Chiral *N*-heterocyclic carbene ligands for asymmetric oxindole synthesis

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CONTENTS:

General.

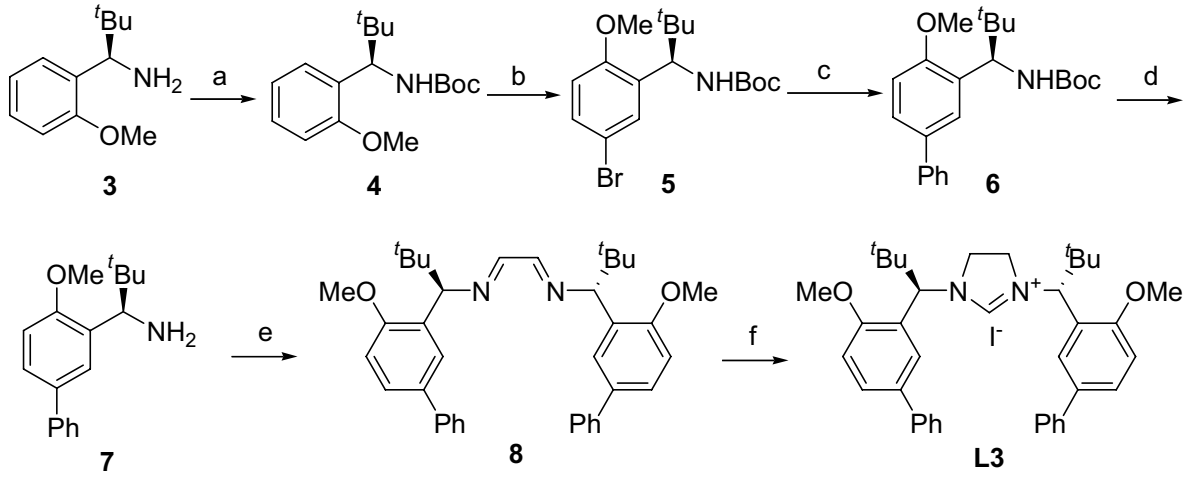
Solvents were purified by filtration on Al_2O_3 drying columns using a Solvtek system or by distillation over Na and benzophenone. Reactions and manipulations involving organometallic or moisture sensitive compounds were carried out under dry nitrogen and glassware heated under vacuum prior to use. Analytical HPLC was performed using an

Agilent 1100 series chromatograph with a JASCO PU–980 pump and Agilent 1100 Series detection system.

^{1}H- and ^{13}C-NMR spectra were recorded on Bruker AMX-500, AMX-400 or AMX-300 FT spectrometers using an internal deuterium lock. Chemical shifts are quoted in parts per million (ppm) downfield of tetramethylsilane. Coupling constants *J* are quoted in Hz. Infrared spectra were recorded on a Perkin–Elmer Spectrum One spectrophotometer. Electron impact (EI) mass spectra were obtained using Varian CH–4 or SM–1 instruments operating at 40–70eV.Electrospray ionization (ESI) HRMS analyses were measured on a VG analytical 7070E instrument. Optical rotations were measured on a Perkin Elmer 241 polarimeter using a quartz cell (l = 10 cm) with a Na high-pressure lamp (λ = 589 nm). Melting points were determined on a Büchi 510 instrument and are uncorrected.

Ligands **L1**, **L2** and chiral amine (*R*)-**3** were prepared according to literature methods.[1]

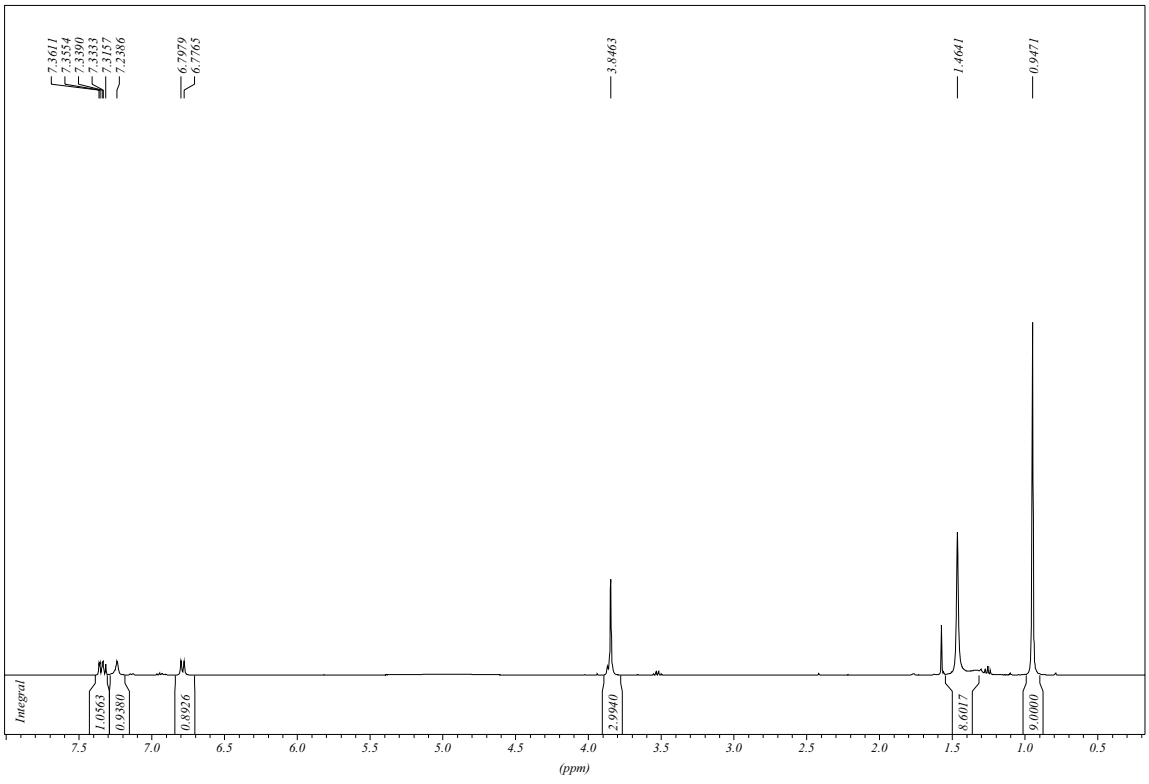
1. Synthesis of the chiral carbene ligand precursor:



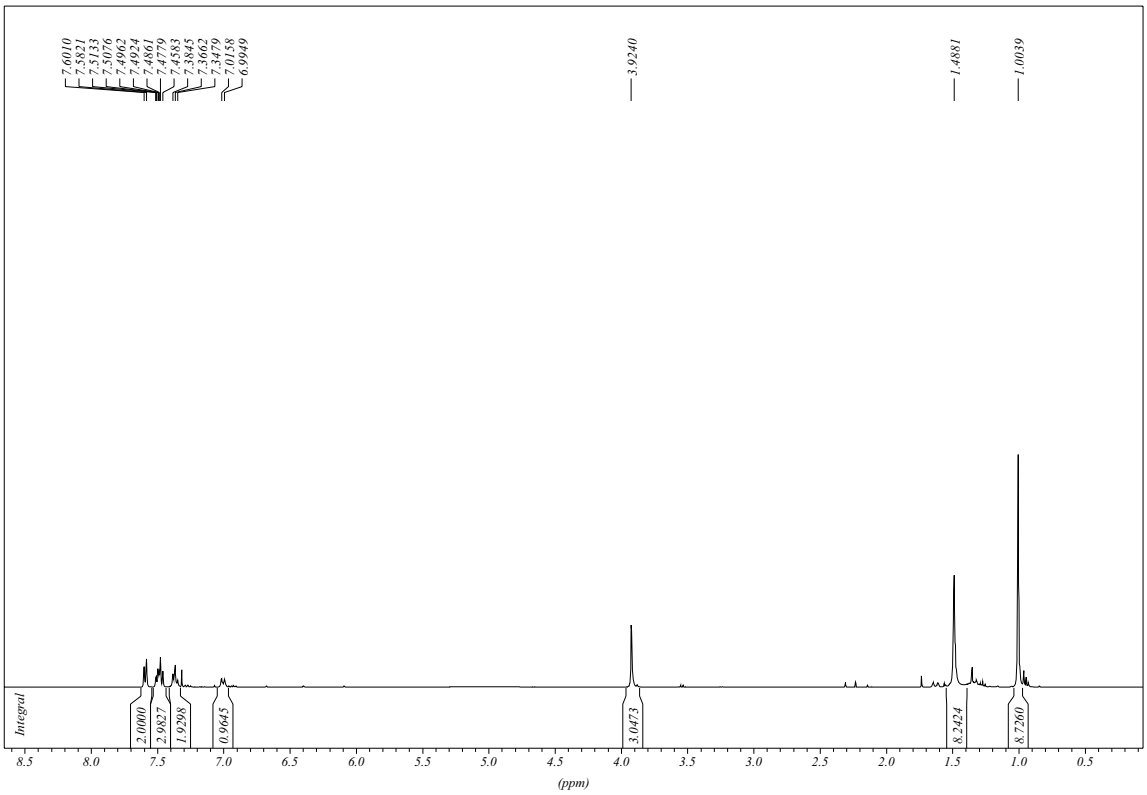
(*R*)-tert-butyl-1-(2-methoxyphenyl)-2,2-dimethylpropylcarbamate (4). To a solution of (*R*)-1-(2-methoxyphenyl)-2,2-dimethylpropan-1-amine (**3**) (1.32 g, 6.83 mmol) and

triethylamine (2.1 mL, 14.6 mmol) in dichloromethane (40 mL) was added di-*tert*butyl dicarbonate (3.2 g, 98%, 14.3 mmol) at room temperature, and the reaction mixture was stirred at room temperature for 18 h. The reaction was quenched with sat. aq. NH_4Cl, the aqueous layer was extracted with dichloromethane and the combined organic layers were dried over magnesium sulfate and concentrated in *vacuo* to give **4**. The crude product was used without any further purification.

(*R*)-1-(5-bromo-2-methoxyphenyl)-2,2-dimethylpropan-1-amine (5). To a solution of **4** (14.6 mmol) in acetone (30 mL) and 1 N HCl (0.74 mL) was added *N*-bromosuccinimide (1.28 g, 95%, 6.83 mmol), and the reaction mixture was stirred at room temperature for 12 h. Hexane (40 mL) was added, the reaction mixture was cooled to 0 °C, and the precipitate formed was removed by filtration and washed with hexanes. The filtrate was concentrated in *vacuo* to give the crude product **5** as a glassy solid (2.31 g, 91% over two steps). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.94 (s, 9H), 1.46 (s, 9H), 3.84 (s, 3H), 6.78 (d, J = 8.6 Hz, 1H), 7.23 (s, 1H), 7.35 (dd, J = 2.3, 8.8 Hz, 1H).



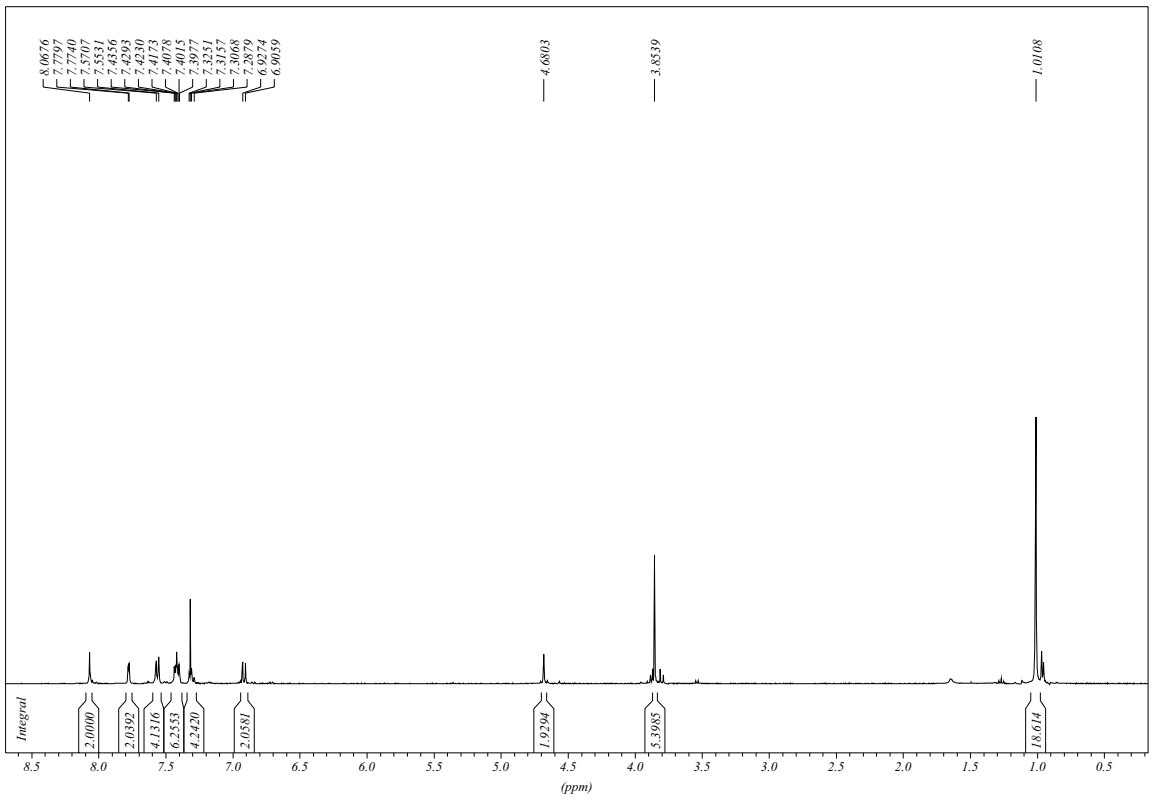
Compound 6. A dried Schlenk tube was charged with [P^{t}Bu$_3$H][BF$_4$] (78 mg, 0.269 mmol), Pd(dba)$_2$ (78 mg, 0.136 mmol), ^{t}BuONa (30 mg, 0.312 mmol) and 5 mL DME under N_2. The mixture was stirred at room temperature for 0.5 h. Then K_2CO_3 (2.8g, 20.3 mmol), PhB(OH)$_2$ (2.4 g, 19.7 mmol), and **6** (2.12 g, 5.7 mmol) (in 20 mL DME and 25 mL degassed water) were added. The stirred mixture was then heated to 80 ^{o}C for 36 h. The reaction mixture was cooled to room temperature, quenched with sat. aq. $NaHCO_3$ and extracted with ethyl acetate. The combined organics were dried over magnesium sulfate, filtered and concentrated in *vacuo*. The resultant oil was purified by column chromatography to yield **6** (2.17g, 5.48 mmol, 96%) as a yellow glassy solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.0 (s, 9H), 1.49 (s, 9H), 3.92 (s, 3H), 7.0 (d, J = 8.4 Hz, 1H), 7.37 (t, J = 7.3, 2H), 7.45-7.51 (m, 3H), 7.59 (d, J = 7.6 Hz, 2H).

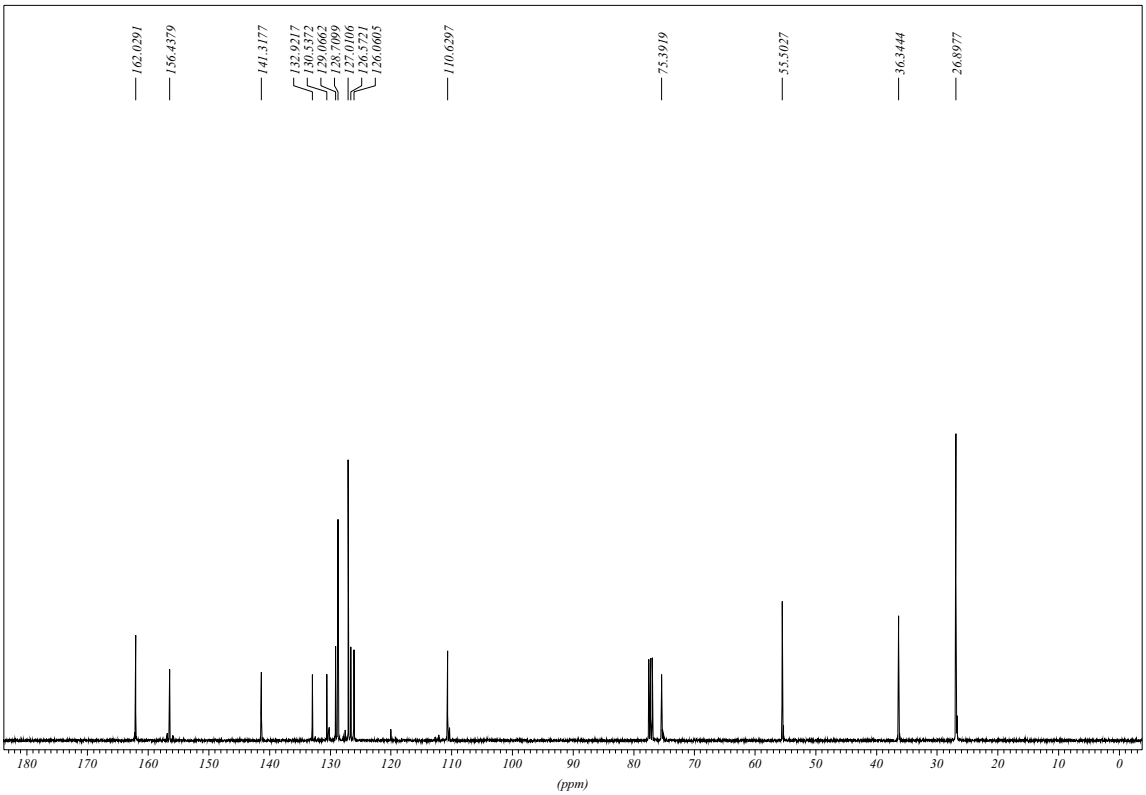


Compound 7. To a solution of **6** (2.1 g, 5.69 mmol) in water (1.4 mL) was added trifluoroacetic acid (25 mL), and the reaction mixture was stirred at room temperature for 4 h. The reaction mixture was neutralized with saturated sodium bicarbonate, the aqueous

layer extracted with ethyl acetate, and the combined organic layers were dried, filtered and concentrated in *vacuo* to give **7** (1.41 g, 92%), which was used without any further purification.

Compound 8. Aq. glyoxal (40%) (300 μL, 2.6 mmol) was introduced into dichloromthane (15 mL) and vigorously stirred with freshly dehydrated sodium sulfate (6.0 g). After the addition of formic acid (98%) (13 μL, 7 mol%) and **7** (1.4 g, 5.2 mmol), the mixture was allowed to stir for overnight at room temperature. The mixture was then filtered, and the solvent was removed *in vacuo*. The residue was purified by column chromatography to yield **8** (1.03g, 71%) as a pale-brown solid. $[\alpha]_D^{25}$ = +291.6 (*c* = 1.0 in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.01 (s, 18H), 3.85 (s, 6H), 4.68 (s, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 7.31 (t, *J* = 3.6 Hz, 2H), 7.39-7.43 (m, 6H), 7.56 (d, *J* = 7.1 Hz, 4H), 7.77 (d, *J* = 2.1 Hz, 2H), 8.07 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.9, 36.3, 55.5, 75.3, 110.6, 126.0, 126.5, 127.0, 128.7, 129.0, 130.5, 132.9, 141.3, 156.4, 162.0.

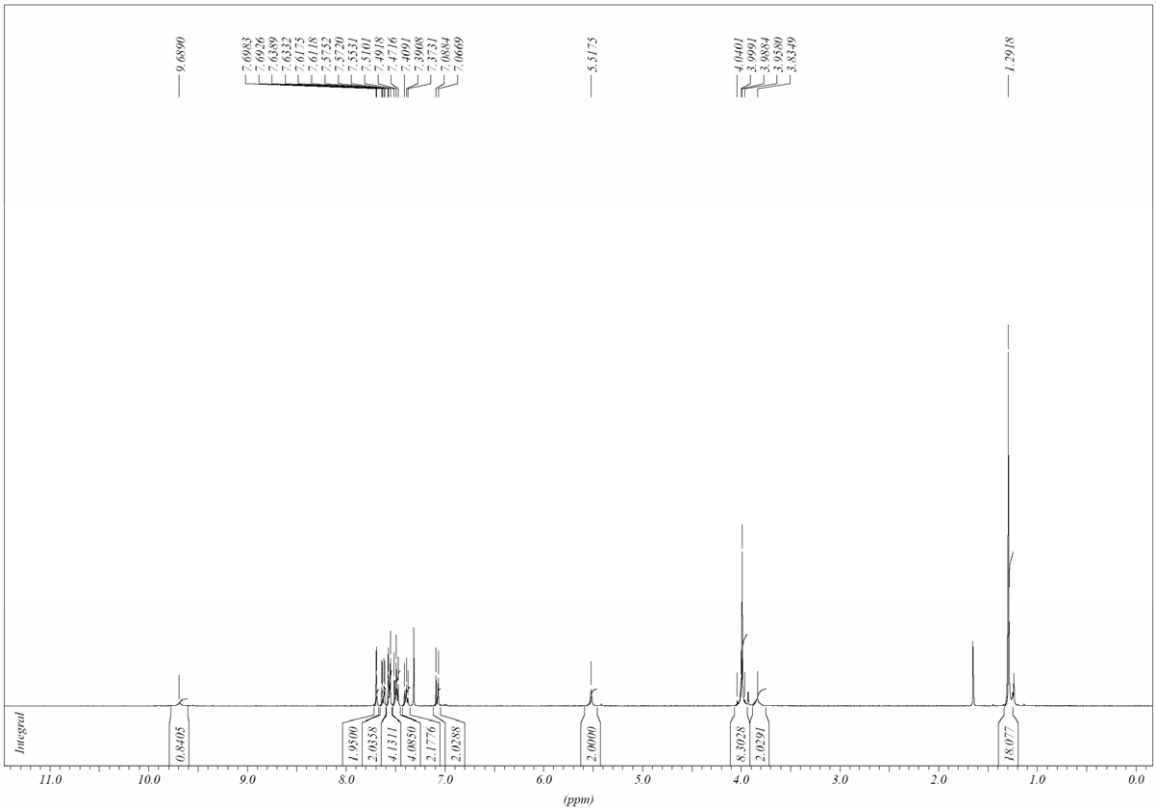


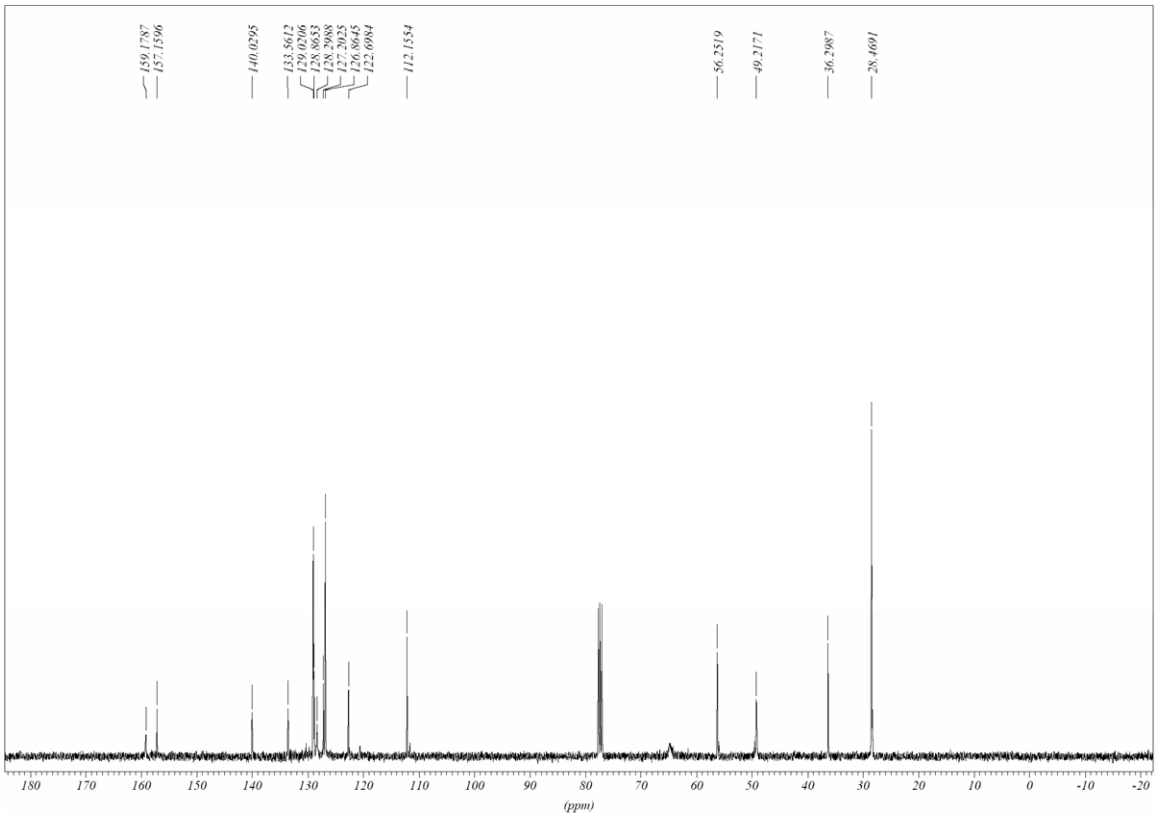


Carbene ligand precursor L3.

To a solution of **8** (340 mg, 0.61 mmol) in methanol (18 mL) was added $NaBH_4$ (461 mg, 12.1 mmol) at 0 ^oC. The reaction mixture was stirred overnight at room temperature. The mixture was then filtered through a short pad of silica gel, the pad washed with ether, and volatiles were removed *in vacuo* to give a pale-yellow oil (334 mg). This was taken up in $HC(OEt)_3$ (3mL), NH_4BF_4 (65 mg, 0.61 mmol) was added and the mixture was heated to 125 ^oC for 12 hours. The excess of $HC(OEt)_3$ was removed under vacuum. The residual oil was dissolved in 6 mL acetone and NaI (887 mg, 6.1 mmol) was added. After stirring overnight, acetone was removed in vacuo and the resultant solid was dissolved in CH_2Cl_2. The solution was filtered and washed with CH_2Cl_2. After removal of CH_2Cl_2, the residue was dissolved in 6 mL of acetone, treated with NaI (436 mg, 3 mmol) and stirred overnight. Solvent removal followed by flash chromatography (Ether/CH_2Cl_2 1/1) afforded **L3** (378 mg, 88%) as pale-yellow solid. $[\alpha]_D^{25}$ = +125.8 (*c* = 0.5 in acetone). ^1H NMR (400 MHz, $CDCl_3$): δ 1.29 (s, 18H), 3.83 (t,

J = 16.4 Hz, 2H), 3.98 (s, 6H), 3.99 (t, *J* = 16.4 Hz, 2H), 5.51 (s, 2H), 7.08 (d, *J* = 8.6 Hz, 2H), 7.39 (t, *J* = 7.1 Hz, 2H), 7.49 (t, *J* = 8.1 Hz, 4H), 7.56 (dd, *J* = 1.3, 7.6 Hz, 4H), 7.62 (dd, *J* = 2.3, 8.6 Hz, 2H), 7.69 (d, *J* = 2.3 Hz, 2H), 9.69 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.4, 36.2, 49.2, 56.2, 112.1, 122.6, 126.8, 127.2, 128.2, 128.8, 129.0, 133.5, 140.0, 157.1, 159.1. ν_{max}/cm^{-1}: 2961, 2186, 1620, 1542, 1509, 1486, 1462, 1400, 1369; HRMS: *m/z* (ESI+) calculated for $C_{39}H_{47}N_2O_2$ ($[M–I]^+$): 575.3632, found: 575.3652.

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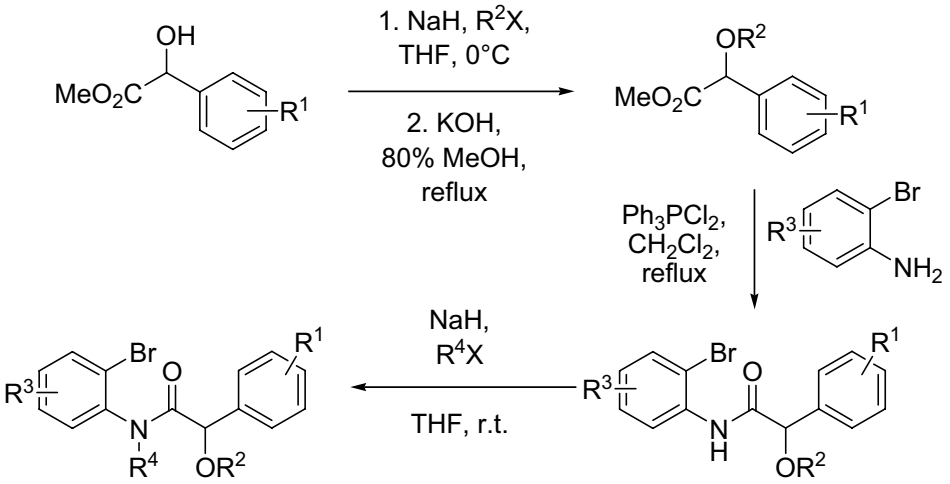
49.2171
36.2087
28.4691
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
(ppm)

2 Synthesis of the substrates:

Substrates **1a**, **1f**, **1g**, **1j** and **1k** were synthesized according to general procedure **A**. **1b-e**, **1h** and **1i** were synthesized according to general procedure **B**. **1l-o** were prepared as detailed in general procedure **C**.

General Procedure A:

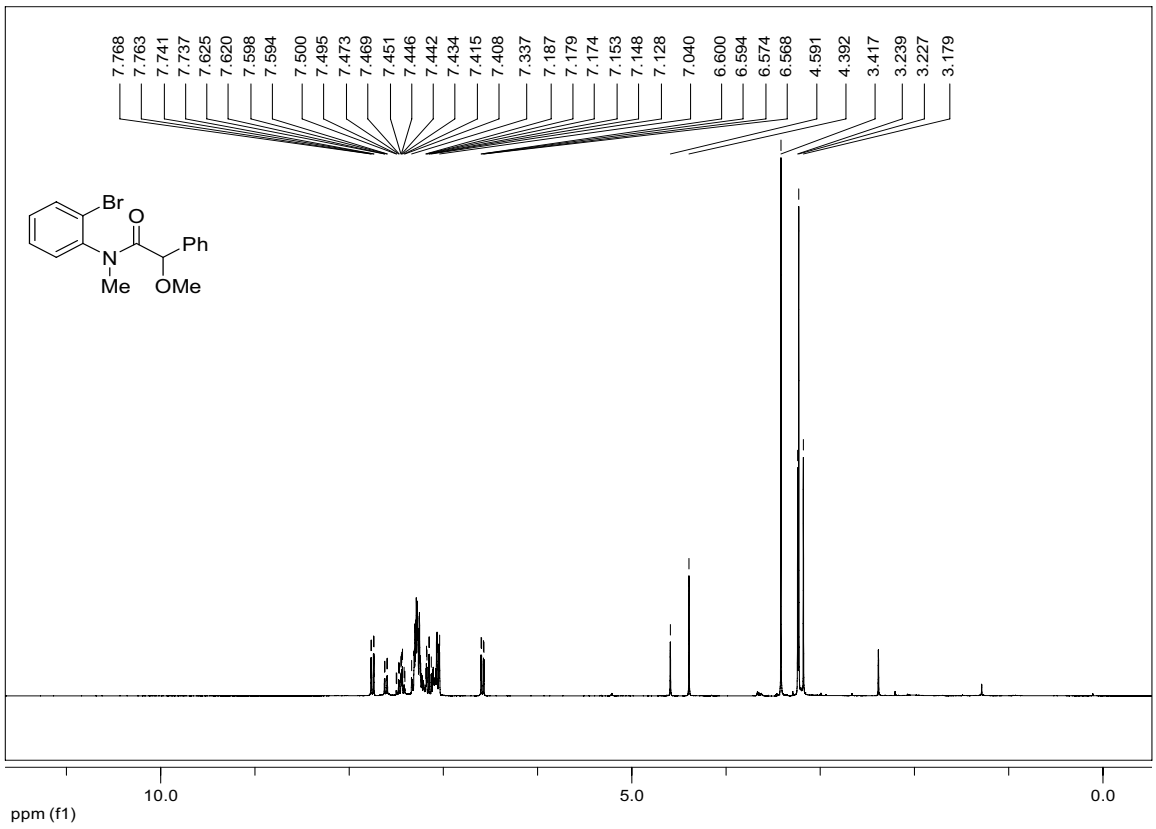


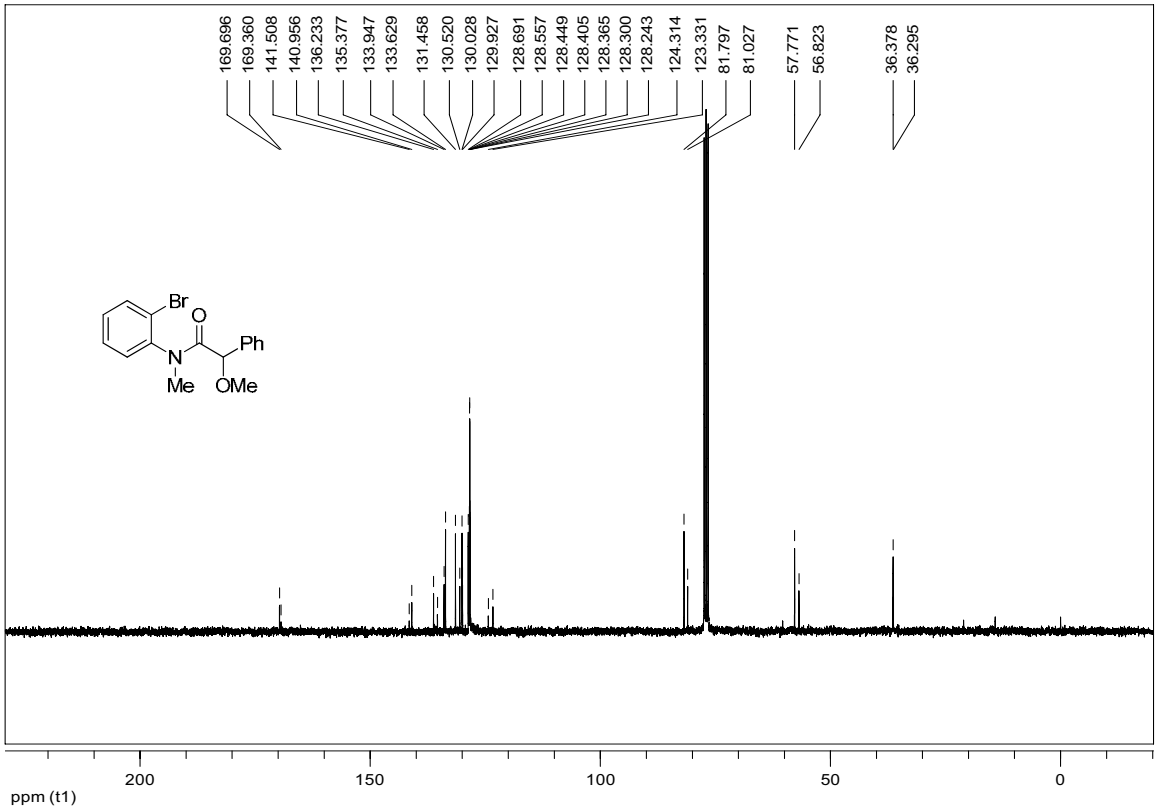
Individual details of the syntheses are not given. Commercial mandelic acids were protected as the methyl esters according to Carboni *et al.*[2] and subsequently *O*-alkylated and deprotected as described by Greenberg *et al* and Khumtaveeporn *et al.*[3] The anilide coupling was facilitated by the method of Azumaya *et al.*,[4] and the anilides *N*-methylated according to Hartwig and Lee.[5]

***N*-(2-Bromophenyl)-*N*-methyl-2-phenyl-2-methoxyacetamide (1a)**

^{1}H NMR (300 MHz, $CDCl_3$): δ 3.19 (s, 0.9H), 3.23 (s, 2.1H), 3.25 (s, 0.9H), 3.42 (s, 2.1H), 4.40 (s, 0.7H), 4.60 (s, 0.3H), 6.59 (dd, *J* = 1.7, 7.8 Hz, 0.7H), 7.05-7.12 (m, 2H), 7.16 (td, *J* = 1.5, 7.7 Hz, 0.7H), 7.19-7.34 (m, 4H), 7.43 (dd, *J* = 1.7, 7.8 Hz, 0.3H), 7.48 (td, *J* = 1.5, 7.7 Hz, 0.3H), 7.62 (dd, *J* = 1.4, 8.0 Hz, 0.3H), 7.76 (dd, *J* = 1.4, 8.0 Hz, 0.7H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 36.3, 36.4, 56.8, 57.8, 81.1, 81.8, 123.4, 124.3, 128.2, 128.30, 128.37, 128.41, 128.45, 128.56, 128.58, 128.7, 130.0, 130.1, 130.6, 131.5, 133.7, 134.0, 135.4, 136.3, 141.0, 141.5, 169.4, 169.7. ν_{max}/cm^{-1}: 2926, 1676, 1477,

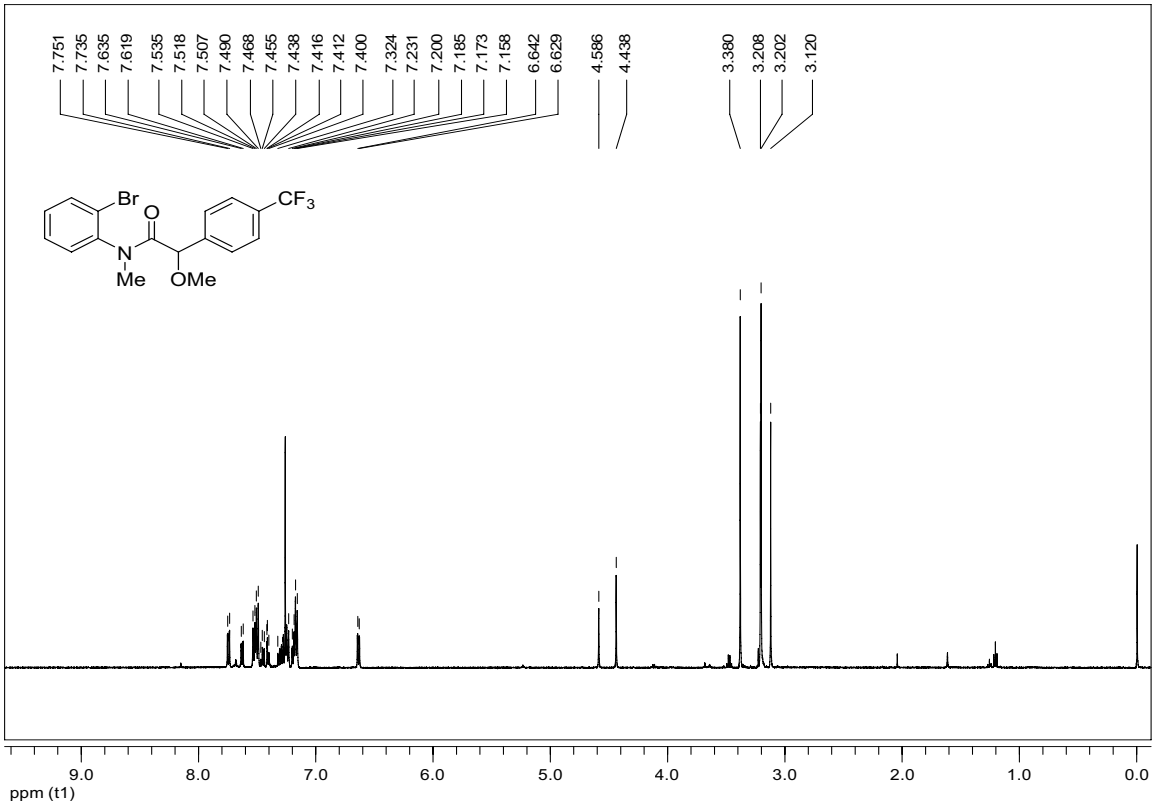
1454, 1379, 1103; HRMS: *m/z* (EI+) calculated for $C_{16}H_{16}{}^{81}BrNO_2Na$ ($[M(^{81}Br)+Na]^+$): 358.0237, Found: 358.0221.





_N_-(2-Bromophenyl)-_N_-methyl-2-methoxy-2-(4-trifluoromethylphenyl)acetamide (1f)

^{1}H NMR (300 MHz, $CDCl_3$): δ 3.13 (s, 0.9H), 3.21 (s, 2.1H), 3.21 (s, 0.9H), 3.39 (s, 2.1H), 4.44 (s, 0.7H), 4.59 (s, 0.3H), 6.64 (dd, *J* = 1.7, 7.8 Hz, 0.7H), 7.15-7.34 (m, 3.3H), 7.40-7.47 (m, 1H), 7.52 (t, *J* = 8.1 Hz, 2H), 7.63 (dd, *J* = 1.4, 8.0 Hz, 0.3H), 7.75 (dd, *J* = 1.4, 8.0 Hz, 0.7H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 36.6, 36.7, 57.5, 58.2, 80.7, 81.3, 123.6, 124.2, 124.3, 124.4, 125.5, 128.96, 129.05, 129.3, 130.7, 130.8, 130.9, 131.5, 134.27, 134.34, 140.9, 169.0, 169.4. ν_{max}/cm^{-1}: 3063, 2989, 2933, 2826, 1682, 1619, 1584, 1477, 1326, 1165, 1124; HRMS: *m/z* (EI−) calculated for $C_{17}H_{14}F_3BrNO_2$ ($[M-H]^-$): 400.0165, Found: 400.0179.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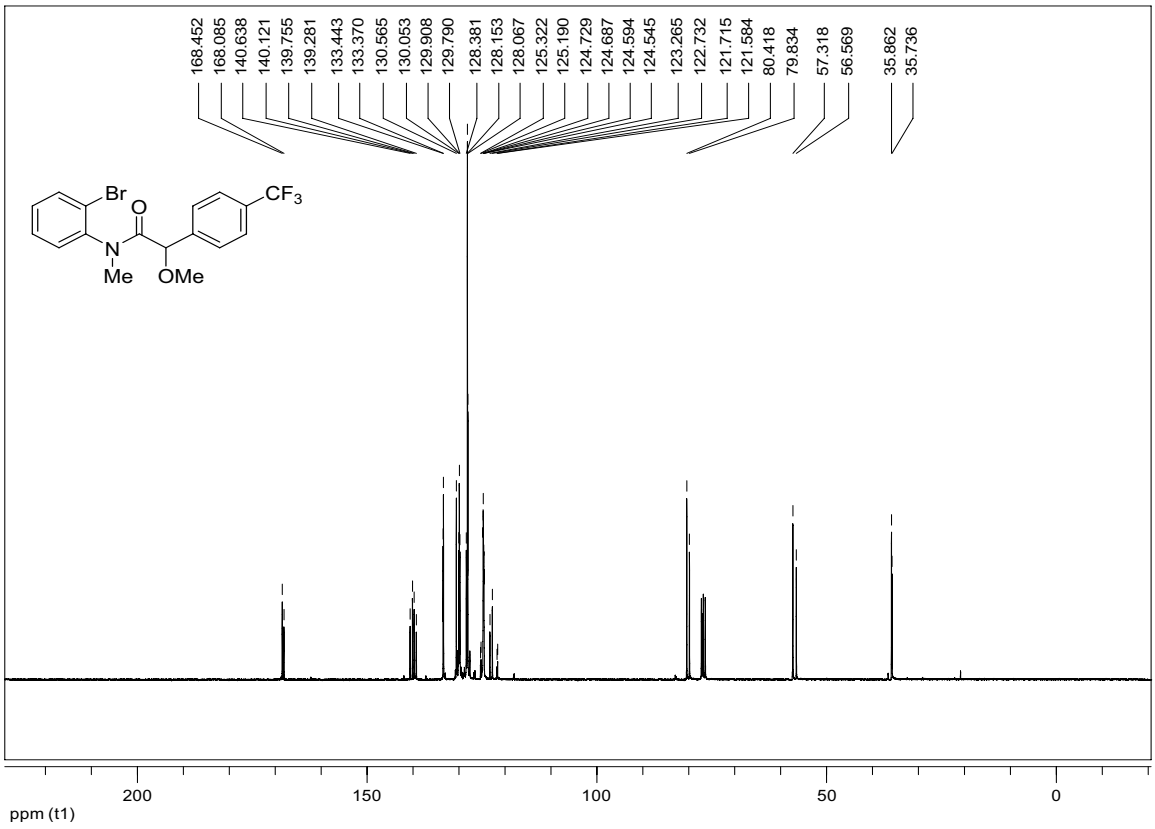
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150
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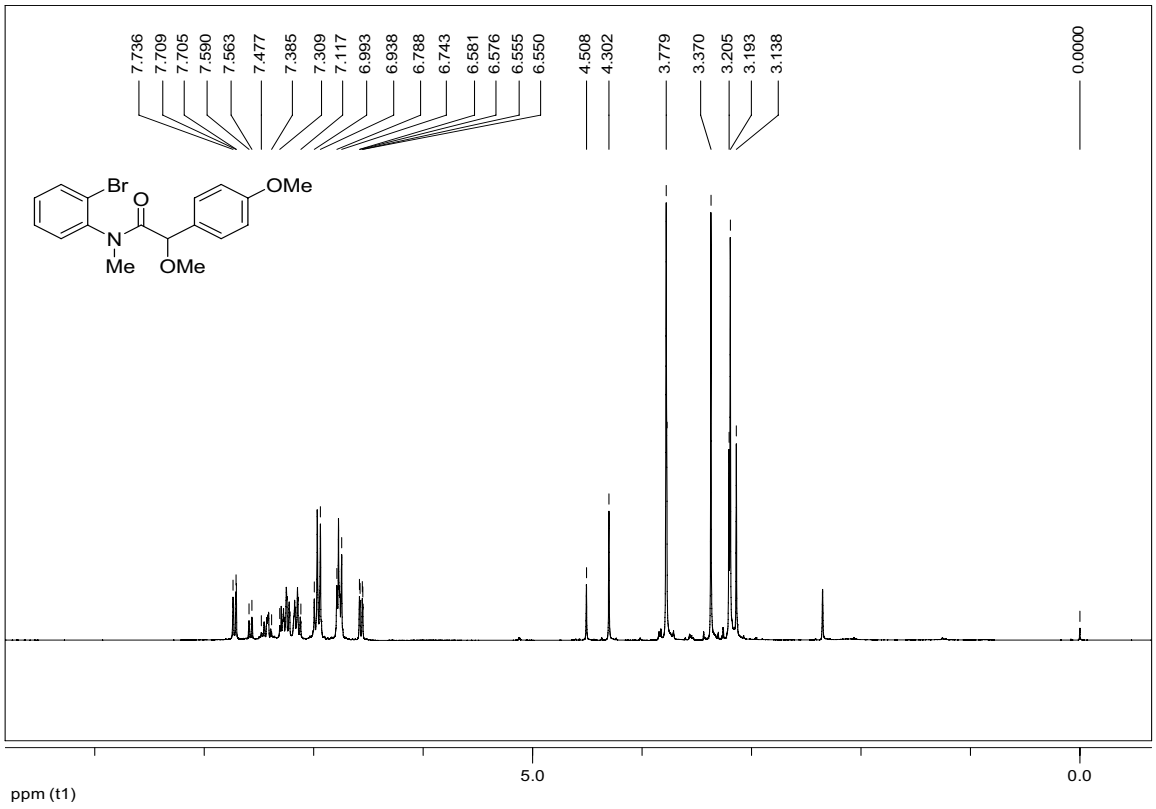
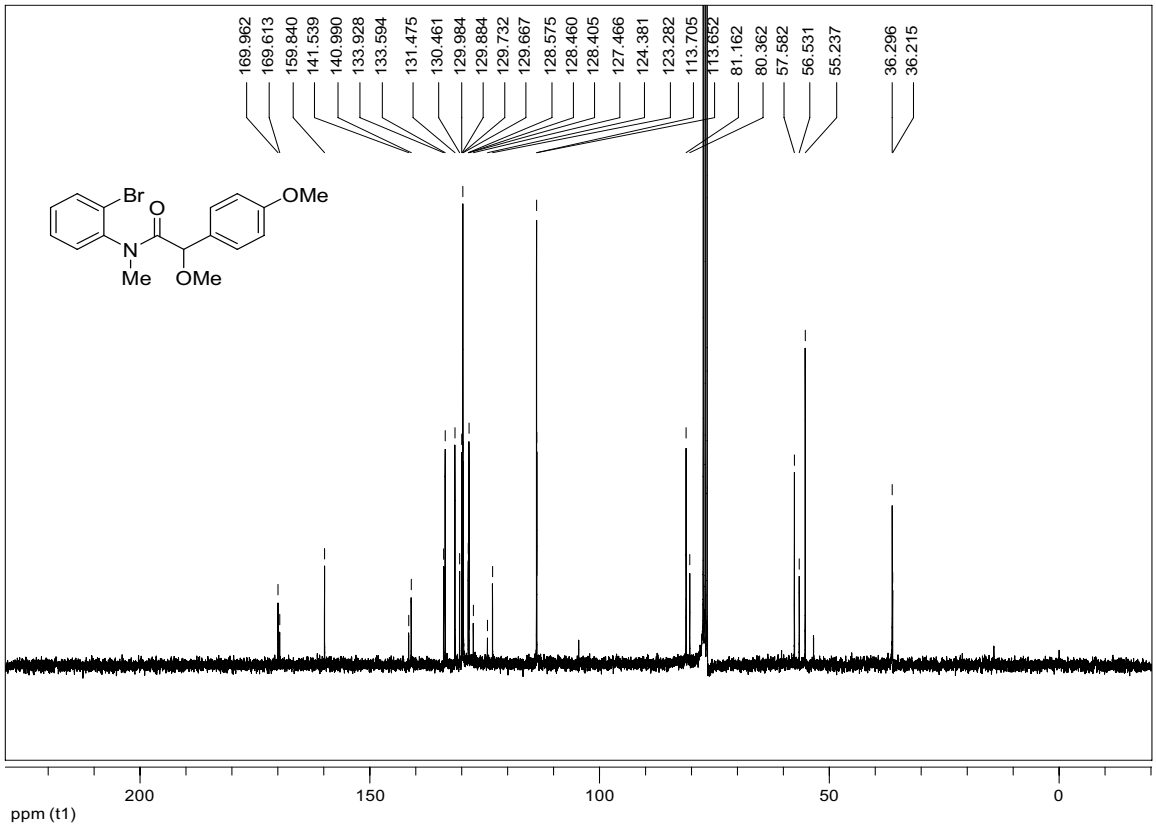
ppm (t1)

_N_-(2-Bromophenyl)-_N_-methyl-2-methoxy-2-(4-methoxyphenyl)acetamide (1g)

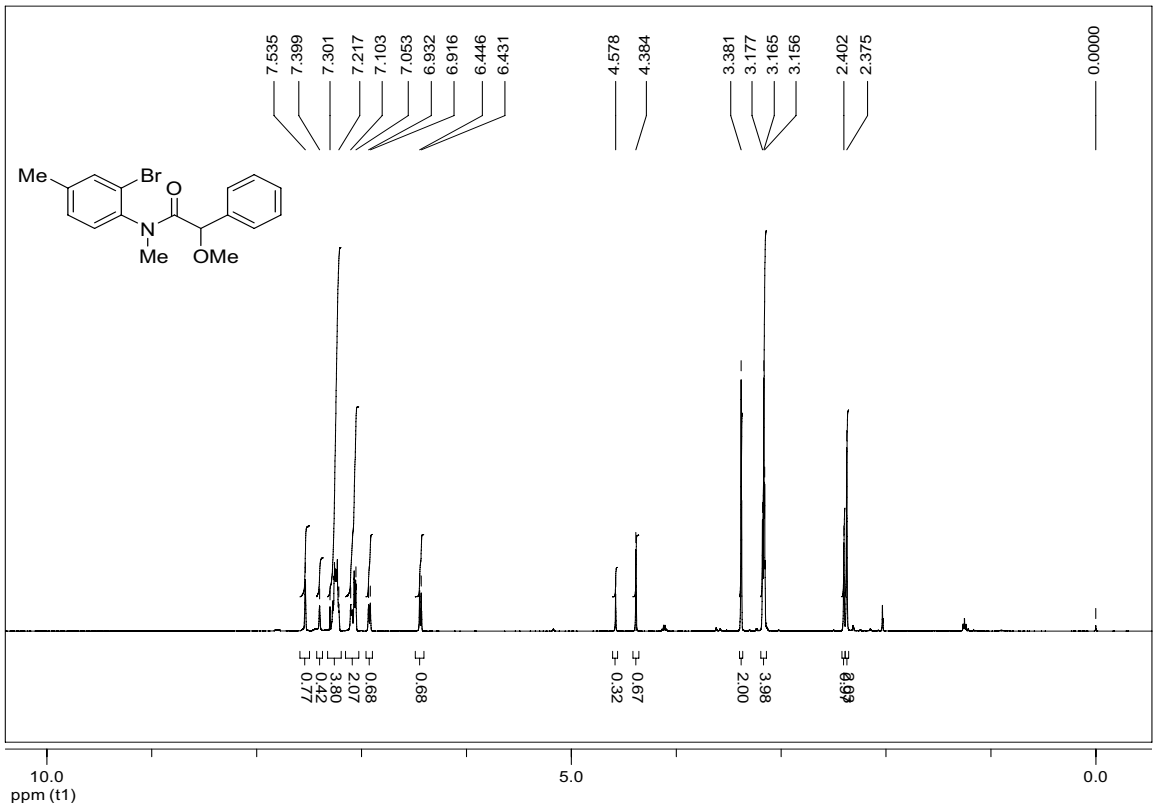
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.14 (s, 0.9H), 3.20 (s, 2.1H), 3.21 (s, 0.9H), 3.37 (s, 2.1H), 3.79 (s, 3H), 4.30 (s, 0.7H), 4.50 (s, 0.3H), 6.56 (dd, *J* = 1.3, 7.7 Hz, 0.7H), 6.74-6.79 (m, 2H), 6.94-6.99 (m, 2H), 7.12-7.31 (m, 1.6H), 7.41 (t, *J* = 8.5 Hz, 0.7H), 7.58 (d, *J* = 8.0 Hz, 0.3H), 7.72 (d, *J* = 8.0 Hz, 0.7H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 36.2, 36.3, 55.3, 56.6, 57.6, 80.4, 81.2, 113.7, 113.8, 123.3, 124.4, 127.5, 128.4, 128.5, 128.6, 129.7, 129.9,130.0, 130.5, 131.5, 133.6, 134.0, 141.0, 141.6, 159.9, 169.7, 170.0. ν_{max}/cm^{-1}: 3061, 2934, 2835, 1675, 1512, 1476; HRMS: *m/z* (EI+) calculated for $C_{17}H_{18}Br\,NO_3Na$ ($[M+Na]^+$): 386.0362, found: 386.0365.





_N_-(2-Bromo-4-methylphenyl)-_N_-methyl-2-methoxy-2-phenylacetamide (1j)

^{1}H NMR (300 MHz, $CDCl_3$): δ 2.38 (s, 1.8H), 2.41 (s, 1.2H), 3.16 (s, 1.2H), 3.17 (s, 1.8H), 3.18 (s, 1.2H), 3.39 (s, 1.8H), 4.42 (s, 0.6H), 4.57 (s, 0.4H), 6.44 (d, J = 8.0 Hz, 0.6H), 6.92 (dd, J = 1.8, 8.0 Hz, 0.6H), 7.04-7.10 (m, 1.8H), 7.21-7.29 (m, 4H), 7.40 (s, 0.4H), 7.54 (s, 0.6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.3, 36.8, 36.9, 57.2, 58.2, 81.2, 82.0, 123.2, 124.2, 128.6, 128.8, 128.9, 128.9, 129.1, 129.6, 129.8, 130.4, 131.3, 134.4, 134.7, 135.9, 136.7, 138.6, 139.2, 140.9, 141.0, 170.0, 170.4. ν_{max}/cm^{-1}: 3060, 3030, 2978, 2924, 2822, 1675, 1494; HRMS: *m/z* (EI+) calculated for $C_{17}H_{18}BrNO_2Na$ ($[M+Na]^+$): 370.0413, found: 370.0402.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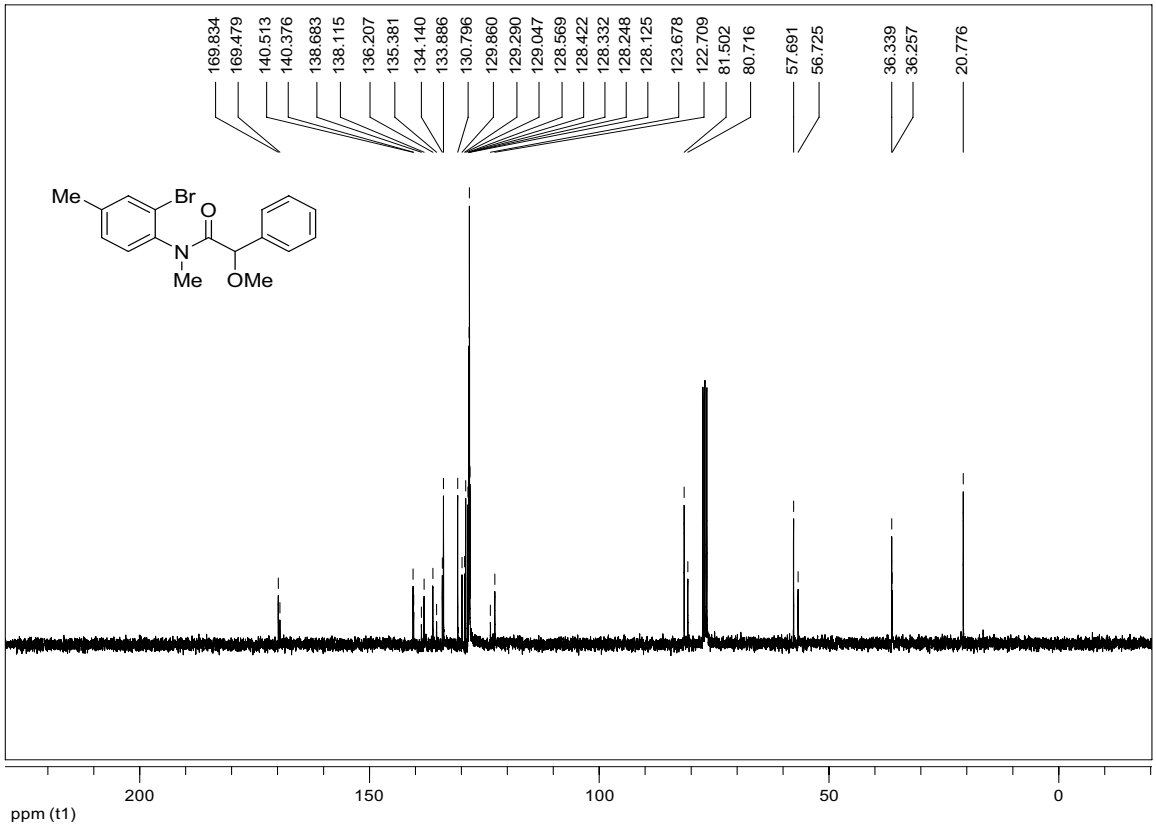
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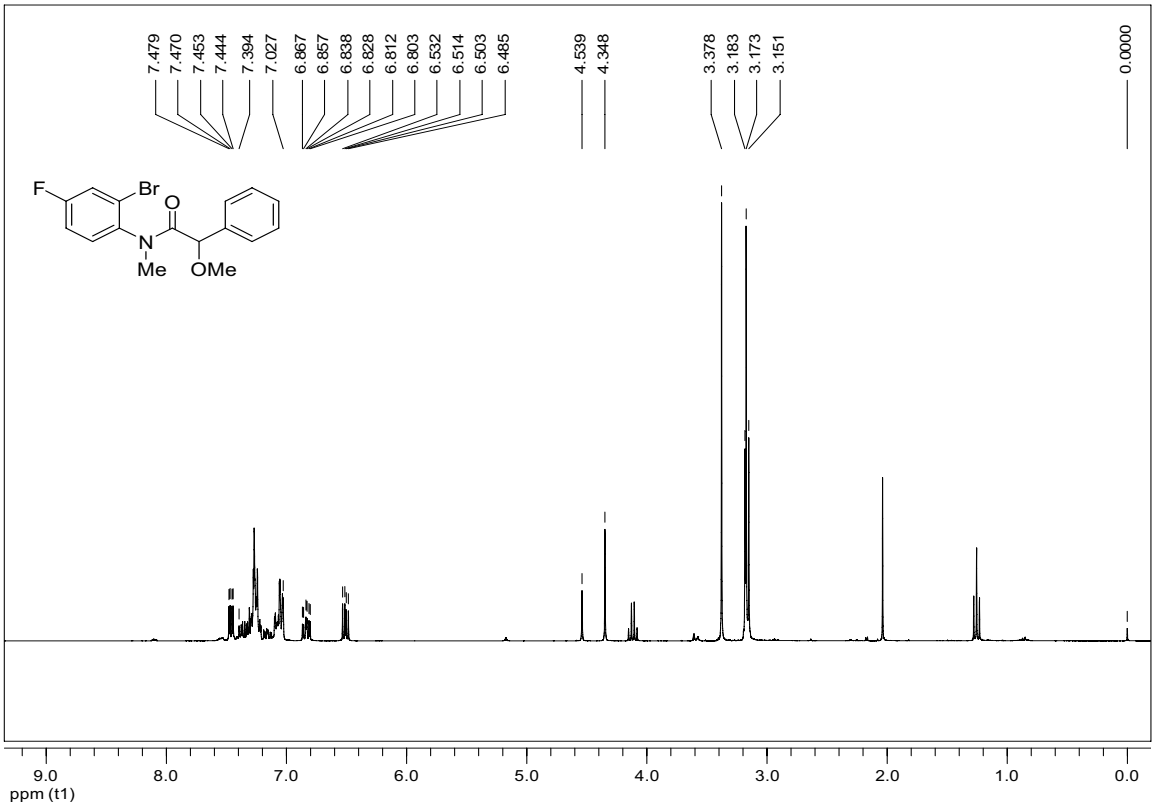
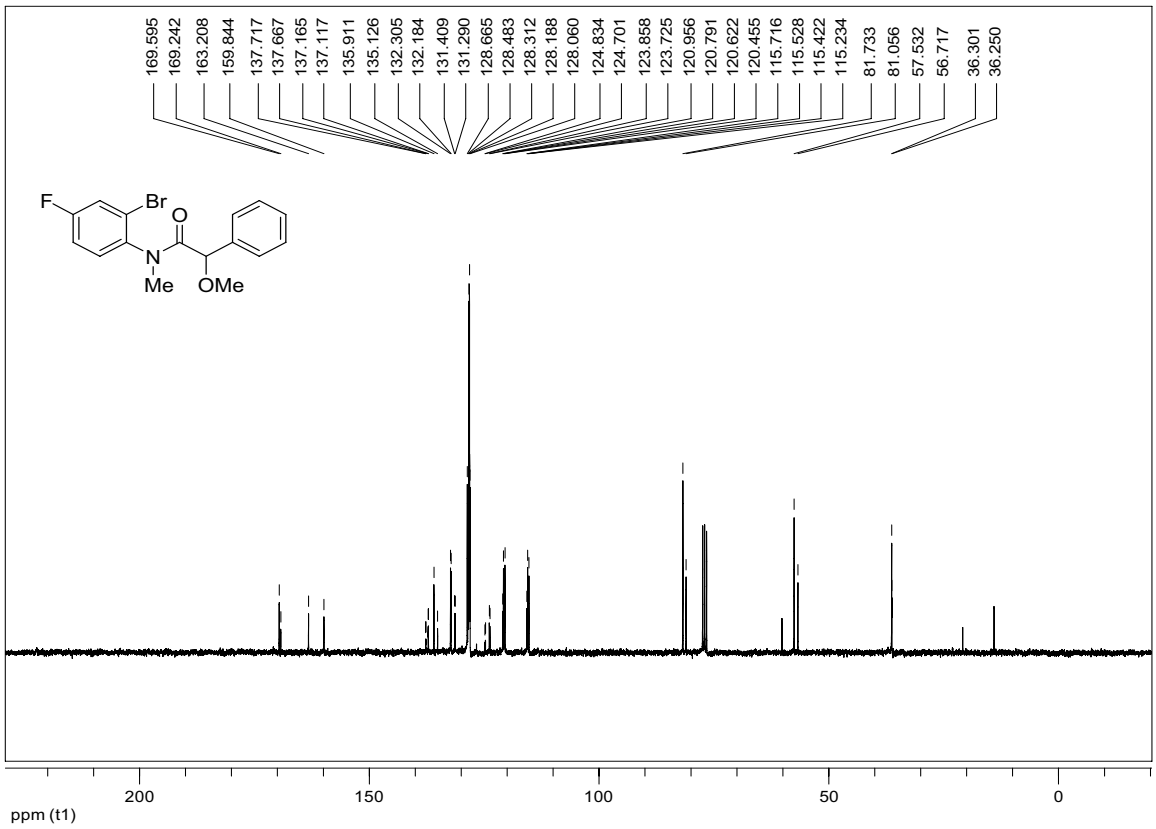
Br
O
N
Me
OMe
200
150
100
50
0
ppm (t1)

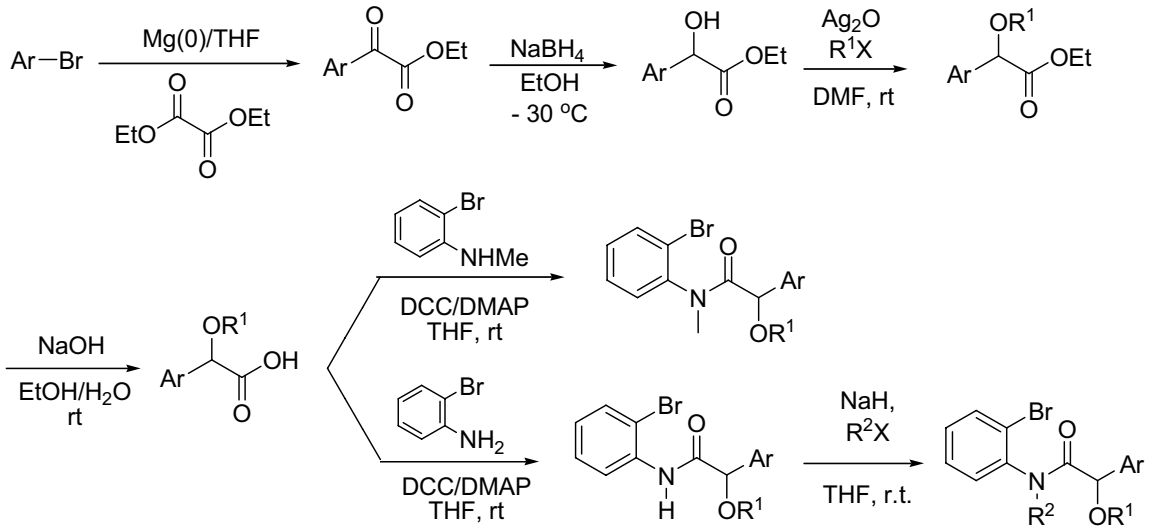
_N_-(2-Bromo-4-fluorophenyl)-_N_-methyl-2-methoxy-2-phenylacetamide (1k)

^{1}H NMR (300 MHz, $CDCl_3$): δ 3.15 (s, 1.2H), 3.18 (s, 1.8H), 3.19 (s, 1.2H), 3.39 (s, 1.8H), 4.34 (s, 0.6H), 4.53 (s, 0.4 H), 6.50 (dd, J = 5.5, 8.8 Hz, 0.6H), 6.83 (ddd, J = 2.8, 7.7, 8.8 Hz, 0.6H), 7.02-7.39 (m, 6.2H), 7.46 (dd, J = 2.8, 7.7 Hz, 0.6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 36.9, 36.9, 57.3, 58.2, 81.6, 82.3, 116.0, 116.2, 121.2, 121.4, 124.4, 128.7, 128.8, 128.9, 129.3, 131.9, 132.8, 135.6, 136.4, 137.7, 162.1, 169.9, 170.2. ν_{max}/cm^{-1}: 3064, 2934, 2825, 1735, 1681, 1594, 1489; HRMS: *m/z* (EI+) calculated for $C_{16}H_{15}BrFNO_2Na$ ($[M+Na]^+$): 374.0173, found: 374.0160.




169.595
169.242
163.208
159.844
137.717
137.667
137.165
137.117
135.911
135.126
132.305
132.184
131.409
131.290
128.665
128.483
128.312
128.188
128.060
124.834
124.701
123.858
123.725
120.956
120.791
120.622
120.455
115.716
115.528
115.422
115.234
81.733
81.056
57.532
56.717
36.301
36.250
F
Br
O
N
Me
OMe
200
150
100
50
0
ppm (t1)

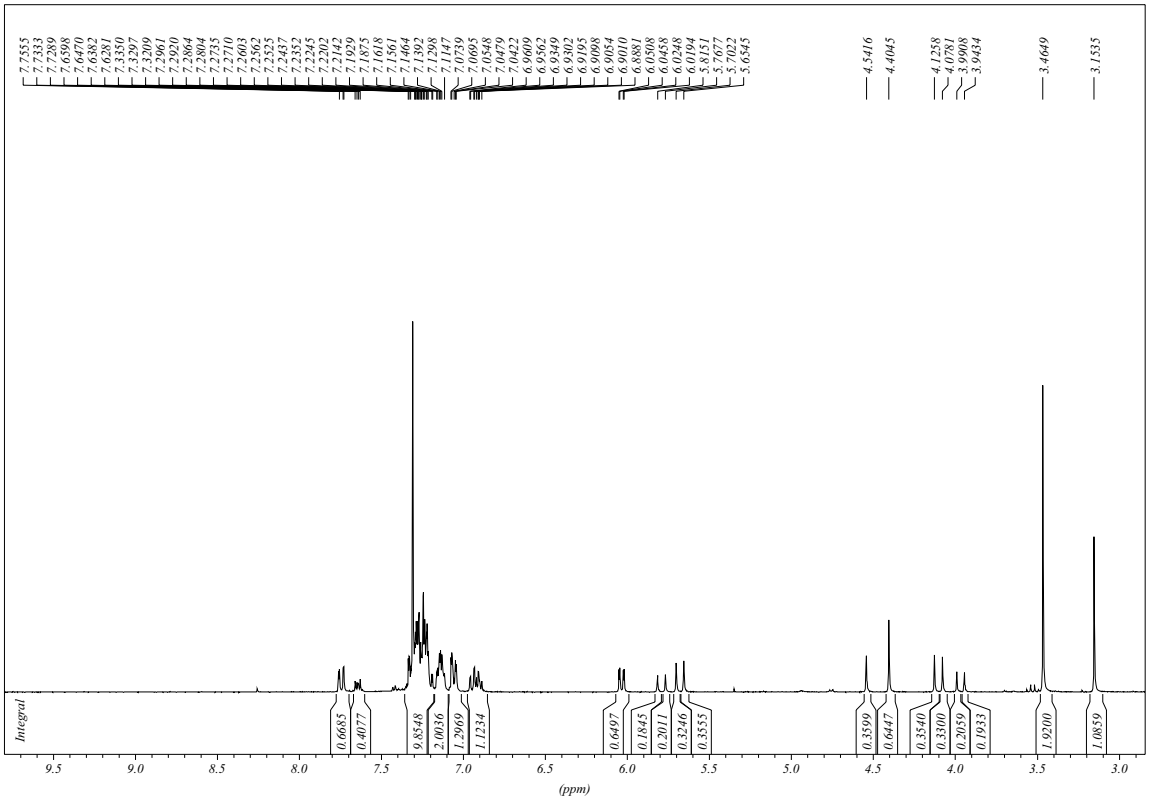
General Procedure B:

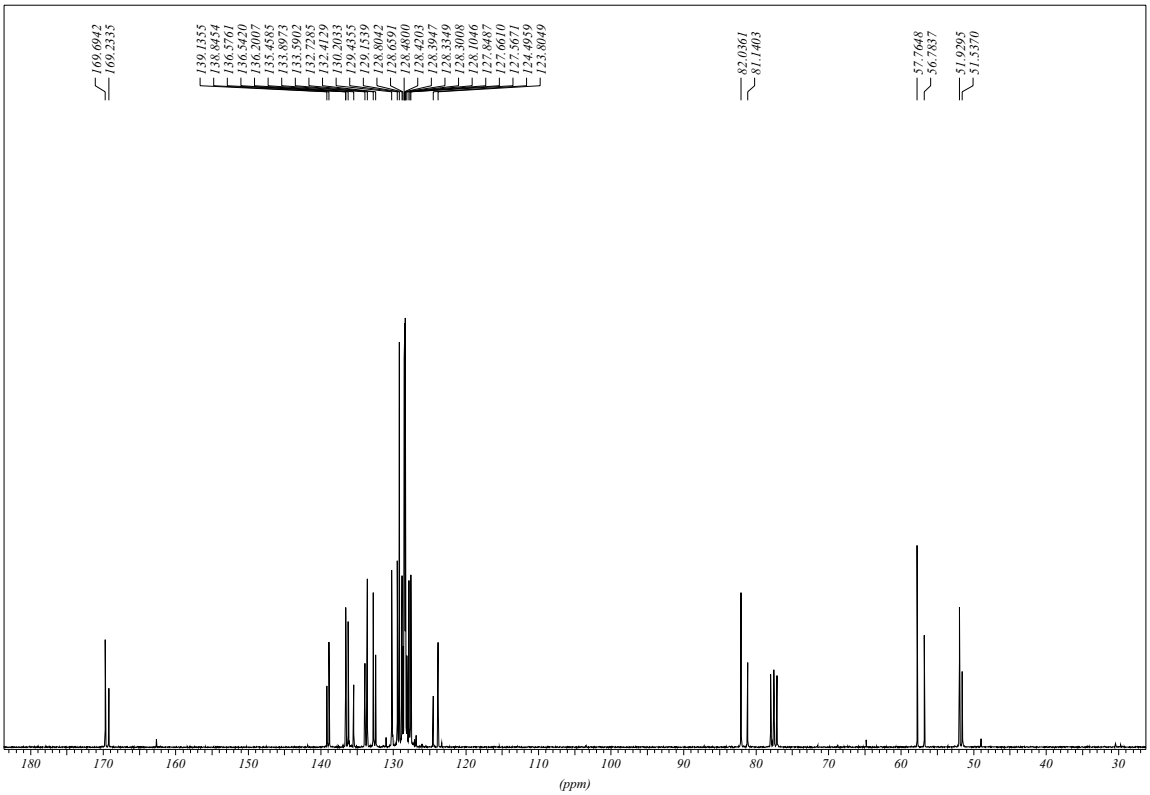


Individual details of the syntheses are not given. Aryl α-ketoester were prepared from commercial arylbromides and reduced to mandelic acids according to Saito *et al*.[6] Condensation reaction to amides were carried out according to Suna.[7] *N*-alkylated amides were prepared according to Hartwig and Lee.[5]

***N*-benzyl-*N*-(2-bromophenyl)-2-methoxy-2-phenylacetamide (1b)**

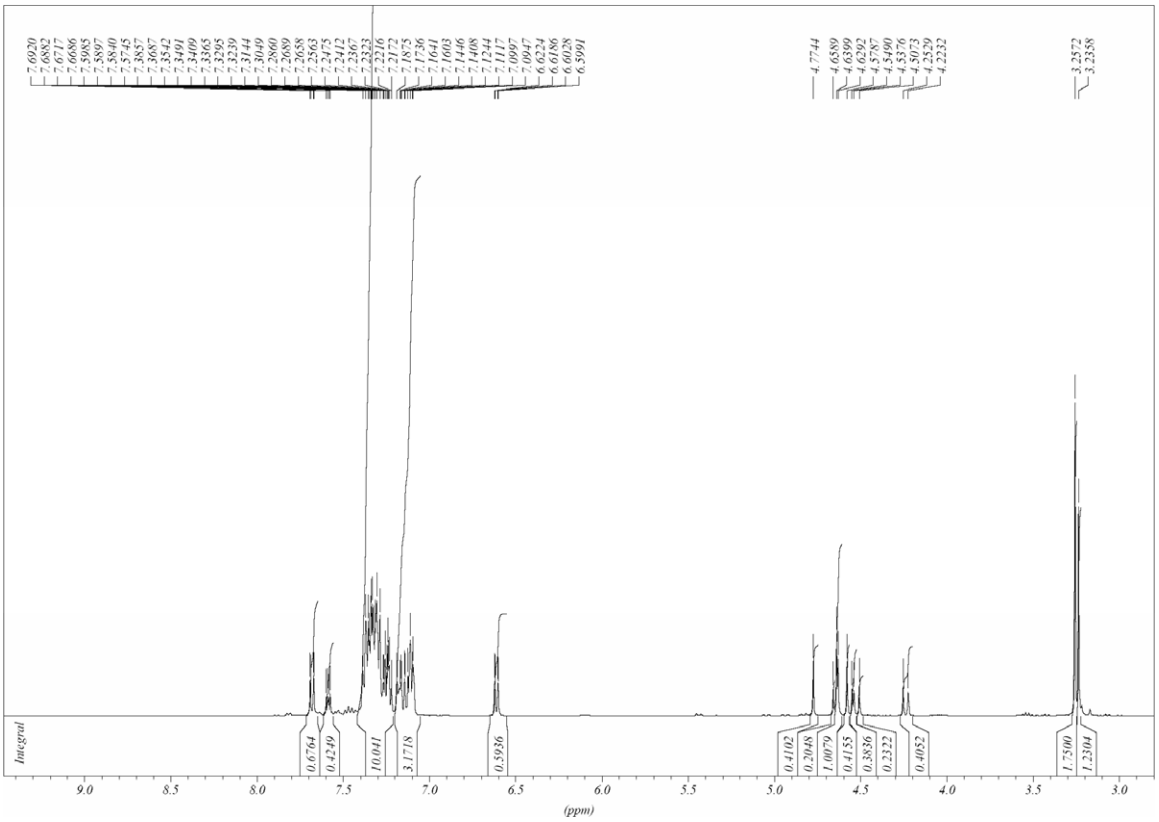
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.15 (s, 1.1H), 3.46 (s, 1.9H), 3.94 (s, 0.2H), 3.99 (s, 0.2H), 4.07 (s, 0.3H), 4.12 (s, 0.3H), 4.40 (s, 0.6H), 4.54 (s, 0.4H), 5.65 (s, 0.3H), 5.70 (s, 0.3H), 5.76 (s, 0.2H), 5.81 (s, 0.2H), 6.03 (dd, *J* = 1.5, 7.8 Hz, 0.7H), 6.88-6.96 (m, 1.1H), 7.04-7.07 (m, 1.3H), 7.11-7.16 (m, 2H), 7.18-7.33 (m, 9.9H), 7.62-7.65 (m, 0.4H), 7.74 (dd, *J* = 1.3, 8.0 Hz, 0.6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 51.5, 51.9, 56.7, 57.7, 81.1, 82.0, 123.8, 124.4, 127.5, 127.6, 127.8, 128.1, 128.30, 128.33, 128.39, 128.42, 128.48, 128.6, 128.8, 129.1, 129.4, 130.2, 132.4, 132.7, 133.5, 133.8, 135.4, 136.2, 136.54, 136.57, 138.8, 139.1, 169.2, 169.6. ν_{max}/cm^{-1}: 3031, 2928, 2825, 1676, 1584, 1495, 1474, 1455; HRMS: *m/z* (ESI+) calculated for $C_{22}H_{21}BrNO_2$ ($[M+H]^+$): 410.0750, found: 410.0750.

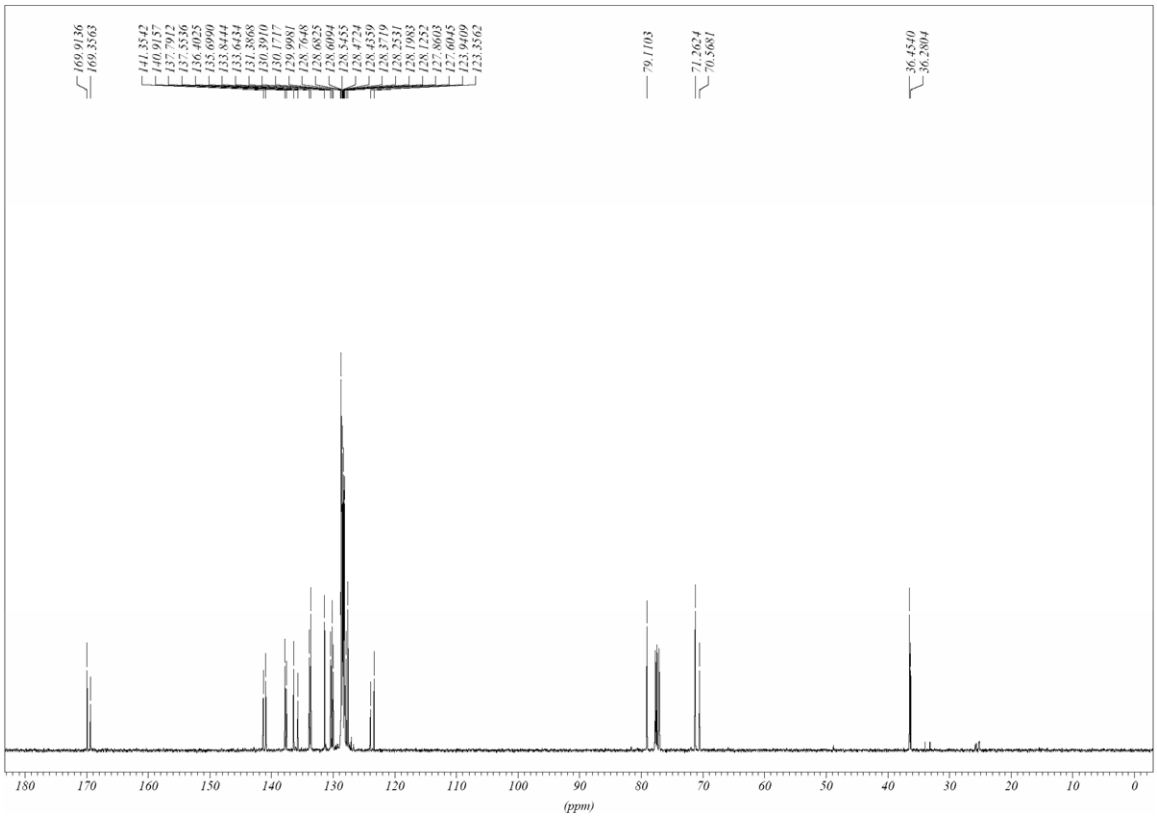

7.7555
7.7333
7.7289
7.6598
7.6470
7.6382
7.6281
7.3350
7.3297
7.3209
7.2961
7.2920
7.2864
7.2804
7.2715
7.2710
7.2603
7.2562
7.2525
7.2437
7.2352
7.2245
7.2202
7.2142
7.1929
7.1875
7.1618
7.1561
7.1464
7.1392
7.1298
7.1147
7.0739
7.0695
7.0548
7.0479
7.0422
6.9609
6.9562
6.9349
6.9302
6.9195
6.9098
6.9054
6.9010
6.8881
6.0508
6.0458
6.0348
6.0294
5.8151
5.7671
5.7022
5.6545
4.5416
4.4045
4.1258
4.0781
3.9908
3.9434
3.4649
3.1535
Integral
0.6685
0.4077
9.8548
2.0036
1.2969
1.1234
0.6497
0.1845
0.2011
0.3246
0.3555
0.3599
0.6447
0.3540
0.3300
0.2059
0.1933
1.9200
1.0859
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
(ppm)


169.6942
169.2335
139.1355
138.8454
136.5761
136.5420
136.2007
135.4585
133.8973
133.5902
132.7285
132.4129
130.2033
129.4355
129.1539
128.8042
128.6591
128.4800
128.4203
128.3947
128.3349
128.3008
128.1046
127.8487
127.6610
127.5671
124.4959
123.8049
82.0361
81.1403
57.7648
56.7837
51.9295
51.5570
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
(ppm)

2-(Benzyloxy)-*N*-(2-bromophenyl)-*N*-methyl-2-phenylacetamide (1c)

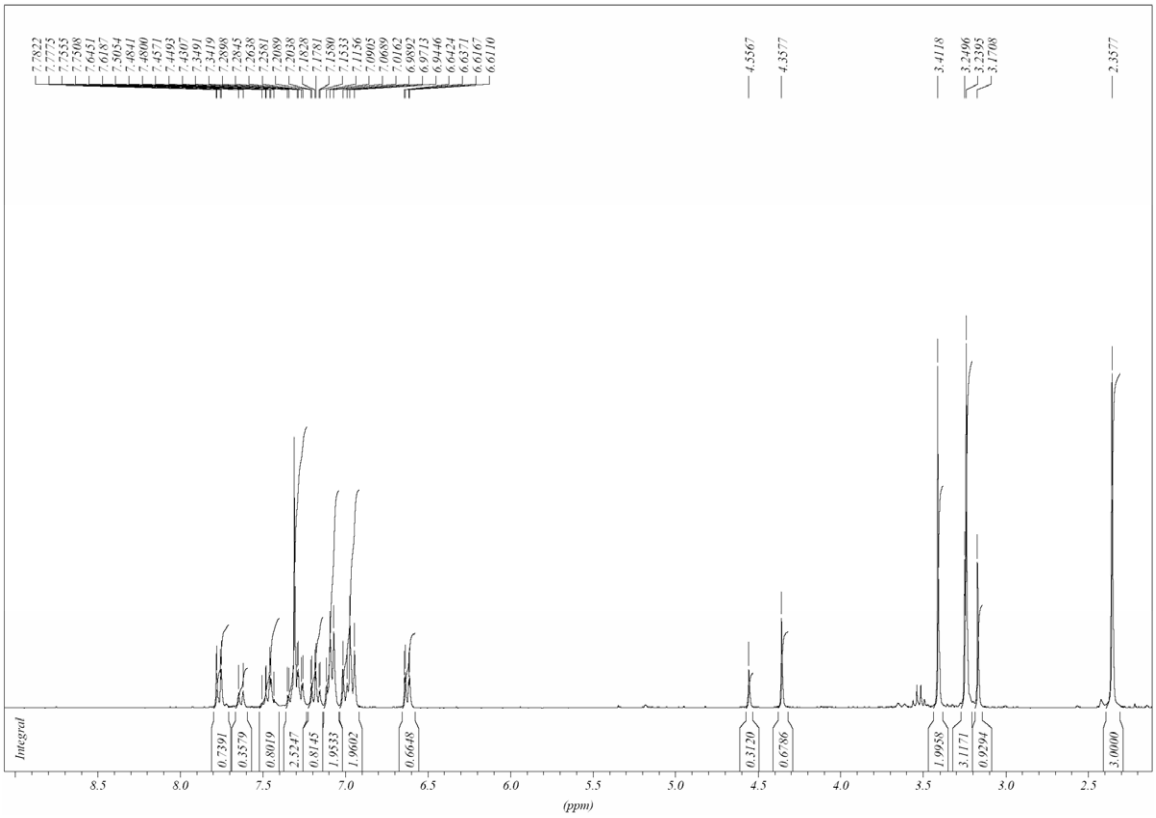
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.23 (s, 1.2H), 3.25 (s, 1.8H), 4.22 (s, 0.2H), 4.25 (s, 0.2H), 4.50 (s, 0.2H), 4.53 (s, 0.2H), 4.54 (s, 0.2H), 4.57 (s, 0.4H), 4.62 (s, 0.4H), 4.64 (s, 0.6H), 4.65 (s, 0.2H), 4.77 (s, 0.4H), 6.61 (dd, *J* = 1.5, 7.8 Hz, 0.6H), 7.09-7.18 (m, 3.2H), 7.21-7.39 (m, 10H), 7.58-7.33 (dd, *J* = 3.6, 5.8 Hz, 0.4H), 7.68 (dd, *J* = 1.5, 8.1 Hz, 0.7H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 36.2, 36.4, 70.5, 71.2, 79.1, 123.3, 123.9, 127.6, 127.8, 128.12, 128.19, 128.2, 128.3, 128,43, 128.47, 128.5, 128.60, 128.68, 128.7, 129.9, 130.1, 130.3, 131.3, 133.6, 133.8, 135.6, 136.4, 137.5, 137.7, 140.9, 141.3, 169.3, 169.9. ν_{max}/cm^{-1}: 3030, 2930, 1675, 1584, 1476, 1454; HRMS: *m/z* (ESI+) calculated for $C_{22}H_{21}BrNO_2$ ($[M+H]^+$): 410.0750, found: 410.0736.

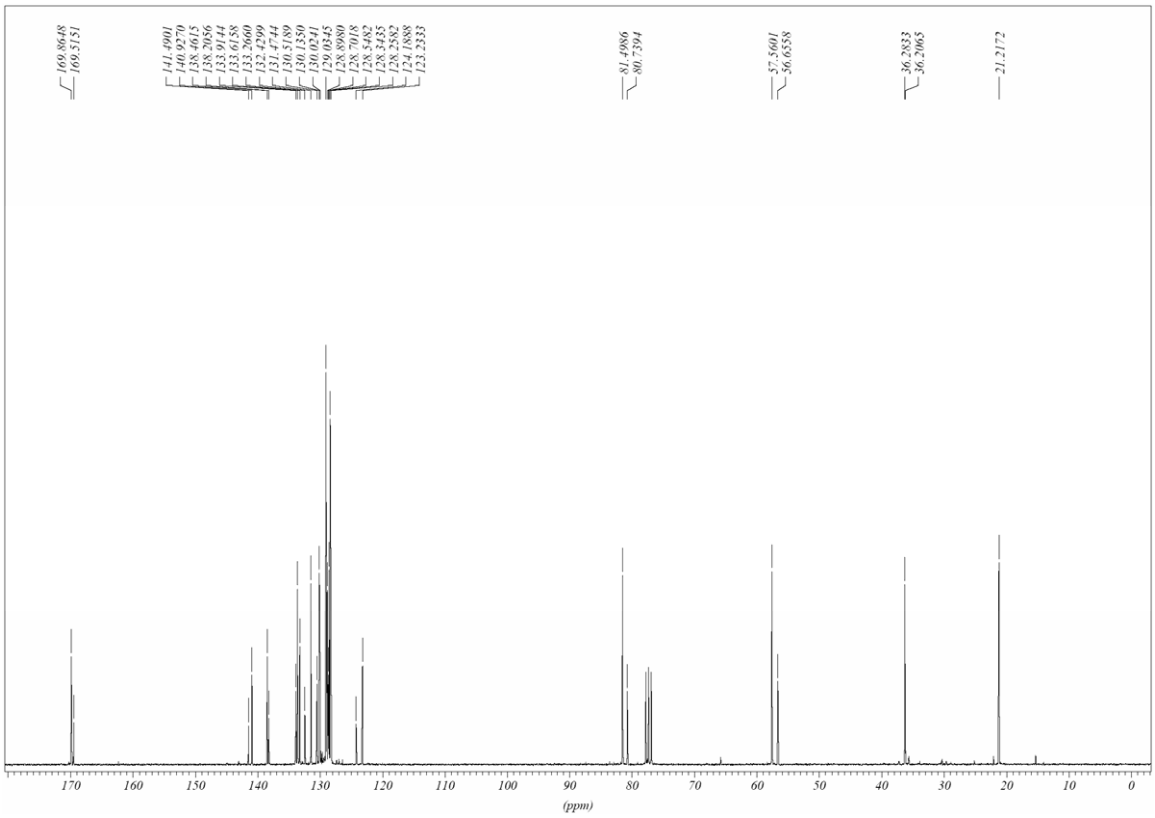




***N*-(2-bromophenyl)-2-methoxy-*N*-methyl-2-p-tolylacetamide (1d)**

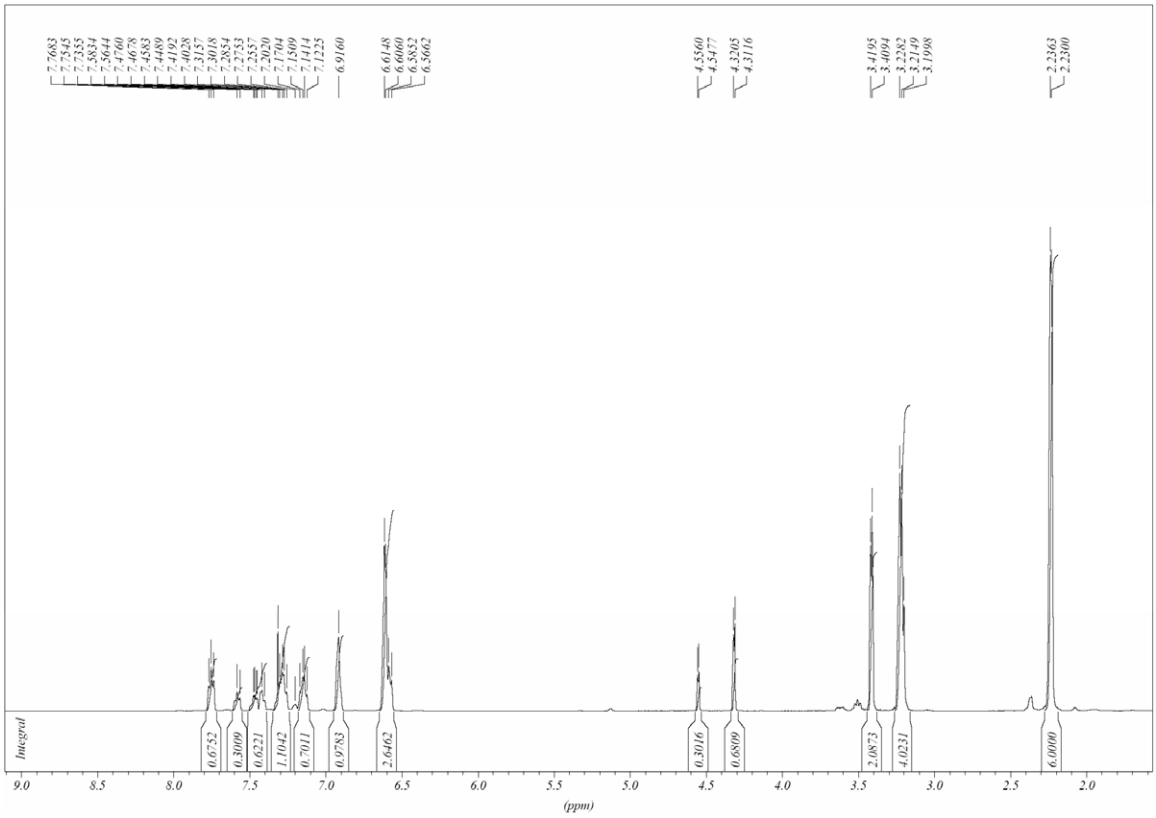
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.35 (s, 3H), 3.17 (s, 0.9H), 3.24 (s, 2.1H), 3.25 (s, 1H), 3.41 (s, 2H), 4.35 (s, 0.7H), 4.55 (s, 0.3H), 6.63 (dd, *J* = 1.7, 7.8 Hz, 0.7H), 6.94-7.02 (m, 2H), 7.09 (t, *J* = 6.6 Hz, 2H), 7.18 (dt, *J* = 1.5, 7.8 Hz, 0.8H), 7.25-7.35 (m, 0.8H), 7.43-7.51 (m, 0.8H), 7.63 (d, *J* = 7.9 Hz, 0.4H), 7.77 (dd, *J* = 1.4, 8.0 Hz, 0.7H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.2, 36.20, 36.28, 56.6, 57.5, 80.7, 81.4, 123.2, 124.1, 128.2, 128.3, 128.5, 128.7, 128.8, 129.0, 130.0, 130.1, 130.5, 131.4, 132.4, 133.2, 133.6, 133.9, 138.2, 138.4, 140.9, 141.4, 169.5, 169.8. ν_{max}/cm^{-1}: 2923, 1676, 1584, 1514, 1476; HRMS: *m/z* (ESI+) calculated for $C_{17}H_{19}BrNO_2$ ($[M+H]^+$): 348.0593, found: 348.0587.

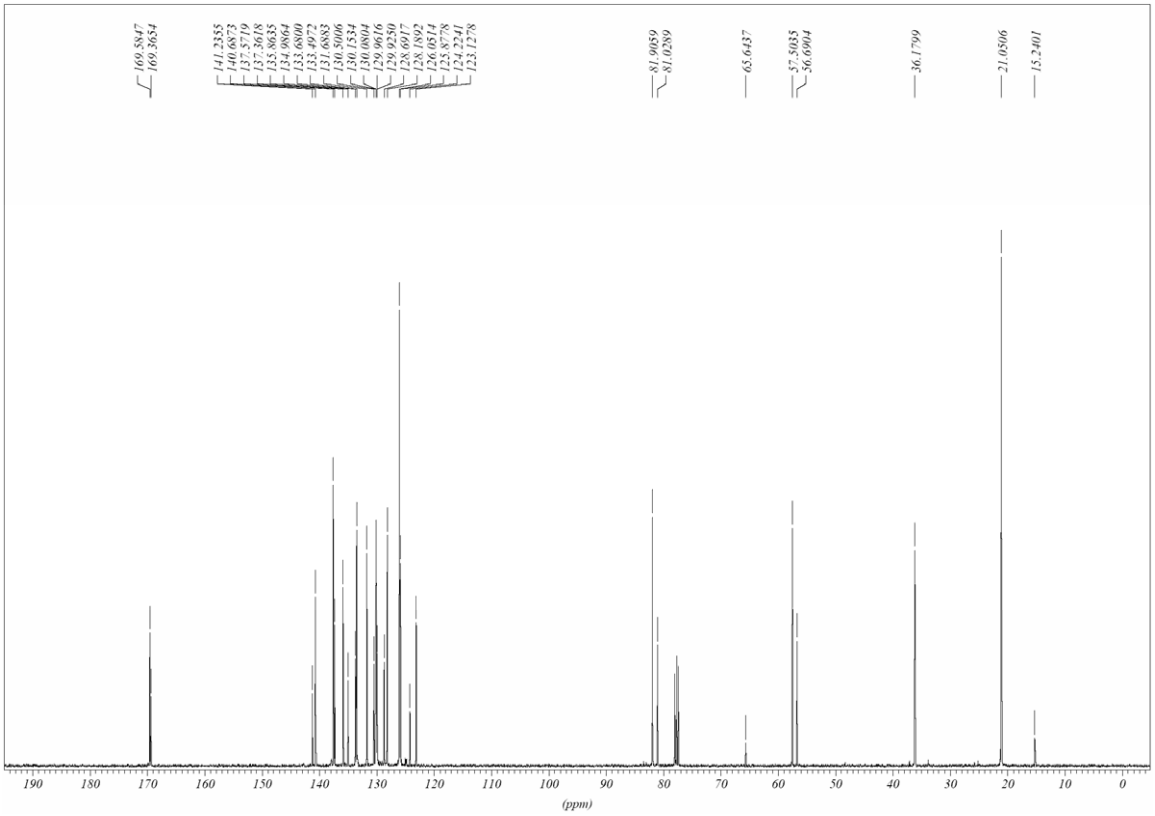




N-(2-bromophenyl)-2-methoxy-N-methyl-2-(3,5-dimethylphenyl)acetamide (1e)

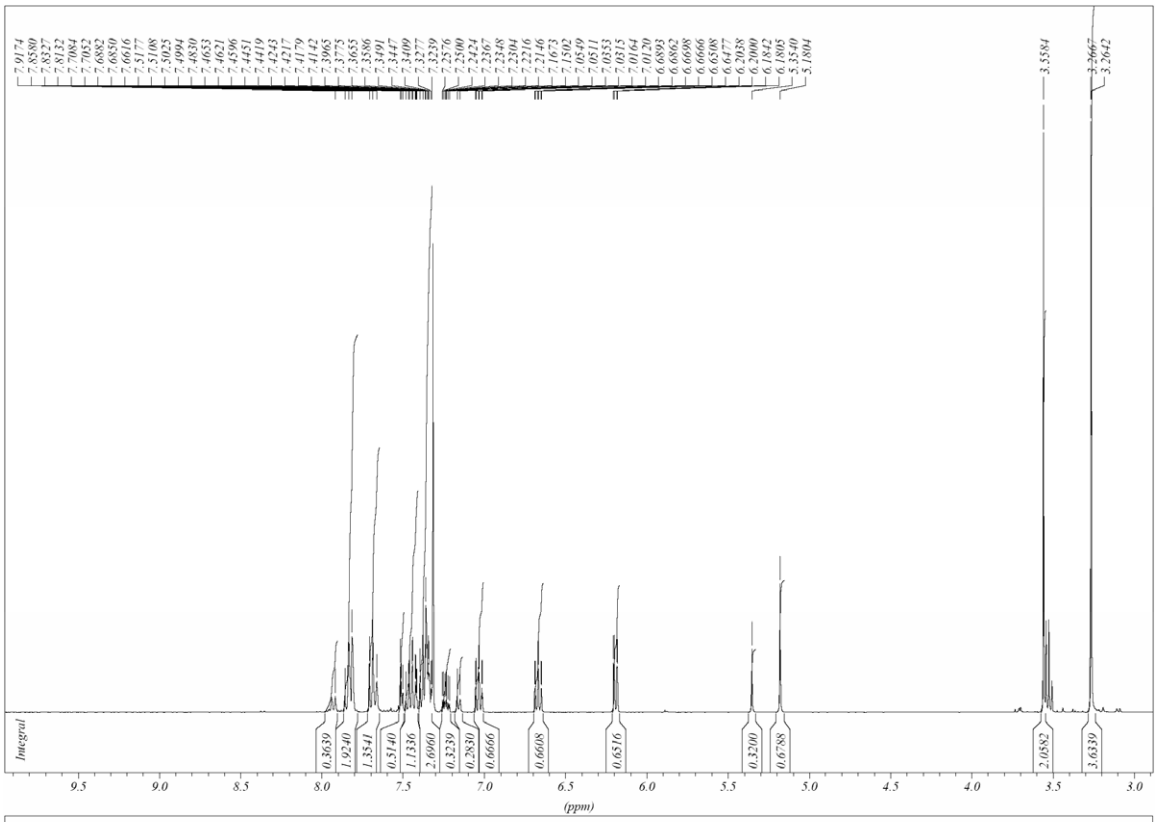
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.23 (s, 3H), 2.24 (s, 3H), 3.19 (s, 0.5H), 3.21 (s, 1.4H), 3.23 (s, 2.1H), 3.41 (s, 1H), 3.42 (s, 1H), 4.31 (d, *J* = 3.6 Hz, 0.7H), 4.55 (d, *J* = 3.3 Hz, 0.3H), 6.56-7.11 (m, 2.7H), 6.91 (s, 1H), 7.12-7.20 (m, 0.7H), 7.25-7.33 (m, 1.1H), 7.40-7.49 (m, 0.6H), 7.58 (t, *J* = 7.6 Hz, 0.3H), 7.75 (t, *J* = 7.6 Hz, 0.7H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.2, 21.0, 36.1, 56.6, 57.5, 65.6, 81.0, 81.9, 123.1, 124.2, 125.8, 126.0, 128.1, 128.6, 129.92, 129.96, 130.0, 130.1, 130.5, 131.6, 133.4, 133.6, 134.9, 135.8, 137.3, 137.5, 140.6, 141.2, 169.3, 169.5. ν_{max}/cm^{-1}: 2916, 2821, 1800, 1672, 1609, 1583, 1475, 1436; HRMS: *m/z* (ESI+) calculated for $C_{18}H_{21}BrNO_2$ ($[M+H]^+$): 362.0750, found: 362.0741.

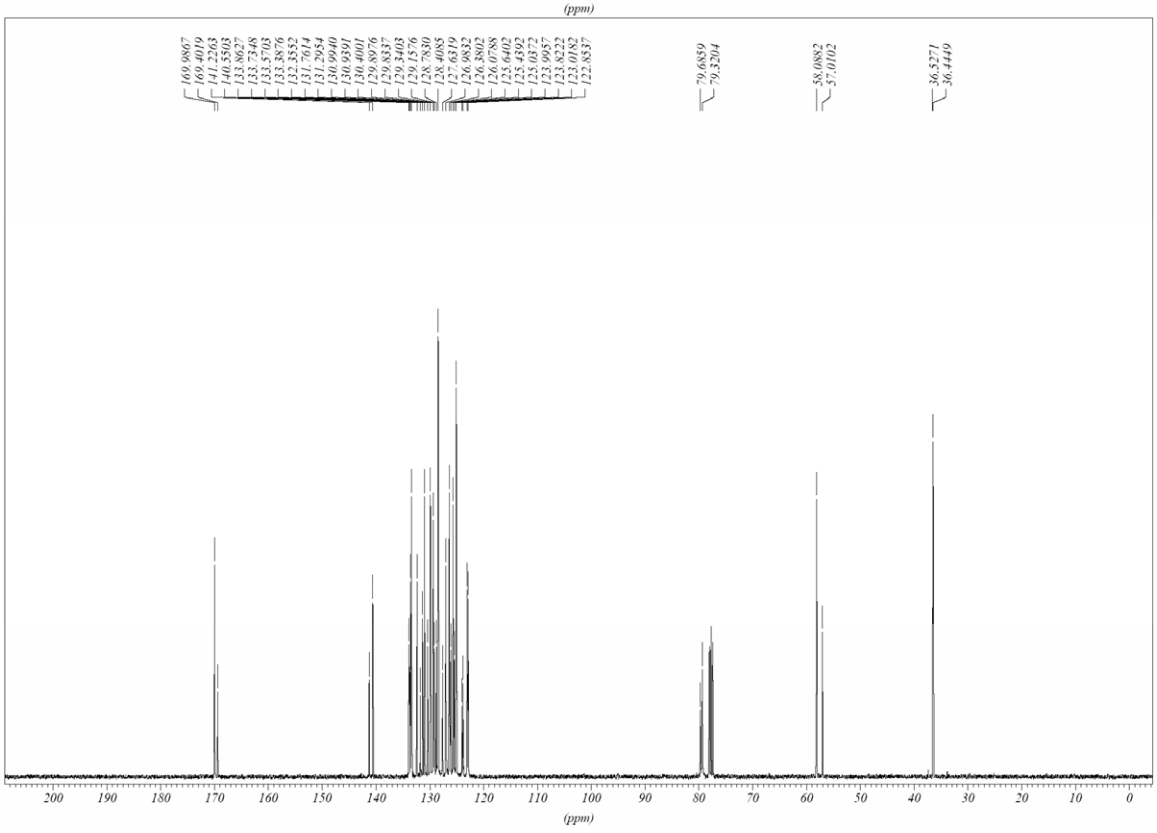




N-(2-bromophenyl)-2-methoxy-N-methyl-2-(naphthalen-1-yl)acetamide (1h)

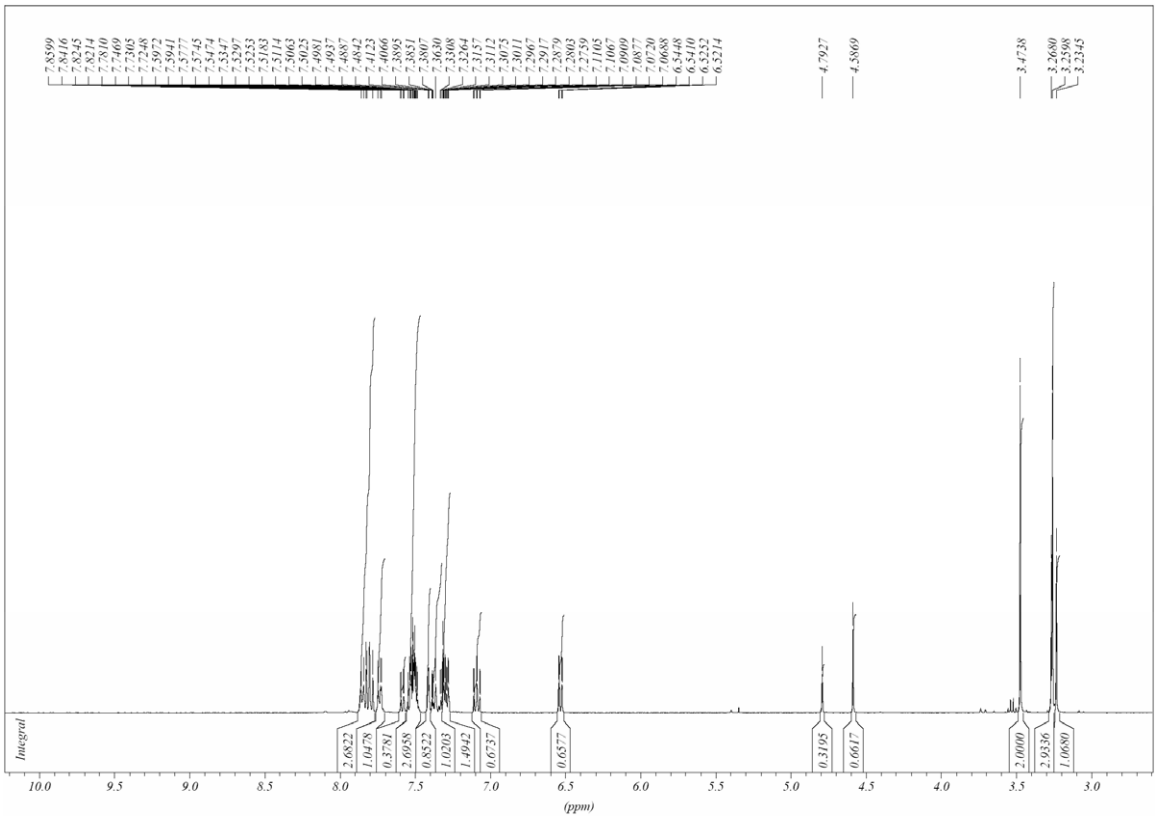
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.26 (s, 1.7H), 3.27 (s, 2H), 3.54 (s, 0.3H), 3.55 (s, 2H), 5.18 (s, 0.7H), 5.35 (s, 0.3H), 6.19 (dd, *J* = 1.5, 6.3 Hz, 0.7H), 6.66 (dt, *J* = 1.2, 7.8 Hz, 0.7H), 7.03 (dt, *J* = 1.5, 7.8 Hz, 0.7H), 7.16 (d, *J* = 6.1 Hz, 0.3H), 7.21-7.26 (m, 0.3H), 7.32-7.40 (m, 2.8H), 7.41-7.53 (m, 1.7H), 7.68 (dt, *J* = 1.2, 8.1 Hz, 1.4H), 7.82 (d, *J* = 7.8Hz, 2H), 7.92 (d, *J* = 8.6 Hz, 0.3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 36.4, 36.5, 57.0, 58.0, 79.3, 79.6, 122.8, 123.0, 123.8, 123.9, 125.0, 125.4, 125.6, 126.0, 126.3, 126.9, 127.6, 128.4, 128.7, 129.1, 129.3, 129.83, 129.89, 130.4, 130.93, 130.99, 131.2, 131.7, 132.3, 133.3, 133.5, 133.7, 133.8, 140.5, 141.2, 169.4, 169.9. ν_{max}/cm^{-1}: 2923, 2822, 1710, 1672, 1597, 1583, 1510, 1475, 1435; HRMS: *m/z* (ESI+) calculated for $C_{20}H_{19}BrNO_2$ ($[M+H]^+$): 384.0593, found: 384.0584.

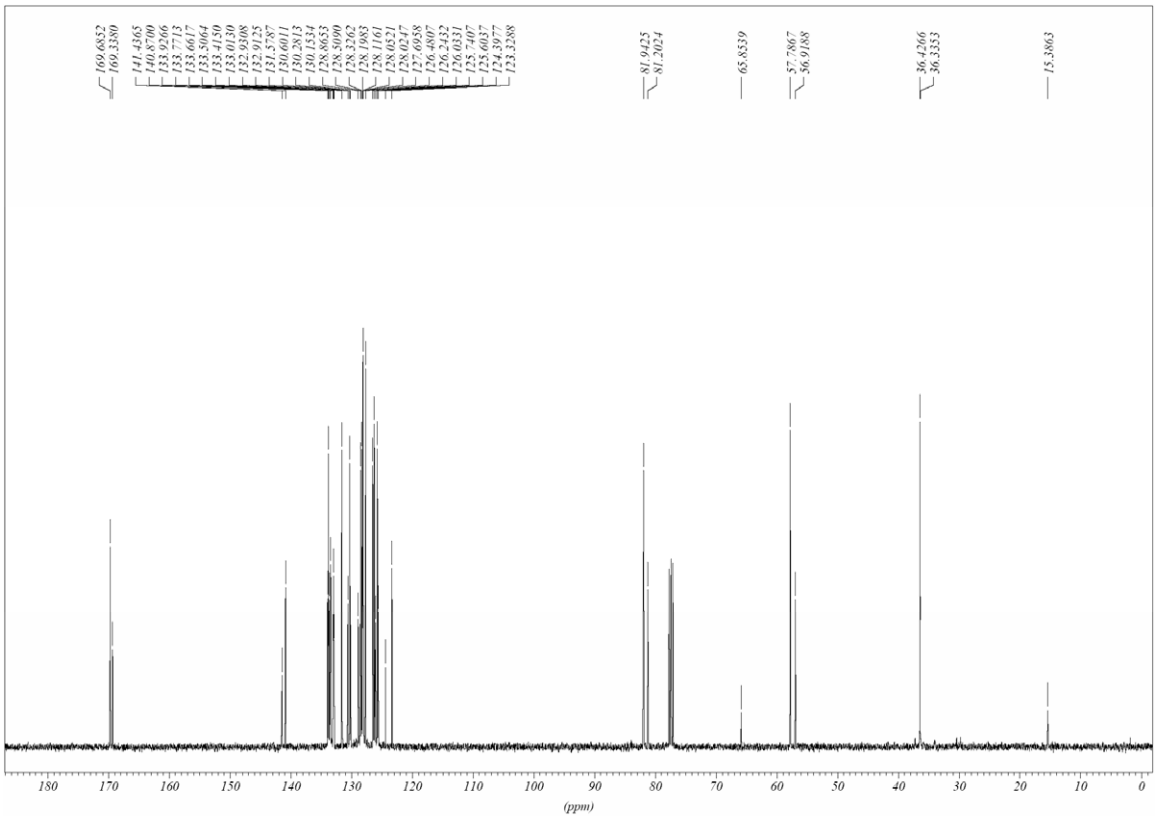

Integral
0.3639
1.9240
1.3541
0.5140
1.1336
2.6960
0.3239
0.2830
0.6666
0.6608
0.6516
0.3200
0.6788
2.0582
3.6339
(ppm)


79.6859
79.3204
58.0882
57.0102
36.5271
36.4449
(ppm)

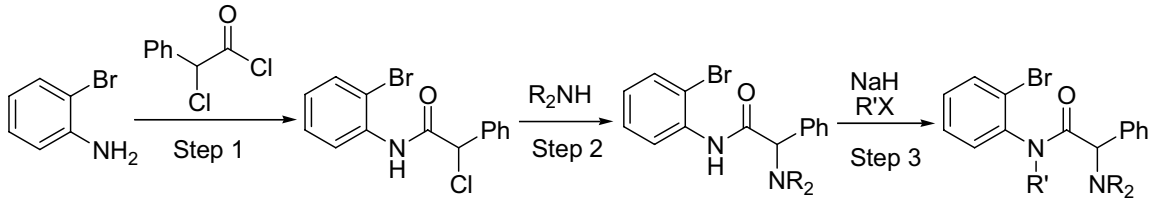
_N_-(2-bromophenyl)-2-methoxy-_N_-methyl-2-(naphthalen-2-yl)acetamide (1i)

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.23 (s, 1.1H), 3.26 (s, 1.9H), 3.27 (s, 1H), 3.47 (s, 2H), 4.58 (s, 0.7H), 4.79 (s, 0.3H), 6.53 (dd, *J* = 1.5, 7.8 Hz, 0.7H), 7.09 (dt, *J* = 1.5, 7.8 Hz, 0.7H), 7.27-7.31 (m, 1.1H), 7.32-7.39 (m, 1H), 7.41 (s, 0.8H), 7.47-7.53 (m, 2.7H), 7.58 (dd, *J* = 1.2, 7.8 Hz, 0.4H), 7.74 (dd, *J* = 2.3, 8.8 Hz, 1H), 7.78-7.86 (m, 2.7H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.3, 36.3, 36.4, 56.9, 57.7, 65.8, 81.2, 81.9, 123.3, 124.3, 125.6, 125.7, 126.0, 126.2, 126.4, 127.6, 128.02, 128.05, 128.11, 128.19, 128.3, 128.5, 128.8, 130.1, 130.2, 130.6, 131.5, 132.91, 132.93, 133.0, 133.4, 133.5, 133.6, 133.7, 133.9, 140.8, 141.4, 169.3, 169.6. ν_{max}/cm^{-1}: 3057, 2927, 2822, 1672, 1583, 1508, 1475, 1436; HRMS: *m/z* (ESI+) calculated for $C_{20}H_{19}BrNO_2$ ($[M+H]^+$): 384.0593, found: 384.0599.




169.6852
169.3380
141.4365
140.6700
140.0766
133.7713
133.6617
133.5064
133.4159
133.0130
132.9308
132.9125
131.5787
130.6011
130.2813
130.1534
128.8653
128.5090
128.3262
128.1983
128.1161
128.0521
128.0247
127.6958
126.4007
126.2432
126.1431
125.7407
125.6037
124.3977
123.3288
81.9425
81.2024
65.8539
57.7867
56.9188
36.4266
36.3353
15.3863
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

General Procedure C:



Step 1: To a solution of 2-bromoaniline (1 eq) in DCM (*ca* 0.025 M) was added pyridine (1.3 eq) and chlorophenylacetyl chloride (1.3 eq). The mixture was stirred for 3 hours then diluted with DCM (equivalent volume to that of DCM used in the reaction), washed with water (equivalent volume to DCM), 1 M NaOH (equivalent volume toDCM) and brine, dried ($MgSO_4$) and concentrated under reduced pressure, to yield an orange oily solid; the product was recrystallised from methanol / water to give *N*-(2-bromophenyl)-2-chloro-2-phenylacetamide as a pale yellow crystalline solid (93 %).

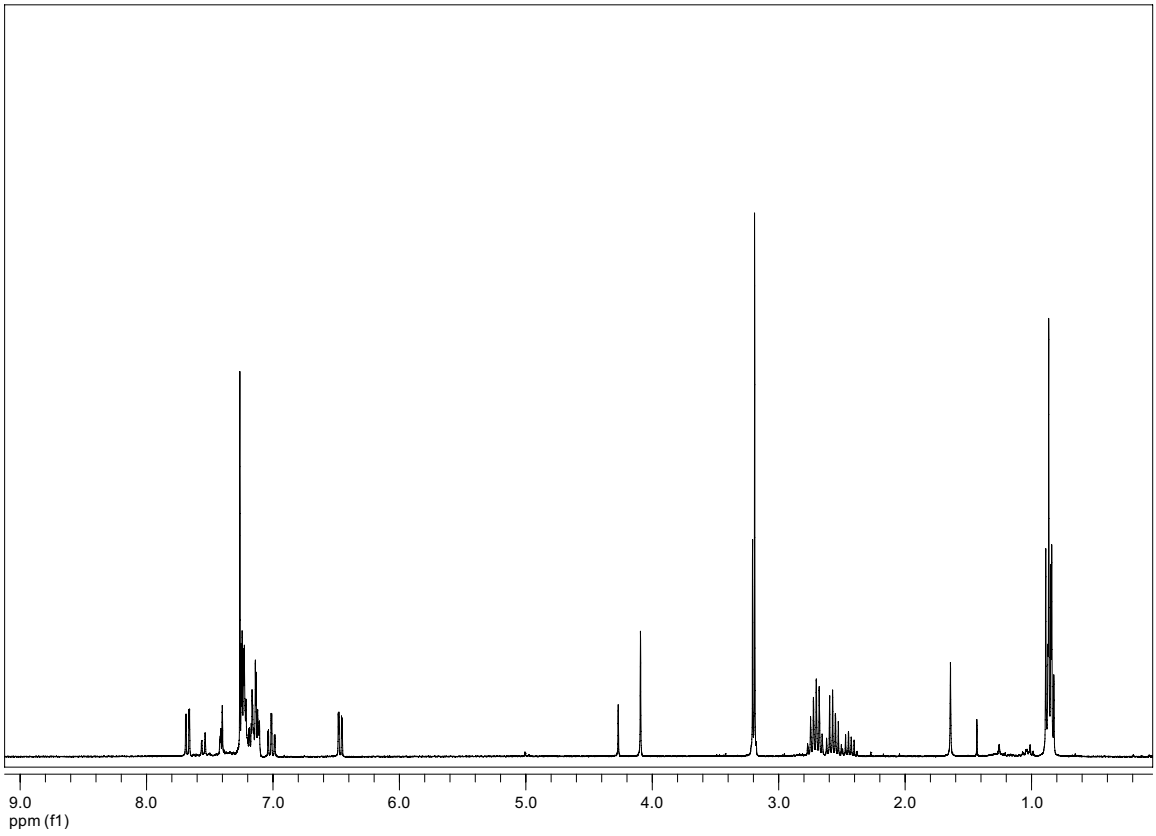
Step 2: To a solution of the amine (1.2 eq) and diisopropylethylamine (1.2 eq) in acetonitrile (*ca* 0.025 M) was added the *N*-(2-bromophenyl)-2-chloro-2-phenylacetamide (1 eq); the solution was then heated under reflux for ~10 hours, and then allowed to cool to room temperature. The reaction mixture was diluted with diethyl ether (equivalent volume to that of acetonitrile used in the reaction) and washed with water (equivalent to volume of diethyl ether). The aqueous layer was washed with diethyl ether, and the combined organics were washed with brine, then dried ($MgSO_4$) and concentrated under reduced pressure to give the crude product, which was purified by flash column chromatography.

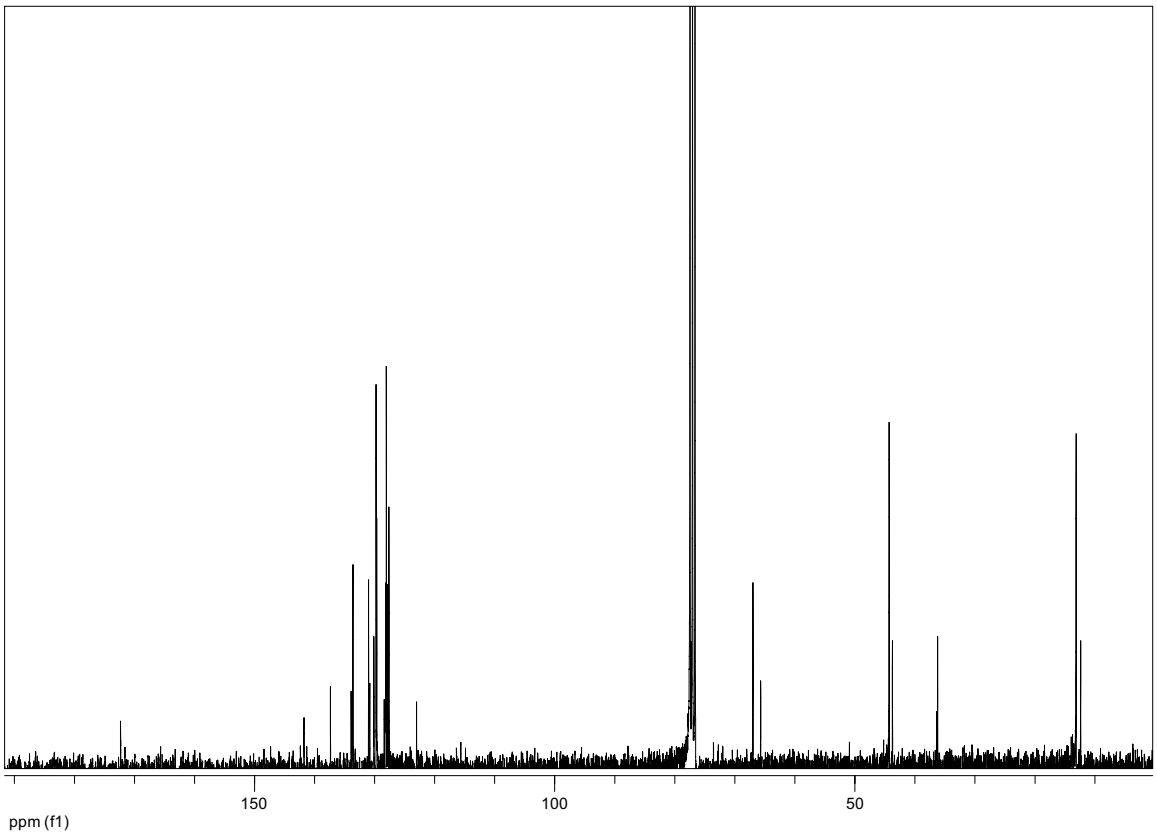
Step 3: To a suspension of NaH (1.2 eq) in acetonitrile (*ca* 0.025 M) at 0 ^{o}C was added the amide (from step 2) (1 eq, as a solution in acetonitrile), and MeI or benzyl bromide (1.2 eq). The reaction mixture was allowed to warm to room temperature over 4 hours. The reaction was quenched with 1 M NaOH (aq) (equivalent to the volume of acetonitrile used in the reaction) and diluted with ethyl acetate (equivalent to the volume of acetonitrile used in the reaction). The layers were separated and the aqueous layer washed with ethyl acetate. The combined organics were then washed with brine, dried

($MgSO_4$), and concentrated under reduced pressure; the crude product was purified by flash column chromatography.

***N*-(2-Bromophenyl)-2-(diethylamino)-*N*-methyl-2-phenylacetamide (1l)**

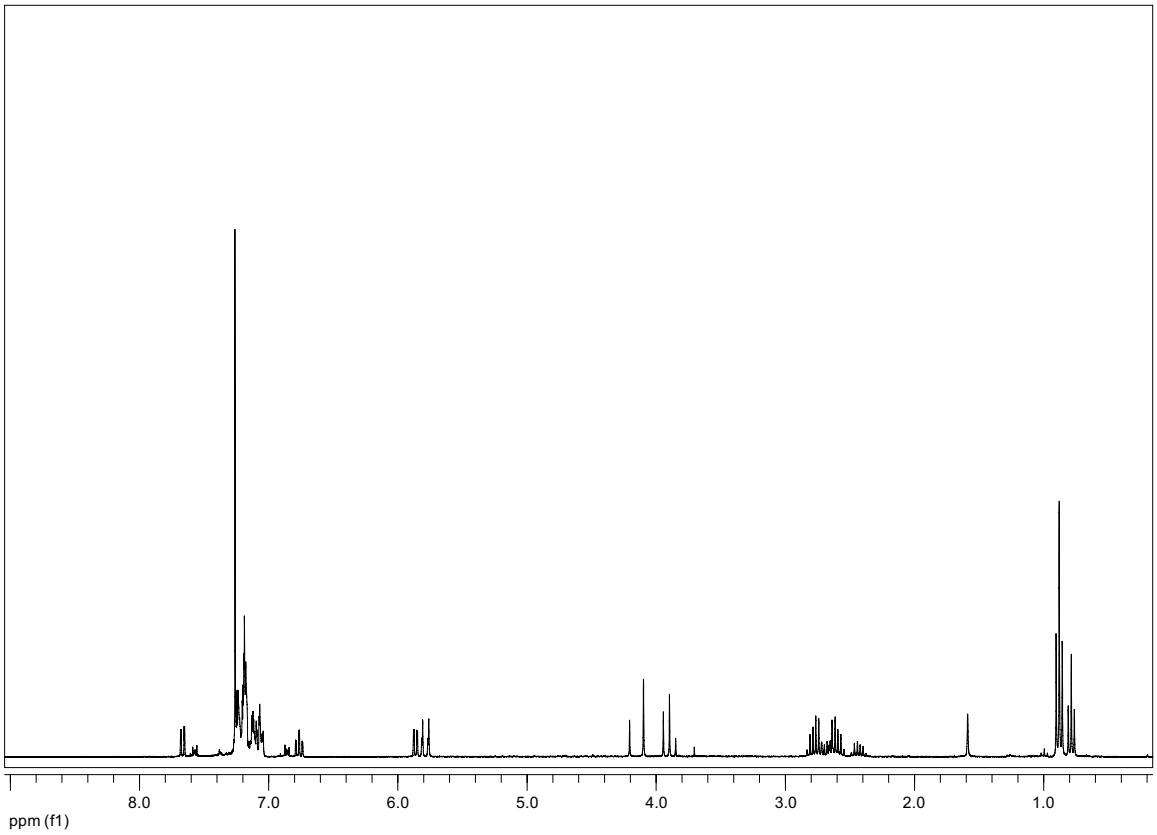
^{1}H NMR (300 MHz, $CDCl_3$): δ 0.82-0.89 (m, 6H), 2.77-2.38 (4H, m), 3.19 (s, 2.1H), 3.21 (s, 0.9H), 4.09 (s, 0.7H), 4.27 (s, 0.3H), 6.47 (d, *J* = 7.8 Hz, 0.7H), 7.01 (t, *J* = 7.8 Hz, 0.7H), 7.11-7.25 (m, 5.9H), 7.41 (d, *J* =7.5 Hz, 0.7H), 7.55 (d, *J* = 7.8 Hz, 0.3H), 7.67 (d, *J* = 7.8 Hz, 0.7H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.1, 36.2, 44.3, 67.0, 123.0, 127.9, 128.1, 128.1, 129.7, 129.8, 131.0, 133.6, 137.3, 141.8,172.3. ν_{max}/cm^{-1}: 3033, 2953, 2861, 1670; HRMS: *m/z* (EI+) calculated for $C_{19}H_{24}BrN_2O$ ($[M+H]^+$): 375.1067; found: 375.1058.

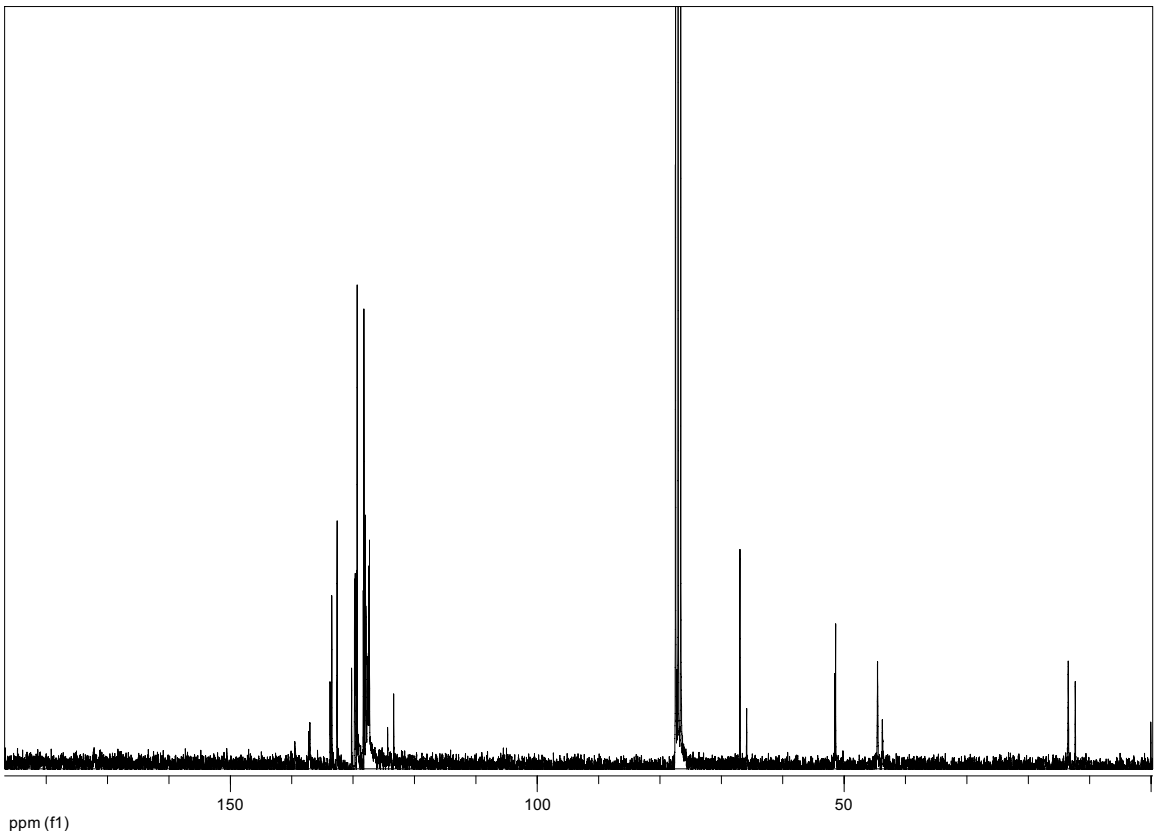




_N_-Benzyl-_N_-(2-bromophenyl)-2-(diethylamino)-2-phenylacetamide (1m)

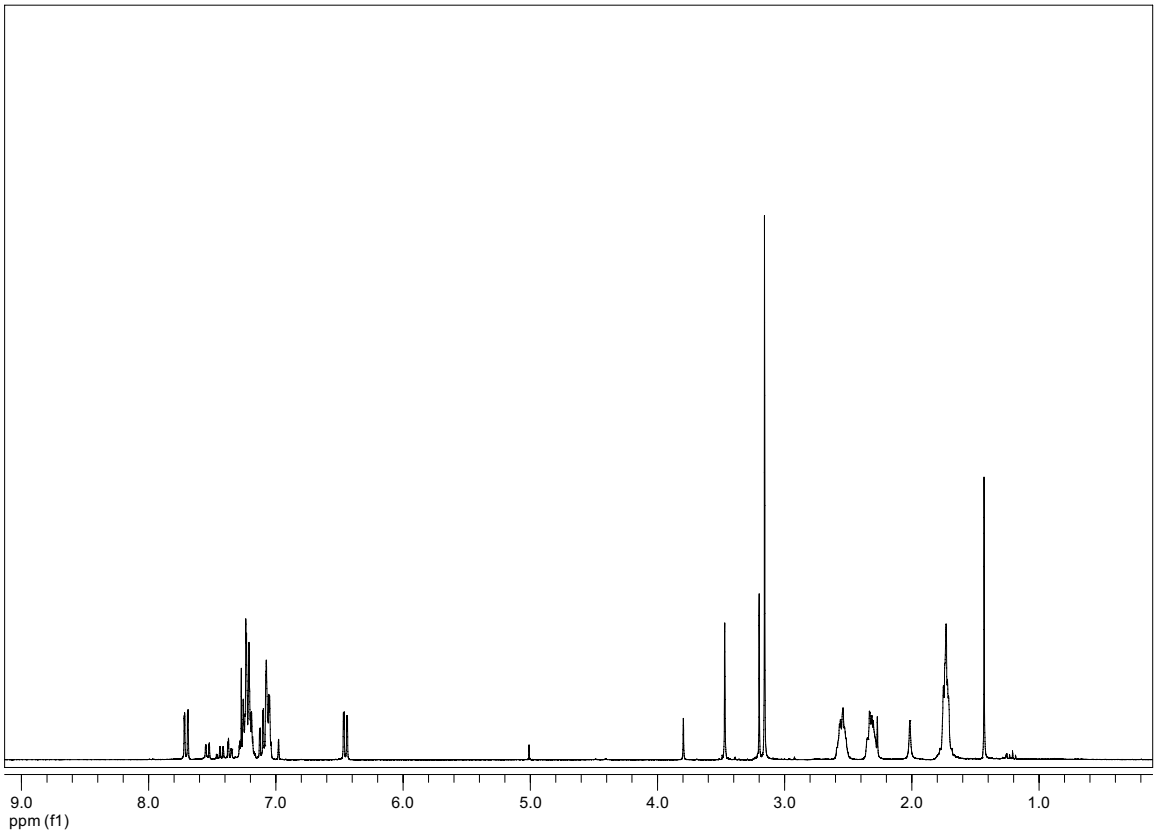
^{1}H NMR (300 MHz, $CDCl_3$): δ 0.79 (t, J = 7.0 Hz, 2.4H), 0.88 (t, J = 7.0 Hz, 3.6H), 2.40-2.83 (m, 4H), 3.94 (d, J = 14.1 Hz, 0.6H), 4.10 (s, 0.6H), 4.21 (s, 0.4H), 5.76-5.87 (m, 1H), 6.76 (t, J = 7.8 Hz. 0.6H), 6.84-6.87 (m, 0.4H), 7.04-7.25 (m, 12H), 7.56-7.59 (m, 0.4H), 7.68 (d, J = 8.1 Hz, 0.6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.5, 44.5, 51.5, 67.0, 123.4, 124.4, 139.5, 127.3, 127.4, 127.5, 127.7, 127.9, 128.0, 128.2, 128.3, 129.3, 129.4, 129.7, 130.2, 132.6, 133.5, 133.7, 137.2. ν_{max}/cm^{-1}: 3077, 2965, 1872, 1659; HRMS: *m/z* (EI+) calculated for $C_{25}H_{28}BrN_2O$ ($[M+H]^+$): 451.1380, found: 451.1390.

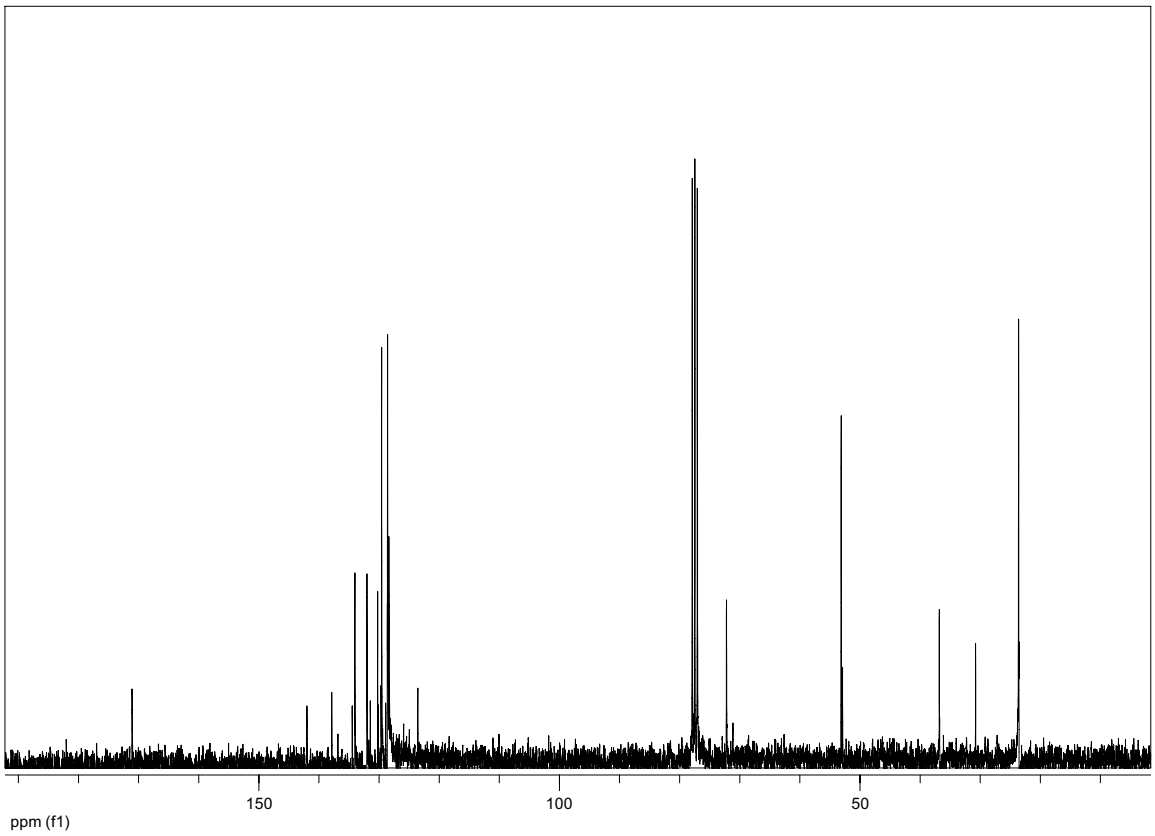

8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)


150
100
50
ppm (f1)

_N_-(2-Bromophenyl)-_N_-methyl-2-phenyl-2-(pyrrolidin-1-yl)acetamide (1n)

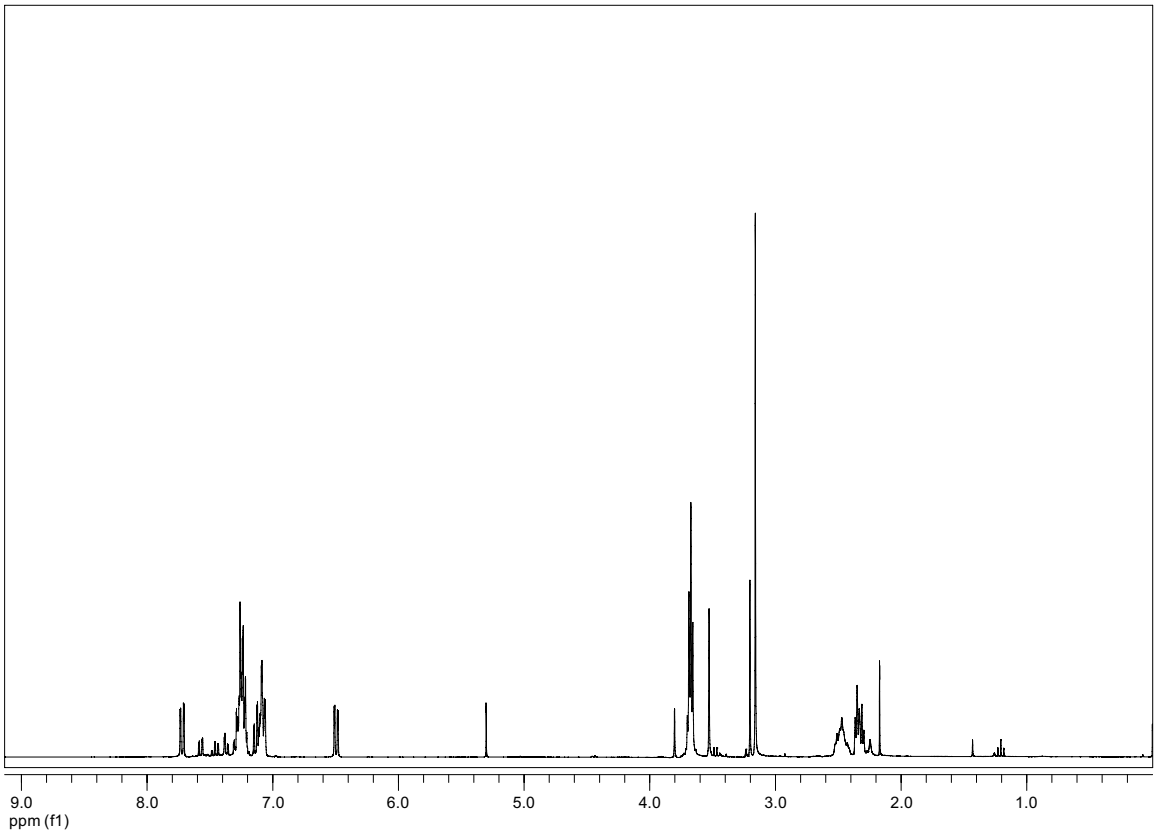
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.71-1.75 (m, 4H), 2.27-2.35 (m, 2H), 2.53-2.59 (m, 2H), 3.16 (s, 2.1H), 3.20 (s, 0.9H), 3.47 (s, 0.7H), 3.80 (s, 0.3H), 6.45 (d, *J* = 7.8 Hz.0.7H), 6.98-7.29 (m, 6.7H), 7.36 (d, *J* = 7.8 Hz, 0.3H), 7.44 (t, *J* = 7.5 Hz, 0.3H), 7.54 (d, *J* = 7.8 Hz, 0.3H), 7.70 (d, *J* = 7.8 Hz. 0.7H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.6, 36.8, 53.1, 72.2, 123.5, 128.3, 128.5, 128.8, 129.6, 130.1, 131.9, 133.9, 137.9, 142.1, 171.1. ν_{max}/cm^{-1}: 3021, 2956, 2875, 1661;HRMS: *m/z* (EI+) calculated for $C_{19}H_{22}BrN_2O$ ($[M+H]^+$): 373.0910, found: 373.0898.





_N_-(2-Bromophenyl)-_N_-methyl-2-morpholin-4-yl-2-phenylacetamide (1o)

^{1}H NMR (300 MHz, $CDCl_3$): δ 2.30-2.37 (m, 2H), 2.42-2.52 (m, 2H), 3.16 (s, 2.25H), 3.20 (s, 0.75H), 3.53 (s, 0.75H), 3.66-3.70 (m, 4H), 3.80 (s, 0.25H), 6.50 (d, J = 7.8 Hz, 0.75H), 7.06-7.31 (m, 6.75H), 7.37 (d, J = 7.8 Hz, 0.25H), 7.46 (t, J = 7.8 Hz, 0.25H), 7.57 (d, J = 8.0 Hz, 0.25H), 7.72 (d, J = 8.0 Hz, 0.75H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 36.2, 36.3, 51.6, 51.9, 66.9, 67.1, 71.3, 72.3, 123.0, 124.2, 127.9, 128.0, 128.1, 128.2, 128.3, 128.6, 129.7, 129.8, 129.9, 130.0, 130.9, 131.4, 133.7, 134.1, 134.4, 135.3, 141.4, 142.0, 170.0, 170.2. ν_{max}/cm^{-1}: 3048, 2960, 2857, 1664; HRMS: *m/z* (EI+) calculated for $C_{19}H_{22}BrN_2O_2$ ($[M+H]^+$): 389.0859, found 389.0845.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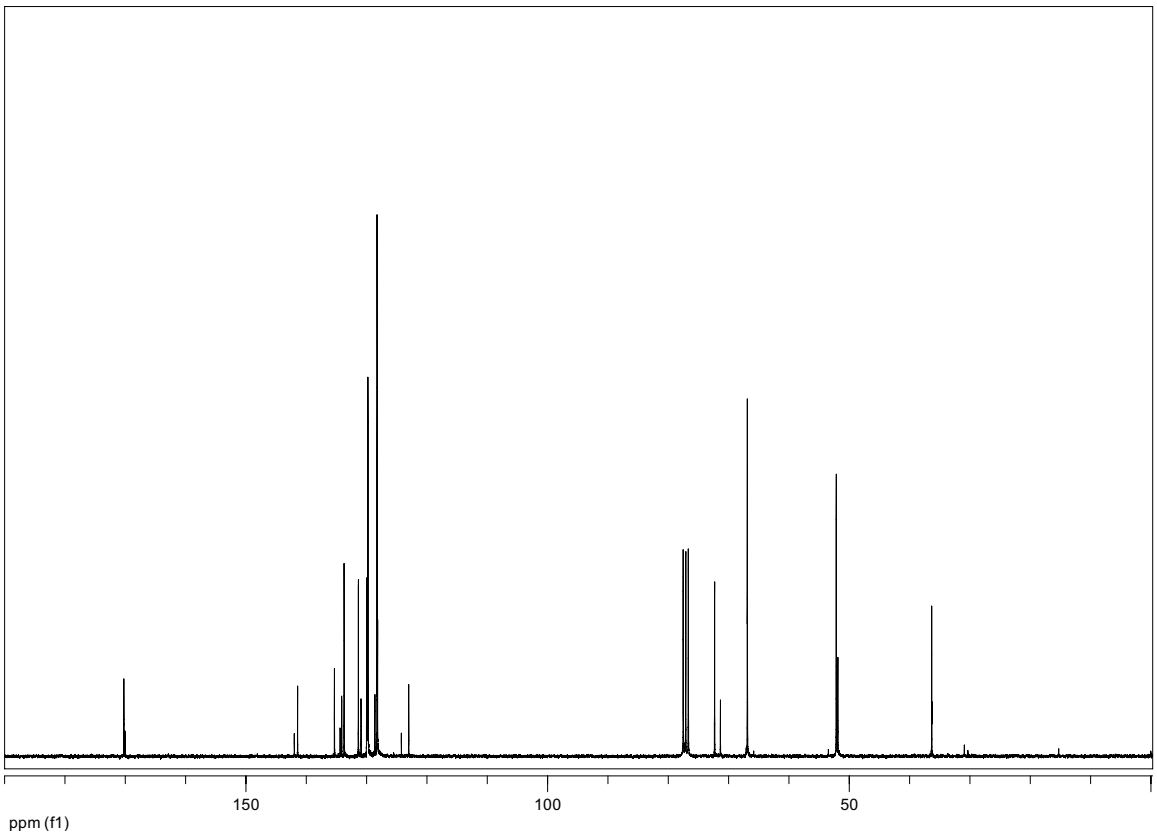
2.0
1.0
ppm (f1)


150
100
50
ppm (f1)

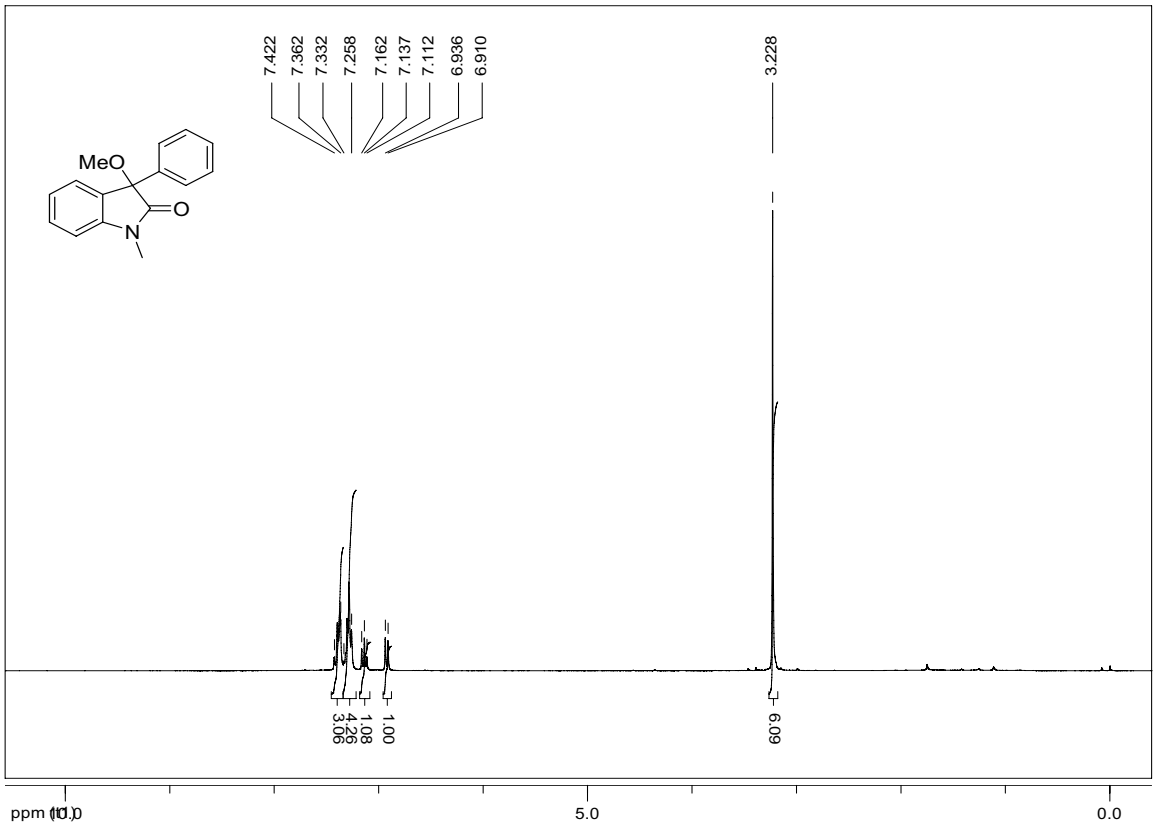
3. Catalytic asymmetric intramolecular α-arylation reactions

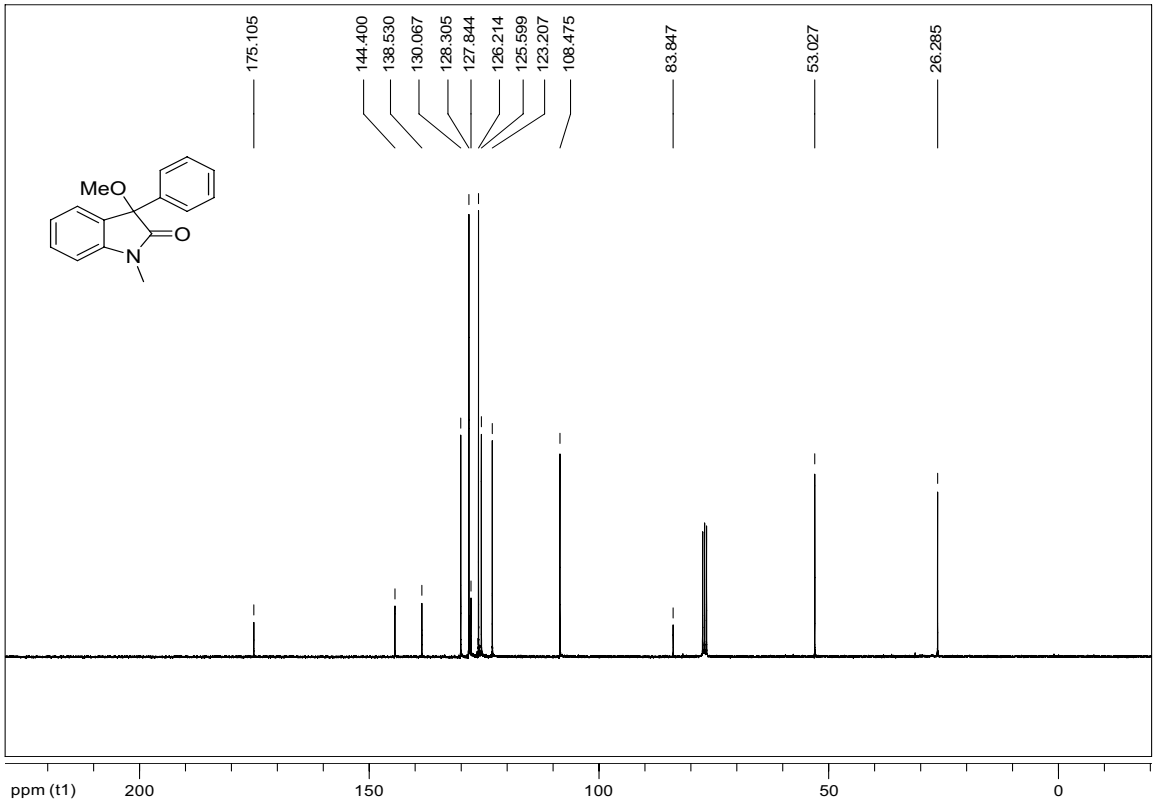
General procedure:

A dry Schlenk tube was charged with $Pd(dba)_2$ (5.8 mg, 0.01 mmol), **L3** (7.8 mg, 0.011 mmol) and ^{t}BuONa (29 mg, 0.3 mmol) under N_2. Toluene (2mL) was added and the mixture was stirred for 0.5 h before addition of a solution of the amide (0.2 mmol in 2.0 mL toluene. The reaction mixture was stirred at the indicated temperature / time. Flash chromatography afforded the product oxindoles, the ee values were determined by chiral HPLC.

3-Methoxy-1-methyl-3-phenyloxindole (2a)[8]

91% yield. $[\alpha]_D^{25}$ = +79.3 (*c* = 0.5 in acetone). 97% ee [Chiralcel AD column, *n*-hexane/*i*-PrOH = 98:2, 1.0 mL/min, 254 nm; t_R = 11.72 min (minor) and 14.13 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.23 (s, 3H), 3.23 (s, 3H), 6.93 (d, *J* = 7.8 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.26-7.33 (m, 4H), 7.33-7.43 (m, 3H).

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130.067
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127.844
126.214
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123.207
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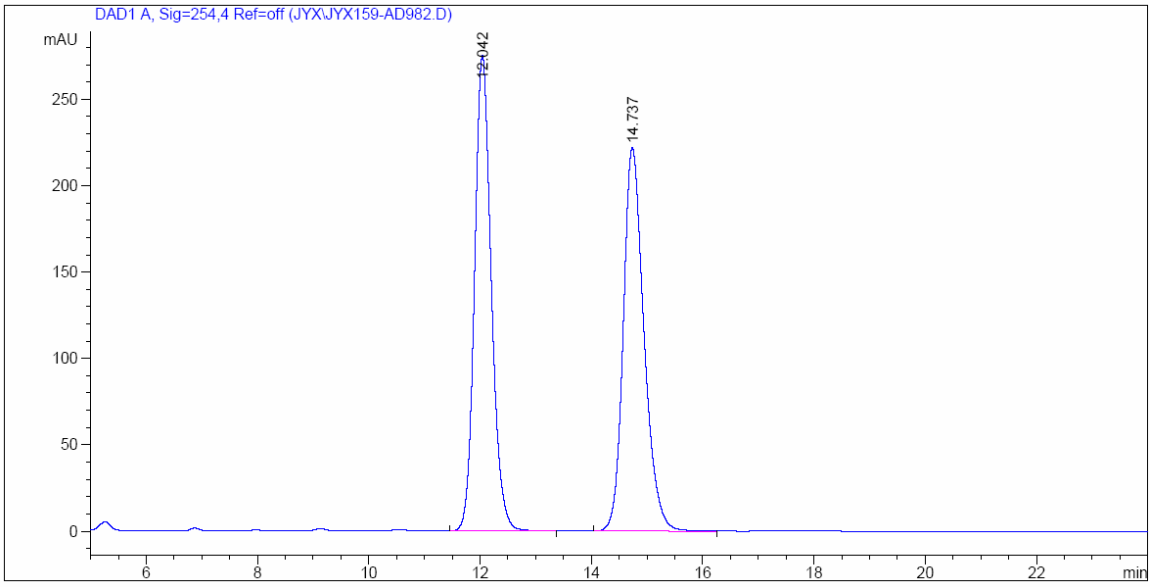
O
N
ppm (t1)
200
150
100
50
0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150
100
50
0
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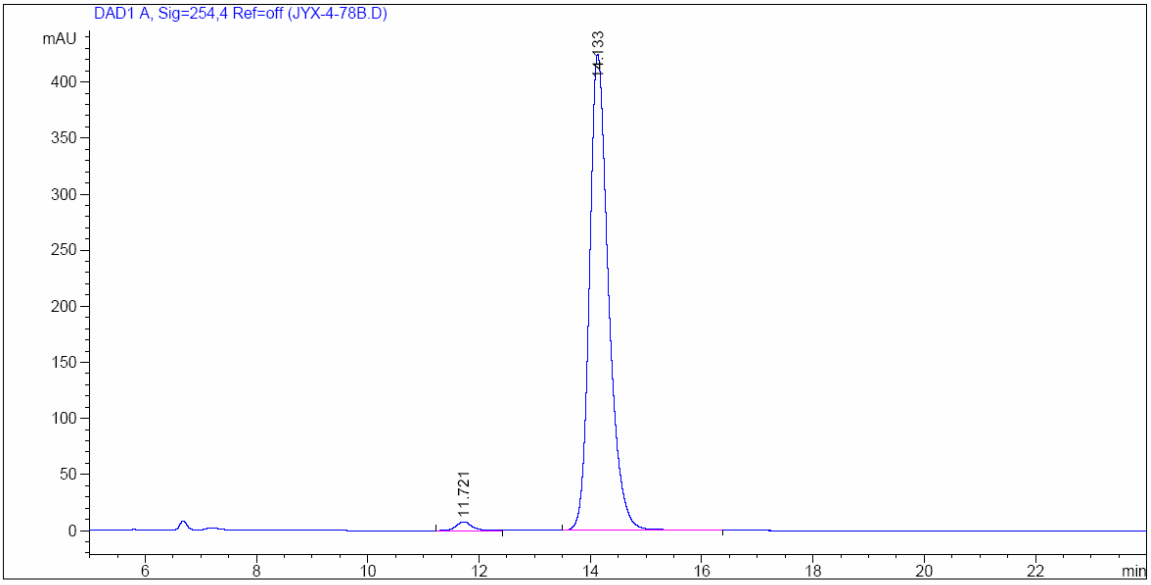
6
8
10
12
14
16
18
20
22
min

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Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


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Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
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   2  14.133 BB    0.3614 1.00916e4   424.43036  98.5210

Totals :                  1.02431e4   432.33494

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                      *** End of Report ***
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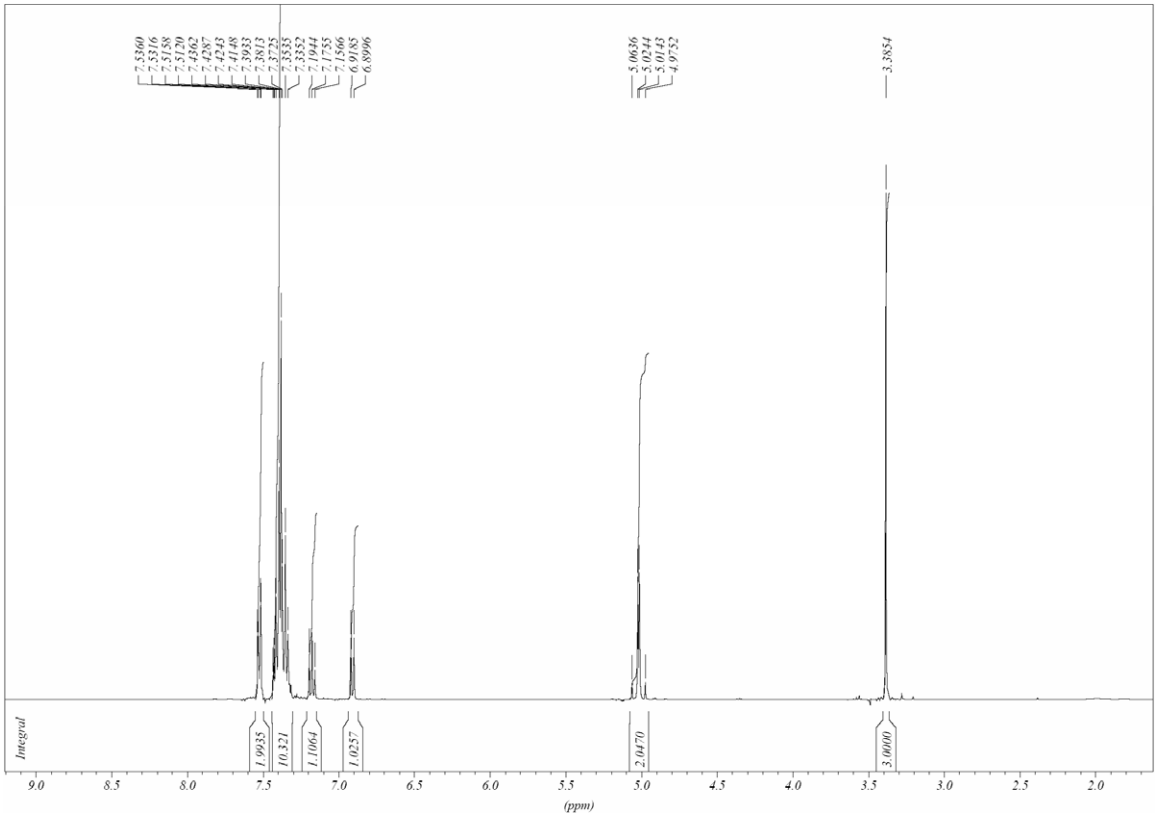
1-Benzyl-3-methoxy-3-phenyoxindole (2b)

93% yield. $[\alpha]_D^{25}$ = +49.1 (*c* = 1.0 in acetone). 85% ee [Chiralcel AS-H column, *n*-hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm; t_R = 9.25 min (minor) and 12.31 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.38 (s, 3H), 5.01 (dd, *J* = 15.7, 19.7 Hz, 2H), 6.90 (d, *J* = 7.6 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.33-7.44 (m, 10H), 7.51 (d, *J* = 1.5Hz, 1H), 7.53 (d, *J* = 1.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 44.0, 53.3, 84.0, 109.8, 123.4, 125.8, 126.4, 127.4, 127.8, 128.1, 128.52, 128.57, 128.9, 130.1, 135.7, 138.9, 143.7, 175.4. ν_{max}/cm^{-1}: 3061, 3031, 2929, 2826, 2248, 1717, 1610, 1485, 1465, 1454; HRMS: *m/z* (ESI+) calculated for $C_{22}H_{19}NO_2Na$ ($[M+Na]^+$): 352.1308, found 352.1321.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7.4362
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7.4243
7.4148
7.3983
7.3813
7.3725
7.3535
7.3352
7.1944
7.1755
7.1566
6.9185
6.8996
5.0636
5.0244
5.0143
4.9752
3.3854
Integral
1.9935
10.321
1.1064
1.0257
2.0470
3.0000
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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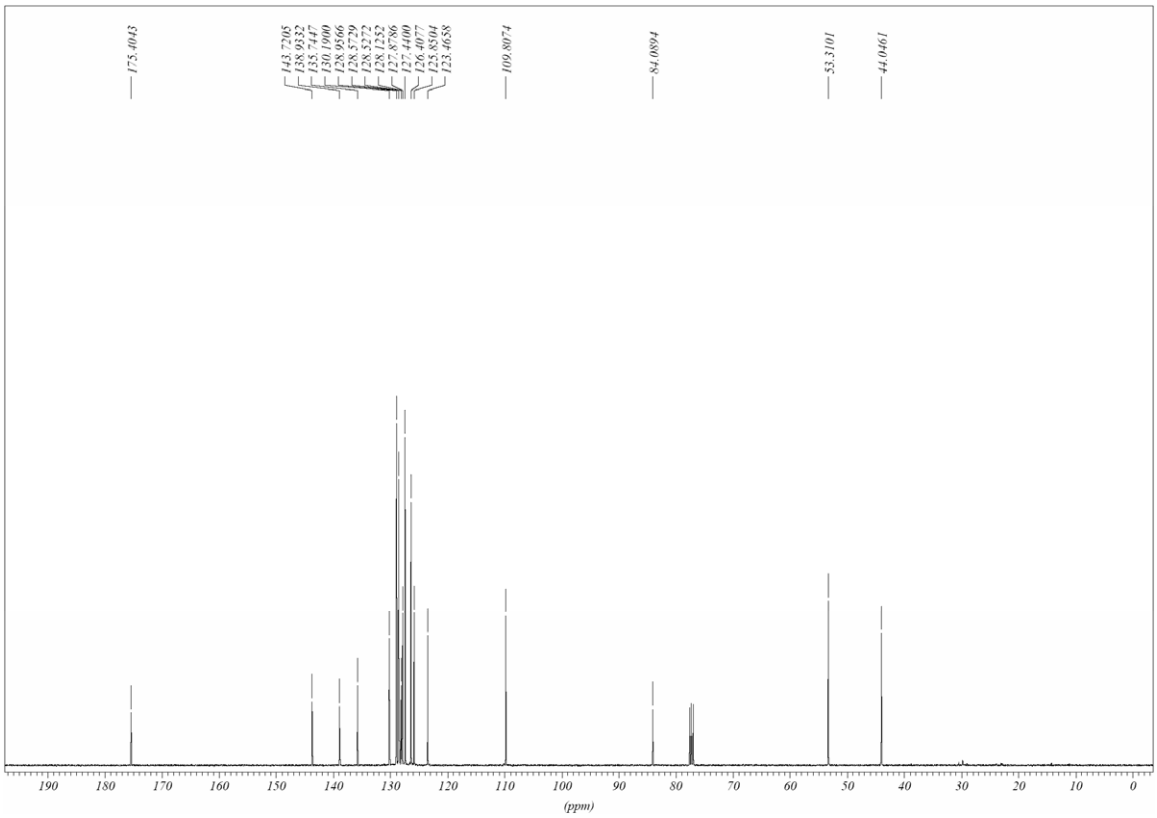
4.0
3.5
3.0
2.5
2.0
(ppm)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126.4077
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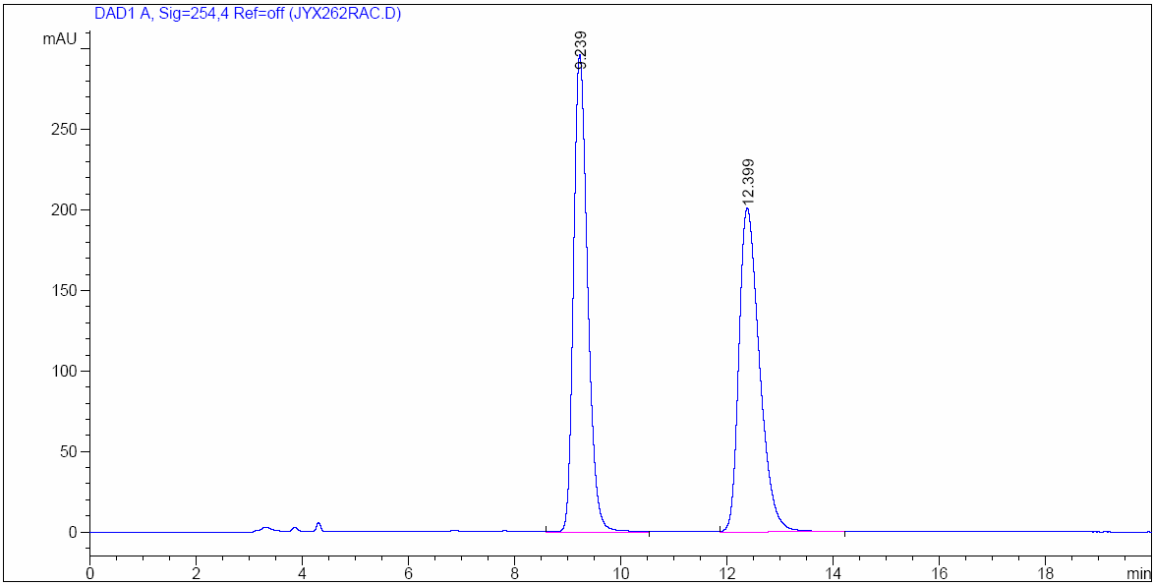
109.8074
84.0894
53.3101
44.0461
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)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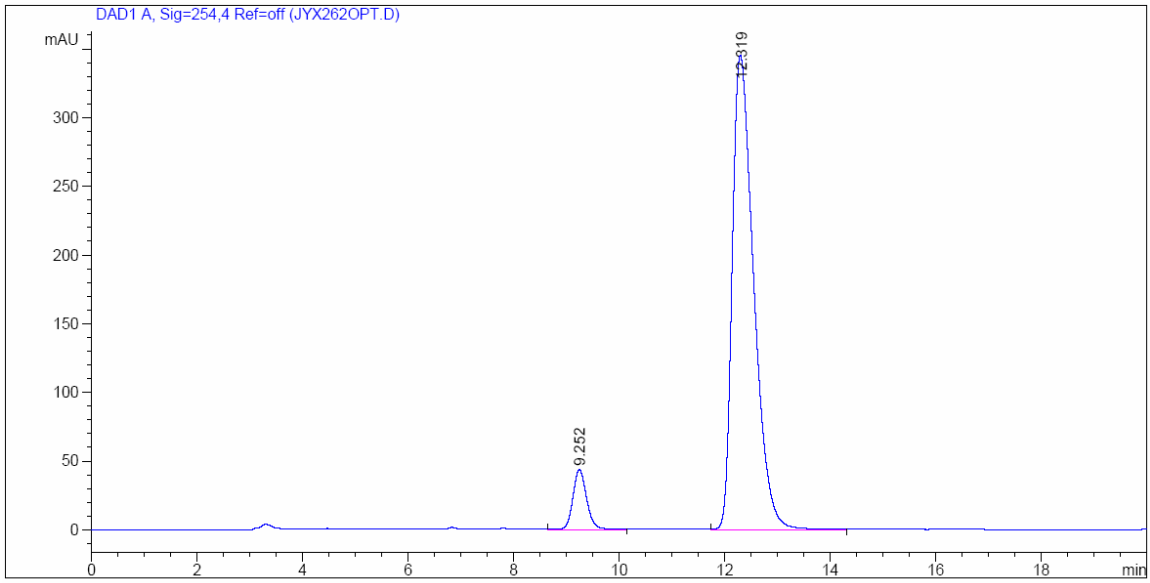
12.399
0 2 4 6 8 10 12 14 16 18 min

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Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


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Peak RetTime Type  Width     Area      Height     Area
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   2  12.319 BB    0.4648 9695.25488  335.83481  92.4362

Totals :                  1.04886e4   379.08820

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                        *** End of Report ***
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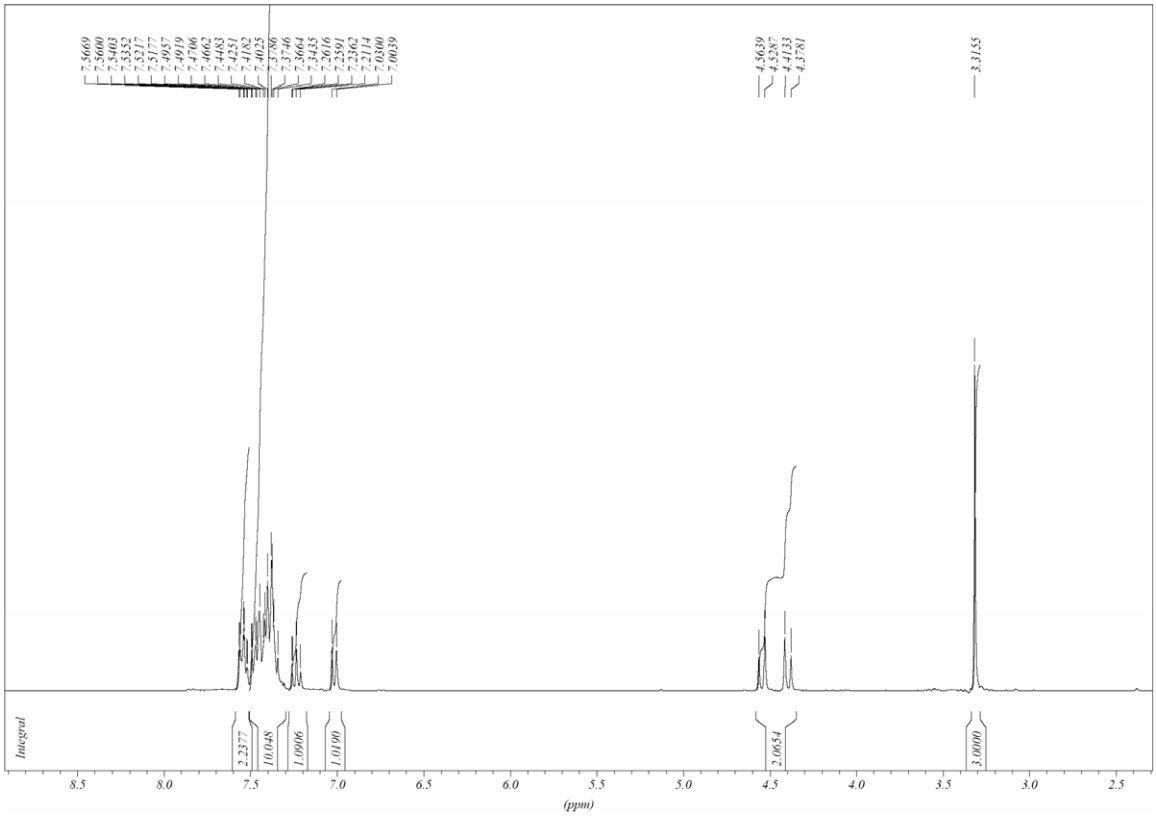
3-(Benzyloxy)-1-methyl-3-phenyloxindole (2c)

94% yield. $[\alpha]_D^{25}$ = +184.2 (*c* = 1.0 in CH_2Cl_2). 79% ee [Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm; t_R = 7.42 min (minor) and 9.28 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.31 (s, 3H), 4.47 (dd, *J* = 10.6, 45.2 Hz, 2H), 7.01 (d, *J* = 7.8 Hz, 1H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.34-7.49 (m, 10H), 7.51-7.57 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.4, 67.6, 83.7, 108.7, 123.4, 125.8, 126.5, 127.7, 128.0, 128.3, 128.42, 128.49, 130.3, 137.7, 138.8, 144.4, 175.2. ν_{max}/cm^{-1}: 3059, 3031, 2924, 1720, 1610, 1491, 1468, 1448, 1419; HRMS: *m/z* (ESI+) calculated for $C_{22}H_{19}NO_2Na$ ($[M+Na]^+$): 352.1308, found 352.1324.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7.3435
7.2616
7.2591
7.2362
7.2114
7.0300
7.0039
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4.5287
4.4133
4.3781
3.3155
Integral
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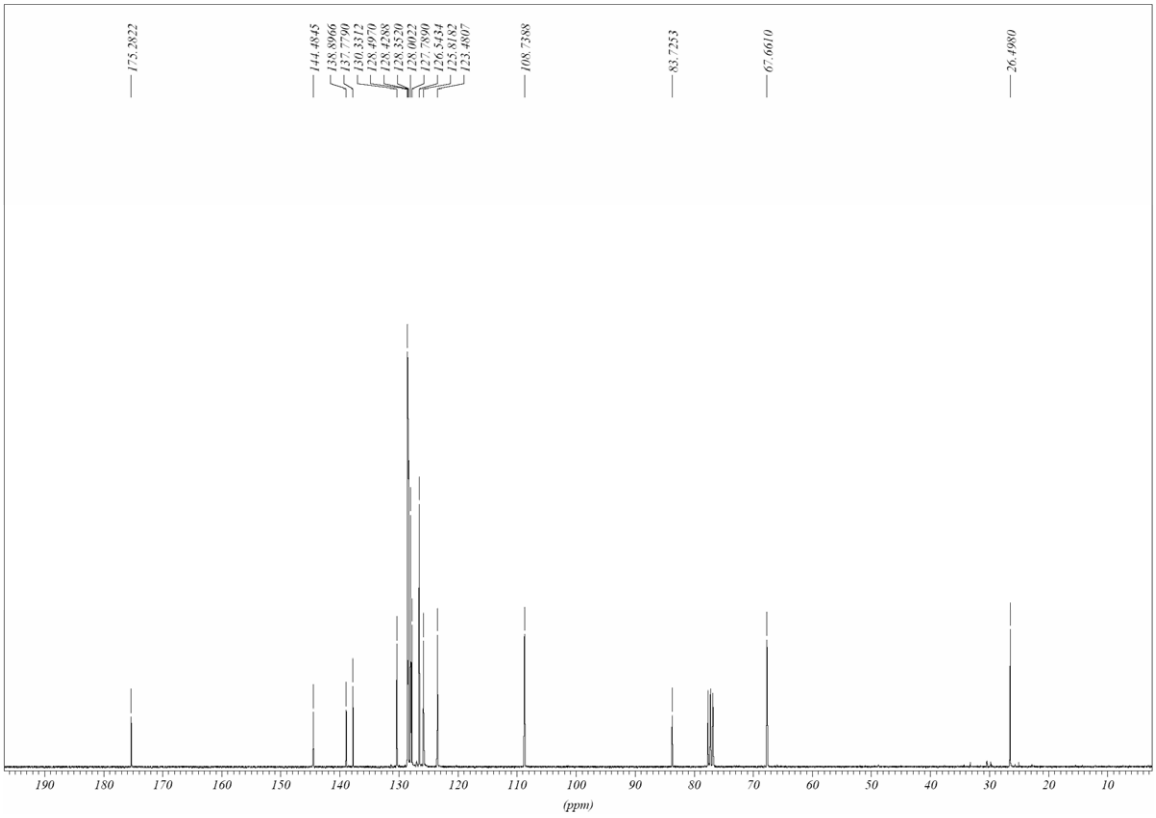
2.5
(ppm)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83.7253
67.6610
26.4980
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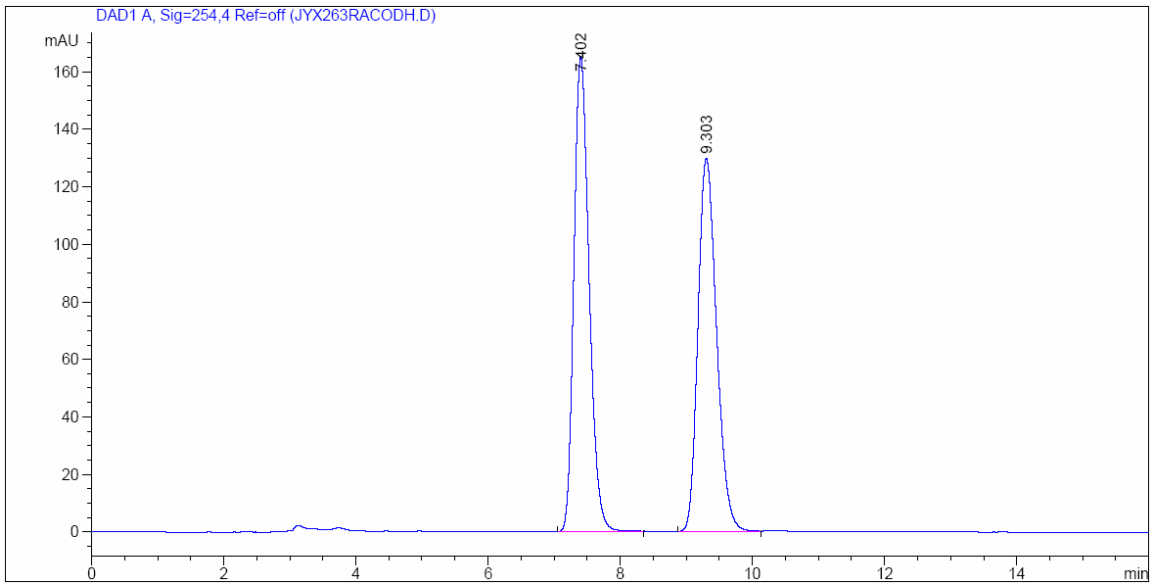
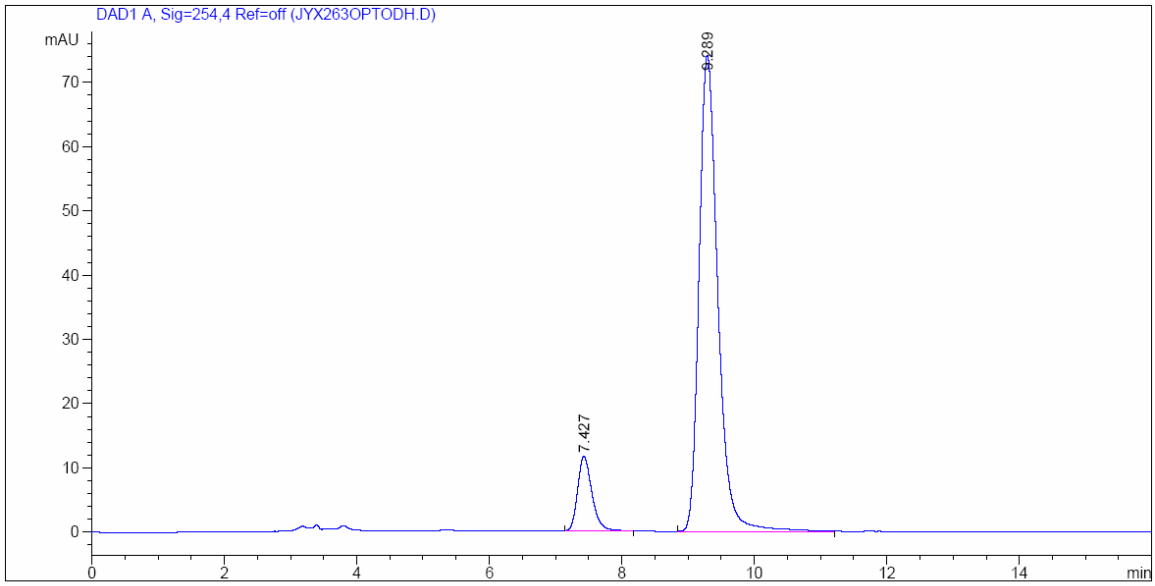
10
(ppm)



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


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Peak RetTime Type  Width     Area      Height     Area
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   2   9.289 BB    0.3015 1457.74878   74.09422  89.2900

Totals :                   1632.60103   85.68899

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                      *** End of Report ***
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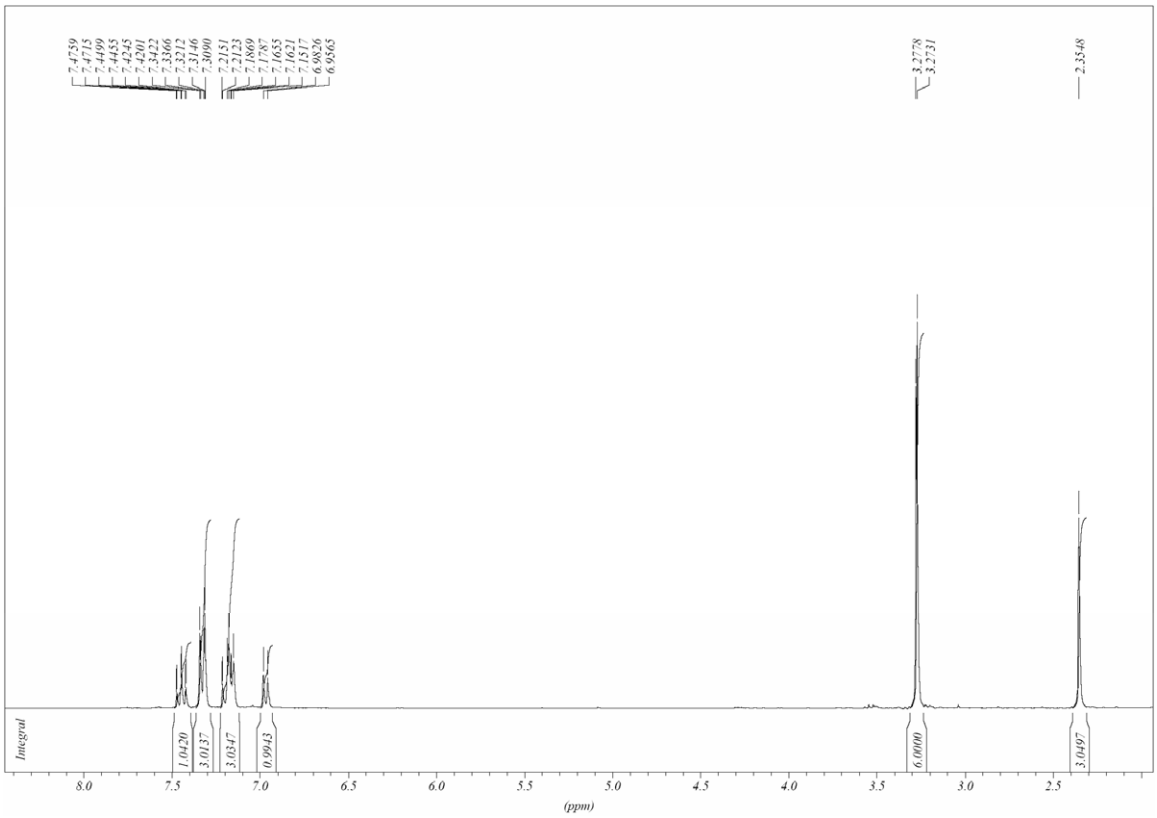
3-Methoxy-1-methyl-3-(4-tolyl)oxindole (2d)

99% yield. $[\alpha]_D^{25}$ = +81.7 (*c* = 1.0 in acetone). 91% ee [Chiralcel AS-H column, *n*-hexane/*i*-PrOH = 95:5, 1.0 mL/min, 254 nm; t_R = 8.08 min (minor) and 9.04 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.35 (s, 3H), 3.27 (s, 3H), 3.28 (s, 3H), 6.97 (d, *J* = 7.8 Hz, 1H), 7.15-7.22 (m, 3H), 7.32 (td, *J* = 1.7, 8.3 Hz, 3H), 7.45 (dt, *J* = 1.3, 7.6 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.1, 26.3, 53.1, 83.8, 108.5, 123.2, 125.6, 126.3, 128.1, 129.1, 130.1, 135.6, 138.2, 144.5, 175.3. ν_{max}/cm^{-1}: 2929, 2826, 1720, 1609, 1509, 1492, 1468, 1420; HRMS: *m/z* (EI) calculated for $C_{17}H_{17}O_2N$ ($[M]^+$): 267.1259, found 267.1262.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7.1517
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6.9565
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3.2731
2.3548
Integral
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3.0347
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6.0000
3.0497
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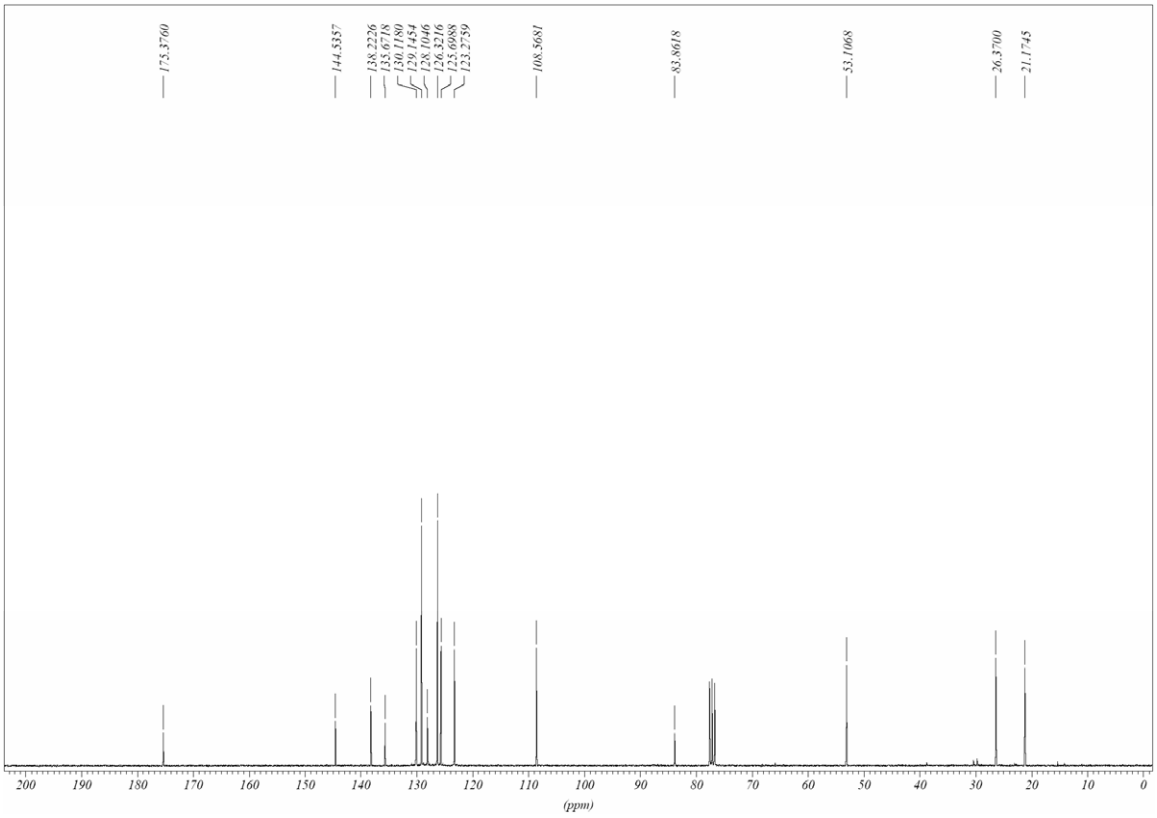
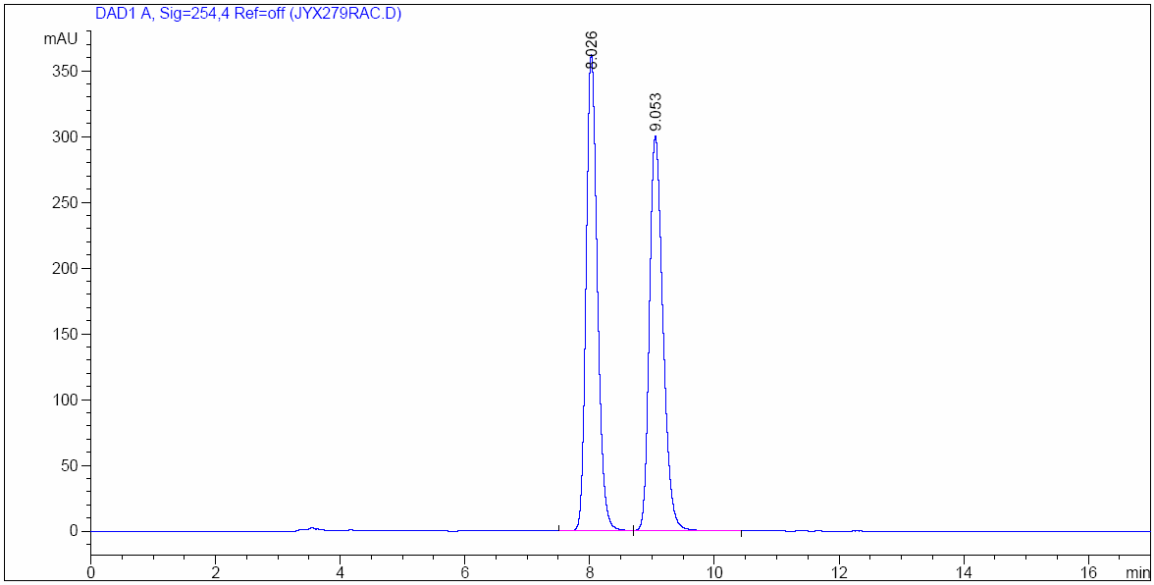
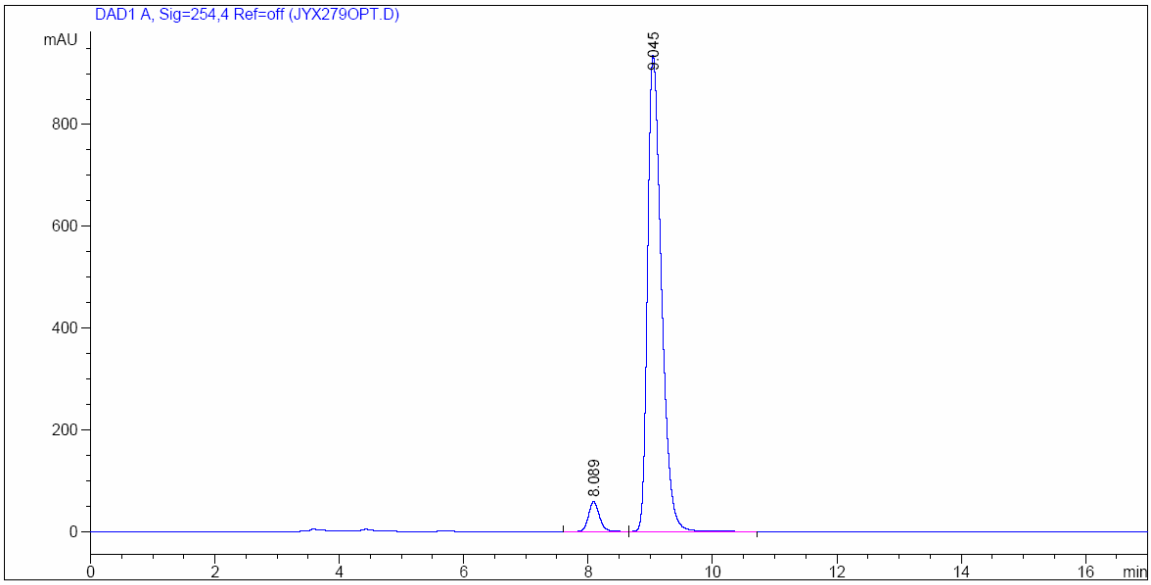
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
(ppm)


175.3760
144.5357
138.2226
135.6718
130.1180
129.1454
128.1046
126.3216
125.6988
123.2759
108.5681
83.8618
53.1068
26.3700
21.1745
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)



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


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.089 VV    0.1848  704.85931   58.38619   4.6451
   2   9.045 VB    0.2383 1.44694e4   936.22797  95.3549

Totals :                  1.51743e4   994.61416

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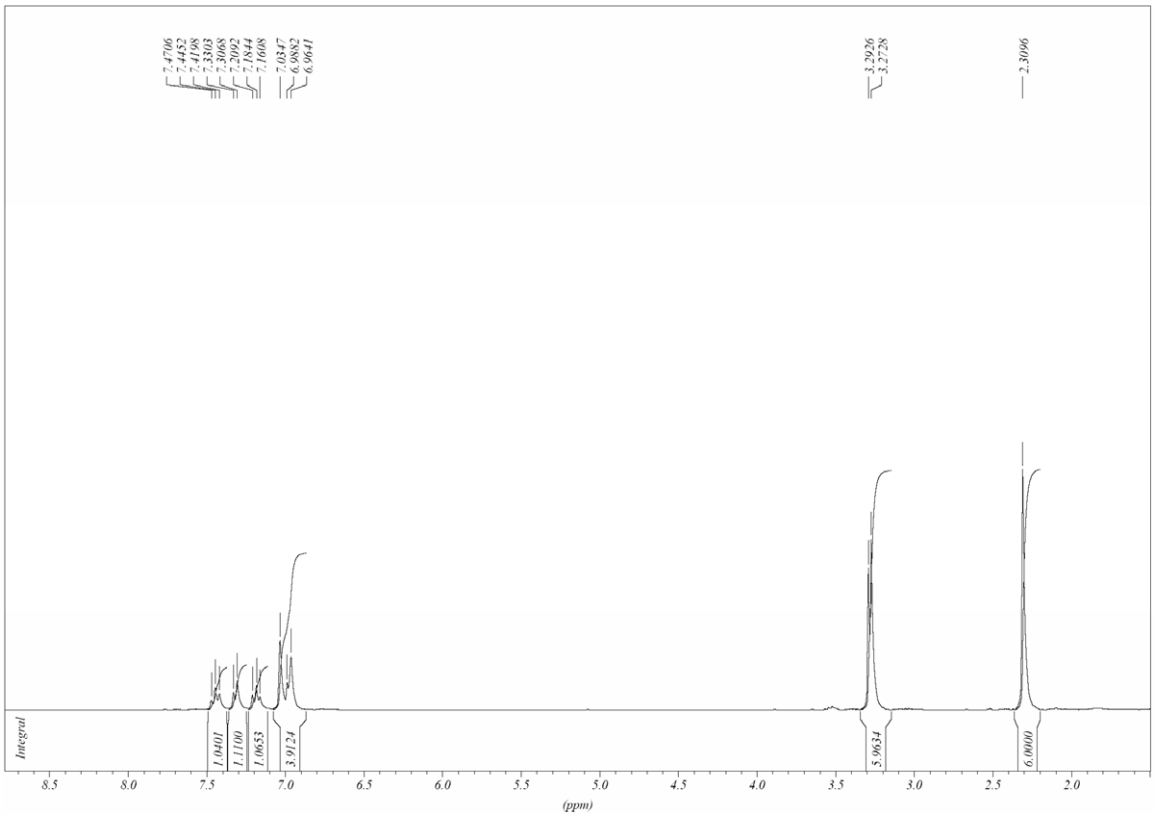
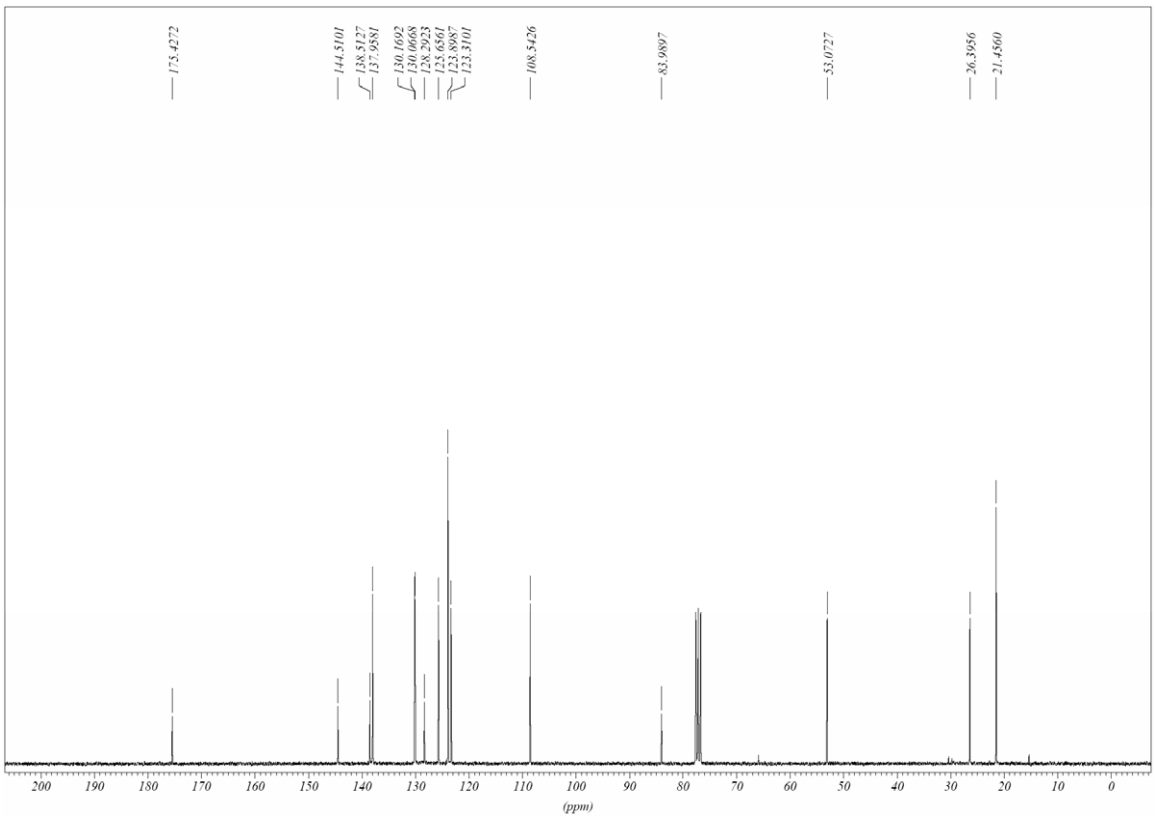
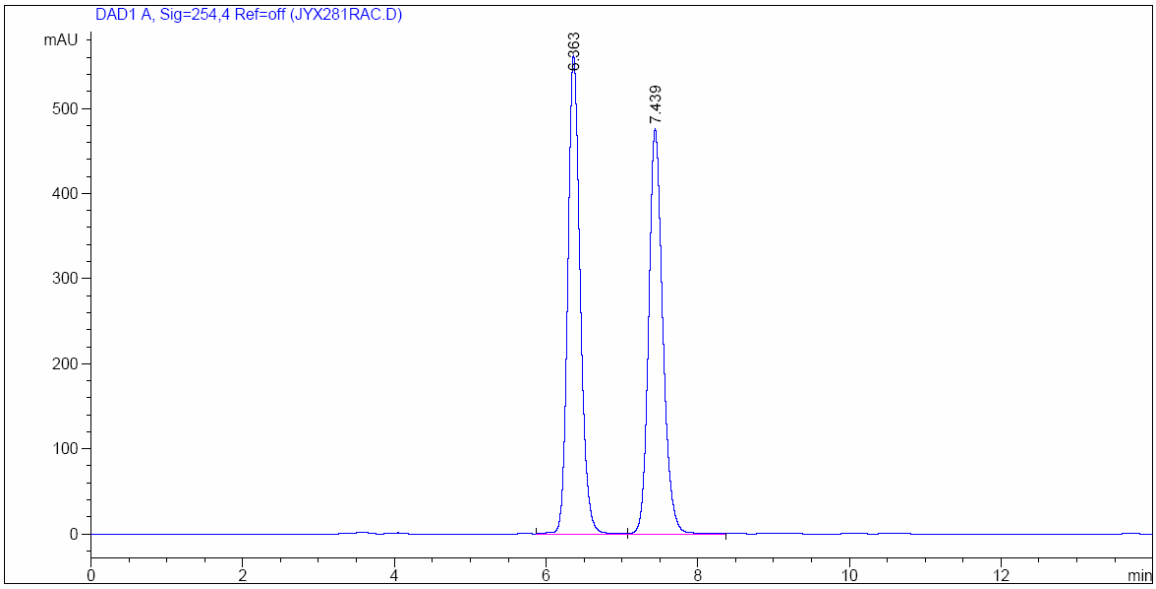
                         *** End of Report ***
```

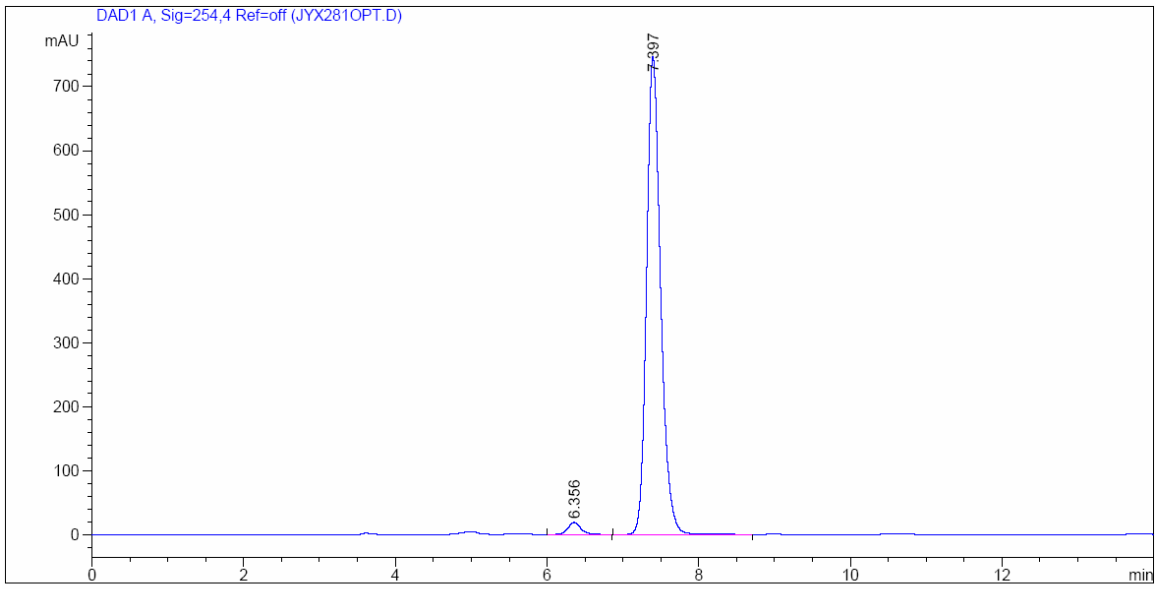
3-Methoxy-1-methyl-3-(3,5-dimethylphenyl)oxindole (2e)

89% yield. $[\alpha]_D^{25}$ = +60.5 (*c* = 1.0 in acetone). 96% ee [Chiralcel AD column, *n*-hexane/*i*-PrOH = 95:5, 1.0 mL/min, 254 nm; t_R = 6.35 min (minor) and 7.39 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.31 (s, 6H), 3.27 (s, 3H), 3.29 (s, 3H), 6.96-7.03 (m, 4H), 7.18 (t, *J* = 7.1 Hz, 1H), 7.32 (d, *J* = 7.1 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.4, 26.3, 53.0, 83.9, 108.5, 123.3, 123.8, 125.6, 128.2, 130.0, 130.1, 137.9, 138.5, 144.5, 175.4. ν_{max}/cm^{-1}: 2927, 2826, 1721, 1608, 1491, 1468, 1420; HRMS: *m/z* (EI) calculated for $C_{18}H_{19}NO_2$ ($[M]^+$): 281.1416, found 281.1412.


7.4706
7.4452
7.4198
7.3303
7.3068
7.2092
7.1844
7.1668
7.0347
6.9882
6.9641
3.2936
3.2728
2.3096
Integral
1.0401
1.1100
1.0653
3.9124
5.9634
6.0000
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
(ppm)


173.4272
144.5101
139.5127
137.9581
130.1692
130.0668
128.2923
123.6561
123.8987
123.3101
108.5426
83.9897
53.0727
26.3956
21.4560
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)



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

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


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.356 BB    0.1771  217.25282   18.48446   2.2141
   2   7.397 BV    0.1984 9594.88672  744.49866  97.7859

Totals :                   9812.13954  762.98312

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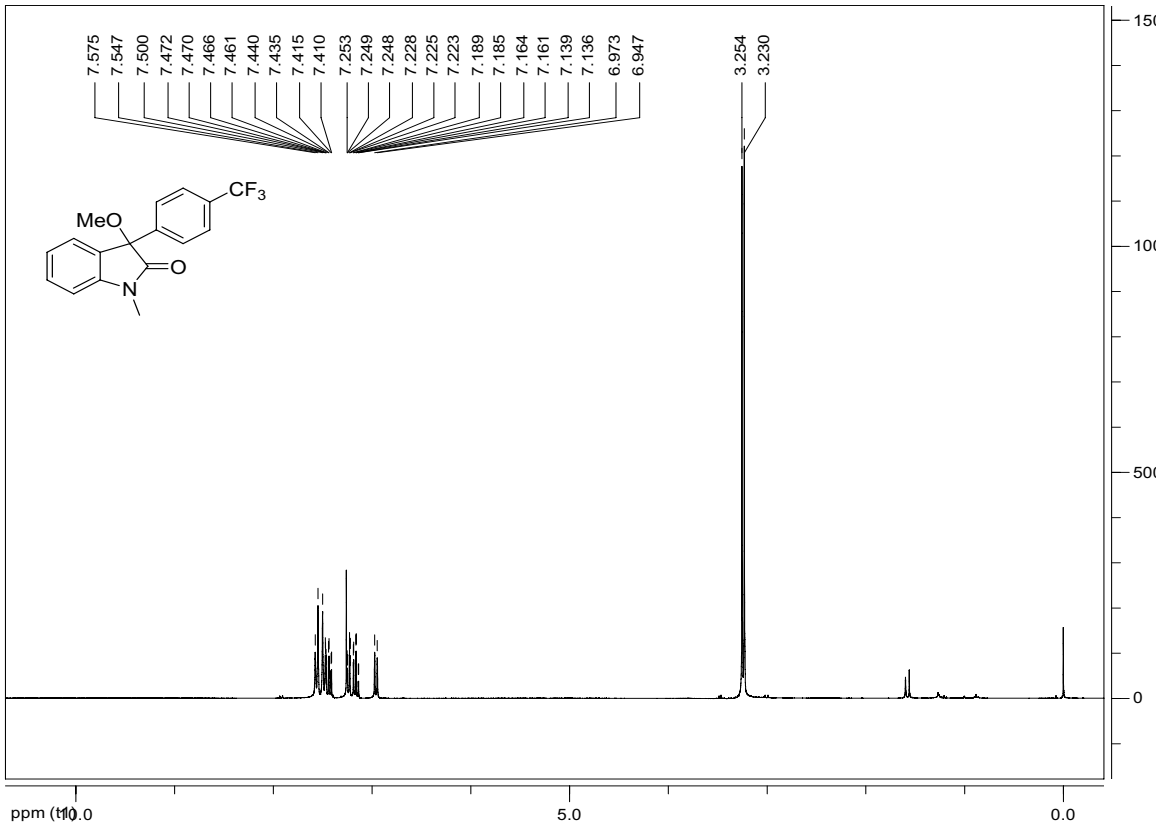
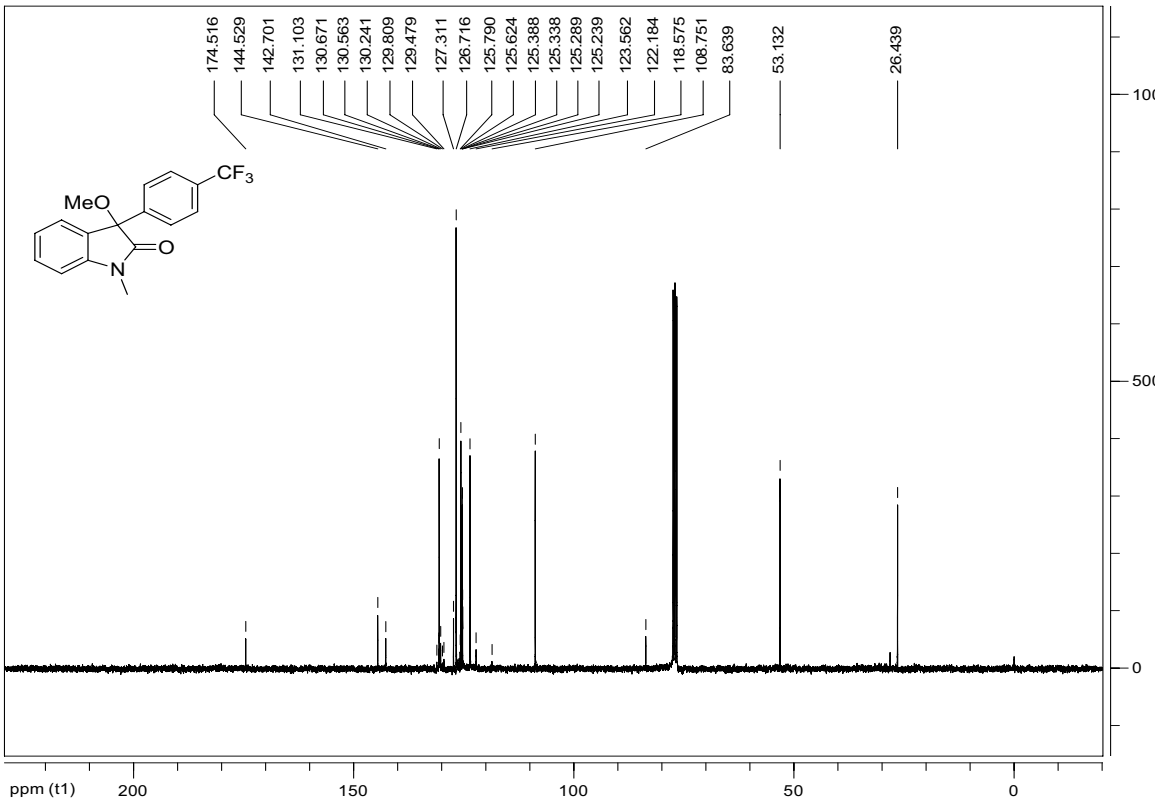
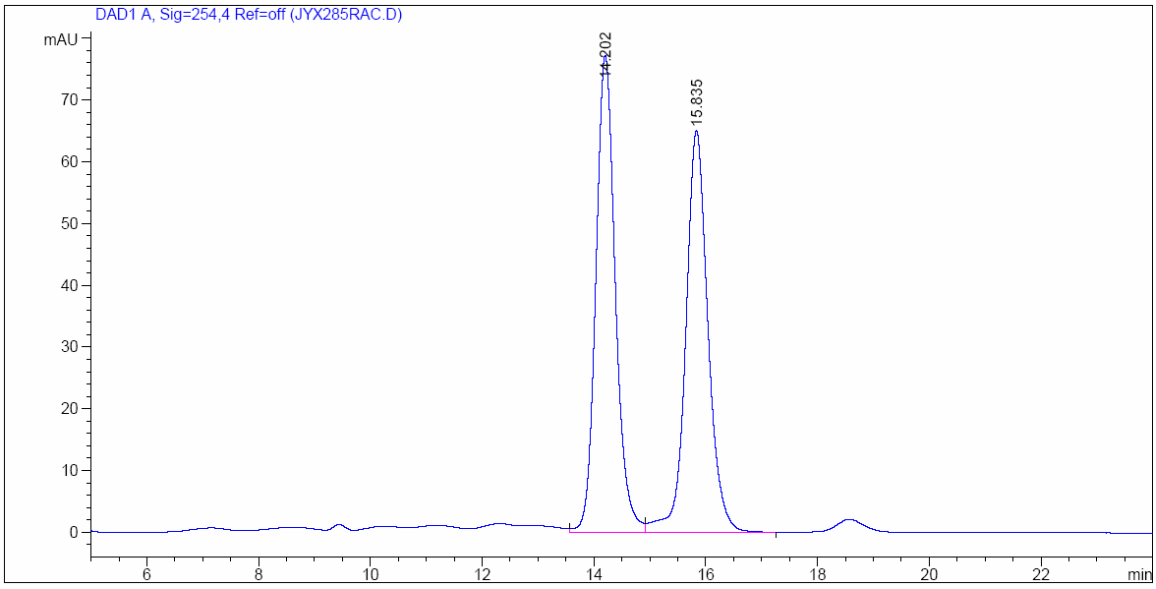
                      *** End of Report ***
```

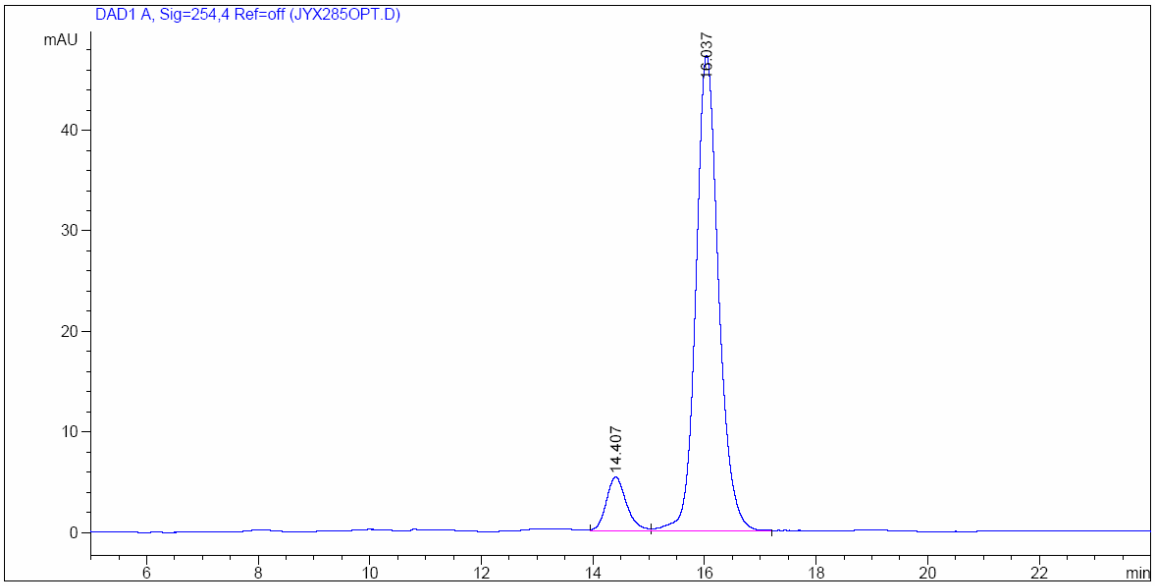
3-Methoxy-1-methyl-3-(4-trifluoromethylphenyl)oxindole (2f)

45% yield. $[\alpha]_D^{25}$ = +40.1 (*c* = 1.0 in acetone). 82% ee [Chiralcel AD column, *n*-hexane/*i*-PrOH = 99:1, 1.0 mL/min, 254 nm; t_R = 14.41 min (minor) and 16.03 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.23 (s, 3H), 3.25 (s, 3H), 6.96 (d, *J* = 7.7 Hz, 1H), 7.16 (td, *J* = 0.9, 7.5 Hz, 1H), 7.24 (ddd, *J* =0.5, 1.5, 7.5 Hz, 1H), 7.44 (td, *J* = 7.7, 1.5 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.4, 53.1, 83.6, 108.8, 123.6, 124.0, 125.3, 125.6, 126.7, 127.3, 130.5, 130.6, 142.7, 144.5, 174.5. ν_{max}/cm^{-1}: 2950, 2928, 1731, 1612, 1470, 1326, 1166, 1127, 1103; HRMS: *m/z* (EI+) calculated for $C_{17}H_{14}F_3NO_2Na$ ($[M+Na]^+$): 344.0869, found: 344.0858.


7.575
7.547
7.500
7.472
7.470
7.466
7.461
7.440
7.435
7.415
7.410
7.253
7.249
7.248
7.228
7.225
7.223
7.189
7.185
7.164
7.161
7.139
7.136
6.973
6.947
3.254
3.230
CF3
MeO
O
N
150
100
50
0
ppm (t1)
10.0
5.0
0.0


174.516
144.529
142.701
131.103
130.671
130.563
130.241
129.809
129.479
127.311
126.716
125.790
125.624
125.388
125.338
125.289
125.239
123.562
122.184
118.575
108.751
83.639
53.132
26.439
CF3
MeO
O
N
ppm (t1)
200
150
100
50
0


DAD1 A, Sig=254,4 Ref=off (JYX285RAC.D)
mAU
14.202
15.835
min

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

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


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  14.407 BV    0.3859  134.90701    5.35591   9.1835
   2  16.037 VB    0.4294 1334.10779   47.25684  90.8165

Totals :                  1469.01480   52.61276

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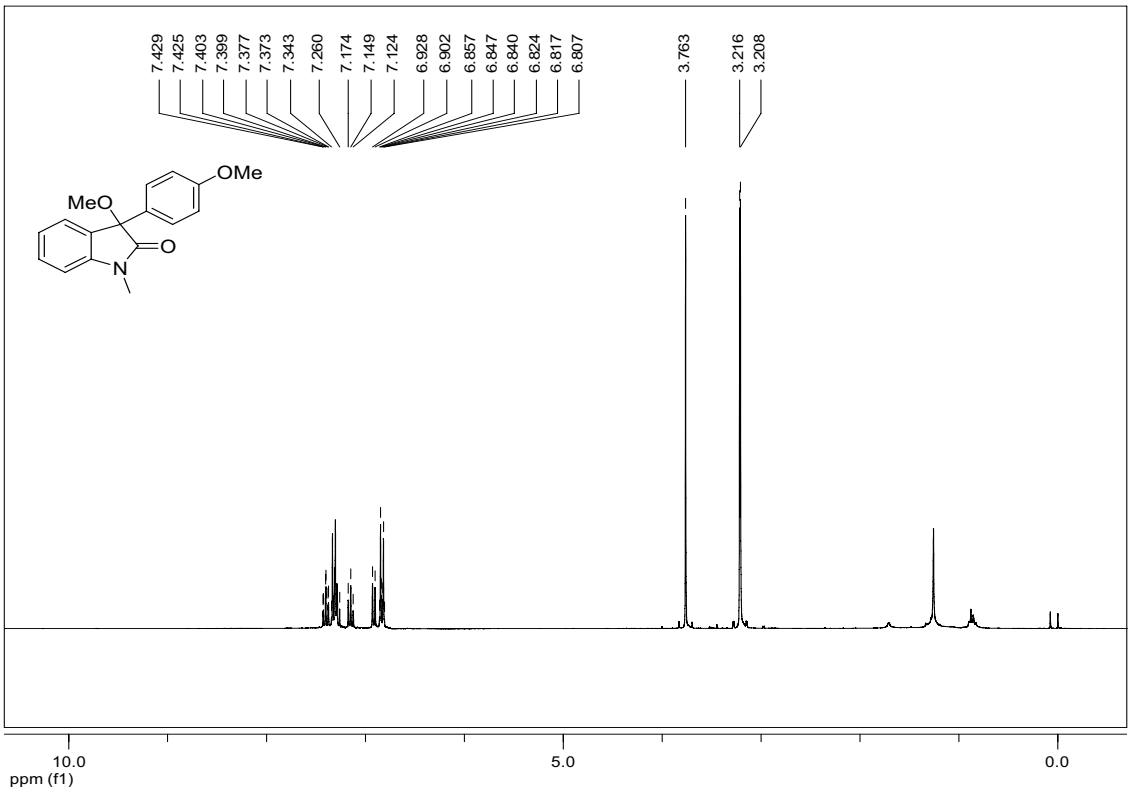
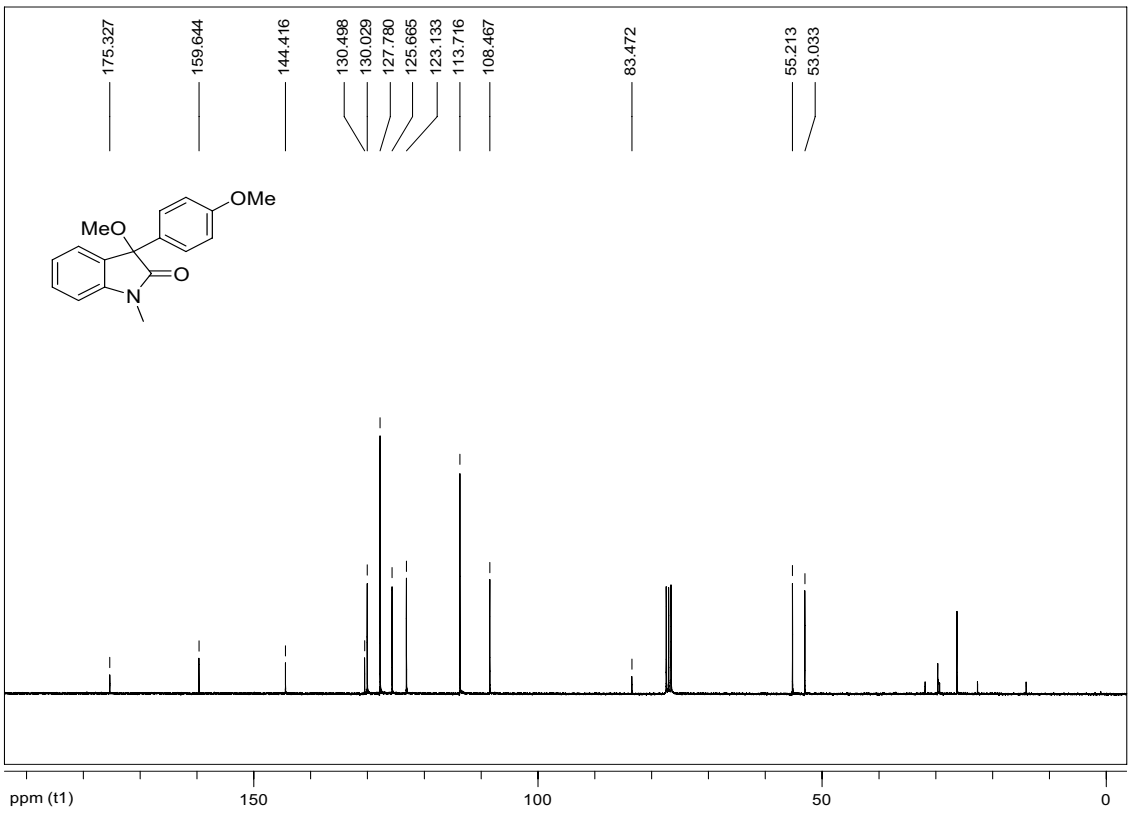
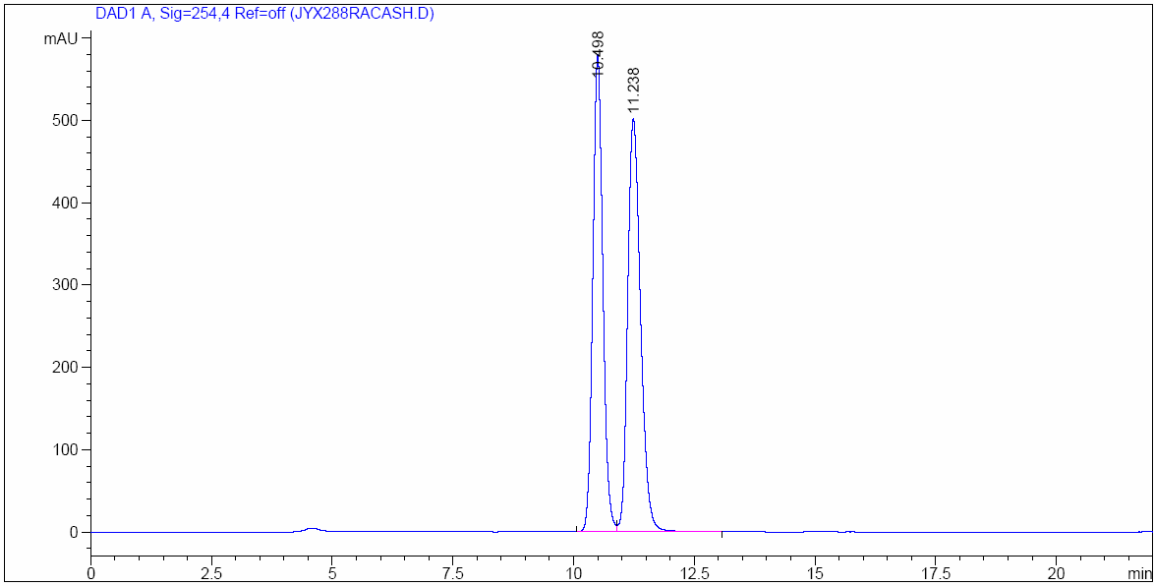
                      *** End of Report ***
```

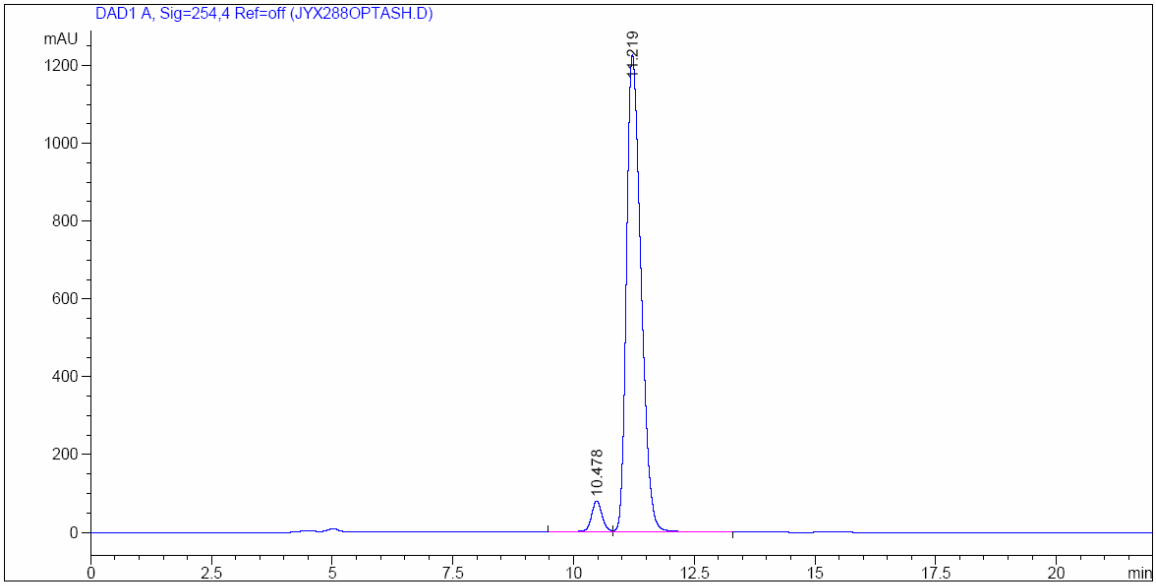
3-Methoxy-3-(4-methoxyphenyl)-1-methyloxindole (2g)

90% yield. $[\alpha]_D^{25}$ = +105.3 (*c* = 1.0 in acetone). 91% ee [Chiralcel AS-H column, *n*-hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm; t_R = 10.47 min (minor) and 11.21 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.21 (s, 3H), 3.22 (s, 3H), 3.76 (s, 3H), 6.83 (dt, *J* = 2.5, 8.9 Hz, 2H), 6.92 (d, *J* = 7.8 Hz, 1H), 7.15 (td, *J* = 0.7, 7.5 Hz, 1H), 7.28-7.34 (m,3H), 7.40 (td, *J* = 1.3, 7.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.3, 52.1, 54.2, 82.5, 107.5, 112.8, 122.2, 124.7, 126.8, 129.1, 129.5, 143.5, 158.7, 174.4. ν_{max}/cm^{-1}: 2928, 2829, 1724, 1610, 1510, 1467; HRMS: *m/z* (EI+) calculated for $C_{17}H_{17}NO_3Na$ ($[M+Na]^+$): 306.1101, found: 306.1091.


7.429
7.425
7.403
7.399
7.377
7.373
7.343
7.260
7.174
7.149
7.124
6.928
6.902
6.857
6.847
6.840
6.824
6.817
6.807
3.763
3.216
3.208
OMe
MeO
O
N
10.0
5.0
0.0
ppm (f1)


175.327
159.644
144.416
130.498
130.029
127.780
125.665
123.133
113.716
108.467
83.472
55.213
53.033
OMe
MeO
O
N
ppm (t1)
150
100
50
0



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


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.478 VV    0.2423 1270.98364   79.58650   4.7163
   2  11.219 VB    0.3328 2.56777e4  1223.60144  95.2837

Totals :                  2.69487e4  1303.18794

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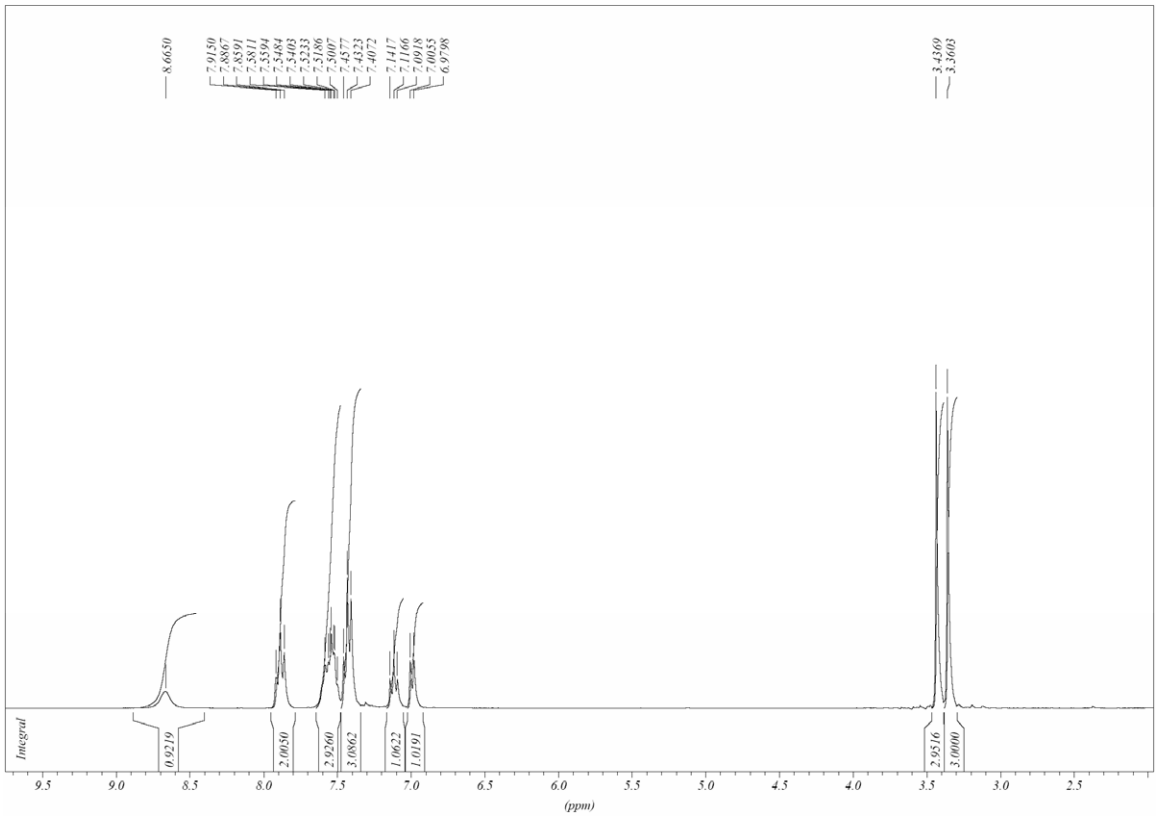
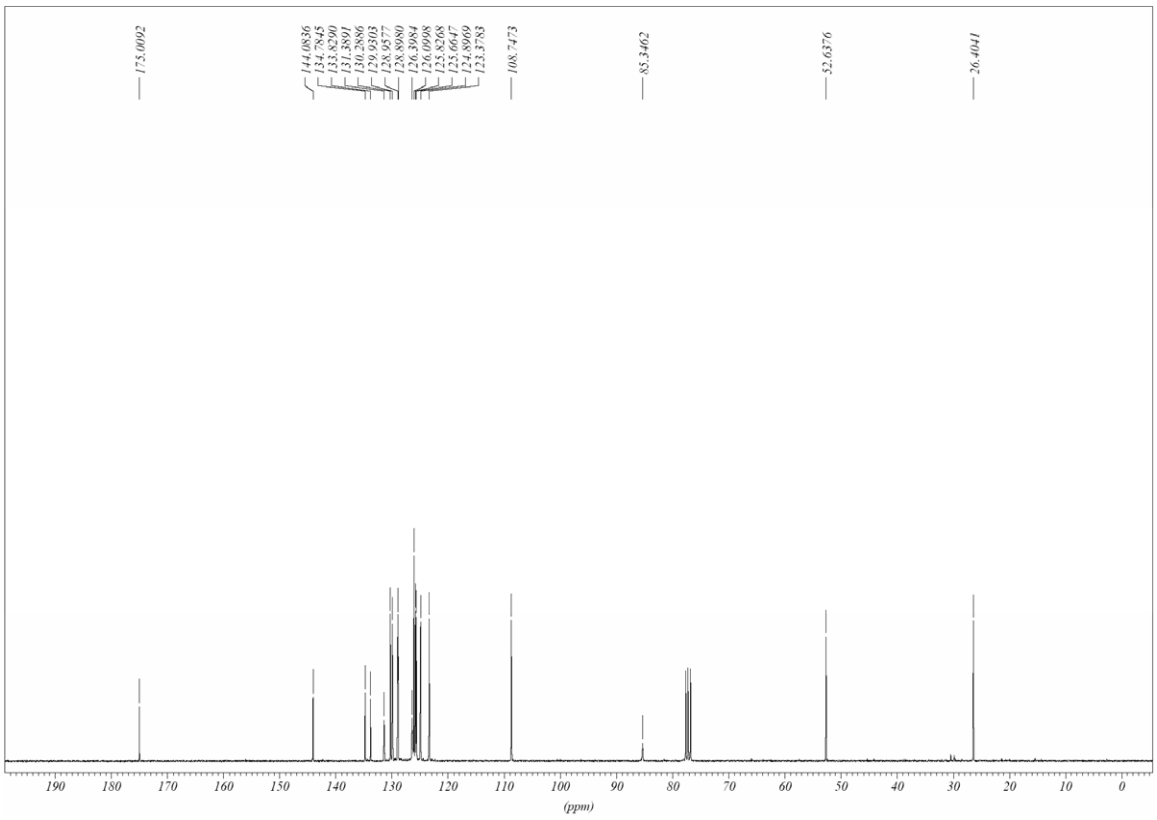
                          *** End of Report ***
```

3-Methoxy-1-methyl-3-(naphthalen-1-yl)oxindole (2h)

99% yield. $[\alpha]_D^{25}$ = –33 (*c* = 1.0 in acetone). 86% ee [Chiralcel AD column, *n*-hexane/*i*-PrOH = 95:5, 1.0 mL/min, 254 nm; t_R = 10.02 min (minor) and 13.76 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.36 (s, 3H), 3.43 (s, 3H), 6.99 (d, *J* = 7.7 Hz, 1H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 3H), 7.50-7.58 (m, 3H), 7.88 (t, *J* = 8.3 Hz, 2H), 8.66 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.4, 52.6, 85.3, 108.7, 123.3, 124.8, 125.6, 125.8, 126.0, 126.3, 128.8, 128.9, 129.9, 130.2, 131.3, 133.8, 134.7, 144.0, 175.0. ν_{max}/cm^{-1}: 3053, 2932, 2827, 1713, 1609, 1509, 1491, 1469, 1420; HRMS: *m/z* (EI) calculated for $C_{20}H_{17}NO_2$ ($[M]^+$): 303.1259, found 303.1261.


8.6650
7.9150
7.8867
7.8591
7.3811
7.3594
7.3484
7.3403
7.3233
7.3096
7.3007
7.2577
7.4323
7.4072
7.1417
7.1166
7.0918
7.0053
6.9798
3.4369
3.3603
Integral
0.9219
2.0050
2.9260
3.0862
1.0622
1.0191
2.9516
3.0000
(ppm)


175.0092
144.0836
134.7945
133.8290
131.8901
131.2886
129.9303
128.9577
128.8080
126.3984
126.0998
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125.6647
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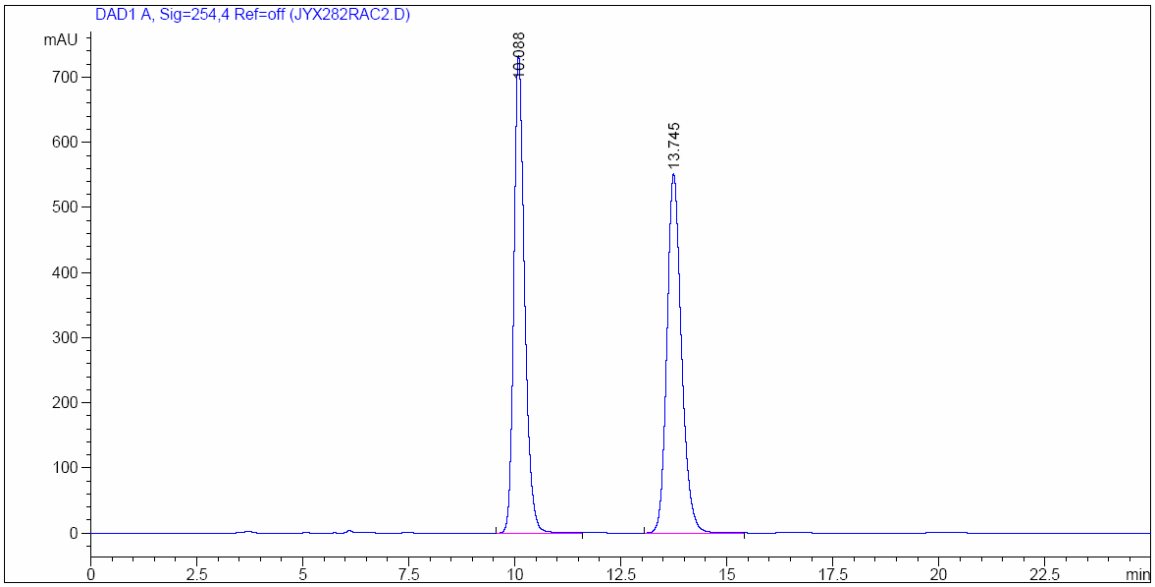
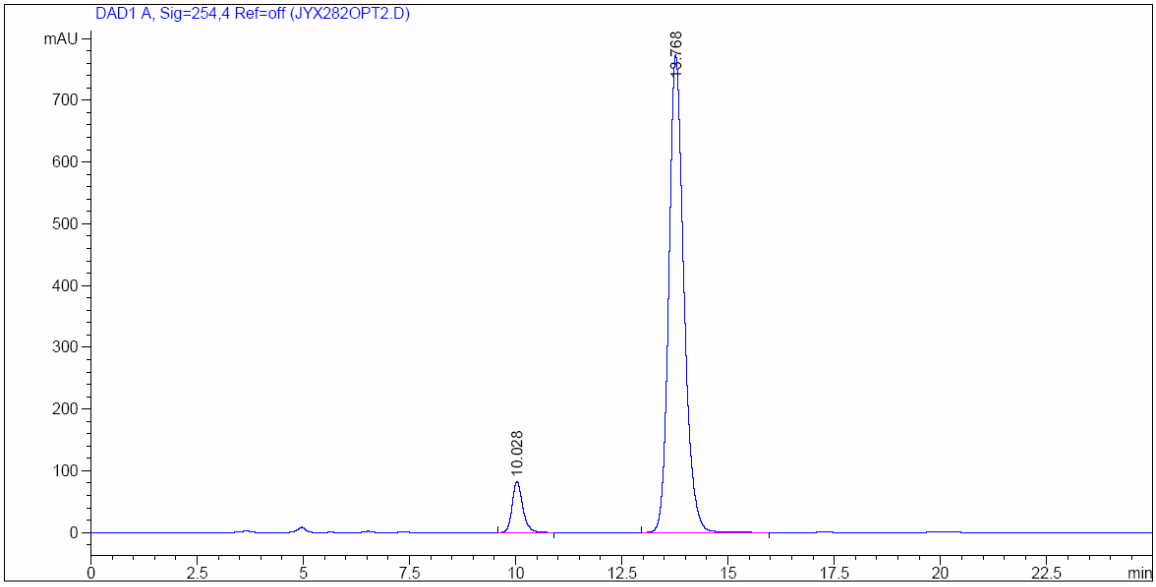
123.3783
108.7473
85.3462
52.6376
26.4041
(ppm)



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


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.028 BB    0.2616 1418.88281   82.12312   6.9434
   2  13.768 BB    0.3706 1.90162e4   774.03448  93.0566

Totals :                  2.04350e4   856.15760

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                      *** End of Report ***
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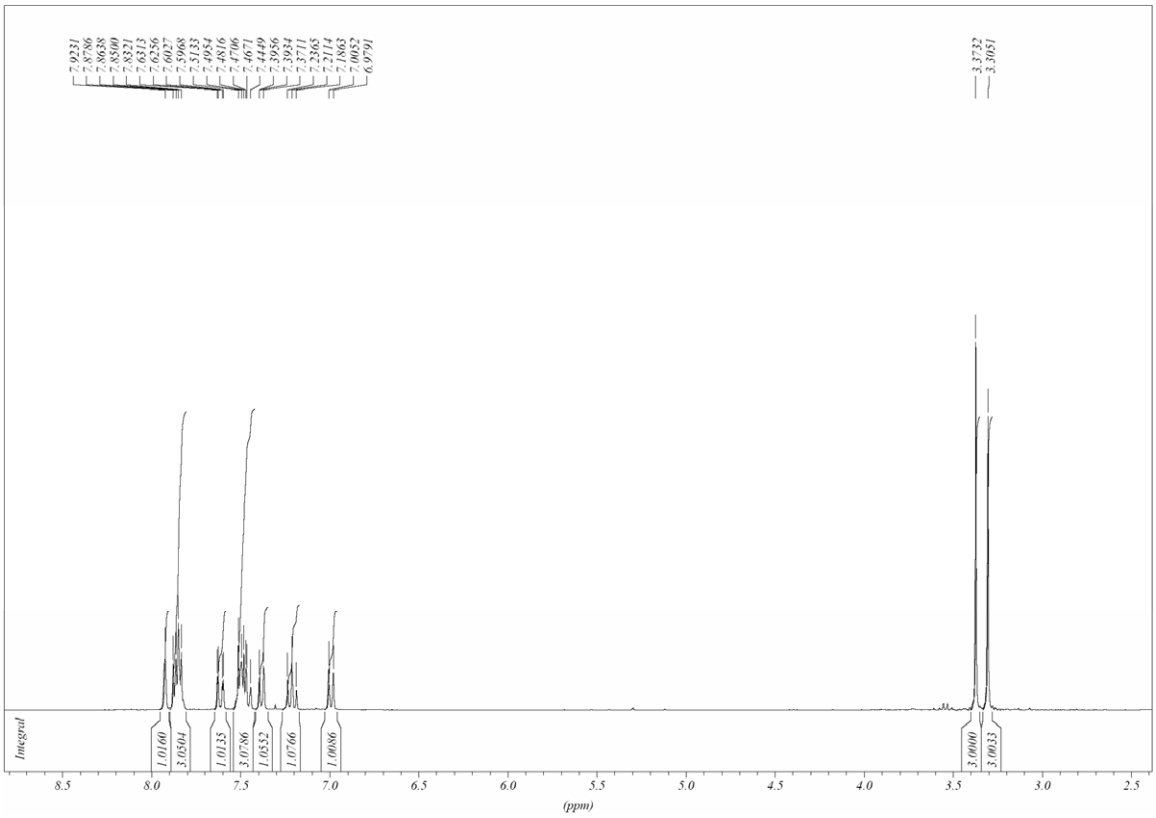
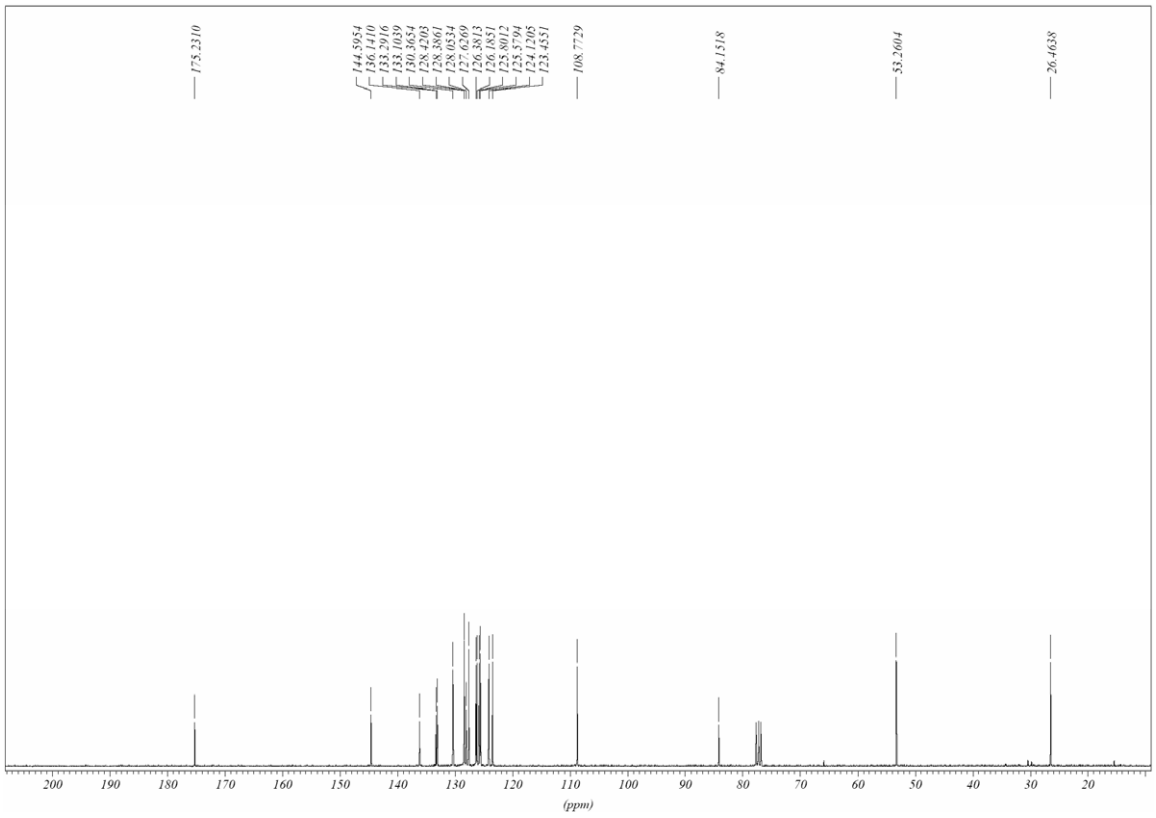
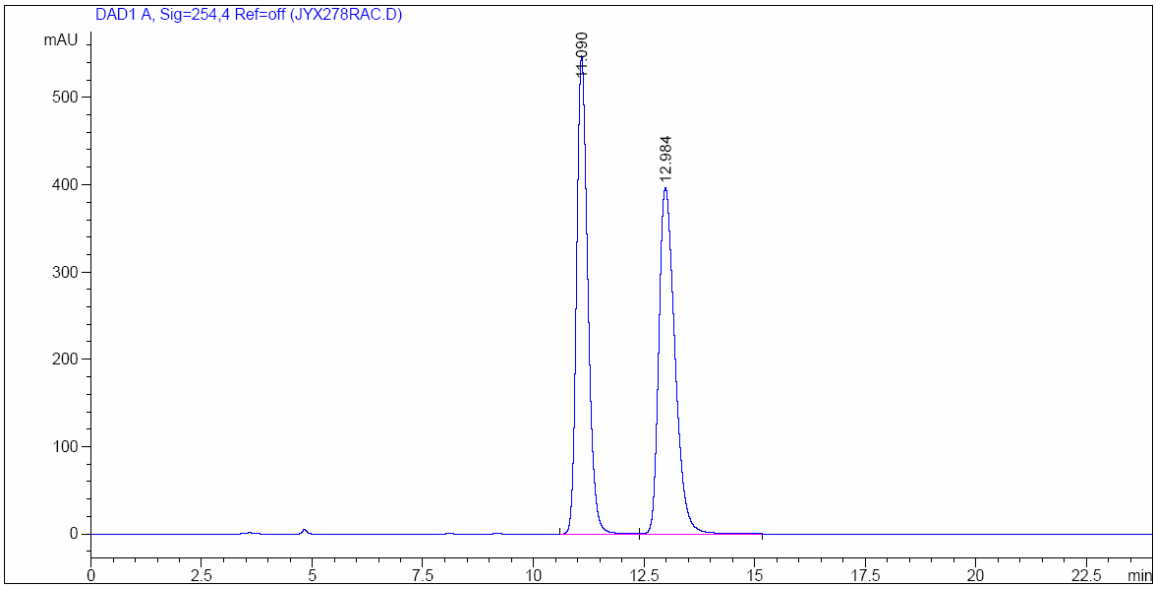
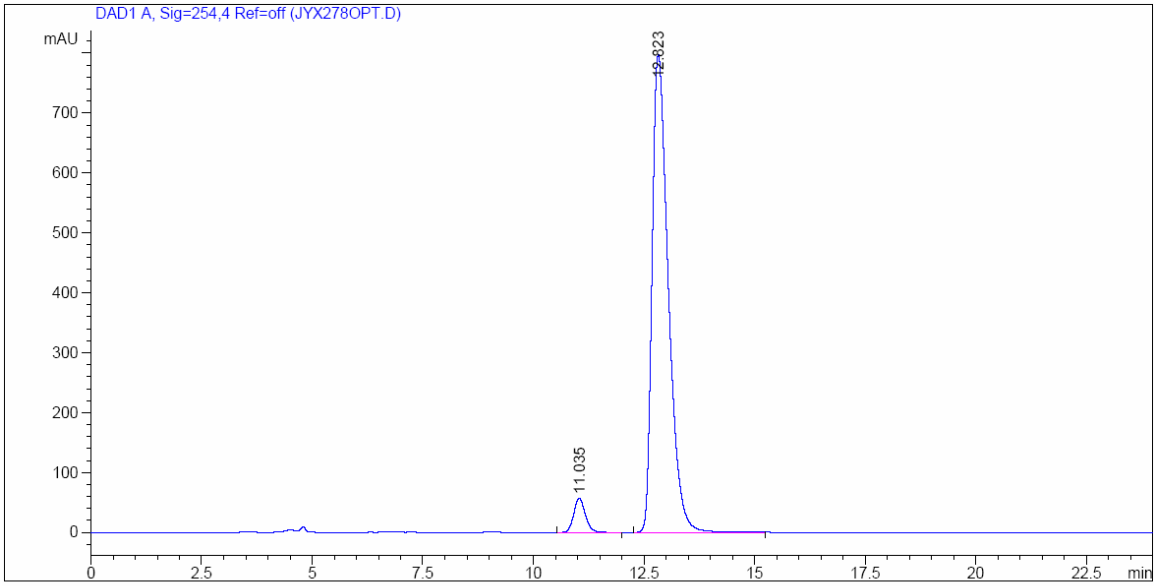
3-Methoxy-1-methyl-3-(naphthalen-2-yl)oxindole (2i)

92% yield. $[\alpha]_D^{25}$ = +62.4 (*c* = 1.0 in acetone). 90% ee [Chiralcel AS-H column, *n*-hexane/*i*-PrOH = 95:5, 1.0 mL/min, 254 nm; t_R = 11.03 min (minor) and 12.82 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.30 (s, 3H), 3.37 (s, 3H), 6.99 (d, *J* = 7.8 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.38 (d, *J* = 6.7 Hz, 1H), 7.44-7.53 (m, 3H), 7.61 (dd, *J* = 1.7, 8.6 Hz, 1H), 7.82-7.88 (m, 3H), 7.92 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.4, 53.2, 84.1, 108.7, 123.4, 124.1, 125.5, 125.8, 126.1, 126.3, 127.6, 128.0, 128.3, 128.4, 130.3, 133.1, 133.2, 136.1, 144.5, 175.2. ν_{max}/cm^{-1}: 3056, 2931, 2826, 1718, 1609, 1491, 1468, 1419; HRMS: *m/z* (EI) calculated for $C_{20}H_{17}NO_2$ ($[M]^+$): 303.1259, found 303.1260.


7.9231
7.8786
7.8638
7.8500
7.8321
7.6313
7.6256
7.6027
7.5968
7.5133
7.4954
7.4816
7.4706
7.4671
7.4440
7.3956
7.3934
7.3711
7.2365
7.2114
7.1863
7.0052
6.9791
3.3732
3.3651
Integral
1.0160
3.0504
1.0135
3.0786
1.0552
1.0766
1.0086
3.0000
3.0033
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
(ppm)


175.2310
144.5954
136.1410
133.2916
133.1039
130.3654
128.4203
128.3861
128.0534
127.6269
126.3813
126.1851
125.8012
125.5794
124.1205
123.4551
108.7729
84.1518
53.2604
26.4638
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
(ppm)



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

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


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.035 VB    0.2817 1030.24084   56.77153   4.8330
   2  12.823 BB    0.3887 2.02867e4   797.57813  95.1670

Totals :                  2.13169e4   854.34966

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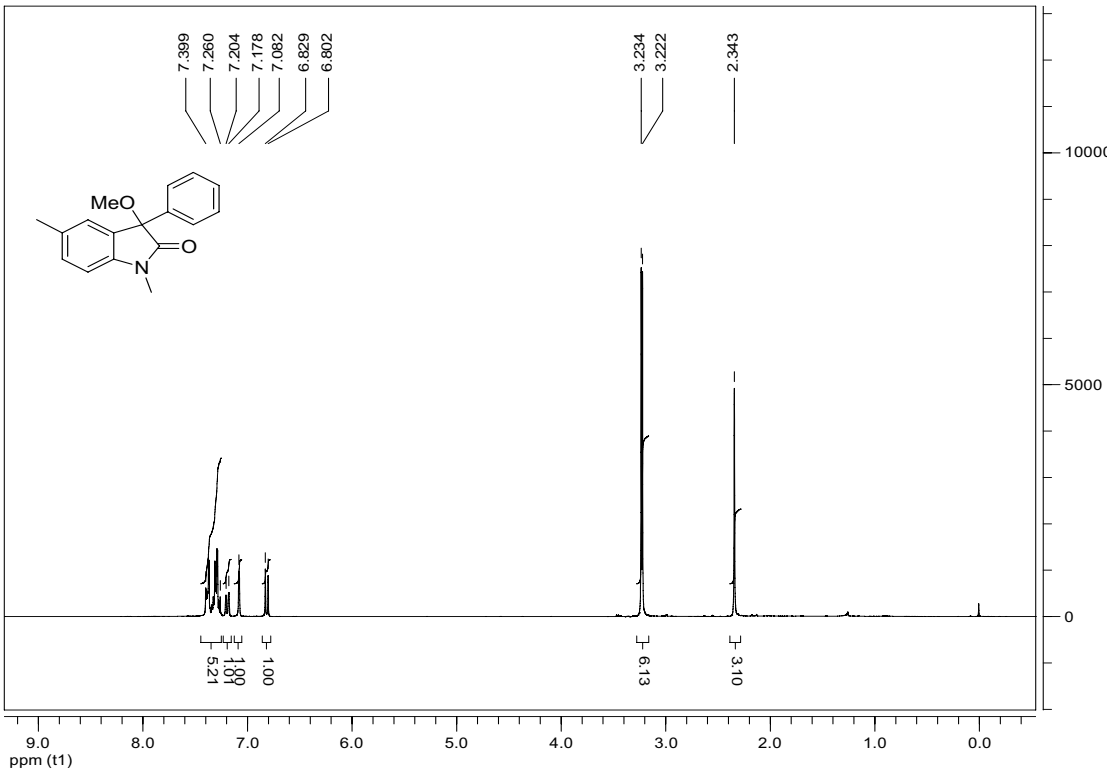
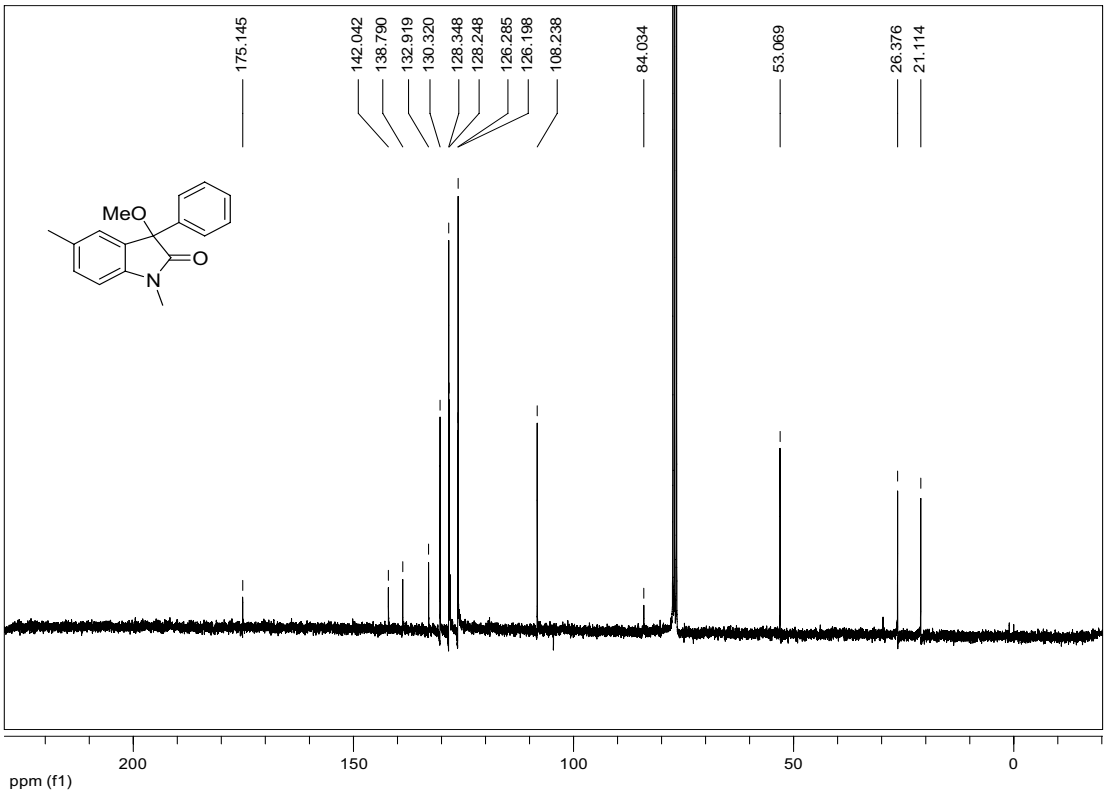
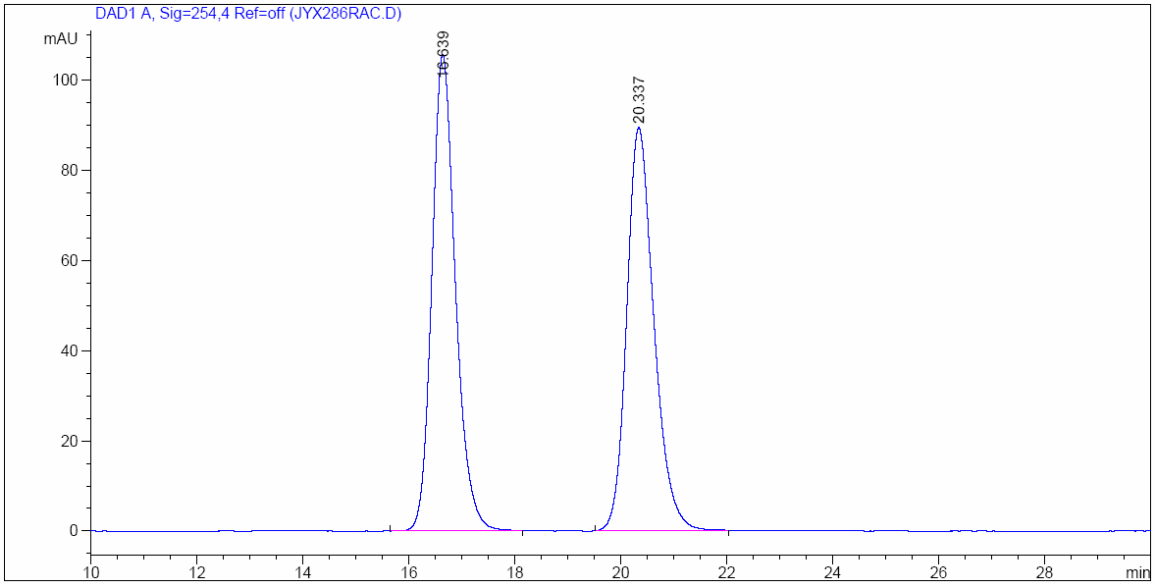
                      *** End of Report ***
```

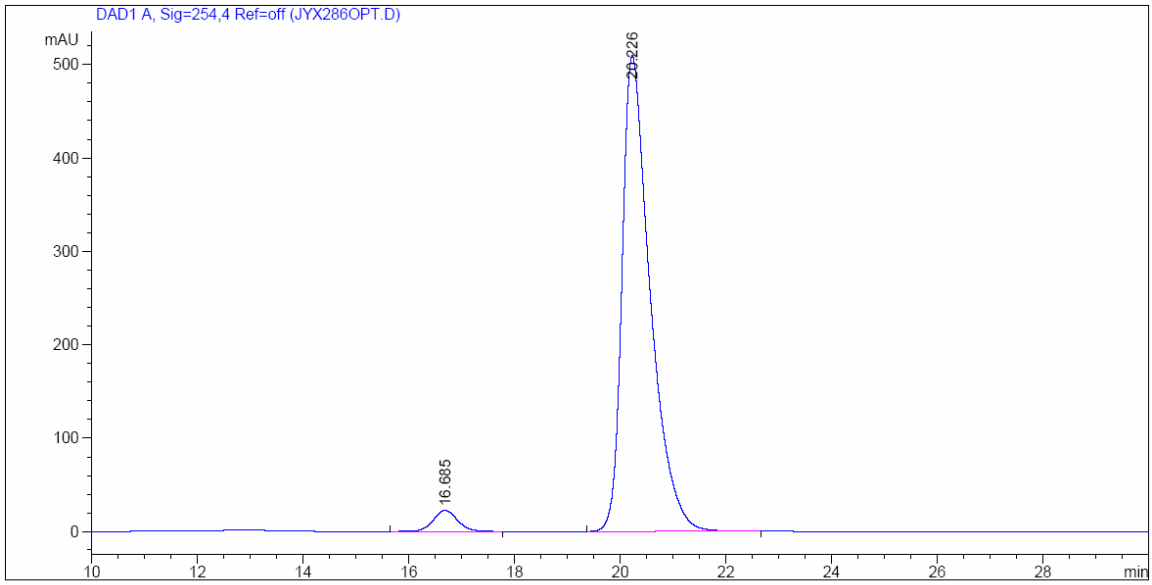
3-Methoxy-1,5-dimethyl-3-phenyloxindole (2j)

95% yield. $[\alpha]_D^{25}$ = +110.8 (*c* = 1.0 in acetone). 93% ee [Chiralcel AD column, *n*-hexane/*i*-PrOH = 99:1, 1.0 mL/min, 254 nm; t_R = 16.68 min (minor) and 20.22 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.34 (s, 3H), 3.23 (s, 3H), 3.23 (s, 3H), 6.82 (d, *J* = 7.9 Hz, 1H), 7.08 (s, 1H), 7.19 (dd, *J* = 0.8, 7.9 Hz, 1H), 7.25-7.39 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.6, 26.8, 54.5, 84.5, 108.7, 126.7, 128.5, 128.7, 128.8, 130.8, 133.4, 139.2, 142.5, 175.6. ν_{max}/cm^{-1}: 3060, 3021, 2929, 2824, 1725, 1619, 1602, 1498; HRMS: *m/z* (EI+) calculated for $C_{17}H_{17}NO_2Na$ ($[M+Na]^+$): 290.1151, found: 290.1146.


7.399
7.260
7.204
7.178
7.082
6.829
6.802
3.234
3.222
2.343
MeO
O
N
10000
5000
0
5.21
1.01
1.00
6.13
3.10
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


175.145
142.042
138.790
132.919
130.320
128.348
128.248
126.285
126.198
108.238
84.034
53.069
26.376
21.114
MeO
O
N
200
150
100
50
0
ppm (f1)



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

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


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  16.685 BB    0.4948  724.92938   22.56577   3.7088
   2  20.226 BB    0.5430 1.88213e4   509.51117  96.2912

Totals :                  1.95462e4   532.07694

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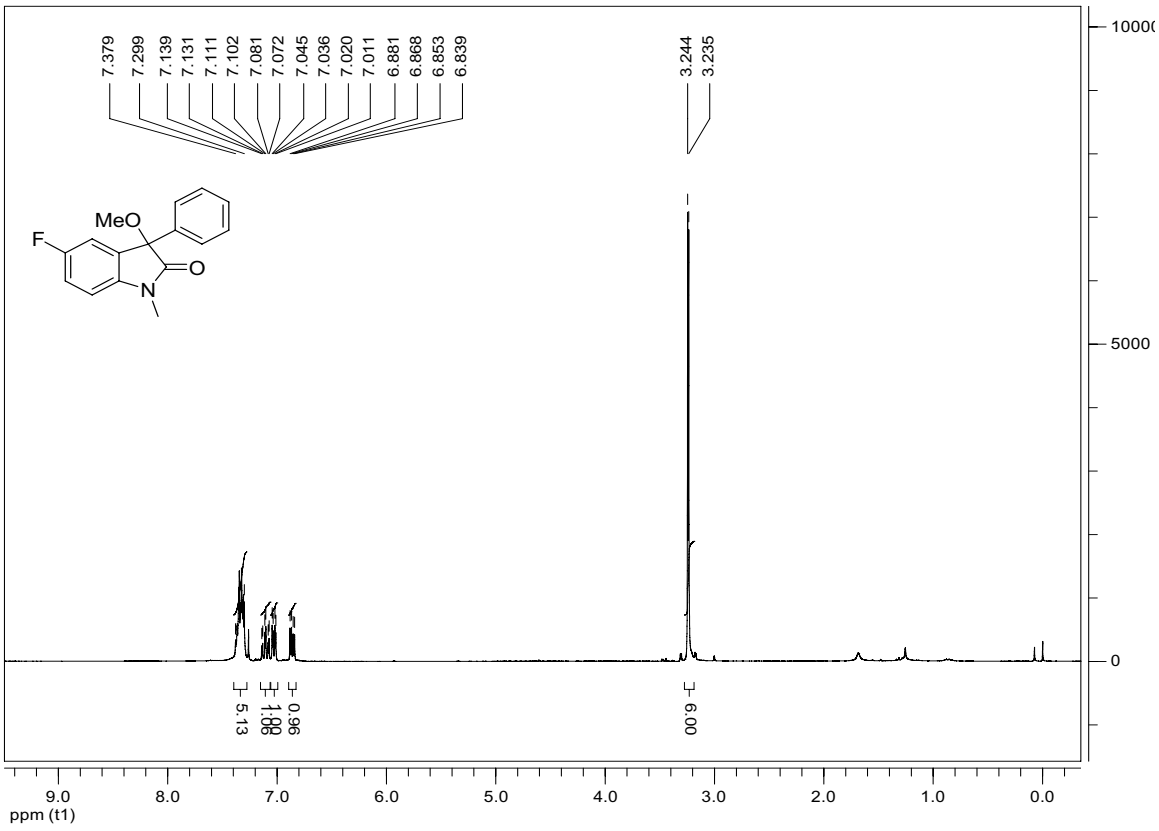
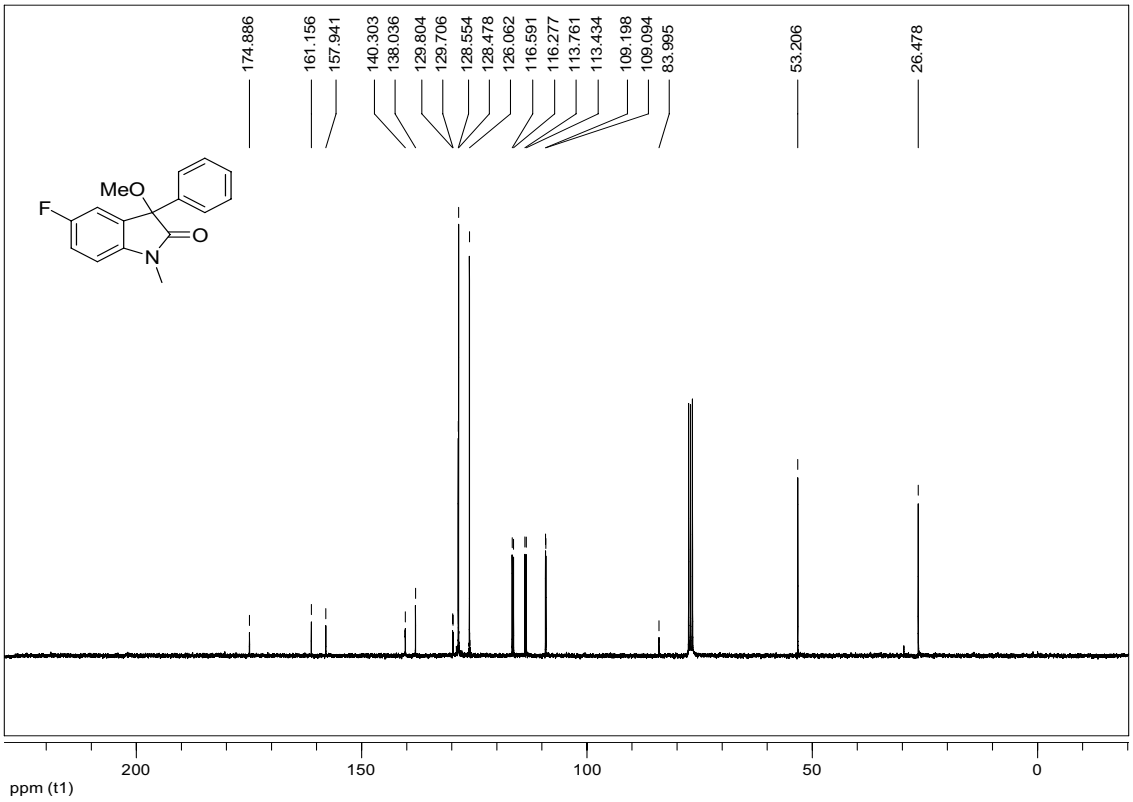
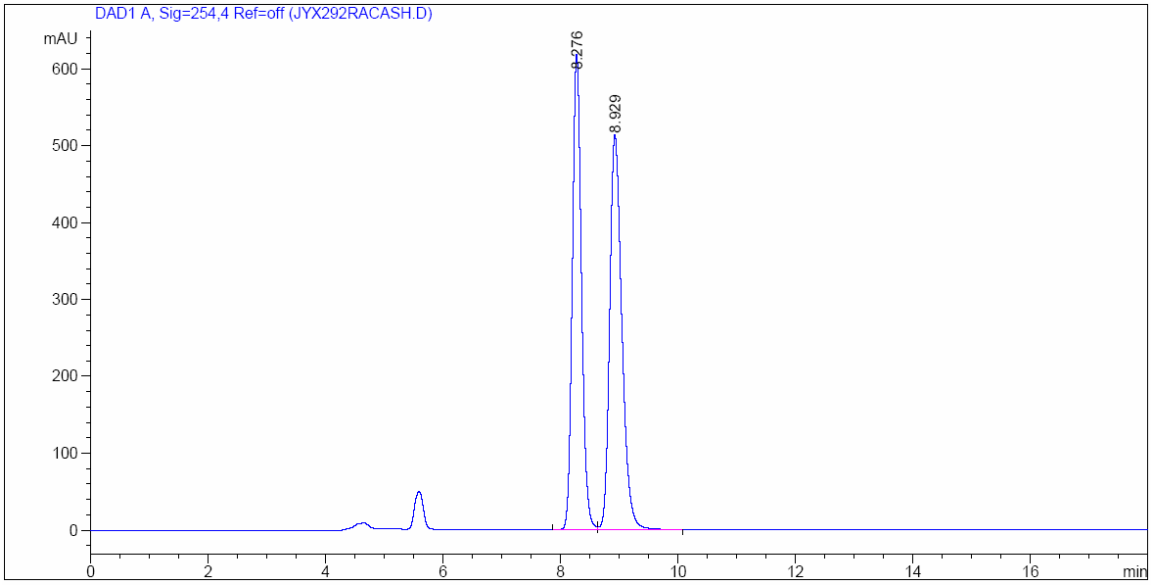
                      *** End of Report ***
```

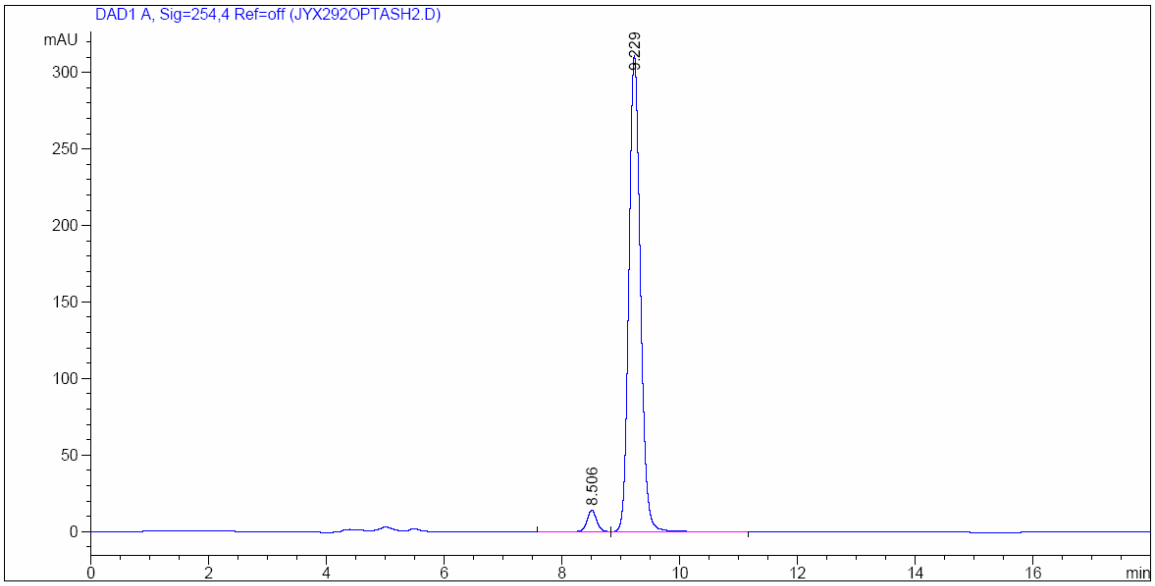
5-Fluoro-3-methoxy-1-methyl-3-phenyloxindole (2k)

76% yield. $[\alpha]_D^{25}$ = +46.7 (*c* = 1.0 in acetone). 93% ee [Chiralcel AS-H column, *n*-hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm; t_R = 8.50 min (minor) and 9.23 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.24 (s, 3H), 3.25 (s, 3H), 6.86 (dd, *J* = 4.0, 8.5 Hz, 1H,), 7.03 (dd, *J* = 2.6, 7.5 Hz, 1H), 7.11 (td, *J* = 2.6, 8.8 Hz, 1H,), 7.30-7.38 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.9, 53.7, 84.5, 109.6, 114.1, 116.9, 126.5, 128.9, 129.0, 130.2, 138.5, 140.8, 160.0, 175.4. ν_{max}/cm^{-1}: 3060, 2932, 2828, 1727, 1619, 1494; HRMS *m/z* (EI+) calculated for $C_{16}H_{14}FNO_2Na$ ($[M+Na]^+$): 294.0901, found: 294.0894.


7.379
7.299
7.139
7.131
7.111
7.102
7.081
7.072
7.045
7.036
7.020
7.011
6.881
6.868
6.853
6.839
3.244
3.235
MeO
F
O
N
5.13
1.00
0.96
6.00
10000
5000
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


174.886
161.156
157.941
140.303
138.036
129.804
129.706
128.554
128.478
126.062
116.591
116.277
113.761
113.434
109.198
109.094
83.995
53.206
26.478
MeO
F
O
N
200
150
100
50
0
ppm (t1)


DAD1 A, Sig=254,4 Ref=off (JYX292RACASH.D)
mAU
600
500
400
300
200
100
0
8.276
8.929
0
2
4
6
8
10
12
14
16
min

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

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


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.506 BV    0.1816  161.47610   14.09918   3.6788
   2   9.229 VB    0.2151 4227.85889  309.93079  96.3212

Totals :                   4389.33499  324.02996

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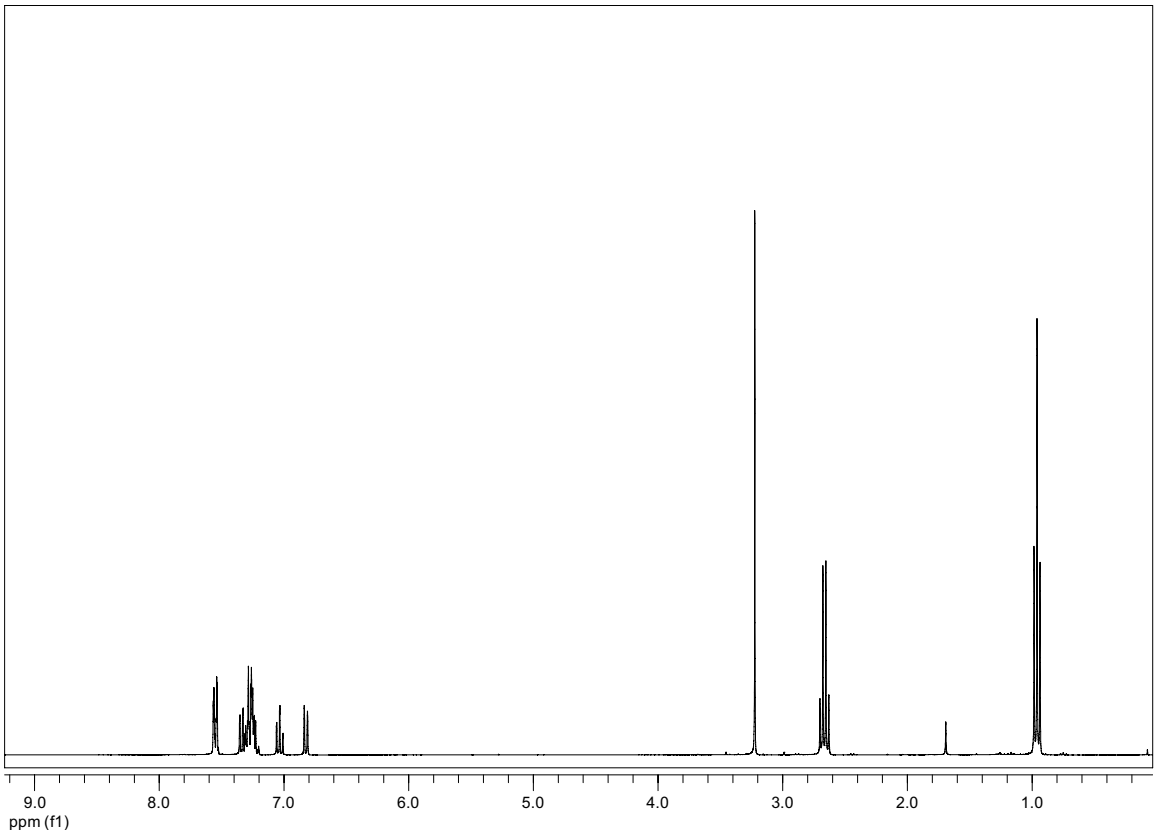
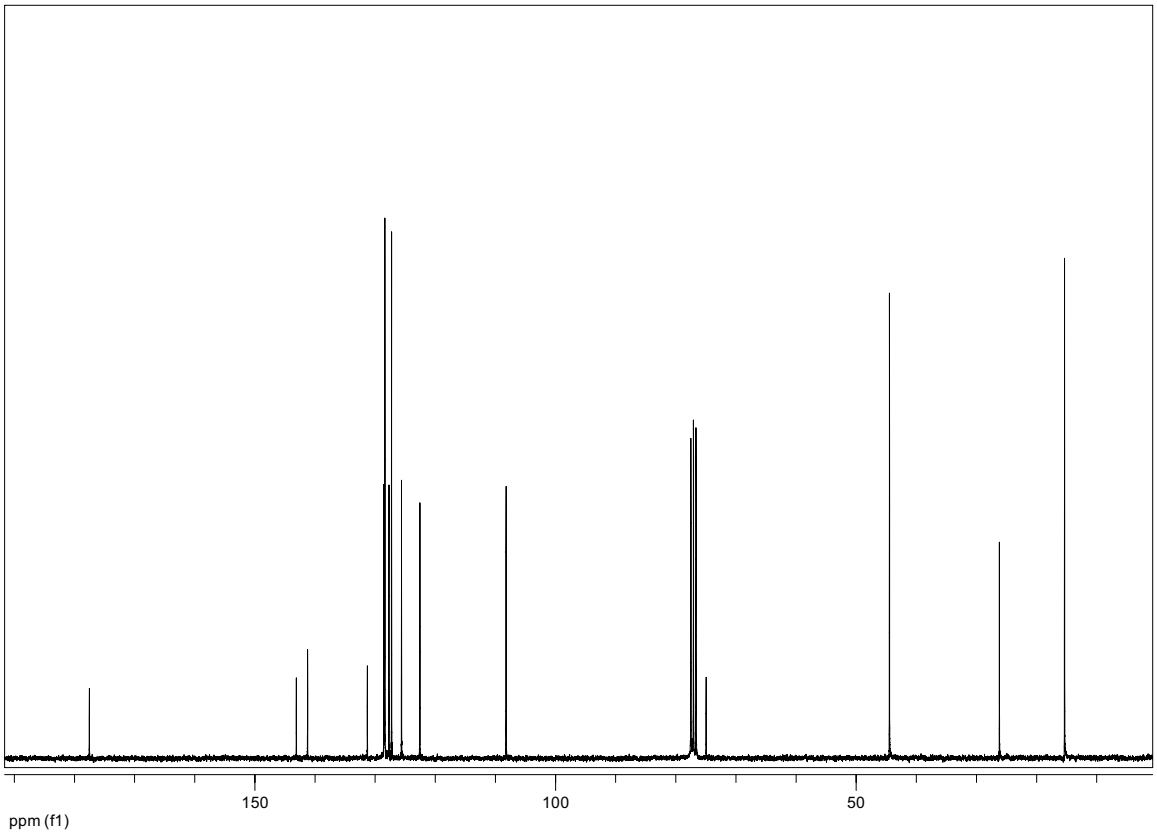
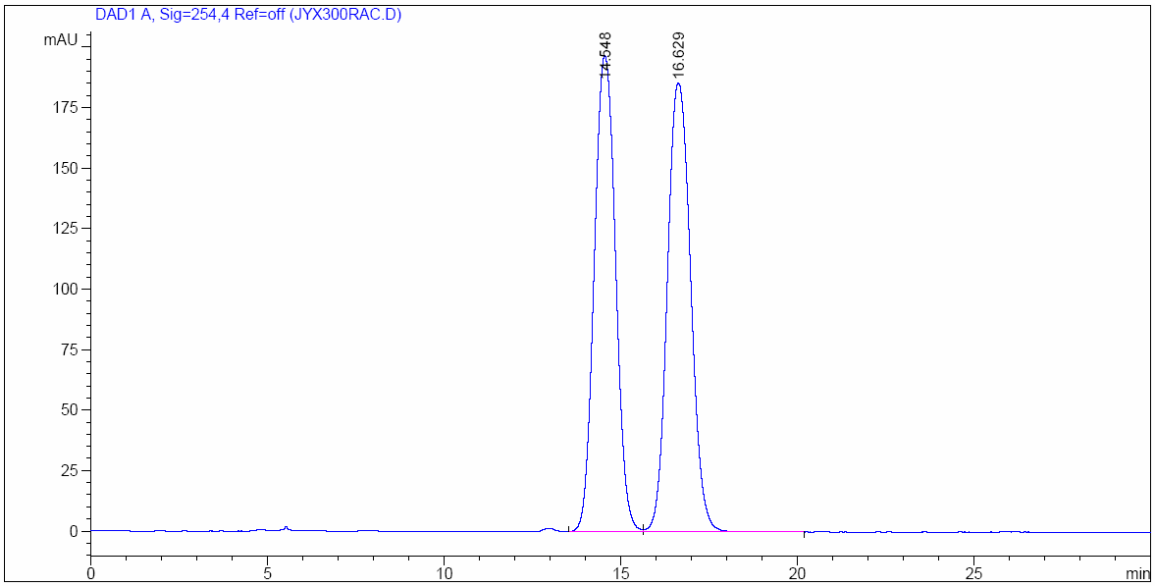
                      *** End of Report ***
```

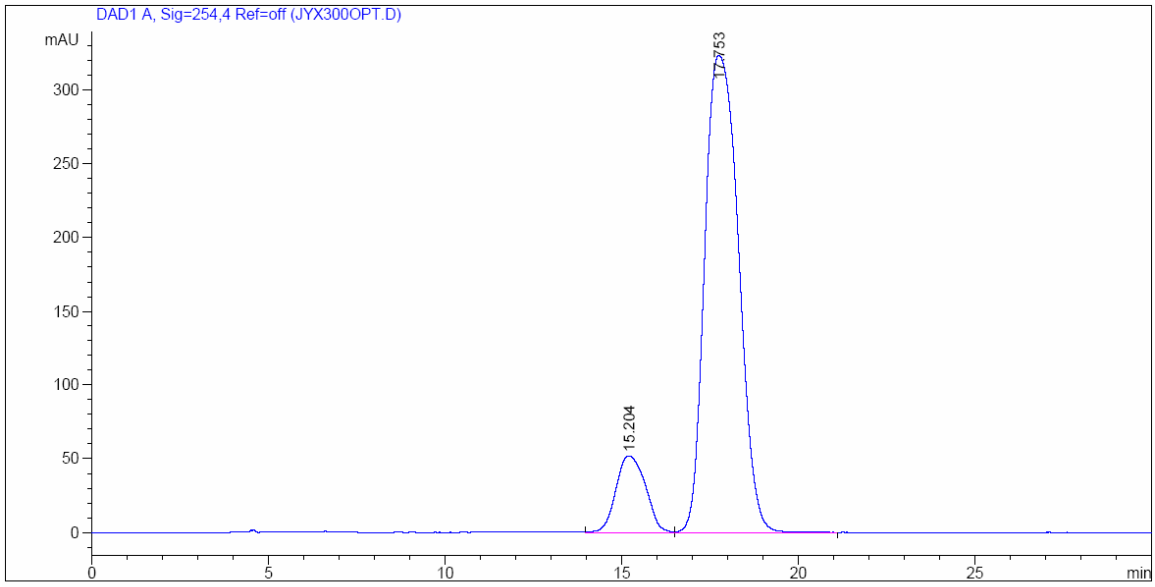
3-(Diethylamino)-1-methyl-3-phenyloxindole (2l)

93% yield. $[\alpha]_D^{25}$ = –128.9 (*c* = 1.0 in acetone). 75% ee [Chiralcel AD column, *n*-hexane/*i*-PrOH = 99.5:0.5, 1.0 mL/min, 254 nm; t_R = 15.20 min (minor) and 17.75 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.96 (t, *J* = 7.1 Hz, 6H), 2.67 (q, *J* = 7.1, 7.1 Hz, 4H), 3.22 (s, 3H), 6.82 (d, *J* = 7.8 Hz, 1H), 7.04 (t, *J* = 7.8 Hz, 1H), 7.21-7.36 (m, 5H), 7.55 (d, *J* = 8.1 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.3, 26.2, 44.4, 74.9, 108.2, 122.5, 125.6, 127.2, 127.7, 128.4, 128.5, 131.3, 141.2, 143.1, 177.5. ν_{max}/cm^{-1}: 3057, 2970, 2869, 1713, 1610; HRMS: *m/z* (EI+) calculated for $C_{19}H_{23}N_2O$ ($[M+H]^+$): 295.1805, found: 295.1791.







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


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  15.204 VV    0.9492 3001.68579   51.71533  12.2712
   2  17.753 VB    1.0620 2.14596e4   323.48184  87.7288

Totals :                  2.44613e4   375.19717

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                      *** End of Report ***
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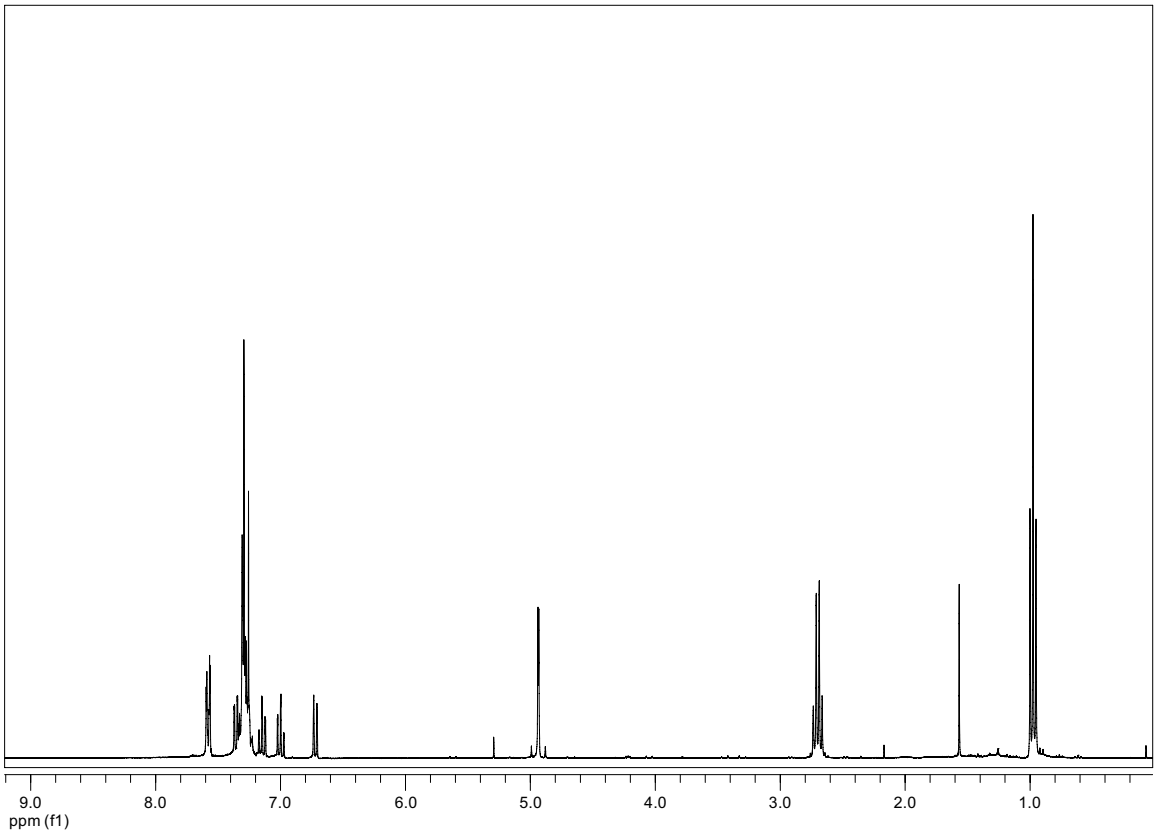
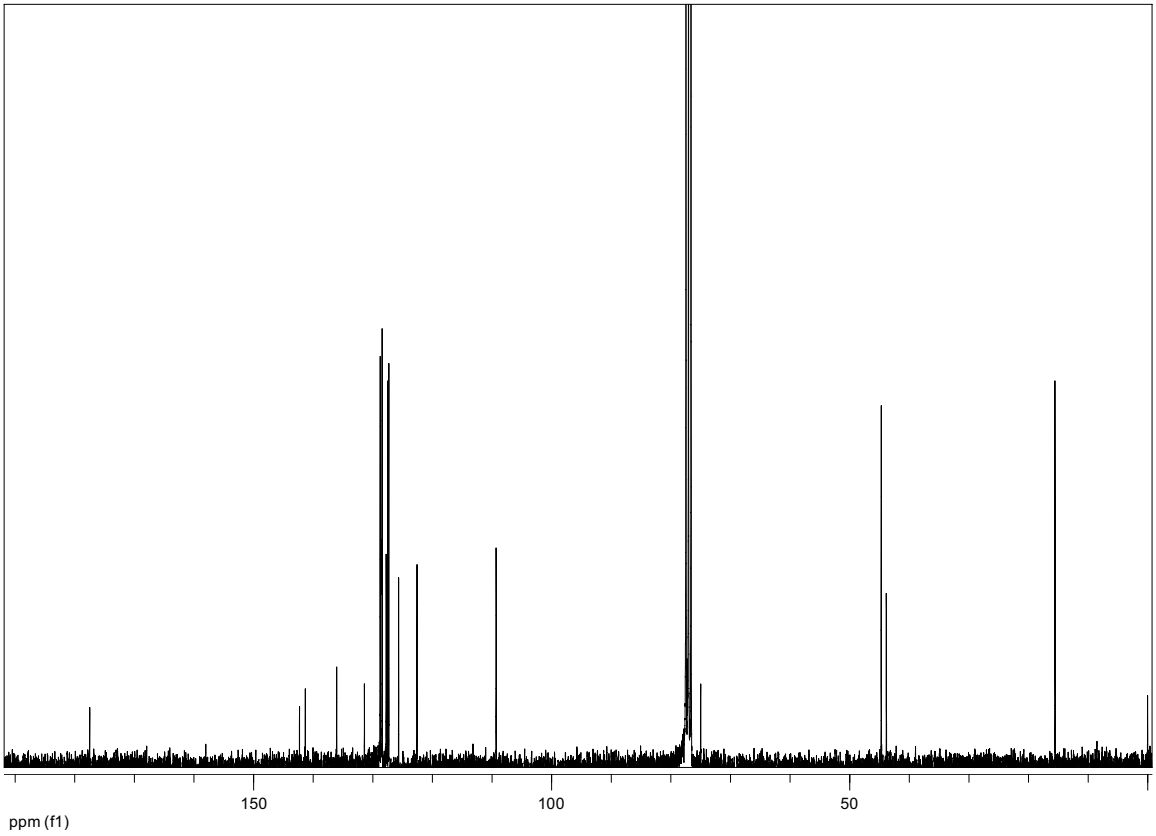
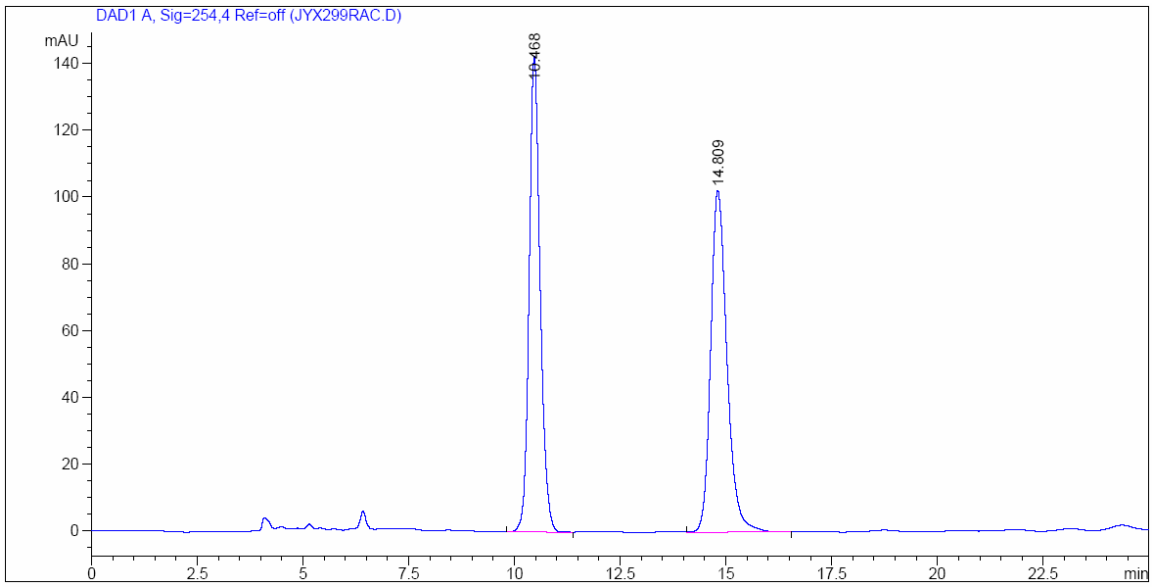
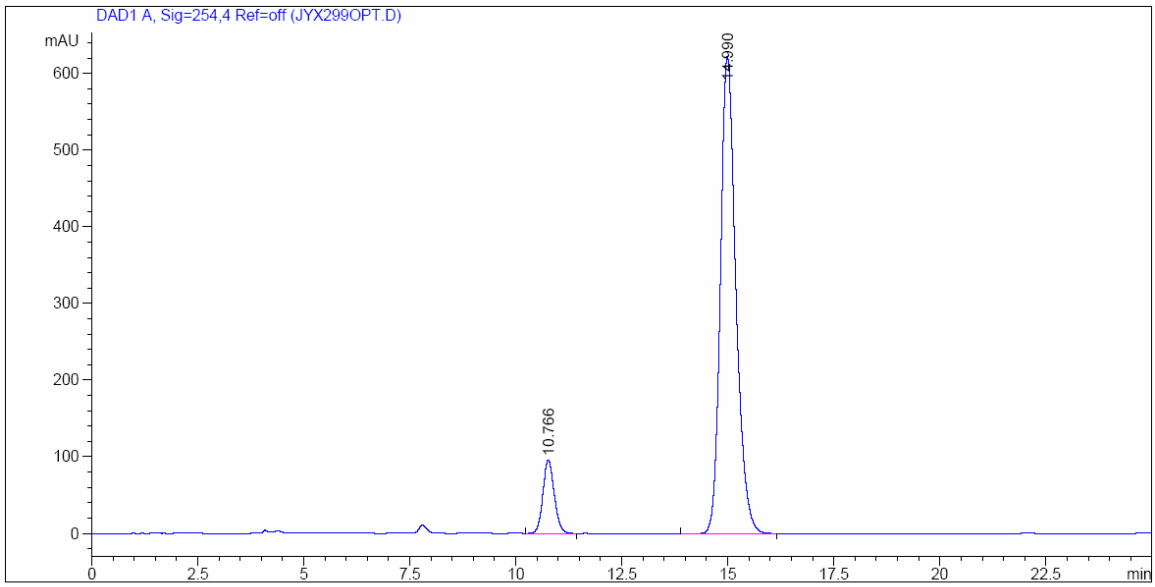
1-Benzyl-3-(diethylamino)-3-phenyloxindole (2m)

94% yield. $[\alpha]_D^{25}$ = –98.9 (*c* = 1.0 in acetone). 80% ee [Chiralcel AD column, *n*-hexane/*i*-PrOH = 95:5, 1.0 mL/min, 254 nm; t_R = 10.76 min (minor) and 14.99 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.98 (t, *J* = 7.2 Hz, 6H), 2.70 (q, *J* = 7.1, 7.1 Hz, 4H,), 4.94 (s, 2H), 6.73 (d, *J* = 7.8 Hz, 1H), 7.00 (t, *J* = 7.8 Hz, 1H), 7.15 (t, *J* = 7.8 Hz, 1H), 7.23-7.37 (m, 10H), 7.59 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.5, 43.8, 44.7, 75.0, 76.6, 109.3, 122.6, 125.6, 127.3, 127.4, 127.6, 127.7, 128.4, 128.7, 131.4, 136.0, 141.3, 142.3, 177.5. ν_{max}/cm^{-1}: 2991, 2830, 1669; HRMS: *m/z* (EI+) calculated for $C_{25}H_{27}N_2O$ ($[M+H]^+$): 371.2118, found: 371.2120.


9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)


150
100
50
ppm (f1)



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

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


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.766 VV    0.2816 1785.58105   95.72770  10.1689
   2  14.990 BV    0.3841 1.57737e4   621.50018  89.8311

Totals :                  1.75593e4   717.22788

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                      *** End of Report ***
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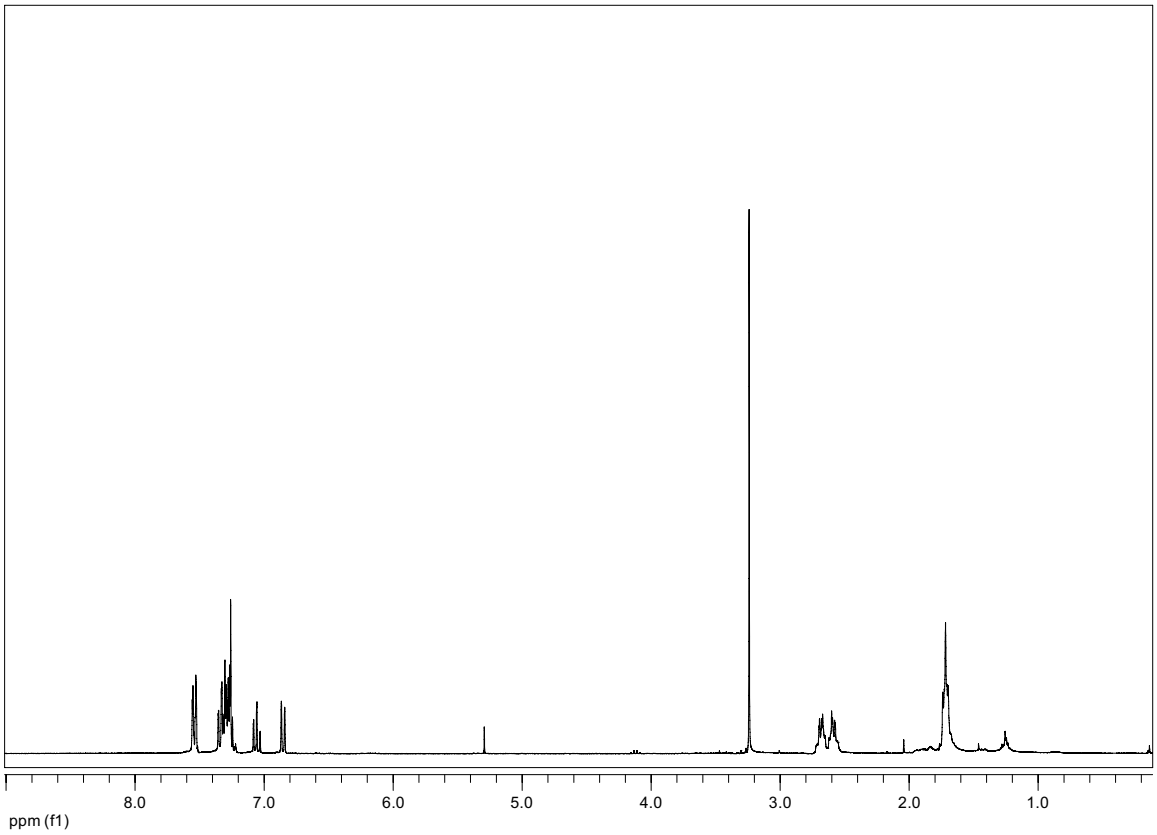
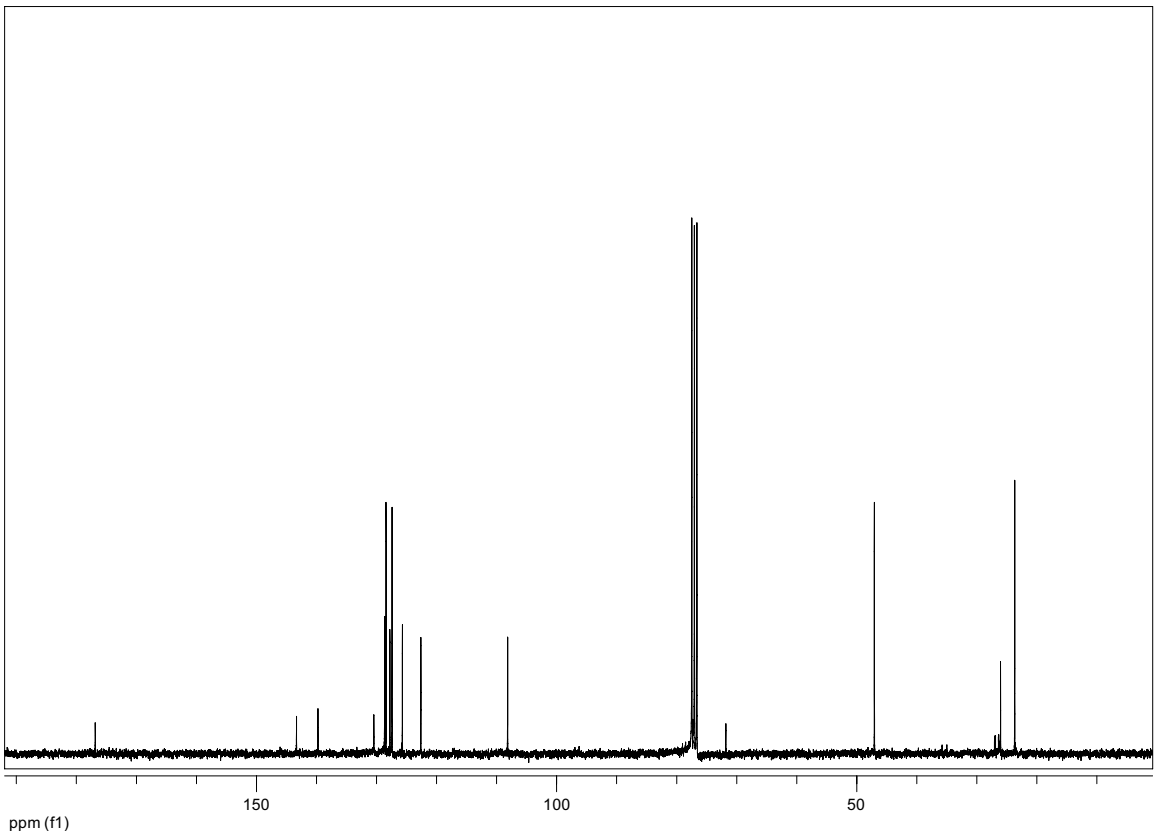
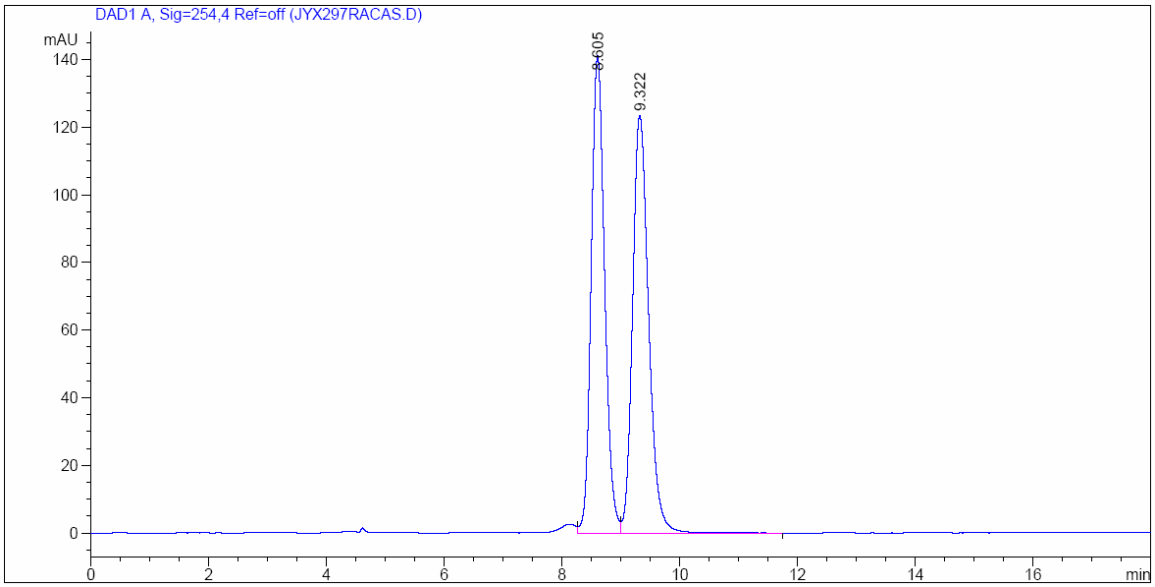
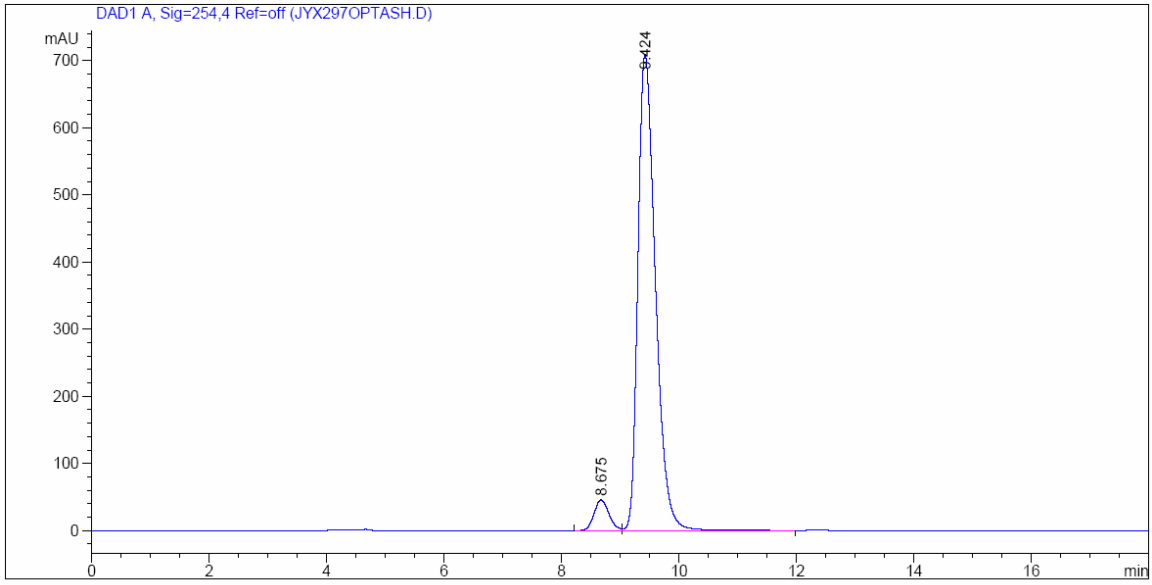
1-Methyl-3-phenyl-3-(pyrrolidin-1-yl)oxindole (2n)

96% yield. $[\alpha]_D^{25} = -115.3$ (c = 1.0 in acetone). 90% ee [Chiralcel AS-H column, *n*-hexane/*i*-PrOH = 99:1, 1.0 mL/min, 254 nm; t_R = 8.67 min (minor) and 9.42 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.70-1.74 (m, 4H), 2.72 (m, 4H), 3.24 (s, 3H), 6.85 (d, J = 7.8 Hz, 1H), 7.06 (t, J = 7.5 Hz, 1H), 7.23-7.36 (m, 5H), 7.55 (d, J = 6.6 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.7, 26.3, 47.0, 71.8, 108.1, 122.6, 125.7, 127.4, 127.7, 128.4, 130.4, 139.7, 143.3, 176.8. ν_{max}/cm^{-1}: 3058, 2962, 2874, 1704; HRMS: *m/z* (EI+) calculated for $C_{19}H_{21}N_2O$ ($[M+H]^+$): 293.1654, found: 293.1616.







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

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


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.675 BV    0.2787  807.18787   45.56599   5.2273
   2   9.424 VV    0.3210 1.46347e4   708.47565  94.7727

Totals :                   1.54419e4   754.04164

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                        *** End of Report ***
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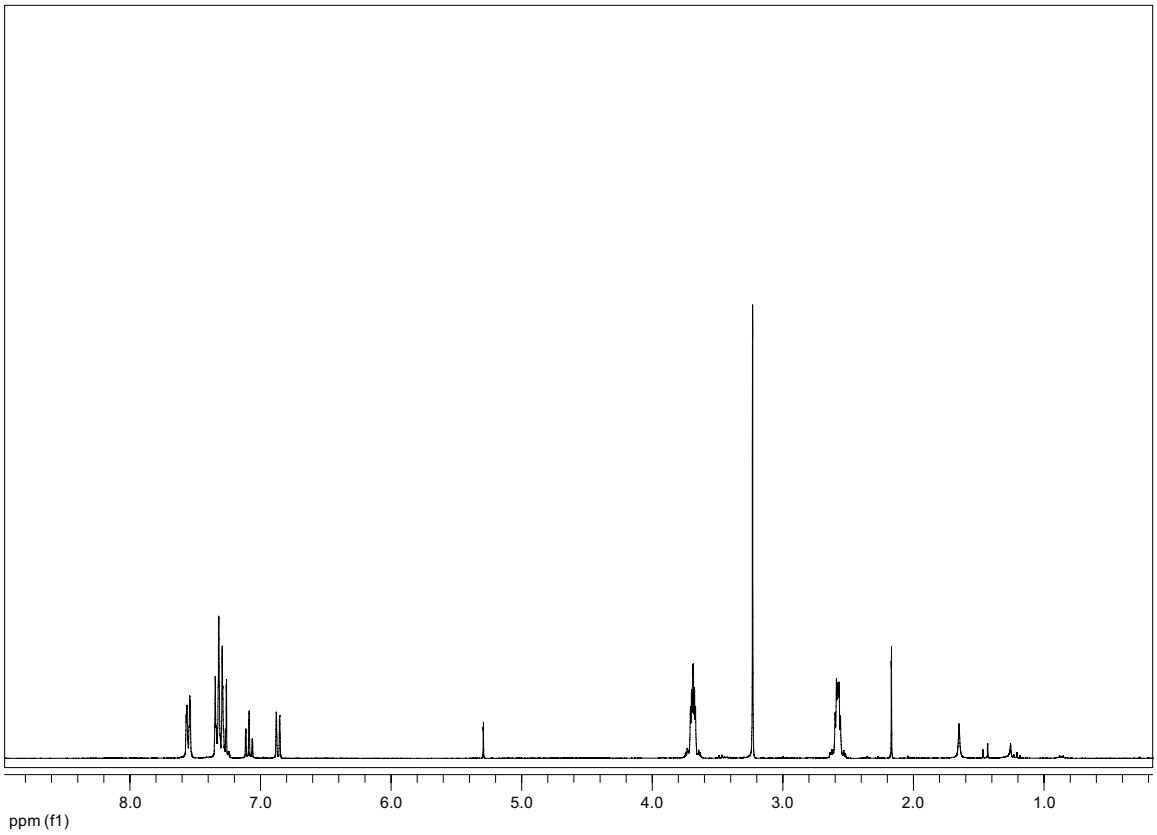
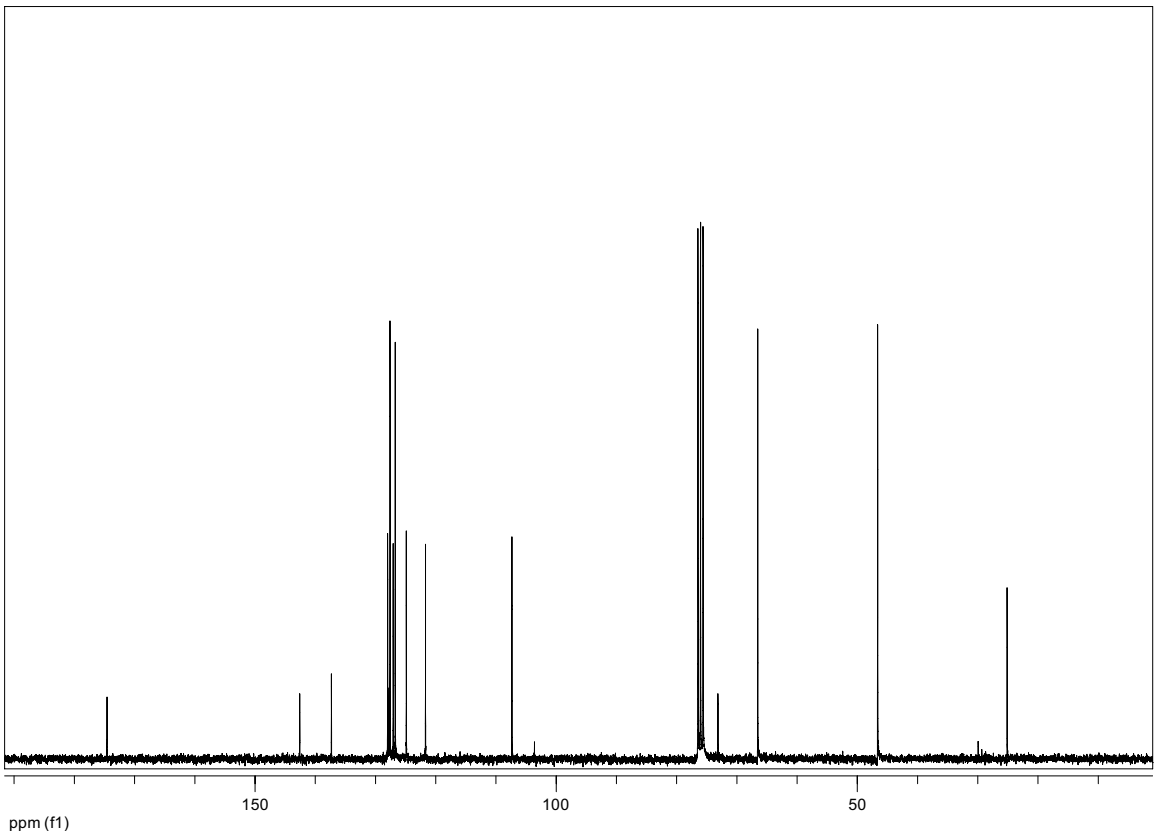
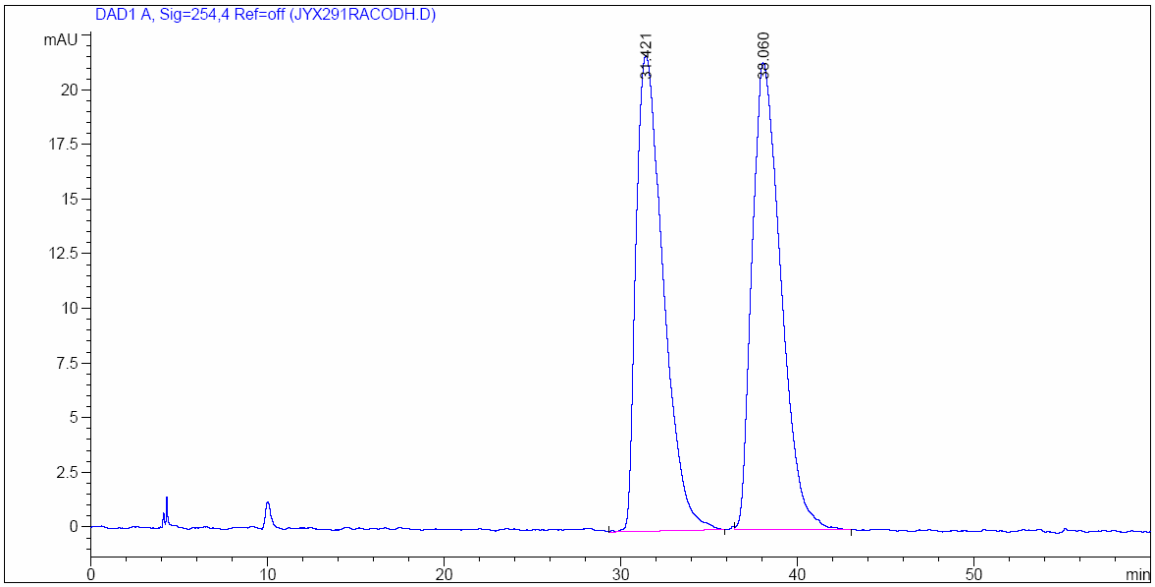
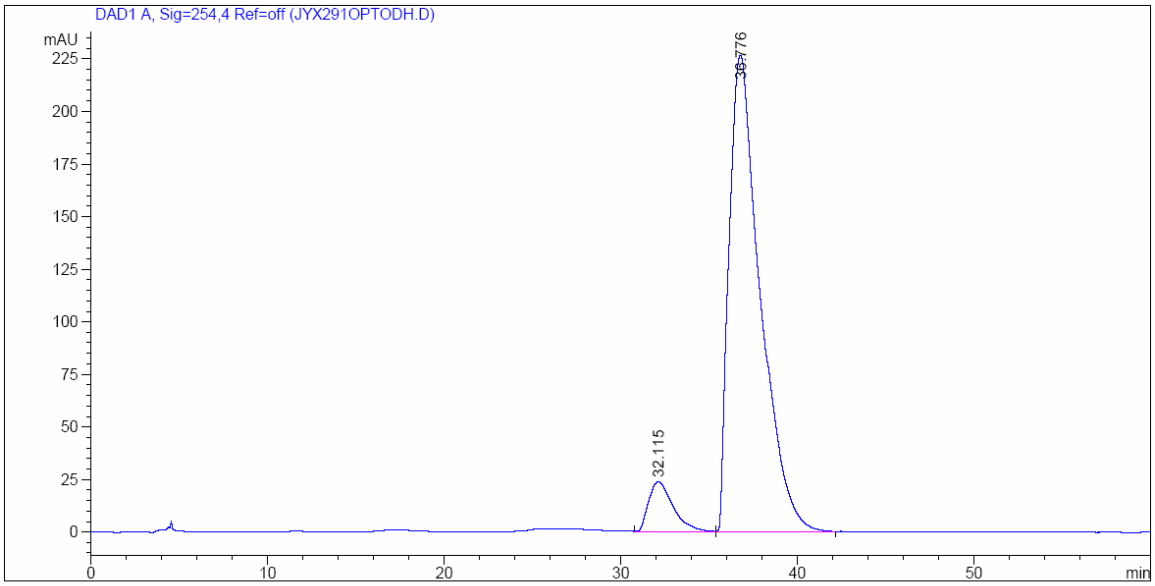
1-Methyl-3-morpholin-4-yl-3-phenyloxindole (2o)

88% yield. $[\alpha]_D^{25} = -88.1$ (c = 1.0 in acetone). 85% ee [Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 99:1, 1.0 mL/min, 254 nm; t_R = 32.11 min (minor) and 36.77 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.56-2.60 (m, 4H), 3.23 (s, 3H), 3.67-3.71 (m, 4H), 6.87 (d, J = 7.5 Hz, 1H), 7.08 (t, J = 7.8 Hz, 1H), 7.26-7.35 (m, 5H), 7.53 (d, J = 7.5 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 5.1, 46.6, 66.5, 73.1, 107.3, 121.7, 124.9, 126.7, 127.0, 127.6, 127.7, 128.0, 137.3, 142.6, 174.6. ν_{max}/cm^{-1}: 3061, 2963, 2854, 1715, 1606; HRMS: *m/z* (EI+) calculated for $C_{19}H_{21}N_2O_2$ ($[M+H]^+$): 309.1598, found: 309.1588.







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


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  32.115 VB    1.5044 2284.58496   23.78917   7.6354
   2  36.776 BV    1.8565 2.76362e4   226.34825  92.3646

Totals :                  2.99208e4   250.13742

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                      *** End of Report ***
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[1] (a) E. P. Kündig, T. M. Seidel, Y.-X. Jia, G. Bernardinelli, *Angew. Chem., Int. Ed.*, **2007**, *46*, 8484; (b) G. Bernardinelli, D. Fernandez, R. Gosmini, P. Meier, A. Ripa, P. Schupfer, B. Treptow, E. P. Kündig, *Chirality*, **2000**, *12*, 529.

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[3] (a) B. C.Bales, J. H.Horner, X. Huang, M. Newcomb, D. Crich, M. M. Greenberg, *J. Am. Chem. Soc.* **2001**, *123*, 3623; (b) K. Khumtaveeporn, A. Ullmann, K. Matsumoto, B. G. Davis, J. B. Jones, *Tetrahedron: Asymm.,* **2001**, *12*, 249.

[4] I. Azumaya, T. Okamoto, F. Imabeppu, H. Takayanagi, *Tetrahedron,* **2003**, *59*, 2325.

[5] .J. F. Hartwig, S. Lee, *J. Org. Chem.* **2001**, *66*, 3402.

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