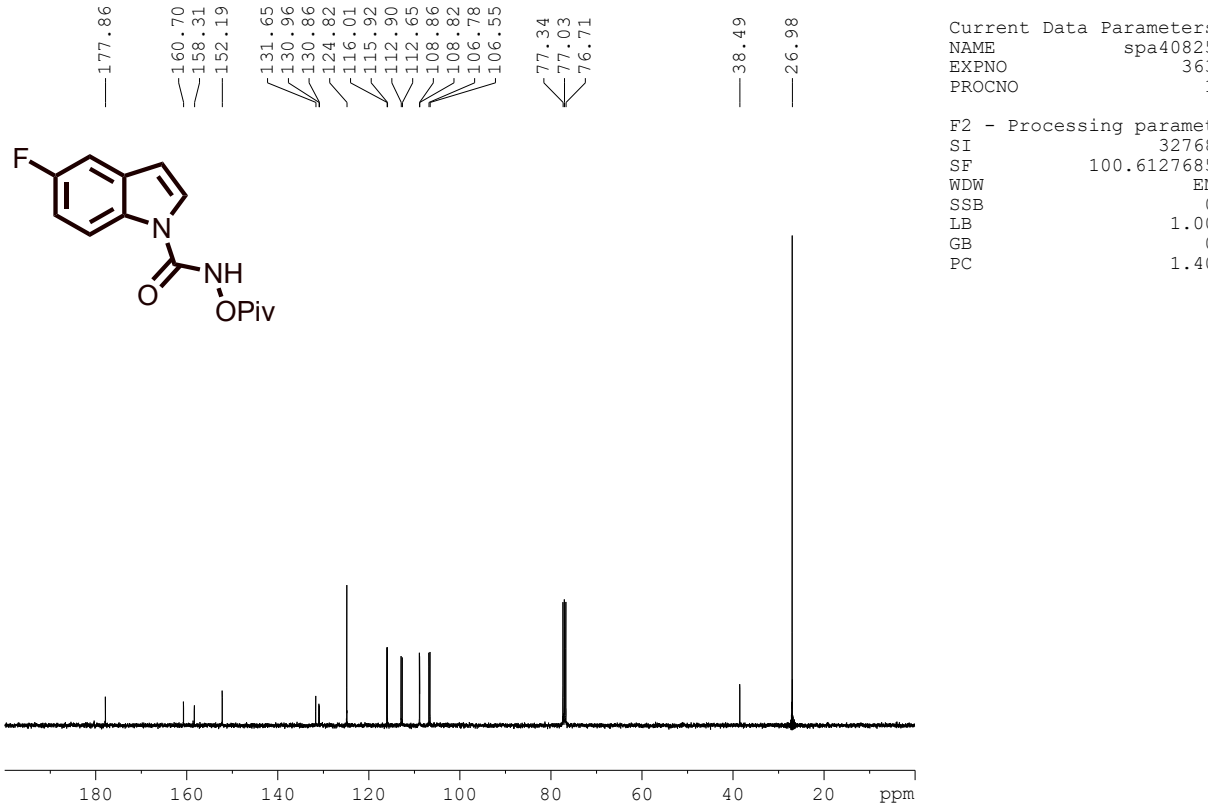


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 1f

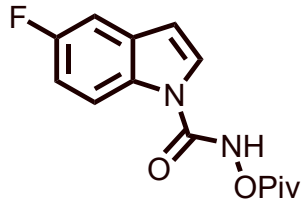
5-fluoro-N-(pivaloyloxy)-1H-indole-1-carboxamide (1g)

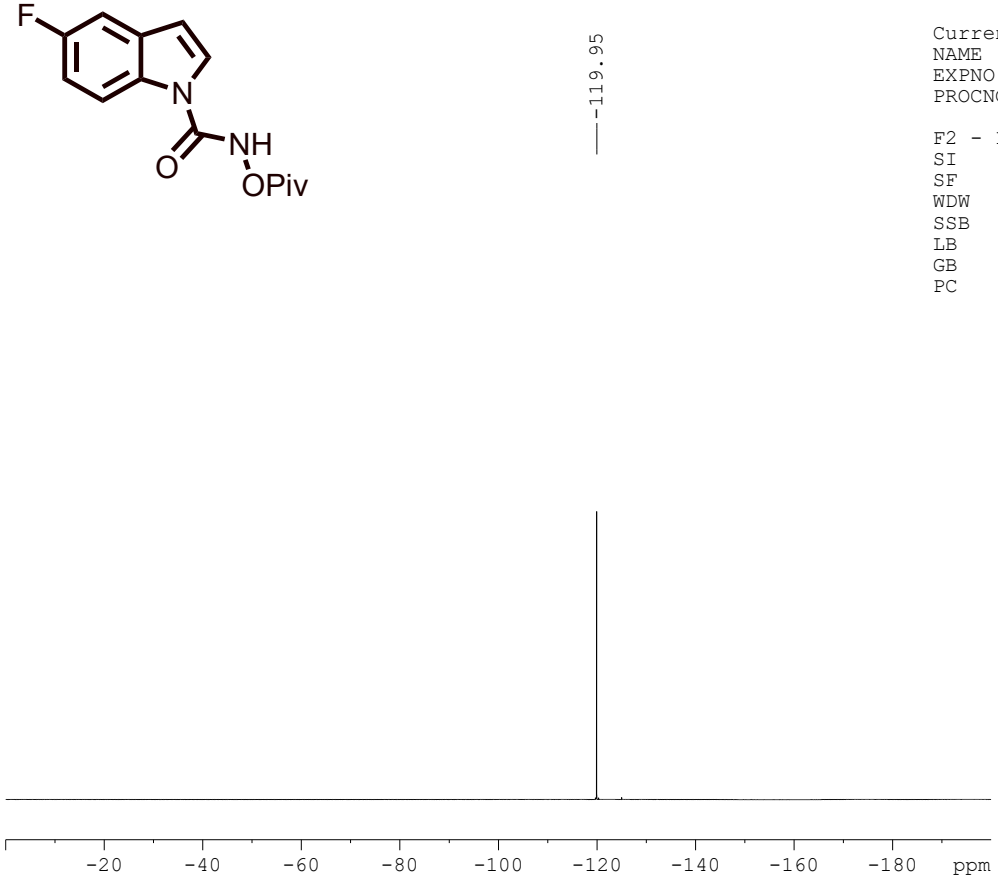


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1g



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 1g



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Current Data Parameter
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EXPNO                36
PROCNO

F2 - Processing parame
SI                 6553
SF          376.498366
WDW                   E
SSB
LB                  0.3
GB
PC                  1.0
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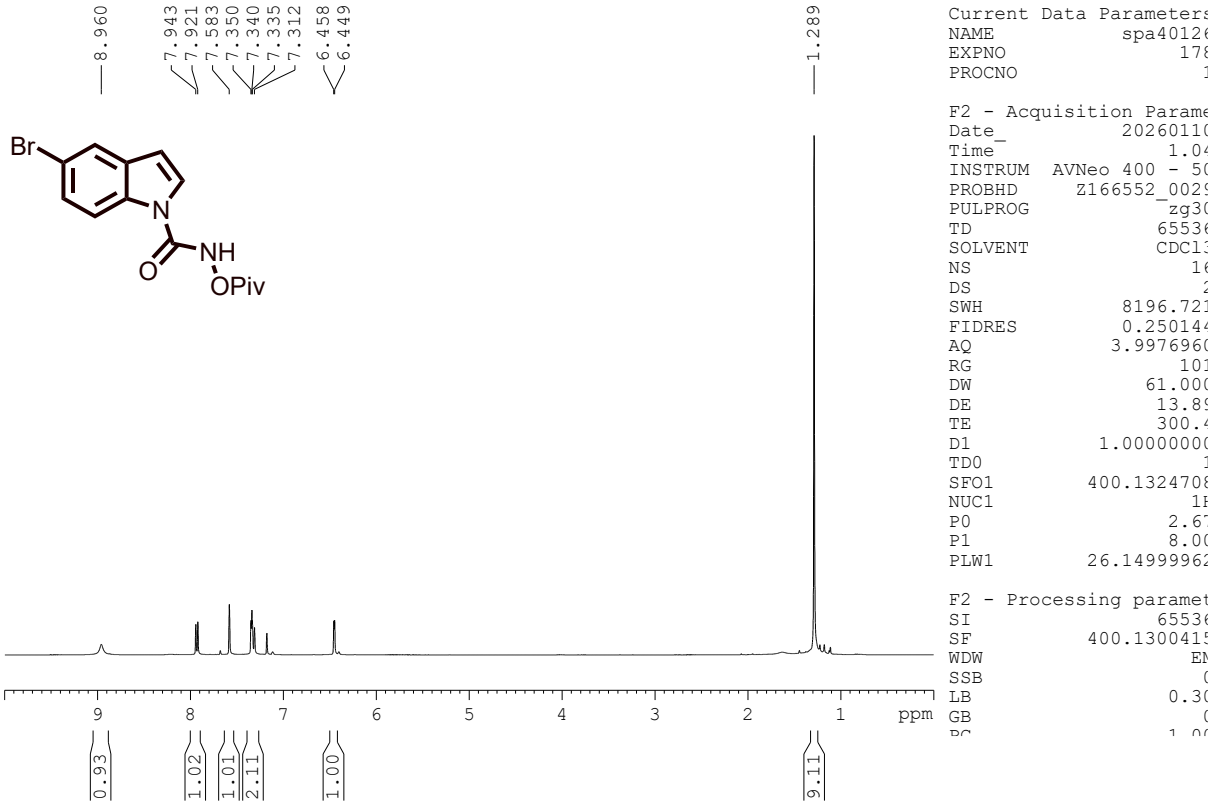
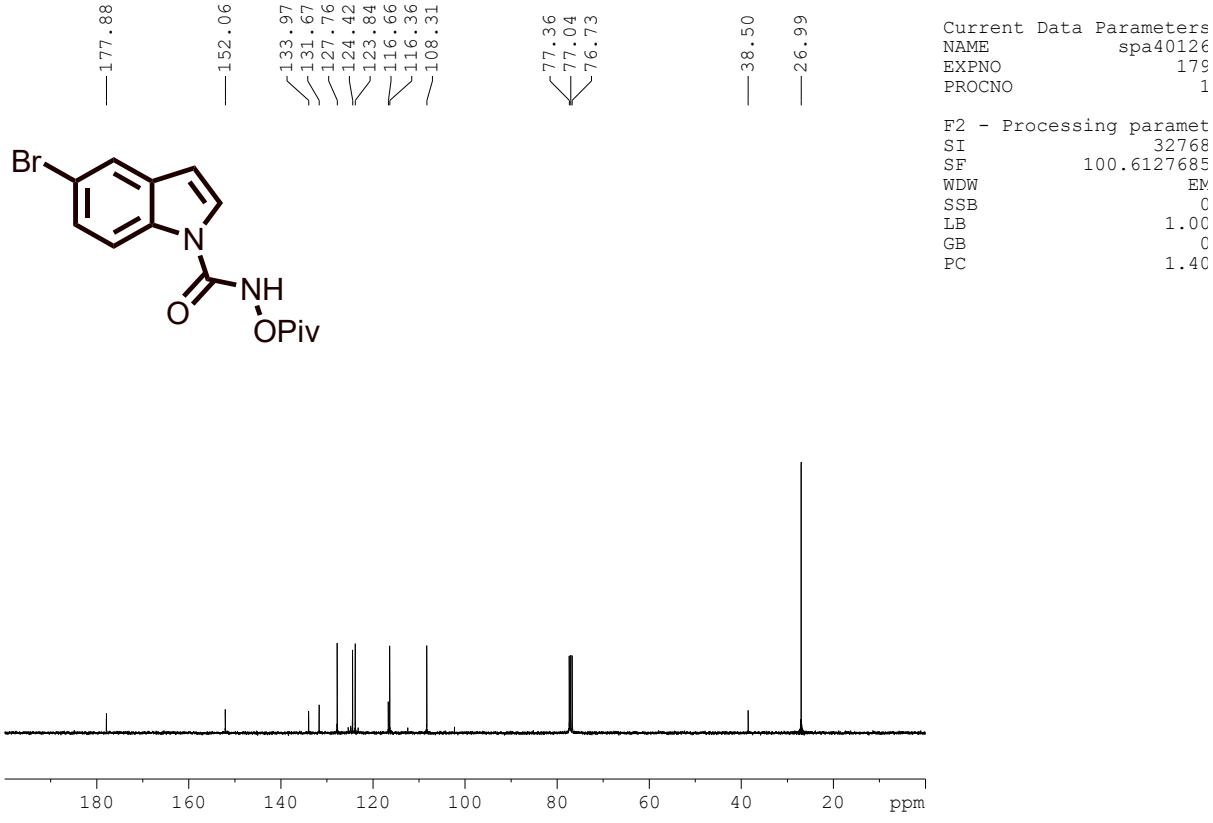
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 1g

5-bromo-N-(pivaloyloxy)-1H-indole-1-carboxamide (1h)

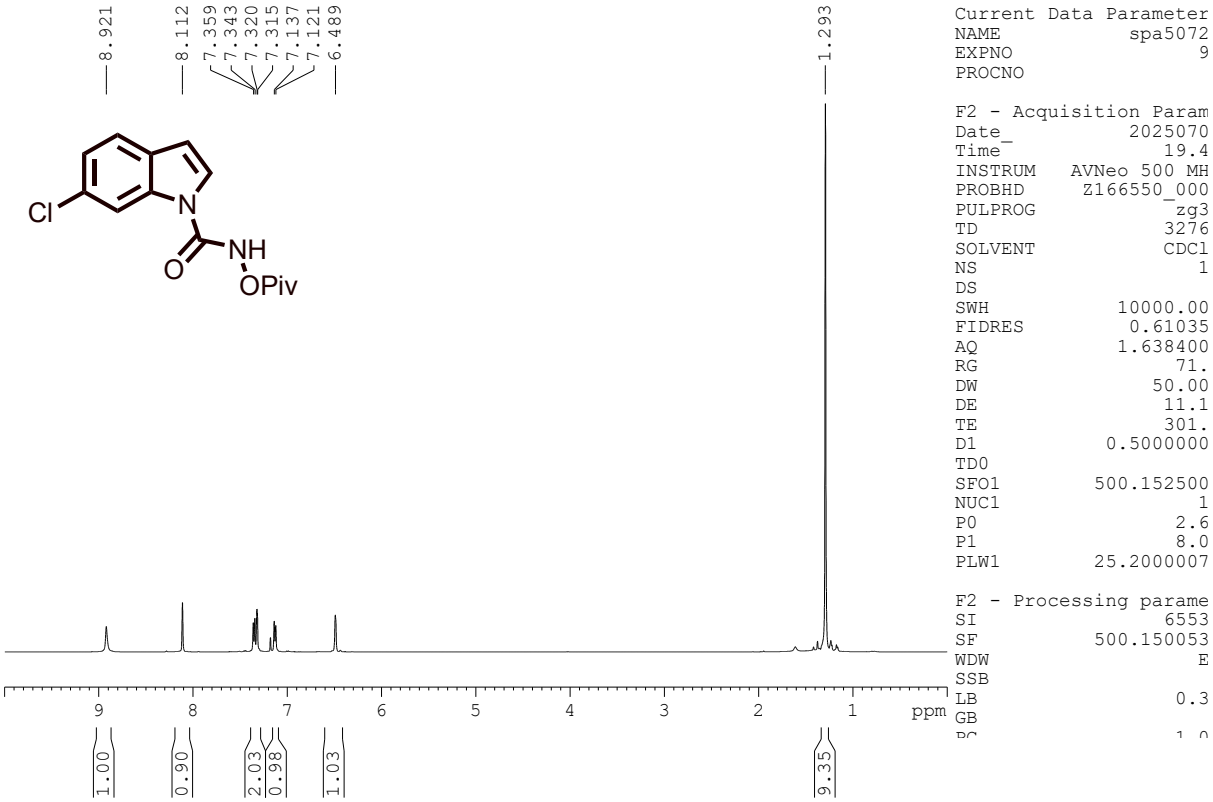


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1h

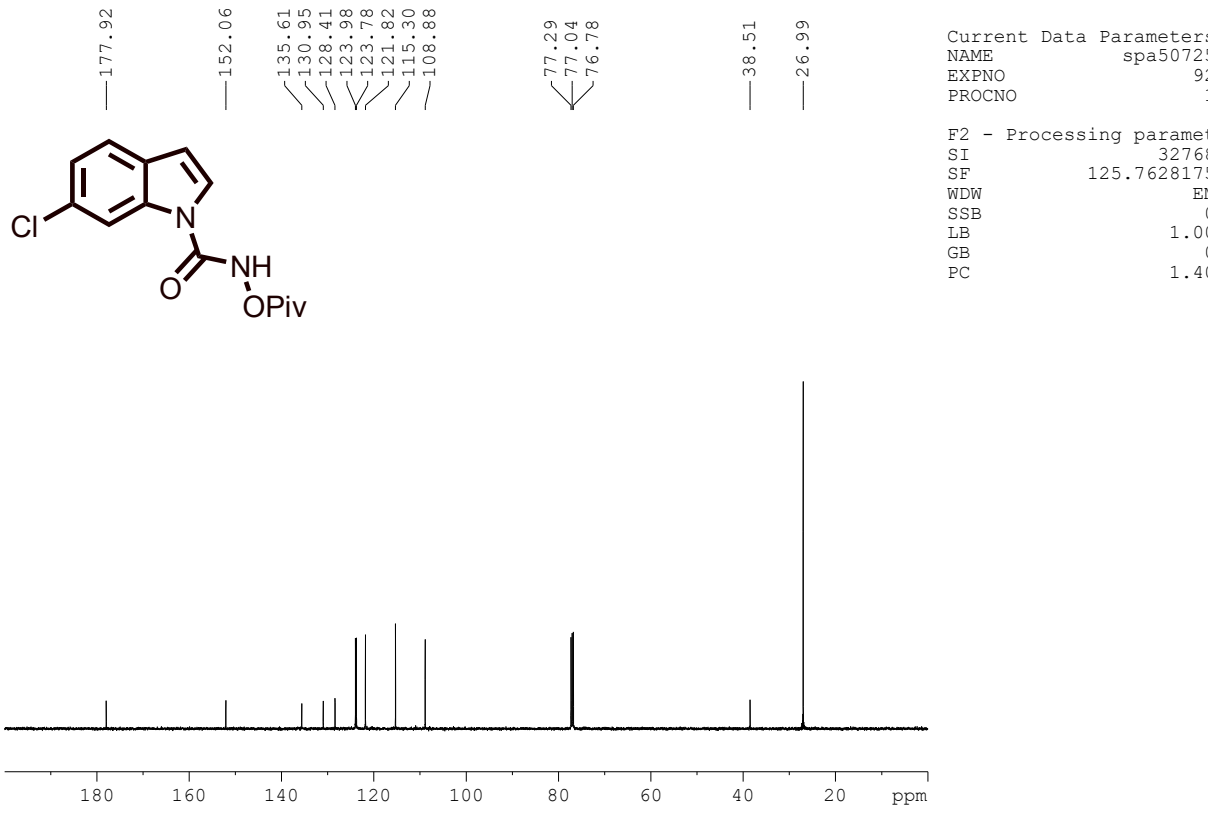


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 1h

6-chloro-N-(pivaloyloxy)-1H-indole-1-carboxamide (1j)

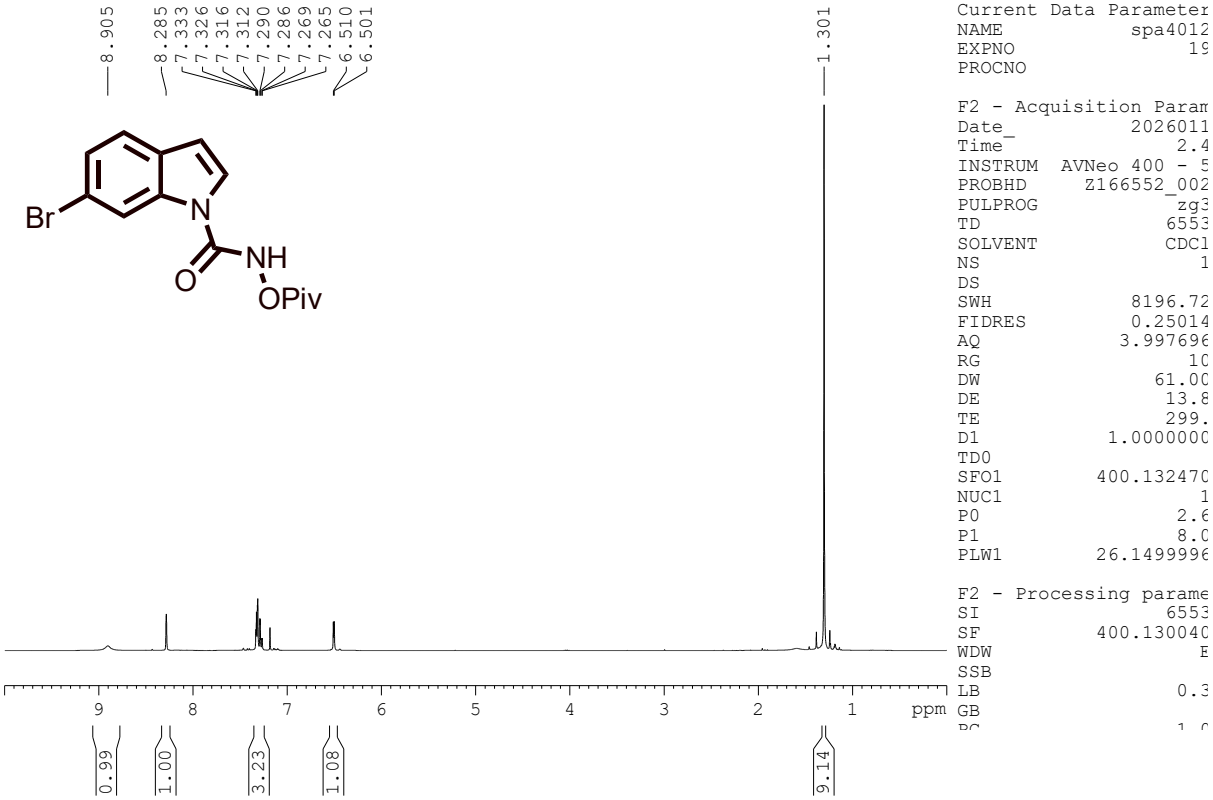


^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 1j

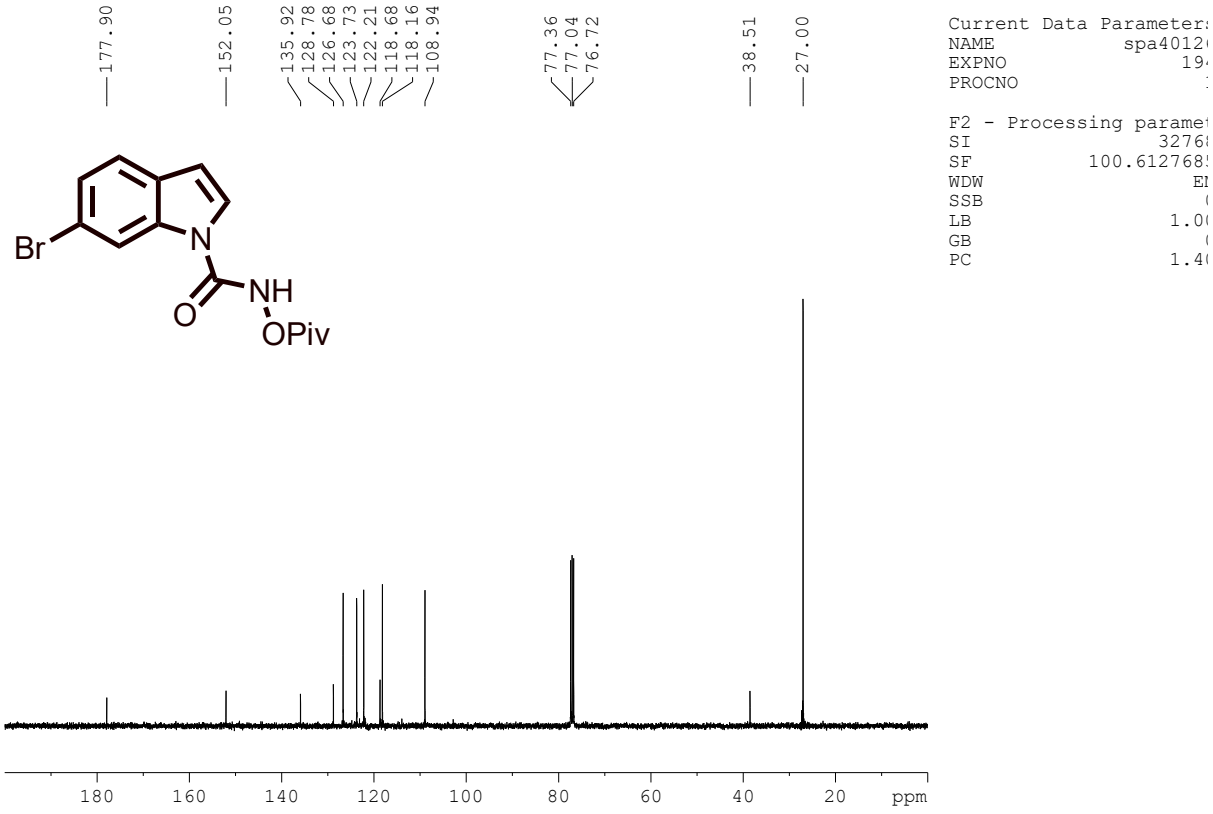


^{13}C NMR (125 MHz, $CDCl_3$) spectrum of 1j

6-bromo-N-(pivaloyloxy)-1H-indole-1-carboxamide (1k)

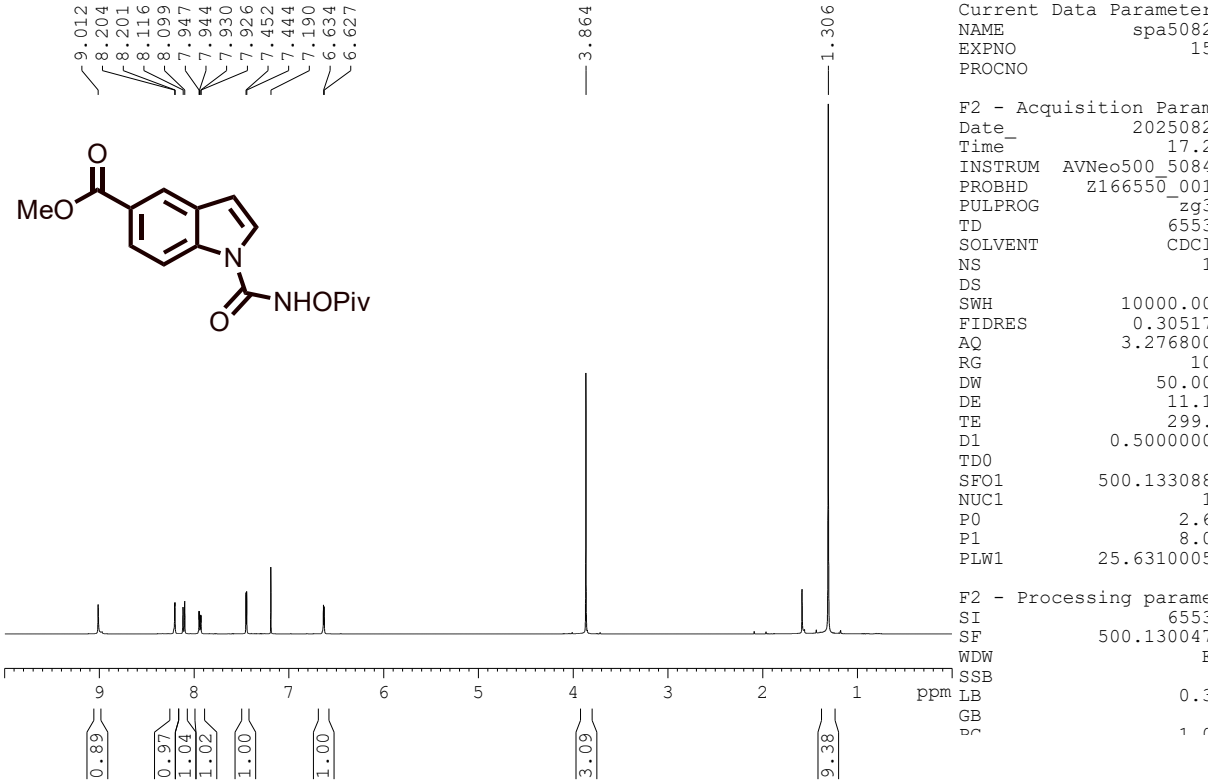


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1k

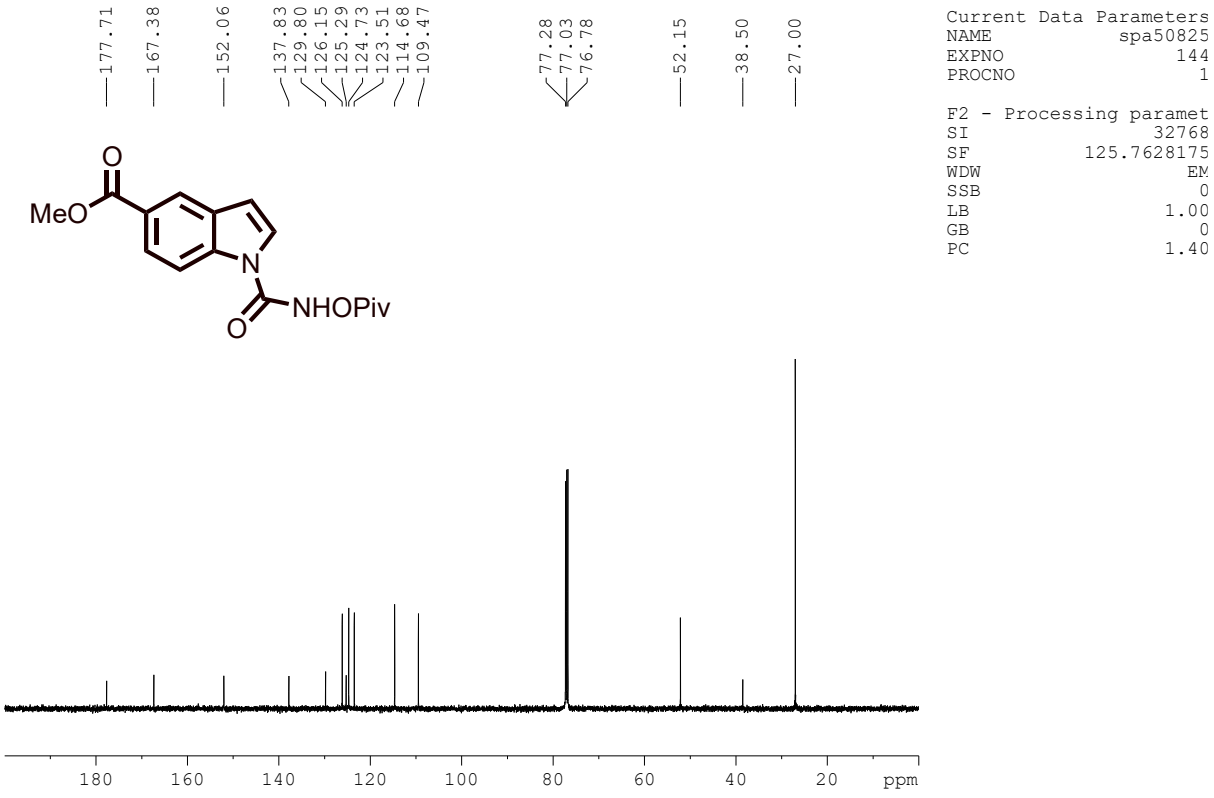


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 1k

methyl 1-((pivaloyloxy)carbamoyl)-1H-indole-5-carboxylate (1l)

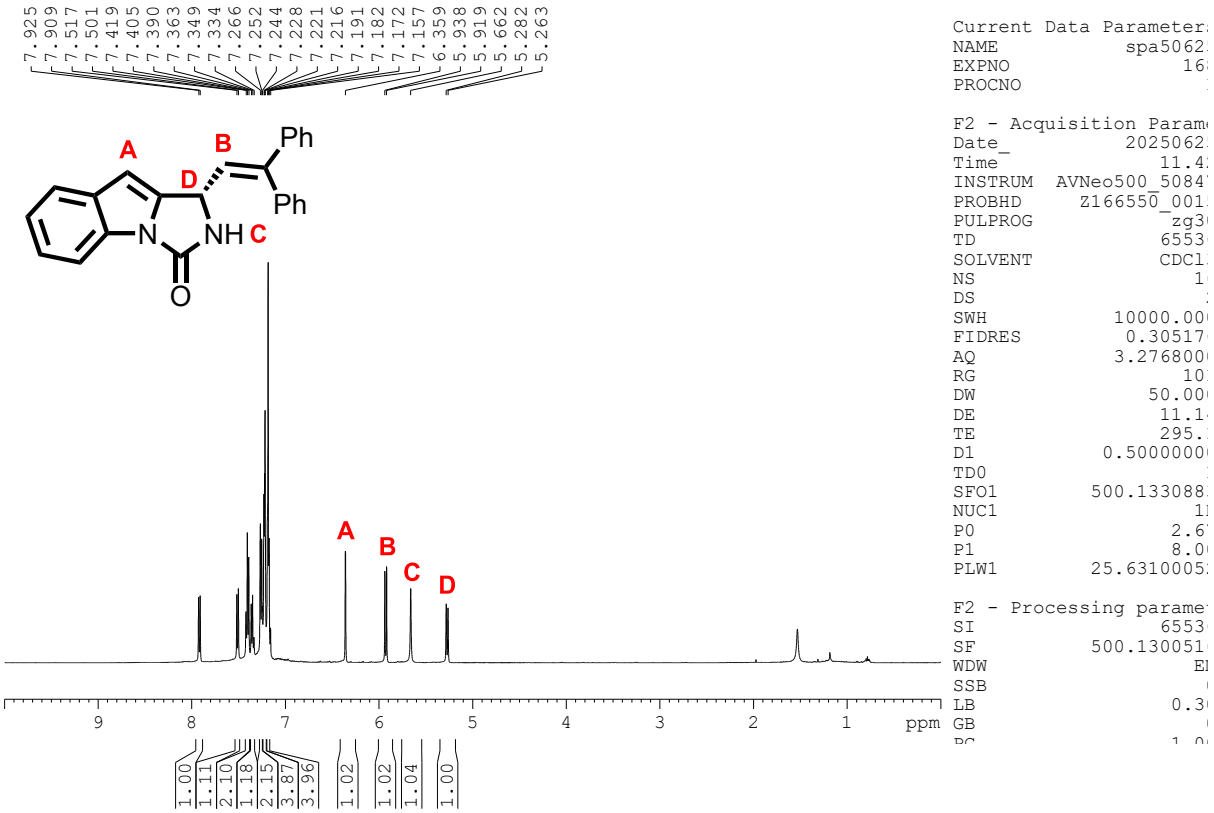


^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 1l



^{13}C NMR (125 MHz, $CDCl_3$) spectrum of 1l

(*S*)-1-(2,2-diphenylvinyl)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3a)



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EXPNO 16
PROCNO

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Time 11.4
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TD 6553
SOLVENT CDCl
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FIDRES 0.30517
AQ 3.276800
RG 10
DW 50.00
DE 11.1
TE 295.
D1 0.5000000
TD0
SFO1 500.133088
NUC1 1
P0 2.6
P1 8.0
PLW1 25.6310005

F2 - Processing parame
SI 6553
SF 500.130051
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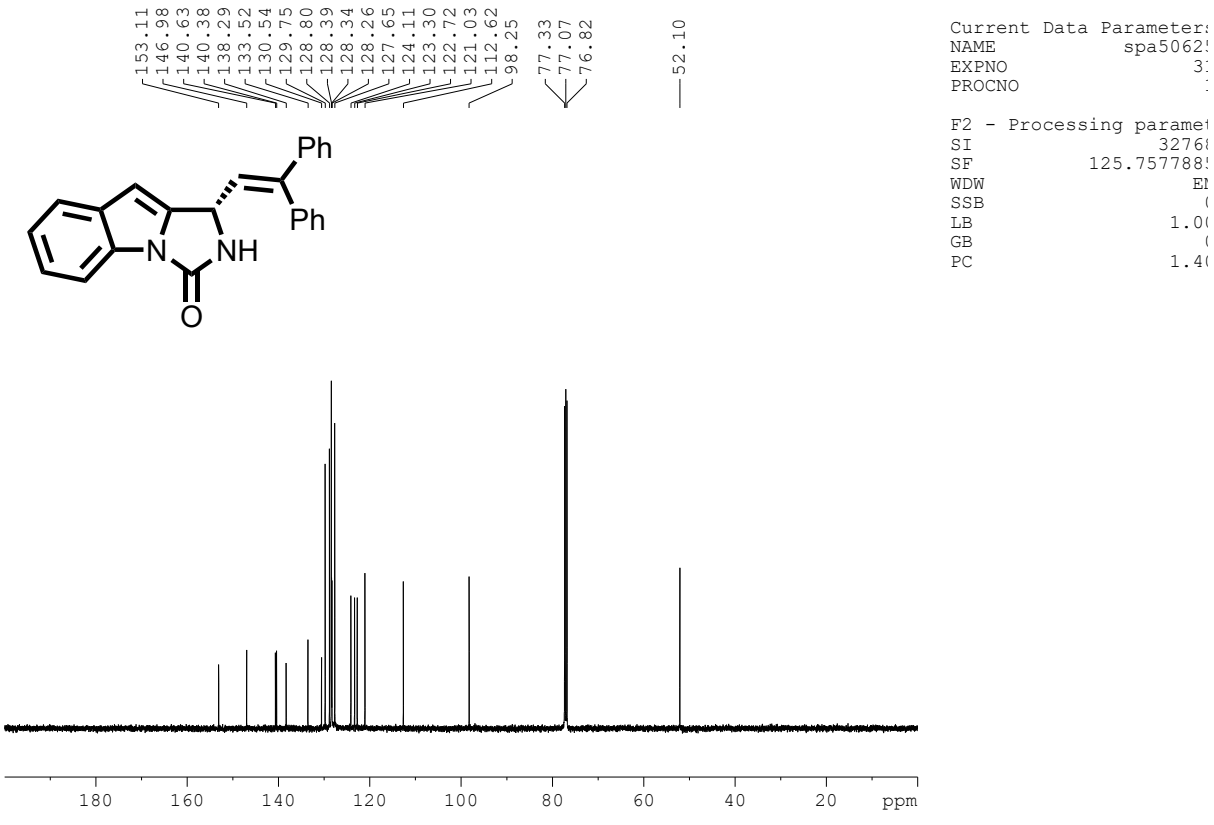
SSB
LB 0.3
GB
PC 1.0

^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3a

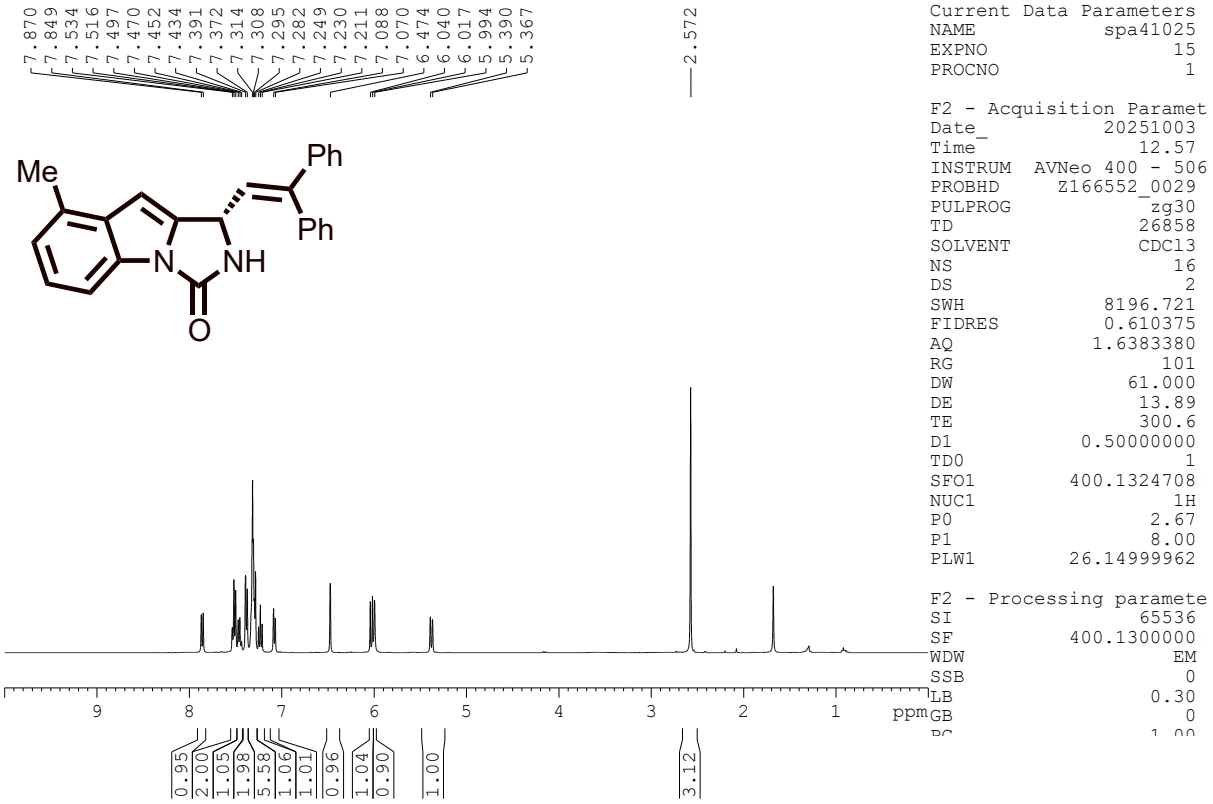


Current Data Parameter
NAME spa5062
EXPNO 3
PROCNO 1

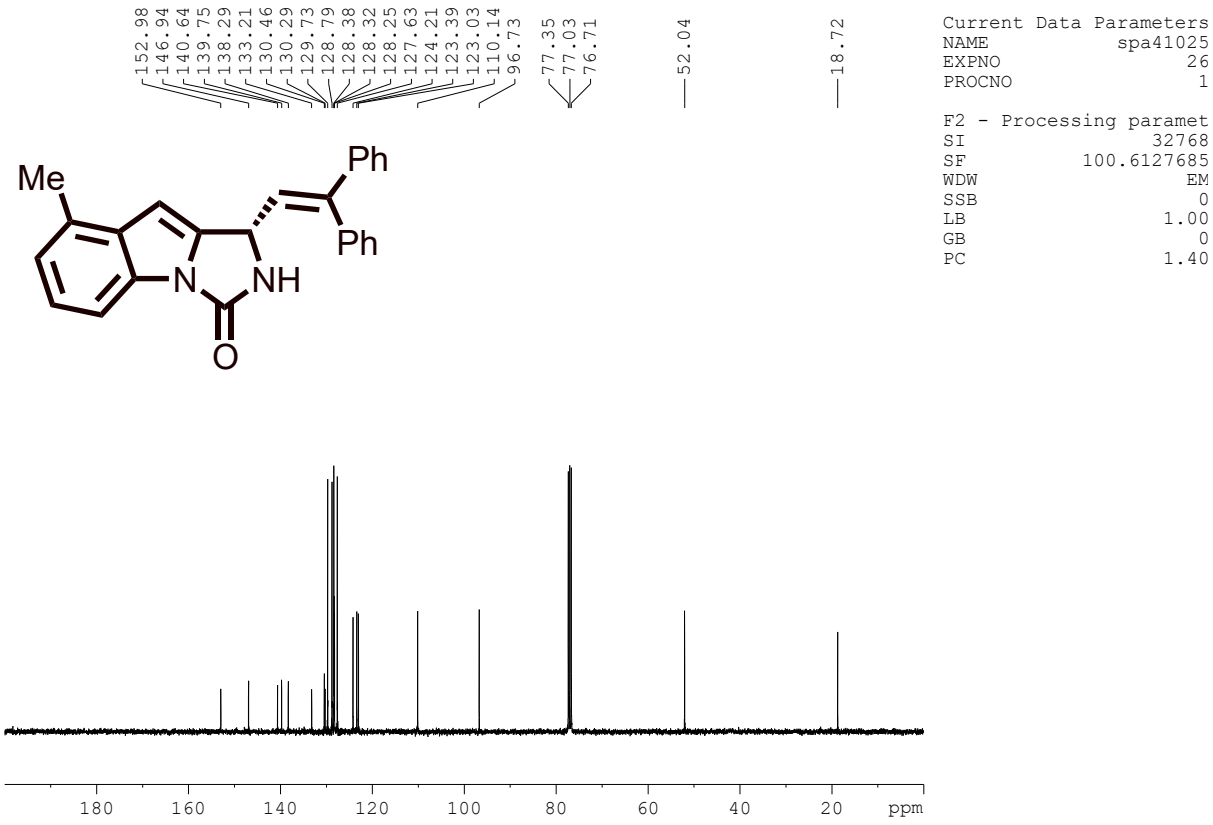
F2 - Processing parame
SI 3276
SF 125.757788
WDW E
SSB
LB 1.0
GB
PC 1.4

^{13}C NMR (125 MHz, $CDCl_3$) spectrum of 3a

(*S*)-1-(2,2-diphenylvinyl)-8-methyl-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3b)

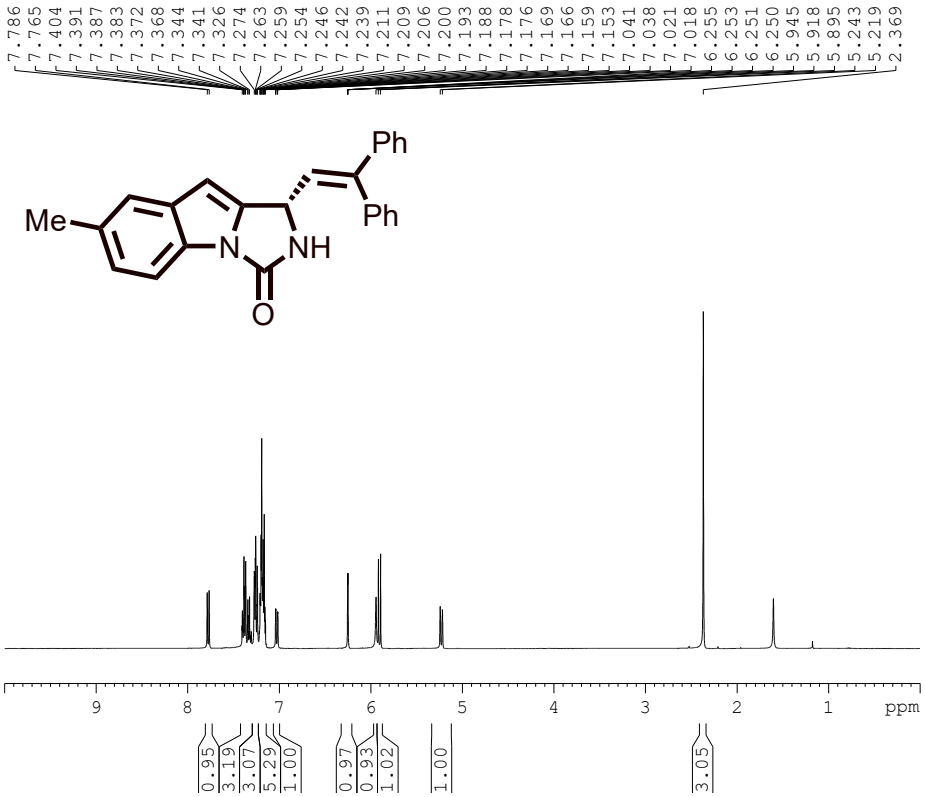


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3b



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3b

(*S*)-1-(2,2-diphenylvinyl)-7-methyl-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3c)



Current Data Parameters
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EXPNO 16
PROCNO 1

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Time 13.04
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PULPROG zg30
TD 26858
SOLVENT CDCl3
NS 16
DS 2
SWH 8196.721
FIDRES 0.610375
AQ 1.6383380
RG 101
DW 61.000
DE 13.89
TE 300.4
D1 0.50000000
TD0 1
SFO1 400.1324708
NUC1 1H
P0 2.67
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PLW1 26.14999962

F2 - Processing paramete
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SSB 0
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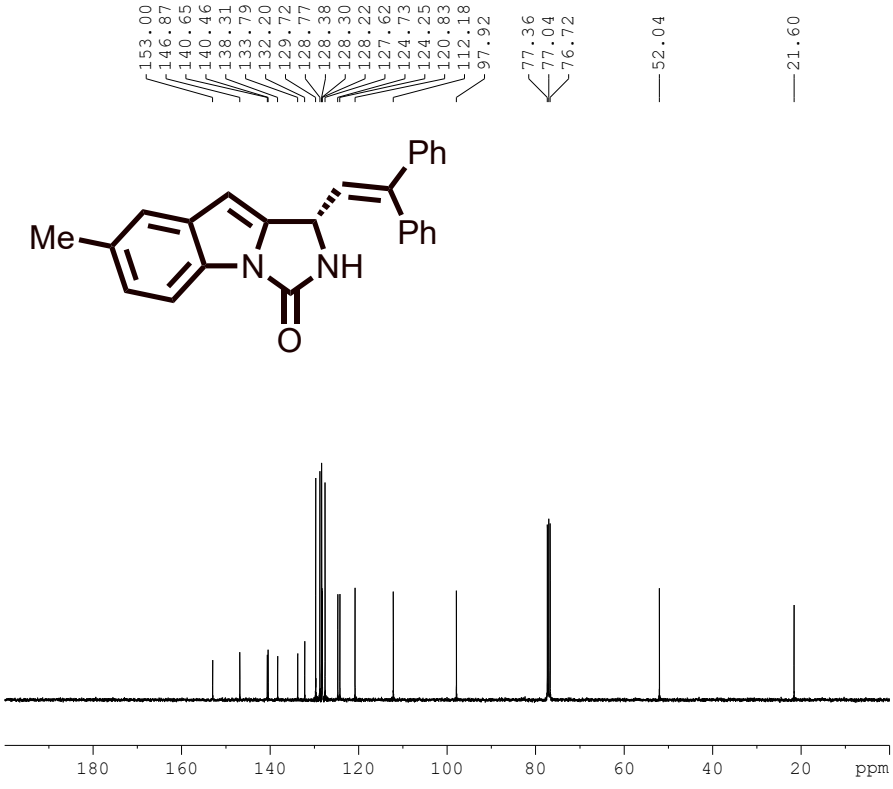
GB 0

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3c



Current Data Parameters
NAME spa41025
EXPNO 28
PROCNO 1

F2 - Processing parameters
SI 32768
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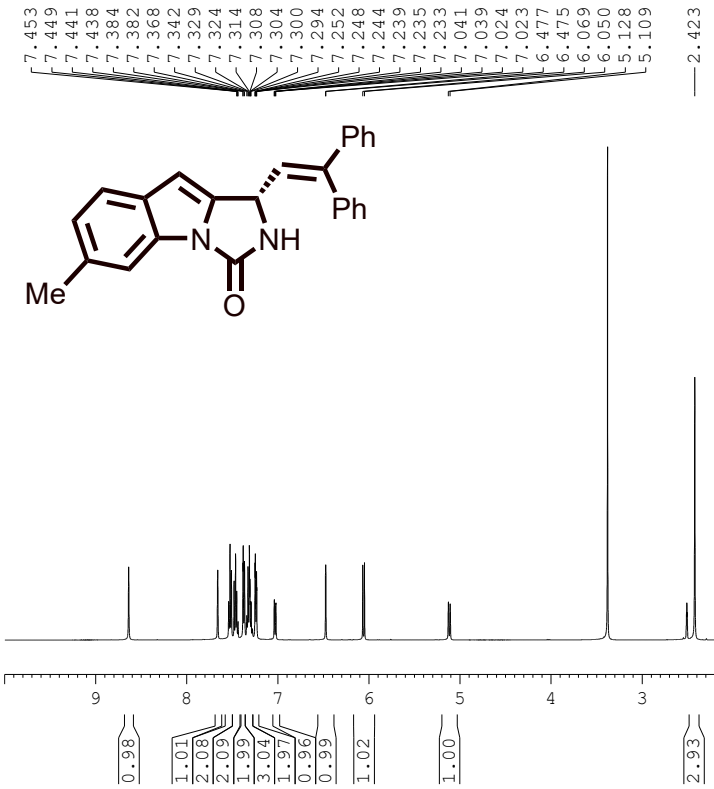
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3c

(*S*)-1-(2,2-diphenylvinyl)-6-methyl-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3d)

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PROCNO                  

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TD                 6553
SOLVENT             DMS
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DS                    
SWH            10000.00
FIDRES          0.30517
AQ             3.276800
RG                 80.
DW                50.00
DE                11.1
TE                295.
D1             0.500000
TD0                   
SFO1          500.13308
NUC1                  1
P0                 2.6
P1                 8.0
PLW1          25.631000

F2 - Processing parame
SI                 6553
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WDW                   E
SSB                   
LB                 0.3
GB                    
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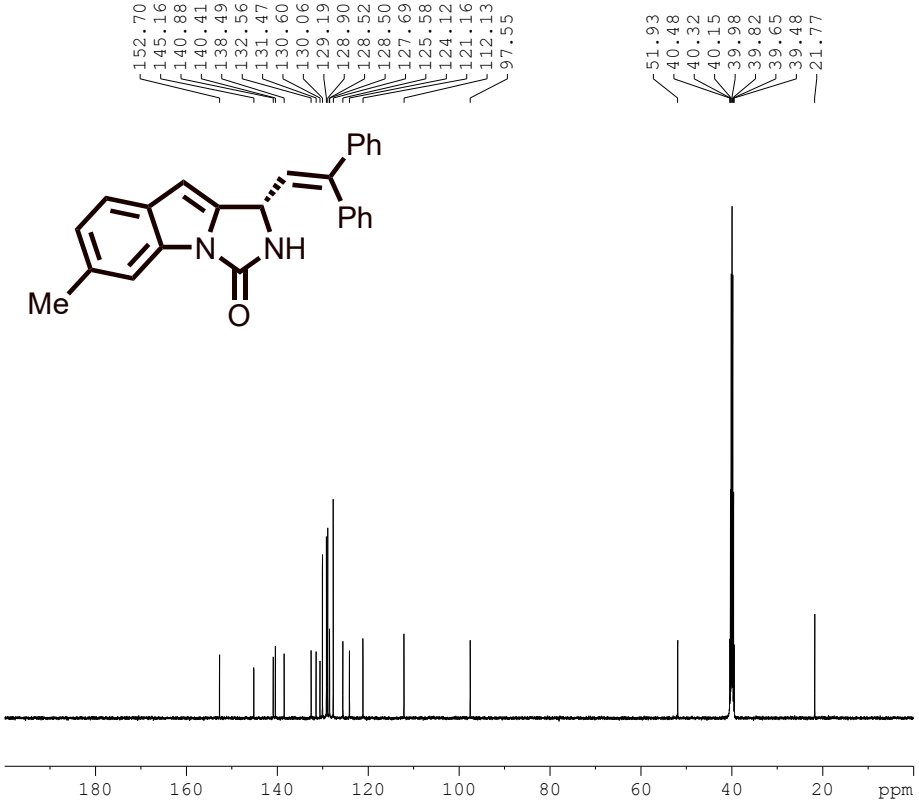
^{1}H NMR (500 MHz, DMSO-d_6) spectrum of 3d

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Current Data Parameter
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EXPNO                   
PROCNO                  

F2 - Processing parame
SI                 3276
SF           125.757788
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SSB                   
LB                 1.0
GB                    
PC                 1.4
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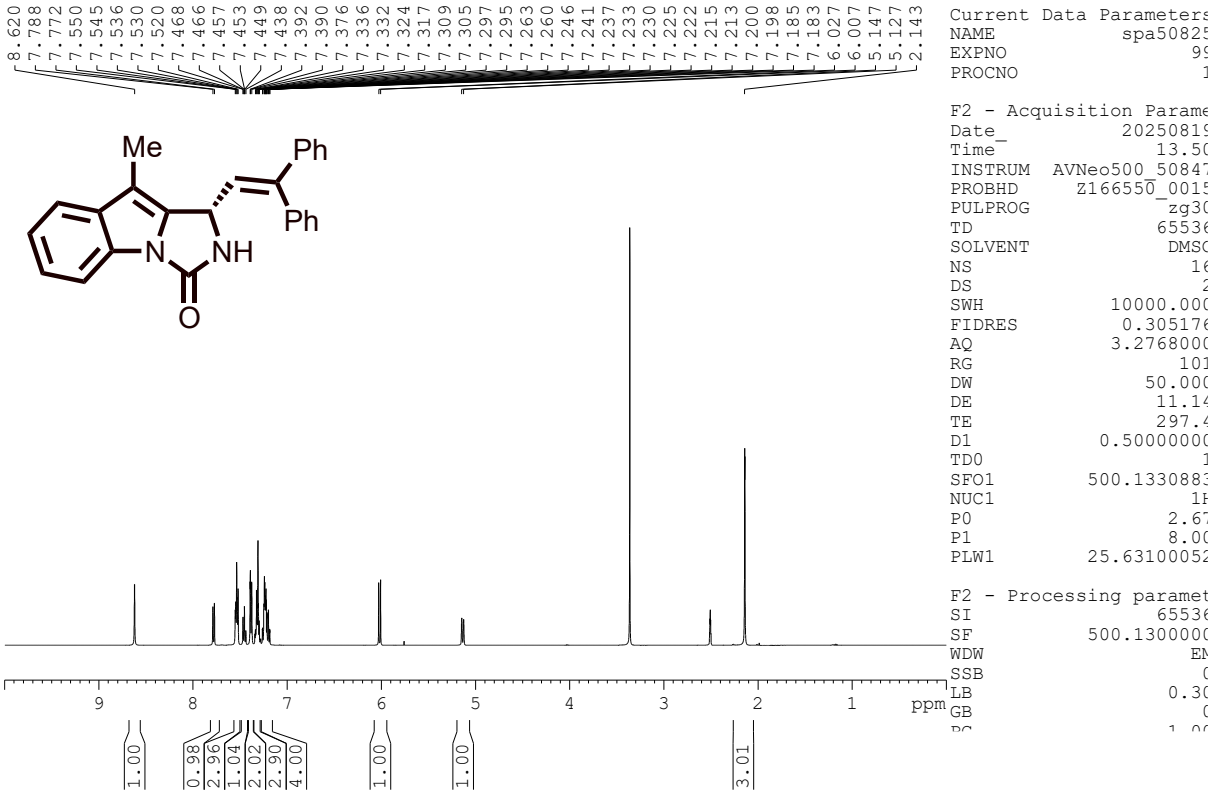
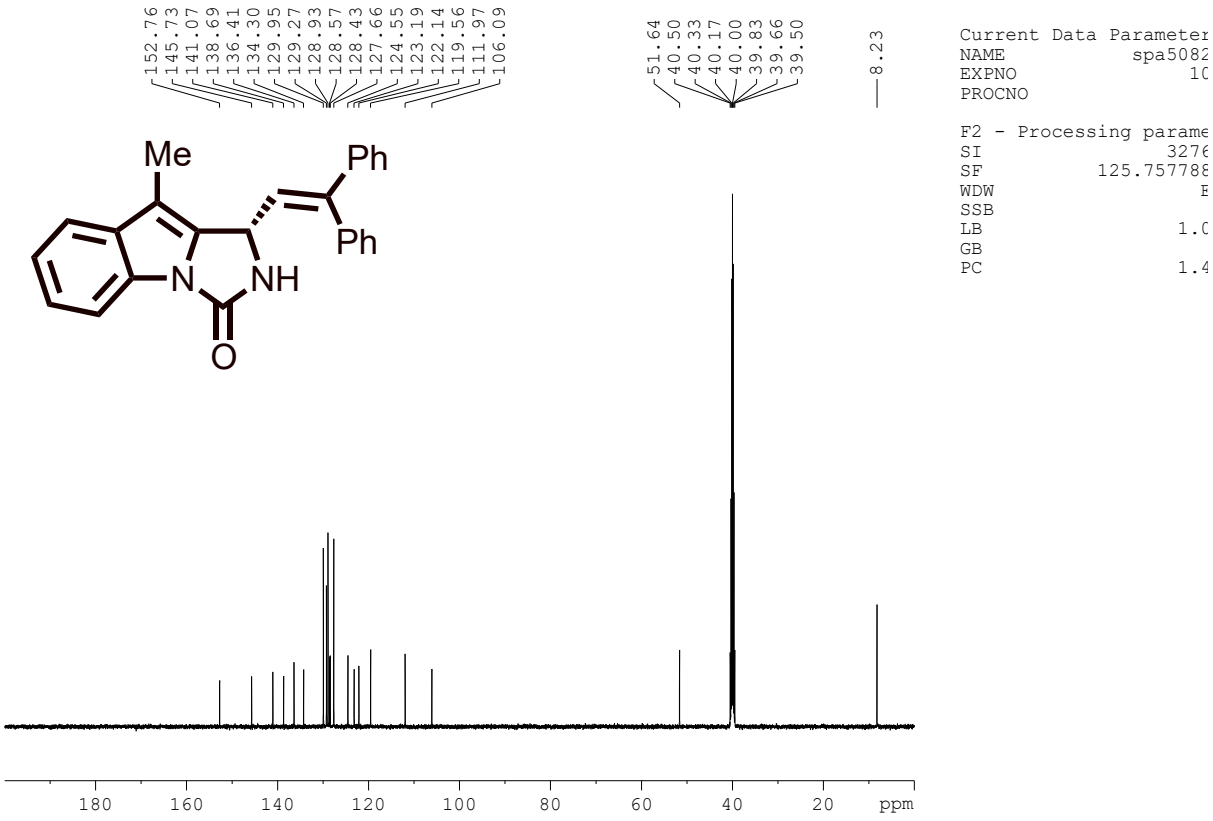
^{13}C NMR (125 MHz, DMSO-d_6) spectrum of 3d

(*S*)-1-(2,2-diphenylvinyl)-9-methyl-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3e)

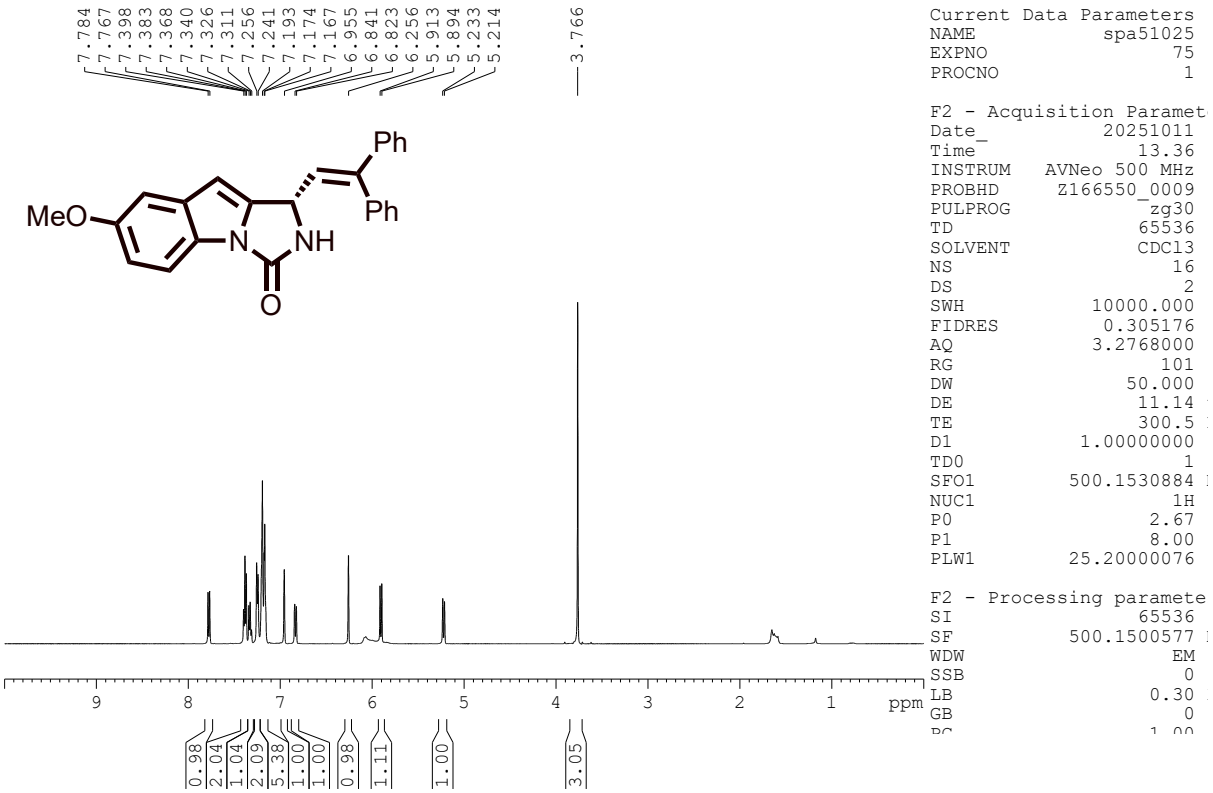


^{1}H NMR (500 MHz, DMSO-*d*$_6$) spectrum of 3e

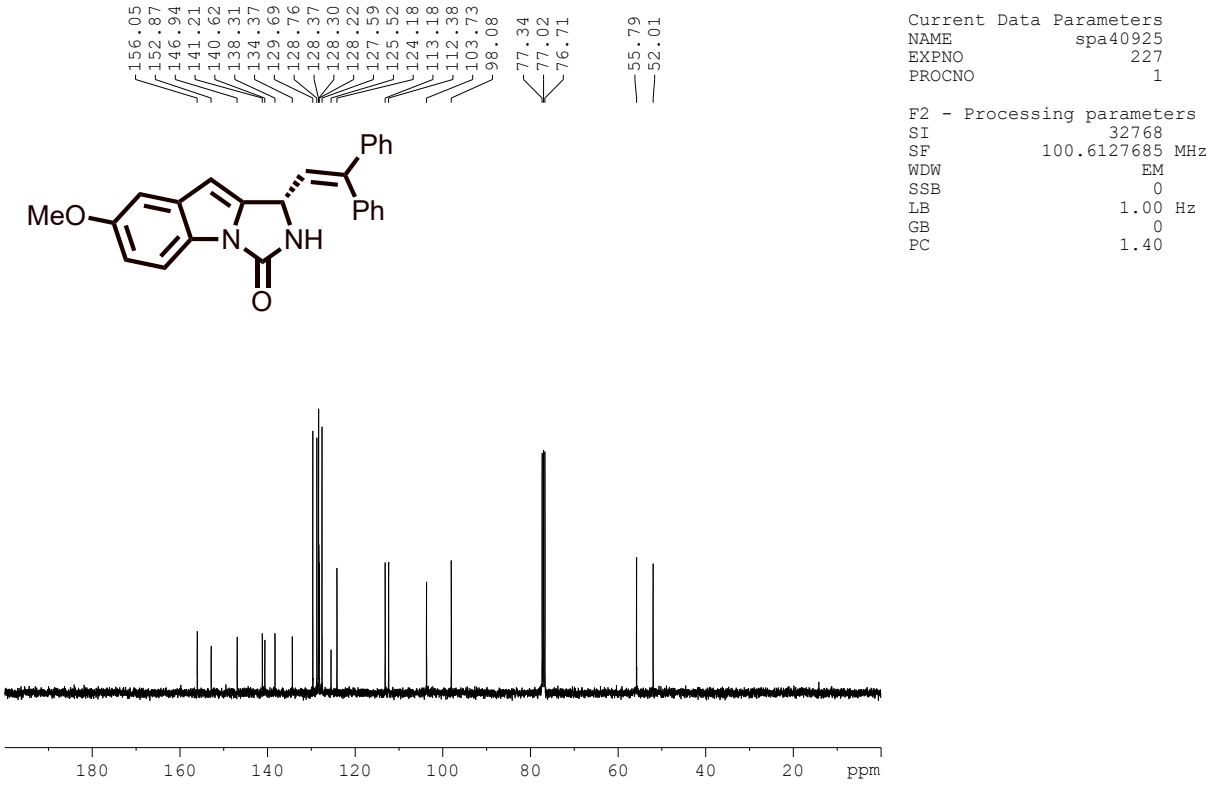


^{13}C NMR (125 MHz, DMSO-*d*$_6$) spectrum of 3e

(*S*)-1-(2,2-diphenylvinyl)-7-methoxy-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3f)

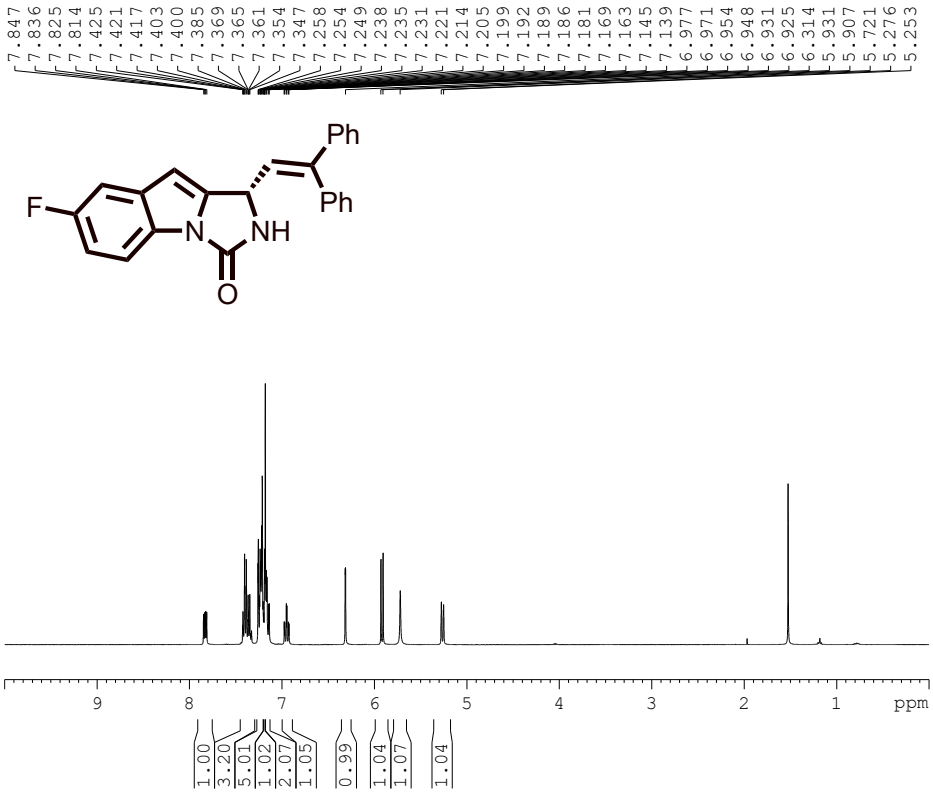


^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3f



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3f

(*S*)-1-(2,2-diphenylvinyl)-7-fluoro-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3g)

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PROCNO

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FIDRES         0.61037
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P1                 8.0
PLW1        26.1499996

F2 - Processing parame
SI                6553
SF          400.130040
WDW                  E
SSB
LB                 0.3
GB
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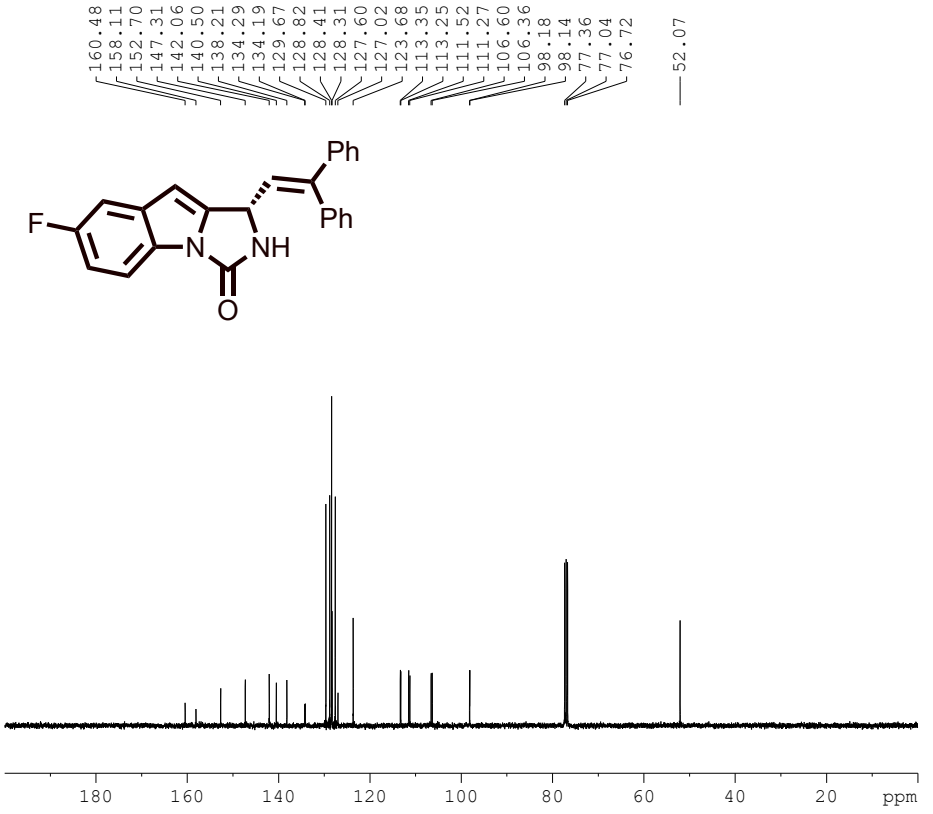
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3g

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Current Data Parameter
NAME            spa4092
EXPNO                 23
PROCNO

F2 - Processing parame
SI                3276
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SSB
LB                 1.0
GB
PC                 1.4
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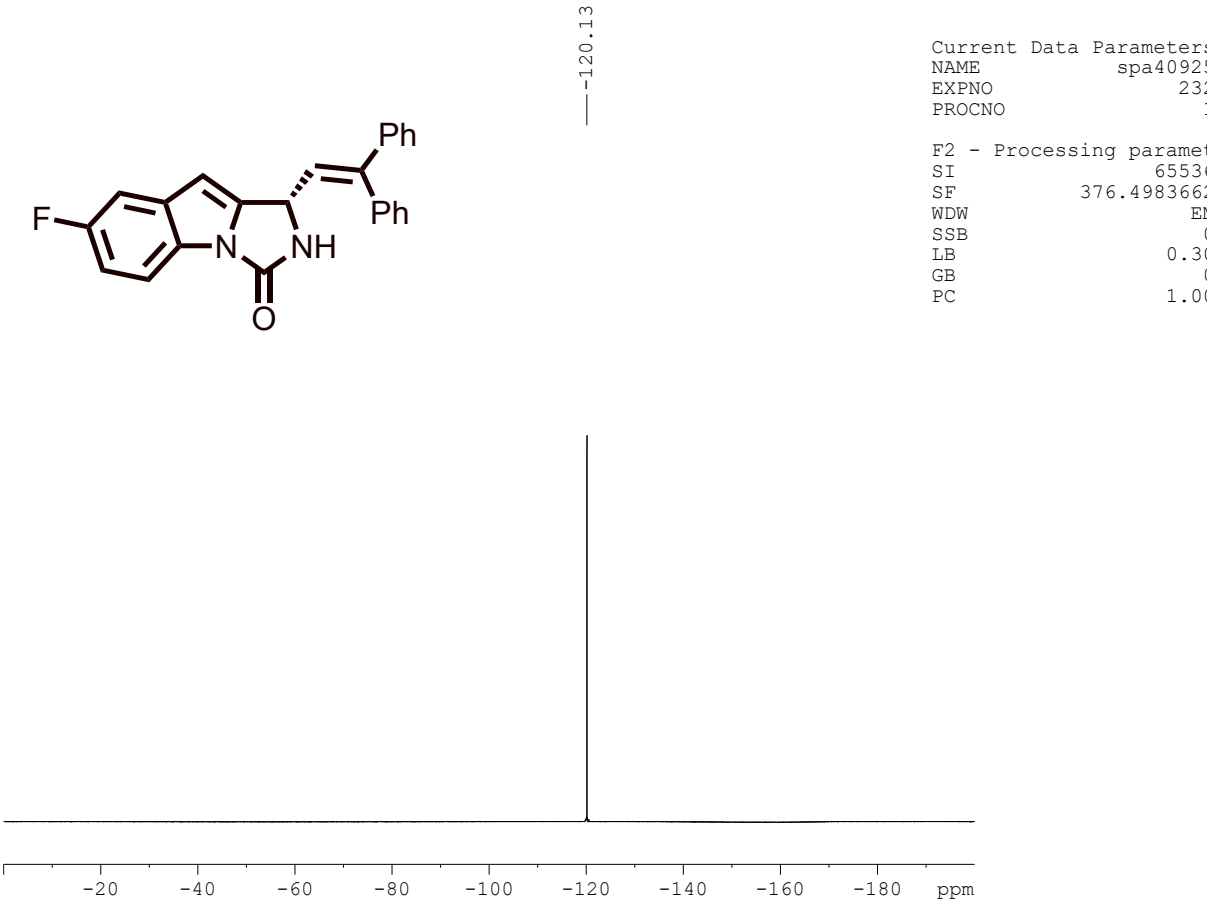
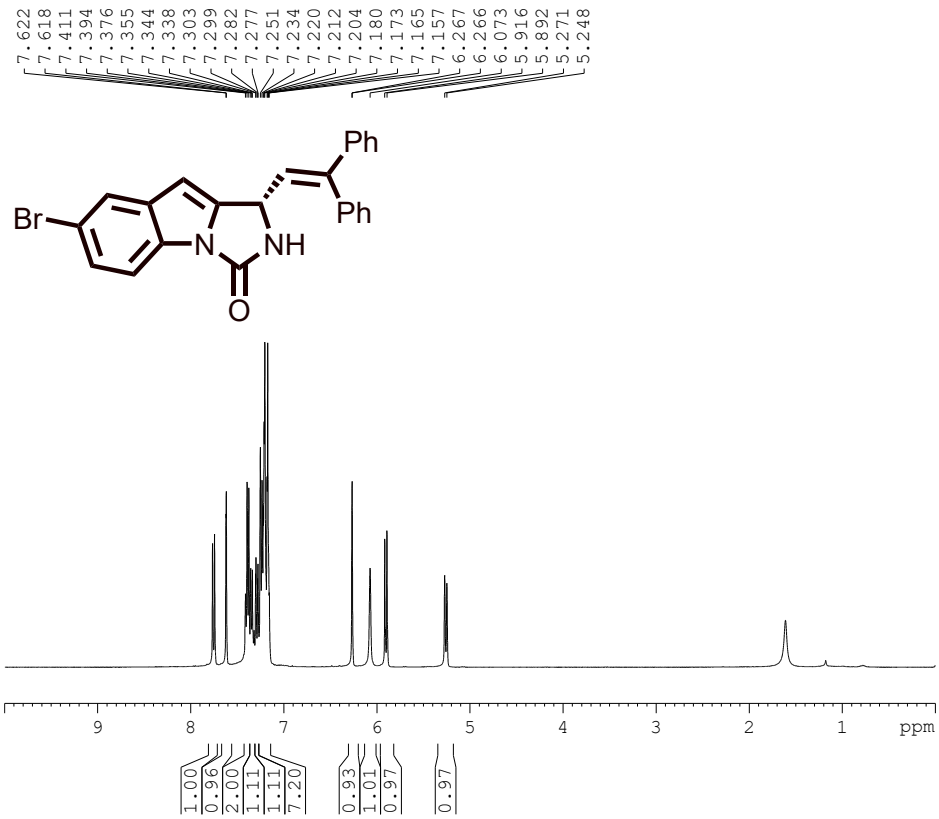
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3g



^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3g

(*S*)-7-bromo-1-(2,2-diphenylvinyl)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3h)

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EXPNO                 9
PROCNO

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PULPROG              zg3
TD                2685
SOLVENT           CDCl
NS                   1
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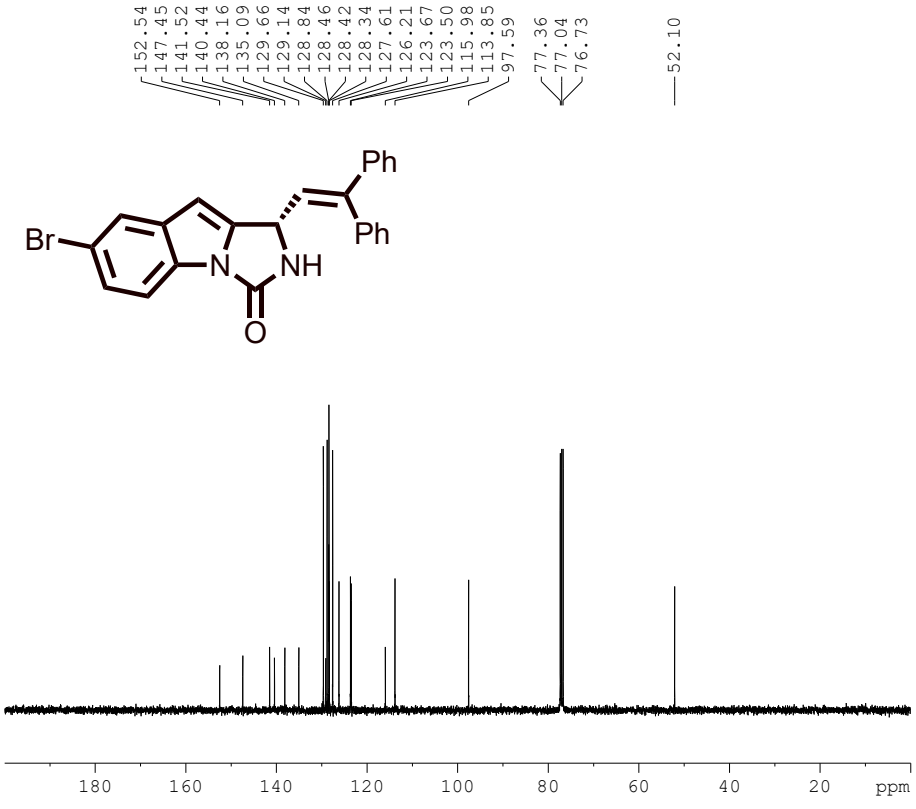
SWH            8196.72
FIDRES         0.61037
AQ            1.638338
RG                  10
DW                61.00
DE                 13.8
TE                300.
D1           0.5000000
TD0
SFO1        400.132470
NUC1                 1
P0                 2.6
P1                 8.0
PLW1        26.1499996

F2 - Processing parame
SI                6553
SF          400.130044
WDW                  E
SSB
LB                 0.3
GB
```

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3h

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Current Data Parameters
NAME            spa40925
EXPNO                 84
PROCNO                 1

F2 - Processing paramet
SI                32768
SF          100.6127685
WDW                  EM
SSB                   0
LB                 1.00
GB                    0
PC                 1.40
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^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3h

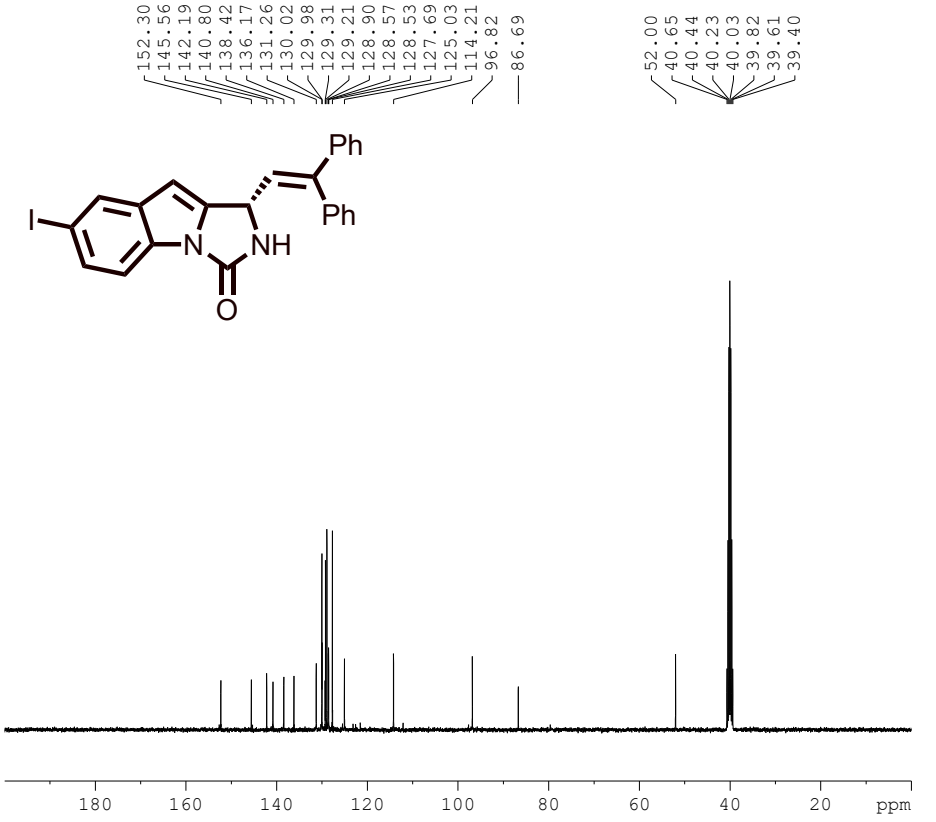
(*S*)-1-(2,2-diphenylvinyl)-7-iodo-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3i)

Current Data Parameters
NAME spa41025
EXPNO 34
PROCNO 1

F2 - Acquisition Parame
Date_ 20251004
Time 0.56
INSTRUM AVNeo 400 - 50
PROBHD Z166552_0029
PULPROG zg30
TD 26858
SOLVENT DMSO
NS 16
DS 2
SWH 8196.721
FIDRES 0.610375
AQ 1.6383380
RG 101
DW 61.000
DE 13.89
TE 300.9
D1 0.50000000
TD0 1
SFO1 400.1324708
NUC1 1H
P0 2.67
P1 8.00
PLW1 26.14999962

F2 - Processing paramet
SI 65536
SF 400.1300000
WDW EM
SSB 0
LB 0.30
GB 0

^{1}H NMR (400 MHz, DMSO-*d*$_6$) spectrum of 3i

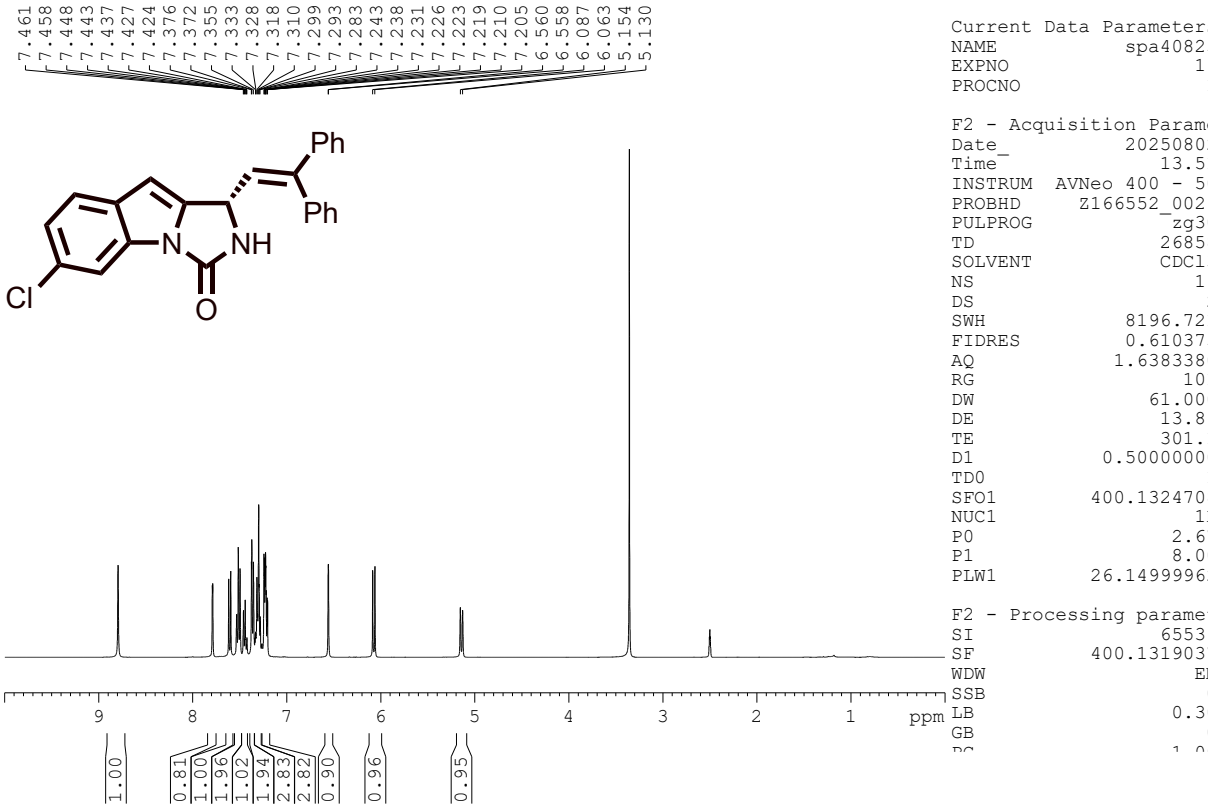


Current Data Parameters
NAME spa41025
EXPNO 35
PROCNO 1

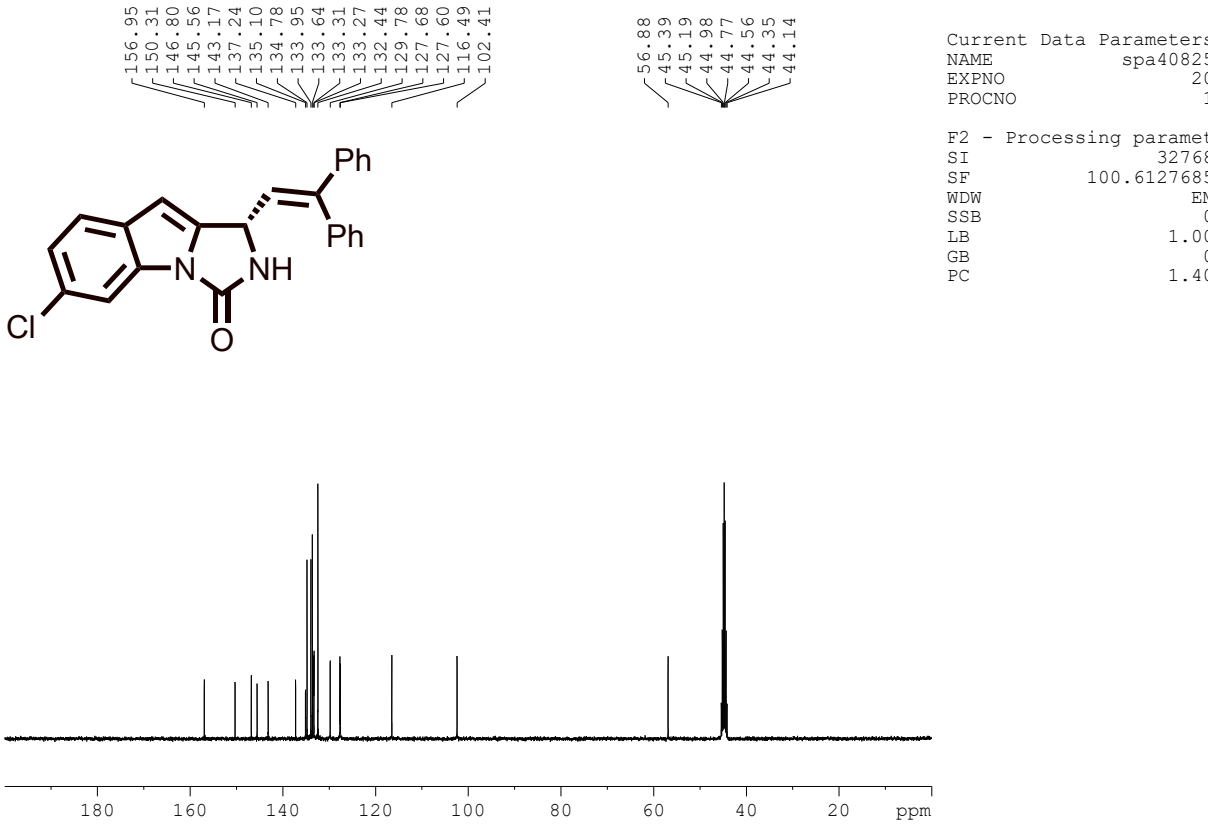
F2 - Processing paramet
SI 32768
SF 100.6127685
WDW EM
SSB 0
LB 1.00
GB 0
PC 1.40

^{13}C NMR (100 MHz, DMSO-*d*$_6$) spectrum of 3i

(*S*)-6-chloro-1-(2,2-diphenylvinyl)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3j)



^{1}H NMR (400 MHz, DMSO-*d*$_6$) spectrum of 3j



^{13}C NMR (100 MHz, DMSO-*d*$_6$) spectrum of 3j

(*S*)-6-bromo-1-(2,2-diphenylvinyl)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3k)


```
Current Data Parameters
NAME            spa51025
EXPNO                 62
PROCNO                 1

F2 - Acquisition Parame
Date_           20251011
Time                13.09
INSTRUM  AVNeo500_50847
PROBHD     Z166550_0015
PULPROG             zg30
TD                 65536
SOLVENT             DMSO
NS                    16
DS                     2
SWH            10000.000
FIDRES          0.305176
AQ             3.2768000
RG                   101
DW                50.000
DE                11.14
TE                295.8
D1           0.50000000
TD0                    1
SFO1         500.1330883
NUC1                  1H
P0                 2.67
P1                 8.00
PLW1         25.631000520

F2 - Processing paramet
SI                 65536
SF           500.1300000
WDW                   EM
SSB                    0
LB                  0.30
GB                     0
PC                  1.00
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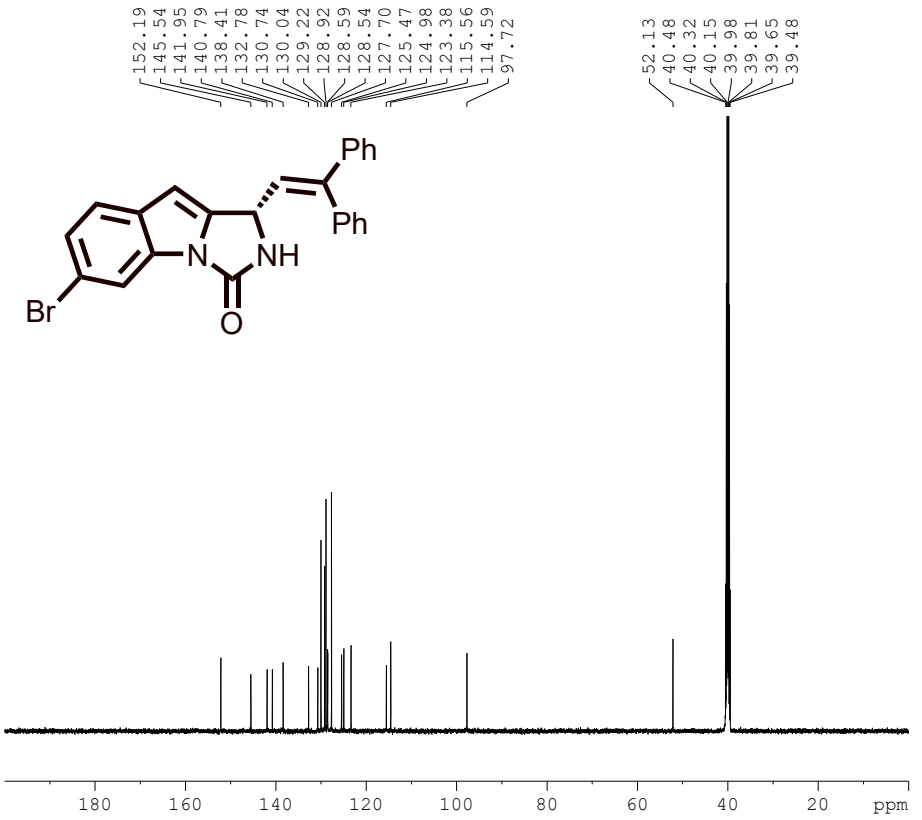
^{1}H NMR (500 MHz, DMSO-*d*$_6$) spectrum of 3k

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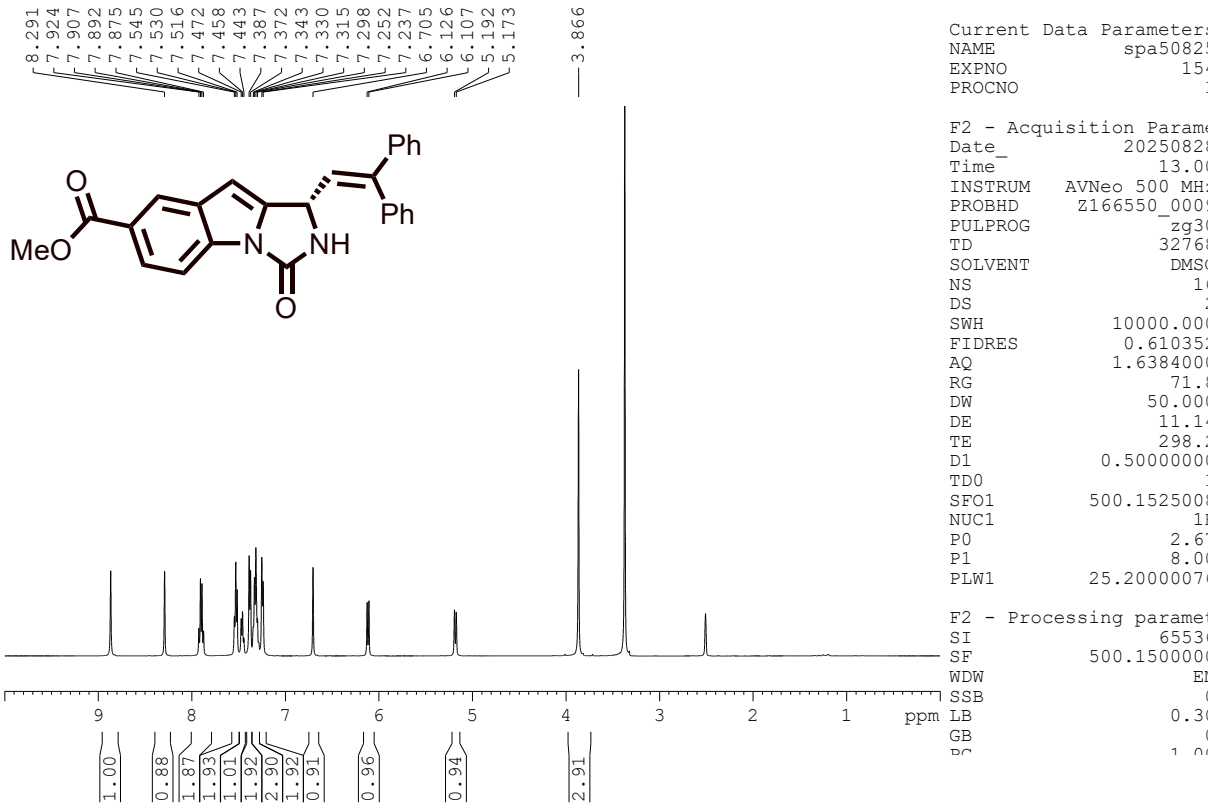
Current Data Parameter
NAME            spa5102
EXPNO                 6
PROCNO

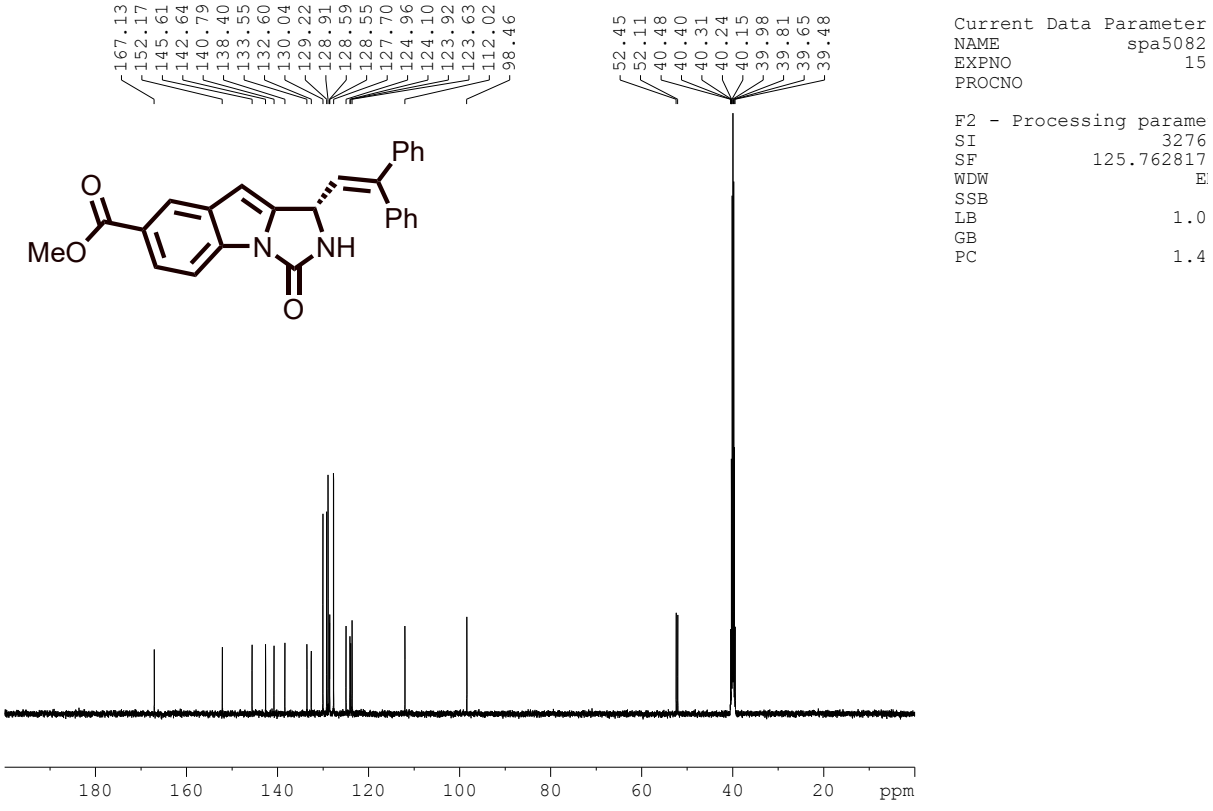
F2 - Processing parame
SI                 3276
SF          125.7577888
WDW                   E
SSB
LB                  1.00
GB
PC                  1.40
```

^{13}C NMR (125 MHz, DMSO-*d*$_6$) spectrum of 3k

methyl (*S*)-1-(2,2-diphenylvinyl)-3-oxo-2,3-dihydro-1H-imidazo[1,5-a]indole-7-carboxylate (3l)

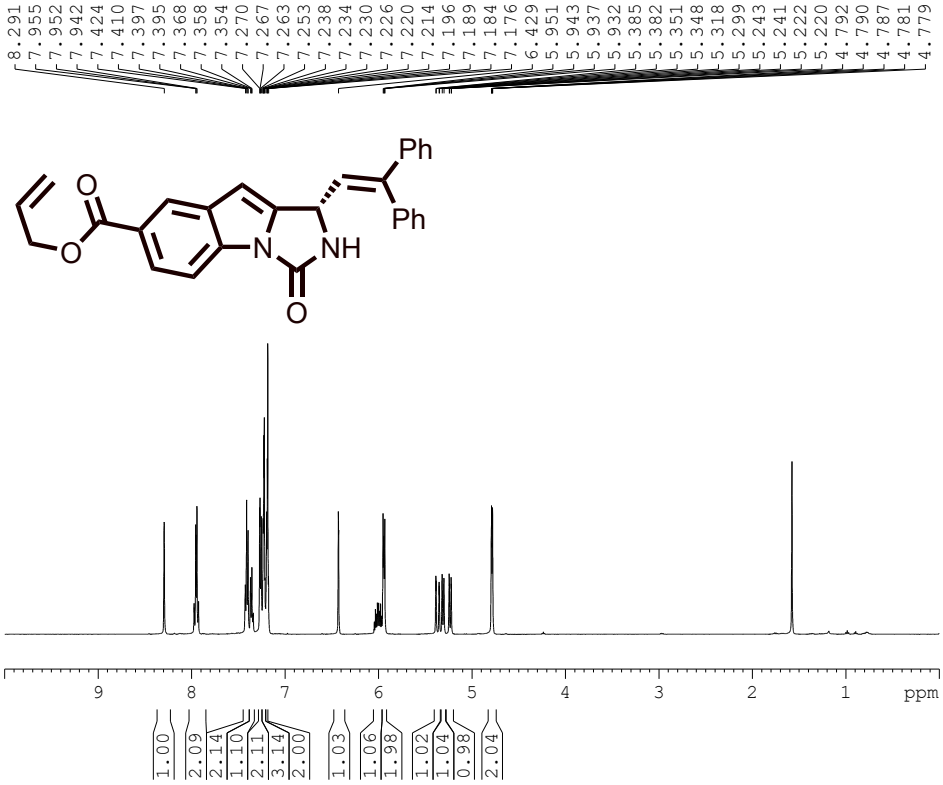


^{1}H NMR (500 MHz, DMSO-d_6) spectrum of 3l



^{13}C NMR (125 MHz, DMSO-d_6) spectrum of 3l

allyl (*S*)-1-(2,2-diphenylvinyl)-3-oxo-2,3-dihydro-1H-imidazo[1,5-a]indole-7-carboxylate (3m)

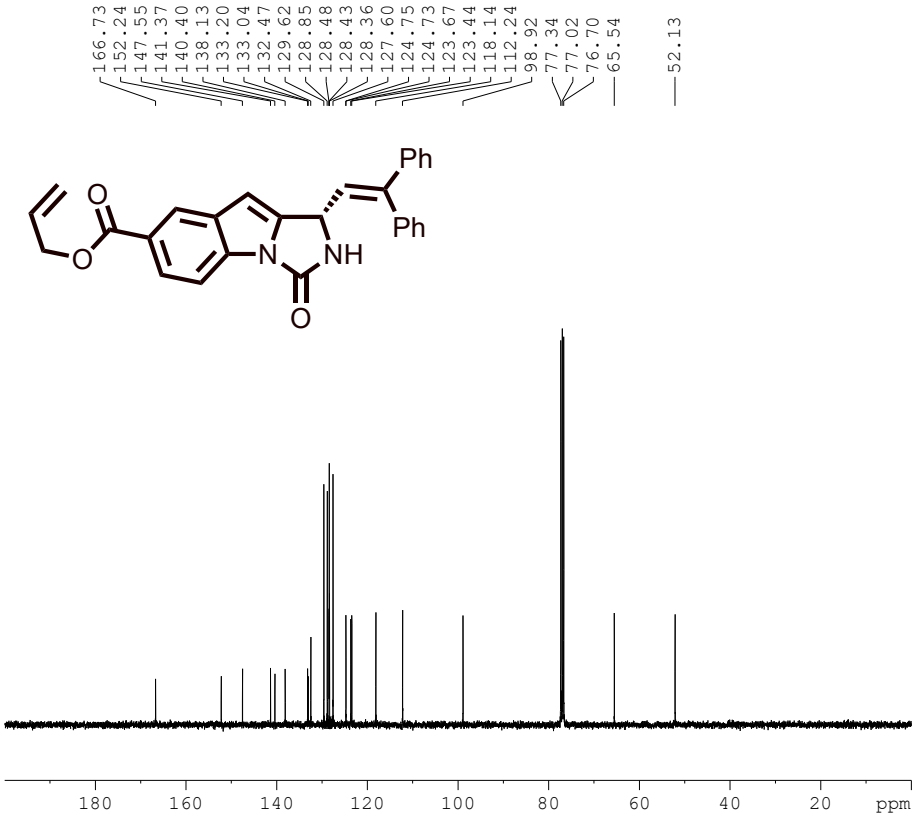


Current Data Parameters
NAME spa50925
EXPNO 133
PROCNO 1

F2 - Acquisition Parame
Date_ 20251001
Time 11.46
INSTRUM AVNeo500_5084
PROBHD Z166550_0015
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10000.000
FIDRES 0.305176
AQ 3.2768000
RG 101
DW 50.000
DE 11.14
TE 294.4
D1 0.50000000
TD0 1
SFO1 500.1330883
NUC1 1H
P0 2.67
P1 8.00
PLW1 25.63100052

F2 - Processing paramet
SI 65536
SF 500.1300495
WDW EM
SSB 0
LB 0.30
GB 0

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3m

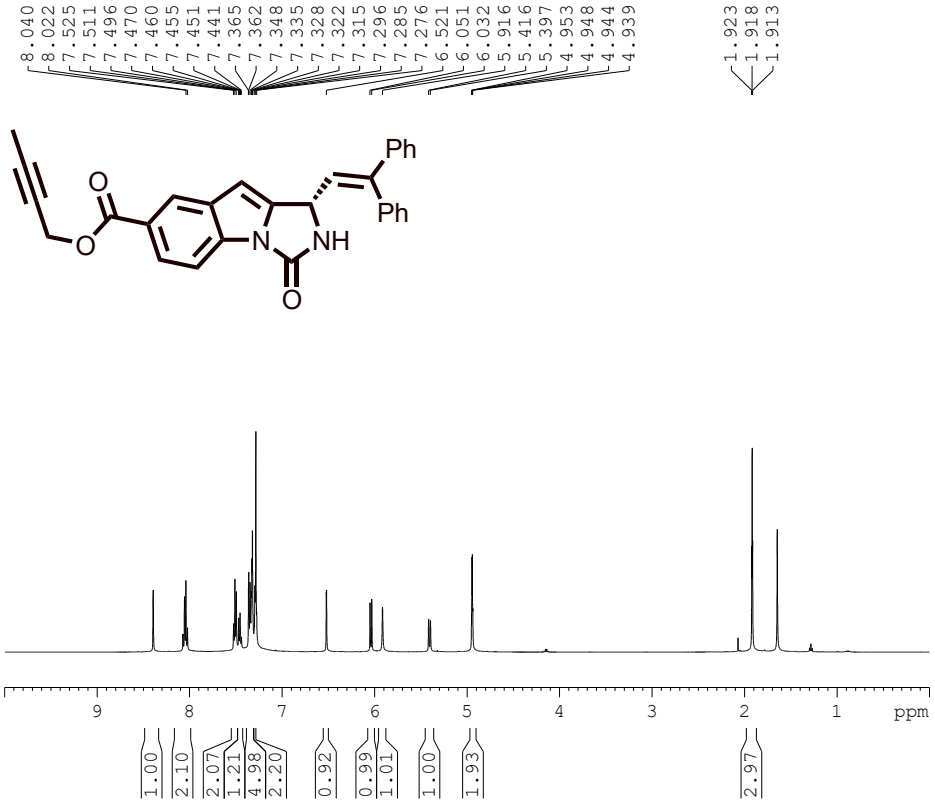


Current Data Parameters
NAME spa41025
EXPNO 1
PROCNO 1

F2 - Processing paramet
SI 32768
SF 100.6127685
WDW EM
SSB 0
LB 1.00
GB 0
PC 1.40

^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3m

but-2-yn-1-yl (*S*)-1-(2,2-diphenylvinyl)-3-oxo-2,3-dihydro-1H-imidazo[1,5-a]indole-7-carboxylate (3n)

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Current Data Parameters
NAME            spa50925
EXPNO                131
PROCNO                 1

F2 - Acquisition Parame
Date_           20250930
Time                11.59
INSTRUM  AVNeo500_50847
PROBHD     Z166550_0015
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            10000.000
FIDRES          0.305176
AQ             3.2768000
RG                   101
DW                50.000
DE                 11.14
TE                 297.1
D1            0.50000000
TD0                    1
SFO1          500.1330883
NUC1                  1H
P0                  2.67
P1                  8.00
PLW1          25.63100052

F2 - Processing paramet
SI                 65536
SF            500.1300000
WDW                   EM
SSB                    0
LB                  0.30
GB                     0
```
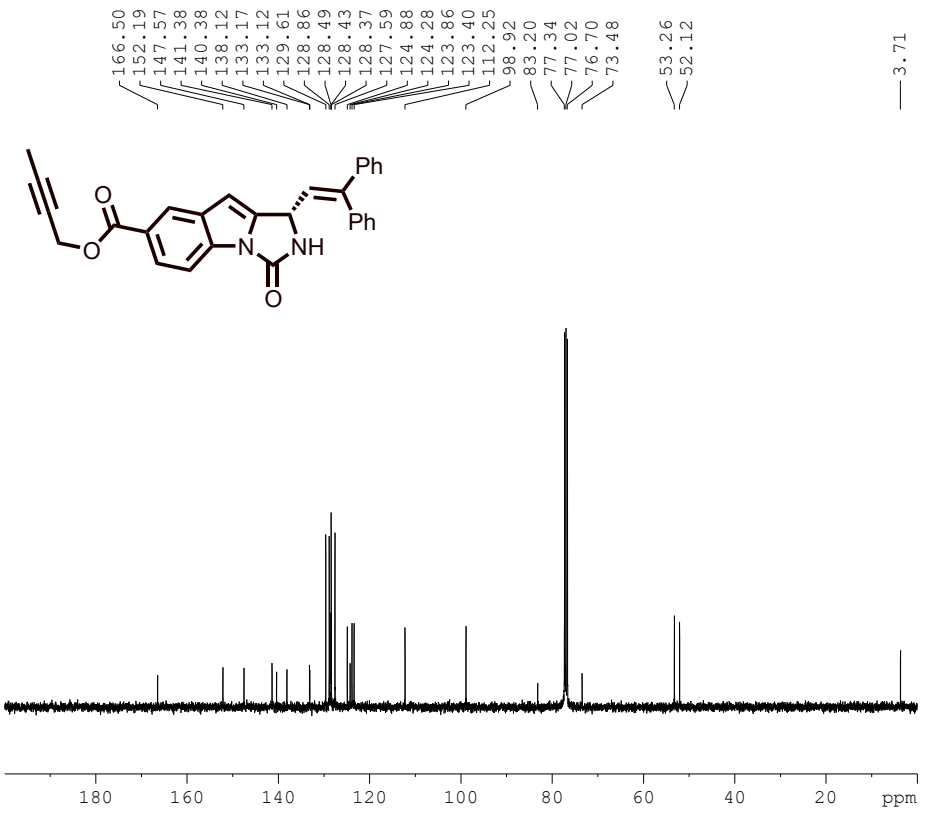

^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3n

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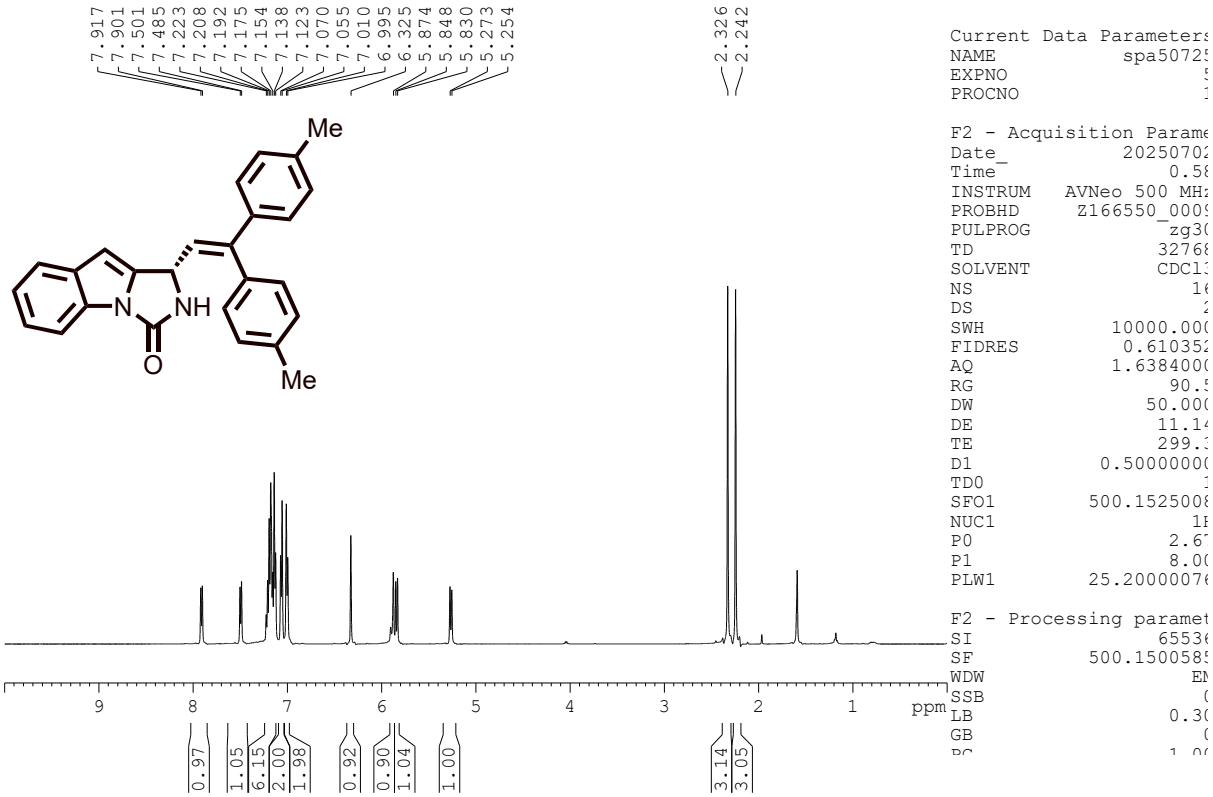
Current Data Parameter
NAME            spa4102
EXPNO
PROCNO

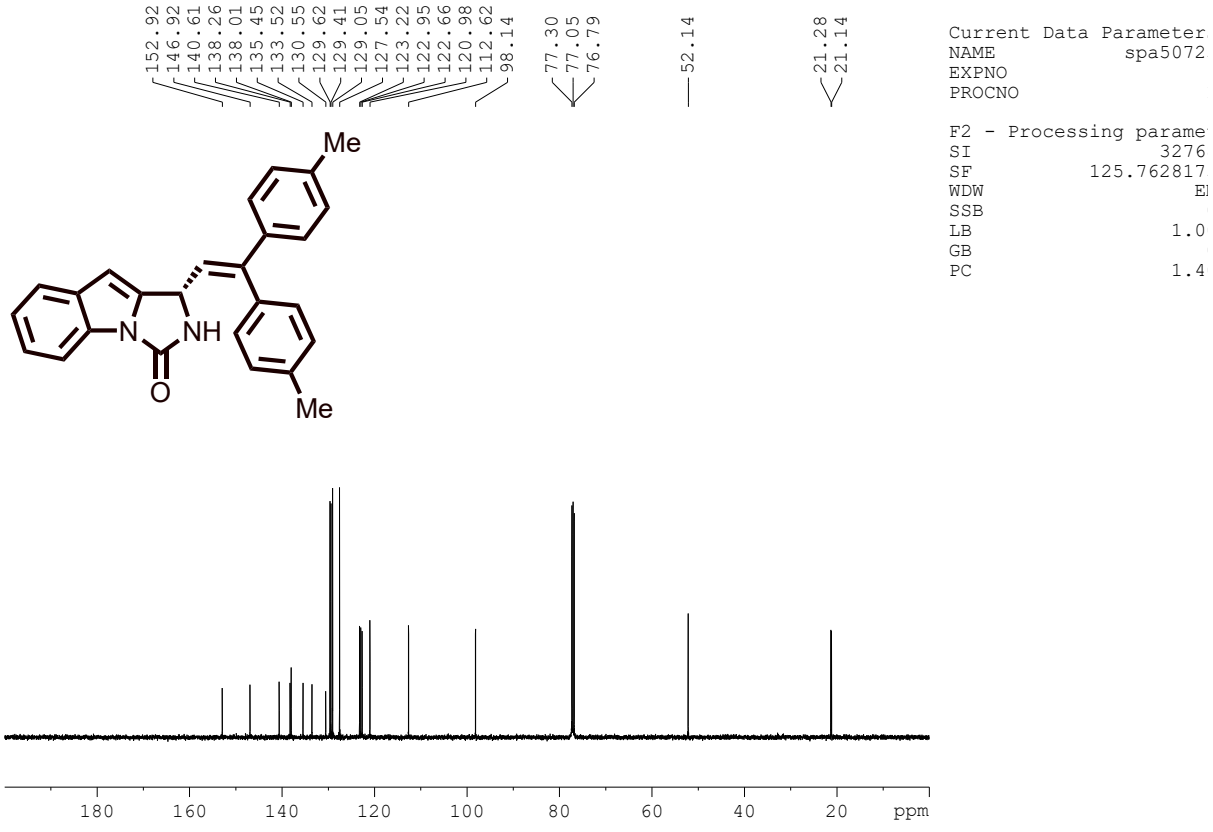
F2 - Processing parame
SI                 3276
SF          100.612768
WDW                   E
SSB
LB                  1.0
GB
PC                  1.4
```

^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3n

(*S*)-1-(2,2-di-p-tolylvinyl)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3o)

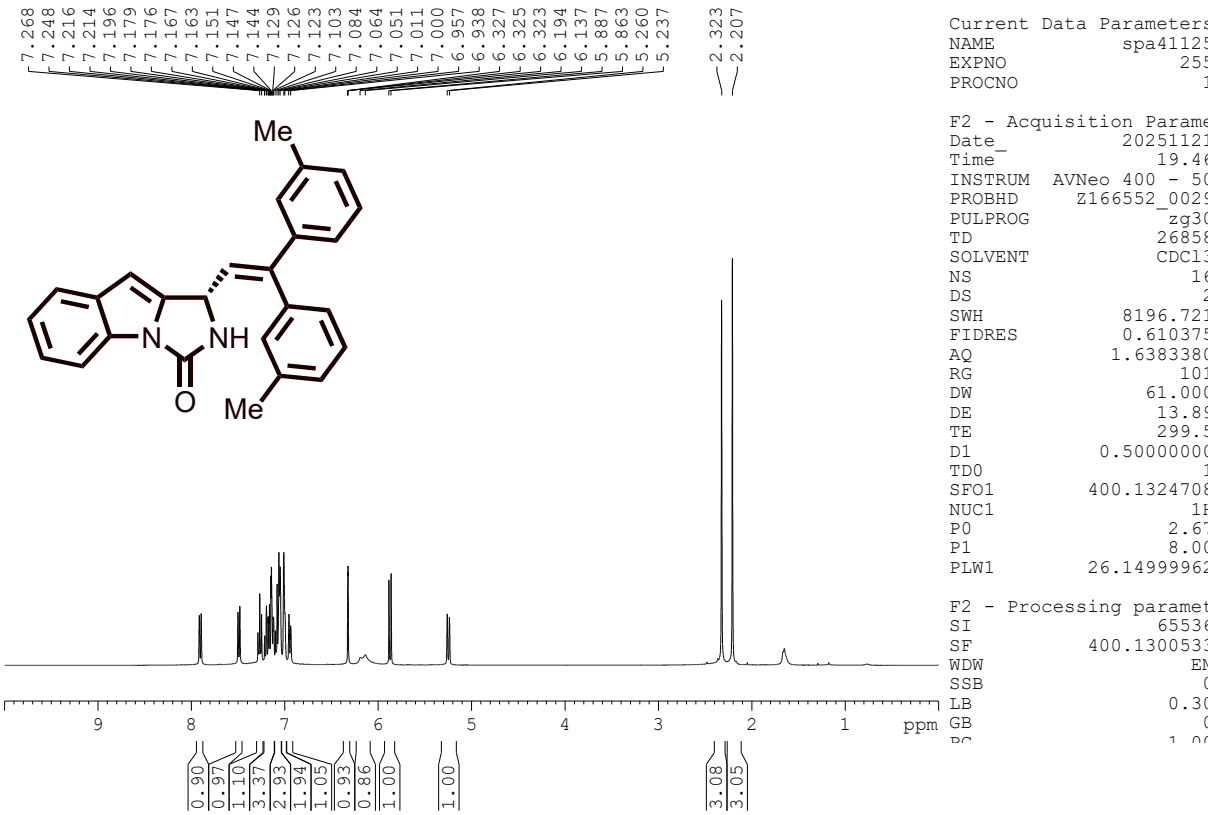


^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3o



^{13}C NMR (125 MHz, $CDCl_3$) spectrum of 3o

(*S*)-1-(2,2-di-m-tolylvinyl)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3p)

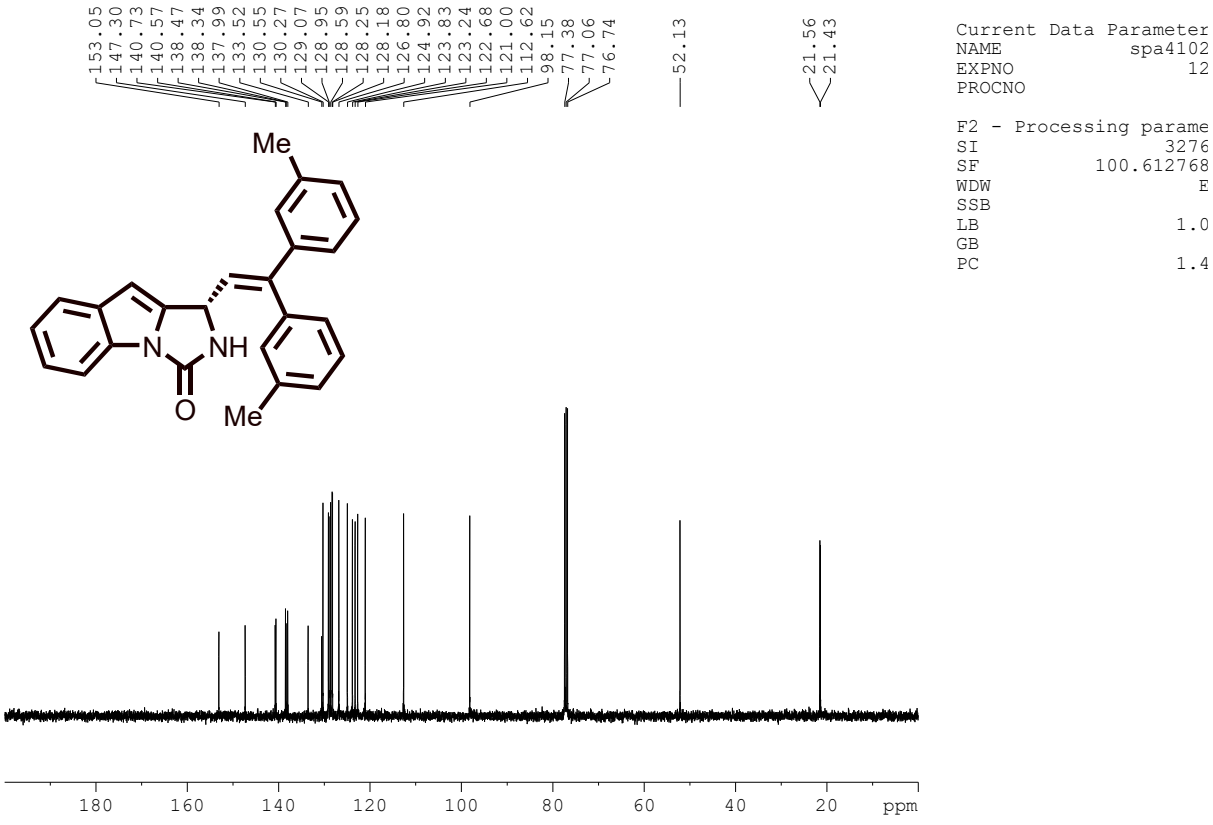


Current Data Parameters
NAME spa4112
EXPNO 25
PROCNO 1

F2 - Acquisition Parame
Date_ 2025112
Time 19.4
INSTRUM AVNeo 400 - 5
PROBHD Z166552_002
PULPROG zg3
TD 2685
SOLVENT CDCl
NS 1
DS 2
SWH 8196.72
FIDRES 0.61037
AQ 1.638338
RG 10
DW 61.00
DE 13.8
TE 299.5
D1 0.5000000
TD0 1
SFO1 400.132470
NUC1 1
P0 2.6
P1 8.0
PLW1 26.14999962

F2 - Processing paramet
SI 6553
SF 400.130053
WDW E
SSB 0
LB 0.3
GB 0

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3p

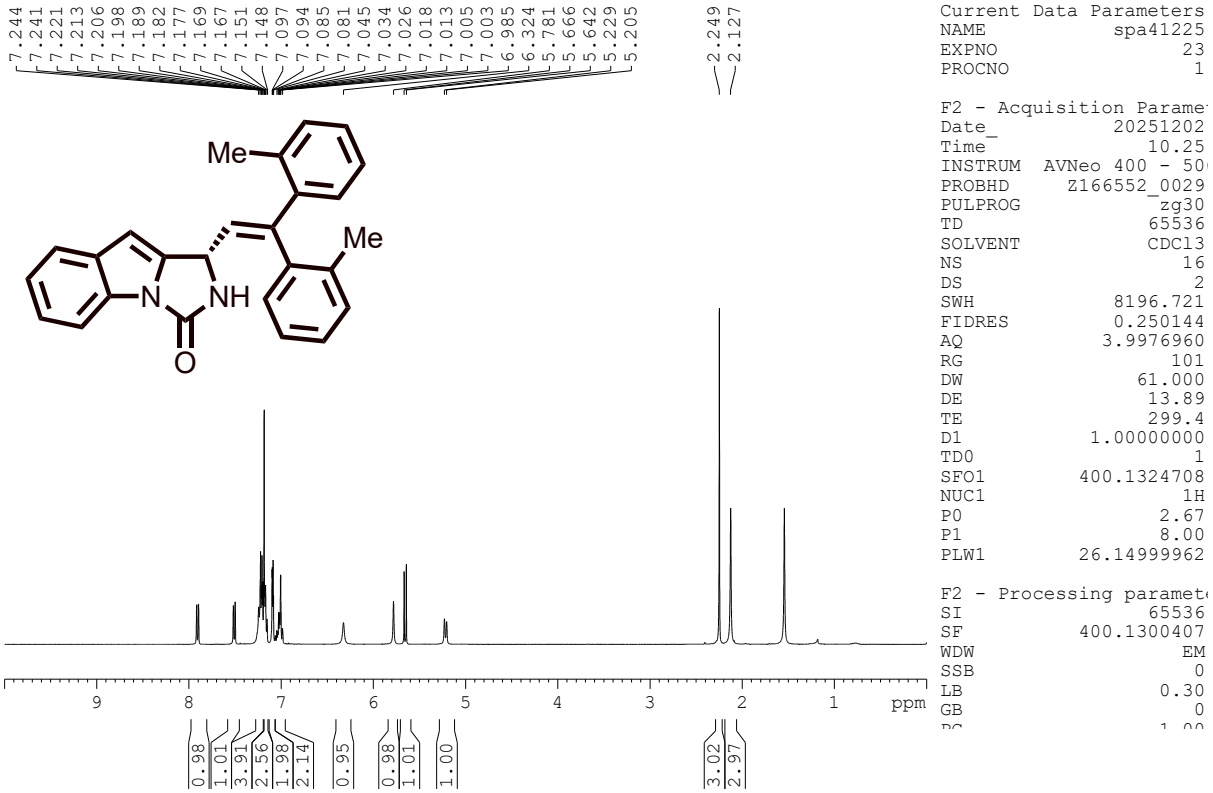


Current Data Parameter
NAME spa4102
EXPNO 12
PROCNO

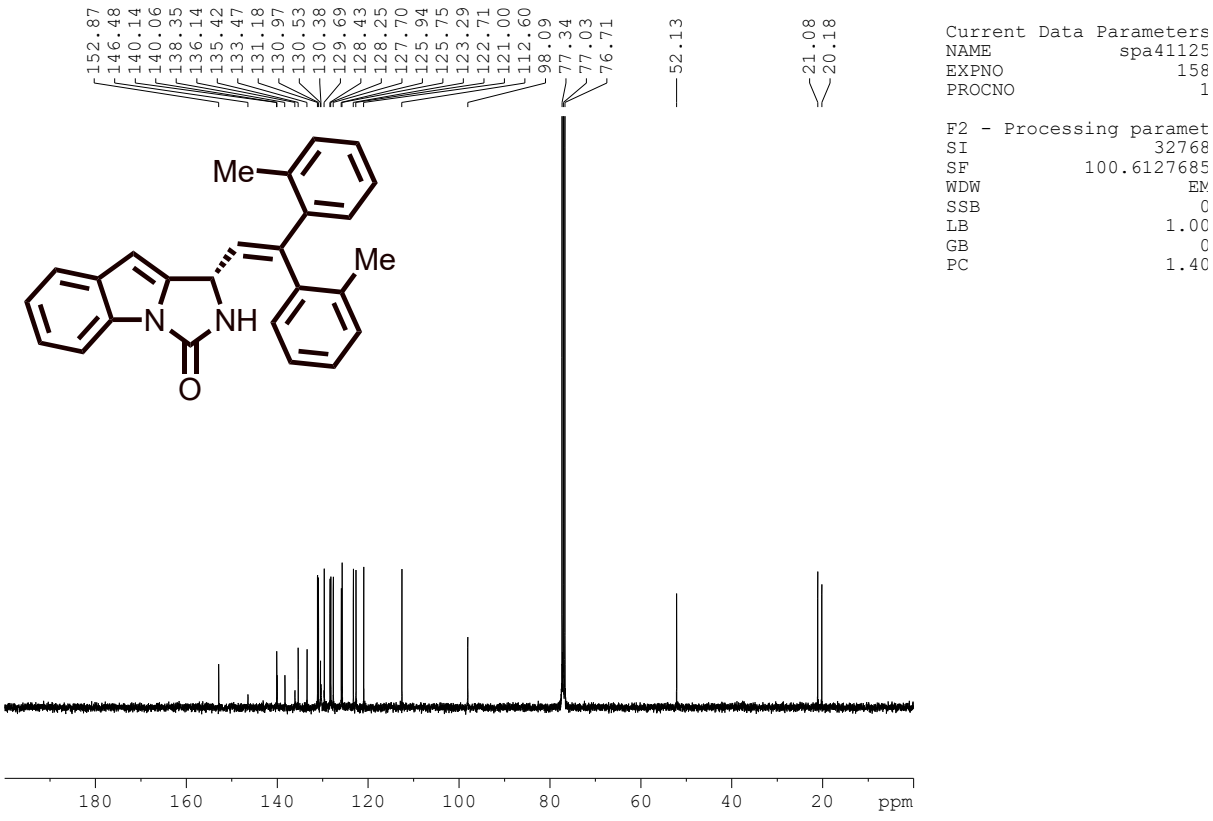
F2 - Processing parame
SI 3276
SF 100.612768
WDW E
SSB
LB 1.0
GB
PC 1.4

^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3p

(*S*)-1-(2,2-di-o-tolylvinyl)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3q)

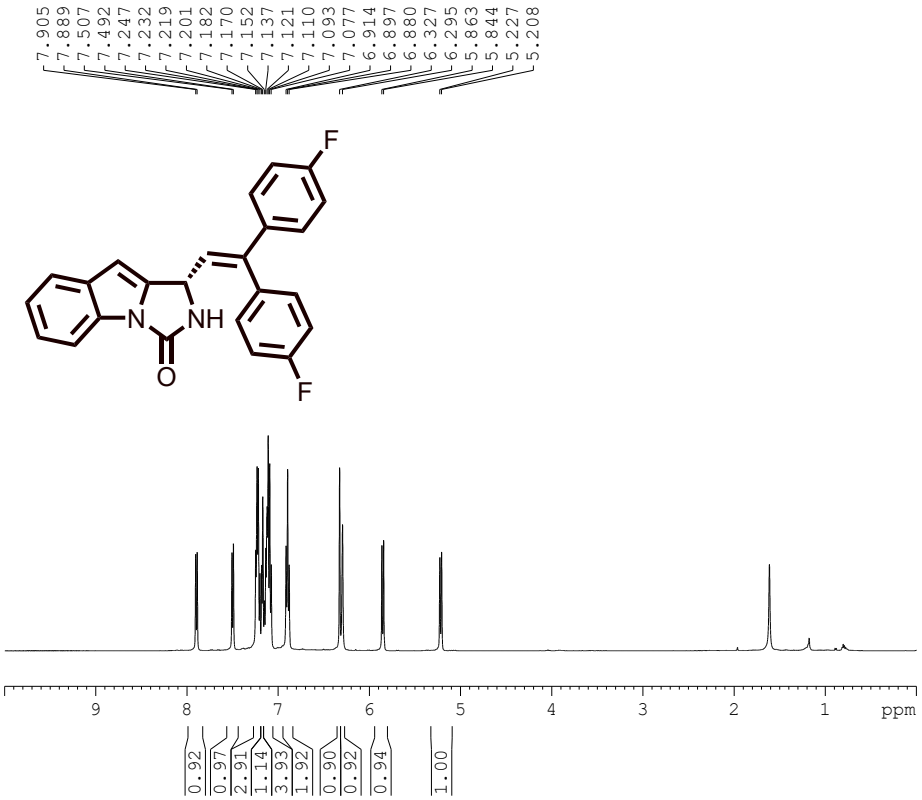


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3q



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3q

(*S*)-1-(2,2-bis(4-fluorophenyl)vinyl)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3r)

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Current Data Parameters
NAME            spa50625
EXPNO                174
PROCNO                 1

F2 - Acquisition Paramet
Date_           20250621
Time                13.46
INSTRUM   AVNeo 500 MHz
PROBHD     Z166550_0009
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    32
DS                     2
SWH            10000.000
FIDRES          0.610352
AQ             1.6384000
RG                   101
DW                50.000
DE                 11.14
TE                 299.3
D1            0.50000000
TD0                    1
SFO1          500.1525008
NUC1                  1H
P0                  2.67
P1                  8.00
PLW1          25.20000076

F2 - Processing paramete
SI                 65536
SF            500.1500566
WDW                   EM
SSB                    0
LB                  0.30
GB                     0
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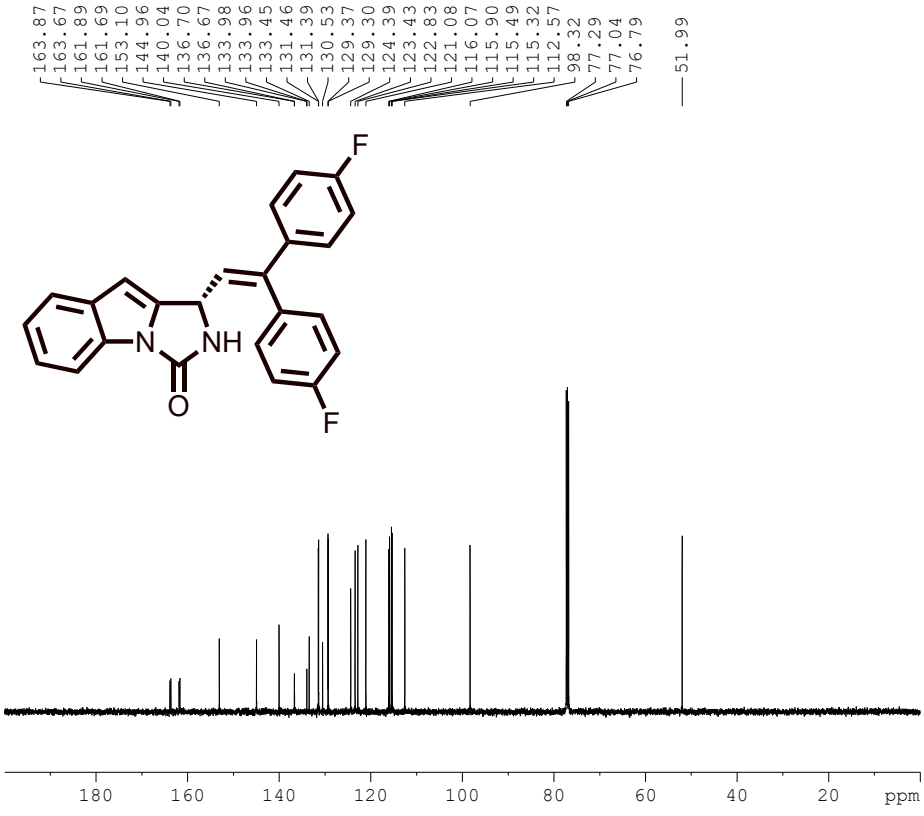
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3r

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Current Data Paramete
NAME            spa506
EXPNO                1
PROCNO

F2 - Processing param
SI                  327
SF           125.76281
WDW                   1
SSB
LB                  1.
GB
PC                  1.
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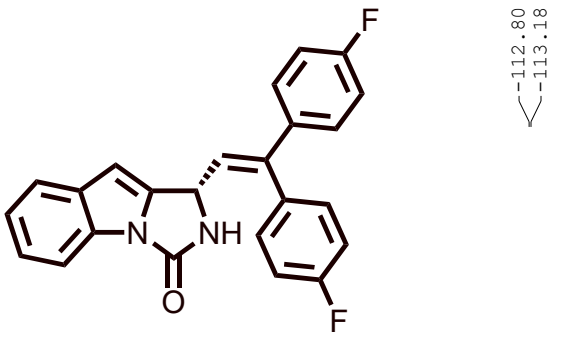
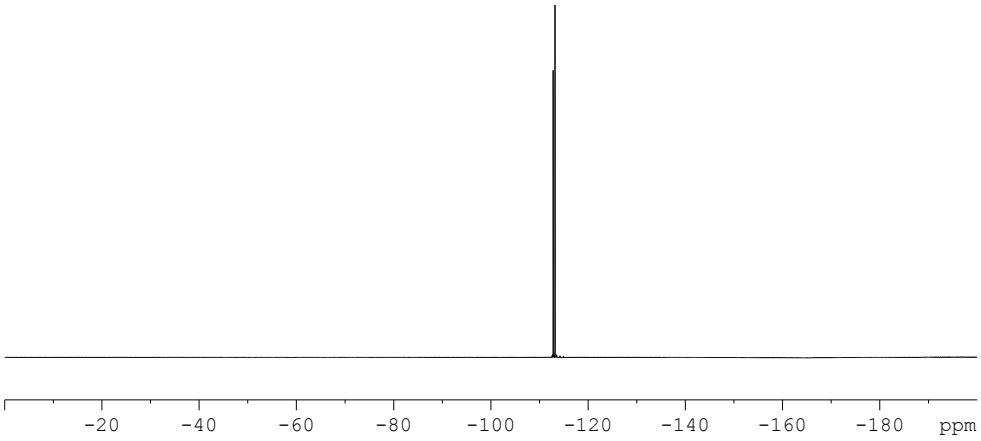
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of 3r



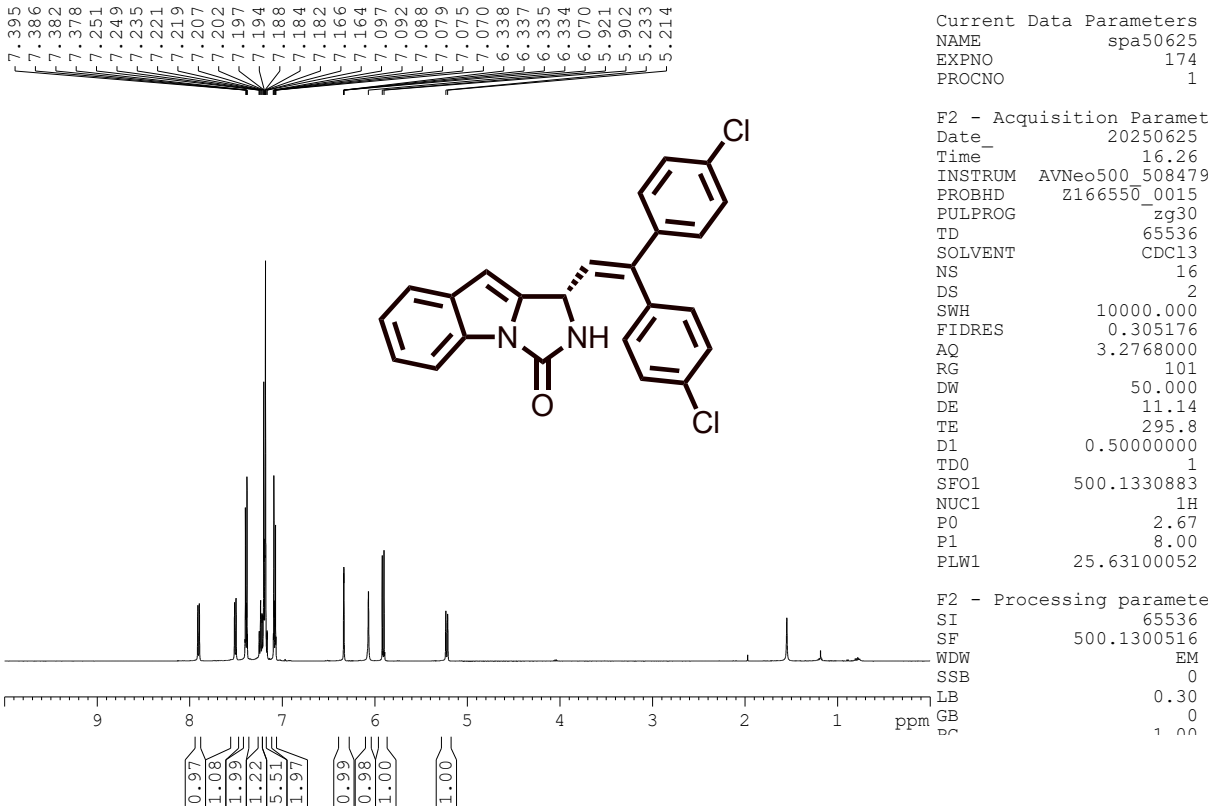
Current Data Parameters
NAME spa5062
EXPNO 17
PROCNO 1

F2 - Processing paramet
SI 6553
SF 470.611196
WDW EM
SSB 0
LB 0.3
GB 0
PC 1.0



^{19}F NMR (470 MHz, $CDCl_3$) spectrum of 3r

(*S*)-1-(2,2-bis(4-chlorophenyl)vinyl)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3s)

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Current Data Parameters
NAME            spa50625
EXPNO                174
PROCNO                 1

F2 - Acquisition Paramet
Date_           20250625
Time               16.26
INSTRUM  AVNeo500_508479
PROBHD     Z166550_0015
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            10000.000
FIDRES          0.305176
AQ             3.2768000
RG                   101
DW                50.000
DE                 11.14
TE                 295.8
D1            0.50000000
TD0                    1
SFO1          500.1330883
NUC1                  1H
P0                  2.67
P1                  8.00
PLW1          25.63100052

F2 - Processing paramete
SI                 65536
SF            500.1300516
WDW                   EM
SSB                    0
LB                  0.30
GB                     0
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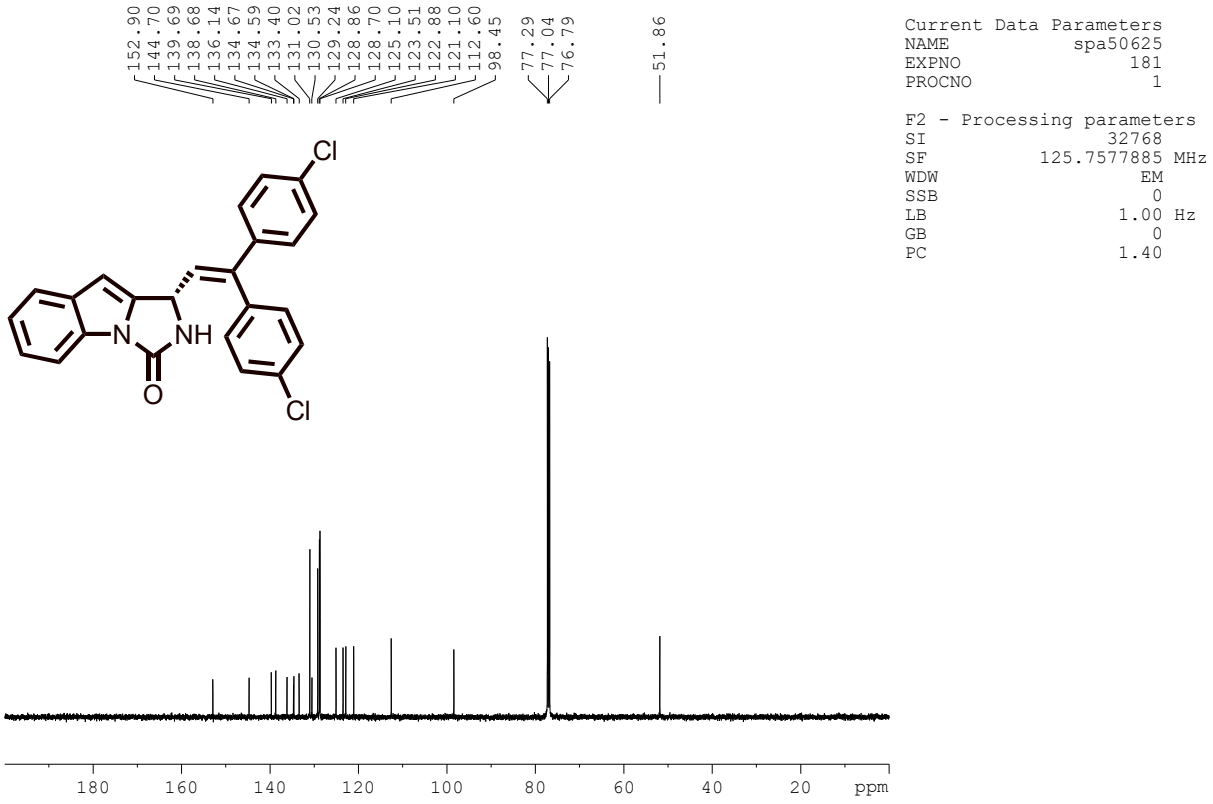
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3s

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Current Data Parameters
NAME            spa50625
EXPNO                181
PROCNO                 1

F2 - Processing parameters
SI                 32768
SF          125.7577885 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
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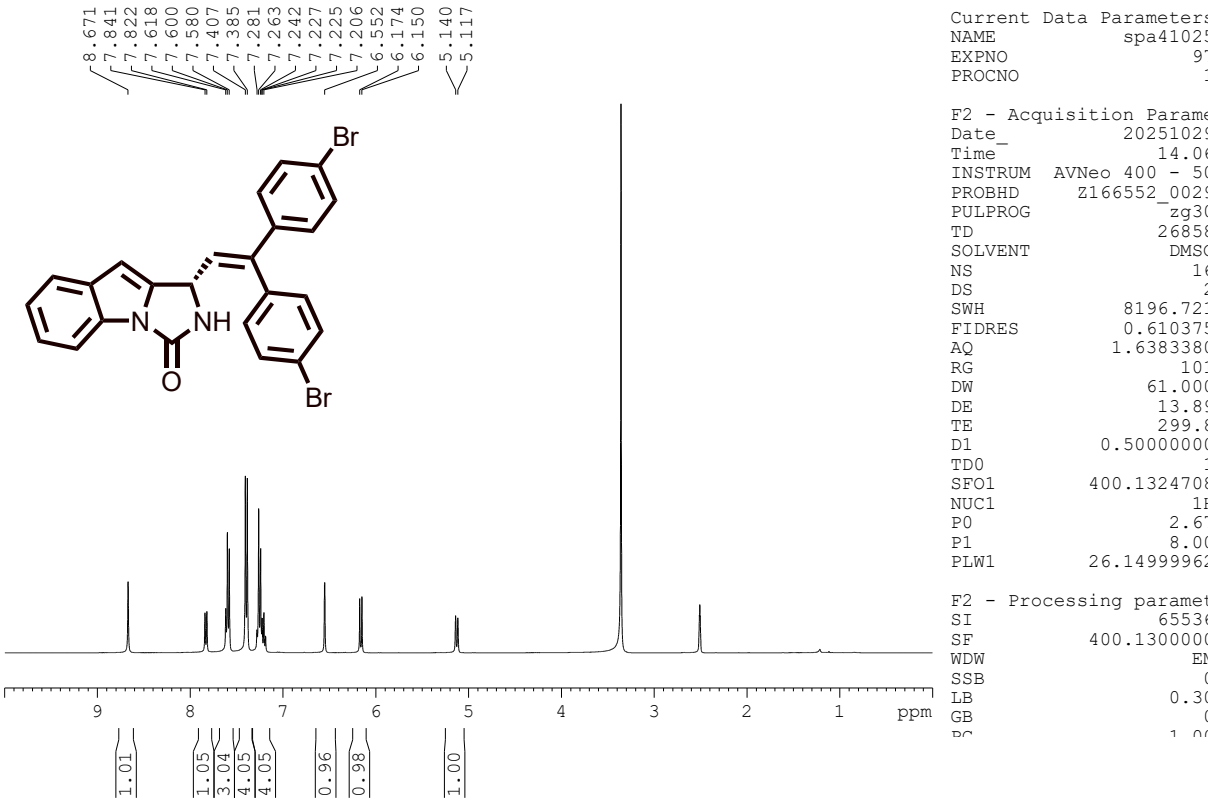
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of 3s

(*S*)-1-(2,2-bis(4-bromophenyl)vinyl)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3t)

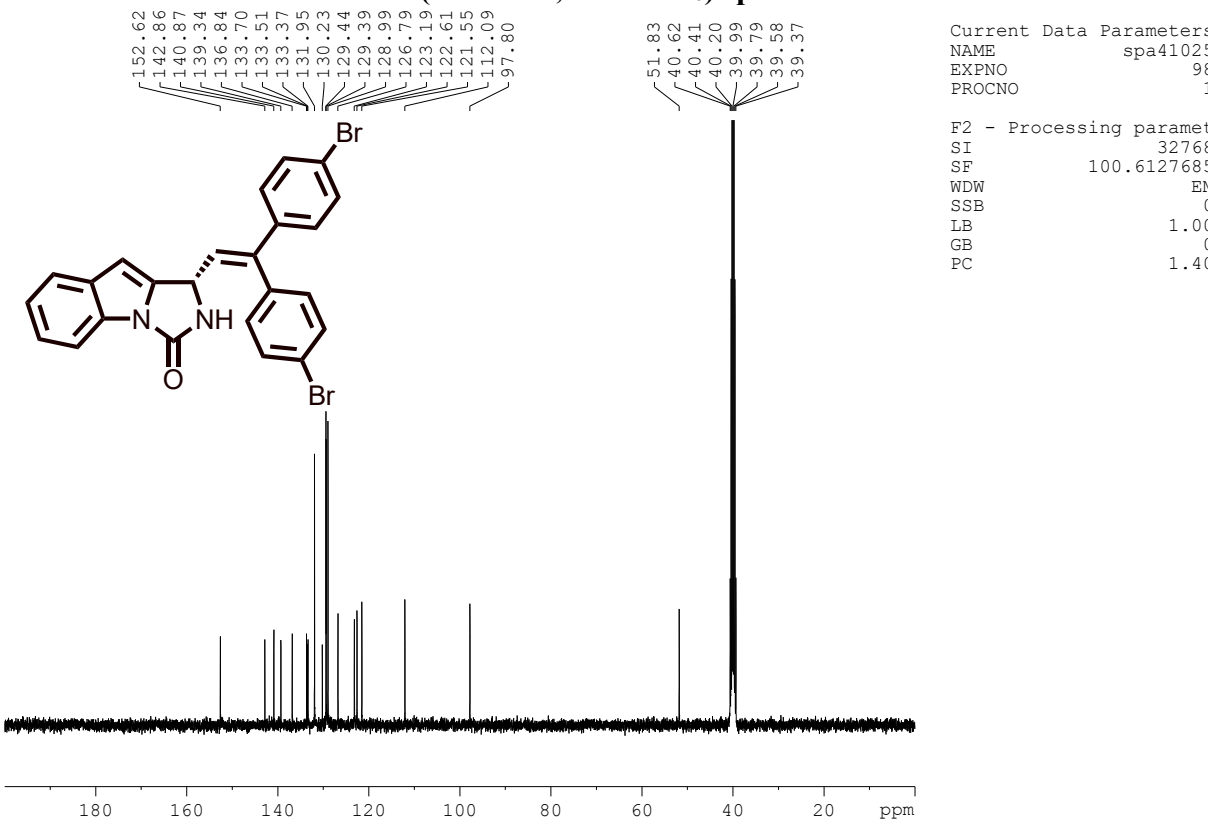


Current Data Parameters
NAME spa41025
EXPNO 9
PROCNO 1

F2 - Acquisition Parame
Date_ 2025102
Time 14.0
INSTRUM AVNeo 400 - 5
PROBHD Z166552_002
PULPROG zg3
TD 2685
SOLVENT DMS
NS 1
DS 2
SWH 8196.72
FIDRES 0.61037
AQ 1.638338
RG 10
DW 61.00
DE 13.8
TE 299.8
D1 0.5000000
TD0 1
SFO1 400.132470
NUC1 1
P0 2.6
P1 8.0
PLW1 26.14999962

F2 - Processing paramet
SI 6553
SF 400.130000
WDW EM
SSB 0
LB 0.3
GB 0

^{1}H NMR (400 MHz, DMSO-*d*$_6$) spectrum of 3t

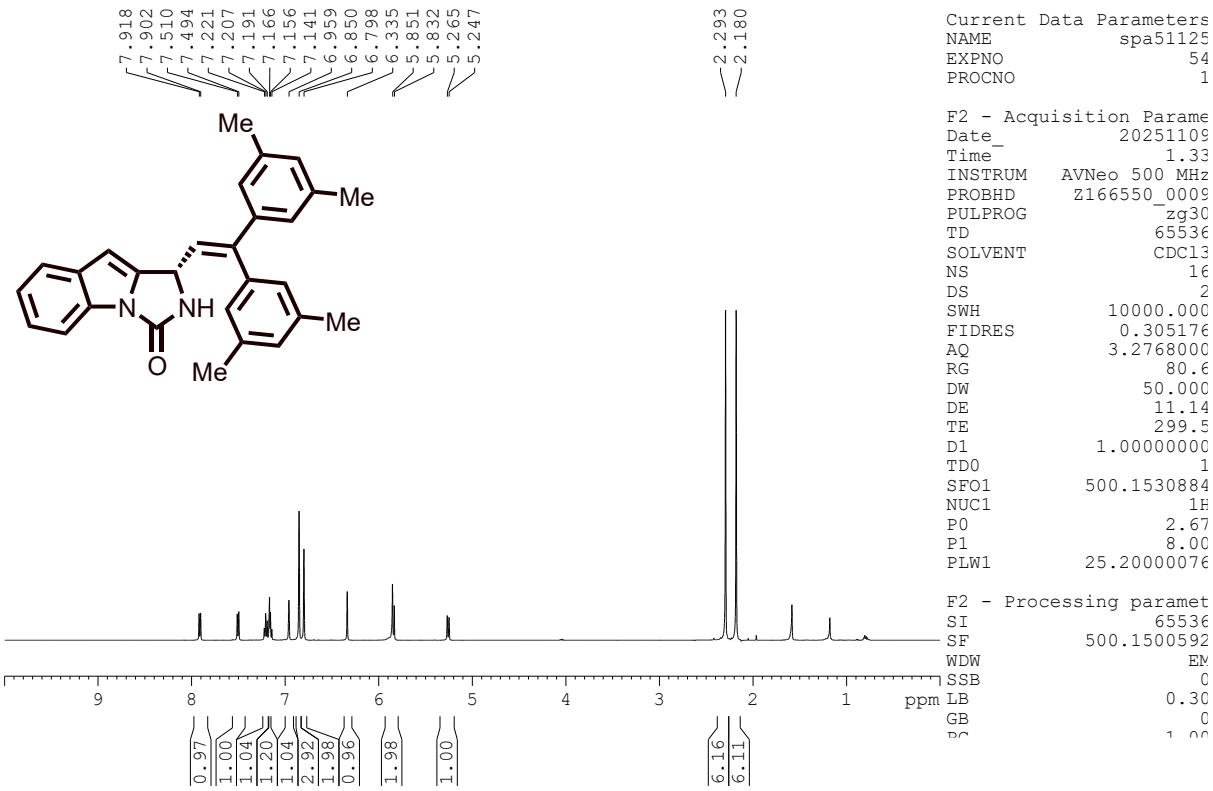


Current Data Parameters
NAME spa41025
EXPNO 9
PROCNO 1

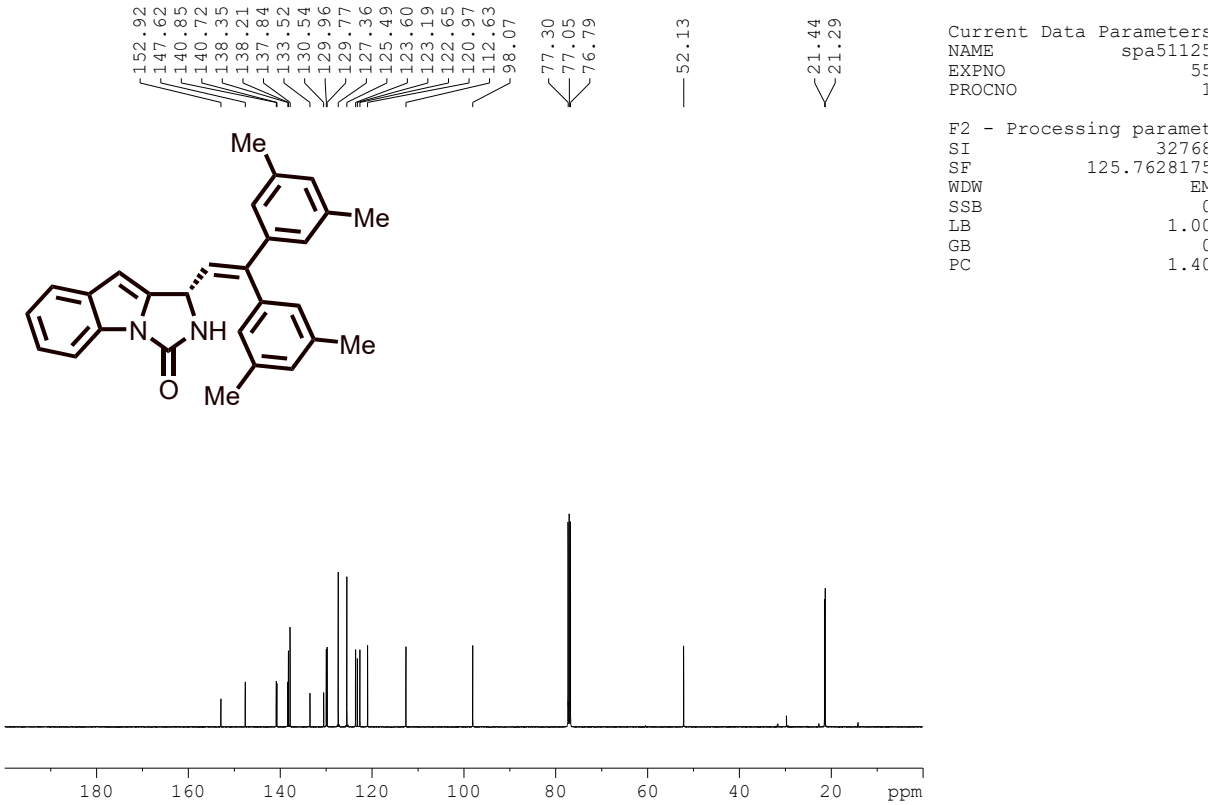
F2 - Processing paramet
SI 3276
SF 100.612768
WDW EM
SSB 0
LB 1.0
GB 0
PC 1.4

^{13}C NMR (100 MHz, DMSO-*d*$_6$) spectrum of 3t

(*S*)-1-(2,2-bis(3,5-dimethylphenyl)vinyl)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3u)

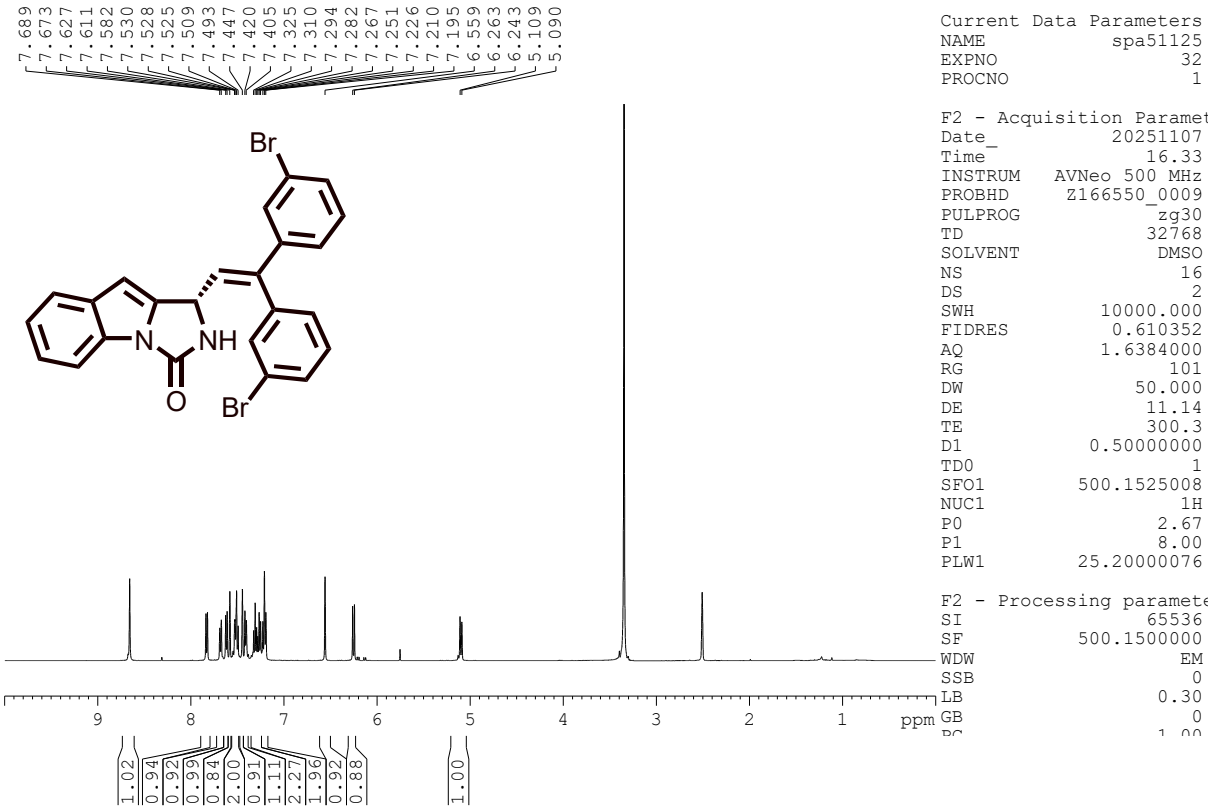


^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3u

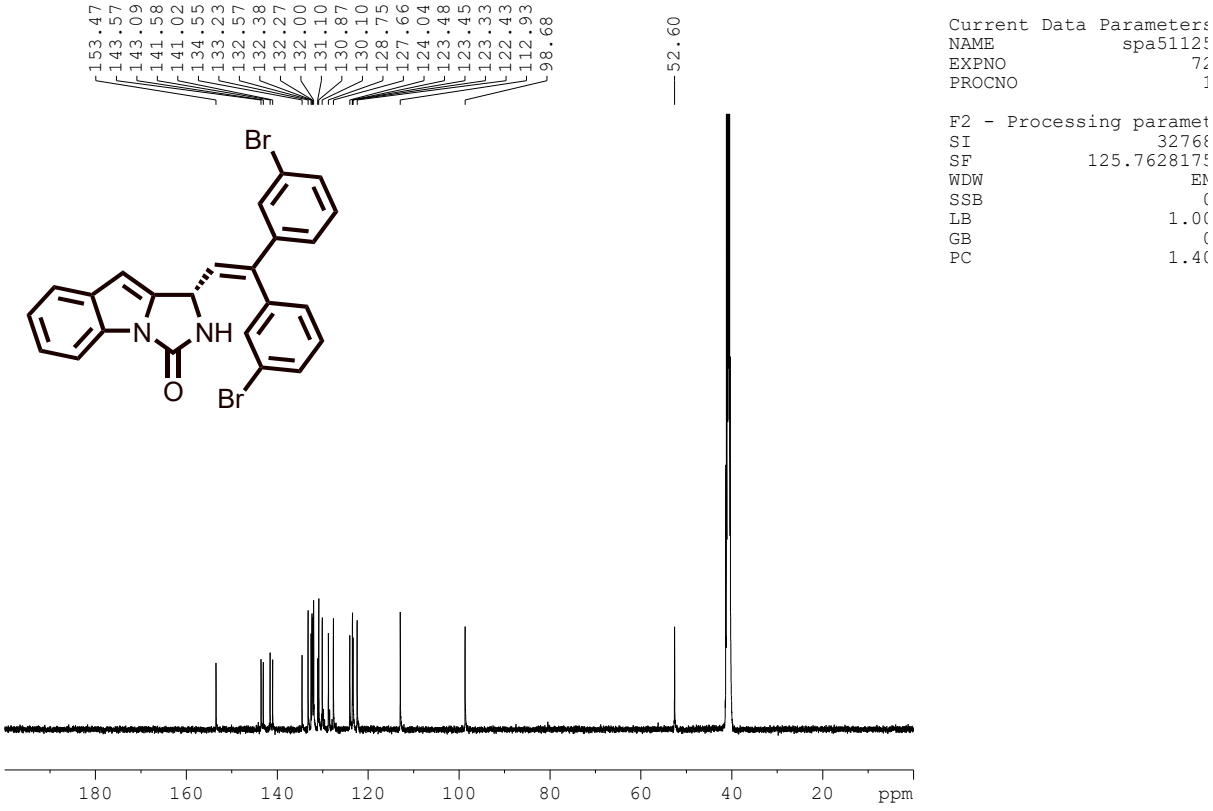


^{13}C NMR (125 MHz, $CDCl_3$) spectrum of 3u

(*S*)-1-(2,2-bis(3-bromophenyl)vinyl)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3v)

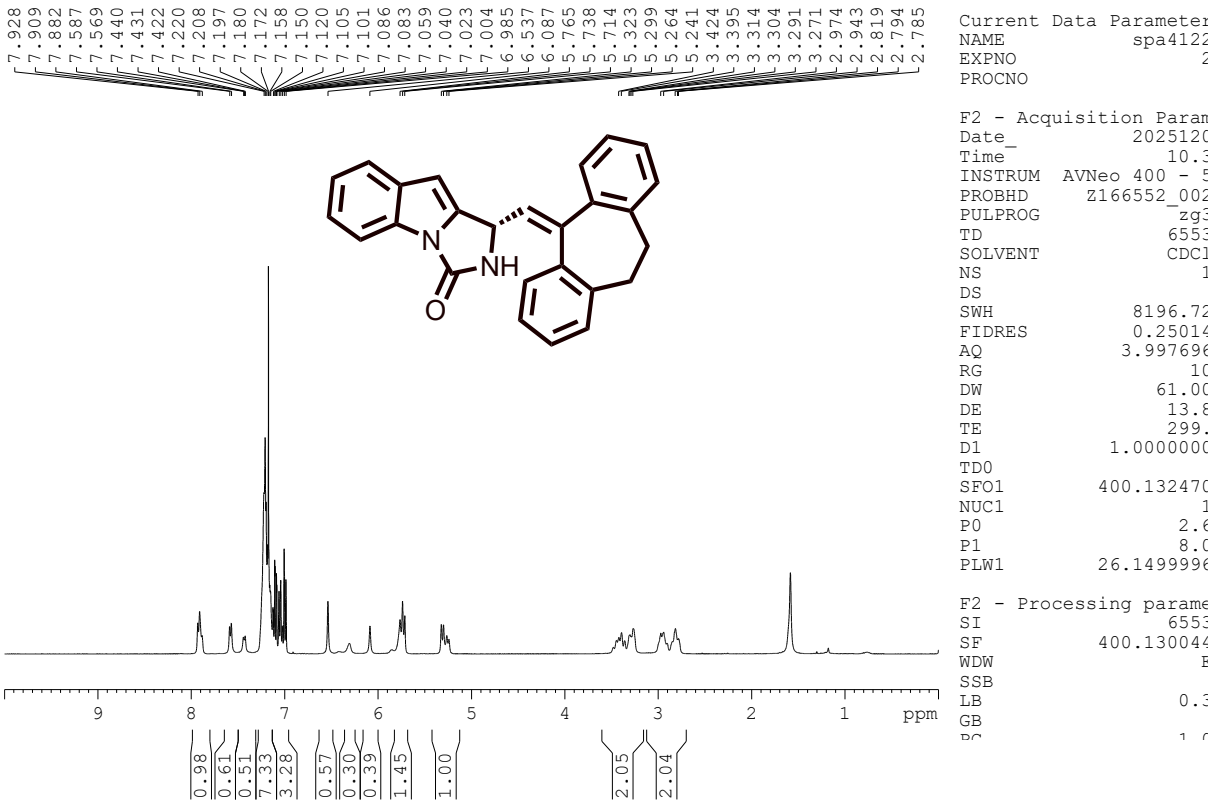


^{1}H NMR (500 MHz, DMSO-d_6) spectrum of 3v



^{13}C NMR (125 MHz, DMSO-d_6) spectrum of 3v

(*S*)-1-((10,11-dihydro-5H-dibenzo[a,d][7]annulen-5-ylidene)methyl)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3w)

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Current Data Parameter
NAME            spa4122
EXPNO                  2
PROCNO

F2 - Acquisition Param
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Time                10.3
INSTRUM  AVNeo 400 - 5
PROBHD     Z166552_002
PULPROG             zg3
TD                 6553
SOLVENT            CDCl
NS                    1
DS
SWH             8196.72
FIDRES          0.25014
AQ              3.997696
RG                    1(
DW                61.00
DE                 13.8
TE                 299.
D1            1.0000000
TD0
SFO1         400.132470
NUC1                  1
P0                  2.6
P1                  8.0
PLW1         26.1499996

F2 - Processing parame
SI                 6553
SF          400.130044
WDW                   E
SSB
LB                  0.3
GB
PC                  1.0
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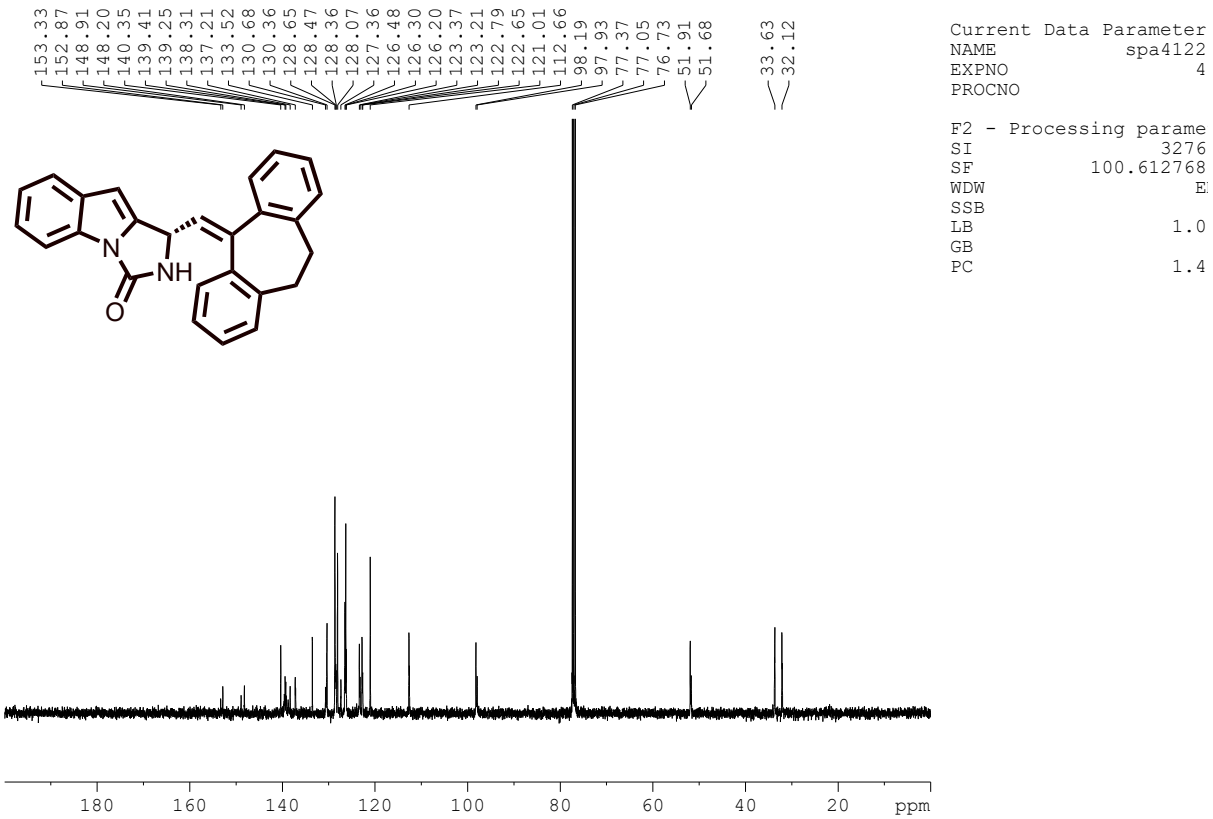
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4w

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Current Data Parameter
NAME            spa4122
EXPNO                  4
PROCNO

F2 - Processing parame
SI                  3276
SF          100.612768
WDW                   E
SSB
LB                  1.0
GB
PC                  1.4
```
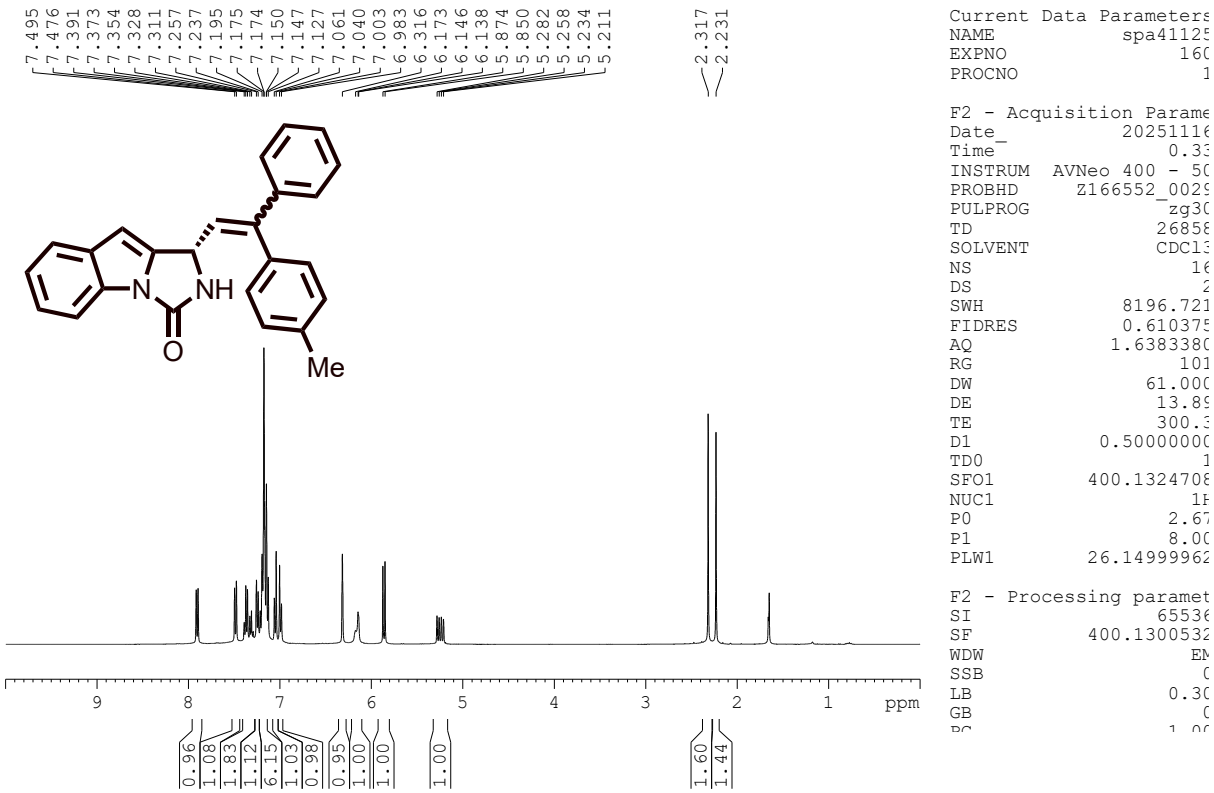
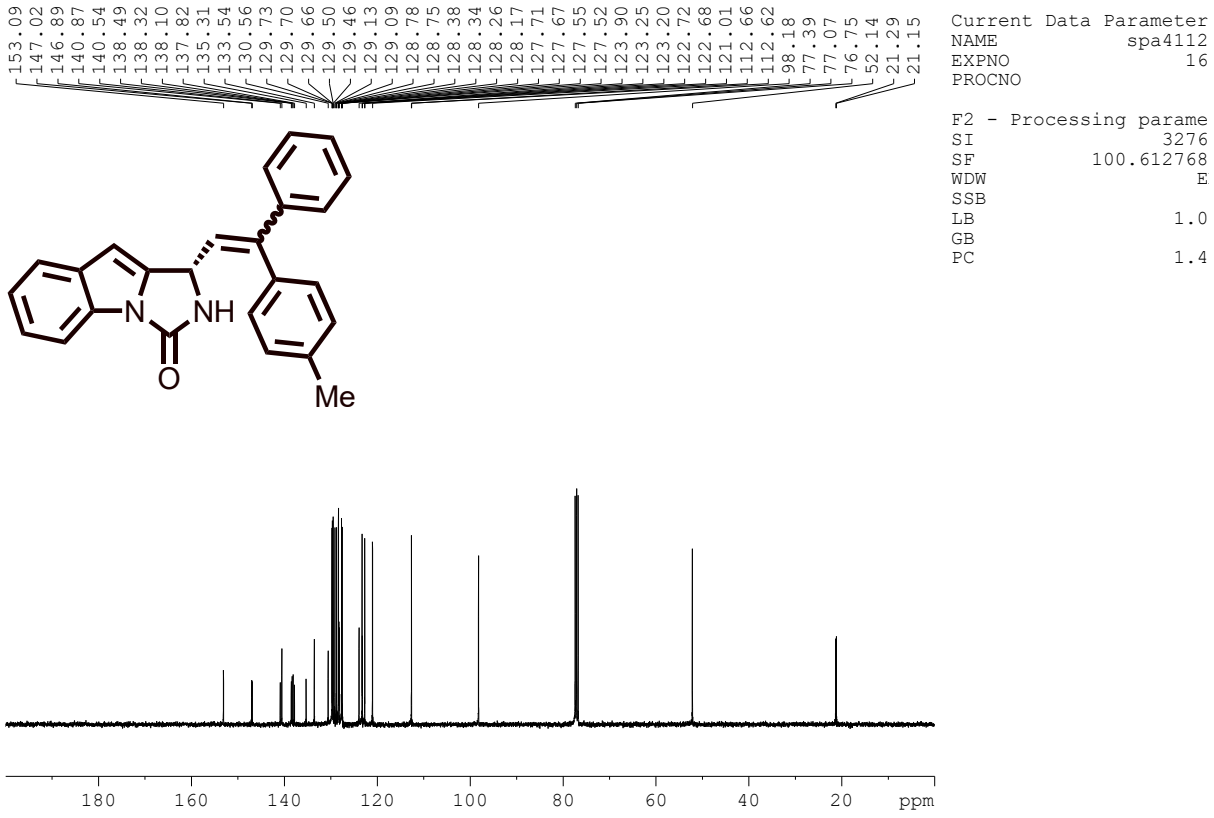

^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3w

(*S*)-1-(2-phenyl-2-(p-tolyl)vinyl)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3x)

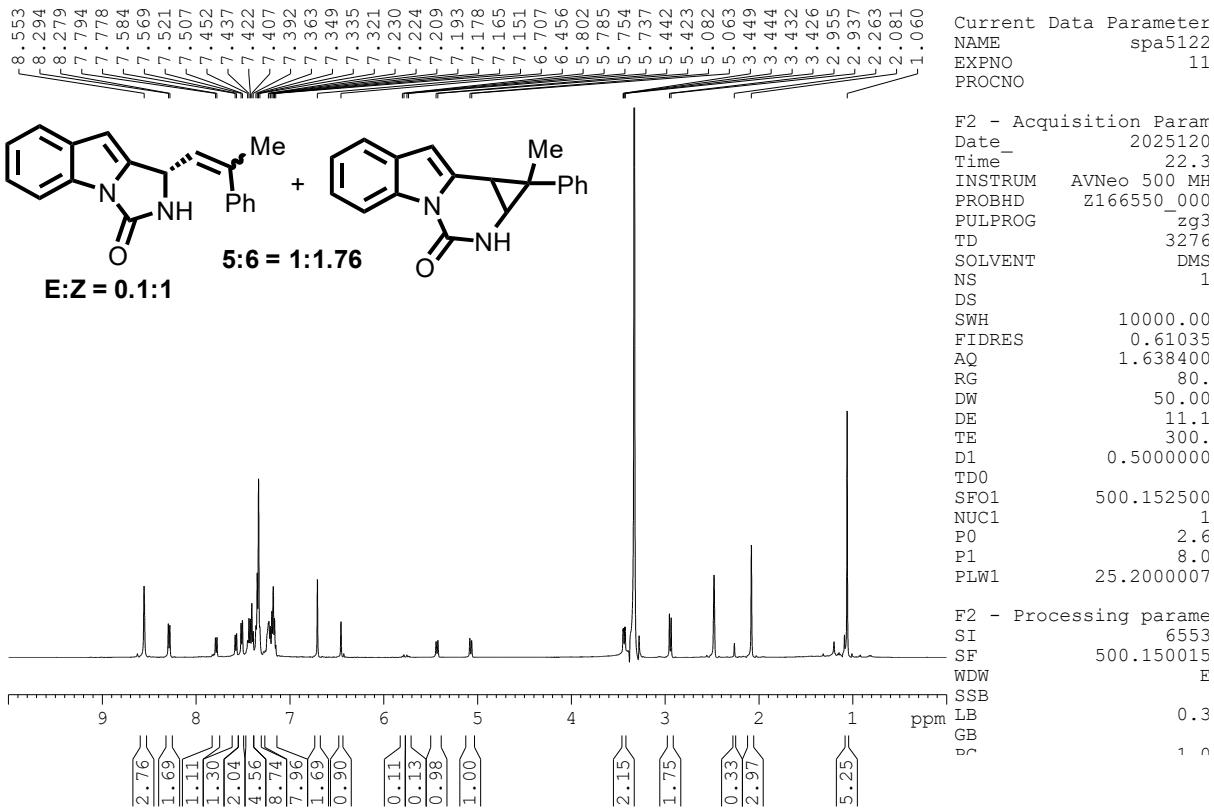


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3x



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3x

(*S*)-1-(2-phenylprop-1-en-1-yl)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (3y)



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EXPNO 11
PROCNO

F2 - Acquisition Param
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Time 22.3
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PULPROG zg3
TD 3276
SOLVENT DMS
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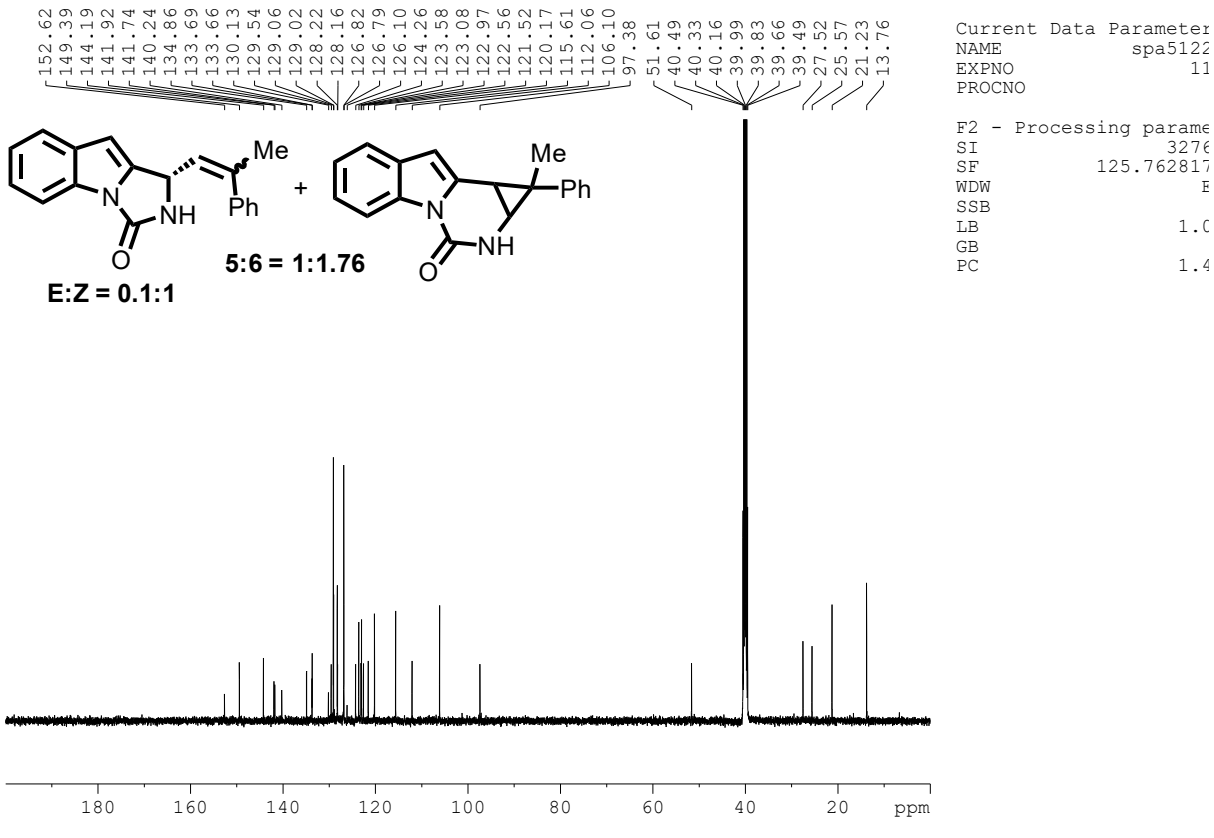
DS
SWH 10000.00
FIDRES 0.61035
AQ 1.638400
RG 80.
DW 50.00
DE 11.1
TE 300.
D1 0.5000000
TD0
SFO1 500.152500
NUC1 1
P0 2.6
P1 8.0
PLW1 25.2000007

F2 - Processing parame
SI 6553
SF 500.150015
WDW E
SSB
LB 0.3
GB

^{1}H NMR (500 MHz, DMSO-*d*$_6$) spectrum of 3y

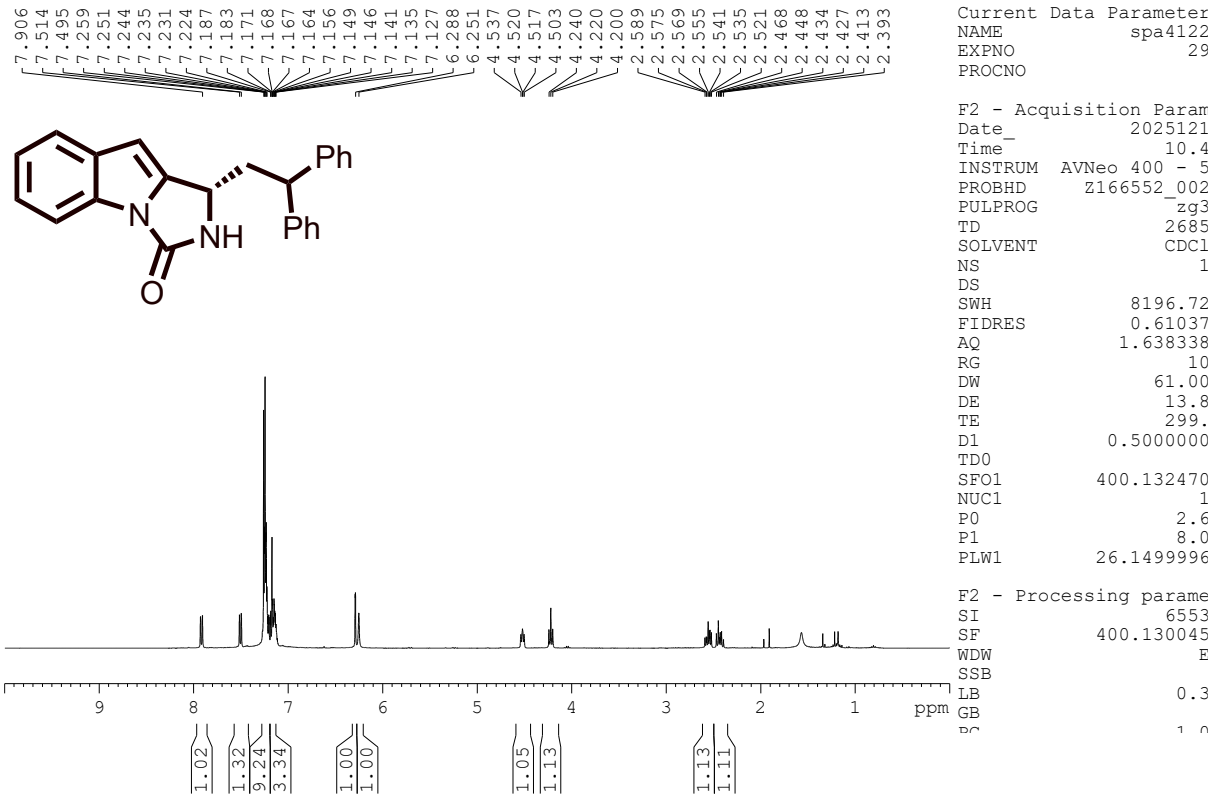


Current Data Parameter
NAME spa5122
EXPNO 11
PROCNO

F2 - Processing parame
SI 3276
SF 125.762817
WDW E
SSB
LB 1.0
GB
PC 1.4

^{13}C NMR (125 MHz, DMSO-*d*$_6$) spectrum of 3y

(*S*)-1-(2,2-diphenylethyl)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (4)



Current Data Parameter
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EXPNO 29
PROCNO

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Date_ 2025121
Time 10.4
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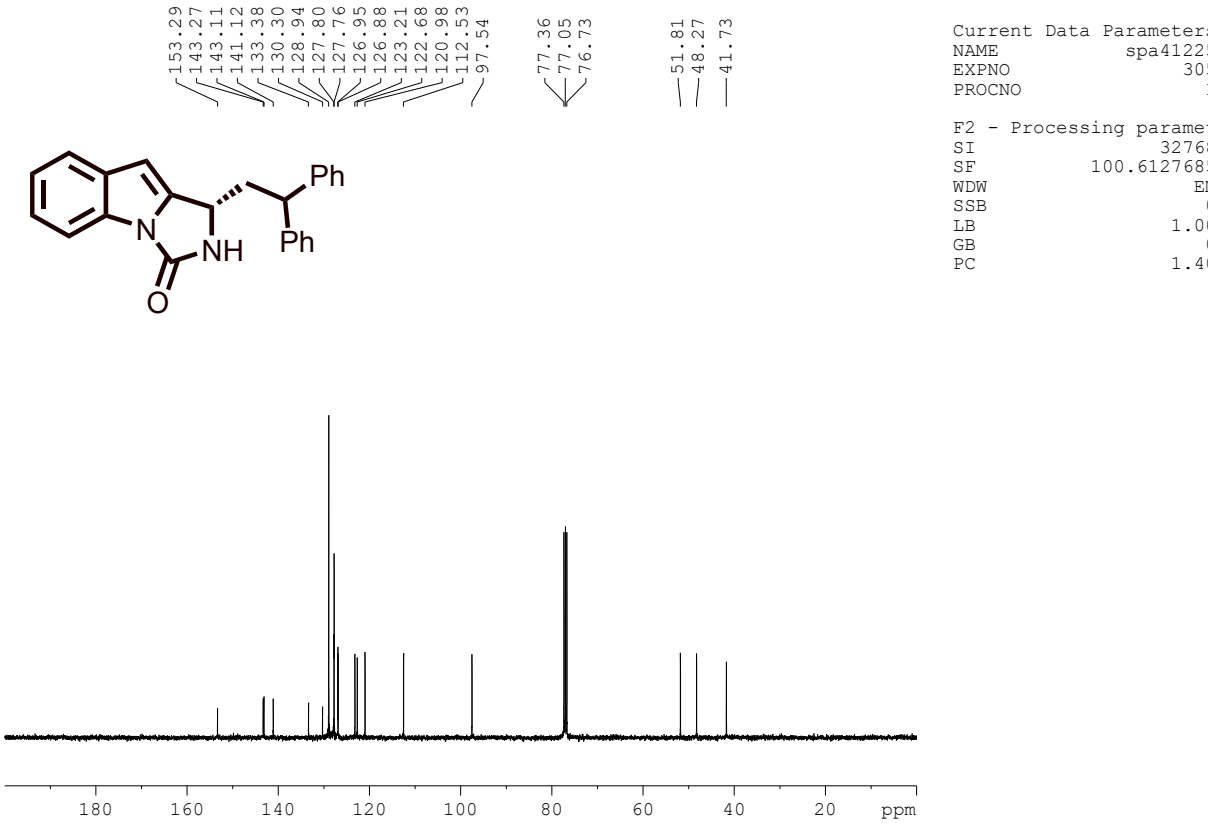
PROBHD Z166552_002
PULPROG zg3
TD 2685
SOLVENT CDCl
NS 1
DS
SWH 8196.72
FIDRES 0.61037
AQ 1.638338
RG 10
DW 61.00
DE 13.8
TE 299.
D1 0.5000000
TD0
SFO1 400.132470
NUC1 1
P0 2.6
P1 8.0
PLW1 26.1499996

F2 - Processing parame
SI 6553
SF 400.130045
WDW E
SSB
LB 0.3
GB

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4

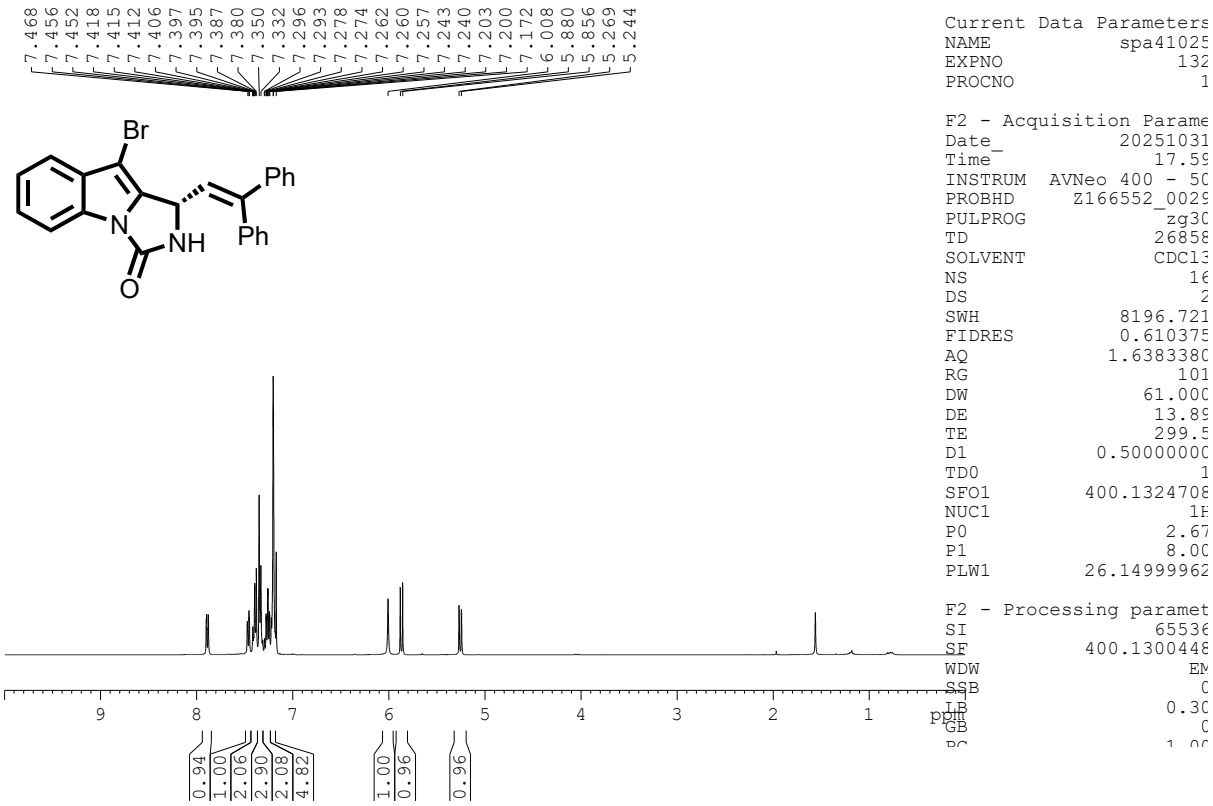


Current Data Parameter:
NAME spa4122
EXPNO 30
PROCNO

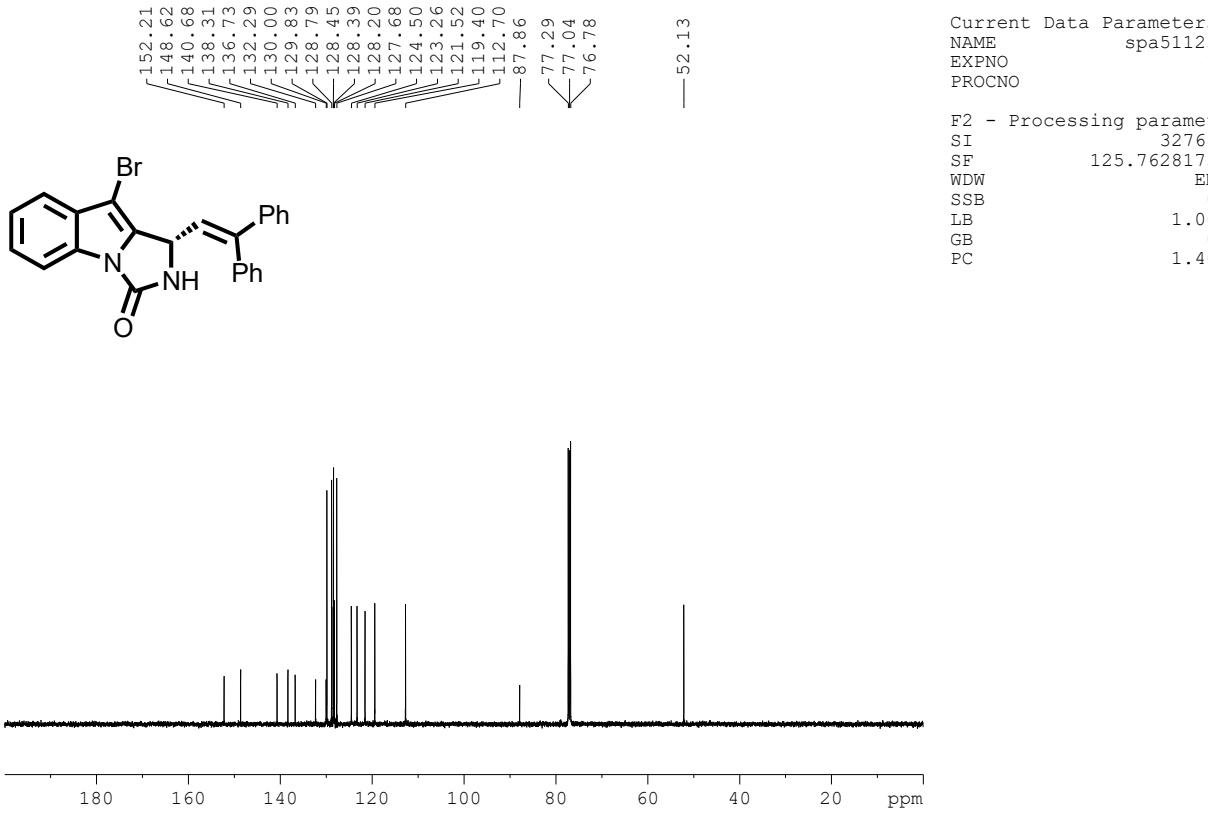
F2 - Processing parame
SI 3276
SF 100.612768
WDW E
SSB
LB 1.0
GB
PC 1.4

^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 4

(*S*)-9-bromo-1-(2,2-diphenylvinyl)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (5)

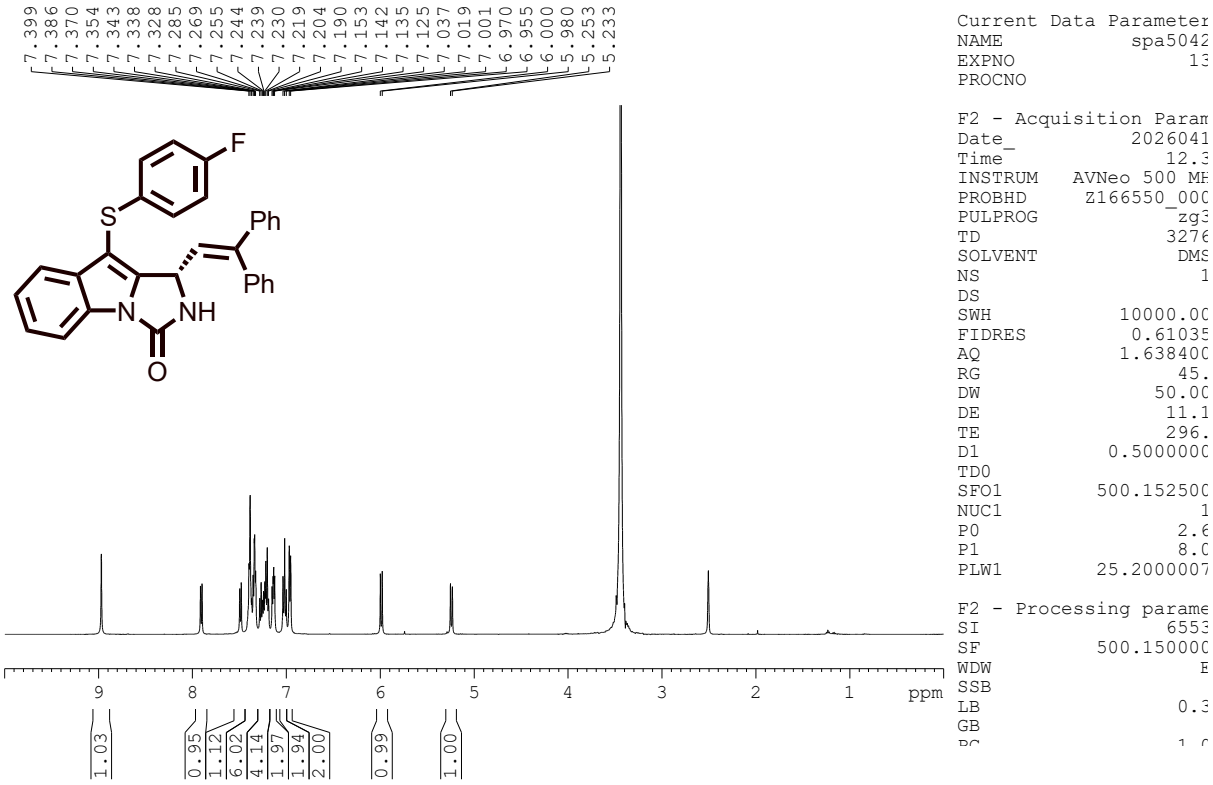


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 5

(*S*)-1-(2,2-diphenylvinyl)-9-((4-fluorophenyl)thio)-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one (6)



Current Data Parameter
NAME spa5042
EXPNO 13
PROCNO

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SOLVENT DMS
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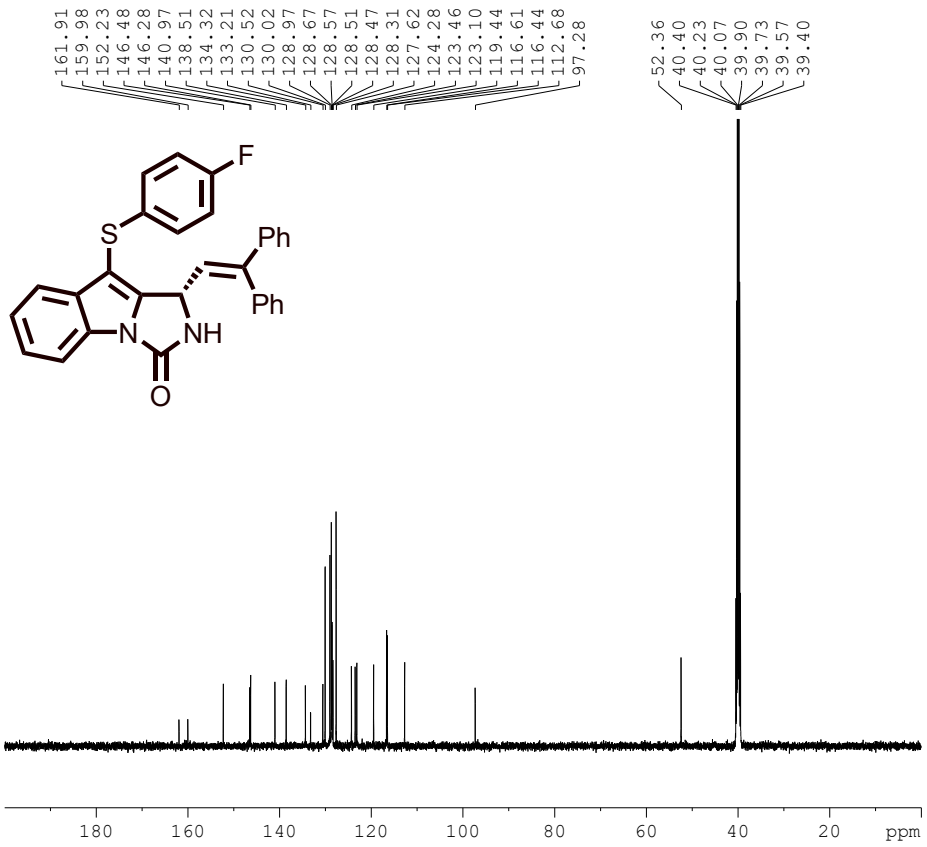
DS
SWH 10000.00
FIDRES 0.61035
AQ 1.638400
RG 45.
DW 50.00
DE 11.1
TE 296.
D1 0.5000000
TD0
SFO1 500.152500
NUC1 1
P0 2.6
P1 8.0
PLW1 25.2000007

F2 - Processing parame
SI 6553
SF 500.150000
WDW E
SSB
LB 0.3
GB
PC 1.0

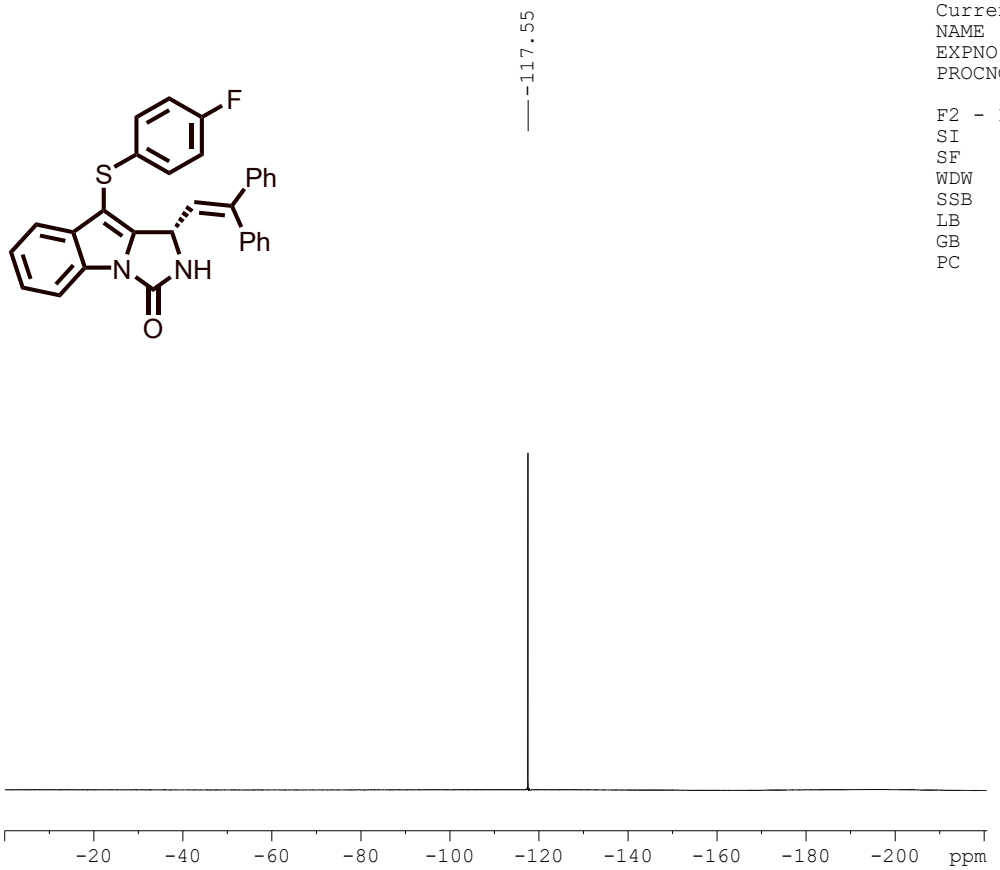
^{1}H NMR (500 MHz, DMSO-d_6) spectrum of 6



Current Data Parameter
NAME spa5042
EXPNO 13
PROCNO

F2 - Processing parame
SI 3276
SF 125.762817
WDW E
SSB
LB 1.0
GB
PC 1.4

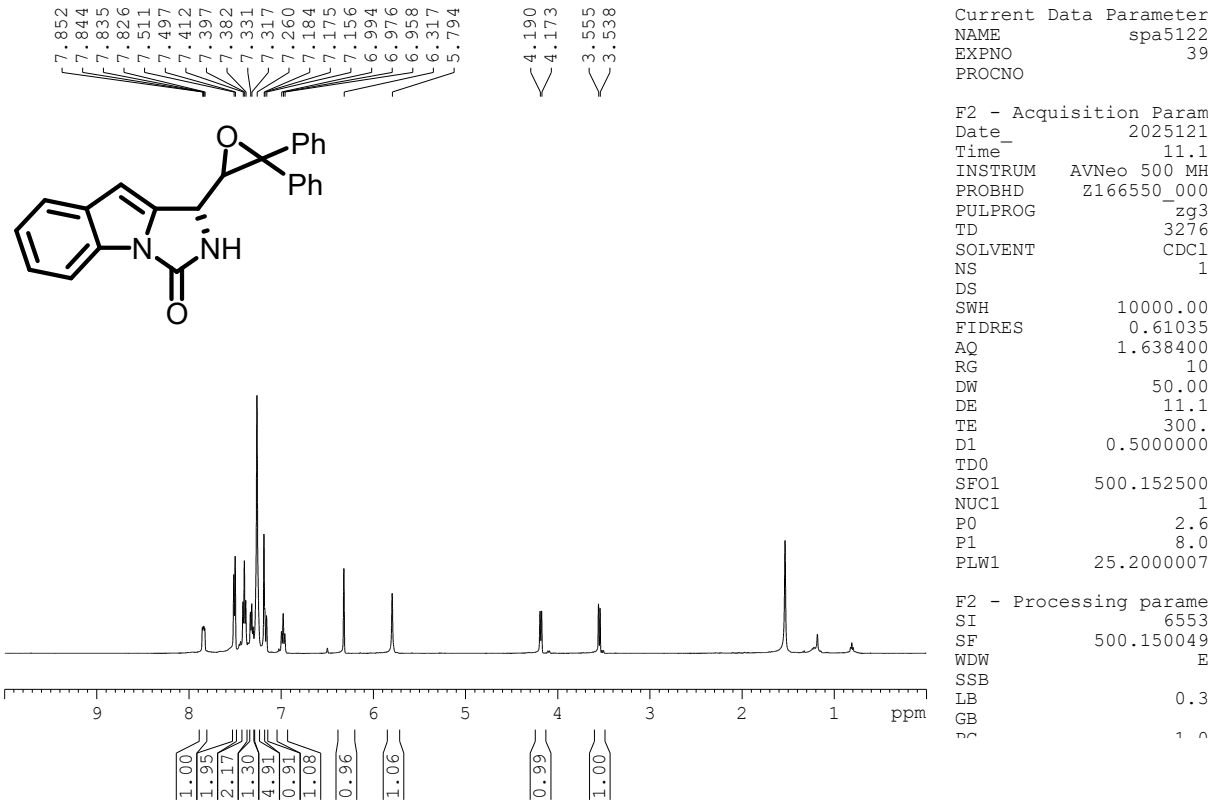
^{13}C NMR (125 MHz, DMSO-d_6) spectrum of 6



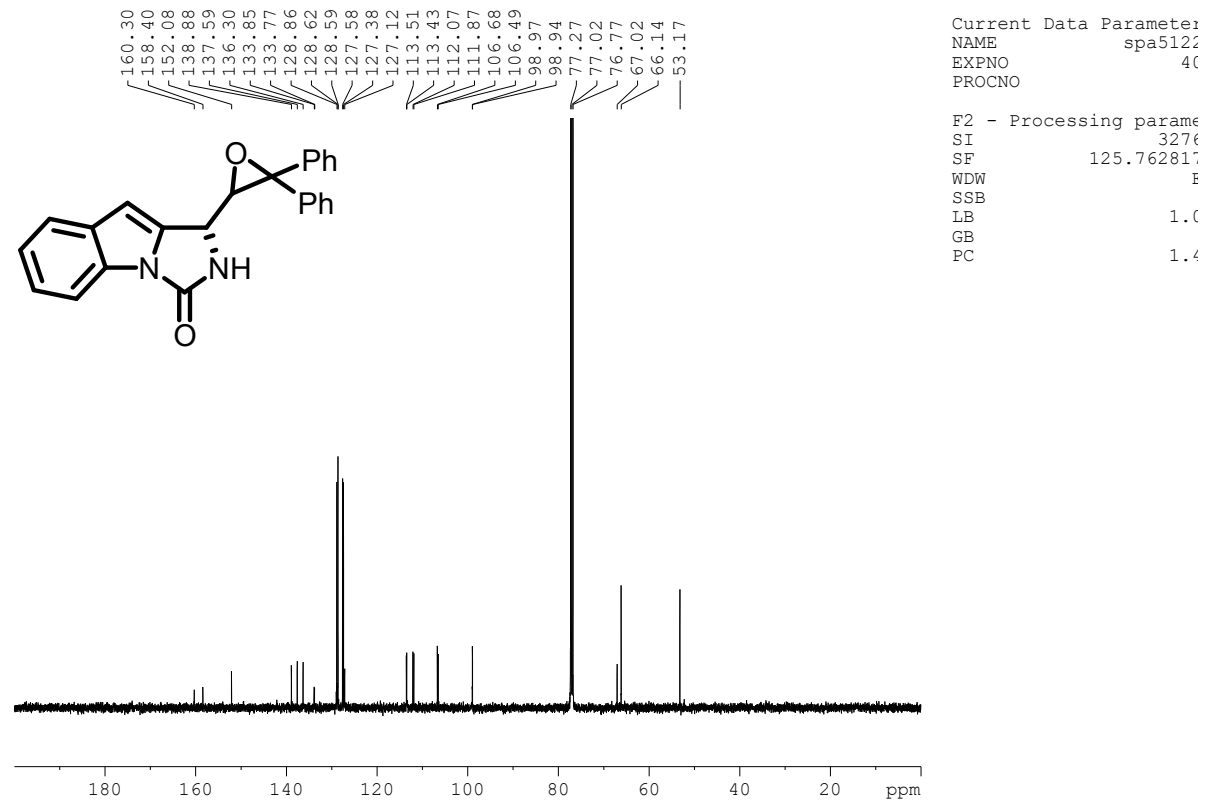
^{19}F NMR (470 MHz, $CDCl_3$) spectrum of 6

(*R*)-1-((S)-3,3-diphenyloxiran-2-yl)-7-fluoro-1,2-dihydro-3H-imidazo[1,5-a]indol-3-one

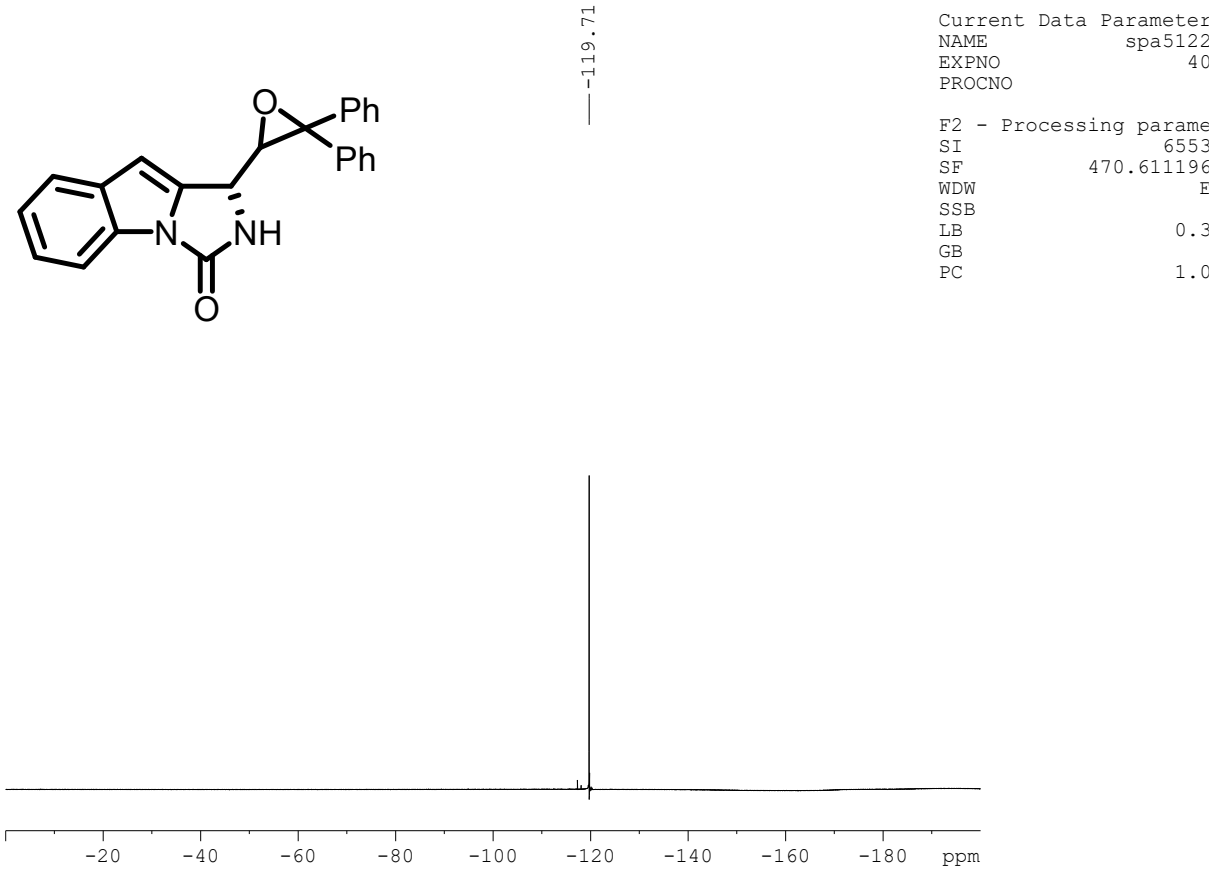
(7)



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 7

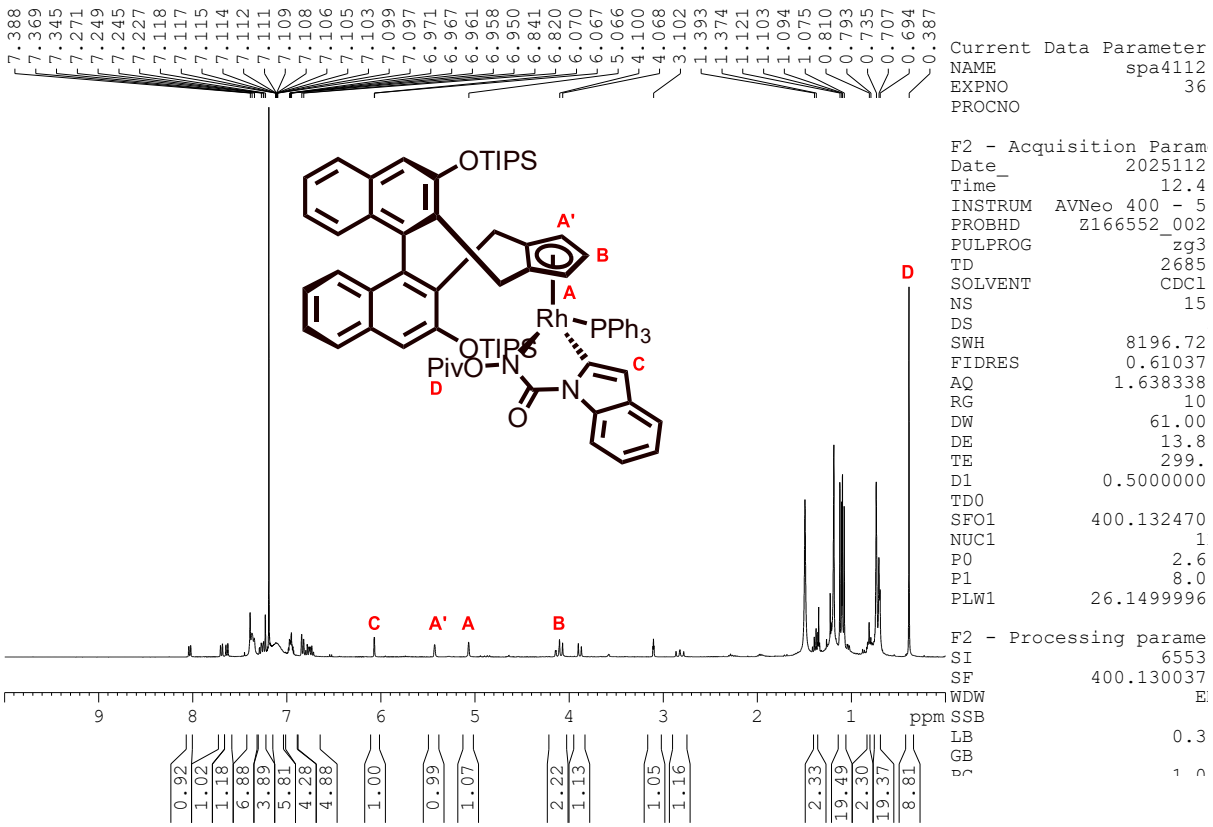


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 7

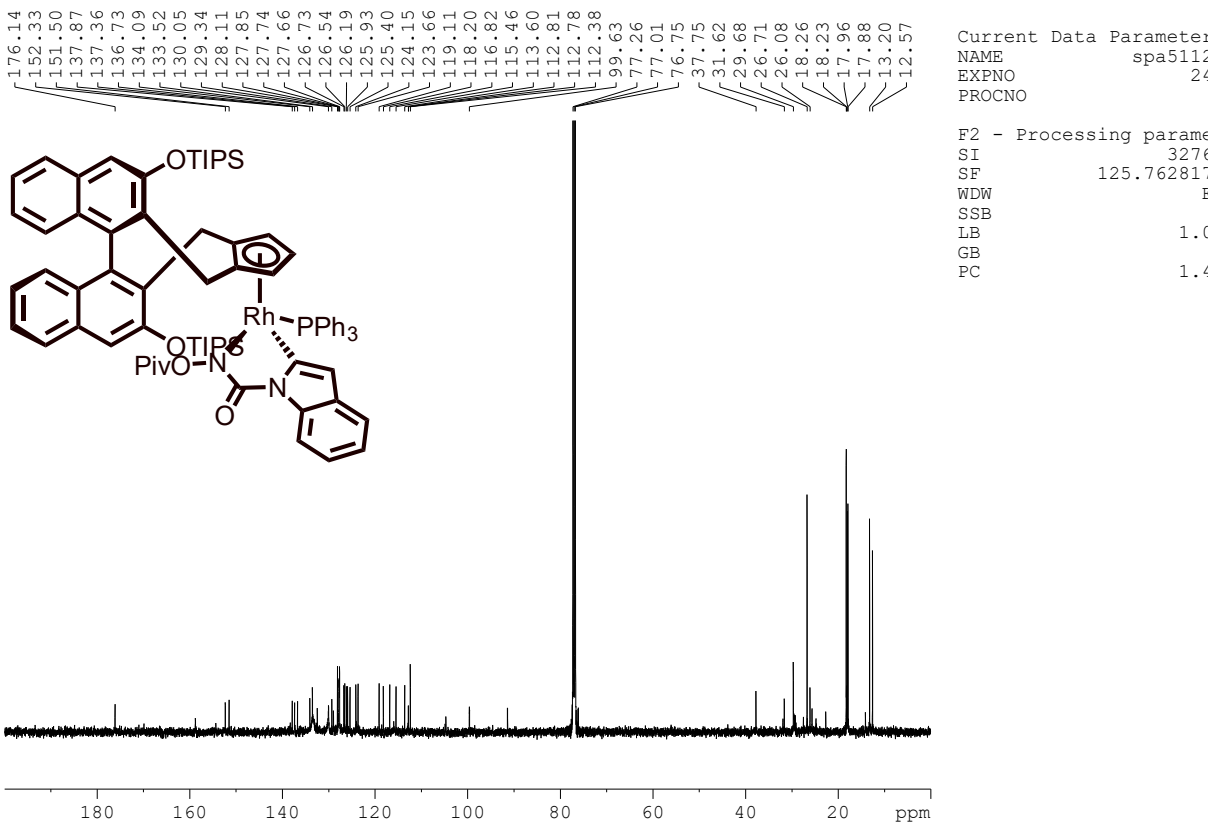


^{19}F NMR (470 MHz, $CDCl_3$) spectrum of 7

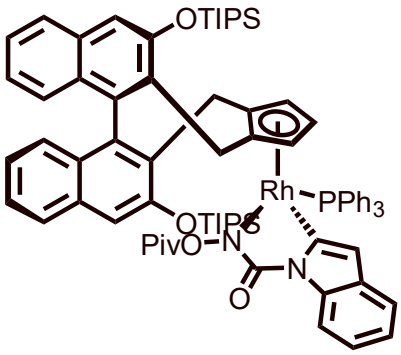
Isolated intermediate (8)



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 8



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 8



35.61
34.88

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Current Data Parameter
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EXPNO                24
PROCNO

F2 - Processing parame
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WDW                   E
SSB
LB                  1.0
GB
PC                  1.4
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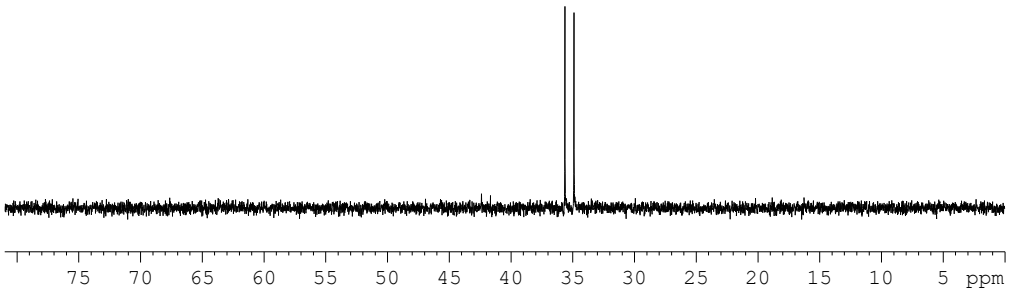
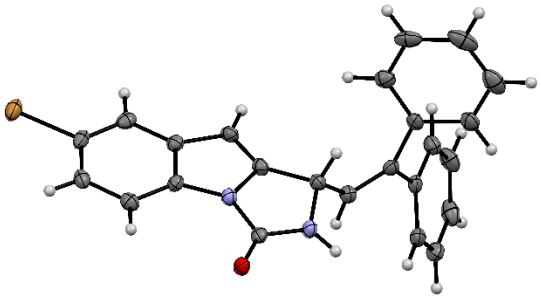


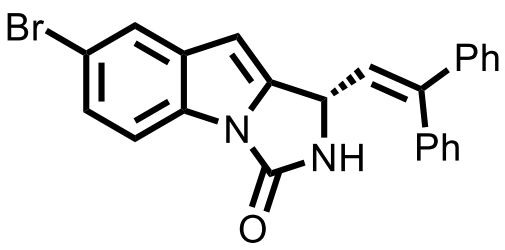
^{31}P NMR (202 MHz, $CDCl_3$) spectrum of 8

13. Crystal data:

Crystallographic data and structure refinement for compound (*S*)-3h

Compound **(*S*)-3h** was recrystallized from Ethylacetate: hexane (1:3) through the slow evaporation method, in a vial with a diameter of 0.75 cm and a length of 5 cm at room temperature, which afforded suitable-sized and quality crystals for X-ray diffraction.



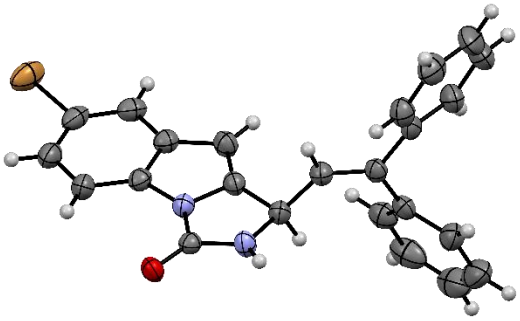


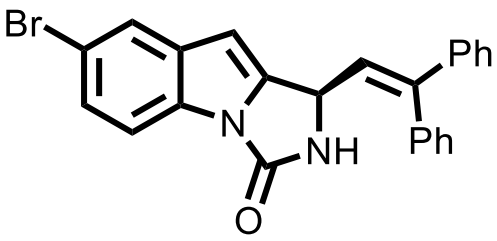
DATA	**(*S*)-3h**
Formula	$C_{24}H_{17}BrN_2O$
Formula weight	429.30
Colour	colourless
Temperature/K	100(2)/K
Wavelength/Å	0.71073 Å
Crystal system	monoclinic
Space group	4, P 21, P 2yb
Unit cell dimensions	a = 5.9099 (3) Å alpha = 90 deg. b = 31.2632 (15) Å beta = 103.579(2) deg. c = 10.5445 (5) Å gamma = 90 deg.
Volume	1893.77(16) A^3
Z, Calculated density	4, 1.506 Mg/m^3
Absorption coefficient	2.188 mm^-1
F(000)	872
Crystal size	0.271 x 0.081 x 0.018 mm
Theta range for data collection	1.987 to 28.315 deg.
Limiting indices	-7 <=h<=7, -41<=k<=41, -14<=l<=14

Reflections collected / unique	54474 / 9360
Data / restraints / parameters	9360 / 1 / 505
Goodness-of-fit on F^2	0.999
Final R indices [I>2sigma(I)]	R1 = 0.0427, wR2 = 0.0862
R indices (all data)	R1 = 0.0545, wR2 = 0.0903
Absolute structure parameter	0.025(4)
Largest diff. peak and hole	1.391 and -0.305 e.A^-3

Crystallographic data and structure refinement for compound (*R*)-3h

Compound **(*R*)-3h** was recrystallized from Ethylacetate: hexane (1:3) through the slow evaporation method, in a vial with a diameter of 0.75 cm and a length of 5 cm at room temperature, which afforded suitable-sized and quality crystals for X-ray diffraction.





DATA	**(*R*)-3h**
Formula	$C_{24}H_{17}BrN_2O$
Formula weight	429.30
Colour	clear light colourless
Temperature/K	301.15/K
Wavelength/Å	0.71073 Å
Crystal system	monoclinic
Space group	4, P 21, P 2yb
Unit cell dimensions	a = 6.0257(6) Å alpha = 90 deg. b = 31.476(3) Å beta = 104.128(3) deg. c = 10.6328(11) Å gamma = 90 deg.

Volume	1955.7(3) A^3
Z, Calculated density	4, 1.458 Mg/m^3
Absorption coefficient	2.119 mm^-1
F(000)	872
Crystal size	0.144 x 0.084 x 0.026 mm
Theta range for data collection	2.3614 to 21.7967 deg.
Limiting indices	-8 <=h<=7, -41<=k<=41, -14<=l<=14
Reflections collected / unique	43869 / 9630
Data / restraints / parameters	9630 / 1 / 505
Goodness-of-fit on F^2	0.985
R indices (all data)	R1 = 0.0351, wR2 = 0.0755
Absolute structure parameter	0.022(4)
Largest diff. peak and hole	0.30 and -0.339 e.A^-3

14. References:

1. J. Liu, D.-Y. Liu, Q. Yang, Y.-F. Zeng, X.-L. Wang, P.-F. Wang, Y.-J. Ruan, M.-M. Wen, S.-S. Zhang, L.-d. Du and X.-G. Liu, *Chem. Commun.*, **2024**, *60*, 598-601.

2. K. Ramachandran, P. Anbarasan, *Chem. Sci.* **2021**, *12*, 13442-13449.

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4. B. Ye, N. Cramer, *J. Am. Chem. Soc.* **2013**, *135*, 636-639.

5. Y. Sun, N. Cramer, *Chem. Sci.* **2018**, *9*, 2981-2985.

6. B. Audic, M. D. Wodrich, N. Cramer, *Chem. Sci.* **2019**, *10*, 781-787.

7. T. Ooi, M. Kameda, K. Maruoka, *J. Am. Chem. Soc.* **2003**, *125*, 5139-5151.