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Synthesis of Dihydroisoquinolinone-4-methylboronic Esters *via* Domino Heck/borylation using a Structurally Characterized Palladacycle as a Catalyst

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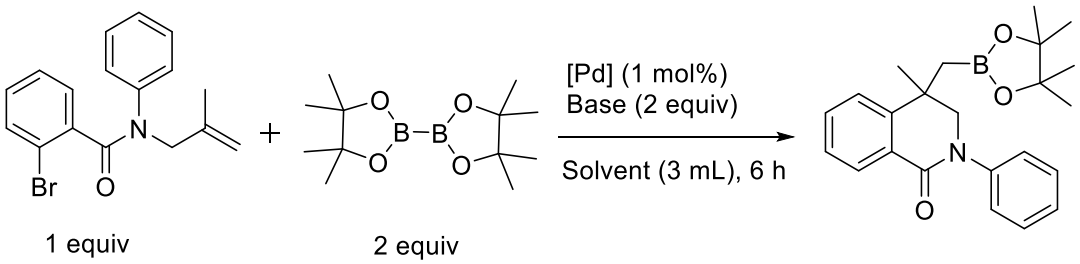
Supporting Information

Table of contents

1. General Information.

All the chemicals were purchased from commercial sources and used without further purification unless otherwise stated. Reactions were monitored by analytical thin-layer chromatography (TLC). Purification of the products was done by column chromatography with 100−200 mesh silica gel. Melting points were determined on a melting point apparatus in open capillaries. Infrared spectra of samples were recorded from 4000 to 500 cm^{-1} in ATR (attenuated total reflectance) mode using a Thermo Nicolet 6700 FT-IR spectrometer. ^{1}H, ^{13}C and ^{31}P spectra were recorded on a Bruker 400 MHz instrument. ^{19}F spectra were recorded on a Bruker 500 MHz instrument. Unless otherwise stated, deuterochloroform ($CDCl_3$) was used as solvents. Chemical shifts (δ) for hydrogen and carbon resonances are reported in parts per million and are referenced to the hydrogen and carbon resonance of the solvent $CHCl_3$ (δ = 7.26 ppm and δ = 77.16 ppm) and DMSO (δ = 2.5 ppm and δ = 39.5 ppm). The splitting patterns are reported as s (singlet), d (doublet), dd (doublet of a doublet), td (triplet of a doublet), t (triplet), q (quartet), br (broad), and m (multiplet). Coupling constants are given in hertz. High-resolution mass spectra were recorded on an Agilent 6540 UHD Q-TOF mass spectrometer equipped with an electrospray ion source (ESI), operated in the positive mode. Elemental analyses were performed using a Thermo Scientific Flash 2000 CHNS analyzer. *N*-Methyl-*N*-(2-methylallyl)benzamide,[1] bromobenzamides,[2-7] 2-bromo-N-(2-phenylallyl)benzamide,[8] N-phenylmethacrylamide,[9] (Z)-N-methoxy-2,3-diphenylacrylamide,[10] and substrates **5a** – **f** were prepared by following methods reported in the literature.[11-13]

2. Table S1. Optimization of Base and Solvents[a]



Entry	Base	Solvent	Temp (°C)	Yield (%)[b]
1	K_2CO_3	DCE	90	91
2	Cs_2CO_3	DCE	90	70

3	Et_3N	DCE	90	0
4	Na_2CO_3	DCE	90	89
5	KO^tBu	DCE	90	0
6	KOAC	DCE	90	62
7	K_3PO_4	DCE	90	80
8	K_2CO_3	MeCN	60	43
9	K_2CO_3	DMF	90	10
10	K_2CO_3	H_2O	90	16
11	K_2CO_3	THF	90	<5
12	K_2CO_3	PhMe	90	78
13	K_2CO_3	DMA	90	60
14	K_2CO_3	DMSO	90	0
15	K_2CO_3	1,4-Dioxane	60	35
16	K_2CO_3	DCE/H_2O (2.5 mL/0.5 mL)	90	94
17	K_2CO_3	PhMe/H_2O (2.5 mL/0.5 mL)	90	84
18	K_2CO_3	MeCN/H_2O (2.5 mL/0.5 mL)	90	0
19	K_2CO_3	1,4-Dioxane/H_2O (2.5 mL/0.5 mL)	90	0

[a] Reaction conditions: **1a** (0.5 mmol), $B_2(Pin)_2$ (1.0 mmol), [Pd(C∧C:)(PPh_3)Cl] (1 mol%), Base (1.0 mmol), and Solvent (3 mL), 90 °C under N_2 for 6 h. [b]Isolated yield.

3. Synthesis of imidazolium salt (ImidHCl).

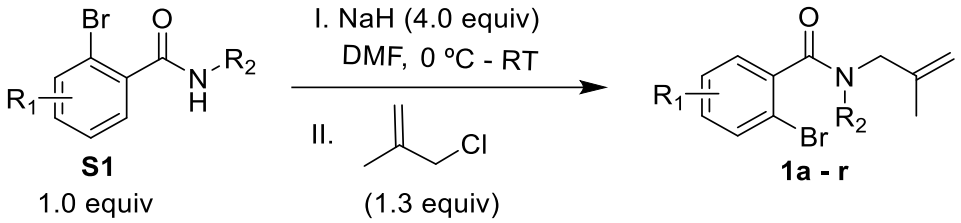
To a mixture of 2-chloro-3-(1H-imidazol-1-yl)quinoxaline (0.231 g, 1 mmol) and 2-chloro-*N*-phenylacetamide (0.187 g, 1.1 mmol) was added toluene (0.5 mL). The resulting solution was stirred for 1 hour at 100 °C and brought to rt. Diethyl ether (5 mL) was added and the mixture was filtered. The crude solid was washed with diethyl ether (2 X 5 mL) and dried under vacuum.

4. Synthesis of palladacycle [Pd(C∧C:)(PPh_3)Cl].

Method A: To an acetonitrile solution (20 mL) of the imidazolium salt **ImidHCl** (0.400 g, 1.0 mmol) was added tetrakis(triphenylphosphine)palladium(0) [$Pd(PPh_3)_4$] (1.155 g, 1.0 mmol,) and stirred the mixture for 4 h at 50 °C. Then the reaction mixture was allowed to cool to room temperature before adding 4-dimethylaminopyridine (DMAP) (0.122 g, 1.0 mmol) and stirred for 2 h. The resultant mixture was filtered and the precipitate was washed with diethyl ether (2 X 5 mL). The crude product was dissolved in hot acetonitrile and kept at room temperature to obtain pale yellow crystals of [Pd(C∧C:)PPh_3Cl]. Yield: 83% (0.608 g).

Method B: Same procedure as method A, except that [$Pd_2(dba)_3$] and PPh_3 were used instead of [$Pd(PPh_3)_4$]. [$Pd_2(dba)_3$] (0.457 g, 0.5 mmol), PPh_3 (0.262 g, 1.0 mmol), acetonitrile (20 mL), **ImidHCl** (0.400 g, 1.0 mmol), DMAP (0.122 g, 1.0 mmol) was added and stirred for 2 h. Yield: 80% (0.586 g).

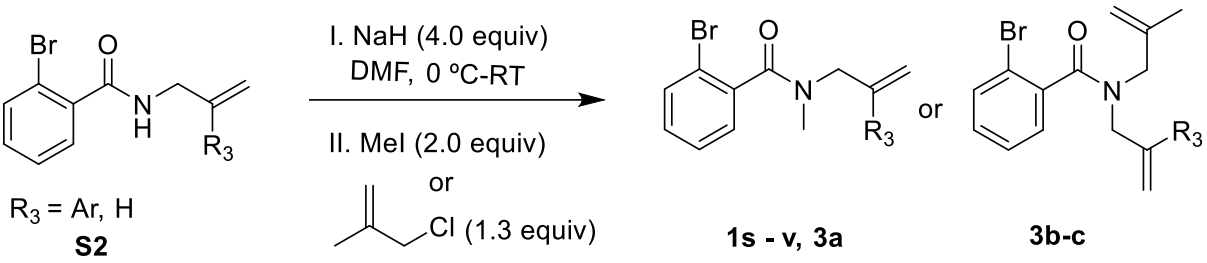
5. General Procedure for the Synthesis of Substrates 1a – r



The methodology was adopted from the literature.[14-15] The corresponding 2-bromobenzamide **S1** (4.0 mmol) was dissolved in dry DMF (5 mL) and cooled to 0 ºC. A 60% dispersion of NaH in mineral oil (16.0 mmol) was added portion wise and stirred for 10 min. The mixture was allowed to come to room temperature and stirred for further 30 min. The mixture was cooled again to 0 ºC and 2-methylallyl chloride (5.2 mmol) was added dropwise and stirred for 10 min before warming it up to room temperature. The mixture was stirred for 12 h before adding a mixture of water (100 mL) and EtOAc (20 mL). Organic layer was separated, washed with water (3 X 10 mL) and brine solution, dried over Na_2SO_4, filtered, and the volatiles were

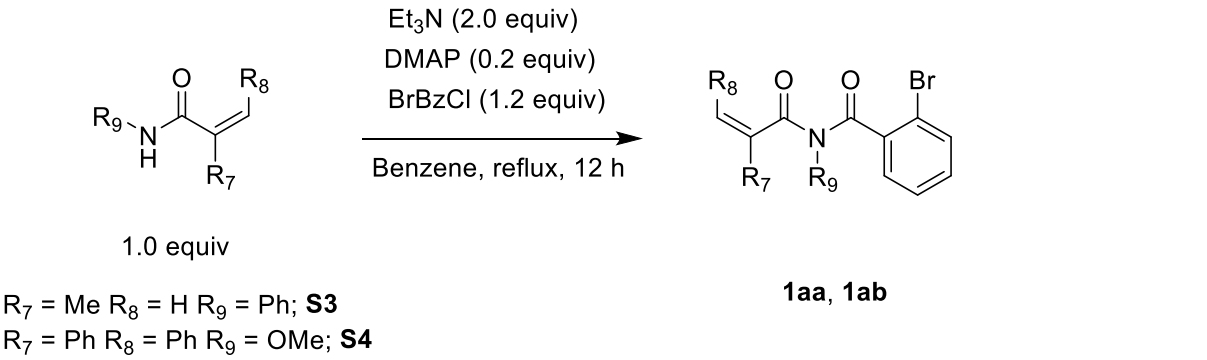
removed under vacuum. The residue was purified by using silica gel column with a mixture of hexane/EtOAc as the eluent to obtain pure **1a-r**.

5.1. General Procedure for the Synthesis of the Substrates 1s-v and 3a-c.



The methodology was adopted from the literature.[8] The corresponding 2-bromo-N-allylbenzamide **S2** (4.0 mmol) was dissolved in dry DMF (5 mL) and cooled to 0 ºC. A 60% dispersion of NaH in mineral oil (16.0 mmol) was added portion wise and stirred for 10 min. The mixture was allowed to come to room temperature and stirred for further 30 min. The mixture was cooled again to 0 ºC and methyl iodide (8.0 mmol) or 2-methylallyl chloride (5.2 mmol) was added dropwise and stirred for 10 min before warming it up to room temperature. The mixture was stirred for 12 h before adding a mixture of water (100 mL) and EtOAc (20 mL). Organic layer was separated, washed with water (3 X 10 mL) and brine solution, dried over Na_2SO_4, filtered, and the volatiles were removed under vacuum. The residue was purified by using silica gel column with a mixture of hexane/EtOAc as the eluent to obtain pure **1s-v** and **3a-c**.

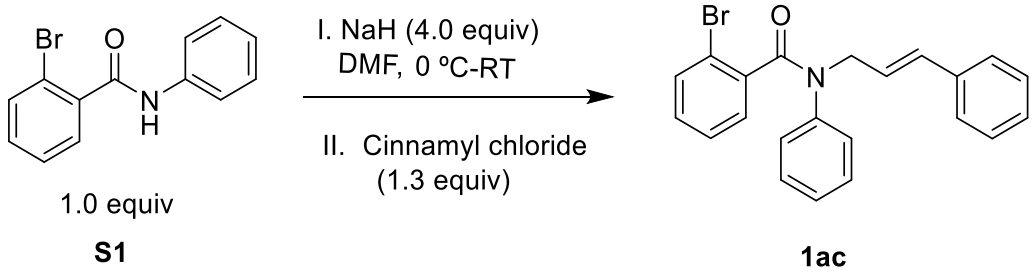
5.2. General Procedure for the Synthesis of the Substrates 1aa, 1ab



The methodology was adopted from the literature.[16] To a solution of corresponding acrylamide **S3** or **S4** (5.0 mmol) in benzene (10 mL) was added Et_3N (10.0 mmol) followed by DMAP (1.0 mmol) at room temperature. The mixture was cooled to 0 ºC and a solution of 2-bromobenzoyl

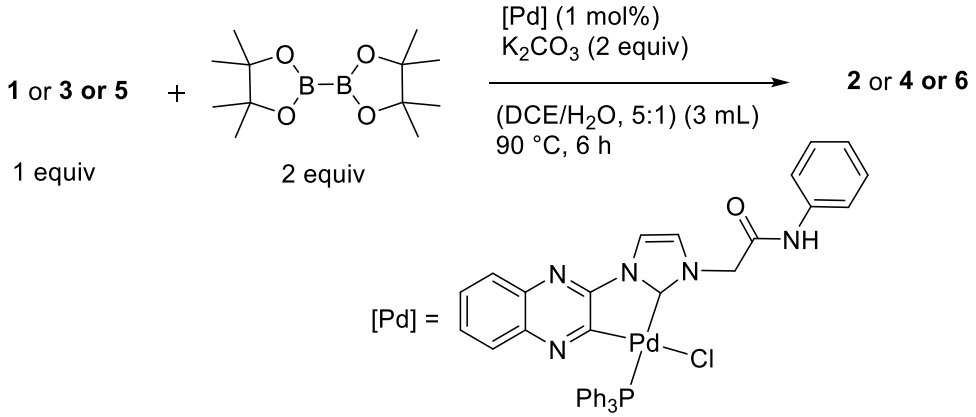
chloride (6 mmol) was added dropwise and stirred for 10 min. It was allowed to coe to room temperature and refluxed for 12 h. The resultant mixture was concentrated and diluted with water and extracted with EtOAc (2 X 20 mL), washed with saturated $NaHCO_3$ solution, water, brine, dried over $MgSO_4$ and the volatiles were removed under vacuum. The residue was purified by using silica gel column with a mixture of hexane/EtOAc as the eluent to obtain pure **1aa** and **1ab**.

5.3. Synthesis of substrate 1ac



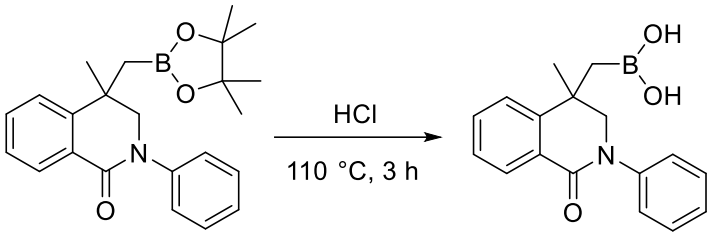
2-Bromo-N-phenylbenzamide **S1** (4.0 mmol) was dissolved in dry DMF (5 mL) and cooled to 0 ^oC. A 60% dispersion of NaH in mineral oil (16.0 mmol) was added portion wise and stirred for 10 min. the mixture was allowed to come to room temperature and stirred for further 30 min. The mixture was cooled again to 0 ^oC and cinnamyl chloride (5.2 mmol) was added dropwise. The resultant mixture was stirred for 10 min at this temperature before it was allowed to come room temperature and stirred for 12 h. The mixture was then treated with H_2O (100 mL) and EtOAc (20 mL). The organic layer was separated and washed with water (3 X 10 mL), brine solution, dried over Na_2SO_4, filtered and the volatiles were removed under vacuum. The residue was purified by using silica gel column with a mixture of hexane/EtOAc as the eluent to obtain pure **1ac**.

6. General Procedure for Heck/Borylation Reactions



An oven dried Schlenk tube (18 mm X 150 mm) containing a magnetic stir-bar was charged with **1** or **3** or **5** (0.5 mmol), K_2CO_3 (1.0 mmol) and [Pd(C∧C:)(PPh_3)Cl] (1.0 mol%), and purged with nitrogen for 10 minutes. DCE/H_2O (5:1) (3 mL) and $B_2(Pin)_2$ (1.0 mmol) were added in sequence. The resultant mixture was gently refluxed at 90 °C for 6 h after which time the reaction mixture was brought to room temperature. The contents were filtered through a Celite bed, which was washed with ethyl acetate (10 mL) and the washing was collected in the same filtration flask. The filtrate was treated with water (10 mL) and the mixture was extracted with ethyl acetate (2 X 10 mL). The ethyl acetate portion was dried over Na_2SO_4, filtered and subjected to vacuum in order to remove the volatiles. The crude product was purified by column chromatography using a mixture of hexane/EtOAc as eluent on silica gel (100-200).

7. Synthesis of 7a

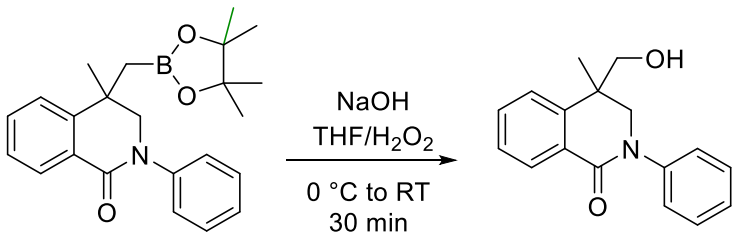


3a, 0.5 mmol

7a (80%)

A mixture of **3a** (0.2 g, 0.5 mmol) in 4 mL 20% HCl (v/v) was stirred at 110 ^oC for 3 h. Once complete consumption of starting material **3a** as monitored by TLC, the reaction mixture was diluted with diethyl ether and water. Separate the two layers and the organic layer was washed with brine solution. Drying over Na_2SO_4 and filtered and concentrated in vaccum. The residue was purified by column silica gel chromatography with hexane/EtOAc as the eluent to provide the product with the 80% (0.125 g) yield of **7a.**

Synthesis of 7b



3a, 0.5 mmol

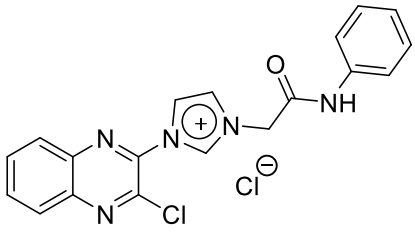
7b (92%)

To a stirred solution of **3a** (0.2 g, 0.5 mmol) in tetrahydrofuran (1.5 mL) and 3M NaOH (0.8 mL) solution was added dropwise at 0 ^oC. Subsequently 30% H_2O_2 solution in water (0.4 mL) was added and stirred for 30 min at room temperature. The reaction mixture was diluted with

H_2O and EtOAc. Separate the two layers and the organic layer was washed with H_2O (10 mL) and brine solution. Drying over Na_2SO_4 and filtered and concentrated in vacuum. The residue was purified by column silica gel chromatography with hexane/ EtOAc as the eluent to afford a white solid of **7b** with the high yield of 92% (0.130 g).

8. Characterization of the Compounds:

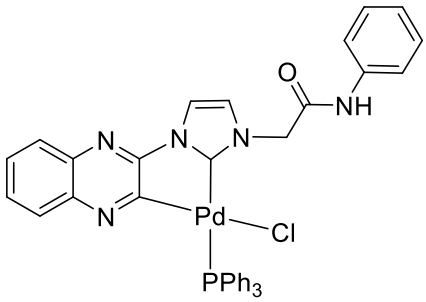
ImidHCl.



ImidHCl

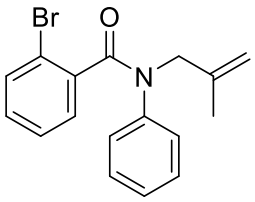
Light yellow solid (0.380 g, 95%). mp: 231 – 232 ^{o}C. ^{1}H NMR (400 MHz, DMSO): δ 11.39 (s, 1H), 10.04 (s, 1H), 8.39 (t, J = 1.7 Hz, 1H), 8.33 – 8.16 (m, 3H), 8.15 – 8.01 (m, 2H), 7.71 (d, J = 7.7 Hz, 2H), 7.34 (t, J = 7.9 Hz, 2H), 7.09 (t, J = 7.4 Hz, 1H), 5.61 (s, 2H) ppm. ^{13}C NMR (100 MHz, DMSO): δ 163.45, 141.48, 141.40, 140.11, 139.39, 138.57, 138.53, 133.33, 132.44, 128.87, 128.76, 128.01, 124.38, 123.78, 122.70, 119.20, 52.11, 40.14, 39.93, 39.73, 39.52, 39.31, 39.10, 38.89 ppm. HRMS (ESI): m/z calcd for $C_{19}H_{16}ClN_5O$ $[M - Cl]^+$ 364.1043, found 364.0973. IR (KBr): $\tilde{\nu}$ = 3468, 3164, 3136, 2974, 2895, 1621, 1539, 1488, 1463, 1441, 1387, 1314, 1262, 1227, 1193, 1100, 1073, 1039, 949, 872, 803, 760, 731, 664, 617, 594, 532, 429 cm^{-1}.

[Pd(C∧C:)(PPh$_3$)Cl].



Light yellow solid. Yield: Method A (0.608 g, 83%) and Method B (0.586 g, 80%) mp: 214 – 215 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.39 (s, 1H), 7.82 – 7.71 (m, 9H), 7.64 – 7.59 (m, 2H), 7.48 – 7.43 (m, 1H), 7.42 – 7.31 (m, 10H), 7.31 – 7.27 (m, 2H), 7.08 (t, J = 7.4 Hz, 1H), 6.96 (dd, J = 8.2, 0.9 Hz, 1H), 5.57 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.97, 176.60, 164.92, 162.53, 152.25, 141.15, 138.13, 137.60, 135.18, 135.12, 135.01, 134.89, 131.95, 131.49, 130.60, 129.95, 129.71, 128.85, 128.23, 128.15, 127.98, 127.88, 127.80, 124.41, 119.89, 114.89, 77.48, 77.16, 76.84, 54.16 ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ 33.61 ppm. HRMS (ESI): m/z calcd for $C_{37}H_{31}ClN_5OPPd$ $[M + H]^+$ 732.0911, found 732.0935. IR (KBr): $\tilde{\nu}$ = 3423, 3161, 3119, 3040, 1674, 1609, 1482, 1415, 1321, 1283, 1257, 1233, 1162, 1108, 1064, 1031, 949, 876, 838, 790, 750, 652, 623, 597, 466 cm^{-1}. Anal. Calcd for $C_{37}H_{29}ClNOPPd$: C, 60.67; H, 3.99; N, 9.56. Found: C, 60.108; H, 3.959; N, 9.330.

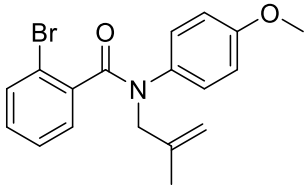
2-Bromo-N-(2-methylallyl)-N-phenylbenzamide (1a).



1a

White solid (1.10 g, 83%), mp: 71 – 72 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, J = 7.8 Hz, 1H), 7.16 – 7.12 (m, 4H), 7.10 – 7.07 (m, 1H), 7.07 – 7.03 (m, 2H), 7.02 – 6.97 (m, 1H), 4.87 (d, J = 0.8 Hz, 2H), 4.53 (s, 2H), 1.87 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.72, 141.81, 140.46, 138.67, 132.76, 129.83, 128.88, 127.62, 127.35, 126.72, 119.97, 113.83, 77.48, 77.16, 76.84, 54.96, 20.60 ppm. HRMS (ESI): m/z calcd for $C_{17}H_{17}BrNO$ $[M + H]^+$ 330.0493, found 330.0492. IR (KBr): $\tilde{\nu}$ = 3064, 2976, 2928, 1813, 1645, 1588, 1493, 1469, 1430, 1388, 1289, 1259, 1204, 1158, 1053, 1024, 902, 756 cm^{-1}.

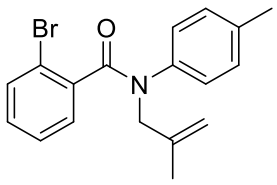
2-Bromo-N-(4-methoxyphenyl)-N-(2-methylallyl)benzamide (1b).



1b

Yellow oil (1.07 g, 74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (dd, J = 7.9, 0.5 Hz, 1H), 7.10 – 7.03 (m, 4H), 7.01 – 6.97 (m, 1H), 6.67 – 6.63 (m, 2H), 4.85 (d, J = 7.6 Hz, 2H), 4.48 (s, 1.8H), 3.80 (s, 0.2H), 3.68 (s, 3H), 1.87 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.01, 158.38, 140.55, 138.91, 134.56, 132.75, 129.72, 128.84, 128.78, 126.80, 119.78, 114.39, 113.99, 77.48, 77.16, 76.84, 55.34, 55.18, 20.64 ppm. HRMS (ESI): m/z calcd for $C_{18}H_{19}BrNO_2$ $[M + H]^+$ 360.0599, found 360.0595. IR (KBr): $\tilde{\nu}$ =3494, 2926, 1650, 1511, 1465, 1433, 1391 1295, 1250, 1171, 1030, 952, 836, 769, 744 cm^{-1}.

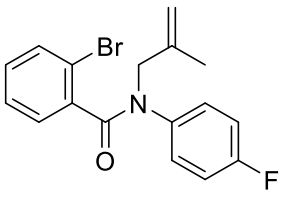
2-Bromo-N-(2-methylallyl)-N-(*p*-tolyl)benzamide (1c).



1c

Yellow oil (1.21 g, 88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, J = 8.0 Hz, 1H), 7.07 – 6.97 (m, 5H), 6.93 (d, J = 8.1 Hz, 2H), 4.86 (d, J = 1.0 Hz, 2H), 4.50 (s, 2H), 2.19 (s, 3H), 1.86 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.81, 140.52, 139.13, 138.83, 137.12, 132.71, 129.71, 129.50, 128.84, 127.35, 126.72, 119.88, 113.75, 77.48, 77.16, 76.84, 55.00, 21.04, 20.59 ppm. HRMS (ESI): m/z calcd for $C_{18}H_{19}BrNO$ $[M + H]^+$ 344.0650, found 344.0646. IR (KBr): $\tilde{\nu}$ =3068, 2922, 1728, 1654, 1512, 1469, 1430, 1385, 1295, 1250, 1164, 1050, 1026, 900, 824, 767, 744 cm^{-1}.

2-Bromo-N-(4-fluorophenyl)-N-(2-methylallyl)benzamide (1d).

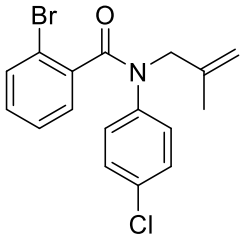


1d

White solid (1.25 g, 90%), mp: 98 – 99 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, J = 8.1 Hz, 1H), 7.14 – 6.99 (m, 5H), 6.82 (t, J = 8.6 Hz, 2H), 4.85 (d, J = 14.8 Hz, 2H), 4.48 (s, 2H), 1.86 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.68, 162.49, 160.03, 140.26, 138.48, 137.69 (d, J = 3.3 Hz), 132.78, 129.95, 129.43 (d, J = 8.7 Hz), 128.73, 126.86, 119.70, 115.90, 115.67, 114.24, 77.48, 77.16, 76.84, 55.05, 20.54 ppm. ^{19}F NMR (471 MHz, $CDCl_3$):

δ -113.74 ppm. HRMS (ESI): m/z calcd for $C_{17}H_{16}BrFNO$ $[M + H]^+$ 348.0399, found 348.0393. IR (KBr): $\tilde{\nu}$ =3062, 2921, 2854, 1640, 1590, 1506, 1465, 1427, 1387, 12926, 1206, 1156, 1054, 1025, 896, 844, 744 cm^{-1}.

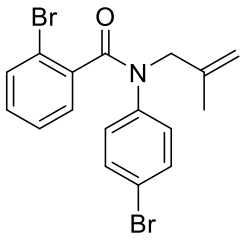
2-Bromo-N-(4-chlorophenyl)-N-(2-methylallyl)benzamide (1e).



1e

White solid (1.24 g, 85%), mp: 58 – 60 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, J = 7.8 Hz, 2H), 7.05 – 6.90 (m, 6H), 4.77 (d, J = 9.3 Hz, 2H), 4.41 (s, 2H), 1.76 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.33, 140.16, 140.07, 138.24, 132.84, 132.70, 129.97, 128.92, 128.83, 128.67, 126.82, 119.62, 114.10, 77.48, 77.16, 76.84, 54.77, 20.39 ppm. HRMS (ESI): m/z calcd for $C_{17}H_{16}BrClNO$ $[M + H]^+$ 364.0103, found 364.0121. IR (KBr): $\tilde{\nu}$ = 3068, 2970, 2920, 1907, 1803, 1643, 1587, 1488, 1379, 1290, 1212, 1160, 1092, 1019, 958, 899, 836, 739 cm^{-1}.

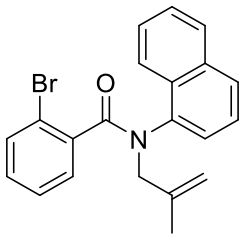
2-Bromo-N-(4-bromophenyl)-N-(2-methylallyl)benzamide (1f).



1f

Yellow oil (1.05g, 64%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 – 7.23 (m, 2H), 7.20 (d, J = 8.6 Hz, 2H), 7.06 – 6.91 (m, 5H), 4.79 (d, J = 13.5 Hz, 2H), 4.43 (s, 0.8H), 3.95 (d, J = 13.0 Hz, 0.2H), 1.78 (s, 3H) ppm.^{13}C NMR (100 MHz, $CDCl_3$): δ 168.46, 140.81, 140.20, 138.33, 132.90, 132.07, 130.15, 129.27, 128.80, 126.99, 121.05, 119.80, 114.25, 77.48, 77.16, 76.84, 54.89, 20.54 ppm. HRMS (ESI): m/z calcd for $C_{17}H_{16}Br_2NO$ $[M + H]^+$ 409.9578, found 409.9565. IR (KBr): $\tilde{\nu}$ = 3438.38, 3072.47, 2971.97, 2917.91, 1654.34, 1586.93, 1489.45, 1471.08, 1432.20, 1407.84, 1378.95, 1291.24, 1257.94, 1161.73, 1072.36, 1055.92, 1045.24, 1027.47, 1011.77, 902.90, 833.53, 768.89, 741.72, 611.73, 525.91 cm^{-1}.

2-Bromo-N-(2-methylallyl)-N-(naphthalen-1-yl)benzamide (1g).

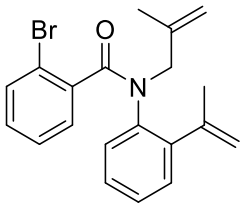


1g

White solid (0.988 g, 65%), mp: 62 – 65 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 8.2 Hz, 1H), 7.63 (dd, J = 11.6, 4.5 Hz, 2H), 7.54 – 7.49 (m, 1H), 7.45 (d, J = 7.2 Hz, 1H), 7.34 (d, J = 8.0 Hz, 1H), 7.24 – 7.19 (m, 1H), 6.85 (m, 2H), 6.71 (dt, J = 7.5, 3.8 Hz, 1H), 5.41 (d, J = 14.4 Hz, 1H), 4.85 (s, 1H), 4.76 (s, 1H), 3.78 (d, J = 14.4 Hz, 1H), 1.98 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.47, 140.51, 138.46, 137.38, 134.45, 132.64, 129.89, 129.78, 128.87, 128.84, 127.29, 127.01, 126.40, 126.35, 125.21, 122.64, 119.86, 114.71, 77.48, 77.16, 76.84, 54.50, 21.08 ppm. HRMS (ESI): m/z calcd for $C_{21}H_{19}BrNO$ $[M + H]^+$ 380.0650, found 380.0642. IR (KBr): $\tilde{\nu}$ = 3061.67, 2928.13, 1651.87, 1595.69, 1508.42, 1471.81, 1432.29, 1403.21, 1382.38 cm-1.

2-Bromo-N-(2-methylallyl)-N-(2-(prop-1-en-2-yl)phenyl)benzamide (1h).

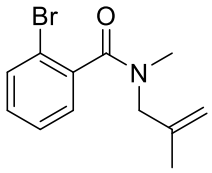
This compound exists as a mixture of rotamers. Colorless oil (0.859 g, 58%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, J = 8.0 Hz, 0.2H), 7.45 (d, J = 3.7 Hz, 0.7H), 7.36 – 7.20 (m, 1.9H), 7.12 (dd, J = 7.7, 2.0 Hz, 1.3H), 7.06 (td, J = 7.5, 1.2 Hz, 0.8H), 7.01 – 6.91 (m, 3H), 5.31 – 5.27 (m, 0.7H), 5.23 (d, J = 20.4 Hz, 0.7H), 5.16 (d, J = 8.7 Hz, 0.7H), 5.04 (s, 0.7H), 4.83 (d, J = 9.5 Hz, 1.5H), 4.65 (s, 0.3H), 4.53 (s, 0.2H), 3.95 (d, J = 47.3 Hz, 0.5H), 3.71 (d, J = 14.8 Hz, 0.7H), 2.10 (2s, 3H), 1.85 (s, 2H), 1.75 (s, 0.4H), 1.59 (s, 0.6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.29, 142.91, 141.37, 140.70, 139.00, 138.59, 137.91, 133.27, 130.38, 129.89, 129.83, 129.56, 128.14, 127.75, 127.64, 127.32, 126.44, 121.41, 117.84, 113.94, 77.48, 77.16, 76.84, 53.54, 23.41, 21.02 ppm. HRMS (ESI): m/z calcd for $C_{20}H_{21}BrNO$ $[M + H]^+$ 370.0806, found 370.0882. IR (KBr): $\tilde{\nu}$ = 3074, 2972, 1811, 1654, 1593, 1487, 1436, 1378, 1296, 1249, 1216, 1161, 1028, 949, 902, 768, 742 cm^{-1}.



1h

2-Bromo-N-methyl-N-(2-methylallyl)benzamide (1i).

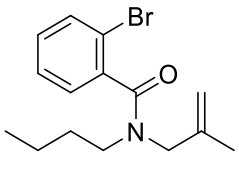
This compound exists as a mixture of rotamers. Colorless oil (0.707 g, 66%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 – 7.48 (m, 1H), 7.33 – 7.24 (m, 1H), 7.22 – 7.15 (m, 2H), 4.92 – 4.89 (m, 1H), 4.87 – 4.84 (m, 0.5H), 4.80 (s, 0.5H), 4.19 (d, J = 13.9 Hz, 0.5H), 3.98 (d, J = 13.8 Hz, 0.5H), 3.65 (d, J = 15.8 Hz, 0.5H), 3.55 (d, J = 15.7 Hz, 0.5H), 3.00 (1s, 1.4H), 2.69 (1s, 1.6H), 1.76 (1s, 1.6H), 1.52 (1s, 1.4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.56, 169.12, 140.07, 139.84, 138.58, 138.01, 132.74, 132.66, 130.19, 130.11, 127.80, 127.71, 127.62, 127.43, 119.23, 118.81, 113.22, 113.20, 77.48, 77.16, 76.84, 56.52, 52.32, 35.32, 32.10, 20.14, 19.82 ppm. HRMS (ESI): m/z calcd for $C_{12}H_{15}BrNO$ $[M + H]^+$ 268.0337, found 268.0333. IR (KBr): $\tilde{\nu}$ = 2977, 1716, 1645, 1435, 1398, 1285, 1173, 1082, 1029, 903, 767 cm^{-1}.



1i

2-Bromo-N-butyl-N-(2-methylallyl)benzamide (1j).

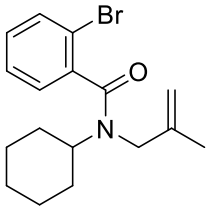
This compound exists as a mixture of rotamers. Yellow oil (0.881 g, 71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (m, 1H), 7.37 – 7.27 (m, 1H), 7.26 – 7.17 (m, 2H), 4.97 (d, J = 10.1 Hz, 1H), 4.88 (dd, J = 10.9, 9.6 Hz, 1.2H), 4.47 (d, J = 15.0 Hz, 0.4H), 3.97 – 3.88 (m, 0.6H), 3.85 (d, J = 15.1 Hz, 0.5H), 3.64 (s, 1H), 3.08 – 2.95 (m, 1.5H), 1.82 (s, 1.4H), 1.55 (s, 2H), 1.47 – 1.30 (m, 2H), 1.13 – 1.04 (m, 1H), 0.96 (t, J = 7.3 Hz, 1.8H), 0.73 (t, J = 7.4 Hz, 1.4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.04, 168.99, 140.41, 140.11, 138.51, 138.22, 132.67, 132.48, 129.94, 127.78, 127.69, 127.31, 119.07, 118.90, 113.24, 112.85, 77.48, 77.16, 76.84, 54.03, 49.05, 46.88, 43.98, 29.72, 28.70, 20.30, 20.23, 19.85, 19.62, 13.77, 13.37 ppm. HRMS



1j

(ESI): m/z calcd for $C_{15}H_{21}BrNO$ $[M + H]^+$ 310.0806, found 310.0796. IR (KBr): ṽ = 3076, 2961, 2931, 2868, 1641, 1425, 1289, 1243, 1162, 1107, 1028, 954, 900, 770, 746 cm^{-1}.

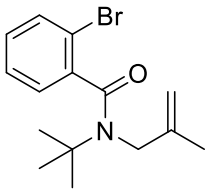
2-Bromo-N-cyclohexyl-N-(2-methylallyl)benzamide (1k).



1k

This compound exists as a mixture of rotamers. Yellow oil (0.928 g, 69%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 – 7.40 (m, 1H), 7.31 – 7.07 (m, 3H), 4.98 (d, J = 0.4 Hz, 0.5H), 4.86 – 4.79 (m, 1H), 4.76 (d, J = 1.3 Hz, 0.4H), 4.36 – 4.29 (m, 0.4H), 4.13 – 4.01 (m, 0.6H), 3.88 (d, J = 16.2 Hz, 0.5H), 3.58 (d, J = 17.1 Hz, 0.5H), 3.44 (d, J = 16.9 Hz, 0.4H), 3.21 – 3.14 (m, 0.5H), 1.89 (d, J = 11.1 Hz, 1.5H), 1.77 (s, 1.7H), 1.72 (s, 0.5H), 1.69 – 1.49 (m, 3H), 1.42 (d, J = 7.1 Hz, 3H), 1.39 – 1.33 (m, 1H), 1.10 – 0.76 (m, 2.7H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.69, 169.14, 142.08, 141.95, 139.11, 138.77, 132.83, 132.28, 129.84, 129.80, 128.14, 127.49, 127.33, 127.12, 118.98, 118.91, 112.06, 110.85, 77.48, 77.16, 76.84, 59.30, 54.99, 50.69, 46.49, 31.49, 31.26, 25.74, 25.57, 25.52, 25.04, 20.76, 20.24 ppm. HRMS (ESI): m/z calcd for $C_{17}H_{23}BrNO$ $[M + H]^+$ 336.0963, found 336.0952. IR (KBr): ṽ = 3846.31, 3664.55, 3439.47, 3075.53, 3048.42, 2945.57, 2856.95, 2670.39, 2431.96, 2241.07, 1960.85, 1925.18, 1807.49, 1720.58, 1643.97, 1565.38, 1416.12, 1374.41 $cm^{-1.}$

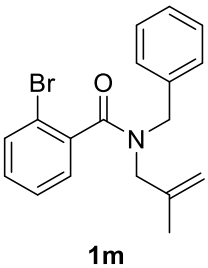
2-Bromo-N-(tert-butyl)-N-(2-methylallyl)benzamide (1l).



1l

Colorless oil (0.955 g, 77%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 – 7.45 (m, 1H), 7.26 – 7.21 (m, 2H), 7.16 – 7.10 (m, 1H), 5.00 (s, 1H), 4.91 (d, J = 1.2 Hz, 1H), 3.78 (d, J = 18.8 Hz, 1H), 3.49 (d, J = 18.7 Hz, 1H), 1.56 (s, 9H), 1.45 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.36, 143.41, 140.30, 132.41, 129.54, 127.46, 127.20, 118.84, 111.28, 77.48, 77.16, 76.84, 58.33, 52.19, 28.36, 20.25 ppm. HRMS (ESI): m/z calcd for C15H21BrNO [M + H]+ 310.0806, found 310.0796. IR (KBr): ṽ = 3064, 2917, 1640, 1437, 1392, 1365, 1275, 1239, 1199, 1166, 1129, 1028, 949, 895,768, 746 cm^{-1}.

N-Benzyl-2-bromo-N-(2-methylallyl)benzamide (1m).

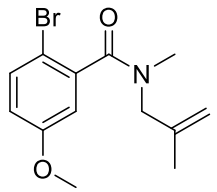


1m

This compound exists as a mixture of rotamers. Colorless oil (1.14 g, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 – 7.53 (m, 1H), 7.46 – 7.42 (m, 1H), 7.37 – 7.27 (m, 5H), 7.23 – 7.18 (m, 1H), 7.17 – 7.10 (m, 1H), 5.39 (d, J = 14.4 Hz, 0.5H), 4.96 (dd, J = 6.4, 5.2 Hz, 1H), 4.87 (d, J = 18.3 Hz, 1H), 4.61 (d, J = 14.9 Hz, 0.4H), 4.43 – 4.25 (m, 1H), 4.15 (d, J = 14.4 Hz, 0.6H), 3.61 (d, J = 15.0 Hz, 0.5H), 3.56 (d, J = 4.5 Hz, 1H), 1.86 (s, 1.2H), 1.56 (s, 1.8H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.82, 169.57, 140.03, 139.77, 138.32, 138.02, 136.63, 136.06, 133.03, 132.90, 130.33, 130.31, 129.07, 128.79, 128.56, 128.24, 128.06,

127.78, 127.68, 127.64, 127.50, 127.43, 119.42, 119.35, 114.09, 113.59, 77.48, 77.16, 76.84, 53.00, 50.80, 48.84, 46.72, 20.74, 20.14 ppm. HRMS (ESI): m/z calcd for $C_{18}H_{19}BrNO$ [M + H]+ 344.0650, found 344.1158. IR (KBr): $\tilde{\nu}$ = 3054.03, 2753.20, 2629.92, 2479.92, 2363.41, 2193.83, 1530.62, 1321.06, 1350.75 cm^{-1}.

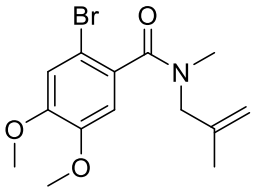
2-Bromo-5-methoxy-N-methyl-N-(2-methylallyl)benzamide (1n).



1n

This compound exists as a mixture of rotamers. Colorless oil (1.03 g, 56%).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 – 7.38 (m, 1H), 6.78 – 6.73 (m, 2H), 4.93 (dd, *J* = 2.5, 1.2 Hz, 1H), 4.88 (dd, *J* = 13.3, 12.1 Hz, 1H), 4.23 (d, *J* = 14.4 Hz, 0.5H), 3.97 (d, *J* = 14.5 Hz, 0.5H), 3.76 (s, 1.5H), 3.73 (s, 1.5H), 3.71 – 3.67 (m, 0.4H), 3.57 (dd, *J* = 14.5, 7.0 Hz, 0.5H), 3.01 (s, 1.4H), 2.74 (s, 1.6H), 1.78 (s, 1.6H), 1.57 (s, 1.4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.47, 169.04, 159.19, 158.92, 140.18, 140.04, 139.36, 138.78, 133.68, 133.56, 116.53, 116.38, 113.35, 113.30, 113.26, 113.03, 109.53, 109.17, 77.48, 77.16, 76.84, 56.62, 55.66, 55.62, 52.46, 35.38, 32.17, 20.26, 19.98 ppm. HRMS (ESI): m/z calcd for $C_{13}H_{17}BrNO_2$ [M + H]+ 298.0000, found 298.0435. IR (KBr): $\tilde{\nu}$ = 3077, 2940, 1643, 1594, 1571, 1465, 1405, 1288, 1237, 1086, 1042, 1017, 900, 816 cm^{-1}.

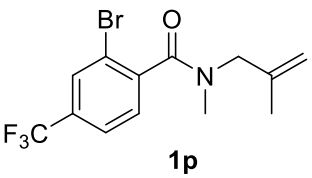
2-Bromo-4,5-dimethoxy-N-methyl-N-(2-methylallyl)benzamide (1o).



1o

This compound exists as a mixture of rotamers. Yellow oil (1.09 g, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.93 – 6.85 (m, 1H), 6.70 – 6.61 (m, 1H), 4.83 (s, 1H), 4.77 (d, *J* = 21.3 Hz, 1H), 4.32 – 3.86 (m, 1H), 3.78 – 3.72 (m, 4.7H), 3.69 (d, *J* = 1.3 Hz, 1.5H), 3.65 – 3.43 (m, 1H), 2.92 (d, *J* = 1.3 Hz, 1.5H), 2.67 (d, *J* = 1.3 Hz, 1.5H), 1.69 (s, 1.5H), 1.47 (s, 1.5H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.40, 168.96, 149.60, 149.55, 148.54, 148.18, 139.98, 139.94, 130.24, 129.60, 115.02, 115.00, 113.04, 112.79, 110.30, 110.04, 109.47, 109.05, 77.48, 77.16, 76.84, 56.47, 56.02, 55.93, 55.86, 52.30, 35.24, 32.11, 20.07, 19.76 ppm. HRMS (ESI): m/z calcd for $C_{14}H_{19}BrNO_3$ $[M + H]^+$ 328.0548, found 328.0542. IR (KBr): $\tilde{\nu}$ = 3480, 2936, 2842, 1640, 1601, 1506, 1440, 1401, 1369, 1331, 1259, 1211, 1160, 1089, 1029, 858, 794 cm^{-1}.

2-Bromo-N-methyl-N-(2-methylallyl)-4-(trifluoromethyl)benzamide (1p).

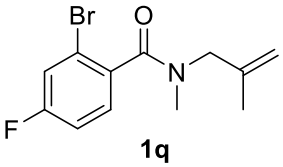


1p

This compound exists as a mixture of rotamers. White solid (1.02 g, 76%), mp: 50 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 7.1 Hz, 1H), 7.64 – 7.55 (m, 1H), 7.37 (d, *J* = 7.8 Hz, 1H), 4.95 (dd, *J* = 9.8, 0.6 Hz, 1H), 4.93 – 4.82 (m, 1H), 4.26 (d, *J* = 14.5 Hz, 0.5H), 4.00 (d, *J* = 14.4 Hz, 0.5H), 3.68 – 3.55 (m, 1H), 3.05 (s, 1.4H), 2.73 (s, 1.6H), 1.79 (s, 1.5H),

1.56 (s, 1.5H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.41, 168.02, 142.30, 141.76, 139.88, 139.59, 132.57 (d, J = 4.3 Hz), 132.26, 129.92, 128.29, 124.96 – 124.91 (m), 124.71 (d, J = 29.1 Hz), 124.23, 121.52, 119.65 (d, J = 41.9 Hz), 113.60 (d, J = 21.2 Hz), 77.48, 77.00 (d, J = 32.0 Hz), 56.54, 52.55, 35.33, 32.40, 20.24, 19.95 ppm. ^{19}F NMR (471 MHz, $CDCl_3$): δ -62.98, -62.99 ppm. HRMS (ESI): m/z calcd for $C_{13}H_{14}BrF_3NO$ $[M + H]^+$ 336.0210, found 336.0197. IR (KBr): $\tilde{\nu}$ = 3089, 2969, 2913, 1643, 1562, 1502, 1436, 1455, 1391, 1326, 1285, 1251, 1171, 1128, 1076, 1033, 910, 885, 856, 750, 706 cm^{-1}.

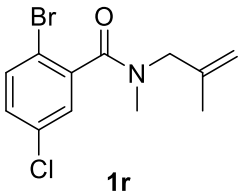
2-Bromo-4-fluoro-N-methyl-N-(2-methylallyl)benzamide (1q).



1q

This compound exists as a mixture of rotamers. Yellow oil (0.972 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 – 7.21 (m, 1H), 7.19 – 7.15 (m, 1H), 7.03 – 6.94 (m, 1H), 4.91 – 4.81 (m, 1.6H), 4.76 (s, 0.5H), 4.05 (d, J = 80.8 Hz, 1H), 3.56 (q, J = 15.3 Hz, 1H), 2.97 (s, 1.5H), 2.67 (s, 1.5H), 1.72 (s, 1.5H), 1.49 (s, 1.5H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.96, 168.53, 163.47 (d, J = 4.5 Hz), 160.96 (d, J = 4.4 Hz), 139.98, 139.76, 134.88 (d, J = 3.7 Hz), 134.29 (d, J = 3.8 Hz), 129.36 – 128.80 (m), 120.51 – 119.75 (m), 119.47 (d, J = 9.6 Hz), 115.33, 115.07 (d, J = 7.4 Hz), 114.82, 113.30 (d, J = 15.3 Hz), 77.48, 77.16, 76.84, 56.63, 52.53, 35.45, 32.43, 20.19, 19.89 ppm. ^{19}F NMR (471 MHz, $CDCl_3$): δ -109.75, -109.94 ppm. HRMS (ESI): m/z calcd for $C_{12}H_{14}BrFNO$ $[M + H]^+$ 286.0242, found 286.0233. IR (KBr): $\tilde{\nu}$ = 3668.61, 3470.33, 3080.40, 3046.54, 2964.81, 2732.52, 2546.02, 2462.15, 2327.01, 2077.10, 1890.46, 1636.10, 1420.30, 1341.53 cm^{-1}.

2-Bromo-5-chloro-N-methyl-N-(2-methylallyl)benzamide (1r).

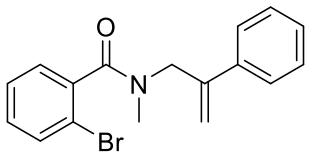


1r

This compound exists as a mixture of rotamers. White solid (0.968 g, 80%), mp: 64 – 66 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (dd, J = 7.9, 6.6 Hz, 1H), 7.25 – 7.16 (m, 2H), 4.96 (s, 0.6H), 4.93 (s, 1H), 4.84 (s, 0.4H), 4.22 (d, J = 14.1 Hz, 0.5H), 4.00 (d, J = 14.3 Hz, 0.5H), 3.74 – 3.54 (m, 1H), 3.03 (s, 1.3H), 2.75 (s, 1.7H), 1.79 (s, 1.7H), 1.59 (s, 1.3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.26, 167.85, 140.13, 139.97, 139.71, 139.58, 134.14, 134.08, 134.05, 133.84, 130.44, 130.37, 128.00, 127.84, 117.36, 116.95, 113.61, 77.48, 77.16, 76.84, 56.66, 52.57, 35.42, 32.37, 20.27, 19.99 ppm. HRMS (ESI): m/z calcd for $C_{12}H_{14}BrClNO$ $[M + H]^+$ 301.9947, found 301.9937. IR (KBr): $\tilde{\nu}$ = 3090.39, 3057.12, 2925.59, 2853.66, 1676.74, 1639.55, 1583.43, 1496.52, 1476.23, 1453.51, 1429.41, 1336.63, 1253.78, 1240.69 cm-1.

2-Bromo-N-methyl-N-(2-phenylallyl)benzamide (1s).

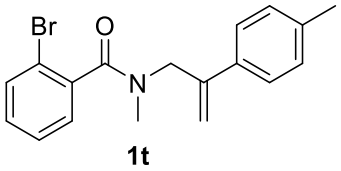
This compound exists as a mixture of rotamers. White solid (0.766 g, 58%), mp: 145 – 147 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 – 7.44 (m, 1.7H), 7.41 (d, J = 8.0 Hz, 0.7H), 7.31 – 7.14 (m, 5H), 7.14 – 7.00 (m, 2H), 6.92 (d, J = 7.5 Hz, 0.7H), 5.46 (s, 0.7H), 5.33 (s, 0.3H), 5.25 (s, 0.7H), 5.13 (s, 0.3H), 4.72 (d, J = 14.9 Hz, 0.7H), 4.52 (d, J = 14.8 Hz, 0.7H), 4.15 (d, J = 16.4 Hz, 0.3H), 3.97 (d, J = 16.4 Hz, 0.3H), 3.02 (d, J = 0.5 Hz, 1H), 2.58 (d, J = 0.6 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.62, 169.00, 143.39, 143.20, 138.59, 138.36, 138.09, 137.76, 132.63, 132.58, 130.34, 130.05, 128.38, 128.09, 128.05, 127.91, 127.57, 127.46, 127.37, 126.46, 126.17, 119.23, 118.73, 115.37, 114.72, 77.48, 77.16, 76.84, 54.47, 49.77, 34.95, 32.56 ppm. HRMS (ESI): m/z calcd for $C_{17}H_{17}BrNO$ $[M + H]^+$ 330.0493, found 330.0492. IR (KBr): $\tilde{\nu}$ = 3855, 3759, 3052, 2924, 2331, 1642, 1490, 1447, 1399, 1277, 1168, 1079, 1030, 980, 909, 773, 746, 705 cm^{-1}.



1s

2-Bromo-N-methyl-N-(2-(p-tolyl)allyl)benzamide (1t).

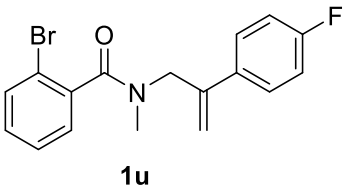
This compound exists as a mixture of rotamers. Yellow oil (0.895 g, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, J = 7.6 Hz, 0.3H), 7.49 (d, J = 8.0 Hz, 0.6H), 7.41 (d, J = 8.1 Hz, 1.3H), 7.29 – 7.13 (m, 4H), 7.07 (d, J = 8.0 Hz, 0.7H), 7.02 – 6.98 (m, 1.3H), 5.50 (s, 0.6H), 5.38 (s, 0.3H), 5.26 (s, 0.6H), 5.14 (s, 0.3H), 4.80 (d, J = 15.0 Hz, 0.6H), 4.52 (d, J = 15.0 Hz, 0.6H), 4.20 (d, J = 16.4 Hz, 0.3H), 4.02 (d, J = 16.4 Hz, 0.3H), 3.08 (s, 1H), 2.65 (s, 2H), 2.32, 2.29 (2s, 3.2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.74, 169.10, 143.13, 143.03, 138.51, 138.05, 137.92, 135.72, 135.27, 132.73, 132.66, 130.39, 130.11, 129.15, 128.00, 127.65, 127.59, 127.44, 126.36, 126.08, 119.34, 118.86, 114.57, 113.96, 77.48, 77.16, 76.84, 54.50, 49.89, 35.02, 32.65, 21.20, 21.14 ppm. HRMS (ESI): m/z calcd for $C_{18}H_{19}BrNO$ $[M + H]^+$ 344.0650, found 344.0640. IR (KBr): $\tilde{\nu}$ = 3084, 3054, 3022, 2922, 2865, 1654, 1565, 1509, 1488, 1449, 1398, 1277, 1079, 1030, 904, 826, 769, 740 cm^{-1}.



1t

2-Bromo-N-(2-(4-fluorophenyl)allyl)-N-methylbenzamide (1u).

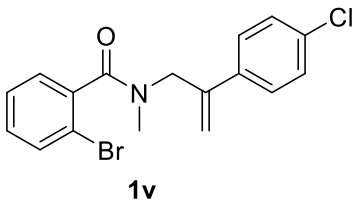
This compound exists as a mixture of rotamers. Yellow oil (0.849 g, 61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 – 7.45 (m, 2.6H), 7.29 – 7.11 (m, 3H), 7.07 – 6.90 (m, 3.8H), 5.47 (s, 0.7H), 5.34 (s, 0.3H), 5.29 (s, 0.7H), 5.17 (s, 0.3H), 4.69 (d, J = 13.4 Hz, 0.7H), 4.59 (d, J = 13.8 Hz, 0.7H), 4.16 (d, J = 16.4 Hz, 0.3H), 4.00 (d, J = 16.3 Hz, 0.3H), 3.07 (s, 1H), 2.64 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.62, 169.07, 163.85 (d, J = 12.7 Hz), 161.39 (d, J = 13.1 Hz), 219.44 – 130.05 (m), 142.43 (d, J = 17.6 Hz), 138.32, 137.78, 134.76 (d, J = 3.1 Hz), 134.46 (dd, J = 58.8, 3.1 Hz), 137.53 – 130.53 (m), 128.30 (d, J = 8.0



1u

Hz), 128.10 – 127.82 (m), 127.76 – 127.24 (m), 119.33, 118.74, 115.29 (dt, *J* = 24.2, 12.9 Hz), 77.48, 77.16, 76.84, 54.60, 49.87, 34.91, 32.57 ppm. ^{19}F NMR (471 MHz, $CDCl_3$): δ -113.68, -114.03, -115.92, -115.96, -116.47, -116.51 ppm. HRMS (ESI): m/z calcd for $C_{17}H_{16}BrFNO$ $[M + H]^+$ 348.0399, found 348.0396. IR (KBr): $\tilde{\nu}$ = 3063, 2965, 2927, 1598, 1508, 1453, 1400, 1226, 1080, 1031, 839, 770, 744 cm^{-1}.

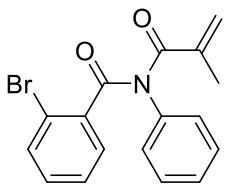
2-Bromo-N-(2-(4-chlorophenyl)allyl)-N-methylbenzamide (1v).



1v

This compound exists as a mixture of rotamers. Yellow oil (0.670 g, 46%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 8.0, 1.0 Hz, 0.3H), 7.53 – 7.46 (m, 2.3H), 7.35 – 7.14 (m, 5H), 7.06 – 7.01 (m, 1.3H), 5.54 (s, 0.7H), 5.41 (s, 0.3H), 5.35 (s, 0.7H), 5.23 (s, 0.3H), 4.67 (q, *J* = 14.7 Hz, 1.6H), 4.20 (d, *J* = 16.4 Hz, 0.3H), 4.03 (d, *J* = 16.5 Hz, 0.3H), 3.09 (s, 0.9H), 2.66 (s, 2.1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.77, 169.23, 142.53, 142.34, 138.33, 137.80, 137.15, 136.59, 134.15, 134.07, 132.85, 130.57, 130.29, 128.72, 128.68, 128.05, 127.99, 127.78, 127.65, 127.63, 127.55, 119.44, 118.86, 116.23, 115.52, 77.48, 77.16, 76.84, 54.50, 49.84, 35.04, 32.72 ppm. HRMS (ESI): m/z calcd for $C_{17}H_{16}BrClNO$ $[M + H]^+$ 364.0103, found 364.0110. IR (KBr): $\tilde{\nu}$ = 2923, 1722, 1641, 1490, 1432, 1399, 1277, 1083, 1031, 910, 835, 768, 744 cm^{-1}.

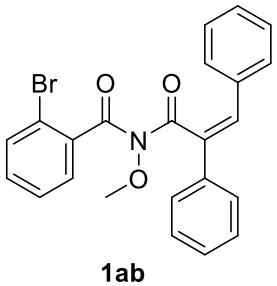
2-Bromo-N-methacryloyl-N-phenylbenzamide (1aa).



1aa

White solid (1.20 g, 70%), mp: 60 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 7.9 Hz, 1H), 7.38 – 7.33 (m, 1H), 7.29 (q, *J* = 7.3 Hz, 2H), 7.22 (t, *J* = 7.5 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.13 (td, *J* = 7.9, 1.3 Hz, 1H), 5.68 (s, 1H), 5.36 (s, 1H), 1.67 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.82, 170.70, 141.30, 138.49, 137.86, 134.69, 133.45, 133.35, 132.21, 131.44, 129.44, 129.36, 128.26, 127.82, 127.26, 123.74, 122.29, 119.94, 77.48, 77.16, 76.84, 18.56 ppm. HRMS (ESI): m/z calcd for $C_{17}H_{15}BrNO_2$ $[M + H]^+$ 344.0286, found 344.0279. IR (KBr): $\tilde{\nu}$ = 3325, 3199, 3064, 2981, 2924, 2853, 1710, 1594, 1536, 1494, 1436, 1290, 1166, 1030, 917, 749, 603 cm^{-1}.

(Z)-2-Bromo-N-(2,3-diphenylacryloyl)-N-methoxybenzamide (1ab).

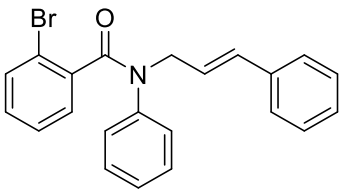


1ab

White solid (1.88 g, 86%), mp: 61 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 – 7.99 (m, 1H), 7.77 – 7.73 (m, 1H), 7.45 – 7.40 (m, 2H), 7.40 – 7.36 (m, 5H), 7.28 (s, 1H), 7.16 – 7.10 (m, 3H), 7.01 – 6.97 (m, 2H), 3.87 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.03, 150.30, 135.43, 135.31, 134.81, 133.61, 133.18, 132.27, 131.79, 130.32, 130.23, 129.99, 128.64, 128.18, 128.12, 128.04, 127.41, 122.66, 77.48,

77.16, 76.84, 63.08 ppm. HRMS (ESI): m/z calcd for $C_{23}H_{19}BrNO_3$ $[M + H]^+$ 436.0548, found 436.0536. IR (KBr): $\tilde{\nu}$ = 2938, 1757, 1635, 1584, 1491, 1466, 1437, 1263, 1288, 1229, 1158, 1129, 1076, 1045, 1018, 963, 910, 778, 738, 706 cm^{-1}.

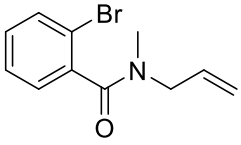
2-Bromo-N-cinnamyl-N-phenylbenzamide (1ac).



1ac

Yellow oil (1.02 g, 65%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.32 – 7.28 (m, 3H), 7.23 (d, J = 7.7 Hz, 2H), 7.19 – 7.17 (m, 1H), 7.13 – 7.06 (m, 4H), 7.06 – 6.98 (m, 3H), 6.93 (td, J = 7.7, 2.1 Hz, 1H), 6.47 (d, J = 15.9 Hz, 1H), 6.35 (dt, J = 15.9, 6.5 Hz, 1H), 4.62 (d, J = 6.3 Hz, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.52, 141.76, 138.46, 136.73, 133.70, 132.68, 129.88, 128.99, 128.87, 128.63, 128.02, 127.81, 127.60, 126.73, 126.58, 123.98, 119.77, 77.48, 77.16, 76.84, 51.85 ppm. HRMS (ESI): m/z calcd for $C_{22}H_{19}BrNO$ $[M + H]^+$ 392.0650, found 392.0644 IR (KBr): $\tilde{\nu}$ = 2977.91, 2928.10, 2857.69, 2551.30, 2333.64, 1951.90, 1881.00, 1805.94, 1276.47, 1263.87, 1250.10, 1250.37, 1157.72, 1122.02, 1076.23, 1026.79 cm-1.

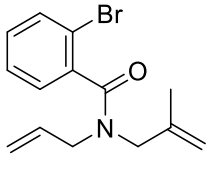
N-Allyl-2-bromo-N-methylbenzamide (3a).



3a

This compound exists as a mixture of rotamers. Colorless oil (0.813 g, 80%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.49 (dd, J = 7.5, 1.0 Hz, 1H), 7.31 – 7.13 (m, 3H), 5.87 – 5.76 (m, 0.5H), 5.66 – 5.57 (m, 0.5H), 5.25 – 5.17 (m, 1H), 5.14 – 5.04 (m, 1H), 4.22 (s, 0.5H), 4.01 (s, 0.5H), 3.71 – 3.57 (m, 1H), 3.01 (s, 1.5H), 2.71 (s, 1.5H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.37, 169.03, 138.56, 138.29, 132.85, 132.83, 132.65, 132.37, 130.31, 130.26, 127.83, 127.72, 127.70, 127.60, 119.23, 119.05, 118.17, 118.12, 77.48, 77.16, 76.84, 53.47, 49.50, 35.61, 32.26 ppm. HRMS (ESI): m/z calcd for $C_{11}H_{13}BrNO$ $[M + H]^+$ 254.0180, found 254.0174. IR (KBr): $\tilde{\nu}$ = 3076, 2924, 1637, 1591, 1487, 1426, 1400, 1289, 1252, 1117, 1079, 1030, 994, 926, 771, 748, 688 cm^{-1}.

N-Allyl-2-bromo-N-(2-methylallyl)benzamide (3b).

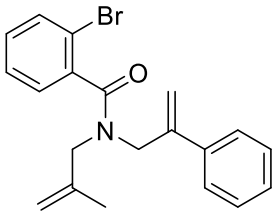


3b

This compound exists as a mixture of rotamers. Colorless oil (0.706 g, 60%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.49 (t, J = 7.5 Hz, 1H), 7.31 – 7.12 (m, 3.2H), 5.96 – 5.78 (m, 0.5H), 5.62 – 5.52 (m, 0.5H), 5.29 – 4.77 (m, 4.5H), 4.62 (d, J = 14.4 Hz, 0.5H), 4.45 (d, J = 14.9 Hz, 0.5H), 3.76 – 3.50 (m, 3.2H), 1.76 (s, 1.5H), 1.49 (s, 1.5H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.38, 169.31, 140.16, 139.88, 138.35, 138.01, 132.92, 132.76, 132.47, 132.35, 130.29, 127.85, 127.81, 127.53, 119.31, 119.05, 118.38, 118.35, 113.53, 113.23, 77.48, 77.16, 76.84, 53.20, 49.87, 48.85, 46.39, 20.53, 20.10 ppm. HRMS (ESI): m/z calcd for $C_{14}H_{17}BrNO$ [M +

H]$^+$ 294.0493, found 294.0482. IR (KBr): $\tilde{\nu}$ = 3078, 2977, 2919, 1640, 1592, 1416, 1340, 1291, 1246, 1159, 1116, 1027, 989, 908, 771, 751 cm^{-1}.

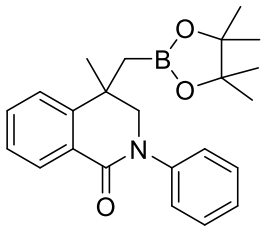
2-Bromo-N-(2-methylallyl)-N-(2-phenylallyl)benzamide (3c).



3c

This compound exists as a mixture of multiple rotamers. Yellow oil (0.829 g, 56%).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 – 6.80 (m, 9H), 5.43 (d, J = 0.6 Hz, 0.3H), 5.32 (d, J = 0.7 Hz, 0.2H), 5.26 (d, J = 1.1 Hz, 0.3H), 5.07 (dd, J = 12.92 Hz, 0.6H), 4.93 – 4.76 (m, 2H), 4.65 (d, J = 5.8 Hz, 0.2H), 4.14 (d, J = 15.3 Hz, 0.3H), 4.01 (s, 0.6H), 3.50 (t, J = 20.6 Hz, 1H), 3.39 – 3.01 (m, 1H), 1.85 – 1.67 (m, 1.6H), 1.46 (2s, 1.4H), 1.37 (s, 0.4H), 1.31 – 1.25 (m, 0.7H), 1.02 (dd, J = 23.6, 7.0 Hz, 0.3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.82, 169.54, 143.41, 143.09, 140.30, 139.63, 139.05, 138.81, 138.26, 137.91, 137.89, 132.88, 132.80, 130.39, 130.22, 130.15, 128.72, 128.50, 128.16, 128.10, 127.70, 127.56, 127.35, 127.29, 126.86, 126.70, 126.30, 119.18, 119.12, 115.98, 114.17, 113.98, 113.31, 77.48, 77.16, 76.84, 52.70, 50.69, 49.31, 46.43, 20.77, 20.22 ppm. HRMS (ESI): m/z calcd for $C_{20}H_{21}BrNO$ $[M + H]^+$ 370.0806, found 370.0853. IR (KBr): $\tilde{\nu}$ = 3078, 2969, 2923, 1642, 1423, 1279, 1244, 1156, 1099, 1025, 992, 944, 903, 772, 750, 703 cm^{-1}.

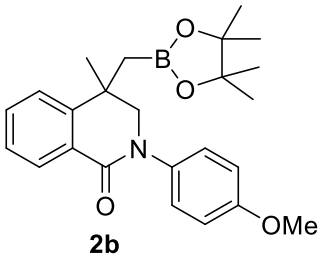
4-Methyl-2-phenyl-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-3,4-dihydroisoquinolin-1(2H)-one (2a).



2a

White solid, (0.177 g, 94%), mp: 88 – 90 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (dd, J = 7.7, 1.3 Hz, 1H), 7.50 – 7.44 (m, 1H), 7.44 – 7.38 (m, 4H), 7.37 (dd, J = 3.7, 1.3 Hz, 1H), 7.35 – 7.30 (m, 1H), 7.26 – 7.21 (m, 1H), 4.03 (d, J = 12.3 Hz, 1H), 3.77 (d, J = 12.3 Hz, 1H), 1.49 (s, 3H), 1.41 (d, J = 15.7 Hz, 1H), 1.33 (d, J = 15.7 Hz, 1H), 1.14 (s, 6H), 1.08 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.18, 147.95, 143.31, 132.25, 128.96, 128.89, 128.26, 126.69, 126.18, 125.56, 123.82, 83.25, 77.48, 77.16, 76.84, 60.67, 36.22, 25.87, 24.77, 24.71 ppm. HRMS (ESI): m/z calcd for $C_{23}H_{29}BNO_3$ $[M + H]^+$ 378.2240, found 378.2248. IR (KBr): $\tilde{\nu}$ = 3449, 3046, 2979, 2923, 1649, 1599, 1470, 1417, 1379, 1355, 1298, 1266, 1220, 1172, 1140, 1090, 1070, 1032, 990, 968, 896, 845, 802, 771, 750 cm^{-1}.

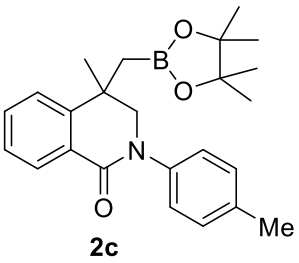
2-(4-Methoxyphenyl)-4-methyl-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-3,4-dihydroisoquinolin-1(2H)-one (2b).



2b

White solid (0.155 g, 76%), mp: 88 – 90 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (dd, J = 7.7, 1.3 Hz, 1H), 7.47 (td, J = 7.6, 1.5 Hz, 1H), 7.40 – 7.30 (m, 4H), 6.96 – 6.90 (m, 2H), 3.96 (d, J = 12.3 Hz, 1H), 3.82 (s, 3H), 3.72 (d, J = 12.3 Hz, 1H), 1.48 (s, 3H), 1.40 (d, J = 15.7 Hz, 1H), 1.33 (d, J = 15.7 Hz, 1H), 1.15 (s, 6H), 1.10 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.41, 157.84, 147.93, 136.36, 132.19, 128.97, 128.36, 126.95, 126.73, 123.88, 114.27, 83.33, 77.48, 77.16, 76.84, 61.10, 55.61, 36.24, 25.98, 24.86, 24.80 ppm. HRMS (ESI): m/z calcd for $C_{24}H_{31}BNO_4$ $[M + H]^+$ 408.2346, found 408.2333. IR (KBr): $\tilde{\nu}$ = 3449, 2979, 2926, 1651, 1602, 1510, 1479, 1442, 1413, 1362, 1329, 1301, 1276, 1231, 1183, 1143, 1069, 1034, 871, 849, 829, 802, 771 cm^{-1}.

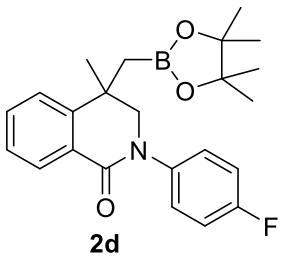
4-Methyl-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-2-(p-tolyl)-3,4-dihydroisoquinolin-1(2H)-one (2c).



2c

White solid (0.136 g, 70%), mp: 102 – 104 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (dd, J = 7.7, 1.3 Hz, 1H), 7.47 (td, J = 7.6, 1.5 Hz, 1H), 7.38 (dd, J = 7.7, 0.8 Hz, 1H), 7.35 – 7.29 (m, 3H), 7.21 (d, J = 8.1 Hz, 2H), 3.99 (d, J = 12.3 Hz, 1H), 3.74 (d, J = 12.3 Hz, 1H), 2.36 (s, 3H), 1.48 (s, 3H), 1.40 (d, J = 15.5 Hz, 1H), 1.34 (d, J = 15.7 Hz, 1H), 1.15 (s, 6H), 1.10 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.29, 147.93, 140.83, 136.03, 132.20, 129.59, 129.01, 128.43, 126.73, 125.52, 123.91, 83.32, 77.48, 77.16, 76.84, 60.94, 36.27, 26.06, 24.86, 24.80, 21.16 ppm. HRMS (ESI): m/z calcd for $C_{24}H_{31}BNO_3$ $[M + H]^+$ 392.2397, found 392.2382. IR (KBr): $\tilde{\nu}$ = 3473, 3060, 3038, 2969, 2912, 1656, 1603, 1577, 1513, 1468, 1404, 1366, 1325, 1276, 1258, 1226, 1186, 1164, 1141, 1109, 1030, 990, 867, 849, 791, 761, 699 cm^{-1}.

2-(4-Fluorophenyl)-4-methyl-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-3,4-dihydroisoquinolin-1(2H)-one (2d).

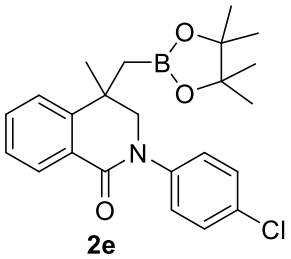


2d

White solid (0.176 g, 89%), mp: 95 – 97 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, J = 7.7 Hz, 1H), 7.47 (t, J = 7.5 Hz, 1H), 7.38 (dd, J = 8.3, 4.2 Hz, 3H), 7.30 (t, J = 7.7 Hz, 1H), 7.11 – 7.02 (m, 2H), 3.97 (d, J = 12.2 Hz, 1H), 3.73 (d, J = 12.3 Hz, 1H), 1.47 (s, 3H), 1.40 (d, J = 15.6 Hz, 1H), 1.30 (d, J = 15.7 Hz, 1H), 1.14 (s, 6H), 1.09 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.20, 161.78, 159.35, 147.94, 139.17 (d, J = 3.2 Hz), 132.28, 128.82, 127.90, 127.25 (d, J = 8.3 Hz), 126.61, 123.73, 115.64,

115.41, 83.18, 77.48, 77.16, 76.84, 60.66, 36.10, 25.58, 24.64 (d, J = 5.5 Hz) ppm. ^{19}F NMR (471 MHz, $CDCl_3$): δ -115.98 ppm. HRMS (ESI): m/z calcd for $C_{23}H_{28}BFNO_3$ $[M + H]^+$ 396.2146, found 396.2151. IR (KBr): $\tilde{\nu}$ = 3449, 3347, 2974, 2923, 2885, 1654, 1599, 1512, 1469, 1423, 1409, 1358, 1301, 1325, 1298, 1217, 1139, 1030, 842, 770, 754, 735 cm^{-1}.

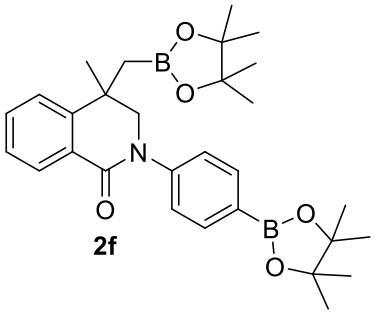
2-(4-Chlorophenyl)-4-methyl-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-3,4-dihydroisoquinolin-1(2H)-one (2e).



2e

White solid (0.152 g, 74%), mp: 88 – 90 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (dd, J = 7.7, 1.1 Hz, 1H), 7.48 (td, J = 7.7, 1.3 Hz, 1H), 7.40 – 7.30 (m, 6H), 3.99 (d, J = 12.2 Hz, 1H), 3.74 (d, J = 12.2 Hz, 1H), 1.47 (s, 3H), 1.39 (d, J = 15.6 Hz, 1H), 1.30 (d, J = 15.7 Hz, 1H), 1.14 (s, 6H), 1.09 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.19, 148.01, 141.83, 132.46, 131.45, 129.00, 128.94, 127.99, 126.84, 126.78, 123.84, 83.33, 77.48, 77.16, 76.84, 60.50, 36.25, 25.80, 24.79, 24.75 ppm. HRMS (ESI): m/z calcd for $C_{23}H_{28}BClNO_3$ $[M + H]^+$ 412.1850 found 412.1854. IR (KBr): $\tilde{\nu}$ = 3063.73, 2989.90, 2889.50, 1654.65, 1593.16, 1496.46, 1467.95, 1421.58, 1402.68, 1327.73, 1140.60, 1088.71, 1031.73, 968.58, 843.62, 771.49, 706.27, 508.58 cm^{-1}.

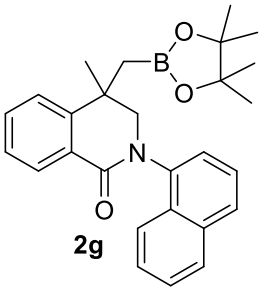
4-methyl-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-3,4-dihydroisoquinolin-1(2H)-one (2f).



2f

White solid (0.156 g, 62%), mp: 168 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, J = 7.7 Hz, 1H), 7.85 (d, J = 8.1 Hz, 2H), 7.48 (dd, J = 14.0, 4.6 Hz, 3H), 7.40 – 7.30 (m, 2H), 4.05 (d, J = 12.2 Hz, 1H), 3.78 (d, J = 12.3 Hz, 1H), 1.47 (s, 3H), 1.36 (d, J = 9.9 Hz, 14H), 1.15 (s, 6H), 1.10 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.13, 148.03, 146.07, 135.53, 132.36, 129.10, 128.34, 126.77, 124.60, 123.88, 83.92, 83.36, 77.48, 77.16, 76.84, 60.45, 36.32, 26.07, 24.96, 24.95, 24.86, 24.81 ppm. HRMS (ESI): m/z calcd for $C_{29}H_{40}B_2NO_5$ $[M + H]^+$ 504.3092 found 504.3085. IR (KBr): $\tilde{\nu}$ = 3436.14, 2978.03, 2927.41, 2883.40, 1656.53, 1603.88, 1467.23, 1401.47, 1361.14, 1308.72, 1275.21, 1230.35, 1143.59, 1108.92, 1093.23, 1065.79, 965.25, 861.17, 842.24, 763.19, 700.70, 661.60 ppm.

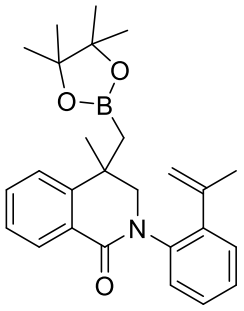
4-Methyl-2-(naphthalen-1-yl)-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-3,4-dihydroisoquinolin-1(2H)-one (2g).



2g

This title compound exists as a mixture of multiple rotamers. Colorless oil (0.165 g, 77%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, J = 7.7 Hz,1H), 7.94 – 7.82 (m, 3H), 7.58 – 7.42 (m, 6H), 7.41 – 7.35 (m, 1H), 4.15 (d, J = 12.3 Hz, 0.5H), 4.01 (d, J = 12.4 Hz, 0.5H), 3.91 (d, J = 12.4 Hz, 0.5H), 3.83 (d, J = 12.3 Hz, 0.5H), 1.58 (d, J = 4.6 Hz, 3H), 1.54 (t, J = 8.0 Hz, 1H), 1.49 – 1.40 (m, 1H), 1.26 (s, 1H), 1.21 (s, 1H), 1.17 (s, 3H), 1.11 (s, 3H), 1.06 (s, 2H), 0.98 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.92, 164.86, 148.25, 140.74, 140.45, 134.67, 132.45, 129.97, 129.19, 128.66, 128.53, 128.15, 128.03, 126.84, 126.78, 126.28, 125.93, 124.78, 124.16, 124.06, 123.87, 123.67, 123.34, 83.37, 83.27, 77.48, 77.16, 76.84, 61.70, 36.41, 26.82, 26.09, 24.94, 24.93, 24.83, 24.76, 24.69, 24.67 ppm. HRMS (ESI): m/z calcd for $C_{27}H_{31}BNO_3$ [M + H]+ 428.2397 found 428.2395. IR (KBr): $\tilde{\nu}$ = 3409, 3061, 2977, 2929, 1662, 1599, 1509, 1474, 1418, 1361, 1326, 1270, 1225, 1141, 971, 849, 766, 700 cm^{-1}.

4-Methyl-2-(2-(prop-1-en-2-yl)phenyl)-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-3,4-dihydroisoquinolin-1(2H)-one (2h).

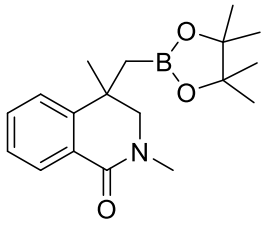


2h

Colourless oil (0.140 g, 67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (dd, J = 7.7, 1.4 Hz, 1H), 7.47 (td, J = 7.6, 1.5 Hz, 1H), 7.38 (dd, J = 7.8, 0.9 Hz, 1H), 7.36 – 7.26 (m, 5H), 5.12 – 5.08 (m, 1H), 5.01 (s, 1H), 4.17 (d, J = 11.3 Hz, 0.3H), 3.74 (d, J = 12.2 Hz, 0.6H), 3.60 (d, J = 12.2 Hz, 0.6H), 3.35 (d, J = 11.2 Hz, 0.3H), 2.05 (s, 3H), 1.47 (s, 3H), 1.28 – 1.19 (m, 2H), 1.13 (s, 6H), 1.07 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.62, 148.11, 143.72, 141.54, 140.57, 132.11, 129.42, 128.83, 128.20, 127.35, 126.61, 123.93, 115.60, 83.19, 77.48, 77.16, 76.84, 61.07, 36.13, 24.81, 24.74, 23.69 ppm. HRMS (ESI): m/z calcd for $C_{26}H_{33}BNO_3$ [M + H]$^+$ 418.2553, found 418.2559. IR (KBr): $\tilde{\nu}$ = 3683.29, 3400.58, 3060.67, 2980.81, 2929.17, 1651.89, 1603.13, 1575.22, 1490.07, 1474.65, 1445.91, 1420.27, 1360.01, 1327.83 cm^{-1}.

2,4-Dimethyl-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-3,4-dihydroisoquinolin-1(2H)-one (2i).

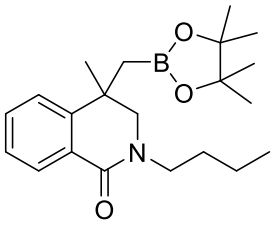
Colourless oil (0.132 g, 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (dd, J = 7.7, 1.2 Hz, 1H), 7.38 – 7.33 (m, 1H), 7.25 – 7.19 (m, 2H), 3.54 (d, J = 12.4 Hz, 1H), 3.27 (d, J = 12.4 Hz, 1H), 3.10 (s, 3H), 1.32 (s, 3H), 1.21 (s, 1H), 1.18 (s, 1H), 1.12 (s, 6H), 1.08 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.86, 147.76, 131.86, 128.42, 127.96, 126.61, 123.74, 83.35, 77.48, 77.16, 76.84, 59.58, 35.86, 35.45, 26.41, 24.90 ppm. HRMS (ESI): m/z calcd for $C_{18}H_{27}BNO_3$ $[M + H]^+$ 315.2006, found 316.2089. IR (KBr): $\tilde{\nu}$ = 3048.24, 2986.92, 2929.68, 1652.09, 1594.85, 1566.23, 1496.73, 1480.38, 1482.42, 1359.77, 1335.24, 1296.40, 1268.50, 1196.24, 1167.62, 1145.14, 1091.99 cm^{-1}.



2i

2-Butyl-4-methyl-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-3,4-dihydroisoquinolin-1(2H)-one (2j).

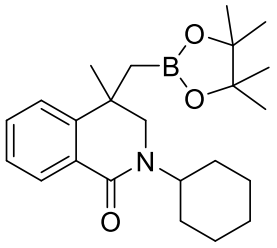
Yellow oil (0.164 g, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (dd, J = 7.7, 1.3 Hz, 1H), 7.37 – 7.30 (m, 1H), 7.25 – 7.17 (m, 2H), 3.56 – 3.39 (m, 3H), 3.26 (d, J = 12.4 Hz, 1H), 1.60 – 1.51 (m, 2H), 1.36 – 1.28 (m, 5H), 1.19 (s, 1H), 1.15 (s, 1H), 1.11 (s, 6H), 1.08 (s, 6H), 0.88 (t, J = 7.4 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.19, 147.55, 131.64, 128.36, 128.14, 126.45, 123.62, 83.19, 77.48, 77.16, 76.84, 57.34, 47.06, 35.58, 29.50, 26.03, 24.83, 24.78, 20.29, 13.93 ppm. HRMS (ESI): m/z calcd for $C_{21}H_{33}BNO_3$ $[M + H]^+$ 358.2553, found 358.2558. IR (KBr): $\tilde{\nu}$ = 3420, 2962, 2929, 2872, 1652, 1604, 1575, 1484, 1429, 1360, 1317, 1268, 1227, 1193, 1143, 1110, 1035, 969, 848, 799, 765, 702 cm^{-1}.



2j

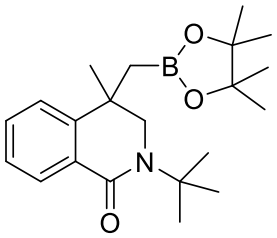
2-Cyclohexyl-4-methyl-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-3,4-dihydroisoquinolin-1(2H)-one (2k).

Yellow oil (0.167 g, 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (dd, J = 7.7, 1.3 Hz, 1H), 7.42 – 7.37 (m, 1H), 7.31 – 7.25 (m, 2H), 4.68 – 4.63 (m, 1H), 3.47 (d, J = 12.5 Hz, 1H), 3.25 (d, J = 12.5 Hz, 1H), 1.81 – 1.71 (m, 5H), 1.52 – 1.39 (m, 4H), 1.37 (s, 3H), 1.24 (s, 1H), 1.23 (s, 1H), 1.19 (s, 6H), 1.17 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.81, 147.43, 131.68, 128.71, 126.53, 123.69, 83.28, 77.48, 77.16, 76.84, 51.88, 51.62, 35.37, 30.10, 29.94, 25.95, 25.89, 25.80, 25.73, 24.99, 24.89 ppm. HRMS (ESI): m/z calcd for $C_{23}H_{34}BNO_3$ $[M + H]^+$ 384.2710, found 384.2715. IR (KBr): $\tilde{\nu}$ = 3451, 2976, 2929, 2856, 1646, 1601, 1479, 1451, 1429, 1361, 1318, 1275, 1254, 1197, 1142, 1036, 969, 894, 849, 798, 765 cm^{-1}.



2k

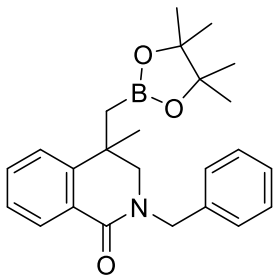
2-(Tert-butyl)-4-methyl-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-3,4-dihydroisoquinolin-1(2H)-one (2l).



2l

White solid (0.161 g, 90%), mp: 71 – 73 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 – 8.01 (m, 1H), 7.39 – 7.35 (m, 1H), 7.28 – 7.22 (m, 2H), 3.59 (d, J = 12.6 Hz, 1H), 3.40 (d, J = 12.6 Hz, 1H), 1.54 (s, 9H), 1.35 (s, 3H), 1.25 (s, 1H), 1.21 (s, 1H), 1.20 (s, 6H), 1.17 (s, 6H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.35, 147.80, 131.37, 130.25, 128.39, 126.33, 123.21, 83.21, 77.48, 77.16, 76.84, 57.03, 53.62, 35.77, 28.68, 25.36, 24.93, 24.81 ppm. HRMS (ESI): m/z calcd for $C_{21}H_{33}BNO_3$ $[M + H]^+$ 358.2553, found 358.2553. IR (KBr): $\tilde{\nu}$ = 2979, 2931, 2882, 1648, 1460, 1416, 1357, 1317, 1276, 1197, 1140, 1089, 965, 849, 764, 703 cm^{-1}.

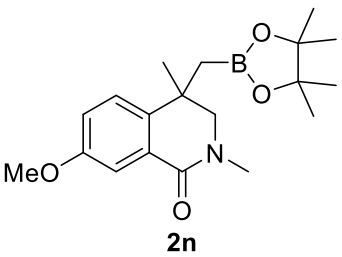
2-Benzyl-4-methyl-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-3,4-dihydroisoquinolin-1(2H)-one (2m).



2m

Yellow solid (0.172 g, 88%), mp: 97 – 99 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 – 8.14 (m, 1H), 7.48 – 7.42 (m, 1H), 7.39 – 7.26 (m, 7H), 5.18 (d, J = 14.4 Hz, 1H), 4.45 (d, J = 14.4 Hz, 1H), 3.54 (d, J = 12.5 Hz, 1H), 3.29 (d, J = 12.5 Hz, 1H), 1.25 (s, 3H), 1.21 (s, 2H), 1.16 (d, J = 12.8 Hz, 12H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.56, 147.86, 137.28, 132.00, 128.74, 128.60, 127.98, 127.50, 126.60, 123.76, 83.26, 77.48, 77.16, 76.84, 56.64, 50.73, 35.64, 26.44, 24.88, 24.85 ppm. HRMS (ESI): m/z calcd for $C_{24}H_{31}BNO_3$ $[M + H]^+$ 392.2397, found 392.2402. IR (KBr): $\tilde{\nu}$ = 3436, 3067, 3030, 2975, 1645, 1600, 1568, 1484, 1451, 1430, 1382, 1358, 1320, 1298, 1261, 1208, 1190, 1141, 1092,998, 967, 847, 826, 803, 768, 739, 704 cm^{-1}.

7-Methoxy-2,4-dimethyl-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-3,4-dihydroisoquinolin-1(2H)-one (2n).

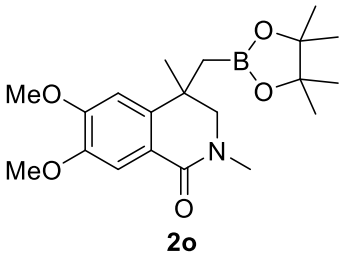


2n

White solid (0.136 g, 79%), mp: 131 – 133 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 2.9 Hz, 1H), 7.19 (d, J = 8.5 Hz, 1H), 6.94 (dd, J = 8.5, 2.9 Hz, 1H), 3.79 (s, 3H), 3.54 (d, J = 12.3 Hz, 1H), 3.28 (d, J = 12.4 Hz, 1H), 3.13 (s, 3H), 1.32 (s, 3H), 1.20 (s, 1H), 1.17 (s, 1H), 1.15 (s, 6H), 1.12 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.66, 158.20, 140.06, 128.96, 125.11, 119.01, 111.55, 83.25, 77.48, 77.16, 76.84, 59.85, 55.51, 35.44, 35.25, 26.44, 24.85 ppm. HRMS (ESI): m/z calcd for $C_{19}H_{29}BNO_4$ $[M + H]^+$ 346.2189, found 346.2202. IR

(KBr): $\tilde{\nu}$ = 3437, 2973, 1648, 1608, 1575, 1494, 1442, 1362, 1321, 1275, 1224, 1143, 1101, 1030, 972, 888, 850, 787, 580 cm^{-1}.

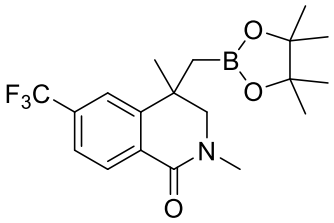
6,7-Dimethoxy-2,4-dimethyl-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-3,4-dihydroisoquinolin-1(2H)-one (2o).



2o

White solid (0.158 g, 84%), mp: 133 – 135 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, J = 1.9 Hz, 1H), 6.79 (d, J = 1.5 Hz, 1H), 3.89 (dd, J = 5.8, 1.9 Hz, 6H), 3.59 (dd, J = 12.3, 1.6 Hz, 1H), 3.24 (dd, J = 12.2, 1.5 Hz, 1H), 3.12 (d, J = 2.0 Hz, 3H), 1.32 (s, 3H), 1.24 (s, 1H), 1.18 (s, 1H), 1.15 (s, 6H), 1.11 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.70, 151.65, 147.36, 141.32, 120.69, 110.56, 106.51, 83.30, 77.48, 77.16, 76.84, 59.96, 56.07, 55.94, 35.56, 35.35, 26.96, 24.95, 24.78 ppm. HRMS (ESI): m/z calcd for $C_{20}H_{31}BNO_5$ $[M + H]^+$ 376.2295, found 376.2310. IR (KBr): $\tilde{\nu}$ = 3479, 3079, 3004, 2979, 1645, 1601, 1494, 1463, 1392, 1360, 1341, 1324, 1286, 1265, 1216, 1183, 1139, 1109, 1086, 1051, 999, 971, 881, 844, 757 cm^{-1}.

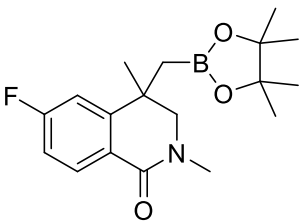
2,4-Dimethyl-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-6-(trifluoromethyl)-3,4-dihydroisoquinolin-1(2H)-one (2p).



2p

White solid (0.172 g, 90%), mp: 54 – 55 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, J = 8.1 Hz, 1H), 7.58 (s, 1H), 7.54 (dd, J = 8.1, 0.9 Hz, 1H), 3.59 (d, J = 12.5 Hz, 1H), 3.35 (d, J = 12.5 Hz, 1H), 3.17 (s, 3H), 1.41 (s, 3H), 1.27 (s, 2H), 1.16 (s, 6H), 1.12 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.49, 148.08, 133.32, 133.01, 131.12, 129.02, 125.38, 123.47 (d, J = 3.8 Hz), 122.68, 121.41 (d, J = 3.7 Hz), 83.48, 77.48, 77.16, 76.84, 59.82, 36.01, 35.53, 26.26, 24.80 (d, J = 14.5 Hz) ppm. ^{19}F NMR (471 MHz, $CDCl_3$): δ -62.88 ppm. HRMS (ESI): m/z calcd for $C_{19}H_{26}BF_3NO_3$ $[M + H]^+$ 384.1957, found 384.1956. IR (KBr): $\tilde{\nu}$ = 2979, 1661, 1503, 1453, 1363, 1331, 1256, 1229, 1166, 1128, 1077, 969, 849, 762, 726, 702 cm^{-1}.

6-Fluoro-2,4-dimethyl-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-3,4-dihydroisoquinolin-1(2H)-one (2q).

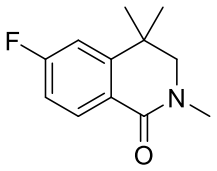


2q

Yellow oil (0.053 g, 32%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 – 8.02 (m, 1H), 7.01 – 6.90 (m, 2H), 3.55 (d, J = 12.4 Hz, 1H), 3.33 (d, J = 12.4 Hz, 1H), 3.13 (d, J = 0.6 Hz, 3H), 1.36 (s, 3H), 1.22 (s, 1H), 1.20 (s, 1H), 1.17 (s, 6H), 1.15 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.31, 164.02, 163.81, 150.68 (d, J = 7.8 Hz), 131.21 (d, J = 9.3 Hz), 124.30, 113.77, 113.56, 111.15, 110.93, 83.43, 77.48, 77.16, 76.84,

59.63, 36.02, 35.37, 26.10, 24.88 (d, J = 1.8 Hz) ppm. ^{19}F NMR (471 MHz, $CDCl_3$): δ -107.72 ppm. HRMS (ESI): m/z calcd for $C_{18}H_{26}BFNO_3$ $[M + H]^+$ 334.1989, found 334.1983. IR (KBr): $\tilde{\nu}$ = 3054, 2983, 1652, 1608, 1480, 1439, 1361, 1333 cm^{-1}.

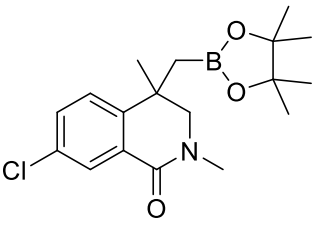
6-Fluoro-2,4,4-trimethyl-3,4-dihydroisoquinolin-1(2H)-one (2q1).



2q$_1$

Yellow oil (0.055 g, 53%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (dd, J = 8.4, 6.1 Hz, 1H), 6.97 – 6.90 (m, 2H), 3.28 (s, 2H), 3.12 (s, 3H), 1.28 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.43, 163.85 (d, J = 15.5 Hz), 149.71 (d, J = 7.9 Hz), 131.30 (d, J = 9.3 Hz), 124.31 (d, J = 2.8 Hz), 113.94, 113.72, 110.60, 110.38, 77.48, 77.16, 76.84, 60.38, 35.37, 34.44 (d, J = 1.2 Hz), 26.50 ppm. ^{19}F NMR (471 MHz, $CDCl_3$): δ -107.23 ppm. HRMS (ESI): m/z calcd for $C_{12}H_{15}FNO$ $[M + H]^+$ 208.1137, found 208.1587. IR (KBr): $\tilde{\nu}$ = 2971.71, 1659.17, 1607.28, 1585.05, 1481.25, 1439.86, 1361.85, 1328.80, 1260.60, 1209.32, 1168.33, 1142.26, 1066.12, 967.83, 937.13, 893.91, 848.47, 779.86, 699.62, 606.90 cm^{-1}.

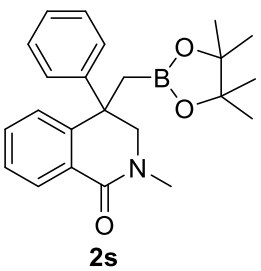
7-Chloro-2,4-dimethyl-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-3,4-dihydroisoquinolin-1(2H)-one (2r).



2r

Yellow oil (0.133 g, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, J = 2.3 Hz, 1H), 7.35 (dd, J = 8.3, 2.3 Hz, 1H), 7.23 (d, J = 8.3 Hz, 1H), 3.57 (d, J = 12.5 Hz, 1H), 3.31 (d, J = 12.5 Hz, 1H), 3.14 (s, 3H), 1.35 (s, 3H), 1.23 (s, 2H), 1.17 (s, 6H), 1.14 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.58, 146.07, 132.68, 131.65, 129.63, 128.32, 125.55, 83.43, 77.48, 77.16, 76.84, 59.48, 35.67, 35.47, 26.29, 24.89 ppm. HRMS (ESI): m/z calcd for $C_{18}H_{26}BClNO_3$ [M + H]+ 350.1694, found 350.1696. IR (KBr): $\tilde{\nu}$ = 2977.11, 2928.05, 2859.36, 2363.86, 2340.96, 1649.22, 1606.70, 1577.27, 1493.87, 1402.29, 1330.61, 1255.11, 1096.48 cm^{-1}.

2-Methyl-4-phenyl-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-3,4-dihydroisoquinolin-1(2H)-one (2s).

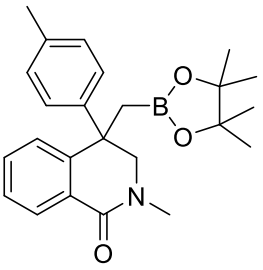


2s

This compound exists as a mixture of multiple rotamers. Colorless oil (0.132 g, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (dd, J = 7.6, 1.3 Hz, 1H), 7.55 – 7.49 (m, 0.7H), 7.43 (td, J = 7.6, 1.5 Hz, 1.4H), 7.39 – 7.31 (m, 2H), 7.31 – 7.27 (m, 1H), 7.25 – 7.14 (m, 6H), 7.14 – 7.10 (m, 2H), 4.10 (d, J = 12.7 Hz, 1H), 3.80 (d, J = 12.7 Hz, 1H), 3.64 (s, 0.35H), 3.06 (s, 1H), 3.05 (s, 3H), 2.46 (s, 2.5H), 1.71 (d, J = 5.9 Hz, 0.25H), 1.66 (d, J = 5.1 Hz, 1.75H), 1.24 (d, J = 10.0 Hz, 1.6H), 1.10 (s, 6H), 1.04 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.80, 145.94, 132.51, 131.66, 129.33, 129.27, 128.44,

128.27, 127.06, 127.02, 126.93, 126.64, 126.45, 126.31, 118.47, 83.43, 77.48, 77.16, 76.84, 59.19, 44.40, 43.29, 35.19, 24.82, 24.61 ppm. HRMS (ESI): m/z calcd for $C_{23}H_{29}BNO_3$ $[M + H]^+$ 378.2240, found 378.2238. IR (KBr): $\tilde{\nu}$ = 3444, 3060, 2977, 2931, 1651, 1601, 1495, 1476, 1450, 1358, 1332, 1263, 1143, 1107, 1036, 766, 701 cm^{-1}.

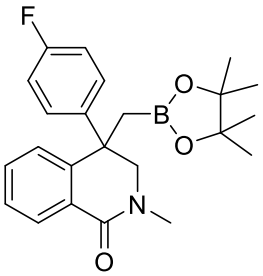
2-Methyl-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-4-(p-tolyl)-3,4-dihydroisoquinolin-1(2H)-one (2t).



2t

White solid (0.153g, 78%), mp: 91 – 93 ^oC. ^1H NMR (400 MHz, $CDCl_3$): δ 8.16 – 8.09 (m, 1H), 7.41 (td, J = 7.5, 1.5 Hz, 1H), 7.33 (td, J = 7.5, 1.1 Hz, 1H), 7.17 (d, J = 7.7 Hz, 1H), 7.07 – 6.99 (m, 4H), 4.08 (d, J = 12.7 Hz, 1H), 3.77 (d, J = 12.7 Hz, 1H), 3.05 (s, 3H), 2.28 (s, 3H), 1.70 – 1.65 (m, 1H), 1.61 (d, J = 15.7 Hz, 1H), 1.11 (s, 6H), 1.05 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.83, 146.30, 143.01, 136.20, 131.63, 129.31, 128.97, 128.41, 126.99, 126.47, 83.41, 77.48, 77.16, 76.84, 59.28, 44.16, 35.20, 24.86, 24.64, 20.98 ppm. HRMS (ESI): m/z calcd for $C_{24}H_{31}BNO_3$ $[M + H]^+$ 392.2319, found 392.2433. IR (KBr): $\tilde{\nu}$ = 3433, 2977, 2926, 1653, 1601, 1496, 1476, 1455, 1357, 1264, 1216, 1193, 1143, 1079, 967, 847, 817, 766, 705 cm^{-1}.

4-(4-Fluorophenyl)-2-methyl-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-3,4-dihydroisoquinolin-1(2H)-one (2u).

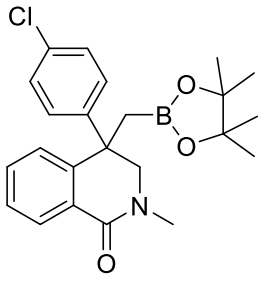


2u

Colorless oil (0.158 g, 80%).^1H NMR (400 MHz, $CDCl_3$): δ 8.13 (dd, J = 15.1, 7.6 Hz, 1H), 7.43 (t, J = 7.1 Hz, 1H), 7.38 – 7.30 (m, 1H), 7.20 (d, J = 7.6 Hz, 1H), 7.08 (dd, J = 7.7, 5.3 Hz, 2H), 6.90 (t, J = 8.4 Hz, 2H), 4.08 (d, J = 12.8 Hz, 1H), 3.78 – 3.69 (m, 1H), 3.04 (s, 3H), 1.70 (t, J = 10.0 Hz, 0.7H), 1.64 (d, J = 4.1 Hz, 1.5H), 1.22 (s, 2.6H), 1.10 (s, 6H), 1.03 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.72, 162.70, 160.26, 145.64, 141.69, 131.78, 129.26, 128.79 – 128.36 (m), 127.23, 126.24, 115.09, 114.89, 83.50, 77.48, 77.16, 76.84, 75.09, 59.30, 43.94, 35.20, 24.87 (d, J = 11.7 Hz), 24.60 ppm. ^{19}F NMR (471 MHz, $CDCl_3$): δ -116.62 ppm. HRMS (ESI): m/z calcd for $C_{23}H_{28}BFNO_3$ $[M + H]^+$ 396.2146, found 396.2145. IR (KBr): $\tilde{\nu}$ = 3415, 2978, 2930, 1648, 1603, 1508, 1453, 1361, 1334, 1266, 1228, 1145, 1014, 843, 704 cm^{-1}.

4-(4-Chlorophenyl)-2-methyl-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-3,4-dihydroisoquinolin-1(2H)-one (2v).

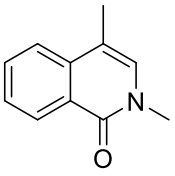
This compound exists as a mixture of multiple rotamers. Colourless oil (0.109 g, 53%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (dd, J = 7.7, 1.3 Hz, 0.6H), 8.13 (dd, J = 7.7, 1.1 Hz, 1H), 7.49 – 7.42 (m, 2H), 7.41 – 7.28 (m, 5H), 7.25 – 7.18 (m, 5H), 7.11 – 7.05 (m, 4H), 4.11 (d, J = 12.8 Hz, 1H), 3.75 (dd, J = 12.7, 6.2 Hz, 1.5H), 3.57 (d, J = 12.7 Hz, 0.6H), 3.15 (s, 0.7H), 3.06 (s, 4.8H), 1.73 (d, J = 12.7 Hz, 2.3H), 1.65 (d, J = 7.6 Hz, 1.5H), 1.25 (d, J = 10.1 Hz, 2.5H), 1.12 (s, 6H), 1.05 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.68, 164.47, 145.33, 144.91, 144.64, 143.72, 132.86, 132.50, 132.15, 131.81, 129.29, 129.23, 128.75, 128.60, 128.50, 128.37, 127.53, 127.32, 126.26, 125.85, 84.18, 83.54, 77.48, 77.16, 76.84, 60.91, 59.16, 44.10, 42.56, 35.38, 35.23, 25.66, 24.95, 24.83, 24.62 ppm. HRMS (ESI): m/z calcd for $C_{23}H_{28}BClNO_3$ $[M + H]^+$ 412.1850, found 412.1868. IR (KBr): $\tilde{\nu}$ = 2971.11, 2928.05, 2859.36, 2363.86, 2340.96, 1649.22, 1606.70, 1577.27, 1493.87, 1402.29, 1333.61, 1274.73, 1255.11, 1142.27, 1096.48, 1013.08 cm^{-1}.



2v

2,4-Dimethylisoquinolin-1(2H)-one (4a).

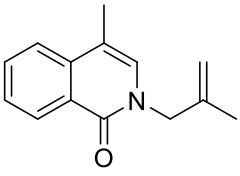
White solid (0.072 g, 83%), mp: 59 – 60 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (dd, J = 8.0, 0.8 Hz, 1H), 7.63 – 7.57 (m, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.46 – 7.40 (m, 1H), 6.83 – 6.76 (m, 1H), 3.49 (s, 3H), 2.17 (d, J = 0.9 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.23, 137.27, 131.80, 130.17, 127.89, 126.51, 125.81, 122.97, 111.85, 77.48, 77.16, 76.84, 36.63, 15.23 ppm. . HRMS (ESI): m/z calcd for $C_{11}H_{12}NO$ $[M + H]^+$ 174.0918, found 174.0916. IR (KBr): $\tilde{\nu}$ = 2965, 2902, 2863, 2744, 1651, 1629, 1598, 1473, 1491, 1444, 1417, 1356, 1328, 1178, 1069, 1046, 1026, 838, 801, 772, 745 cm^{-1}.



4a

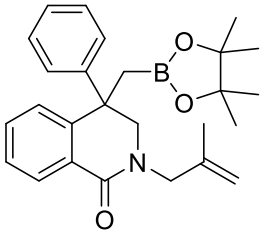
4-Methyl-2-(2-methylallyl)isoquinolin-1(2H)-one (4b).

Colorless oil (0.066 g, 62%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 – 8.40 (m, 1H), 7.63 – 7.59 (m, 1H), 7.52 (d, J = 8.0 Hz, 1H), 7.45 – 7.40 (m, 1H), 6.77 (d, J = 1.1 Hz, 1H), 4.88 – 4.85 (m, 1H), 4.72 – 4.69 (m, 1H), 4.48 (s, 2H), 2.20 (d, J = 1.2 Hz, 3H), 1.68 – 1.65 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.96, 140.95, 137.37, 132.16, 128.77, 128.52, 126.74, 126.09, 123.13, 113.07, 112.23, 77.48, 77.16, 76.84, 53.20, 20.10, 15.48 ppm. HRMS (ESI): m/z calcd for $C_{14}H_{16}NO$ $[M + H]^+$ 214.1231, found 214.1221. IR (KBr): $\tilde{\nu}$ = 3064, 2974, 2925, 1693, 1657, 1628, 1603, 1488, 1441, 1374, 1318, 1169, 1124, 900, 848, 768 cm^{-1}.



4b

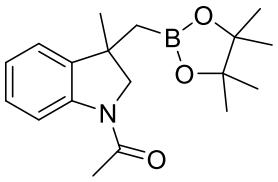
2-(2-Methylallyl)-4-phenyl-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-3,4-dihydroisoquinolin-1(2H)-one (4c).



4c

Colourless oil (0.121 g, 58%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 – 7.97 (m, 0.9H), 7.46 (dd, J = 7.2, 1.2 Hz, 0.9H), 7.43 – 6.93 (m, 7H), 5.50 (s, 0.4H), 5.22 (t, J = 7.2 Hz, 0.8H), 4.69 (d, J = 20.7 Hz, 0.2H), 4.36 – 4.24 (m, 0.1H), 4.14 (d, J = 15.1 Hz, 0.6H), 4.02 – 3.87 (m, 0.2H), 3.61 (dd, J = 13.6, 4.1 Hz, 0.2H), 3.42 (dt, J = 17.4, 5.8 Hz, 0.8H), 3.28 – 3.09 (m, 1H), 3.03 (d, J = 12.4 Hz, 0.2H), 1.30 – 0.93 (m, 17H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.75, 164.35, 147.77, 144.03, 138.26, 131.94, 128.64, 128.46, 128.04, 127.81, 127.48, 127.40, 126.47, 123.71, 115.92, 83.26, 77.48, 77.16, 76.84, 55.26, 49.92, 35.52, 26.87, 24.86, 19.62 ppm. HRMS (ESI): m/z calcd for $C_{26}H_{33}BNO_3$ $[M + H]^+$ 418.2553, found 418.2571. IR (KBr): $\tilde{\nu}$ = 3439, 2976, 2926, 1651, 1483, 1359, 1329, 1262, 1143, 764, 701 cm^{-1}.

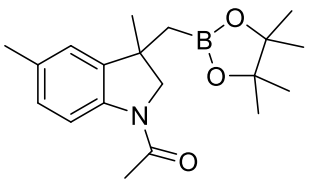
1-(3-Methyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-1-yl)ethan-1-one (6a).



6a

White solid (0.142 g, 90%), mp: 68 – 70 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, J = 8.1 Hz, 1H), 7.08 (t, J = 7.6 Hz, 2H), 6.94 (t, J = 7.4 Hz, 1H), 3.99 (d, J = 10.2 Hz, 1H), 3.68 (d, J = 10.2 Hz, 1H), 2.14 (s, 3H), 1.31 (s, 3H), 1.18 (d, J = 2.5 Hz, 1H), 1.16 (d, J = 2.1 Hz, 1H), 1.03 (s, 12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.76, 141.57, 140.94, 127.56, 123.76, 122.15, 116.90, 83.23, 77.48, 77.16, 76.84, 62.90, 41.56, 29.88, 24.88, 24.80, 24.69, 24.31 ppm. HRMS (ESI): m/z calcd for $C_{18}H_{27}BNO_3$ $[M + H]^+$ 316.2084, found 316.2092. IR (KBr): $\tilde{\nu}$ = 3058.53, 2972.59, 2924.89, 2744.69, 1982.18, 1862.14, 1761.89, 1621.69, 1587.10, 1502.03, 1319.78, 1272.98, 1240.80, 1196.95, 1133.74, 1113.44, 1072.25, 1055.02, 926.01, 814.04, 602.35 cm^{-1}.

1-(3,5-Dimethyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-1-yl)ethan-1-one (6b).

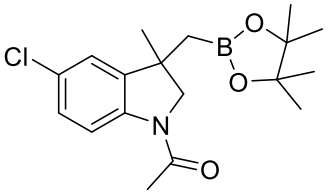


6b

White solid (0.140 g, 85%), mp: 89 – 91 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, J = 7.9 Hz, 1H), 7.04 – 6.90 (m, 2H), 4.01 (d, J = 10.2 Hz, 1H), 3.71 (d, J = 10.3 Hz, 1H), 2.27 (s, 3H), 2.18 (s, 3H), 1.35 (s, 2.5H), 1.31 (s, 0.5 H) 1.22 (t, J = 13.3 Hz, 2H), 1.13 (d, J = 9.1 Hz, 2H), 1.09 (s, 10H). ppm. ^{13}C NMR (100 MHz,

$CDCl_3$): δ 168.39, 141.01, 139.30, 133.20, 128.03, 122.77, 116.62, 83.21, 77.48, 77.16, 76.84, 63.11, 41.51, 29.75, 24.83, 24.67, 24.21, 21.17 ppm. HRMS (ESI): m/z calcd for $C_{19}H_{29}BNO_3$ $[M + H]^+$ 330.2440, found 330.2282. IR (KBr): $\tilde{\nu}$ = 2976, 2919, 1666, 1612, 1591, 1489, 1390, 1326, 1273, 1213, 1142, 847, 822 cm^{-1}.

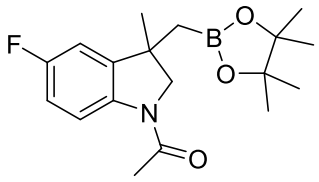
1-(5-Chloro-3-methyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-1-yl)ethan-1-one (6c).



6c

White solid (0.152 g, 87%), mp: 102 – 103 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J = 9.2 Hz, 1H), 7.12 – 7.07 (m, 2H), 4.03 (d, J = 10.2 Hz, 1H), 3.74 (d, J = 10.2 Hz, 1H), 2.19 (s, 3H), 1.37 (s, 3H), 1.22 (s, 1H), 1.19 (s, 1H), 1.12 (s, 6H), 1.11 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.81, 142.92, 140.32, 128.54, 127.53, 122.69, 117.92, 83.42, 77.48, 77.16, 76.84, 63.25, 41.71, 29.58, 24.86, 24.74, 24.20 ppm. HRMS (ESI): m/z calcd for $C_{18}H_{26}BrClNO_3$ $[M + H]^+$ 350.1694, found 350.1704. IR (KBr): $\tilde{\nu}$ = 3317.77, 3113.64, 2981.15, 2929.28, 2873.80, 1671.09, 1667.41, 1595.33, 1478.70, 1394.02, 1331.87, 1263.66, 1213.80 cm^{-1}.

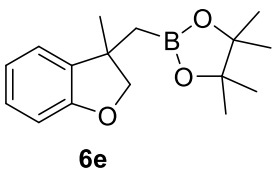
1-(5-Fluoro-3-methyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-1-yl)ethan-1-one (6d).



6d

White solid (0.147 g, 88%), mp: 70-72 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 – 8.07 (m, 1H), 6.87 – 6.81 (m, 2H), 4.05 (d, J = 10.3 Hz, 1H), 3.77 (d, J = 10.3 Hz, 1H), 2.20 (s, 3H), 1.38 (s, 3H), 1.23 (s, 1H), 1.21 (s, 1H), 1.12 (d, J = 1.2 Hz, 12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.5, 160.86, 158.46, 143.09, 137.73, 117.88 (d, J = 8.0 Hz), 113.99, 113.76, 109.76, 109.52, 83.46, 77.48, 77.16, 76.84, 63.28, 41.72, 29.60, 24.83 (d, J = 11.8 Hz), 24.16 ppm. ^{19}F NMR (471 MHz, $CDCl_3$) δ -119.04 ppm. HRMS (ESI): m/z calcd for $C_{18}H_{26}BFNO_3$ $[M + H]^+$ 334.1989, found 334.2000. IR (KBr): $\tilde{\nu}$ = 2981.26, 2929.64, 2878.99, 2358.95, 2331.15, 1667.42, 1607.85, 1485.02, 1403.97, 1362.38, 1337.84, 1277.33, 1275.56, 1271.91, 1264.05, 1256.35, 1214.45, 1184.10, 1167.18, 1142.33, 1022.79 cm^{-1}.

4,4,5,5-Tetramethyl-2-((3-methyl-2,3-dihydrobenzofuran-3-yl)methyl)-1,3,2-dioxaborolane (6e).

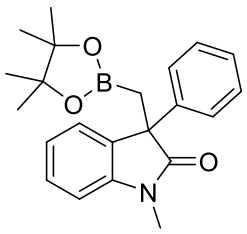


6e

Colorless oil (0.104 g, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 – 7.13 (m, 1H), 7.12 – 7.06 (m, 1H), 6.85 (td, J = 7.4, 1.0 Hz, 1H), 6.78 – 6.73 (m, 1H), 4.42 (d, J = 8.6 Hz, 1H), 4.26 (d, J = 8.6 Hz, 1H), 1.37 (s, 3H), 1.31 (d, J = 15.5 Hz, 1H), 1.24 (d, J = 11.3 Hz, 1H), 1.20 (s,

6H), 1.19 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.12, 137.49, 127.84, 122.74, 120.51, 109.59, 84.23, 83.33, 77.47, 77.16, 76.84, 43.29, 28.21, 24.92, 24.87 ppm. HRMS (ESI): m/z calcd for $C_{16}H_{24}BO_3$ $[M + H]^+$ 275.1818, found 275.1824. IR (KBr): $\tilde{\nu}$ = 2976, 1599, 1478, 1362, 1324, 1262, 1212, 1144, 1103, 1017, 976, 845, 804, 748 cm^{-1}.

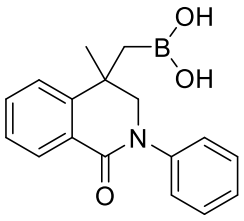
1-Methyl-3-phenyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (6f)[17].



6f

Colorless oil (0.136 g, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 – 7.17 (m, 6H), 7.07 (t, J = 7.5 Hz, 1H), 6.87 (d, J = 7.7 Hz, 1H), 3.21 (s, 3H), 1.99 (d, J = 15.2 Hz, 1H), 1.87 (d, J = 15.1 Hz, 1H), 0.97 (s, 6H), 0.86 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.74, 144.57, 141.95, 134.43, 128.47, 128.13, 127.09, 126.72, 124.86, 122.52, 108.05, 83.19, 77.48, 77.16, 76.84, 53.21, 26.65, 24.78, 24.34 ppm. HRMS (ESI): m/z calcd for $C_{22}H_{27}BNO_3$ $[M + H]^+$ 364.2084, found 364.2163. IR (KBr): $\tilde{\nu}$ = 3433, 2976, 2930, 1718, 1649, 1608, 1491, 1468, 1352, 1266, 1210, 1143, 1076, 1027, 966, 936, 883, 850, 803, 752 cm^{-1}.

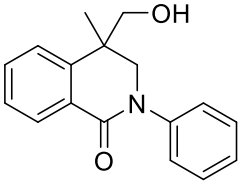
((4-Methyl-1-oxo-2-phenyl-1,2,3,4-tetrahydroisoquinolin-4-yl)methyl)boronic acid (7a)



7a

White solid (0.125 g, 80%). mp: 164 ^{o}C. ^{1}H NMR (400 MHz, DMSO): δ 7.94 (d, J = 7.1 Hz, 1H), 7.67 (s, 2H), 7.55 (d, J = 6.8 Hz, 1H), 7.42 (s, 4H), 7.26 (s, 1H), 3.99 (d, J = 12.1 Hz, 1H), 3.79 (d, J = 12.1 Hz, 1H), 1.42 (s, 3H), 1.19 (s, 2H) ppm. ^{13}C NMR (100 MHz, DMSO): δ 162.97, 149.32, 143.47, 132.33, 128.73, 127.97, 127.82, 126.21, 125.91, 125.60, 124.03, 59.70, 40.12, 39.92, 39.71, 39.50, 39.29, 39.08, 38.87, 35.93, 25.43 ppm. HRMS (ESI): m/z calcd for $C_{17}H_{19}BNO_3$ $[M + H]^+$ 296.1458, found 296.1457. IR (KBr): $\tilde{\nu}$ = 3326, 2976, 2901, 2882, 1642, 1596, 1572, 1480, 1451, 1420, 1366, 1329, 1266, 1236, 1092, 1043, 961, 908, 818, 780, 730, 606 cm^{-1}.

4-(hydroxymethyl)-4-methyl-2-phenyl-3,4-dihydroisoquinolin-1(2H)-one (7b)



7b

White solid (0.130 g, 92%). mp: 148 – 151 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (dd, J = 7.8, 1.3 Hz, 1H), 7.51 (td, J = 7.6, 1.4 Hz, 1H), 7.41 – 7.34 (m, 1H), 7.32 (dd, J = 8.5, 1.8 Hz, 4H), 7.30 – 7.27 (m, 1H), 7.20 – 7.16 (m, 1H), 3.87 (d, J = 12.5 Hz, 1H), 3.73 – 3.64 (m, 2H), 3.41 (dd, J = 10.9, 4.5 Hz, 1H), 3.09 (s, 1H), 1.34 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.00, 143.35, 142.78, 132.49, 129.13, 129.03, 128.96, 127.38, 126.55, 125.83, 124.63, 67.08, 56.20, 39.65, 20.28 ppm. HRMS (ESI): m/z calcd for $C_{17}H_{19}BNO_3$ $[M + H]+$

268.1337, found 268.1344. IR (KBr): $\tilde{\nu}$ = 3413, 3052, 2968, 2900, 2870, 1639, 1597, 1571, 1494, 1458, 1427, 1405, 1334, 1263, 1227, 1062, 1028, 761, 734, 697 cm^{-1}.

9. Table S2. Crystal data for compounds **[Pd(C∧C:)(PPh$_3$)Cl]** and **2o**

	[Pd(C∧C:)(PPh$_3$)Cl]	**2o**
empirical formula	C_{43} H_{41} Cl N_5 O_3 P Pd	C_{20} H_{30} B N O_5
formula wt	848.63	375.26
temp (K)	293(2)0	293(2)
cryst syst	Monoclinic	Monoclinic
space group	P 21/a	P 21/c
a (Å)	9.5617(4)	9.3411(14)
b (Å)	39.7290(15)	10.4942(16)
c (Å)	10.2744(4)	21.238(4)
α (deg)	90	90
β (deg)	92.477(3)	88.740(14)
γ (deg)	90	90
V (Å^3)	3899.4(3)	2081.5(6)
Z	4	4
*ρ*calcd (Mg m^{-3})	1.446	1.197
μ (mm^{-1})	0.632	0.084
F(000)	1744	808
cryst size (mm)	0.55 x 0.14 x 0.08	0.84 x 0.72 x 0.48
θ range (deg)	3.929 – 29.104	3.468 – 29.578
no. of collected/unique rflns	29580 / 9220 (R(int) = 0.0785)	22829 / 5058 (R(int) = 0.0342)
no. of data/restraints/ params	9220 / 0 / 481	5058 / 0 / 252
*R*1, *wR*2 ($I > 2\sigma(I)$)[a]	0.1159, 0.2262	0.0571, 0.1346
*R*1, *wR*2 (all data)[a]	0.1401, 0.2373	0.0884, 0.1554

GOF	1.060	1.033
$\Delta\rho$max/$\Delta\rho$min (e Å^{-3})	1.243/-3.942	0.394/-0.219

$^{a}R1 = \sum||Fo| - |Fc||/\sum|Fo|$; $wR2 = [\sum w(Fo^2 - Fc^2)^2/\sum w(Fo^2)^2]^{0.5}$.

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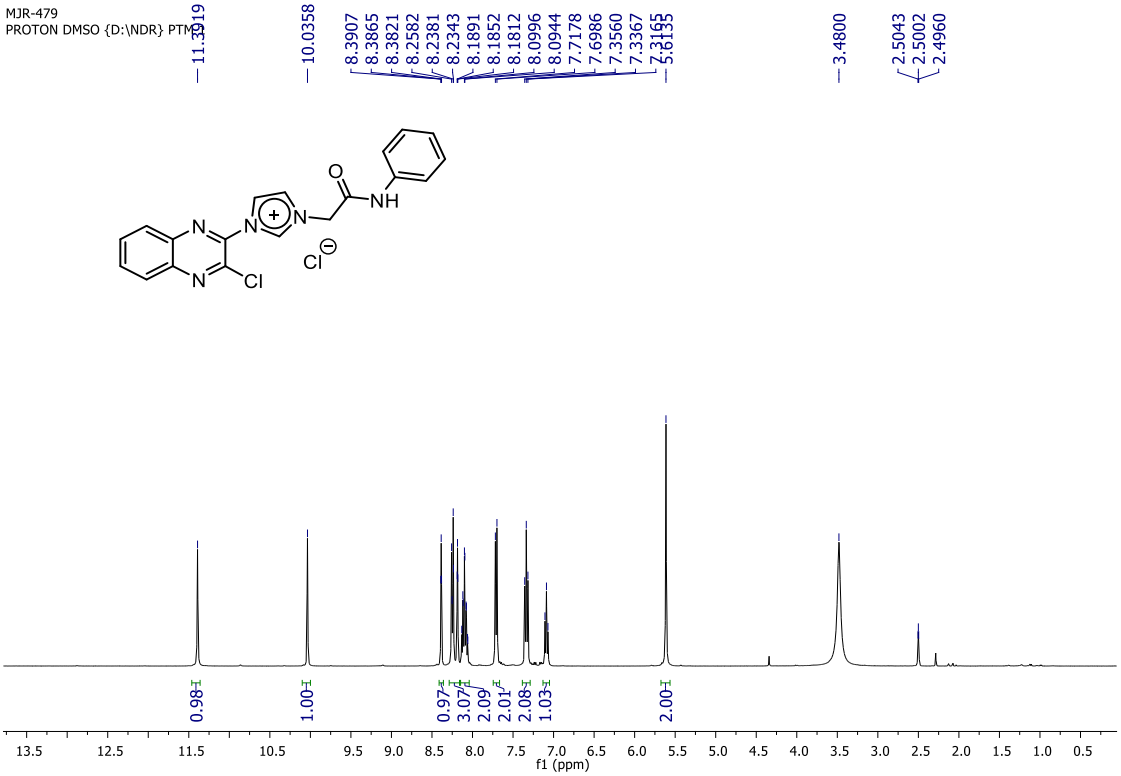
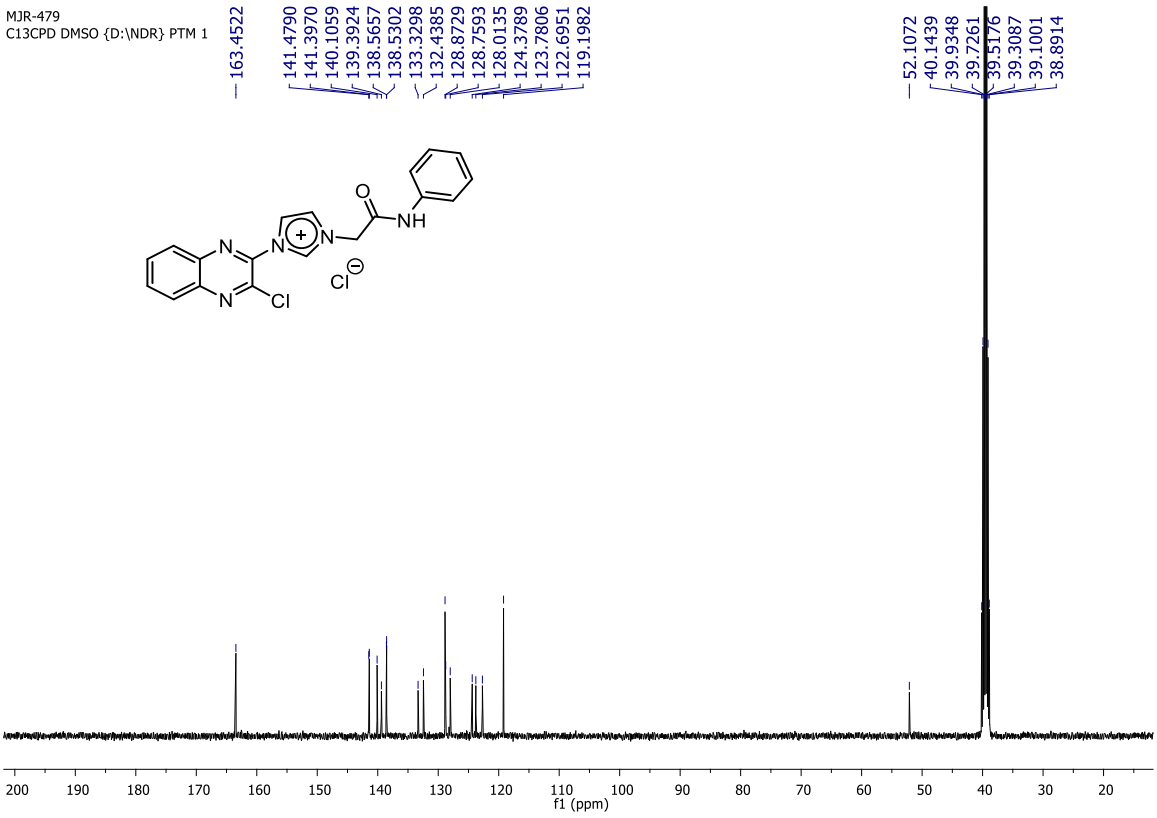
11. NMR Spectra

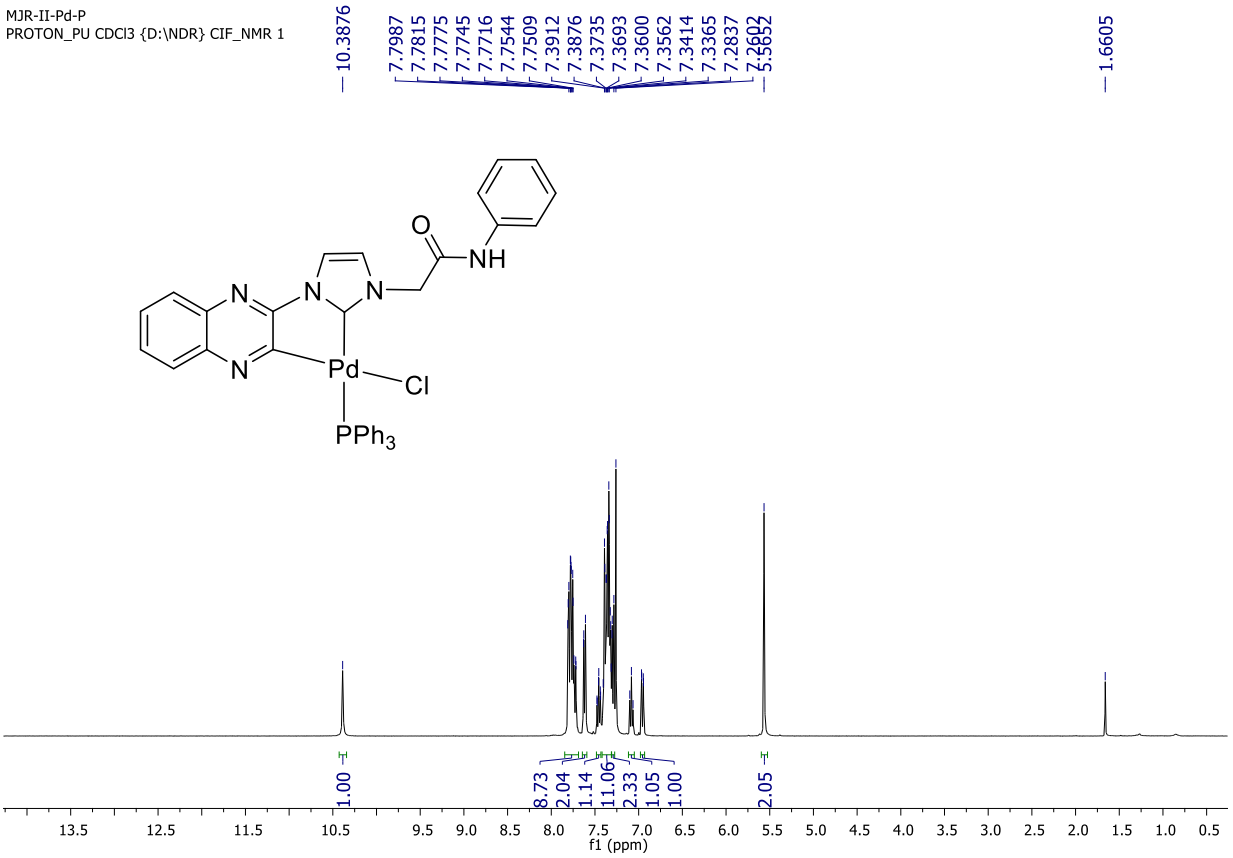
^{1}H **NMR**-spectrum (400 MHz, DMSO-d_6) of **ImidHCl**



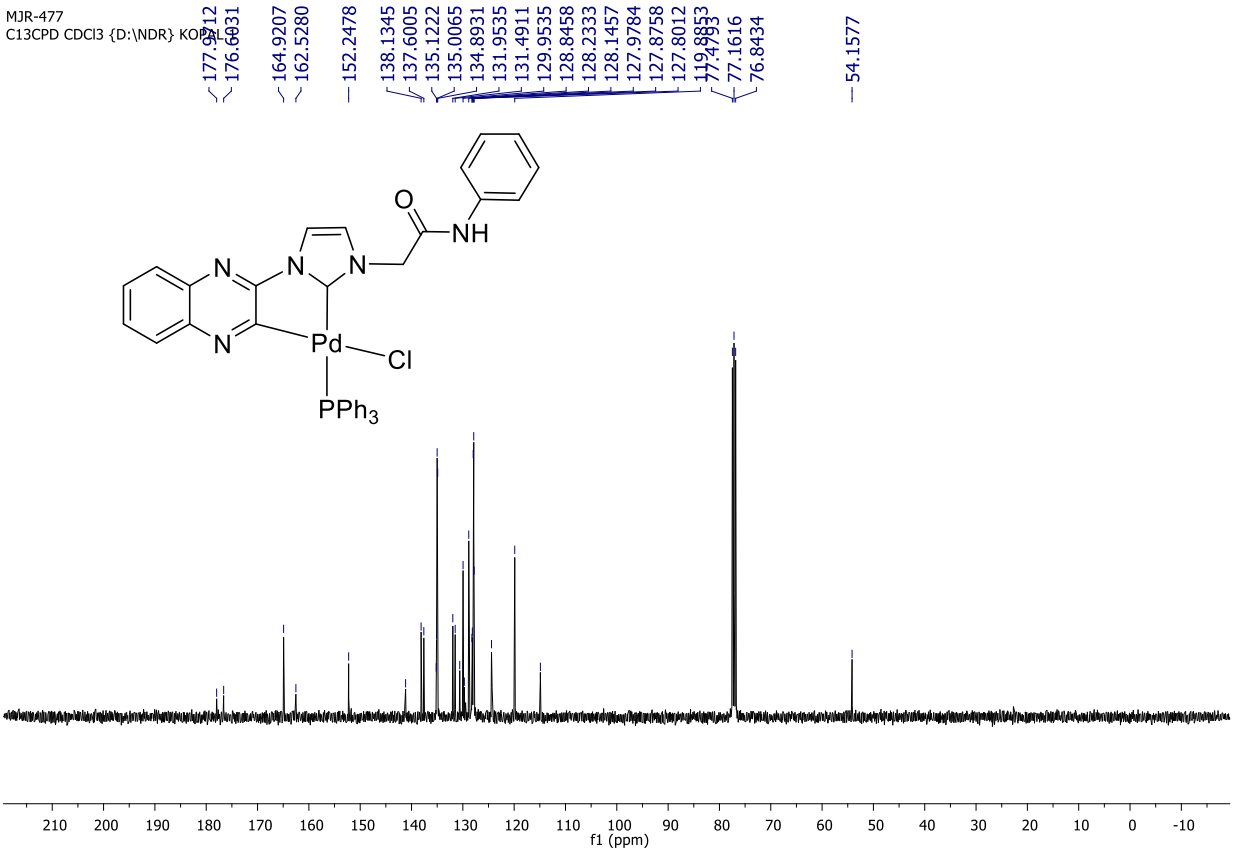
^{13}C **NMR**-spectrum (100 MHz, DMSO-d_6) of **ImidHCl**



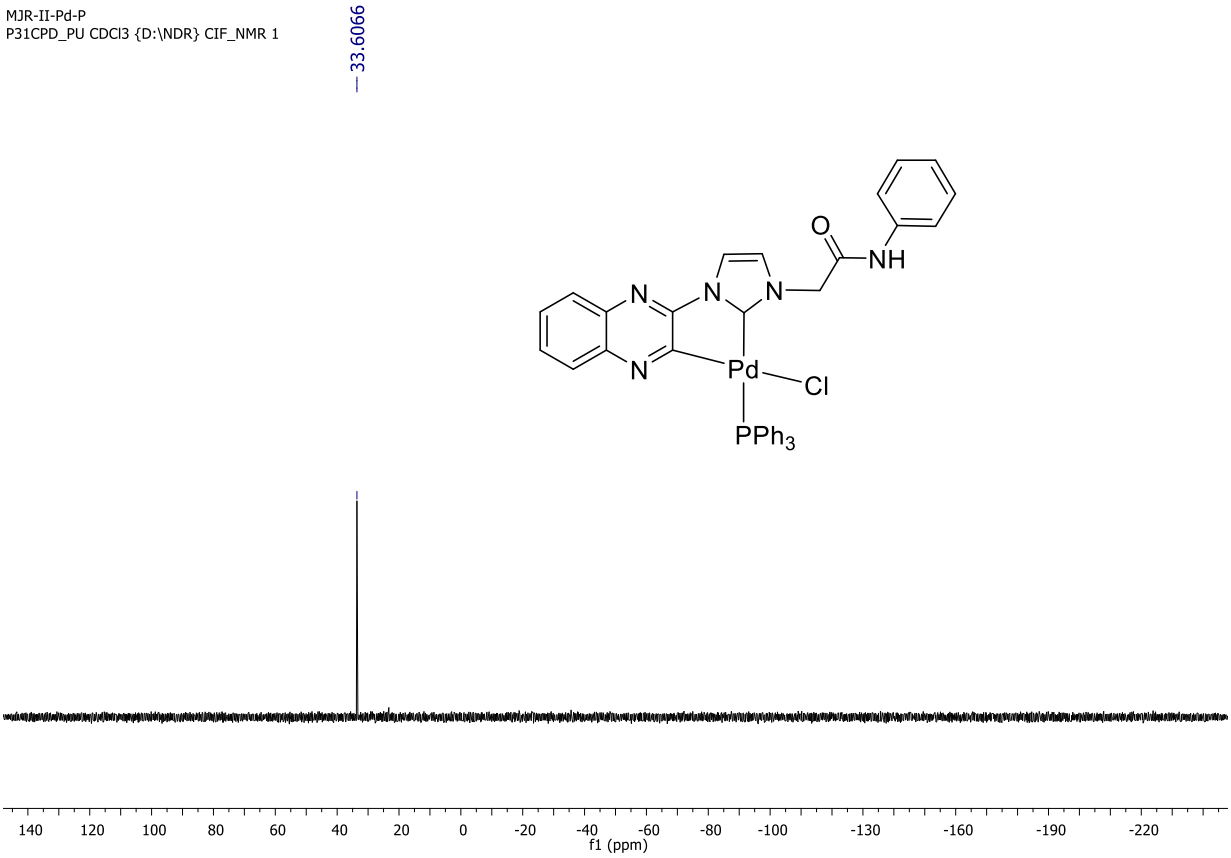
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **[Pd(C∧C:)PPh$_3$Cl]**



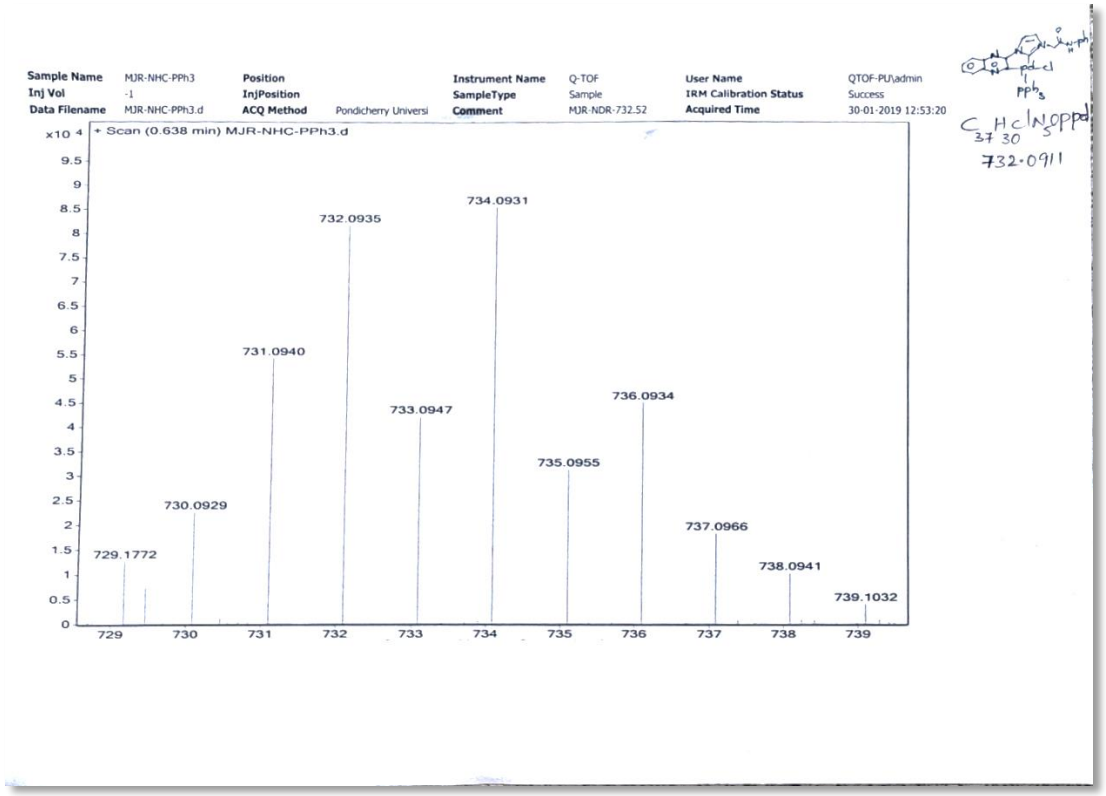
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **[Pd(C∧C:)PPh$_3$Cl]**



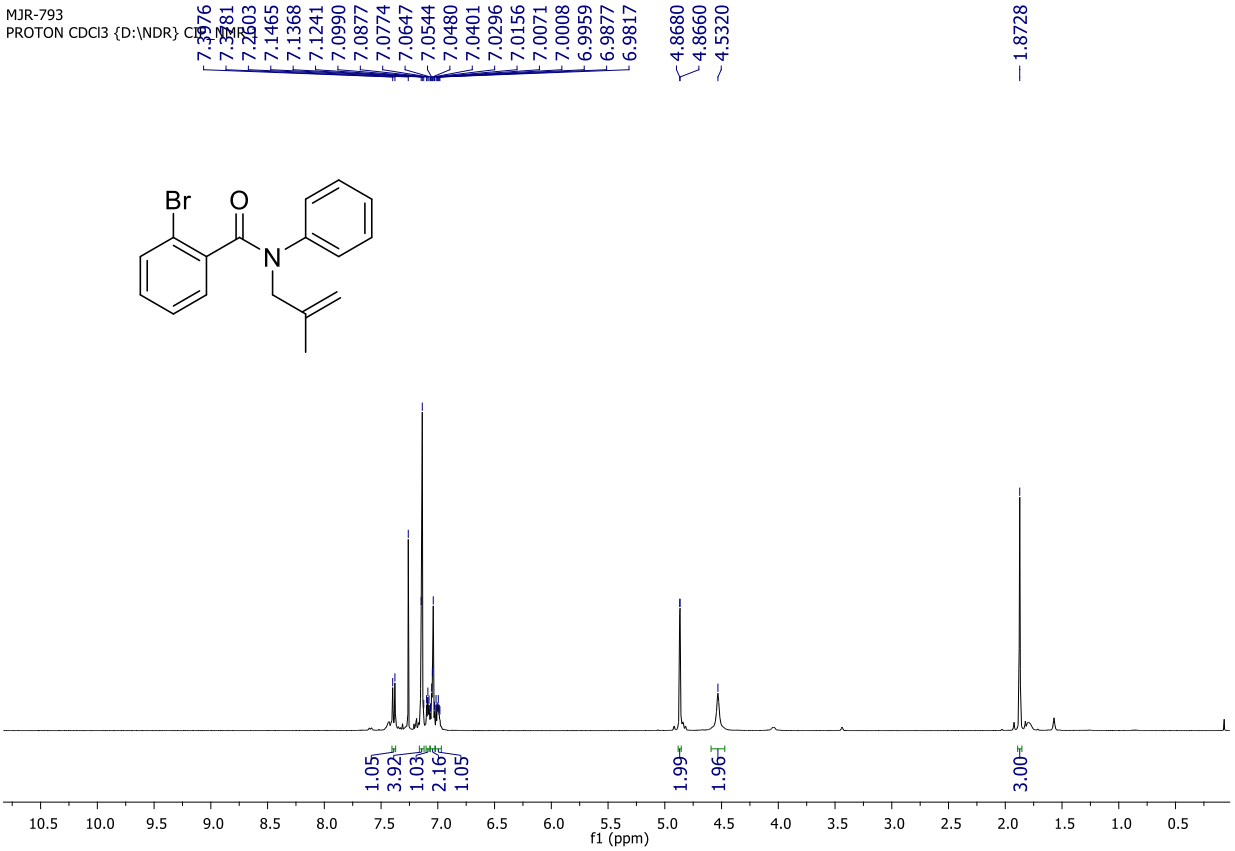
^{31}P NMR spectrum (162 MHz, $CDCl_3$) of **[Pd(CΛC:)PPh$_3$Cl]**



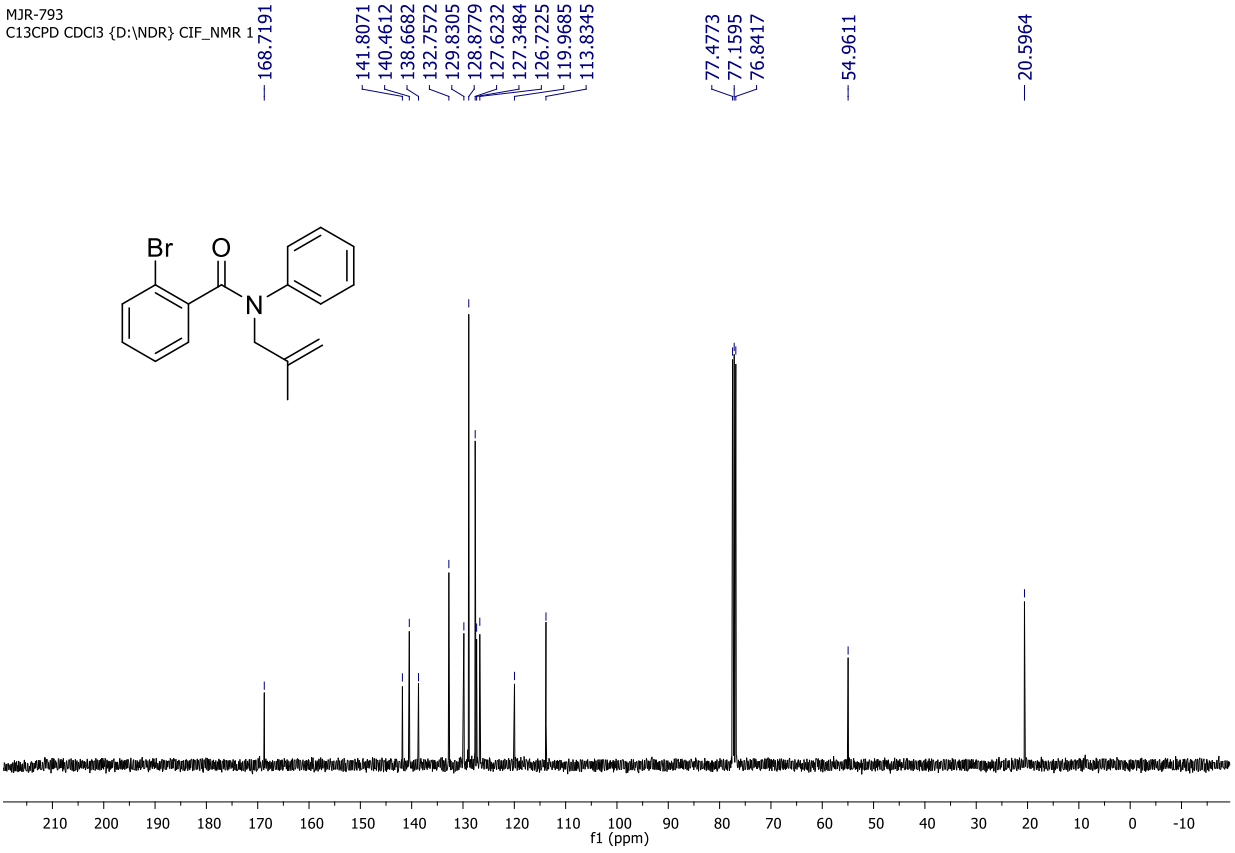
ESI Spectrum of **[Pd(CΛC:)PPh$_3$Cl]**



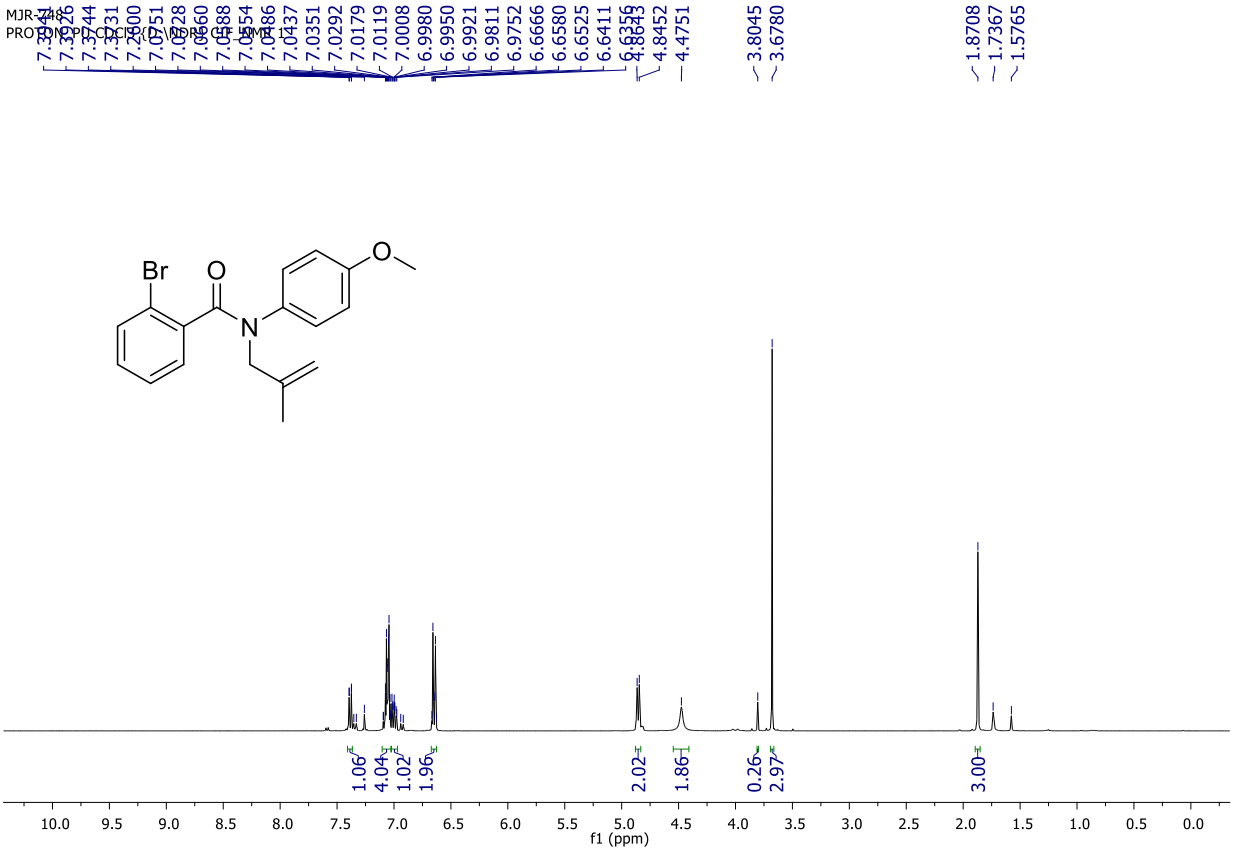
^{1}H **NMR**-spectrum (400 MHz, $CDCl_3$) of **1a**



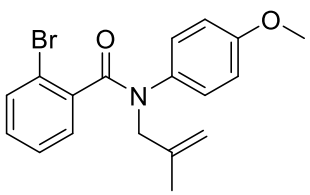
^{13}C **NMR**-spectrum (100 MHz, $CDCl_3$) of **1a**

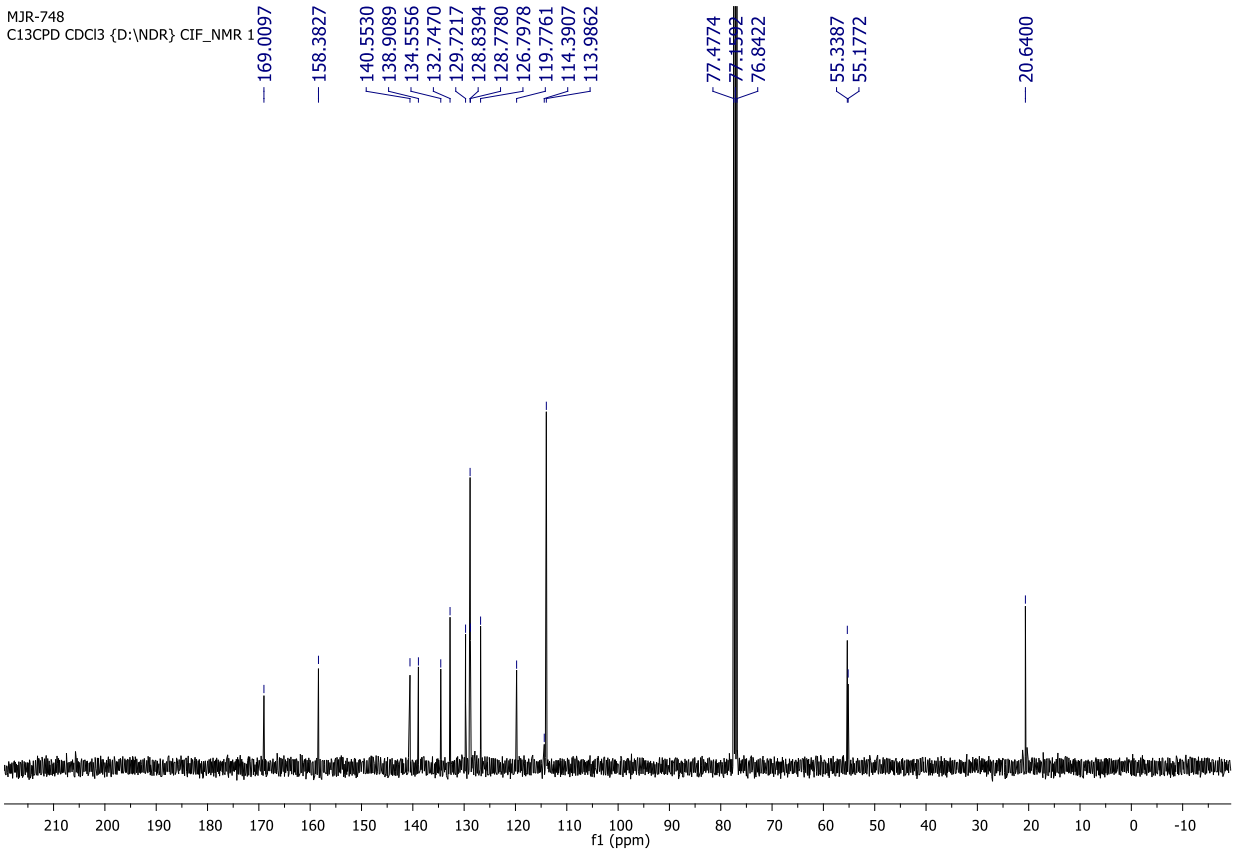


^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **1b**

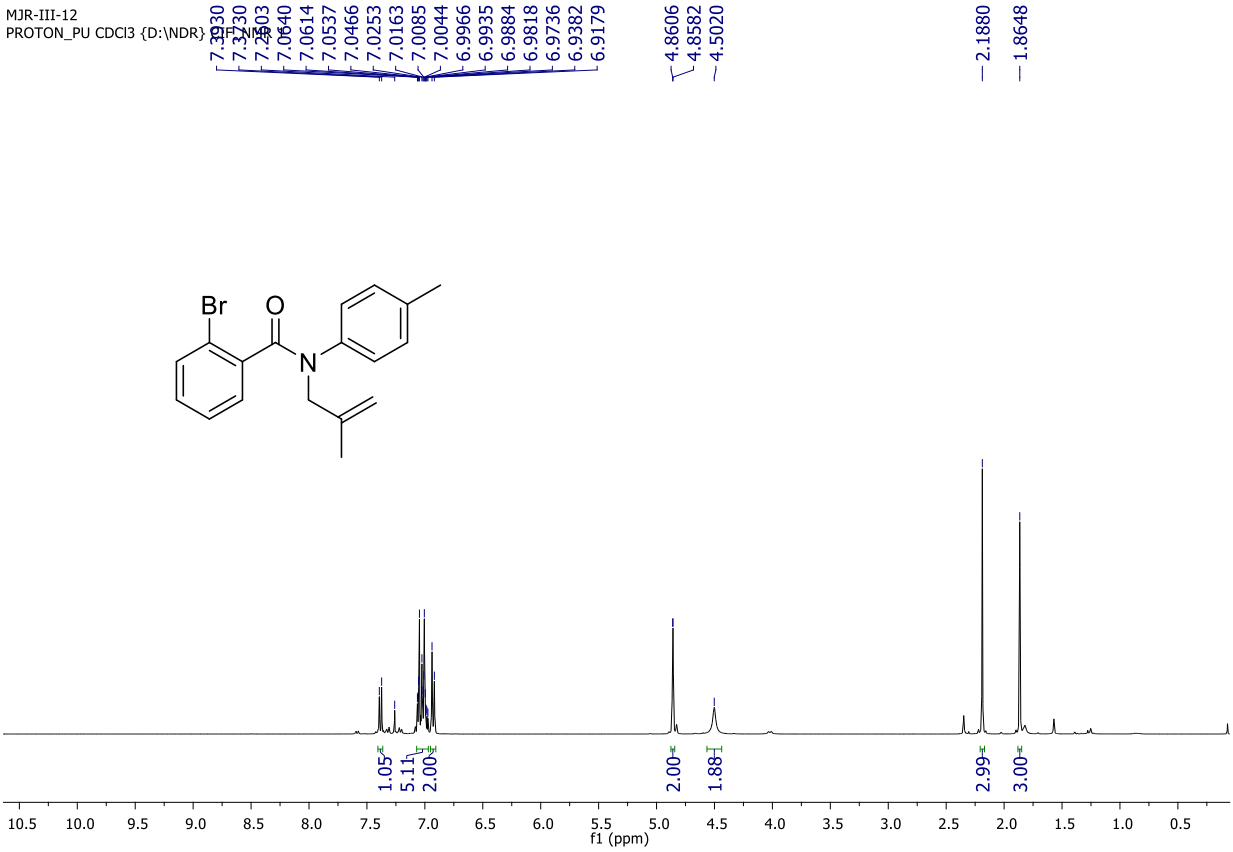


^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **1b**

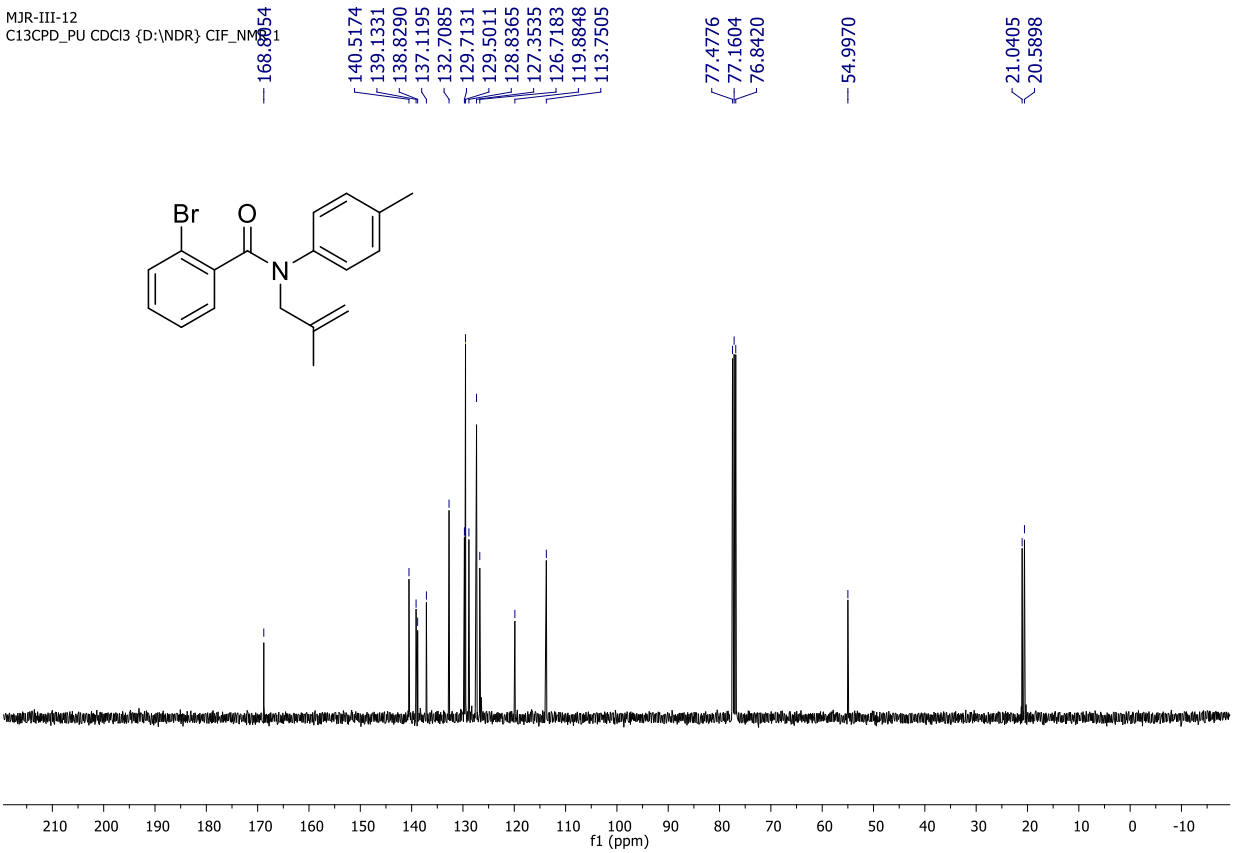




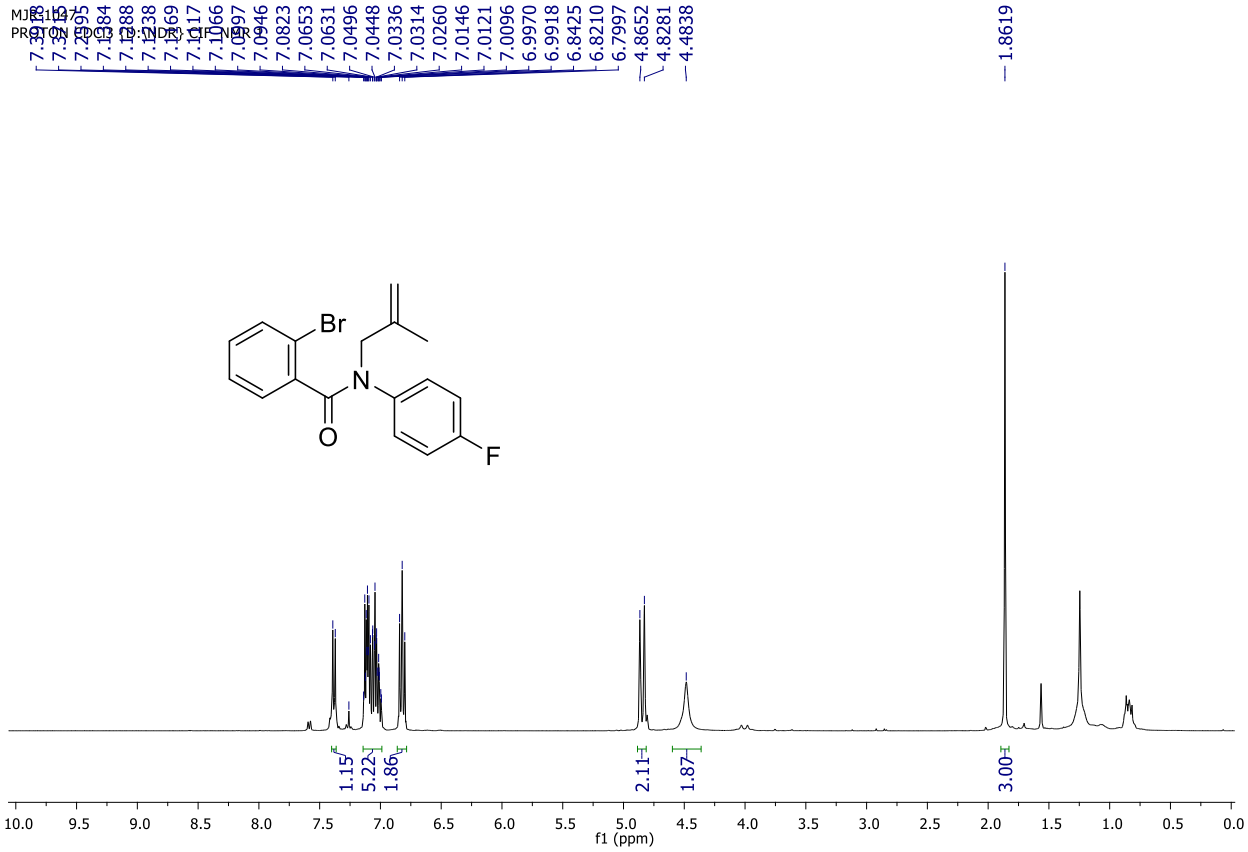
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **1c**



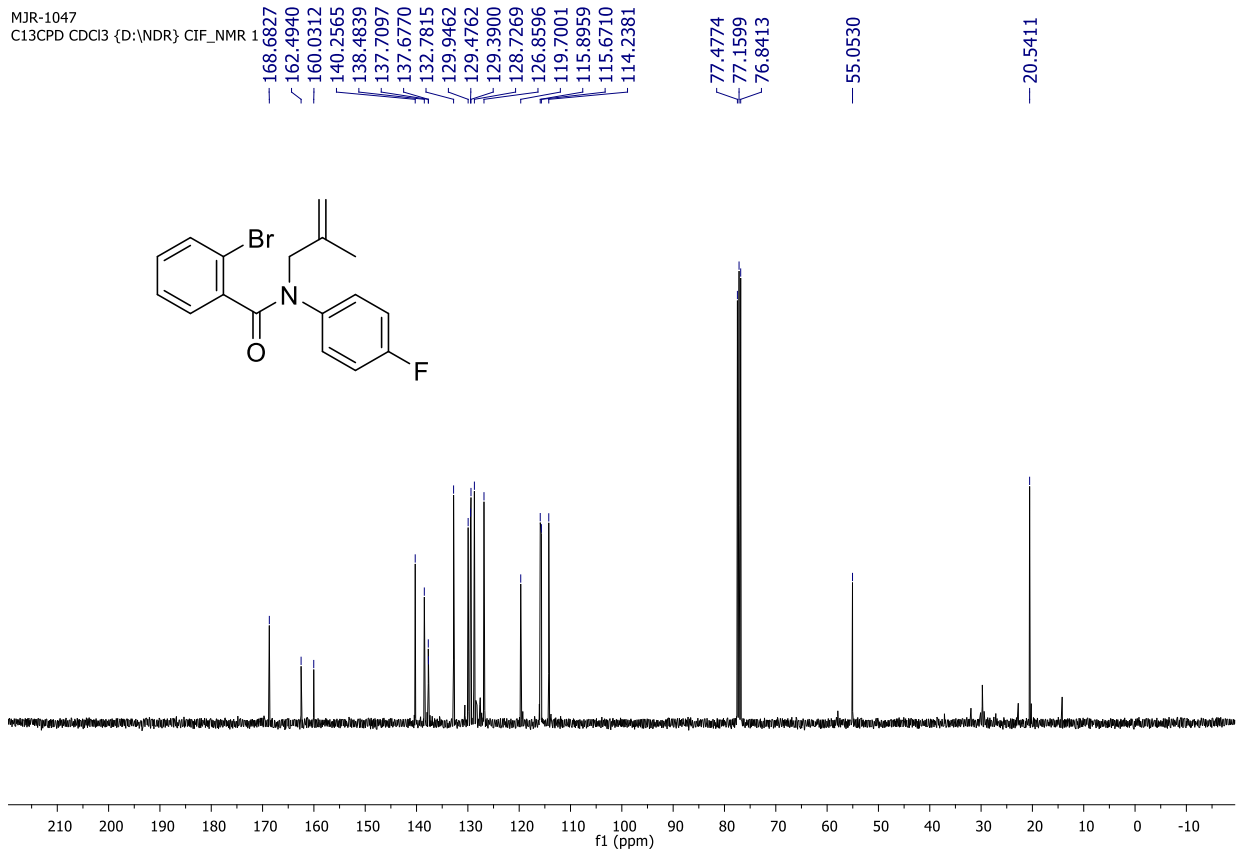
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **1c**



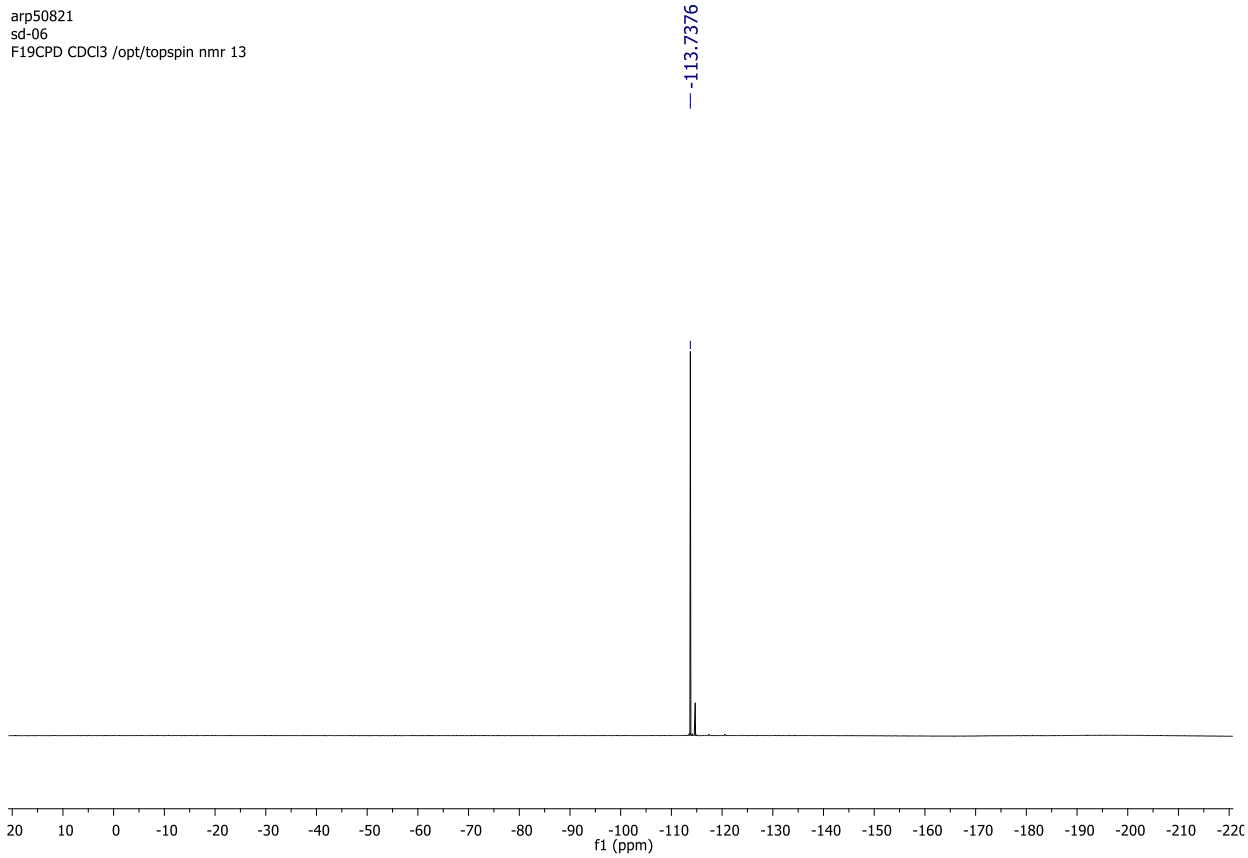
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **1d**



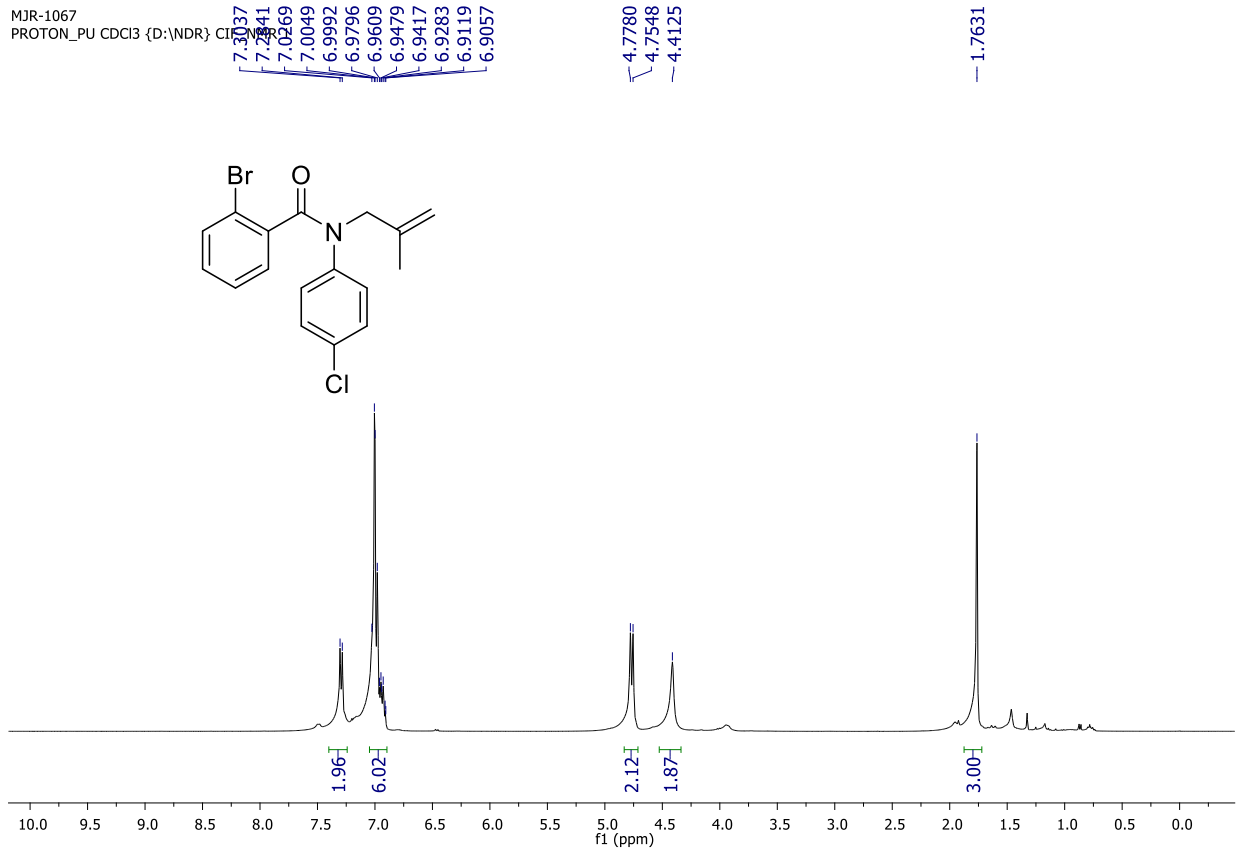
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **1d**



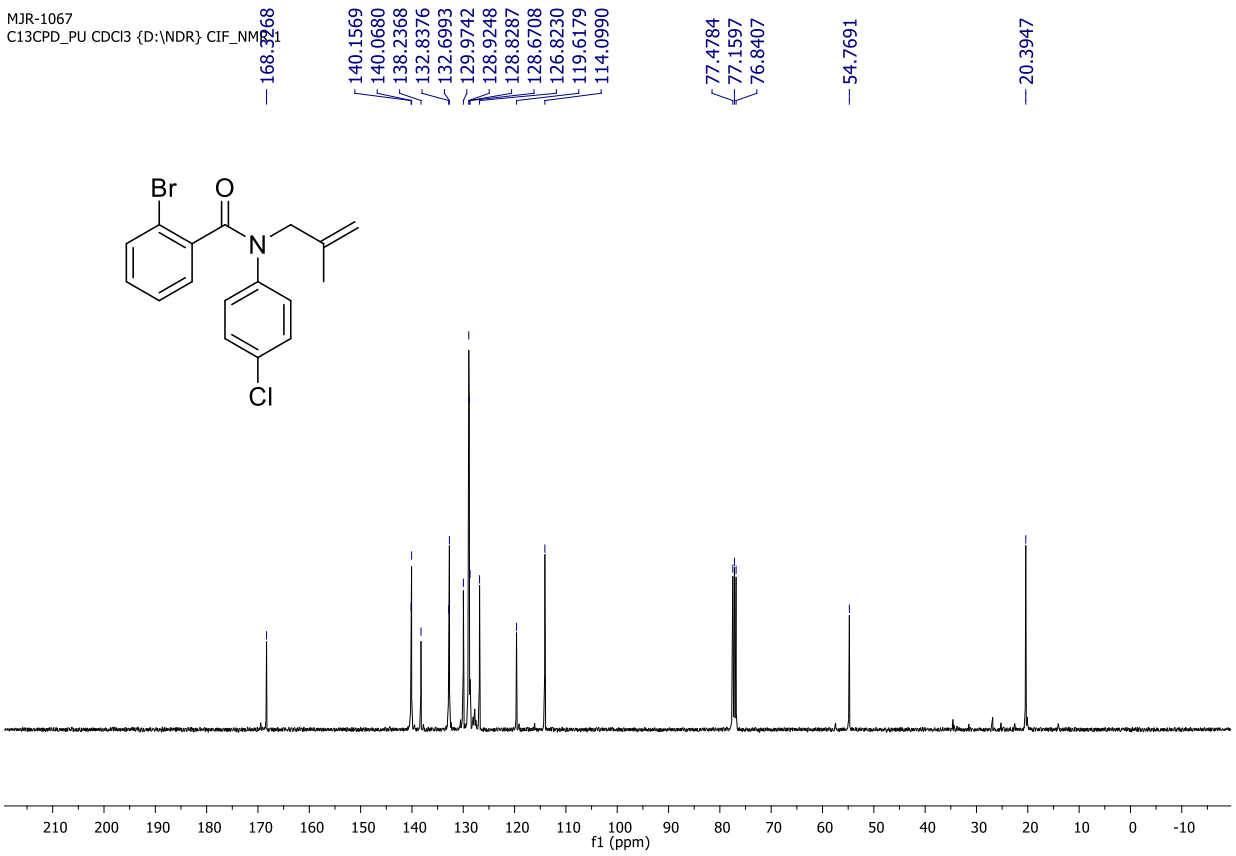
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **1d**



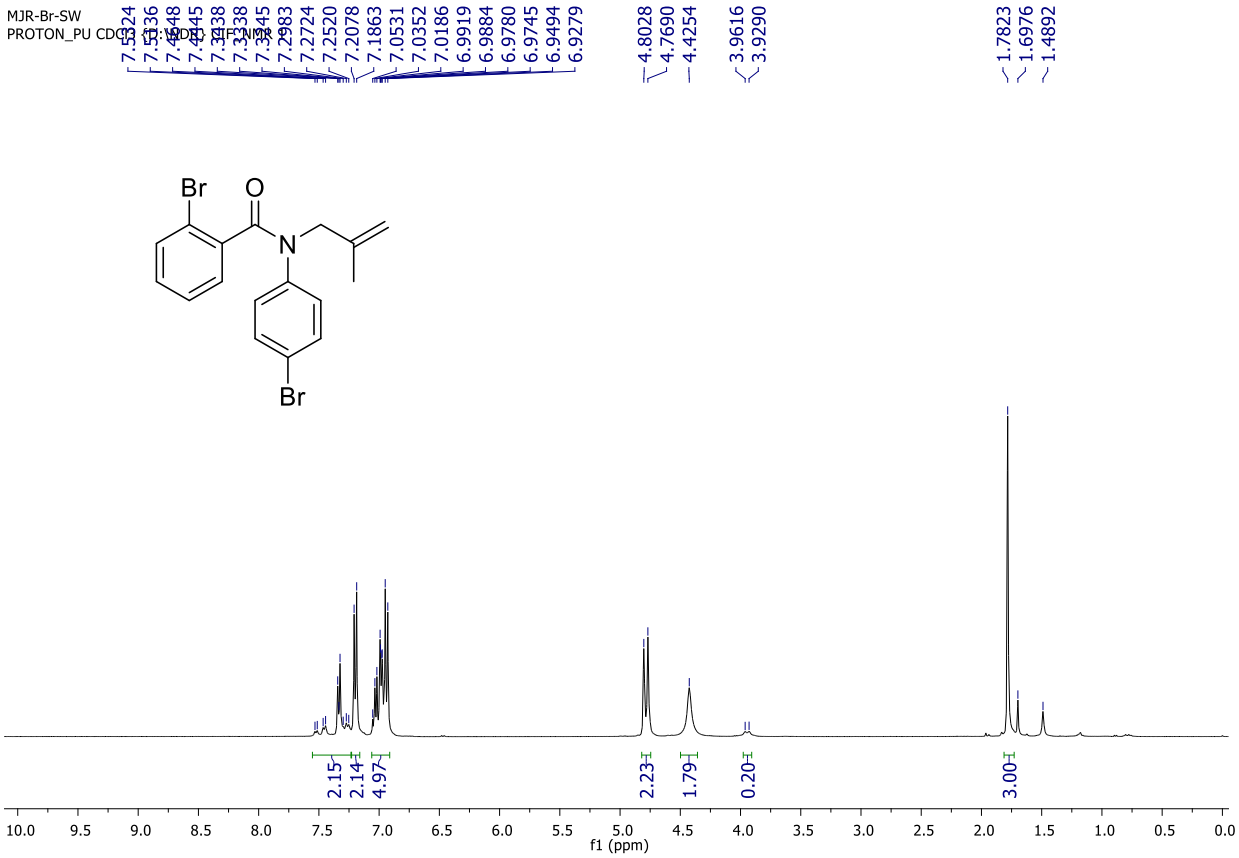
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **1e**



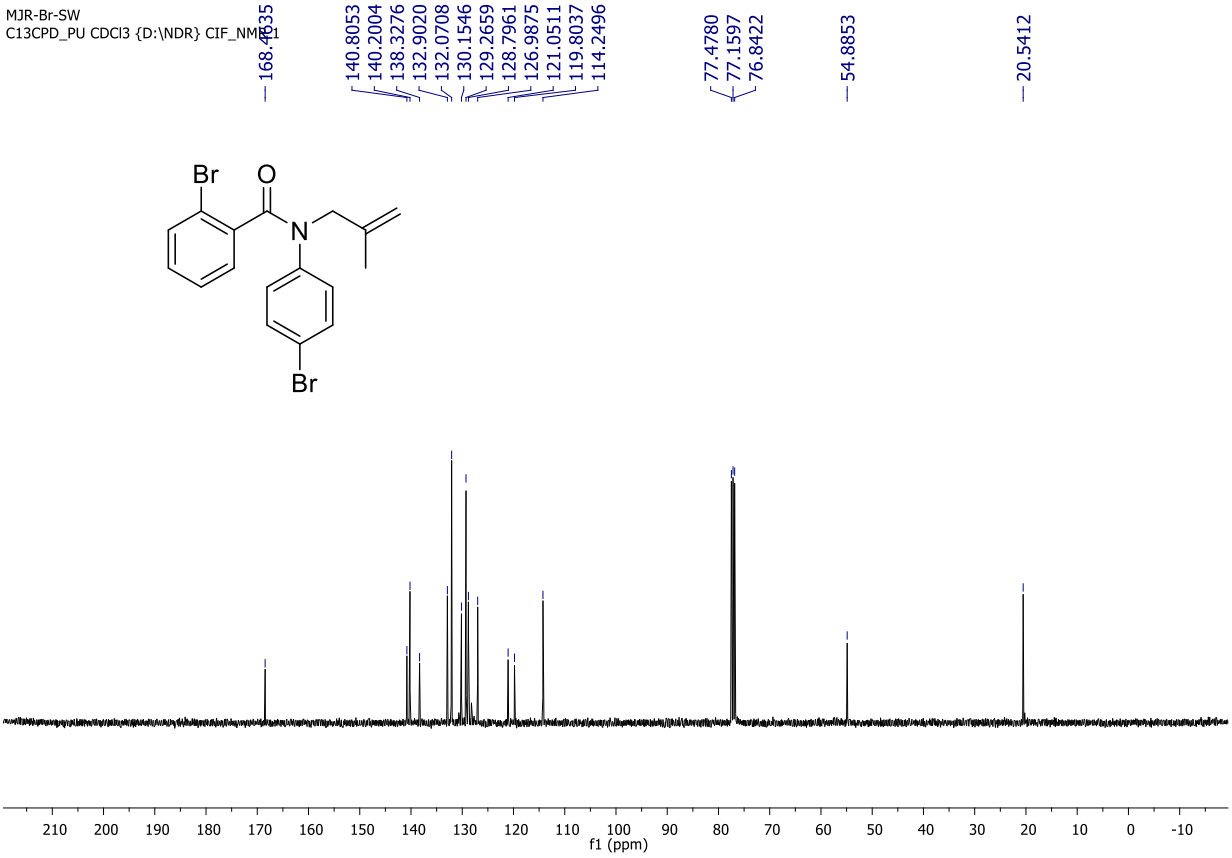
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **1e**



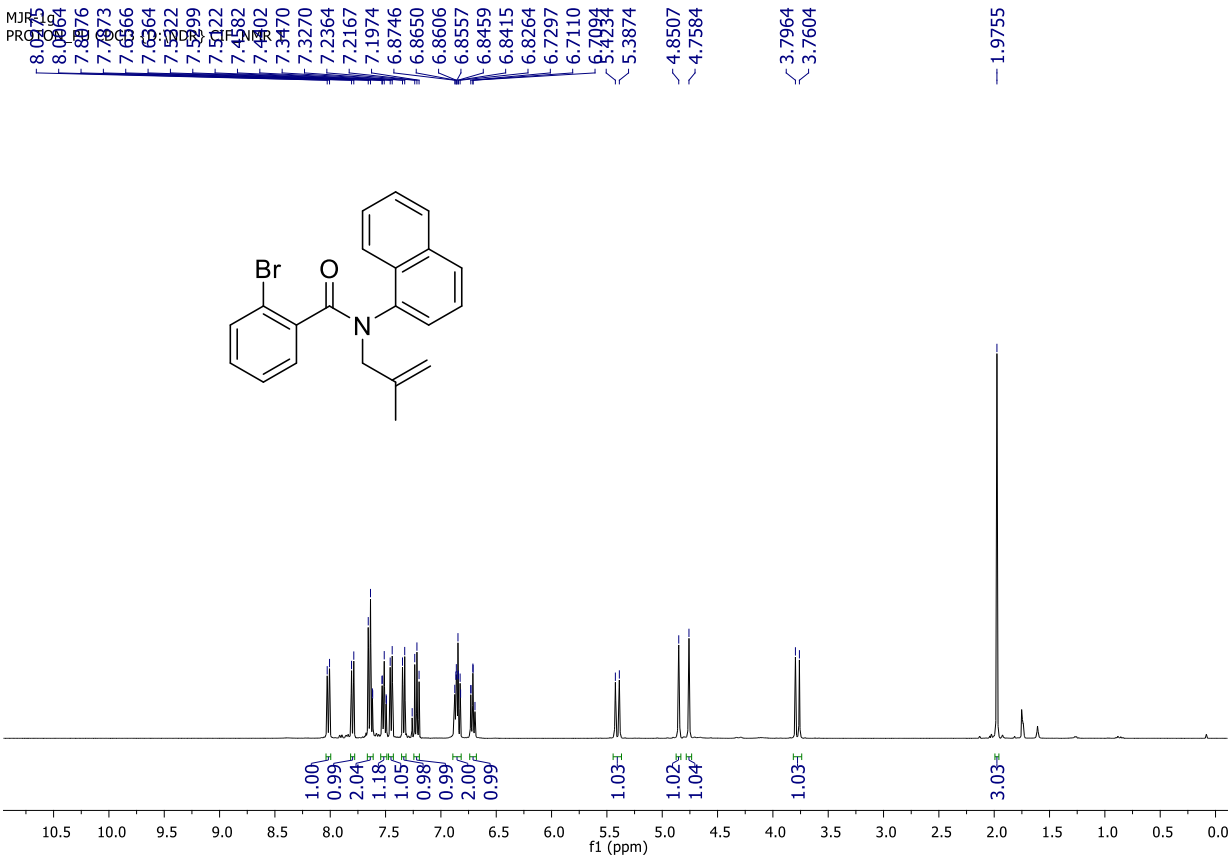
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **1f**



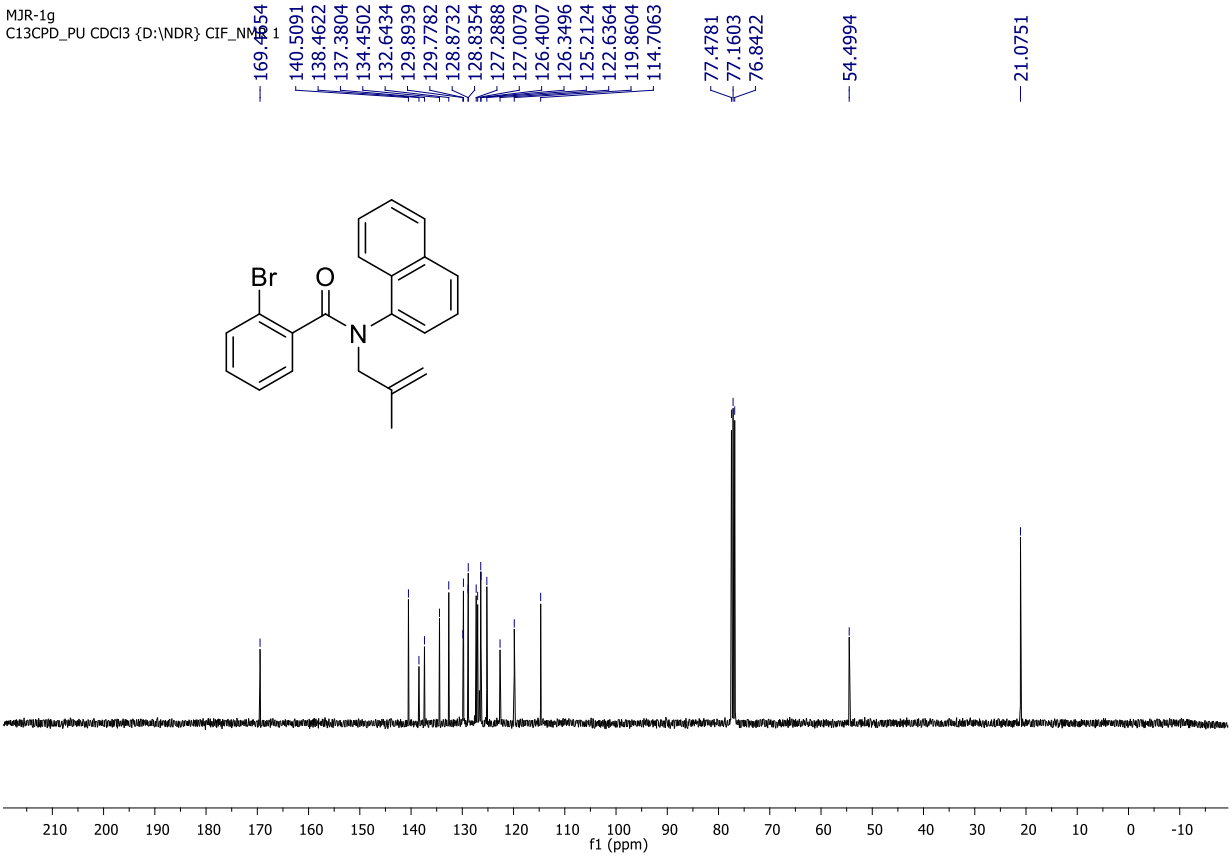
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **1f**



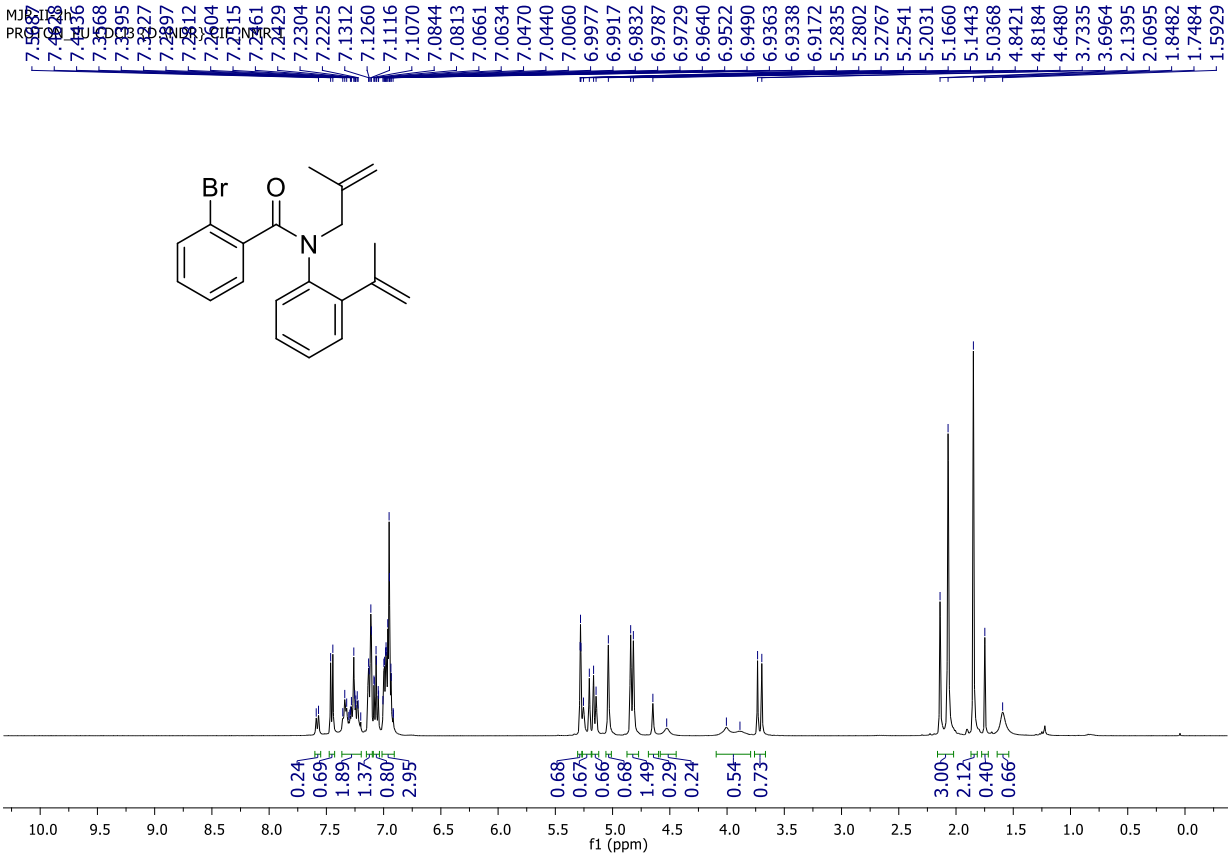
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **1g**



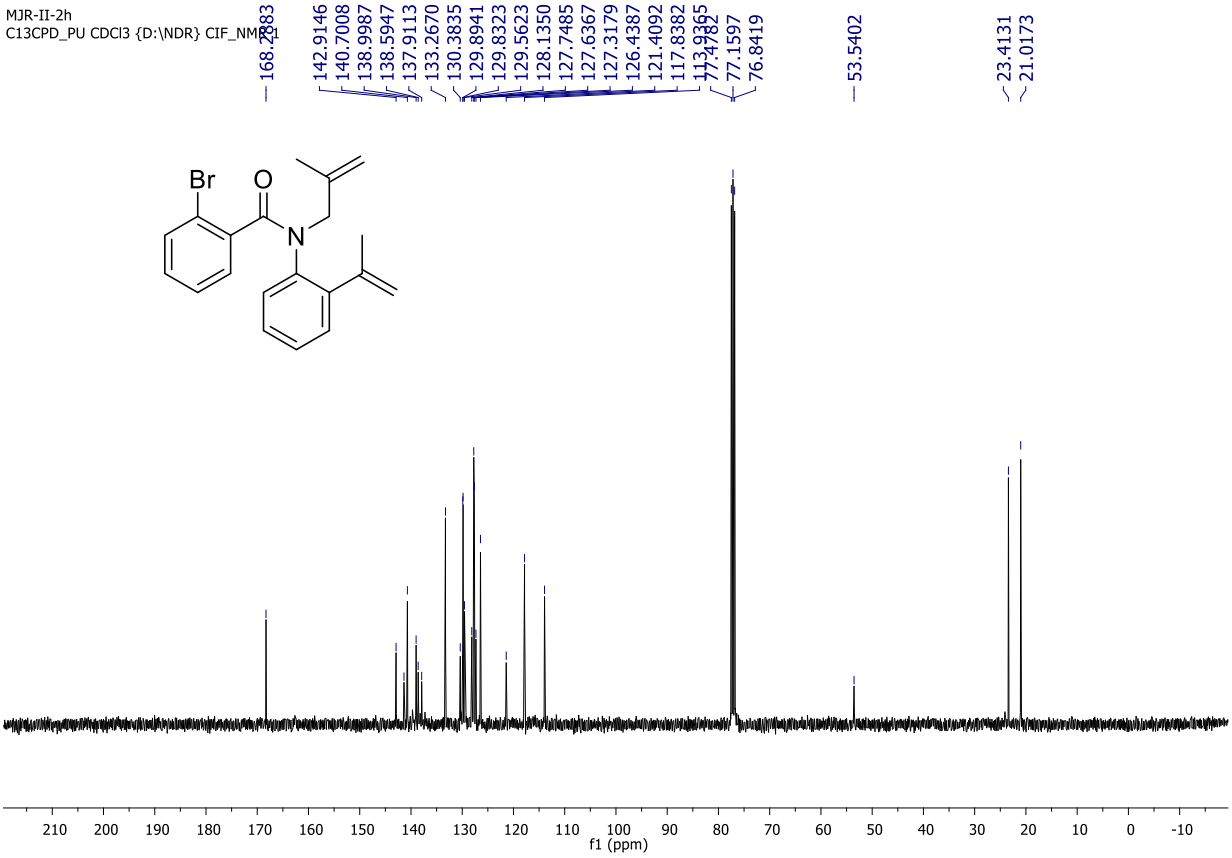
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **1g**



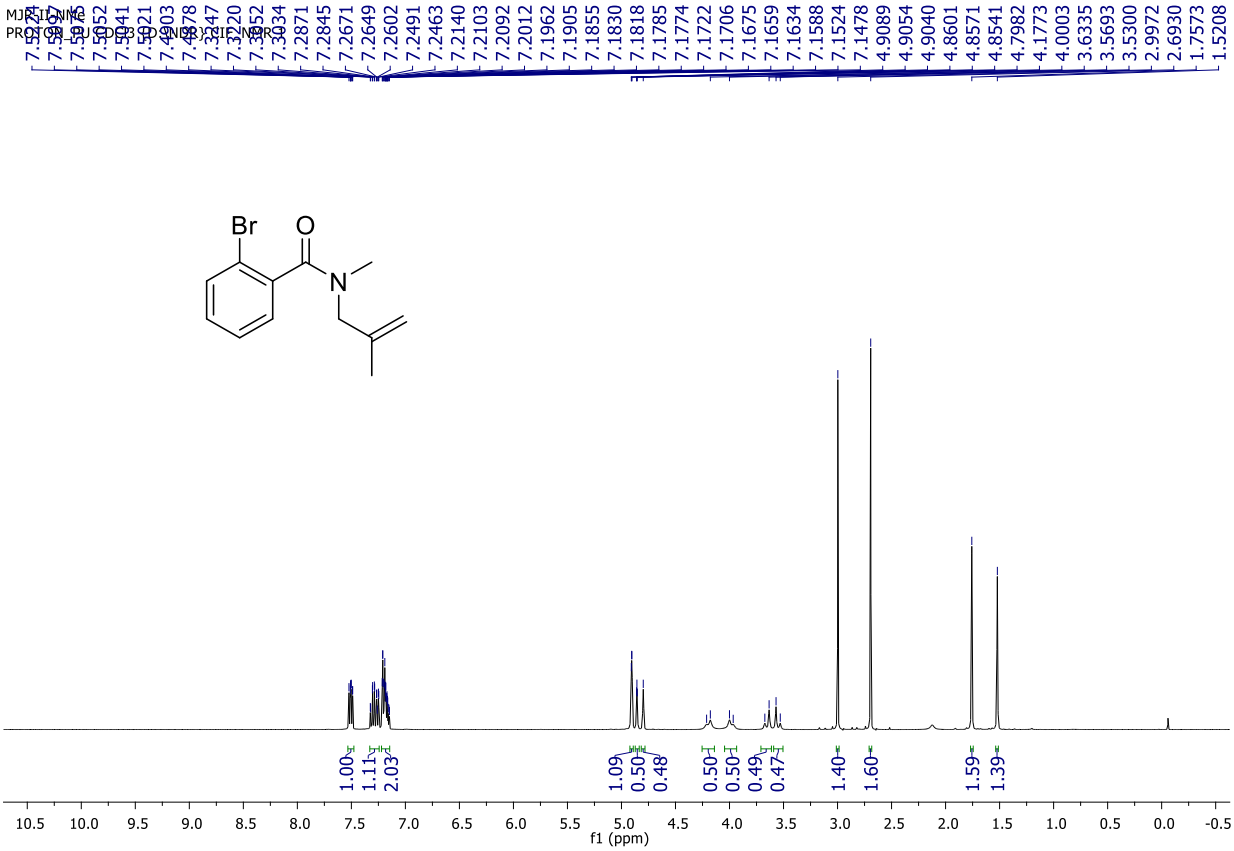
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **1h**



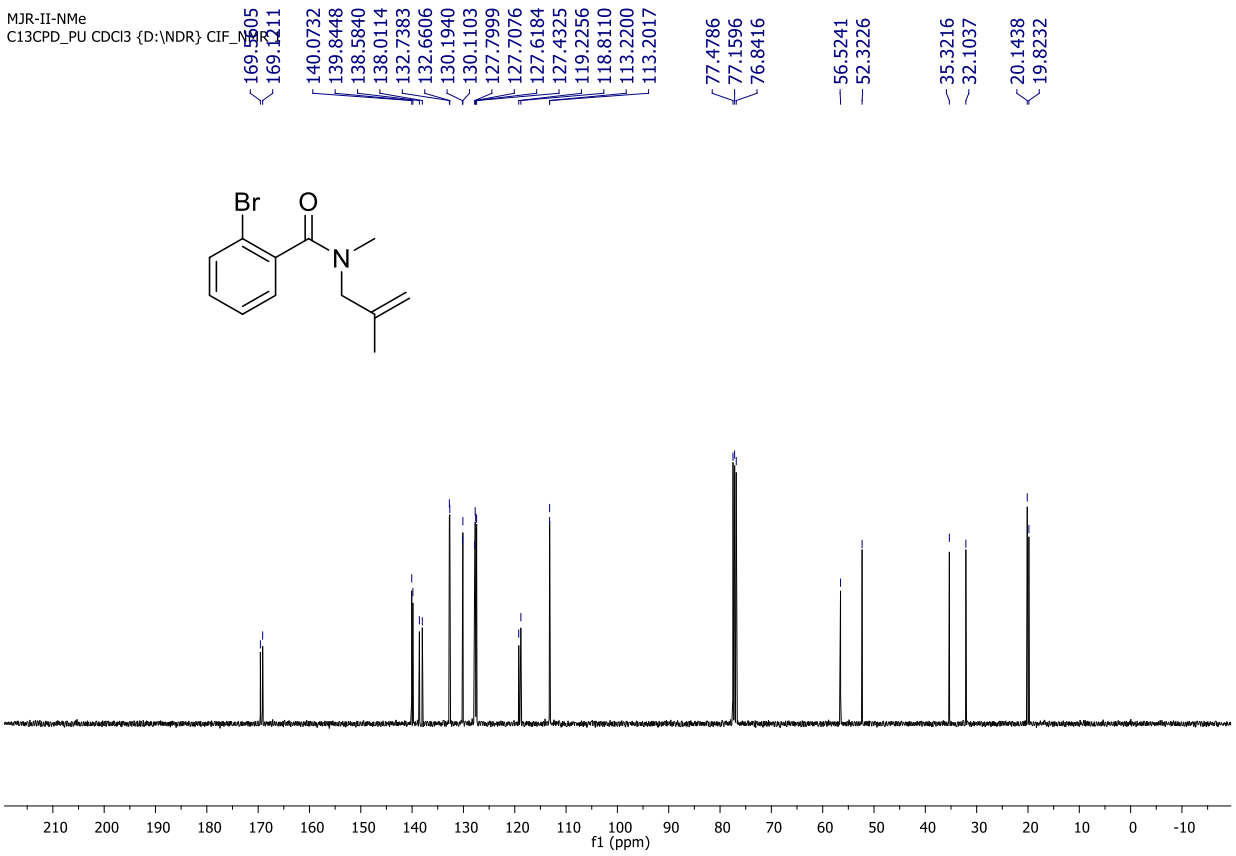
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **1h**



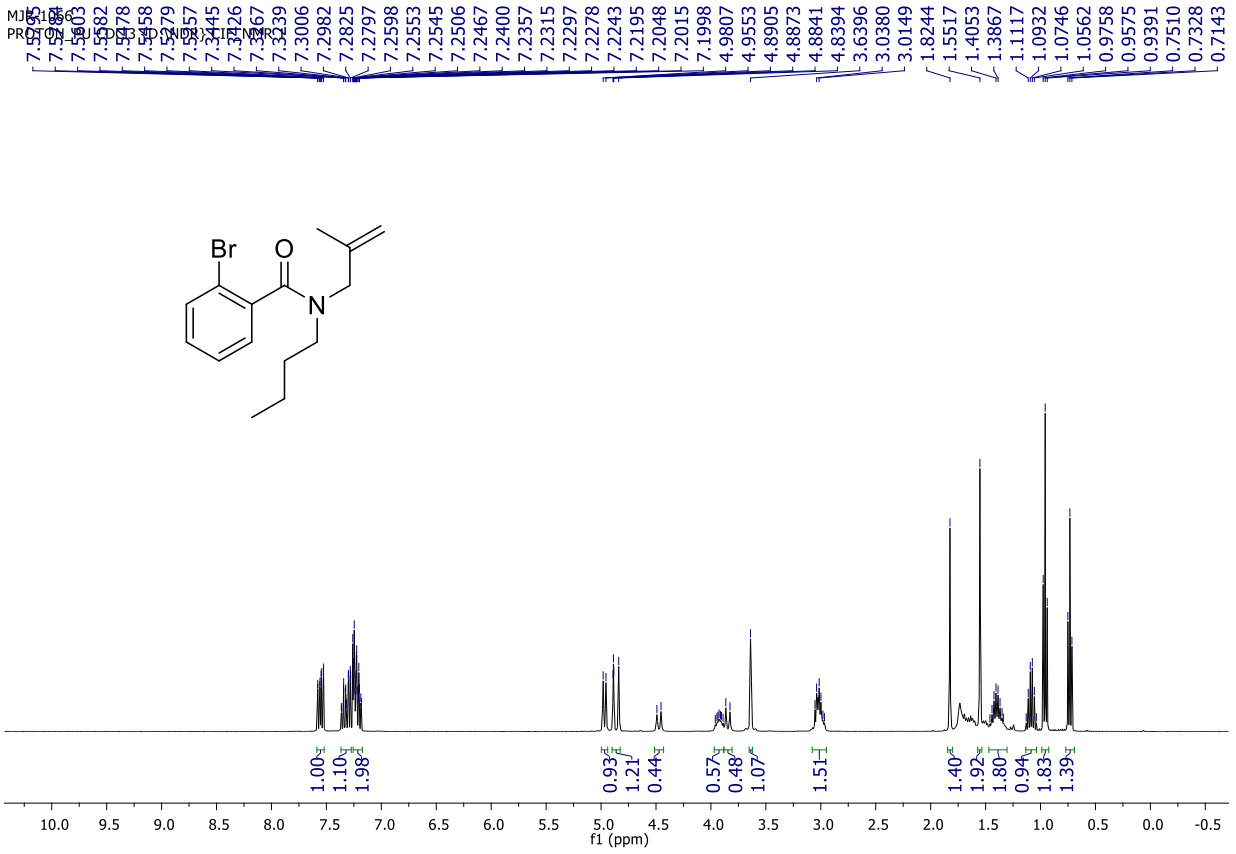
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **1i**



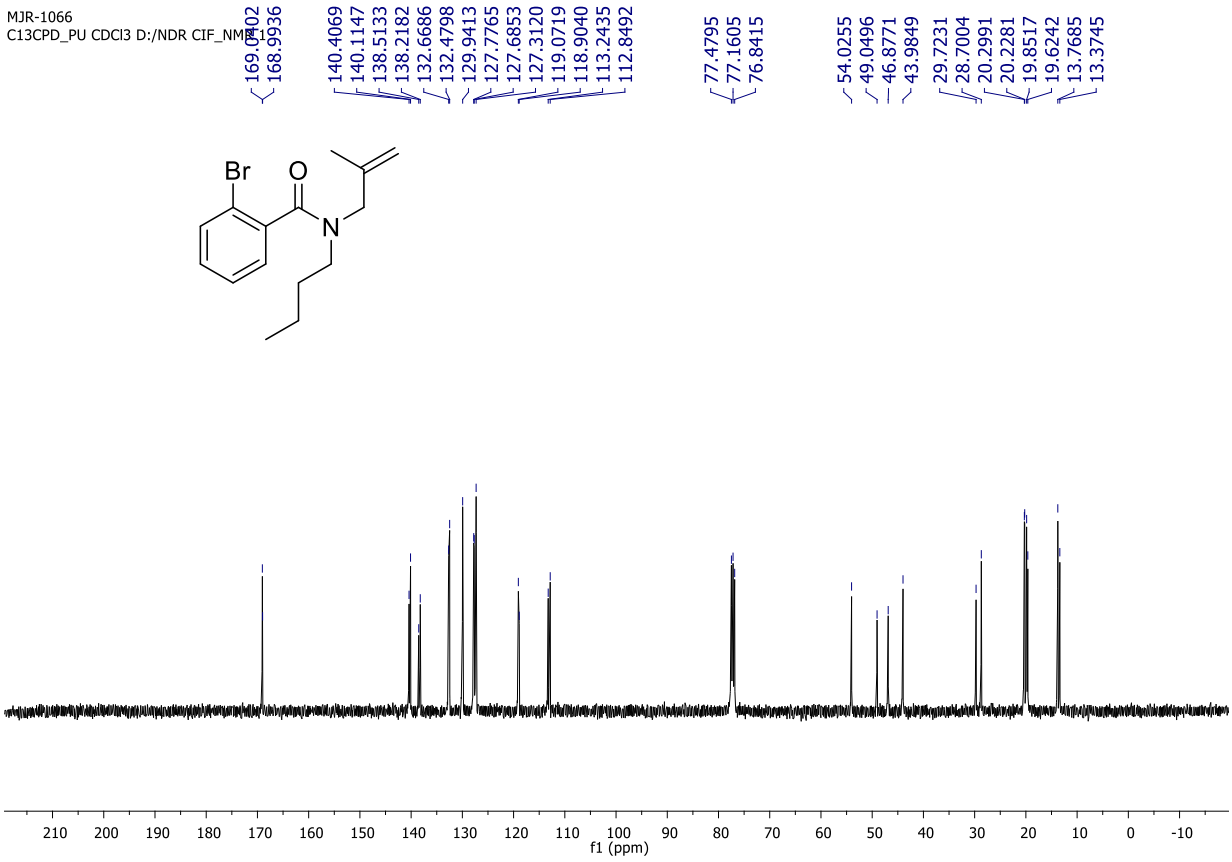
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **1i**



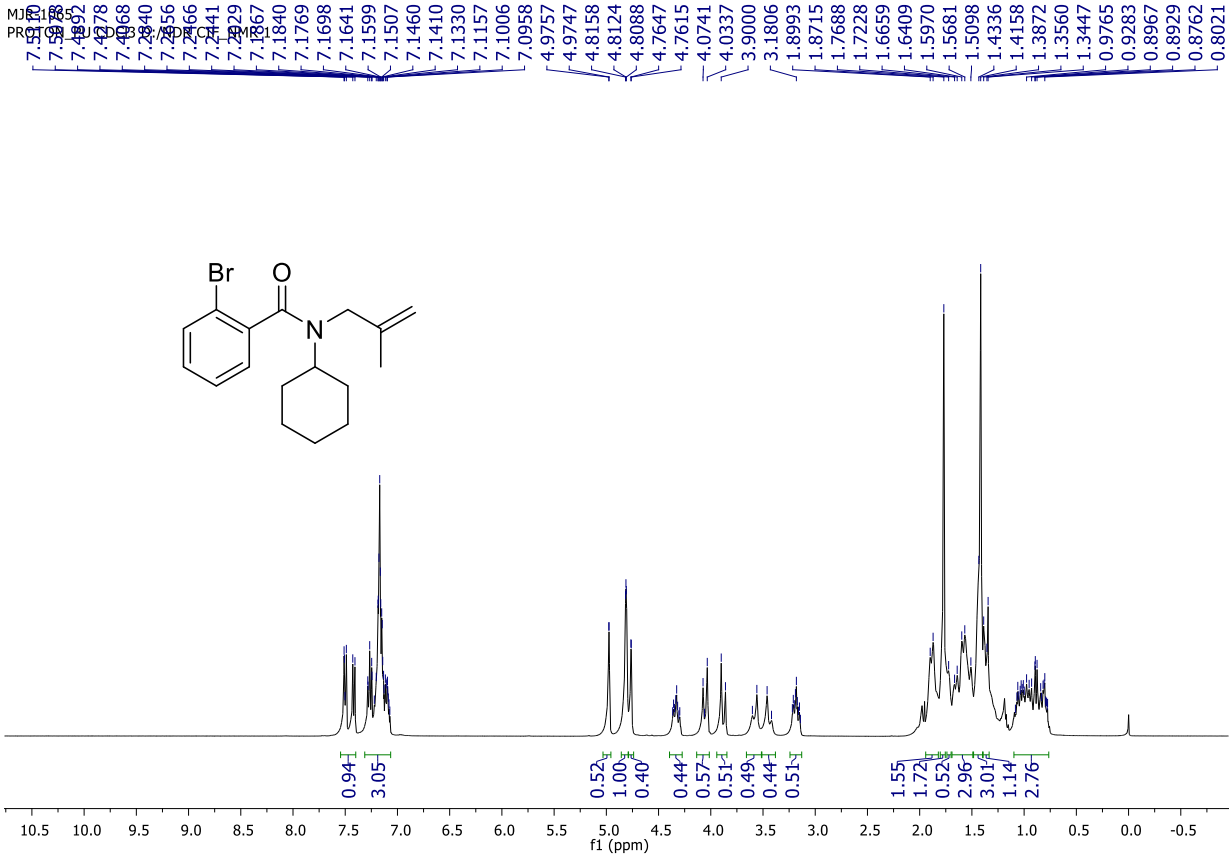
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **1j**



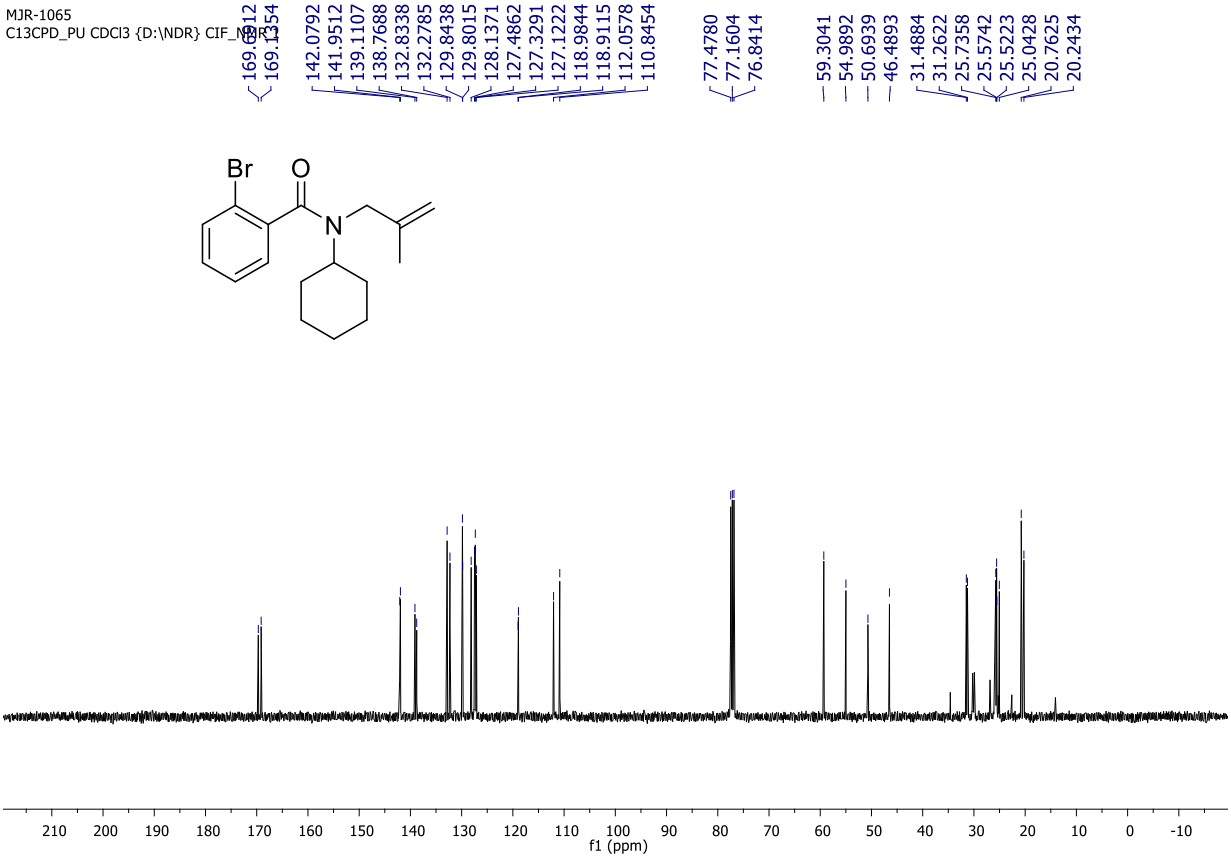
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **1j**



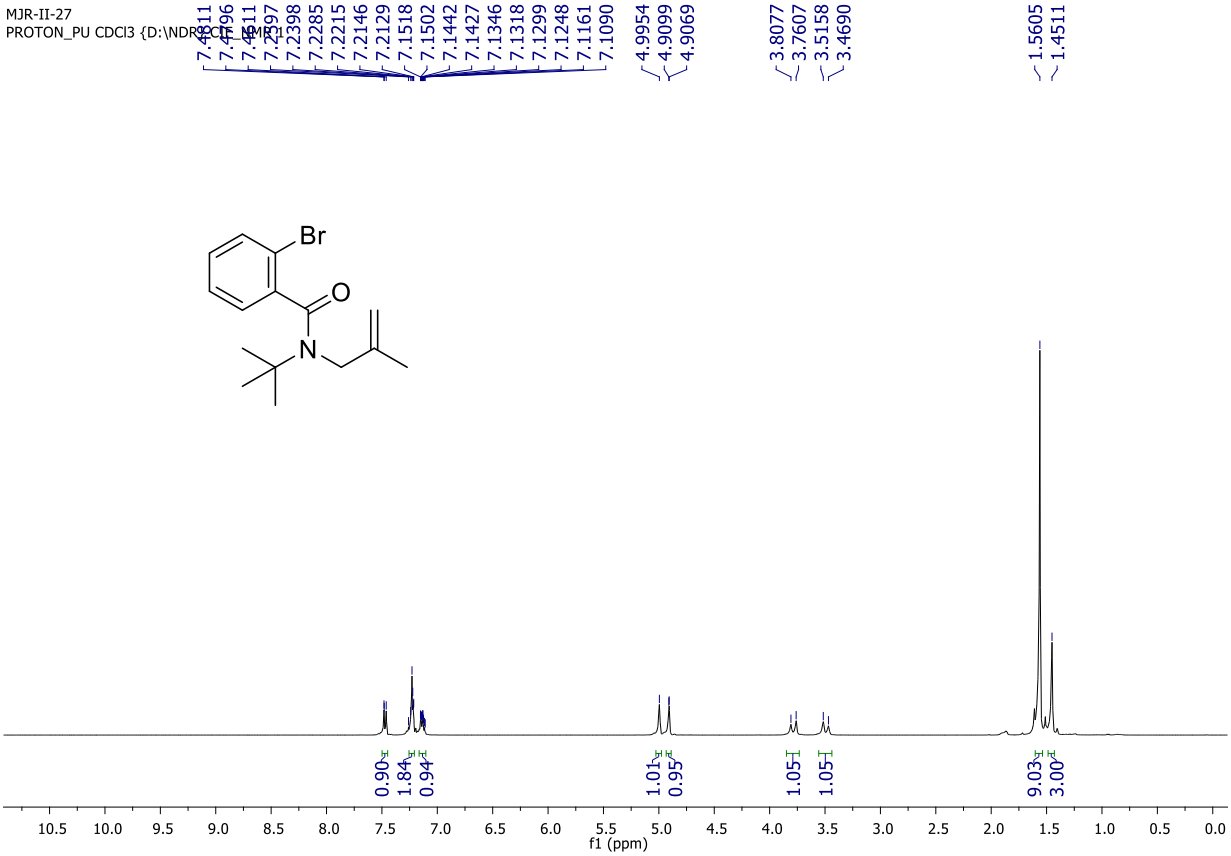
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **1k**



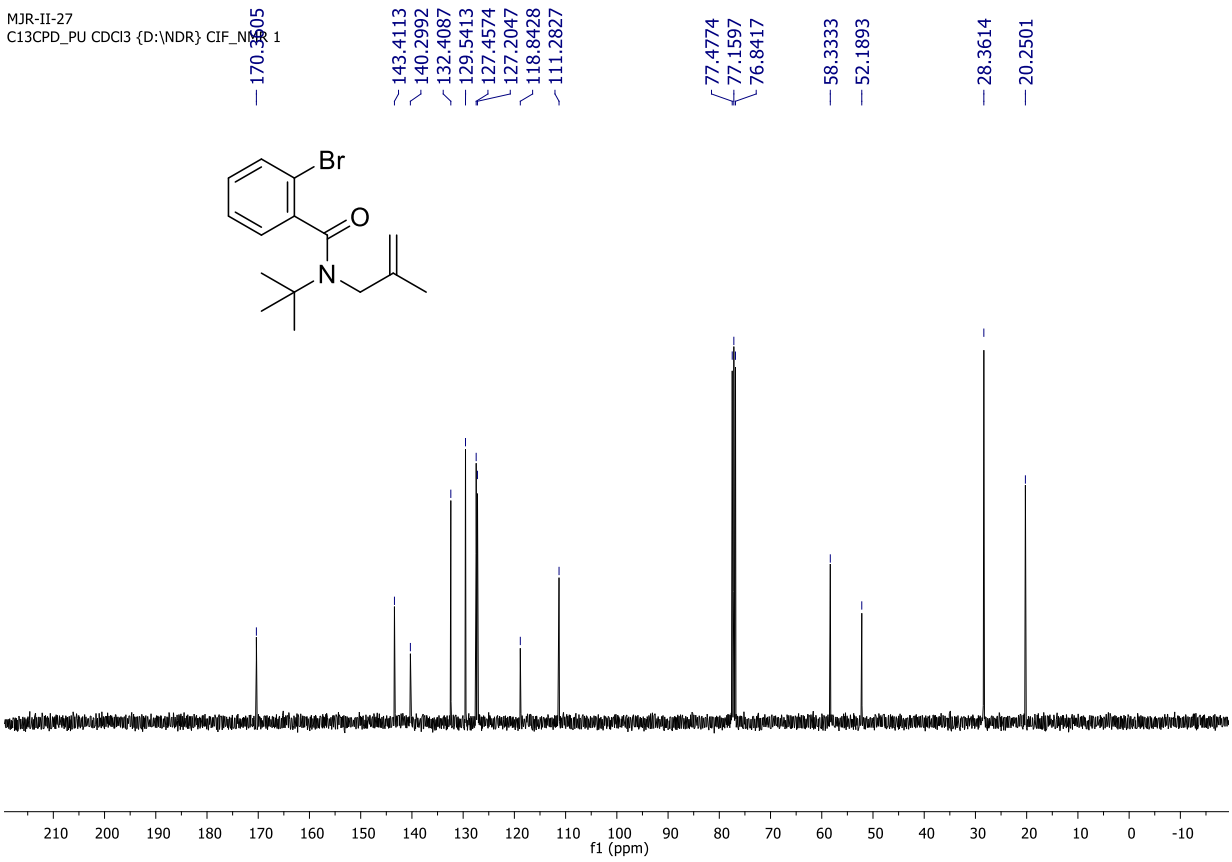
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **1k**



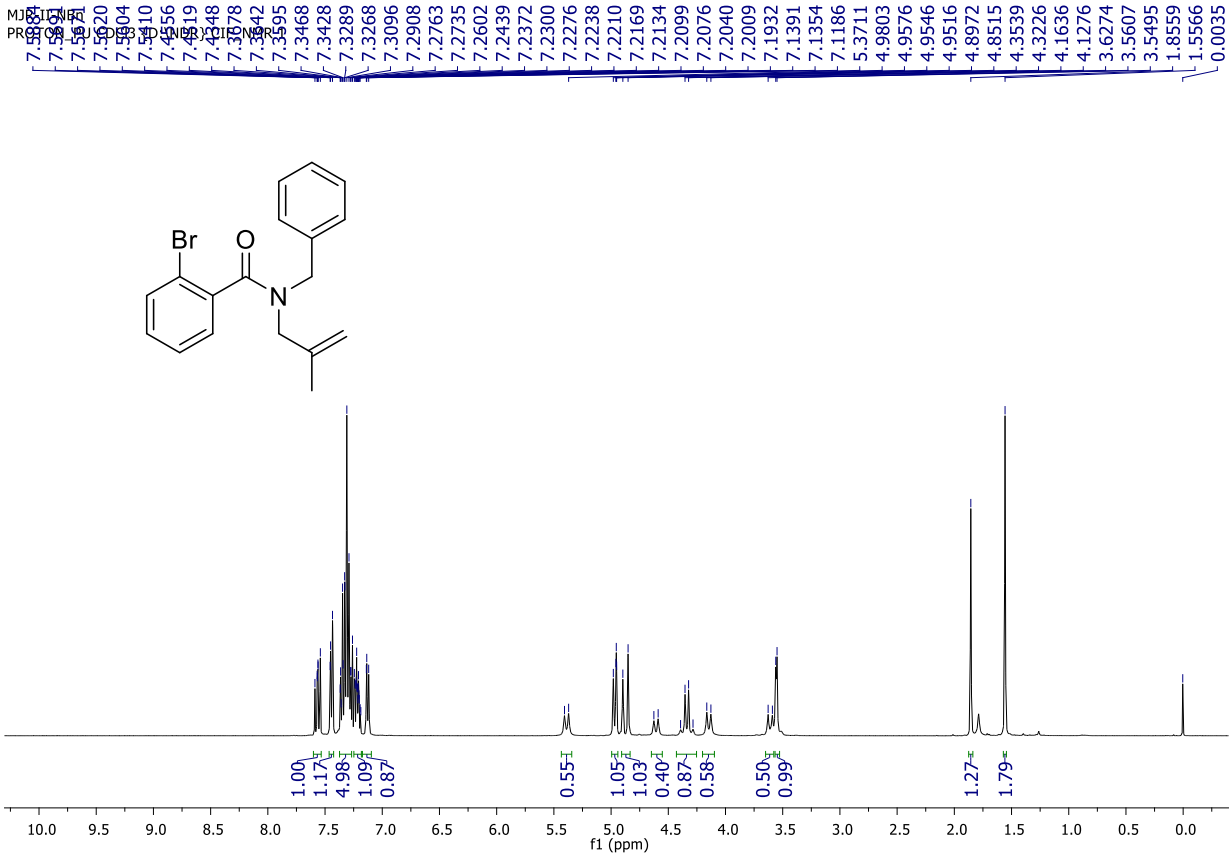
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **1l**



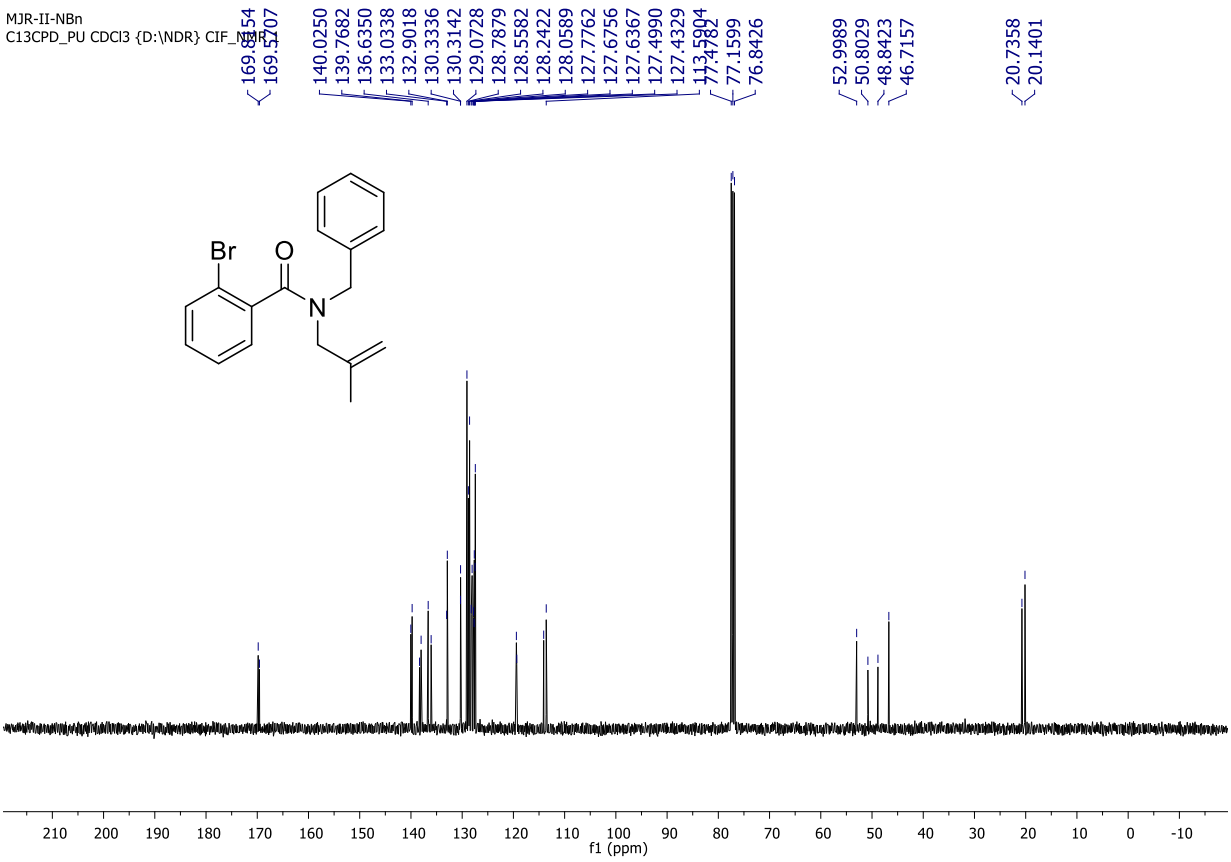
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **1l**



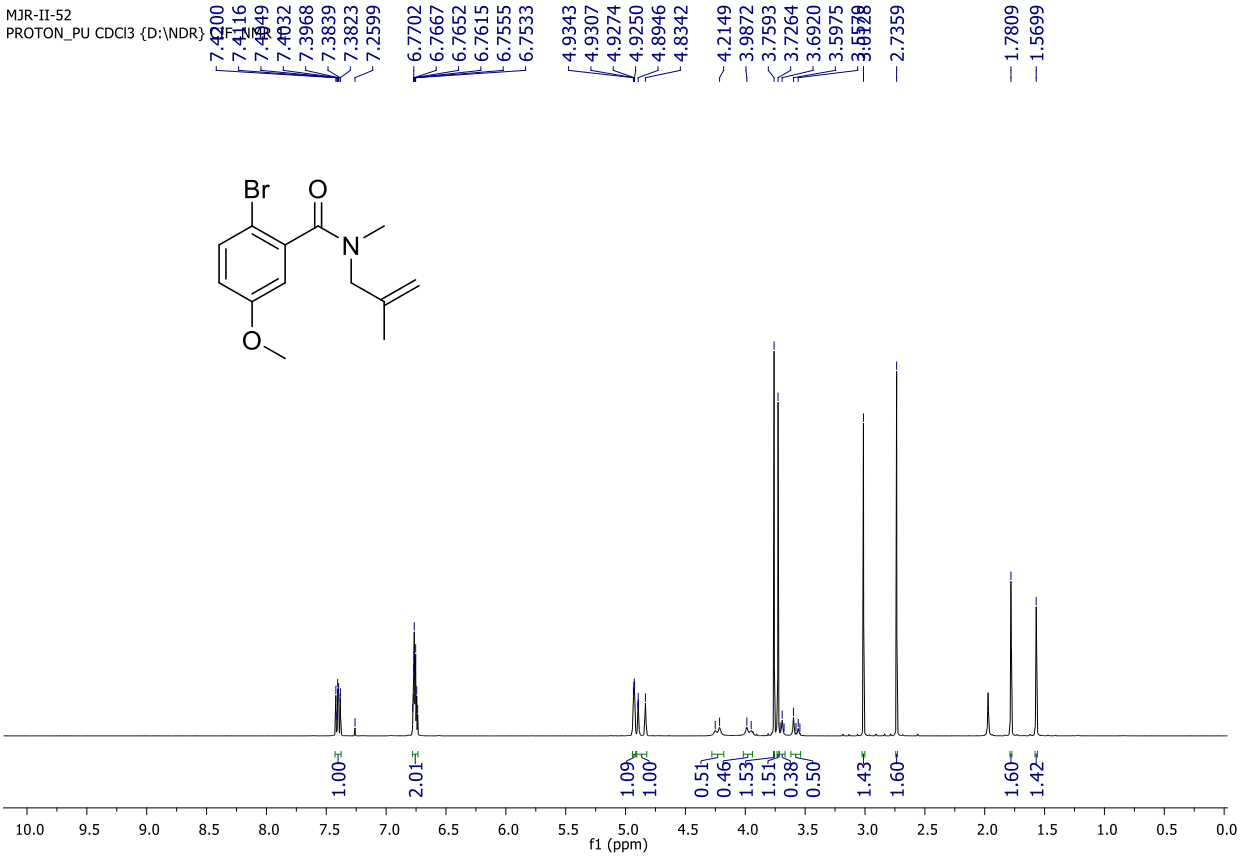
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **1m**



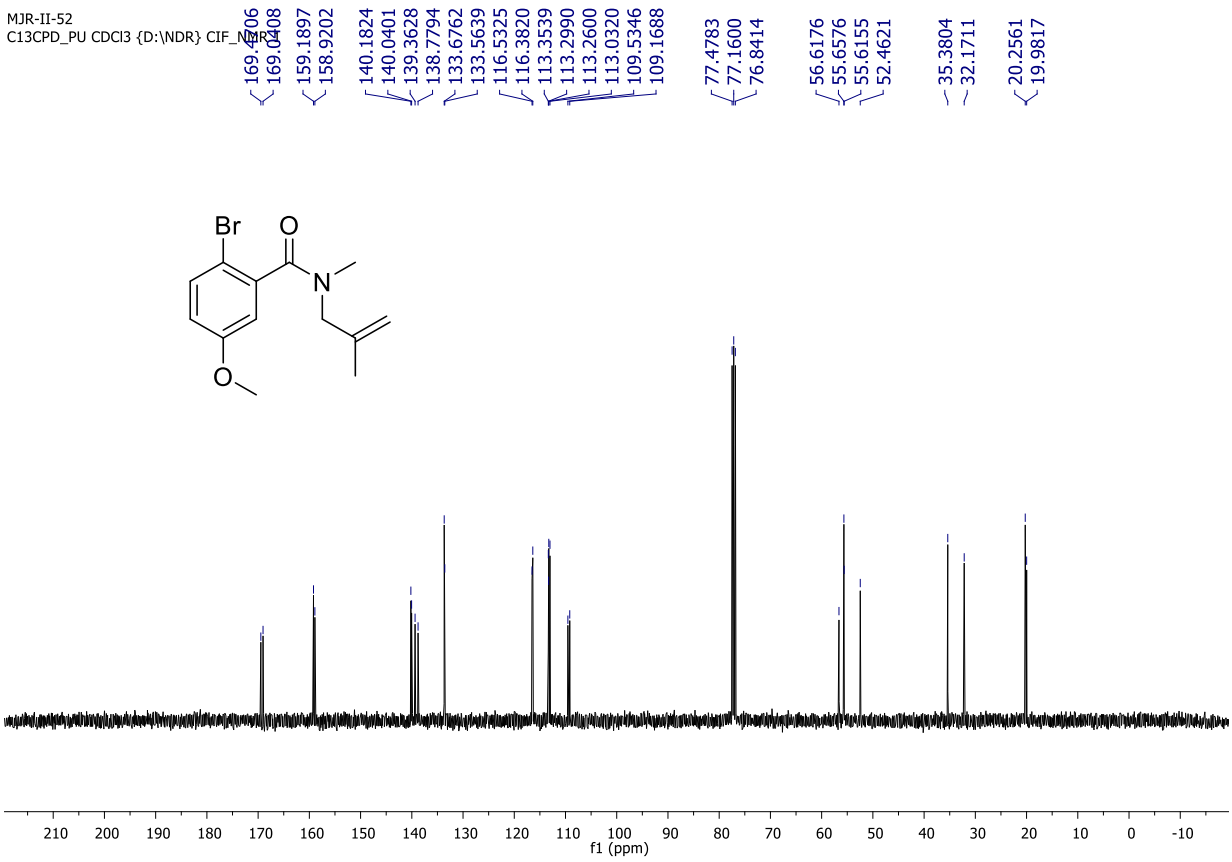
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **1m**



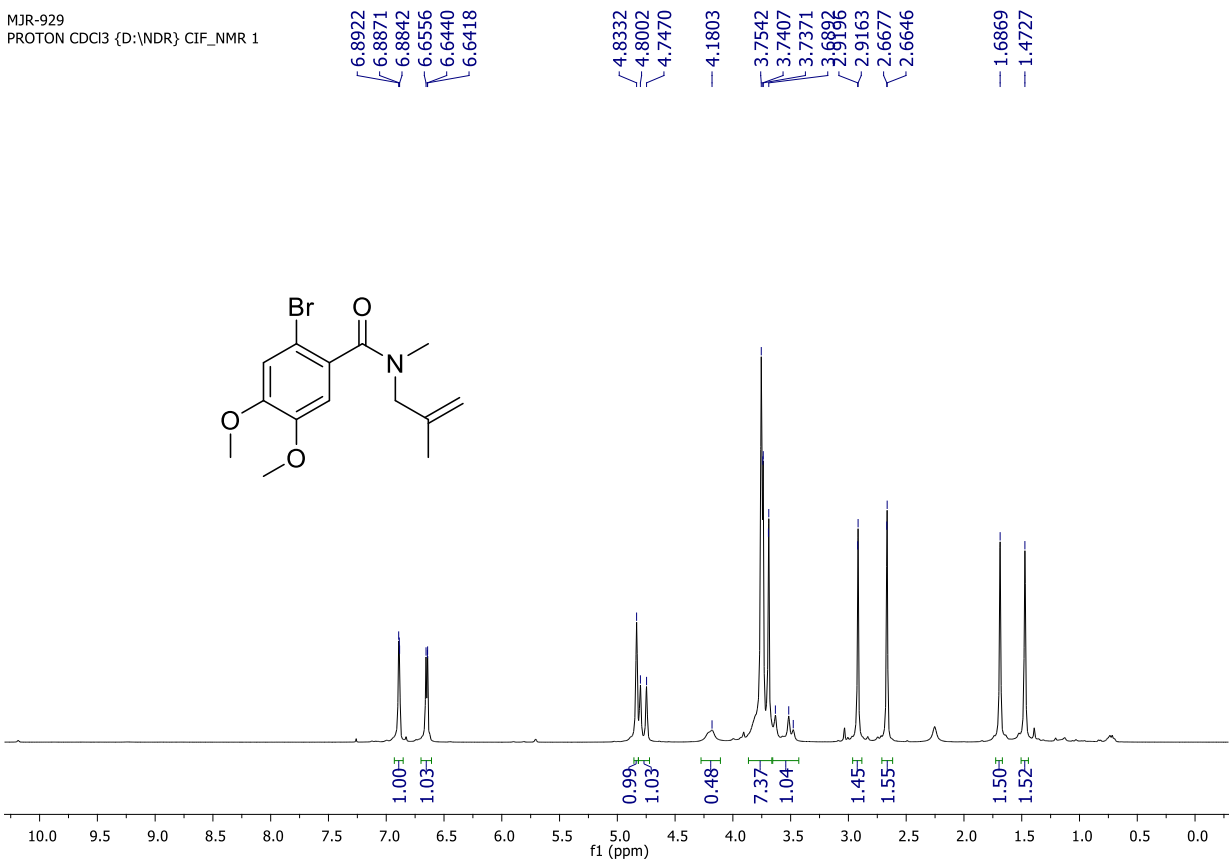
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **1n**



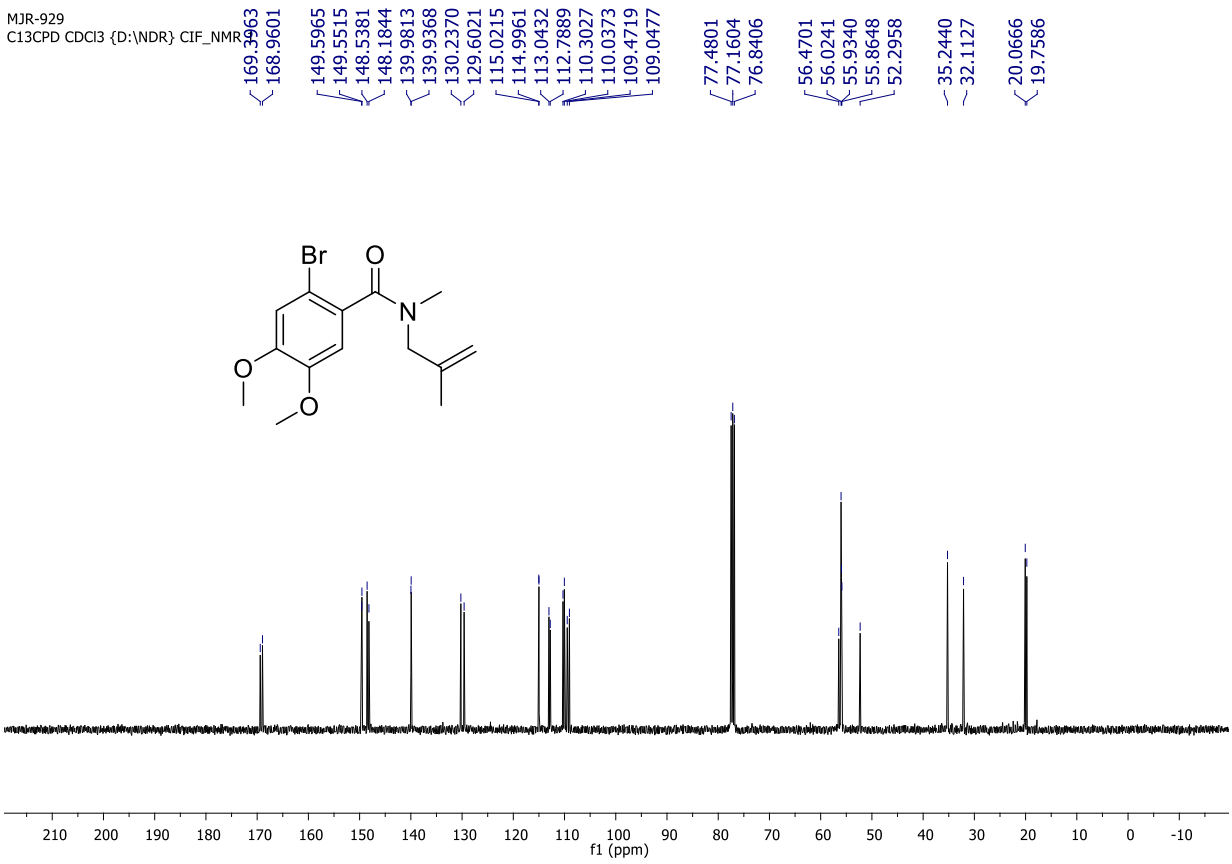
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **1n**



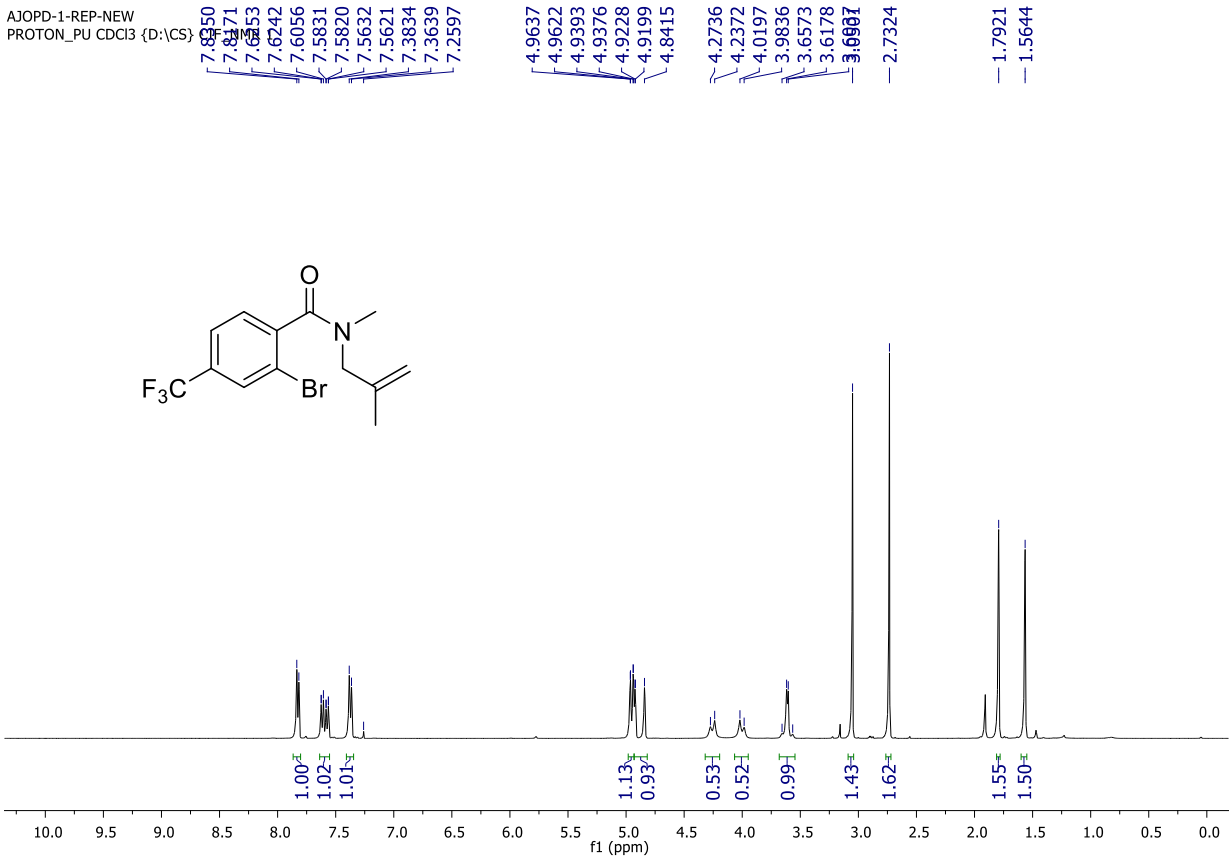
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **1o**



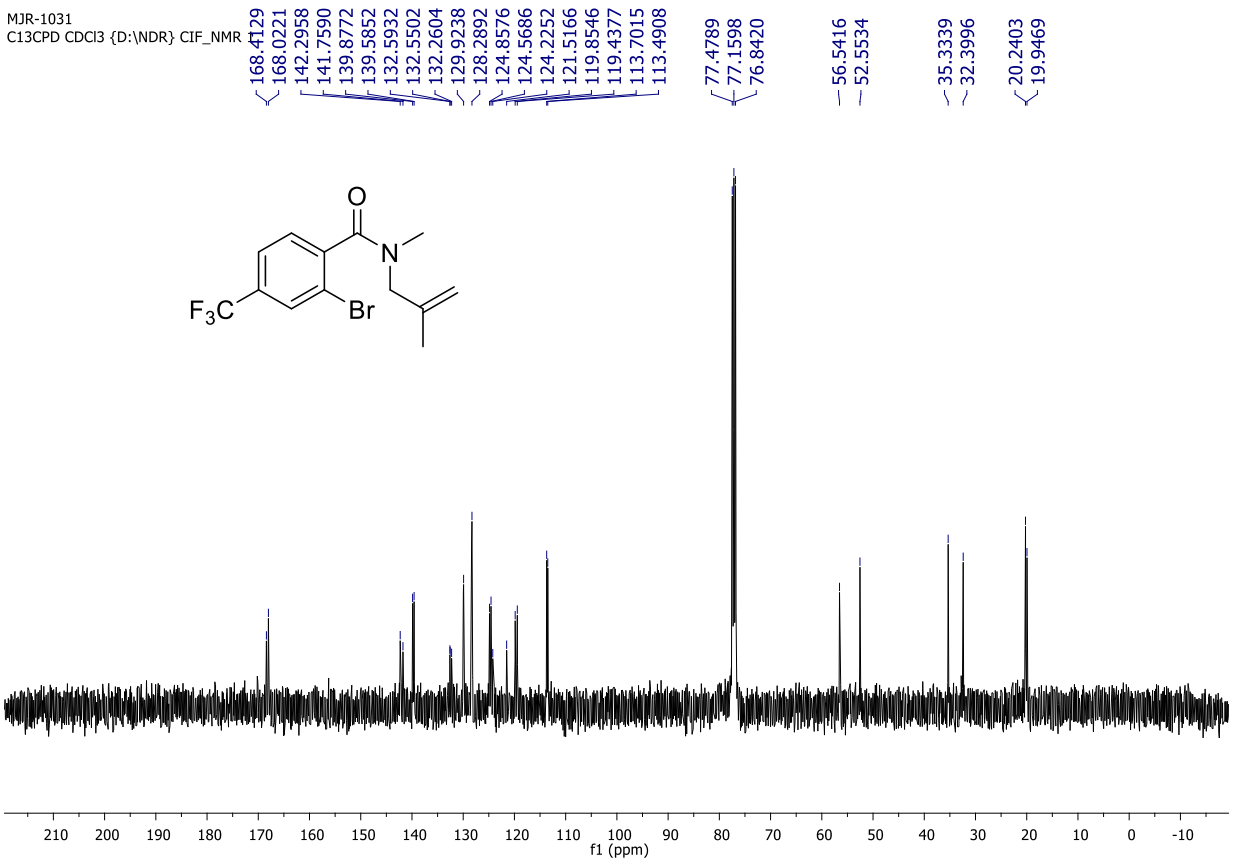
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **1o**



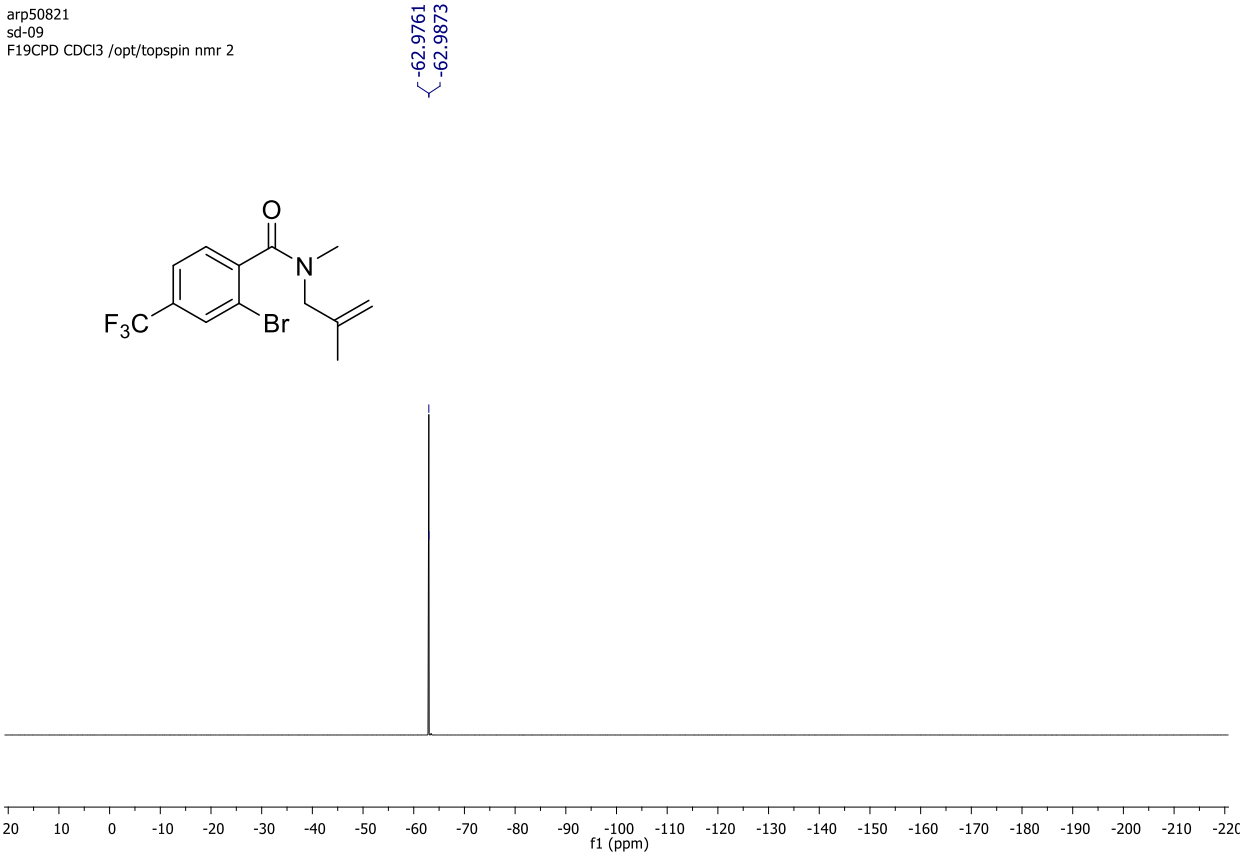
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **1p**



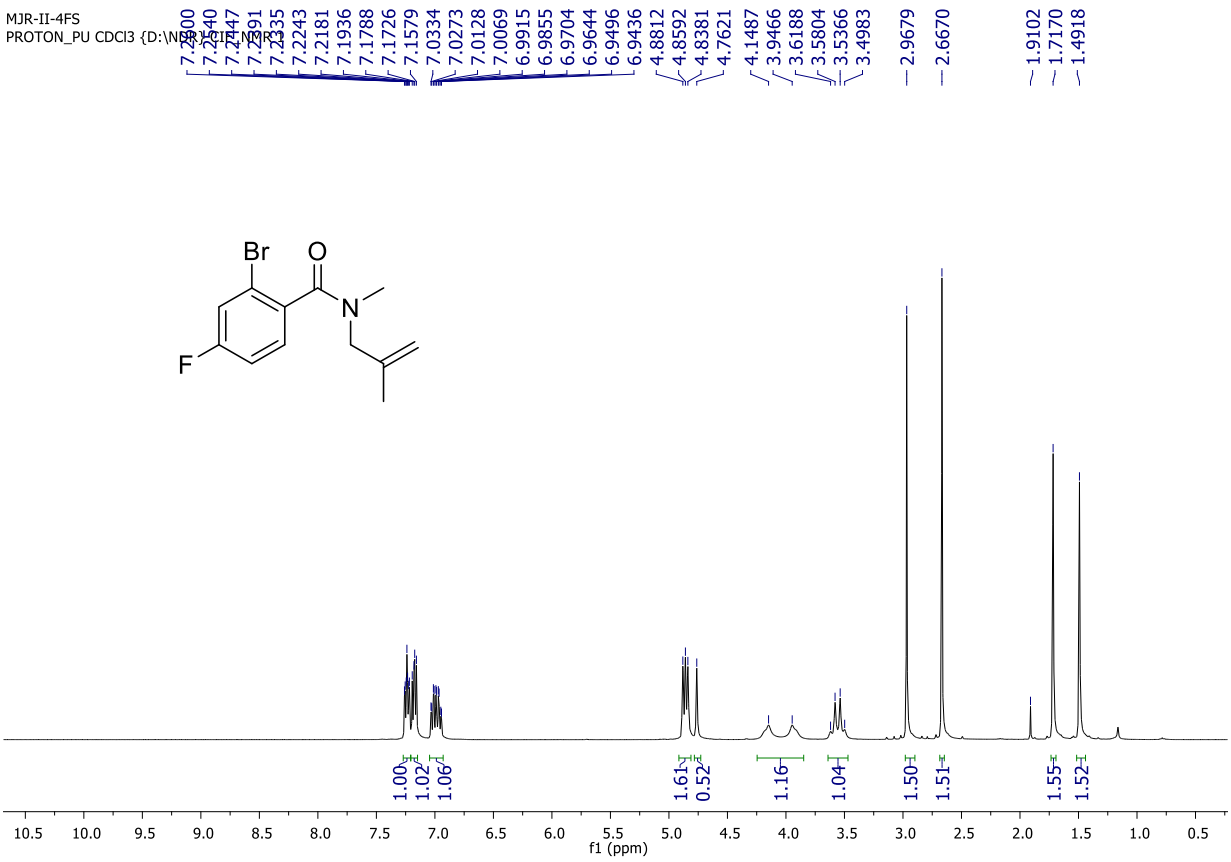
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **1p**



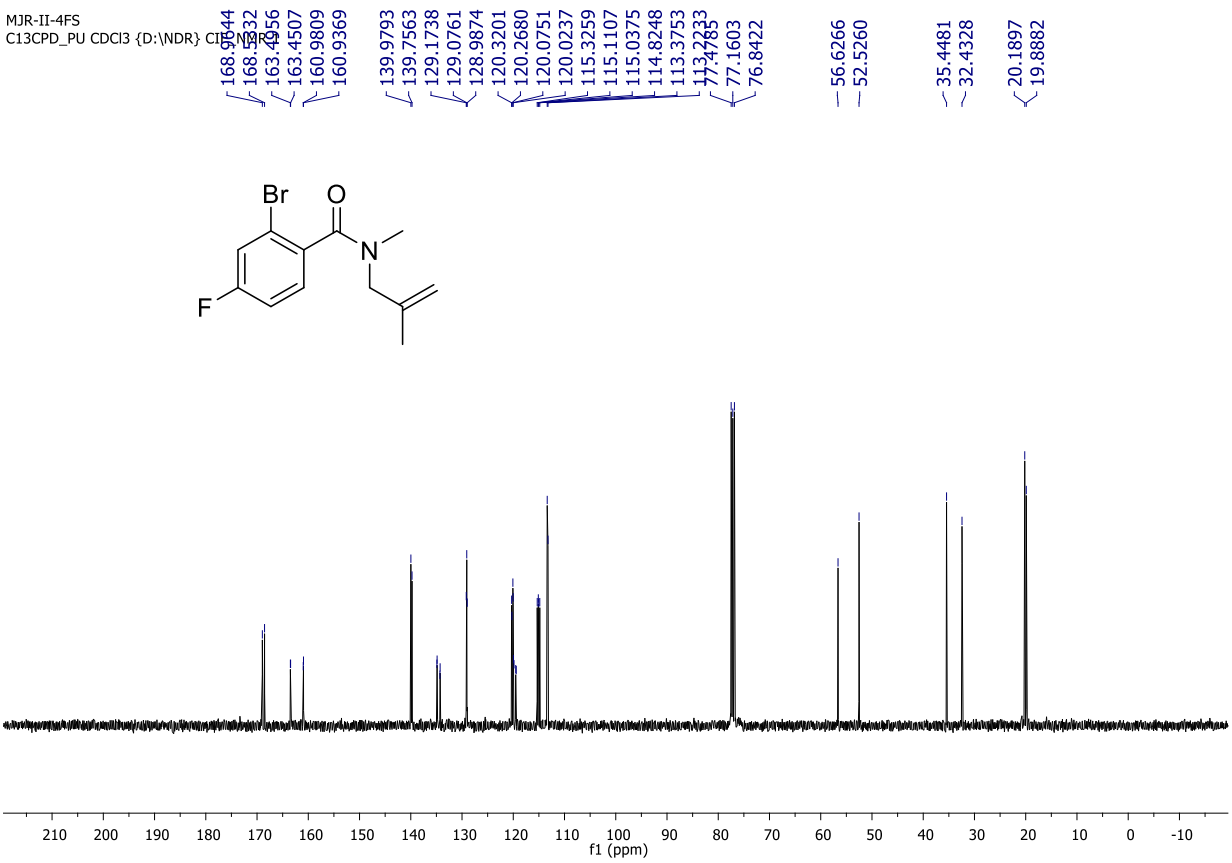
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **1p**



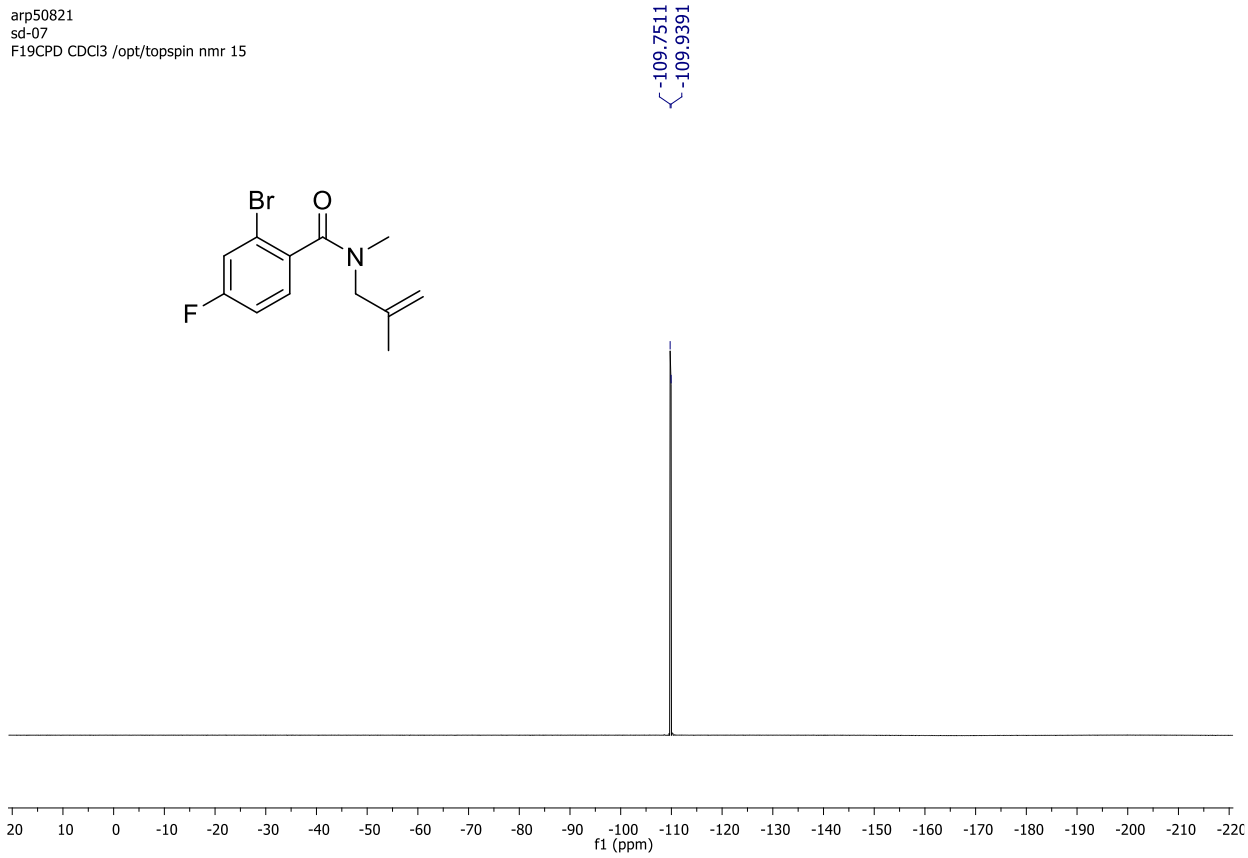
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **1q**



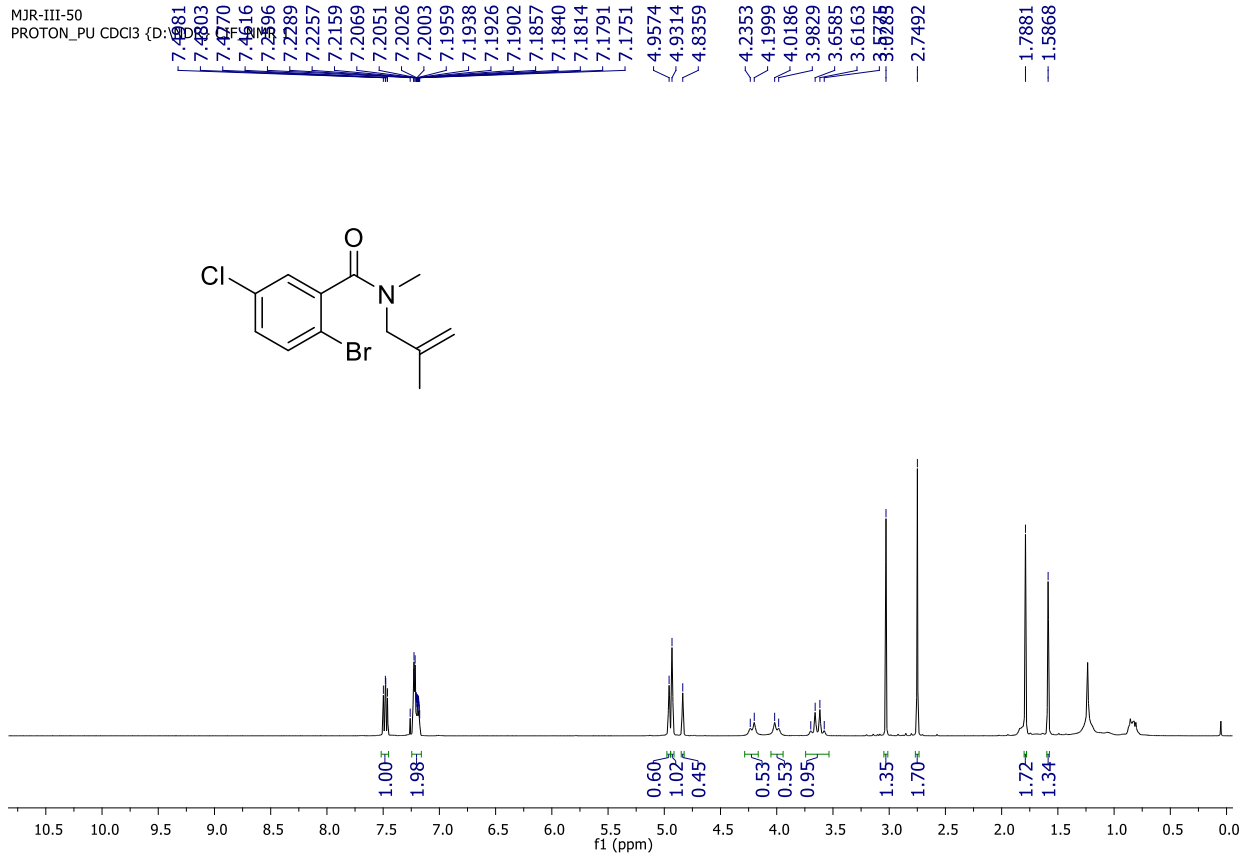
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **1q**



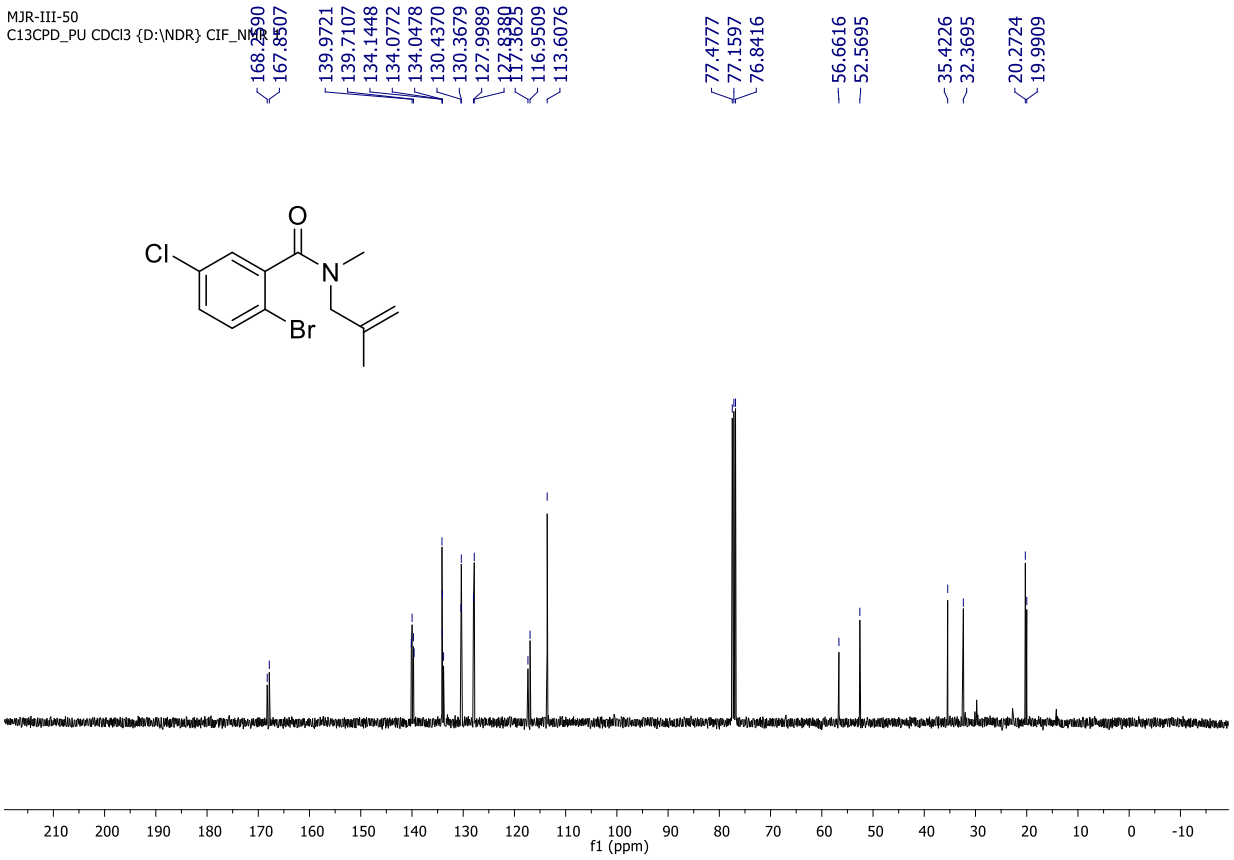
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **1q**



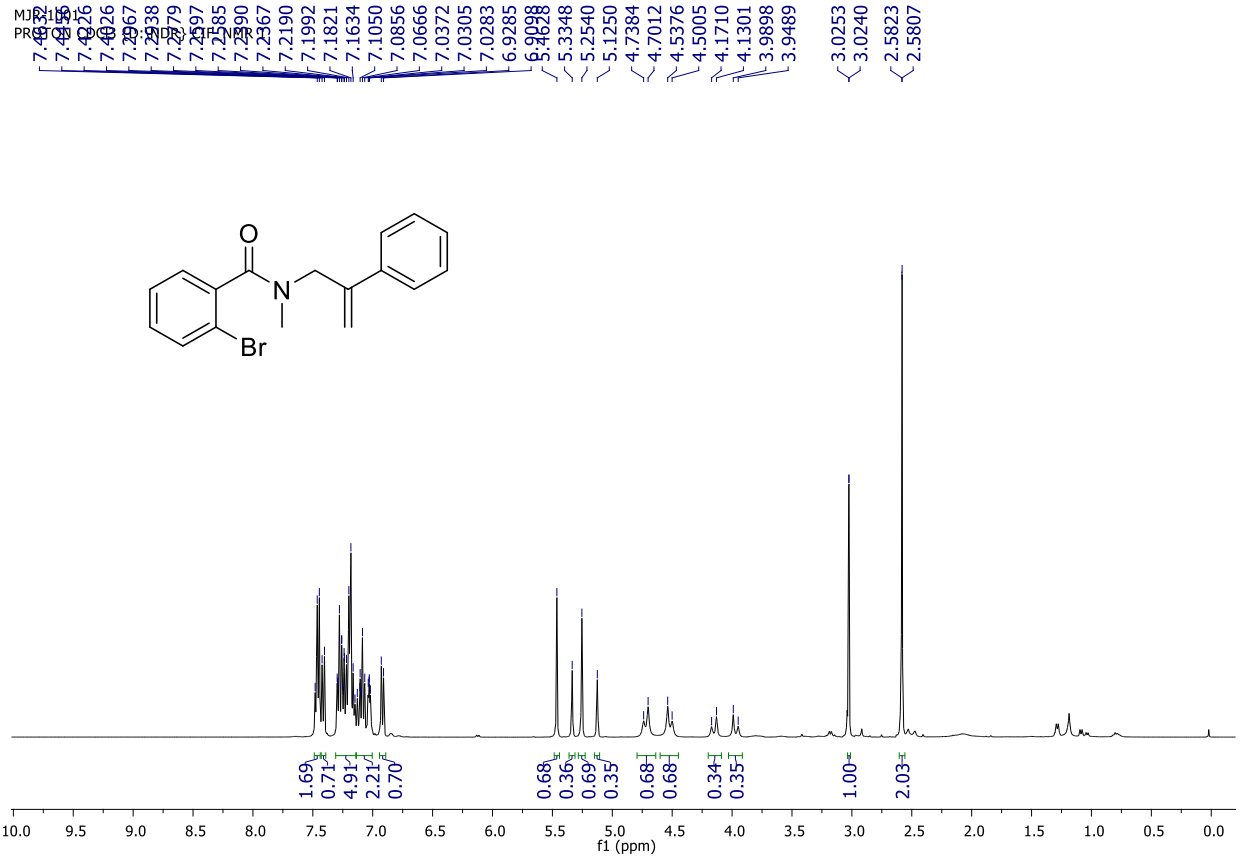
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **1r**



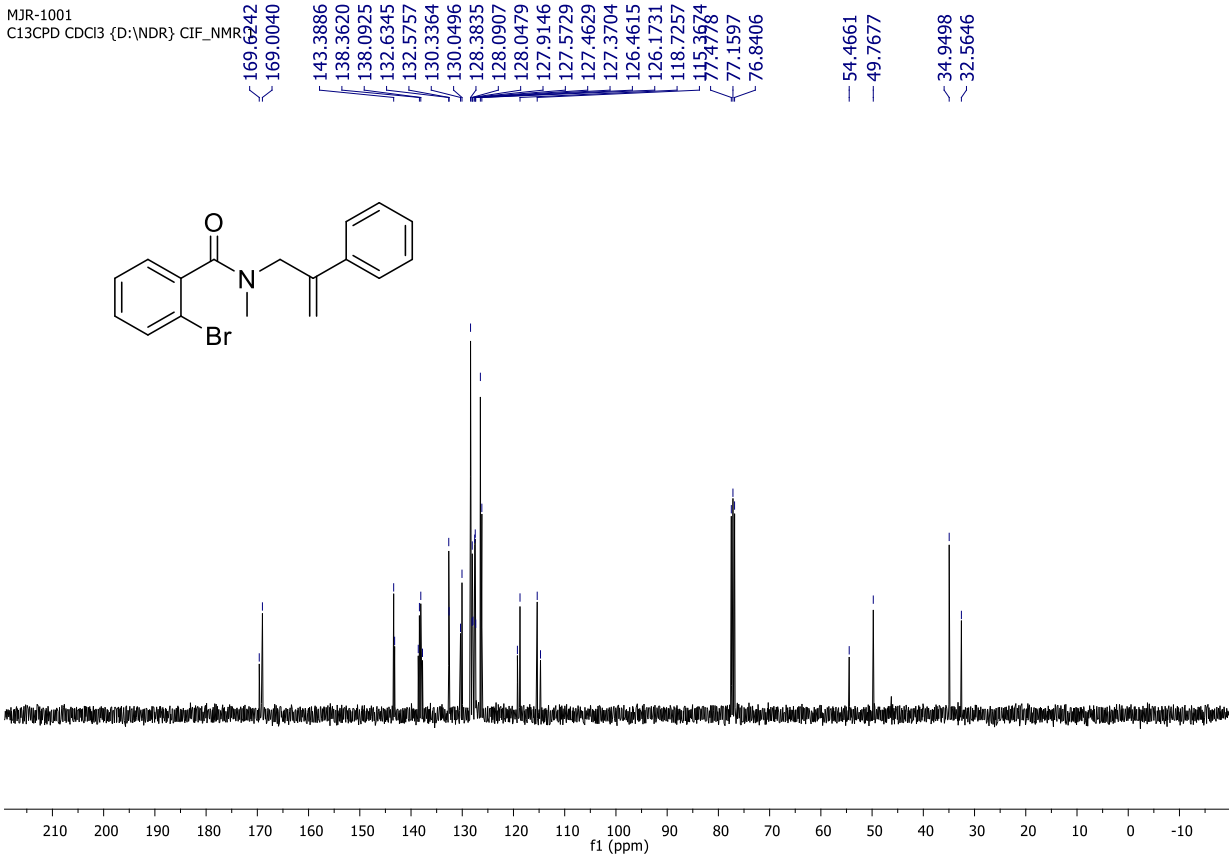
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **1r**



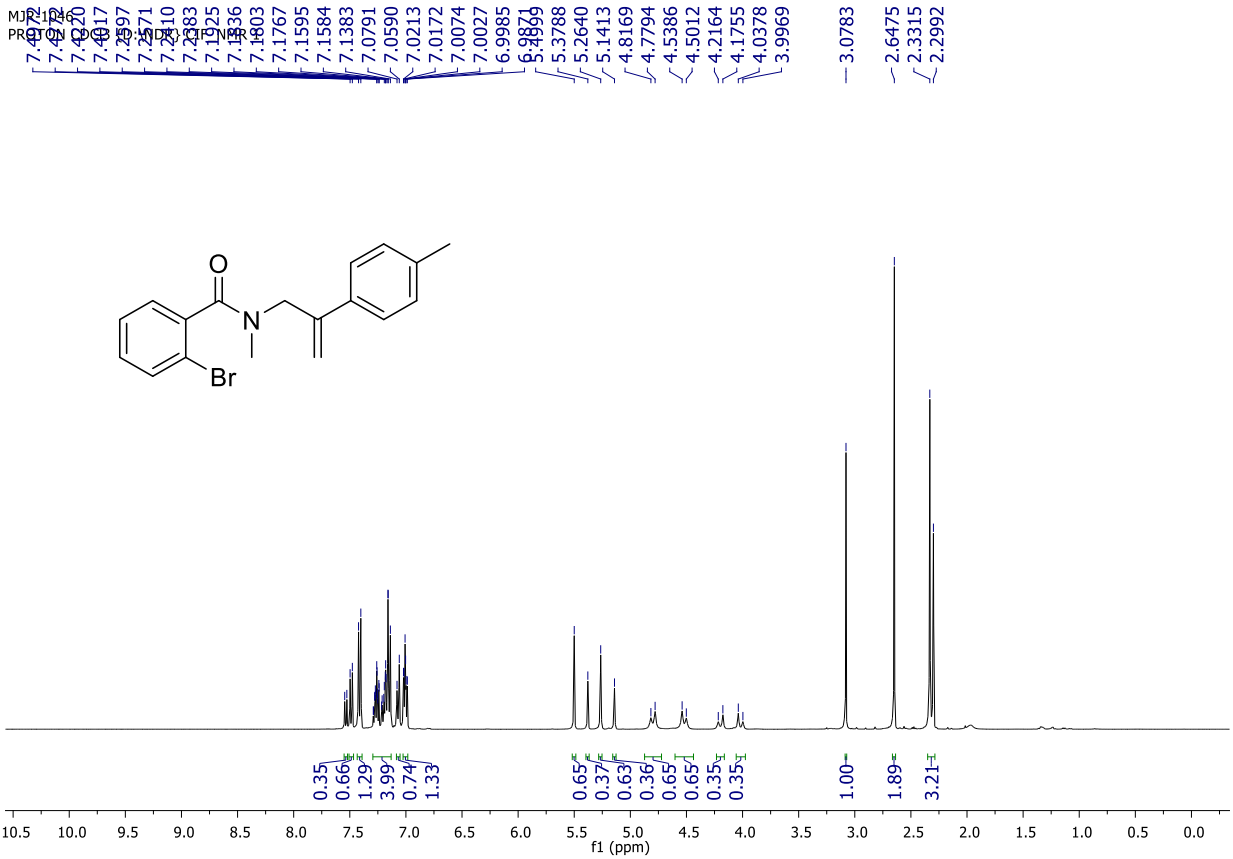
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **1s**



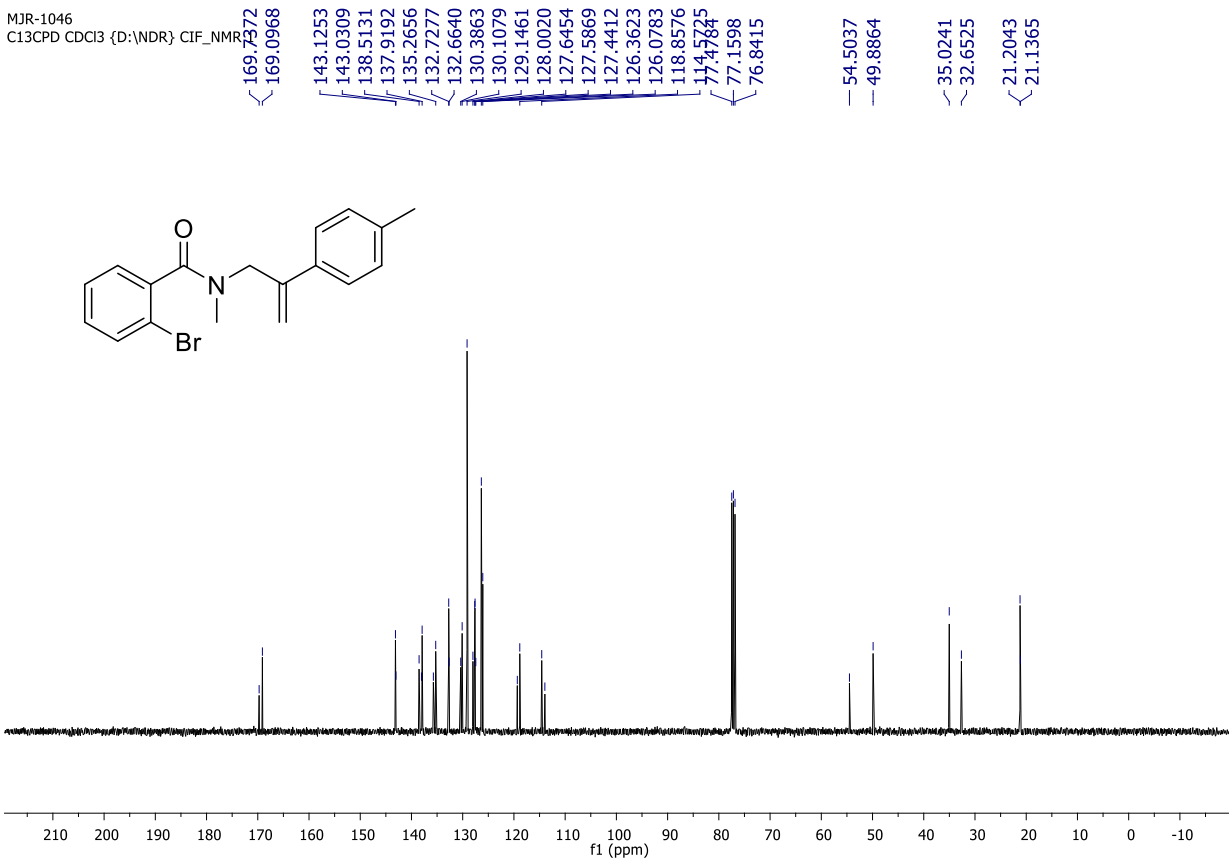
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **1s**



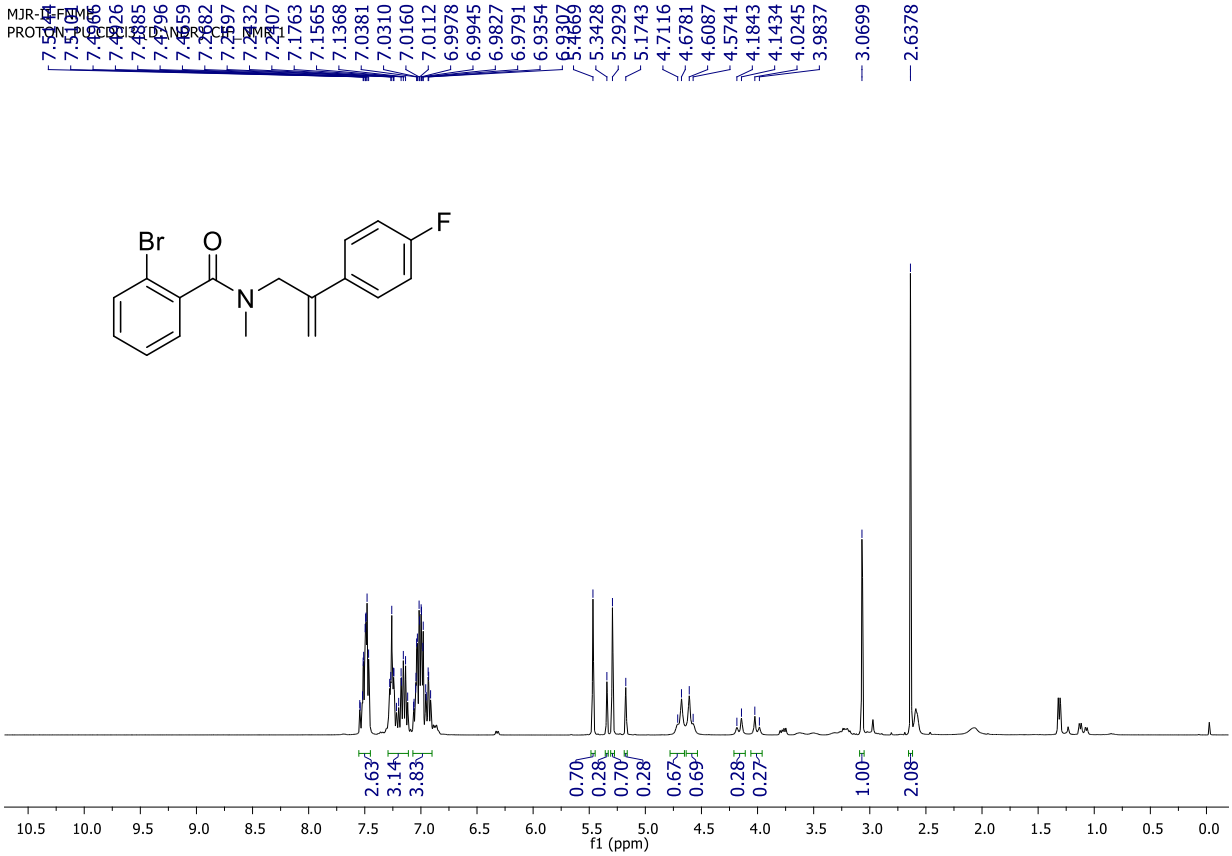
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **1t**



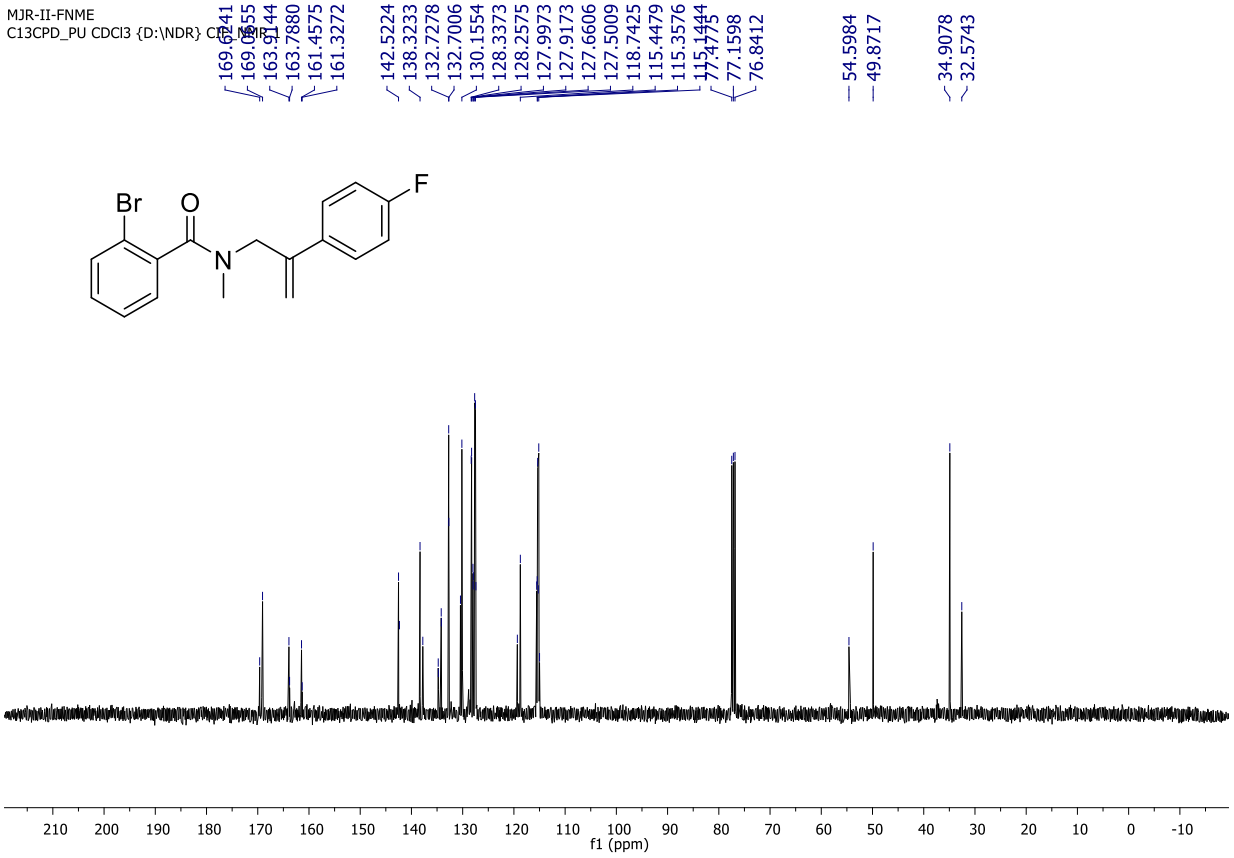
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **1t**



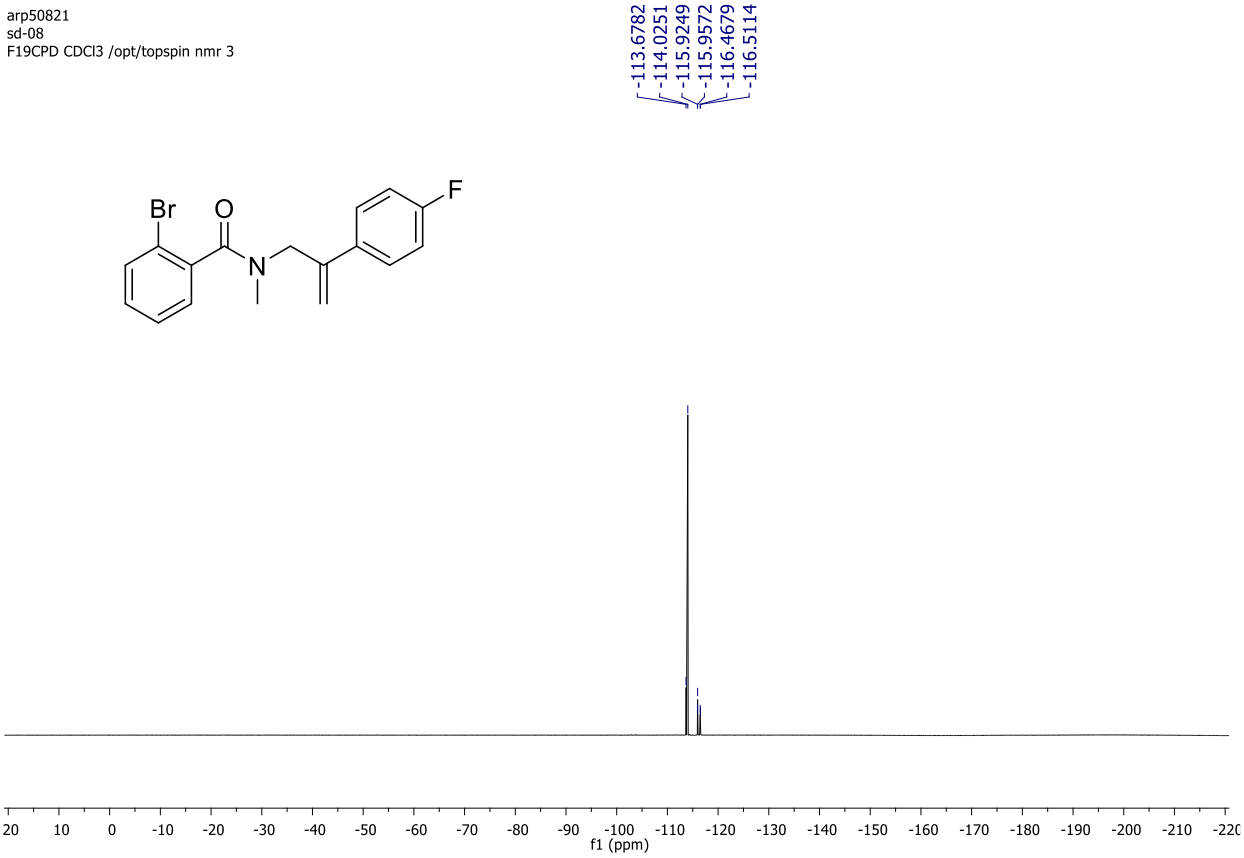
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **1u**



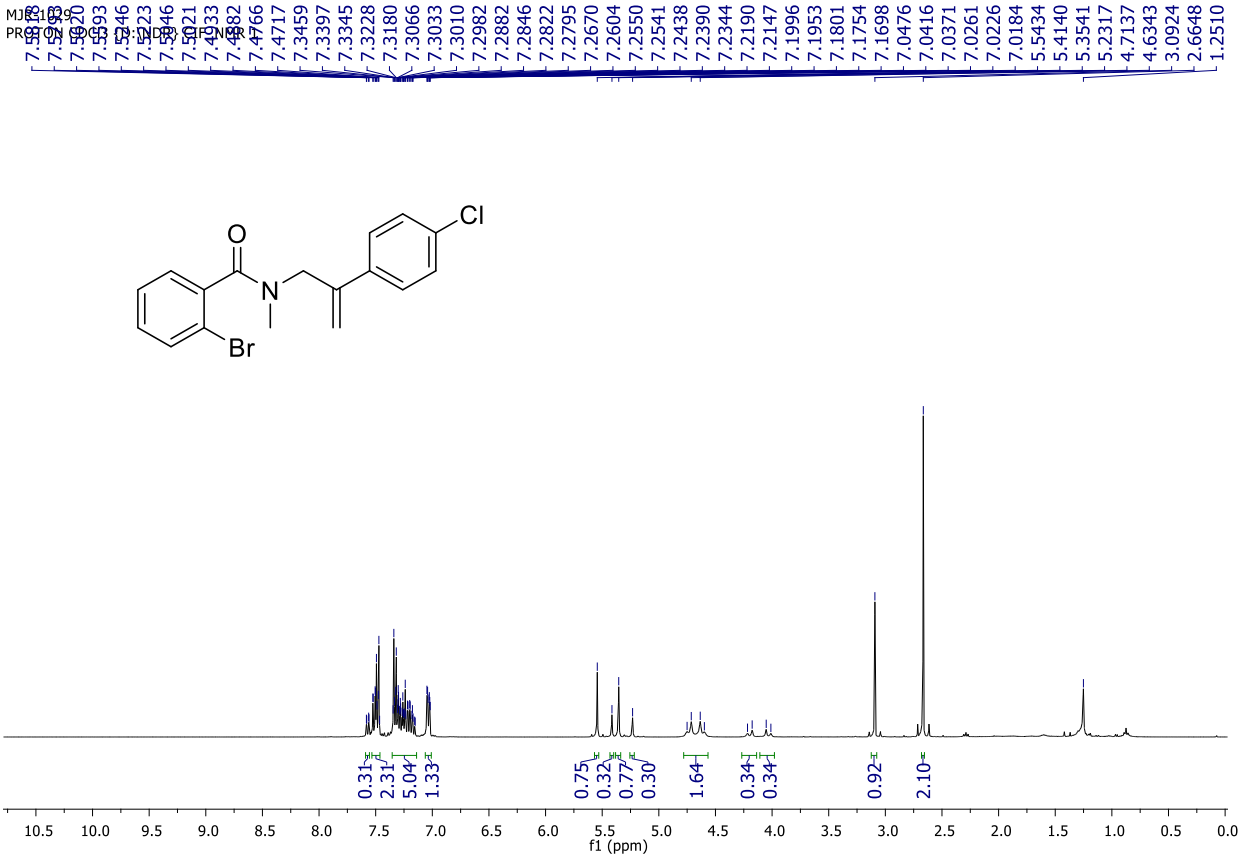
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **1u**



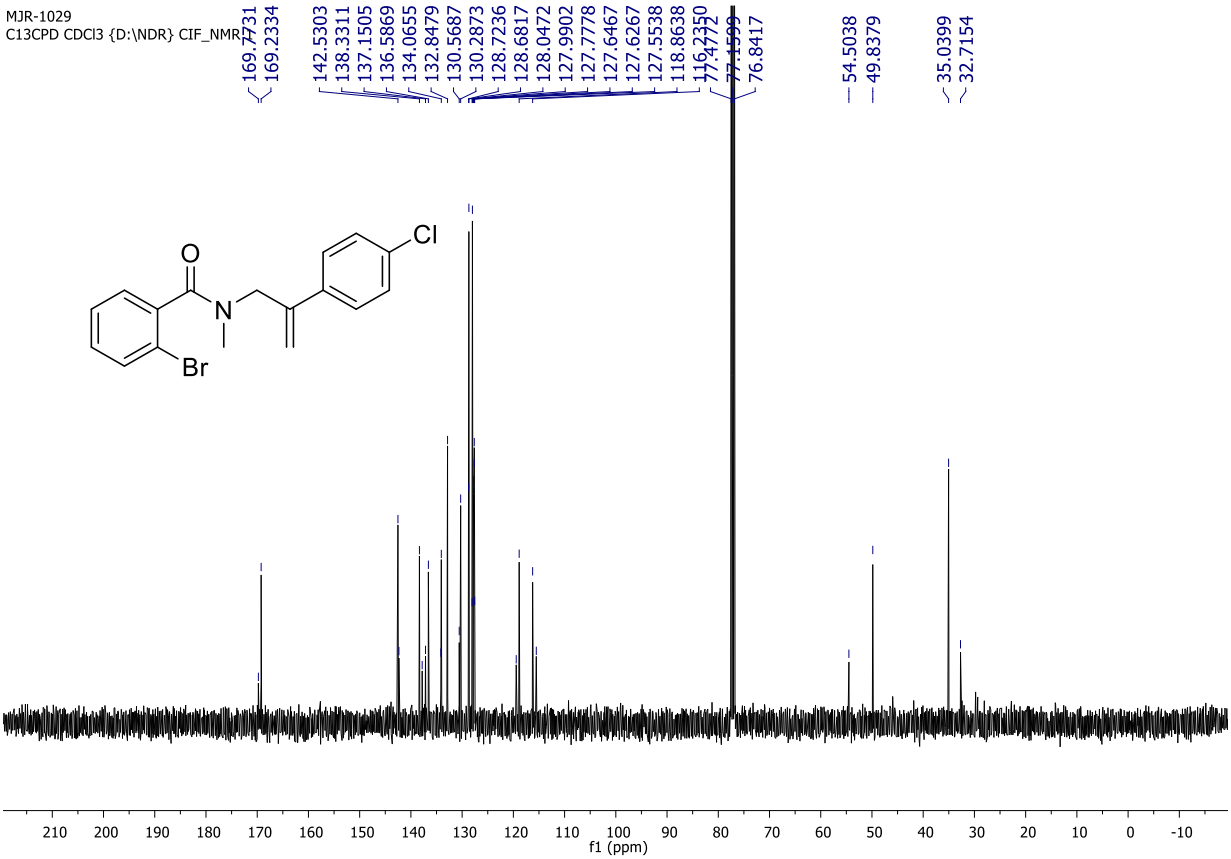
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **1u**



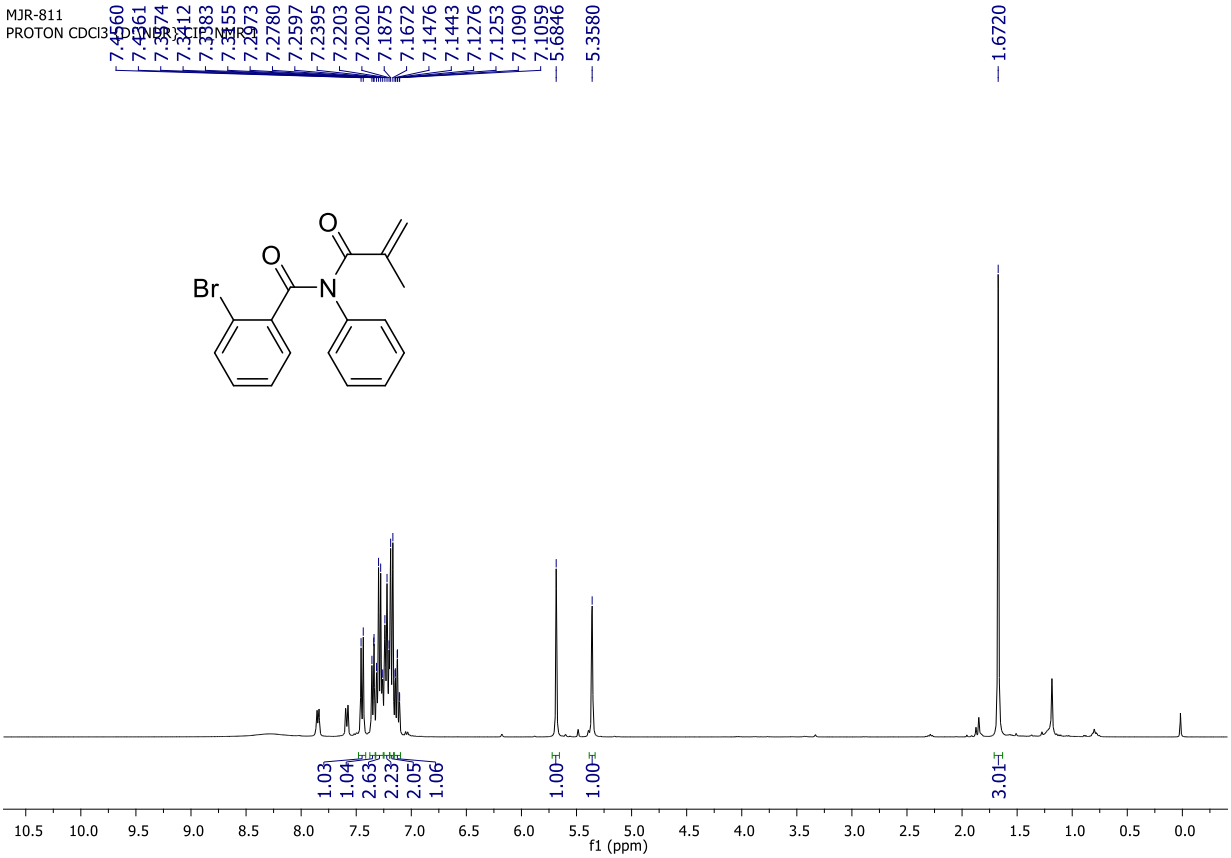
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **1v**



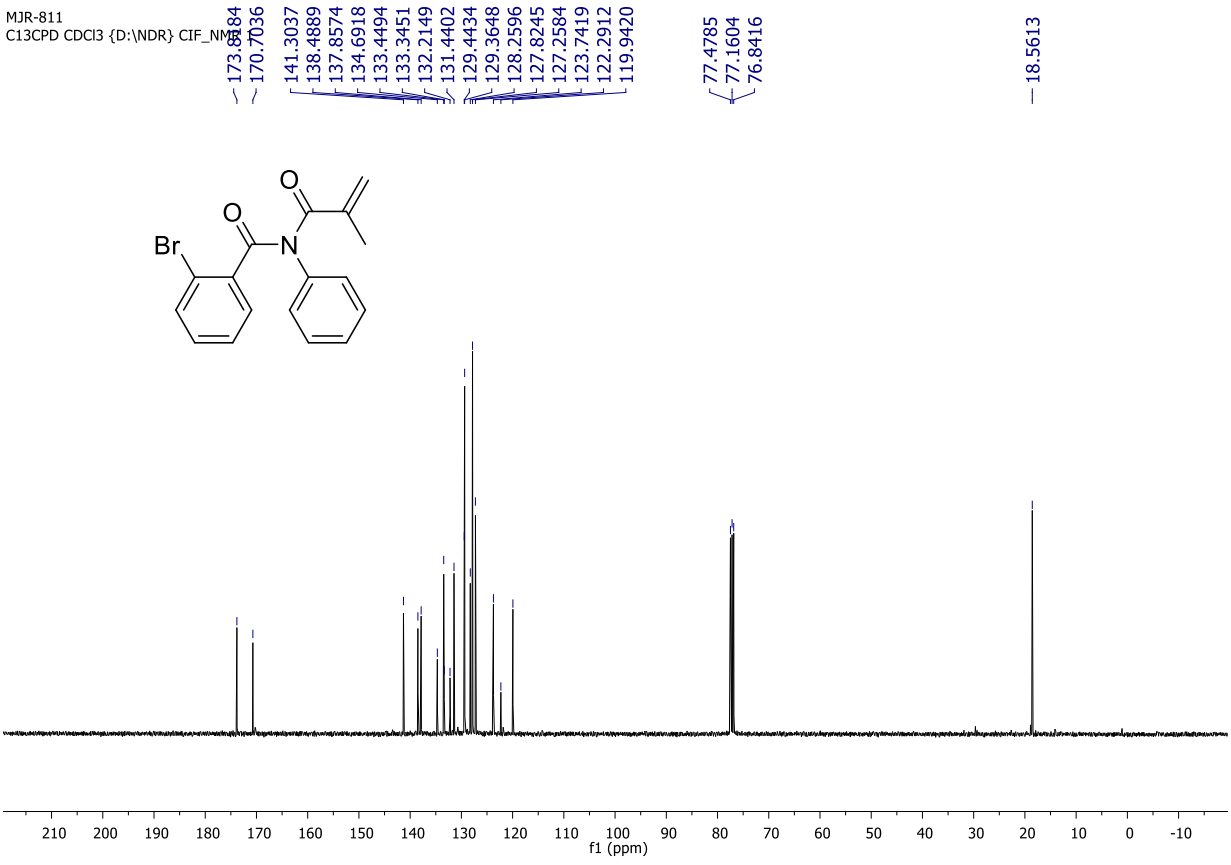
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **1v**



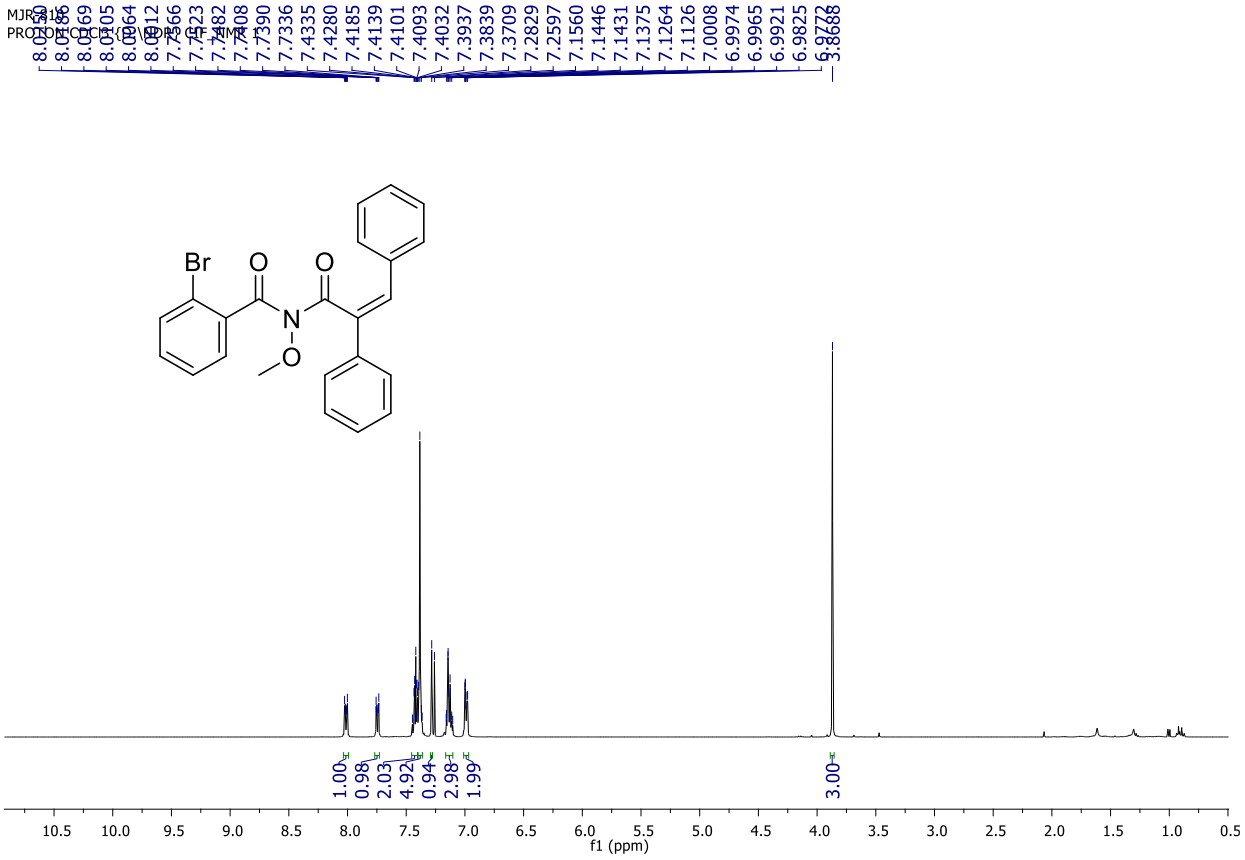
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **1aa**



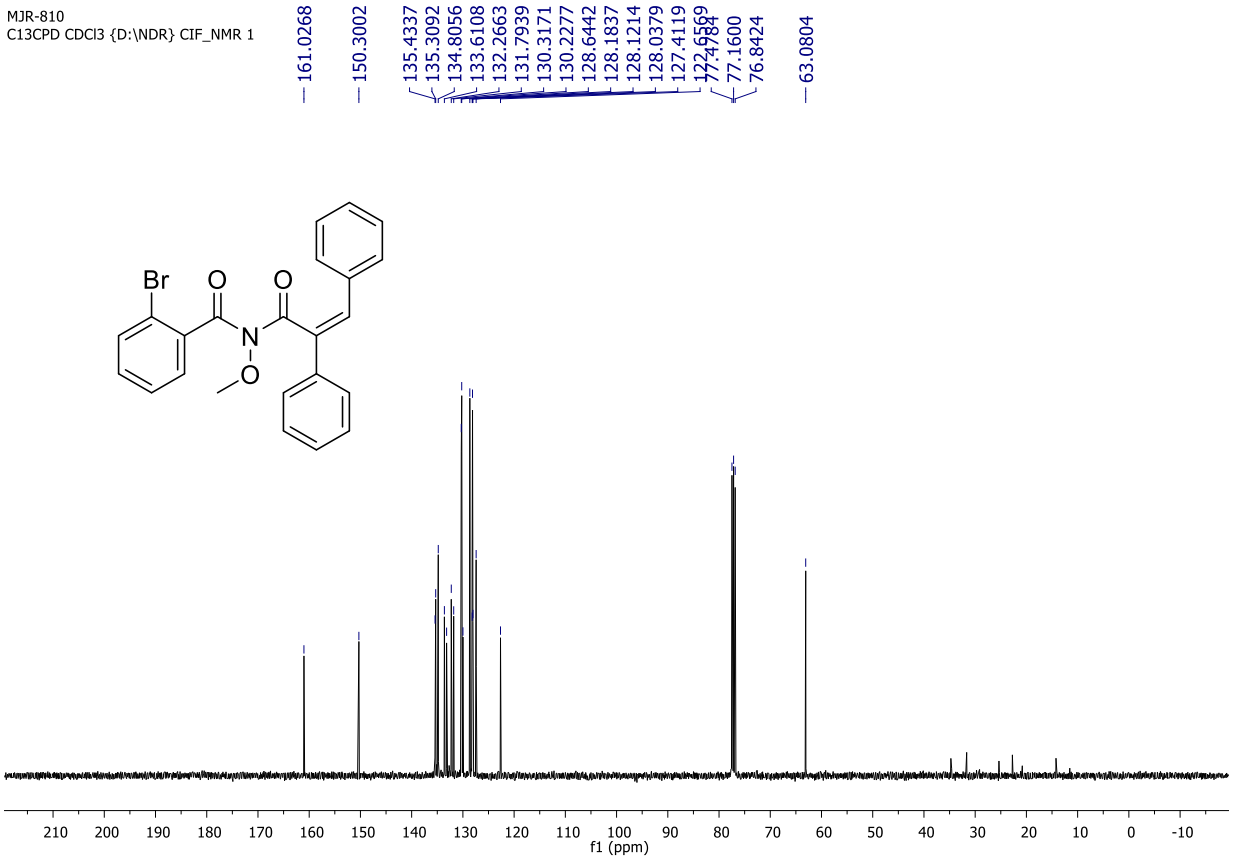
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **1aa**



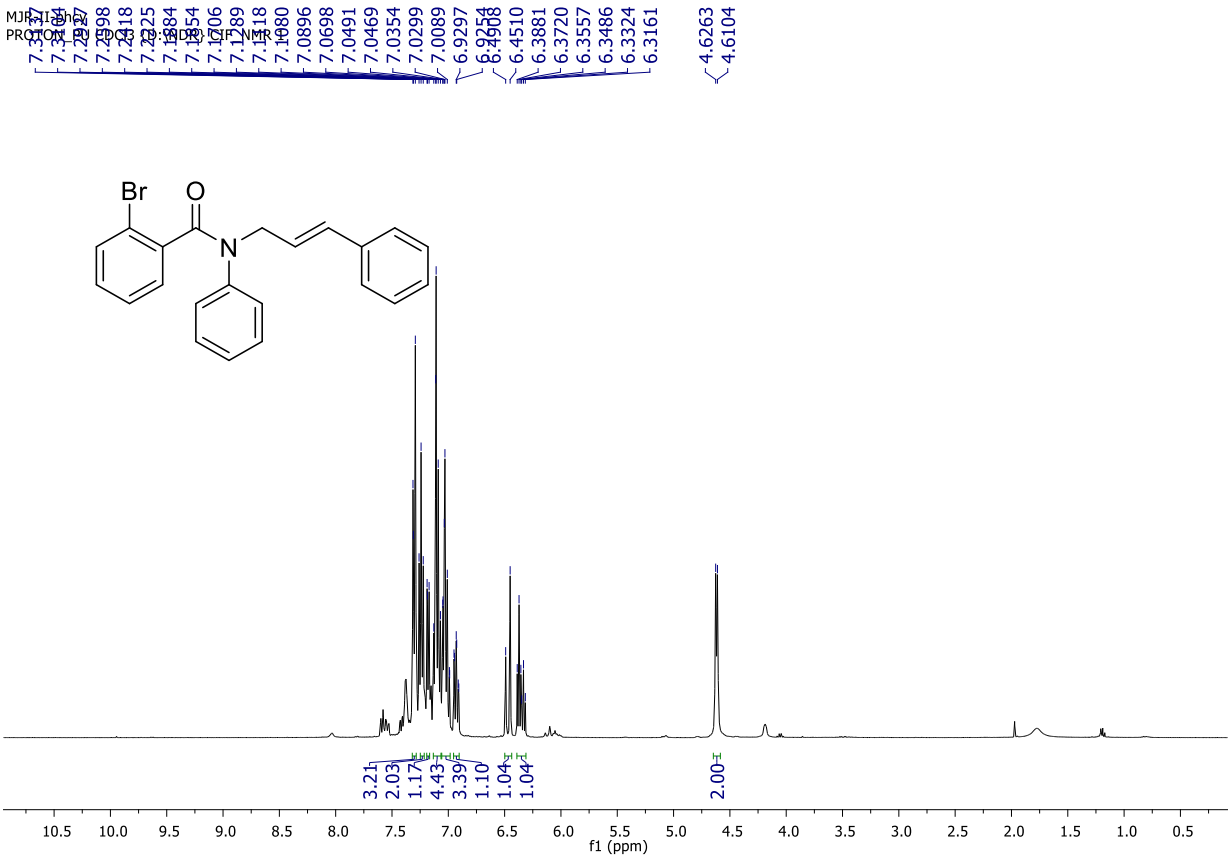
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **1ab**



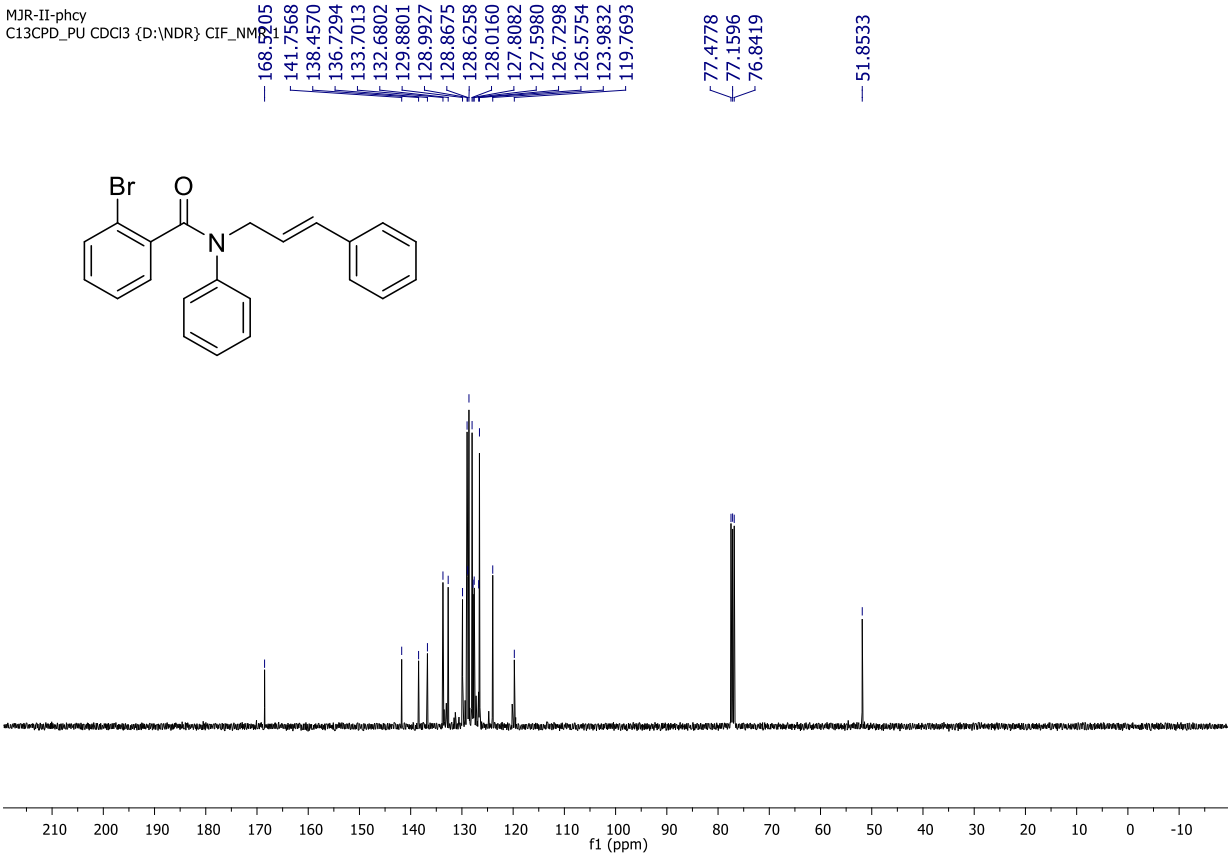
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **1ab**



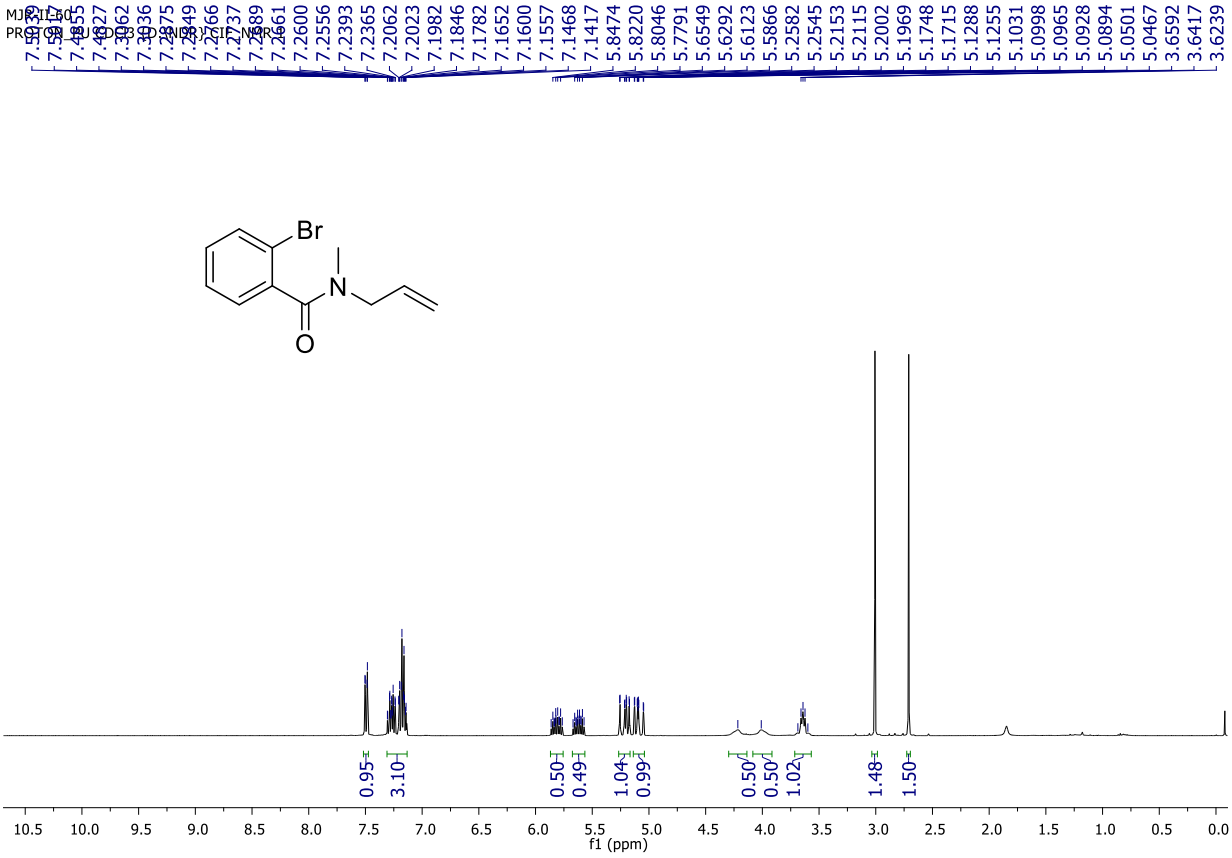
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **1ac**



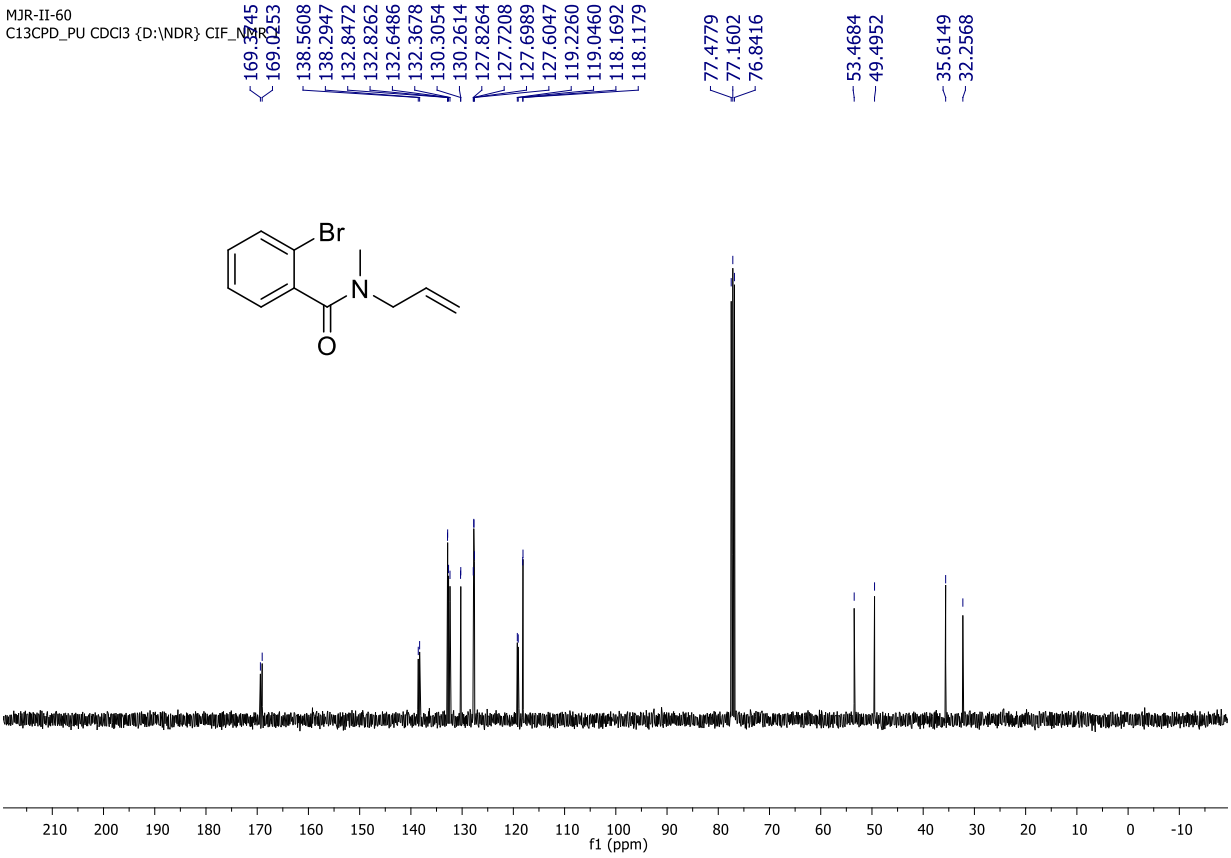
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **1ac**



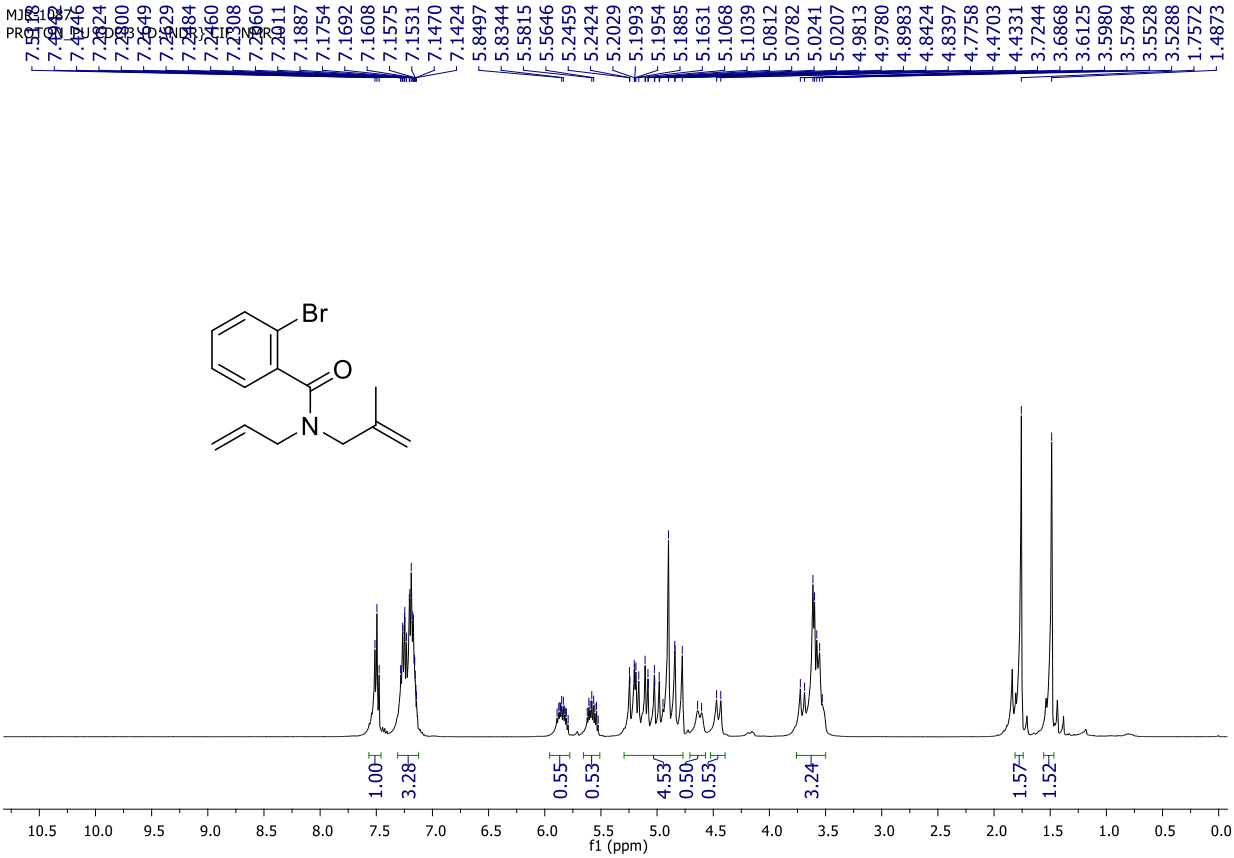
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3a**



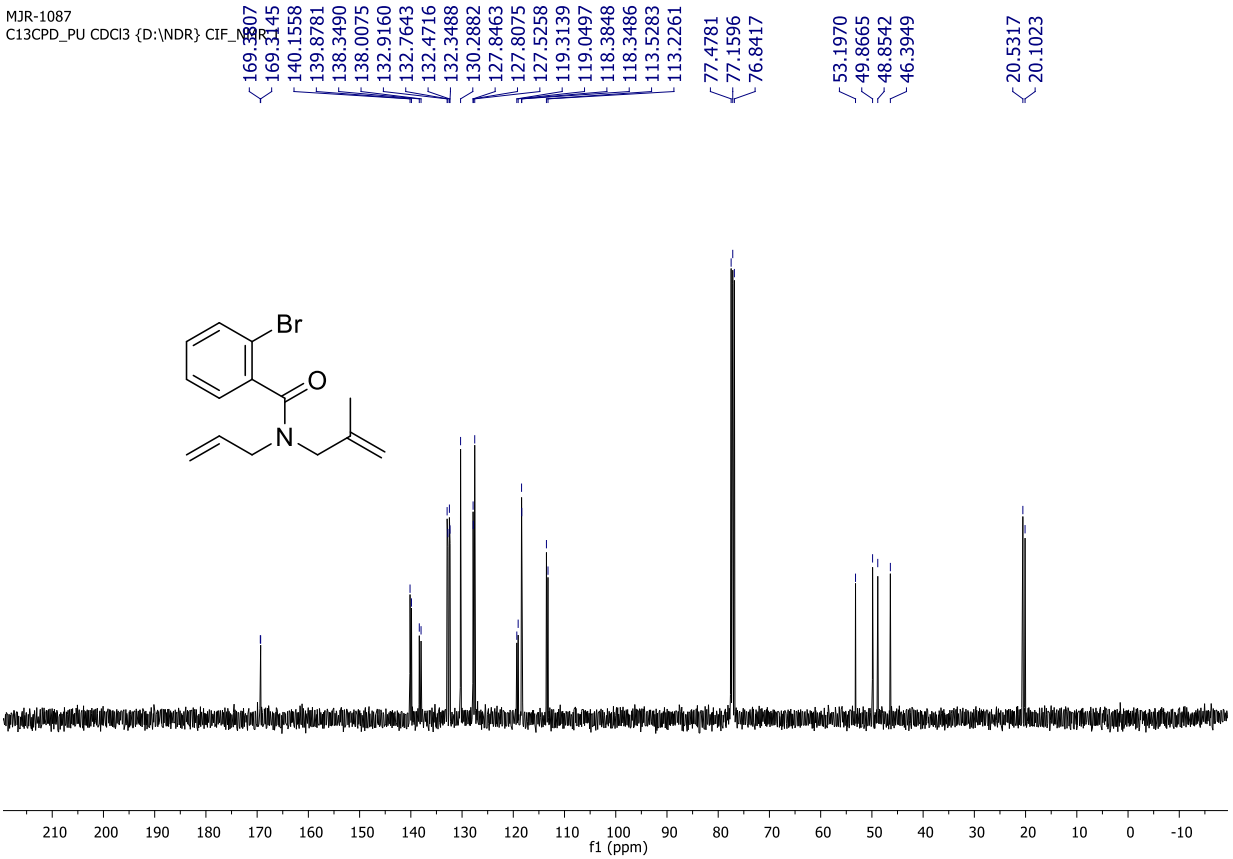
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3a**



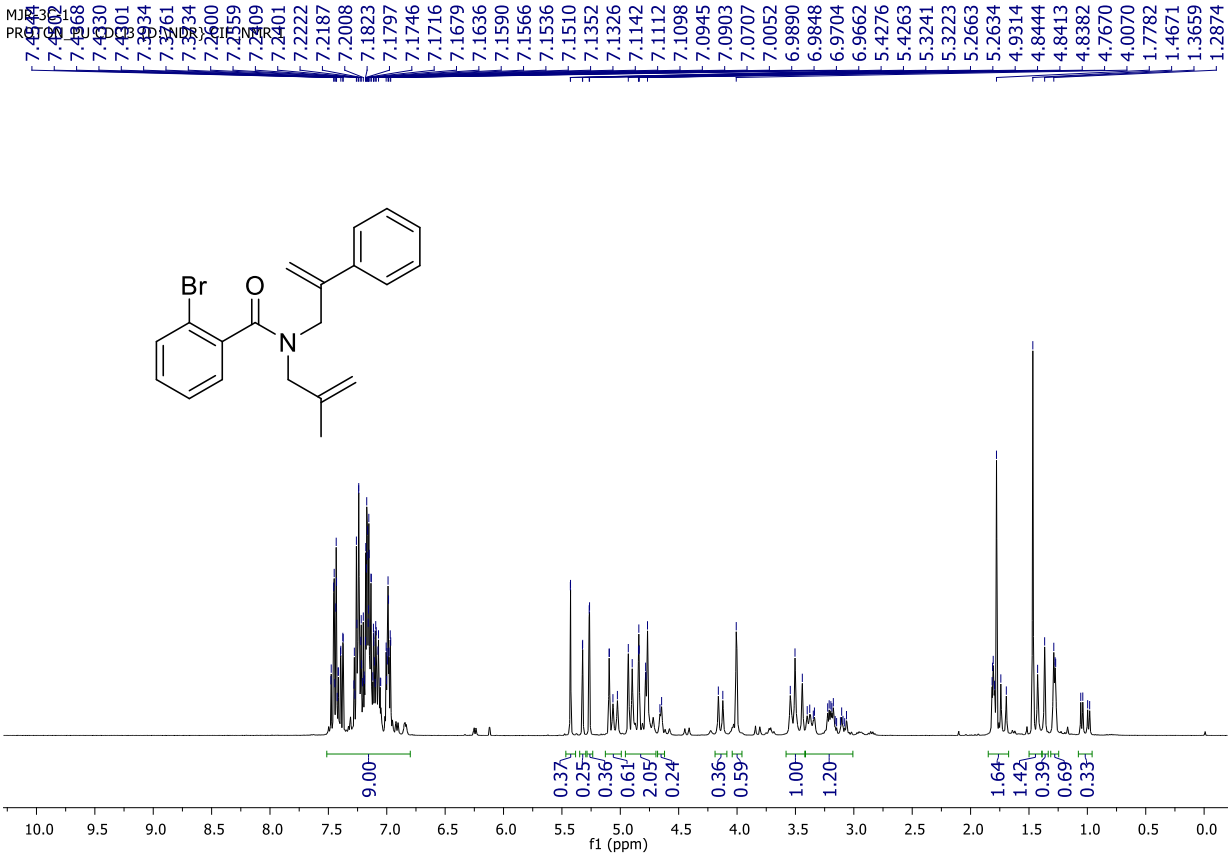
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3b**



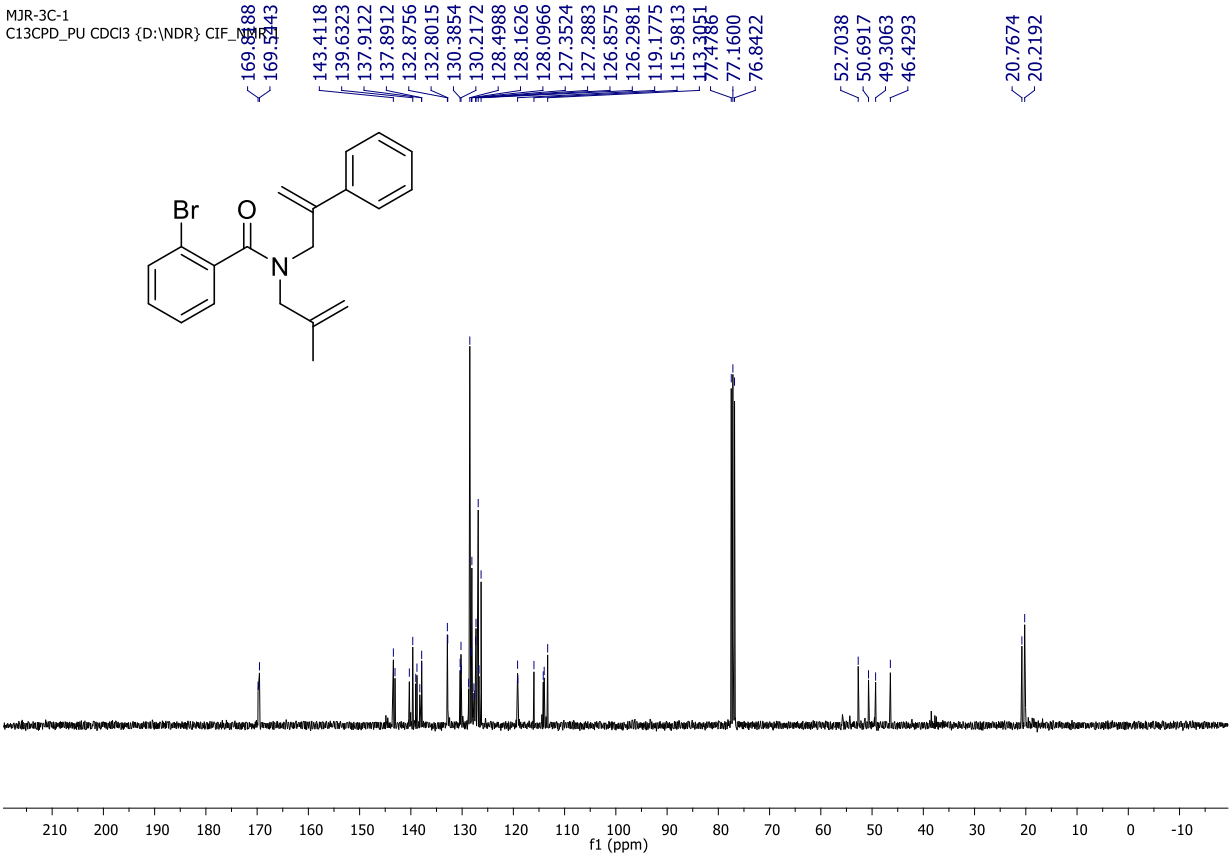
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3b**



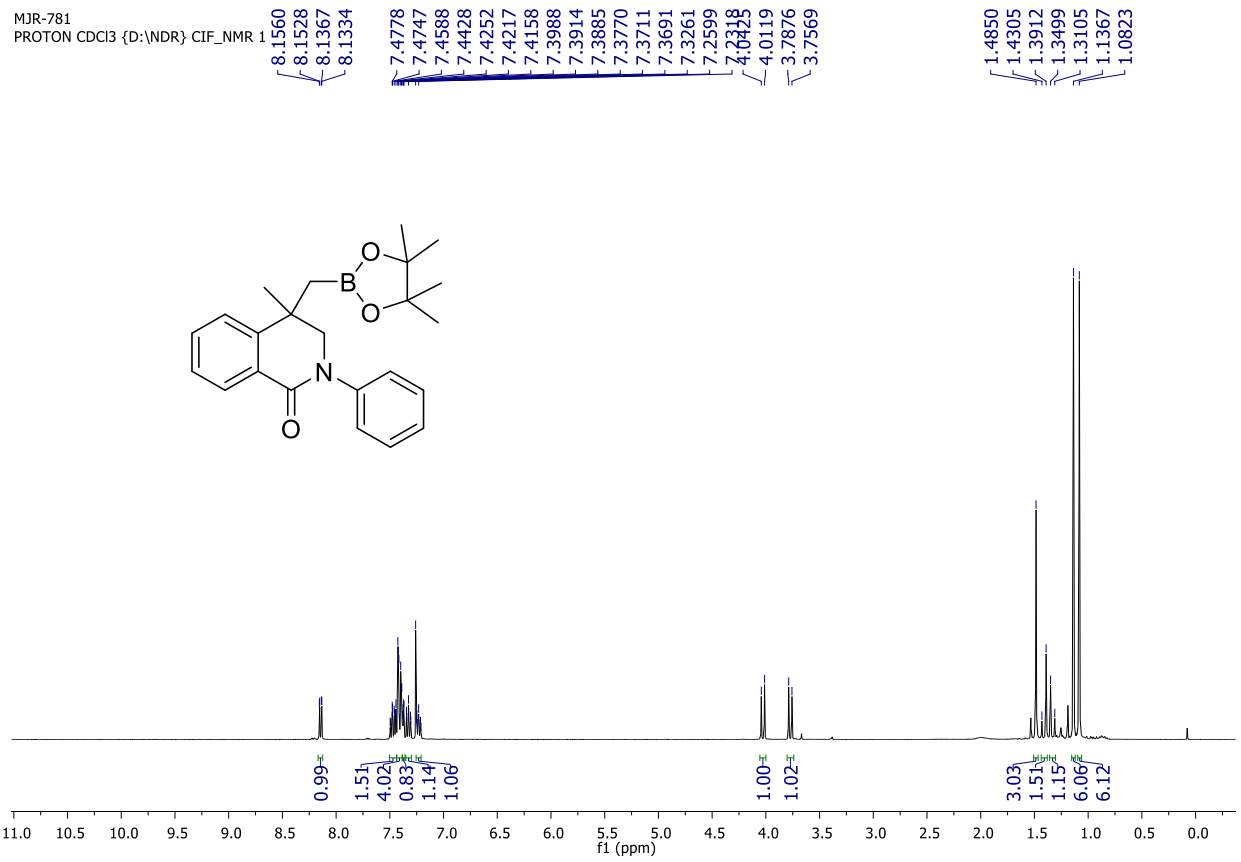
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3c**



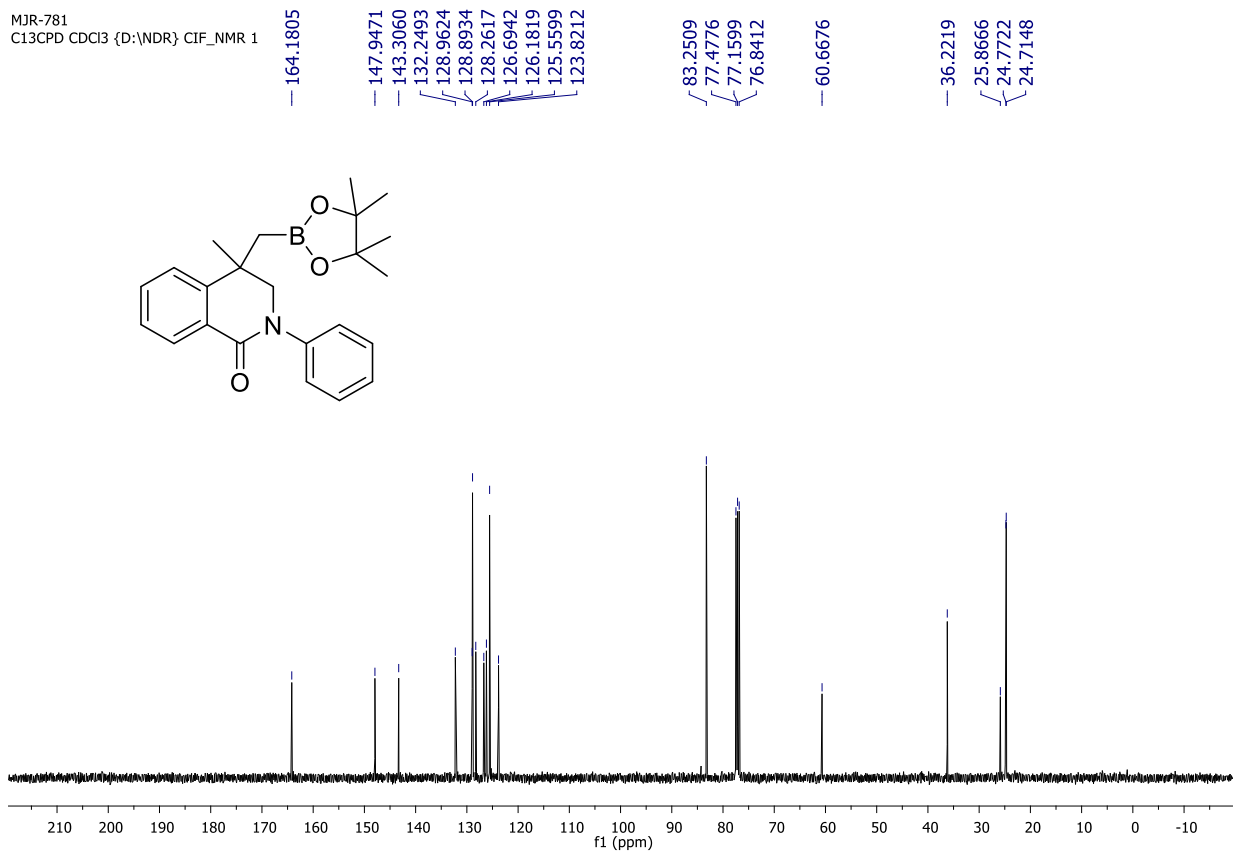
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3c**



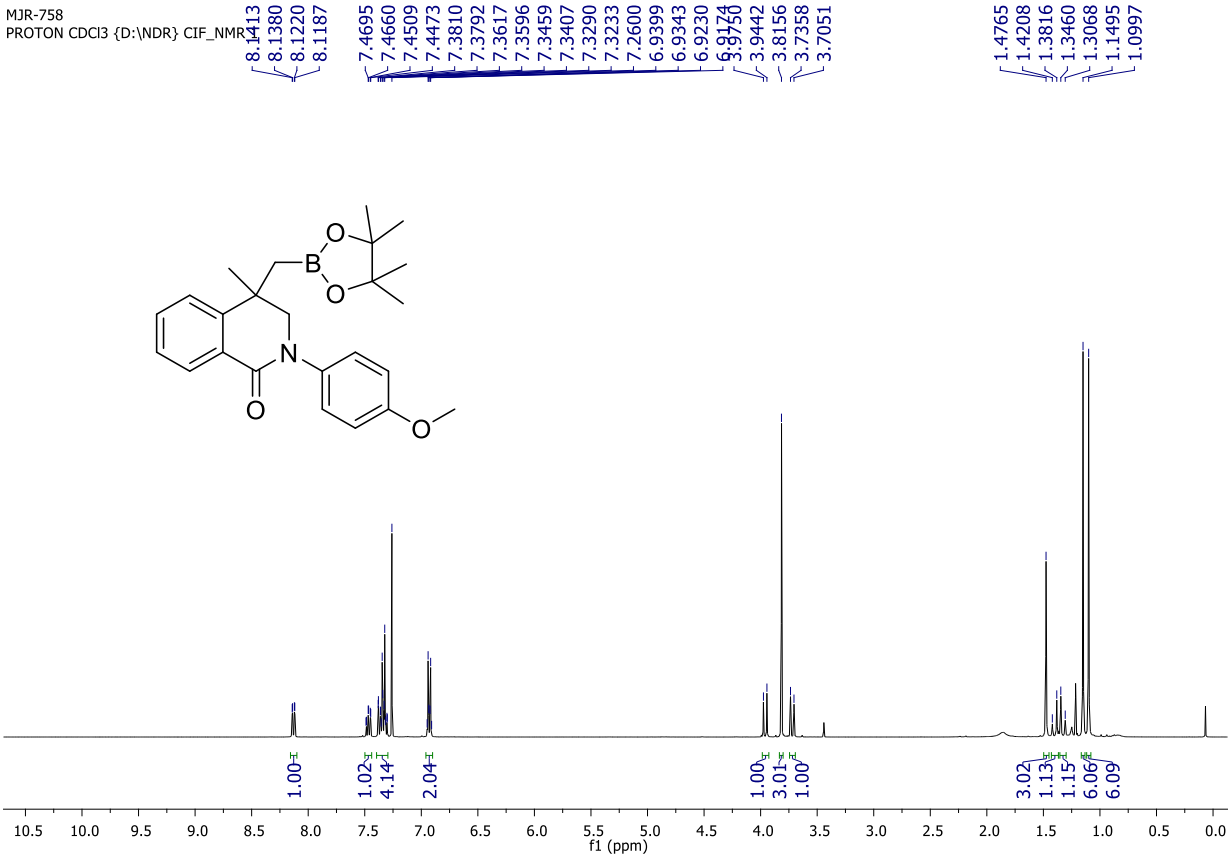
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **2a**



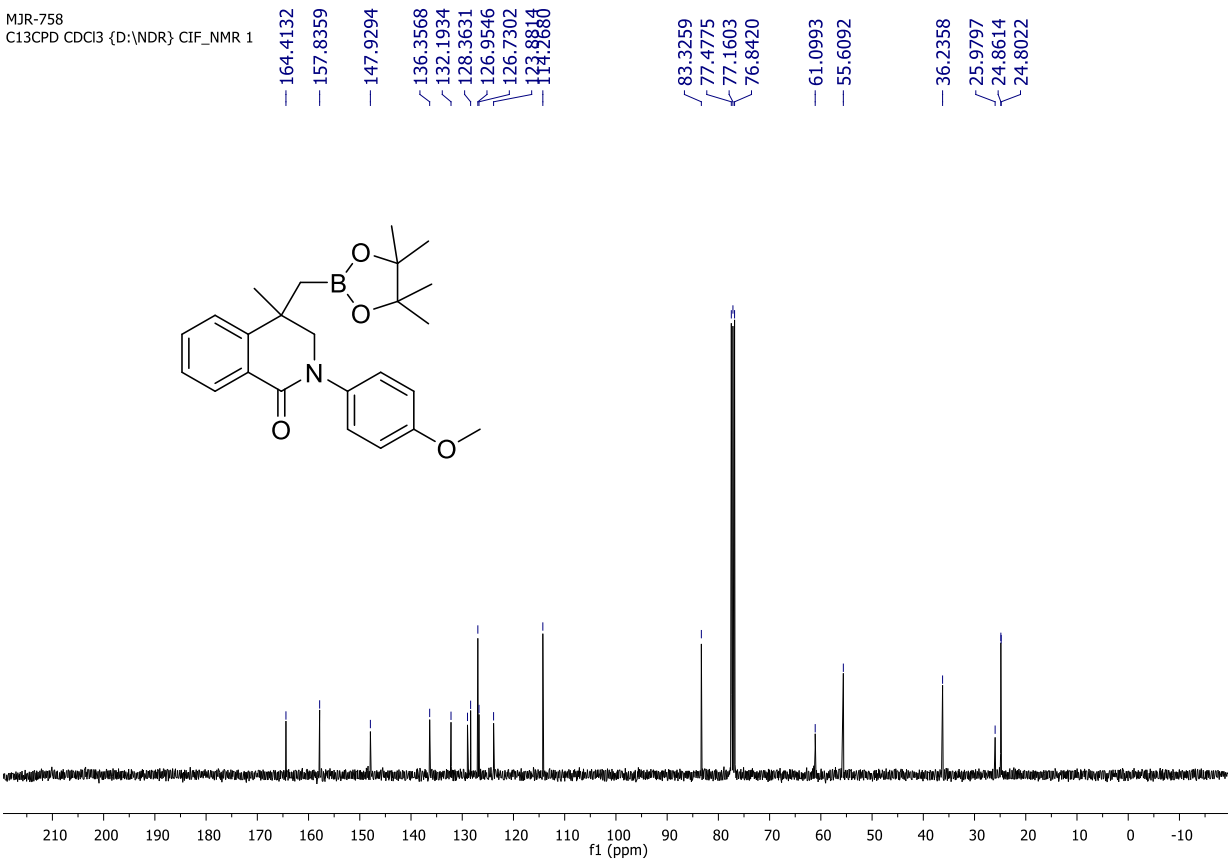
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **2a**



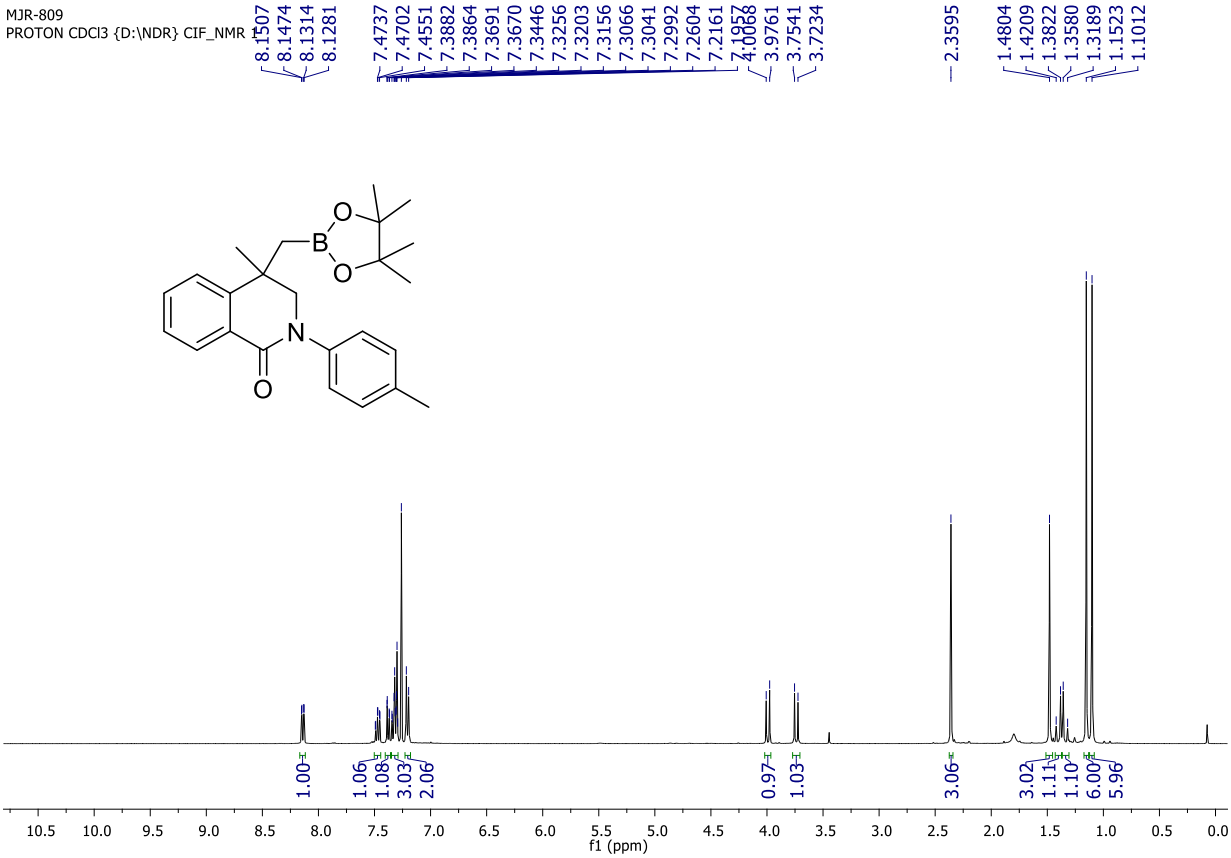
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **2b**



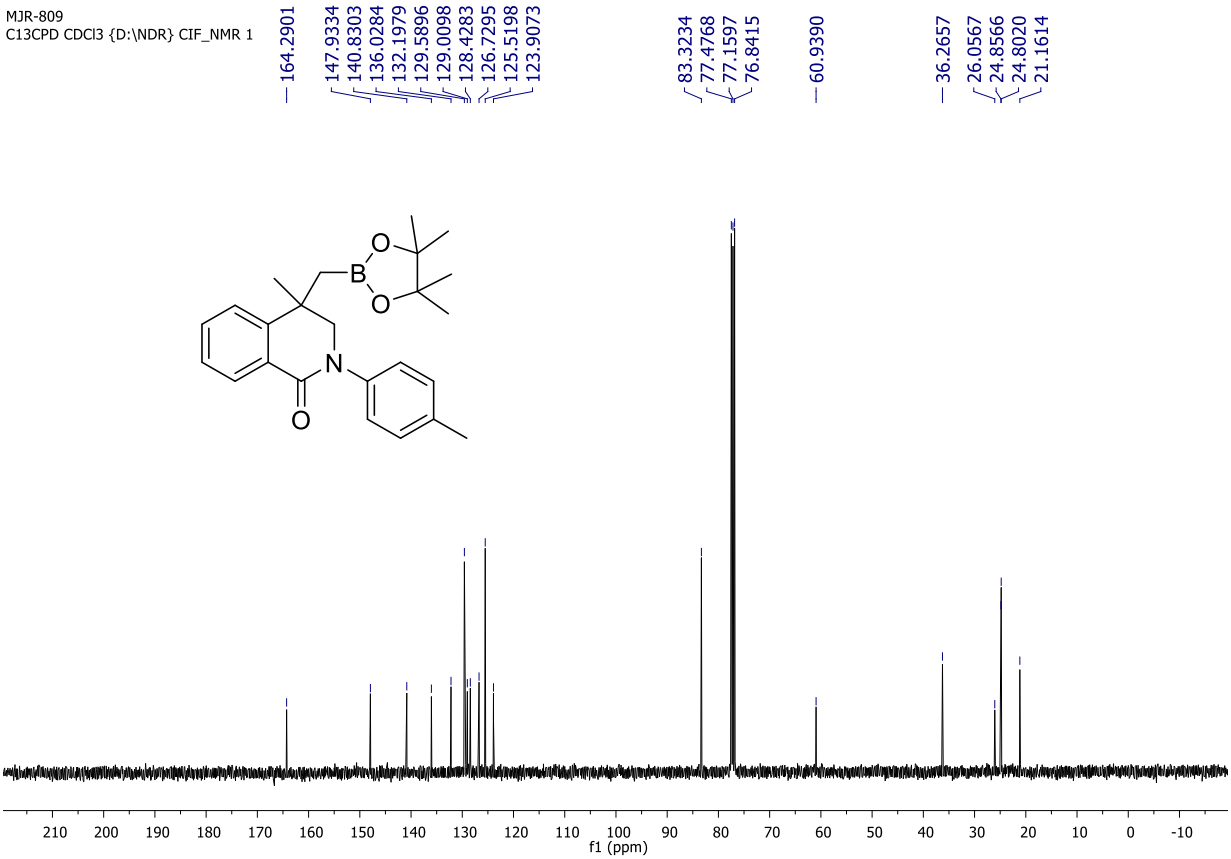
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **2b**



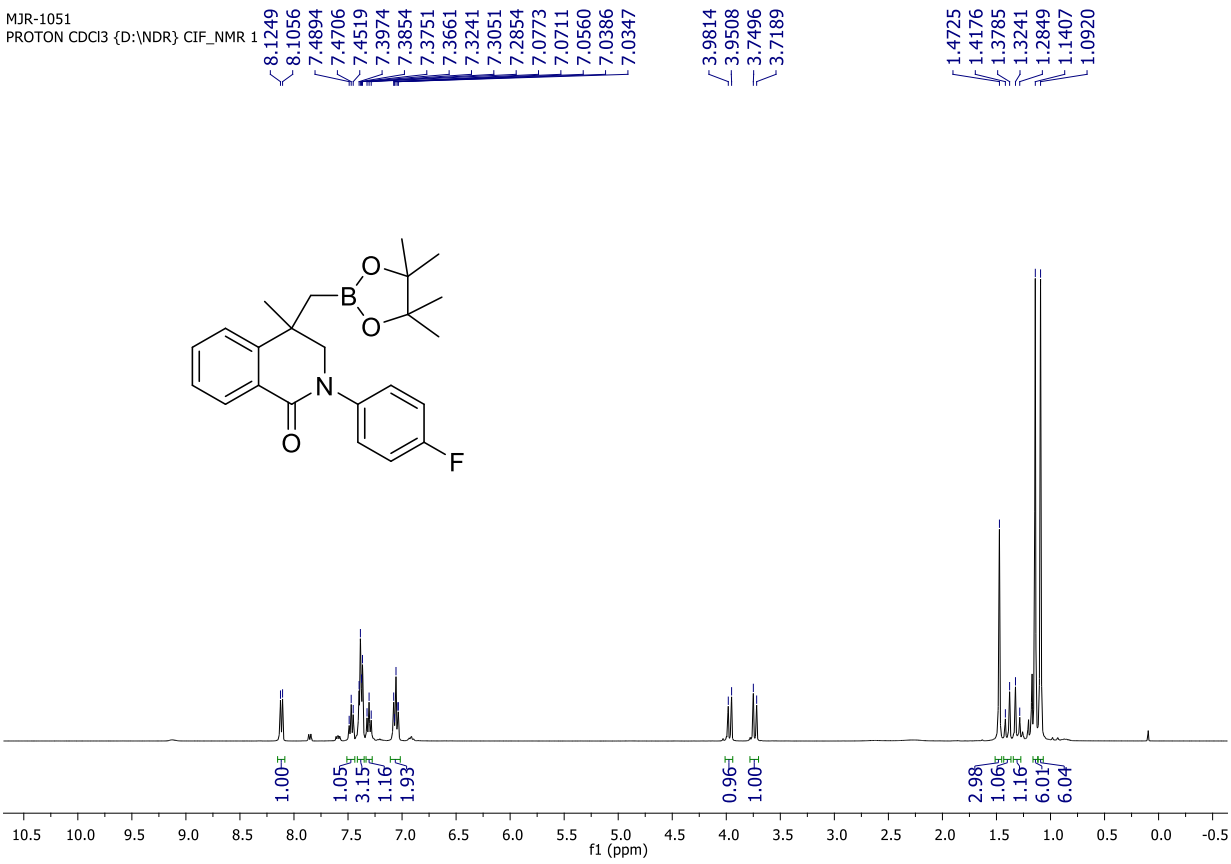
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **2c**



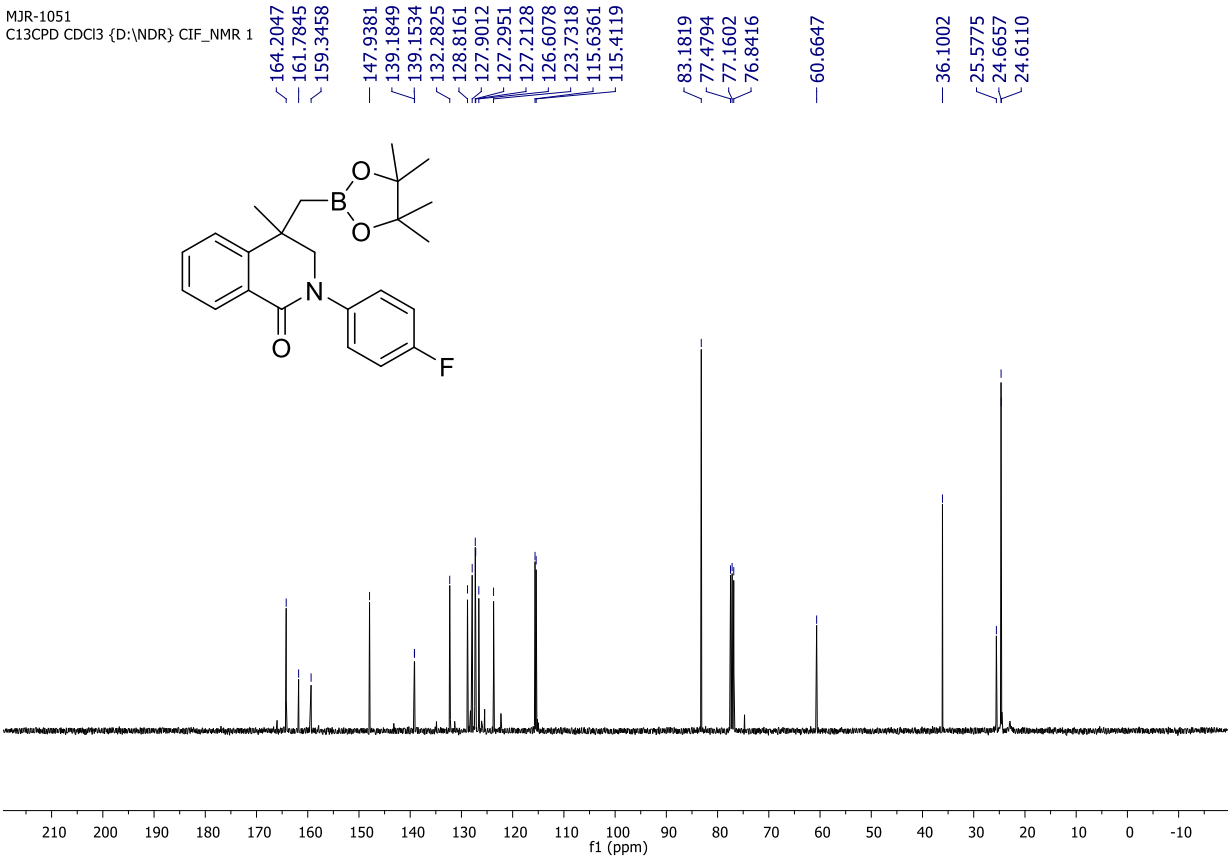
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **2c**



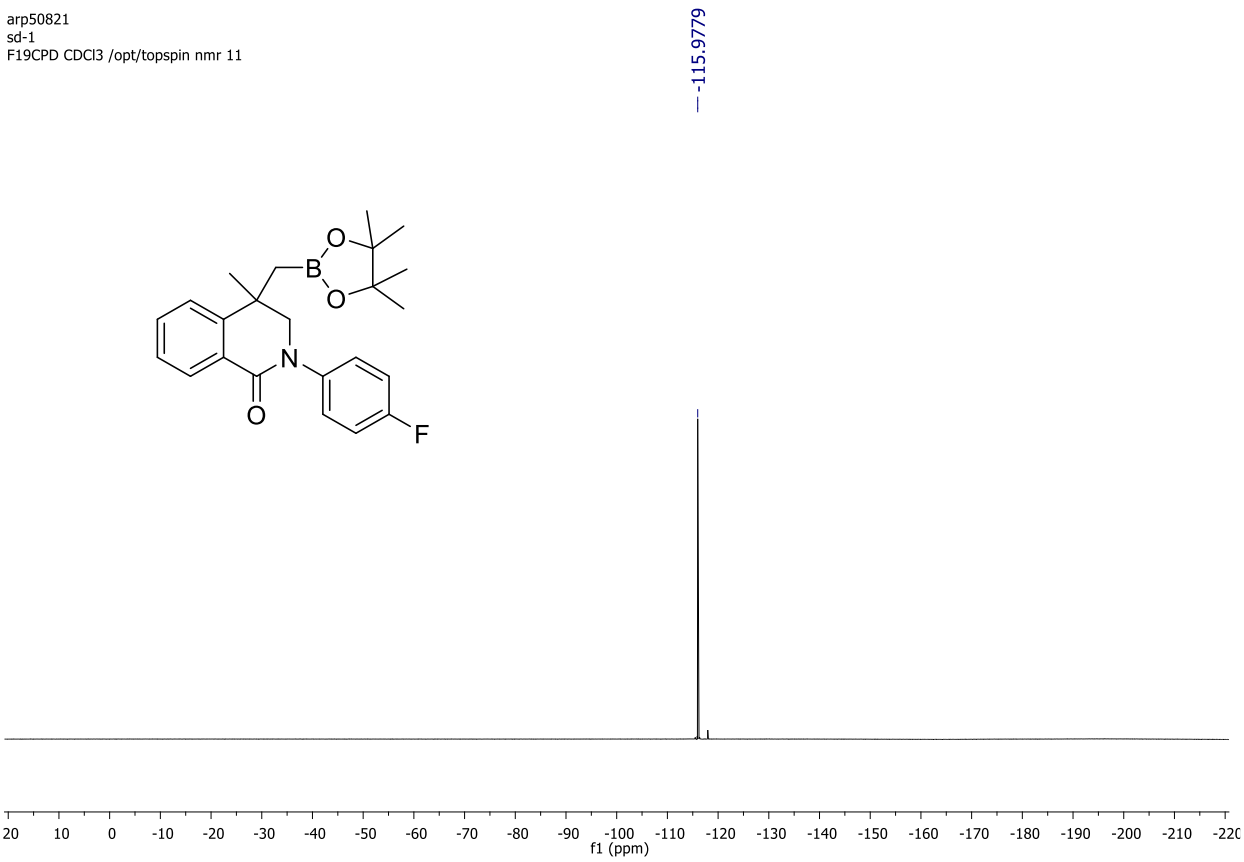
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **2d**



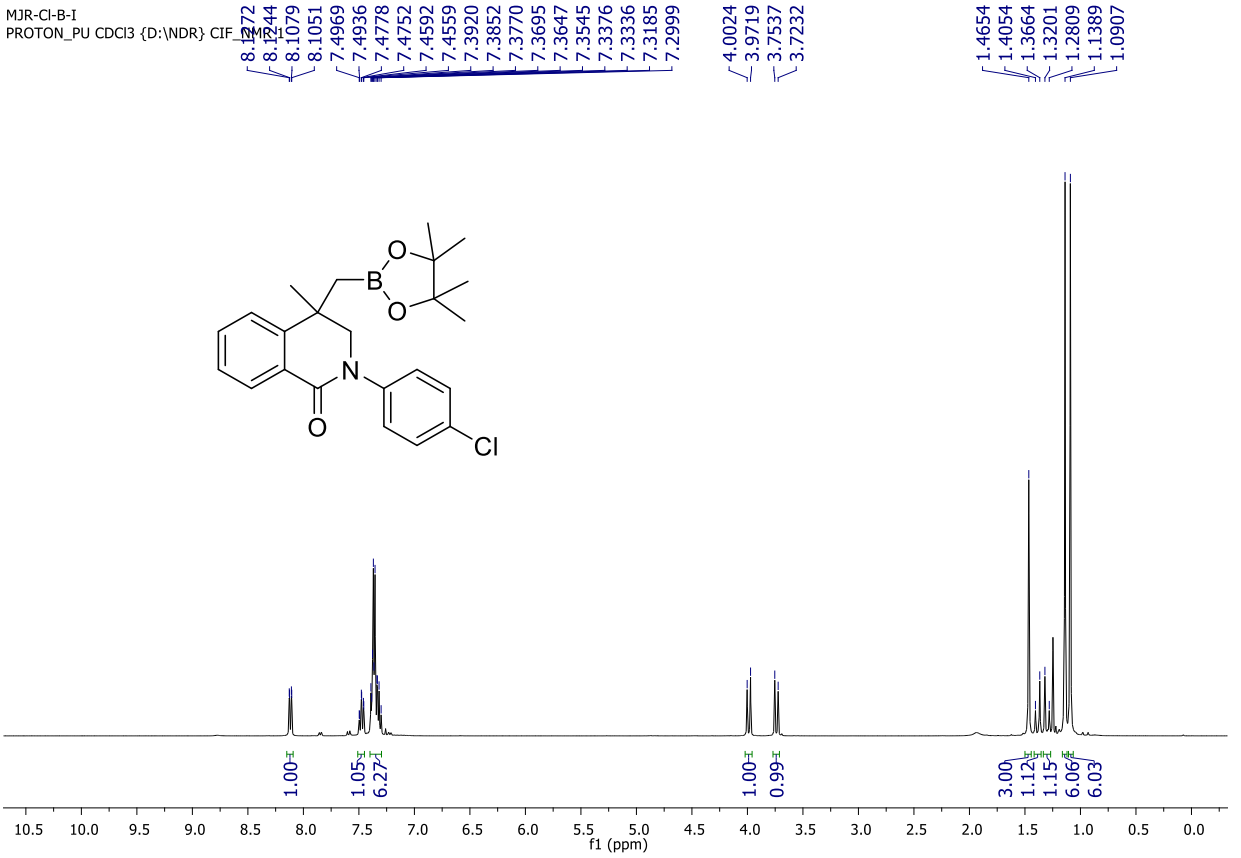
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **2d**



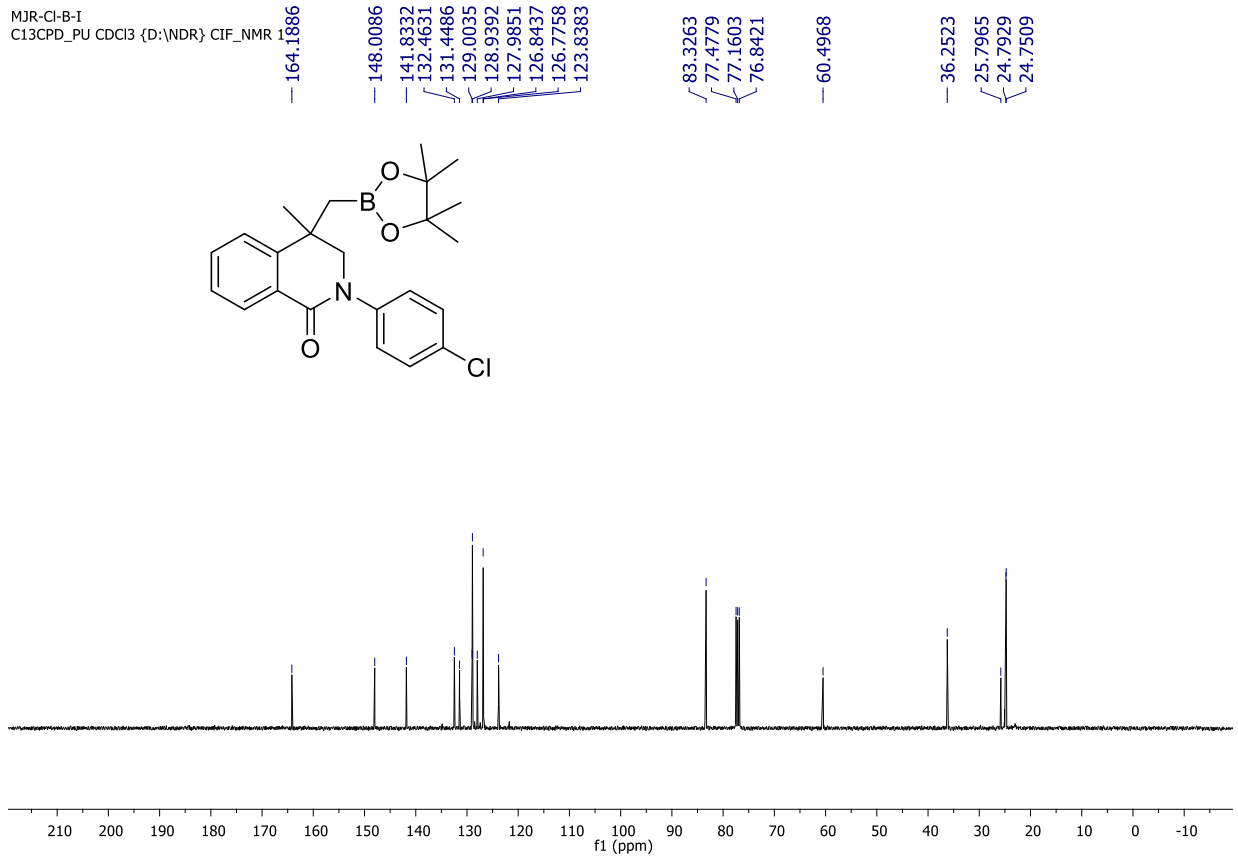
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **2d**



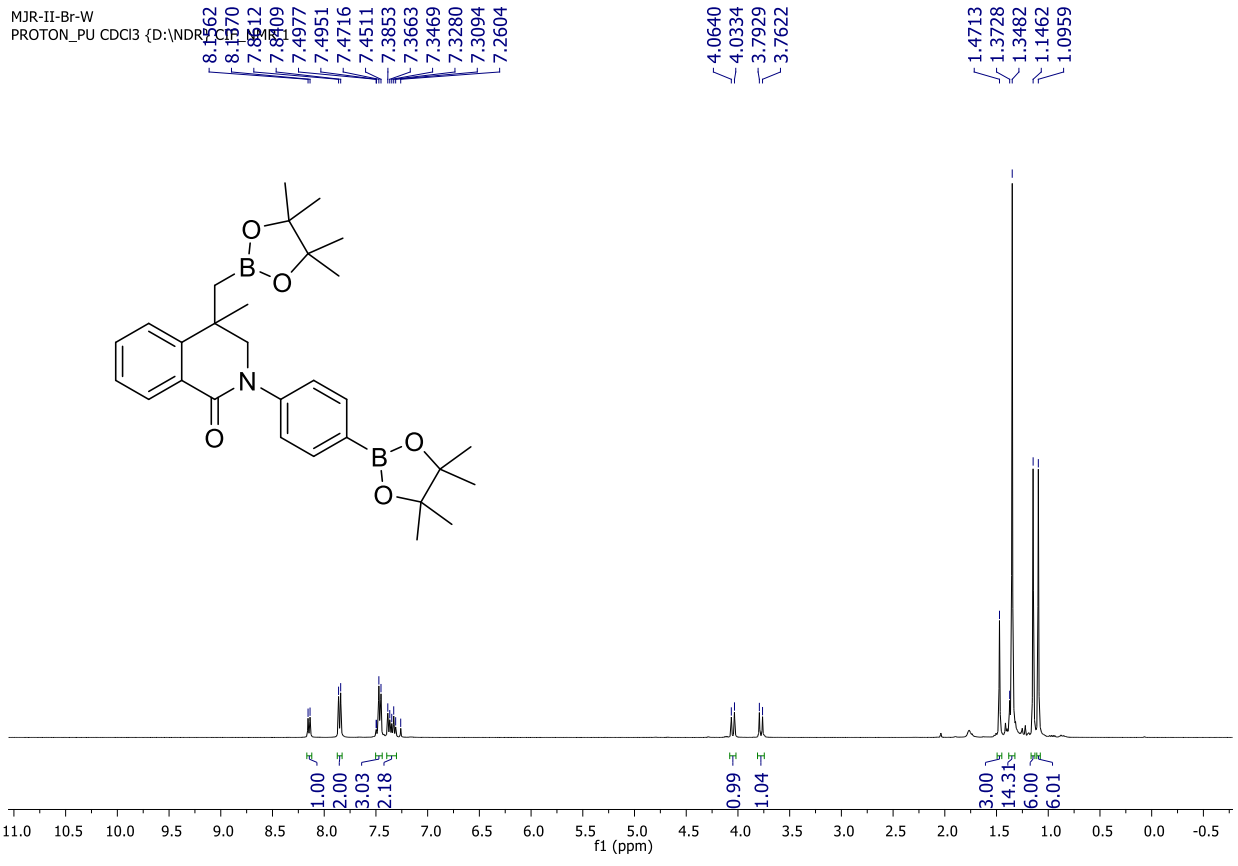
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **2e**



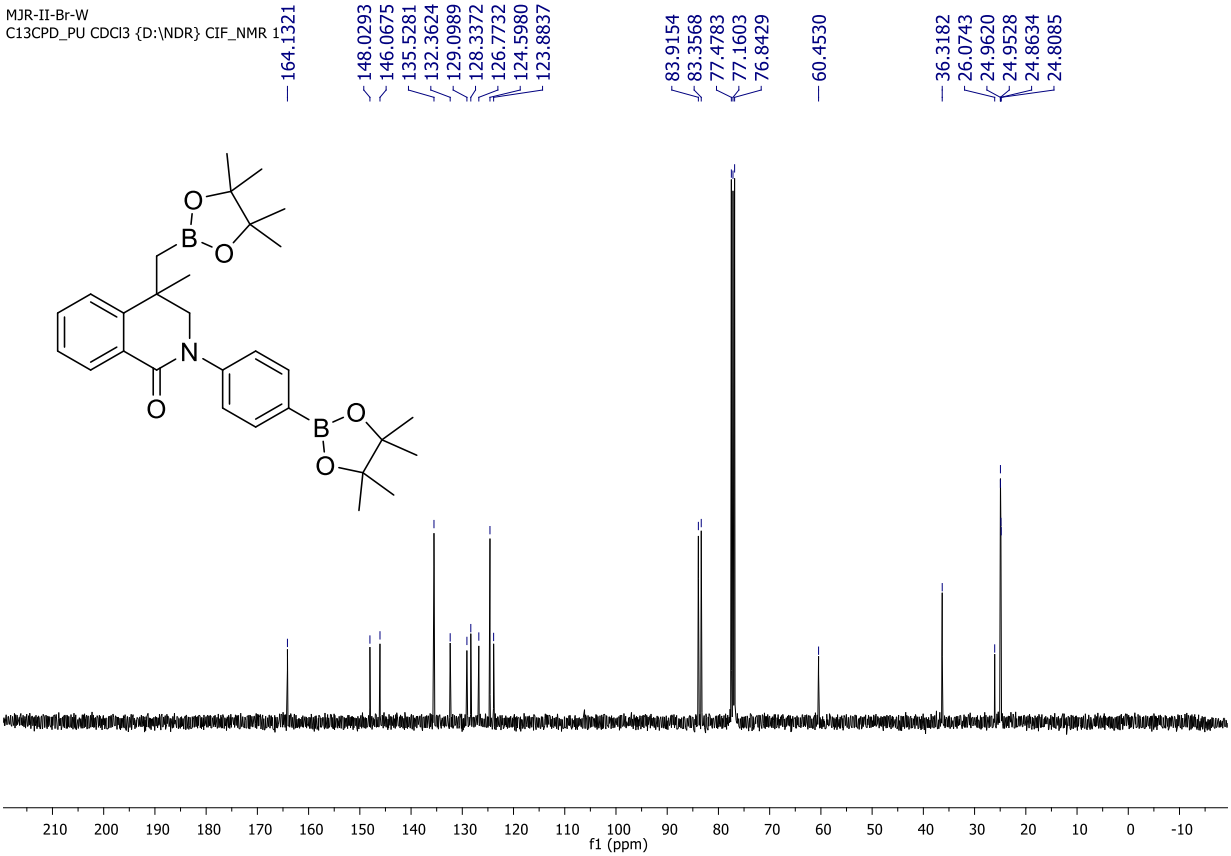
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **2e**



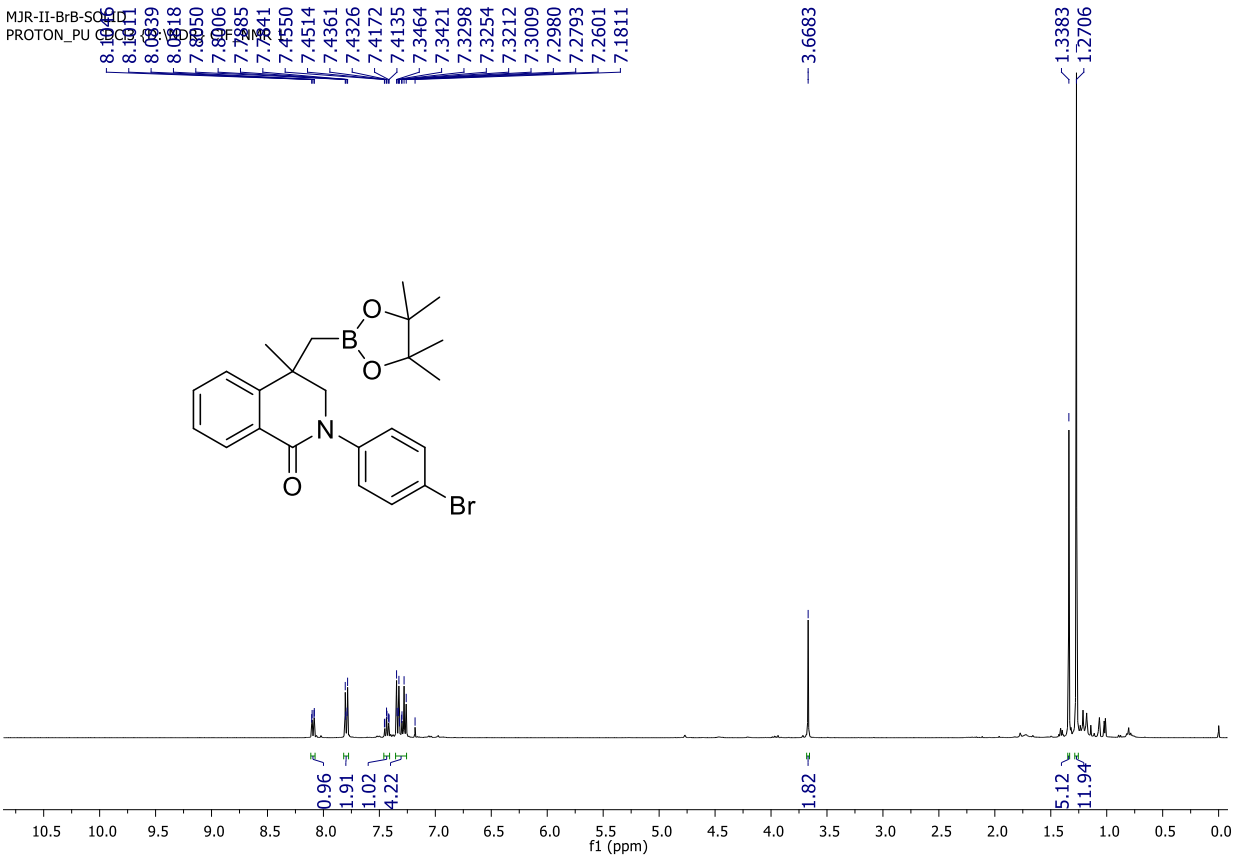
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **2f**



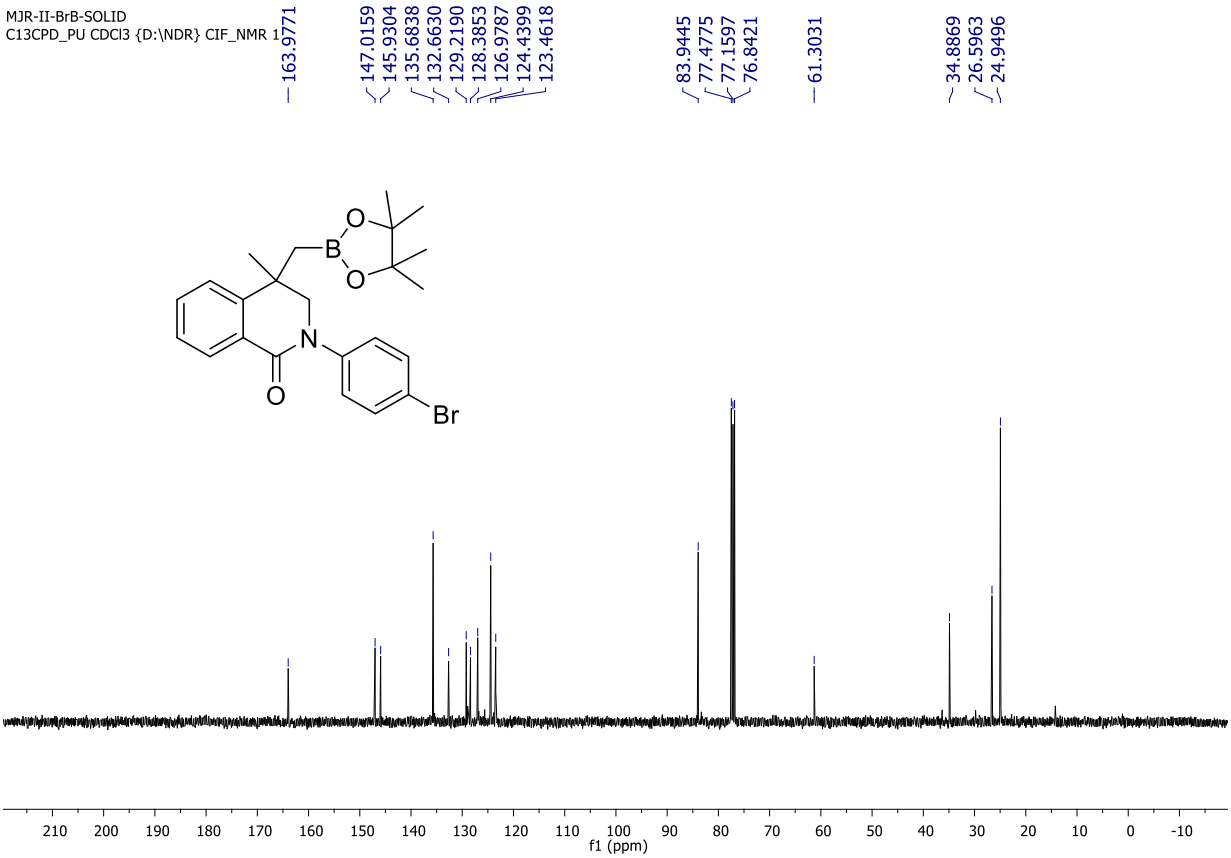
^{13}C **NMR**-spectrum (100 MHz, $CDCl_3$) of **2f**



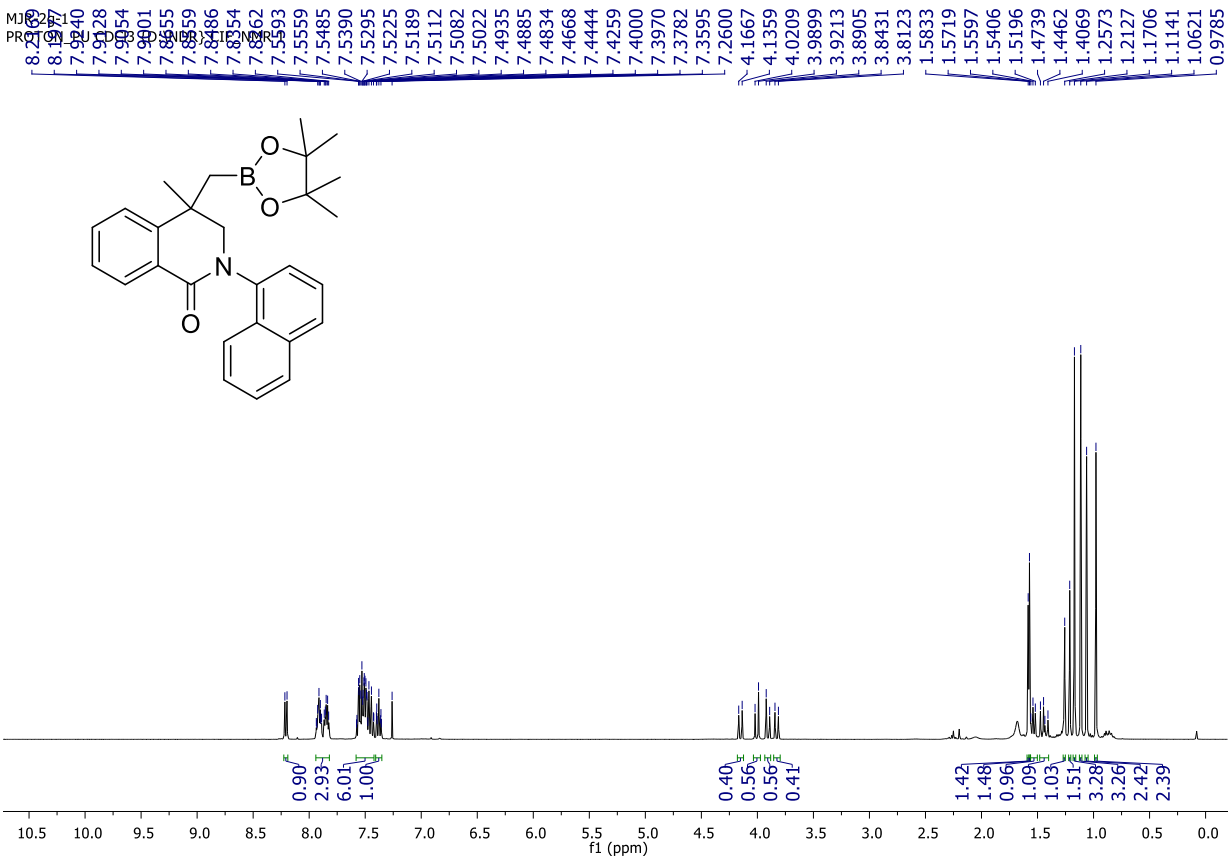
^{1}H **NMR**-spectrum (400 MHz, $CDCl_3$) of **2f**



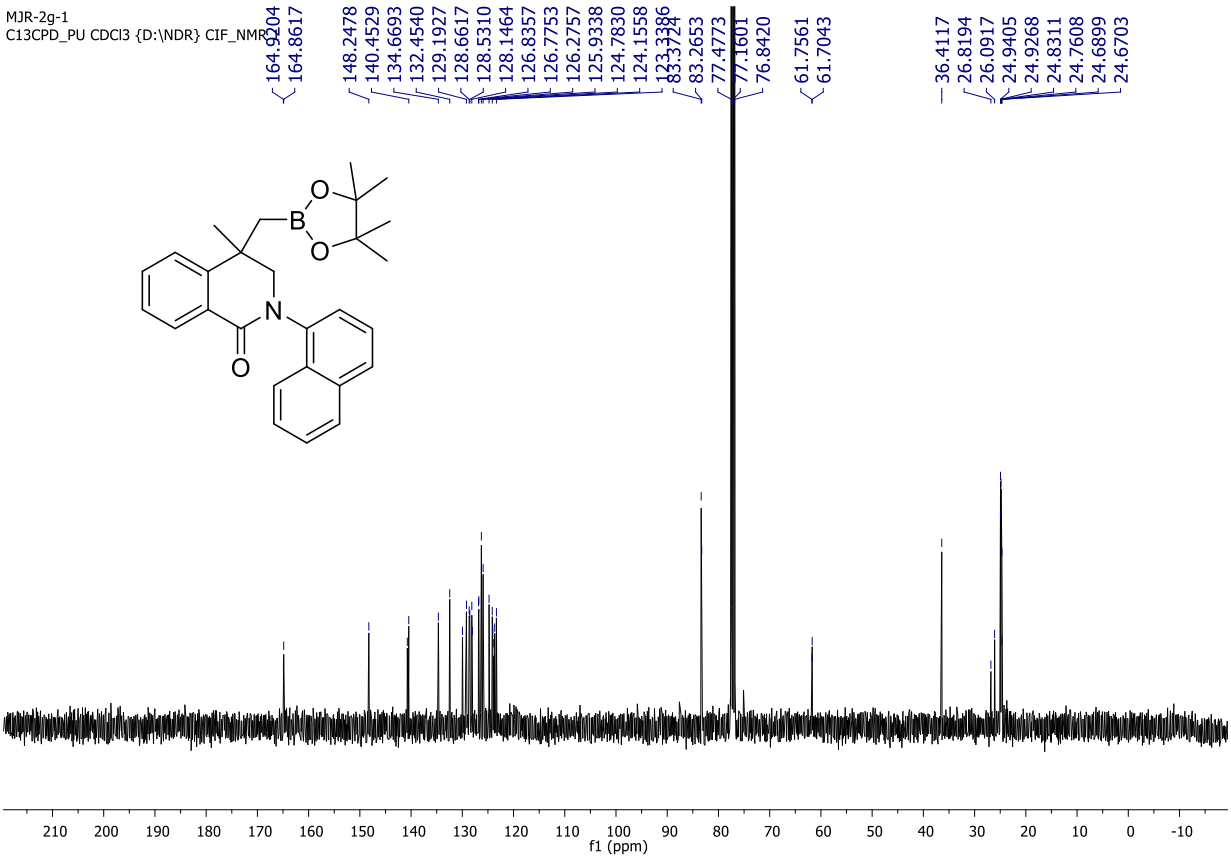
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **2f**



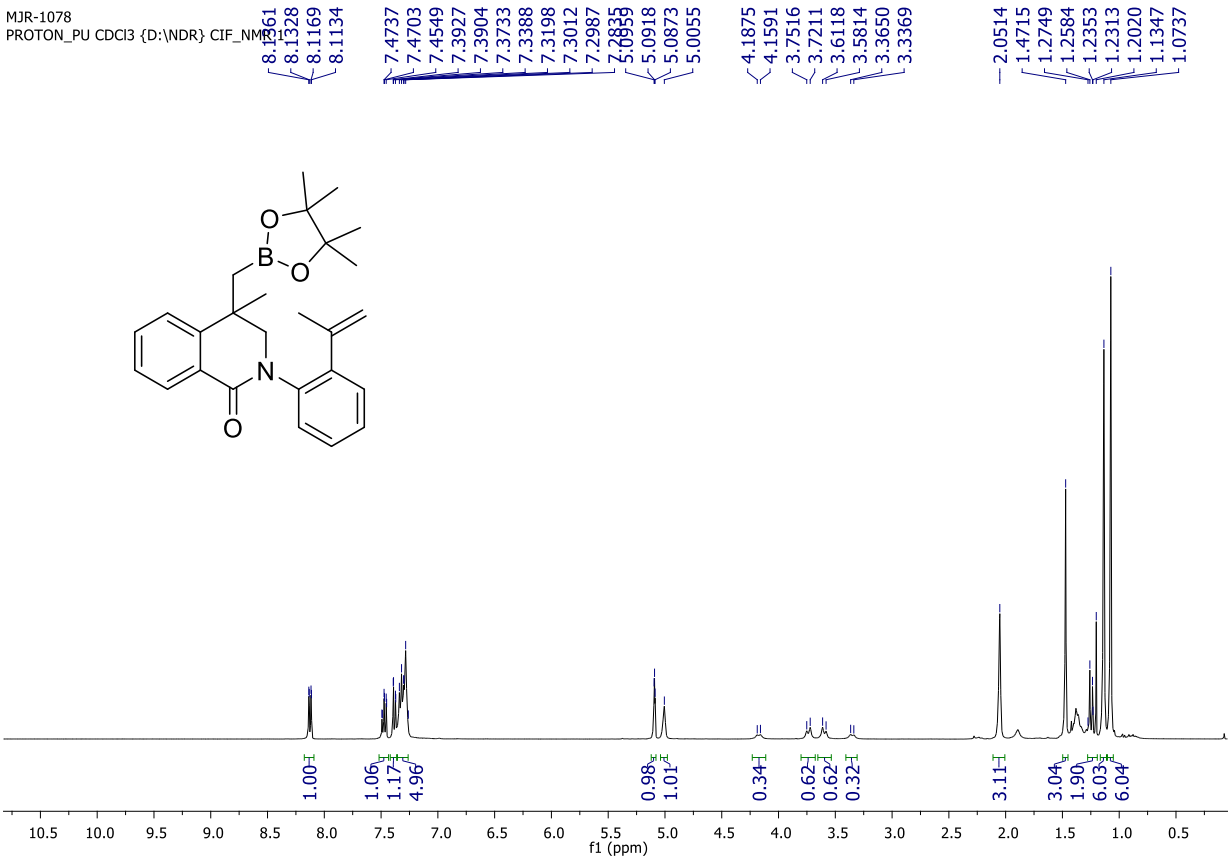
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **2g**



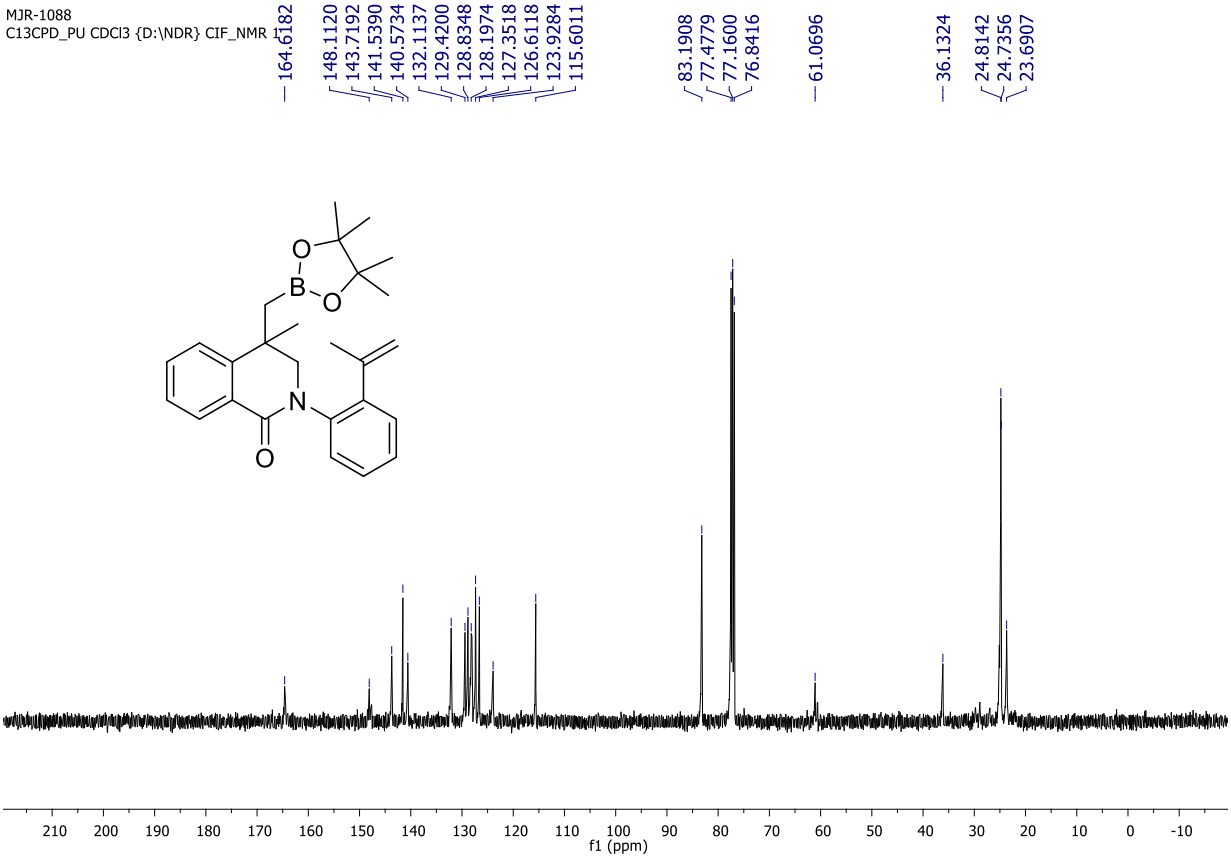
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **2g**



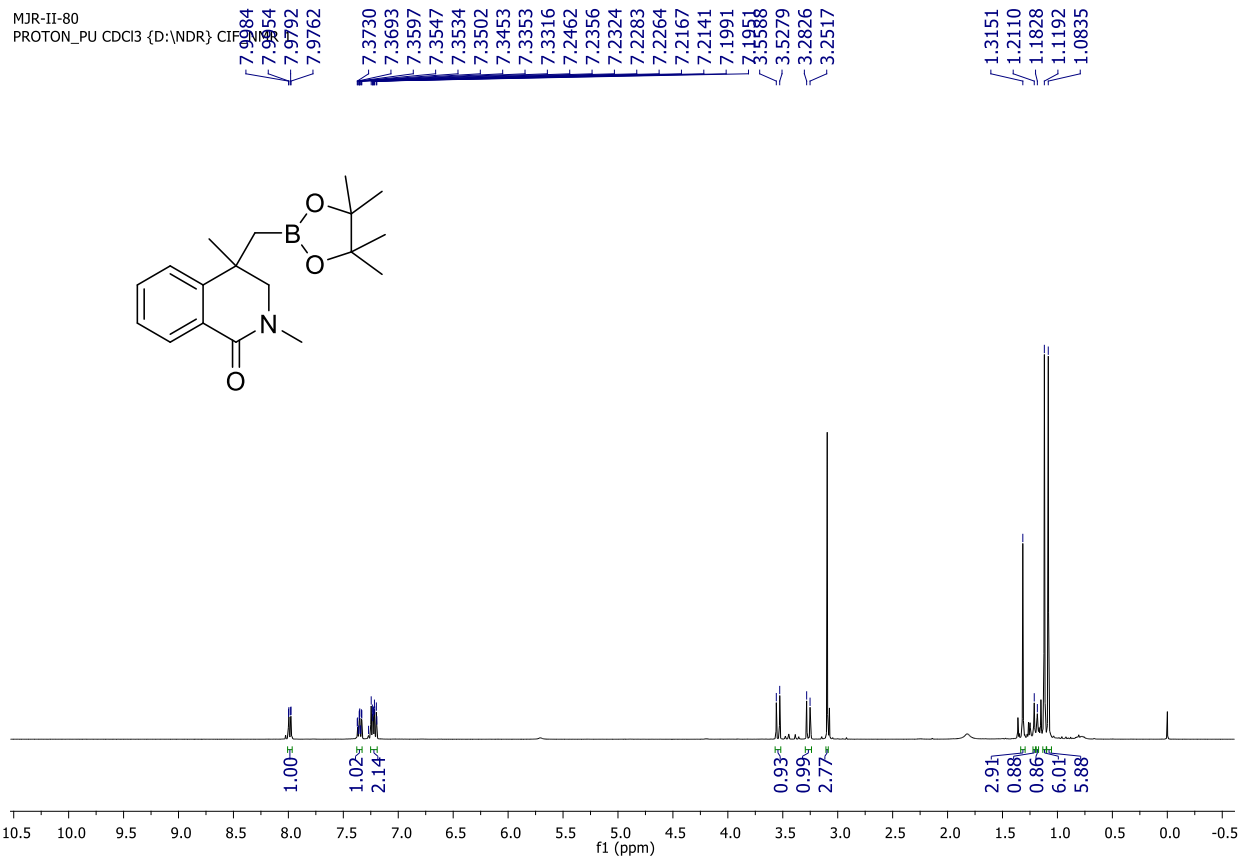
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **2h**



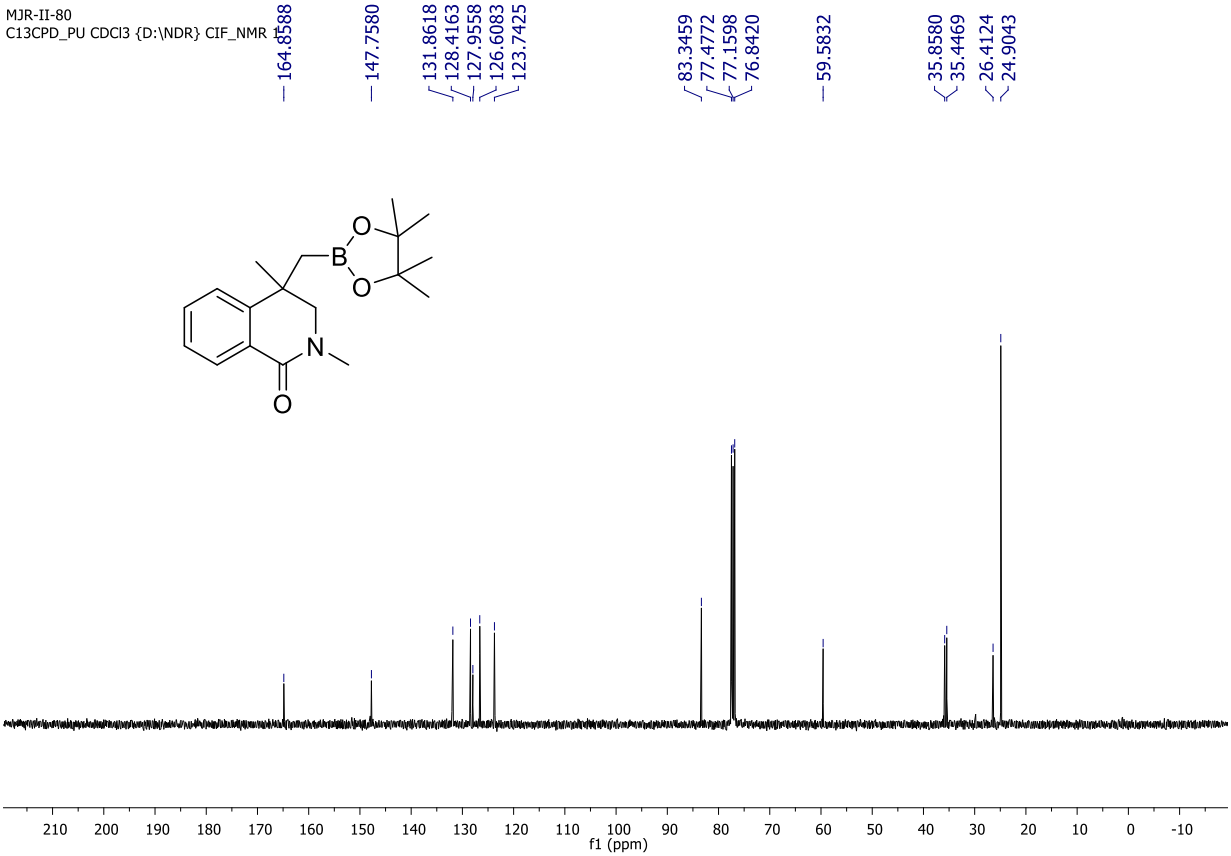
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **2h**



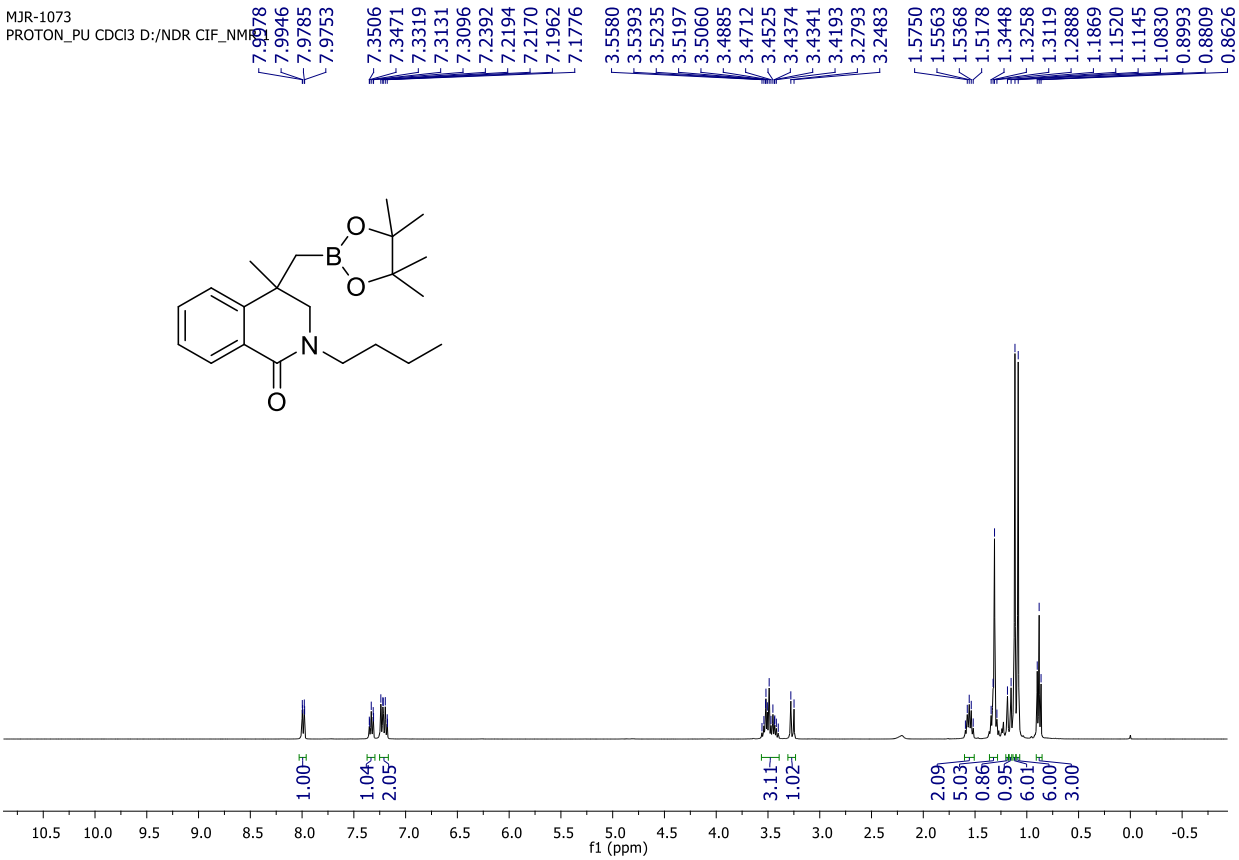
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **2i**



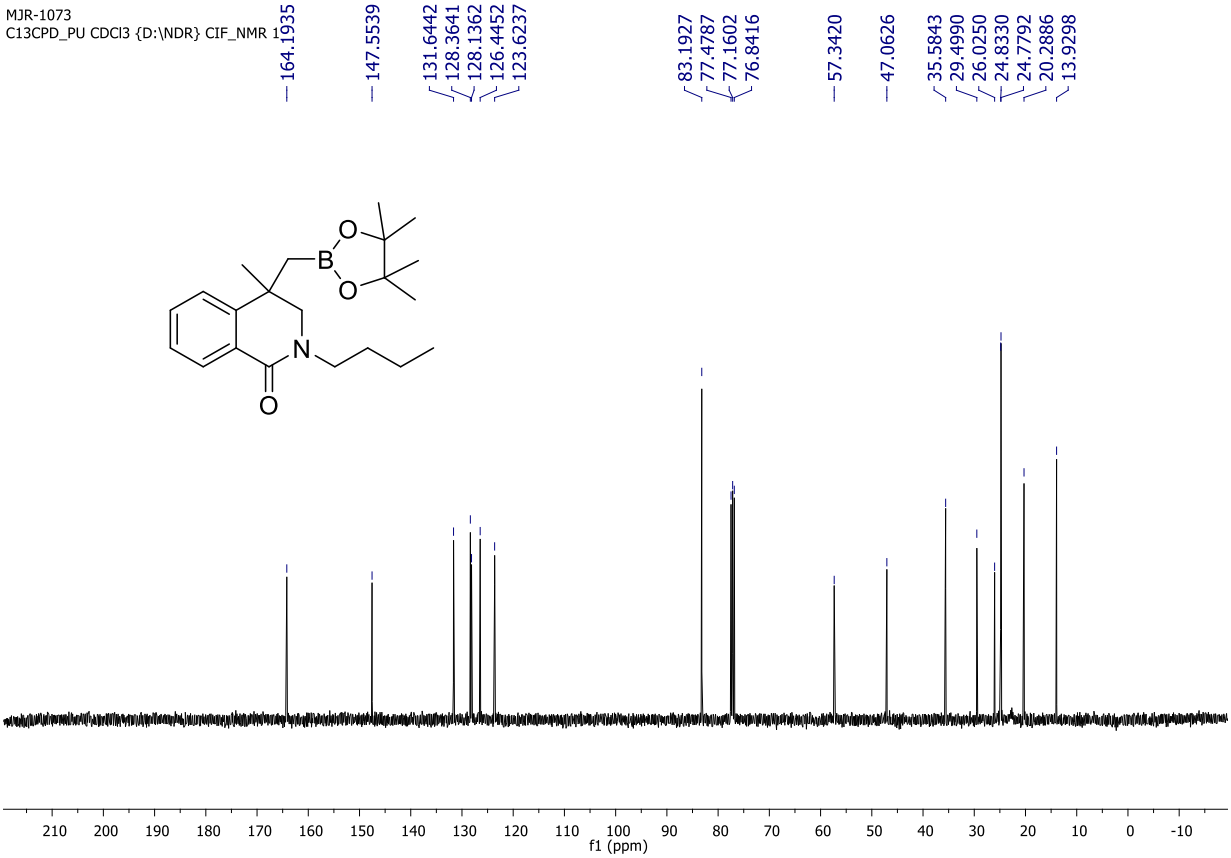
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **2i**



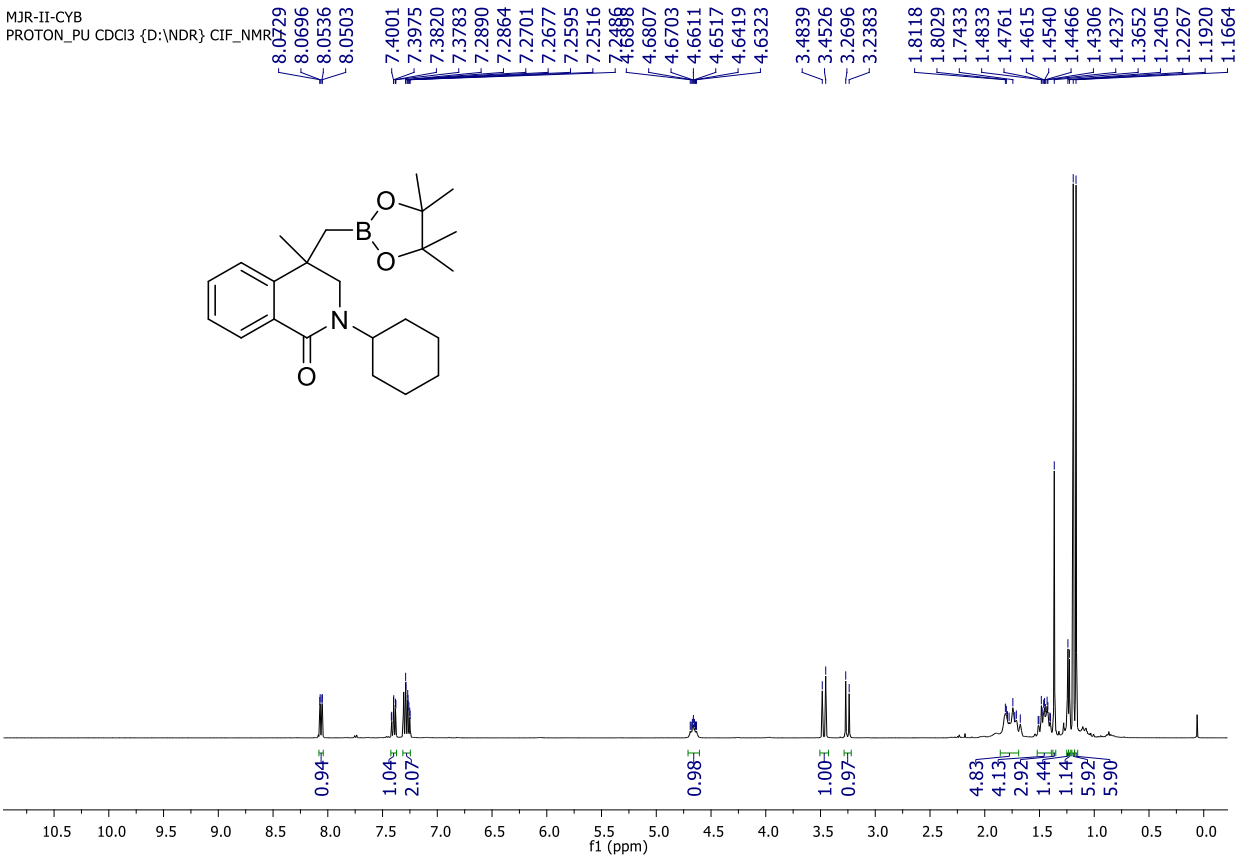
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **2j**



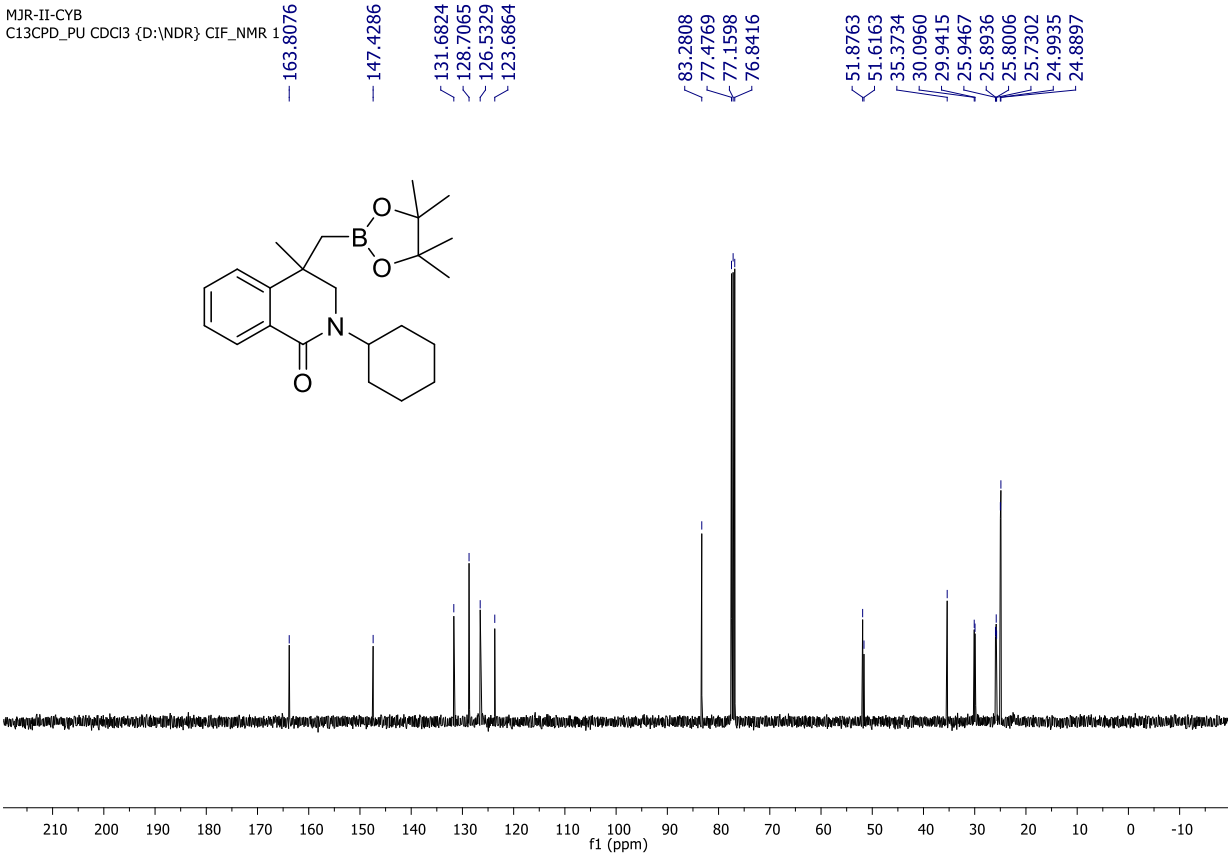
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **2j**



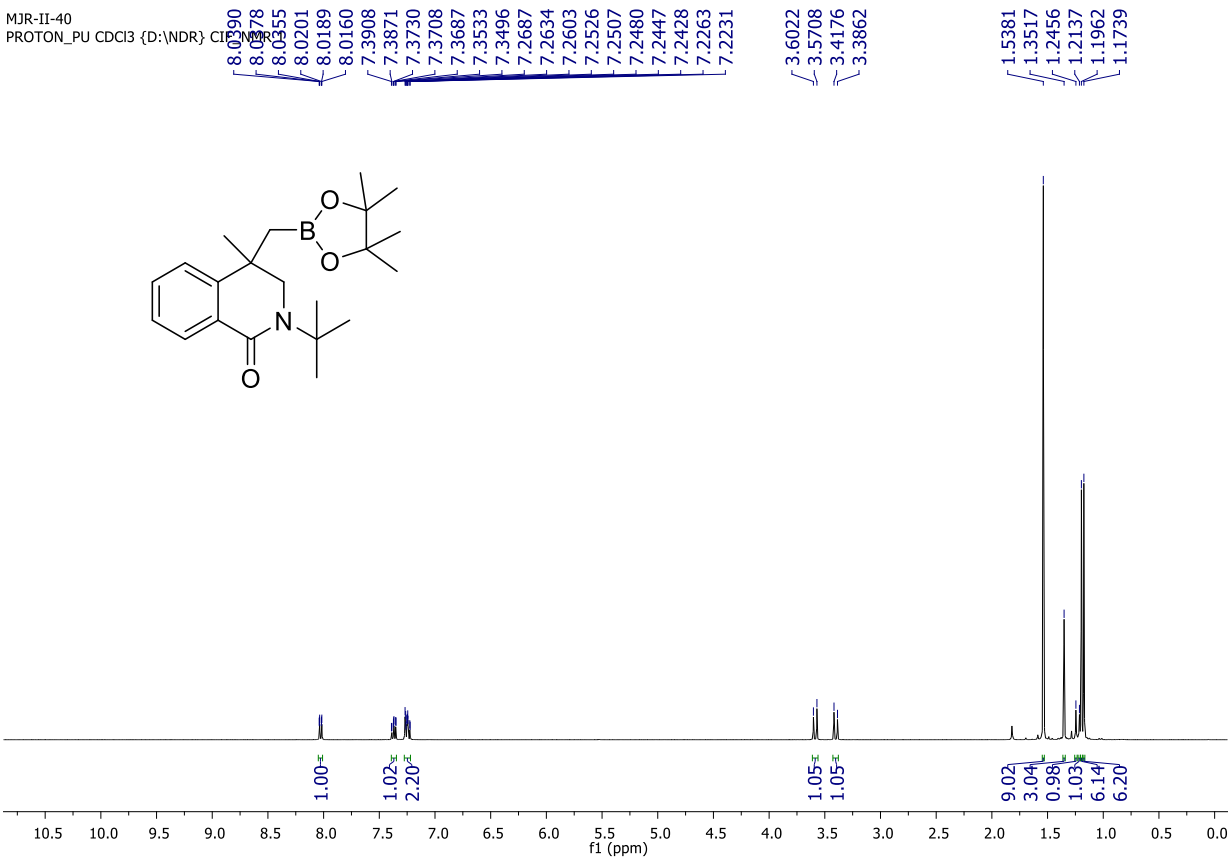
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **2k**



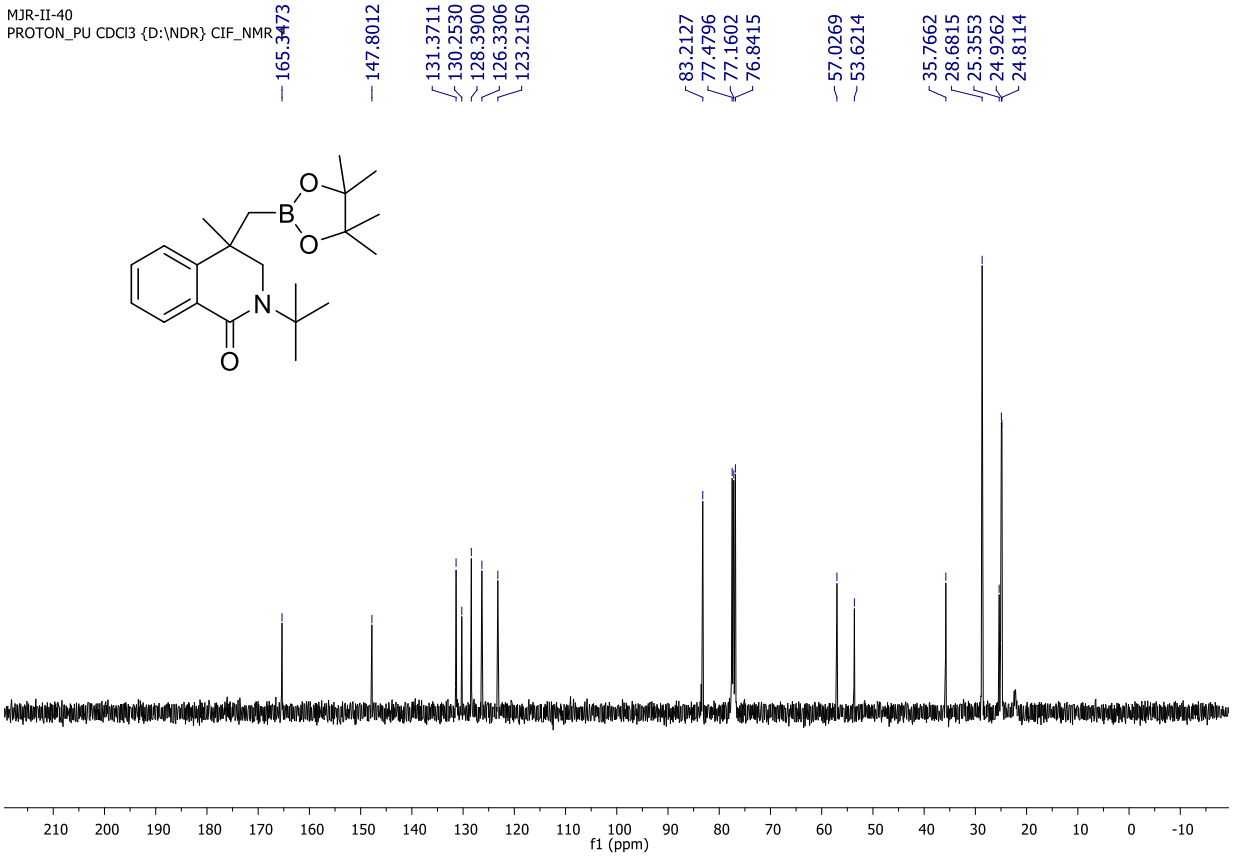
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **2k**



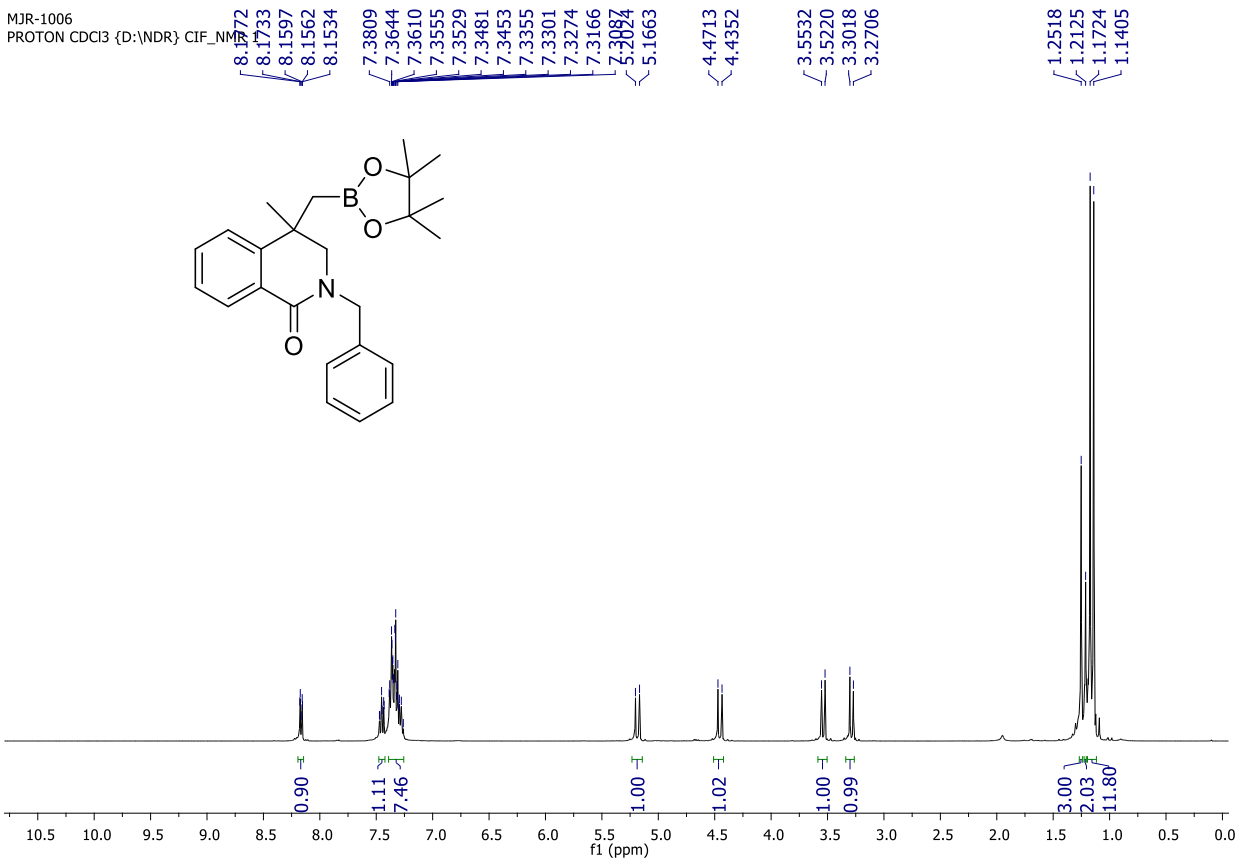
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **2l**



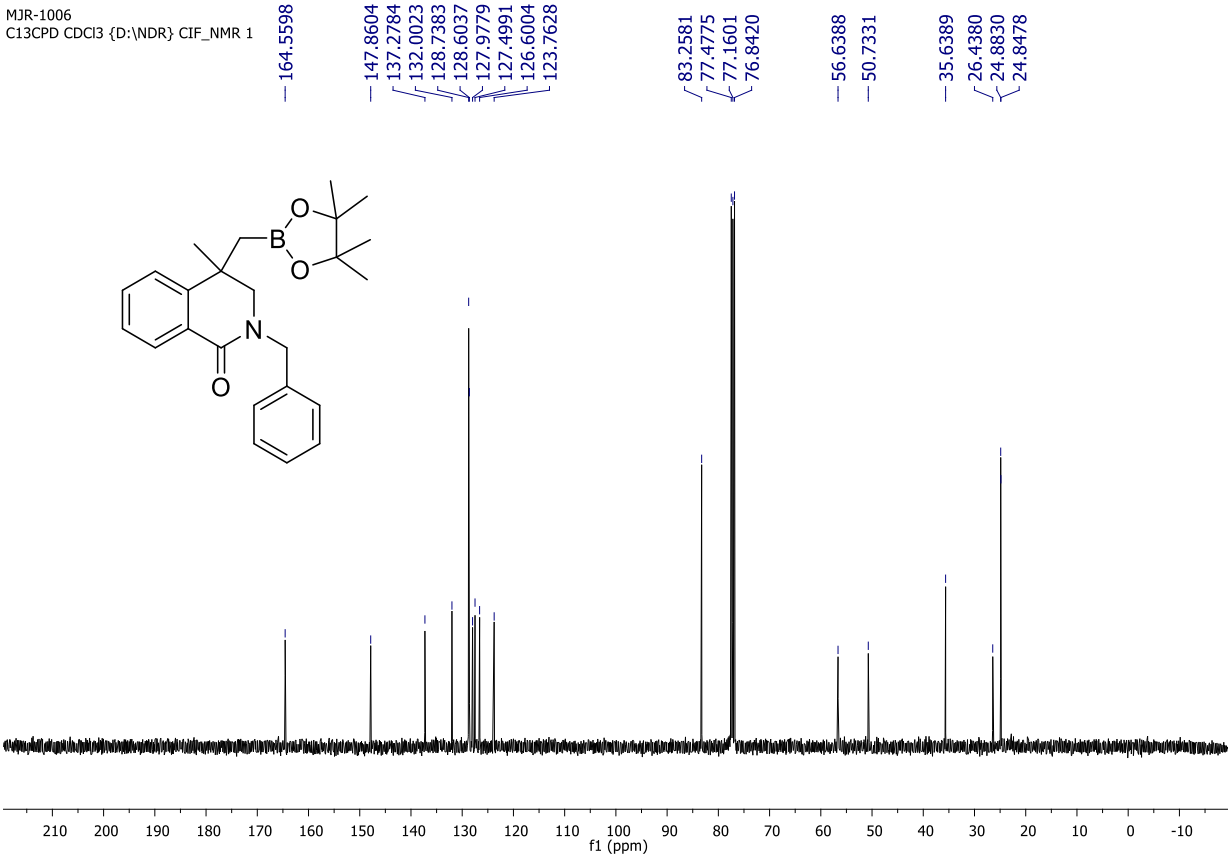
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **2l**



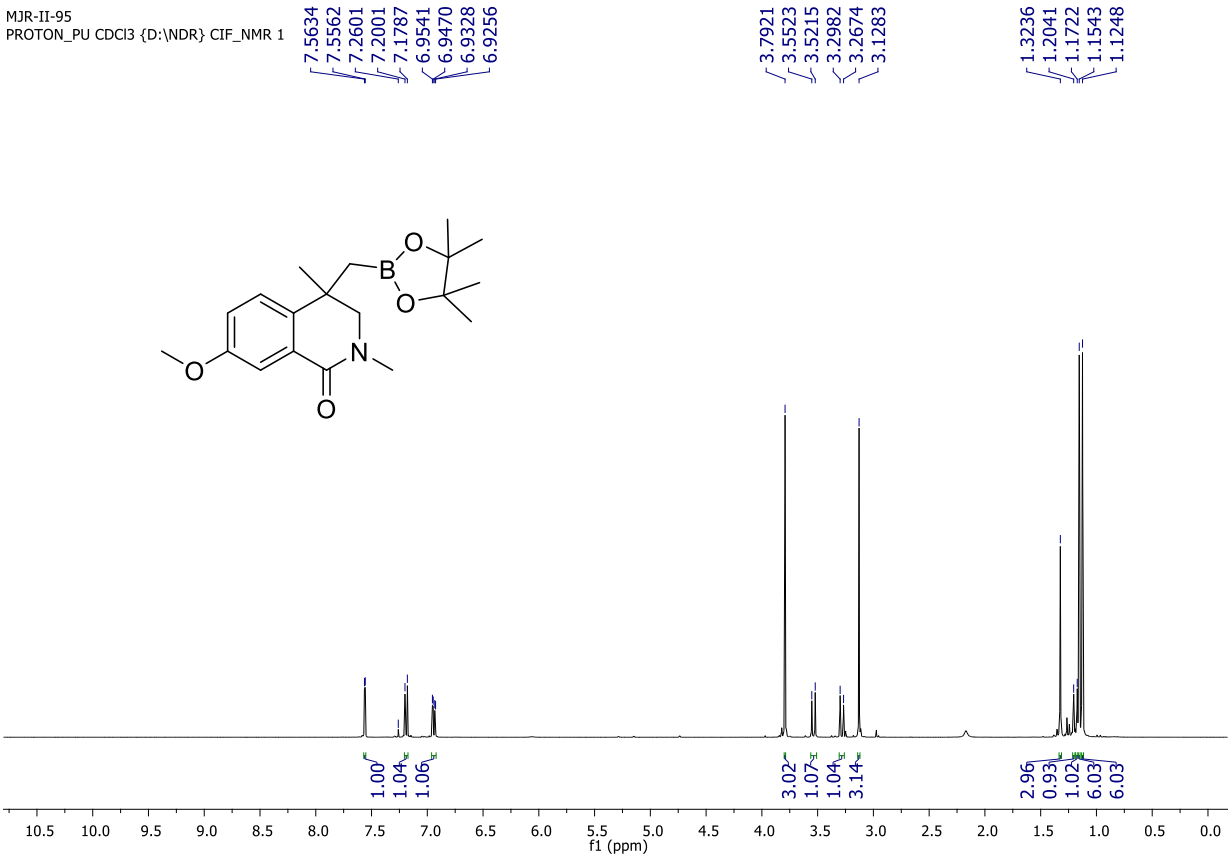
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **2m**



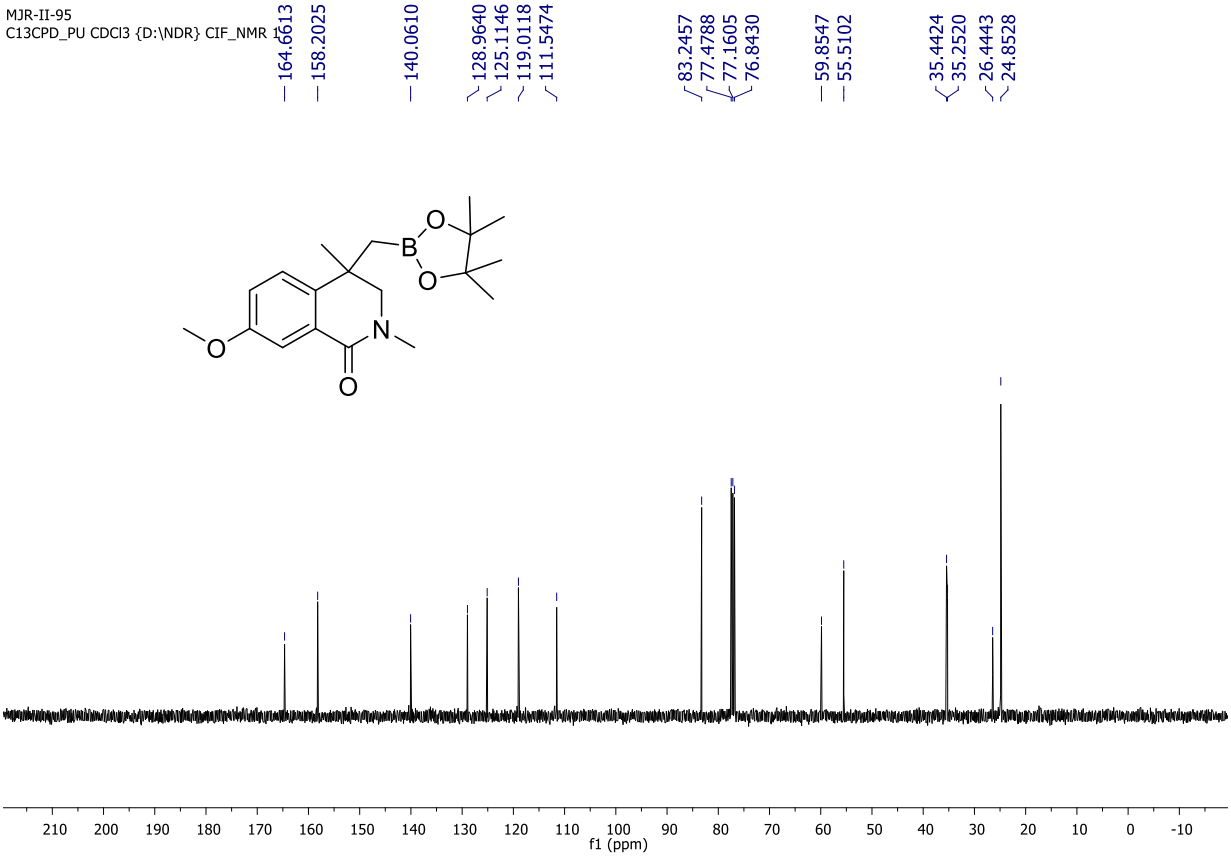
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **2m**



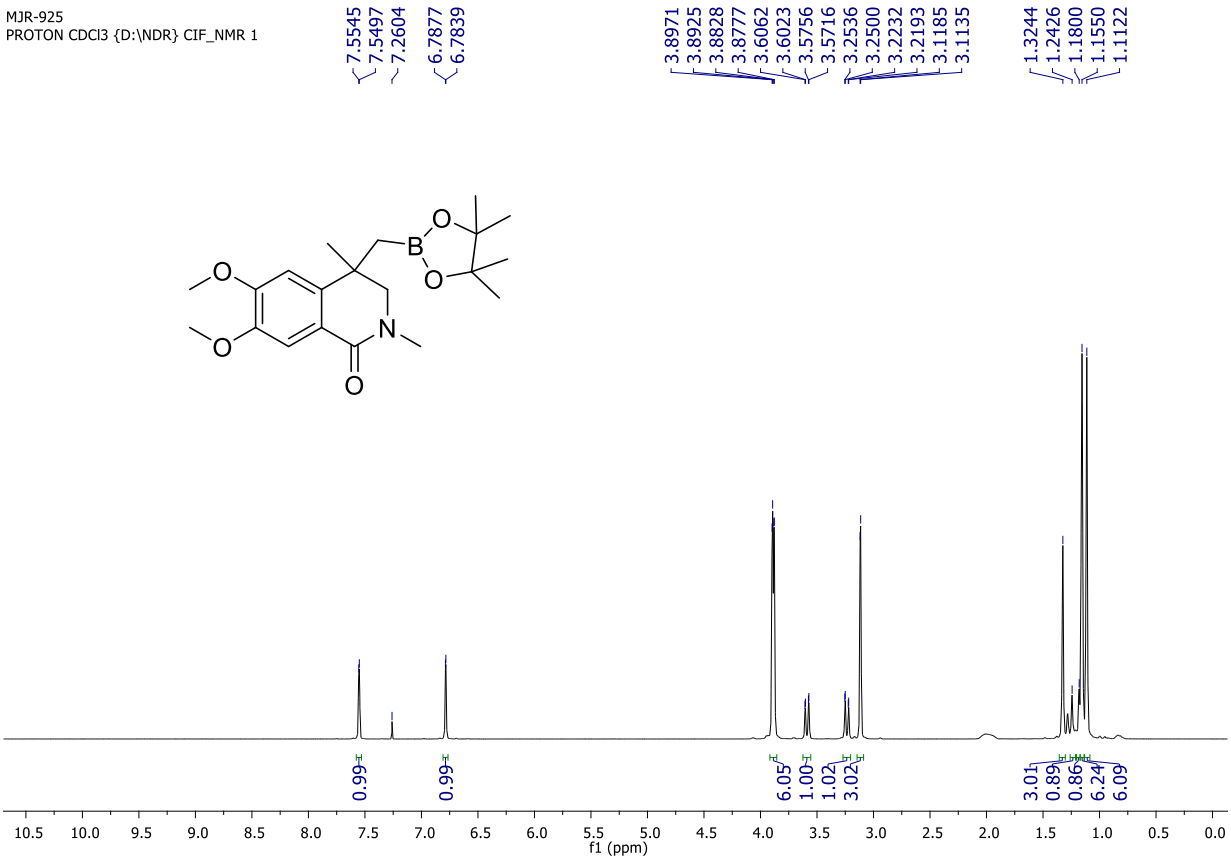
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **2n**



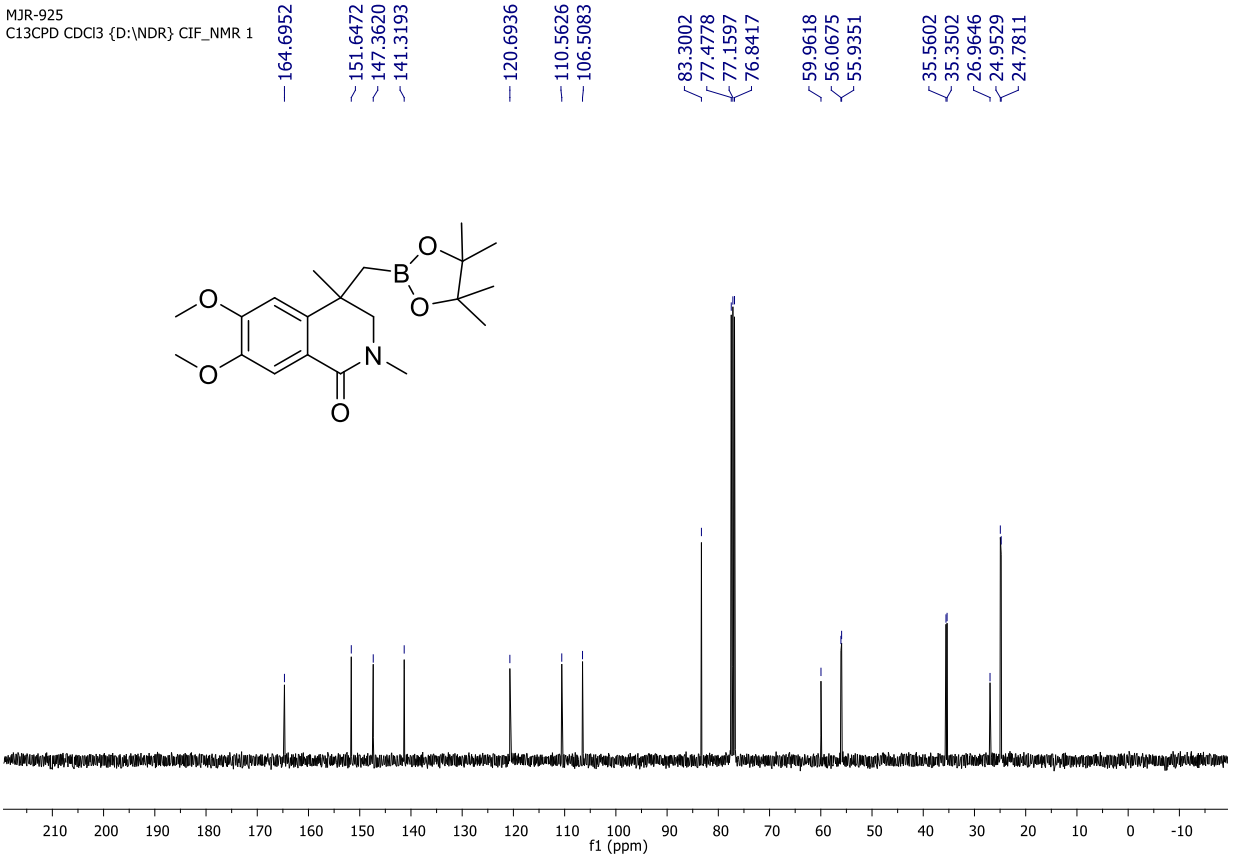
^{13}C **NMR**-spectrum (100 MHz, $CDCl_3$) of **2n**



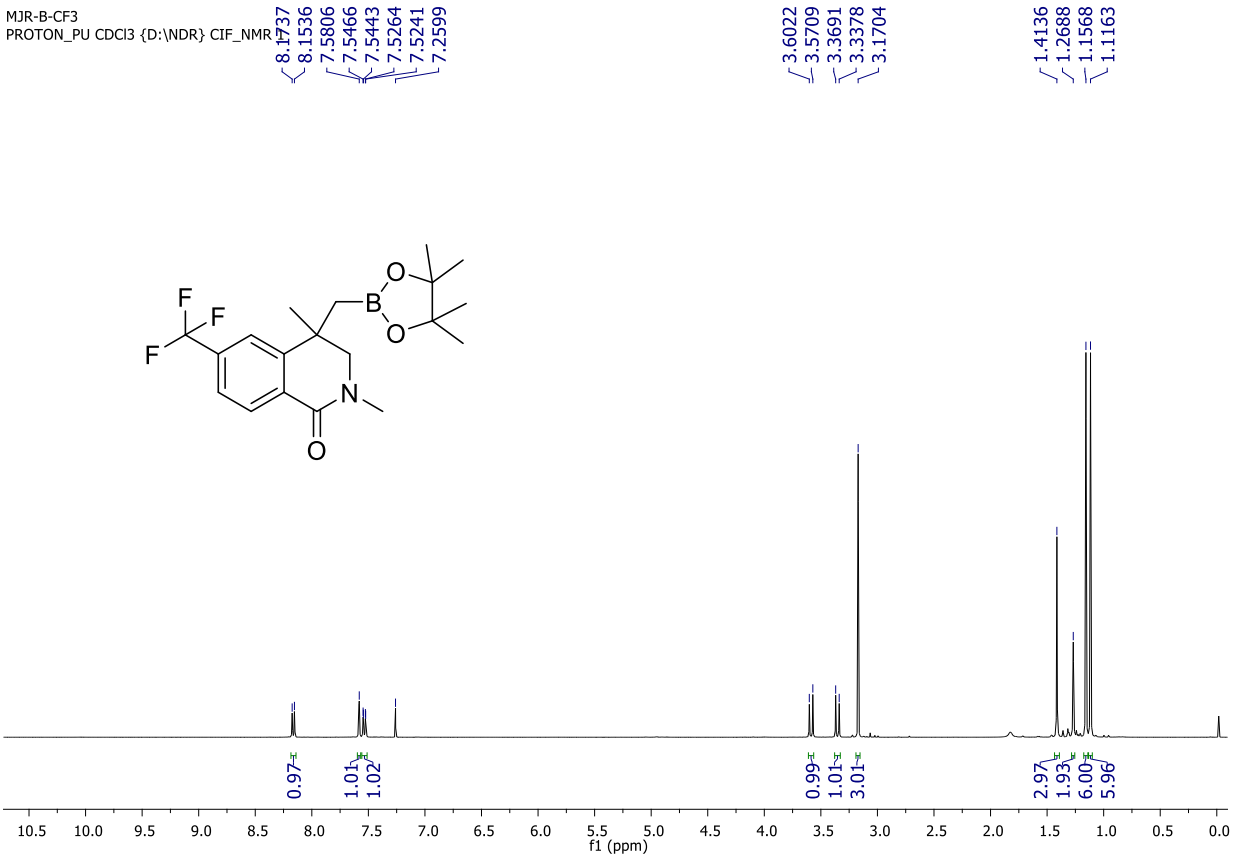
^{1}H **NMR**-spectrum (400 MHz, $CDCl_3$) of **2o**



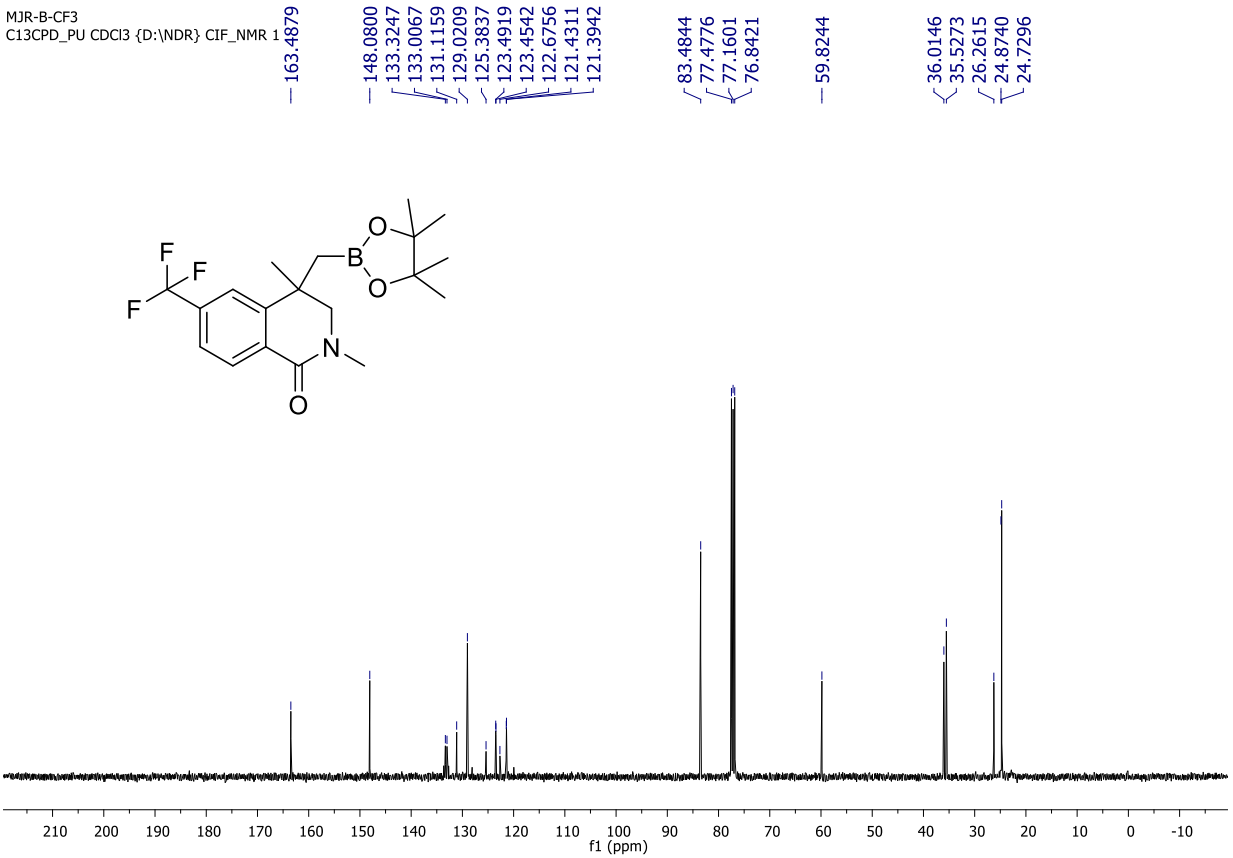
^{13}C **NMR**-spectrum (100 MHz, $CDCl_3$) of **2o**



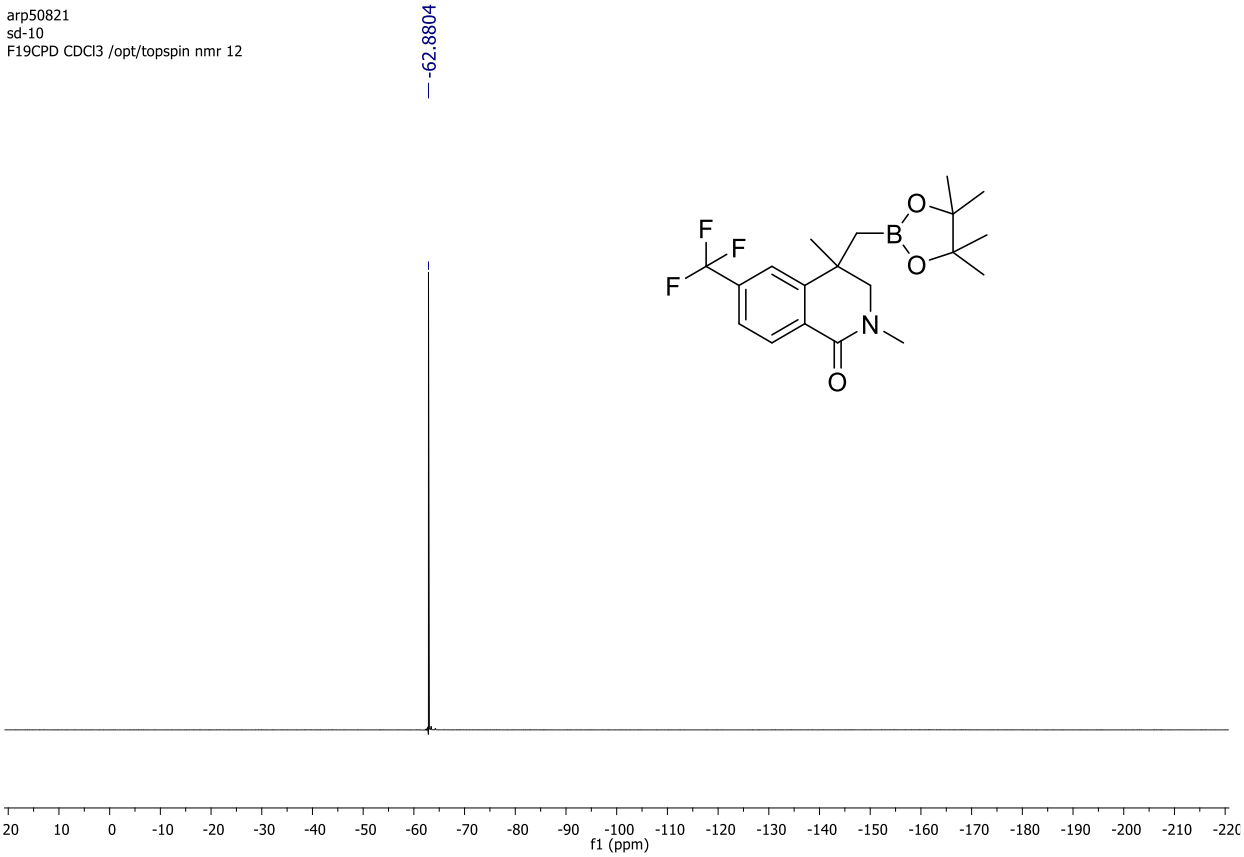
^{1}H **NMR**-spectrum (400 MHz, $CDCl_3$) of **2p**



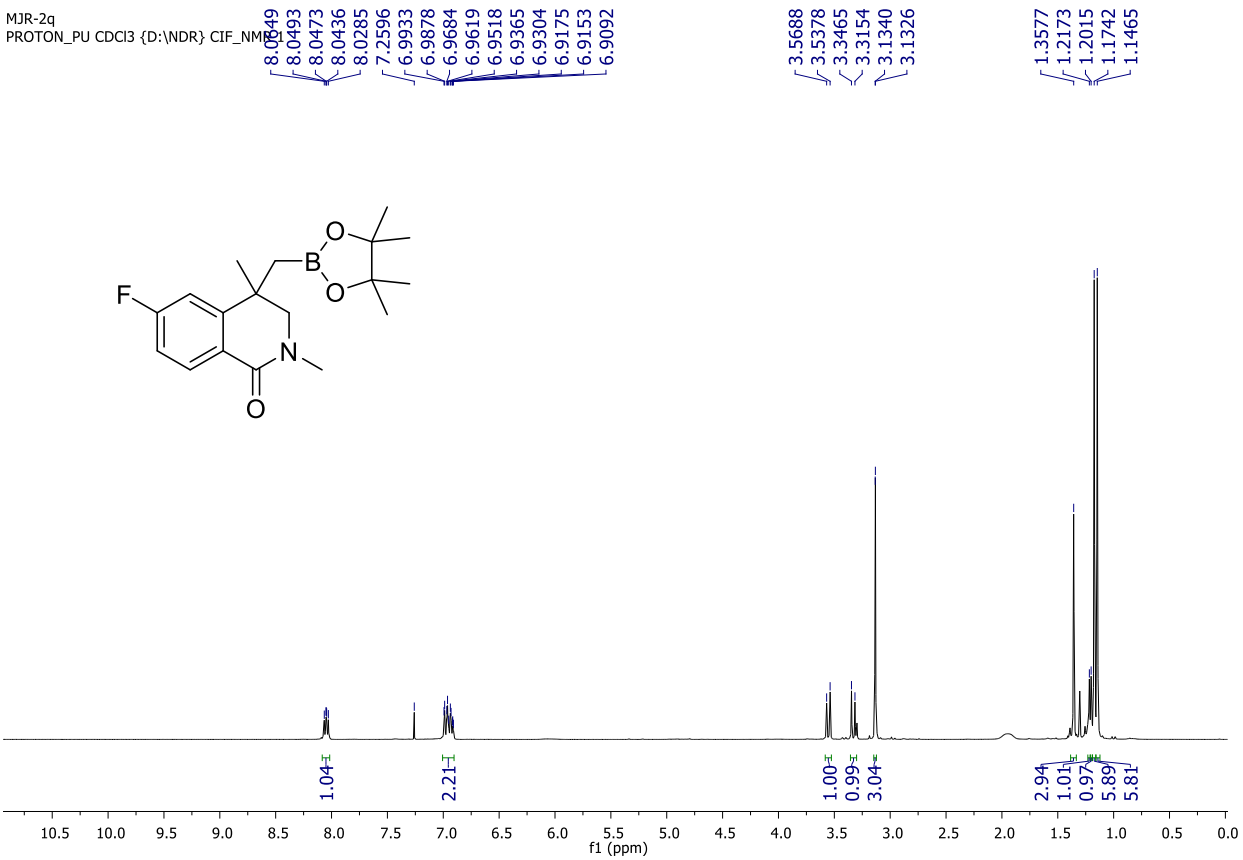
^{13}C **NMR**-spectrum (100 MHz, $CDCl_3$) of **2p**



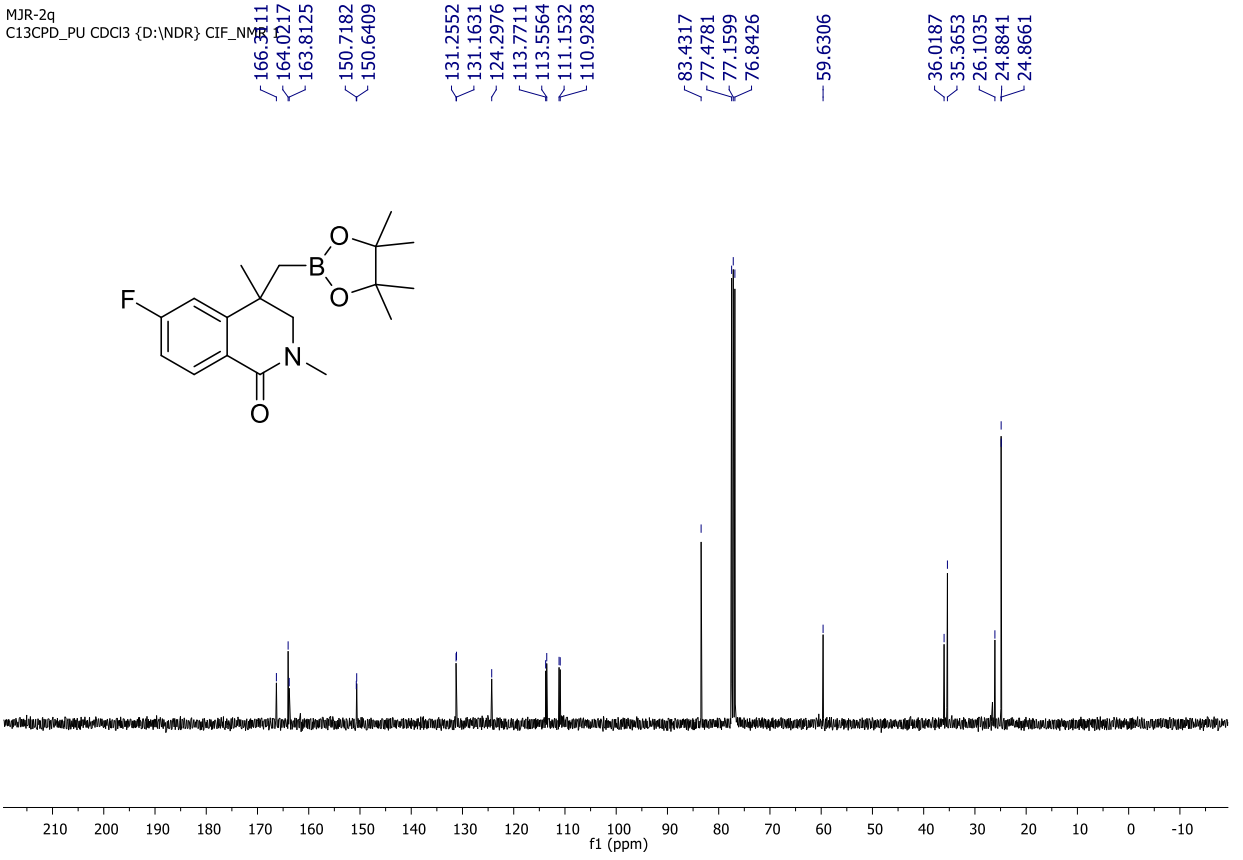
^{19}F **NMR**-spectrum (471 MHz, $CDCl_3$) of **2p**



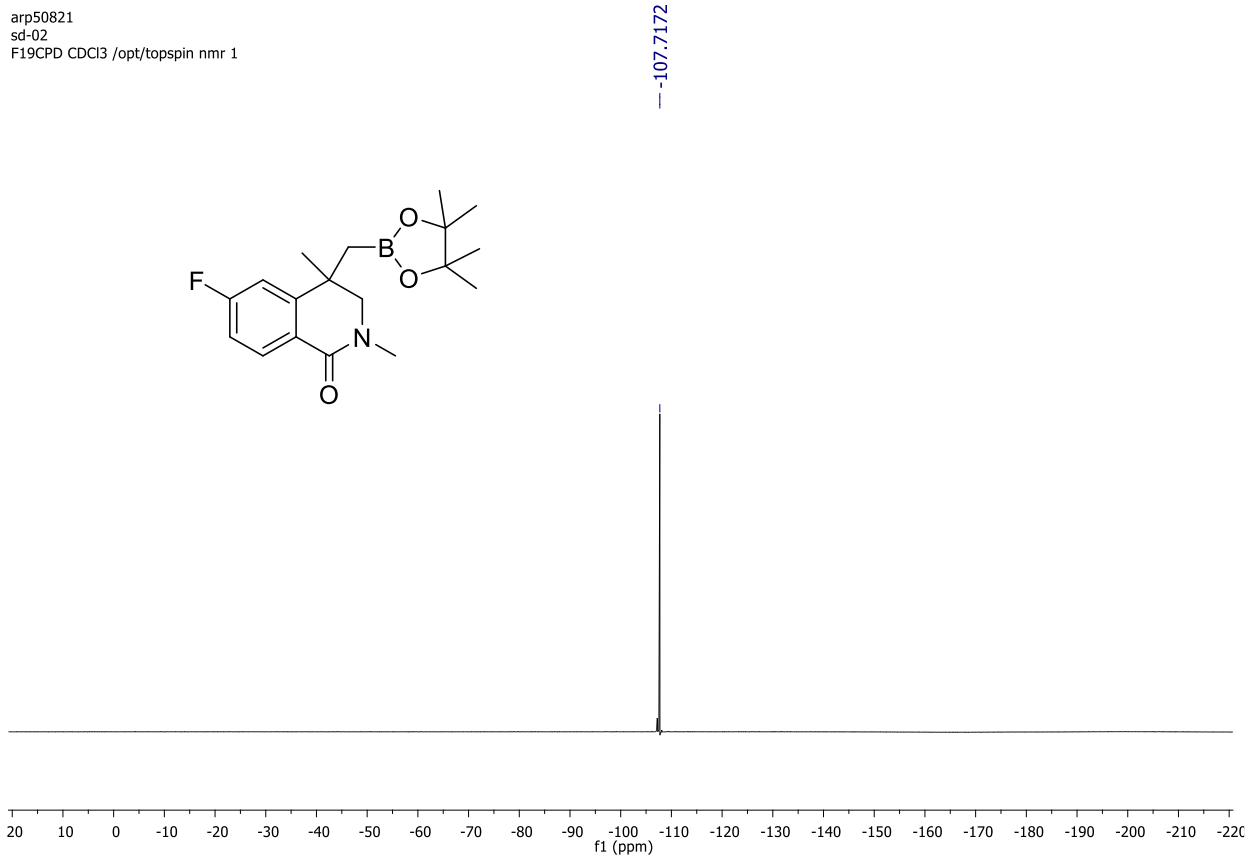
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **2q**



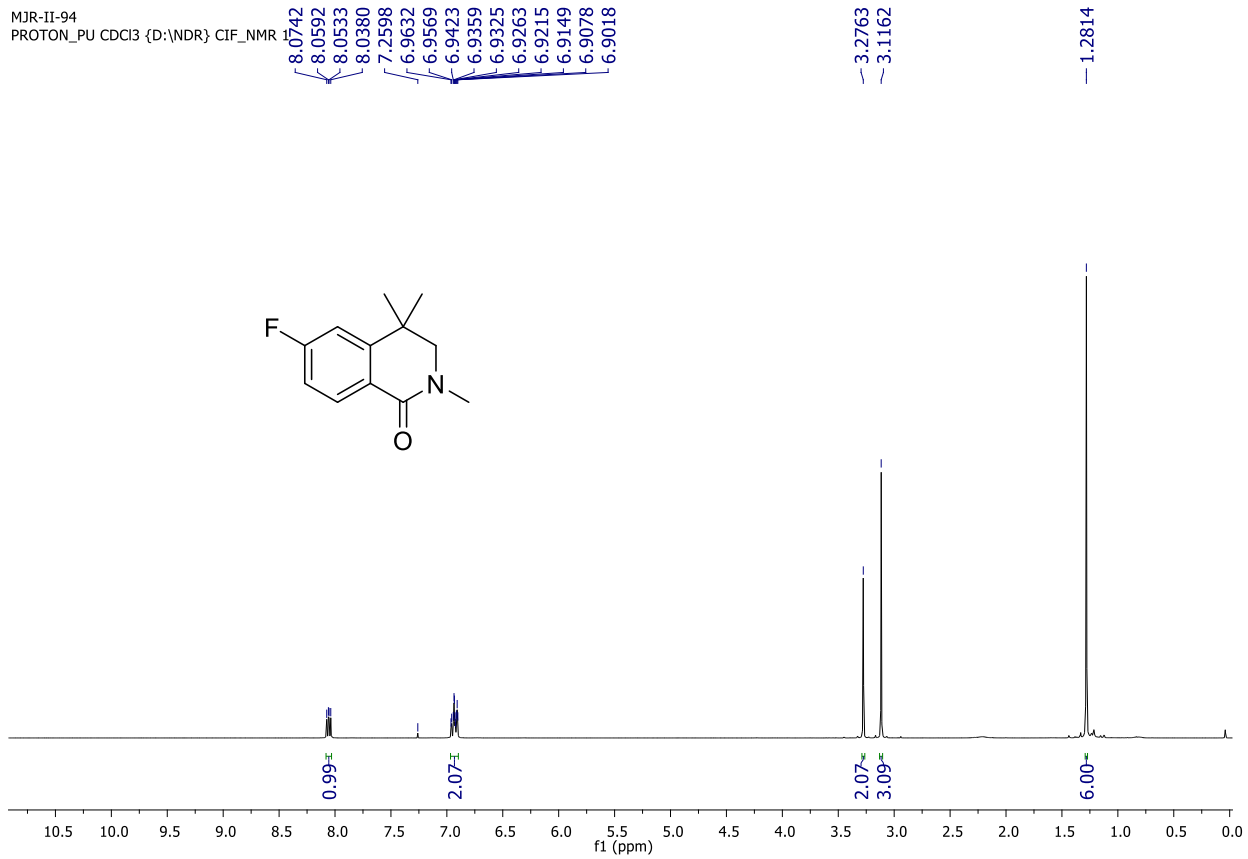
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **2q**



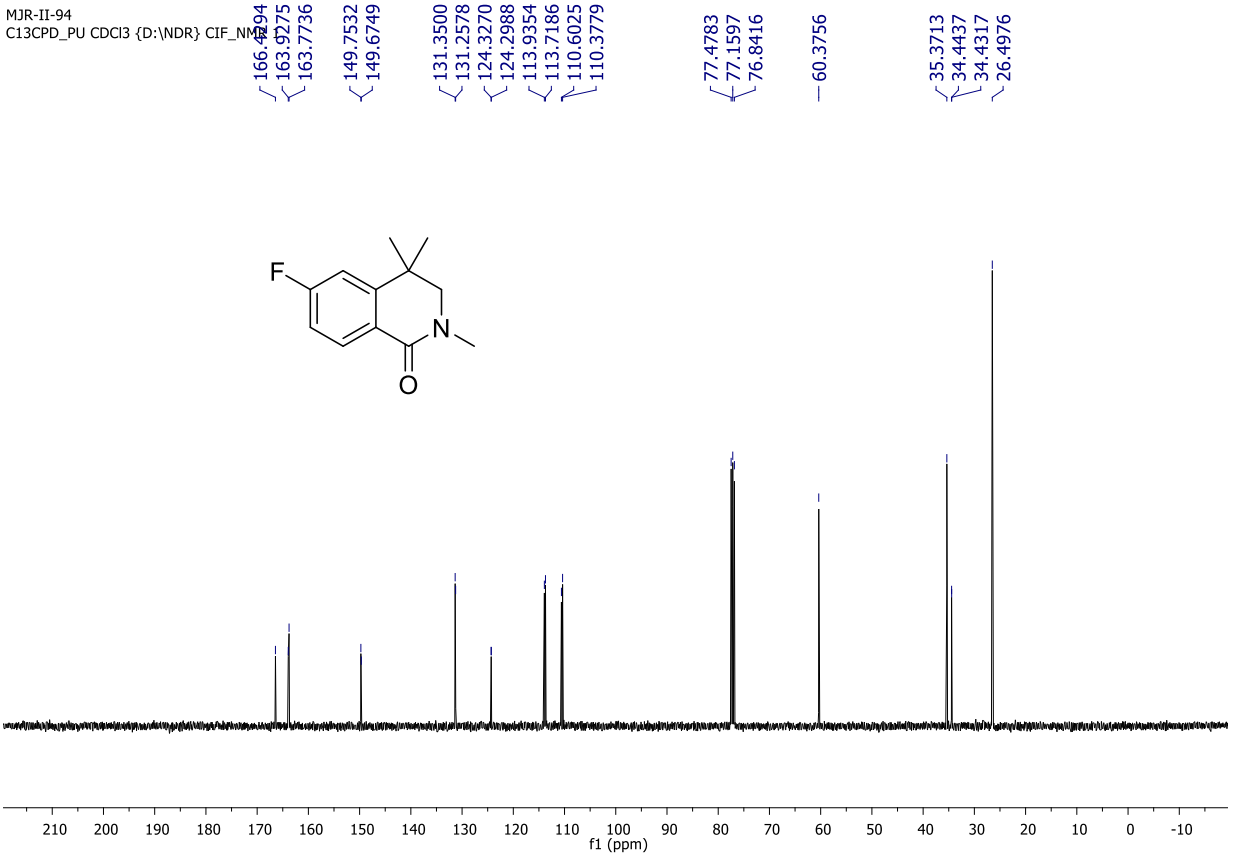
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **2q**



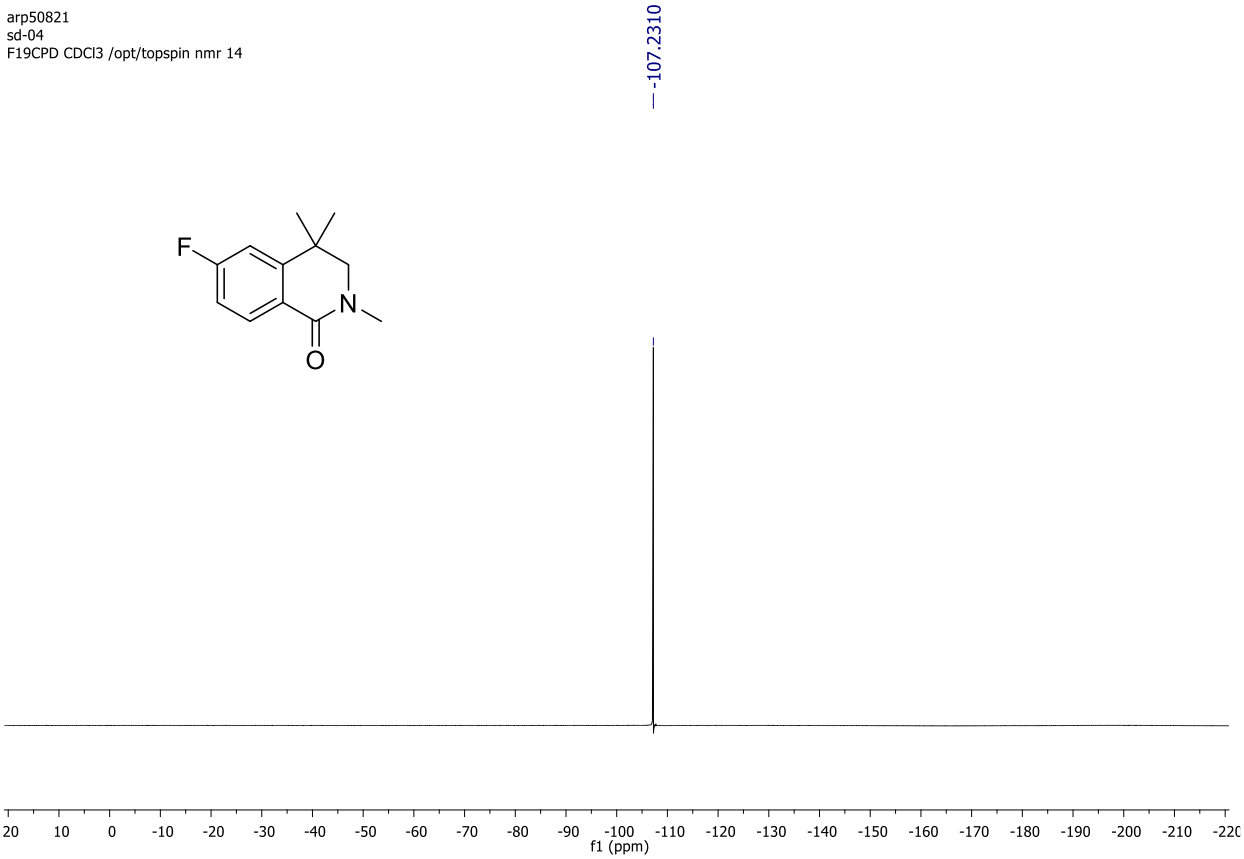
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **2q$_1$**



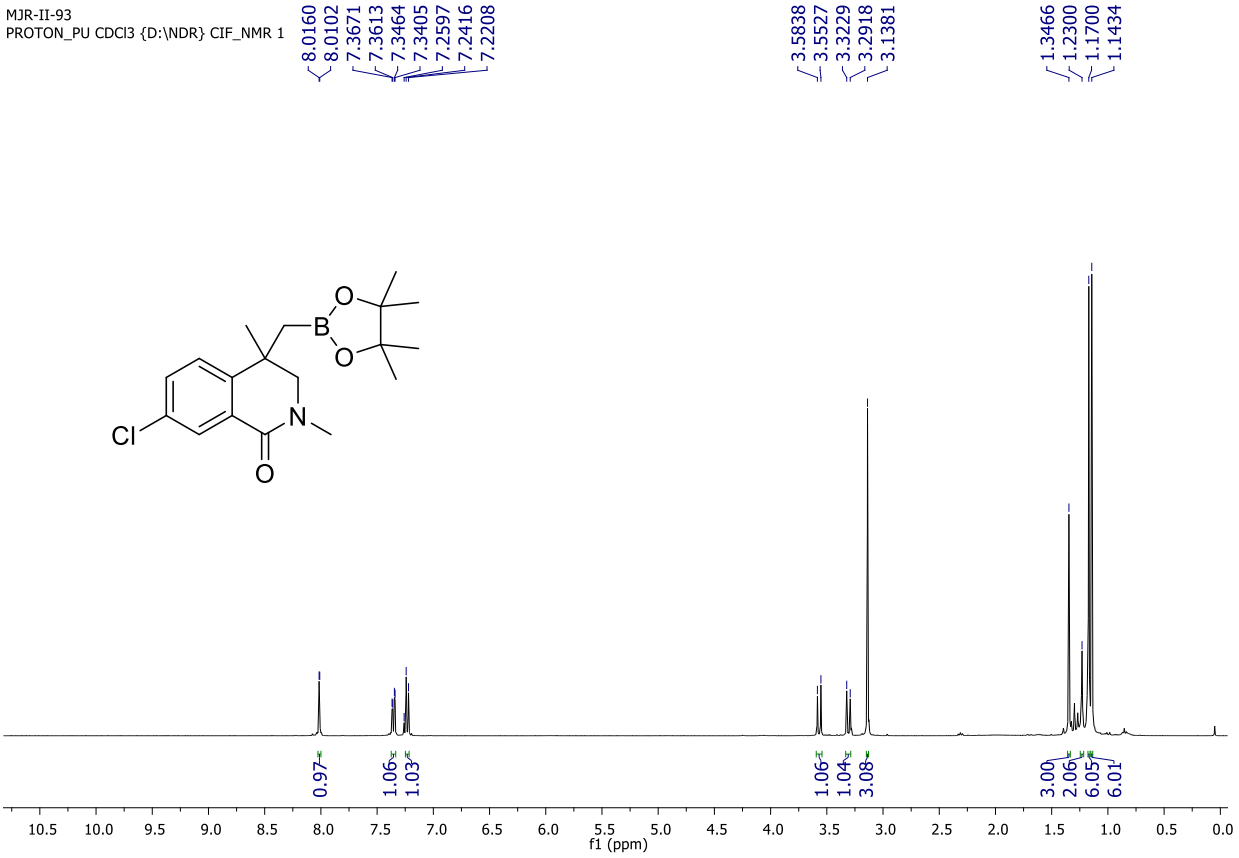
^{13}C **NMR**-spectrum (100 MHz, $CDCl_3$) of **2q1**



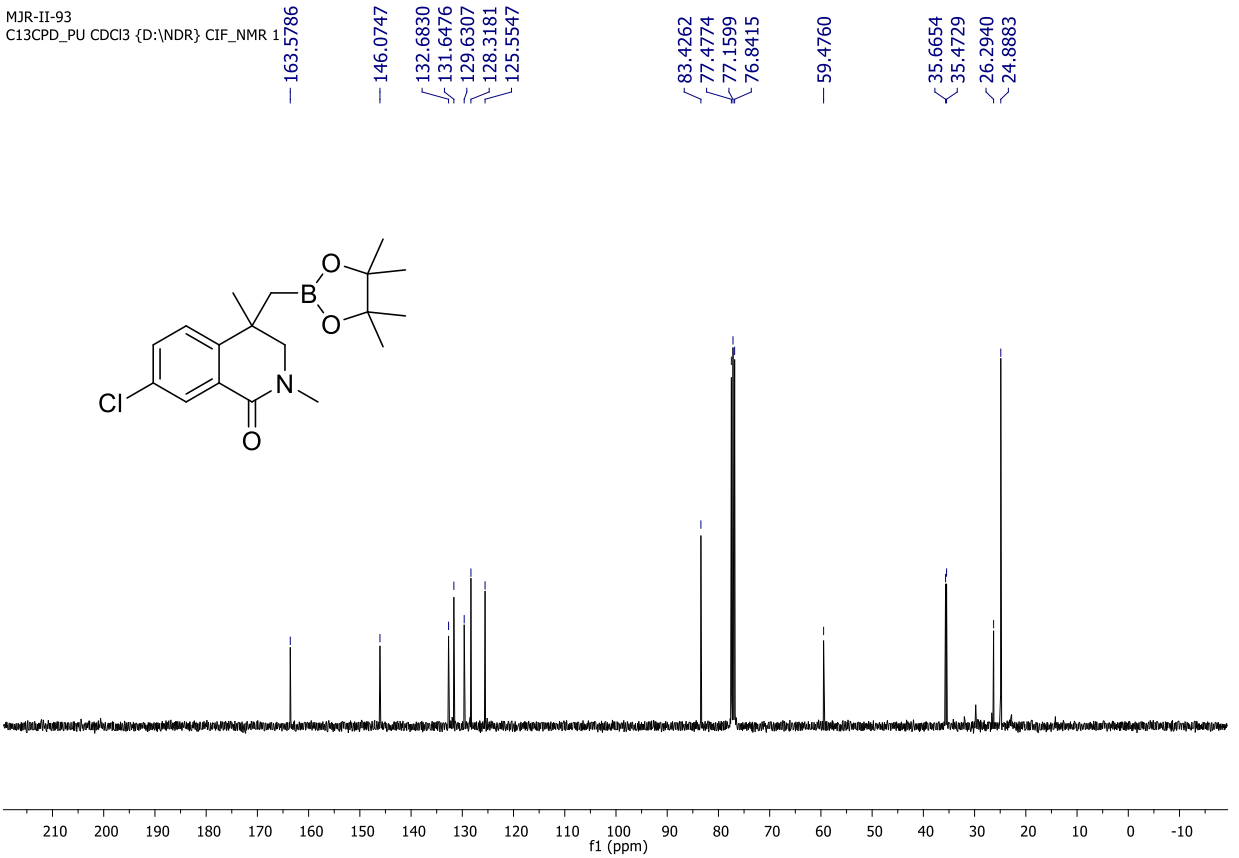
^{19}F **NMR**-spectrum (471 MHz, $CDCl_3$) of **2q1**



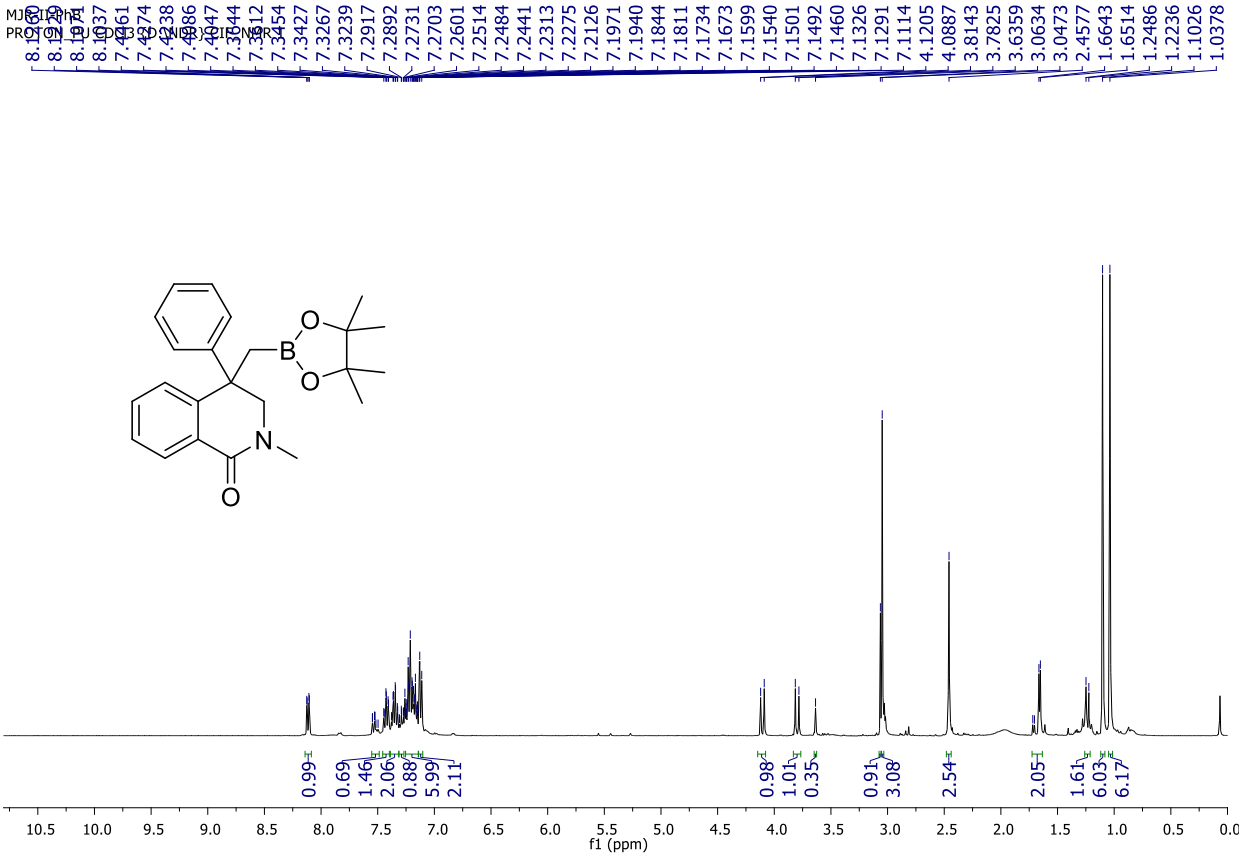
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **2r**



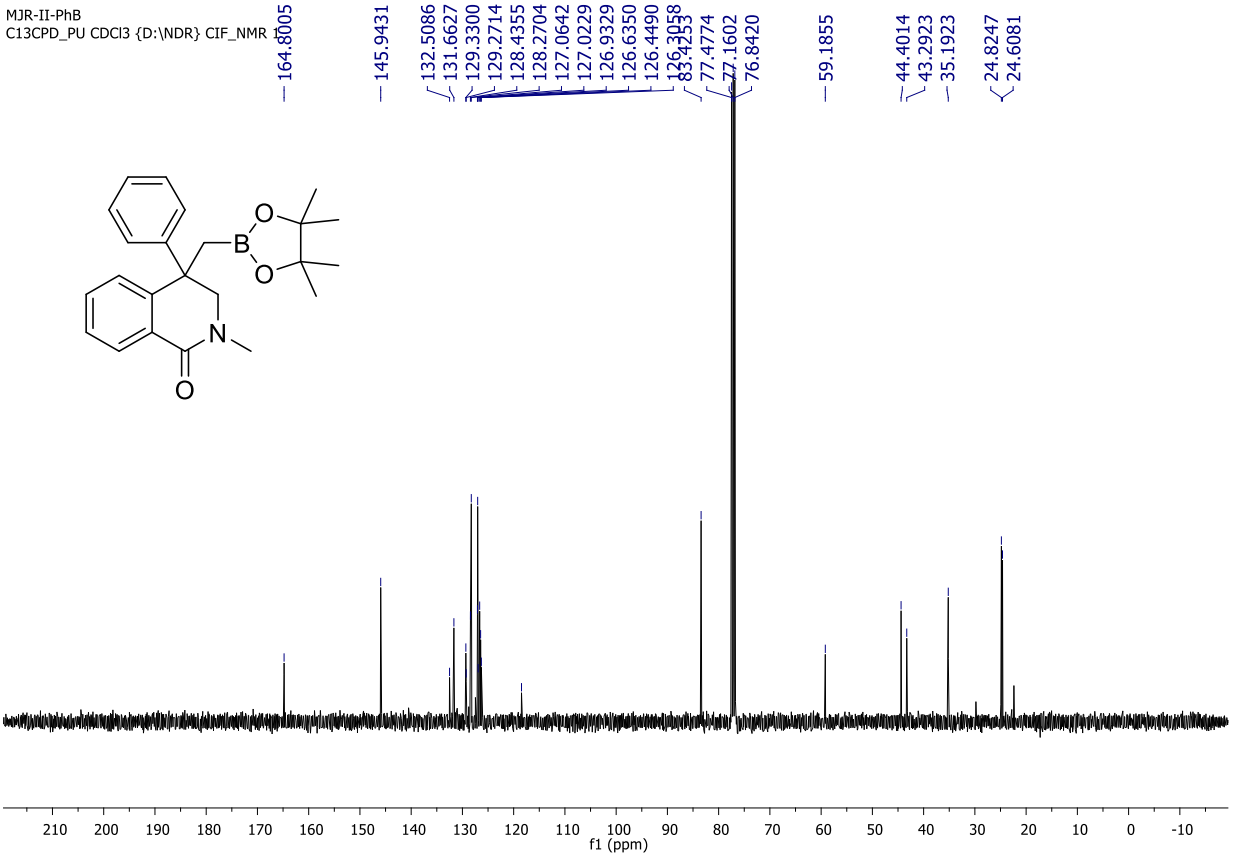
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **2r**



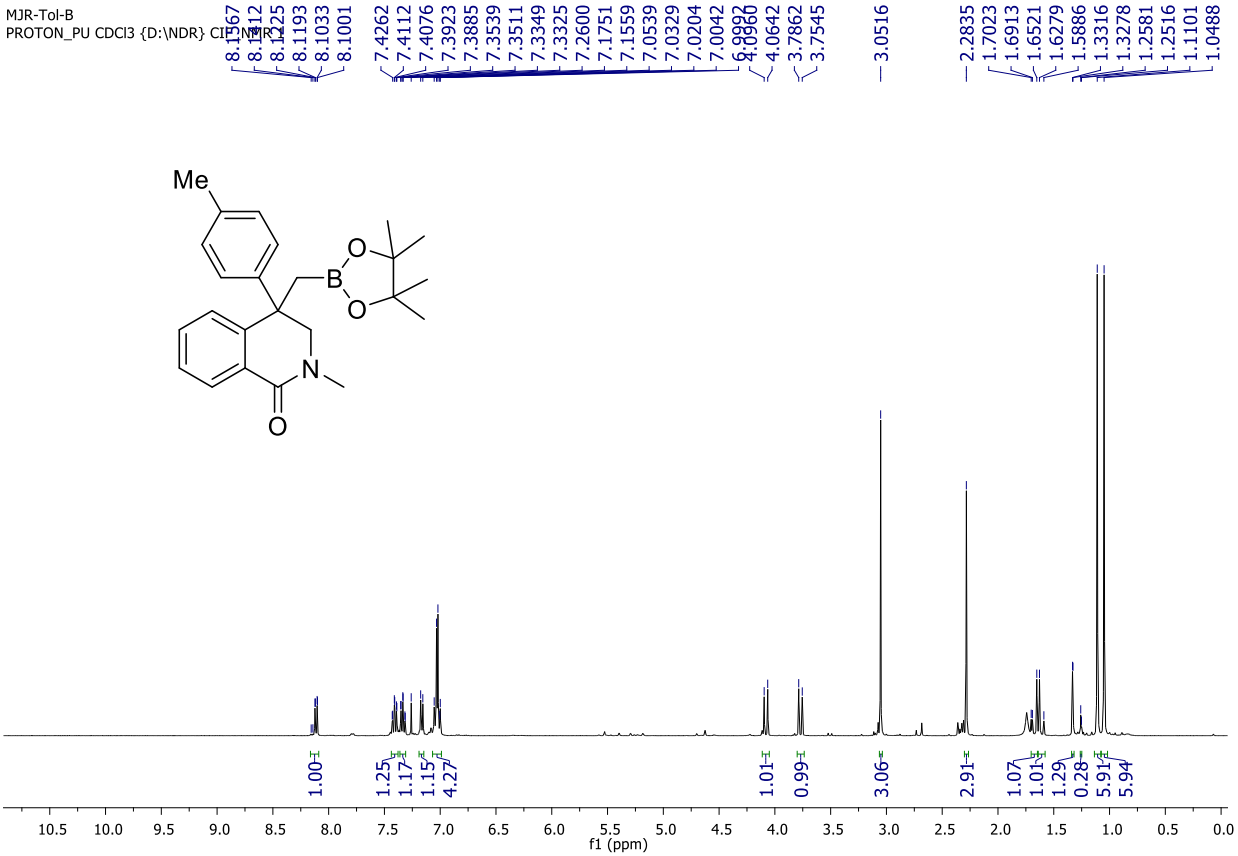
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **2s**



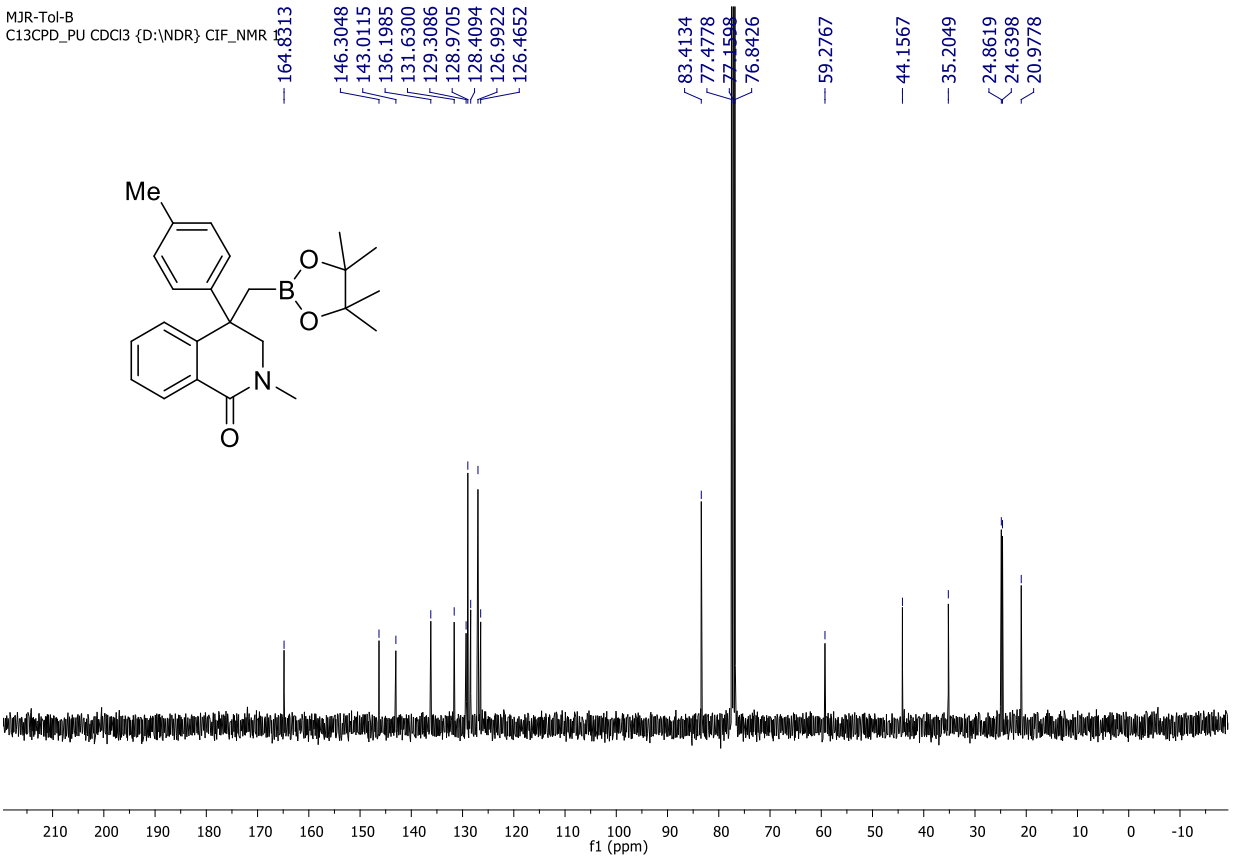
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **2s**



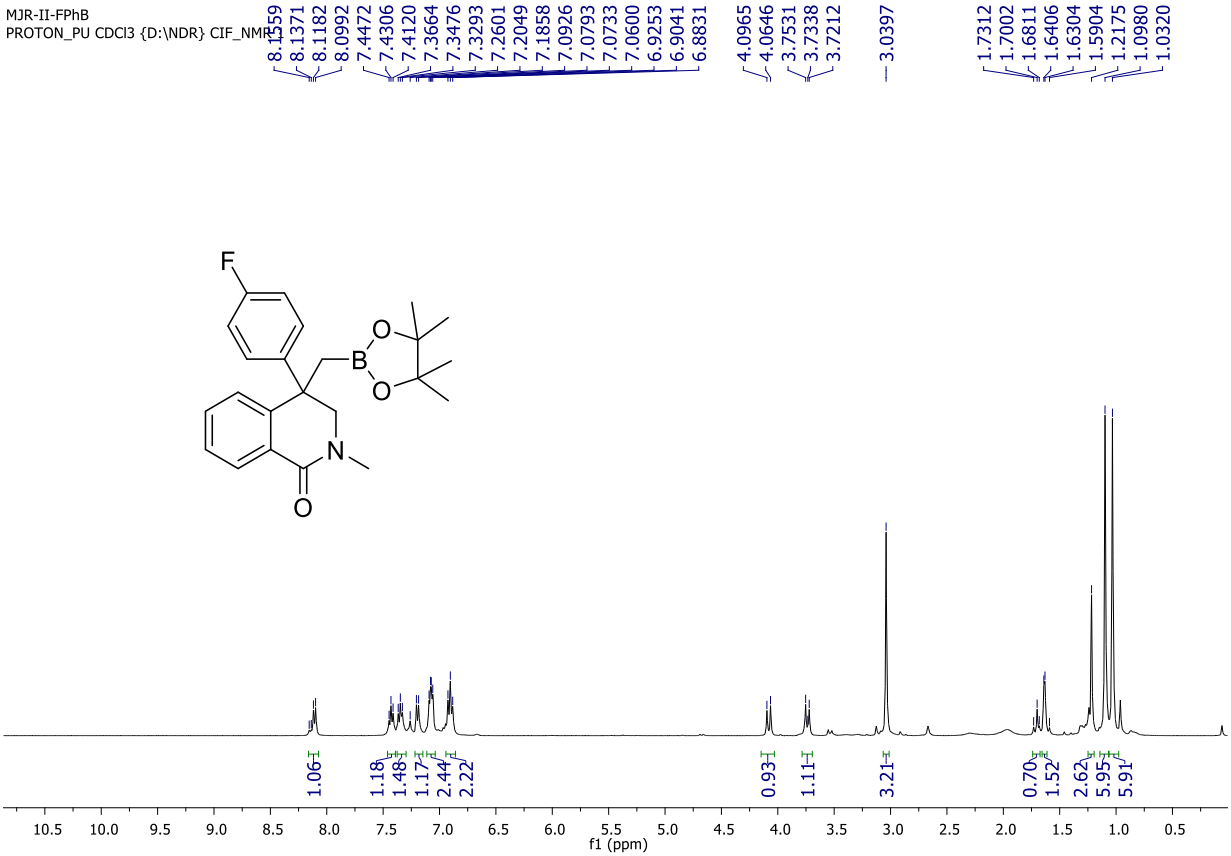
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **2t**



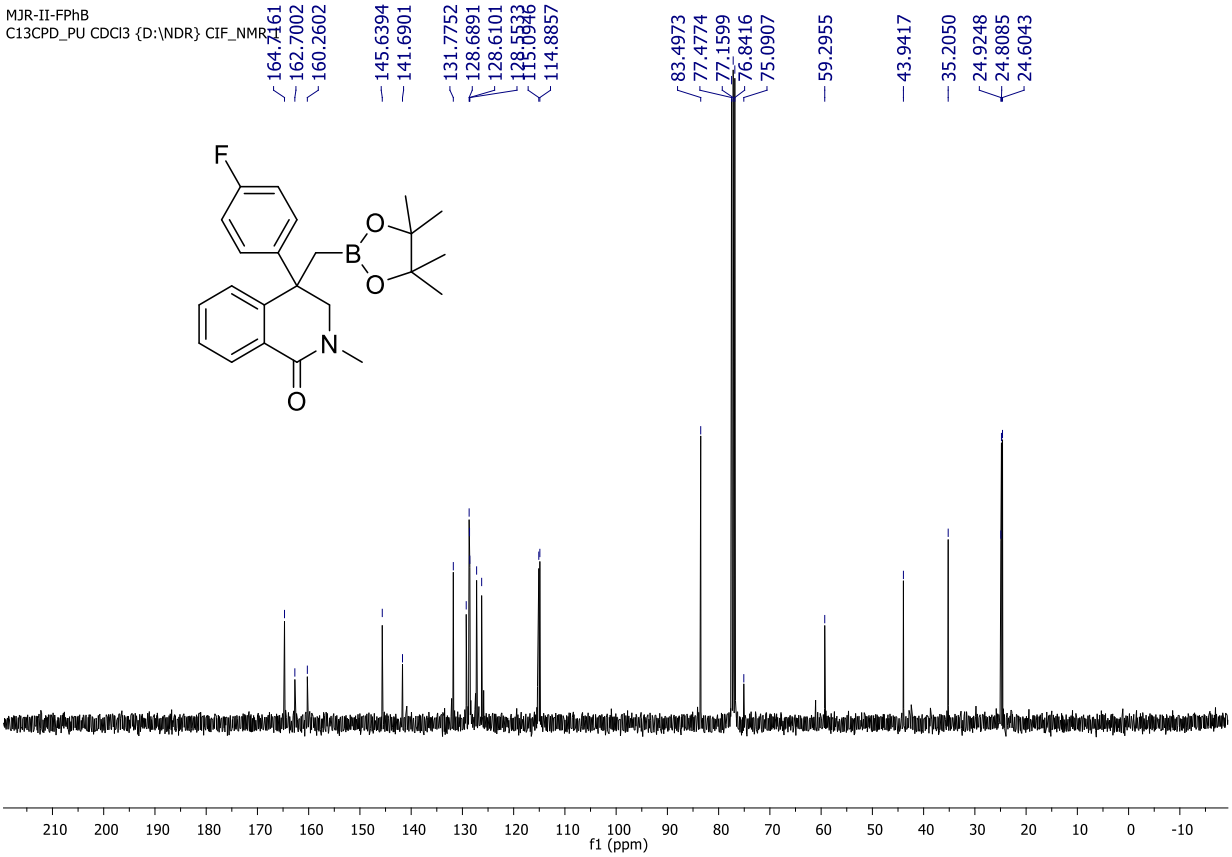
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **2t**



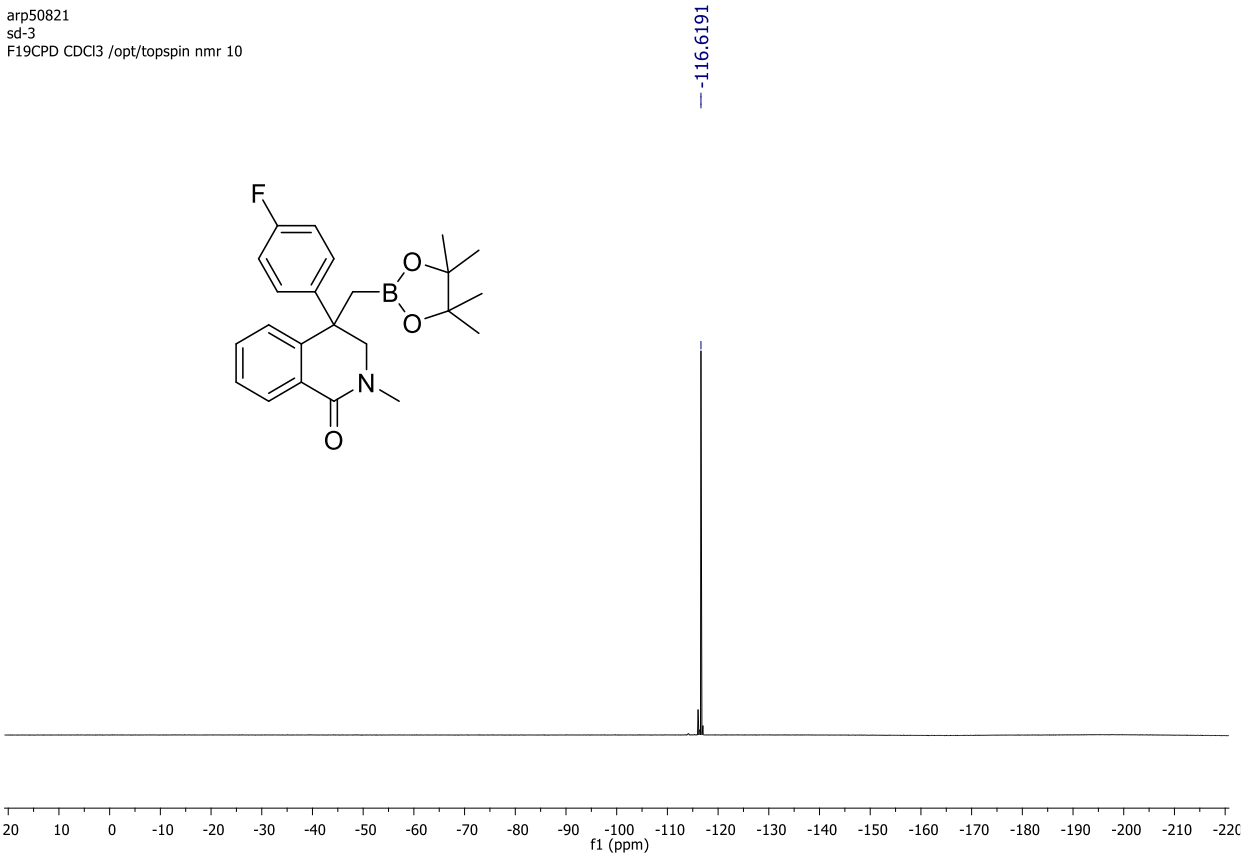
^{1}H **NMR**-spectrum (400 MHz, $CDCl_3$) of **2u**



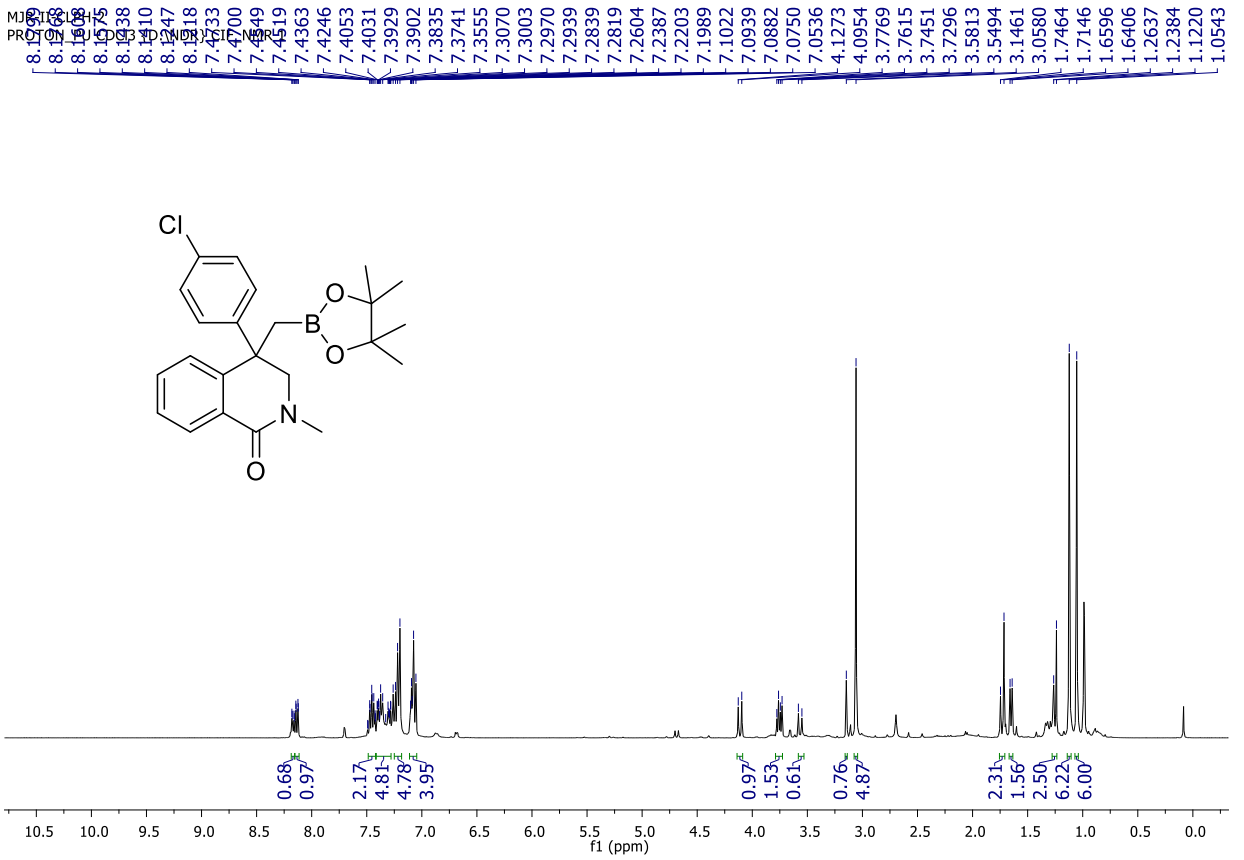
^{13}C **NMR**-spectrum (100 MHz, $CDCl_3$) of **2u**



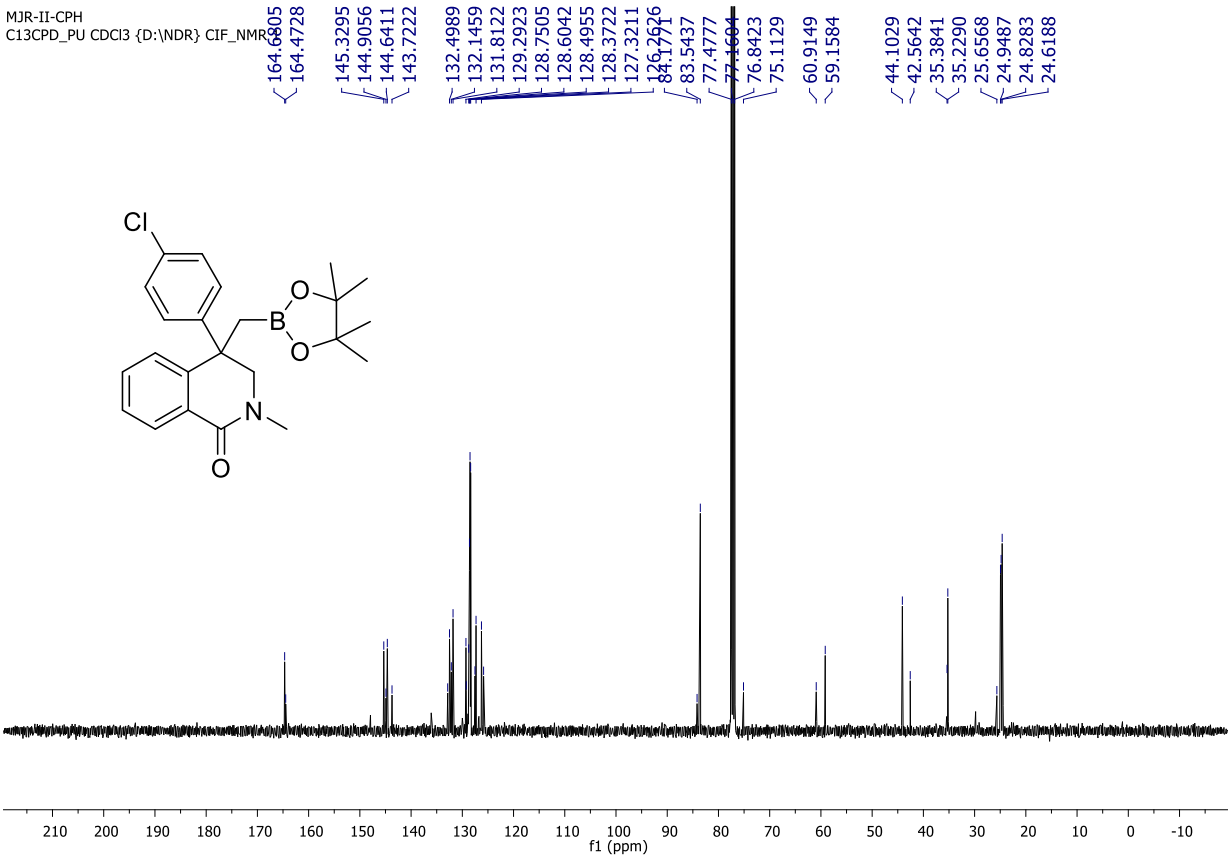
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **2u**



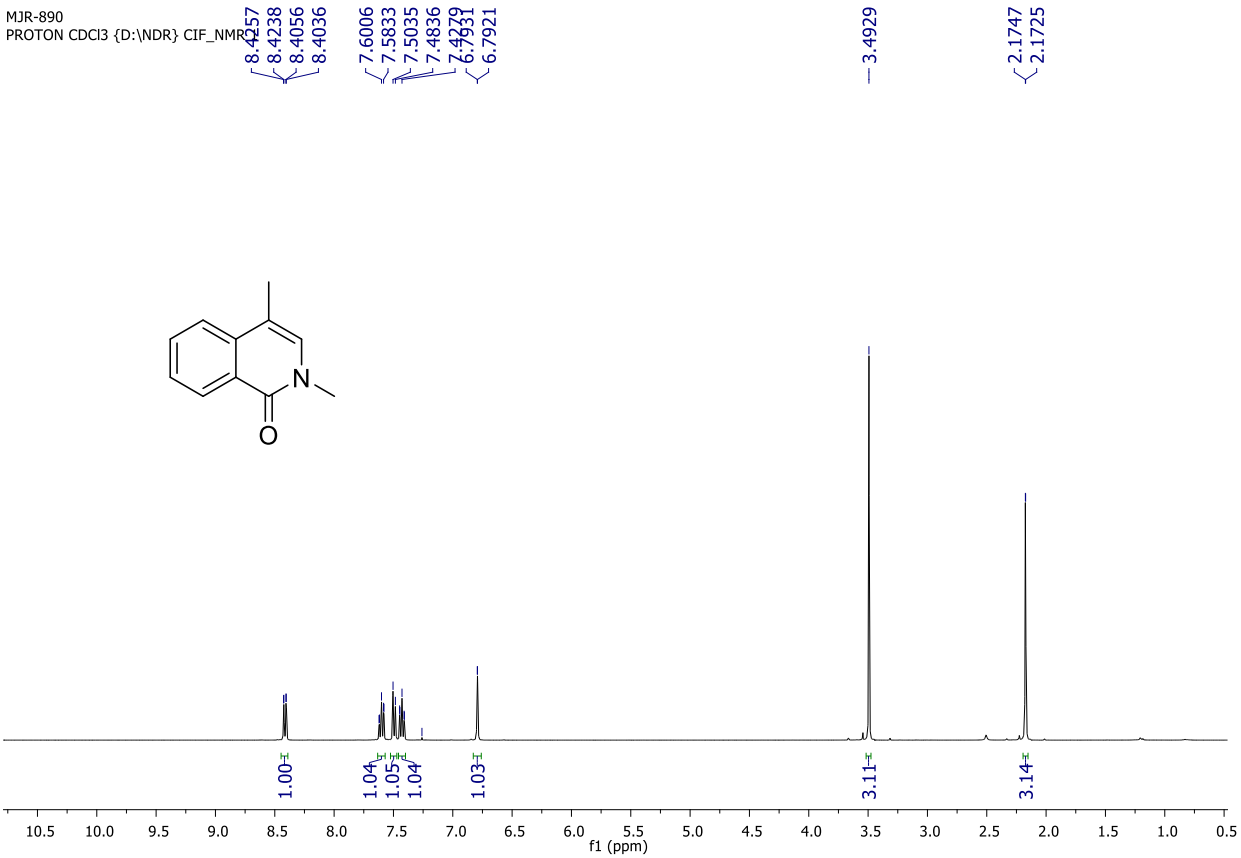
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **2v**



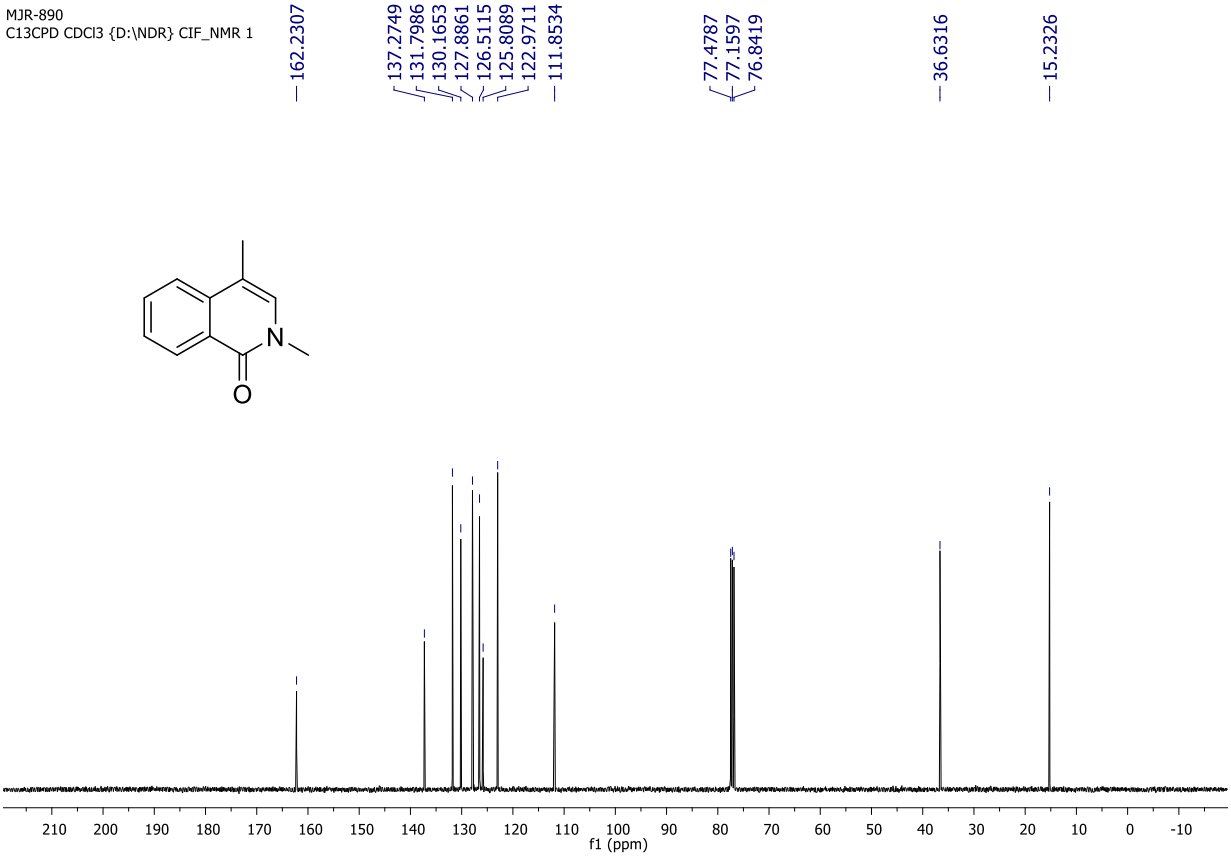
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **2v**



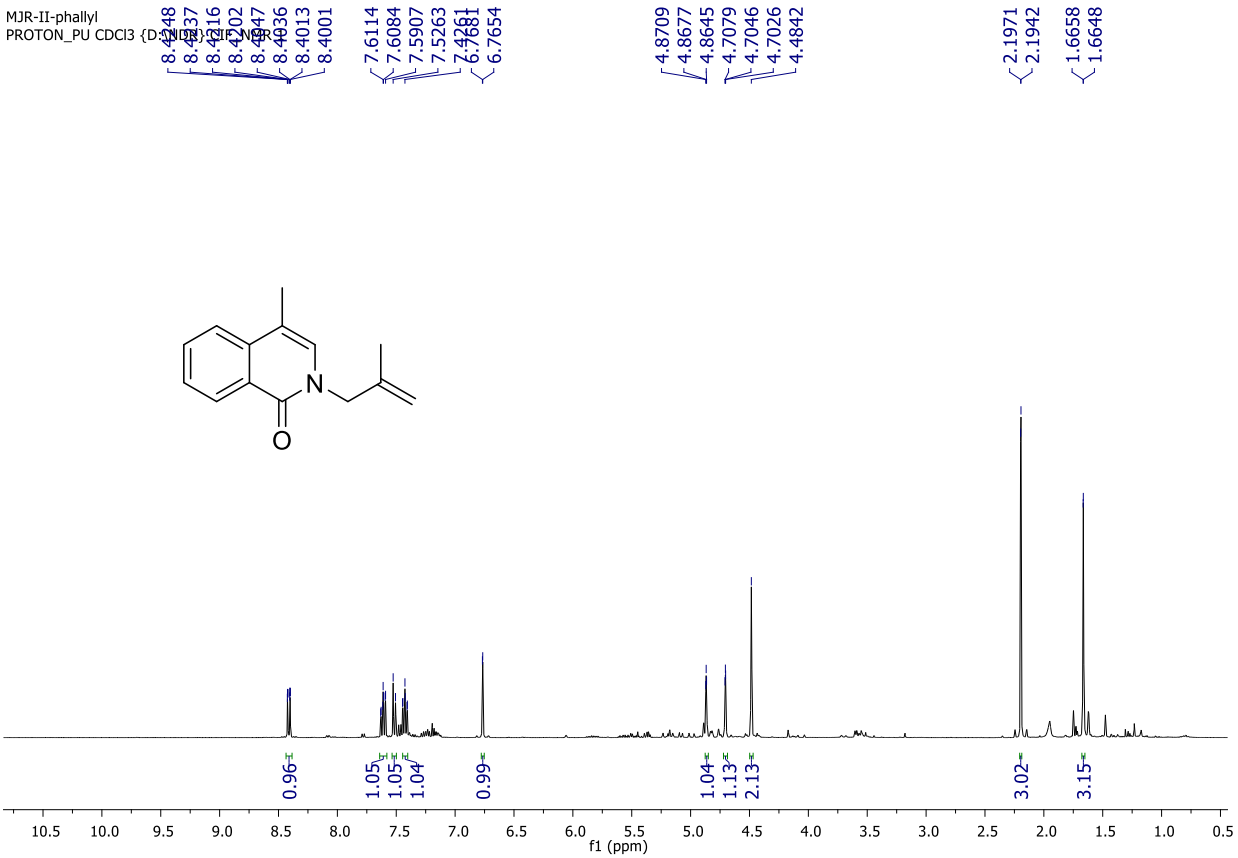
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4a**



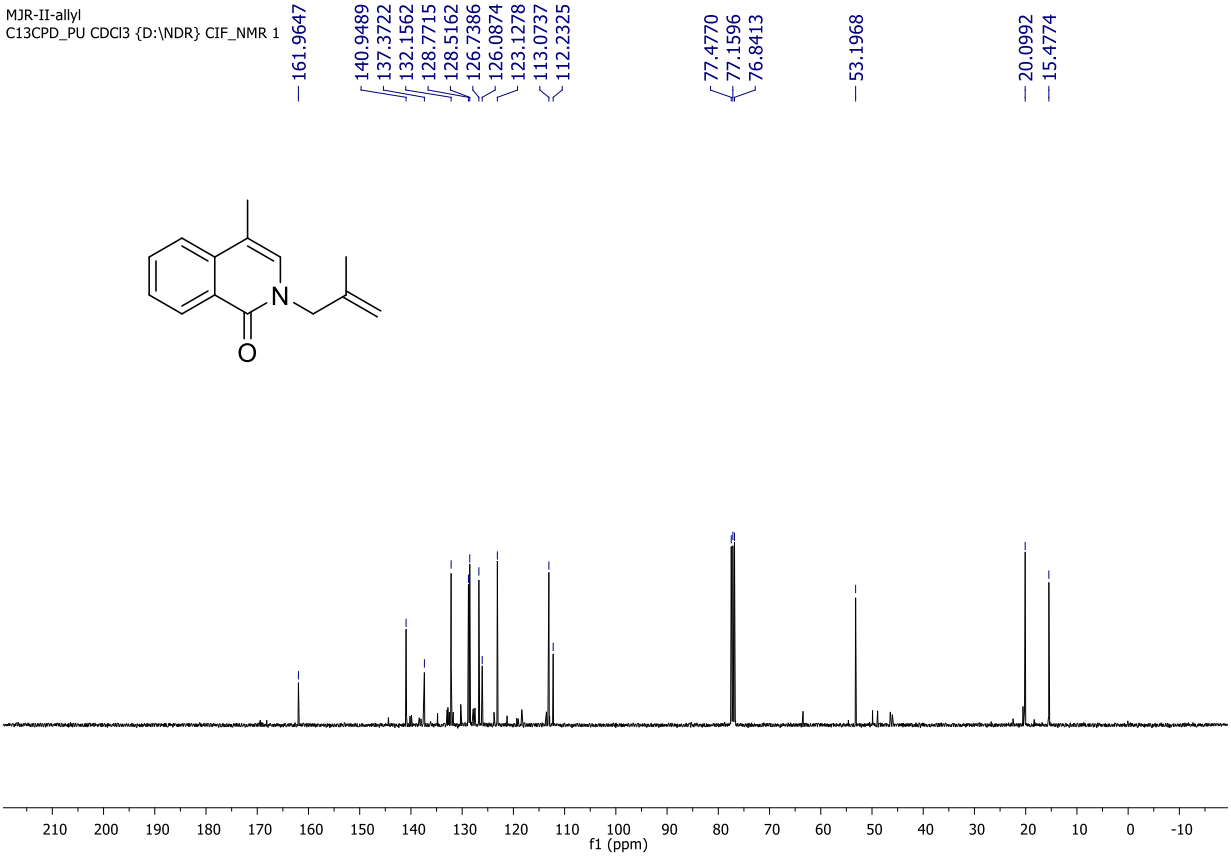
^{13}C **NMR**-spectrum (100 MHz, $CDCl_3$) of **4a**



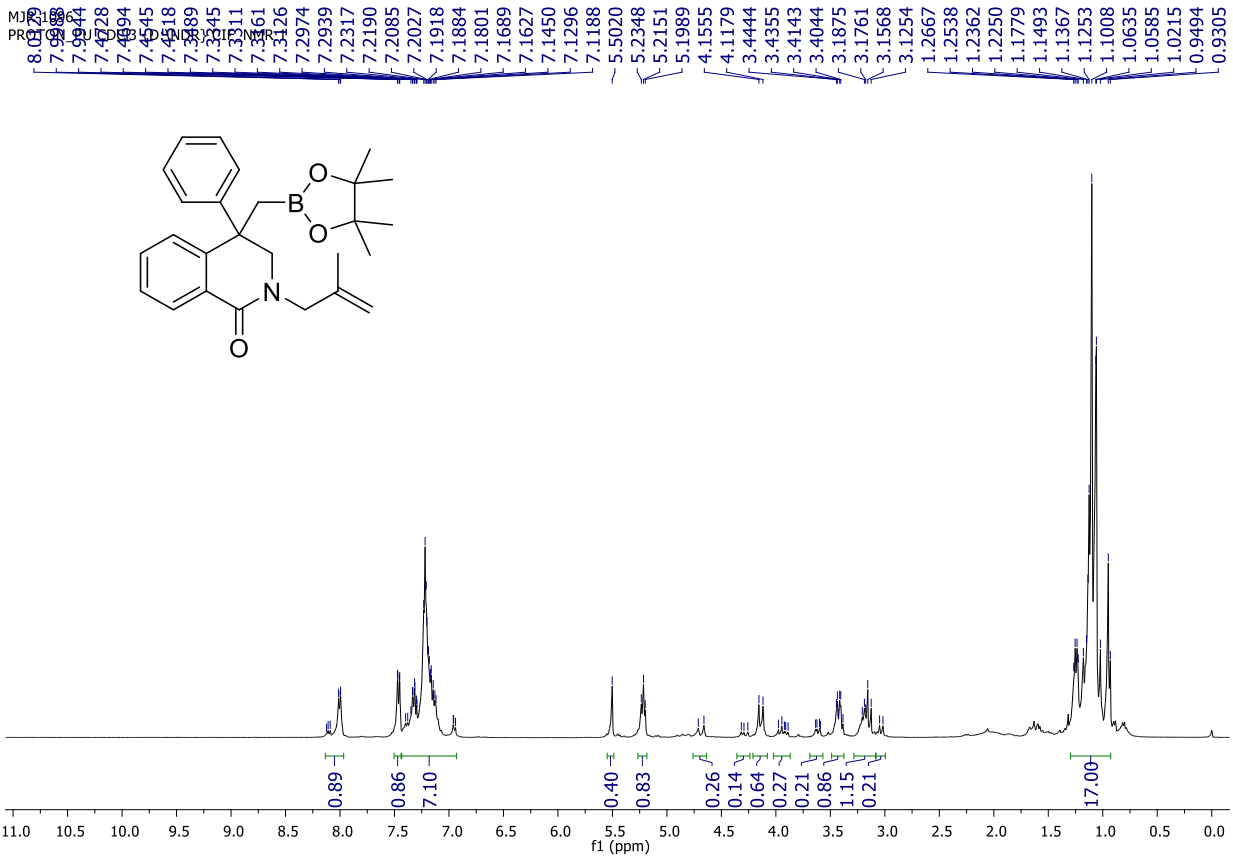
^{1}H **NMR**-spectrum (400 MHz, $CDCl_3$) of **4b**



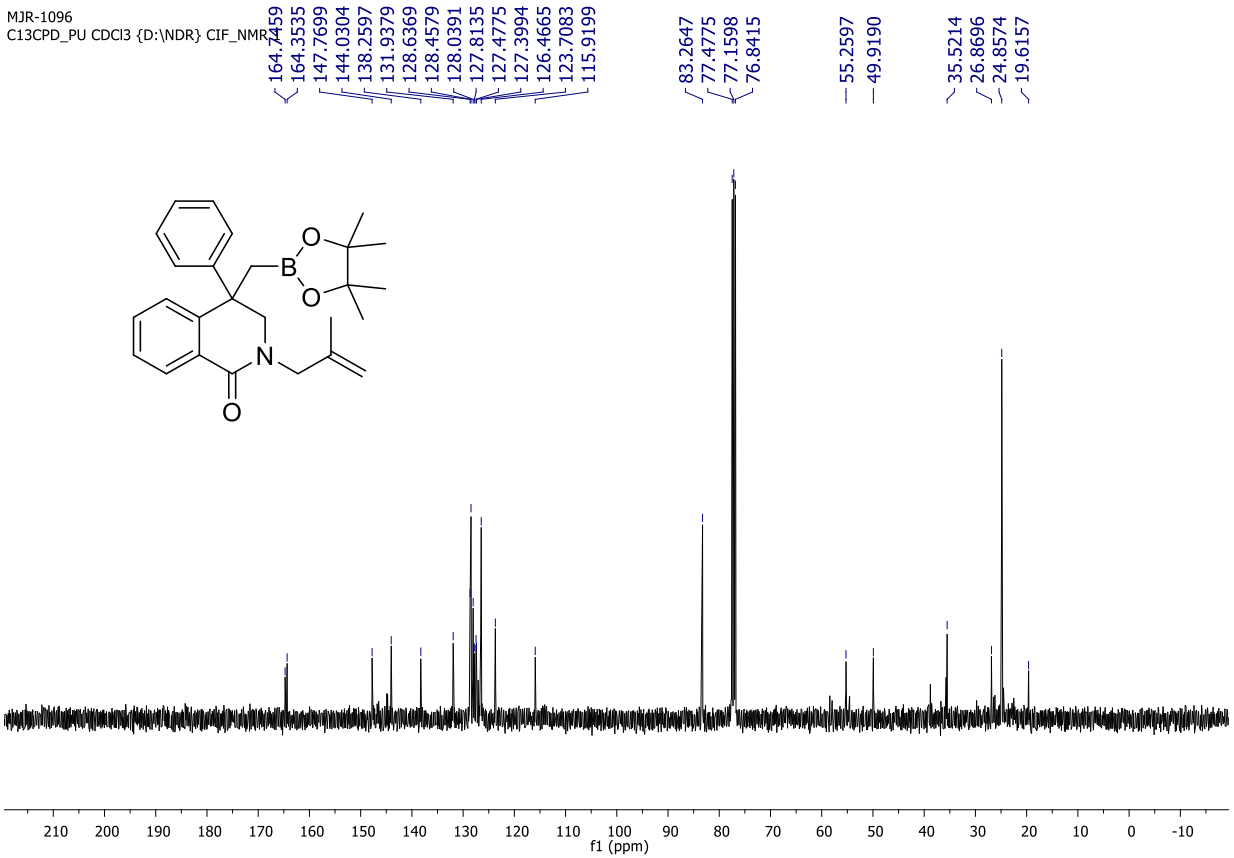
^{13}C **NMR**-spectrum (100 MHz, $CDCl_3$) of **4b**



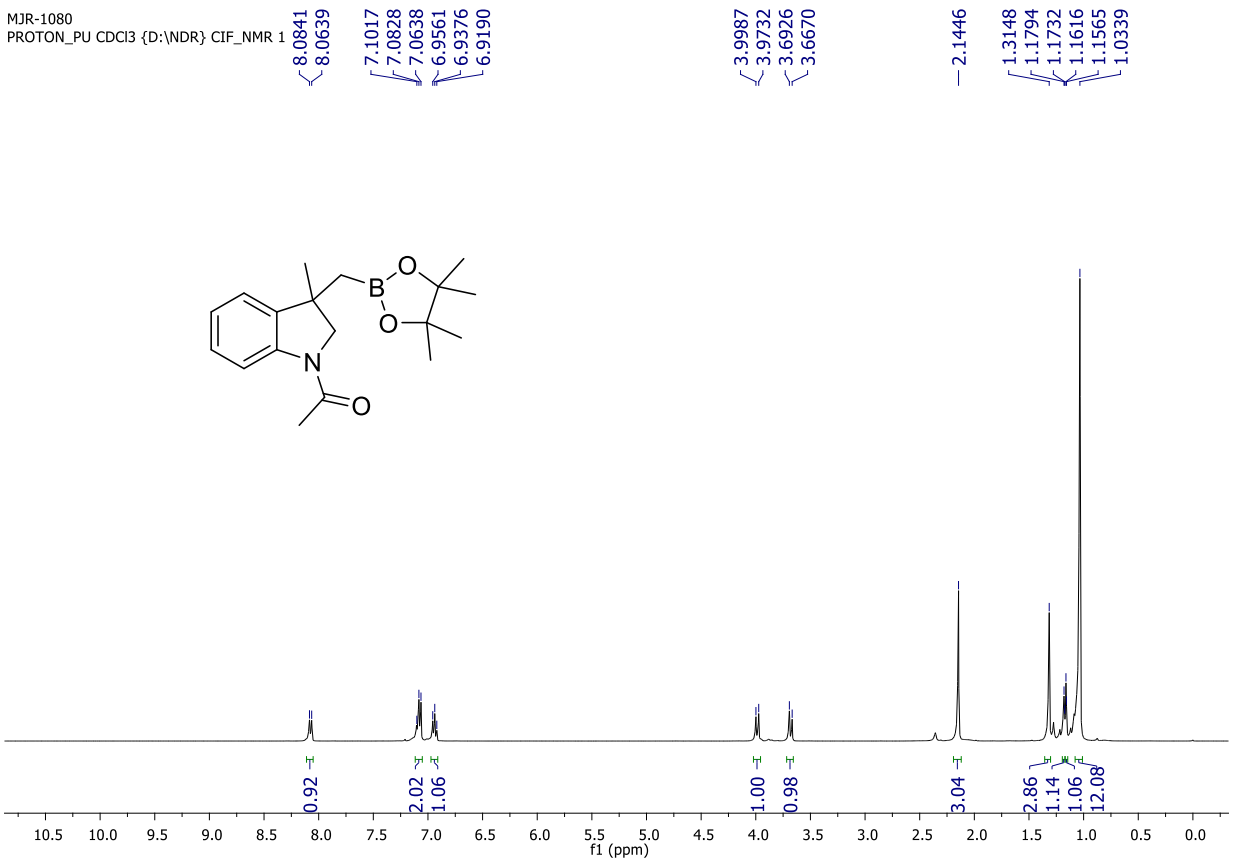
^{1}H **NMR**-spectrum (400 MHz, $CDCl_3$) of **4c**



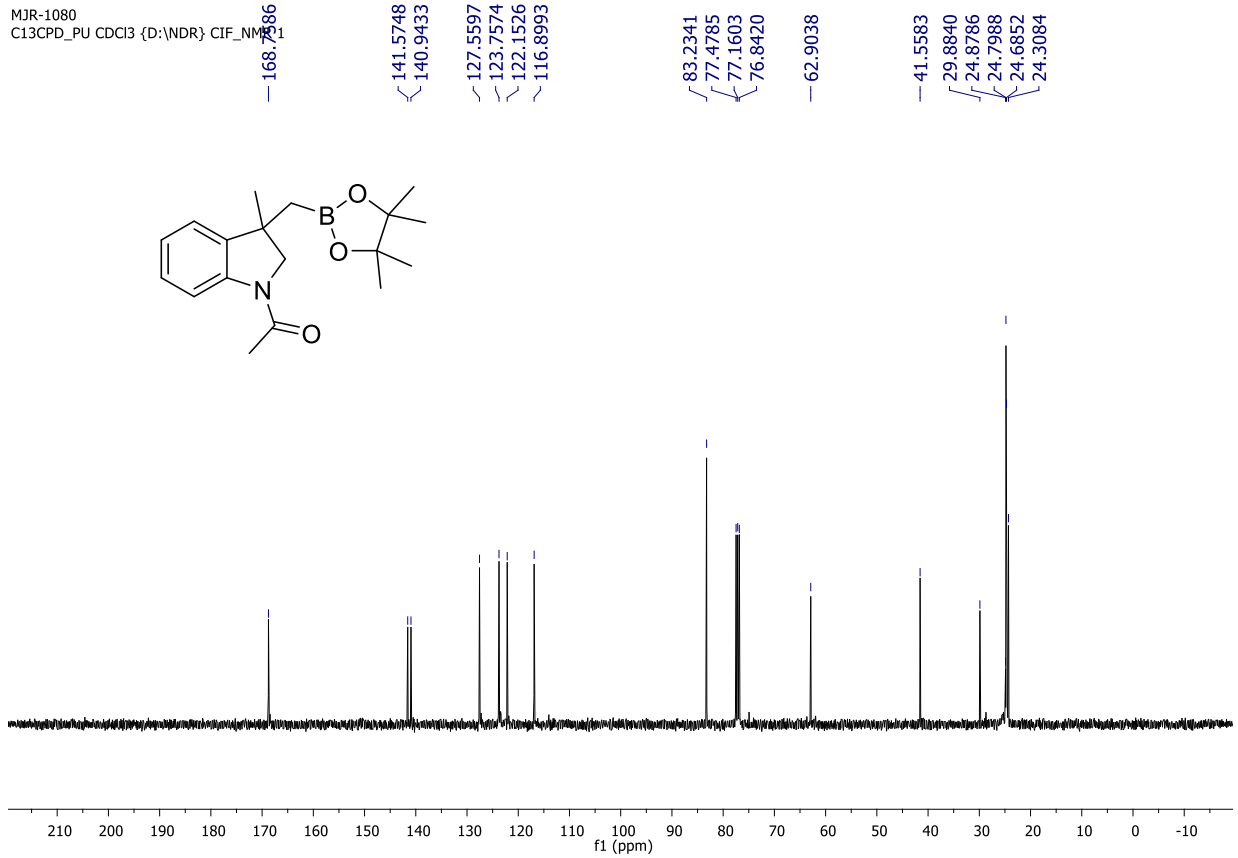
^{13}C **NMR**-spectrum (100 MHz, $CDCl_3$) of **4c**



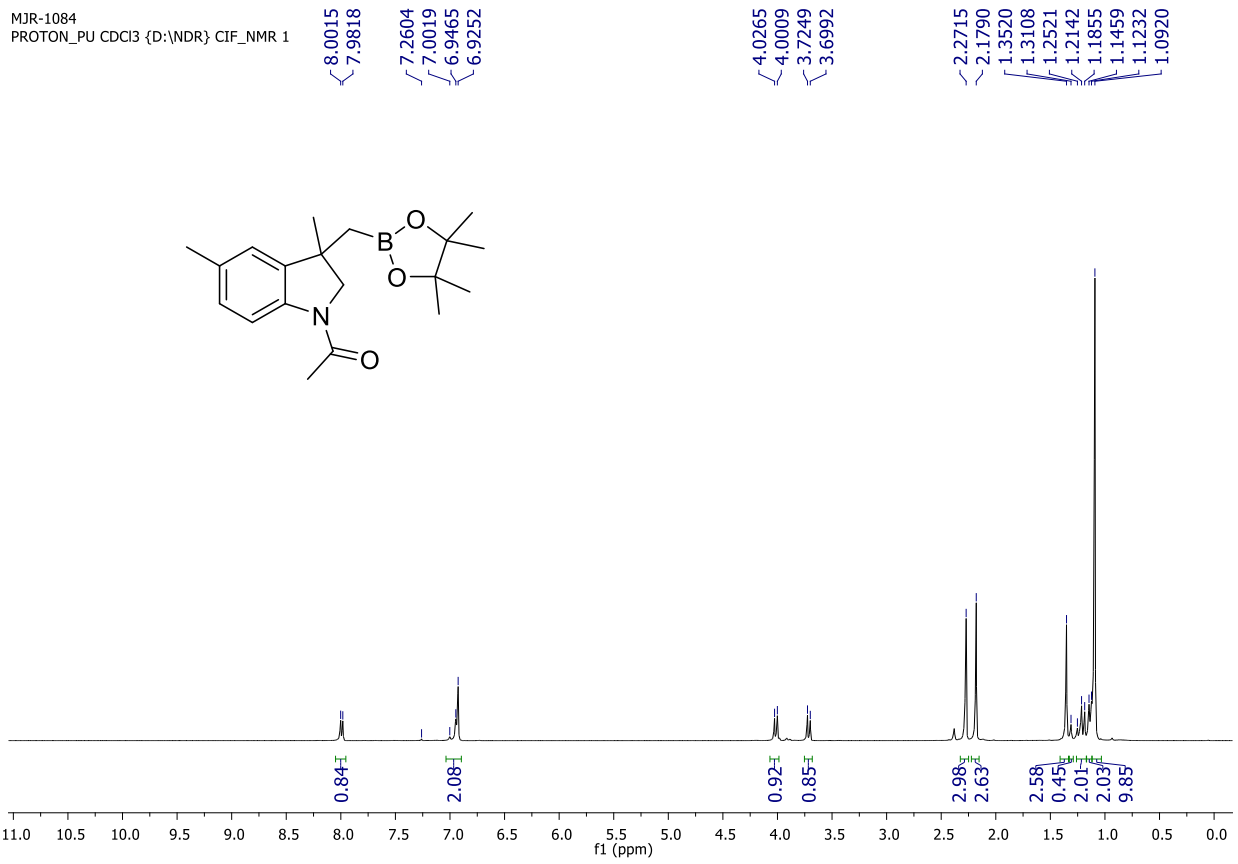
^{1}H **NMR**-spectrum (400 MHz, $CDCl_3$) of **6a**



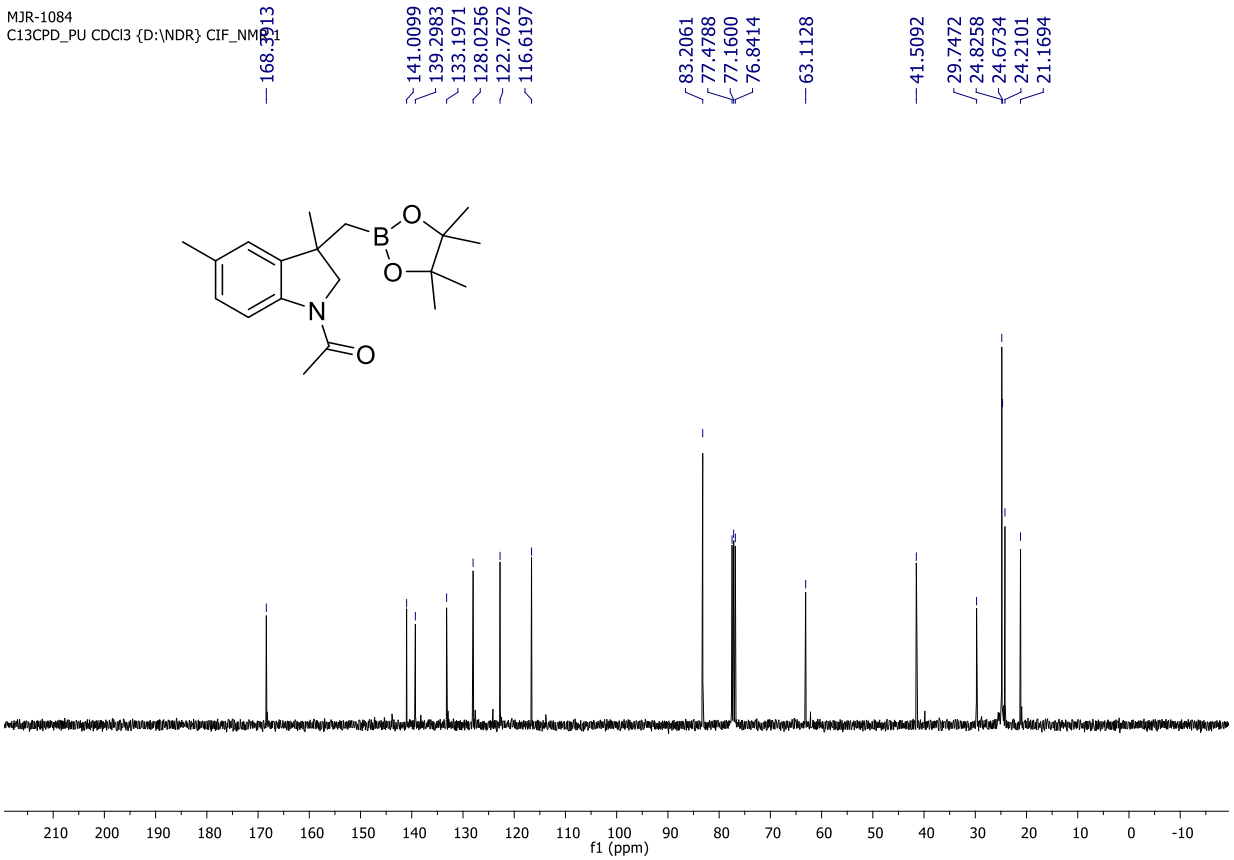
^{13}C **NMR**-spectrum (100 MHz, $CDCl_3$) of **6a**



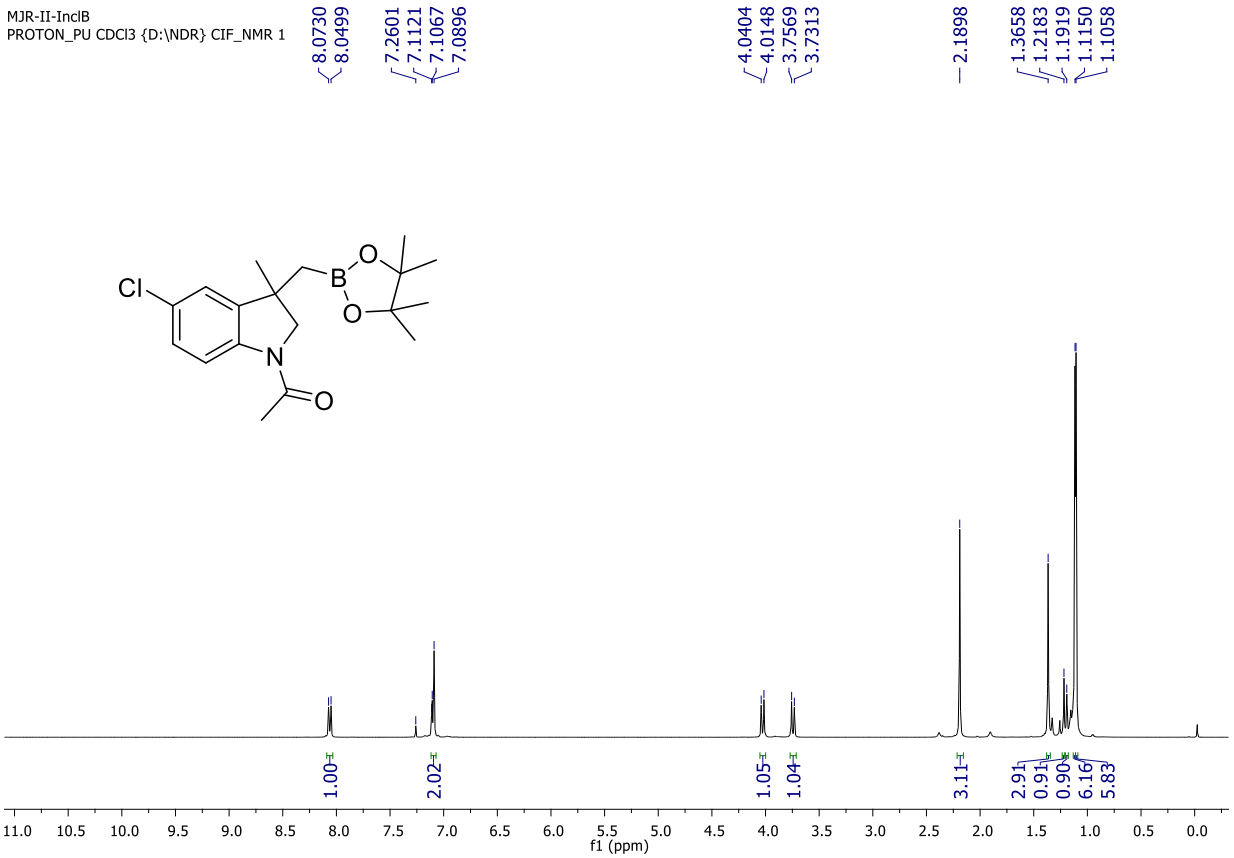
^{1}H **NMR**-spectrum (400 MHz, $CDCl_3$) of **6b**



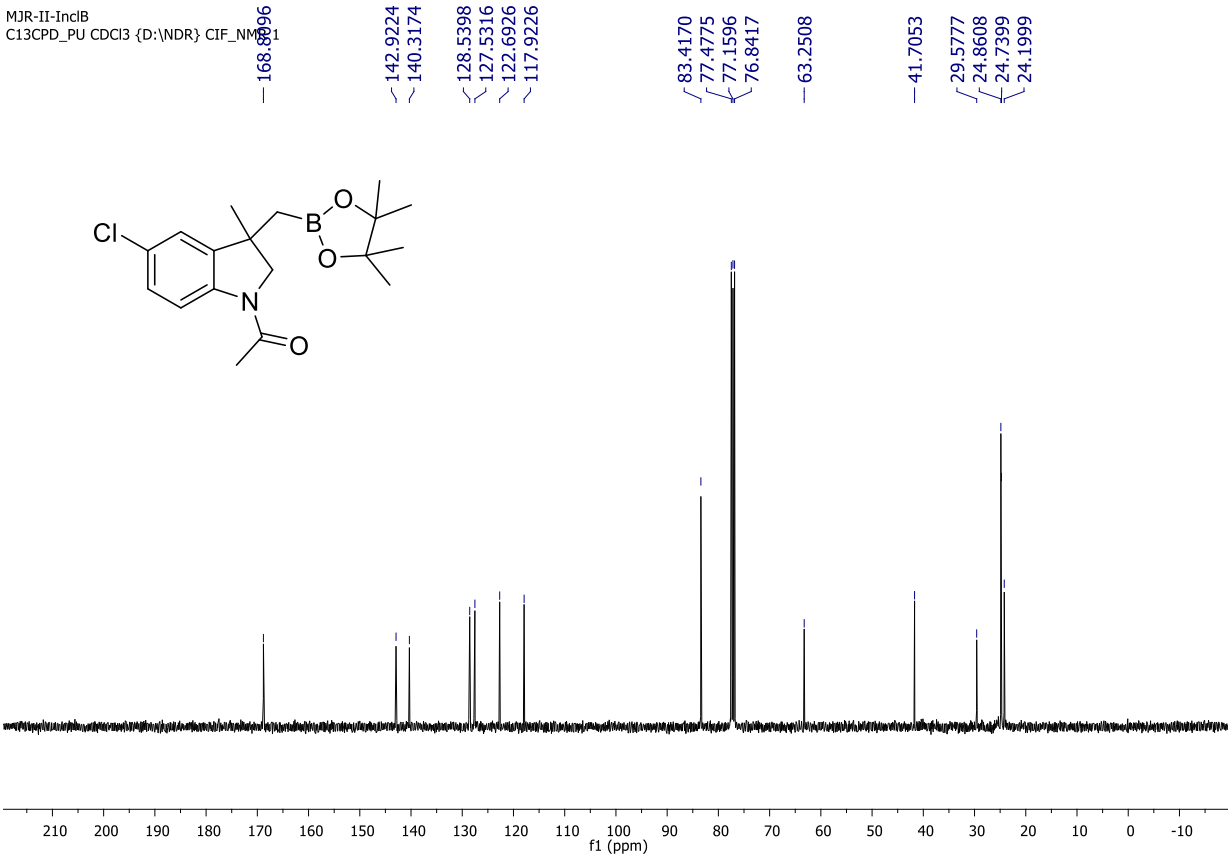
^{13}C **NMR**-spectrum (100 MHz, $CDCl_3$) of **6b**



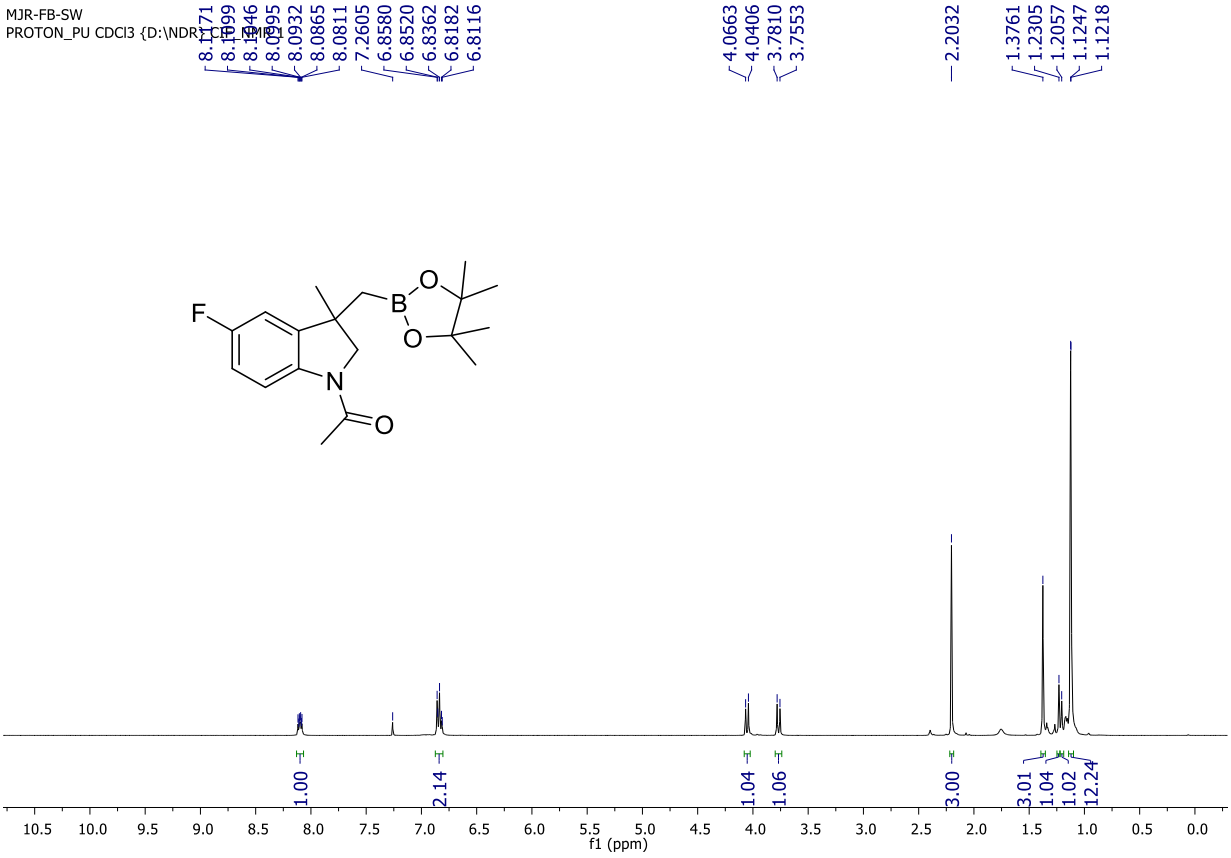
^{1}H **NMR**-spectrum (400 MHz, $CDCl_3$) of **6c**



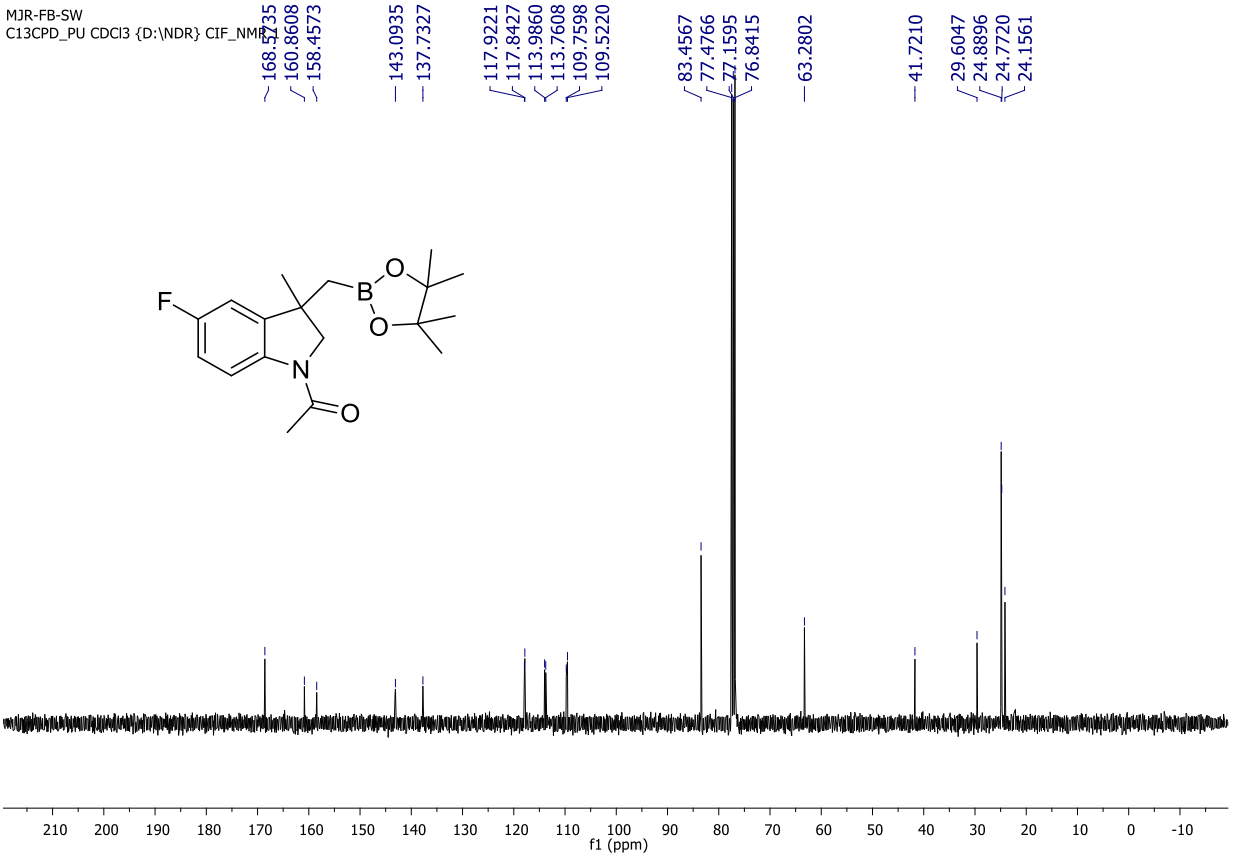
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **6c**



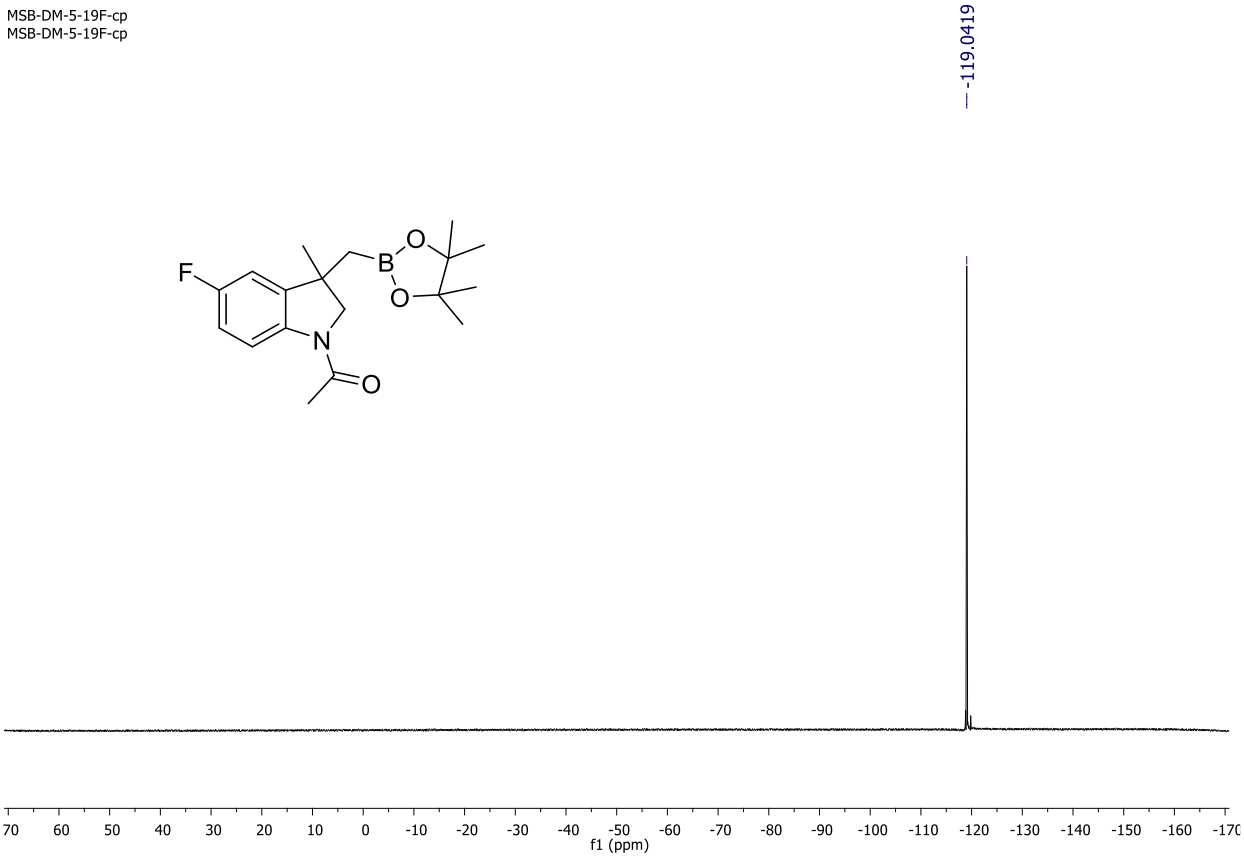
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **6d**



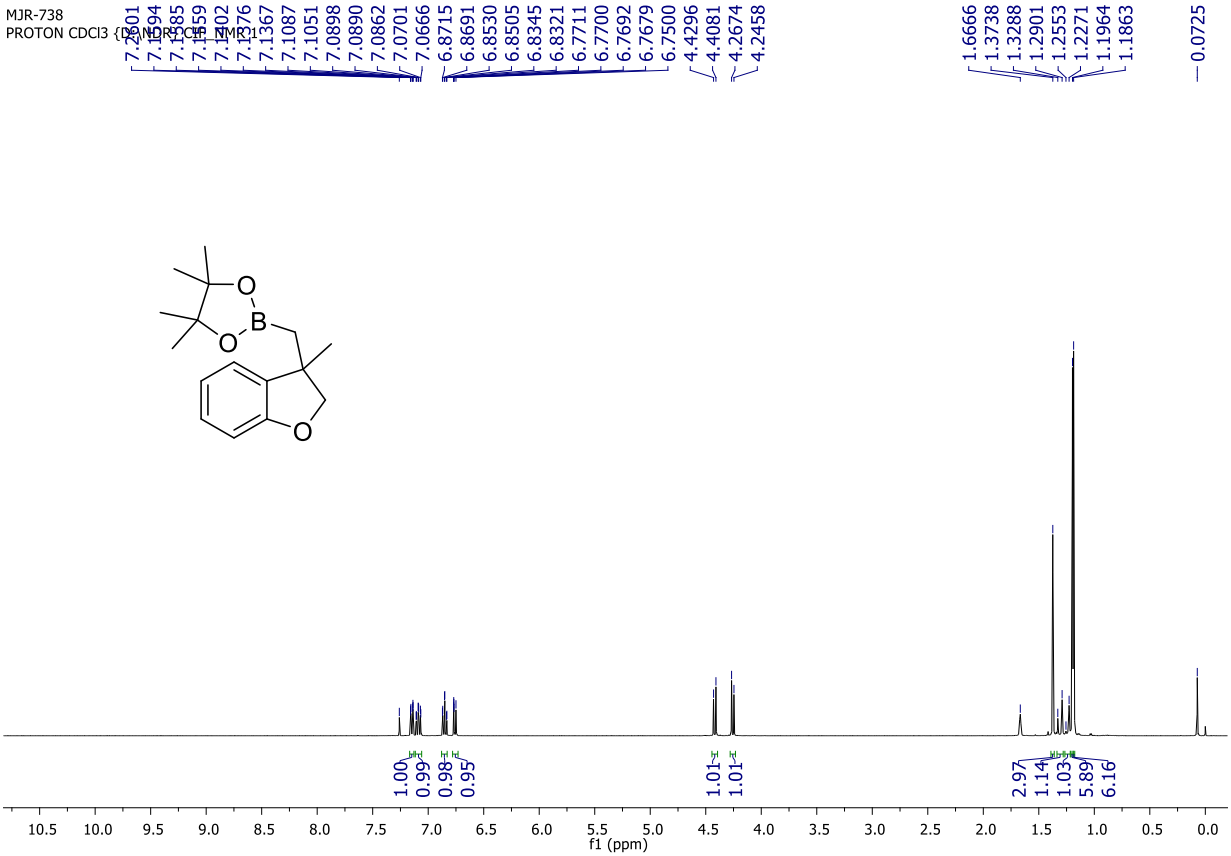
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **6d**



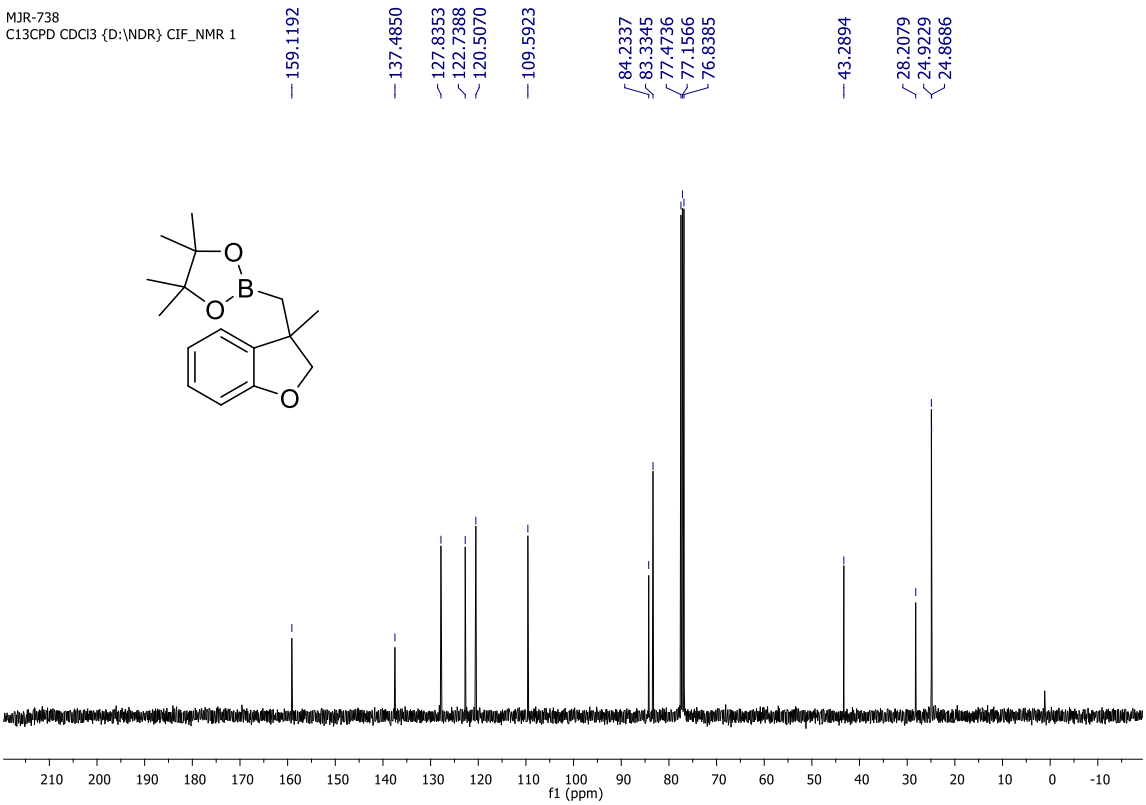
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **6d**



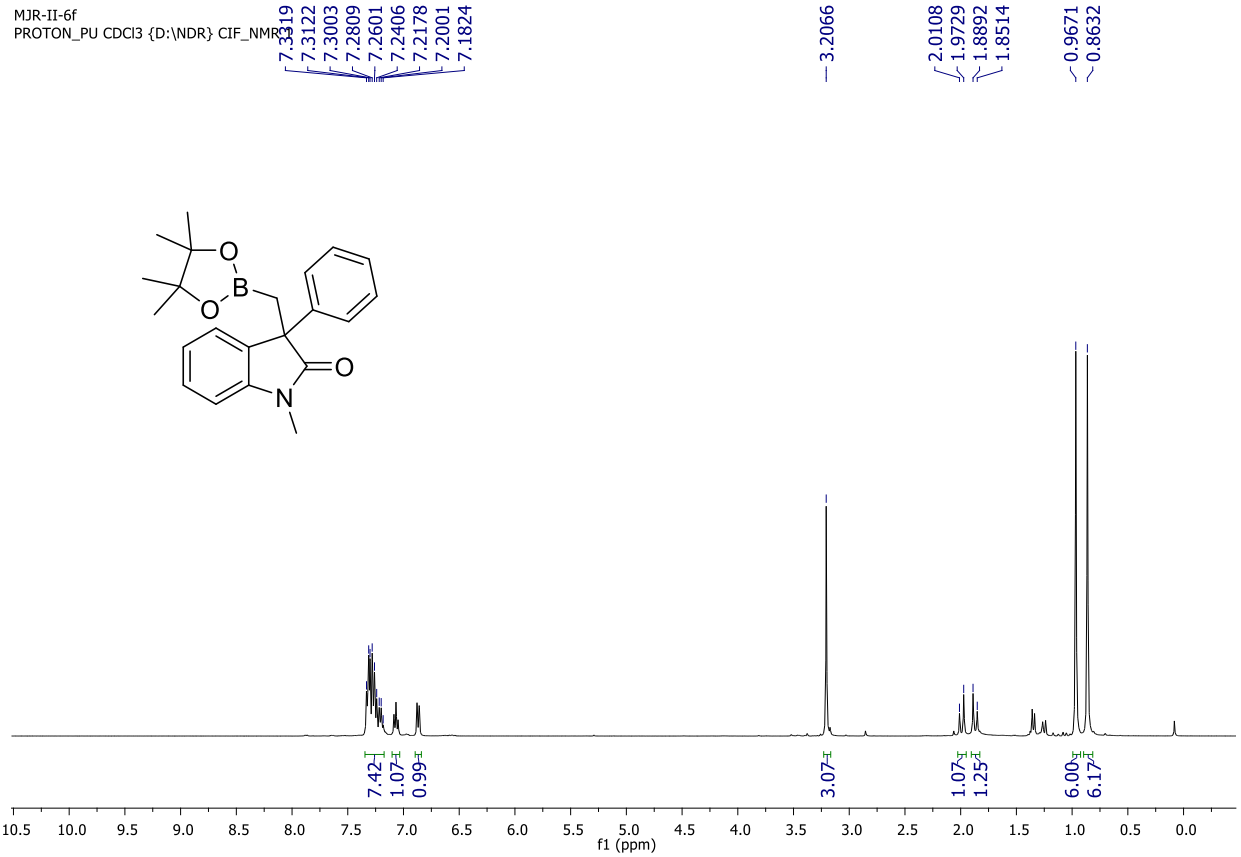
^{1}H **NMR**-spectrum (400 MHz, $CDCl_3$) of **6e**



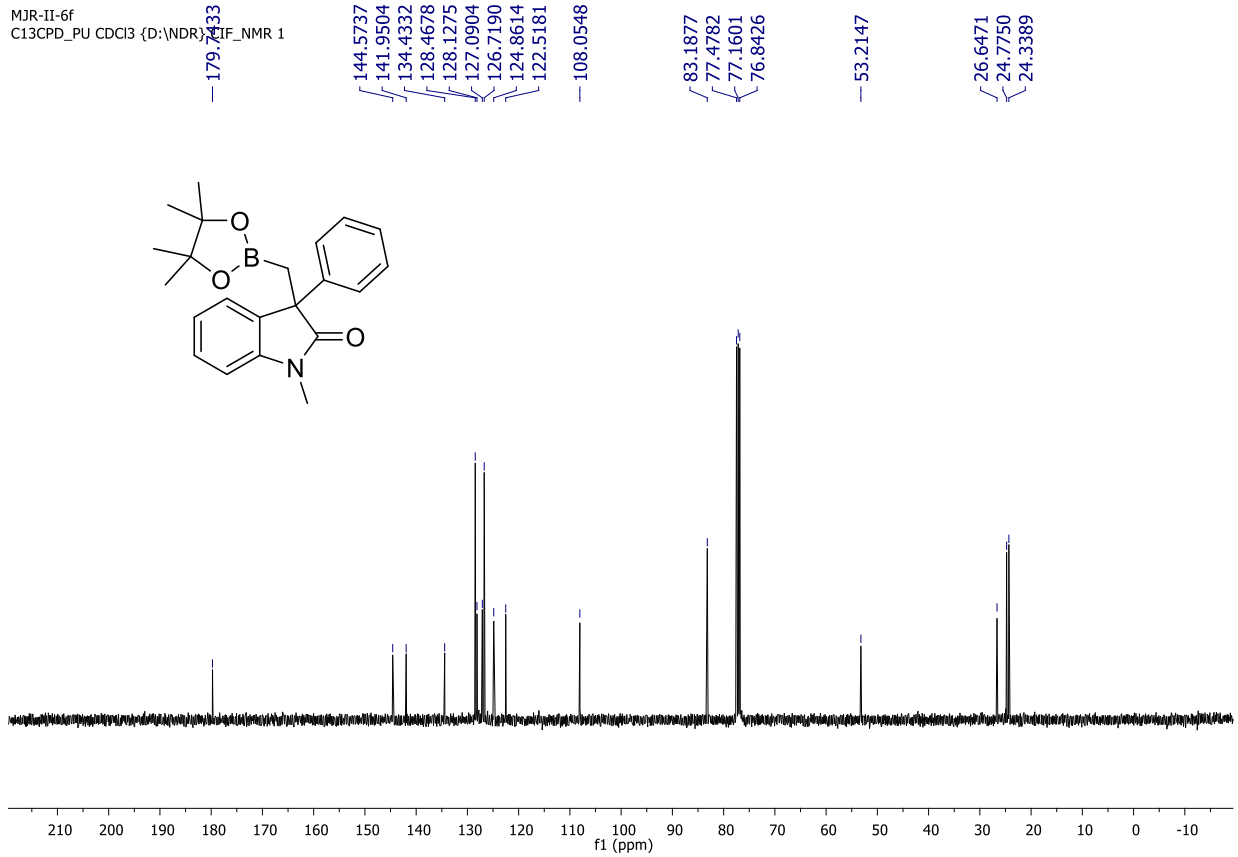
^{13}C **NMR**-spectrum (100 MHz, $CDCl_3$) of **6e**



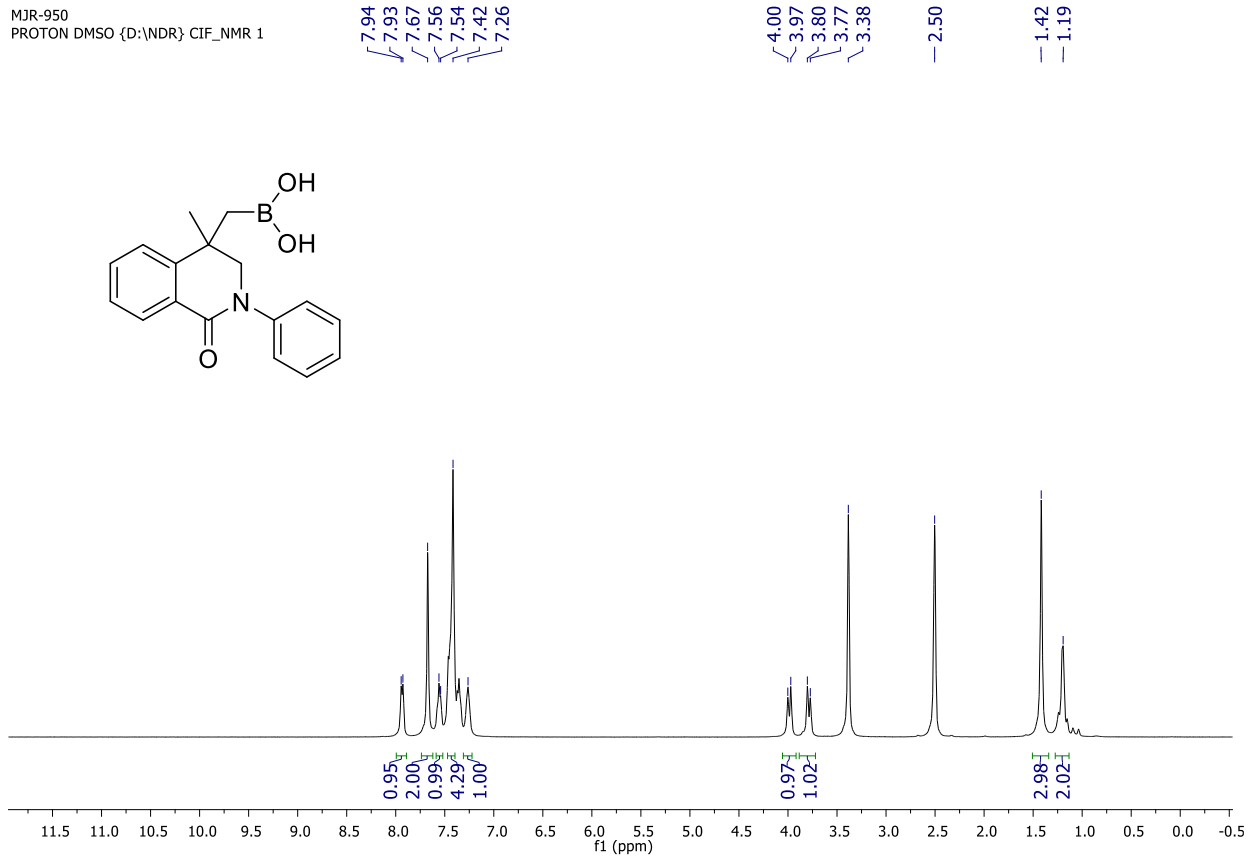
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **6f**



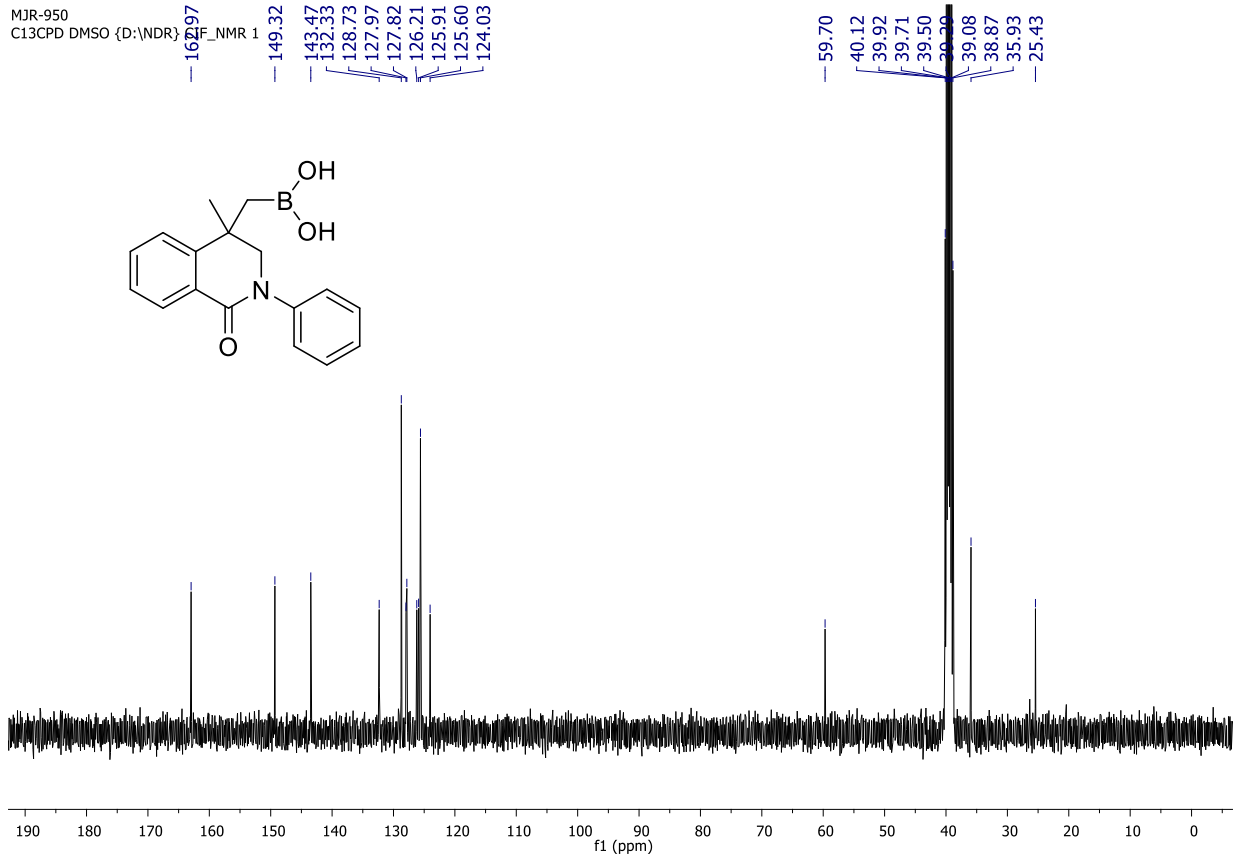
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **6f**



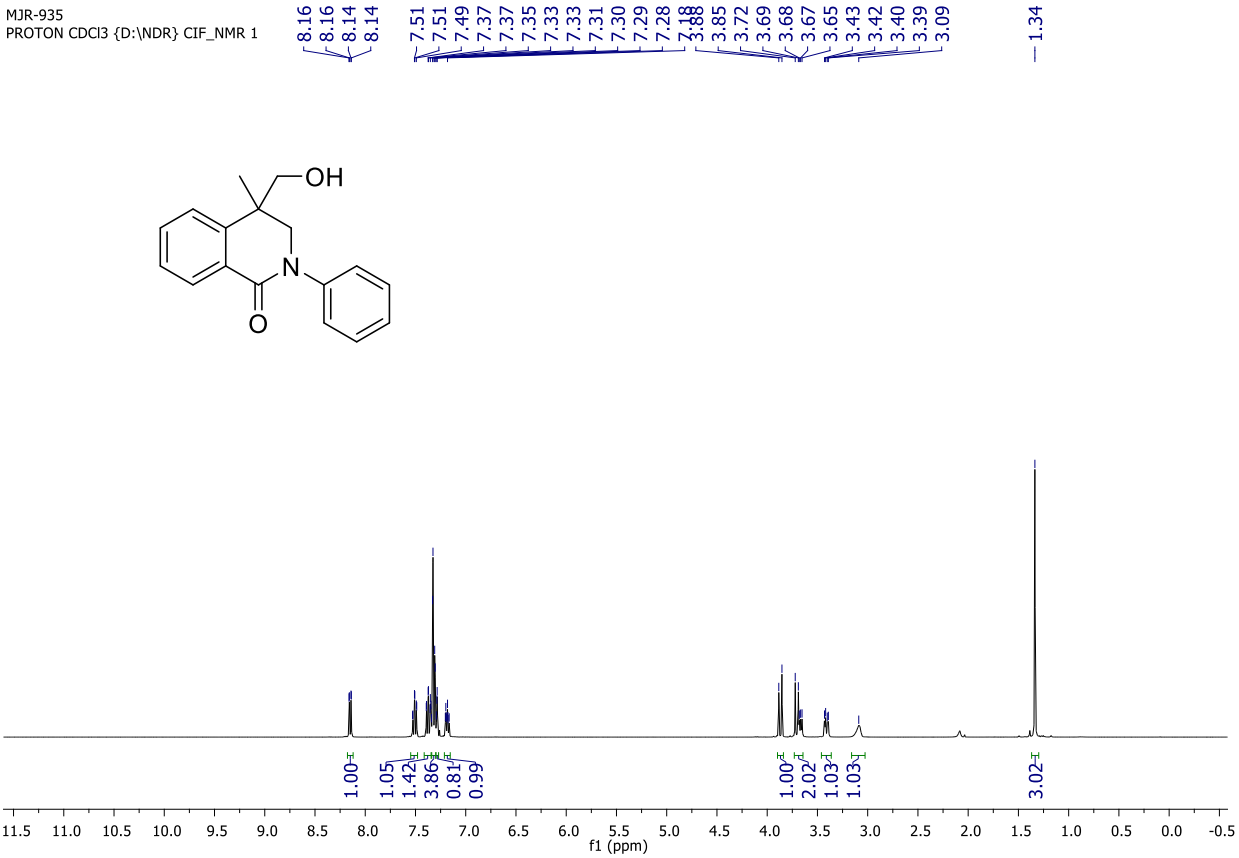
^{1}H **NMR**-spectrum (400 MHz, DMSO) of **7a**



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



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



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