Supporting Information

Pd/Cu-Catalyzed Domino Cyclization/Deborylation of Alkene-Tethered Carbamoyl Chloride and 1,1-Diborylmethane

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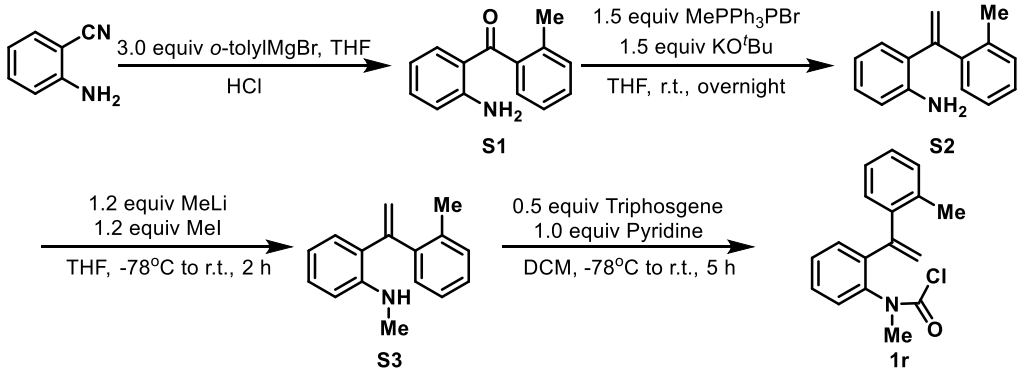
General Experimental

All reactions were carried out under nitrogen atmosphere and anhydrous conditions unless otherwise indicated. All manipulations of air-sensitive or moisture-sensitive compounds were performed in a glovebox under an atmosphere of nitrogen. Unless otherwise noted, all catalytic reactions were run in dried glassware. Toluene and THF were distilled from sodium/benzophenone. DCM was distilled over CaH_2. $Pd(PPh_3)_4$ (CAS 14221-01-3) was purchased from Adamas; CuCl (CAS 7758-89-6) was purchased from Energy Chemical; Benzene (CAS 71-43-2) was purchased from J & K (99.8%, SafeDry, with molecular sieves, Water ≤ 50 ppm (by K.F.), SafeSeal); Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.20 mm Huanghai silica gel plates (HSGF 254) using UV light as the visualizing agent or by iodine staining. All new compounds were characterized by means of GC, ^{1}H-NMR, ^{13}C-NMR, and HR-MS. GC analysis was performed on Agilent Technologies 7820A GC system. GC runs were performed with the following method: GC; HP-5 column; inlet temperature 100 ℃; column temperature 100 ℃ for 1 min, then 50 ℃ /min to 280 ℃, then 280 ℃ for 6 min. NMR spectra were recorded using a Bruker AVANCE Ⅲ 400 MHz NMR spectrometer and can be found at the end of the paper. High-resolution mass spectra (HRMS) were recorded on a Agilent Technologies 7250 GCQTOF using EI-TOF (electron ionization-time of flight) or on a JEOC AccuTOF LC-plus 4G mass spectrometer using ESI (electrospray ionization). All ^{1}H-NMR data are reported in δ units, parts per million (ppm), and were calibrated relative to the signals for residual chloroform (7.26 ppm) in deuterochloroform ($CDCl_3$). All ^{13}C-NMR data are reported in ppm relative to $CDCl_3$ (77.16 ppm) and were obtained with ^{1}H decoupling. The following abbreviations or combinations thereof were used to explain the multiplicities: s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

Experimental Procedures for Substrates

Compounds **1a**[2], **1b**[1], **1c**[3], **1d**[3], **1e**[1], **1f**[1], **1h**[3], **1i**[3], **1j**[3], **1k**[1], **1l**[1], **1m**[3], **1n**[1], **1o**[3], **1p**[3], **1q**[1], **1s**[1], **1t**[3] were synthesized according to the published procedures.

Procedure for carbamoyl chlorides 1r



To a round-bottomed flask charged with the 2-aminoacetophenone (1.0 equiv) in THF (1.0 M), the o-tolylmagnesium bromide (3.0 equiv) in THF was added dropwise via syringe at 0 ℃. The reaction mixture was warmed to room temperature. When the starting material was consumed as monitored by TLC, the reaction mixture was quenched by 6 M HCl, extracted with EtOAc (three times). The separated organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica gel column chromatography to afford ketone **S1**.

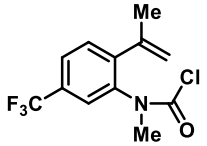
Potassium *tert*-butoxide (1.5 equiv) was added in portions to the solution of methyl triphenyl-phosphonium bromide (1.5 equiv) in THF (0.3 M) at 0 °C. The suspension turned bright yellow upon addition of the base. The suspension was warmed to room temperature and stirred for 30 minutes, the reaction mixture was cooled to 0 °C. The solution of ketone intermediate **S1** in THF was slowly added into the reaction mixture. The resulting reaction mixture was warmed to room temperature and stirred until consumption of starting material was observed by TLC. Upon completion the reaction was concentrated *in vacuo* and the residue diluted with PE, filtered, and concentrated under reduced pressure to afford alkene **S2**.

To the solution of alkene intermediate **S2** in THF (0.3 M) was added methyllithium (1.2 equiv, 1.6 M in diethoxymethane) dropwise at –78 °C. The resultant yellow solution was stirred for 1 h at –78 °C. Iodomethane (1.2 equiv) was added and the reaction was warmed to room temperature and stirred until consumption of the starting material. The reaction was quenched with H_2O then extracted with EtOAc. The combined extracts were washed by brine. The organic layer was separated, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give amine **S3**, which could be used without further purification.

To a solution of **S3** (1.0 equiv) in DCM was added pyridine (2.0 equiv) and triphosgene (0.35 equiv) in sequence at 0 ℃. The mixture was then allowed to warm to room temperature for enough time (TLC monitor), and then was quenched with 1 M HCl, diluted with DCM, dried over Na_2SO_4. After removing the solvent, the residue was purified by column chromatography to give substrate **1r**.

Characterization Data for Substrates

methyl(2-(prop-1-en-2-yl)-5-(trifluoromethyl)phenyl)carbamic chloride (1g)

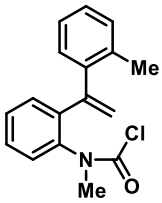


General procedure A was followed and purification by flash column chromatography on silica gel (PE/EtOAc = 50/1) afforded **1g** as a yellow solid (234.3 mg, 21% over 4 steps). Product was isolated as a 4:1 mixture of rotamers. ^{1}H and ^{13}C NMR data listed is for the major rotamer.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 8.0 Hz, 1H), 7.40 (s, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 5.27 (s, 1H), 5.03 (s, 1H), 3.22 (s, 3H), 2.05 (s, 3H).

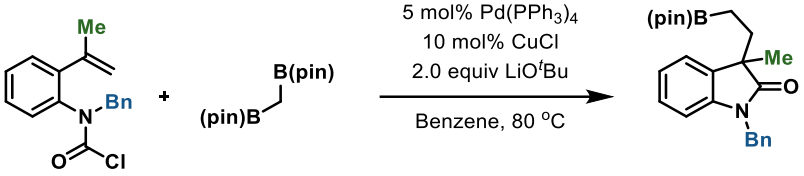
^{13}C NMR (101 MHz, $CDCl_3$): δ 149.1, 145.2, 141.3, 140.4, 130.8 (q, J_{C-F} = 33.3 Hz), 130.6, 126.2 (q, J_{C-F} = 3.7 Hz), 125.7 (q, J_{C-F} = 3.5 Hz), 123.3 (q, J_{C-F} = 270.6 Hz), 118.1, 39.8, 23.1.
^{19}F NMR (376 MHz, $CDCl_3$): δ -62.6
HRMS (EI): [M-HCl] Calcd for $C_{12}H_{10}NO$: 241.0709; found: 241.0706.

methyl(2-(1-(o-tolyl)vinyl)phenyl)carbamic chloride (1r)



General procedure A was followed and purification by flash column chromatography on silica gel (PE/EtOAc = 10/1–5/1) afforded **1r** as an orange solid (704.3 mg, 61% over 2 steps). Product was isolated as a 5:1 mixture of rotamers. ^{1}H and ^{13}C NMR data listed is for the major rotamer.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44–7.39 (m, 3H), 7.23–7.17 (m, 3H), 6.86–6.82 (m, 2H), 5.65 (s, 1H), 5.27 (s, 1H), 3.80 (s, 3H), 2.87 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 159.7, 146.3, 141.1, 140.9, 140.6, 133.0, 131.7, 129.1, 129.0, 128.9, 128.6, 128.2, 128.1, 116.2, 113.9, 55.4, 39.5.
HRMS (EI): $[M-Cl]^+$ Calcd for $C_{17}H_{16}NO^+$: 250.1226; found: 250.1226.

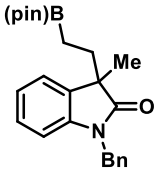
Experimental Procedures for the Catalytic Reaction



To an oven-dried sealed tube was added CuCl (10 mol%), carbamoyl chloride (1.0 equiv) (if solid) and LiO^tBu (2.0 equiv). $Pd(PPh_3)_4$ (5 mol%) was added in a nitrogen-filled glove-box. Then benzene (0.1 M), 1,1-bis[(pinacolato)boryl]methane (1.5 equiv) were added. The tube was sealed strictly and heated in 80 °C preheated oil bath with a reaction time of 12 h. After completion of starting material as monitored by TLC, The solution was cooled to room temperature and filtered through a pad of celite and washed with EA. The reaction mixture was concentrated under reduced pressure and purified by silica gel flash column chromatography.

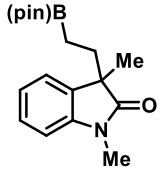
Characterization Data for Products

1-benzyl-3-methyl-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)indolin-2-one (3a)



General Procedure was followed on 0.2 mmol scale, purification by flash column chromatography on silica gel (PE/Acetone = 50/1–20/1) afforded **3a** as a pale yellow oil (64.5 mg, 82%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.33–7.22 (m, 5H), 7.18 (dd, J = 7.2, 0.4 Hz, 1H), 7.11 (td, J = 7.6, 1.2 Hz, 1H), 7.00 (td, J = 7.6, 0.4 Hz, 1H), 6.67 (d, J = 7.6 Hz, 1H), 4.94 (d, J = 16.0 Hz, 1H), 4.86 (d, J = 15.6 Hz, 1H), 2.06 (td, J = 13.2, 4.8 Hz, 1H), 1.90 (td, J = 13.2, 4.4 Hz, 1H), 1.41 (s, 3H), 1.20 (s, 6H), 1.18 (s, 6H), 0.56 (ddd, J = 15.6, 12.8, 4.4 Hz, 1H), 0.40 (ddd, J = 15.6, 12.8, 4.4 Hz, 1H);
^{13}C NMR (100 MHz, $CDCl_3$): δ 180.9, 142.8, 136.2, 134.0, 128.9, 127.6, 127.6, 127.3, 122.9, 122.5, 109.0, 83.2, 49.6, 43.7, 32.9, 25.0, 24.9, 23.6.
^{11}B NMR (128 MHz, $CDCl_3$): δ 33.40.
R_f = 0.50 (PE/Acetone = 5/1).
HRMS (EI): Calcd for $C_{24}H_{30}BNO_3$: 391.2319; found: 391.2314.

1,3-dimethyl-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)indolin-2-one (3b)



General Procedure was followed on 0.2 mmol scale, purification by flash column chromatography on silica gel (PE/Acetone = 50/1–20/1–10/1) afforded **3b** as an orange solid (50.7 mg, 80%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.23 (td, *J* = 8.0, 0.8 Hz, 1H), 7.15 (d, *J* = 7.2 Hz, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.79 (d, *J* = 7.6 Hz, 1H), 3.18 (s, 3H), 1.98 (td, *J* = 13.6, 4.8 Hz, 1H), 1.83 (td, *J* = 13.2, 4.8 Hz, 1H), 1.34 (s, 3H), 1.17 (s, 6H), 1.16 (s, 6H), 0.44 (ddd, *J* = 16.0, 13.2, 4.8 Hz, 1H), 0.30 (ddd, *J* = 16.0, 12.8, 4.4 Hz, 1H);

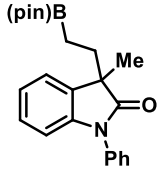
^{13}C NMR (100 MHz, $CDCl_3$): δ 180.8, 143.7, 133.9, 127.7, 122.8, 122.5, 107.8, 83.1, 49.5, 33.0, 26.1, 24.9, 24.9, 23.0.

^{11}B NMR (128 MHz, $CDCl_3$): δ 33.80.

R_f = 0.43 (PE/Acetone = 5/1).

HRMS (EI): Calcd for $C_{18}H_{26}BNO_3$: 315.2006; found: 315.2001.

3-methyl-1-phenyl-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)indolin-2-one (3c)



General Procedure was followed on 0.2 mmol scale, purification by flash column chromatography on silica gel (Hexane/EA = 50/1–20/1) afforded **3c** as an yellow solid (66.5 mg, 88%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.52-7.48 (m, 2H), 7.42-7.36 (m, 3H), 7.24 (d, *J* = 7.2 Hz, 1H), 7.17 (td, *J* = 7.6, 1.2 Hz, 1H), 7.08 (t, *J* = 7.2 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 2.12 (td, *J* =13.2, 4.4 Hz, 1H), 1.93 (td, *J* = 13.6, 4.4 Hz, 1H), 1.48 (s, 3H), 1.19 (s, 6H), 1.19 (s, 6H), 0.63 (ddd, *J* = 15.6, 13.2, 4.8 Hz, 1H), 0.44 (ddd, *J* = 15.6, 12.8, 4.4 Hz, 1H);

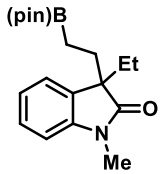
^{13}C NMR (100 MHz, $CDCl_3$): δ 180.3, 143.6, 134.8, 133.7, 129.6, 128.0, 127.6, 126.8, 123.1, 123.0, 109.2, 83.2, 49.6, 33.6, 25.0, 24.9, 23.5.

^{11}B NMR (128 MHz, $CDCl_3$): δ 33.97.

R_f = 0.56 (PE/Acetone = 5/1).

HRMS (EI): Calcd for $C_{23}H_{28}BNO_3$: 377.2162; found: 377.2156.

3-ethyl-1-methyl-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)indolin-2-one (3d)



General Procedure was followed on 0.2 mmol scale, purification by flash column chromatography on silica gel (Hexane/EA = 50/1–20/1–5/1) afforded **3d** as an orange oil (45.2 mg, 69%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.24 (td, *J* = 7.6, 0.8 Hz, 1H), 7.12 (d, *J* = 6.8 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.79 (d, *J* = 7.6 Hz, 1H), 3.18 (s, 3H), 2.04–1.73 (m, 4H), 1.17 (s, 6H), 1.16 (s, 6H), 0.54 (t, *J* = 7.2 Hz, 3H), 0.42 (ddd, *J* = 16.0, 13.2, 4.8 Hz, 1H), 0.27 (ddd, *J* = 16.0, 12.8, 4.4 Hz, 1H);

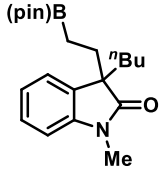
^{13}C NMR (100 MHz, $CDCl_3$): δ 180.2, 144.5, 132.0, 127.6, 123.0, 122.4, 107.7, 83.1, 55.1, 32.2, 30.3, 26.0, 24.9, 24.9, 9.0.

^{11}B NMR (128 MHz, $CDCl_3$): δ 33.67.

R_f = 0.53 (PE/Acetone = 5/1).

HRMS (EI): Calcd for $C_{19}H_{28}BNO_3$: 329.2162; found: 329.2156.

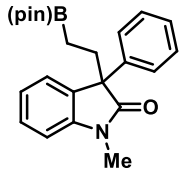
3-butyl-1-methyl-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)indolin-2-one (3e)



General Procedure was followed on 0.2 mmol scale, purification by flash column chromatography on silica gel (Hexane/EA = 50/1–20/1–10/1) afforded **3e** as a white solid (57.8 mg, 81%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.22 (t, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 7.2 Hz, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 3.17 (s, 3H), 1.96 (td, *J* = 13.2, 4.8 Hz, 1H), 1.90–1.79 (m, 2H), 1.72 (td, *J* = 12.8, 4.4 Hz, 1H), 1.20–1.09 (m, 14H), 1.00–0.84 (m, 2H), 0.73 (dd, *J* = 7.6 Hz, 3H), 0.41 (ddd, *J* = 16.4, 13.2, 4.8 Hz, 1H), 0.25 (ddd, *J* = 16.4, 13.2, 4.8 Hz, 1H);

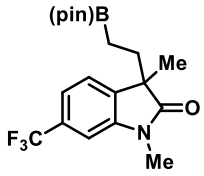
^{13}C NMR (100 MHz, $CDCl_3$): δ 180.3, 144.4, 132.4, 127.6, 122.9, 122.4, 107.7, 83.1, 54.4, 37.2, 32.5, 26.6, 26.0, 24.9, 24.8, 23.0, 13.9.
^{11}B NMR (128 MHz, $CDCl_3$): δ 33.54.
R_f = 0.45 (PE/EtOAc = 5/1).
HRMS (ESI$^+$): $[M+Na]^+$ Calcd for $C_{21}H_{32}BNNaO_3^+$: 380.2368; found: 380.2366.

1-methyl-3-phenyl-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)indolin-2-one (3f)



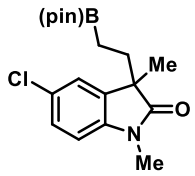
General Procedure was followed on 0.2 mmol scale with a reaction time of 12 h at 110 °C, purification by flash column chromatography on silica gel (PE/Acetone = 50/1–20/1–5/1) afforded **3f** as an orange oil (52.6 mg, 70%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.35–7.33 (m, 2H), 7.26–7.13 (m, 5H), 7.03 (td, *J* = 7.6, 0.8 Hz, 1H), 6.82 (d, *J* = 7.6 Hz, 1H), 3.14 (s, 3H), 2.44 (td, *J* = 13.2, 4.4 Hz, 1H), 2.24 (td, *J* = 13.6, 4.4 Hz, 1H), 1.13 (s, 6H), 1.12 (s, 6H), 0.51 (ddd, *J* = 16.0, 13.2, 4.4 Hz, 1H), 0.30 (ddd, *J* = 16.4, 12.8, 4.0 Hz, 1H);
^{13}C NMR (100 MHz, $CDCl_3$): δ 178.7, 144.3, 140.2, 132.1, 128.5, 128.1, 127.2, 127.2, 125.0, 122.7, 108.2, 83.2, 58.0, 32.4, 26.4, 24.9, 24.9.
^{11}B NMR (128 MHz, $CDCl_3$): δ 33.27.
R_f = 0.42 (PE/Acetone = 5/1).
HRMS (EI): Calcd for $C_{23}H_{28}BNO_3$: 377.2162; found: 377.2152.

1,3-dimethyl-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-6-(trifluoromethyl)indolin-2-one (3g)



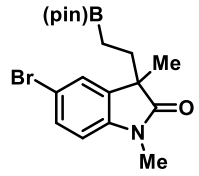
General Procedure was followed on 0.2 mmol scale, purification by flash column chromatography on silica gel (Hexane/EA = 50/1-20/1–10/1) afforded **3g** as a yellow solid (45.7 mg, 60%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.32 (d, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 8.4 Hz, 1H), 7.01 (s, 1H), 3.22 (s, 3H), 2.02 (td, *J* = 13.6, 4.8 Hz, 1H), 1.85 (td, *J* = 13.2, 4.8 Hz, 1H), 1.36 (s, 3H), 1.18 (s, 6H), 1.16 (s, 6H), 0.44 (ddd, *J* = 16.0, 12.8, 4.8 Hz, 1H), 0.27 (ddd, *J* = 16.0, 12.8, 4.4 Hz, 1H);
^{13}C NMR (100 MHz, $CDCl_3$): δ 180.4, 144.3, 138.0 (q, J_{C-F} = 3.0 Hz), 130.3 (q, J_{C-F} = 32.1 Hz), 124.2 (q, J_{C-F} = 270.5 Hz). 123.0, 119.6 (q, J_{C-F} = 3.3 Hz), 104.5 (q, J_{C-F} = 3.9 Hz), 83.3, 49.7, 33.0, 26.3, 25.0, 24.9, 22.8.
^{19}F NMR (376 MHz, $CDCl_3$): δ -62.3
^{11}B NMR (128 MHz, $CDCl_3$): δ 34.15.
R_f = 0.40 (PE/Acetone = 5/1).
HRMS (EI): Calcd for $C_{19}H_{25}BF_3NO_3$: 383.1880; found: 383.1867.

5-chloro-1,3-dimethyl-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)indolin-2-one (3h)



General Procedure was followed on 0.2 mmol scale, purification by flash column chromatography on silica gel (PE/Acetone = 50/1–20/1–5/1) afforded **3h** as an orange solid (38.3 mg, 55%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.20 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.13 (d, *J* = 2.0 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 3.16 (s, 3H), 1.99 (td, *J* = 13.6, 4.8 Hz, 1H), 1.81 (td, *J* = 13.2, 4.8 Hz, 1H), 1.33 (s, 3H), 1.18 (s, 6H), 1.17 (s, 6H), 0.44 (ddd, *J* = 15.6, 12.8, 4.8 Hz, 1H), 0.29 (ddd, *J* = 16.0, 12.8, 4.8 Hz, 1H);
^{13}C NMR (100 MHz, $CDCl_3$): δ 180.3, 142.3, 135.7, 127.9, 127.6, 123.4, 108.8, 83.3, 49.9, 32.9, 26.2, 25.0, 24.9, 22.9.
^{11}B NMR (128 MHz, $CDCl_3$): δ 33.72.
R_f = 0.45 (PE/Acetone = 5/1).
HRMS (EI): Calcd for $C_{18}H_{25}BClNO_3$: 349.1616; found: 349.1608.

5-bromo-1,3-dimethyl-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)indolin-2-one (3i)



General Procedure was followed on 0.2 mmol scale, purification by flash column chromatography on silica gel (PE/Acetone = 50/1–20/1) afforded **3i** as a yellow solid (40.6 mg, 52%).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.35 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.26 (d, *J* = 2.0 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 3.16 (s, 3H), 1.98 (td, *J* = 13.6, 4.8 Hz, 1H), 1.80 (td, *J* = 13.6, 4.8 Hz, 1H), 1.33 (s, 3H), 1.19 (s, 6H), 1.17 (s, 6H), 0.44 (ddd, *J* = 16.0, 12.8, 4.8 Hz, 1H), 0.30 (ddd, *J* = 16.0, 12.8, 4.8 Hz, 1H);

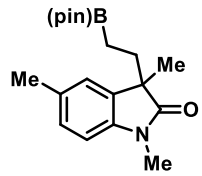
^{13}C NMR (100 MHz, $CDCl_3$): δ 180.2, 142.7, 136.1, 130.6, 126.1, 115.3, 109.3, 83.3, 49.9, 32.9, 26.2, 25.0, 24.9, 22.9.

^{11}B NMR (128 MHz, $CDCl_3$): δ 33.15.

R_f = 0.38 (PE/Acetone = 5/1).

HRMS (EI): Calcd for $C_{18}H_{25}BBrNO_3$: 393.1111; found: 393.1101

1,3,5-trimethyl-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)indolin-2-one (3j)



General Procedure was followed on 0.2 mmol scale, purification by flash column chromatography on silica gel (PE/Acetone = 50/1–20/1) afforded **3j** as an orange solid (41.9 mg, 64%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.02 (d, *J* = 7.6 Hz, 1H), 6.97 (s, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 3.16 (s, 3H), 2.33 (s, 3H), 1.96 (td, *J* = 13.6, 4.8 Hz, 1H), 1.80 (td, *J* = 13.2, 4.8 Hz, 1H), 1.33 (s, 3H), 1.18 (s, 6H), 1.17 (s, 6H), 0.45 (ddd, *J* = 16.0, 12.8, 4.4 Hz, 1H), 0.32 (ddd, *J* = 16.0, 12.8, 4.4 Hz, 1H);

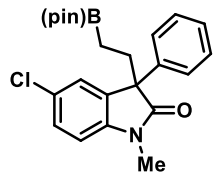
^{13}C NMR (100 MHz, $CDCl_3$): δ 180.8, 141.3, 134.0, 131.9, 127.9, 123.7, 107.6, 83.2, 49.6, 33.1, 26.2, 25.0, 24.9, 23.0, 21.3.

^{11}B NMR (128 MHz, $CDCl_3$): δ 33.98.

R_f = 0.40 (PE/Acetone = 5/1).

HRMS (EI): Calcd for $C_{19}H_{28}BNO_3$: 329.2162; found: 329.2152.

5-chloro-1-methyl-3-phenyl-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)indolin-2-one (3k)



General Procedure was followed on 0.2 mmol scale with a reaction time of 12 h at 110 °C, purification by flash column chromatography on silica gel (Hexane/EA = 50/1–20/1-10/1) afforded **3k** as a white solid (60.5 mg, 73%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.39–7.24 (m, 6H), 7.22 (d, *J* = 2.0 Hz , 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 3.22 (s, 3H), 2.52 (td, *J* = 13.2, 4.4 Hz, 1H), 2.30 (td, *J* = 13.2, 4.4 Hz, 1H), 1.23 (s, 6H), 1.22 (s, 6H), 0.58 (ddd, *J* = 16.0, 13.2, 4.4 Hz, 1H), 0.38 (ddd, *J* = 16.8, 12.8, 4.4 Hz, 1H);

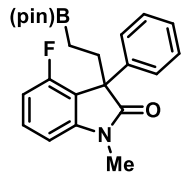
^{13}C NMR (100 MHz, $CDCl_3$): δ 178.2, 142.8, 139.5, 134.0, 128.7, 128.2, 128.0, 127.5, 127.0, 125.3, 109.1, 83.3, 58.2, 32.2, 26.5, 25.0, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$): δ 33.24.

R_f = 0.32 (PE/EtOAc = 5/1).

HRMS (ESI$^+$): $[M+Na]^+$ Calcd for $C_{23}H_{27}BClNO_3Na^+$: 434.1665; found: 434.1669.

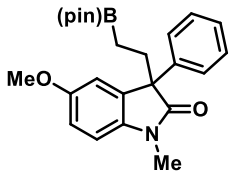
4-fluoro-1-methyl-3-phenyl-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)indolin-2-one (3l)



General Procedure was followed on 0.2 mmol scale with a reaction time of 12 h at 110 °C, purification by flash column chromatography on silica gel (PE/Acetone = 50/1–20/1–5/1) afforded **3l** as an orange solid (51.5 mg, 65%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.32 (d, *J* = 7.6 Hz, 2H), 7.24–7.13 (m, 4H), 6.71 (t, *J* = 8.8 Hz, 1H), 6.60 (d, *J* = 8.0 Hz, 1H), 3.11 (s, 3H), 2.51 (td, *J* = 13.2, 4.8 Hz, 1H), 2.36 (td, *J* = 13.6, 4.8 Hz, 1H), 1.11 (s, 12H), 0.42 (ddd, *J* = 16.0, 13.2, 4.4 Hz, 1H), 0.30 (ddd, *J* = 16.8, 13.2, 4.4 Hz, 1H);

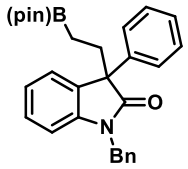
^{13}C NMR (100 MHz, $CDCl_3$): δ 178.1, 159.0 (d, $J_{C–F}$ = 247.0 Hz), 146.2 (d, $J_{C–F}$ = 9.5 Hz), 138.9, 130.2 (d, $J_{C–F}$ = 8.6 Hz), 128.5, 127.5, 126.9, 117.3 (d, $J_{C–F}$ = 19.5 Hz), 110.5 (d, $J_{C–F}$ = 21.1 Hz), 104.3 (d, $J_{C–F}$ = 2.9 Hz), 83.2, 58.4 (d, $J_{C–F}$ = 2.4 Hz), 30.9, 26.8, 24.9, 24.9;
^{19}F NMR (376 MHz, $CDCl_3$): δ -115.8 (dd, *J* = 8.6, 5.6 Hz).
^{11}B NMR (128 MHz, $CDCl_3$): δ 33.76.
R_f = 0.31 (PE/EtOAc = 5/1).
HRMS (ESI$^+$): $[M+Na]^+$ Calcd for $C_{23}H_{27}BFNO_3Na^+$: 418.1960; found: 418.1960.

5-methoxy-1-methyl-3-phenyl-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)indolin-2-one (3m)



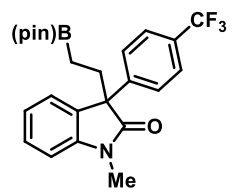
General Procedure was followed on 0.2 mmol scale with a reaction time of 12 h at 110 °C, purification by flash column chromatography on silica gel (Hexane/EA = 50/1–20/1–5/1) afforded **3m** as an orange oil (64.2 mg, 79%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 7.6 Hz, 2H), 7.29–7.25(m, 2H), 7.23–7.19 (m, 1H), 6.82 (dd, *J* = 6.4, 2.4 Hz, 2H), 6.77 (dd, *J* = 6.4, 3.2 Hz, 1H), 3.79 (s, 3H), 3.18 (s, 3H), 2.50 (td, *J* = 13.2, 4.4 Hz, 1H), 2.26 (td, *J* = 13.2, 4.4 Hz, 1H), 1.19 (s, 6H), 1.19 (s, 6H), 0.55 (ddd, *J* = 16.0, 13.2, 4.4 Hz, 1H), 0.36 (ddd, *J* = 16.0, 12.8, 4.0 Hz, 1H);
^{13}C NMR (100 MHz, $CDCl_3$): δ 178.3, 156.0, 140.2, 137.9, 133.6, 128.5, 127.2, 127.2, 112.6, 112.1, 108.4, 83.2, 58.4, 55.8, 32.3, 26.4, 24.9, 24.9.
^{11}B NMR (128 MHz, $CDCl_3$): δ 33.98.
R_f = 0.36 (PE/Acetone = 5/1).
HRMS (EI): Calcd for $C_{24}H_{30}BNO_4$: 407.2268; found: 407.2259.

1-benzyl-3-phenyl-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)indolin-2-one (3n)



General Procedure was followed on 0.2 mmol scale with a reaction time of 12 h at 110 °C, purification by flash column chromatography on silica gel (PE/Acetone = 50/1–20/1–10/1) afforded **3n** as a white solid (80.7 mg, 89%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.44 (d, *J* = 8.0 Hz, 2H), 7.34–7.24 (m, 9H), 7.19 (td, *J* = 7.6, 1.2 Hz, 1H), 7.08 (t, *J* = 7.2 Hz, 1H), 6.77 (d, *J* = 7.6 Hz, 1H), 5.02 (d, *J* = 15.6 Hz, 1H), 4.86 (d, *J* = 16.0 Hz, 1H), 2.60 (td, *J* = 13.2, 4.4 Hz, 1H), 2.39 (td, *J* = 13.6, 4.0 Hz, 1H), 1.24 (s, 6H), 1.23 (s, 6H), 0.69 (ddd, *J* = 15.2, 13.6, 4.4 Hz, 1H), 0.45 (ddd, *J* = 15.6, 13.2, 4.0 Hz, 1H);
^{13}C NMR (100 MHz, $CDCl_3$): δ 178.8, 143.3, 140.3, 136.1, 132.2, 128.8, 128.6, 128.0, 127.6, 127.3, 127.2, 127.2, 125.0, 122.7, 109.3, 83.2, 57.9, 43.9, 32.3, 24.9, 24.9.
^{11}B NMR (128 MHz, $CDCl_3$): δ 33.25.
R_f = 0.45 (PE/EtOAc = 5/1).
HRMS (ESI$^+$): $[M+H]^+$ Calcd for $C_{29}H_{33}BNO_3^+$: 454.2548; found: 454.2537

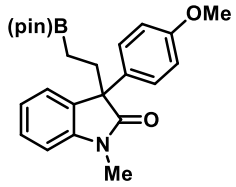
1-methyl-3-(4-(trifluoromethyl)phenyl)-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)indolin-2-one (3o)



General Procedure was followed on 0.2 mmol scale with a reaction time of 12 h at 110 °C, purification by flash column chromatography on silica gel (PE/Acetone = 50/1–20/1) afforded **3o** as an orange solid (40.1 mg, 45%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.53 (s, 4H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 7.2 Hz, 1H), 7.13 (td, *J* = 7.6 Hz, 1H), 6.90 (d. *J* = 8.0 Hz, 1H), 3.21 (s, 3H), 2.48 (td, *J* = 13.2, 4.8 Hz, 1H), 2.29 (td, *J* = 13.2, 4.0 Hz, 1H), 1.19 (s, 6H), 1.18 (s, 6H), 0.57 (ddd, *J* = 16.0, 13.6, 4.4 Hz, 1H), 0.35 (ddd, *J* = 16.4, 12.8, 4.0 Hz, 1H);
^{13}C NMR (100 MHz, $CDCl_3$): δ 178.0, 144.2, 131.3, 129.5 (q, $J_{C–F}$ = 32.3 Hz), 128.6, 127.8, 125.4 (q, $J_{C–F}$ = 3.7 Hz), 125.0, 124.2 (q, $J_{C–F}$ = 270.4 Hz), 122.9, 108.5, 83.3, 57.9, 32.7, 26.5, 25.0, 24.9;
^{19}F NMR (376 MHz, $CDCl_3$): δ -62.6.
^{11}B NMR (128 MHz, $CDCl_3$): δ 33.44.

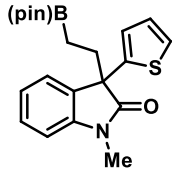
R_f = 0.48 (PE/Acetone = 5/1).
HRMS (EI): Calcd for $C_{24}H_{27}BF_3NO_3$: 445.2036; found: 445.2022.

3-(4-methoxyphenyl)-1-methyl-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)indolin-2-one (3p)



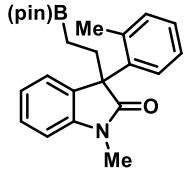
General Procedure was followed on 0.2 mmol scale with a reaction time of 12 h at 110 °C, purification by flash column chromatography on silica gel (Hexane/EA = 50/1–20/1–5/1) afforded **3p** as a yellow oil (71.9 mg, 88%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.32–7.28 (m, 3H), 7.21 (d, *J* = 6.8 Hz, 1H), 7.09 (t, *J* = 7.2 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.80 (d, *J* = 8.8 Hz, 2H), 3.75 (s, 3H), 3.19 (s, 3H), 2.45 (td, *J* = 13.2, 4.4 Hz, 1H), 2.24 (td, *J* = 13.2, 4.0 Hz, 1H), 1.19 (s, 6H), 1.18 (s, 6H), 0.55 (ddd, *J* = 15.6, 13.2, 4.4 Hz, 1H), 0.34 (ddd, *J* = 15.6, 13.2, 4.4 Hz, 1H);
^{13}C NMR (100 MHz, $CDCl_3$): δ 179.0, 158.7, 144.3, 132.3, 132.3, 128.4, 128.1, 125.0, 122.6, 113.9, 108.2, 83.2, 57.3, 55.4, 32.6, 26.4, 25.0, 24.9.
^{11}B NMR (128 MHz, $CDCl_3$): δ 33.79.
R_f = 0.32 (PE/Acetone = 5/1).
HRMS (EI): Calcd for $C_{24}H_{30}BNO_3$: 407.2268; found: 407.2259

1-methyl-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-3-(thiophen-2-yl)indolin-2-one (3q)



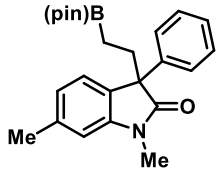
General Procedure was followed on 0.2 mmol scale with a reaction time of 12 h at 110 °C, purification by flash column chromatography on silica gel (Hexane/EA = 20/1–5/1) afforded **3q** as a yellow solid (54.5 mg, 71%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 7.2 Hz, 1H), 7.32 (t, *J* = 6.8 Hz, 1H), 7.16 (dd, *J* = 5.2, 0.8 Hz, 1H), 7.12 (t, *J* = 7.6, 0.8 Hz, 1H), 6.98 (dd, *J* = 3.6, 1.2 Hz, 1H), 6.90 (dd, *J* = 5.2, 3.6 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 3.20 (s, 3H), 2.43 (td, *J* = 13.6, 4.8 Hz, 1H), 2.28 (td, *J* = 13.2, 4.0 Hz, 1H), 1.18 (s, 6H), 1.17 (s, 6H), 0.58 (ddd, *J* = 16.0, 13.6, 4.8 Hz, 1H), 0.39 (ddd, *J* = 16.8, 12.8, 4.0 Hz, 1H);
^{13}C NMR (100 MHz, $CDCl_3$): δ 177.4, 144.0, 144.0, 131.5, 128.6, 126.6, 124.9, 124.8, 124.7, 122.7, 108.3, 83.2, 55.6, 34.9, 26.5, 24.9, 24.9.
^{11}B NMR (128 MHz, $CDCl_3$): δ 33.16.
R_f = 0.39 (PE/Acetone = 5/1).
HRMS (EI): Calcd for $C_{21}H_{26}BNO_3S$: 383.1726; found: 383.1717.

1-methyl-3-(o-tolyl)-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)indolin-2-one (3r)



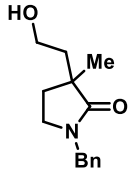
General Procedure was followed on 0.2 mmol scale with a reaction time of 12 h at 110 °C, purification by flash column chromatography on silica gel (PE/Acetone = 50/1–20/1–5/1) afforded **3r** as an orange solid (54.8 mg, 70%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 7.6 Hz, 1H), 7.21–7.16 (m, 2H), 7.08 (t, *J* = 7.2 Hz, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 6.88 (d, *J* = 7.6 Hz, 1H), 6.77 (d, *J* = 7.6 Hz, 1H), 6.73 (d, *J* = 7.6 Hz, 1H), 3.20 (s, 3H), 2.41 (td, *J* = 12.8, 4.0 Hz, 1H), 2.29 (td, *J* = 12.8, 4.0 Hz, 1H), 1.55 (s, 3H), 1.13 (s, 6H), 1.12 (s, 6H), 0.49 (ddd, *J* = 16.0, 13.2, 4.4 Hz, 1H), 0.34 (ddd, *J* = 15.6, 13.2, 4.4 Hz, 1H);
^{13}C NMR (100 MHz, $CDCl_3$): δ 179.0, 144.4, 138.5, 137.1, 132.9, 131.9, 127.9, 127.7, 127.4, 126.0, 123.4, 123.0, 107.6, 83.2, 56.9, 32.4, 26.2, 25.0, 24.9, 19.5.
^{11}B NMR (128 MHz, $CDCl_3$): δ 33.87.
R_f = 0.40 (PE/Acetone = 5/1).
HRMS (EI): Calcd for $C_{24}H_{30}BNO_3$: 391.2319; found: 391.2312.

1,6-dimethyl-3-phenyl-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)indolin-2-one (3s)



General Procedure was followed on 0.2 mmol scale with a reaction time of 12 h at 110 °C, purification by flash column chromatography on silica gel (PE/Acetone = 50/1–20/1–5/1) afforded **3s** as an white solid (60.0 mg, 77%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 7.2 Hz, 2H), 7.31 (t, *J* = 7.2, 2H), 7.28–7.24 (m, 1H), 7.17 (d, *J* = 7.6, 1H), 6.97 (d, *J* = 7.2 Hz, 1H), 6.77 (s, 1H), 6.77 (d, *J* = 7.6 Hz, 1H), 3.24 (s, 3H), 2.53 (td, *J* = 13.6, 4.8 Hz, 1H), 2.47 (s, 3H), 2.33 (td, *J* = 13.2, 4.0 Hz, 1H), 1.25 (s, 6H), 1.24 (s, 6H), 0.62 (ddd, *J* = 16.0, 13.2, 4.4 Hz, 1H), 0.44 (ddd, *J* = 15.6, 13.2, 4.4 Hz, 1H);
^{13}C NMR (100 MHz, $CDCl_3$): δ 178.9, 144.3, 140.4, 138.2, 129.1, 128.4, 127.2, 127.1, 124.7, 123.1, 109.1, 83.1, 57.7, 32.5, 26.3, 24.9, 24.9, 21.9.
^{11}B NMR (128 MHz, $CDCl_3$): δ 33.33.
R_f = 0.43 (PE/EtOAc = 5/1).
HRMS (ESI$^+$): $[M+Na]^+$ Calcd for C24H30BNNaO3+: 414.2211; found: 414.2213.

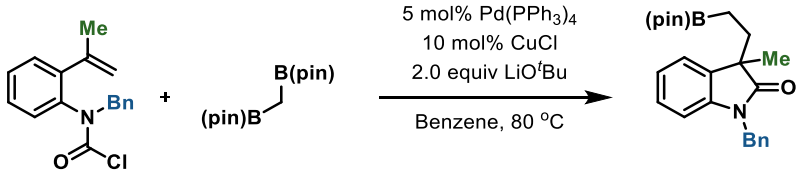
1-benzyl-3-(2-hydroxyethyl)-3-methylpyrrolidin-2-one (3t)



General Procedure was followed on 0.2 mmol scale with a reaction time of 12 h at 80 °C, subsequent oxidation by 5.0 equiv $NaBO_3$•$4H_2O$. Purification by flash column chromatography on silica gel (PE/Acetone = 5/1–2/1) afforded **3t** as an orange solid (20.2 mg, 43%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.35–7.21 (m, 5H), 4.47 (d, *J* = 14.8 Hz, 1H), 4.42 (d, *J* = 14.4 Hz, 1H), 3.90 (ddd, *J* = 12.0, 9.2, 3.2 Hz, 1H), 3.68 (ddd, *J* = 9.6, 9.6, 4.4 Hz, 1H), 3.27–3.19 (m, 2H), 2.88 (bs, 1H), 1.98–1.86 (m, 2H), 1.82–1.76 (m, 1H), 1.70–1.64 (m, 1H), 1.23 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$): δ 180.2, 136.3, 128.9, 128.2, 127.8, 59.0, 47.2, 44.1, 44.0, 40.6, 33.7, 21.8.
R_f = 0.60 (PE/Acetone = 2/1).
HRMS (ESI$^+$): $[M+Na]^+$ Calcd for $C_{14}H_{19}NNaO_2^+$: 256.1308; found: 256.1313.

Derivatization Experiment

a) Gram-scale reaction

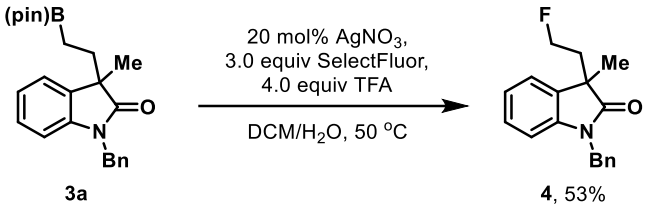


1a (4.0 mmol) **2** (6.0 mmol) **3a**, 1.2 g, 76%

To an oven-dried sealed tube was added CuCl (10 mol%, 0.4 mmol, 40 mg), carbamoyl chloride **1a** (4.0 mmol, 1.1 g) and LiO^tBu (2.0 equiv, 8.0 mmol, 640.0 mg). $Pd(PPh_3)_4$ (5 mol%, 0.2 mmol, 231.2 mg) was added inside a nitrogen-filled glove-box. Then benzene (0.2 M, 20 mL), 1,1-bis[(pinacolato)boryl]methane (1.5 equiv, 6.0 mmol, 1.8 mL) were added by syringe outside the glove-box. The tube was sealed strictly and heated in 80 °C oil bath. After completion (TLC monitor), The solution was cooled to room temperature and filtered through a pad of celite and the celite was thoroughly washed with EA. Then the resulted filtrate was concentrated under reduced pressure to yield the crude product, which was purified by silica gel flash column chromatography (PE/Acetone = 20/1–5/1) to afford **3a** as pale yellow oil (1.2 g, 76%).

b) Procesure for Derivatization Experiment

Procedure for Fluorination of Compound 3a



1-benzyl-3-(2-fluoroethyl)-3-methylindolin-2-one (**4**) was synthesized according to the following procedure.[4] To an oven-dried sealed tube was added compound **3a** (1.0 equiv, 0.2 mmol), $AgNO_3$ (20 mol%, 0.04 mmol), Selectfluor (3.0 equiv, 0.6 mmol). The reaction vessel was evacuated and filled with nitrogen for three times. Then DCM (1.0 mL), TFA (58 μL) and distilled water (1.0 mL) were added successively at r.t.. The reaction mixture was stirred at 50 °C for 8 hours. The resulting mixture was cooled down to room temperature and extracted with DCM. The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (PE/DCM = 1/1–1/3) afforded **4** as a yellow solid (29.9 mg, 53%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33–7.25 (m, 5H), 7.20 (d, *J* = 7.6 Hz, 1H), 7.16 (t, *J* = 8.0 Hz, 1H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.73 (d, *J* = 7.6 Hz, 1H), 4.97 (d, *J* = 15.6 Hz, 1H), 4.86 (d, *J* = 15.6 Hz, 1H), 4.39–4.30 (m, 1H), 4.28–4.18 (m, 1H), 2.55–2.43 (m, 1H), 2.23–2.09 (m, 1H), 1.47 (s, 3H);

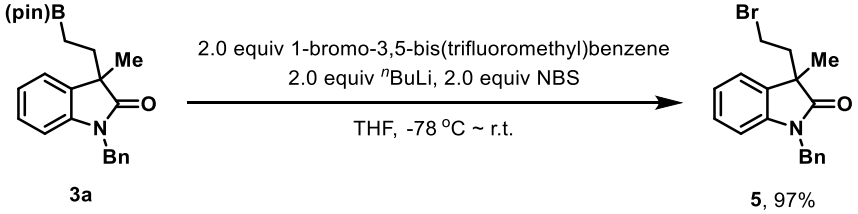
^{13}C NMR (100 MHz, $CDCl_3$): δ 180.3, 142.4, 136.1, 133.0, 128.9, 128.1, 127.7, 127.4, 123.0, 122.7, 109.5, 80.8 (d, $J_{C–F}$ = 165.2 Hz), 46.2 (d, $J_{C–F}$ = 4.4 Hz), 43.9, 38.2 (d, $J_{C–F}$ = 19.7 Hz), 24.7;

^{19}F NMR (376 MHz, $CDCl_3$): δ -218.17–-218.55 (m).

R_f = 0.59 (PE/DCM = 1/3).

HRMS (ESI$^+$): $[M+H]^+$ Calcd for $C_{18}H_{19}FNO^+$: 284.1445; found: 284.1443.

Procedure for Bromination of Compound 3a



1-benzyl-3-(2-bromoethyl)-3-methylindolin-2-one (**5**) was synthesized according to the following procedure.[5] An oven-dried vessel was charged with 1-bromo-3,5-bis(trifluoromethyl)benzene (2.0 equiv, 0.4 mmol) and THF (1.0 mL). The vessel was cooled to -78 °C. A solution of ^{n}BuLi (2.0 equiv, 2.4 M in hexanes) was added dropwise. The resulting mixture was allowed to stir at -78 °C for 1 h. A separate vessel was charged with **3a** (1.0 equiv, 0.2 mmol) and THF (1.0 mL) in the drybox. The solution of **3a** was then dropwise added to the solution of aryllithium. The reaction mixture was allowed to stir at -78 ℃ for 30 min and at r.t. for 30 min. The resulting solution was added a solution of NBS (2.0 equiv, 0.4 mmol) in THF (1.0 mL) dropwise. After stirring at r.t. for 1 h, 20% $Na_2S_2O_3$ solution was added. The mixture was extracted with ethyl acetate twice. The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1-10/1) afforded **5** as a yellow solid (66.7 mg, 97%).

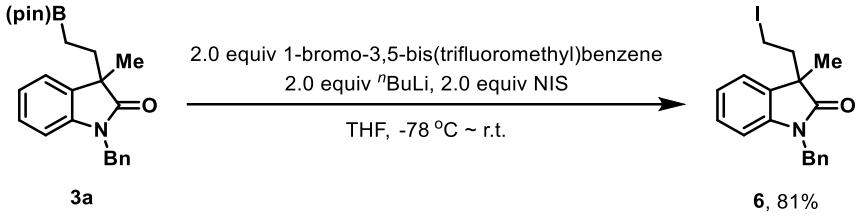
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26–7.18 (m, 5H), 7.13–7.08 (m, 2H), 7.98 (t, *J* = 7.6 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 4.83 (s, 2H), 3.03 (ddd, *J* = 11.6, 10.0, 5.6 Hz, 1H), 2.90 (ddd, *J* = 11.6, 10.0, 4.8 Hz, 1H), 2.50 (ddd, *J* = 16.8, 11.6, 5.6 Hz, 1H), 2.28 (ddd, *J* = 16.8, 12.0, 4.8 Hz, 1H), 1.37 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 179.6, 142.3, 135.9, 132.5, 129.0, 128.3, 127.8, 127.4, 123.0, 122.8, 109.5, 48.7, 43.9, 41.3, 27.3, 24.3.

R_f = 0.73 (PE/EtOAc = 5/1).

HRMS (EI): Calcd for $C_{18}H_{18}BrNO$: 343.0572; found: 343.0559

Procedure for Iodization of Compound 3a



1-benzyl-3-(2-iodoethyl)-3-methylindolin-2-one (**6**) was synthesized according to the following procedure.[5]. An oven-dried vessel was charged with 1-bromo-3,5-bis(trifluoromethyl)benzene (2.0 equiv, 0.4 mmol) and THF (1.0 mL). The vessel was cooled to -78 °C. A solution of ^{n}BuLi (2.0 equiv, 2.4 M in hexanes) was added dropwise. The resulting mixture was allowed to stir at -78 °C for 1 h. A separate vessel was charged with **3a** (1.0 equiv, 0.2 mmol) and THF (1.0 mL) in the drybox. The solution of **3a** was then dropwise added to the solution of aryllithium. The reaction mixture was allowed to stir at -78 ℃ for 30 min and at r.t. for 30 min. The resulting solution was added a solution of NIS (2.0 equiv, 0.4 mmol) in THF (1.0 mL) dropwise. After stirring at r.t. for 1 h, 20% $Na_2S_2O_3$ solution was added. The mixture was extracted with ethyl acetate twice. The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1–10/1) afforded **6** as a yellow solid (63.2 mg, 81%).

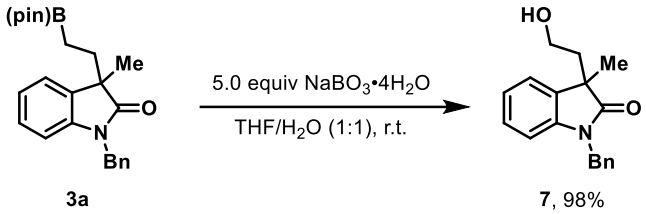
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.22 (m, 5H), 7.15 (t, *J* = 8.0 Hz , 2H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.73 (d, *J* = 7.6 Hz, 1H), 4.88 (s, 2H), 2.82 (ddd, *J* = 12.8, 9.2, 4.8 Hz, 1H), 2.68 (ddd, *J* = 12.4, 9.2, 4.0 Hz, 1H), 2.57 (td, *J* = 12.8, 4.8 Hz, 1H), 2.37 (td, *J* = 12.8, 4.0 Hz, 1H), 1.40 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 179.7, 142.3, 135.8, 132.3, 129.0, 128.4, 127.9, 127.3, 123.1, 122.8, 109.6, 50.4, 44.0, 42.8, 23.9, -2.2.

R_f = 0.78 (PE/EtOAc = 5/1).

HRMS (EI): Calcd for $C_{18}H_{18}INO$: 391.0433; found: 391.0416.

Procedure for Oxidation of Compound 3a

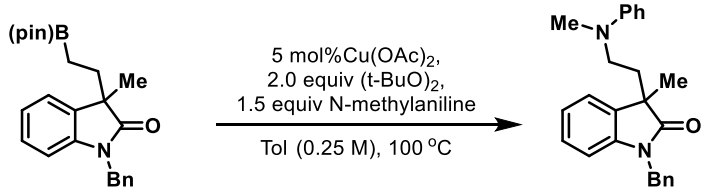


1-benzyl-3-(2-fluoroethyl)-3-methylindolin-2-one (**7**) was synthesized according to the following procedure. [6] A vial containing **3a** (1.0 equiv, 0.2 mmol) was charged with THF (1 mL) and H_2O (1 mL), then $NaBO_3$•$4H_2O$ (5.0 equiv, 1.0 mmol) was added in one portion. The reaction mixture was stirred at room temperature for 3 hours in open flask. The reaction was quenched with a saturated aqueous solution of NH_4Cl. The aqueous layer was extracted for three times with EtOAc and separated organic layer was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (PE/EtOAc = 10/1–2/1) afforded **7** as a white solid (55.0 mg, 98%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29–7.21 (m, 5H), 7.14 (d, 1H), 7.10 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.70 (d, *J* = 7.6 Hz, 1H), 4.91 (d, *J* = 15.6 Hz, 1H), 4.85 (d, *J* = 15.6 Hz, 1H) , 3.59 (dt, *J* = 11.2, 6.4 Hz, 1H), 3.43 (dt, *J* = 11.2, 6.4 Hz, 1H), 2.53 (br s, 1H), 2.21 (dt, *J* = 14.4, 6.4 Hz, 1H), 2.01 (dt, *J* = 14.0, 6.4 Hz, 1H), 1.42 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 181.6, 142.1, 135.9, 134.0, 128.9, 127.9, 127.7, 127.3, 122.8, 122.6, 109.4, 59.3, 47.0, 43.9, 40.2, 24.3.
R_f = 0.43 (PE/EtOAc = 2/1).
HRMS (EI): Calcd for $C_{18}H_{19}NO_2$: 281.1416; found: 281.1405

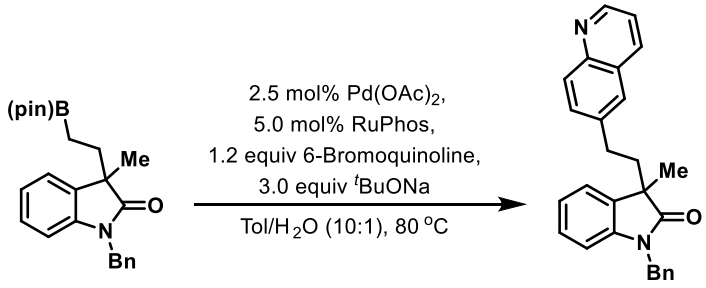
Procedure for Amination of Compound 3a



3a **8**, 40%

1-benzyl-3-methyl-3-(2-(methyl(phenyl)amino)ethyl)indolin-2-one (**8**) was synthesized according to the following procedure.[7] A solution of **3a** (1.0 equiv, 0.20 mmol), N-methylaniline (1.5 equiv, 0.3 mmol), di-tert-butyl peroxide (2.0 equiv, 0.4 mmol) and $Cu(OAc)_2$ (5 mol%) in toluene (0.5 mL) was stirred at 50 ℃ for 24 h in a sealed tube. The reaction mixture was diluted with ethyl acetate, then filtered through a pad of celite and the celite was thoroughly washed with EA. The resulted filtrate was concentrated under reduced pressure to yield the crude product, which was purified by silica gel flash column chromatography (PE/EtOAc = 100:1-20:1) afforded **8** as an orange oil. (29.8 mg, 40%).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30–7.22 (m, 6H), 7.19–7.14 (m, 3H), 7.08 (t, *J* = 7.2 Hz, 1H), 6.71–6.48 (m, 4H), 4.88 (d, *J* = 15.6 Hz, 1H), 4.79 (d, *J* = 16.0 Hz, 1H), 3.12–3.05 (m, 1H), 2.92–2.86 (m, 1H), 2.77 (s, 3H), 2.36–2.29 (m, 1H) , 2.01 (t, *J* = 10.0 Hz, 1H), 1.42 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$): δ 180.2, 142.5, 136.2, 133.4, 129.3, 128.9, 128.8, 128.4, 128.1, 127.7, 127.4, 122.8, 122.6, 109.4, 109.3, 46.9, 43.8, 43.7, 34.3, 24.9, 24.7.
R_f = 0.59 (PE/EtOAc = 5/1).
HRMS (EI): Calcd for $C_{25}H_{26}N_2O$: 370.2045; found: 370.2034

Procedure for Suzuki coupling of Compound 3a

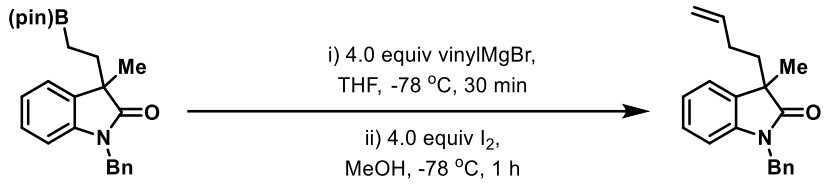


3a **9**, 90%

1-benzyl-3-methyl-3-(2-(quinolin-5-yl)ethyl)indolin-2-one (**9**) was synthesized according to the following procedure.[8] In an oven-dried vessel, **3a** (1.0 equiv, 0.20 mmol), $Pd(OAc)_2$ (2.5 mol%, 0.005 mmol), RuPhos (5 mol%, 0.01 mmol) and ^{t}BuONa (3.0 equiv, 0.60 mmol) were weighted as solid and suspended in 1.0 mL of toluene. To this mixture, 6-bromoquinoline (1.2 equiv, 0.24 mmol) and degassed water (0.1 mL) were added in the order by syringe. The reaction mixture was heated at 80 ℃ for 24 h, then diluted with ethyl acetate (5 mL) and filtered over celite and the celite was thoroughly washed with EA. The resulted filtrate was concentrated under reduced pressure to yield the crude product, which was purified by silica gel flash column chromatography (PE/EtOAc = 20:1–2:1) afforded **9** as an orange solid. (70.6 mg, 90% yield).
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.85 (dd, *J* = 4.0, 1.2 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 9.2 Hz, 1H), 7.45–7.28 (m, 9H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.08 (td, *J* = 7.6 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H),

4.96 (d, *J* = 15.6 Hz, 1H), 4.90 (d, *J* = 15.6 Hz, 1H), 2.58 (td, *J* = 10.8, 3.2 Hz, 1H), 2.48–2.34 (m, 2H), 2.15 (td, *J* = 13.2, 4.0 Hz, 1H), 1.50 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$): δ 180.5, 149.8, 147.2, 142.6, 139.9, 136.2, 135.7, 133.6, 130.9, 129.3, 128.9, 128.3, 128.0, 127.7, 127.4, 126.2, 122.8, 122.7, 121.2, 109.3, 48.5, 43.8, 40.1, 31.2, 24.5.
R_f = 0.56 (PE/EtOAc = 2/1).
HRMS (EI): Calcd for $C_{27}H_{24}N_2O$: 392.1889; found: 392.1880

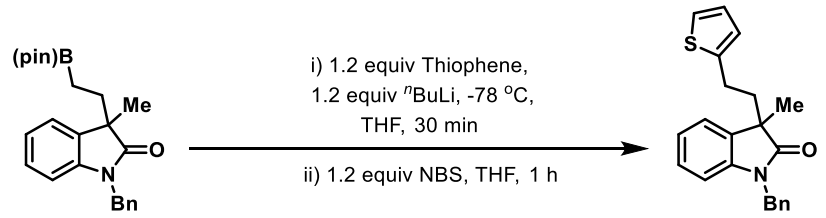
Procedure for Alkenylation of Compound 3a



3a **10**, 97%

1-benzyl-3-(but-3-en-1-yl)-3-methylindolin-2-one (**10**) was synthesized according to the following procedure.[8] Vinylmagnesium bromide solution (4.0 equiv, 0.74 M in THF, 0.8 mmol) was added to a solution of compound **3a** (1.0 equiv, 0.2 mmol) in THF (2.0 mL) and the reaction mixture was stirred for 30 min at -78 ℃. A solution of iodine (4.0 equiv, 1.6 mmol) in MeOH (2.0 mL) was added in a dropwise manner. The mixture was stirred for another 30 min, and allowed to warm to 0 ℃. Upon completion of the reaction, the reaction mixture was quenched with sat. aq. $Na_2S_2O_3$ (4 mL), and extracted with ethyl acetate. The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (PE/EtOAc = 40/1–20/1) afforded **10** as a colorless oil (56.3 mg, 97%).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30–7.19 (m, 5H), 7.16–7.09 (m, 2H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.69 (d, *J* = 7.6 Hz, 1H), 5.69–5.59 (m, 1H), 4.88–4.81 (m, 4H), 2.10–2.03 (m, 1H), 1.88–1.73 (m, 2H), 1.70–1.59 (m, 1H), 1.40 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$): δ 180.7, 142.5, 137.8, 136.2, 133.8, 128.8, 127.7, 127.6, 127.4, 122.7, 122.6, 114.8, 109.1, 48.2, 43.7, 37.6, 29.1, 24.4.
R_f = 0.82 (PE/EtOAc = 5/1).
HRMS (EI): Calcd for $C_{20}H_{21}NO$: 291.1623; found: 291.1614

Procedure for Heterocyclization of Compound 3a



3a **11**, 68%

1-benzyl-3-methyl-3-(2-(thiophen-2-yl)ethyl)indolin-2-one (**11**) was synthesized according to the following procedure. [9] A solution of thiophene (1.2 equiv, 0.24 mmol) in THF (1.0 mL) was cooled to -78 ℃ and treated with ^{n}BuLi (1.2 equiv, 2.4 M in hexanes, 0.24 mmol). The cooling bath was removed and the mixture was stirred at room temperature for 1 hour. The mixture was cooled to -78 ℃ and a solution of compound **3a** (1.0 equiv, 0.2 mmol) in THF (1.0 mL) was added. The mixture was stirred at -78 ℃ for 1 hour and then, a solution of NBS (1.2 equiv, 0.24 mmol) in THF (1.0 mL) was added. After 1 hour at -78 ℃, sat. aq. $Na_2S_2O_3$ (2.0 mL) was added and the reaction mixture was allowed to warm to room temperature. The mixture was extracted with ethyl acetate twice. The combined organic layer was

dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1–20/1) afforded **11** as an orange oil (47.2 mg, 68%).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33–7.27 (m, 5H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.19 (td, *J* = 8.0, 1.2 Hz, 1H), 7.09–7.06 (m, 2H), 6.87 (dd, *J* = 4.8, 3.2 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.68 (d, *J* = 2.8 Hz, 1H), 4.98 (d, *J* = 15.6 Hz, 1H), 4.92 (d, *J* = 15.6 Hz, 1H), 2.68–2.56 (m, 1H), 2.47–2.37 (m, 2H), 2.24–2.11 (m, 1H), 1.48 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$): δ 180.3, 144.3, 142.5, 136.2, 133.5, 128.9, 128.0, 127.7, 127.4, 126.7, 124.2, 123.2, 122.8, 122.7, 109.3, 48.3, 43.8, 40.4, 25.3, 24.3.
R_f = 0.62 (PE/EtOAc = 5/1).
HRMS (EI): Calcd for $C_{22}H_{21}NOS$: 347.1343; found: 347.1331

References

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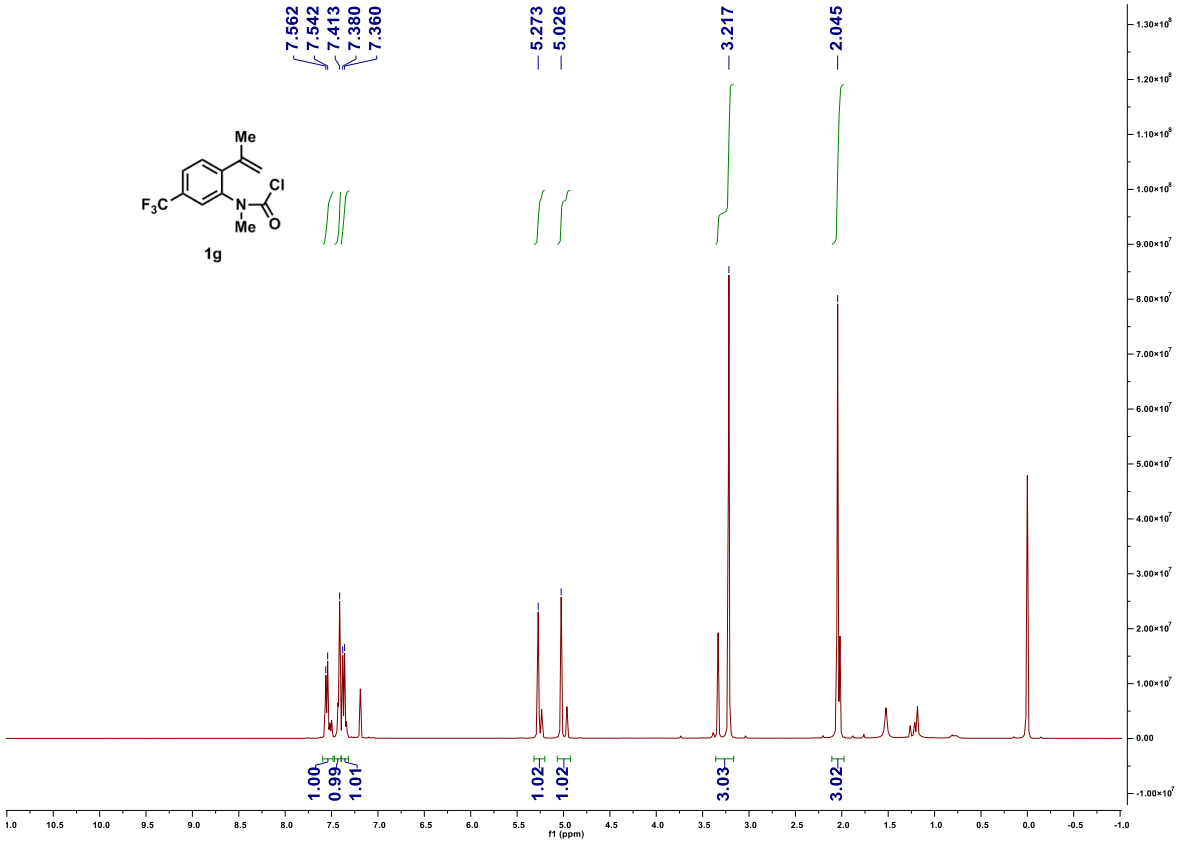
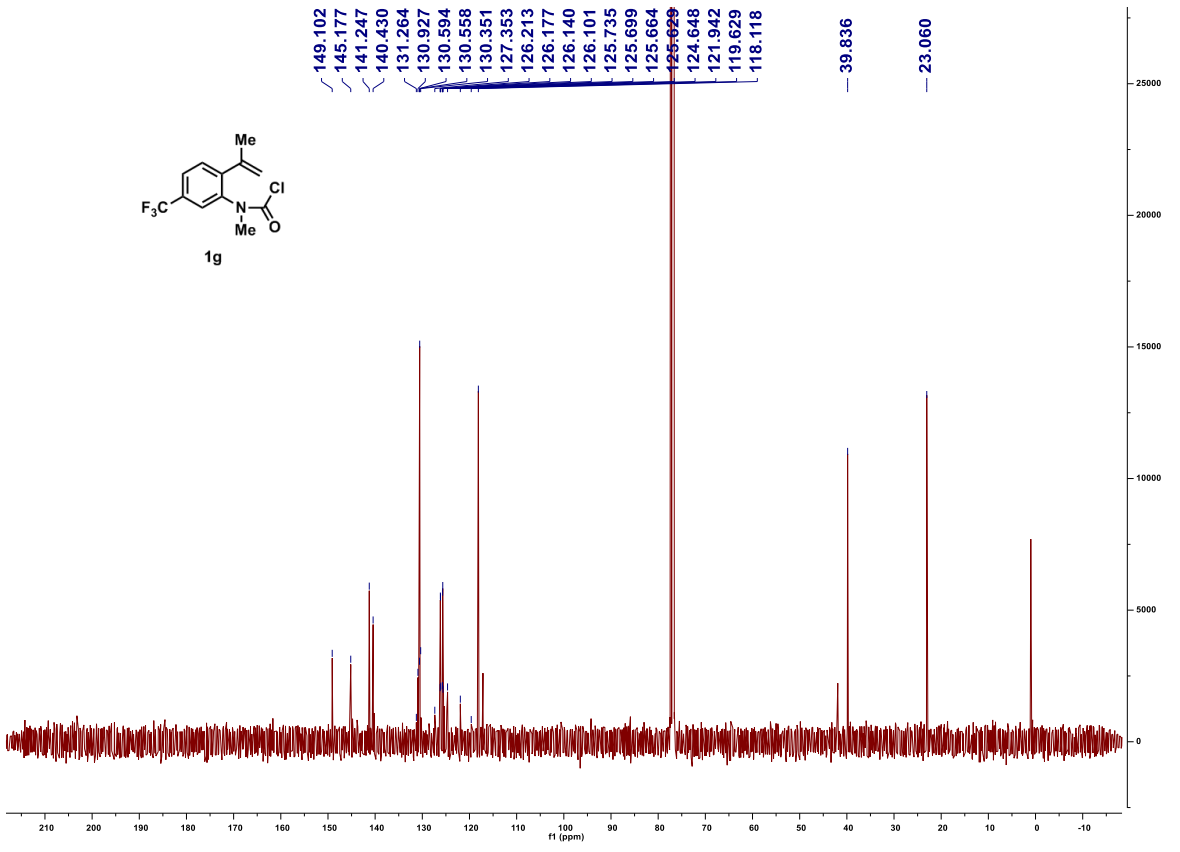
NMR spectra

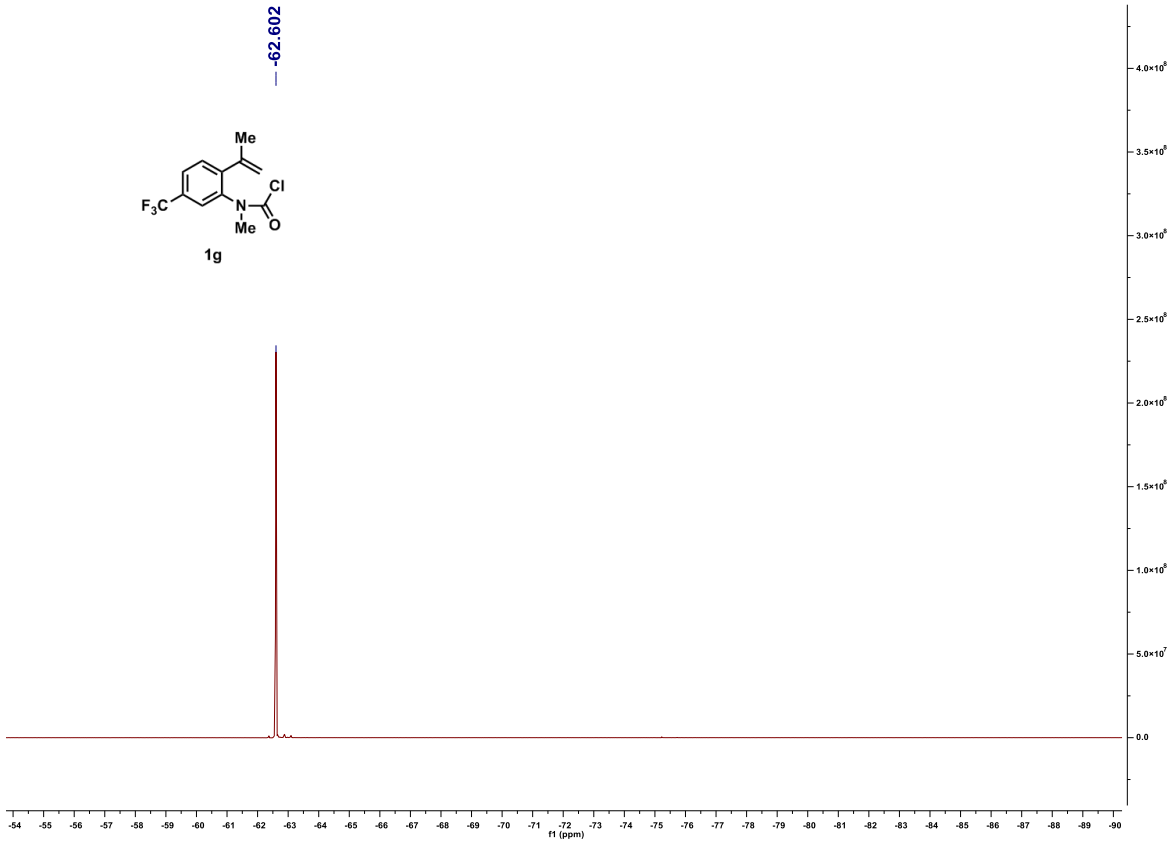
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **1g**



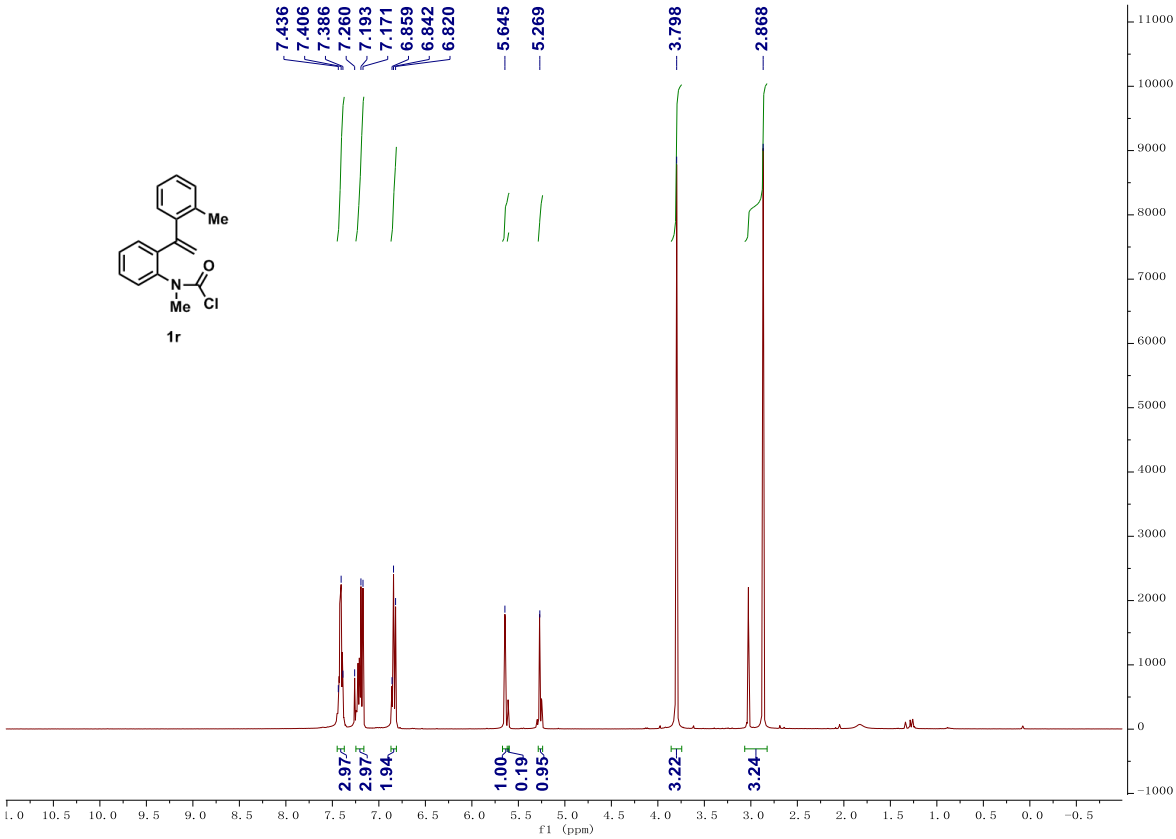
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **1g**



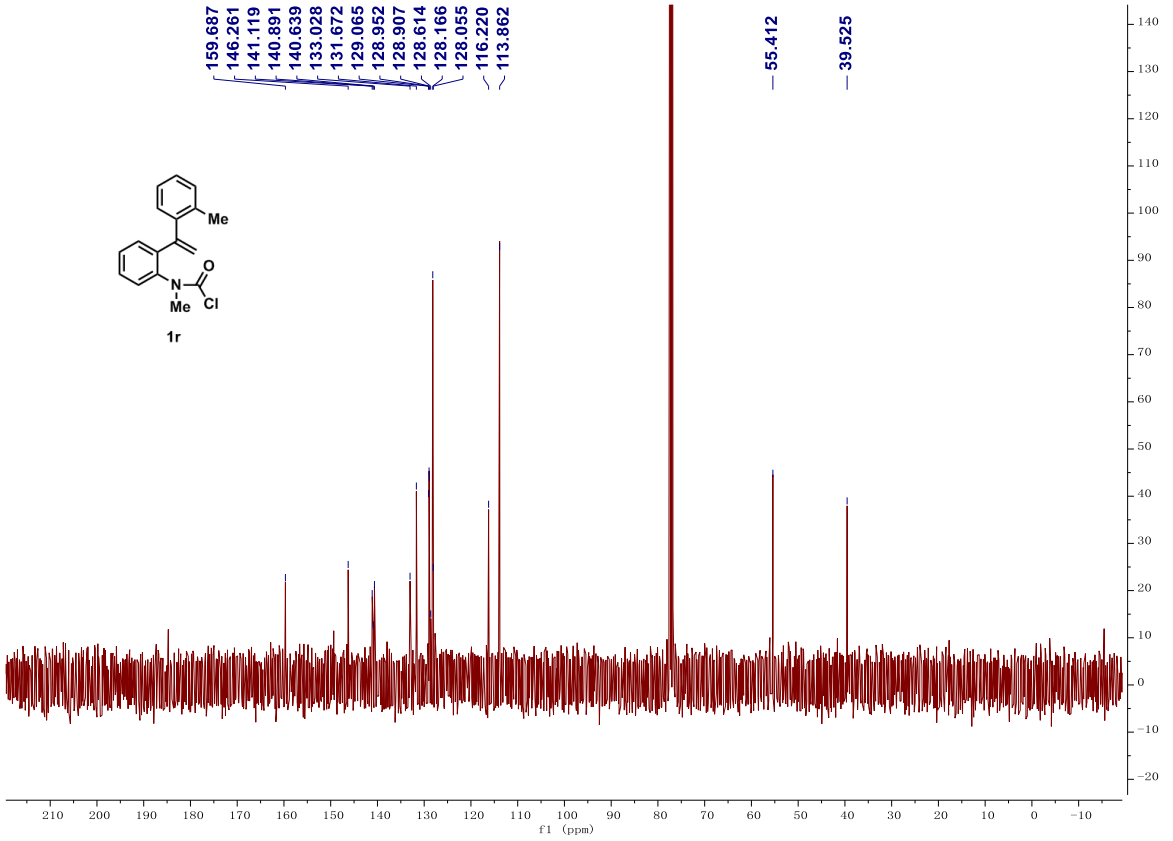
^{19}F NMR-spectrum (376 MHz, $CDCl_3$) of **1g**



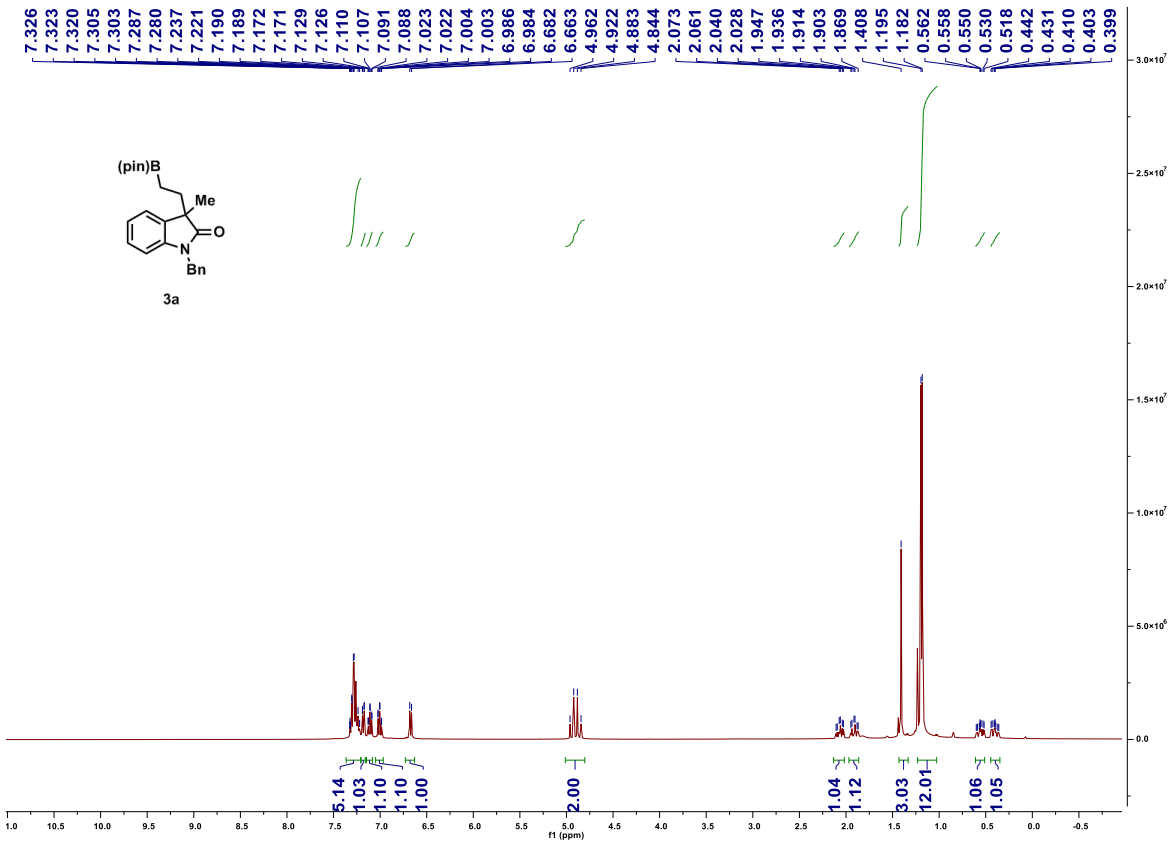
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **1r**



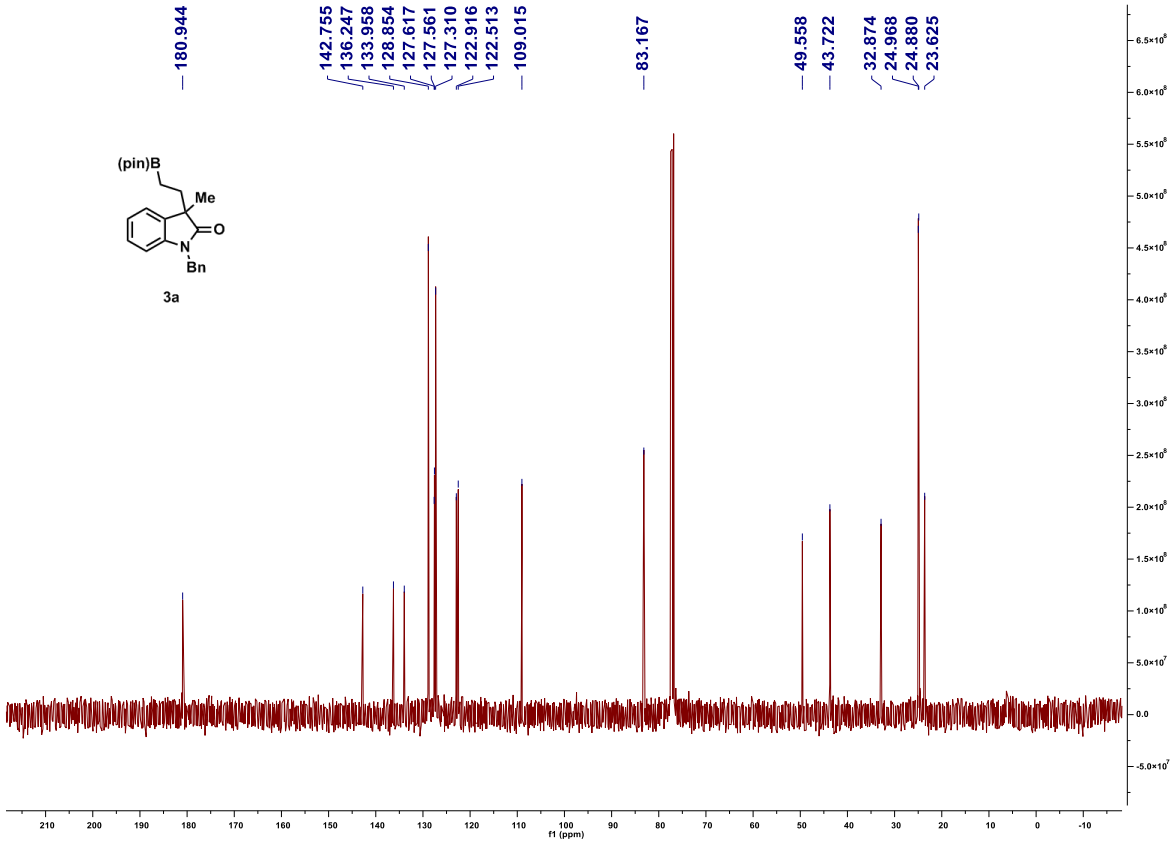
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **1r**



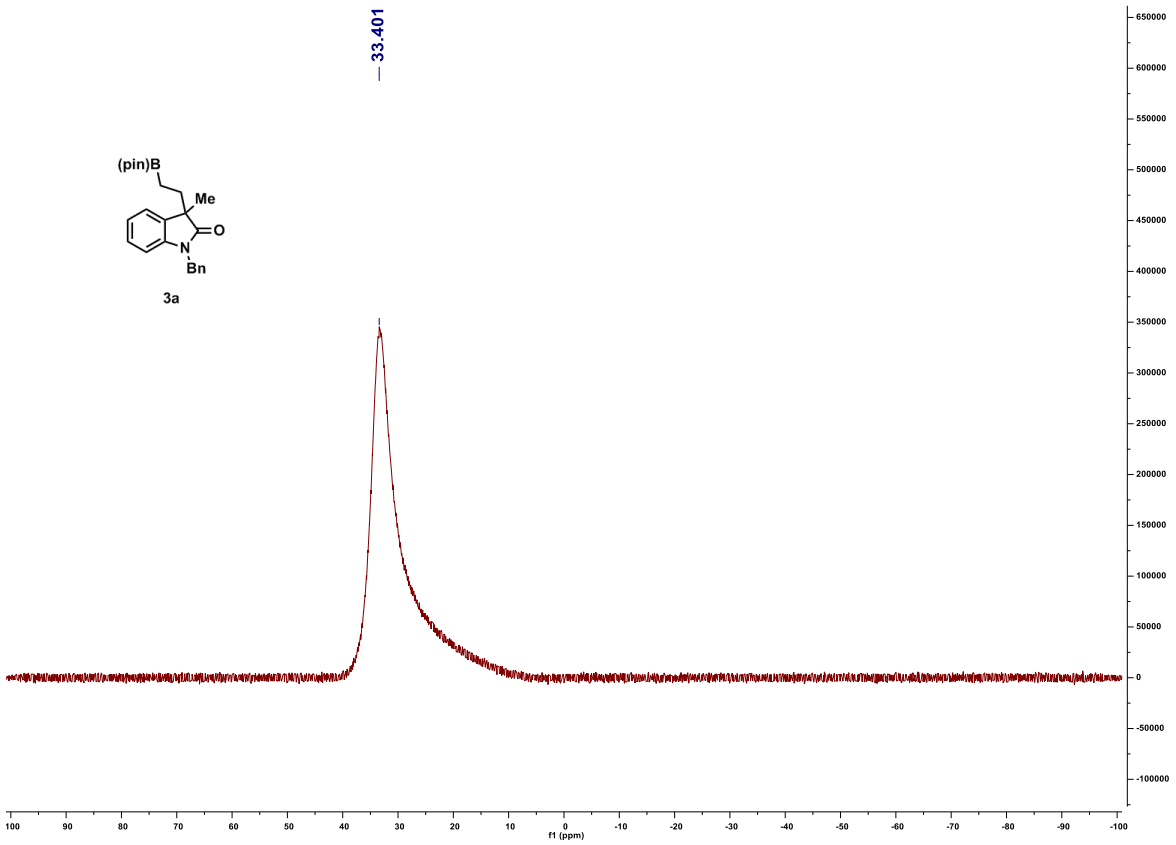
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3a**



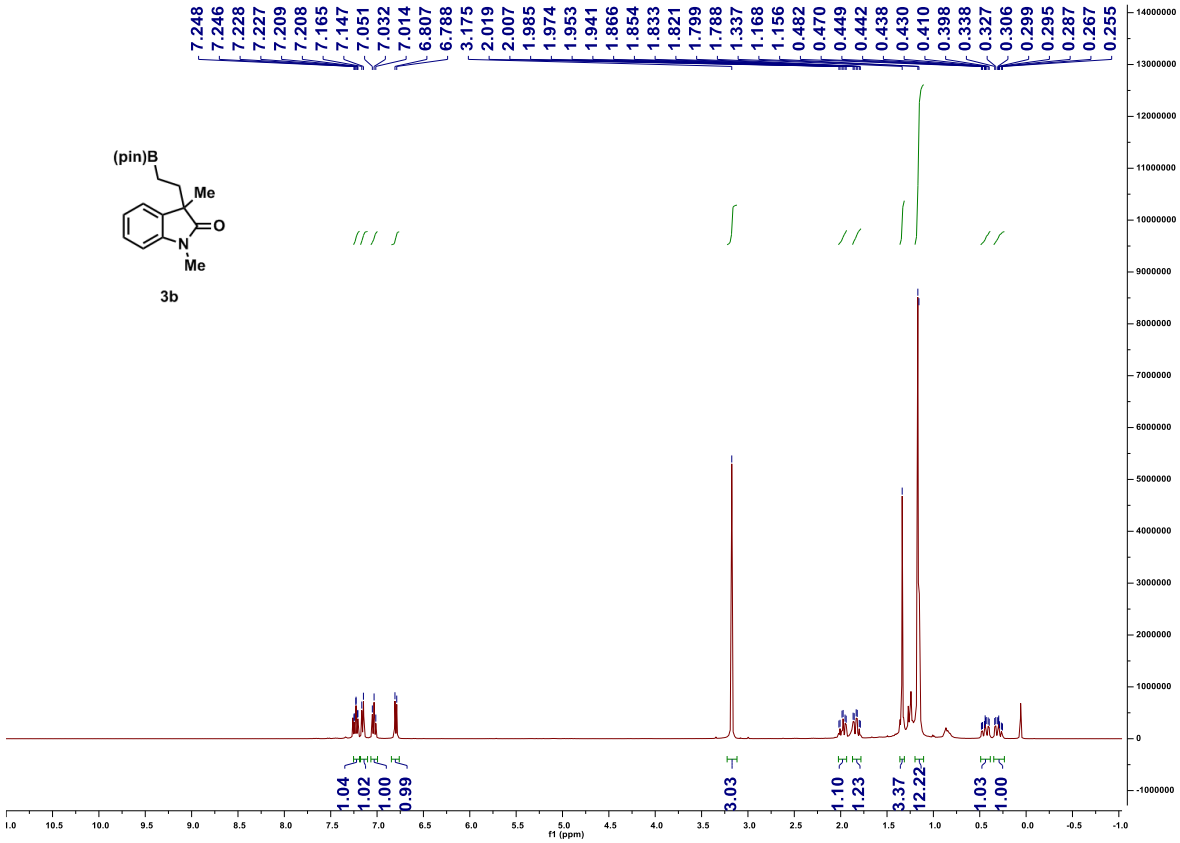
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3a**



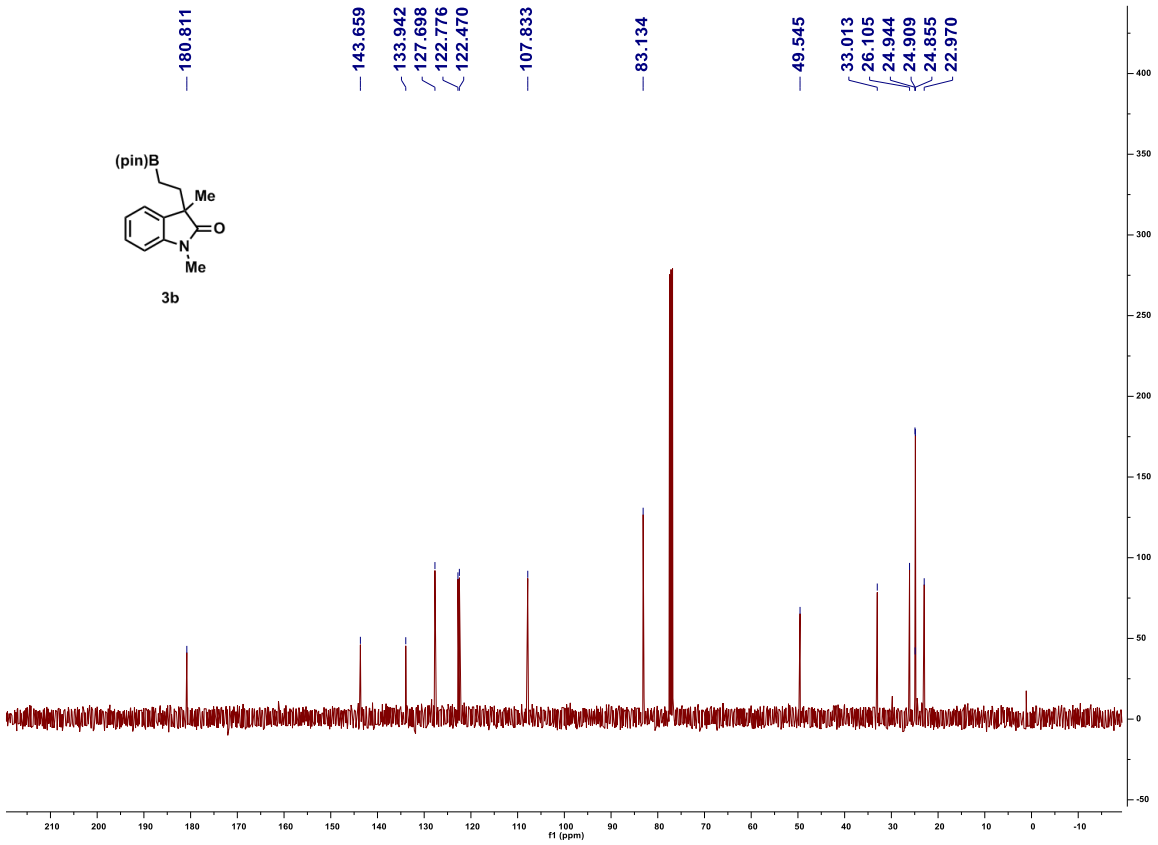
^{11}B NMR-spectrum (128 MHz, $CDCl_3$) of **3a**



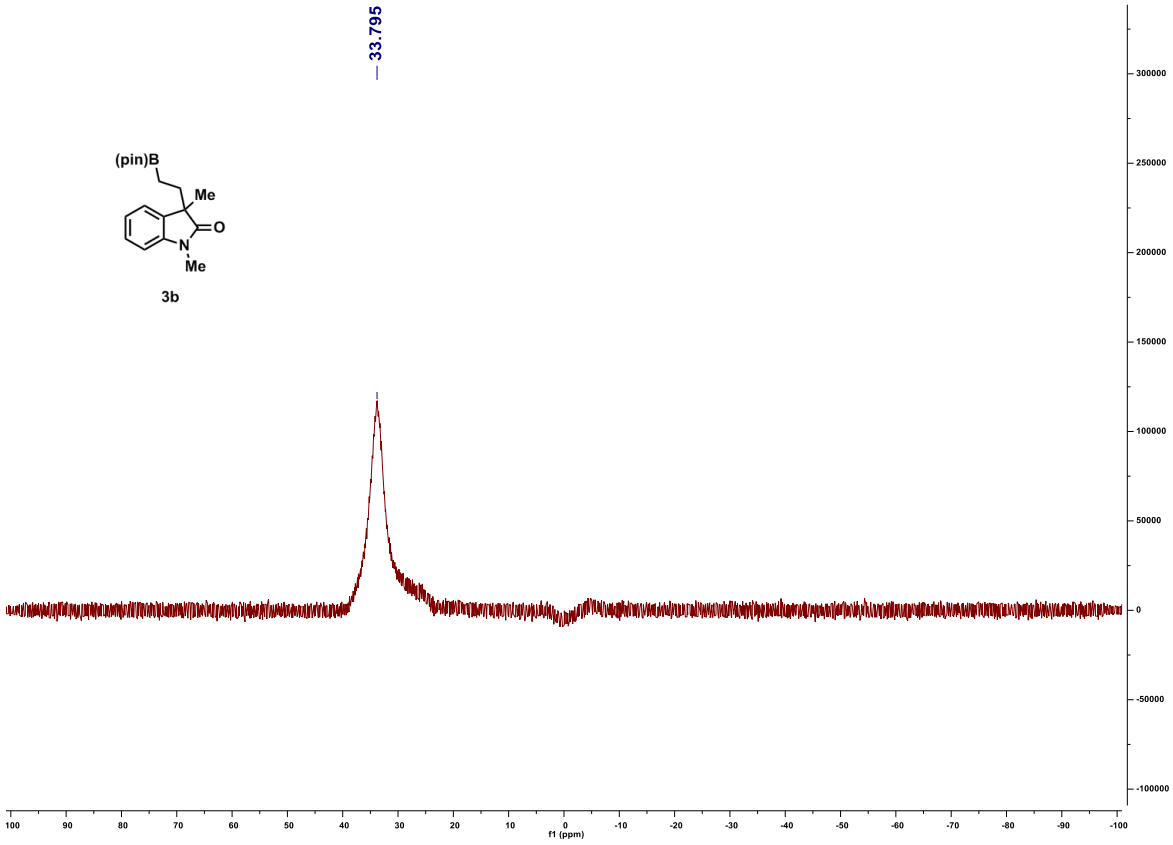
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3b**



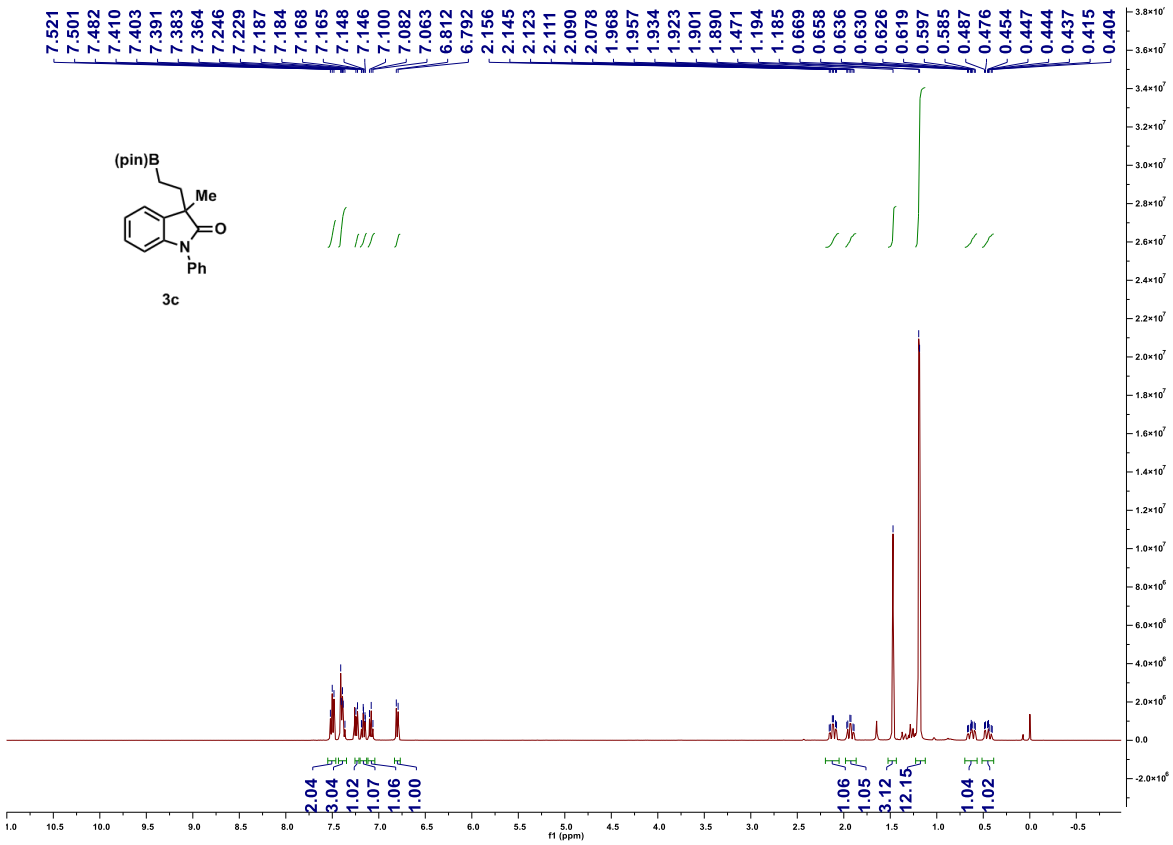
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3b**



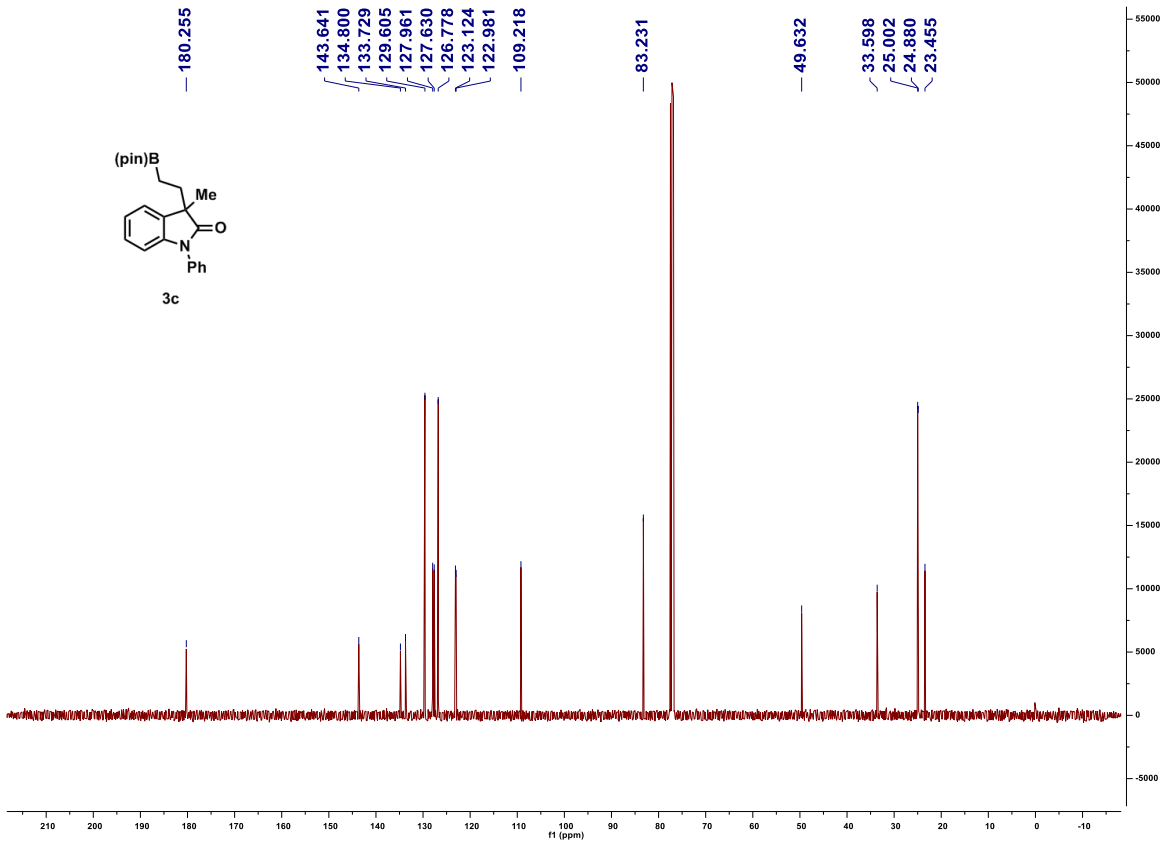
^{11}B NMR-spectrum (128 MHz, $CDCl_3$) of **3b**



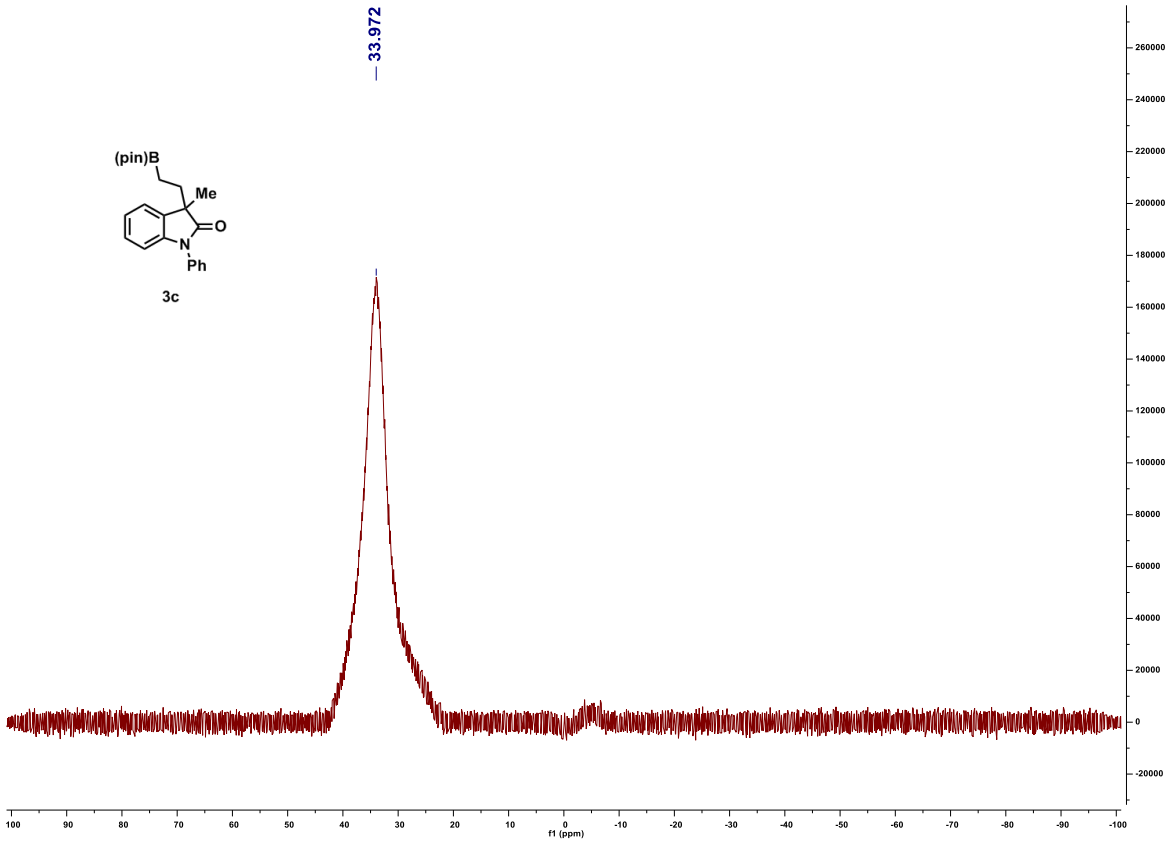
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3c**



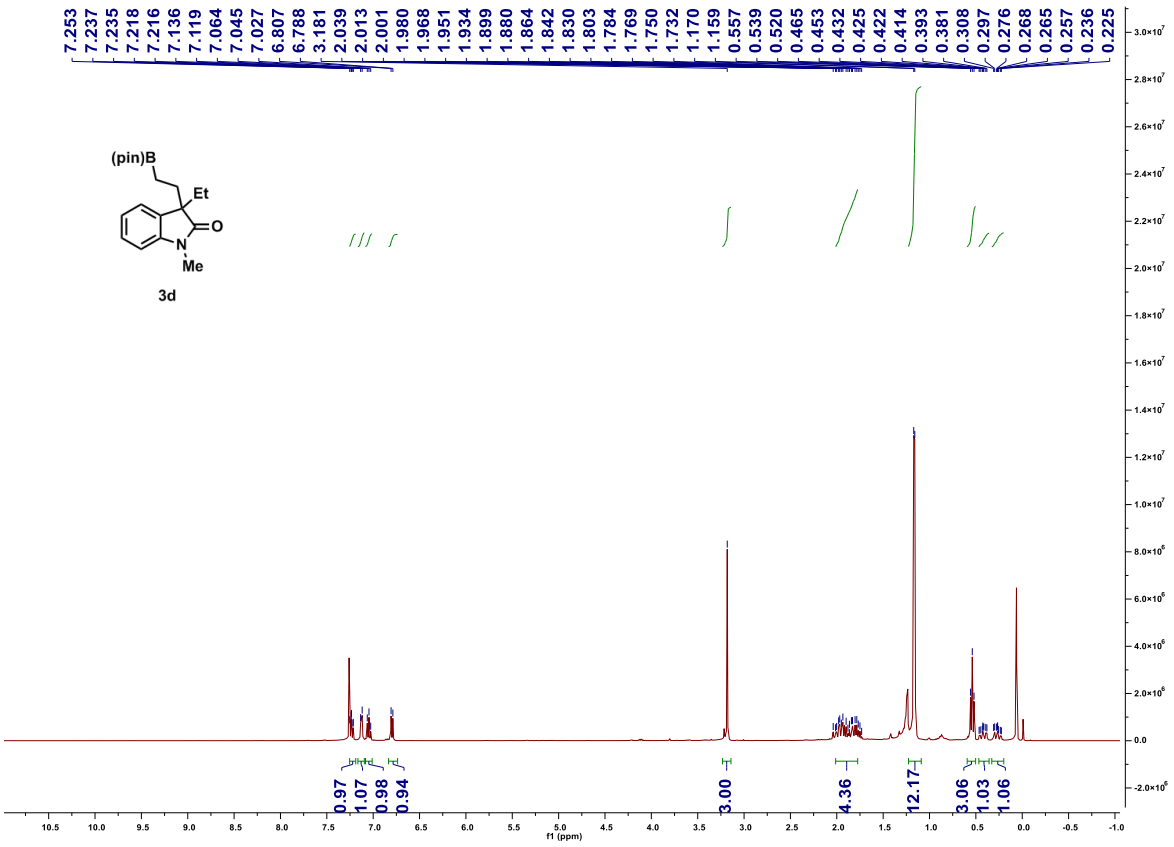
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3c**



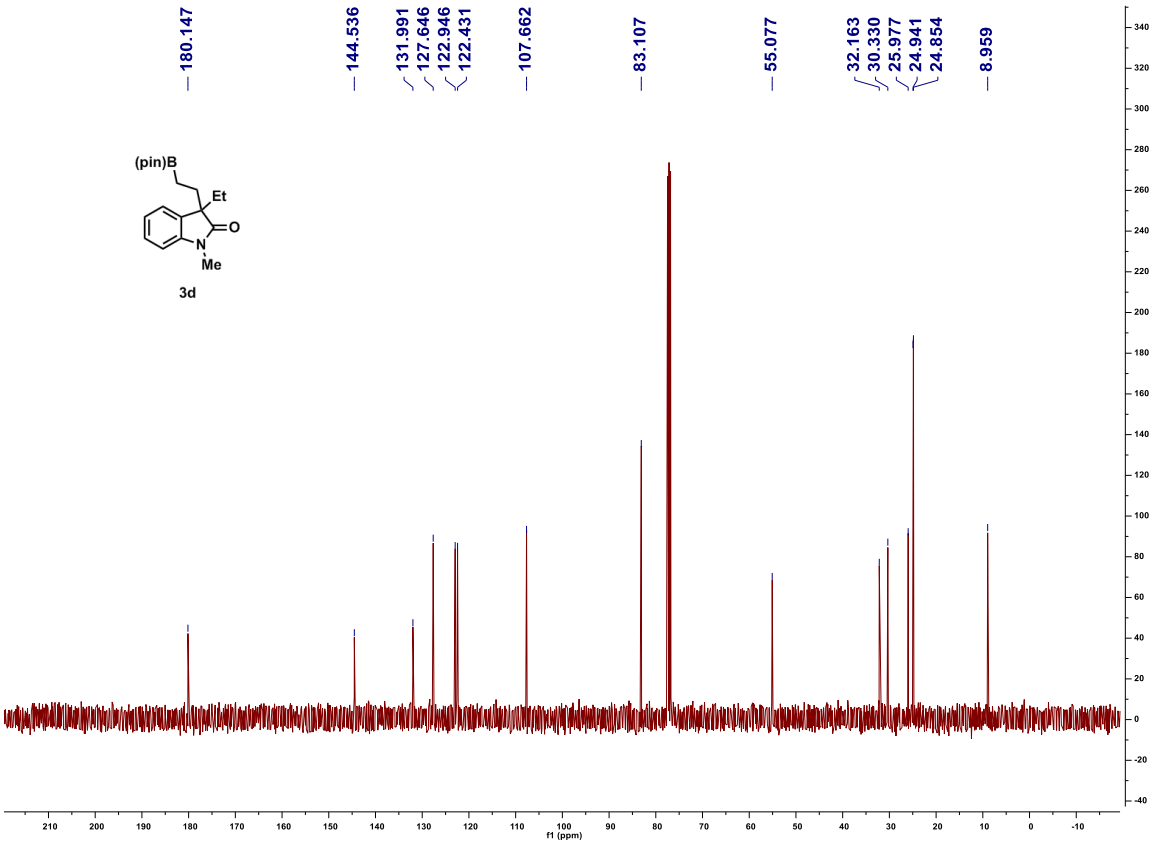
^{11}B NMR-spectrum (128 MHz, $CDCl_3$) of **3c**



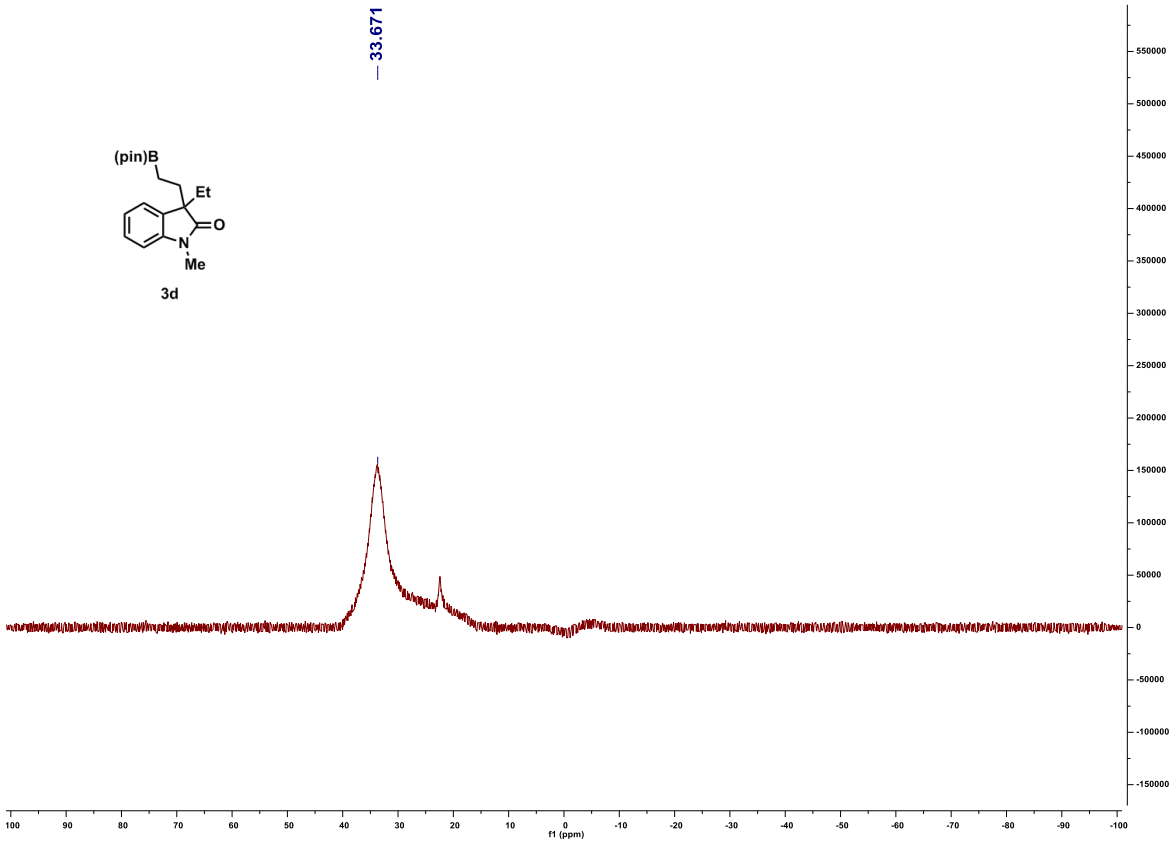
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3d**



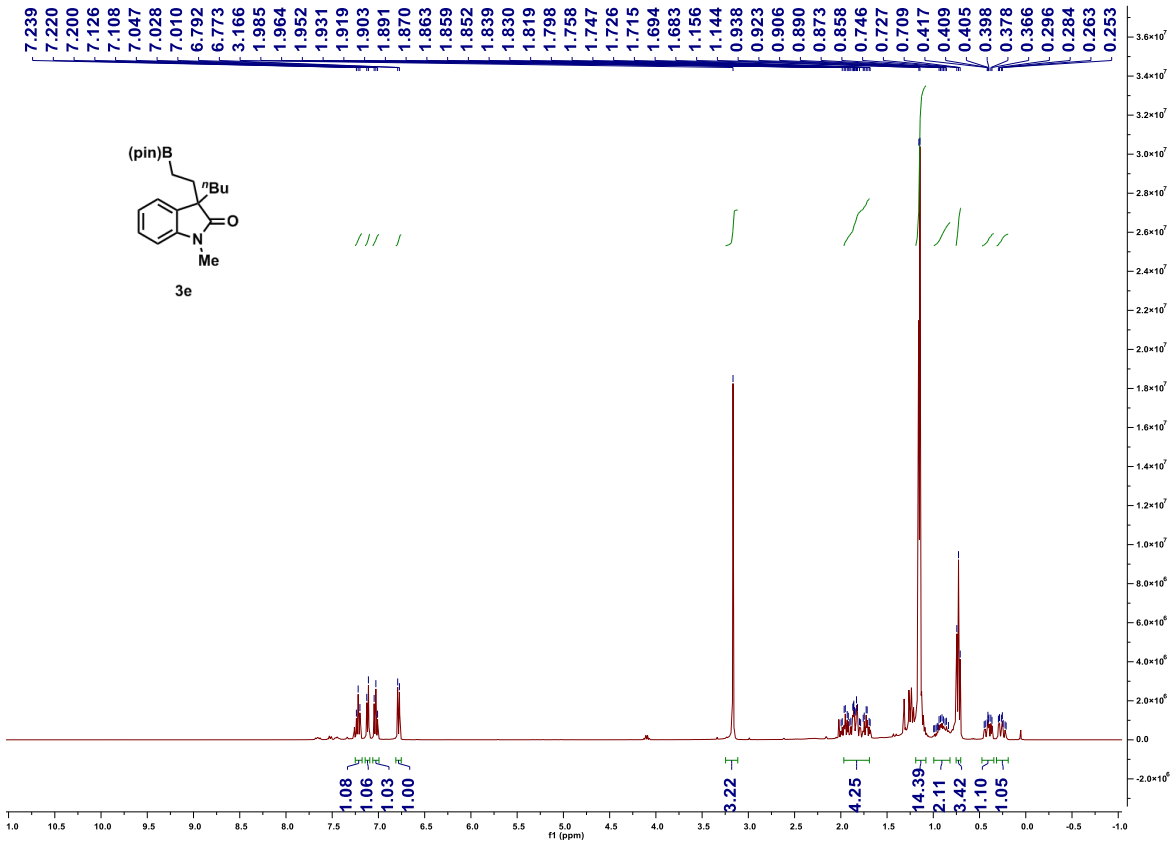
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3d**



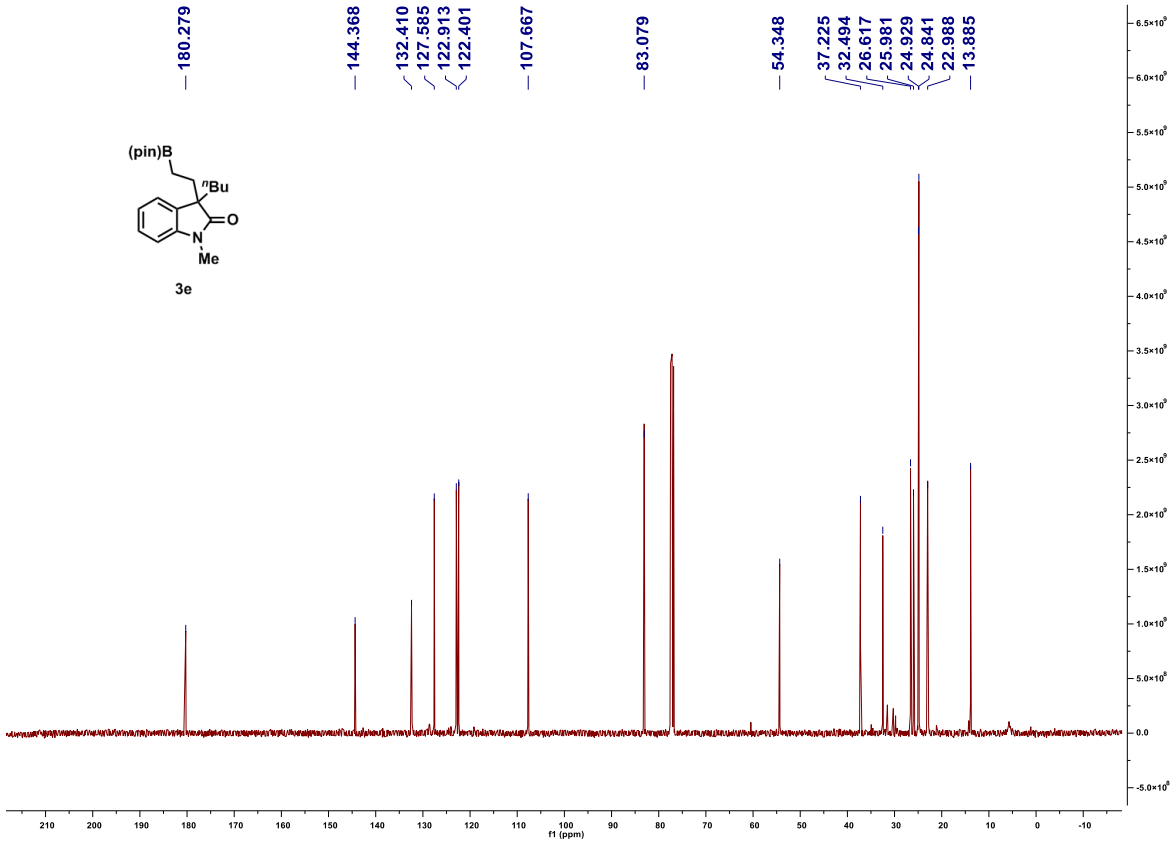
^{11}B NMR-spectrum (128 MHz, $CDCl_3$) of **3d**



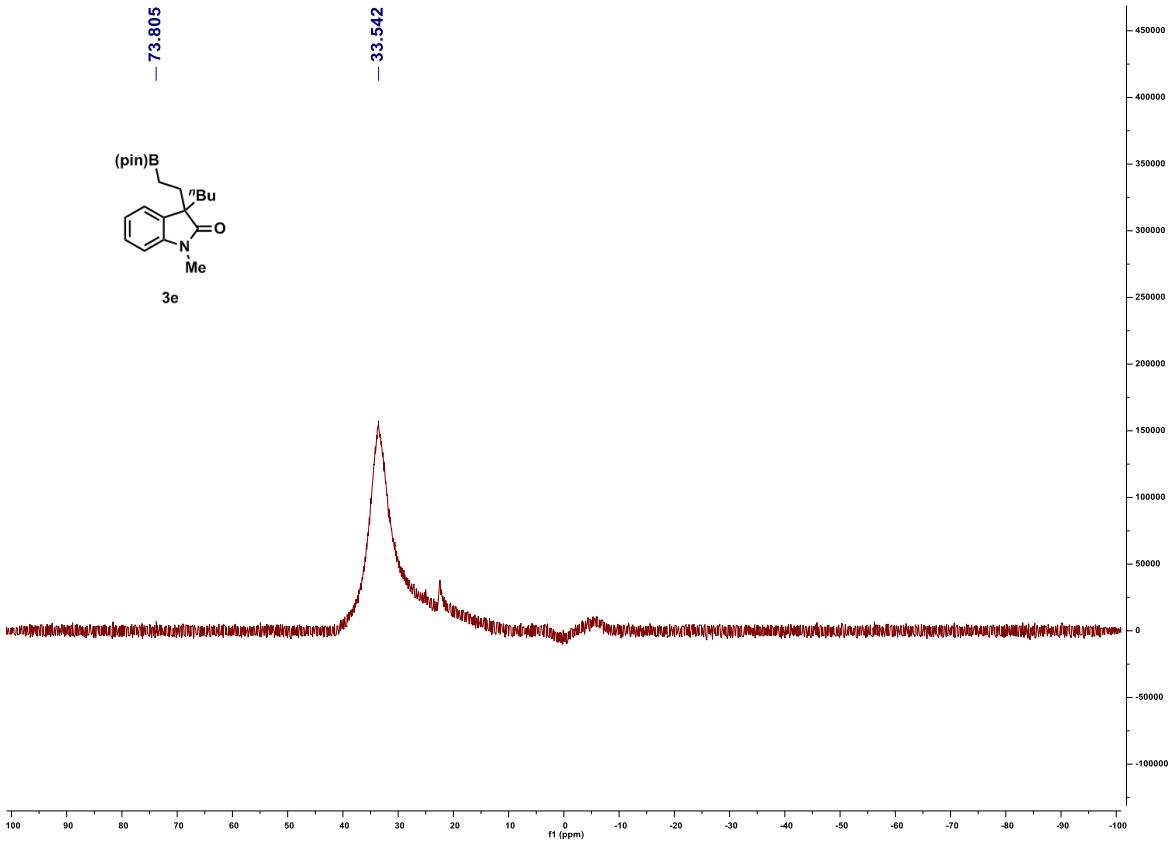
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3e**



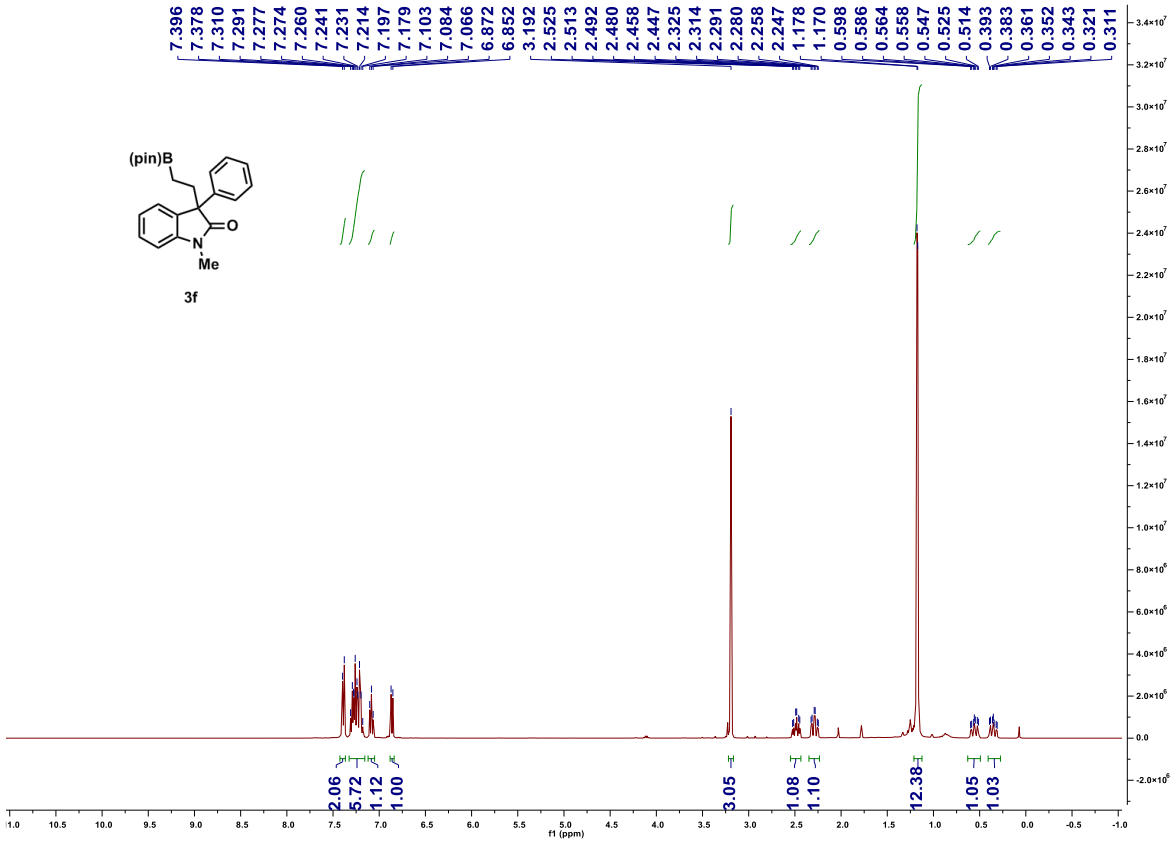
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3e**



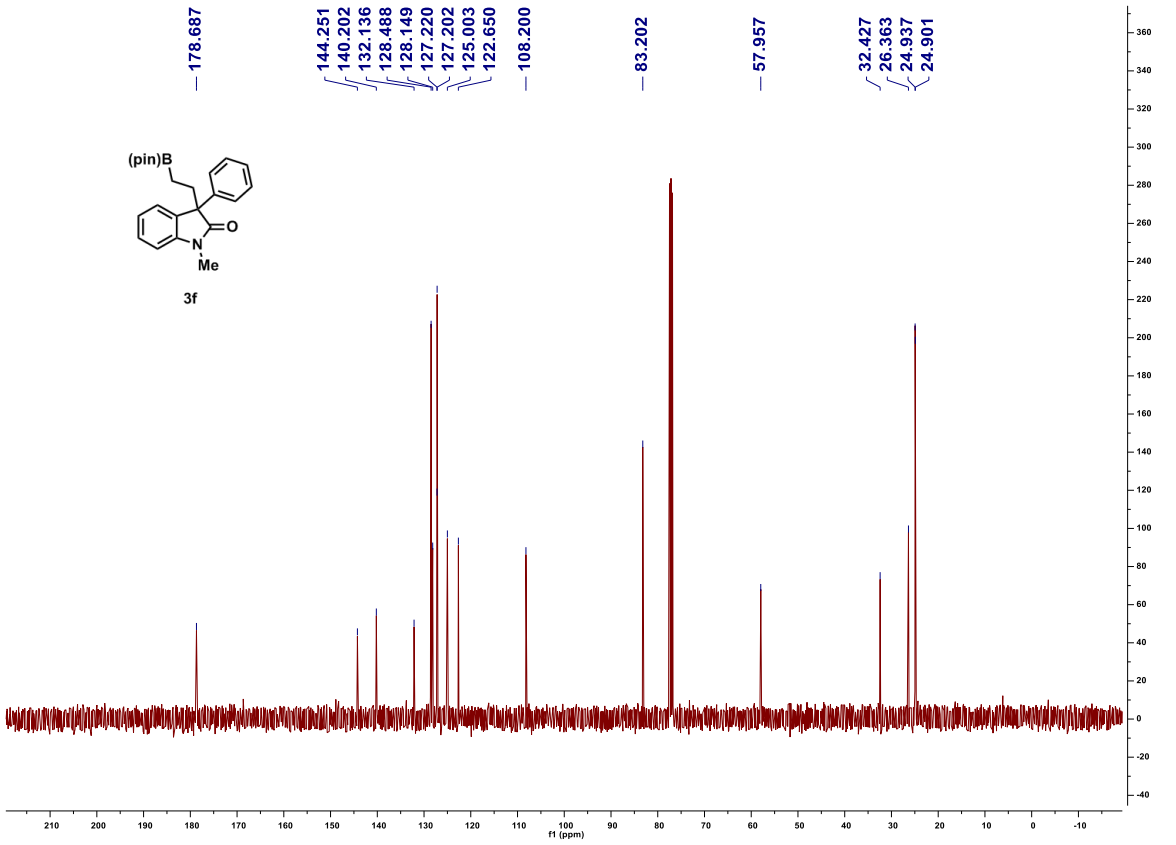
^{11}B NMR-spectrum (128 MHz, $CDCl_3$) of **3e**



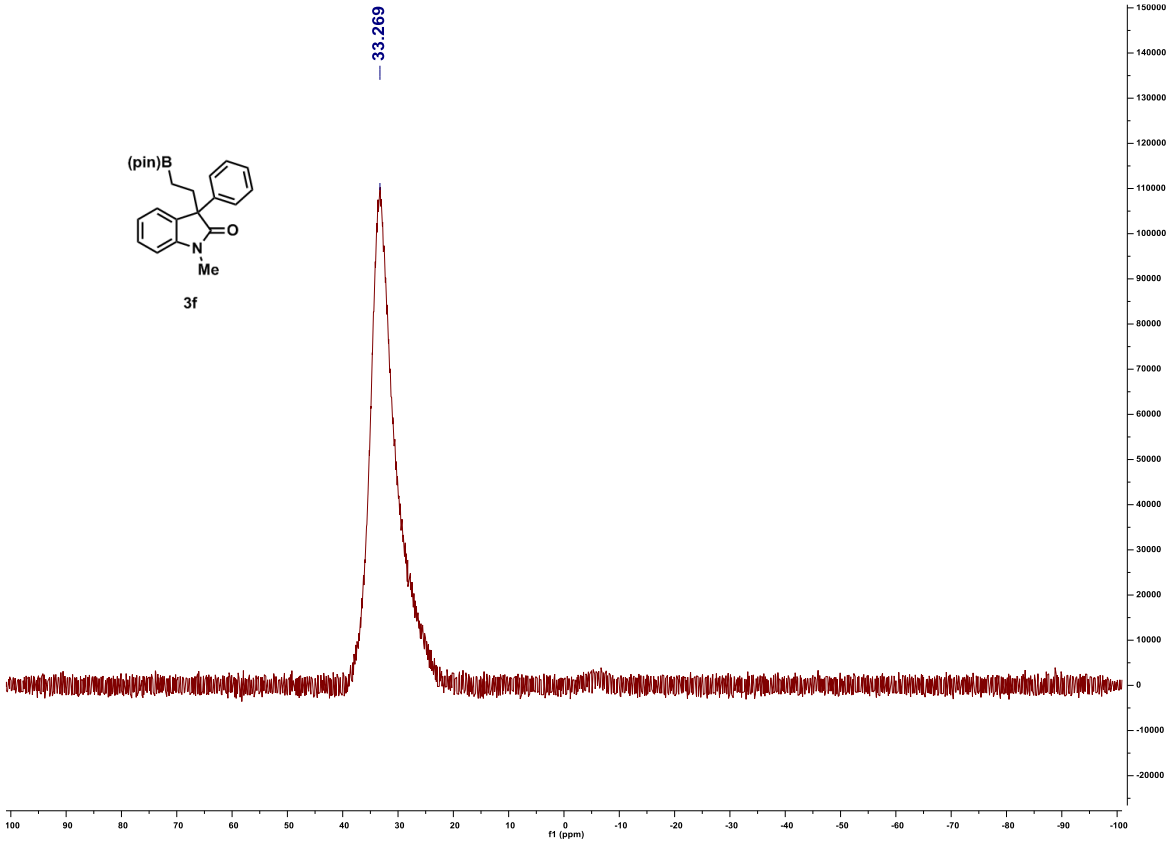
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3f**



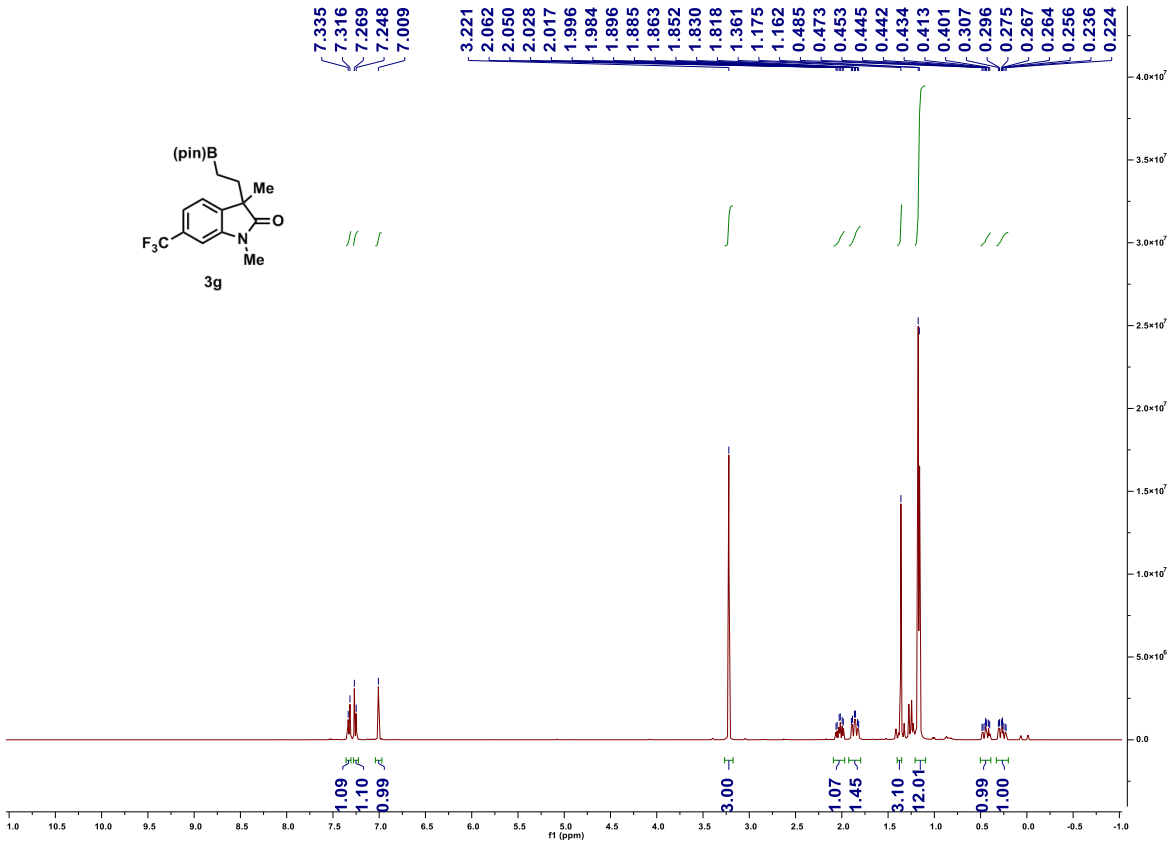
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3f**



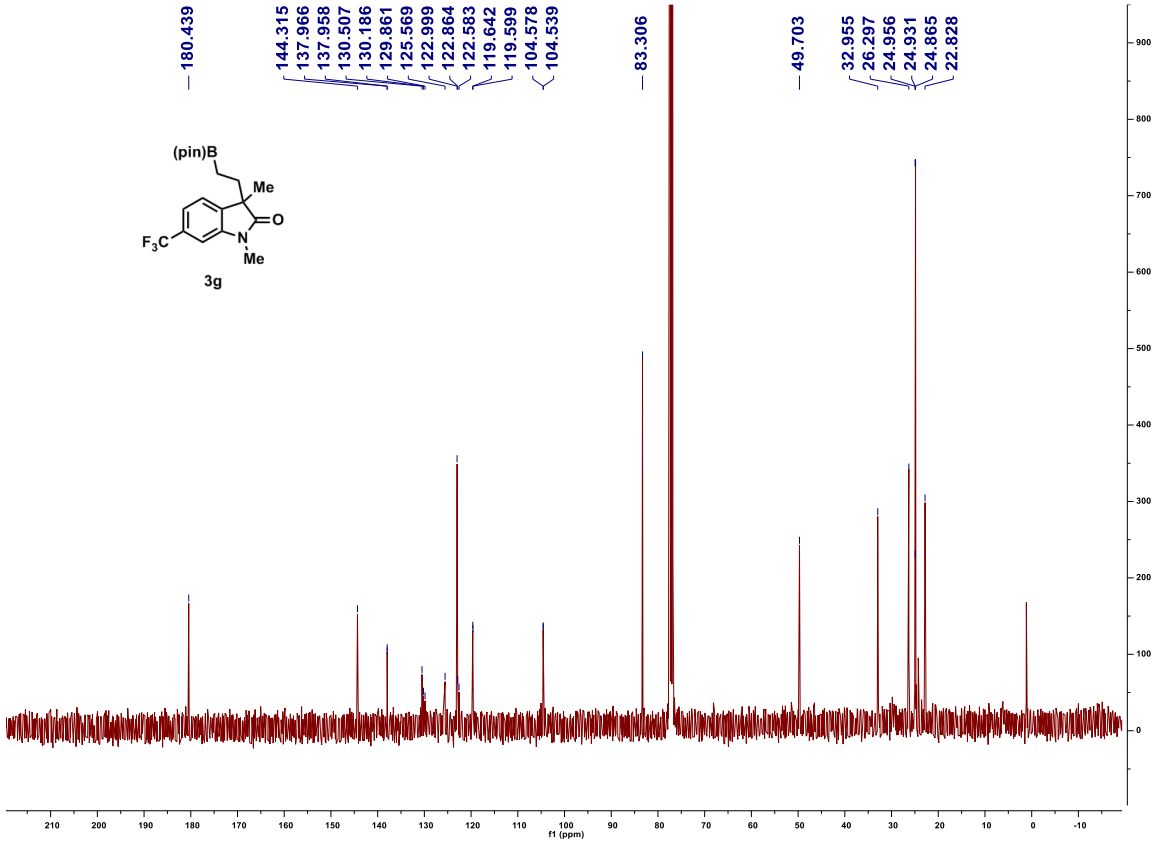
^{11}B NMR-spectrum (128 MHz, $CDCl_3$) of **3f**



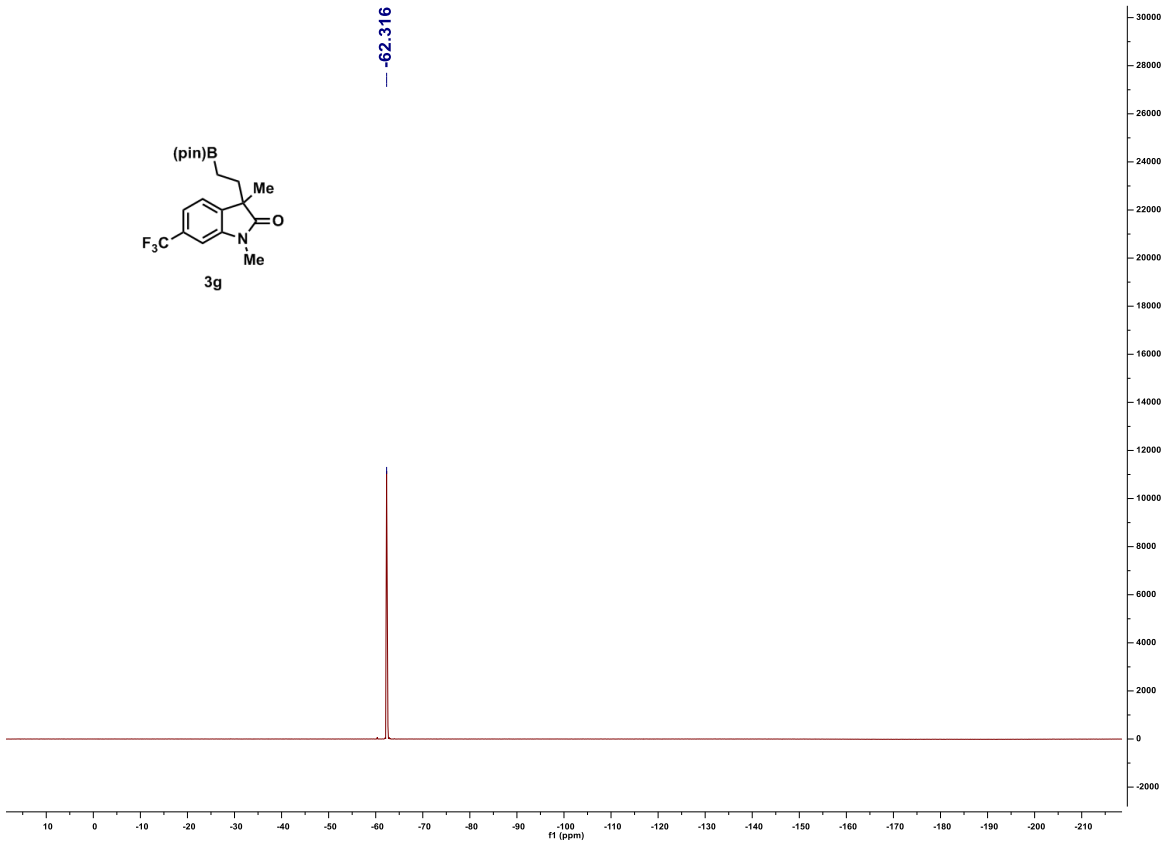
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3g**



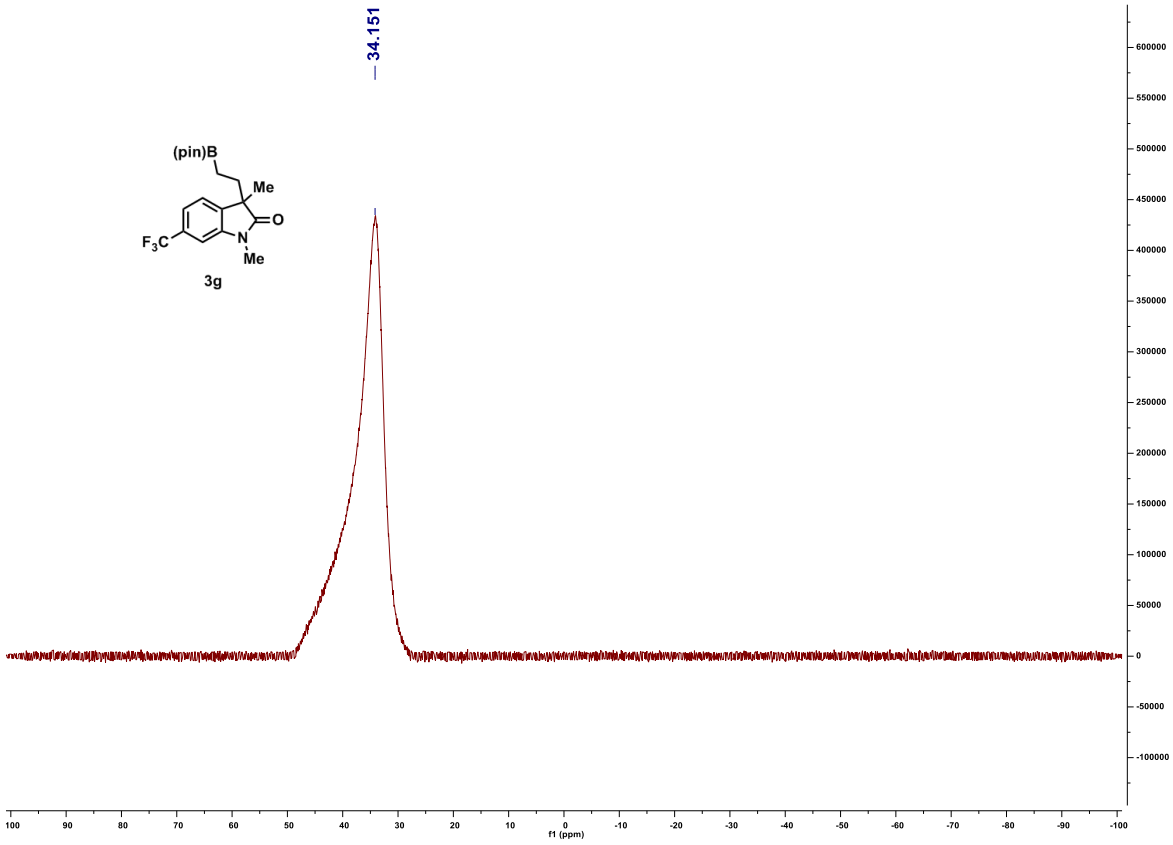
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3g**



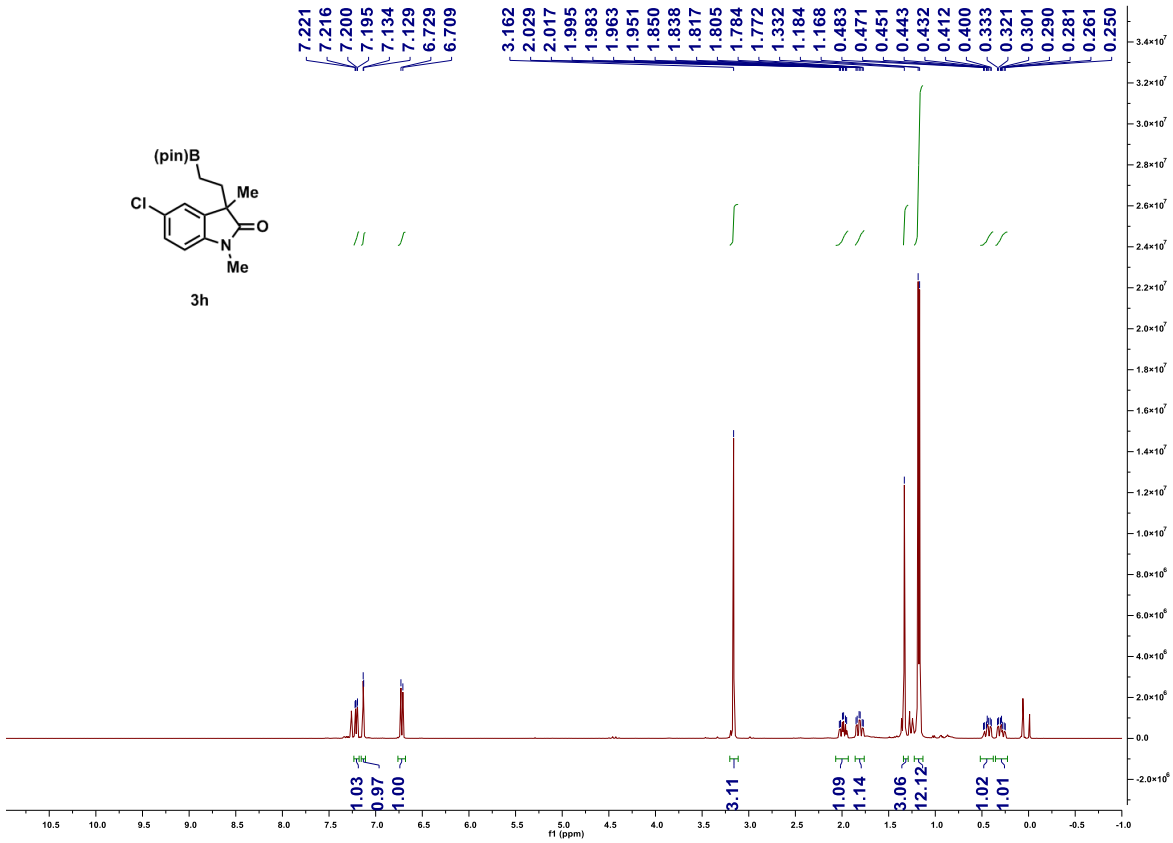
^{19}F NMR-spectrum (376 MHz, $CDCl_3$) of **3g**



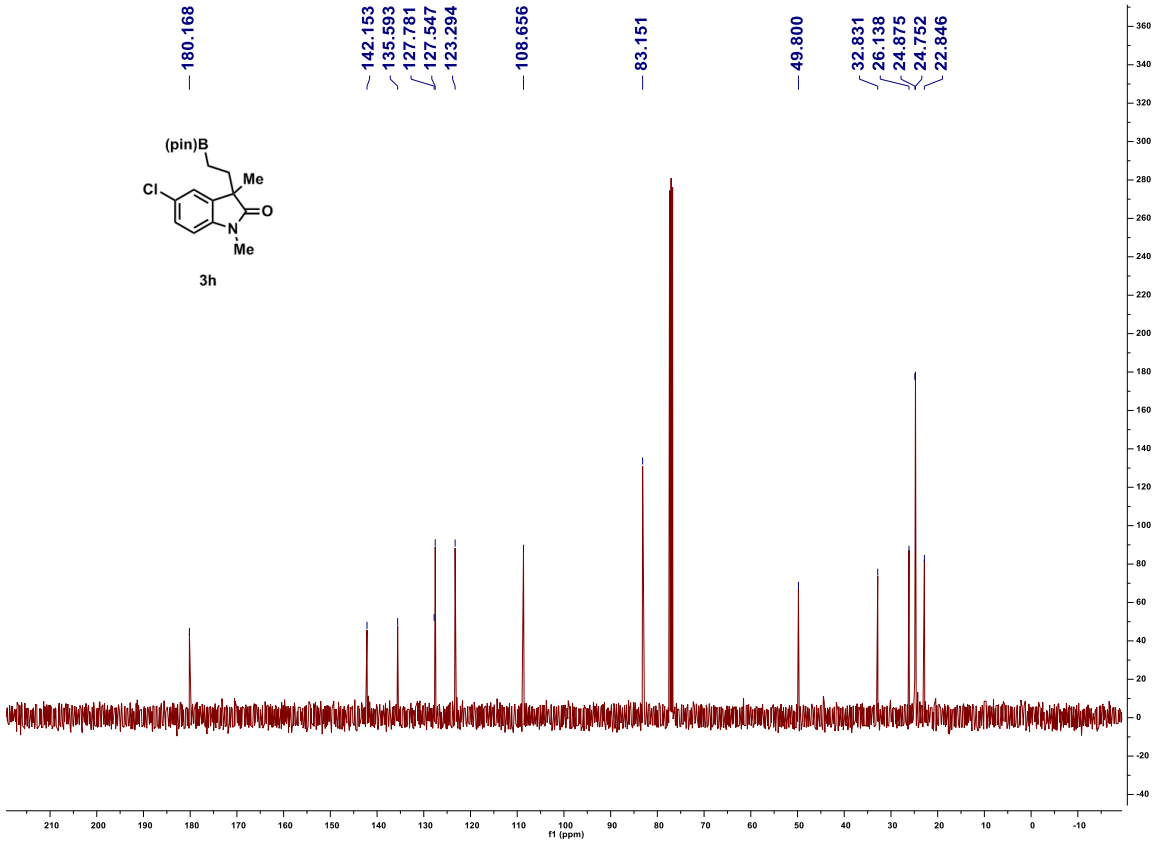
^{11}B NMR-spectrum (128 MHz, $CDCl_3$) of **3g**



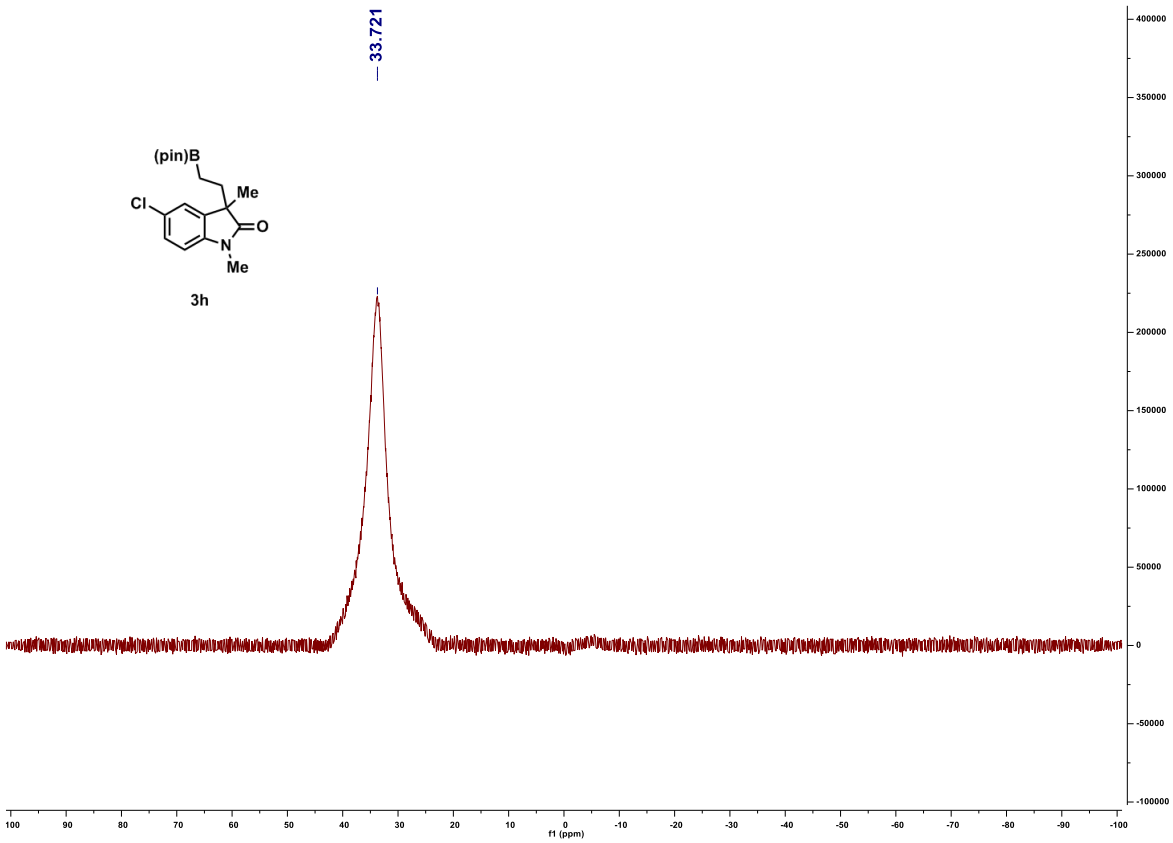
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3h**



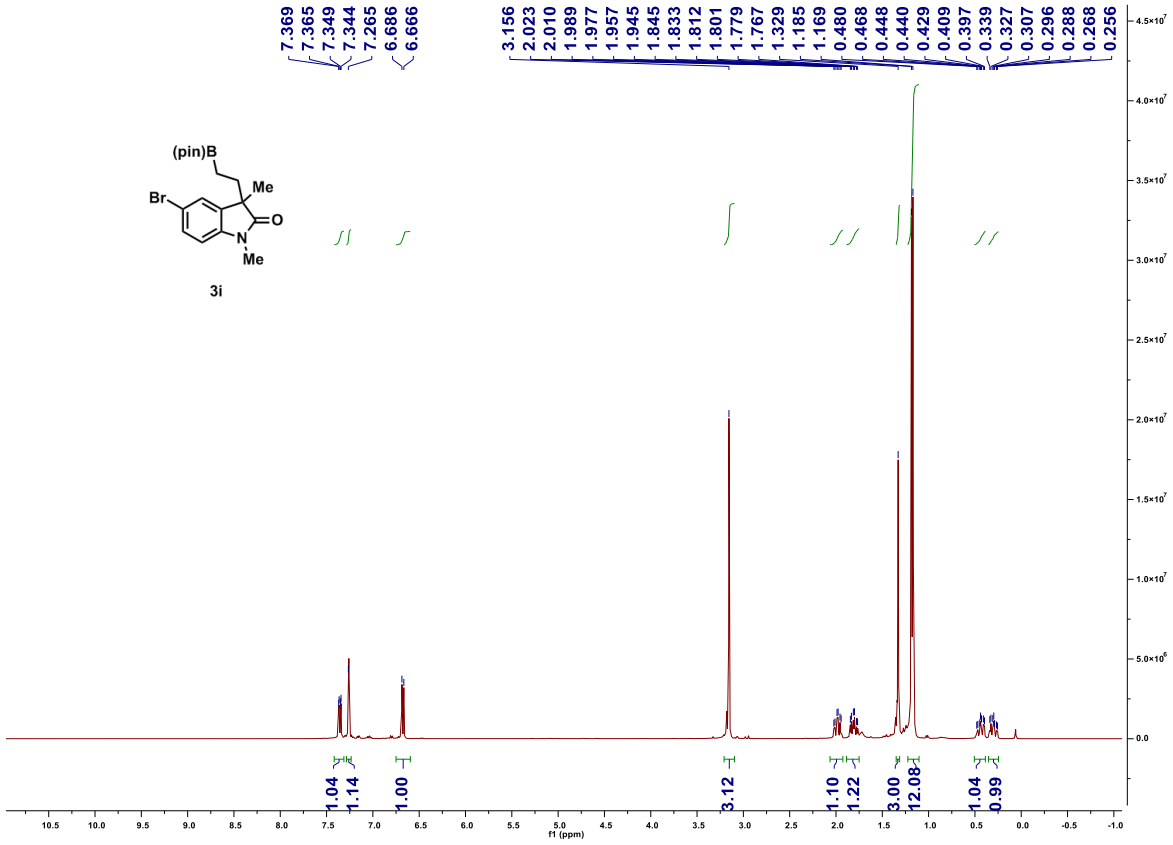
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3h**



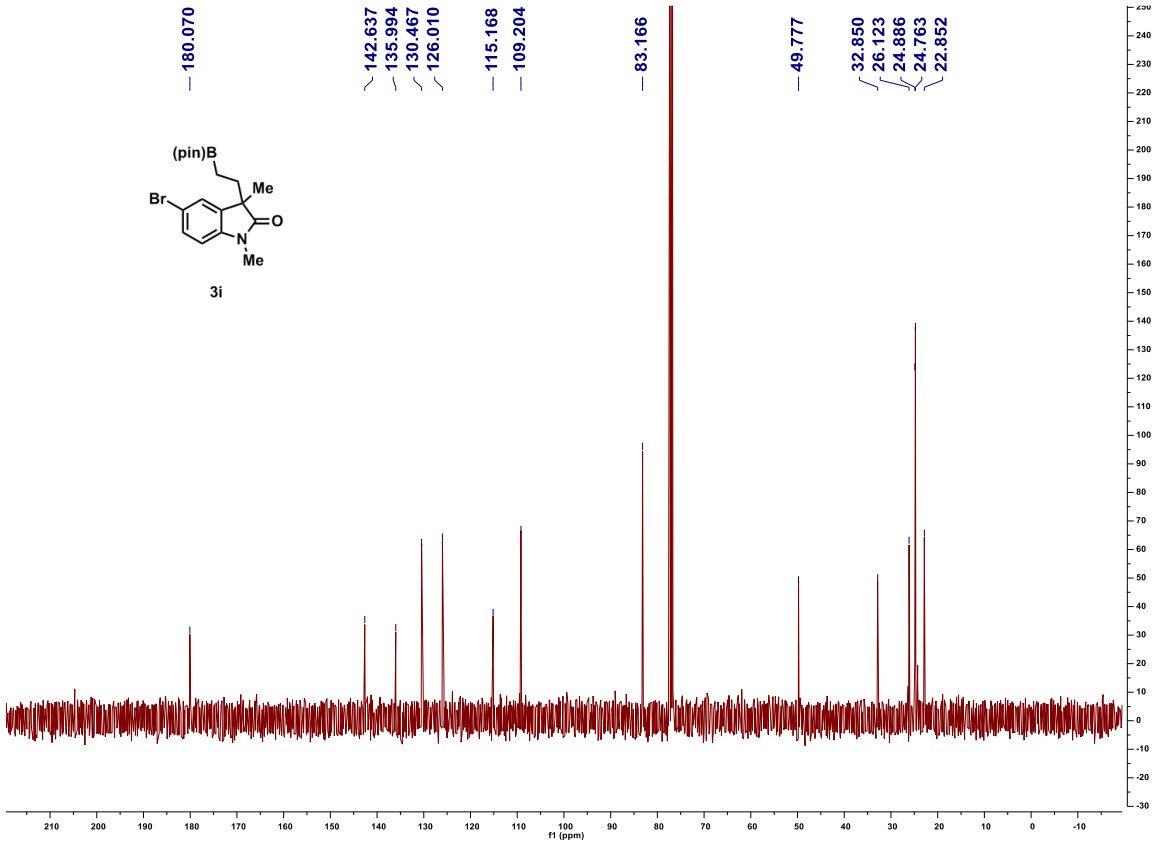
^{11}B NMR-spectrum (128 MHz, $CDCl_3$) of **3h**



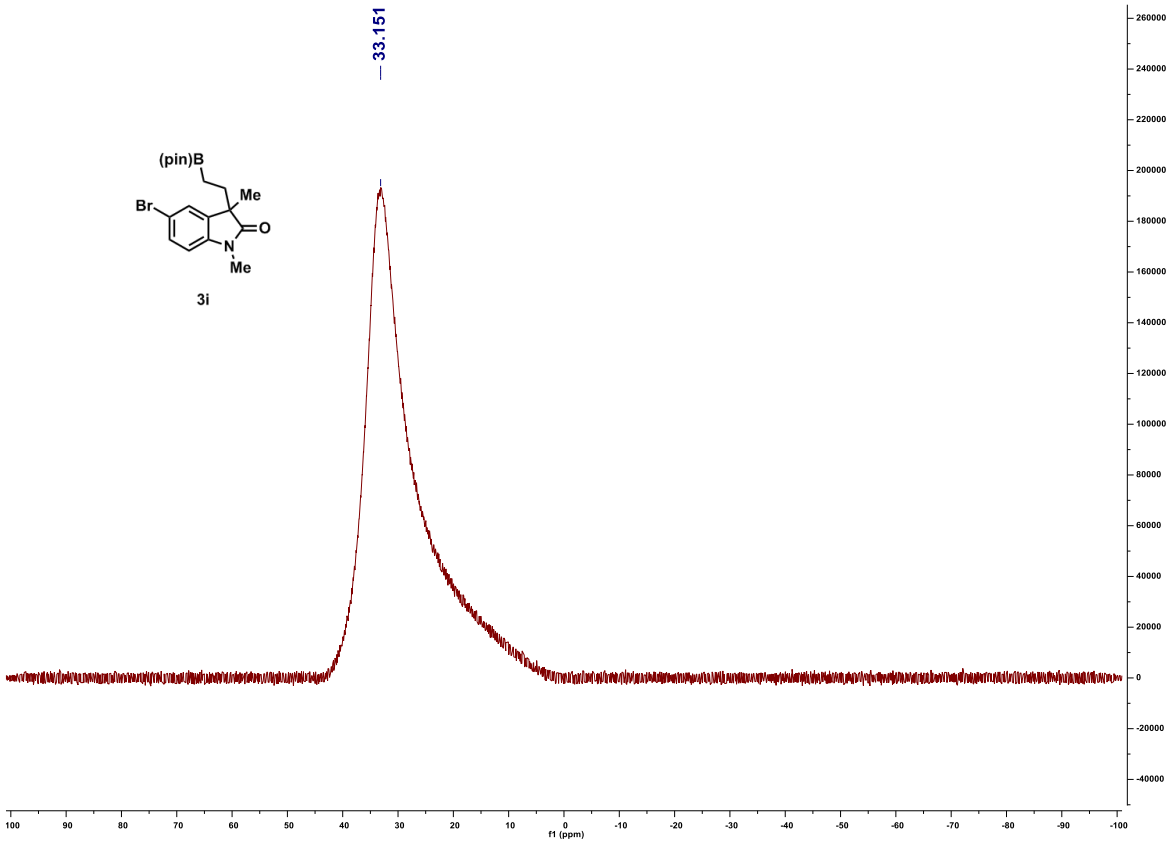
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3i**



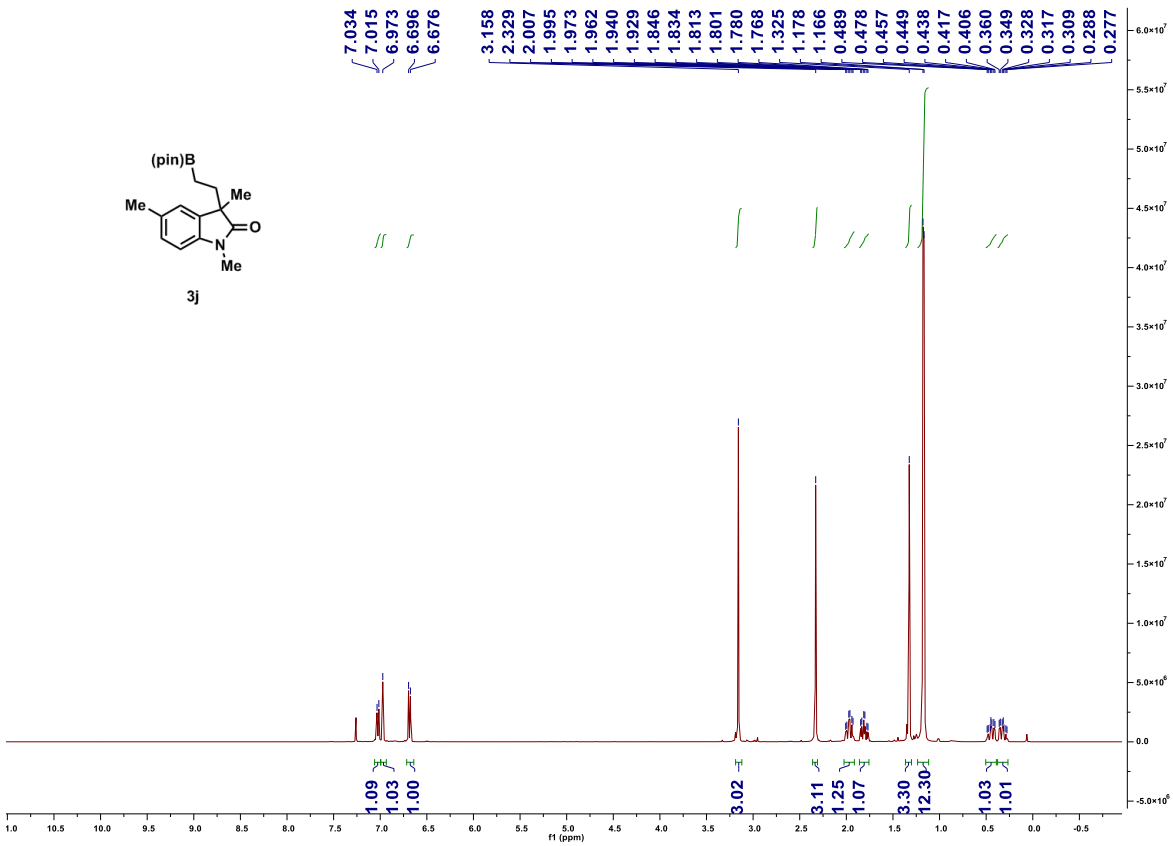
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3i**



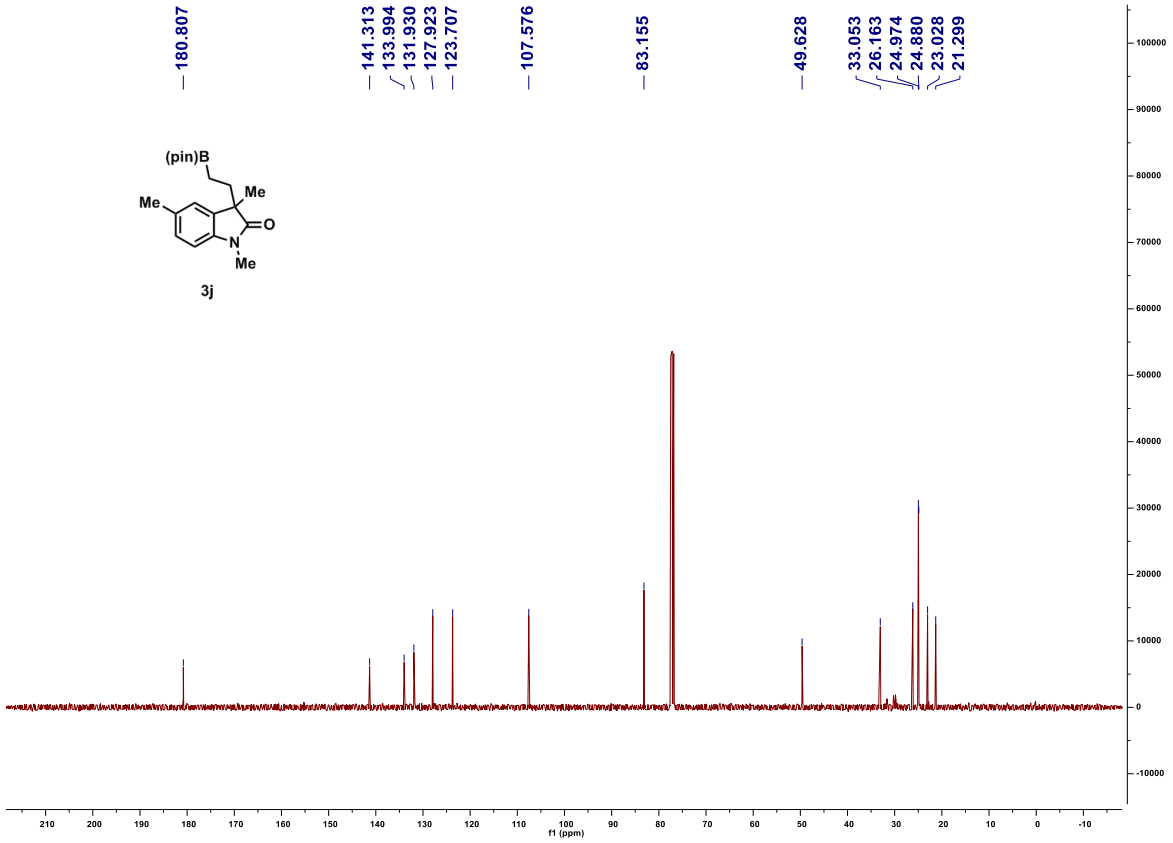
^{11}B NMR-spectrum (128 MHz, $CDCl_3$) of **3i**



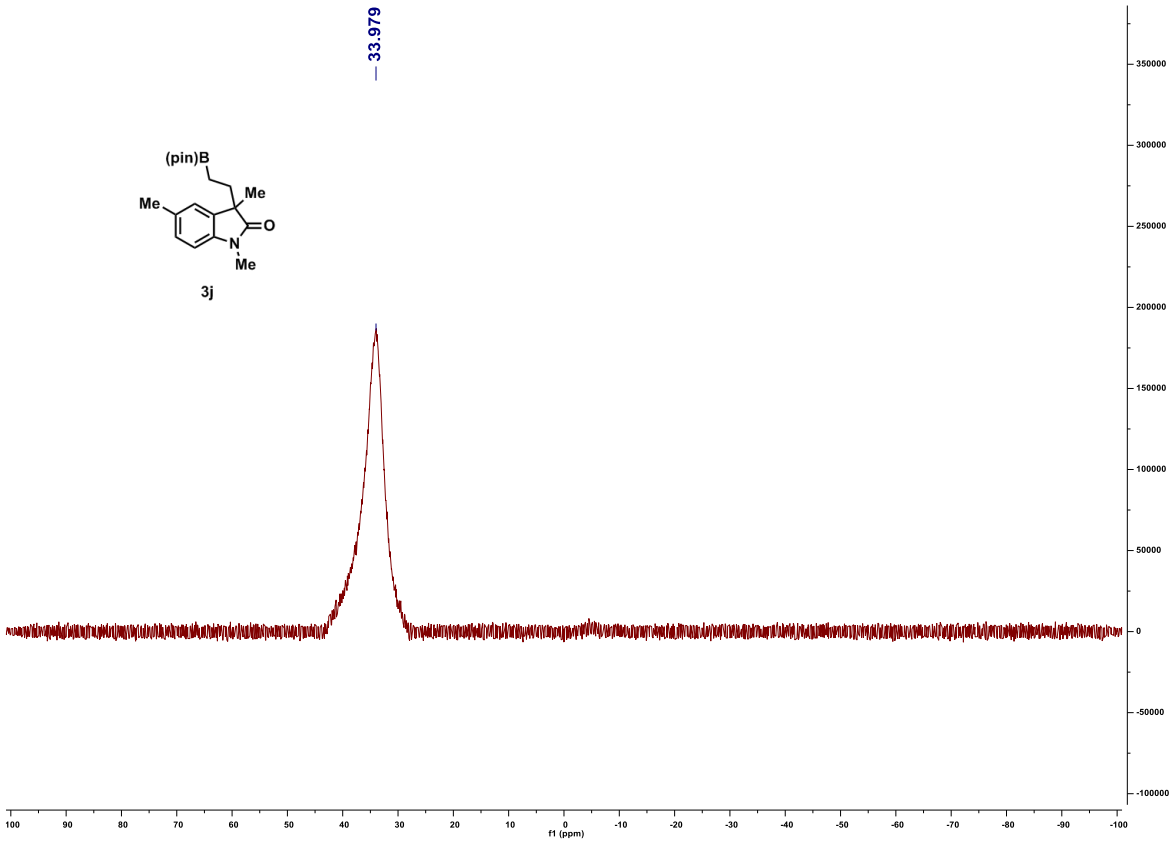
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3j**



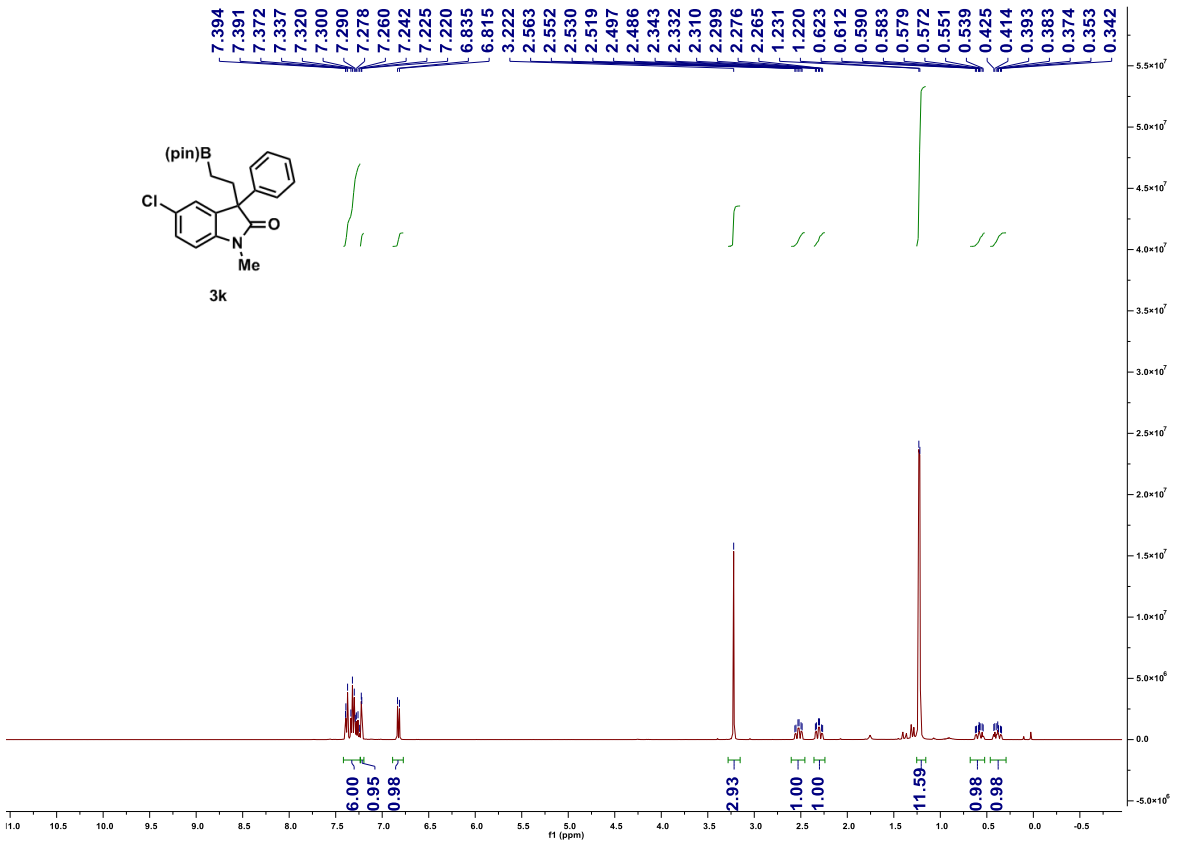
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3j**



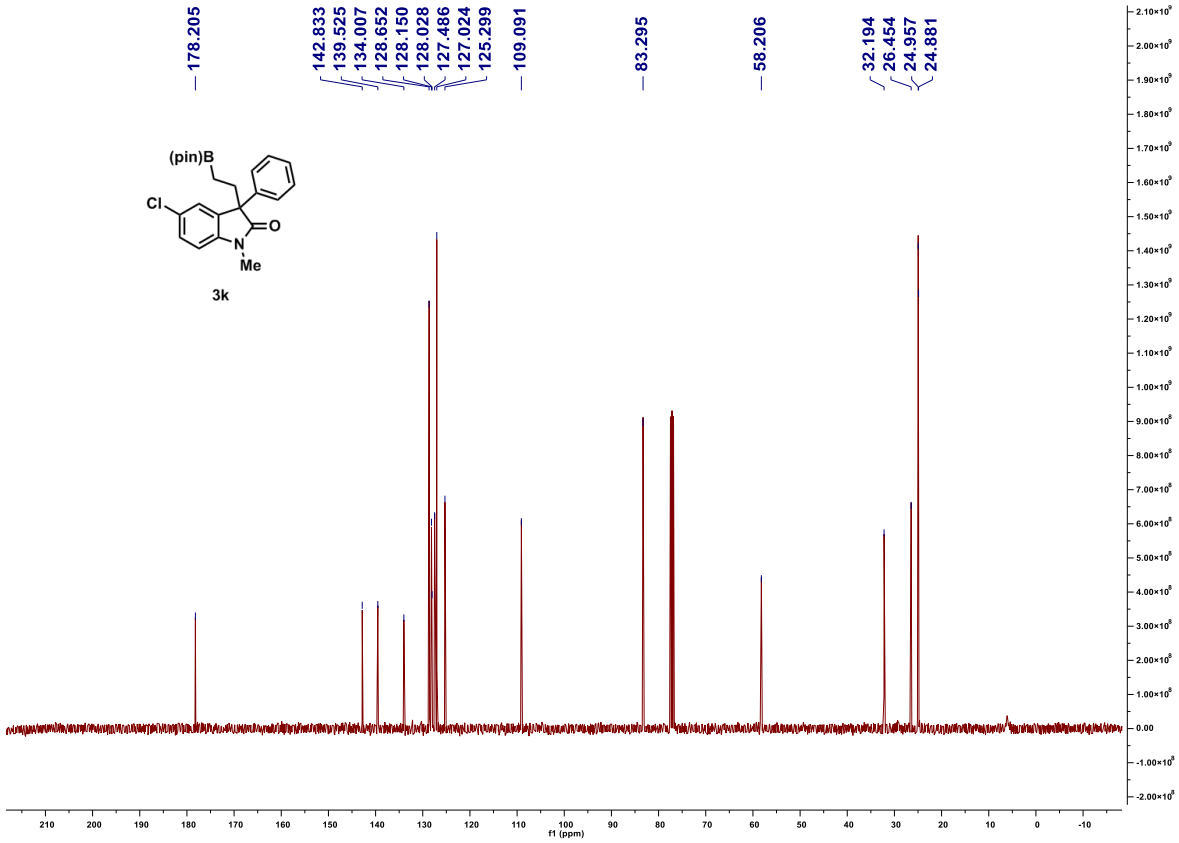
^{11}B NMR-spectrum (128 MHz, $CDCl_3$) of **3j**



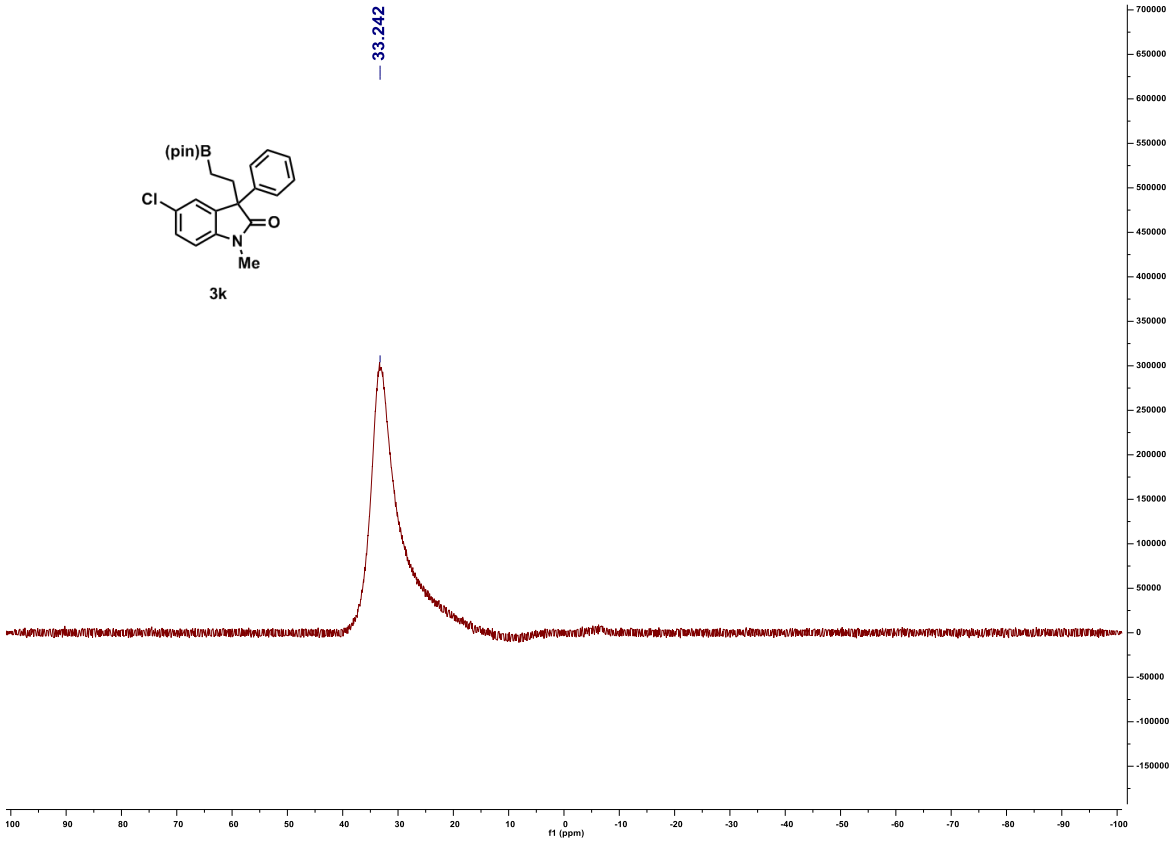
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3k**



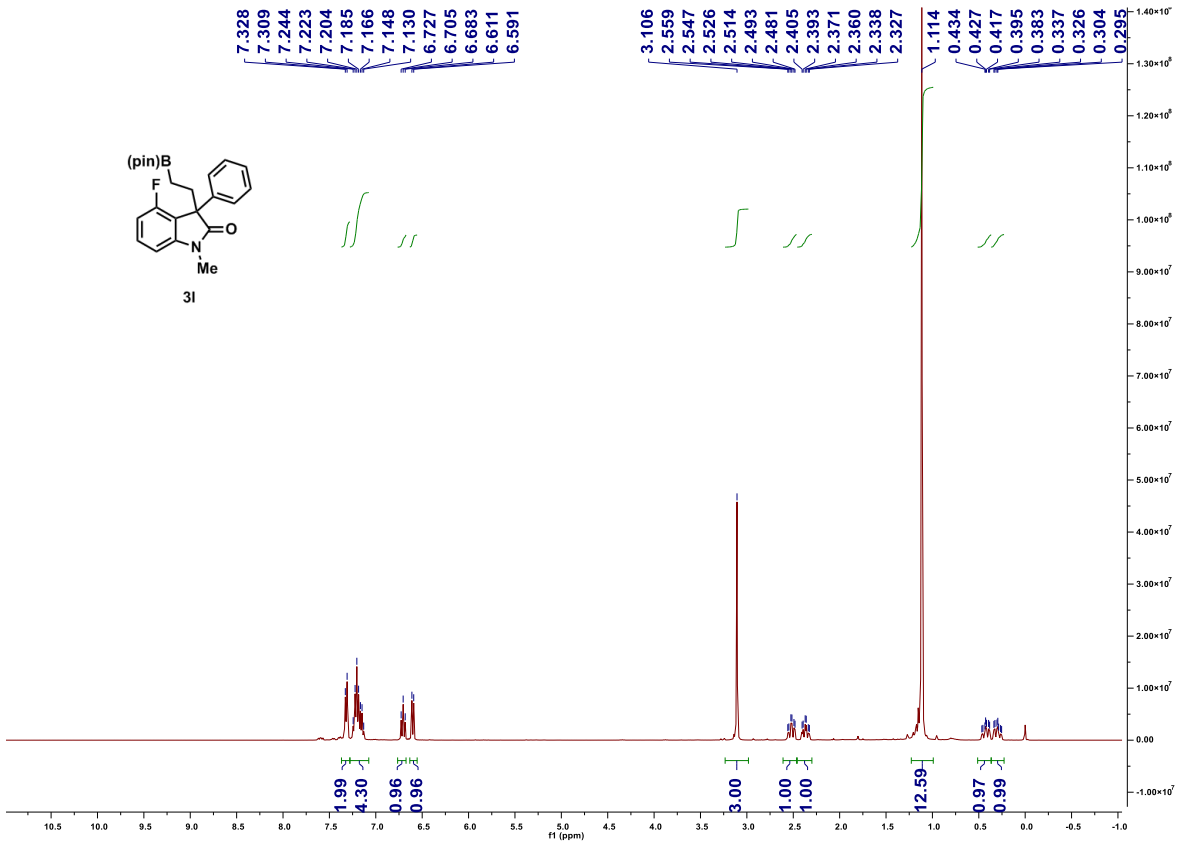
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3k**



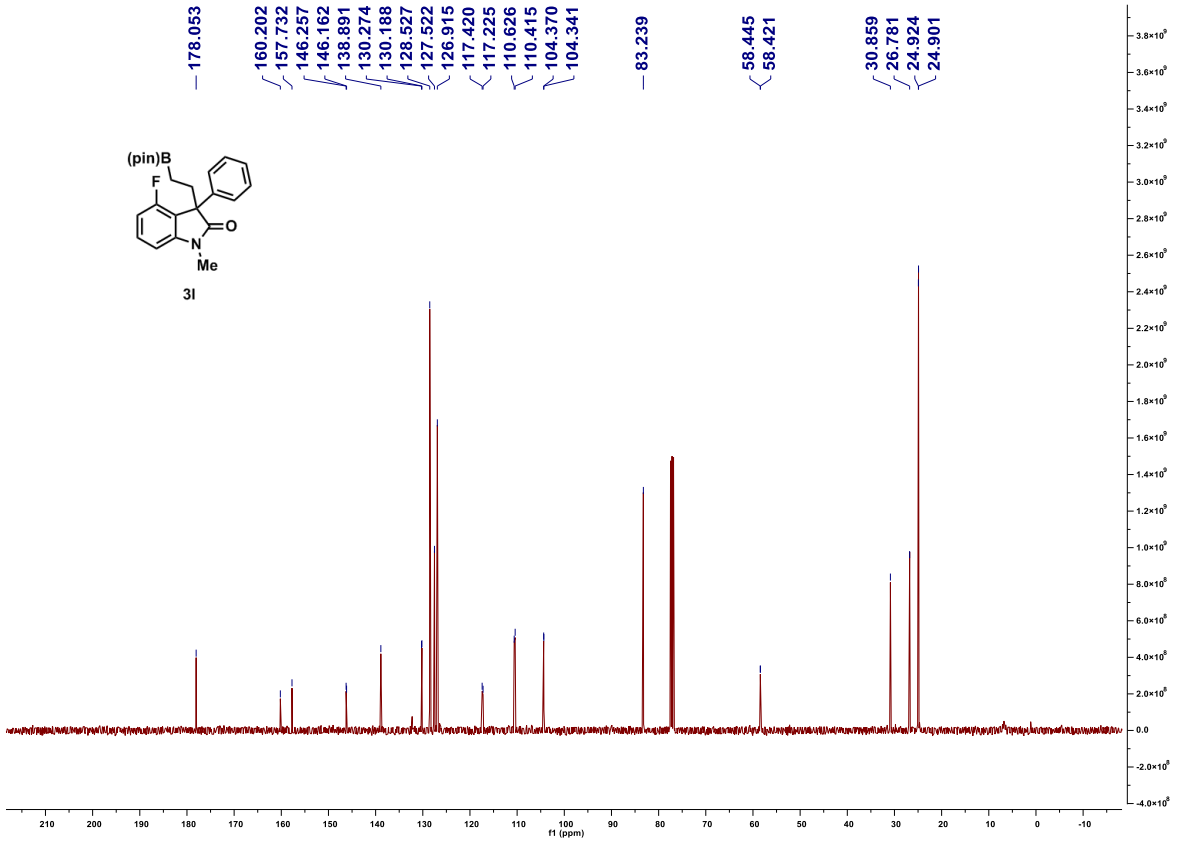
^{11}B NMR-spectrum (128 MHz, $CDCl_3$) of **3k**



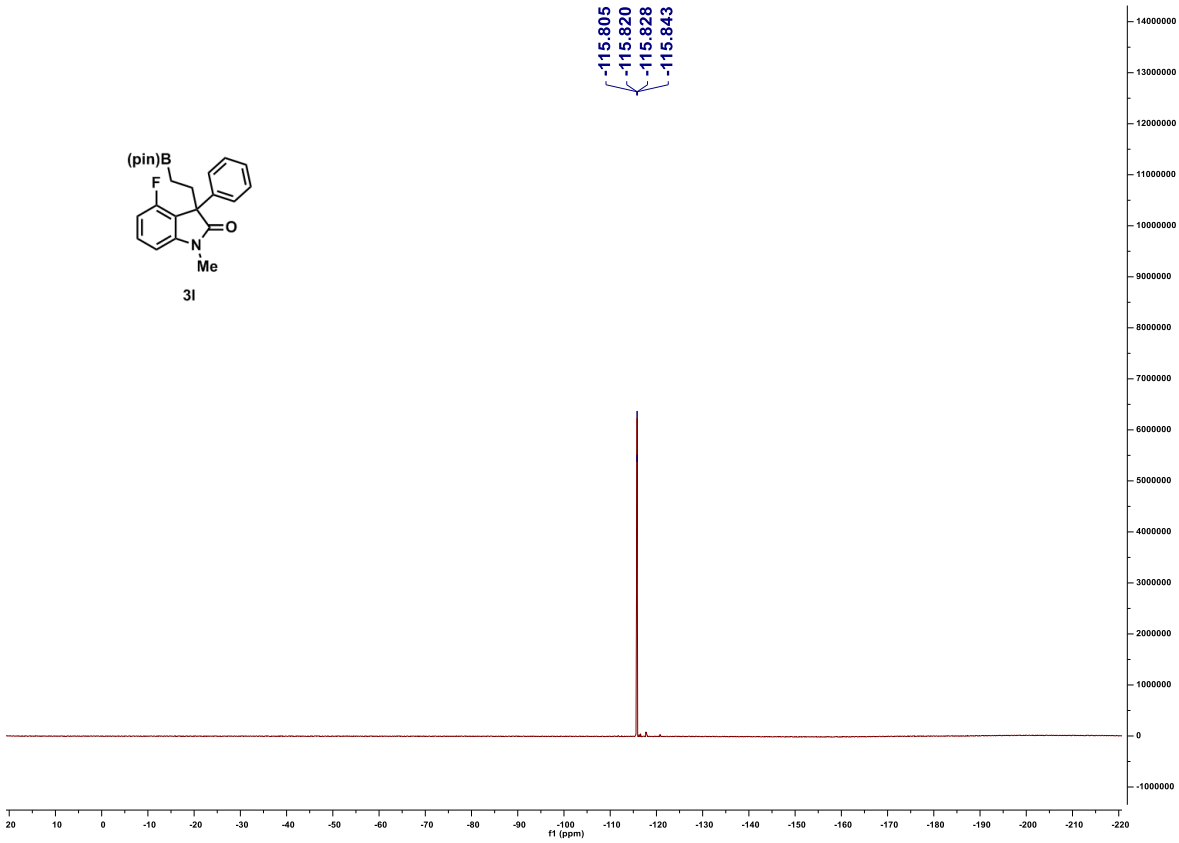
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3l**



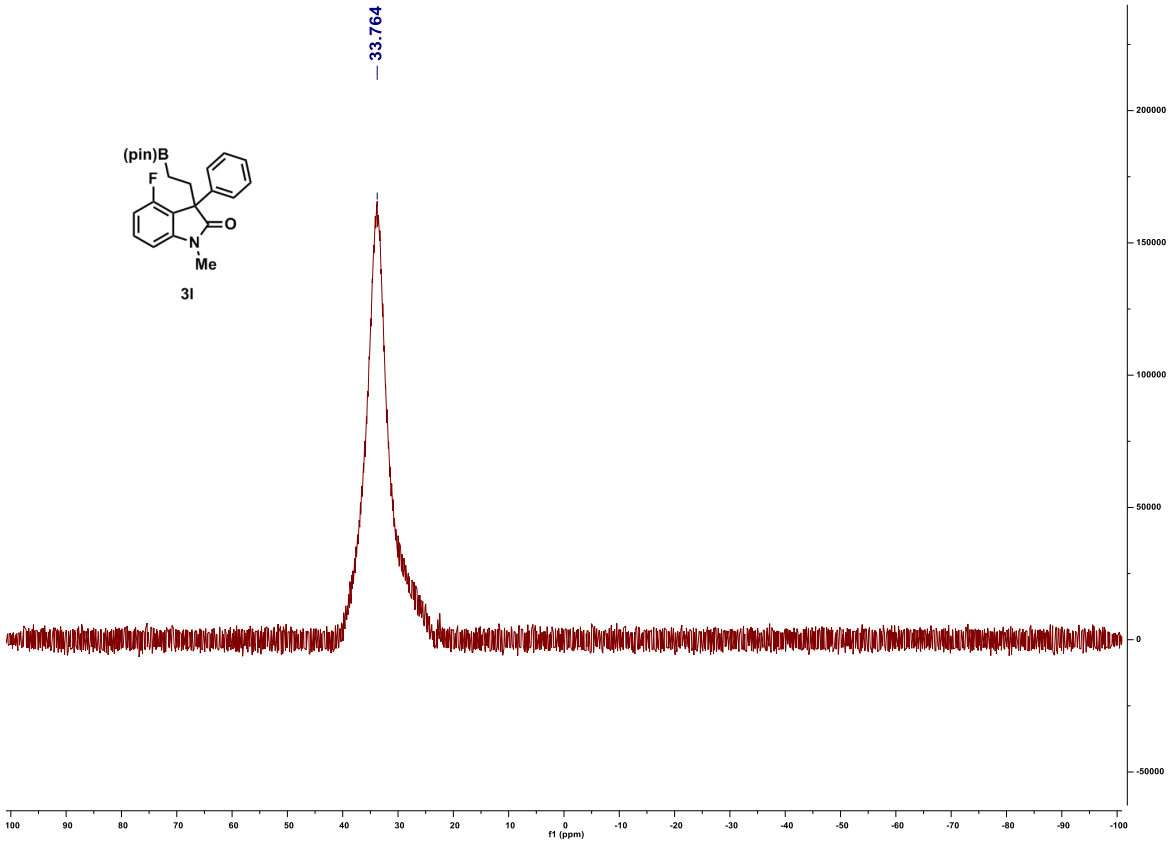
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3l**



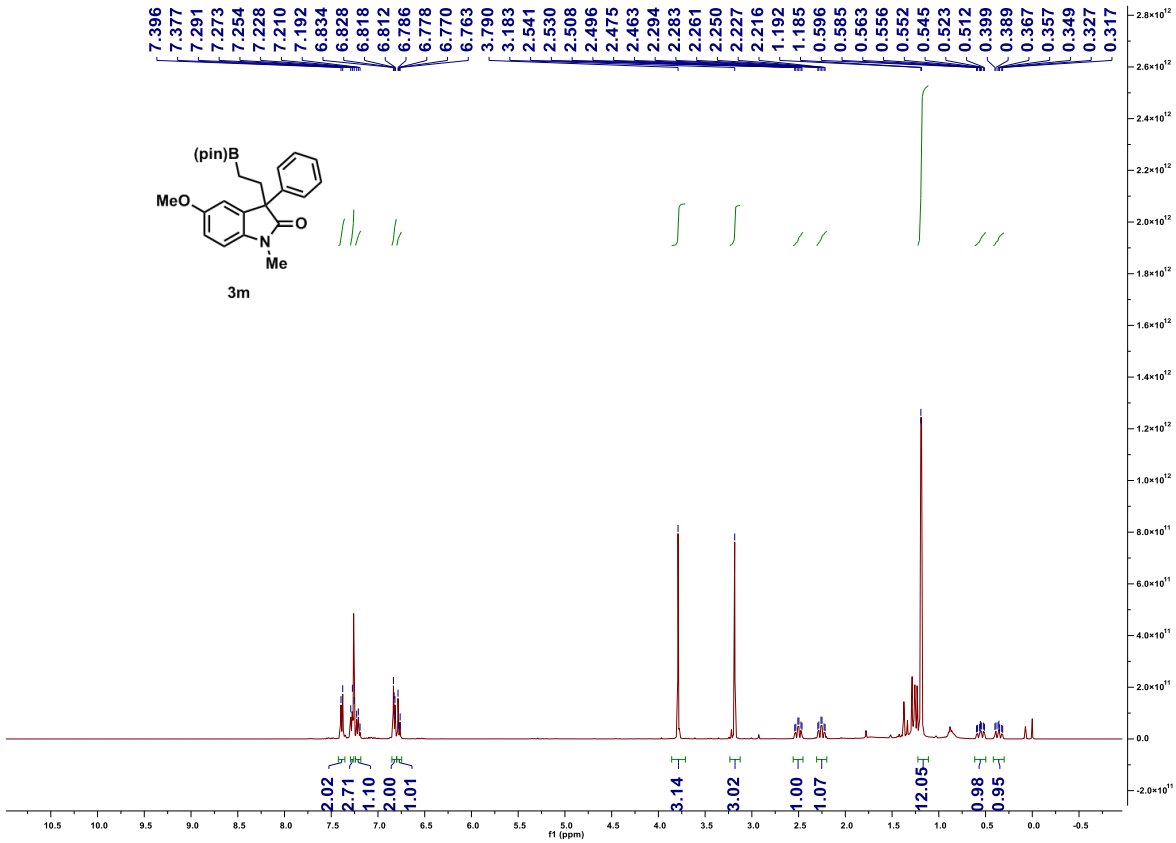
^{19}F NMR-spectrum (376 MHz, $CDCl_3$) of **3l**



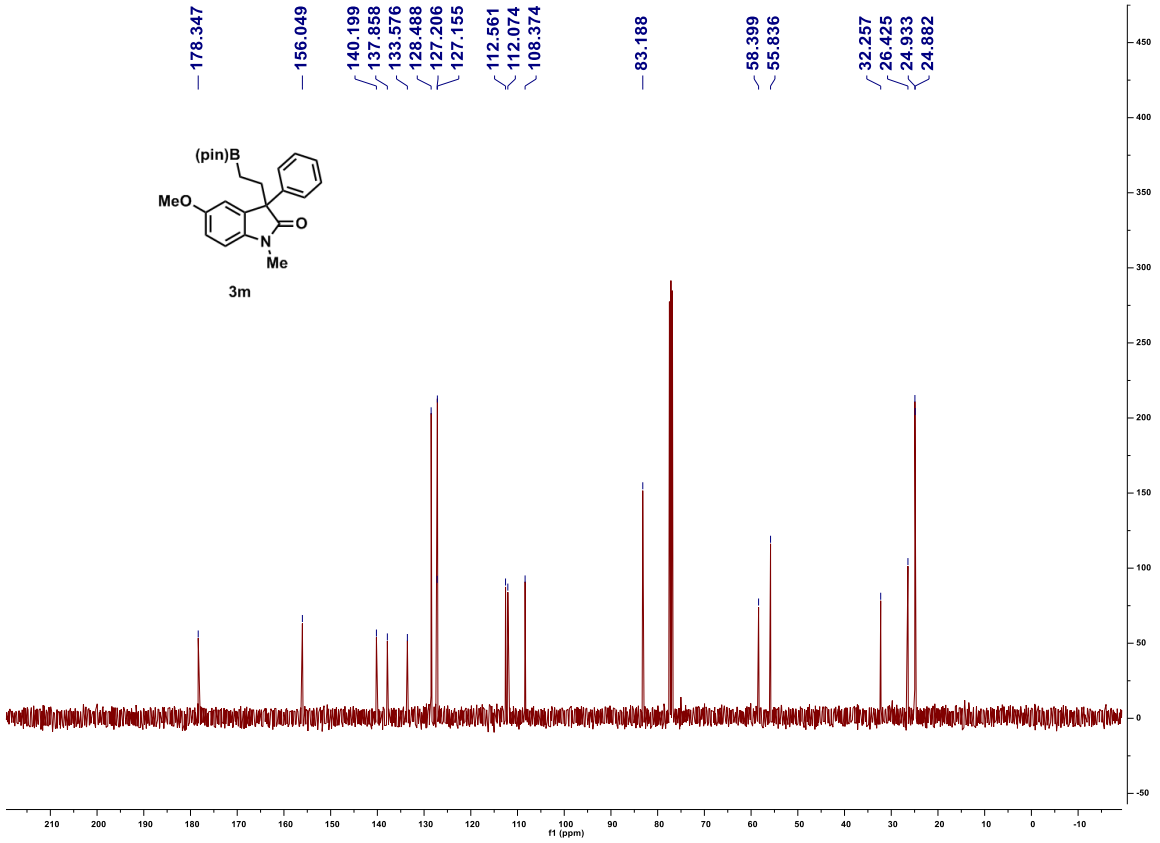
^{11}B NMR-spectrum (128 MHz, $CDCl_3$) of **3l**



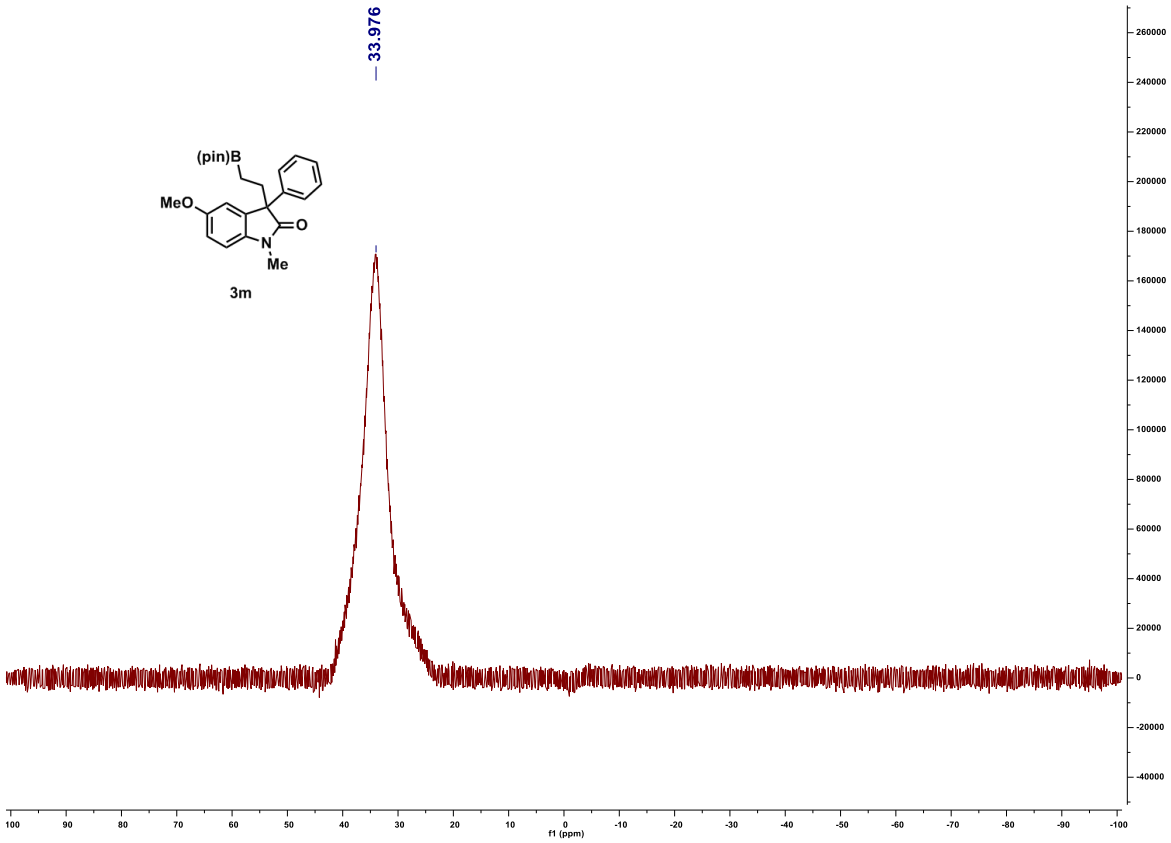
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3m**



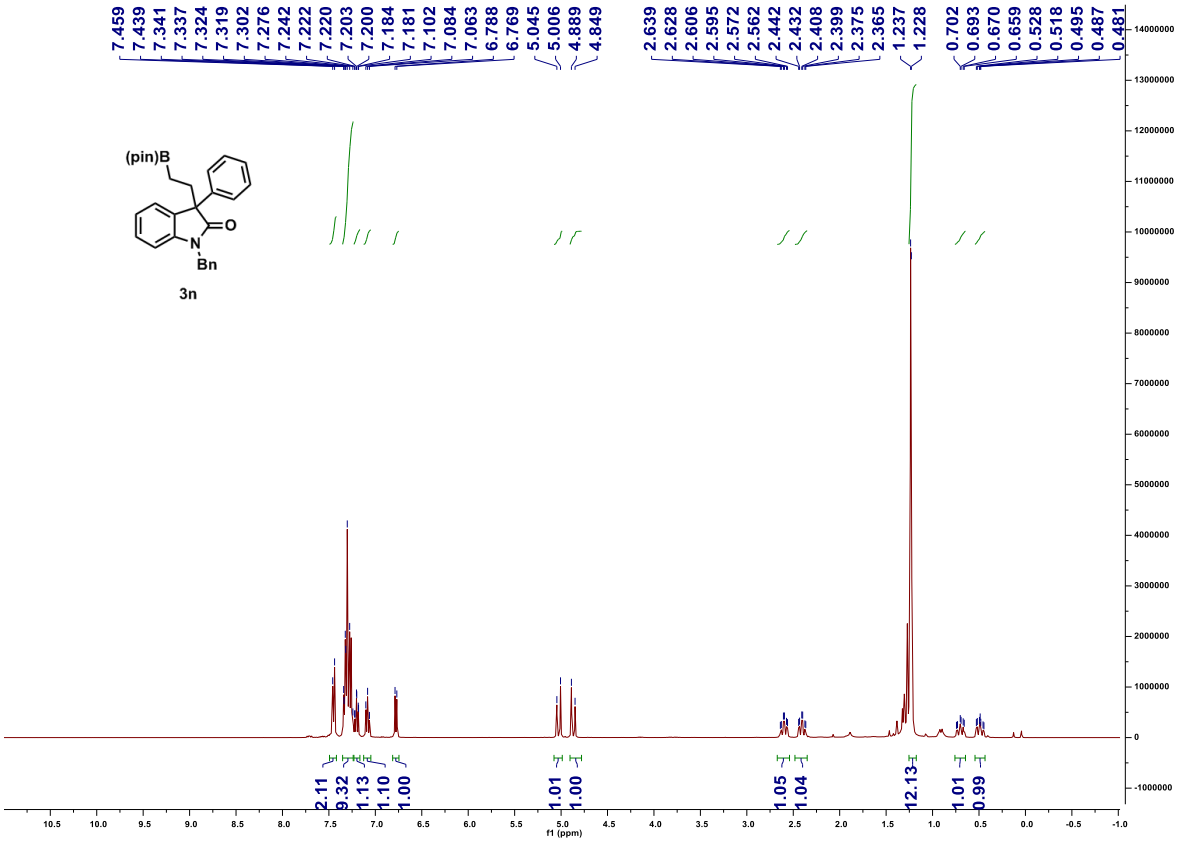
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3m**



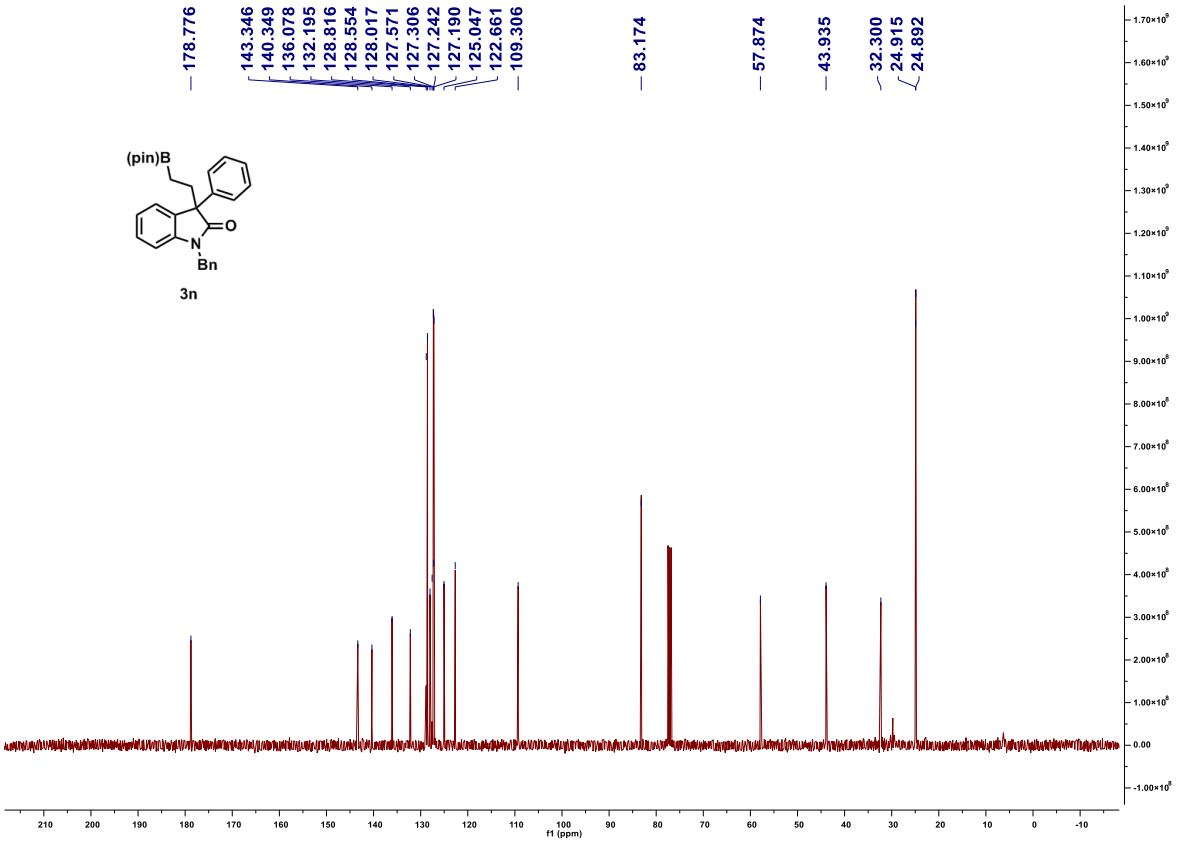
^{11}B NMR-spectrum (128 MHz, $CDCl_3$) of **3m**



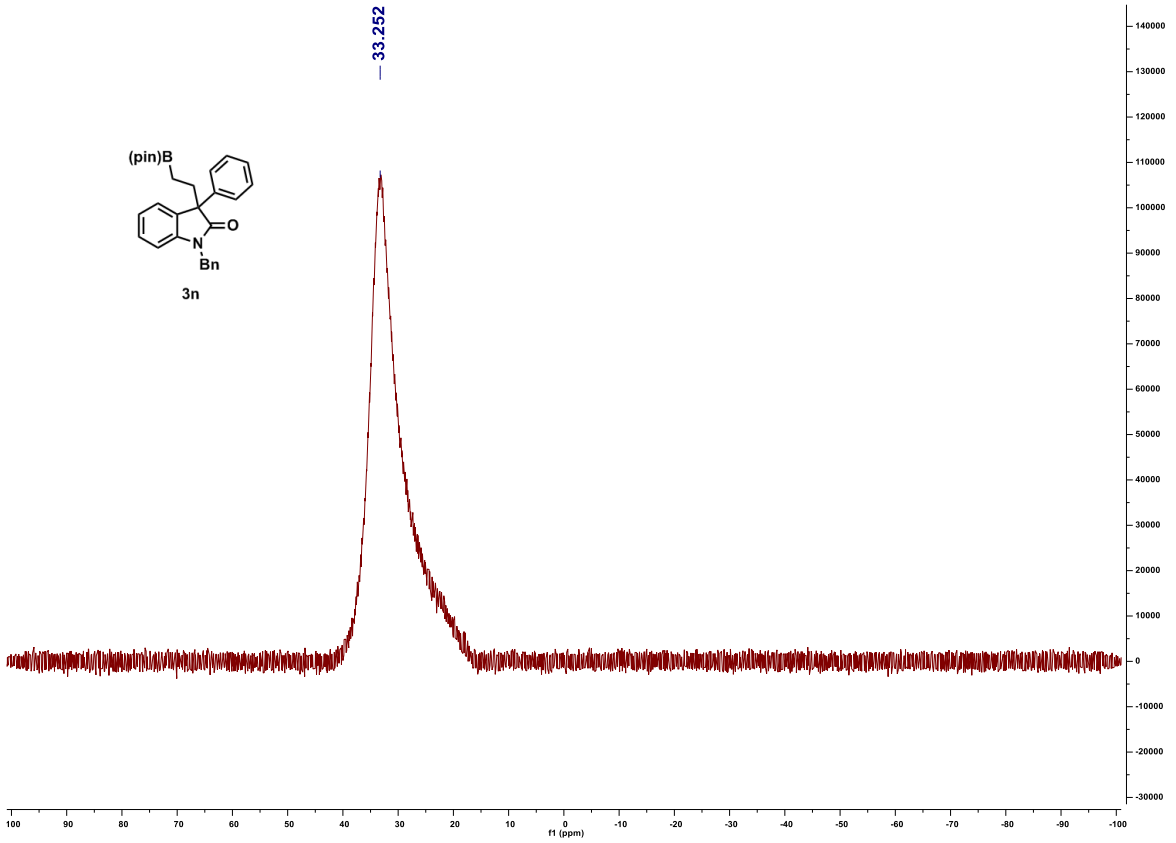
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3n**



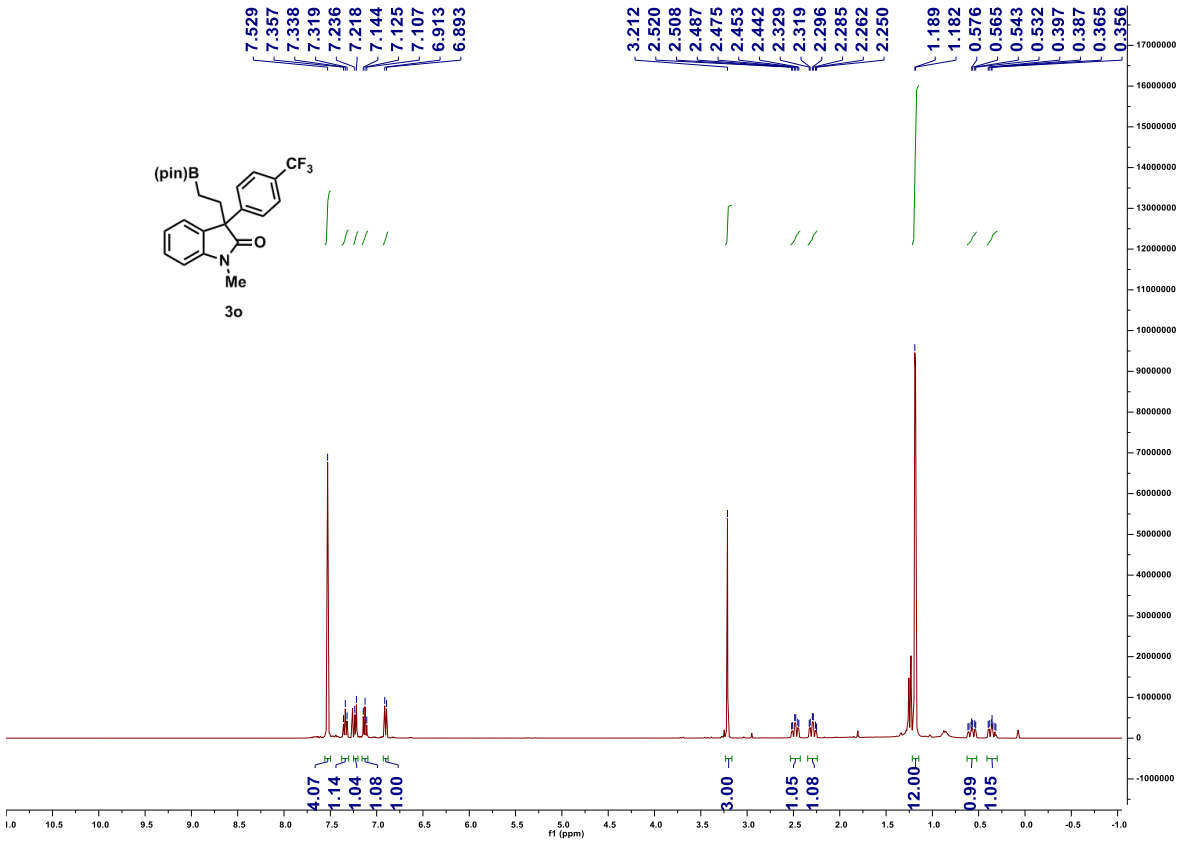
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3n**



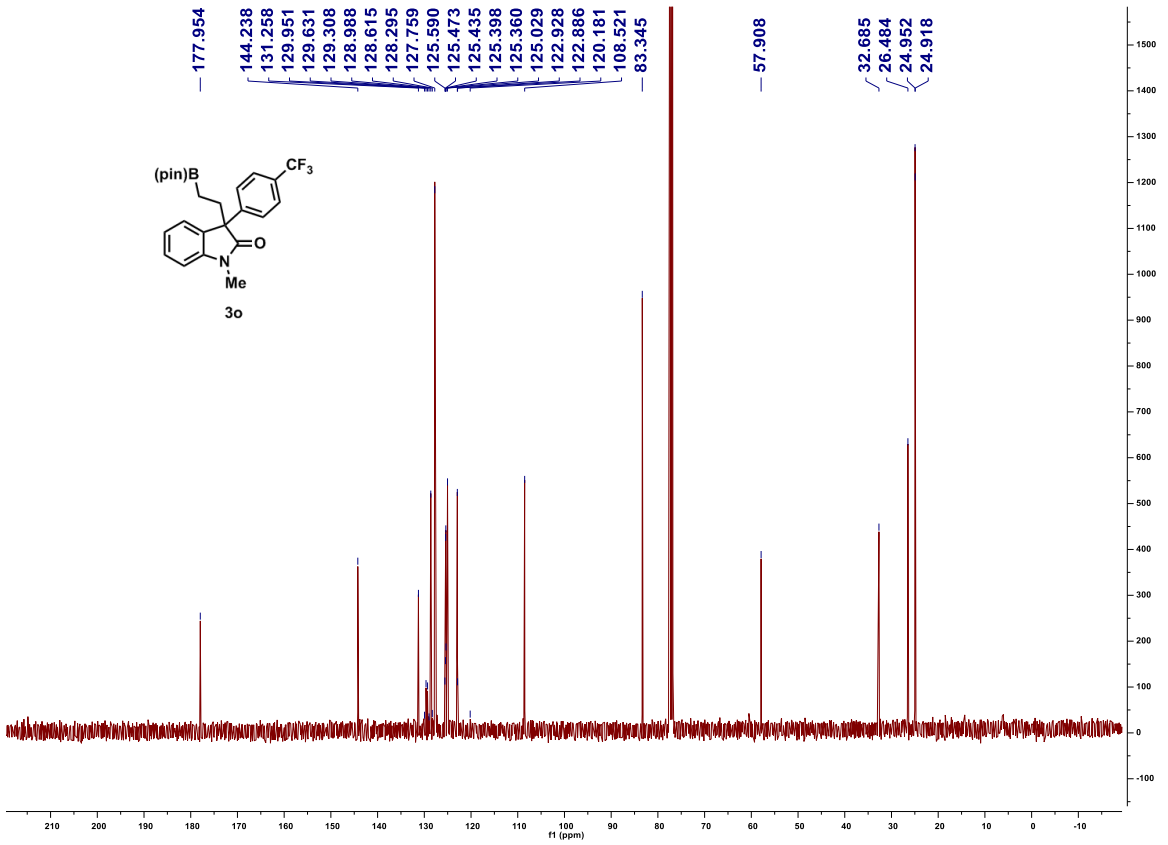
^{11}B NMR-spectrum (128 MHz, $CDCl_3$) of **3n**



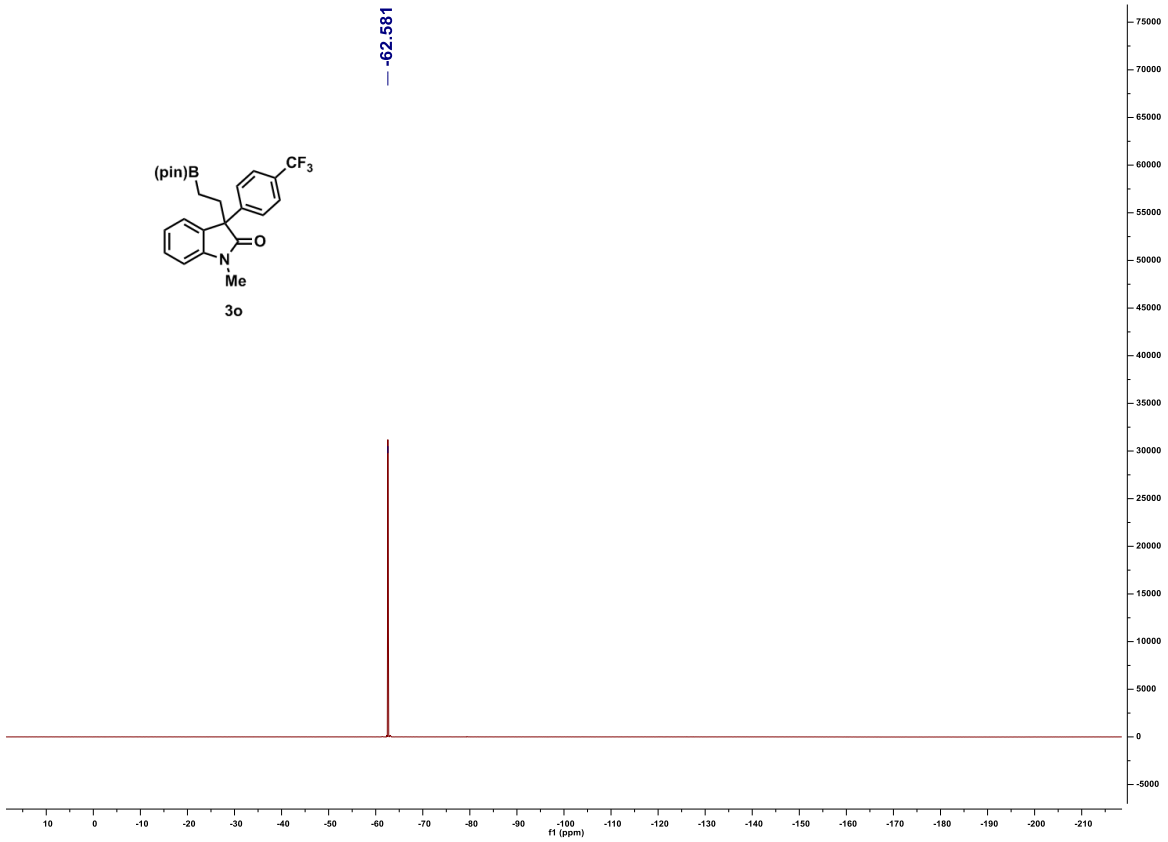
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3o**



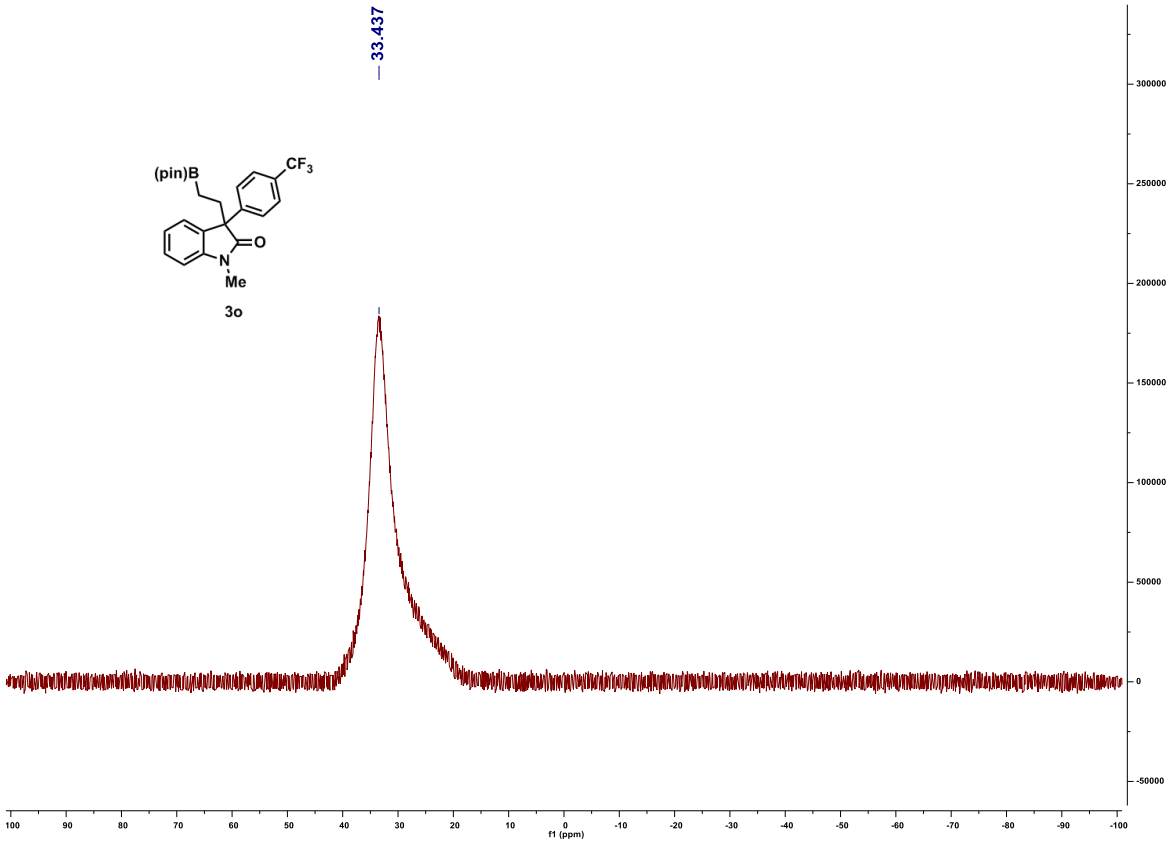
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3o**



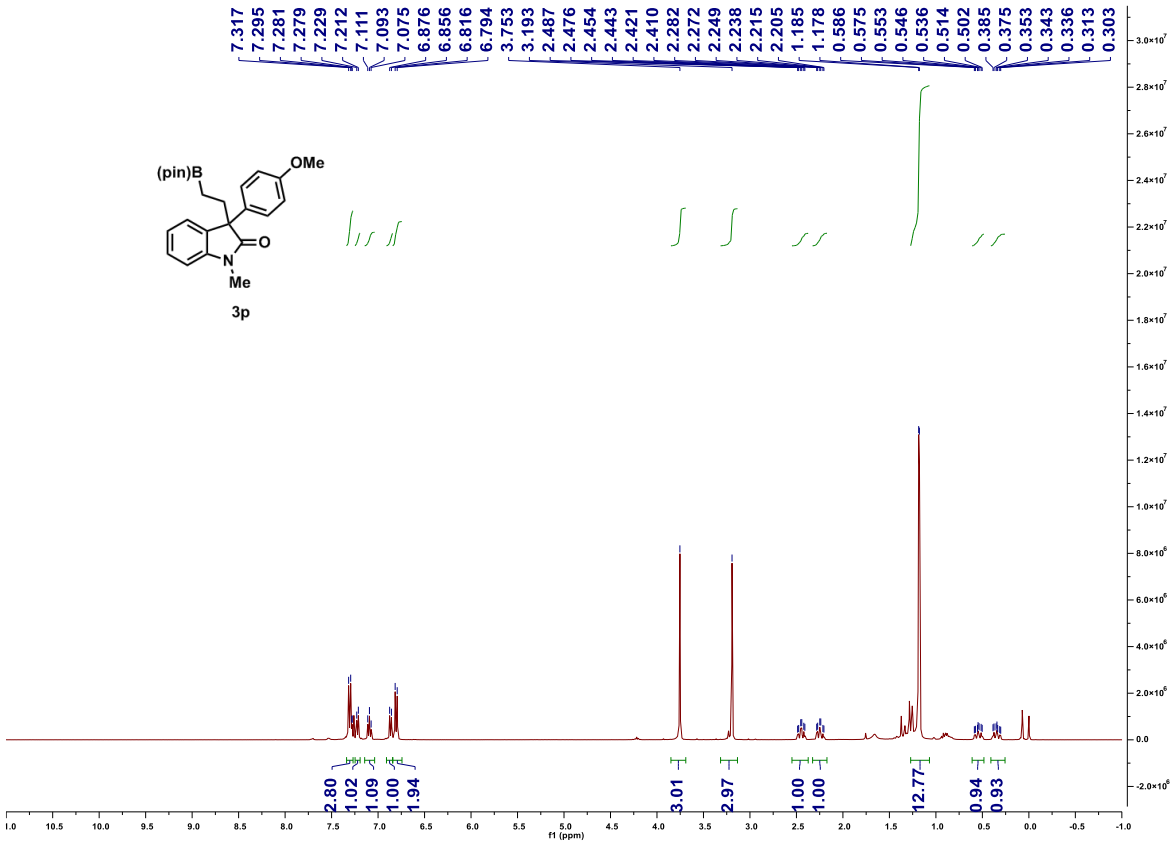
^{19}F NMR-spectrum (376 MHz, $CDCl_3$) of **3o**



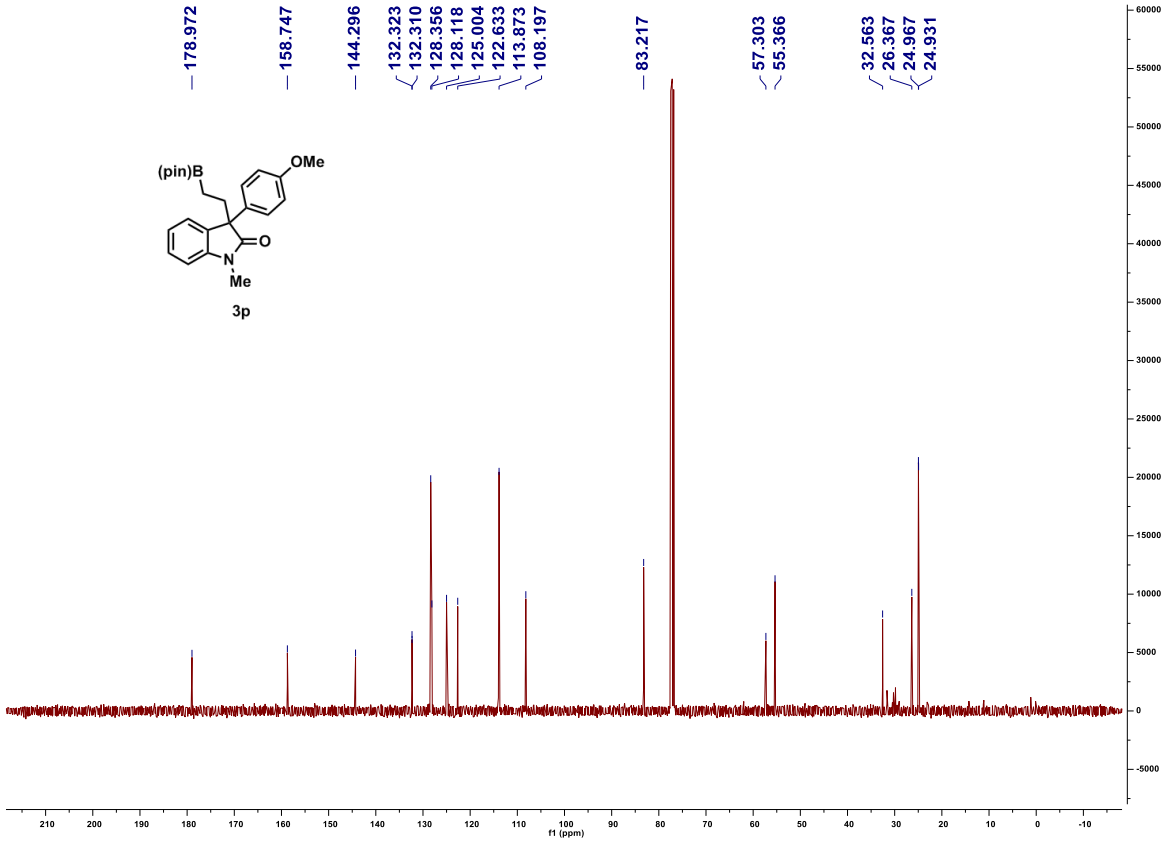
^{11}B NMR-spectrum (128 MHz, $CDCl_3$) of **3o**



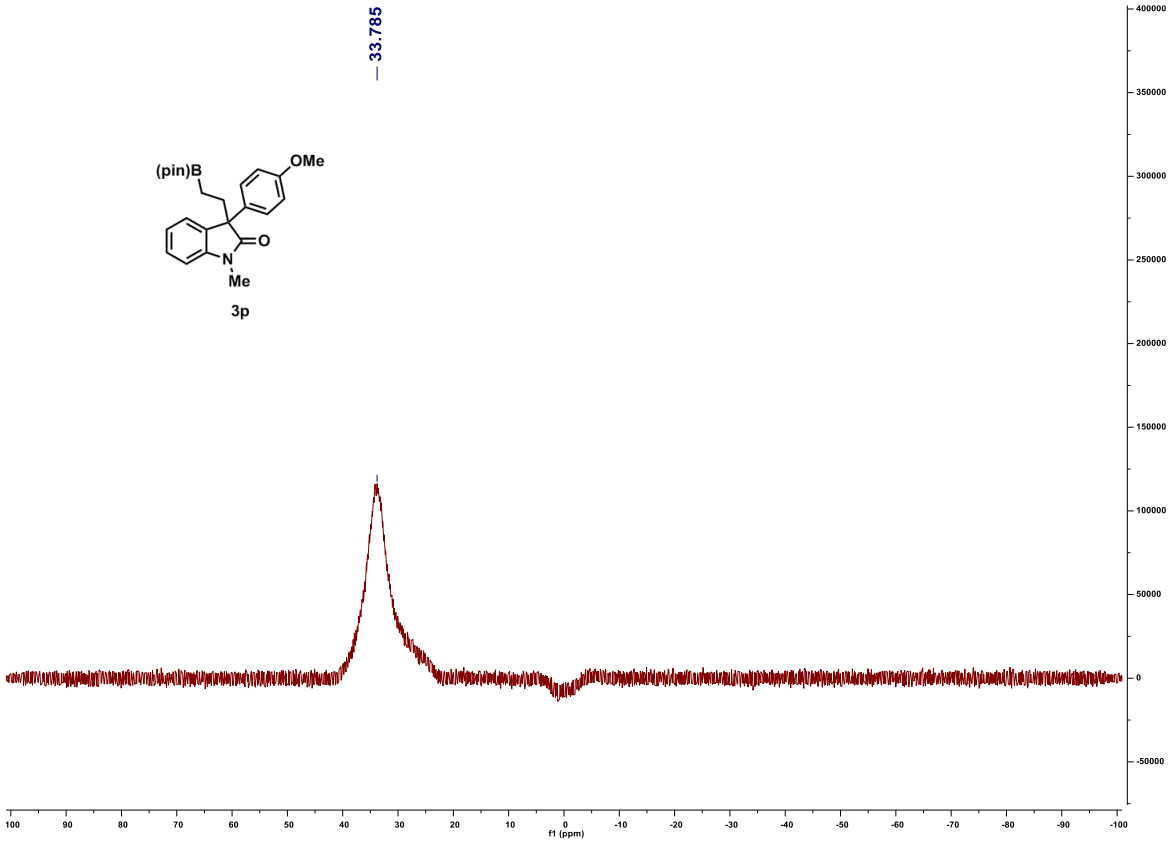
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3p**



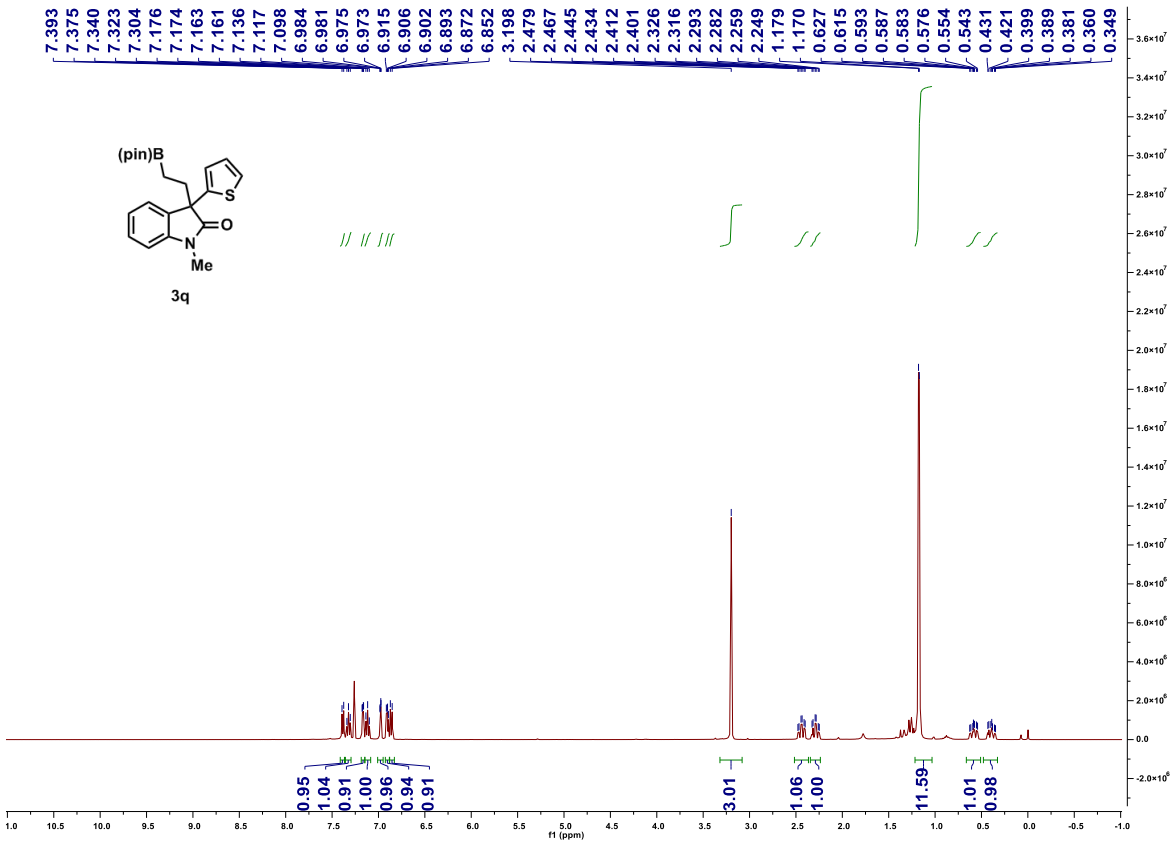
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3p**



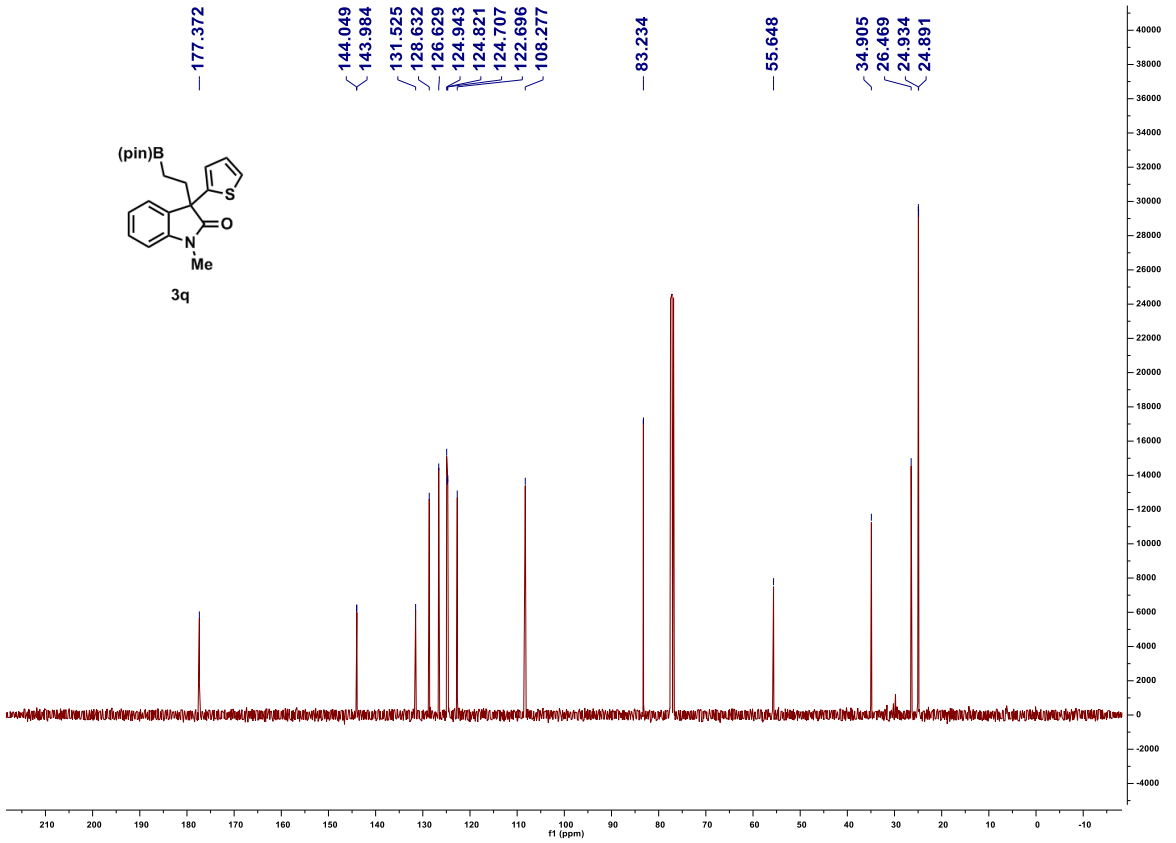
^{11}B NMR-spectrum (128 MHz, $CDCl_3$) of **3p**



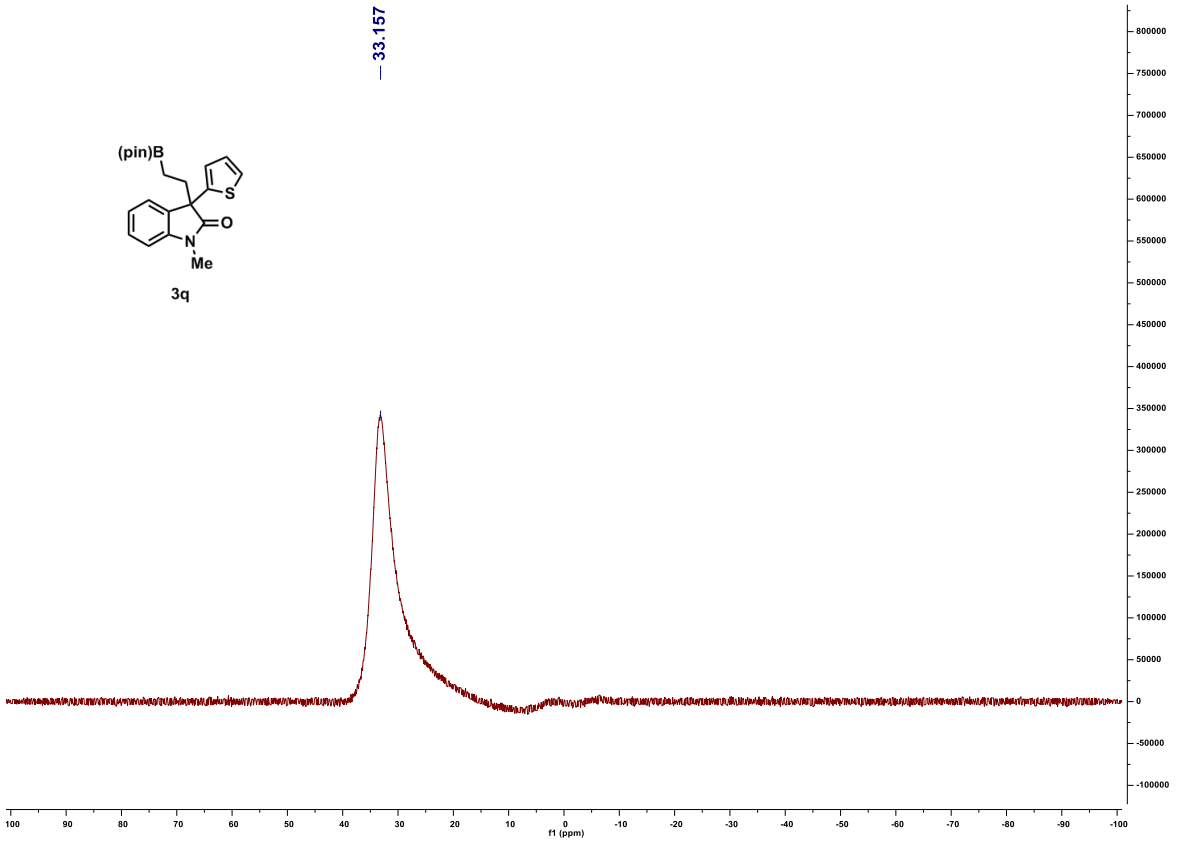
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3q**



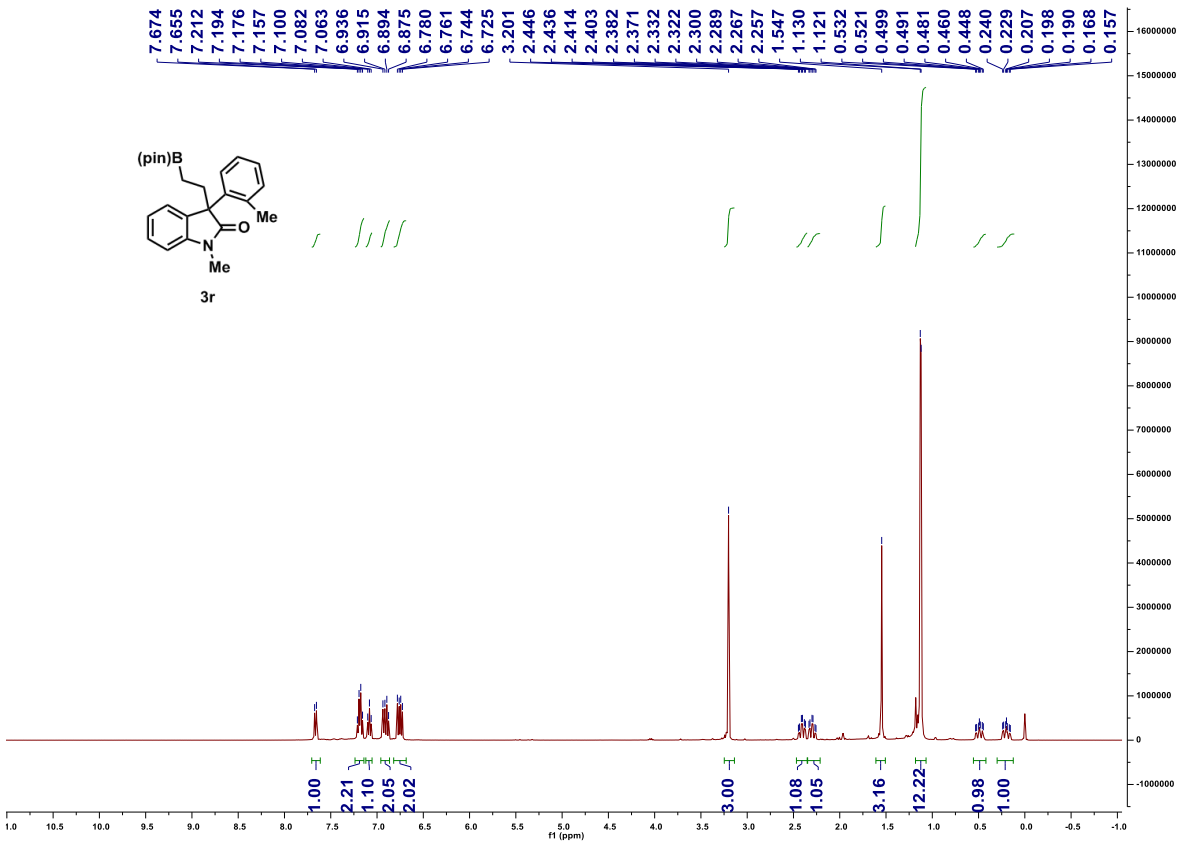
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3q**



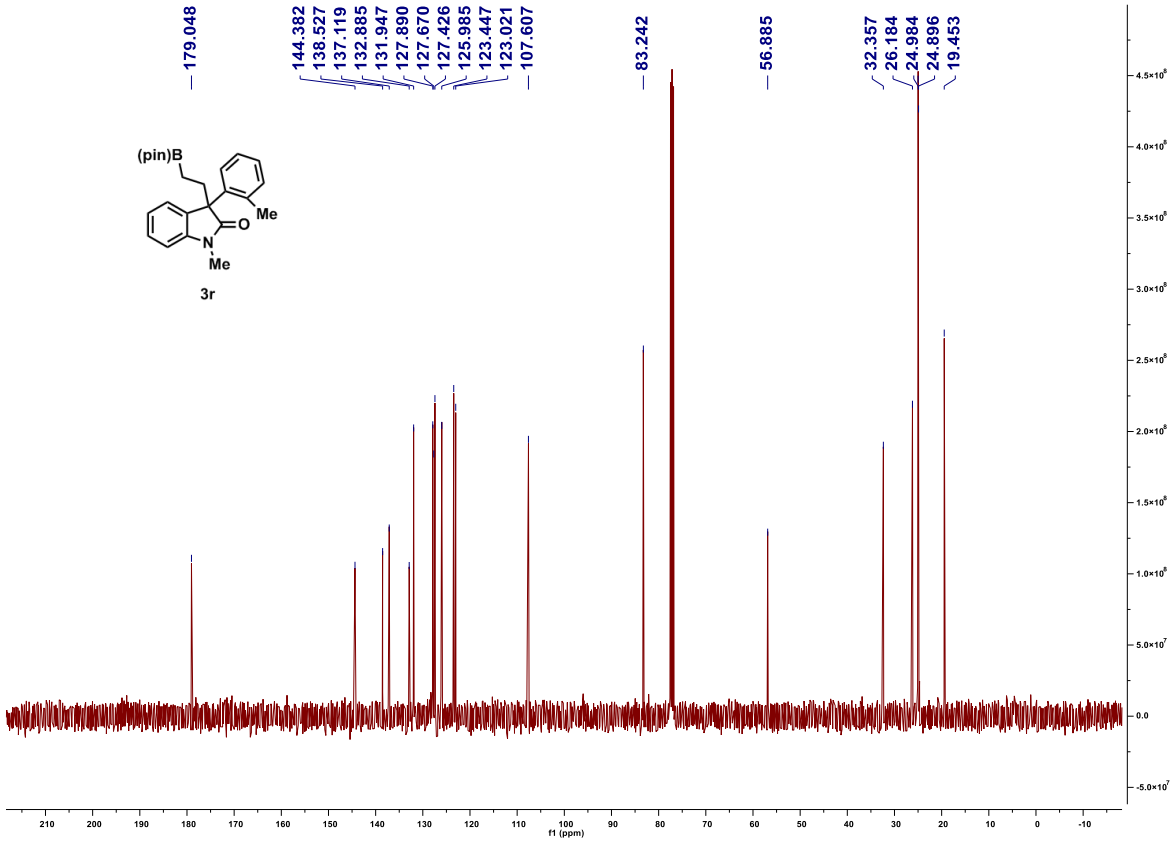
^{11}B NMR-spectrum (128 MHz, $CDCl_3$) of **3q**



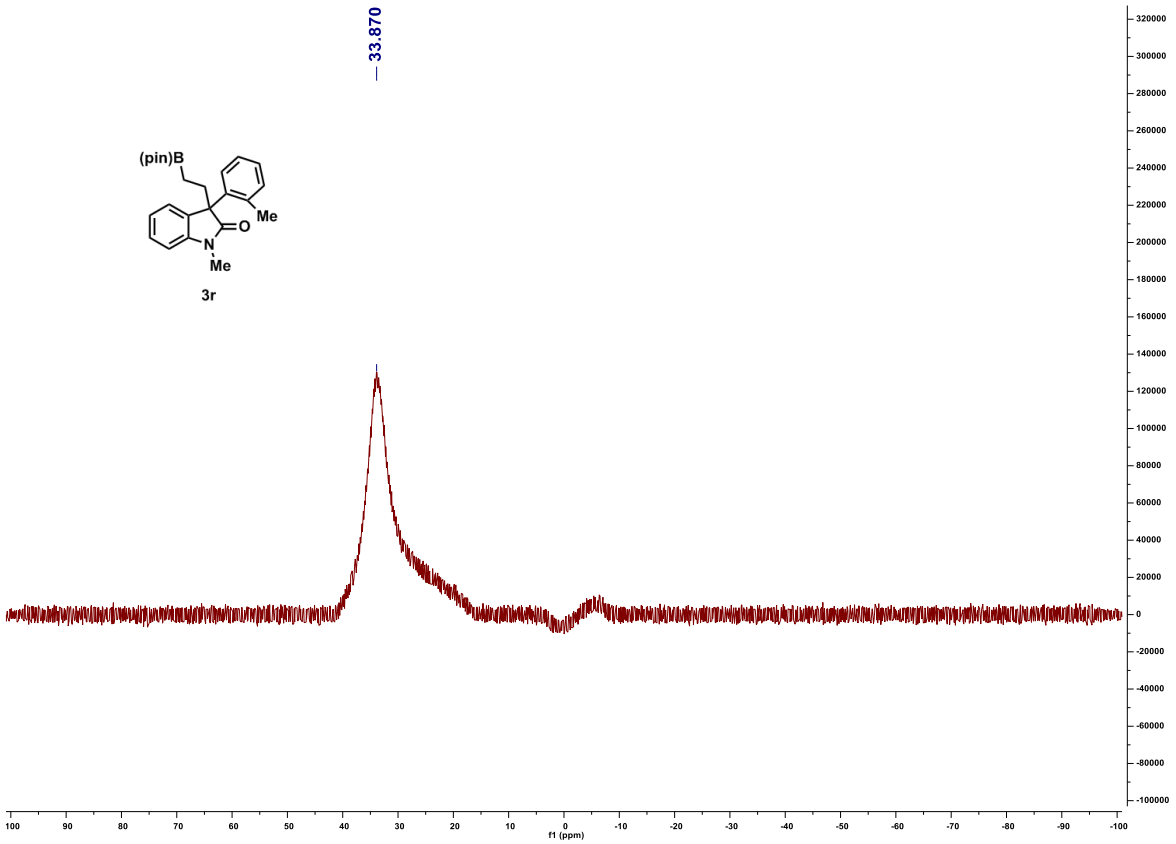
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3r**



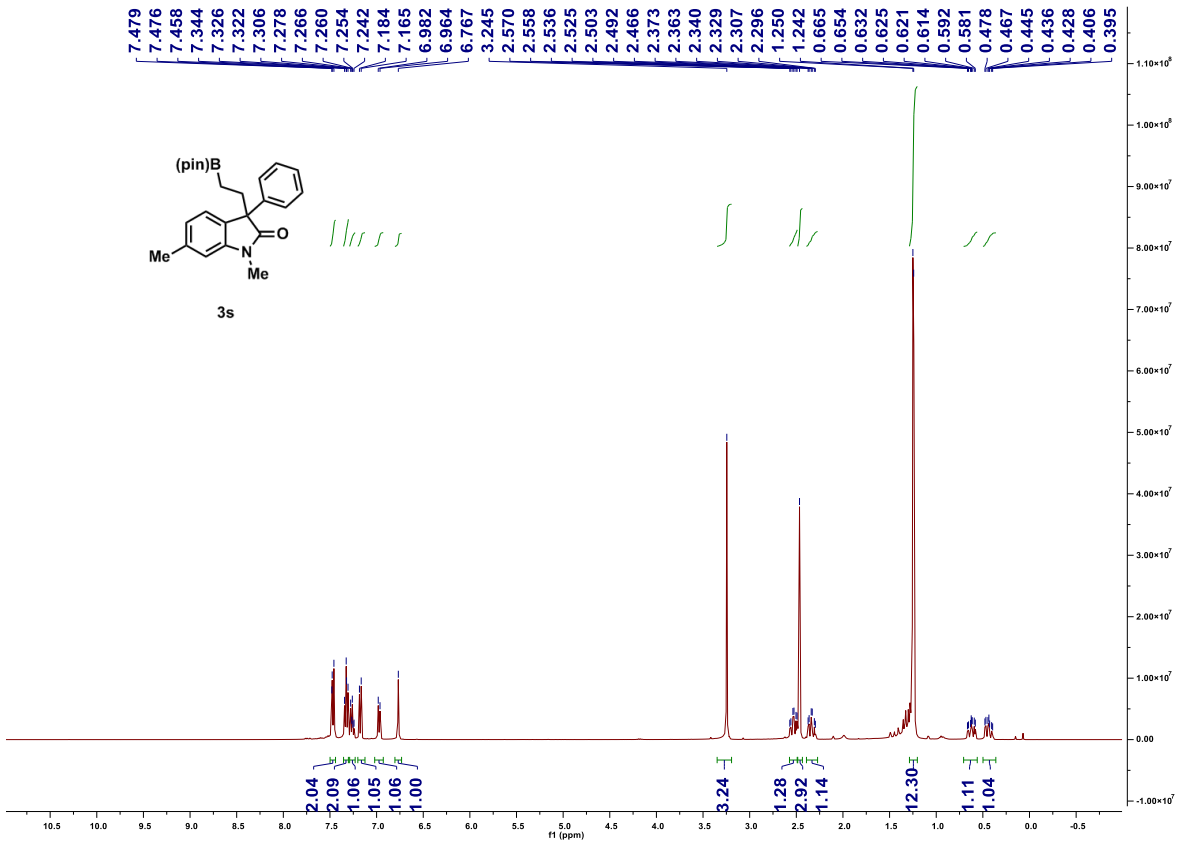
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3r**



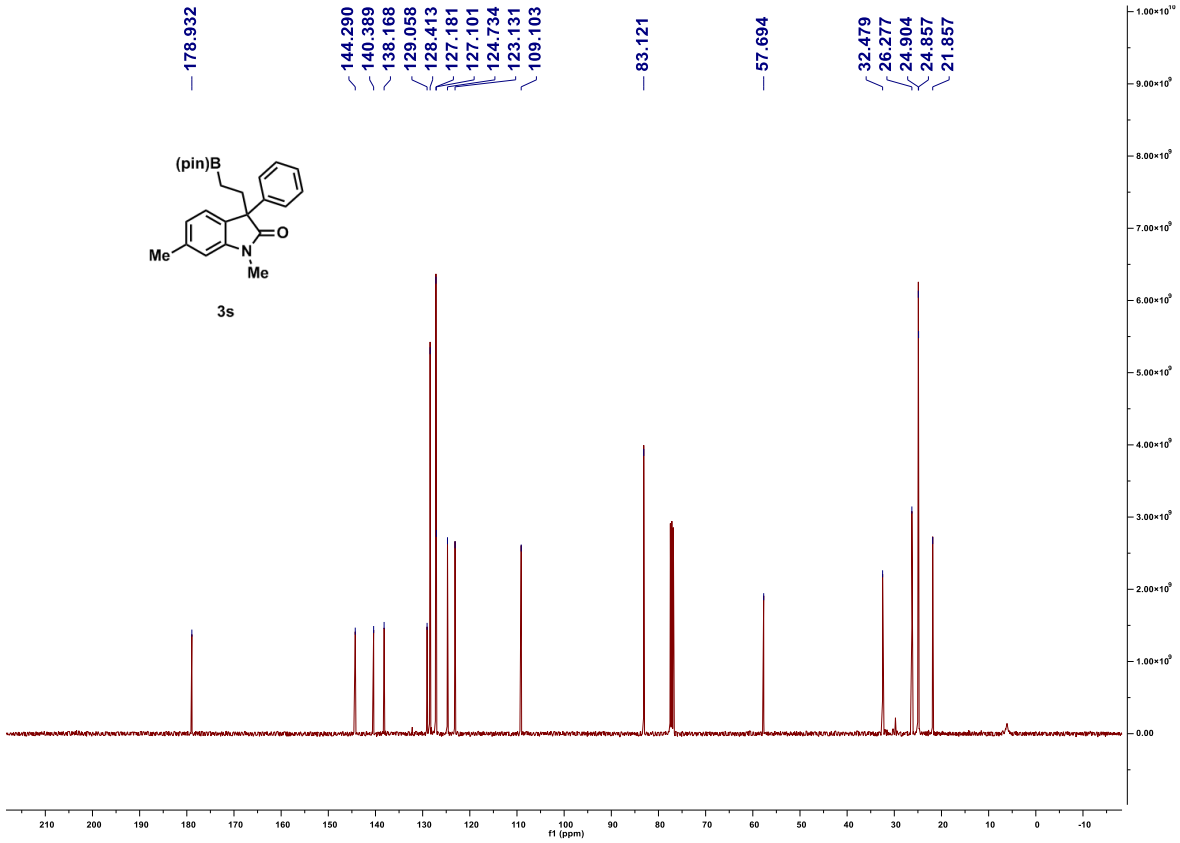
^{11}B NMR-spectrum (128 MHz, $CDCl_3$) of **3r**



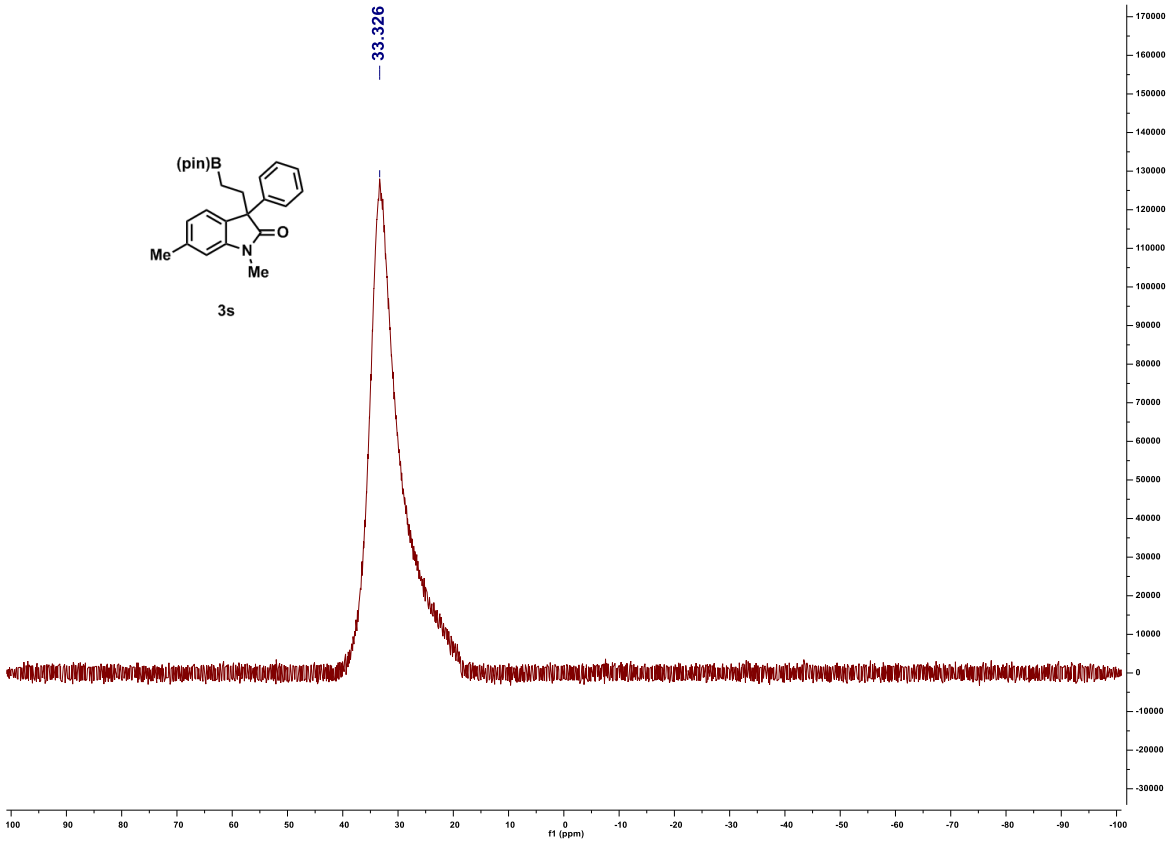
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3s**



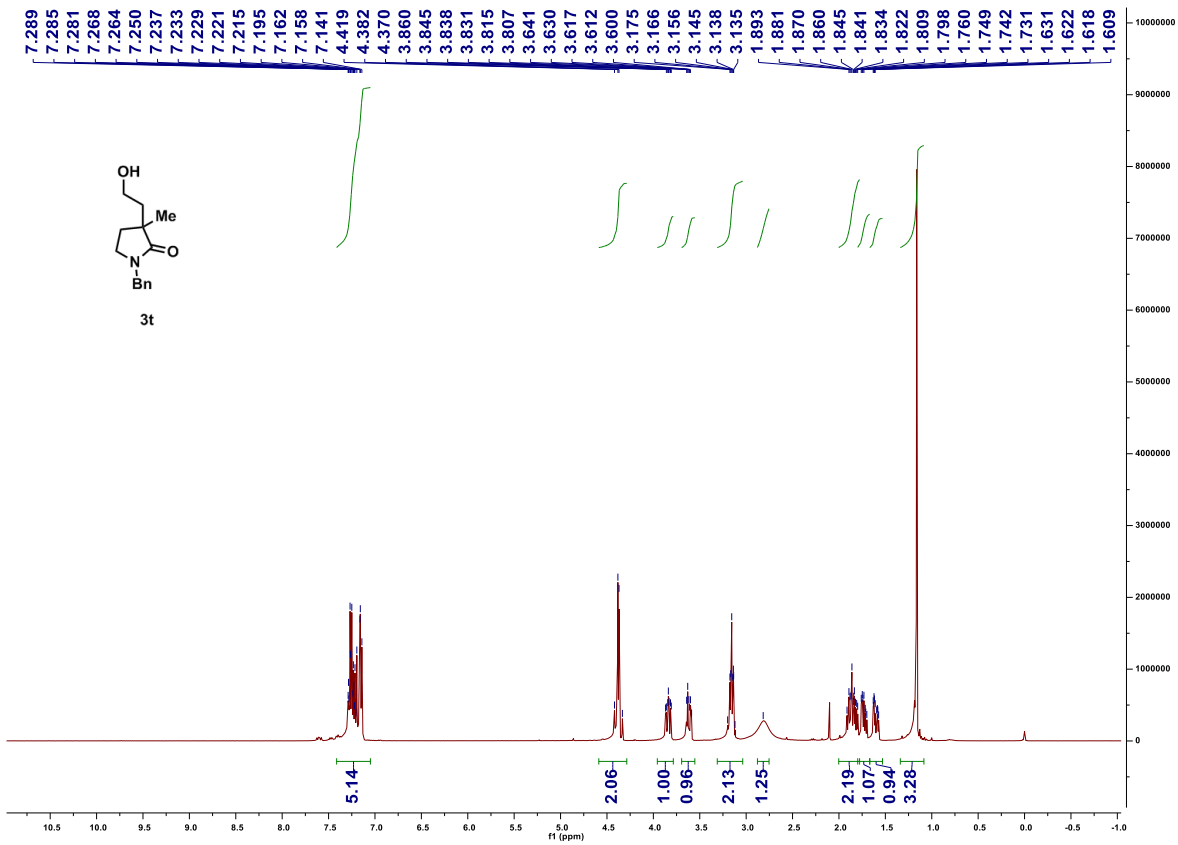
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3s**



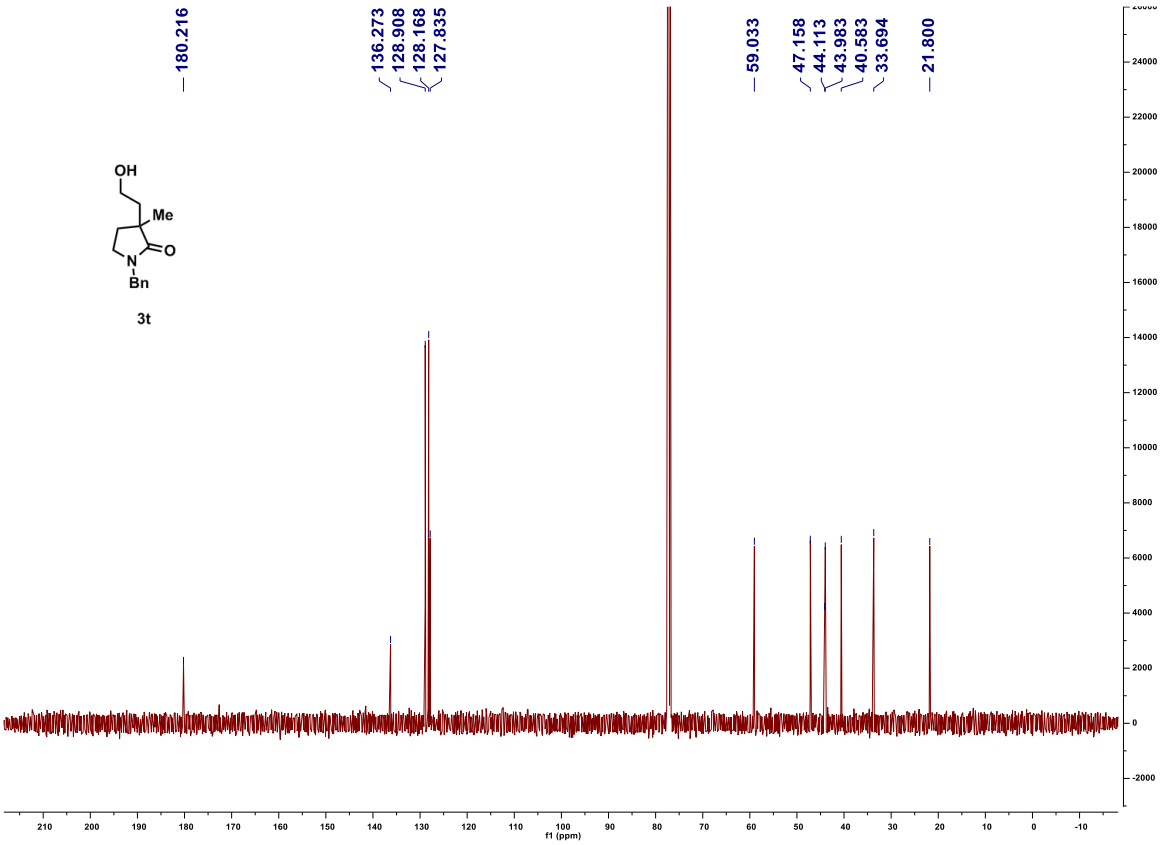
^{11}B NMR-spectrum (128 MHz, $CDCl_3$) of **3s**



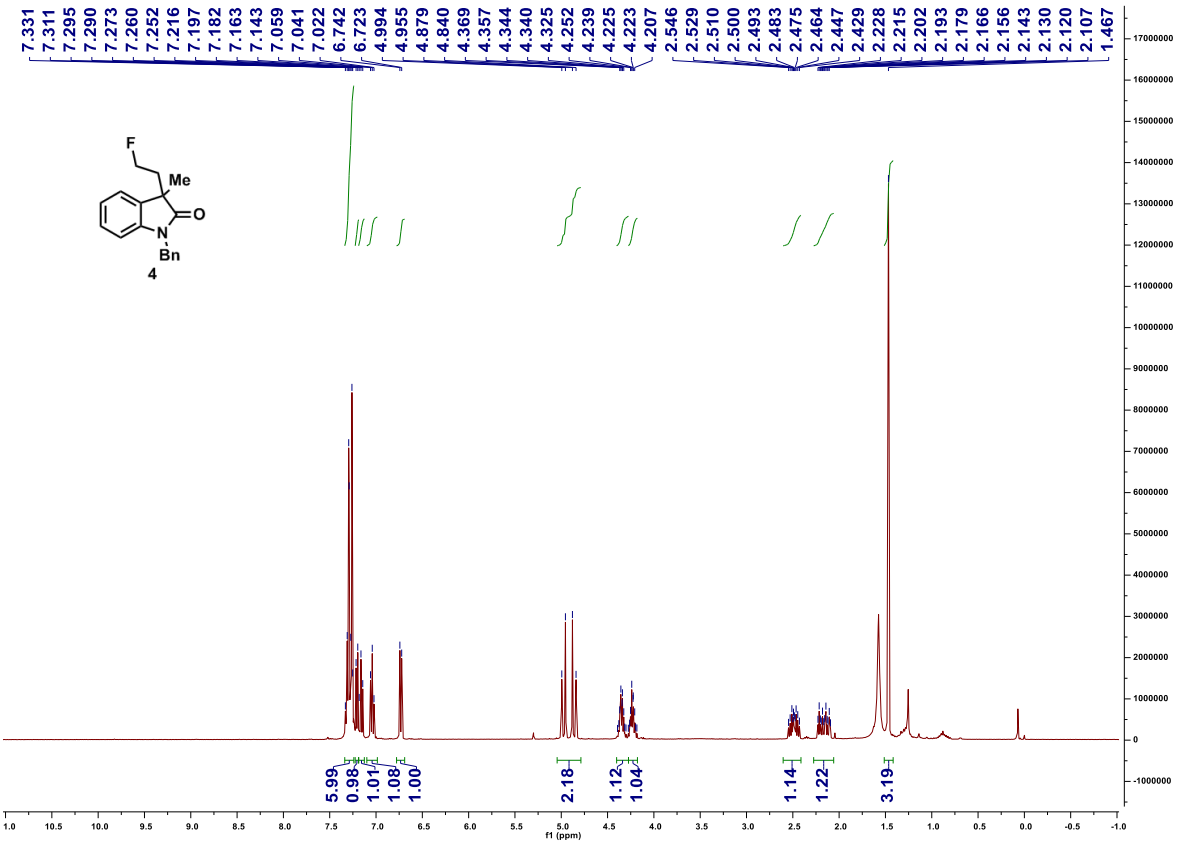
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3t**



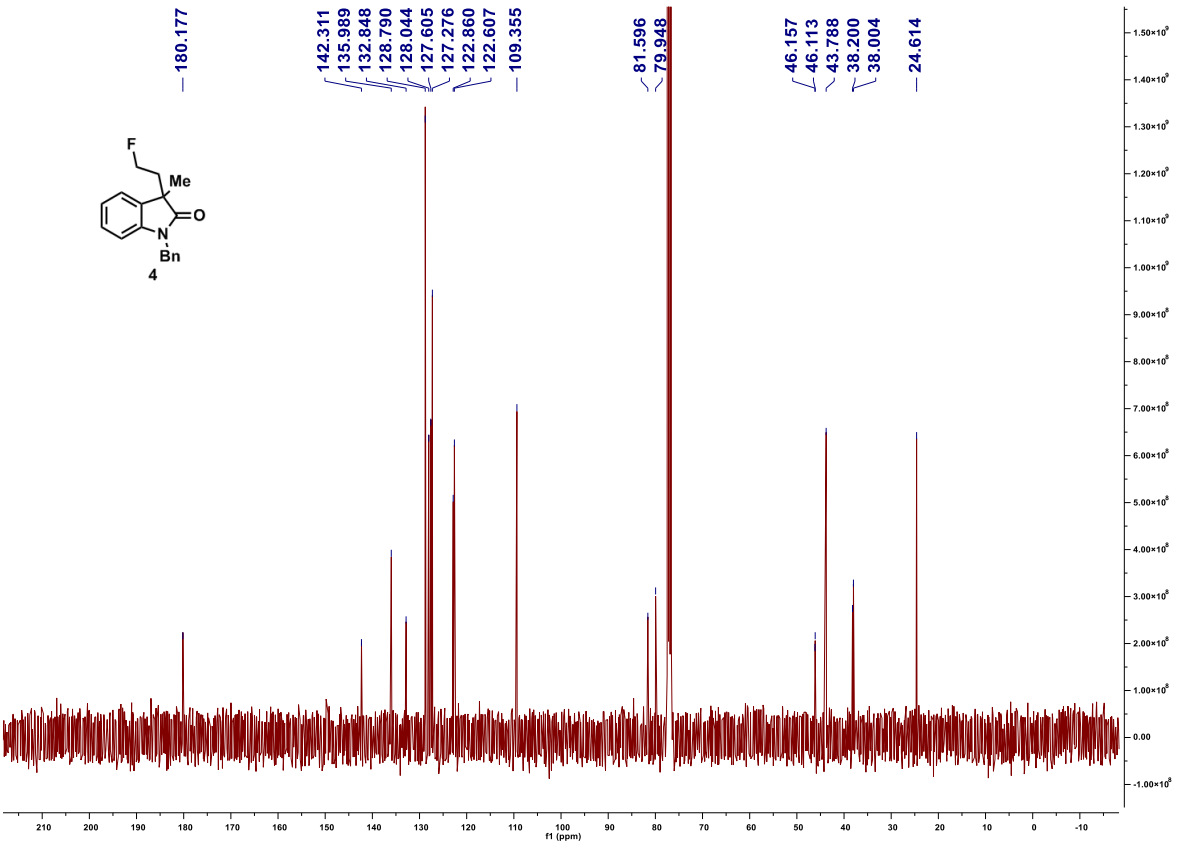
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3t**



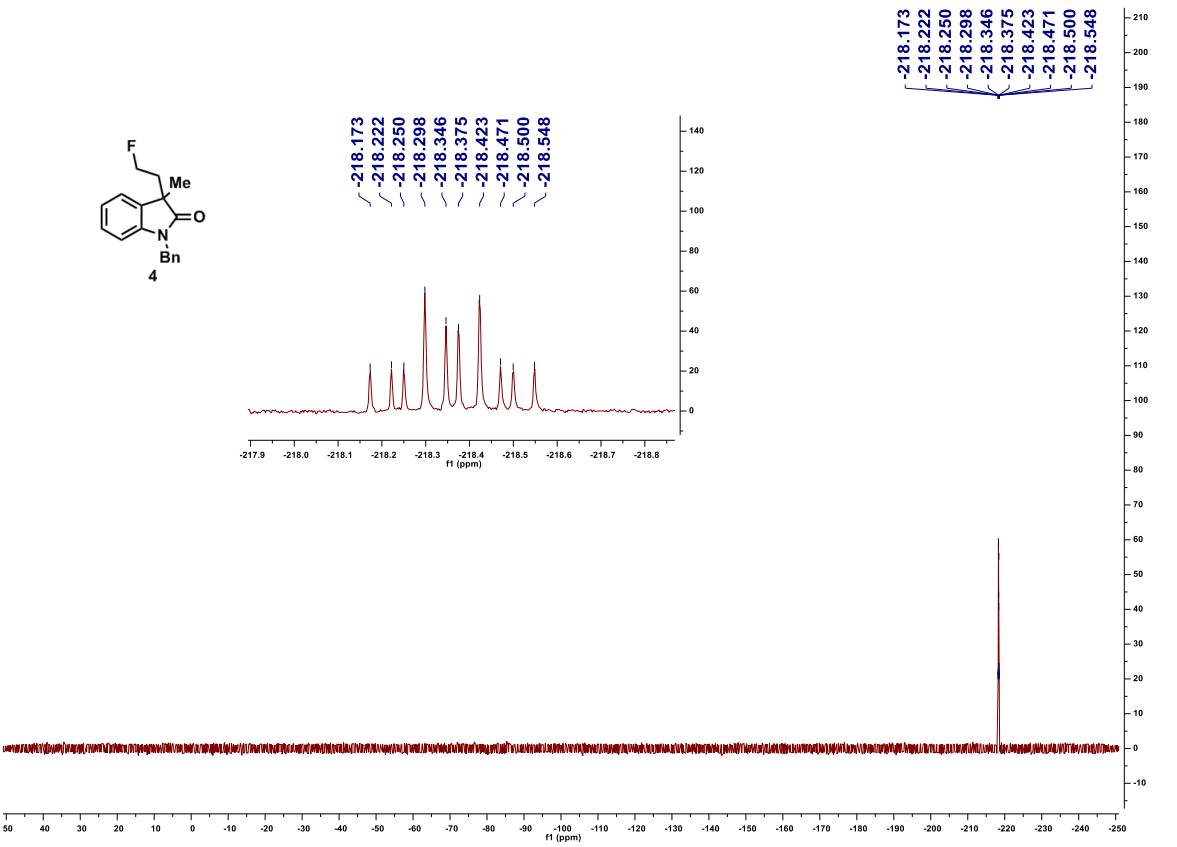
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4**



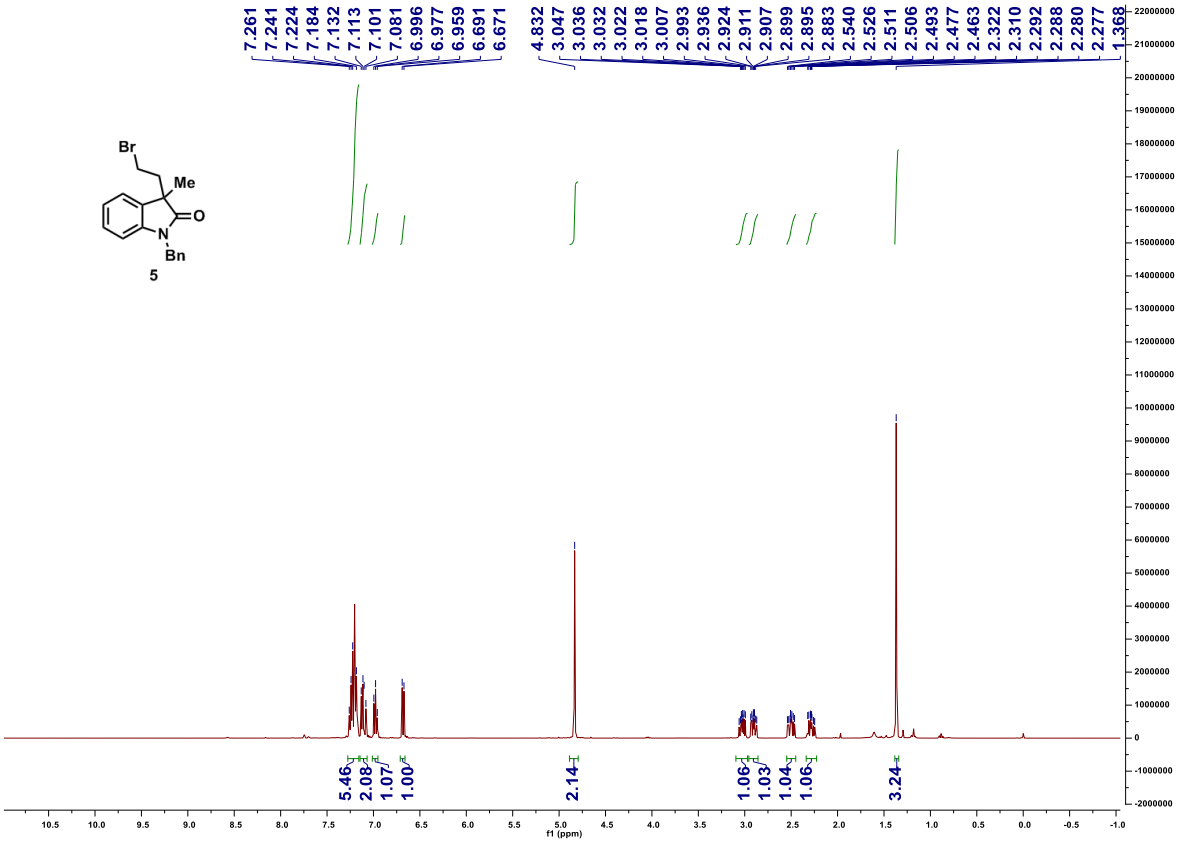
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **4**



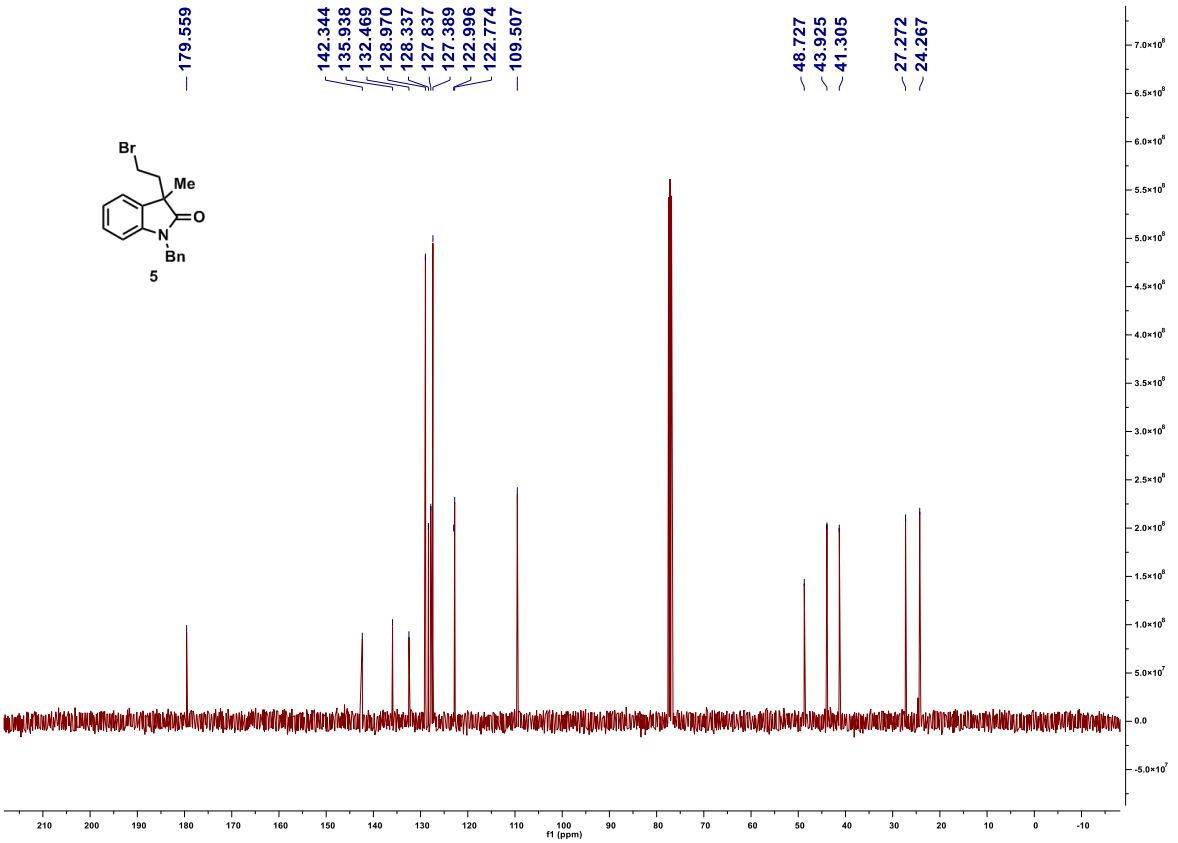
^{19}F NMR-spectrum (376 MHz, $CDCl_3$) of **4**



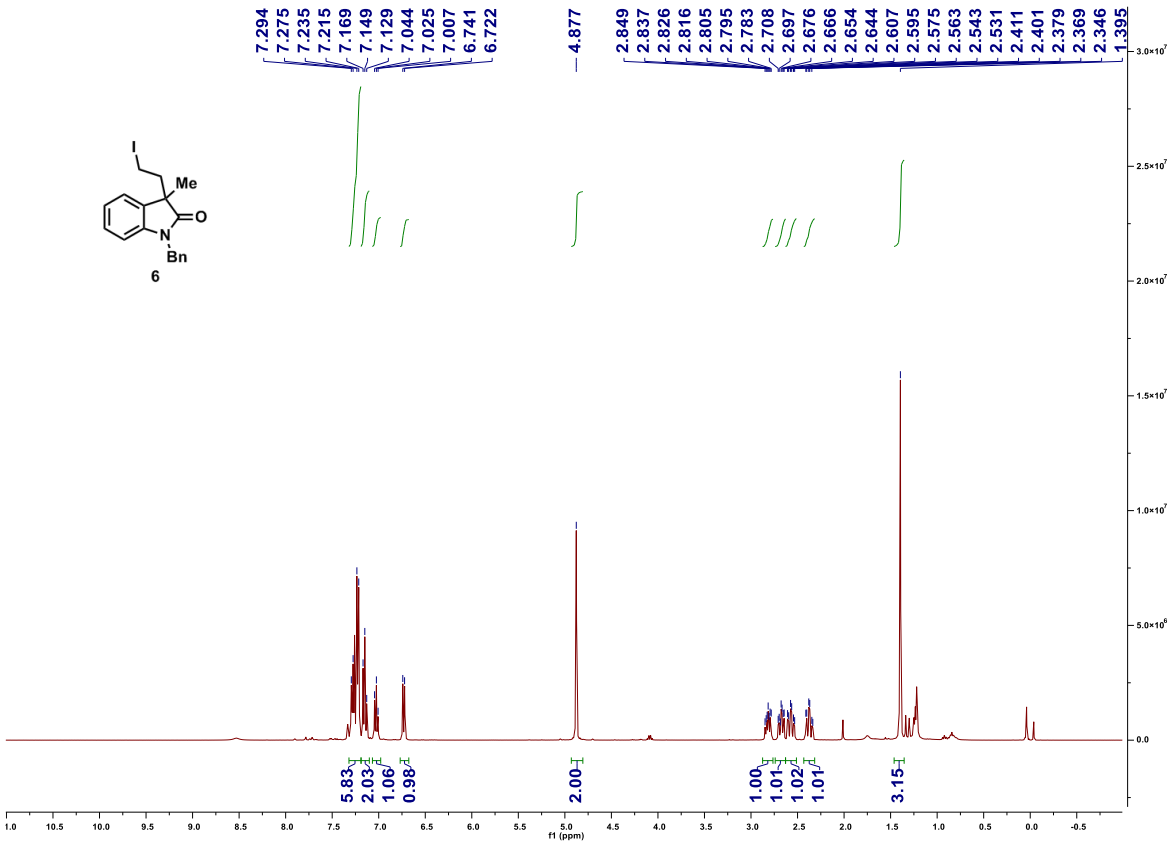
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **5**



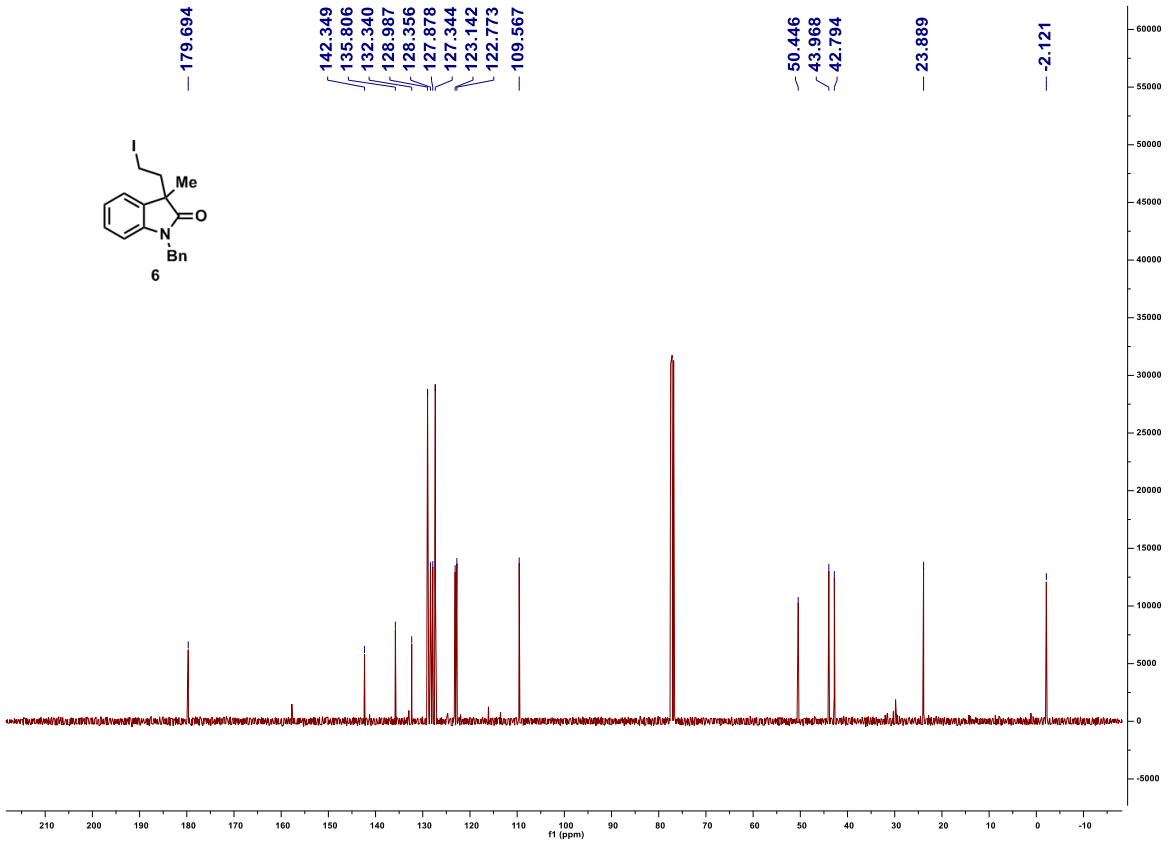
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **5**



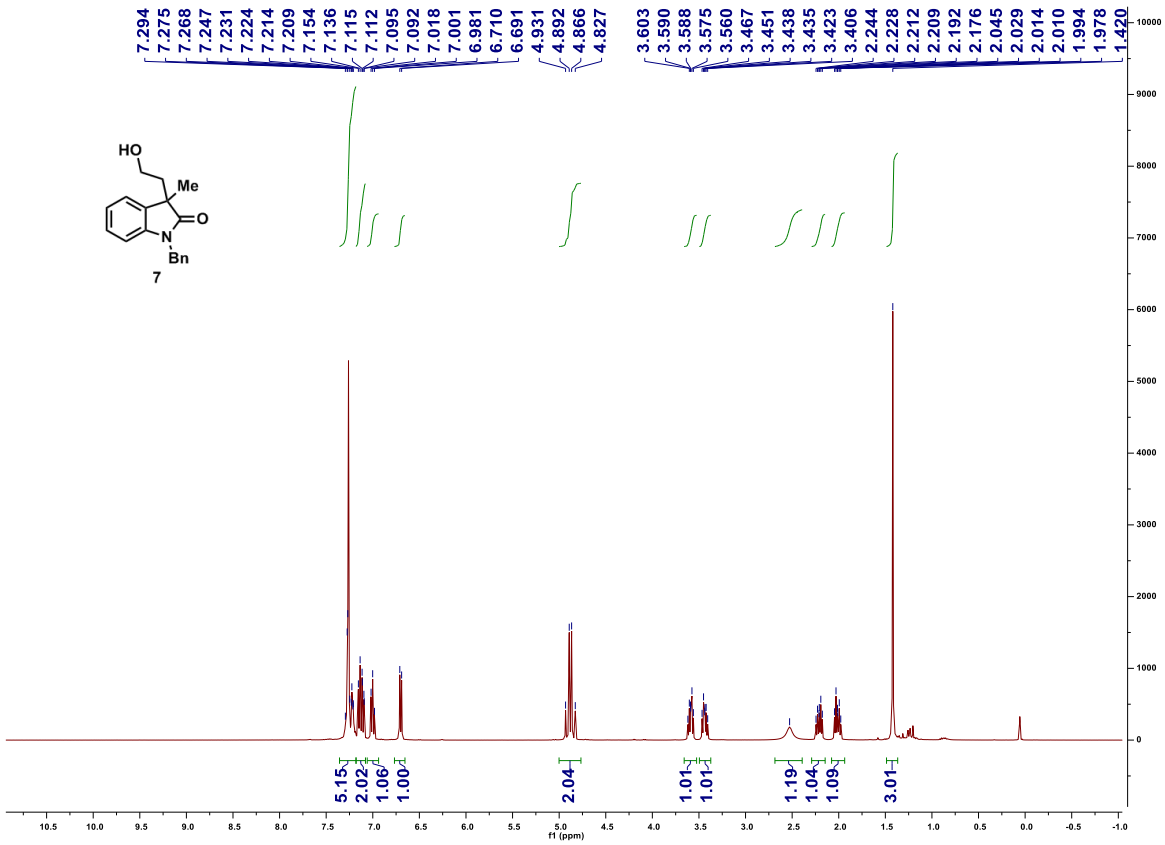
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **6**



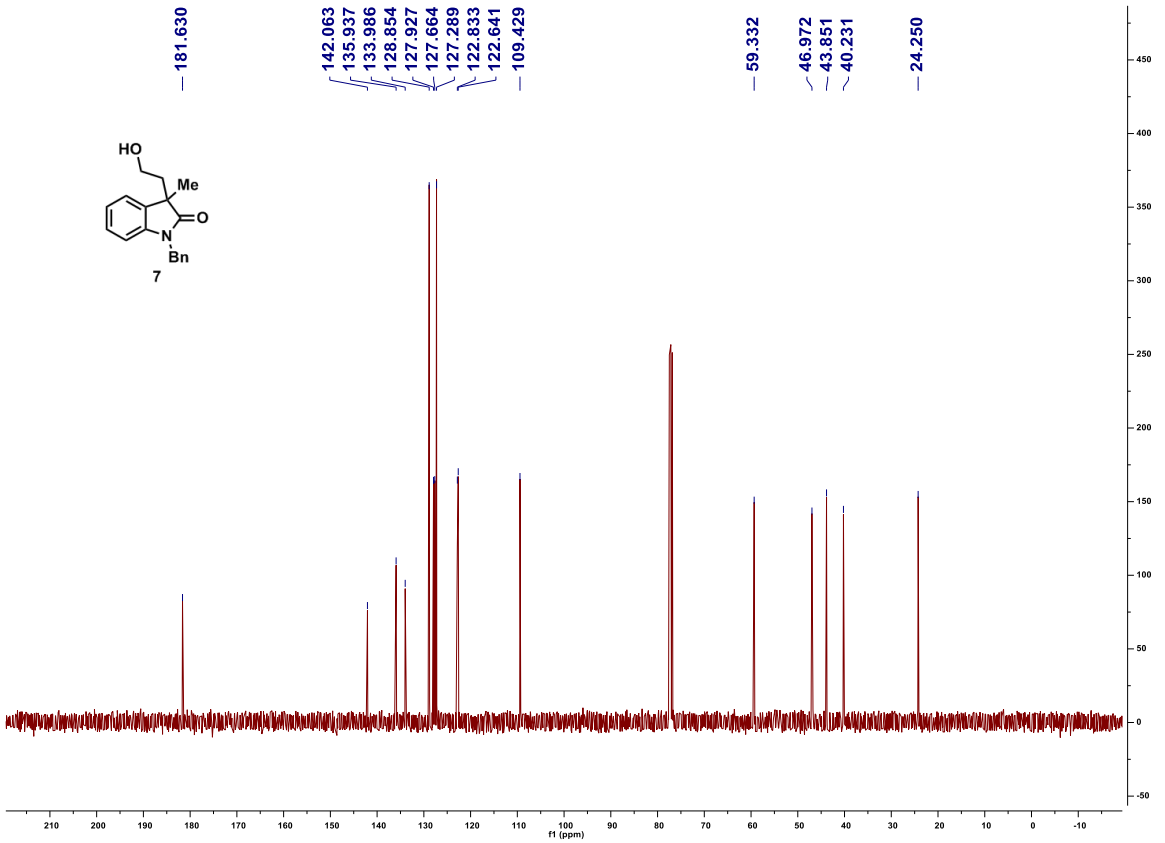
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **6**



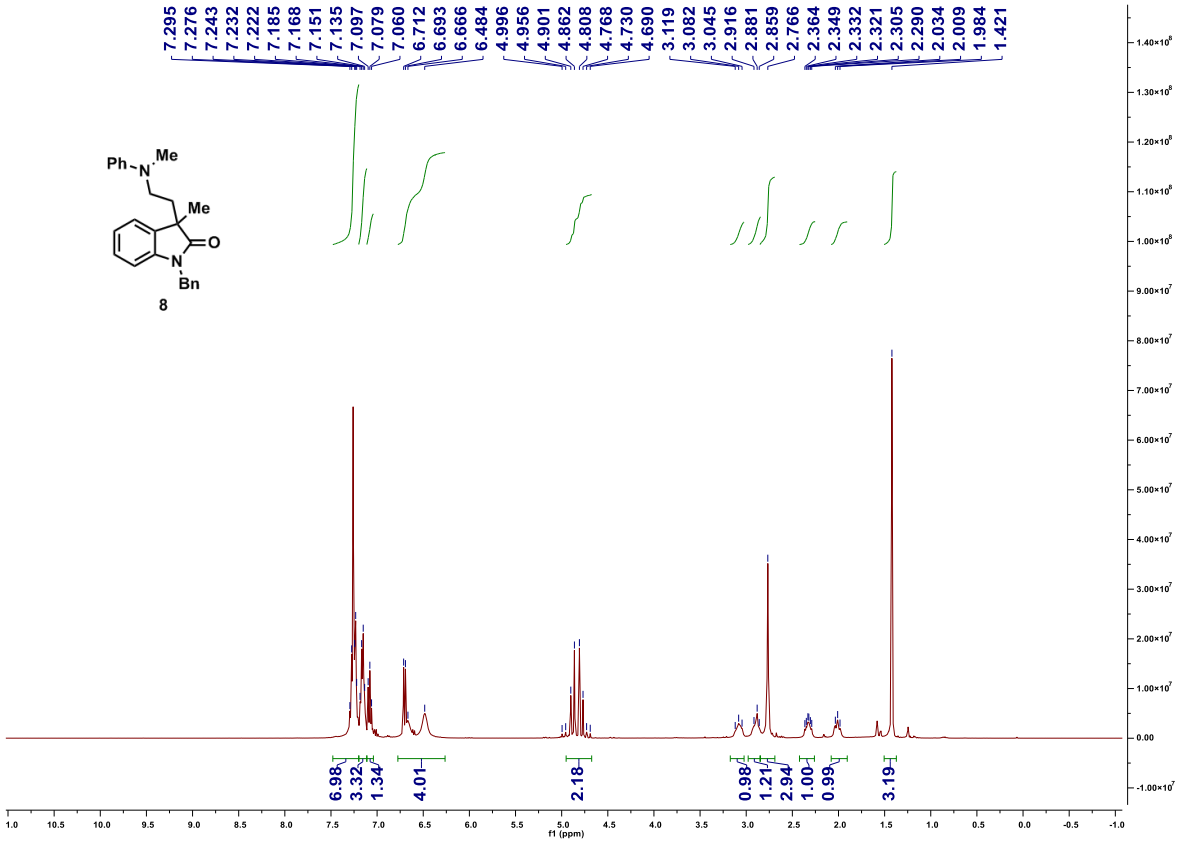
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **7**



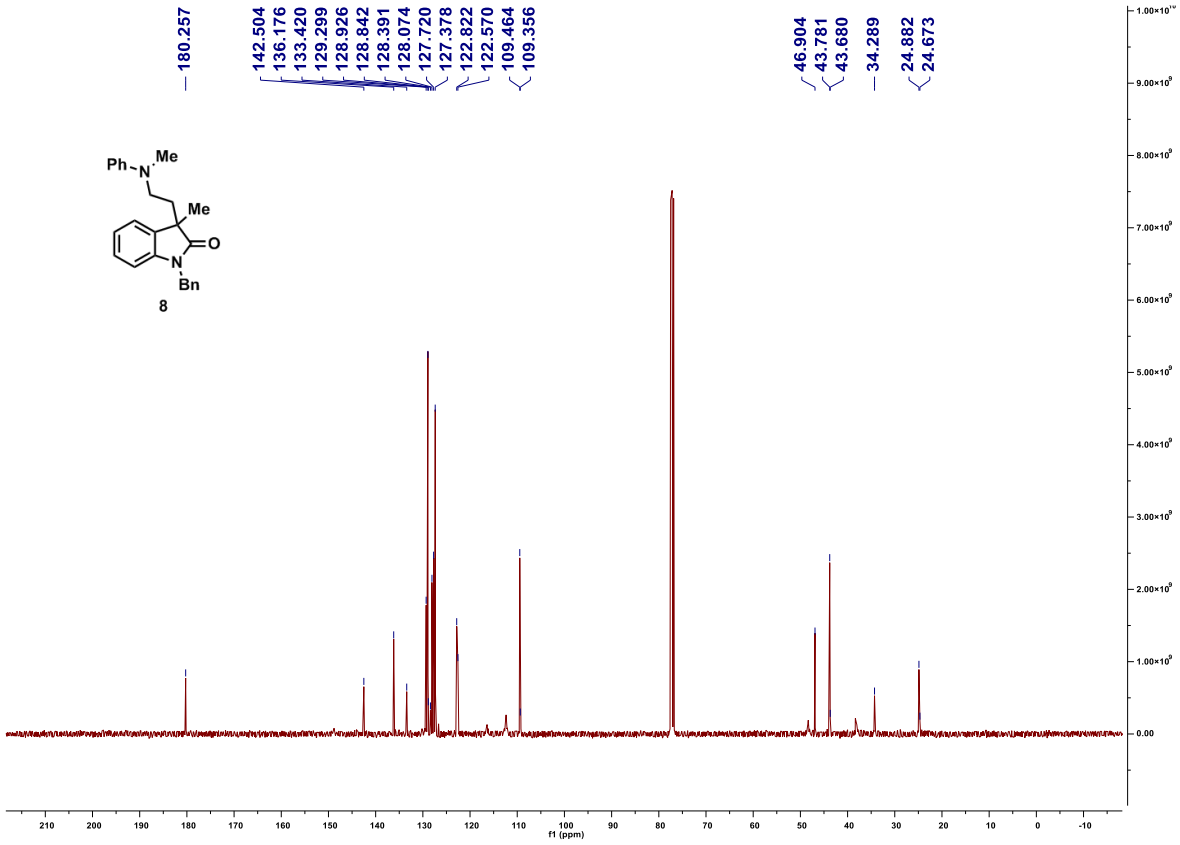
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **7**



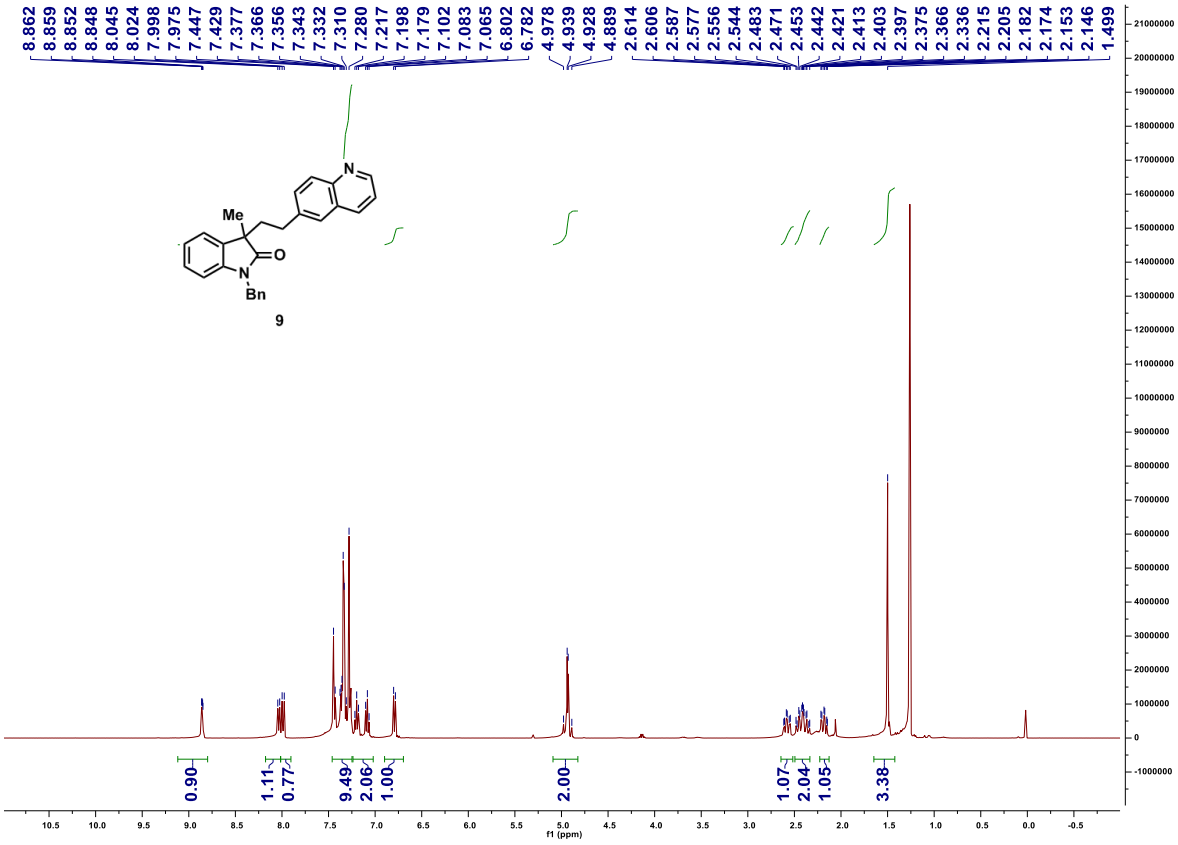
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **8**



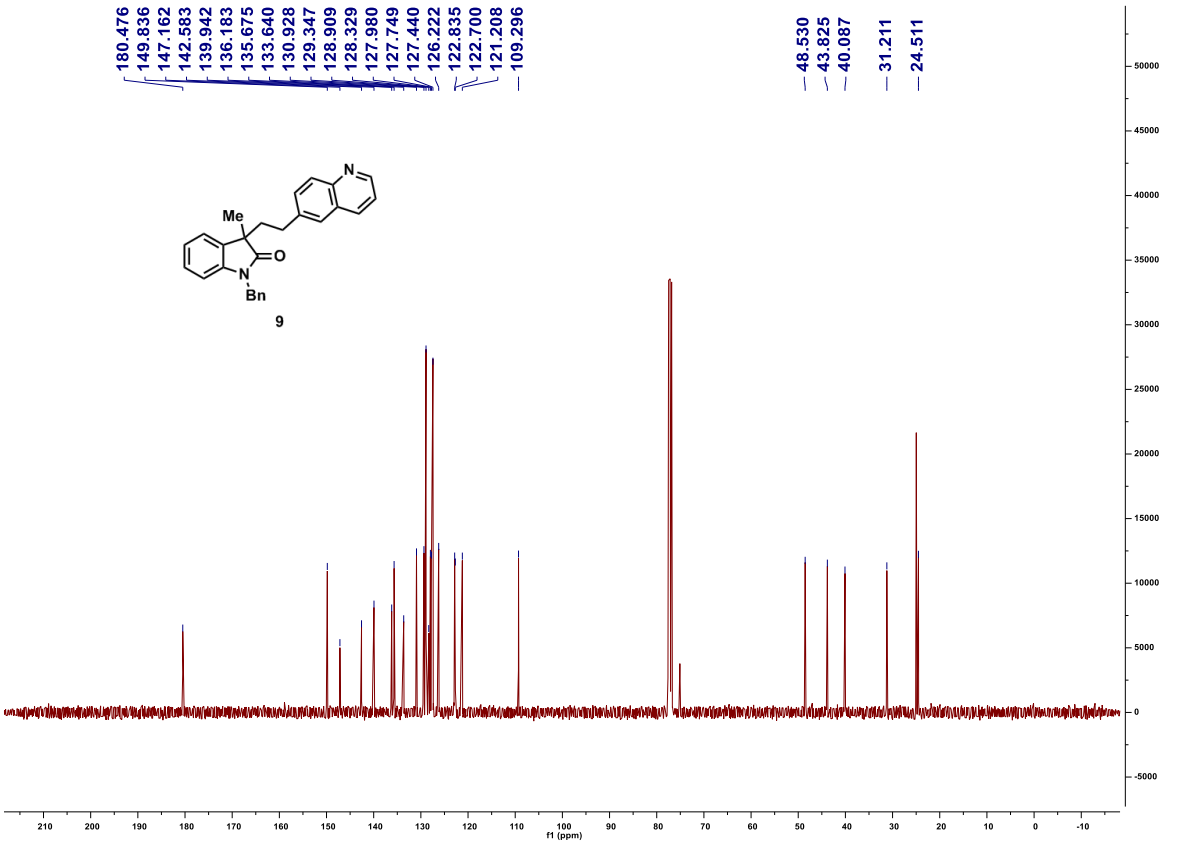
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **8**



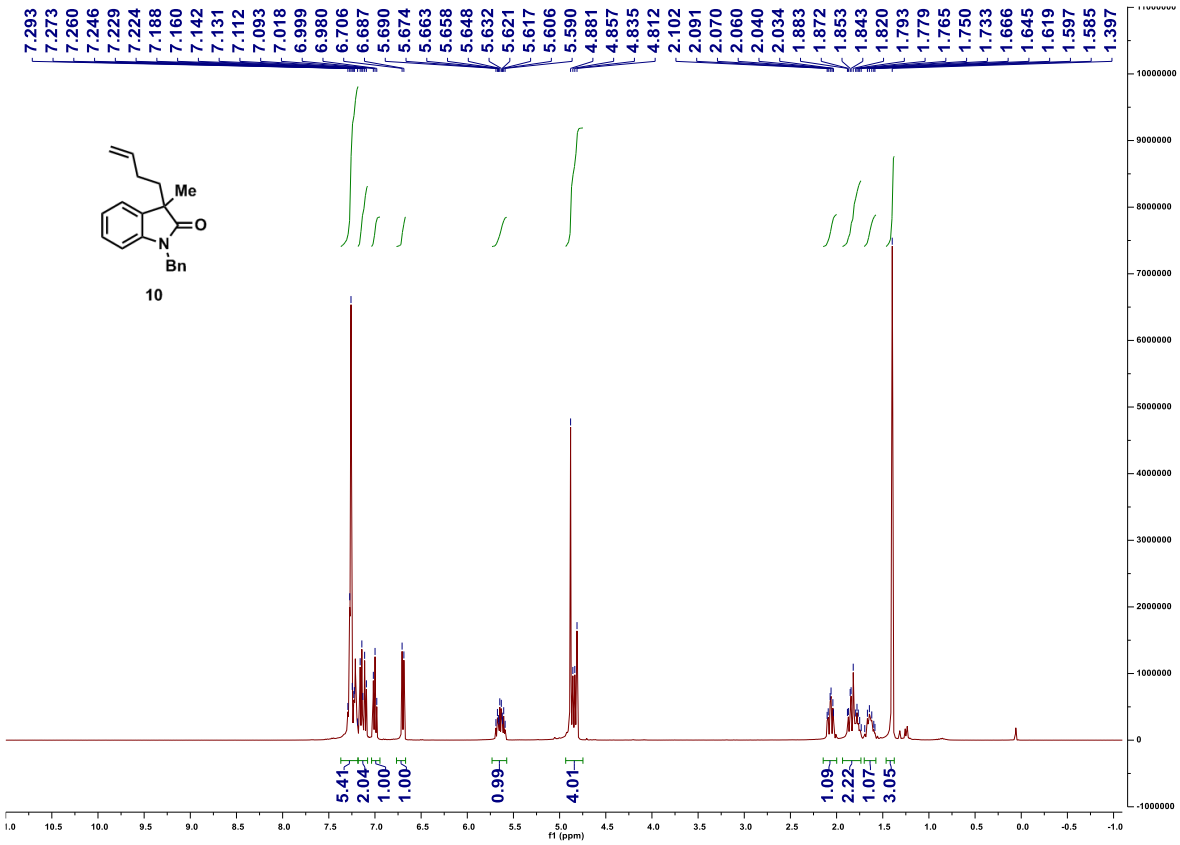
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **9**



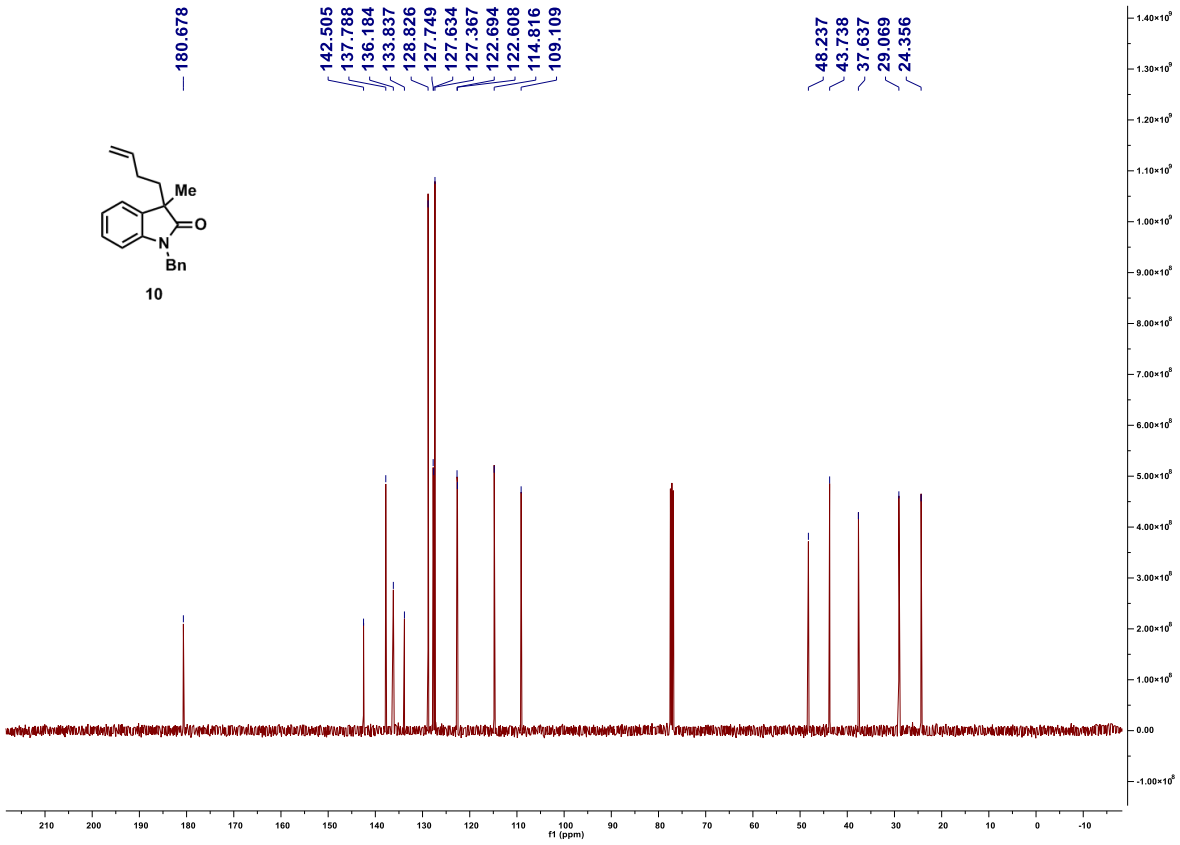
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **9**



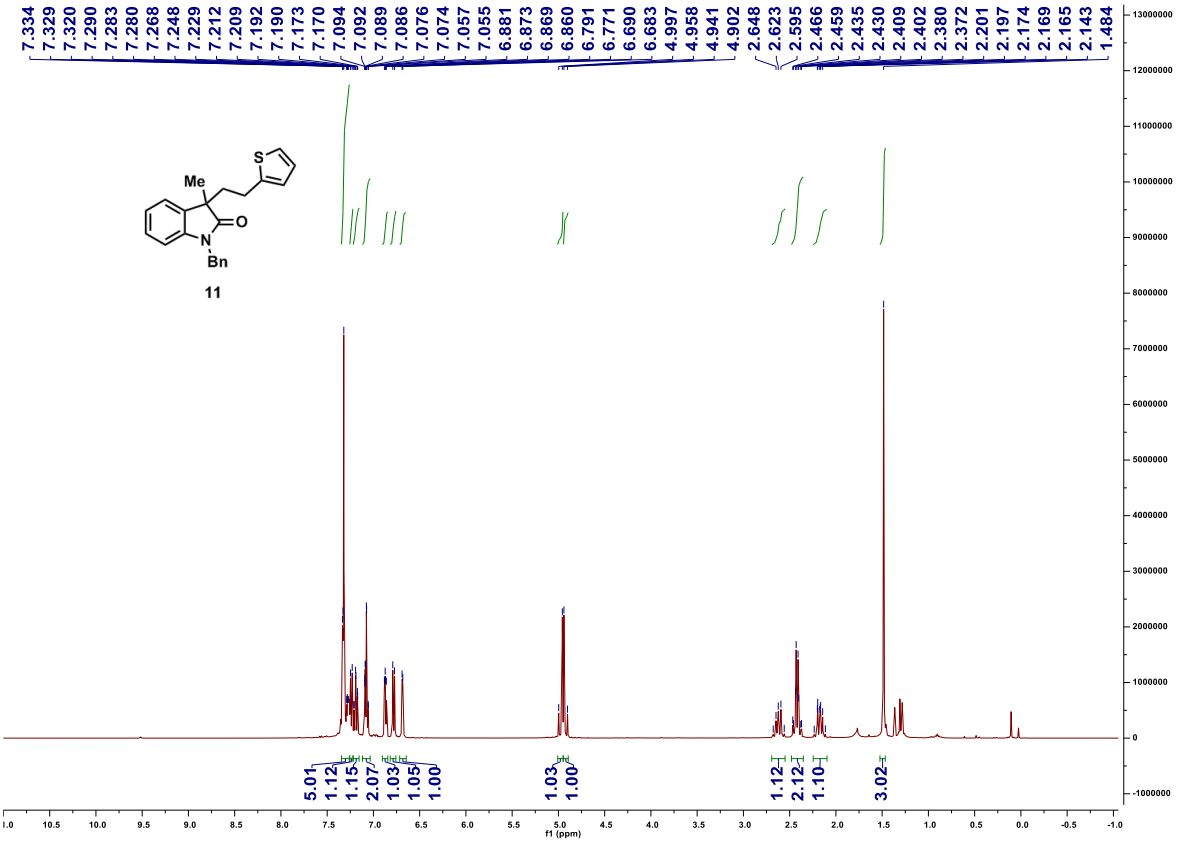
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **10**



^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **10**



^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **11**



^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **11**