Supporting Information for

Substrate-Controlled Divergent Synthesis of Substituted Carbazoles through Cascade Reaction of 2-Alkenylndoles with α,β-Unsaturated Ketones

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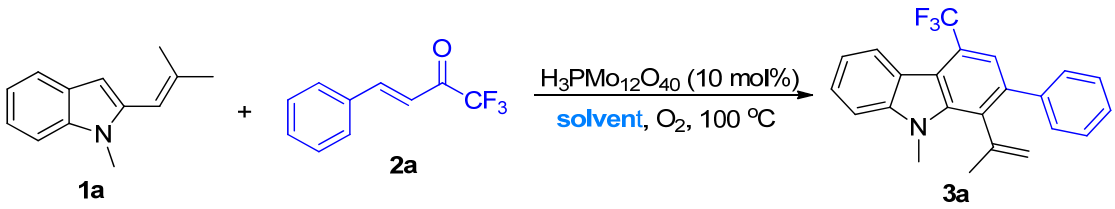
1. General information

All manipulations were carried out in an oven-dried pressure tube under noted conditions. Commercial reagents were purchased from Adamas, Aladdin, Merck, and used without further purification. The products were purified by column chromatography with Huanghai Silica Gel (200-300 mesh) as the stationary phase. All reaction solvents were purchased from Adamas, Aladdin, Merk and used without further purification. (200-300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-D_6 on a Bruker Avance NEO 400 spectrometer with TMS as internal standard (400 MHz ^{1}H, 101 MHz ^{13}C) at ambient temperature. The structures of known compounds were further corroborated by comparing their ^{1}H NMR, ^{13}C NMR data with those of the literature. Any chemical shifts (δ) are reported as parts per million (ppm) with reference to tetramethylsilane (TMS) (δ H = 0.00 ppm) unless otherwise stated. The coupling constants (J) are reported in Hz, and signal multiplicities are reported as singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), multiplet (m), or broad (br). Data for ^{13}C NMR are reported in terms of chemical shift (ppm, scale), multiplicity, and coupling constant (Hz). HRMS were obtained on a Waters G2-Xs Q-TOF mass spectrometer by the ESI method.

2. Additional optimization data

Table S1. Solvent Screen for 1,2-Addition Cascade Approach[a]

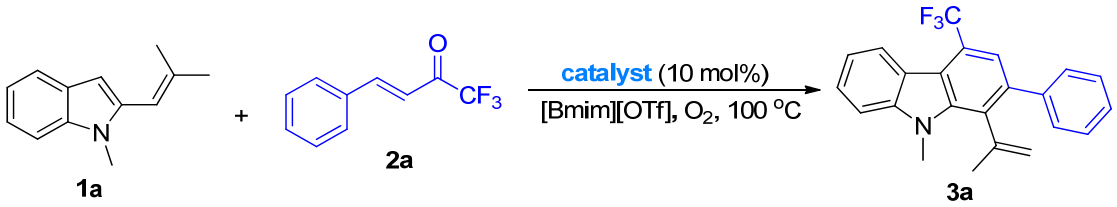


entry	solvent	yield (%)[b]
1	[Bmim][OTf]	84
2	DCE	nd
3	Dioxane	nd
4	THF	trace
5	DMF	nd
6	DMSO	nd
7	Toluene	nd
8	HFIP	nd
9	choline chloride/ethylene glycol (1:2)	trace
10	Choline chloride/1,4-butanediol (1:2)	trace
11	choline chloride/urea (1:2)	nd
12	choline chloride/thiourea (1:2)	nd
13	[Bmim]NTf_2	15
14	[Bmim]PF_6	35

15	[Bmim]BF_4	trace
16	[Bmim]Br	trace
17	[Bmim]Cl	nd
18	[Bmim][OAc]	nr
19	[Emim][OTf]	47
20	[Hmim][OTf]	78
21	[Omim][OTf]	83

[a]**1a** (0.20 mmol), **2a** (0.30 mmol), $H_3PMo_{12}O_{40}$ (10 mol%), and solvent (2 mL) at 100 °C for 24 h under O_2 atmosphere. Isolated yield after column chromatography. nd = not detected, nr = no reaction, DCE = 1,2-dicholoroethane, THF = tetrahydrofuran, HFIP = hexafluoroisopropanol.

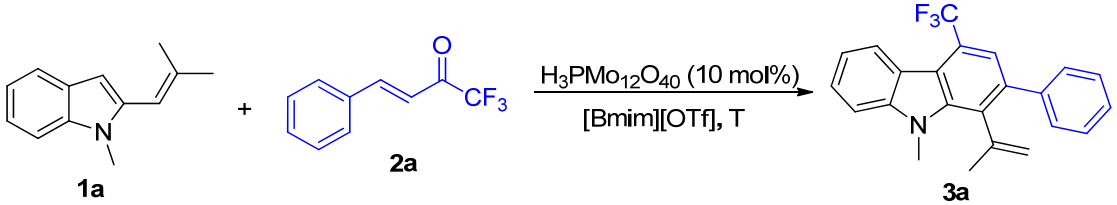
Table S2. Catalyst Screen 1,2-Addition Cascade Approach[a]



entry	catalyst	yield (%)[b]
1	$H_3PW_{12}O_{40}$	56
2	$H_4SiW_{12}O_{40}$	57
3	$HNTf_2$	50
4	HOTf	45
5	PTSA	nd
6	Mont-K 10	nd
7	MeOTf	22
8	TMSOTf	22
9	I_2	77
10	$Cu(OTf)_2$	nd
11	$Sc(OTf)_3$	25
12	$Y(OTf)_3$	33
13	$Yb(OTf)_3$	22
14	$Zn(OTf)_2$	nd
15	$In(OTf)_3$	20

[a]**1a** (0.20 mmol), **2a** (0.30 mmol), catalyst (10 mol%), and [Bmim][OTf] (2 mL) at 100 °C for 24 h under O_2 atmosphere. [b]Isolated yield after column chromatography.

Table S3. Other Parameters Screen 1,2-Addition Cascade Approach[a]

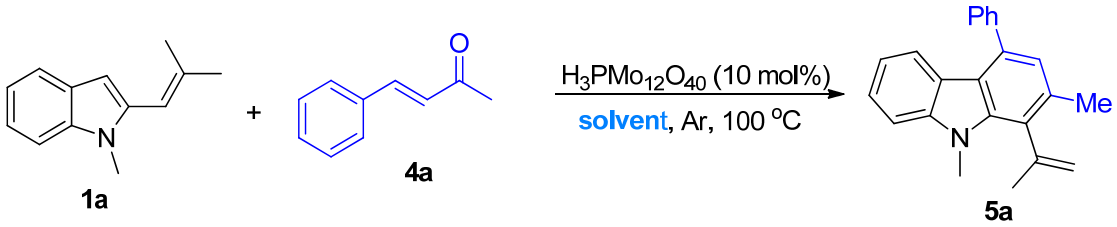


entry	atmosphere	Temp.(°C)	ratio of **1a**:**2a**	yield (%)[b]

1	O_2	120	1:1.5	48
2	O_2	80	1:1.5	80
3[c]	O_2	100	1:1.5	77
4[d]	O_2	100	1:1.5	70
5	O_2	100	1:2.0	76
6	O_2	100	1:1.2	72
7	Air	100	1:1.5	76
8[e]	O_2	100	1:1.5	69
9[f]	O_2	100	1:1.5	77

[a]**1a** (0.20 mmol), **2a** (0.30 mmol), catalyst (10 mol%), and [Bmim][OTf] (2 mL) at 100 °C for 24 h under O_2 atmosphere. [b]Isolated yield after column chromatography. [c]$H_3PMo_{12}O_{40}$ (20 mol%). [d]$H_3PMo_{12}O_{40}$ (5 mol%). [e][Bmim][OTf] (1 mL). [f][Bmim][OTf] (3 mL).

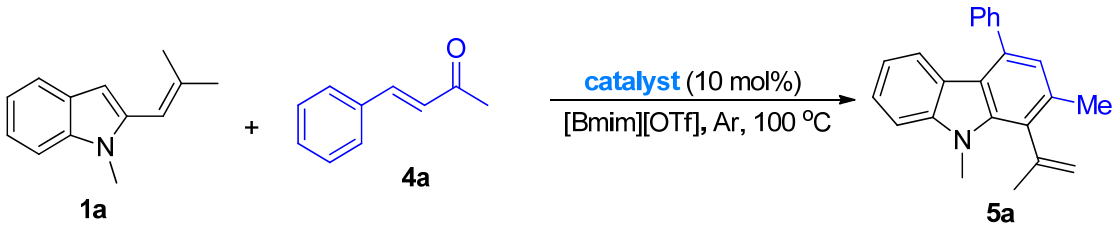
Table S4. Solvent Screen for 1,4-Addition Cascade Approach[a]



entry	solvent	Yield (%)[b]
1	[Bmim][OTf]	55
2	DCE	nd
3	TFE	nd
4	HFIP	nd
5	Dioxane	nd
6	DMSO	nd
7	Toluene	trace
8	HFIP	nd
9	[Bmim]PF_6	23
10	[Bmim]BF_4	nd
11	[Bmim]Br	15
12	[Bmim]Cl	10
13	[Bmim][OAc]	nd
14	[Emim][OTf]	48
15	[Hmim][OTf]	56
16	[Omim][OTf]	52
17	[SO_3H-Bmim][OTf]	30

[a]**1a** (0.20 mmol), **3a** (0.20 mmol), $H_3PMo_{12}O_{40}$ (10 mol%), and solvent (2 mL) at 100 °C for 30 h under argon atmosphere. Isolated yield after column chromatography.

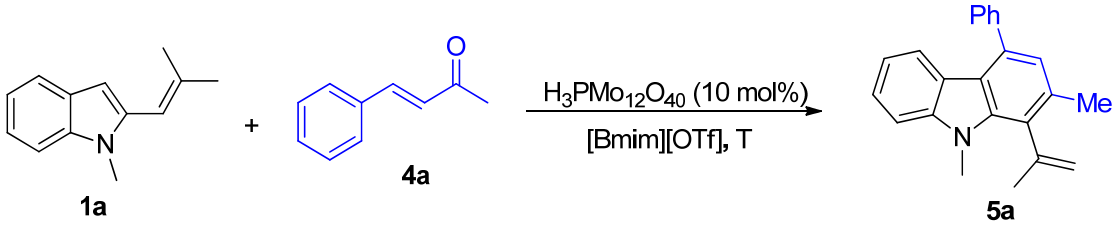
Table S5. Catalyst Screen for 1,4-Addition Cascade Approach[a]



entry	catalyst	Yield (%)[b]
1	$H_3PW_{12}O_{40}$	38
2	$H_4SiW_{12}O_{40}$	31
3	$HNTf_2$	24
4	HOTf	23
5	PTSA	20
6	TMSOTf	27
7	$FeCl_3$	trace
8	$BiCl_3$	trace
9	$BF_3{\cdot}OEt_2$	16

[a]**1a** (0.20 mmol), **2a** (0.320 mmol), catalyst (10 mol%), and [Bmim][OTf] (2 mL) at 100 °C for 30 h under argon atmosphere. [b]Isolated yield after column chromatography.

Table S6. Other Parameters Screen for 1,4-Addition Cascade Approach[a]



entry	atmosphere	Oxidant	Temp.(°C)	Ratio of **1a**:3**a**	Yield (%)[b]
1	O_2	-	120	1:1	38
2	Ar	$K_2S_2O_8$	100	1:1	10
3	Ar	$Na_2S_2O_8$	100	1:1	14
4	Ar	PhIO	100	1:1	trace
5	Ar	TEMPO	100	1:1	nd
6	Ar	DDQ	100	1:1	nd
7	Ar	-	100	1:1.5	54
8	Ar	-	120	1:1	52
9	Ar	-	80	1:1	45
10[c]	Ar	-	100	1.1	55
11[d]	Ar	-	100	1.1	30
12[e]	Ar	-	100	1.1	38
13[f]	Ar	-	100	1.1	56
14[g]	Ar	-	100	1.1	52
15[h]	Ar	-	100	1.1	55

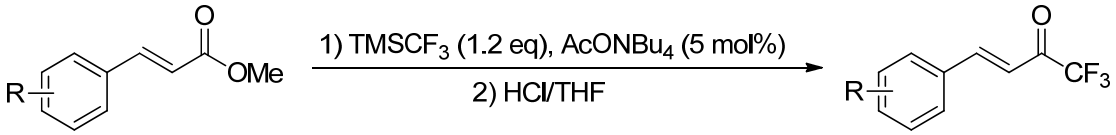
[a]**1a** (0.20 mmol), **2a** (0.30 mmol), $H_3PMo_{12}O_{40}$ (10 mol%), oxidant (1.1 eq.), and [Bmim][OTf] (2 mL) for 30 h.

[b]Isolated yield after column chromatography. [c]$H_3PMo_{12}O_{40}$ (20 mol%). [d]$H_3PMo_{12}O_{40}$ (5 mol%). [e][Bmim][OTf] (1 mL). [f][Bmim][OTf] (3 mL). [g]24h. [h]36h.

3. Preparation of starting materials

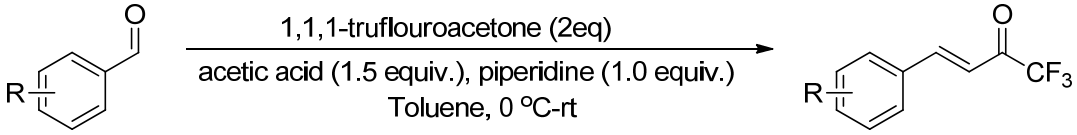
3.1 Preparation of α, β-unsaturated trifluoromethyl ketones

General Procedure A: the synthesis of α, β-unsaturated trifluoromethyl ketones from ester and $TMSCF_3$.

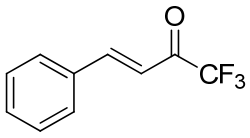


Following Mukaiyama's procedure,[1] α,β-unsaturated ester (5 mmol) in toluene (10 mL), and $TMSCF_3$ (0.89 mL, 6 mmol, 1.2 eq) were added to a solution of $AcONBu_4$ (75 mg, 0.25 mmol, 5 mol%) in toluene (10 mL) at 0 °C. The reaction was allowed to stir at room temperature for over 1 h and quenched with saturated aqueous NH_4Cl (10 mL). The mixture was extracted with Et_2O, and dried over anhydrous Na_2SO_4, then evaporated under reduced pressure. The residue was dissolved in a mixture of HCl (1.0 M, 10.0 mL) and THF (10 mL), and the mixture was stirred for 16 h. The mixture was extracted with EtOAc and the organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Finally, the crude product was purified by silica gel column chromatography (ethyl acetate/petroleum ether as the eluent) to afford the corresponding α, β-unsaturated trifluoromethyl ketones.

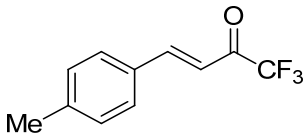
General Procedure B: the Synthesis of α,β-unsaturated trifluoromethyl ketones from aldehyde and trifluoroacetone.



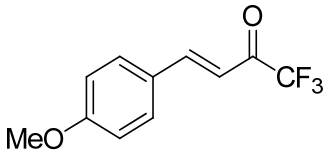
Following literature procedure,[2] to an oven-dried 35 mL pressure tube equipped with magnetic bar, were quickly added aldehyde (5 mmol), acetic acid (0.43 mL, 7.5 mmol, 1.5 equiv.), piperidine (0.496 mL, 5 mmol, 1.0 eq.), and 1,1,1-truflouroacetone (0.895 mL, 10 mmol，2eq.), and 5 mL of dry toluene at 0 °C. Then the tube was sealed and the reaction mixture was stirred for 2 h at this temperature and 16-24 h at room temperature. Upon completion, the mixture was quenched with a saturated aqueous solution of ammonium chloride and was extracted with EtOAc (3×15 mL). The organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (ethyl acetate/petroleum ether as the eluent) to give the corresponding α,β-unsaturated trifluoromethyl ketones.



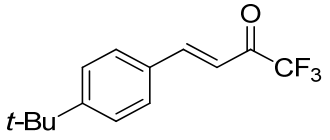
(*E*)-1,1,1-trifluoro-4-phenylbut-3-en-2-one (**2a**). The title compound was synthesized via the General Procedure A. The crude material was purified by ethyl acetate/petroleum ether = 1:50 as an eluent, colorless liquid, 65% yield (1.30 g, 10 mmol scale). All spectral data are in accord with the literature. [1] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 16.0 Hz, 1H), 7.66-7.63 (m, 2H), 7.53-7.43 (m, 3H), 7.05 (dd, *J* = 16.0, 0.8 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 180.55 (q, *J* = 35.6 Hz), 150.17, 133.34, 132.35, 129.25, 120.74 (q, *J* = 291.8 Hz), 116.65. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -77.61.



(*E*)-1,1,1-trifluoro-4-(p-tolyl)but-3-en-2-one (2b). The title compound was synthesized via the General Procedure A. The crude material was purified by ethyl acetate/petroleum ether = 1:50 as an eluent, colorless liquid, 60% yield (0.642 g, 5 mmol scale). All spectral data are in accord with the literature. [1] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 16.0 Hz, 1H), 7.55-7.53 (m, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 16.0 Hz, 1H), 2.42 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 180.56 (q, *J* = 35.4 Hz), 150.27, 143.40, 130.70, 130.02, 129.36, 120.82 (q, *J* = 292.0 Hz), 115.04, 21.69. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = 77.56.

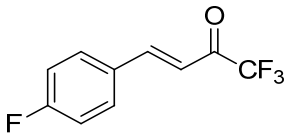


(*E*)-1,1,1-trifluoro-4-(4-methoxyphenyl)but-3-en-2-one (2c): The title compound was synthesized via the General Procedure A. The crude material was purified by ethyl acetate/petroleum ether = 1:50 as an eluent, light yellow solid, 46% yield (0.265 g, 2.5 mmol scale). All spectral data are in accord with the literature. [1] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 15.6 Hz, 1H), 7.62 (dt, *J* = 10.0, 3.2 Hz, 2H), 6.97 (dt, *J* = 9.6, 2.4 Hz, 2H), 6.91 (dq, *J* = 15.6, 0.8 Hz, 1H), 3.87 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 180.42 (q, *J* = 35.0 Hz), 163.21, 149.98, 131.41, 126.17, 120.91 (q, *J* = 292.0 Hz), 114.76, 114.03, 55.52. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -77.50.

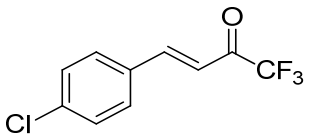


(*E*)-4-(4-(tert-butyl)phenyl)-1,1,1-trifluorobut-3-en-2-one (2d). The title compound was synthesized via the General Procedure B. The crude material was purified by ethyl acetate/petroleum ether = 1:50 as an eluent, light yellow liquid, 62% yield (0.318 g, 2 mmol scale). All spectral data

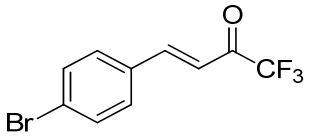
are in accord with the literature. [5] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 15.6 Hz, 1H), 7.60 (dd, *J* = 6.0, 1.6 Hz, 2H), 7.50 (dd, *J* = 6.4, 2.0 Hz, 2H), 7.03 (d, *J* = 16.0 Hz, 1H), 1.36 (d, *J* = 1.2 Hz, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 180.56 (q, *J* = 35.2 Hz), 156.44, 150.15, 130.68, 129.24, 126.28, 120.84 (q, *J* = 291.9 Hz), 115.76, 35.17, 31.02. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -77.53.



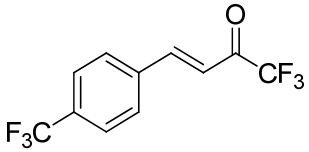
(*E*)-1,1,1-trifluoro-4-(4-fluorophenyl)but-3-en-2-one (2e): The title compound was synthesized via the General Procedure A. The crude material was purified by ethyl acetate/petroleum ether = 1:50 as an eluent, white solid, 38% yield (0.207 g, 2.5 mmol scale). All spectral data are in accord with the literature. [1] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 15.6 Hz, 1H), 7.68-7.63 (m, 2H), 7.18-7.12 (m, 2H), 6.97 (d, *J* = 16.0 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 180.41 (q, *J* = 35.6 Hz), 166.38 (d, *J* = 256.0 Hz), 131.45 (d, *J* = 9.1 Hz), 129.68 (d, *J* = 3.3 Hz), 120.70 (q, *J* = 291.8 Hz), 116.71, 116.49, 116.36 (d, *J* = 2.5 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -77.67, -105.59.



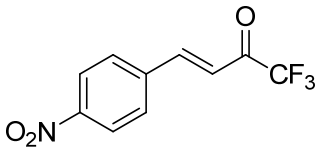
(*E*)-4-(4-chlorophenyl)-1,1,1-trifluorobut-3-en-2-one (2f): The title compound was synthesized via the General Procedure A. The crude material was purified by ethyl acetate/petroleum ether = 1:50 as an eluent, white solid, 58% yield (0.679 g, 5 mmol scale). All spectral data are in accord with the literature. [1] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 16.0 Hz, 1H), 7.58 -7.56 (m, 2H), 7.43-7.41 (m, 2H), 7.01 (dt, *J* = 16.0, 1.2 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 180.38 (q, *J* = 35.8 Hz), 148.53, 138.47, 131.79, 130.35, 129.59, 120.65 (q, *J* = 291.8 Hz), 117.02. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -77.69.



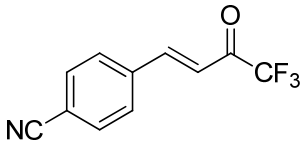
(*E*)-4-(4-bromophenyl)-1,1,1-trifluorobut-3-en-2-one (2g): The title compound was synthesized via the General Procedure A. The crude material was purified by ethyl acetate/petroleum ether = 1:50 as an eluent, white solid, 54% yield (0.375 g, 2.5 mmol scale). All spectral data are in accord with the literature. [1] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 16.0 Hz, 1H), 7.62 (dt, *J* = 8.8, 2.4 Hz, 2H), 7.53 (dt, *J* = 8.8, 2.4 Hz, 2H), 7.04 (dt, *J* = 16.0, 0.8 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 180.41 (q, *J* = 35.7 Hz), 148.64, 132.59, 132.20, 130.48, 127.00, 120.65 (q, *J* = 291.8 Hz), 117.12. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -77.66.



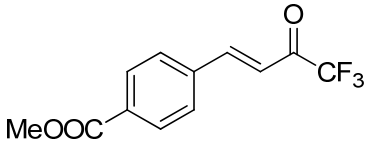
(*E*)-1,1,1-trifluoro-4-(4-(trifluoromethyl)phenyl)but-3-en-2-one (2h): The title compound was synthesized via the General Procedure A. The crude material was purified by ethyl acetate/petroleum ether = 1:50 as an eluent, colorless liquid, 34% yield (0.228 g, 2.5 mmol scale). All spectral data are in accord with the literature. [1] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 16.0 Hz, 1H), 7.77 (q, *J* = 8.4 Hz, 4H), 7.11-7.07 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 180.35 (q, *J* = 36.1 Hz), 147.91, 136.53 (d, *J* = 1.5 Hz, CF_3), 133.93 (q, *J* = 32.9 Hz), 129.26, 127.62 (q, *J* = 273.5 Hz), 126.23 (q, *J* = 3.7 Hz, CF_3-Ph-C2), 120.54 (q, *J* = 291.6 Hz), 118.87. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -63.20, -77.82.



(*E*)-1,1,1-trifluoro-4-(4-nitrophenyl)but-3-en-2-one (2i): The title compound was synthesized via the General Procedure B. The crude material was purified by ethyl acetate/petroleum ether = 1:50 as an eluent, white solid, 32% yield (0.118 g, 1.5 mmol scale). All spectral data are in accord with the literature. [1] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.31-8.29 (m, 2H), 8.00 (d, *J* = 16.0 Hz, 1H), 7.83-7.81 (m, 2H), 7.15 (dd, *J* = 16.0, 1.2 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 180.19 (q, *J* = 36.4 Hz), 149.52, 146.68, 139.04, 129.78, 124.39, 120.44, 120.27 (q, *J* = 291.6 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -77.78.

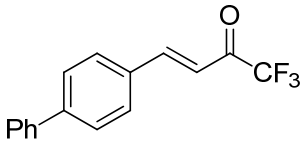


(*E*)-1,1,1-trifluoro-4-(4-(trifluoromethyl)phenyl)but-3-en-2-one (2j): The title compound was synthesized via the General Procedure B. The crude material was purified by ethyl acetate/petroleum ether = 1:50 as an eluent, white solid, 48% yield (0.270 g, 2.5 mmol scale). All spectral data are in accord with the literature. [1] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.99(d, *J* = 16.0 Hz, 1H), 7.77 (q, *J* = 8.4 Hz, 4H), 7.11-7.07 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 180.35 (q, *J* = 36.1 Hz), 147.91, 136.53 (d, *J* = 1.5 Hz), 133.93 (q, *J* = 32.9 Hz), 129.26, 127.62 (q, *J* = 273.5 Hz), 126.23 (q, *J* = 3.7 Hz), 120.54 (q, *J* = 291.6 Hz), 118.87. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -77.76.

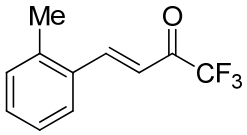


(*E*)-methyl 4-(4,4,4-trifluoro-3-oxobut-1-en-1-yl)benzoate (2k): The title compound was synthesized via the General Procedure B. The crude material was purified by ethyl acetate/petroleum ether = 1:50 as an eluent, white solid, 95% yield (0.368 g, 1.5 mmol scale). All spectral data are in accord with the literature. [3] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.10 (d, *J* = 8.4 Hz, 2H), 7.97 (d, *J* = 16.0 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 16.0 Hz, 1H), 3.94 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 180.38 (q, *J* = 36.1 Hz), 166.07, 148.42, 137.22, 133.05, 130.31, 128.99, 120.57

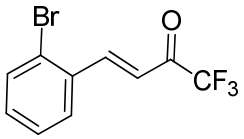
(q, *J* = 294.9 Hz), 118.65, 52.44. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -77.71.



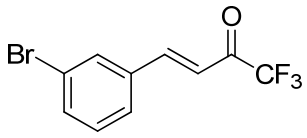
(*E*)-4-([1,1'-biphenyl]-4-yl)-1,1,1-trifluorobut-3-en-2-one (2l): The title compound was synthesized via the General Procedure A. The crude material was purified by ethyl acetate/petroleum ether = 1:50 as an eluent, white solid, 40% yield (0.276 g, 2.5 mmol scale). All spectral data are in accord with the literature. [4] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 16.0 Hz, 1H), 7.74-7.68 (m, 4H), 7.65 (dd, *J* = 7.2, 1.6 Hz, 2H), 7.51-7.47 (m, 2H), 7.44-7.40 (m, 1H), 7.08 (d, *J* = 16.0 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 180.52 (q, *J* = 35.5 Hz), 149.70, 145.14, 139.67, 132.26, 129.85, 129.04, 128.36, 127.84, 127.14, 120.80 (q, *J* = 291.8 Hz), 116.36. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -77.51.



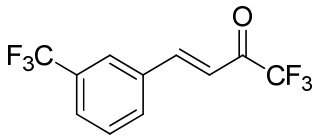
(*E*)-1,1,1-trifluoro-4-(o-tolyl)but-3-en-2-one (2m): The title compound was synthesized via the General Procedure B. The crude material was purified by ethyl acetate/petroleum ether = 1:50 as an eluent, colorless liquid, 40% yield (0.128 g, 1.5 mmol scale). All spectral data are in accord with the literature. [2] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.35 (d, *J* = 15.6 Hz, 1H), 7.72-7.69 (m, 1H), 7.43 (td, *J* = 7.6, 1.2 Hz, 1H), 7.31 (t, *J* = 6.8 Hz, 1H), 7.01 (d, *J* = 15.6 Hz, 1H), 2.51 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 180.35 (q, *J* = 36.1 Hz), 147.91, 136.53 (d, *J* = 1.5 Hz), 133.93 (q, *J* = 32.9 Hz), 129.26, 127.62 (q, *J* = 273.5 Hz), 126.23 (q, *J* = 3.7 Hz), 120.54 (q, *J* = 291.6 Hz), 118.87, 180.55 (q, *J* = 35.4 Hz), 147.56, 139.57, 132.22, 132.10, 131.29, 126.84, 126.66, 120.80 (q, *J* = 291.9 Hz), 117.33, 19.66. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -77.66.



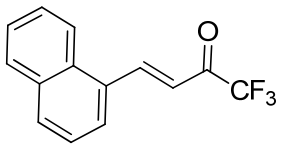
***(E)*-4-(2-bromophenyl)-1,1,1-trifluorobut-3-en-2-one (2n):** The title compound was synthesized via the General Procedure A. The crude material was purified by ethyl acetate/petroleum ether = 1:50 as an eluent, light yellow liquid, 51% yield (0.354 g, 2.5 mmol scale). All spectral data are in accord with the literature. [2] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.39 (d, *J* = 16.0 Hz, 1H), 7.74 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.69 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.41 (td, *J* = 8.4, 1.2 Hz, 1H). 7.35 (td, *J* = 7.6, 2.0 Hz, 1H), 6.99 (dd, *J* = 16.0, 0.8 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 180.29 (q, *J* = 35.8 Hz), 148.28, 133.93, 133.35, 133.01, 128.16, 127.97, 126.94, 120.61 (q, *J* = 292.0 Hz), 119.13. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -77.49.



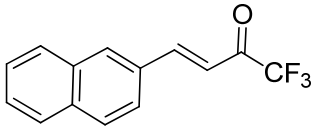
(*E*)-4-(3-bromophenyl)-1,1,1-trifluorobut-3-en-2-one (2o): The title compound was synthesized via the General Procedure A. The crude material was purified by ethyl acetate/petroleum ether = 1:50 as an eluent, light yellow liquid, 60% yield (0.417 g, 2.5 mmol scale). All spectral data are in accord with the literature. [2] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.86 (d, *J* = 16.0 Hz, 1H), 7.75 (t, *J* =1.6 Hz, 1H), 7.60 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.55-7.53 (m, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.01 (d, *J* = 16.0 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 180.28 (q, *J* = 35.8 Hz), 148.16, 135.30, 134.95, 131.64, 130.69, 127.82, 123.34, 120.59 (q, *J* = 291.9 Hz), 117.85. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -77.71



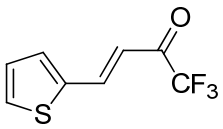
(*E*)-1,1,1-trifluoro-4-(3-(trifluoromethyl)phenyl)but-3-en-2-one (2p): The title compound was synthesized via the General Procedure A. The crude material was purified by ethyl acetate/petroleum ether = 1:50 as an eluent, light yellow liquid, 30% yield (0.201 g, 2.5 mmol scale). All spectral data are in accord with the literature. [4] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 16.0 Hz, 1H), 7.88 (d, *J* = 2.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 16.0 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 180.34 (q, *J* = 36.1 Hz), 148.03, 134.04, 132.42 (q, *J* = 33.1 Hz), 132.11, 129.88, 128.57 (q, *J* = 3.7 Hz), 127.60 (q *J* = 273.5 Hz), 125.67 (q, *J* = 3.7 Hz), 123.49 (q, *J* = 291.7 Hz),118.35. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -63.01 -77.71.



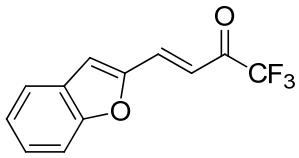
(*E*)-1,1,1-trifluoro-4-(naphthalen-1-yl)but-3-en-2-one (2q): The title compound was synthesized via the General Procedure A. The crude material was purified by ethyl acetate/petroleum ether = 1:50 as an eluent, light yellow liquid, 35% yield (0.438 g, 5 mmol scale). All spectral data are in accord with the literature. [2] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.86 (d, *J* = 15.6 Hz, 1H), 8.20 (d, *J* = 8.4 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 7.2 Hz, 2H), 7.65-7.51 (m, 3H), 7.16 (d, *J* = 15.6 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 180.46 (q, *J* = 35.6 Hz), 146.71, 133.79, 132.85, 131.80, 130.33, 129.06, 127.69, 126.68, 126.10, 125.42, 122.83, 120.87 (q, *J* = 292.0 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -77.49.



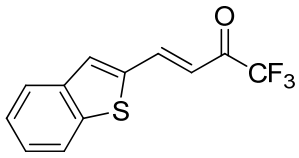
(*E*)-1,1,1-trifluoro-4-(naphthalen-2-yl)but-3-en-2-one (2r): The title compound was synthesized via the General Procedure A. The crude material was purified by ethyl acetate/petroleum ether = 1:50 as an eluent, white solid, 63% yield (0.394 g, 2.5 mmol scale). All spectral data are in accord with the literature. [2] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.15 (d, *J* = 16.0 Hz, 1H), 8. 06 (d, *J* = 2.0 Hz, 1H), 7.91 (q, *J* = 7.6 Hz, 3H), 7.75 (dd, *J* = 8.4, 1.6 Hz, 1H). 7.61-7.54 (m, 2H), 7.14 (d, *J* = 15.6 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 180.54 (q, *J* = 35.5 Hz), 150.21, 135.17, 133.17, 132.68, 130.88, 129.17, 129.04, 128.42, 127.94, 127.18, 123.32, 120.82 (q, *J* = 291.8 Hz), 116.65. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -77.49.



(*E*)-1,1,1-trifluoro-4-(thiophen-2-yl)but-3-en-2-one (2s): The title compound was synthesized via the General Procedure B. The crude material was purified by ethyl acetate/petroleum ether = 1:50 as an eluent, yellow liquid, 42% yield (0.216 g, 2.5 mmol scale). All spectral data are in accord with the literature. [1] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.08 (d, *J* = 15.2 Hz, 1H), 7.58 (d, *J* = 5.2 Hz, 1H), 7.47 (d, *J* = 3.6 Hz, 1H), 7.15 (dd, *J* = 3.6, 1.2 Hz, 1H), 6.79 (d, *J* = 15.6 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 180.18 (q, *J* = 35.4 Hz), 142.06, 139.02, 134.76, 131.95, 128.94, 120.75 (q, *J* = 291.8 Hz), 115.10. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -77.52.

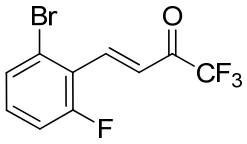


(*E*)-4-(benzofuran-2-yl)-1,1,1-trifluorobut-3-en-2-one (2t): The title compound was synthesized via the General Procedure B. The crude material was purified by ethyl acetate/petroleum ether = 1:50 as an eluent, light yellow solid, 42% yield (0.202 g, 2 mmol scale). All spectral data are in accord with the literature. [3] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 16.0 Hz, 1H), 7.66 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.54 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.47 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.32-7.28 (m, 1H), 7.19 (s, 1H), 7.16 (d, *J* = 15.6 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 180.36 (q, *J* = 35.9 Hz), 156.21, 151.58, 135.20, 128.19, 123.91, 122.47, 120.70 (q, *J* = 291.7 Hz), 116.49, 116.08, 111.74. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -77.70.

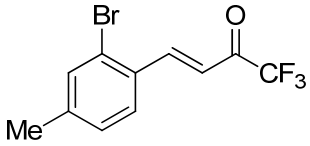


(E)-4-(benzo[b]thiophen-2-yl)-1,1,1-trifluorobut-3-en-2-one (2u): The title compound was synthesized via the General Procedure B. The crude material was purified by ethyl acetate/petroleum ether = 1:50 as an eluent, light yellow solid, 46 % yield (0.236 g, 2 mmol scale). All spectral data are in accord with the literature. [5] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.17 (d, *J* = 15.6 Hz, 1H), 7.84-7.82 (m, 2H), 7.69 (s, 1H), 7.48 (td, *J* = 6.8, 1.2 Hz, 1H), 7.43 (td, *J* = 8.0, 1.6 Hz, 1H), 6.84 (d, *J* =

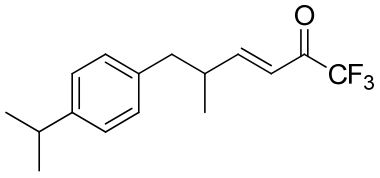
15.6 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 180.14 (q, *J* = 35.9 Hz), 142.63, 141.24, 139.36, 138.76, 132.98, 127.62, 125.36, 125.22, 122.70, 120.68 (q, *J* = 291.7 Hz), 117.36. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -77.47.



(*E*)-4-(2-bromo-6-fluorophenyl)-1,1,1-trifluorobut-3-en-2-one (2w): The title compound was synthesized via the General Procedure B. The crude material was purified by ethyl acetate/petroleum ether = 1:50 as an eluent, yellow liquid, 50% yield (0.222 g, 1.5 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.18 (d, *J* = 16.0 Hz, 1H), 7.51 (dd, *J* = 9.2, 1.2 Hz, 1H), 7.31-7.24 (m, 2H), 7.17 (dd, *J* = 10.8, 8.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 180.93 (q, *J* = 35.4 Hz), 163.63 (d, *J* = 260.8 Hz), 142.46 (d, *J* = 2.7 Hz), 132.99 (d, *J* = 10.2 Hz), 129.77 (d, *J* = 3.5 Hz), 127.64 (d, *J* = 3.9 Hz), 123.07(d, *J* = 16.3 Hz), 122.30 (d, *J* = 13.0 Hz), 120.57 (q, *J* = 291.7 Hz), 115.99 (d, *J* = 23.4 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -77.94, -104.96. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{10}H_6BrF_4O$ 296.9538, found 296.9539.

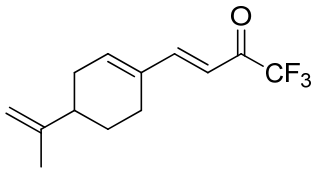


(*E*)-4-(2-bromo-4-methylphenyl)-1,1,1-trifluorobut-3-en-2-one (2x): The title compound was synthesized via the General Procedure B. The crude material was purified by ethyl acetate/petroleum ether = 1:50 as an eluent, light white liquid; 87% yield (0.381 g, 1.5 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.35 (d, *J* = 16.0 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 1.6 Hz, 1H), 7.19 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.95 (d, *J* = 16.0 Hz, 1H), 2.38 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 180.29 (q, *J* = 35.5 Hz), 148.24, 144.44, 134.38, 130.40, 128.92, 127.85, 127.07, 120.68 (q, *J* = 291.9 Hz), 117.95, 21.22. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -77.48. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{11}H_9BrF_3O$ 292.9789, found 292.9786.

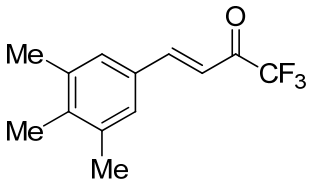


(*E*)-1,1,1-trifluoro-6-(4-isopropylphenyl)-5-methylhex-3-en-2-one (2y): The title compound was synthesized via the General Procedure B. The crude material was purified by ethyl acetate/petroleum ether = 1:40 as an eluent, colorless liquid, 45 % yield (0.639 g, 5 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.35 (dd, *J* = 16.0, 6.4 Hz, 1H), 7.19-7.16 (m, 2H), 7.09-7.06 (m, 2H), 6.34 (dt, *J* = 15.6, 1.2 Hz, 1H), 2.94 (p, *J* = 6.8 Hz, 1H), 2.79-2.72 (m, 2H), 2.69-2.64 (m, 1H), 1.27 (d, *J* = 6.8 Hz, 6H), 1.15 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 180.46 (q, *J* = 35.2 Hz), 160.74, 147.11, 136.02, 129.02, 126.50, 120.58 (q, *J* = 227.0 Hz), 119.93, 41.68, 39.42, 33.74, 24.01, 18.38.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -77.51. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for$C_{16}H_{20}F_3O$ 285.1466, found 285.1467.



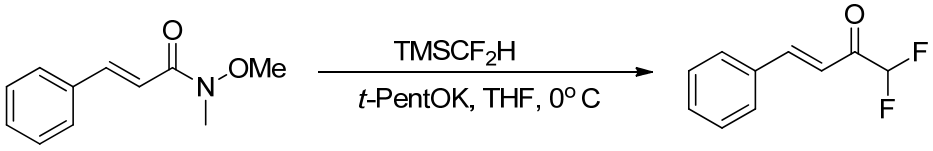
(*E*)-1,1,1-trifluoro-4-(4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)but-3-en-2-one (2z): The title compound was synthesized via the General Procedure B. The crude material was purified by ethyl acetate/petroleum ether = 1:40 as an eluent, light yellow liquid, 32 % yield (0.391 g, 5 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.59 (d, *J* = 15.6 Hz, 1H), 6.50 (d, *J* = 4.8 Hz, 1H), 6.35 (d, *J* = 15.6 Hz, 1H), 4.78 (t, *J* = 1.6 Hz, 1H), 4.73 (s, 1H), 2.46-2.32 (m, 2H), 2.26-2.18 (m, 3H), 1.98-1.93 (m, 1H), 1.76 (t, *J* = 1.2 Hz, 3H), 1.60-1.50 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 180.85 (q, *J* = 34.9 Hz), 152.77, 148.36, 145.16, 135.25, 120.80 (q, *J* = 292.1 Hz), 114.09, 109.49, 40.31, 32.35, 26.64, 24.19, 20.70. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -77.55. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{16}F_3O$ 245.1153, found 245.1157.



(*E*)-1,1,1-trifluoro-4-(3,4,5-trimethylphenyl)but-3-en-2-one (2aa): The title compound was synthesized via the General Procedure A. The crude material was purified by ethyl acetate/petroleum ether = 1:60 as an eluent, light yellow solid; 78 % yield (0.944 g, 5 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 15.6 Hz, 1H), 6.93 (dd, *J* = 15.6, 1.2 Hz, 1H), 6.87 (s, 2H), 3.93 (s, 3H), 3.92 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 180.31 (q, *J* = 35.4 Hz), 153.57, 150.24, 142.06, 128.66, 120.79 (q, *J* = 292.0 Hz), 115.66, 106.53, 61.05, 56.24. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -77.43. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{14}F_3O$ 243.0997, found 243.0991.

3.2 Preparation of α, β-unsaturated ketones with other EWGs

3.2.1 Synthesis of (E)-1,1-difluoro-4-phenylbut-3-en-2-one

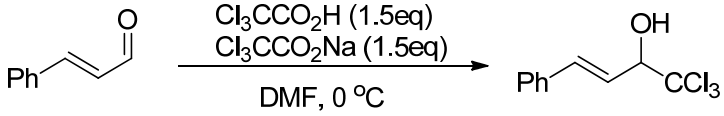


Following Pace's procedure,[7] to a solution of N-methoxy-N-methylcinnamamide (0.382 g, 2 mmol, 1 eq.) in dry THF (10 mL) precooled at 0 °C was added (difluoromethyl)trimethylsilane (0.497 g, 4 mmol, 2 eq.) under an Argon atmosphere. Then potassium *tert*-pentoxide (3.6 mmol, 1.8 eq.) was added dropwise at the same temperature during a period of 15 min. The reaction mixture was further stirred for an additional 4 h. Upon completion, the reaction mixture was quenched with

saturated ammonium chloride solution (5 mL) and extracted with Et_2O (3 × 15 mL). The organic layer was washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude was purified via column chromatography on silica gel to afford the corresponding (*E*)-1,1-difluoro-4-phenyl-3-buten- 2-one **2ad** in 80% yield (0.291 g) as a transparent oil after column chromatography on silica gel (PE/EtOAc =30:1 -20:1 as eluent). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 16.4 Hz, 1H), 7.64-7.62 (m, 2H), 7.49-7.41 (m, 3H), 7.08 (dt, *J* = 16.0, 1.2 Hz, 1H), 6.07 (t, *J* = 54 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 188.04 (t, *J* = 25.9 Hz), 148.22, 148.21, 148.19, 133.77, 131.80, 129.15, 129.01, 117.91, 113.10 (t, *J* = 507.6 Hz). Spectral data are in accord with the literature.

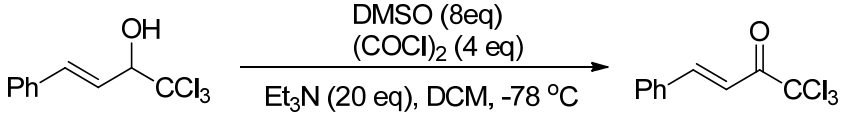
3.2.2 Synthesis of (E)-1,1,1-trichloro-4-phenylbut-3-en-2-one

Step 1



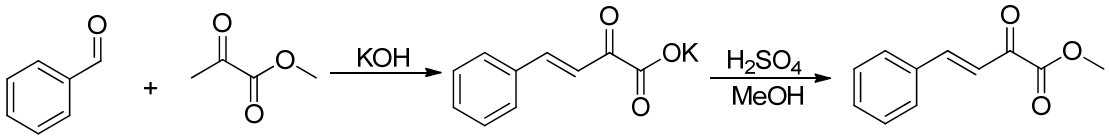
Following literature procedure,[8] to a solution of cinnamaldehyde (1 mL, 5 mmol, 1.0 eq.) in DMF (5 mL) at 0 °C added trichloroacetic acid (1.225 g, 7.5 mmol, 1.5 eq.) and sodium trichloroacetate (1.390 g, 7.5 mmol, 1.5 eq.). The reaction was allowed to warm slowly to rt over 16 h. The mixture was diluted with water and extracted with EtOAc (3×30 mL). The combined organics were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (PE/EtOAc) to afford the (*E*)-1,1,1-trichloro-4-phenylbut-3-en-2-ol.

Step 2



According classic Swern oxidation procedure. A solution of DMSO (1.09 mL, 16 mmol, 8 eq.) in anhydrous CH_2Cl_2 (4 mL) was added dropwise to a solution of oxalyl chloride (0.69 mL, 8 mmol, 4 eq.) in CH_2Cl_2 (30 mL) at –78 °C. After 5 min, a solution of (E)-1,1,1-trichloro-4-phenylbut-3-en-2-ol (0.50 g, 2 mmol, 1 eq.) in CH_2Cl_2 (2 mL) was added dropwise. After a further 15 min, Et_3N (5.58 mL, 40 mmol, 20 eq.) was added dropwise and the reaction stirred for 0.5 h, allowing warm to room temperature. Then, the reaction mixture was quenched with 2 M HCl and extracted with CH_2Cl_2 (3×30 mL). The combined organics were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (PE/EtOAc = 30:1) to afford the (*E*)-1,1,1-trichloro-4-phenylbut-3-en-2-one **2ae** (0.476 g, 96% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 15.6 Hz, 1H), 7.67-7.65 (m, 2H), 7.50-7.43 (m, 3H), 7.37 (d, *J* = 15.6 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 180.08, 149.70, 133.79, 131.79, 129.16, 129.01, 115.84, 96.47. Spectral data are in accord with the literature.

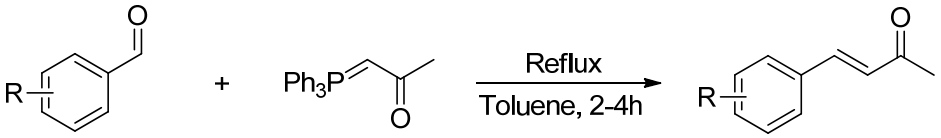
3.2.3 Synthesis of (E)-methyl 2-oxo-4-phenylbut-3-enoate



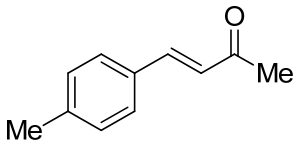
According to the literature procedure,[9] to a solution of methylpyruvate (0.9 mL, 10 mmol, 1.0 eq.) and benzaldehyde (1.02 mL, 10 mmol, 1.0 eq.) in methanol (2 mL) was added at 0 °C a solution of potassium hydroxide (15 mmol, 1.5 eq.) in methanol (3 mL). The first two-thirds of alkali were added dropwise, then the ice-bath was removed and the rest of the potassium hydroxide was run rapidly to complete the condensation before precipitation of potassium pyruvate could occur. The mixture was held at 40 °C for 1h and then at 0 °C overnight. The solvent was removed in vacuo, and the solid was filtered and washed with a little cold methanol to give the potassium salt as a yellow solid.

A saturated solution of potassium salt (10 mmol, 1 eq.) in water (20 mL) at 40° C was rapidly poured into an excess of 1.6 M HCl. The acid precipitated from water was filtered and dissolved in CH_2Cl_2, dried over anhydrous Na_2SO_4, and the solvent evaporated in vacuo. Without further purification, the residue was dissolved in methanol (2.5 mL), and sulfuric acid (98 %, 0.05 eq.) was added. The mixture was refluxed overnight. The cooled mixture was concentrated in vacuo, diluted with CH_2Cl_2, and washed with saturated brine. The aqueous phase was extracted with DCM (3×40 mL), and dried over anhydrous Na_2SO_4, then evaporated under reduced pressure. The residue yellow solid was recrystallized from hexane to give the (*E*)-methyl 2-oxo-4-phenylbut-3-enoate product **2af** (0.931 g, 49% yield of two steps). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 16.0 Hz, 1H), 7.62-7.60 (m, 2H), 7.45-7.38 (m, 3H), 7.37 (d, *J* = 16.0 Hz, 1H), 3.92 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 182.41, 162.54, 148.64, 133.97, 131.72, 129.12, 129.09, 120.44, 53.05. Spectral data are in accord with the literature.

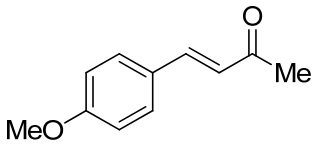
3.3 Preparation of 4-phenylbut-3-en-2-one derivatives



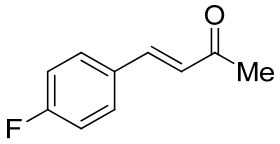
According to the literature classic procedure,[10] to an oven-dried flask equipped with a stir bar and a condenser was added aldehyde (2 mmol), 1-(triphenylphosphoranylidene)-2-propanone (0.764 g, 2.4 mmol, 1.2 eq.), and dry toluene (5 mL). The reaction mixture was refluxed for 2-4 h. Once completed, the reaction mixture was concentrated under reduced pressure, and the residue was purified by flash column chromatography on silica gel (PE/EtOAc as eluent). Data matches that reported in the literature. (*E*)-4-phenylbut-3-en-2-one **4a** was purchased from Adamas.



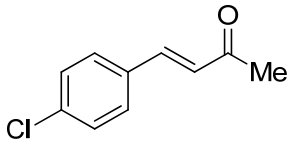
(*E*)-4-(p-tolyl)but-3-en-2-one (4b): ethyl acetate/petroleum ether = 1:20 as an eluent, White solid, 78% yield (0.256 g, 2 mmol scale). All spectral data are in accord with the literature. [10] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.49 (d, *J* = 16.4 Hz, 1H), 7.45-7.43 (m, 2H), 7.20 (d, *J* = 7.6 Hz, 2H), 6.69 (d, *J* = 16.4 Hz, 1H), 2.37 (d, *J* = 3.2 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 198.50, 143.54, 141.05, 131.68, 129.74, 128.28, 126.28, 27.45, 21.51.



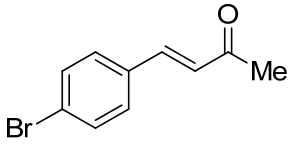
(*E*)-4-(4-methoxyphenyl)but-3-en-2-one (4c): ethyl acetate/petroleum ether = 1:20 as an eluent, White solid, 76% yield (0.268 g, 2 mmol scale). All spectral data are in accord with the literature. [10] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.50 – 7.45 (m, 3H), 6.92 (dt, *J* = 10.0, 3.2 Hz, 2H), 6.62 (d, *J* = 16.0 Hz, 1H), 3.83 (s, 3H), 2.35 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 198.40, 161.63, 143.25, 129.97, 127.07, 125.04, 114.45, 55.40, 27.41.



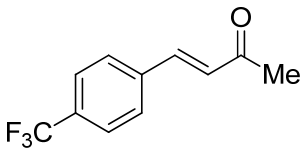
(*E*)-4-(4-fluorophenyl)but-3-en-2-one (4d): ethyl acetate/petroleum ether = 1:20 as an eluent, White solid, 82% yield (0.269 g, 2 mmol scale). All spectral data are in accord with the literature. [10] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.54-7.51 (m, 2H), 7.49 (d, *J* = 16.0 Hz, 1H), 7.10-7.06 (m, 2H), 6.66 (d, *J* = 16.4 Hz, 1H), 2.37 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 198.14, 165.28 (d, *J* = 252.7 Hz), 142.06, 130.69 (d, *J* = 3.3 Hz), 130.19 (d, *J* = 8.7 Hz), 126.87 (d, *J* = 2.3 Hz), 116.27 (d, *J* = 4.8 Hz), 27.61. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -109.2.



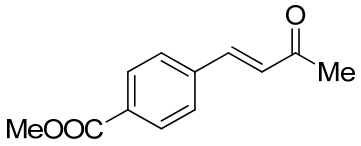
(*E*)-4-(4-chlorophenyl)but-3-en-2-one (4e): ethyl acetate/petroleum ether = 1:20 as an eluent, White solid, 84% yield (0.304 g, 2 mmol scale). All spectral data are in accord with the literature. [10] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.48 – 7.43 (m, 3H), 7.38 (dt, *J* = 8.8, 2.4 Hz, 2H), 6.70 (d, *J* = 16.4 Hz, 1H), 2.37 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 198.06, 141.86, 136.44, 132.94, 129.40, 129.28, 127.49, 27.69.



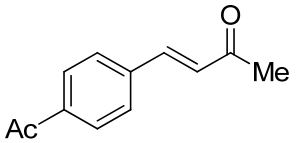
(*E*)-4-(4-bromophenyl)but-3-en-2-one (4f): ethyl acetate/petroleum ether = 1:20 as an eluent, White solid, 80% yield (0.360 g, 2 mmol scale). All spectral data are in accord with the literature. [11] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.54-7.51 (m, 2H), 7.45 -7.38 (m, 3H), 6.71 (d, *J* = 16.4 Hz, 1H), 2.37 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 198.12, 141.96, 133.37, 132.24, 129.62, 127.56, 124.81, 27.71.



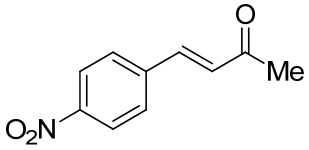
(*E*)-4-(4-(trifluoromethyl)phenyl)but-3-en-2-one (4g): ethyl acetate/petroleum ether = 1:20 as an eluent, White solid, 80% yield (0.343 g, 2 mmol scale). All spectral data are in accord with the literature. [10] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.67-7.62 (m, 4H), 7.53 (d, *J* = 16.0 Hz, 1H), 6.79 (d, *J* = 16.4 Hz, 1H), 2.40 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 197.89, 141.29, 137.89 (d, *J* = 1.5 Hz), 132.43 (q, *J* = 32.8 Hz), 129.10, 128.35, 127.85 (q, *J* = 273.3 Hz), 125.98 (q, *J* = 3.7 Hz), 27.82. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -62.9.



methyl (*E*)-4-(3-oxobut-1-en-1-yl)benzoate (4h): ethyl acetate/petroleum ether = 1:20 as an eluent, White solid, 70% yield (0.286 g, 2 mmol scale). All spectral data are in accord with the literature. [12] **^{1}H NMR** (400 MHz, $CDCl_3$)): δ = 8.05 (d, *J* = 8.4 Hz, 2H), 7.59 (dd, *J* = 6.4, 1.6 Hz, 2H), 7.53 (d, *J* = 16.4 Hz, 1H), 6.79 (d, *J* = 16.4 Hz, 1H), 3.92 (s, 3H), 2.39 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 198.00, 166.39, 141.79, 138.70, 131.57, 130.15, 128.99, 128.08, 52.31, 27.78.

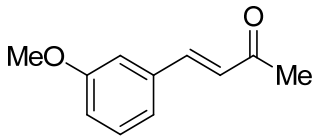


(*E*)-4-(4-acetylphenyl)but-3-en-2-one (4i): ethyl acetate/petroleum ether = 1:20 as an eluent, White solid, 72% yield (0.271 g, 2 mmol scale). All spectral data are in accord with the literature. [13]**^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 8.0 Hz, 2H), 7.62 (dd, *J* = 6.4, 1.6 Hz, 2H), 7.53 (d, *J* = 16.0 Hz, 1H), 6.79 (d, *J* = 16.4 Hz, 1H), 2.60 (s, 3H), 2.39 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 198.01, 197.30, 141.66, 138.82, 138.16, 129.09, 128.91, 128.33, 27.82, 26.72.

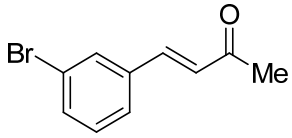


(*E*)-4-(4-nitrophenyl)but-3-en-2-one (4j): ethyl acetate/petroleum ether = 1:20 as an eluent, Yellow solid, 73% yield (0.279 g, 2 mmol scale). All spectral data are in accord with the literature. [14] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.26 (d, *J* = 8.8 Hz, 2H), 7.70 (d, *J* = 8.8 Hz, 2H), 7.55 (d, *J* =

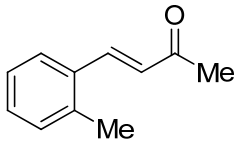
16.0 Hz, 1H), 6.83 (d, *J* = 16.4 Hz, 1H), 2.41 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 197.54, 148.60, 140.68, 140.07, 130.39, 128.82, 124.22, 28.06.



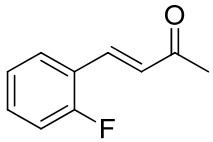
(*E*)-4-(3-methoxyphenyl)but-3-en-2-one (4k): ethyl acetate/petroleum ether = 1:20 as an eluent, Colorless oily liquid, 78% yield (0.275 g, 2 mmol scale). All spectral data are in accord with the literature. [10] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.51 (d, *J* = 16.4 Hz, 1H), 7.32 (t, *J* = 8.0 Hz, 1H), 7.12 (dt, *J* = 7.6, 1.6 Hz, 1H), 7.05 (t, *J* = 1.6 Hz, 1H), 6.97-7.94 (m, 1H), 6.72 (d, *J* = 16.0 Hz, 1H), 3.84 (s, 3H), 2.39 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 198.42, 159.95, 143.38, 135.80, 129.98, 127.42, 121.01, 116.41, 113.04, 55.31, 27.51.



(*E*)-4-(3-bromophenyl)but-3-en-2-one (4l): ethyl acetate/petroleum ether = 1:20 as an eluent, White solid, 83% yield (0.372 g, 2 mmol scale). All spectral data are in accord with the literature. [11] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.67 (t, *J* = 4.0 Hz, 1H), 7.50 (ddd, *J* = 2.8, 2, 0.8 Hz, 1H), 7.46 – 7.39 (m, 2H), 7.26 (t, *J* = 4.0 Hz, 1H), 6.69 (d, *J* = 16.0 Hz, 1H), 2.37 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 197.91, 141.50, 136.58, 133.25, 130.93, 130.47, 128.18, 126.84, 123.10, 27.80.

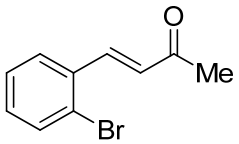


(*E*)-4-(*o*-tolyl)but-3-en-2-one (4m): ethyl acetate/petroleum ether = 1:20 as an eluent, colorless oily liquid, 76% yield (0.244 g, 2 mmol scale). All spectral data are in accord with the literature.[10] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 16.0 Hz, 1H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.24 – 7.20 (m, 2H), 6.65 (d, *J* = 16.4 Hz, 1H), 2.45 (s, 3H), 2.39 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 198.36, 140.86, 137.87, 133.38, 130.88, 130.25, 128.11, 126.46, 126.42, 27.81, 19.79.

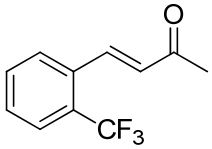


(*E*)-4-(2-fluorophenyl)but-3-en-2-one (4n): ethyl acetate/petroleum ether = 1:20 as an eluent, Yellow solid, 80% yield (0.263 g, 2 mmol scale). All spectral data are in accord with the literature. [10] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.68 (d, *J* = 16.8 Hz, 1H), 7.56 (td, *J* = 7.6, 1.6 Hz, 1H), 7.40 – 7.34 (m, 1H), 7.17 (td, *J* = 7.6, 1.2 Hz, 1H), 7.10-7.07 (m, 1H), 6.79 (d, *J* = 16.4 Hz, 1H), 2.39 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 198.42, 162.63 (d, *J* = 254.6 Hz), 135.69 (d, *J* = 3.5 Hz), 132.01 (d, *J* = 8.9 Hz), 129.27 (d, *J* = 5.5 Hz), 128.71 (d, *J* = 2.6 Hz), 124.58 (d, *J* = 3.6 Hz), 122.57

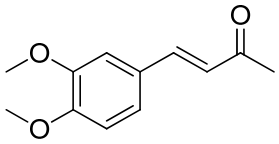
(d, *J* = 11.6 Hz), 116.32 (d, *J* = 22.1 Hz), 27.49. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -114.78 (dd, *J* = 5,6, 2.3 Hz).



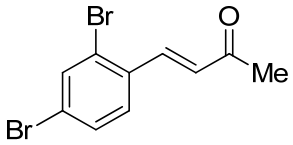
(*E*)-4-(2-bromophenyl)but-3-en-2-one (4o): ethyl acetate/petroleum ether = 1:20 as an eluent, White solid, 82% yield (0.367 g, 2 mmol scale). All spectral data are in accord with the literature. [11] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 16.0 Hz, 1H), 7.62-7.60 (m, 2H), 7.33-7.31 (m, 1H), 7.26 – 7.21 (m, 1H), 6.63 (d, *J* = 16.0 Hz, 1H), 2.41 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 198.34, 141.92, 134.44, 133.47, 131.44, 129.85, 127.85, 127.77, 125.59, 27.21.



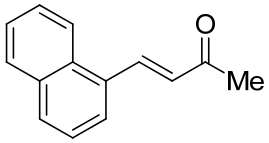
(*E*)-4-(2-(trifluoromethyl)phenyl)but-3-en-2-one (4p): ethyl acetate/petroleum ether = 1:20 as an eluent, White solid, 82% yield (0.351 g, 2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.90 (dq, *J* = 16.4, 2.4 Hz, 1H), 7.86-7.72 (m, 2H), 7.70 -7.58 (m, 1H), 7.56-7.47 (m, 1H), 6.65 (d, *J* = 16.0 Hz, 1H), 2.41 (s, 3H). All spectral data are in accord with the literature. [10] **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 198.14, 138.95 (q, *J* = 2.2 Hz), 133.44 (d, *J* = 1.8 Hz), 132.23, 131.24, 129.78, 129.39 (q, *J* = 30.5 Hz), 128.07 (q, *J* = 275.1 Hz), 127.86, 126.33 (q, *J* = 5.6 Hz), 27.13. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -58.9 (d, *J* = 2.3 Hz).



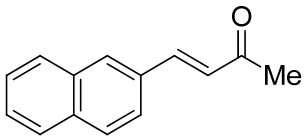
(*E*)-4-(3,4-dimethoxyphenyl)but-3-en-2-one (4q): ethyl acetate/petroleum ether = 1:20 as an eluent, Colorless oily liquid, 71% yield (0.293 g, 2 mmol scale). All spectral data are in accord with the literature. [15] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 16.0 Hz, 1H), δ = 7.09-7.06 (m, 1H), 7.02 (d, *J* = 2.0 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 1H), 6.57 (d, *J* = 16.4 Hz, 1H), 3.86 (s, 6H), 2.32 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 198.29, 151.34, 149.26, 143.50, 127.30, 125.21, 123.00, 111.08, 109.63, 55.95, 55.86, 27.32.



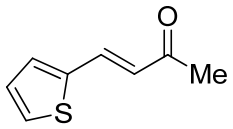
(*E*)-4-(2,4-Dibromophenyl)-3-buten-2-one (4r): ethyl acetate/petroleum ether = 1:20 as an eluent, White solid, mp 112.5℃-113.1℃, 75% yield (0.456 g, 2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.81 -7.76 (m, 2H), 7.47 (d, *J* = 0.8 Hz, 2H), 6.61 (d, *J* = 16.0 Hz, 1H), 2.41 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 197.96, 140.62, 135.86, 133.47, 131.16, 130.07, 128.60, 125.96, 124.65, 27.39. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{10}H_9Br_2O$ 302.9020, found 302.9022.



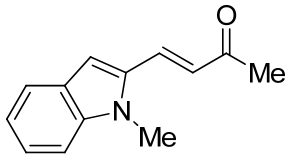
(*E*)-4-(naphthalen-1-yl)but-3-en-2-one (4s): ethyl acetate/petroleum ether = 1:20 as an eluent, Yellow oily liquid, 69% yield (0.271 g, 2 mmol scale). All spectral data are in accord with the literature. [10] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.39 (d, *J* = 16.0 Hz, 1H), 8.19 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.92 – 7.87 (m, 2H), 7.78-7.86 (m, 1H), 7.61 – 7.47 (m, 3H), 6.82 (d, *J* = 16.0 Hz, 1H), 2.47 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 198.22, 140.15, 133.73, 131.73, 131.54, 130.79, 129.57, 128.88, 126.97, 126.30, 125.52, 125.16, 123.18, 27.96.



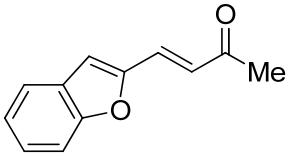
(*E*)-4-(naphthalen-2-yl)but-3-en-2-one (4t): ethyl acetate/petroleum ether = 1:20 as an eluent, Yellow solid, 70% yield (0.275 g, 2 mmol scale). All spectral data are in accord with the literature. [10] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.96 – 7.95(m, 1H), 7.86 – 7.82 (m, 3H), 7.70 – 7.65 (m, 2H), 7.53 – 7.51 (m, 2H), 6.83 (d, *J* = 16.4 Hz, 1H), 2.42 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 198.37, 143.51, 134.36, 133.32, 131.97, 130.35, 128.82, 128.59, 127.84, 127.41, 127.30, 126.81, 123.53, 27.64.



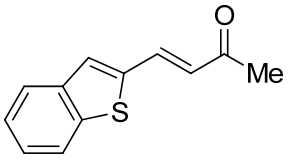
(*E*)-4-(thiophen-2-yl)but-3-en-2-one (4u): ethyl acetate/petroleum ether = 1:20 as an eluent, Yellow solid, 62% yield (0.189 g, 2 mmol scale). All spectral data are in accord with the literature. [10] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.64 (d, *J* = 16.0 Hz, 1H), 7.40 – 7.38 (m, 1H), 7.29 – 7.27 (m, 1H), 7.06 (dd, *J* = 5.2, 3.6 Hz, 1H), 6.52 (d, *J* = 16.0 Hz, 1H), 2.32 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 197.75, 139.75, 135.74, 131.53, 128.92, 128.29, 125.82, 27.69.



(E)-4-(2-(trifluoromethyl)phenyl)but-3-en-2-one (4v): ethyl acetate/petroleum ether = 1:20 as an eluent, yellow solid, 56% yield (0.223 g, 2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.67 – 7.60 (m, 2H), 7.33 – 7.26 (m, 2H), 7.12-7.10 (m, 1H), 7.01 (s, 1H), 6.83 (d, *J* = 15.6 Hz, 1H), 3.83 (s, 3H), 2.39 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 197.52, 139.41, 134.93, 130.97, 127.47, 126.36, 123.90, 121.52, 120.59, 109.68, 104.27, 30.09, 28.41. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{14}NO$ 200.1075, found 200.1076.



(*E*)-4-(benzofuran-2-yl)but-3-en-2-one (4w): ethyl acetate/petroleum ether = 1:20 as an eluent, White solid, 65% yield (0.242 g, 2 mmol scale). All spectral data are in accord with the literature. [10] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.60 (ddd, *J* = 2.0, 1.2, 0.8 Hz, 1H), 7.49-7.47 (m, 1H), 7.41-7.34 (m, 2H), 7.26-7.22 (m, 1H), 6.98 (s, 1H), 6.88 (d, *J* = 15.6 Hz, 1H), 2.38 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 197.59, 155.63, 152.41, 129.50, 128.43, 126.71, 126.68, 123.42, 121.79, 112.06, 111.45, 28.33.

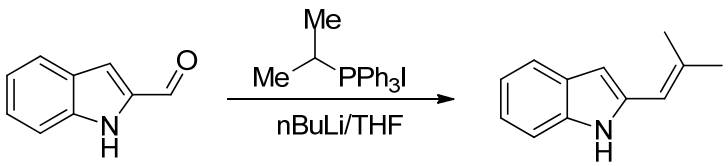


(*E*)-4-(benzo[b]thiophen-2-yl)but-3-en-2-one (4x): ethyl acetate/petroleum ether = 1:20 as an eluent, Yellow solid, 66% yield (0.267 g, 2 mmol scale). All spectral data are in accord with the literature. [10] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.81-7.75 (m, 2H), 7.73 (d, *J* = 15.6 Hz, 1H), 7.50 (s, 1H), 7.40-7.33 (m, 2H), 6.60 (d, *J* = 16.0 Hz, 1H), 2.37 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 197.54, 140.31, 139.75, 139.61, 136.17, 129.39, 127.91, 126.43, 124.95, 124.47, 122.52, 27.97.

3.4 Preparation of 2-vinylindole derivatives

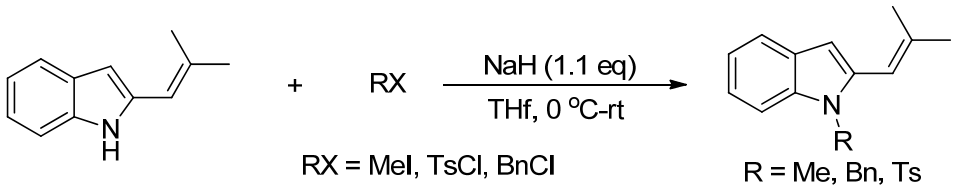
General procedure for the synthesis of unsubstituted 2-vinyl-indole derivatives

Step 1

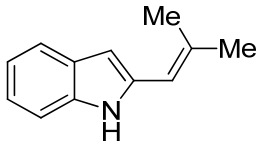


According to the classical Wittig olefination procedure. A 50 mL round-bottom flask equipped with a magnetic stir bar was charged with Wittig salt (1.1 eq.) under an argon atmosphere. Dry THF (0.3 M) was added, and cooled to 0 ºC with low-temperature reactor followed by *n*-BuLi addition (1.2 eq.). After stirring for 30 min at 0 °C, the 1*H*-indole-2-carbaldehyde derivatives (1.0 eq.) in THF were added dropwise while keeping the internal temperature below 0 °C. After the completion of the addition, the mixture was allowed to warm to room temperature and stirred until judged complete by TLC analysis (12 h). The reaction mixture was then cooled to 0 °C and quenched with aqueous ammonium chloride. The biphasic solution was extracted with ethyl acetate. The combined organic phases were washed with brine, dried over anhydrous sodium sulphate, and concentrated under reduced pressure. The crude product was purified via column chromatography on silica gel using EtOAc/petroleum ether as eluent to afford the desired 1*H*-indole-2-carbaldehyde derivatives.

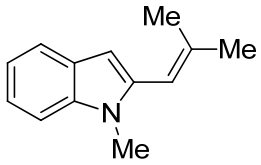
Step 2



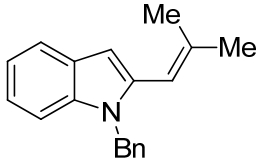
NaH (88 mg, 2.2 mmol, 1.1eq.) was added to a solution of 2-(2-methylprop-1-en-1-yl)-1*H*-indole (0.342 g, 2 mmol, 1eq.) in dry THF (10 mL) at 0 °C under an argon atmosphere. The mixture was stirred at 0 °C for 30 min. Then, RX (4 mmol, 2 eq.) was added to the reaction mixture at 0 °C. The resulting mixture was warmed slowly to room temperature, stirred for 10-12 h, then quenched with H_2O. The mixture was extracted with ether. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under pressure. The residue was purified by flash chromatography with PE/EtOAc (50:1-20:1) to afford the desired *N*-protected 2-(2-methylprop-1-en-1-yl)-1*H*-indole product.



2-(2-methylprop-1-en-1-yl)-1*H*-indole (1b): ethyl acetate/petroleum ether = 1:30 as an eluent, white solid, mp 102-103℃, 85% yield (1.455 g, 10 mmol scale). All spectral data are in accord with the literature.[16] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.88 (s, 1H), 7.60 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.21-7.11 (m, 2H), 6.46 (t, *J* = 1.2 Hz, 1H), 6.18 (d, *J* = 2.0 Hz, 1H), 2.07 (d, *J* = 1.2 Hz, 3H), 1.99 (d, *J* = 1.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 137.38, 136.34, 135.53, 129.06, 121.66, 120.18, 119.88, 116.01, 110.46, 101.55, 27.28, 20.37.

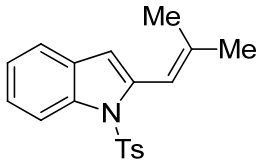


methyl-2-(2-methylprop-1-en-1-yl)-1*H*-indole (1a): ethyl acetate/petroleum ether = 1:30 as an eluent, colorless liquid, 72% yield (1.332 g, 10 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.63 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.32 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.26-7.20 (m, 1H), 7.14-7.10 (m, 1H), 6.45 (s, 1H), 6.26 (t, *J* = 1.6 Hz, 1H), 3.70 (s, 3H), 2.04 (d, *J* = 1.6 Hz, 3H), 2.02 (d, *J* = 1.2 Hz, 3H). **^{13}C NMR** (101 MHz, CDCl3): δ = 139.63, 137.63, 136.81, 128.04, 121.07, 120.10, 119.39, 114.53, 108.98, 101.17, 29.78, 27.02, 20.27. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{16}N$ 186.1282, found 186.1282.

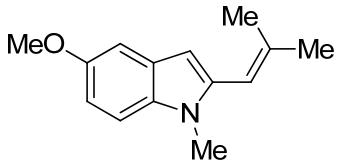


benzyl-2-(2-methylprop-1-en-1-yl)-1*H*-indole (1c): ethyl acetate/petroleum ether = 1:30 as an eluent, light yellow solid, mp 80-83 ℃, 82% yield (0.428 g, 2 mmol scale). All spectral data are in accord with the literature. [17]**^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.63 – 7.61 (m, 1H), 7.30 – 7.19 (m,

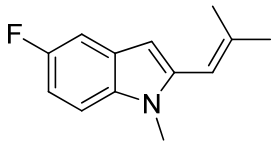
4H), 7.14 – 7.09 (m, 2H), 7.04 – 7.01 (m, 2H), 6.50 (s, 1H), 6.15 – 6.13 (m, 1H), 5.33 (s, 2H), 1.99 (d, *J* = 1.2 Hz, 3H), 1.93 (d, *J* = 2.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 140.27, 138.09, 137.50, 136.51, 128.70, 128.28, 127.18, 126.09, 121.34, 120.16, 119.66, 114.32, 109.47, 101.86, 46.67, 26.92, 20.32.



2-(2-methylprop-1-en-1-yl)-1-tosyl-1*H*-indole (1d): ethyl acetate/petroleum ether = 1:30 as an eluent, yellow liquid, 72% yield (0.468 g, 2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.26 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.44-7.42 (m, 1H), 7.31-7.27 (m, 1H), 7.24 (td, *J* = 7.2, 1.2 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.61 (dd, *J* = 2.8, 1.2 Hz, 1H), 6.38 (s, 1H), 2.31 (s, 3H), 2.00 (d, *J* = 1.6 Hz, 3H), 1.71 (d, *J* = 1.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 144.48, 139.63, 137.85, 136.62, 135.92, 130.13, 129.44, 126.64, 124.25, 123.65, 120.33, 116.39, 115.12, 111.30, 26.59, 21.54, 19.82. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{20}NO_2S$ 326.1215, found 326.1219.

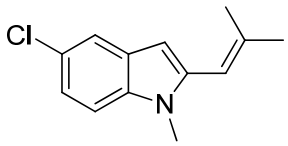


5-methoxy-1-methyl-2-(2-methylprop-1-en-1-yl)-1*H*-indole (1e): Wittig olefination was conducted at 90 ºC for 16 h; ethyl acetate/petroleum ether = 1:60 as an eluent, white solid, mp 60.5-63.4 ℃, 85% yield (0.183 g, 1 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.19 (t, *J* = 8.0 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.60(s, 1H), 6.59 (d, *J* = 7.6 Hz, 1H), 6.27 (p, *J* = 1.6 Hz, 1H), 4.02 (s, 3H), 3.69 (s, 3H), 2.06 (t, *J* = 1.6 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 153.02, 139.10, 138.28, 136.23, 121.86, 118.57, 114.46, 102.67, 99.41, 98.36, 55.39, 30.09, 27.07, 20.35. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{18}NO$ 216.1388, found 216.1371.

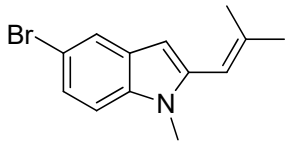


5-fluoro-1-methyl-2-(2-methylprop-1-en-1-yl)-1*H*-indole (1f): Wittig olefination was conducted at 90 ºC for 16 h; ethyl acetate/petroleum ether = 1:60 as an eluent, yellow solid, mp 76.8-77.4 ℃, 85% yield (0.173 g, 1 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.26 (dd, *J* = 9.6, 2.4 Hz, 1H), 7.20 (dd, *J* = 9.2, 4.4 Hz, 1H), 6.97 (td, *J* = 9.2, 2.8 Hz, 1H), 6.39 (s, 1H), 6.22 (p, *J* = 1.6 Hz, 1H), 3.66 (s, 3H), 2.03 (d, *J* = 1.6 Hz, 3H), 2.00 (d, *J* = 1.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 159.09 (d, *J* = 234.3 Hz), 140.30, 139.22, 133.46, 128.18 (d, *J* = 10.2 Hz), 114.34, 109.47 (d, *J* = 9.8 Hz), 109.29(d, *J* = 26.3 Hz), 104.85(d, *J* = 23.4 Hz), 101.09 (d, *J* = 4.6 Hz), 29.95, 27.00, 20.27.

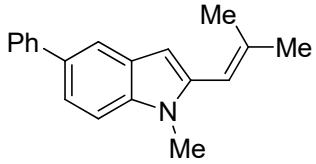
^{19}F NMR (376 MHz, $CDCl_3$): δ = -125.53. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{15}FN$ 204.1189, found 204.1192.



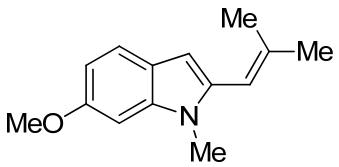
5-chloro-1-methyl-2-(2-methylprop-1-en-1-yl)-1*H*-indole (1g): Wittig olefination was conducted at 90 °C for 16 h; ethyl acetate/petroleum ether = 1:60 as an eluent, yellow solid, mp 71.1-72.8°C, 86% yield (0.188 g, 1 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.54 (d, *J* = 2.0 Hz, 1H), 7.19 (d, *J* = 8.4 Hz, 1H), 7.14 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.35 (s, 1H), 6.20 (t, *J* = 1.6 Hz, 1H), 3.65 (s, 3H), 2.02 (d, *J* = 1.6 Hz, 3H), 1.98 (d, *J* = 1.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 140.57, 138.94, 135.21, 128.95, 124.97, 121.18, 119.33, 114.16, 109.89, 100.68, 29.93, 27.01, 20.28. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{15}ClN$ 220.0893, found 220.0894.



5-bromo-1-methyl-2-(2-methylprop-1-en-1-yl)-1*H*-indole (1h): Wittig olefination was conducted at 90 °C for 16 h; ethyl acetate/petroleum ether = 1:60 as an eluent, yellow solid, mp 91.7-93.0 °C, 82% yield (0.216 g, 1 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 2.0 Hz, 1H), 7.26 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.14 (d, *J* = 8.8 Hz, 1H), 6.35 (s, 1H), 6.20 (t, *J* = 1.6 Hz, 1H), 3.64 (s, 3H), 2.02 (d, *J* = 1.6 Hz, 3H), 1.98 (d, *J* = 1.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 140.65, 138.79, 135.46, 129.64, 123.72, 122.40, 114.11, 112.55, 110.36, 100.59, 29.91, 27.01, 20.28. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{15}BrN$ 264.0388, found 264.0391.



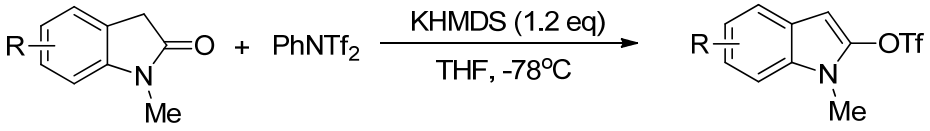
1-methyl-2-(2-methylprop-1-en-1-yl)-5-phenyl-1*H*-indole (1i): Wittig olefination was conducted at 90 °C for 16 h; ethyl acetate/petroleum ether = 1:100 as an eluent, yellow solid, mp 94.5-96.0 °C, 86% yield (total yield of Wittig olefination and Suzuki coupling, 0.225 g, 1 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.90 (d, *J* =1.6 Hz, 1H), 7.77-7.75 (m, 2H), 7.54-7.50 (m, 3H), 7.41-7.37 (m, 2H), 6.55 (s, 1H), 6.31 (t, *J* = 1.6 Hz, 1H), 3.74 (s, 3H), 2.09 (d, *J* = 1.6 Hz, 3H), 2.08 (d, *J* = 1.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ =142.86, 139.92, 138.39, 136.47, 132.96, 128.71, 128.57, 127.42, 126.24, 121.00, 118.66, 114.53, 109.28, 101.59, 29.94, 27.09, 20.37. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{20}N$ 262.1596, found 262.1592.



6-methoxy-1-methyl-2-(2-methylprop-1-en-1-yl)-1*H*-indole (1j): Wittig olefination was conducted at 90 °C for 16 h; ethyl acetate/petroleum ether = 1:60 as an eluent, yellow solid, mp 119.3-120.8 °C, 95% yield (0.204 g, 1 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.20 (d, *J* = 8.8 Hz, 1H), 7.09 (d, *J* = 2.4 Hz, 1H), 6.89 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.42-6.31 (m, 1H), 6.23 (p, *J* = 1.6 Hz, 1H), 3.89 (s, 3H), 3.66 (d, *J* = 1.6 Hz, 3H), 2.03 (d, *J* = 1.2 Hz, 3H), 2.01 (d, *J* = 1.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 154.07, 139.37, 138.19, 132.22, 128.26, 114.60, 111.21, 109.65, 101.93, 100.76, 55.94, 29.87, 27.02, 20.27. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{18}NO$ 216.1388, found 216.1389.

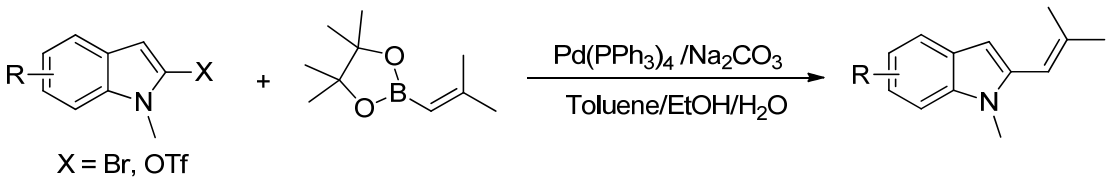
General procedure for the synthesis of substituted 2-vinyl-indole derivatives

Step 1



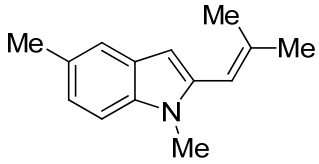
Following literature procedure,[18] to an oven-dried round-bottom flask equipped with a stir bar was added the corresponding 1-methylindolin-2-one (2 mmol, 1eq.) in dry THF (5 mL) at -78 °C under argon atmosphere. A solution of KHMDS (2.4 mL, 1 M in THF, 1.2 eq.) was added dropwise via syringe and the reaction mixture was stirred for 30 minutes, followed by slowly adding N,N-bis(trifluoromethylsulfonyl)aniline (2 mmol, 1eq., 0.715g). The mixture was stirred 2-3h at -78 °C. Upon completion, the solution was warmed to rt, then quenched with saturated NH_4Cl solution (5 mL). The aqueous phase was extracted by EtOAc (3 × 20 mL). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford the 1-methyl-1H-indol-2-yl trifluoromethanesulfonate product.

Step 2

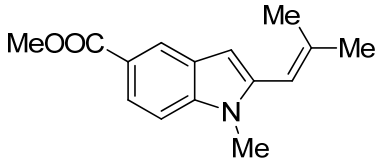


The synthesis of 2-vinyl-indole derivatives were according to the classical Suzuki coupling procedures.[19] $Pd(PPh_3)_4$ (1 mol%, 46.5 mg) and Na_2CO_3 (1.272 g, 12 mmol, 3 eq.) were added to a oven-dried round-bottom flask at rt under Ar atmosphere. Then toluene (14 mL), EtOH (4 mL), distilled water (2 mL), 2-bromo-1-methyl-1H-indole derivatives (4 mmol, 1eq.), and 2,2-dimethylethenylboronic acid pinacol ester (0.874 g, 4.8 mmol, 1.2 eq.), were added successively via

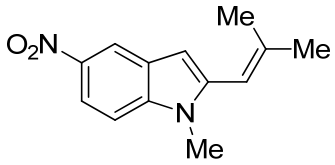
syringe. The mixture was refluxed with stirring until completion (monitored by TLC). The resulting mixture was cooled to rt, added water (30 mL), and extracted with EtOAc (3×30 mL). The combined organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EtOAc = 60/1 to 40/1) to afford the target product.



1,5-dimethyl-2-(2-methylprop-1-en-1-yl)-1*H*-indole (1k): prepared from 1,5-dimethylindolin-2-one, ethyl acetate/petroleum ether = 1:150 as an eluent, white solid, mp 73.7-74.4 ºC; 65% yield (total yield of trifluoromethane sulfonic acid esterification and Suzuki cross-coupling step, 0.129 g, 1 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.37 (dt, *J* = 2.4, 0.8 Hz, 1H), 7.18 (d, *J* = 8.4 Hz, 1H), 7.02 (dd, *J* = 8.0, 1.6 Hz), 6.33 (s, 1H), 6.22 (p, *J* = 1.2 Hz), 3.66 (s, 3H), 2.45 (s, 3H), 2.01 (d, *J* = 1.6 Hz, 3H), 1.98 (d, *J* = 1.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 139.28, 137.63, 135.21, 128.50, 128.21, 122.61, 119.74, 114.61, 108.62, 100.59, 29.79, 26.99, 21.44, 20.24. **IR** (UATR): 2959.5, 2904.6,1712.3, 1655.0, 1572.2, 1483.2, 1444.8, 1369.0, 1321.4, 1179.7, 1050.5, 885.9, 843.7, 789.0, 587.7, 442.0 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{18}N$ 200.1439, found 200.1438.

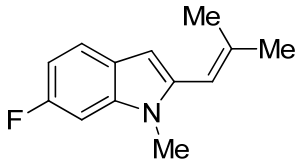


methyl 1-methyl-2-(2-methylprop-1-en-1-yl)-1*H*-indole-5-carboxylate (1l): prepared from methyl 2-bromo-1-methyl-1H-indole-5-carboxylate; ethyl acetate/petroleum ether = 1:40 as an eluent, white solid, mp 114.1-115.4 ºC; 15% yield (yield of Suzuki cross-coupling step, 0.109 g, 3 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.34 (d, *J* = 1.6 Hz, 1H), 7.90 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.27 (d, *J* = 8.8 Hz, 1H), 6.48 (s, 1H), 6.19 (t, *J* = 1.6 Hz, 1H), 3.93 (s, 3H), 3.68 (s, 3H), 2.01 (d, *J* = 1.6 Hz, 3H), 1.98 (d, *J* = 1.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 168.37, 140.83, 139.27, 139.06, 127.51, 123.00, 122.53, 121.30, 113.98, 108.53, 102.45, 51.78, 30.02, 27.00, 20.27. **IR** (UATR): 2969.7, 2943.0, 1698.3, 1607.2, 1534.3, 1431.9, 1365.5, 1306.7, 1257.7, 1086.9, 840.5, 763.5, 605.8, 433.9 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{15}H_{18}NO_2$ 244.1338, found 244.1340.

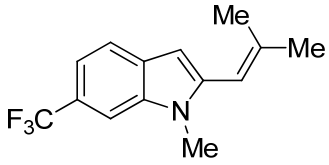


1-methyl-2-(2-methylprop-1-en-1-yl)-5-nitro-1*H*-indole (1m): prepared from 2-bromo-1-methyl-5-nitro-1H-indole; ethyl acetate/petroleum ether = 1:50 as an eluent, yellow solid, mp 87.6-88.6 ºC; 52% yield (yield of Suzuki cross-coupling step, 0.191 g, 1.6 mmol scale). **^{1}H NMR** (400

MHz, $CDCl_3$): δ = 8.50 (d, *J* = 2.0 Hz, 1H), 8.07 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.24 (s,1H), 6.54 (s, 1H), 6.18 (t, *J* = 1.6 Hz, 1H), 3.71 (s, 3H), 2.03 (s, 3H), 1.98 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 142.35, 141.47, 140.93, 139.63, 127.16, 117.09, 116.79, 113.49, 108.65, 103.30, 30.31, 27.04, 20.33. **IR** (UATR): 2964.5, 2935.1, 1647.3, 1608.4, 1580.6, 1510.7, 1481.5, 1365.9, 1309.2, 1148.1, 1055.2, 829.7, 751.0, 609.4, 431.4 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{15}N_2O_2$ 231.1134, found 231.1130.



6-fluoro-1-methyl-2-(2-methylprop-1-en-1-yl)-1*H*-indole (1n): prepared from 6-fluoro-1-methylindolin-2-one; ethyl acetate/petroleum ether = 1:50 as an eluent, pale yellow solid, mp 47.7-49.0 ºC; 81% yield (total yield of trifluoromethane sulfonic acid esterification and Suzuki cross-coupling step, 0.165 g, 1 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.50 (dd, *J* = 12.8, 7.0 Hz, 1H), 6.98 (dd, *J* = 10.0, 2.4 Hz, 1H), 6.89 (ddd, *J* = 10.0, 8.8, 2.4 Hz, 1H), 6.39 (s, 1H), 6.21 (p, *J* = 1.6 Hz, 1H), 3.63 (s, 3H), 2.02 (d, *J* = 1.2 Hz, 3H), 1.99 (d, *J* = 1.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 160.76 (d, *J* = 237.6 Hz), 139.60, 138.17 (d, J = 3.8 Hz), 136.92 (d, *J* = 12.1 Hz), 124.43, 120.70 (d, *J* = 10.0 Hz), 114.23, 108.01 (d, *J* = 24.5 Hz), 101.19, 95.58 (d, *J* = 26.4 Hz), 29.95, 26.97, 20.23. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -121.49. **IR** (UATR): 2974.3, 2911.9, 1659.0, 1615.1, 1530.5, 1467.0, 1357.7, 1233.0, 1080.4, 963.8, 819.5, 612.2, 562.4 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{15}FN$ 204.1189, found 204.1188.

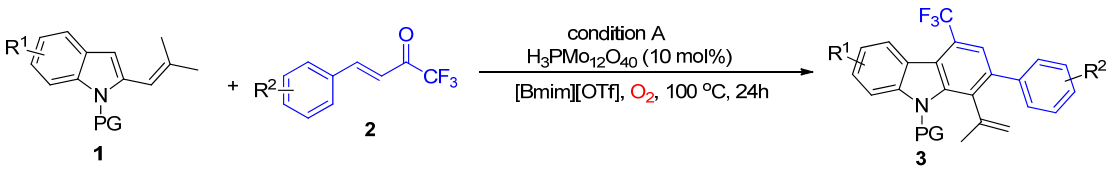


1-methyl-2-(2-methylprop-1-en-1-yl)-6-(trifluoromethyl)-1*H*-indole (1o): prepared from 1-methyl-6-(trifluoromethyl)indolin-2-one; ethyl acetate/petroleum ether = 1:100 as an eluent, white solid, mp 53.2-54.3 ºC; 97% yield (total yield of trifluoromethane sulfonic acid esterification and Suzuki cross-coupling step, 0.246 g, 1 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.68 (d, *J* = 8.4 Hz, 1H), 7.59 (s, 1H), 7.38 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.50 (s, 1H), 6.26 (t, *J* = 1.6 Hz, 1H), 3.74 (s, 3H), 2.07 (d, *J* = 1.2 Hz, 3H), 2.03 (d, *J* = 1.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 141.38, 140.40, 135.72, 130.34, 129.59 (q, *J* = 272.4 Hz), 123.34 (q, *J* = 31.7 Hz), 120.20, 116.09 (q, *J* = 3.5 Hz), 114.00, 106.52 (q, *J* = 4.4 Hz), 101.36, 29.91, 26.99, 20.26. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -60.2. **IR** (UATR): 2920.0, 1616.2, 1524.3, 1453.7, 1352.2, 1284.4, 1132.1, 1095.1, 1053.7, 935.7, 813.3, 650.4, 433.7 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{15}F_3N$ 254.1157, found 254.1160.

4. Synthesis and characterization of products

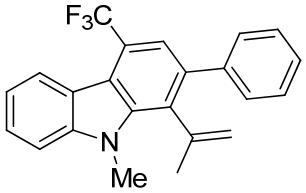
4.1 Carbazole derivatives through 1,2-addition cascade approach

Representative procedure for standard condition A



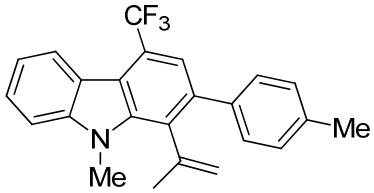
A flame-dried Schlenk tube was charged with 2-(2-methylprop-1-en-1-yl)-1H-indole derivatives (**1**, 0.2 mmol, 1 eq.), (*E*)-1,1,1-trifluoro-4-phenylbut-3-en-2-one derivatives (**2**, 0.3 mmol, 1.5 eq.), [Bmim][OTf] (2 mL), and $H_3PMo_{12}O_{40}$ (10 mol%) under an O_2 atmosphere at room temperature. The mixture was stirred at 100 °C for 24 h. The progress of the reaction was monitored by the disappearance of the starting material as visualized by TLC. After completion of the reaction, the mixture was cooled to room temperature, extracted with toluene (3×15 mL), the combined oragnic layers were then concentrated under reduced pressure and purified by flash chromatography on silica gel using petroleum ether/EtOAc (50:1-20:1) as eluent to afford target product. The ionic liquid of [Bmim][OTf] could be recycled up to 3 times using the follows procedure: after removing water and toluene from the ionic liquid under vacuum, it was necessary to add 3 mol%, 5 mol%, and 8 mol% phosphomolybdic acid in the second, third, and fourth cycle, respectively, due to the partial leaching of the catalyst caused by toluene extraction during each cycle.

Characterization data of carbazole derivatives through 1,2-addition cascade approach

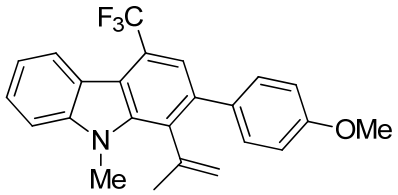


9-methyl-2-phenyl-1-(prop-1-en-2-yl)-4-(trifluoromethyl)-9*H*-carbazole (3a): ethyl acetate/petroleum ether = 1:150 as an eluent; white solid, mp 162.9-163.8 °C; 84% yield (61.3 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.43 (d, *J* = 8.4 Hz, 1H), 7.60 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.52 (s, 1H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.44-7.39 (m, 5H), 7.37 (ddd, *J* = 7.2, 6.4, 1.2 Hz, 1H), 5.49 (p, *J* = 1.6 Hz, 1H), 5.15-5.14 (m, 1H), 4.03 (s, 3H), 1.93 (t, *J* = 1.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 142.89, 141.29 (d, *J* = 3.6 Hz), 138.62, 137.72, 129.83, 129.42, 128.98 (q, *J* = 273.2 Hz), 127.69, 127.04, 126.79, 123.43 (q, *J* = 5.2 Hz), 121.26, 120.93, 120.70, 120.03, 119.58, 119.50 (q, *J* = 6.1 Hz), 119.29, 109.10, 32.26, 25.94. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -61.96. **IR** (UATR): 2948.9, 1613.8, 1561.5, 1440.0, 1389.1, 1372.2, 1250.8, 1142.6, 1113.7, 1072.7, 950.5, 883.0, 742.5, 707.9, 569.5 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{19}F_3N$

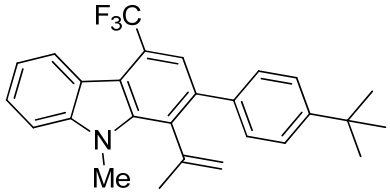
366.1469, found 366.1468.



9-methyl-1-(prop-1-en-2-yl)-2-(p-tolyl)-4-(trifluoromethyl)-9*H*-carbazole (3b): ethyl acetate/petroleum ether = 1:80 as an eluent; white solid, mp 181.7-182.6 ºC; 82% yield (62.2 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.38 (d, *J* = 8.0 Hz, 1H), 7.58 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.47-7.45 (m, 2H), 7.34-7.29 (m, 3H), 7.21 (d, *J* = 7.6 Hz, 2H), 5.47 (t, *J* = 1.6 Hz, 1H), 5.13-5.12 (m, 1H), 4.02 (s, 3H), 2.43 (s, 3H), 1.91 (t, *J* = 1.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 142.82, 141.39, 138.61, 138.28, 137.67, 136.67, 129.66, 129.40, 128.39, 126.69, 126.24 (q, *J* = 273.3 Hz), 123.33 (q, *J* = 5.2 Hz), 121.17, 120.84, 120.57, 119.95, 119.57 (q, *J* = 6.9 Hz), 119.12, 109.04, 32.28, 25.94, 21.27. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -62.03. **IR** (UATR): 2968.3, 1613.1, 1570.7, 1470.7, 1437.6, 1372.1, 1326.7, 1257.7, 1156.1, 1126.9, 1069.8, 906.8, 738.4, 523.9 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{21}F_3N$ 380.1626, found 280.1628.

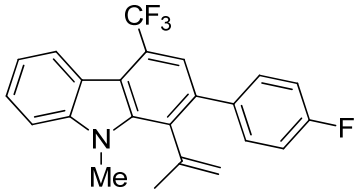


2-(4-methoxyphenyl)-9-methyl-1-(prop-1-en-2-yl)-4-(trifluoromethyl)-9H-carbazole (3c): ethyl acetate/petroleum ether = 1:60 as an eluent; white solid, mp 194.6-195.2 ºC; 75% yield (59.3 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.39 (dt, *J* = 8.0, 1.6 Hz, 1H), 7.58 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.47-7.45 (m, 2H), 7.36-7.30 (m, 3H), 6.95 (dt, *J* = 9.2, 2.8 Hz, 2H), 5.48 (p, *J* = 1.6 Hz, 1H), 5.13-5.12 (m, 1H), 4.01 (s, 3H), 3.88 (s, 3H), 1.90 (t, *J* = 1.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 158.69, 142.83, 141.48, 138.67, 137.31, 133.50, 130.88, 129.49, 128.96 (q, *J* = 273.2 Hz), 126.69, 123.37 (q, *J* = 5.3 Hz), 121.50 (q, *J* = 32.8 Hz), 120.59, 119.95, 119.71 (q, *J* = 6.0 Hz), 119.56, 119.09, 113.10, 109.05, 55.29, 32.32, 25.84. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -62.01. **IR** (UATR): 2950.9, 2850.6, 1610.8, 1564.4, 1515.5, 1439.3, 1371.3, 1303.0, 1244.9, 1122.2, 1104.2,1074.1, 834.8, 739.1, 596.3 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{21}F_3NO$ 396.1575, found 396.1573.

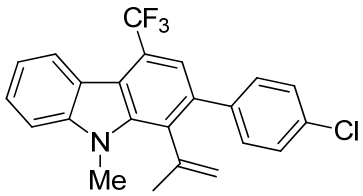


2-(4-(tert-butyl)phenyl)-9-methyl-1-(prop-1-en-2-yl)-4-(trifluoromethyl)-9*H*-carbazole (3d): ethyl acetate/petroleum ether = 1:60 as an eluent; white solid, mp 199.6-200.8 ºC; 80% yield (67.4 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.42 (d, *J* = 8.0 Hz, 1H), 7.59-7.55 (m, 1H), 7.53 (s, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.44 (dd, *J* = 6.4, 2.4 Hz, 2H), 7.37-7.32 (m, 3H), 5.50-5.49

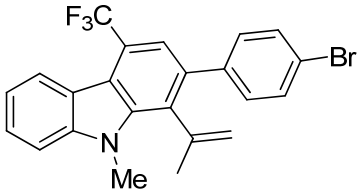
(m, 1H), 5.16-5.15 (m, 1H), 4.03 (s, 3H), 1.92 (s, 3H), 1.42 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 149.89, 142.89, 141.36, 138.71, 138.18, 137.69, 129.46, 129.42, 129.02 (q, *J* = 273.4 Hz), 126.69, 124.58, 123.40 (q, *J* = 5.1 Hz), 121.53 (q, *J* = 32.7 Hz), 120.62, 120.62, 119.96, 119.77 (q, *J* = 6.1 Hz), 119.62, 119.17 (d, *J* = 1.9 Hz), 34.59, 32.35, 31.47, 25.87. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -61.94. **IR** (UATR): 2956.1, 1614.6, 1567.0, 1470.4, 1435.0, 1376.3, 1325.5, 1263.6, 1135.1, 1027.1, 949.3, 742.3, 606.7, 504.7 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{27}F_3N$ 422.2096, found 422.2089.



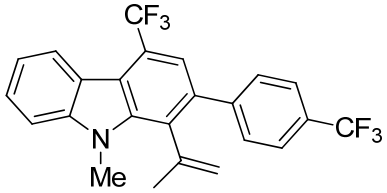
9-methyl-2-phenyl-1-(prop-1-en-2-yl)-4-(trifluoromethyl)-9*H*-carbazole (3e): ethyl acetate/petroleum ether = 1:60 as an eluent; white solid, mp 187.1-188.3 ºC; 96% yield (73.6 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.40 (d, *J* = 8.0 Hz, 1H), 7.60 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.48 (d, *J* = 10.4 Hz, 2H), 7.39-7.32 (m, 3H), 7.11-7.07 (m, 2H), 5.48 (t, *J* = 1.6 Hz, 1H), 5.13-5.12 (m, 1H), 4.02 (s, 3H), 1.90 (t, *J* = 1.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 163.31 (d, *J* = 246.9 Hz), 142.86, 141.22, 138.57, 137.07 (d, *J* = 3.4 Hz), 136.54, 131.43 (d, *J* = 8.0 Hz), 129.48, 128.87 (q, *J* = 273.2 Hz), 126.88, 123.44 (q, *J* = 5.2 Hz), 121.63 (q, *J* = 32.8 Hz), 120.84, 120.07, 119.48, 119.44 (d, *J* = 2.0 Hz), 119.38 (q, *J* = 6.1 Hz), 114.72 (d, *J* = 21.4 Hz), 109.11, 32.26, 25.90. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -62.05, -115.56. **IR** (UATR): 2969.5, 1599.9, 1512.6, 1472.0, 1390.4, 1326.4, 1257.1, 1216.7, 1144.4, 1109.9, 905.2, 840.0, 746.5, 553.8 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{18}F_4N$ 384.1375, found 384.1371.



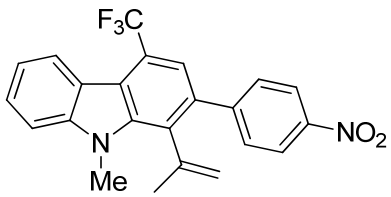
2-(4-chlorophenyl)-9-methyl-1-(prop-1-en-2-yl)-4-(trifluoromethyl)-9*H*-carbazole (3f): ethyl acetate/petroleum ether = 1:80 as an eluent; white solid, mp 190.2-190.8 ºC; 72% yield (57.5 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.41-8.39 (m, 1H), 7.60 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.49-7.46 (m, 2H), 7.40-7.32 (m, 5H), 5.50 (t, *J* = 1.6 Hz, 1H), 5.133-5.126 (m, 1H), 4.02 (s, 3H), 1.92-1.91 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 142.90, 141.08, 139.65, 138.56, 136.30, 133.19, 131.15, 129.38, 128.86 (q, *J* = 273.1 Hz), 127.92, 126.95, 123.47 (q, *J* = 5.4 Hz), 121.73 (q, *J* = 32.9 Hz), 120.97, 120.11, 119.57, 119.47, 119.18 (q, *J* = 6.0 Hz), 109.13, 32.24, 25.98. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -62.07. **IR** (UATR): 2945.2, 1613.5, 1562.6, 1469.8, 1373.1, 1305.7, 1261.3, 1128.5, 1015.7, 883.4, 835.6, 740.6, 530.8 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{18}ClF_3N$ 400.1080, found 400.1079.



2-(4-bromophenyl)-9-methyl-1-(prop-1-en-2-yl)-4-(trifluoromethyl)-9*H*-carbazole (3g): ethyl acetate/petroleum ether = 1:80 as an eluent; white solid, mp 204.1-205.1 °C; 70% yield (62.0 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.40 (d, *J* = 8.4 Hz, 1H), 7.60 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.55 (dt, *J* = 9.2, 1.2 Hz, 2H), 7.48 (dt, *J* = 8.4, 0.8 Hz, 1H), 7.44 (s, 1H), 7.36 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.31 (dt, *J* = 9.2, 2.4 Hz, 2H), 5.49 (p, *J* = 1.6 Hz, 1H), 5.13-5.12 (m, 1H), 4.02 (s, 3H), 1.92 (t, *J* = 1.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 142.89, 141.04, 140.13, 138.55, 136.27, 131.49, 130.86, 129.31, 128.83 (q, *J* = 273.2 Hz), 126.95, 123.37 (q, *J* = 5.2 Hz), 121.74 (q, *J* = 33.0 Hz), 121.37, 120.99, 120.12, 119.58, 119.46, 119.10 (q, *J* = 6.2 Hz), 109.12, 32.24, 26.00. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -61.07. **IR** (UATR): 2946.0, 1613.5, 1563.0, 1470.0, 1389.4, 1373.3, 1322.1, 1026.4, 1260.8, 1117.4, 1011.8, 949.0, 882.3, 633.0 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{18}BrF_3N$ 444.0575, found 444.0578.

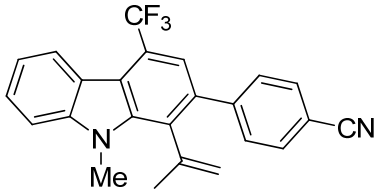


9-methyl-1-(prop-1-en-2-yl)-4-(trifluoromethyl)-2-(4-(trifluoromethyl)phenyl)-9*H*-carbazole (3h): ethyl acetate/petroleum ether = 1:100 as an eluent; white solid, mp 189.3-190.4 °C; 73% yield (63.2 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.40 (dt, *J* = 8.0, 1.6 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.61 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 2H), 7.50 (dt, *J* = 8.4, 0.8 Hz, 1H), 7.44 (s, 1H), 7.36 (ddd, *J* = 8.0, 6.8, 0.8 Hz, 1H), 5.49 (p, *J* = 1.6 Hz, 1H), 5.14 (dd, *J* =1.6, 0.8 Hz, 1H), 4.03 (s, 3H), 1.91 (t, *J* = 1.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 144.97, 142.94, 140.85, 138.49, 136.08, 130.16, 129.44, 129.30, 129.12, 127.07, 126.07, 125.65, 124.70 (q, *J* = 3.6 Hz), 123.53 (q, *J* = 5.1 Hz), 122.95, 121.53, 121.16, 120.20, 119.82, 119.41, 118.97 (q, *J* = 6.1 Hz), 109.15, 32.22, 26.04. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -62.11, -62.36. **IR** (UATR): 2952.6, 1617.7 1563.1, 1439.3, 1375.3, 1321.8, 1262.8, 1150.9, 1113.8, 1061.5, 886.9, 846.9, 741.5, 634.4 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{18}F_6N$ 434.1343, found 434.1342.

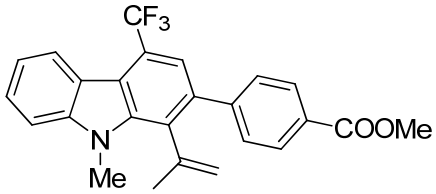


9-methyl-2-(4-nitrophenyl)-1-(prop-1-en-2-yl)-4-(trifluoromethyl)-9*H*-carbazole (3i): ethyl acetate/petroleum ether = 1:20 as an eluent; white solid, mp 216.9-218.2 °C; 55% yield (45.1 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.40-8.37 (m, 1H), 8.28 (dt, *J* = 9.2, 2.4 Hz, 2H), 7.62-7.57 (m, 3H), 7.50 (dt, *J* = 8.4, 0.8 Hz, 1H), 7.43 (s, 1H), 7.37 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H),

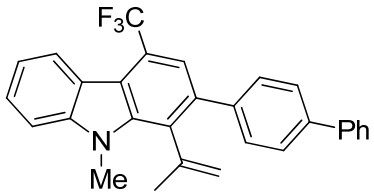
5.50 (p, *J* = 1.6 Hz, 1H), 5.155-5.148 (m, 1H), 4.04 (s, 3H), 1.92 (t, *J* = 1.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 148.23, 147.03, 143.03, 140.67, 138.46, 135.11, 130.74, 129.21, 127.31, 125.98 (q, *J* = 273.4 Hz), 123.60 (q, *J* = 5.3 Hz), 122.96, 122.07 (q, *J* = 33.2 Hz), 121.49, 120.35, 120.24, 119.33, 118.56 (q, *J* = 6.1Hz), 109.23, 32.22, 26.11. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -62.15. **IR** (UATR): 2957.5, 1598.5, 1514.8, 1471.4, 1392.4, 1342.3, 1264.1, 1104.9, 1070.5, 912.0, 846.5, 741.5, 716.8, 576.9 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{18}F_3N_2O_2$ 411.1320, found 411.1315.



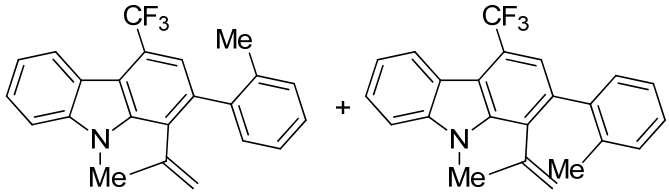
4-(9-methyl-1-(prop-1-en-2-yl)-4-(trifluoromethyl)-9*H*-carbazol-2-yl)benzonitrile (3j): ethyl acetate/petroleum ether = 1:20 as an eluent; white solid, mp 223.7-224.8 ºC; 43% yield (33.6 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.40-8.37 (m, 1H), 7.71-7.68 (m, 2H), 7.61 (ddd, *J* = 8.0, 6.8, 0.8 Hz, 1H), 7.54-7.52 (m, 2H), 7.50 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.41 (s, 1H), 7.36 (ddd, *J* = 8.0, 7.2, 0.8 Hz, 1H) 5.50 (p, *J* = 1.6 Hz, 1H), 5.14-5.13 (m, 1H), 4.03 (s, 3H), 1.91 (t, *J* = 1.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 146.19, 142.99, 140.69, 138.45, 135.50, 131.55, 130.60, 129.16, 128.70 (q, *J* = 273.2 Hz), 127.25, 123.57 (q, *J* = 5.3 Hz), 122.01 (q, *J* = 33.0 Hz), 121.39, 121.39 (d, *J* = 2.3 Hz), 120.31, 120.09, 119.34, 118.91, 118.58 (q, *J* = 6.2 Hz), 111.02, 109.21, 32.24, 26.08. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -61.13. **IR** (UATR): 2958.7, 2228.5, 1607.1, 1564.1, 1470.0, 1391.8, 1374.7, 1261.2, 1166.3, 1105.6, 1071.0, 948.4, 859.0, 738.7, 597.1, 500.5 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{18}F_3N_2$ 391.1422, found 391.1418.



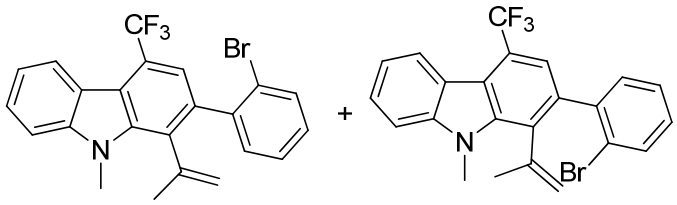
methyl 4-(9-methyl-1-(prop-1-en-2-yl)-4-(trifluoromethyl)-9*H*-carbazol-2-yl)benzoate (3k): ethyl acetate/petroleum ether = 1:30 as an eluent; white solid, mp 187.3-188.4 ºC; 50% yield (42.3 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.41 (d, *J* = 8.4 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.60 (ddd, *J* = 8.0, 6.8, 0.8 Hz, 1H), 7.51-7,46 (m, 4H), 7.36 (td, *J* = 6.8, 0.8 Hz,1H), 5.46 (t, *J* = 1.6 Hz, 1H), 5.133-5.126 (m, 1H), 4.02 (s, 3H), 3.97 (s, 3H), 1.91 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 167.07, 146.13, 142.94, 140.91, 138.53, 136.53, 129.91, 129.28, 128.99, 128.86, 127.02, 126.13, 123.50 (q, *J* = 5.3 Hz), 121.80 (q, *J* = 33.0 Hz), 121.08, 120.16, 119.76 (d, *J* = 2.0 Hz), 119.46, 118.93 (q, *J* = 6.1 Hz), 109.15, 52.19, 32.23, 26.00. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -62.05. **IR** (UATR): 2961.3, 1714.1 1581.1, 1467.8, 1433.7, 1385.2, 1319.1, 1238.5, 1141.4, 1084.0, 925.3, 736.1, 701.1, 554.9 cm^{-1}. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{21}F_3NO_2$ 424.1524, found 424.1526.



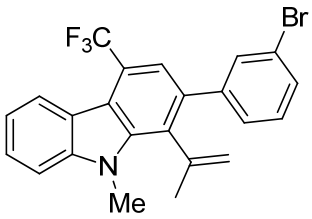
2-([1,1'-biphenyl]-4-yl)-9-methyl-1-(prop-1-en-2-yl)-4-(trifluoromethyl)-9*H*-carbazole (3l): ethyl acetate/petroleum ether = 1:50 as an eluent; white solid, mp 208.4-210.0 ºC; 97% yield (85.6 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.42-8.40 (m, 1H), 7.71-7.68 (m, 2H), 7.66 -7.63 (m, 2H), 7.60 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1H), 7.55 (s, 1H), 7.51-7.47 (m, 5H), 7.41-7.37 (m, 1H), 7.366 (ddd, *J* = 8.0, 7.2, 1.2 Hz, 1H), 5.52 (p, *J* = 1.6 Hz, 1H), 5.18 (dd, *J* = 2.0, 1.2 Hz, 1H), 4.04 (s, 3H), 1.96 (t, *J* = 1.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 142.90, 141.27, 140.74, 140.26, 139.77, 138.66, 137.26, 130.24, 129.86, 129.45, 129.06, 128.86, 128.38 (q, J = 52.7 Hz), 127.39, 127.16, 127.10, 126.81, 126.37, 126.25 (q, *J* = 273.2 Hz), 123.45 (q, *J* = 5.1 Hz), 121.66 (q, *J* = 32.9 Hz), 120.83, 120.04, 119.57, 119.52 (q, *J* = 6.0 Hz), 109.10, 32.32, 26.01. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -61.98. **IR** (UATR): 3033.9, 2960.9, 1717.0, 1598.4, 1557.3, 1487.4, 1327.0, 1261.9, 1144.9, 1056.6, 1002.7, 834.2, 769.8, 741.8, 691.1, 582.0 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{29}H_{23}F_3N$ 442.1783, found 442.1782.



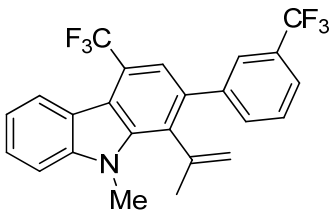
9-methyl-1-(prop-1-en-2-yl)-2-(o-tolyl)-4-(trifluoromethyl)-9*H*-carbazole (3m and 3m'): ethyl acetate/petroleum ether = 1:60 as an eluent; an inseparable mixture of atropisomers (1.17:1) as white solid, mp 132.2-135.1 ºC; isolated yield 66% (50.0 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.44 (dt, *J* = 8.4, 2.0 Hz, 1H), 7.61 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 11.2 Hz, 1H), 7.37-7.35 (m, 1H), 7.34-7.29 (m, 2H), 7.24-7.18 (m, 2H), 5.43 (t, *J* = 1.6 Hz, 0.45H), 5.24 (p, *J* = 1.6 Hz, 0.53H), 5.11-5.10 (m, 0.45H), 5.03-5.02 (s, 0.52H), 4.07 (s, 1.62H), 4.03 (1.38), 2.16 (s, 1.38H), 2.12 (s, 1.62H), 2.05 (t, *J* = 1.2 Hz, 1.62H), 1.84 (t, J = 1.2 Hz, 1.37H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 142.71, 142.64, 141.75, 141.17, 140.83, 139.96, 138.98, 138.67, 137.87, 136.98, 136.61, 135.88, 131.71, 129.86, 129.80, 129.73, 129.64, 129.28, 129.01 (q, *J* = 273.2 Hz), 127.58, 127.47, 126.73, 124.85, 124.78, 123.38 (q, *J* = 5.2 Hz), 121.29, 121.15, 120.96, 120.83, 120.09, 120.04, 119.63, 119.15, 119.11, 118.84 (q, *J* = 5.9 Hz), 118.04, 109.09, 32.34, 31.89, 26.58, 24.74, 20.56, 20.53. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -61.92. **IR** (UATR): 2923.8, 1615.0, 1592.4, 1470.8, 1437.3, 1389.5, 1327.5, 1258.6, 1157.0, 1111.5, 948.8, 909.0, 740.4, 621.5, 455.7 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{21}F_3O$ 380.1626, found 380.1622.



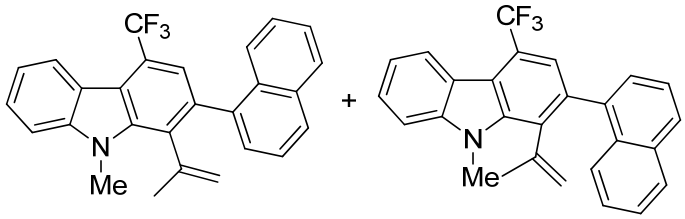
2-(2-bromophenyl)-9-methyl-1-(prop-1-en-2-yl)-4-(trifluoromethyl)-9*H*-carbazole (3n and 3n'): ethyl acetate/petroleum ether = 1:50 as an eluent; an inseparable mixture of atropisomers (1:1) as yellow solid, mp 155.9-156.8 ºC; isolated yield 62% (54.9 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.41 (d, *J* = 8.4 Hz, 1H), 7.69-7.65 (m, 1H), 7.60-7.56 (m, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 4.9 Hz), 7.36-7.29 (m, 3H), 7.27-7.23 (m, 1H), 5.41 (t, *J* = 1.6 Hz, 0.5H), 5.30 (s, 0.5H), 5.23 (t, *J* = 2.0 Hz, 0.5H), 5.07 (d, *J* = 2.0 Hz, 0.5H), 4.08 (s, 1.5H), 4.03 (s, 1.5H), 2.04 (t, *J* = 1.2 Hz, 1.5H), 1.94 (t, *J* = 1.2 Hz, 1.5H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 142.77, 142.68, 142.11, 141.33, 141.11, 140.62, 138.56, 138.32, 137.14, 136.49, 133.27, 132.48 (d, *J* = 5.5 Hz), 130.44, 129.57 (d, *J* = 4.2 Hz), 129.01, 126.86, 126.52, 126.33, 126.20, 125.00, 123.87, 123.47 (q, *J* = 6.1 Hz), 121.31 (q, *J* = 15.6 Hz), 120.11, 120.05, 119.59, 119.50, 119.44, 119.38, 118.85, 118.80, 118.74, 109.11, 109.10, 32.18, 31.60, 26.71, 25.01. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -61.98. **IR** (UATR): 2923.5, 1613.9, 1561.2, 1475.7, 1371.7, 1325.6, 1268.8, 1143.7, 1106.8, 1036.5, 949.8, 737.0, 616.7, cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{18}BrF_3N$ 444.0575, found 444.0570.



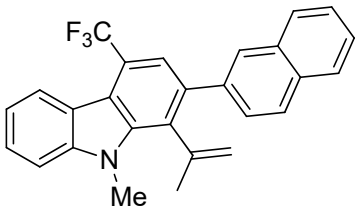
2-(3-bromophenyl)-9-methyl-1-(prop-1-en-2-yl)-4-(trifluoromethyl)-9*H*-carbazole (3o): ethyl acetate/petroleum ether = 1:60 as an eluent; white solid, mp 155.8-156.5 ºC; 54% yield (47.8 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.42 (d, *J* = 8.0 Hz, 1H), 7.61-7.57 (m, 2H), 7.54 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.49 (d, *J* = 7.2 Hz, 2H), 7.37-7.33 (m, 2H), 7.30 (t, *J* = 7.6 Hz, 1H), 5.51 (t, *J* = 1.6 Hz, 1H), 5.14 (s, 1H), 4.03 (s, 3H), 1.94 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 143.27, 142.93, 140.94, 138.51, 135.99, 132.78, 130.15, 129.38, 129.23, 128.85 (q, *J* = 273.3 Hz), 128.52, 127.01, 123.50 (q, *J* = 5.2 Hz), 121.74, 121.44, 121.11, 121.03, 120.16, 119.71 (d, *J* = 1.8 Hz), 119.46, 119.10 (q, *J* = 6.2 Hz), 109.15, 32.22, 26.05. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -62.03. **IR** (UATR): 2971.3, 1591.0, 1557.4, 1468.8, 1438.9, 1370.6, 1325.9, 1271.8, 1118.3, 1077.3, 912.0, 878.0, 742.1 665.0 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{18}BrF_3N$ 444.0575, found 444.0569.



9-methyl-1-(prop-1-en-2-yl)-4-(trifluoromethyl)-2-(3-(trifluoromethyl)phenyl)-9*H*-carbazole (3p): ethyl acetate/petroleum ether = 1:50 as an eluent; white solid, mp 134.9-135.7 ºC; 46% yield (39.8 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.40 (dt, *J* = 8.0, 1.6 Hz, 1H), 7.69 (d, *J* = 2.0 Hz, 1H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.61-7.57 (m, 2H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.50-7.46 (m, 2H), 7.36 (ddd, *J* = 8.0, 6.8, 0.8 Hz, 1H), 5.48 (t, *J* = 1.6 Hz, 1H), 5.143-5.136 (m, 1H), 4.04 (d, *J* = 1.2 Hz, 3H), 1.90 (t, *J* = 1.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 142.93, 141.90, 140.91, 138.49, 135.97, 133.11, 130.55(q, *J* = 32.3 Hz), 129.42, 128.78 (q, *J* = 273.0 Hz), 128.19, 127.06, 126.69 (q, *J* = 3.7 Hz), 125.52 (q, *J* = 273.4 Hz), 123.91(q, *J* = 3.5 Hz), 123.53 (q, *J* = 5.2 Hz), 121.56, 121.24, 121.17, 120.18, 119.81, 119.43, 119.00 (q, *J* = 6.0 Hz), 109.14, 32.18, 25.99. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -62.09, -62.59. **IR** (UATR): 2971.9, 2901.4, 1616.0, 1566.6, 1473.8, 1393.1, 1376.3, 1320.2, 1236.7, 1118.0, 1067.2, 951.2, 872.0, 742.3, 659.7, 568.5 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{18}F_6N$ 434.1343, found 434.1345.

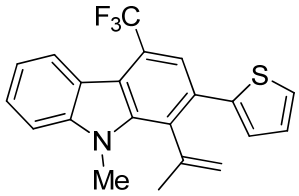


9-methyl-2-(naphthalen-1-yl)-1-(prop-1-en-2-yl)-4-(trifluoromethyl)-9*H*-carbazole (3q and 3q'): ethyl acetate/petroleum ether = 1:80 as an eluent; an inseparable mixture of atropisomers (1:1) as white solid, mp 183.7-184.4 ºC; isolated yield 50% (41.5 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.45 (d, *J* = 8.0 Hz, 1H), 7.93 (t, *J* = 8.8 Hz, 2H), 7.62 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1H), 7.54-7.43 (m, 5H), 7.43-7.35 (m, 3H), 5.36 (t, *J* = 1.6 Hz, 0.5H), 5.11 (s, 0.5H), 4.97 (t, *J* = 1.6 Hz, 0.5H), 4.81 (s, 0.5H), 4.08 (s, 1.5H), 4.05 (s, 1.5H), 2.04 (s, 1.5H), 1.65 (s, 1.5H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 142.79, 142.66, 141.39, 141.03, 139.03, 138.80, 138.45, 137.82, 136.44, 135.76, 133.49, 133.30, 132.75, 130.73, 129.35, 128.24, 128.05, 127.85, 127.66, 126.97, 126.83, 126.55, 126.29, 126.25, 126.04, 125.83, 125.74 (d, *J* = 1.9 Hz), 124.75, 123.58, 123.46 (q, *J* = 5.1 Hz), 121.21, 120.88, 120.30, 120.10, 120.03 (q, *J* = 6.2 Hz), 119.72, 119.65, 119.37, 119.00, 109.15, 32.25, 31.70, 26.63, 25.28. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -61.90, -61.93. **IR** (UATR): 2968.4, 1614.8, 1566.7, 1474.0, 1388.0, 1327.2, 1302.7, 1270.1, 1155.3, 1112.2, 1053.5, 846.7, 777.8, 741.3, 552.3 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{21}F_3N$ 416.1626, found 416.1620.

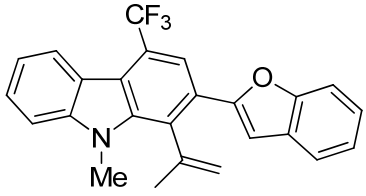


9-methyl-2-(naphthalen-2-yl)-1-(prop-1-en-2-yl)-4-(trifluoromethyl)-9*H*-carbazole (3r): ethyl acetate/petroleum ether = 1:50 as an eluent; white solid, mp 198.3-200.1 ºC; 46% yield (38.2 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.42 (d, *J* = 8.0 Hz, 1H), 7.93-7.86 (m, 4H),

7.61-7.51 (m, 5H), 7.52 (dt, *J* = 8.4, 1.2 Hz, 1H), 7.37 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 5.46 (p, *J* = 1.6 Hz, 1H), 5.19 (dd, *J* = 2.0, 0.8 Hz, 1H), 4.04 (s, 3H), 1.92 (t, *J* = 1.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 142.91, 141.28, 138.84, 138.63, 137.57, 132.95, 132.35, 129.61, 128.57, 128.22, 128.08, 127.72, 127.05, 126.83, 126.24, 126.05, 123.54, 123.46 (q, *J* = 5.2 Hz), 121.31 (q, *J* = 32.9 Hz), 120.82, 120.05, 119.71 (q, *J* = 5.9 Hz), 119.59, 119.39, 109.11, 32.28, 26.04. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -61.95. **IR** (UATR): 3047.0, 2921.0, 1590.7, 1474.6, 1389.4, 1330.6, 1264.2, 1145.0, 1114.1, 947.5, 819.5, 741.9, 475.0 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{21}F_3N$ 416.1626, found 416.1625.

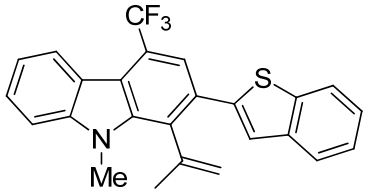


9-methyl-1-(prop-1-en-2-yl)-2-(thiophen-2-yl)-4-(trifluoromethyl)-9*H*-carbazole (3s): ethyl acetate/petroleum ether = 1:100 as an eluent; white solid, mp 129.5-130.8 ºC; 60% yield (44.5 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.39 (d, *J* = 8.0 Hz, 1H), 7.67 (s, 1H), 7.59 (ddd, *J* = 8.0, 6.8, 0.8 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.39 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.35 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.22 (dd, *J* = 3.2, 1.2 Hz, 1H), 7.10 (dd, *J* = 5.2, 3.6 Hz, 1H), 5.59 (t, *J* = 1.6 Hz, 1H), 5.25-5.24 (m, 1H), 4.04 (s, 3H), 2.05 (t, *J* = 1.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 142.94, 141.79, 141.41, 138.71, 129.97, 129.74, 128.80 (q, *J* = 273.2 Hz), 127.77, 126.99, 126.72, 125.94, 123.49 (q, *J* = 5.2 Hz), 121.75 (q, *J* = 32.9 Hz), 121.30, 120.12, 120.06 (q, *J* = 6.1 Hz), 119.68 (d, *J* = 1.9 Hz), 119.45, 109.10, 32.23, 25.75. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -62.13. **IR** (UATR): 2943.8, 1593.0, 1472.4, 1441.1, 1389.0, 1321.3, 1253.4, 1142.0, 1111.7, 1027.5, 906.2, 741.5, 707.7, 568.3 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{17}F_3NS$ 372.1034, found 372.1033.

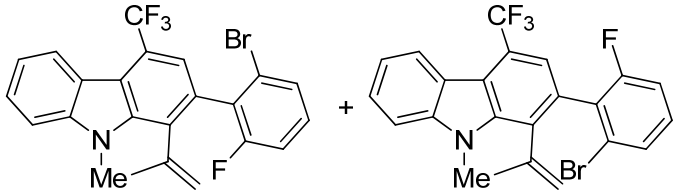


2-(benzofuran-2-yl)-9-methyl-1-(prop-1-en-2-yl)-4-(trifluoromethyl)-9*H*-carbazole (3t): ethyl acetate/petroleum ether = 1:60 as an eluent; light yellow solid, mp 127.6-129.0 ºC; 50% yield (40.5 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.40 (d, *J* = 8.0 Hz, 1H), 8.14 (s, 1H), 7.64 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.60-7.56 (m, 2H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.36 (td, *J* = 7.2, 1.6 Hz, 2H), 7.29-7.25 (m, 1H), 7.23 (d, *J* = 0.8 Hz, 1H), 5.69 (t, *J* = 1.6 Hz, 1H), 5.32 (t, *J* = 1.6 Hz, 1H), 4.10 (s, 3H), 2.29 (t, *J* = 1.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 154.46, 154.28, 143.09, 142.01, 138.63, 129.25, 129.20, 127.22, 126.11(q, *J* = 273.4 Hz), 125.60, 124.48, 123.55 (q, *J* = 5.4 Hz), 121.94 (q, *J* = 33.2 Hz), 121.06, 120.49, 120.25, 120.10, 119.37, 117.70 (q, *J* = 6.4 Hz), 111.15, 109.11, 105.87, 32.21, 25.61. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -62.20. **IR** (UATR): 2970.9, 1613.4, 1571.2, 1472.8, 1438.7, 1389.6, 1327.0, 1233.6, 1144.2, 1106.2, 1063.9, 947.3, 879.4, 737.5,702.5,

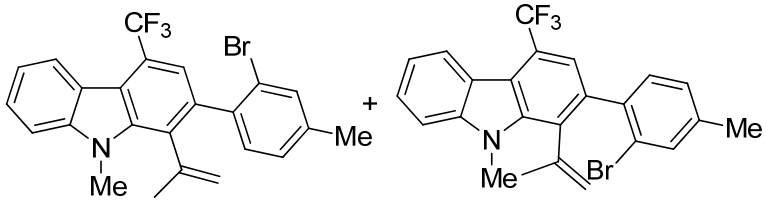
555.5 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{19}F_3NO$ 406.1419, found 406.1419.



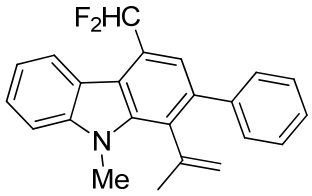
2-(benzo[b]thiophen-2-yl)-9-methyl-1-(prop-1-en-2-yl)-4-(trifluoromethyl)-9*H*-carbazole (3u): ethyl acetate/petroleum ether = 1:60 as an eluent; white solid, mp 206.7-207.3 ºC; 45% yield (37.9 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.40 (d, *J* = 8.0 Hz, 1H), 7.87-7.85 (m, 1H), 7.83-7.81 (m, 1H), 7.73 (s, 1H), 7.61 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.42-7.32 (m, 4H), 5.61 (p, *J* = 1.6 Hz, 1H), 5.30-5.29 (m, 1H), 4.06 (s, 3H), 2.10 (t, *J* = 0.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 143.02, 142.36, 141.14, 140.56, 139.73, 138.63, 130.09, 129.87, 127.17, 126.04 (q, *J* = 273.4 Hz), 124.44, 124.39, 124.28, 123.60, 123.53 (q, *J* = 5.1 Hz), 121.95, 121.51 (q, *J* = 33.0 Hz), 121.41, 120.22, 120.07 (q, *J* = 6.1 Hz), 119.40, 109.17, 32.25, 26.02. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -62.13. **IR** (UATR): 2922.6, 2853.9, 1614.9, 1562.3, 1471.0, 1389.4, 1322.3, 1243.9, 1112.4, 1026.5, 910.4, 740.7, 604.7, 490.4 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{19}F_3NS$ 422.1190, found 422.1193.



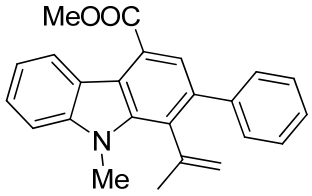
2-(2-bromo-6-fluorophenyl)-9-methyl-1-(prop-1-en-2-yl)-4-(trifluoromethyl)-9*H*-carbazole (3w and 3w'): ethyl acetate/petroleum ether = 1:100 as an eluent; an inseparable mixture of atropisomers (1:1) as white solid, mp 128.5-130.3 ºC; isolated yield 41% (36.9 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.44 (d, *J* = 8.0 Hz, 1H), 7.61 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.51-7.47 (m, 2H), 7.39-7.34 (m, 2H), 7.30 (tt, *J* = 12.0, 6.0 Hz, 1H), 7.16-7.08 (m, 1H), 5.35 (t, *J* =1.6 Hz, 0.5H), 5.27 (dd, *J* = 2.8, 1.2 Hz, 1H), 5.24-5.22 (m, 0.5H), 4.09 (s, 1.5H), 4.07 (s, 1.5H), 2.10 (t, *J* = 1.2 Hz, 1.5H), 2.05 (t, *J* = 1.2 Hz, 1.5H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 161.76 (d, *J* = 249.5 Hz), 161.34 (d, *J* = 248.2 Hz), 142.80, 142.72, 141.09, 140.97, 138.51, 138.40, 130.75, 130.60, 130.51, 130.40, 130.33, 130.29, 130.21, 130.13, 129.97, 129.88, 128.89 (q, *J* =273.3 Hz) , 128.15 (t, *J* = 3.1 Hz), 127.05, 126.62 (d, *J* = 2.9 Hz), 125.08 (d, *J* = 3.0 Hz), 123.55 (q, *J* =5.3 Hz), 122.11 (q, *J* = 33.1 Hz), 121.84 (q, *J* = 33.0 Hz), 120.21, 120.15, 120.12, 119.61 (d, *J* = 6.3 Hz), 119.04 (q, *J* = 6.2 Hz), 118.79, 118.73, 118.71, 118.47, 114.56, 114.34 (d, *J* =1.4 Hz), 109.19, 109.13, 31.72, 31.62, 25.16, 25.13, 25.10. **^{19}F NMR** (376 MHz, DMSO-D_6): δ = -61.03, -105.21, -106.98. **IR** (UATR): 2923.4, 1614.2, 1562.4, 1440.0, 1391.6, 1325.8, 1262.9, 1106.9, 1050.0, 856.7, 777.4, 740.9, 708.7, cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{17}BrF_4N$ 462.0480, found 462.0473.



2-(2-bromo-4-methylphenyl)-9-methyl-1-(prop-1-en-2-yl)-4-(trifluoromethyl)-9*H*-carbazole (3x and 3x'): ethyl acetate/petroleum ether = 1:100 as an eluent; an inseparable mixture of atropisomers (1:1) as white solid, mp 189.2-192.3 ºC; isolated yield 70% (64.0 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.40 (d, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.51 (dd, *J* = 13.2, 8.0 Hz, 2H), 7.40-7.41 (m, 2H), 7.20-7.12 (m, 2H), 5.41 (t, *J* = 1.6 Hz, 0.5H), 5.29 (s, 0.5H), 5.24 (t, *J* = 1.6 Hz, 0.5H), 5.06(s, 0.5H), 4.07 (s, 1.5H), 4.02 (s, 1.5H), 2.41 (s, 3H), 2.04 (s, 1.5H), 1.94 (s, 1.5H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 142.76, 142.68, 141.47, 140.71, 139.15, 139.11, 138.59, 138.36, 138.09, 137.16, 136.50, 132.90, 132.86, 130.12, 129.80, 129.72, 127.34, 127.23, 126.80, 126.24, 124.67, 123.55, 123.44 (q, *J* = 5.1 Hz), 121.25 (q, *J* = 15.8 Hz), 120.07, 120.03, 119.92, 119.73, 119.63, 119.37, 119.10 (q, *J* = 6.0 Hz), 118.81, 109.09, 109.08, 32.16, 31.59, 26.71, 25.04, 20.90. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -61.94. **IR** (UATR): 2966.5, 1615.0, 1571.2, 1469.5, 1435.8, 1380.3, 1328.6, 1274.6, 1143.0, 1113.8, 948.5, 828.6, 740.9, 551.3 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{20}BrF_3N$ 458.0731, found 458.0724.

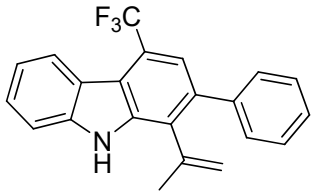


4-(difluoromethyl)-9-methyl-2-phenyl-1-(prop-1-en-2-yl)-9*H*-carbazole (3y): ethyl acetate/petroleum ether = 1:100 as an eluent; white solid, mp 124.6-125.3 ºC; 44% yield (30.5 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.33 (d, *J* = 8.0 Hz, 1H), 7.59 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.45-7.34 (m, 7H), 7.34-7.29 (m, 1H), 5.47 (p, *J* = 1.6 Hz, 1H), 5.14 (dd, *J* = 2.0, 1.2 Hz, 1H), 4.03 (s, 3H), 1.93 (t, *J* = 1.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 142.78, 141.58, 141.49, 138.38, 138.02, 129.86, 128.34 (t, *J* = 2.0 Hz), 127.62, 126.89, 126.42, 125.88 (t, *J* = 22.5 Hz), 123.27 (t, *J* = 4.0 Hz), 120.53, 120.36, 119.88, 119.84, 119.81 (t, J = 6.3 Hz),117.58 (t, J = 239.0 Hz), 109.08, 32.19, 26.03. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -112.24. **IR** (UATR): 2961.9, 1614.0, 1568.5, 1469.7, 1439.4, 1395.0, 1328.3, 1301.2, 1124.2, 1077.3, 1020.2, 976.1, 821.5, 739.4, 702.0, 535.9 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for for $C_{23}H_{20}NF_2$ 348.1564, found 348.1559.

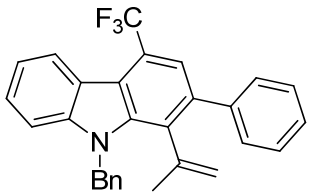


methyl 9-methyl-2-phenyl-1-(prop-1-en-2-yl)-9*H*-carbazole-4-carboxylate (3aa): ethyl acetate/petroleum ether = 1:50 as an eluent, light yellow solid, 25% yield (17.8 mg, 0.2 mmol scale).

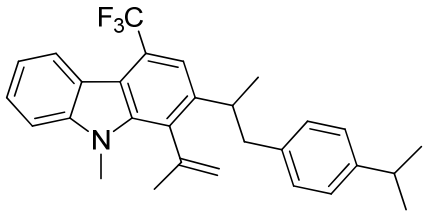
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.84 (dt, *J* = 8.4, 0.8 Hz, 1H), 7.74 (s, 1H), 7.57 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1H), 7.45-7.35 (m, 6H), 7.31 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 5.45 (t, *J* = 2.0 Hz, 1H), 5.11 (dd, *J* = 2.0, 1.2 Hz, 1H), 4.05 (s, 3H), 4.01 (s, 3H), 1.91 (t, *J* = 1,2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 168.51, 143.25, 141.60, 141.54, 138.68, 137.69, 129.85, 129.60, 127.58, 126.83, 126.72, 125.05, 124.52, 123.53, 121.71, 120.95, 120.42, 119.49, 108.69, 52.16, 32.33, 25.95. **IR** (UATR): 2951.3, 1714.1, 1581.1, 1467.8, 1433.7, 1385.2, 1319.1, 1238.5, 1141.4, 1084.0, 1024.3, 925.3, 736.1, 701.1, 554.9 cm^{-1}. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{24}H_{21}NO_2Na$ 378.1470, found 378.1465.



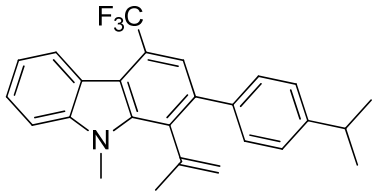
2-phenyl-1-(prop-1-en-2-yl)-4-(trifluoromethyl)-9*H*-carbazole (3ab): ethyl acetate/petroleum ether = 1:50 as an eluent; white solid, mp 186.3-188.6 ºC; 22% yield (15.4 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.55 (s, 1H), 8.36 (d, *J* = 8.4 Hz, 1H), 7.58-7.54 (m, 3H), 7.51 (d, *J* = 4.0 Hz, 2H), 7.46-7.39 (m, 3H), 7.34-7.30 (m, 1H), 5.62 (p, *J* = 1.6 Hz, 1H), 5.45-5.44 (m, 1H), 1.72 (t, *J* = 1.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 142.26, 140.74, 139.79, 138.31, 135.77, 129.27, 128.47, 128.29, 127.40, 126.85, 126.20, 123.53 (q, *J* = 4.5 Hz), 121.69 (q, *J* = 33.1Hz), 120.99, 120.29, 119.57 (q, *J* = 6.1 Hz), 118.67, 118.13, 110.79, 23.23. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -62.15. **IR** (UATR): 3443.7, 2959.7, 2924.3, 1619.2, 1599.2, 1564.3, 1461.8, 1353.9, 1302.2, 1282.6, 1148.2, 1121.2, 965.5, 748.1, 704.6, 454.4 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{17}F_3N$ 352.1313, found 352.1306.



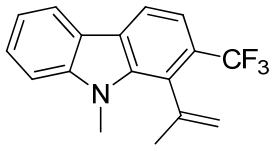
9-benzyl-2-phenyl-1-(prop-1-en-2-yl)-4-(trifluoromethyl)-9*H*-carbazole (3ac): ethyl acetate/petroleum ether = 1:80 as an eluent; white solid, mp 198.4-200.8 ºC; 53% yield (46.8 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.50 (d, *J* = 8.0 Hz, 1H), 7.59 (s, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.44 -7.32 (m, 7H), 7.29-7.22 (m, 3H), 6.97-6.95 (m, 2H), 5.95 (dd, *J* = 28.8, 17.6 Hz, 2H), 5.20 (t, *J* = 1.6 Hz, 1H), 4.95 (s, 1H), 1.70 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 142.51, 141.10, 140.25, 138.07, 137.96, 137.73, 129.98, 129.64, 129.03 (q, *J* = 273.2 Hz), 128.69, 127.65, 127.09 (d, *J* = 1.2 Hz), 127.02, 125.61, 123.53 (q, *J* = 5.3 Hz), 121.71 (q, *J* = 32.8 Hz), 120.52, 120.46, 119.90, 119.83, 119.77, 119.67, 110.03, 48.02, 25.21. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -61.91. **IR** (UATR): 2963.0, 2924.2, 1613.0, 1593.1, 1495.3, 1452.1, 1396.1, 1331.2, 1281.9, 1143.2, 1108.2, 906.0, 743.2, 698.7, 612.1 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{29}H_{23}F_3N$ 442.1783, found 442.1780.



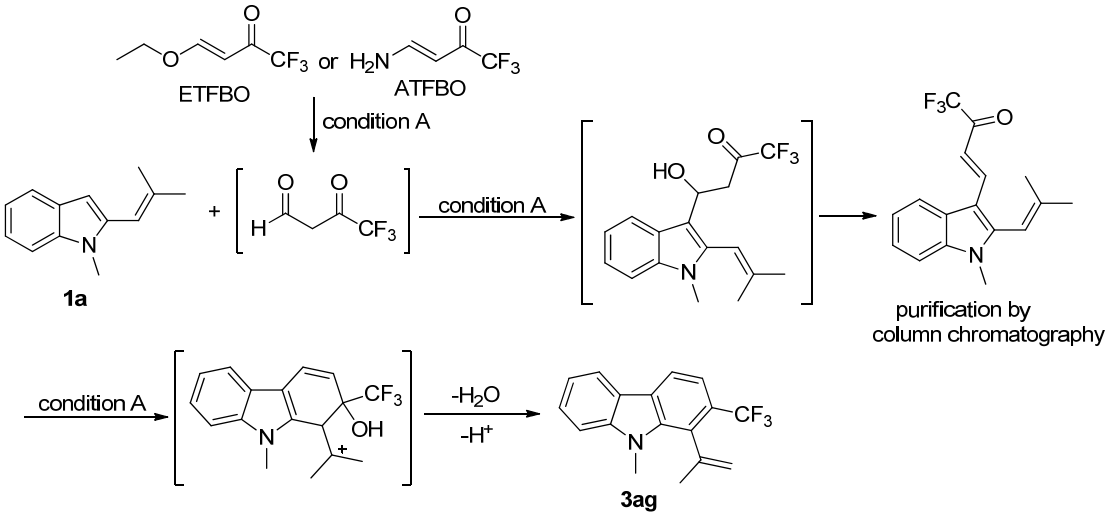
2-(1-(4-isopropylphenyl)propan-2-yl)-9-methyl-1-(prop-1-en-2-yl)-4-(trifluoromethyl)-9*H*-carbazole (3ae+3ae'): ethyl acetate/petroleum ether = 1:50 as an eluent; an inseparable mixture of atropisomers (0.9:1), milky white oil, 31% yield (27.9 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.43 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 24.0 Hz, 1H), 7.59-7.55 (m, 1H), 7.48 (d, *J* = 8.4, 2.0 Hz, 1H), 7.37-7.33 (m, 1H), 7.14-7.11 (m, 2H), 7.04 (d, *J* = 7.6 Hz, 2H), 5.56 (d, *J* = 2.0 Hz, 0.47H), 5.52 (d, *J* = 1.6 Hz, 0.52H), 5.13-5.12 (m, 0.47H), 4.64-4.63 (m 0.52H), 4.05 (s, 3H), 3.52 (p, *J* = 2.8 Hz, 1H), 3.10-2.80 (m, 3H), 2.22 (d, *J* = 1.6 Hz, 1.56H), 1.85 (d, *J* = 1.2 Hz, 1.41H), 1.40 (ddd, *J* = 8.4, 7.2, 1.6 Hz, 3H), 1.29 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 146.61, 146.54, 142.32, 142.30, 142.13, 141.53, 141.51, 141.42, 138.37, 138.22, 138.04, 129.57, 129.36, 129.24 (q, *J* = 273.0 Hz), 129.12, 129.03, 126.31, 126.24, 126.16, 123.06, 123.01, 123.00, 122.17 (q, *J* = 32.6 Hz), 119.84, 119.79, 119.69, 119.67, 119.01, 118.63, 117.68, 117.58, 115.30 (q, *J* = 2.4 Hz), 108.92, 108.88, 45.40, 44.34, 37.91, 37.13, 33.75, 33.73, 31.53, 31.40, 26.93, 26.10, 24.15, 24.09, 24.06, 23.38, 21.98. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -61.93. **IR** (UATR): 2961.0, 1571.0, 1472.9, 1438.8, 1338.3, 1253.9, 1151.9, 1113.3, 953.4, 809.1, 738.9, 549.4 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{29}H_{31}F_3N$ 450.2409, found 450.2413.



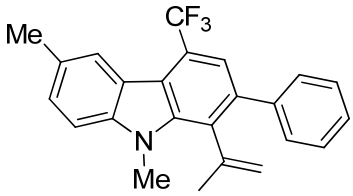
2-(4-isopropylphenyl)-9-methyl-1-(prop-1-en-2-yl)-4-(trifluoromethyl)-9H-carbazole (3af): ethyl acetate/petroleum ether = 1:150 as an eluent; white solid, mp 138.2-140.7 ºC; 28% yield (45.6 mg, 0.4 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.43 (dt, *J* = 8.4, 1.6 Hz, 1H), 7.60 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.53 (s, 1H), 7.49 (dt, *J* = 8.4, 0.8 Hz, 1H), 7.37-7.32 (m, 3H), 7.29-7.26 (m, 2H), 5.50 (q, *J* = 1.6 Hz, 1H), 5.15 (q, *J* = 1.2 Hz, 1H), 4.03 (s, 3H), 3.06 (sep, *J* = 6.8 Hz, 1H), 1.93 (s, 3H), 1.36 (d, *J* = 6.8 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 147.61, 142.89, 141.39, 138.70, 138.56, 137.76, 129.70, 129.45, 129.02 (q, *J* = 273.2 Hz), 126.70, 125.74, 123.40 (q, *J* = 3.0 Hz), 121.52 (q, *J* = 32.6 Hz), 120.61, 119.97, 119.74 (q, *J* = 6.0 Hz), 119.17, 119.15, 109.07, 33.85, 32.33, 25.87, 24.09, 24.05. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -61.94. **IR** (UATR): 2965.9, 1570.8, 1469.5, 1437.5, 1373.1, 1261.5, 1147.1, 1108.5, 1048.5, 882.5, 838.5, 744.6, 599.0, 557.1 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{25}NF_3$ 408.1939, found 408.1936.



After conducting the reaction under condition A (0.4 mmol scale), purified by column chromatography to give the intermediate of (*E*)-1,1,1-trifluoro-4-(1-methyl-2-(2-methylprop-1-en-1-yl)-1*H*-indol-3-yl)but-3-en-2-one, further stirring it under condition A for 20 h led to the product **3ag**. A plausible mechanism was depicted as follows:

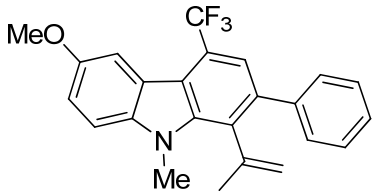


9-methyl-1-(prop-1-en-2-yl)-2-(trifluoromethyl)-9*H*-carbazole (**3ag**): ethyl acetate/petroleum ether = 1:150 as an eluent; white solid, mp 86.4-88.2 ºC; 55% yield (63.6 mg, 0.4 mmol scale, using (E)-4-ethoxy-1,1,1-trifluorobut-3-en-2-one as starting material), 30% yield (34.7 mg, 0.4 mmol, using 4-amino-1,1,1-trifluorobut-3-en-2-one as starting material). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.42 (dt, *J* = 9.2, 1.6 Hz, 1H), 7.60-7.56 (m, 1H), 7.54 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.48 (dt, *J* = 8.4, 0.8 Hz, 1H), 7.36-7.32 (m, 1H), 7.27 (dd, *J* = 7.6, 1.2 Hz, 1H), 5.47 (t, *J* = 1.6 Hz, 1H), 5.18 (dd, *J* = 2.0, 0.8 Hz, 1H), 4.01 (s, 3H), 2.26 (t, *J* = 1.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 143.95, 142.44, 138.18, 131.68, 129.06 (q, *J* = 273.0 Hz), 126.82, 123.53 (q, *J* = 5.2 Hz), 122.33 (q, *J* = 32.7 Hz), 120.05, 120.03, 119.98, 119.95, 117.26, 116.71 (q, *J* = 6.1 Hz), 109.08, 31.89, 25.91. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -62.01. **IR** (UATR): 2922.0, 1614.9, 1588.3, 1473.4, 1393.1, 1313.2, 1279.8, 1154.4, 1104.1, 1076.3, 945.7, 817.4, 737.8, 660.2, 558.2 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{15}NF_3$ 290.1157, found 290.1161.

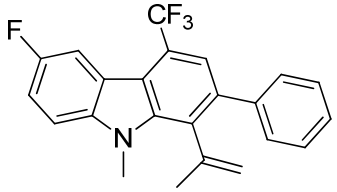


6,9-dimethyl-2-phenyl-1-(prop-1-en-2-yl)-4-(trifluoromethyl)-9*H*-carbazole (3ah): ethyl acetate/petroleum ether = 1:150 as an eluent; white solid, mp 155.8-156.7 ºC; 62% yield (47 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.17 (d, *J* = 1.2 Hz, 1H), 7.47 (s, 1H), 7.43-7.35 (m, 7H), 5.46 (p, *J* = 1.6 Hz, 1H), 5.124-5.117 (m, 1H), 3.99 (s, 3H), 2.59 (s, 3H), 1.91 (t, *J* = 0.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 141.32, 141.28, 138.78, 137.43, 129.82, 129.29, 129.24, 128.22, 127.66, 126.97, 126.28 (q, *J* = 273.3 Hz), 123.17 (q, *J* = 5.2 Hz), 121.13 (q, *J* = 32.8 Hz), 120.81, 119.64, 119.24 (q, *J* = 6.2 Hz), 119.09, 108.77, 32.28, 25.93, 21.67. **^{19}F NMR** (376 MHz,

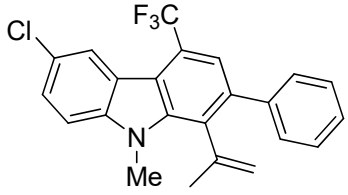
$CDCl_3$): δ = -61.78. **IR** (UATR): 2917.9, 1594.3, 1566.9, 1492.0, 1371.6, 1306.0, 1236.6, 1142.7, 1105.4, 963.2, 881.3, 799.3, 701.6, 591.1 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{21}F_3N$ 380.1626, found 380.1626.



6-methoxy-9-methyl-2-phenyl-1-(prop-1-en-2-yl)-4-(trifluoromethyl)-9H-carbazole (3ai): ethyl acetate/petroleum ether = 1:100 as an eluent; light white solid, mp 128.2-129.2 ºC; 82% yield (64.8 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.88 (t, *J* = 1.6 Hz, 1H), 7.47 (s, 1H), 7.42-7.36 (m, 6H), 7.24 (dd, *J* = 8.8, 2.4 Hz, 1H), 5.46 (t, *J* = 2.0 Hz, 1H), 5.13 (t, *J* = 1.6 Hz, 1H), 3.99 (s, 3H), 3.97 (s, 3H), 2.59 (s, 3H), 1.91 (d, *J* = 2.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 154.04, 141.28 (d, *J* = 3.1 Hz), 139.04, 138.06, 137.52, 129.81, 129.48, 128.97 (q, *J* = 273.2 Hz), 127.67, 127.00, 121.44 (q, *J* = 32.9 Hz), 120.62, 119.78, 119.15 (q, *J* =6.1 Hz), 119.00, 116.35, 109.77, 105.89 (q, *J* = 5.4 Hz), 56.01, 32.31, 25.89. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -61.56. **IR** (UATR): 2950.4, 1623.8, 1582.3, 1486.7, 1375.5, 1332.8, 1226.8, 1145.0, 1107.1, 1049.2, 897.6, 802.7, 701.7, 613.3, 515.5 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{21}F_3NO$ 396.1575, found 379.1579.

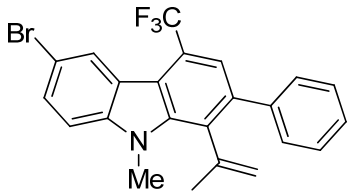


6--fluoro-9-methyl-2-phenyl-1-(prop-1-en-2-yl)-4-(trifluoromethyl)-9*H*-carbazole (3aj): ethyl acetate/petroleum ether = 1:100 as an eluent; yellow solid, mp 175.8-176.5 ºC; 98 % yield (75.1 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.07 (ddd, *J* = 4.0, 2.4, 1.2 Hz, 1H), 7.49 (s, 1H), 7.42-7.36 (m, 6H), 7.32 (td, *J* = 8.8, 2.4 Hz, 1H), 5.47 (t, *J* = 1.6 Hz, 1H), 5.13 (dd, *J* = 2.0, 1.2 Hz, 1H), 4.01 (s, 3H), 1.91 (t, *J* = 1.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 158.75 (d, *J* = 236.1 Hz), 141.03, 139.36, 139.28, 138.26, 129.74, 129.69, 128.75 (q, *J* = 273.0 Hz), 127.72, 127.13, 121.71 (q, *J* = 32.9 Hz), 120.83, 119.84 (d, *J* = 10.2 Hz), 119.53(q, *J* = 6.1 Hz), 118.74, 114.89 (d, *J* = 25.8 Hz), 109.73 (d, *J* = 9.2 Hz), 109.07 (q, *J* = 5.4 Hz), 108.82 (q, *J* = 5.5 Hz), 32.41, 25.86. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -61.88, -123.61. **IR** (UATR): 2937.5, 1586.1, 1477.2, 1377.6, 1281.7, 1260.4, 1122.3, 1071.9, 973.1, 897.9, 794.9, 700.2, 589.7, 444.4 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{18}F_4N$ 384.1375, found 384.1369.

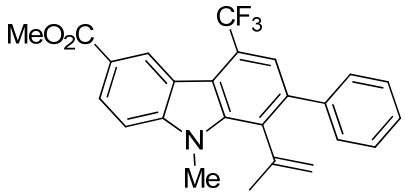


6-chloro-9-methyl-2-phenyl-1-(prop-1-en-2-yl)-4-(trifluoromethyl)-9*H*-carbazole (3ak): ethyl

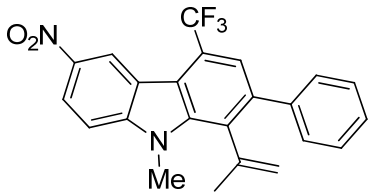
acetate/petroleum ether = 1:100 as an eluent; light yellow solid, mp 156.4-157.2 ºC; 95 % yield (75.8 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.32 (t, *J* = 1.6 Hz, 1H), 7.52-7.49 (m, 2H), 7.41-7.36 (m, 6H), 5.47 (q, *J* = 1.6 Hz, 1H), 5.13 (dd, *J* = 1.6, 1.2 Hz, 1H), 4.00 (s, 3H), 1.90 (t, *J* = 1.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 141.16, 140.96, 140.92, 139.03, 138.41, 129.81, 129.72, 129.44, 128.69 (q, *J* = 273.3 Hz), 127.72, 127.16, 126.90, 122.86 (q, *J* = 5.6 Hz), 121.43 (q, *J* = 33.0 Hz), 120.90, 120.56, 119.80 (q, *J* = 6.1 Hz), 118.31, 110.09, 32.42, 25.87. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -61.97. **IR** (UATR): 2961.3, 1594.4, 1470.9, 1439.8, 1371.1, 1280.5, 1256.1, 1140.0, 1150.9, 955.1, 880.2, 739.4, 702.9, 588.9 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{18}NF_3Cl$ 400.1080, found 400.1075.



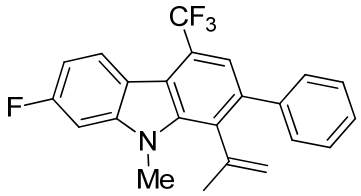
6-methoxy-9-methyl-2-phenyl-1-(prop-1-en-2-yl)-4-(trifluoromethyl)-9H-carbazole (3al): ethyl acetate/petroleum ether = 1:100 as an eluent; yellow solid, mp 153.2-154.4 ºC; 94 % yield (83.3 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.47 (t, *J* = 1.2 Hz, 1H), 7.64 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.49 (s, 1H), 7.43-7.32 (m, 5H), 7.34 (d, *J* = 8.8 Hz, 1H), 5.47 (p, *J* = 1.6 Hz, 1H), 5.13 (dd, *J* = 2.0, 1.2 Hz, 1H), 4.00 (s, 3H), 1.90 (t, *J* = 1.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 141.45, 140.94, 140.90, 138.87, 138.45, 129.72, 129.52, 128.69 (q, *J* = 273.2 Hz), 128.07, 127.73, 127.17, 125.84 (q, *J* = 5.6 Hz), 121.76 (q, *J* = 33.0 Hz), 121.18, 120.92, 119.91 (q, *J* = 6.2 Hz), 118.18, 112.93, 110.54, 32.40, 25.87. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -61.97. **IR** (UATR): 2944.2, 1567.0, 1500.7, 1468.8, 1441.7, 1372.0, 1280.4, 1259.5, 1148.9, 1114.8, 1073.8, 952.9, 883.7, 801.3, 700.1, 615.0 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{18}BrF_3N$ 444.0575, found 444.0571.



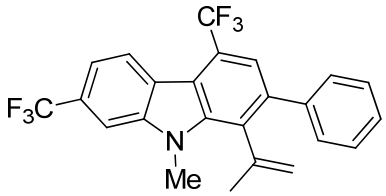
9-methyl-2-phenyl-1-(prop-1-en-2-yl)-4-(trifluoromethyl)-9H-carbazole (3am): ethyl acetate/petroleum ether = 1:30 as an eluent; white solid, mp 173.3-174.5 ºC; 52% yield (44 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 9.10 (s, 1H), 8.28 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.53 (s, 1H), 7.48 (d, *J* = 8.8 Hz, 1H), 7.39-7.36 (m, 5H), 5.48 (t, *J* = 1.6 Hz, 1H), 5.14 (s, 1H), 4.04 (s, 3H), 4.00 (s, 3H), 1.90 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 167.74, 145.31, 140.90, 140.82, 139.22, 138.56, 129.85, 129.74, 128.21, 127.74, 127.20, 125.97 (q, *J* = 273.4 Hz), 125.90 (q, *J* = 5.5 Hz), 122.00, 121.59 (d, *J* = 33.0 Hz), 121.00, 120.26 (q, *J* = 6.1 Hz), 119.48, 119.26, 108.78, 52.09, 32.58, 25.89. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -62.11. **IR** (UATR): 2945.7, 1720.6, 1615.6, 1563.3, 1430.8, 1313.9, 1238.3, 1110.7, 1072.2, 997.2, 877.5, 762.8, 699.4, 590.5 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{21}F_3NO_2$ 424.1524, found 424.1525.



9-methyl-6-nitro-2-phenyl-1-(prop-1-en-2-yl)-4-(trifluoromethyl)-9*H*-carbazole (3an): ethyl acetate/petroleum ether = 1:20 as an eluent; white solid, mp 221.4-222.7 ºC; 68% yield (55.8 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 9.24 (d, *J* = 2.0 Hz, 1H), 8.41 (dd, *J* = 9.2, 2.4 Hz, 1H), 7.57 (s, 1H), 7.47 (d, *J* = 9.2 Hz, 1H), 7.44-7.37 (m, 5H), 5.53 (p, *J* = 1.6 Hz, 1H), 5.18 (t, *J* = 1.2 Hz, 1H), 4.09 (s, 3H), 1.91 (t, *J* = 1.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 145.53, 141.38, 140.47, 140.37, 139.82, 139.70, 130.49, 129.66, 127.85, 127.45, 125.73 (q, *J* = 273.3 Hz), 122.21, 121.83, 121.50, 121.10 (q, *J* = 5.8 Hz), 120.22 (q, *J* = 5.8 Hz), 119.20 (d, *J* = 2.2 Hz), 119.09, 108.98, 32.90, 25.82. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -62.22. **IR** (UATR): 2966.3, 1615.4, 1597.01, 1568.3, 1518.3, 1384.5, 1326.7, 1132.9, 1101.1, 1071.8, 904.2, 807.4, 697.0, 617.5 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{18}F_3N_2O_2$ 411.1320, found 411.1319.



7-fluoro-9-methyl-2-phenyl-1-(prop-1-en-2-yl)-4-(trifluoromethyl)-9*H*-carbazole (3ao): ethyl acetate/petroleum ether = 1:150 as an eluent; white solid, mp 198.8-200.4 ºC; 70% yield (53.6 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.34 (ddd, *J* = 6.8, 5.2, 1.2 Hz, 1H), 7.52 (s, 1H), 7.44-7.38 (m, 5H), 7.13 (dd, *J* = 9.6, 2.4 Hz, 1H), 7.09 (td, *J* = 8.8, 2.0 Hz, 1H), 5.48 (t, *J* = 1.6 Hz, 1H), 5.15-5.14 (m, 1H), 3.97 (s, 3H), 1.92 (t, *J* = 1.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 163.78 (d, *J* = 244.9 Hz), 143.94 (d, *J* = 12.0 Hz), 141.08 (d, *J* = 3.6 Hz), 139.14 (d, *J* = 2.0 Hz), 137.51, 130.43, 129.81, 129.59, 129.48, 128.89 (q, *J* = 273.1 Hz), 128.67, 127.72, 127.11, 124.81(m, *J* = 5.4 Hz, 6C), 121.18 (q, *J* = 33.0 Hz), 120.84, 119.87 (q, *J* = 5.9 Hz), 119.13, 116.03, 108.47 (d, *J* = 48.1 Hz), 95.93 (d, *J* = 26.7 Hz), 32.48, 25.88. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -62.10, -113.29. **IR** (UATR): 2969.8, 1623.8, 1567.3, 1435.4, 1391.7, 1373.5, 1330.1, 1233.3, 1153.7, 1101.6, 1046.3, 969.0, 834.4, 772.4, 705.0, 557.0 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{18}F_4N$ 384.1375, found 384.1366.

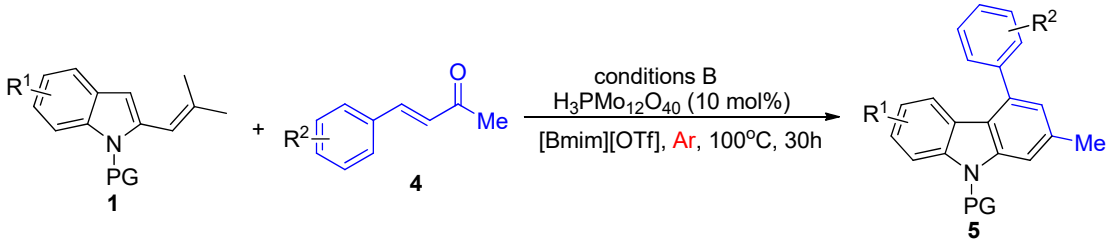


9-methyl-2-phenyl-1-(prop-1-en-2-yl)-4,7-bis(trifluoromethyl)-9*H*-carbazole (3ap): ethyl acetate/petroleum ether = 1:80 as an eluent; white solid, mp 202.2-203.5 ºC; 64% yield (55.4 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.49 (d, *J* = 8.4 Hz, 1H), 7.76 (s, 1H), 7.59-7.56 (m, 2H), 7.45-7.39 (m, 5H), 5.51 (t, *J* = 1.6 Hz, 1H), 5.16 (d, *J* = 1.6 Hz, 1H), 4.09 (s, 3H), 1.94 (t,

J = 1.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 141.97, 140.89, 140.78, 139.63, 139.07, 129.88, 129.70, 128.91 (q, J = 32.1 Hz), 128.84 (q, J = 273.2 Hz), 128.70 (q, J = 273.1 Hz), 127.78, 127.28, 123.85 (q, J = 5.4 Hz), 122.20 (q, J = 33.0 Hz), 122.10, 121.08, 120.28 (q, J = 6.0 Hz), 118.37, 116.57 (d, J = 3.6 Hz), 106.50 (q, J = 4.1 Hz), 32.45, 25.84. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -61.24, -62.04. **IR** (UATR): 2976.3, 1596.6, 1569.1, 1497.3, 1467.3, 1375.9, 1337.5, 1281.7, 1153.7, 1106.2, 1068.4, 954.1, 864.9, 699.1, 626.8 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{18}F_6N$ 434.1343, found 434.1349.

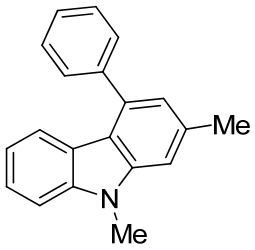
5.2 Carbazole derivatives through 1,4-addition cascade approach

Representative procedure for standard condition B



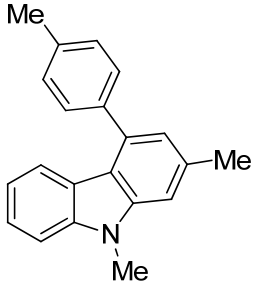
A flame-dried sealed tube was charged with 2-(2-methylprop-1-en-1-yl)-1H-indole **1** (0.2 mmol), (*E*)-4-phenylbut-3-en-2-one **4** (0.4 mmol), [Bmim][OTf] (1 mL), and $H_3PMo_{12}O_{40}$ (10 mol%) under an argon atmosphere at room temperature. The mixture was stirred at 100 °C for 30 h. The progress of the reaction was monitored by the disappearance of the starting material as visualized by TLC. After completion of the reaction, the mixture was cooled to room temperature, extracted with toluene (10 mL × 2), the combined organic layers were then concentrated under reduced pressure and purified by flash chromatography on silica gel using petroleum ether/EtOAc (50:1-30:1) as eluent to afford target product **5**. The ionic liquid of [Bmim][OTf] could be recycled up to 3 times using the follows procedure: after removing acetone and toluene from the ionic liquid under vacuum, it was necessary to add 3 mol%, 5 mol%, and 8 mol% phosphomolybdic acid in the second, third, and fourth cycle, respectively, due to the partial leaching of the catalyst caused by toluene extraction during each cycle.

Characterization data of carbazole derivatives through 1,4-addition cascade approach

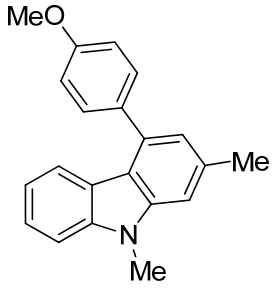


2,9-dimethyl-4-phenyl-9*H*-carbazole (5a): ethyl acetate/petroleum ether = 1:50 as an eluent, white solid, 55% yield (29.8 mg, 0.2 mmol scale). All spectral data are in accord with the literature. [20] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.69-7.67 (m, 2H), 7.59-7.49 (m, 4H), 7.45-7.38 (m, 2H), 7.24 (s, 1H), 7.03-6.99 (m, 2H), 3.88 (s, 3H), 2.64 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 141.88, 141.45,

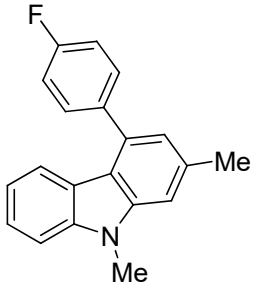
141.28, 137.44, 135.67, 129.26, 128.41, 127.46, 125.06, 122.53, 122.24, 122.01, 118.47, 118.00, 108.20, 107.70, 29.12, 22.16. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{18}N$ 272.1439, found 272.1436.



2,9-dimethyl-4-(p-tolyl)-9*H*-carbazole (5c): ethyl acetate/petroleum ether = 1:50 as an eluent; white solid, mp 110.1-111.2 ºC; 56% yield (31.9 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.59-7.55 (m, 3H), 7.44-7.45 (m, 4H), 7.22 (s, 1H), 7.03-7.00 (m, 1H), 6.98 (d, *J* = 1.2 Hz, 1H), 3.87 (s, 3H), 2.63 (s, 3H), 2.52 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 141.89, 141.26, 138.47, 137.47, 137.08, 135.65, 129.10, 124.98, 122.61, 122.29, 122.08, 118.40, 118.03, 108.14, 107.51, 29.11, 22.15, 21.41. **IR** (UATR): 2916.0, 1599.3, 1470.5, 1410.5, 1320.5, 1117.2, 815.7, 745.0, 728.6, 638.7, 567.8, 446.1 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{20}N$ 286.1596, found 286.1592.

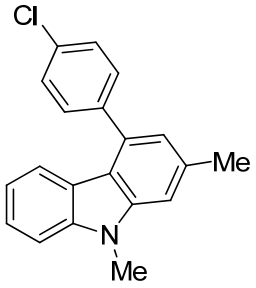


4-(4-methoxyphenyl)-2,9-dimethyl-9*H*-carbazole (5d): ethyl acetate/petroleum ether = 1:50 as an eluent; white solid, mp 96.3- 98.5 ºC; 30 % yield (18 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.76-7.71 (m, 3H), 7.55-7.50 (m, 1H), 7.30 (s, 1H), 7.22-7.19 (m, 2H), 7.17-7.13 (m, 1H), 7.11-7.10 (m, 1H), 4.03 (d, *J* = 1.6 Hz, 3H), 3.90 (s, 3H), 2.74 (d, *J* = 2.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 159.26, 142.01, 141.37, 137.24, 135.74, 133.95, 130.45, 125.11, 122.75, 122.43, 122.11, 118.56, 118.24, 113.93, 108.30, 107.55, 55.46, 29.12, 22.26. **IR** (UATR): 2913.5, 1598.6, 1515.5, 1469.5, 1321.7, 1296.5, 1244.5, 1177.4, 1030.1, 838.4, 748.6, 730.7, 638.2, 565.7 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{20}NO$ 302.1545, found 302.1549.

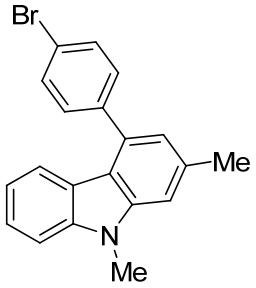


4-(4-fluorophenyl)-2,9-dimethyl-9*H*-carbazole (5e): ethyl acetate/petroleum ether = 1:50 as an

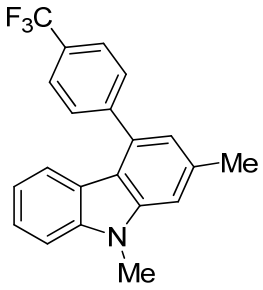
eluent; white solid, mp 96.3-97.5 ºC; 63% yield, (36.4 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.62-7.59 (m, 2H), 7.48 (dt, *J* = 8.0, 0.8 Hz, 1H), 7.44-7.38 (m, 2H), 7.25-7.21 (m, 3H), 7.03 (ddd, *J* = 8.0, 6.4, 2.0 Hz, 1H), 6.94 (d, *J* = 1.6 Hz, 1H), 3.87 (s, 3H), 2.62 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 163.68 (d, *J* = 246.6 Hz), 141.85, 141.27, 137.39 (d, *J* = 3.3 Hz), 136.29, 135.70, 130.85 (d, *J* = 11.0 Hz), 125.14, 122.37, 122.23, 121.78, 118.53, 118.03, 115.41, 115.20, 108.28 (d, *J* = 45.6 Hz), 29.12, 22.11. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -115.31 (d, *J* = 3.4 Hz). **IR** (UATR): 2916.4, 1601.5, 1509.5, 1471.3, 1322.1, 1217.9, 1154.3, 831.6, 728.8, 636.3, 563.1 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{17}FN$ 290.1345, found 290.1346.



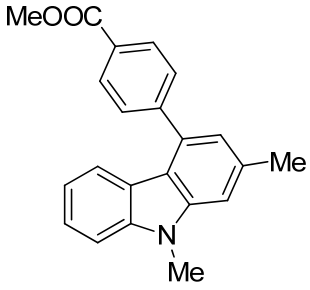
4-(4-chlorophenyl)-2,9-dimethyl-9*H*-carbazole (5f): ethyl acetate/petroleum ether = 1:50 as an eluent; white solid, mp 112.7-114.0 ºC; 54% yield (32.9 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.63-7.61 (m, 2H), 7.56-7.53 (m, 3H), 7.47-7.39 (m, 2H), 7.26-7.25 (m, 1H), 7.07 (ddd, *J* = 8.0, 6.8, 1.6 Hz, 1H), 6.96 (d, *J* = 1.6 Hz, 1H), 3.87 (s, 3H), 2.64 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 141.90, 141.31, 139.93, 136.05, 135.75, 133.43, 130.65, 128.64, 125.25, 122.29, 122.16, 121.85, 118.62, 117.86, 108.36, 108.06, 29.13, 22.15. **IR** (UATR): 2969.0, 1598.7, 1469.5, 1392.5, 1322.6, 1118.4, 1083.2, 1012.6, 824.0, 748.5, 565.0, 504.0 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{17}ClN$ 306.1050, found 306.1052.



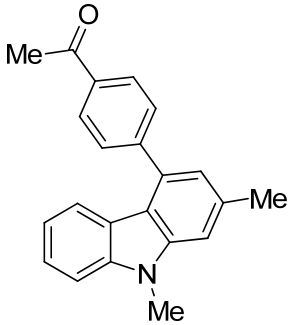
4-(4-bromophenyl)-2,9-dimethyl-9*H*-carbazole (5g): ethyl acetate/petroleum ether = 1:50 as an eluent, light yellow oil, 43% yield (30 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.67(d, *J* = 8.4 Hz, 2H), 7.53-7.49 (m, 3H), 7.42-7.38 (m, 2H), 7.24 (s, 1H), 7.04 (ddd, *J* = 8.0, 6.4, 2.0 Hz, 1H), 6.92 (d, *J* = 1.6 Hz, 1H), 3.87 (s, 3H), 2.61 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 141.88, 141.28, 140.37, 136.00, 135.74, 131.55, 130.95, 125.22, 122.23, 122.06, 121.82, 121.57, 118.59, 117.76, 108.31, 108.03, 29.13, 22.09. **IR (UATR):** 2922.0, 1600.5, 1572.7, 1469.9, 1321.3, 1289.4, 1118.8, 1070.8, 1010.1, 822.5, 728.6, 685.8, 565.4 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{17}BrN$ 350.0544, found 350.0540.



2,9-dimethyl-4-(4-(trifluoromethyl)phenyl)-9*H*-carbazole (5h): ethyl acetate/petroleum ether = 1:50 as an eluent; white solid, mp 140.1-141.0 ºC; 58% yield (39.3 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.81-7.76 (m, 4H), 7.45-7.39 (m, 3H), 7.27 (t, *J* = 1.2 Hz, 1H), 7.03 (ddd, *J* = 6.8, 5.6, 2.0 Hz, 1H), 6.94 (d, *J* = 1.2 Hz, 1H), 3.88 (s, 3H), 2.62 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 145.17, 141.88, 141.30, 135.79, 135.74, 129.75, 129.61, 129.42, 128. 51(q, *J* = 273.1 Hz), 125.42 (q, *J* = 3.7 Hz), 122.16, 122.06, 121.70, 118.66, 117.69, 108.40, 108.38, 29.14, 22.08. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -62.19. **IR** (UATR): 2968.3, 1601.9, 1569.9, 1470.6, 1400.2, 1321.5, 1117.6, 1103.9, 1067.8, 832.0, 748.0, 637.0, 593.1 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{17}F_3N$ 340.1313, found 340.1319.

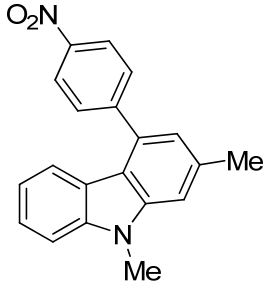


methyl 4-(2,9-dimethyl-9*H*-carbazol-4-yl)benzoate (5i): ethyl acetate/petroleum ether = 1:20 as an eluent, light yellow oil, 40% yield (26.3 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.22-8.20 (m, 2H), 7.74-7.71 (m, 2H), 7.47-7.44 (m, 1H), 7.41-7.38 (m, 2H), 7.25 (s, 1H), 6.70-6.95 (m, 2H), 4.00 (s, 3H), 3.87 (s, 3H), 2.61 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 167.23, 146.29, 141.88, 141.29, 136.18, 135.73, 129.73, 129.69, 129.35, 129.30, 129.15, 125.27, 122.13, 122.01, 121.88, 121.85, 118.59, 117.69, 108.33, 108.30, 108.27, 52.22, 29.14, 22.09. **IR** (UATR): 2948.3, 1716.9, 1600.2, 1471.1, 1434.7, 1321.5, 1271.3, 1175.2, 1099.2, 1019.1, 831.0, 729.0, 707.5, 566.6, 445.2 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{20}NO_2$ 330.1494, found 330.1499.

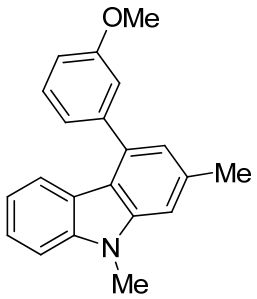


1-(4-(2,9-dimethyl-9*H*-carbazol-4-yl)phenyl)ethenone (5j): ethyl acetate/petroleum ether = 1:30 as an eluent; white solid, mp 151.8-153.8 ºC; 61% yield (38.2 mg, 0.2 mmol scale). **^{1}H NMR** (400

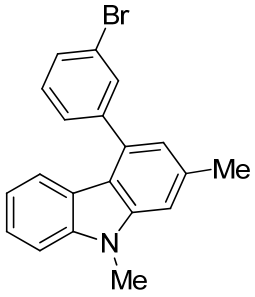
MHz, $CDCl_3$): δ = 8.14 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.49 (dt, *J* = 7.6, 0.8 Hz, 1H), 7.44-7.38 (m, 2H), 7.26 (s, 1H), 7.02 (ddd, *J* = 8.0, 6.0, 1.6 Hz, 1H), 6.96 (t, *J* = 0.8 Hz, 1H), 3.87 (s, 3H), 2.73 (s, 3H), 2.62 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 146.52, 141.91, 141.32, 136.17, 136.06, 135.76, 129.54, 128.53, 125.32, 122.12, 122.04, 121.82, 118.62, 117.67, 108.39, 29.14, 26.78, 22.10. **IR** (UATR): 2915.1, 1680.8, 1597.8, 1472.0, 1396.4, 1320.2, 1262.7, 957.1, 830.5, 750.5, 729.3, 590.9, 446.5 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{20}NO$ 314.1545, found 314.1547.



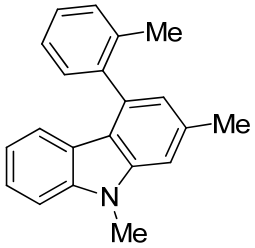
2,9-dimethyl-4-(4-nitrophenyl)-9*H*-carbazole (5k): ethyl acetate/petroleum ether = 1:30 as an eluent; yellow solid, mp 187.5-189.0 ºC; 24% yield (15.2 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.40-8.37 (m, 2H), 7.83-7.79 (m, 2H), 7.44-7.41 (m, 3H), 7.30 (t, *J* = 0.8 Hz, 1H), 7.03 (ddd, *J* = 8.0, 6.0, 2.0 Hz, 1H), 6.94 (d, *J* = 1.2 Hz, 1H), 3.89 (s, 3H), 2.62 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 148.40, 147.30, 141.91, 141.34, 135.87, 134.75, 130.19, 125.56, 123.73, 122.03, 121.76, 121.54, 118.78, 117.49, 108.95, 108.59, 29.18, 22.08. **IR** (UATR): 2911.6, 1622.7, 1595.3, 1511.7, 1471.2, 1346.8, 1321.1, 1100.0, 1012.3, 845.9, 750.3, 699.9, 563.8, 445.1 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{17}N_2O_2$ 317.1290, found 317.1285.



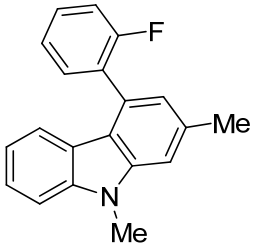
4-(3-methoxyphenyl)-2,9-dimethyl-9*H*-carbazole (5l): ethyl acetate/petroleum ether = 1:50 as an eluent, white solid, mp 76.2- 77.5 ºC; 18% yield (10.8 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.57 (dt, *J* =8.0, 0.8 Hz, 1H), 7.47 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.41-7.38 (m, 2H), 7.26-7.23 (m, 2H), 7.20 (dd, *J* = 2.8, 1.6 Hz, 1H), 7.06-6.99 (m, 3H), 3.872 (s, 3H), 3.870 (s, 3H), 2.62 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 159.58, 142.81, 141.85, 141.26, 137.24, 135.64, 129.41, 125.06, 122.43, 122.13, 122.06, 121.67, 118.49, 117.91, 114.31, 113.49, 108.18, 107.76, 55.36, 29.12, 22.13. **IR** (UATR): 2929.9, 1598.4, 1574.9, 1470.5, 1319.7, 1286.2, 1149.2, 1044.9, 838.5, 783.8, 746.4, 702.5, 580.6 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{20}NO$ 302.1545, found 302.1547.



4-(3-bromophenyl)-2,9-dimethyl-9*H*-carbazole (5m): ethyl acetate/petroleum ether = 1:50 as an eluent, colorless liquid, 52% yield (36.3 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 7.6 Hz, 1H), 7.48 (d, *J* = 4.4 Hz, 2H), 7.45-7.35 (m, 3H), 7.28 (s, 1H), 7.03-6.96 (m, 1H), 6.94 (s, 1H), 3.87 (s, 3H), 2.64 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 142.04, 141.37, 141.15, 135.69, 135.47, 132.79, 131.29, 129.18, 127.48, 125.15, 123.80, 122.40, 121.64, 121.50, 118.80, 118.49, 108.26, 108.21, 29.11, 22.25. **IR** (UATR): 2920.3, 1600.3, 1556.9, 1467.9, 1320.9, 1288.3, 1072.0, 830.8, 728.9, 696.3, 583.8 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{17}BrN$ 350.0544, found 350.0541.

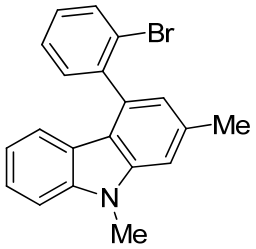


2,9-dimethyl-4-(o-tolyl)-9*H*-carbazole (5n): ethyl acetate/petroleum ether = 1:50 as an eluent; white solid, mp 132.4-133.0 ºC; 50% yield (28.5 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.44-7.35 (m, 6H), 7.24 (d, *J* = 0.8 Hz, 1H), 6.98-6.93 (m, 2H), 6.91 (d, *J* = 0.8 Hz,1H), 3.88 (s, 3H), 2.63 (s, 3H), 2.13 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 141.44, 141.10, 140.93, 136.58, 136.45, 135.63, 129.93, 129.48, 127.64, 125.89, 124.93, 122.81, 121.59, 121.35, 118.78, 118.61, 108.04, 107.45, 29.09, 22.24, 19.85. **IR** (UATR): 2919.8, 1599.0, 1469.5, 1410.5, 1322.1, 1121.4, 1043.3, 839.8, 749.5, 731.3, 568.6, 445.6 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{20}N$ 286.1596, found 286.1590.

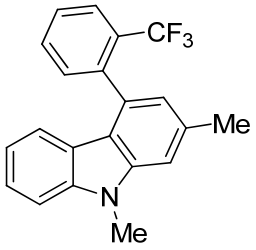


4-(2-fluorophenyl)-2,9-dimethyl-9*H*-carbazole (5o): ethyl acetate/petroleum ether = 1:50 as an eluent; white solid, mp 150.1-151.6 ºC; 58% yield (33.5 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.57 (td, *J* = 7.2, 1.6 Hz, 1H), 7.53-7.47 (m, 1H), 7.43-7.37 (m, 2H), 7.34-7.29 (m, 3H), 7.26 (s, 1H), 7.03-6.96 (m, 2H), 3.86 (s, 3H), 2.63 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 161.32 (d, *J* = 247.7 Hz), 141.61, 141.23, 135.54, 131.83 (d, *J* = 3.4 Hz), 130.18, 129.50 (d, *J* = 8.0 Hz),

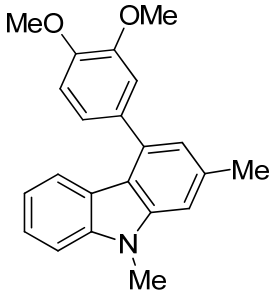
128.91, 128.74, 125.18, 124.22 (d, J = 3.6 Hz), 122.47, 122.45, 121.42, 118.76 (d, J = 5.2 Hz), 115.96, 115.73, 108.41(d, J = 18.6 Hz), 29.07, 22.15. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -114.98 (m). **IR** (UATR): 2928.7, 1597.2, 1574.1, 1470.8, 1319.6, 1207.4, 1155.5, 841.1, 767.4, 750.8, 529.1cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{17}FN$ 290.1345, found 290.1346.



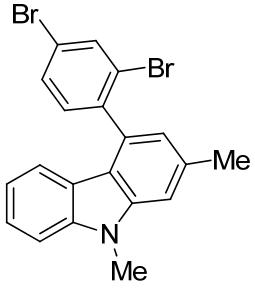
4-(2-bromophenyl)-2,9-dimethyl-9*H*-carbazole (5p): ethyl acetate/petroleum ether = 1:50 as an eluent; white solid, mp 178.1-179.2 °C; 39% yield (27.2 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.82 (d, J = 8.0 Hz, 1H), 7.48 (d, J = 4.4 Hz, 2H), 7.40-7.35 (m, 3H), 7.27 (s, 1H), 7.02-6.96 (m, 2H), 6.94 (d, J = 1.2 Hz, 1H), 3.87 (s, 3H), 2.64 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 142.04, 141.37, 141.16, 135.69, 135.46, 132.79, 131.28, 129.17, 127.47, 125.14, 123.80, 122.40, 121.64, 121.49, 118.80, 118.50, 108.25, 108.20, 29.11, 22.24. **IR** (UATR): 2913.6, 1598.9, 1466.8, 1410.7, 1322.4, 1294.2, 1020.2, 834.5, 747.6, 678.4, 643.8, 445.4 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{17}BrN$ 350.0544, found 350.0541.



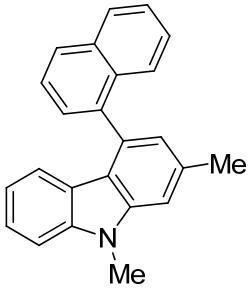
2,9-dimethyl-4-(2-(trifluoromethyl)phenyl)-9*H*-carbazole (5q): ethyl acetate/petroleum ether = 1:50 as an eluent; white solid, mp 137.1-138.2 °C; 60% yield (40.7 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.92 (dd, J = 7.6, 1.6 Hz, 1H), 7.68-7.60 (m, 2H), 7.50-7.47 (m, 1H), 7.37-7.36 (m, 2H), 7.26 (t, J = 1.2 Hz, 1H), 6.95 (s, 1H), 6.93 (dt, J = 13.2, 8.8 Hz, 1H), 6.73 (dt, J = 8.0, 1.2 Hz, 1H), 3.86 (s, 3H), 2.62 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 141.17 (d, J = 3.8 Hz), 140.12 (d, J = 2.1 Hz), 134.95, 133.49, 132.03, 131.57, 129. 5(q, J = 30.0 Hz), 128.19 (q, J = 275.3 Hz), 127.74, 126.29 (q, J = 5.2 Hz), 124.99, 122.47, 121.95, 121.93, 121.92, 121.39, 118.95, 118.56, 108.21, 29.06, 22.18. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -58.58. **IR** (UATR): 2968.7, 1602.0, 1573.9, 1470.0, 1315.6, 1111.7, 1035.0, 954.5, 837.5, 745.2, 733.0, 668.9, 567.2 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{17}F_3N$ 340.1313, found 340.1317.



4-(3,4-dimethoxyphenyl)-2,9-dimethyl-9*H*-carbazole (5r): ethyl acetate/petroleum ether = 1:40 as an eluent; white solid, mp 137.3-138.5 °C; 55% yield (36.4 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.59 (dt, *J* = 8.0, 0.8 Hz, 1H), 7.43-7.39 (m, 2H), 7.22-7.17 (m, 3H), 7.06 (d, *J* = 8.8 Hz, 1H), 7.02-6.99 (m, 1H), 6.98-6.97 (m, 1H), 4.02 (s, 3H), 3.90 (s, 3H), 3.87 (s, 3H), 2.61 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 148.64, 148.42, 141.89, 141.26, 137.17, 135.67, 134.10, 125.02, 122.52, 122.13, 122.08, 121.23, 118.44, 118.07, 112.55, 111.14, 108.20, 107.53, 56.00, 55.94, 29.12, 22.13. **IR** (UATR): 2946.5, 1602.4, 1511.4, 1471.9, 1323.4, 1245.2, 1213.3, 1130.8, 1021.3, 1034.6, 815.8, 741.8, 665.5, 598.2 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{22}NO_2$ 332.1651, found 332.1658.

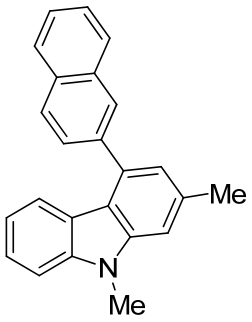


4-(2,4-dibromophenyl)-2,9-dimethyl-9*H*-carbazole (5s): ethyl acetate/petroleum ether = 1:40 as an eluent, colorless oil, 52% yield (44.4 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 1.6 Hz, 1H), 7.61 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.43-7.36 (m, 2H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.27-7.16 (m, 1H), 7.05-6.98 (m, 2H), 6.87 (dd, *J* = 1.2, 0.4 Hz, 1H), 3.87 (s, 3H), 2.62 (d, *J* = 0.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 141.36, 141.13, 141.08, 135.52, 135.12, 134.43, 132.35, 130.66, 125.30, 124.56, 122.13, 121.87, 121.52, 121.37, 118.91, 118.27, 108.53, 108.30, 29.12, 22.19. **IR** (UATR): 2918.7, 1727.5, 1600.3, 1545.1, 1462.1, 1320.8, 1154.0, 1118.4, 1080.6, 1032.5, 820.1, 723.5, 569.2 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{16}Br_2N$ 427.9649, found 427.9643.

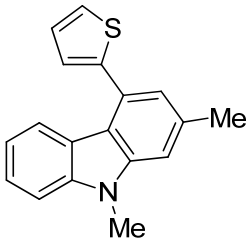


2,9-dimethyl-4-(naphthalen-1-yl)-9*H*-carbazole (5t): ethyl acetate/petroleum ether = 1:50 as an

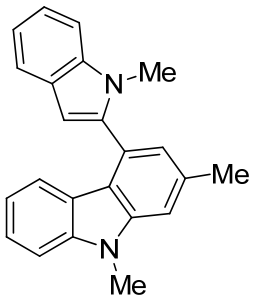
eluent; white solid, mp 140.6-141.7 ºC; 45% yield (28.9 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.03 (tt, *J* = 8.0, 2.4, 1.2 Hz, 2H), 7.66-7.60 (m, 3H), 7.51 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1H), 7.37-7.27 (m, 4H), 7.07 (d, *J* = 1.6 Hz, 1H), 6.77 (ddd, *J* = 8.0, 7.2, 1.2 Hz, 1H), 6.73 (dt, *J* = 7.6, 0.8 Hz, 1H), 3.90 (s, 3H), 2.66 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 141.55, 141.19, 139.15, 135.59, 135.08, 133.61, 132.15, 128.15, 127.84, 126.83, 126.44, 126.09, 125.88, 125.60, 124.88, 122.90, 122.45, 121.95, 119.49, 118.56, 108.00, 107.86, 29.14, 22.23. **IR** (UATR): 2914.7, 1599.2, 1567.6, 1470.4 1402.1, 1323.1, 1127.0, 1017.6, 840.7, 775.2, 747.9, 727.3, 603.8, 531.4 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{20}N$ 322.1596, found 322.1598.



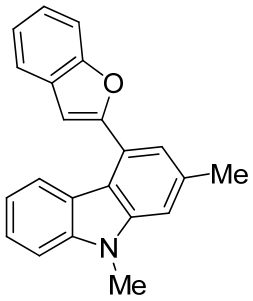
2,9-dimethyl-4-(naphthalen-2-yl)-9*H*-carbazole (5u): ethyl acetate/petroleum ether = 1:50 as an eluent; white solid, mp 155.9-157.7 ºC; 42% yield (27.0 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.12 (t, *J* = 0.8 Hz, 1H), 8.03-7.98 (m, 2H), 7.95-7.92 (m, 1H), 7.83 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.59-7.56 (m, 2H), 7.51 (dt, *J* = 7.6, 0.8 Hz, 1H), 7.41-7.39 (m, 2H), 7.27 (t, *J* = 1.2 Hz, 1H), 7.08 (d, *J* = 1.6 Hz, 1H), 6.95 (dt, *J* = 12.0 ,4.4 Hz, 1H), 3.89 (s, 3H), 2.65 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 141.96, 141.32, 138.99, 137.26, 135.75, 133.60, 132.83, 128.24, 127.91, 127.85 (d, *J* = 1.5 Hz), 127.73, 126.23, 125.98, 125.09, 122.52, 122.50, 122.09, 118.51, 118.12, 108.20, 107.83, 29.16, 22.17. **IR** (UATR): 2915.3, 1599.9, 1564.2, 1472.0, 1322.9, 1195.8, 895.1, 818.0, 744.7, 729.2, 674.2, 602.8, 477.4 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{20}N$ 322.1596, found 322.1597.



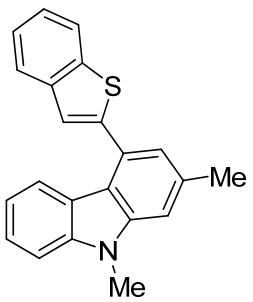
2,9-dimethyl-4-(thiophen-2-yl)-9*H*-carbazole (5v): ethyl acetate/petroleum ether = 1:50 as an eluent, white solid, mp 93.8-95.2 ºC; 18% yield (15.0 mg, 0.3 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.76-7.74 (m, 1H), 7.48 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.46 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.40-7.37 (m, 2H), 7.25-7.23 (m, 2H), 7.10 (t, *J* = 0.8 Hz, 1H), 7.08 (ddd, *J* = 8.4, 6.8, 1.6 Hz, 1H), 3.85 (s, 3H), 2.61 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 142.46, 141.82, 141.26, 135.46, 129.40, 127.22, 126.62, 125.42, 125.31, 123.46, 122.33, 121.98, 118.78, 118.62, 108.57, 108.26, 29.11, 22.03. **IR** (UATR): 2967.4, 2917.1, 1598.0, 1472.0, 1319.2, 1286.9, 1050.0, 823.1, 747.9, 700.8, 643.2, 447.1 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{16}NS$ 278.1003, found 278.1005.



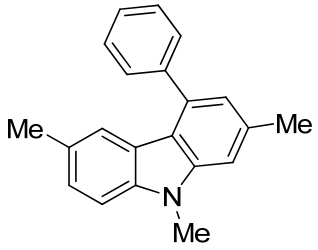
2,9-dimethyl-4-(1-methyl-1H-indol-2-yl)-9*H*-carbazole (5w): ethyl acetate/petroleum ether = 1:50 as an eluent, white solid, mp 187.3-189.5 ºC; 10% yield (9.7 mg, 0.3 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.78 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.42-7.39 (m, 2H), 7.37-7.33 (m, 2H), 7.28-7.24 (m, 1H), 7.12-7.09 (m, 2H), 6.99 (ddd, *J* = 8.0, 6.0, 2.8 Hz, 1H), 6.70 (s, 1H), 3.90 (s, 3H), 3.53 (s, 3H), 2.66 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 141.43, 141.27, 140.52, 137.62, 135.64, 128.40, 126.68, 125.42, 123.54, 122.22, 121.44, 121.39, 120.72, 119.90, 119.73, 119.30, 109.70, 109.06, 108.23, 101.44, 30.42, 29.17, 22.18. **IR** (UATR): 2970.9, 1599.6, 1470.5, 1412.1, 1320.7, 1235.2, 1061.4, 1056.1, 839.9, 731.8, 684.7, 599.5, 443.0 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{21}N_2$ 325.1705, found 325.1713.



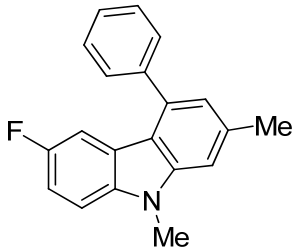
4-(4-bromophenyl)-2,9-dimethyl-9*H*-carbazole (5x): ethyl acetate/petroleum ether = 1:50 as an eluent; white solid, mp 99.3-101.2 ºC; 28% yield (17.4 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.22 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.76-7.73 (m, 1H), 7.71 (d, *J* = 8.0, 1H), 7.51 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.43-7.35 (m, 4H), 7.29 (d, *J* = 1.6 Hz, 1H), 7.20-7.16 (m, 2H), 3.86 (s, 3H), 2.64 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 156.68, 154.97, 142.17, 141.52, 135.55, 129.29, 125.59, 125.08, 124.25, 123.03, 122.86, 121.98, 121.94, 121.04, 118.95, 117.94, 111.45, 109.71, 108.34, 104.75, 29.13, 22.07. **IR** (UATR): 2967.6, 2912.7, 1625.1, 1590.4, 1471.2, 1452.5, 1323.4, 1255.8, 1054.8, 946.0, 741.7, 724.2, 690.0, 596.6, 431.3 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{18}NO$ 312.1388, found 312.1390.



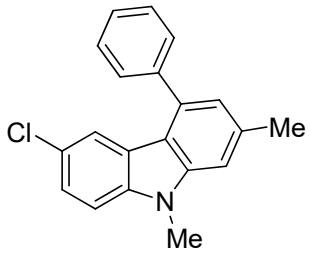
4-(benzo[b]thiophen-2-yl)-2,9-dimethyl-9*H*-carbazole (5y): ethyl acetate/petroleum ether = 1:50 as an eluent; white solid, mp 144.8-145.5 ºC; 40% yield (26.2 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.96-7.94 (m, 1H), 7.90-7.83 (m, 2H), 7.58 (d, *J* = 0.8 Hz, 1H), 7.48-7.39 (m, 4H), 7.27 (t, *J* = 1.2 Hz, 1H), 7.17 (dd, *J* = 1.6, 0.8 Hz, 1H), 7.05 (ddd, *J* = 8.4, 6.8, 1.6 Hz, 1H), 3.87 (s, 3H), 2.62 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 143.01, 141.86, 141.32, 140.43, 140.31, 135.52, 129.24, 125.45, 124.40, 124.16, 123.69, 123.41, 123.11, 122.35, 122.20, 122.14, 118.75, 118.61, 109.00, 108.32, 29.14, 22.05. **IR** (UATR): 2911.7, 1625.7, 1600.9, 1471.8, 1435.2, 1323.0, 1022.6, 825.9, 744.6, 719.9, 650.7, 575.4, 429.7 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{18}NS$ 328.1160, found 328.1164.



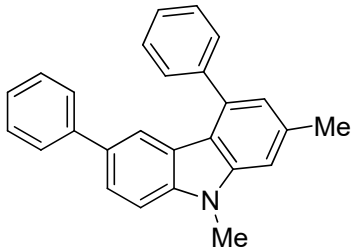
2,6,9-trimethyl-4-phenyl-9*H*-carbazole (5z): ethyl acetate/petroleum ether = 1:50 as an eluent; white solid, mp 118.0-119.1 ºC; 57% yield (32.5 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.68-7.66 (m, 2H), 7.57-7.48 (m, 3H), 7.30-7.27 (m, 2H), 7.24-7.20 (m, 2H), 6.96 (t, *J* = 0.8 Hz, 1H), 3.84 (s, 3H), 2.62 (s, 3H), 2.35 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 142.12, 141.51, 139.64, 137.39, 135.42, 129.26, 128.31, 127.56, 127.43, 126.33, 122.61, 122.05, 122.01, 117.78, 107.86, 107.61, 29.13, 22.11, 21.51. **IR** (UATR): 2912.7, 1623.4, 1603.3, 1485.0, 1440.9, 1328.1, 1302.0, 1026.2, 869.0, 830.1, 791.5, 699.9, 588.9, 444.1 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{20}N$ 286.1596, found 286.1594.



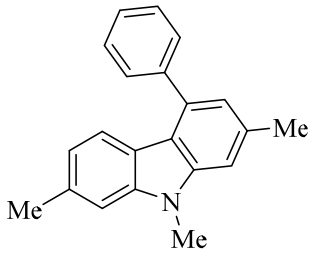
6-fluoro-2,9-dimethyl-4-phenyl-9*H*-carbazole (5aa): ethyl acetate/petroleum ether = 1:50 as an eluent; white solid, mp 90.8-92.9ºC; 48% yield (27.8 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.66-7.63 (m, 2H), 7.60-7.50 (m, 3H), 7.28 (dd, *J* = 8.4, 4.0 Hz, 1H), 7.22-7.17 (m, 2H), 7.17 (td, *J* = 8.8, 2.4 Hz, 1H), 7.00 (d, *J* = 1.2 Hz, 1H), 3.83 (s, 3H), 2.64 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 157.88 (d, *J* = 234.4 Hz), 142.69, 140.92, 137.71 (d, *J* = 5.9 Hz), 136.36, 129.10, 128.57, 127.73, 122.87 (d, *J* = 9.9 Hz), 122.22, 117.64 (d, *J* = 4.1 Hz), 112.75 (d, *J* = 25.8 Hz), 108.54 (d, *J* = 9.3 Hz), 107.93, 107.87, 107.62, 29.25, 22.18. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -125.13. **IR** (UATR): 2916.7, 1602.0, 1475.8, 1307.4, 1270.2, 1159.4, 959.5, 830.6, 776.3, 703.3, 595.7, 511.3, 440.7 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{17}FN$ 290.1345, found 290.1341.



6-chloro-2,9-dimethyl-4-phenyl-9*H*-carbazole (5ab): ethyl acetate/petroleum ether = 1:50 as an eluent, white solid; mp 106.8-108.2 ºC; 54% yield (32.9 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.67-7.64 (m, 2H), 7.62 (ddd, *J* = 6.4, 3.6, 1.6 Hz, 2H), 7.57-7.52 (m, 1H), 7.50 (d, *J* = 2.0 Hz, 1H), 7.38 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.22 (t, *J* = 1.2 Hz, 1H), 7.02 (t, *J* = 0.8 Hz, 1H), 3.83 (s, 3H), 2.65 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 142.32, 140.84, 139.60, 137.66, 136.49, 129.07, 128.58, 127.82, 125.03, 123.85, 123.59, 122.62, 121.54, 117.16, 109.09, 107.90, 29.21, 22.16. **IR** (UATR): 3021.8, 2920.4, 1598.2, 1566.4, 1463.2, 1298.5, 1223.8, 1119.1, 1075.4, 1010.8, 876.7, 794.0, 701.3, 587.0, 439.5 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{17}ClN$ 306.1050, found 306.1052.

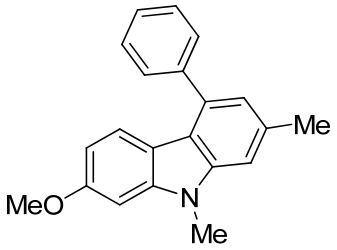


2,9-dimethyl-4,6-diphenyl-9*H*-carbazole (**5ac)**: ethyl acetate/petroleum ether = 1:60 as an eluent, white solid; mp 161.2-162.9 ºC; 58% yield (40.3 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.78 (d, J = 1.6 Hz, 1H), 7.73-7.67 (m, 3H), 7.59-7.55 (m, 2H), 7.53-7.49 (m, 3H), 7.44 (td, *J* = 8.4, 2.4 Hz, 3H), 7.32 (tt, *J* = 6.8 1.2 Hz, 1H), 7.24 (s, 1H), 7.03 (d, *J* = 1.6 Hz, 1H), 3.88 (s, 3H), 2.65 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 142.34, 142.09, 141.28, 140.85, 137.59, 135.91, 131.62, 129.27, 128.72, 128.40, 127.65, 126.99, 126.17, 124.44, 123.06, 122.30, 120.53, 118.21, 108.43, 107.85, 29.23, 22.17. **IR** (UATR): 3028.7, 2923.2, 1597.3, 1565.2, 1468.5, 1300.8, 1217.9, 1122.1, 1027.5, 956.9, 890.1, 828.1, 751.6, 693.3, 581.9, 502.5 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{22}N$ 348.1752, found 348.1748.

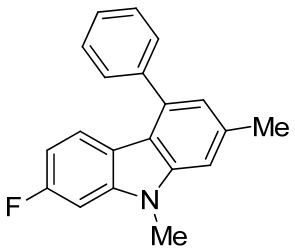


2,7,9-trimethyl-4-phenyl-9*H*-carbazole (5ad): ethyl acetate/petroleum ether = 1:50 as an eluent, white solid; mp 100.5-100.9 ºC; 60% yield (34.2 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$):

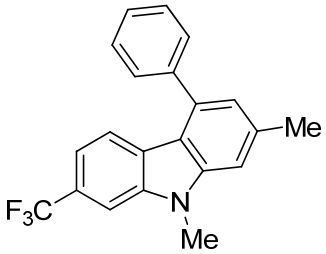
δ = 7.68-7.65 (m, 2H), 7.57-7.47 (m, 3H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.21-7.19 (m, 2H), 6.97 (t, *J* = 1.2 Hz, 1H), 6.84-6.81 (m, 1H), 3.84 (s, 3H), 2.62 (s, 3H), 2.54 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 141.91, 141.76, 141.54, 137.00, 135.20, 135.10, 129.25, 128.36, 127.36, 122.07, 121.68, 120.21, 119.95, 118.09, 108.45, 107.62, 29.03, 22.13, 22.09. **IR** (UATR): 2913.5, 1603.4, 1567.3, 1467.3, 1310.9, 1140.0, 1028.7, 826.5, 771.0, 698.9, 574.2, 443.4 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{20}N$ 286.1596, found 286.1594.



7-methoxy-2,9-dimethyl-4-phenyl-9*H*-carbazole (5ae): ethyl acetate/petroleum ether = 1:50 as an eluent; white solid, mp 103.8-105.1 ºC; 62 % yield (37.3 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.69-7.67 (m, 2H), 7.58-7.54 (m, 2H), 7.52-7.48 (m, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.20 (s, 1H), 6.98 (d, *J* = 1.2 Hz, 1H), 6.87 (d, *J* = 2.4 Hz, 1H), 6.65 (ddd, *J* = 3.2, 2.4, 0.8 Hz, 1H), 3.93 (s, 3H), 2.83 (s, 3H), 2.63 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 158.59, 142.73, 142.00, 141.51, 136.41, 134.41, 129.23, 128.39, 127.36, 122.68, 122.20, 118.17, 116.47, 107.56, 106.61, 92.76, 55.63, 29.13, 22.03. **IR** (UATR): 2918.3, 1605.7, 1568.5, 1452.1, 1427.3, 1331.8, 1232.4, 1111.1, 1063.9, 1035.8, 903.4, 819.7, 771.3, 702.7, 577.5 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{20}NO$ 302.1545, found 302.1551.



7-fluoro-2,9-dimethyl-4-phenyl-9*H*-carbazole (5af): ethyl acetate/petroleum ether = 1:50 as an eluent; white solid, mp 101.9-103.4 ºC; 50% yield (28.9 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.63-7.61 (m, 2H), 7.56-7.47 (m, 3H), 7.40 (dd, *J* = 8.4, 6.4 Hz, 1H), 7.20 (s, 1H), 7.04 (dd, *J* = 9.6, 6.4 Hz, 1H), 6.98 (d, *J* = 1.2 Hz, 1H), 6.73 (td, *J* = 9.2, 2.4 Hz, 1H), 3.81 (s, 3H), 2.61 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 162.88 (d, J = 242.2 Hz), 142.36 (d, *J* = 2.0 Hz), 142.15 (d, *J* = 12.0 Hz), 141.17, 136.95, 135.36, 129.14, 128.47, 127.54, 122.88 (d, *J* = 10.2 Hz), 122.58, 118.92 (d, *J* = 1.5 Hz), 117.75, 107.76, 106.48 (d, *J* = 23.5 Hz), 95.19 (d, *J* = 26.8 Hz), 29.26, 22.04. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -116.03 (d, *J* = 5.6 Hz). **IR** (UATR): 2922.4, 1601.7, 1569.6, 1468.6, 1410.8, 1309.1, 1227.6, 1106.2, 973.9, 922.1, 817.4, 772.8, 701.7, 519.6, 440.5 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{17}FN$ 302.1345, found 302.1349.

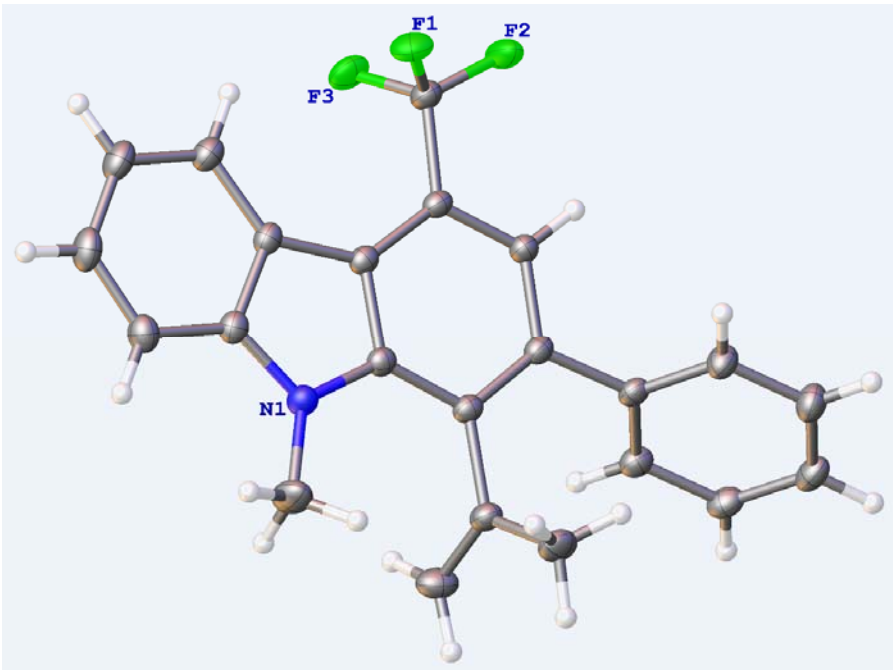


2,9-dimethyl-4-phenyl-7-(trifluoromethyl)-9*H*-carbazole (5ag): ethyl acetate/petroleum ether = 1:50 as an eluent, white solid, mp 129.7-131.1 °C; 32% yield (21.7 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.67-7.64 (m, 3H), 7.61-7.53 (m, 4H), 7.29-7.26 (m, 2H), 7.06 (d, *J* = 1.6 Hz, 1H), 3.88 (s, 3H), 2.66 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 142.84, 140.91, 140.40, 138.07, 137.19, 129. 16 (q, *J* = 273.0 Hz), 129.14, 128.58, 127.79, 127.23 (q, *J* = 32.0 Hz), 125.16, 122.94, 122.12, 117.30, 115.23 (q, *J* = 3.7 Hz), 108.01, 105.46 (q, *J* = 4.2 Hz), 29.20, 22.20. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -60.78. **IR** (UATR): 2920.7, 1629.8, 1603.6, 1571.0, 1468.5, 1322.1, 1284.8, 1159.7, 1098.9, 1067.7, 820.2, 763.1, 702.8, 624.8, 577.7 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{17}F_3N$ 340.1313, found 340.1316.

5. X–Ray data for 3a and 3ao

Method for crystal growth of 3a: Dissolve 10 mg **3a** in $CHCl_3$/hexane (1/5, 6 mL) and keep away from light, crystals are precipitated when some of the solvent evaporates.

X–Ray Data for 3a: A suitable crystal was selected on a ROD, Synergy Custom system, HyPix-Arc 150 diffractometer. The crystal was kept at 170.00(10) K during data collection. Using Olex2, the structure was solved with the SHELXS structure solution program using direct methods and refined with the SHELXL refinement package using Least Squares minimisation.

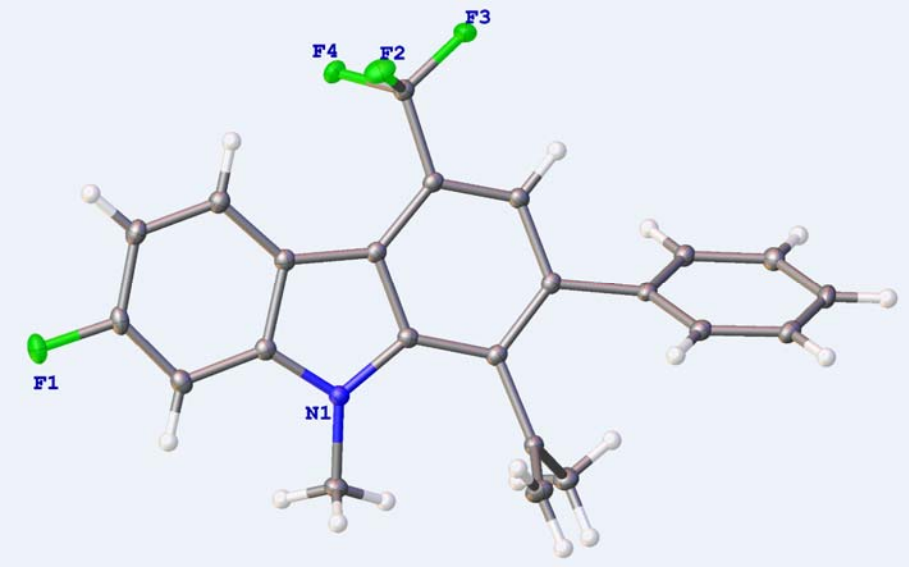


CCDC No.: 2449182, the thermal ellipsoids were drawn at the 50% probability level.

Empirical formula	$C_{26}H_{25}F_3N$
Formula weight	408.47
Temperature/K	170.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.0837(2)
b/Å	10.11921(18)
c/Å	12.4621(3)
α/°	72.752(2)
β/°	75.888(2)
γ/°	86.8218(17)
Volume/Å^3	1060.80(5)
Z	2
ρ_{calc}g/cm^3	1.279
μ/mm^{-1}	0.758
F(000)	430.0
Crystal size/mm^3	0.13 × 0.12 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.648 to 145.726
Index ranges	-11 ≤ h ≤ 11, -11 ≤ k ≤ 8, -15 ≤ l ≤ 15
Reflections collected	14404
Independent reflections	3950 [R_{int} = 0.0469, R_{sigma} = 0.0202]
Data/restraints/parameters	3950/0/292
Goodness-of-fit on F^2	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0546, wR_2 = 0.1610
Final R indexes [all data]	R_1 = 0.0574, wR_2 = 0.1640
Largest diff. peak/hole / e Å^{-3}	0.38/-0.45

Method for crystal growth of 3ao: Dissolve 10 mg **3ao** in CH_2Cl_2/hexane (1/5, 6 mL) and keep away from light, crystals are precipitated when some of the solvent evaporates.

X–Ray Data for 3ao: A suitable crystal was selected on a ROD, Synergy Custom system, HyPix diffractometer. The crystal was kept at 100.00(10) K during data collection. Using Olex2, the structure was solved with the SHELXS structure solution program using Direct Methods and refined with the SHELXL refinement package using Least Squares minimisation..

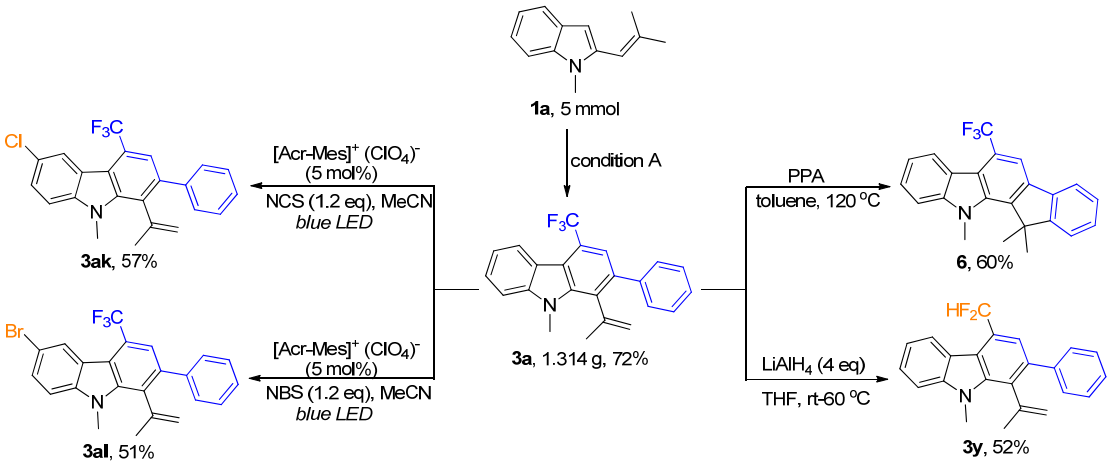


CCDC No.: 2449181, the thermal ellipsoids were drawn at the 50% probability level.

Empirical formula	$C_{23}H_{17}F_4N$
Formula weight	383.38
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.9386(5)
b/Å	11.3326(5)
c/Å	18.1315(9)
α/°	74.496(4)
β/°	87.854(4)
γ/°	65.355(4)
Volume/Å^3	1782.20(16)
Z	4
ρ_{calc}g/cm^3	1.429
μ/mm^{-1}	0.952
F(000)	792.0
Crystal size/mm^3	0.15 × 0.13 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.076 to 149.136
Index ranges	-12 ≤ h ≤ 12, -14 ≤ k ≤ 12, -22 ≤ l ≤ 22
Reflections collected	18902
Independent reflections	6892 [R_{int} = 0.0172, R_{sigma} = 0.0122]
Data/restraints/parameters	6892/18/525
Goodness-of-fit on F^2	1.083
Final R indexes [I>=2σ (I)]	R_1 = 0.0407, wR_2 = 0.1018
Final R indexes [all data]	R_1 = 0.0416, wR_2 = 0.1024

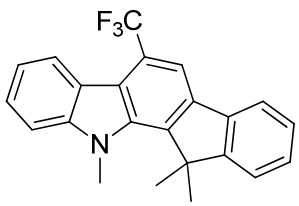
Largest diff. peak/hole / e Å^{-3}	0.42/-0.43

6. Scaled-up reaction and transformations



General Procedures for Scaled-up reaction: A flame-dried 100 mL round bottom falsk was charged with 2-(2-methylprop-1-en-1-yl)-1H-indole (**1a**, 0.926 g, 5 mmol, 1eq.), (*E*)-1,1,1-trifluoro-4-phenylbut-3-en-2-one (**2a**, 1.5 g, 7.5 mmol, 1.5 eq.), [Bmim][OTf] (30 mL), and $H_3PMo_{12}O_{40}$ (10 mol%) under O_2 atmosphere at room temperature. The mixture was stirred at 100 °C for 24 h. The progress of the reaction was monitored by the disappearance of the starting material as visualized by TLC. After completion of the reaction, the mixture was cooled to room temperature, extracted with toluene (4×40 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure and purified by flash chromatography on silica gel using petroleum ether/EtOAc (50:1-20:1) as eluent to afford target product **3a** as a white solid (1.314 g, 72% yield).

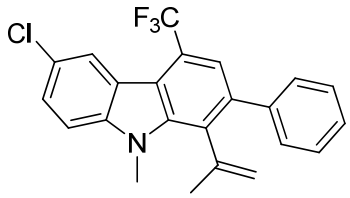
General Procedures for transformation 3a to 6: A mixture of **3a** (73.0 mg, 0.2 mmol), PPA (2.0 mL), and toluene (1.0 mL) in a sealed tube quipped with a magnetic stir bar was heated to 130 °C at an aluminum block heater for 6h. After completion, the mixture was cooled to room temperature, poured into a sat. NaOH to make the solution basic, extracted with EtOAc (3×15 mL), the combined organic layers were washed with brine, concentrated under reduced pressure, and purified by flash chromatography (silica gel, eluent: petroleum ether/EtOAc = 100:1) to give product **6**.



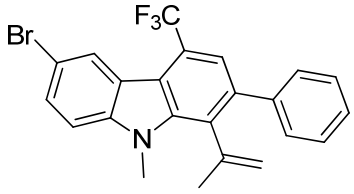
11,12,12-trimethyl-6-(trifluoromethyl)-11,12-dihydroindeno[2,1-*a*]carbazole (6): ethyl acetate/petroleum ether = 1:100 as an eluent; white solid, mp 204.4-205.6 °C; 60 % yield (43.8 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.42 (dt, *J* = 8.0,1.6 Hz, 1H), 8.02 (s, 1H), 7.85-

7.83 (m, 1H), 7.59-7.55 (m, 1H), 7.51-7.48 (m, 2H), 7.44-7.39 (m, 2H), 7.36-7.32 (m, 1H), 4.3 3(s, 3H), 1.87 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 154.89, 142.29, 139.21, 138.40, 137.99, 137.62, 129.16 (q, *J* =273.3 Hz), 127.80, 127.28, 126.61, 123.36 (q, *J* = 5.6 Hz), 122.84, 122.51, 122.16, 120.63, 120.24, 119.69, 110.15 (q, *J* = 6.3 Hz), 109.04, 48.29, 34.33, 27.43. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -61.96. **IR** (UATR): 2980.9, 2938.2, 1612.1, 1569.3, 1471.4, 1391.9, 1303.1, 1266.6, 1136.9, 1114.4, 1055.7, 941.6, 872.0, 748.0, 701.0, 566.9 cm^{-1}. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{19}NF_3$ 366.1470, found 366.1472.

General Procedures for transformation 3a to 3ak or 3al: In a pressure tube quipped with a magnetic stir bar, carbazole **3a** (0.110 g, 0.3 mmol, 1eq.), $[Mes\text{-}Acr]^+(ClO_4)^-$ (5 mol%), NCS (0.36 mmol, 1.2 eq.) or or NBS (0.36 mmol, 1.2 eq.), and MeCN (5 mL) were added in sequence. The tube was sealed, and the mixture was stirred at 60 ºC for 12 h under irradiation of 25 W blue LED. After completion, the mixture was cooled to room temperature, quenched with saturated sodium bicarbonate aqueous solution, extracted with EtOAc (3×15 mL), the combined organic layers were dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and purified by flash chromatography (silica gel, eluent: petroleum ether/EtOAc = 100:1) to afford product **3ak** or **3al**.



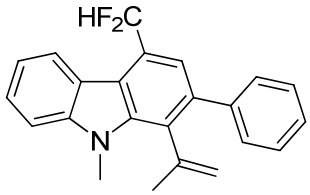
6-chloro-9-methyl-2-phenyl-1-(prop-1-en-2-yl)-4-(trifluoromethyl)-9*H*-carbazole (3ak): ethyl acetate/petroleum ether = 1:100 as an eluent; yellow solid, mp 155.7-157.0 ºC; 57 % yield (68.2 mg, 0.3 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.33 (t, *J* = 1.6 Hz, 1H), 7.51-7.48 (m, 2H), 7.42-7.36 (m, 6H), 5.47 (t, *J* = 1.6 Hz, 1H), 5.13 (dd, *J* = 2.0, 1.2 Hz, 1H), 4.00 (s, 3H), 1.91 (t, *J* = 1.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 141.15, 140.95, 140.92, 139.03, 138.42, 129.73, 129.45, 128.72 (q, *J* = 273.3 Hz), 127.74, 127.17, 126.89, 122.89 (q, *J* = 5.6 Hz), 121.74 (q, *J* = 33.0 Hz), 120.92, 120.62, 120.55, 119.86 (q, *J* = 5.9 Hz), 118.30 (d, *J* = 1.9 Hz), 110.11, 32.41, 25.87. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -61.94.



6-bromo-9-methyl-2-phenyl-1-(prop-1-en-2-yl)-4-(trifluoromethyl)-9H-carbazole (3al): ethyl acetate/petroleum ether = 1:100 as an eluent; yellow solid, mp 152.5-154.1 ºC; 51 % yield (67.8 mg, 0.3 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.49 (t, *J* = 1.6 Hz, 1H), 7.66 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.52 (s, 1H), 7.45-7.39 (m, 5H), 7.36 (d, *J* = 8.8 Hz, 1H), 5.49 (t, *J* = 1.6 Hz, 1H), 5.15 (dd, *J* = 2.0, 0.8 Hz, 1H), 4.02 (s, 3H), 1.92 (t, *J* = 1.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 141.45, 140.94, 140.90, 138.87, 138.45, 129.73, 129.51, 128.69 (q, *J* = 273.2 Hz), 128.08, 127.73, 127.17,

125.88 (q, *J* = 5.5 Hz), 121.76 (q, *J* = 33.0 Hz), 121.18, 120.93, 119.91 (q, *J* = 6.1 Hz), 118.18 (d, *J* = 1.9 Hz), 112.92, 110.55, 32.40, 25.87. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -61.96.

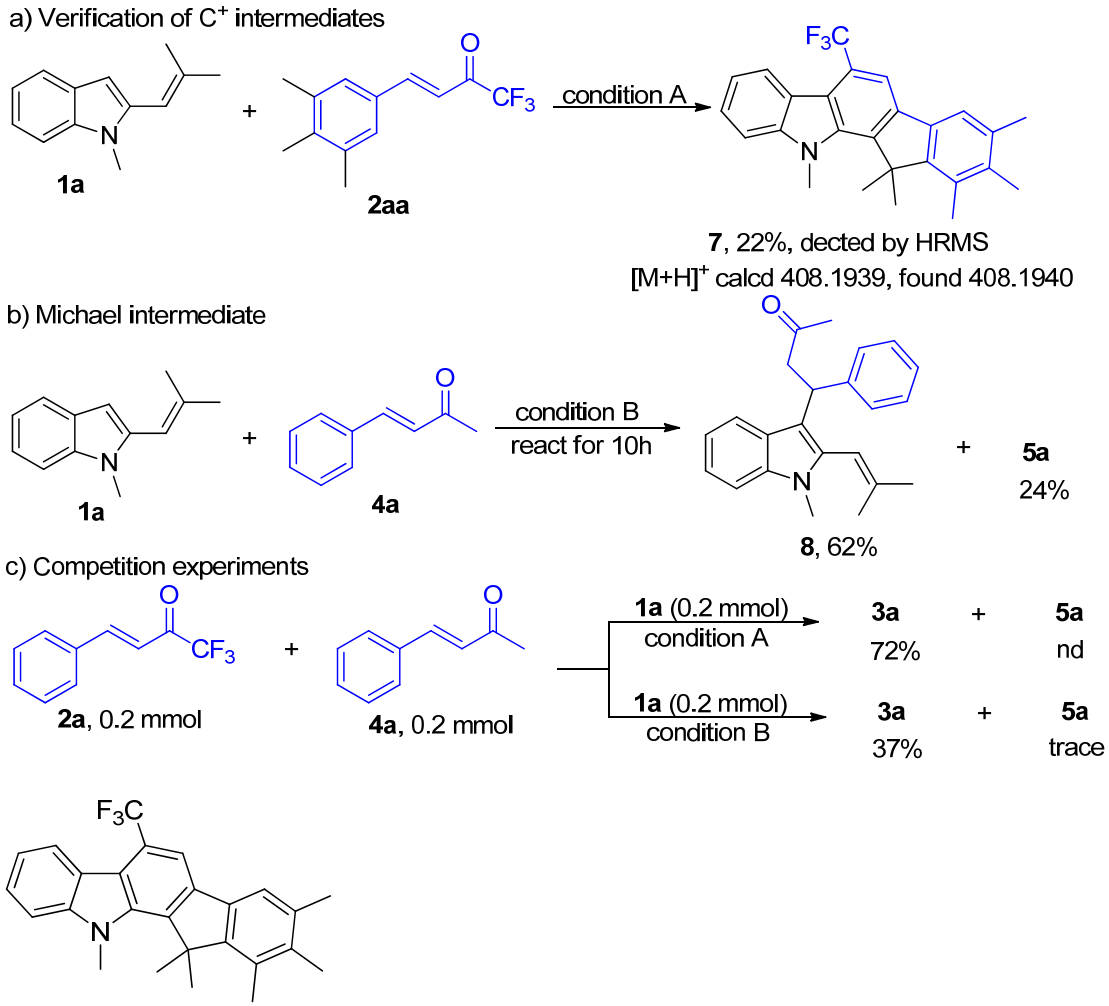
General Procedures for transformation 3a to 3y: The compound **3a** (73 mg, 0.2 mmol, 1eq.) was dissolved in anhydrous THF (5 mL), then $LiAlH_4$ (1 mmol, 5 eq.) was added portionwise at 0 °C. The reaction mixture was then stirred at room temperature for 30 min, then for 12h at 60 °C. Once completion, the reaction mixture was quenched with saturated ammonium chloride solution and extracted with EtOAc (3 × 15 mL). The organic layer was washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated under vacuum. The crude was purified via column chromatography on silica gel to afford the corresponding product **3y** in 52% yield.



4-(difluoromethyl)-9-methyl-2-phenyl-1-(prop-1-en-2-yl)-9*H*-carbazole (3y): ethyl acetate/petroleum ether = 1:100 as an eluent; white solid, mp 124.5-125.4 °C; 52 % yield (36.1 mg, 0.2 mmol scale). All spectral data are in accord with the aforementioned **3y**. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.31 (dt, *J* = 8.0,1.2 Hz, 1H), 7.58 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.44-7.26 (m, 8H), 5.46 (t, *J* = 1.6 Hz, 1H), 5.13 (dd, *J* = 2.0, 1.2 Hz, 1H), 4.02 (s, 3H), 1.92 (t, *J* = 1.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 142.76, 141.56, 141.48, 138.36, 138.00, 129.85, 128.32 (t, *J* = 2.1 Hz), 127.61, 126.88, 126.41, 125.86 (t, *J* = 22.6 Hz),123.26 (t, *J* = 3.9 Hz), 120.52, 120.35, 119.87, 119.82 (t, *J* = 8.6 Hz), 119.79, 117.57 (t, *J* = 239.0 Hz), 109.07, 32.19, 26.03. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -112.22. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{20}NF_2$ 348.1564, found 348.1556.

7. Mechanistic studies

7.1 Control experiments



1,2,3,11,12,12-hexamethyl-6-(trifluoromethyl)-11,12-dihydroindeno[2,1-*a*]carbazole (**7**): ethyl acetate/petroleum ether = 1:100 as an eluent; an inseparable mixture of **9** and unknown compound (0.25:1); 22 % yield (yields were determined by ^{1}H NMR, 195 mg, 0.4 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.41 (s, 0.25H), 7.3 (s, 0.25H), 7.58-7.54 (m, 0.25H), 7.43 (d, *J* = 4.0 Hz, 0.25H), 7.37-7.33 (m, 0.25H), 7.15 (s, 0.25H), 4.30 (s, 0.75H), 4.13 (s, 0.75H), 4.04 (s, 0.75H), 3.98 (s, 0.75H),1.97(s, 1.5H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -61.79. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{25}NF_3$ 408.1939, found 408.1940. **HRMS** (ESI) m/z: $[M+H]^+$ for unknown: 454.1673.

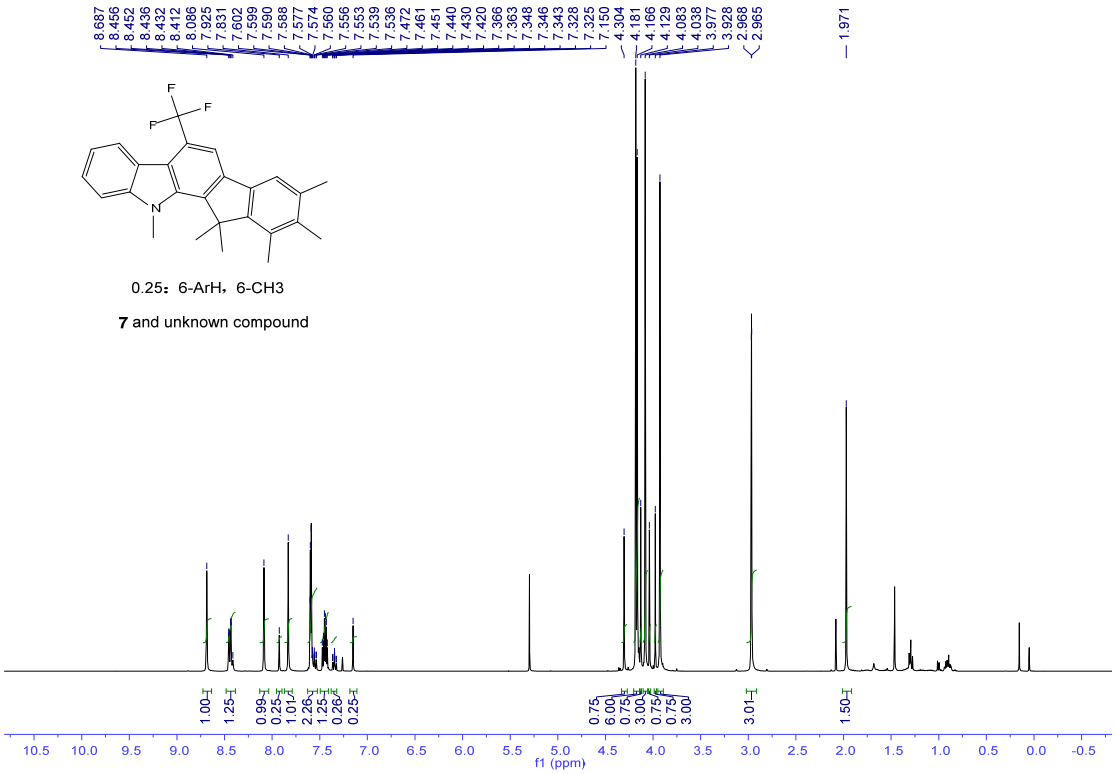


Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **7** and unknown compound

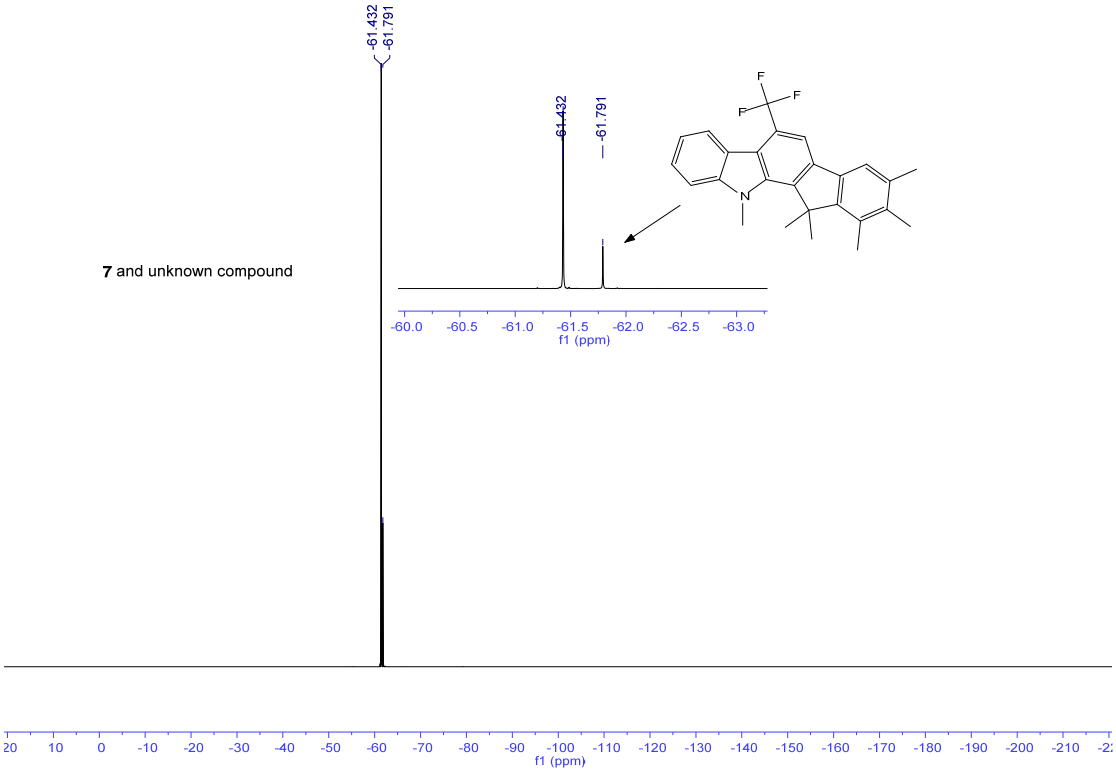


Figure S2. ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **7** and unknown compound

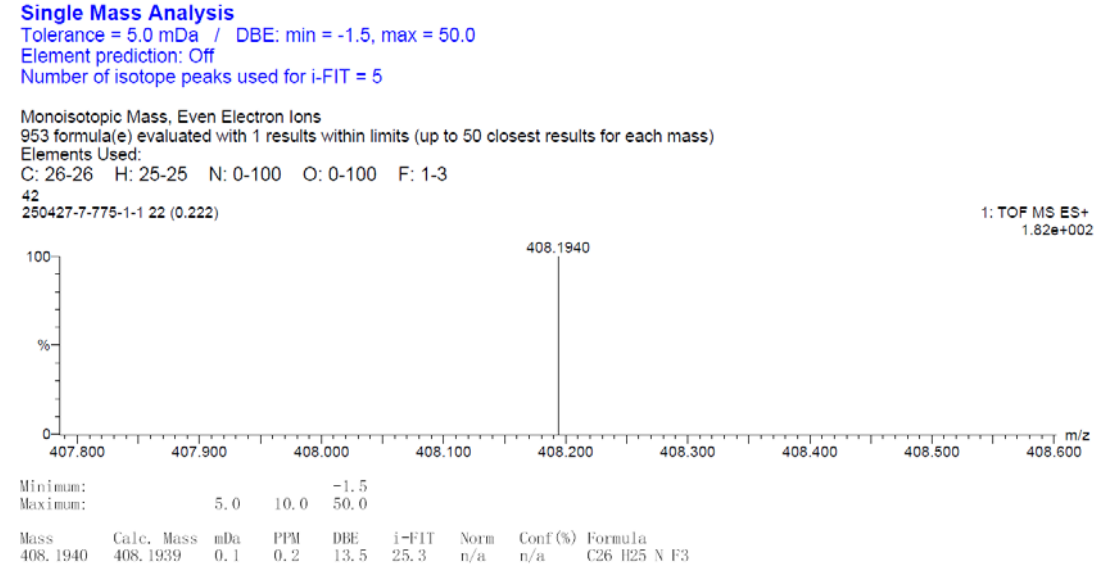
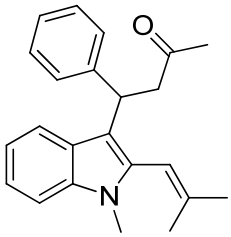


Figure S3. HRMS for compound **7**



4-(1-methyl-2-(2-methylprop-1-en-1-yl)-1H-indol-3-yl)-4-phenylbutan-2-one (**8**): ethyl acetate/petroleum ether = 1:100 as an eluent; light yellow liquid; 62 % yield (41.0 mg, 0.2 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.59 (dt, *J* = 8.0,1.2 Hz, 1H), 7.33-7.29 (m, 3H), 7.25-7.17 (m, 3H), 7.16-7.12 (m, 1H), 7.09 (ddd, *J* = 8.0, 6.8, 0.8 Hz, 1H), 6.15 (q, *J* = 1.2 Hz, 1H), 4.84 (t, *J* = 7.6 Hz, 1H), 3.58 (s, 3H), 3.38 (d, *J* = 7.6 Hz, 2H), 2.04 (s, 3H), 2.01 (d, *J* = 1.2 Hz, 3H), 1.50 (d, *J* = 1.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 207.88, 144.34, 143.60, 137.12, 135.48, 128.19, 127.53, 126.52, 125.80, 120.82, 119.66, 118.95, 114.97, 113.69, 109.35, 48.99, 37.83, 30.58, 30.11, 25.39, 20.26. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{26}NO$ 332.2014, found 332.2011.

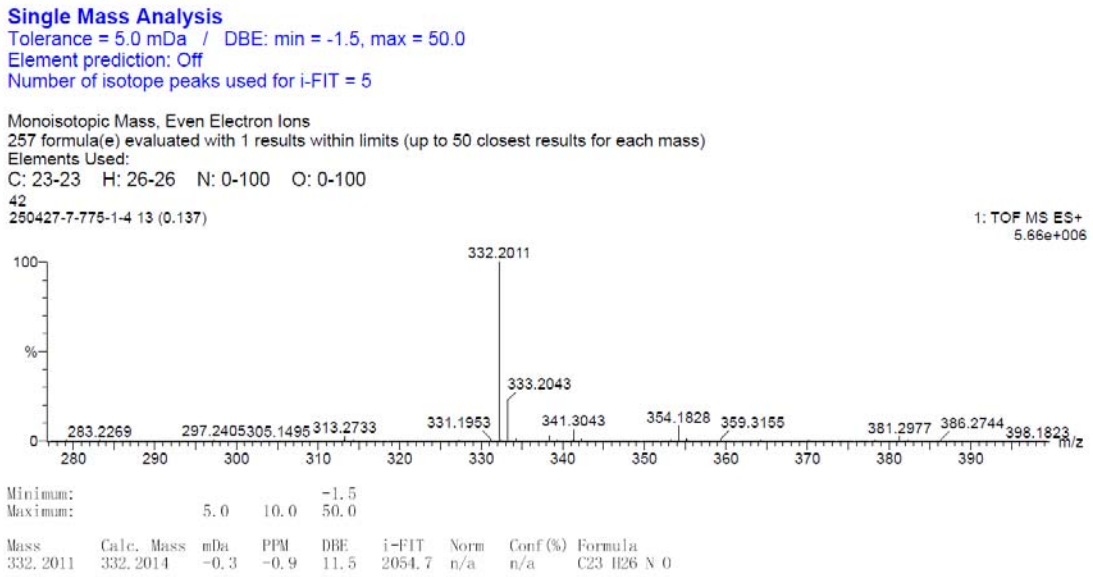


Figure S4. HRMS for compound **8**

7.2 Real-time NMR experiments

Procedure for real-time ^{1}H NMR monitoring program for product 3a: Under standard reaction conditions A, seven groups of reactions were administered in parallel, with a scale of 0.1 mmol per group, labeled at 0 min, 15 min, 30 min, 1h, 2h, 6h, and 12h, respectively. After reaching the corresponding reaction time, completely cool down, extracted with 5 mL of toluene, concentrated the extract under reduced pressure, dissolved in 0.6 mL of deuterated chloroform, and then performed ^{1}H NMR testing.

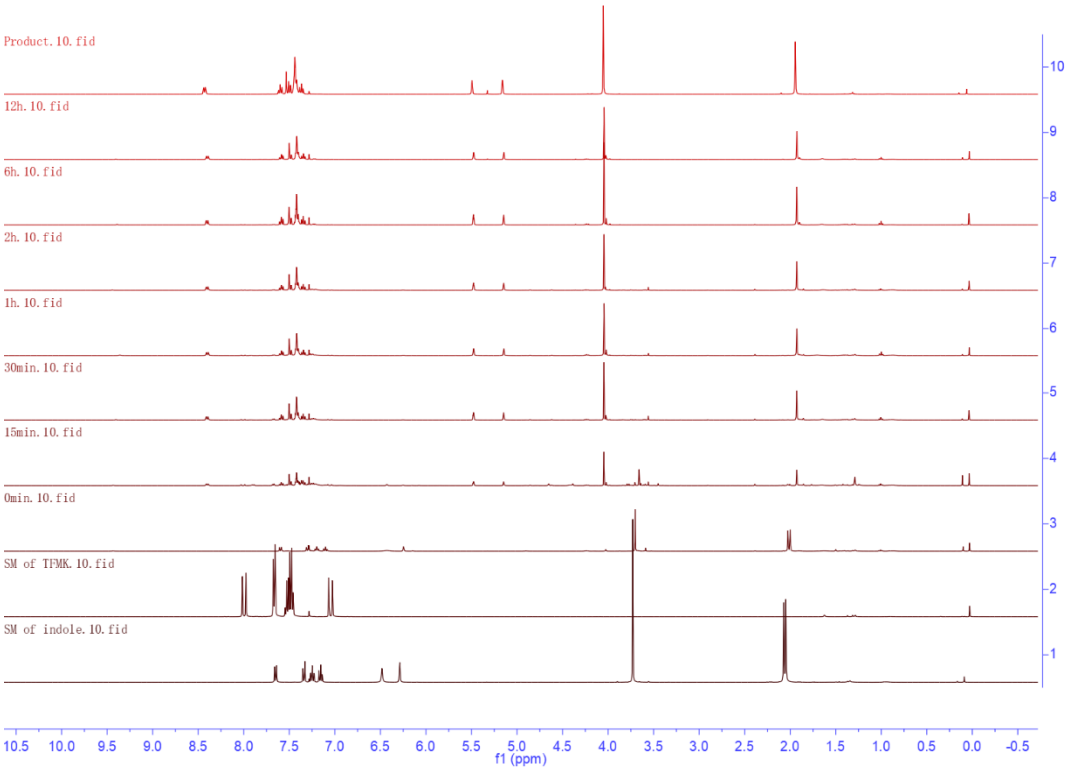


Figure S5. Real-time ^{1}H NMR experiments (full ^{1}H NMR spectra). From bottom to top: 1) ^{1}H NMR of substrate

1a (pure, in $CDCl_3$) (bottom). 2) ^1H NMR of substrate **2a** (pure, in $CDCl_3$). 3-9) Reaction mixture of substrate **1a**, **2a**, and 10 mol% $H_3PMo_{12}O_{40}$ in [Bmim][OTf] at 100°C under O_2 atmosphere after 0 min, 15 min, 30 min, 1, 2, 6 and 12 hours. 10) ^1H NMR of product **3a** (in $CDCl_3$) (top).

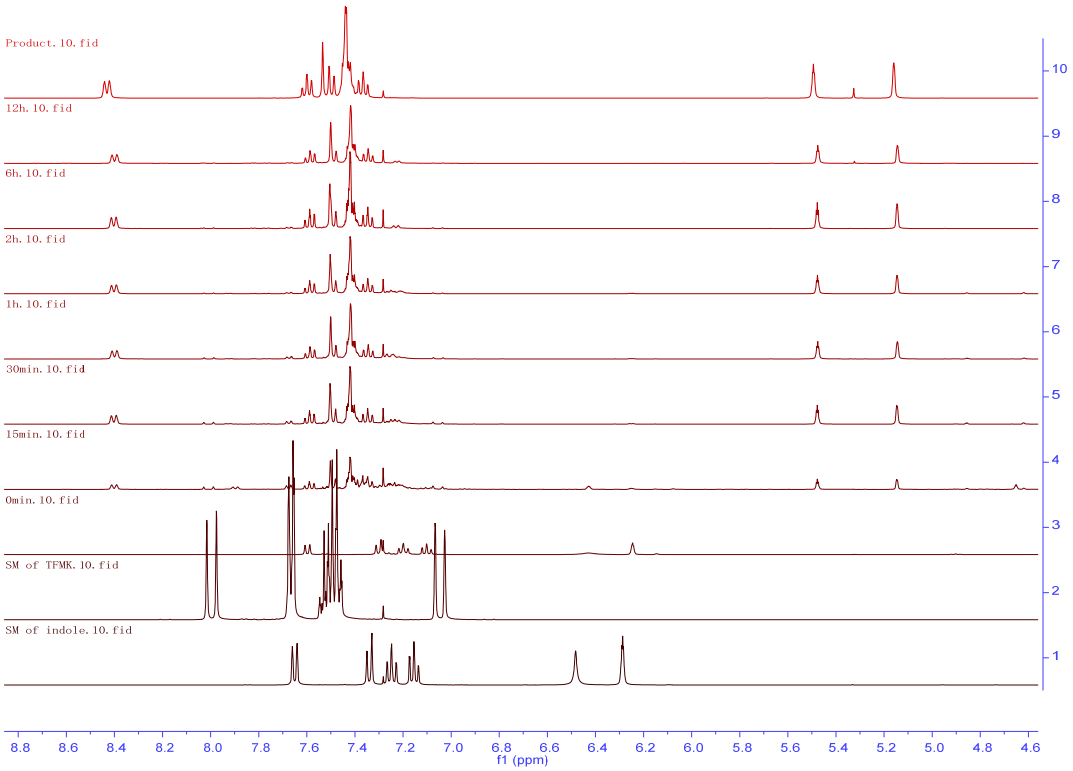


Figure S6. zoomed real-time ^1H NMR (400 MHz) spectra from ppm 8.8-4.6.

Procedure for real-time ^{19}F NMR monitoring program for product 3a: Under standard reaction conditions A, four groups of reactions were administered in parallel, with a scale of 0.1 mmol per group, labeled at 15 min, 30 min, 1h, and 2h, respectively. After reaching the corresponding reaction time, completely cool down, extracted with 5 mL of toluene, concentrated the extract under reduced pressure, dissolved in 0.6 mL of deuterated chloroform, and performed ^{19}F NMR testing.

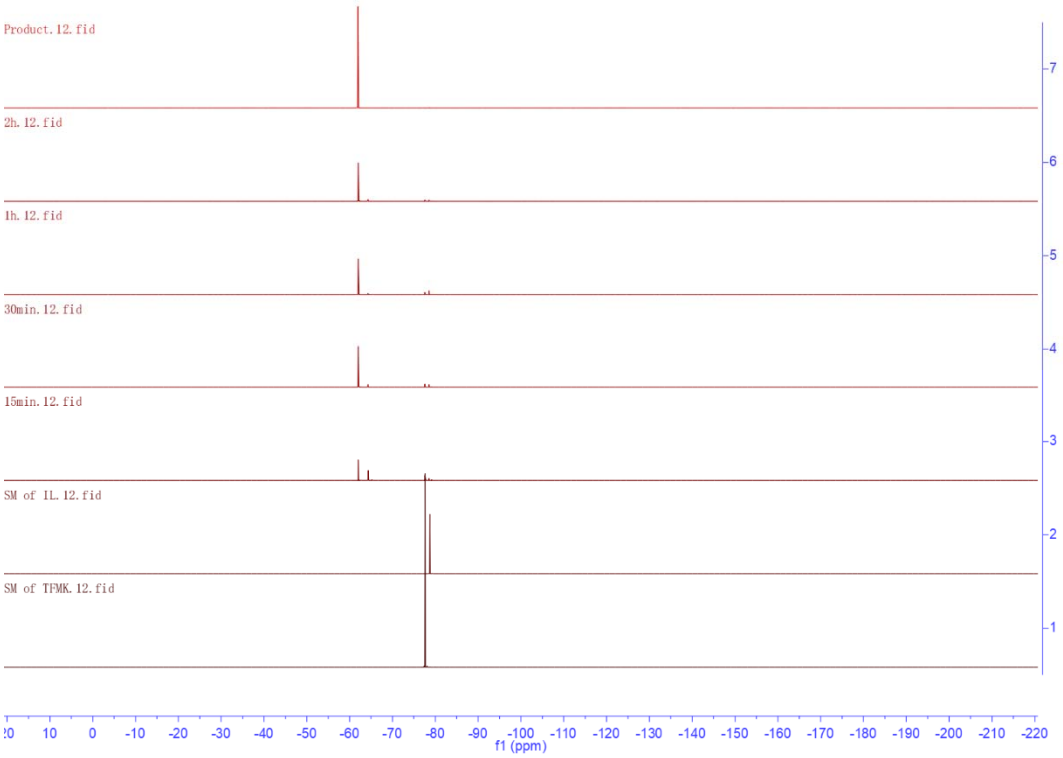


Figure S7. Real-time NMR (full ^{19}F NMR spectra), from bottom to top: 1) ^{19}F NMR of substrate **1a** (pure, in $CDCl_3$) (bottom). 2) ^{19}F NMR of [Bmim][OTf] (pure, in $CDCl_3$). 3-6) Reaction mixture of substrate **1a**, **2a**, and 10 mol% $H_3PMo_{12}O_{40}$ in [Bmim][OTf] at 100°C under O_2 atmosphere after 15 min, 30 min, 1, 2 hours. 7) ^{19}F NMR of product **3a** (in $CDCl_3$) (top).

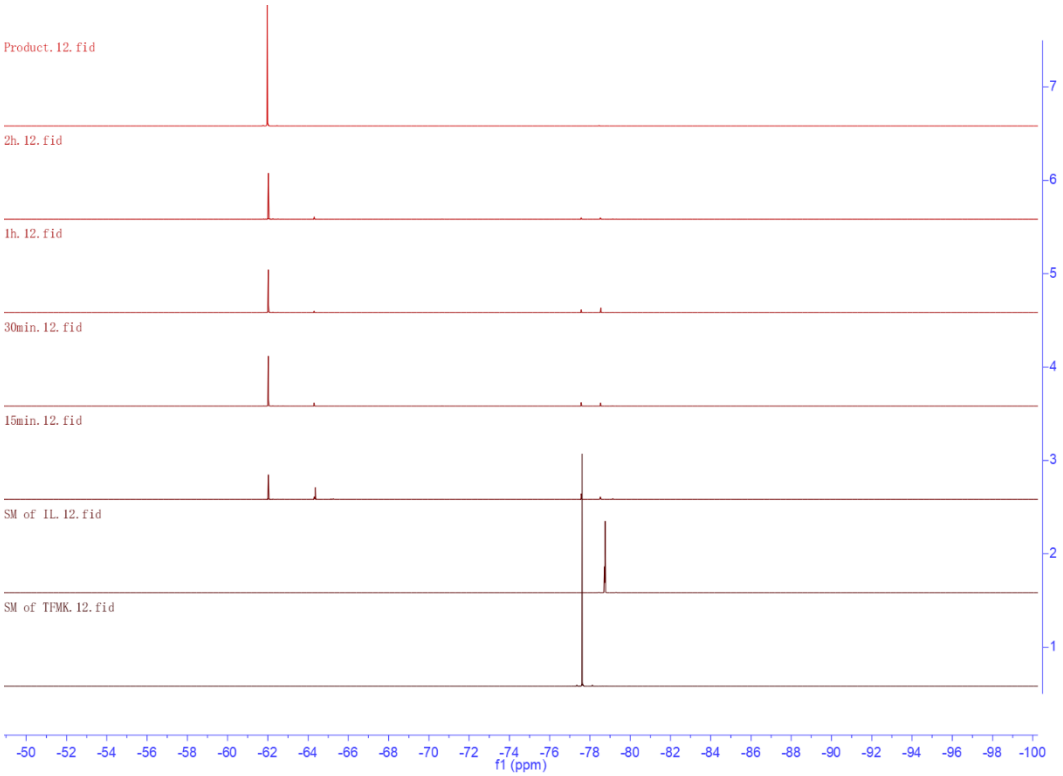


Figure S8. Real-time NMR (zoomed in ^{19}F NMR spetra)

Procedure for real-time ^1H NMR monitoring program for product 5a: Under standard reaction conditions B, six groups of reactions were administered in parallel, with a scale of 0.1 mmol per group,

labeled at 0.5h, 1h, 2h, 4h, 16h, and 24h, respectively. After reaching the corresponding reaction time, completely cool down, dissolve 100 μL of solvent ([Bmim][OTf]) in 0.6 mL of deuterated chloroform, and perform ^{1}H NMR testing.

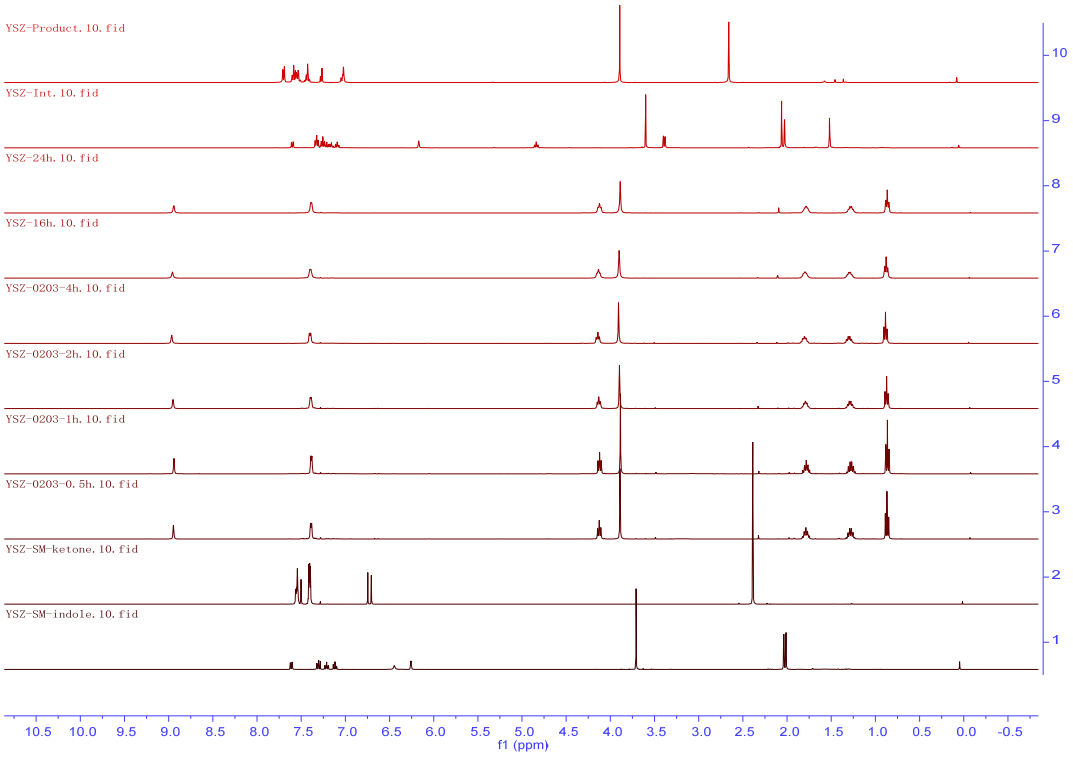


Figure S9. Real-time ^{1}H NMR experiments (full ^{1}H NMR spectra). From top to bottom: 1) ^{1}H NMR of substrate **1a** (pure, in $CDCl_3$) (bottom). 2) ^{1}H NMR of substrate **4a** (pure, in $CDCl_3$). 3-8) Reaction mixture of substrate **1a**, **2a**, and 10 mol% $H_3PMo_{12}O_{40}$ in [Bmim][OTf] at 100°C under argon atmosphere after 0.5, 1, 2, 4, 16, and 24 hours. 9-10) ^{1}H NMR of compound **7** and product **5a** (in $CDCl_3$) (top).

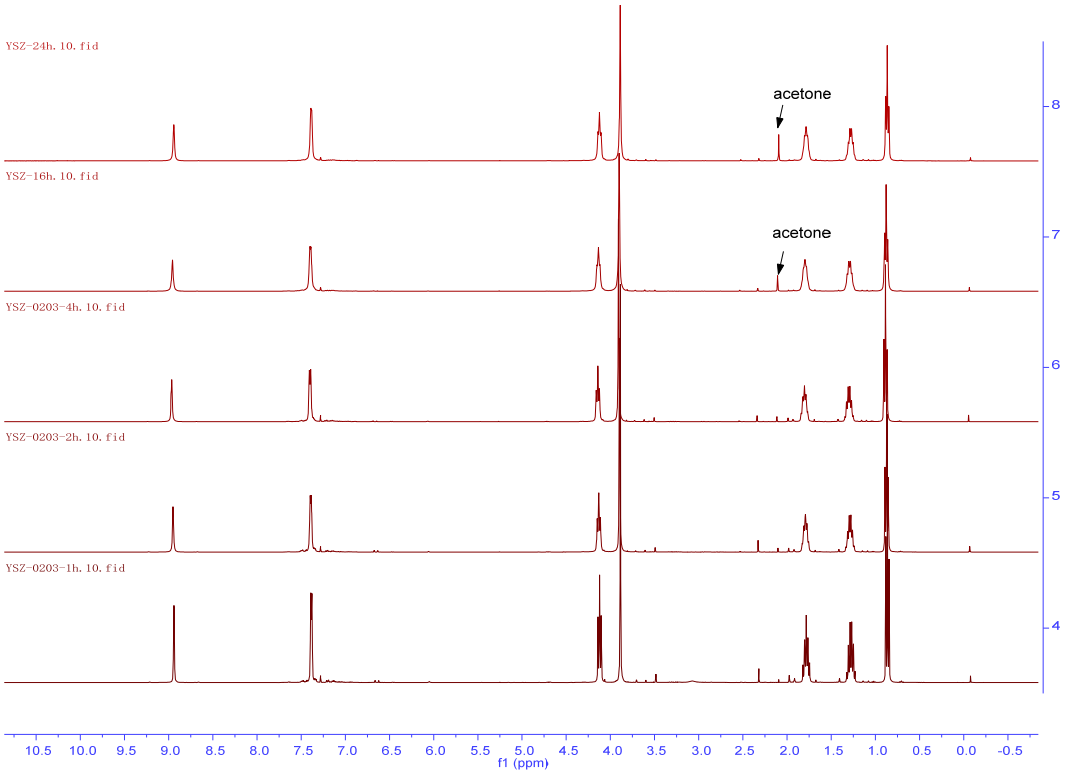


Figure S10. zoomed real-time ^{1}H NMR (400 MHz) spectra (***Note***: δ 2.37 for methyl proton signal of **4a**, δ 2.07 for methyl proton signal of acetone, due to the interference of ionic liquids, ***the spectrum needs to be fully enlarged***).

7.3 Proposed mechanism

For the 1,2-addition cascade pathway, first, under the synergistic effect of phosphomolybdic acid /ionic liquid, indole **1a** and unsaturated ketone **2a** are activated, 1,2-addition follows dehydration to generate the **int-I**. Due to the destabilization effect of trifluoromethyl, **int-I** rapidly isomerizes to form **int-II**. Afterward, intramolecular electrophile addition occurs, forming the more stable **int-III**. Finally, **int-III** would be oxidized by O_2 to give the desired product **3a**. For the 1,4-addition cascade approach, initially, Michael conjugate addition occurs preferentially, followed by intramolecular carbonyl-olefin metathesis reaction and dehydrogenation, giving the target carbazole product **4a**. The dehydrogenation aromatization is possibly promoted by phosphomolybdic acid/ionic liquid. In these two divergent pathways, it is conceivable that the synergistic effect of HPA/IL plays a significant role in substrate activation and enhancing reaction selectivity.

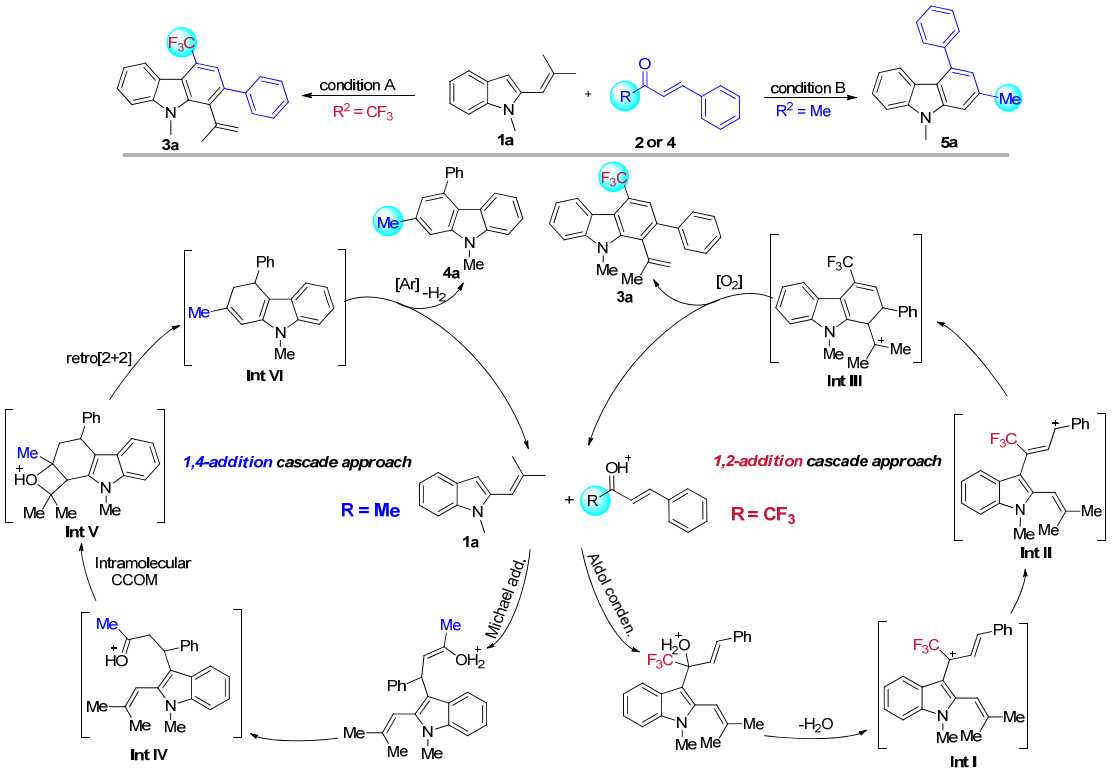


Figure S7. Proposed Mechanism

8. References

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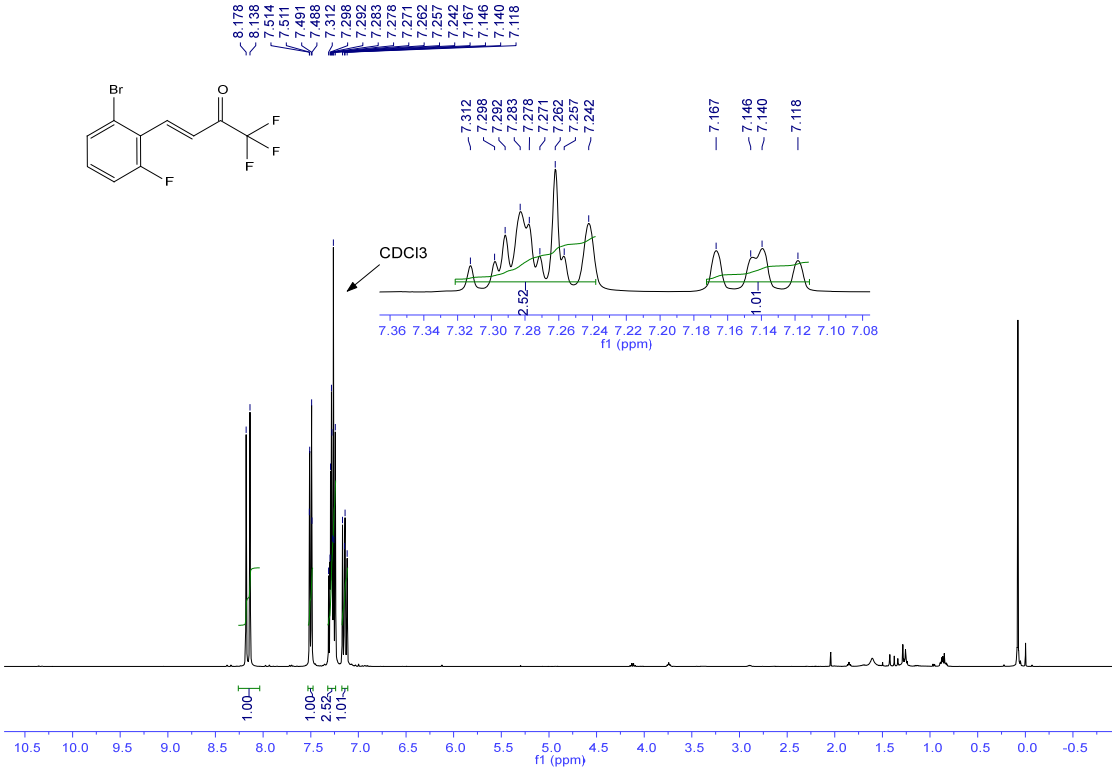
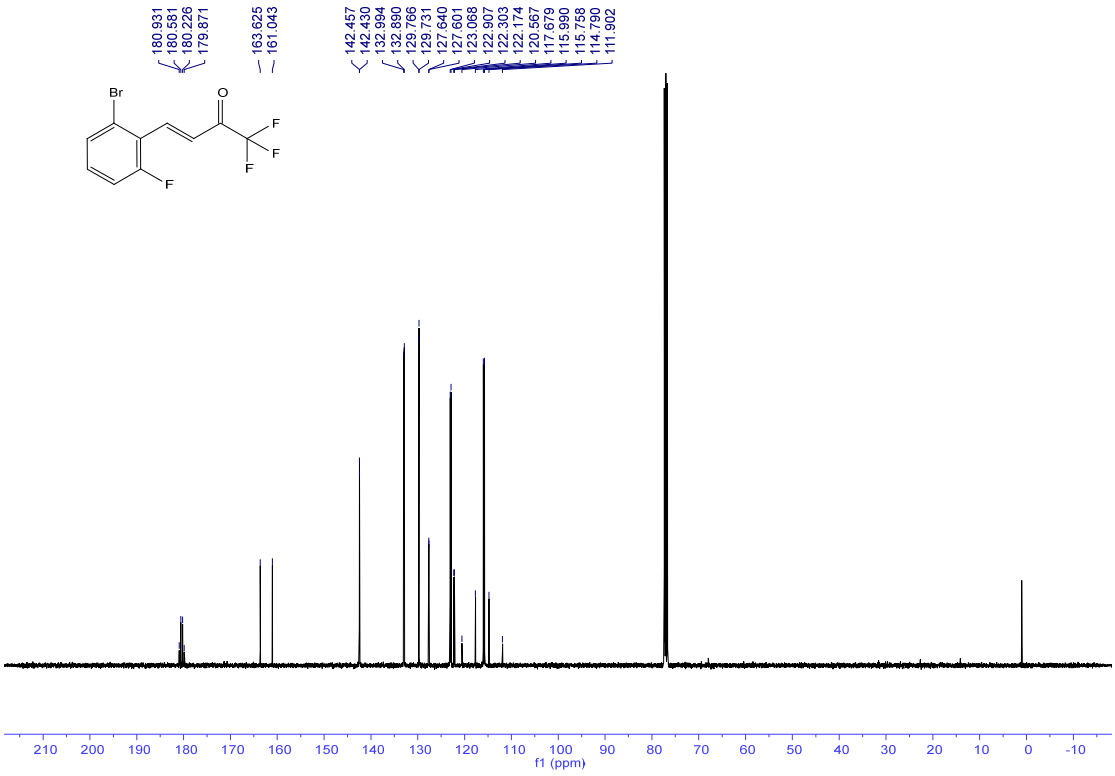
9. NMR spectra

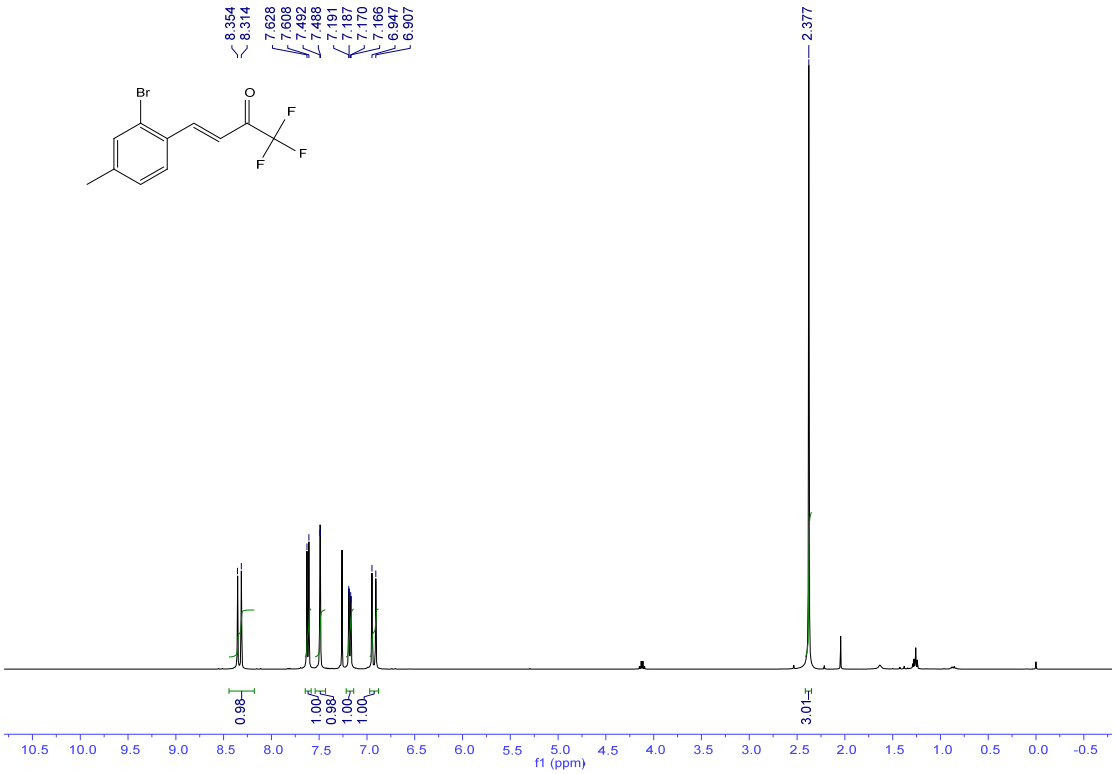


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **2w**

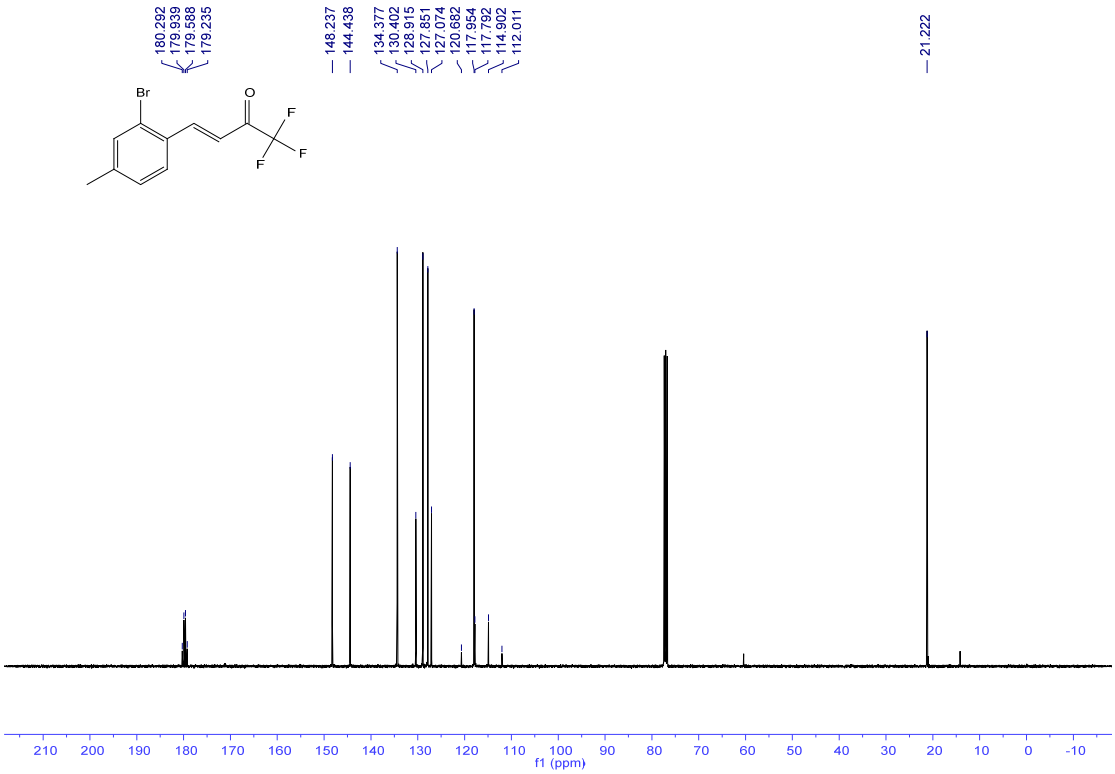


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of compound **2w**

^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **2w**



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



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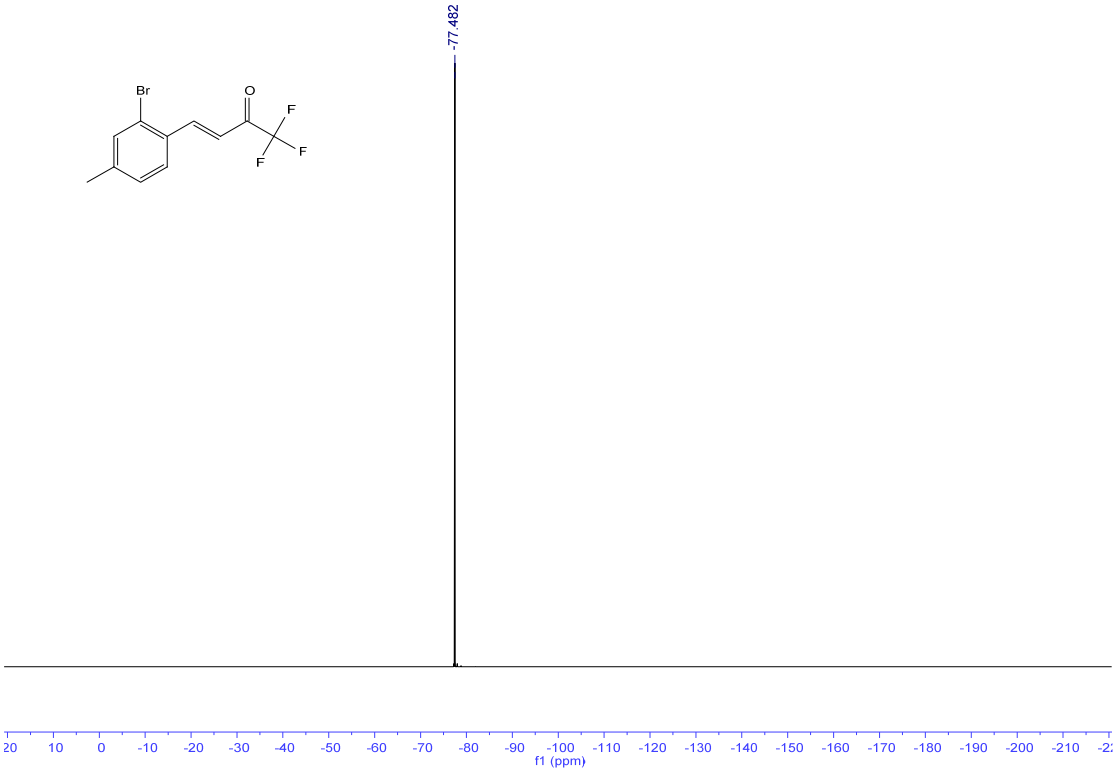
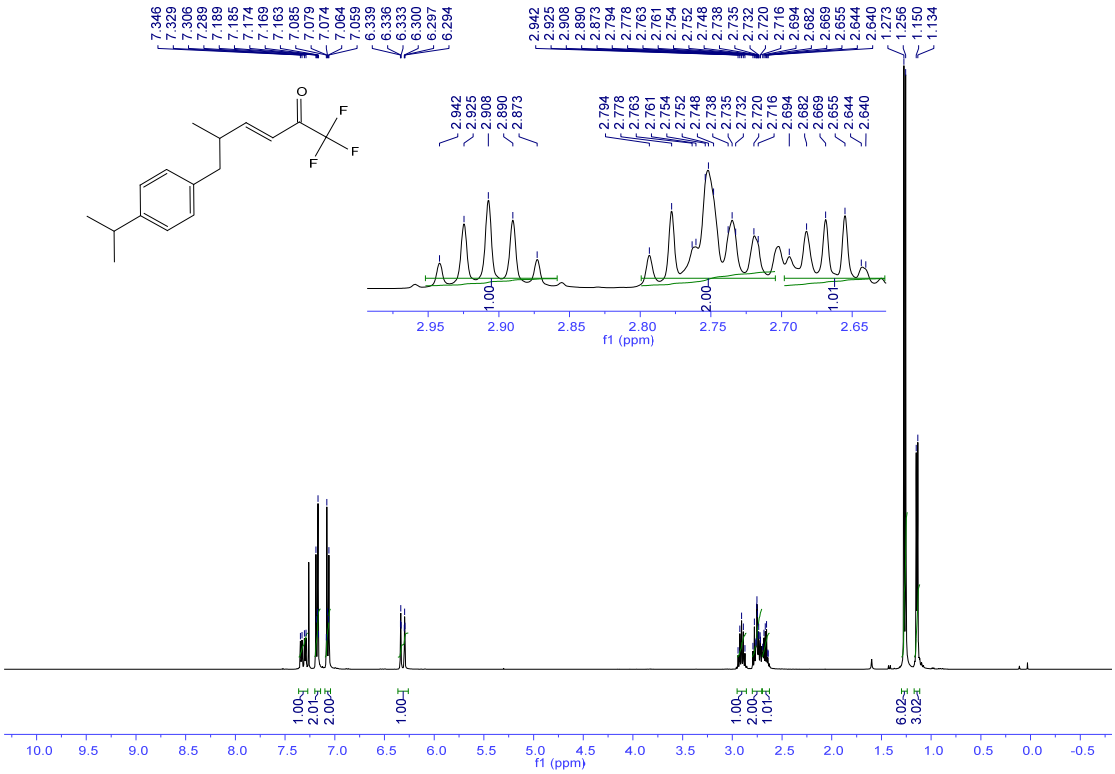
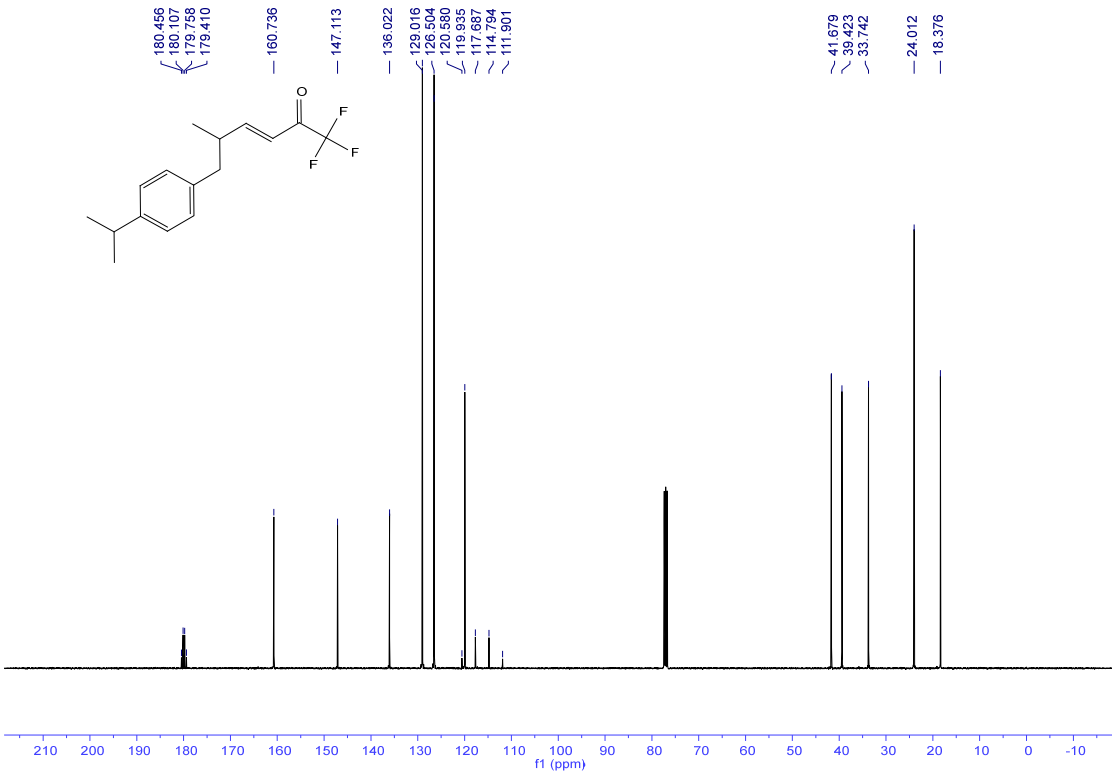


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **2x**

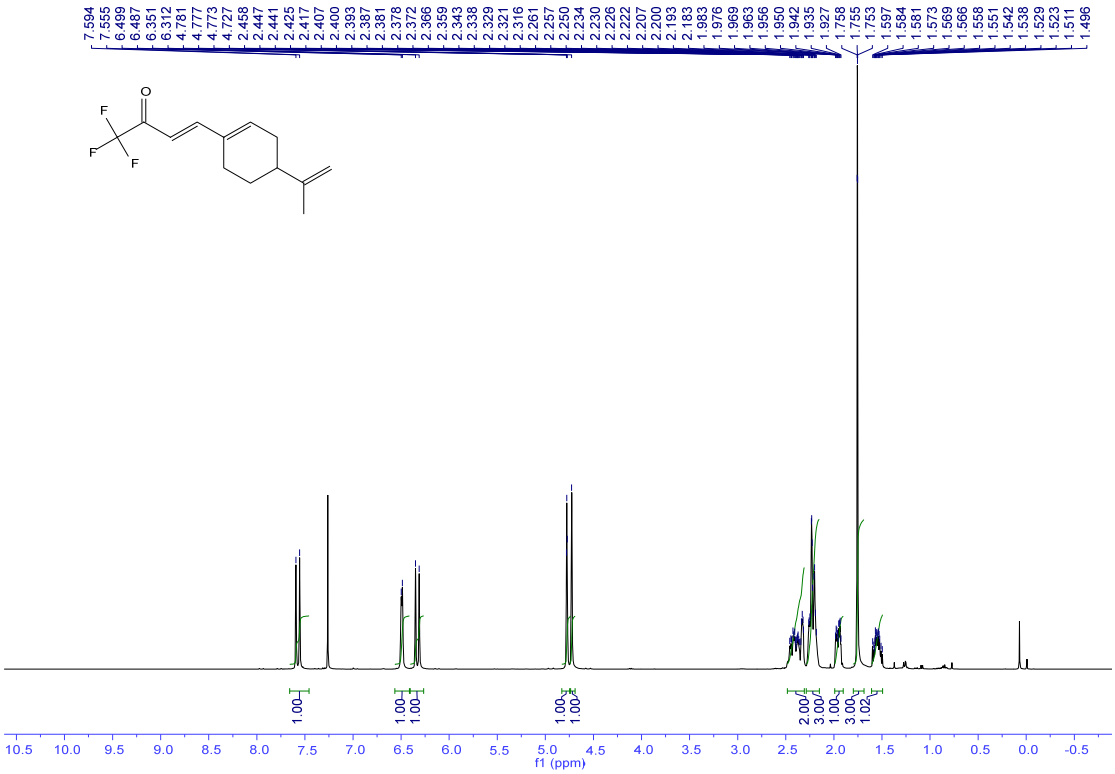


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **2y**



^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of compound **2y**

^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **2y**



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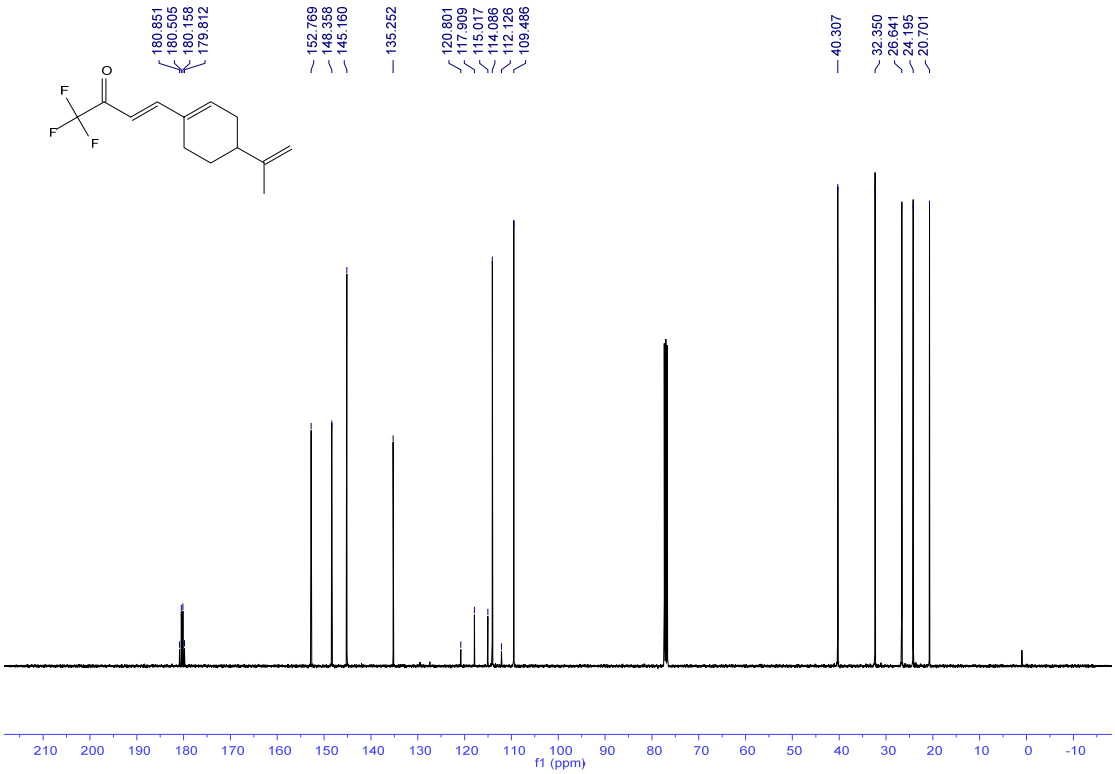
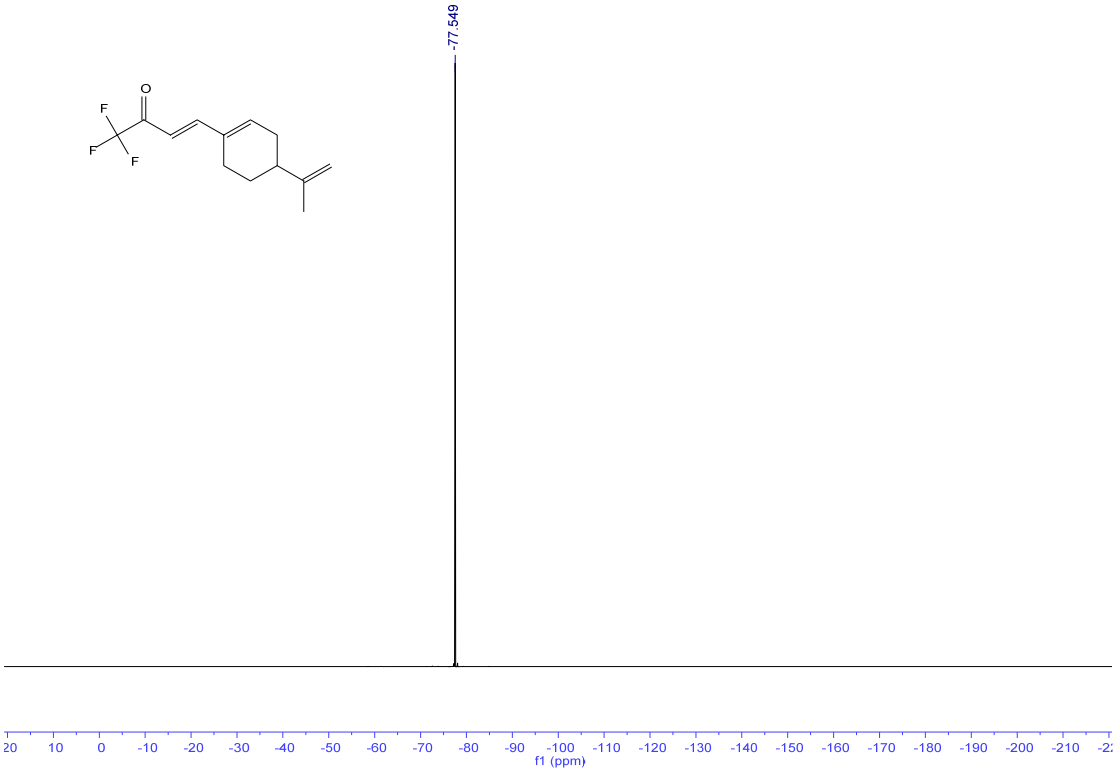
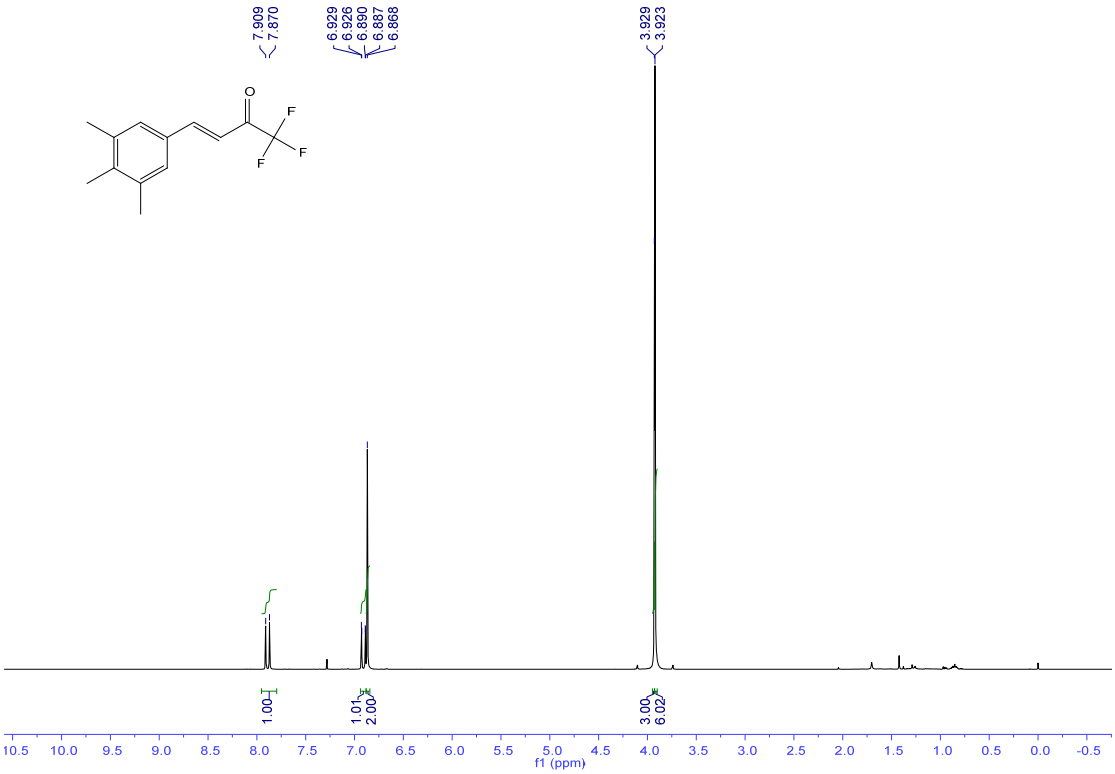


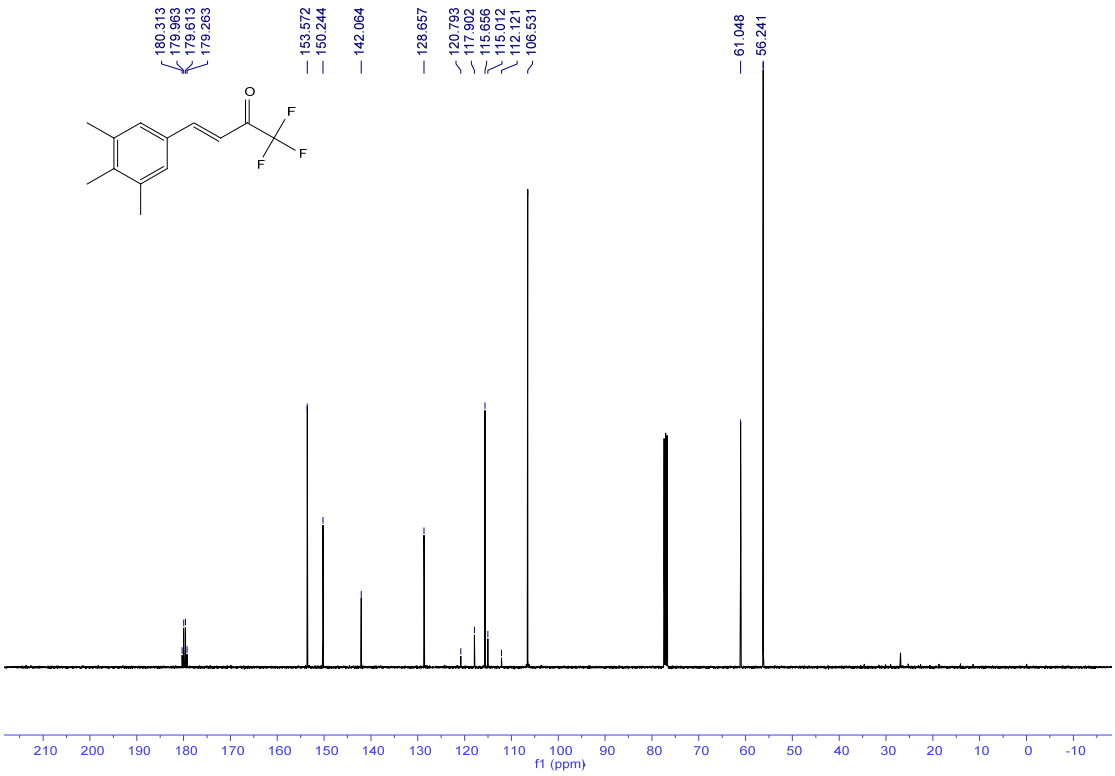
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **2z**



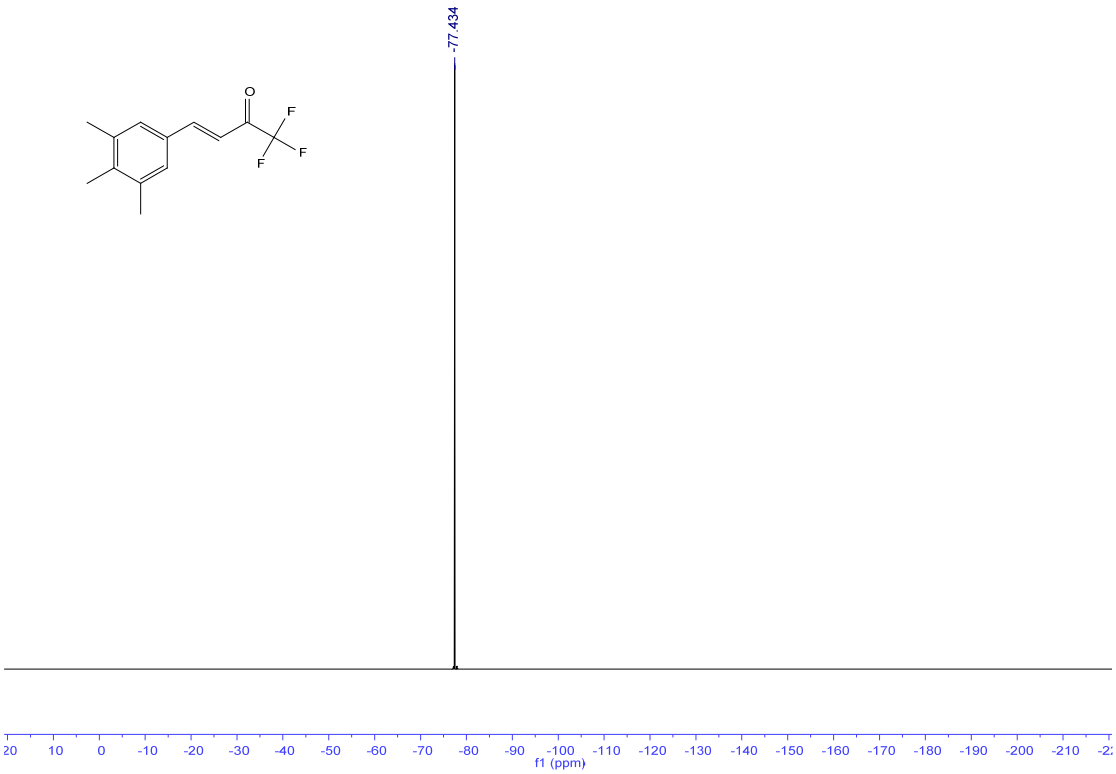
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **2z**



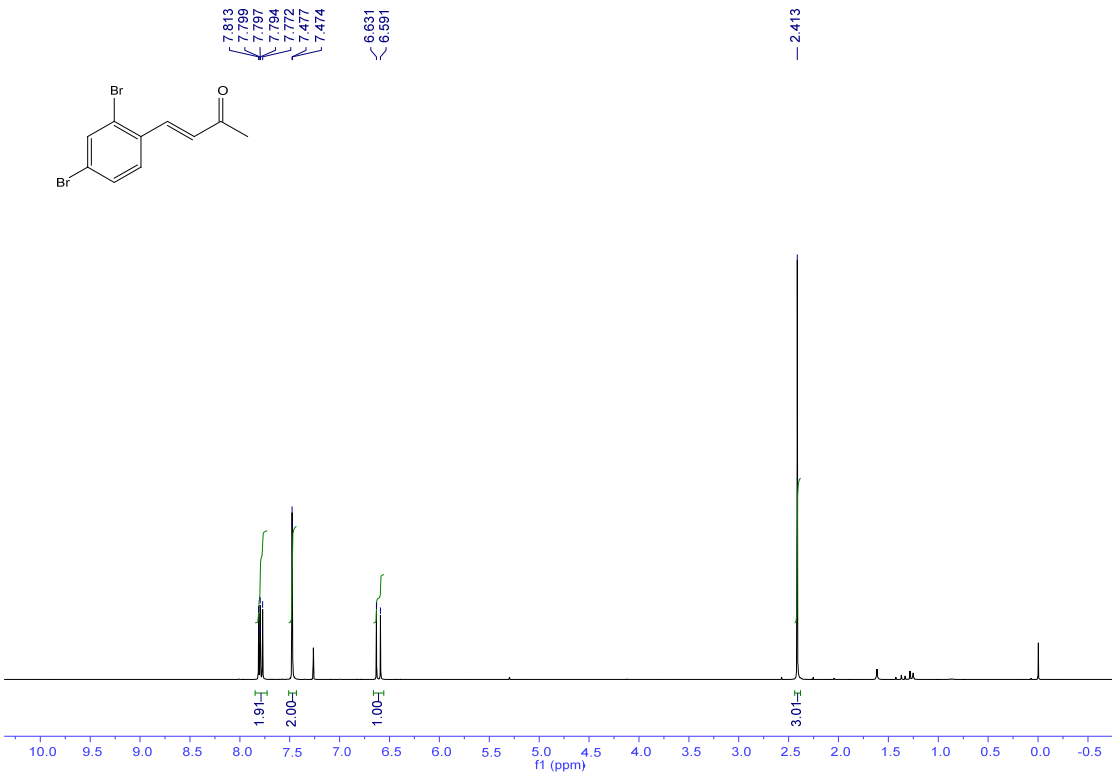
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **2aa**



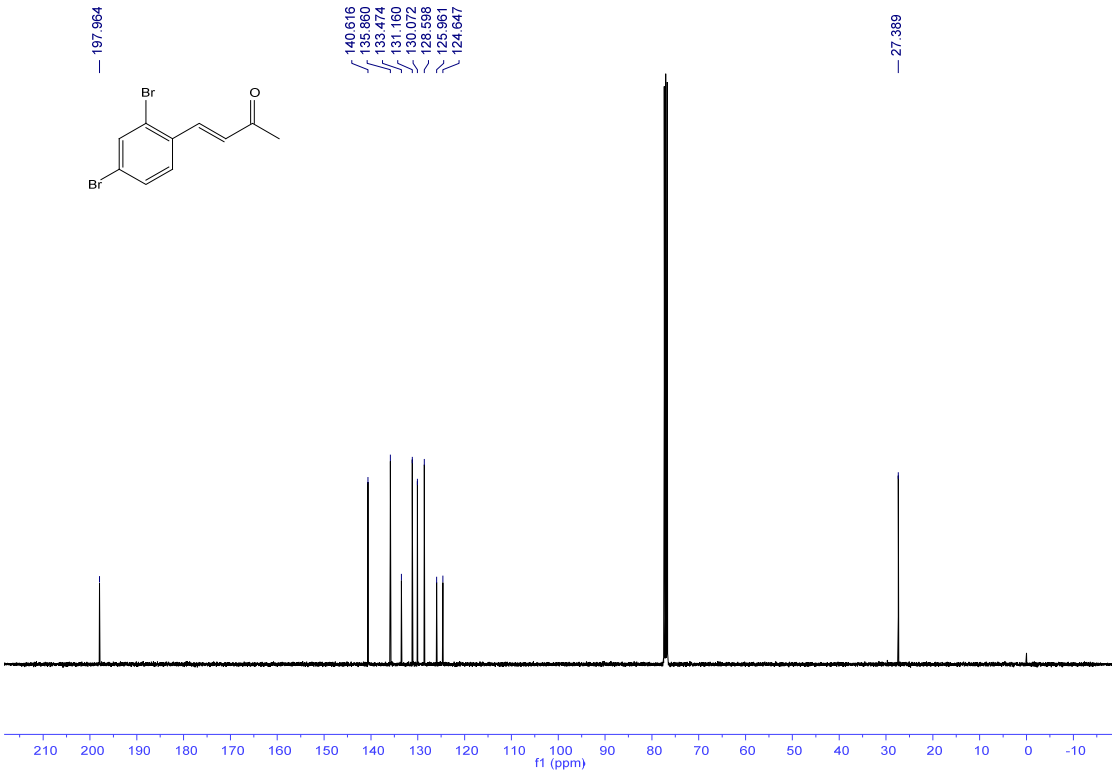
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of compound **2aa**



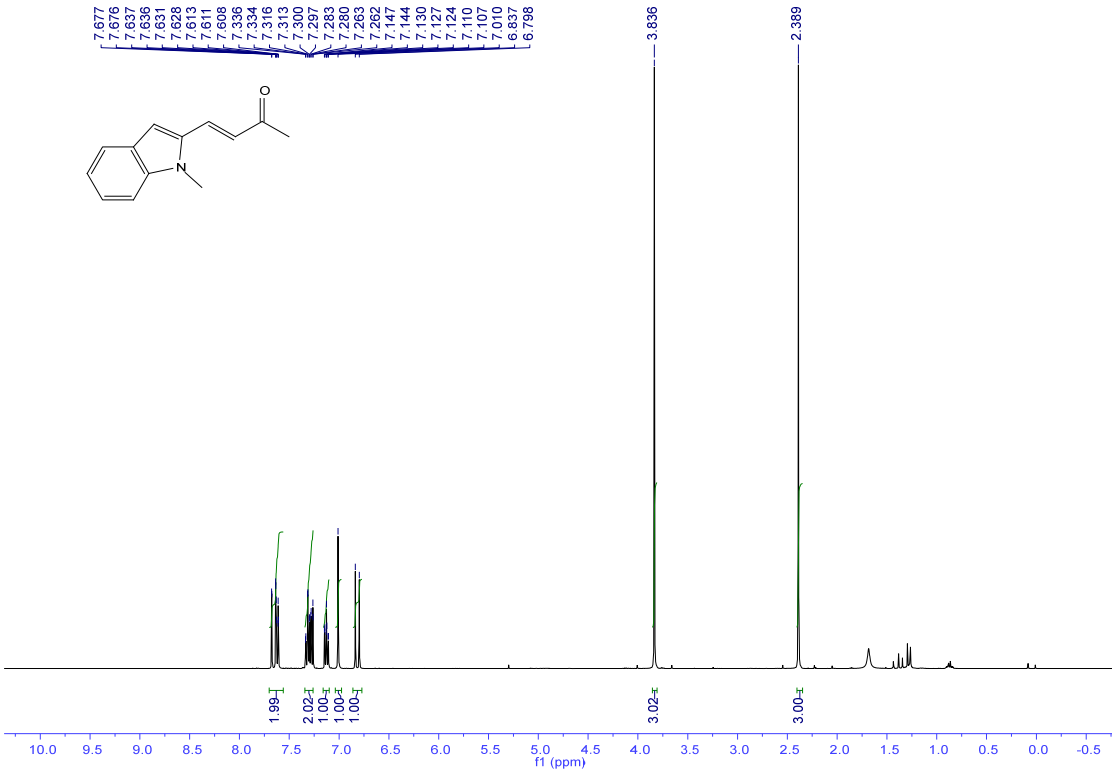
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **2aa**



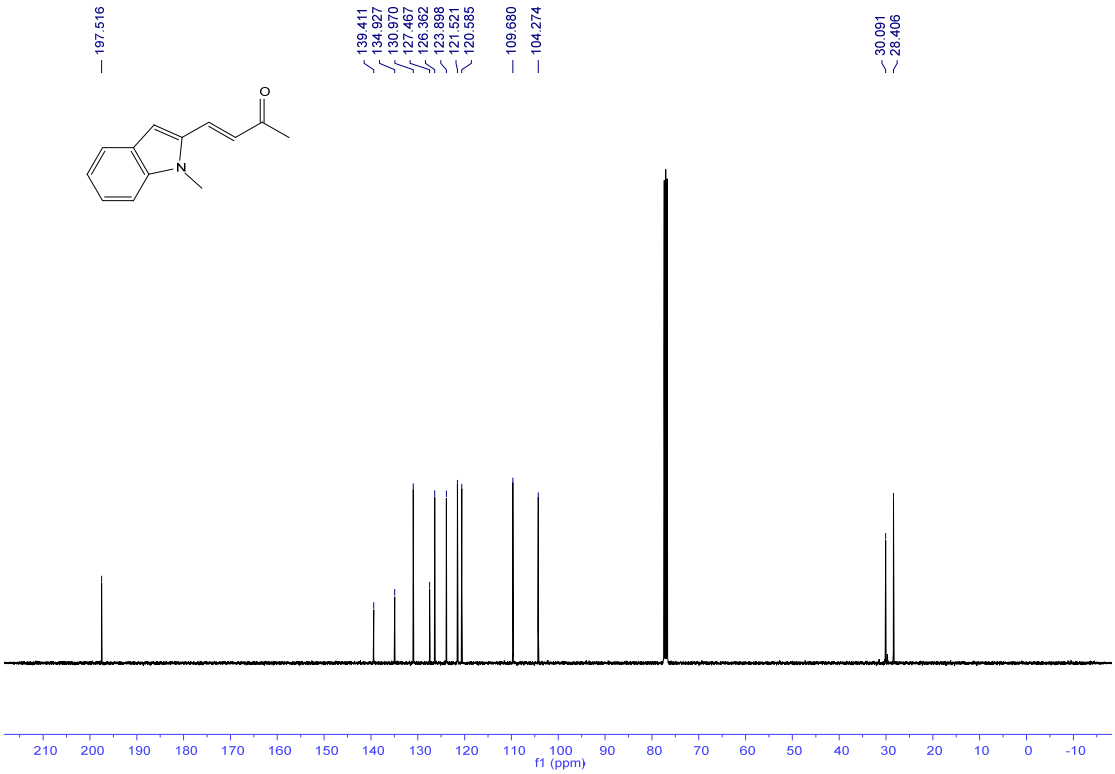
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4r**



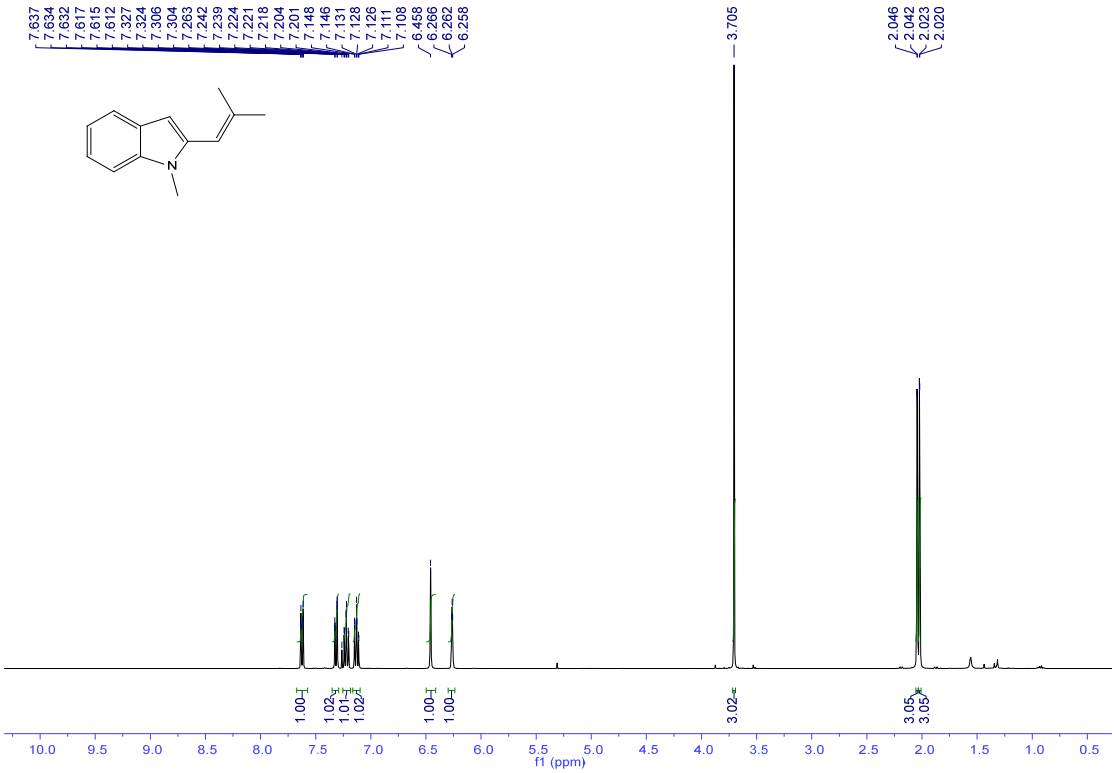
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **4r**



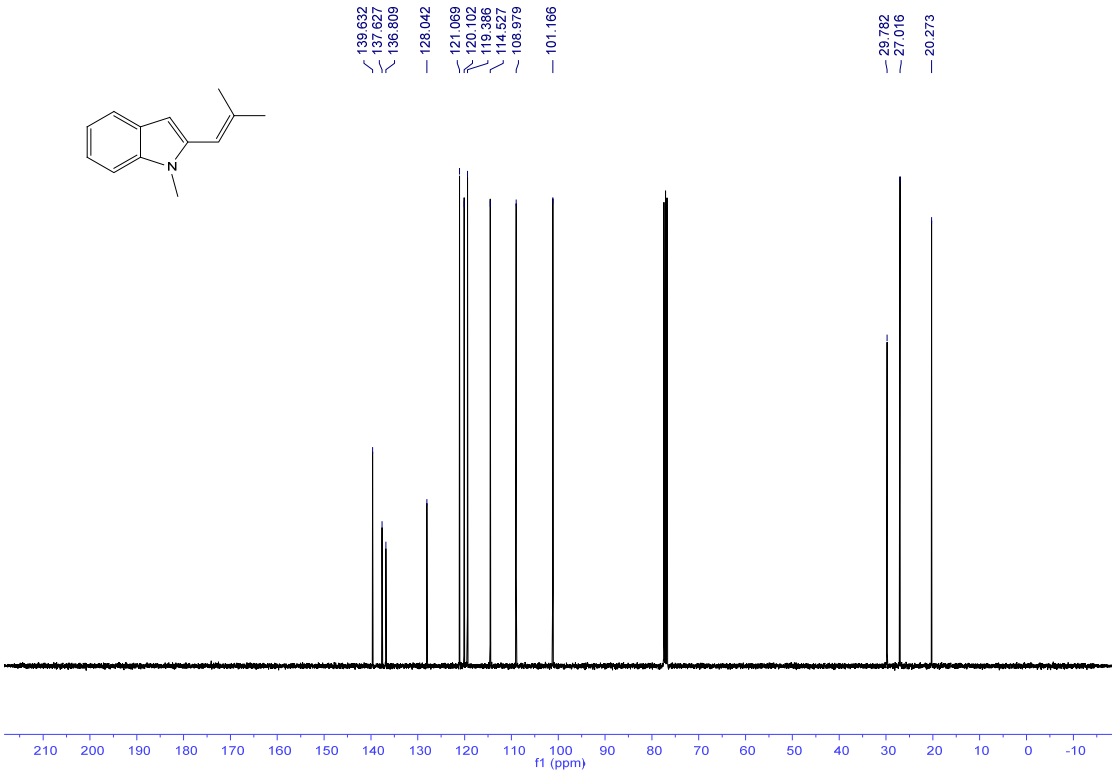
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4v**



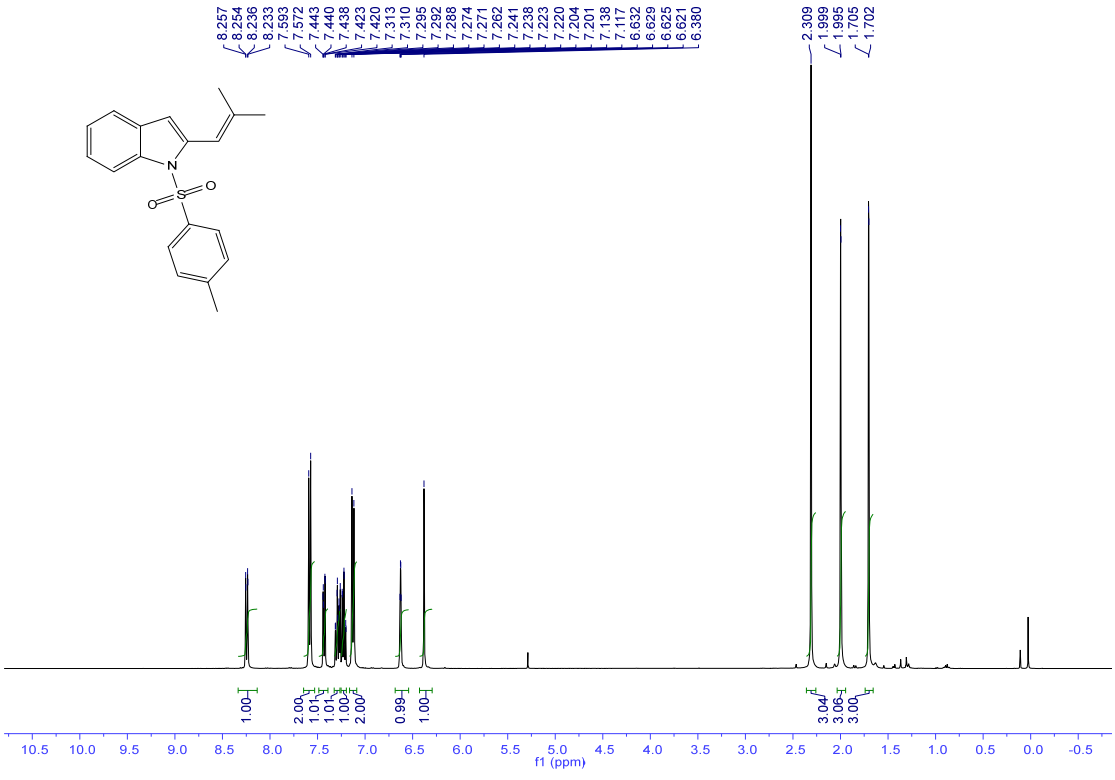
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **4v**



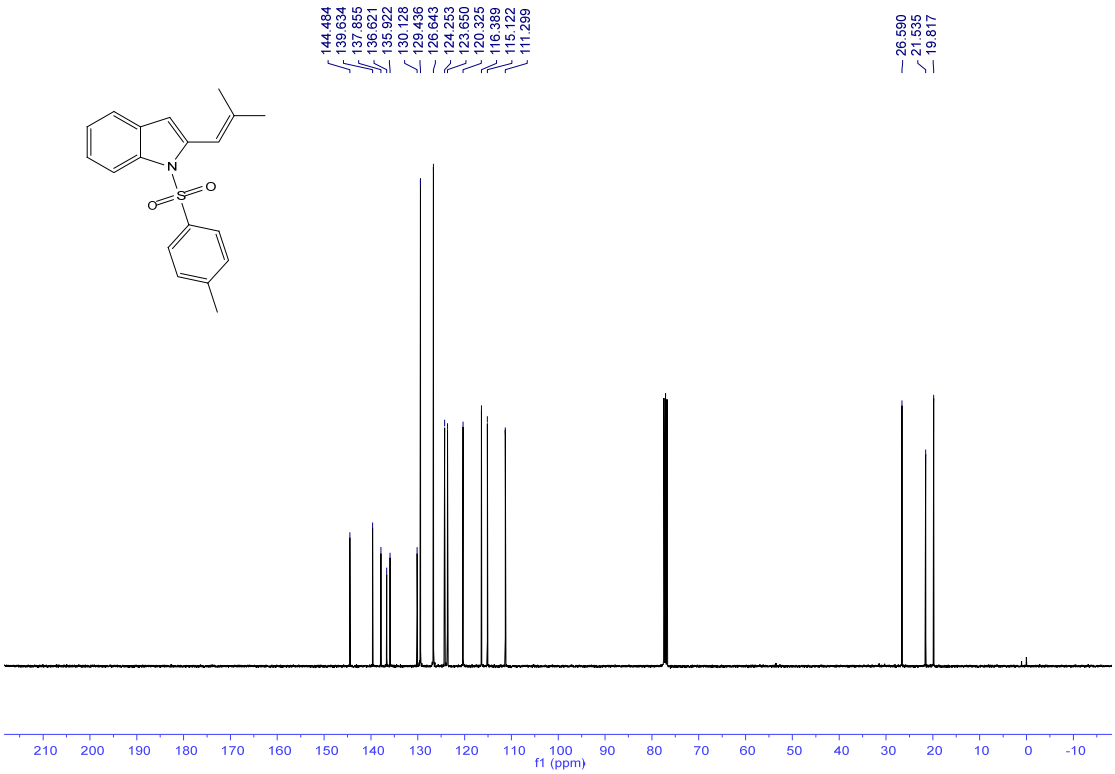
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1a**



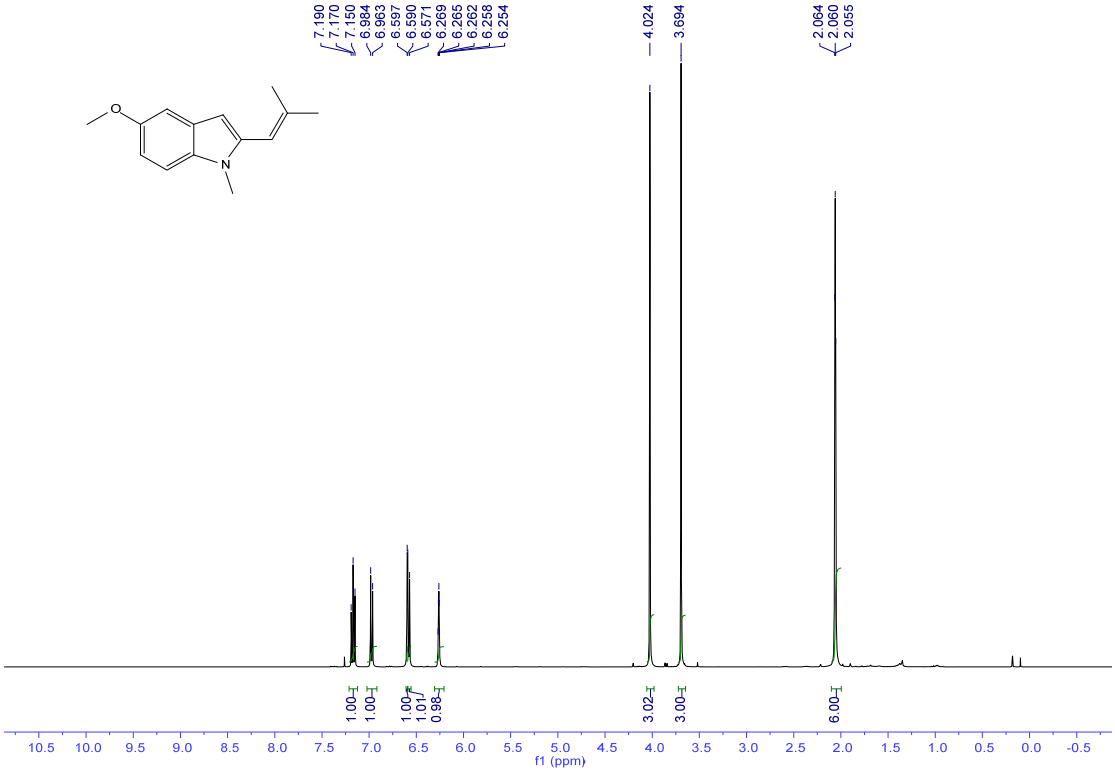
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **1a**



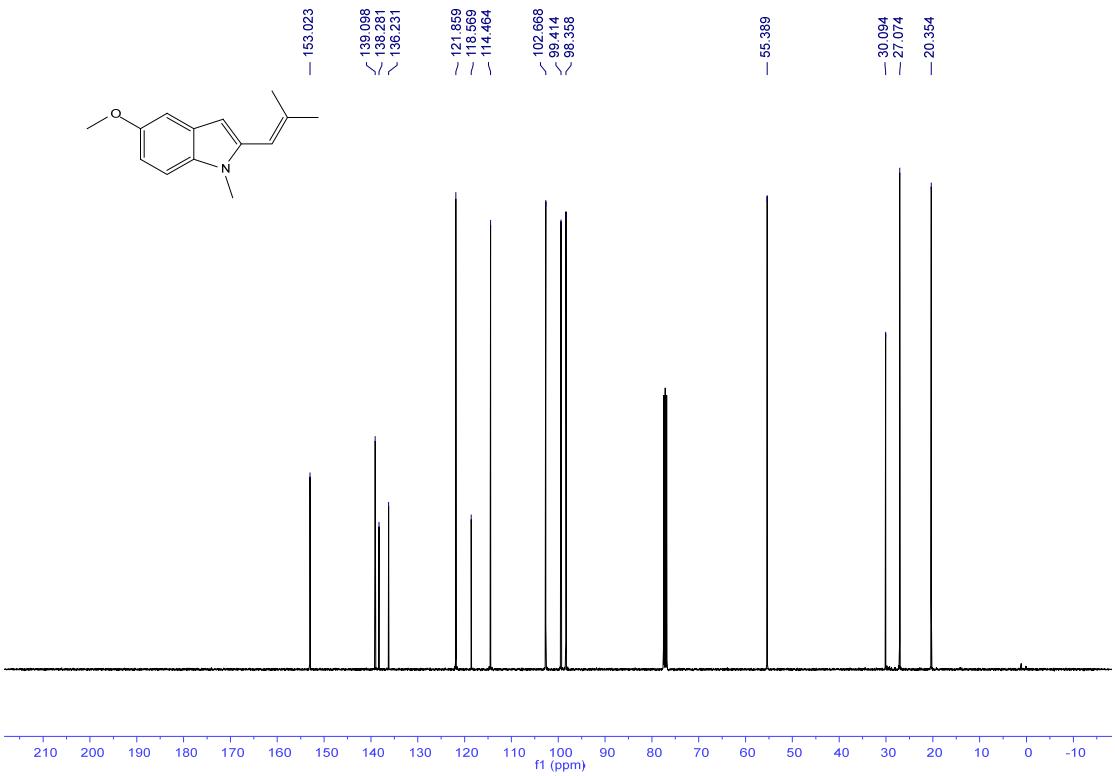
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1d**



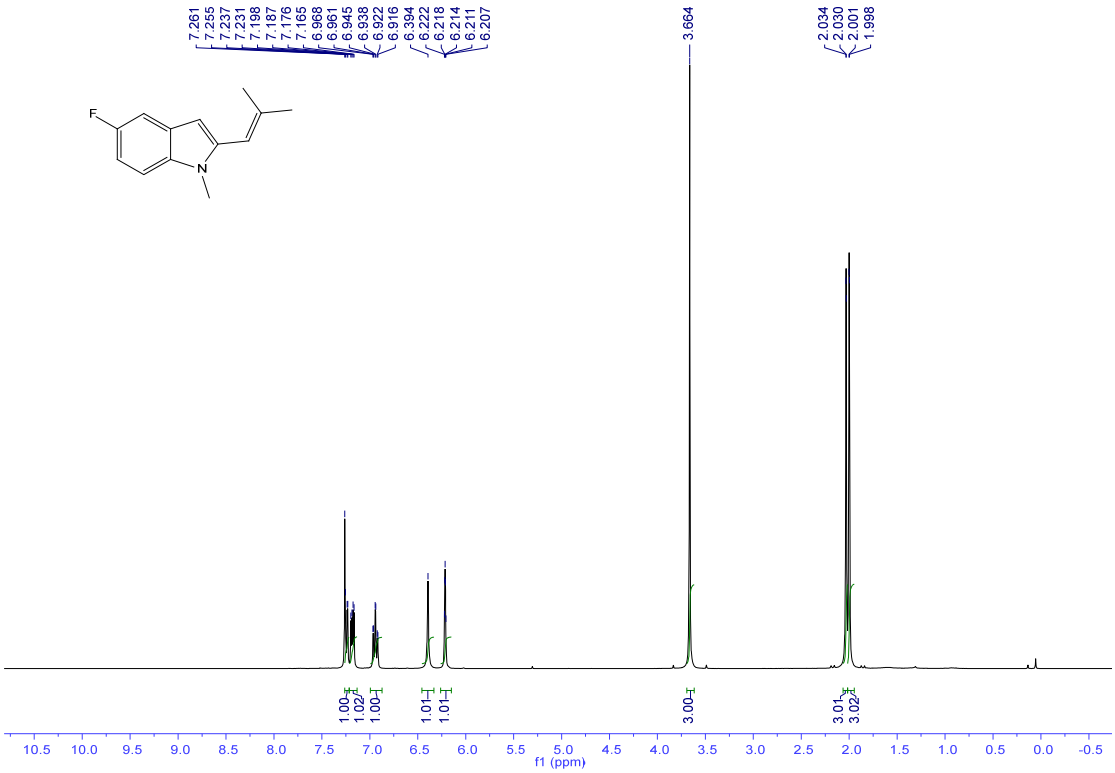
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **1d**



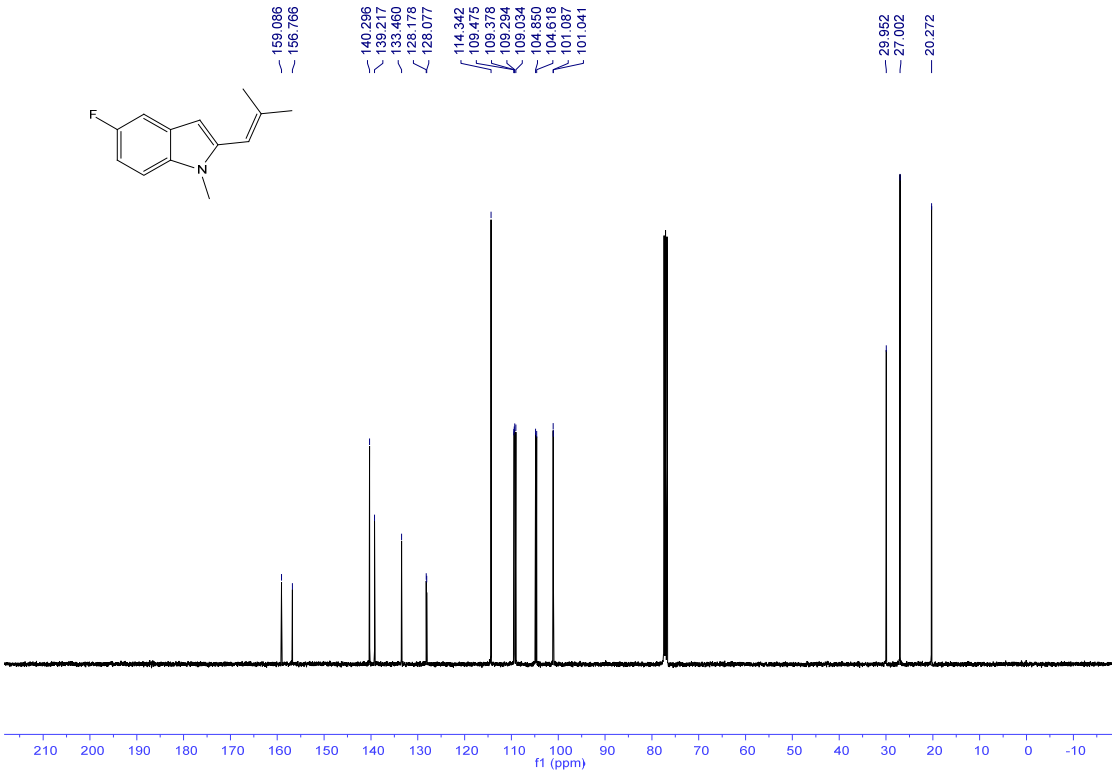
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1e**



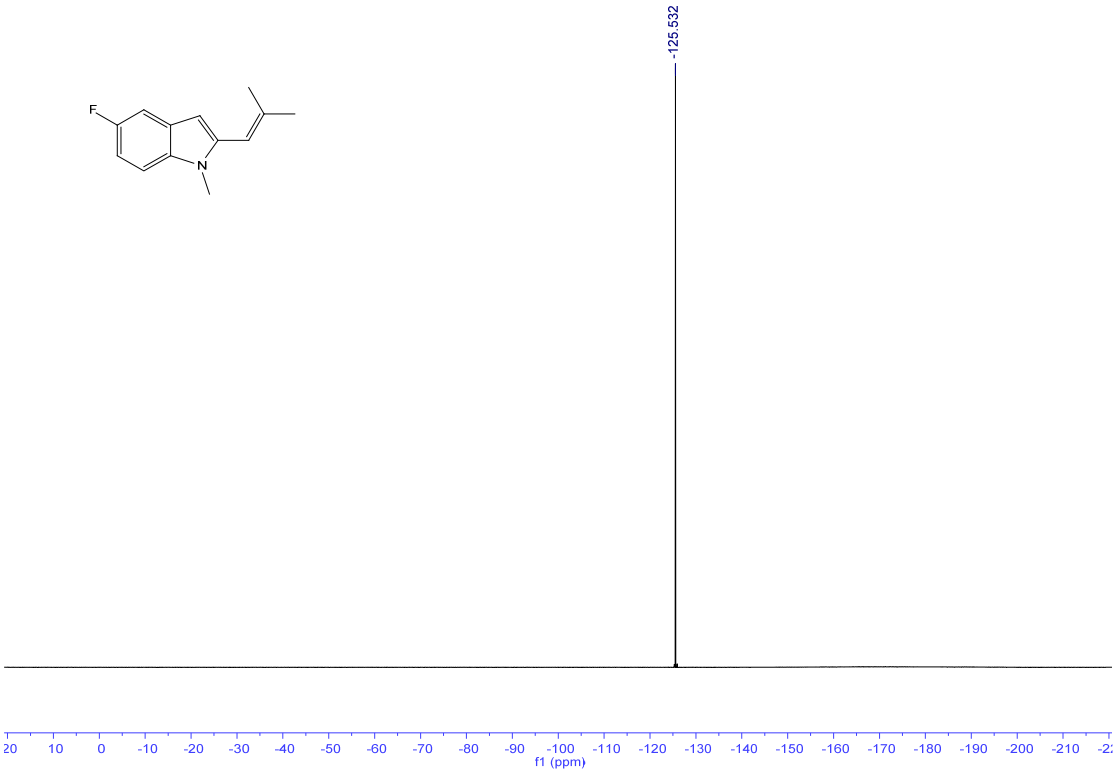
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **1e**



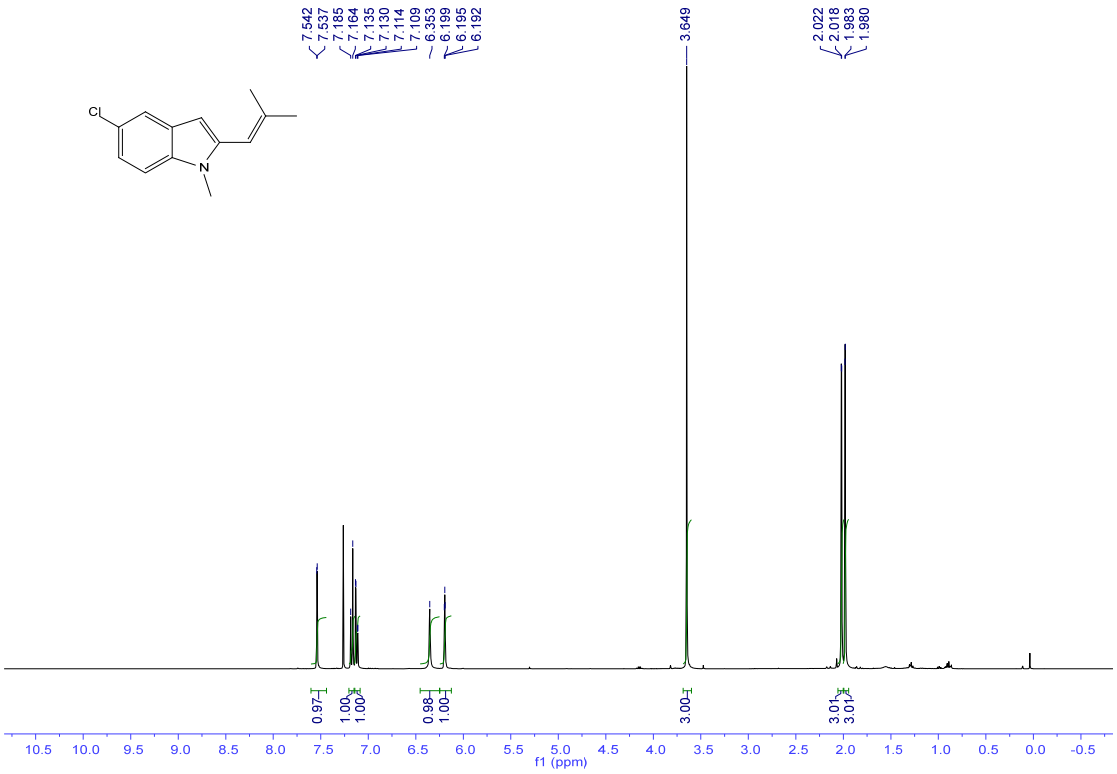
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1f**



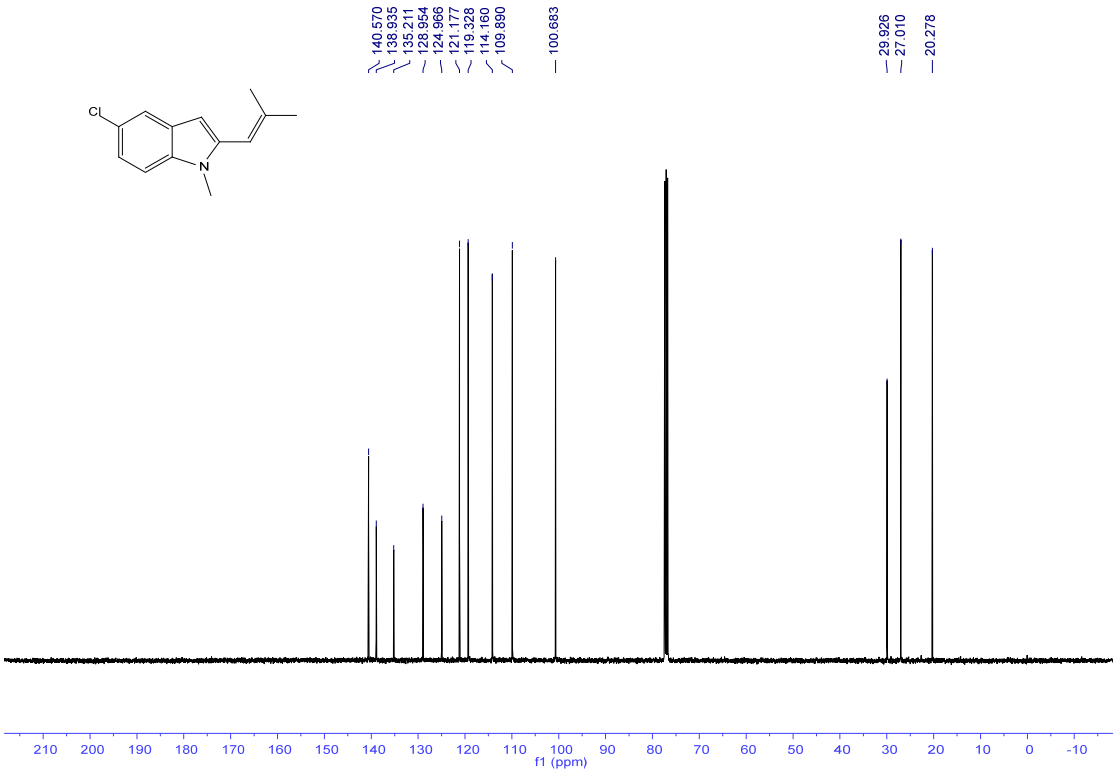
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **1f**



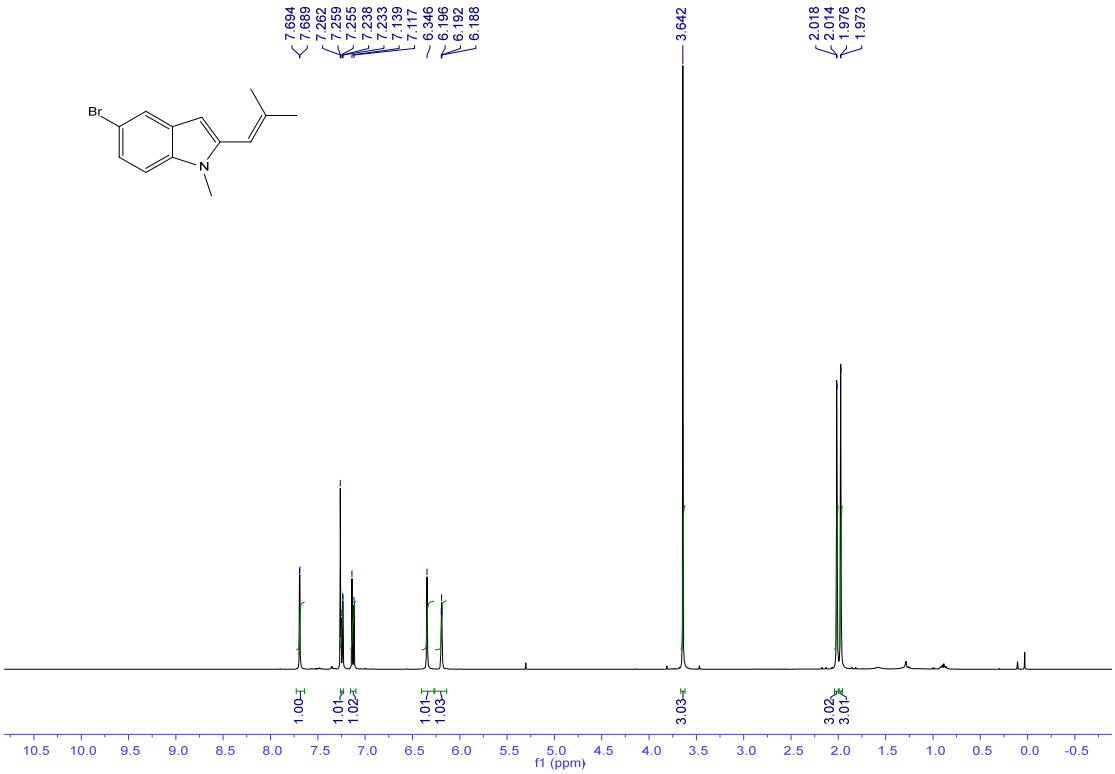
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **1f**



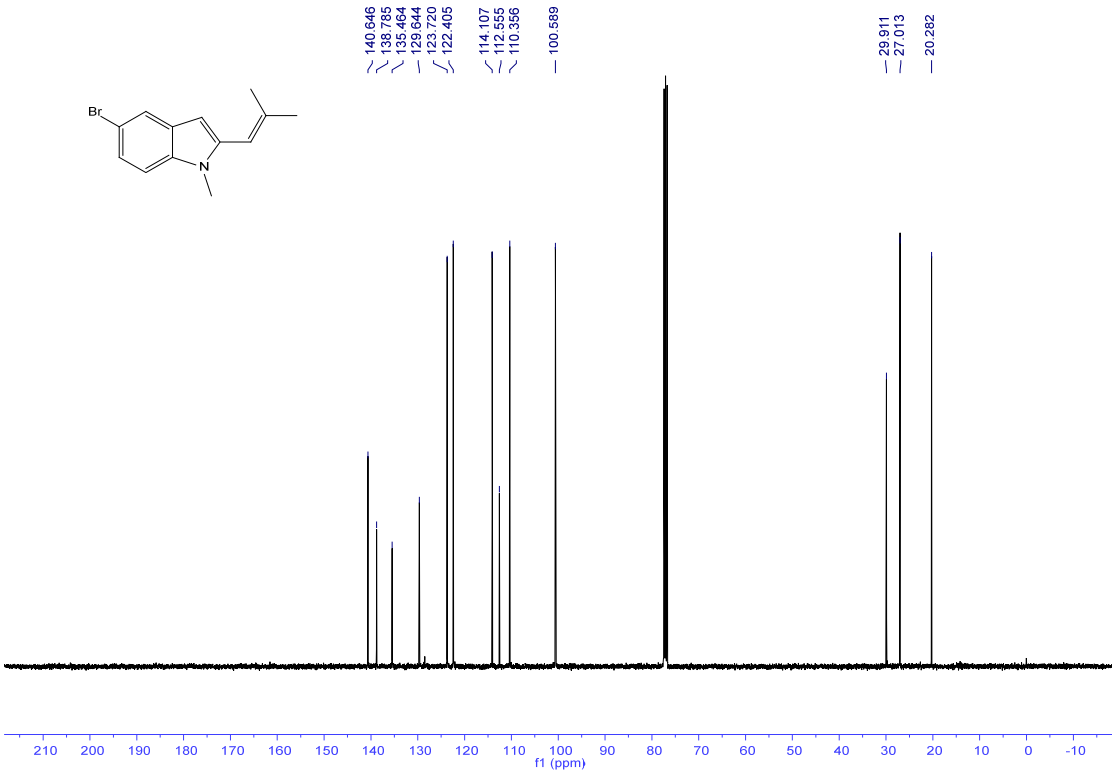
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1g**



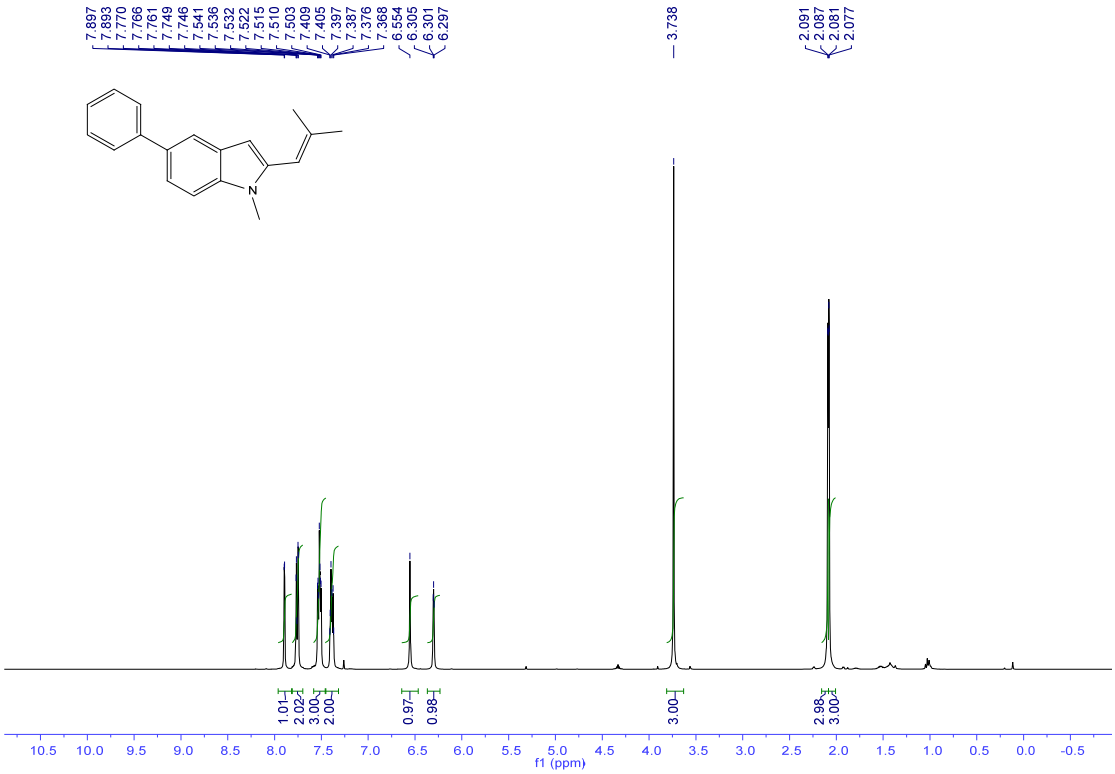
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of compound **1g**



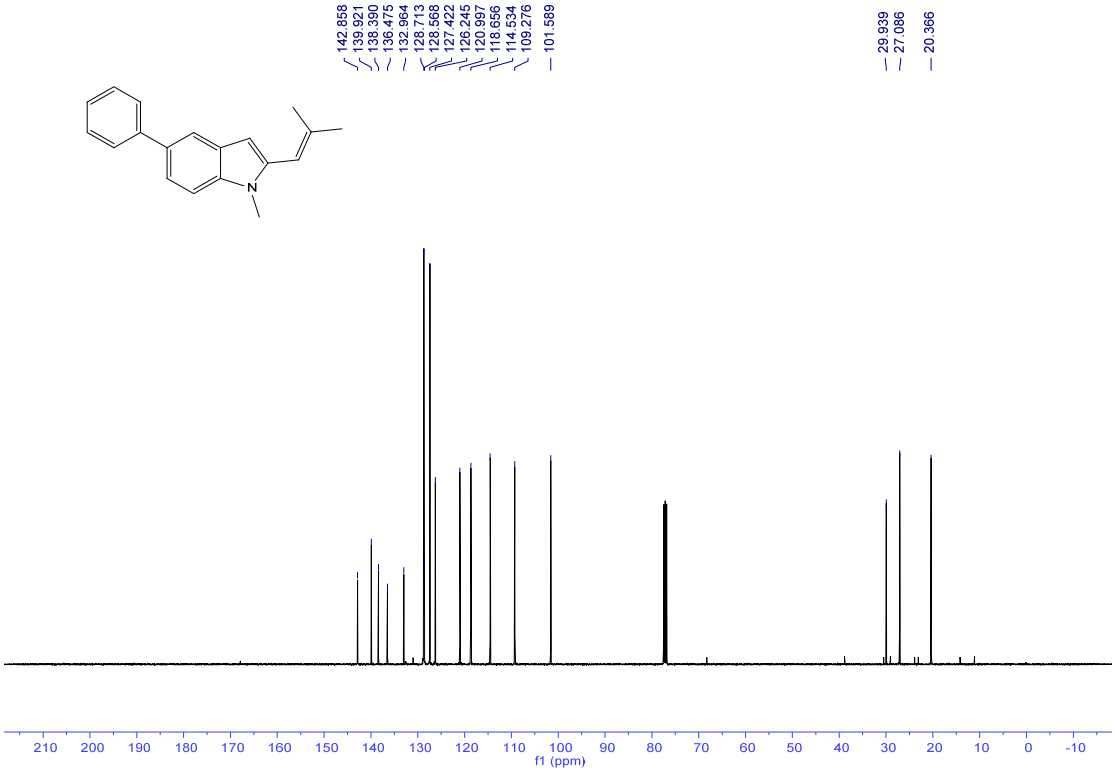
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1h**



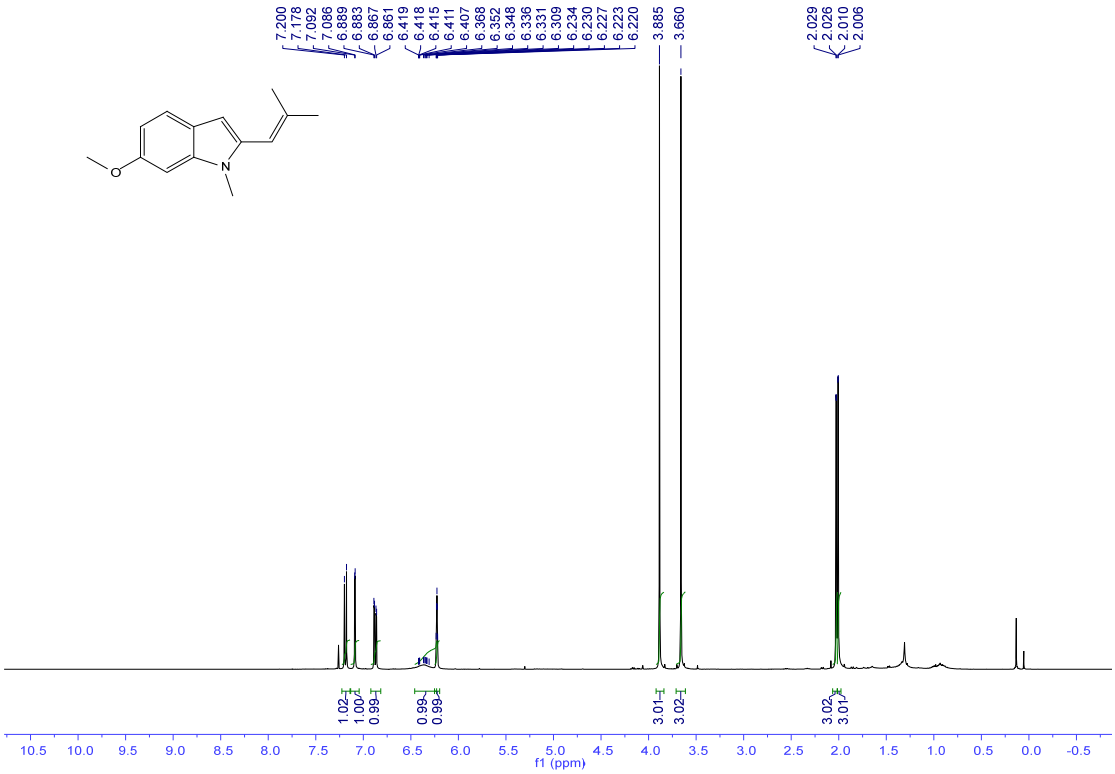
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **1h**



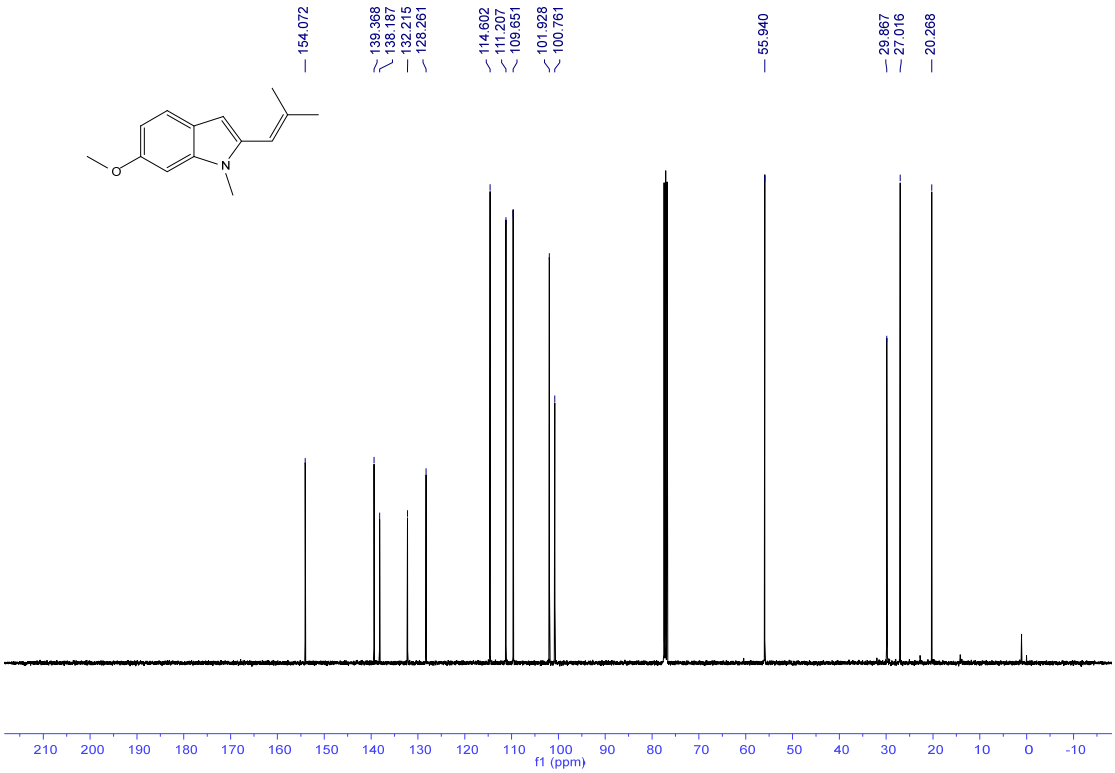
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1i**



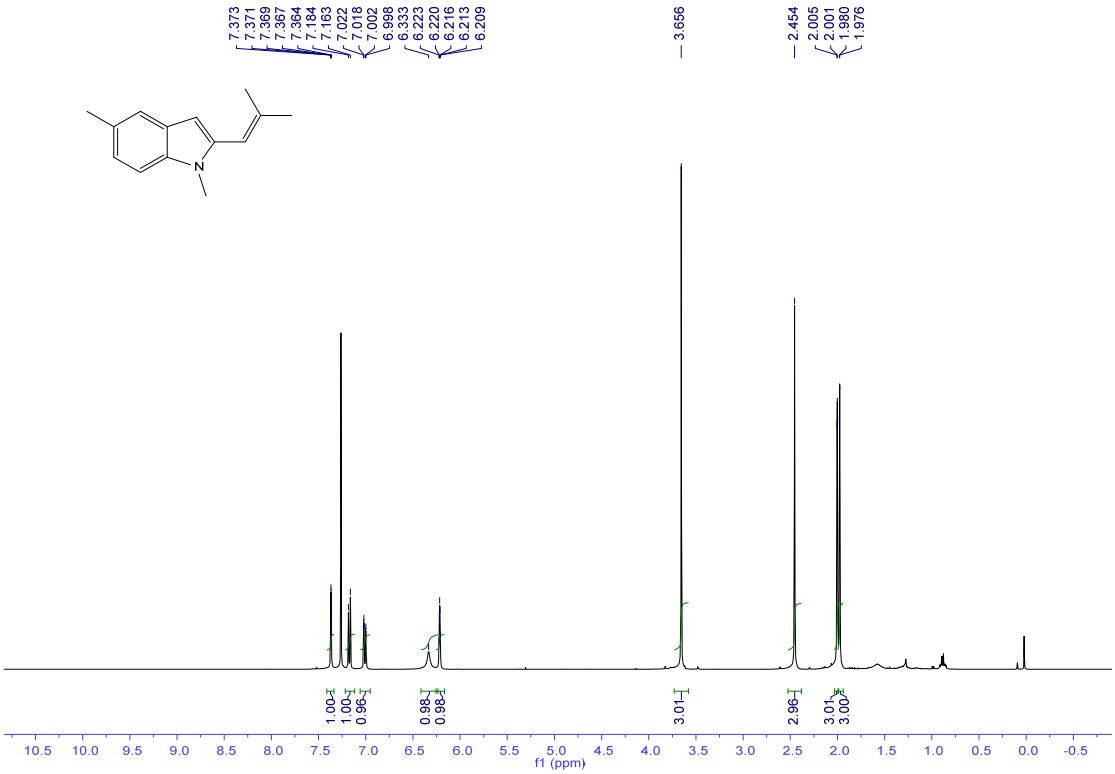
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of compound **1i**



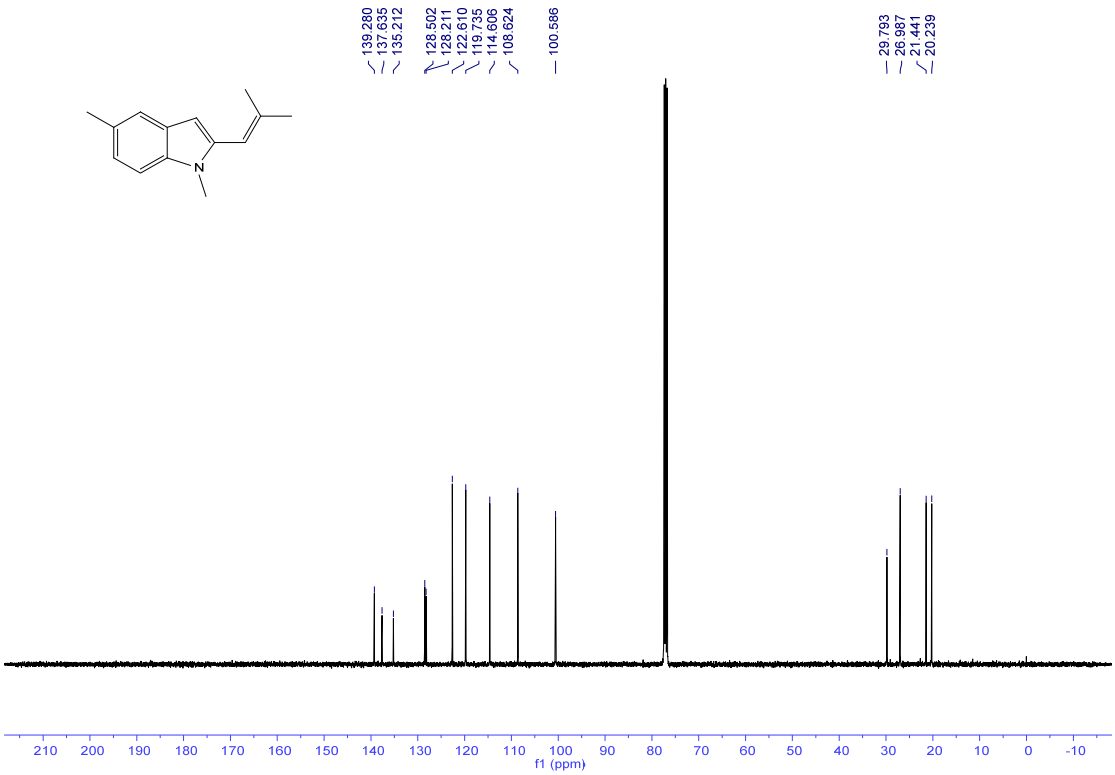
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1j**



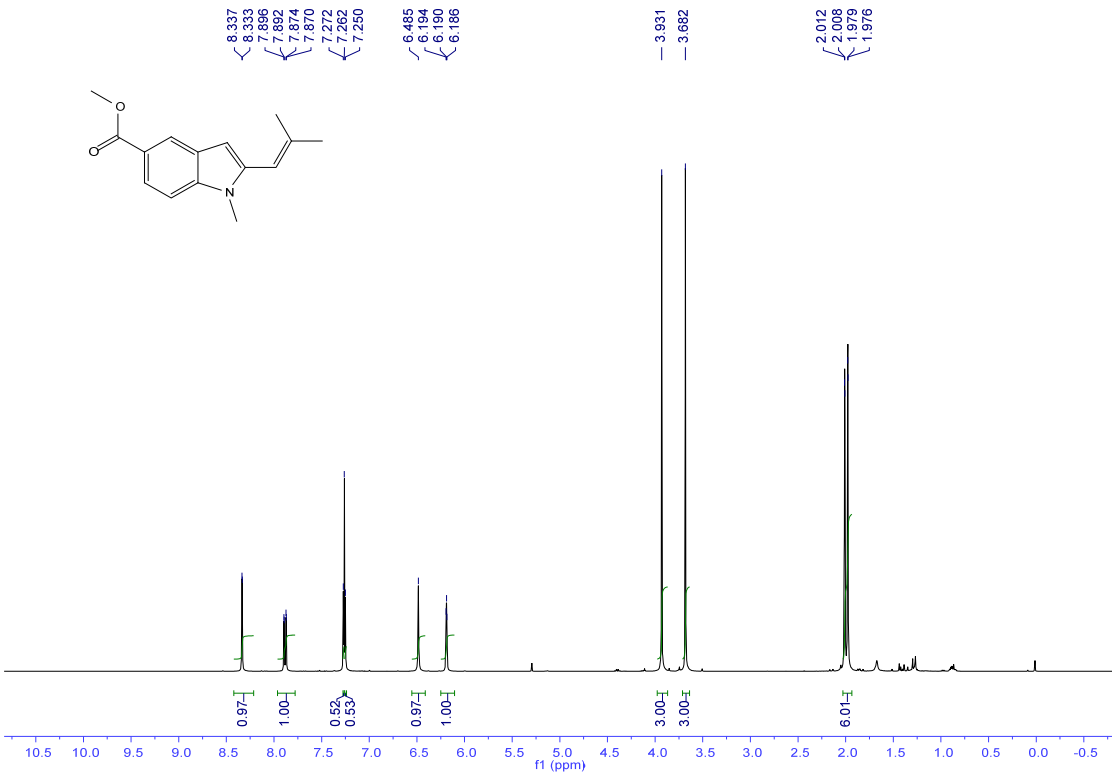
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of compound **1j**



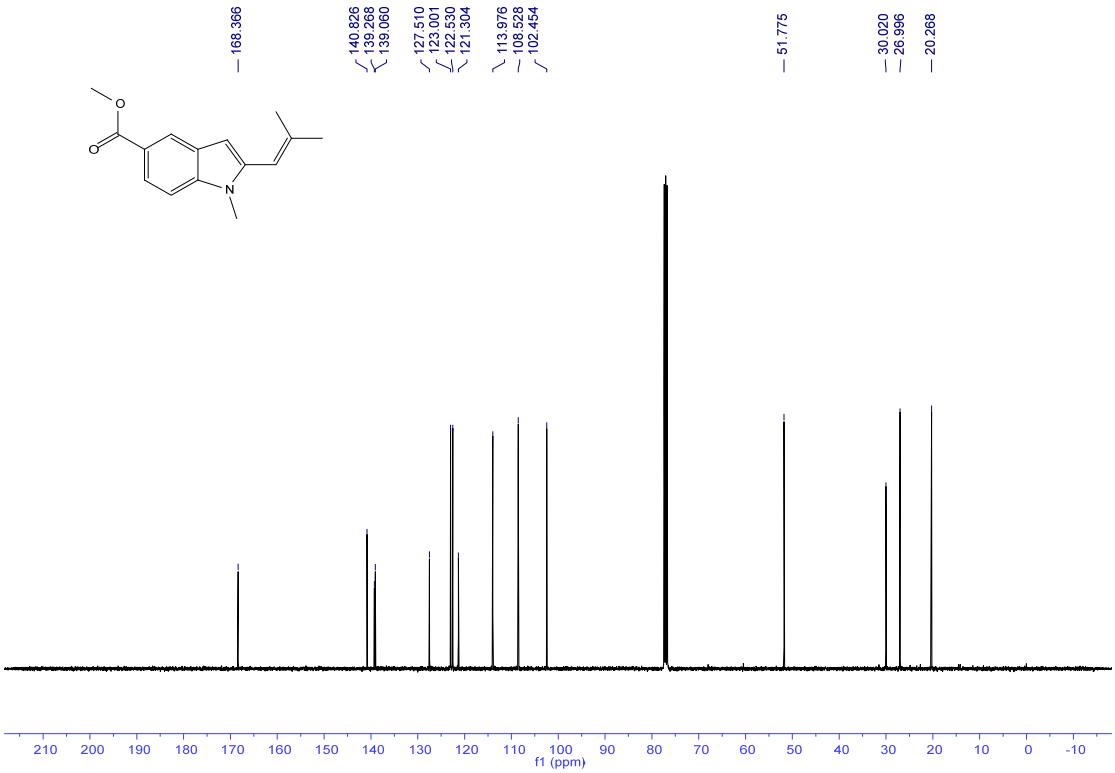
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1k**



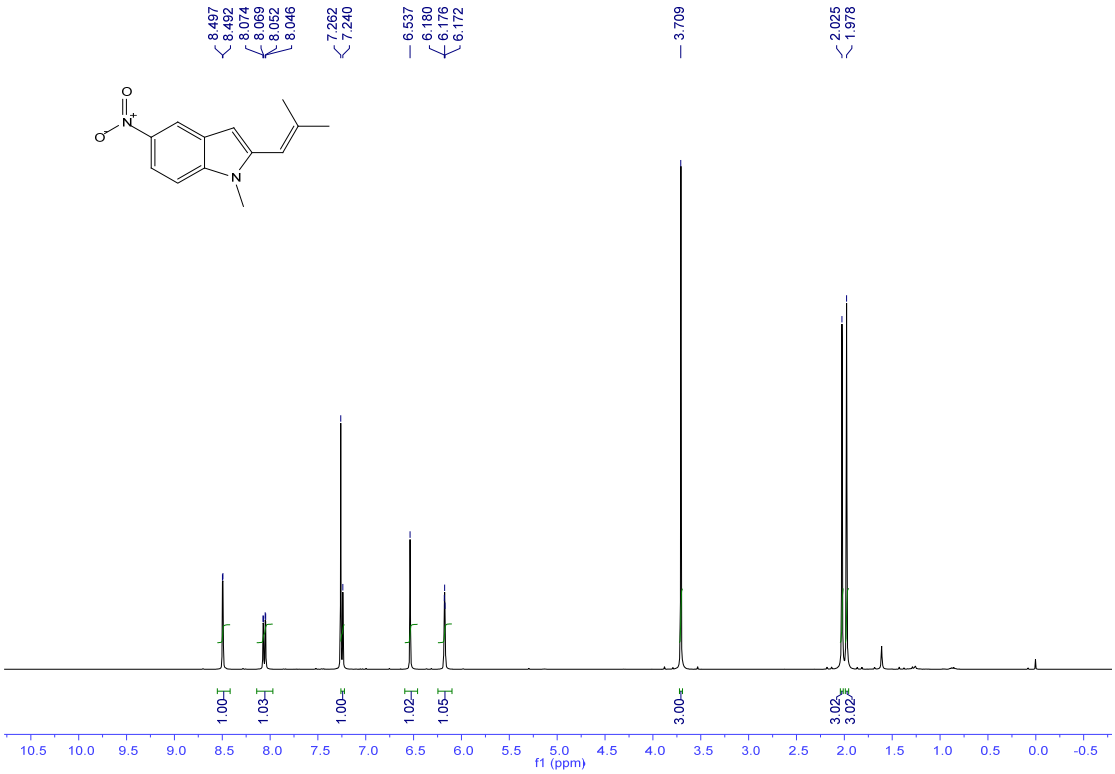
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of compound **1k**



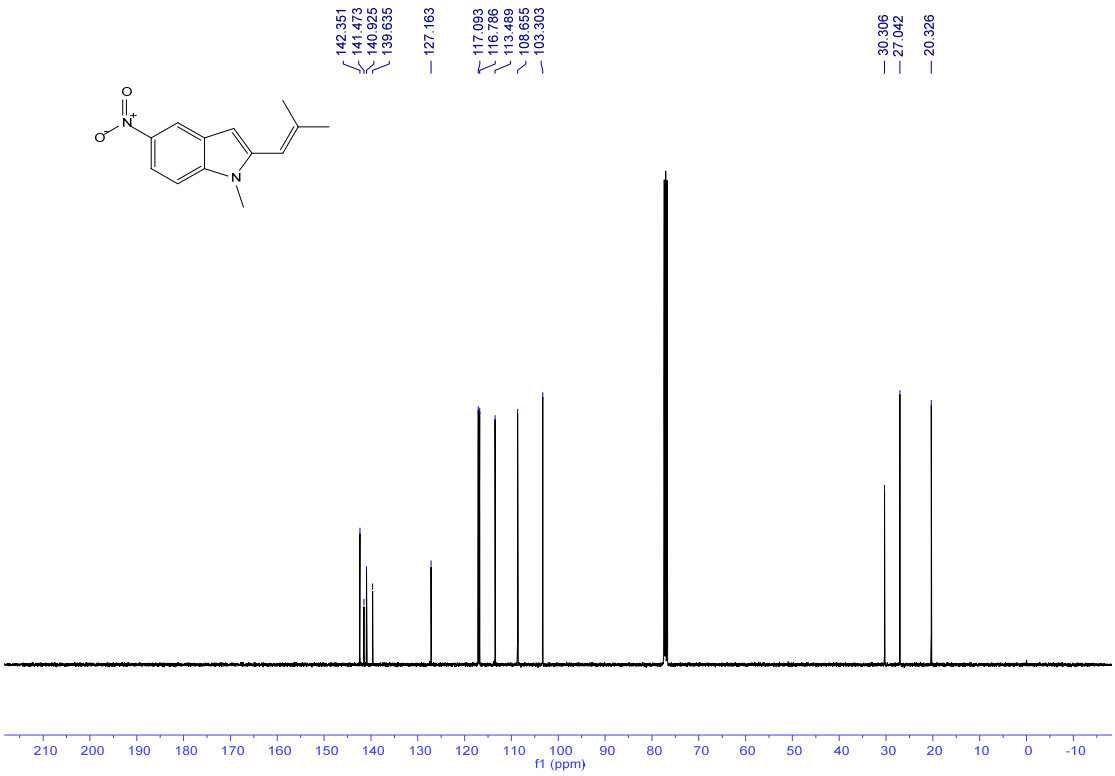
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1l**



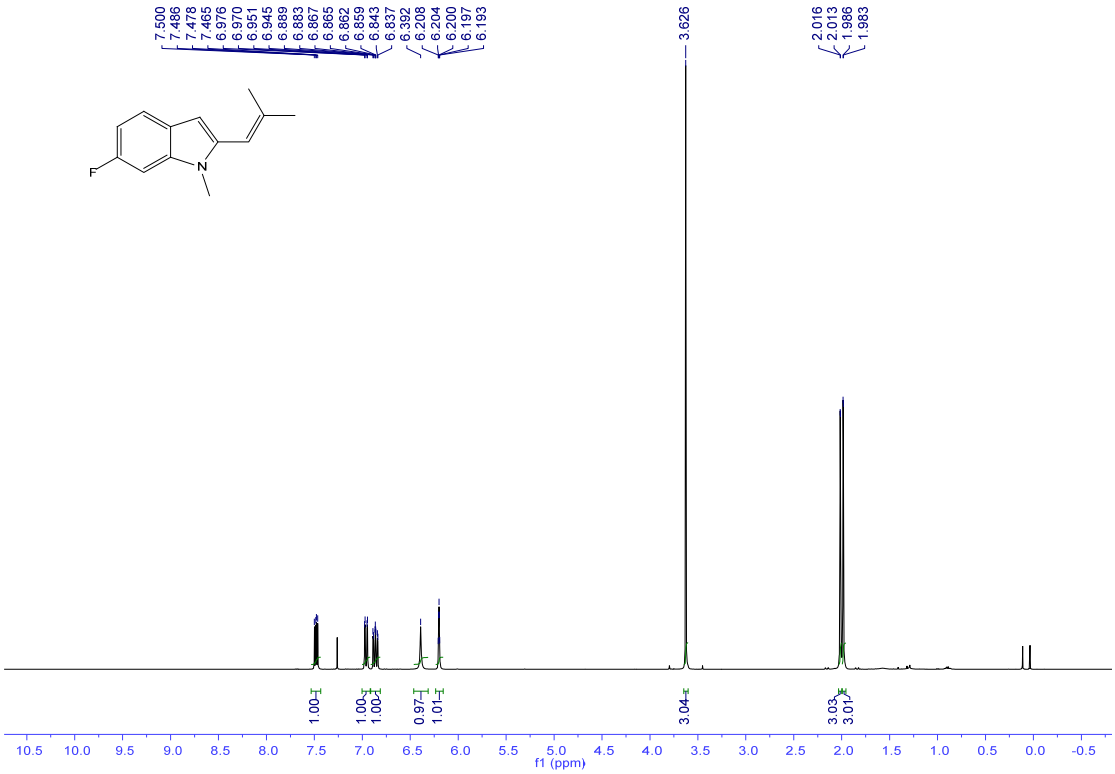
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of compound **1l**



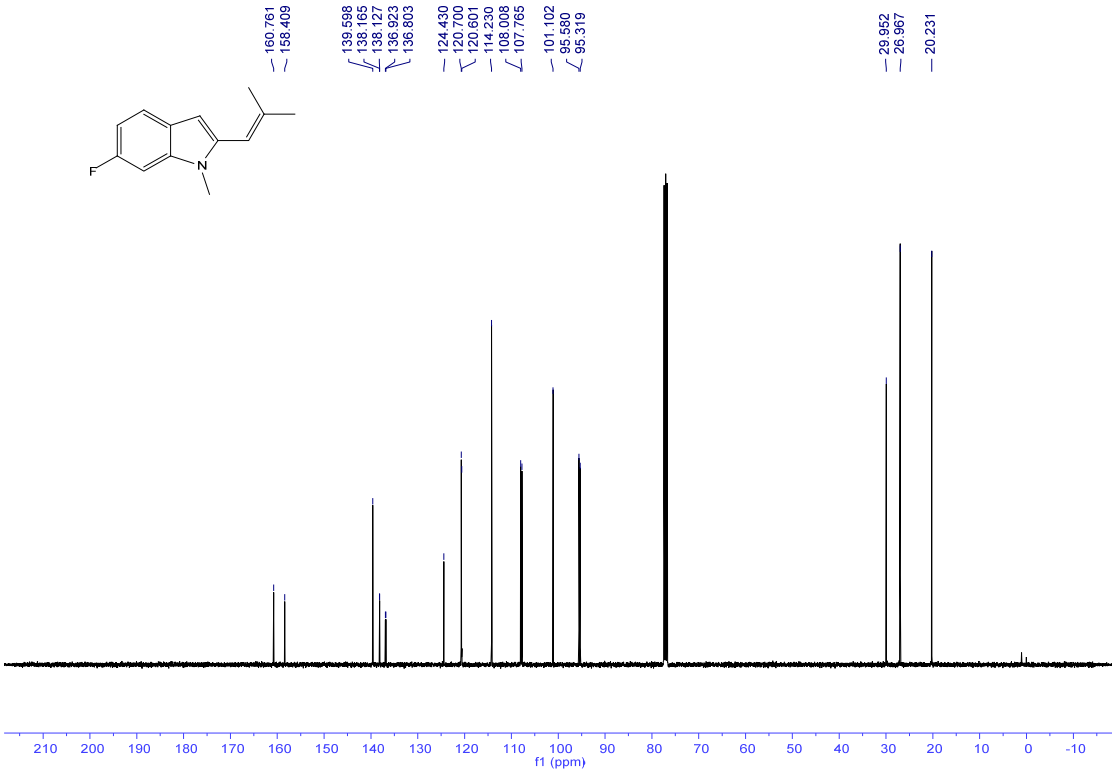
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1m**



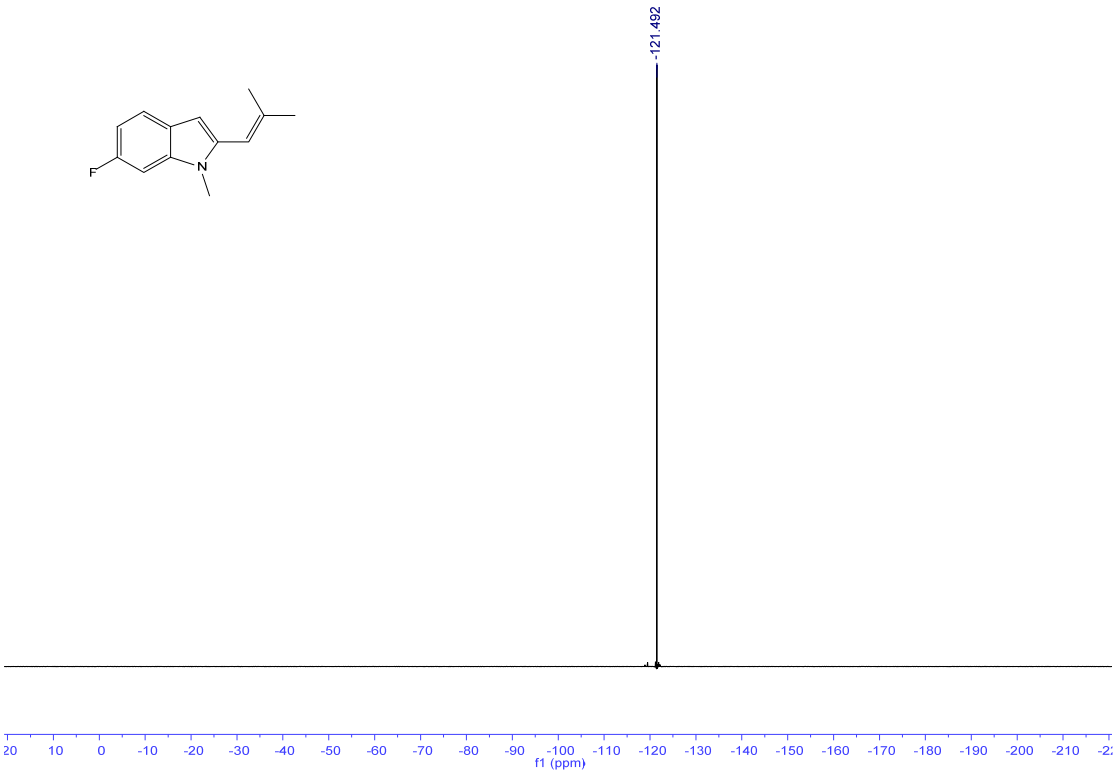
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of compound **1m**



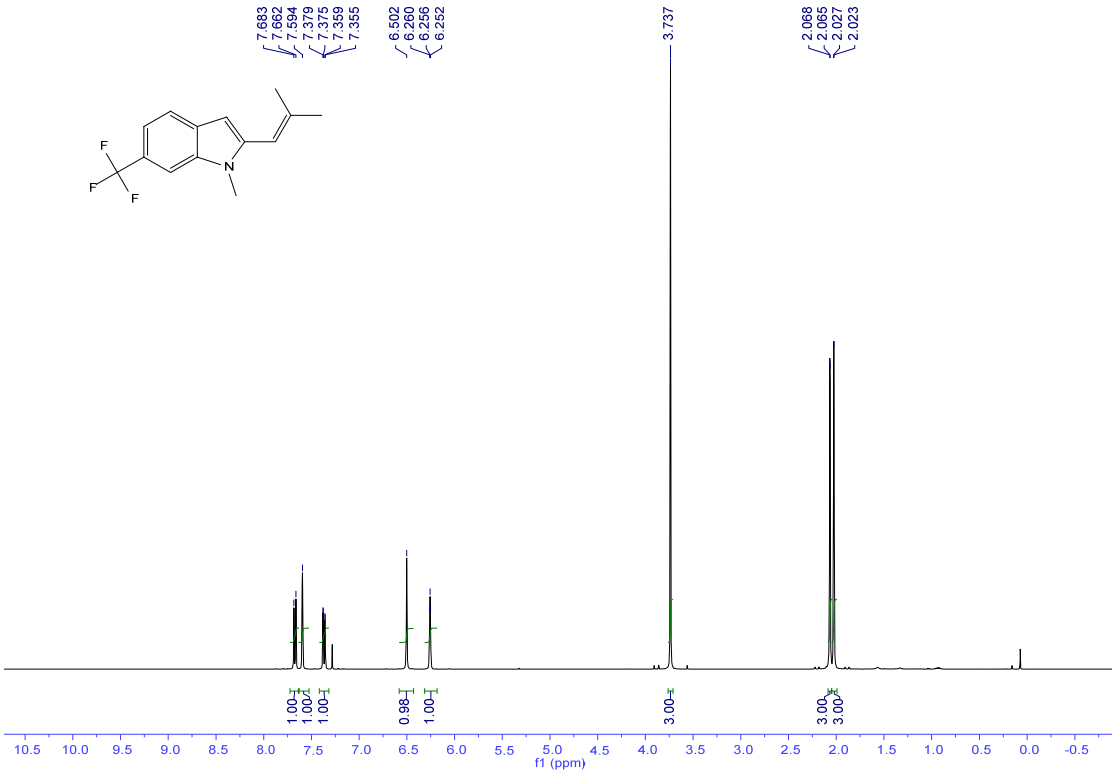
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1n**



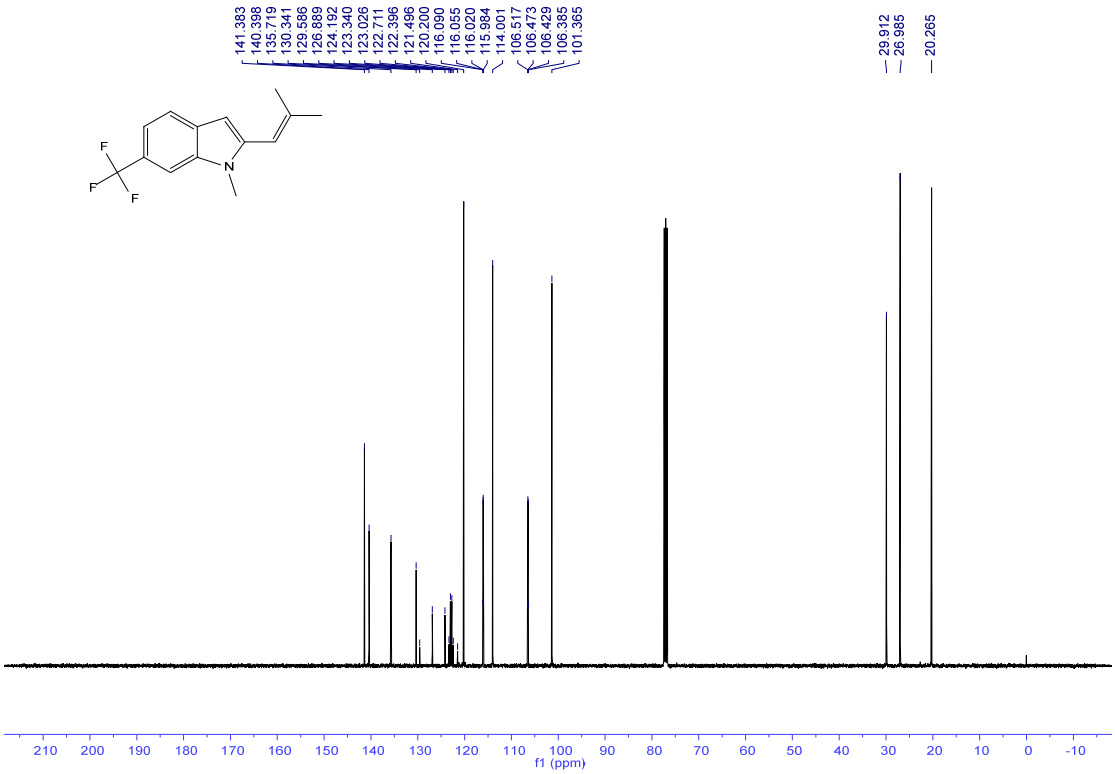
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of compound **1n**



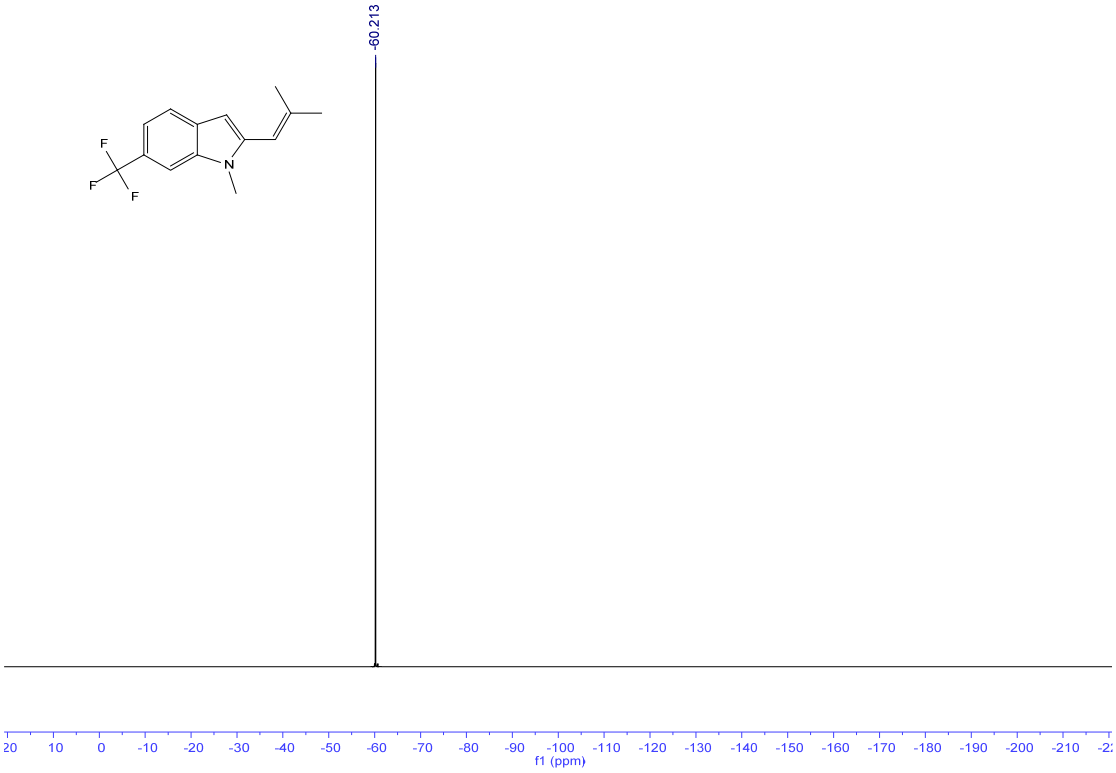
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **1n**



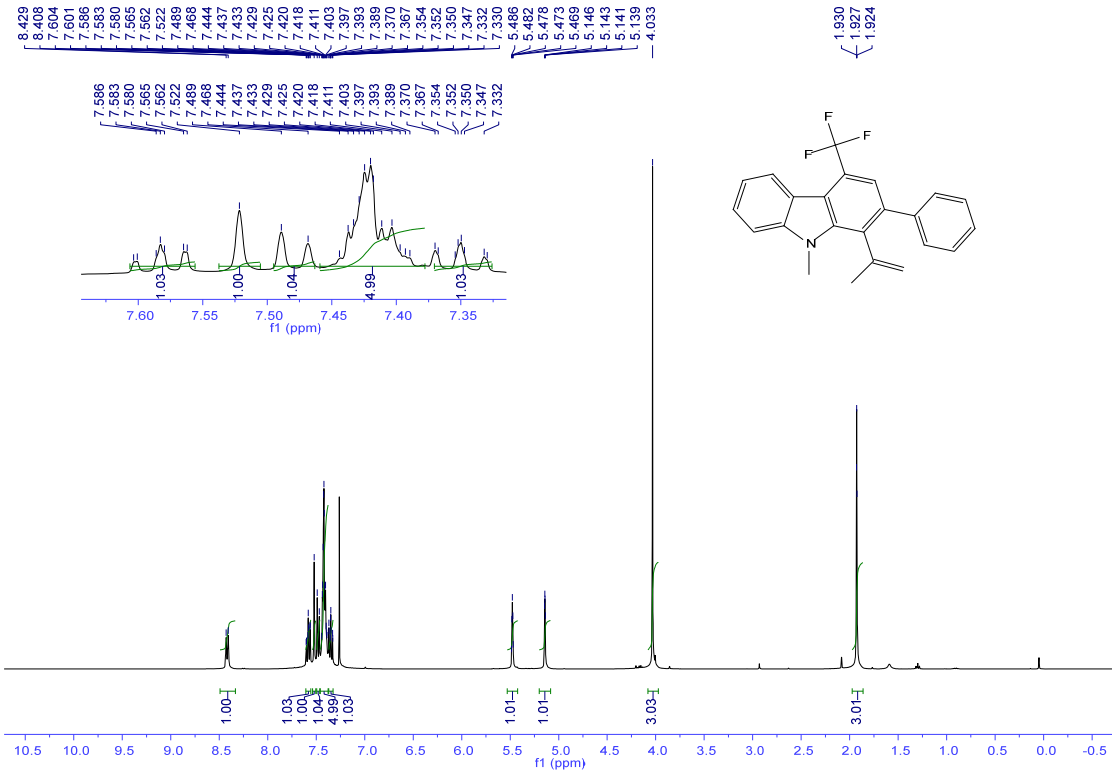
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1o**



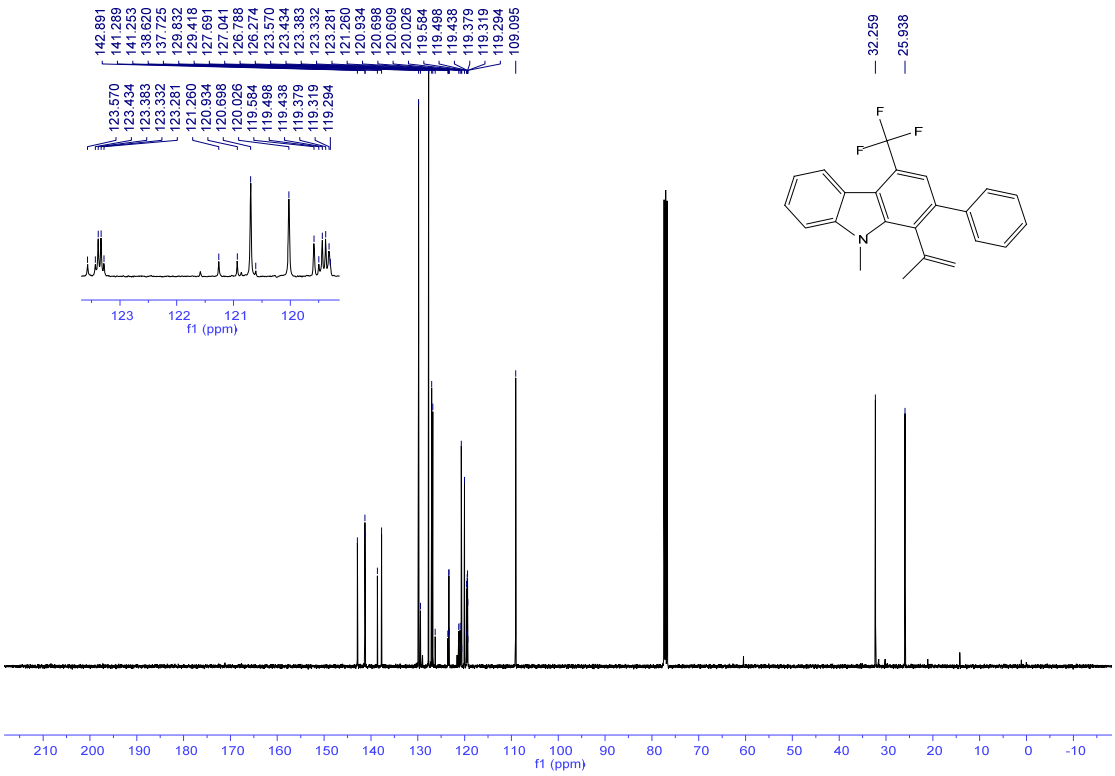
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **1o**



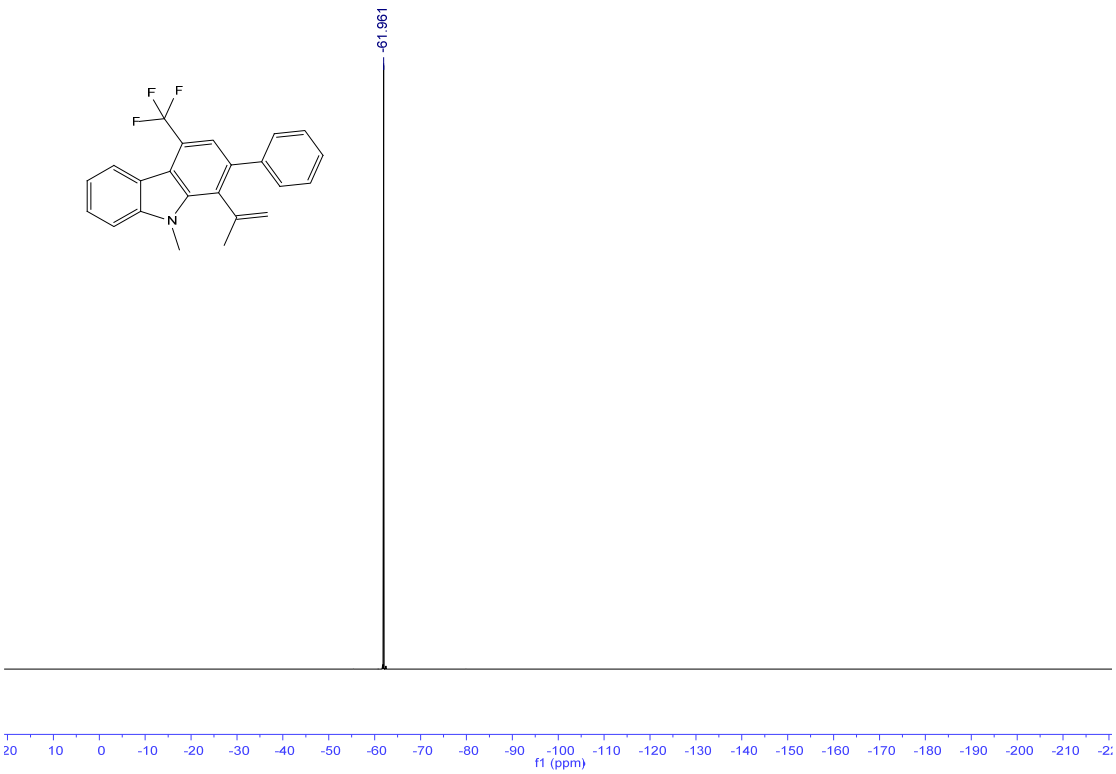
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **1o**



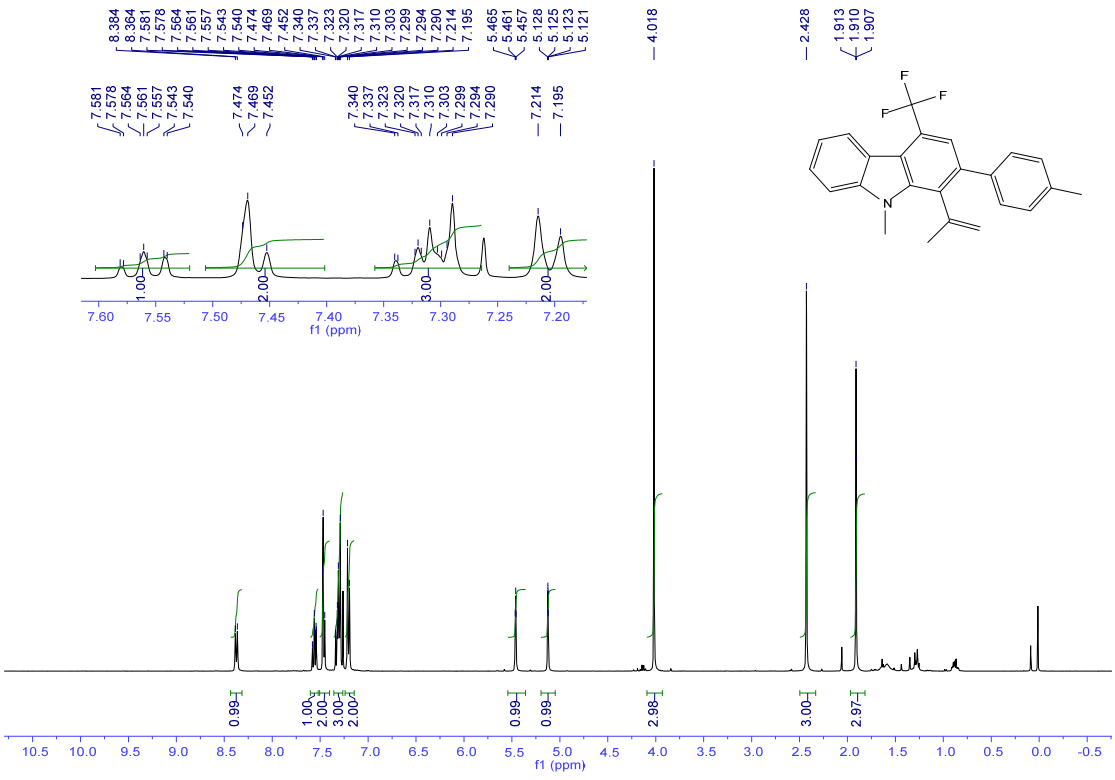
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3a**



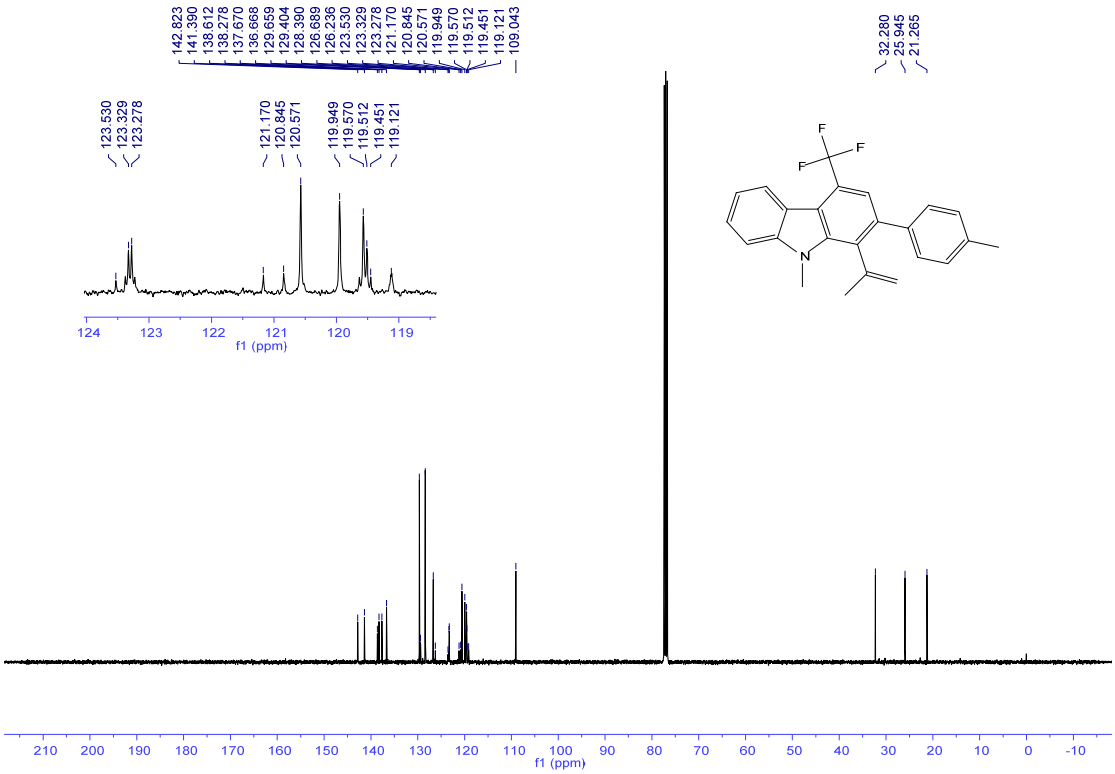
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3a**



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

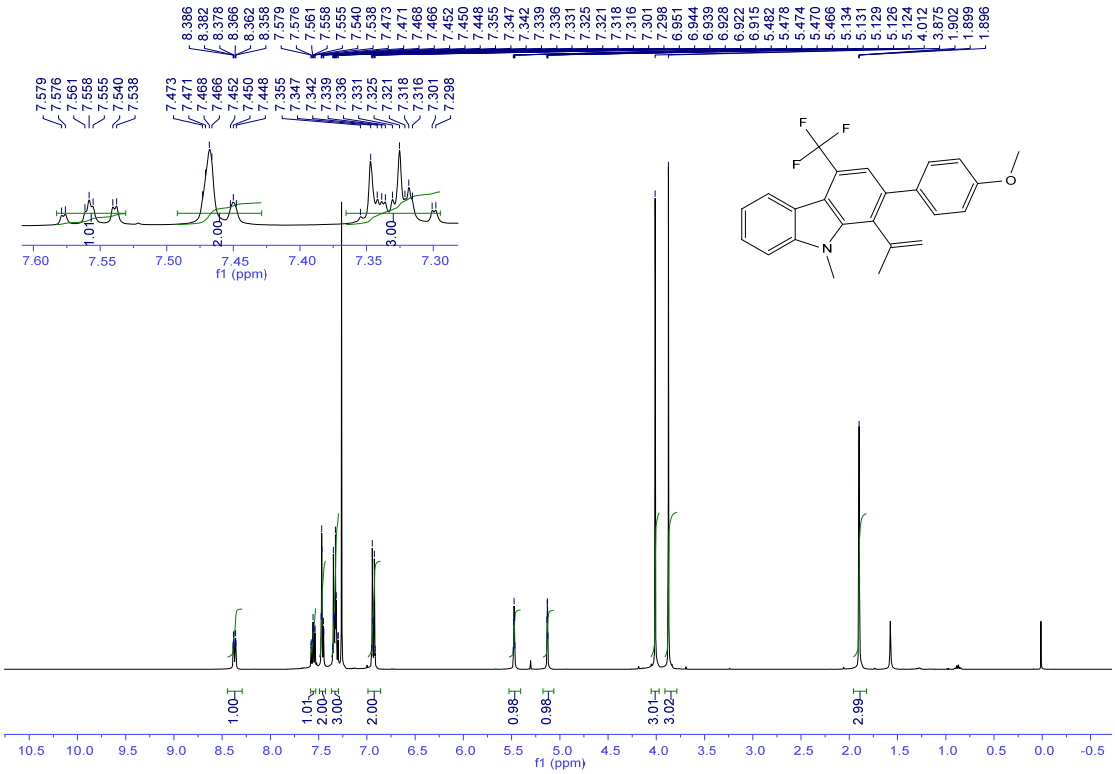


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3b**

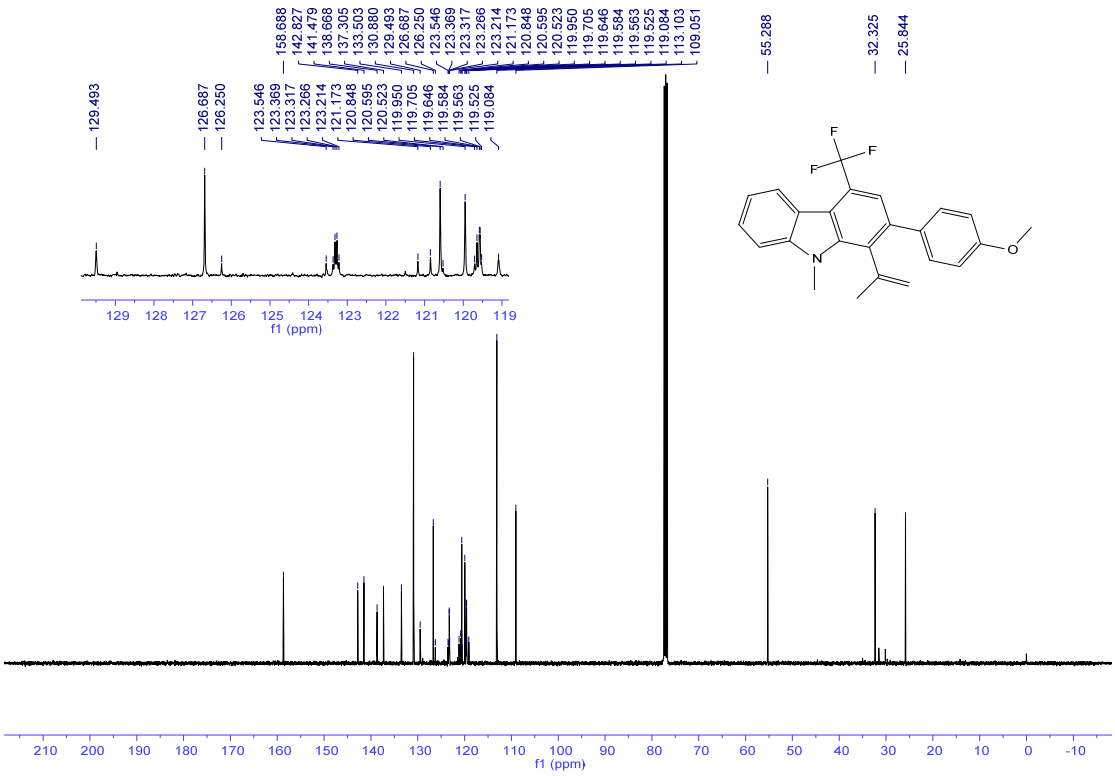


$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3b**

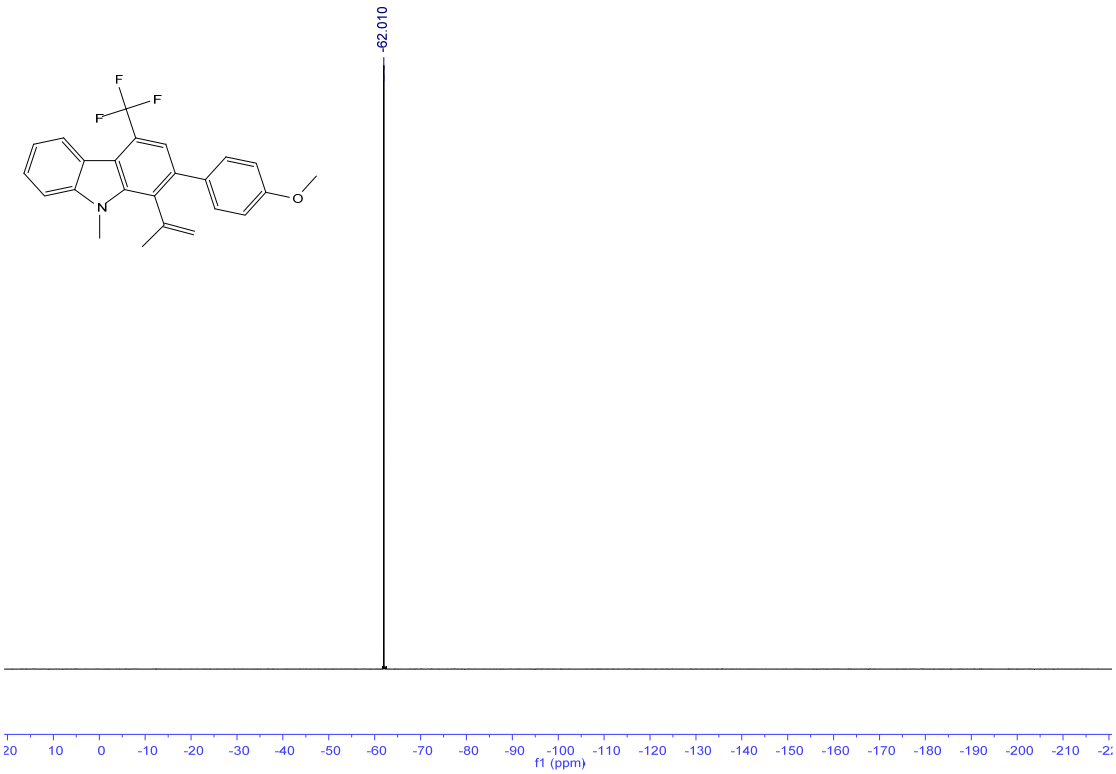
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3b**



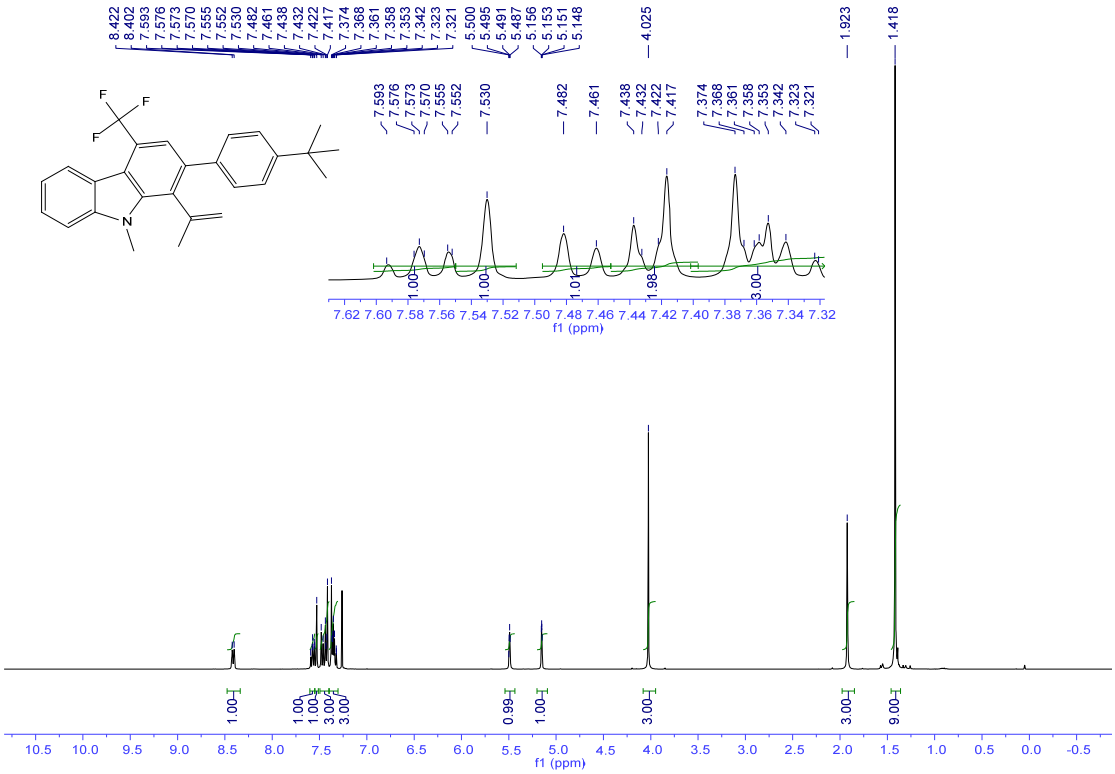
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3c**



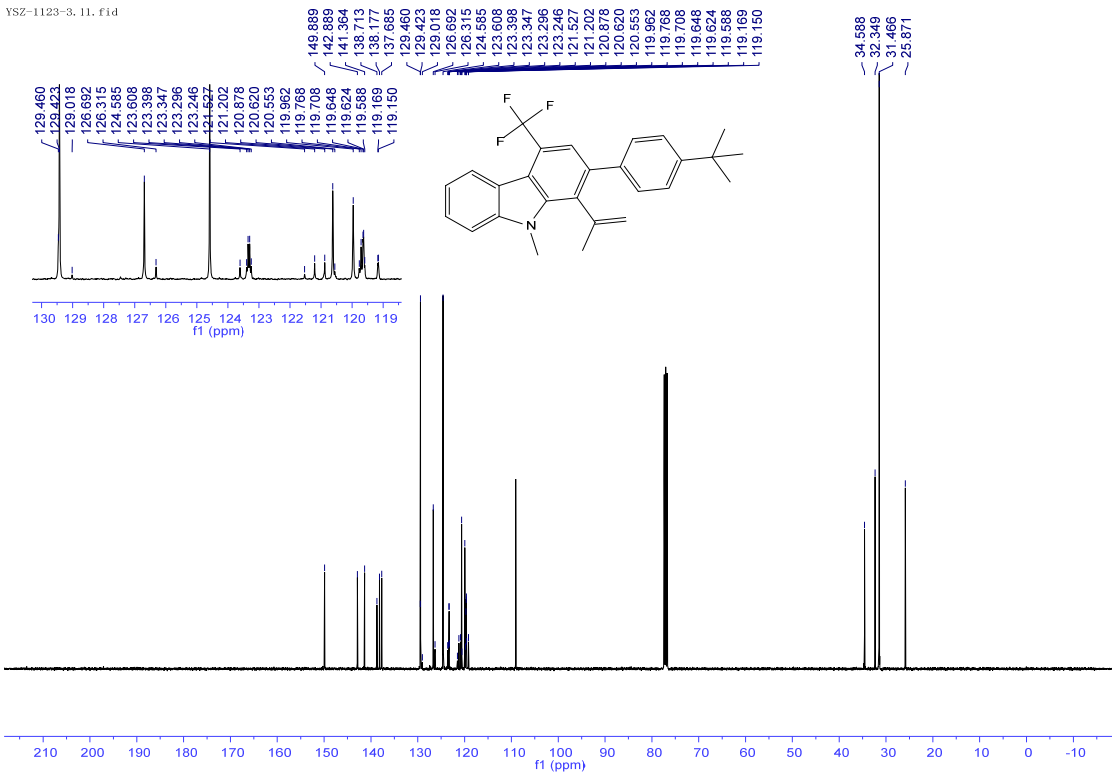
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3c**



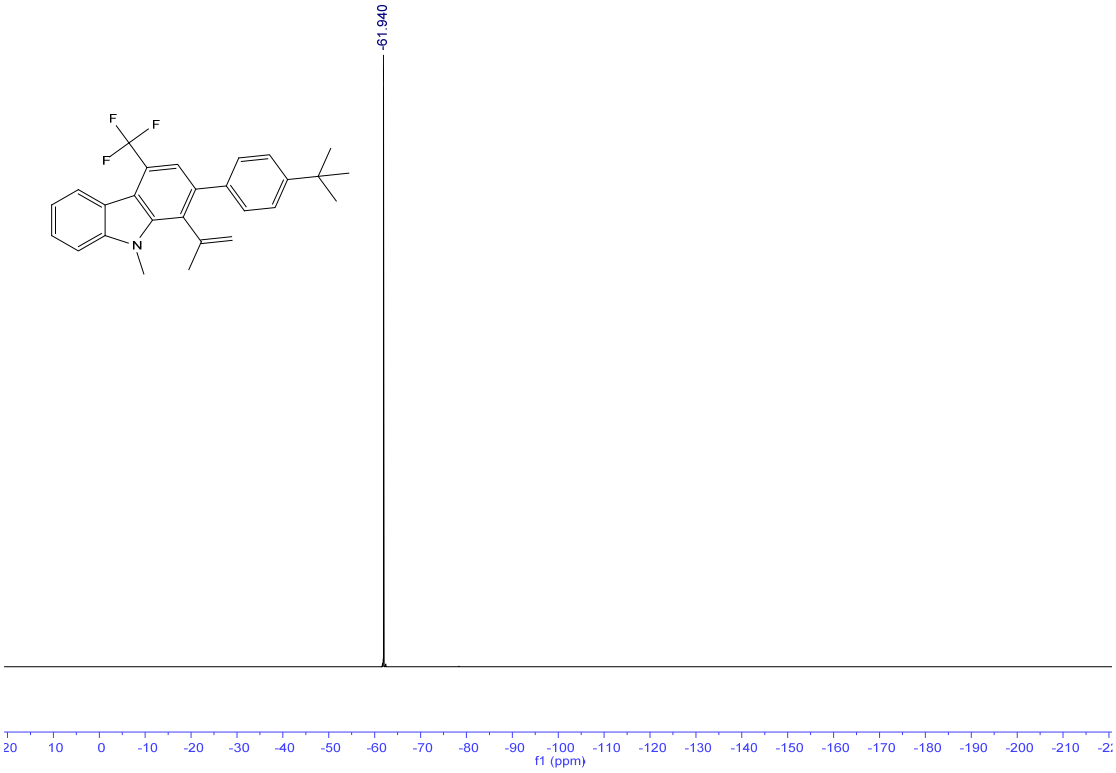
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3c**



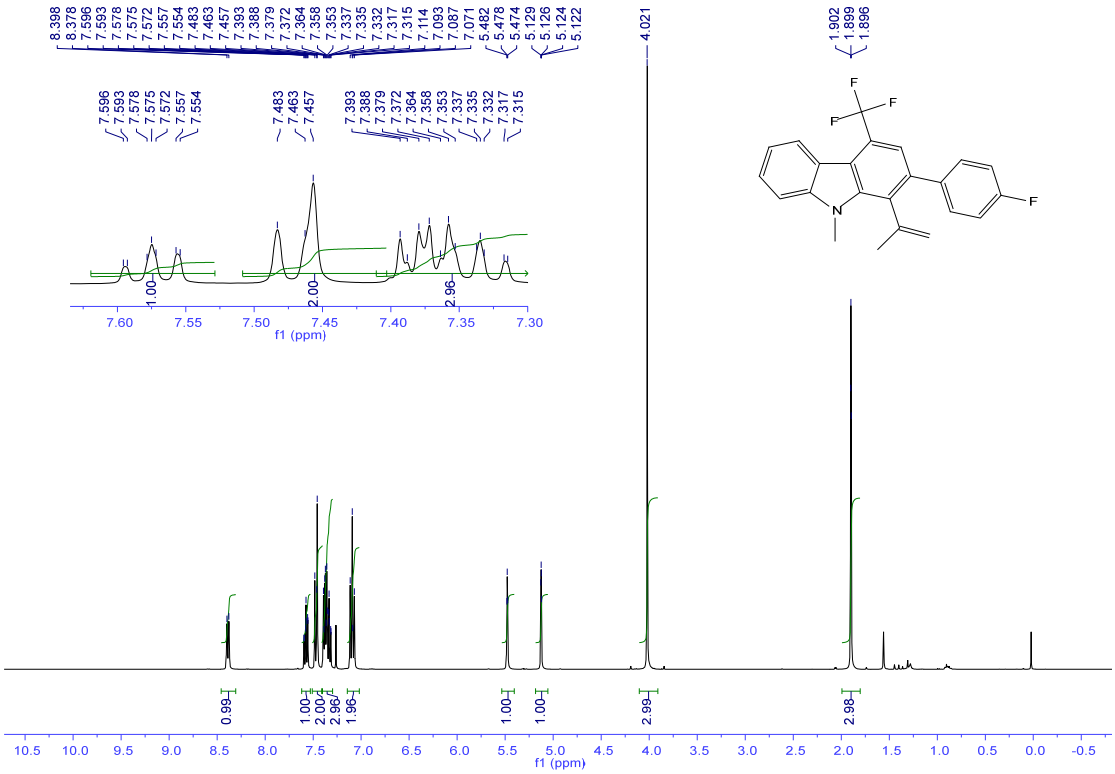
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3d**



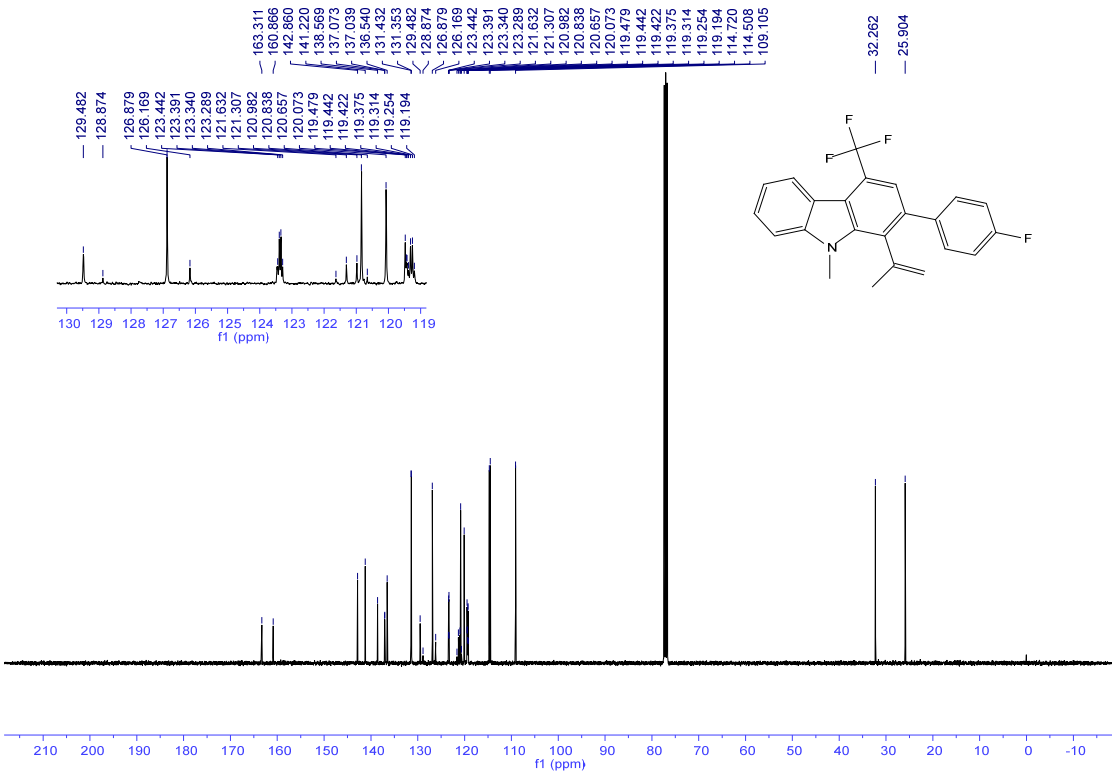
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3d**



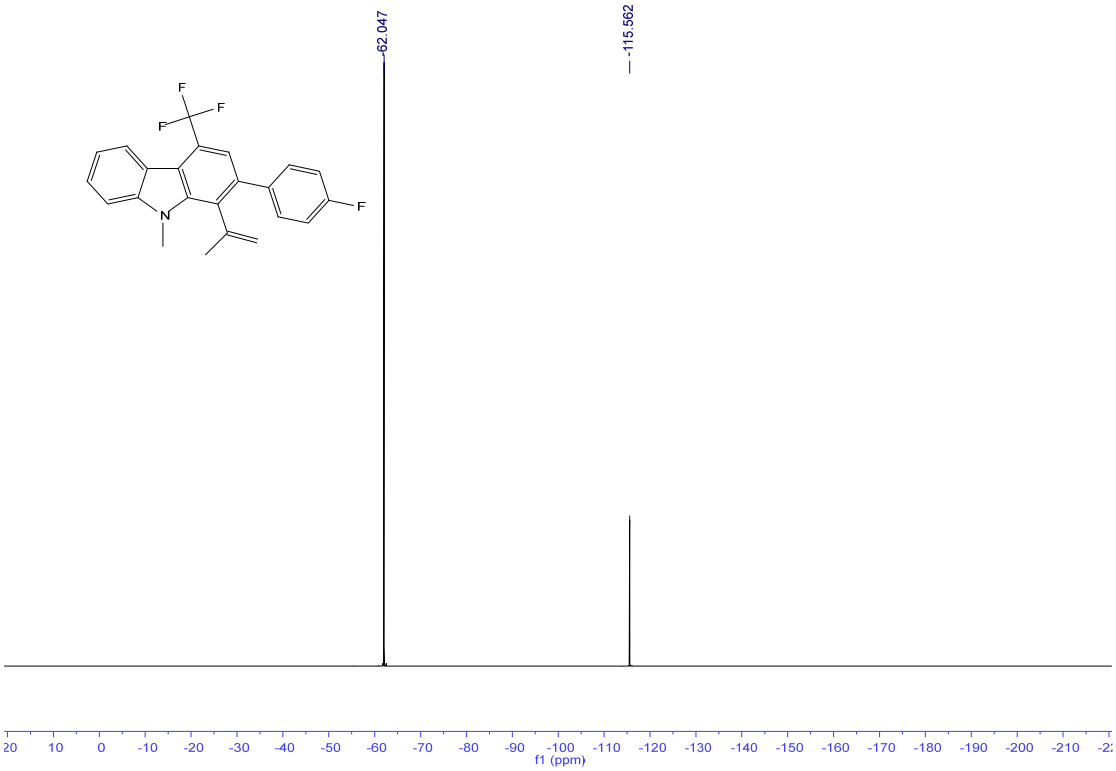
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3d**



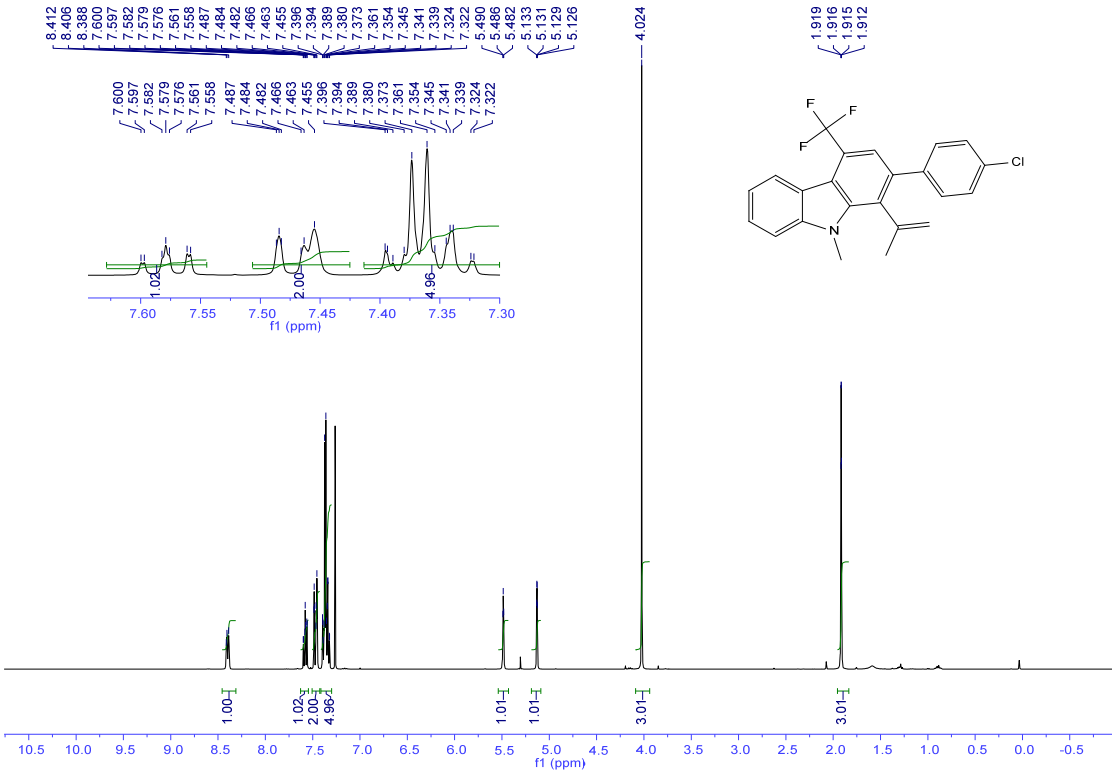
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3e**



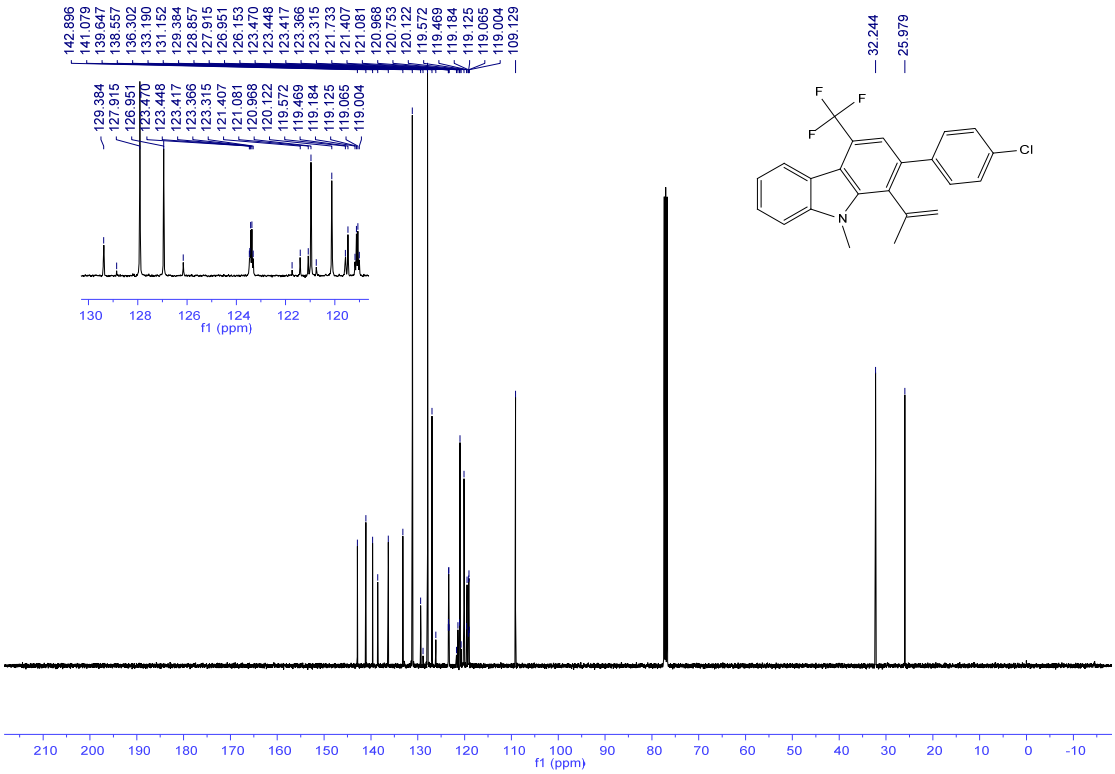
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3e**



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

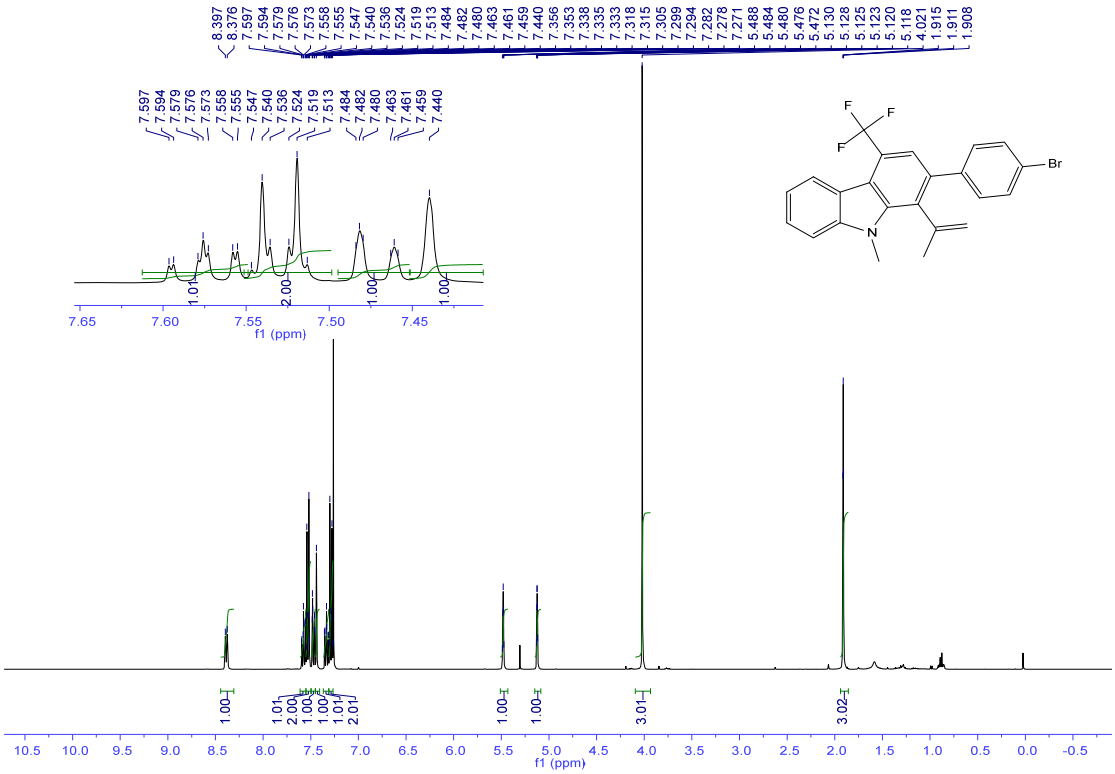


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3f**

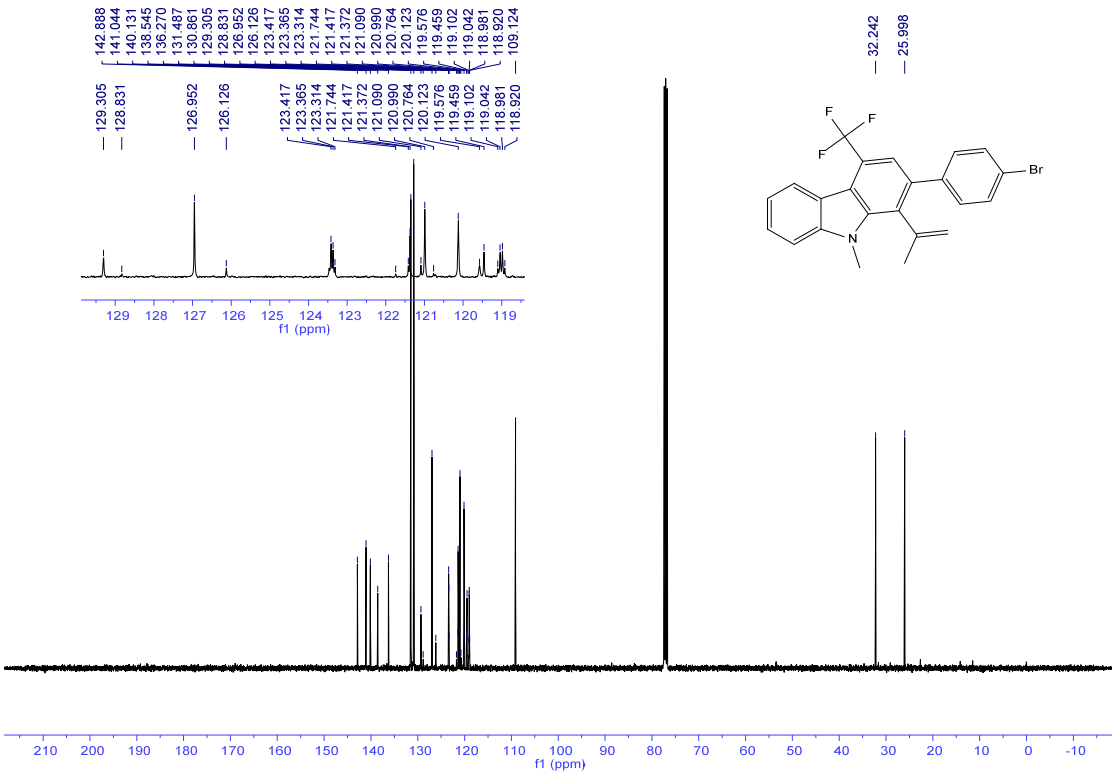


$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3f**

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

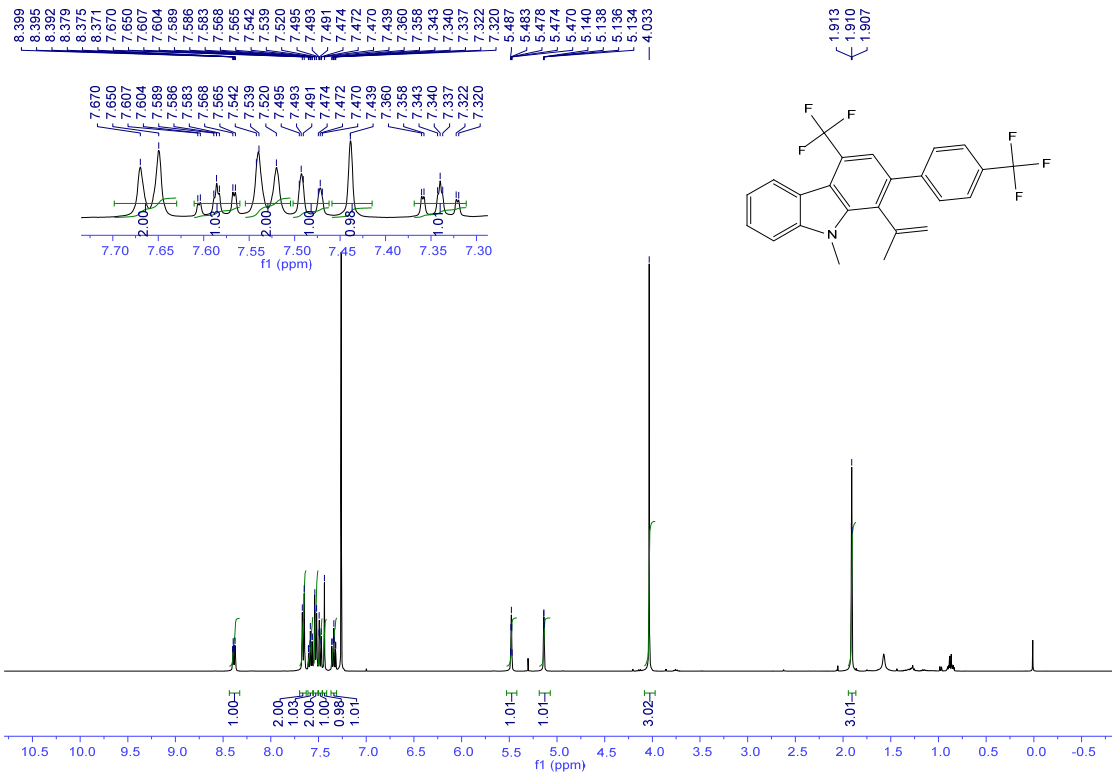


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3g**

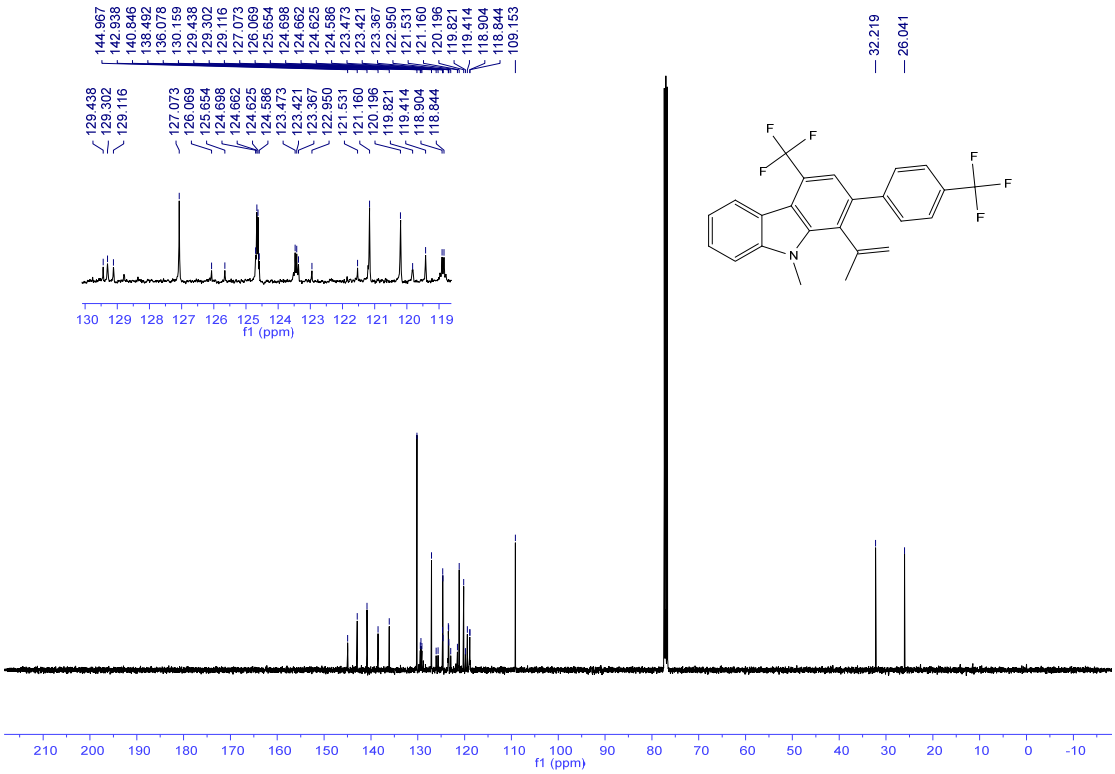


$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3g**

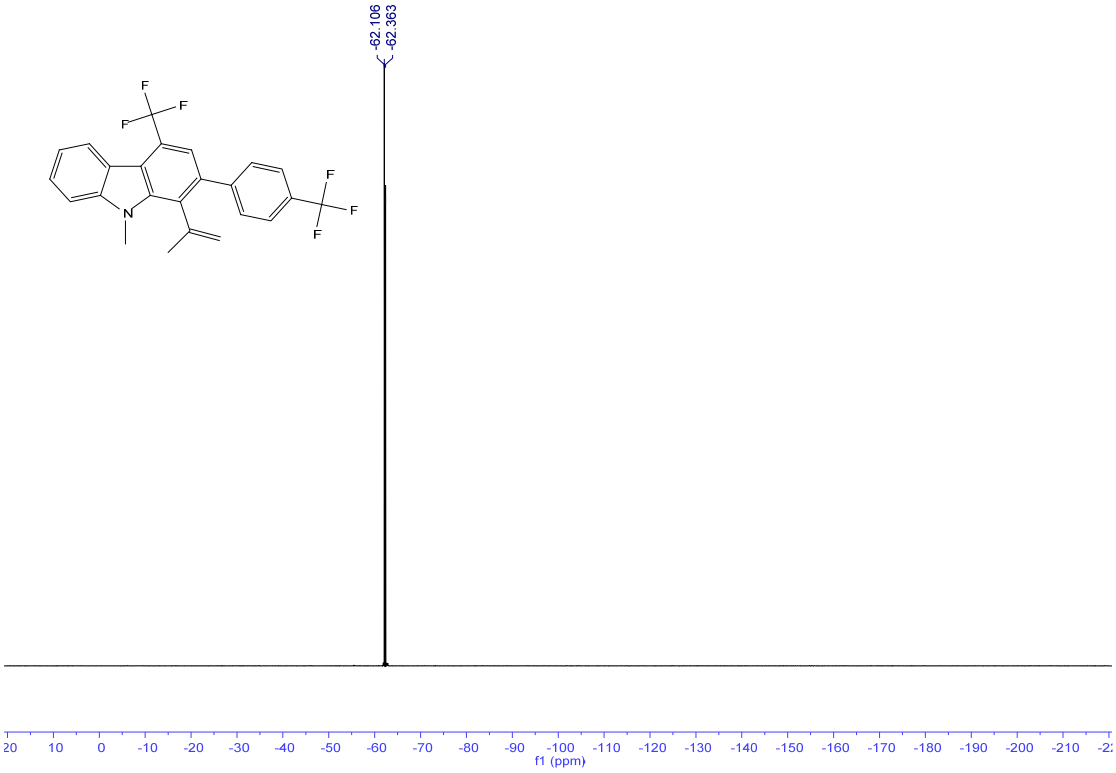
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3g**



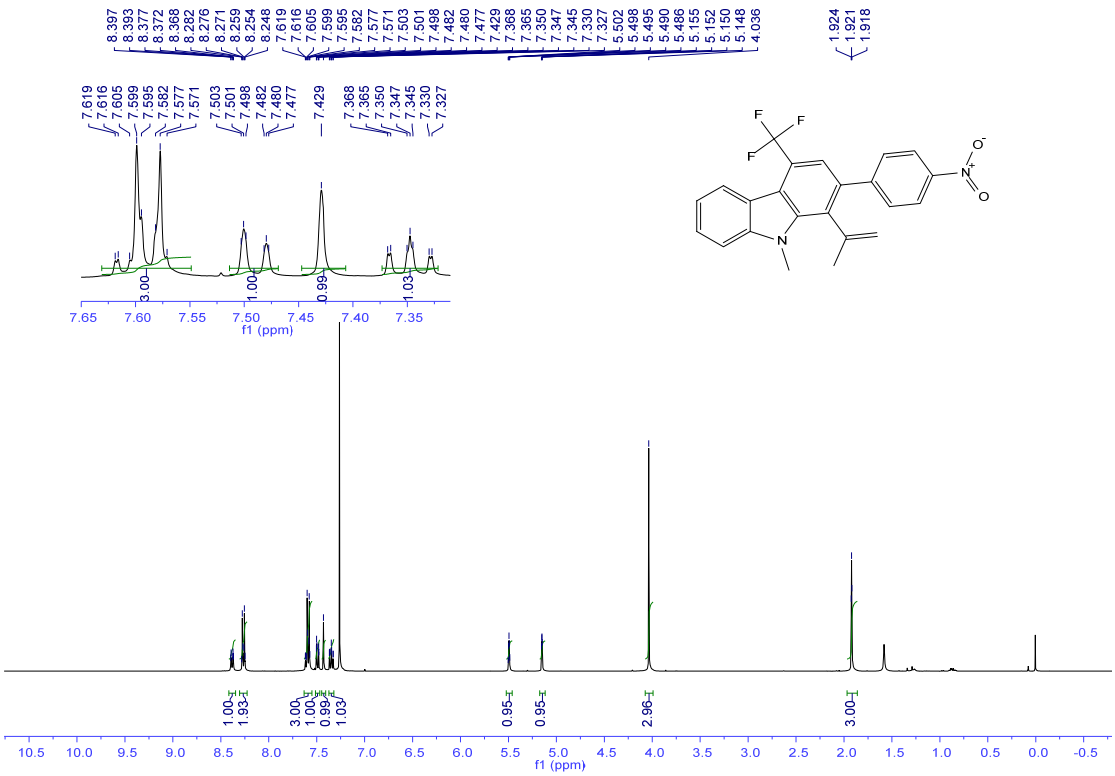
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3h**



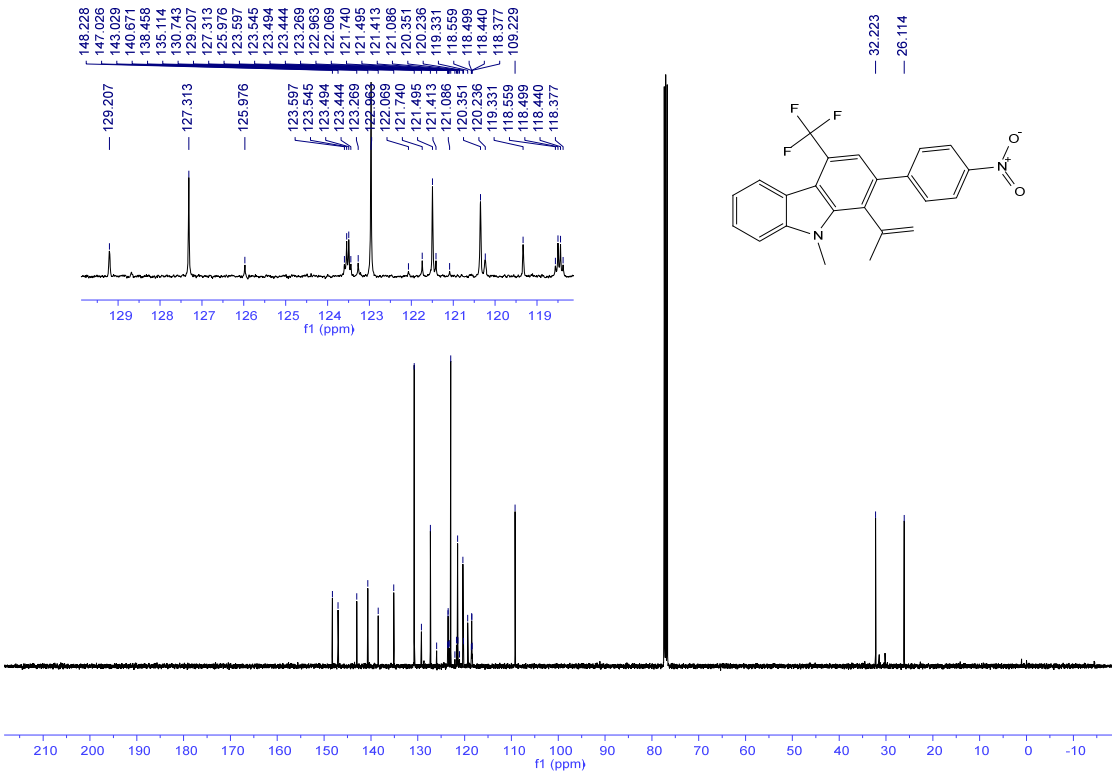
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3h**



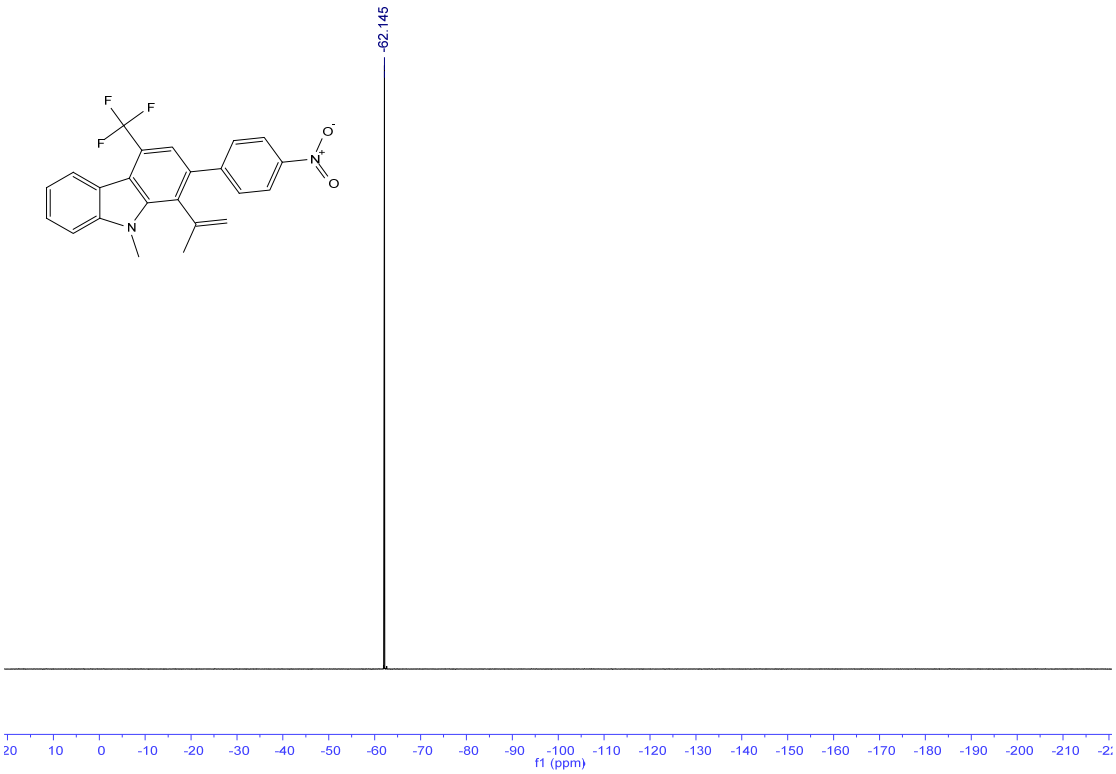
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3h**



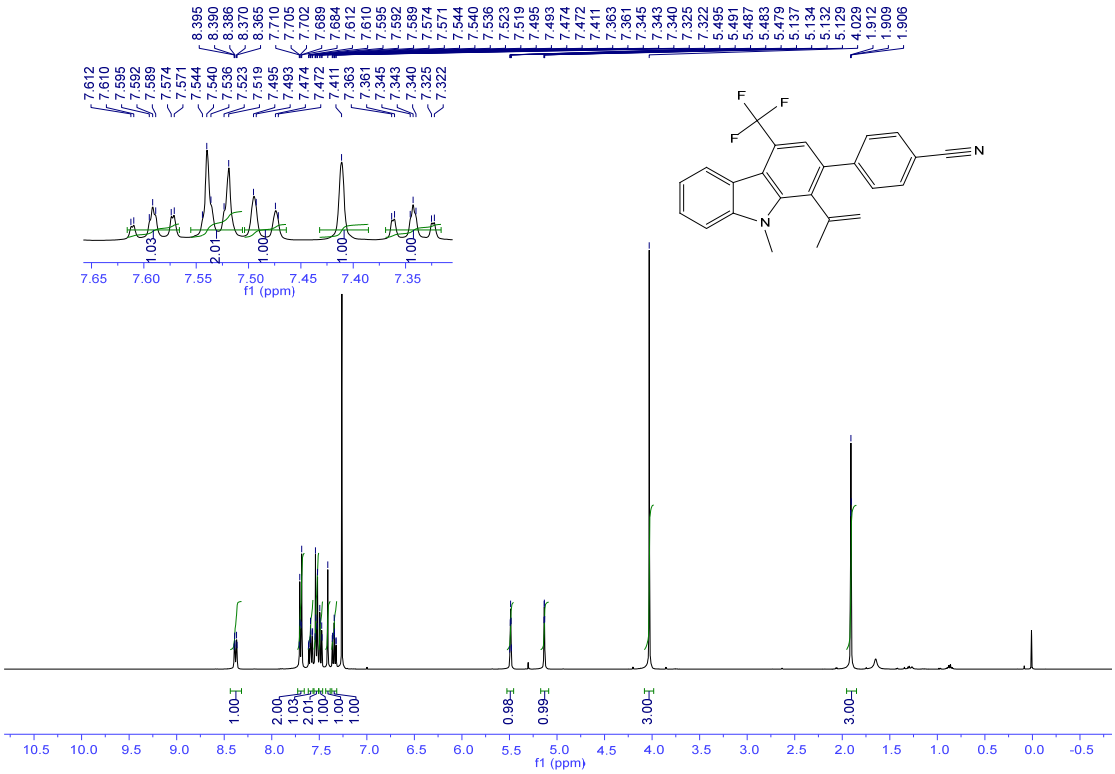
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3i**



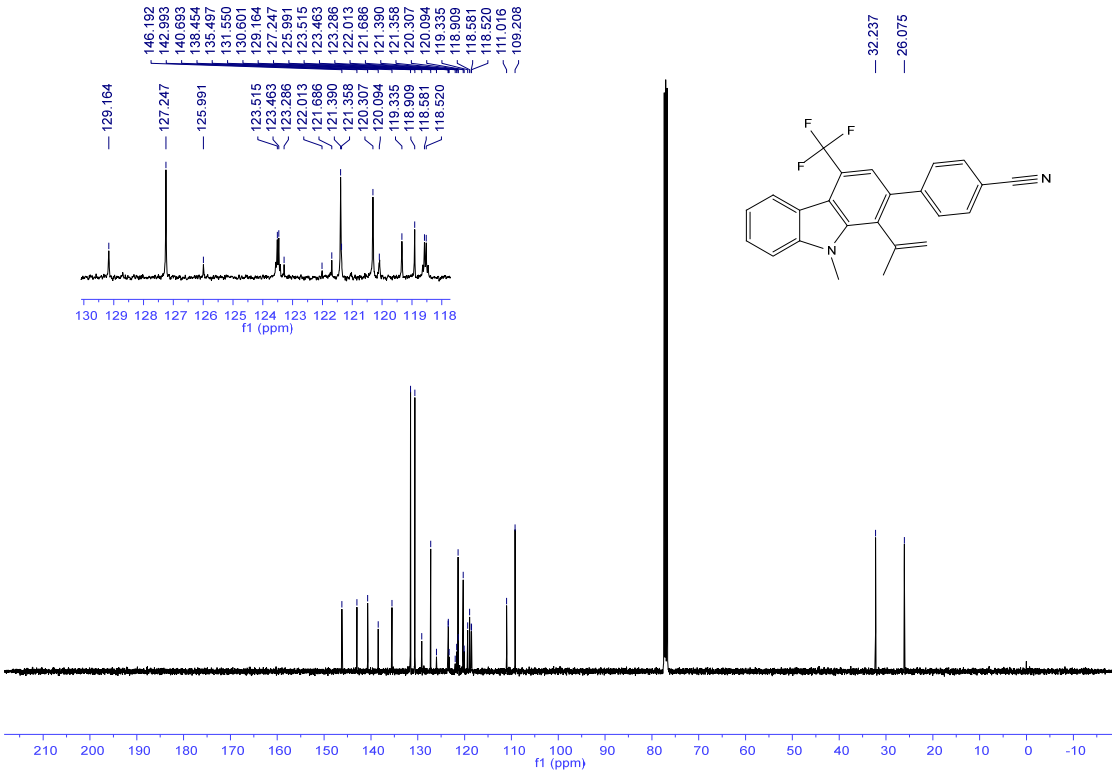
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3i**



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

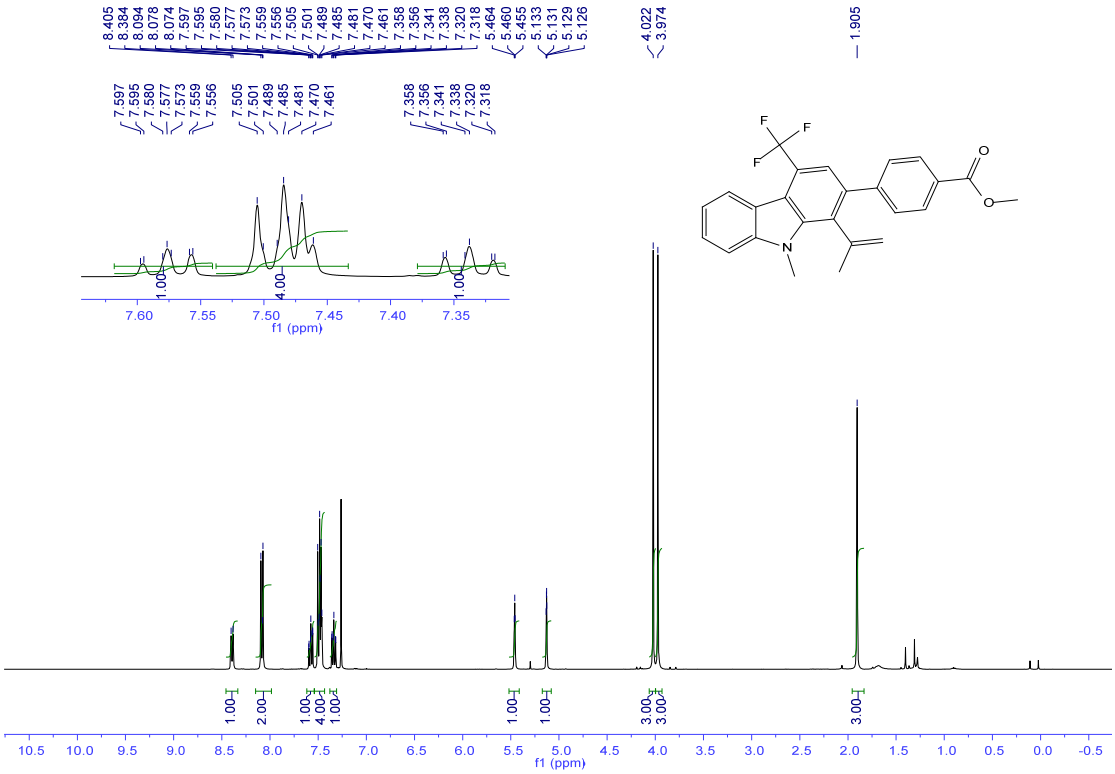


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3j**

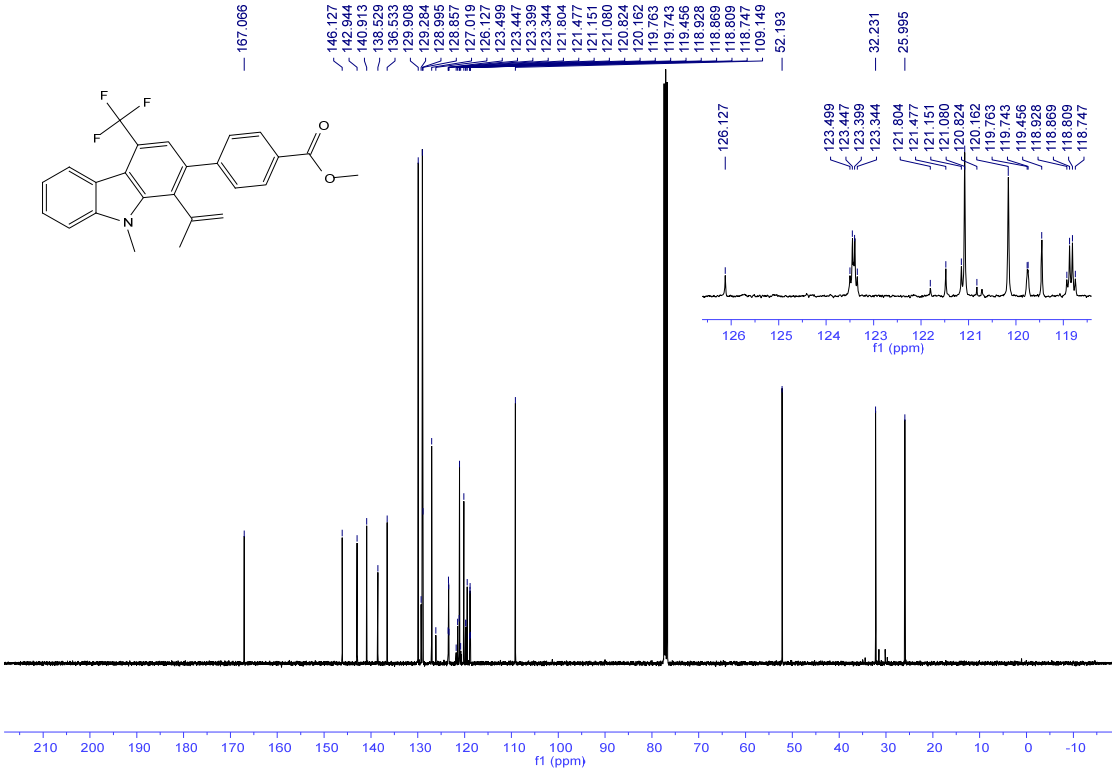


$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3j**

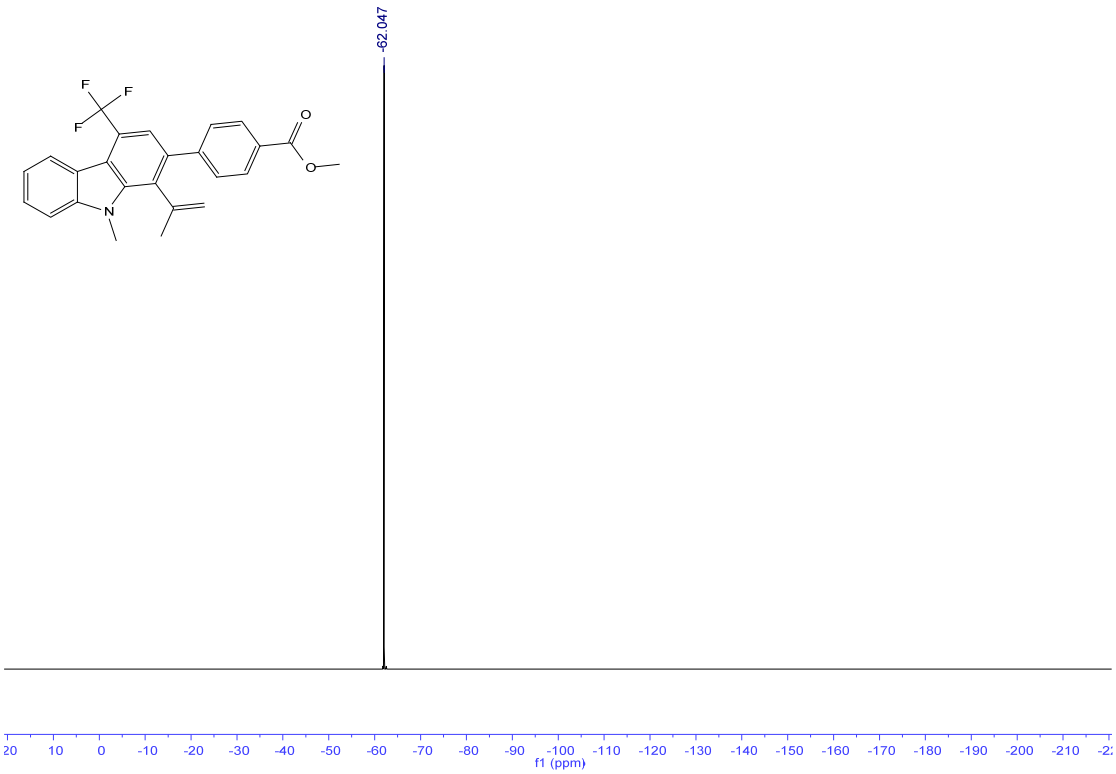
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3j**



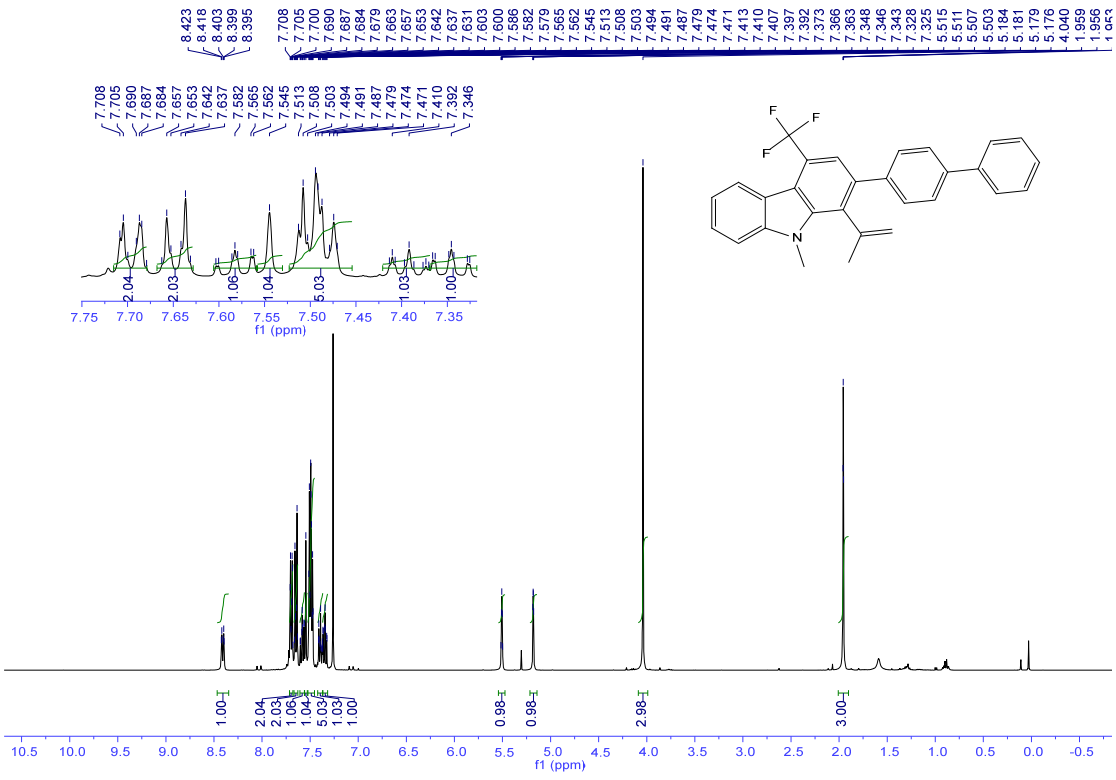
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3k**



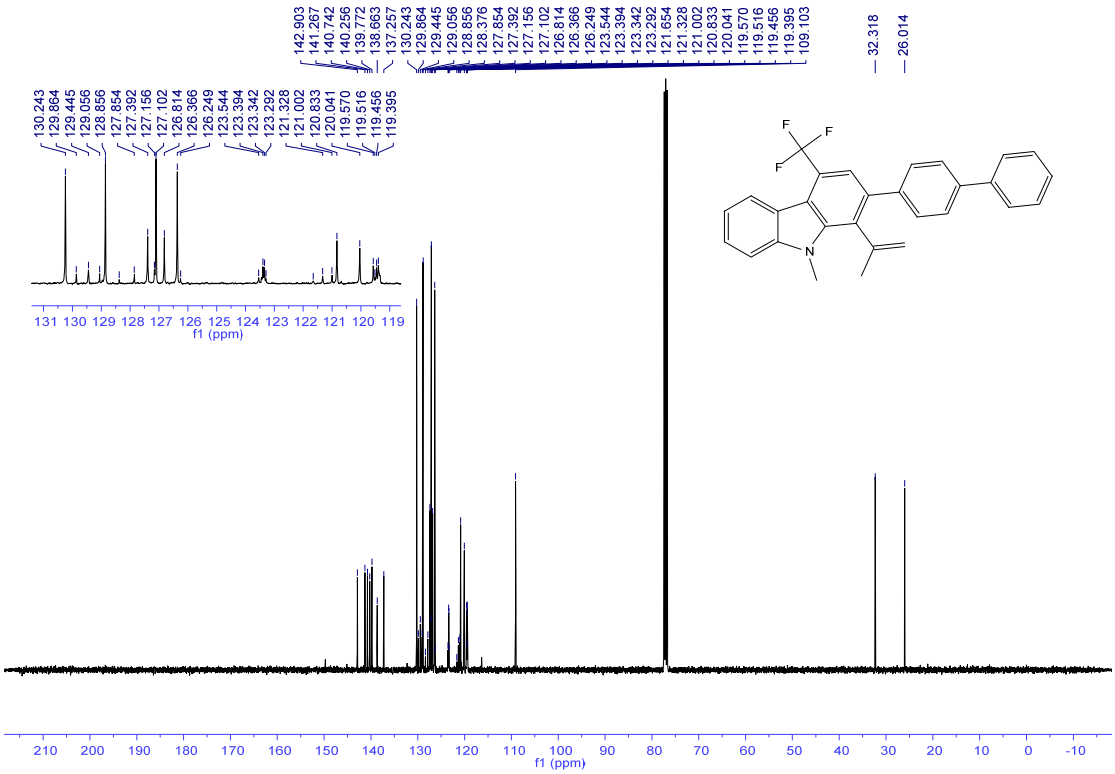
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3k**



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

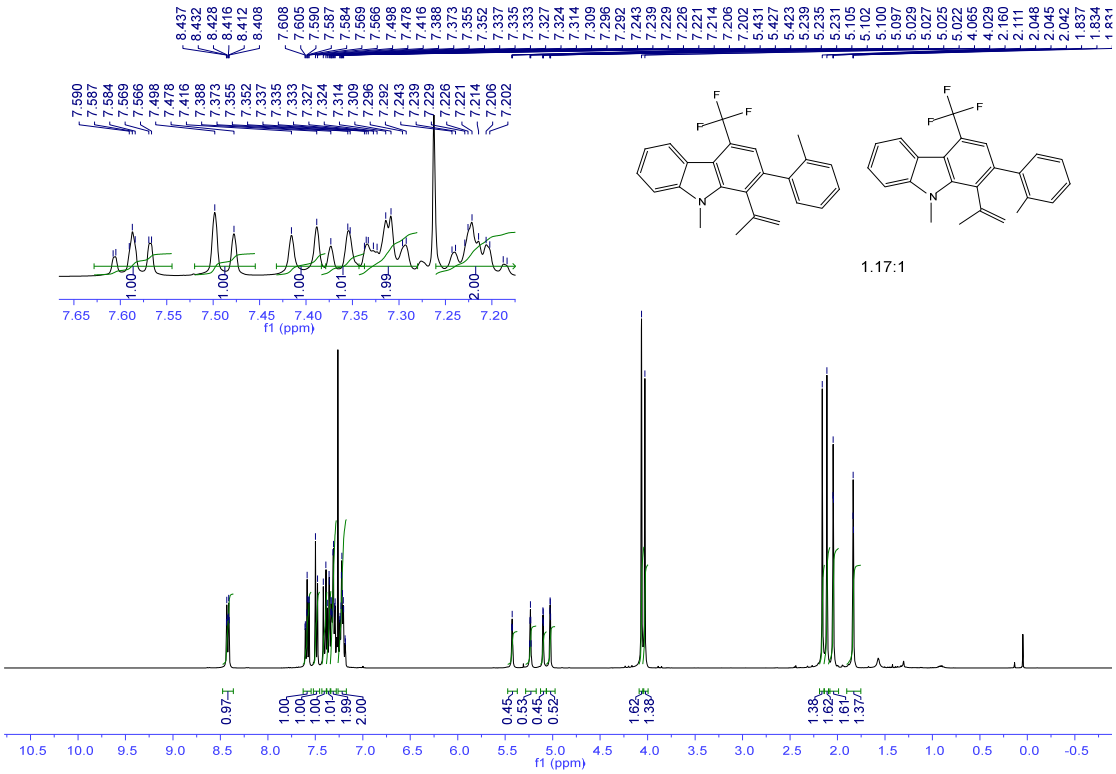


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3l**

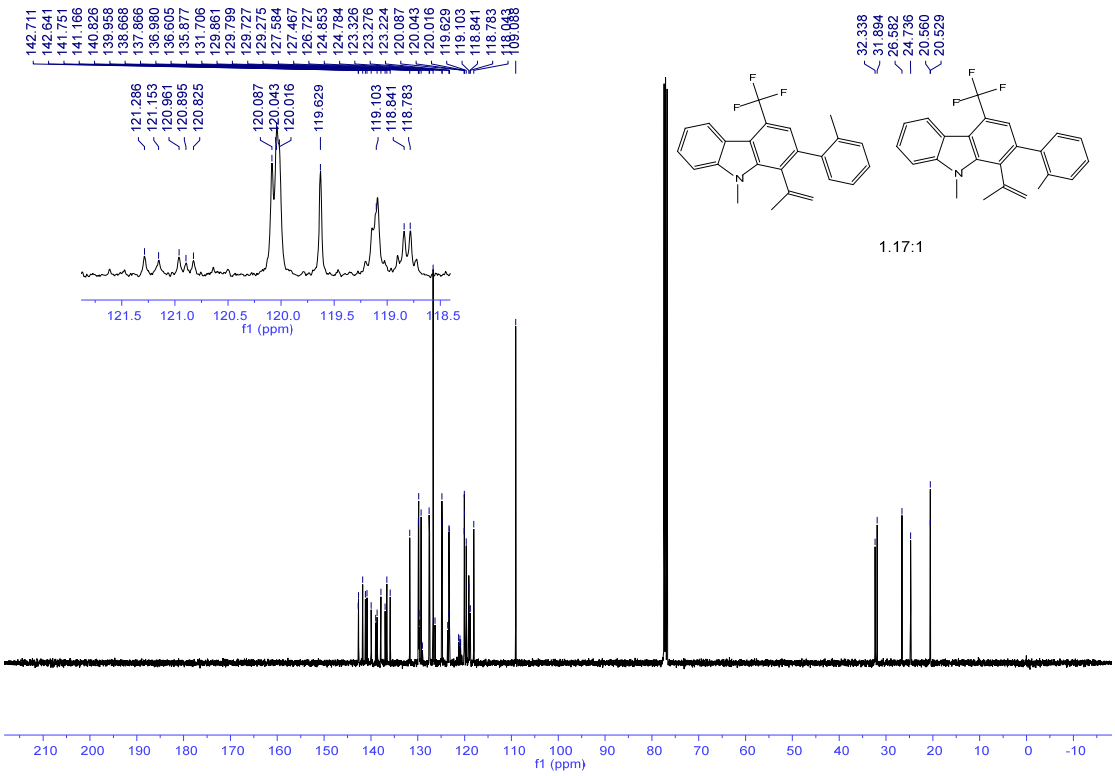


$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3l**

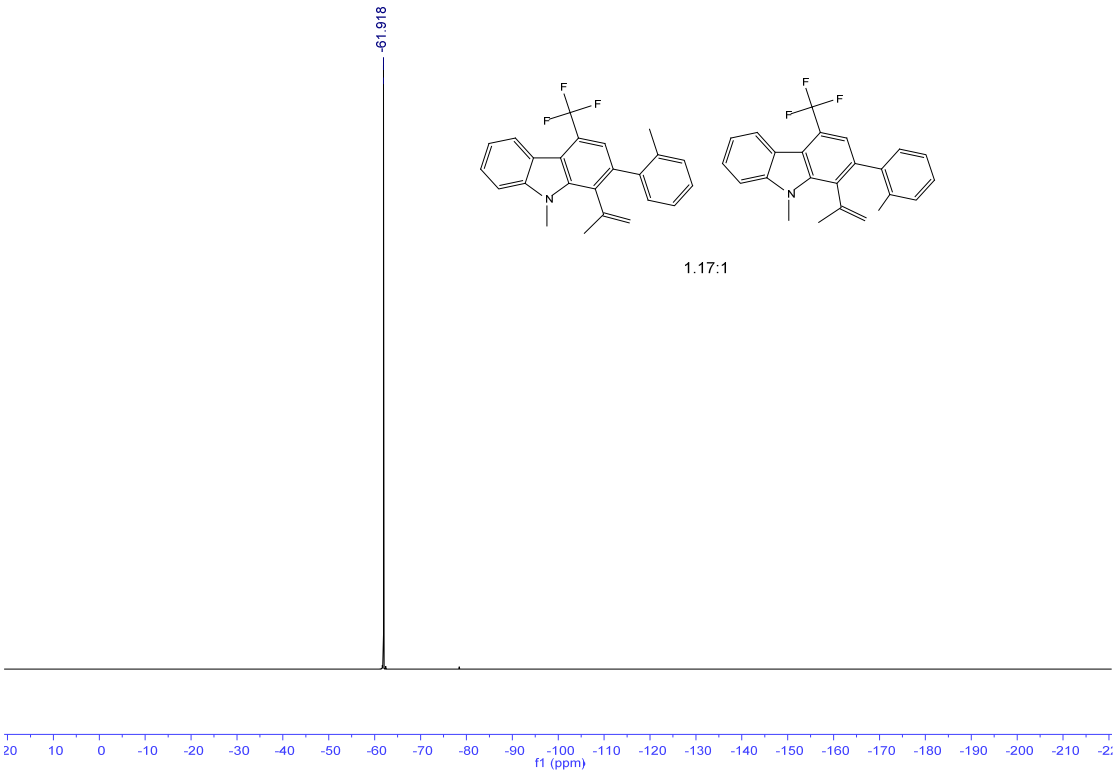
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3l**



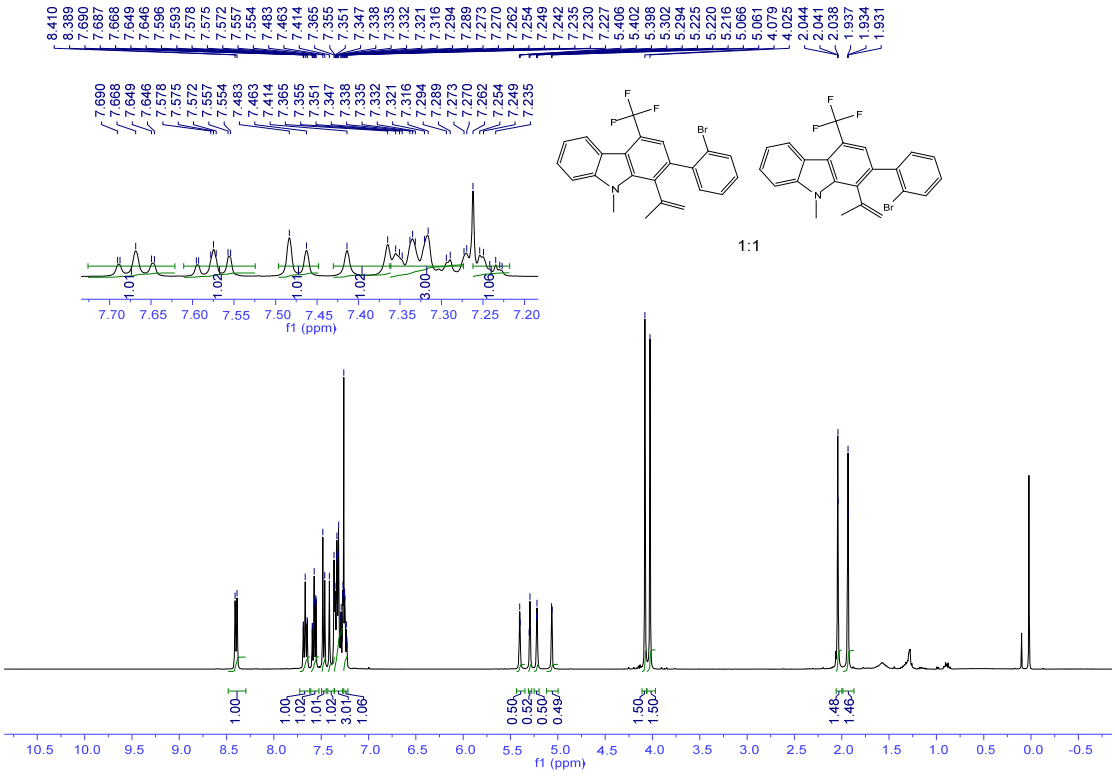
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compounds **3m** and **3m'**



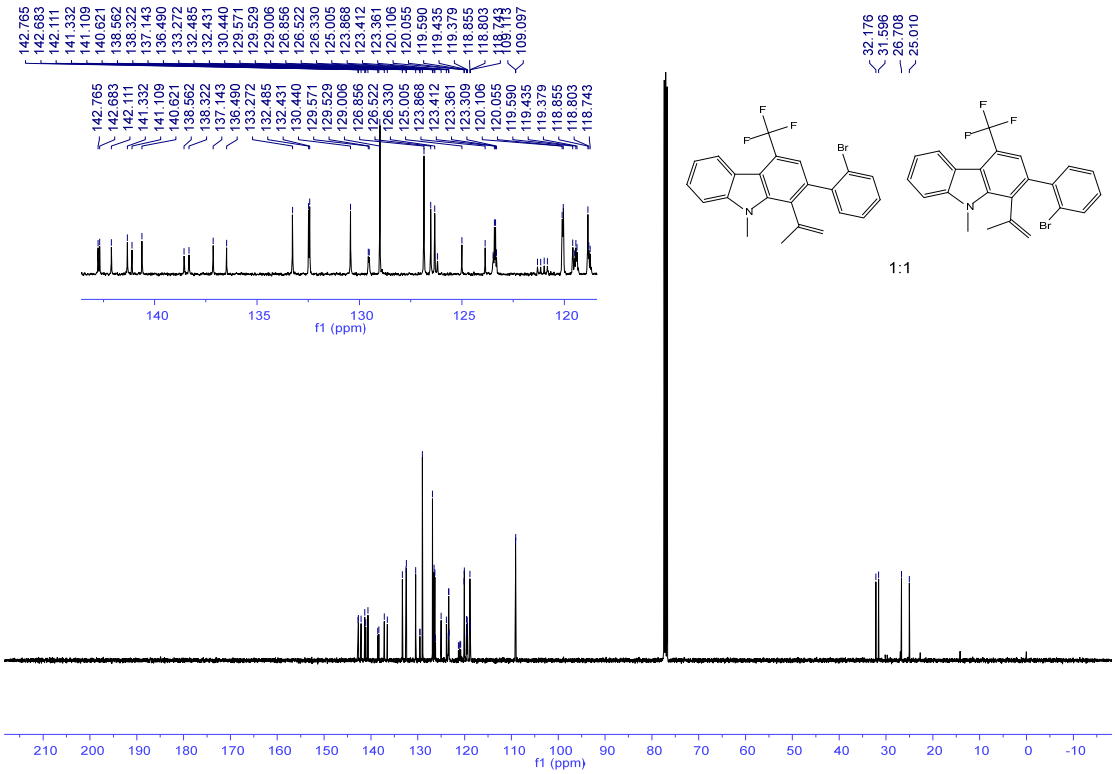
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compounds **3m** and **3m'**



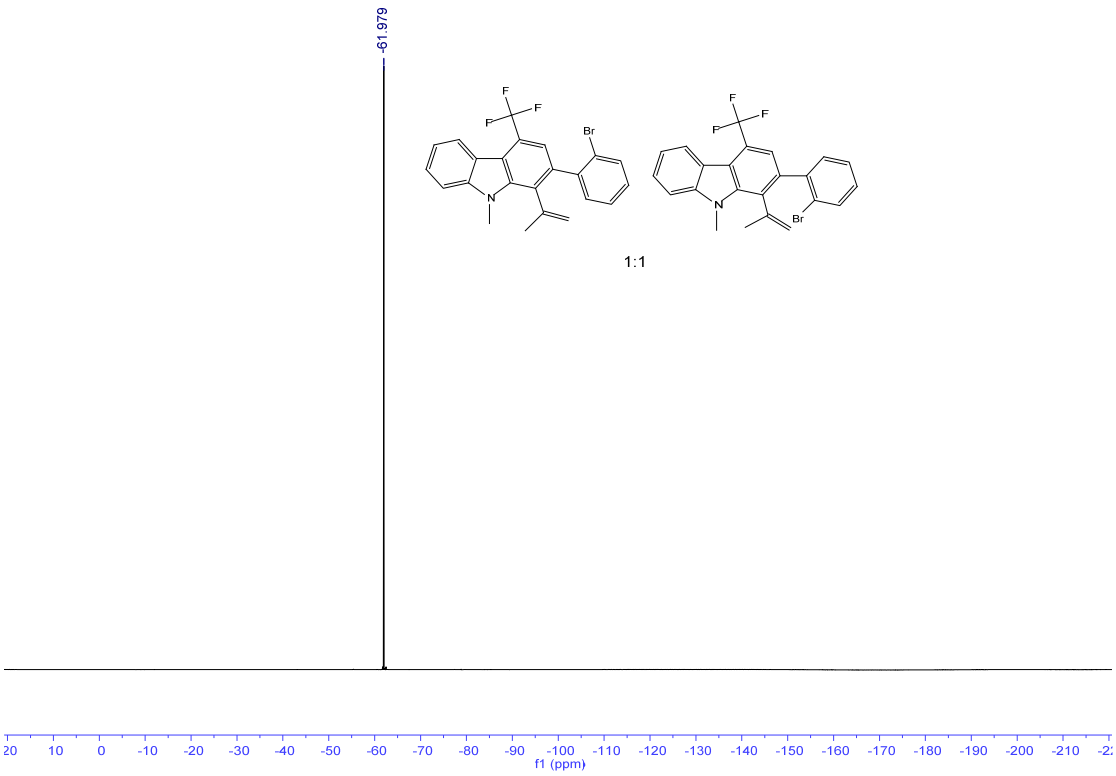
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compounds **3m** and **3m'**



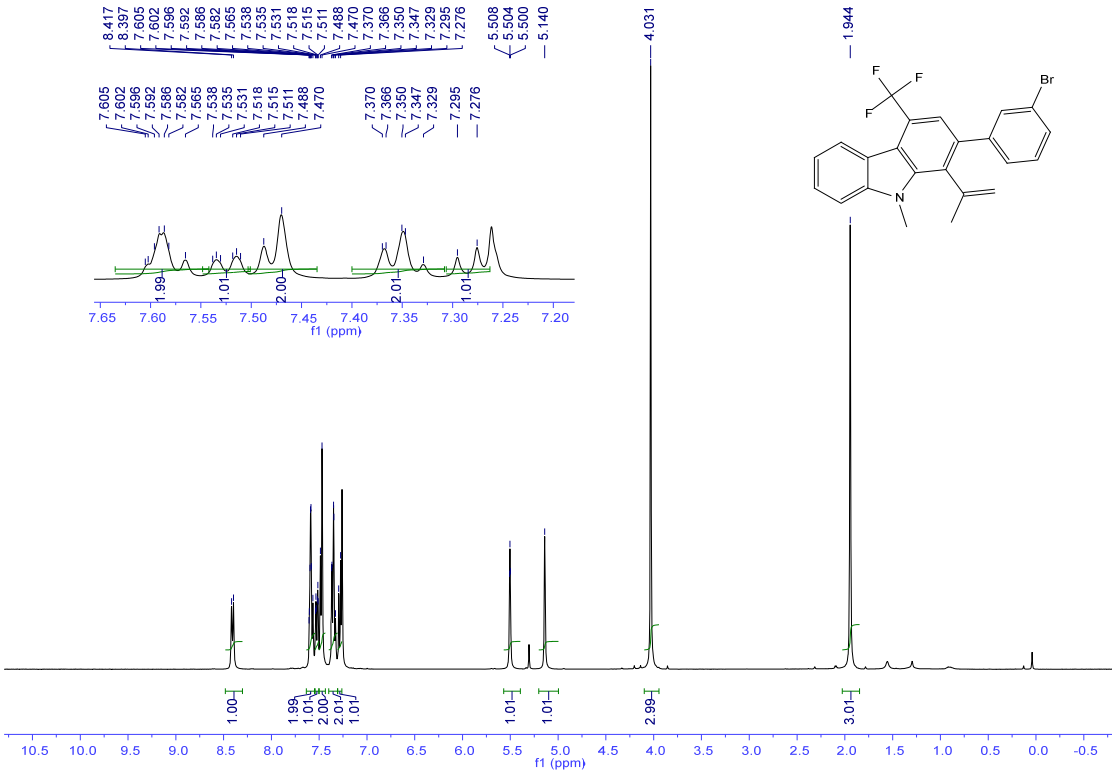
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compounds **3n** and **3n'**



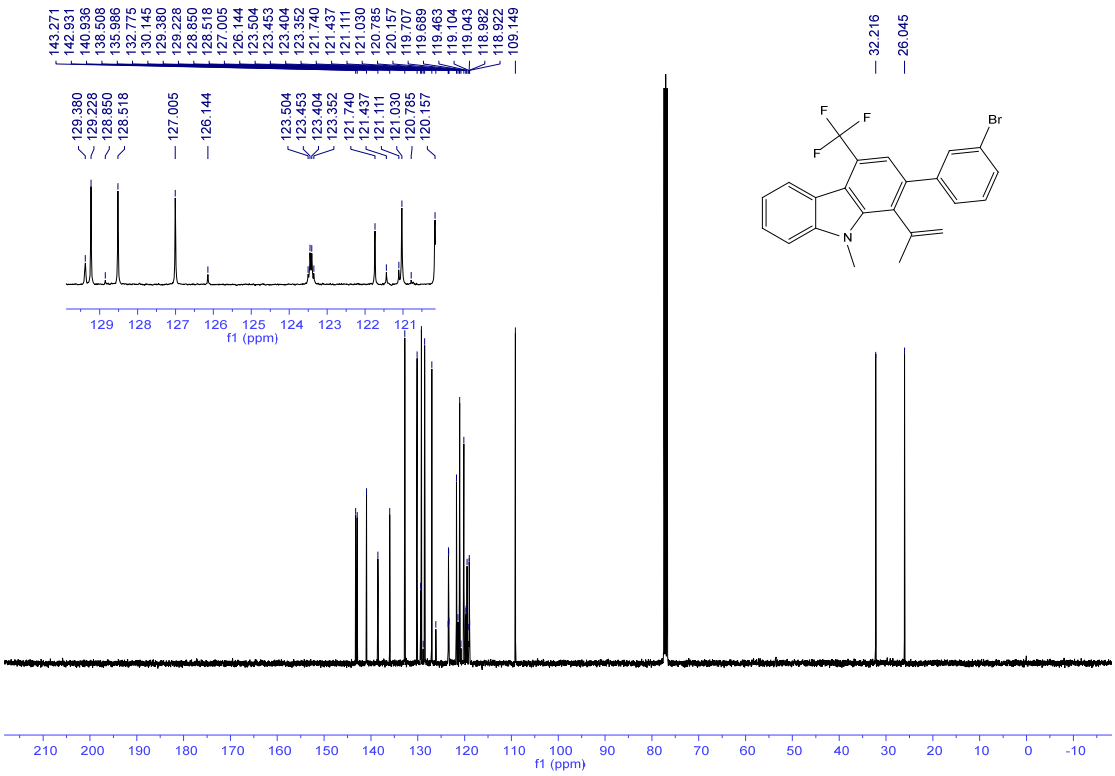
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compounds **3n** and **3n'**



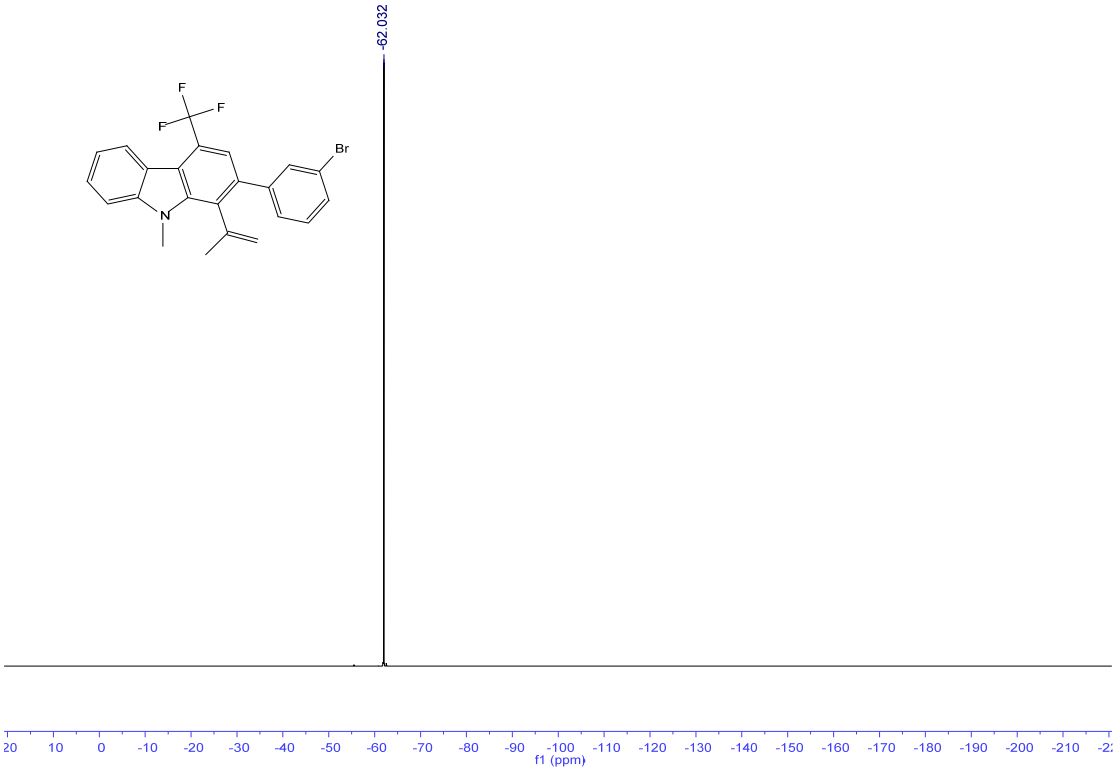
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compounds **3n** and **3n'**



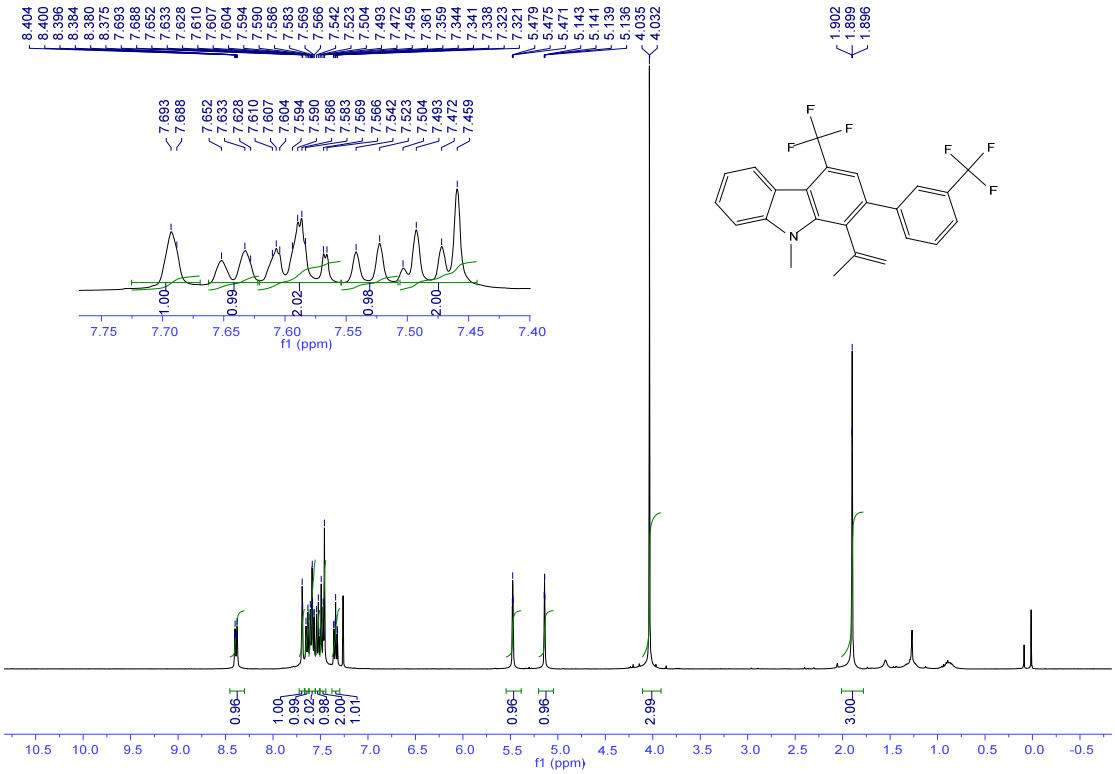
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3o**



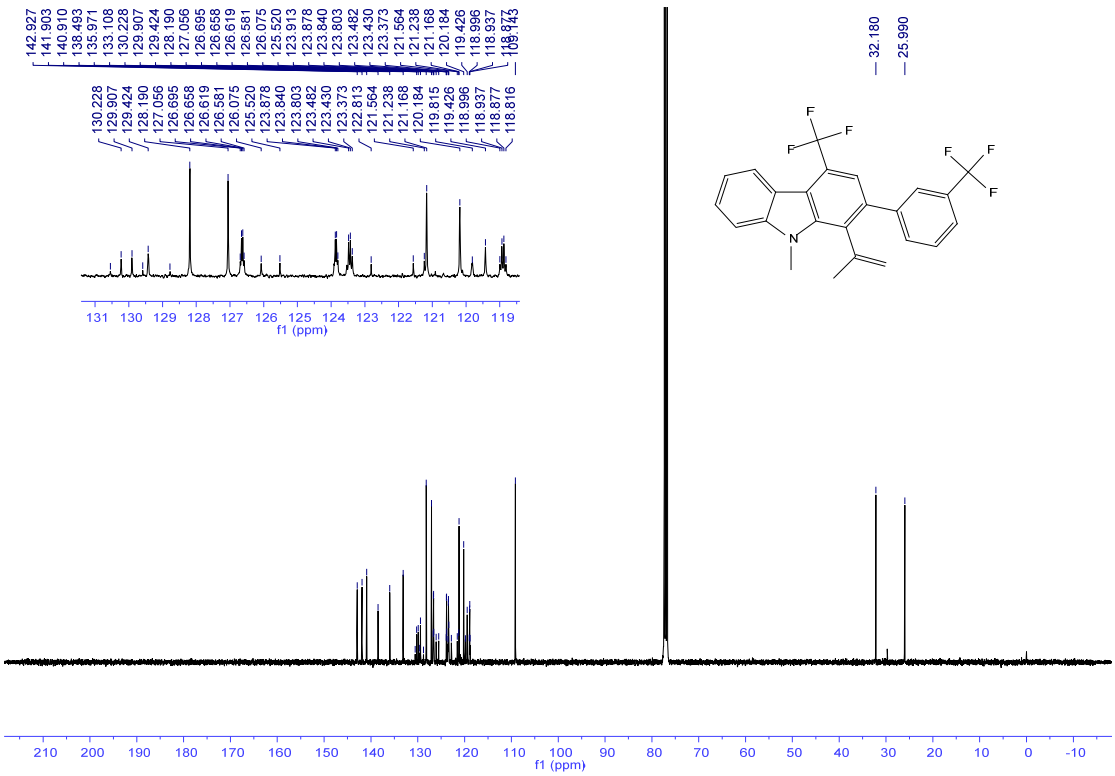
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of compound **3o**



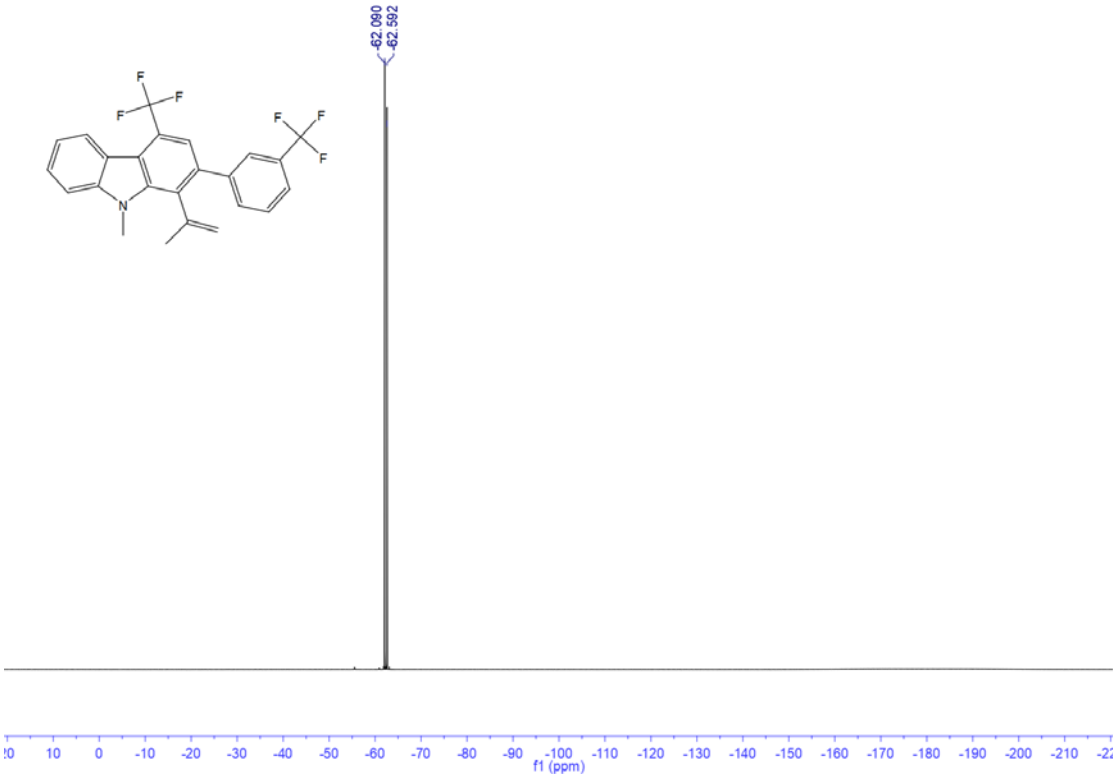
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3o**



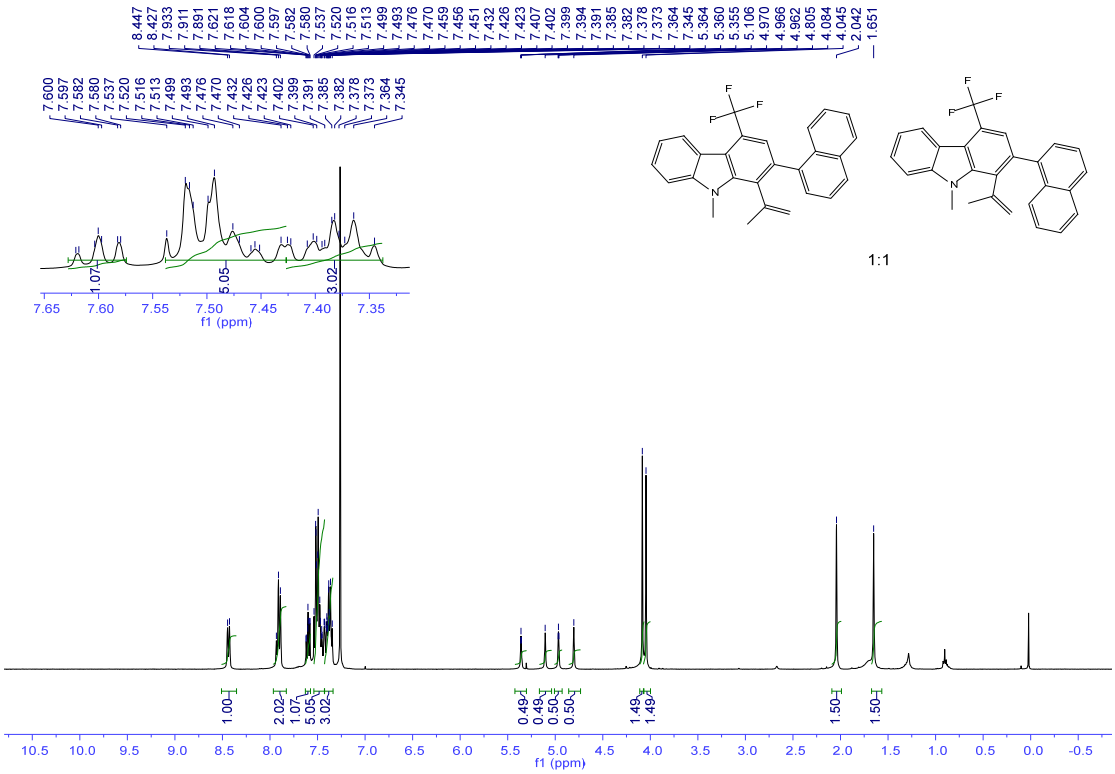
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3p**



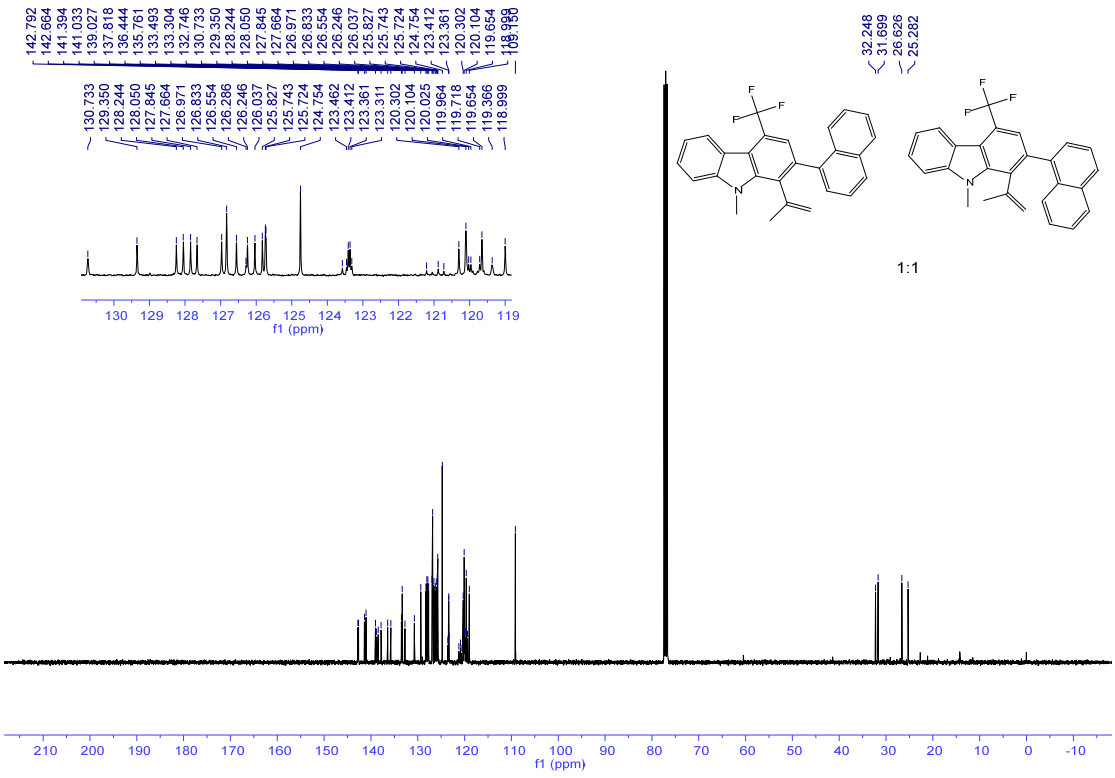
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3p**



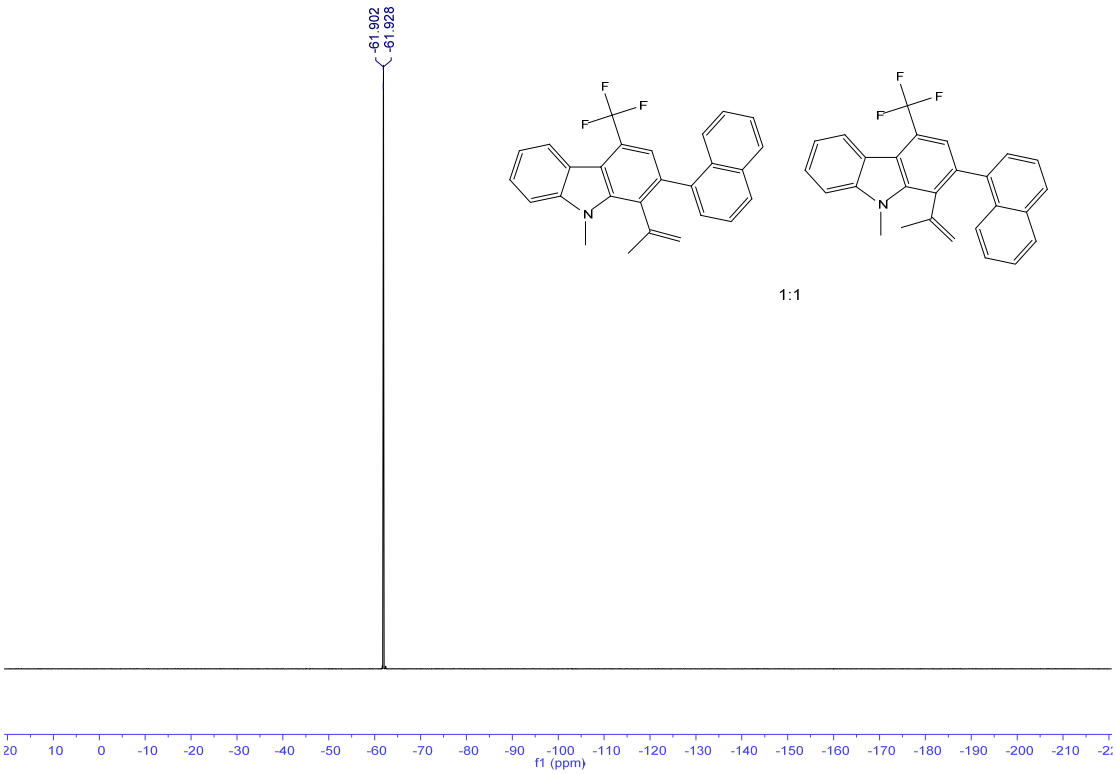
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3p**



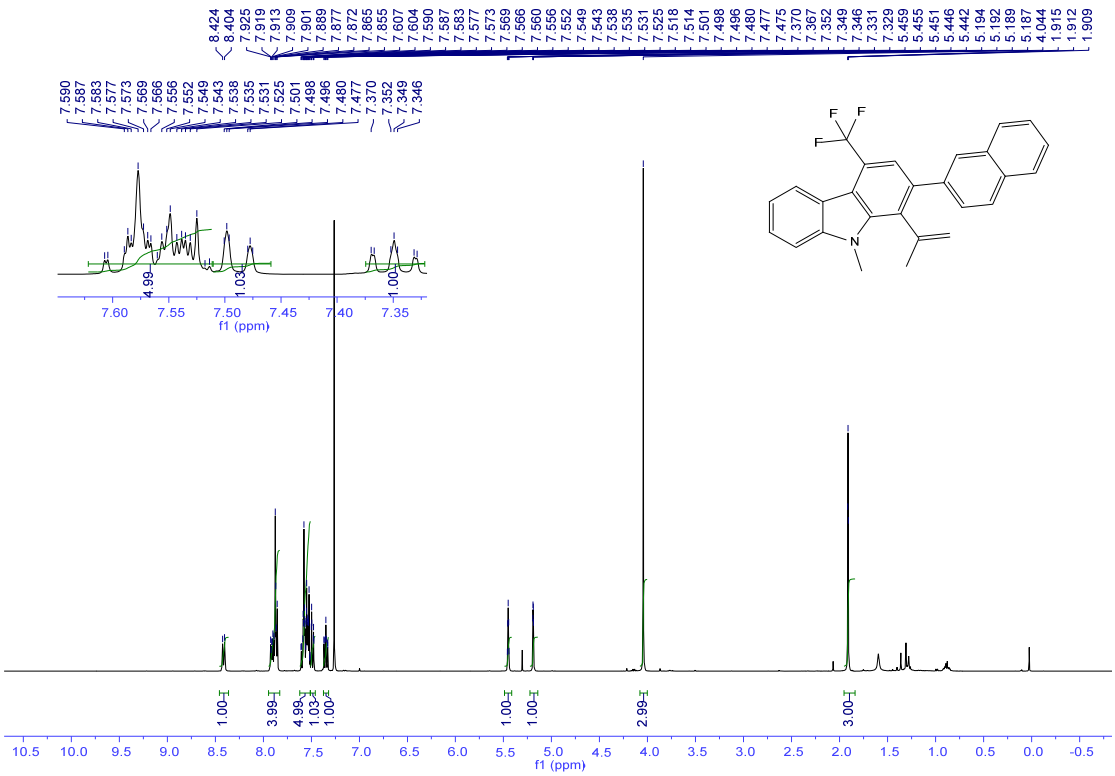
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compounds **3q** and **3q'**



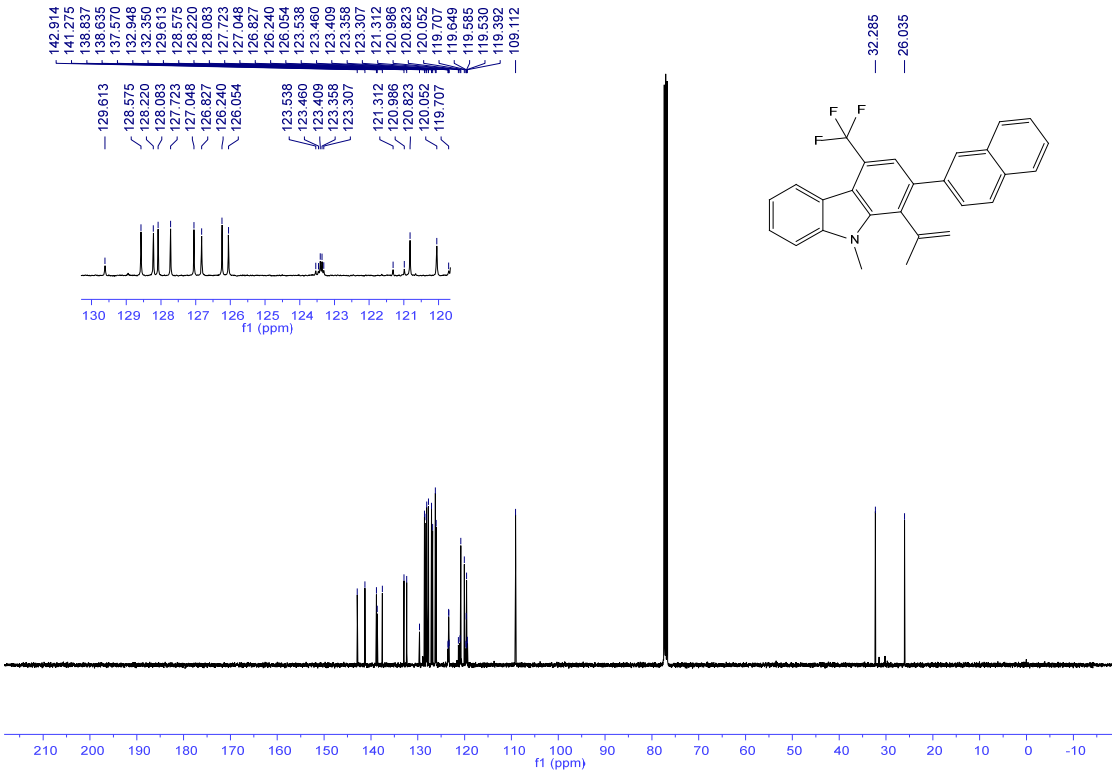
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compounds **3q** and **3q'**



^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compounds **3q** and **3q'**

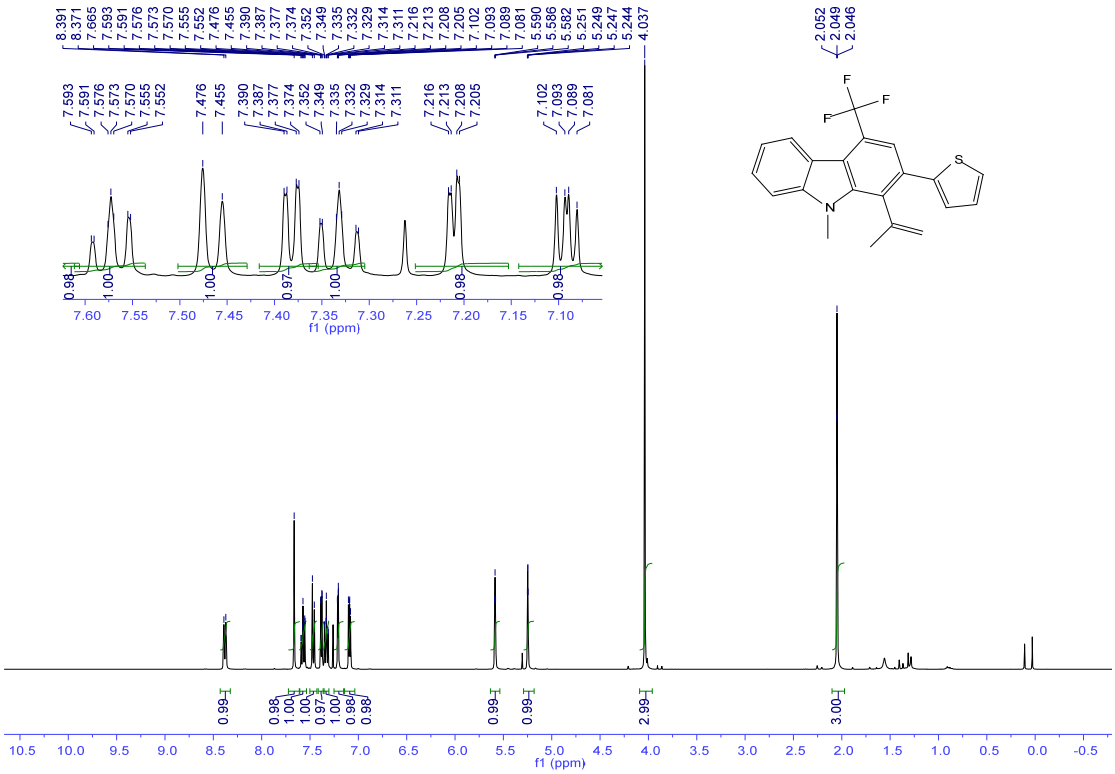


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3r**

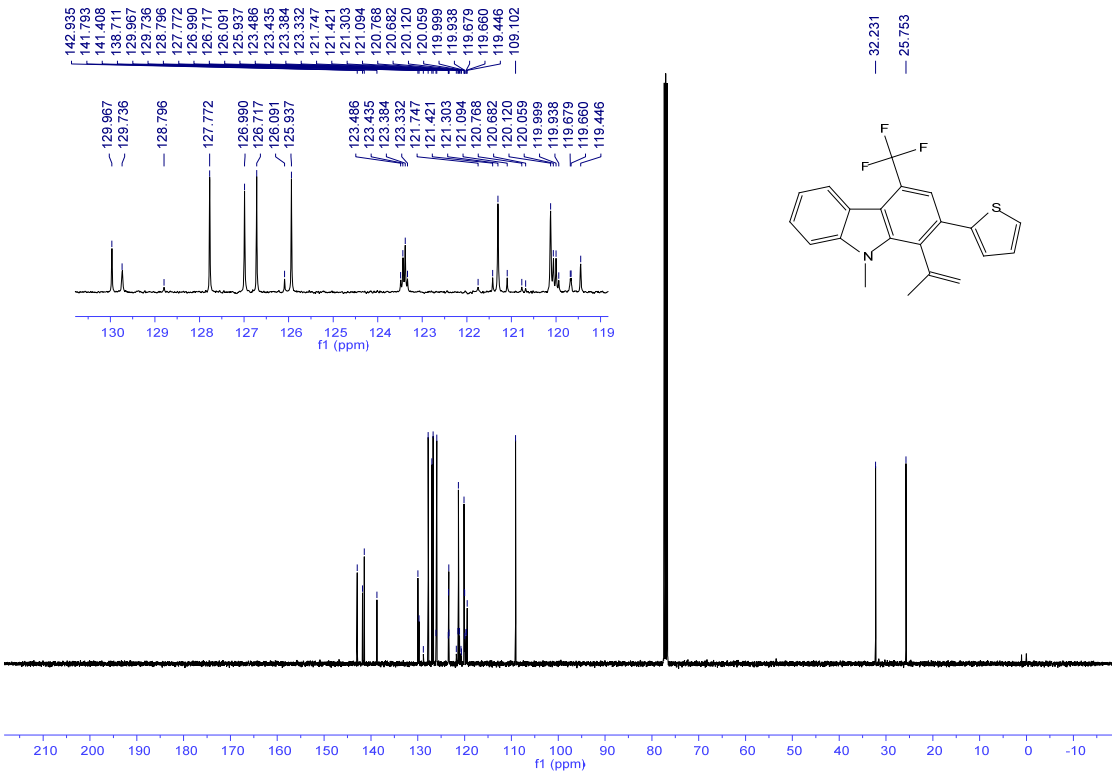


$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3r**

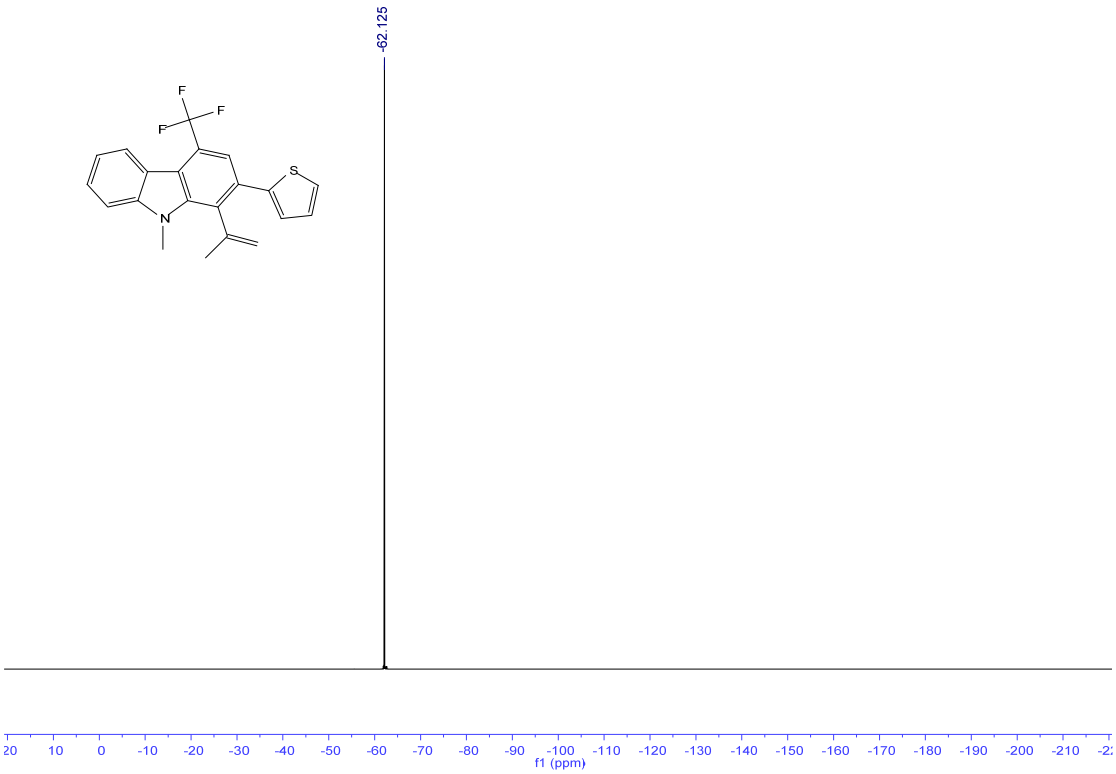
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3r**



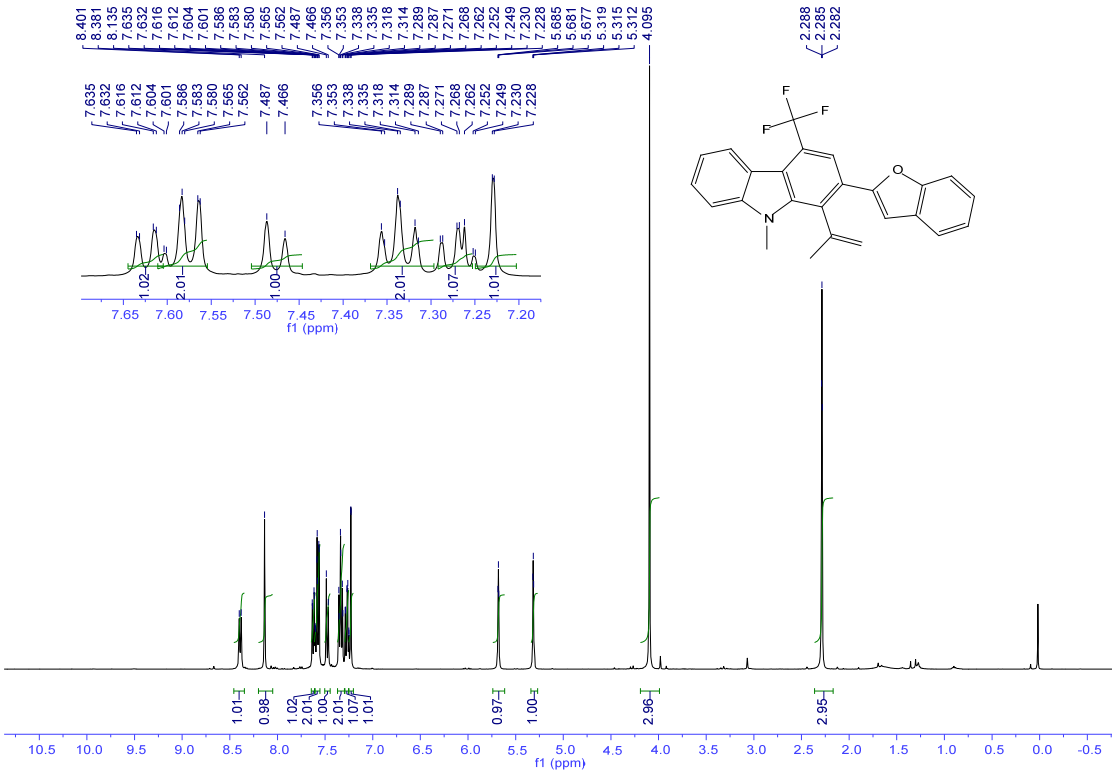
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3s**



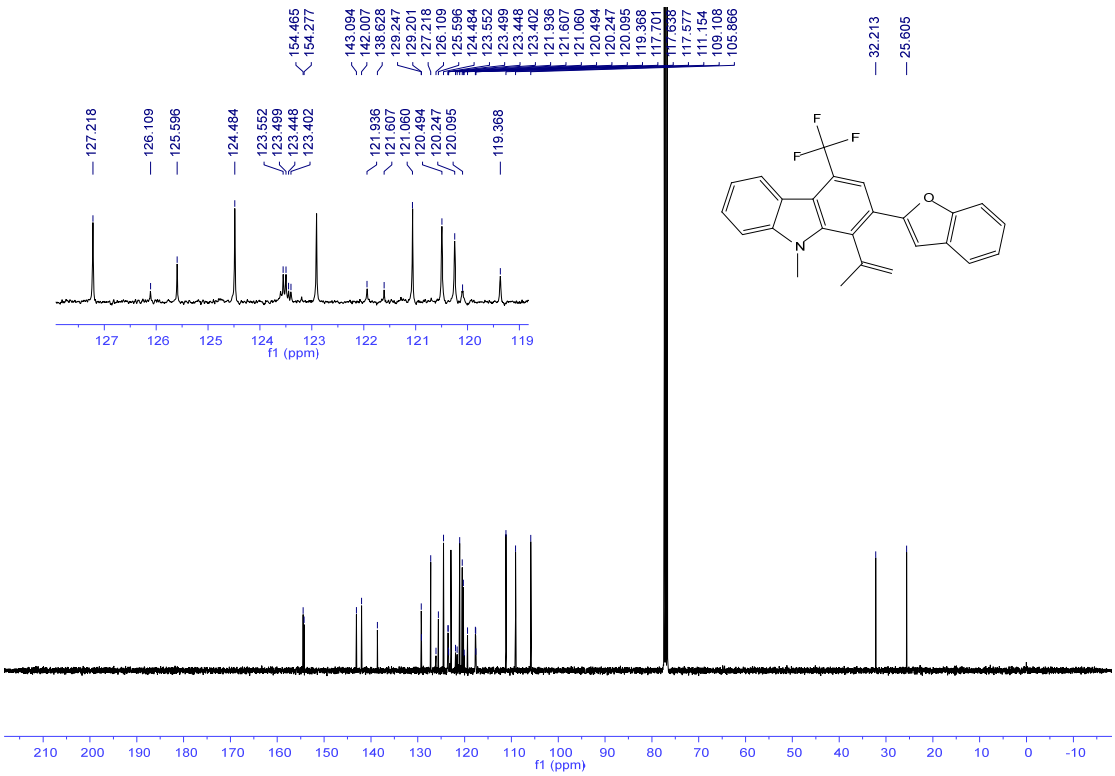
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3s**



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

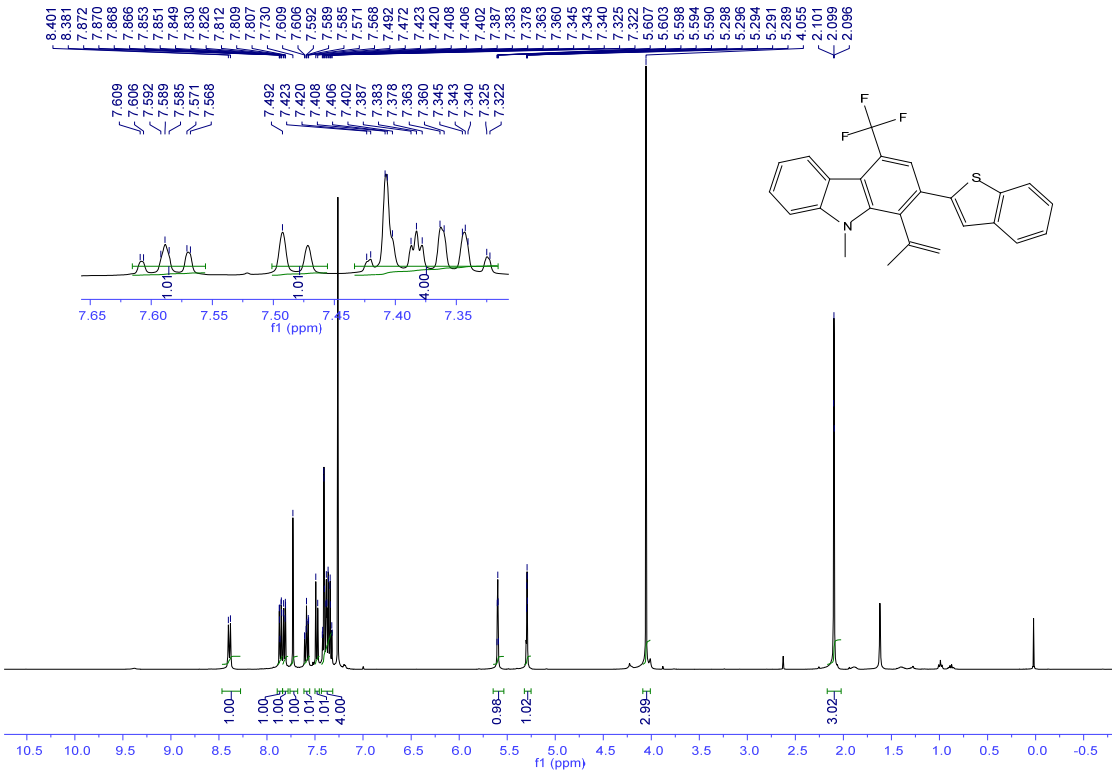


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3t**

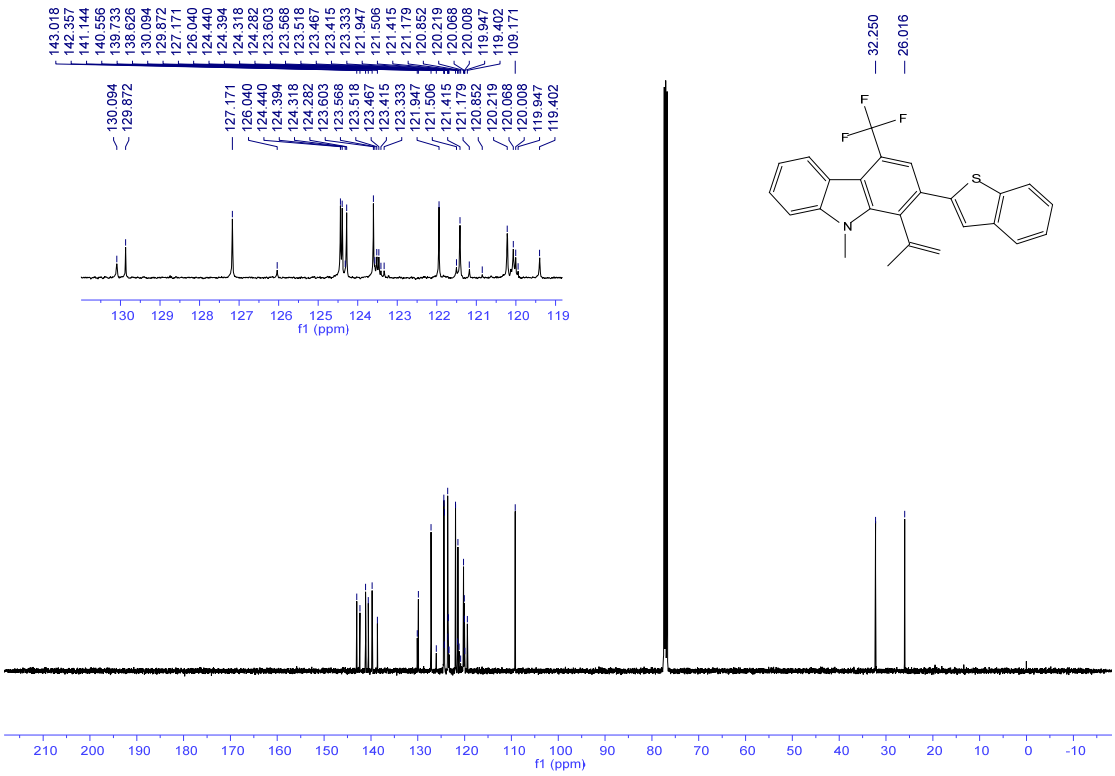


$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3t**

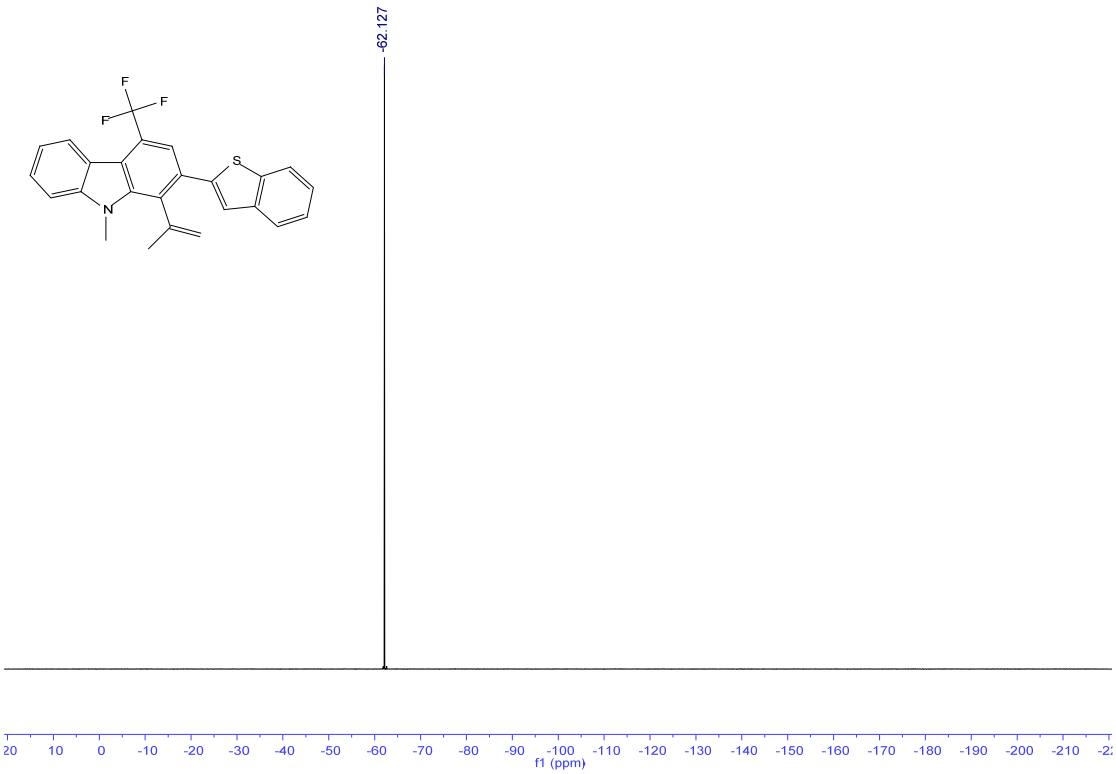
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3t**



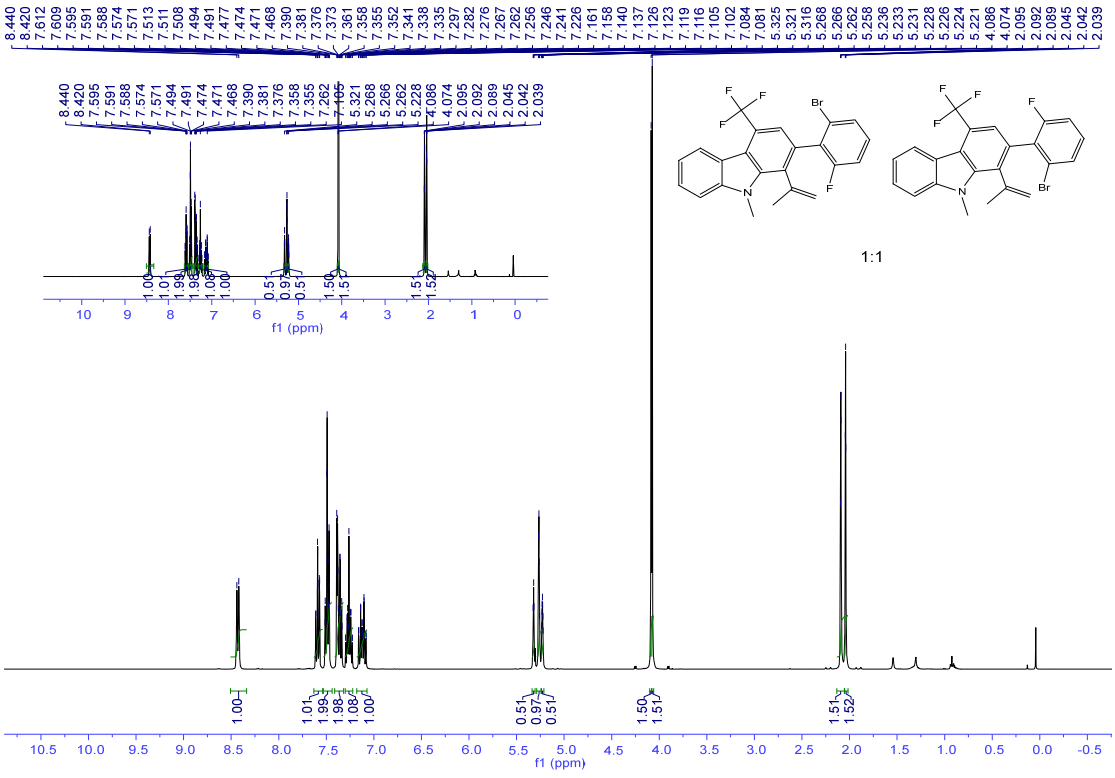
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3u**



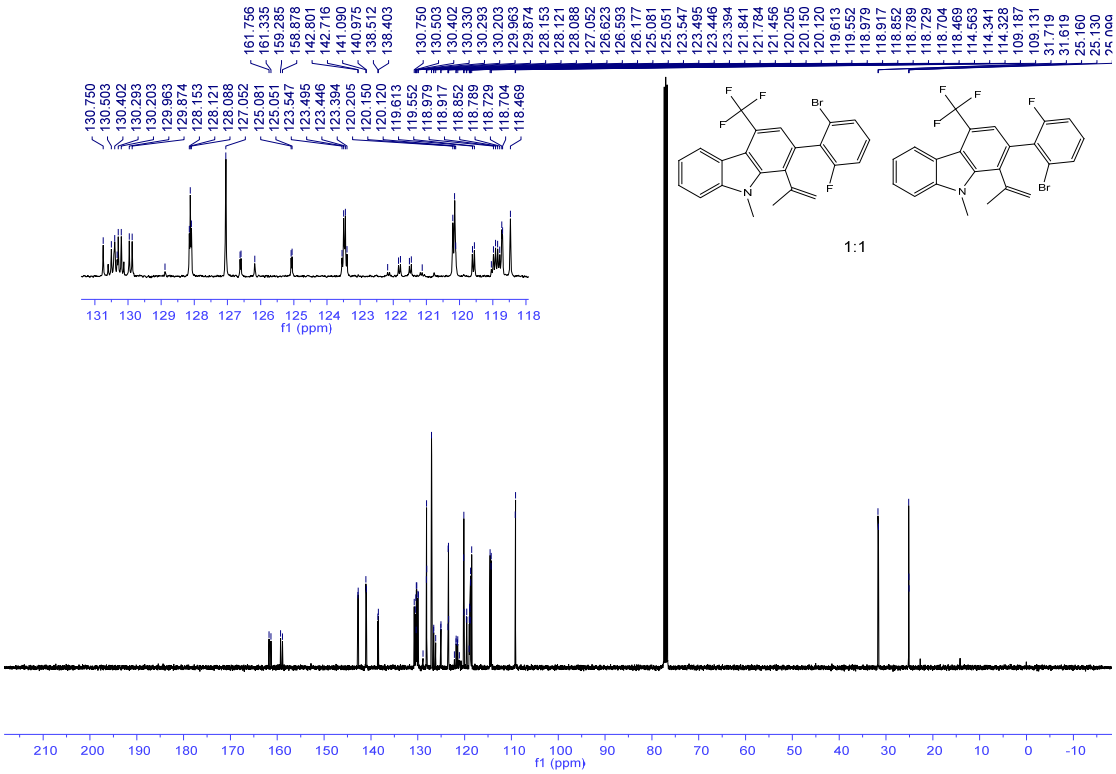
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3u**



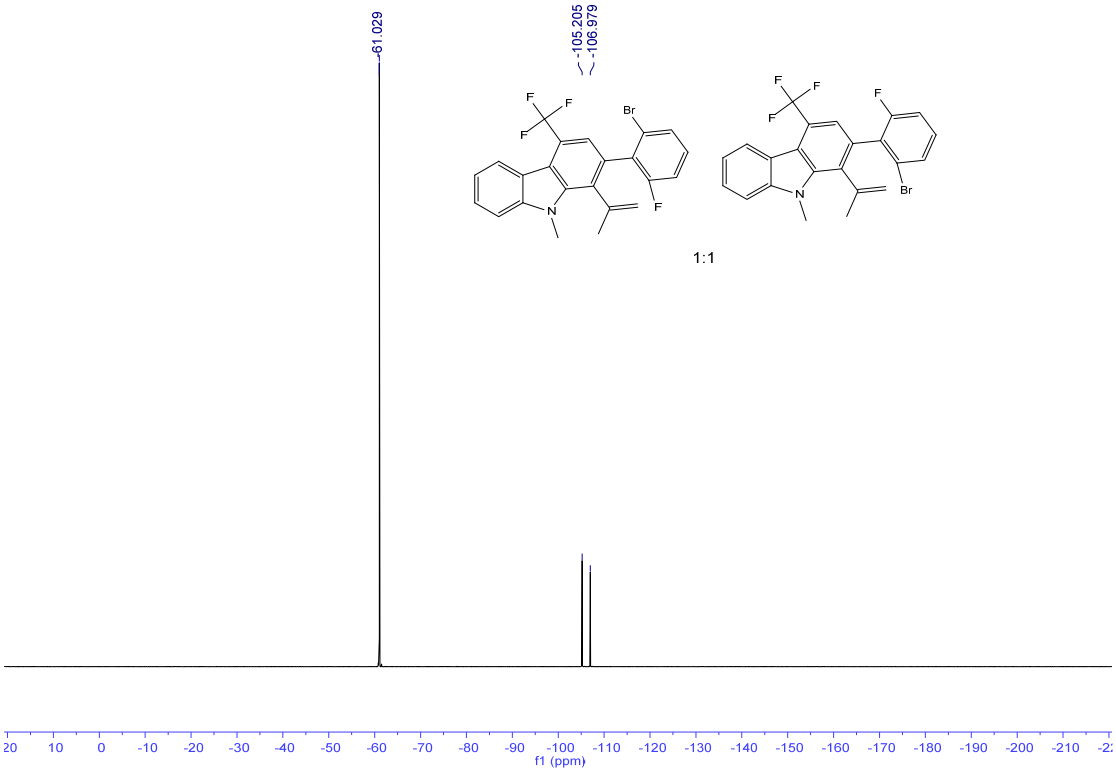
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3u**



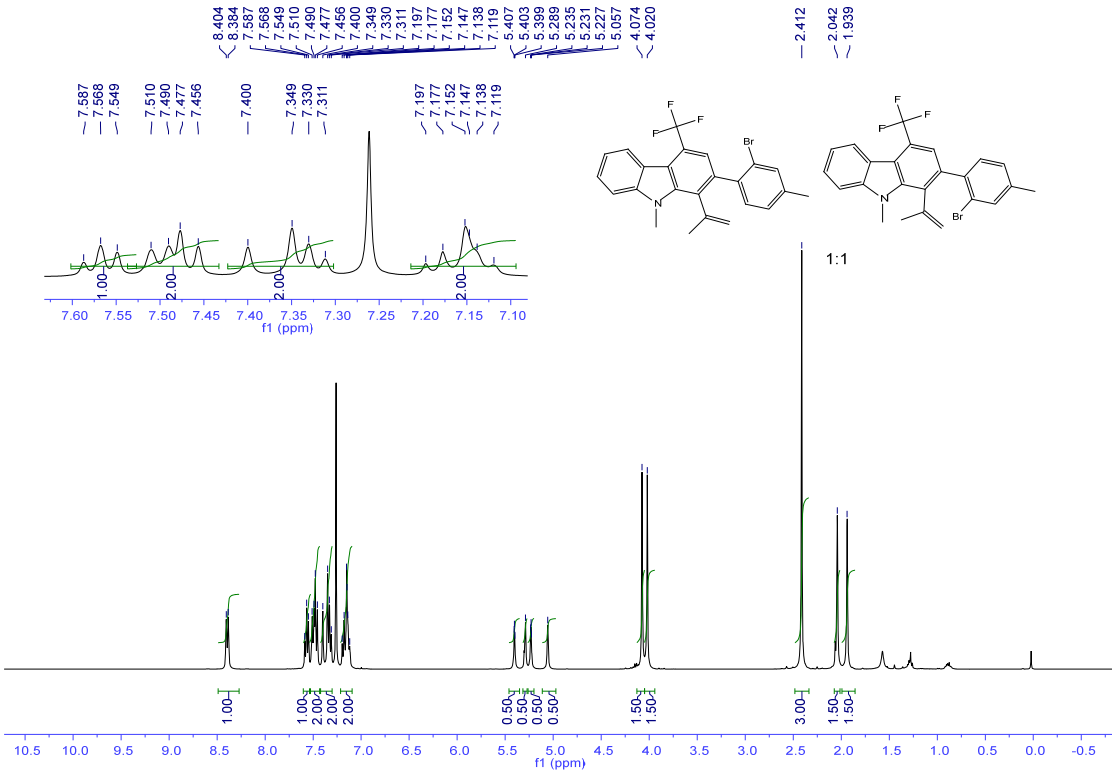
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compounds **3w** and **3w'**



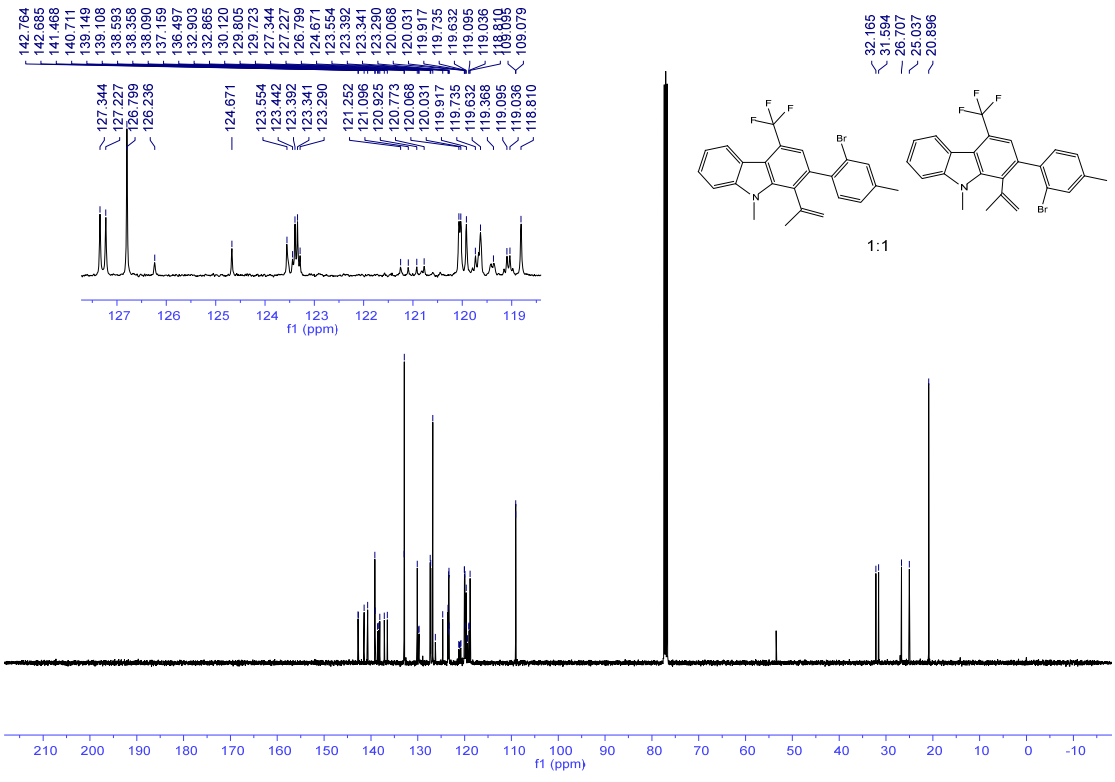
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compounds **3w** and **3w'**



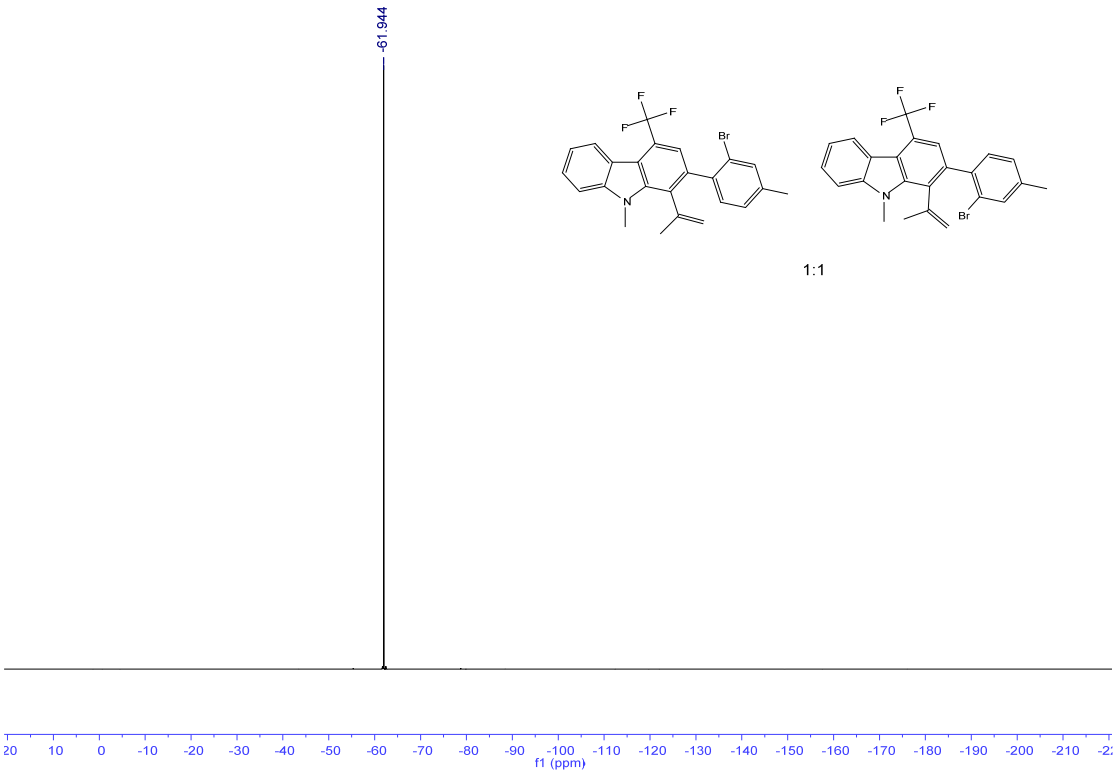
^{19}F NMR (376 MHz, DMSO-D_6) spectrum of compounds **3w** and **3w'**



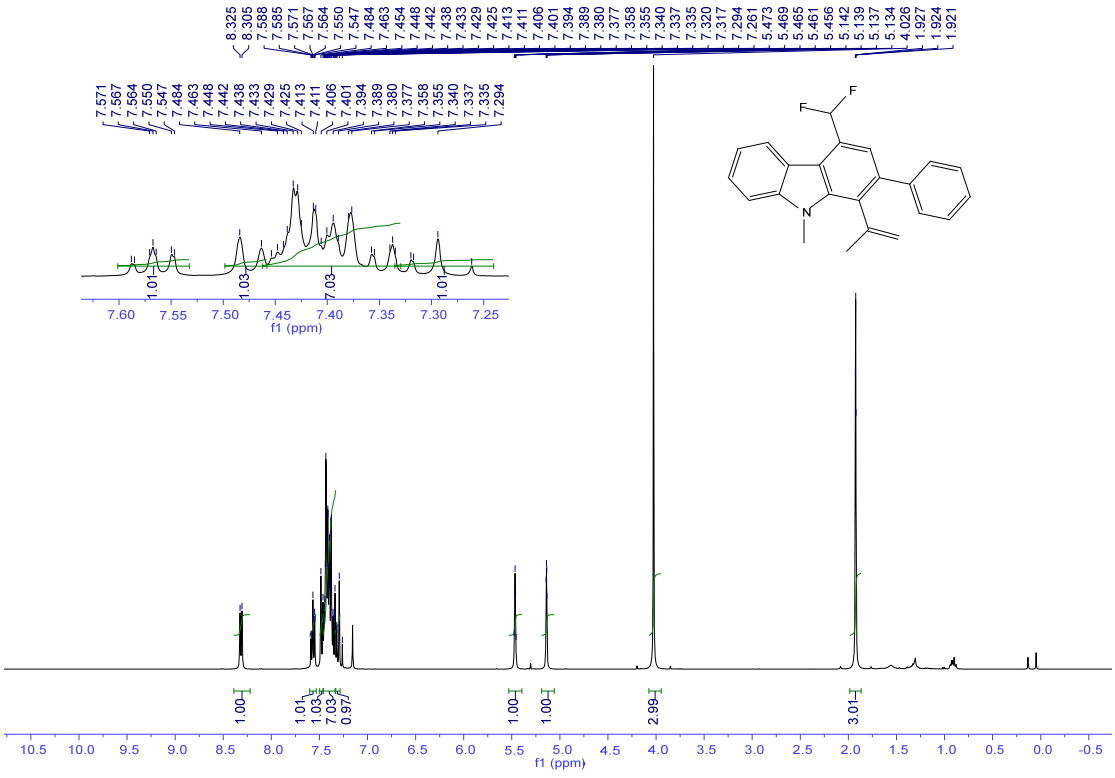
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compounds **3x** and **3x'**



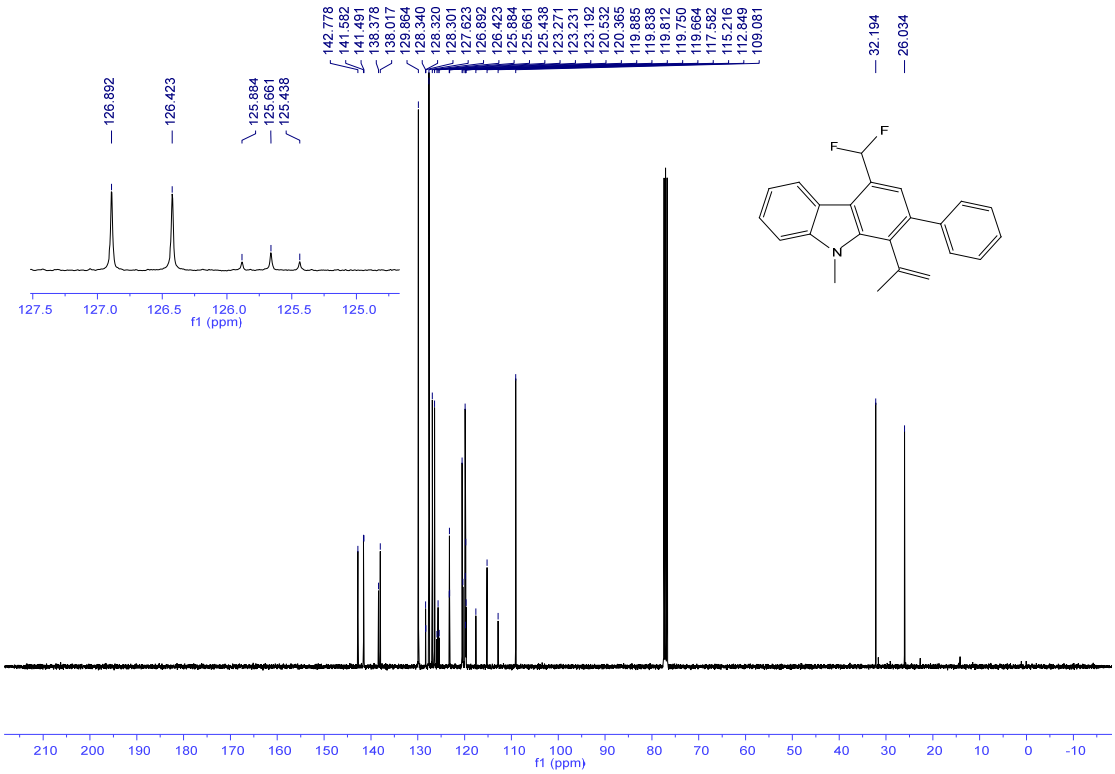
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of compounds **3x** and **3x'**



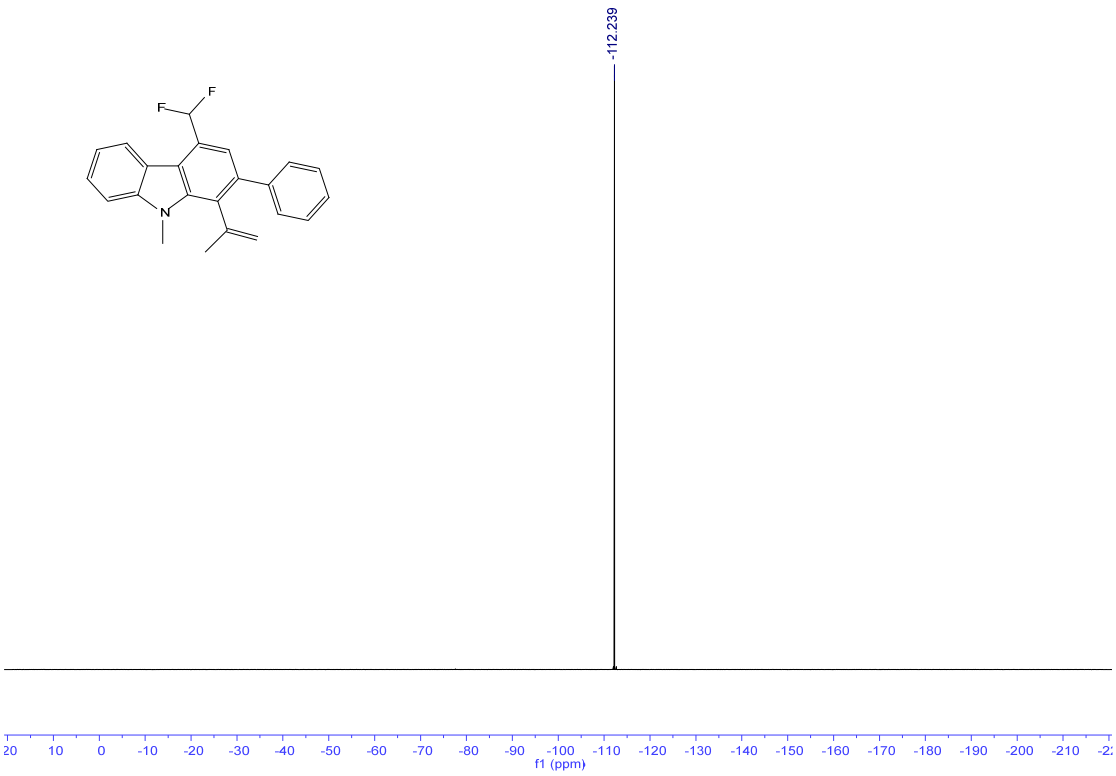
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compounds **3x** and **3x'**



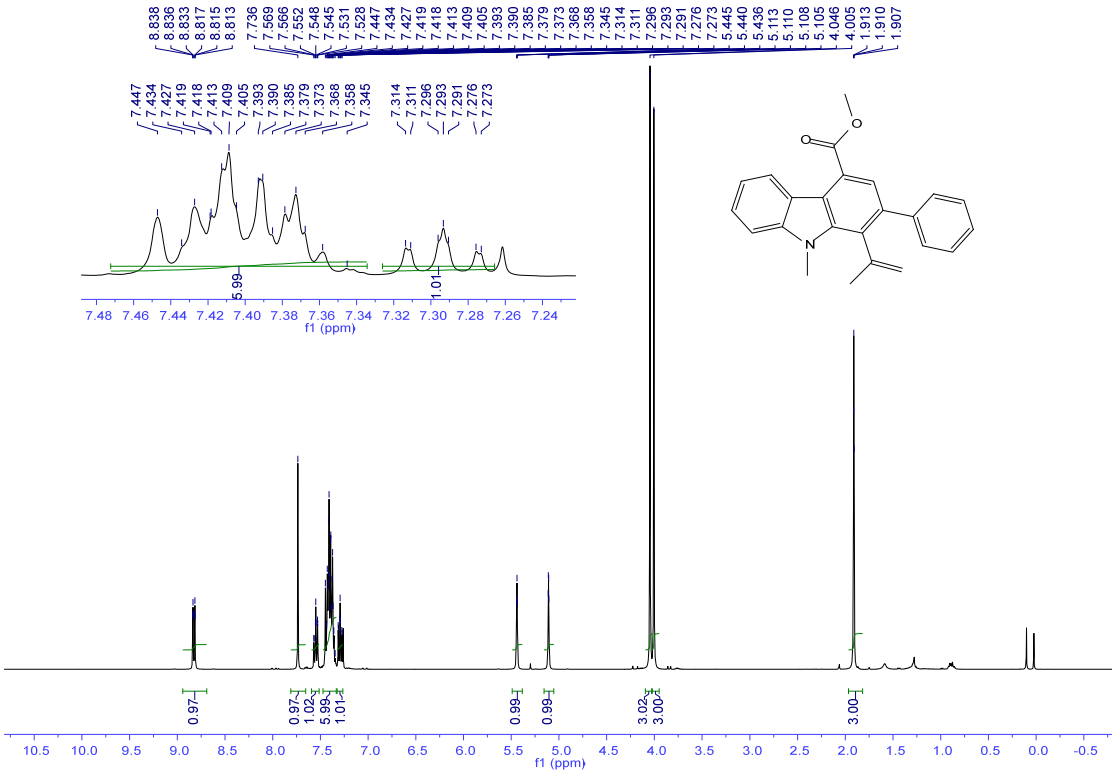
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3y**



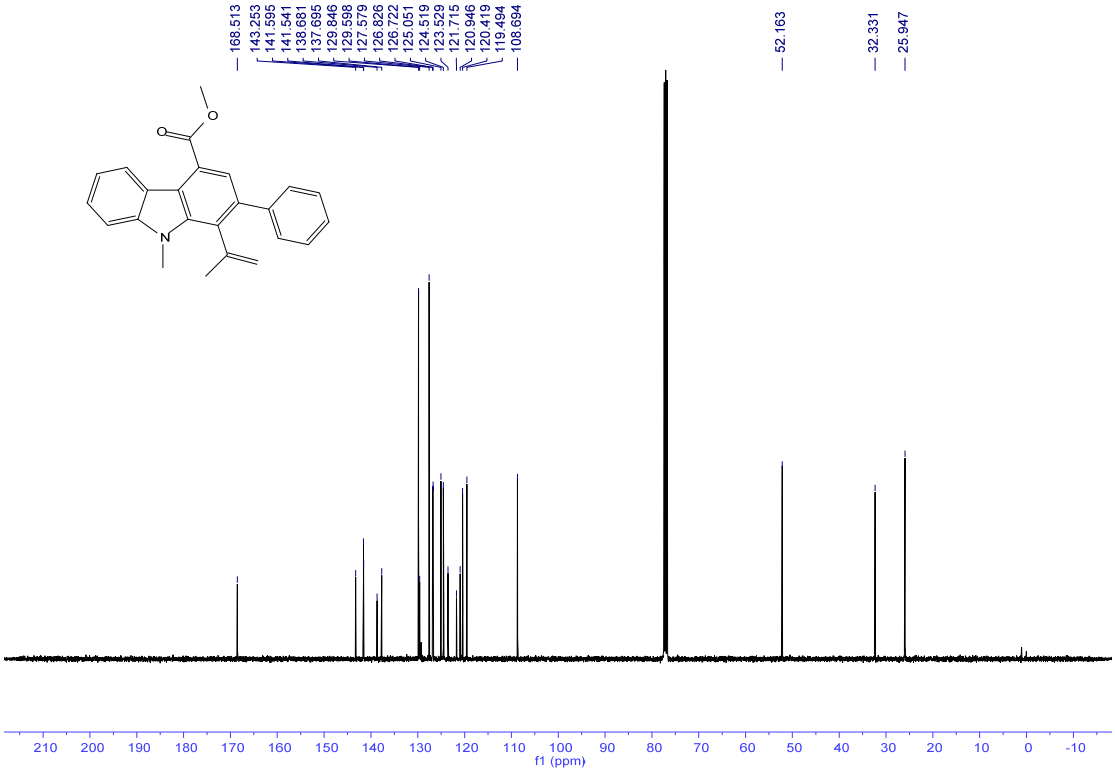
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3y**



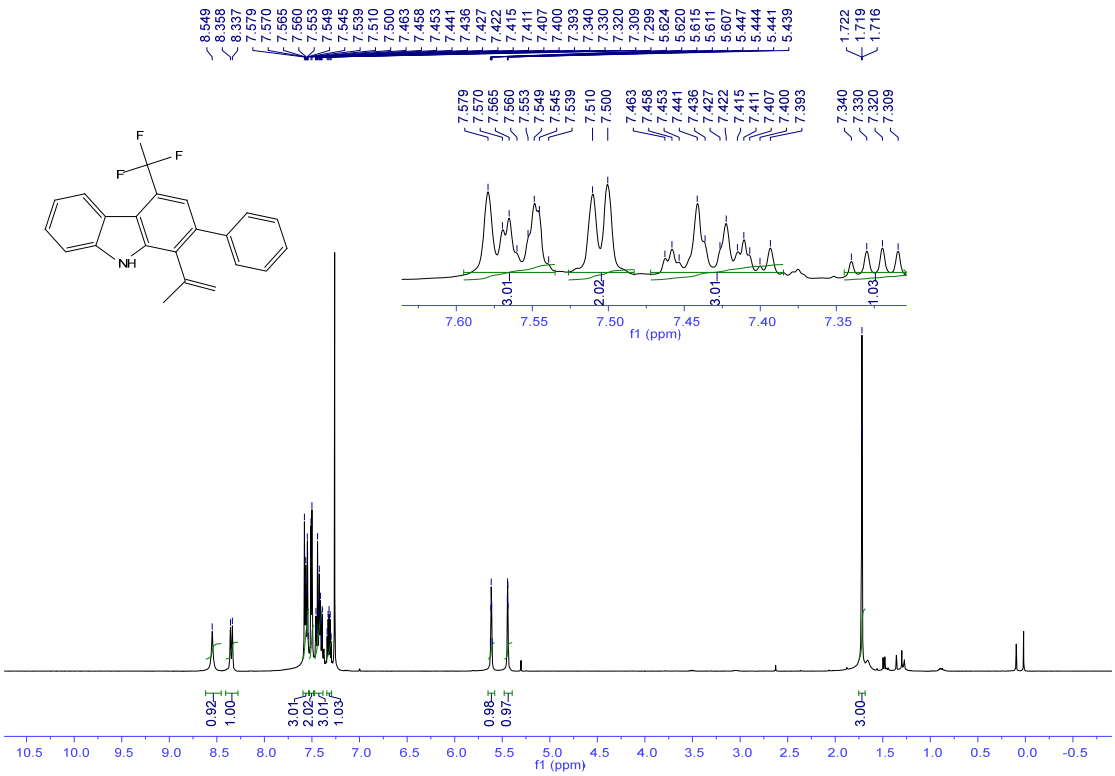
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3y**



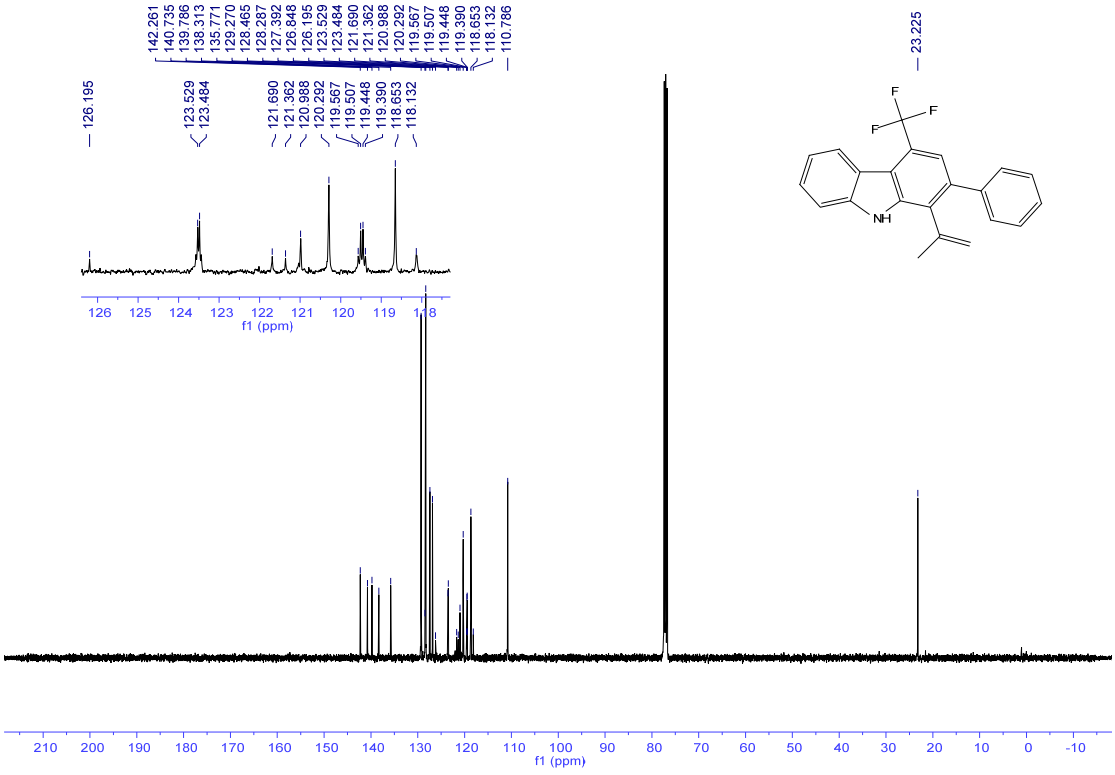
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3aa**



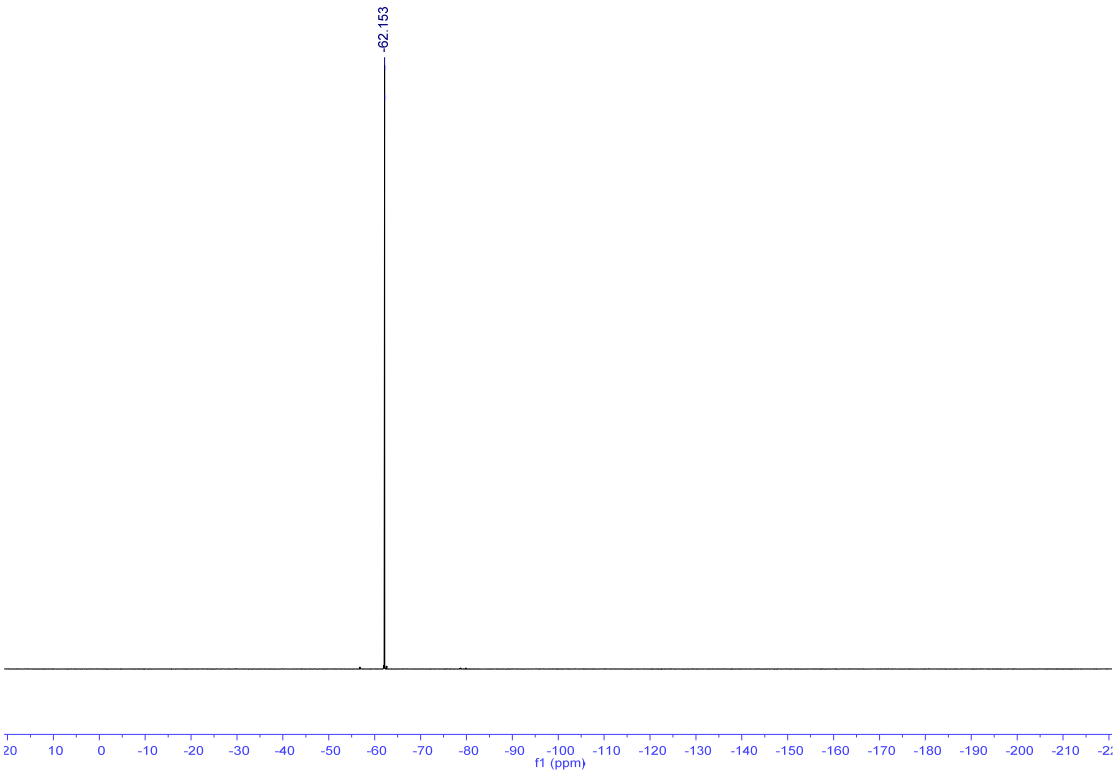
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3aa**



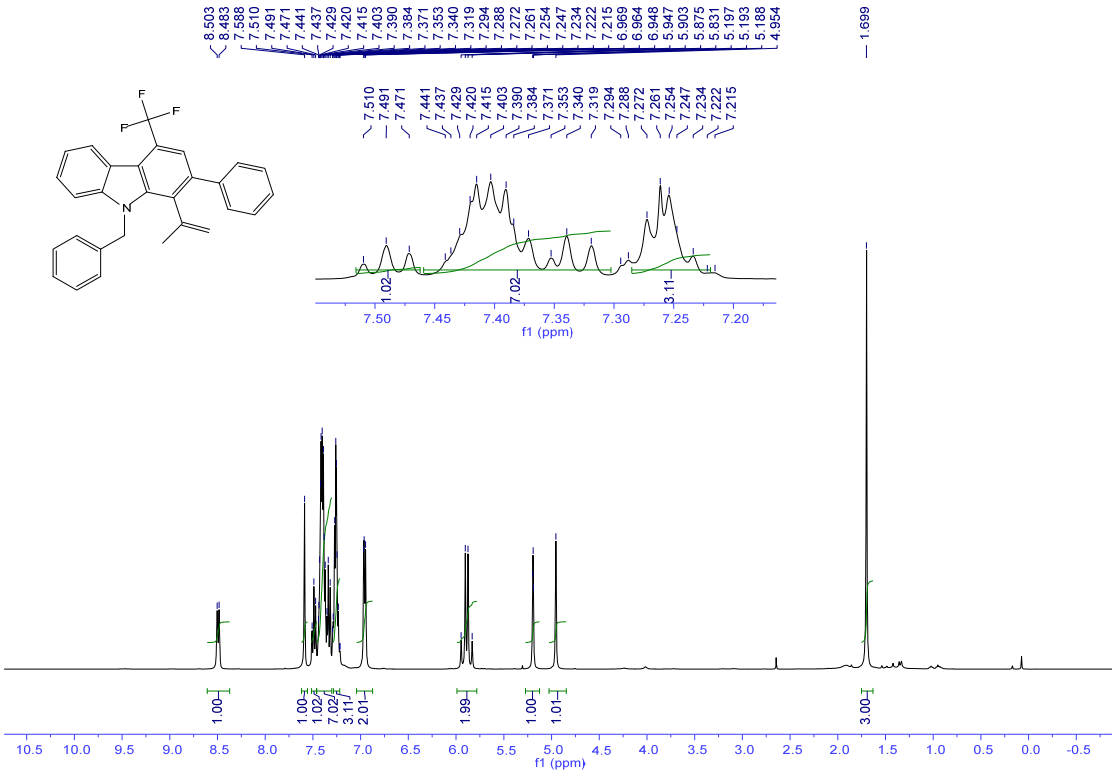
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ab**



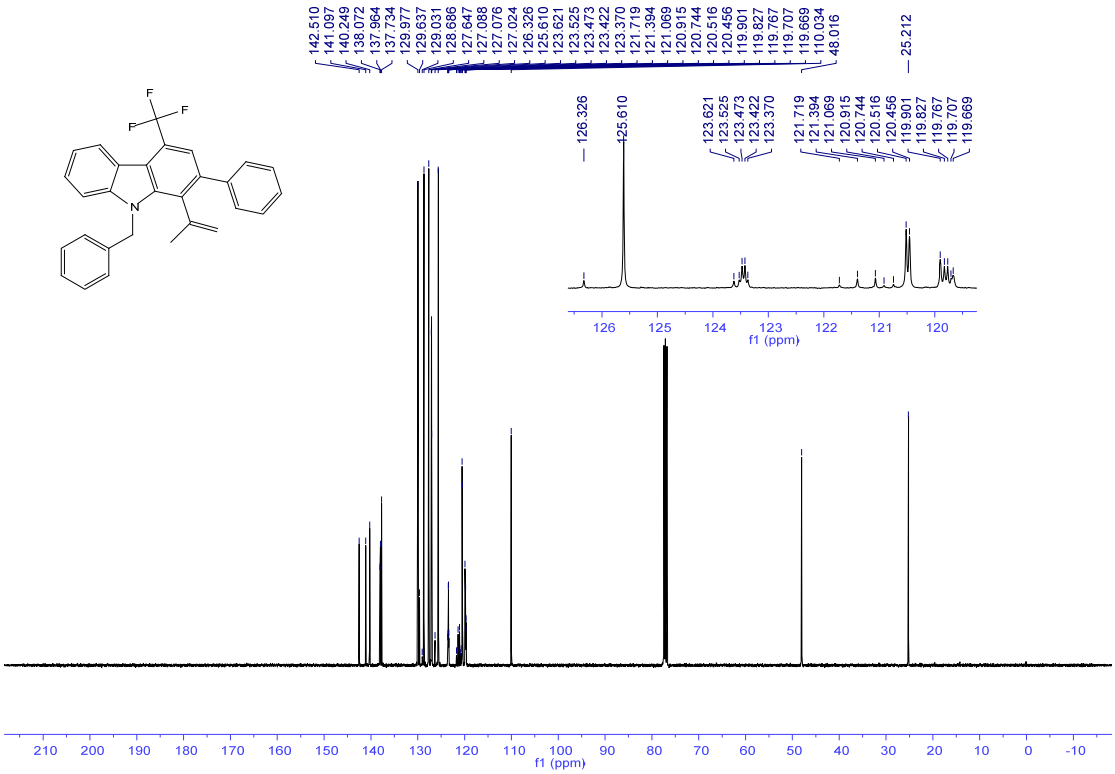
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3ab**



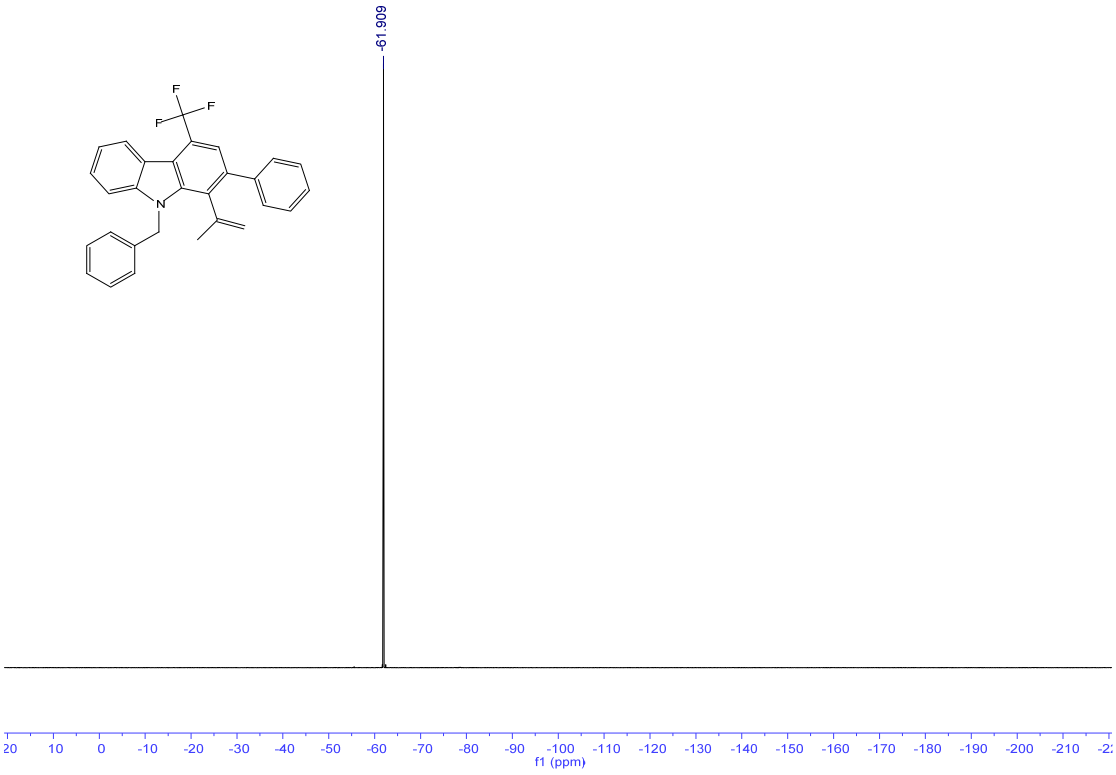
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3ab**



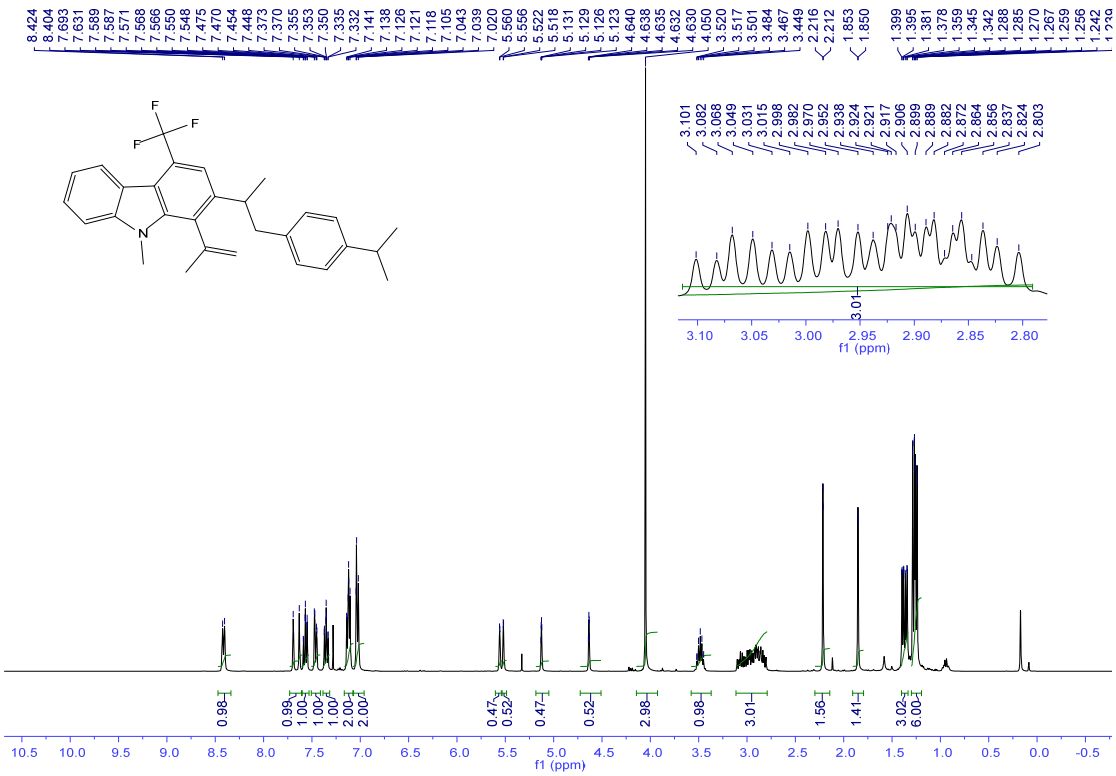
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ac**



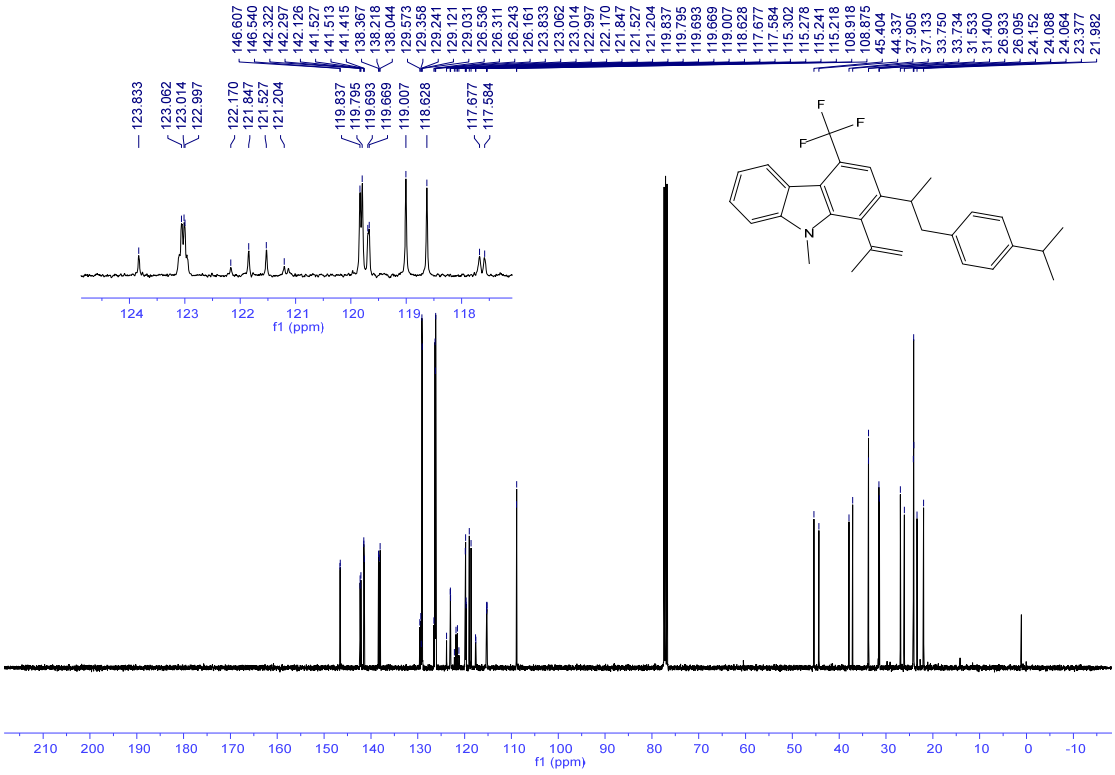
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3ac**



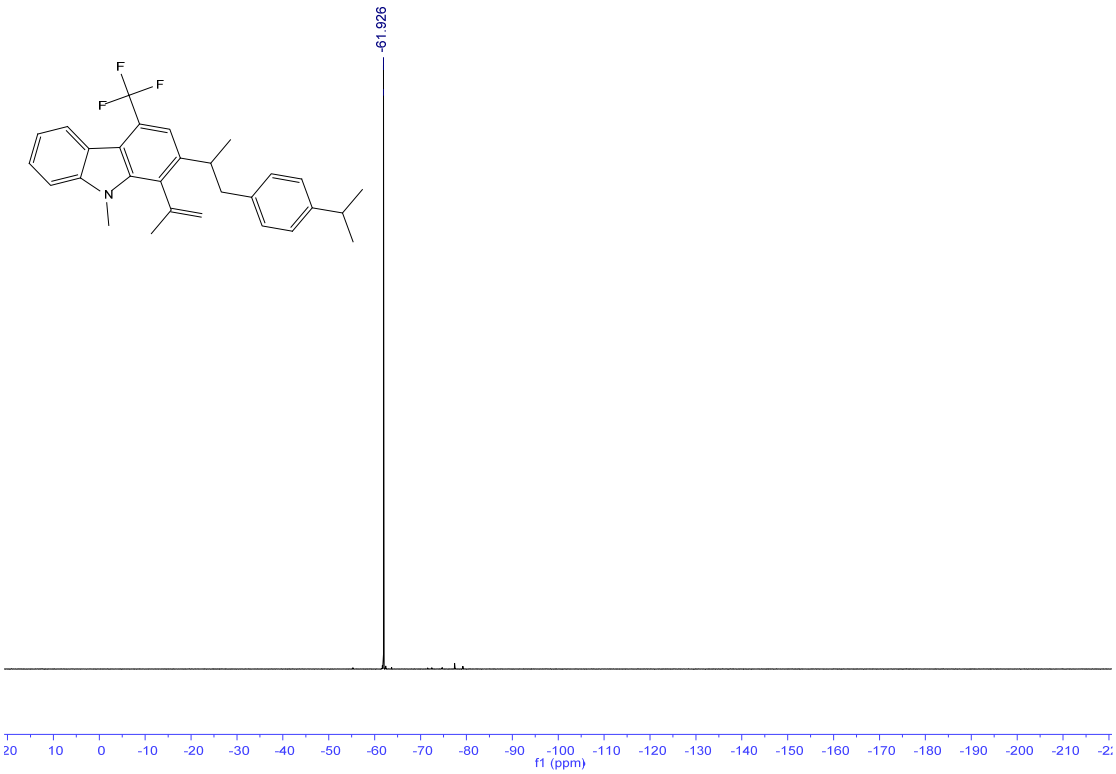
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3ac**



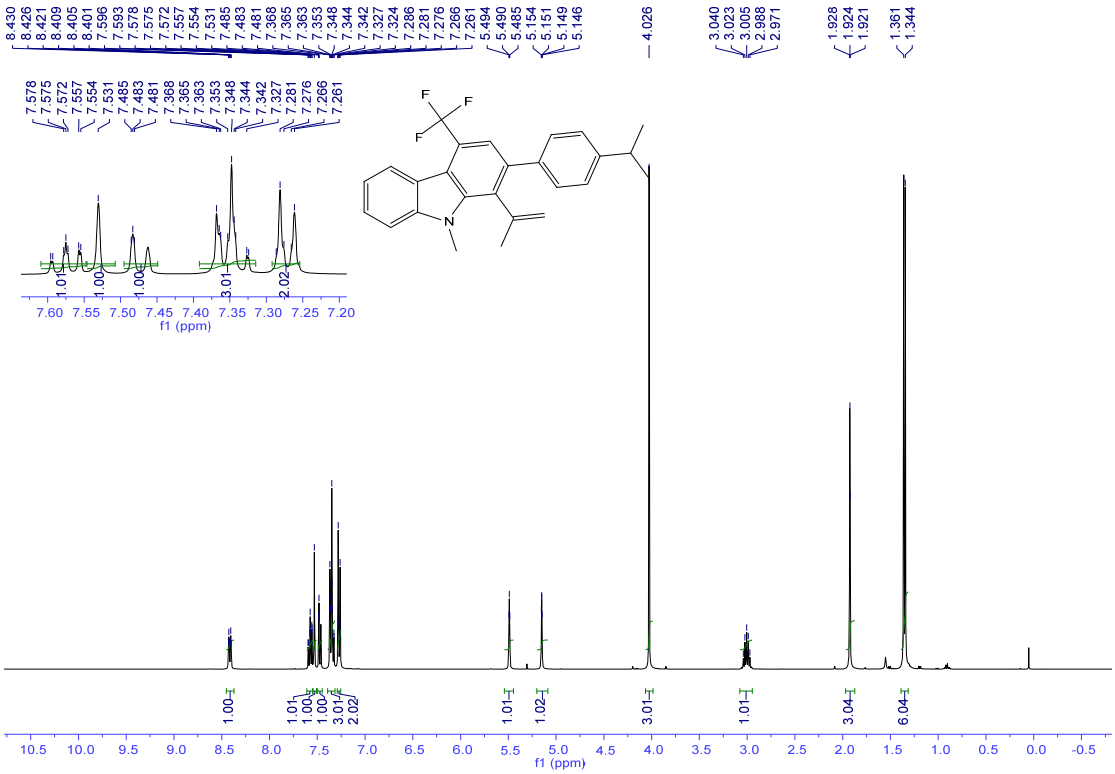
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compounds **3ae** and **3ae'**



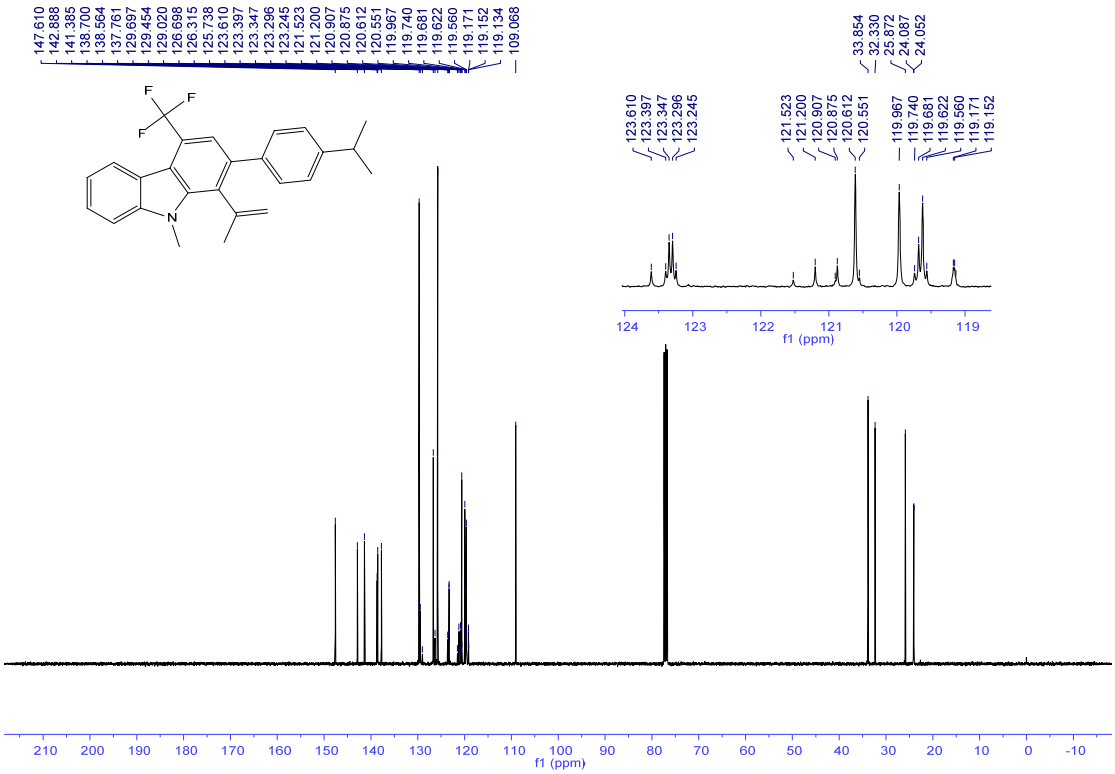
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compounds **3ae** and **3ae'**



^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compounds **3ae** and **3ae'**

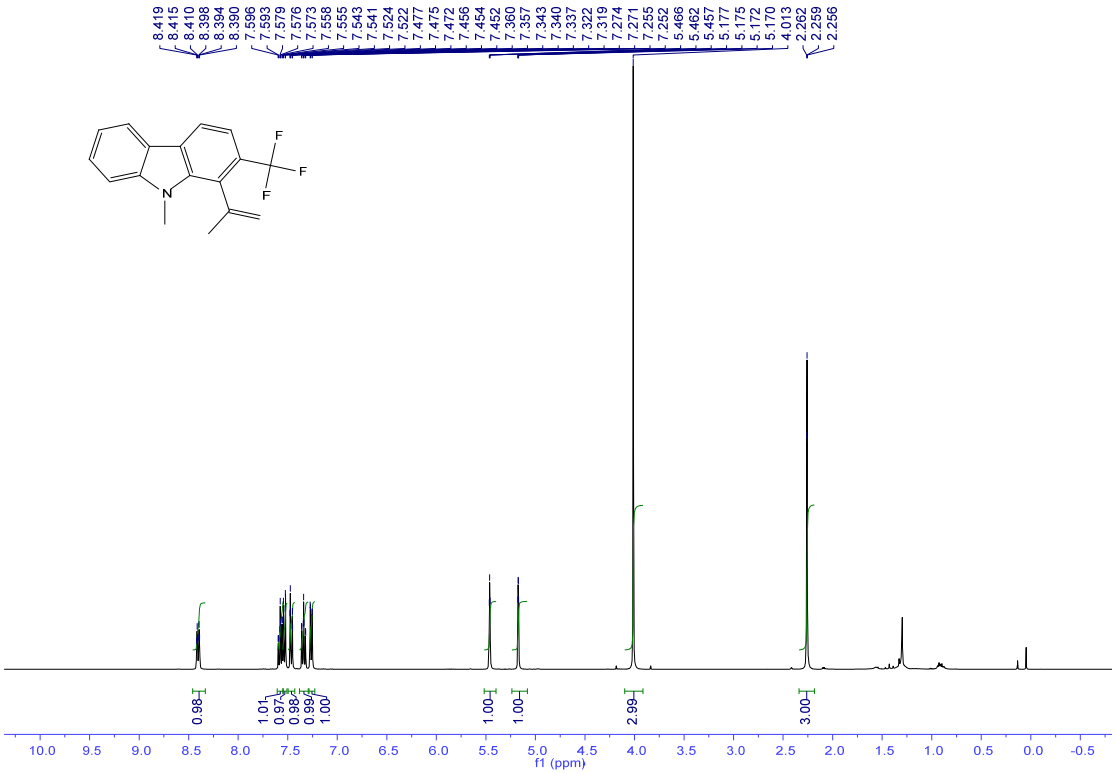


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3af**

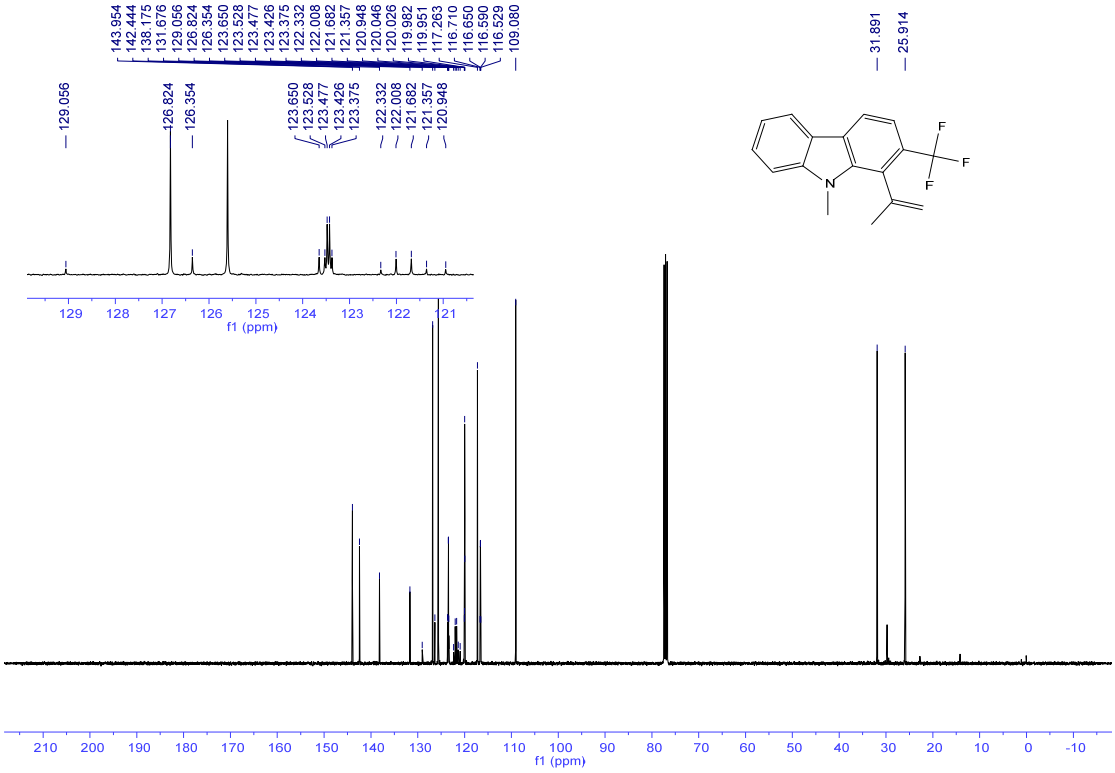


$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3af**

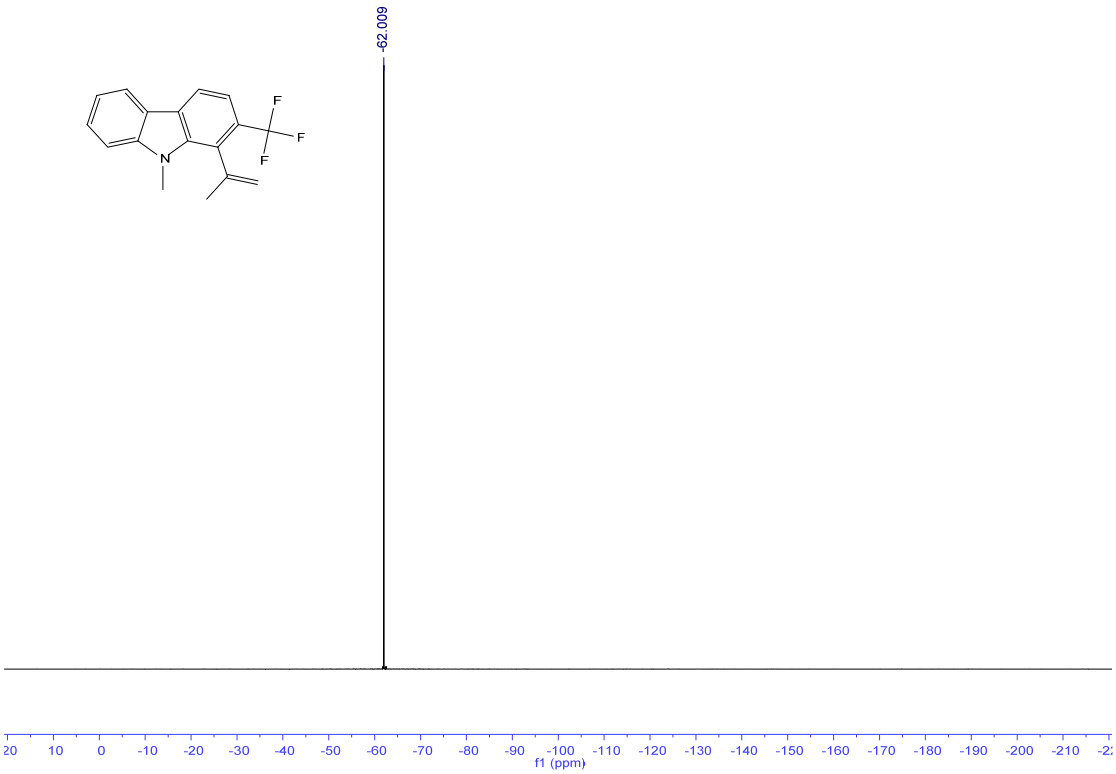
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3af**



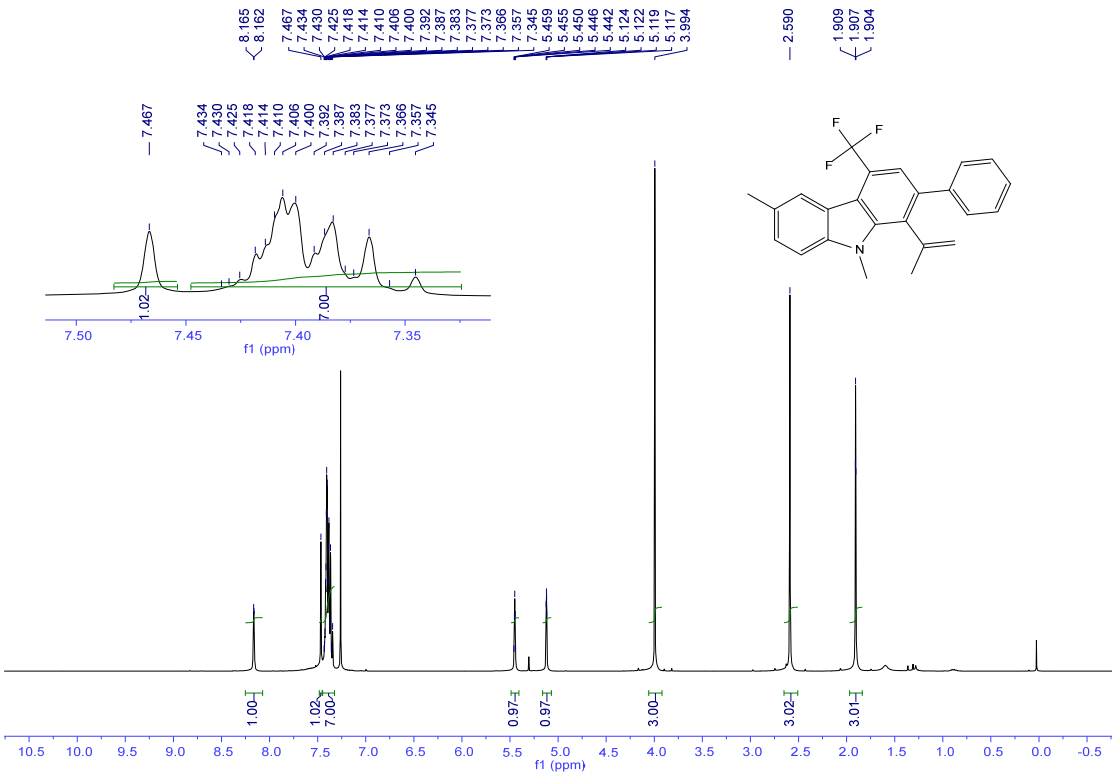
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ag**



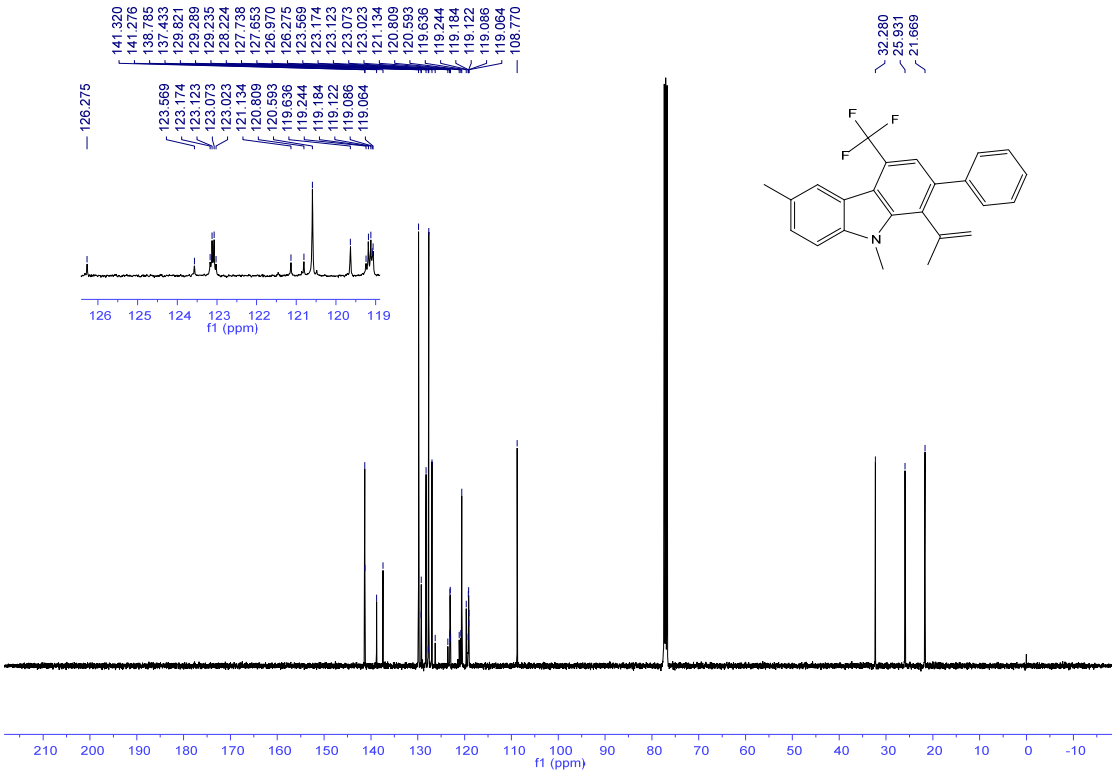
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of compound **3ag**



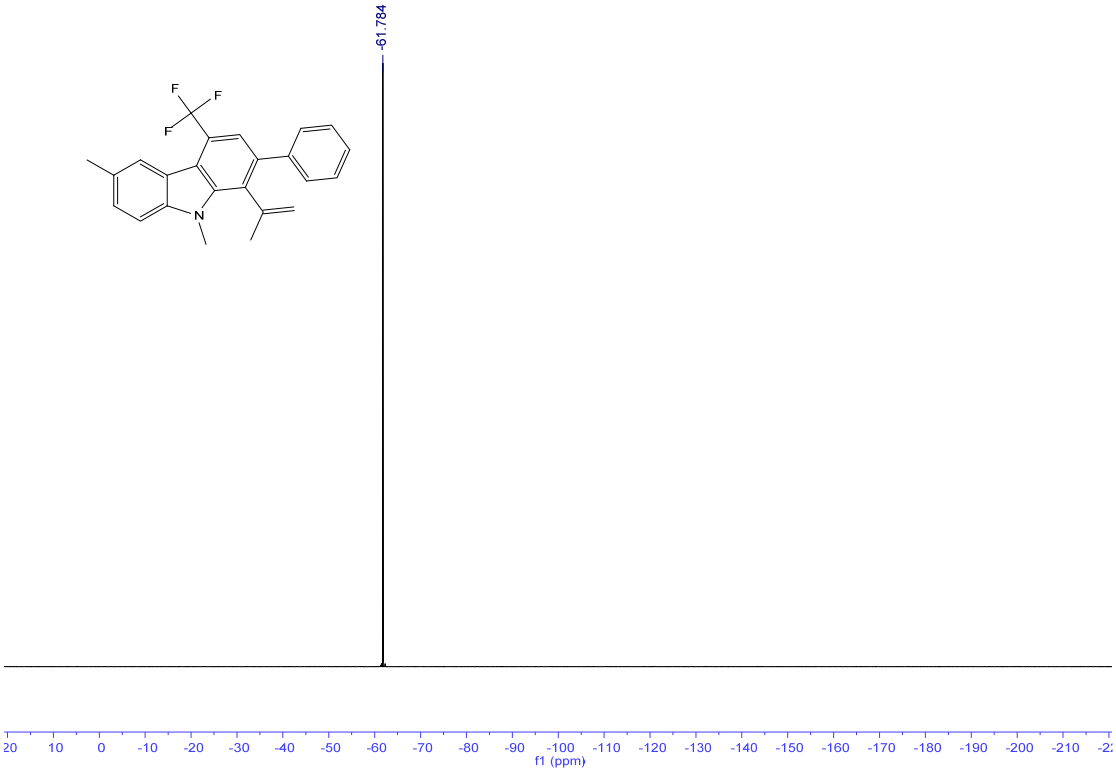
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3ag**



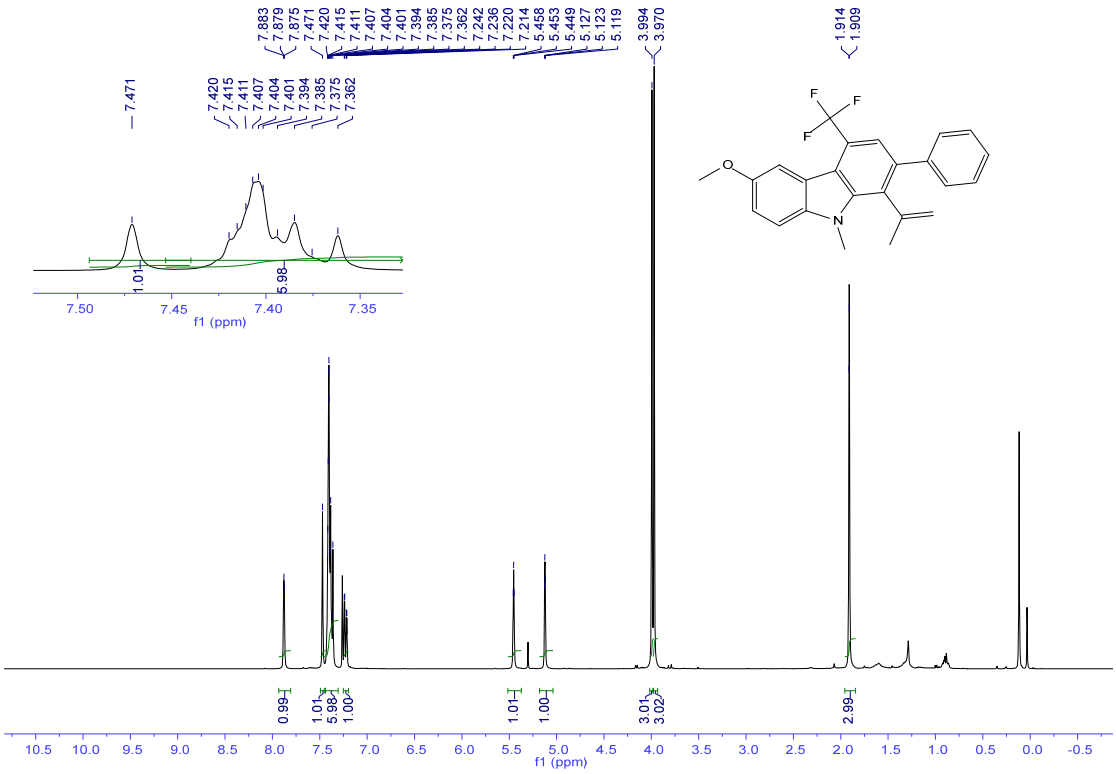
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ah**



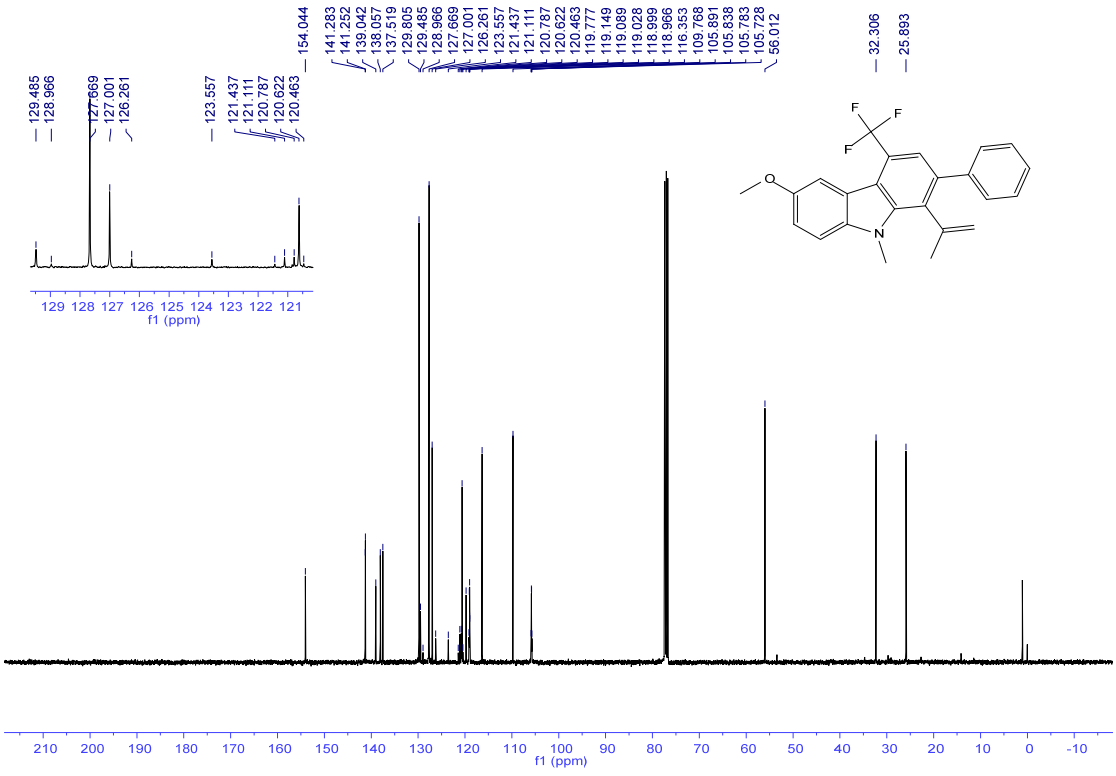
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3ah**



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

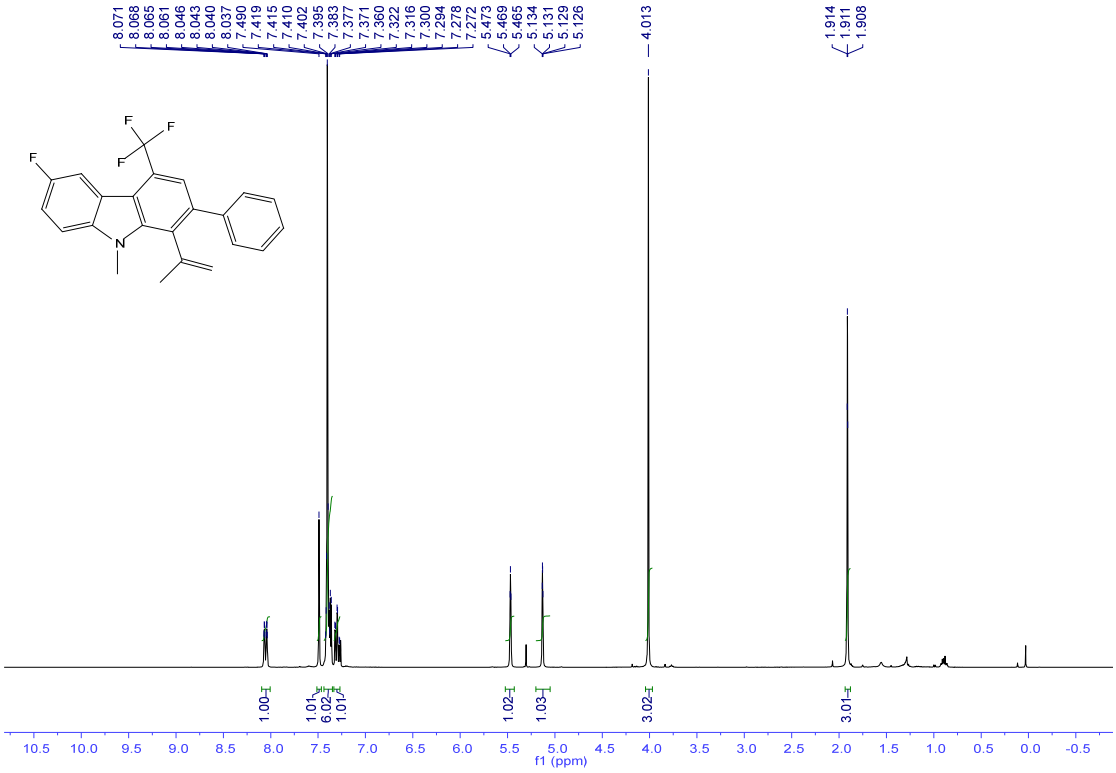


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ai**

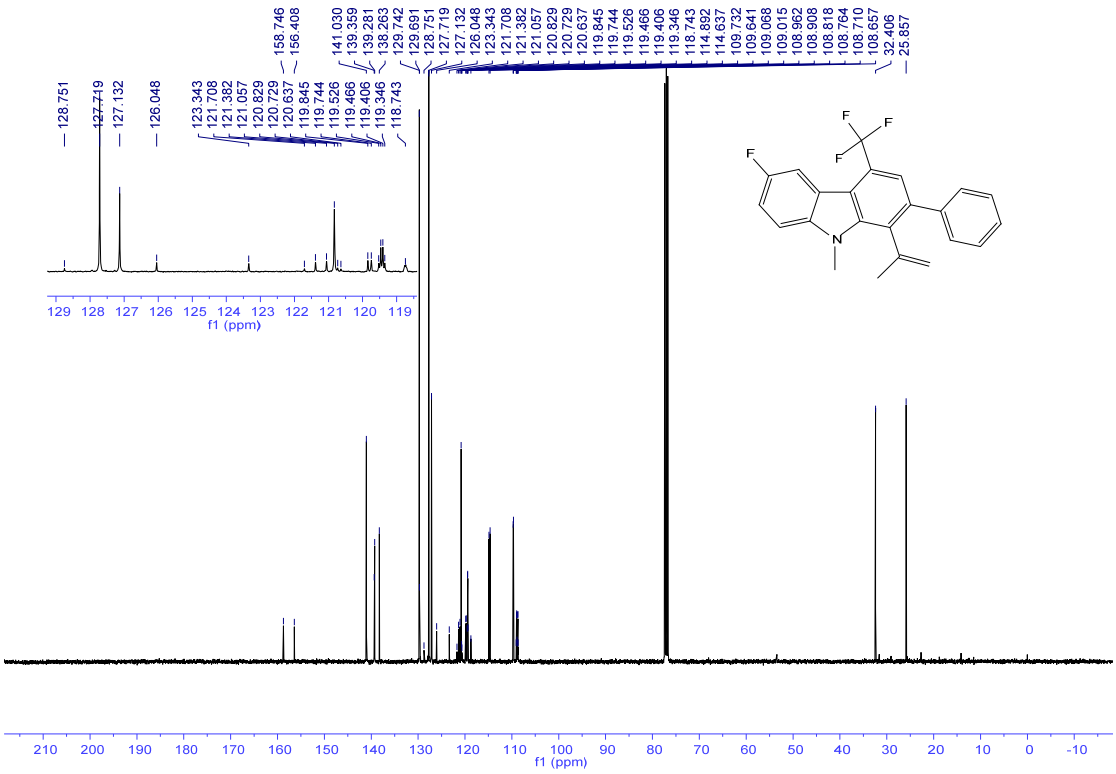


$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3ai**

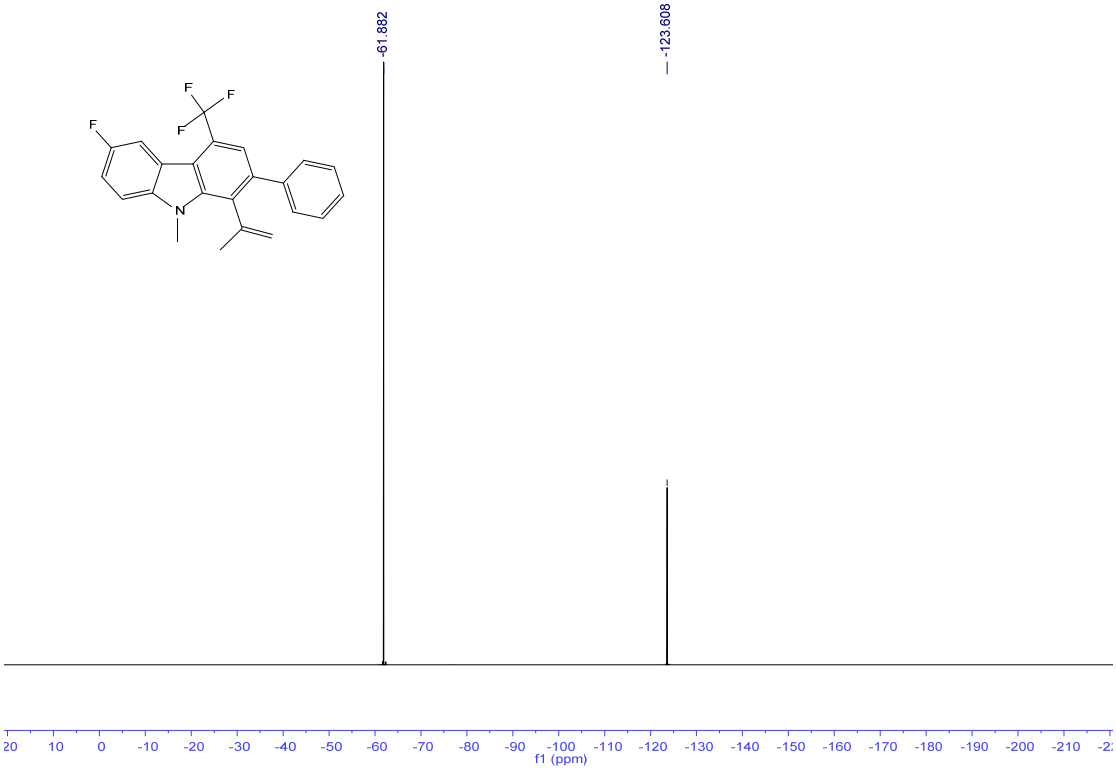
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3ai**



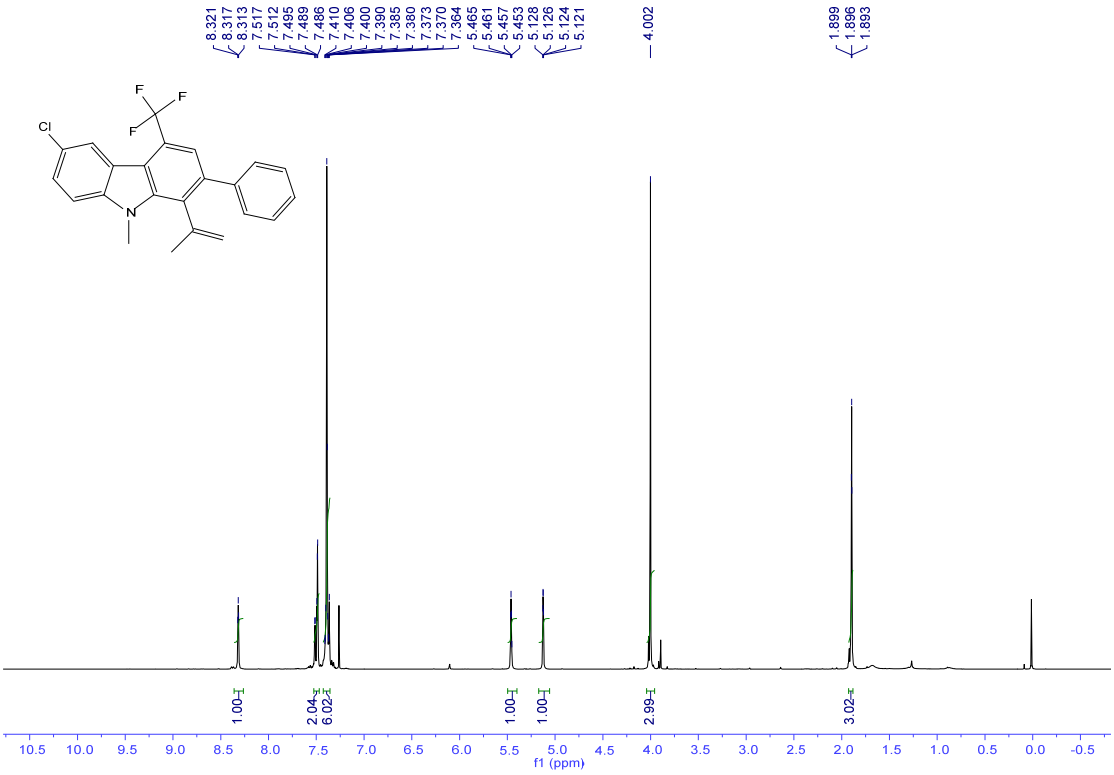
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3aj**



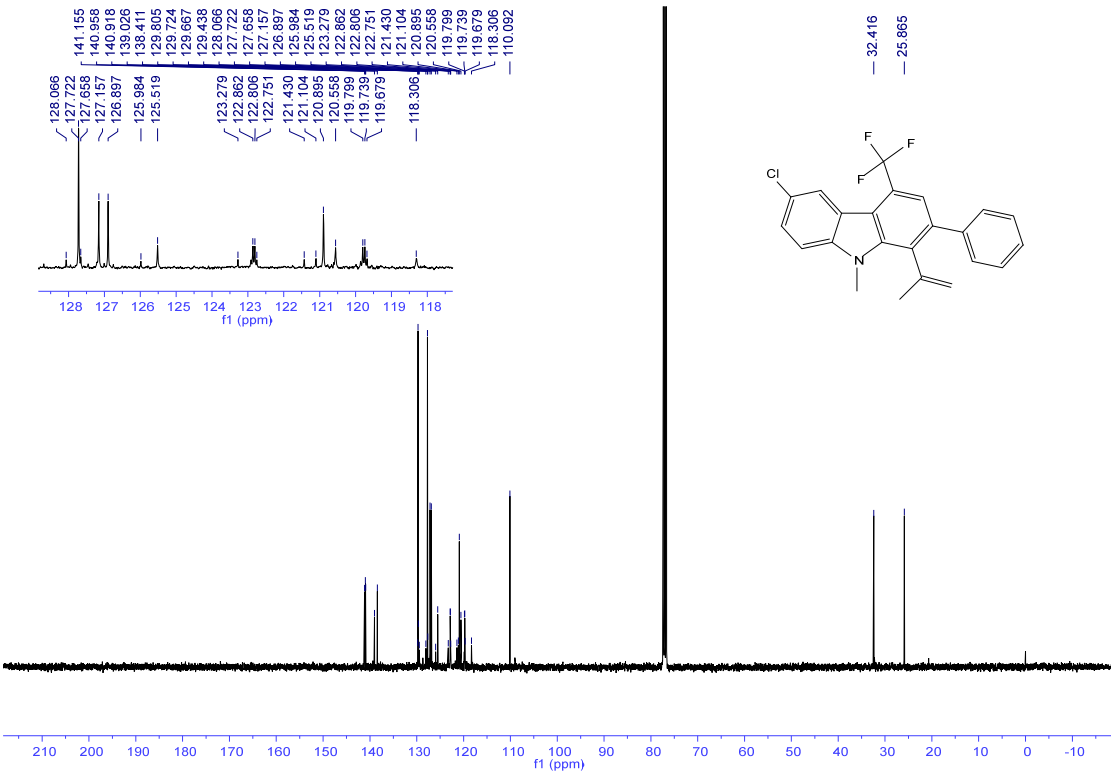
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3aj**



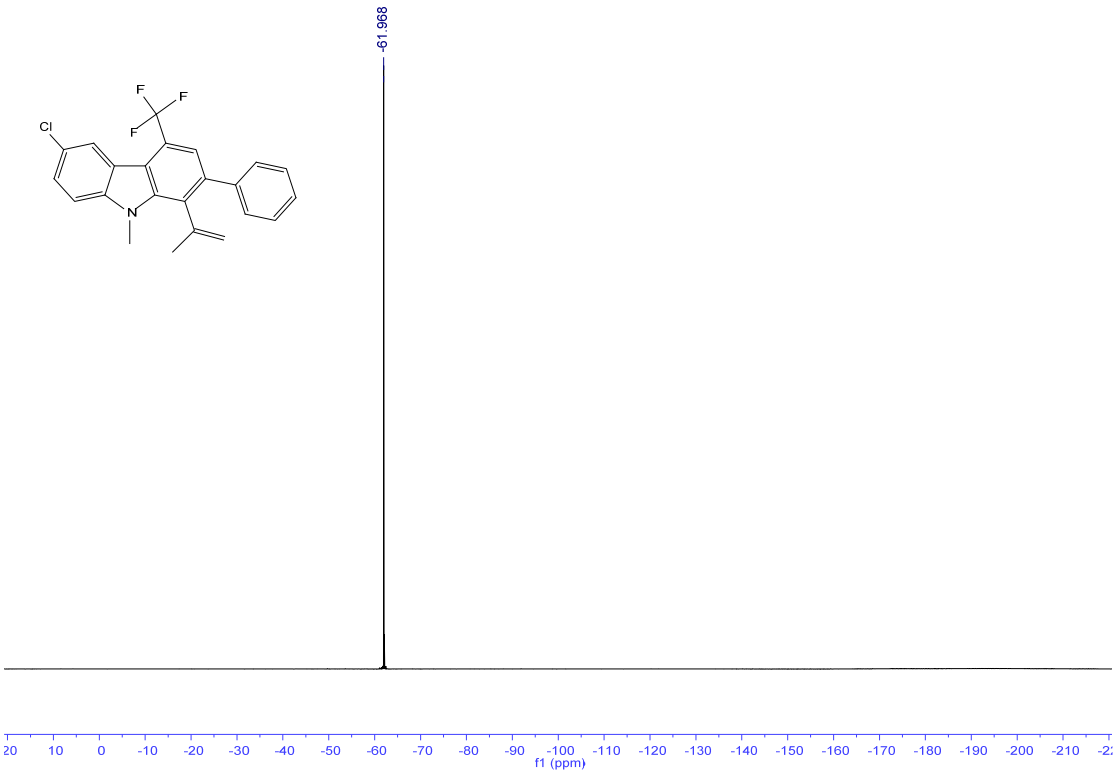
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3aj**



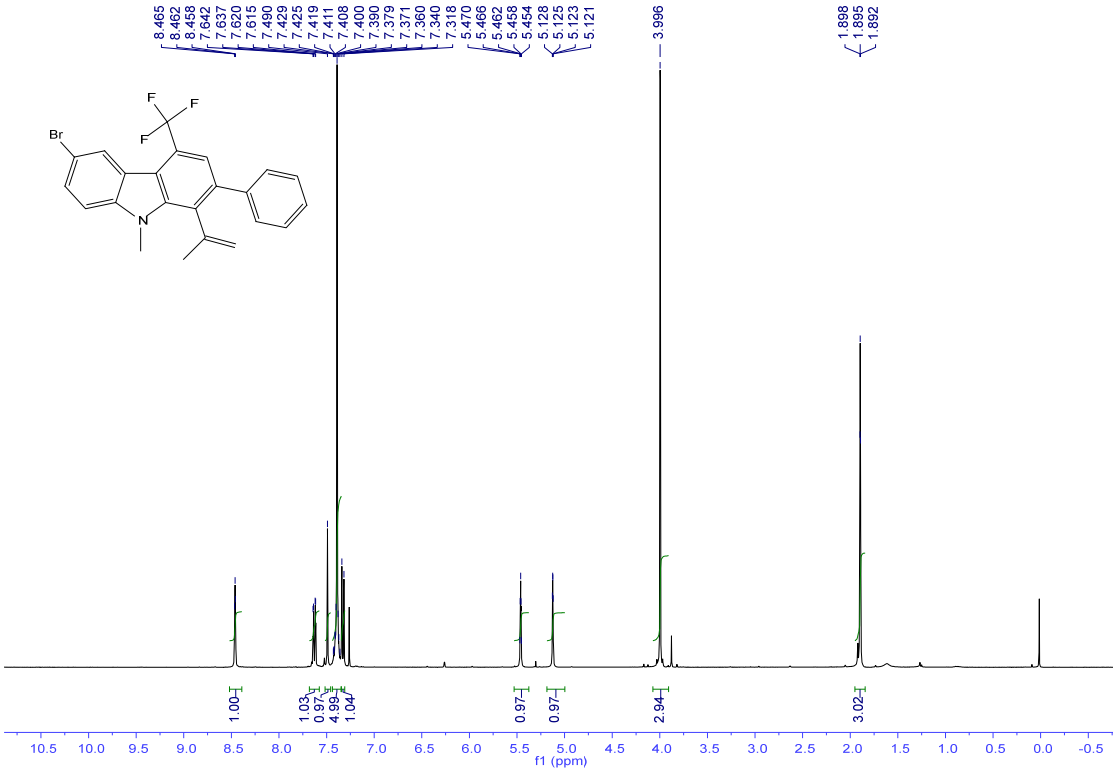
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ak**



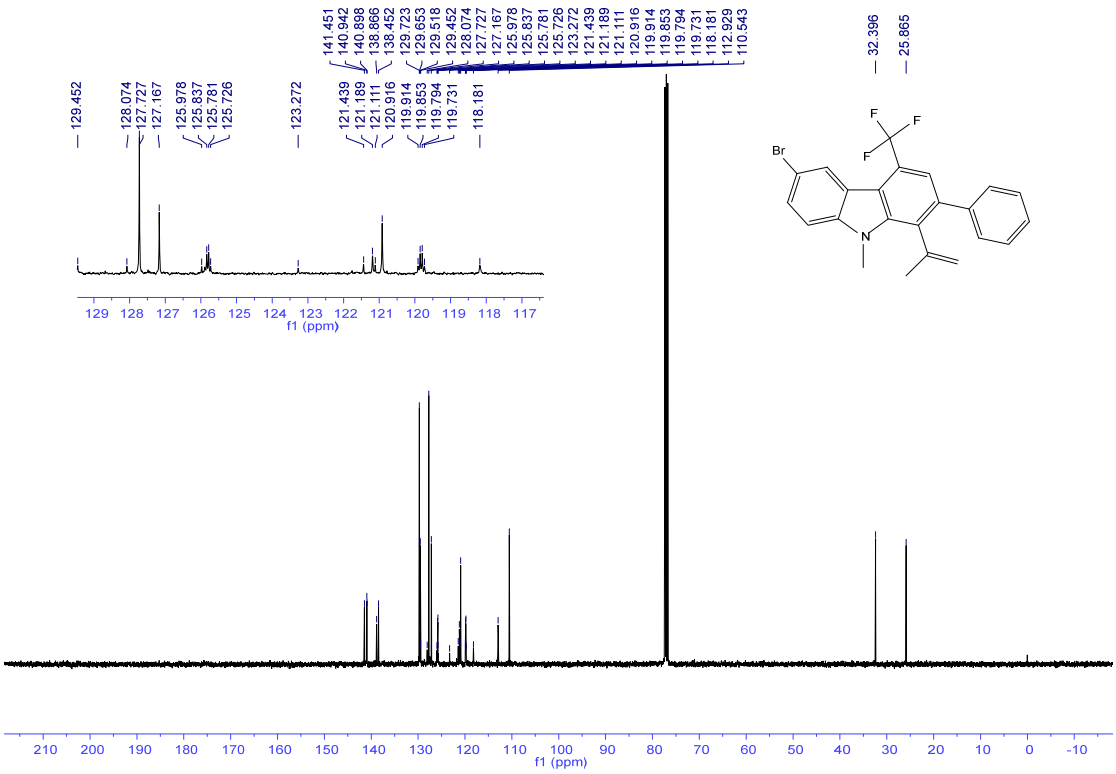
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of compound **3ak**



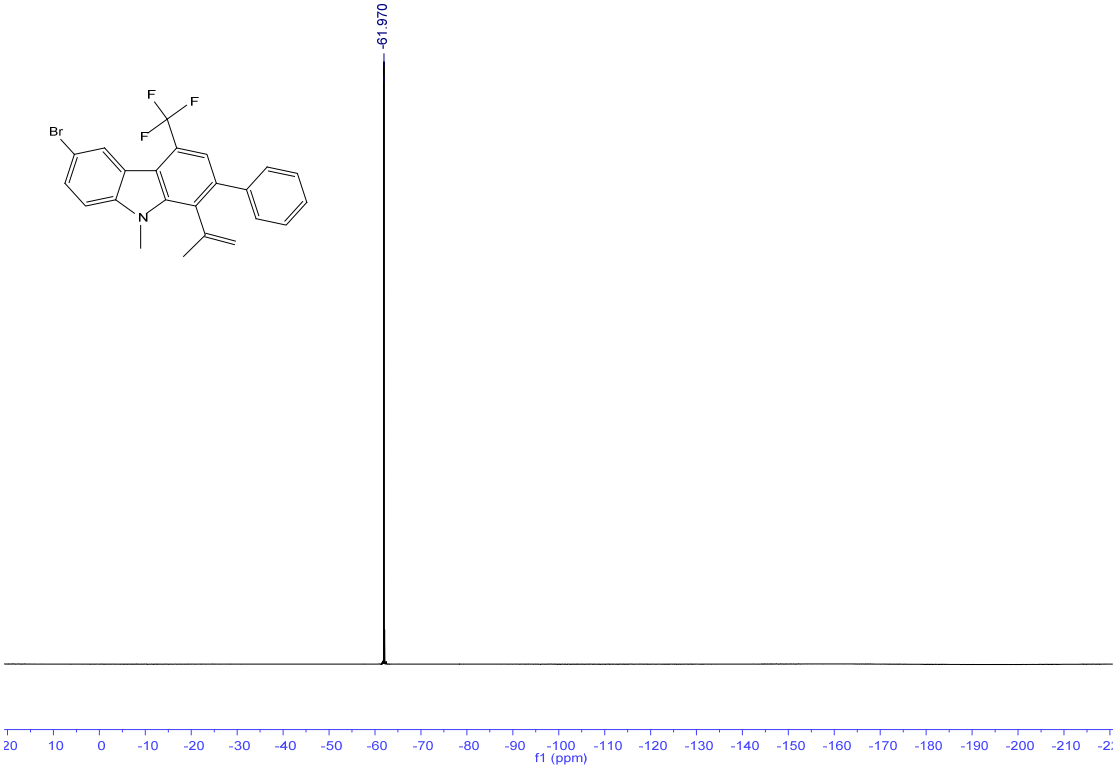
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3ak**



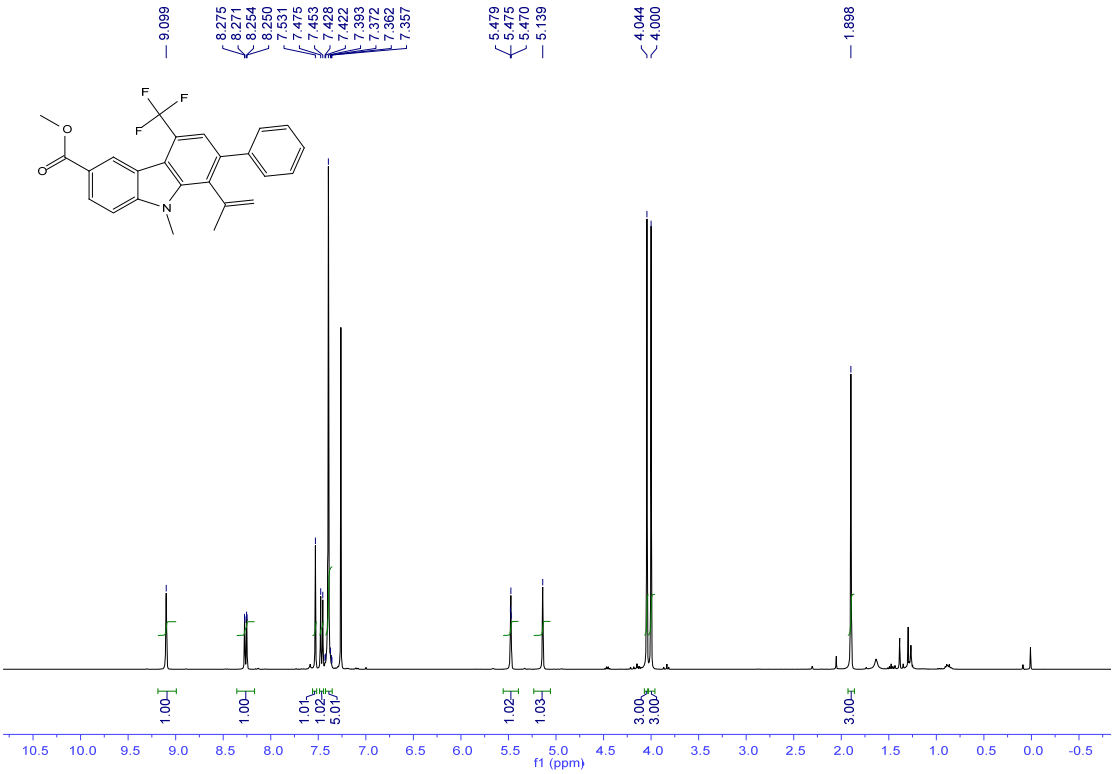
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3al**



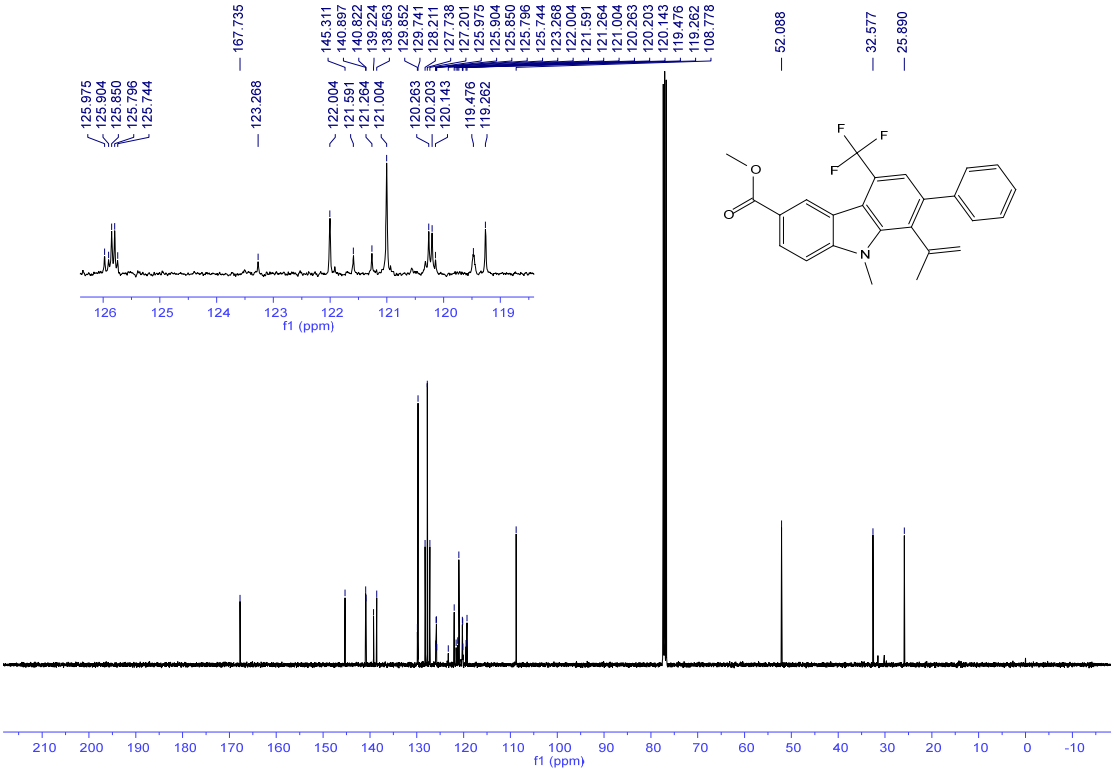
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3al**



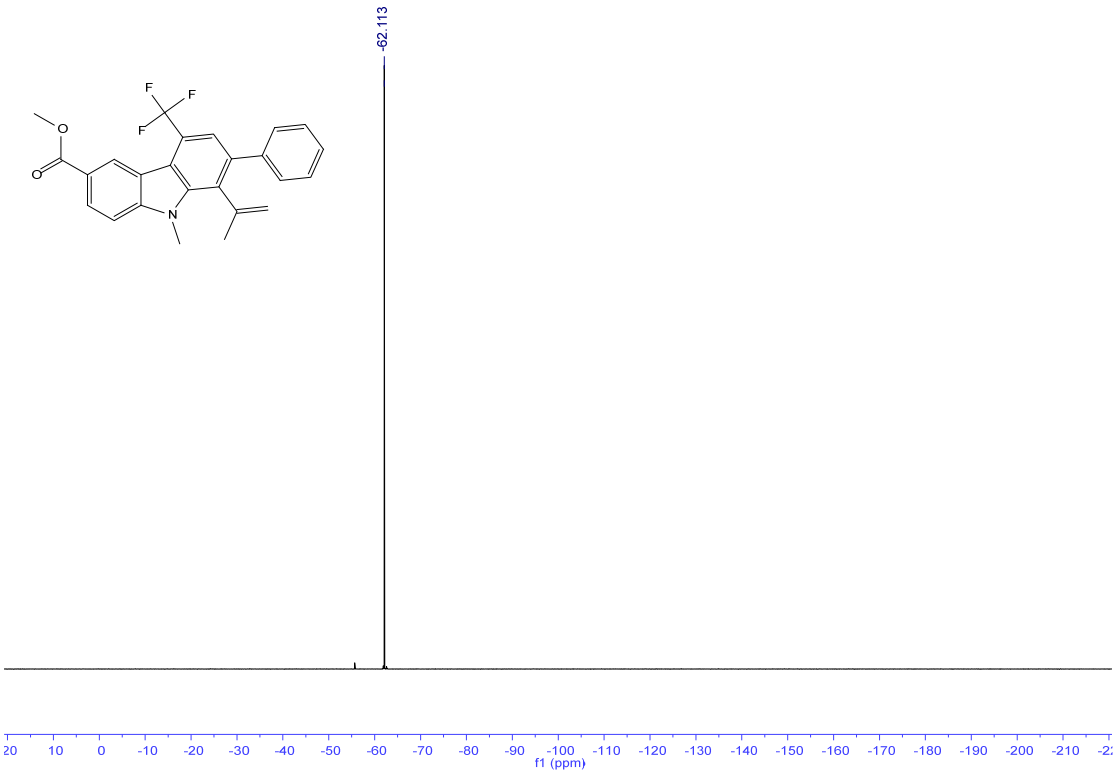
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3al**



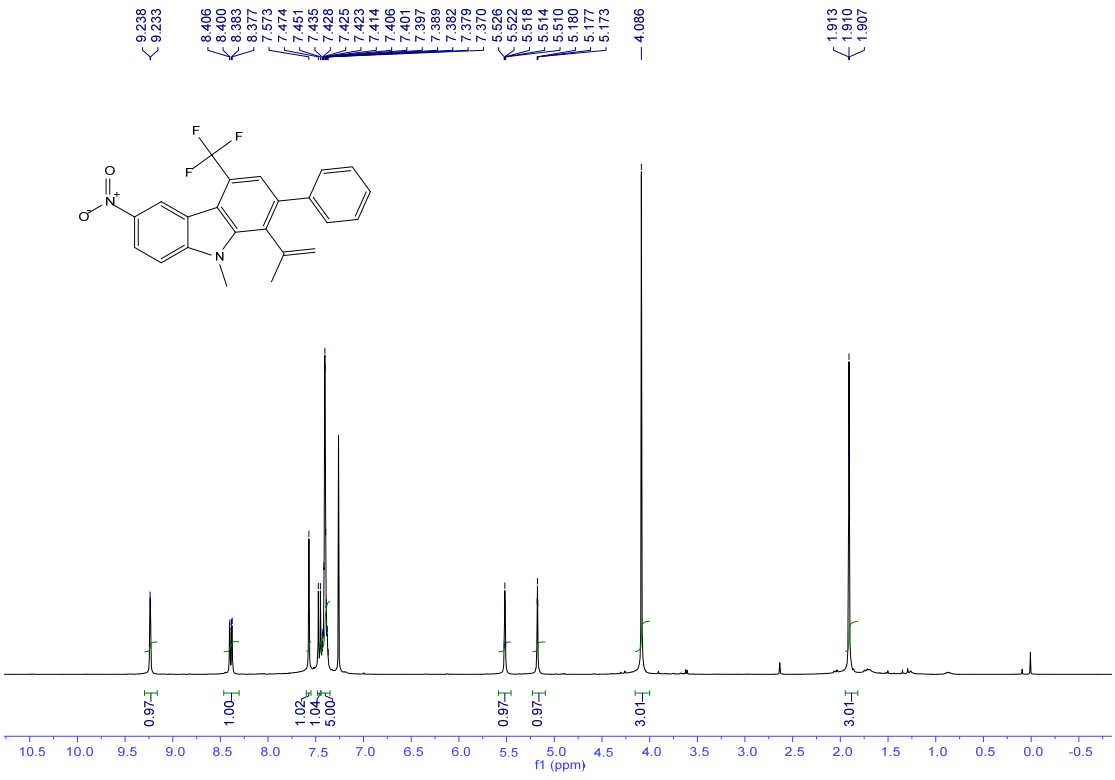
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3am**



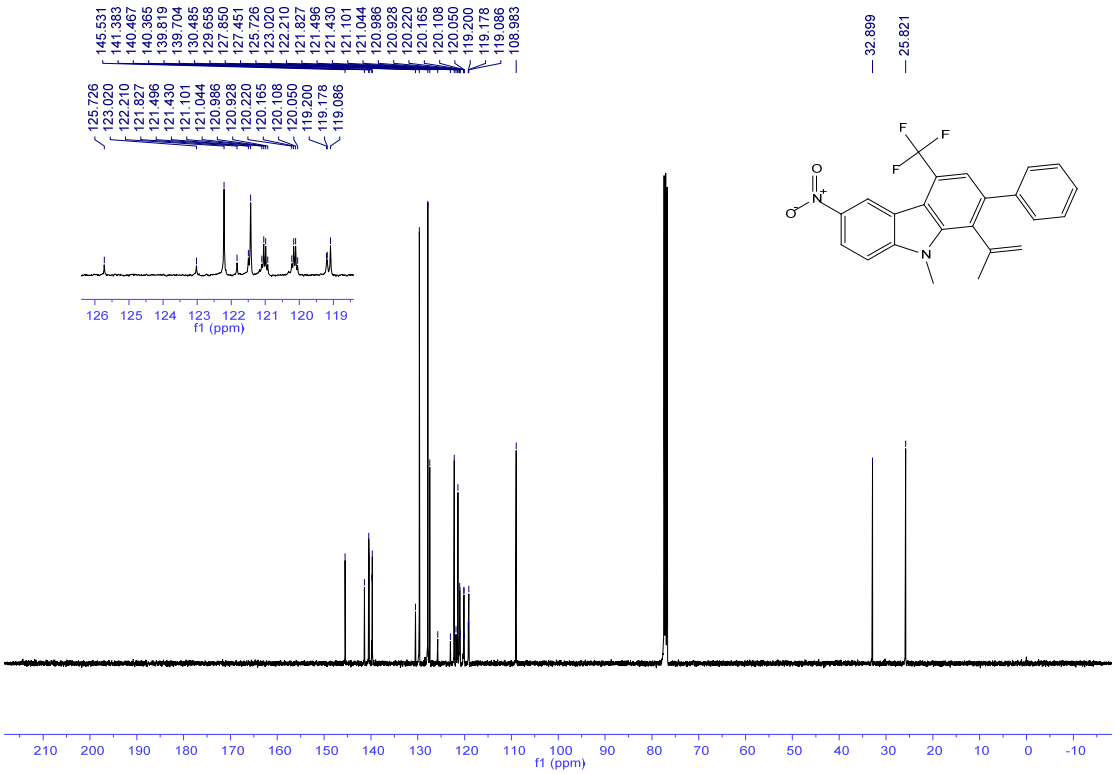
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of compound **3am**



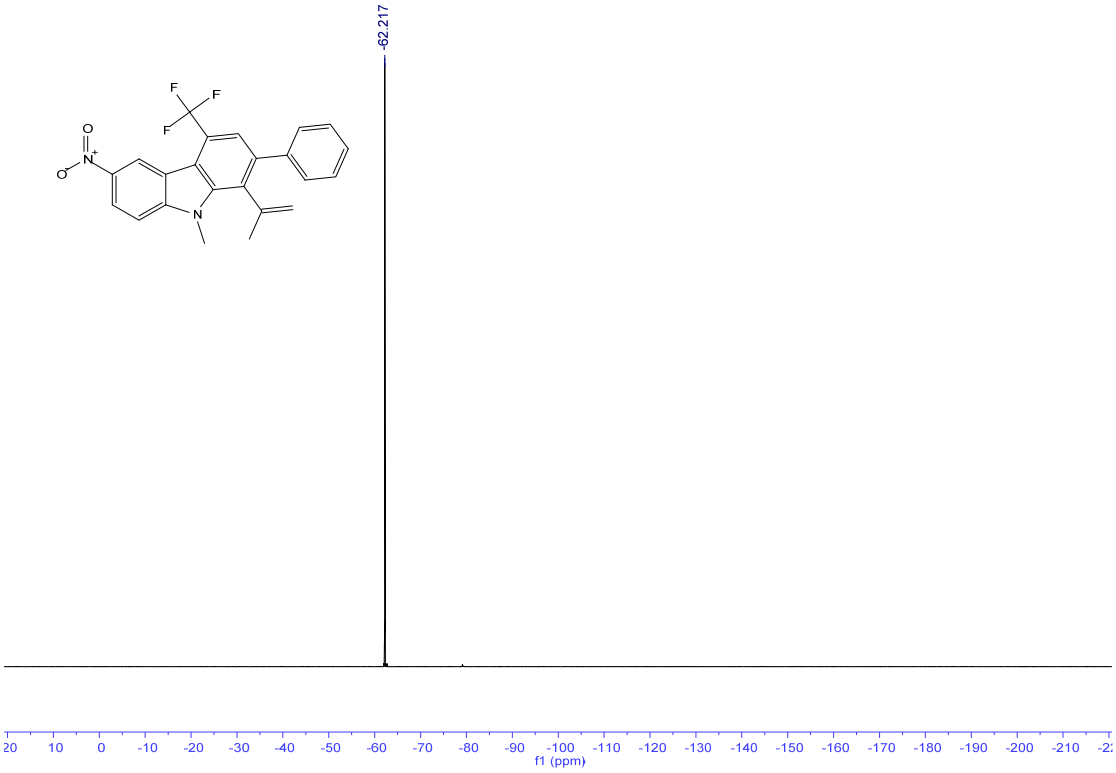
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3am**



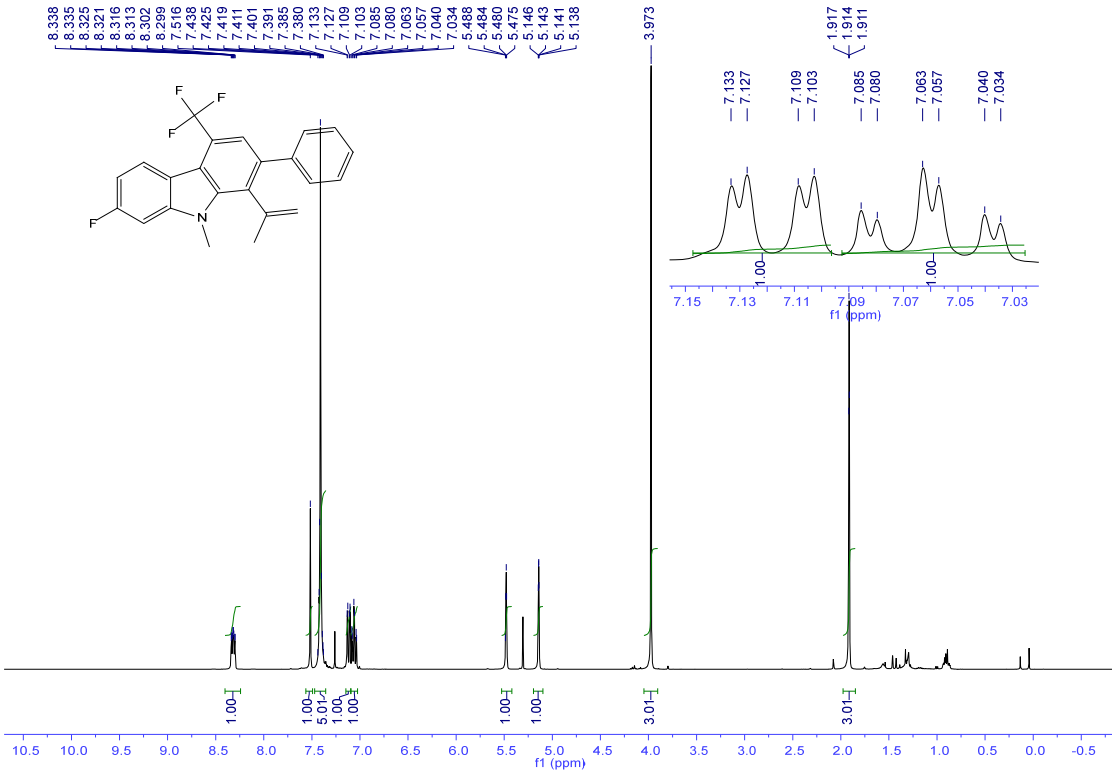
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3an**



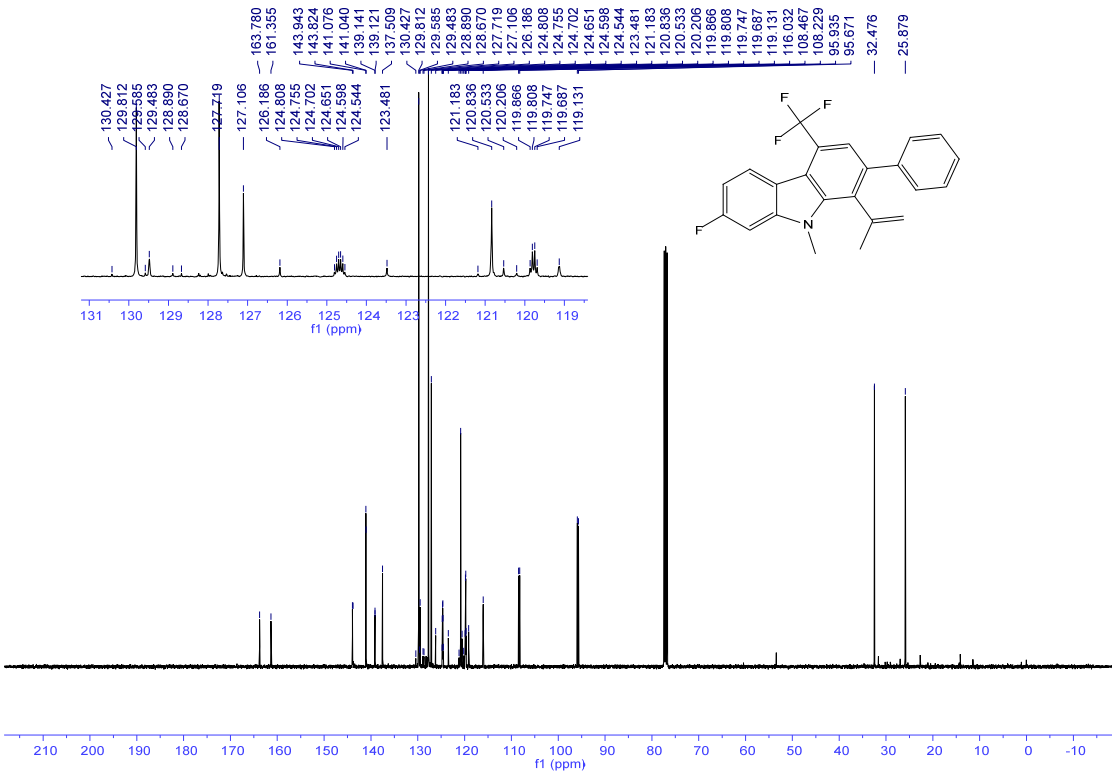
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3an**



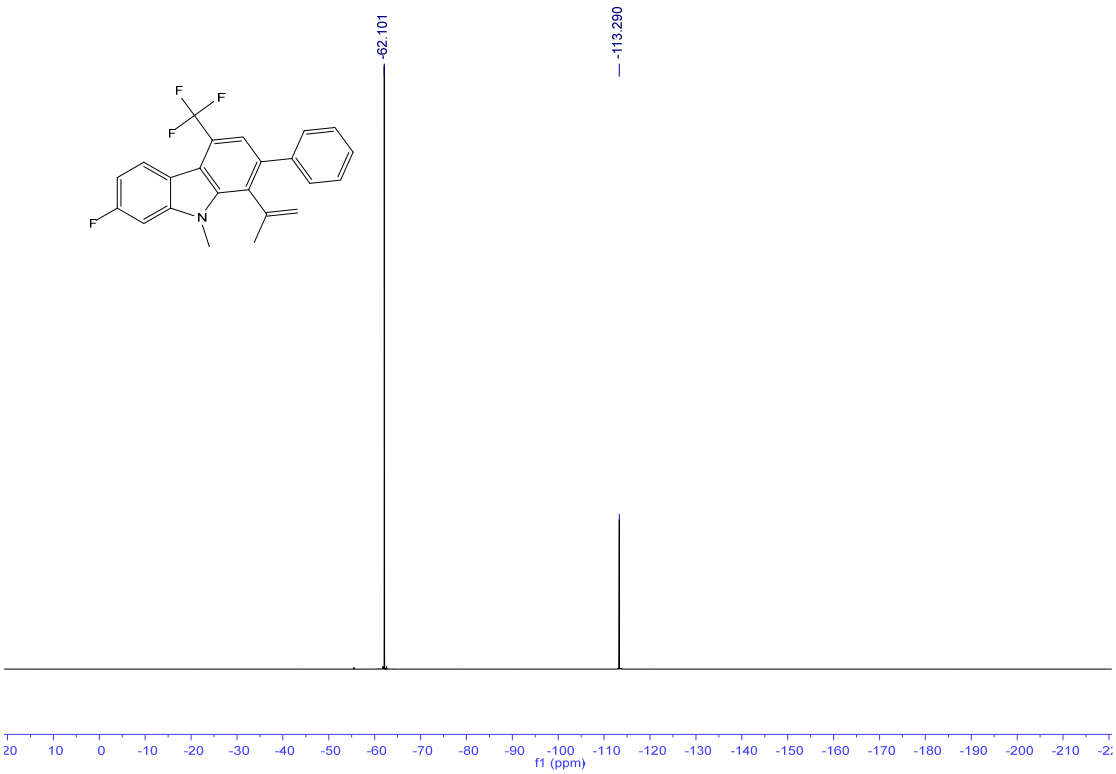
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3an**



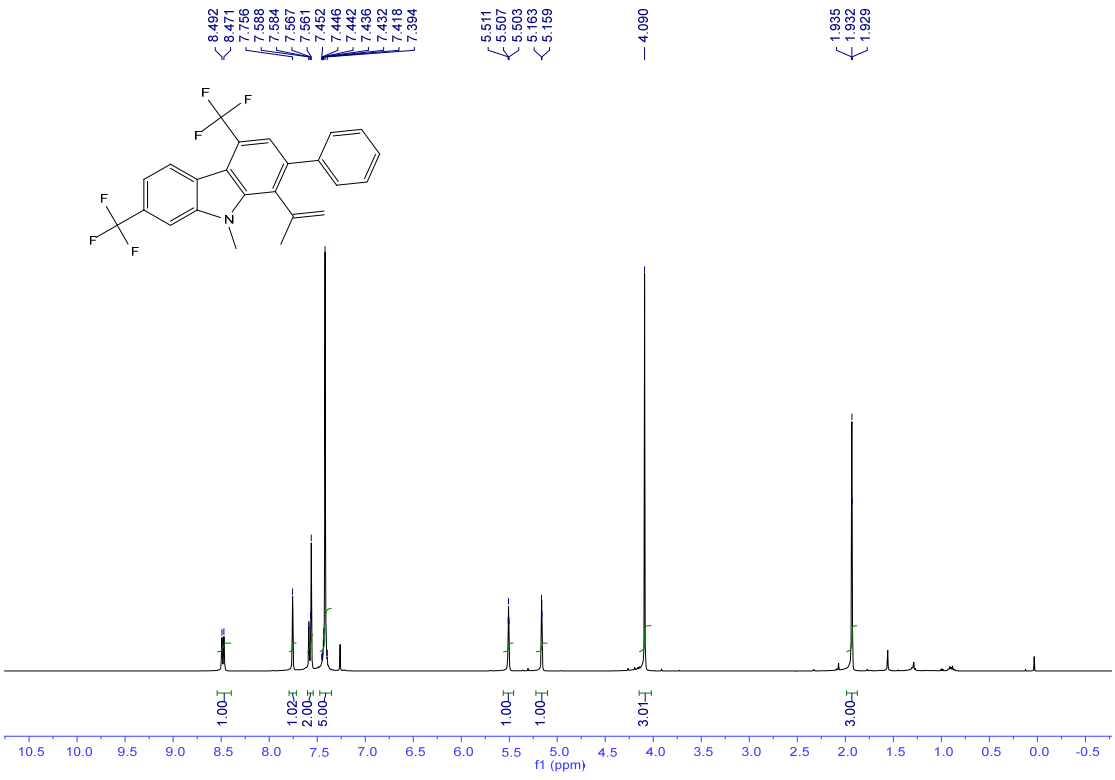
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ao**



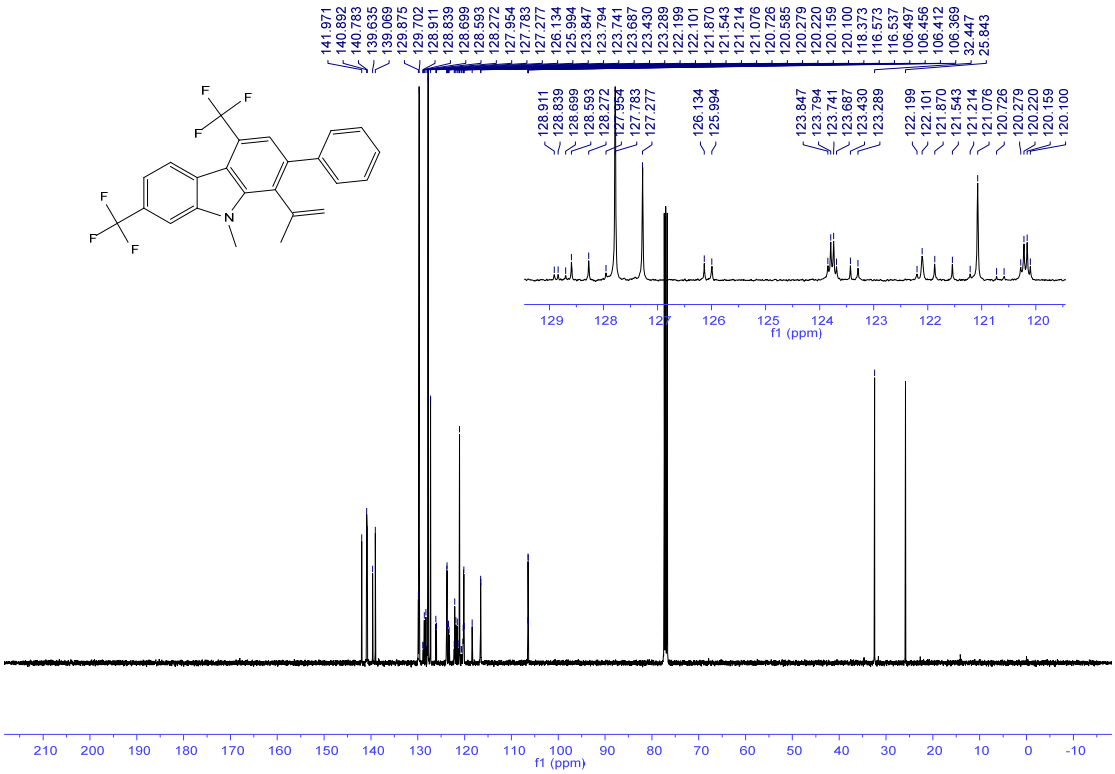
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3ao**



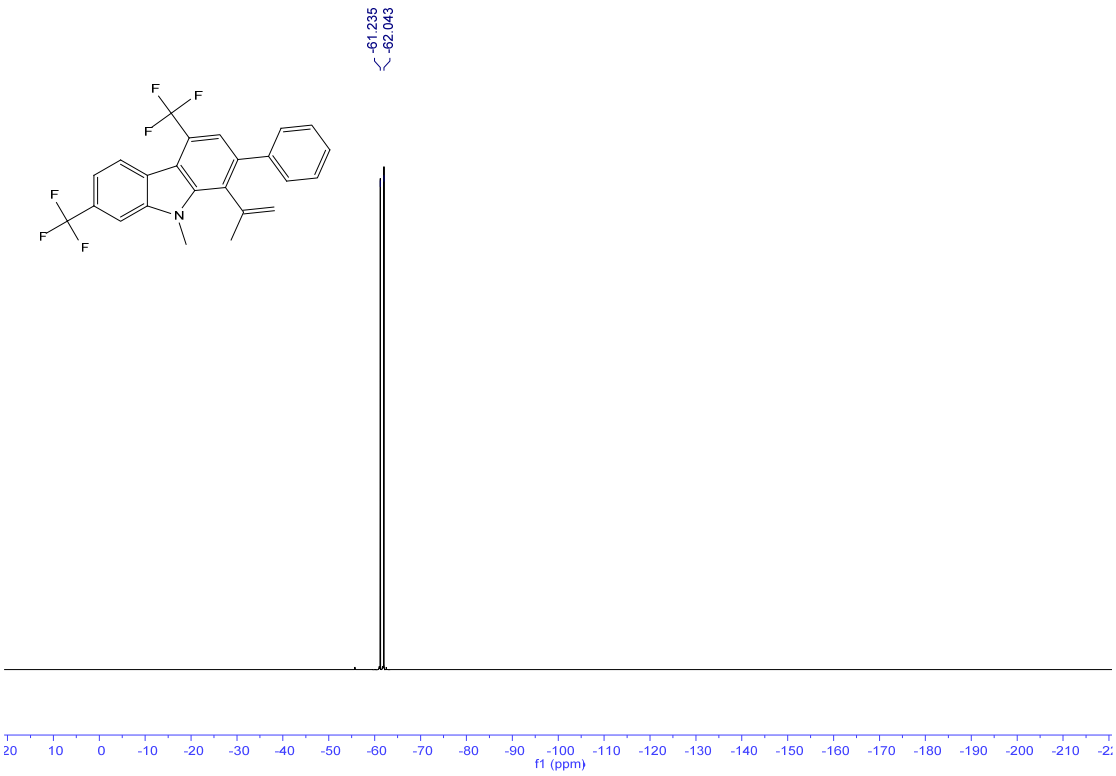
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3ao**



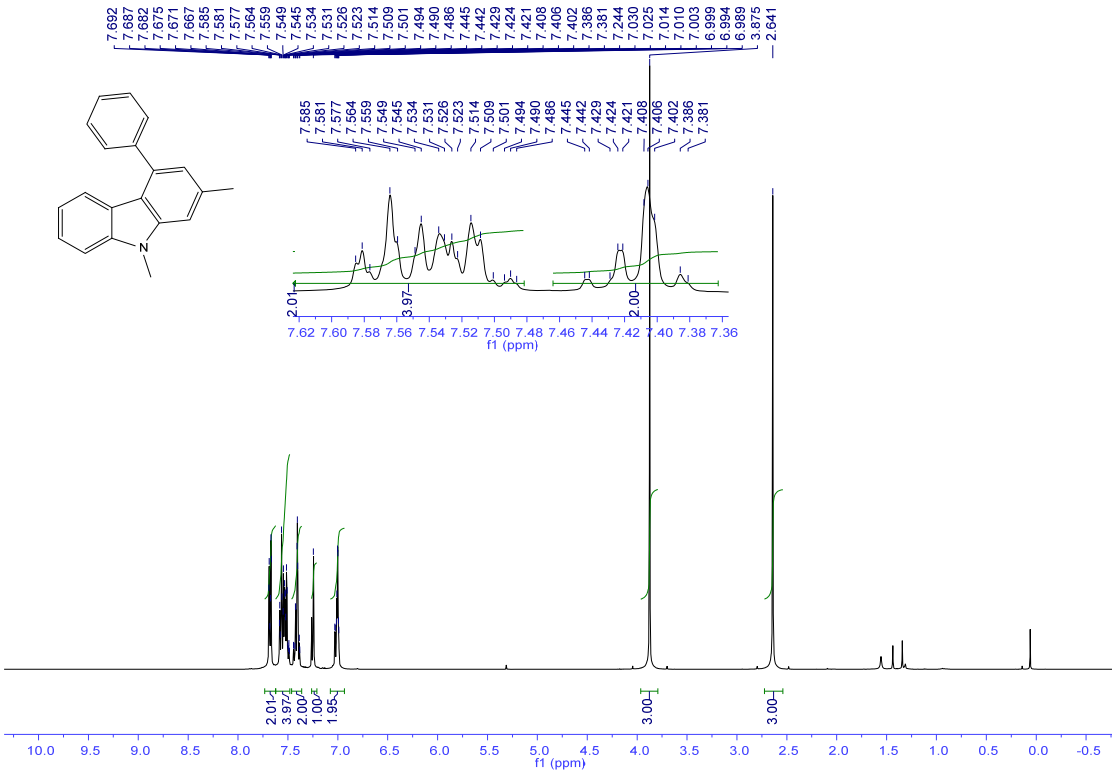
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ap**



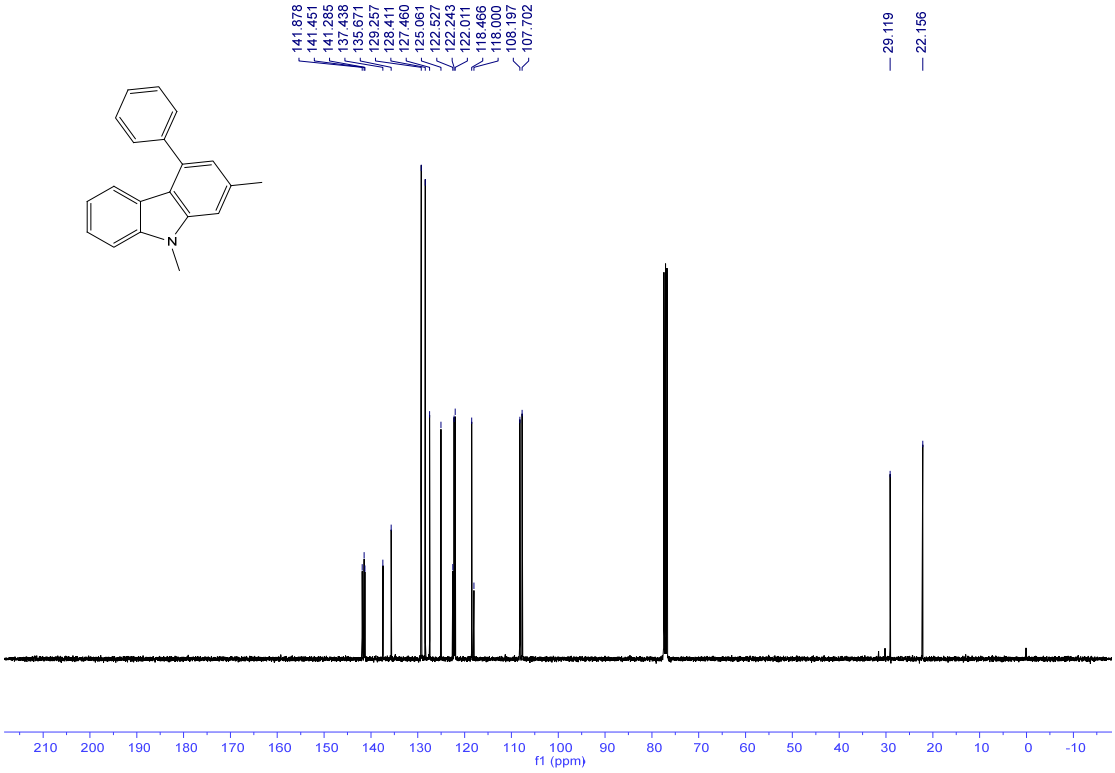
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3ap**



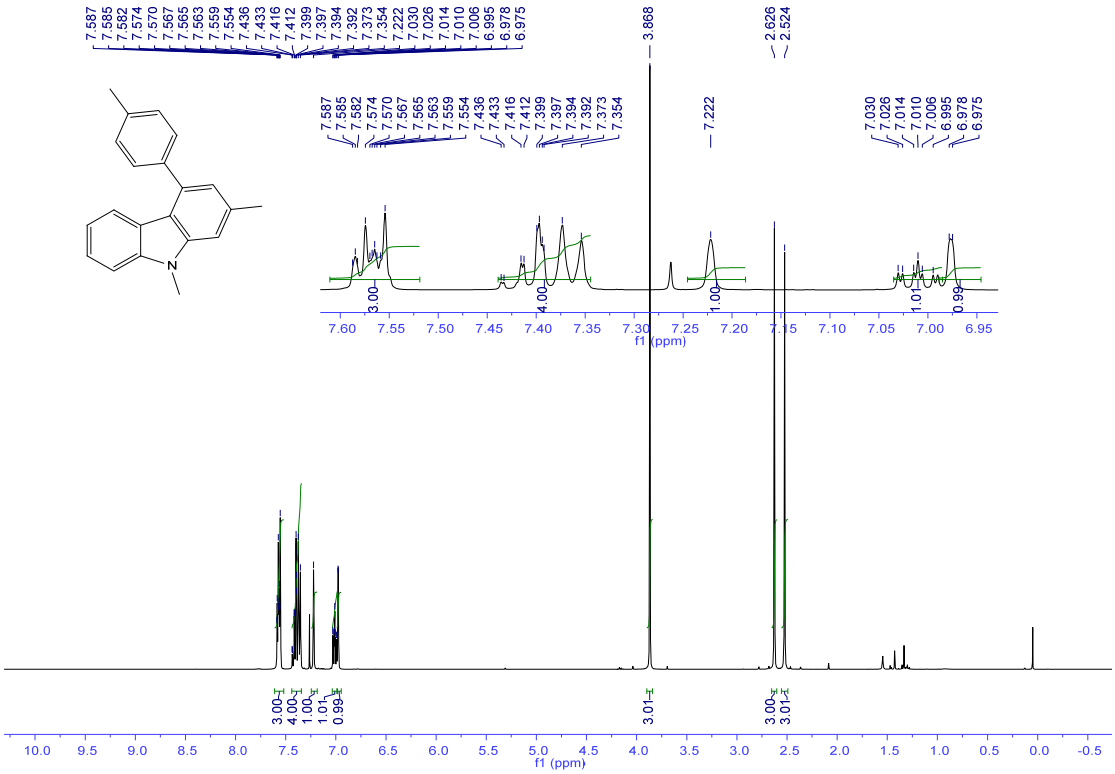
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3ap**



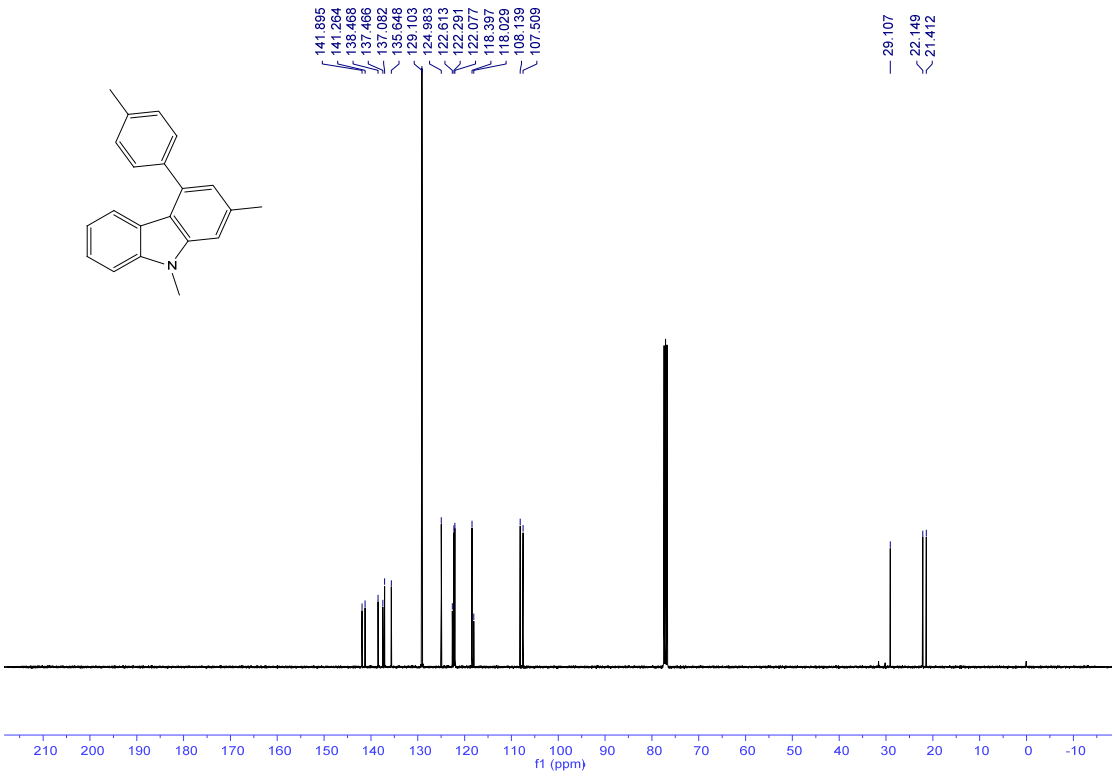
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5a**



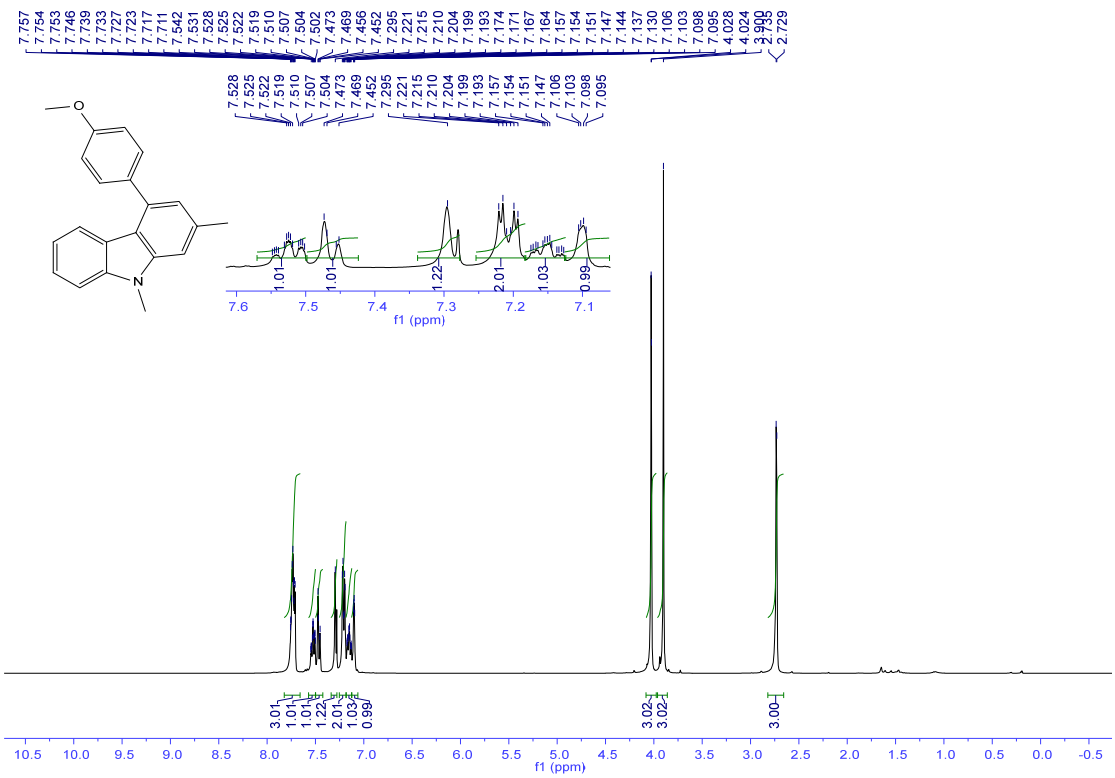
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **5a**



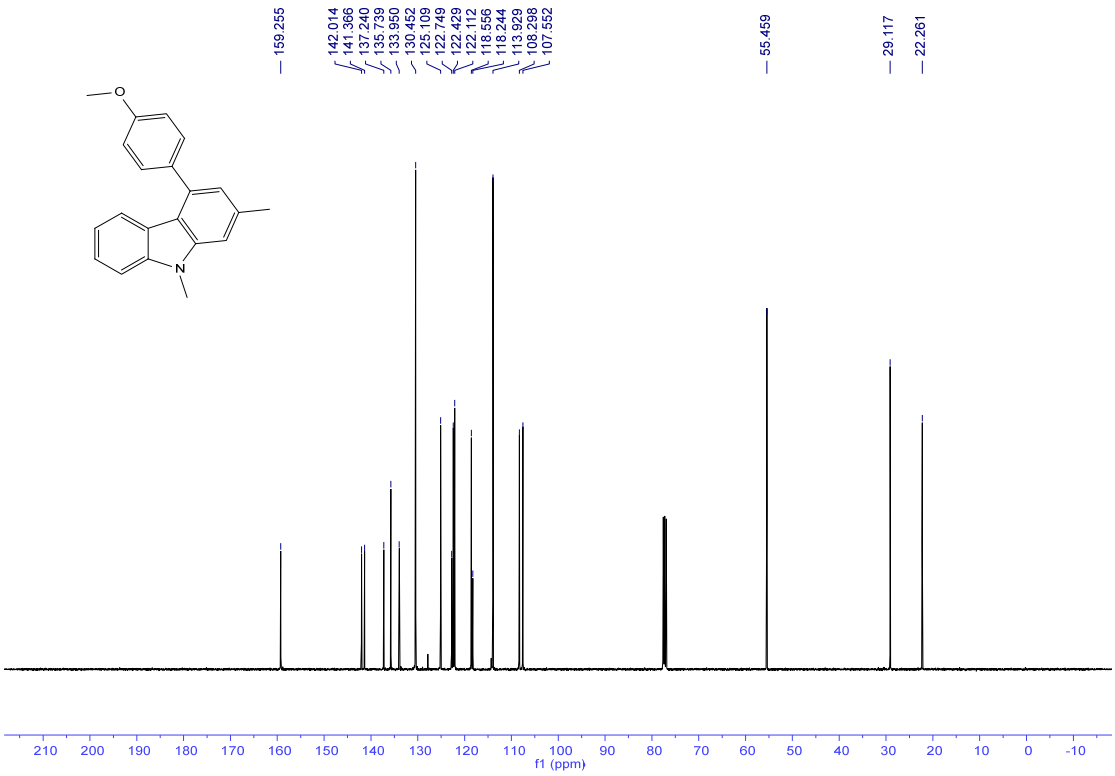
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5c**



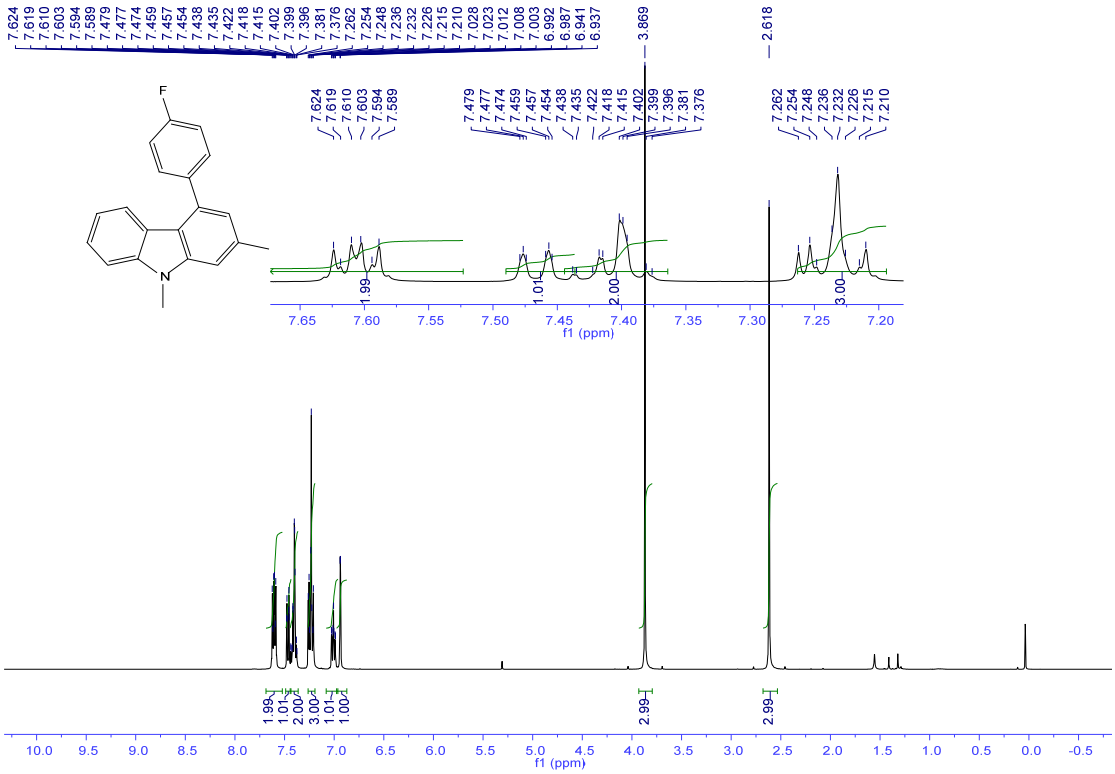
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **5c**



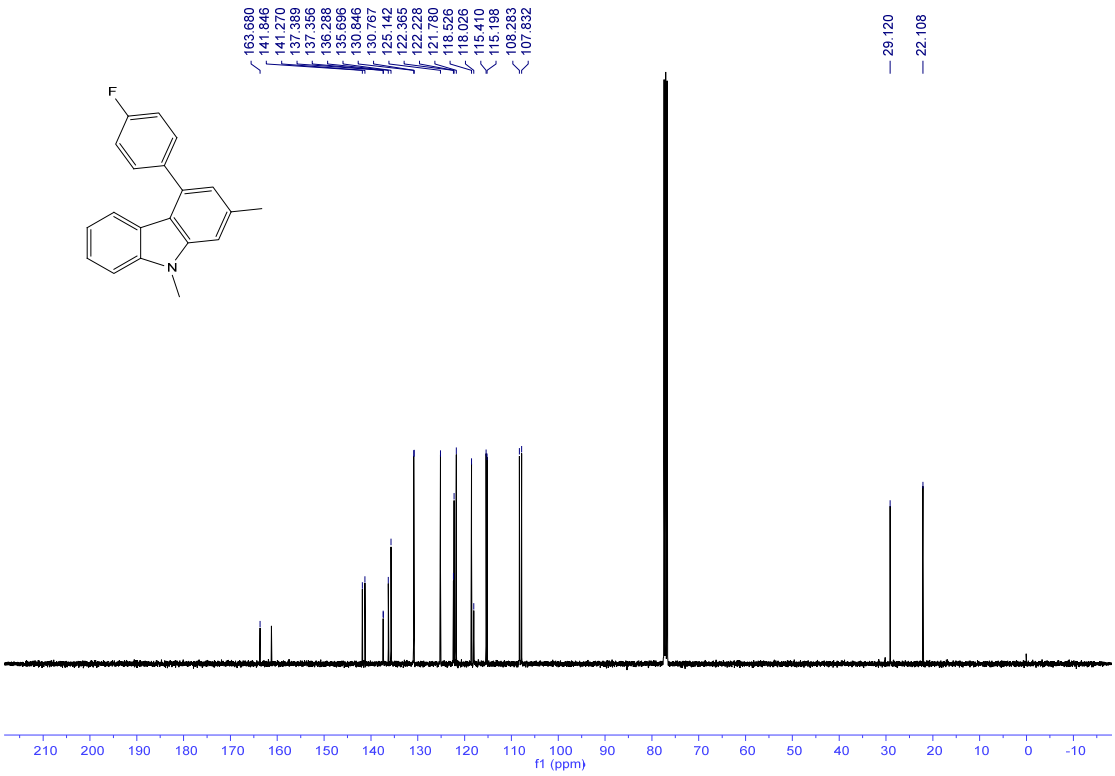
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5d**



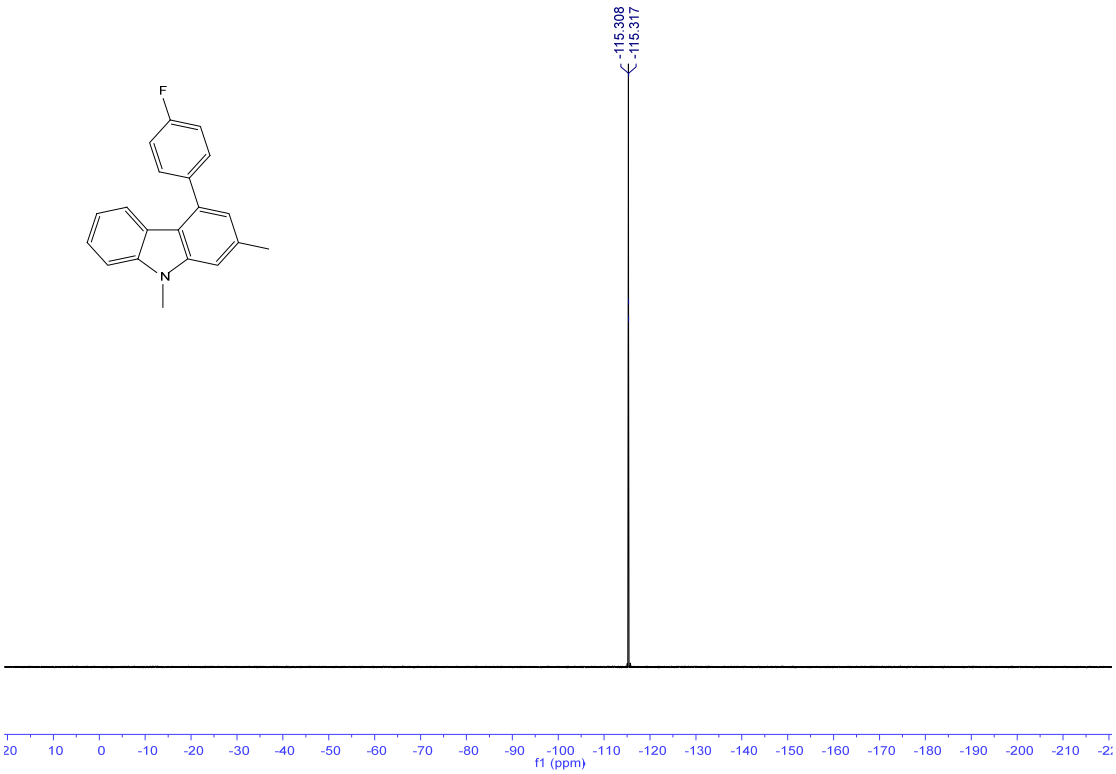
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **5d**



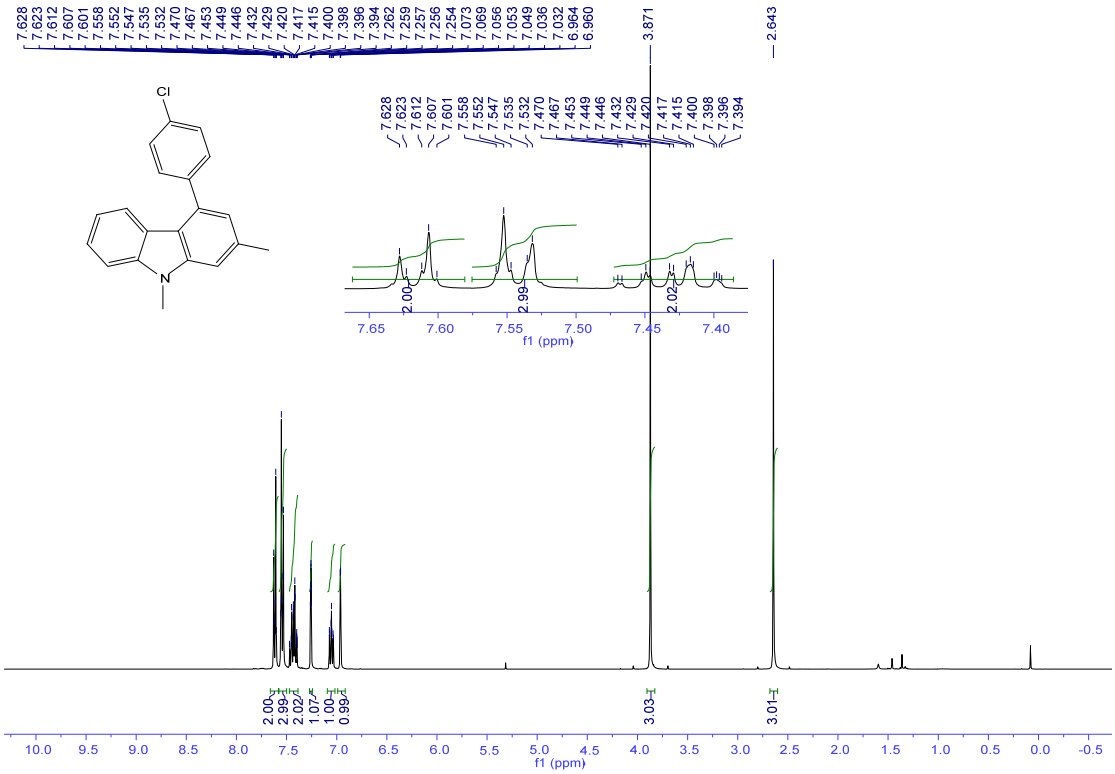
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5e**



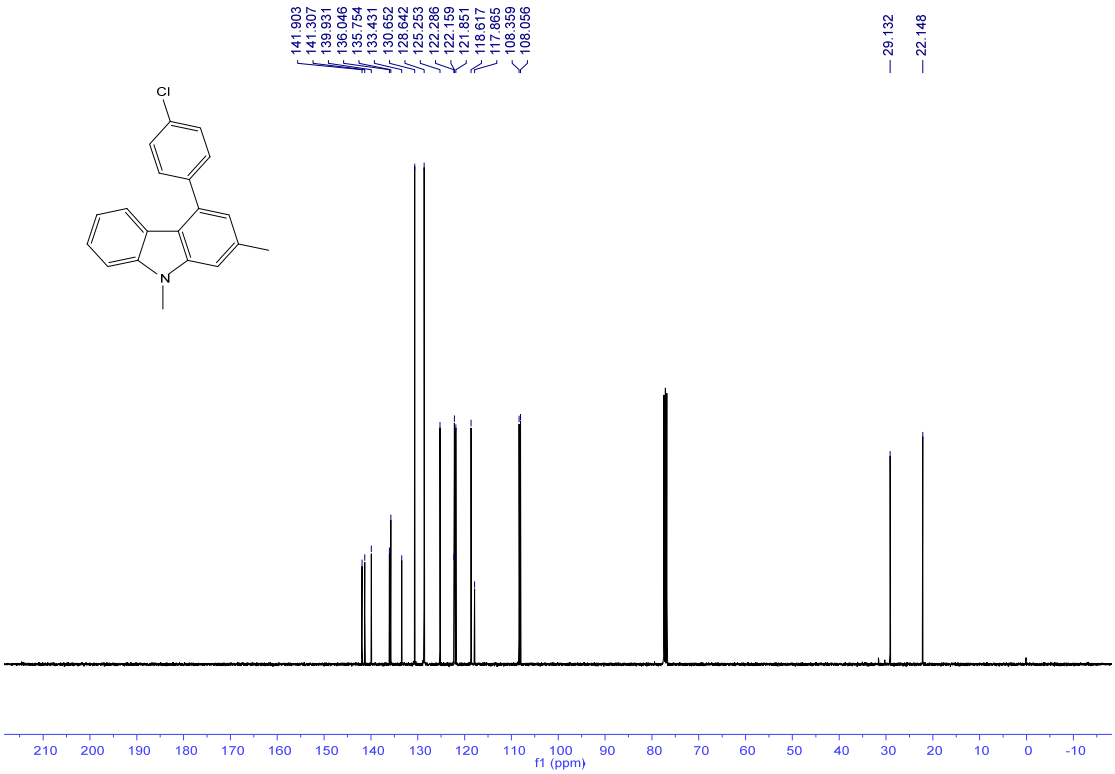
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **5e**



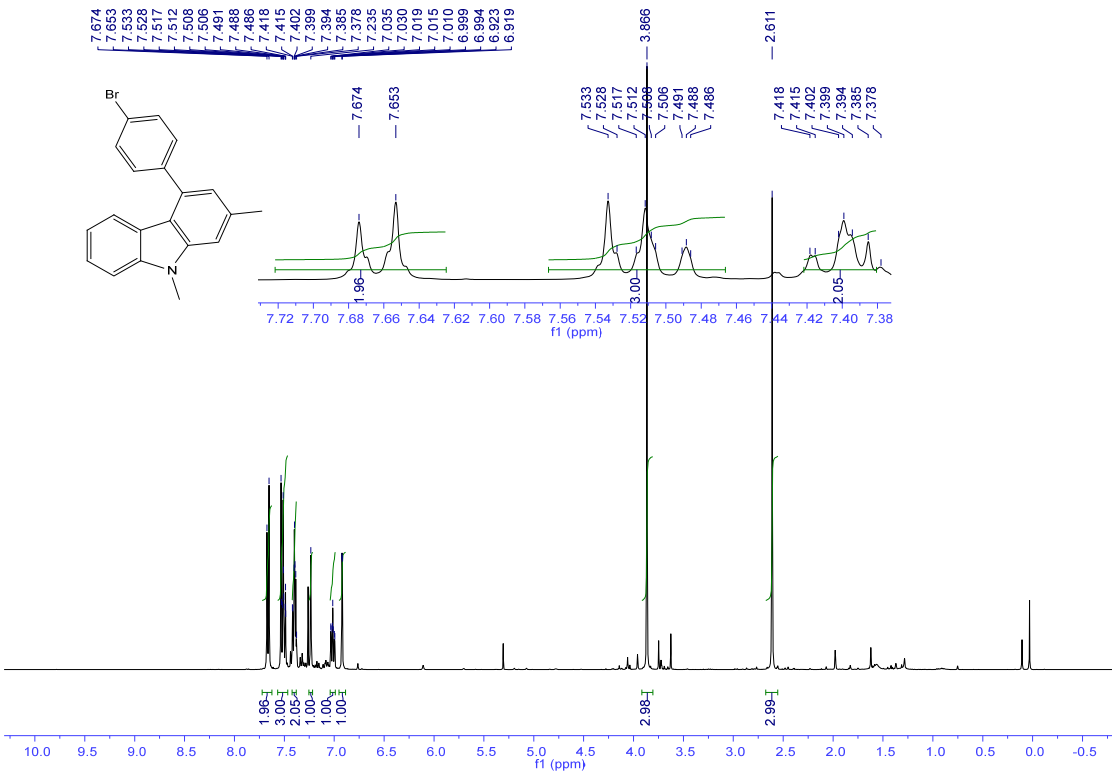
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5e**



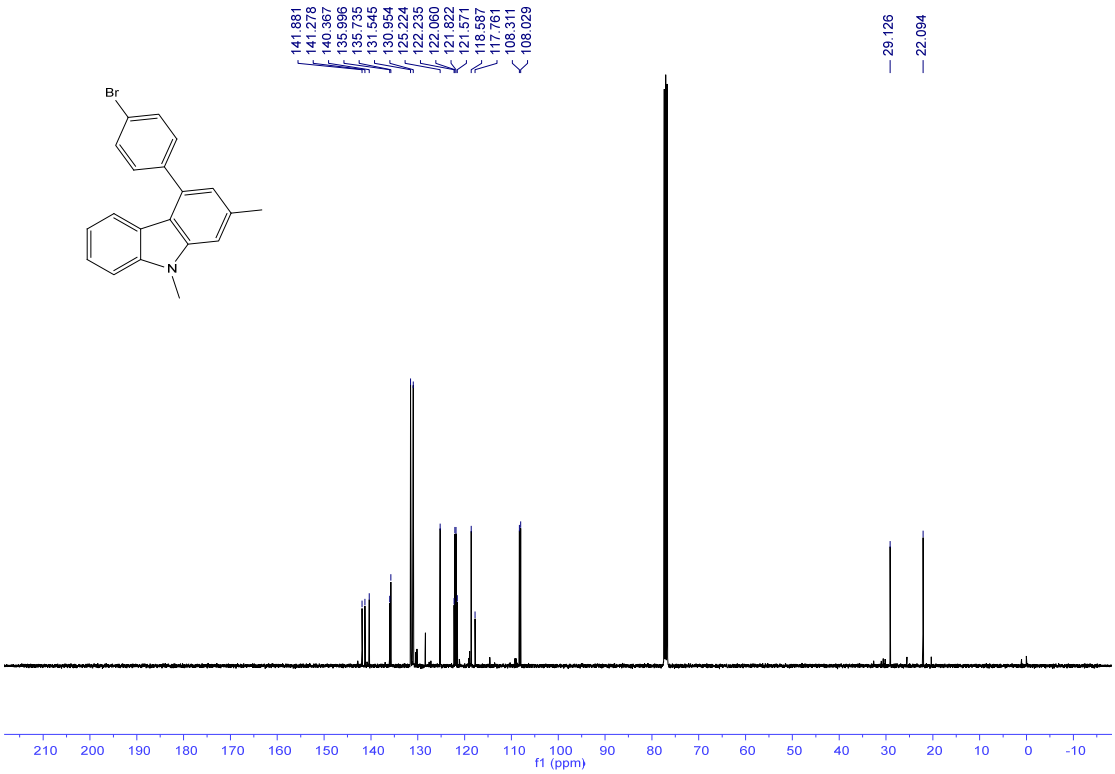
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5f**



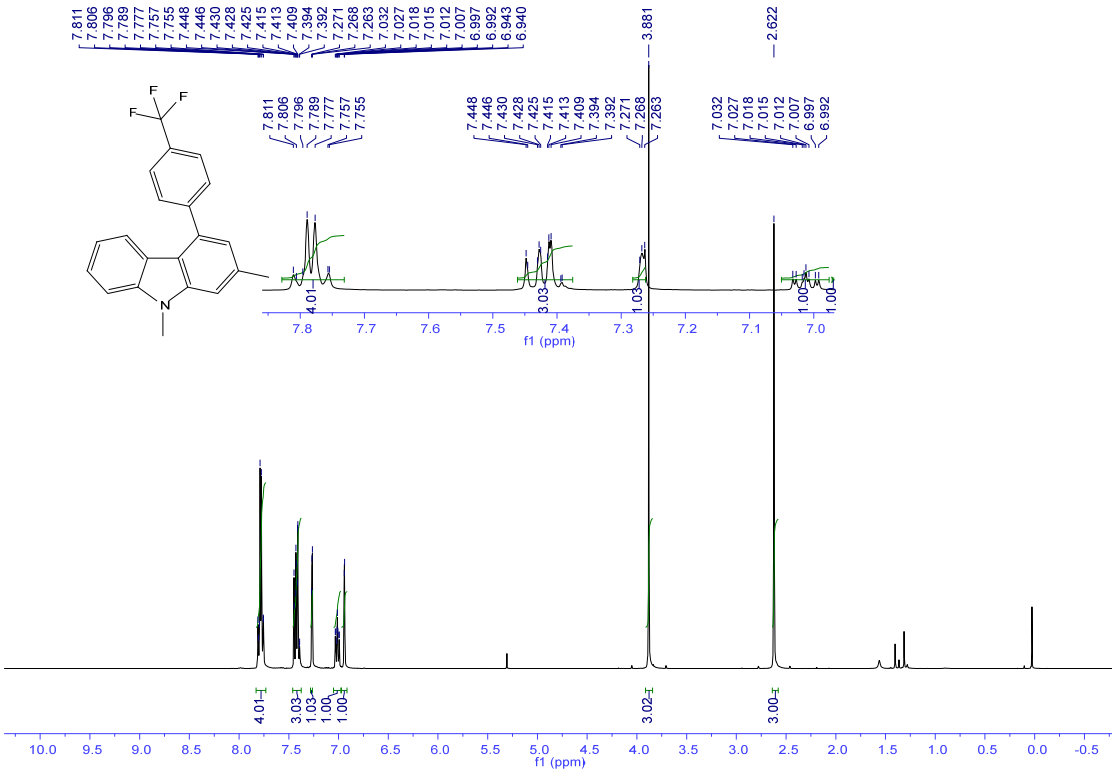
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **5f**



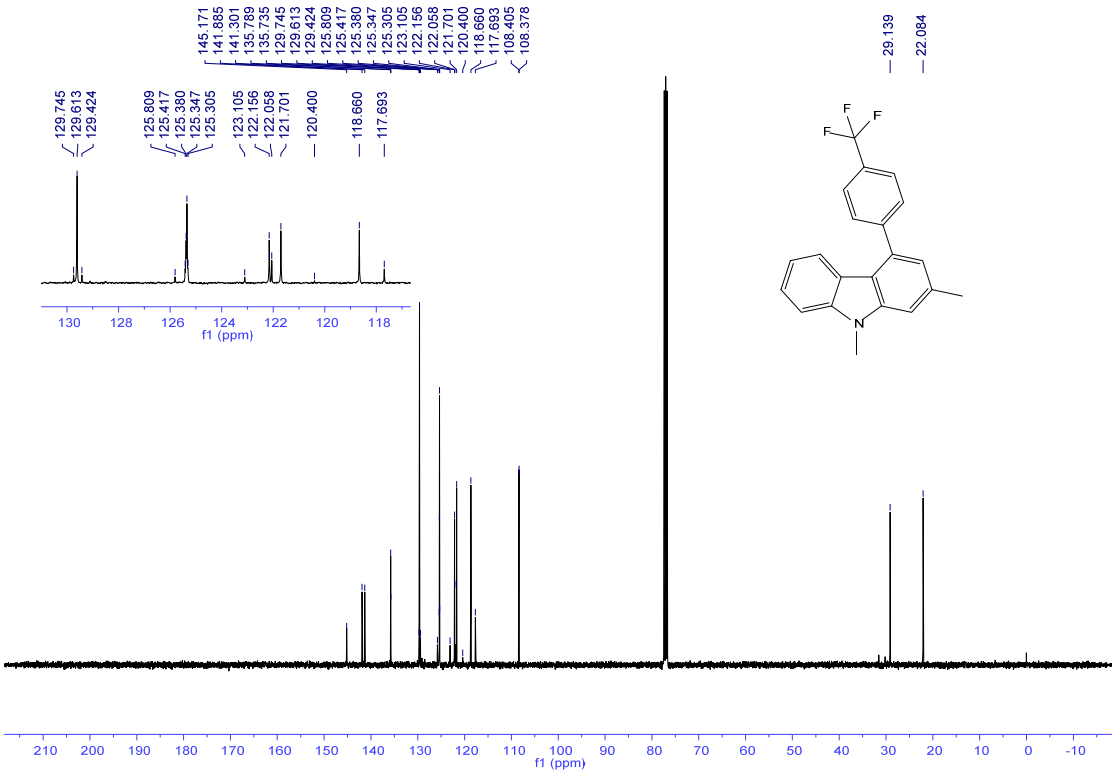
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5g**



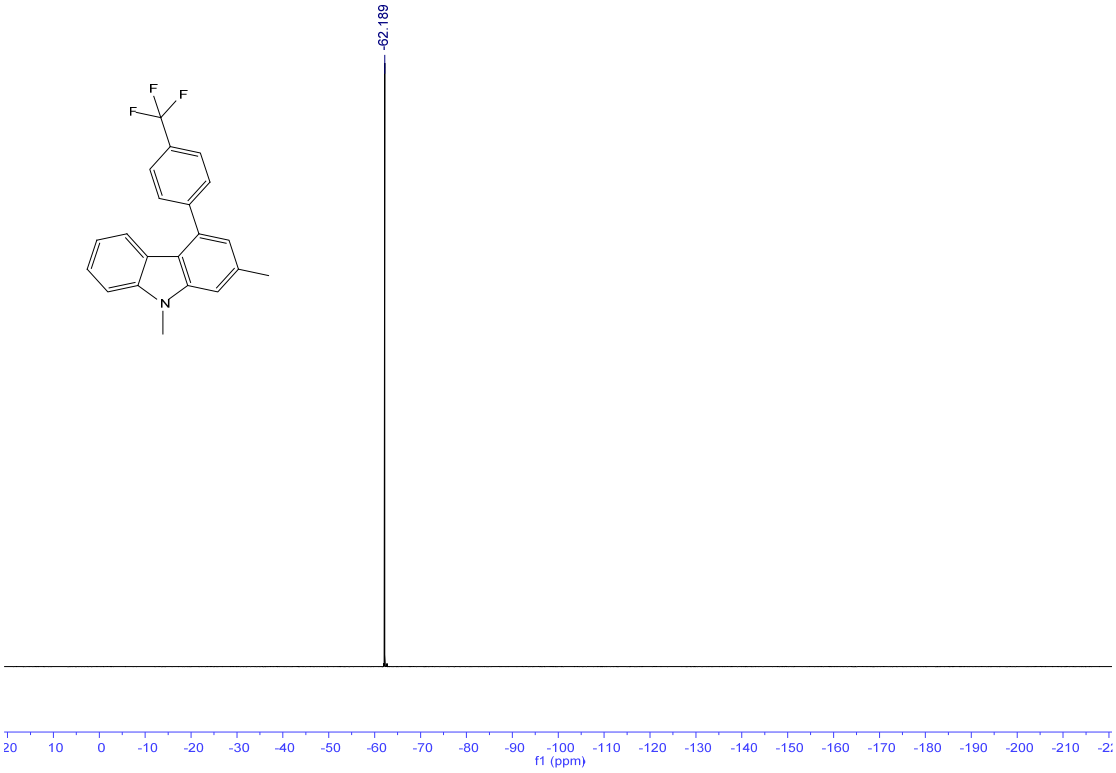
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **5g**



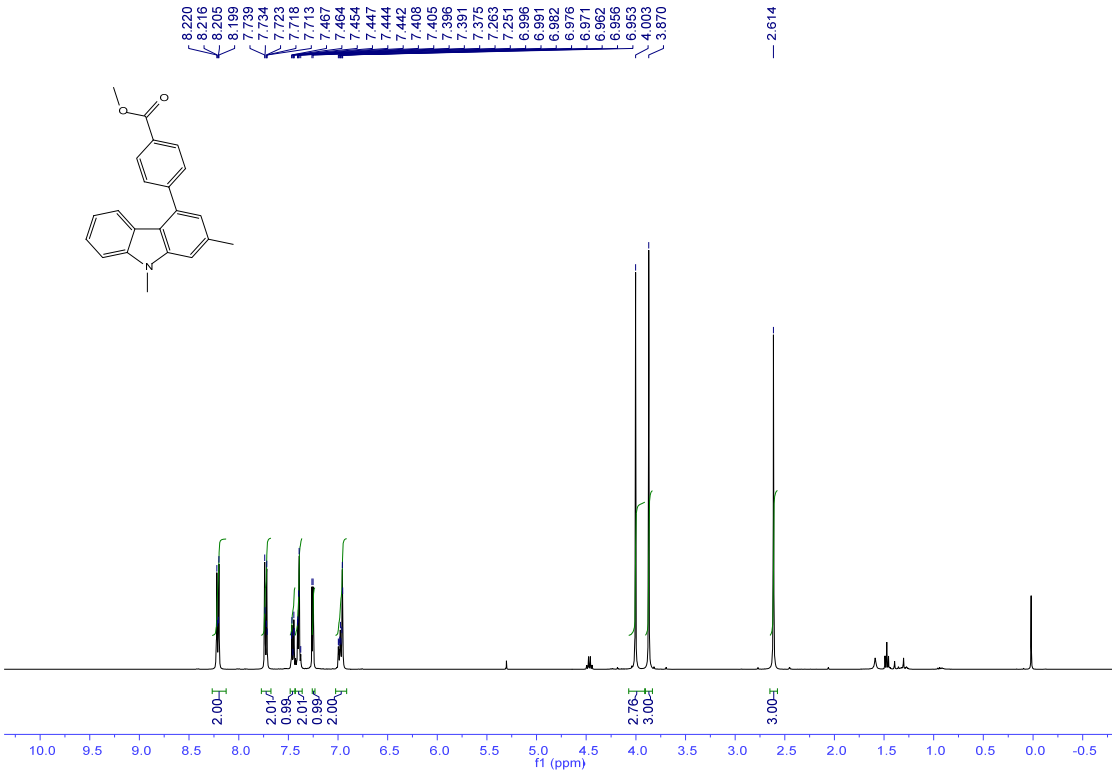
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5h**



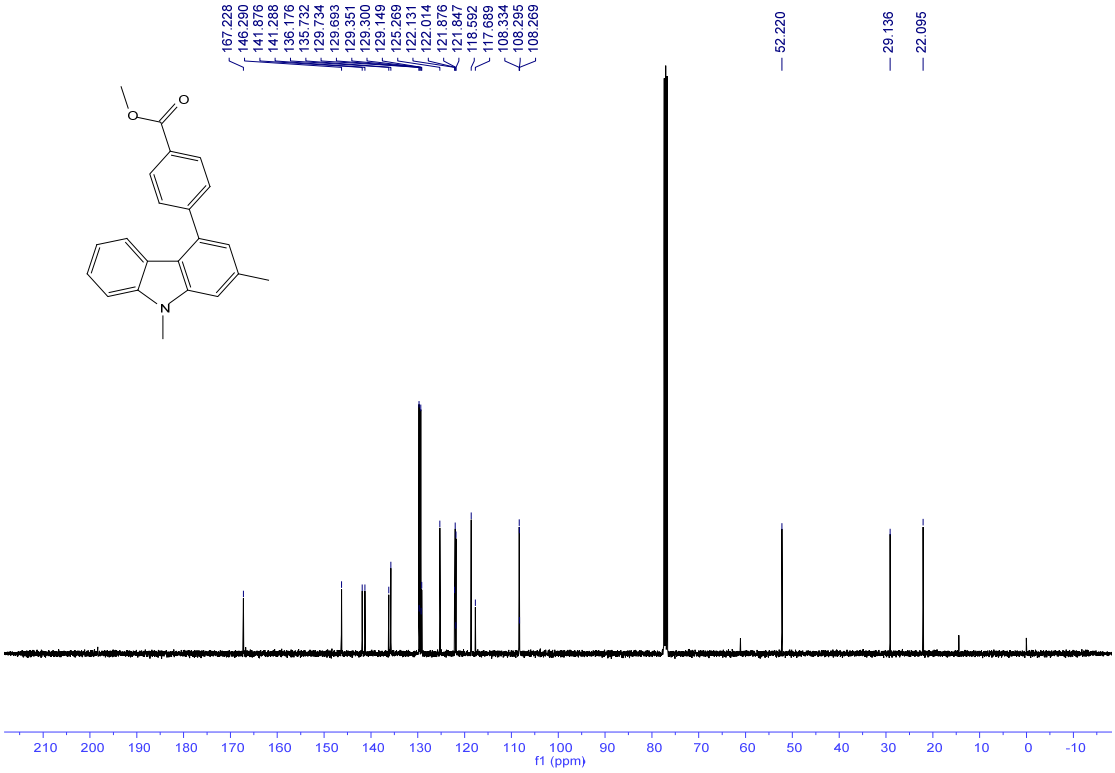
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **5h**



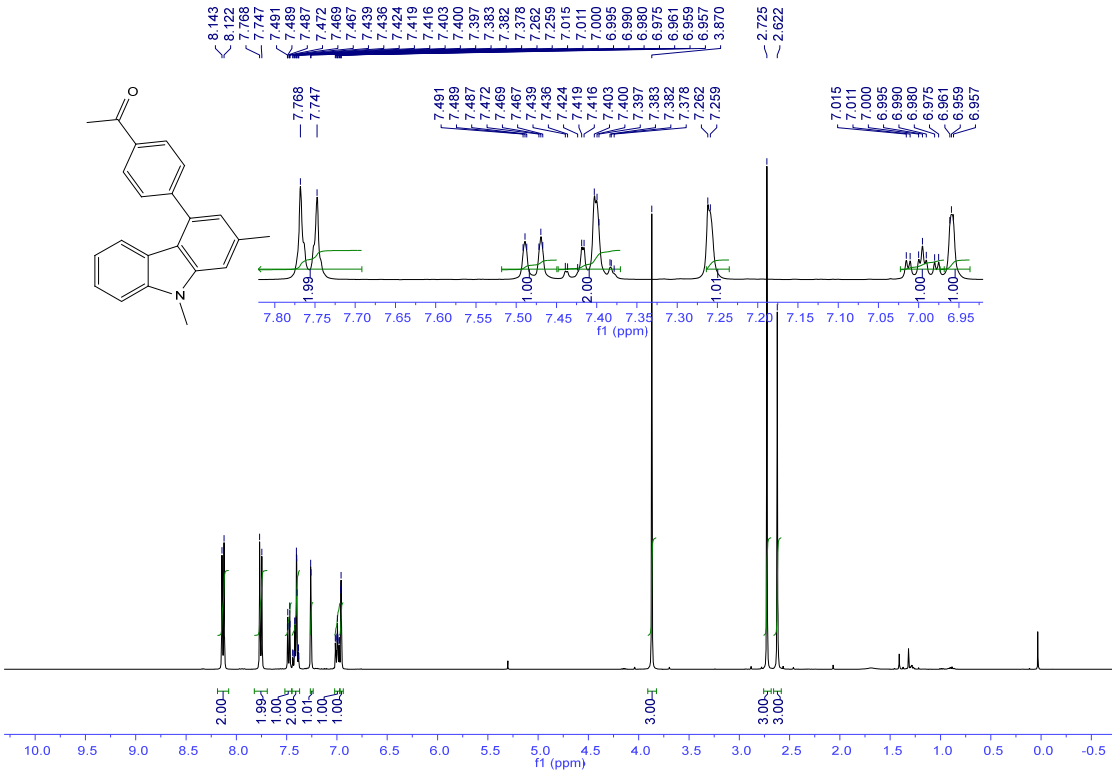
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5h**



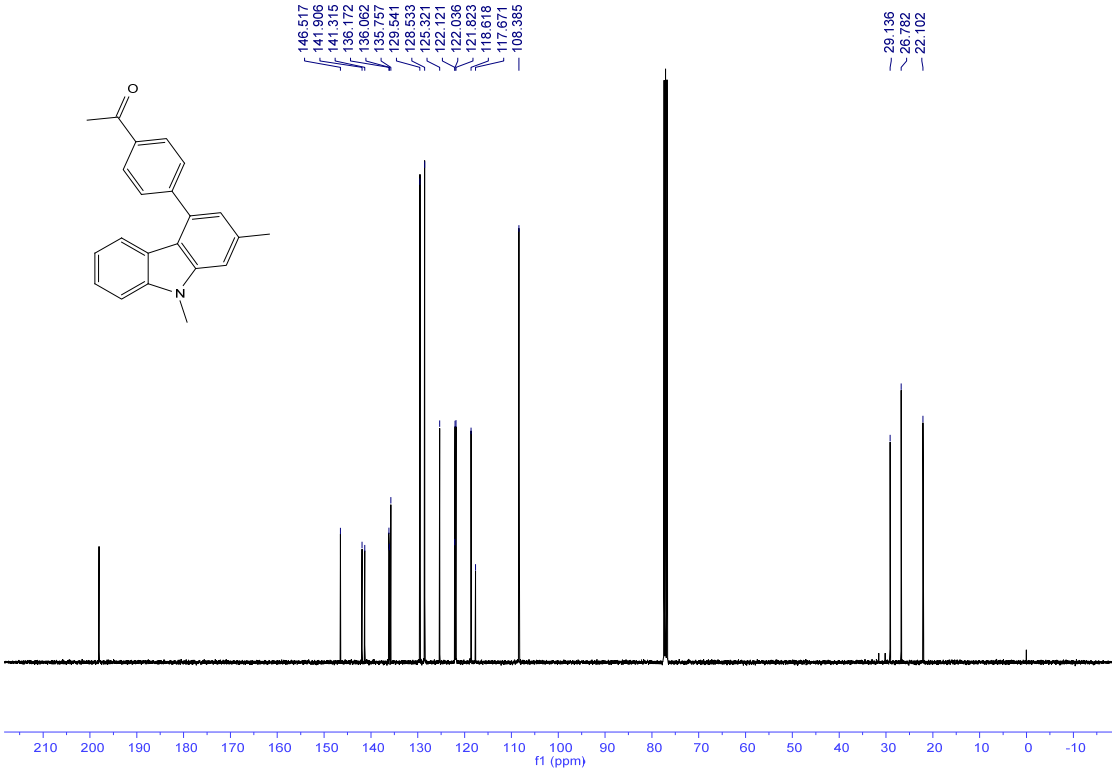
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5i**



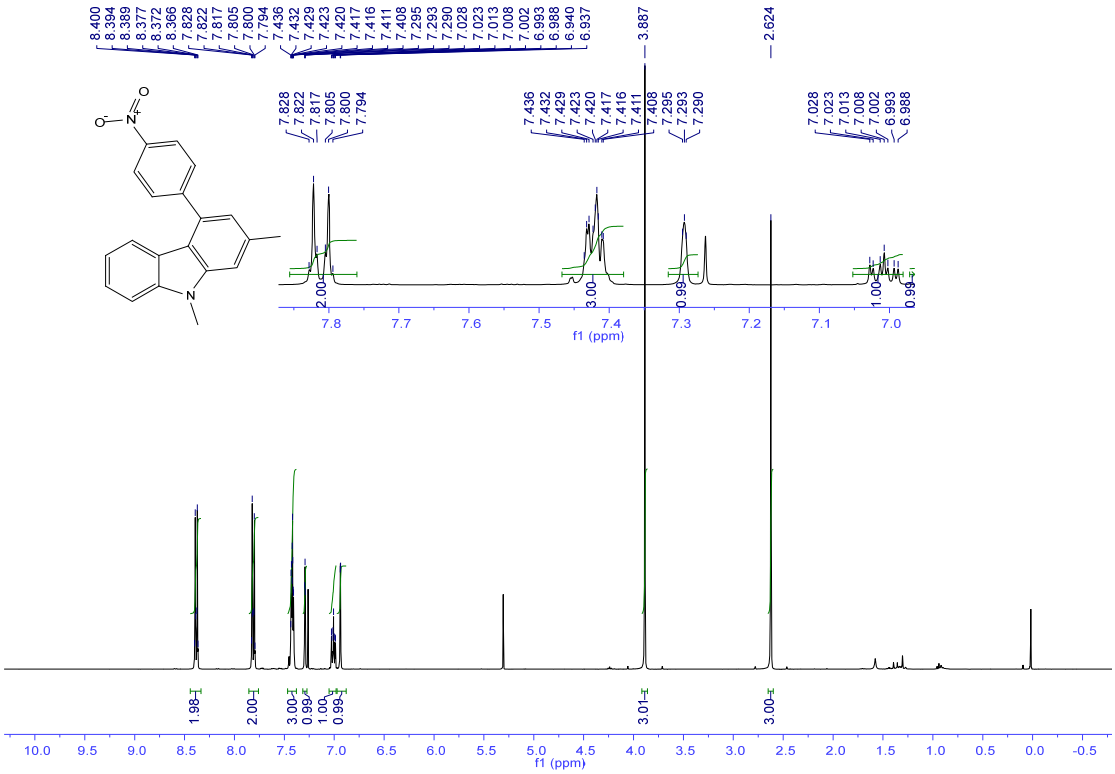
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of compound **5i**



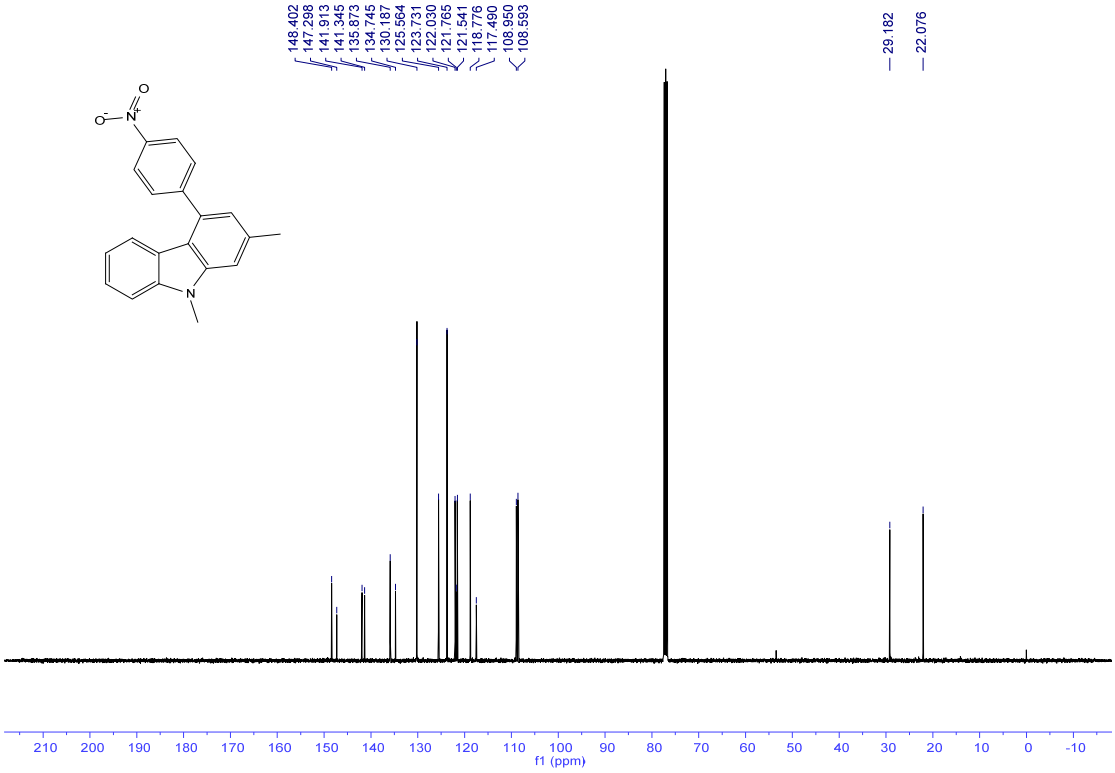
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5j**



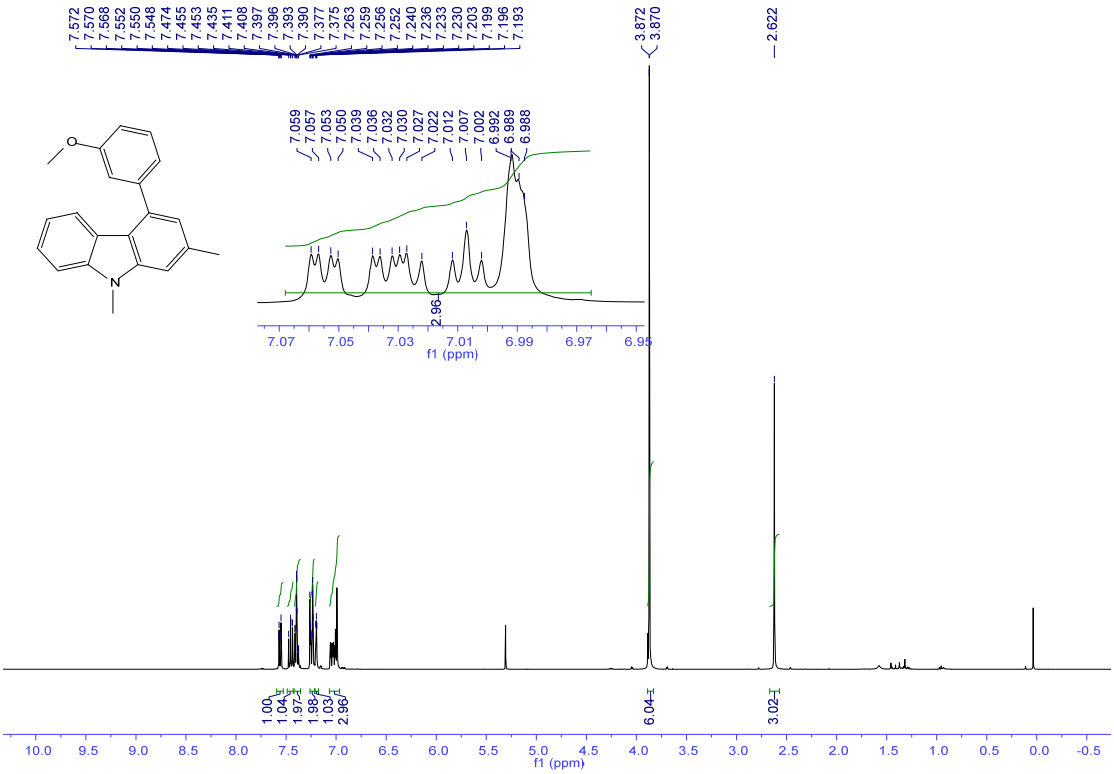
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **5j**



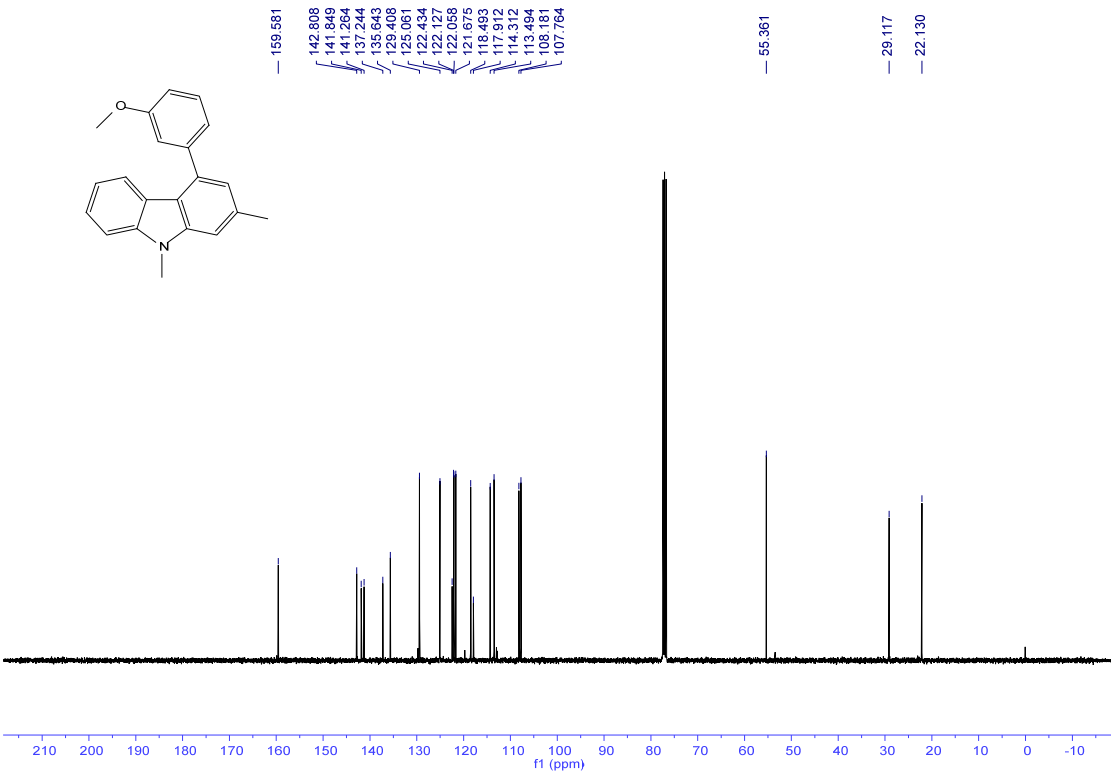
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5k**



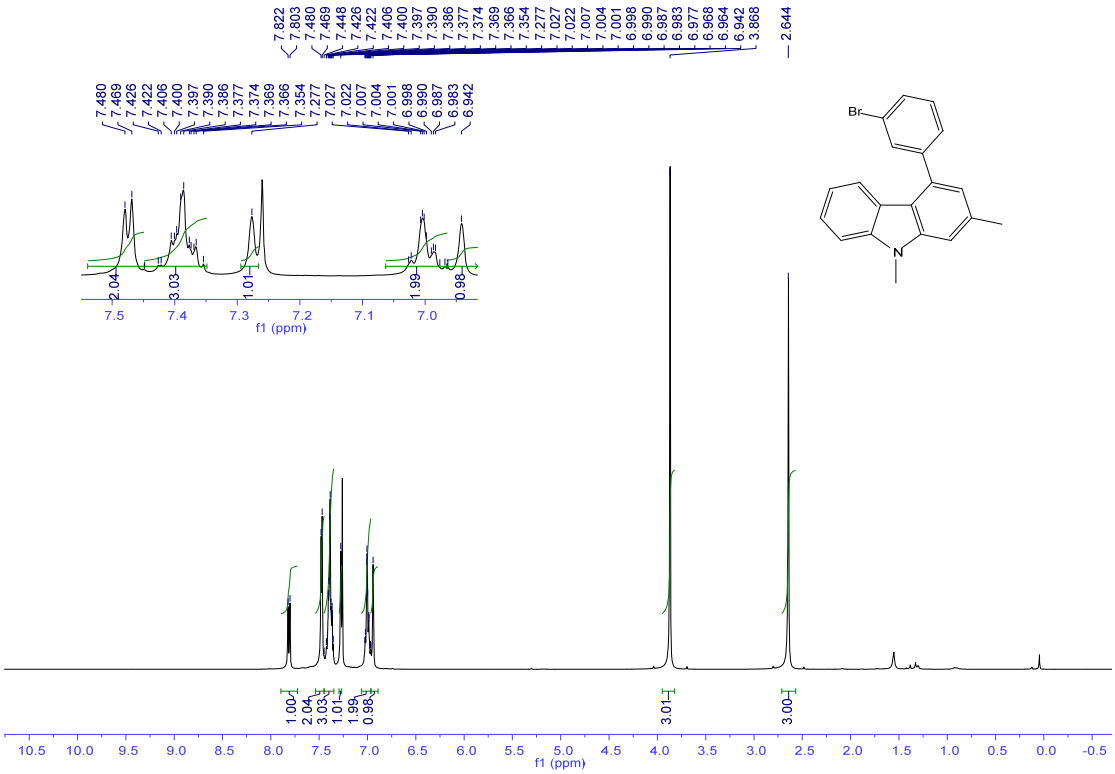
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **5k**



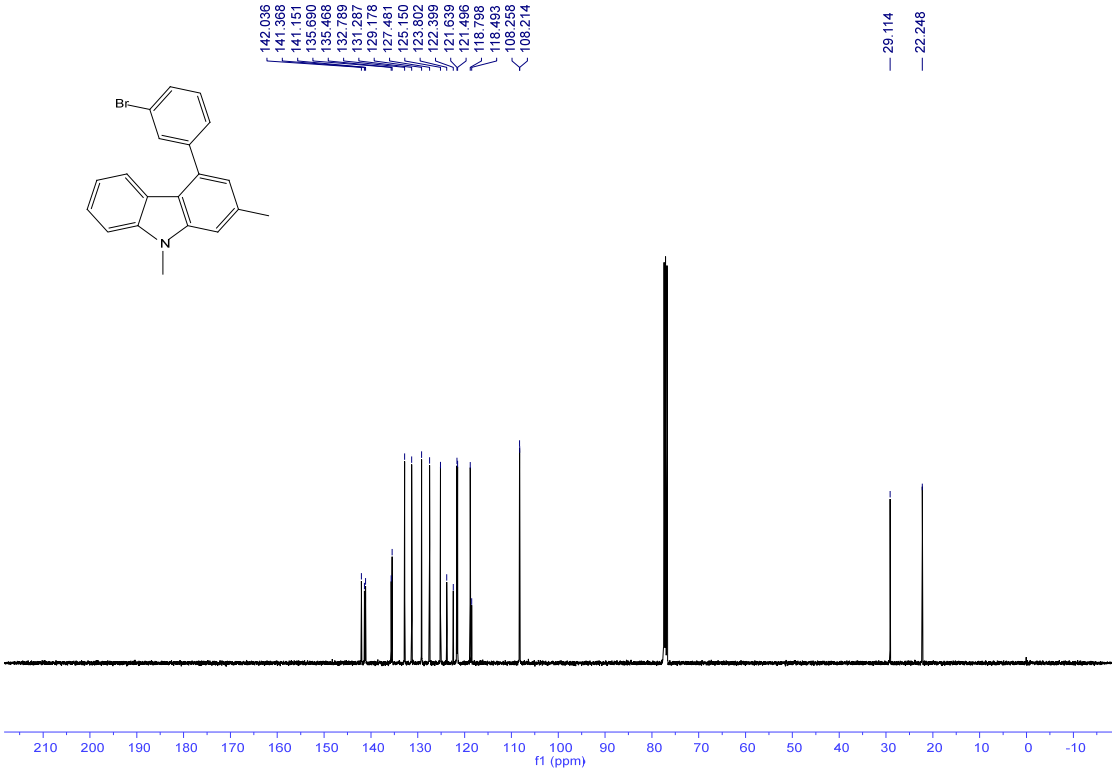
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5l**



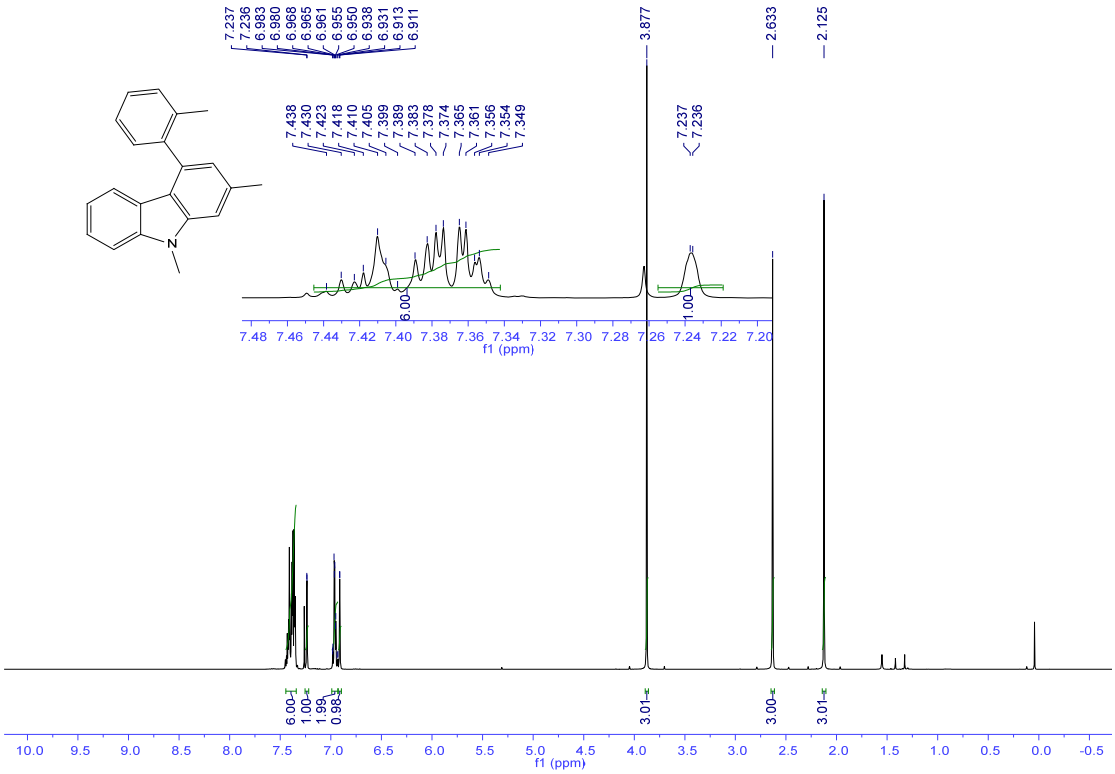
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of compound **5l**



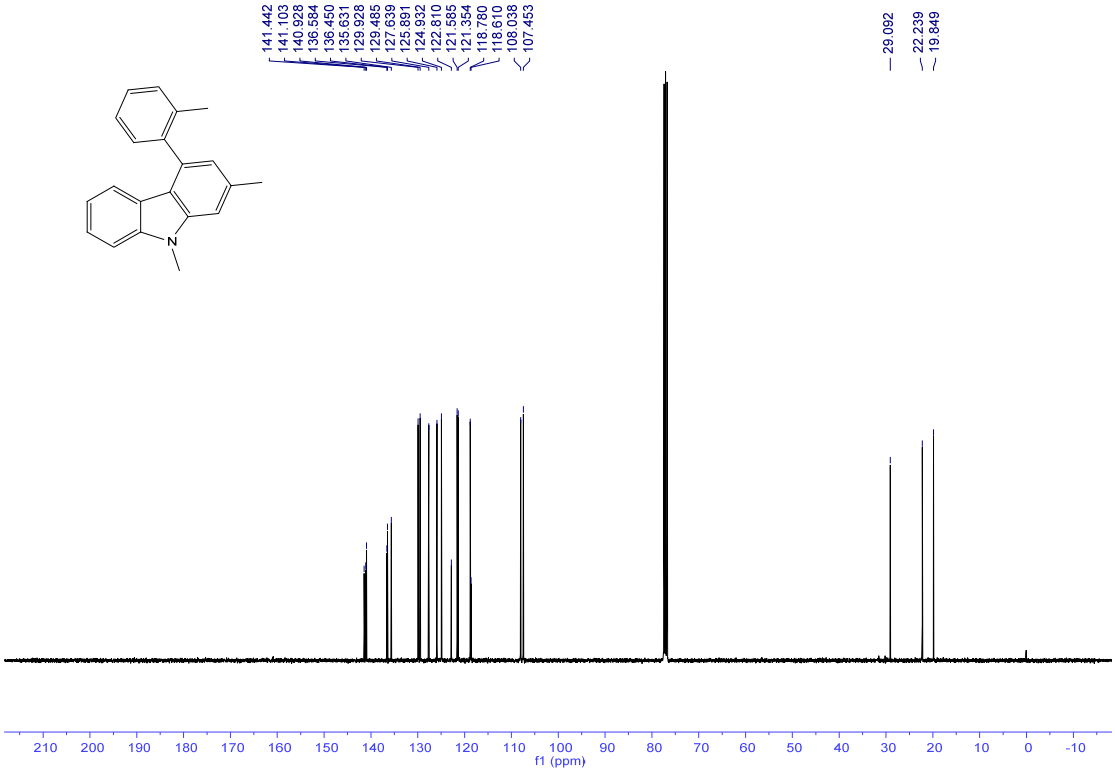
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5m**



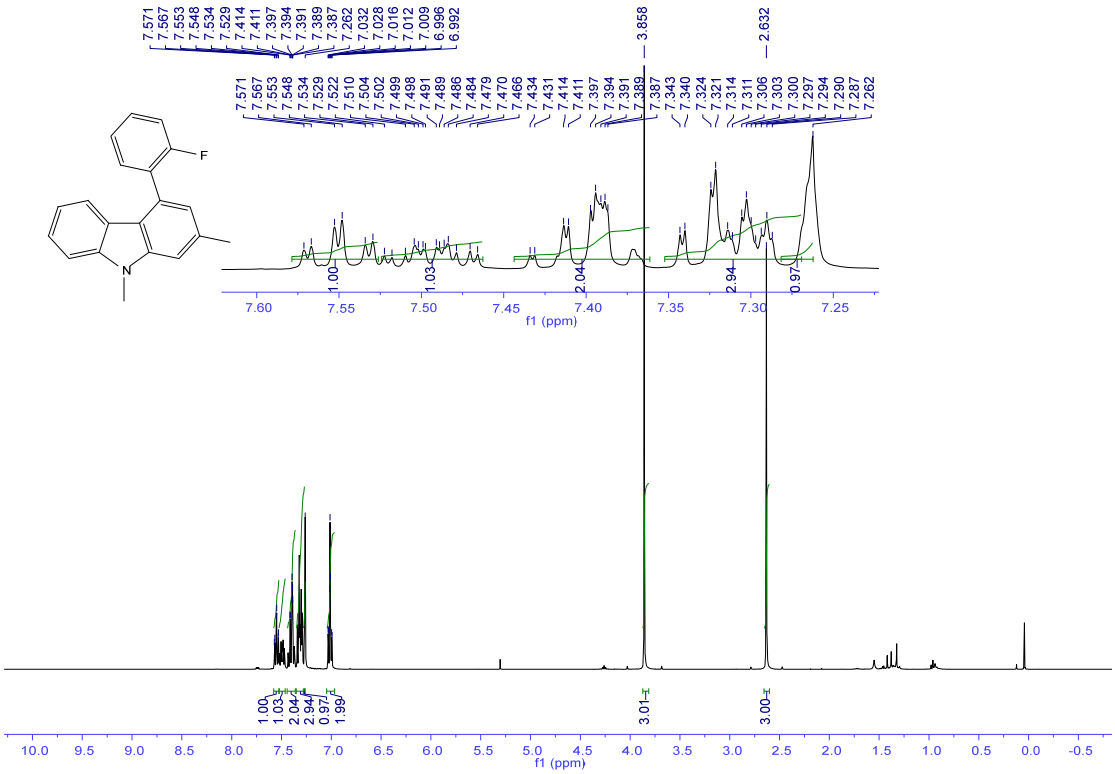
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of compound **5m**



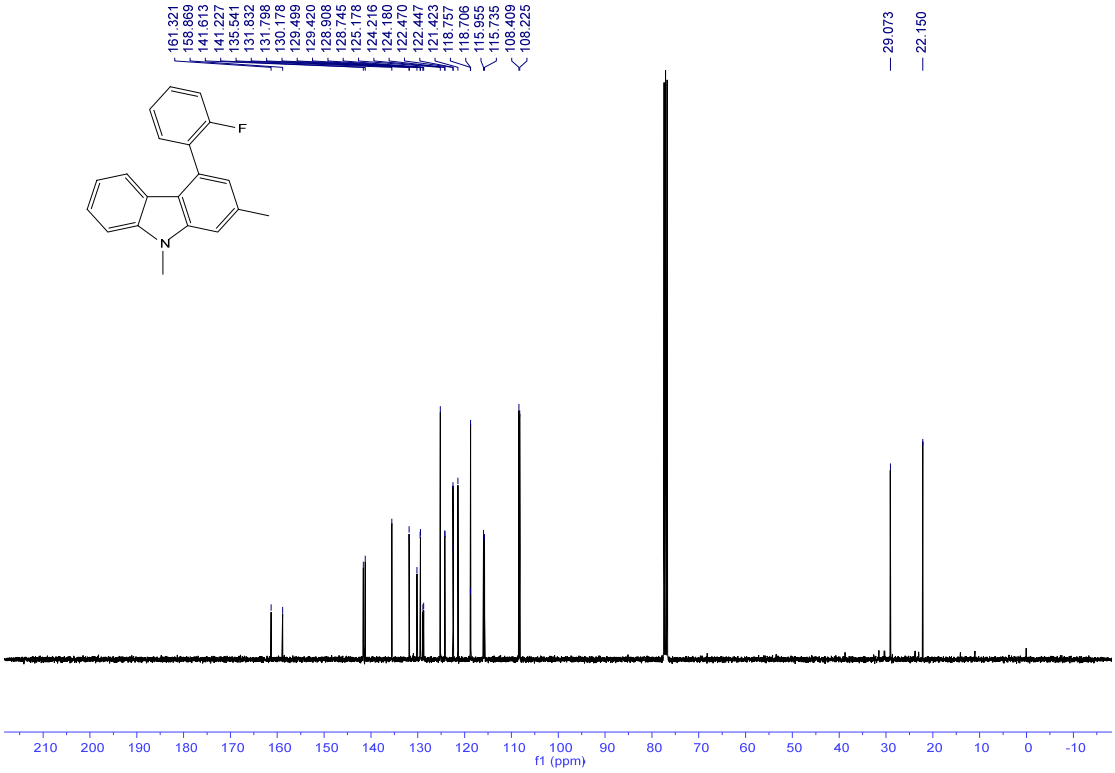
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5n**



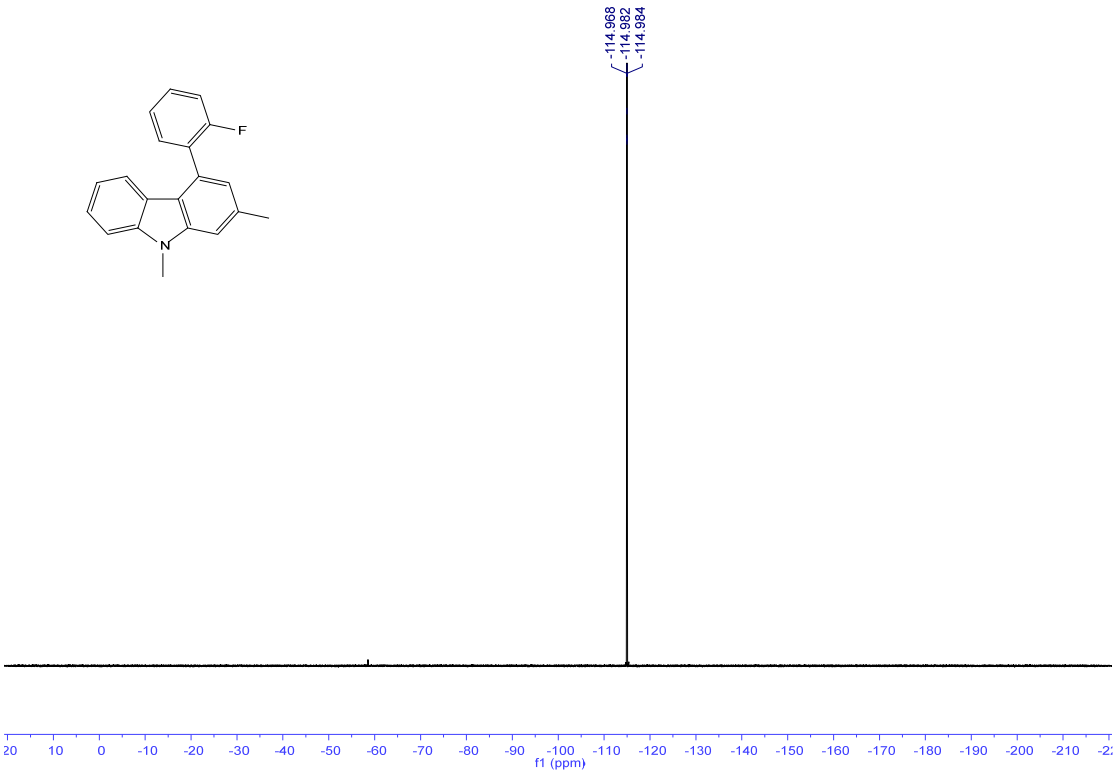
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of compound **5n**



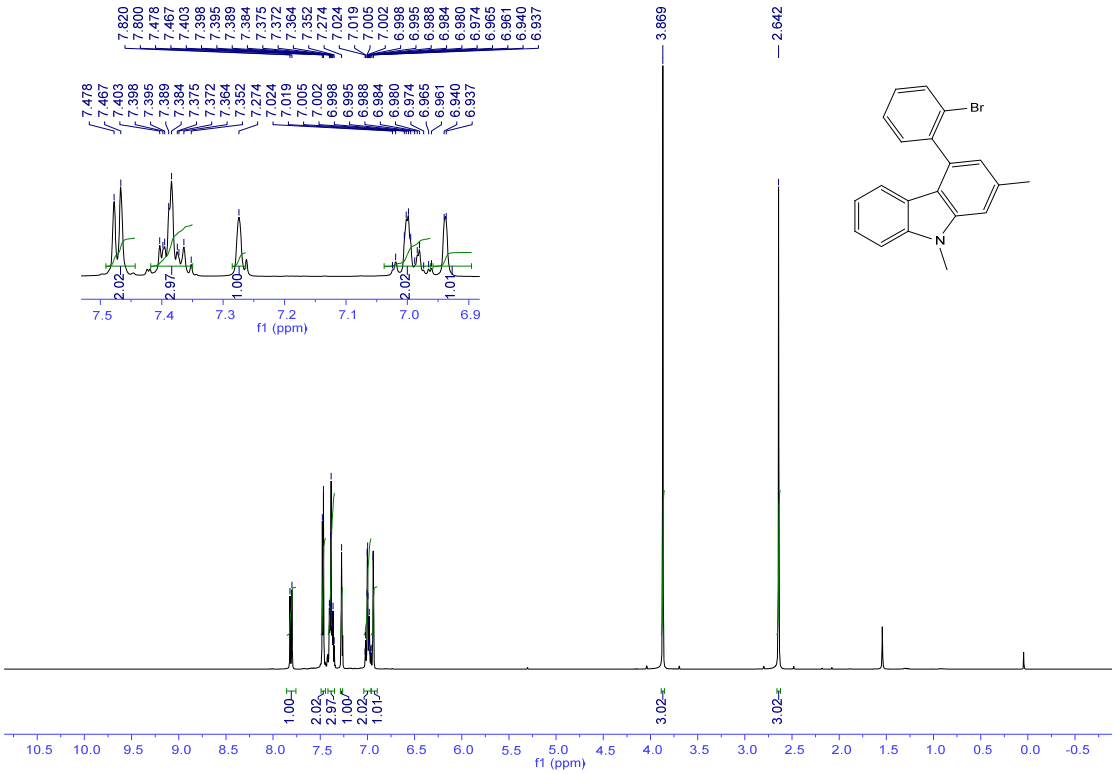
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5o**



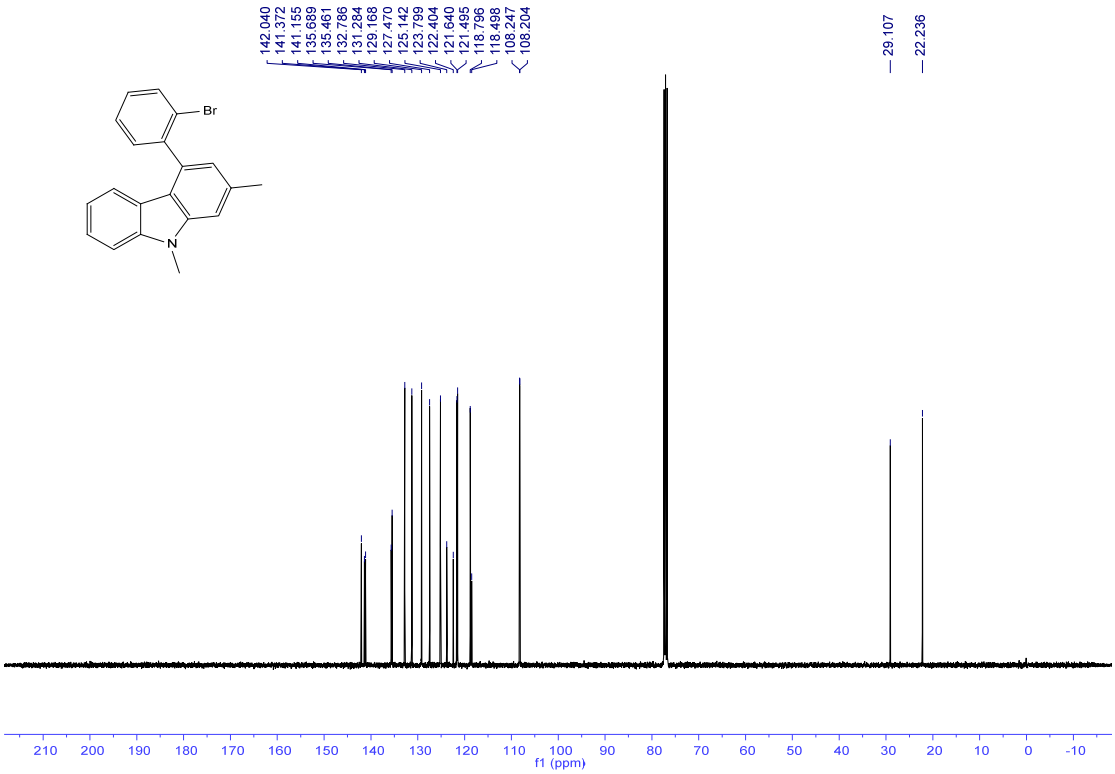
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **5o**



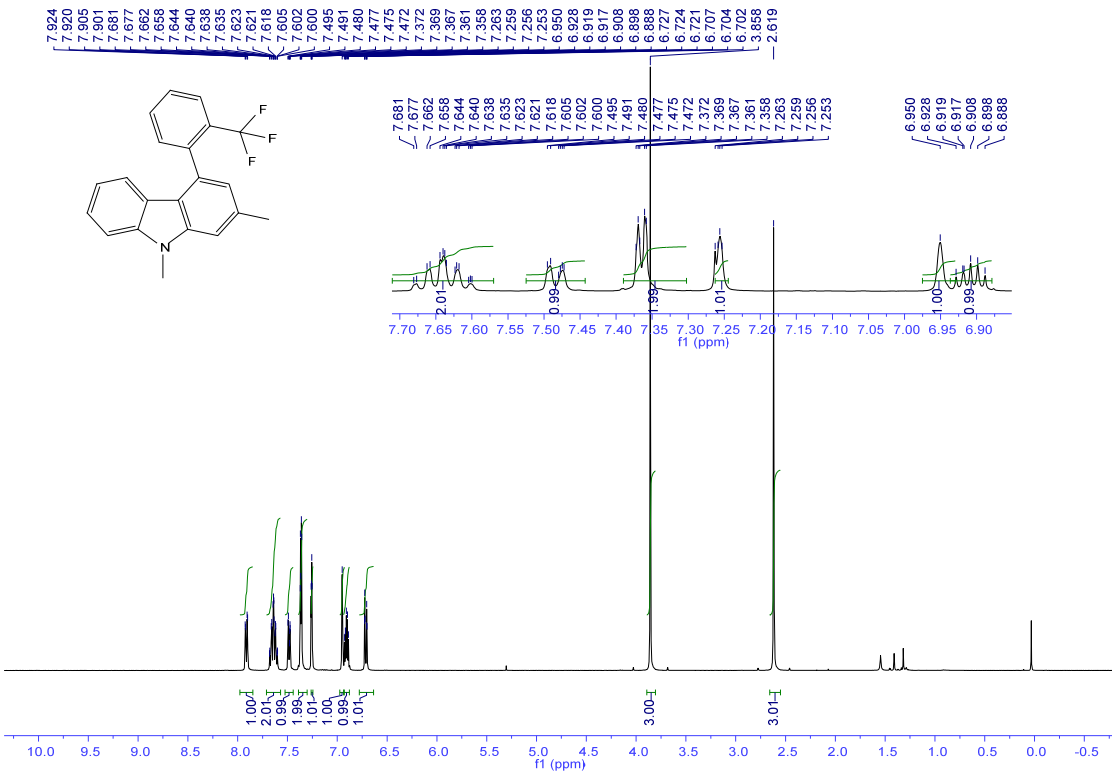
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5o**



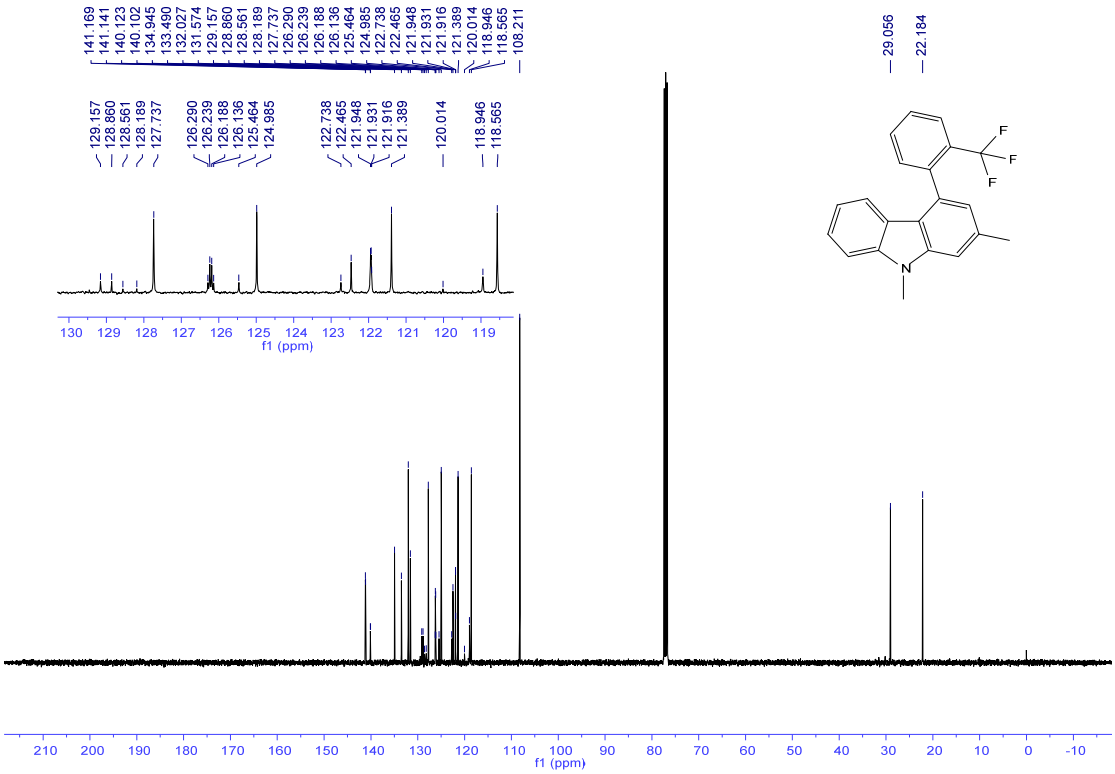
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5p**



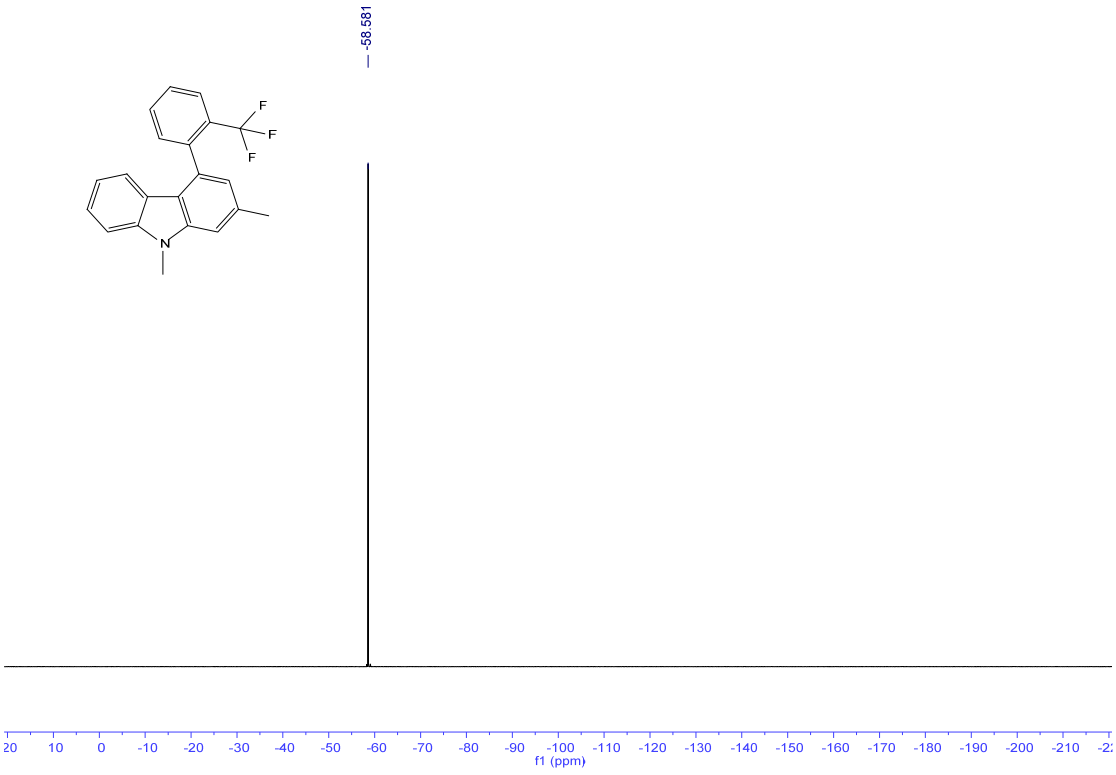
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **5p**



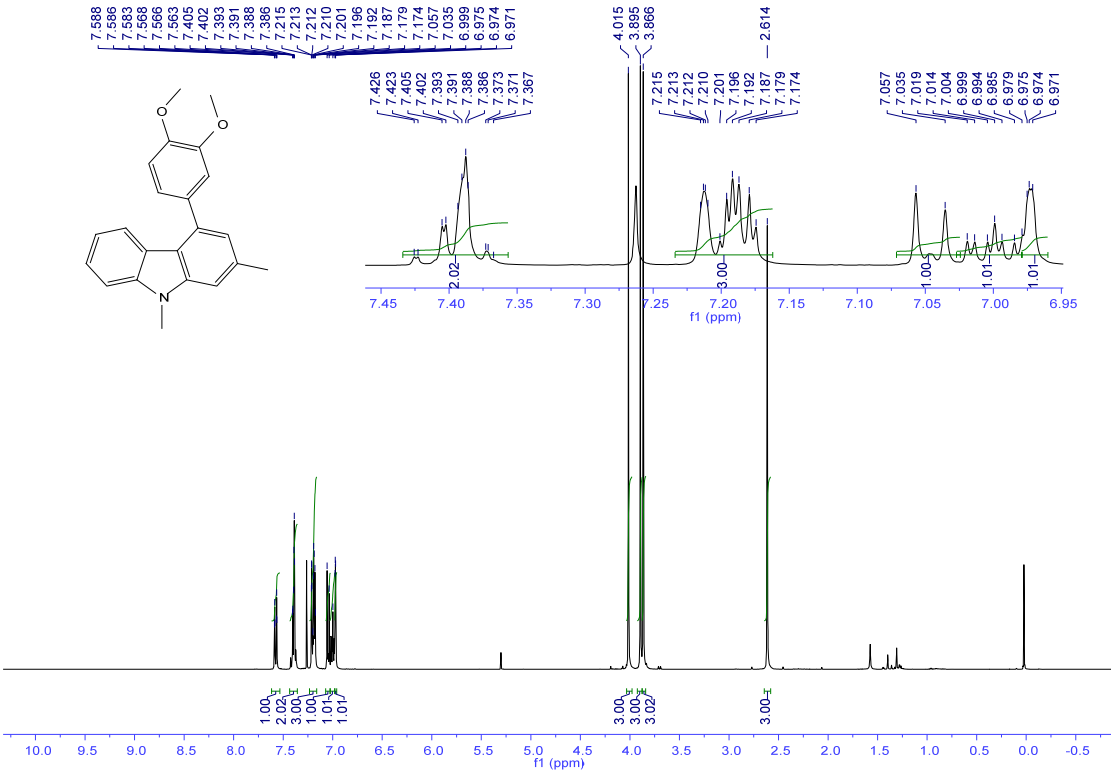
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5q**



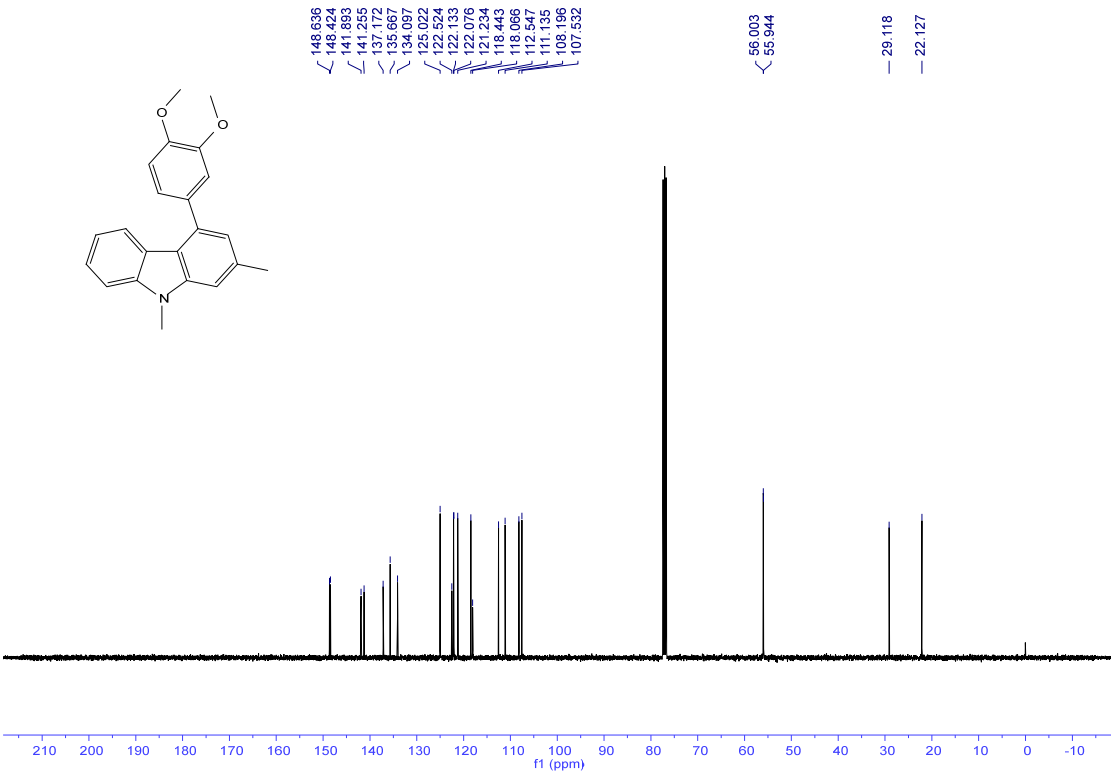
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **5q**



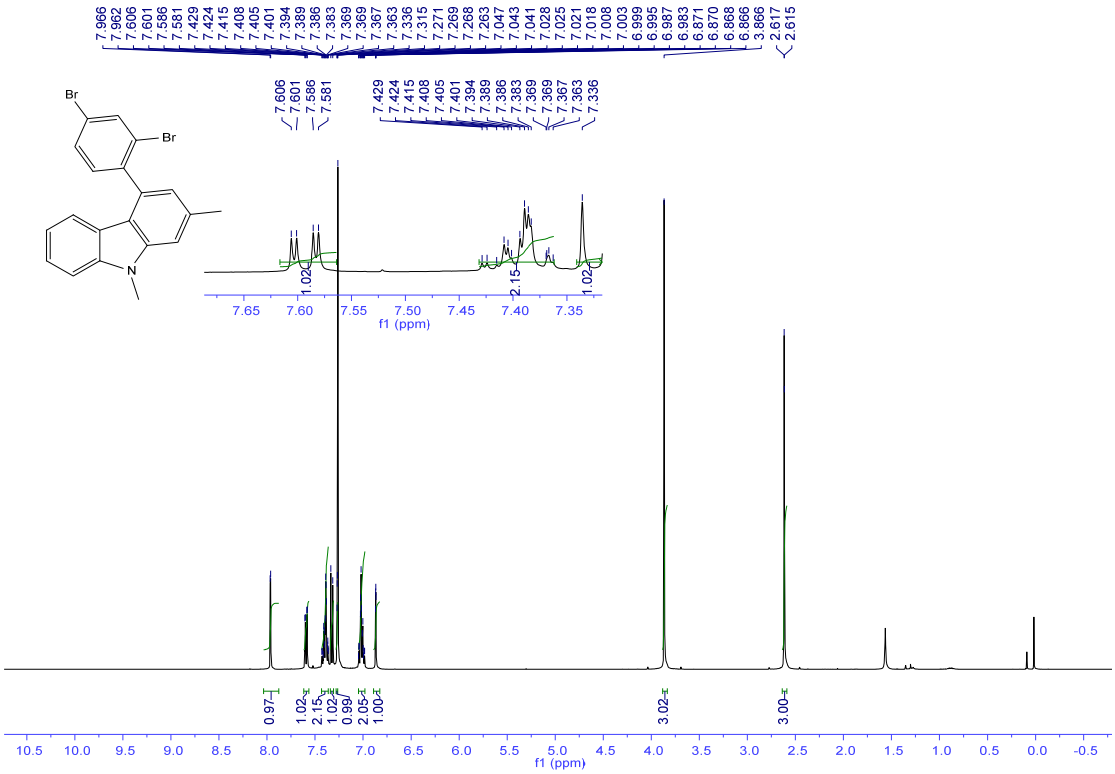
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5q**



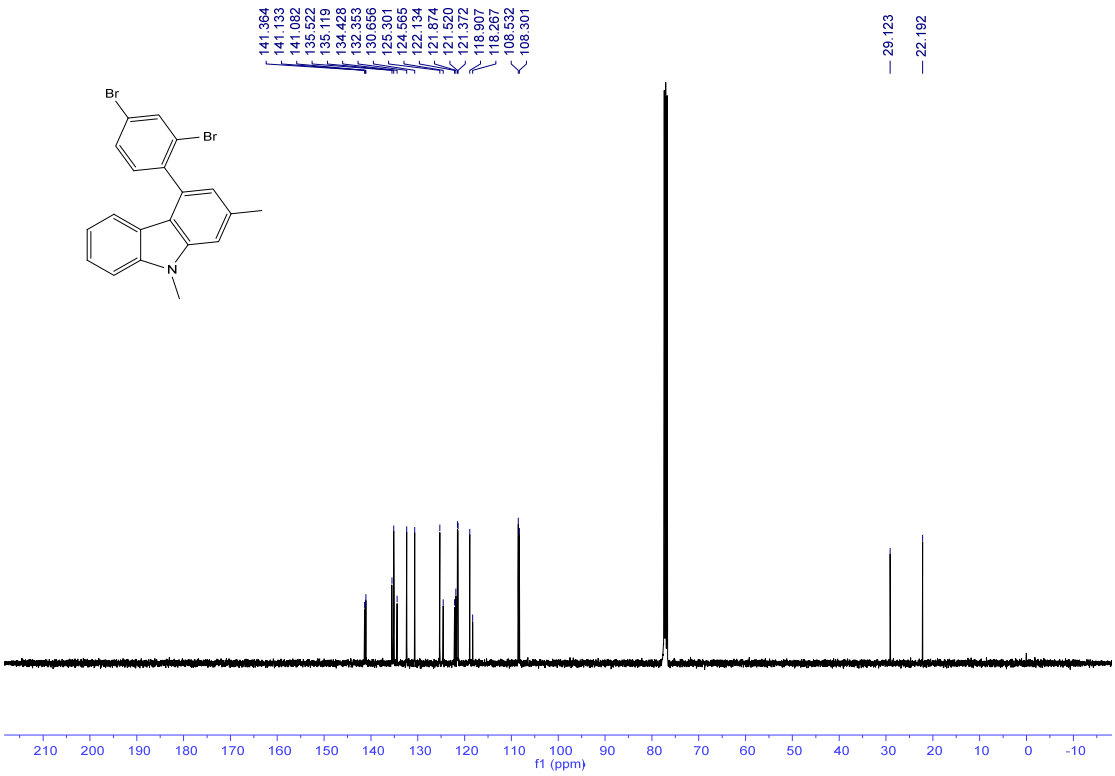
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5r**



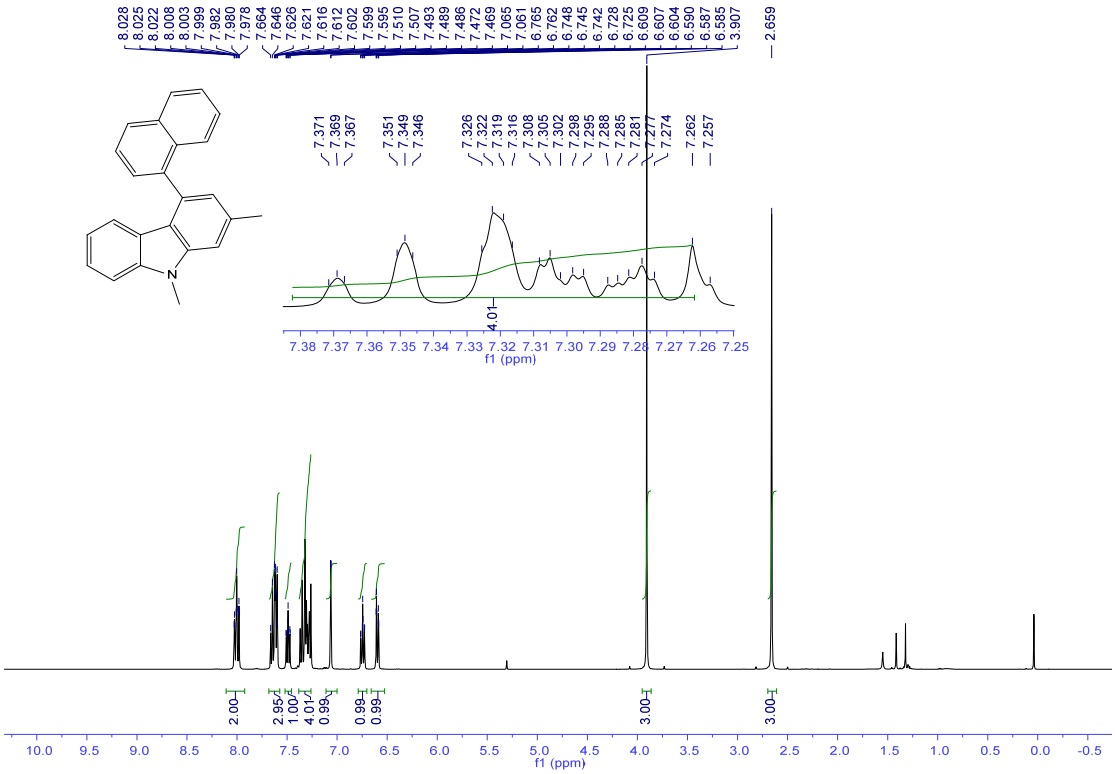
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **5r**



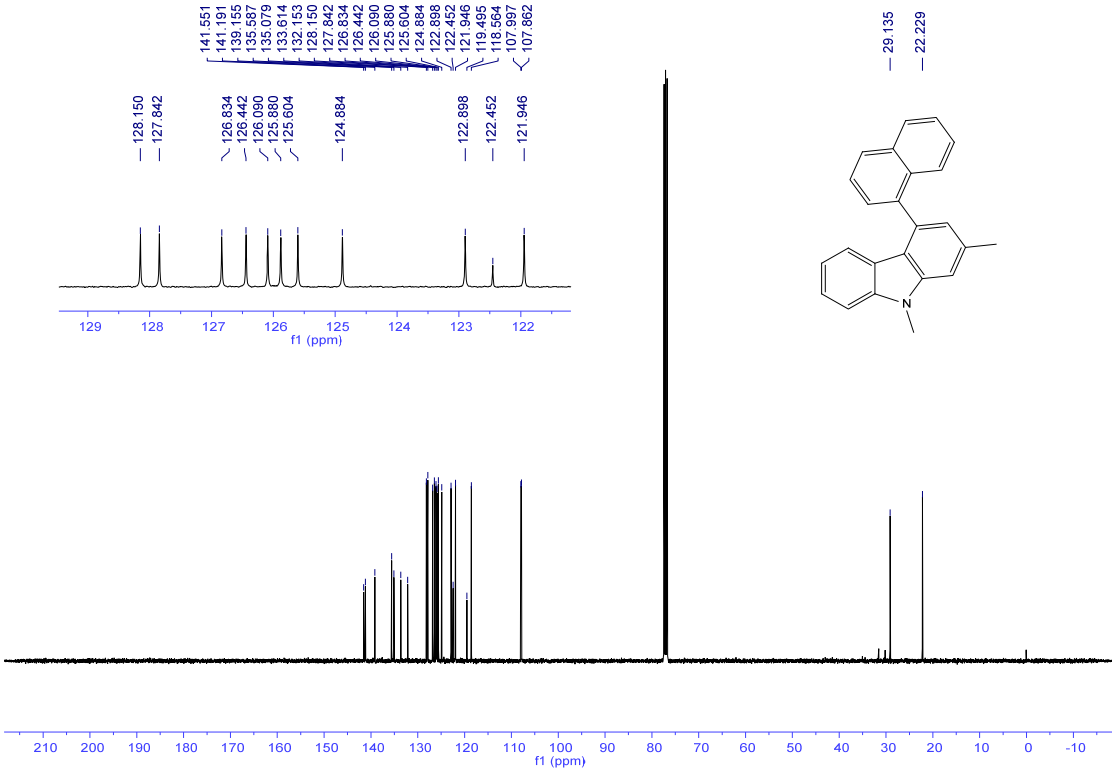
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5s**



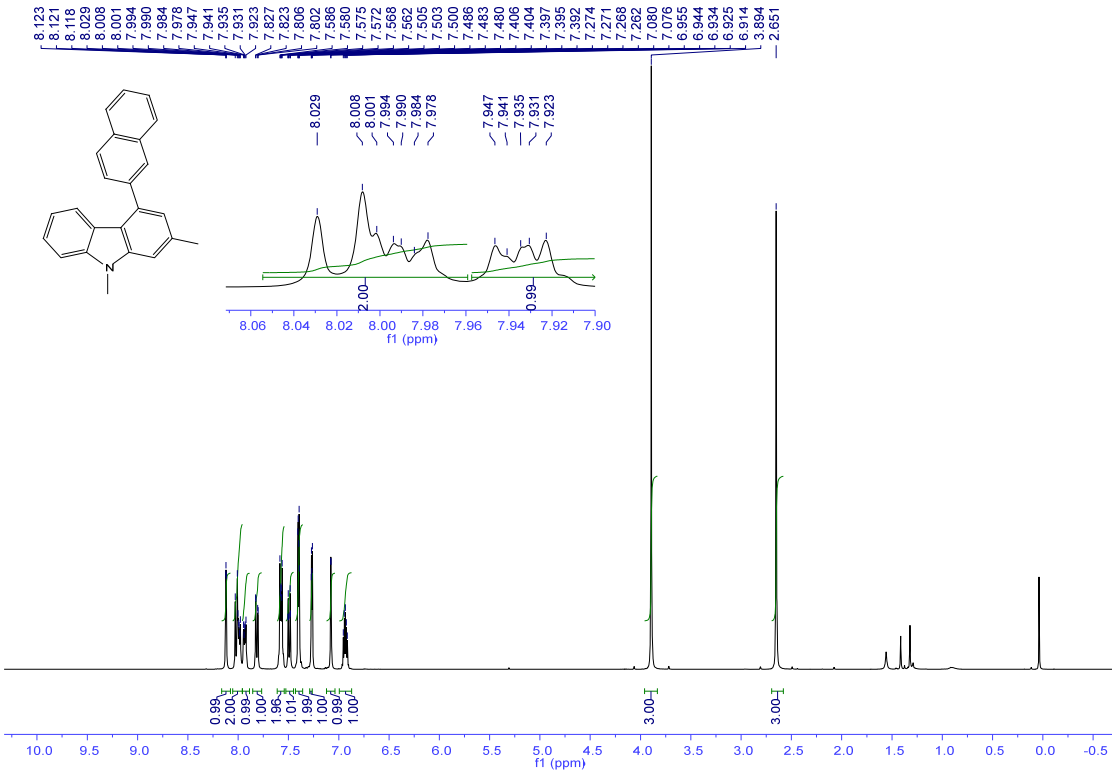
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of compound **5s**



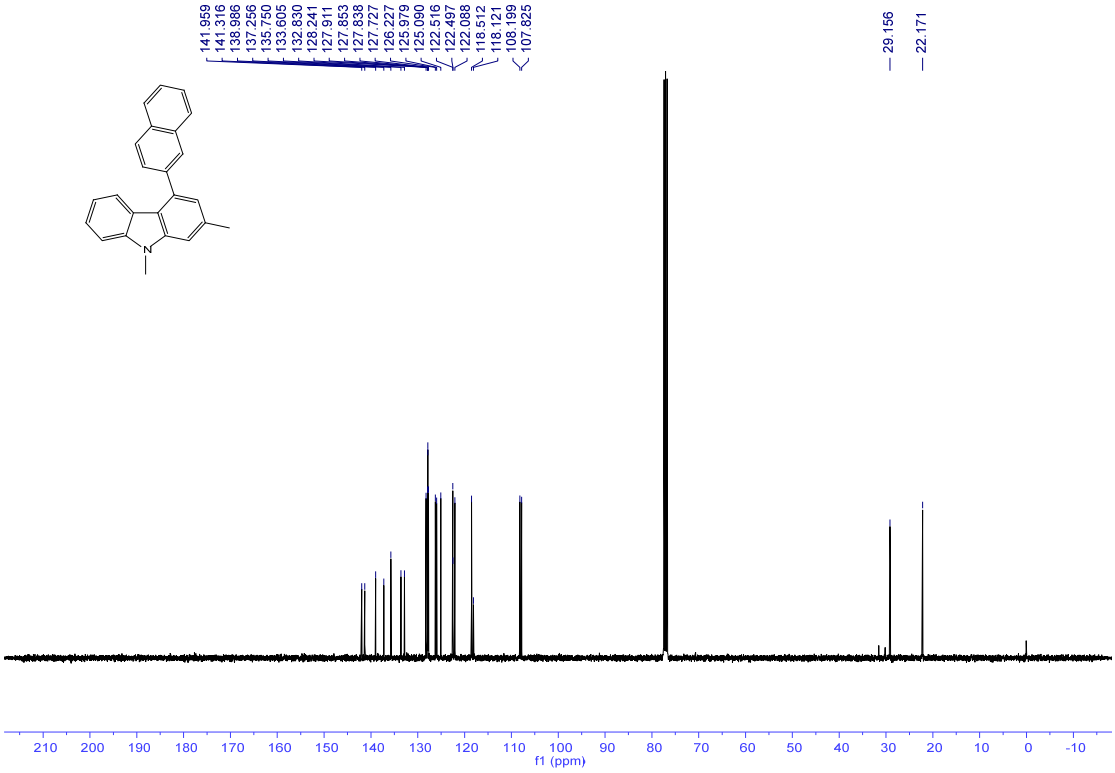
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5t**



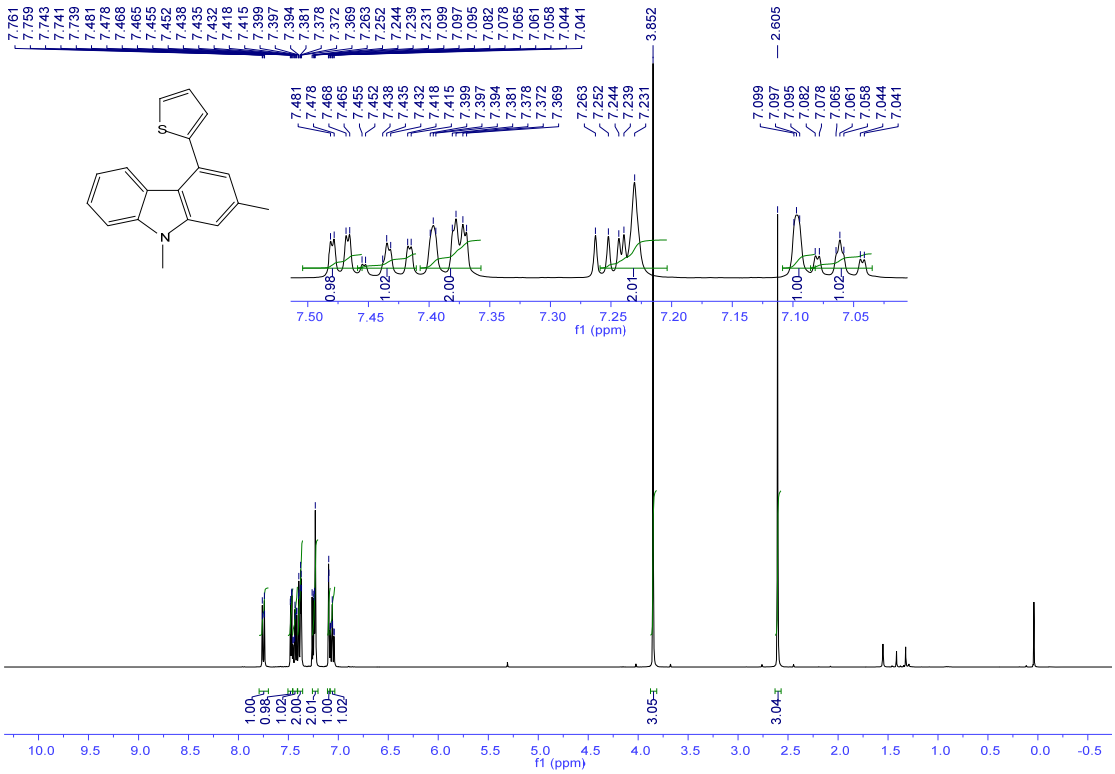
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **5t**



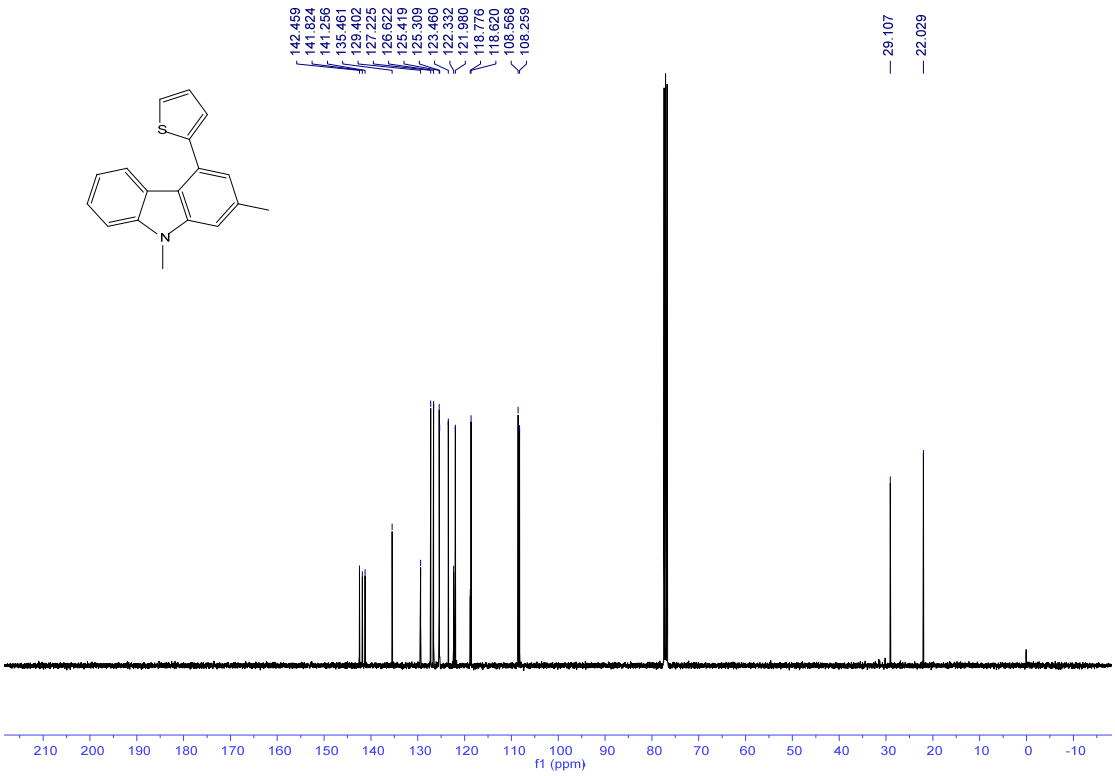
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5u**



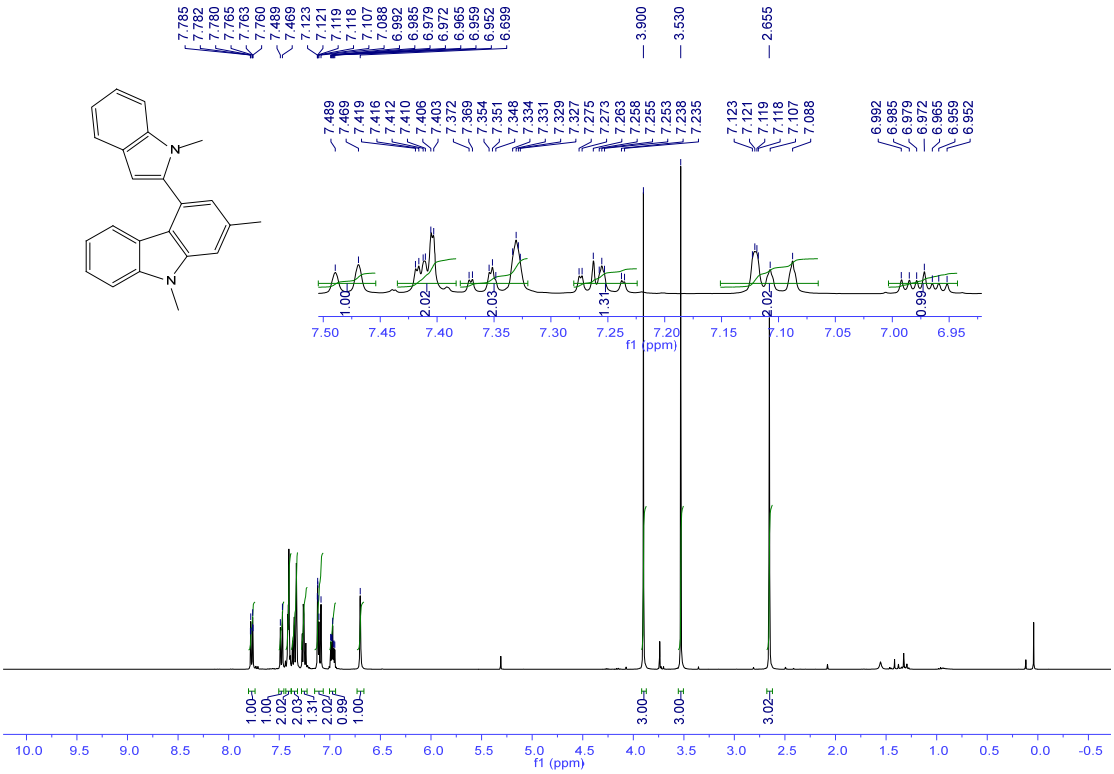
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **5u**



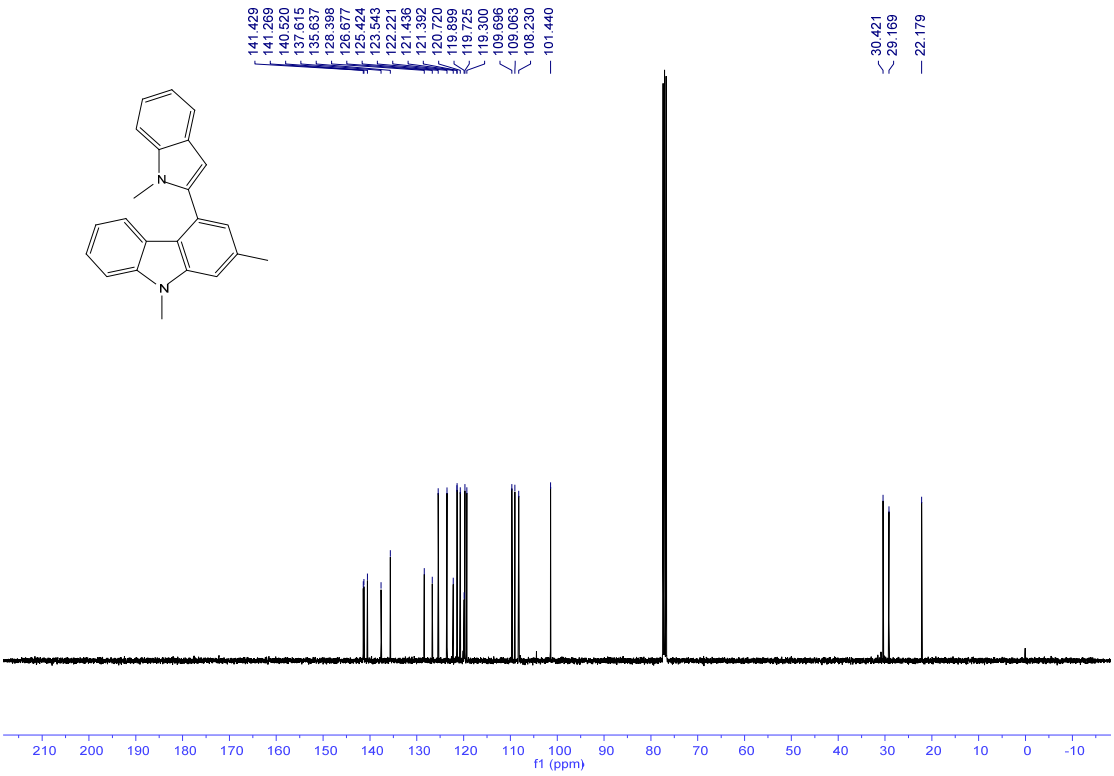
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5v**



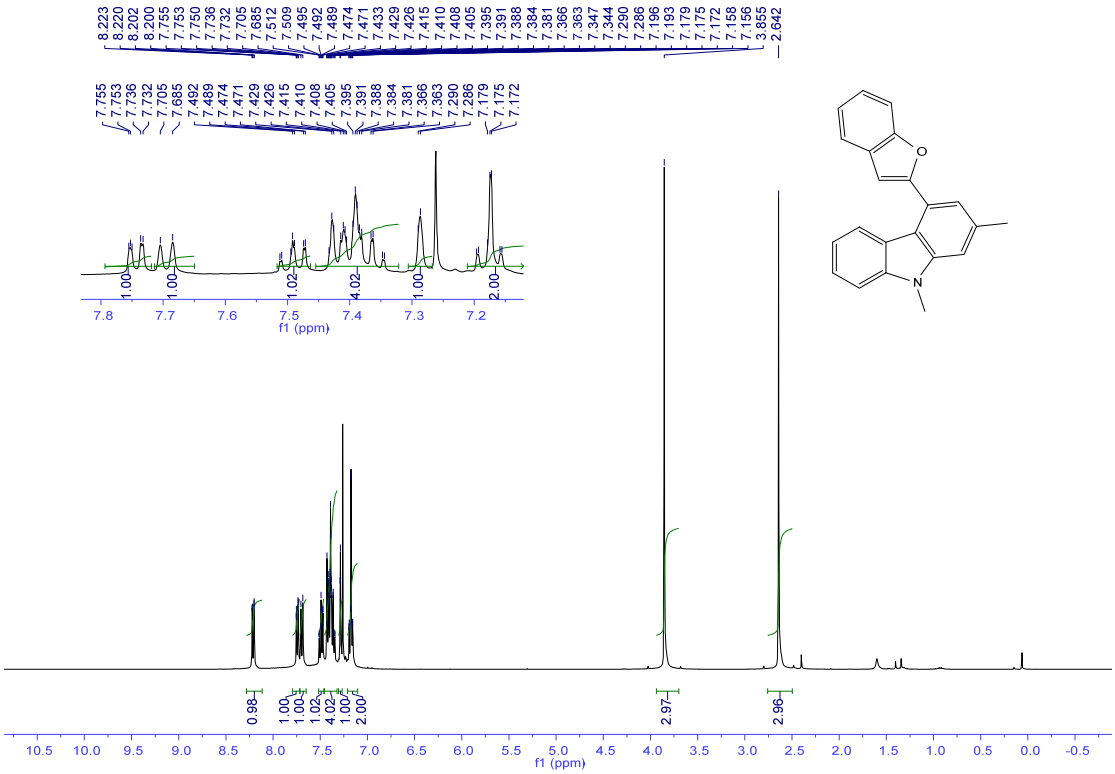
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of compound **5v**



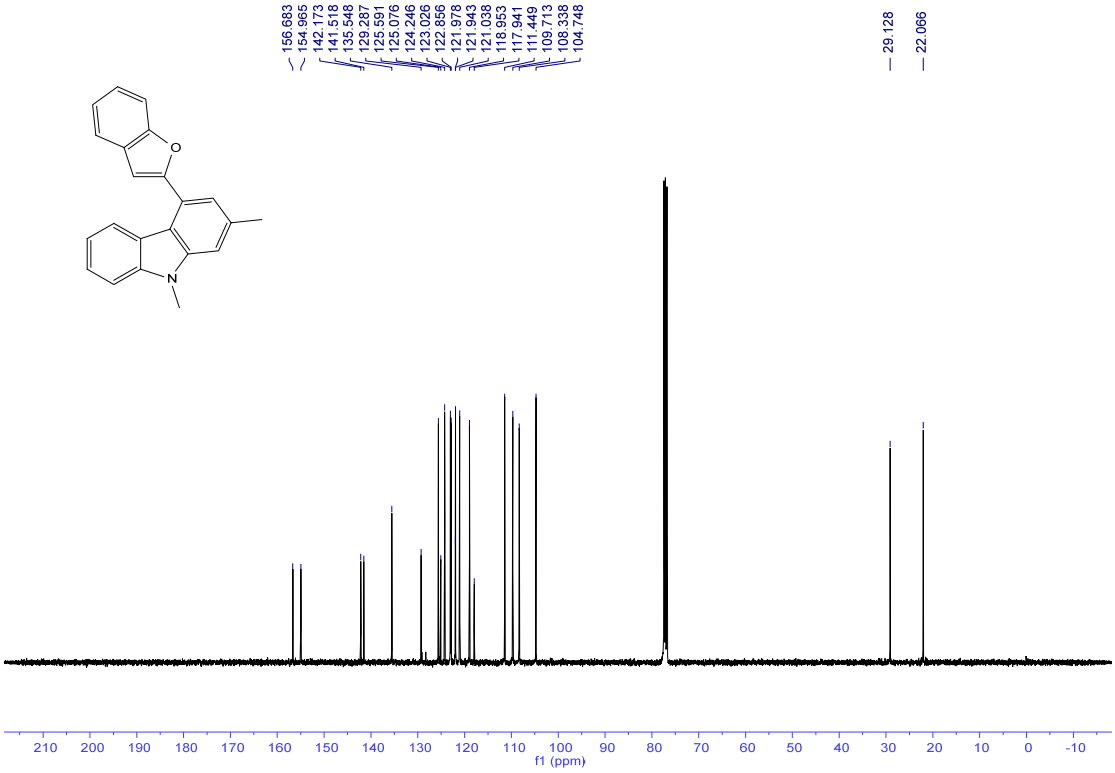
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5w**



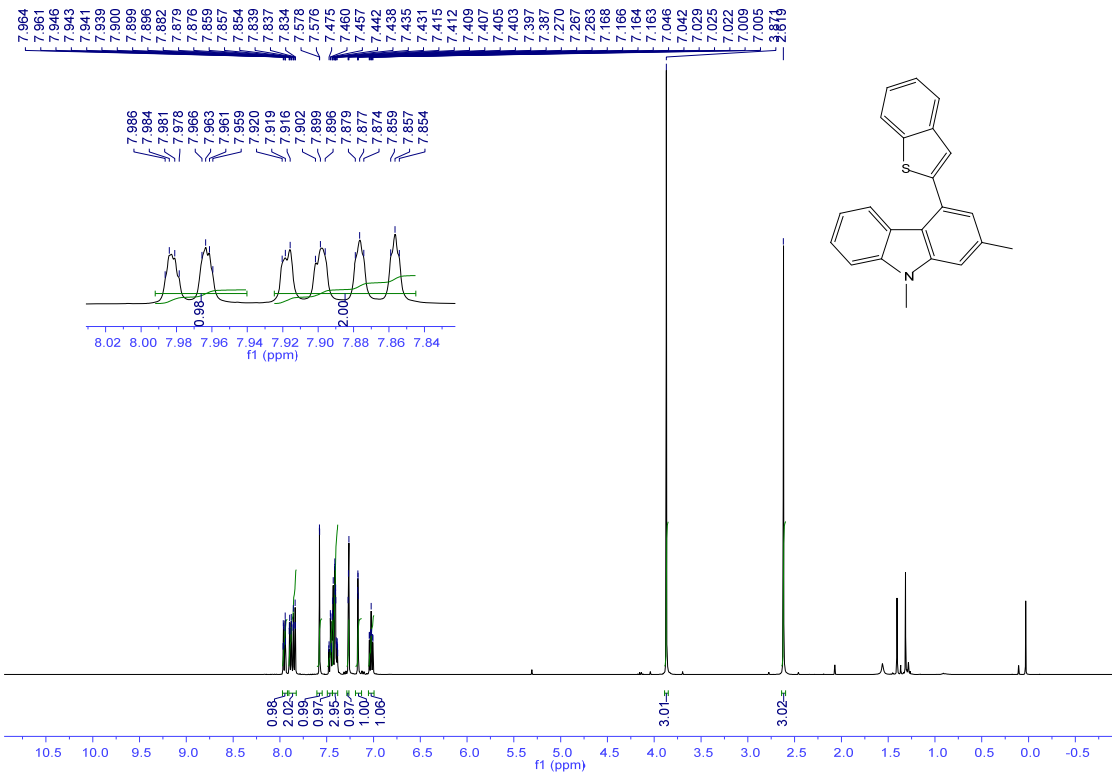
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **5w**



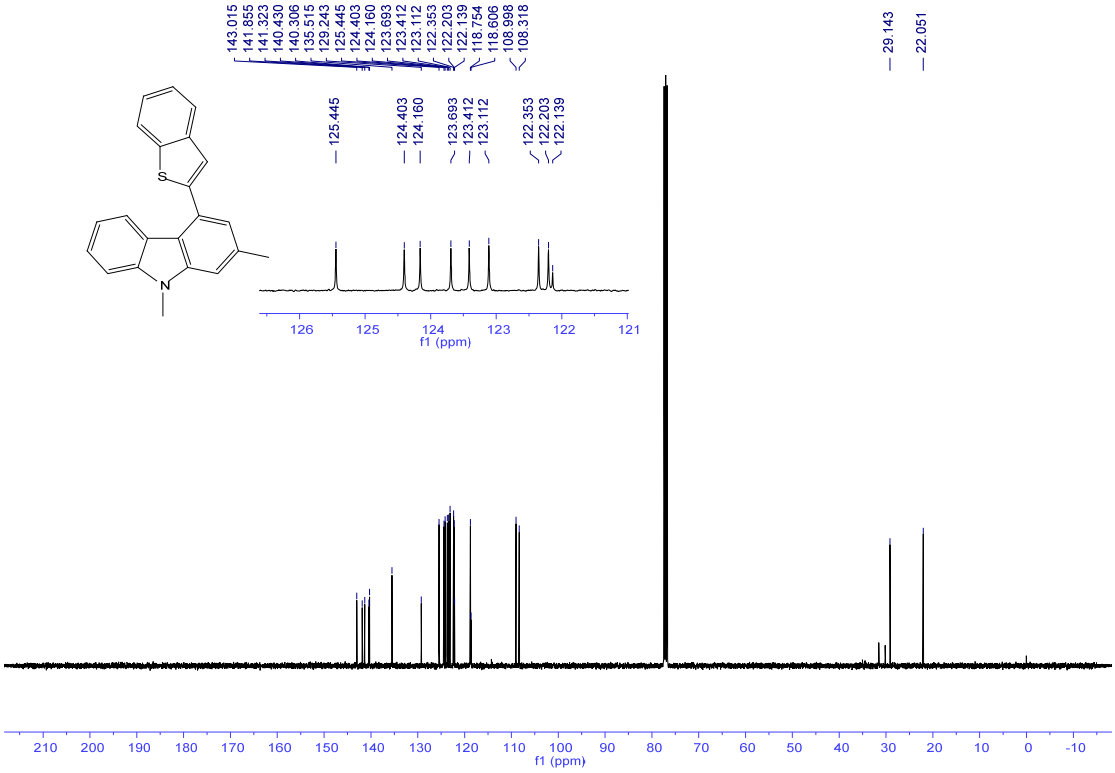
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5x**



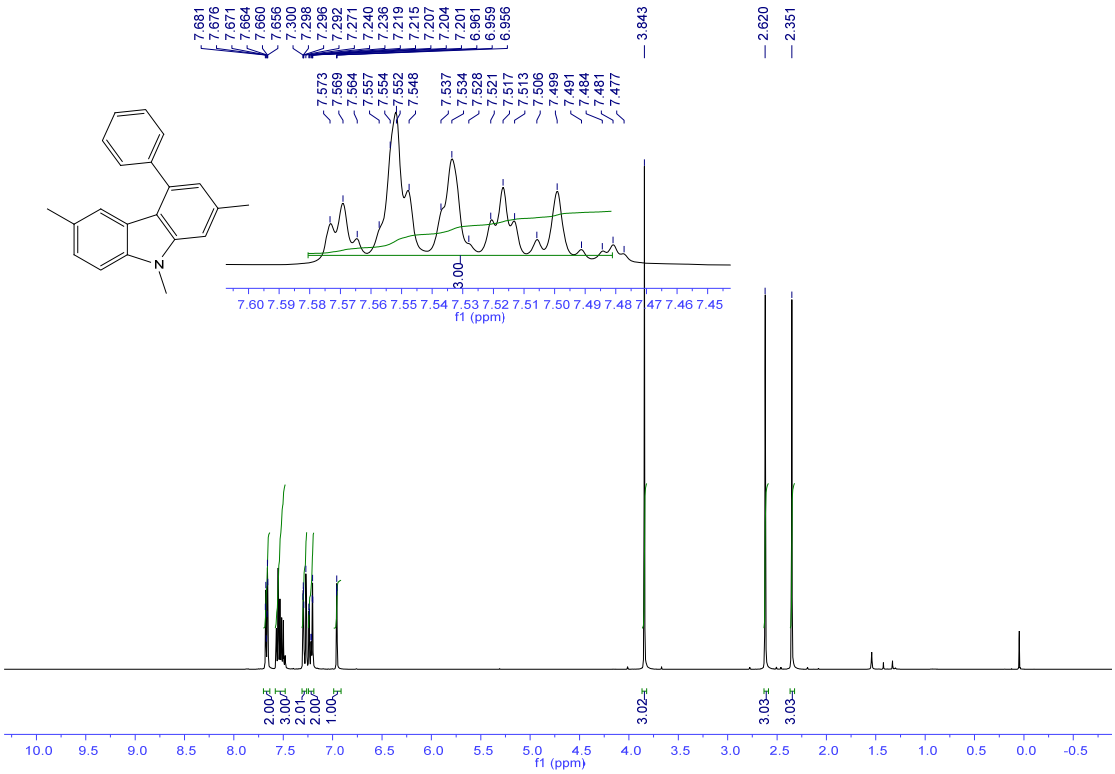
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of compound **5x**



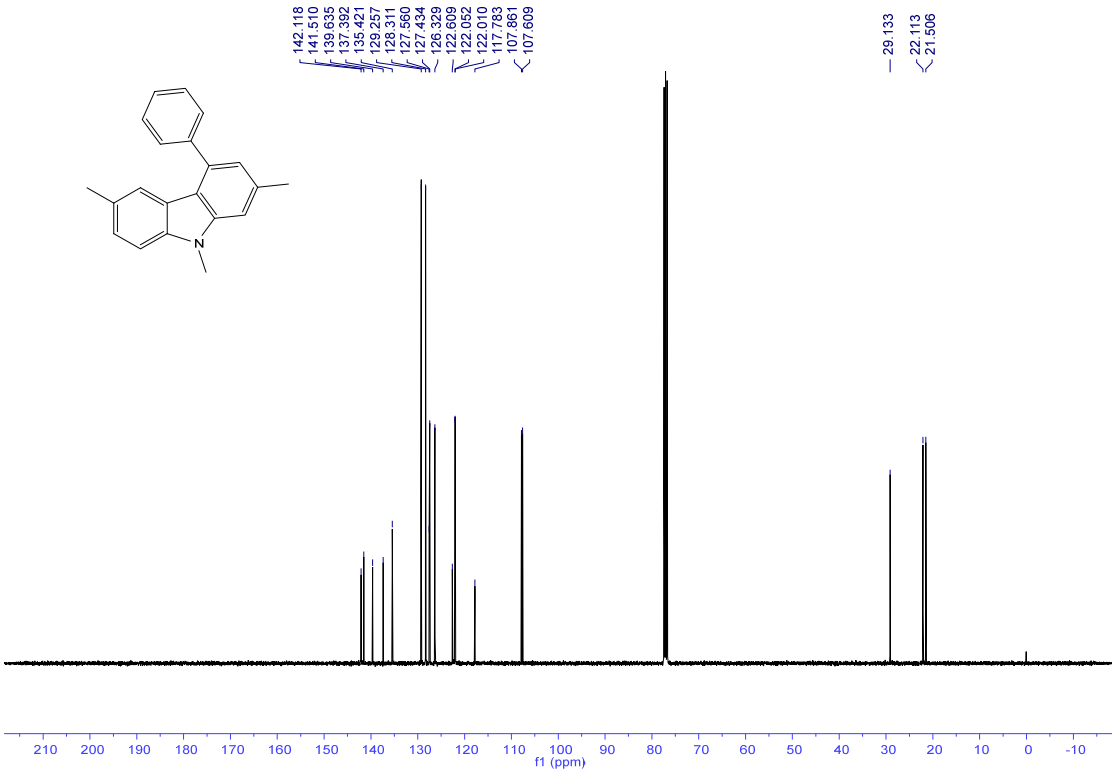
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5y**



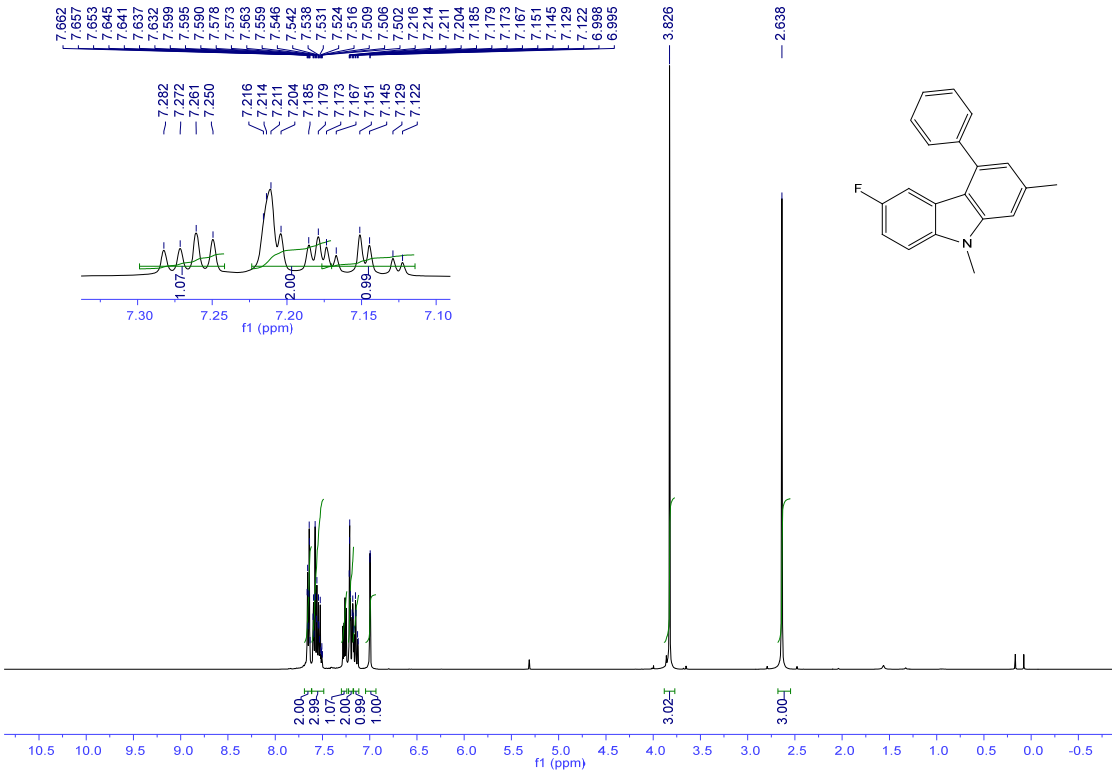
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **5y**



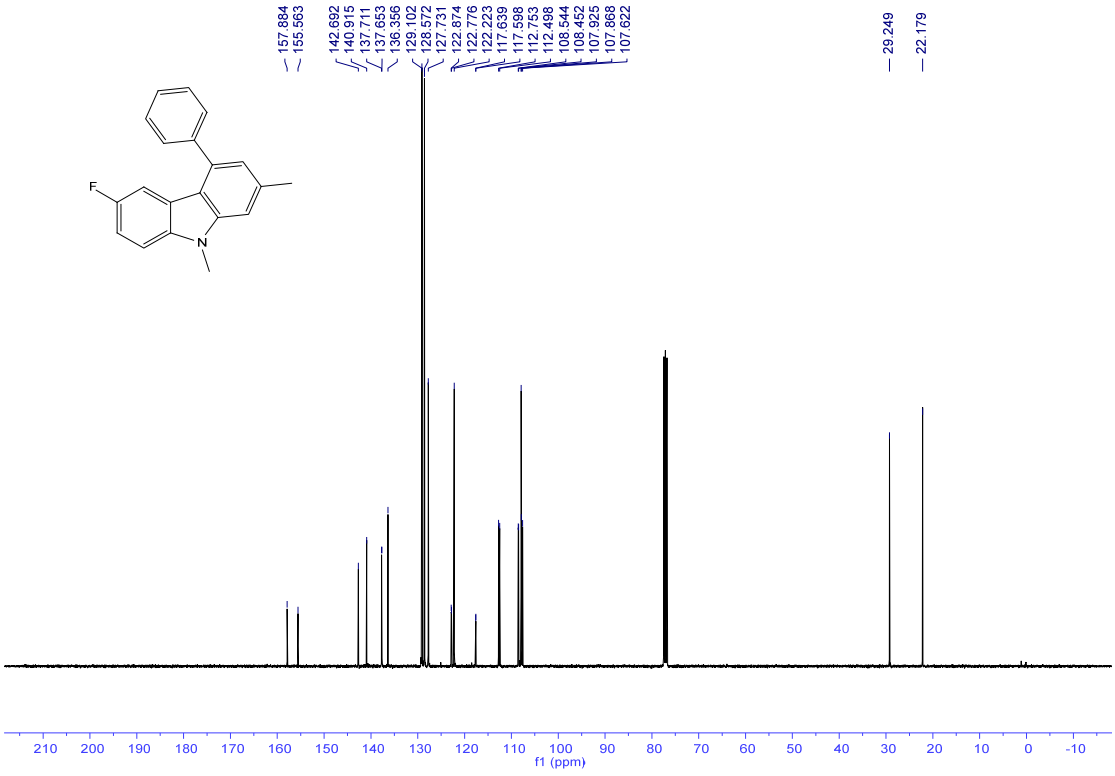
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5z**



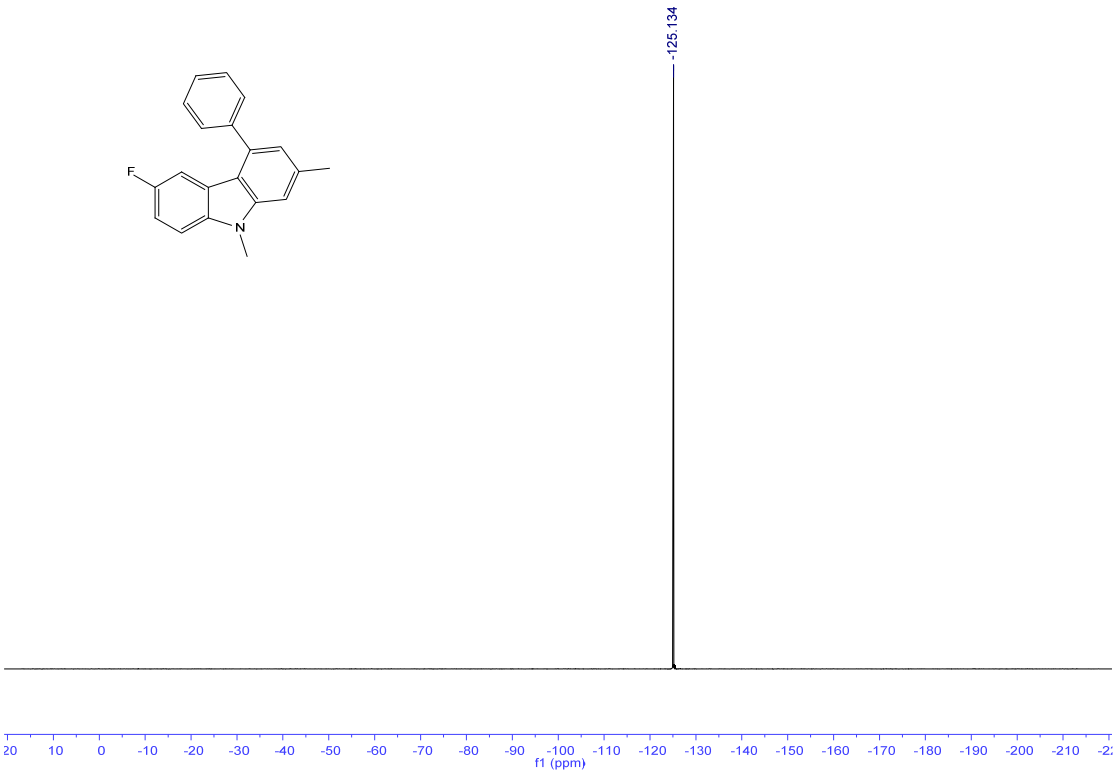
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **5z**



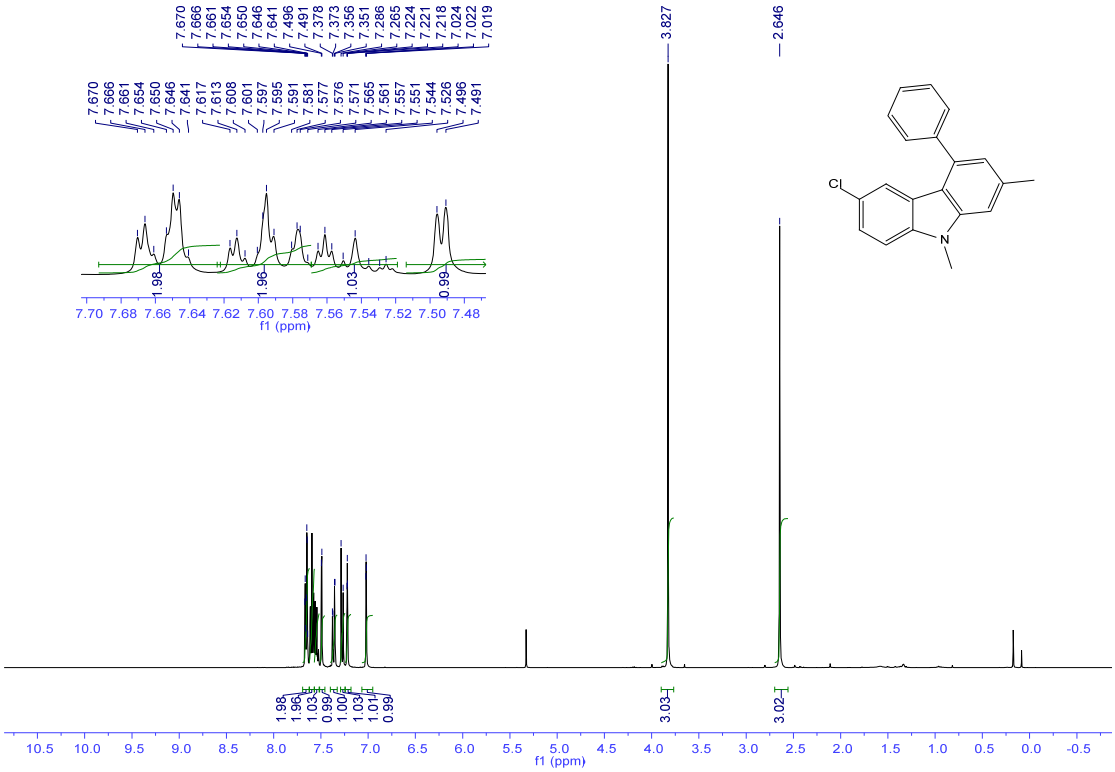
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5aa**



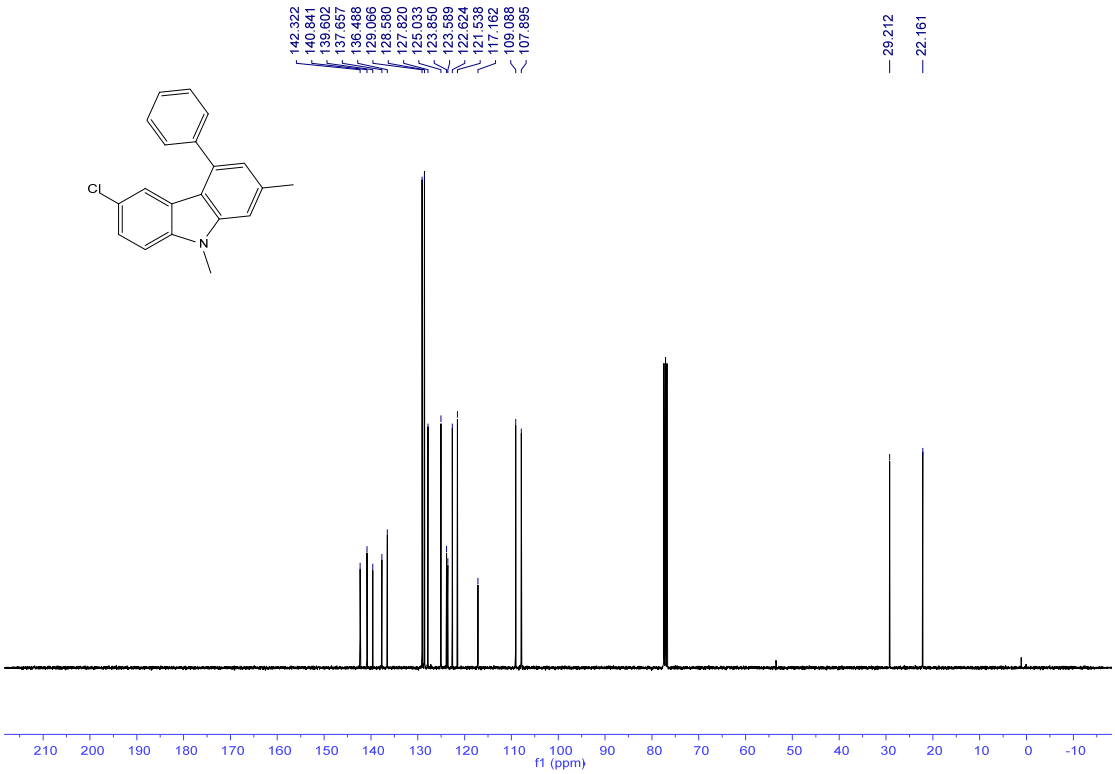
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of compound **5aa**



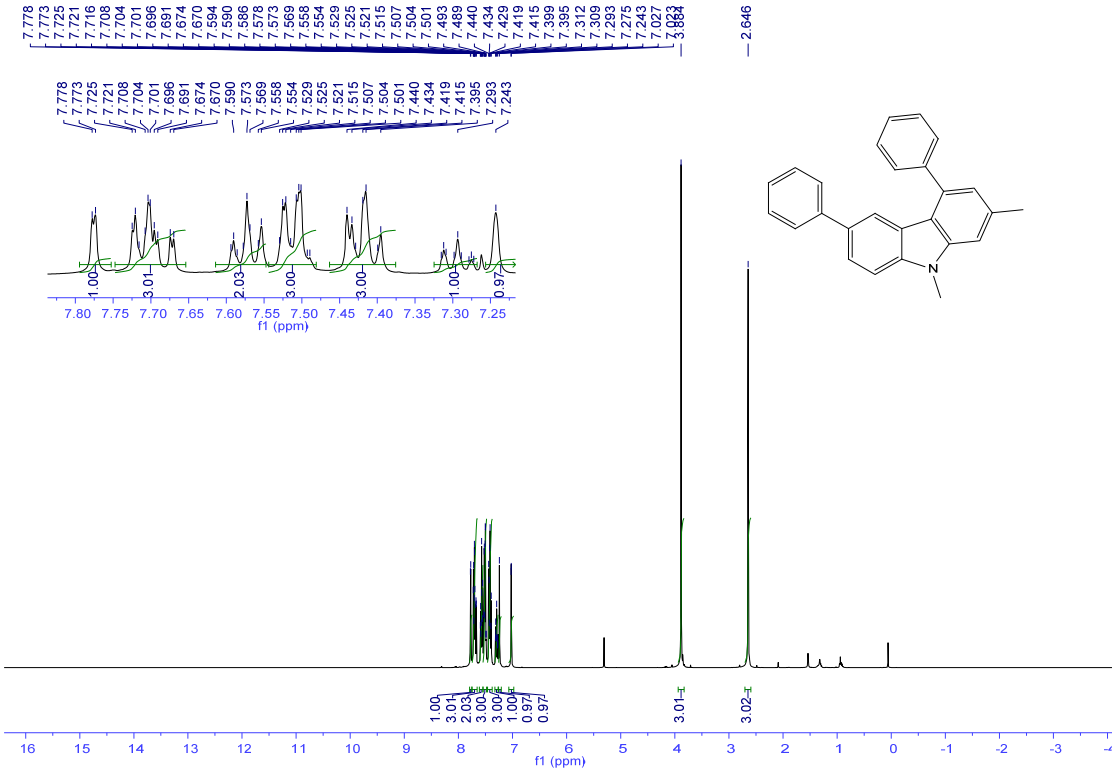
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5aa**



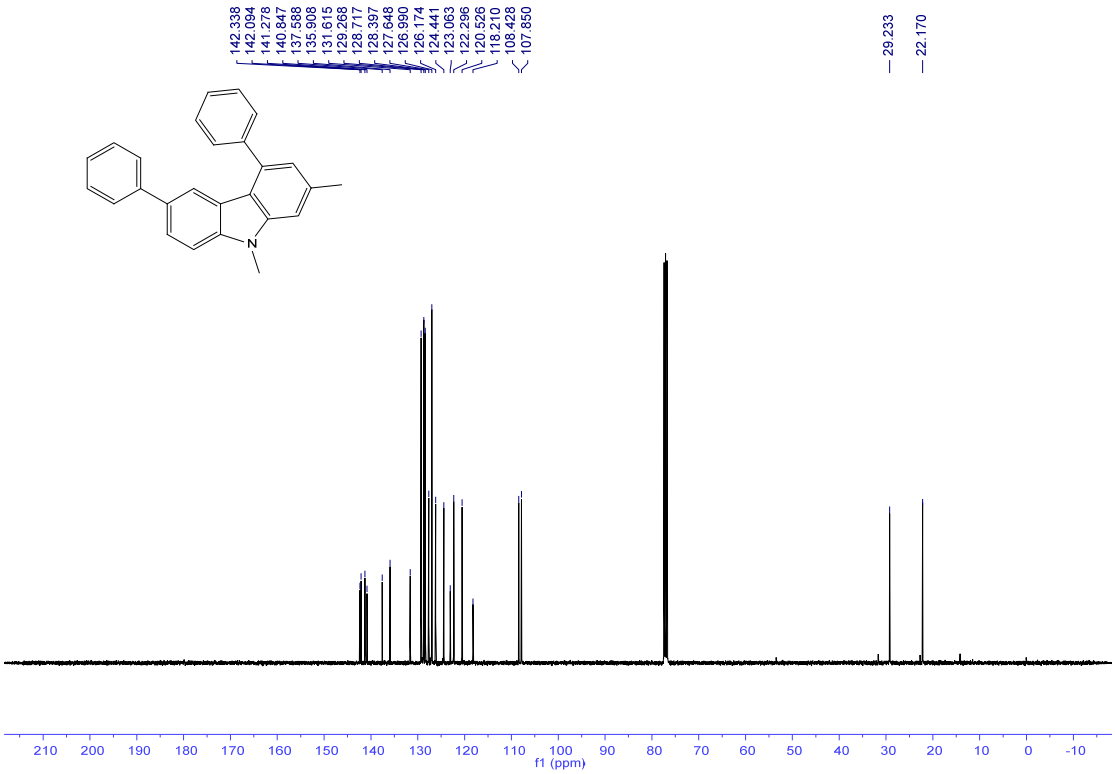
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5ab**



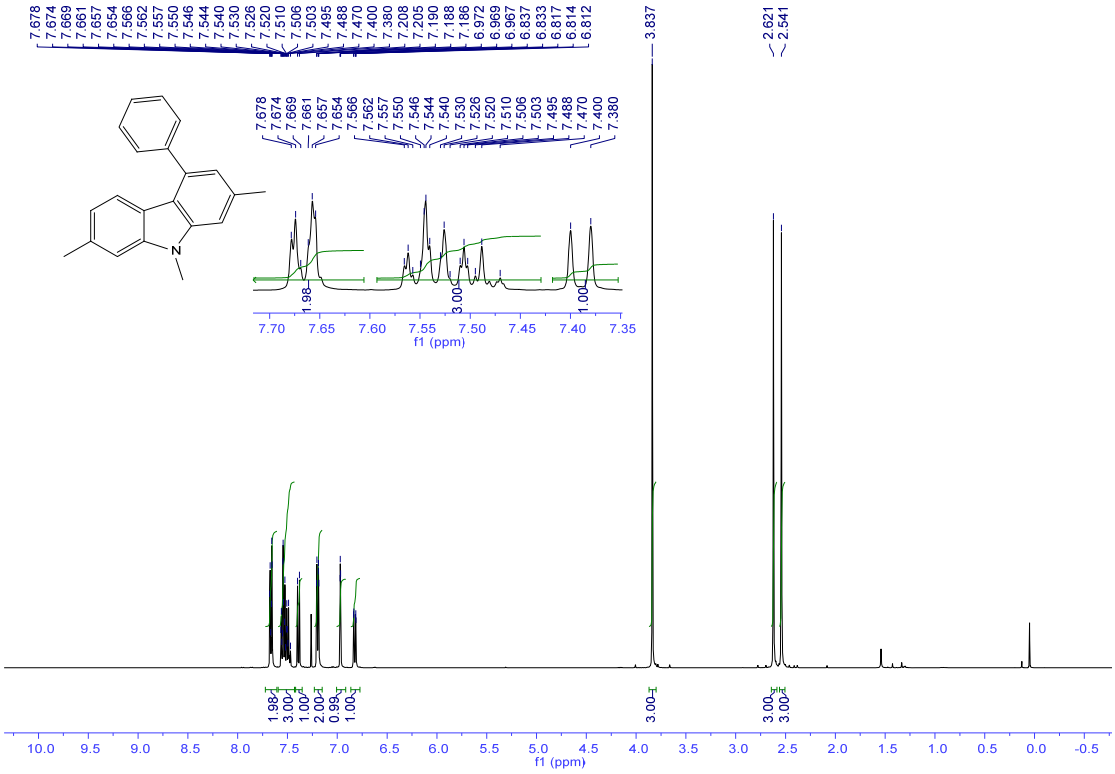
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **5ab**



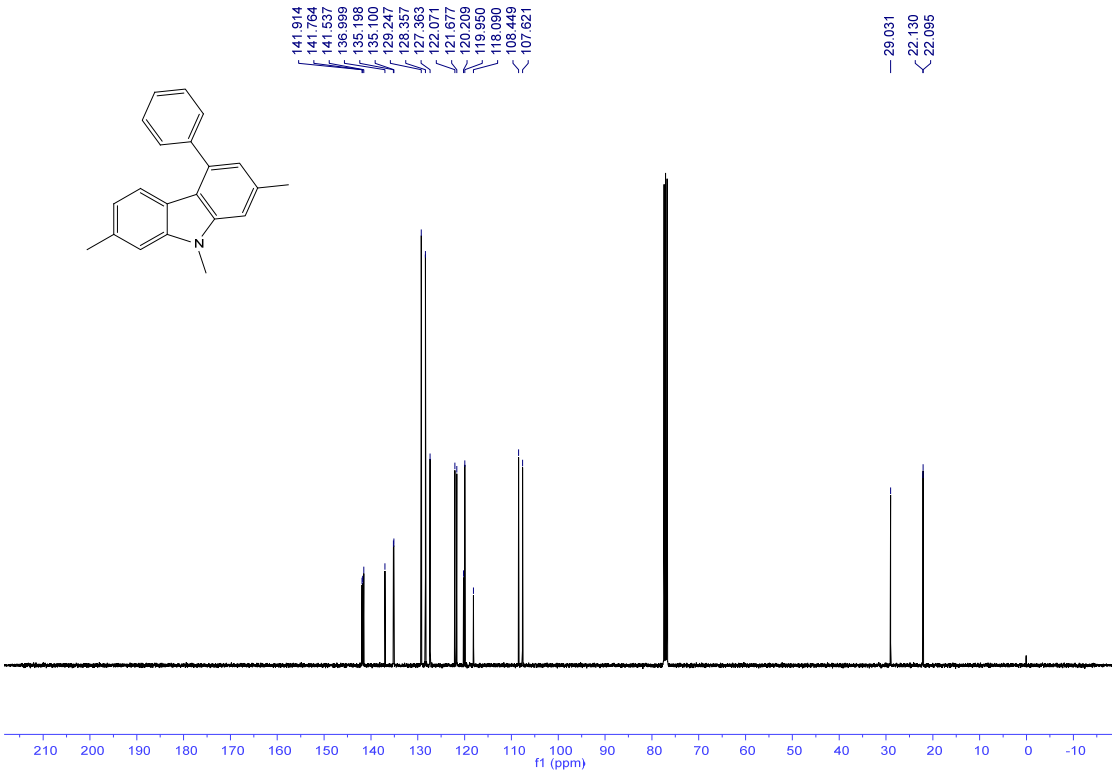
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5ac**



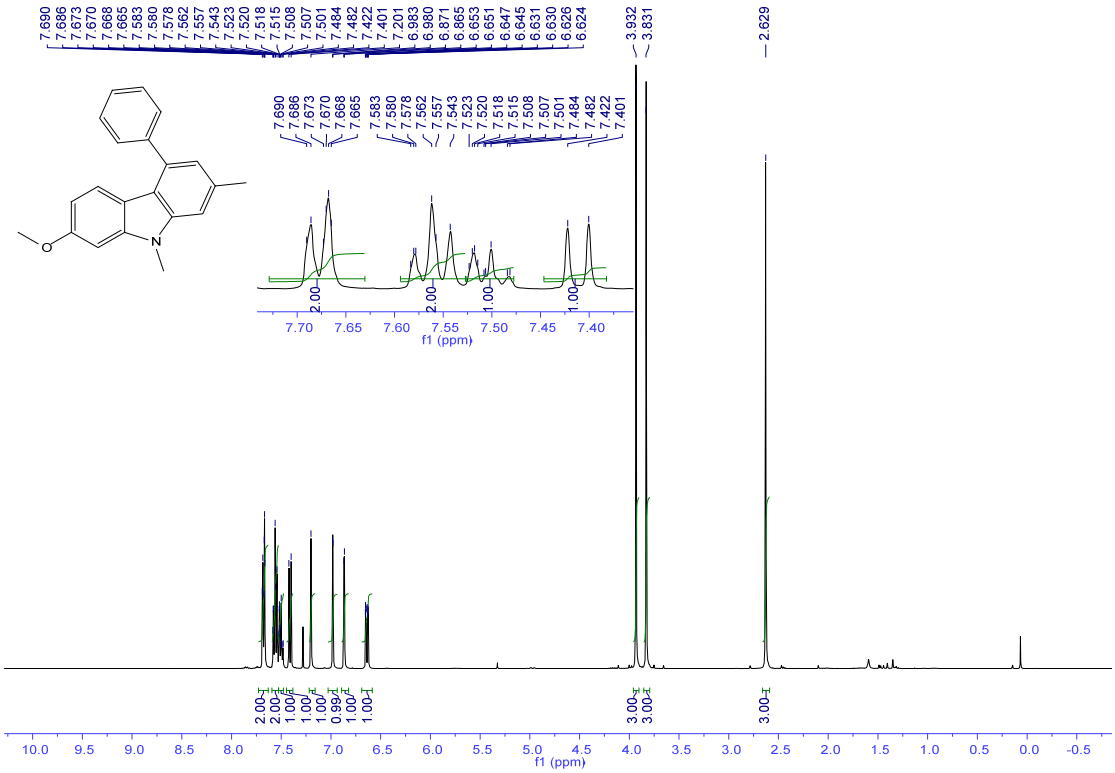
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **5ac**



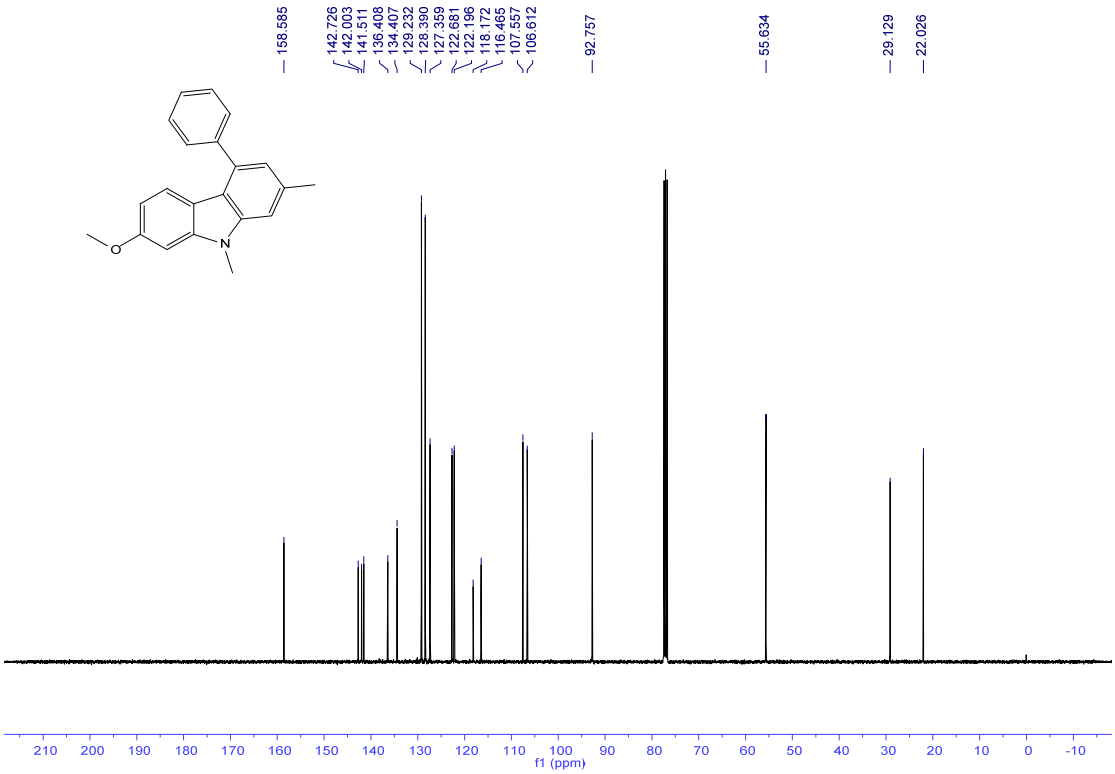
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5ad**



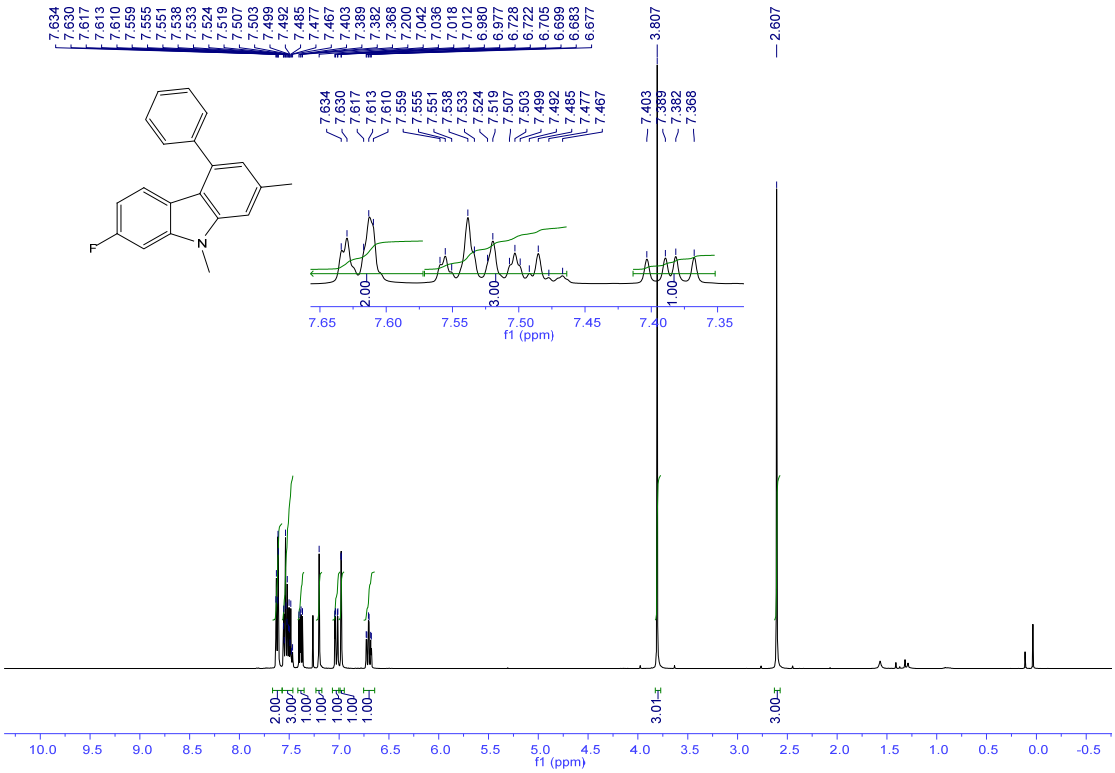
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **5ad**



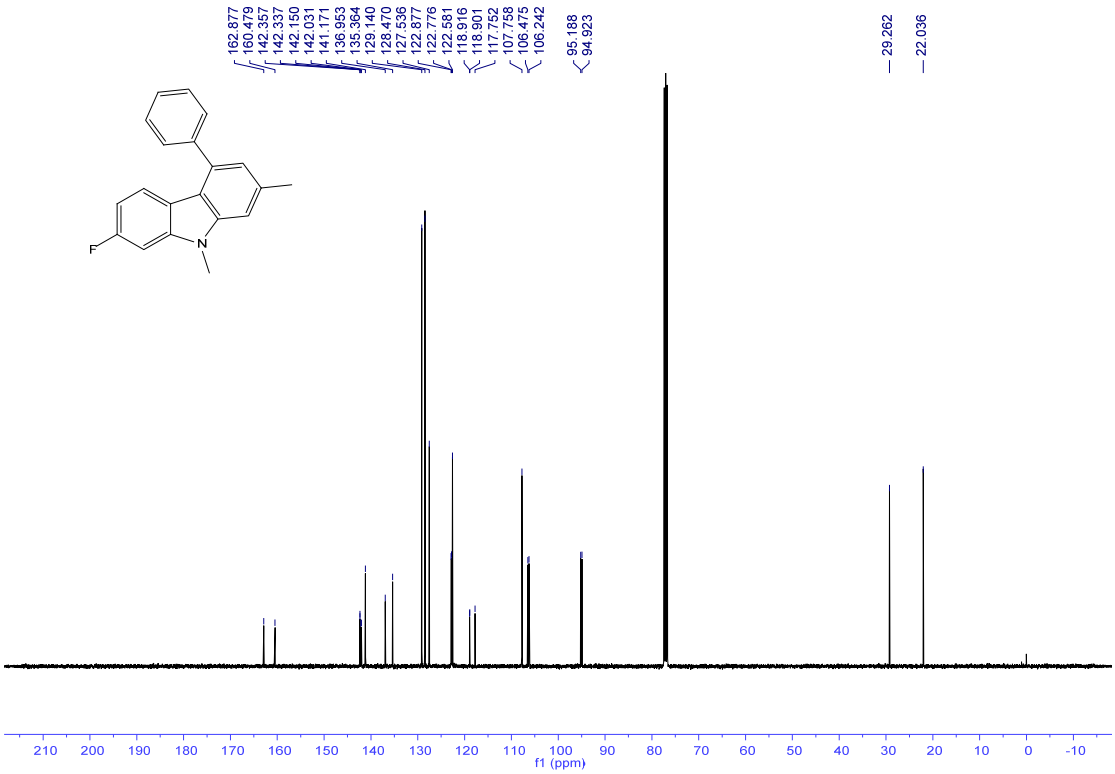
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5ae**



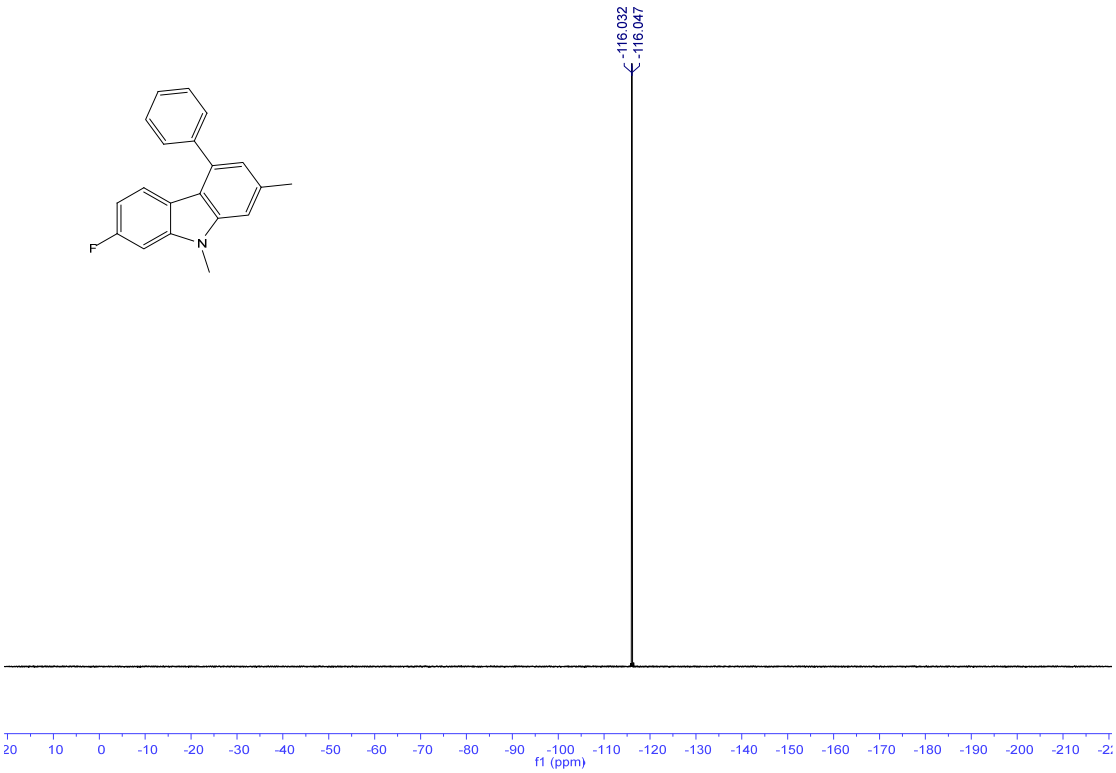
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **5ae**



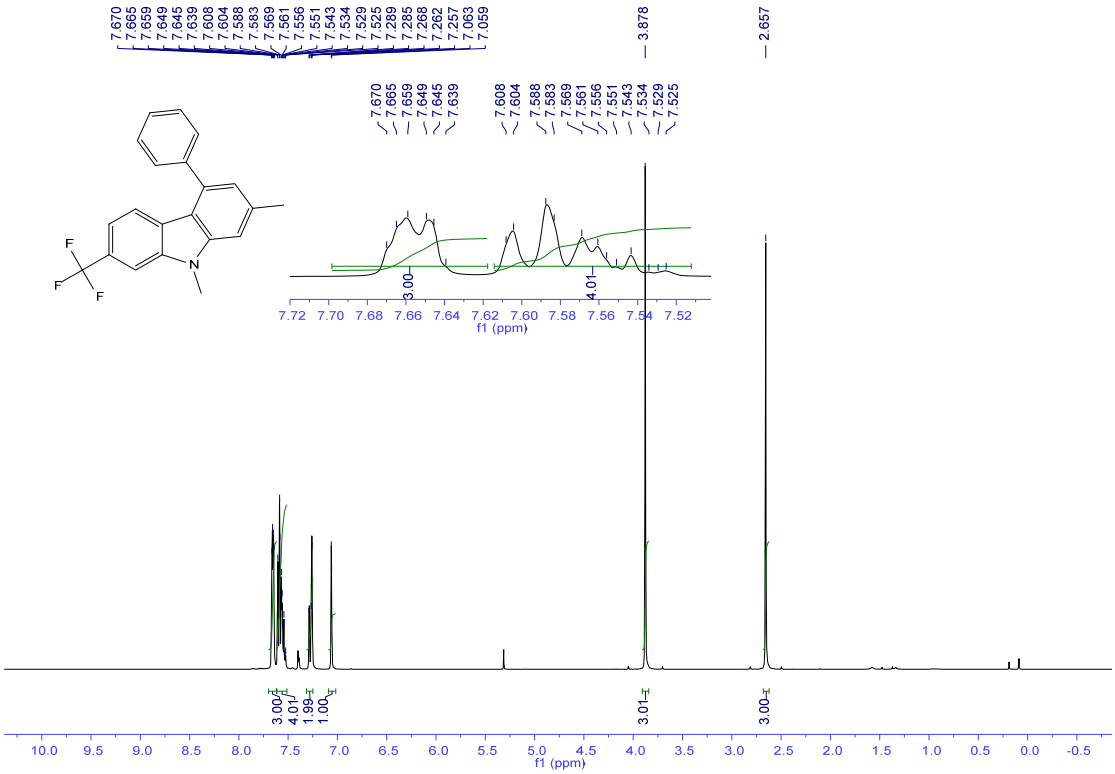
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5af**



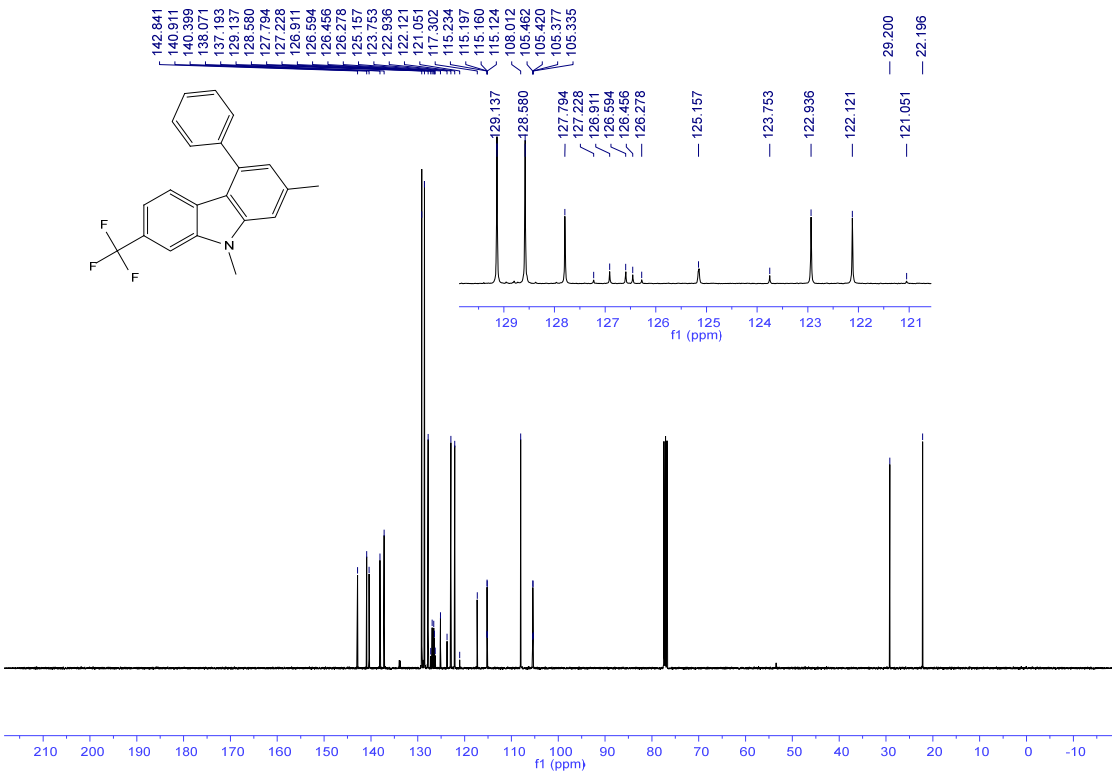
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **5af**



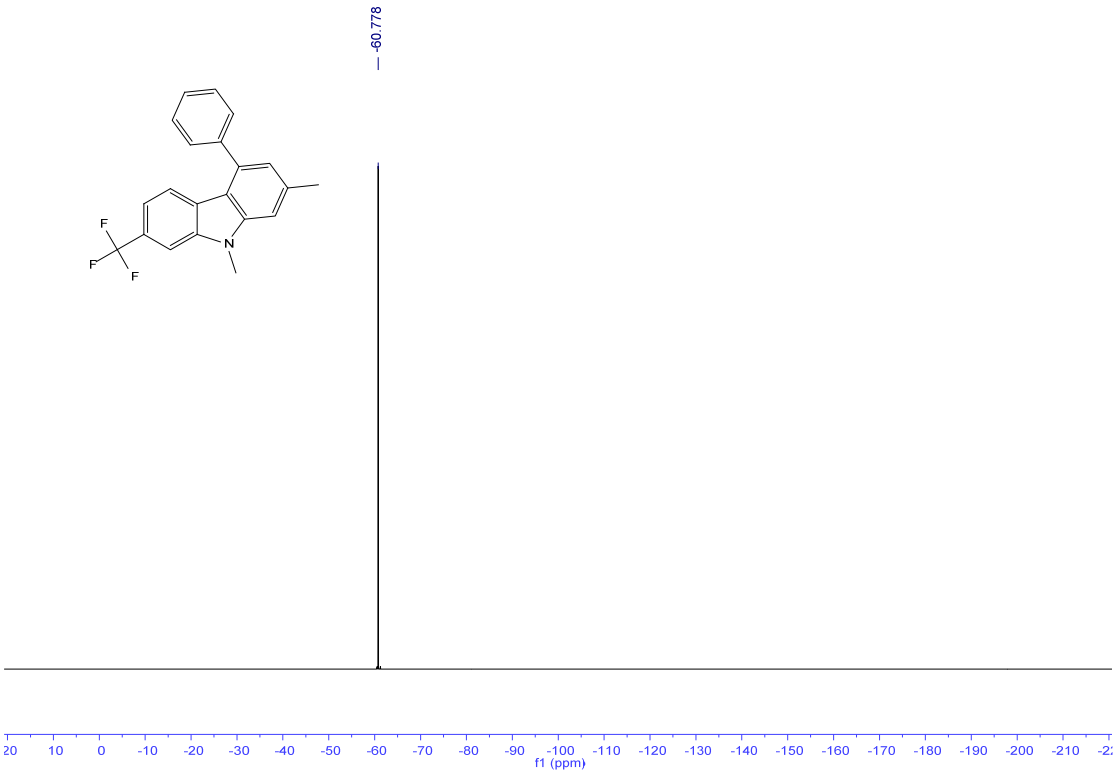
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5af**



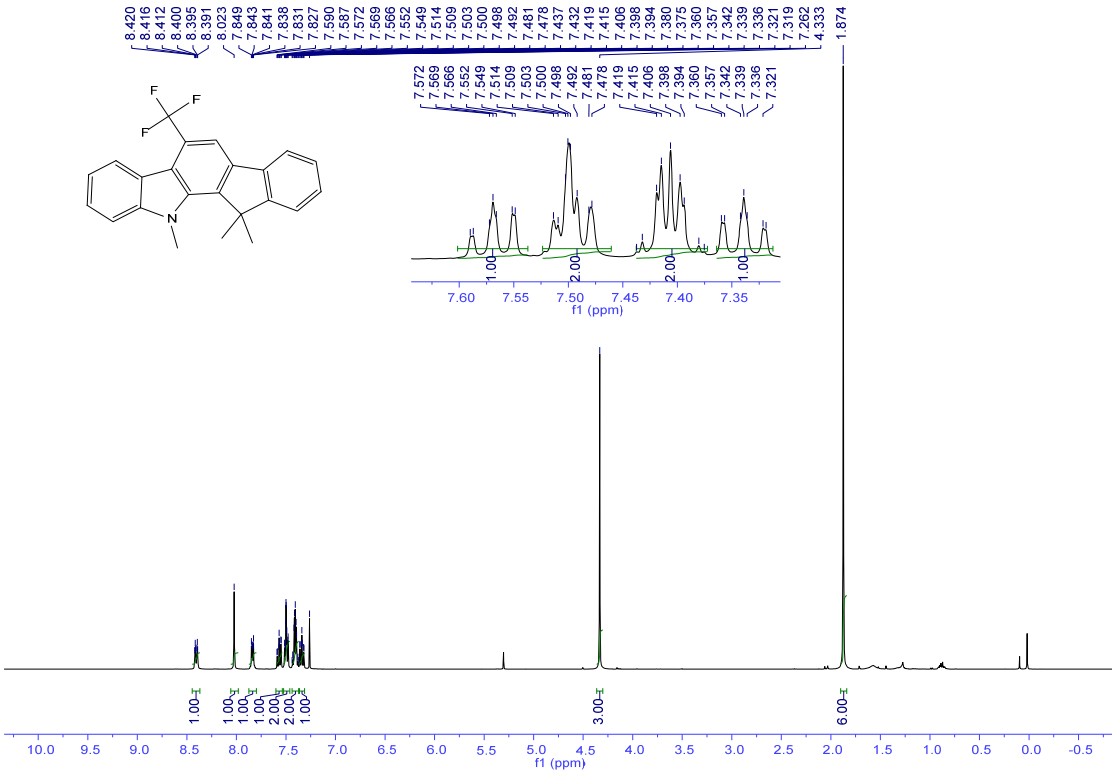
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5ag**



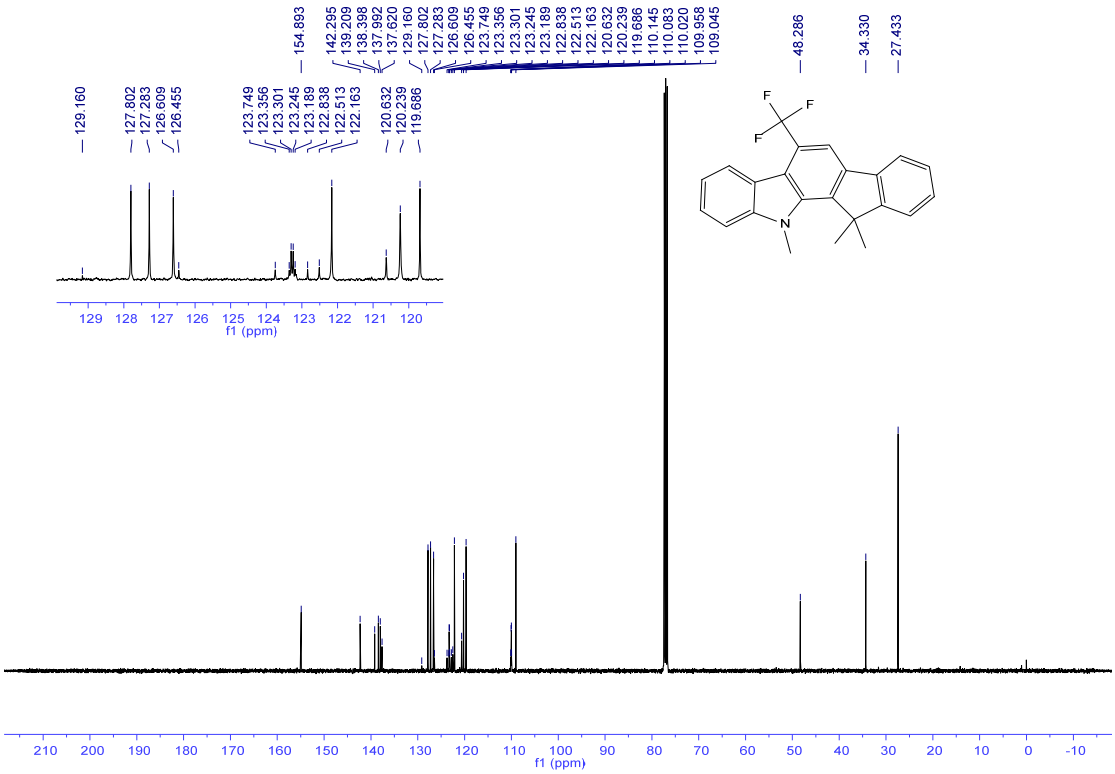
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **5ag**



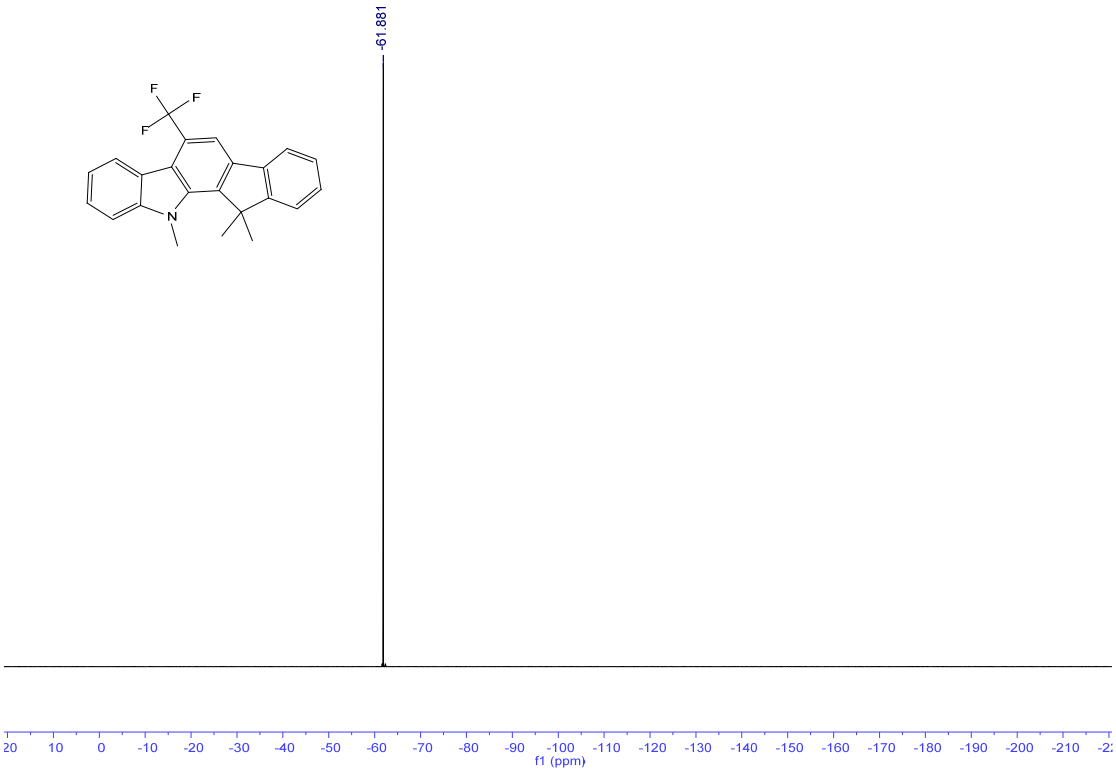
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5ag**



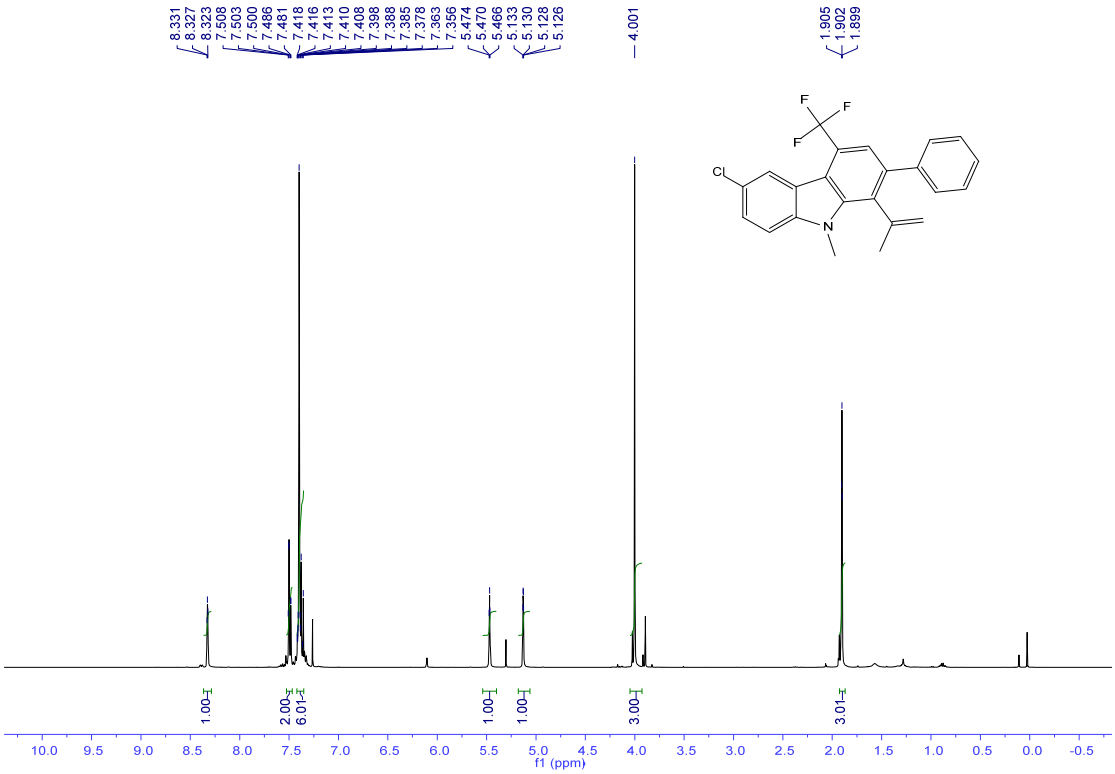
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6**



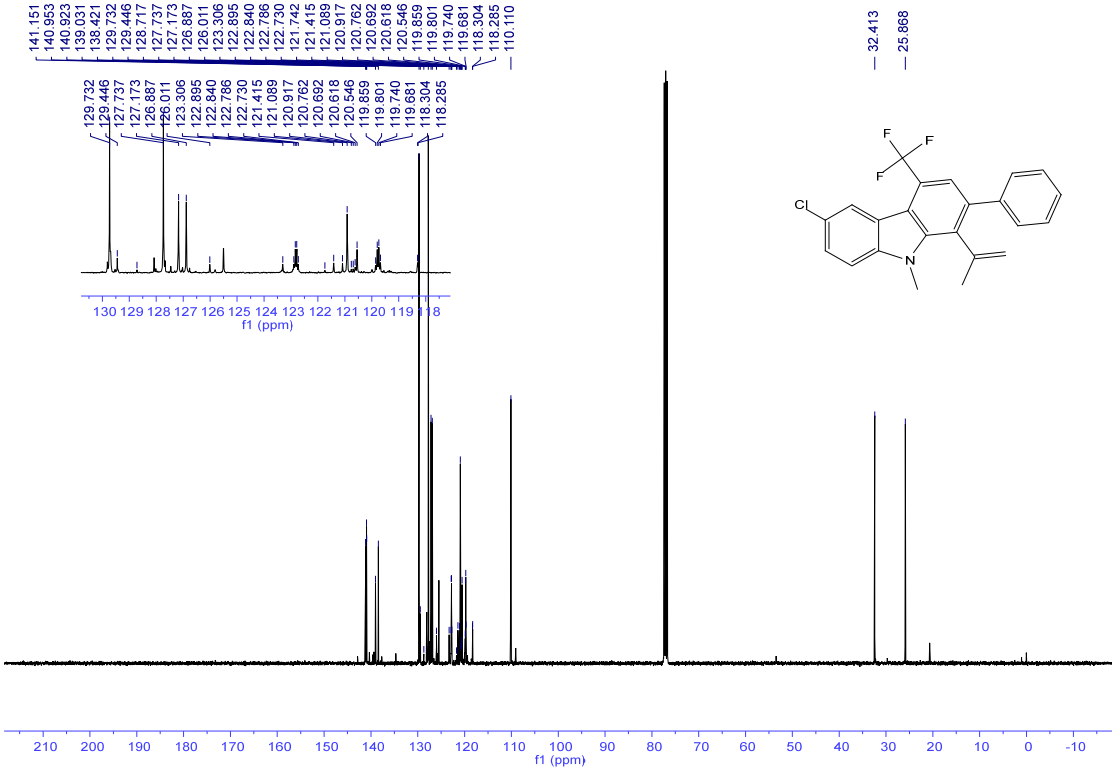
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **6**



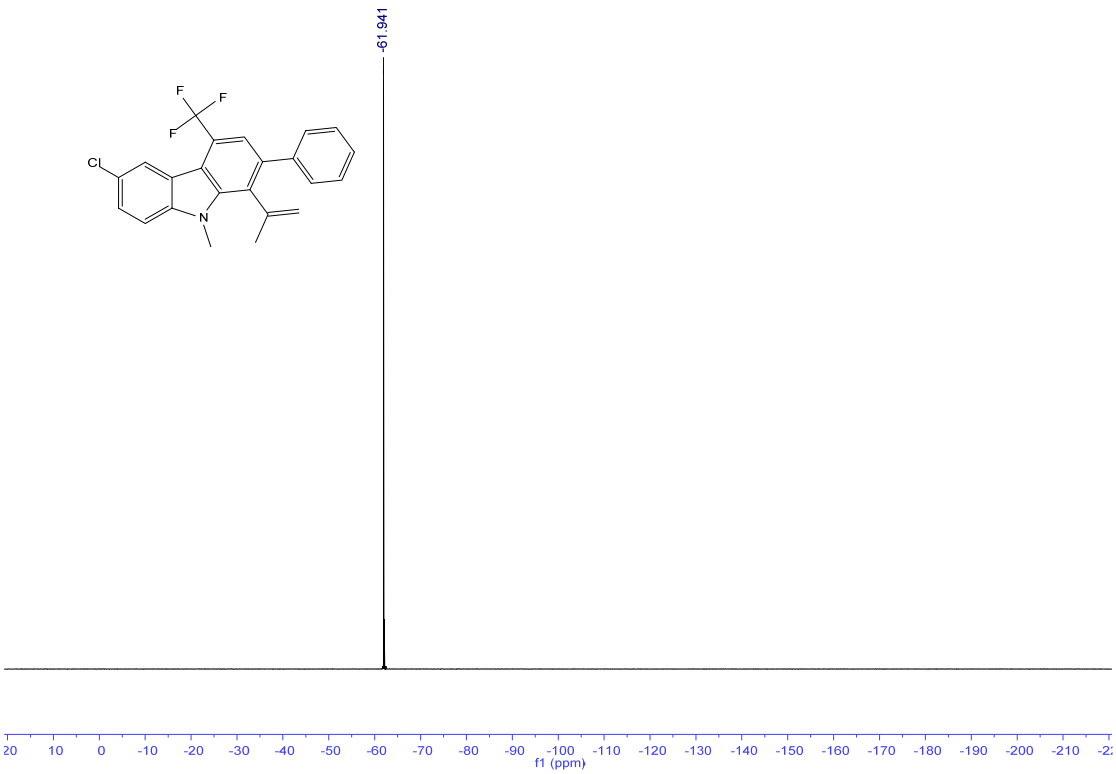
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **6**



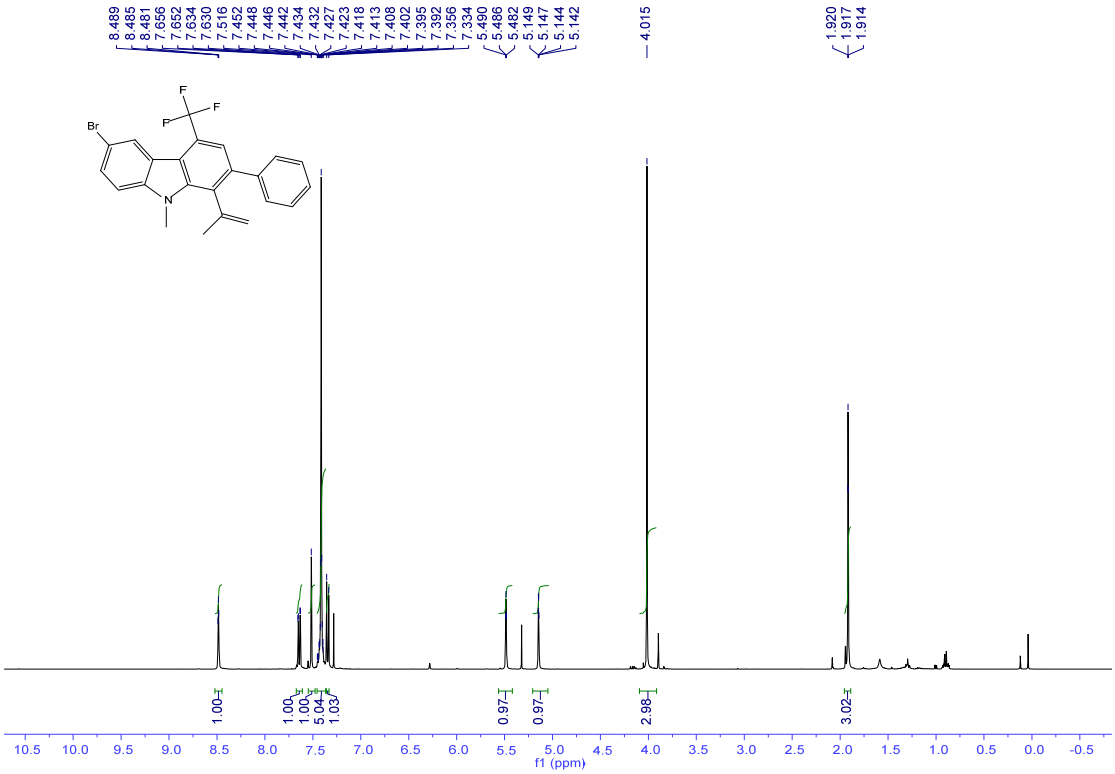
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ak** (from direct chlorination)



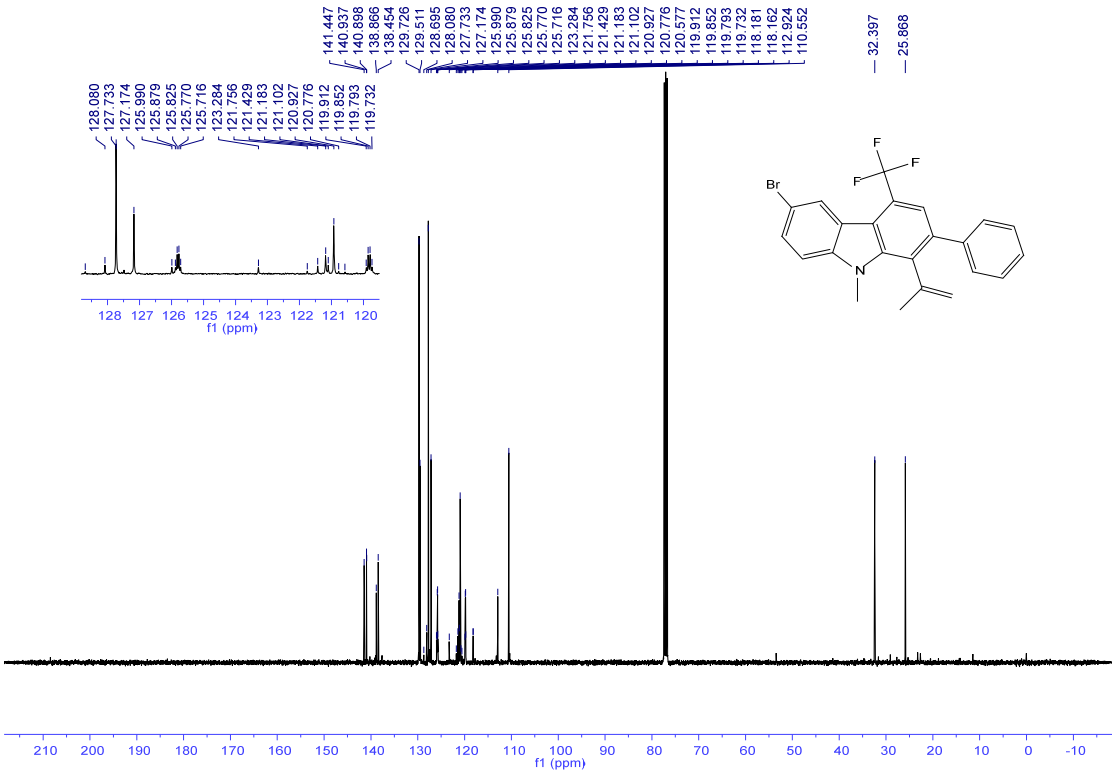
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of compound **3ak** (from direct chlorination)



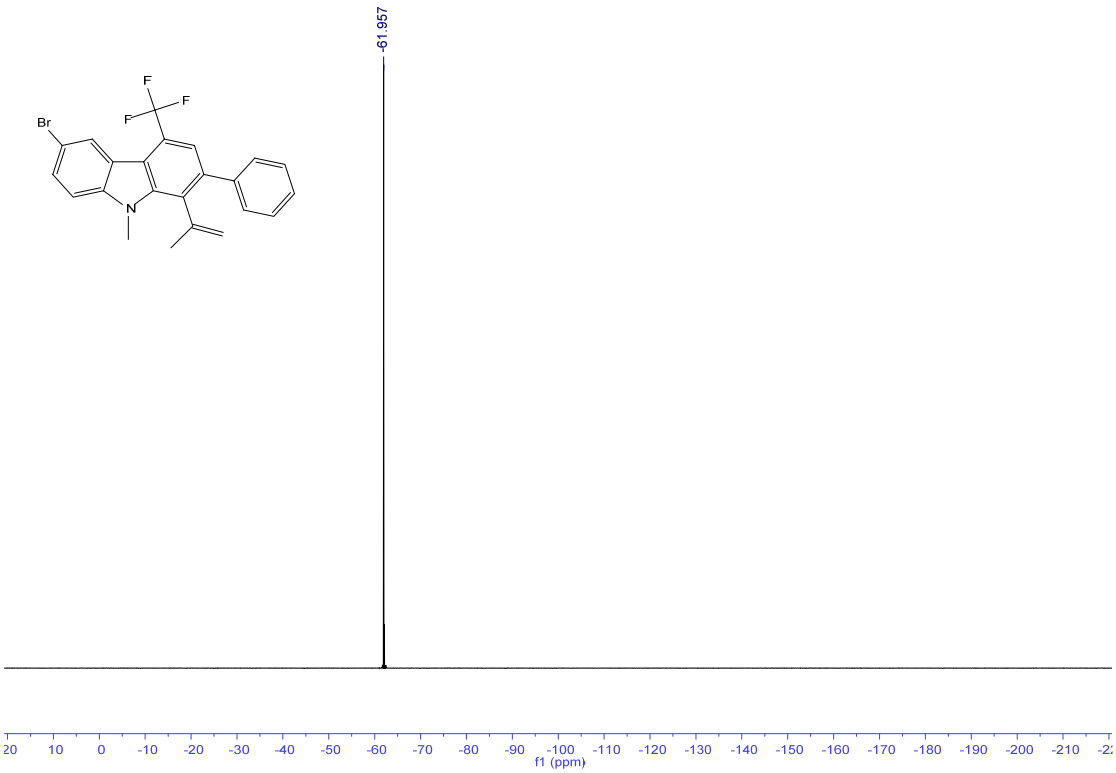
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3ak** (from direct chlorination)



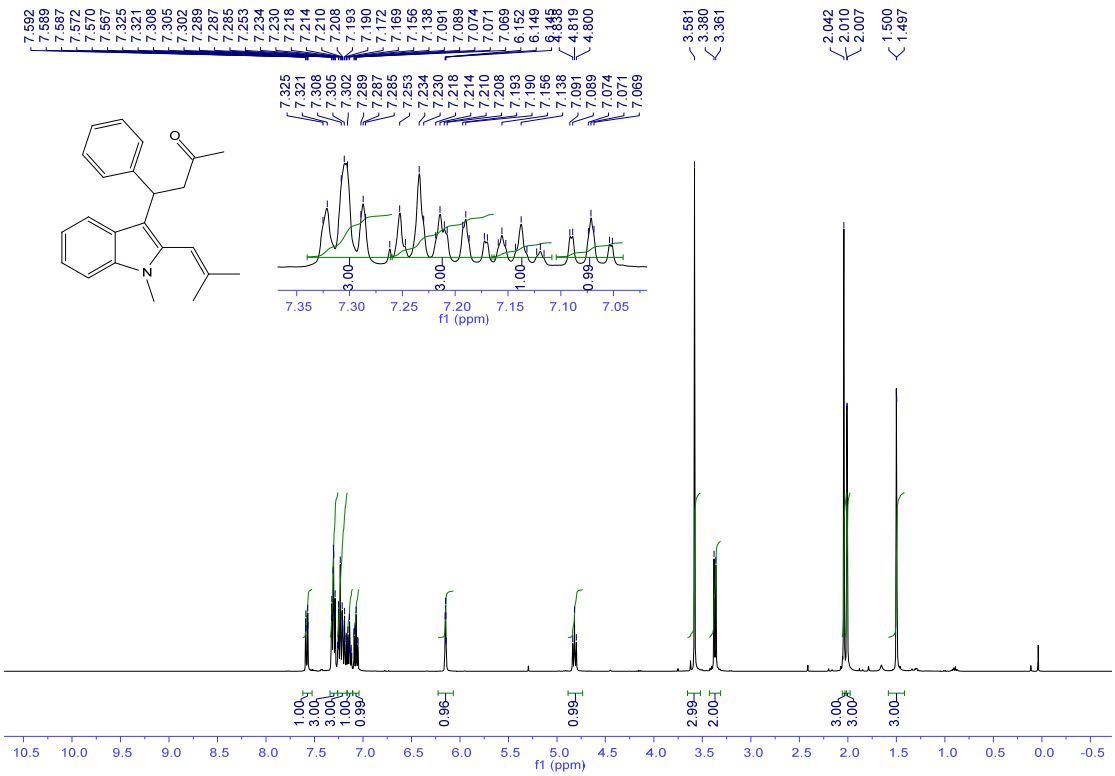
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3al** (from direct bromination)



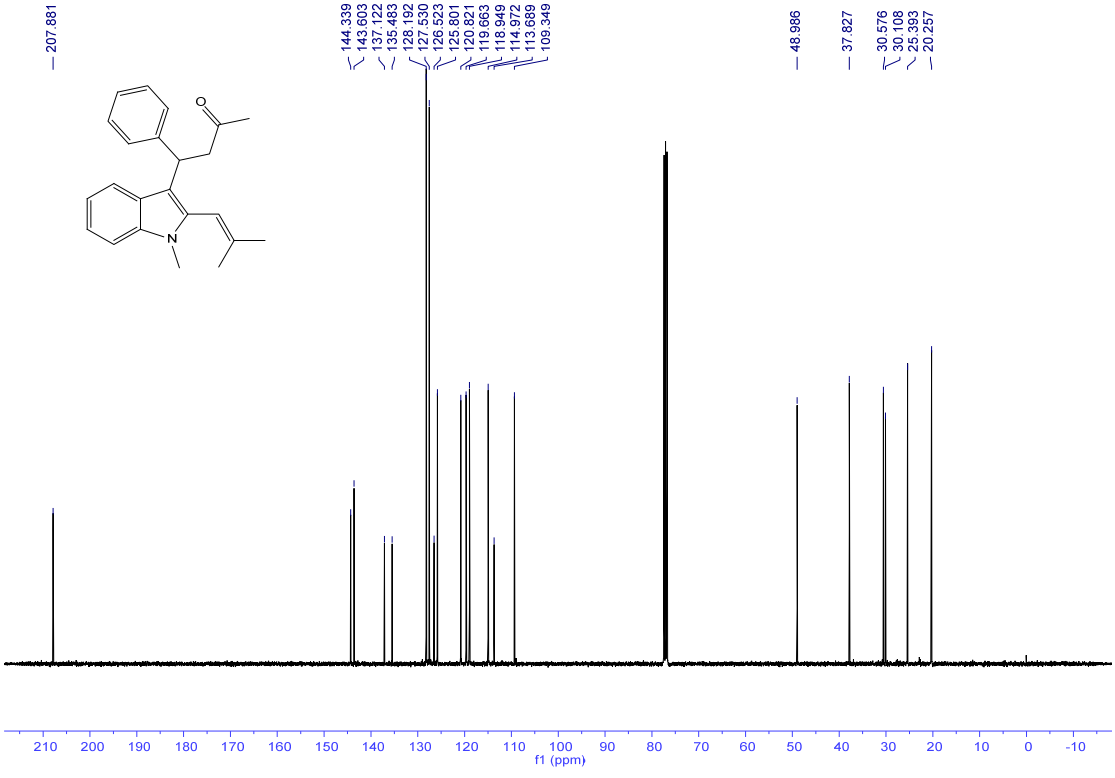
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3al** (from direct bromination)



^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3al** (from direct bromination)



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



$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **8**