Supporting Information For:

Enantioselective Friedel-Crafts Reaction of 4,7-dihydroindoles with *β*-CF_3-*β*-disubstituted Nitroalkenes

Hao Wu, Ren-Rong Liu, Chong Shen, Min-Di Zhang, Jianrong Gao, and Yi-Xia Jia*

College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, China

Email: yxjia@zjut.edu.cn

Contents :

General information:

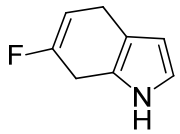
NMR spectra were recorded on 500 MHz spectrometers for ^{1}H NMR and 125 MHz spectrometer for ^{13}C NMR with deuterated chloroform ($CDCl_3$) as a solvent at 298 K. Chemical shifts are expressed in δ ppm according to $SiMe_4$ as an internal standard (δ = 0) for ^{1}H NMR, chloroform-*d* (δ = 77.0) for ^{13}C NMR. HRMS were obtained with a TOF MS spectrometer. Melting points were uncorrected. Anhydrous toluene and ether were freshly distilled over Na and benzophenone. Anhydrous DCE was freshly distilled over calcium hydride. Chiral bisoxazoline ligands **L1**-**L6**[1] and **L7**-**L8** [2] were synthesized according to the literatures. Substrates *β*-CF_3-*β*-disubstituted nitroalkenes **1a**-**1m**[3] and 4,7-dihydroindoles **2a**,[4] **2b**,[5] **2c**,[6] and

[1] Evans, D. A.; Peterson, G. S.; Johnson, J. S.; Barnes, D. M.; Campos, K. R.; Woerpel, K. A. *J. Org. Chem.* **1998**, *63,* 4541.
[2] Desimoni, G.; Faita, G.; Mella, M. *Tetrahedron*, **1996**, *52*, 13649.
[3] Gao, J.-R.; Wu, H.; Xiang, B.; Yu, W.-B.; Han, L.; Jia, Y.-X. *J. Am. Chem. Soc.* **2013**, *135*, 2983.
[4] Çavdar, H.; Saraçoğlu, N. *Tetrahedron* **2005**, *61*, 2401.
[5] Takenaka, N.; Chen, J.; Captain, B.; Sarangthem, R. S.; Chandrakuma, A. *J. Am. Chem. Soc.* **2010**, *132*, 4536.
[6] Kang, Q.; Zheng, X.-J.; You, S.-L. *Chem. Eur. J.* **2008**, *14*, 3539.

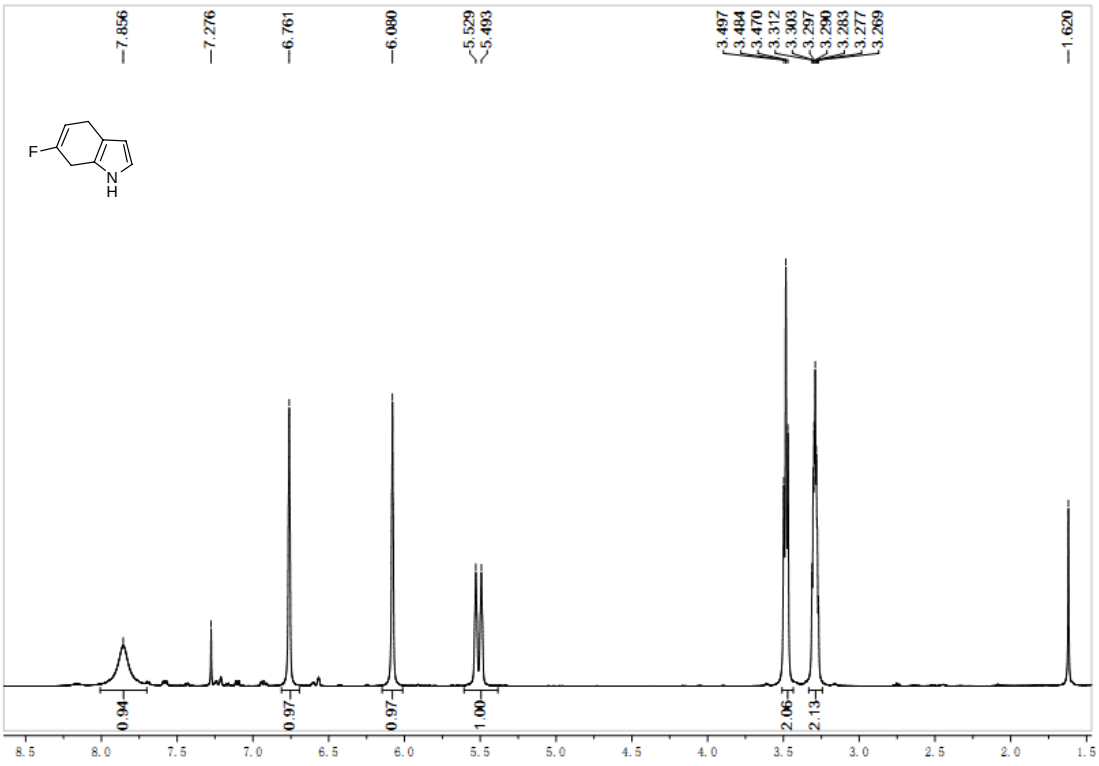
2d were prepared according to the reported methods.

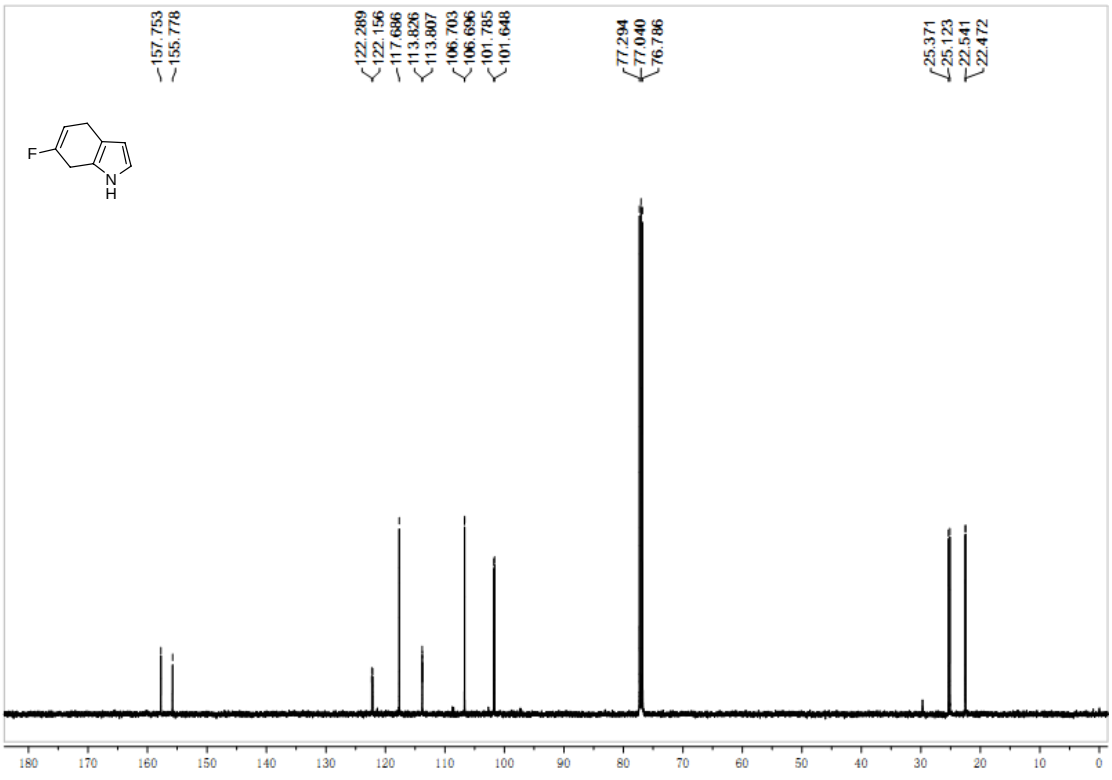
Synthesis of substrate:

6-fluoro-4,7-dihydro-1H-indole (**2d**):



The solution of the 6-fluoro-indole (1 g, 7.4 mmol) in dry methanole (6 mL) was added to liquid ammonia (20 mL) under N_2 .When the resulting solution was cooled to -40 ^{o}C, lithium metal (0.21 g, 29.6 mmol) was added in small pieces for 5–10 min. The resulting deep blue solution was stirred at the same temperature for 1h and then was allowed to warm to rt. After the excess ammonia had evaporated, saturated aq. NH4Cl were carefully added to the mixture and extracted with Et_2O. The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel eluting with ethyl acetate/petroleum ether (1:20) to give the 6-fluoro-4,7-dihydro-1H-indole (**2d**) as a yellow liquid (0.57g, 4.2mmol, 56%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.26-3.31 (m, 2H), 3.48 (t, J = 7.0 Hz, 2H), 5.51 (d, J = 18.0 Hz, 1H), 6.08 (s, 1H), 6.76 (s, 1H), 7.85 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 22.5 (d, J = 8.6 Hz), 25.2 (d, J = 31.0 Hz), 101.7 (d, J = 17.1 Hz), 106.7 (d, J = 0.9 Hz), 113.8 (d, J = 2.4 Hz), 117.6, 122.2 (d, J = 16.6 Hz), 156.7 (d, J =246.9 Hz); HRMS *m/z* (EI+): Calculated for C_8H_8NF ($[M]^+$): 137.0641, Found 137.0648.

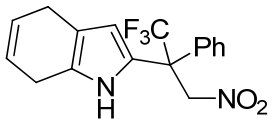

7.856
7.276
6.761
6.080
5.529
5.493
3.497
3.484
3.470
3.312
3.303
3.297
3.290
3.283
3.277
3.269
1.620
F
N
H
0.94
0.97
0.97
1.00
2.06
2.13
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5


157.753
155.778
122.289
122.156
117.686
113.826
113.807
106.703
106.696
101.785
101.648
77.294
77.040
76.786
25.371
25.123
22.541
22.472
F
N
H
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

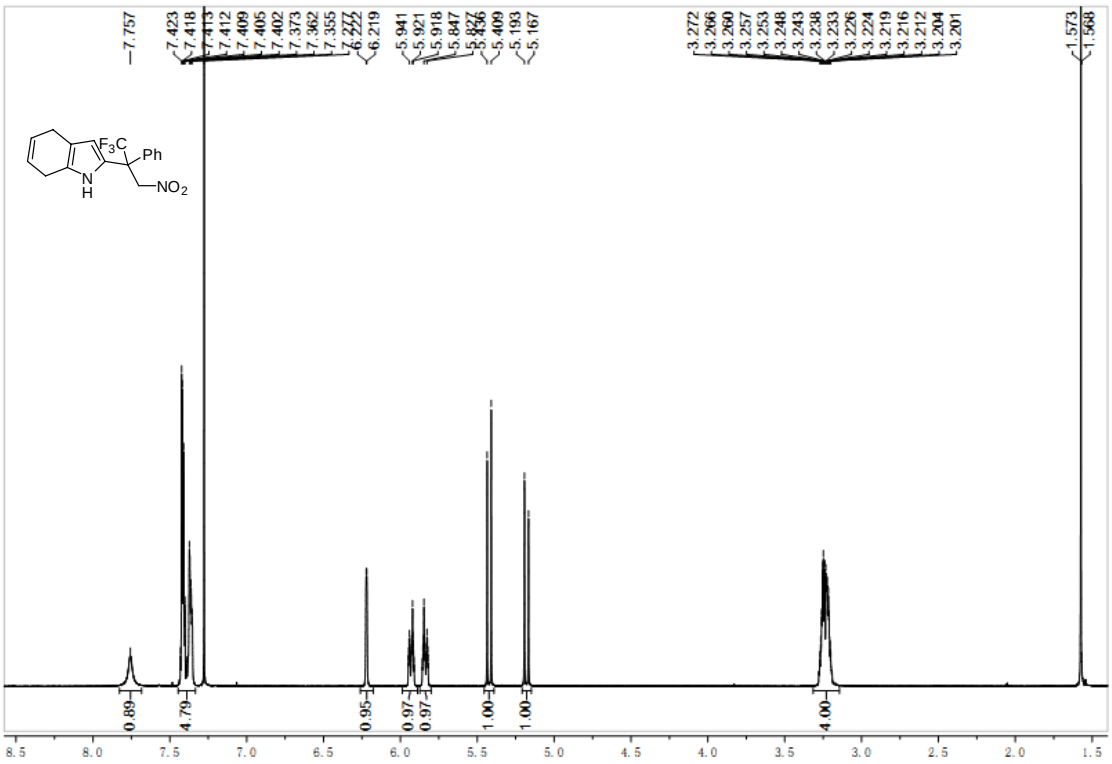
General procedure for Friedel-Crafts reaction:

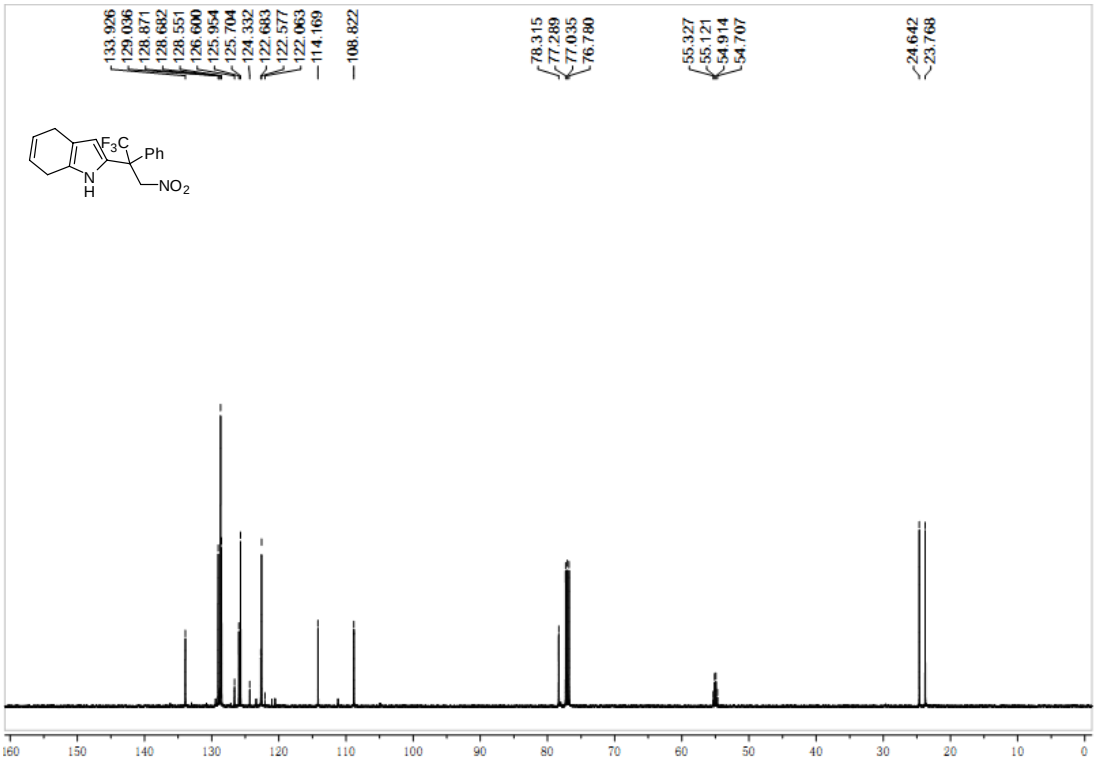
To a dried Schlenk tube were added $Ni(ClO_4)_2 \cdot 6H_2O$ (7.3 mg, 0.02 mmol) and ligand **L7** (11.7 mg, 0.024 mmol) under N_2, 2.0 mL toluene was then added through syringe. The resulting mixture was stirred at 80 °C for 1h, after which the nitroalkene (0.2 mmol) and 4,7-dihydroindole (0.3 mmol) were added. The mixture was stirred at 80 °C until the reaction was completed (monitored by TLC). The solvent was then evaporated under vacuum and the residue was purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether (1:10~1:5) to afford the product.

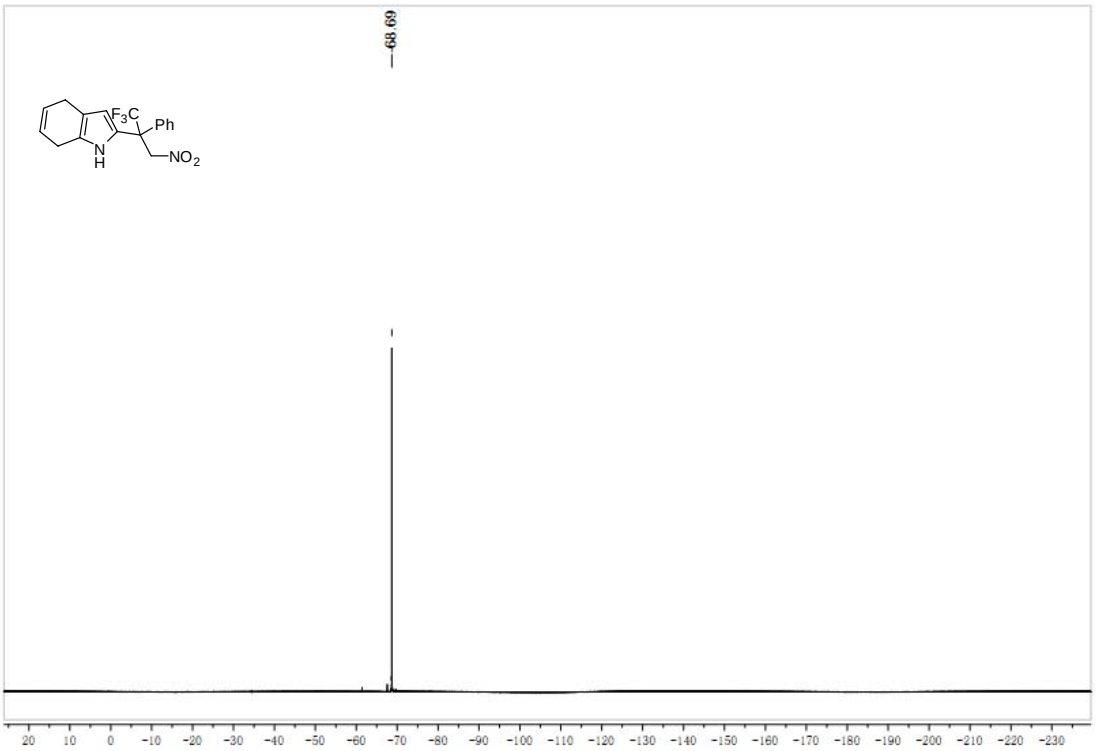
2-(1,1,1-trifluoro-3-nitro-2-phenylpropan-2-yl)-4,7-dihydro-1H-indole (**3aa**):

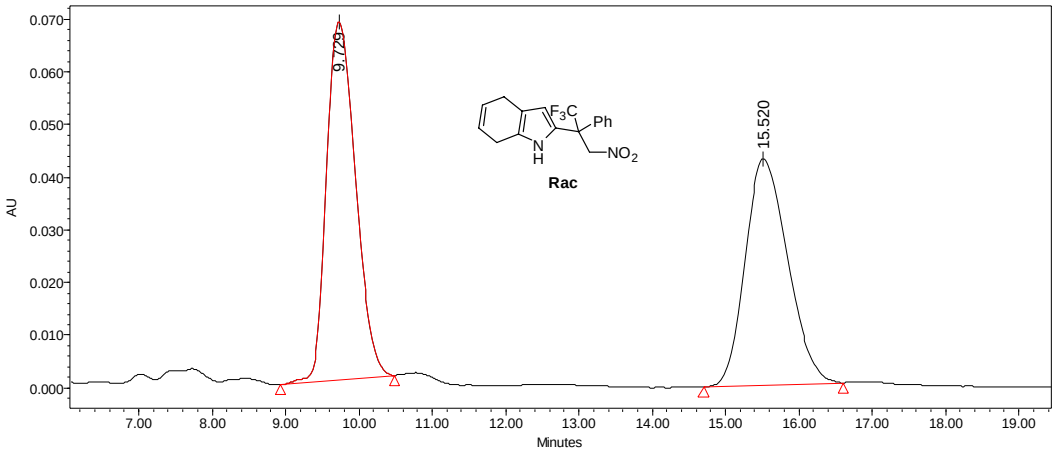


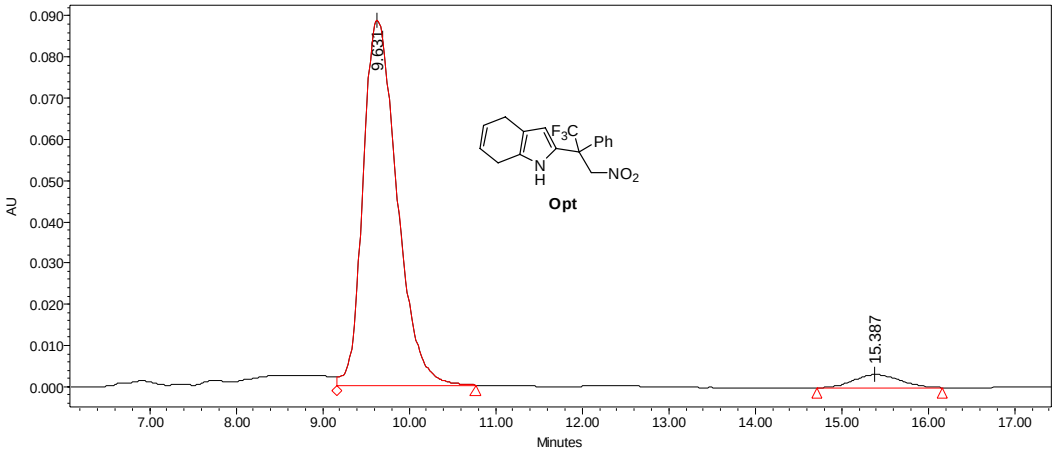
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); Yellow oil, 94% yield, $[\alpha]_D^{25}$ = + 38.2 (*c* 1.0, CH_2Cl_2), 91% ee [Daicel Chiralpak AS-H column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 85/15, 1.0 mL/min, 254 nm; t_{minor} = 15.3 min, t_{major} = 9.6 min]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.20-3.27 (m, 4H), 5.18 (d, *J* = 13.0 Hz, 1H), 5.42 (d, *J* = 13.5 Hz, 1H), 5.82-5.85 (m, 1H), 5.91-5.94 (m, 1H), 6.22 (d, *J* = 1.5 Hz, 1H), 7.35-7.43 (m, 5H), 7.75 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -68.6 (s, 3F); ^{13}C NMR (125 MHz, $CDCl_3$): δ 23.7, 24.6, 55.0 (q, *J* = 25.9 Hz), 78.3, 108.8, 114.1, 122.5, 122.6, 125.4 (q, *J* = 283.5 Hz), 125.7, 125.9, 128.5, 128.6, 129.0, 133.9; HRMS m/z (ESI+): Calculated for $C_{17}H_{16}F_3N_2O_2$ ($[M+H]^+$): 337.1164, Found 337.1151.


7.757
7.423
7.418
7.413
7.412
7.409
7.405
7.402
7.373
7.362
7.355
6.219
5.941
5.921
5.918
5.847
5.409
5.193
5.167
3.272
3.266
3.260
3.257
3.253
3.248
3.243
3.238
3.233
3.226
3.224
3.219
3.216
3.212
3.204
3.201
1.573
1.568
F3C
Ph
N
H
NO2
0.89
4.79
0.95
0.97
0.97
1.00
1.00
4.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5


133.926
129.036
128.871
128.682
128.551
126.600
125.954
125.704
124.332
122.683
122.577
122.063
114.169
108.822
78.315
77.289
77.035
76.780
55.327
55.121
54.914
54.707
24.642
23.768
F3C
Ph
N
H
NO2
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

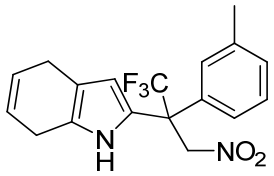




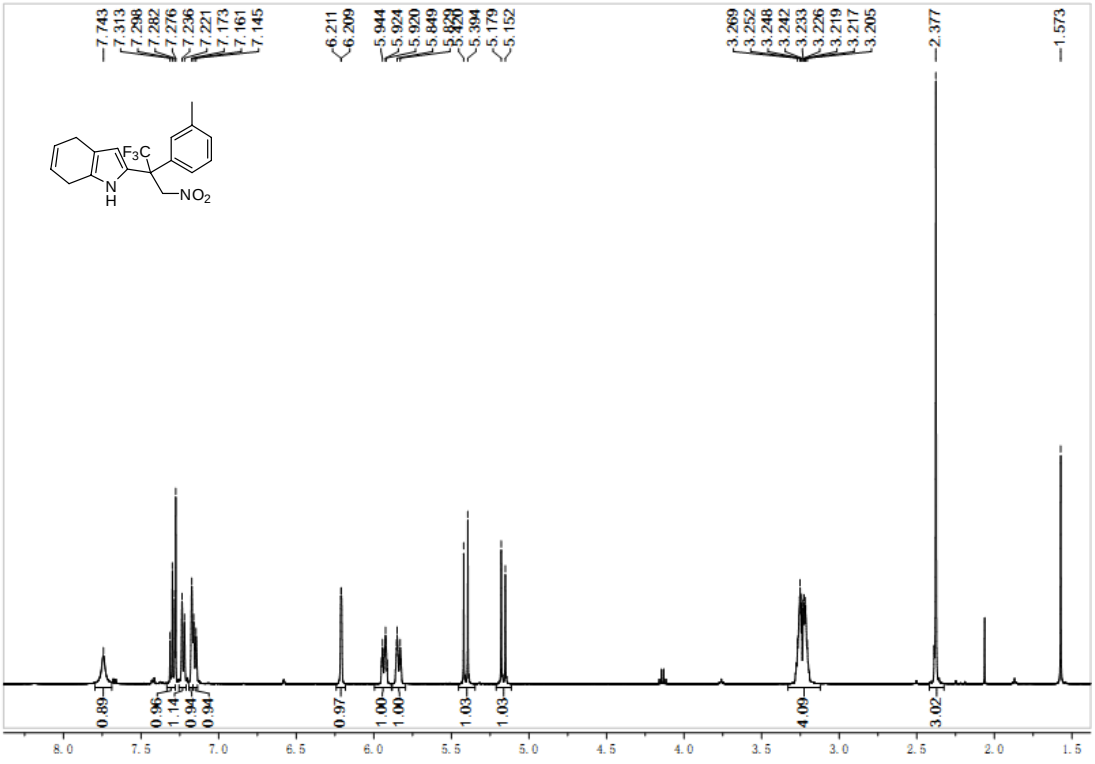


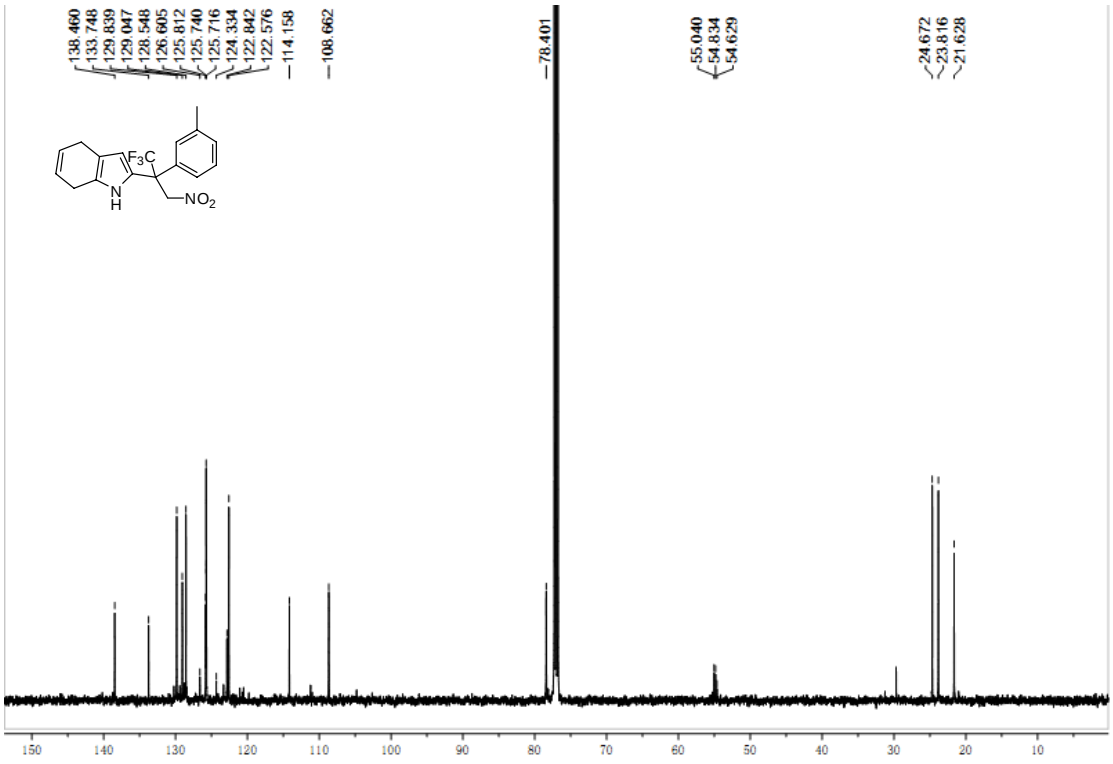
	Retention Time	Height	Area	% Area
1	9.631	88677	2414824	95.34
2	15.387	3170	118155	4.66

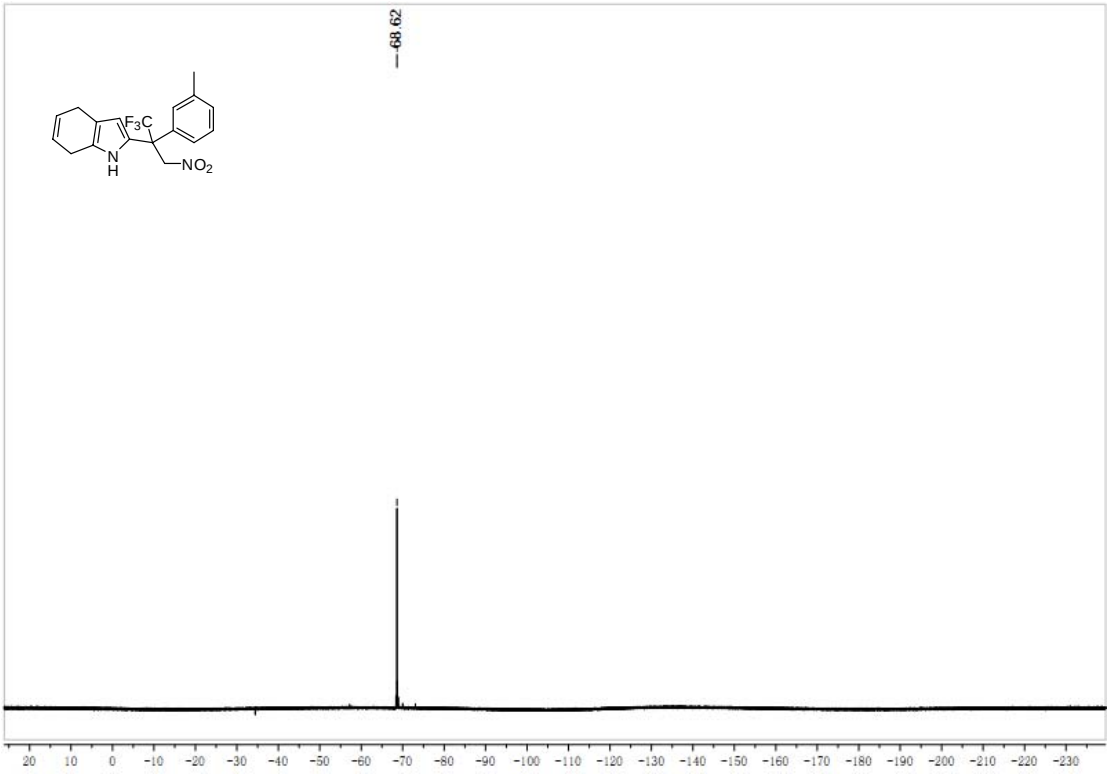
2-(1,1,1-trifluoro-3-nitro-2-*m*-tolylpropan-2-yl)-4,7-dihydro-1H-indole (**3ba**):

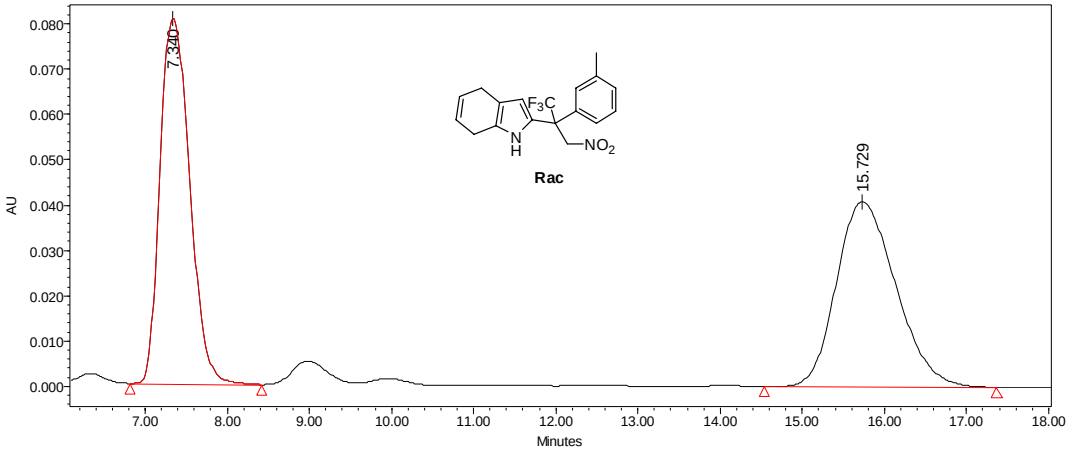


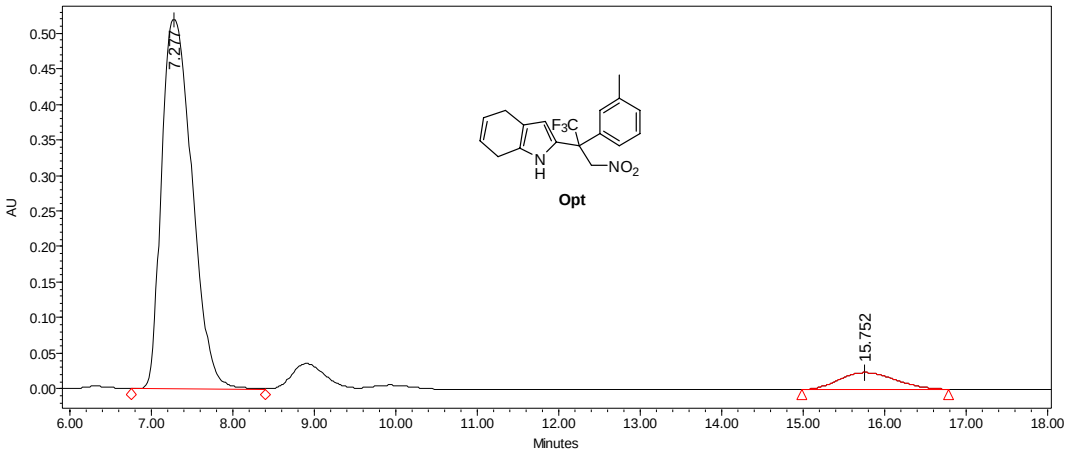
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); Yellow oil, 95% yield, $[\alpha]_D^{27}$ = + 26.0 (*c* 1.0, CH_2Cl_2), 85% ee [Daicel Chiralpak AS-H column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 85/15, 1.0 mL/min, 254 nm; t_{minor} =15.7 min, t_{major} = 7.2 min]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.37 (s, 3H), 3.20-3.26 (m, 4H), 5.16 (d, *J* = 13.5 Hz, 1H), 5.40 (d, *J* = 13.0 Hz, 1H), 5.82-5.85 (m, 1H), 5.91-5.95 (m, 1H), 6.21 (d, *J* = 1.0 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.17 (s, 1H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.29 (t, *J* = 8.0 Hz, 1H), 7.74 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -68.6 (s, 3F); ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.6, 23.8, 24.6, 54.9 (q, *J* = 25.8 Hz), 78.4, 108.6, 114.1, 122.5, 122.8, 125.4 (q, *J* = 283.9 Hz), 125.71, 125.74, 125.8, 128.5, 129.0, 129.8, 133.7, 138.4; HRMS *m/z* (EI+): calculated for $C_{18}H_{17}N_2O_2F_3$ ($[M]^+$): 350.1242, found 350.1249.




138.460
133.748
129.839
129.047
128.548
126.605
125.812
125.740
125.716
124.334
122.842
122.576
114.158
108.662
78.401
55.040
54.834
54.629
24.672
23.816
21.628
F3C
N
H
NO2
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

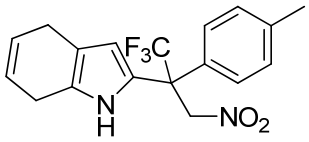

68.62
F3C
N
H
NO2
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230





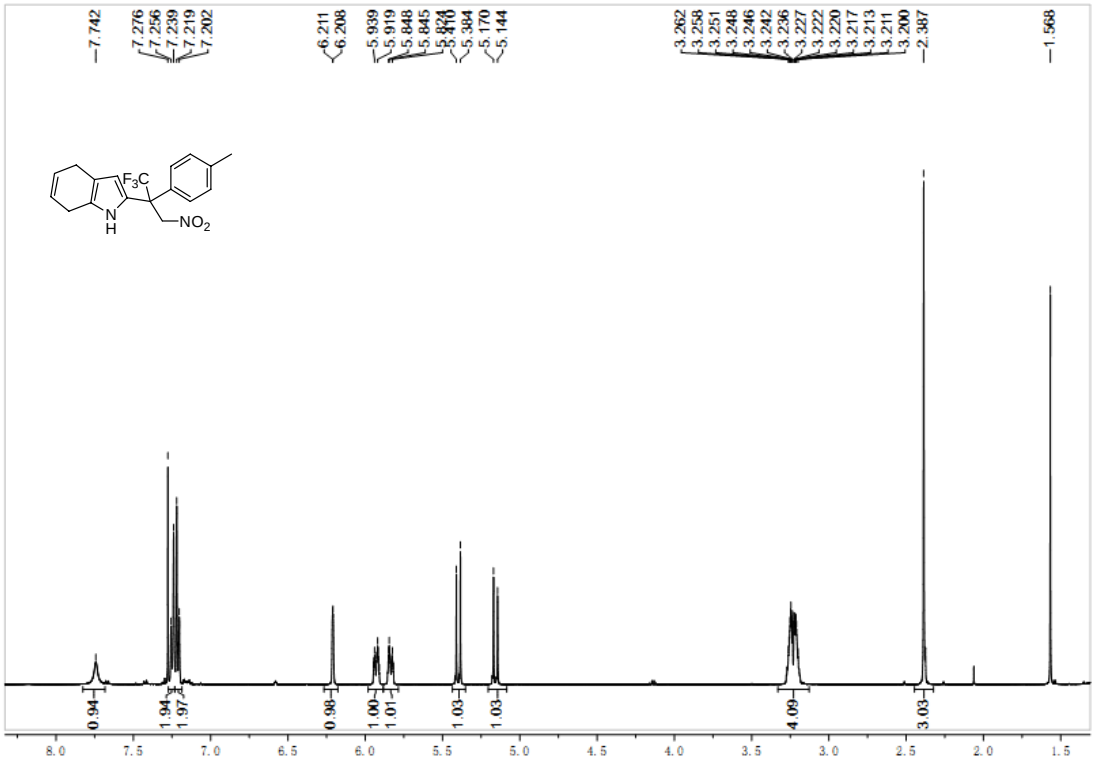
	Retention Time	Height	Area	% Area
1	7.277	519475	13544335	92.23
2	15.752	23753	1141786	7.77

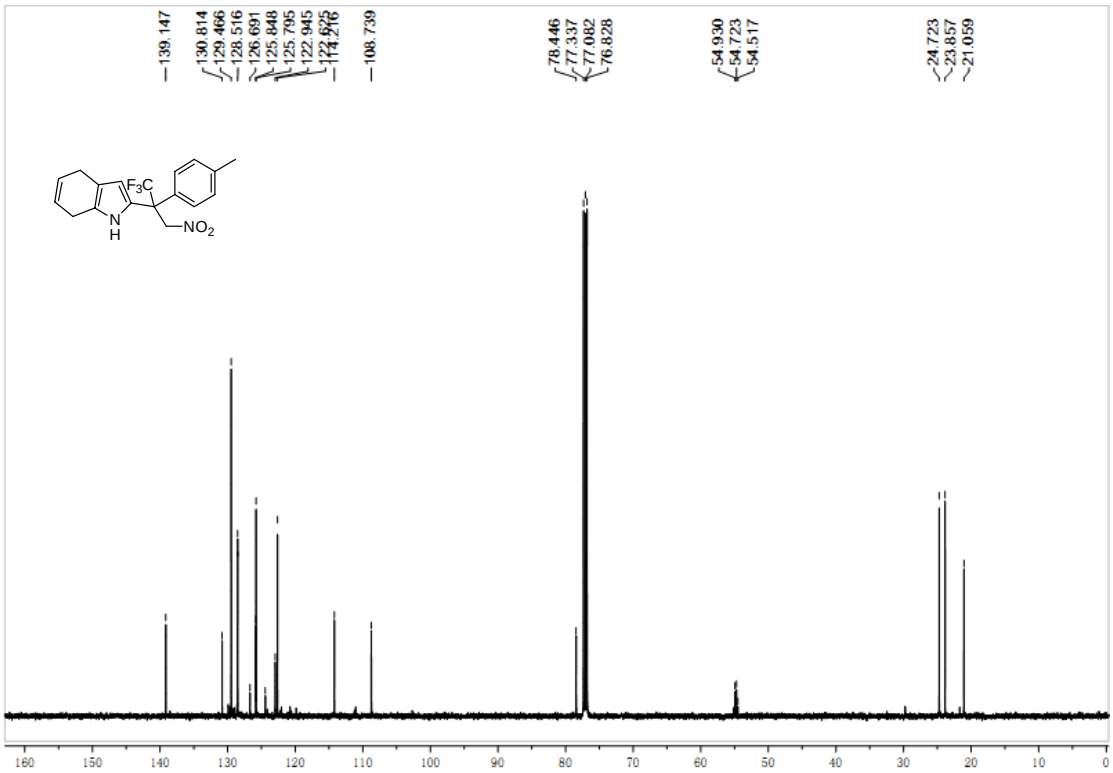
2-(1,1,1-trifluoro-3-nitro-2-*p*-tolylpropan-2-yl)-4,7-dihydro-1H-indole (**3ca**):

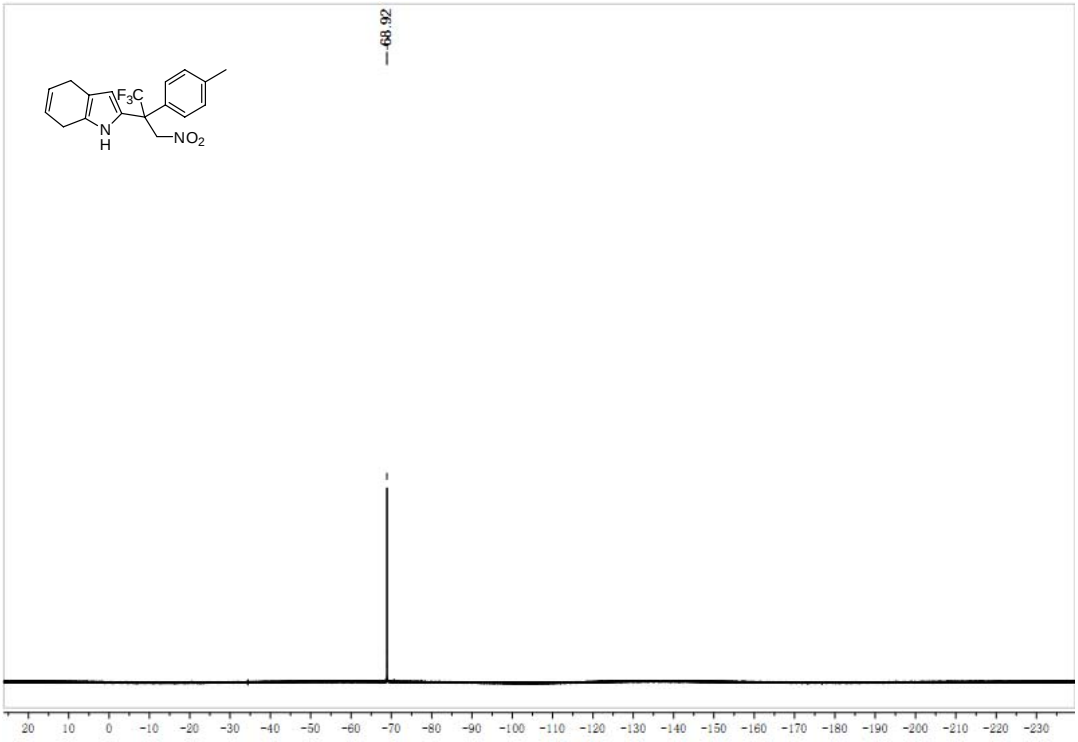


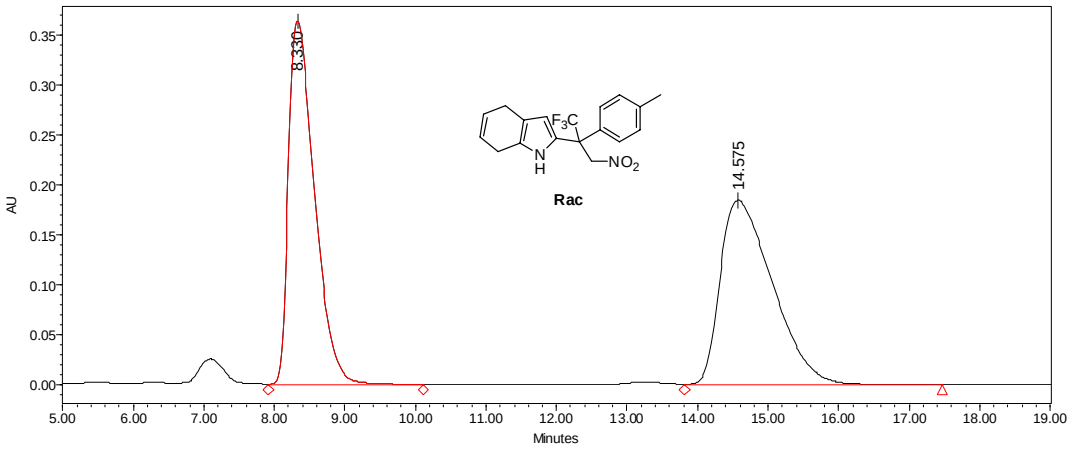
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); Yellow oil, 92% yield, $[\alpha]_D^{27}$ = + 30.5 (*c* 1.0, CH_2Cl_2), 88% ee [Daicel Chiralpak AS-H column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 85/15, 1.0 mL/min, 254 nm; t_{minor} = 15.3 min, t_{major} = 8.4 min]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.38 (s, 3H), 3.20-3.26 (m, 4H), 5.15 (d, *J* = 13.0 Hz, 1H), 5.39 (d, *J* = 13.0 Hz, 1H), 5.81-5.84 (m, 1H), 5.90-5.94 (m, 1H), 6.20 (d, *J* = 1.5 Hz, 1H), 7.21 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 7.74 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -68.9 (s,

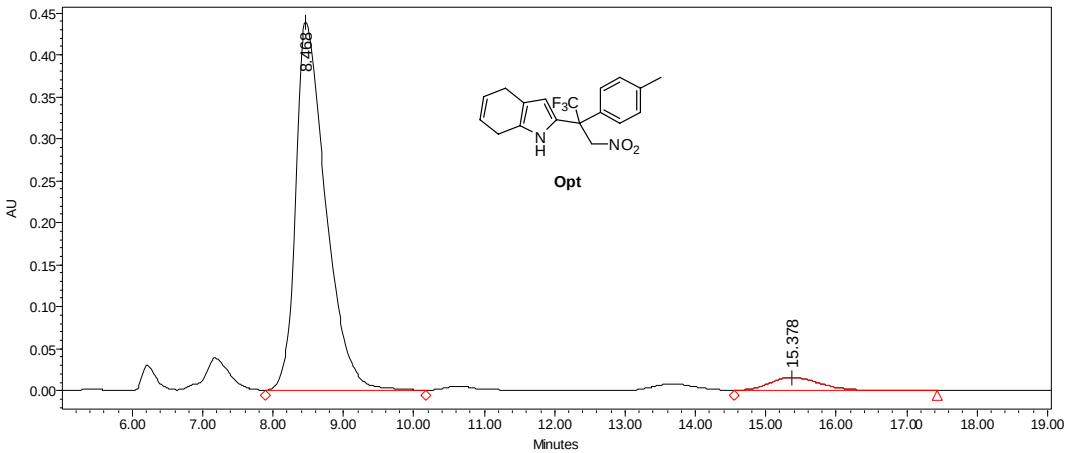
3F); ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.0, 23.8, 24.7, 54.8 (q, J = 25.9 Hz), 78.4, 108.7, 114.2, 122.6, 122.9, 125.5 (q, J = 283.4 Hz), 125.7, 125.8, 128.5, 129.4, 130.8, 139.1; HRMS *m/z* (EI+): Calculated for $C_{18}H_{17}N_2O_2F_3$ ($[M]^+$): 350.1242, Found 350.1265.





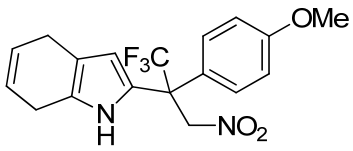




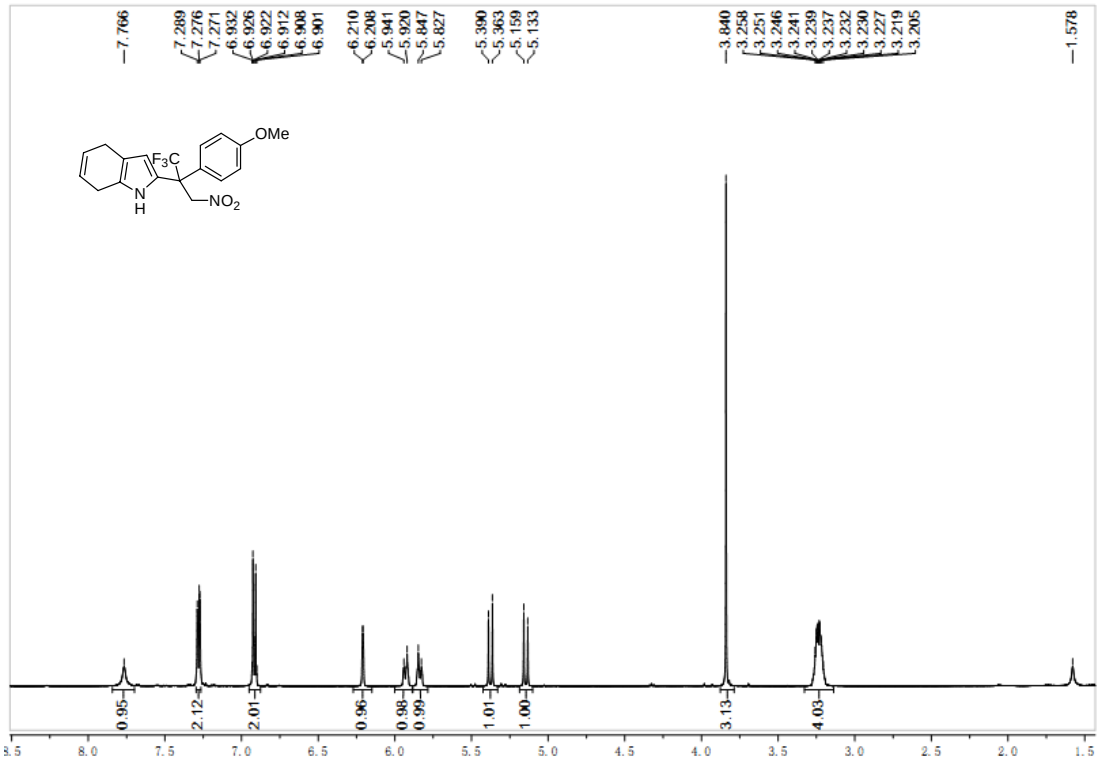


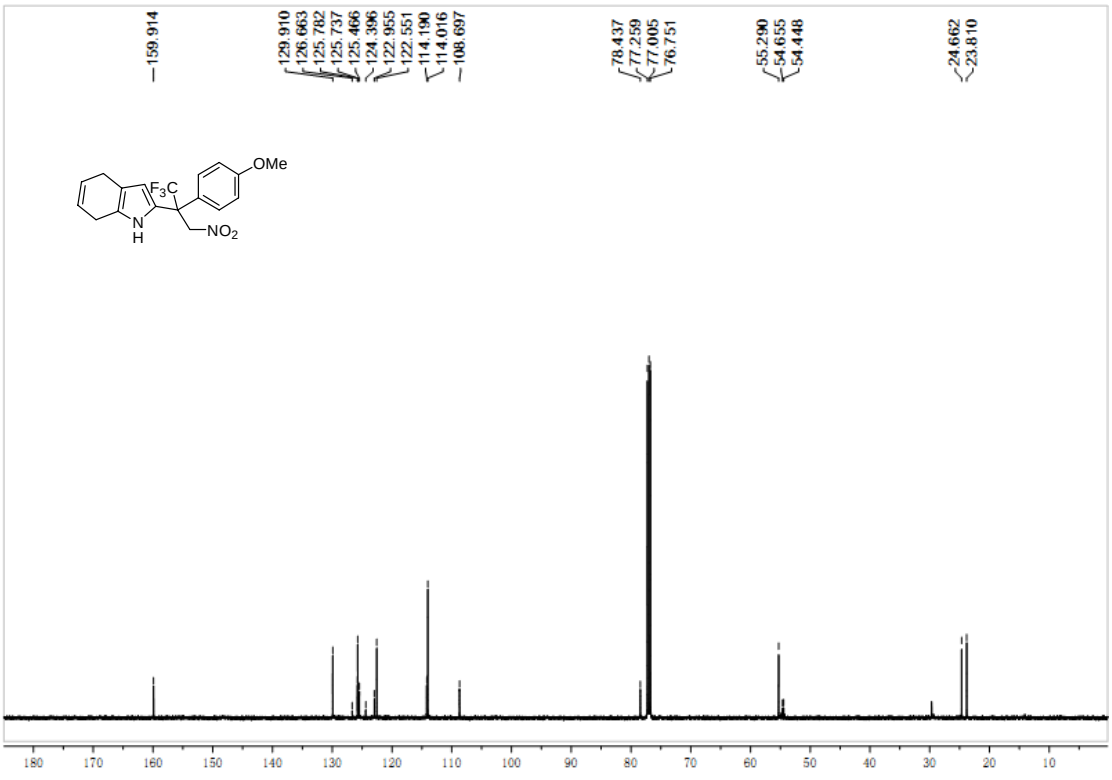
	Retention Time	Height	Area	% Area
1	8.468	439485	13056508	94.12
2	15.378	15981	815773	5.88

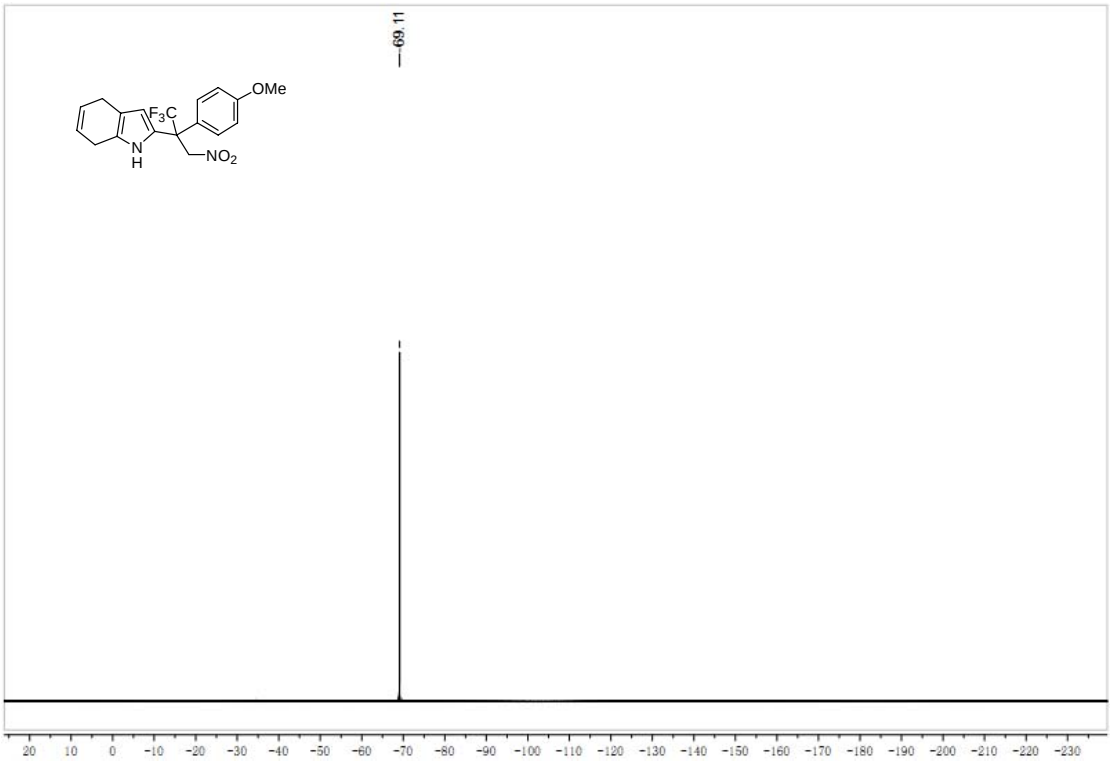
2-(1,1,1-trifluoro-2-(4-methoxyphenyl)-3-nitropropan-2-yl)-4,7-dihydro-1H-indole (**3da**):

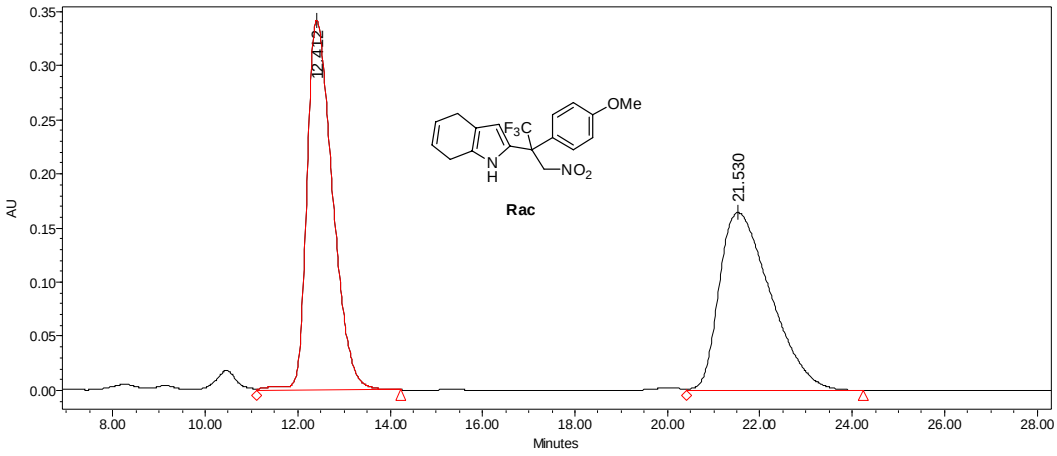


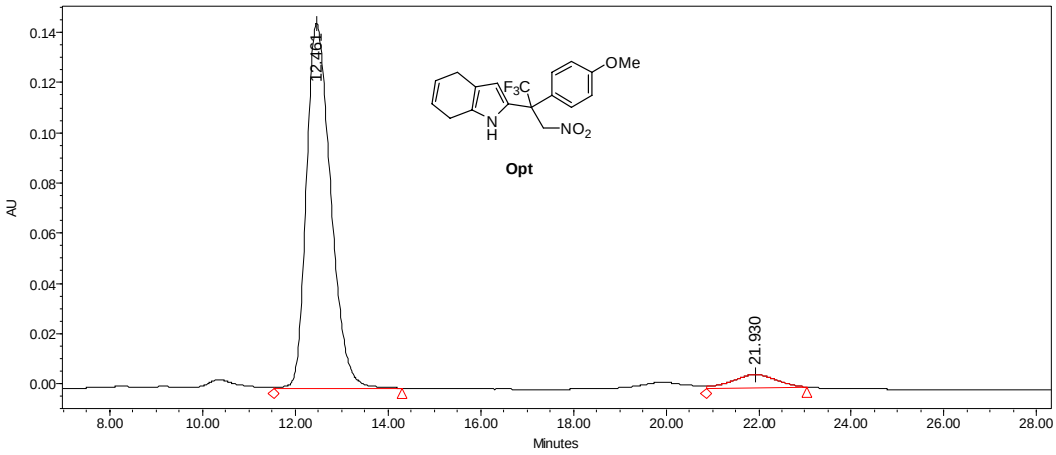
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); Yellow oil, 90% yield, $[\alpha]_D^{27}$ = + 30.6 (*c* 1.0, CH_2Cl_2), 88% ee [Daicel Chiralpak AS-H column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 85/15, 1.0 mL/min, 254 nm; t_{minor} = 21.9 min, t_{major} = 12.4 min]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.20-3.25 (m, 4H), 3.84 (s, 3H), 5.14 (d, *J* = 13.0 Hz, 1H), 5.37 (d, *J* = 13.5 Hz, 1H), 5.83 (d, *J* = 10.0 Hz, 1H), 5.93 (d, *J* = 10.5 Hz, 1H), 6.20 (d, *J* = 1.0 Hz, 1H), 6.91 (dt, *J* = 2.5, 9.0 Hz, 2H), 7.28 (d, *J* = 9.0 Hz, 2H), 7.76 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -69.1 (s, 3F); ^{13}C NMR (125 MHz, $CDCl_3$): δ 23.8, 24.6, 54.5 (q, *J* = 25.9 Hz), 55.2, 78.4, 108.6, 114.0, 114.1, 122.5, 122.9, 125.4, 125.5 (q, *J* = 283.4 Hz), 125.73, 125.78, 129.9, 159.9; HRMS *m/z* (EI+): Calculated for $C_{18}H_{17}N_2O_3F_3$ ($[M]^+$): 366.1191, Found 366.1211.




159.914
129.910
126.663
125.782
125.737
125.466
124.396
122.955
122.551
114.190
114.016
108.697
78.437
77.259
77.005
76.751
55.290
54.655
54.448
24.662
23.810
OMe
F3C
N
H
NO2
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

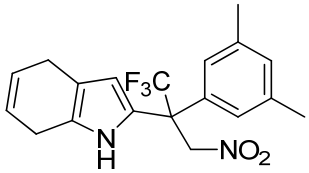

69.11
OMe
F3C
N
H
NO2
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230





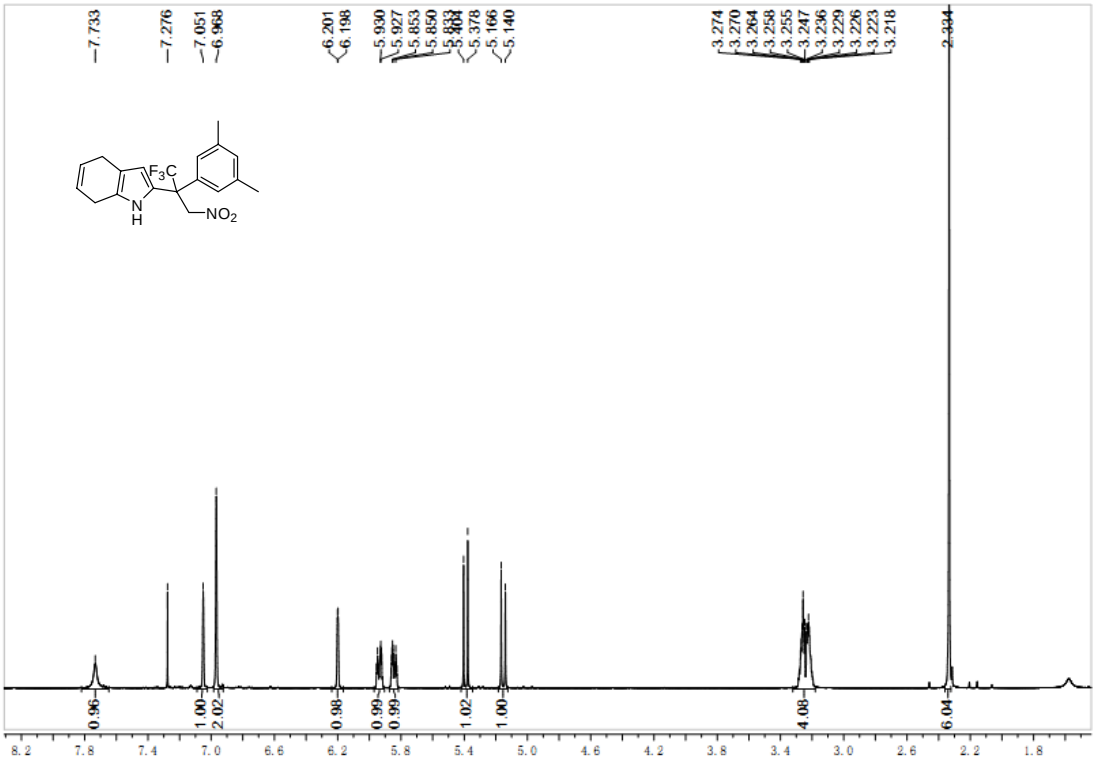
	Retention Time	Height	Area	% Area
1	12.461	145355	5291570	93.98
2	21.930	5167	339178	6.02

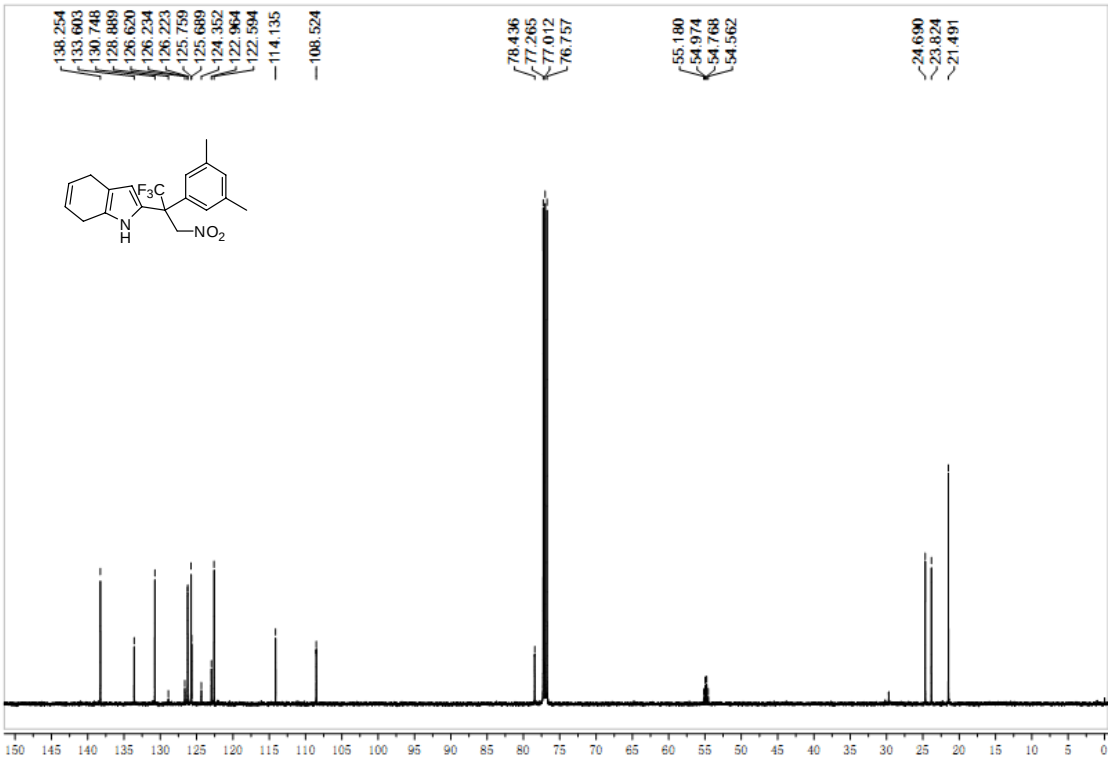
2-(2-(3,5-dimethylphenyl)-1,1,1-trifluoro-3-nitropropan-2-yl)-4,7-dihydro-1H-indole (**3ea**):

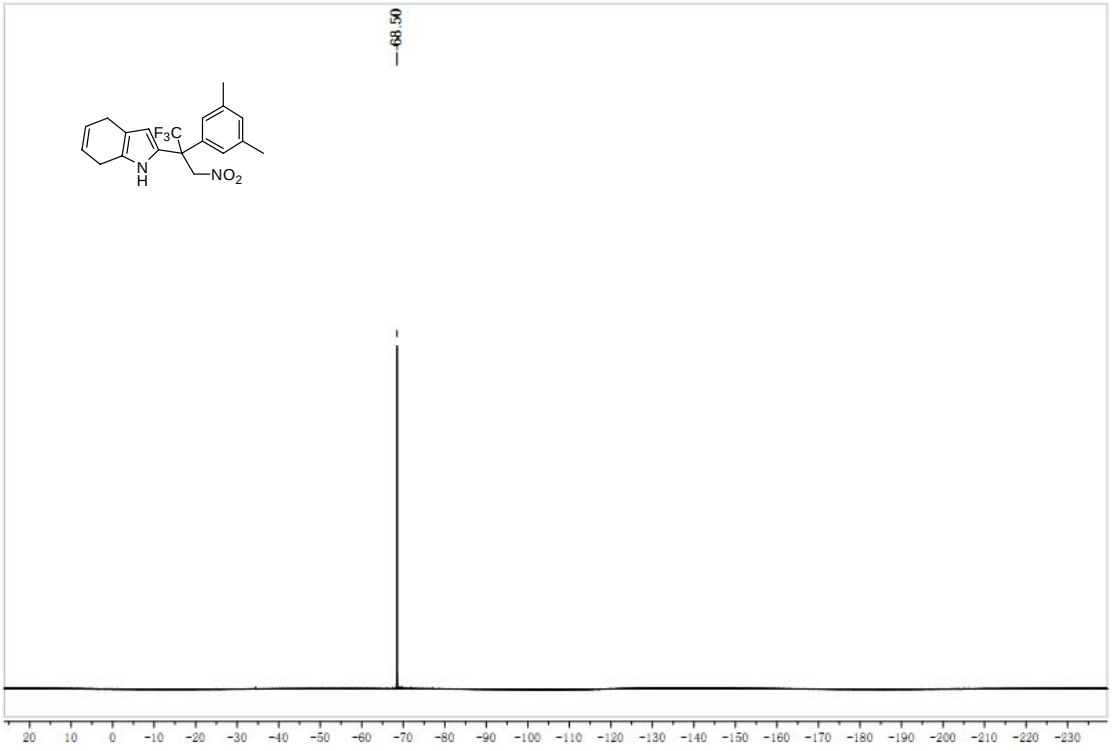


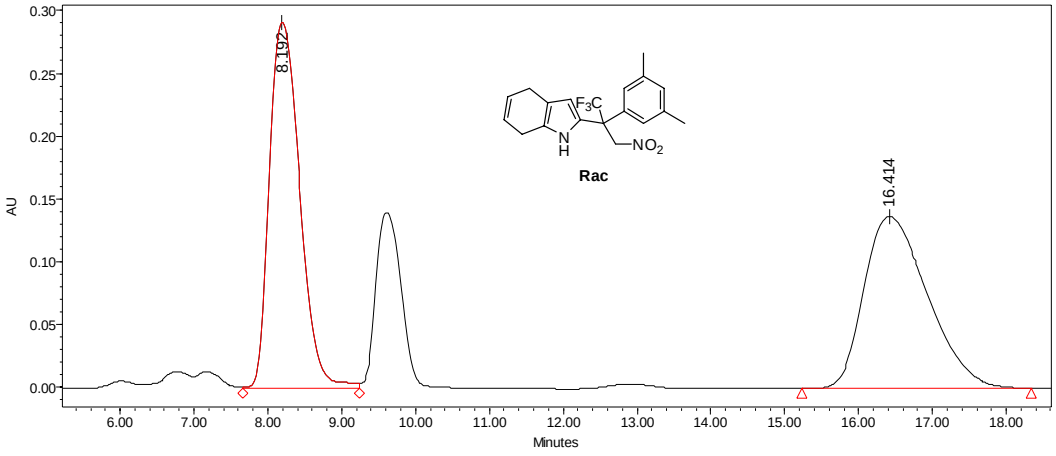
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); Yellow oil, 90% yield, $[\alpha]_D^{27}$ = + 37.2 (*c* 0.5, CH_2Cl_2), 84% ee [Daicel Chiralpak AS-H column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 93/7, 1.0 mL/min, 254 nm; t_{minor} = 16.6 min, t_{major} = 8.2 min]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.33 (s, 6H), 3.21-3.27 (m, 4H), 5.15 (d, *J* = 13.0 Hz, 1H), 5.39 (d, *J* = 13.0 Hz, 1H), 5.82-5.86 (m, 1H), 5.92-5.95 (m, 1H), 6.20 (d, *J* = 1.5 Hz, 1H), 6.96 (s, 2H), 7.05 (s,

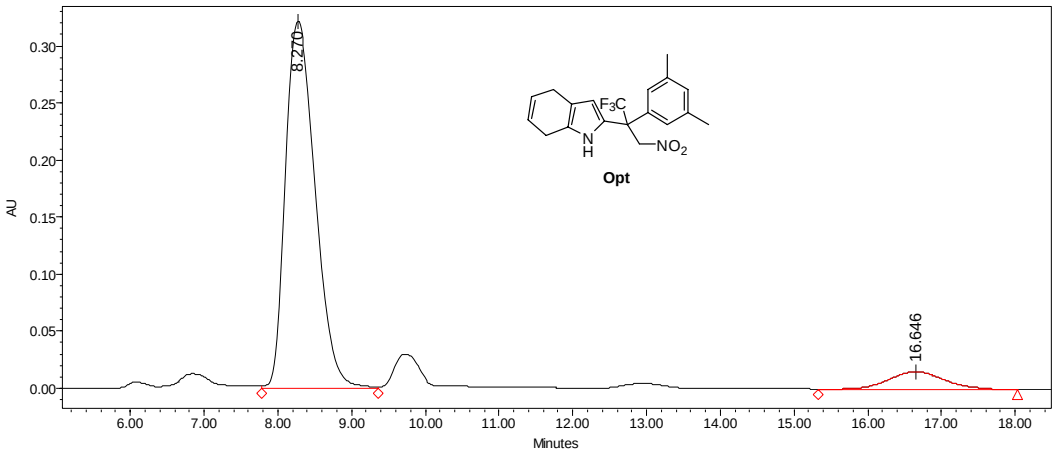
1H), 7.73 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -68.5 (s, 3F); ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.4, 23.8, 24.6, 54.8 (q, J = 25.8 Hz), 78.4, 108.5, 114.1, 122.5, 122.9, 125.4 (q, J = 283.5 Hz), 125.6, 125.7, 126.2 (d, J = 1.4 Hz), 130.7, 133.6, 138.2; HRMS *m/z* (EI+): Calculated for $C_{19}H_{19}N_2O_2F_3$ ($[M]^+$): 364.1399, Found 364.1402.





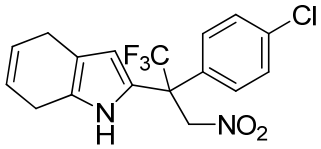




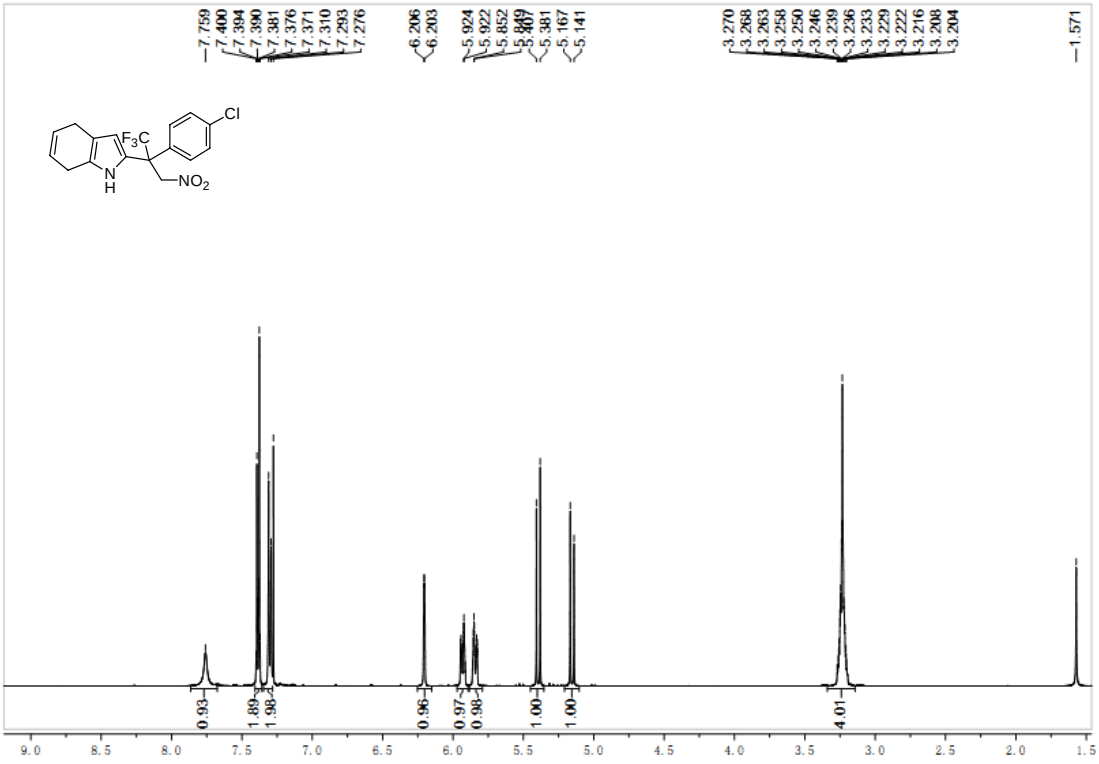


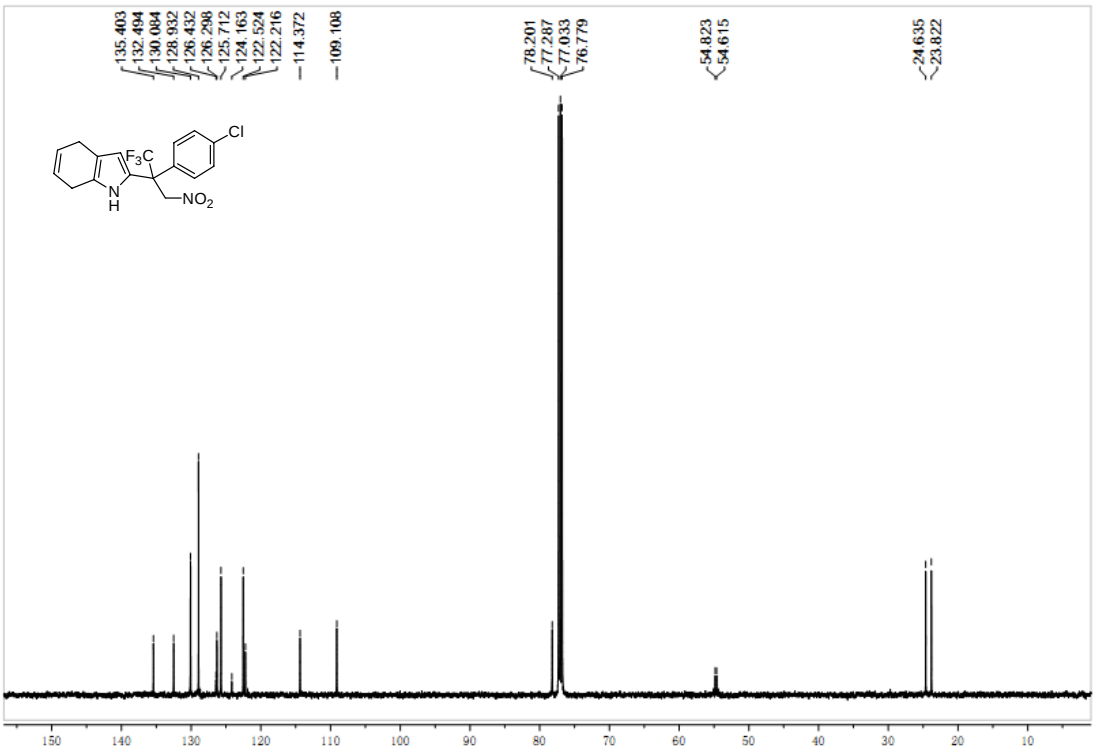
	Retention Time	Height	Area	% Area
1	8.270	321657	9111087	91.89
2	16.646	15281	804641	8.11

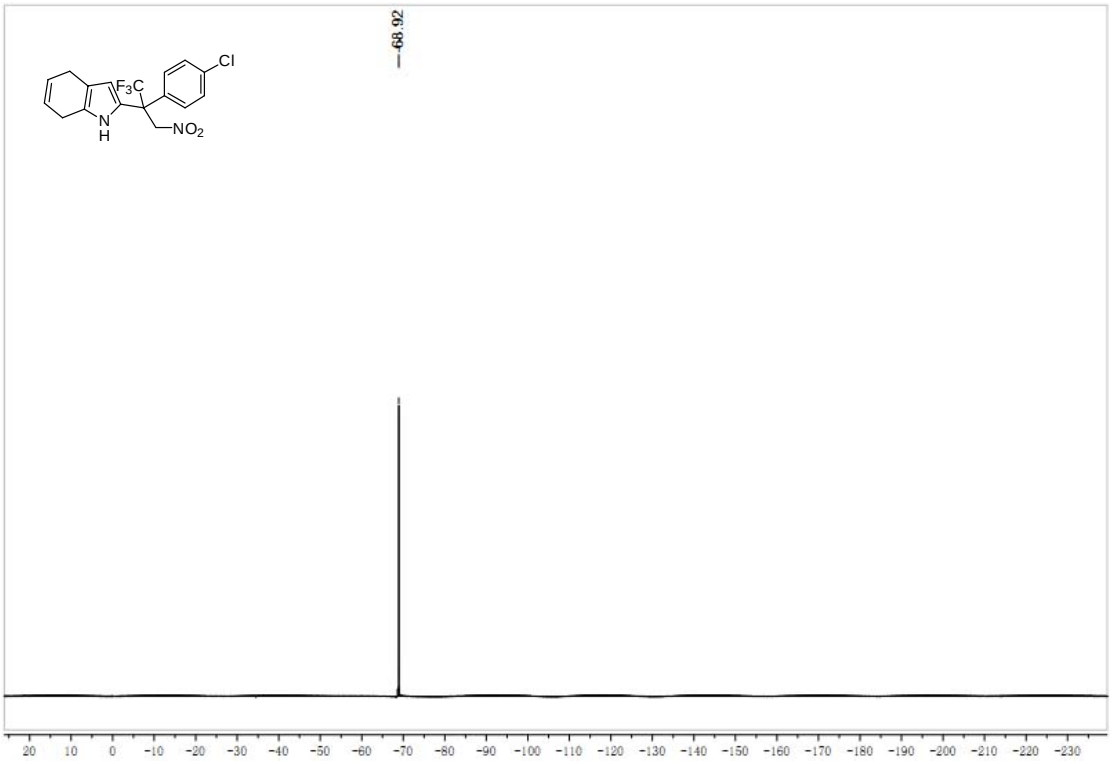
2-(2-(4-chlorophenyl)-1,1,1-trifluoro-3-nitropropan-2-yl)-4,7-dihydro-1H-indole (**3fa**):

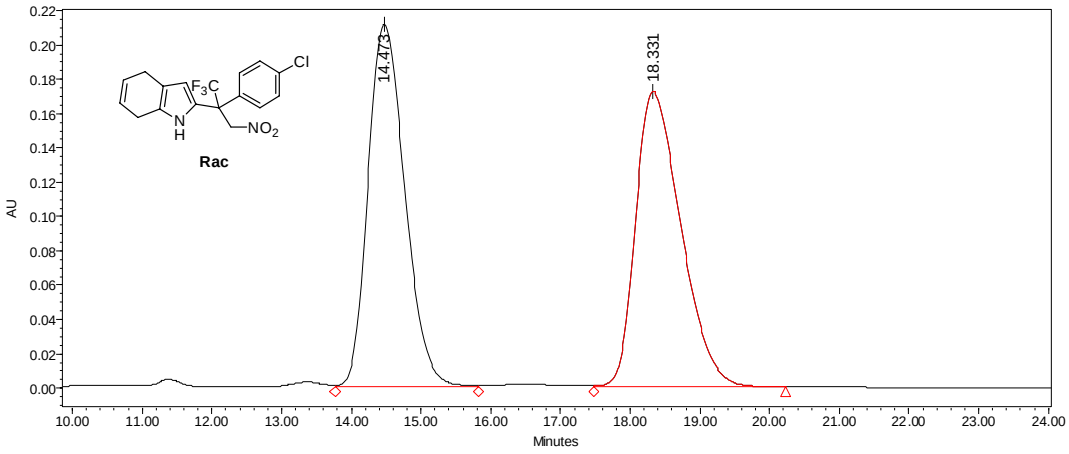


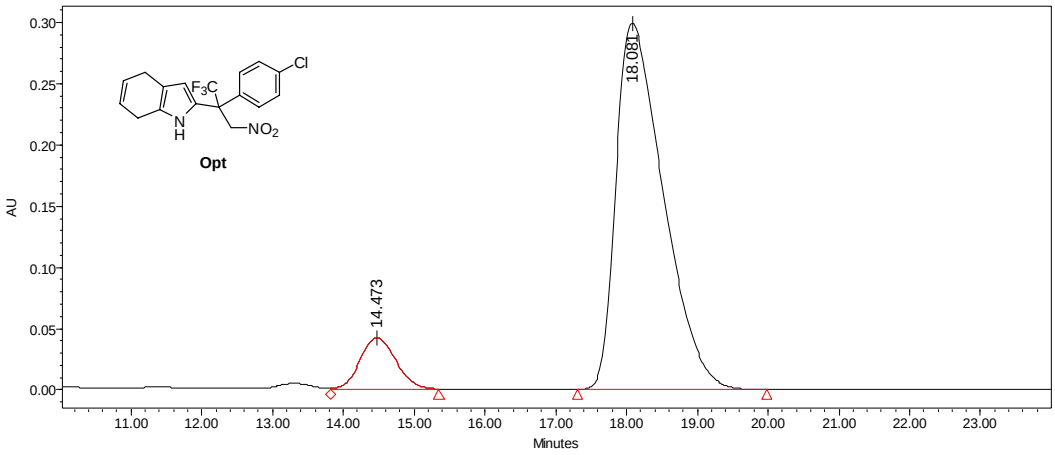
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); Yellow oil, 89% yield, $[\alpha]_D^{27}$ = + 36.5 (*c* 1.0, CH_2Cl_2), 81% ee [Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 85/15, 1.0 mL/min, 254 nm; t_{minor} = 14.4 min, t_{major} = 18.0 min]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.20-3.27 (m, 4H), 5.15 (d, *J* = 13.0 Hz, 1H), 5.39 (d, *J* = 13.0 Hz, 1H), 5.82-5.86 (m, 1H), 5.91-5.94 (m, 1H), 6.20 (d, *J* = 1.5 Hz, 1H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.38 (dt, *J* = 2.5, 9.5 Hz, 2H), 7.75 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -68.9 (s, 3F); ^{13}C NMR (125 MHz, $CDCl_3$): δ 23.8, 24.6, 54.7 (q, *J* = 26.0), 78.2, 109.1, 114.3, 122.2, 122.5, 125.3 (q, *J* = 283.6), 125.7, 126.2, 128.9, 130.0, 132.4, 135.4; HRMS *m/z* (EI+): Calculated for $C_{17}H_{14}N_2O_2F_3Cl$ ([M]$^+$): 370.0696, Found 370.0718.




135.403
132.494
130.084
128.932
126.432
126.298
125.712
124.163
122.524
122.216
114.372
109.108
78.201
77.287
77.033
76.779
54.823
54.615
24.635
23.822
Cl
F3C
N
H
NO2
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

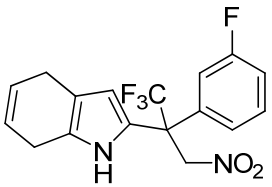

-68.92
Cl
F3C
N
H
NO2
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230





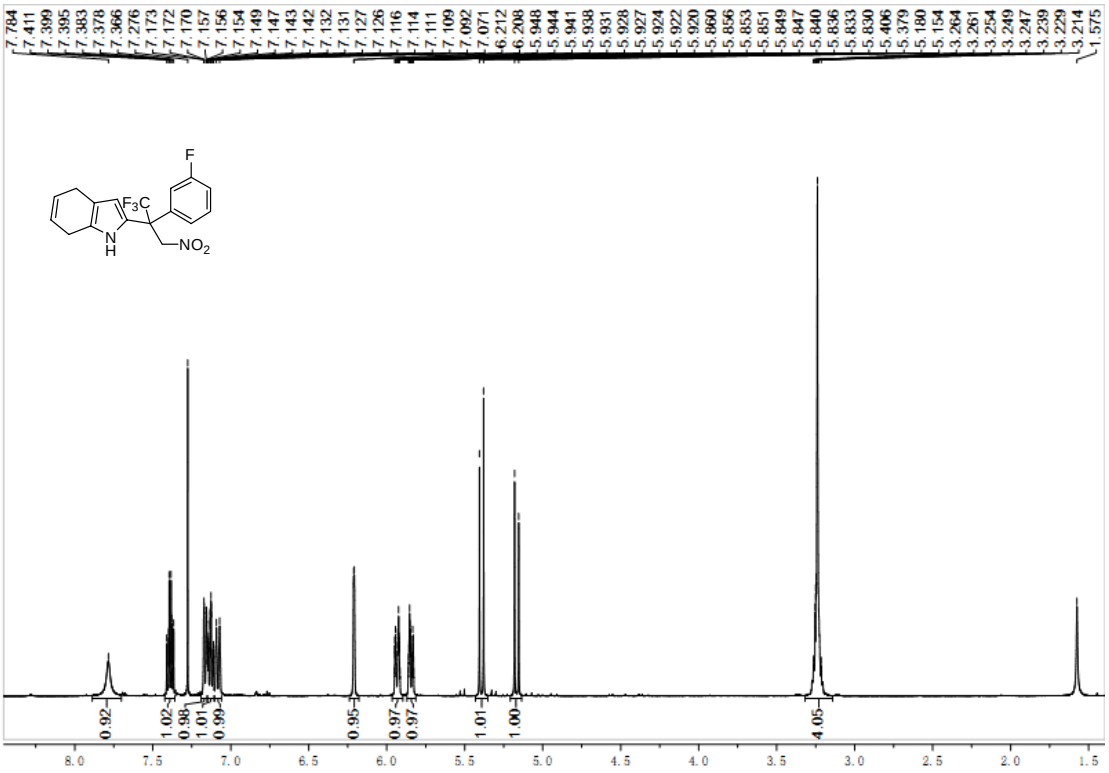
	Retention Time	Height	Area	% Area
1	14.473	41862	1453353	9.48
2	18.081	298824	13874142	90.52

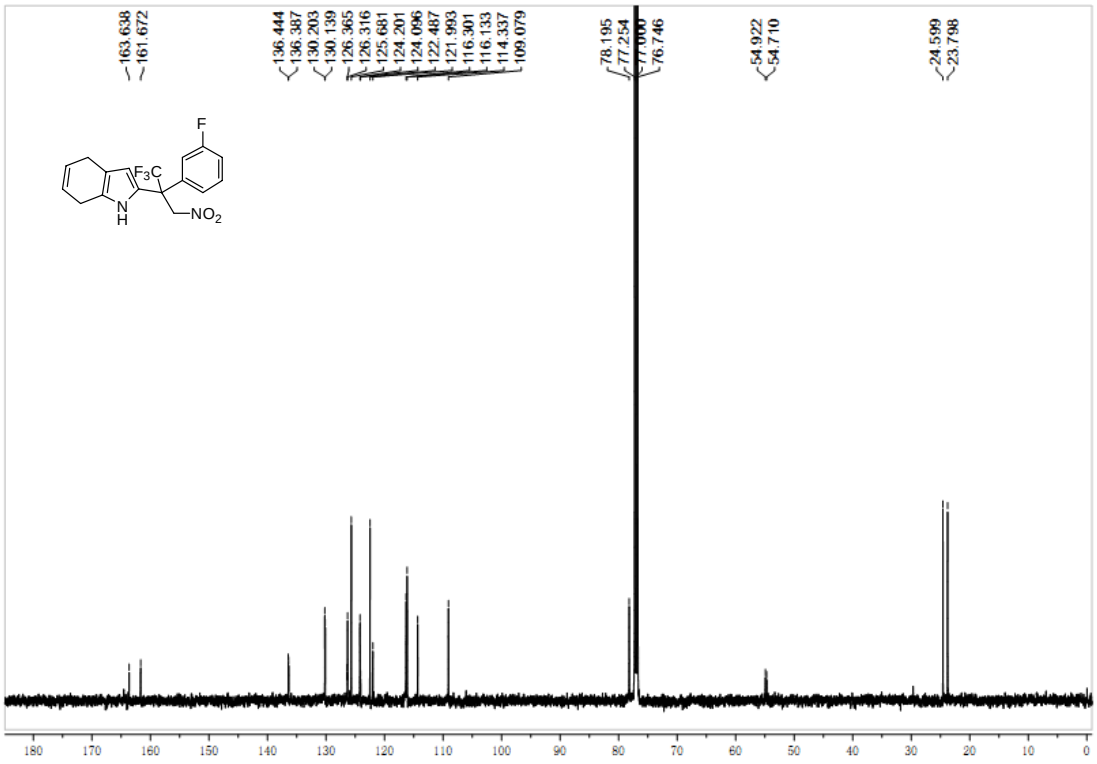
2-(1,1,1-trifluoro-2-(3-fluorophenyl)-3-nitropropan-2-yl)-4,7-dihydro-1H-indole (**3ga**):

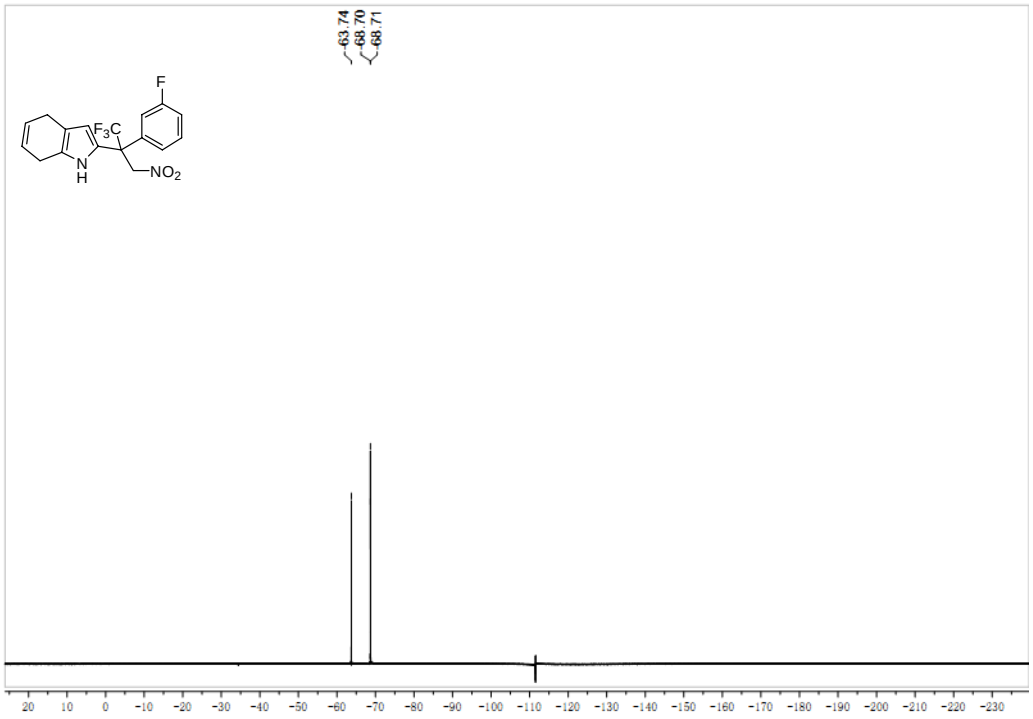


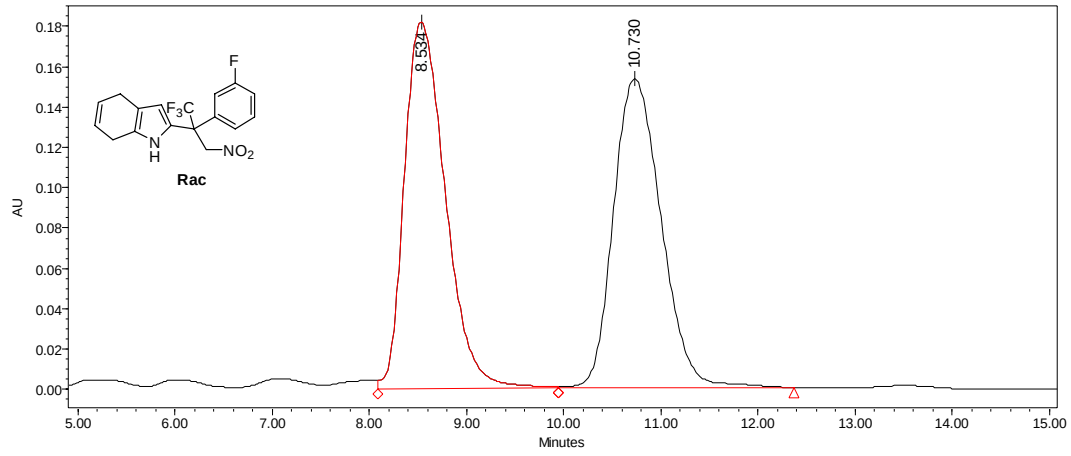
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); Yellow oil, 92% yield, $[\alpha]_D^{27}$ = + 33.6 (*c* 1.0, CH_2Cl_2), 85% ee [Daicel Chiralpak AS-H column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 85/15, 1.0 mL/min, 254 nm; t_{minor} = 10.7 min, t_{major} = 8.3 min]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.21-3.26 (m, 4H), 5.16 (d, *J* = 13.0 Hz, 1H), 5.39 (d, *J* = 13.5 Hz, 1H), 5.82-5.86 (m, 1H), 5.91-5.95 (m, 1H), 6.21 (d, *J* = 2.0 Hz, 1H), 7.08 (d, *J* = 10.5 Hz, 1H), 7.12 (tdd, *J* = 1.0, 2.5, 8.5 Hz, 1H), 7.16 (dt, *J* = 1.0,8.0 Hz, 1H), 7.38 (td, *J* = 6.0, 8.5 Hz, 1H),

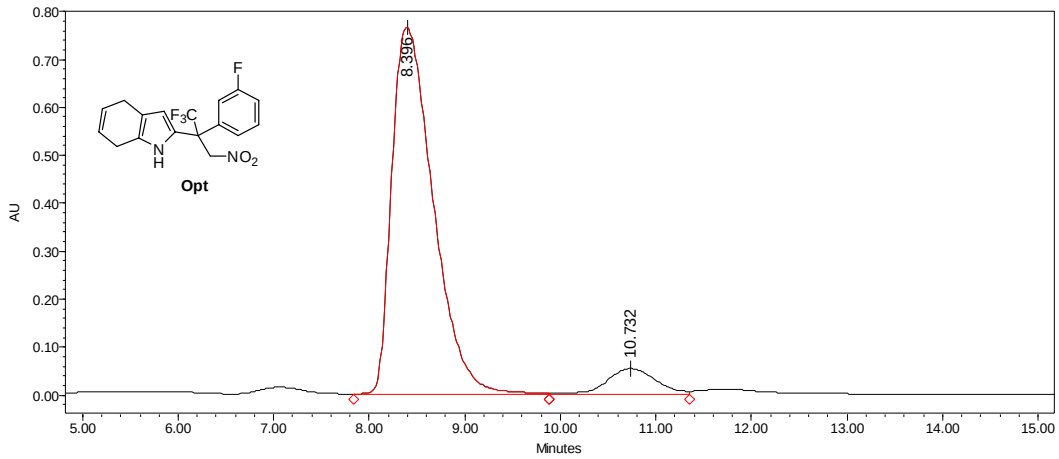
7.78 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.7 (s, 1F), -68.7 (d, *J* = 3.8Hz, 3F); ^{13}C NMR (125 MHz, $CDCl_3$): δ 23.7, 24.5, 54.8 (q, *J* = 26.5 Hz), 78.1, 109.0, 114.3, 116.1, 116.3, 121.9, 122.4, 124.2, 125.2 (q, *J* = 283.8 Hz), 125.6, 126.3, 130.1 (d, *J* = 8.0 Hz), 136.4 (d, *J* = 7.1 Hz), 162.6 (d, *J* = 245.8 Hz); HRMS *m/z* (EI+): Calculated for $C_{17}H_{14}N_2O_2F_4$ ([M]$^+$): 354.0991, Found 354.0991.





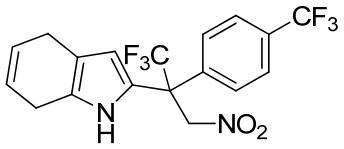




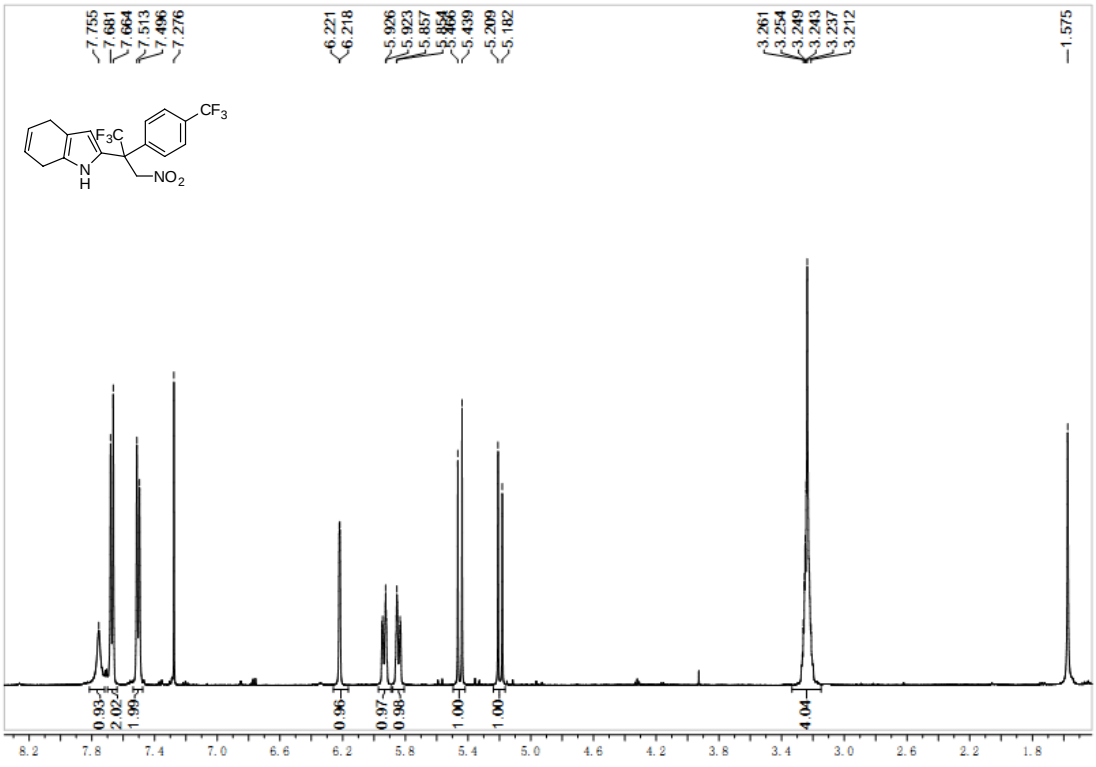


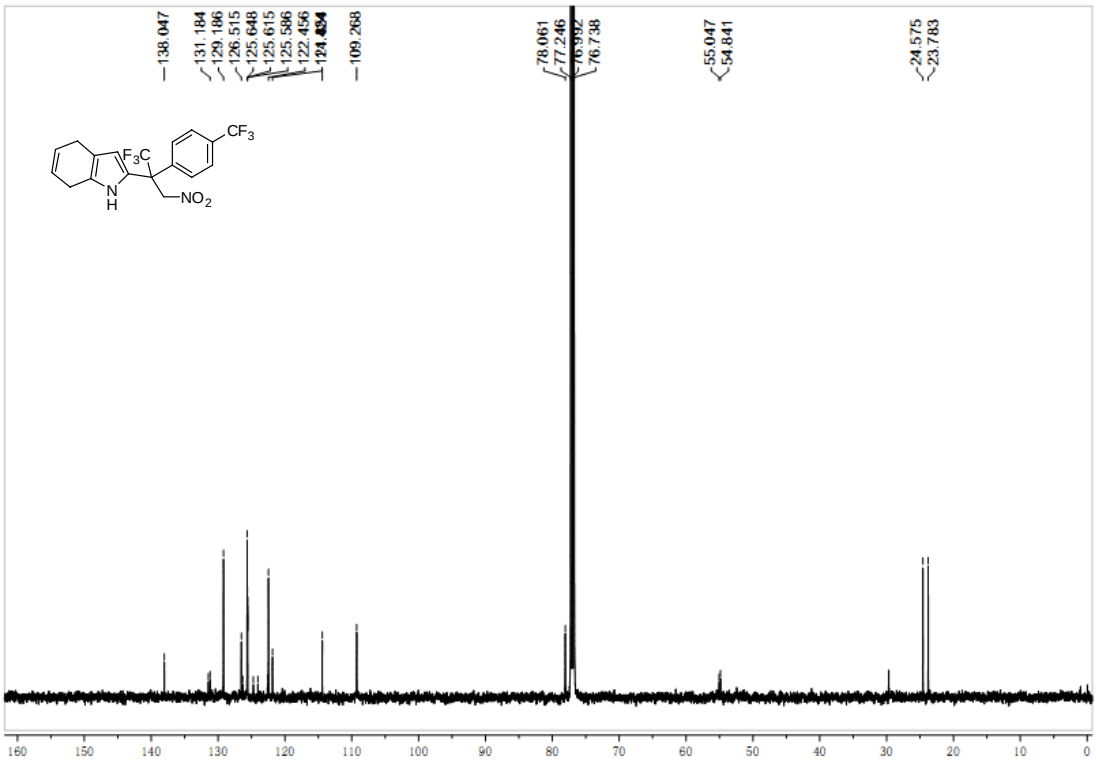
	Retention Time	Height	Area	% Area
1	8.396	766250	23110592	92.42
2	10.732	53360	1895260	7.58

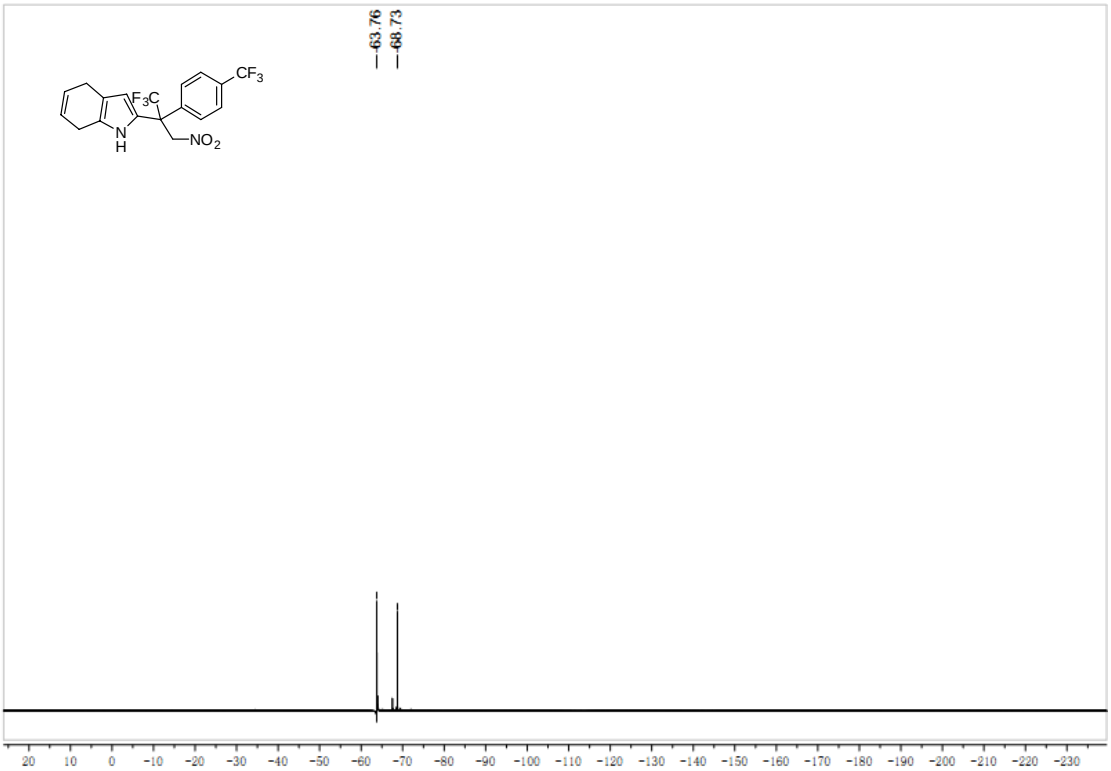
2-(1,1,1-trifluoro-3-nitro-2-(4-(trifluoromethyl)phenyl)propan-2-yl)-4,7-dihydro-1H-indole (**3ha**):

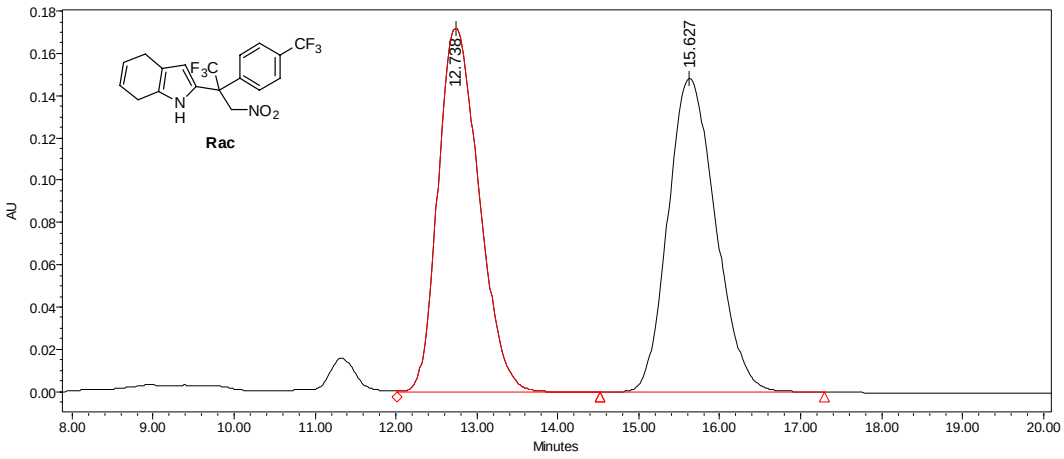


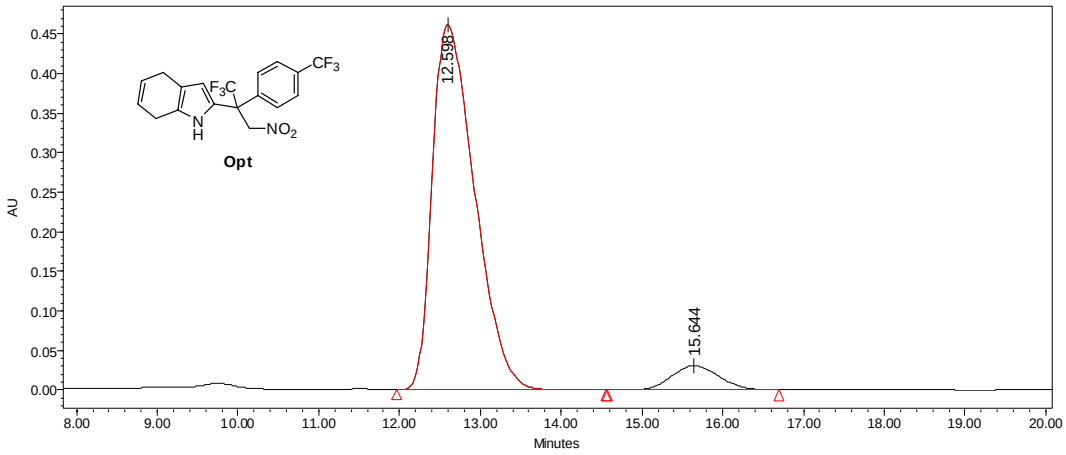
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); Yellow oil, 88% yield, $[\alpha]_D^{27}$ = + 30.0 (*c* 0.5, CH_2Cl_2), 86% ee [Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 85/15, 1.0 mL/min, 254 nm; t_{minor} = 15.6 min, t_{major} = 12.5 min]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.21-3.26 (m, 4H), 5.19 (d, *J* = 13.5 Hz, 1H), 5.45 (d, *J* = 13.5 Hz, 1H), 5.84 (dd, *J* = 1.5, 11.5 Hz, 1H), 5.93 (dd, *J* = 1.5, 11.5 Hz, 1H), 6.21 (d, *J* = 1.5 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.67 (d, *J* = 8.5 Hz, 2H), 7.75 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.7 (s, 3F), -68.7 (s, 3F); ^{13}C NMR (125 MHz, $CDCl_3$): δ 23.7, 24.5, 54.9 (q, *J* = 25.8 Hz), 78.0, 109.2, 114.4, 121.8, 122.4, 123.6 (q, *J* = 270.6 Hz), 125.1 (q, *J* = 283.6 Hz), 125.60 (q, *J* = 3.6 Hz), 125.64, 126.5, 129.1, 131.3 (q, *J* = 32.8 Hz), 138.0; HRMS *m/z* (EI+): Calculated for $C_{18}H_{14}N_2O_2F_6$ ($[M]^+$): 404.0959, Found 404.0981.




138.047
131.184
129.186
126.515
125.648
125.615
125.596
122.456
109.268
78.061
77.246
76.992
76.738
55.047
54.841
24.575
23.783
CF3
F3C
N
H
NO2
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

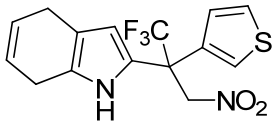

63.76
68.73
CF3
F3C
N
H
NO2
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230





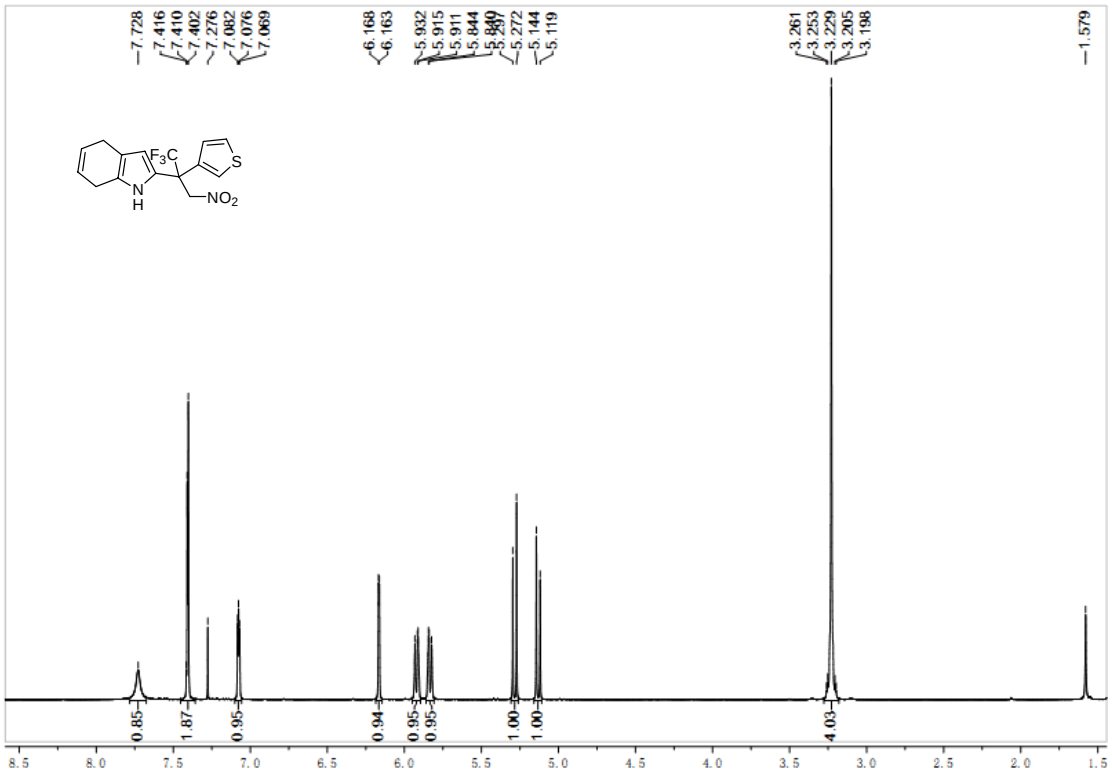
	Retention Time	Height	Area	% Area
1	12.598	461921	16827226	92.96
2	15.644	30775	1274886	7.04

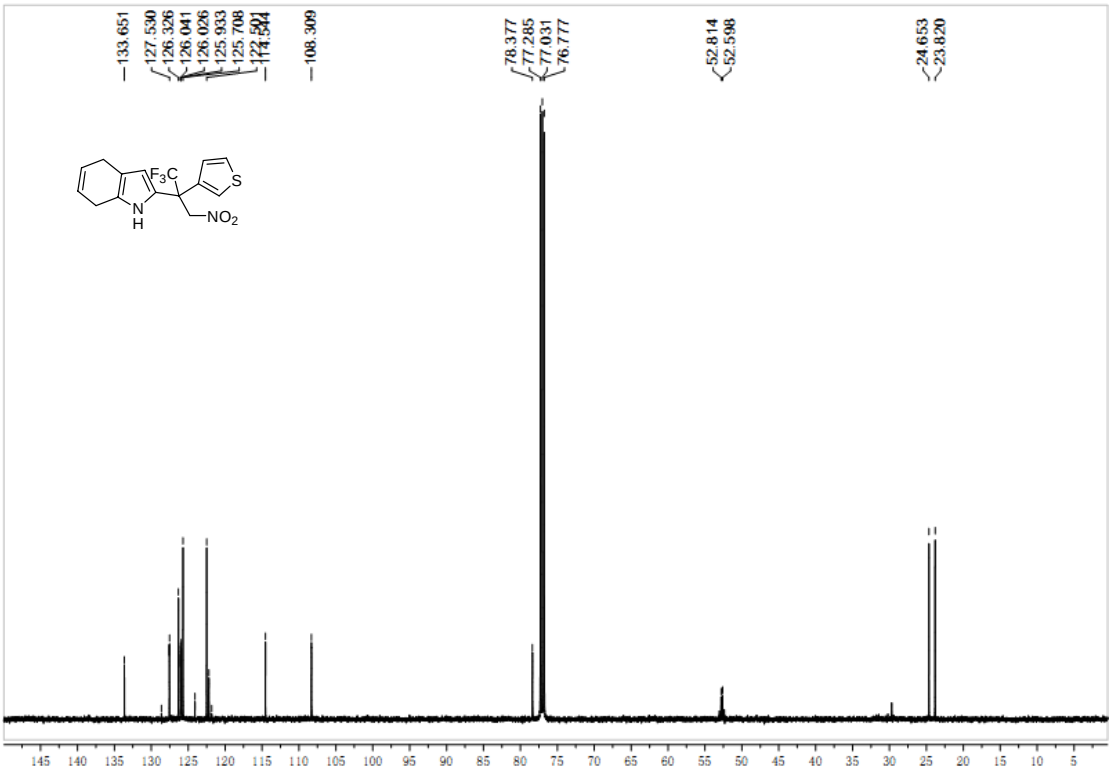
2-(1,1,1-trifluoro-3-nitro-2-(thiophen-3-yl)propan-2-yl)-4,7-dihydro-1H-indole (**3ia**):

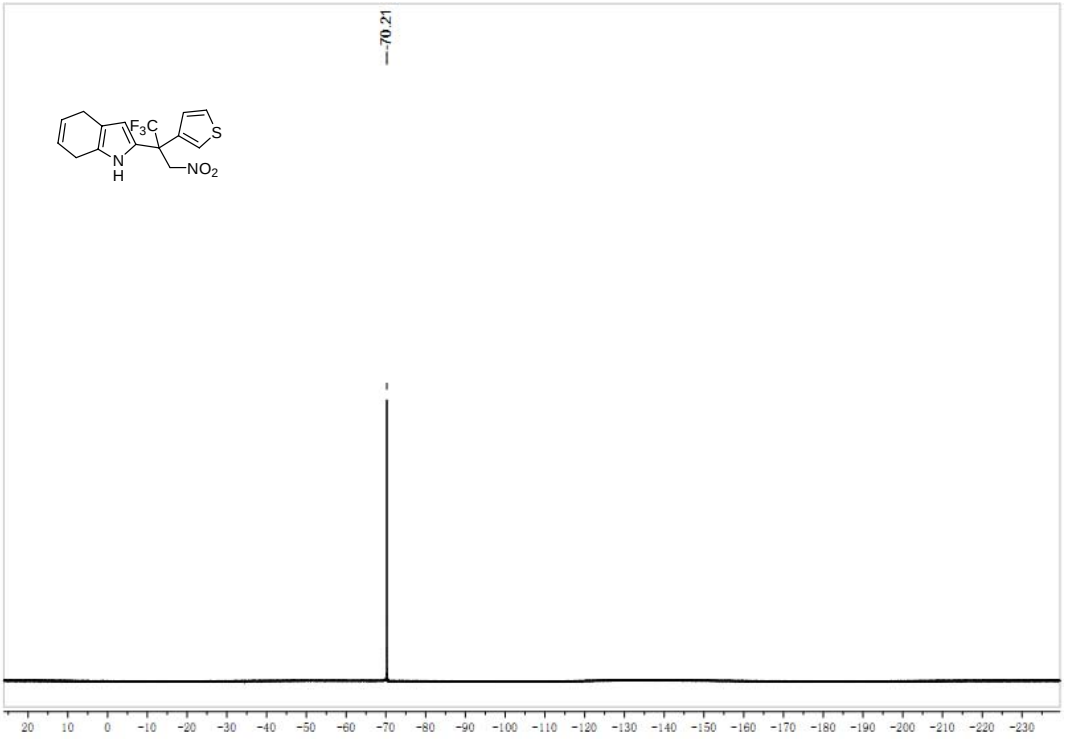


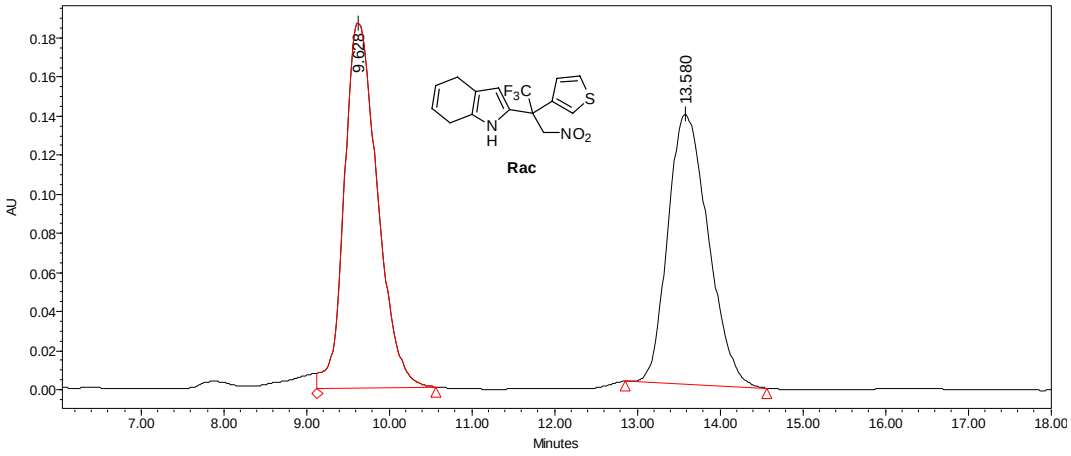
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); Yellow oil, 86% yield, $[\alpha]_D^{27}$ = + 31.3 (*c* 1.0, CH_2Cl_2), 68% ee [Daicel Chiralpak AS-H column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 85/15, 1.0 mL/min, 254 nm; t_{minor} = 13.5 min, t_{major} = 9.5 min]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.19-3.26 (m, 4H), 5.13 (d, *J* = 12.5 Hz, 1H), 5.28 (d, *J* = 12.5 Hz, 1H), 5.82-5.84 (m, 1H), 5.91-5.93 (m, 1H), 6.16 (d, *J* = 2.5 Hz, 1H), 7.07 (d, *J* = 3.0 Hz, 1H), 7.40 (d, *J* = 4.0 Hz, 2H), 7.72 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -70.2 (s, 3F); ^{13}C NMR (125 MHz, $CDCl_3$): δ 23.8, 24.6, 52.7 (q, *J* = 27.0 Hz), 78.3, 108.3, 114.5, 122.1, 122.5, 125.2 (q, *J* = 283.0 Hz), 125.7, 125.9, 126.0 (d, *J* = 1.9 Hz), 126.3, 127.5,

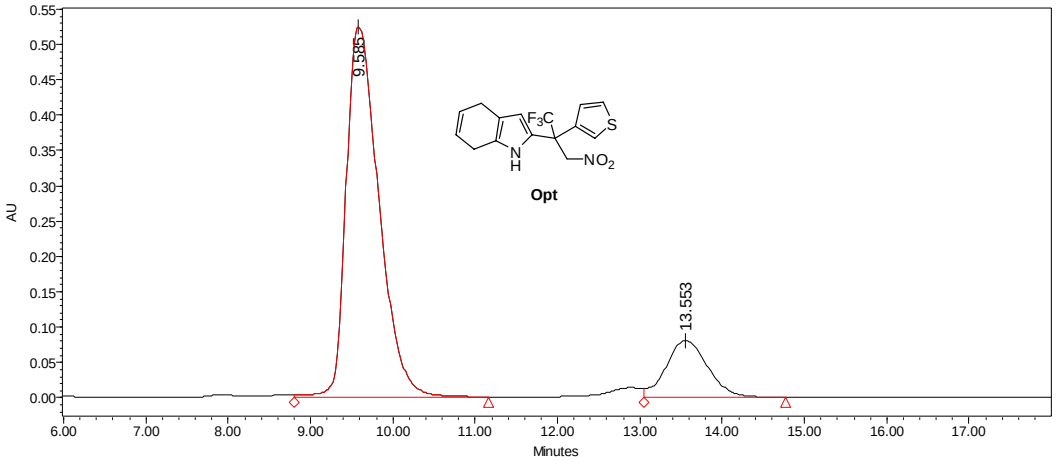
133.6; HRMS *m/z* (EI+): Calculated for $C_{15}H_{13}N_2O_2F_3S$ ($[M]^+$): 342.0650, Found 342.0658.





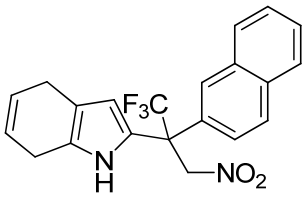




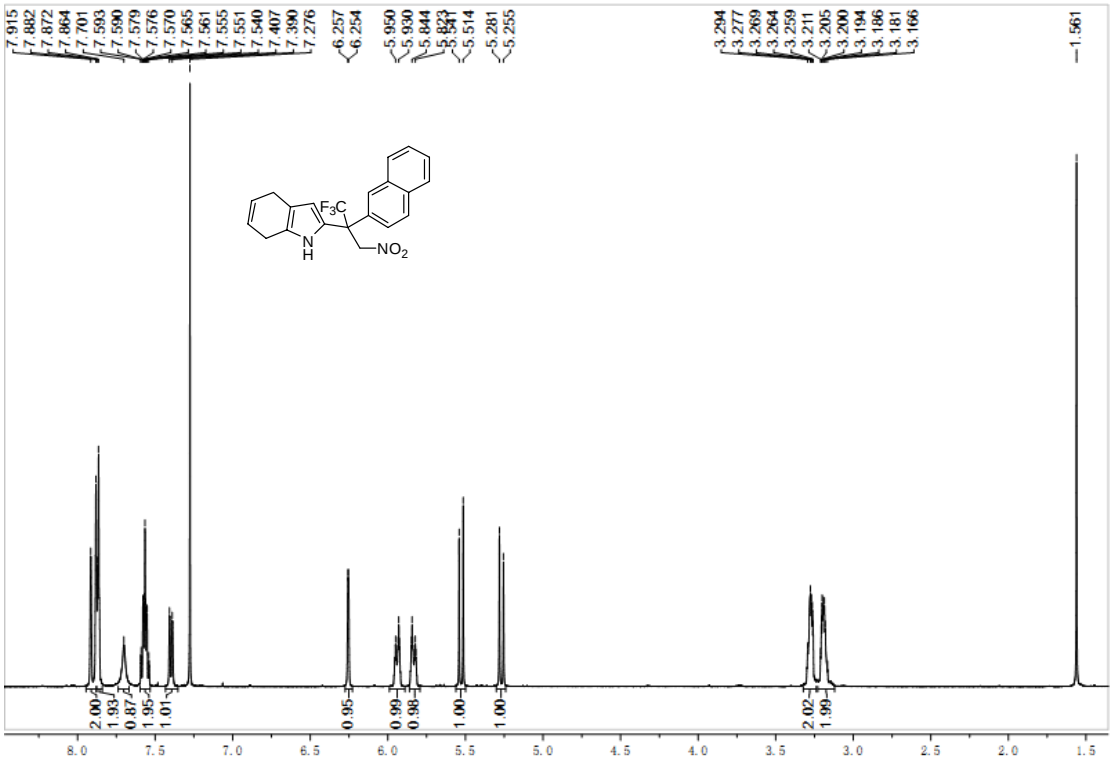


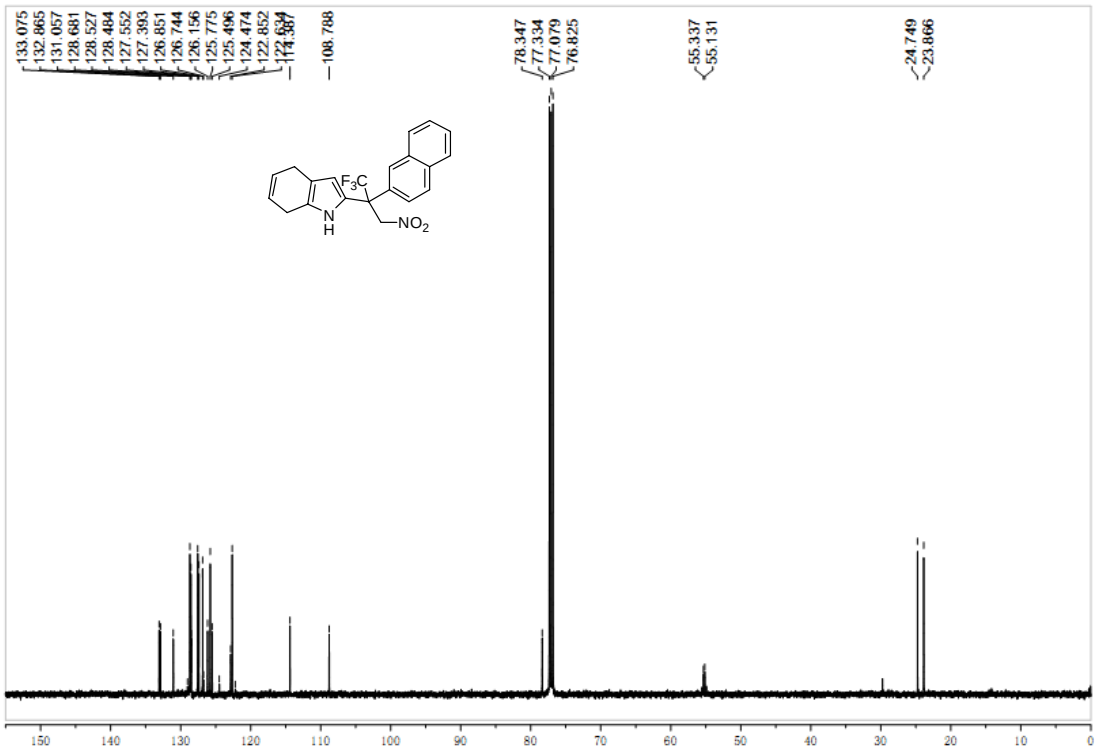
	Retention Time	Height	Area	% Area
1	9.585	524621	14501139	83.79
2	13.553	80432	2804930	16.21

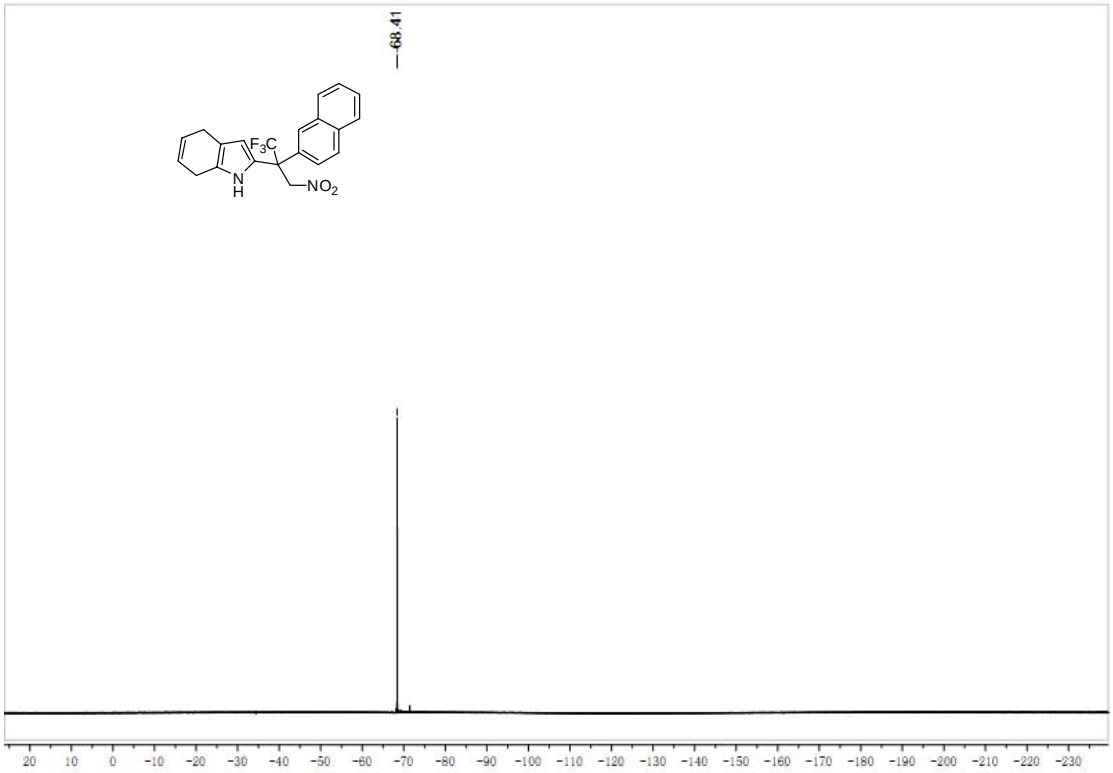
2-(1,1,1-trifluoro-2-(naphthalen-2-yl)-3-nitropropan-2-yl)-4,7-dihydro-1H-indole (**3ja**):

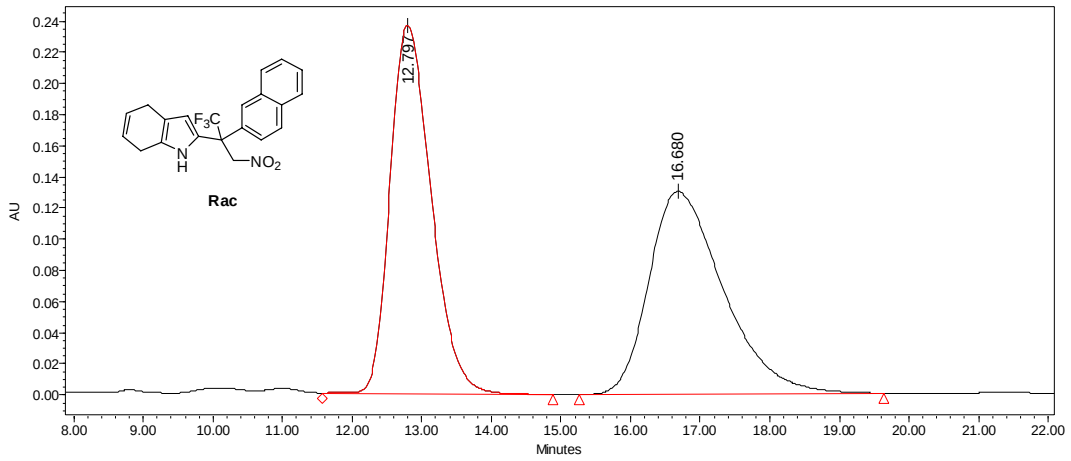


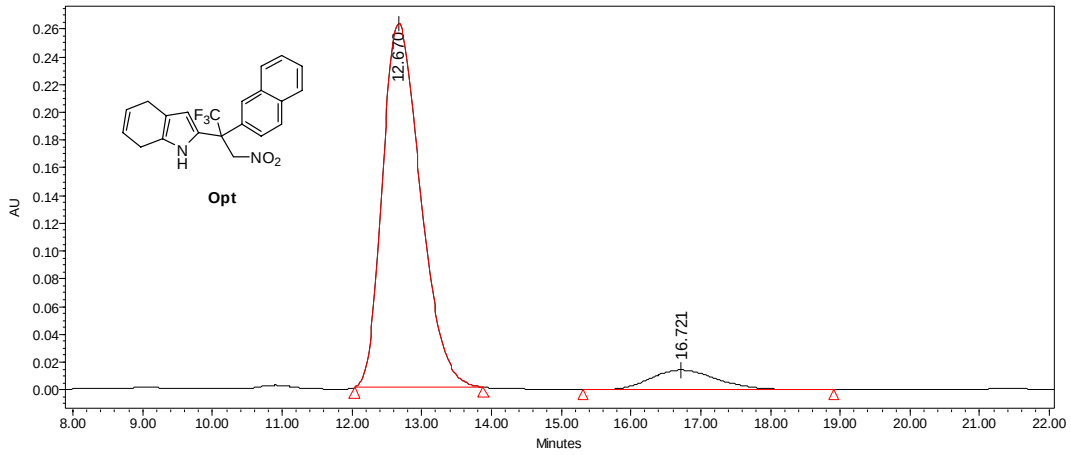
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); Yellow oil, 85% yield, $[\alpha]_D^{27}$ = + 109.0 (*c* 0.5, CH_2Cl_2), 82% ee [Daicel Chiralpak AS-H column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 85/15, 1.0 mL/min, 254 nm; t_{minor} = 16.7 min, t_{major} = 12.6 min]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.16-3.21 (m, 2H), 3.25-3.29 (m, 2H), 5.26 (d, *J* = 13.0 Hz, 1H), 5.52 (d, *J* = 13.5 Hz, 1H), 5.82-5.84 (m, 1H), 5.92-5.95 (m, 1H), 6.25 (d, *J* = 1.5 Hz, 1H), 7.39 (d, *J* = 8.5 Hz, 1H), 7.54-7.59 (m, 2H), 7.70 (s, 1H), 7.86 (t, *J* = 4.0 Hz, 2H), 7.89 (d, *J* = 16.5 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -68.4 (s, 3F); ^{13}C NMR (125 MHz, $CDCl_3$): δ 23.8, 24.7, 55.2 (q, *J* = 25.8 Hz), 78.3, 108.7, 114.3, 122.6, 122.8, 125.4, 125.6 (q, *J* = 283.8 Hz), 125.7, 126.1, 126.8, 127.3, 127.5, 128.4, 128.5, 128.6, 131.0, 132.8, 133.0; HRMS *m/z* (EI+): Calculated for $C_{21}H_{17}N_2O_2F_3$ ($[M]^+$): 386.1242, Found 386.1249.




133.075
132.865
131.057
128.681
128.527
128.484
127.552
127.393
126.851
126.744
126.156
125.775
125.496
124.474
122.852
108.788
78.347
77.334
77.079
76.825
55.337
55.131
24.749
23.866
F3C
N
H
NO2
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

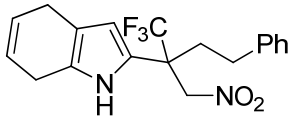

68.41
F3C
N
H
NO2
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230





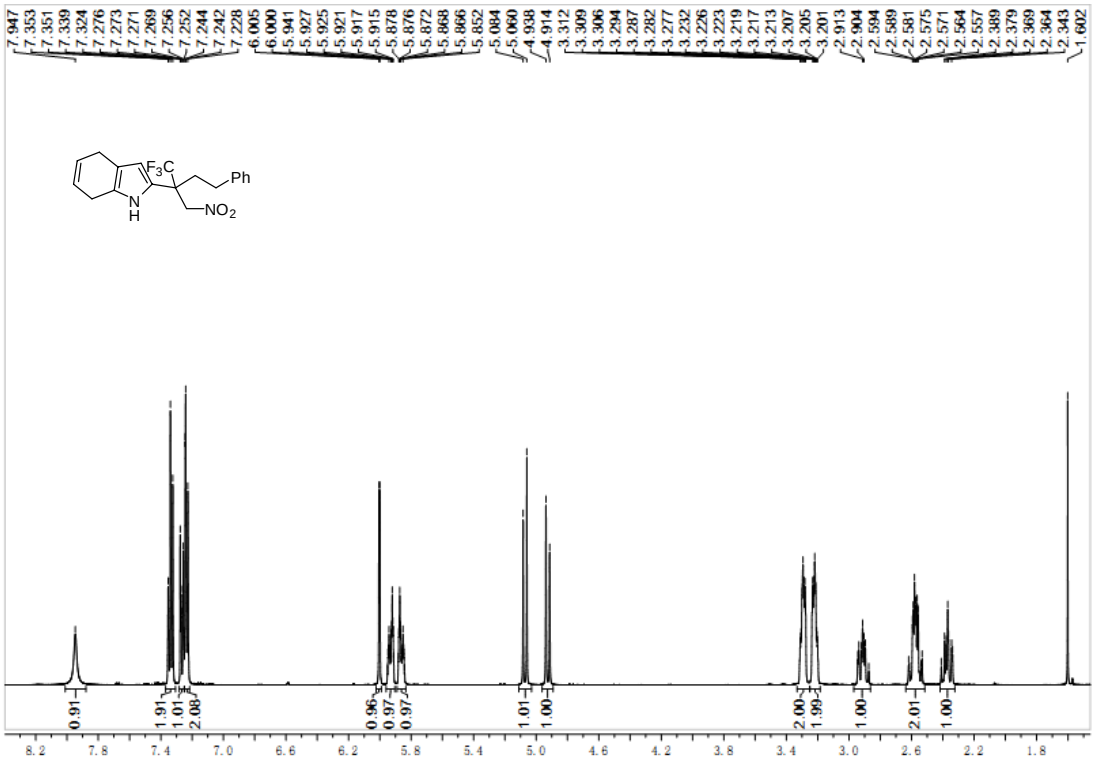
	Retention Time	Height	Area	% Area
1	12.670	262540	9979154	91.12
2	16.721	14250	972038	8.88

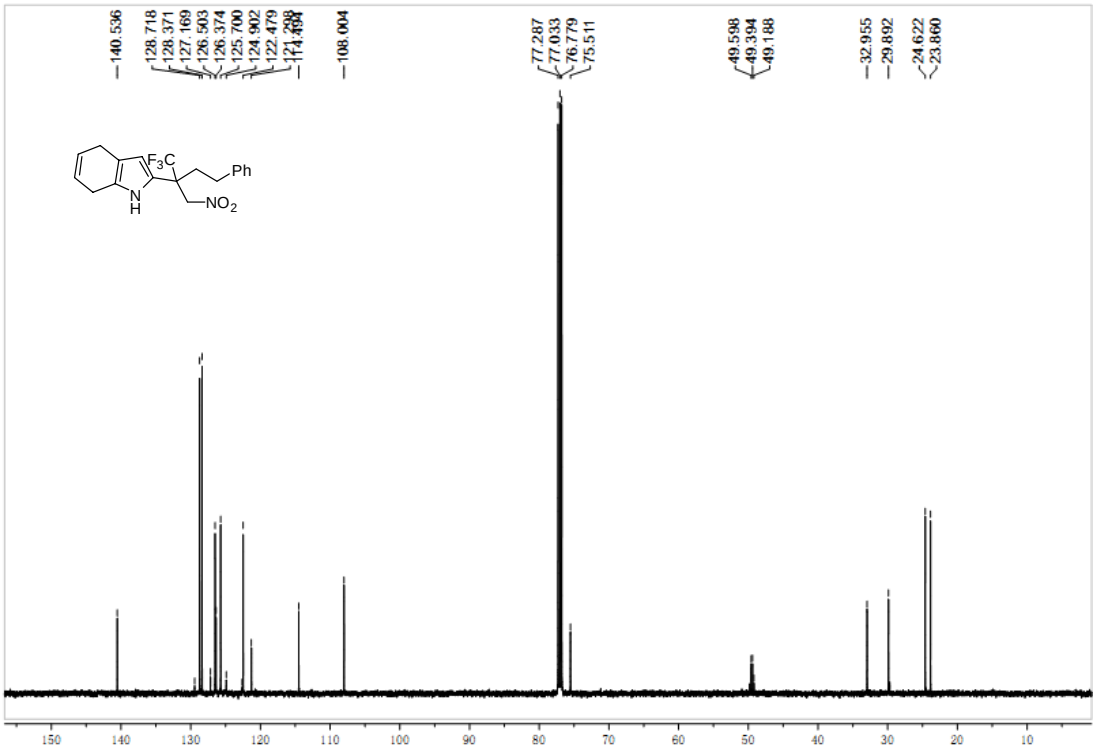
2-(1,1,1-trifluoro-2-(nitromethyl)-4-phenylbutan-2-yl)-4,7-dihydro-1H-indole (**3ka**):

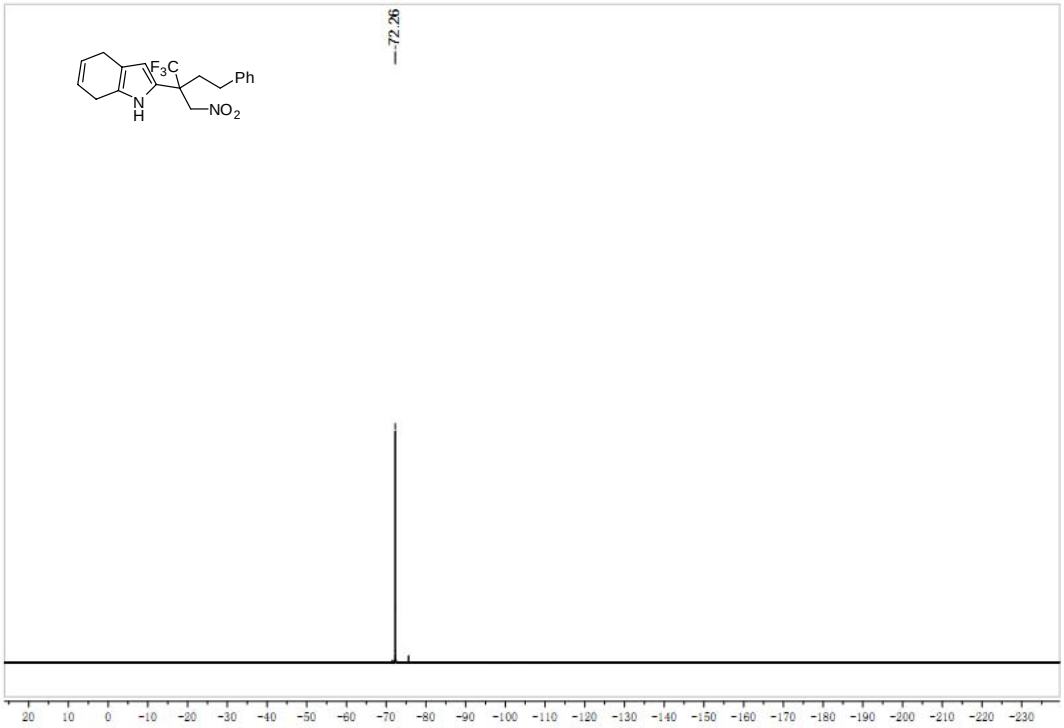


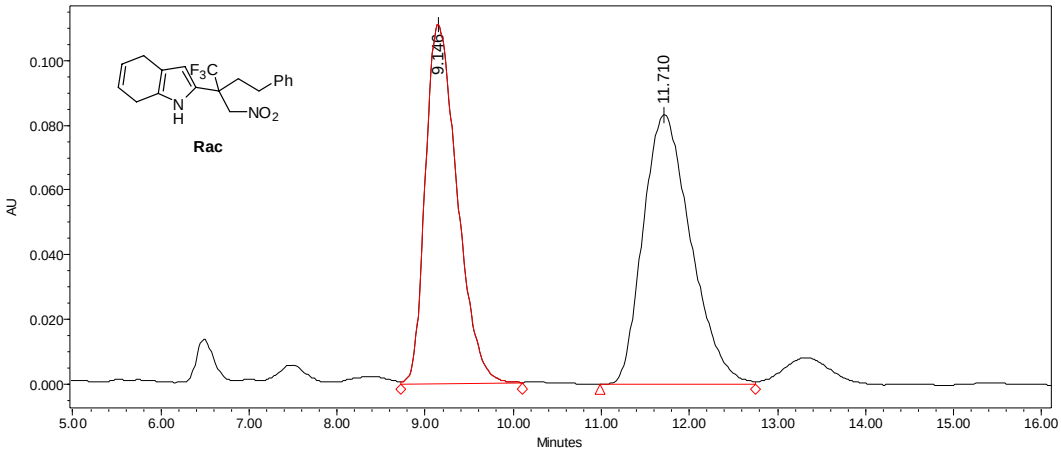
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); Yellow oil, 84% yield, $[\alpha]_D^{27}$ = + 28.6 (*c* 1.0, CH_2Cl_2), 71% ee [Daicel Chiralpak AS-H column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{minor} = 8.9 min, t_{major} = 11.4min]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.33-2.41 (m, 1H), 2.53-2.61 (m, 2H), 2.87-2.94 (m, 1H), 3.20-3.23 (m, 2H), 3.27-3.31 (m, 2H), 4.92 (d, *J* = 12.0 Hz, 1H), 5.07 (d, *J* = 12.0 Hz, 1H), 5.84-5.88 (m, 1H), 5.91-5.95 (m, 1H), 6.00 (d, *J* = 2.5 Hz, 1H), 7.24 (t, *J* = 7.5 Hz, 2H), 7.26 (dt, *J* = 2.0, 7.5 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.94 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -72.2 (s, 3F); ^{13}C NMR (125 MHz, $CDCl_3$): δ 23.8, 24.6, 29.8, 32.9, 49.4 (q, *J* =

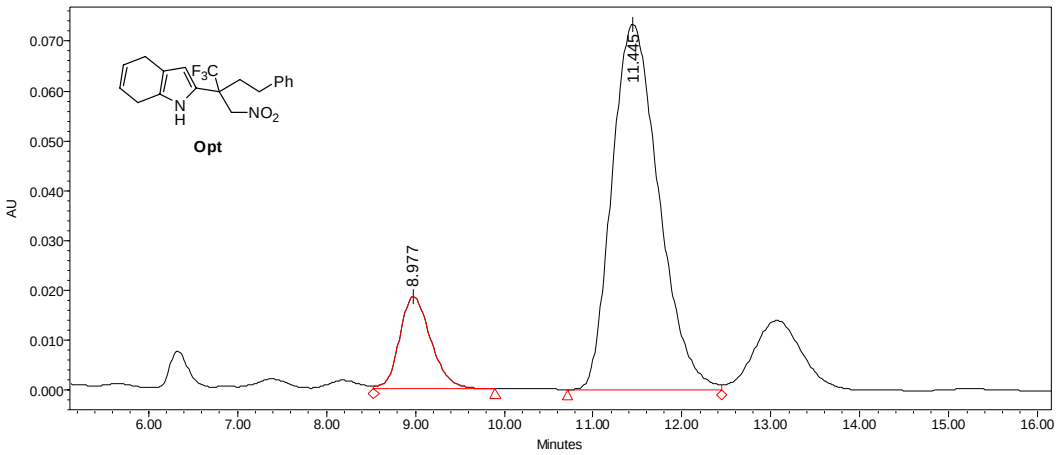
25.5 Hz), 75.5, 108.0, 114.4, 121.2, 122.4, 125.7, 126.0 (q, J = 283.4 Hz), 126.3, 126.5, 128.3, 128.7, 140.5; HRMS *m/z* (EI+): Calculated for $C_{19}H_{19}N_2O_2F_3$ ($[M]^+$): 364.1399, Found 364.1419.





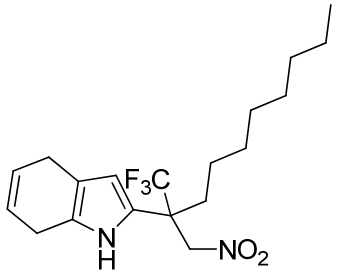




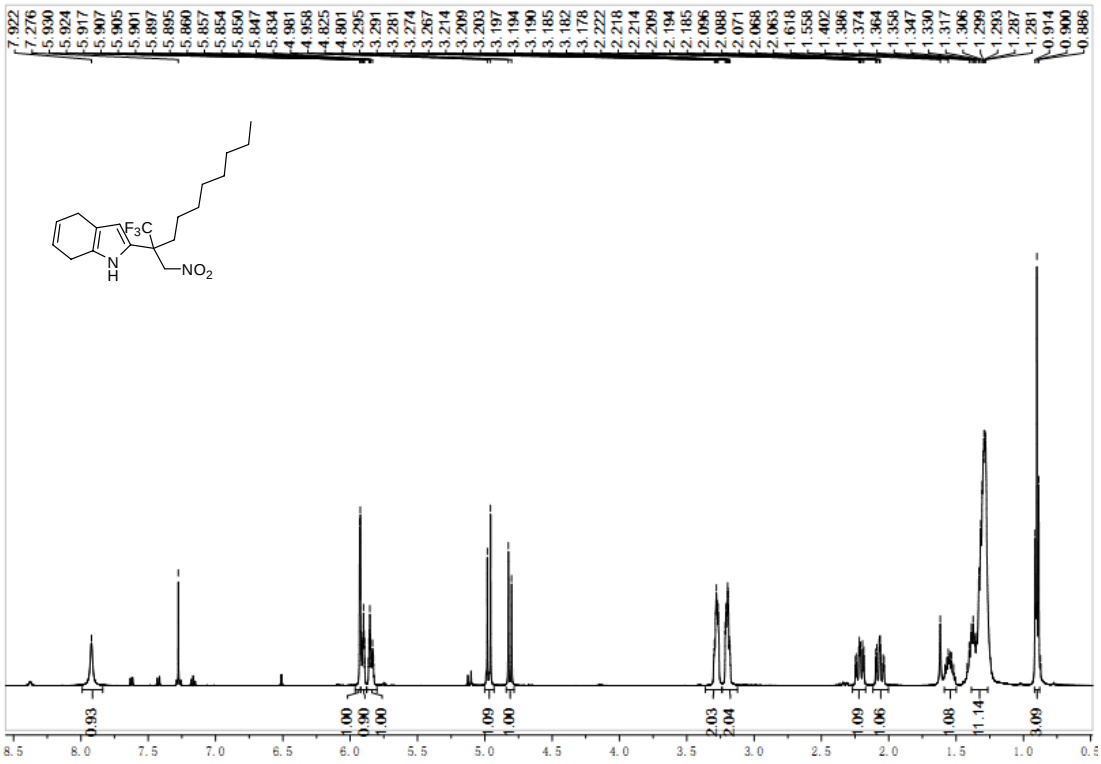


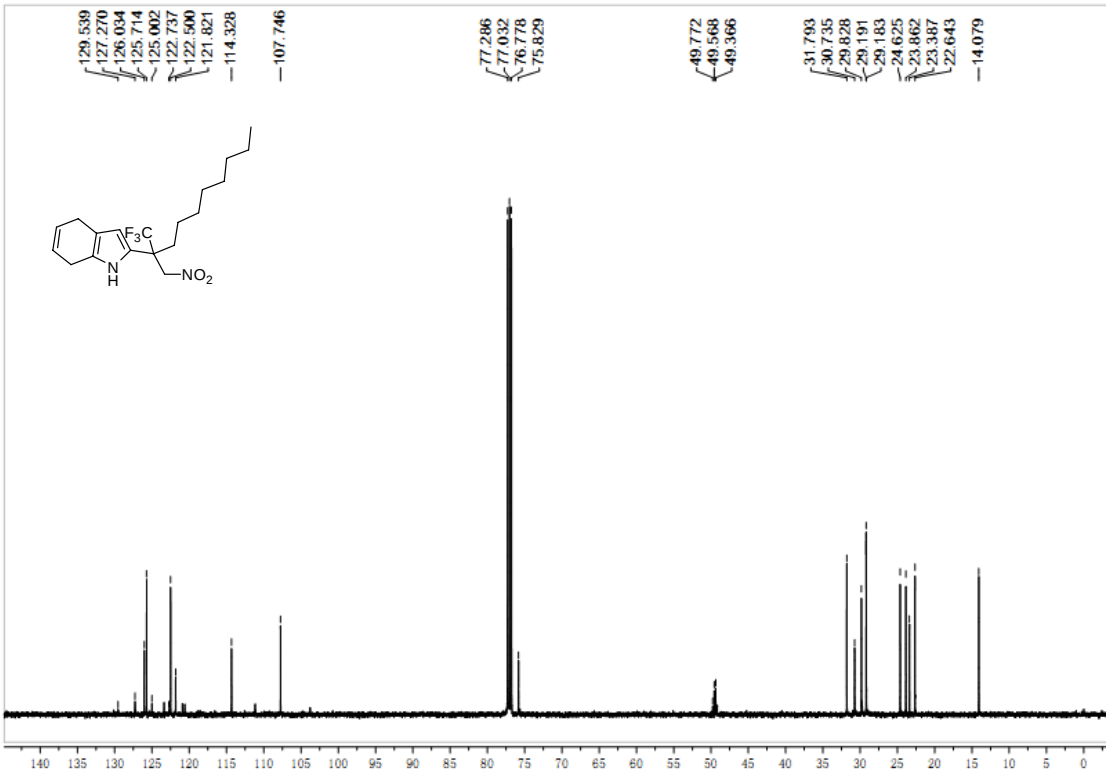
	Retention Time	Height	Area	% Area
1	8.977	18424	453114	14.44
2	11.445	73356	2685259	85.56

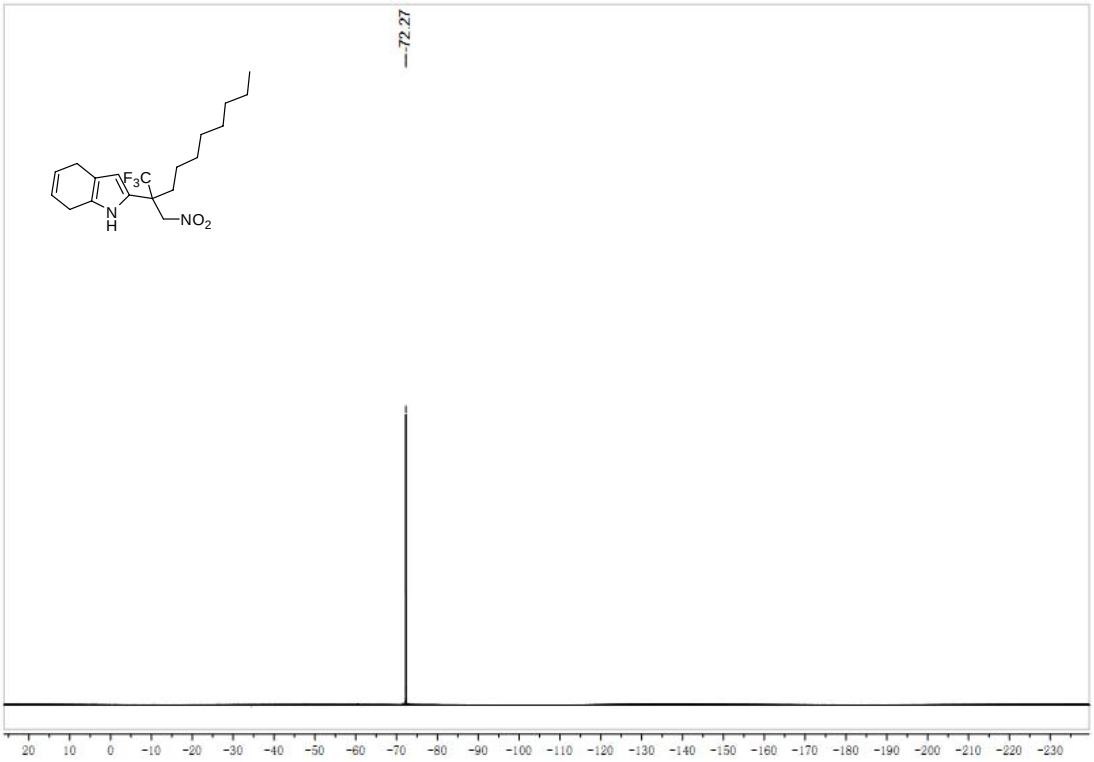
2-(1,1,1-trifluoro-2-(nitromethyl)decan-2-yl)-4,7-dihydro-1H-indole (**3la**):

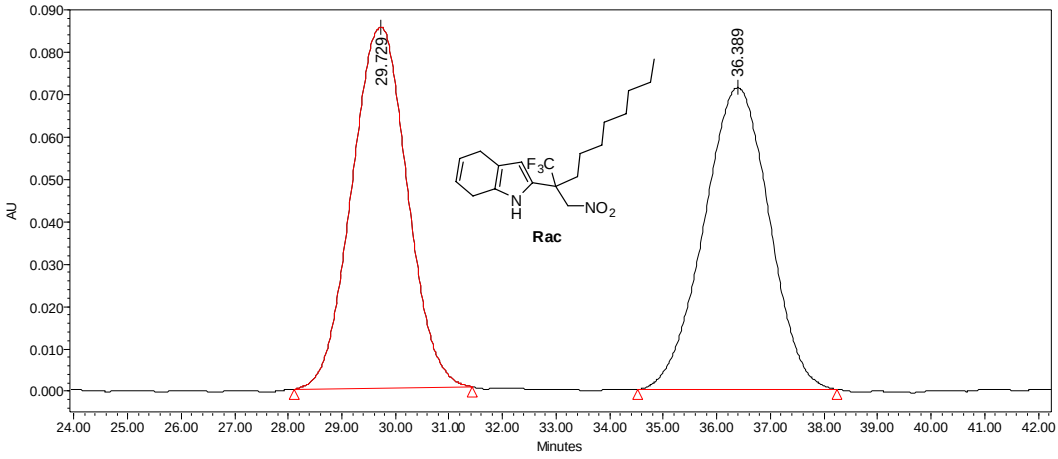


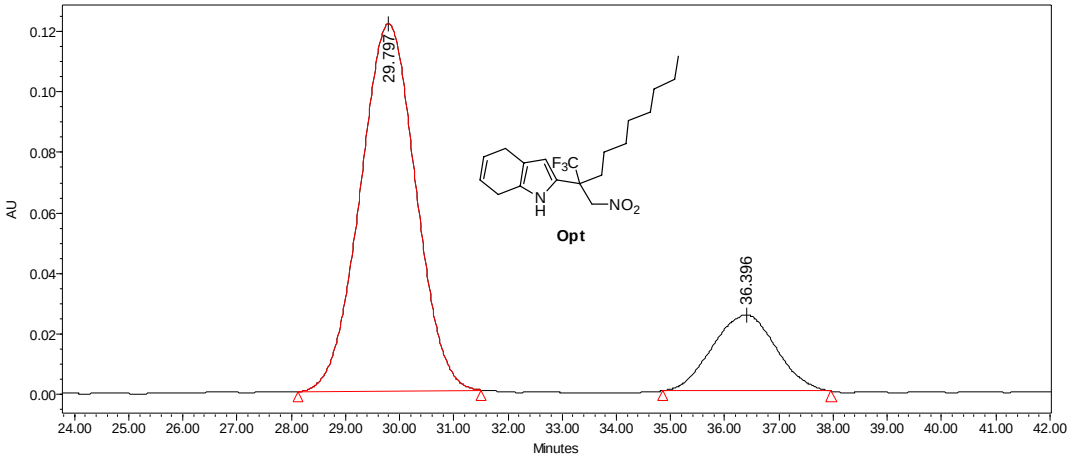
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); Yellow oil, 88% yield, $[\alpha]_D^{27}$ = + 1.7 (*c* 1.0, CH_2Cl_2), 62% ee [Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{minor} = 36.3 min, t_{major} = 29.7 min]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.90 (t, *J* = 7.0 Hz, 3H), 1.28-1.41 (m, 11H), 1.51-1.58 (m, 1H), 2.03-2.09 (m, 1H), 2.18-2.24 (m, 1H), 3.17-3.21 (m, 2H), 3.26-3.29 (m, 2H), 4.81 (d, *J* = 12.0 Hz, 1H), 4.96 (d, *J* = 11.5 Hz, 1H), 5.82-5.86 (m, 1H), 5.89-5.91 (m, 1H), 5.92 (d, *J* = 3.0 Hz, 1H), 7.92 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -72.2 (s, 3F); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.0, 22.6, 23.3, 23.8, 24.6, 29.18, 29.19, 29.8, 30.7, 31.7, 49.4 (q, *J* = 25.3 Hz), 75.8, 107.7, 114.3, 121.8, 122.5, 125.7, 126.0, 126.1 (q, *J* = 283.5 Hz); HRMS *m/z* (EI+): Calculated for $C_{19}H_{27}N_2O_2F_3$ ([M]$^+$): 372.2025, Found 372.2023.




129.539
127.270
126.034
125.714
125.002
122.737
122.500
121.821
114.328
107.746
77.286
77.032
76.778
75.829
49.772
49.568
49.366
31.793
30.735
29.828
29.191
29.183
24.625
23.862
23.387
22.643
14.079
F3C
N
H
NO2
140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0

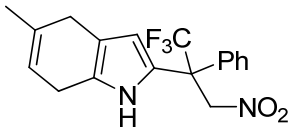

-72.27
F3C
N
H
NO2
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230





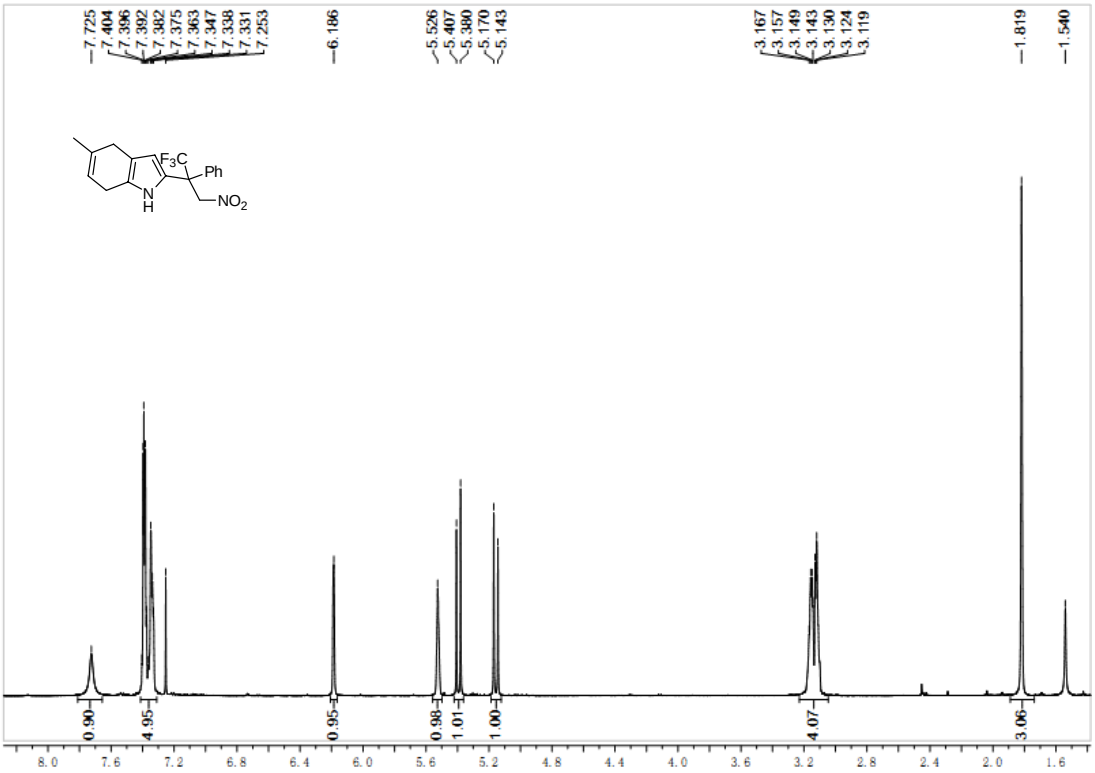
	Retention Time	Height	Area	% Area
1	29.797	121320	8641758	80.79
2	36.396	25176	2054275	19.21

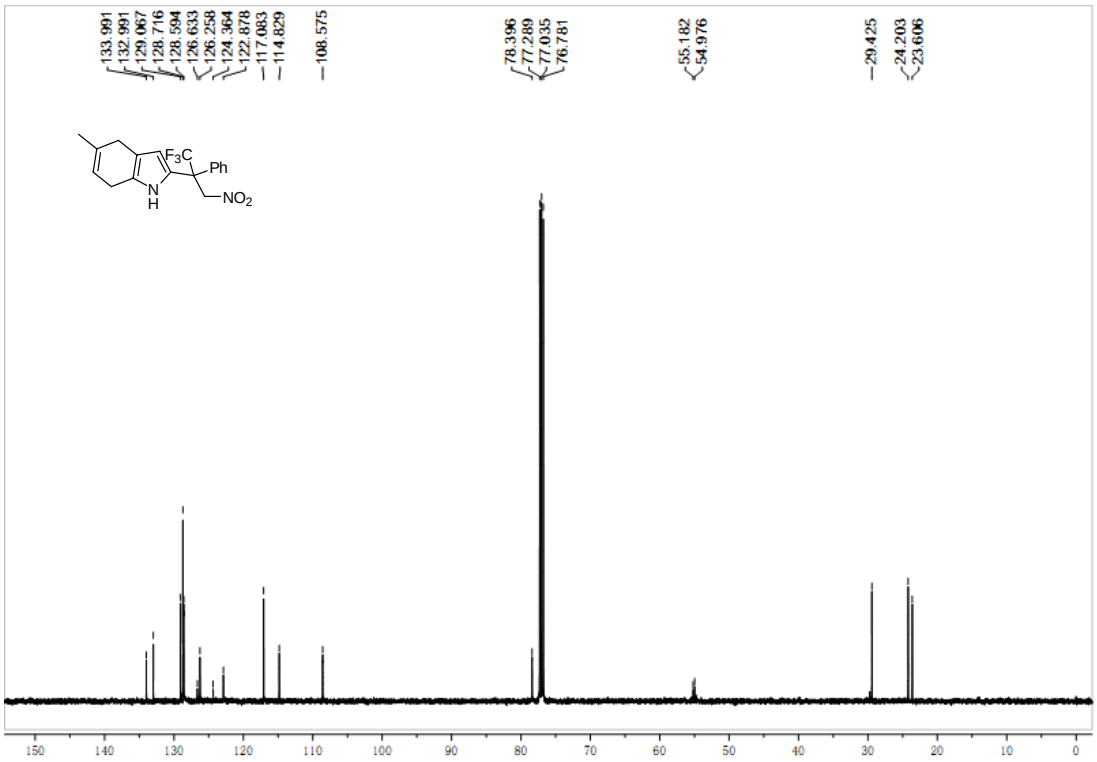
5-methyl-2-(1,1,1-trifluoro-3-nitro-2-phenylpropan-2-yl)-4,7-dihydro-1H-indole (**3ab**):

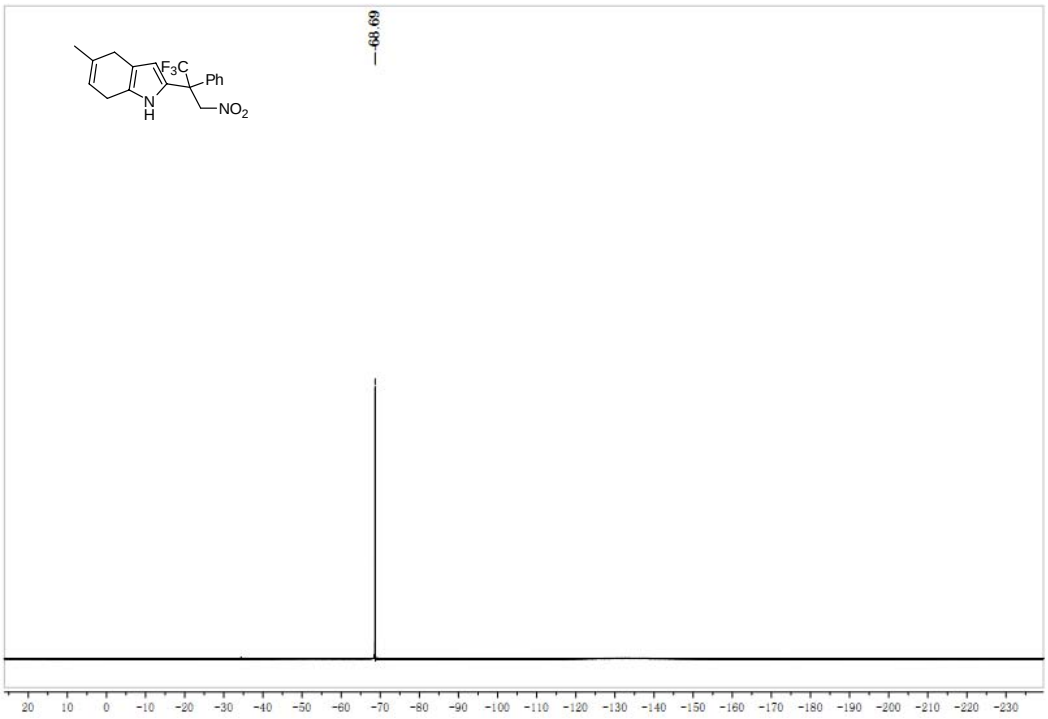


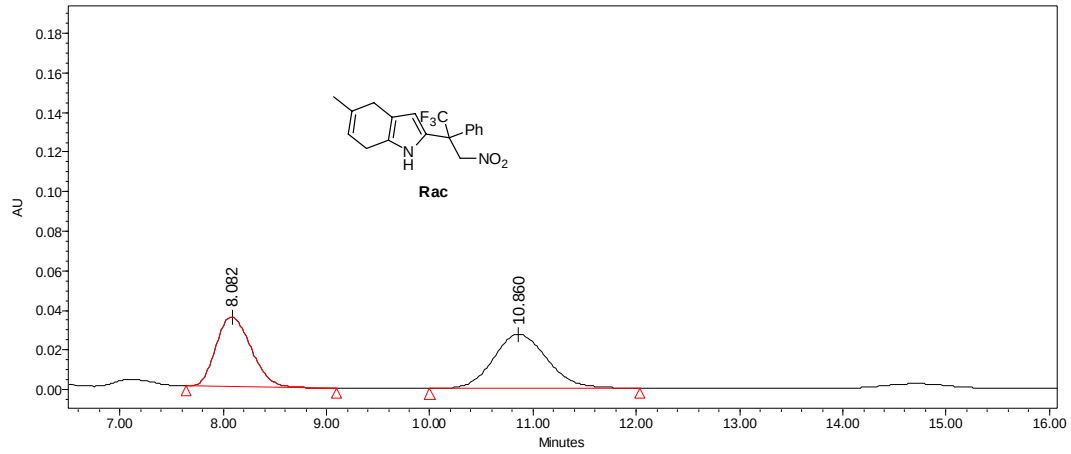
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); Yellow oil, 90% yield, $[\alpha]_D^{27}$ = + 32.6 (*c* 0.5, CH_2Cl_2), 88% ee [Daicel Chiralpak AS-H column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 85/15, 1.0 mL/min, 254 nm; t_{minor} =11.1 min, t_{major} = 8.0 min]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.81 (s, 3H), 3.11-3.16 (m, 4H), 5.15 (d, *J* = 13.5 Hz, 1H), 5.39 (d, *J* = 13.5 Hz, 1H), 5.52 (s, 1H), 6.18 (s, 1H), 7.33-7.40 (m, 5H), 7.72 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -68.6 (s, 3F); ^{13}C NMR (125 MHz, $CDCl_3$): δ 23.6, 24.2, 29.4, 55.0 (q, *J* =

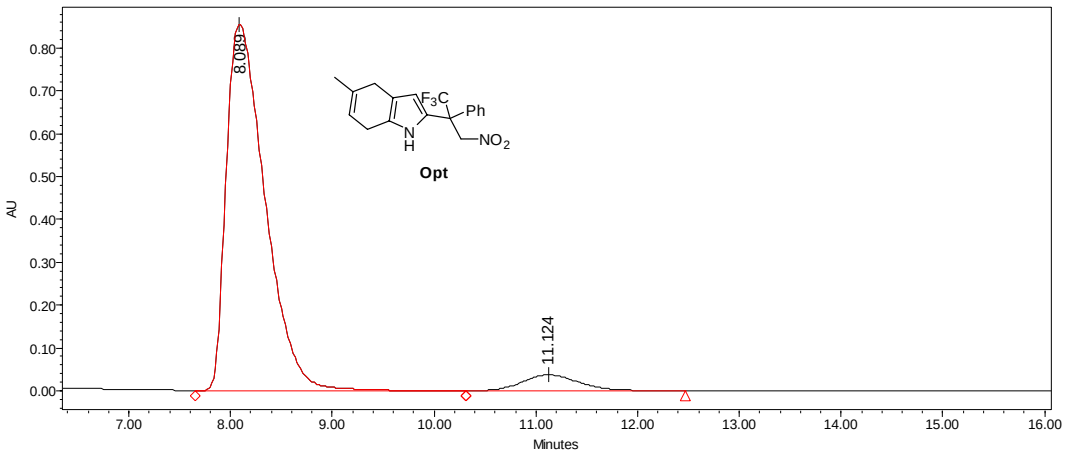
25.8 Hz), 78.3, 108.5, 114.8, 117.0, 122.8, 125.4 (q, J = 283.6 Hz), 126.2, 128.5, 128.7, 129.0, 132.9, 133.9; HRMS *m/z* (EI+): Calculated for $C_{18}H_{17}N_2O_2F_3$ ($[M]^+$): 350.1242, Found 350.1247.





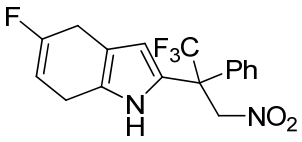




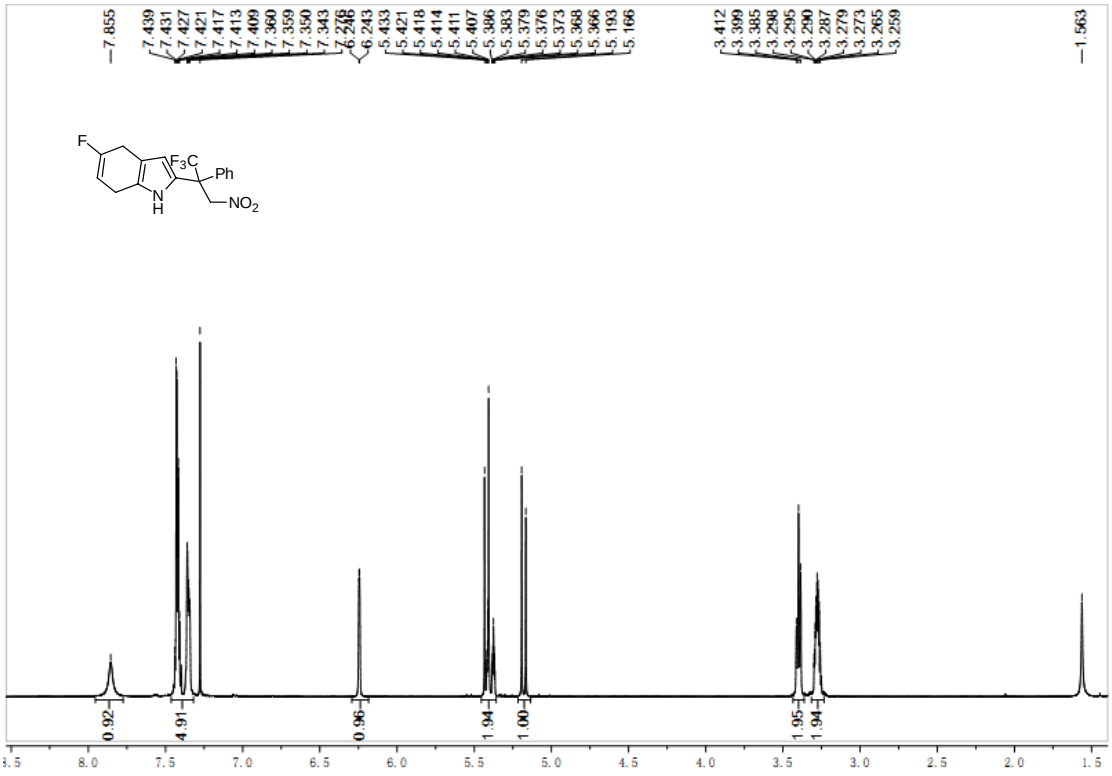


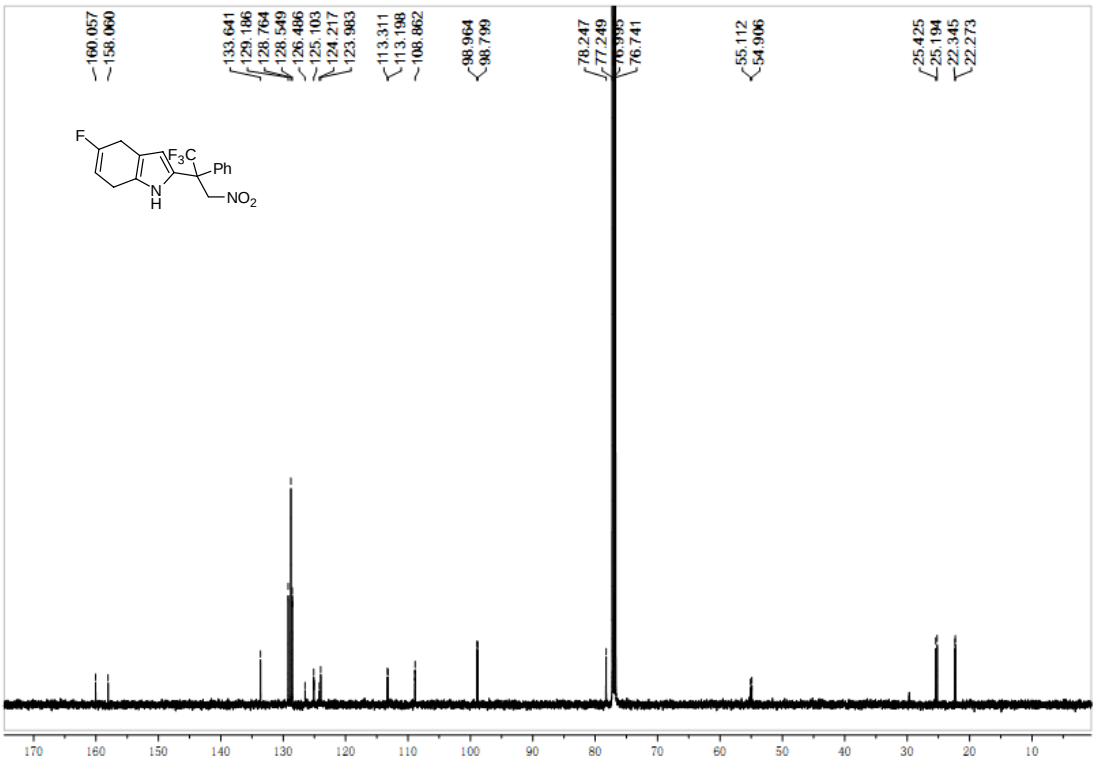
	Retention Time	Height	Area	% Area
1	8.089	856761	22763361	93.90
2	11.124	37232	1478540	6.10

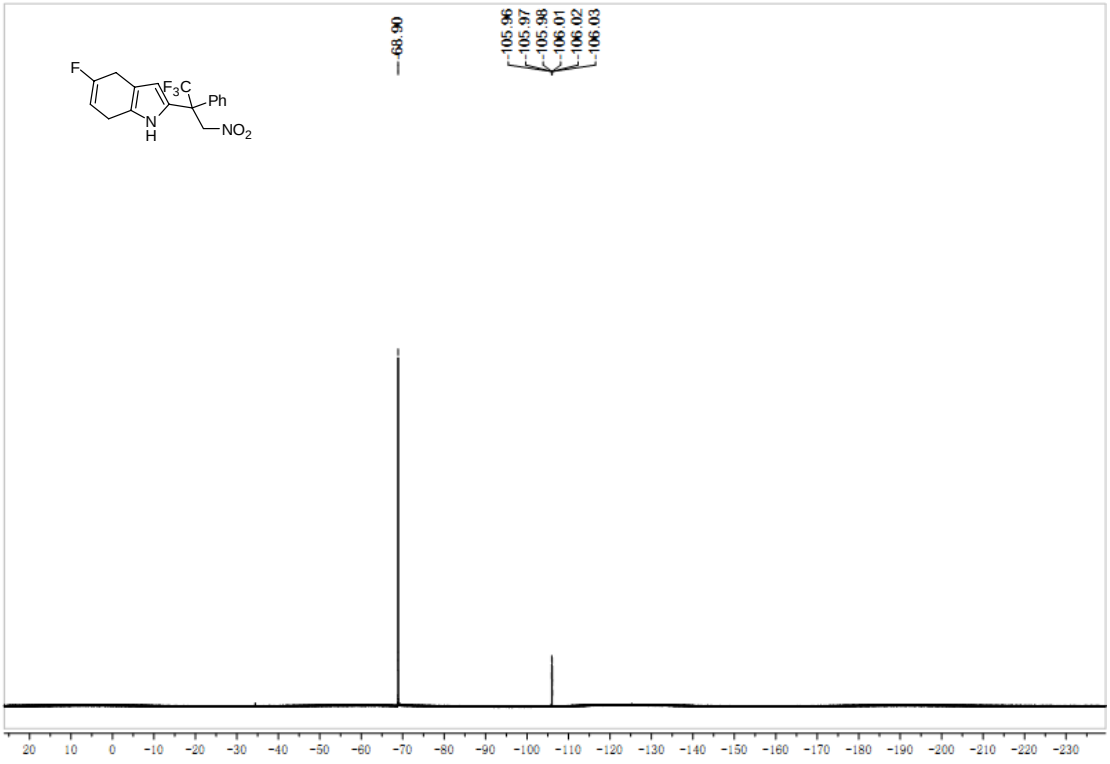
5-fluoro-2-(1,1,1-trifluoro-3-nitro-2-phenylpropan-2-yl)-4,7-dihydro-1H-indole (**2ac**):

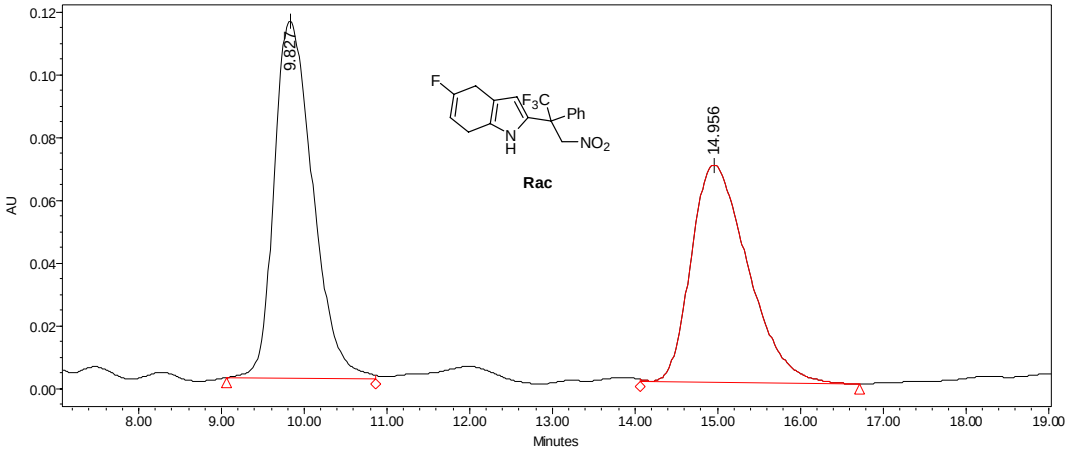


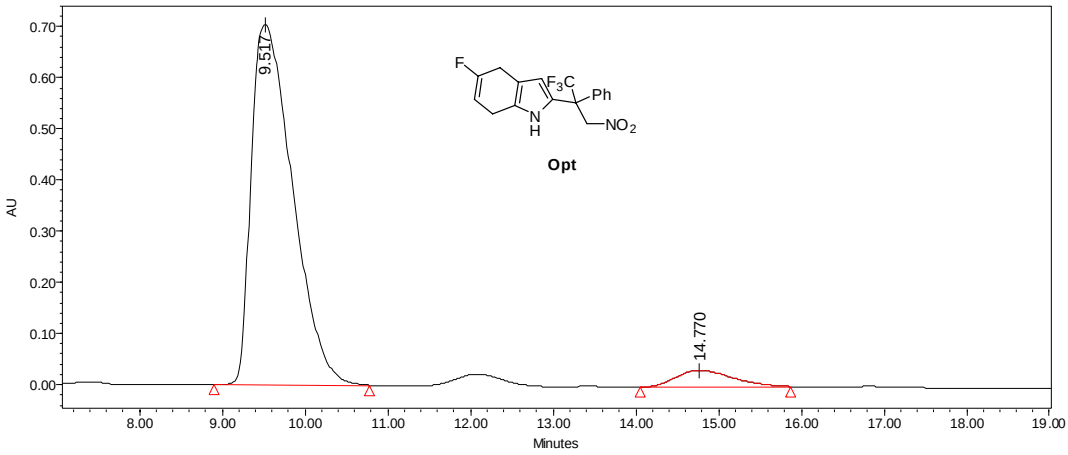
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); Yellow oil, 87% yield, $[\alpha]_D^{27}$ = + 43.0 (*c* 0.5, CH_2Cl_2), 88% ee [Daicel Chiralpak AS-H column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 85/15, 1.0 mL/min, 254 nm; t_{minor} = 14.7 min, t_{major} = 9.5 min]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.25-3.29 (m, 2H), 3.39 (t, *J* = 7.0 Hz, 2H), 5.17 (d, *J* = 13.5 Hz, 1H), 5.36-5.43 (m, 2H), 6.24 (d, *J* = 1.5 Hz, 1H), 7.34-7.43 (m, 5H), 7.85 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -68.9 (s, 3F), -105.9 to -106.0 (m, 1F); ^{13}C NMR (125 MHz, $CDCl_3$): δ 22.3 (d, *J* = 9.0 Hz), 25.3 (d, *J* = 28.9 Hz), 55.0 (q, *J* = 25.8 Hz), 78.2, 98.8 (d, *J* = 20.6 Hz), 108.8, 113.2 (d, *J* = 14.1 Hz), 123.9, 125.1, 125.3 (q, *J* = 283.6 Hz), 128.5, 128.7, 129.1, 133.6, 159.0 (d, *J* = 249.6 Hz); HRMS *m/z* (EI+): Calculated for $C_{17}H_{14}N_2O_2F_4$ ([M]$^+$): 354.0991, Found 354.0999.




160.057
158.060
133.641
129.186
128.764
128.549
126.486
125.103
124.217
123.983
113.311
113.198
108.862
98.964
98.799
78.247
77.249
76.995
76.741
55.112
54.906
25.425
25.194
22.345
22.273
F
F3C
Ph
N
H
NO2
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

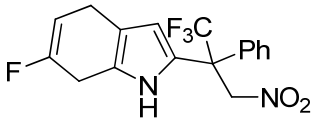

-68.90
-105.96
-105.97
-105.98
-106.01
-106.02
-106.03
F
F3C
Ph
N
H
NO2
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230





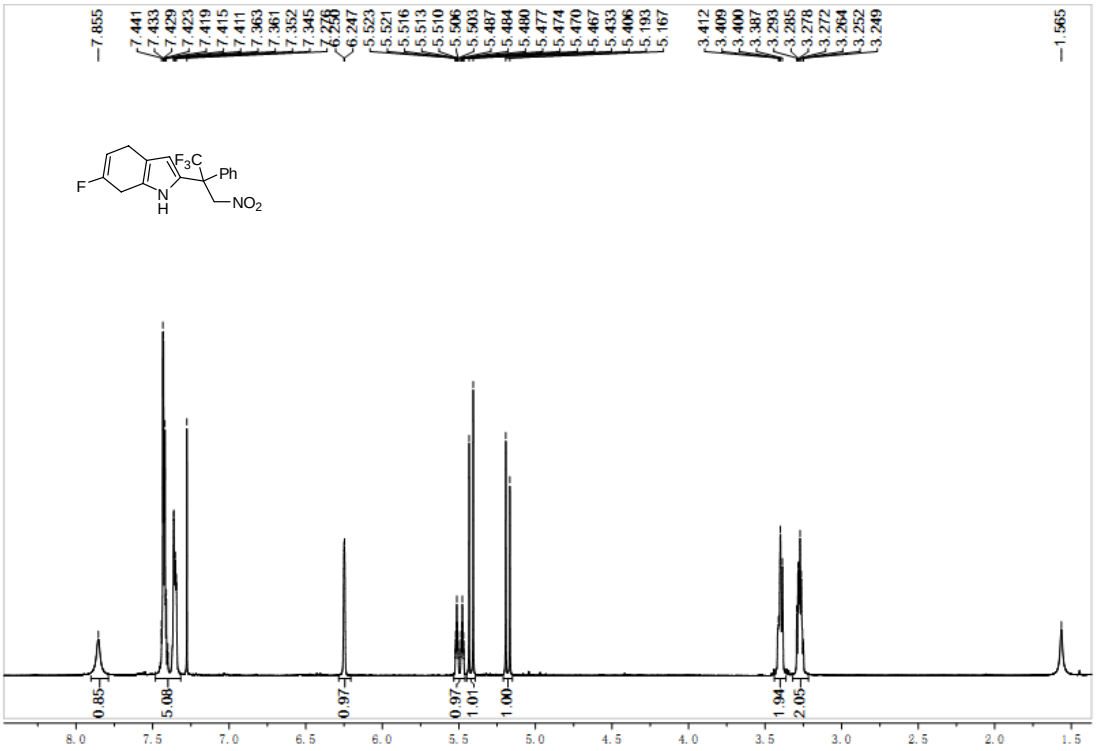
	Retention Time	Height	Area	% Area
1	9.517	704773	24454296	94.02
2	14.770	32362	1554286	5.98

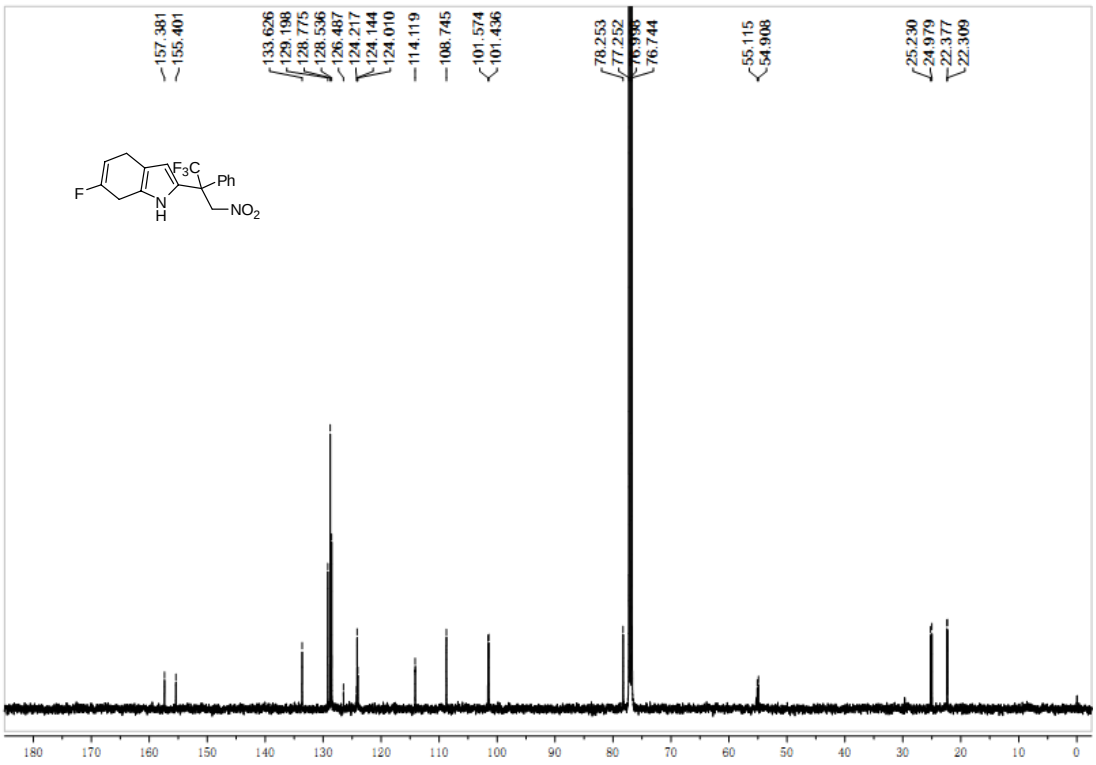
6-fluoro-2-(1,1,1-trifluoro-3-nitro-2-phenylpropan-2-yl)-4,7-dihydro-1H-indole (**3ad**):

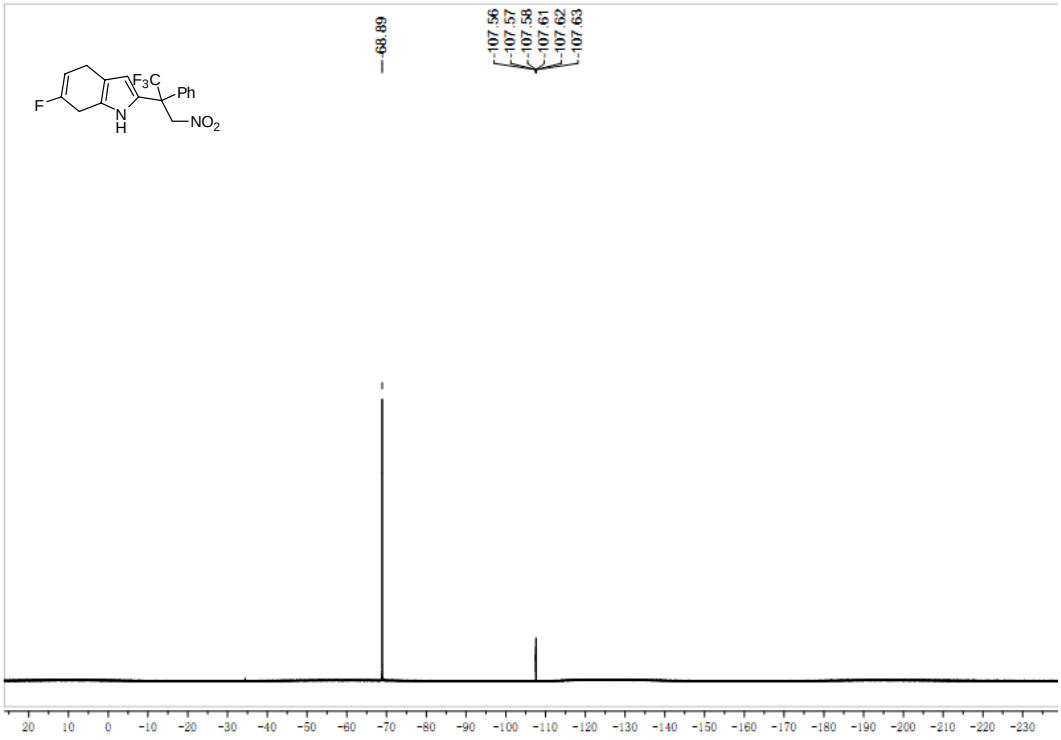


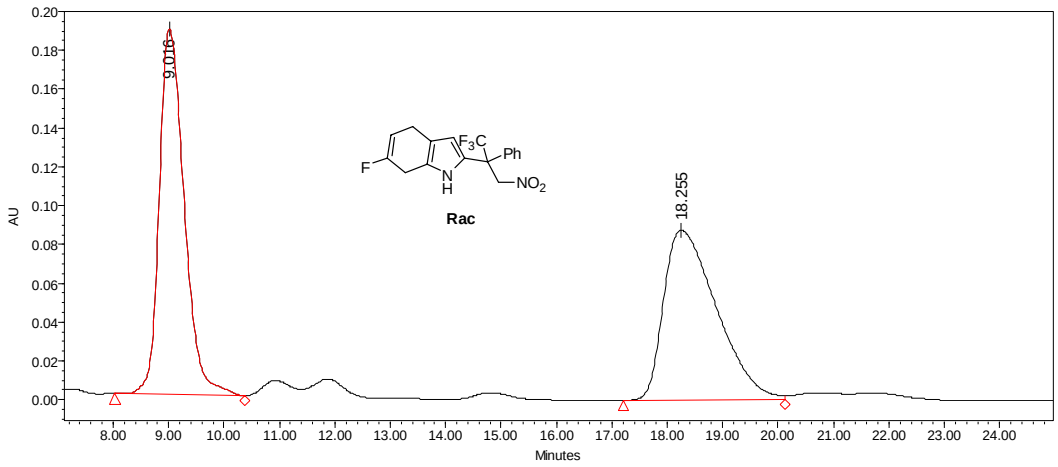
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); Yellow oil, 89% yield, $[\alpha]_D^{27}$ = + 32.6 (*c* 0.5, CH_2Cl_2), 88% ee [Daicel Chiralpak AS-H column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 85/15, 1.0 mL/min, 254 nm; t_{minor} = 18.5 min, t_{major} = 8.9 min]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.24-3.29 (m, 2H), 3.38-3.41(m, 2H), 5.18 (d, *J* = 13.0 Hz, 1H), 5.41 (d, *J* = 13.5 Hz, 1H), 5.46-5.52 (m, 1H), 6.24 (d, *J* = 1.5 Hz, 1H), 7.34-7.44 (m, 5H), 7.85 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -69.8 (s, 3F), -107,5 to -107.6 (m, 1F); ^{13}C NMR (125 MHz, $CDCl_3$): δ 22.3 (d, *J* = 8.5 Hz), 25.1 (d, *J* = 31.4 Hz), 55.0 (q, *J* = 25.9 Hz), 78.2, 101.5 (d, *J* = 17.2 Hz), 108.7, 114.1, 124.0, 124.1, 125.3 (q, *J* = 283.8 Hz), 128.5,

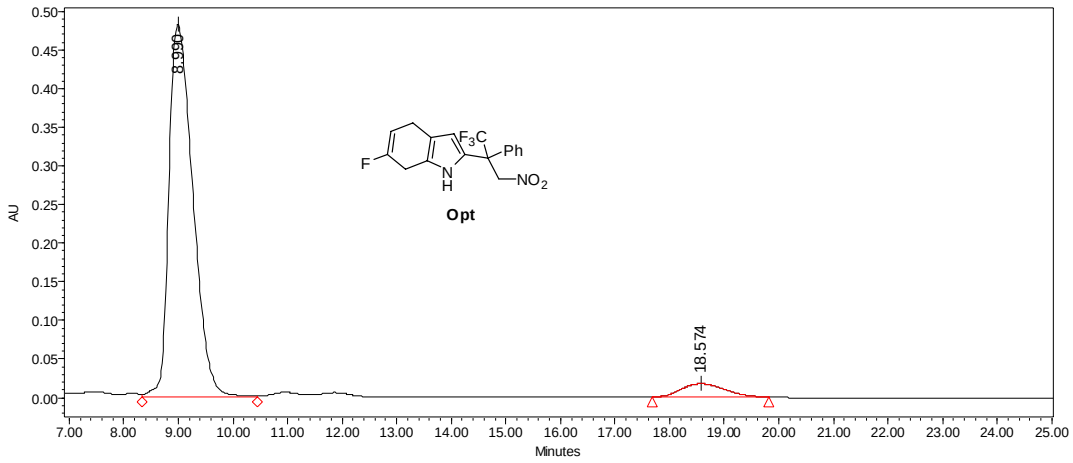
128.7, 129.1, 133.6, 156.3 (d, J = 247.5 Hz); HRMS *m/z* (EI+): Calculated for $C_{17}H_{14}N_2O_2F_4$ ([M]$^+$): 354.0991, Found 354.0997.









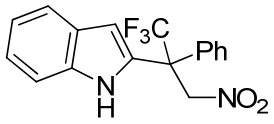


	Retention Time	Height	Area	% Area
1	8.990	483276	14806759	93.81
2	18.574	17472	977302	6.19

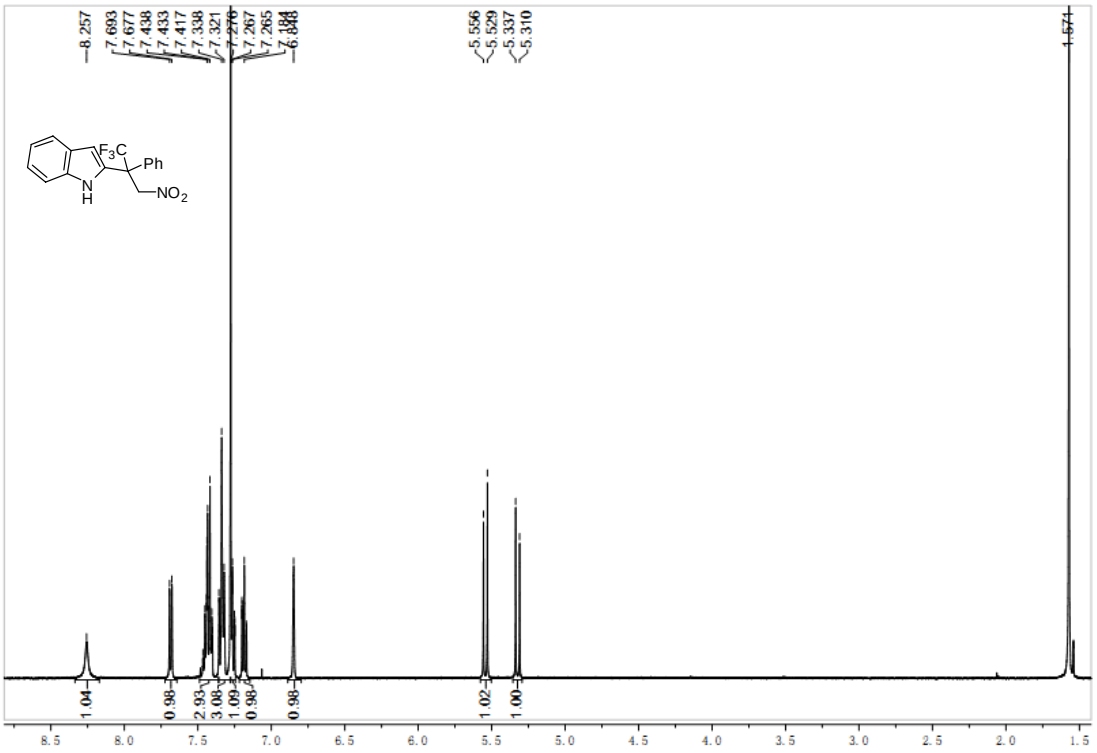
General procedure for one-pot synthesis of 2-alkylated indoles 4:

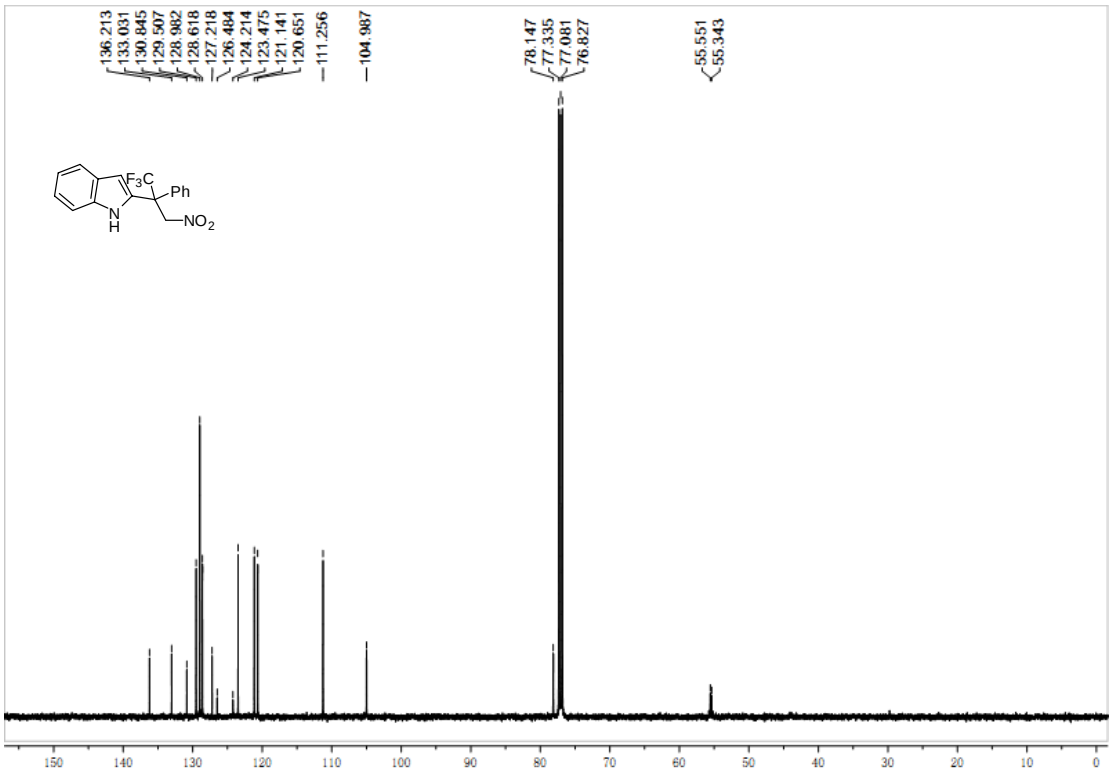
To a dried Schlenk tube were added $Ni(ClO_4)_2 \cdot 6H_2O$ (7.3 mg, 0.02 mmol) and ligand **L7** (11.7 mg, 0.024 mmol) under N_2, 2.0 mL toluene was then added through syringe. The resulting mixture was stirred at 80 °C for 1h, after which the nitroalkene (0.2 mmol) and 4,7-dihydroindole (0.3 mmol) were added. The mixture was stirred at 80 °C until the reaction was completed (monitored by TLC). The reaction mixture was then cooled to room temperature and 10 mL CH_2Cl_2 and 3.0 equiv of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) were added. The resulting mixture was stirred at room temperature for 2 h. The solvent was then evaporated and the residue was purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether (1:5~1:3) to afford the 2-alkylated indole product.

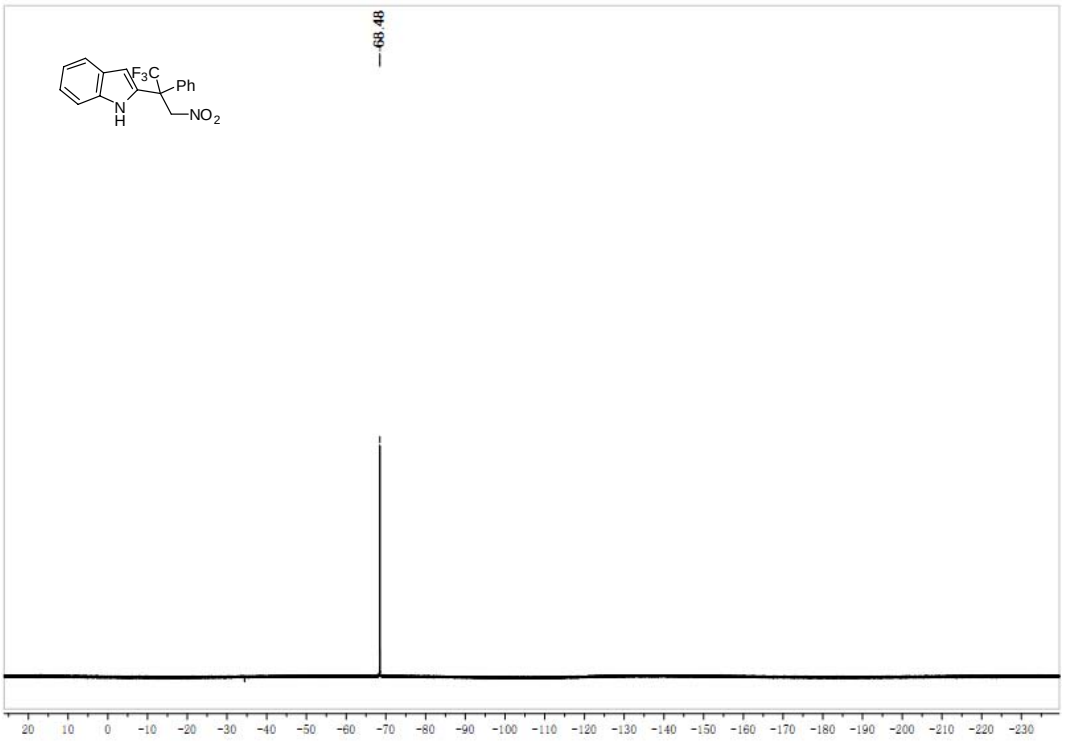
2-(1,1,1-trifluoro-3-nitro-2-phenylpropan-2-yl)-1H-indole (**4a**):

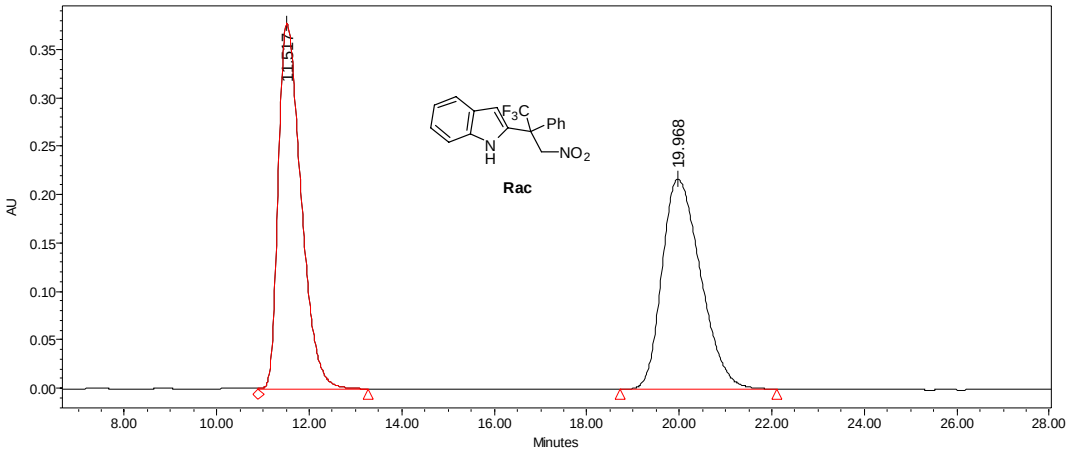


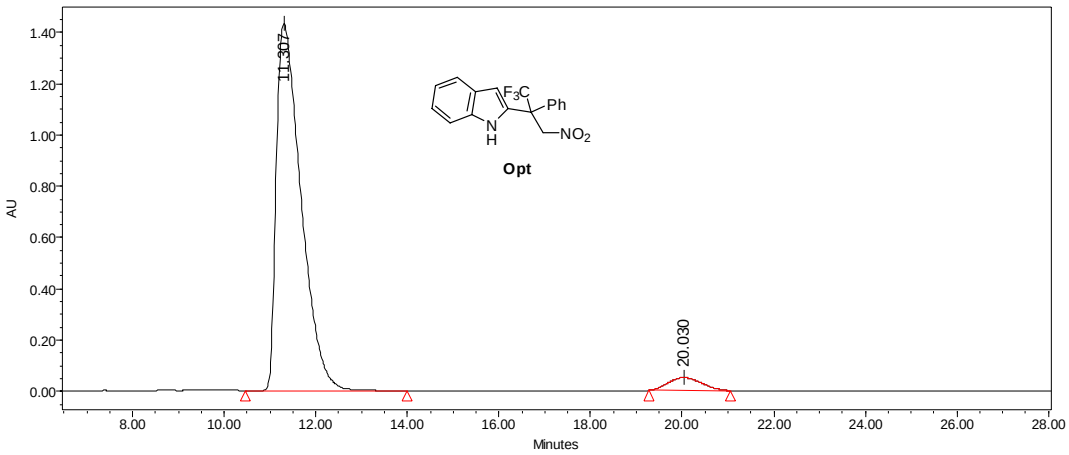
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); White solid, 85% yield, $[\alpha]_D^{27}$ = + 22.5 (*c* 1.0, CH_2Cl_2), 91% ee [Daicel Chiralpak AS-H column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 85/15, 1.0 mL/min, 254 nm; t_{minor} = 20.0 min, t_{major} = 11.3 min]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.32 (d, *J* = 13.5 Hz, 1H), 5.54 (d, *J* = 13.5 Hz, 1H), 6.84 (s, 1H), 7.18 (td, *J* = 1.0, 8.0 Hz, 1H), 7.26 (td, *J* = 1.0, 8.0 Hz, 1H), 7.33 (t, *J* = 8.5 Hz, 3H), 7.40-7.46 (m, 3H), 7.68 (d, *J* = 8.0 Hz, 1H), 8.25 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -68.4 (s, 3F); ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.4 (q, *J* = 26.0 Hz), 78.1, 104.9, 111.2, 120.6, 121.1, 123.4, 125.3 (q, *J* = 283.8 Hz), 127.2, 128.6, 128.9, 129.5, 130.8, 133.0, 136.2; HRMS *m/z* (EI+): Calculated for $C_{17}H_{13}N_2O_2F_3$ ($[M]^+$): 334.0929, Found 334.0941.


8.257
7.693
7.677
7.438
7.433
7.417
7.338
7.321
7.276
7.267
7.265
6.848
5.556
5.529
5.337
5.310
1.671
F3C
Ph
NO2
N
H
1.04
0.98
2.93
3.08
1.09
0.98
0.98
1.02
1.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5


136.213
133.031
130.845
129.507
128.982
128.618
127.218
126.484
124.214
123.475
121.141
120.651
111.256
104.987
78.147
77.335
77.081
76.827
55.551
55.343
F3C
Ph
NO2
N
H
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

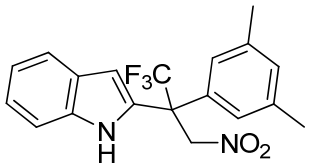




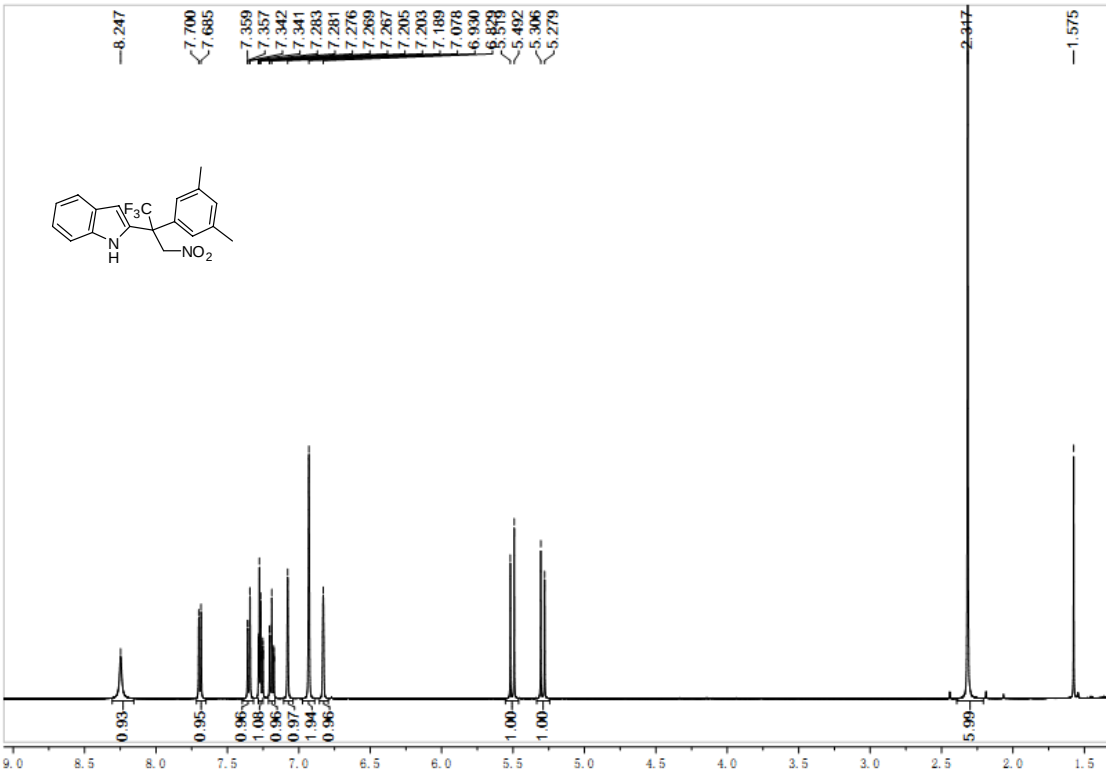


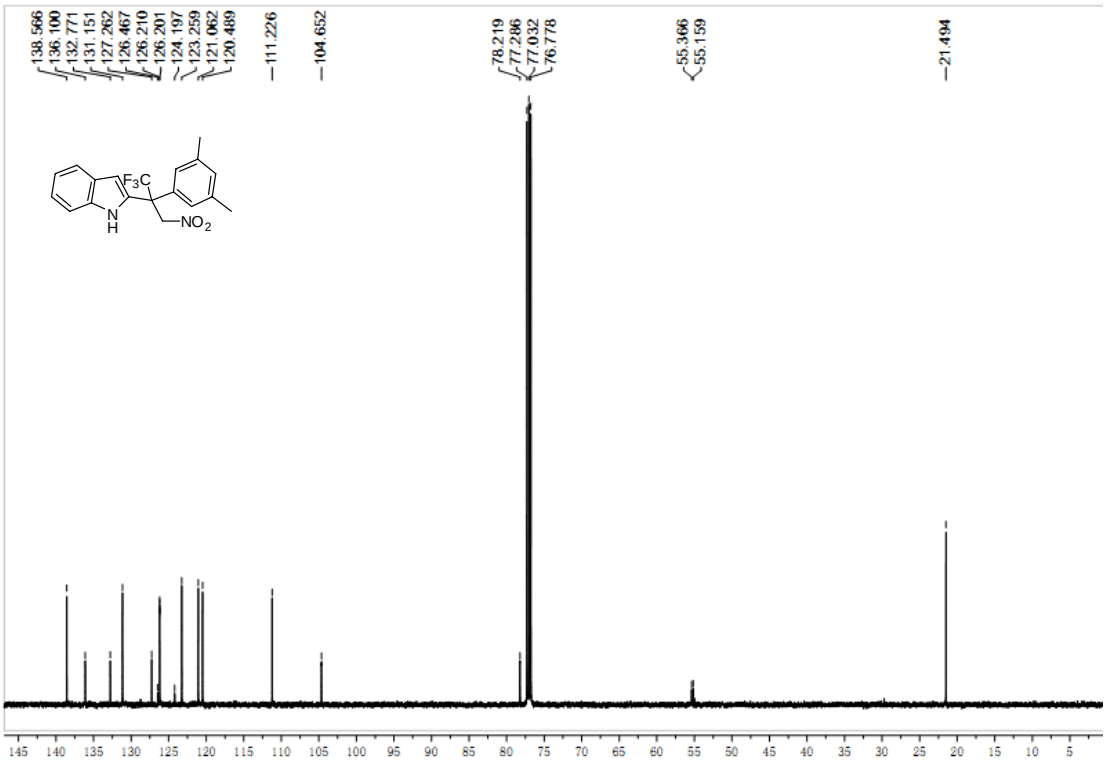
	Retention Time	Height	Area	% Area
1	11.307	1432510	53536996	95.42
2	20.030	50337	2567612	4.58

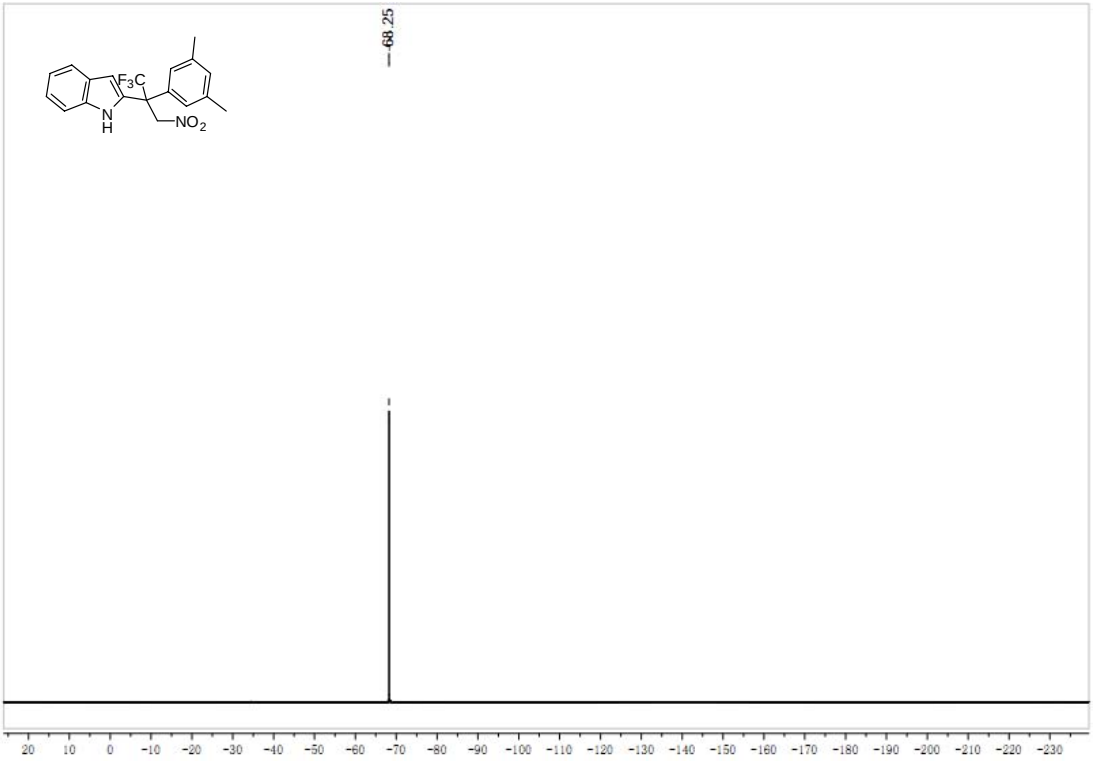
2-(2-(3,5-dimethylphenyl)-1,1,1-trifluoro-3-nitropropan-2-yl)-1H-indole (**4b**):

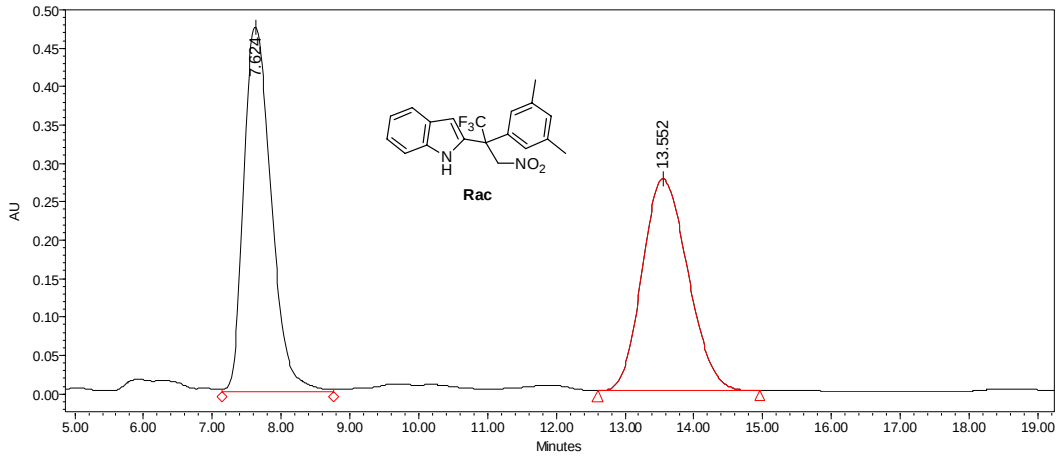


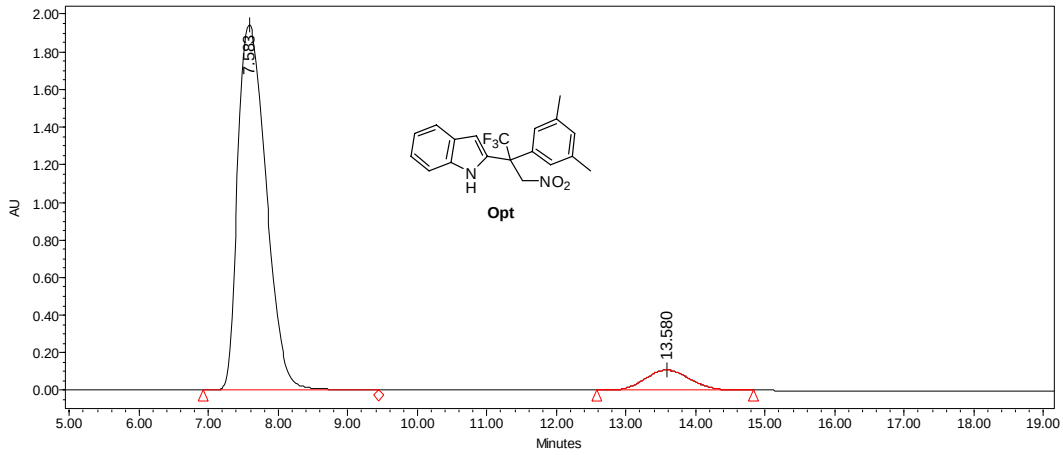
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); White solid, 86% yield, $[\alpha]_D^{27}$ = + 20.4 (*c* 0.5, CH_2Cl_2), 84% ee [Daicel Chiralpak AS-H column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 85/15, 1.0 mL/min, 254 nm; t_{minor} = 13.5 min, t_{major} = 7.5 min]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.31 (s, 6H), 5.29 (d, *J* = 13.5 Hz, 1H), 5.50 (d, *J* = 13.5 Hz, 1H), 6.82 (s, 1H), 6.93 (s, 2H), 7.07 (s, 1H), 7.18 (td, *J* = 1.0, 8.0 Hz, 1H), 7.26 (td, *J* = 1.0,7.0 Hz, 1H), 7.34 (dd, *J* = 1.0, 8.0 Hz, 1H), 7.69 (d, *J* = 7.5 Hz, 1H), 8.24 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -68.2 (s, 3F); ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.4, 55.2 (q, *J* = 25.9 Hz), 78.2, 104.6, 111.2, 120.4, 121.0, 123.2, 125.3 (q, *J* = 283.8 Hz), 126.20, 126.21, 127.2, 131.1, 132.7, 136.1, 138.5; HRMS *m/z* (EI+): Calculated for $C_{19}H_{17}N_2O_2F_3$ ($[M]^+$): 362.1242, Found 362.1234.




138.566
136.100
132.771
131.151
127.262
126.467
126.210
126.201
124.197
123.259
121.062
120.489
111.226
104.652
78.219
77.286
77.032
76.778
55.366
55.159
21.494
F3C
N
H
NO2
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5

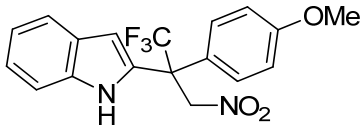

68.25
F3C
N
H
NO2
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230





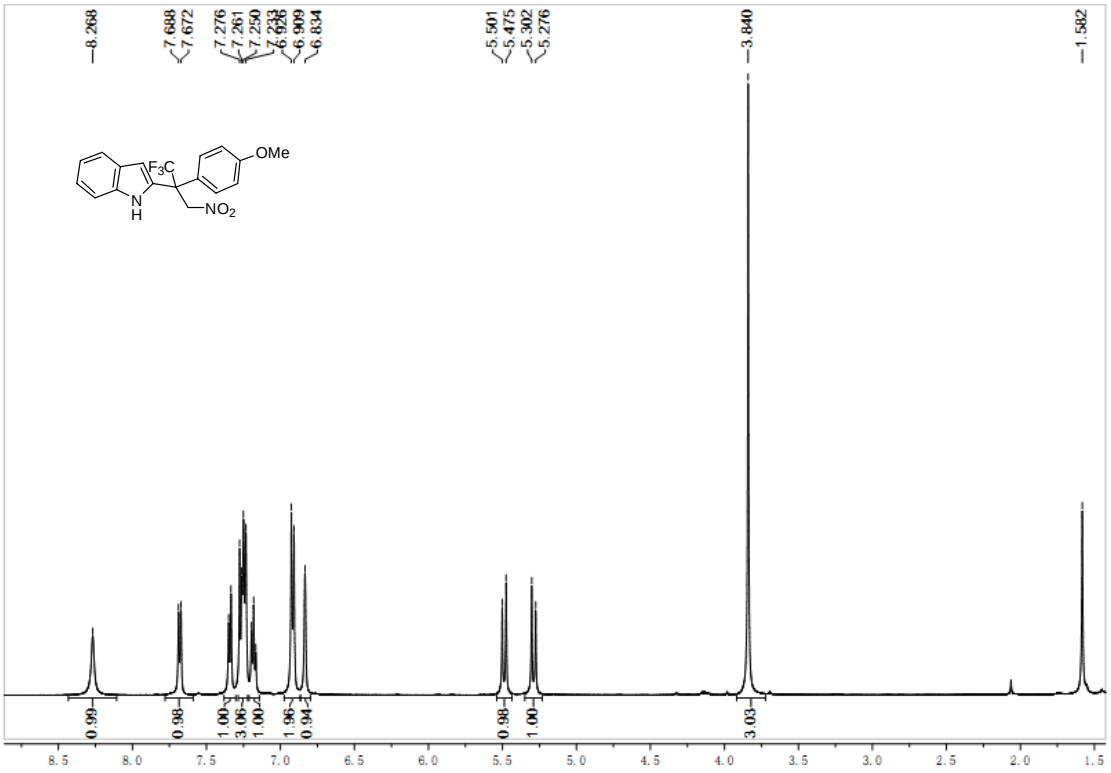
	Retention Time	Height	Area	% Area
1	7.583	1944869	55008455	91.85
2	13.580	107897	4883098	8.15

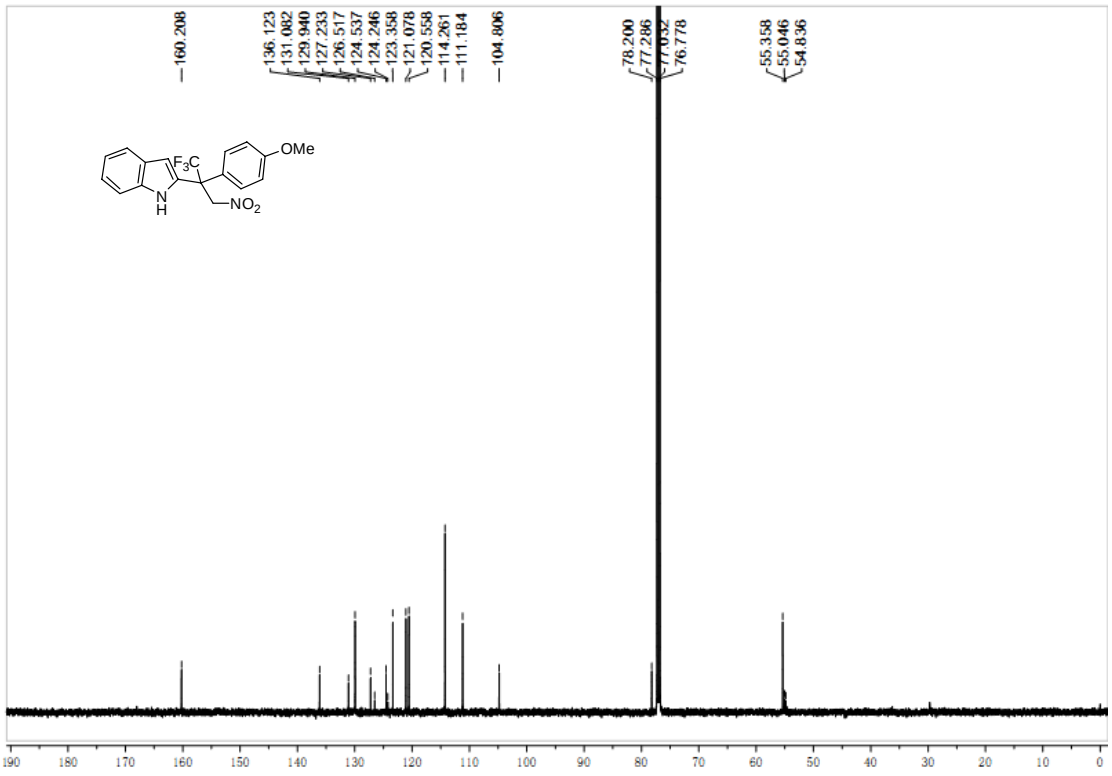
2-(1,1,1-trifluoro-2-(4-methoxyphenyl)-3-nitropropan-2-yl)-1H-indole (**4c**):

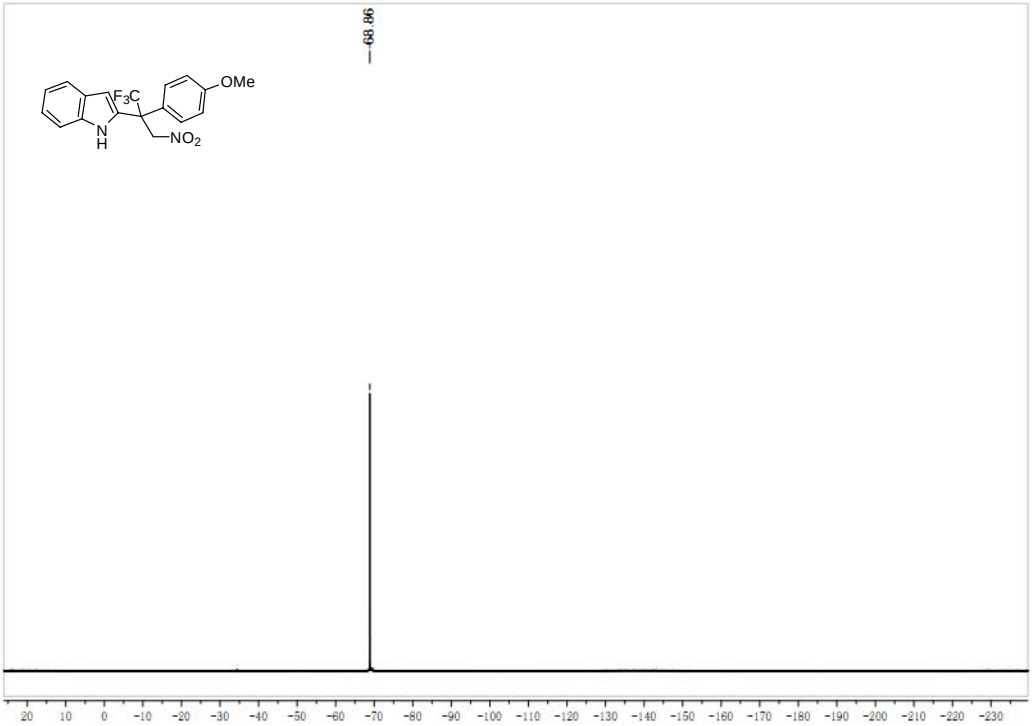


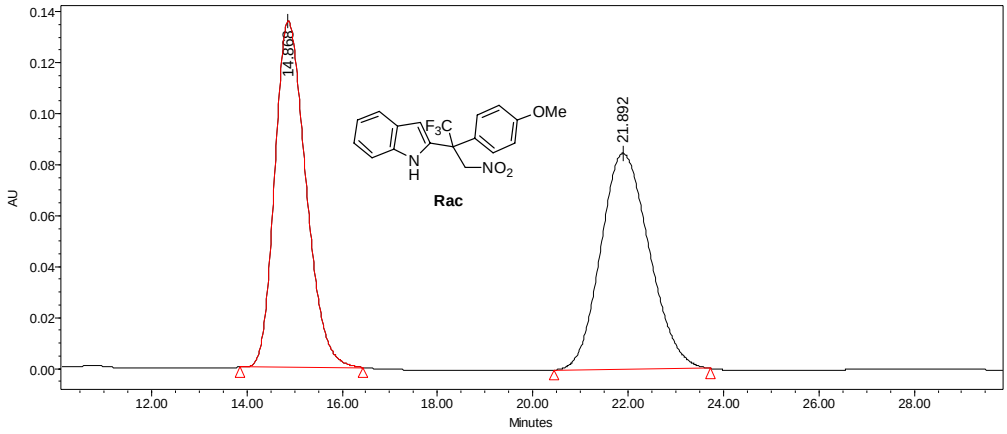
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:3 (v/v); White solid, 82% yield, $[\alpha]_D^{27}$ = + 16.6 (*c* 0.5, CH_2Cl_2), 88% ee [Daicel Chiralpak AS-H column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 254 nm; t_{minor} = 22.2 min, t_{major} = 14.7 min]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.84 (s, 3H), 5.28 (d, *J* = 13.0 Hz, 1H), 5.48 (d, *J* = 13.0 Hz, 1H), 6.83 (s, 1H), 6.91 (d, *J* = 8.5 Hz, 2H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.23-7.27 (m, 3H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 8.26 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -68.8 (s, 3F); ^{13}C NMR (125 MHz, $CDCl_3$): δ 54.9 (q, *J* = 26.3 Hz), 55.3, 78.2, 104.8, 111.1, 114.2,

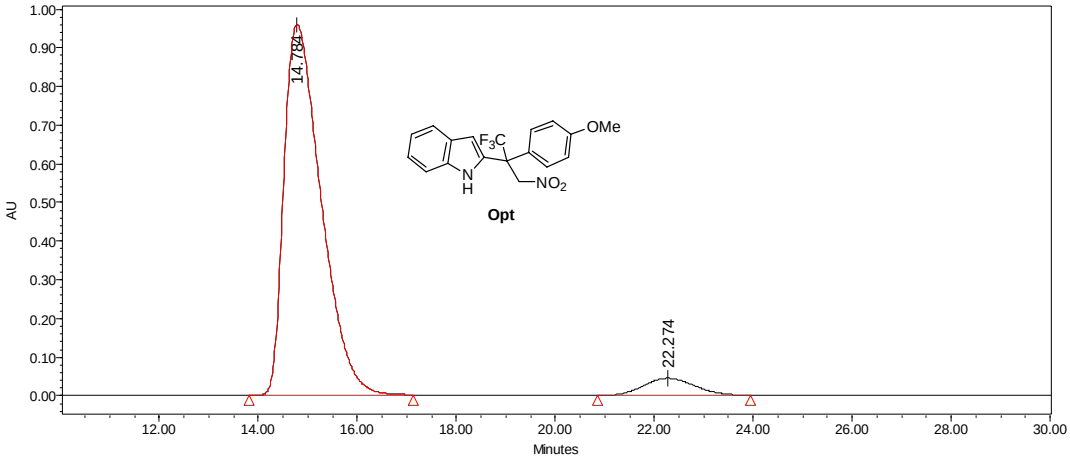
120.5, 121.0, 123.3, 124.5, 125.3 (q, J = 283.9 Hz), 127.2, 129.9, 131.0, 136.1, 160.2; HRMS *m/z* (EI+): Calculated for $C_{18}H_{15}N_2O_3F_3$ ([M]$^+$): 364.1035, Found 364.1039.





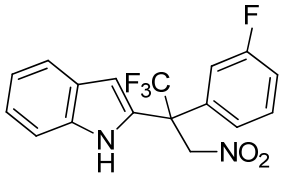




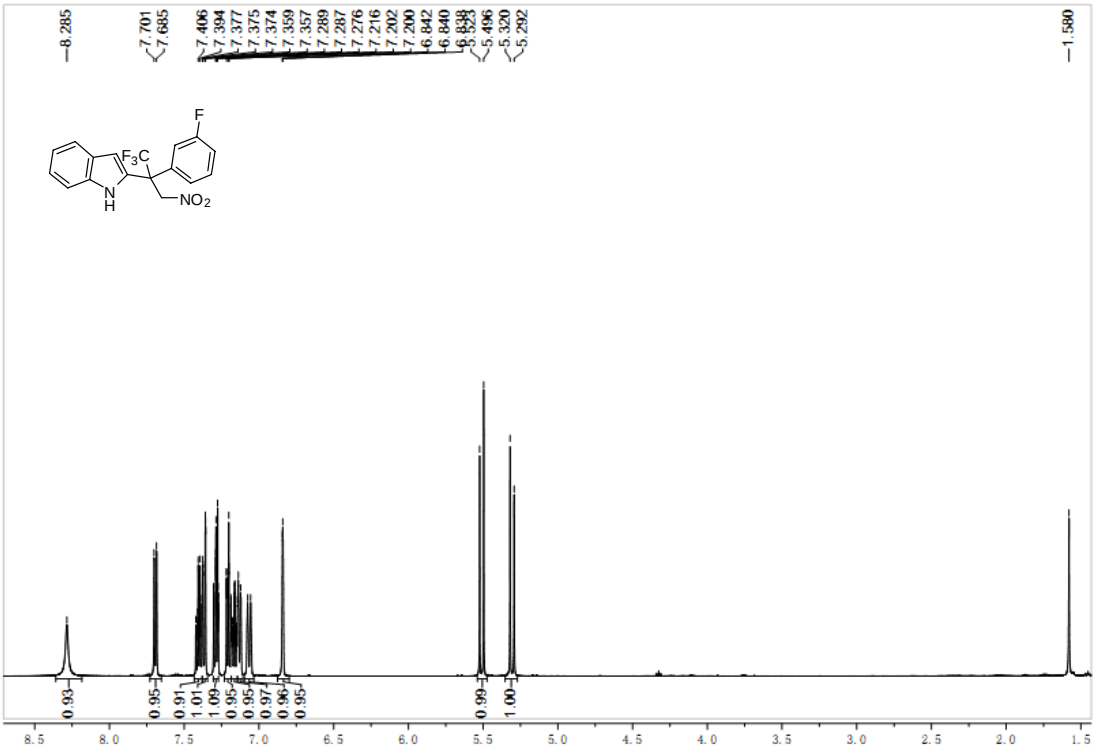


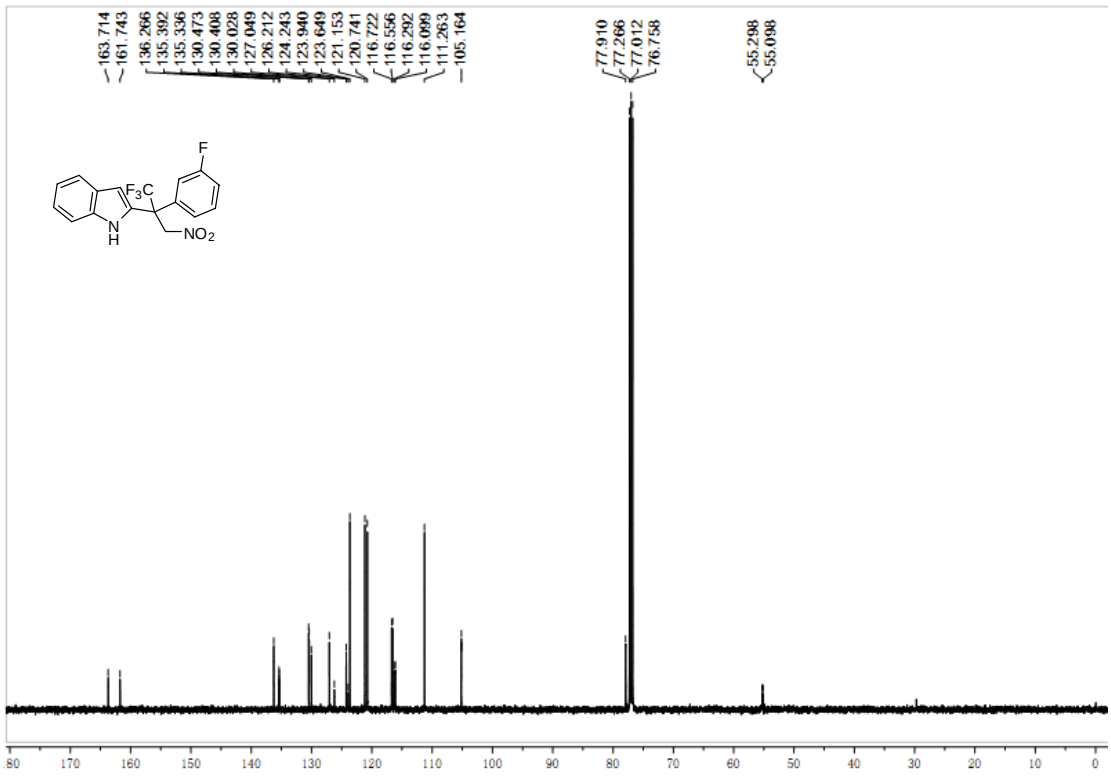
	Retention Time	Height	Area	% Area
1	14.784	959393	49945957	93.88
2	22.274	44735	3253392	6.12

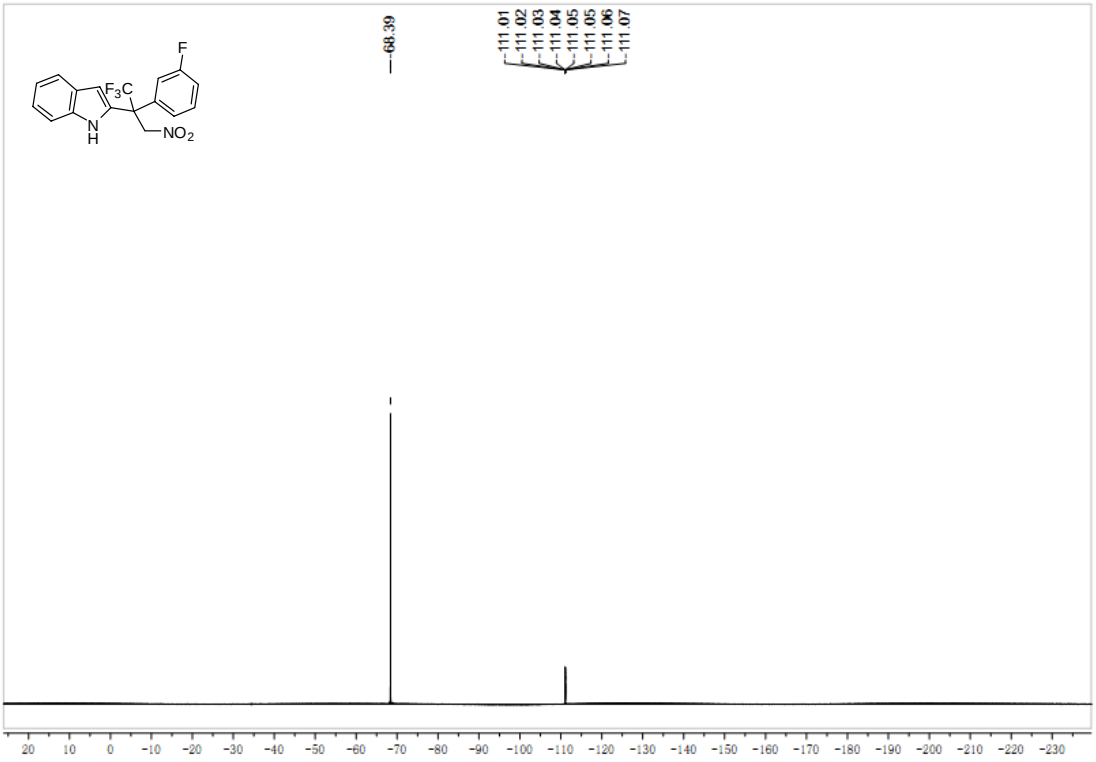
2-(1,1,1-trifluoro-2-(3-fluorophenyl)-3-nitropropan-2-yl)-1H-indole (**4d**):

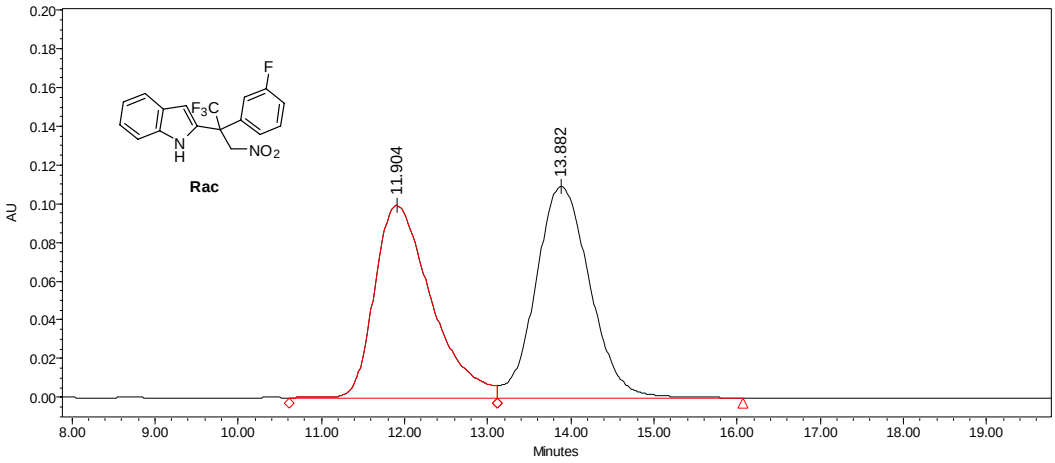


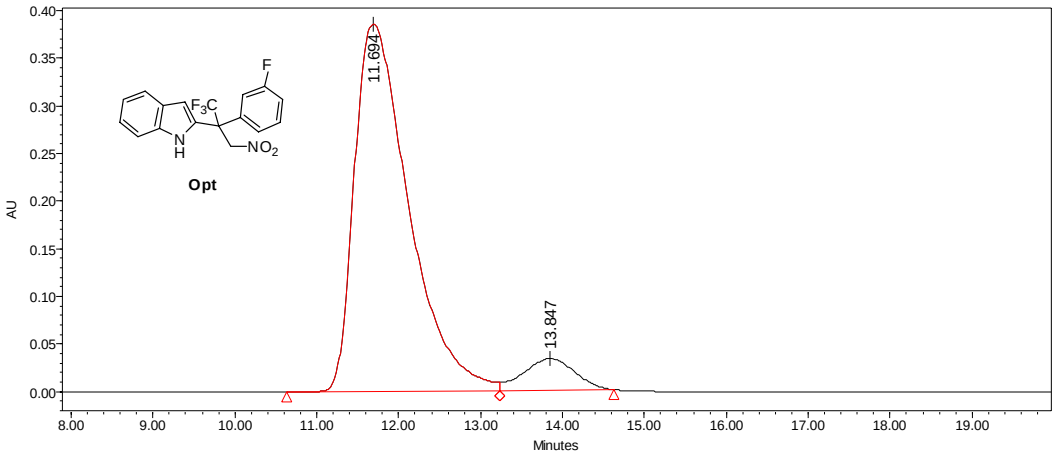
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); White solid, 85% yield, $[\alpha]_D^{27}$ = + 18.2 (*c* 0.5, CH_2Cl_2), 85% ee [Daicel Chiralpak AS-H column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 85/15, 1.0 mL/min, 254 nm; t_{minor} = 13.8 min, t_{major} = 11.6 min]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.30 (d, *J* = 14.0 Hz, 1H), 5.50 (d, *J* = 13.5 Hz, 1H), 6.84 (t, *J* = 1.0 Hz, 1H), 7.06 (d, *J* = 10.0 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.16 (tdd, *J* = 0.5, 2.5, 8.0 Hz, 1H), 7.20 (td, *J* = 0.5, 7.0 Hz, 1H), 7.28 (td, *J* = 1.0, 7.5 Hz, 1H), 7.36 (dd, *J* = 1.0, 8.5 Hz, 1H), 7.40 (td, *J* = 6.5, 8.5 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 8.28 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -68.3 (s, 3F), -111.01 to -111.07 (m, 1F); ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.1 (q, *J* = 25.0 Hz), 77.9, 105.1, 111.2, 116.1 (d, *J* = 24.1 Hz), 116.6 (d, *J* = 20.8 Hz), 120.7, 121.1, 123.6, 124.2, 125.0 (q, *J* = 284.0 Hz), 127.0, 130.0, 130.4 (d, *J* = 8.1 Hz), 135.3 (d, *J* = 7.0 Hz), 136.2, 162.7 (d, *J* = 246.4 Hz); HRMS *m/z* (EI+): Calculated for $C_{17}H_{12}N_2O_2F_4$ ([M]$^+$): 352.0835, Found 352.0833.




163.714
161.743
136.266
135.392
135.336
130.473
130.408
130.028
127.049
126.212
124.243
123.940
123.649
121.153
120.741
116.722
116.556
116.292
116.099
111.263
105.164
77.910
77.266
77.012
76.758
55.298
55.098
F
F3C
N
H
NO2

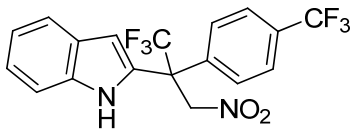

68.39
111.01
111.02
111.03
111.04
111.05
111.05
111.06
111.07
F
F3C
N
H
NO2





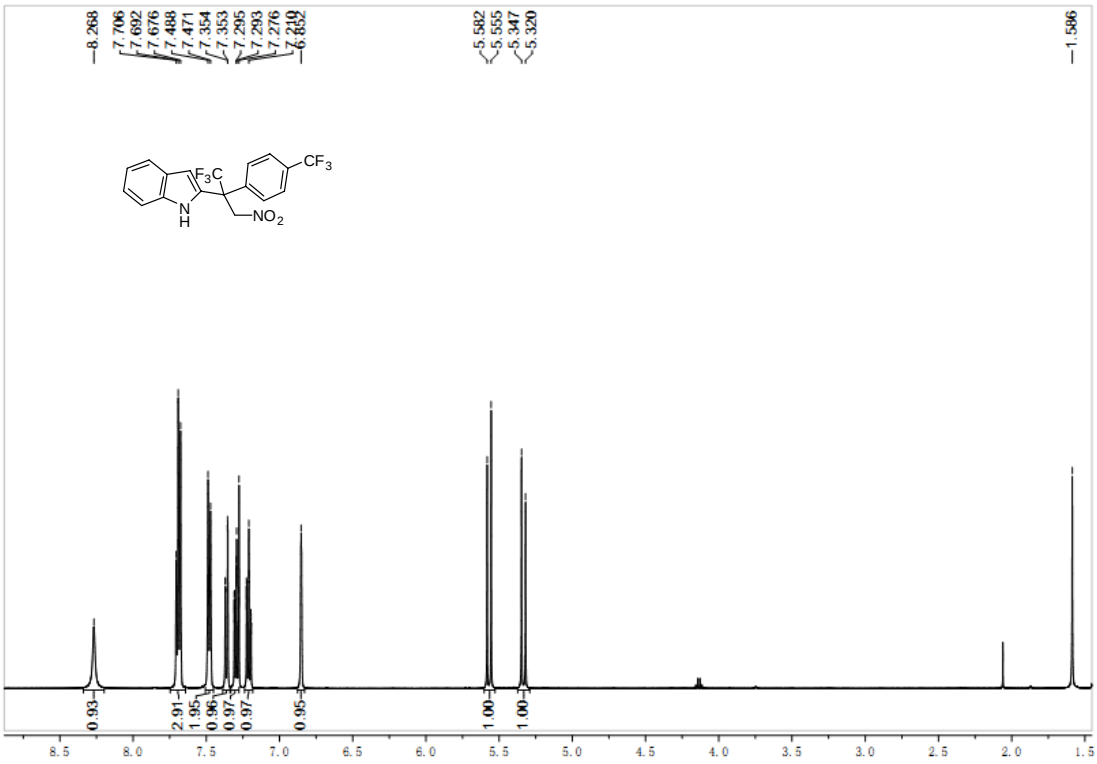
	Retention Time	Height	Area	% Area
1	11.694	385085	17715243	92.49
2	13.847	33059	1437946	7.51

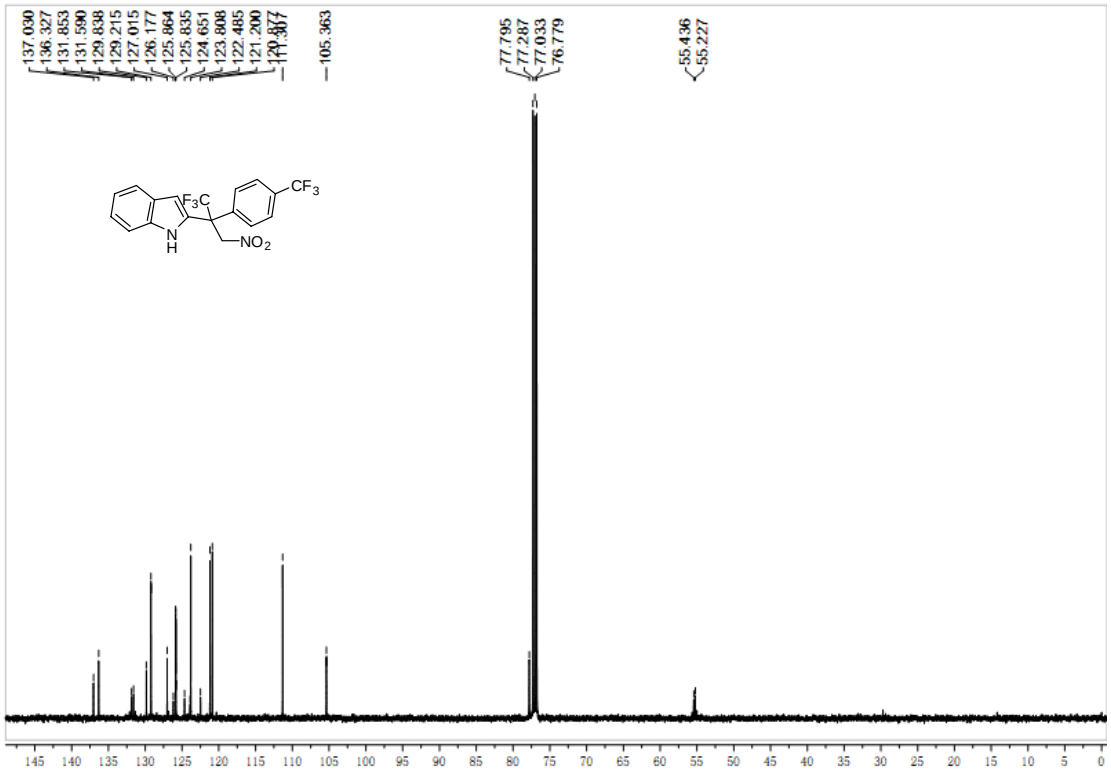
2-(1,1,1-trifluoro-3-nitro-2-(4-(trifluoromethyl)phenyl)propan-2-yl)-1H-indole (**4e**):

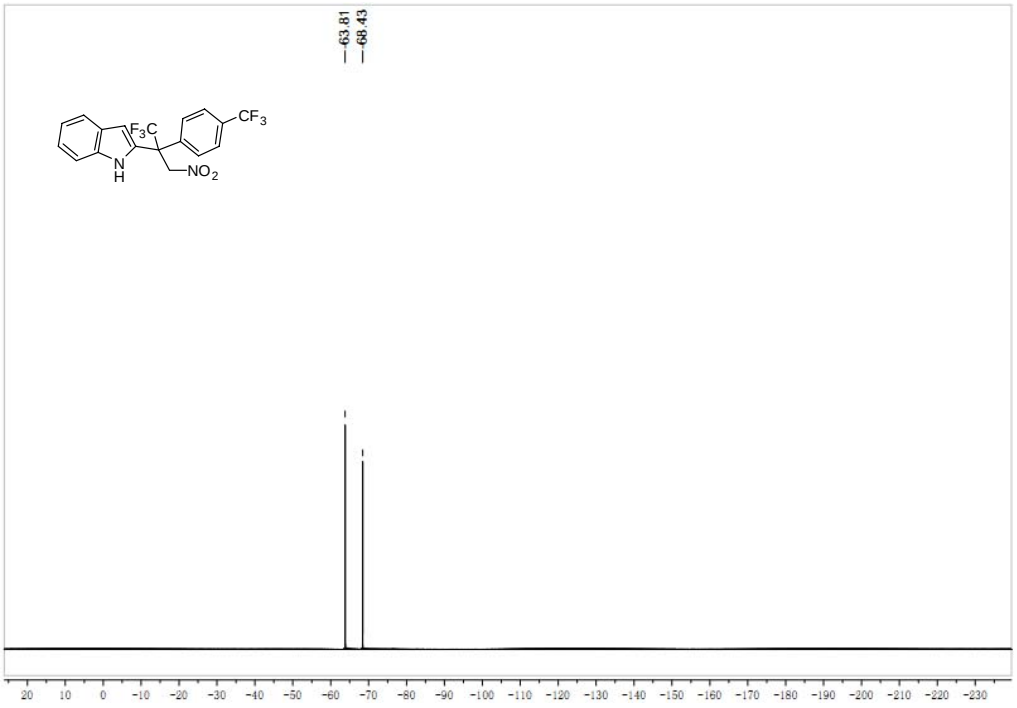


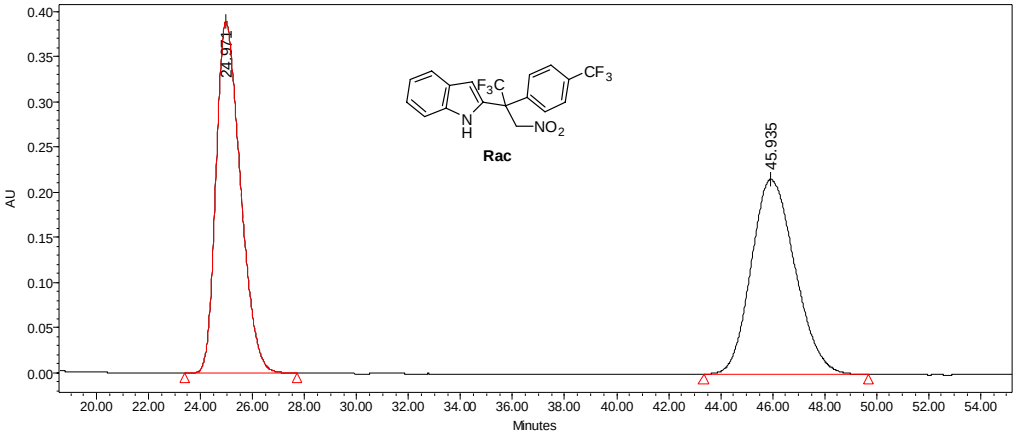
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); White solid, 80% yield, $[\alpha]_D^{27}$ = + 16.4 (*c* 0.5, CH_2Cl_2), 86% ee [Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), *n*-hexane/*i*-PrOH = 85/15, 1.0 mL/min, 254 nm; t_{minor} = 46.4 min, t_{major} = 24.0 min]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.33 (d, *J* = 13.5 Hz, 1H), 5.56 (d, *J* = 13.5 Hz, 1H), 6.85 (s, 1H), 7.20 (td, *J* = 1.0, 7.0 Hz, 1H), 7.29 (td, *J* = 1.0, 7.0 Hz, 1H), 7.36 (dd, *J* = 1.0, 8.0 Hz, 1H), 7.47 (d, *J* = 8.5, 2H), 7.69 (t, *J* = 8.0 Hz, 3H), 8.26 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.8 (s, 3F), -68.4 (s, 3F); ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.3 (q, *J* = 26.1 Hz), 77.7, 105.3, 111.3,

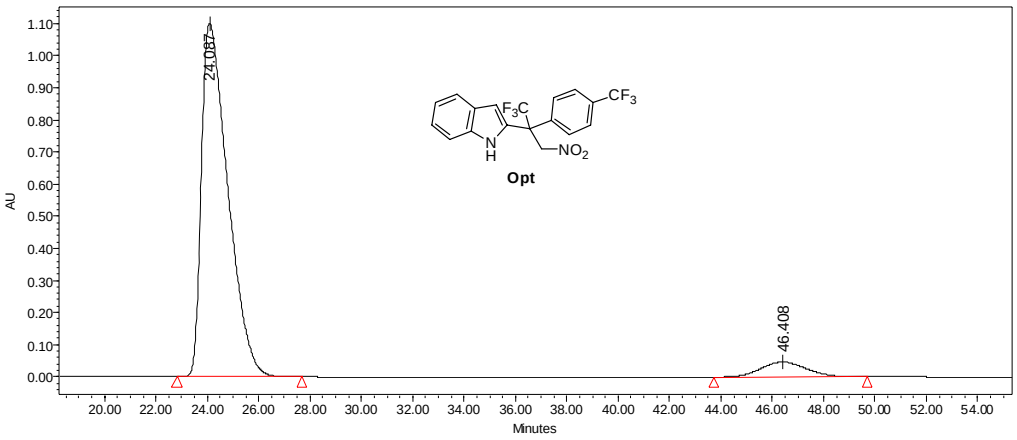
120.8, 121.2, 123.5 (q, J = 270.8 Hz), 123.8, 125.0 (q, J = 284.3 Hz), 125.8 (q, J = 3.6 Hz), 127.0, 129.2, 129.8, 131.7 (q, J = 32.9 Hz), 136.3, 137.0; HRMS *m/z* (EI+): Calculated for $C_{18}H_{12}N_2O_2F_6$ ($[M]^+$): 402.0803, Found 402.0823.











	Retention Time	Height	Area	% Area
1	24.087	1100819	78691143	93.16
2	46.408	46650	5774358	6.84

Determine the absolute configuration of product 4a:

The CD spectrum of product **4a** and its analogous product (**A**) reported in our previous work (Ref.11a, *J. Am Chem. Soc.* 2013, **135**, 2983) were recorded on JASCO J-815 CD spectrometer. Based on the observed cotton effect of these two compounds at around 300 nm and the known *R* configuration for compound **B**, the absolute configuration of the present product **4a** was assigned to be *S*.