Supporting Information for:

Pd-Catalyzed Dearomative Arylborylation of Indoles

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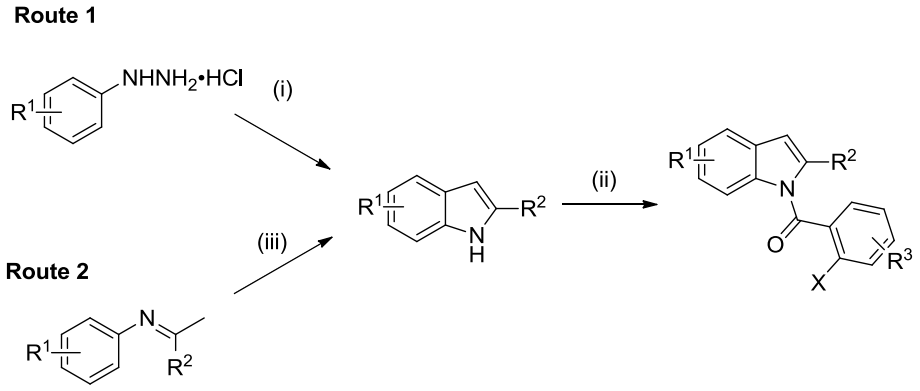
Contents:

1. General information

Reactions and manipulations involving organometallic or moisture sensitive compounds were carried out under dry nitrogen and glassware heated under oven for two hours prior to use. ^{1}H and ^{13}C spectra were recorded on Bruker AVANCE III 500 MHz using $CDCl_3$ or CD_3OD as solvent with TMS as internal standard. Anhydrous THF and toluene were freshly distilled over Na and benzophenone. Anhydrous DCM, DCE, CH_3CN were freshly distilled over calcium hydride. Melting points were measured on a Buchi B-545 apparatus and uncorrected. Commercial reagents were used as received without further purification unless otherwise noticed. HRMS were recorded on Agilent 6210 TOF LC/MS mass spectrometer. Column chromatography was carried out using silica gel (200-300 mesh).

2. Substrate and ligand synthesis

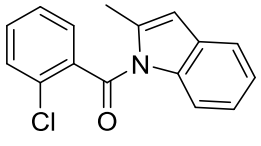
As shown in Scheme S1, all of the substrates were synthesized according to the procedure that we published previously.[1] The bromo-substrates **1a-1q** are known compounds, while the chloro-analogues are new.



Scheme S1. Preparation of *N*-acylindole bromo-substrates. Reaction Conditions: (i) Ketone, polyphosphoric acid, 110 ℃, 4–6 h; (ii) 2-halobenzoyl chloride, NaH, THF, r. t., overnight; (iii) Ketone, $Pd(OAc)_2$, Bu_4NBr, O_2, DMSO, 100 ^oC, 24 h.

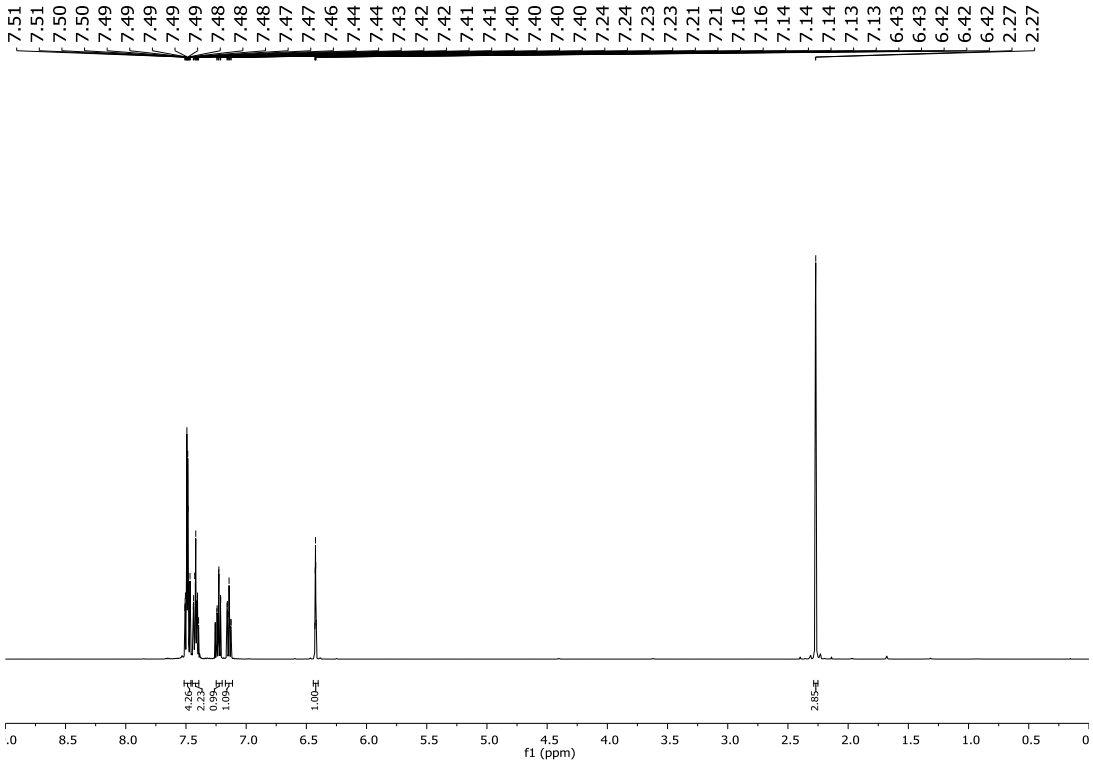
Procedure for the synthesis of chloro-substrates: To a suspension of benzoic acid derivatives (2.2 equiv) in DCM (1 M) and a few drops of DMF, was added oxalyl chloride (2.2 equiv). Stirring was complete when the reaction stopped evolving gas and a homogeneous solution was observed. The solvent was evaporated, and the acyl-chloride formed was redissolved in THF (1 M). In a second flask, a solution of indole (1 equiv) in THF (1 M) was added NaH (1.2 equiv) and was stirred for 10 minutes. The solution of acyl-chloride was added to the deprotonated indole and the reaction was stirred for 2 hours. The reaction was quenched with $NH_4Cl_{(aq)}$ slowly and was extracted with EtOAc. After evaporation, the crude product was columned.

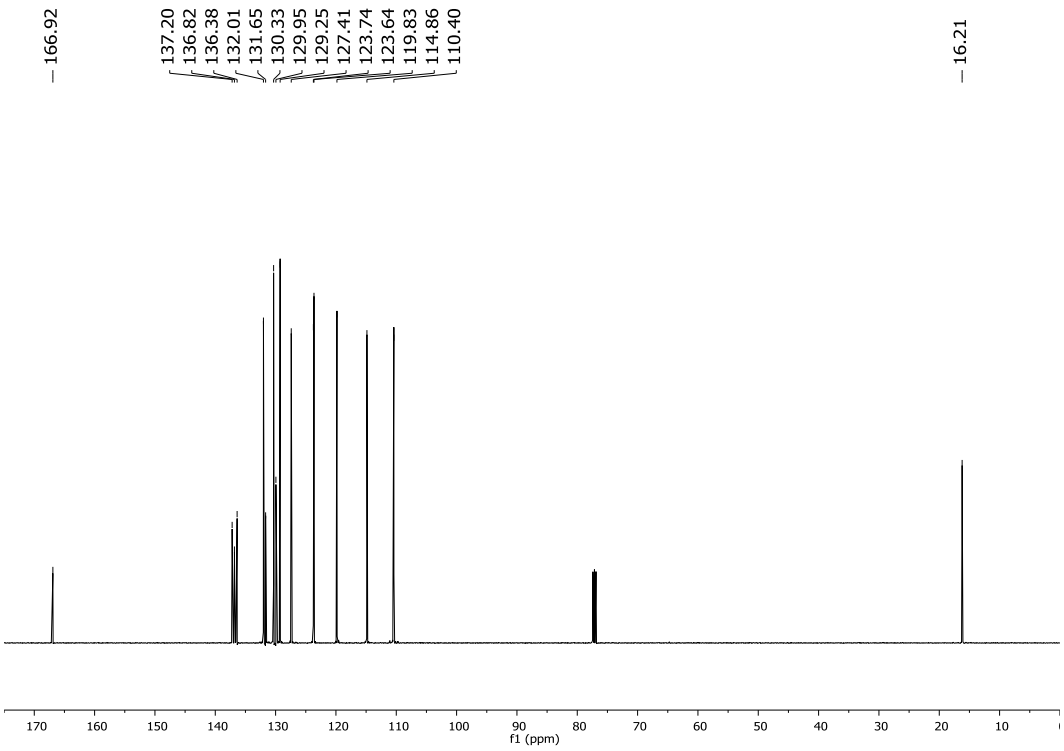
(2-chlorophenyl)(2-methyl-1H-indol-1-yl)methanone **(1a')**



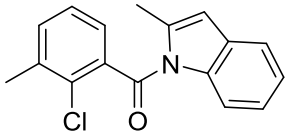
[1] Shen, C.; Liu, R.-R.; Fan, R.-J.; Li, Y.-L.; Xu, T.-F.; Gao, J.-R.; Jia, Y.-X. *J. Am. Chem. Soc.* **2015**, *137*, 4936.

The crude reaction mixture was purified on silica by flash chromatography, eluting with pentanes to pentanes:NEt_3 40:1 (v/v). The product was isolated as a white solid (60% yield, mp = 58–59 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52–7.46 (m, 4H), 7.45–7.39 (m, 2H), 7.23 (td, *J* = 7.5, 1.0 Hz, 1H), 7.14 (ddd, *J* = 8.5, 7.3, 1.3 Hz, 1H), 6.42 (p, *J* = 1.1 Hz, 1H), 2.27 (d, *J* = 1.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.9, 137.2, 136.8, 136.4, 132.0, 131.7, 130.3, 129.9, 129.2, 127.4, 123.7, 123.6, 119.8, 114.9, 110.4, 16.2. HRMS *m/z* (DART+): calculated for $C_{16}H_{13}ClNO$ ($[M+H]^+$) 270.0686, found 270.0685.

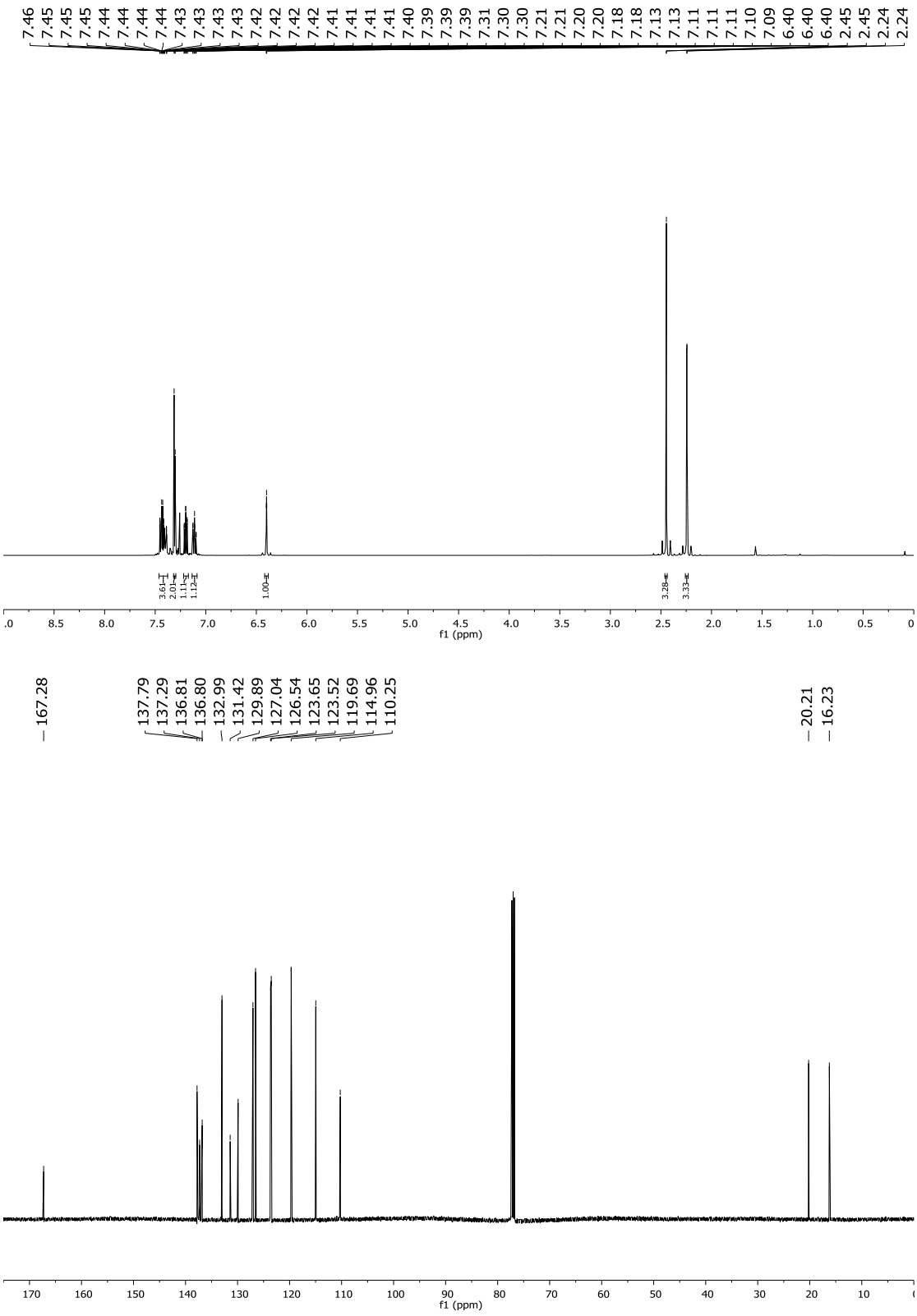




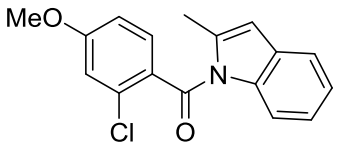
(2-chloro-3-methylphenyl)(2-methyl-1H-indol-1-yl)methanone **(1r)**



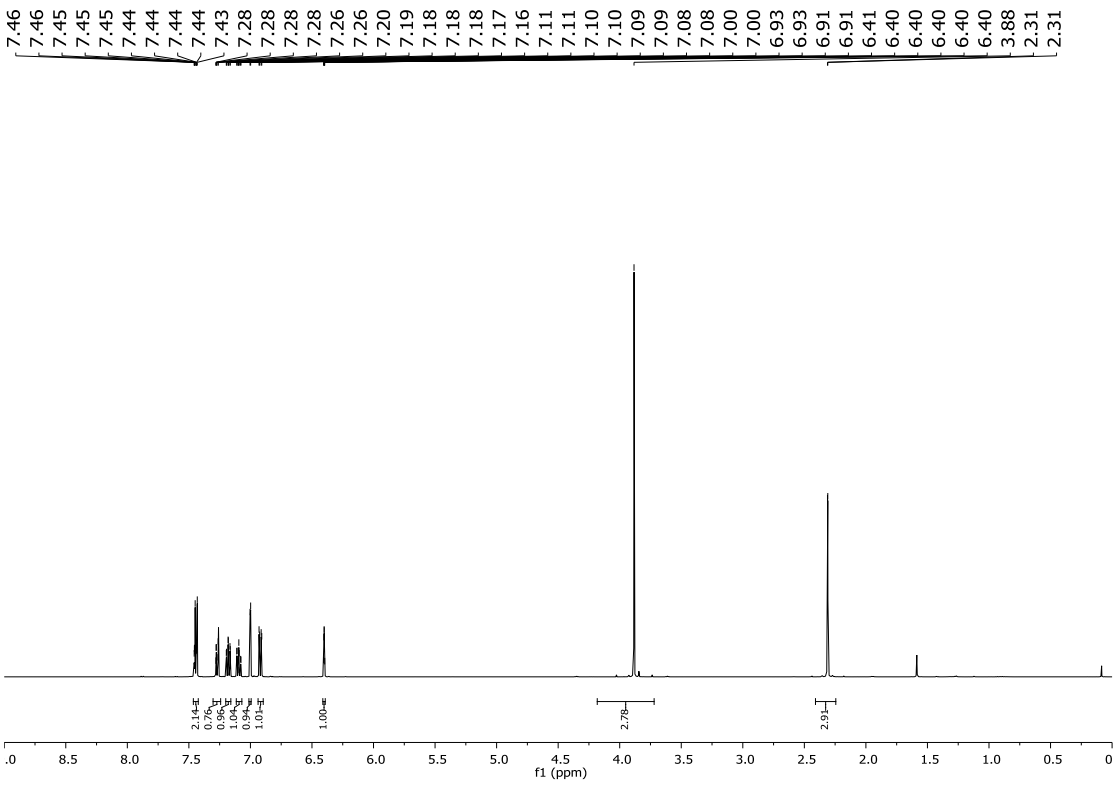
The crude reaction mixture was purified on silica by flash chromatography, eluting with pentanes to pentanes:EtOAc 50:1 (v/v). The product was isolated as a white solid (47% yield, mp = 85–86 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46–7.38 (m, 3H), 7.32–7.30 (m, 2H), 7.20 (td, *J* = 7.5, 1.0 Hz, 1H), 7.11 (ddd, *J* = 8.5, 7.3, 1.3 Hz, 1H), 6.40 (t, *J* = 1.0 Hz, 1H), 2.45 (d, *J* = 0.7 Hz, 3H), 2.24 (d, *J* = 1.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.3, 137.8, 137.3, 136.8, 136.8, 133.0, 131.4, 129.9, 127.0, 126.5, 123.7, 123.5, 119.7, 115.0, 110.3, 20.2, 16.2. HRMS *m/z* (DART+): calculated for $C_{17}H_{15}ClNO$ ($[M+H]^+$) 284.0842, found 284.0849.

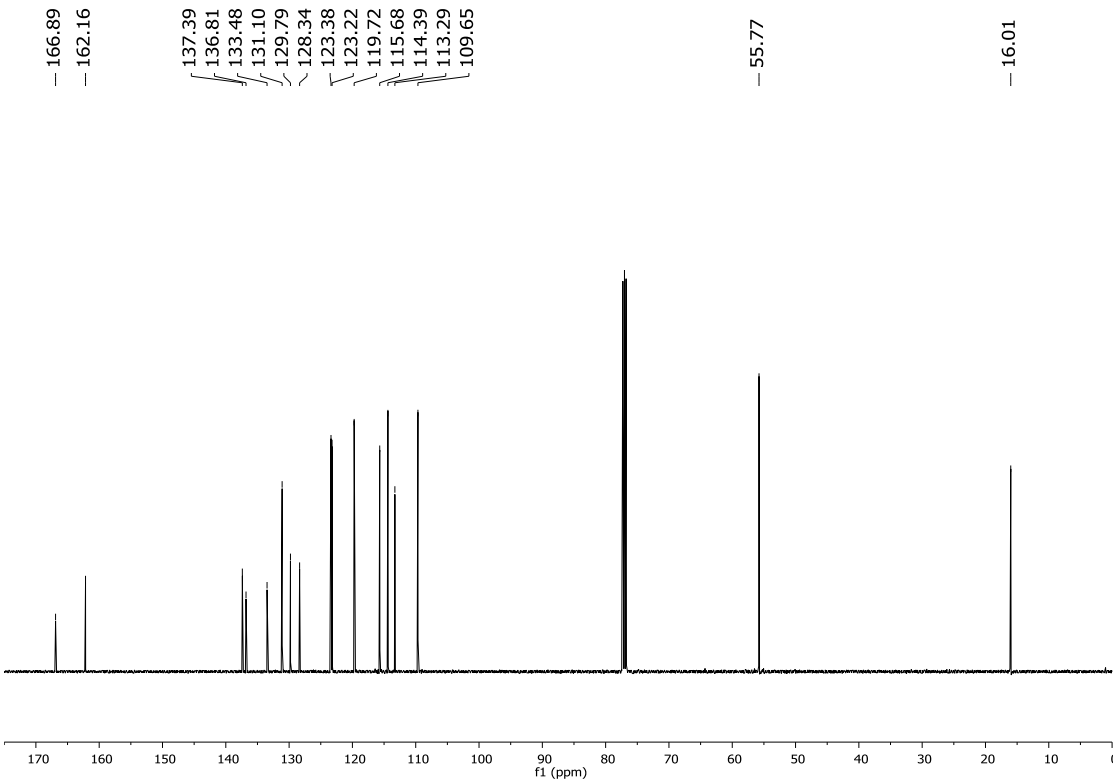


(2-chloro-4-methoxyphenyl)(2-methyl-1H-indol-1-yl)methanone **(1d')**

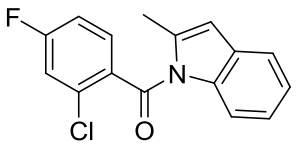


The crude reaction mixture was purified on silica by flash chromatography. Two columns were required, first eluting with pentanes:EtOAc 10:1 (v/v), then pentanes:DCM:toluene 2:2:1 (v/v/v). The product was isolated as a white solid (31% yield, mp = 105–106 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46–7.42 (m, 2H), 7.30–7.24 (m, 1H), 7.20–7.16 (m, 1H), 7.09 (ddd, *J* = 8.5, 7.2, 1.3 Hz, 1H), 7.00 (d, *J* = 2.4 Hz, 1H), 6.92 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.41–6.39 (m, 1H), 3.88 (s, 3H), 2.31 (d, *J* = 1.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.9, 162.2, 137.4, 136.8, 133.5, 131.1, 129.8, 128.3, 123.4, 123.2, 119.7, 115.7, 114.4, 113.3, 109.7, 55.8, 16.0. HRMS *m/z* (DART+): calculated for $C_{17}H_{15}ClNO_2$ ($[M+H]^+$) 300.0791, found 300.0790.



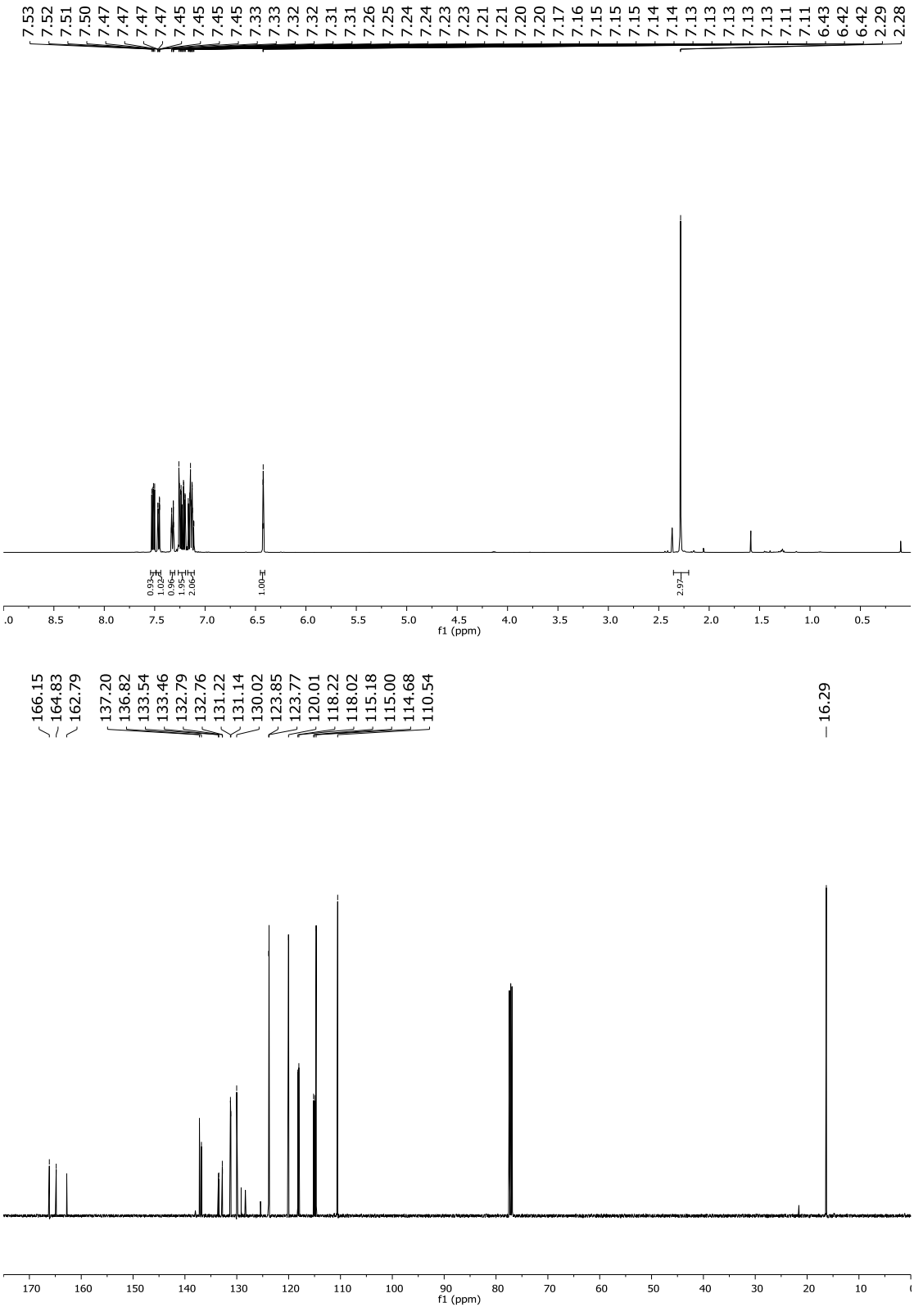


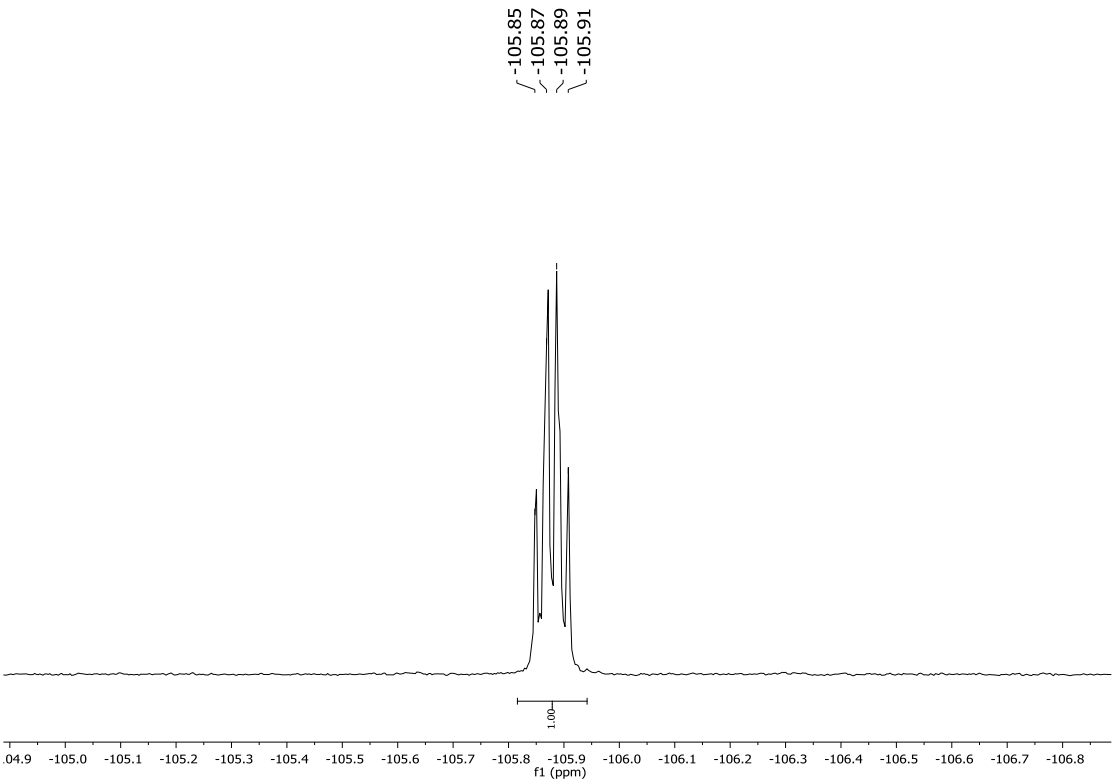
(2-chloro-4-fluorophenyl)(2-methyl-1H-indol-1-yl)methanone **(1s)**



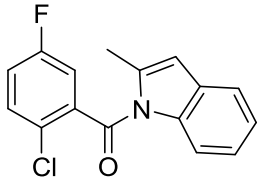
The crude reaction mixture was purified on silica by flash chromatography, eluting with pentanes to pentanes:Et_2O 100:1 (v/v). The product was isolated as a white solid (35% yield, mp = 51–52 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 8.6, 5.8 Hz, 1H), 7.46 (ddd, *J* = 7.7, 1.3, 0.7 Hz, 1H), 7.32 (dq, *J* = 8.3, 0.9 Hz, 1H), 7.27–7.19 (m, 2H), 7.17–7.11 (m, 2H), 6.42 (t, *J* = 1.1 Hz, 1H), 2.28 (d, *J* = 1.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.2, 163.8 (d, *J* = 255.6 Hz), 137.2, 136.8, 133.5 (d, *J* = 10.8 Hz), 132.8 (d, *J* = 3.8 Hz), 131.2 (d, *J* = 9.4 Hz), 130.0, 123.8, 123.8, 120.0, 118.1 (d, *J* = 24.9 Hz), 115.1 (d, *J* = 21.8 Hz), 114.7, 110.5, 16.3. ^{19}F NMR (377 MHz, $CDCl_3$)

δ -105.88 (q, J = 7.9 Hz). HRMS *m/z* (DART+): calculated for $C_{16}H_{12}ClFNO$ ($[M+H]^+$): 288.0591, found 288.0590.





(2-chloro-5-fluorophenyl)(2-methyl-1H-indol-1-yl)methanone **(1t)**



The crude reaction mixture was purified on silica by flash chromatography, eluting with pentanes to pentanes:Et_2O 100:1 (v/v). The product was isolated as a white solid (36% yield, mp = 73–75 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48–7.43 (m, 2H), 7.42–7.39 (m, 1H), 7.25–7.19 (m, 3H), 7.14 (ddd, *J* = 8.5, 7.3, 1.4 Hz, 1H), 6.43 (t, *J* = 1.2 Hz, 1H), 2.28 (d, *J* = 1.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.4 (d, *J* = 2.0 Hz), 161.2 (d, *J* = 250.3 Hz), 137.7 (d, *J* = 7.2 Hz), 136.9, 136.6, 131.9 (d, *J* = 8.0 Hz), 129.9, 126.7 (d, *J* = 3.6 Hz), 123.9, 123.8, 119.9, 119.1 (d, *J* = 22.8 Hz), 116.3 (d, *J* = 24.7 Hz), 114.7, 110.8, 16.2. ^{19}F NMR (377 MHz, $CDCl_3$) δ -112.96 (td, *J* = 8.0, 4.6 Hz). HRMS *m/z* (DART+): calculated for $C_{16}H_{12}ClFNO$ ($[M+H]^+$): 288.0591,

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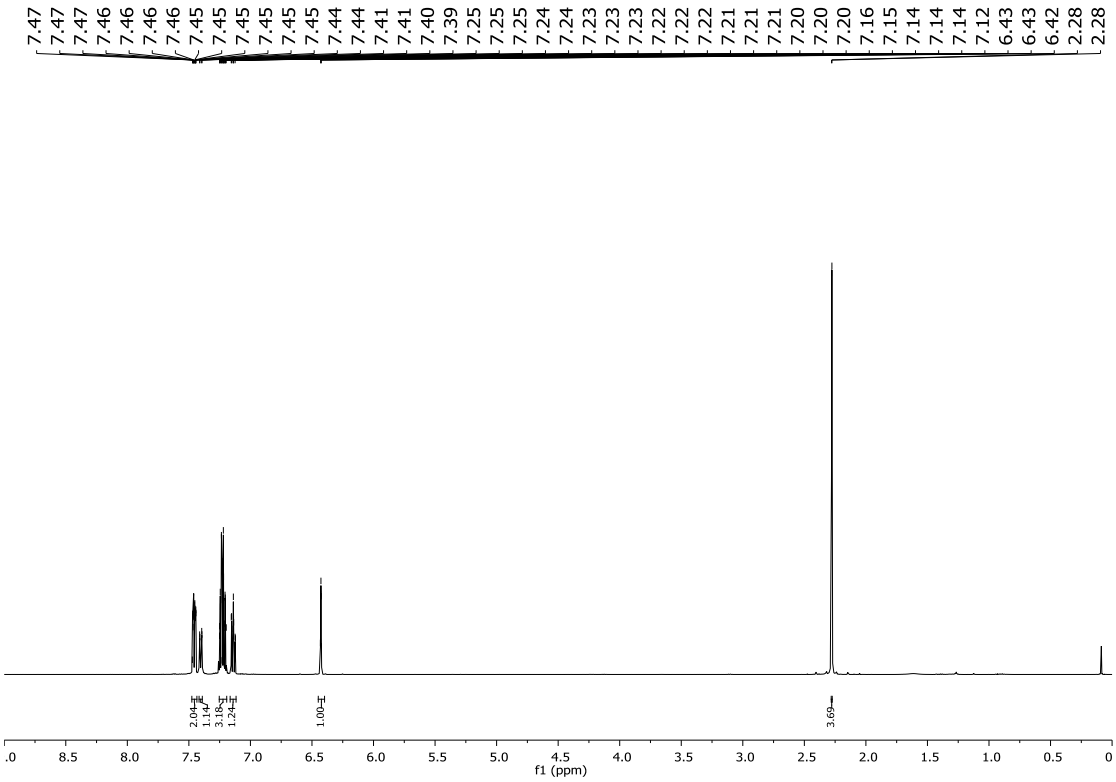
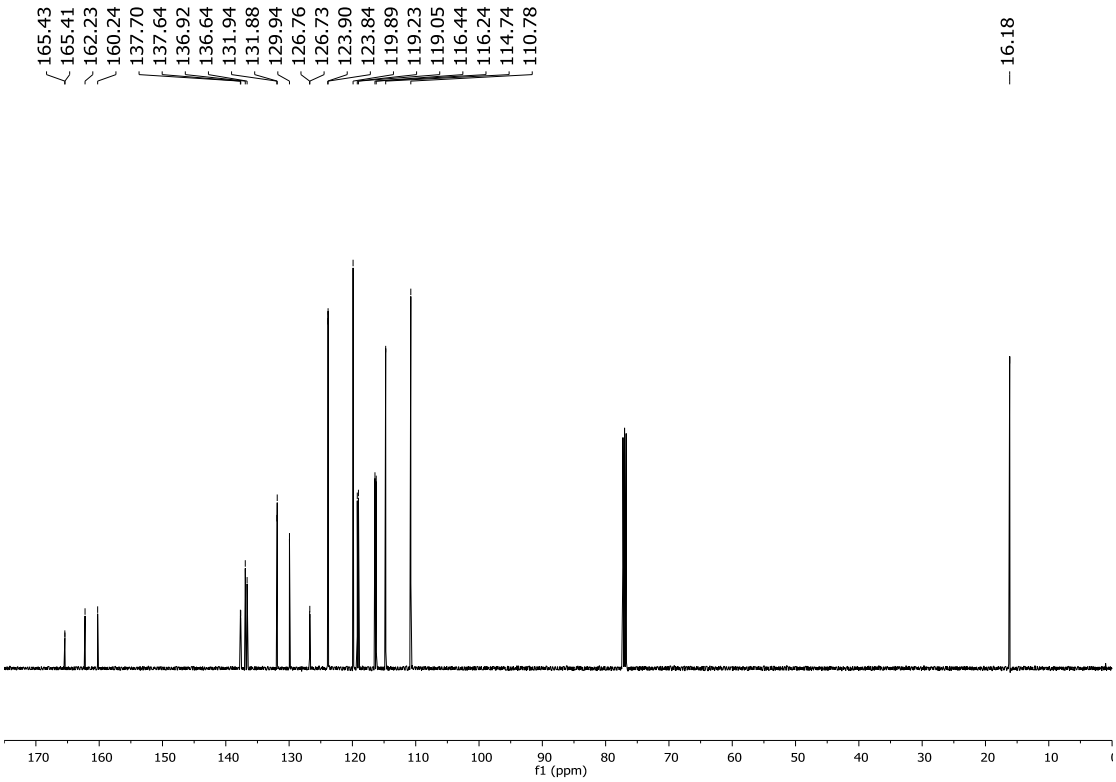
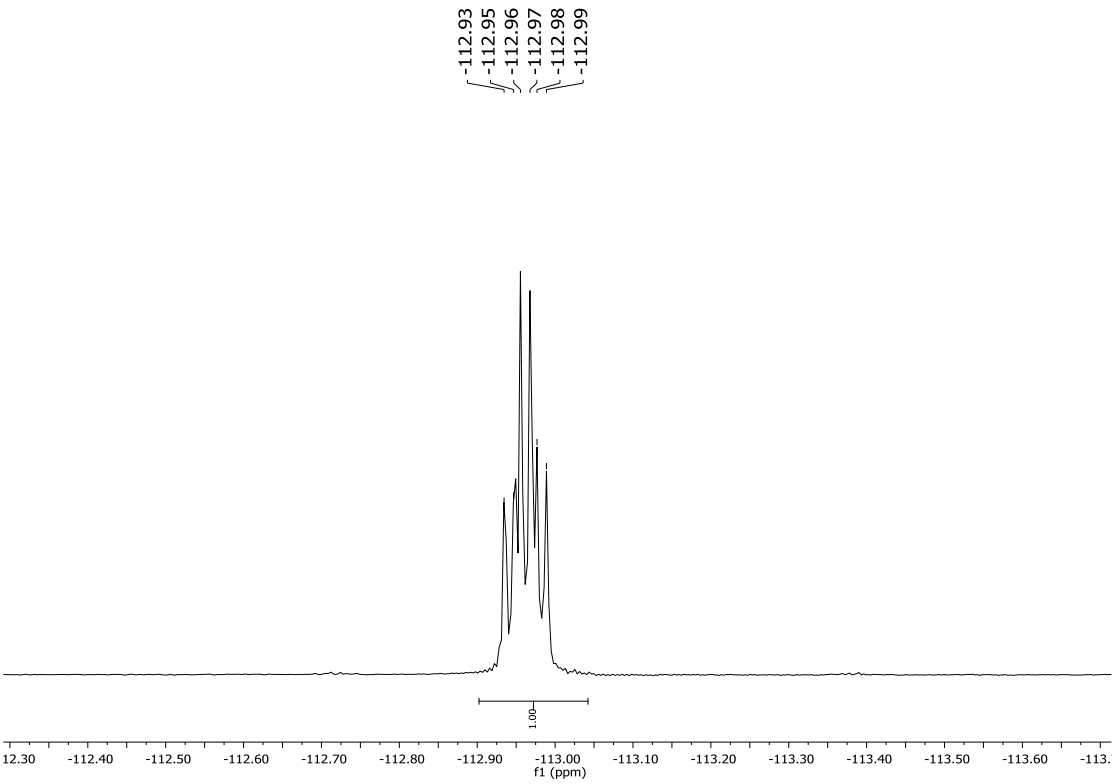
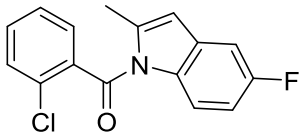




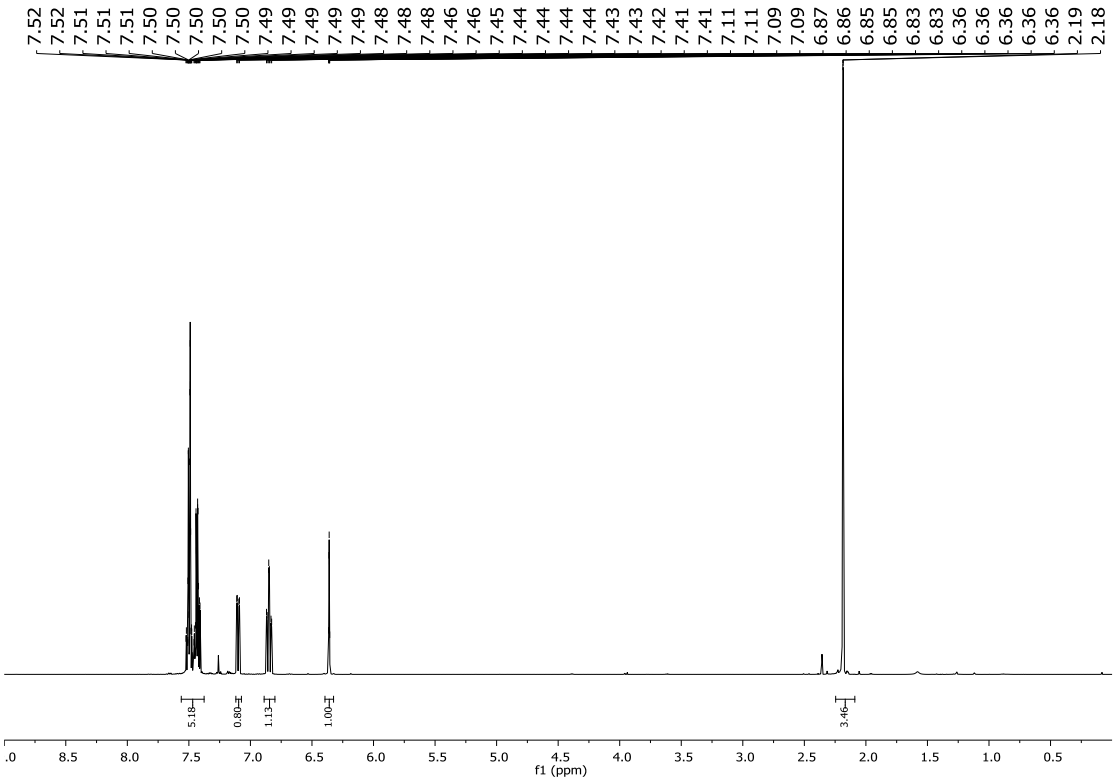


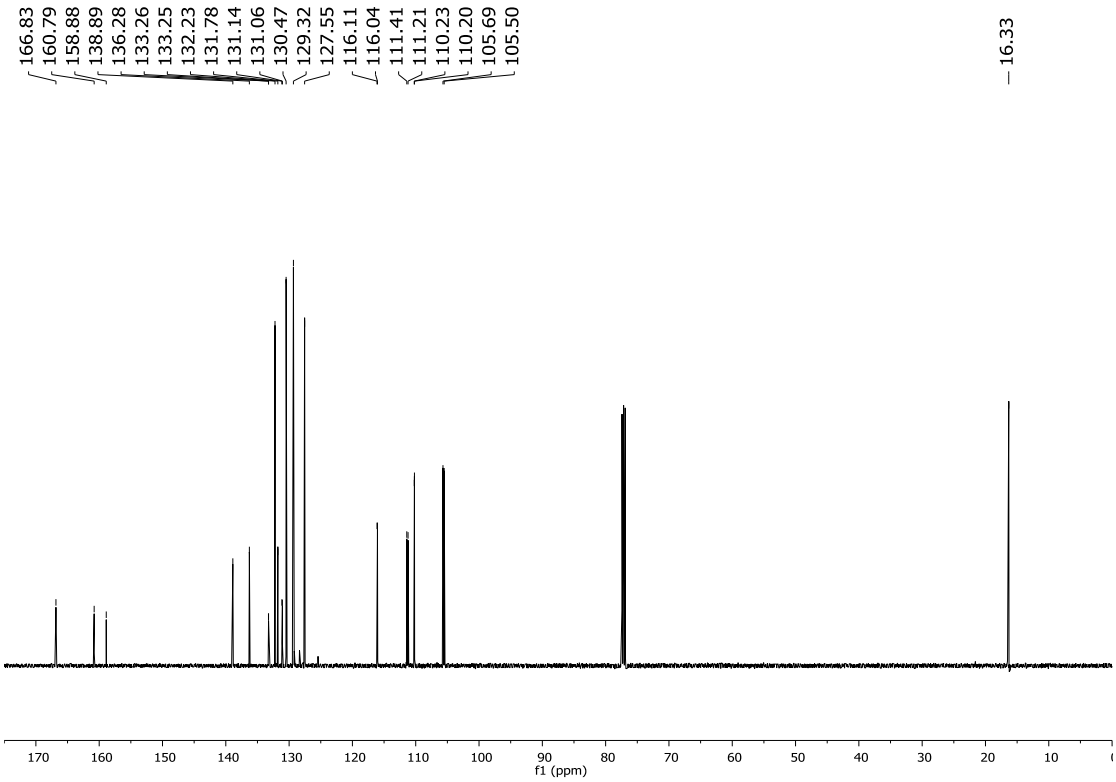
(2-chlorophenyl)(5-fluoro-2-methyl-1H-indol-1-yl)methanone **(1u)**

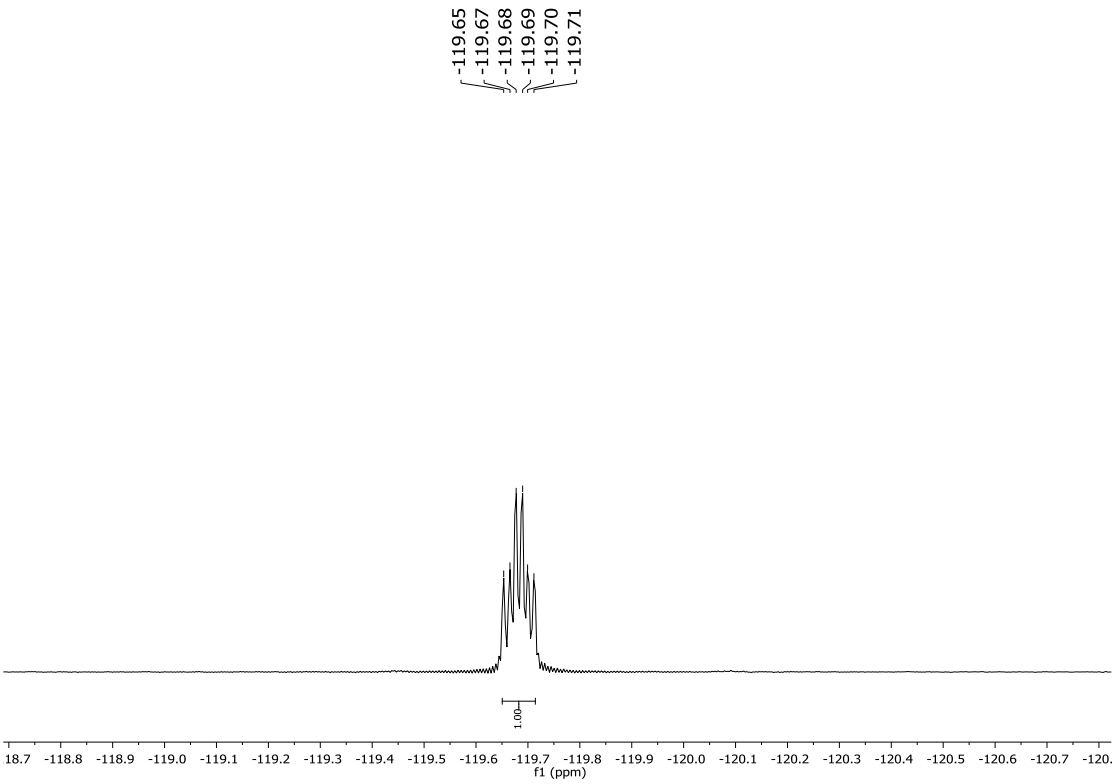


The crude reaction mixture was purified on silica by flash chromatography, eluting with pentanes to pentanes:Et_2O 100:1 (v/v). The product was isolated as a white solid (47% yield, mp = 84–85 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56–7.38 (m, 5H), 7.10 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.85 (td, *J* = 9.1, 2.6 Hz, 1H), 6.36 (p, *J* = 1.2 Hz, 1H), 2.19 (d, *J* = 1.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.8, 159.8 (d, *J* = 240.0 Hz), 138.9, 136.3, 133.2 (d, *J* = 1.4 Hz), 132.2, 131.8, 131.1 (d, *J* = 10.0 Hz), 130.5, 129.3, 127.6, 116.1 (d, *J* = 9.1 Hz), 111.3 (d, *J* = 24.7 Hz), 110.2 (d, *J* = 3.7 Hz), 105.6 (d, *J* = 23.8 Hz), 16.3. ^{19}F NMR (377 MHz, $CDCl_3$) δ -119.68 (td, *J* = 8.6, 8.2, 4.6 Hz). HRMS *m/z* (DART+): calculated for $C_{16}H_{12}ClFNO$ ($[M+H]^+$): 288.0591, found

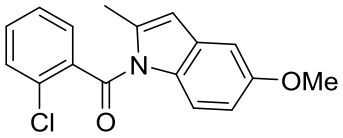
288.0596.


7.52 7.52 7.51 7.51 7.51 7.50 7.50 7.50 7.50 7.50 7.49 7.49 7.49 7.49 7.49 7.48 7.48 7.48 7.46 7.46 7.45 7.44 7.44 7.44 7.44 7.43 7.43 7.42 7.41 7.41 7.11 7.11 7.09 7.09 6.87 6.86 6.85 6.85 6.83 6.83 6.36 6.36 6.36 6.36 2.19 2.18
5.18
0.80
1.13
1.00
3.46
f1 (ppm)

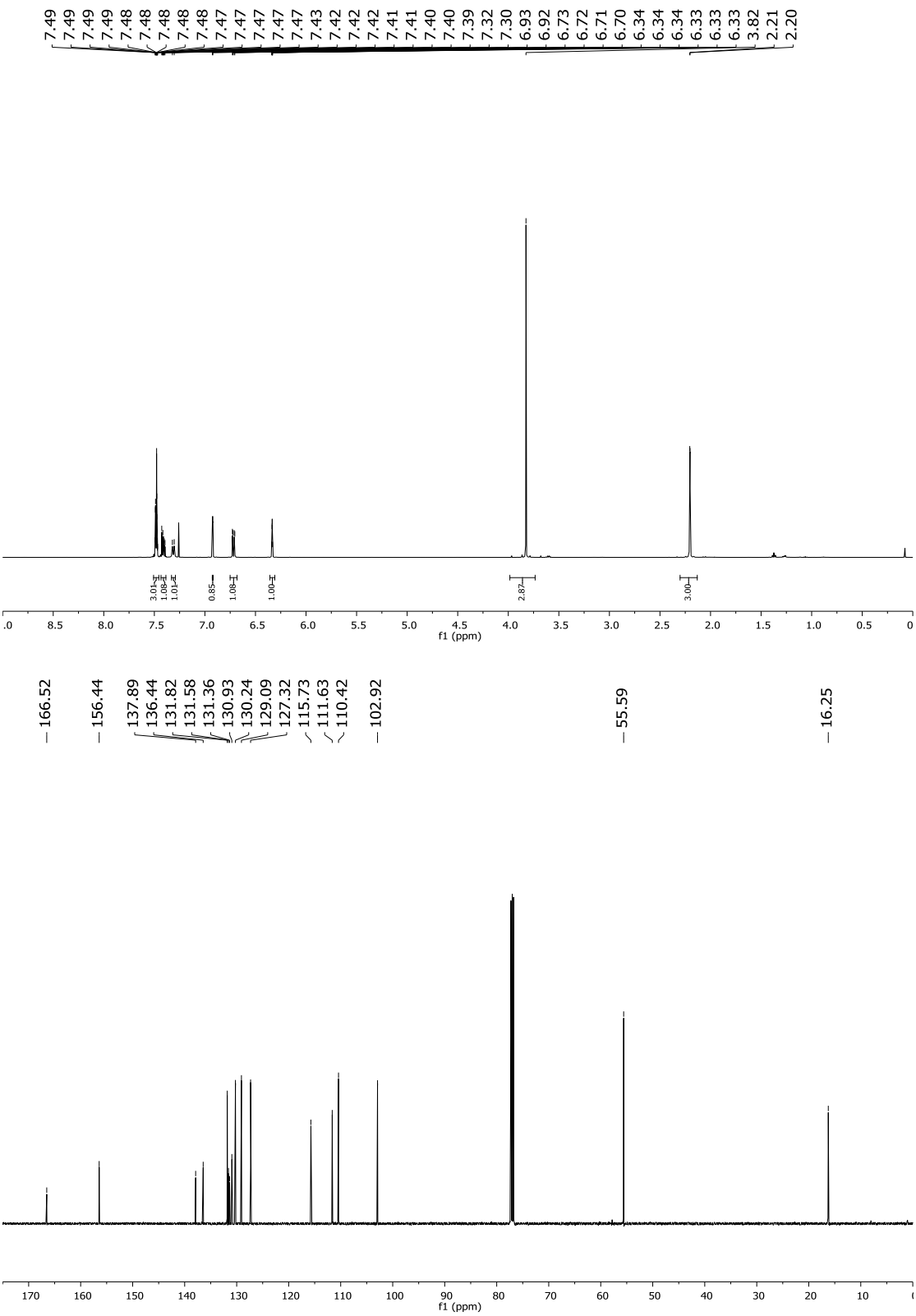

166.83 160.79 158.88 138.89 136.28 133.26 133.25 132.23 131.78 131.14 131.06 130.47 129.32 127.55 116.11 116.04 111.41 111.21 110.23 110.20 105.69 105.50
16.33
f1 (ppm)



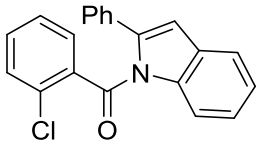
(2-chlorophenyl)(5-methoxy-2-methyl-1H-indol-1-yl)methanone **(1v)**



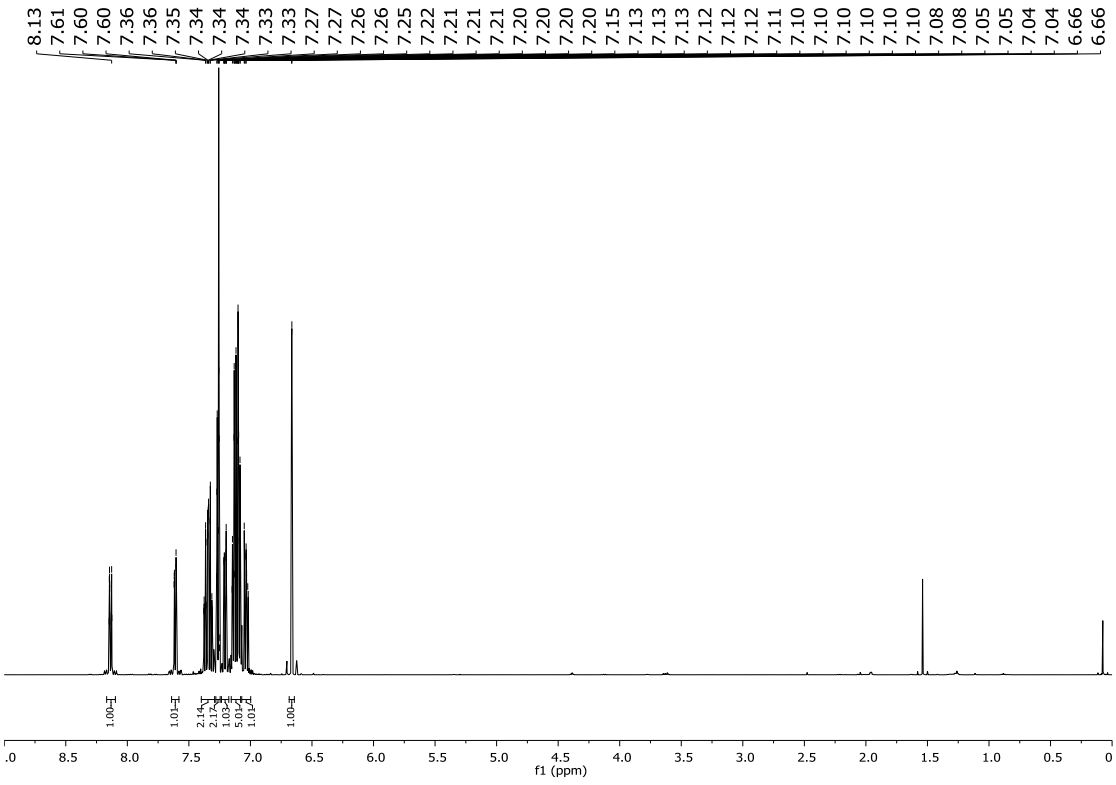
The crude reaction mixture was purified on silica by flash chromatography, eluting with pentanes to pentanes:NEt_3 20:1 (v/v). The product was isolated as a white solid (41% yield, mp = 54–55 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51–7.46 (m, 3H), 7.43–7.39 (m, 1H), 7.31 (d, *J* = 9.0 Hz, 1H), 6.92 (d, *J* = 2.4 Hz, 1H), 6.72 (dd, *J* = 9.0, 2.6 Hz, 1H), 6.33 (dt, *J* = 1.9, 0.9 Hz, 1H), 3.82 (s, 3H), 2.20 (d, *J* = 1.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.5, 156.4, 137.9, 136.4, 131.8, 131.6, 131.4, 130.9, 130.2, 129.1, 127.3, 115.7, 111.6, 110.4, 102.9, 55.6, 16.2. HRMS *m/z* (DART+): calculated for $C_{17}H_{15}ClNO_2$ ($[M+H]^+$): 300.0791, found 300.0784.

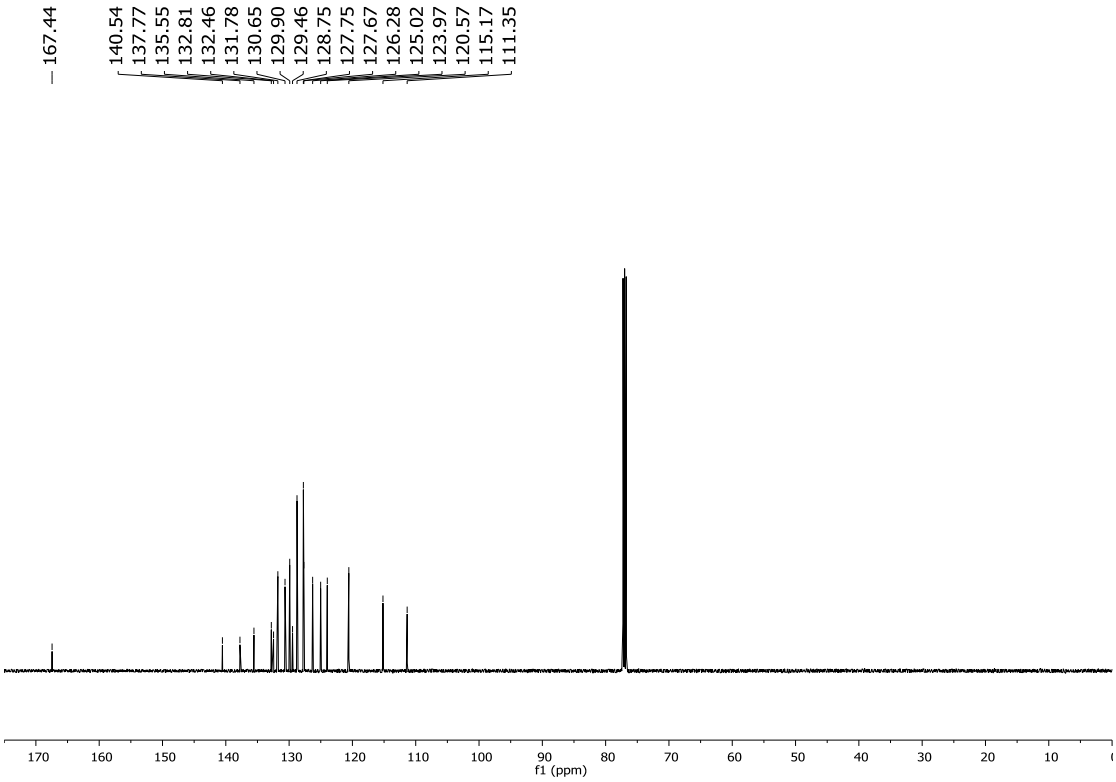


(2-chlorophenyl)(2-phenyl-1H-indol-1-yl)methanone **(1j')**

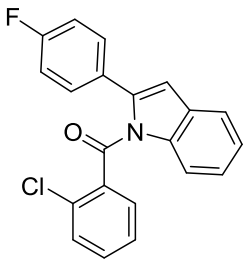


The crude reaction mixture was purified on silica by flash chromatography, eluting with pentanes to pentanes:Et_2O 100:1 (v/v). The product was isolated as a white solid (46% yield, mp = 86–87 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (ddt, *J* = 8.1, 1.4, 0.8 Hz, 1H), 7.61 (ddd, *J* = 7.3, 1.6, 0.7 Hz, 1H), 7.40–7.29 (m, 2H), 7.28–7.25 (m, 2H), 7.21 (ddd, *J* = 7.6, 1.6, 0.6 Hz, 1H), 7.16–7.08 (m, 5H), 7.03 (ddd, *J* = 7.7, 6.7, 1.9 Hz, 1H), 6.66 (d, *J* = 0.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.4, 140.5, 137.8, 135.6, 132.8, 132.5, 131.8, 130.6, 129.9, 129.5, 128.8, 127.7, 127.7, 126.3, 125.0, 124.0, 120.6, 115.2, 111.4. HRMS *m/z* (DART+): calculated for $C_{21}H_{15}ClNO$ ($[M+H]^+$): 332.0842, found 332.0844.



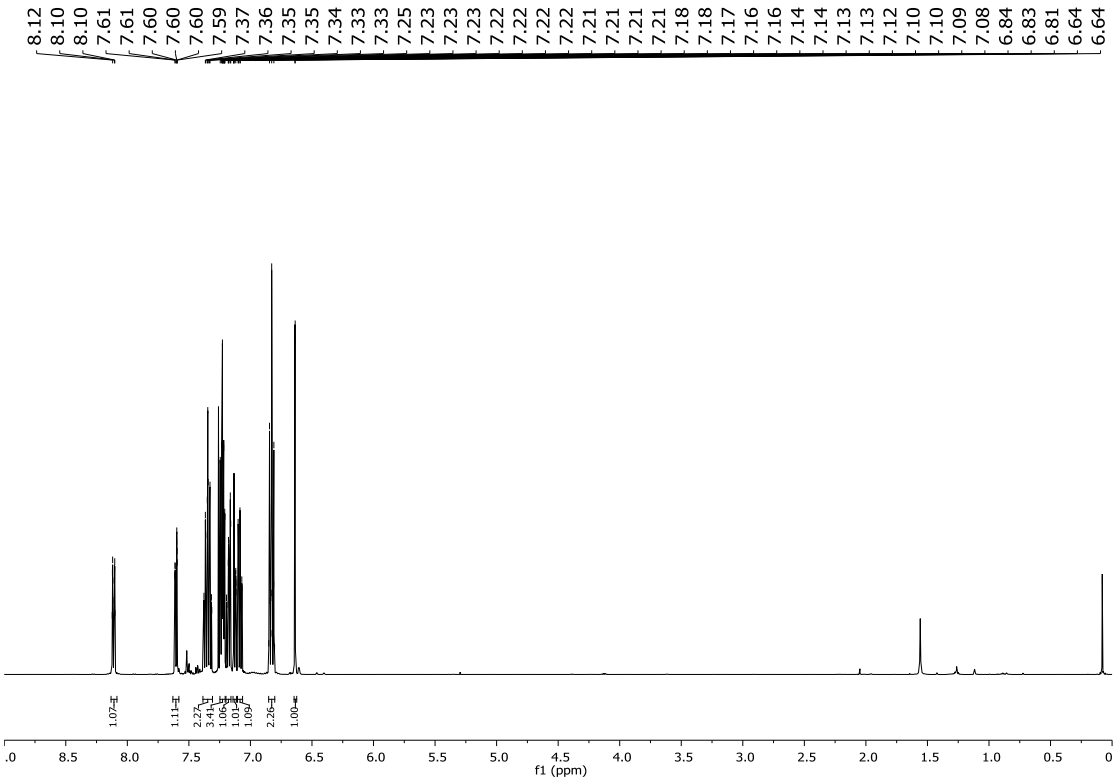


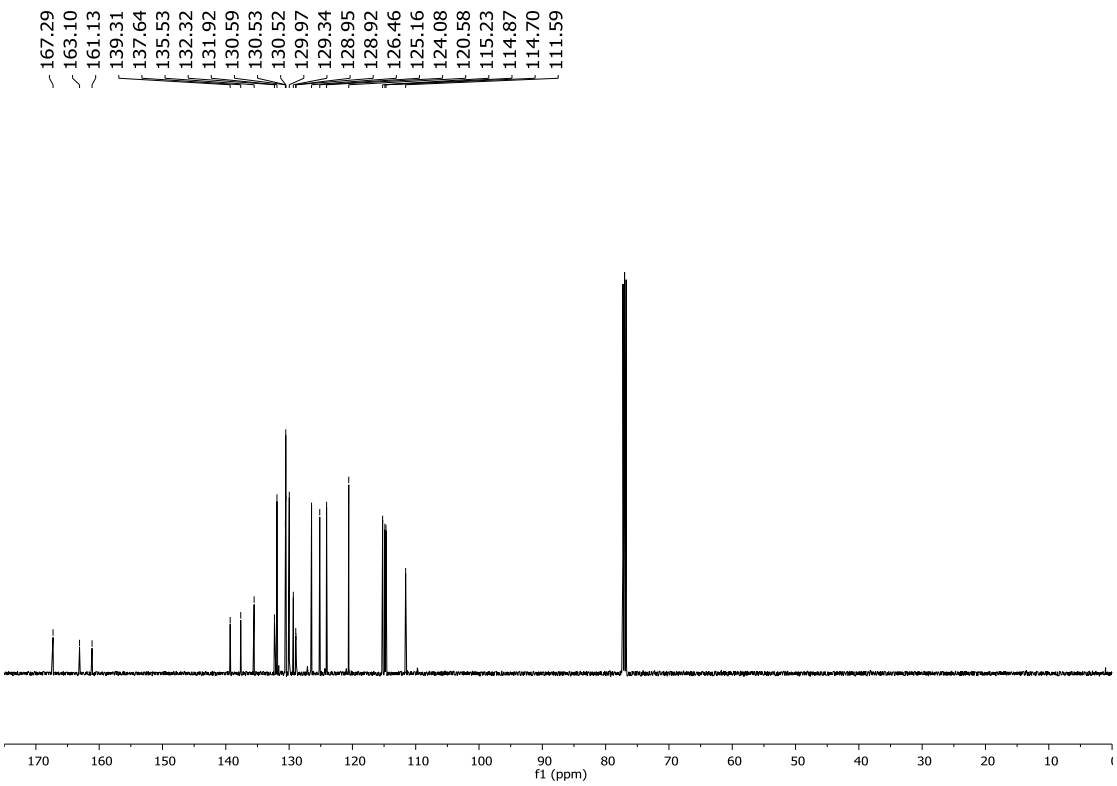
(2-chlorophenyl)(2-(4-fluorophenyl)-1H-indol-1-yl)methanone **(1w)**

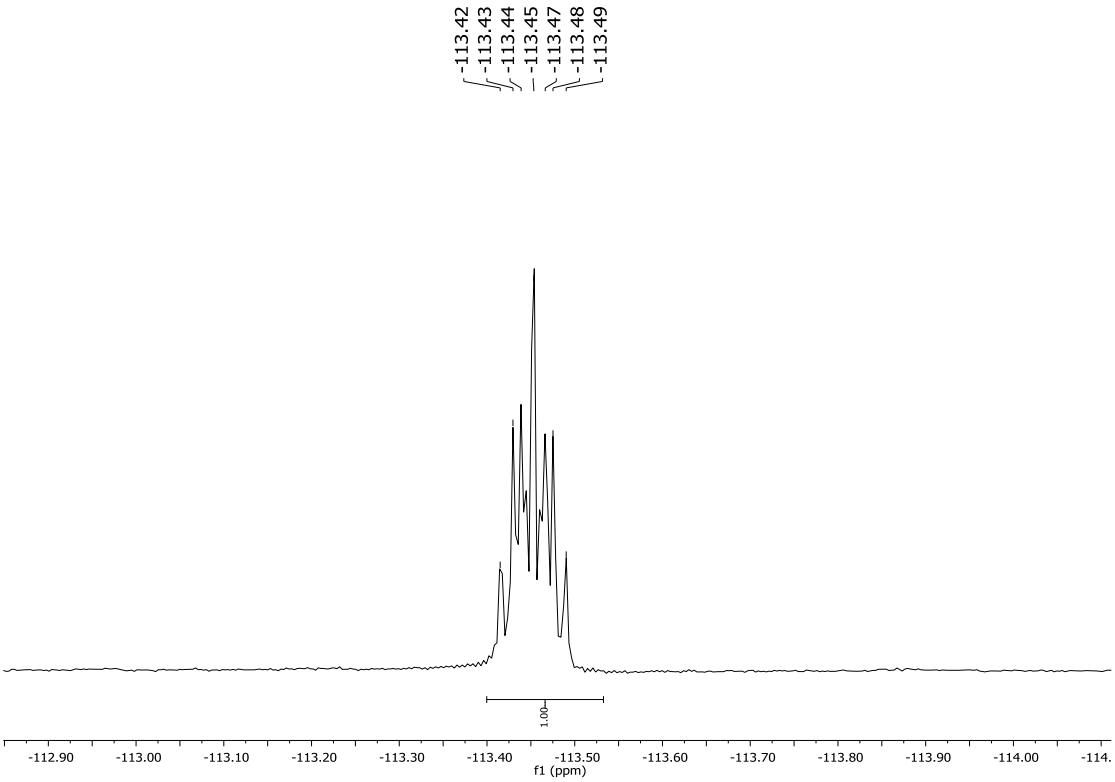


The crude reaction mixture was purified on silica by flash chromatography, eluting with pentanes to pentanes:MTBE 50:1 (v/v). The product was isolated as a white solid (21% yield, mp = 94–96 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (ddt, *J* = 8.2, 1.4, 0.8 Hz, 1H), 7.60 (ddd, *J* = 7.2, 1.7, 0.7 Hz, 1H), 7.39–7.31 (m, 2H), 7.25–7.21 (m, 3H), 7.18 (ddd, *J* = 8.1, 7.2, 1.7 Hz, 1H), 7.13 (ddd, *J* = 8.2, 1.4, 0.5 Hz, 1H), 7.08 (td, *J* = 7.5, 1.3 Hz, 1H), 6.85–6.80 (m, 2H), 6.64 (d, *J* = 0.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.3, 162.1 (d, *J* = 248.2 Hz), 139.3, 137.6, 135.5, 132.3, 131.9,

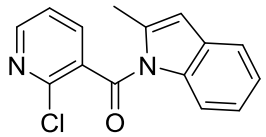
130.6 (d, J = 7.6 Hz), 130.5, 130.0, 129.3, 128.9 (d, J = 3.6 Hz), 126.5, 125.2, 124.1, 120.6, 115.2, 114.8 (d, J = 21.9 Hz), 111.6. ^{19}F NMR (377 MHz, $CDCl_3$) δ -113.45 (ddd, J = 13.9, 9.0, 5.6 Hz). HRMS *m/z* (DART+): calculated for $C_{21}H_{14}ClFNO$ ($[M+H]^+$): 350.0748, found 350.0743.



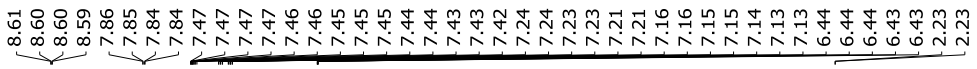


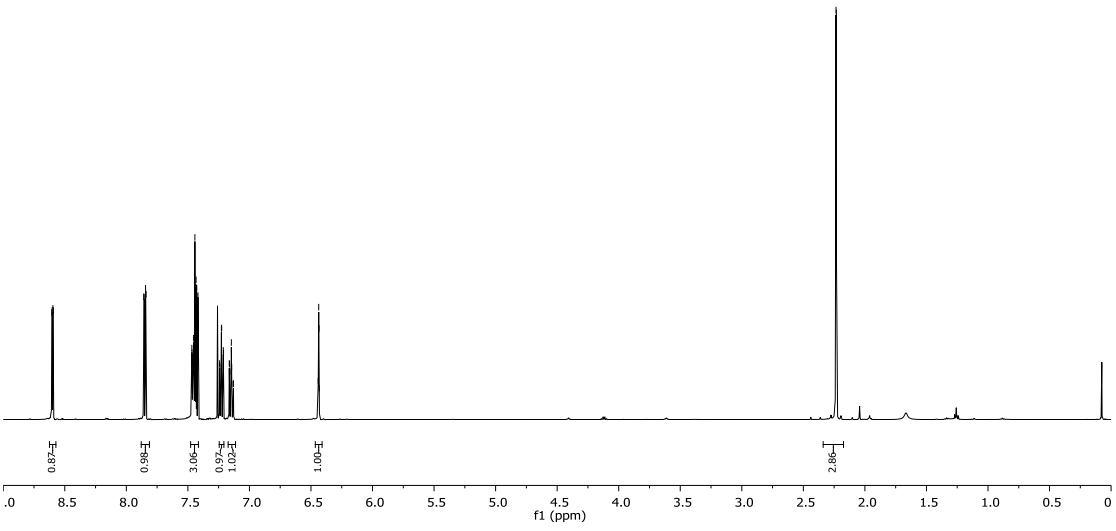


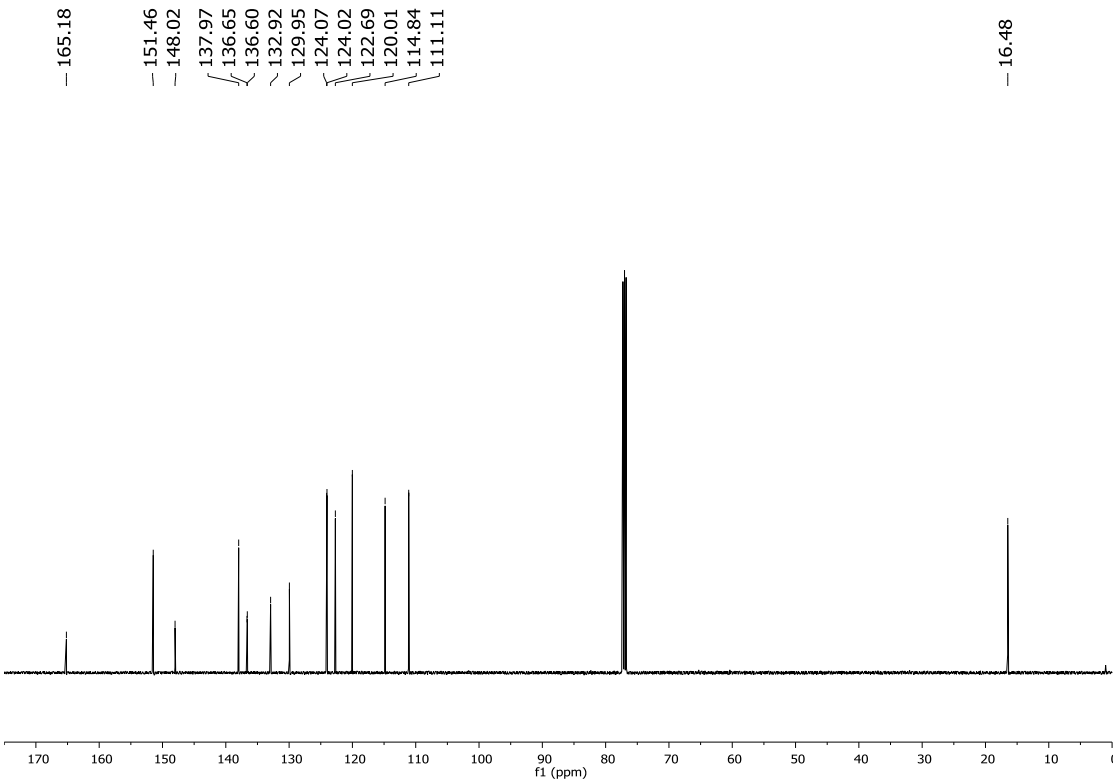
(2-chloropyridin-3-yl)(2-methyl-1H-indol-1-yl)methanone **(1X)**



The crude reaction mixture was purified on silica by flash chromatography, eluting with pentanes:EtOAc 10:1 to 5:1 (v/v). The product was isolated as a white solid (38% yield, mp = 66–67 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (dd, *J* = 4.9, 2.0 Hz, 1H), 7.85 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.48–7.41 (m, 3H), 7.23 (td, *J* = 7.5, 1.0 Hz, 1H), 7.15 (ddd, *J* = 8.6, 7.3, 1.3 Hz, 1H), 6.44 (p, *J* = 1.2 Hz, 1H), 2.23 (d, *J* = 1.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.2, 151.5, 148.0, 138.0, 136.7, 136.6, 132.9, 130.0, 124.1, 124.0, 122.7, 120.0, 114.8, 111.1, 16.5. HRMS *m/z* (DART+): calculated for $C_{15}H_{12}ClN_2O$ ($[M+H]^+$): 271.0638, found 271.0630.



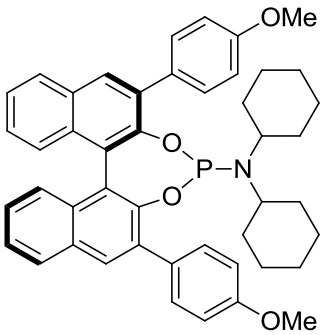




Synthesis of Ligand L1: The preparation of the chiral phosphoramidite ligand was followed literature procedures with some modifications.[2] To a solution of dicyclohexylamine (20.0 mmol) in dry THF (15 mL) at 0 ºC was added *n*-BuLi (2.5 M in hexanes, 20 mmol) dropwise over 5 min under nitrogen atmosphere. After stirring at 0 ºC for 30 min, PCl_3 (60.0 mmol) was added to the reaction mixture in one portion. The resulting mixture was warmed to room temperature, stirred for 1 h, and then concentrated at room temperature. The remaining PCl_3 was removed under vacuum. Dry THF (30 mL) was then added to the resulting residue. After stirring for 10 min, the mixture was cooled to 0 ºC, followed by addition of a solution of 3,3'-disubstituted binaphthyl compound (10.0 mmol) and Et_3N (33.0 mmol) in dry THF

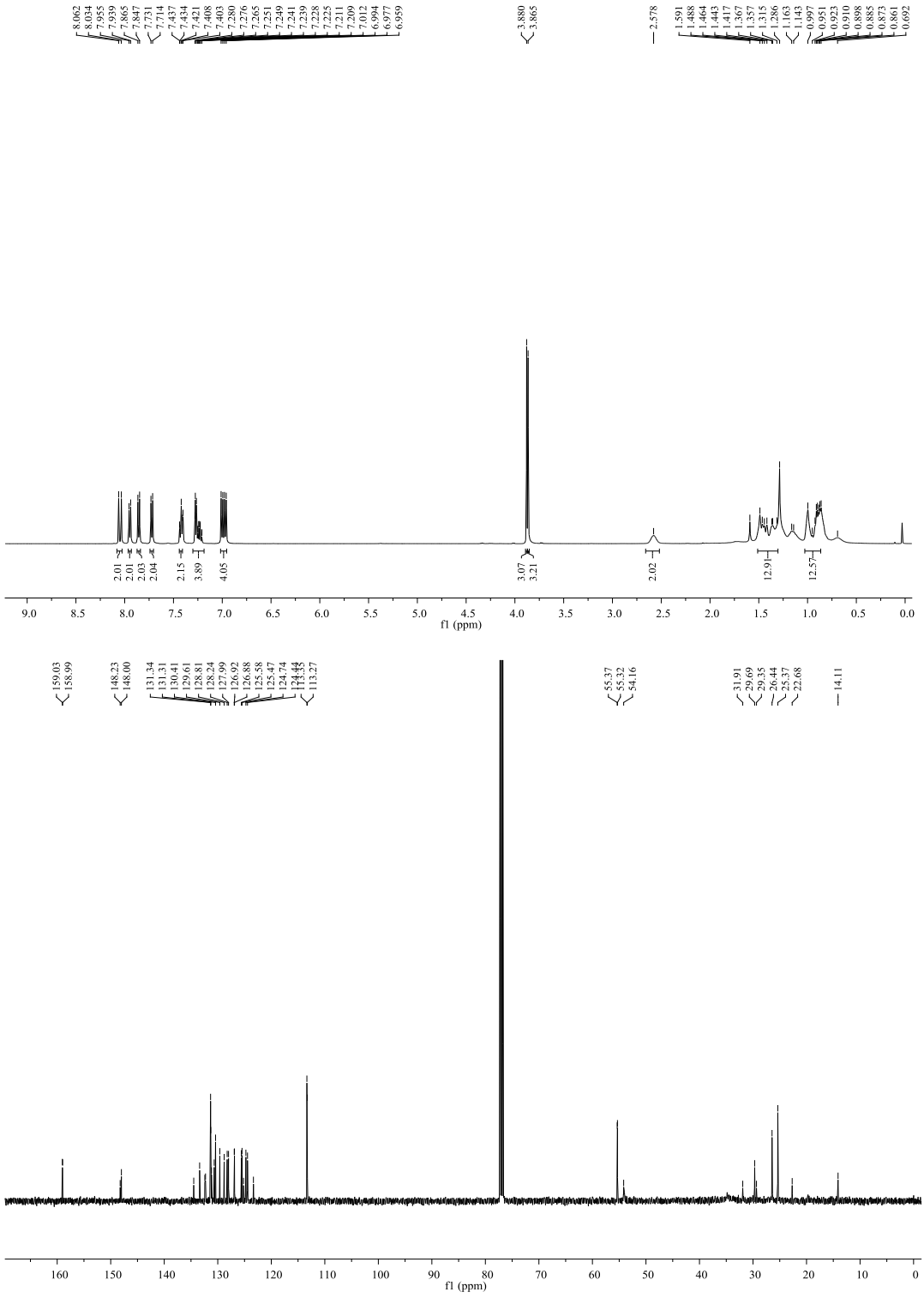
[2] C. R. Smith, T. V. RajanBabu, *Org. Lett.* **2008**, *10*, 1657.

(15 mL). The mixture was warmed to room temperature and stirred for overnight, after which it was filtered and the solid was washed with THF. After evaporation under vacuum, the residue was purified by chromatography on silica gel, eluting with PE: DCM = 10:1 (v/v) to afford the ligands.



L1

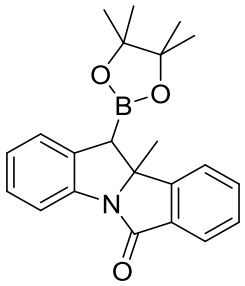
White solid, m.p.: 74-75 ^{o}C, yield 60%, $[\alpha]_D^{20}$ = -293.2 (*c* 0.2, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 (d, *J* = 13.5 Hz, 2H), 7.95 (d, *J* = 8.0 Hz, 2H), 7.86 (d, *J* = 8.5 Hz, 2H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.42-7.40 (m, 2H), 7.30-7.19 (m, 4H), 6.99 (dd, *J* = 17.5, 8.8 Hz, 4H), 3.88 (s, 3H), 3.87 (s, 3H), 2.58 (s, 2H), 1.60-1.20 (m, 8H), 1.00-0.86 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.0, 148.2, 148.0, 134.5, 133.4, 132.4, 131.5, 131.0, 130.7, 130.4, 129.6, 128.8, 128.2, 128.0, 126.9, 125.5, 125.2, 124.7, 124.4, 123.3, 113.3, 55.4, 54.2, 31.9, 29.7, 29.4, 26.4, 25.4, 22.7, 14.1. HRMS *m/z* (ESI^+): calculate for $C_{46}H_{47}NO_4P$ ($[M+H]^+$): 708.3237, found 708.3238.


8.062
8.034
7.955
7.939
7.865
7.847
7.731
7.714
7.437
7.434
7.421
7.408
7.403
7.280
7.276
7.265
7.251
7.249
7.241
7.239
7.228
7.225
7.211
7.209
7.012
6.994
6.977
6.959
3.880
3.865
2.578
1.591
1.488
1.464
1.443
1.417
1.387
1.315
1.286
1.168
1.143
0.997
0.951
0.923
0.910
0.898
0.885
0.873
0.861
0.692
2.01
2.01
2.03
2.04
2.15
3.89
4.05
3.07
3.21
2.02
12.91
12.57
f1 (ppm)
159.03
158.99
148.23
148.00
131.34
131.31
130.41
129.61
128.81
128.24
127.99
126.92
126.88
125.58
125.47
124.74
114.44
114.35
113.27
55.37
55.32
54.16
31.91
29.69
29.35
26.44
25.37
22.68
14.11
f1 (ppm)

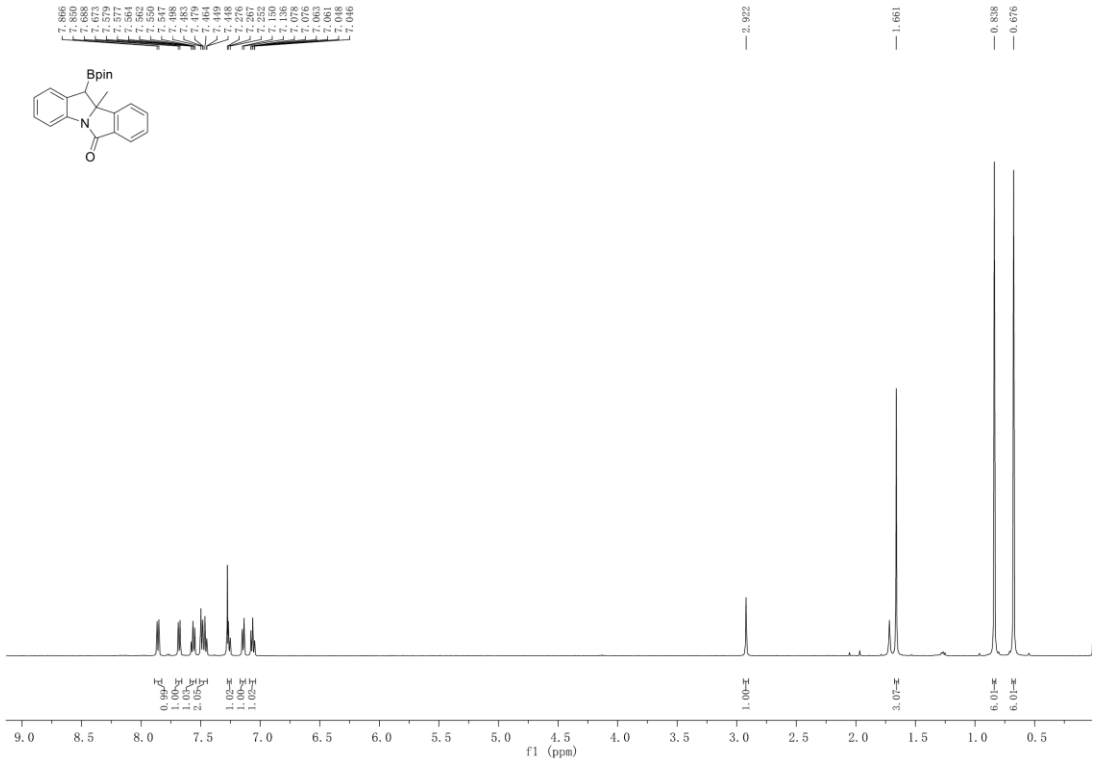
3. Pd-catalyzed dearomative arylborylation of indoles

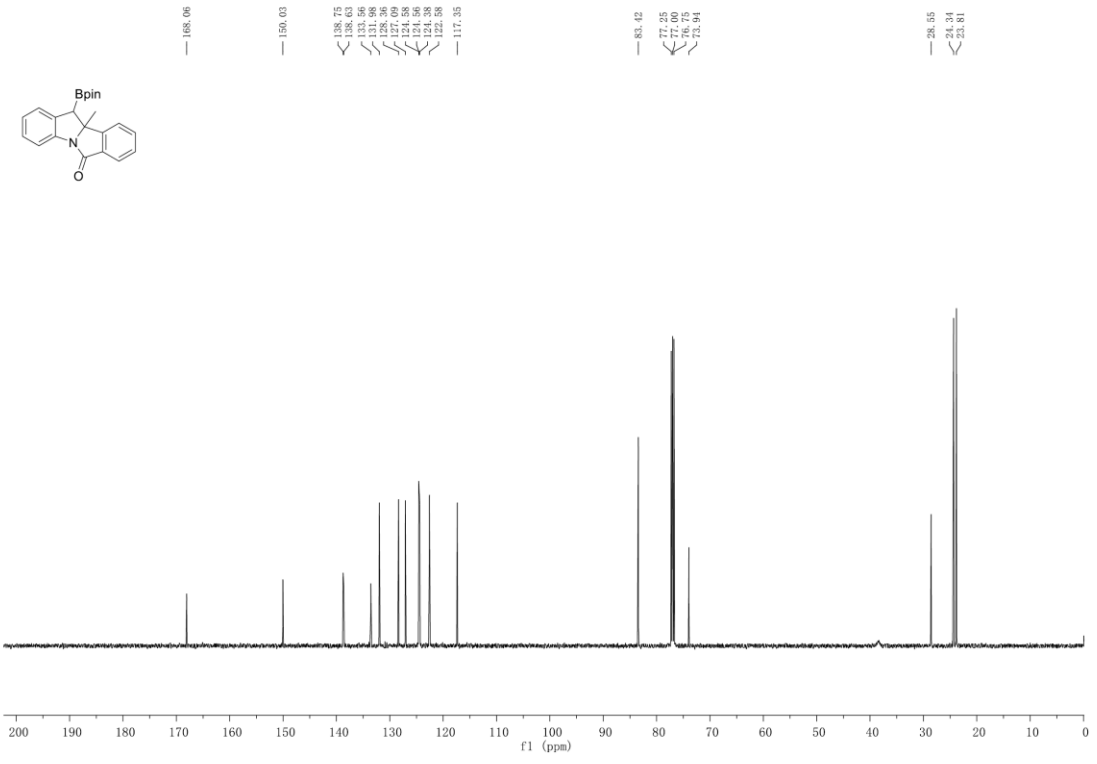
To a dried Schlenk tube were added $Pd(OAc)_2$ (2.3 mg, 0.01 mmol) and PPh_3 (5.2 mg, 0.02 mmol) under N_2, 2.0 mL DCE or DCM was then introduced via a syringe. The resulting mixture was stirred at room temperature for 1 h, after which *N*-benzoylindoles (0.2 mmol) and B_2pin_2 (0.4 mmol) were added and the tube was sealed using Teflon cap. The mixture was stirred at 60 °C or 70 °C (oil bath) until the reaction was complete (monitored by TLC). The solvent was then removed under vacuum and the residue was purified by chromatography on silica gel quickly, eluting with ethyl acetate/petroleum ether 1:5 (v/v) to afford the products.

10b-methyl-11-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**3a**):

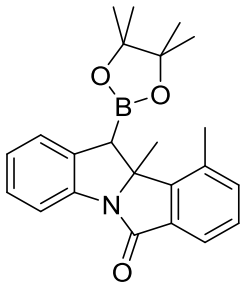


The reaction was in DCE at 60 °C (oil bath). Purified by chromatography on silica gel very quickly, eluting with ethyl acetate/petroleum ether 1:5 (v/v); white solid, Mp = 193-195 °C; 87% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.5 Hz, 1H), 7.68 (d, *J* = 7.5 Hz, 1H), 7.56 (td, *J* = 7.5, 1.0 Hz, 1H), 7.51 – 7.44 (m, 2H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 7.0 Hz, 1H), 7.06 (td, *J* = 7.5, 1.0 Hz, 1H), 2.92 (s, 1H), 1.66 (s, 3H), 0.84 (s, 6H), 0.68 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.1, 150.0, 138.8, 138.6, 133.6, 132.0, 128.4, 127.1, 124.58, 124.56, 124.4, 122.6, 117.4, 83.4, 73.9, 28.6, 24.3, 23.8. HRMS *m/z* (ESI+): Calculated for $C_{22}H_{25}BNO_3$ ($[M+H]^+$): 362.1922, Found 362.1921.

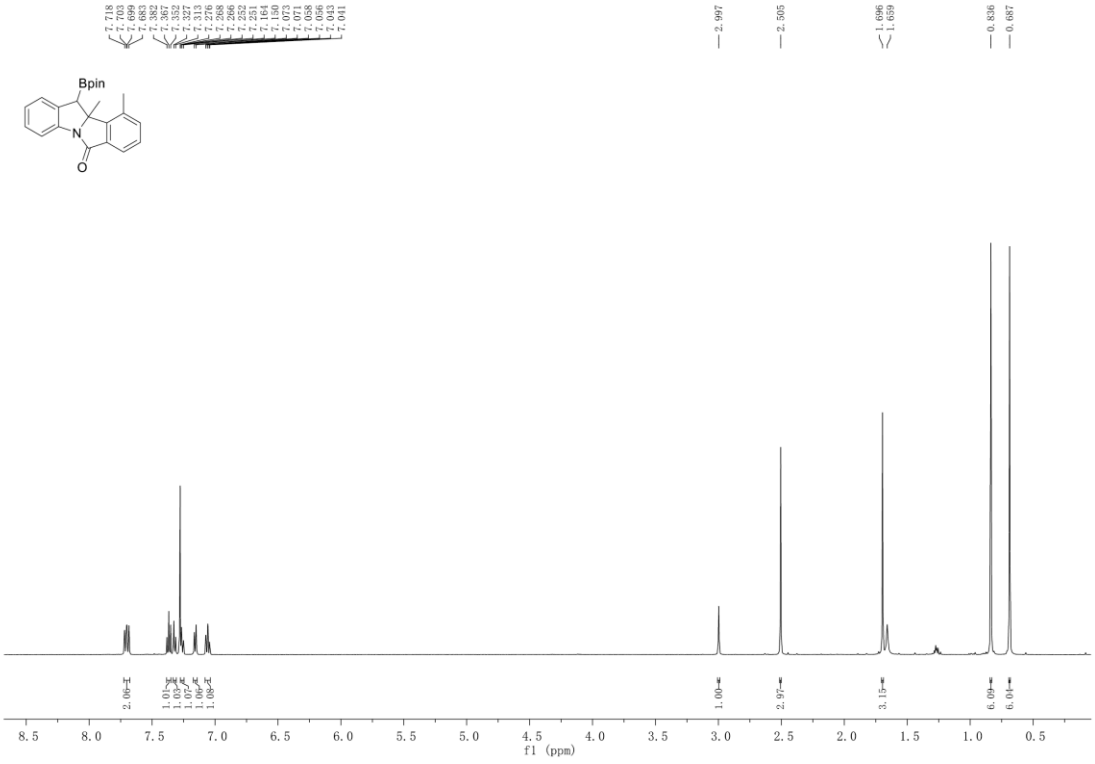

7.866
7.850
7.688
7.673
7.579
7.577
7.564
7.562
7.550
7.547
7.498
7.483
7.479
7.464
7.449
7.448
7.276
7.267
7.252
7.169
7.136
7.078
7.076
7.063
7.061
7.048
7.046
2.922
1.661
0.838
0.676
Bpin
N
O
0.99
1.00
1.05
2.05
1.02
1.00
1.02
1.00
3.07
6.01
6.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

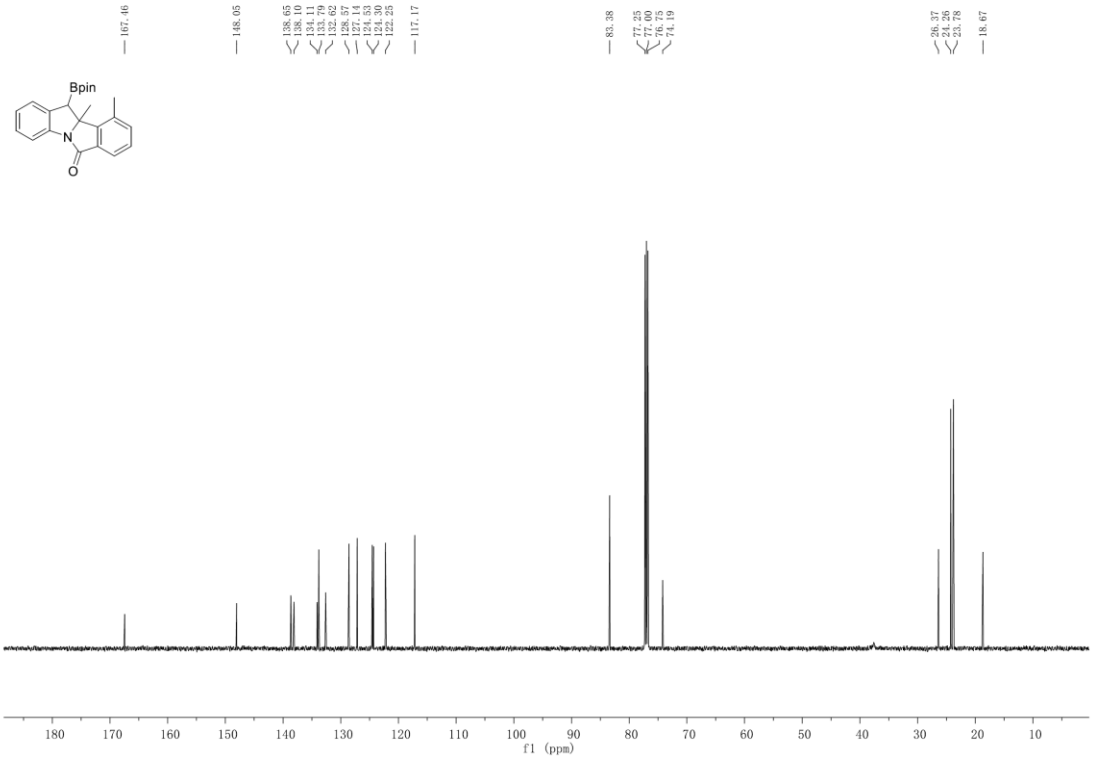

168.06
150.03
138.75
138.63
133.56
131.98
128.36
127.09
124.58
124.56
124.38
122.98
117.35
83.42
77.25
77.00
76.75
73.94
28.55
24.34
23.81
Bpin
N
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

10,10b-dimethyl-11-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**3b**):

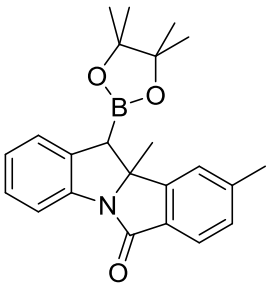


The reaction was in DCE at 60 °C (oil bath). Purified by chromatography on silica gel very quickly, eluting with ethyl acetate/petroleum ether 1:5 (v/v); white solid, Mp = 129-131 °C; 78% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 7.5 Hz, 1H), 7.29 (s, 1H), 7.25 (t, *J* = 7.0 Hz, 2H), 7.13 (d, *J* = 7.5 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 2.90 (s, 1H), 2.47 (s, 3H), 1.65 (s, 3H), 0.85 (s, 6H), 0.70 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.3, 150.5, 142.7, 138.9, 138.6, 130.9, 129.3, 127.1, 124.6, 124.5, 124.3, 123.2, 117.3, 83.4, 73.7, 28.7, 24.3, 23.8, 21.8. HRMS *m/z* (ESI+): Calculated for $C_{23}H_{27}BNO_3$ ([M+H]$^+$): 376.2079, Found 376.2046.



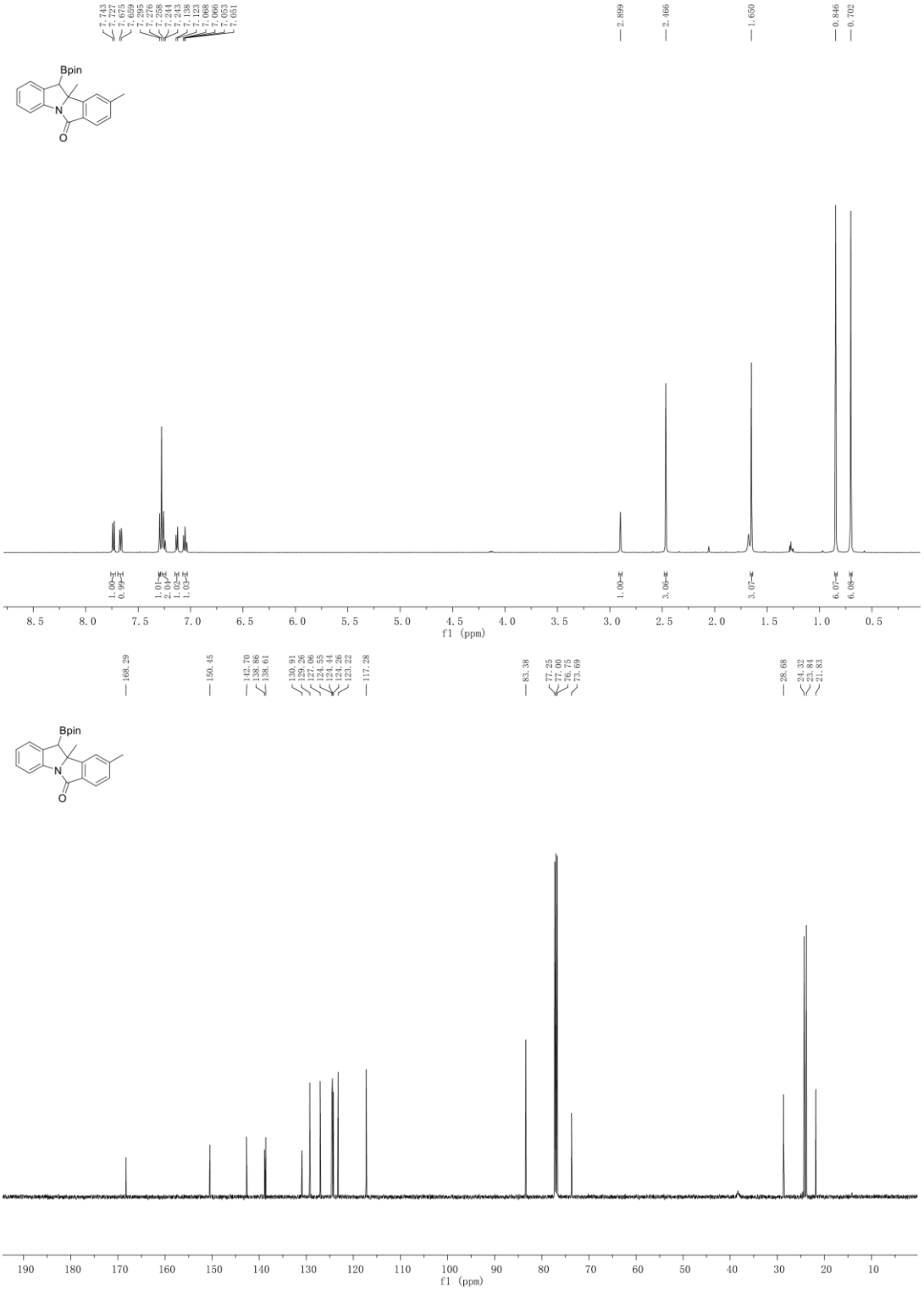


9,10b-dimethyl-11-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**3c**):

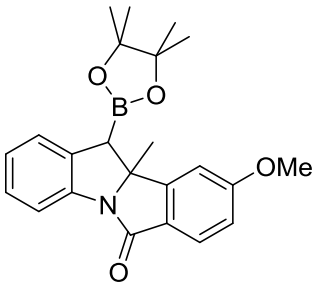


The reaction was in DCE at 60 °C (oil bath). Purified by chromatography on silica gel very quickly, eluting with ethyl acetate/petroleum ether 1:5 (v/v); white solid, Mp = 226-229 °C; 88% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 10.0, 8.0 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 7.0 Hz, 1H), 7.26 (td, *J* = 8.0, 0.5 Hz, 1H), 7.16 (d, *J* = 7.0 Hz, 1H), 7.06 (td, *J* = 7.5, 1.0 Hz, 1H), 3.00 (s, 1H), 2.51 (s, 3H), 1.70 (s, 3H), 0.84 (s, 6H), 0.69 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.5, 148.1, 138.7, 138.1, 134.1, 133.8, 132.6, 128.6, 127.1, 124.5, 124.3, 122.3, 117.2, 83.4, 74.2, 26.4, 24.3, 23.8, 18.7. HRMS *m/z* (ESI+): Calculated for $C_{23}H_{27}BNO_3$ ([M+H] $^{+}$):

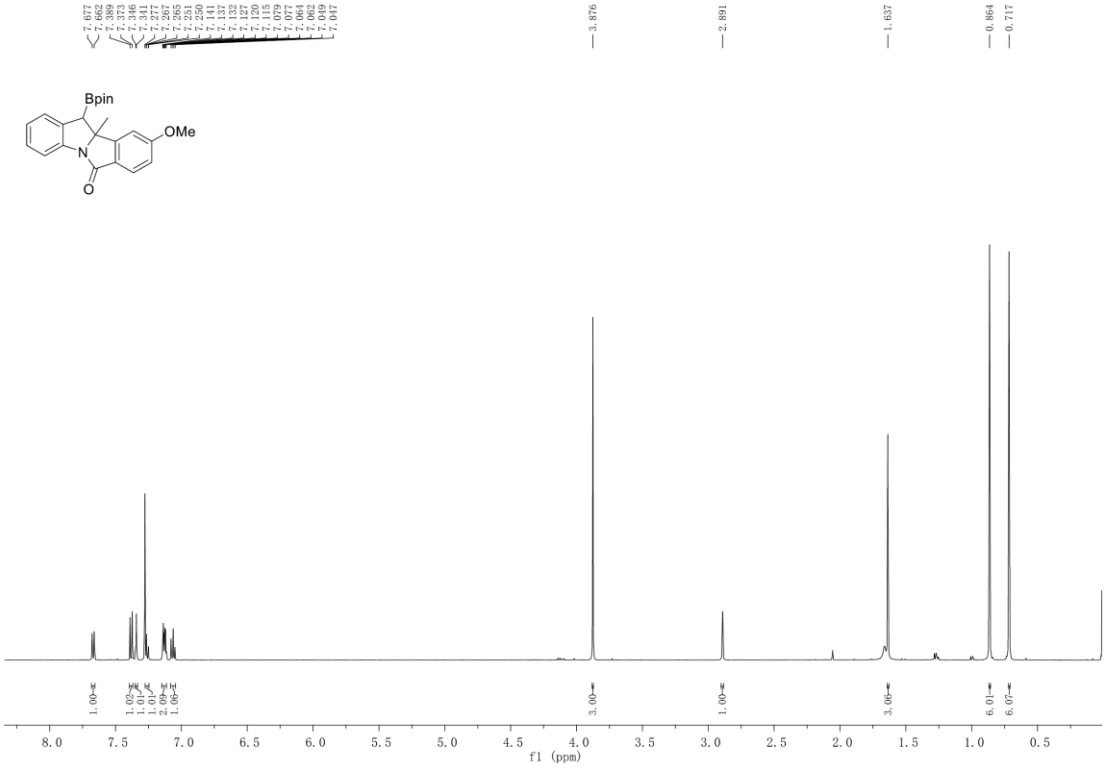
376.2079, Found 376.2052.

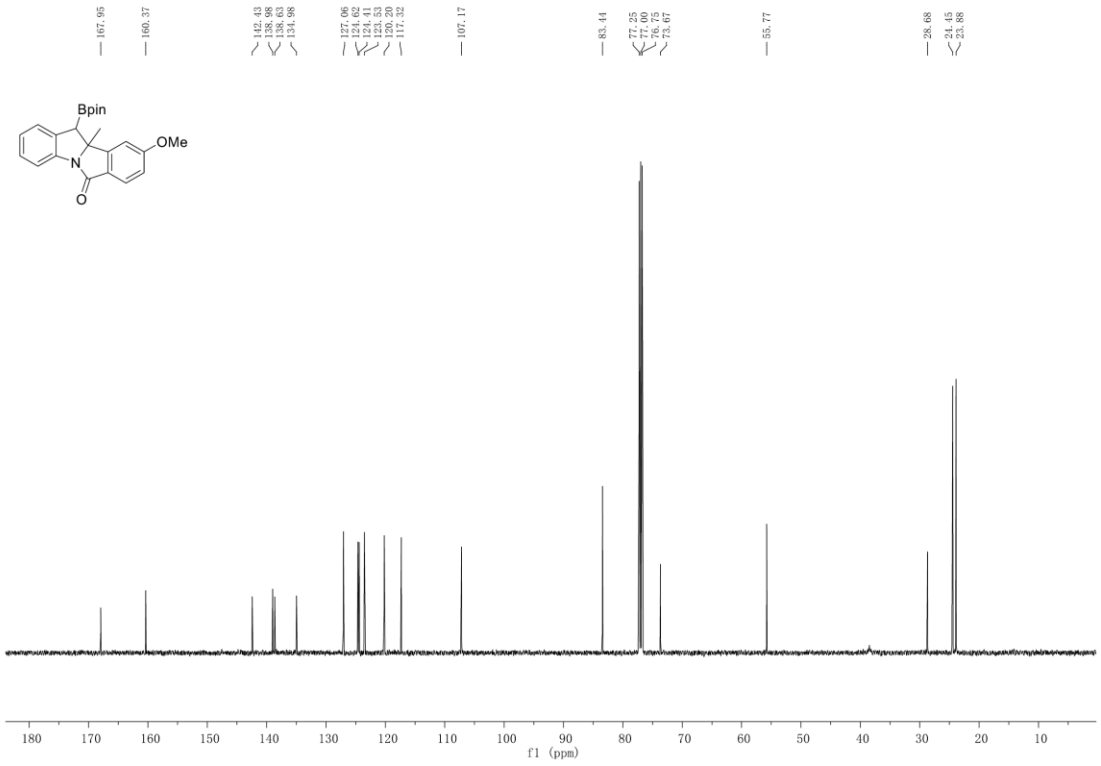


9-methoxy-10b-methyl-11-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**3d**):

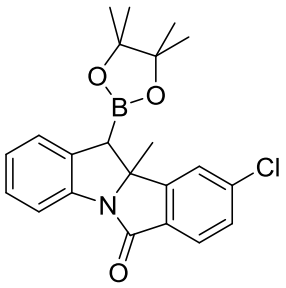


The reaction was in DCE at 60 °C (oil bath). Purified by chromatography on silica gel very quickly, eluting with ethyl acetate/petroleum ether 1:5 (v/v); white solid, Mp = 243-245 °C; 76% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.5 Hz, 1H), 7.38 (d, *J* = 8.5 Hz, 1H), 7.34 (d, *J* = 2.5 Hz, 1H), 7.26 (td, *J* = 7.5, 1.0 Hz, 1H), 7.15 – 7.11 (m, 2H), 7.06 (td, *J* = 7.5, 1.0 Hz, 1H), 3.88 (s, 3H), 2.89 (s, 1H), 1.64 (s, 3H), 0.86 (s, 6H), 0.72 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.0, 160.4, 142.4, 139.0, 138.6, 135.0, 127.1, 124.6, 124.4, 123.5, 120.2, 117.3, 107.2, 83.4, 73.7, 55.8, 28.7, 24.5, 23.9. HRMS *m/z* (ESI+): Calculated for $C_{23}H_{27}BNO_4$ ($[M+H]^+$): 392.2028, Found 392.2044.



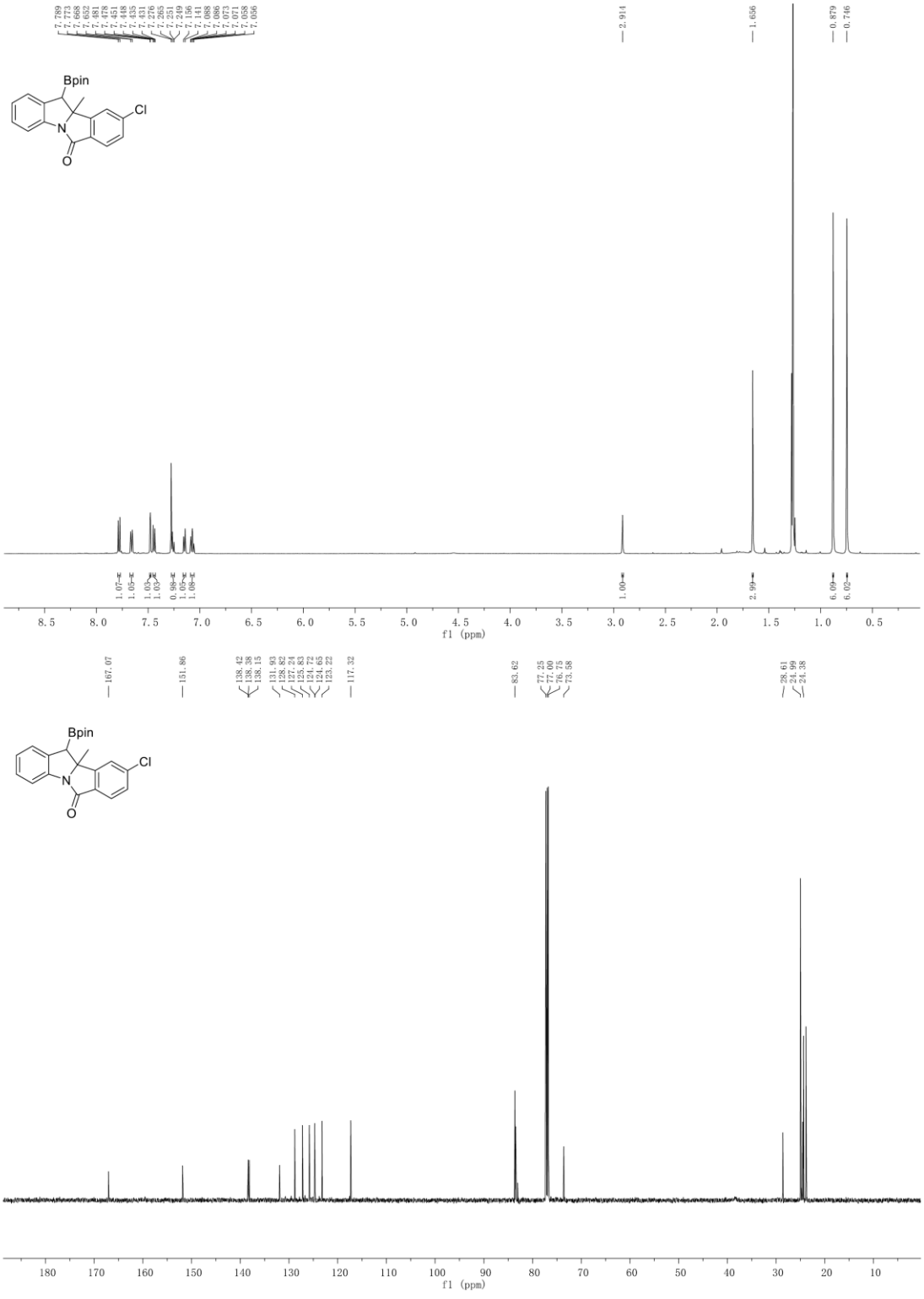


9-chloro-10b-methyl-11-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**3e**):

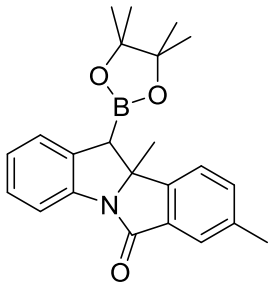


The reaction was in DCE at 60 °C (oil bath). Purified by chromatography on silica gel very quickly, eluting with ethyl acetate/petroleum ether 1:5 (v/v); white solid, Mp = 148-150 °C; 61% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 1.5 Hz, 1H), 7.44 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.27–7.24 (m, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 7.07 (td, *J* = 7.5, 1.0 Hz, 1H), 2.91 (s, 1H), 1.66 (s, 3H), 0.88 (s, 6H), 0.75 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.1, 151.9, 138.42, 138.38, 138.2, 131.9, 128.8, 127.2, 125.8, 124.72, 124.65, 123.2, 117.3, 83.6, 73.6, 28.6, 25.0, 24.4. HRMS *m/z* (ESI+): Calculated for $C_{22}H_{24}BClNO_3$

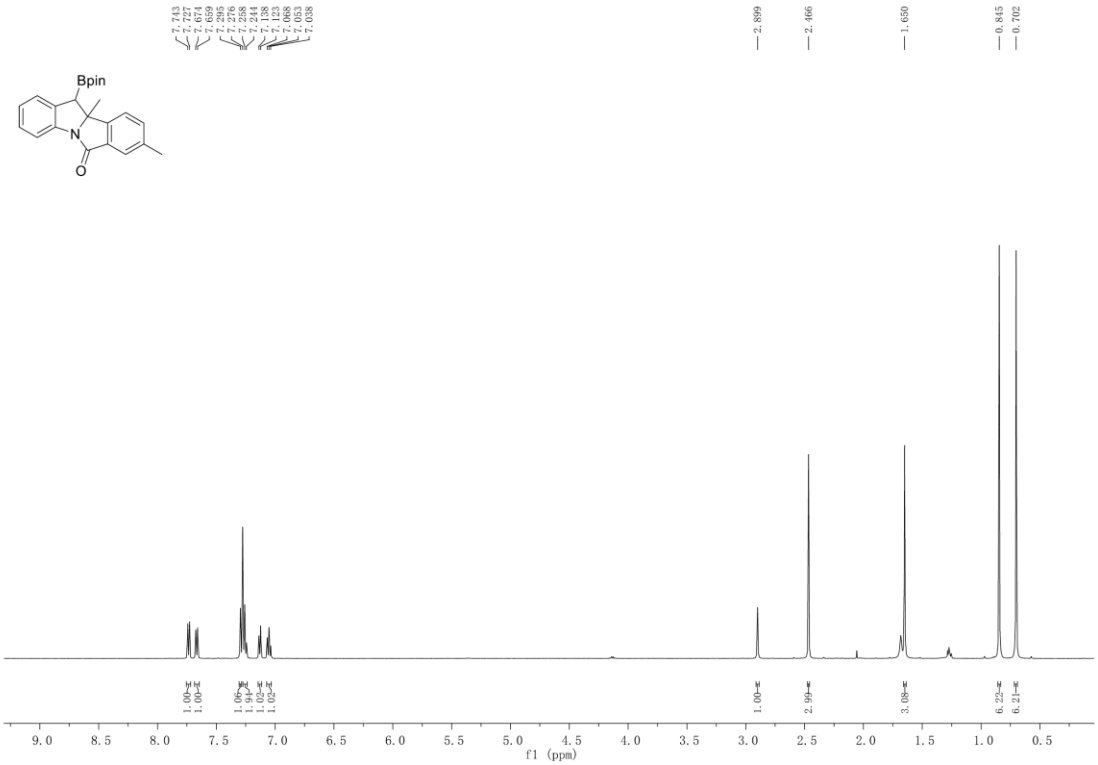
([M+H]$^+$): 396.1532, Found 396.1528.

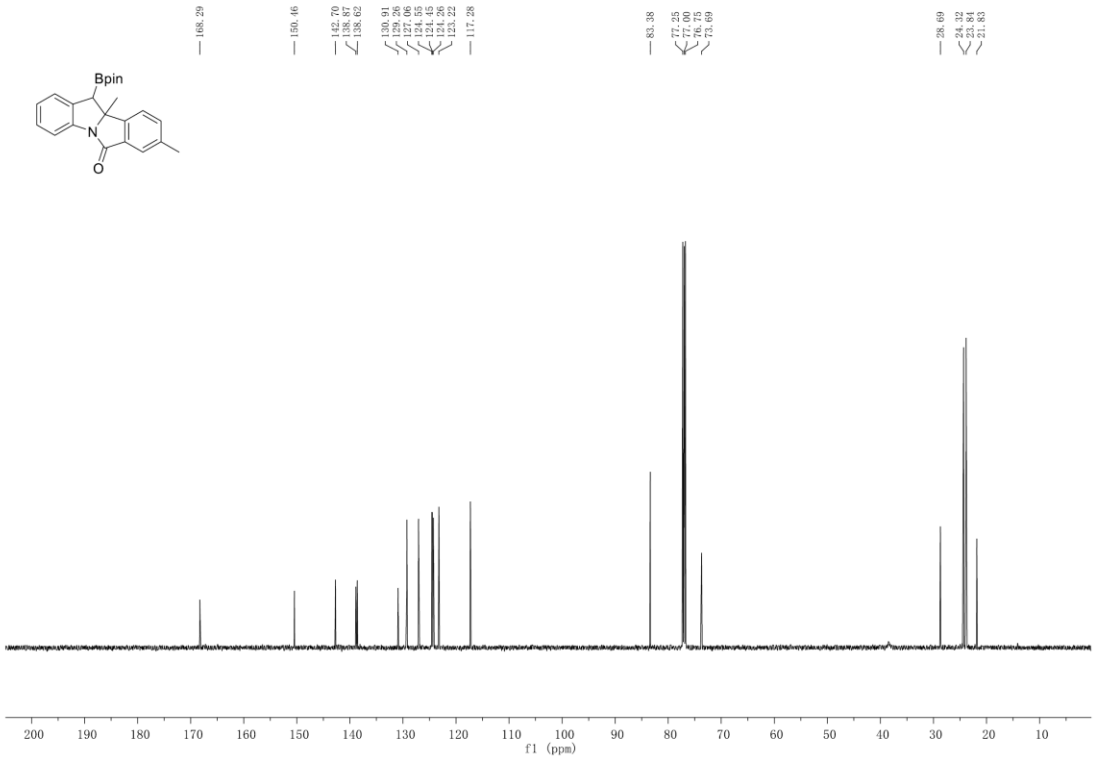


8,10b-dimethyl-11-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**3f**):

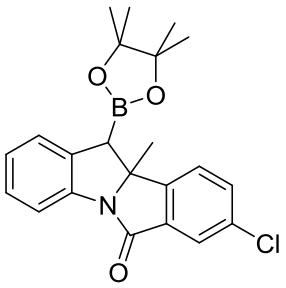


The reaction was in DCE at 60 °C (oil bath). Purified by chromatography on silica gel very quickly, eluting with ethyl acetate/petroleum ether 1:5 (v/v); white solid, Mp = 225-227 °C; 90% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 7.5 Hz, 1H), 7.29 (s, 1H), 7.25 (t, *J* = 7.0 Hz, 2H), 7.13 (d, *J* = 7.5 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 2.90 (s, 1H), 2.47 (s, 3H), 1.65 (s, 3H), 0.85 (s, 6H), 0.70 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.3, 150.5, 142.7, 138.9, 138.6, 130.9, 129.3, 127.1, 124.6, 124.5, 124.3, 123.2, 117.3, 83.4, 73.7, 28.7, 24.3, 23.8, 21.8. HRMS *m/z* (ESI+): Calculated for $C_{23}H_{27}BNO_3$ ($[M+H]^+$): 376.2079, Found 376.2043.



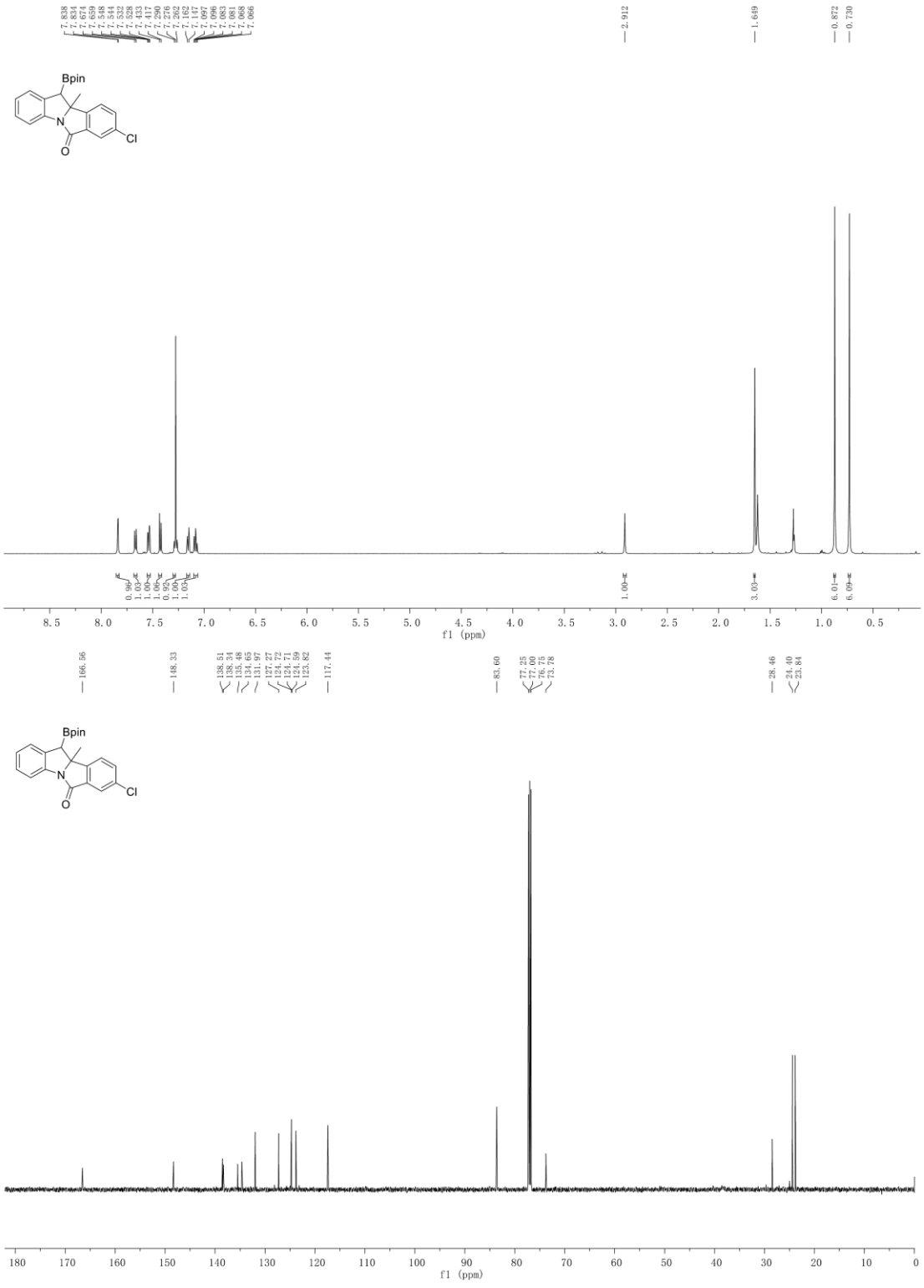


8-chloro-10b-methyl-11-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**3g**):

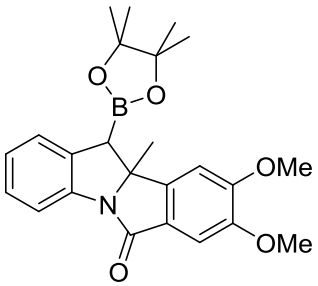


The reaction was in DCE at 60 °C (oil bath). Purified by chromatography on silica gel very quickly, eluting with ethyl acetate/petroleum ether 1:5 (v/v); white solid, Mp = 184-186 °C; 65% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 2.0 Hz, 1H), 7.67 (d, *J* = 7.5 Hz, 1H), 7.54 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.29 (s, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 7.08 (td, *J* = 7.5, 1.0 Hz, 1H), 2.91 (s, 1H), 1.65 (s, 3H), 0.87 (s, 6H), 0.73 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.6, 148.3, 138.5, 138.3, 135.5, 134.7, 132.0, 127.3, 124.72, 124.71, 124.6, 123.8, 117.4, 83.6, 73.8, 28.5, 24.4, 23.8. HRMS *m/z* (ESI+): Calculated for $C_{22}H_{24}BClNO_3$ ($[M+H]^+$):

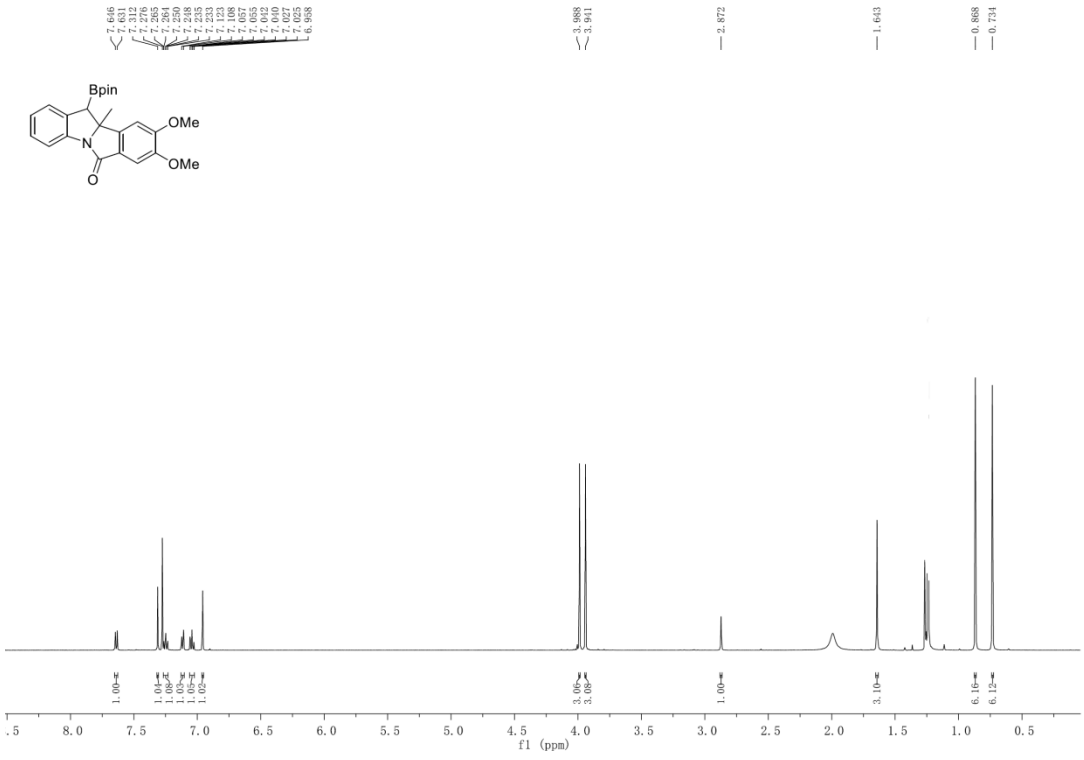
396.1532, Found 396.1507.

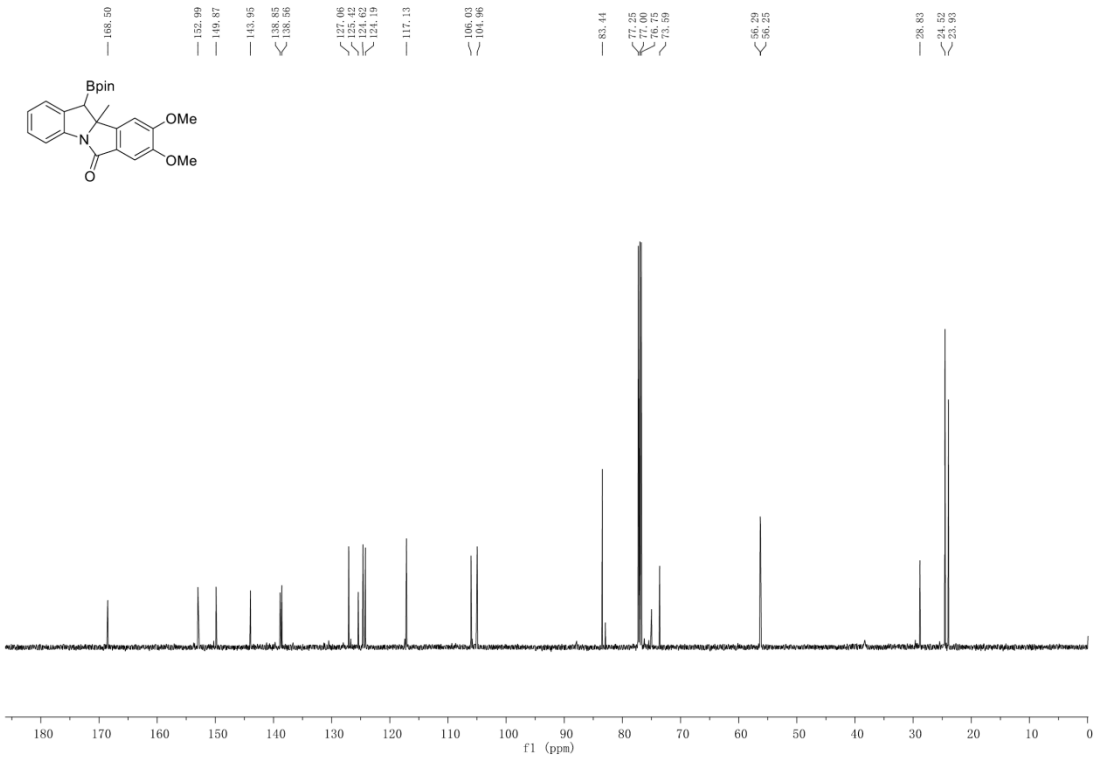


8,9-dimethoxy-10b-methyl-11-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**3h**):

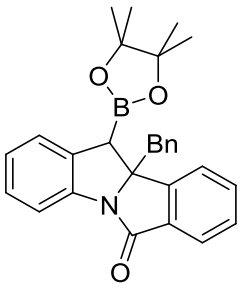


The reaction was in DCE at 60 °C (oil bath). Purified by chromatography on silica gel very quickly, eluting with ethyl acetate/petroleum ether 1:5 (v/v); white solid, Mp = 59-61 °C; 92% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, J = 7.5 Hz, 1H), 7.31 (s, 1H), 7.25 (td, *J* = 7.5, 1.0 Hz, 1H), 7.12 (d, *J* = 7.5 Hz, 1H), 7.04 (td, *J* = 7.5, 1.0 Hz, 1H), 6.96 (s, 1H), 3.99 (s, 3H), 3.94 (s, 3H), 2.87 (s, 1H), 1.64 (s, 3H), 0.87 (s, 6H), 0.73 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.5, 153.0, 149.9, 144.0, 138.9, 138.6, 127.1, 125.4, 124.6, 124.2, 117.1, 106.0, 105.0, 83.4, 73.6, 56.29, 56.25, 28.8, 24.5, 23.9. HRMS *m/z* (ESI+): Calculated for $C_{24}H_{29}BNO_5$ ([M+H] $^{+}$): 422.2133, Found 422.2159.



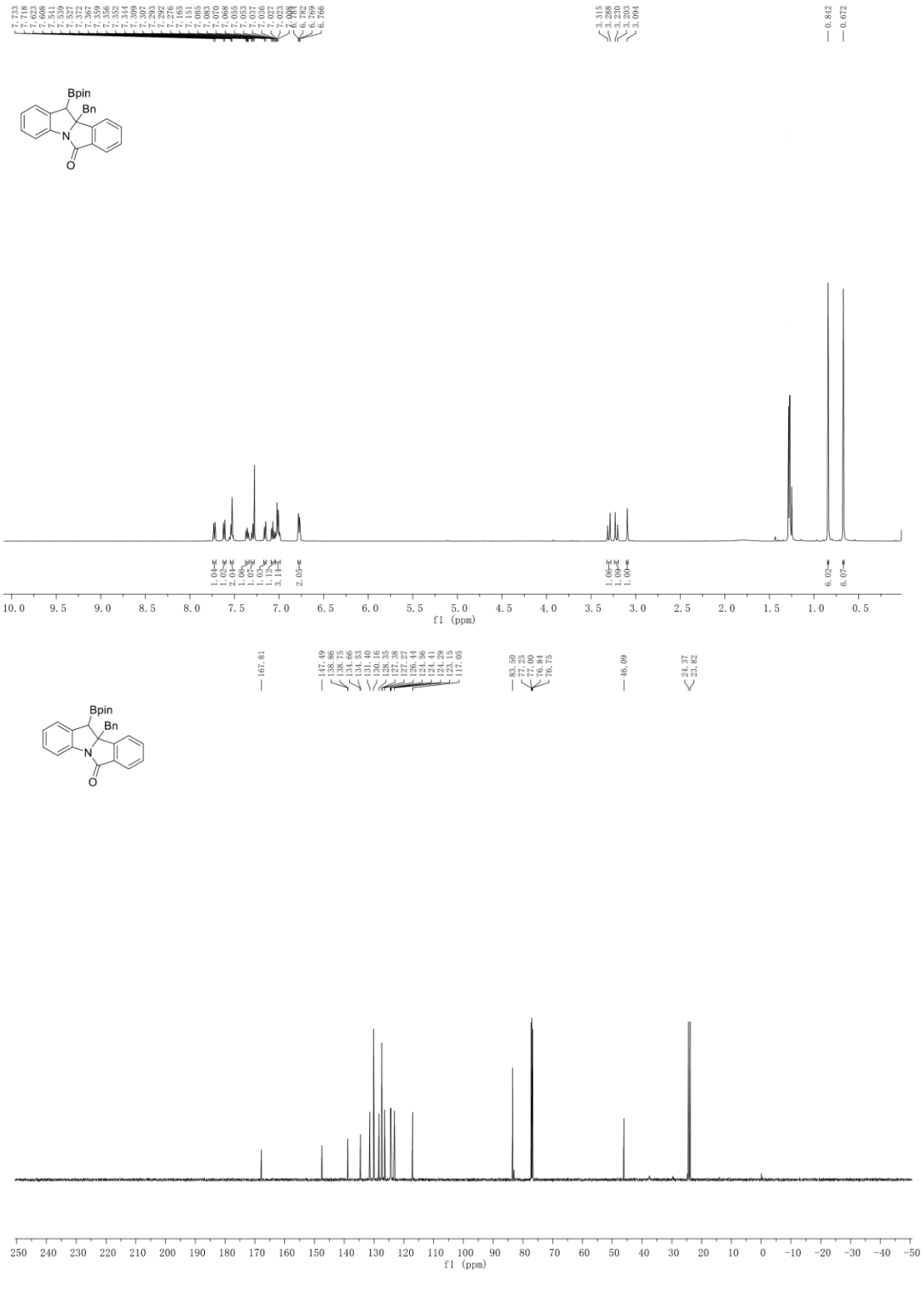


10b-benzyl-11-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**3i**):

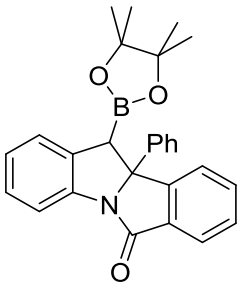


The reaction was in DCM at 70 °C (oil bath). Purified by chromatography on silica gel very quickly, eluting with ethyl acetate/petroleum ether 1:5 (v/v); white solid, Mp = 121-122 °C; 62% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.5 Hz, 1H), 7.62 (d, *J* = 7.5 Hz, 1H), 7.55–7.51 (m, 2H), 7.38 – 7.34 (m, 1H), 7.32–7.27 (m, 1H), 7.16 (d, *J* = 7.0 Hz, 1H), 7.07 (td, *J* = 7.5, 1.0 Hz, 1H), 7.04–6.99 (m, 3H), 6.78 (dd, *J* = 7.5, 1.5 Hz, 2H), 3.30 (d, *J* = 13.5 Hz, 1H), 3.22 (d, *J* = 13.5 Hz, 1H), 3.09 (s, 1H), 0.84 (s, 6H), 0.67 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.8, 147.5, 138.9, 138.8, 134.7, 134.5, 131.4, 130.2, 128.4, 127.4, 127.3, 126.4, 124.6, 124.4, 124.3, 123.2, 117.1, 83.5, 76.8, 46.1, 24.4, 23.8. HRMS *m/z* (ESI+): Calculated for $C_{24}H_{29}BNO_5$ ([M+H] $^{+}$):

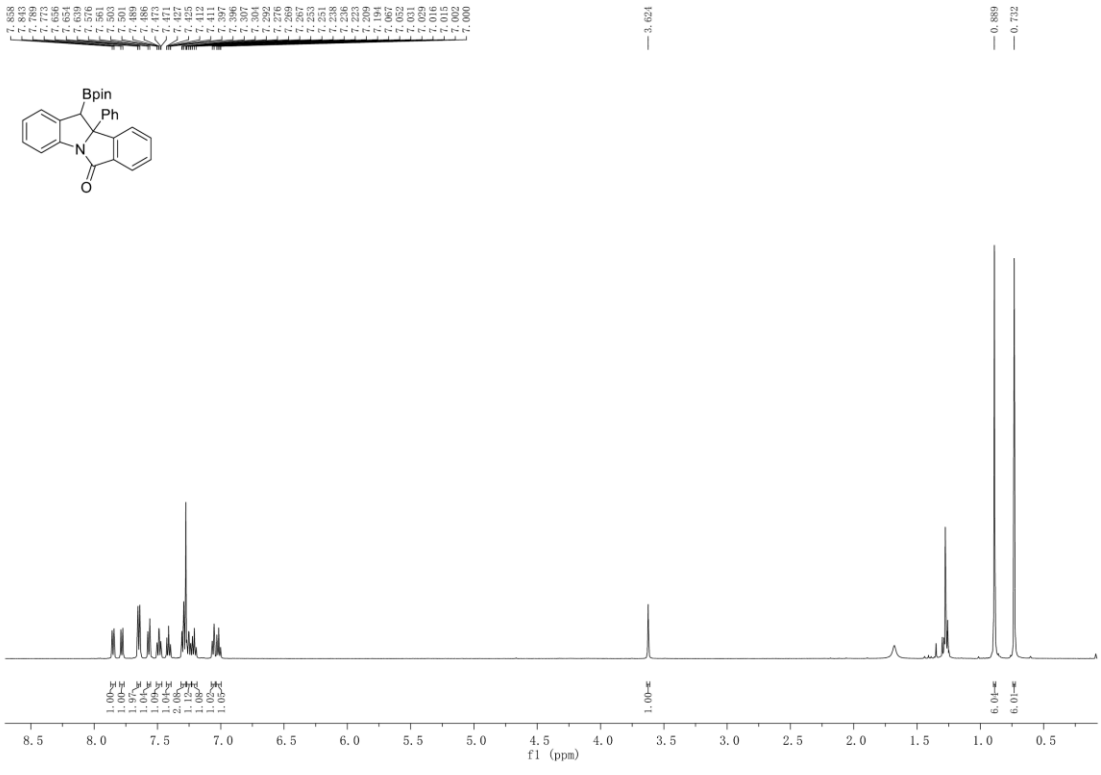
438.2235, Found 438.2245.

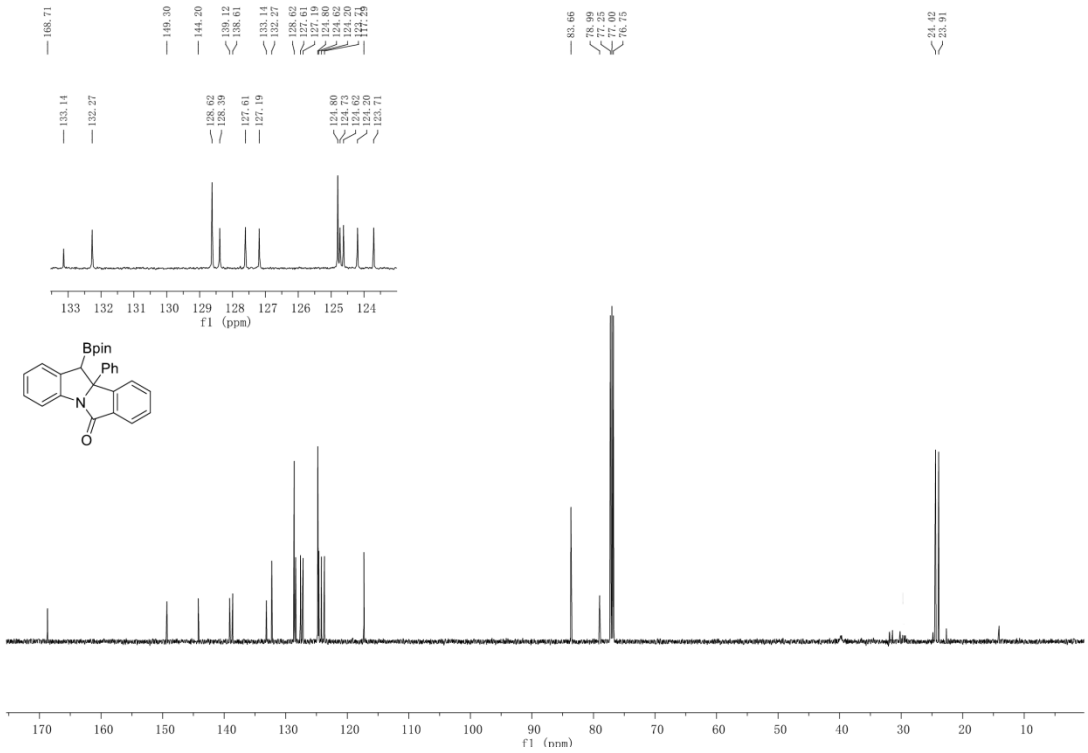


10b-phenyl-11-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**3j**):

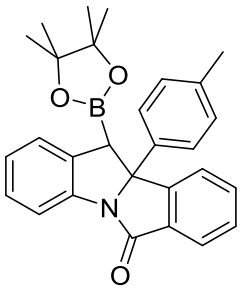


The reaction was in DCM at 70 °C (oil bath). Purified by chromatography on silica gel very quickly, eluting with ethyl acetate/petroleum ether 1:5 (v/v); white solid, Mp = 180-183 °C; 65% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.5 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.66–7.63 (m, 2H), 7.57 (d, *J* = 7.5 Hz, 1H), 7.49 (td, *J* = 7.5, 1.0 Hz, 1H), 7.41 (td, *J* = 7.5, 1.0 Hz, 1H), 7.31 – 7.28 (m, 2H), 7.27–7.23 (m, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.06 (d, *J* = 7.5 Hz, 1H), 7.02 (td, *J* = 7.5, 1.0 Hz, 1H), 3.62 (s, 1H), 0.89 (s, 6H), 0.73 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.7, 149.3, 144.2, 139.1, 138.6, 133.1, 132.3, 128.6, 128.4, 127.6, 127.2, 124.8, 124.7, 124.6, 124.2, 123.7, 117.3, 83.7, 79.0, 24.4, 23.9. HRMS *m/z* (ESI+): Calculated for $C_{27}H_{27}BNO_3$ ($[M+H]^+$): 424.2079, Found 424.2049.



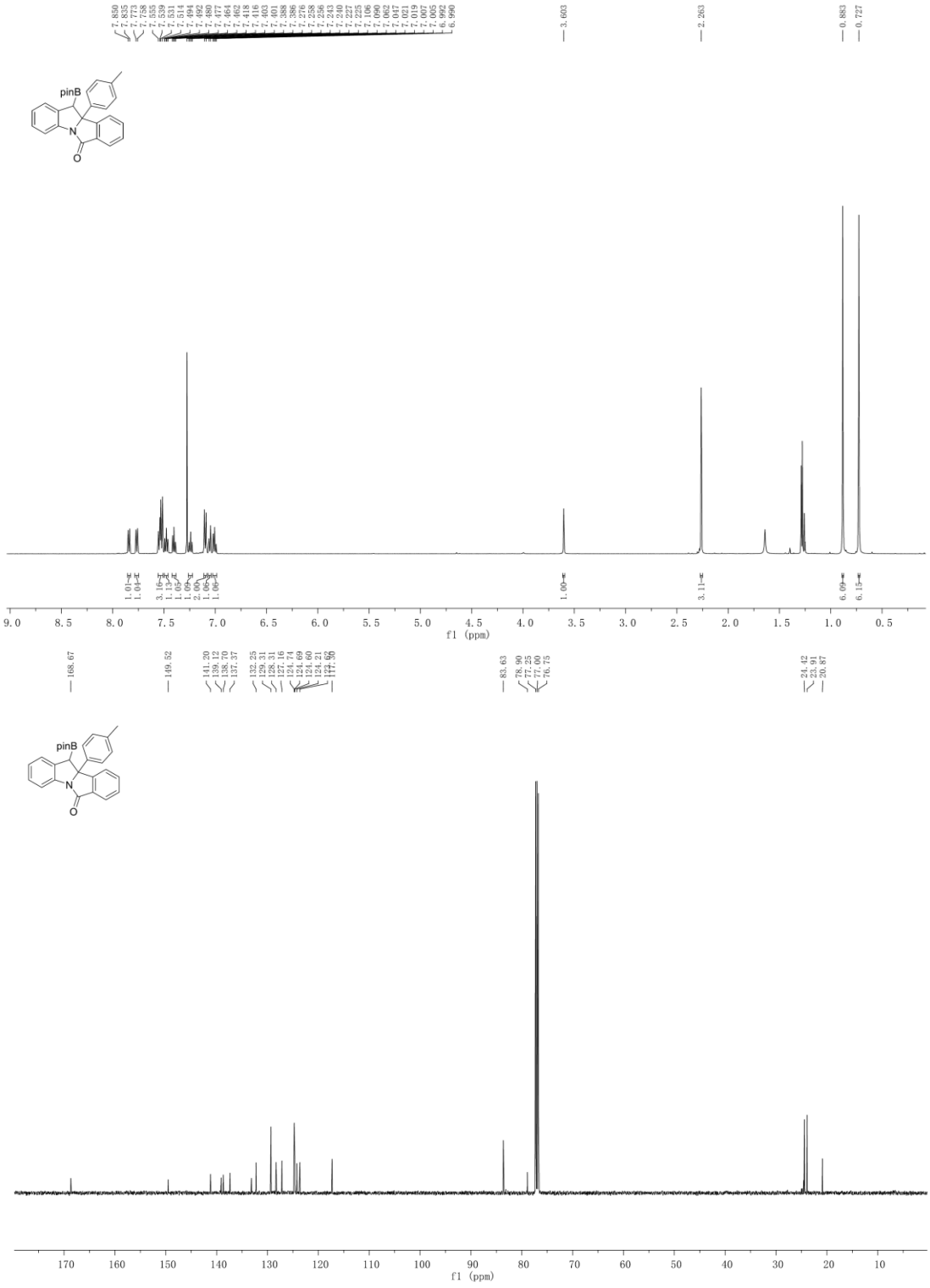


11-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10b-(p-tolyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**3k**):

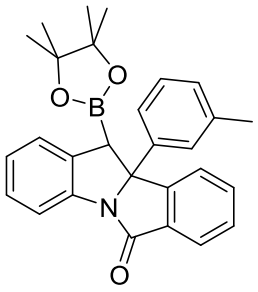


The reaction was in DCM at 70 °C (oil bath). Purified by chromatography on silica gel very quickly, eluting with ethyl acetate/petroleum ether 1:5 (v/v); white solid, Mp = 165–168 °C; 70% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.5 Hz, 1H), 7.77 (d, *J* = 7.5 Hz, 1H), 7.56–7.50 (m, 3H), 7.48 (td, *J* = 7.5, 1.0 Hz, 1H), 7.40 (td, *J* = 7.5, 1.0 Hz, 1H), 7.24 (td, *J* = 7.5, 1.0 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 7.5 Hz, 1H), 7.01 (td, *J* = 7.0, 1.0 Hz, 1H), 3.60 (s, 1H), 2.26 (s, 3H), 0.88 (s, 6H), 0.73 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.7, 149.5, 141.2, 139.1, 138.7, 137.4, 133.2, 132.3, 129.3, 128.3, 127.2, 124.7, 124.7, 124.6, 124.2, 123.6, 117.3, 83.6,

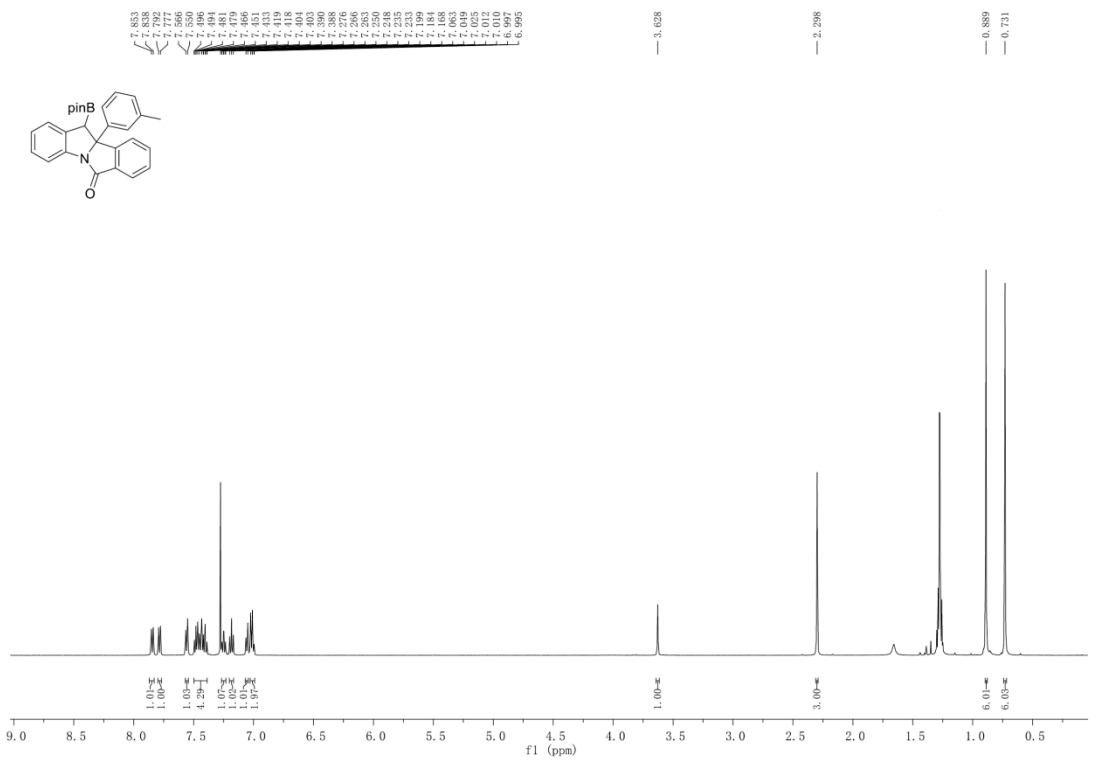
78.9, 24.4, 23.9, 20.9. HRMS *m/z* (ESI+): Calculated for $C_{28}H_{29}BNO_3$ ([M+H] $^+$): 438.2235, Found 438.2214.

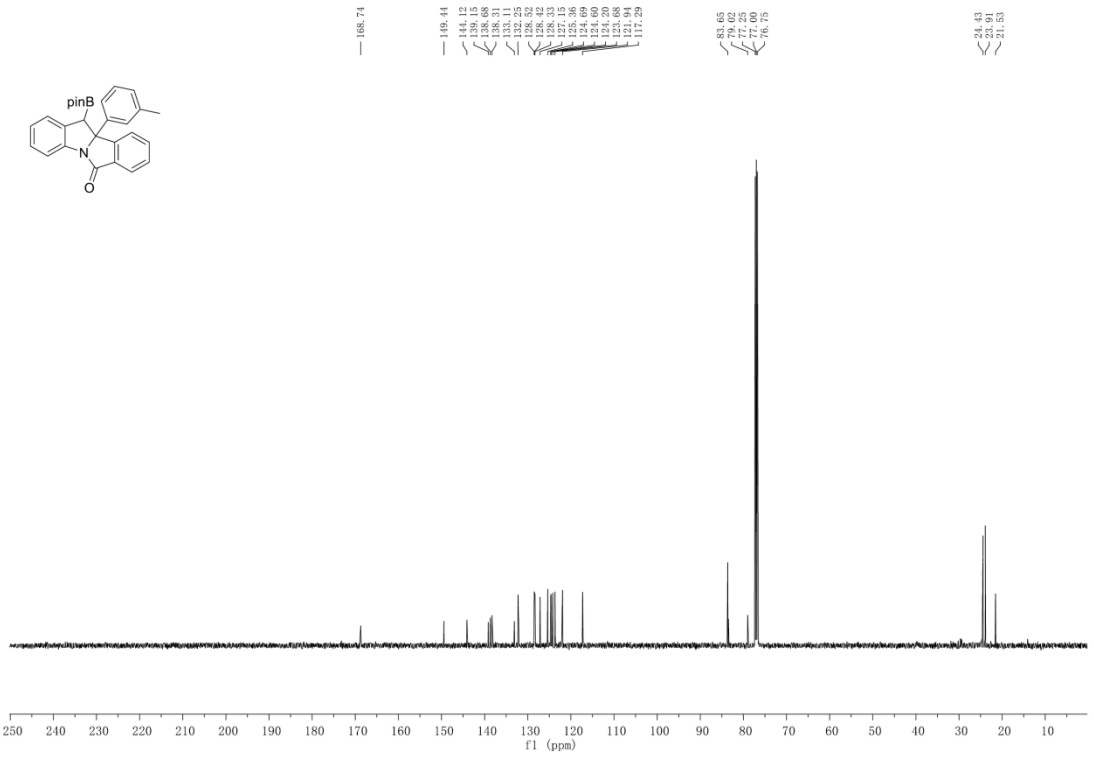


11-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10b-(m-tolyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**3l**):

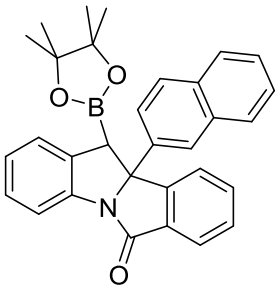


The reaction was in DCM at 70 °C (oil bath). Purified by chromatography on silica gel very quickly, eluting with ethyl acetate/petroleum ether 1:5 (v/v); white solid, Mp = 160–163 °C; 72% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.5 Hz, 1H), 7.78 (d, *J* = 7.5 Hz, 1H), 7.56 (d, *J* = 7.5 Hz, 1H), 7.50 - 7.38 (m, 4H), 7.25 (td, *J* = 7.5, 1.0 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.06 (d, *J* = 7.0 Hz, 1H), 7.03–6.99 (m, 2H), 3.63 (s, 1H), 2.30 (s, 3H), 0.89 (s, 6H), 0.73 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.7, 149.4, 144.1, 139.2, 138.7, 138.3, 133.1, 132.3, 128.5, 128.4, 128.3, 127.2, 125.4, 124.7, 124.6, 124.2, 123.7, 121.9, 117.3, 83.7, 79.0, 24.4, 23.9, 21.5. HRMS *m/z* (ESI+): Calculated for $C_{28}H_{29}BNO_3$ ($[M+H]^+$): 438.2235, Found 438.2245.

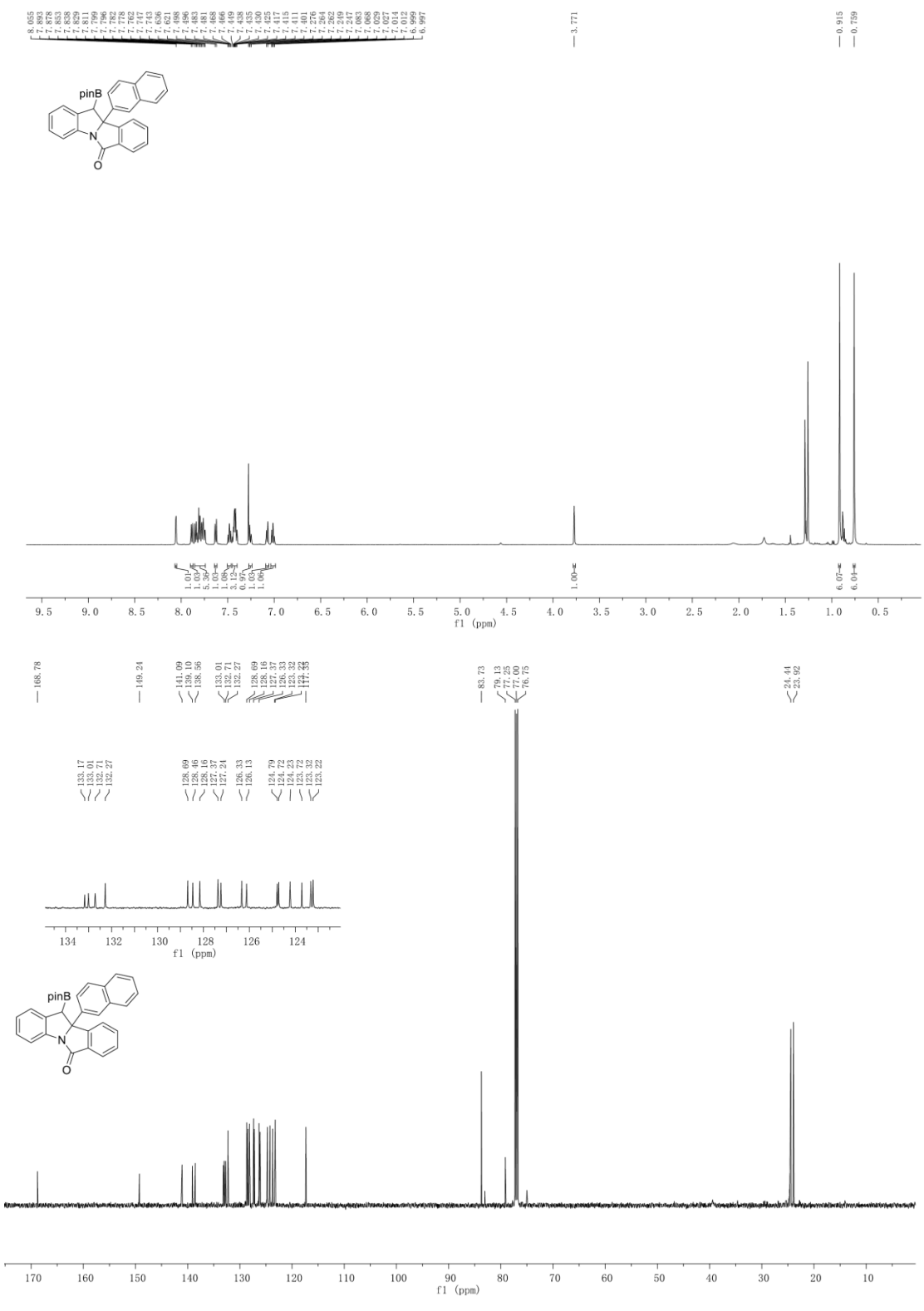

pinB
N
O
f1 (ppm)


pinB
N
O
f1 (ppm)

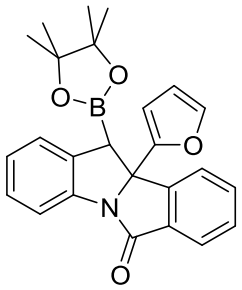
10b-(naphthalen-2-yl)-11-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**3m**):



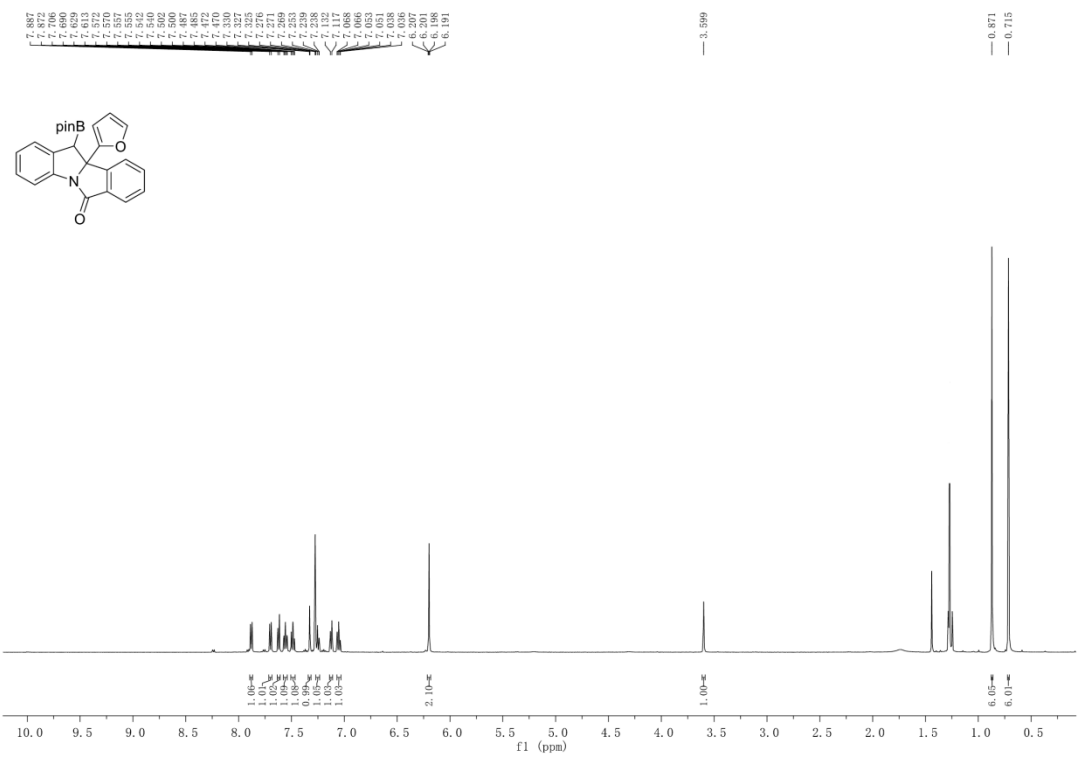
The reaction was in DCM at 70 °C (oil bath). Purified by chromatography on silica gel very quickly, eluting with ethyl acetate/petroleum ether 1:5 (v/v); white solid, Mp = 198-200 °C; 67% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.89 (d, *J* = 7.5 Hz, 1H), 7.86–7.74 (m, 5H), 7.63 (d, *J* = 7.5 Hz, 1H), 7.48 (td, *J* = 7.5, 1.0 Hz, 1H), 7.45–7.40 (m, 3H), 7.26 (td, *J* = 7.5, 1.0 Hz, 1H), 7.08 (d, *J* = 7.5 Hz, 1H), 7.01 (td, *J* = 7.5, 1.0 Hz, 1H), 3.77 (s, 1H), 0.92 (s, 6H), 0.76 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.8, 149.2, 141.1, 139.1, 138.6, 133.2, 133.0, 132.7, 132.3, 128.7, 128.5, 128.2, 127.4, 127.2, 126.3, 126.1, 124.8, 124.7, 124.2, 123.7, 123.3, 123.2, 117.4, 83.7, 79.1, 24.4, 23.9. HRMS *m/z* (ESI+): Calculated for $C_{31}H_{29}BNO_3$ ($[M+H]^+$): 474.2235, Found 474.2257.

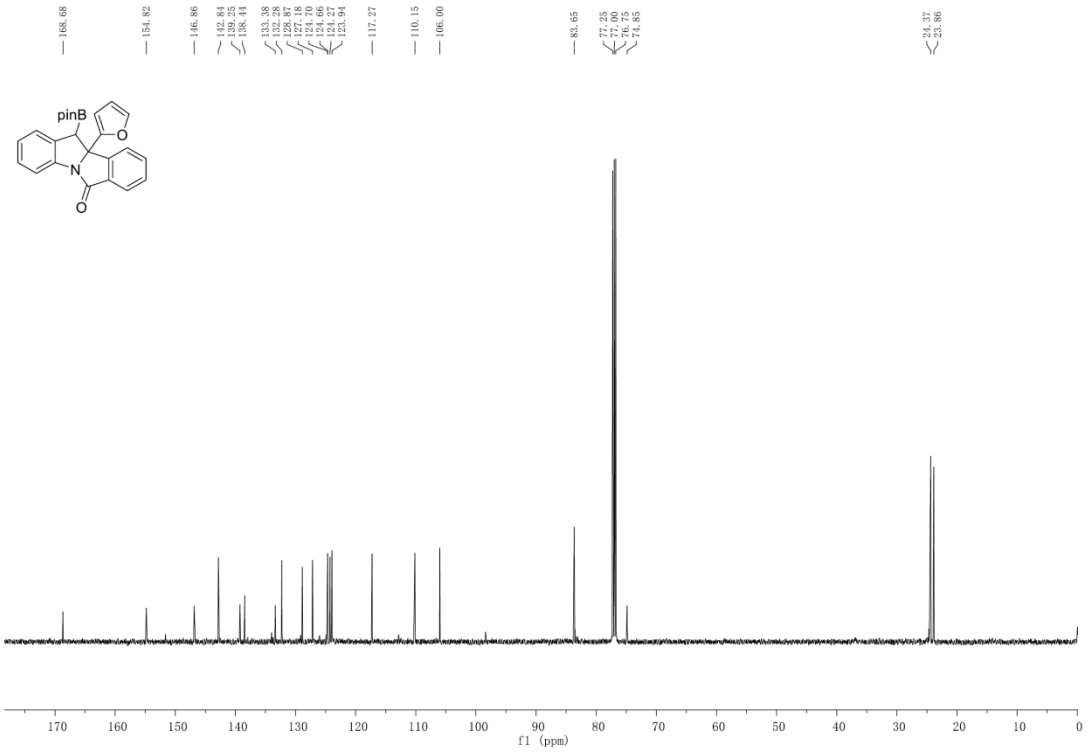

pinB
N
O
f1 (ppm)
pinB
N
O
f1 (ppm)
f1 (ppm)

10b-(furan-2-yl)-11-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**3n**):

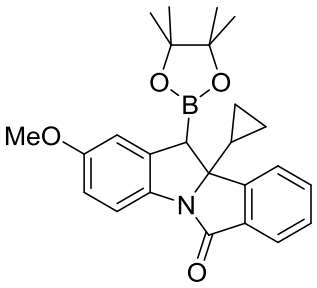


The reaction was in DCM at 70 °C (oil bath). Purified by chromatography on silica gel very quickly, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow solid, Mp = 136-138 °C; 53% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.5 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 7.5 Hz, 1H), 7.56 (td, *J* = 7.5, 1.0 Hz, 1H), 7.49 (td, *J* = 7.5, 1.0 Hz, 1H), 7.34–7.31 (m, 1H), 7.25 (td, *J* = 8.0, 1.0 Hz, 1H), 7.12 (d, *J* = 7.5 Hz, 1H), 7.05 (td, *J* = 7.5, 1.0 Hz, 1H), 6.21 – 6.18 (m, 2H), 3.60 (s, 1H), 0.87 (s, 6H), 0.71 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.7, 154.8, 146.9, 142.8, 139.3, 138.4, 133.4, 132.3, 128.9, 127.2, 124.70, 124.66, 124.3, 123.9, 117.3, 110.2, 106.0, 83.7, 74.9, 24.4, 23.9. HRMS *m/z* (ESI+): Calculated for $C_{25}H_{25}BNO_4$ ($[M+H]^+$): 414.1871, Found 414.1865.

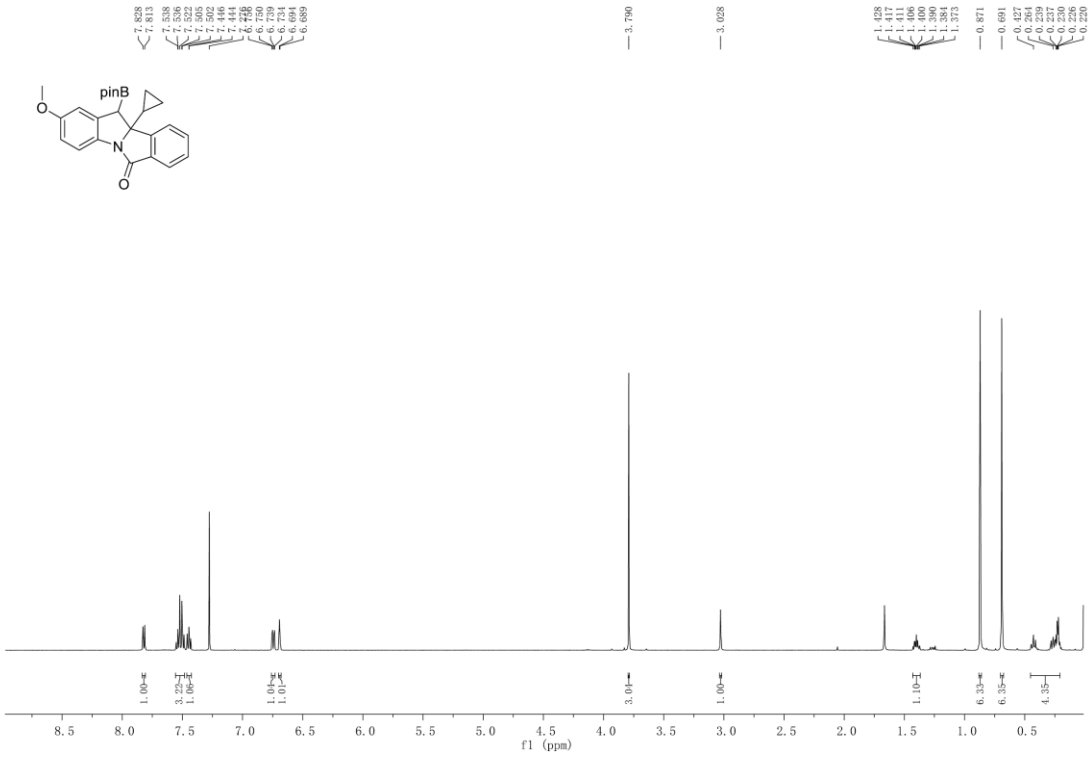

pinB
O
N
O
f1 (ppm)

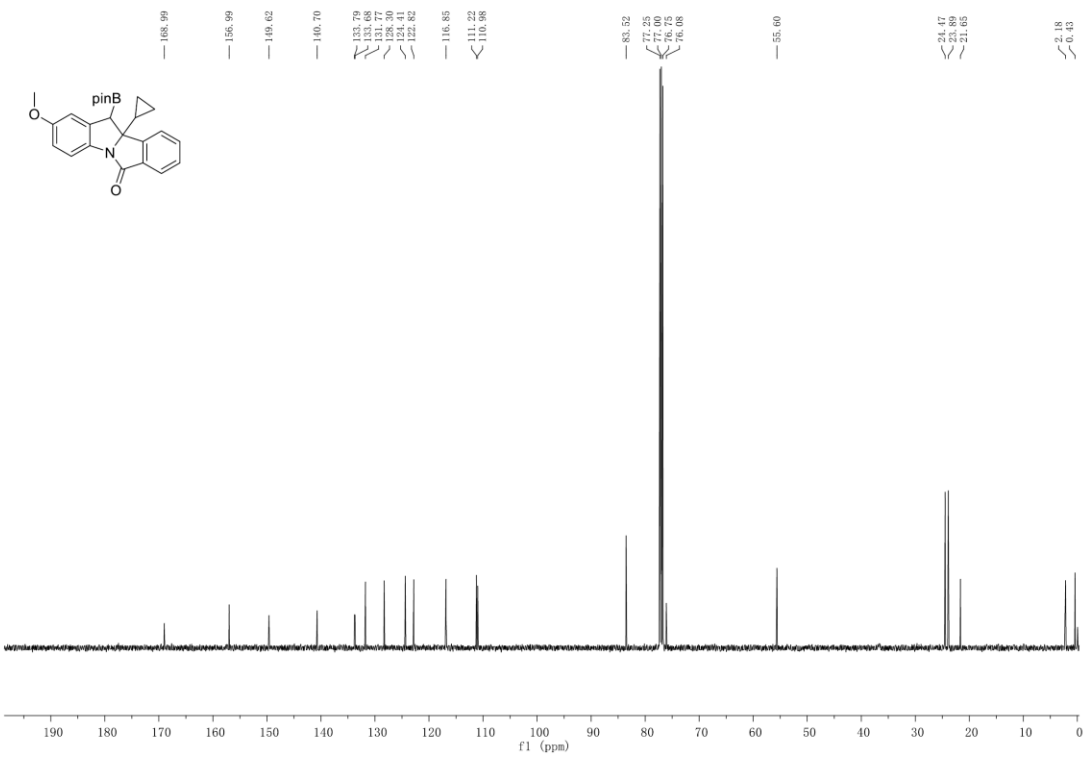

pinB
O
N
O
f1 (ppm)

10b-cyclopropyl-2-methoxy-11-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**3o**):

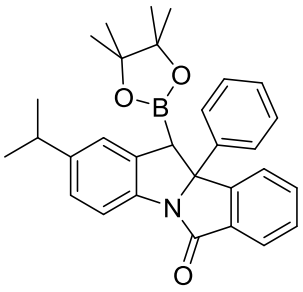


The reaction was in DCM at 70 °C (oil bath). Purified by chromatography on silica gel very quickly, eluting with ethyl acetate/petroleum ether 1:5 (v/v); white solid, Mp = 138-141 °C; 61% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.5 Hz, 1H), 7.56–7.48 (m, 3H), 7.45 (td, *J* = 7.5, 1.0 Hz, 1H), 6.74 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.69 (d, *J* = 2.5 Hz, 1H), 3.79 (s, 3H), 3.03 (s, 1H), 1.43 - 1.37 (m, 1H), 0.87 (s, 6H), 0.69 (s, 6H), 0.45–0.21 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.0, 157.0, 149.6, 140.7, 133.8, 133.7, 131.8, 128.3, 124.4, 122.8, 116.9, 111.2, 111.0, 83.5, 76.1, 55.6, 24.5, 23.9, 21.7, 2.2, 0.4. HRMS *m/z* (ESI+): Calculated for $C_{25}H_{29}BNO_4$ ([M+H]$^{+}$): 418.2184, Found 418.2188.



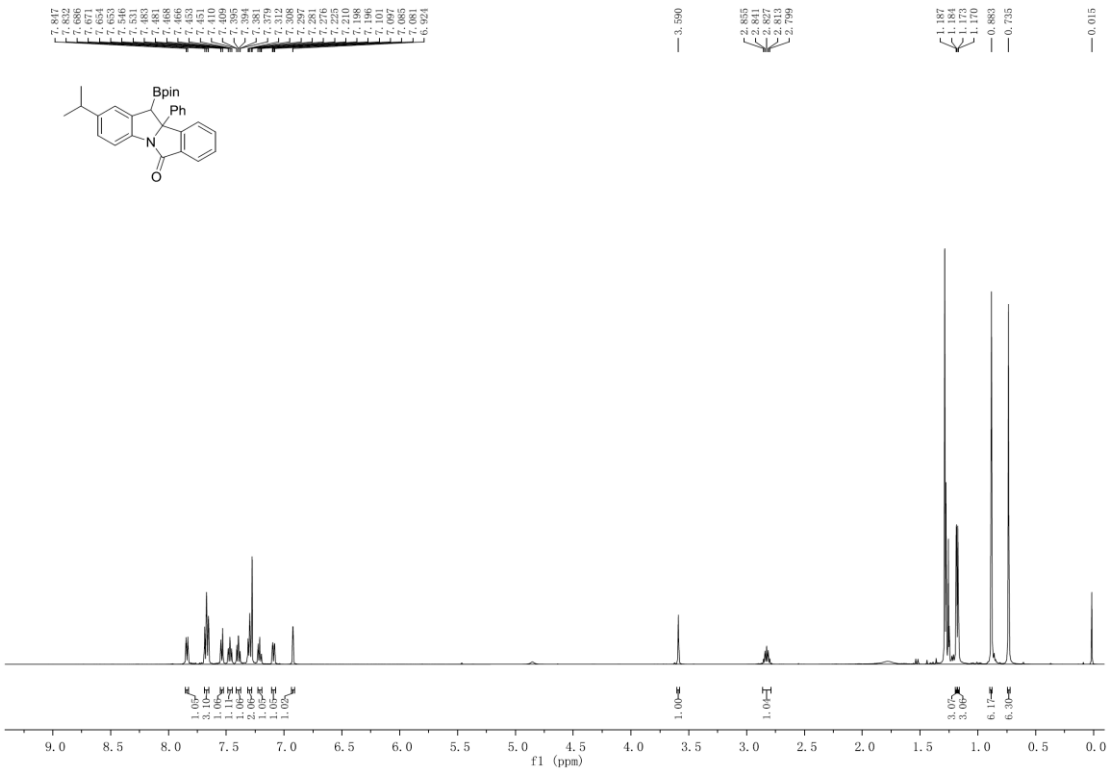


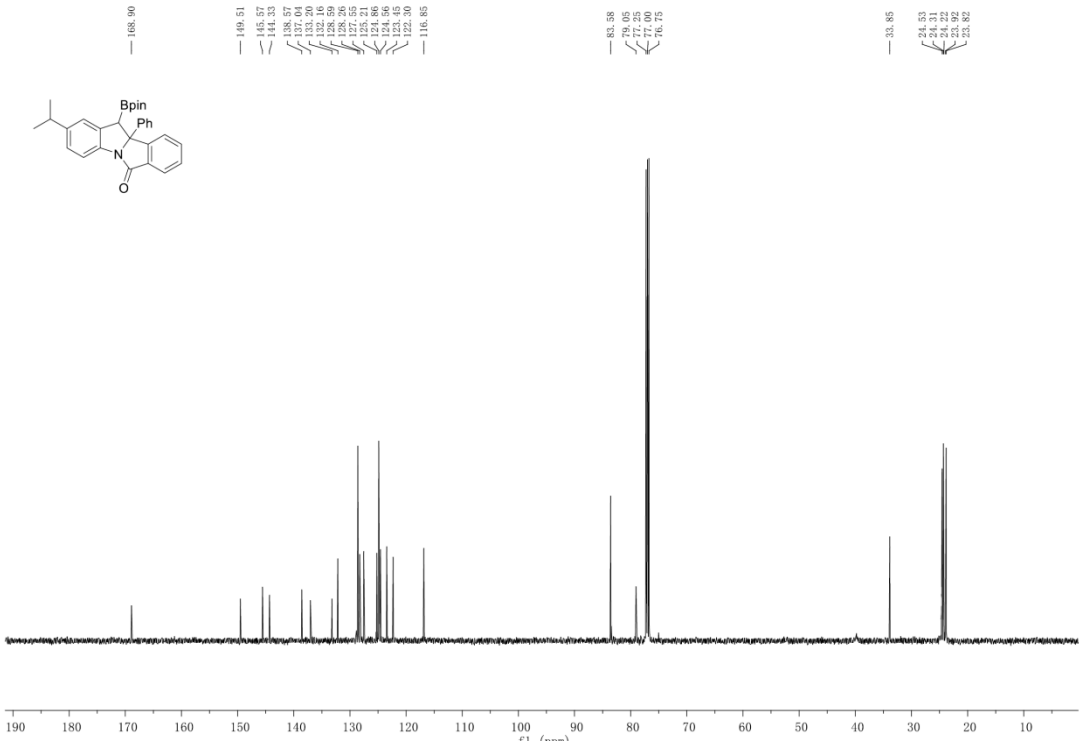
2-isopropyl-10b-phenyl-11-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**3p**):



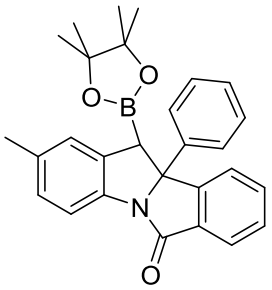
The reaction was in DCE at 60 °C (oil bath). Purified by chromatography on silica gel very quickly, eluting with ethyl acetate/petroleum ether 1:5 (v/v); white solid, Mp = 146-149 °C; 76% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.5 Hz, 1H), 7.70–7.64 (m, 3H), 7.54 (d, *J* = 7.5 Hz, 1H), 7.47 (td, *J* = 7.5, 1.0 Hz, 1H), 7.39 (td, *J* = 7.5, 1.0 Hz, 1H), 7.32 – 7.28 (m, 2H), 7.23–7.19 (m, 1H), 6.92 (s, 1H), 3.59 (s, 1H), 2.83 (hept, *J* = 7.0 Hz, 1H), 1.19 (d, *J* = 1.5 Hz, 3H), 1.17 (d, *J* = 1.5 Hz, 3H), 0.88 (s, 6H), 0.74 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.9, 149.5, 145.6, 144.3, 138.6, 137.0, 133.2, 132.2, 128.6, 128.3, 127.6, 125.2, 124.9, 124.6, 123.5, 122.3, 116.9,

83.6, 79.1, 33.9, 24.5, 24.3, 24.2, 23.9, 23.8. HRMS *m/z* (ESI+): Calculated for $C_{30}H_{33}BNO_3$ ($[M+H]^+$): 466.2548, Found 466.2542.

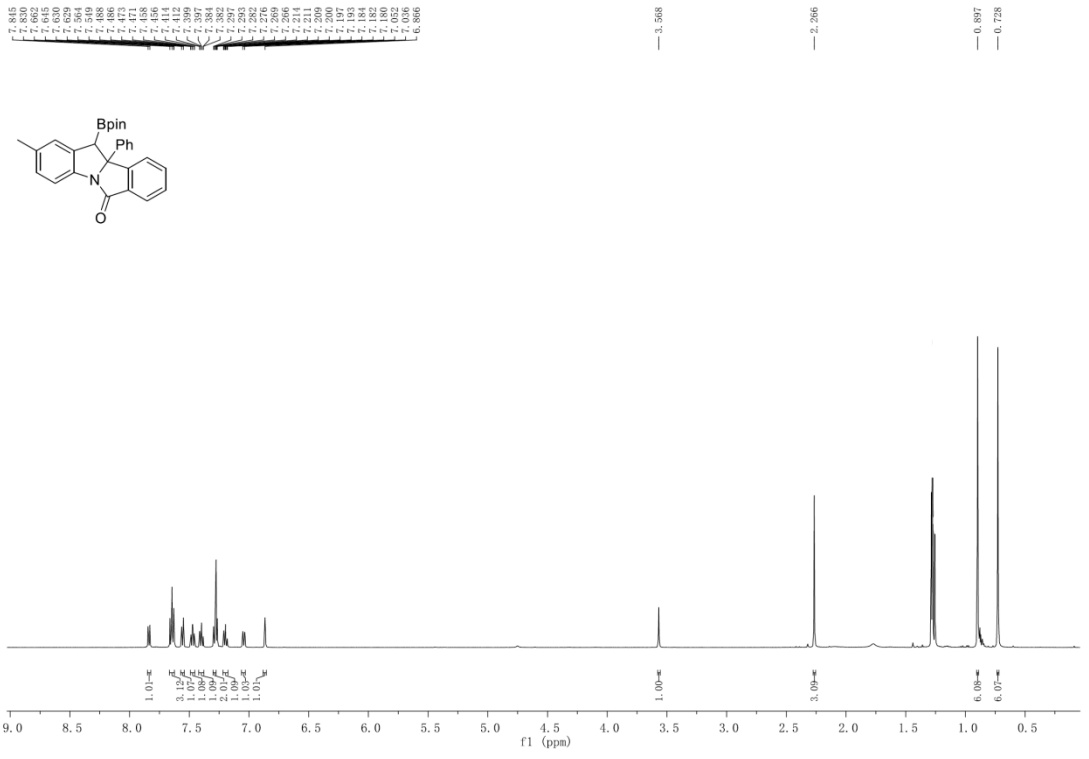


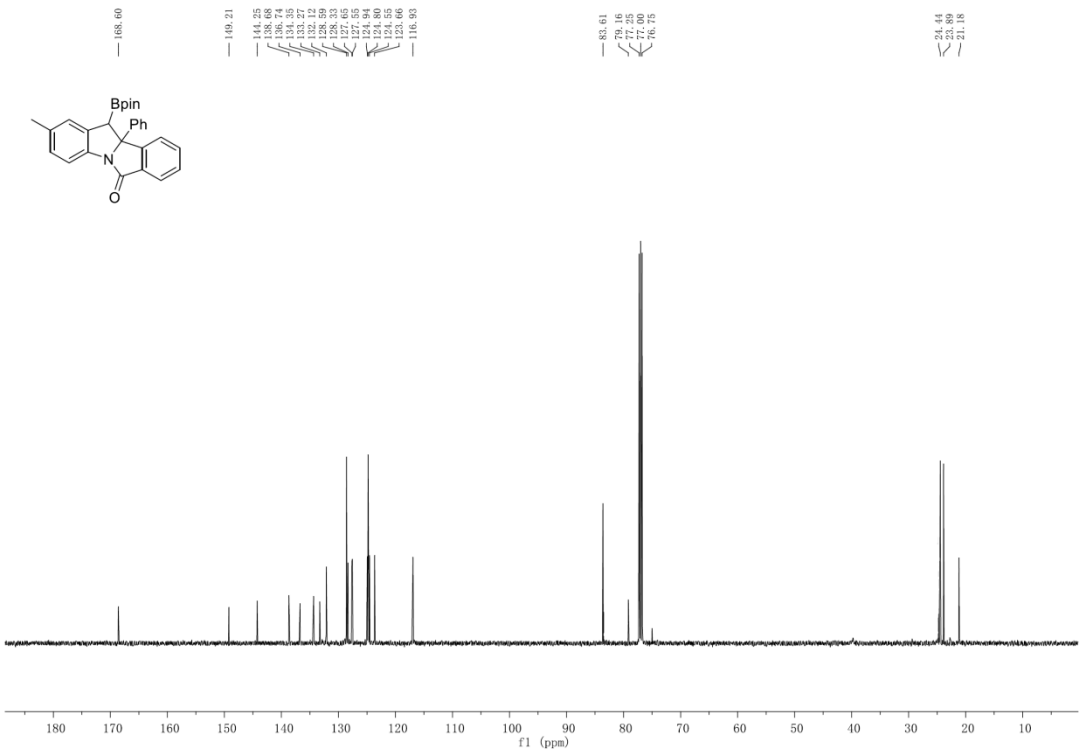


2-methyl-10b-phenyl-11-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**3q**):



The reaction was in DCM at 70 °C (oil bath). Purified by chromatography on silica gel very quickly, eluting with ethyl acetate/petroleum ether 1:5 (v/v); white solid, Mp = 92-94 °C; 64% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.5 Hz, 1H), 7.67–7.62 (m, 3H), 7.56 (d, *J* = 7.5 Hz, 1H), 7.47 (td, *J* = 7.5, 1.0 Hz, 1H), 7.40 (td, *J* = 7.5, 1.0 Hz, 1H), 7.30 – 7.26 (m, 2H), 7.22–7.18 (m, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.87 (s, 1H), 3.57 (s, 1H), 2.27 (s, 3H), 0.90 (s, 6H), 0.73 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.6, 149.2, 144.3, 138.7, 136.7, 134.4, 133.3, 132.1, 128.6, 128.3, 127.7, 127.6, 124.9, 124.8, 124.6, 123.7, 116.9, 83.6, 79.2, 24.4, 23.9, 21.2. HRMS *m/z* (ESI+): Calculated for $C_{28}H_{29}BNO_3$ ([M+H]$^+$): 438.2235, Found 438.2241.

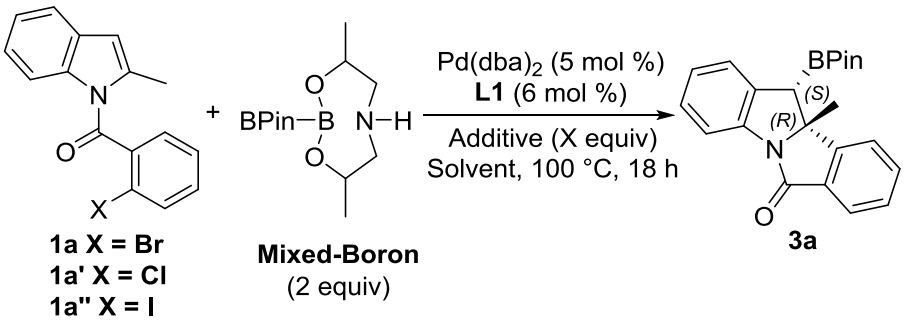



168.60
149.21
144.25
138.68
136.74
134.35
133.27
132.12
128.59
128.33
127.65
127.55
124.94
124.80
124.55
120.66
116.93
83.61
79.16
77.25
77.00
76.75
24.44
23.89
21.18
Bpin
Ph
N
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

4. Enantioselctive Pd-catalyzed dearomative arylborylation of indoles

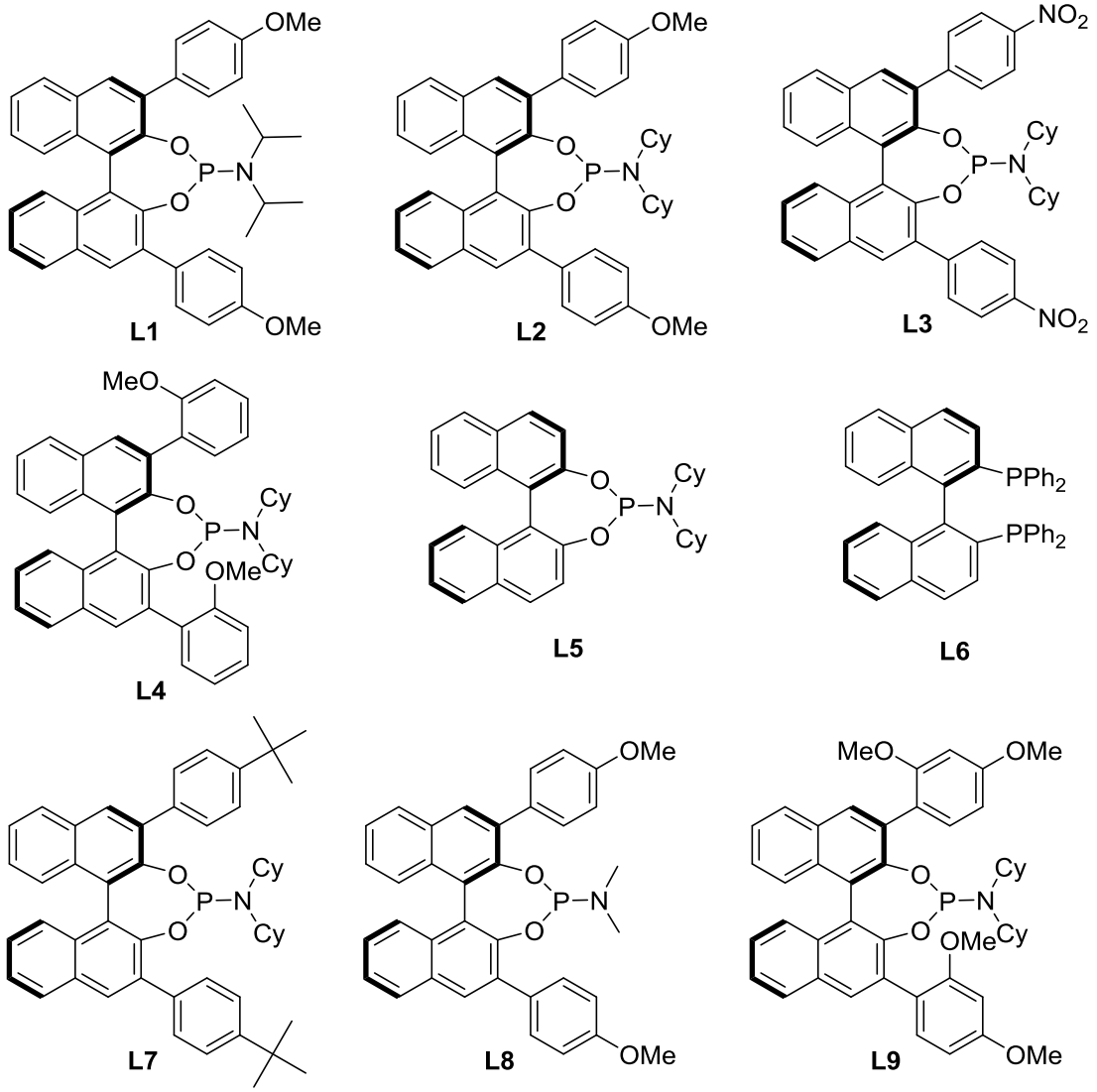
General Procedure: In a dry and purged 1D vial, $Pd(dba)_2$ (5 mol%) and **L2** (10 mol%) were pre-stirred in 2 mL of MTBE at 40 °C for 15 minutes. The catalyst solution was transferred (washing with 2 mL of MTBE, total 4 mL) into a Schlenk tube containing the corresponding aryl-chloride (0.2 mmol) and **Mixed-Boron** (3 equiv). NEt_3 (5 equiv) was added and the reaction was sealed and heated to 100 °C for 18 h. The reaction was filtered through silica and purified by column chromatography.

Optimization: Reactions were run as outlined above. Ligand structures on following page.



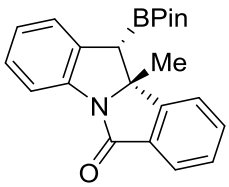
SI-Table 1. Optimization of the enantioselective arylborylation

Entry	X	Solvent	Additive	Changes to condition	Yield (%)	ee (%)
1	Br	PhMe	CsPiv	B_2Pin_2	43	12
2	Br	PhMe	–	–	49	44
3	Br	DCE	–	–	34	20
4	Br	THF:MTBE	–	–	78	38
5	Br	MTBE	–	–	73	64
6	I	MTBE	–	–	40	50
7	Cl	MTBE	–	–	15	88
8	Cl	MTBE	K_2CO_3	B_2Pin_2	n.r	–
9	Cl	MTBE	NEt_3 (3 eq)	–	50	88
*Following entries using **L2***						
10	Cl	MTBE	NEt_3 (3 eq)	–	65	88
11	Cl	MTBE	TMG (3 eq)	–	nr	--
12	Cl	MTBE	$^{i}Pr_2NEt$ (3 eq)	–	27	nd
13	Cl	MTBE	NEt_3 (3 eq)	80 °C	nr	--
14	Cl	MTBE	NEt_3 (3 eq)	10 mol% **L2**	68	91
15	Cl	MTBE	NEt_3 (5 eq)	3 eq mixed-boron	74	94
Ligand screen using conditions in entry 15:						
16	Cl	MTBE	Net_3 (5 eq)	**L3**	17	78
17	Cl	MTBE	Net_3 (5 eq)	**L4**	70	91
18	Cl	MTBE	Net_3 (5 eq)	**L5**	trace	–
19	Cl	MTBE	Net_3 (5 eq)	**L6**	trace	–
20	Cl	MTBE	Net_3 (5 eq)	**L7**	72	87
21	Cl	MTBE	Net_3 (5 eq)	**L8**	12	n.d
22	Cl	MTBE	Net_3 (5 eq)	**L9**	34	86



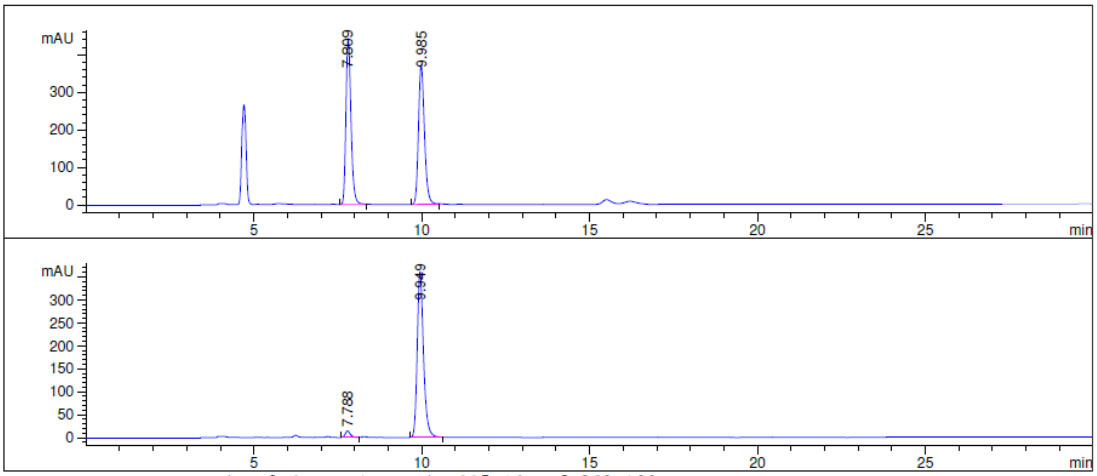
Note: Binap derivatives, basic Josiphos and Walphos ligands, Prophos, Binapine were all ineffective in the reactions (data not shown).

10b-methyl-11-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**3a**):



Product was purified by silica flash chromatography, eluting with pentanes/ethyl acetate/DCM 10:1:1 (v/v/v). Product isolated as a white solid (53.5 mg, 0.148 mmol, 74%). $[\alpha]_D^{20}$ = +90.7 (c 1.0, $CHCl_3$), 94% ee, [Daicel Chiralpak IA column (25 cm × 0.46 cm), *n*-hexane/*i*-PrOH = 90/10,

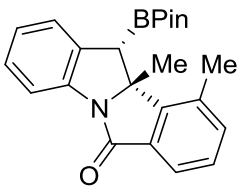
0.75 mL/min, t_{major} = 9.9 min, t_{minor} = 7.8 min.



Signal 2: DAD1 B, Sig=225,16 Ref=360,100

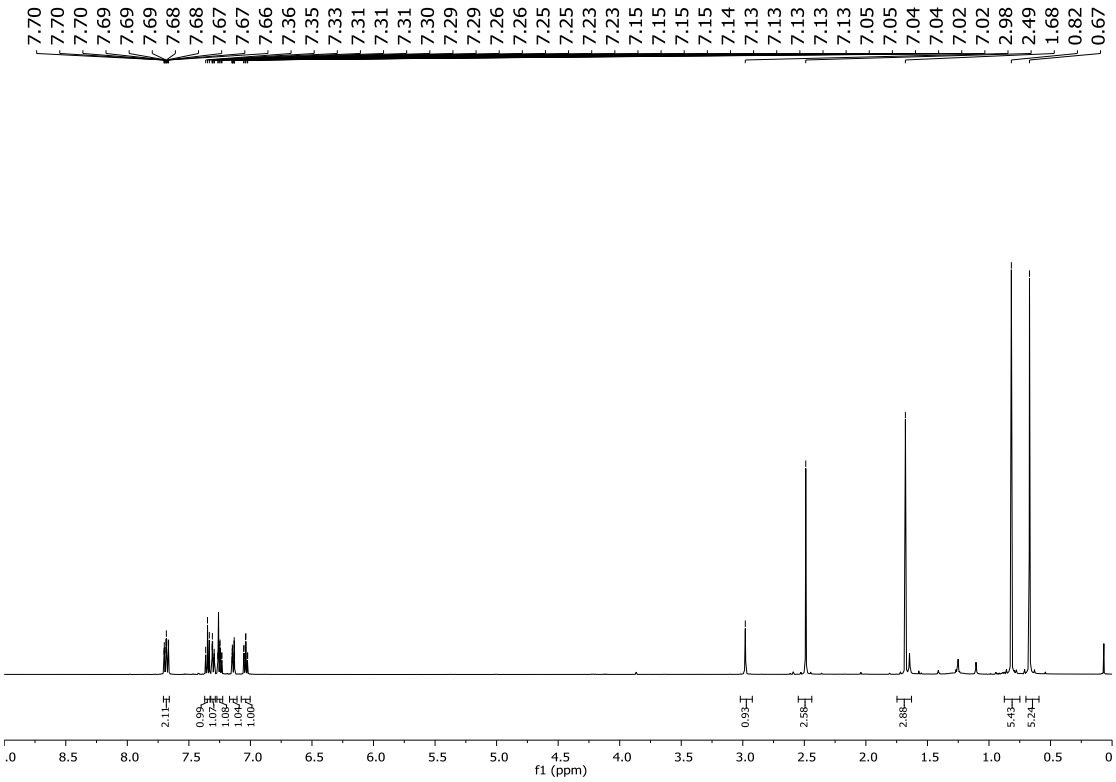
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.788	BB	0.1650	153.18356	14.07136	3.1359
2	9.949	BB	0.1987	4731.71484	361.60074	96.8641
Totals :				4884.89841	375.67210	

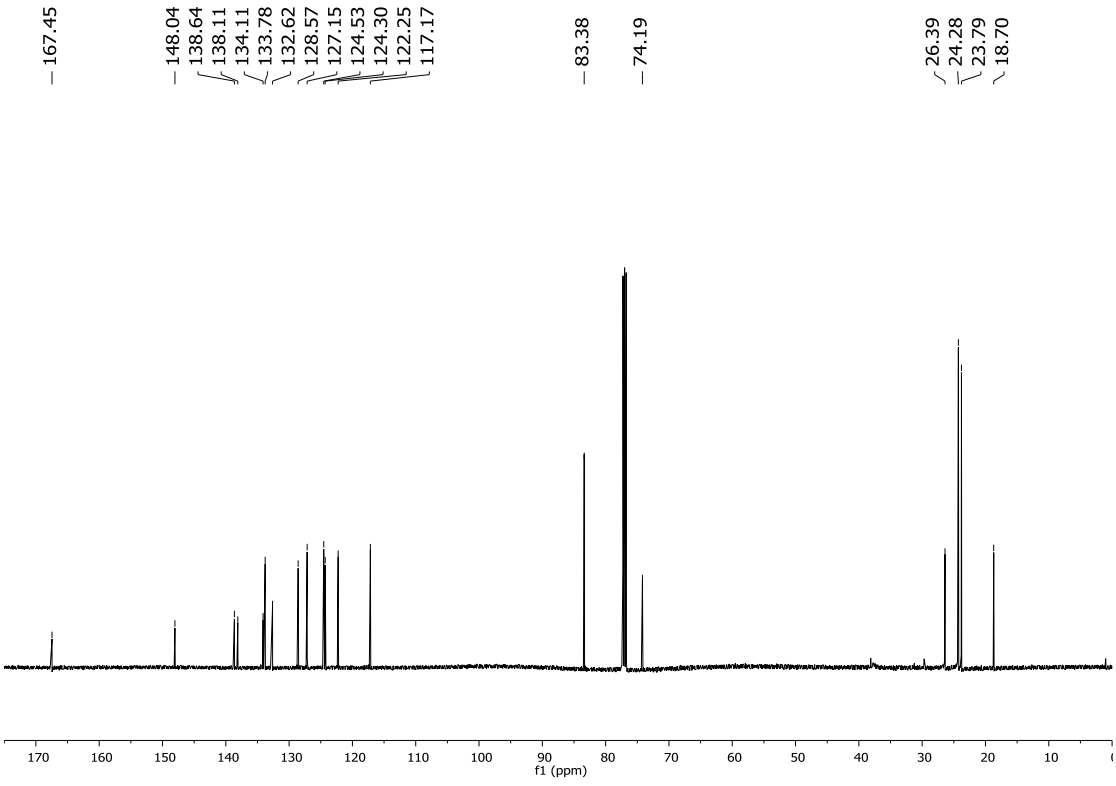
10,10b-dimethyl-11-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**3r**):

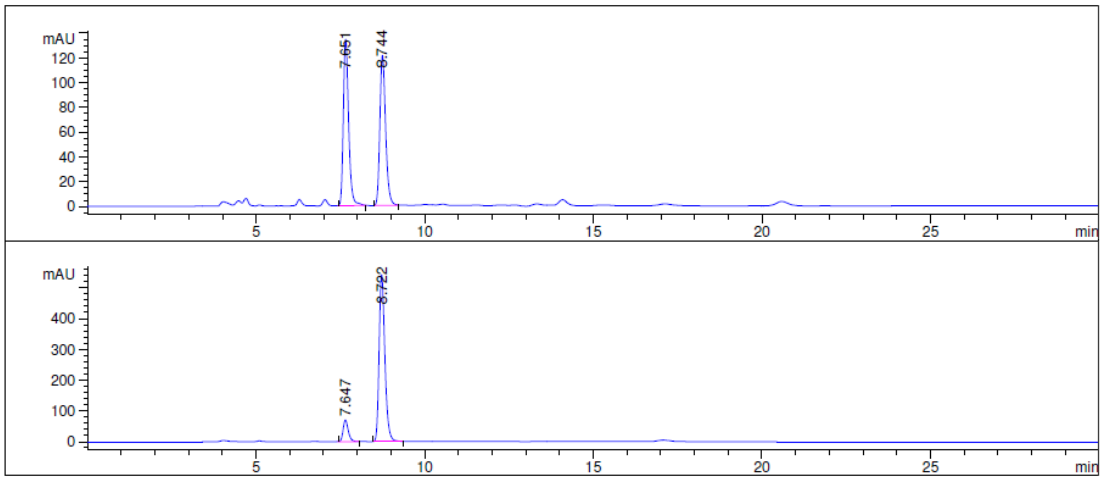


Product was purified by silica flash chromatography, eluting with pentanes/ethyl acetate/DCM 10:1:1 (v/v/v). Product isolated as a white solid (44.4 mg, 0.118 mmol), 59%, mp = 161–162 °C. $[\alpha]_D^{20}$ = +125.2 (c 1.0, $CHCl_3$), 79% ee, [Daicel Chiralpak IA column (25 cm × 0.46 cm), *n*-hexane/*i*-PrOH = 90/10, 0.75 mL/min, t_{major} = 8.7 min, t_{minor} = 7.6 min. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71–7.66 (m, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.30 (dt, *J* = 7.5, 1.0 Hz, 1H), 7.25 (td, *J* = 7.7, 1.4 Hz, 1H), 7.14 (ddt, *J* = 7.5, 1.3, 0.7 Hz, 1H), 7.04 (td, *J* = 7.5, 1.1 Hz, 1H), 2.98 (s, 1H), 2.49 (s, 3H), 1.68 (s, 3H), 0.82 (s, 6H), 0.67 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.5, 148.0, 138.6, 138.1, 134.1, 133.8, 132.6, 128.6, 127.2, 124.5, 124.3, 122.3, 117.2, 83.4, 74.2, 26.4, 24.3, 23.8, 18.7. HRMS *m/z* (DART+): Calculated for $C_{23}H_{27}BNO_3$ ($[M+H]^+$): 376.2079, Found

376.2046.


7.70
7.70
7.70
7.69
7.69
7.69
7.68
7.68
7.67
7.67
7.66
7.36
7.35
7.33
7.31
7.31
7.31
7.30
7.29
7.29
7.26
7.26
7.25
7.25
7.23
7.23
7.15
7.15
7.15
7.15
7.14
7.13
7.13
7.13
7.13
7.13
7.05
7.05
7.04
7.04
7.02
7.02
2.98
2.49
1.68
0.82
0.67
2.11
0.99
1.07
1.08
1.04
1.00
0.93
2.58
2.88
5.43
5.24
f1 (ppm)

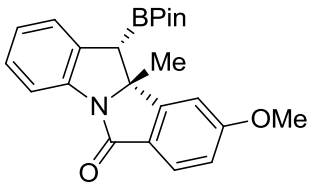

167.45
148.04
138.64
138.11
134.11
133.78
132.62
128.57
127.15
124.53
124.30
122.25
117.17
83.38
74.19
26.39
24.28
23.79
18.70
f1 (ppm)



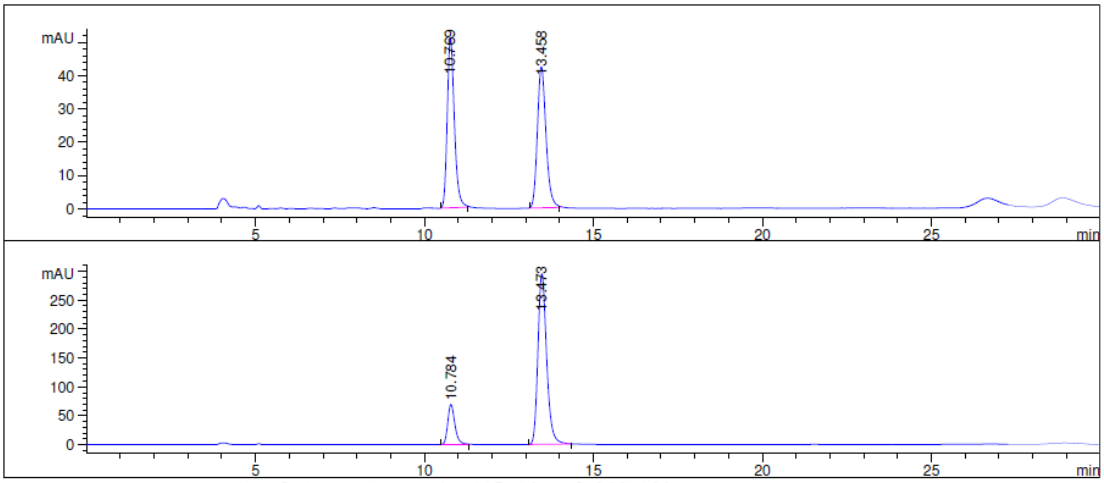
Signal 2: DAD1 B, Sig=225,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.647	BB	0.1662	758.29303	70.11597	10.4601
2	8.722	BB	0.1837	6491.10352	542.11920	89.5399
Totals :				7249.39655	612.23518	

9-methoxy-10b-methyl-11-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**3d**):



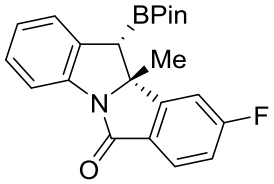
Product was purified by silica flash chromatography, eluting with pentanes/ethyl acetate/DCM 10:1:1 (v/v/v). Product isolated as a white solid (69.2 mg, 0.177 mmol), 88%. $[\alpha]_D^{20}$ = +172.4 (c 1.0, $CHCl_3$), 68% ee, [Daicel Chiralpak IA column (25 cm × 0.46 cm), *n*-hexane/*i*-PrOH = 90/10, 0.75 mL/min, t_{major} = 13.5 min, t_{minor} = 10.8 min.



Signal 2: DAD1 B, Sig=225,16 Ref=360,100

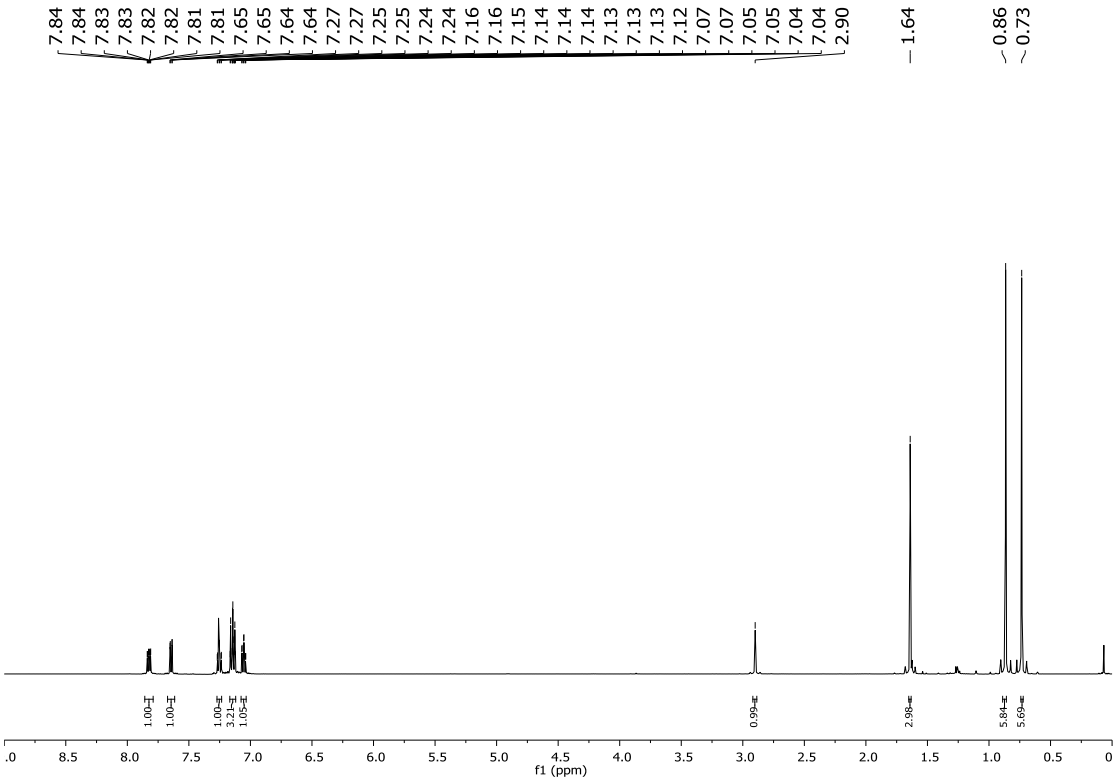
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.784	BB	0.2264	1024.36292	69.31072	16.0744
2	13.473	BB	0.2774	5348.26465	295.20142	83.9256
Totals :				6372.62756	364.51214	

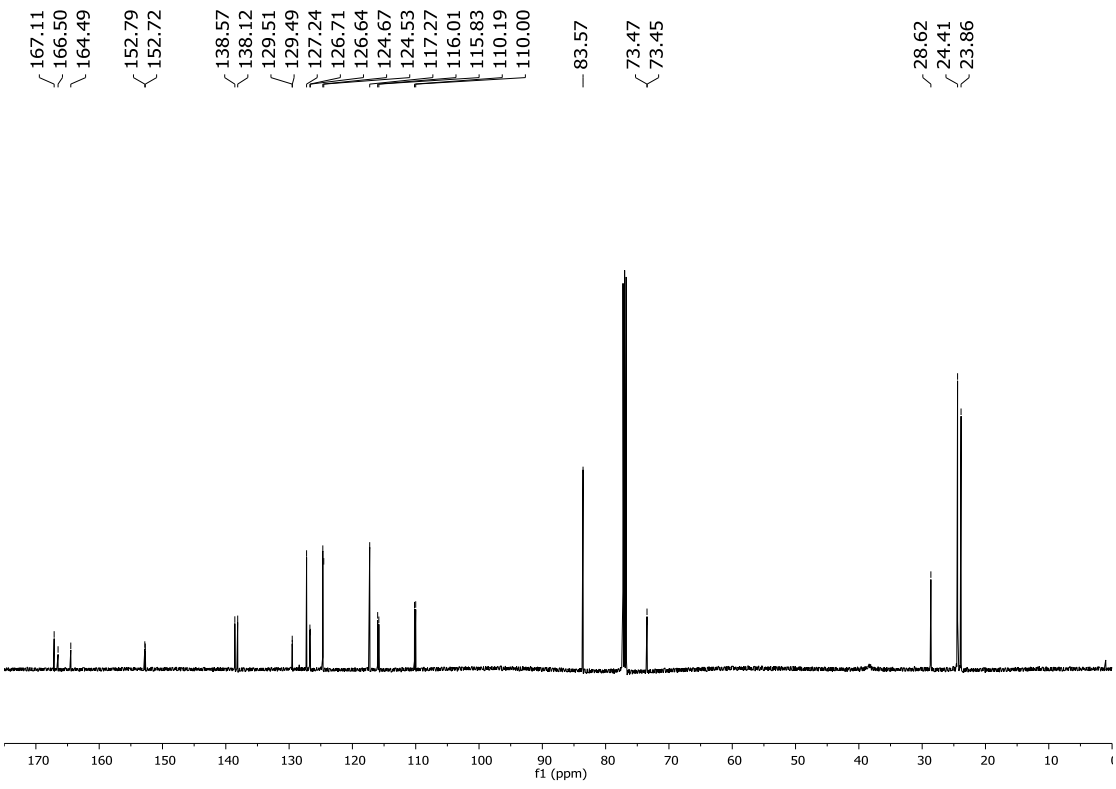
(10bR,11S)-9-fluoro-10b-methyl-11-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**3s**)

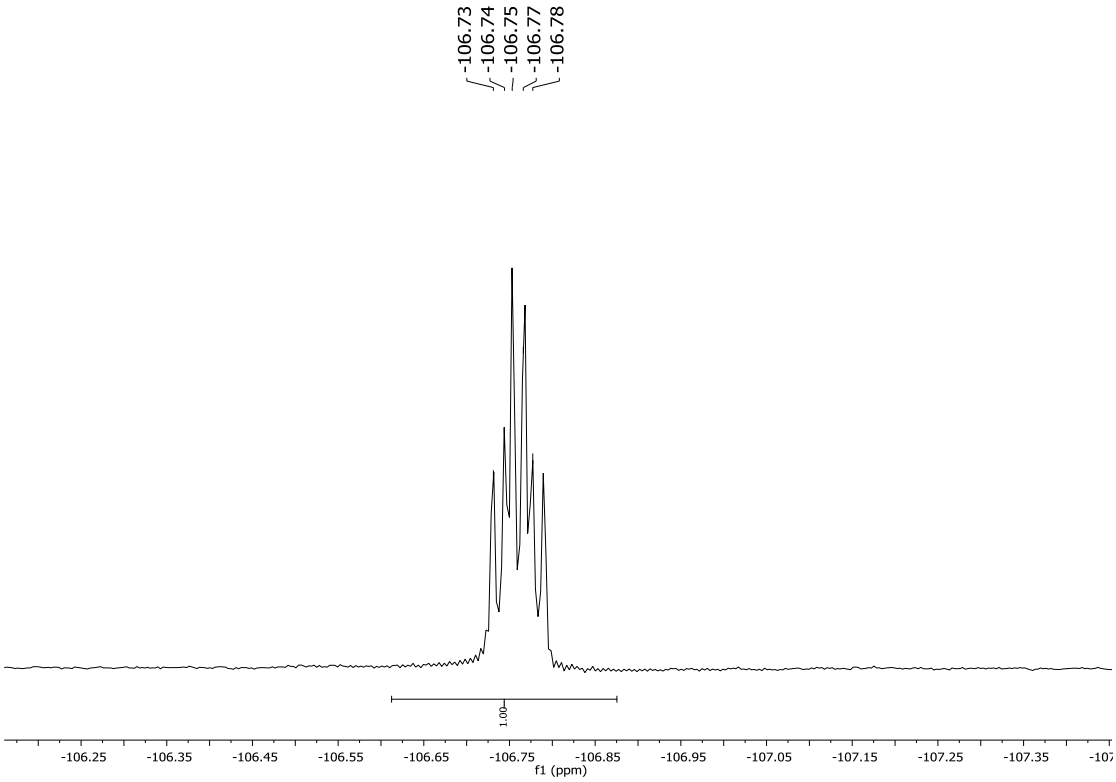


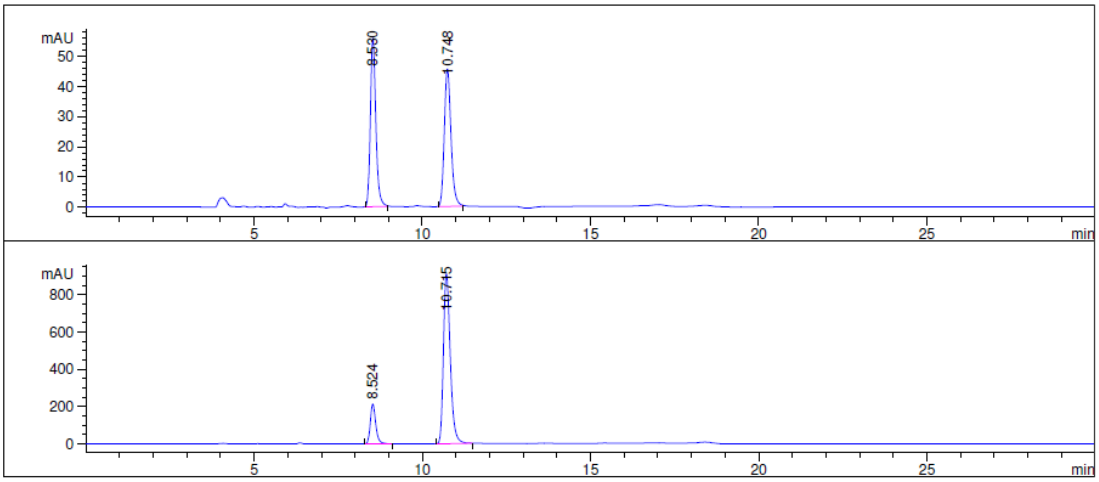
Product was purified by silica flash chromatography, eluting with pentanes/ethyl acetate/DCM 10:1:1 (v/v/v). Product isolated as a white solid (49.0 mg, 0.129 mmol), 65%, mp = 152–154 °C. $[\alpha]_D^{20}$ = +87.3 (c 1.0, $CHCl_3$), 68% ee, [Daicel Chiralpak IA column (25 cm × 0.46 cm), *n*-hexane/*i*-PrOH = 90/10, 0.75 mL/min, t_{major} = 10.7 min, t_{minor} = 8.5 min. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (ddd, *J* = 8.0, 5.1, 0.8 Hz, 1H), 7.64 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.25 (td, *J* = 7.6, 1.3 Hz, 1H), 7.17–7.12 (m, 3H), 7.05 (td, *J* = 7.5, 1.1 Hz, 1H), 2.90 (s, 1H), 1.64 (s, 3H), 0.86 (s, 6H), 0.73 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.1, 165.5 (d, *J* = 252.5 Hz), 152.8 (d, *J* = 9.3 Hz), 138.6, 138.1, 129.5 (d, *J* = 2.2 Hz), 127.2, 126.7 (d, *J* = 9.6 Hz), 124.7, 124.5, 117.3, 115.9 (d, *J* = 23.4 Hz), 110.1 (d, *J* = 23.8 Hz), 83.6, 73.5 (d, *J* = 2.6 Hz), 28.6, 24.4, 23.9. ^{19}F NMR (377 MHz, $CDCl_3$) δ -106.75 (dt, *J* = 9.0, 4.5 Hz). HRMS m/z (DART+): Calculated for $C_{22}H_{24}BFNO_3$

([M+H]$^+$) 380.1833, found 380.1832.





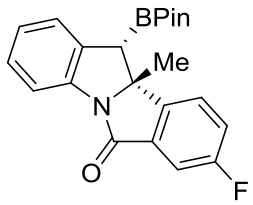




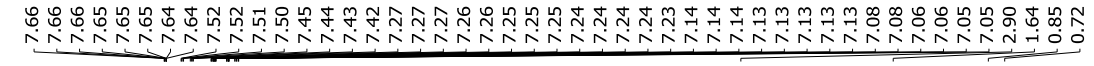
Signal 2: DAD1 B, Sig=225,16 Ref=360,100

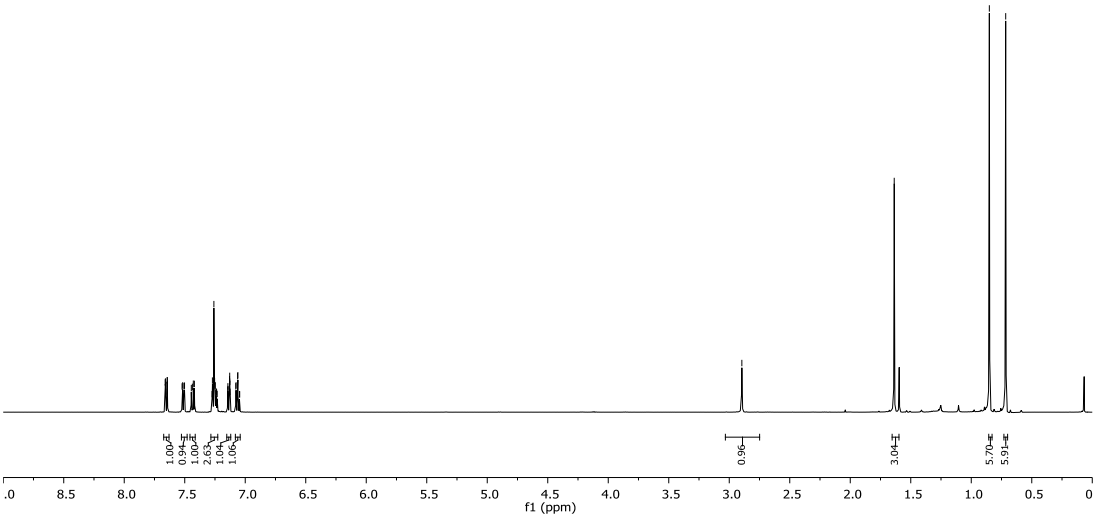
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.524	BB	0.1719	2421.91064	214.24069	15.7650
2	10.715	BB	0.2179	1.29407e4	910.12939	84.2350
Totals :				1.53626e4	1124.37009	

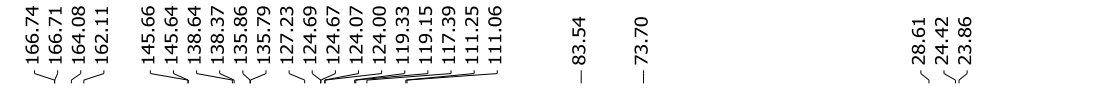
(10bR,11S)-10-fluoro-10b-methyl-11-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**3t**)

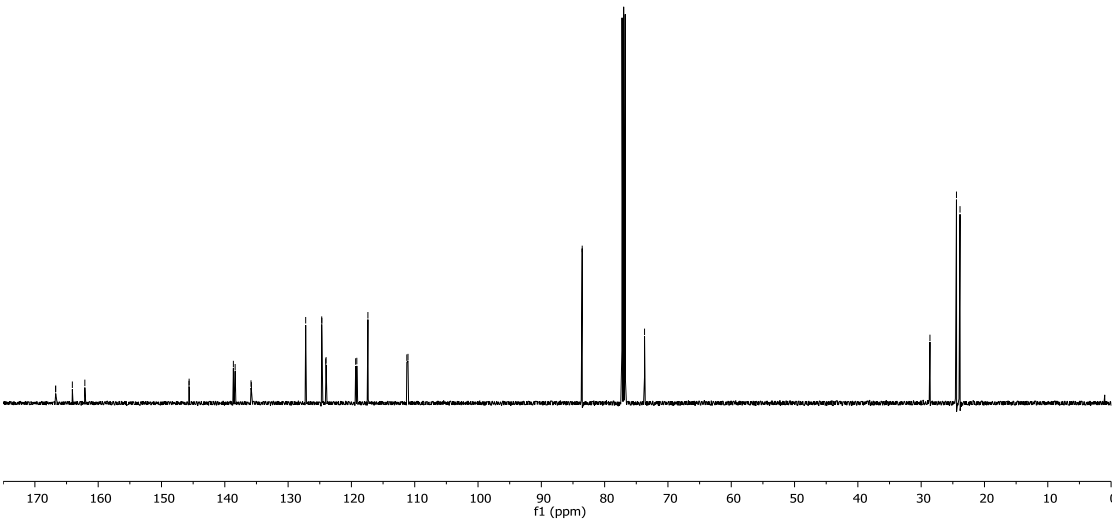


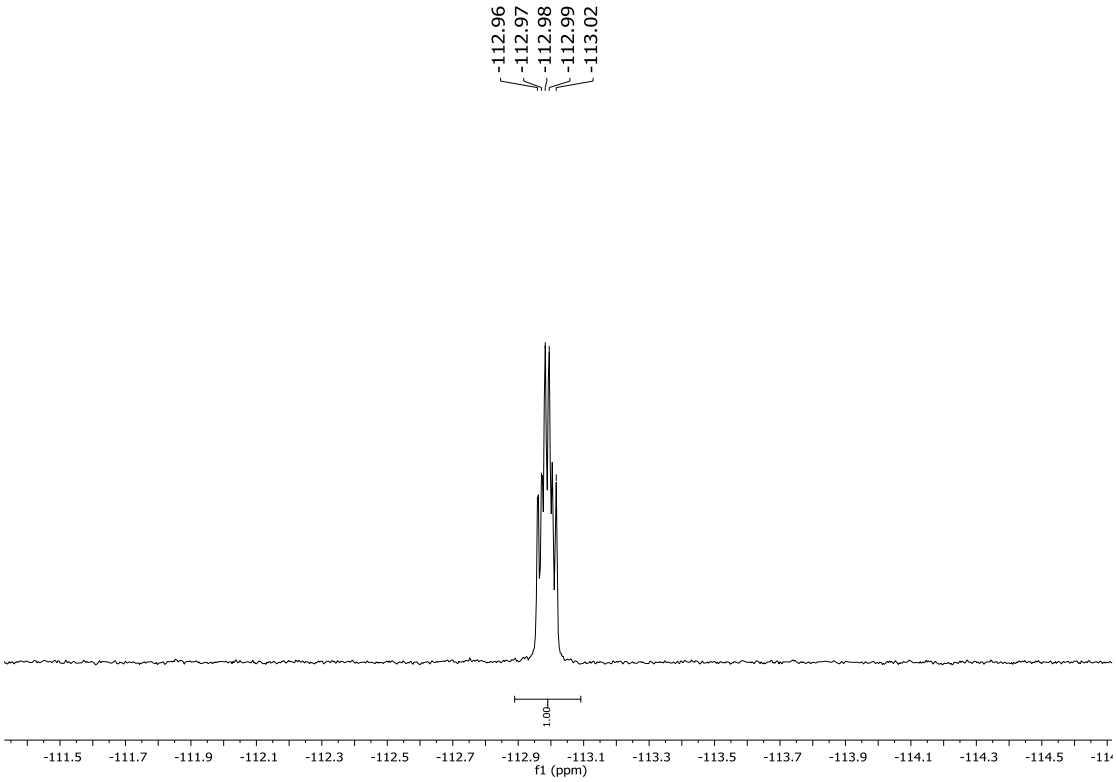
Product was purified by silica flash chromatography, eluting with pentanes/ethyl acetate/DCM 10:1:1 (v/v/v). Product isolated as a white solid (50.3 mg, 0.133 mmol), 66%, mp = 170–172 °C. $[\alpha]_D^{20}$ = +72.7 (c 1.0, $CHCl_3$), 91% ee, [Daicel Chiralpak IA column (25 cm × 0.46 cm), *n*-hexane/*i*-PrOH = 90/10, 0.75 mL/min, t_{major} = 8.6 min, t_{minor} = 6.8 min. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67–7.63 (m, 1H), 7.51 (dd, *J* = 7.7, 2.5 Hz, 1H), 7.43 (dd, *J* = 8.3, 4.4 Hz, 1H), 7.28–7.23 (m, 3H), 7.14 (ddt, *J* = 7.4, 1.3, 0.7 Hz, 1H), 7.06 (td, *J* = 7.5, 1.1 Hz, 1H), 2.90 (s, 1H), 1.64 (s, 3H), 0.85 (s, 6H), 0.72 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.7 (d, J = 3.3 Hz), 163.1 (d, *J* = 247.7 Hz), 145.6 (d, *J* = 2.6 Hz), 138.6, 138.34, 135.8 (d, *J* = 8.4 Hz), 127.2, 124.7, 124.7, 124.0 (d, *J* = 8.4 Hz), 119.2 (d, *J* = 23.5 Hz), 117.4, 111.2 (d, *J* = 23.2 Hz), 83.5, 73.7, 28.6, 24.4, 23.9. ^{19}F NMR (377 MHz, $CDCl_3$) δ -112.89 – -113.09 (m). HRMS m/z (DART+): Calculated for $C_{22}H_{24}BFNO_3$ ($[M+H]^+$) 380.1833, found 380.1836.

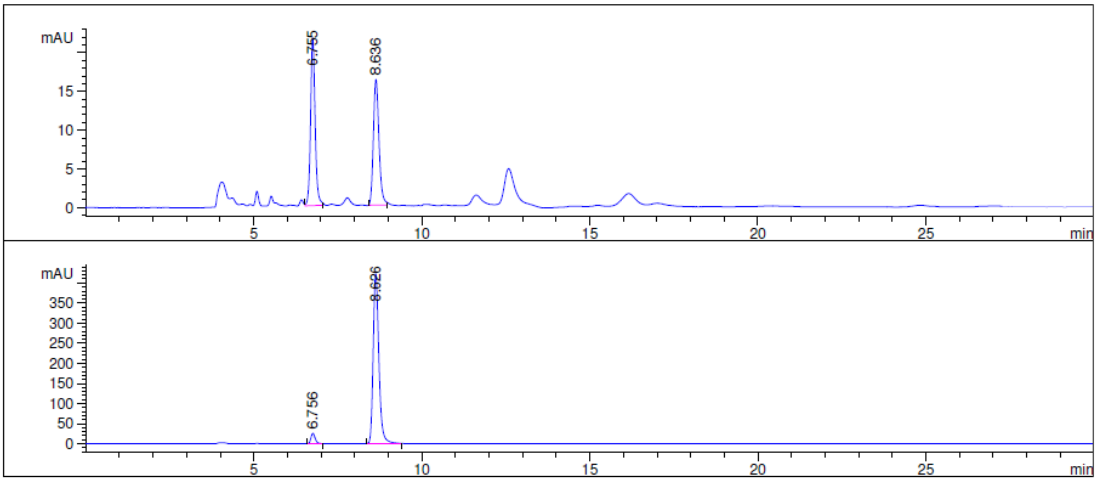

7.66
7.66
7.66
7.65
7.65
7.65
7.64
7.64
7.52
7.52
7.51
7.50
7.45
7.44
7.43
7.42
7.27
7.27
7.27
7.26
7.26
7.25
7.25
7.25
7.24
7.24
7.24
7.24
7.23
7.14
7.14
7.14
7.13
7.13
7.13
7.13
7.13
7.08
7.08
7.06
7.06
7.05
7.05
2.90
1.64
0.85
0.72


1.00
0.94
1.00
2.63
1.04
1.06
0.96
3.04
5.70
5.91
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)


166.74
166.71
164.08
162.11
145.66
145.64
138.64
138.37
135.86
135.79
127.23
124.69
124.67
124.07
124.00
119.33
119.15
117.39
111.25
111.06
83.54
73.70
28.61
24.42
23.86


170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

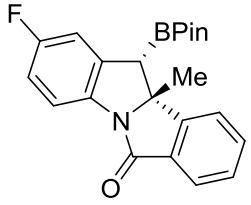




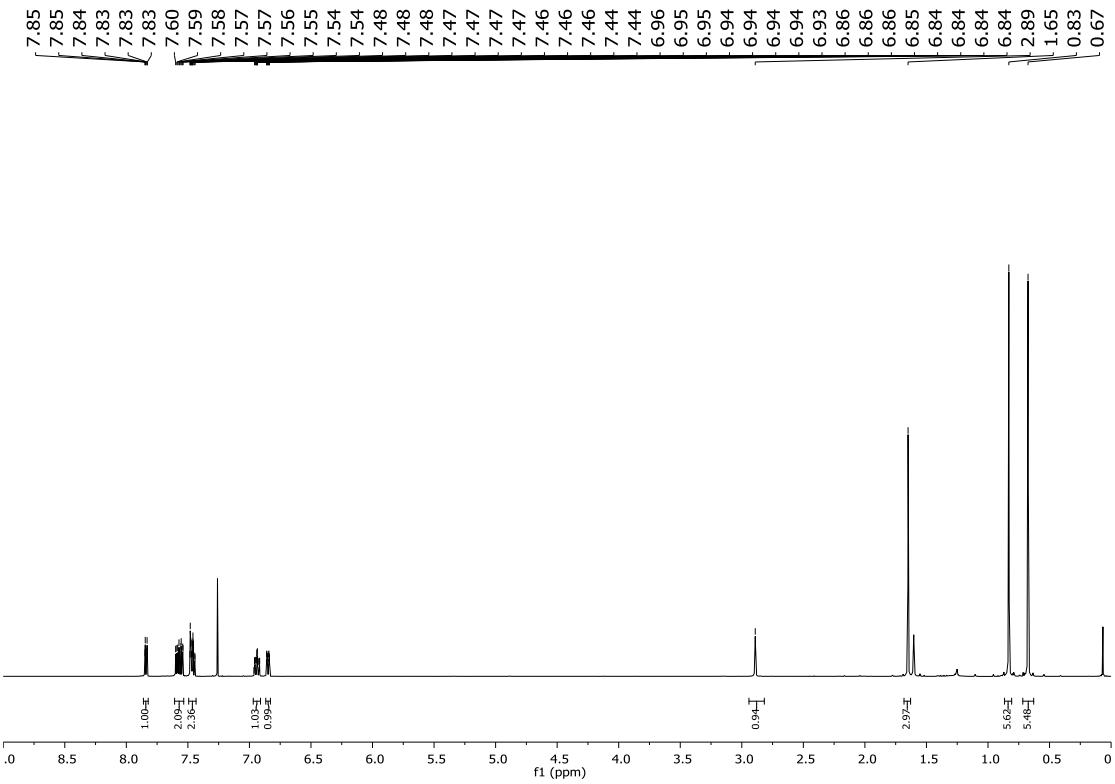
Signal 2: DAD1 B, Sig=225,16 Ref=360,100

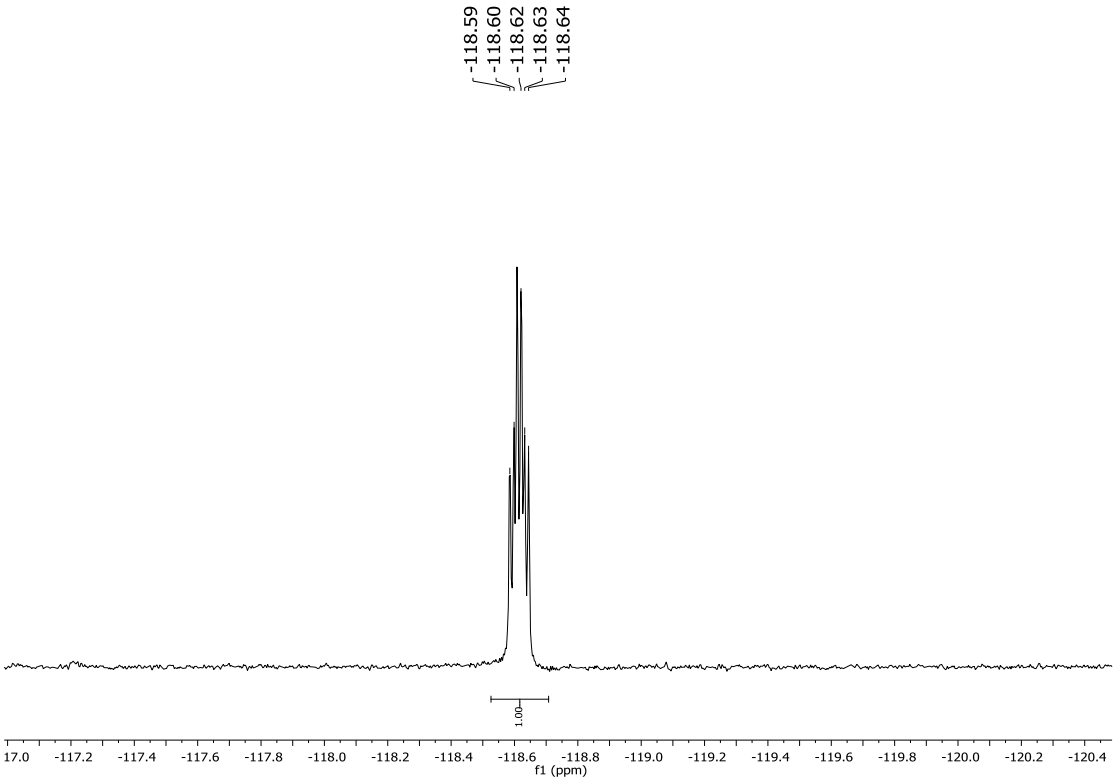
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.756	BB	0.1395	235.39171	26.02644	4.5074
2	8.626	BB	0.1797	4986.97510	422.47775	95.4926
Totals :				5222.36681	448.50419	

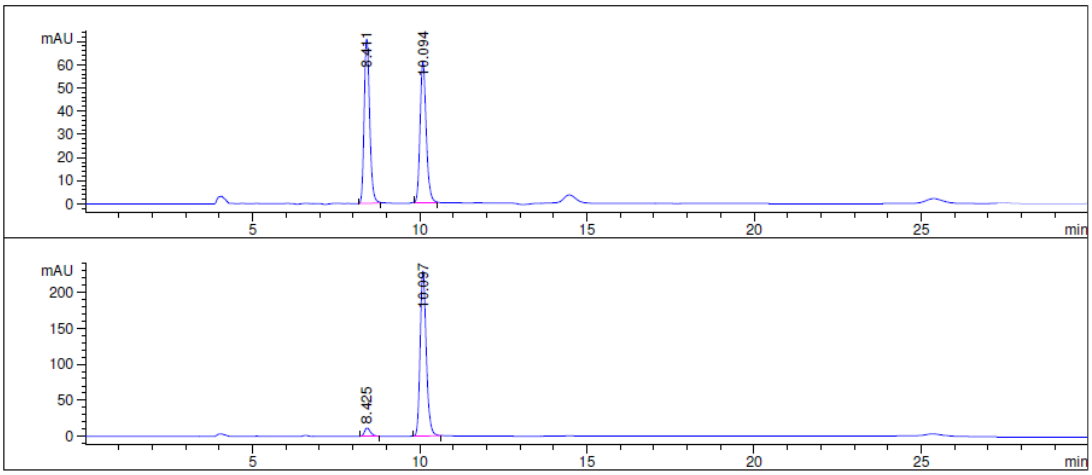
(10bR,11S)-2-fluoro-10b-methyl-11-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**3u**)



Product was purified by silica flash chromatography, eluting with pentanes/ethyl acetate/DCM 10:1:1 (v/v/v). Product isolated as a white solid (44.6 mg, 0.118 mmol), 59%, mp = 193–194 °C. $[\alpha]_D^{20}$ = +86.0 (c 1.0, $CHCl_3$), 91% ee, [Daicel Chiralpak IA column (25 cm × 0.46 cm), *n*-hexane/*i*-PrOH = 90/10, 0.75 mL/min, t_{major} = 10.1 min, t_{minor} = 8.4 min. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (dt, *J* = 7.5, 1.0 Hz, 1H), 7.61–7.53 (m, 2H), 7.49–7.43 (m, 2H), 6.97–6.91 (m, 1H), 6.85 (ddd, *J* = 8.3, 2.5, 0.8 Hz, 1H), 2.89 (s, 1H), 1.65 (s, 3H), 0.83 (s, 6H), 0.67 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.1, 160.2 (d, *J* = 242.2 Hz), 149.7, 140.9 (d, *J* = 8.5 Hz), 134.8 (d, *J* = 2.2 Hz), 133.4, 132.1, 128.6, 124.7, 122.7, 117.9 (d, *J* = 9.0 Hz), 113.5 (d, *J* = 23.5 Hz), 112.2 (d, *J* = 24.3 Hz), 83.7, 74.5, 28.5, 24.4, 23.9. ^{19}F NMR (377 MHz, $CDCl_3$) δ -118.53 – -118.71 (m). HRMS m/z (DART+): Calculated for $C_{22}H_{24}BFNO_3$ ($[M+H]^+$) 380.1833, found 380.1837.


7.85 7.85 7.84 7.83 7.83 7.83 7.60 7.59 7.58 7.57 7.57 7.56 7.55 7.54 7.54 7.48 7.48 7.48 7.47 7.47 7.47 7.47 7.46 7.46 7.46 7.44 7.44 6.96 6.95 6.95 6.94 6.94 6.94 6.94 6.93 6.86 6.86 6.85 6.84 6.84 6.84 6.84 2.89 1.65 0.83 0.67
1.00 2.09 2.36 1.03 0.99 0.94 2.97 5.62 5.48
f1 (ppm)
168.12 161.12 159.19 149.74 140.91 140.84 134.84 134.83 133.37 132.10 128.56 124.66 122.69 117.98 117.90 113.56 113.37 112.26 112.06 83.66 74.47 28.50 24.39 23.89
f1 (ppm)

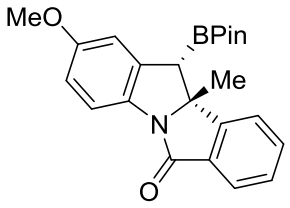




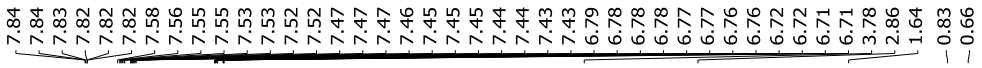
Signal 2: DAD1 B, Sig=225,16 Ref=360,100

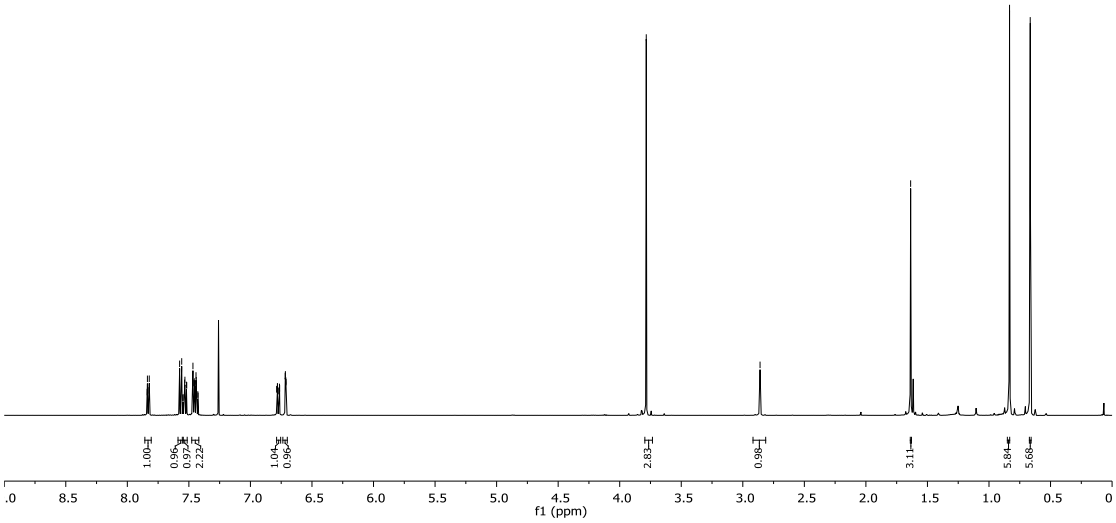
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.425	BB	0.1845	140.36433	11.49218	4.6032
2	10.097	BB	0.1944	2908.91284	228.74794	95.3968
Totals :				3049.27718	240.24012	

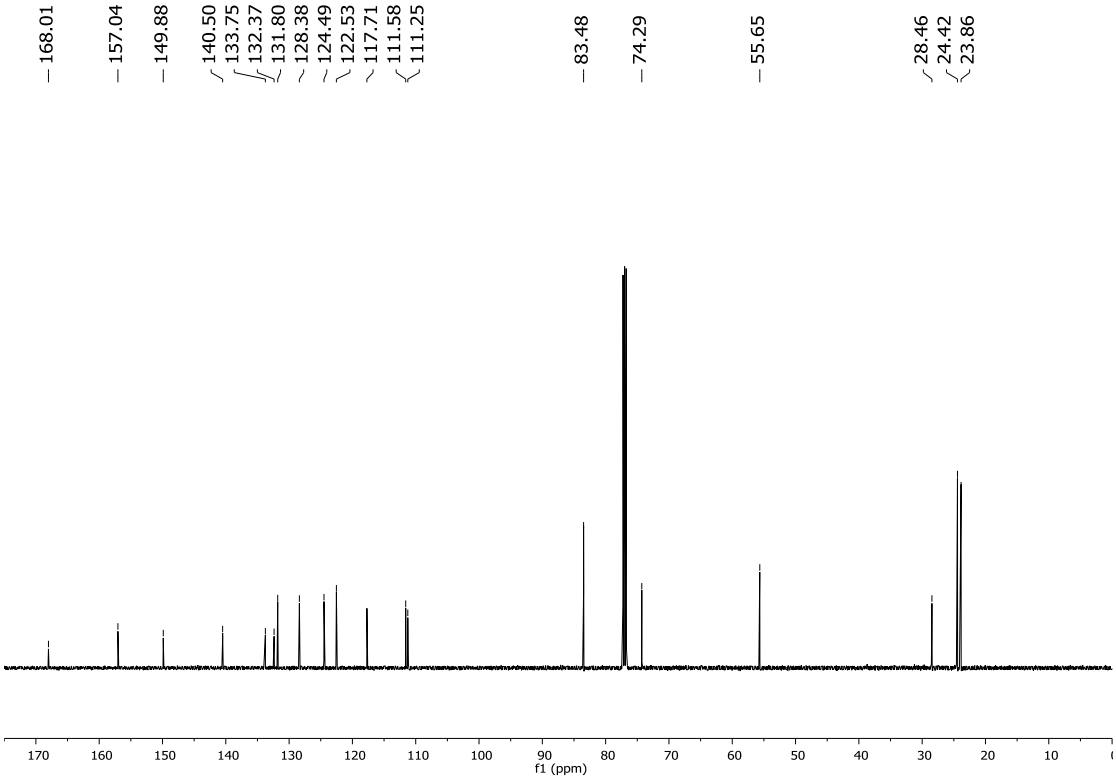
(10bR,11S)-2-methoxy-10b-methyl-11-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**3v**)

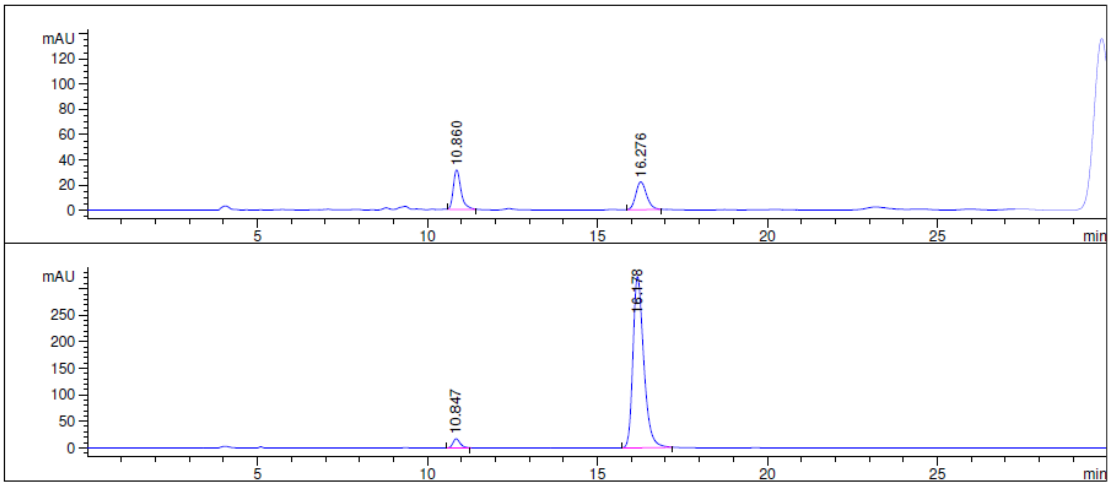


Product was purified by silica flash chromatography, eluting with pentanes/ethyl acetate/DCM 10:1:1 (v/v/v). Product isolated as a white solid (50.7 mg, 0.129 mmol), 65%, mp = 189–191 °C. $[\alpha]_D^{20}$ = +28.6 (c 1.0, CHCl3), 93% ee, [Daicel Chiralpak IA column (25 cm × 0.46 cm), *n*-hexane/*i*-PrOH = 90/10, 0.75 mL/min, t_{major} = 16.2 min, t_{minor} = 10.8 min. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (dt, *J* = 7.5, 1.0 Hz, 1H), 7.57 (d, *J* = 8.5 Hz, 1H), 7.53 (td, *J* = 7.4, 1.2 Hz, 1H), 7.48–7.42 (m, 2H), 6.77 (ddd, *J* = 8.5, 2.6, 0.5 Hz, 1H), 6.71 s(dd, *J* = 2.6, 0.8 Hz, 1H), 3.78 (s, 3H), 2.86 (s, 1H), 1.64 (s, 3H), 0.83 (s, 6H), 0.66 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.0, 157.0, 149.9, 140.5, 133.8, 132.4, 131.8, 128.4, 124.5, 122.5, 117.7, 111.6, 111.3, 83.5, 74.3, 55.6, 28.5, 24.4, 23.9. HRMS m/z (DART+): Calculated for $C_{23}H_{27}BNO_4$ ($[M+H]^+$) 392.2033, found 392.2028.


7.84
7.84
7.83
7.82
7.82
7.82
7.58
7.56
7.55
7.55
7.53
7.53
7.52
7.52
7.47
7.47
7.47
7.46
7.45
7.45
7.45
7.44
7.44
7.43
7.43
6.79
6.78
6.78
6.78
6.77
6.77
6.76
6.76
6.72
6.71
6.71
3.78
2.86
1.64
0.83
0.66


1.00
0.96
0.97
2.22
1.04
0.96
2.83
0.98
3.11
5.84
5.68
f1 (ppm)

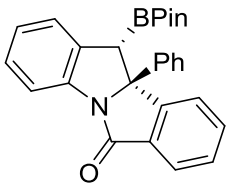

168.01
157.04
149.88
140.50
133.75
132.37
131.80
128.38
124.49
122.53
117.71
111.58
111.25
83.48
74.29
55.65
28.46
24.42
23.86
f1 (ppm)



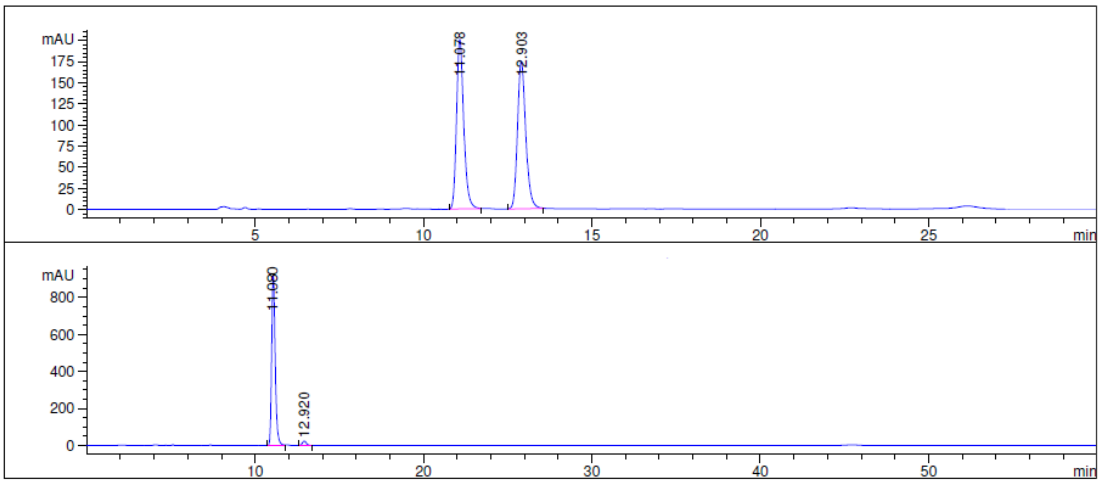
Signal 2: DAD1 B, Sig=225,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.847	BB	0.2297	256.92917	17.25393	3.4551
2	16.178	BB	0.3390	7179.22021	323.39426	96.5449
Totals :				7436.14938	340.64819	

10b-phenyl-11-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**3j**)



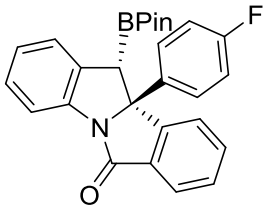
Product was purified by silica flash chromatography, eluting with pentanes/ethyl acetate/DCM 10:1:1 (v/v/v). Product isolated as a white solid (61.8 mg, 0.146 mmol), 73%. $[\alpha]_D^{20}$ = +219.1 (c 1.0, $CHCl_3$), 94% ee, [Daicel Chiralpak IA column (25 cm × 0.46 cm), *n*-hexane/*i*-PrOH = 90/10, 0.75 mL/min, t_{major} = 11.1 min, t_{minor} = 12.9 min.



Signal 2: DAD1 B, Sig=225,16 Ref=360,100

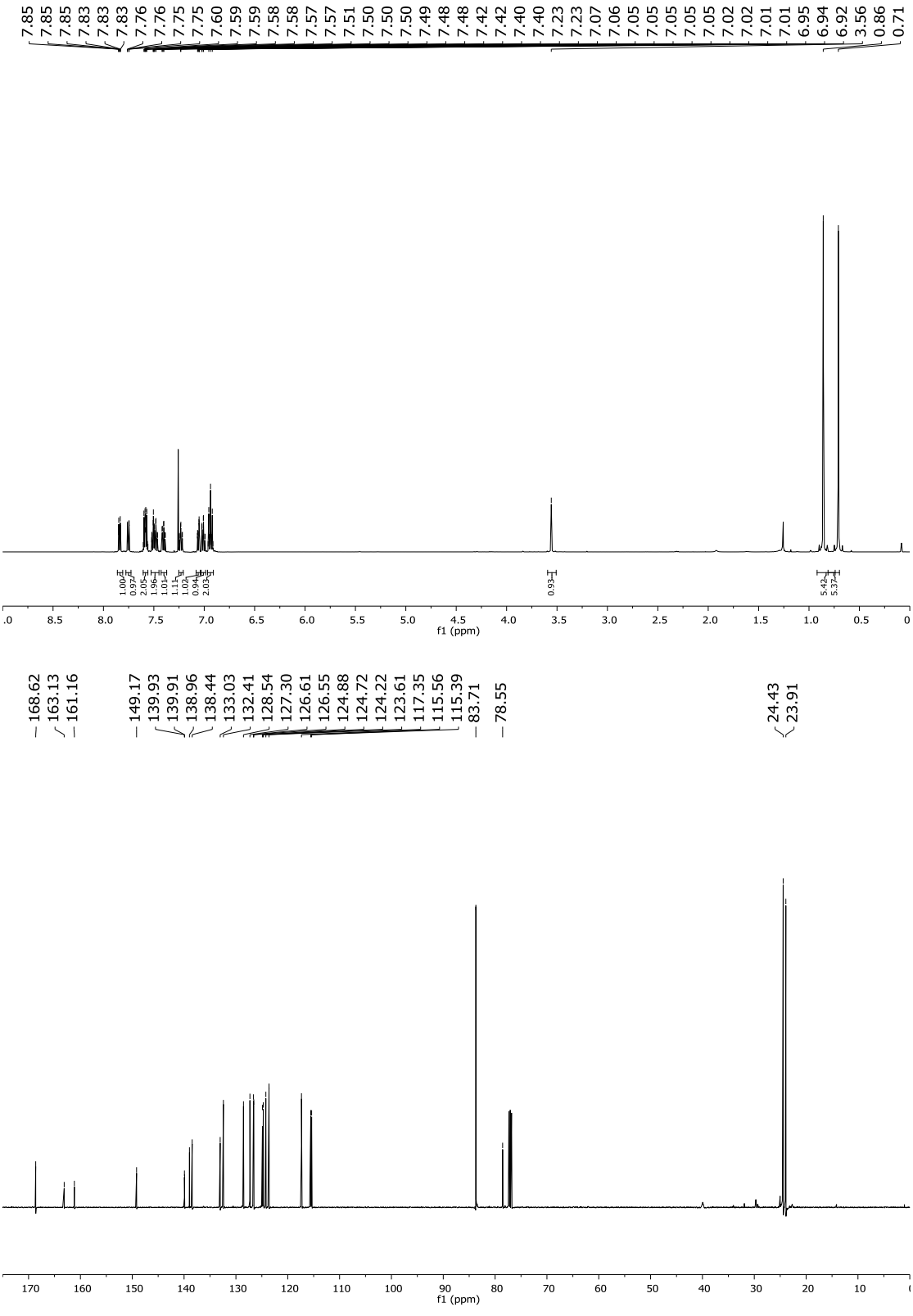
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.080	BB	0.2273	1.36549e4	919.40527	97.1731
2	12.920	BB	0.2576	397.23920	23.93755	2.8269
Totals :				1.40522e4	943.34283	

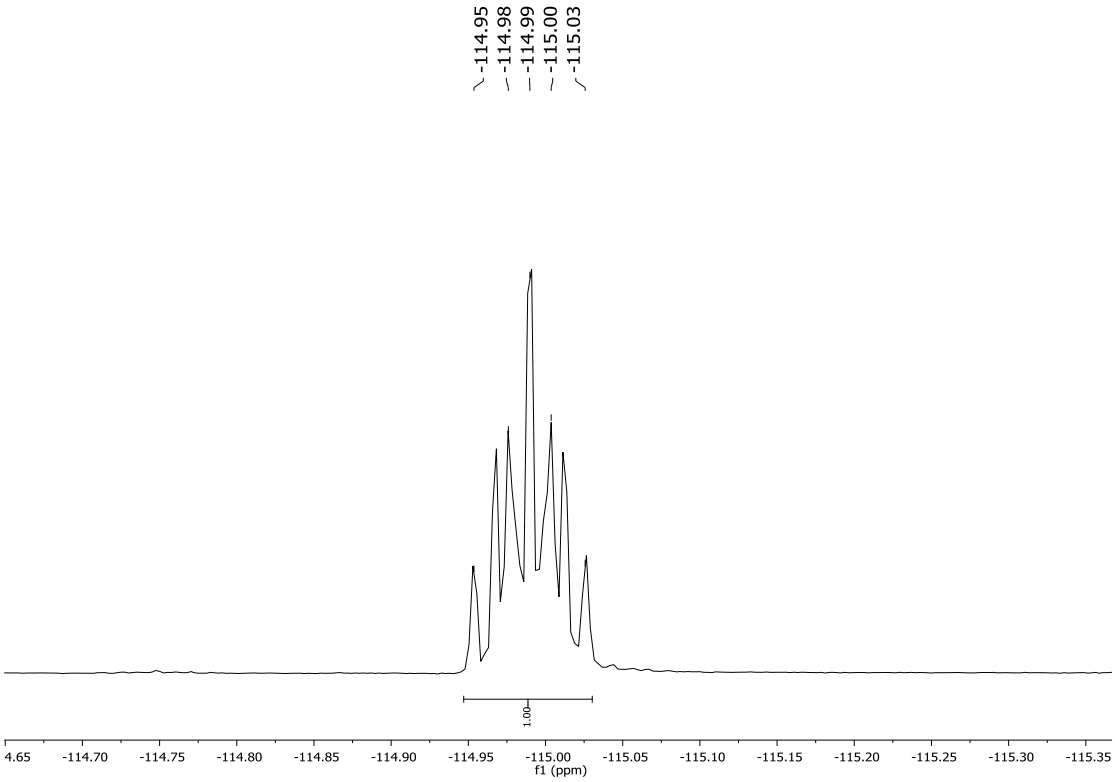
(10bS,11S)-10b-(4-fluorophenyl)-11-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**3w**)

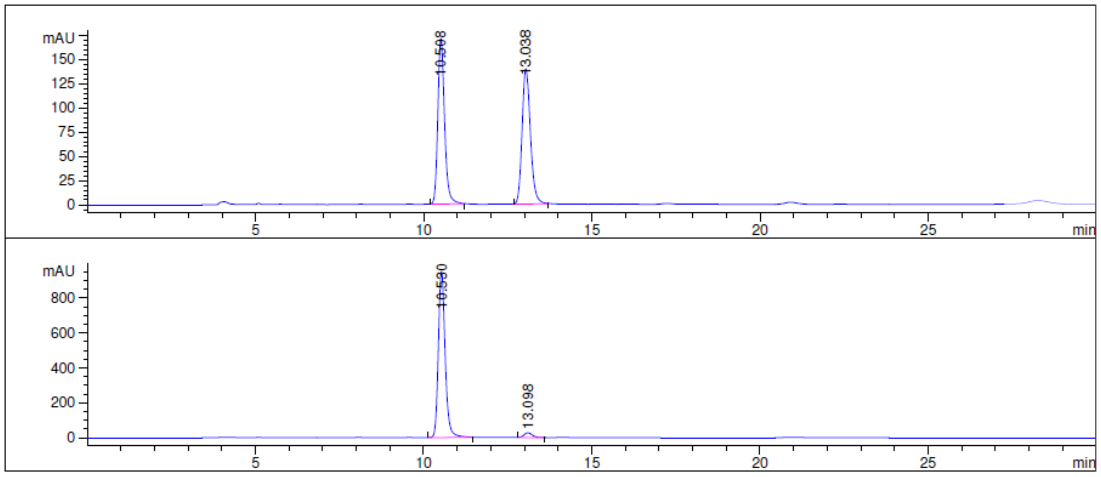


Product was purified by silica flash chromatography, eluting with pentanes/ethyl acetate/DCM 10:1:1 (v/v/v). Product isolated as a white solid (35.0 mg, 0.0793 mmol), 40%, mp = 163–165 °C. $[\alpha]_D^{20}$ = +183.2 (c 1.0, $CHCl_3$), 94% ee, [Daicel Chiralpak IA column (25 cm × 0.46 cm), *n*-hexane/*i*-PrOH = 90/10, 0.75 mL/min, t_{major} = 10.5 min, t_{minor} = 13.1 min. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (dt, *J* = 7.5, 1.0 Hz, 1H), 7.75 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.61–7.56 (m, 2H), 7.53–7.45 (m, 2H), 7.40 (td, *J* = 7.3, 1.3 Hz, 1H), 7.23 (td, *J* = 7.6, 1.4 Hz, 1H), 7.08–7.04 (m, 1H), 7.01 (td, *J* = 7.5, 1.1 Hz, 1H), 6.97–6.91 (m, 2H), 3.56 (s, 1H), 0.86 (s, 6H), 0.71 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.6, 162.1 (d, *J* = 246.6 Hz), 149.2, 139.9 (d, *J* = 3.1 Hz), 139.0, 138.4, 133.0, 132.4, 128.5, 127.3, 126.6 (d, *J* = 8.1 Hz), 124.9, 124.7, 124.2, 123.6, 117.4, 115.5 (d, *J* =

21.6 Hz), 83.7, 78.6, 24.4, 23.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.95 – -115.03 (m). HRMS m/z (DART+): Calculated for $C_{27}H_{26}BFNO_3$ ($[M+H]^+$) 442.1990, found 442.1994.



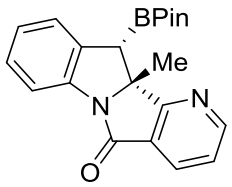




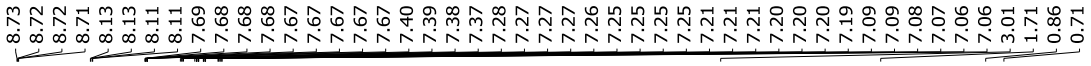
Signal 2: DAD1 B, Sig=225,16 Ref=360,100

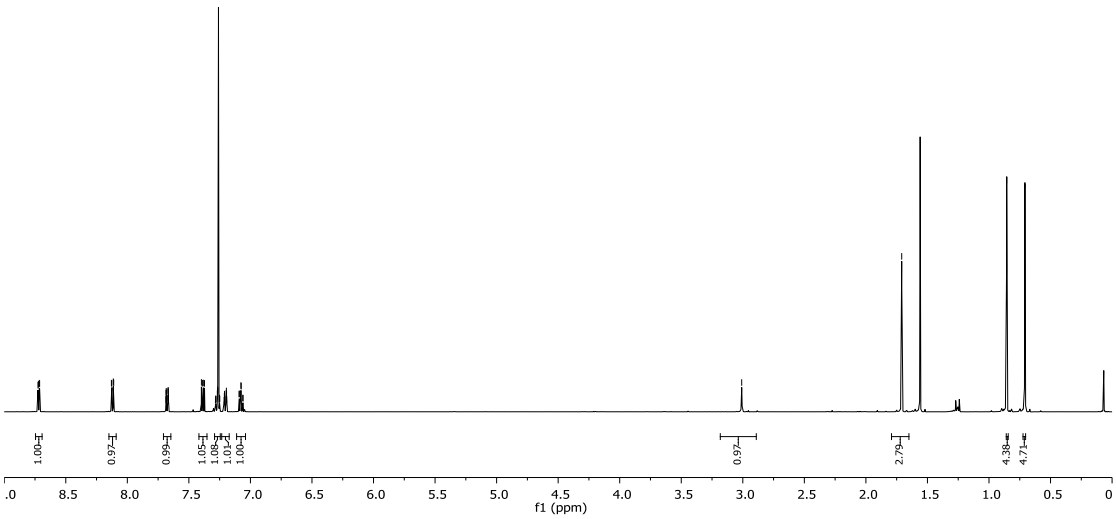
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.530	BB	0.2166	1.34172e4	950.74335	96.7651
2	13.098	BB	0.2583	448.54614	26.66433	3.2349
Totals :				1.38657e4	977.40768	

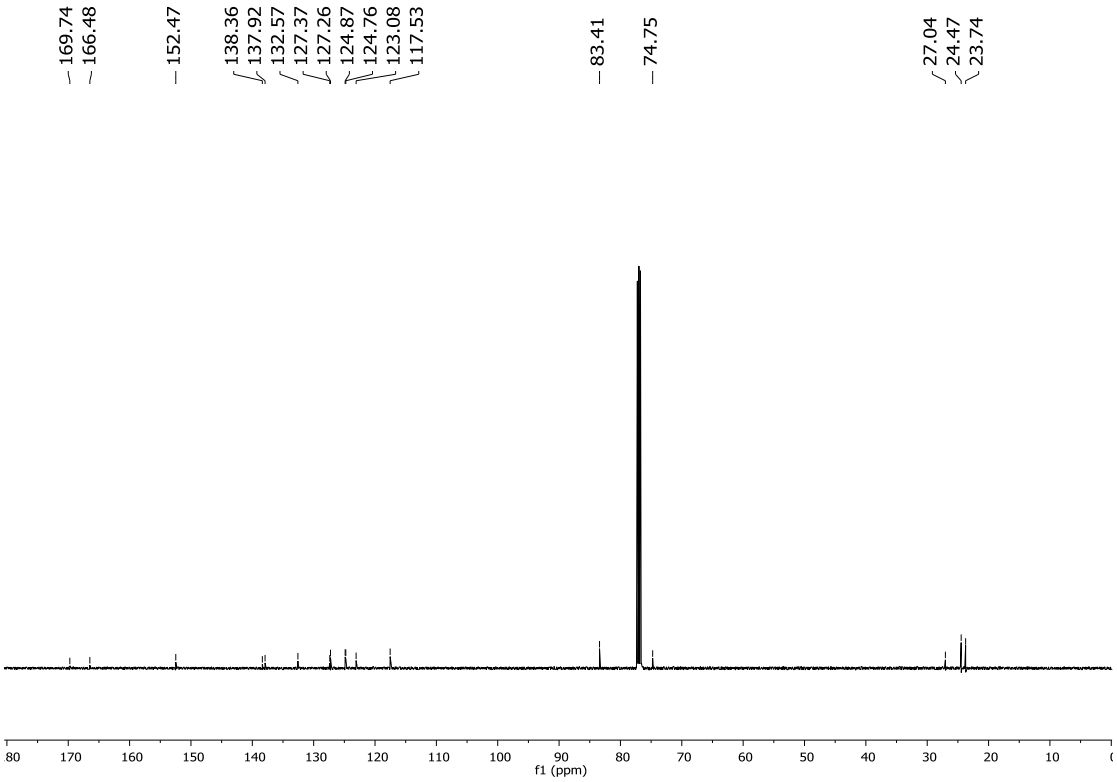
(11S,11aR)-11a-methyl-11-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-11,11a-dihydro-5H-pyrido[2',3':3,4]pyrrolo[1,2-a]indol-5-one (**3X**)

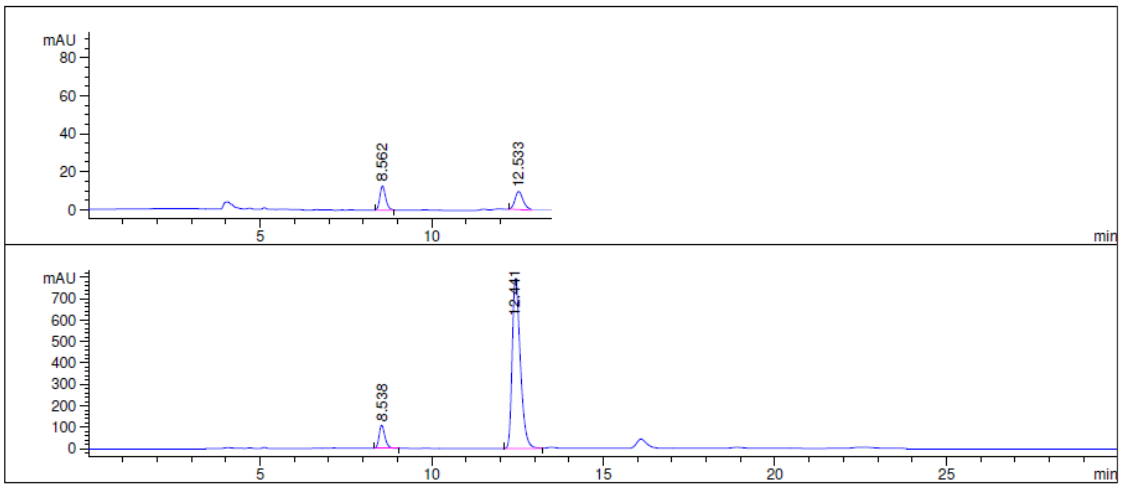


Product was purified by silica flash chromatography, eluting with pentanes/ethyl acetate/DCM 10:1:1 (v/v/v). Product isolated as a white solid (58.7mg, 0.162 mmol), 81%, mp = 120–122 °C. $[\alpha]_D^{20}$ = +105.6 (c 1.0, CHCl3), 82% ee, [Daicel Chiralpak IA column (25 cm × 0.46 cm), *n*-hexane/*i*-PrOH = 90/10, 0.75 mL/min, t_{major} = 12.4 min, t_{minor} = 8.5 min. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72 (dd, *J* = 4.9, 1.6 Hz, 1H), 8.12 (dd, J = 7.7, 1.6 Hz, 1H), 7.68 (ddt, *J* = 7.7, 1.0, 0.5 Hz, 1H), 7.39 (dd, *J* = 7.7, 4.9 Hz, 1H), 7.27 (tdd, *J* = 7.6, 1.3, 0.6 Hz, 1H), 7.20 (ddt, *J* = 7.6, 1.4, 0.7 Hz, 1H), 7.08 (td, *J* = 7.5, 1.2 Hz, 1H), 3.01 (s, 1H), 1.71 (s, 3H), 0.86 (s, 6H), 0.71 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.7, 166.5, 152.5, 138.4, 137.9, 132.6, 127.4, 127.3, 124.9, 124.8, 123.1, 117.5, 83.4, 74.7, 27.0, 24.5, 23.7. HRMS m/z (DART+): Calculated for $C_{21}H_{24}BN_2O_3$ ($[M+H]^+$) 363.1880, found 363.1878.







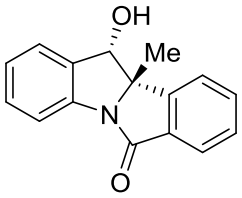


Signal 2: DAD1 B, Sig=225,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.538	BB	0.1834	1296.96045	108.57360	8.9727
2	12.441	BB	0.2536	1.31576e4	792.97217	91.0273
Totals :				1.44546e4	901.54577	

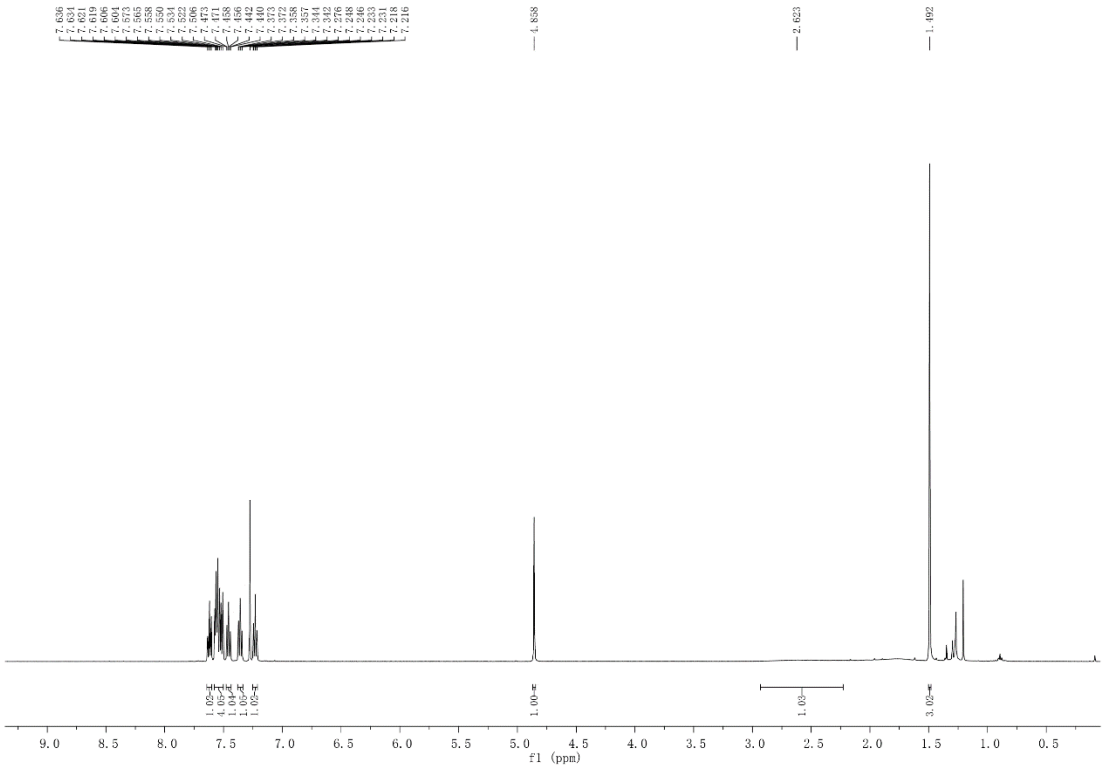
5. Synthetic transformations of product 3a

Oxidation of 3a to 11-hydroxy-10b-methyl-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (4):



The oxidation was performed according to the literature procedure.[3] In a reaction vial, **3a** (72.2 mg, 0.2 mmol) was dissolved in THF/H_2O (1:1, 2 mL). $NaBO_3$•$4H_2O$ (153.9 mg, 1.0 mmol) was then added at room temperature. After stirred for 2 h, the reaction mixture was extracted three times with EtOAc, dried over $MgSO_4$, and filtered. The crude mixture was purified by flash column chromatography (SiO_2, ethyl acetate/ petroleum ether, 1:1) to afford the product **4** as a white solid (50.2 mg, 0.2 mmol), >99%, mp = 99–101 °C. $[\alpha]_D^{20}$ = +178.4 (c 1.0, $CHCl_3$), 93% ee, [Daicel Chiralpak IA column (25 cm × 0.46 cm), *n*-hexane/*i*-PrOH = 70/30, 0.8 mL/min, t_{major} = 11.1 min, t_{minor} = 6.4 min. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (td, *J* = 7.5, 1.0 Hz, 1H), 7.58 – 7.50 (m, 4H), 7.46 (td, *J* = 7.5, 1.0 Hz, 1H), 7.36 (td, *J* = 7.5, 1.0 Hz, 1H), 7.23 (td, *J* = 7.5, 1.0 Hz, 1H), 4.86 (s, 1H), 2.62 (s, 1H), 1.49 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.6, 147.0, 139.2, 137.0, 133.1, 132.5, 130.4, 128.8, 126.7, 124.8, 124.4, 123.2, 117.8, 76.2, 76.0, 24.5. HRMS *m/z* (DART+): Calculated for $C_{16}H_{14}NO_2$ ($[M+H]^+$): 252.1019, Found 252.1022.

[3] Kubota, K.; Hayama, K.; Iwamoto, H.; Ito, H. *Angew. Chem. Int. Ed.* **2015**, *54*, 8809.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7.471
7.458
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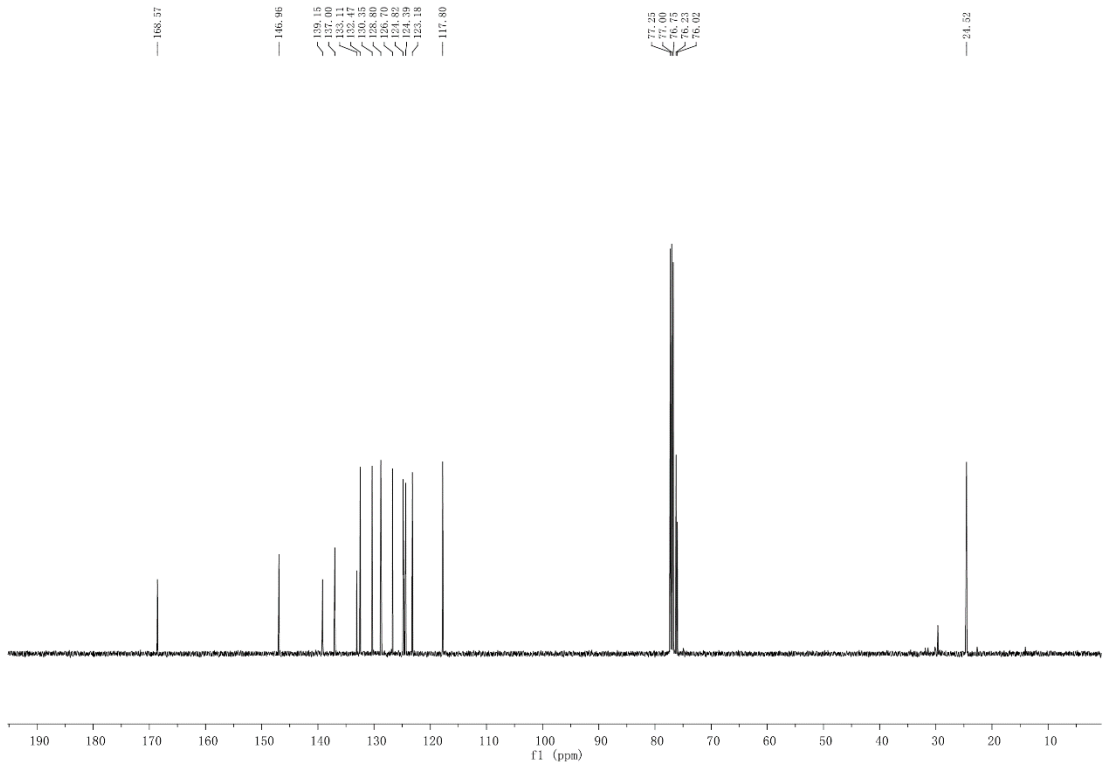
7.442
7.440
7.373
7.372
7.358
7.357
7.344
7.342
7.276
7.248
7.246
7.233
7.231
7.218
7.216
4.838
2.623
1.492
1.02
4.05
1.04
1.05
1.05
1.00
1.03
3.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


168.57
146.96
139.15
137.00
133.11
132.47
130.15
128.80
126.70
124.82
124.39
123.18
117.80
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76.02
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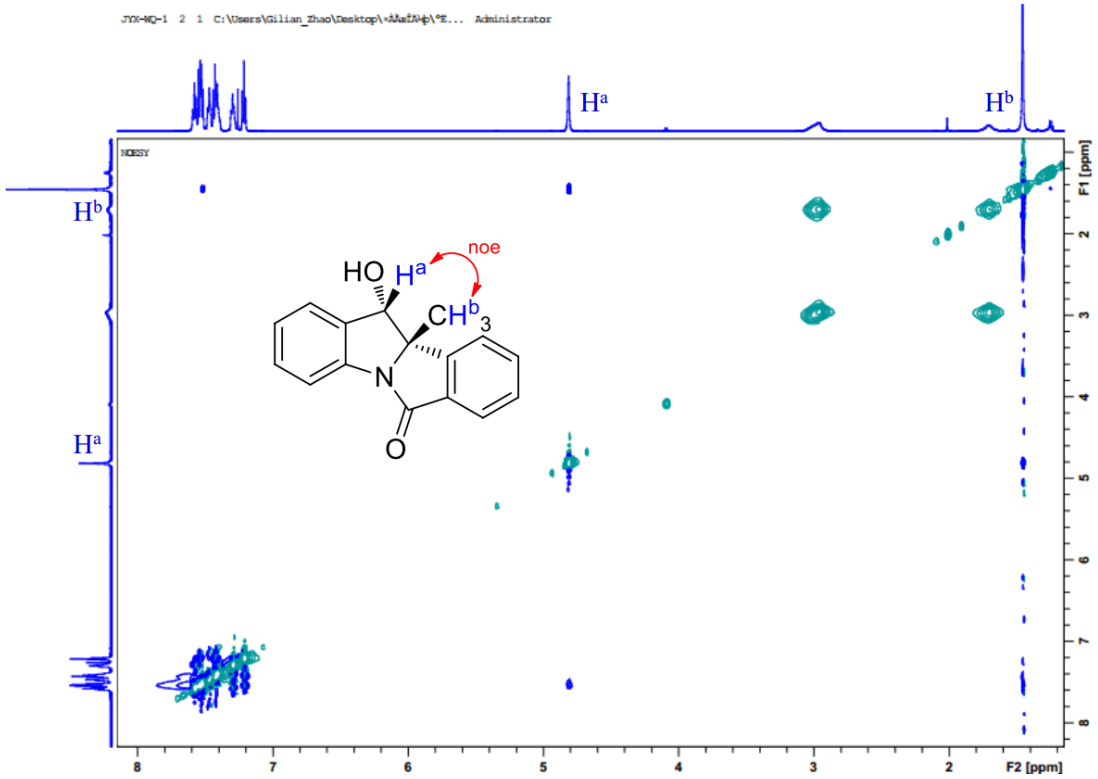
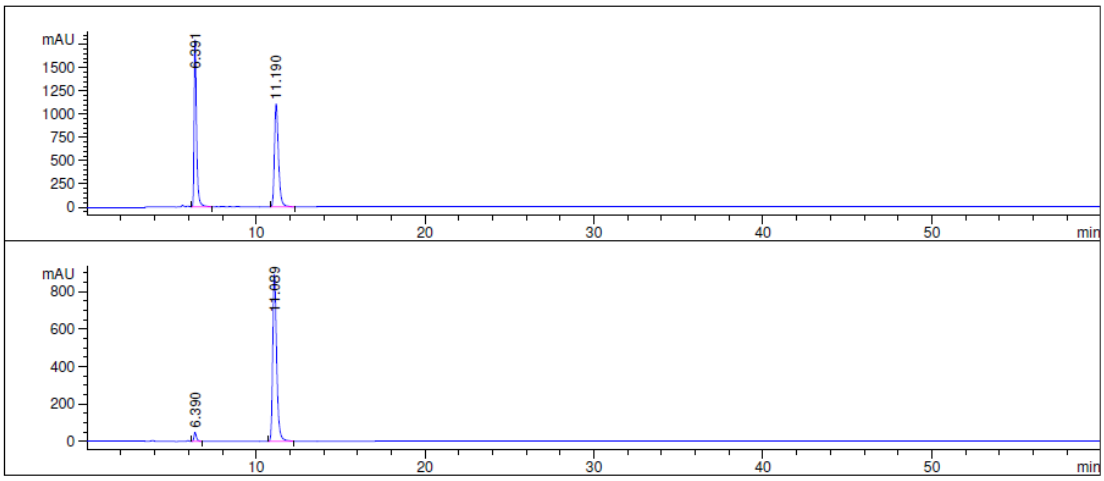
f1 (ppm)

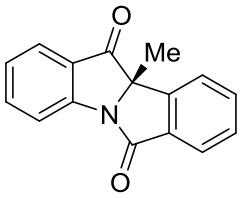




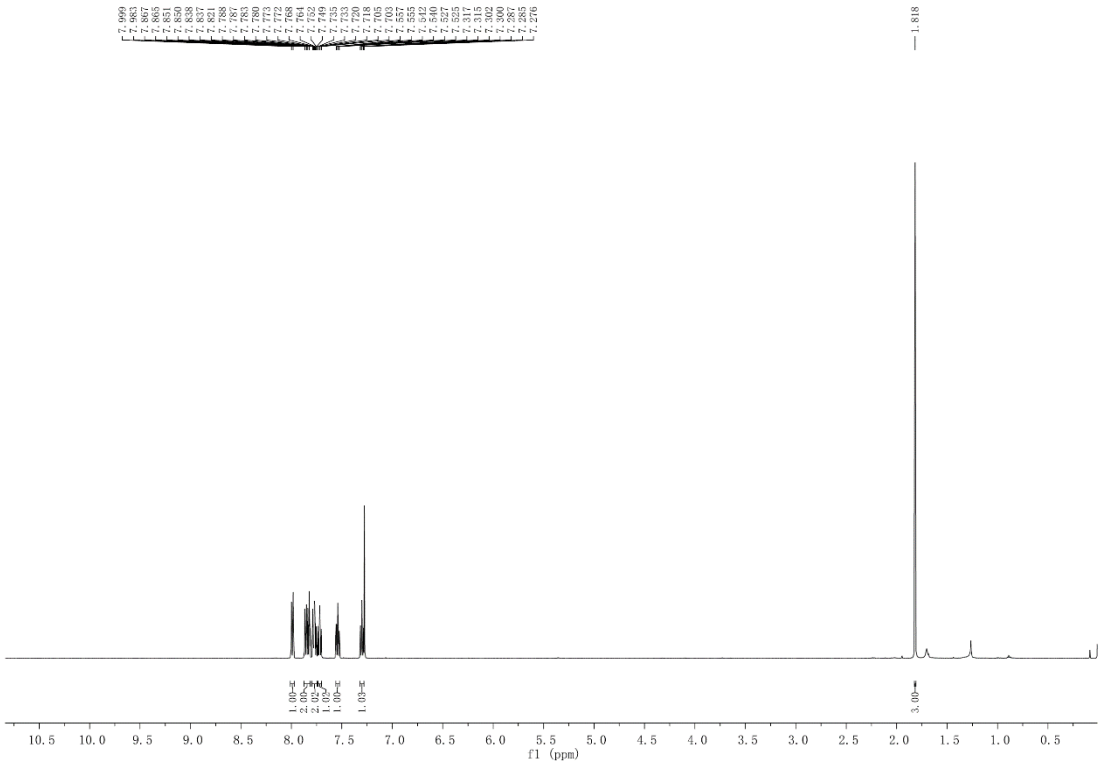
Signal 2: DAD1 B, Sig=225,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.390	VB	0.1557	498.26758	47.77721	3.3091
2	11.089	BB	0.2484	1.45594e4	892.14557	96.6909
Totals :				1.50577e4	939.92278	

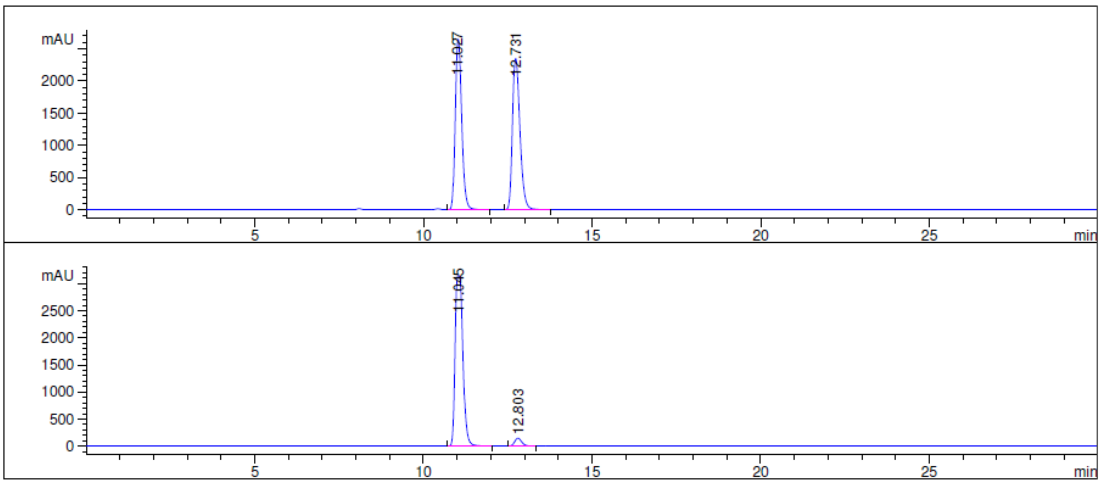
Oxidation of 4 to10b-methyl-6H-isoindolo[2,1-a]indole-6,11(10bH)-dione (5):[4]



In a reaction vial, alcohol **4** (50.3 mg, 0.2 mmol) was dissolved in $CHCl_3$ (2 mL). Pyridinium chlorochromate (64.7 mg, 0.6 mmol) was then added at room temperature. And the reaction mixture was heated to 35 °C and stirred overnight. The solvent was then removed under vacuum and the residue was purified by chromatography on silica gel, eluting with ethyl acetate/pentanes 1:5 (v/v) to afford the product **7** as a white solid (42.4 mg, 0.17 mmol), 85%. $[\alpha]_D^{20}$ = +578.9 (c 1.0, $CHCl_3$), 92% ee, [Daicel Chiralpak IA column (25 cm × 0.46 cm), *n*-hexane/*i*-PrOH = 90/10, 0.75 mL/min, t_{major} = 11.0 min, t_{minor} = 12.8 min. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.0 Hz, 1H), 7.87–7.82 (m, 2H), 7.80 – 7.75 (m, 2H), 7.72 (td, *J* = 7.5, 1.0 Hz, 1H), 7.54 (td, *J* = 7.5, 1.0 Hz, 1H), 7.30 (td, *J* = 7.5, 1.0 Hz, 1H), 1.82 (s, 3H).



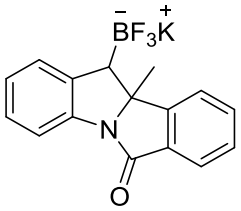
[4] Liu, R.-R.; Wang, Y.-G.; Li, Y.-L.; Huang, B.-B.; Liang, R.-X.; Jia, Y.-X. *Angew. Chem. Int. Ed.* **2017**, *56*, 7475.



Signal 2: DAD1 B, Sig=225,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.045	BB	0.2493	5.00021e4	3148.87427	95.9182
2	12.803	BB	0.2237	2127.85938	146.29939	4.0818
Totals :				5.21299e4	3295.17366	

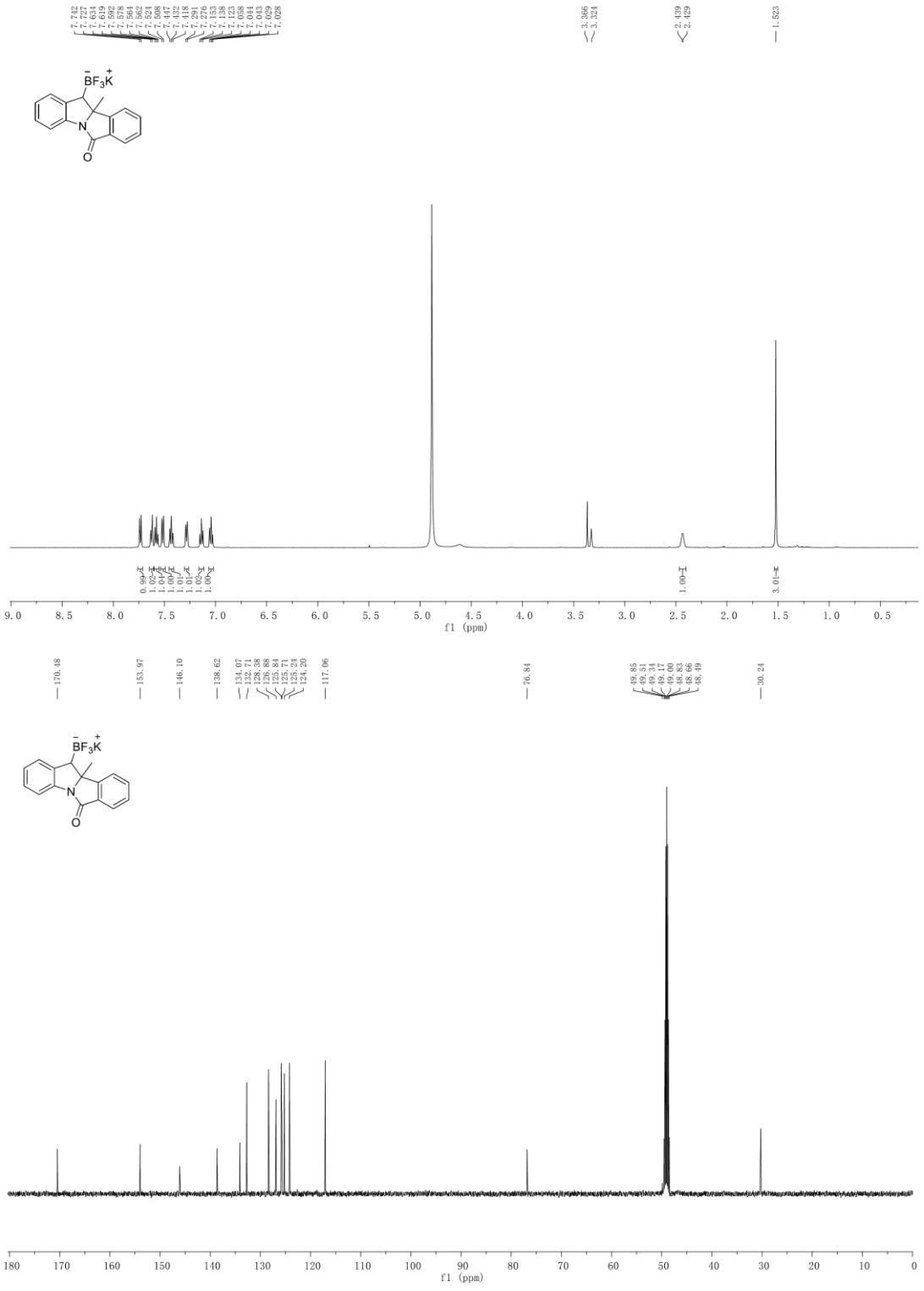
Procedure for the preparation of potassium trifluoro (10b-methyl-6-oxo-10b,11-dihydro-6H-isoindolo[2,1-a]indol-11-yl) borate 6:



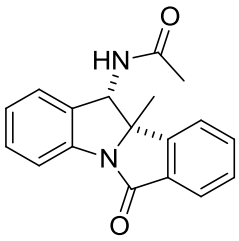
The reaction was performed according to the literature procedure.[5] To a solution of **3a** (144.5mg, 0.40 mmol) in MeOH (1 mL), a saturated aqueous solution of potassium hydrogen fluoride (4.5 M, 0.5 mL) was added dropwise and the mixture was stirred at room temperature for 4 h. The solvent was then removed in vacuo to afford a solid, which was dried under vacuum overnight. The solid was then washed by acetone (3×4.0 mL) and the collected organic phase was concentrated in vacuo to afford a concentrated acetone solution containing product (~1.0 mL). After addition of Et_2O (10 mL) to the acetone solution a precipitate was obtained, which was filtered and dried to give compound **6** as a white solid, Mp = 188-190 °C; 91% yield; ^{1}H NMR (500 MHz, CD_3OD) δ 7.73 (d, *J* = 7.5 Hz, 1H), 7.63 (d, *J* = 7.5 Hz, 1H), 7.60 – 7.55 (m, 1H), 7.52

[5] Feng, Q.; Yang, K.; Song, Q.-L. *Chem. Commun.* **2015**, *51*, 15394.

(d, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 7.0 Hz, 1H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.07–7.02 (m, 1H), 2.43 (d, *J* = 5.0 Hz, 1H), 1.52 (s, 3H). ^{13}C NMR (125 MHz, CD_3OD) δ 170.5, 154.0, 146.1, 138.6, 134.1, 132.7, 128.4, 126.9, 125.8, 125.7, 125.2, 124.2, 117.1, 76.8, 49.9, 30.2. HRMS *m/z* (ESI+): Calculated for $C_{16}H_{12}BF_3NNaO$ ([M-K+Na]$^+$): 325.0862, Found 325.0988.

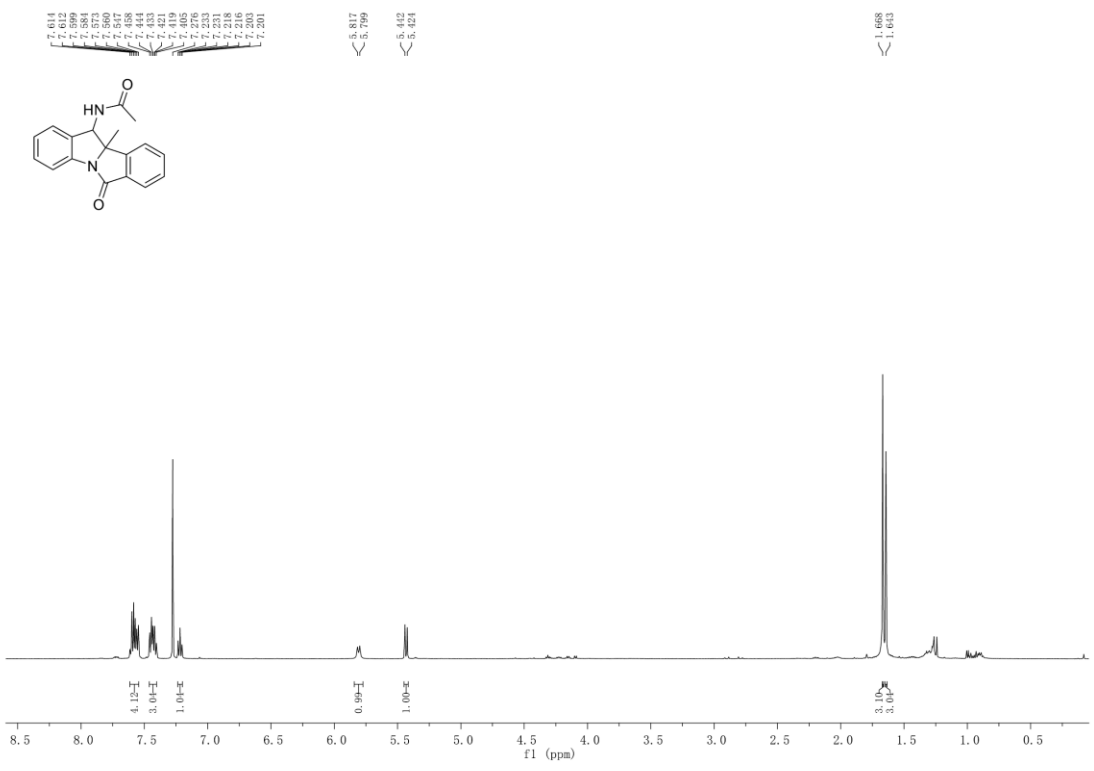


Procedure for the preparation of *N*-(10b-methyl-6-oxo-10b,11-dihydro-6H-isoindolo[2,1-a]indol-11-yl)acetamide (7):



The reaction was performed according to the literature procedure.[6] To a dried Schlenk tube were added copper diacetate monohydrate (59.9 mg, 0.20 mmol) and **6** (58.5 mg, 0.20 mmol), 2.0 mL acetonitrile was then introduced via syringe. 2.0 equivalent boron trifluoride (in solution in ether, ca. 48% BF_3) was then added, and the tube was sealed using Teflon cap. The mixture was stirred 15 h at 100 °C (oil bath). The reaction media was poured in 5 mL of water and extracted with ethyl acetate (3×3 mL). The combined organic layers were washed with brine (5 mL) and dried over $MgSO_4$, filtered, and concentrated under reduce pressure. The crude was purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:1 (v/v) to afford the product **7** as a white solid, Mp = 256-258 °C; 64% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.54 (m, 4H), 7.47 – 7.40 (m, 3H), 7.22 (td, *J* = 7.5, 1.0 Hz, 1H), 5.81 (d, *J* = 9.0 Hz, 1H), 5.43 (d, *J* = 9.0 Hz, 1H), 1.67 (s, 3H), 1.64 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.3, 168.3, 147.3, 139.4, 134.8, 132.8, 132.6, 130.2, 129.0, 126.9, 125.0, 124.4, 123.7, 117.5, 76.1, 56.6, 25.6, 22.6. HRMS *m/z* (ESI+): Calculated for $C_{18}H_{16}N_2NaO_2$ ($[M+Na]^+$): 315.1104, Found 315. 1098.

[6] Cazorla, C.; Métay, E.; Lemaire, M. *Tetrahedron,* **2011**, *67,* 8615.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7.405
7.376
7.255
7.231
7.218
7.216
7.203
7.201
5.817
5.799
5.442
5.424
1.668
1.643
HN
O
N
O
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3.04
1.04
0.99
1.00
3.10
3.04
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8.0
7.5
7.0
6.5
6.0
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5.0
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3.0
2.5
2.0
1.5
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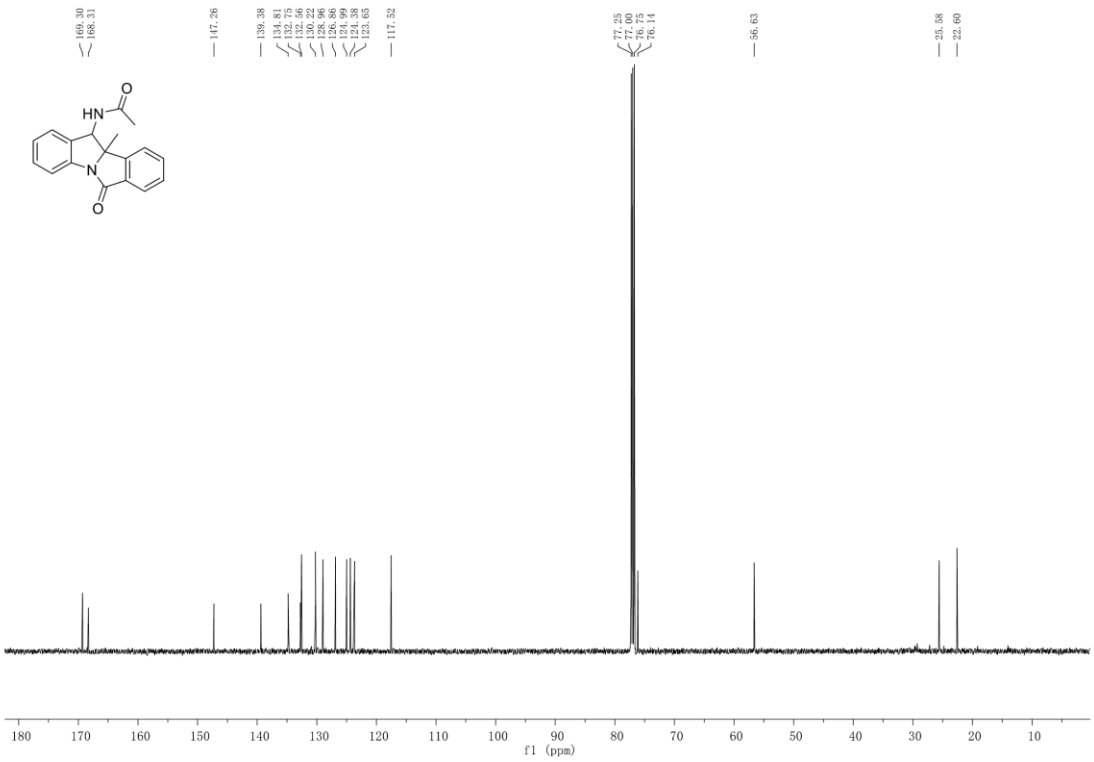
0.5
f1 (ppm)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126.88
124.99
124.38
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117.52
77.25
77.00
76.75
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56.63
25.58
22.60
HN
O
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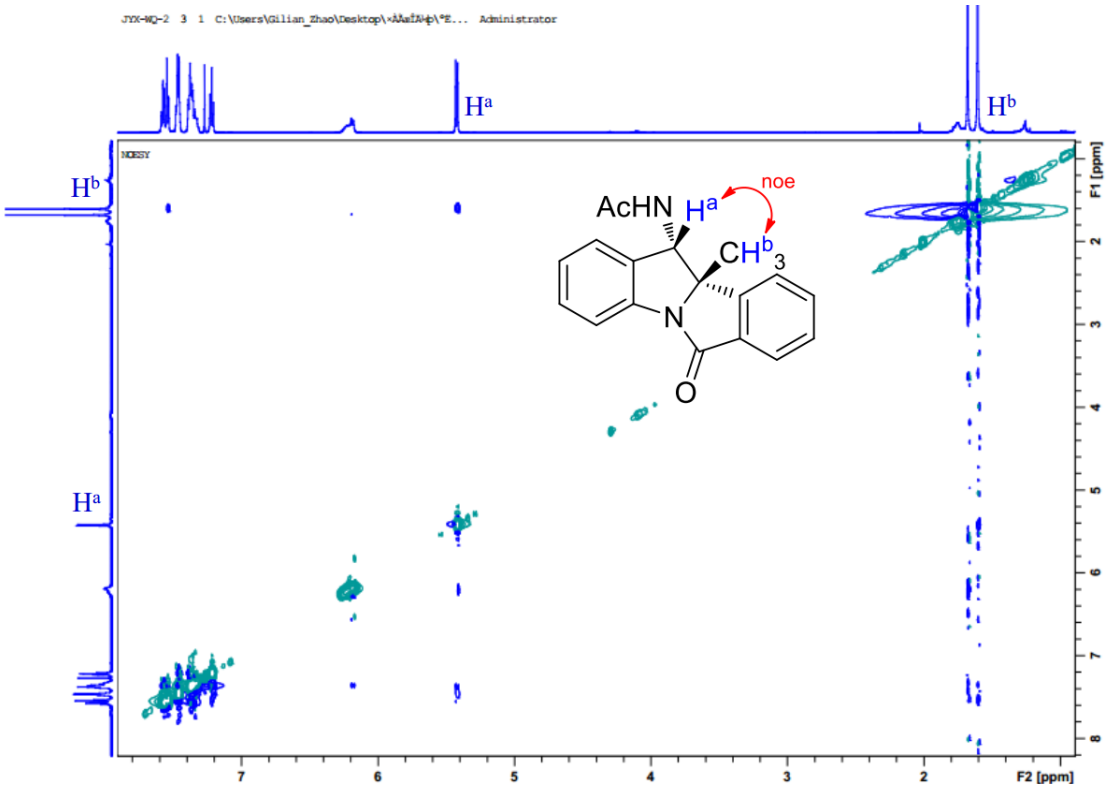
f1 (ppm)


JYX-MQ-2 3 1 C:\Users\Gilian_Zhao\Desktop\ÀÅæÎÄ¼þ*E... Administrator
NOESY
Ha
Hb
Hb
Ha
AcHN
Ha
noe
CHb3
N
O
F1 [ppm]
F2 [ppm]
7
6
5
4
3
2
1
2
3
4
5
6
7
8

6. Single-crystal X-ray of 3a

No syntax errors found. CIF dictionary
Please wait while processing .... Interpreting this report

Datablock: d1866a_a

Bond precision: = 0.0000 A Wavelength=1.54178
Cell: a=9.9629(2) b=10.4616(2) c=18.5419(3)
alpha=90 beta=90.923(1) gamma=90
Temperature: 150 K

	Calculated	Reported
Volume	1932.33(6)	1932.33(6)
Space group	P 21	P 21
Hall group	P 2yb	P 2yb
Moiety formula	C22 H24 B N O3	C22 H24 B N O3
Sum formula	C22 H24 B N O3	C22 H24 B N O3
Mr	361.23	361.23
Dx,g cm-3	1.242	1.242
Z	4	4
Mu (mm-1)	0.646	0.646
F000	768.0	768.0
F000'	770.24	
h,k,lmax	11,12,22	11,12,22
Nref	6984[3699]	6794
Tmin,Tmax	0.877,0.896	0.690,0.753
Tmin'	0.851	

Correction method= # Reported T Limits: Tmin=0.690 Tmax=0.753
AbsCorr = MULTI-SCAN
Data completeness= 1.84/0.97 Theta(max)= 67.563
R(reflections)= 0.0401(6670) wR2(reflections)= 0.1049(6794)
S = 1.043 Npar= 947

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A
PLAT089_ALERT_3_A Poor Data / Parameter Ratio (Zmax < 18) ..... 3.85 Note

Author Response: Data were collected 0.83 A with CuKalpha data. Percentage of I>2sig(I) Data at Theta(Max) Still 93% Note Both molecules in the asymmetric unit have whole molecule disorder and this increases the number of parameters.

Alert level C
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L= 0.600 53 Report

Alert level G
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 108 Note
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ... 108 Report
PLAT175_ALERT_4_G The CIF-Embedded .res File Contains SAME Records 2 Report
PLAT178_ALERT_4_G The CIF-Embedded .res File Contains SIMU Records 2 Report
PLAT230_ALERT_2_G Hirshfeld Test Diff for O2B --B1B . 6.4 s.u.
PLAT301_ALERT_3_G Main Residue Disorder .....(Resd 1) 100% Note
And 3 other PLAT301 Alerts
More ...
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... Resd 1 44.32 Check
And 3 other PLAT304 Alerts
More ...
PLAT395_ALERT_2_G Deviating X-O-Y Angle From 120 for O2A 107.2 Degree
And 7 other PLAT395 Alerts
More ...
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..... 16 Note
PLAT791_ALERT_4_G Model has Chirality at C1A (Chiral SPGR) R Verify
And 3 other PLAT791 Alerts
More ...
PLAT860_ALERT_3_G Number of Least-Squares Restraints ..... 2087 Note
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still 93% Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density. 5 Info

1 ALERT level A = Most likely a serious problem - resolve or explain
0 ALERT level B = A potentially serious problem, consider carefully
1 ALERT level C = Check. Ensure it is not caused by an omission or oversight
29 ALERT level G = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
12 ALERT type 2 Indicator that the structure model may be wrong or deficient
8 ALERT type 3 Indicator that the structure quality may be low
11 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual