Supporting Information

Catalyst-Free and Selective Trifluoromethylative Cyclizations of Acryloanilides Using $PhICF_3Cl$

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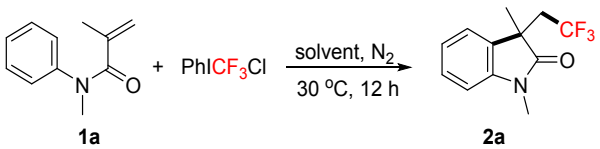
I. General Information

All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. PIFA and $TMSCF_3$ were purchased from Energy Chemical Co. Ltd., Anhydrous MeCN, THF (Tetrahydrofuran), DMF (N, N-dimethylformamide), 1,4-dioxane were purchased from Innochem Co. Ltd., DCM (dichloromethane) was distilled over CaH_2 before use. The products were purified by column chromatography over silica gel (particle size 300-400 mesh ASTM, purchased from Taizhou, China). ^1H NMR, ^{13}C NMR spectra were recorded at 25 ºC on a Bruker 600 MHz or Varian 500 MHz, 400 MHz, and 151 MHz or 125 MHz spectrometer, respectively by using TMS as internal standard. ^{19}F-NMR were recorded at 25 ºC on a Bruker 565 MHz or Varian 470 MHz spectrometer by using (trifluoromethyl)benzene (δ -63.2 ppm) as external standard. Data for ^1H, ^{13}C, ^{19}F were recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, td = triplet of doublets). High-resolution mass spectra (HRMS) were obtained using a Bruker micro TOF II focus spectrometer (ESI). Melting points were uncorrected. $PhICF_3Cl$ reagent was prepared according to literature procedures.[1]

II. Screen of Reaction Conditions

Table S1. Screen of solvents.[a]



1a **2a**

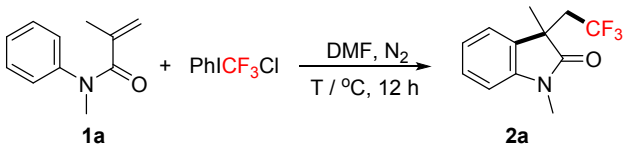
Entry	Solvent	Yield of **2a** [%][b]
1	toluene	0
2	DCE	0
3	MeCN	8
4	CH_2Cl_2	18
5	THF	46
6	1,4-dioxane	82
7	NMP	82

8	DMF	85

[a]Reaction conditions: **1a** (0.1 mmol), $PhICF_3Cl$ (0.15 mmol), solvent (1 mL).

[b]^{19}F NMR yields using $PhCF_3$ as an internal standard.

Table S2. Screen of temperature.[a]



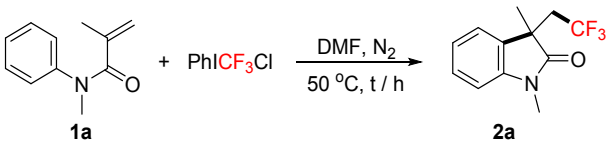
1a **2a**

Entry	*T* [°C]	Yield of **2a** [%][b]
1	rt	0
2	30	85
3	40	90
4	50	96
5	60	95

[a]Reaction conditions: **1a** (0.1 mmol), $PhICF_3Cl$ (0.15 mmol), DMF (1 mL).

[b]^{19}F NMR yields using $PhCF_3$ as an internal standard.

Table S3. Screen of time.[a]



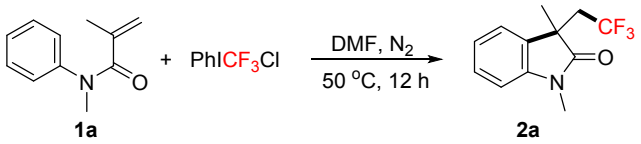
1a **2a**

Entry	t	Yield of **2a** [%][b]
1	2h	62
2	4h	80
3	6h	87
4	8h	92
5	10h	95
6	12h	95

[a]Reaction conditions: **1a** (0.1 mmol), $PhICF_3Cl$ (0.15 mmol), DMF (1 mL).

[b]^{19}F NMR yields using $PhCF_3$ as an internal standard.

Table S4. Screen of reaction concentration.[a]

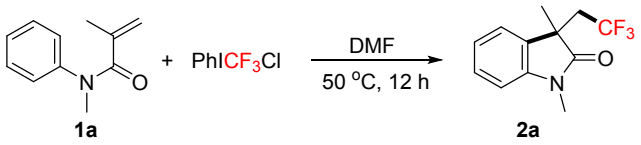


Entry	DMF / mL	Yield of **2a** [%][b]
1	0.5	80
2	1.0	95
3	1.5	95
4	2.0	95

[a]Reaction conditions: **1a** (0.1 mmol), $PhICF_3Cl$ (0.15 mmol), DMF (x mL).

[b]^{19}F NMR yields using $PhCF_3$ as an internal standard.

Table S5. Screen of reaction atomosphere.[a]

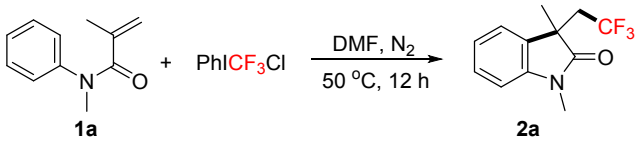


Entry	N_2 or Air	Yield of **2a** [%][b]
1	N_2	96
2	Air	66

[a]Reaction conditions: **1a** (0.1 mmol), $PhICF_3Cl$ (0.15 mmol), DMF (1 mL).

[b]^{19}F NMR yields using $PhCF_3$ as an internal standard.

Table S6. Screen of the ratio of 1a / $PhICF_3Cl$.[a]

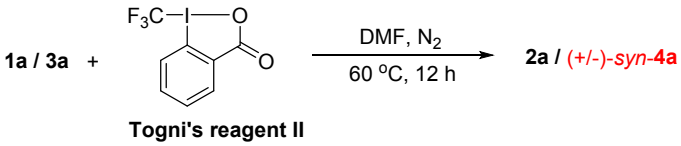


Entry	**1a** : $PhICF_3Cl$	Yield of **2a** [%][b]
1	1 : 1.2	90
2	1 : 1.5	95
3	1 : 2.0	95

[a]Reaction conditions: **1a** (0.1 mmol), $PhICF_3Cl$ (x mmol), DMF (1 mL).

[b]^{19}F NMR yields using $PhCF_3$ as an internal standard.

Table S7. Catalyst-free trifluoromethylative cyclizations using Togni's reagent.[a]



	Yield of **2a** / (+/-)-*syn*-**4a** [%][b]	Recovery of **Togin's reagent II** [%][b]
1a	0	98
3a	0	97

[a]Reaction conditions: **1a / 3a** (0.1 mmol), **Togin's reagent II** (0.15 mmol), DMF (1 mL).

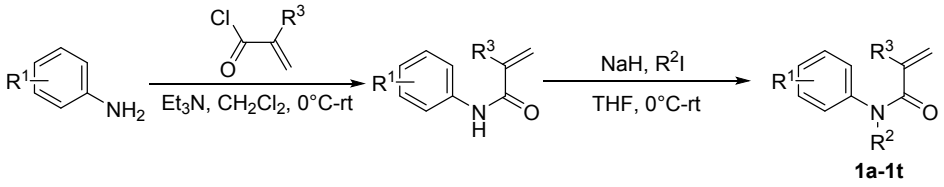
[b]^{19}F NMR yields using $PhCF_3$ as an internal standard.

III. Procedures for the synthesis of substrates

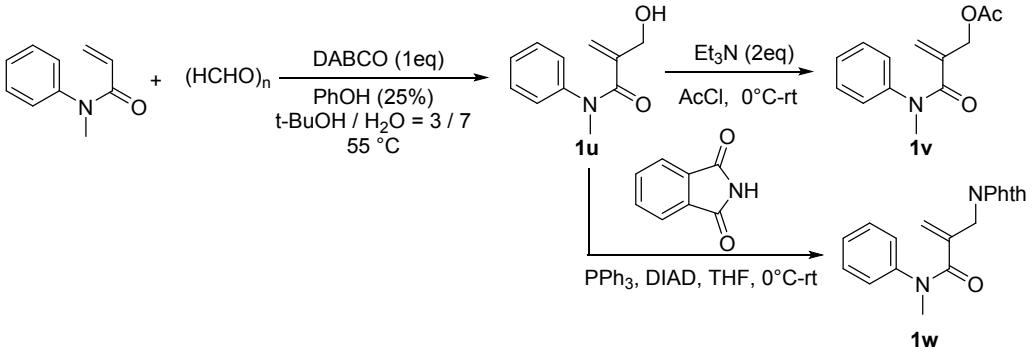
1. Synthesis of substrates 1.

All of compounds in the scheme **1** of the manuscript were synthesized according to the literature, and the NMR spectroscopy were consistented with reported data.[2]

Synthesis of substrates **1a-1t**:



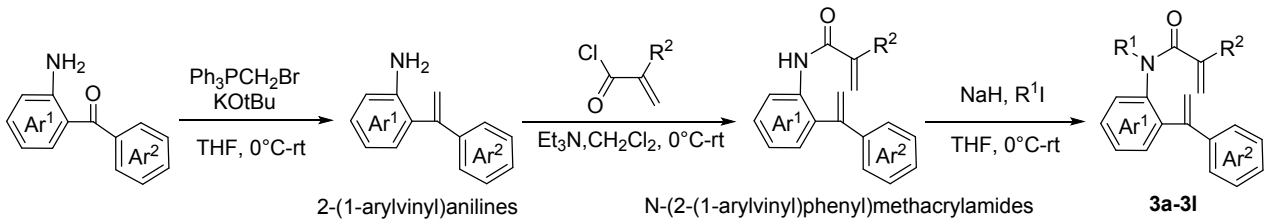
Synthesis of substrates **1u-1w**:



2. Synthesis of substrates 3.

Substrates **3a-3n** were new compounds synthesized according to the literature.[2,3] The NMR spectroscopy were as follow:

Synthesis of substrates **3a-3l** (taking **3a** as an example):



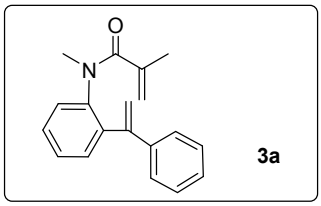
A solution of Ph_3PCH_2Br (3.72 g, 10.4 mmol) and KOtBu (1.60 g, 13.6 mmol) in 20 mL of dry THF was stirred at 0 ºC under N_2 for 30 min. A solution of (2-aminophenyl) (phenyl) methanone (1.58 g, 8.0 mmol) in 20 mL dry THF was then added dropwise and the resulting milky mixture was stirred at room temperature for 12 h. The reaction was quenched with water and extracted with ethyl acetate. The combined organic layers were rinsed with sat. $NaHCO_3$ (2 × 15 mL), and brine, dried over anhydrous $MgSO_4$ and concentrated under reduce pressure. Residues were purified by silica column chromatography (eluent: petroleum ether/EtOAc = 20/1, v/v) to give 1.23 g (85%) of 2-(1-phenylvinyl)aniline as a yellow solid. The yield and NMR spectroscopy were consistented with reported data.[2,3]

A solution of 2-(1-phenylvinyl)aniline (0.91 g, 5.0 mmol) in 13 mL of dry CH_2Cl_2 was stirred at 0 ºC under N_2. Methacryloyl chloride (0.73 mL, 7.5 mmol) and Et_3N (1.05 mL, 7.5 mmol) were slowly added. The reaction was stirred at room temperature for 12 h. Aqueous $NaHCO_3$ (10 mL) was added and reaction mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic phases were washed with 2N HCl (2 x 10 mL), water (2 x 10 mL), and brine (2 x 10 mL). After dried over anhydrous $MgSO_4$, the resulting solution was concentrated under reduce pressure. Residues were purified by silica column chromatography (eluent: petroleum ether/EtOAc = 10/1, v/v) to give 0.99 g (75%) of *N*-(2-(1-phenylvinyl)phenyl)methacrylamide as a yellow solid.

A solution of *N*-(2-(1-phenylvinyl)phenyl)methacrylamide (0.79 g, 3.0 mmol) and NaH (0.15 g, 60%, 4.2 mmol) in 15 mL of dry THF was stirred at 0 ºC under N_2 for 15 min. Then, MeI (0.28 mL, 4.5mmol) was added. The mixture was stirred at room temperature until *N*-(2-(1-phenylvinyl)phenyl)methacrylamide was consumed (monitored by TLC). The reaction was quenched with water and extracted with ethyl acetate. The combined organic layers were rinsed with brine, dried

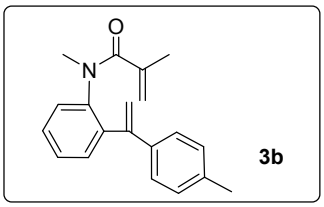
over anhydrous $MgSO_4$ and concentrated under reduce pressure. Residues were purified by silica column chromatography (eluent: petroleum ether/EtOAc = 10/1 to 5/1, v/v) to give **3a** as a white solid.

N-methyl-N-(2-(1-phenylvinyl)phenyl)methacrylamide (3a).



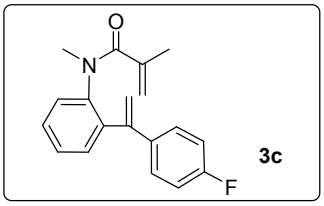
0.66 g, 80% yield. White solid. The amide isomerism was observed by ^{1}H-NMR with a ratio of 3:1. **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.25 - 7.36 (m, 9H), 5.61 (s, 1H), 5.24 (s, 1H), 5.00 (s, 1H), 4.75 (s, 1H), 2.75 (s, 3H), 1.76 (s, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$): δ = 170.7, 147.4, 143.1, 141.1, 140.0, 139.9, 131.7, 128.8, 128.2 (3C), 127.9 (2C), 127.3, 127.0, 120.1, 117.9, 37.6, 20.4. HRMS (ESI): Calcd for $[C_{19}H_{19}NO, M+Na]^+$: 300.1359, measured: 300.1366.

N-methyl-N-(2-(1-(p-tolyl)vinyl)phenyl)methacrylamide (3b).



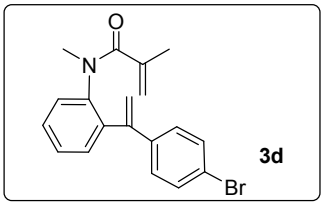
0.74 g, 85% yield. Light yellow oil. The amide isomerism was observed by ^{1}H-NMR with a ratio of 3:1. **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.29 - 7.34 (m, 4H), 7.18 - 7.19 (m, 1H), 7.09 (d, *J* = 7.8 Hz, 3H), 5.59 (s, 1H), 5.18 (s, 1H), 4.99 (s, 1H), 4.76 (s, 1H), 2.78 (s, 3H), 2.32 (s, 3H), 1.75 (s, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$): δ = 170.8, 147.2, 143.1, 140.1, 140.0, 138.3, 137.7, 131.7 (2C), 128.9 (2C), 128.7, 128.2, 127.3, 126.9, 120.1, 117.1, 37.8, 21.1, 20.4. HRMS (ESI): Calcd for $[C_{20}H_{21}NO, M+Na]^+$: 314.1515, measured: 314.1525.

N-(2-(1-(4-fluorophenyl)vinyl)phenyl)-N-methylmethacrylamide (3c).



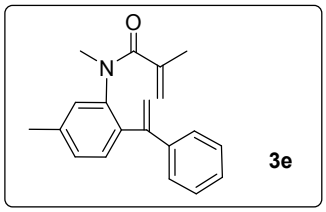
0.75 g, 85% yield. Light yellow oil. The amide isomerism was observed by ^{1}H-NMR with a ratio of 3:1. **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.36 (s, 2H), 7.31 (s,1H), 7.21 (d, *J* = 7.8 Hz, 1H), 7.14 (s, 2H), 6.96 - 7.00 (m, 2H), 5.57 (s, 1H), 5.21 (s, 1H), 5.00 (s, 1H), 4.75 (s, 1H), 2.77 (s, 3H), 1.75 (s, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$): δ = 170.7, 162.6 (d, *J* = 247.8 Hz), 146.4, 143.0, 139.9, 139.7, 137.3, 131.6, 129.0, 128.7, 128.3, 127.7, 127.4, 120.3, 117.9, 115.2, 115.1, 37.7, 20.4. HRMS (ESI): Calcd for [$C_{19}H_{18}FNO$, M+Na]$^+$: 318.1265, measured: 318.1264.

N-(2-(1-(4-bromophenyl)vinyl)phenyl)-N-methylmethacrylamide (3d).



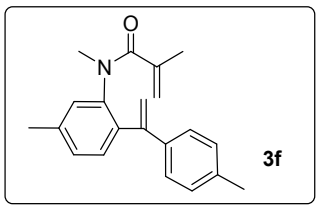
0.74 g, 70% yield. Light yellow oil. The amide isomerism was observed by ^{1}H-NMR with a ratio of 3:1. **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 8.4 Hz, 3H), 7.30 - 7.32 (m, 2H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.04 (d, *J* = 7.8 Hz, 2H), 5.61 (s,1H), 5.25 (s, 1H), 5.01 (s, 1H), 4.74 (s, 1H), 2.79 (s, 3H), 1.75 (s, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$): δ = 170.6, 146.3, 143.1, 140.1, 139.9, 139.3, 131.6 (2C), 131.4 (2C), 129.1, 128.6, 128.3, 127.4, 122.0, 120.4, 118.5, 37.8, 20.4. HRMS (ESI): Calcd for [$C_{19}H_{18}BrNO$, M+Na]$^+$: 378.0464, measured: 378.0460.

N-methyl-N-(5-methyl-2-(1-phenylvinyl)phenyl)methacrylamide (3e).



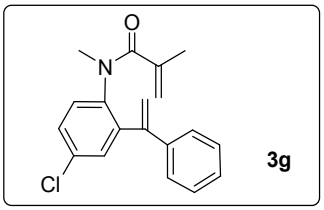
0.74 g, 85% yield. White solid. The amide isomerism was observed by ^{1}H-NMR with a ratio of 3:1. **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.25 - 7.31 (m, 5H), 7.18 (m, 1H), 7.10 (d, *J* = 7.2 Hz, 1H), 7.00 (s, 1H), 5.58 (s, 1H), 5.20 (s, 1H), 5.00 (s, 1H), 4.77 (s, 1H), 2.75 (s, 3H), 2.38 (s, 3H), 1.75 (s, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$): δ = 170.7, 142.3, 142.9, 141.4, 140.1, 138.9, 136.9, 131.5, 128.7, 128.2 (2C), 128.1, 127.8 (2C), 127.1, 120.0, 117.5, 37.6, 21.0, 20.4. HRMS (ESI): Calcd for $[C_{20}H_{21}NO, M+Na]^+$: 314.1515, measured: 314.1523.

N-methyl-N-(5-methyl-2-(1-(p-tolyl)vinyl)phenyl)methacrylamide (3f).



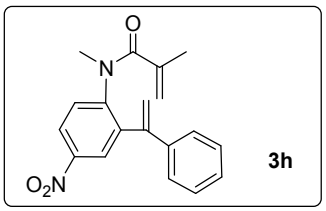
0.78 g, 85% yield. Red solid. The amide isomerism was observed by ^{1}H-NMR with a ratio of 3:1. **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.33 (s, 6H), 7.00 (s, 1H), 5.55 (s, 1H), 5.15 (s, 1H), 4.99 (s, 1H), 4.78 (s, 1H), 2.78 (s, 3H), 2.38 (s, 3H), 2.32 (s, 3H), 1.75 (s, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$): δ = 170.8, 147.0, 142.9, 140.1, 138.7, 138.5, 137.6, 137.0, 131.5 (2C), 128.9 (2C), 128.7, 128.0, 127.0, 120.0, 116.8, 37.1, 21.1, 21.0, 20.4. HRMS (ESI): Calcd for $[C_{21}H_{23}NO, M+Na]^+$: 328.1672, measured: 328.1681.

N-(4-chloro-2-(1-phenylvinyl)phenyl)-N-methylmethacrylamide (3g).



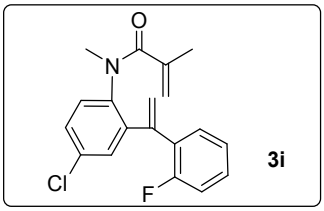
0.66 g, 71% yield. Red oil. The amide isomerism was observed by ^{1}H-NMR with a ratio of 2:1. **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.27 - 7.33 (m, 5H), 7.15 - 7.16 (m, 3H), 5.64 (s, 1H), 5.25 (s, 1H), 5.03 (s, 1H), 4.74 (s, 1H), 2.70 (s, 3H), 1.77 (s, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$): δ = 170.5, 146.4, 141.7, 141.5, 140.4, 139.8, 132.9, 131.4, 129.5, 128.9 (2C), 128.4 (2C), 128.2, 127.0, 120.4, 118.7, 37.5, 20.4. HRMS (ESI): Calcd for $[C_{19}H_{18}ClNO, M+Na]^+$: 334.0969, measured: 334.0974.

N-methyl-N-(4-nitro-2-(1-phenylvinyl)phenyl)methacrylamide (3h).



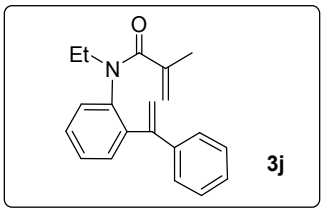
0.68 g, 70% yield. Light yellow oil. **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 8.23 - 8.25 (m, 2H), 7.40 - 7.41 (m, 1H), 7.32 - 7.34 (m, 3H), 7.19 (s, 2H), 5.77 (s, 1H), 5.39 (s, 1H), 5.08 (s, 1H), 4.65 (s, 1H), 287 (s, 3H), 1.78 (s, 3H). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 170.2, 148.9, 148.7, 146.3, 145.5, 140.7, 139.9, 139.6, 130.5, 128.9, 128.8 (2C), 127.0 (2C), 126.3, 124.5, 120.1, 119.8, 20.0. HRMS (ESI): Calcd for $[C_{19}H_{18}N_2O_3, M+Na]^+$: 345.1210, measured: 345.1201.

N-(4-chloro-2-(1-(2-fluorophenyl)vinyl)phenyl)-N-methylmethacrylamide (3i).



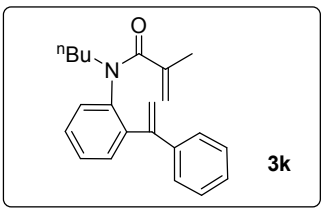
0.74 g, 70% yield. Yellow solid. The amide isomerism was observed by ^{1}H-NMR with a ratio of 3:1. **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.36 (s, 1H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.26 - 7.27 (m, 1H), 7.12 - 7.14 (m, 3H), 7.05 (d, *J* = 11.4 Hz, 1H), 5.66 (s, 1H), 5.50 (s, 1H), 5.02 (s, 1H), 4.74 (s, 1H), 2.68 (s, 3H), 1.79 (s, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$): δ = 170.7, 159.8 (d, *J* = 254.0 Hz), 141.5, 141.3, 141.0, 139.9, 133.1, 131.0, 130.2, 129.8, 129.5, 128.9, 124.2, 122.6, 120.2, 116.1, 115.9, 36.9, 20.4. HRMS (ESI): Calcd for $[C_{19}H_{17}ClFNO, M+Na]^+$: 352.0875, measured: 352.0884.

N-ethyl-N-(2-(1-phenylvinyl)phenyl)methacrylamide (3j).



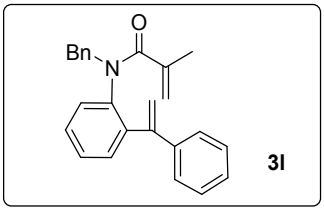
0.70 g, 80% yield. Yellow oil. The amide isomerism was observed by ^{1}H-NMR with a ratio of 2:1. **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.26 - 7.35 (m, 7H), 7.17 - 7.21 (m, 2H), 5.63 (s, 1H), 5.26 (s, 1H), 4.99 (s, 1H), 4.79 (s, 1H), 3.59 - 3.64 (m, 1H), 2.64 (s, 1H), 1.74 (s, 1H), 1.10 (s, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$): δ = 170.4, 147.3, 142.2, 141.2, 140.6, 139.4, 131.8, 131.2, 128.9, 128.4, 128.2 (2C), 127.9, 127.3, 127.1, 119.9, 117.9, 44.8, 20.4, 13.3. HRMS (ESI): Calcd for $[C_{20}H_{21}NO, M+Na]^+$: 314.1515, measured: 314.1528.

N-butyl-N-(2-(1-phenylvinyl)phenyl)methacrylamide (3k).



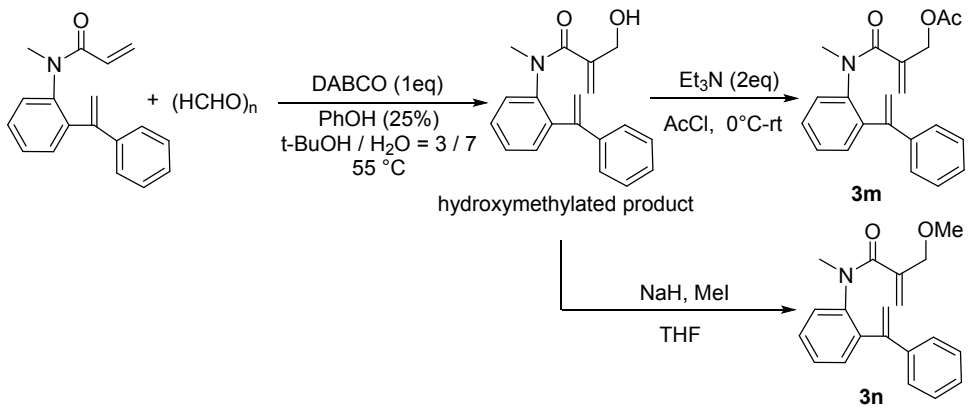
0.73 g, 72% yield. Yellow oil. The amide isomerism was observed by ^{1}H-NMR with a ratio of 2:1. **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.26 - 7.29 (m, 7H), 7.18 (s, 2H), 5.64 (s, 1H), 5.26 (s, 1H), 4.99 (s, 1H), 4.80 (s, 1H), 3.60 (s, 1H), 2.57 (s, 1H), 1.73 (s, 3H), 1.26 - 1.35 (m, 2H), 1.10 - 1.22 (m, 2H), 0.86 (s, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$): δ = 170.6, 147.2, 142.2, 141.2, 140.6, 139.3, 131.9 (2C), 131.1, 129.1, 128.3 (2C), 127.9, 127.3, 127.1, 119.9, 117.9, 49.7, 31.0, 30.1, 20.4, 13.7. HRMS (ESI): Calcd for [$C_{22}H_{25}NO$, M+Na]$^+$: 342.1828, measured: 342.1838.

N-benzyl-N-(2-(1-phenylvinyl)phenyl)methacrylamide (3l).



0.76 g, 71% yield. Yellow oil. The amide isomerism was observed by ^{1}H-NMR with a ratio of 4:1. **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.17 - 7.35 (m, 12H), 7.03 (s, 1H), 6.87(d, *J* = 7.8 Hz, 1H), 5.67 (s, 1H), 5.27 (s, 1H), 5.04 (s, 2H), 4.84 (s, 1H), 3.39 (d, *J* = 15.0 Hz, 1H), 1.78 (s, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$): δ = 170.8, 147.3, 142.0, 141.2, 140.2, 139.6, 138.3, 131.7, 129.0, 128.4 (5C), 128.3 (2C), 128.28, 128.1, 127.5, 127.2, 127.1, 120.5, 118.2, 52.4, 20.4. HRMS (ESI): Calcd for [$C_{25}H_{23}NO$, M+Na]$^+$: 376.1672, measured: 376.1678.

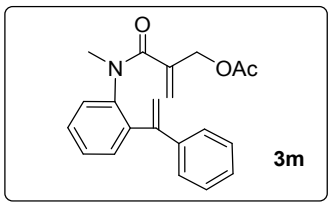
Synthesis of substrates **3m** and **3n**:



To a 10 mL Schlenk tube was sequentially added paraformaldyde (0.92 g, 30.0 mmol), DABCO (0.83g, 7.2 mmol), PhOH (141 mg, 1.5 mmol) and a mixture of t-BuOH and H_2O (2 mL, v/v, 3/7) under N_2. The suspended mixture was stired at 55 ºC untill it was completely dissolved. Then, N-methyl-N-(2-(1-phenylvinyl)phenyl)acrylamide (1.58 g, 6.0 mmol) was added. The resulting mixture was stirred at 55 ºC for 3 days. After evaporation of t-BuOH, the mixture solution was extracted by CH_2Cl_2. The combined organic phase was dried over anhydrous $MgSO_4$, and concentrated under reduce pressure. Resulting residues were purified by silica column chromatography (eluent: petroleum ether/EtOAc = 5/1 to 3/1, v/v) to give 1.23 g (70%) of delivered hydroxymethylated product as a white solid.

A 15 mL Schlenk tube was charged with a stir bar. The tube was evacuated and backfilled with N_2 (3 times). The above hydroxymethylated product (0.59 g, 2.0 mmol) and Et_3N (0.57 mL, 4.0 mmol) was added in CH_2Cl_2 (4.0 mL) at 0 ºC. Then, AcCl (0.28 mL, 4.0 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred over night. Water was added to quench the reaction when the substrate was consumed. The resulting mixture was extracted by CH_2Cl_2, and the organic phase was dried over anhydrous $MgSO_4$, then concentrated under reduce pressure. Residues were purified by silica column chromatography (eluent: petroleum ether/EtOAc = 5/1 to 3/1, v/v) to give **3m** as a yellow oil.

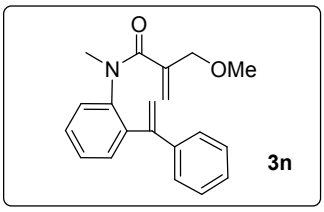
2-(Methyl(2-(1-phenylvinyl)phenyl)carbamoyl)allyl acetate (3m).



0.47 g, 70% yield. Yellow oil. The amide isomerism was observed by ^{1}H-NMR with a ratio of 3:1. **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.15 - 7.42 (m, 9H), 5.62 (s, 1H), 5.27 (s, 1H), 5.23 (s, 1H), 4.96 (s, 1H), 4.72 (d, *J* = 15.0 Hz, 1H), 4.56 (d, *J* = 14.4 Hz, 1H), 2.74 (s, 3H), 2.05 (s, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$): δ = 170.3, 167.8, 147.6, 142.4, 141.0, 139.9, 139.3, 138.7, 131.8, 129.0 (2C), 128.3 (2C), 128.0, 127.7, 127.0, 121.2, 118.1, 64.0, 37.6, 20.9. HRMS (ESI): Calcd for $[C_{21}H_{21}NO_3, M+Na]^+$: 358.1414, measured: 358.1428.

After a solution of hydroxymethylated product (0.59 g, 2.0 mmol) and NaH (0.12 g, 60%, 3.0 mmol) in 10 mL of dry THF was stirred at 0 ºC under N_2 for 15 min, MeI (0.19 mL, 3.0mmol) were added. The reaction mixture was stirred at room temperature for 3 h and was quenched with water. After extraction with ethyl acetate, the combined organic layers were rinsed with brine, dried over anhydrous $MgSO_4$ and concentrated under reduce pressure. Resulting residues were purified by silica column chromatography (eluent: petroleum ether/EtOAc = 5/1 to 3/1, v/v) to give **3n** as a yellow oil.

2-(Methoxymethyl)-N-methyl-N-(2-(1-phenylvinyl)phenyl)acrylamide (3n).



0.43 g, 70% yield. Yellow oil. The amide isomerism was observed by ^{1}H-NMR with a ratio of 3:1. **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.22 - 7.40 (m, 7H), 7.17 (d, *J* = 7.2 Hz, 2H), 5.61 (s, 1H), 5.27 (s, 2H), 4.94 (s, 1H), 4.08 (d, *J* = 13.8 Hz, 1H), 3.79 (d, *J* = 13.8 Hz, 1H), 3.27 (s, 3H), 2.76 (s, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$): δ = 168.7, 147.5, 142.5, 141.1, 139.8, 139.9, 131.7, 128.9, 128.6, 128.3 (2C), 128.0 (2C), 127.6, 127.0, 119.4, 117.8, 72.2, 58.4, 37.5. HRMS (ESI): Calcd for $[C_{20}H_{21}NO_2, M+Na]^+$: 330.1456, measured: 330.1460.

IV. Synthetic Procedures and Analytical Data

1.Catalyst-free intramolecular aryltrifluoromethylation of activated alkenes 1

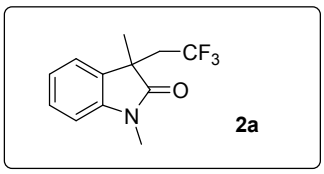
Typical procedures for catalyst-free intramolecular aryltrifluoromethylation of activated alkenes (taking **1a** as an example):

To a dried polytetrafluoroethene (PTFE) sealed pressure tube was added **1a** (52.6 mg, 0.3 mmol), $PhICF_3Cl$ (138.6 mg, 0.45 mmol) and anhydrous DMF (3.0 mL) in sequence under N_2. After the reaction mixture was stirred at 50 °C for 12 h, $PhCF_3$ (30 μL, 0.2436 mmol) was added as the internal standard and the NMR yield of **2a** was calculated from ^{19}F-NMR integrals. Then the mixture was washed with water and brine, extracted by CH_2Cl_2. The combined organic phase was dried over

anhydrous $MgSO_4$ and concentrated under reduce pressure. The residue was purified by silica column chromatography (eluent: petroleum ether/EtOAc = 10/1 to 5/1, v/v) to give **2a** as a white solid. The NMR spectroscopy were consistented with reported data.[2,4-7]

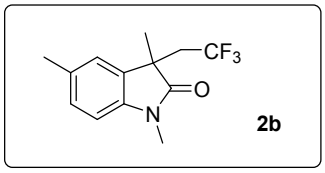
Analytical data for compounds 2a-2w:

1,3-Dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (2a).



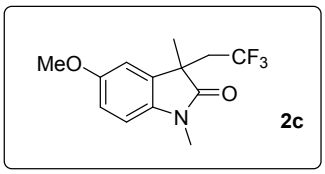
63.2 mg, 87% yield. White solid, mp: 73-74 ºC (lit.[2] mp 45-46 ºC). **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.30 - 7.33 (m, 1H), 7.26 - 7.27 (m, 1H), 7.08 - 7.11 (m, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 3.24 (s, 3H), 2.81 (dq, *J* = 15.6 Hz, 10.8 Hz, 1H), 2.65 (dq, *J* = 15.0 Hz, 10.2 Hz, 1H), 1.41 (s,3H). **^{13}C-NMR** (151 MHz, $CDCl_3$): δ = 178.5, 142.9, 131.0, 128.5, 125.2 (q, *J* = 278.3 Hz), 123.6, 122.6, 108.4, 44.3 (q, *J* = 1.5 Hz), 40.7 (q, *J* = 28.5 Hz), 26.4, 25.0. **^{19}F-NMR** (565 MHz, $CDCl_3$): δ = -61.9 (t, *J* = 10.7 Hz). HRMS (ESI): Calcd for $[C_{12}H_{12}F_3NO, M+H]^+$: 243.0865, measured: 243.0872.

1,3,5-Trimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (2b).



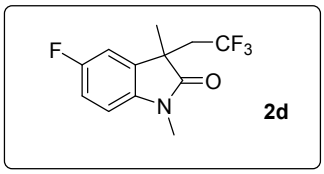
63.2 mg, 82% yield. Yellow solid, mp: 68-69 ºC (lit.[2] mp 70-71 ºC). **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.11 (dd, *J* = 7.8 Hz, 1.8 Hz, 1H), 7.07 (s, 1H), 6,77 (d, *J* = 7.86, 1H), 3.21 (s, 3H), 2.80 (dq, *J* = 15.6 Hz, 10.8 Hz, 1H), 2.63 (dq, *J* = 15.6 Hz, 10.8 Hz, 1H), 2.35 (s, 3H), 1.39 (s, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$): δ = 178.4, 140.5, 132.2, 131.1, 128.8, 125.3 (q, *J* = 278.0 Hz), 124.3, 108.1, 44.4 (d, *J* = 2.3 Hz), 40.6 (q, *J* = 28.2 Hz), 26.4, 25.0, 21.1. **^{19}F-NMR** (565 MHz, $CDCl_3$): δ = -61.9 (t, *J* = 10.7 Hz). HRMS (ESI): Calcd for $[C_{13}H_{14}F_3NO, M+Na]^+$: 280.0920, measured: 280.0919.

5-Methoxy-1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (2c).



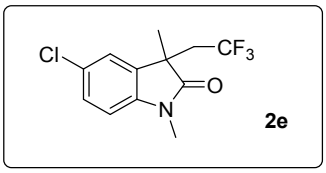
65.6 mg, 81% yield. Yellow solid, mp: 111-112 ºC (lit.[2]107-108 ºC). **^{1}H-NMR** (400 MHz, $CDCl_3$): δ = 6.78 (d, *J* = 2.4 Hz, 1H), 6.74 (dd, *J* = 8.4 Hz, 2.0 Hz, 1H), 6.68 (d, *J* = 8.4, 1H), 3.71 (s, 3H), 3.12 (s, 3H), 2.65 - 2.77 (m, 1H), 2.47 - 2.58 (m, 1H), 1.30 (s, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$): δ = 178.1, 156.1, 136.4, 132.4, 125.2 (q, *J* = 278.1 Hz), 122.6, 111.3, 108.7, 55.9, 44.8 (q, *J* = 1.4 Hz), 40.6 (q, *J* = 28.4 Hz), 26.5, 25.0. **^{19}F-NMR** (470 MHz, $CDCl_3$): δ = -61.9 (t, *J* = 11.3 Hz). HRMS (ESI): Calcd for $[C_{13}H_{14}F_3NO_2$, M+Na$]^+$: 296.0868, measured: 296.0877.

5-Fluoro-1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (2d).



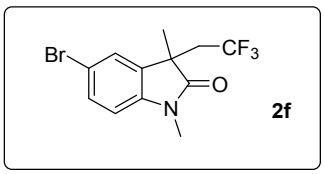
71.3 mg, 91% yield. White solid, mp: 69-70 ºC (lit.[2]56-57 ºC). **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.00 - 7.04 (m, 2H), 6.80 (q, *J* = 4.2 Hz, 1H), 3.23 (s, 3H), 2.82 (dq, *J* = 15.0 Hz, 10.8 Hz, 1H), 2.63 (dq, *J* = 15.0 Hz, 10.2 Hz, 1H), 1.41 (s, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$): δ = 178.1, 159.3 (d, *J* = 240.8 Hz), 138.8, 132.6 (d, *J* = 9.5 Hz), 125.1 (q, *J* = 278.1 Hz), 114.8 (d, *J* = 23.4 Hz), 111.8 (d, *J* = 24.9 Hz), 108.9 (d, *J* = 8.2 Hz), 44.8 (q, *J* = 1.4 Hz), 40.6 (q, *J* = 28.4 Hz), 26.6, 24.9. **^{19}F-NMR** (565 MHz, $CDCl_3$): δ = -62.0 (t, *J* = 10.2 Hz, 3F), -120.4 (m, 1F). HRMS (ESI): Calcd for $[C_{12}H_{11}F_4NO$, M+H$]^+$: 262.0850, measured: 262.0847.

5-Chloro-1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (2e).



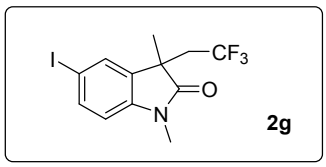
74.0 mg, 89% yield. White solid, mp: 91-92 ºC (lit.[2]100-101 ºC). **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.29 (dd, *J* = 8.4 Hz, 1.8Hz, 1H), 7.24 (d, *J* = 1.8 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 3.22 (s, 3H), 2.83 (dq, *J* = 15.6 Hz, 10.8 Hz, 1H), 2.63 (dq, *J* = 15.0 Hz, 10.2 Hz, 1H), 1.41 (s, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$): δ = 177.9, 141.5, 132.7, 128.5, 128.1, 125.1 (q, *J* = 276.3 Hz), 124.1, 109.4, 44.6 (q, *J* = 2.3 Hz), 40.6 (q, *J* = 28.4 Hz), 26.6, 24.9. **^{19}F-NMR** (565 MHz, $CDCl_3$): δ = -62.0 (t, *J* = 10.2 Hz). HRMS (ESI): Calcd for $[C_{12}H_{11}ClF_3NO, M+H]^+$: 278.0554, measured: 278.0549.

5-Bromo-1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (2f).



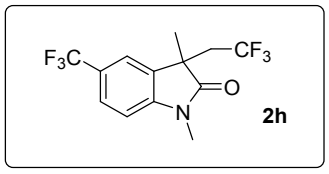
85.7 mg, 89% yield. Yellow solid, mp: 107-108 ºC (lit.[2]106-107 ºC). **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.44 (dd, *J* = 8.4 Hz, 1.8 Hz, 1H), 7.38 (d, *J* = 2.4 Hz, 1H), 6.76 (d, *J* = 8.4, 1H), 3.22 (s, 3H), 2.74 (dq, *J* = 15.6 Hz, 10.8 Hz, 1H), 2.62 (dq, *J* = 15.0 Hz, 10.2 Hz, 1H), 1.41 (s, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$): δ = 177.8, 141.9, 133.1, 131.4, 126.8, 125.0 (q, *J* = 278.0 Hz), 115.3, 109.9, 44.5 (q, J = 1.5 Hz), 40.6 (q, *J* = 28.5 Hz), 26.5, 24.9. **^{19}F-NMR** (565 MHz, $CDCl_3$): δ = -61.9 (t, *J* = 10.7 Hz). HRMS (ESI): Calcd for $[C_{12}H_{11}BrF_3NO, M+Na]^+$: 343.9868, measured: 343.9867.

5-Iodo-1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (2g).



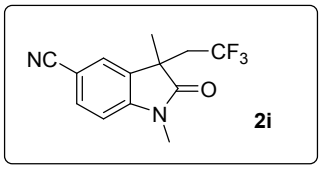
96.3 mg, 87% yield. White solid, mp: 121-122 ºC (lit.[2]110-111 ºC). **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.63 (dd, *J* = 8.4 Hz, 1.8 Hz, 1H), 7.54 (d, *J* = 1.2 Hz, 1H), 6.67 (d, *J* = 8.4, 1H), 3.21 (s, 3H), 2.81 (dq, *J* = 15.6 Hz, 10.8 Hz, 1H), 2.62 (dq, *J* = 15.0 Hz, 10.2 Hz, 1H), 1.40 (s, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$): δ = 177.6, 142.6, 137.4, 133.4, 132.4, 125.0 (q, *J* = 278.4 Hz), 110.5, 85.1, 44.4 (q, *J* = 2.4 Hz), 40.6 (q, *J* = 28.4 Hz), 26.5, 24.9. **^{19}F-NMR** (565 MHz, $CDCl_3$): δ = -61.9 (t, *J* = 10.2 Hz). HRMS (ESI): Calcd for $[C_{12}H_{11}IF_3NO, M+Na]^+$: 391.9730, measured: 391.9733.

1,3-Dimethyl-3-(2,2,2-trifluoroethyl)-5-(trifluoromethyl)indolin-2-one (2h).



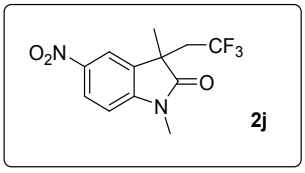
76.5 mg, 82% yield. White solid, mp: 115-116 ºC (lit.[4]109-110 ºC). **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.61 (d, *J* = 7.8 Hz, 1H), 7.50 (s, 1H), 6.96 (d, *J* = 8.4, 1H), 3.27 (s, 3H), 2.86 (dq, *J* = 15.0 Hz, 10.2 Hz, 1H), 2.69 (dq, *J* = 15.0 Hz, 10.2 Hz, 1H), 1.44 (s, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$): δ = 178.3, 145.9, 131.5, 126.4 (q, J = 4.1 Hz), 125.2 (d, *J* = 3.3 Hz), 125.0 (q, *J* = 278.0 Hz), 124.9, 120.7 (d, *J* = 2,7 Hz), 108.3, 44.3 (q, *J* = 2.0 Hz), 40.6 (q, *J* = 28.7 Hz), 26.7, 24.9. **^{19}F-NMR** (565 MHz, $CDCl_3$): δ = -61.5 (s, 3F), -62.1 (t, *J* = 9.6 Hz, 3F). HRMS (ESI): Calcd for $[C_{13}H_{11}F_6NO, M+H]^+$: 312.0817, measured: 312.0810.

1,3-Dimethyl-2-oxo-3-(2,2,2-trifluoroethyl)indoline-5-carbonitrile (2i).



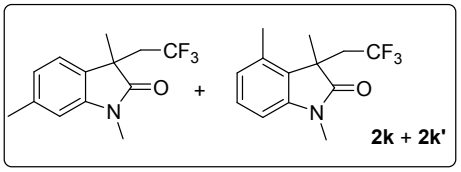
69.4 mg, 86% yield. Yellow solid, mp: 107-108 ºC (lit.[2]141-142 ºC). **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.66 (dd, *J* = 8.4 Hz, 1.8 Hz, 1H), 7.52 (d, *J* = 1.2 Hz, 1H), 6.96 (d, *J* = 8.4, 1H), 3.27 (s, 3H), 2.87 (dq, *J* = 15.6 Hz, 10.8 Hz, 1H), 2.67 (dq, *J* = 15.6 Hz, 10.2 Hz, 1H), 1.44 (s, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$): δ = 178.1, 146.7, 133.9, 132.0, 127.0, 124.9 (q, *J* = 277.8 Hz), 118.9, 109.0, 106.0, 44.2 (q, *J* = 2.0 Hz), 40.6 (q, *J* = 28.7 Hz), 26.7, 24.9. **^{19}F-NMR** (565 MHz, $CDCl_3$): δ = -62.3 (t, *J* = 10.7 Hz). HRMS (ESI): Calcd for $[C_{13}H_{11}F_3N_2O, M+Na]^+$: 291.0716, measured: 291.0708.

1,3-Dimethyl-5-nitro-3-(2,2,2-trifluoroethyl)indolin-2-one (2j).



62.6 mg, 70% yield. Yellow solid, mp: 57-58 ºC.[5] **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 8.31 (dd, *J* = 9.0 Hz, 2.4 Hz, 1H), 8.17 (d, *J* = 1.2 Hz, 1H), 6.98 (d, *J* = 8.6, 1H), 3.32 (s, 3H), 2.91 (dq, *J* = 15.0 Hz, 10.2 Hz, 1H), 2.73 (dq, *J* = 15.6 Hz, 10.2 Hz, 1H), 1.48 (s, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$): δ = 178.4, 148.5, 143.6, 131.8, 125.9, 124.8 (q, *J* = 278.1 Hz), 119.5, 108.1, 44.3 (q, *J* = 1.7 Hz), 40.6 (q, *J* = 28.8 Hz), 26.9, 24.0. **^{19}F-NMR** (565 MHz, $CDCl_3$): δ = -62.1 (t, *J* = 10.7 Hz). HRMS (ESI): Calcd for $[C_{12}H_{11}F_3N_2O_3, M+H]^+$: 299.0794, measured: 299.0789.

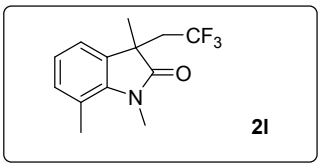
1,3,6-Trimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (2k) and 1,3,4-Trimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (2k').



67.1 mg, 87% yield. Light yellow oil.[2] Two inseperable isomers were obtained with a ratio of 1:2. **2k** **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.14 (d, J = 7.8 Hz, 1H), 6.90 (d, J = 7.8 Hz, 1H), 6.72 (t, J = 7.8, 1H), 3.22 (s, 3H), 2.96 (dq, J = 15.0 Hz, 10.8 Hz, 1H), 2.75 - 2.87 (m, 1H), 2.40 (s, 3H), 1.38 (s, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$): δ = 178.8, 142.9, 138.7, 128.1, 127.8, 125.3 (q, J = 278.1 Hz), 123.3, 109.4, 44.2 (q, J = 2.1 Hz), 40.6 (q, J = 28.1 Hz), 26.4, 25.1, 21.8. **^{19}F-NMR** (470 MHz, $CDCl_3$): δ = -63.9 (t, J = 10.8 Hz). HRMS (ESI): Calcd for $[C_{13}H_{14}F_3NO, M+Na]^+$: 280.0920, measured: 280.0916.

2k' **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.21 (t, J = 7.2 Hz, 1H), 6.86 (d, J = 7.8 Hz, 1H), 6.72 (t, J = 7.8, 1H), 3.22 (s, 3H), 2.75 - 2.87 (m, 1H), 2.63 (dq, J = 15.6 Hz, 10.8 Hz, 1H), 2.38 (s, 3H), 1.45 (s, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$): δ = 178.5, 143.2, 134.8, 128.3, 125.2, 125.1 (q, J = 278.1 Hz), 123.2, 106.2, 44.9 (q, J = 2.3 Hz), 39.7 (q, J = 28.1 Hz), 26.5, 23.1, 18.2. **^{19}F-NMR** (470 MHz, $CDCl_3$): δ = -65.9 (t, J = 10.8 Hz). HRMS (ESI): Calcd for $[C_{13}H_{14}F_3NO, M+Na]^+$: 280.0920, measured: 280.0916.

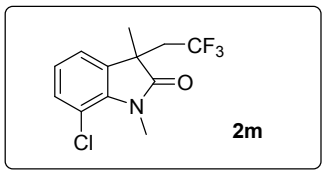
1,3,7-Trimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (2l).



54.0 mg, 72% yield. Colourless oil.[2] **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.08 (d, *J* = 7.2 Hz, 1H), 7.03 (d, *J* = 7.2 Hz, 1H), 6,96 (t, *J* = 7.2, 1H), 3.51 (s, 3H), 2.82 (dq, *J* = 15.6 Hz, 10.8 Hz, 1H), 2.58 - 2.65 (m, 1H), 2.59 (s, 3H), 1.37 (s, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$): δ = 179.2, 140.6, 132.2, 131.6, 125.2 (q, *J* = 278.1 Hz), 122.5, 121.4, 120.1, 43.7 (q, *J* = 2.1 Hz), 40.9 (q, *J* = 28.2 Hz), 29.8, 25.5, 19.1. **^{19}F-NMR** (565 MHz, $CDCl_3$): δ = -62.0 (t, *J* = 10.7 Hz). HRMS (ESI): Calcd for $[C_{13}H_{14}F_3NO, M+Na]^+$: 280.0920,

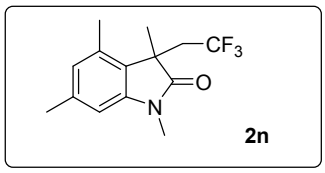
measured: 280.0914.

7-Chloro-1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (2m).



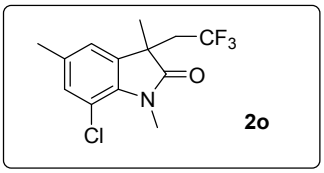
67.3 mg, 81% yield. Colourless oil.[2] **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.23 (dd, *J* = 7.8 Hz, 1.2 Hz, 1H), 7.13 (d, *J* = 7.2 Hz, 1H), 6.99 (t, *J* = 5.2, 1H), 3.61 (s, 3H), 2.85 (dq, *J* = 15.0 Hz, 10.8 Hz, 1H), 2.62 (dq, *J* = 15.6 Hz, 10.8 Hz, 1H), 1.40 (s, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$): δ = 178.7, 138.8, 133.7, 130.9, 125.0 (q, *J* = 278.0 Hz), 123.4, 122.0, 115.9, 44.1 (q, *J* = 2.0 Hz), 40.9 (q, *J* = 28.2 Hz), 29.9, 25.4. **^{19}F-NMR** (565 MHz, $CDCl_3$): δ = -62.0 (t, *J* = 10.2 Hz). HRMS (ESI): Calcd for $[C_{12}H_{11}ClF_3NO, M+Na]^+$: 300.0373, measured: 300.0366.

1,3,4,6-Tetramethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (2n).



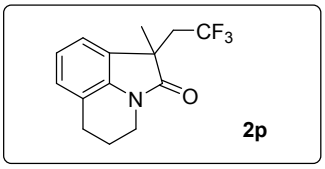
66.2 mg, 82% yield. Red solid, mp: 129-130 ºC.[5] **^{1}H-NMR** (400 MHz, $CDCl_3$): δ = 6.58 (s, 1H), 6.46 (s, 1H), 3.11 (s, 3H), 2.79 - 2.93 (m, 1H), 2.64 - 2.76 (m, 1H), 2.24 (d, *J* = 5.2 Hz, 6H), 1.33 (s, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$): δ = 178.9, 143.3, 138.4, 134.4, 125.7, 125.1 (q, *J* = 278.0 Hz), 124.9, 107.2, 44.7 (q, *J* = 2.3 Hz), 39.7 (q, *J* = 27.9 Hz), 26.5, 23.3, 20.6, 18.1. **^{19}F-NMR** (470 MHz, $CDCl_3$): δ = -63.9 (t, *J* = 10.3 Hz). HRMS (ESI): Calcd for $[C_{14}H_{16}F_3NO, M+Na]^+$: 292.0920, measured: 292.0927.

7-Chloro-1,3,5-trimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (2o).



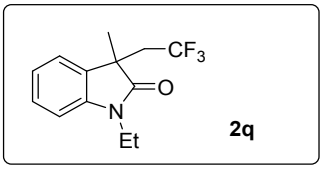
70.7 mg, 81% yield. Yellow solid, mp: 99-100 ºC. **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.04 (d, *J* = 0.6 Hz, 1H), 6.93 (d, *J* = 1.2 Hz, 1H), 3.57 (s, 3H), 2.83 (dq, *J* = 15.0 Hz, 10.8 Hz, 1H), 2.59 (dq, *J* = 15.6 Hz, 10.2 Hz, 1H), 2.31 (s, 3H), 1.38 (s, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$): δ = 178.6, 136.3, 133.7, 133.4, 130.9, 125.0 (q, *J* = 278.1 Hz), 122.9, 115.4, 44.2 (q, *J* = 2.4 Hz), 40.9 (q, *J* = 28.2 Hz), 29.8, 25.5, 20.6. **^{19}F-NMR** (565 MHz, $CDCl_3$): δ = -61.9 (t, *J* = 10.7 Hz). HRMS (ESI): Calcd for $[C_{13}H_{13}ClF_3NO, M+Na]^+$: 314.0530, measured: 314.0534.

1-Methyl-1-(2,2,2-trifluoroethyl)-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinolin-2(1H)-one (2p).



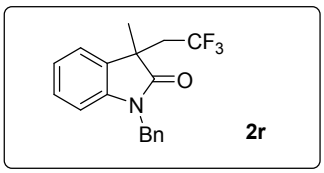
73.4 mg, 91% yield. White solid, mp:74-75 ºC (lit.[2]71-72 ºC). **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.10 (d, *J* = 7.2 Hz, 1H), 7.06 (d, *J* = 7.8 Hz, 1H), 6.97 (t, *J* = 7.8 Hz, 1H), 3.73 (t, *J* = 5.4 Hz, 2H), 2.73 - 2.83 (m, 3H), 2.64 (dq, *J* = 15.6 Hz, 10.8 Hz, 1H), 2.00 - 2.04 (m, 2H), 1.42 (s, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$): δ = 177.3, 138.6, 129.7, 127.3, 125.4 (q, *J* = 279.7 Hz), 122.1, 121.5, 120.5, 45.6 (q, *J* = 2.4 Hz), 40.5 (q, *J* = 28.2 Hz), 39.1, 24.6, 24.5, 21.1. **^{19}F-NMR** (565 MHz, $CDCl_3$): δ = -61.8 (t, *J* = 10.2 Hz). HRMS (ESI): Calcd for $[C_{14}H_{14}F_3NO, M+Na]^+$: 292.0920, measured: 292.0917.

1-Ethyl-3-methyl-3-(2,2,2-trifluoroethyl)indolin-2-one (2q).



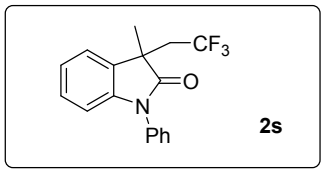
68.6 mg, 85% yield. Yellow solid, mp: 98-99 ºC (lit.[2]52-53 ºC). **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.29 - 7.31 (m, 1H), 7.26 (d, *J* = 7.2 Hz 1H), 7.06 - 7.09 (m, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 3.85 - 3.91 (m, 1H), 3.66 - 3.71 (m, 1H), 2.84 (dq, *J* = 15.6 Hz, 10.8 Hz, 1H), 2.64 (dq, J = 15.6 Hz, 10.8 Hz, 1H), 1.40 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$): δ = 178.0, 141.9, 131.2, 128.4, 125.3 (q, *J* = 278.3 Hz), 123.7, 122.4, 108.6, 44.3 (q, *J* = 2.1 Hz), 40.7 (q, *J* = 28.2 Hz), 34.8, 25.1, 12.2. **^{19}F-NMR** (565 MHz, $CDCl_3$): δ = -61.9 (t, *J* = 10.7 Hz). HRMS (ESI): Calcd for $[C_{13}H_{14}F_3NO, M+Na]^+$: 280.0920, measured: 280.0928.

1-Benzyl-3-methyl-3-(2,2,2-trifluoroethyl)indolin-2-one (2r).



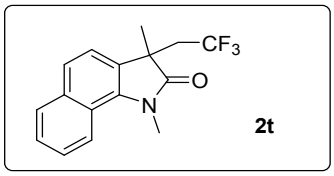
74.7 mg, 82% yield. Colourless oil.[2] **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.30 - 7.32 (m, 2H), 7.24 - 7.28 (m, 4H), 7.17 - 7.19 (m, 1H), 7.03 - 7.06 (m, 1H), 6.75 (d, *J* = 7.8 Hz, 1H), 4.98 (d, *J* = 15.6 Hz, 1H), 4.89 (d, *J* = 15.6 Hz, 1H), 2.87 - 2.94 (m, 1H), 2.66 - 2.74 (m, 1H), 1.46 (s, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$): δ = 178.6, 142.0, 135.7, 131.0, 128.8 (2C), 128.4, 127.6, 127.2 (2C), 125.3 (q, *J* = 278.1 Hz), 123.6, 122.6, 109.6, 44.4 (q, *J* = 2.0 Hz), 44.0, 40.5 (q, *J* = 28.2 Hz), 25.7. **^{19}F-NMR** (470 MHz, $CDCl_3$): δ = -61.7 (t, *J* = 10.3 Hz). HRMS (ESI): Calcd for $[C_{18}H_{16}F_3NO, M+H]^+$: 320.1256, measured: 320.1268.

3-Methyl-1-phenyl-3-(2,2,2-trifluoroethyl)indolin-2-one (2s).



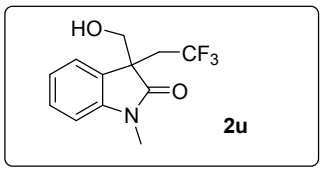
75.1 mg, 82% yield. Yellow solid, mp: 119-120 ºC (lit.[4]116-117 ºC). **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.53 (t, *J* = 7.8 Hz, 2H), 7.42 (d, *J* = 7.2 Hz, 1H), 7.40 (d, *J* = 7.2 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.23 (t, *J* = 7.8 Hz, 1H), 7.12 (t, *J* = 7.2 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 2.96 (dq, *J* = 15.6 Hz, 10.8 Hz, 1H), 2.72 (dq, *J* = 15.0 Hz, 10.2 Hz, 1H), 1.53 (s, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$): δ = 178.0, 143.0, 134.3, 130.7, 129.7 (2C), 128.4, 128.3, 126.6 (2C), 125.3 (q, *J* = 278.1 Hz), 123.8, 123.1, 109.8, 44.5 (q, *J* = 2.0 Hz), 41.1 (q, *J* = 28.2 Hz), 25.5. **^{19}F-NMR** (565 MHz, $CDCl_3$): δ = -61.9 (t, *J* = 10,7 Hz). HRMS (ESI): Calcd for $[C_{17}H_{14}F_3NO, M+Na]^+$: 328.0920, measured: 328.0924.

1,3-Dimethyl-3-(2,2,2-trifluoroethyl)-1,3-dihydro-2H-benzo[g]indol-2-one (2t).



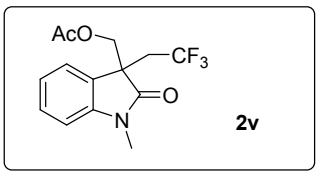
35.2 mg, 40% yield. Colorless oil.[6] **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 8.4 Hz, 1H), 7.54 (t, *J* = 8.4 Hz, 2H), 7.44 (q, *J* = 7.2 Hz, 2H), 6.98 (d, *J* = 7.8 Hz, 1H), 3.56 (s, 3H), 3.44 - 3.52 (m, 1H), 2.74 - 2.81 (m, 1H), 1.73 (s, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$): δ = 171.4, 136.2, 134.9, 133.5, 126.7, 126.7, 126.5, 125.5 (q, *J* = 279.4 Hz), 123.4, 122.8, 119.0, 108.8, 45.4 (q, *J* = 26.9 Hz), 43.8 (q, *J* = 2.1 Hz), 33.1, 29.9. **^{19}F-NMR** (470 MHz, $CDCl_3$): δ = -60.9 (t, *J* = 9.9 Hz). HRMS (ESI): Calcd for $[C_{16}H_{14}F_3NO, M+Na]^+$: 316.0920, measured: 316.0909.

3-(Hydroxymethyl)-1-methyl-3-(2,2,2-trifluoroethyl)indolin-2-one (2u).



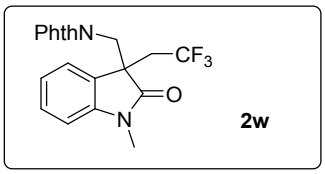
58.3 mg, 75% yield. Colourless oil.[6] **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.37 (t, *J* = 7.8 Hz, 1H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.12 (t, *J* = 7.8 Hz, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 3.75 (t, *J* = 10.8 Hz, 1H), 3.67 (dd, *J* = 10.8 Hz, 3.0 Hz, 1H), 3.26 (s, 3H), 3.08 (dq, *J* = 15.6 Hz, 10.8 Hz, 1H), 2.81 (dq, *J* = 15.6 Hz, 10.2 Hz, 1H), 2.54 (dd, *J* = 9.6 Hz, 3.6 Hz, 1H). **^{13}C-NMR** (151 MHz, $CDCl_3$): δ = 177.1, 143.6, 129.2, 126.9, 125.6 (q, *J* = 277.8 Hz), 124.0, 122.9, 108.7, 67.4, 49.7 (q, *J* = 1.8 Hz), 36.4 (q, *J* = 28.7 Hz), 26.5. **^{19}F-NMR** (565 MHz, $CDCl_3$): δ = -61.5 (t, *J* = 10.7 Hz). HRMS (ESI): Calcd for $[C_{12}H_{12}F_3NO_2, M+Na]^+$: 282.0712, measured: 282.0704.

(1-Methyl-2-oxo-3-(2,2,2-trifluoroethyl)indolin-3-yl)methyl acetate (2v).



60.5 mg, 67% yield. Yellow oil.[2] **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.35 (dt, *J* = 7.8 Hz, 1.2 Hz, 1H), 7.30 (d, *J* = 7.8 Hz, 1H), 7.09 (t, *J* = 7.8 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 4.40 (d, *J* = 10.8 Hz, 1H), 4.08 (d, *J* = 10.8 Hz, 1H), 3.25 (s, 3H), 2.80 - 2.93 (m, 2H), 1.97 (s, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$): δ = 175.1, 170.0, 143.6, 129.3, 126.6, 125.2 (q, *J* = 278.0 Hz), 124.6, 122.7, 108.5, 67.0, 48.2 (q, *J* = 1.8 Hz), 36.8 (q, *J* = 29.1 Hz), 26.5, 20.5. **^{19}F-NMR** (565 MHz, $CDCl_3$): δ = -61.4 (t, *J* = 10.2 Hz). HRMS (ESI): Calcd for $[C_{14}H_{14}F_3NO_3, M+Na]^+$: 324.0818, measured: 324.0826.

2-((1-Methyl-2-oxo-3-(2,2,2-trifluoroethyl)indolin-3-yl)methyl)isoindoline-1,3-dione (2w).

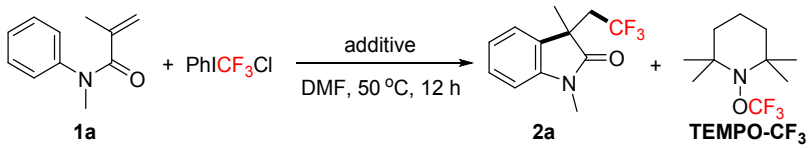


82.7 mg, 71% yield. Yellow solid, mp: 209-210 ºC (lit.[2]167-170 ºC). **^{1}H-NMR** (400 MHz, $CDCl_3$): δ = 7.72 - 7.77 (m, 2H), 7.61 - 7.65 (m, 2H), 7.22 (dt, *J* = 8.0 Hz, 0.8 Hz, 1H), 7.13 (d, *J* = 7.6 Hz, 1H), 6.94 (dt, *J* = 7.6 Hz, 0.8 Hz, 1H), 6.79 (d, *J* = 7.6 Hz, 1H), 3.90 (d, *J* = 14.4 Hz, 1H), 3.78 (d, *J* = 14.0 Hz, 1H), 3.15 (s, 3H), 2.83 - 3.04 (m, 2H). **^{13}C-NMR** (151 MHz, $CDCl_3$): δ = 175.5, 168.0 (2C), 143.4, 134.3 (2C), 131.6, 129.3, 126.7, 125.0 (q, J = 278.3 Hz), 124.4, 123.6 (2C), 122.5 (2C), 108.7, 48.4 (q, *J* = 2.0 Hz), 44.0, 38.1 (q, *J* = 28.5 Hz), 26.6. **^{19}F-NMR** (470 MHz, $CDCl_3$): δ = -61.5 (t, *J* = 10.3 Hz). HRMS (ESI): Calcd for $[C_{20}H_{15}F_3N_2O_3, M+Na]^+$: 411.0927, measured: 411.0934.

V. Mechanistic Study

1. Experimental Procedures: To a dried polytetrafluoroethene (PTFE) sealed pressure tube was added alkene **1a** (35.0 mg, 0.2 mmol), $PhICF_3Cl$ (92.4 mg, 0.3 mmol), TEMPO/BHT and anhydrous DMF (2 mL) in sequence under N_2. The reaction mixture was stirred at 50 °C for 12 h, monitored by ^{19}F NMR using $PhCF_3$ (20 μL, 0.1564 mmol) as the internal standard.

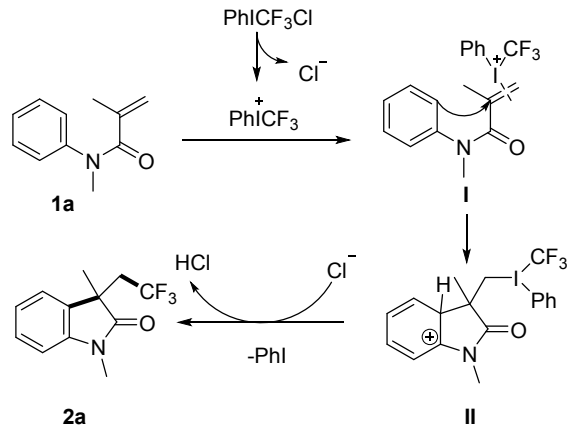
Table S8. Radical trapping experiment for trifluoromethylation of activated alkenes.[a]



Entry	**1a** : $PhICF_3Cl$	additive	eq	Yield of **2a** [%][b]	**TEMPO-CF_3** [%][b]
1	1 : 1.5	--	--	97	--
2	1 : 1.5	TEMPO	1.5	41	0
3	1 : 1.5	BHT	1.5	96	--

[a]Reaction conditions: **1a** (0.2 mmol), $PhICF_3Cl$ (0.30 mmol), DMF (2 mL).

[b]^{19}F NMR yields using $PhCF_3$ as an internal standard.



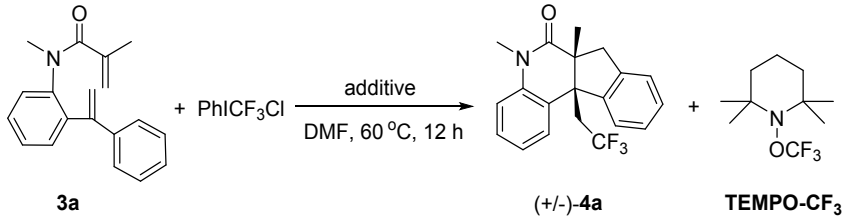
Scheme S1

Plausible mechanistic:

Based on the above expeimantal results (**Table S7)**, an ionic process is proposed as shown in **Scheme S1**. The activation of the alkene double bond of **1a** by $[PhICF_3]^+$ affords iodonium complex **I**. Then exo-cyclization occurs via an attack of the *N*-aryl substituent affording cyclic intermediate **II**. Finally, the deprotonation of **II** gives trifluoromethylated product **2a** along with the elimination of PhI.

2. Experimental Procedures: To a dried polytetrafluoroethene (PTFE) sealed pressure tube was added alkene **3a** (55.5 mg, 0.2 mmol), $PhICF_3Cl$ (92.4 mg, 0.3 mmol), TEMPO/BHT and anhydrous DMF (2 mL) in sequence under N_2. The reaction mixture was stirred at 60 °C for 12 h, monitored by ^{19}F NMR using $PhCF_3$ (20 μL, 0.1564 mmol,) as the internal standard.

Table S9. Radical trapping experiment for trifluoromethylation cyclization of dienes.[a]



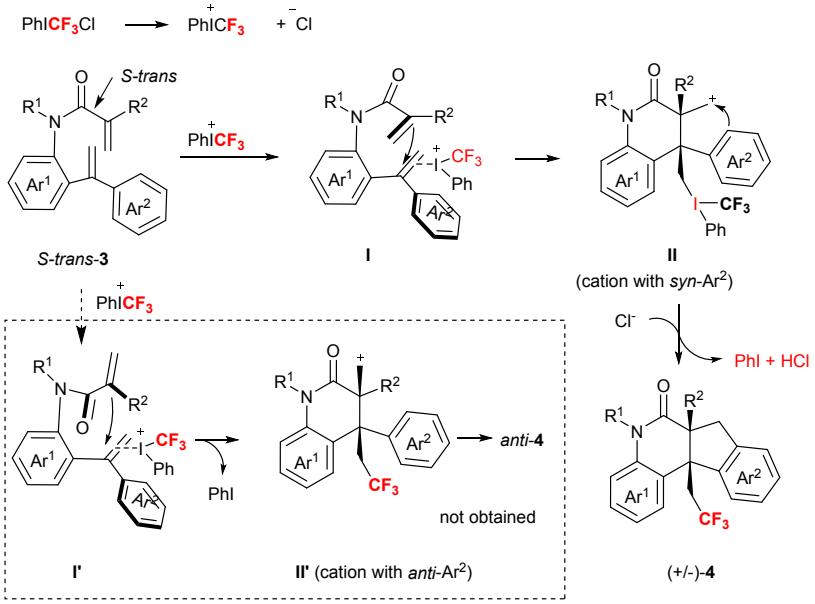
3a (+/-)-**4a** **TEMPO-CF_3**

Entry	additive	eq	Yield of (+/-)-*syn*-**4a** [%][b]	**TEMPO-CF_3** [%][b]
1	--	--	90	--
2	TEMPO	1.5	57	0
3	BHT	1.5	90	--

[a]Reaction conditions: **3a** (0.2 mmol), $PhICF_3Cl$ (0.30 mmol), DMF (2 mL).

[b]^{19}F NMR yields using $PhCF_3$ as an internal standard.

Proposed mechanism I



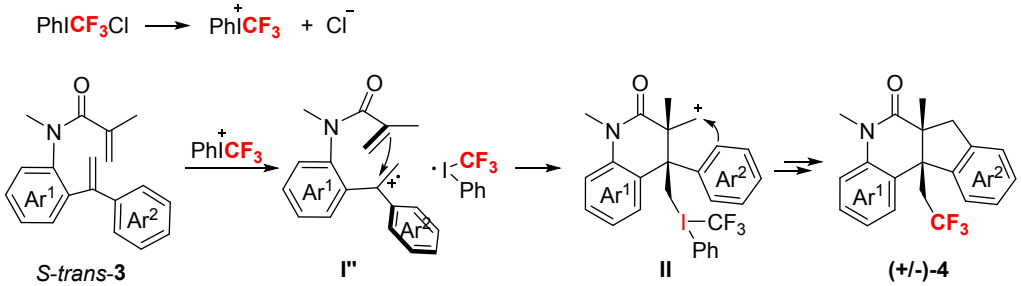
Scheme S2

Proposed mechanism for the transformations of *S-cis*-3 to 4:

A similar sequence was involved in the transformations of *S-cis*-**3** to **4**. As described in Scheme **S2**,

$[PhICF_3]^+$ prefers to activate styrene olefin bond and a following trap of the acryloyl substituent furnishes carbocation **II** or **II′**. The carbocation center in **II** happens to have a *syn*-**Ar²** group for easy trap along with the elimination of PhI. Thus, *syn*-substituted **4** are delivered as the final products. On the contrary, *anti*-substituted **4** could not be isolated from the reaction mixture in all cases. However, **Proposed mechanism II** can not be ruled out.

Proposed mechanism II



Scheme S3

VI. References

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VII. Crystallographic data.

1. Single-crystal X-ray diffraction data for (+/-)-*syn*-**4a** as recorded at a temperature of 294(2) K on a Bruker APEX CCD diffractometer, using a ω scan technique with Mo-Kα radiation (λ = 1.54178 Å). The structure was solved by Direct Method of SHELXS-97 and refined by full-matrix least-squares techniques using the SHELXL-97 program.1 Non-hydrogen atoms were refined with anisotropic temperature parameters, and hydrogen atoms of compound (+/-)-*syn*-**4a** were refined as rigid groups. Basic information pertaining to crystal parameters and structure refinement is summarized in follow. CCDC 1854708 contains the supplementary crystallographic data for (+/-)-*syn*-**4a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S10. Crystal data and structurerefinement for (+/-)-*syn*-4a.

Identification code	**(+/-)-*syn*-4a**
Empirical formula	$C_{20}\ H_{18}\ F_3\ N\ O$
Formula weight	355.12
Temperature	294(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
space group	P121/n1
Unit cell dimensions	a = 8.1844(9) Å alpha = 90.00 ° b = 24.475(3) Å beta = 106.736(6) ° c = 8.6835(9) Å gamma = 90.00 °
Volume	1665.7(3) $Å^3$
Z	19
Calculated density	1.377 mg/m^3
Absorption coefficient	0.908 mm^{-1}
F(000)	720
Crystal size	0.40 x 0.30 x 0.20 mm
Theta range for data collection	3.612 to 72.302°
Limiting indices	-8<=h<=10, -29<=k<=30, -10<=l<=10
Reflections collected	3252
Unique	2586 [R(int) = 0.030]
Completeness to theta = 25.00	99.6 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	3252 / 0 / 298
Goodness-of-fit on F2	1.050
Final R indices [I>2sigma(I)]	R1 = 0.0520, wR2 = 0.1199
R indices (all data)	R1 = 0.0664, wR2 = 0.1280
Largest diff. peak and hole	0.226 and -0.256 e. $Å^{-3}$

Table S11. Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for (+/-)-*syn*-4a. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U^{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
F1	10111(2)	5517.6(8)	9055.8(18)	85.6(5)
O1	7657(2)	6234.0(7)	10727.4(18)	63.7(5)
F3	11209.2(19)	6010.6(8)	7667(2)	94.8(6)
N1	8640(2)	6806.7(7)	9169.7(18)	44.1(4)
F2	11114(3)	5150.4(9)	7316(3)	122.6(8)
C15	8153(2)	6644.5(7)	6293(2)	33.1(4)
C16	8722(2)	6983.1(8)	7643(2)	37.6(4)
C10	7341(2)	6089.0(7)	6408(2)	32.8(4)
C5	5685(2)	6049.2(7)	5015(2)	38.7(4)
C20	8342(3)	6829.0(9)	4842(2)	44.5(5)
C13	7698(3)	6369.2(8)	9385(2)	41.7(4)
C11	8540(3)	5613.0(9)	6304(3)	45.7(5)
C8	6604(2)	6086.0(7)	7885(2)	37.6(4)
C6	4324(2)	6246.4(8)	5507(3)	44.8(5)
C7	4930(3)	6419.9(9)	7229(3)	45.7(5)
C9	6141(3)	5514.2(9)	8324(3)	54.6(6)
C4	5439(3)	5866.4(8)	3451(3)	50.6(5)
C17	9415(3)	7493.5(9)	7490(3)	53.0(6)
C19	9056(3)	7330.8(10)	4712(3)	58.9(6)
C18	9578(3)	7663.9(10)	6033(3)	61.3(6)
C12	10218(3)	5573.5(10)	7567(3)	57.1(6)
C2	2689(3)	6257.2(10)	4433(3)	62.4(7)
C3	3798(4)	5879.6(10)	2389(3)	64.7(7)
C1	2447(4)	6066.6(11)	2883(4)	72.6(8)
C14	9518(5)	7127.9(12)	10589(3)	67.3(7)

Table S12. Anisotropic Displacement Parameters (Å²×10³) for (+/-)-*syn*-4a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F1	65.8(9)	121.7(14)	60.6(9)	22.3(9)	4.7(7)	11.8(9)
O1	87.5(12)	71.0(11)	37.9(8)	5.9(7)	26.1(8)	-5.0(9)
F3	43.5(8)	105.4(13)	123.4(15)	28.6(11)	4.8(8)	-7.3(8)
N1	56.9(10)	43.2(9)	31.0(8)	-6.3(7)	10.9(7)	-6.8(8)
F2	93.5(13)	121.8(16)	132.9(17)	-24.9(13)	1.6(11)	73.0(12)
C15	32.5(9)	34.5(9)	32.5(9)	-2.2(7)	9.7(7)	0.1(7)
C16	39.8(10)	37.3(10)	35.8(10)	-3.2(8)	11.2(8)	-4.2(8)
C10	36.4(9)	29.4(9)	31.7(9)	-2.2(7)	8.7(7)	0.6(7)
C5	42.3(10)	29.3(9)	40.2(10)	-1.1(7)	4.9(8)	-3.5(8)
C20	52.9(12)	46.9(11)	37.2(10)	-4.7(9)	18.6(9)	-6.4(9)
C13	49.8(11)	43.5(11)	33.9(10)	2.4(8)	15.6(8)	5.6(9)

C11	49.8(12)	40.8(11)	46.8(12)	-3.3(9)	14.4(9)	8.4(9)
C8	40.4(10)	34.8(9)	40.4(10)	3.6(8)	16.1(8)	0.0(8)
C6	39.4(10)	36.3(10)	55.4(12)	3.9(9)	8.5(9)	-1.8(8)
C7	40.7(10)	46.3(12)	54.5(12)	1.9(10)	20.7(9)	3.3(9)
C9	62.1(15)	41.8(12)	63.2(15)	8.7(11)	23.1(12)	-6.8(11)
C4	60.9(13)	38.2(11)	45.4(12)	-7.9(9)	3.6(10)	-3.2(10)
C17	61.6(13)	46.4(12)	52.0(13)	-12.6(10)	18.1(11)	-17.7(10)
C19	78.6(16)	56.6(14)	50.5(13)	5.8(11)	33.1(12)	-13.9(12)
C18	77.5(16)	46.5(13)	66.6(15)	-1.0(11)	31.4(13)	-22.6(12)
C12	47.2(12)	59.1(14)	64.6(15)	4.6(11)	15.3(11)	15.3(11)
C2	42.0(12)	58.1(14)	78.1(17)	8.9(12)	3.1(12)	1.9(11)
C3	78.6(17)	47.9(13)	49.3(14)	-5.3(11)	-10.9(12)	-6.6(12)
C1	58.5(15)	58.6(15)	75.8(18)	4.9(13)	-20.3(14)	-8.4(12)
C14	97(2)	60.9(16)	36.6(12)	-11.9(11)	7.2(12)	-12.8(15)

Table S13. Bond Lengths for (+/-)-*syn*-4a.

Atom	Length/Å	Atom	Length/Å
F1-C12	1.328(3)	C5-C6	1.390(3)
O1-C13	1.222(2)	C5-C4	1.388(3)
F3-C12	1.330(3)	C20-C19	1.379(3)
N1-C16	1.414(2)	C13-C8	1.519(3)
N1-C13	1.363(3)	C11C12	1.493(3)
N1C14	1.464(3)	C8-C7	1.556(3)
F2-C12	1.323(3)	C8-C9	1.527(3)
C15-C16	1.401(2)	C6-C7	1.495(3)
C15-C10	1.529(2)	C6-C2	1.393(3)
C15-C20	1.388(3)	C4-C3	1.394(3)
C16-C17	1.394(3)	C17-C18	1.375(3)
C10-C5	1.537(2)	C19-C18	1.371(3)
C10-C11	1.542(3)	C2-C1	1.384(4)
C10-C8	1.567(2)	C3-C1	1.374(4)

Table S14. Bond Angles for (+/-)-*syn*-4a.

Atom	Angle/°	Atom	Angle/°
C16-N1-C14	118.75(18)	C13-C8-C10	115.41(15)

C13-N1-C16	123.34(15)	C13-C8-C7	108.29(16)
C13-N1-C14	117.79(18)	C13-C8-C9	109.35(17)
C16-C15-C10	121.17(15)	C7-C8-C10	101.77(15)
C20-C15-C16	118.00(17)	C9-C8-C10	113.01(17)
C20-C15-C10	120.83(16)	C9-C8-C7	108.49(17)
C15-C16-N1	120.63(16)	C5-C6-C7	109.96(17)
C17-C16-N1	119.56(17)	C5-C6-C2	120.1(2)
C17-C16-C15	119.79(18)	C2-C6-C7	129.9(2)
C15-C10-C5	107.83(14)	C6-C7-C8	102.73(16)
C15-C10-C11	111.84(16)	C5-C4-C3	118.7(2)
C15-C10-C8	109.53(14)	C18-C17-C16	120.6(2)
C5-C10-C11	109.75(15)	C18-C19-C20	119.9(2)
C5-C10-C8	100.60(14)	C19-C18-C17	120.0(2)
C11-C10-C8	116.45(15)	F1-C12-F3	103.2(2)
C6-C5-C10	109.85(16)	F1-C12-C11	114.65(19)
C4-C5-C10	129.53(18)	F3-C12-C11	114.2(2)
C4-C5-C6	120.60(19)	F2-C12-F1	105.9(2)
C19-C20-C15	121.66(19)	F2-C12-F3	106.5(2)
O1-C13-N1	121.05(19)	F2-C12-C11	111.5(2)
O1-C13-C8	121.54(19)	C1-C2-C6	119.0(3)
N1-C13-C8	117.25(16)	C1-C3-C4	120.6(2)
C12-C11-C10	118.19(18)	C3-C1-C2	120.9(2)

Table S15. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for (+/-)-*syn*-4a.

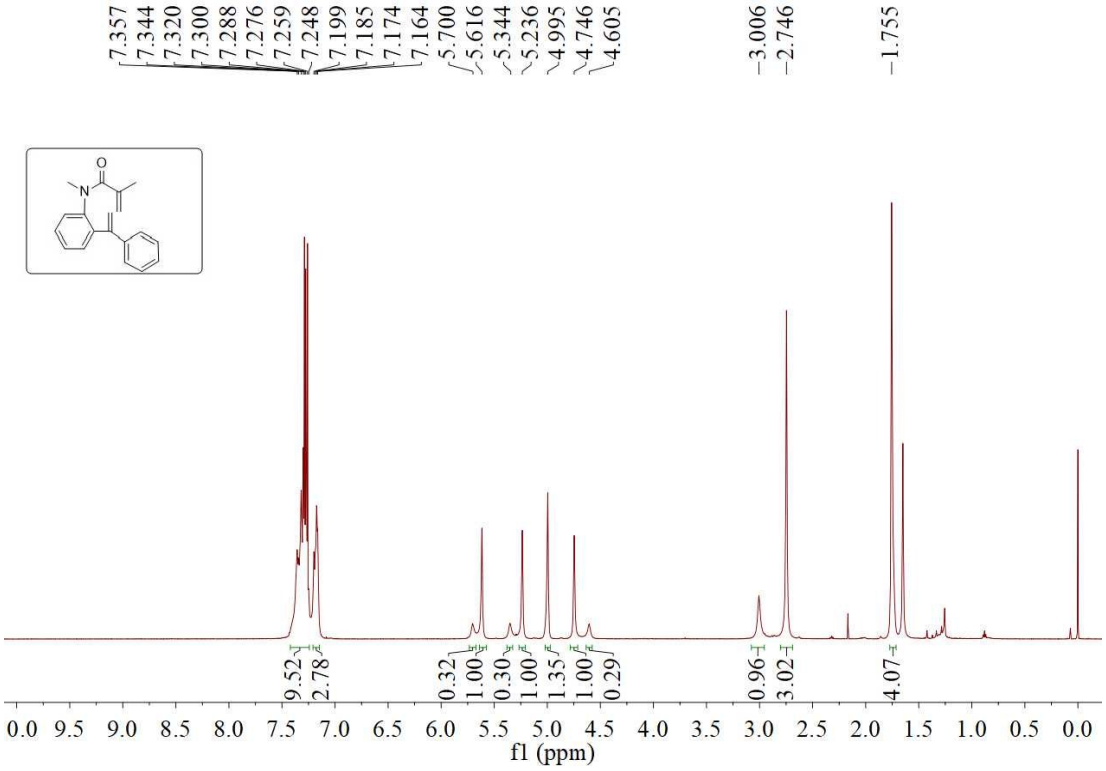
Atom	*x*	*y*	*z*	U(eq)
H9A	5420(30)	5331(11)	7360(30)	62(7)
H9B	5480(40)	5543(13)	9120(40)	95(10)
H9C	7150(30)	5279(11)	8750(30)	66(7)
H14A	9480(40)	6905(12)	11530(40)	83(9)

H14B	10750(40)	7174(12)	10610(30)	86(10)
H14C	8930(40)	7486(13)	10570(40)	91(10)
H7A	5220(30)	6841(10)	7310(30)	51(6)
H7B	4190(30)	6346(10)	7850(30)	61(7)
H20	7940(30)	6598(9)	3890(30)	57(6)
H4	6440(30)	5717(10)	3080(30)	59(7)
H17	9750(30)	7731(11)	8400(30)	66(7)
H1	1300(40)	6056(12)	2110(40)	92(9)
H3	3580(40)	5731(11)	1240(30)	80(8)
H19	9140(40)	7445(11)	3720(40)	81(9)
H2	1760(40)	6376(11)	4830(30)	74(8)
H18	10060(40)	8022(12)	5940(30)	78(8)
H11A	8820(30)	5648(9)	5310(30)	50(6)
H11B	7950(30)	5252(11)	6270(30)	62(7)

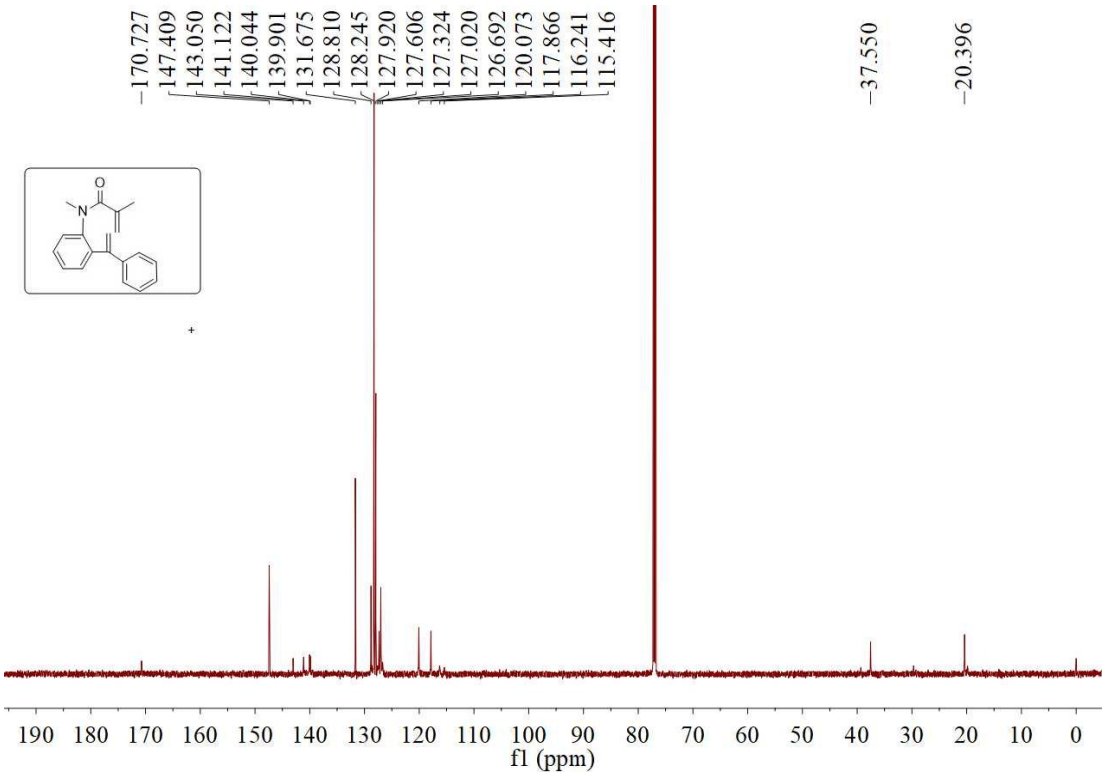
VIII. NMR Spectra

1. NMR Spectra of New Substrates

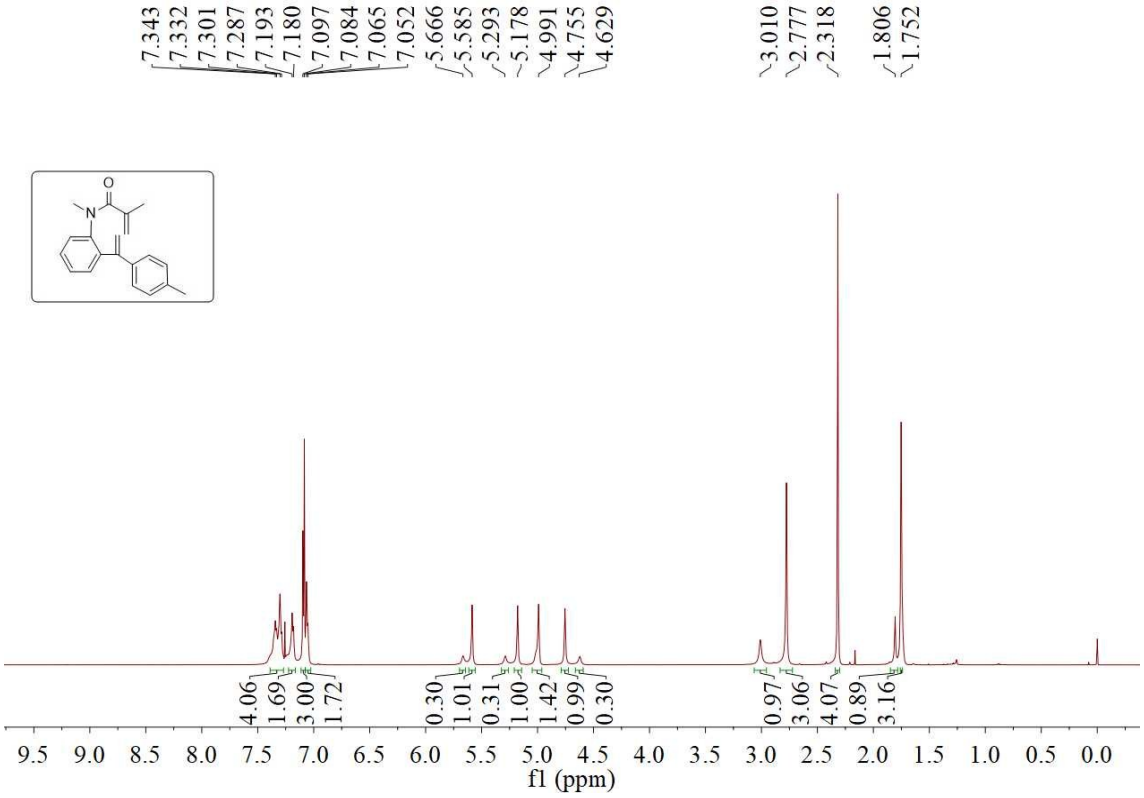
^{13}H-NMR Spectra of 3a



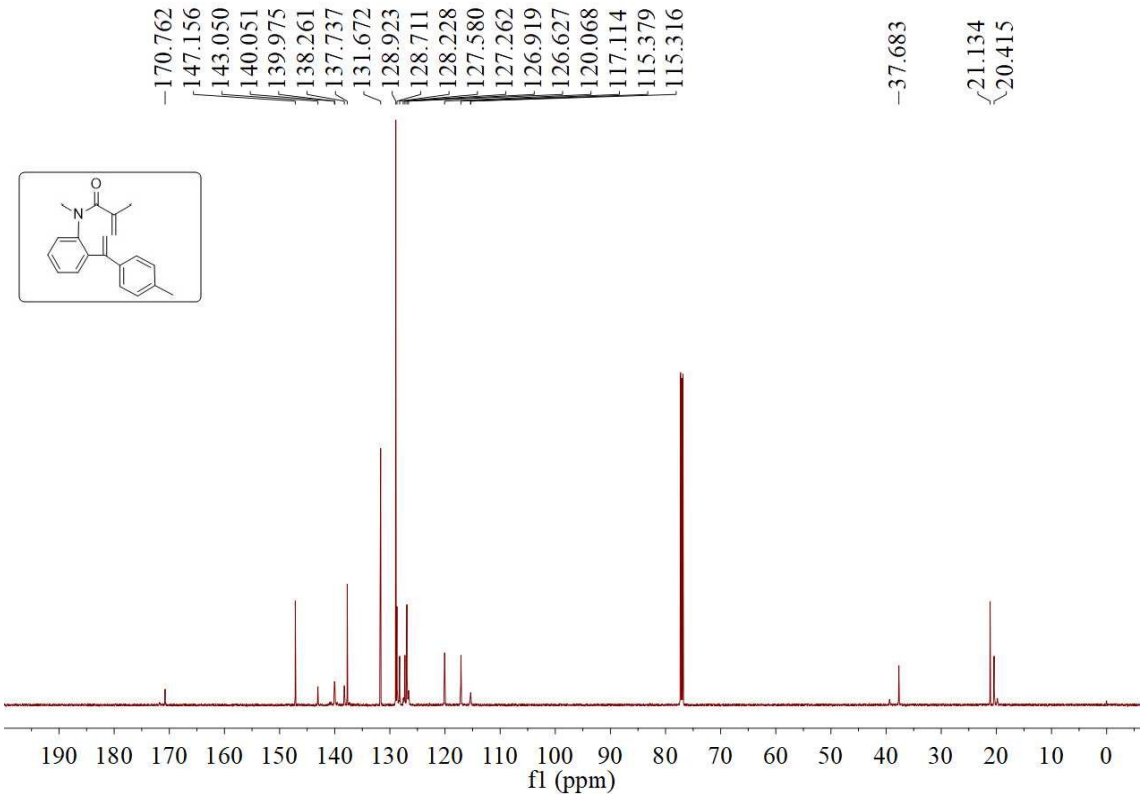
^{13}C-NMR Spectra of 3a



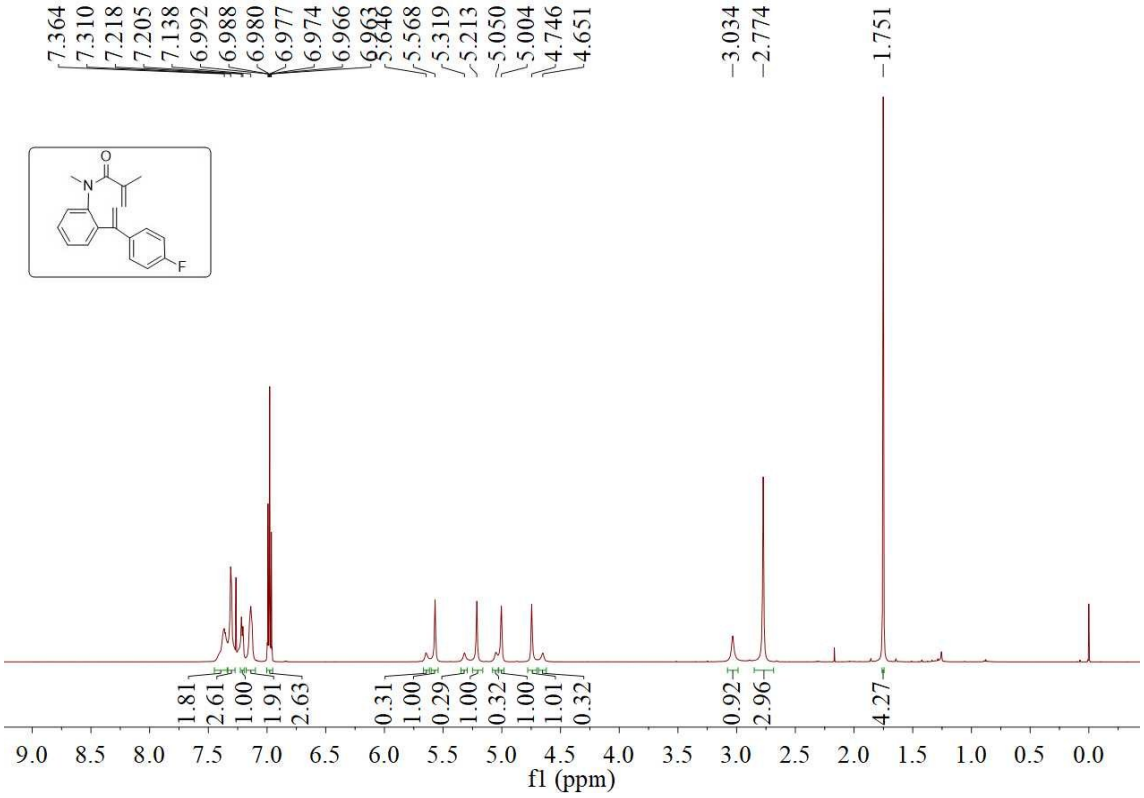
^{1}H-NMR Spectra of 3b



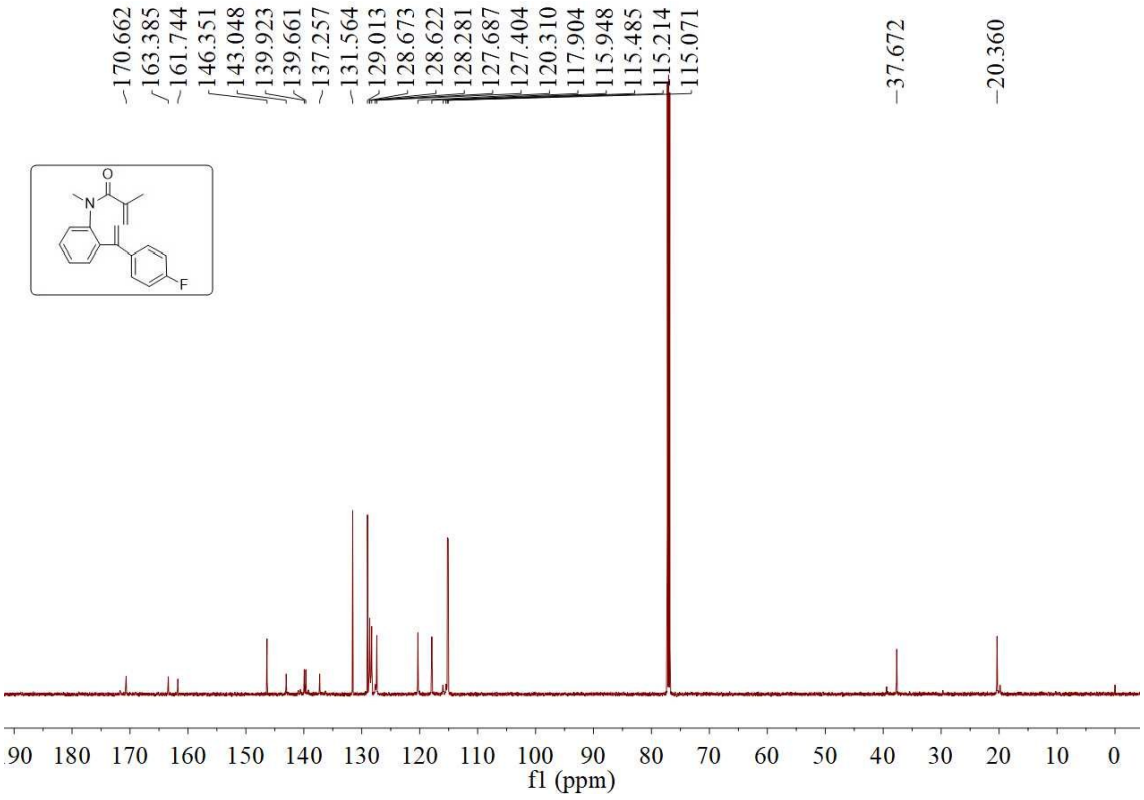
^{13}C-NMR Spectra of 3b



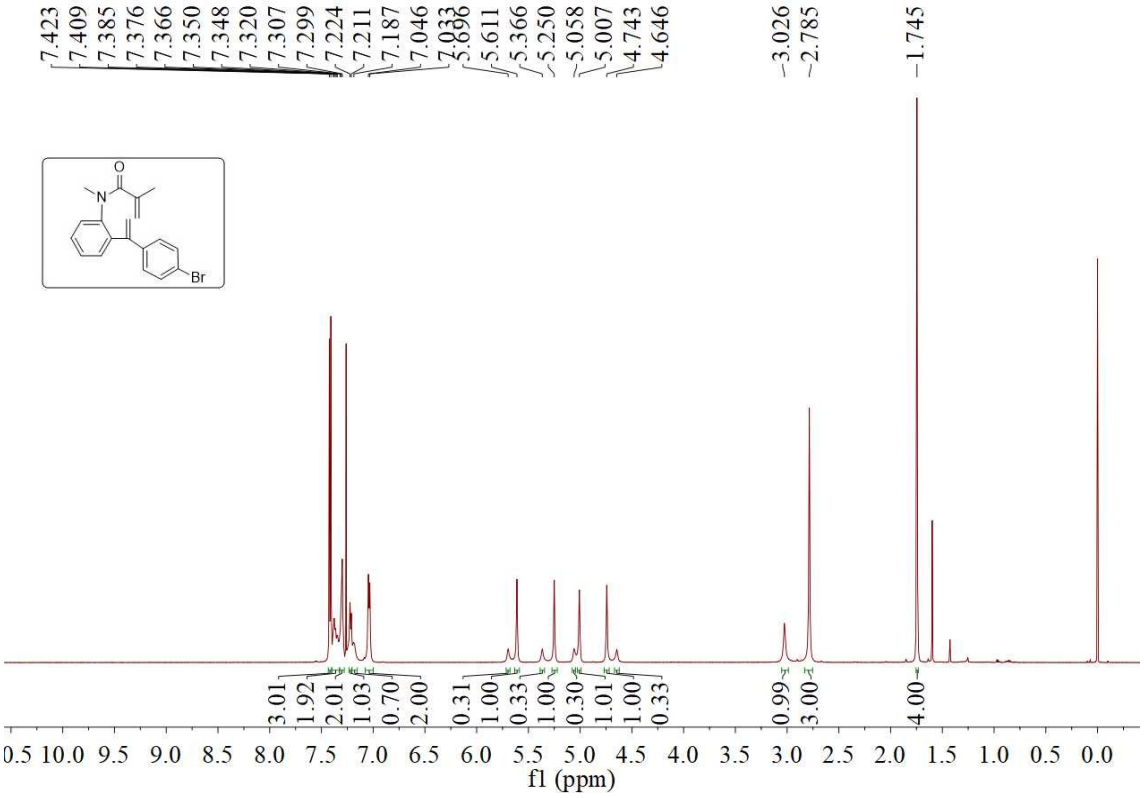
^{1}H-NMR Spectra of 3c



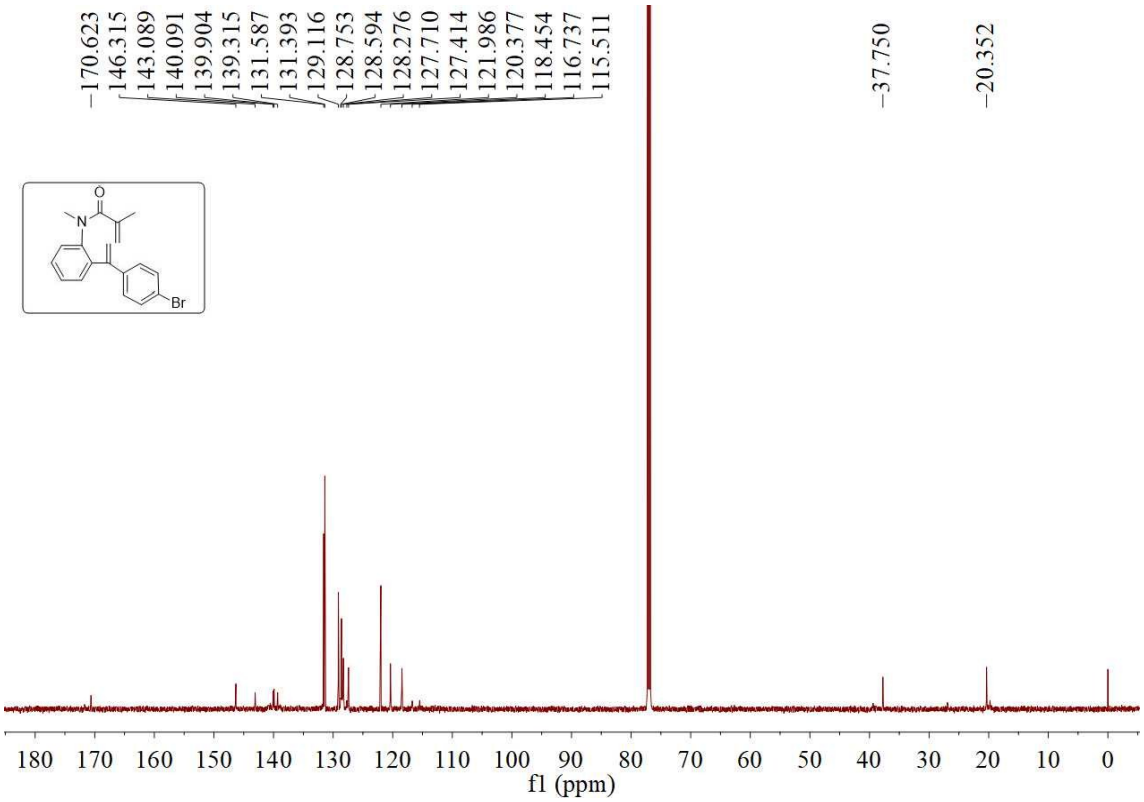
^{13}C-NMR Spectra of 3c



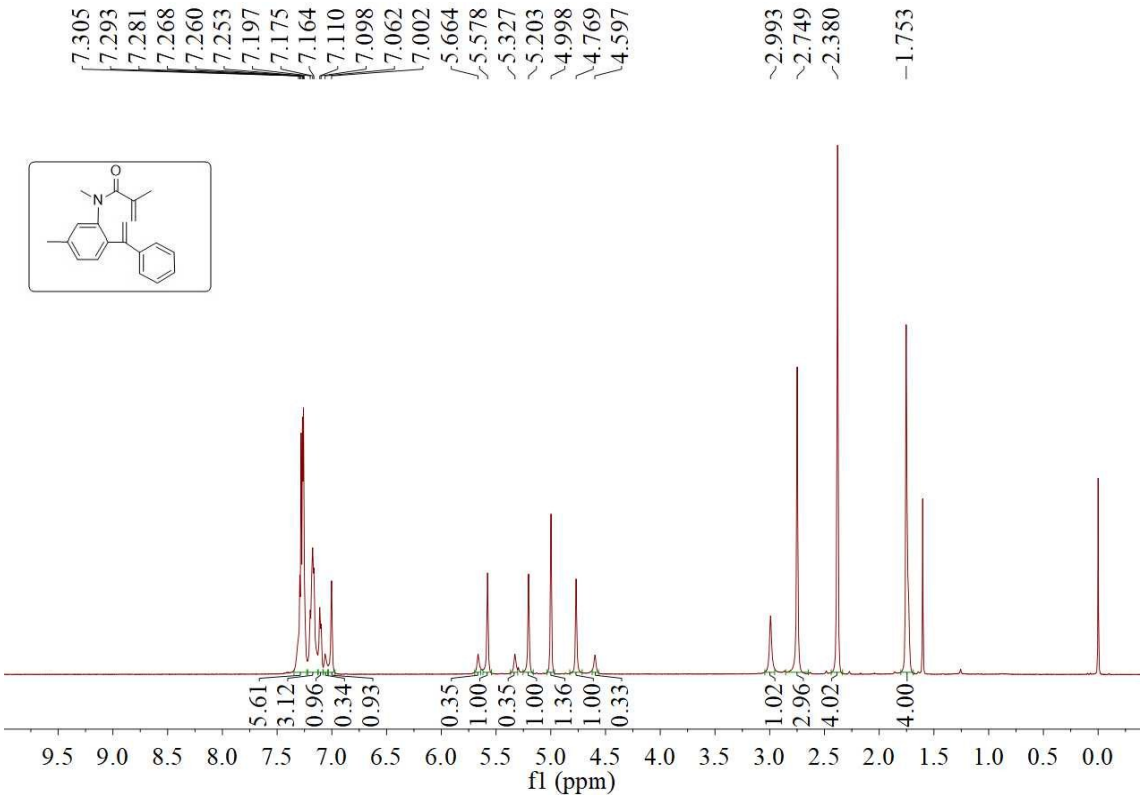
[1]H-NMR Spectra of 3d



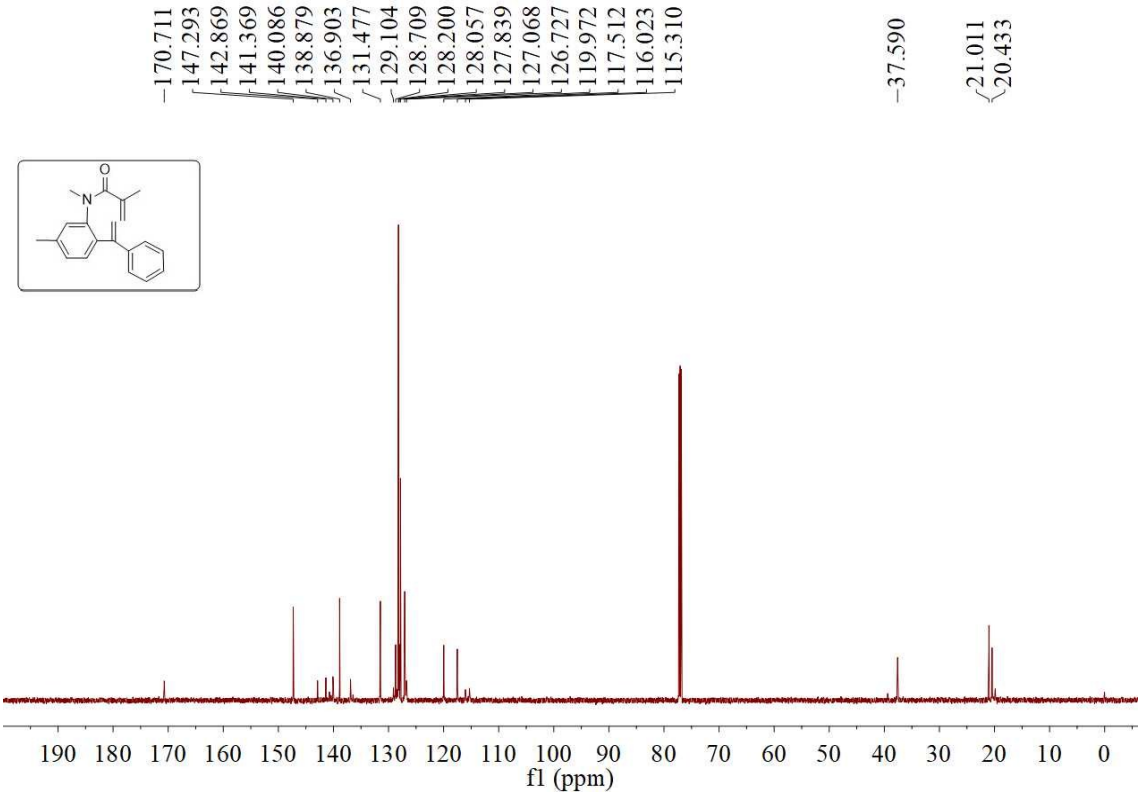
[13]C-NMR Spectra of 3d



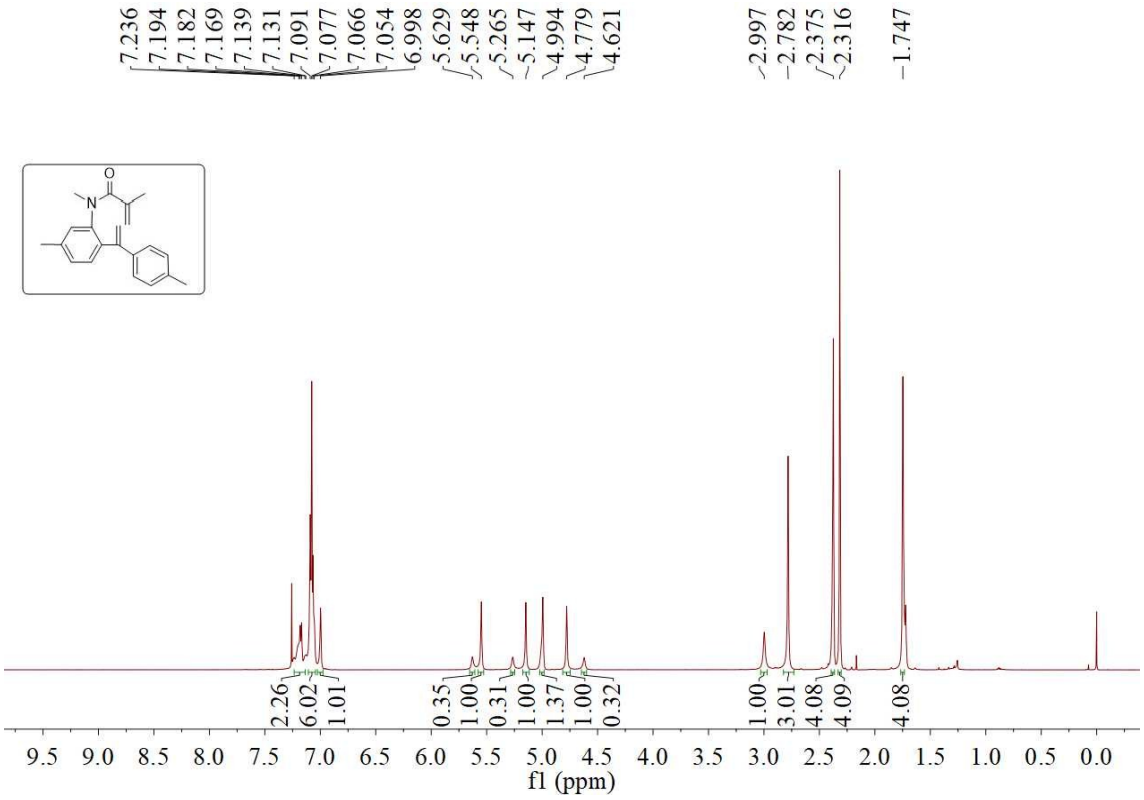
^{1}H-NMR Spectra of 3e



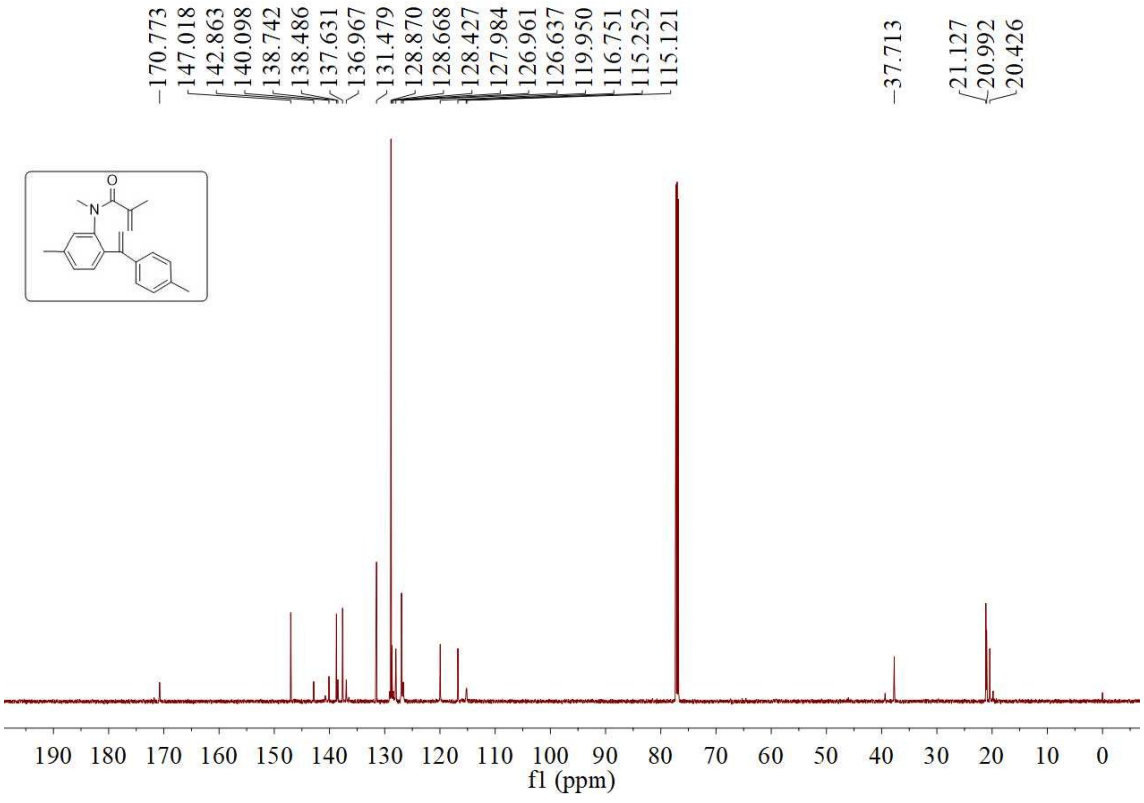
^{13}C-NMR Spectra of 3e



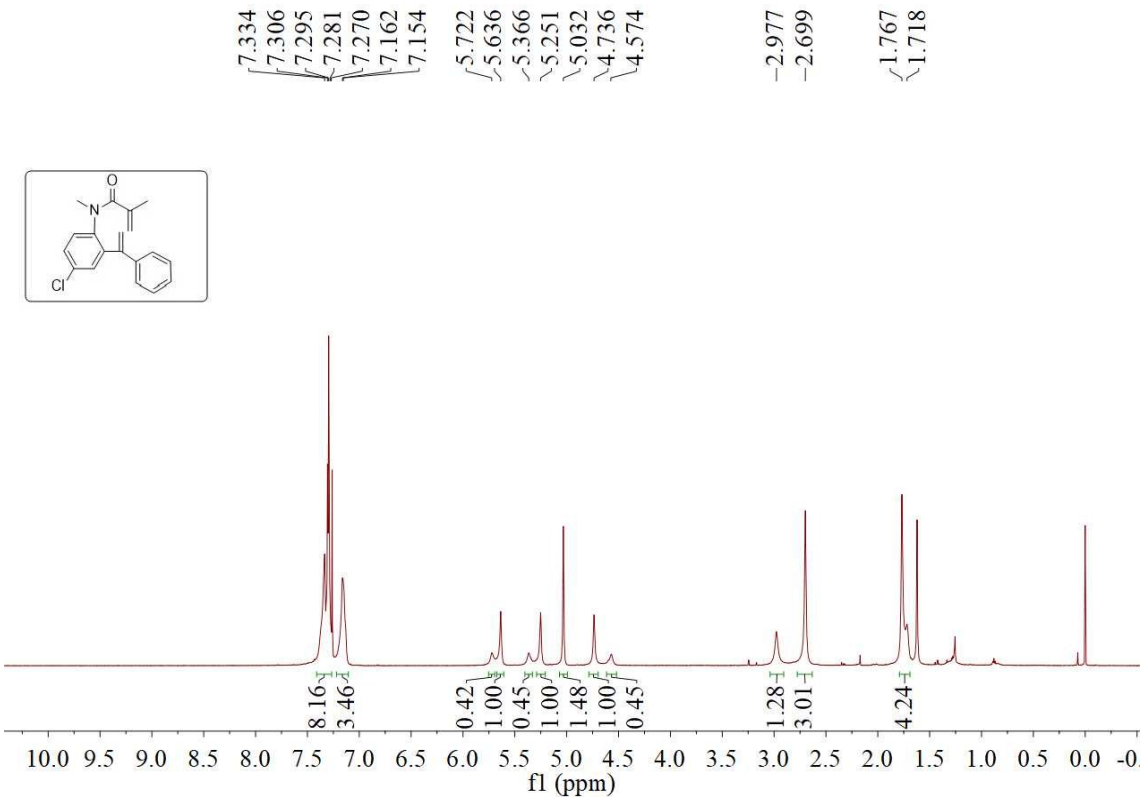
^{1}H-NMR Spectra of 3f



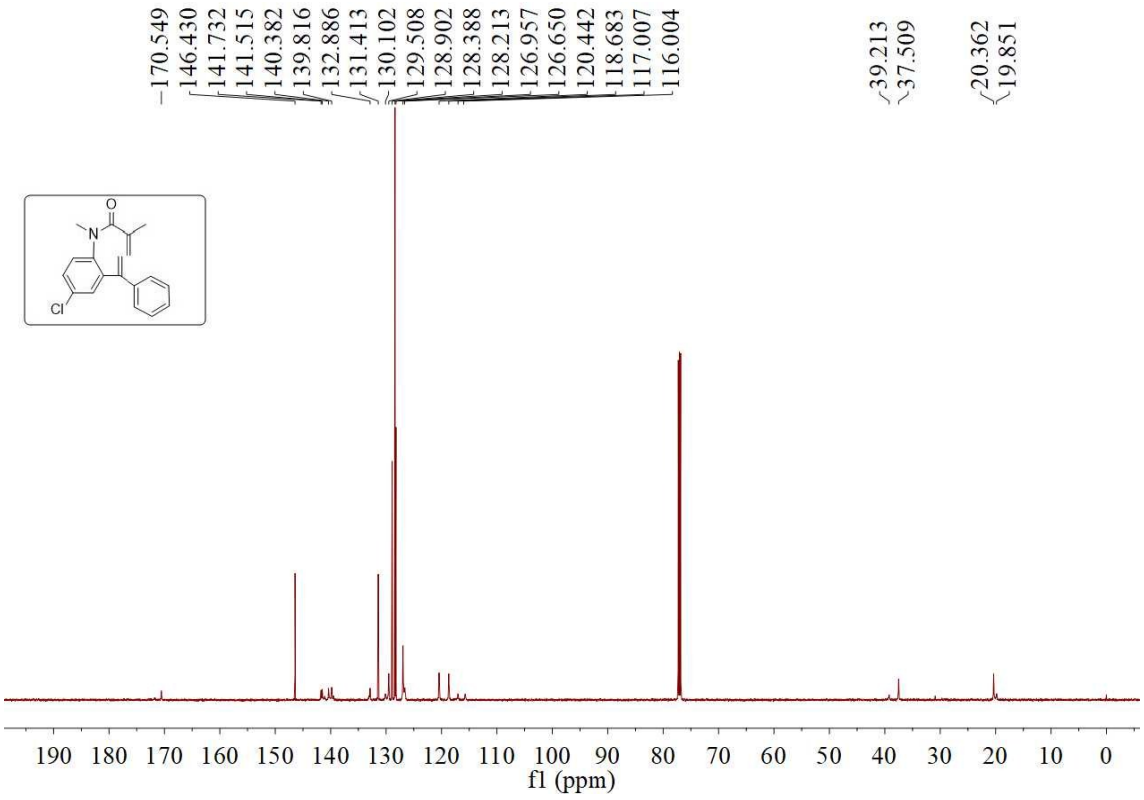
^{13}C-NMR Spectra of 3f



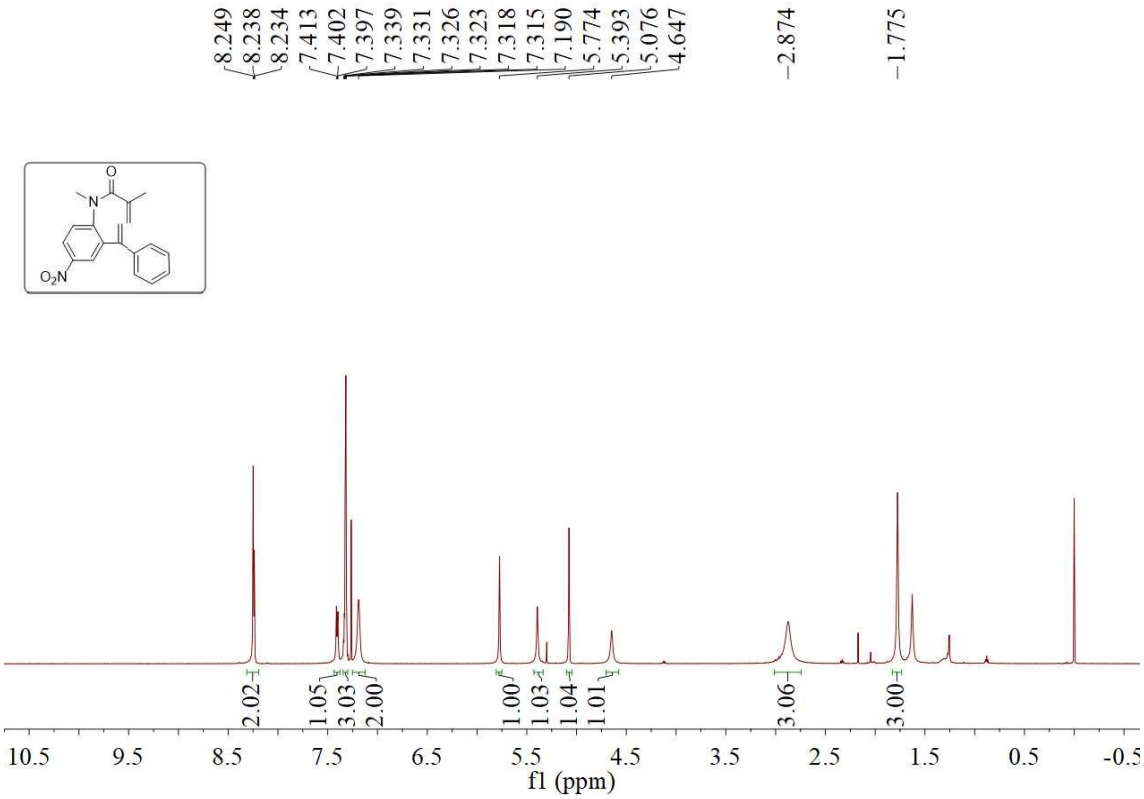
^{1}H-NMR Spectra of 3g



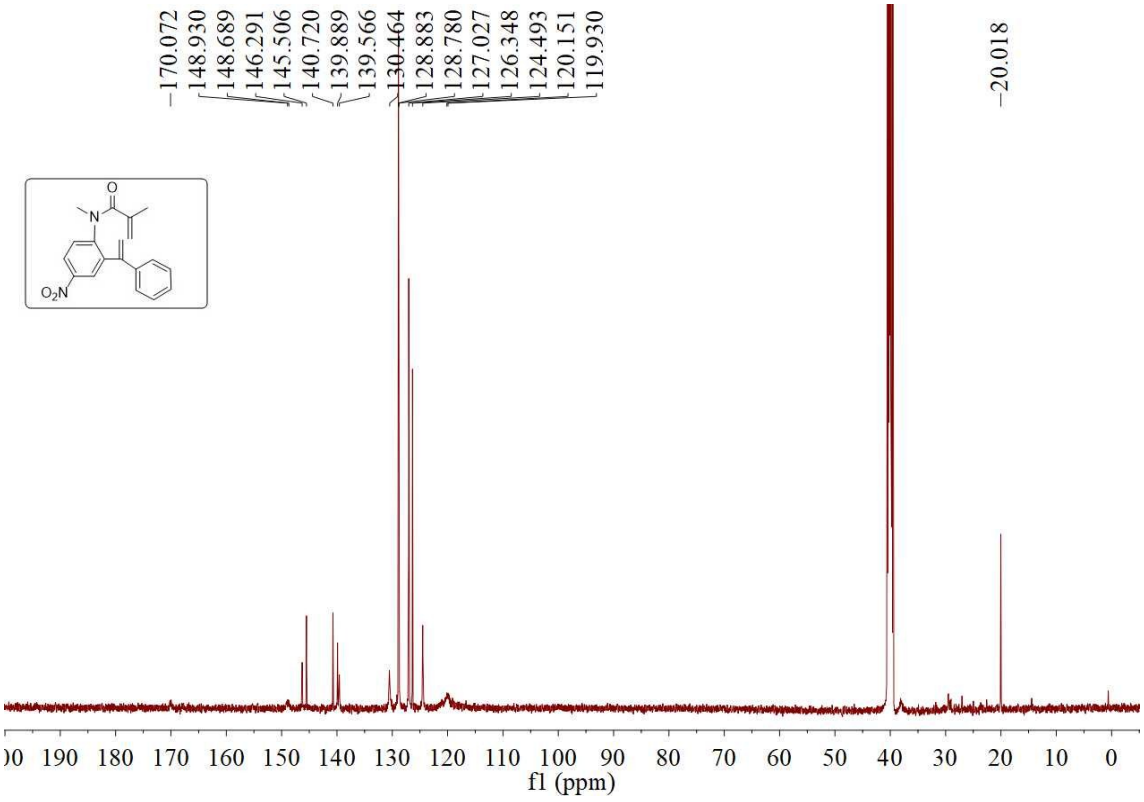
^{13}C-NMR Spectra of 3g



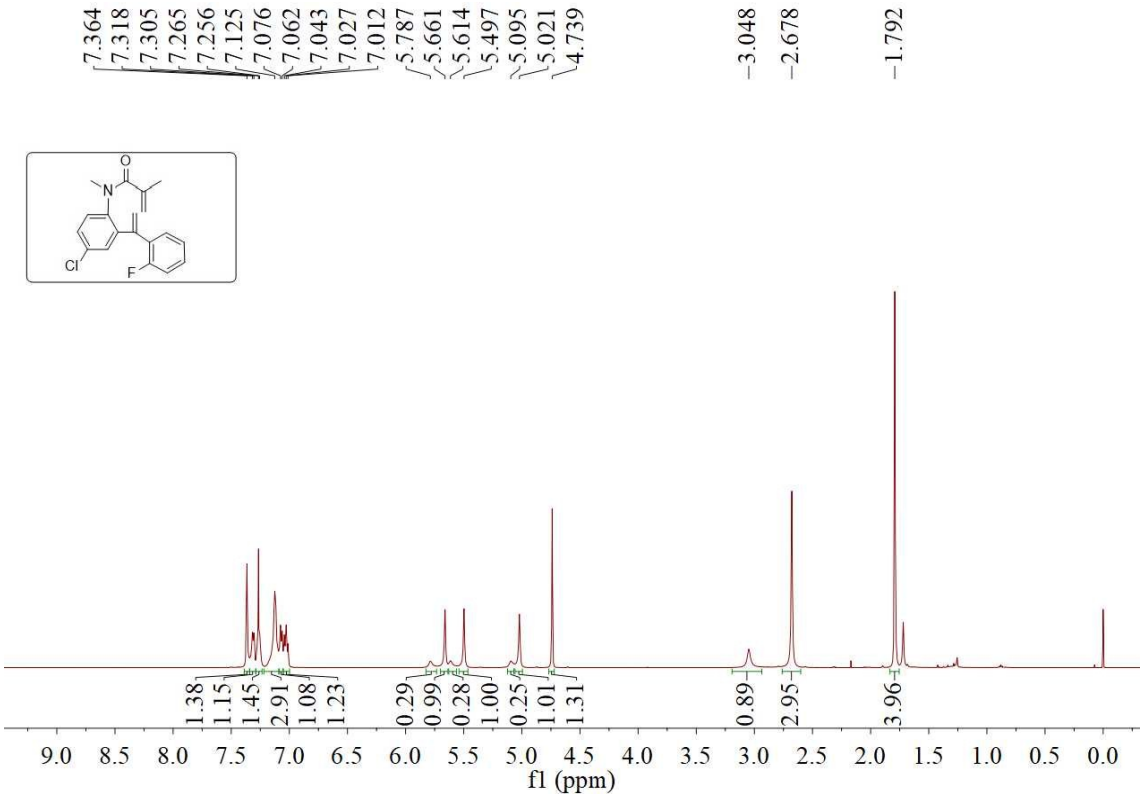
[1]H-NMR Spectra of 3h



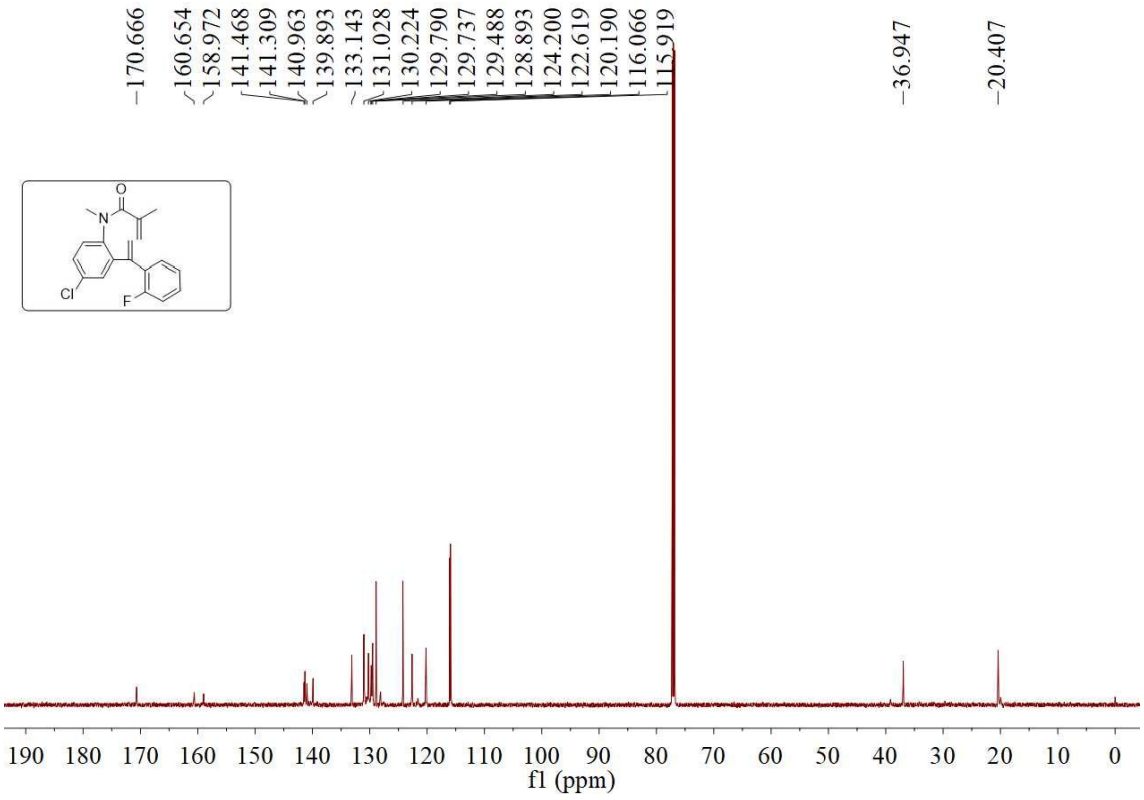
[13]C-NMR Spectra of 3h



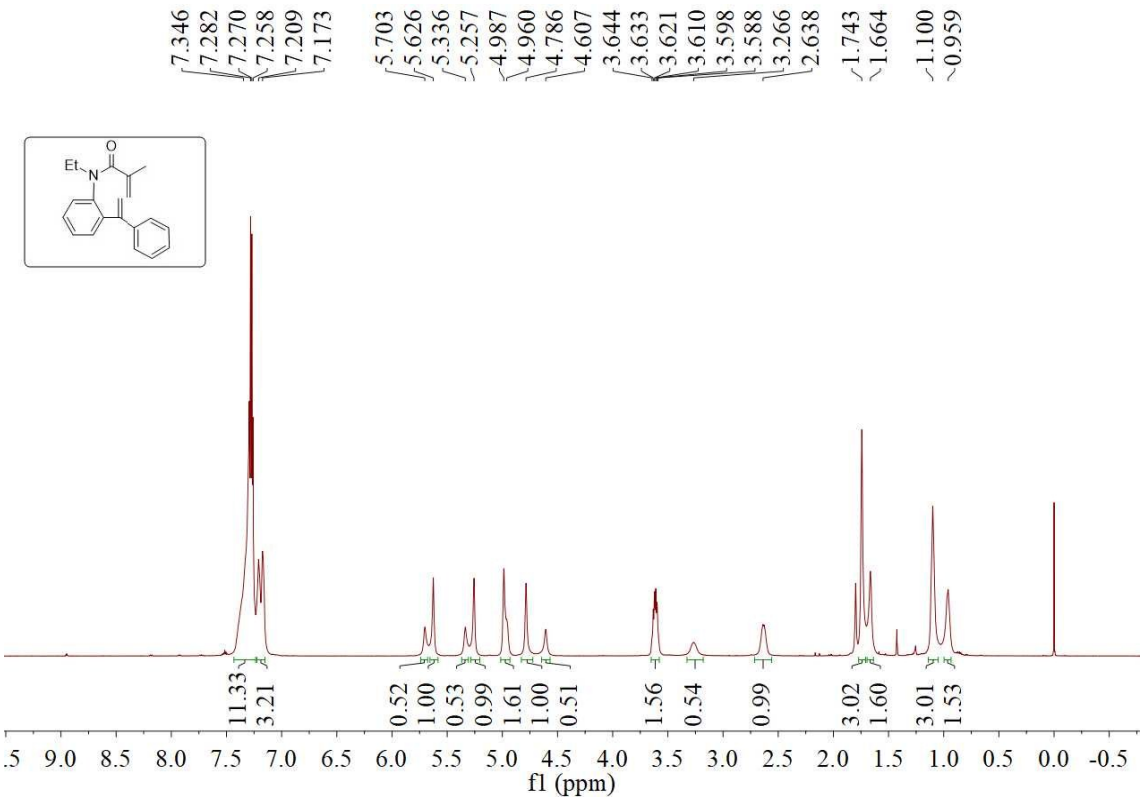
[1]H-NMR Spectra of 3i



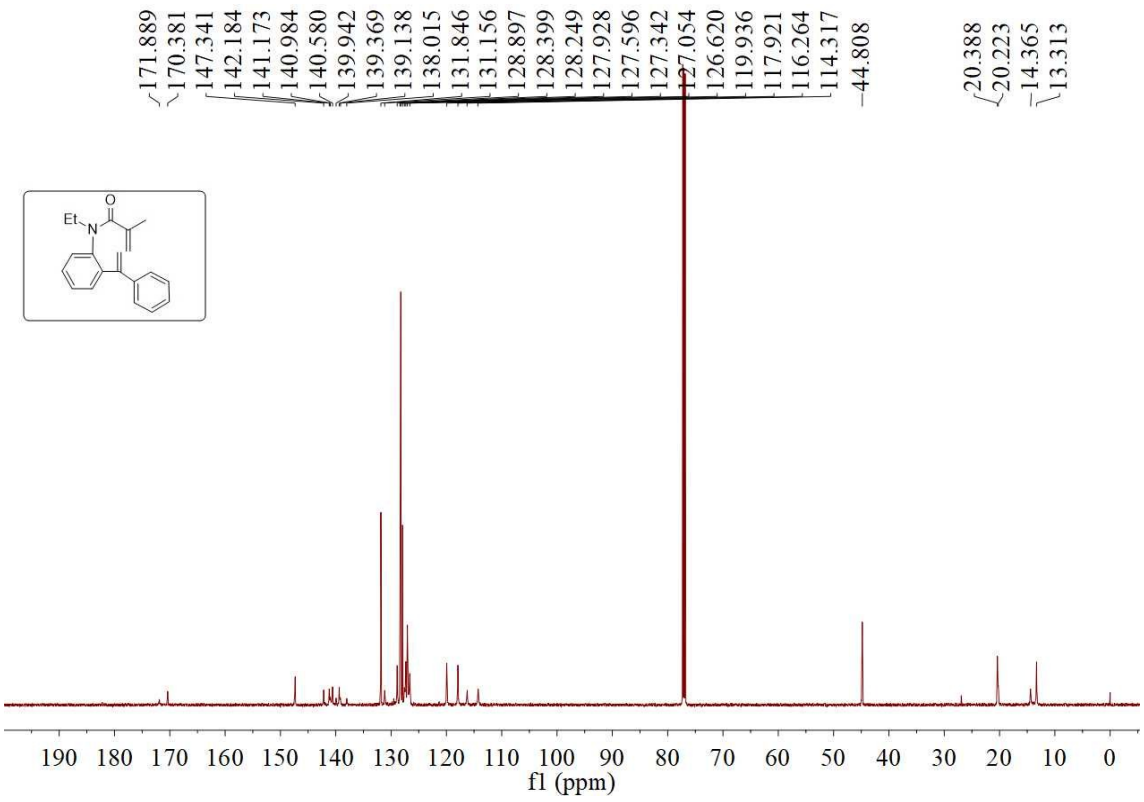
[13]C-NMR Spectra of 3i



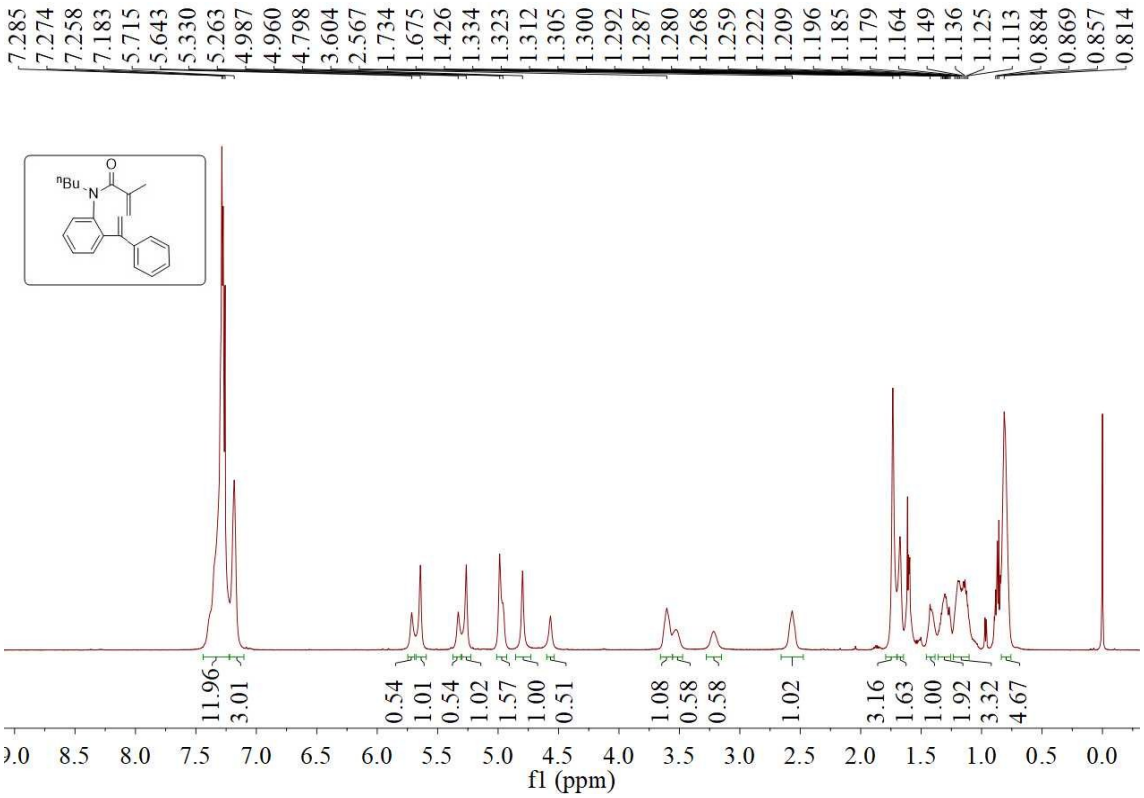
[1]H-NMR Spectra of 3j



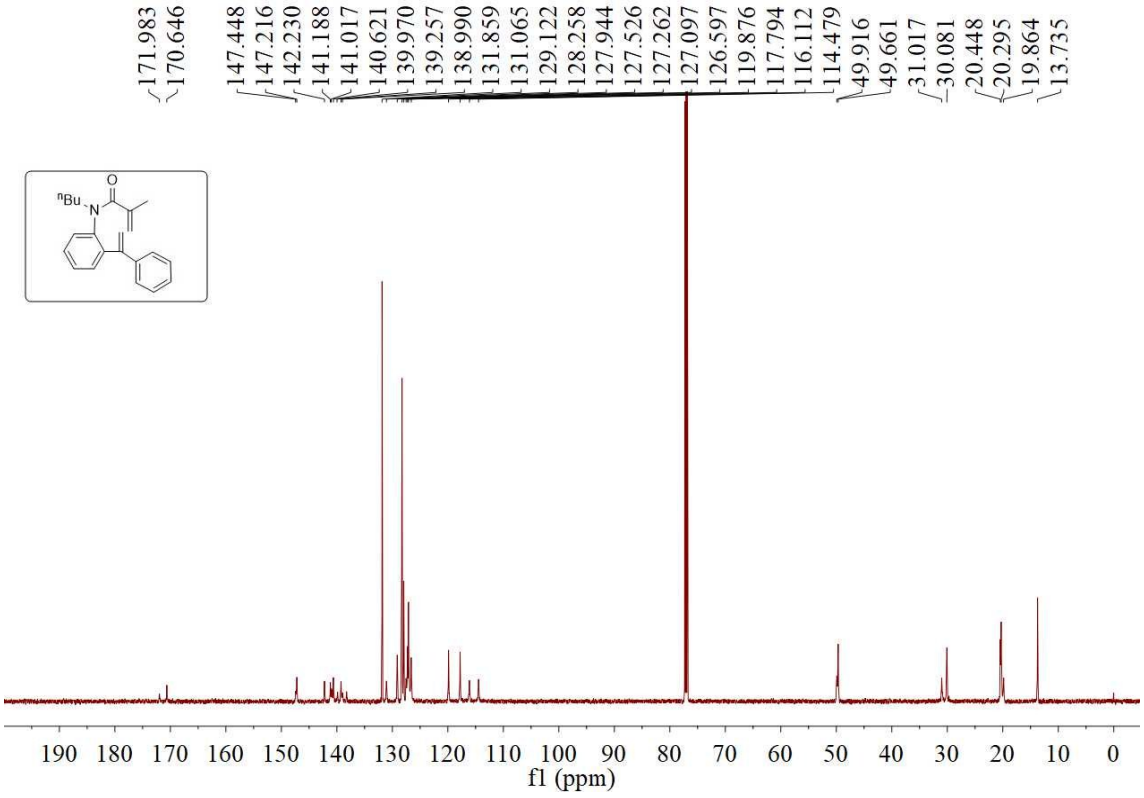
[13]C-NMR Spectra of 3j



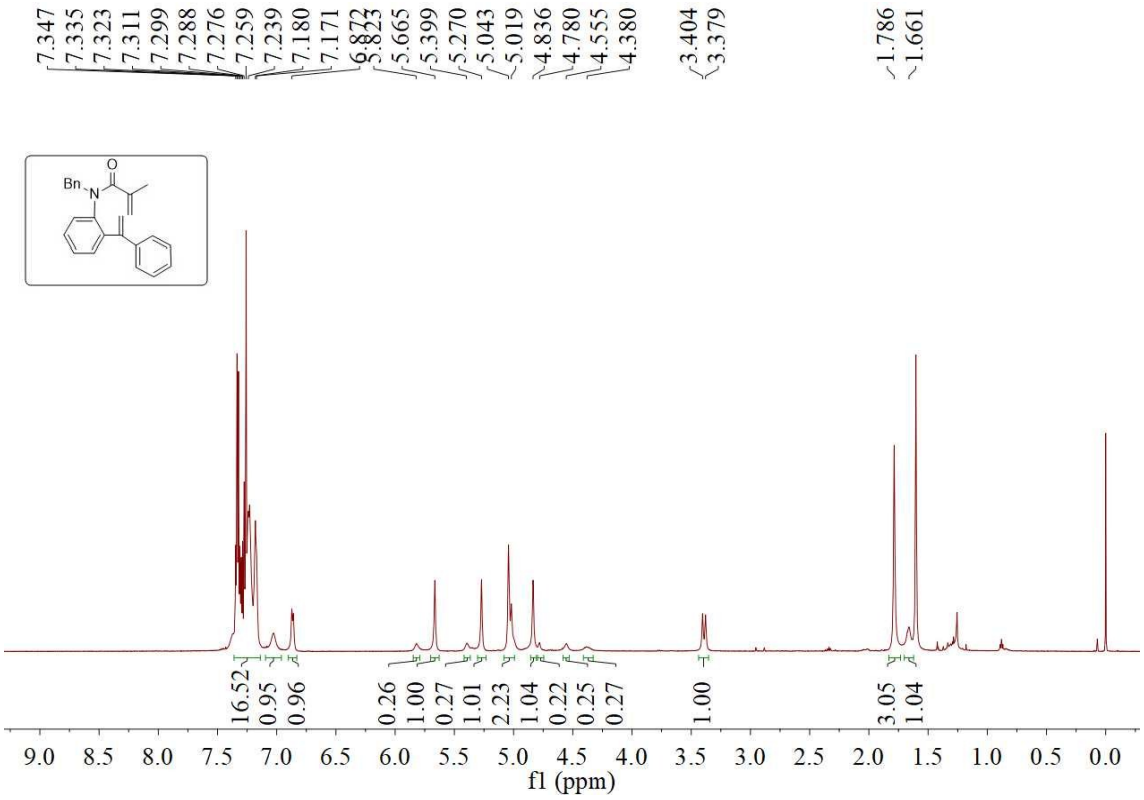
^{1}H-NMR Spectra of 3k



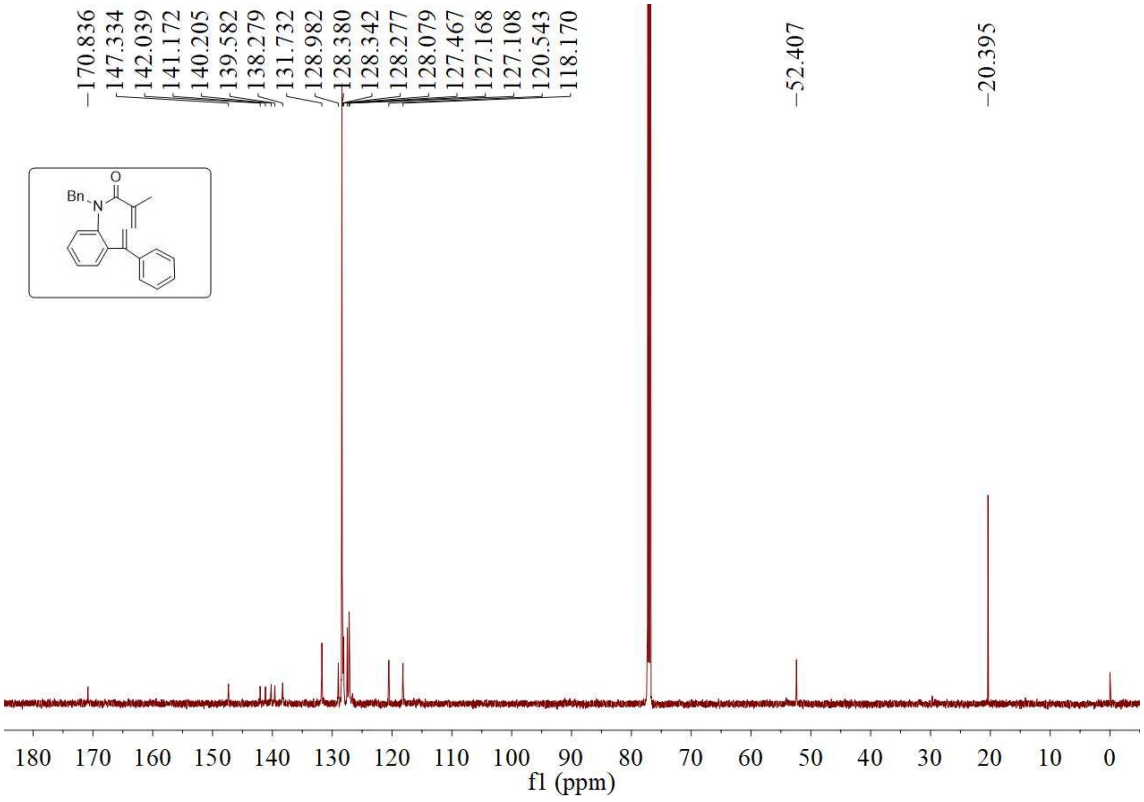
^{13}C-NMR Spectra of 3k



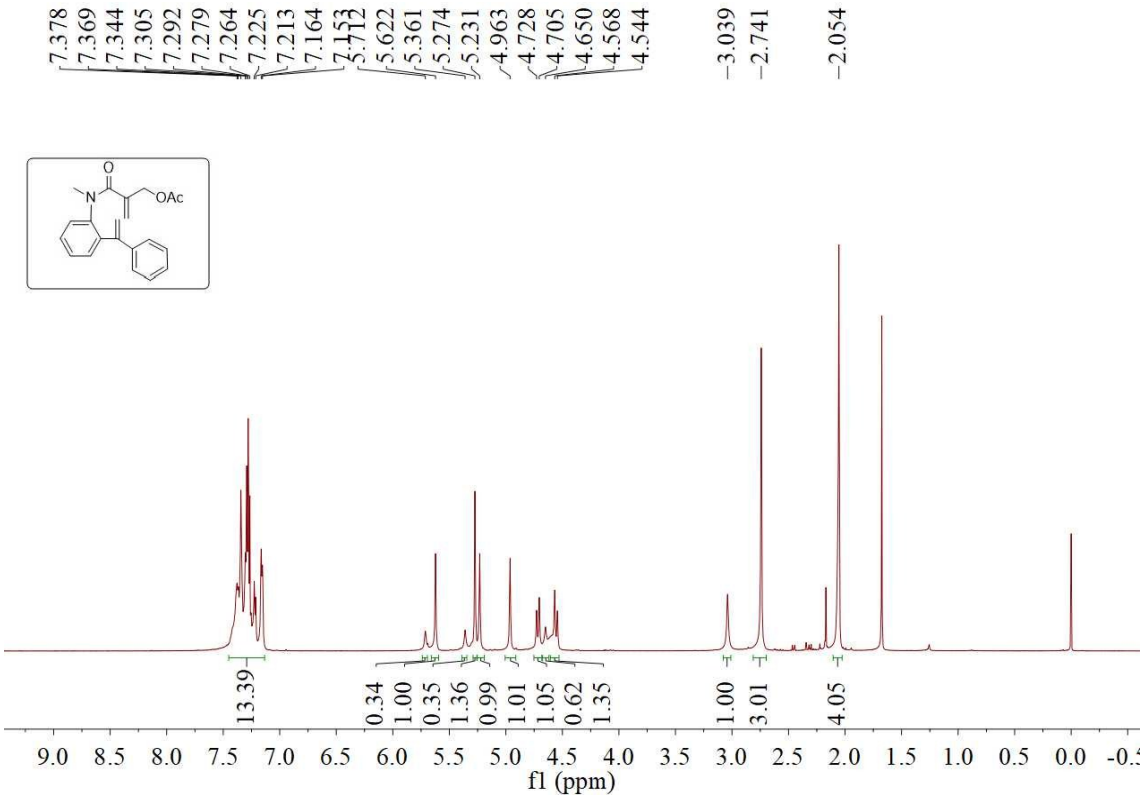
^{1}H-NMR Spectra of 3l



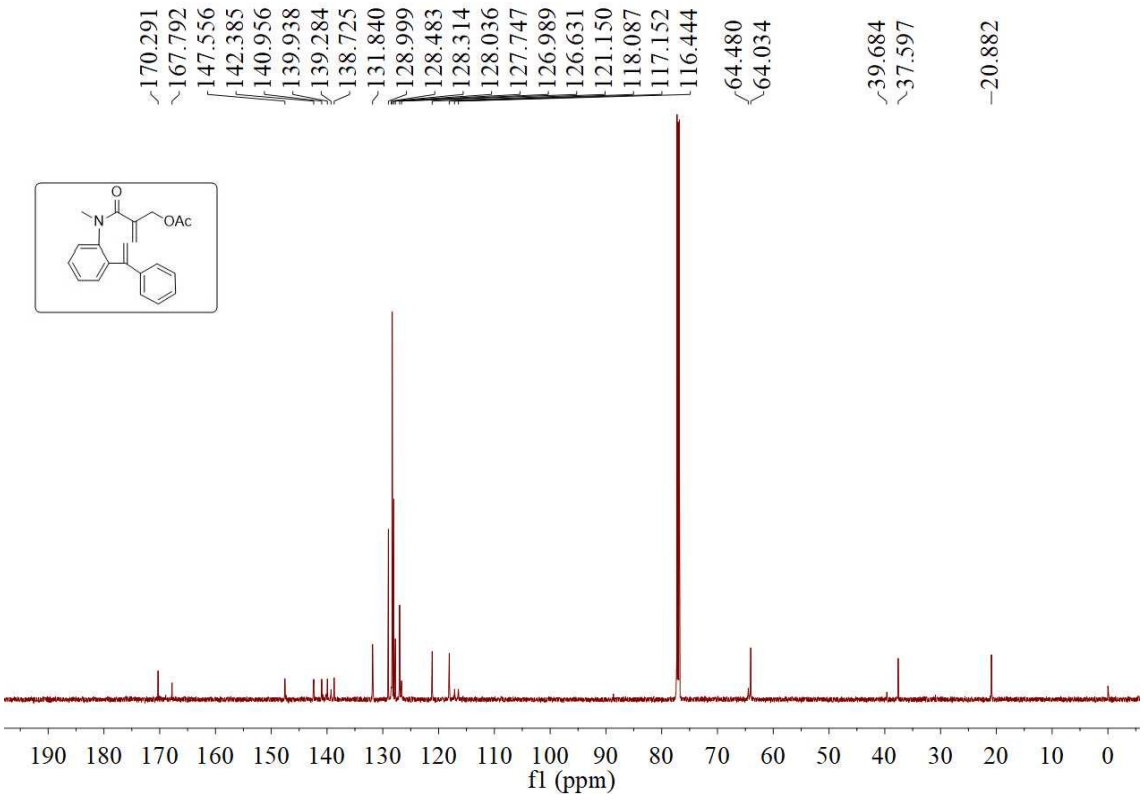
^{13}C-NMR Spectra of 3l



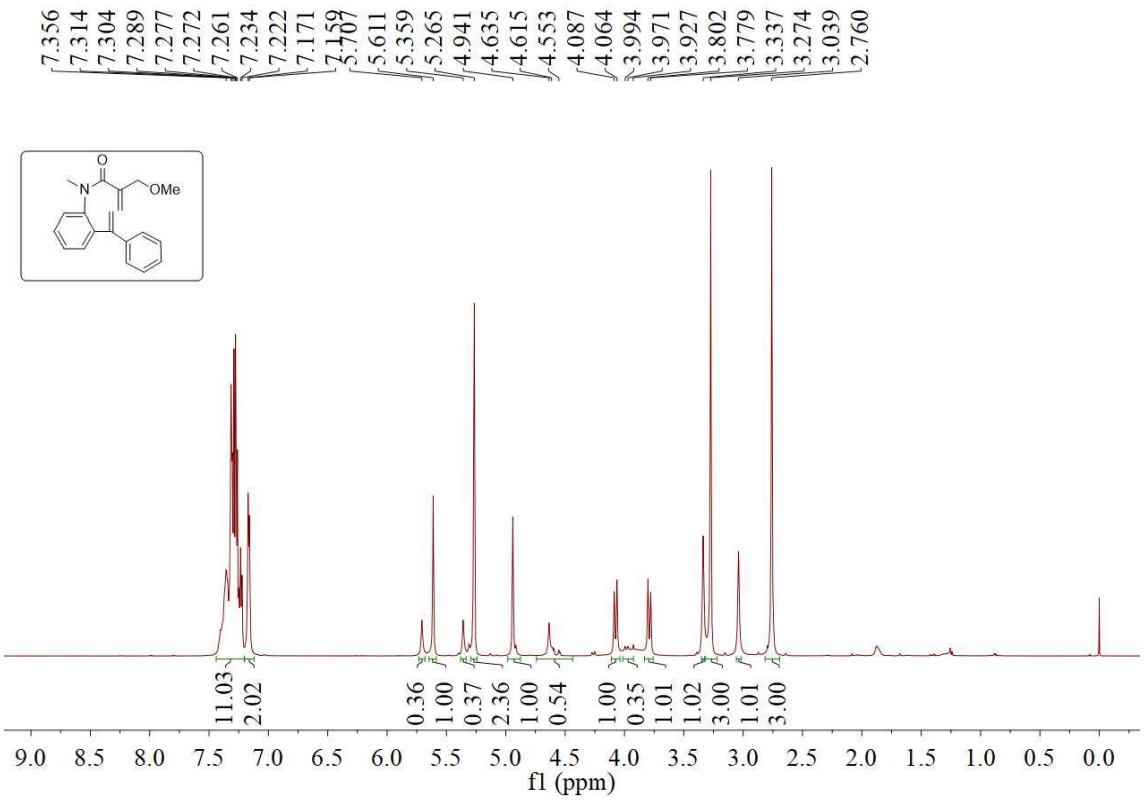
[1]H-NMR Spectra of 3m



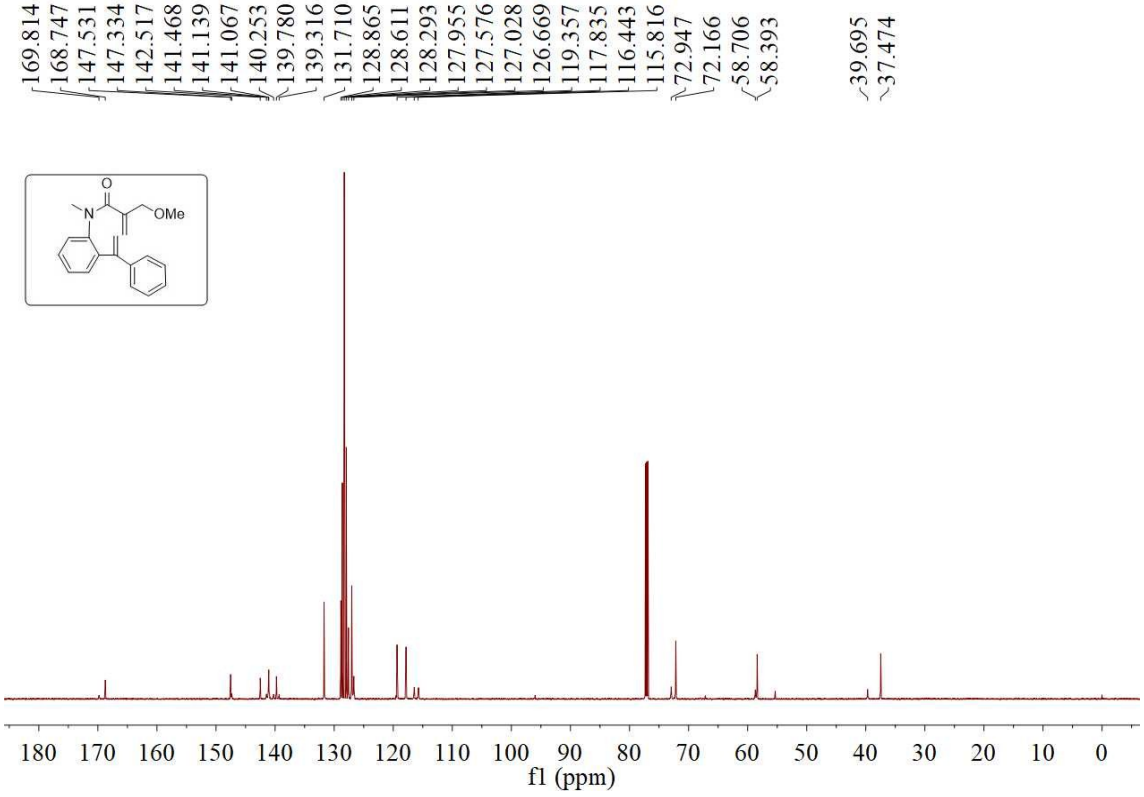
[13]C-NMR Spectra of 3m



[1]H-NMR Spectra of 3n

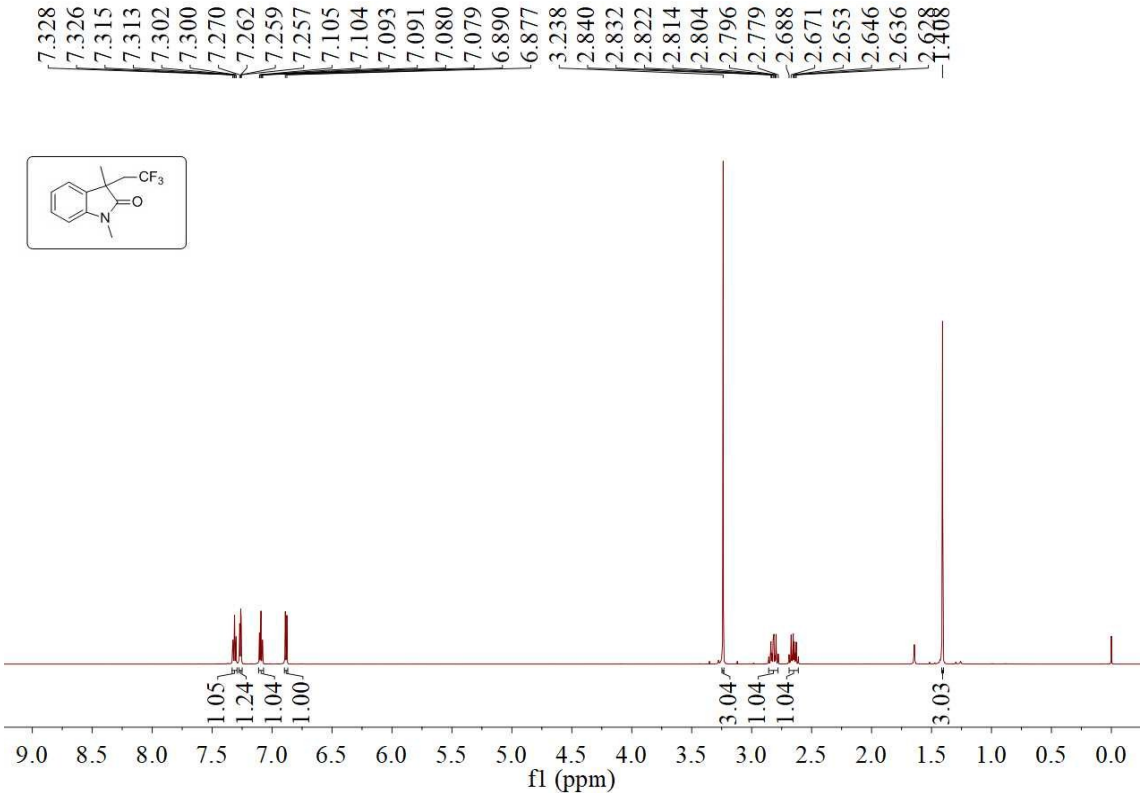


[13]C-NMR Spectra of 3n

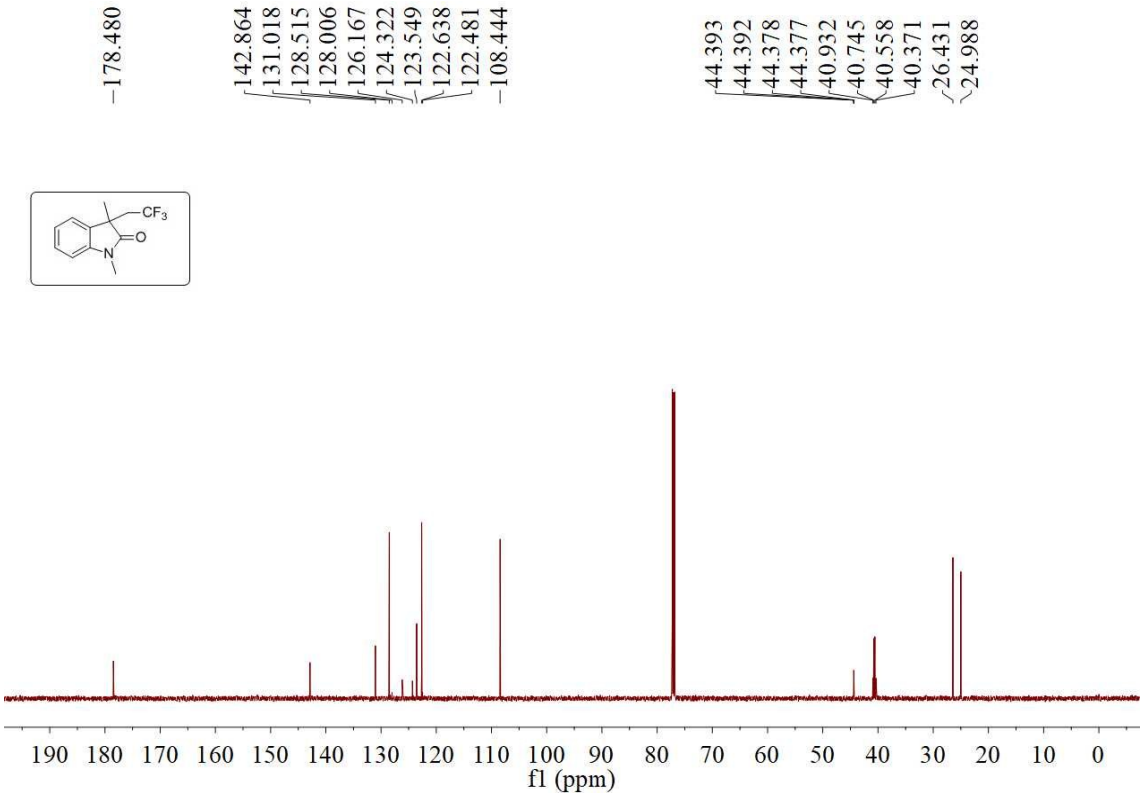


2. NMR Spectra of Products

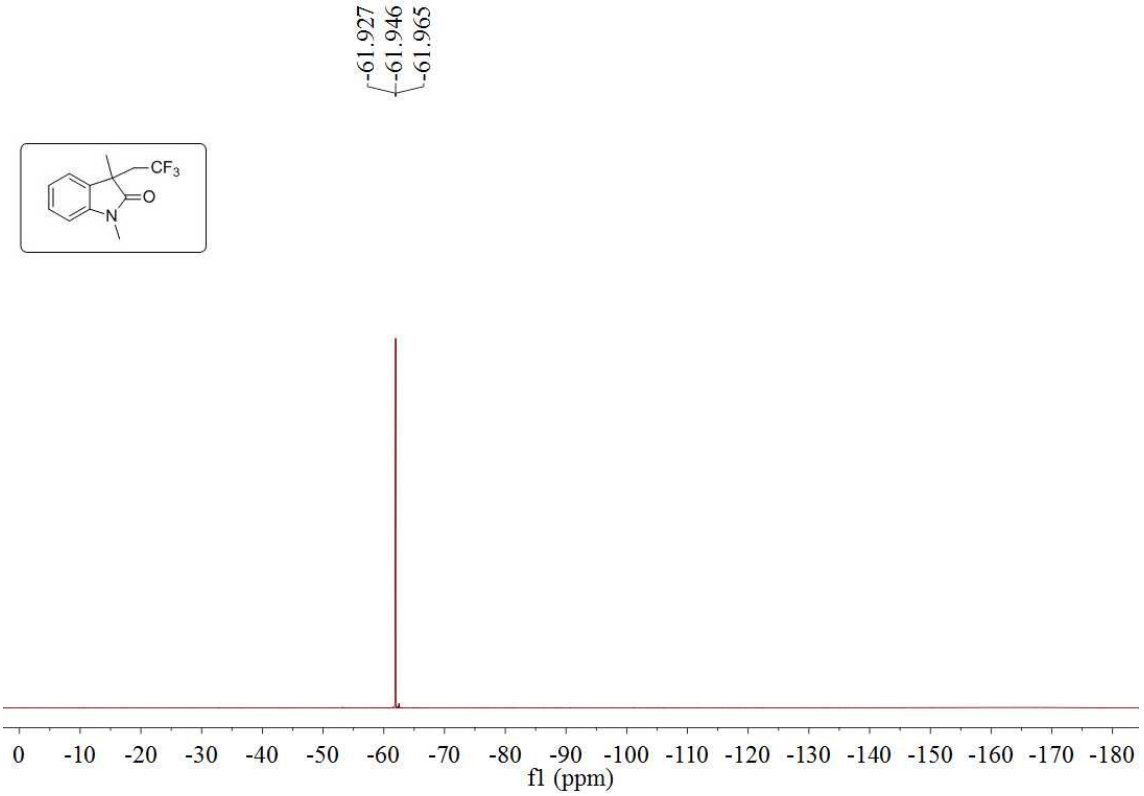
^{1}H-NMR Spectra of 2a



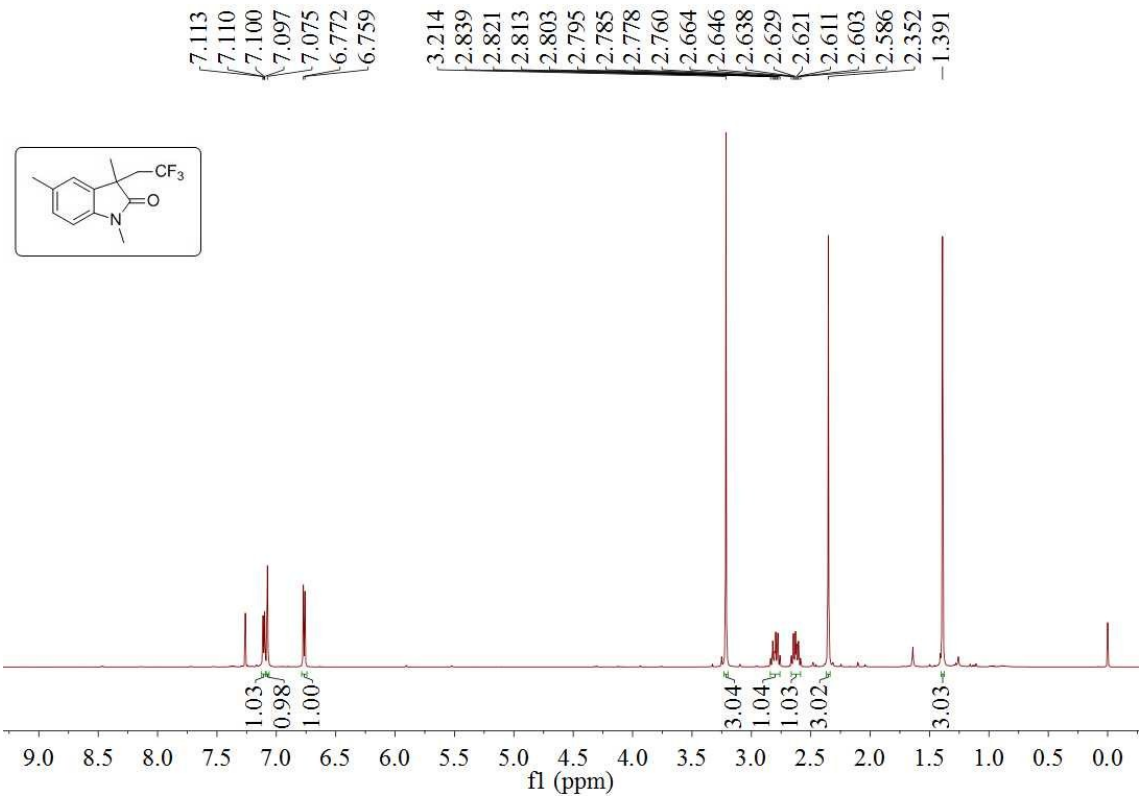
^{13}C-NMR Spectra of 2a



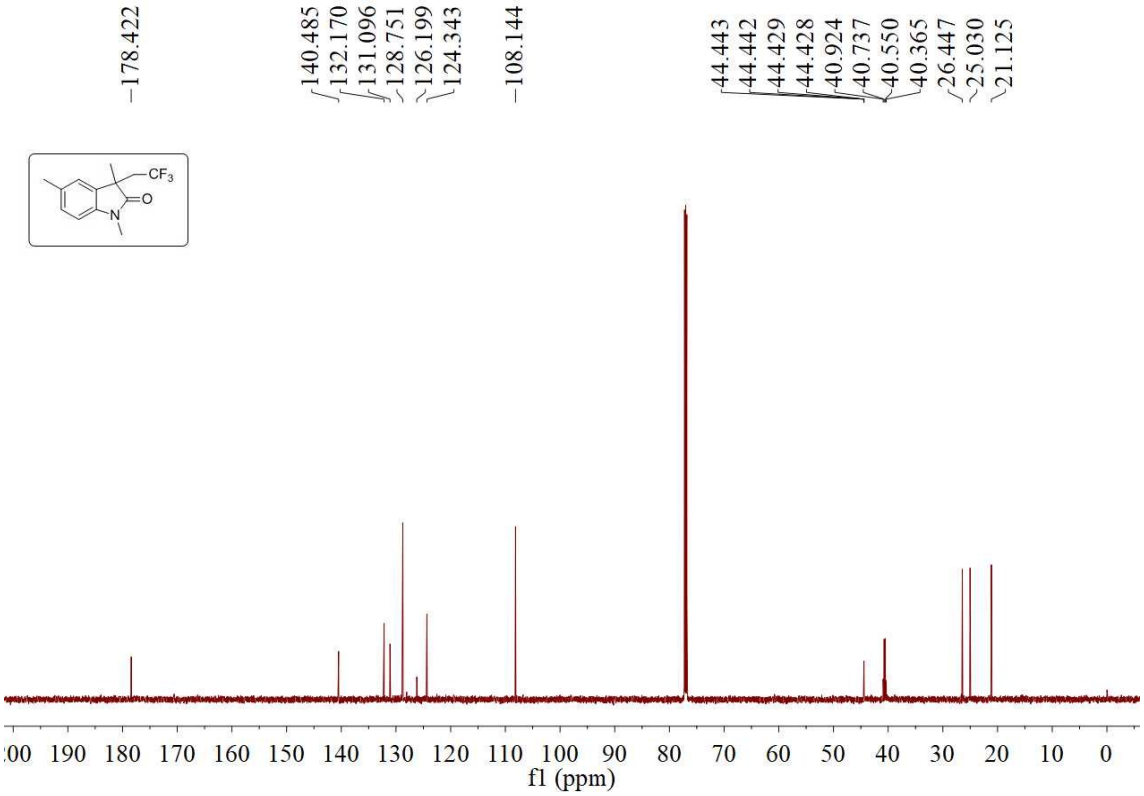
^{19}F-NMR Spectra of 2a



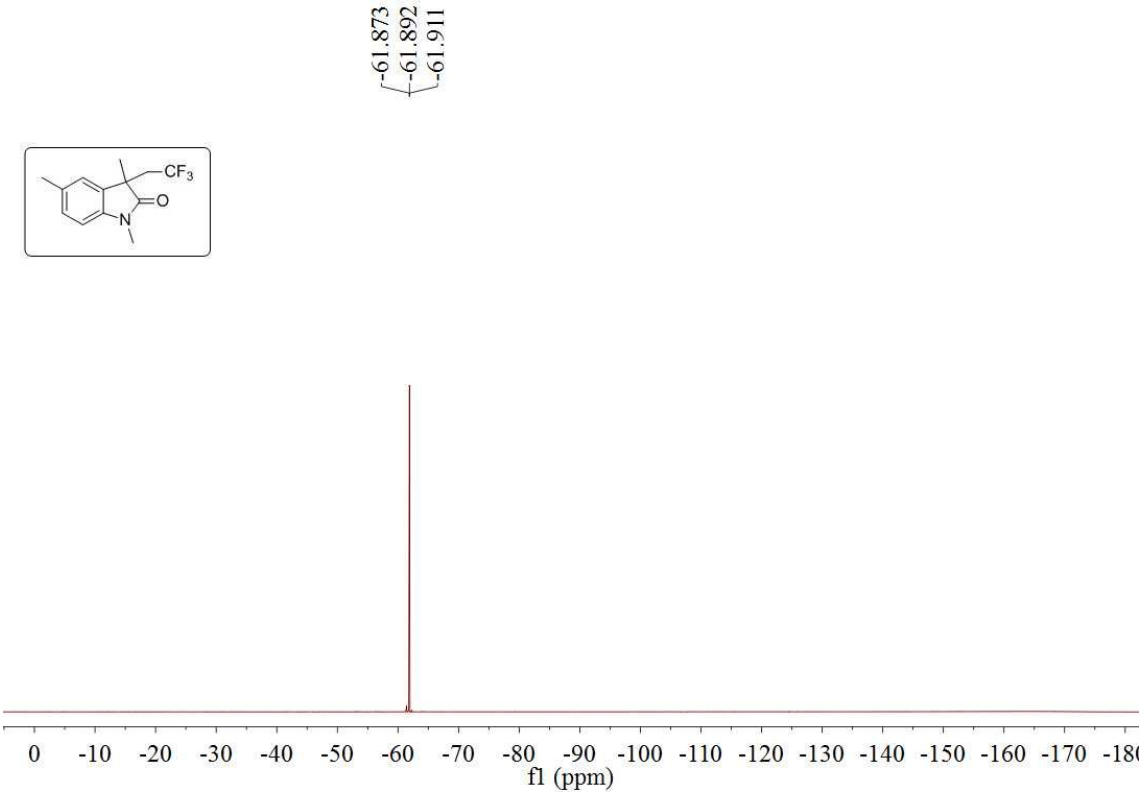
^{1}H-NMR Spectra of 2b



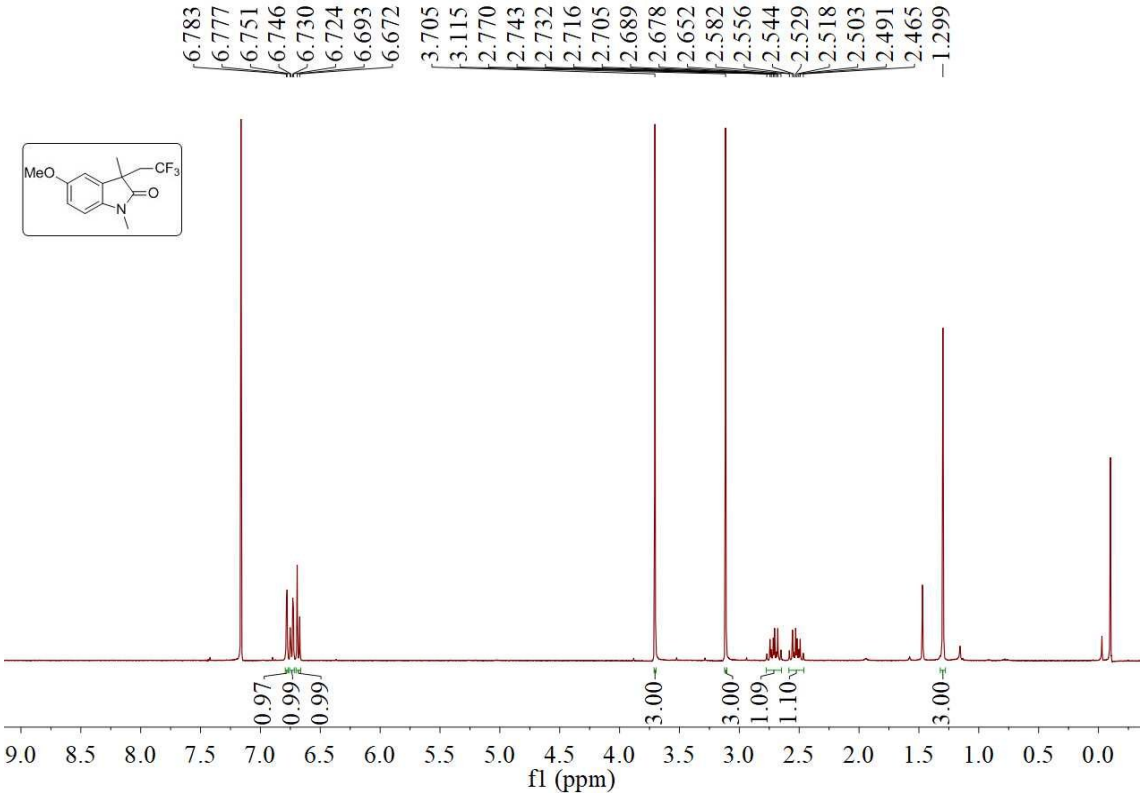
^{13}C-NMR Spectra of 2b



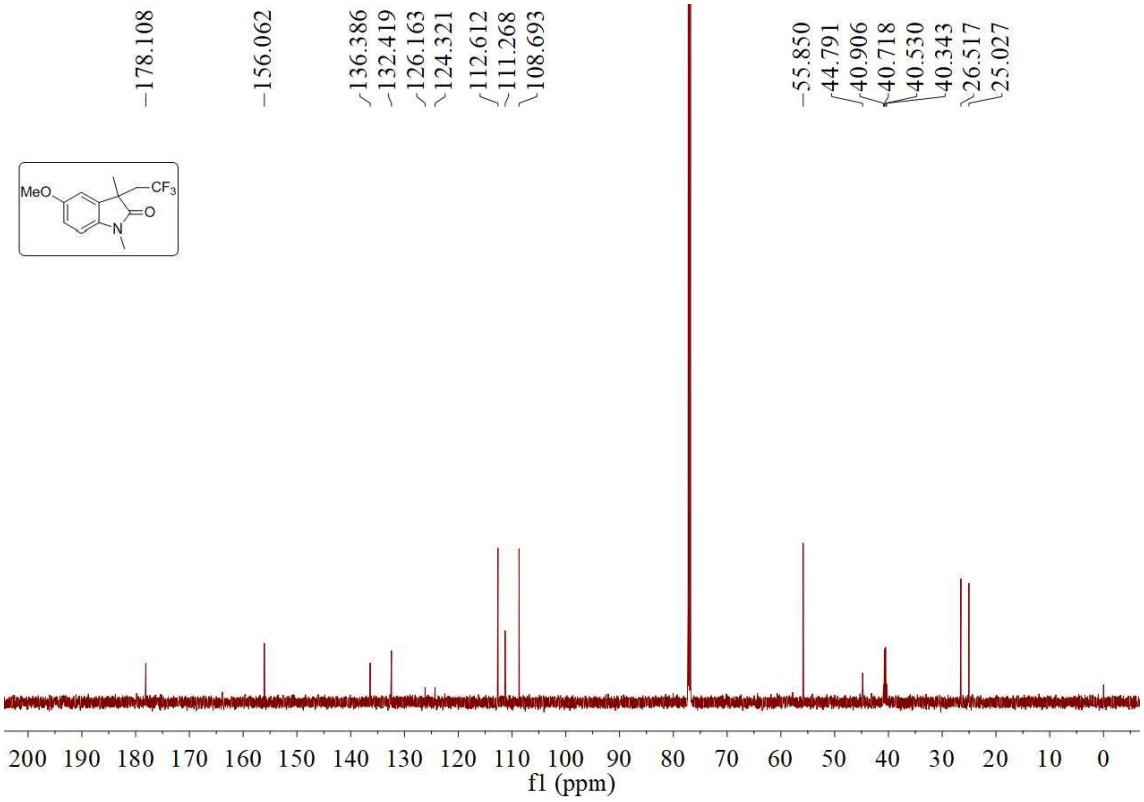
^{19}F-NMR Spectra of 2b



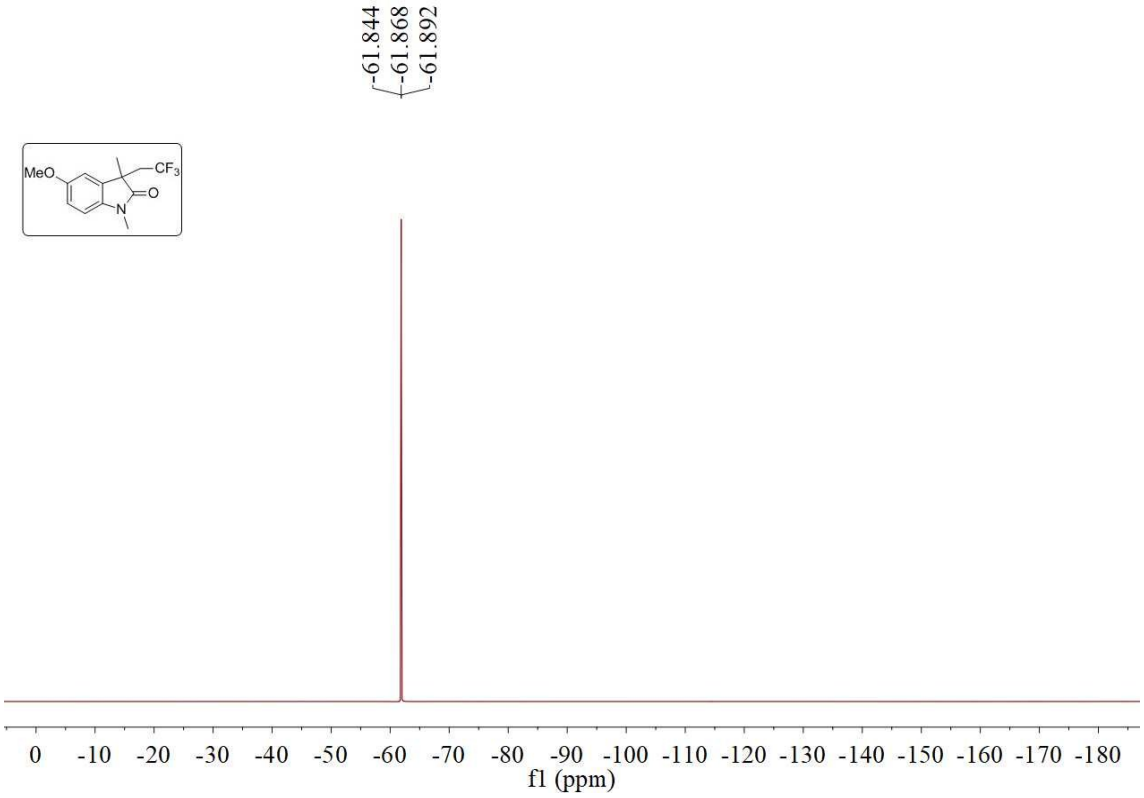
^{1}H-NMR Spectra of 2c



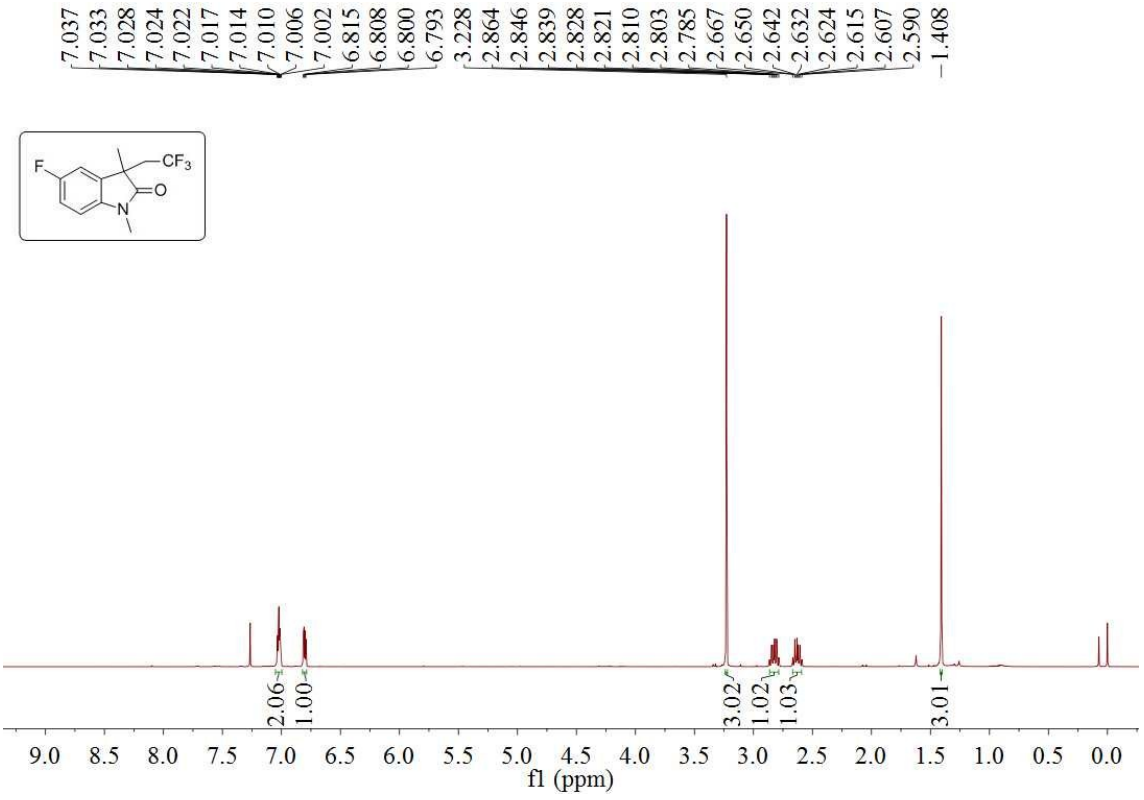
^{13}C-NMR Spectra of 2c



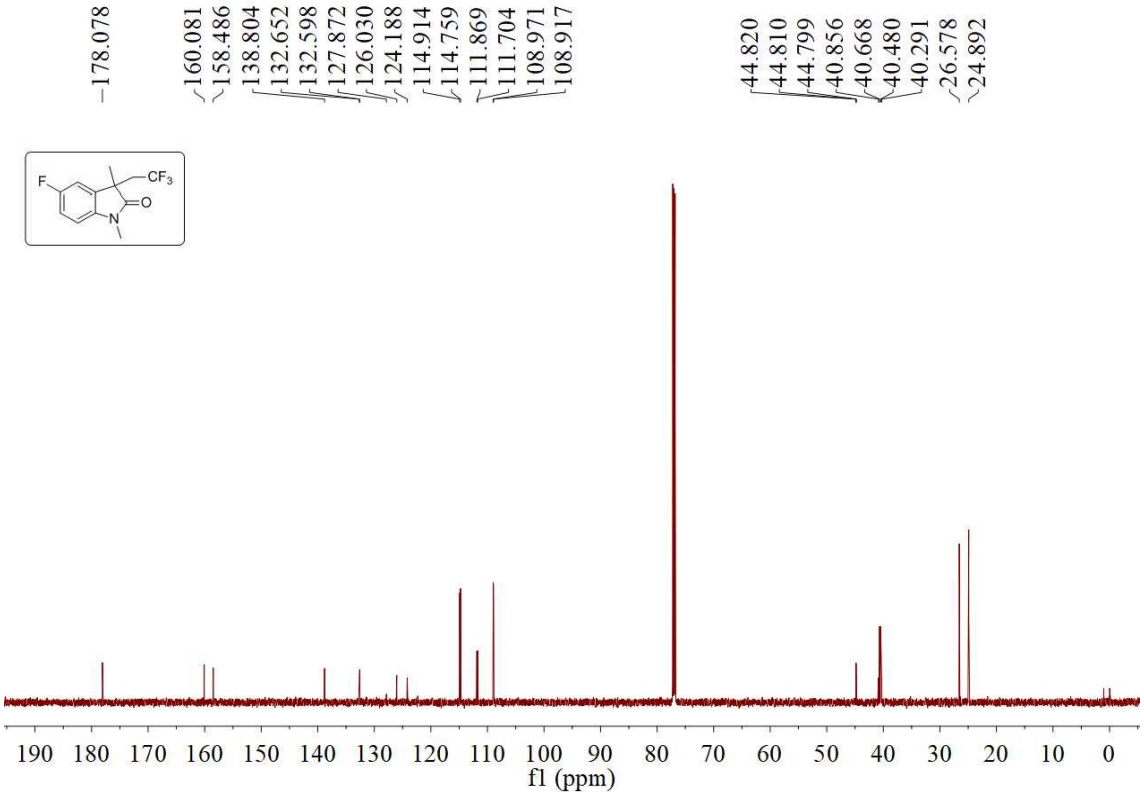
^{19}F-NMR Spectra of 2c



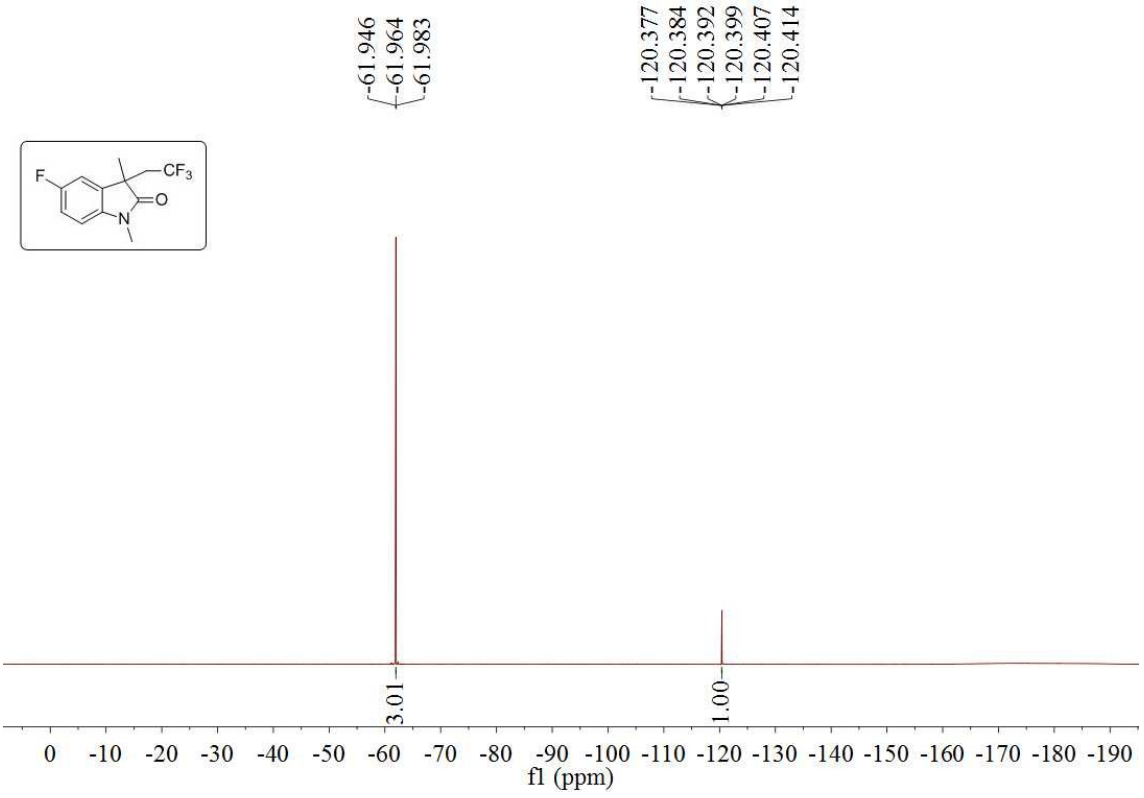
^{1}H-NMR Spectra of 2d



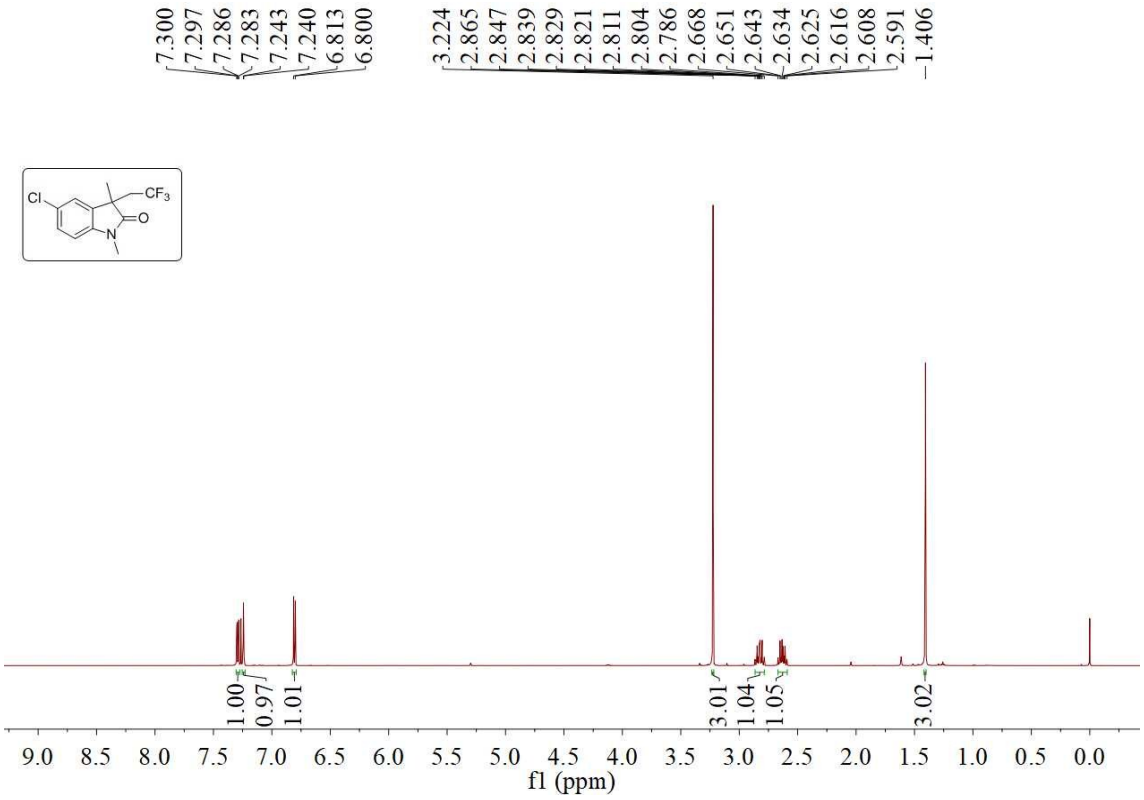
^{13}C-NMR Spectra of 2d



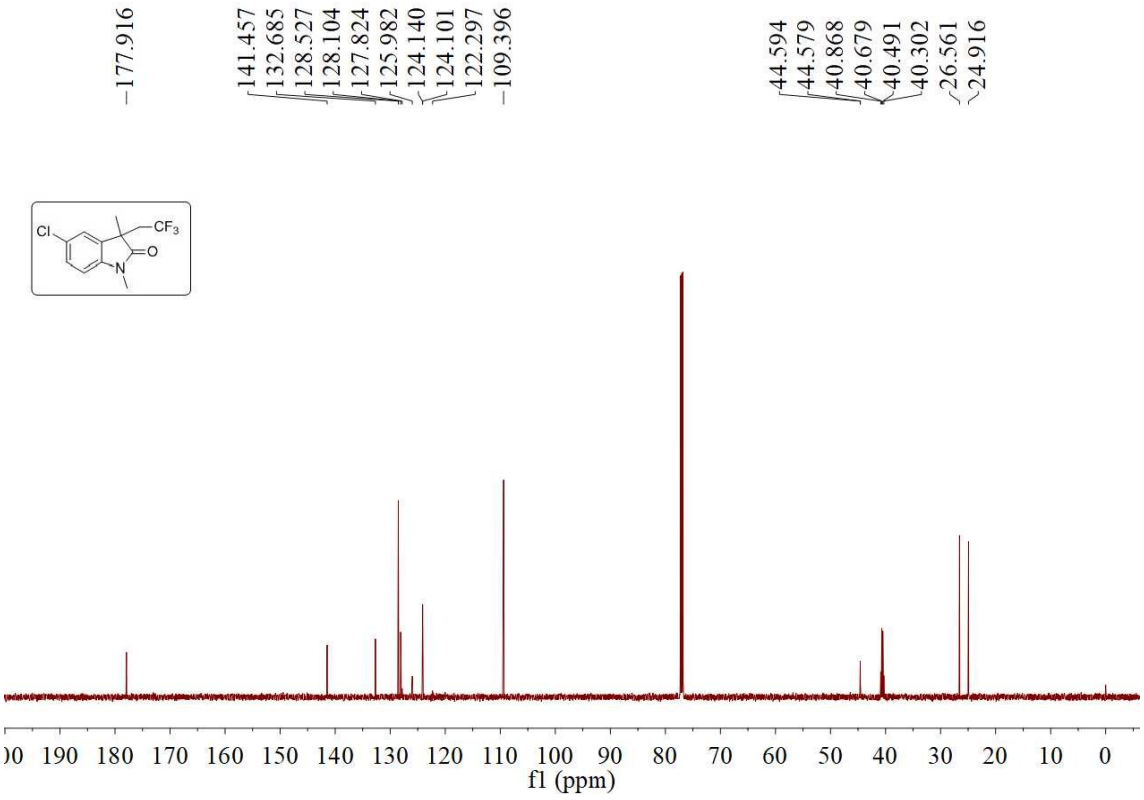
^{19}F-NMR Spectra of 2d



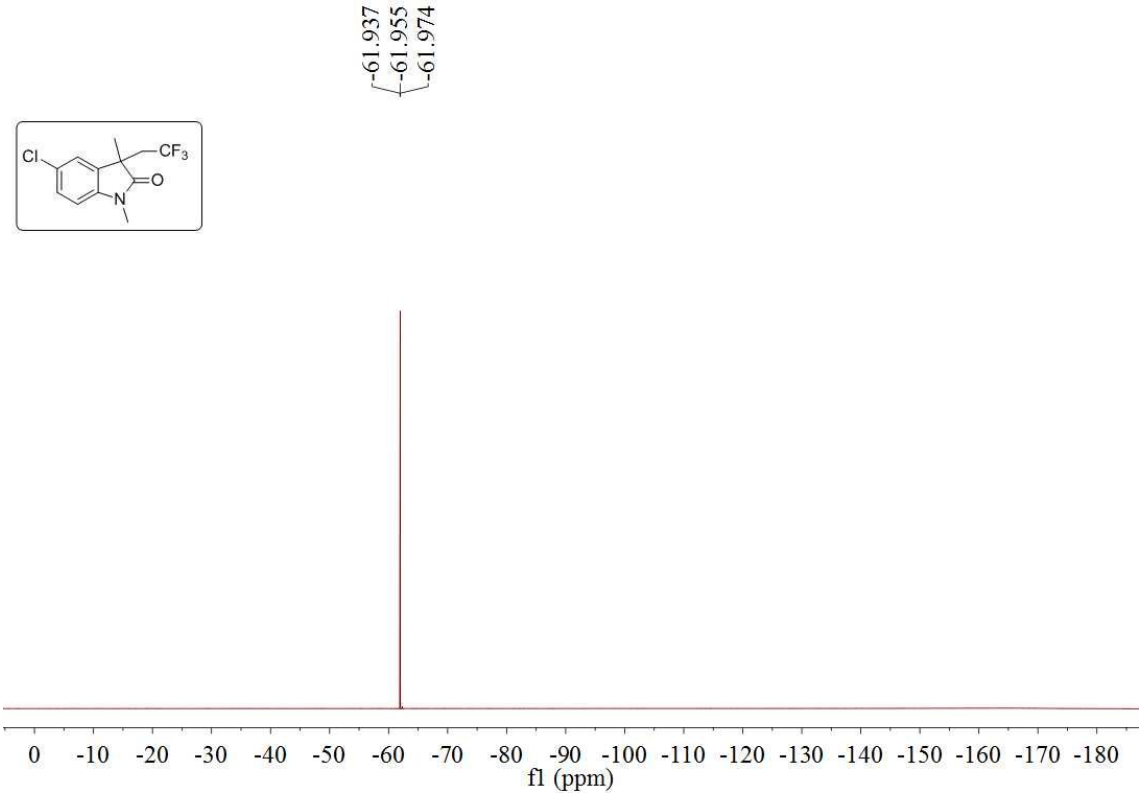
[1]H-NMR Spectra of 2e



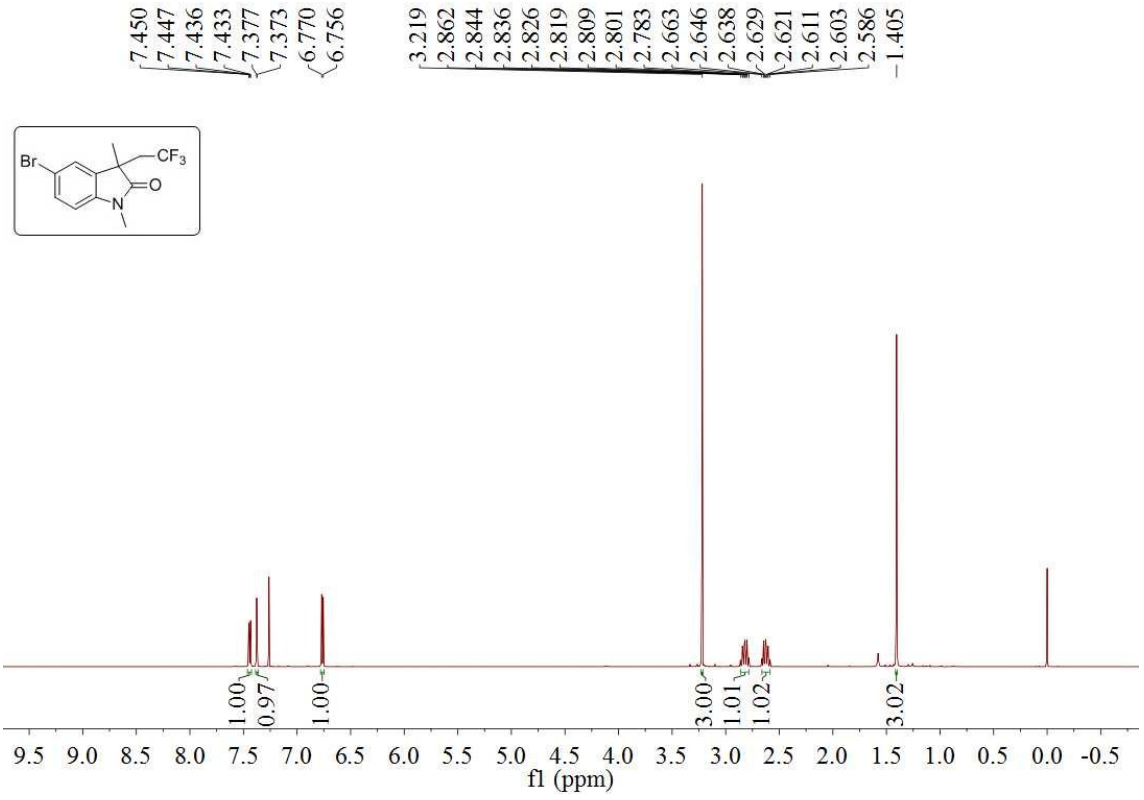
[13]C-NMR Spectra of 2e



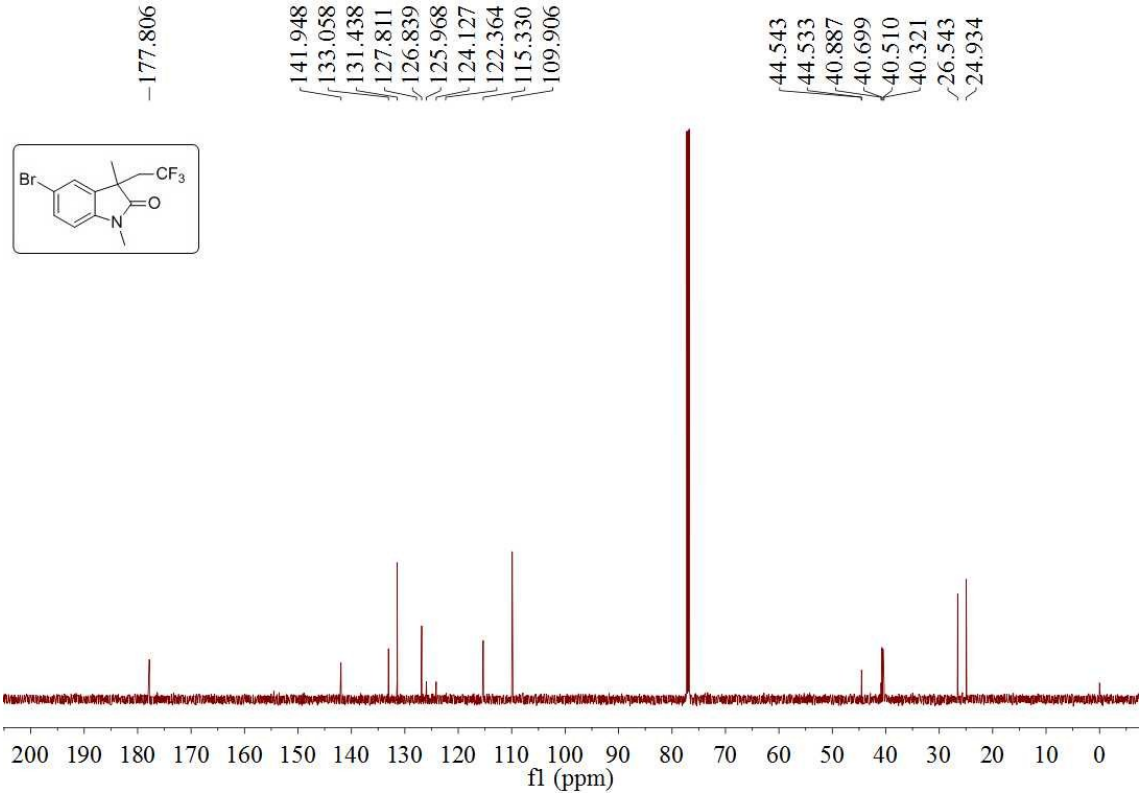
^{19}F-NMR Spectra of 2e



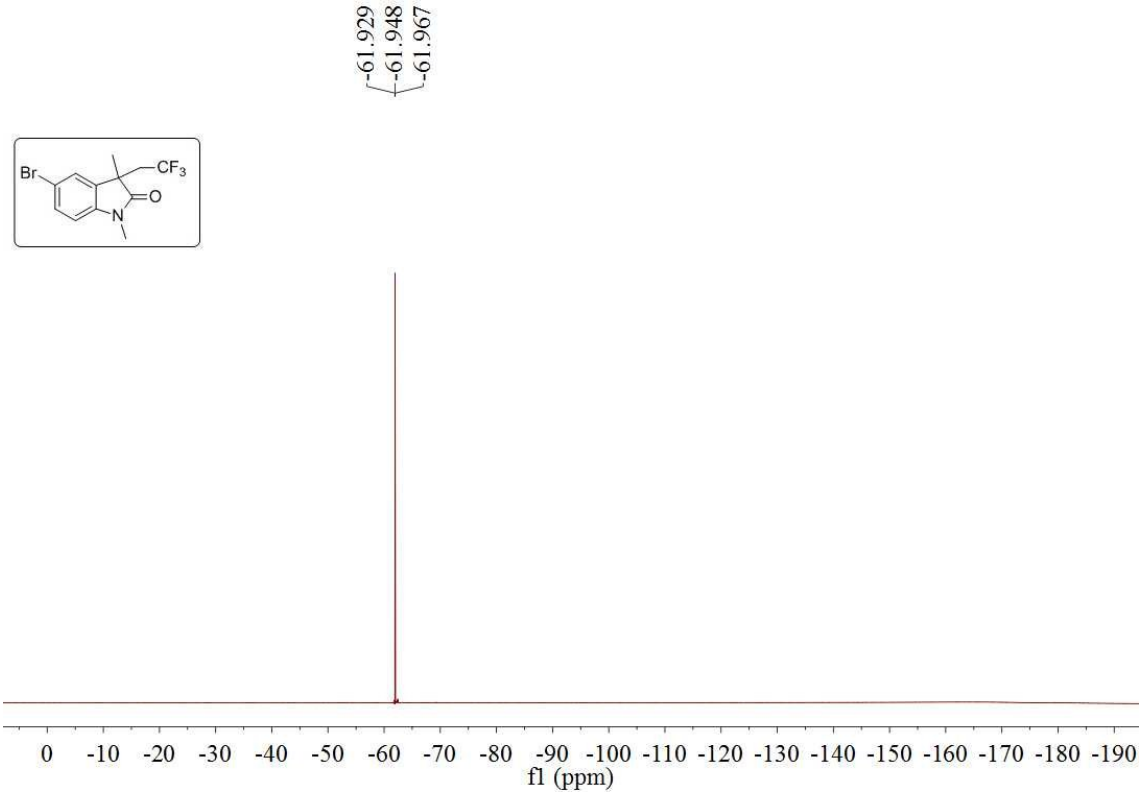
^{1}H-NMR Spectra of 2f



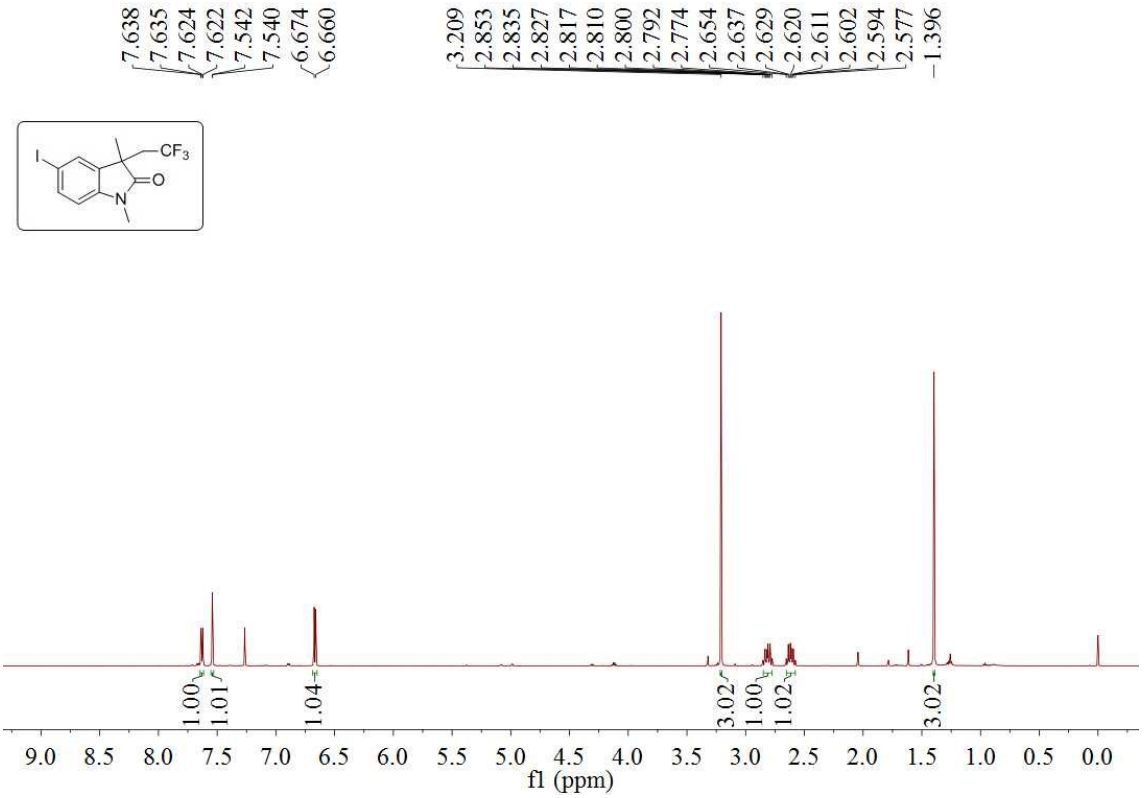
^{13}C-NMR Spectra of 2f



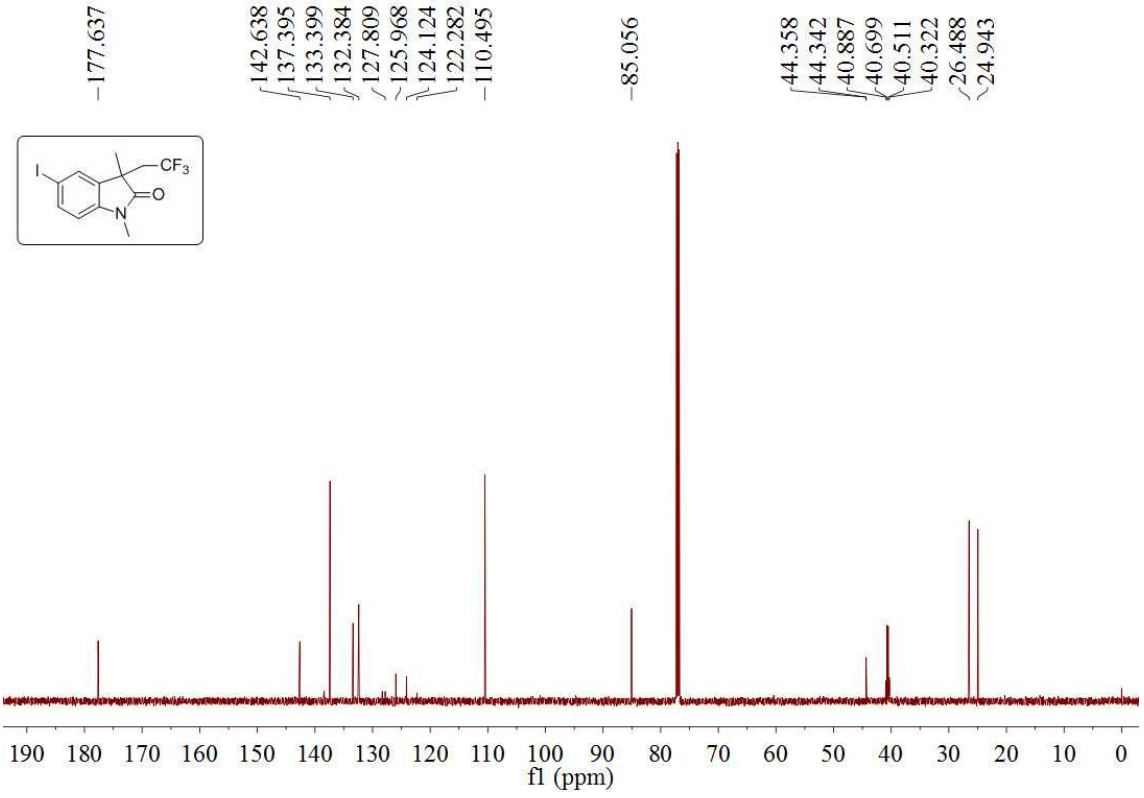
^{19}F-NMR Spectra of 2f



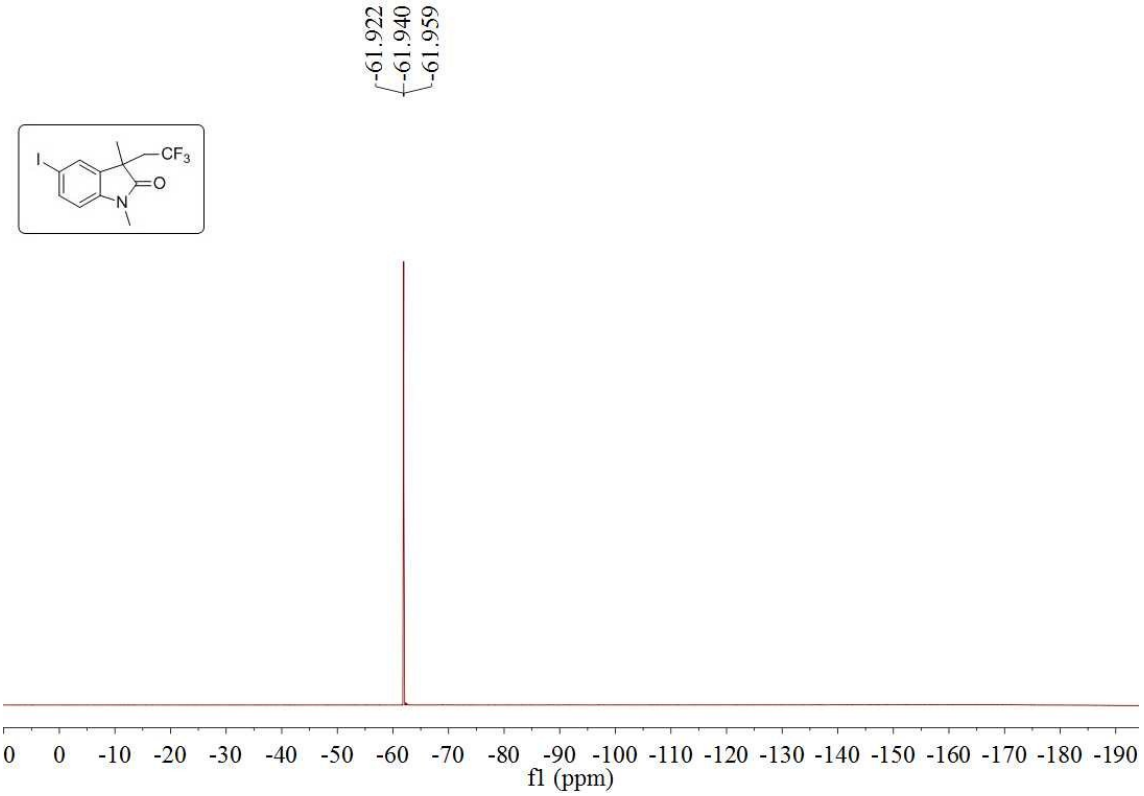
[1]H-NMR Spectra of 2g



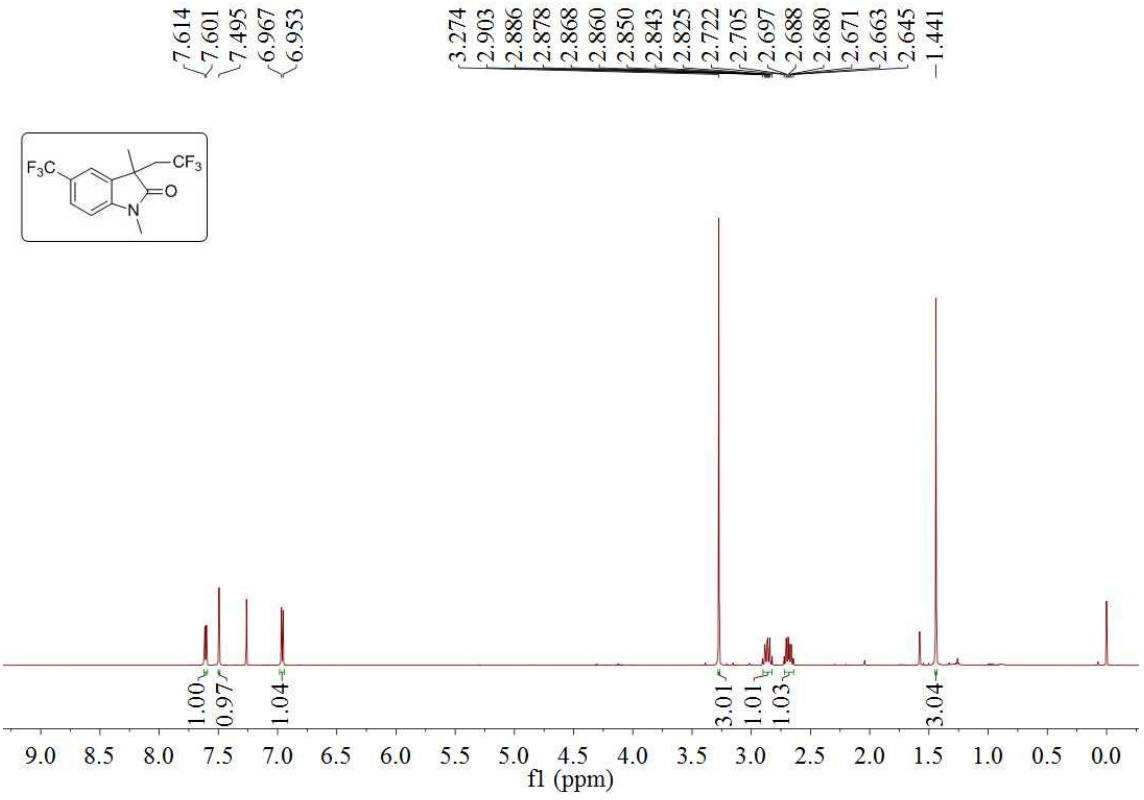
[13]C-NMR Spectra of 2g



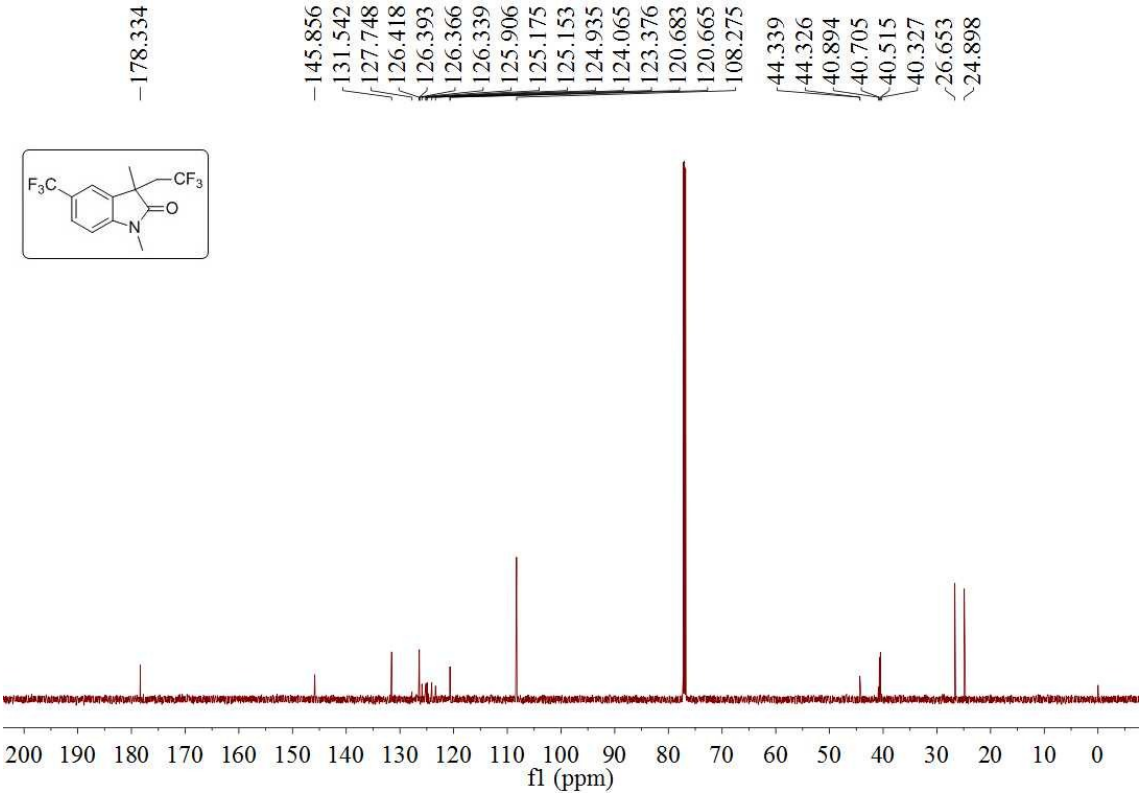
^{19}F-NMR Spectra of 2g



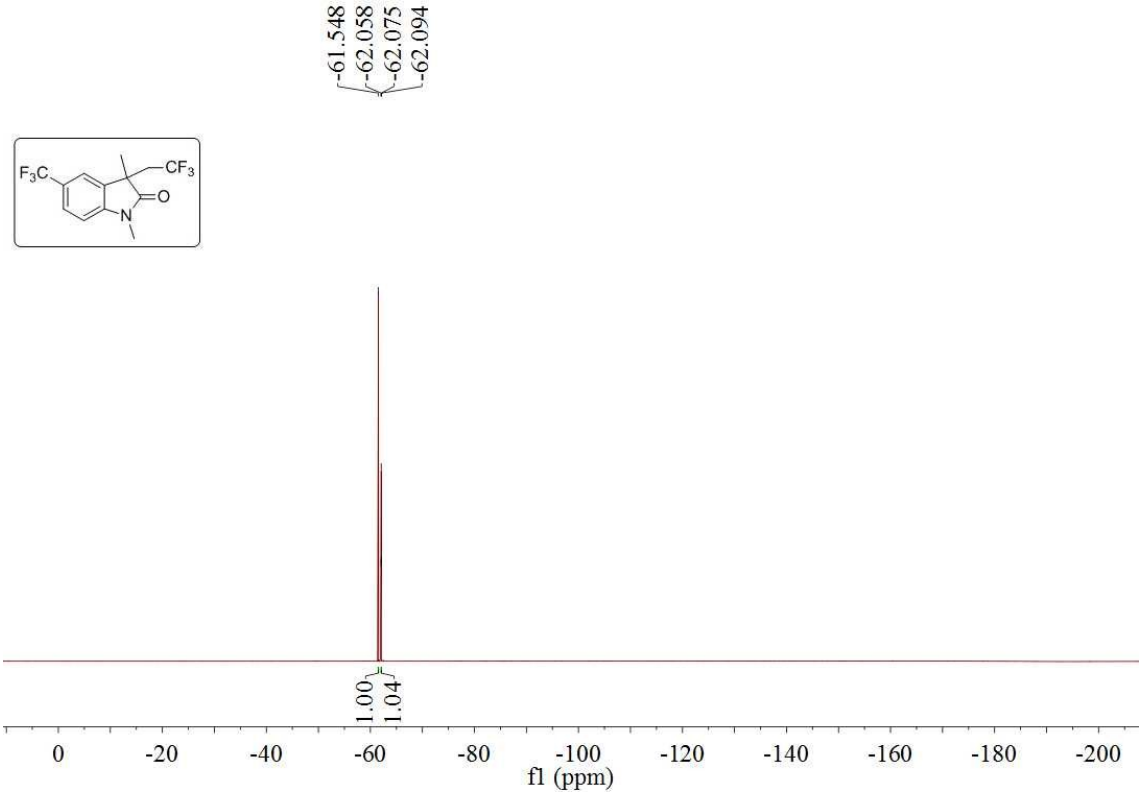
^{1}H-NMR Spectra of 2h



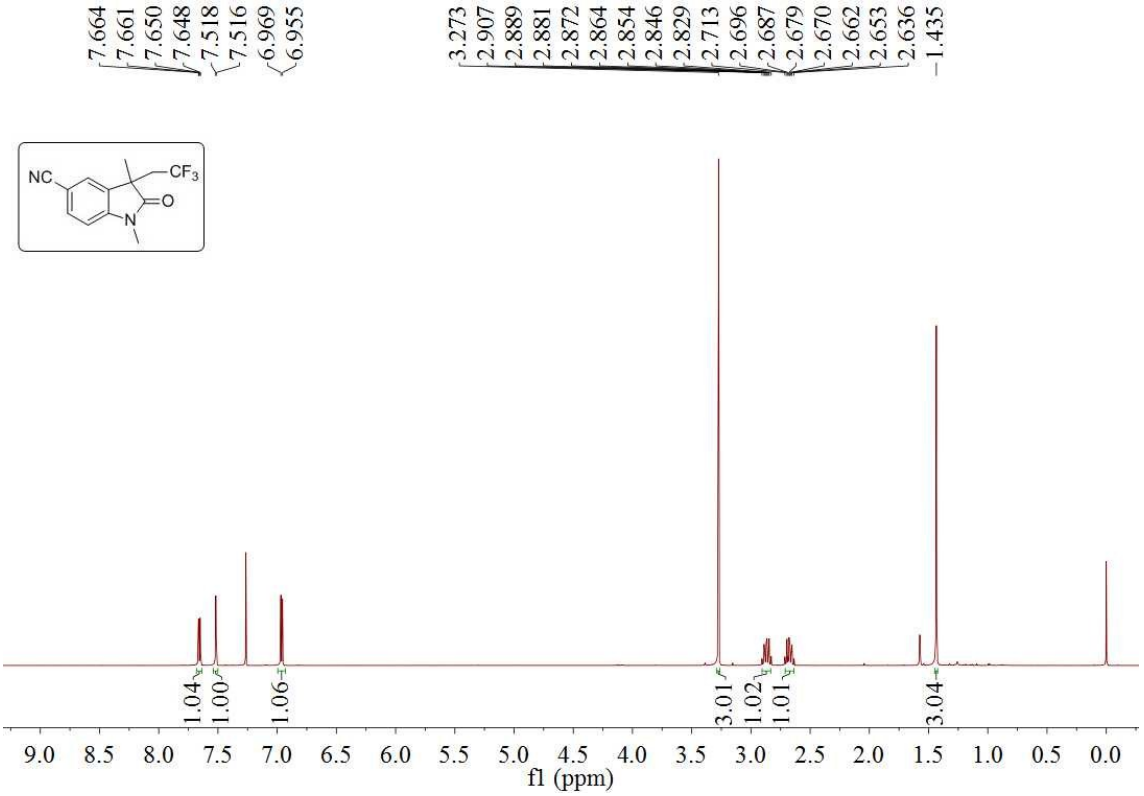
^{13}C-NMR Spectra of 2h



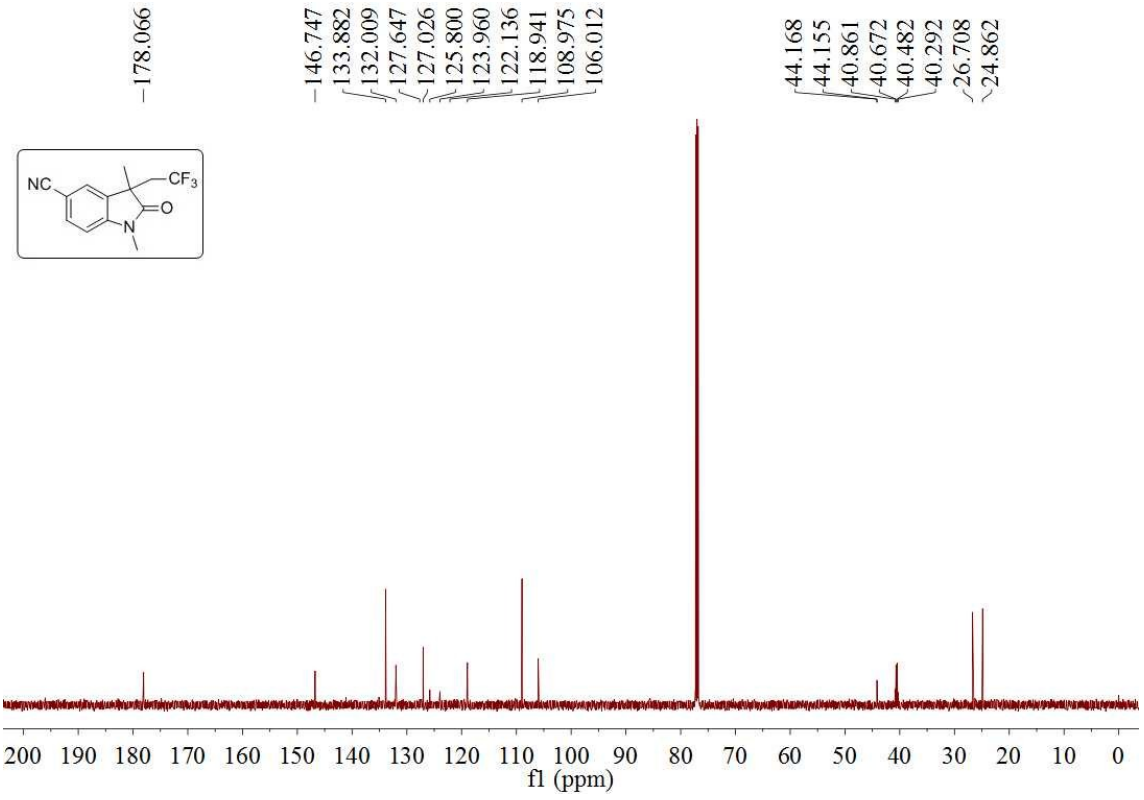
^{19}F-NMR Spectra of 2h



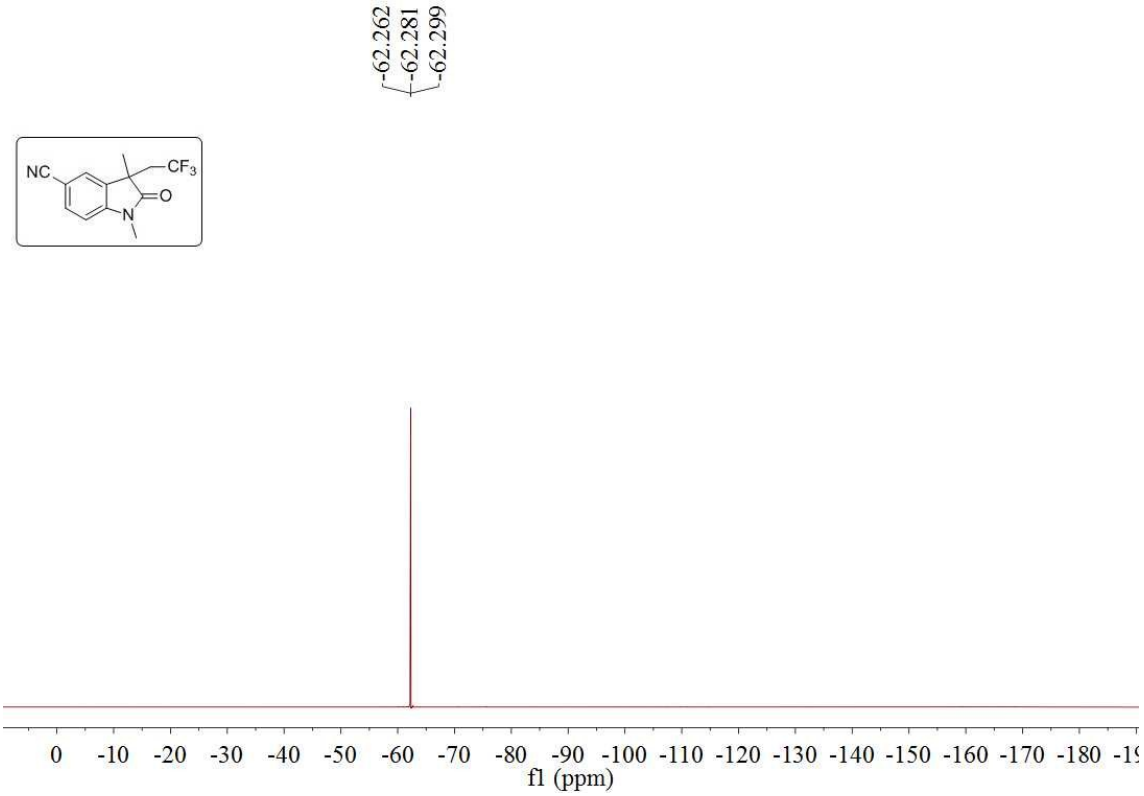
[1]H-NMR Spectra of 2i



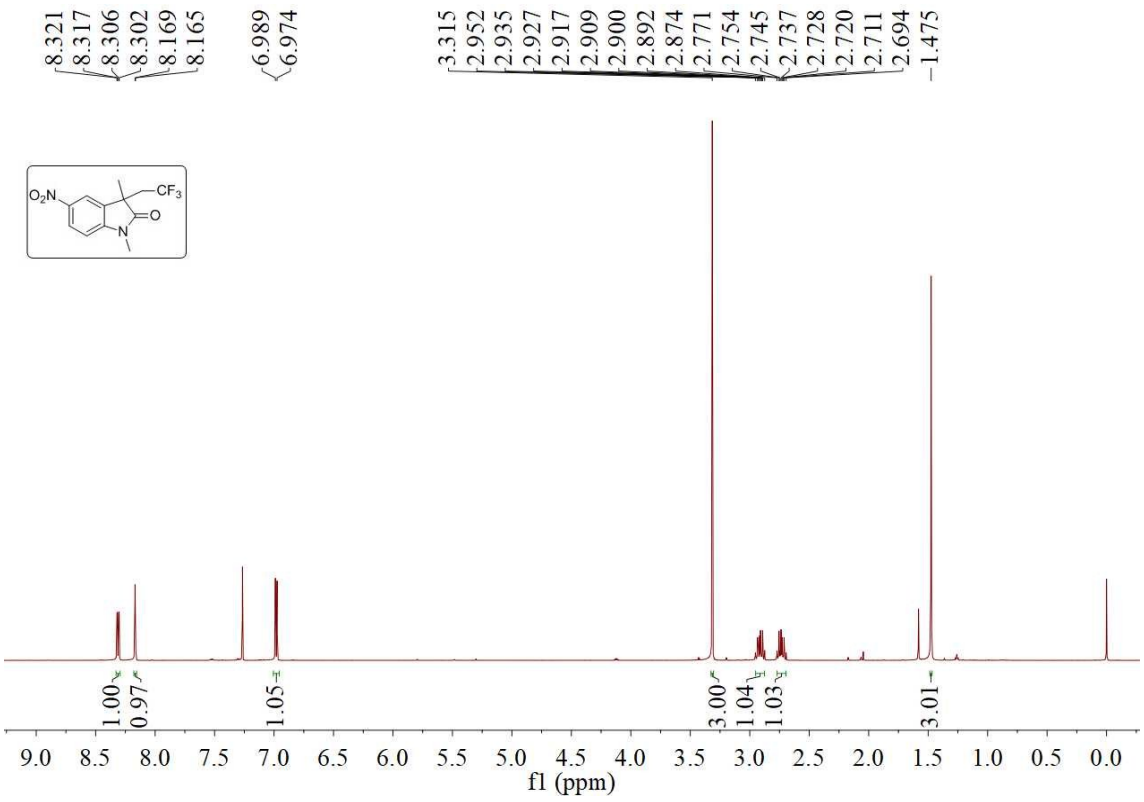
[13]C-NMR Spectra of 2i



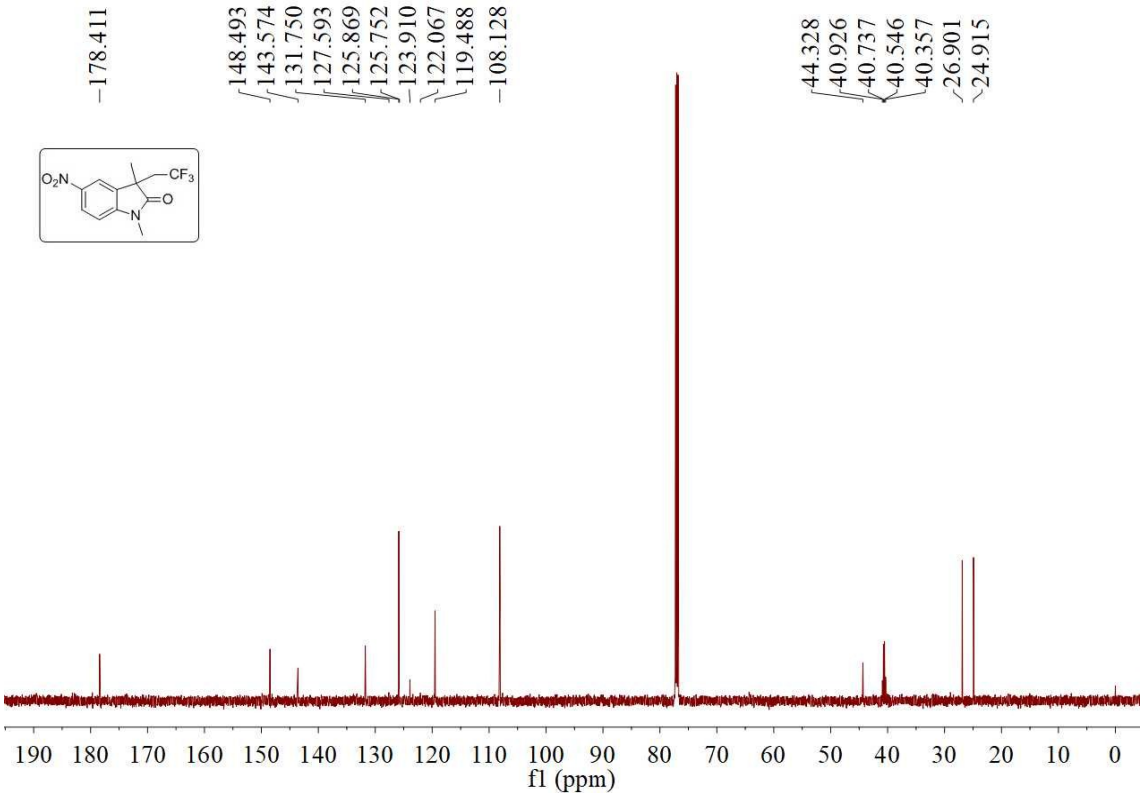
^{19}F-NMR Spectra of 2i



^{1}H-NMR Spectra of 2j



^{13}C-NMR Spectra of 2j



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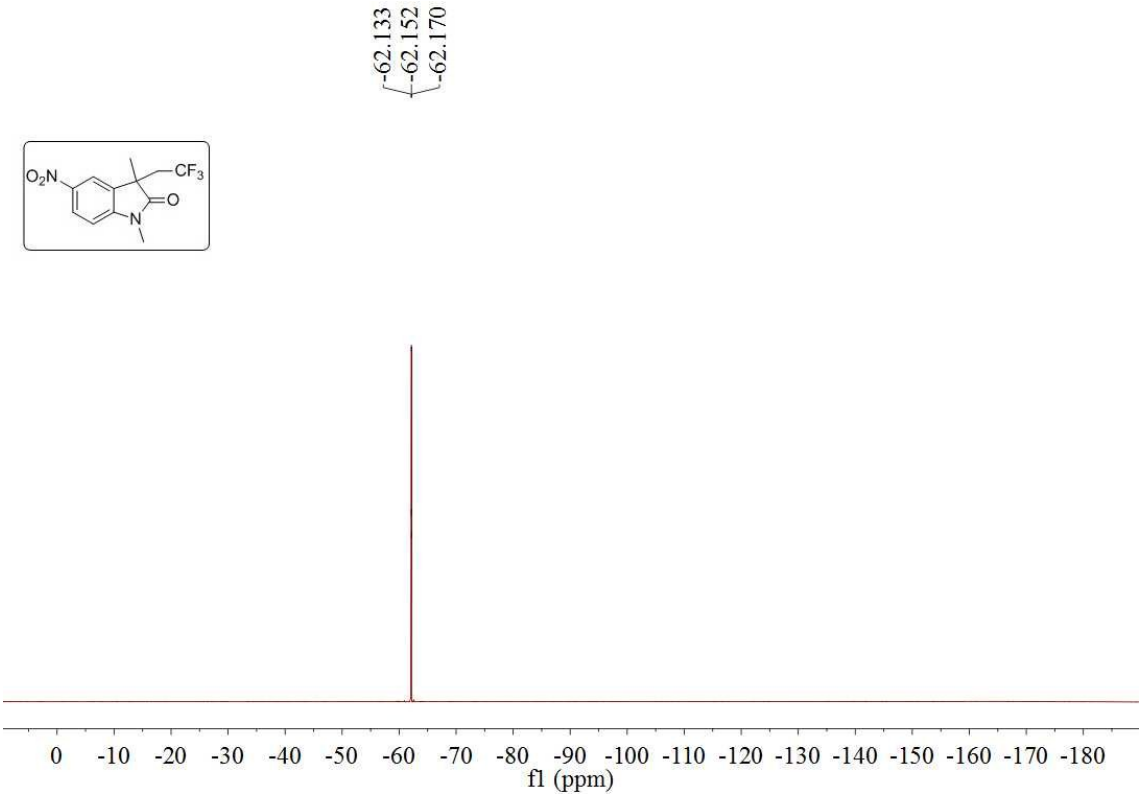
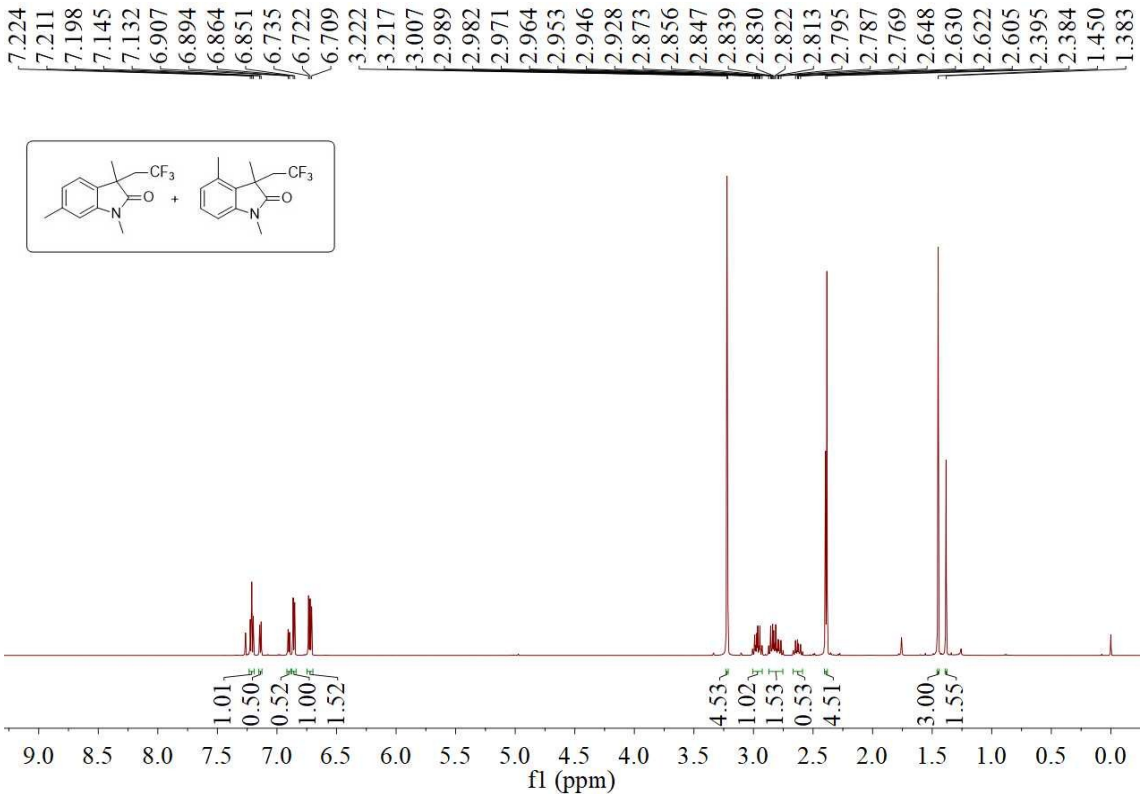
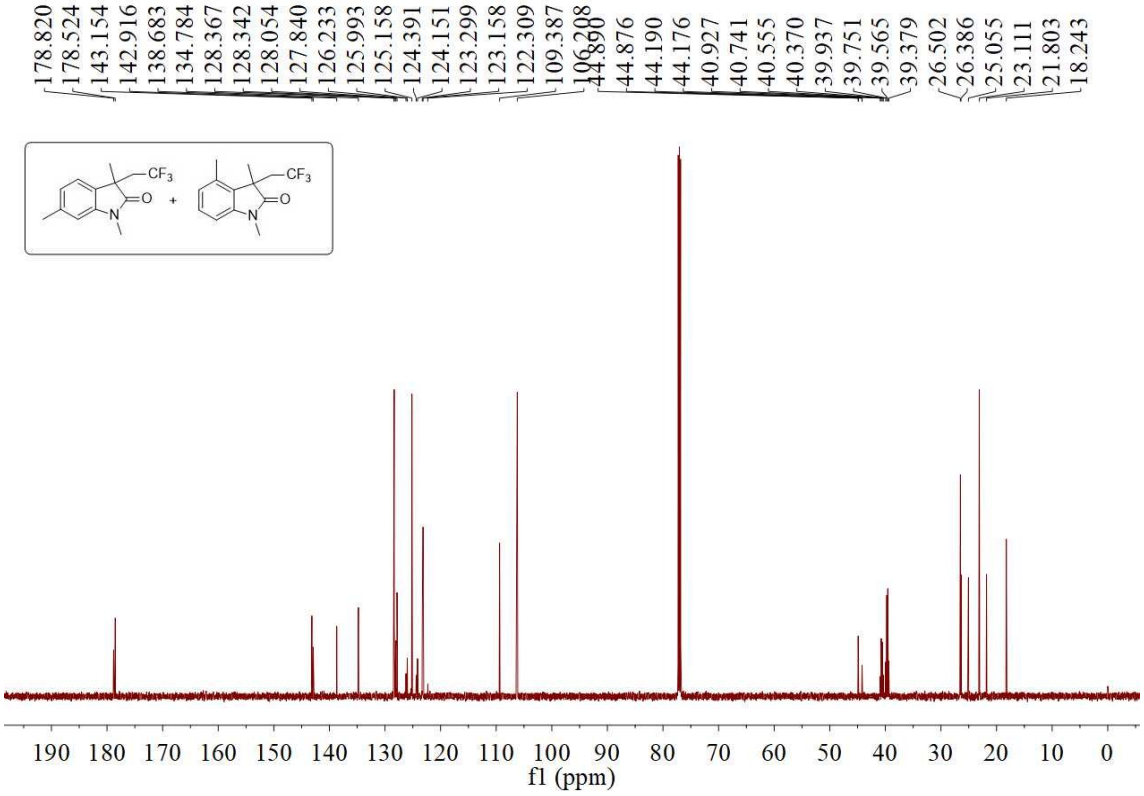


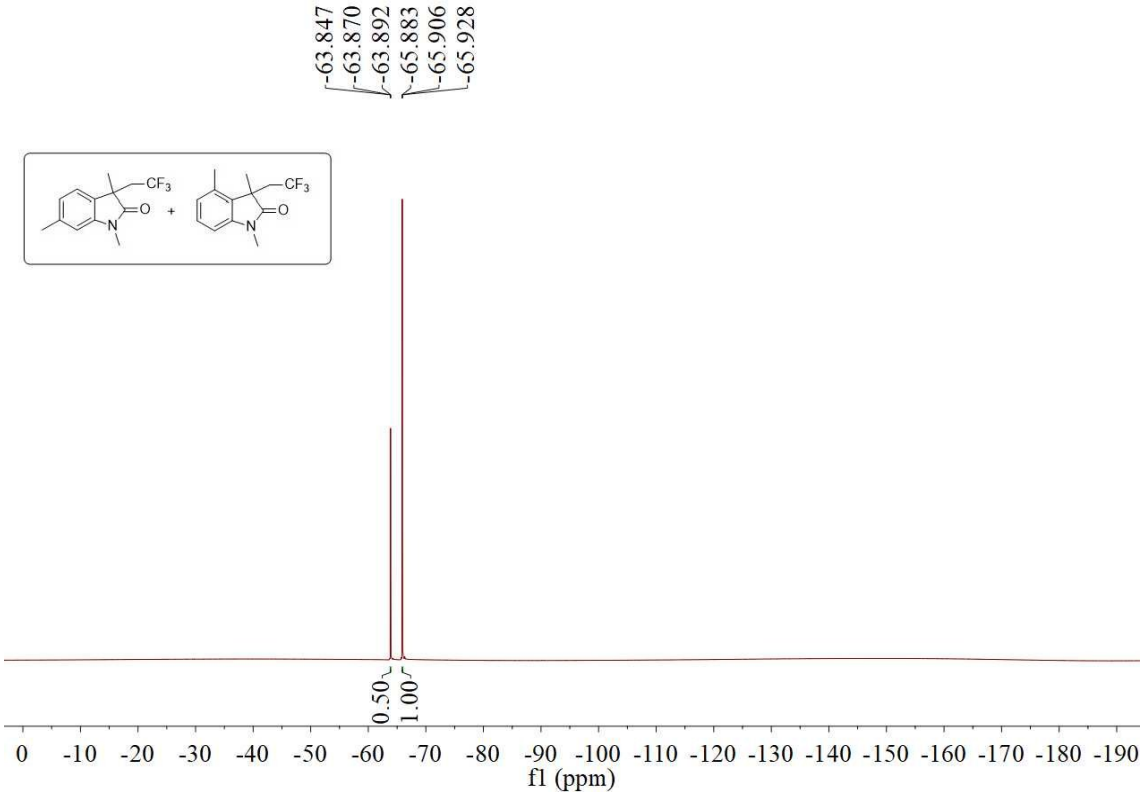
^{1}H-NMR Spectra of 2k



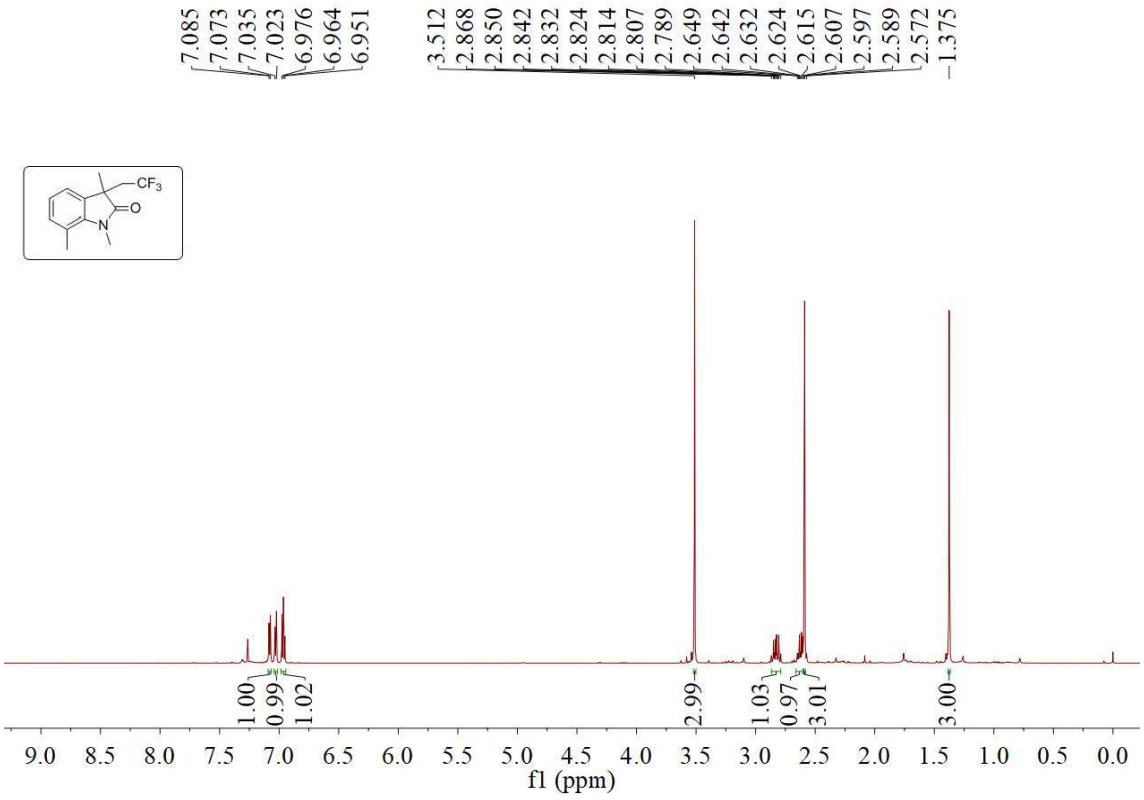
^{13}C-NMR Spectra of 2k



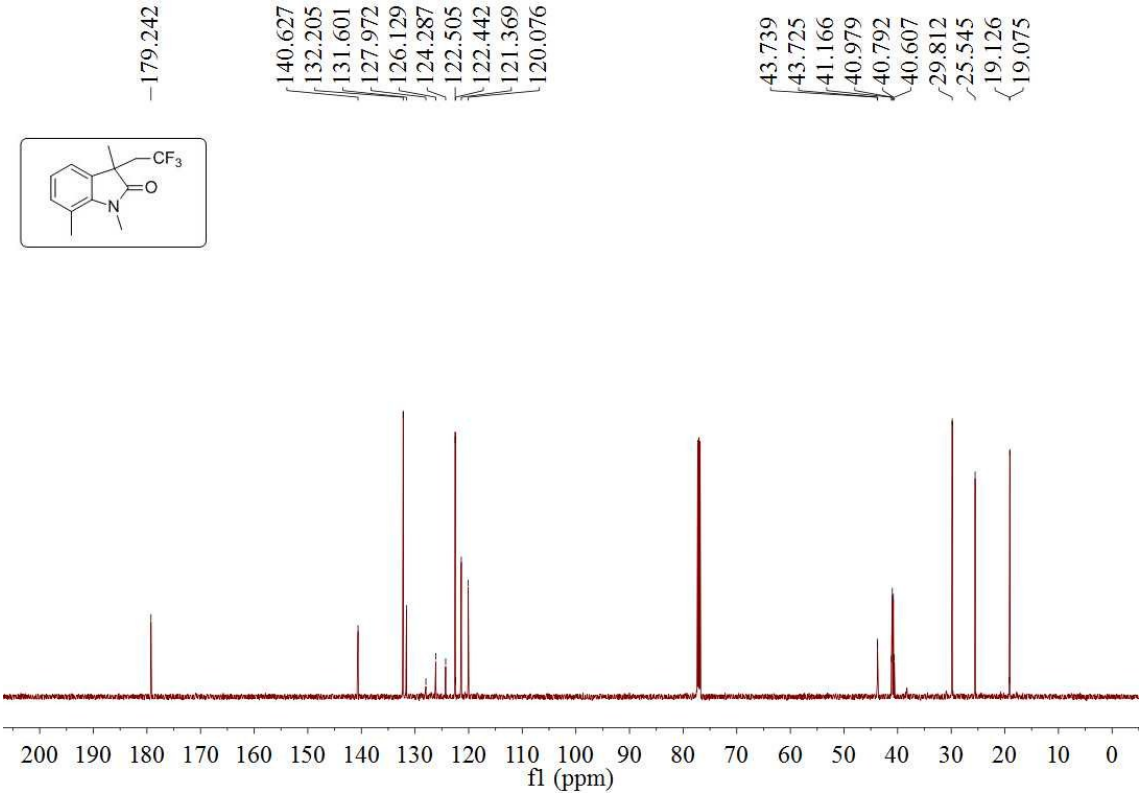
^{19}F-NMR Spectra of 2k



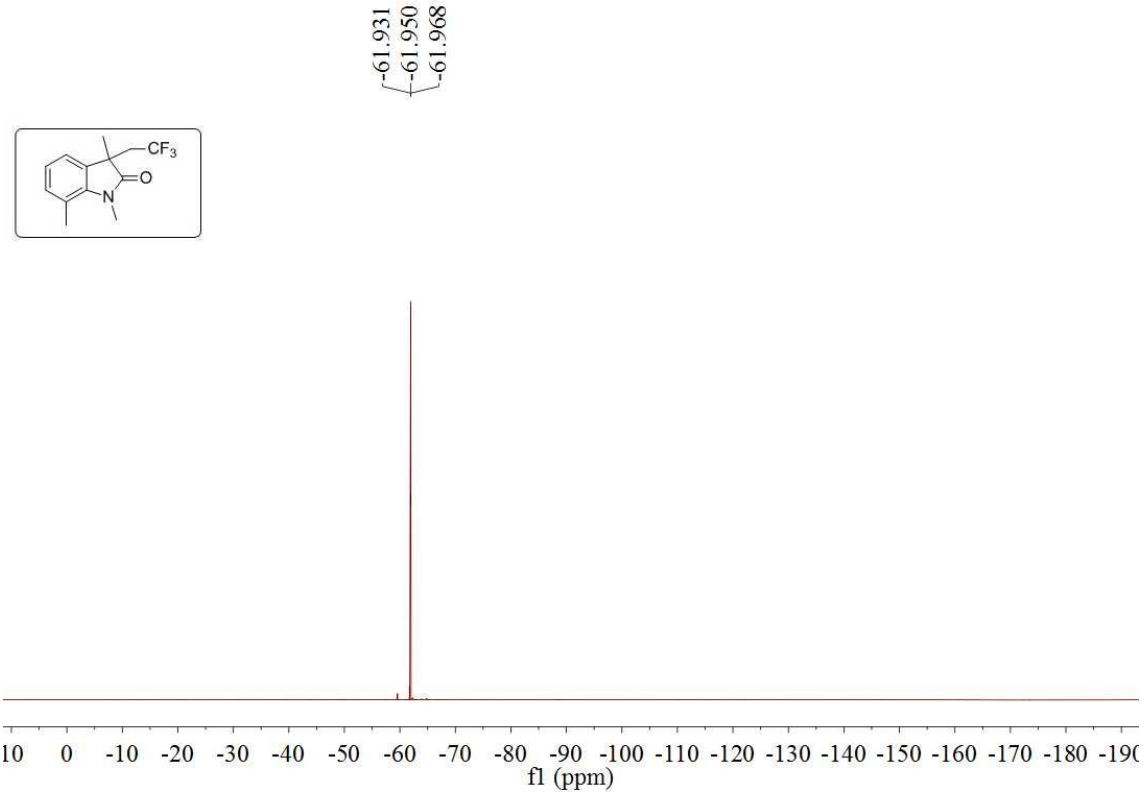
^{1}H-NMR Spectra of 2l



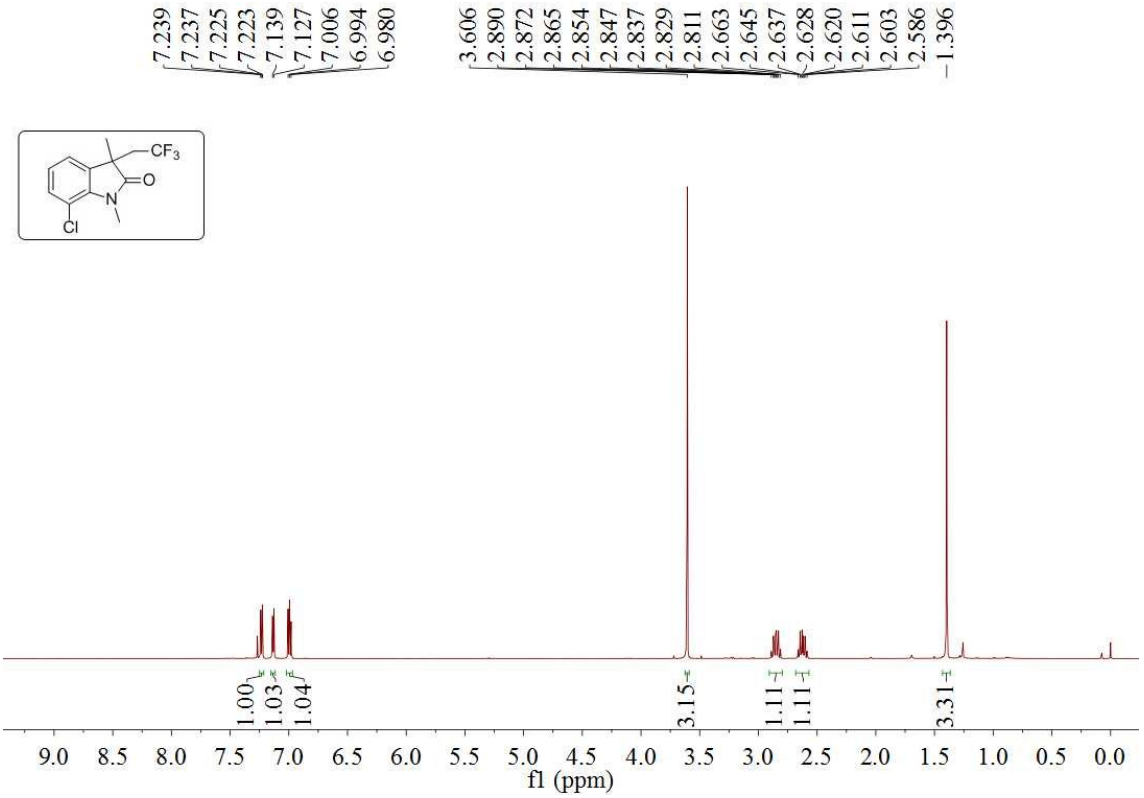
^{13}C-NMR Spectra of 2l



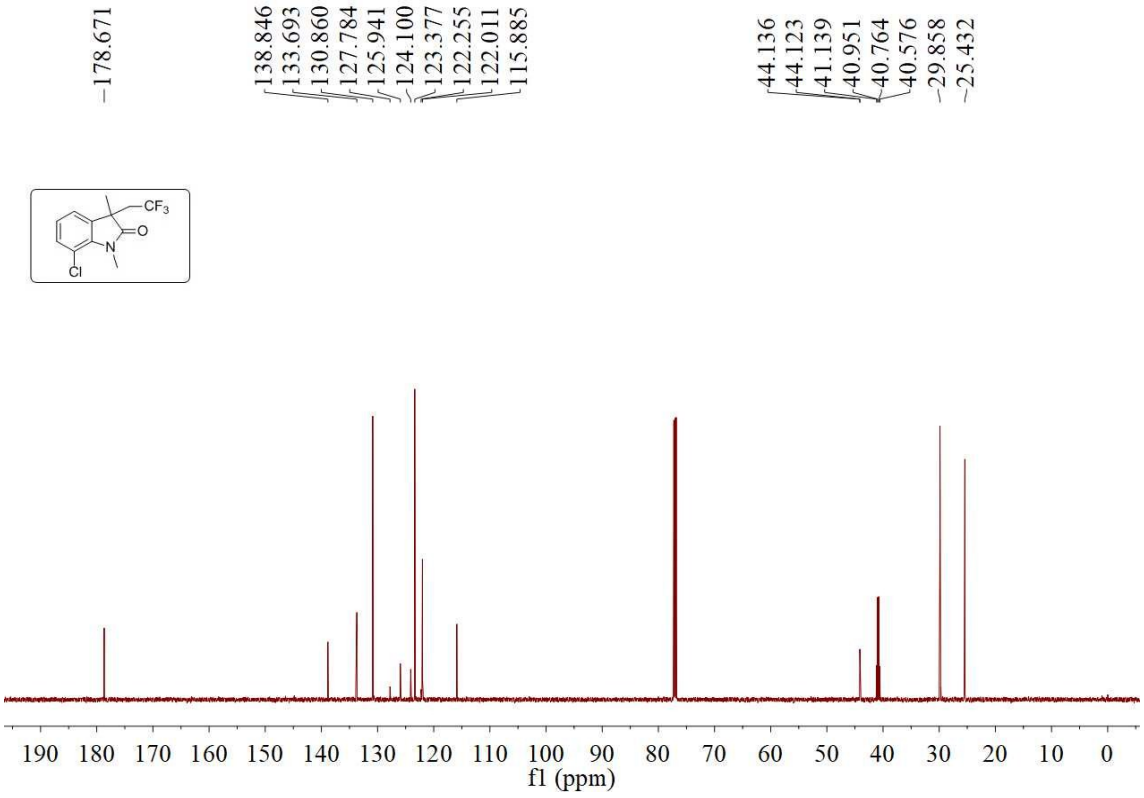
^{19}F-NMR Spectra of 2l



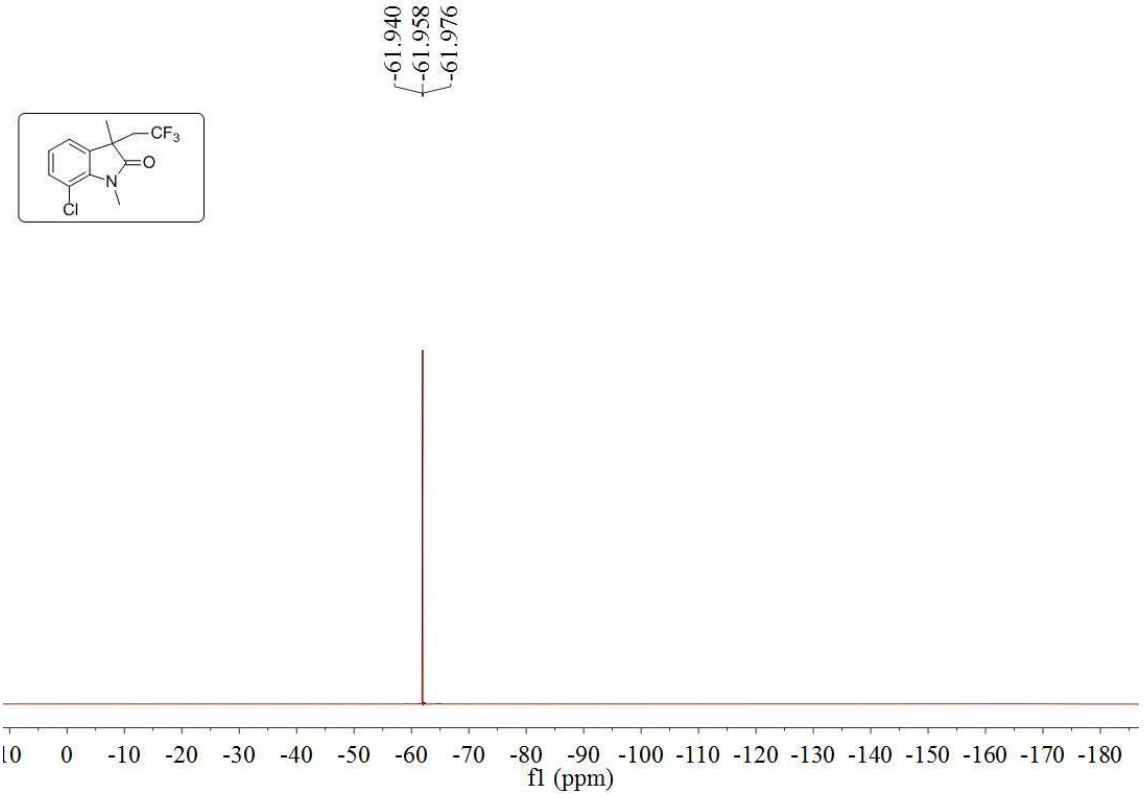
^{1}H-NMR Spectra of 2m



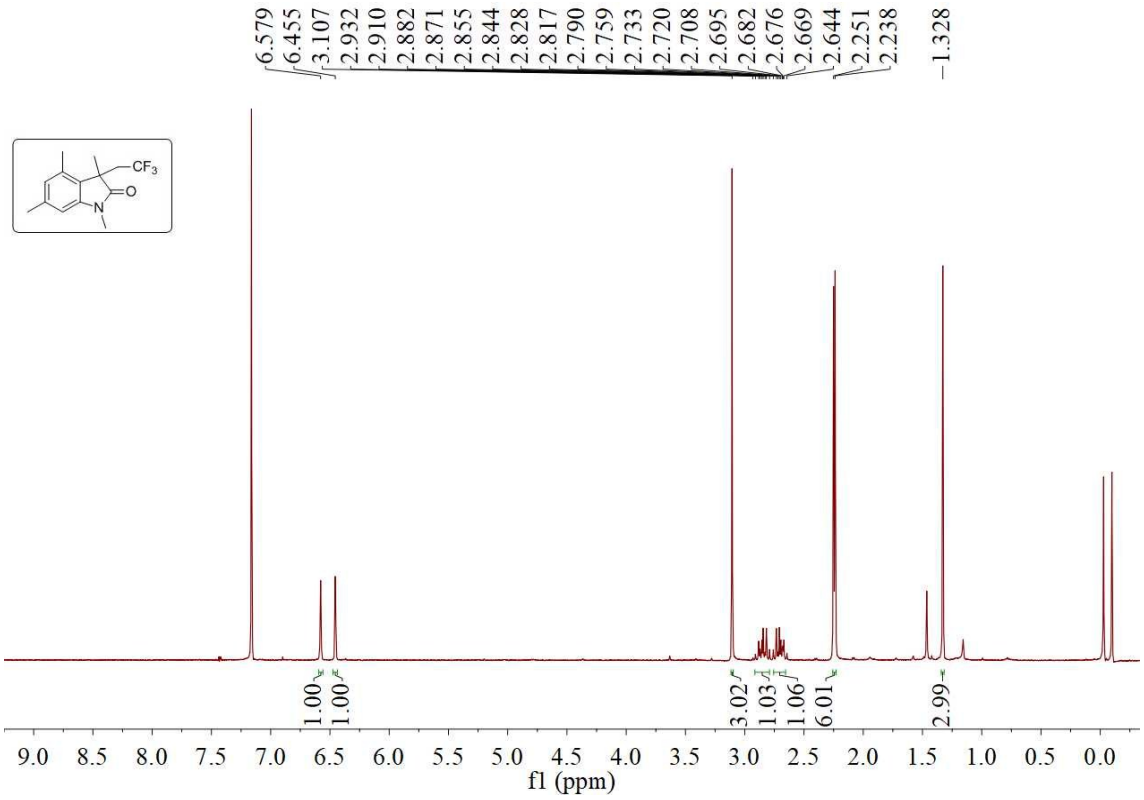
^{13}C-NMR Spectra of 2m



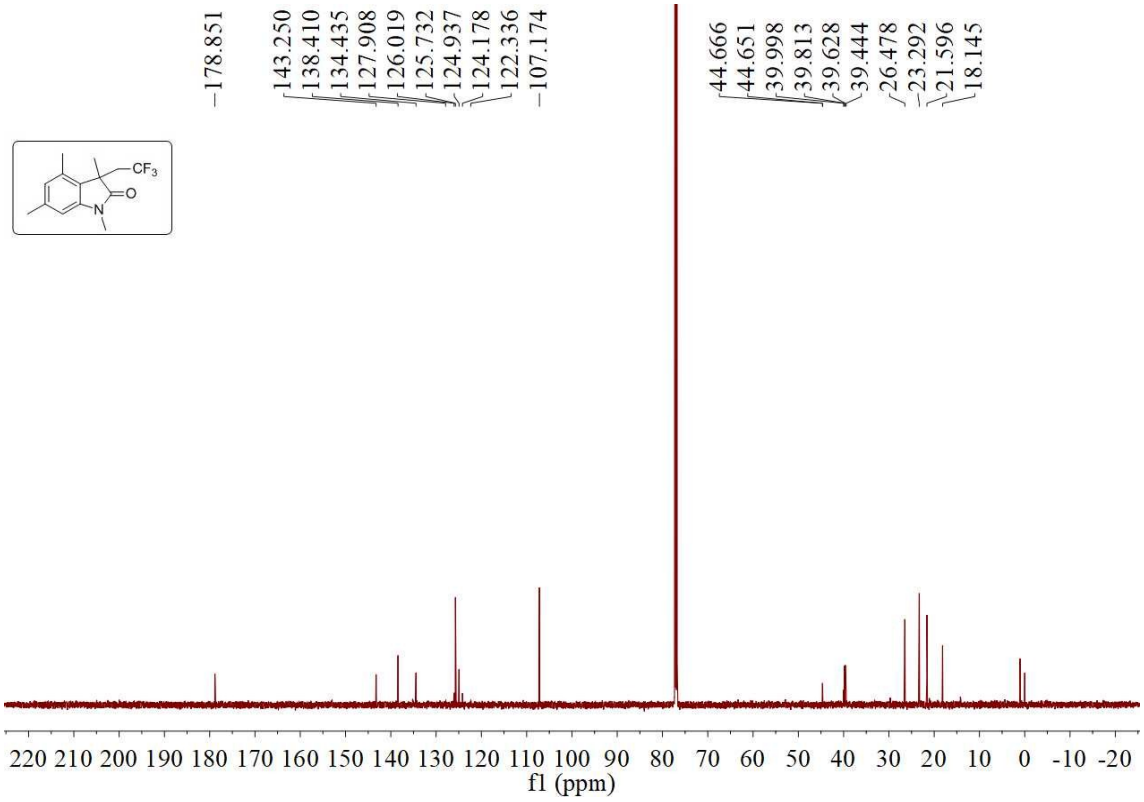
^{19}F-NMR Spectra of 2m



^{1}H-NMR Spectra of 2n



^{13}C-NMR Spectra of 2n



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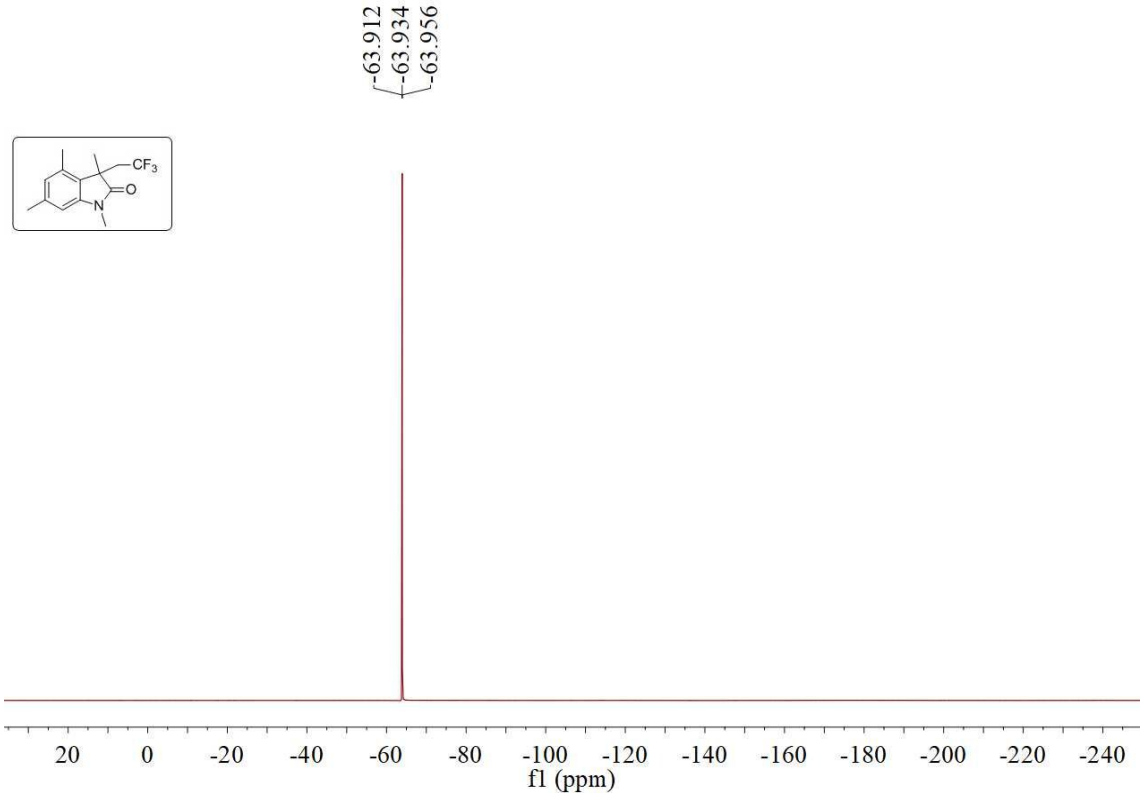
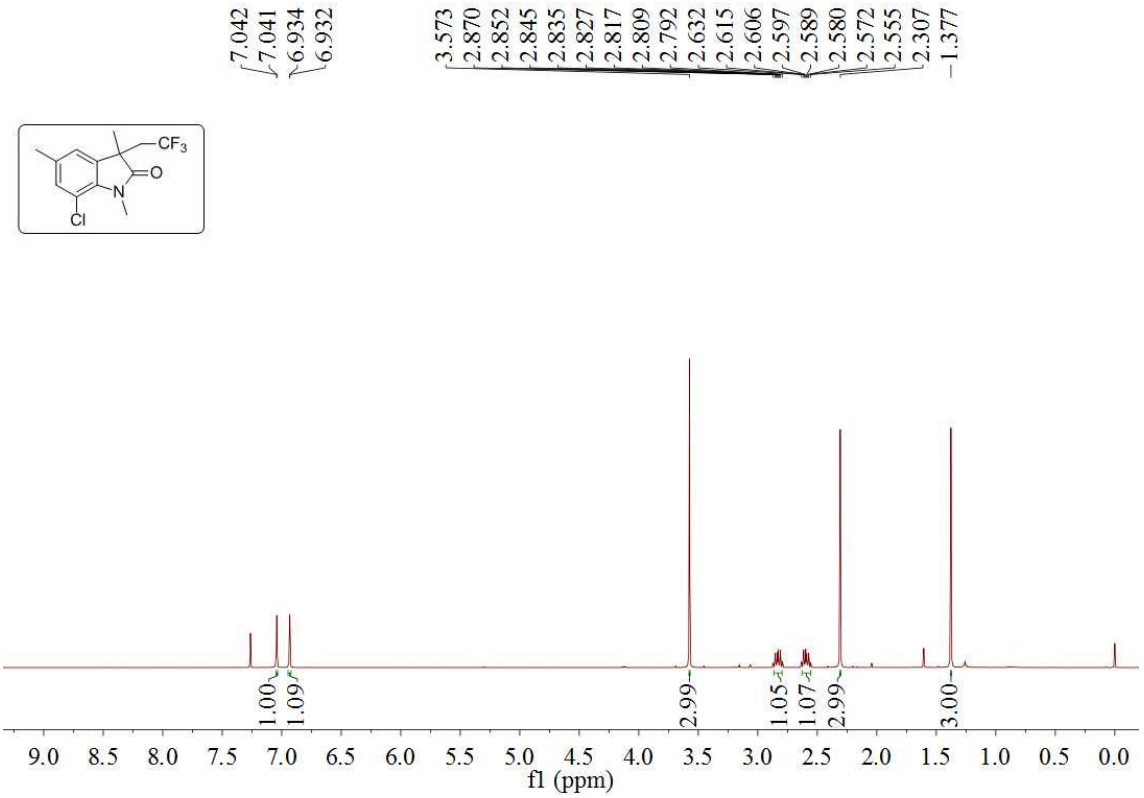
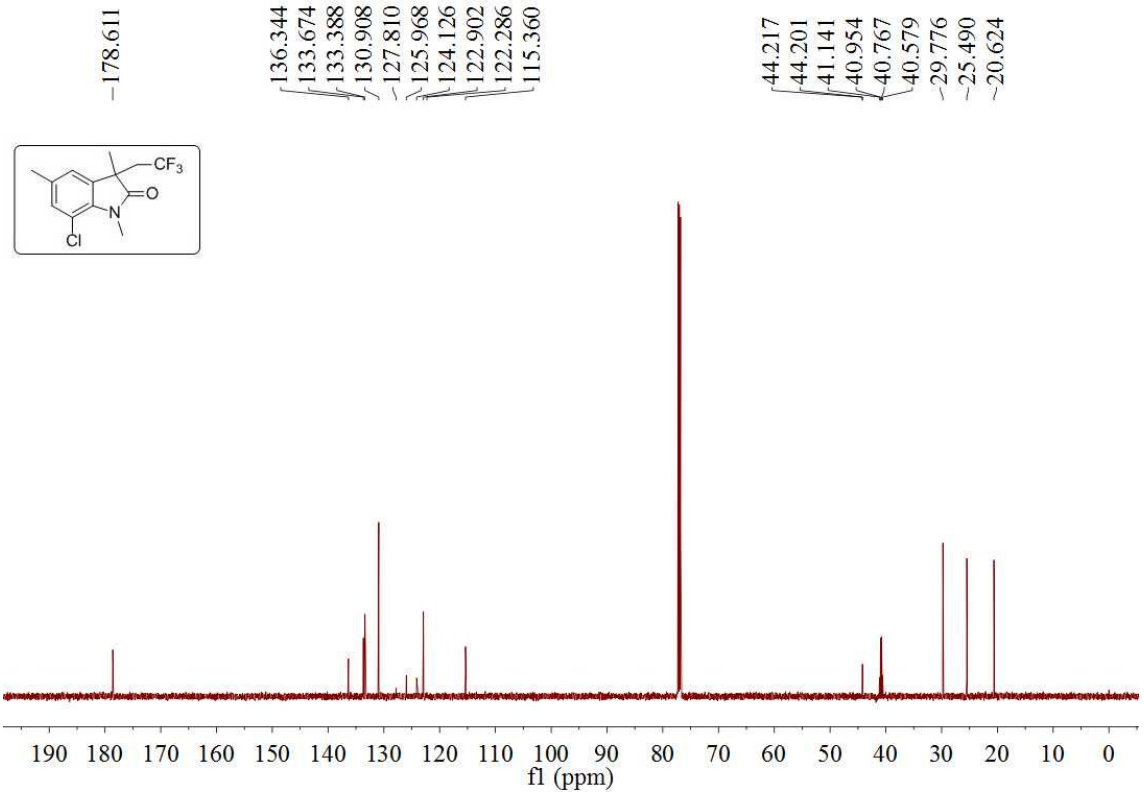


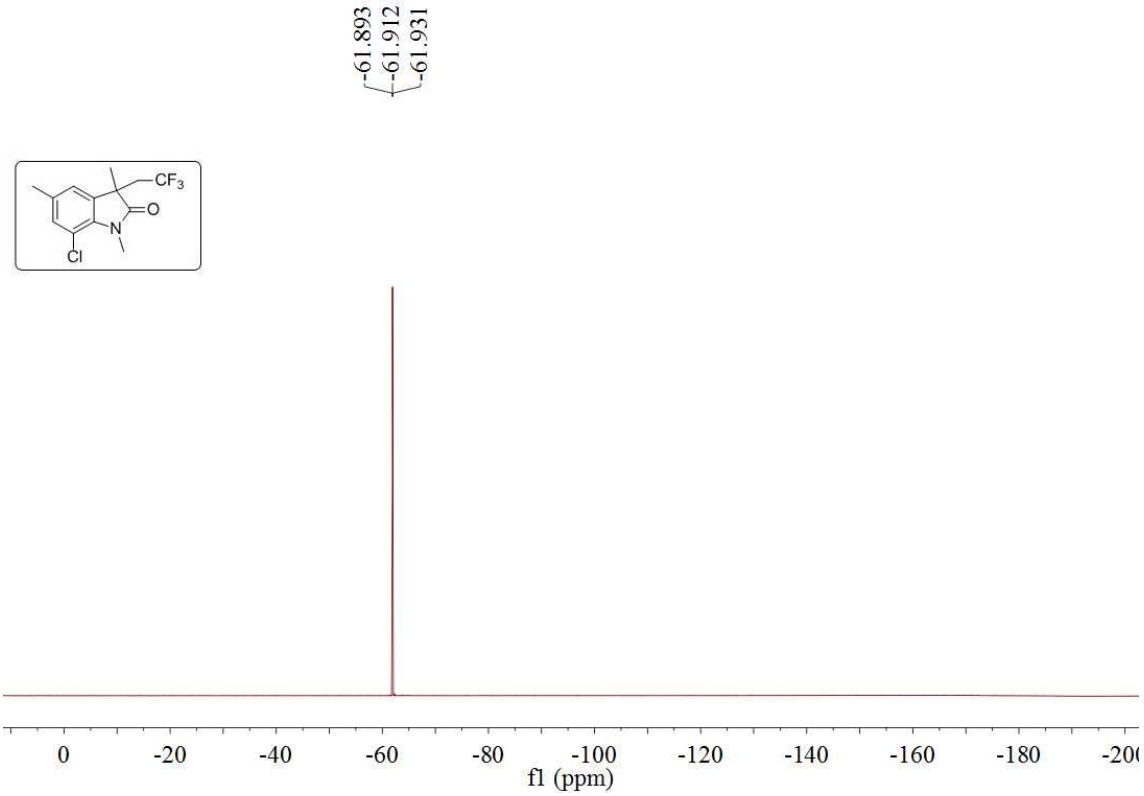
[1]H-NMR Spectra of 2o



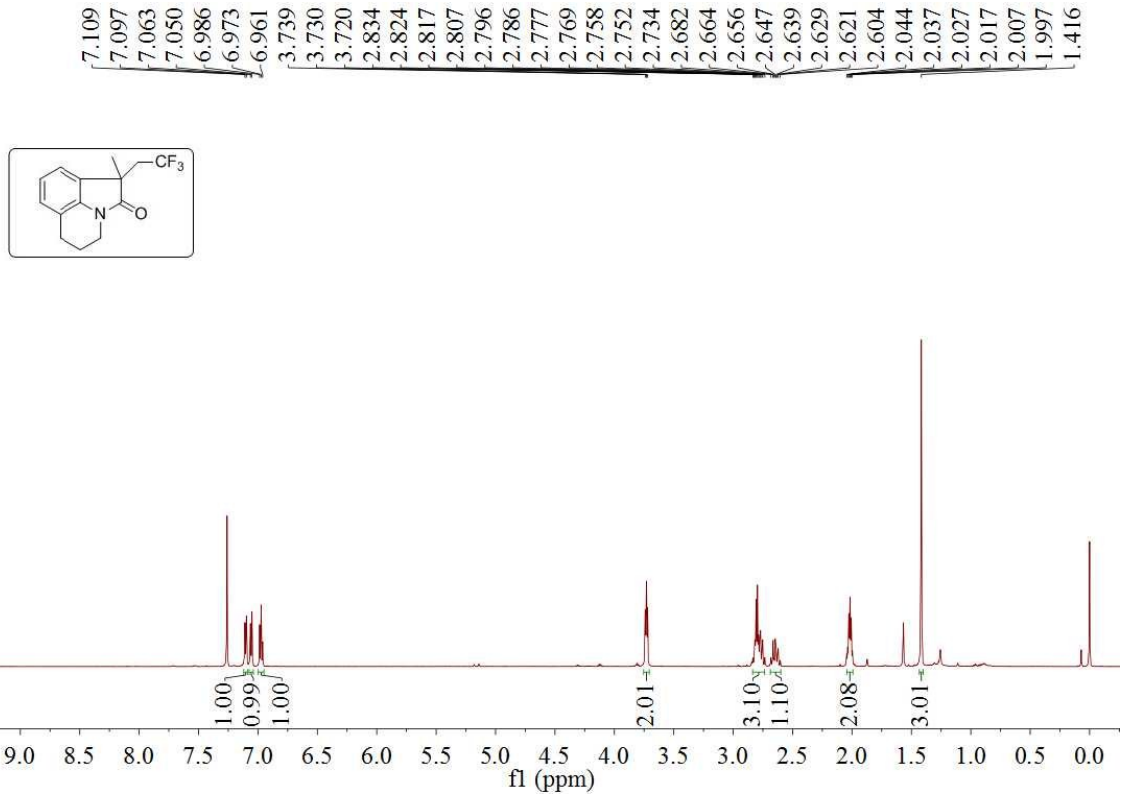
[13]C-NMR Spectra of 2o



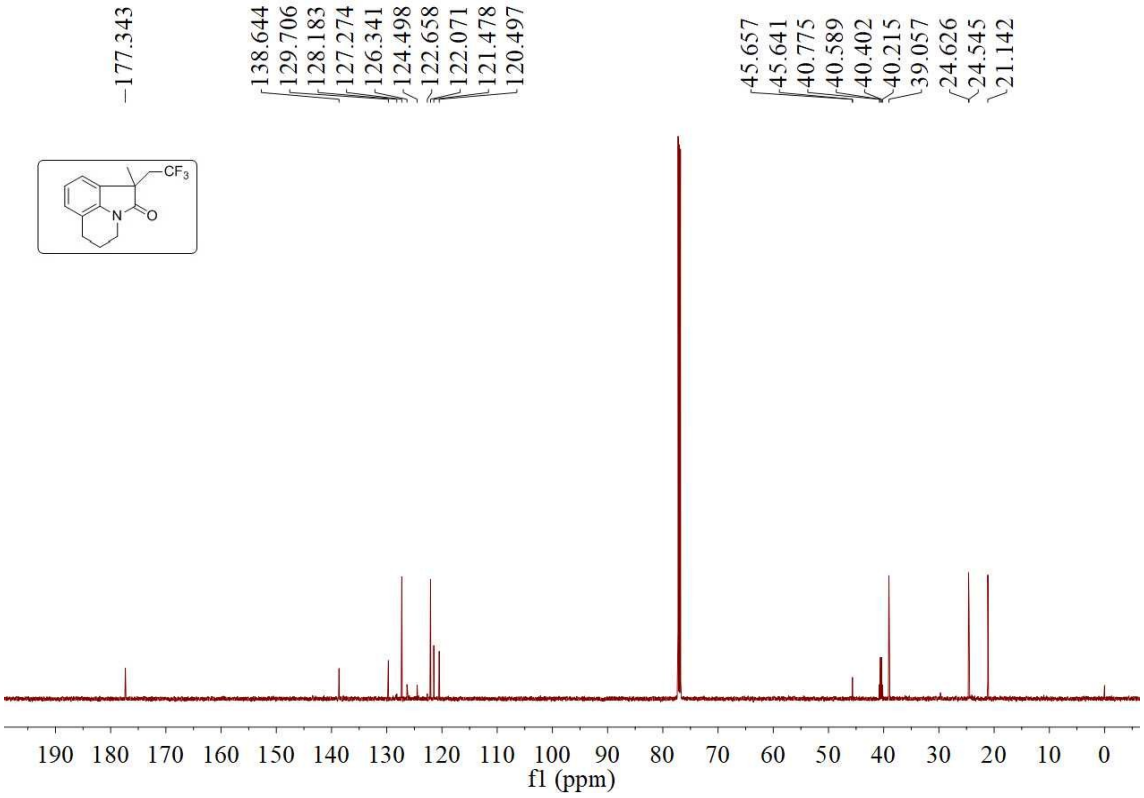
^{19}F-NMR Spectra of 2o



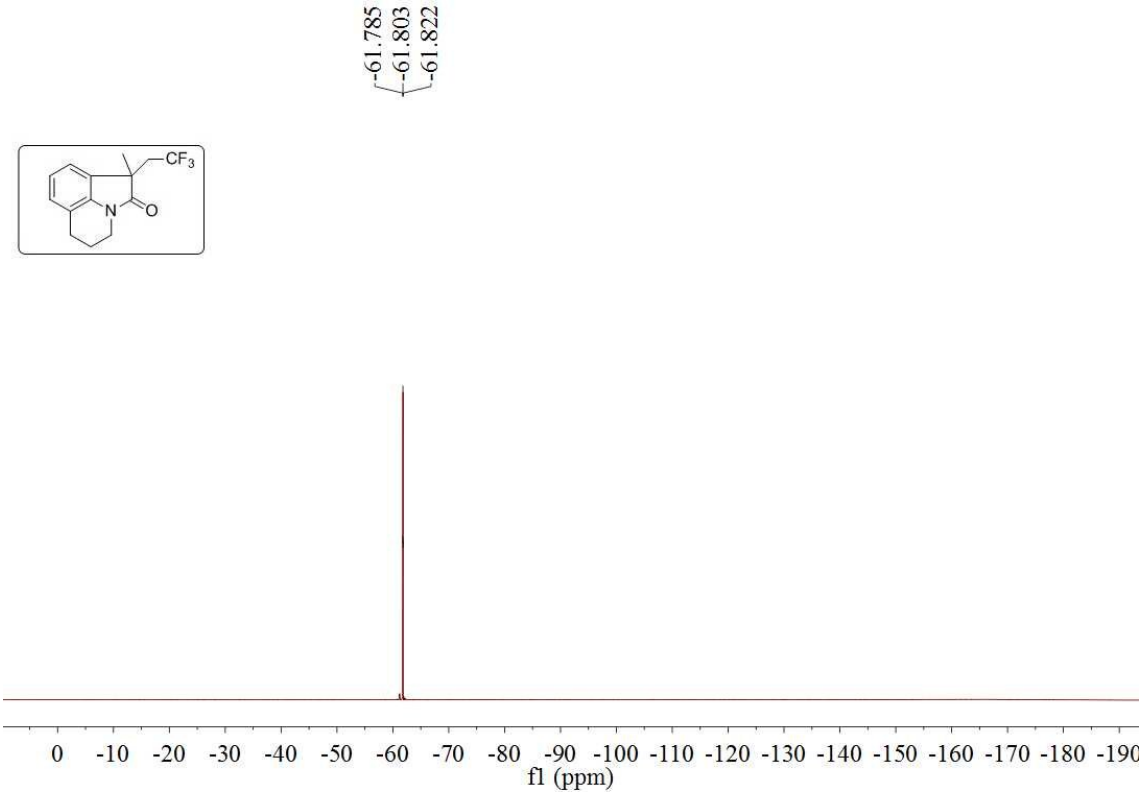
^{1}H-NMR Spectra of 2p



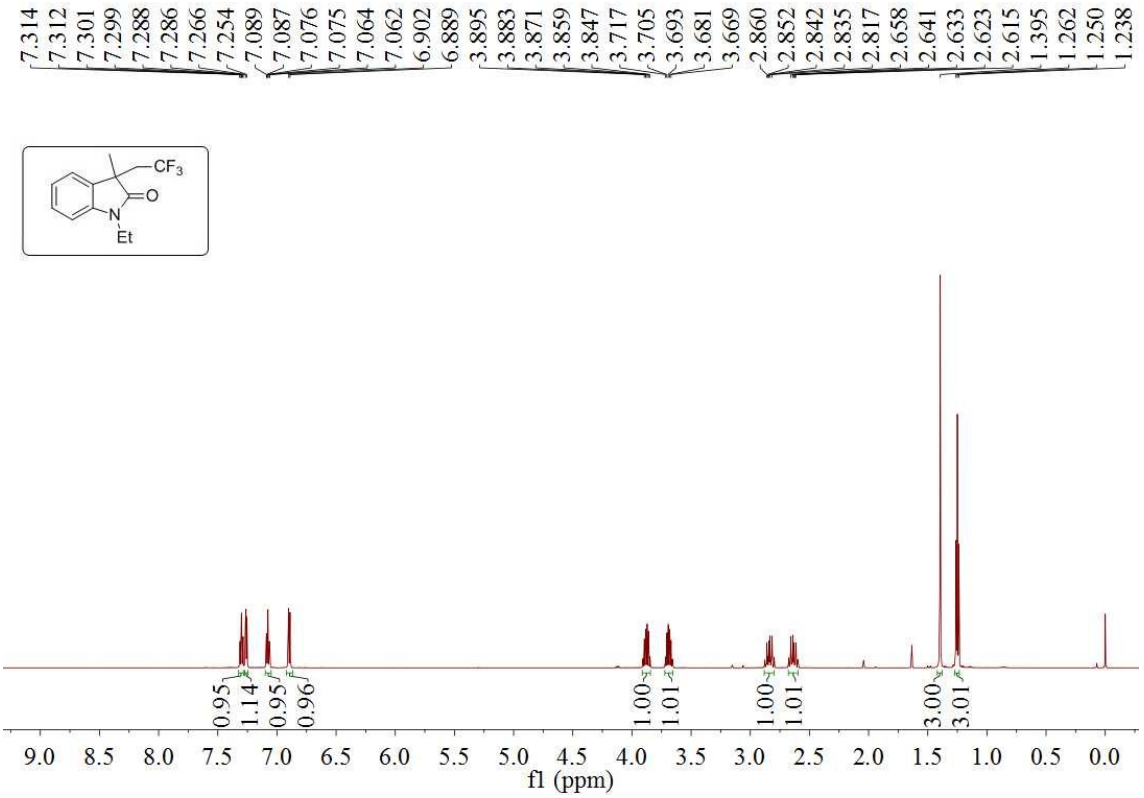
^{13}C-NMR Spectra of 2p



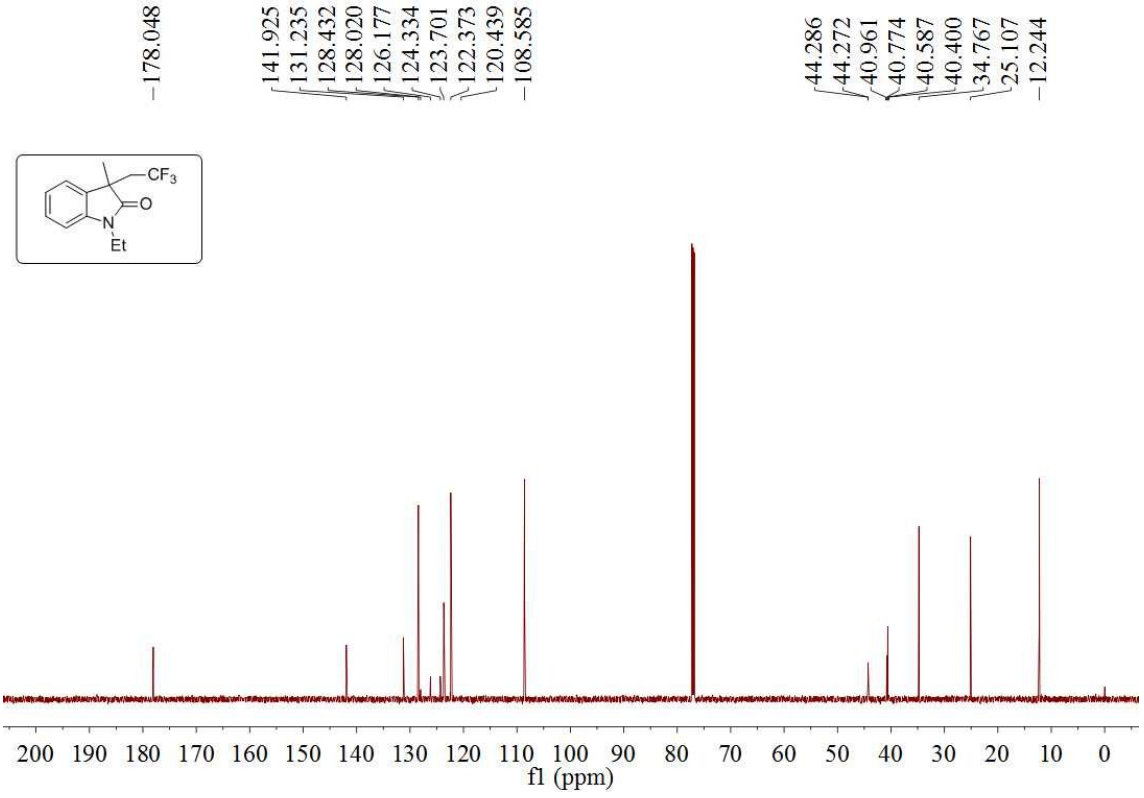
^{19}F-NMR Spectra of 2p



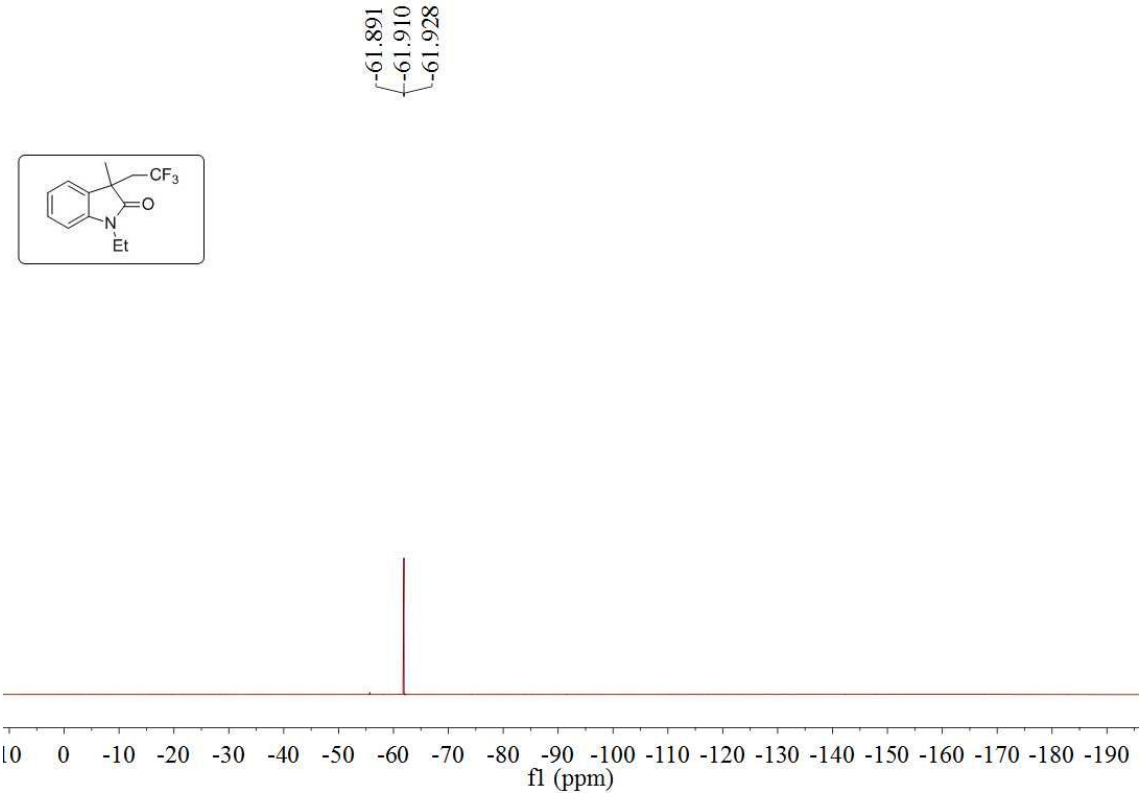
^{1}H-NMR Spectra of 2q



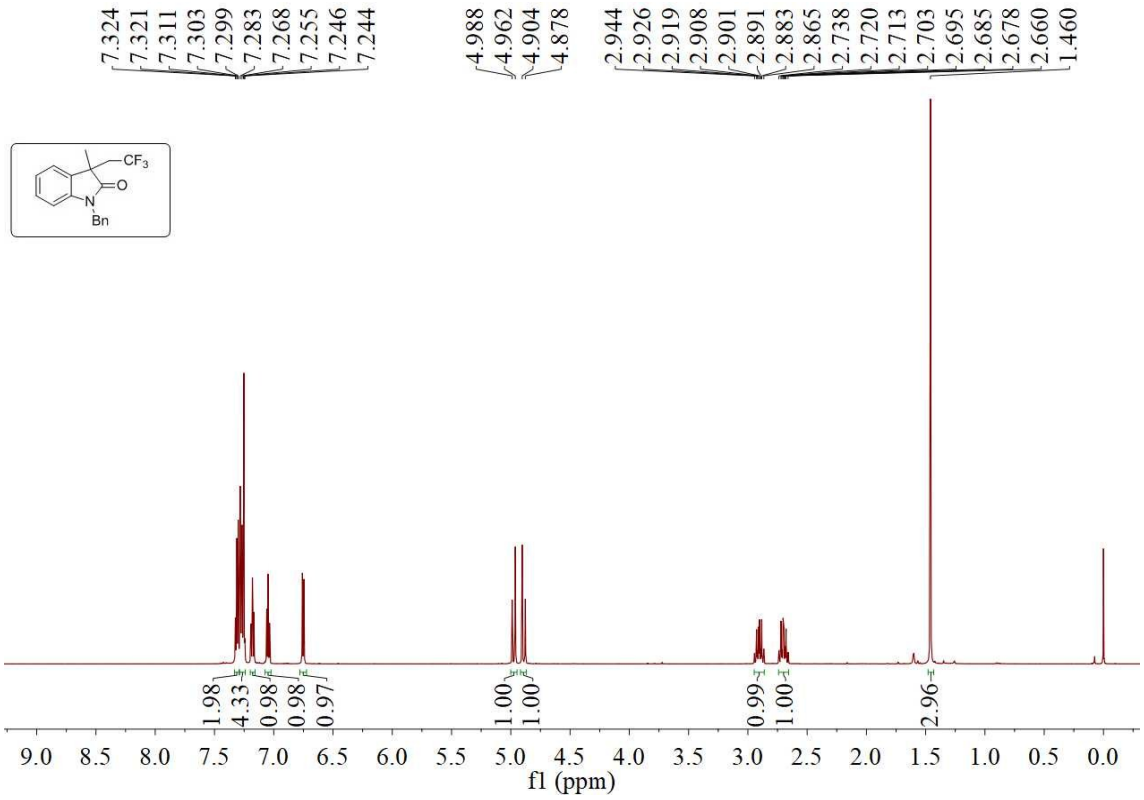
^{13}C-NMR Spectra of 2q



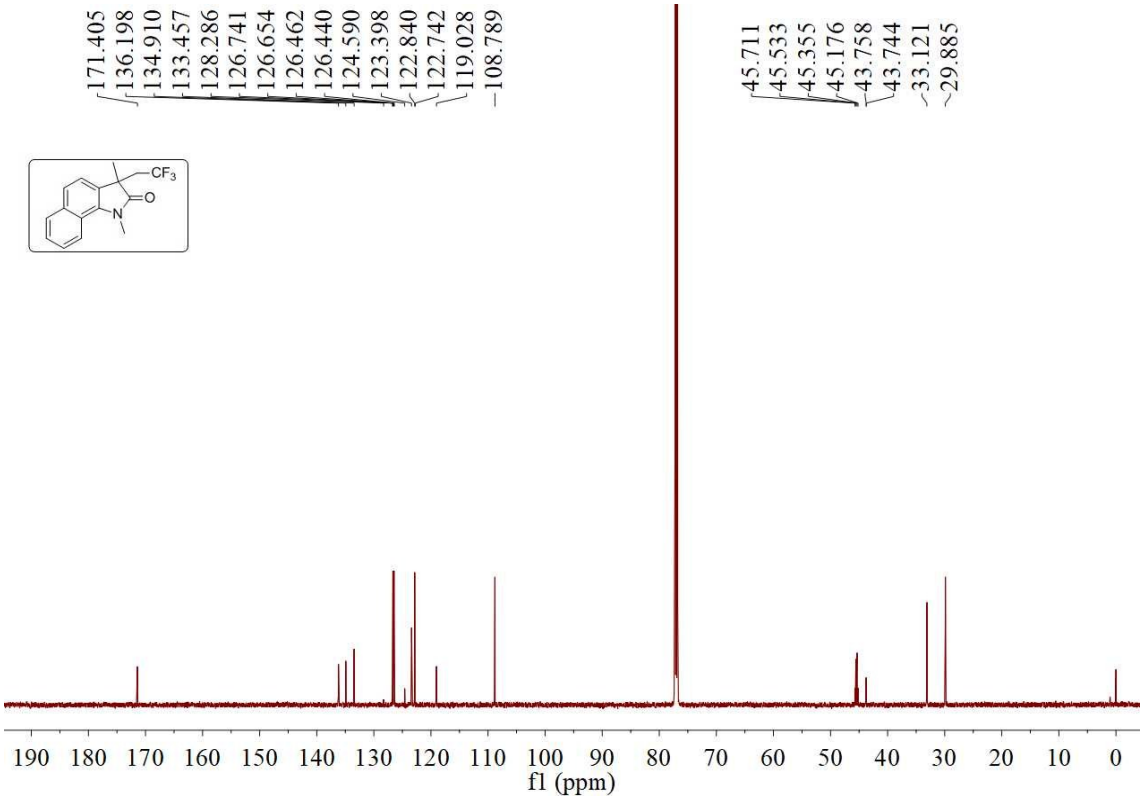
^{19}F-NMR Spectra of 2p



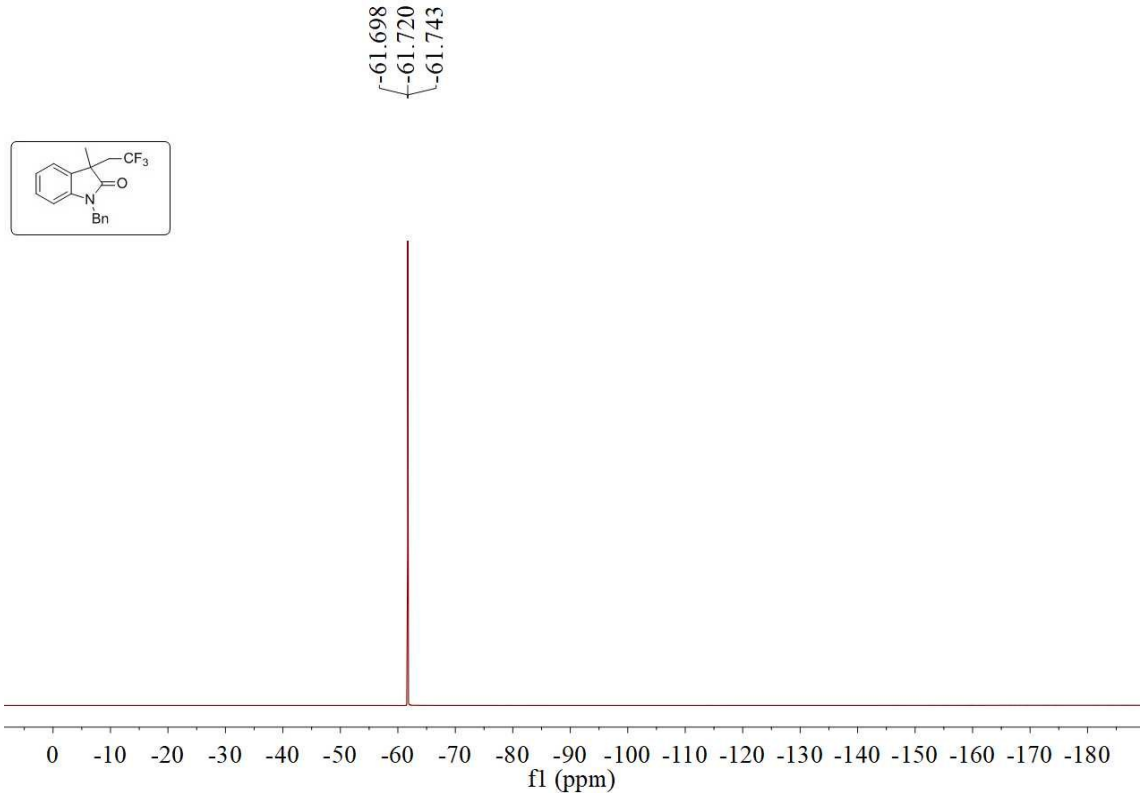
^{1}H-NMR Spectra of 2r



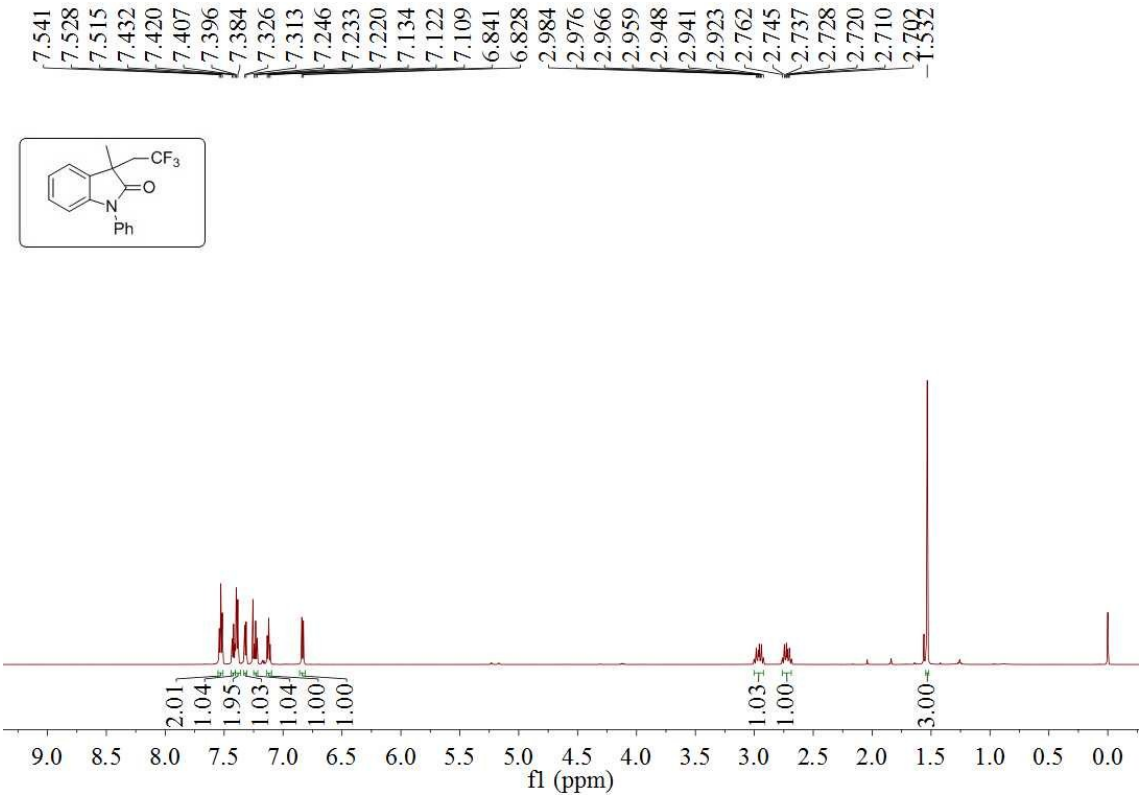
^{13}C-NMR Spectra of 2r



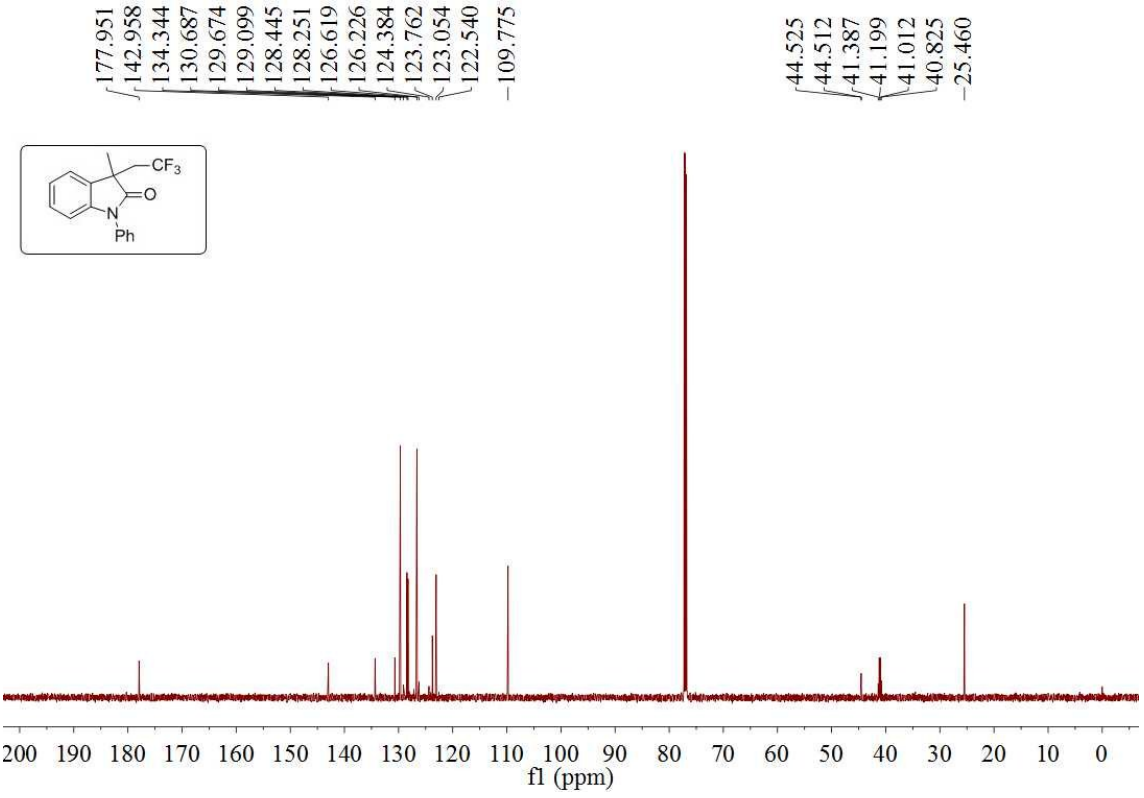
^{19}F-NMR Spectra of 2r



[1]H-NMR Spectra of 2s



[13]C-NMR Spectra of 2s



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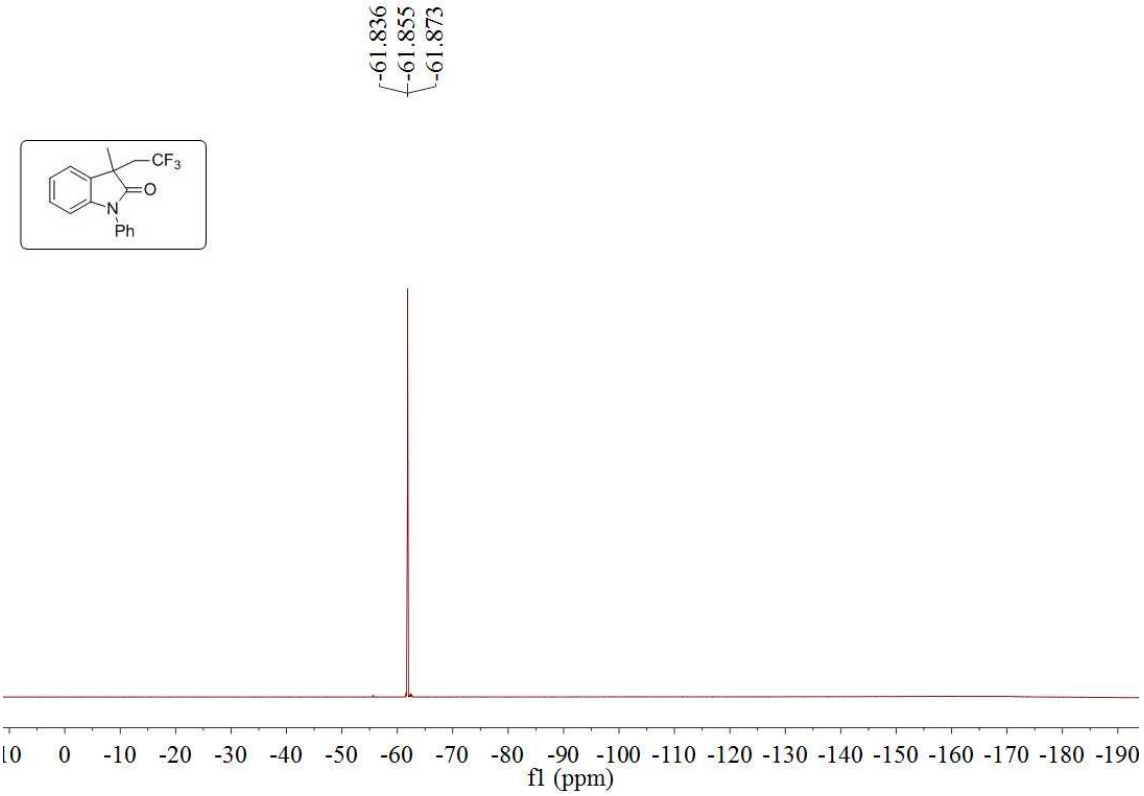
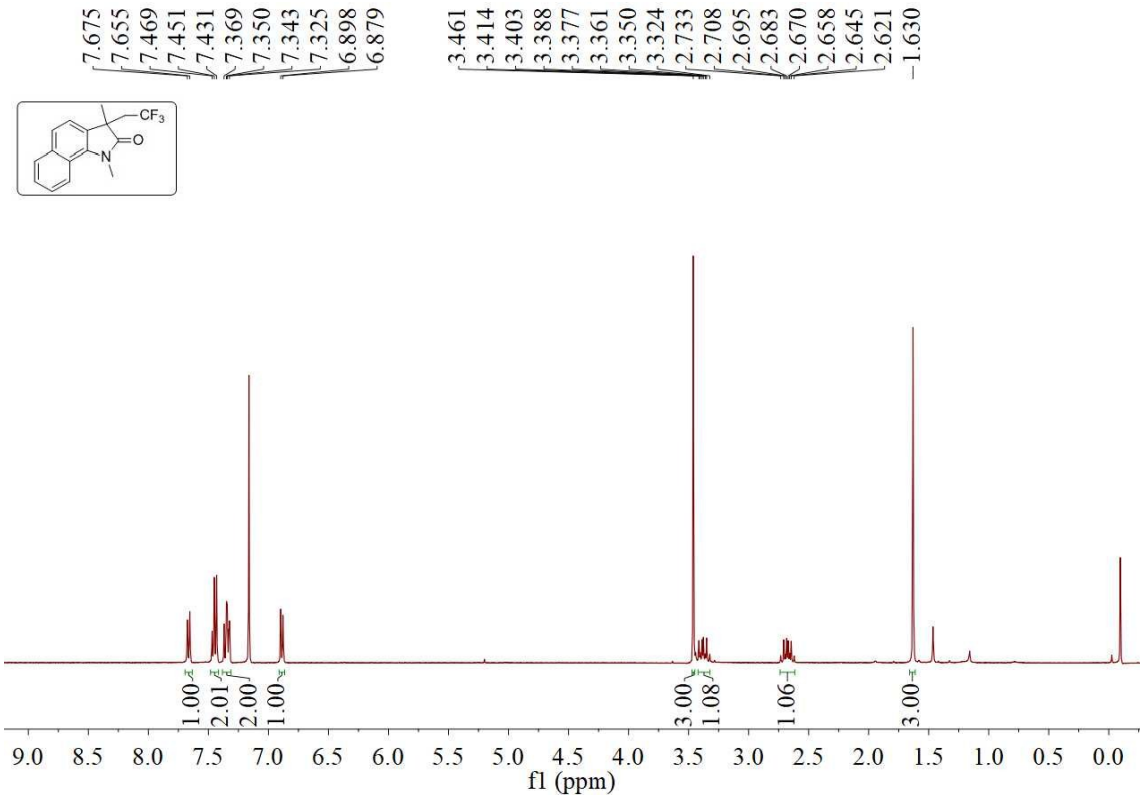
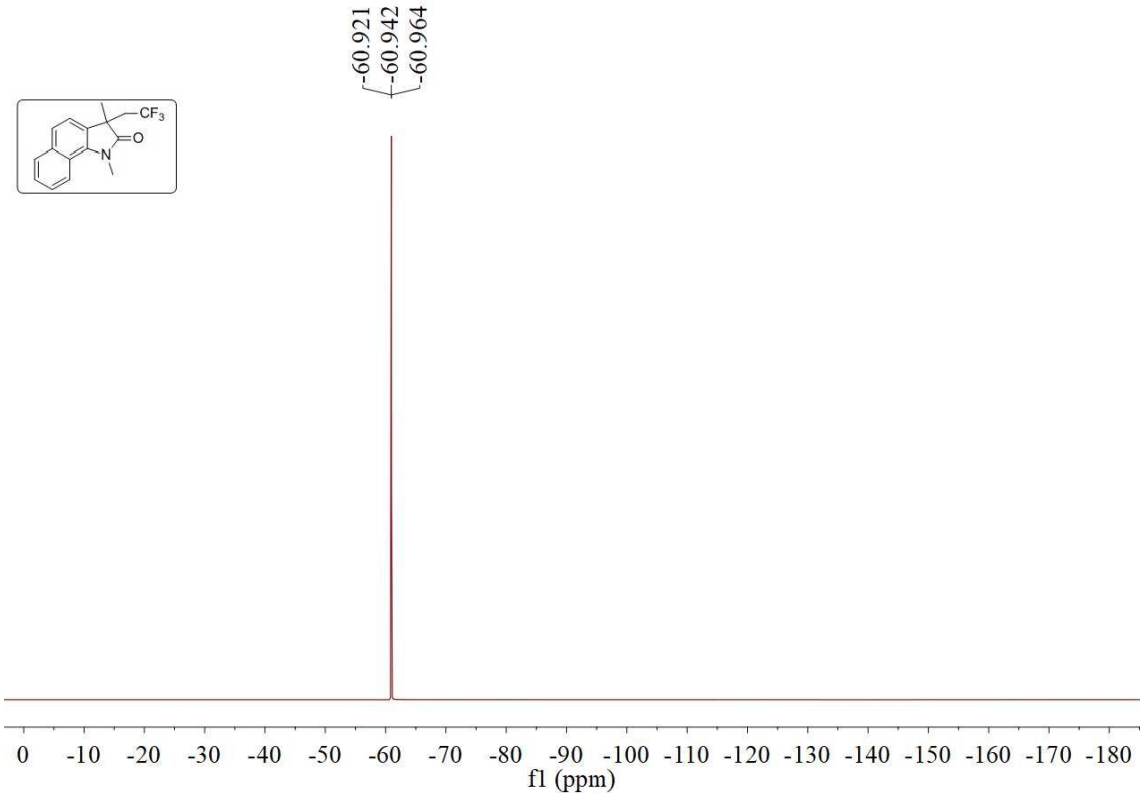


^{1}H-NMR Spectra of 2t

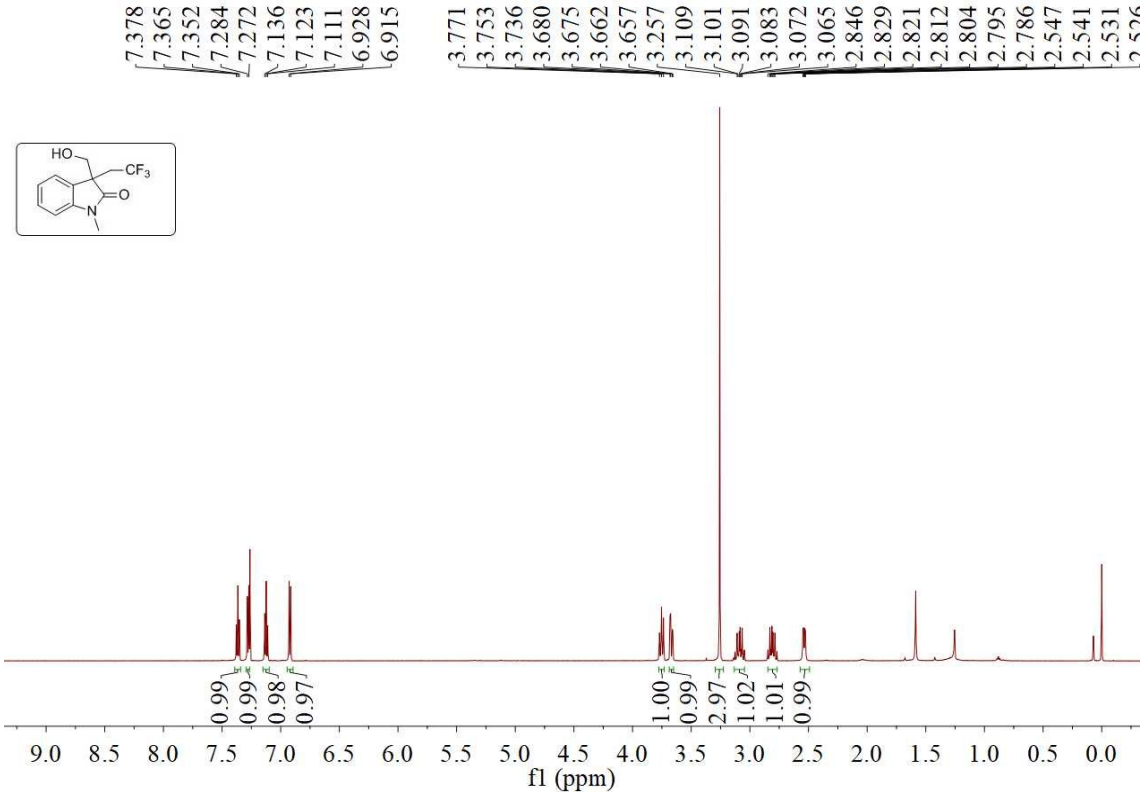


^{13}C-NMR Spectra of 2t

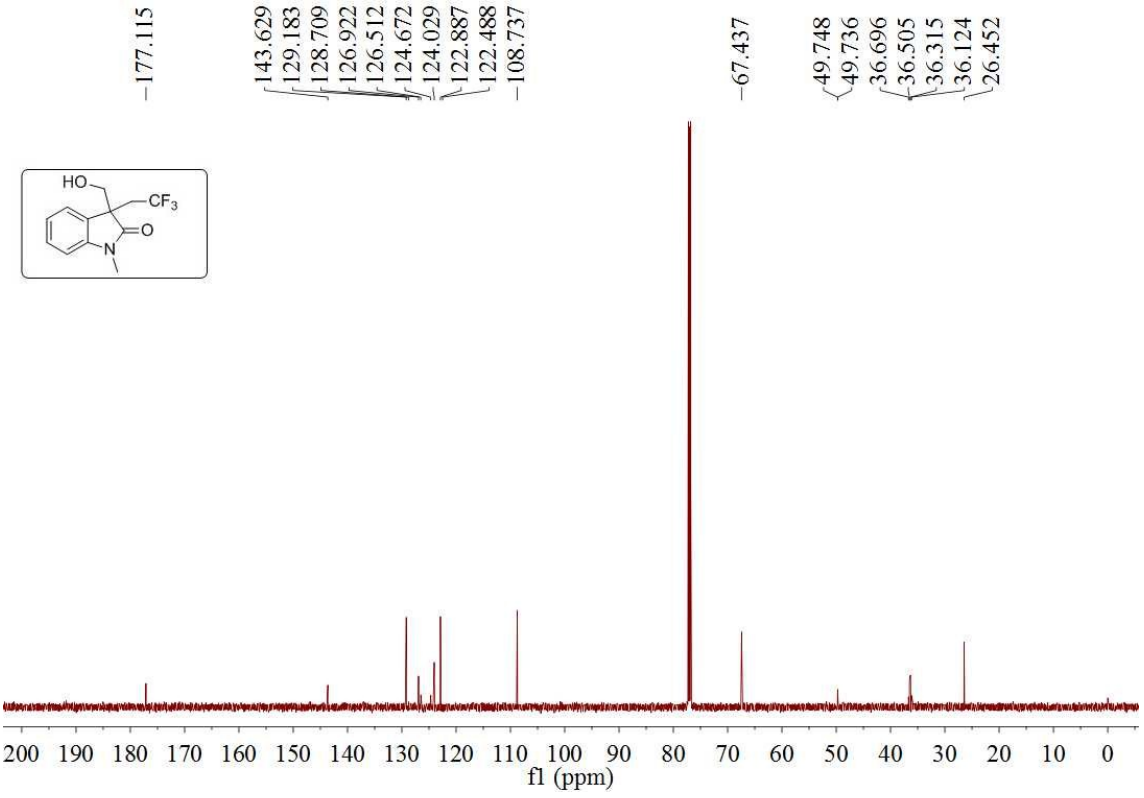
^{19}F-NMR Spectra of 2t



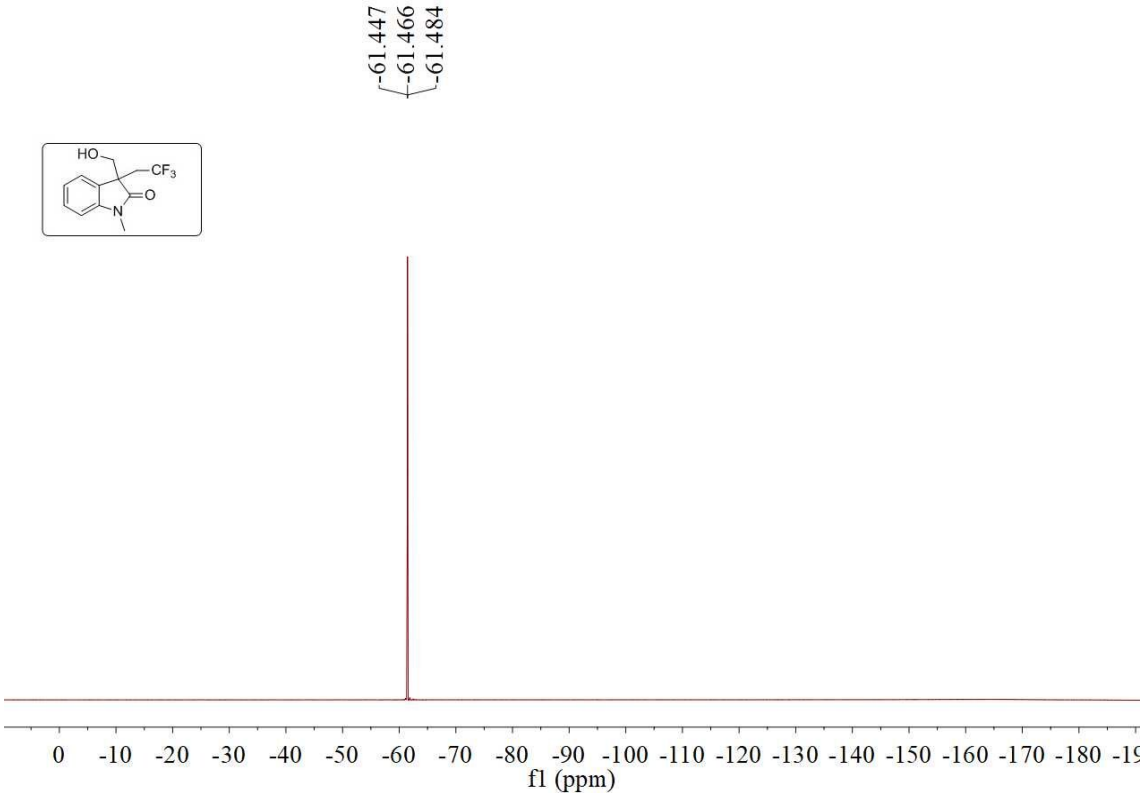
^{1}H-NMR Spectra of 2u



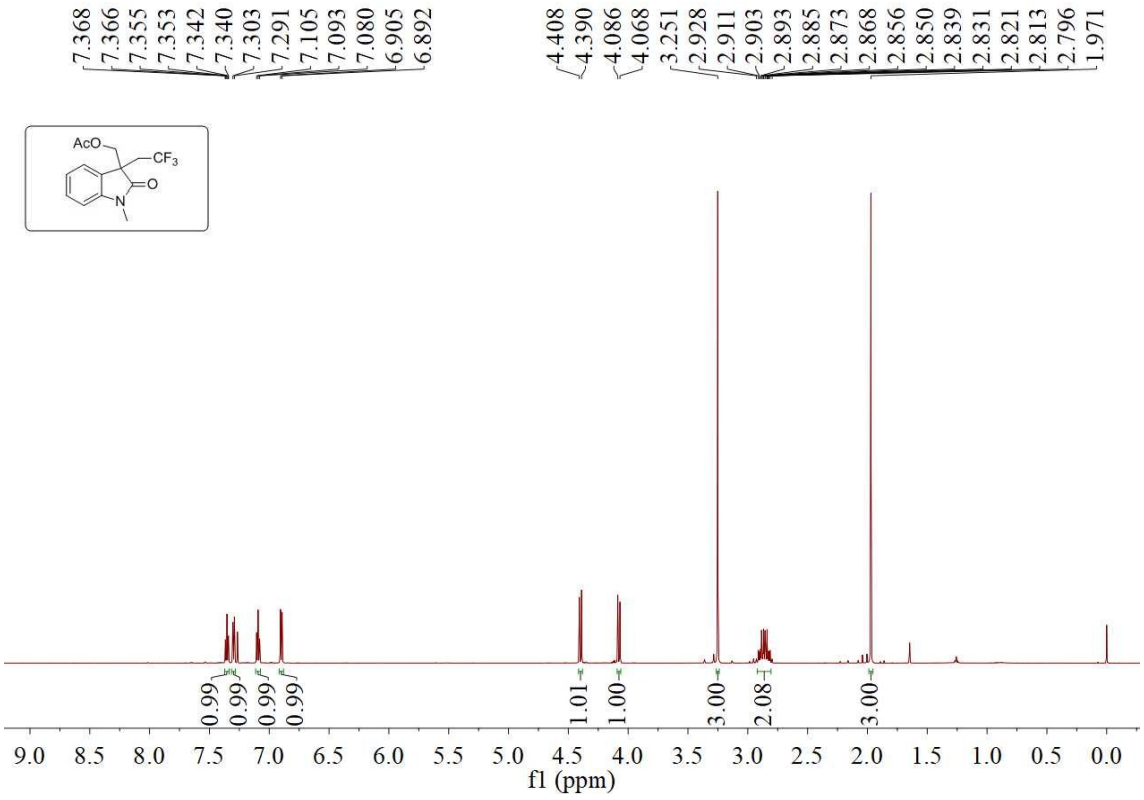
^{13}C-NMR Spectra of 2u



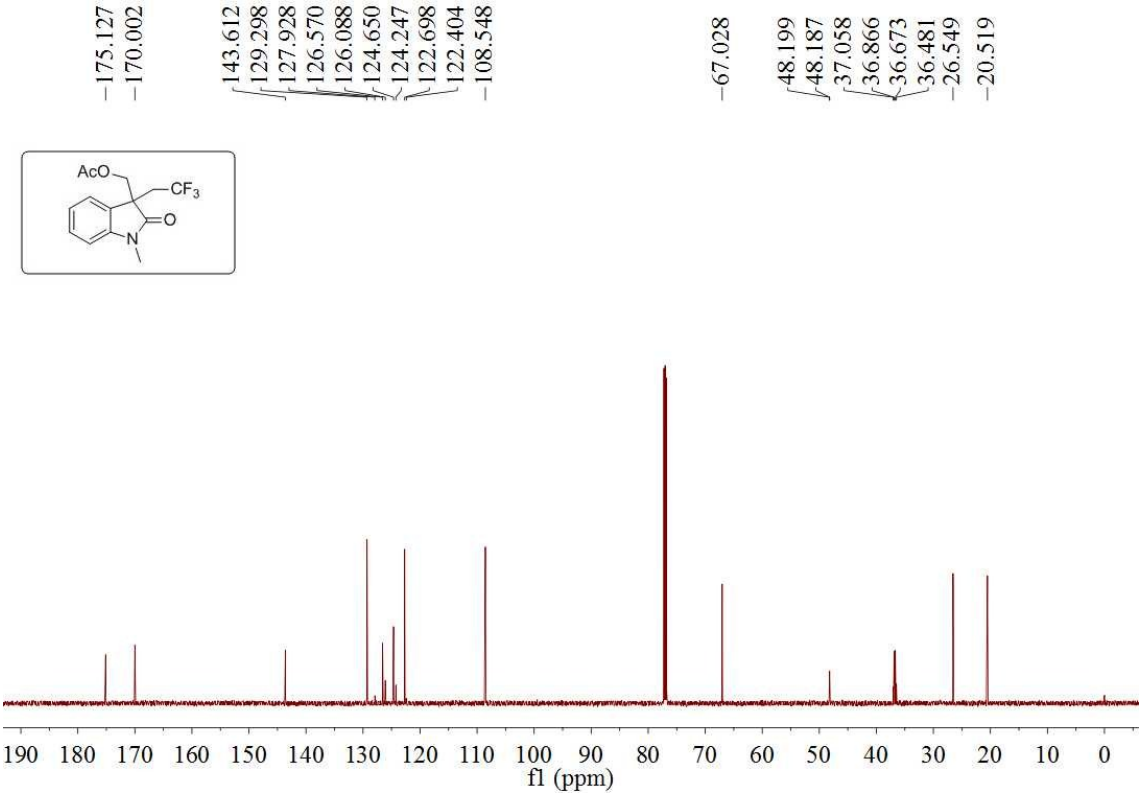
^{19}F-NMR Spectra of 2u



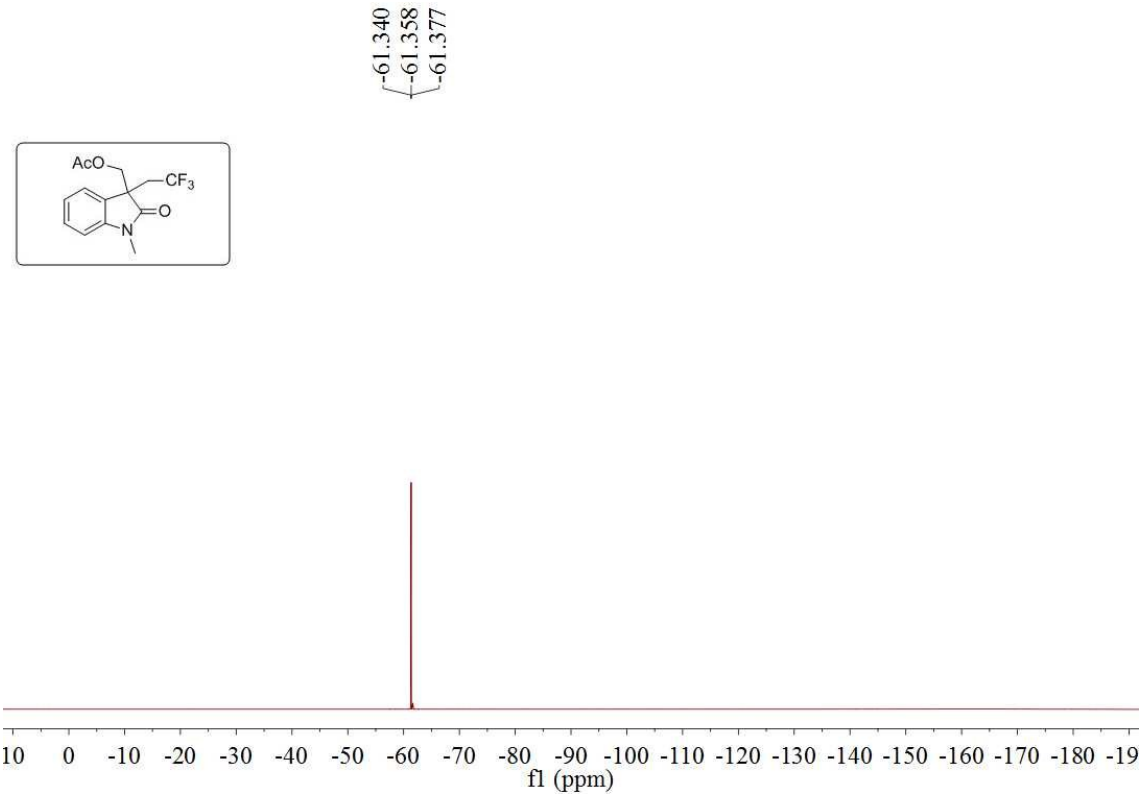
^{1}H-NMR Spectra of 2v



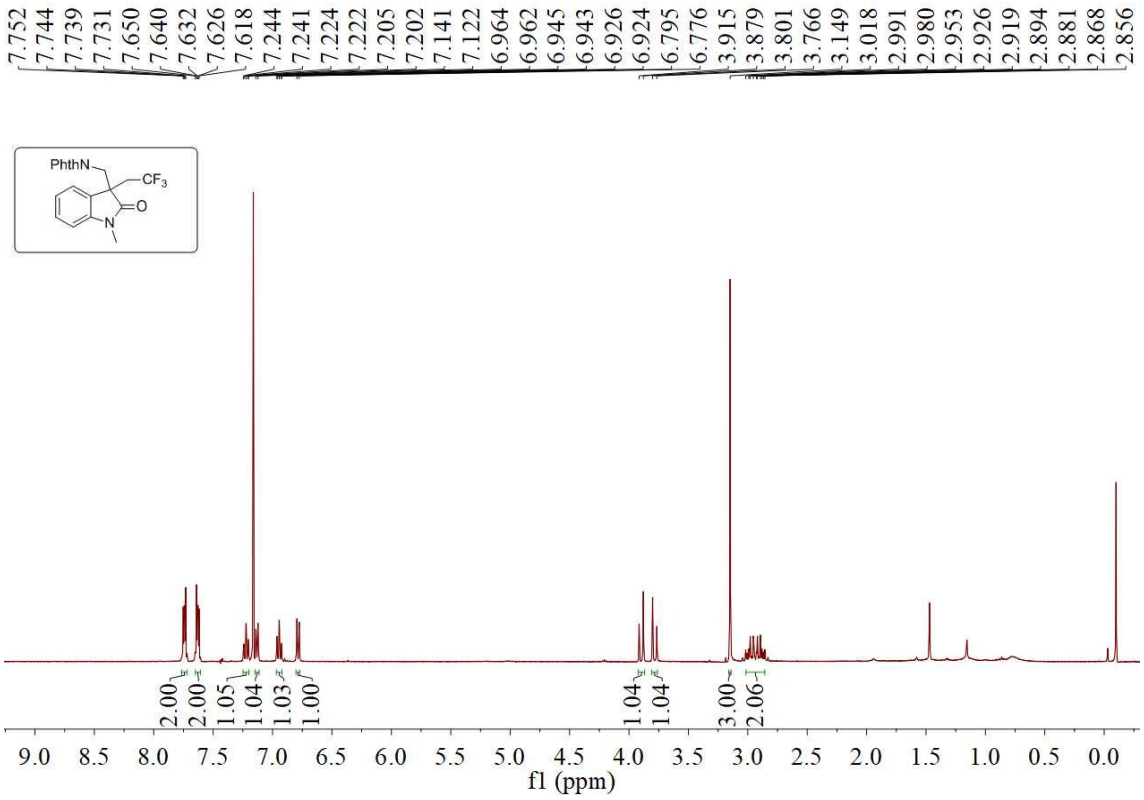
^{13}C-NMR Spectra of 2v



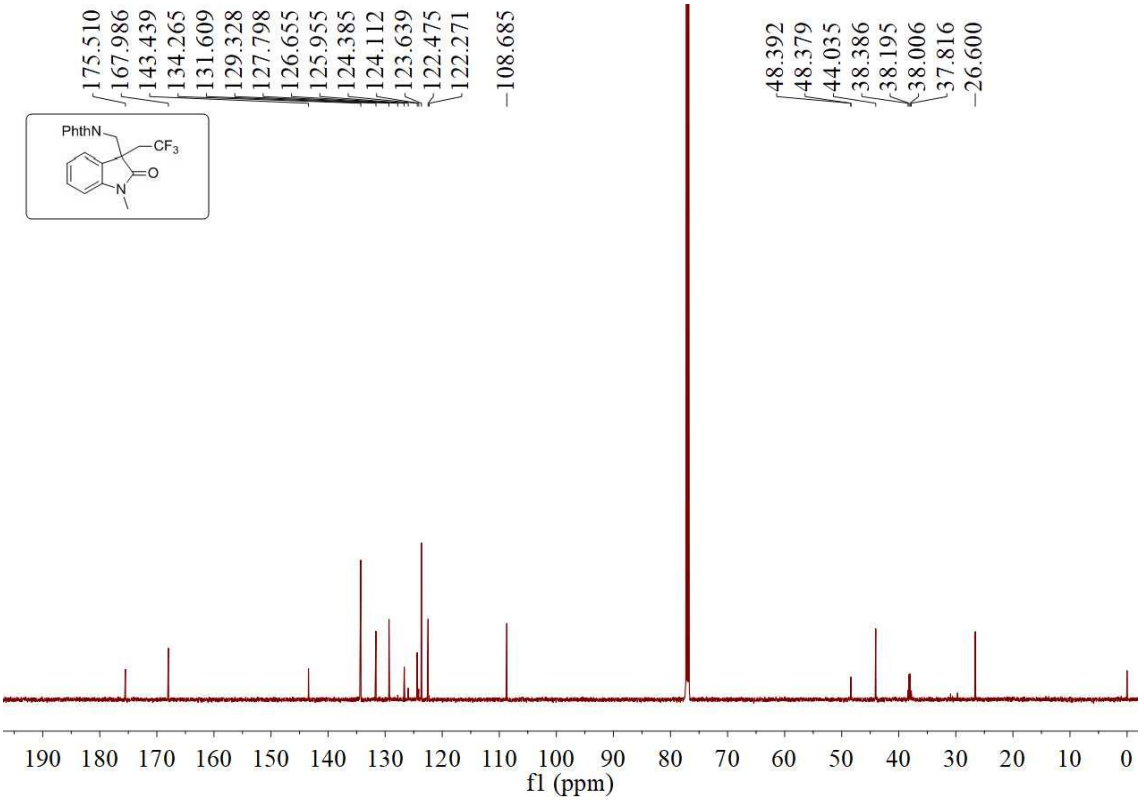
^{19}F-NMR Spectra of 2v



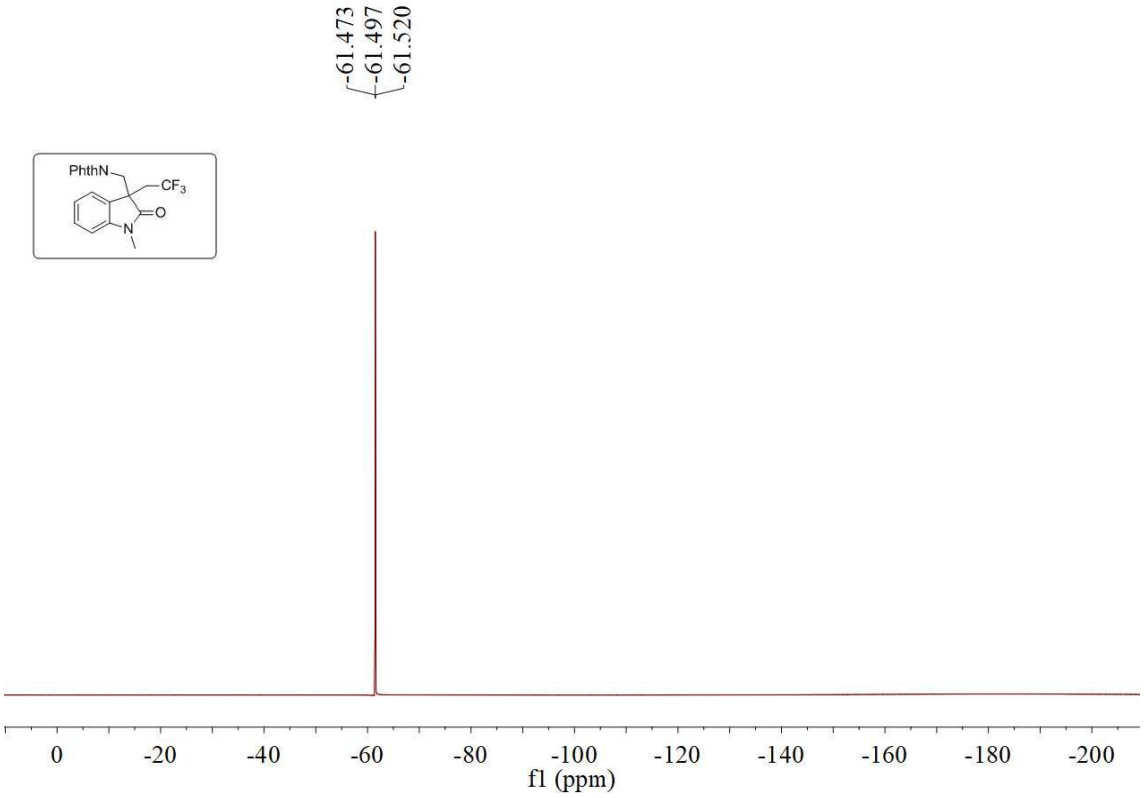
^{1}H-NMR Spectra of 2w



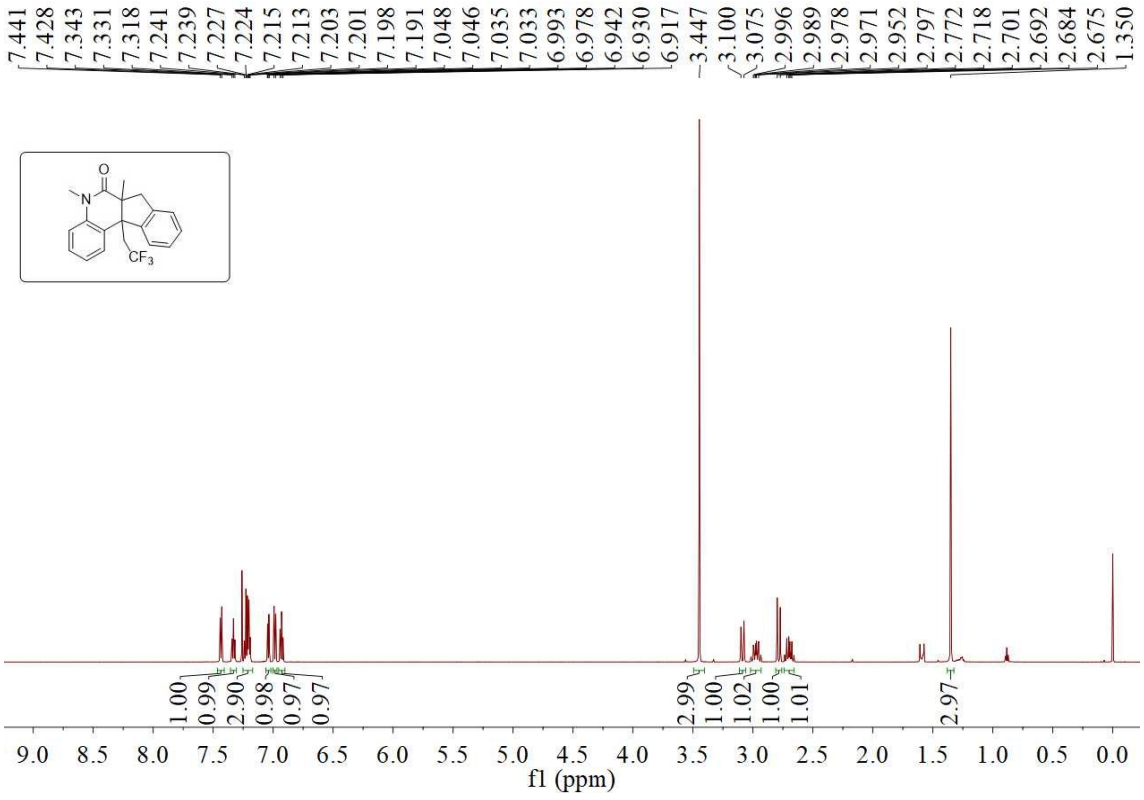
^{13}C-NMR Spectra of 2w



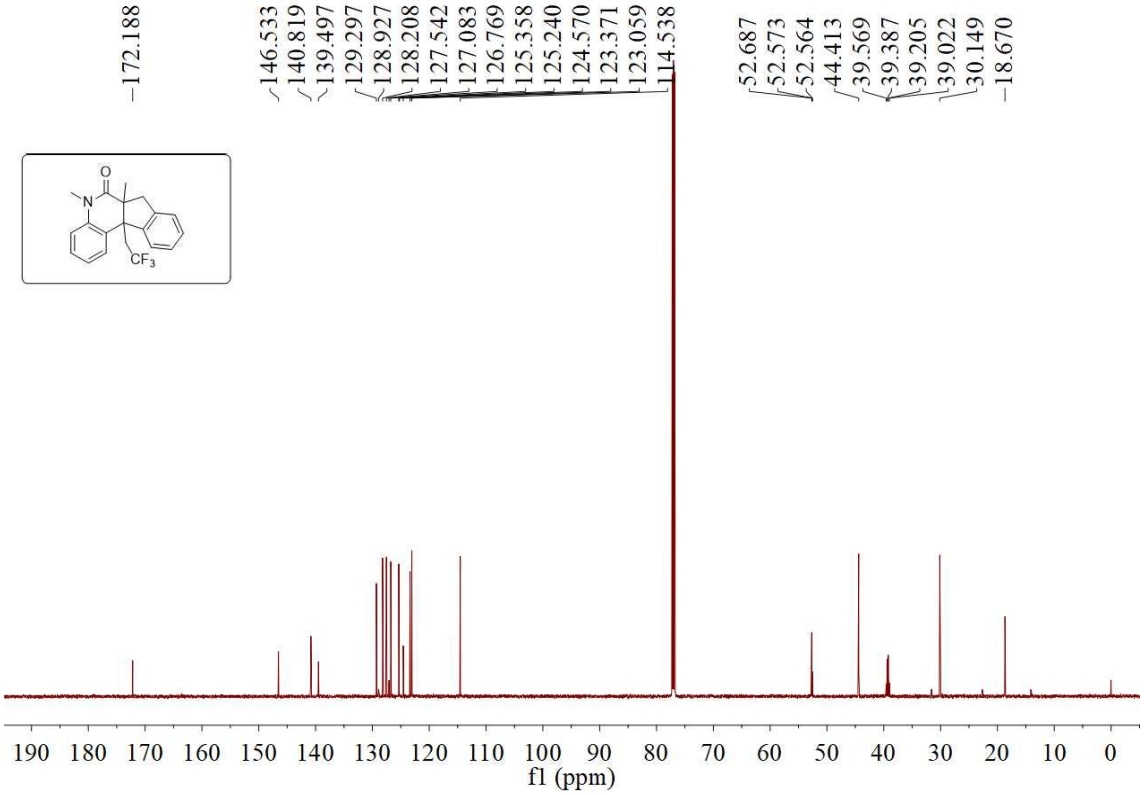
^{19}F-NMR Spectra of 2w



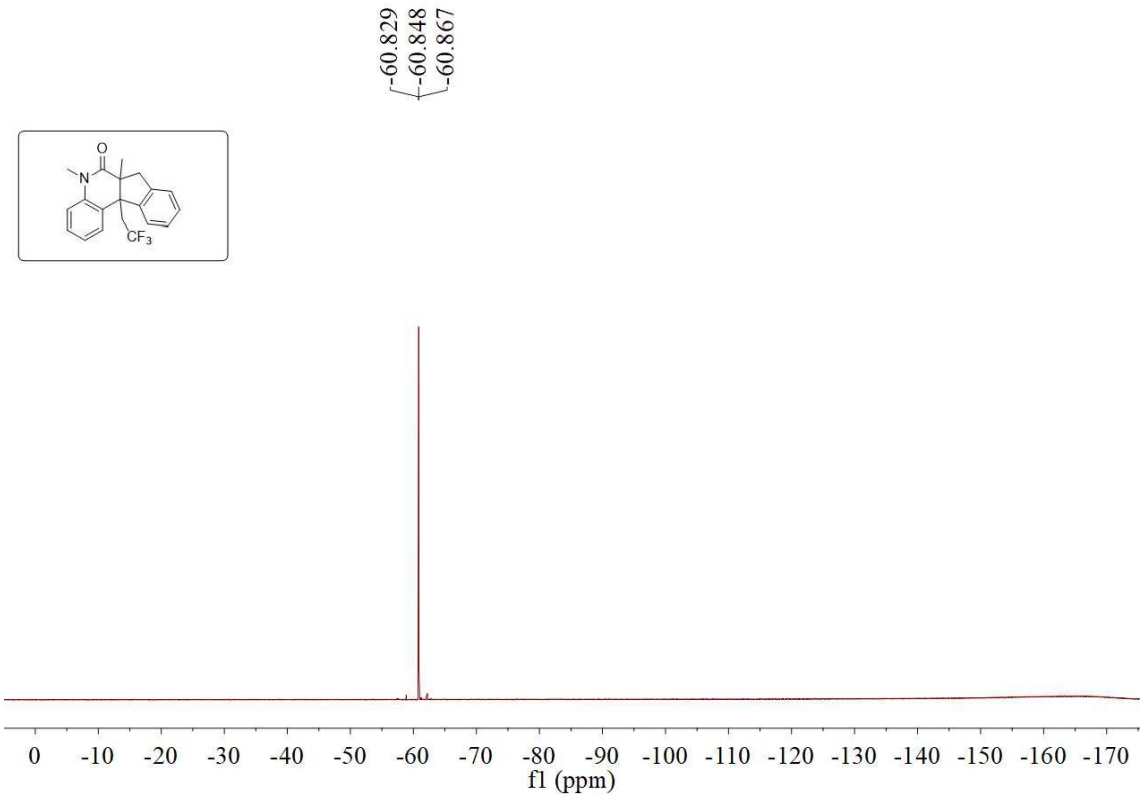
^{1}H-NMR Spectra of (+/-)-*Syn*-4a



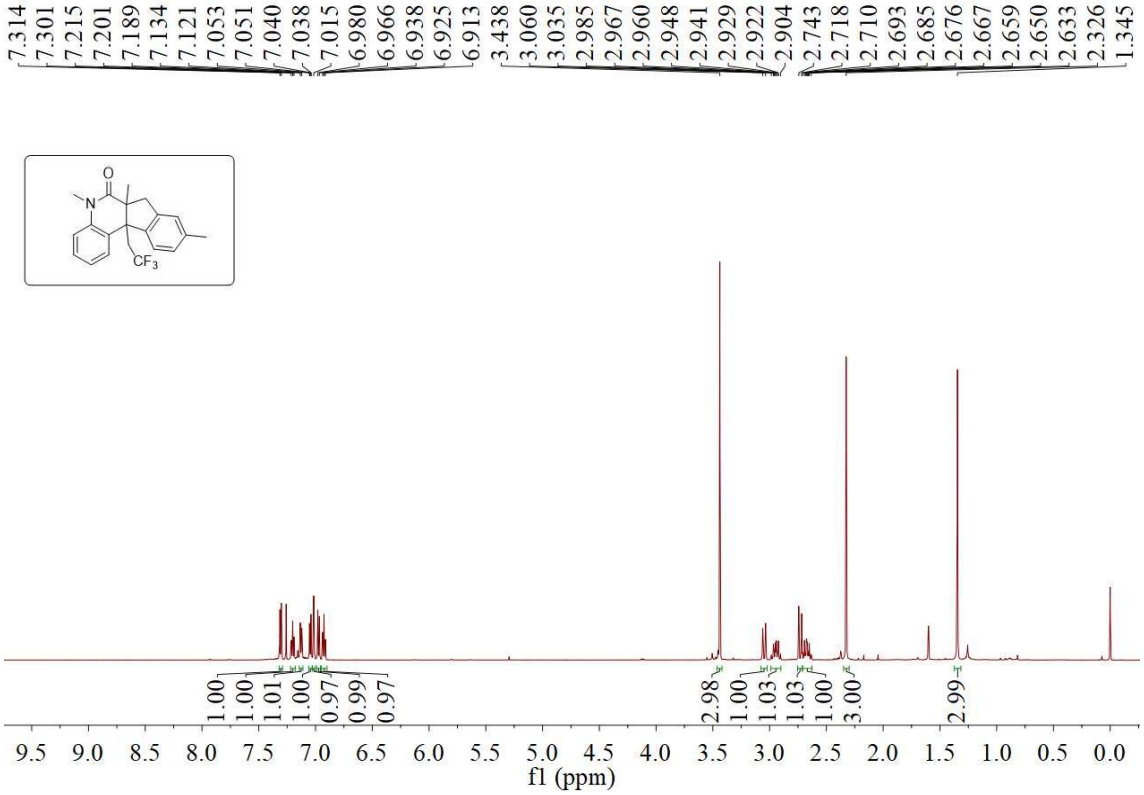
^{13}C-NMR Spectra of (+/-)-*Syn*-4a



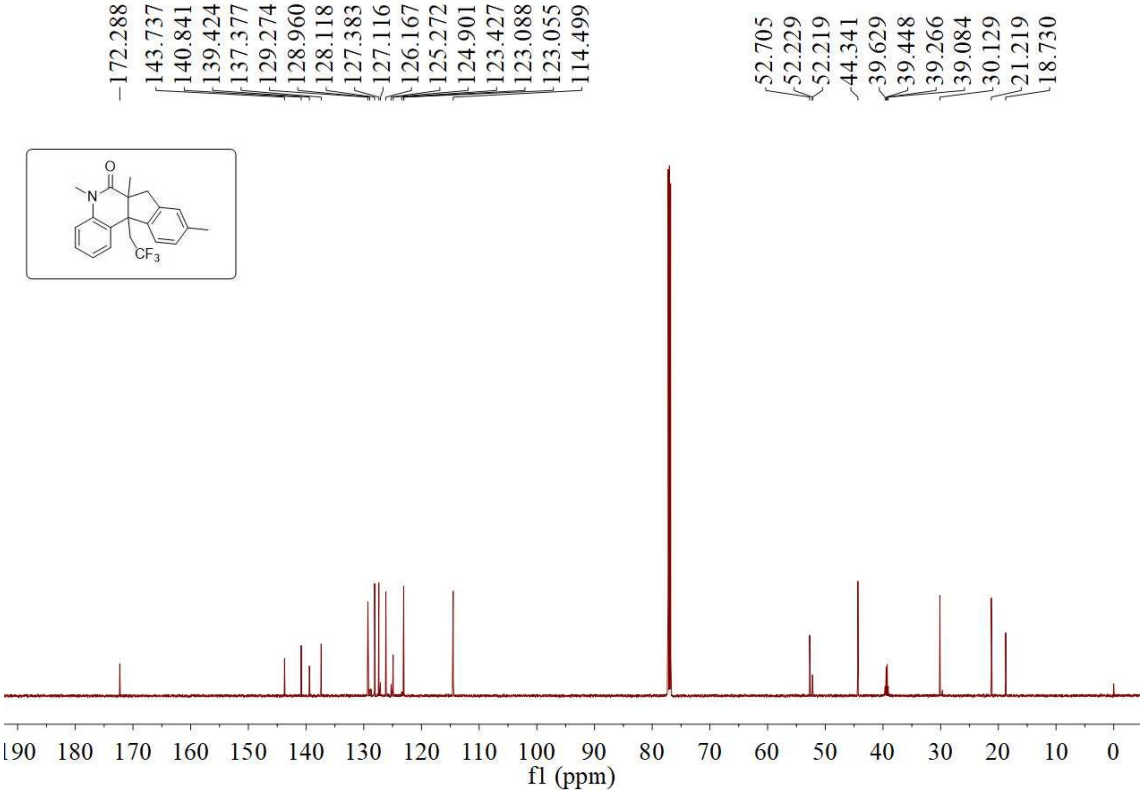
^{19}F-NMR Spectra of (+/-)-*Syn*-4a



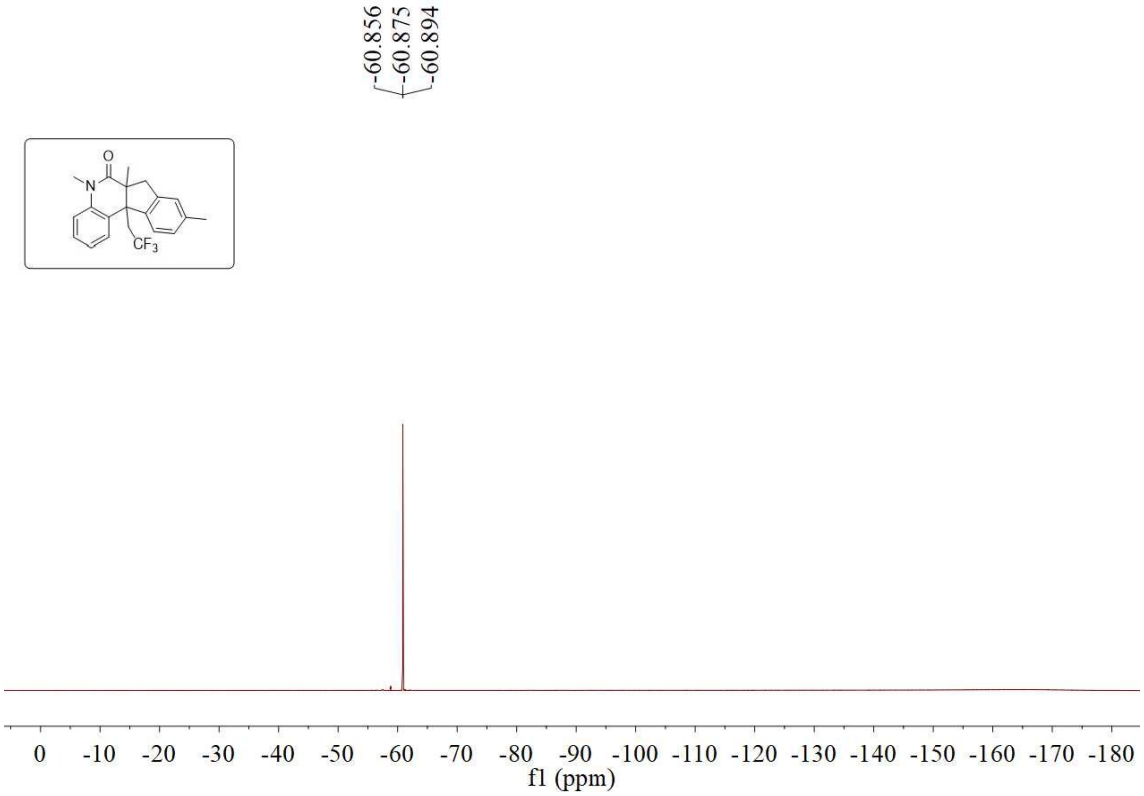
^{1}H-NMR Spectra of (+/-)-*Syn*-4b



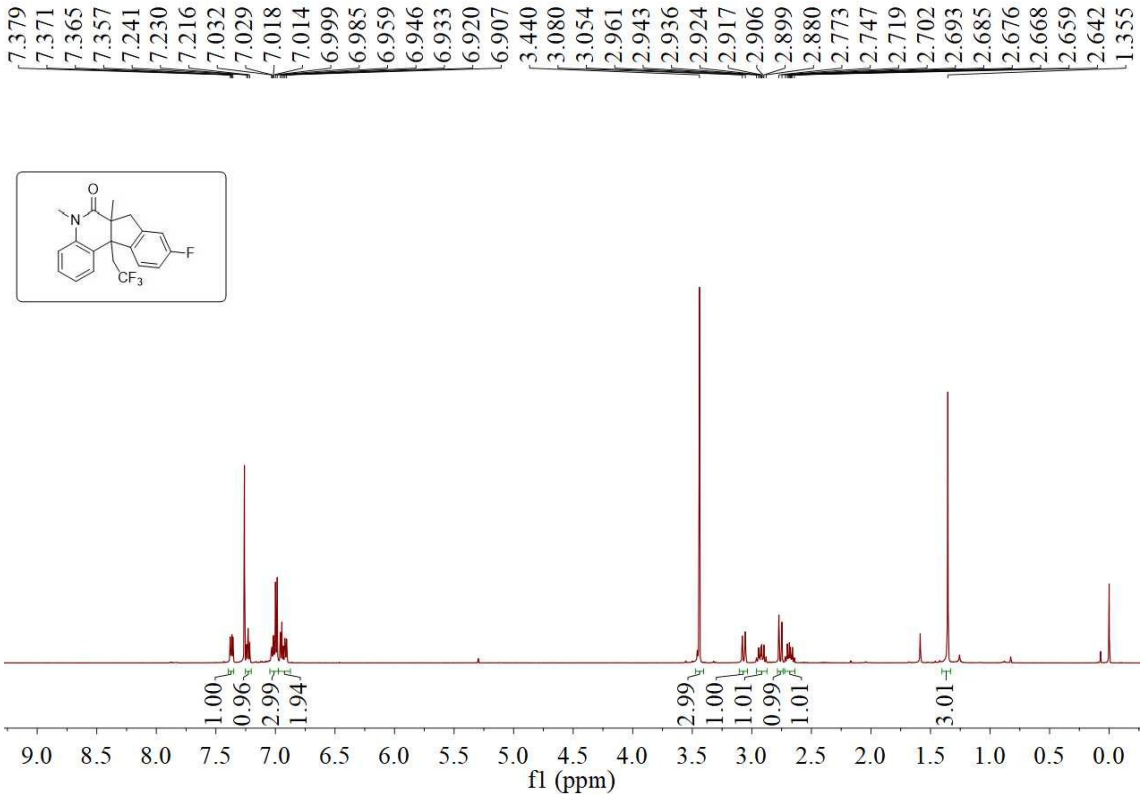
^{13}C-NMR Spectra of (+/-)-*Syn*-4b



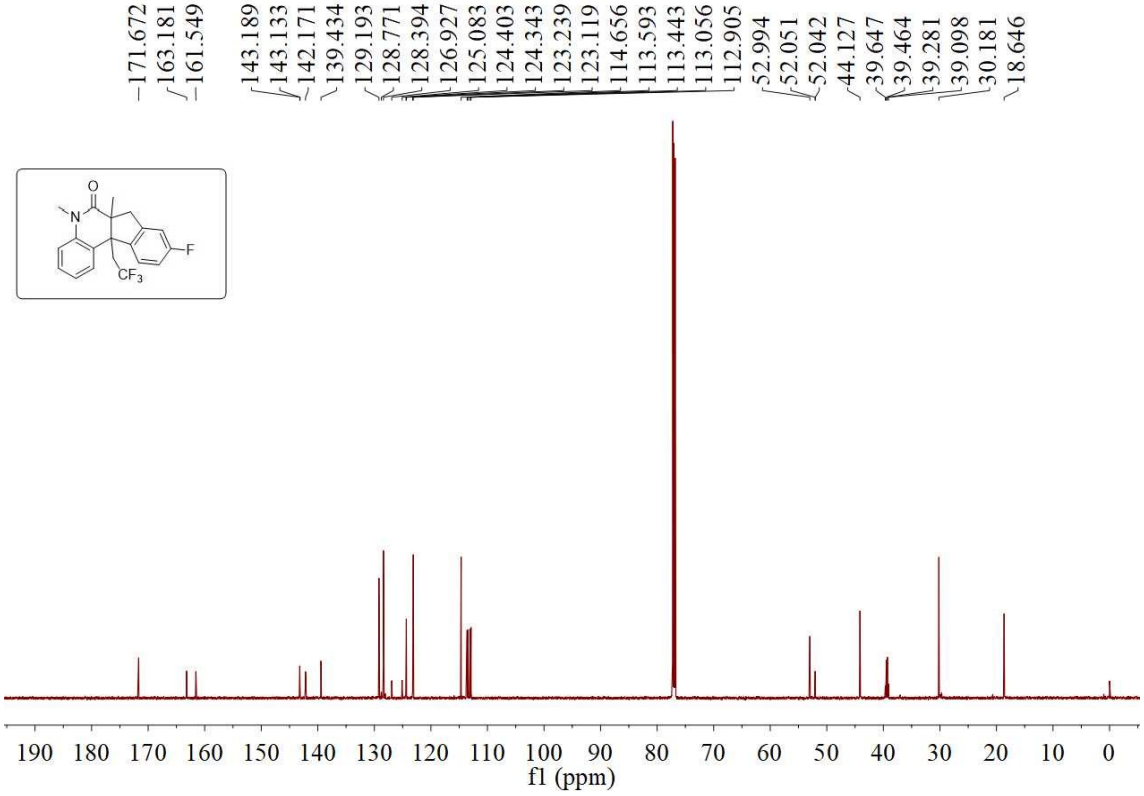
^{19}F-NMR Spectra of (+/-)-*Syn*-4b



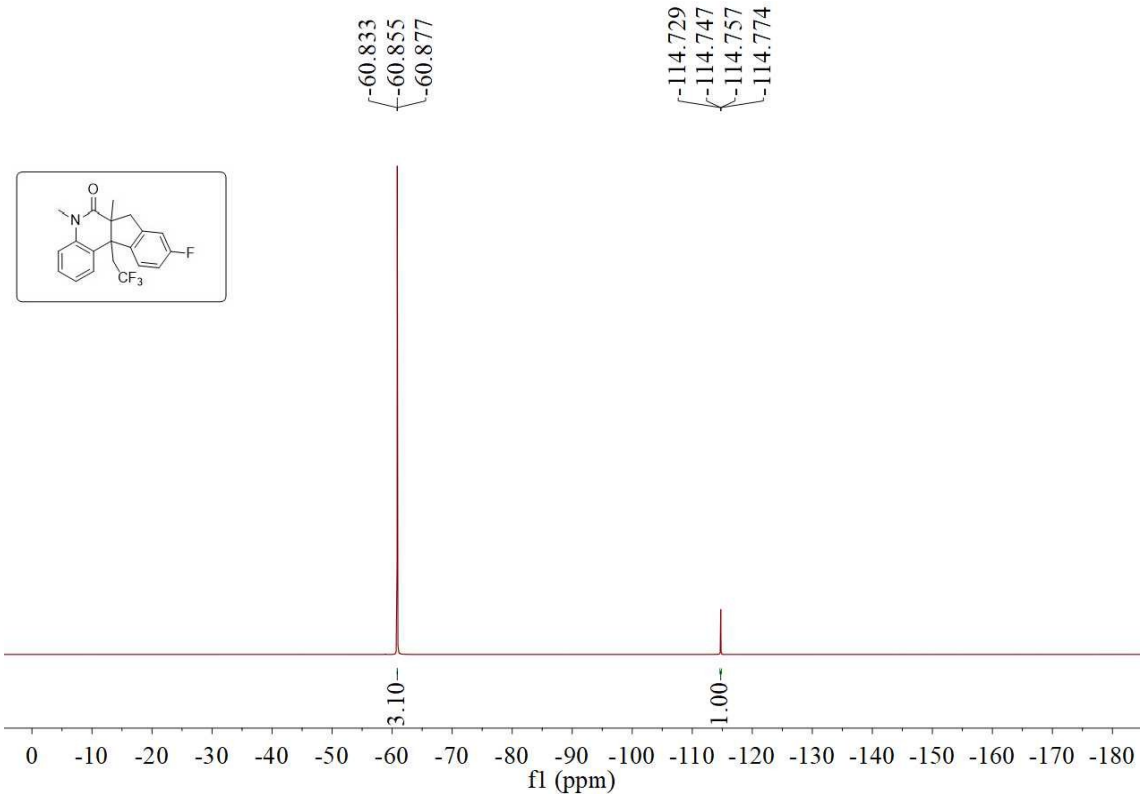
^{1}H-NMR Spectra of (+/-)-*Syn*-4c



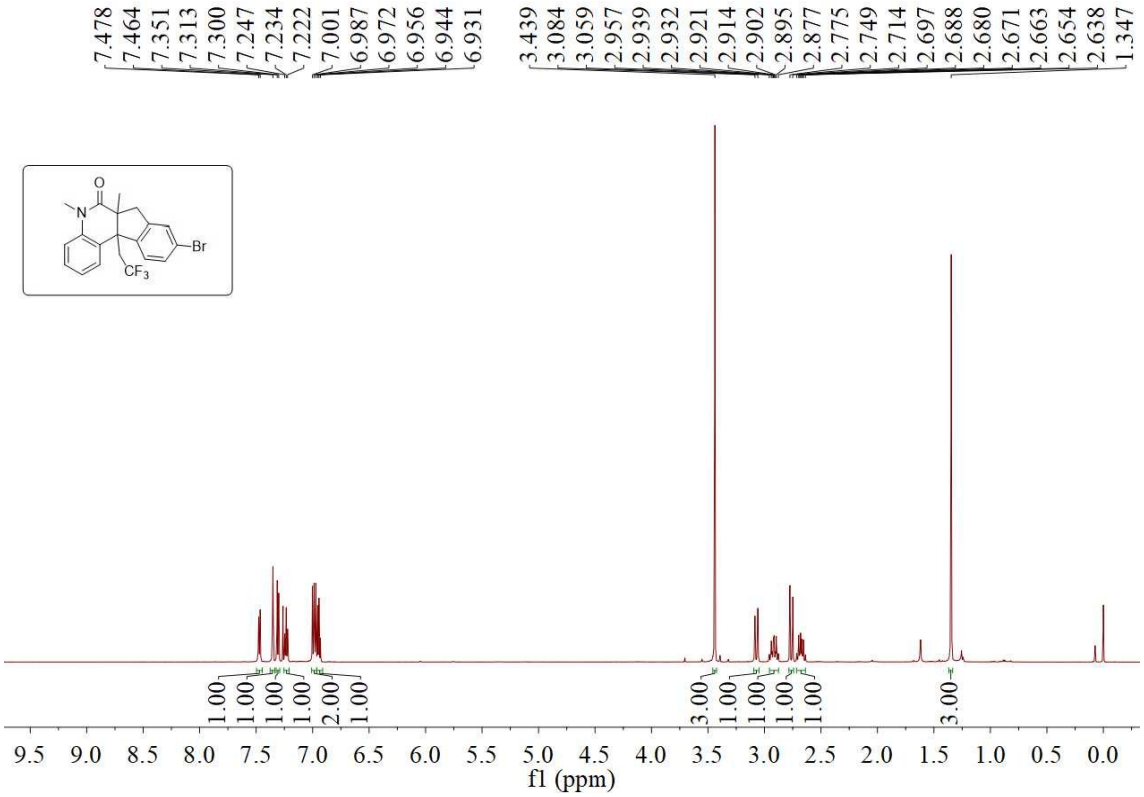
^{13}C-NMR Spectra of (+/-)-*Syn*-4c



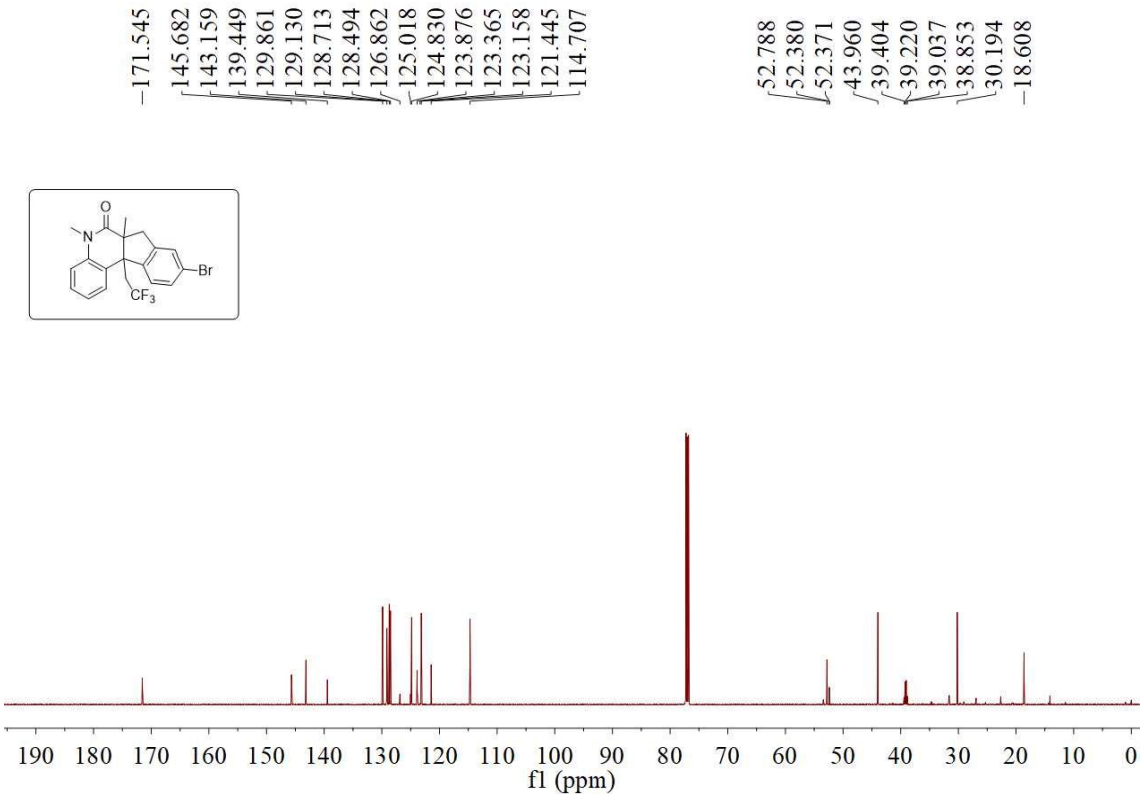
^{19}F-NMR Spectra of (+/-)-*Syn*-4c



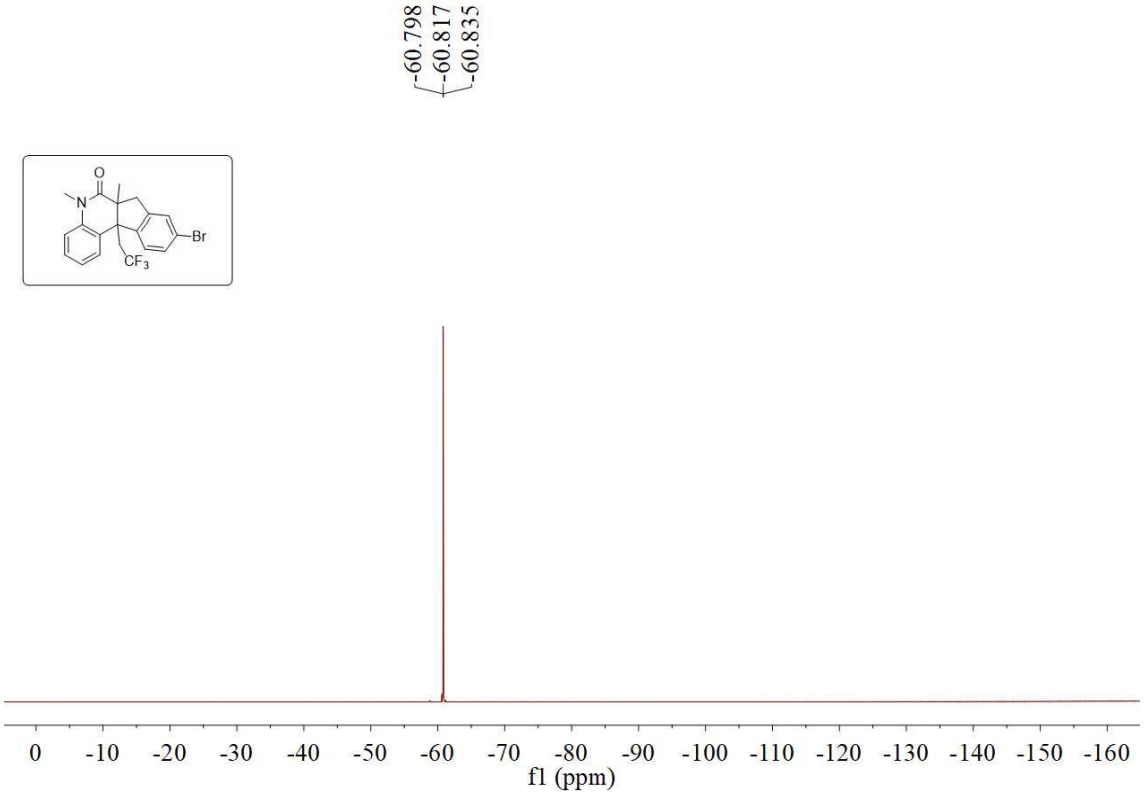
^{1}H-NMR Spectra of (+/-)-*Syn*-4d



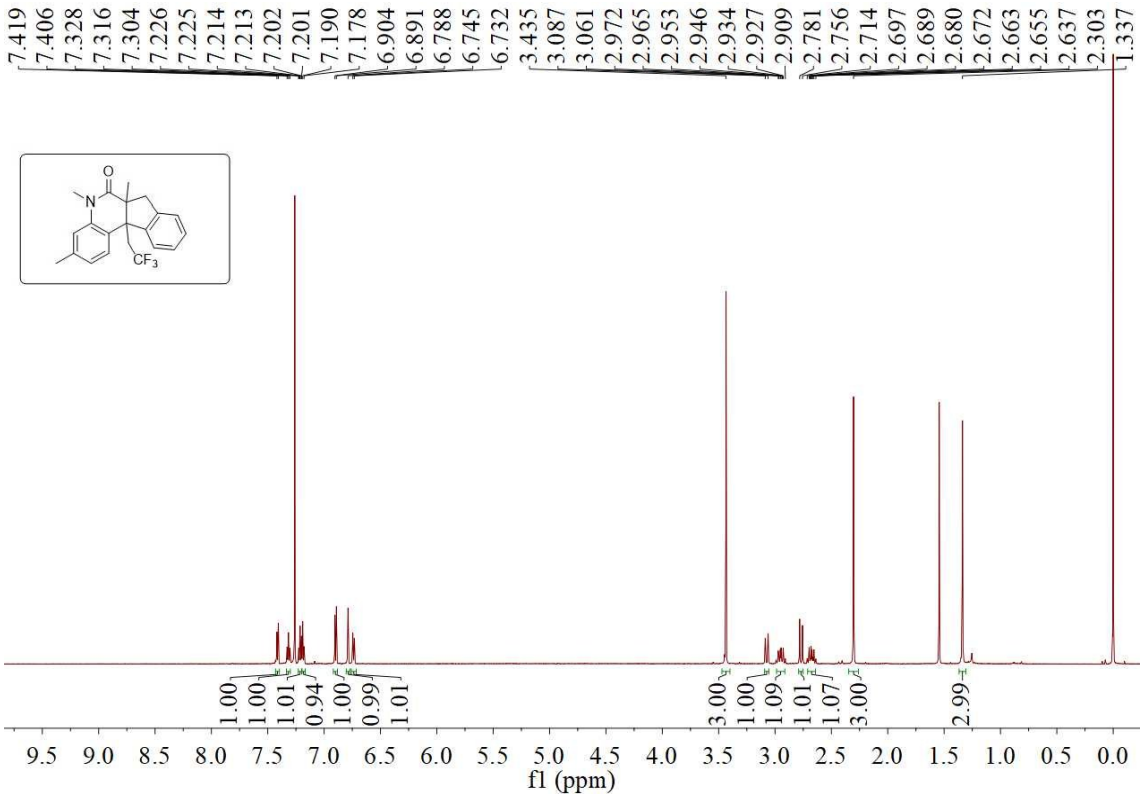
^{13}C-NMR Spectra of (+/-)-*Syn*-4d



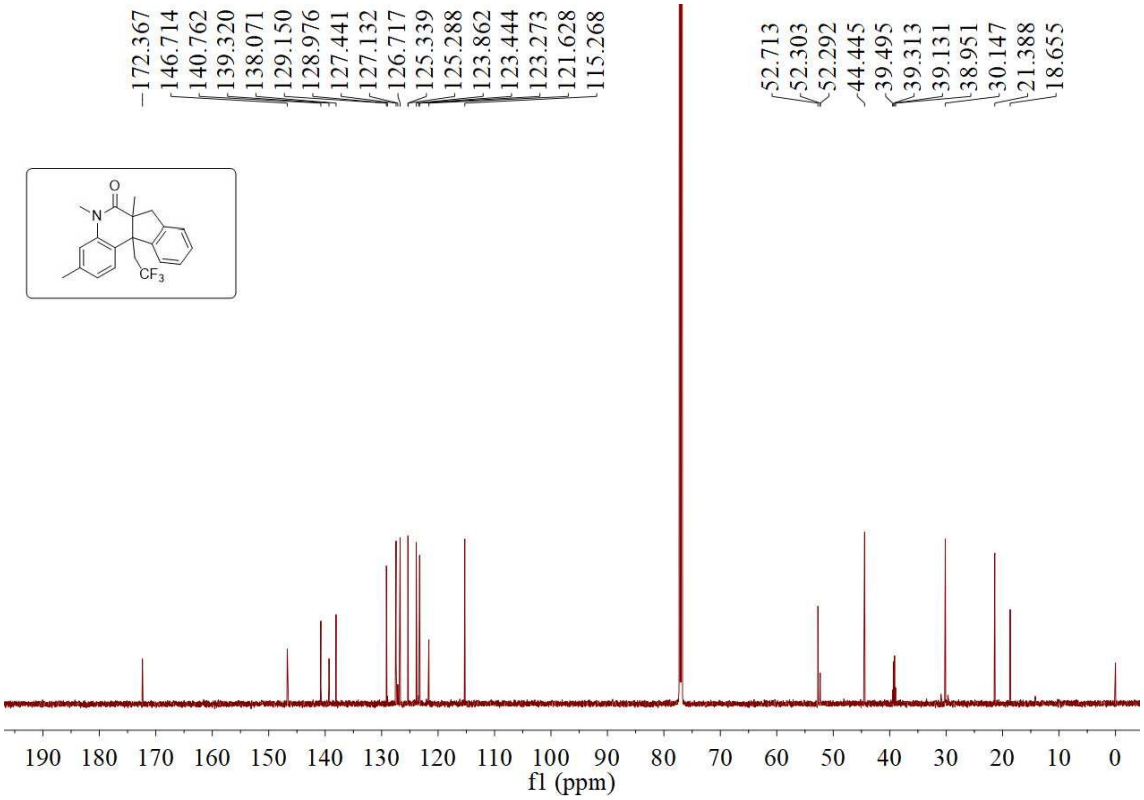
^{19}F-NMR Spectra of (+/-)-*Syn*-4d



^{1}H-NMR Spectra of (+/-)-*Syn*-4e



^{13}C-NMR Spectra of (+/-)-*Syn*-4e



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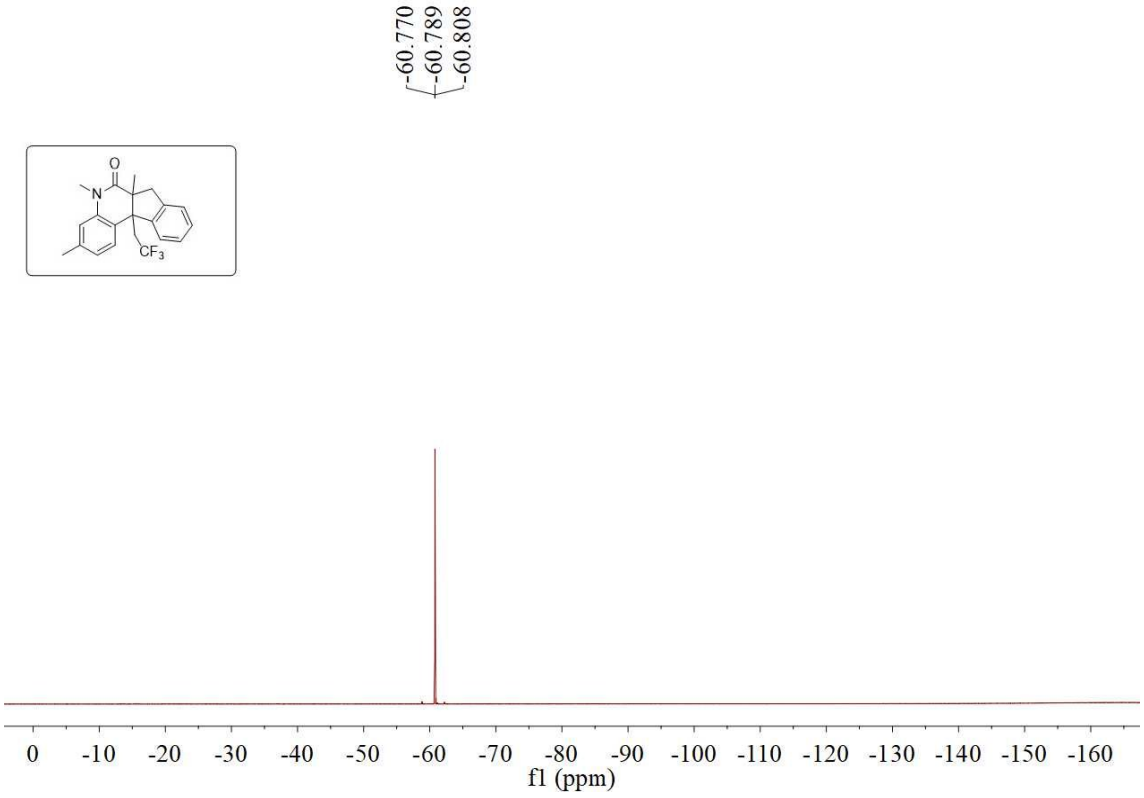
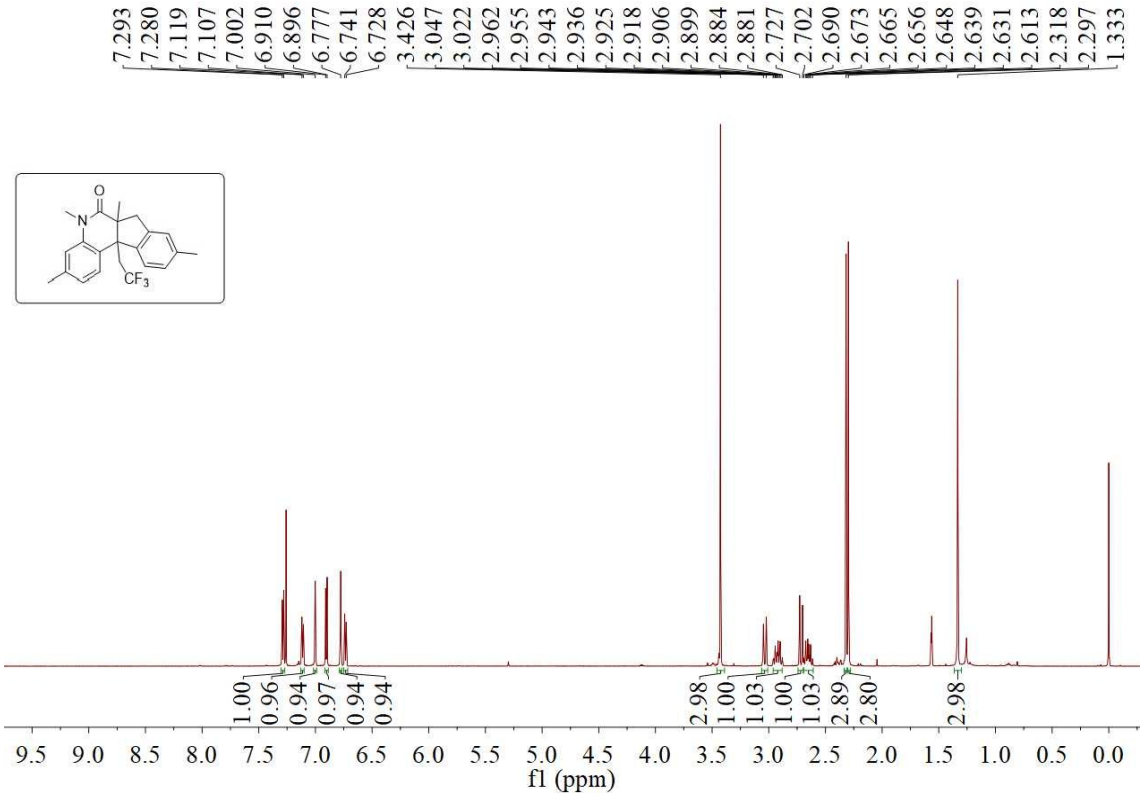
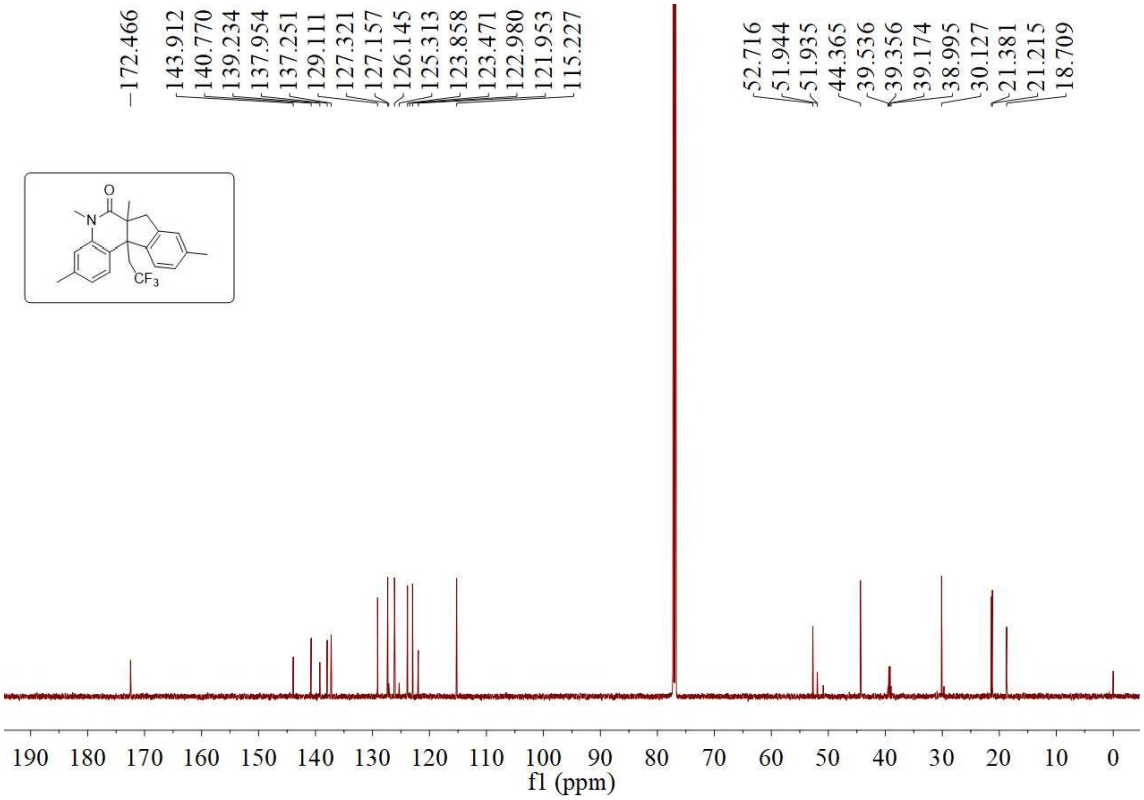


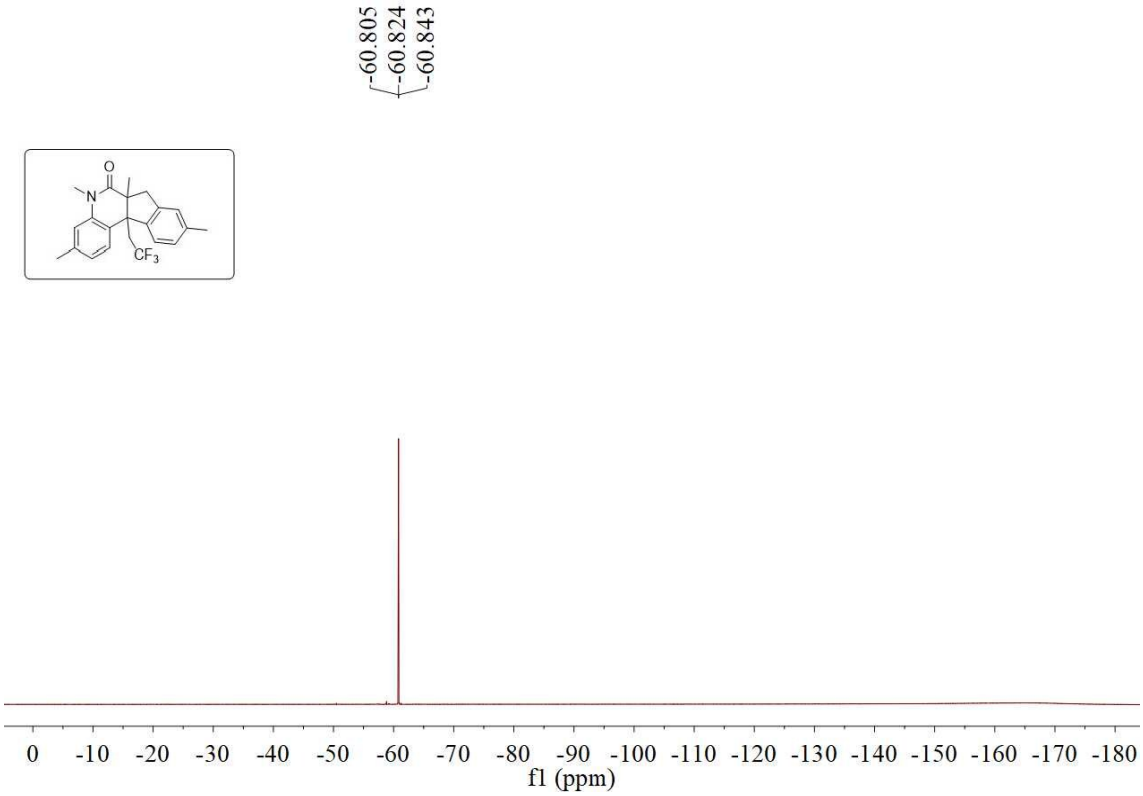
^{1}H-NMR Spectra of (+/-)-*Syn*-4f



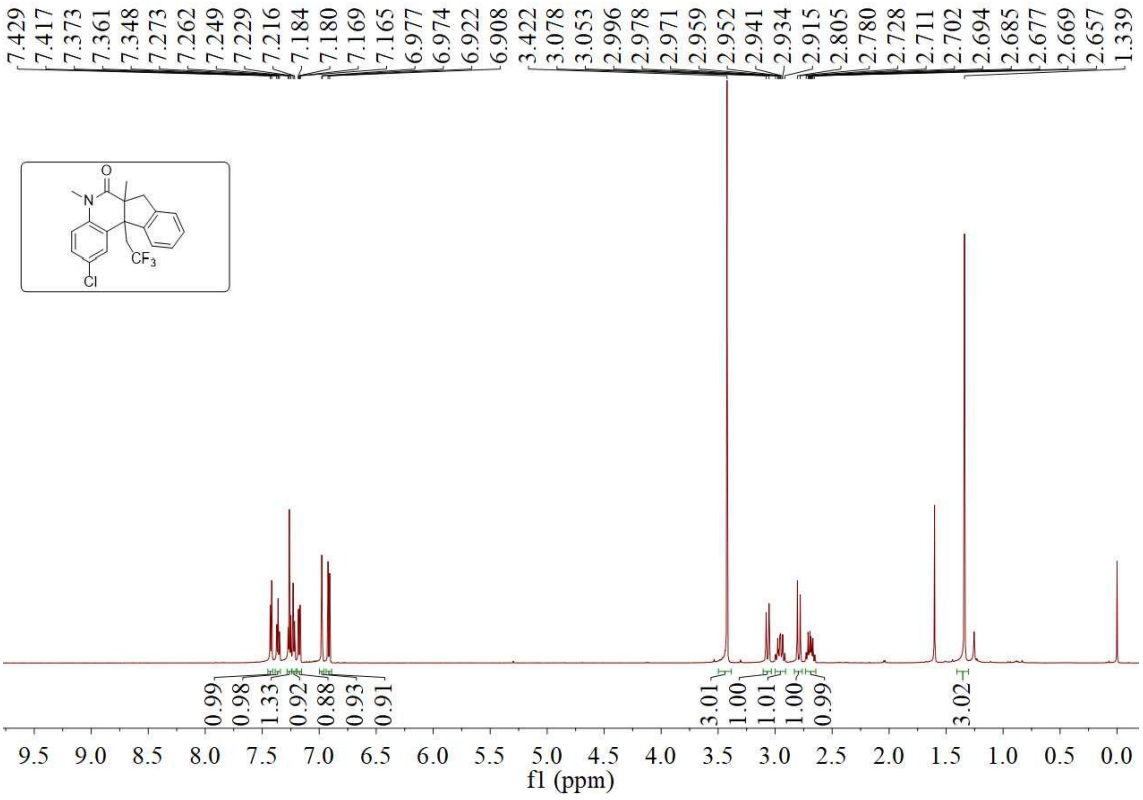
^{13}C-NMR Spectra of (+/-)-*Syn*-4f



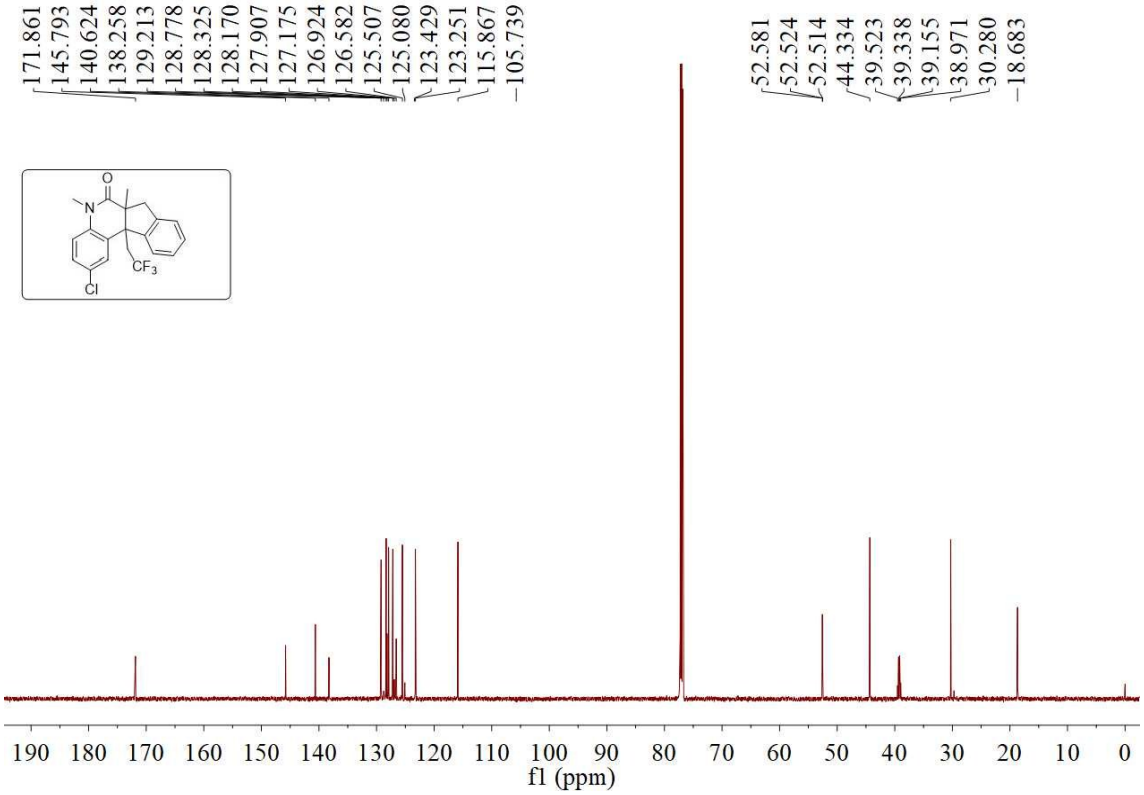
^{19}F-NMR Spectra of (+/-)-*Syn*-4f



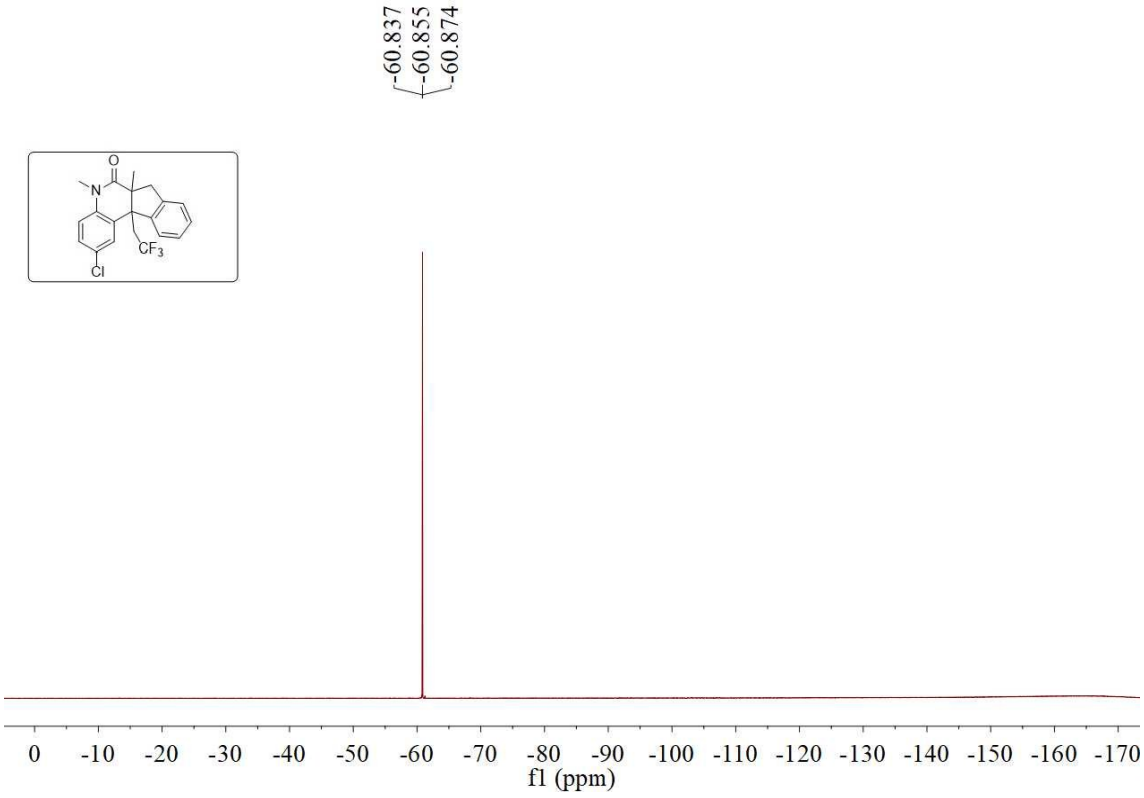
^{1}H-NMR Spectra of (+/-)-*Syn*-4g



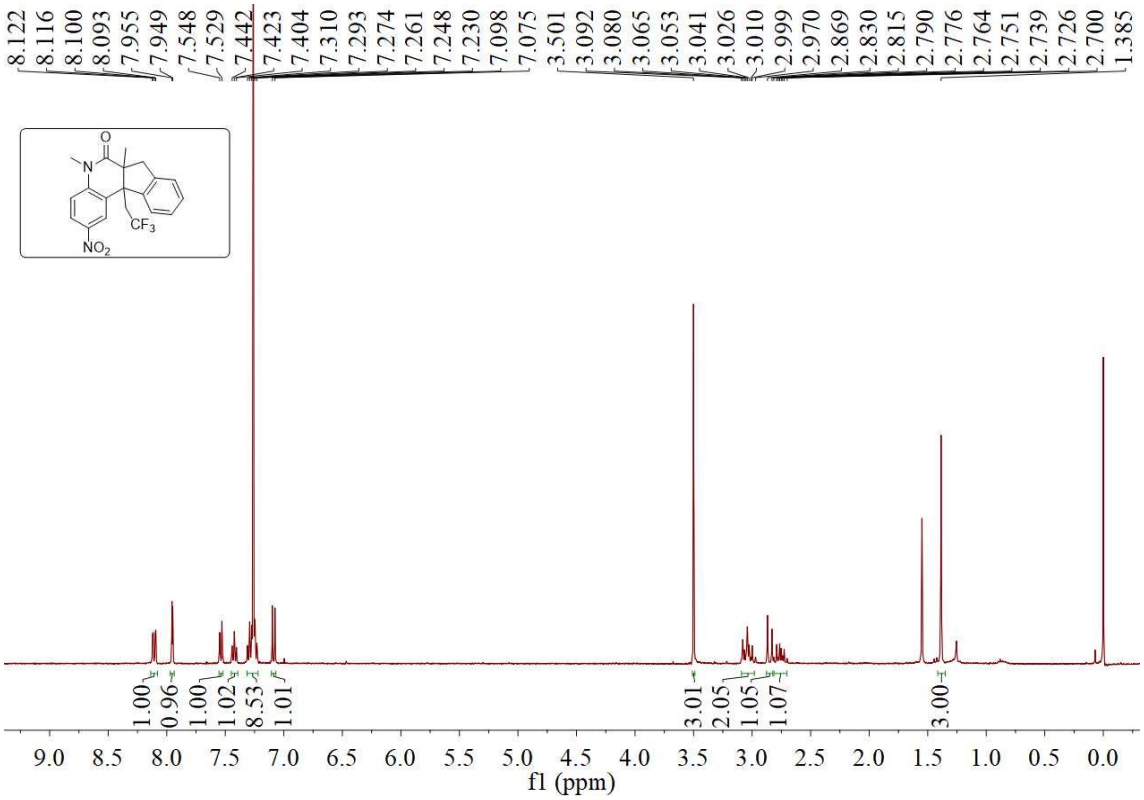
^{13}C-NMR Spectra of (+/-)-*Syn*-4g



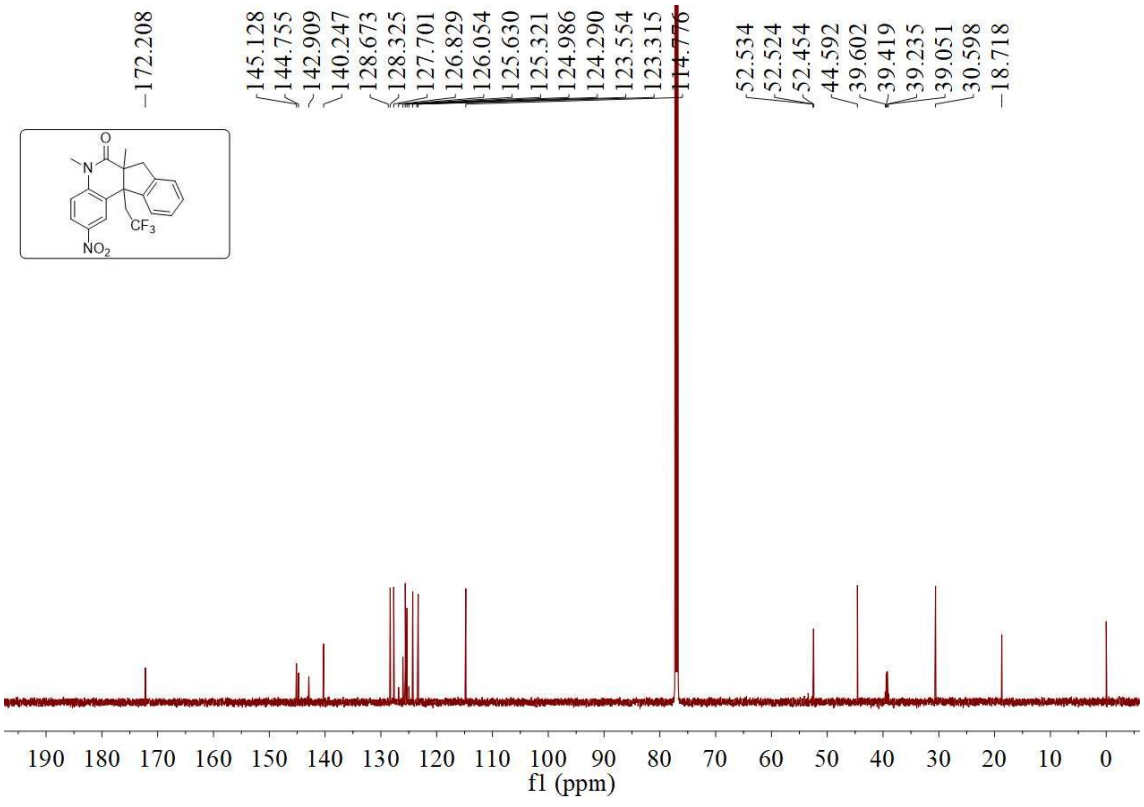
^{19}F-NMR Spectra of (+/-)-*Syn*-4g



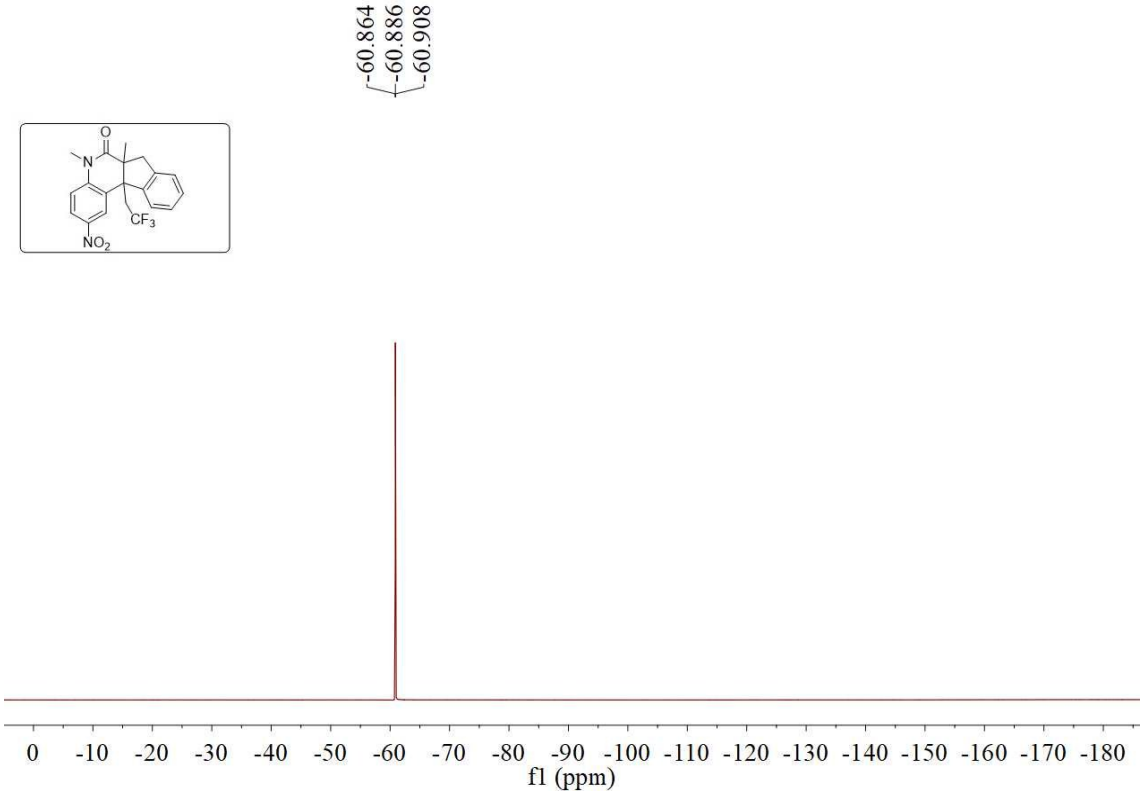
^{1}H-NMR Spectra of (+/-)-*Syn*-4h



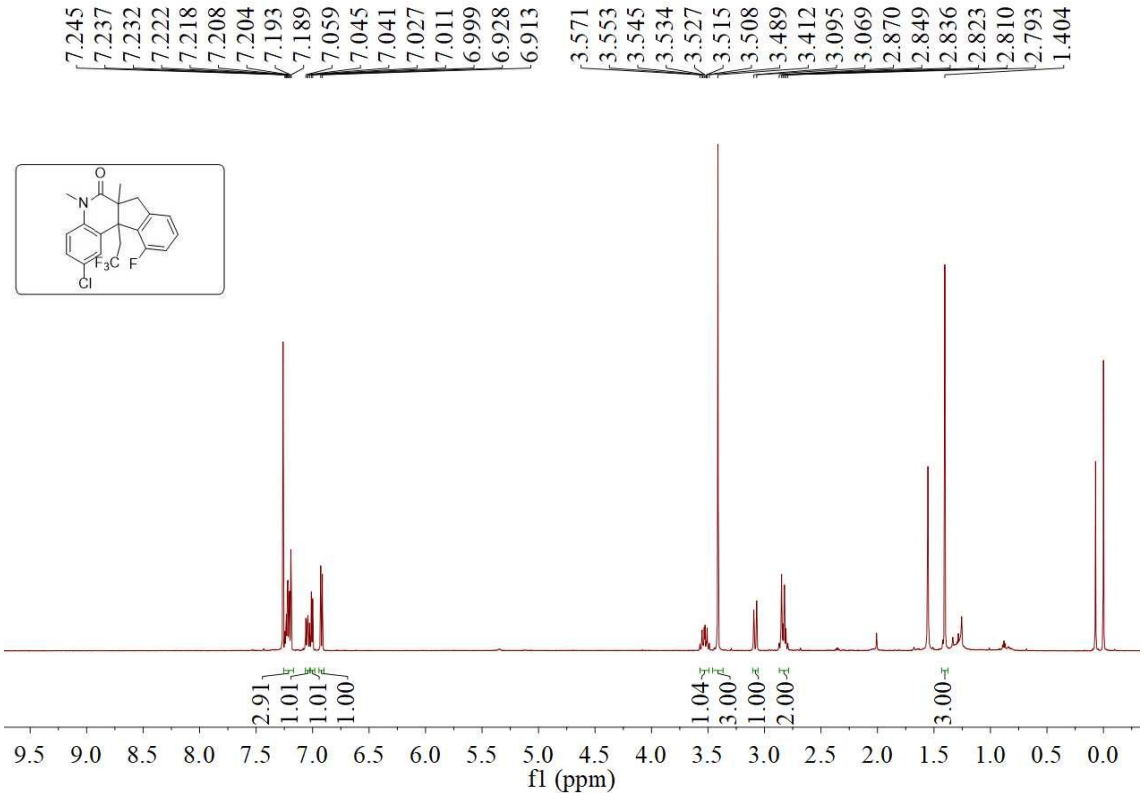
^{13}C-NMR Spectra of (+/-)-*Syn*-4h



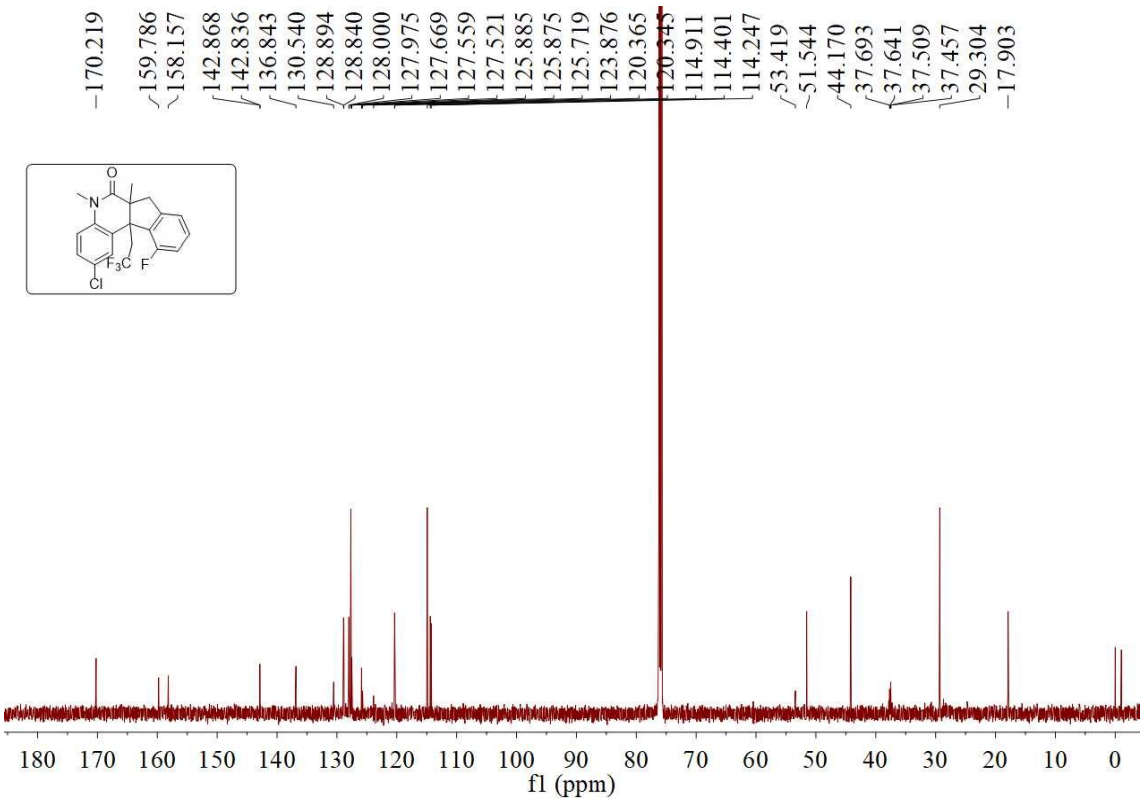
^{19}F-NMR Spectra of (+/-)-*Syn*-4h



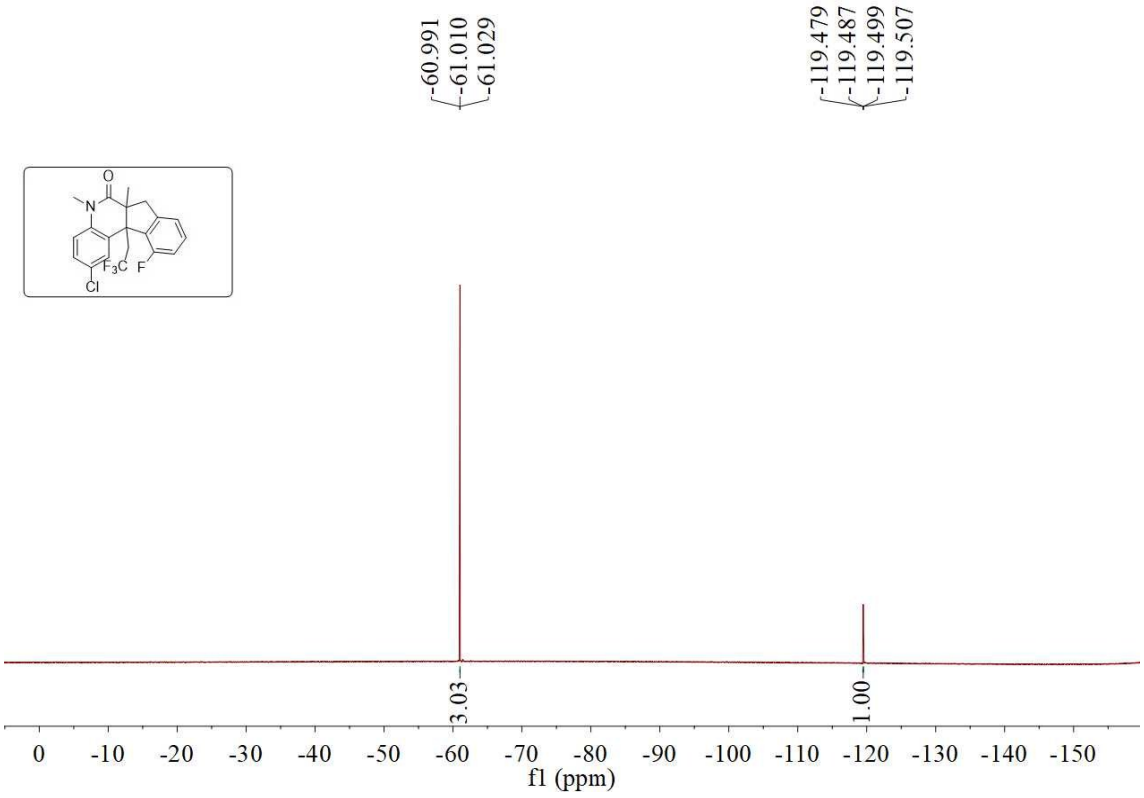
^{1}H-NMR Spectra of (+/-)-*Syn*-4i



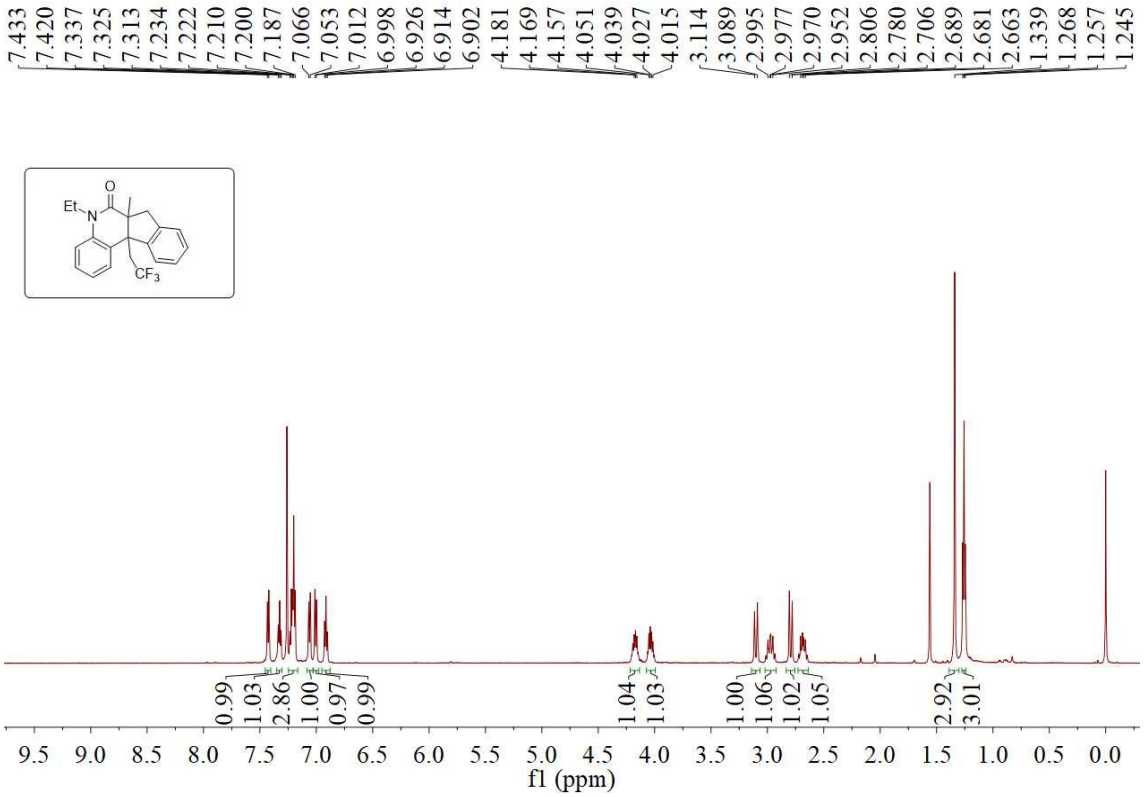
^{13}C-NMR Spectra of (+/-)-*Syn*-4i



^{19}F-NMR Spectra of (+/-)-*Syn*-4i



^{1}H-NMR Spectra of (+/-)-*Syn*-4j



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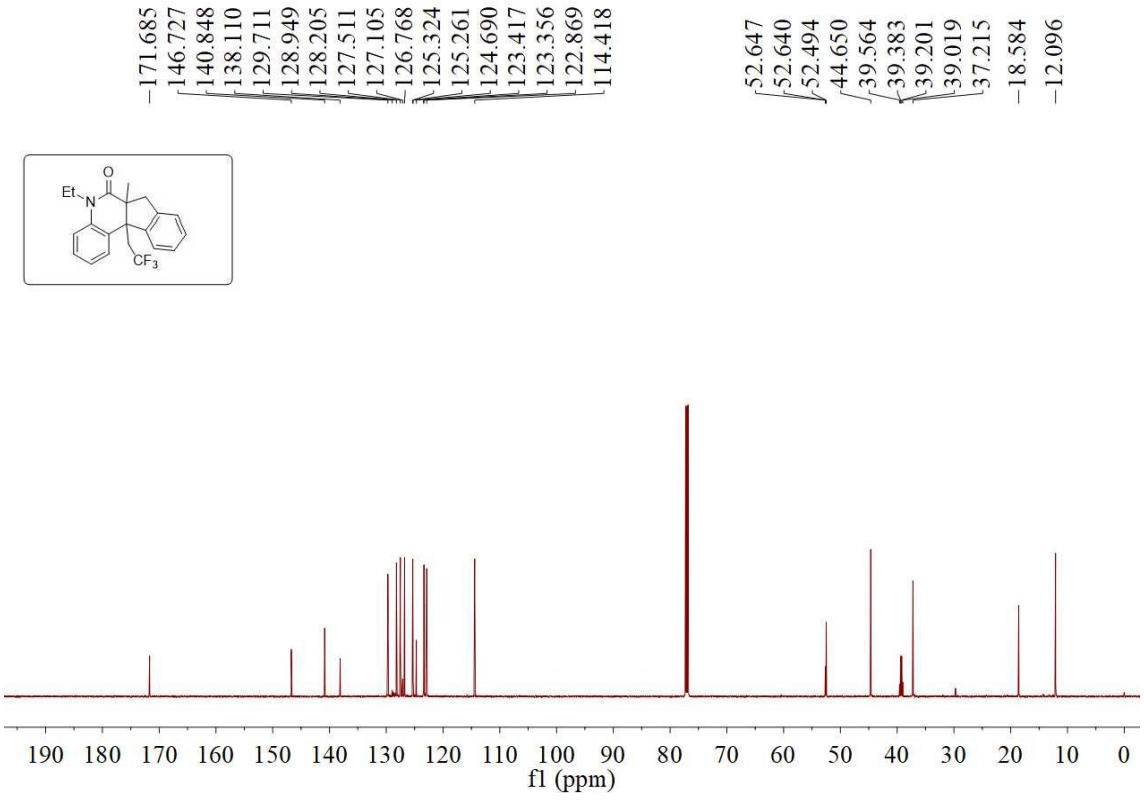
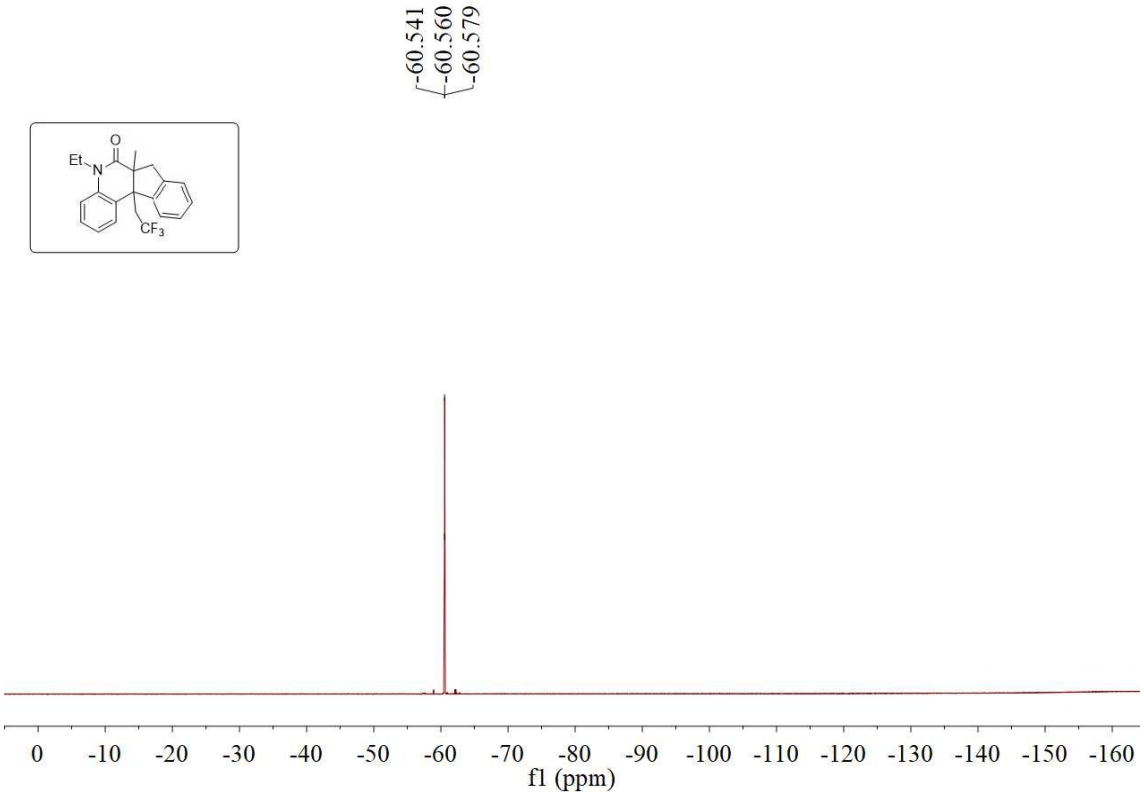
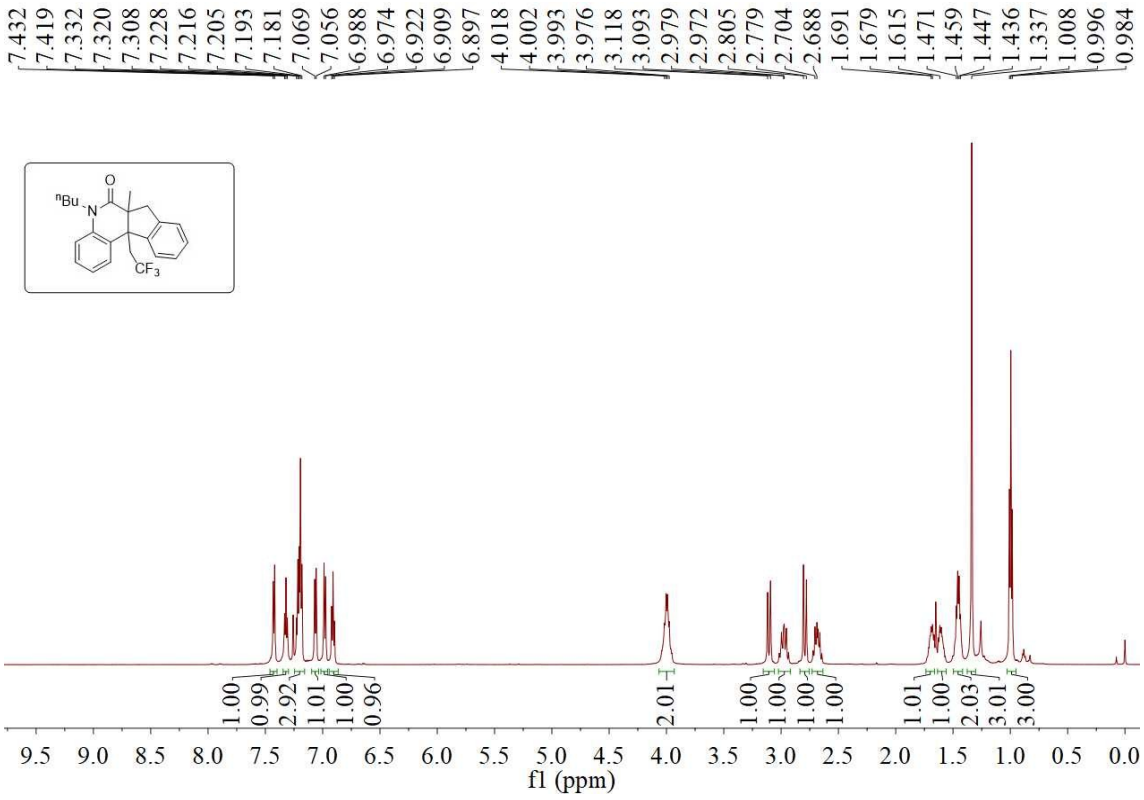


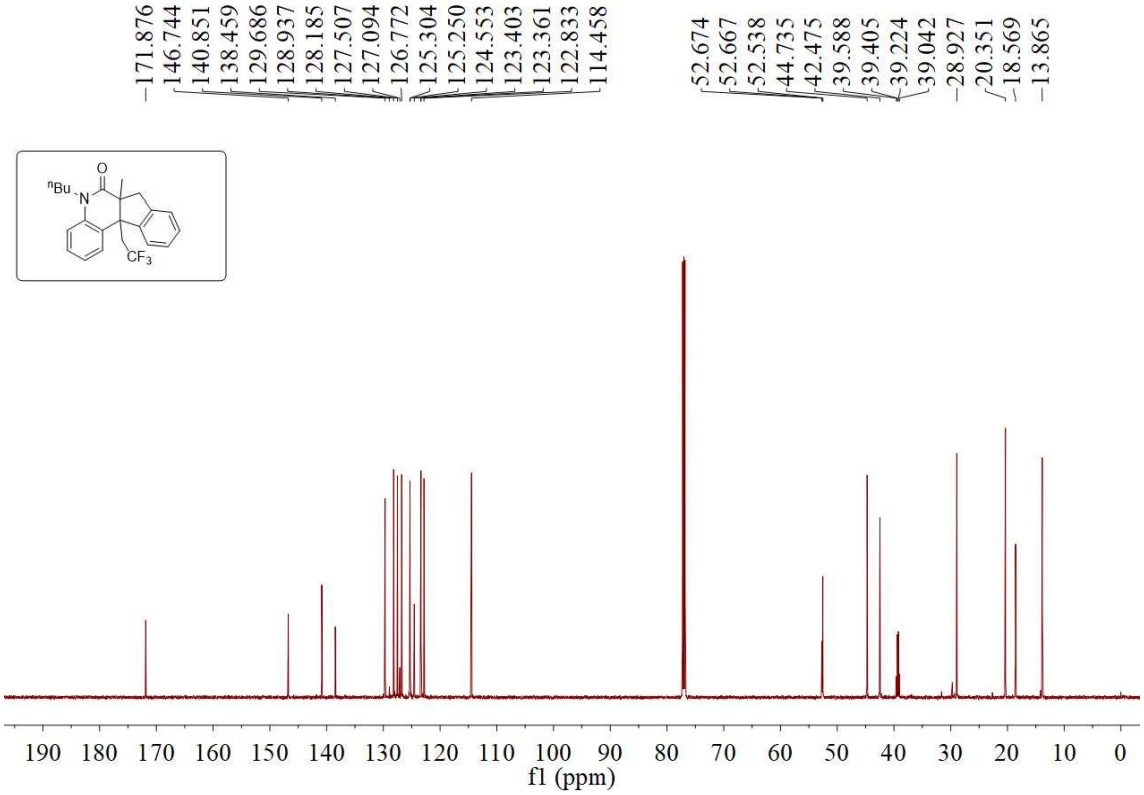
^{19}F-NMR Spectra of (+/-)-*Syn*-4j



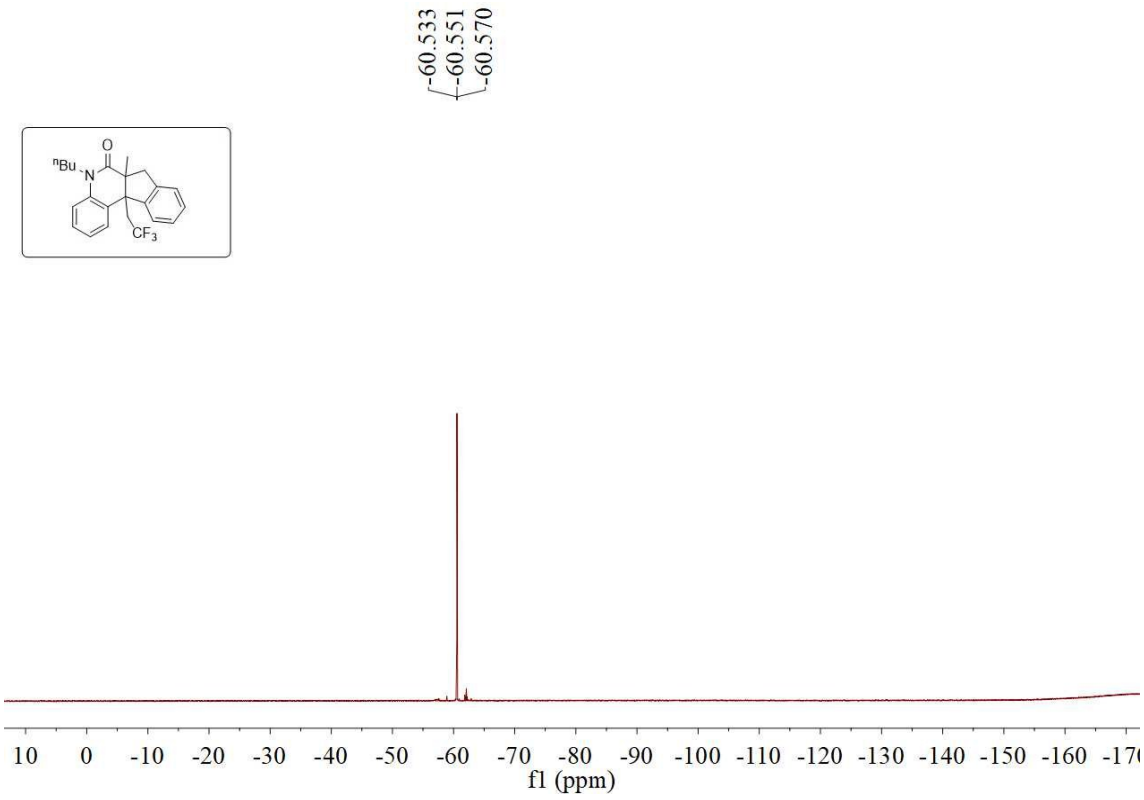
^{1}H-NMR Spectra of (+/-)-*Syn*-4k



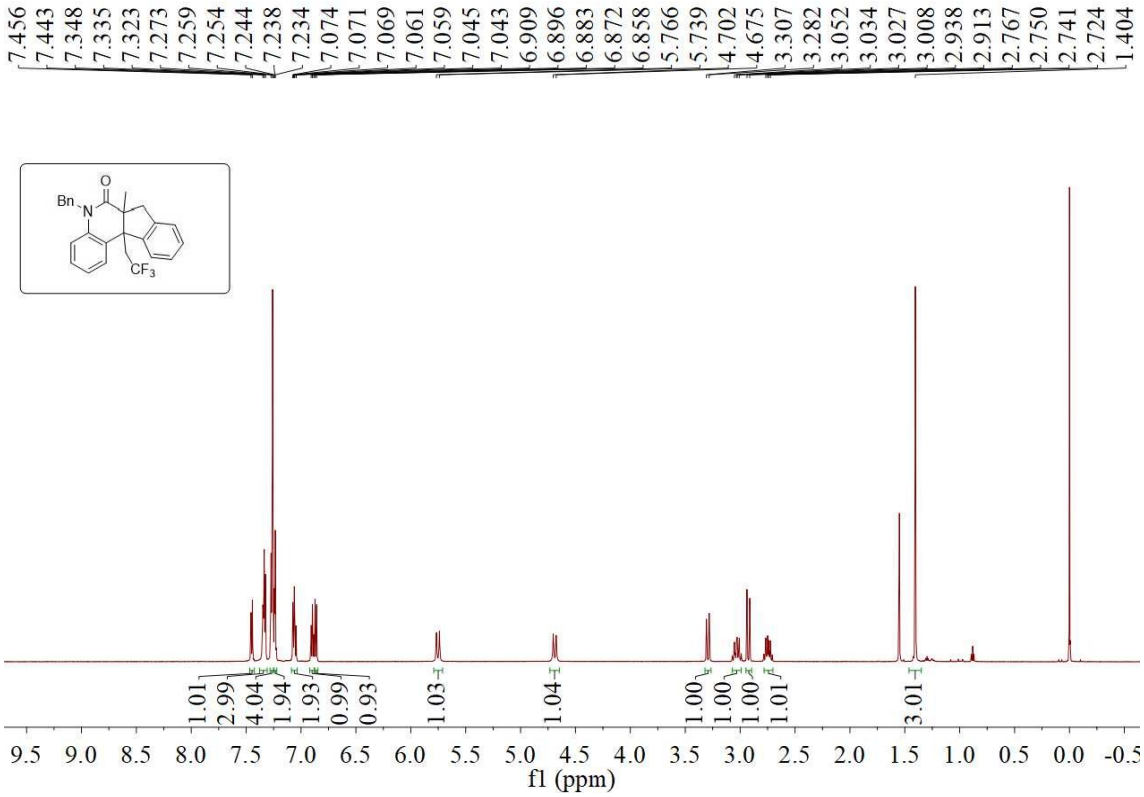
^{13}C-NMR Spectra of (+/-)-*Syn*-4k



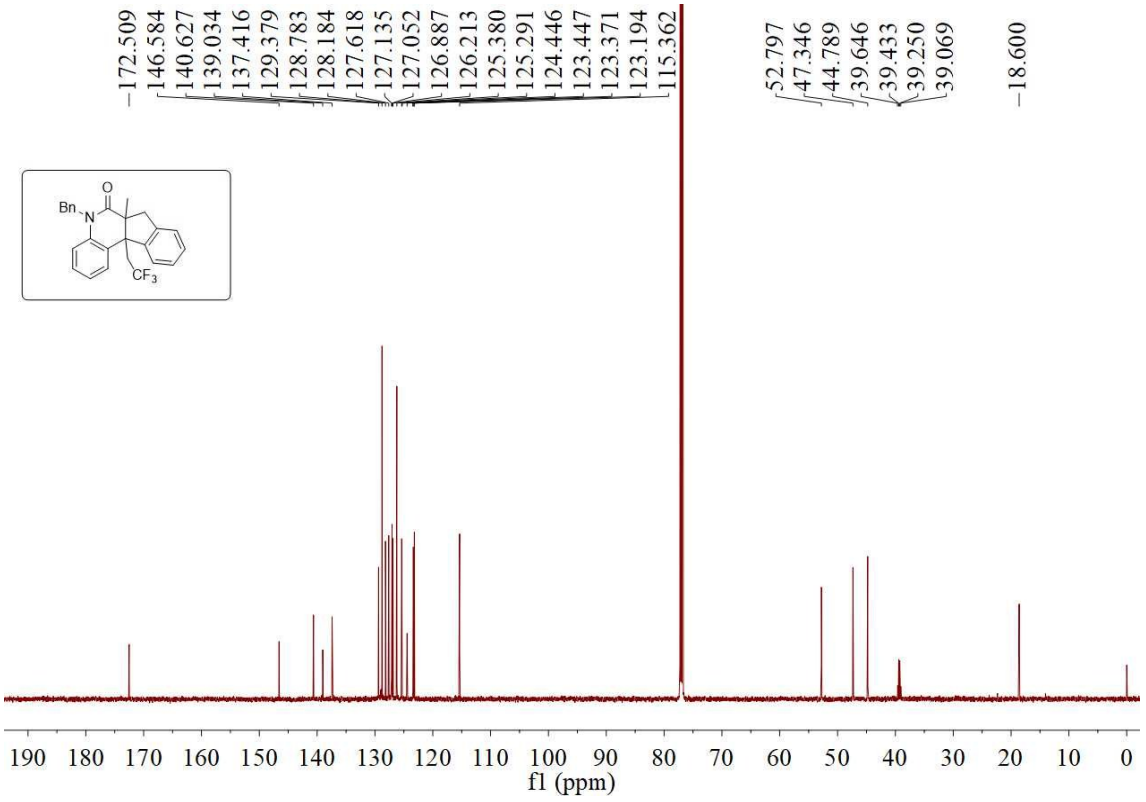
^{19}F-NMR Spectra of (+/-)-*Syn*-4k



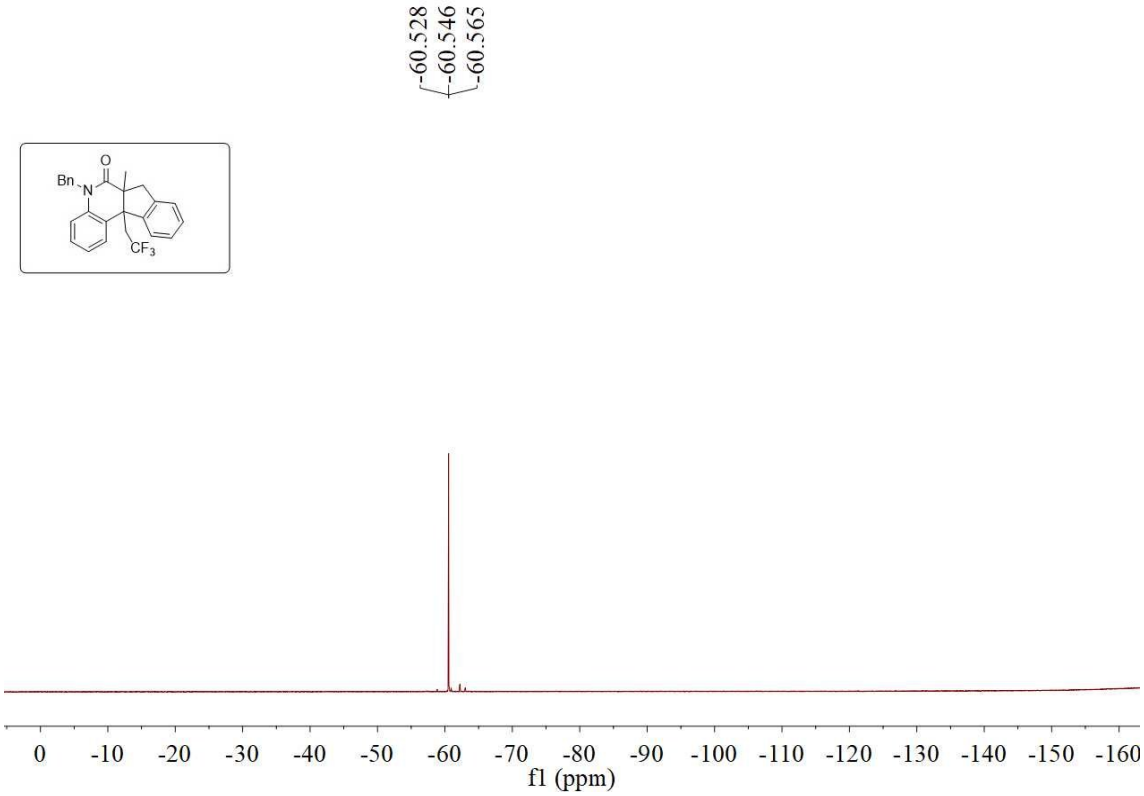
^{1}H-NMR Spectra of (+/-)-*Syn*-4l



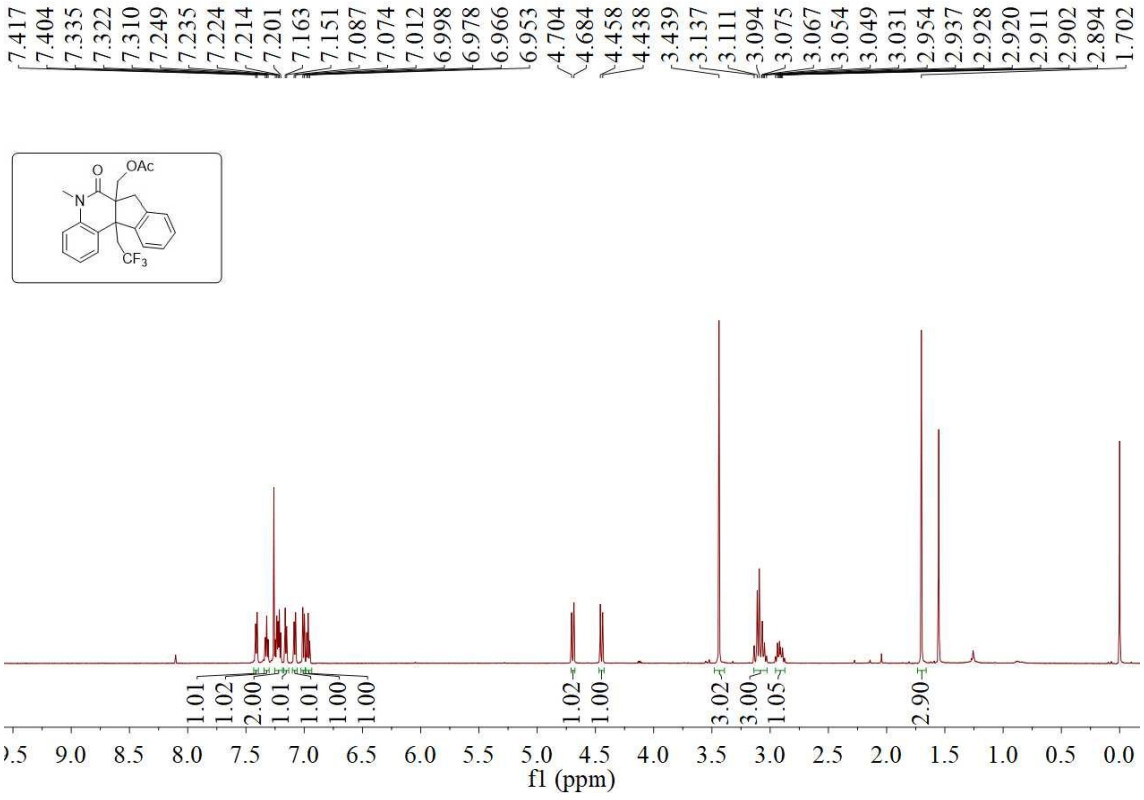
^{13}C-NMR Spectra of (+/-)-*Syn*-4l



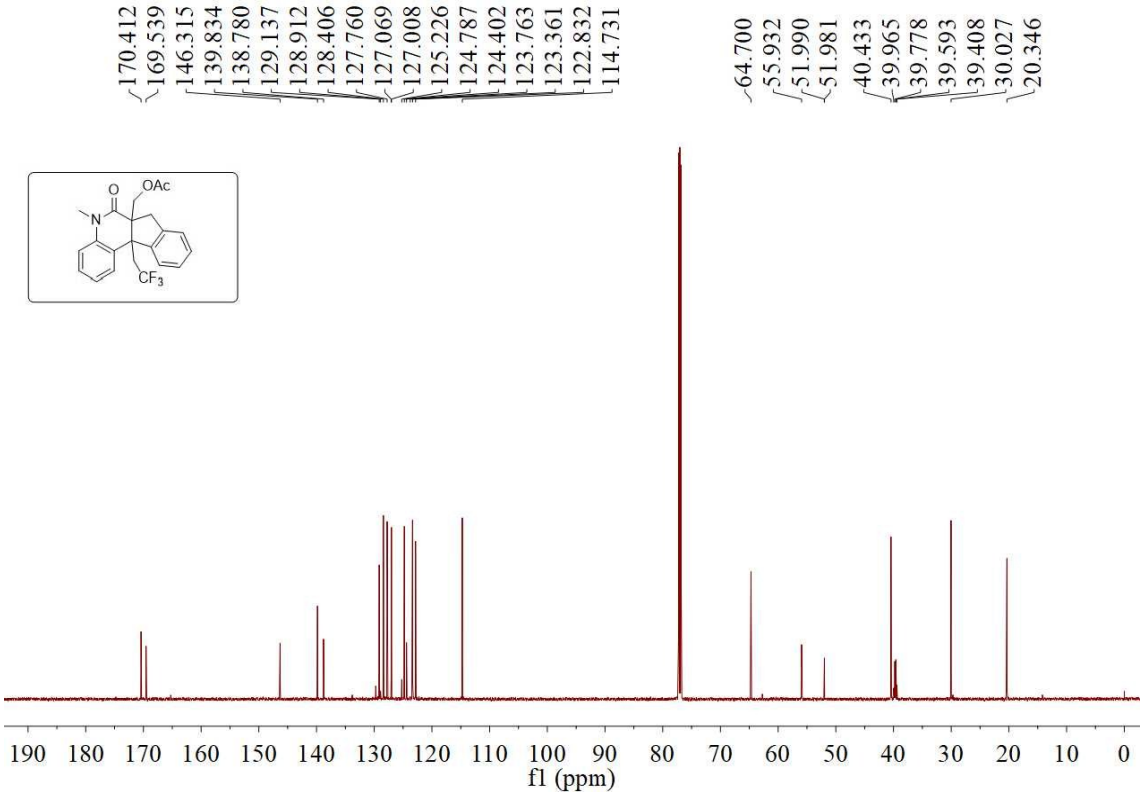
^{19}F-NMR Spectra of (+/-)-*Syn*-4l



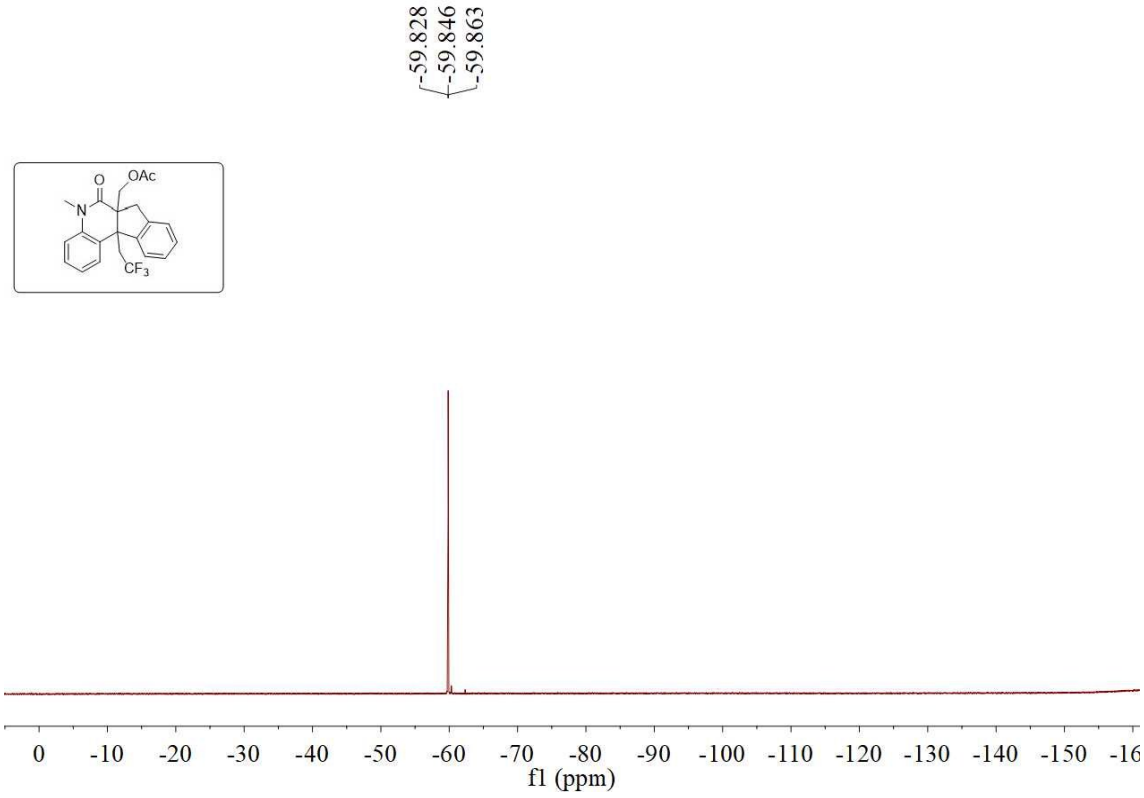
^{1}H-NMR Spectra of (+/-)-*Syn*-4m



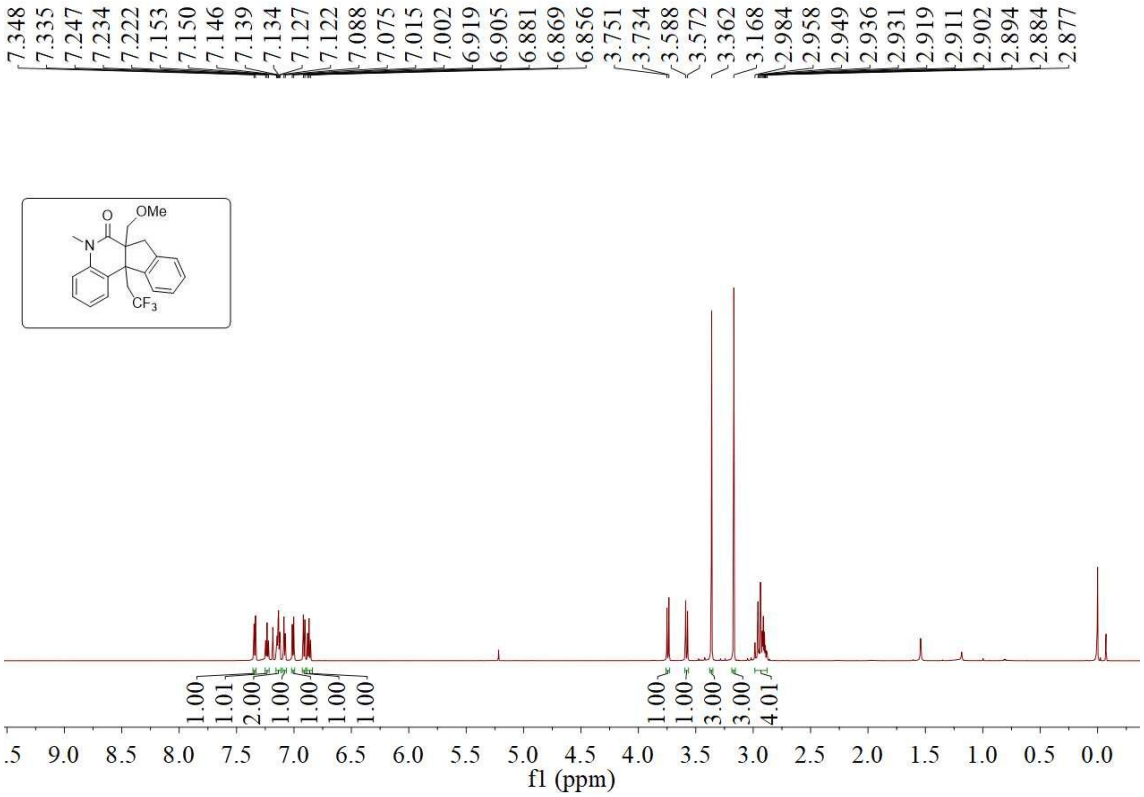
^{13}C-NMR Spectra of (+/-)-*Syn*-4m



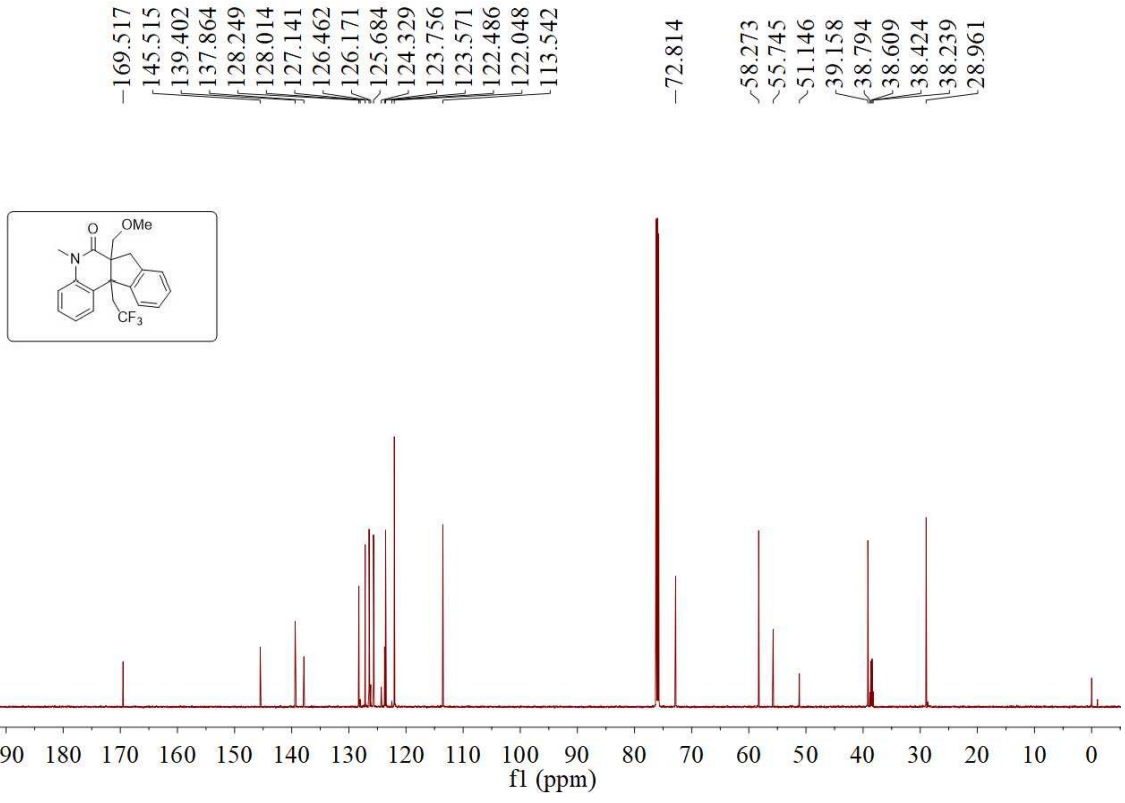
^{19}F-NMR Spectra of (+/-)-*Syn*-4m



^{1}H-NMR Spectra of (+/-)-*Syn*-4n



^{13}C-NMR Spectra of (+/-)-*Syn*-4n



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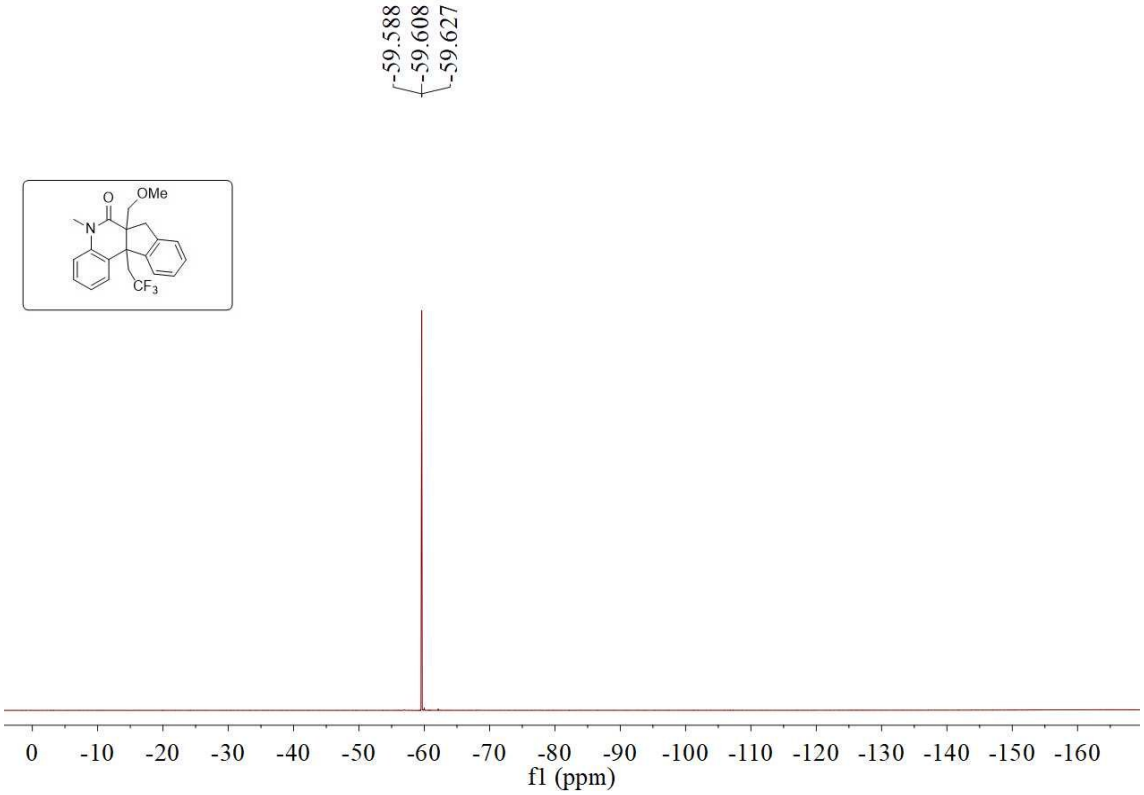
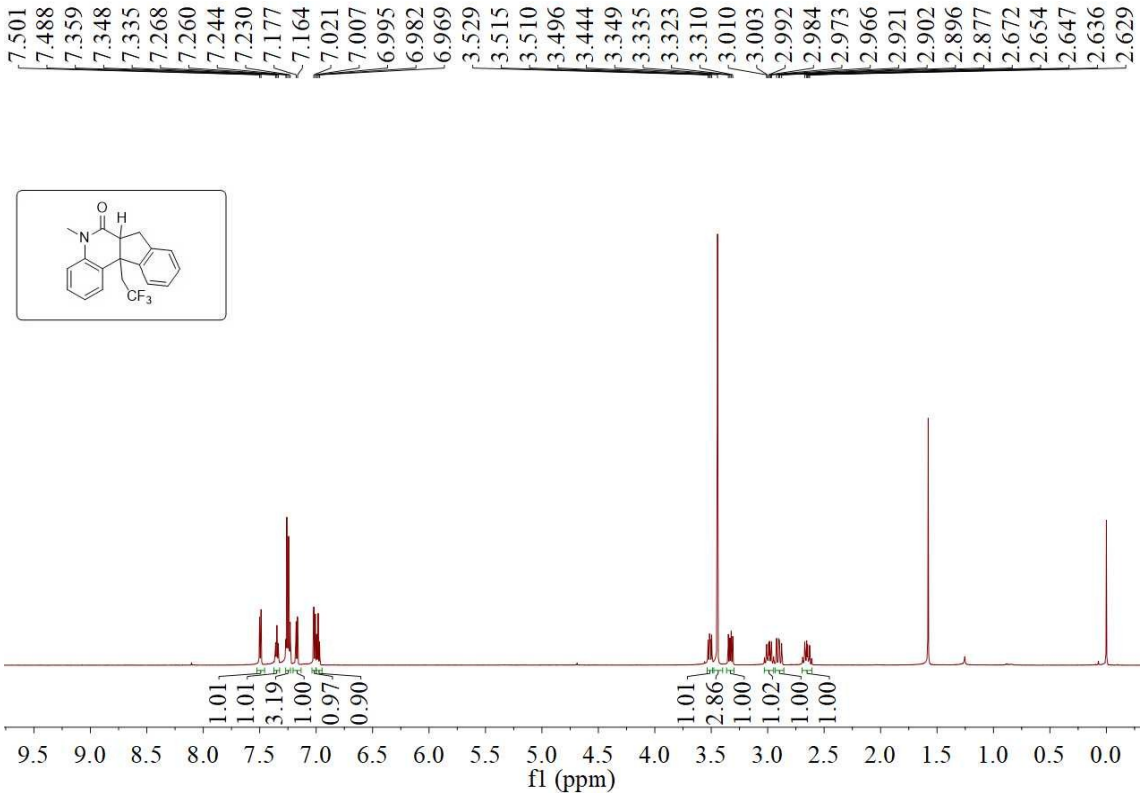
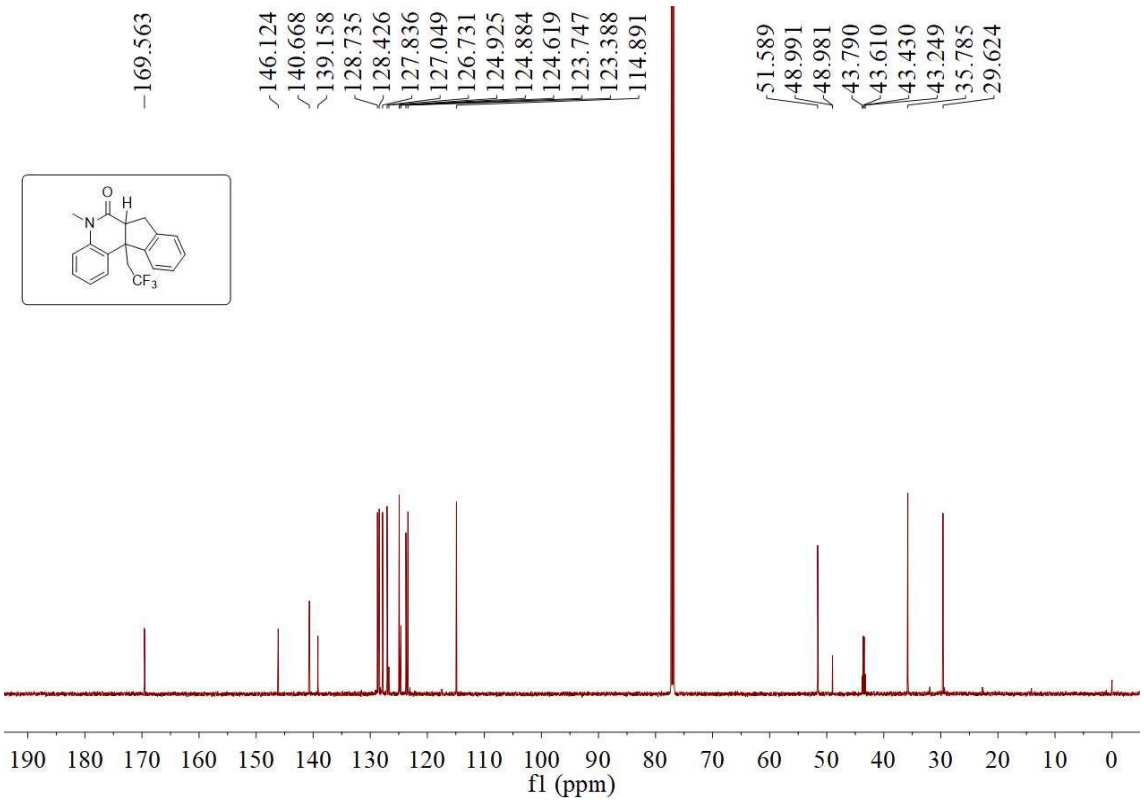


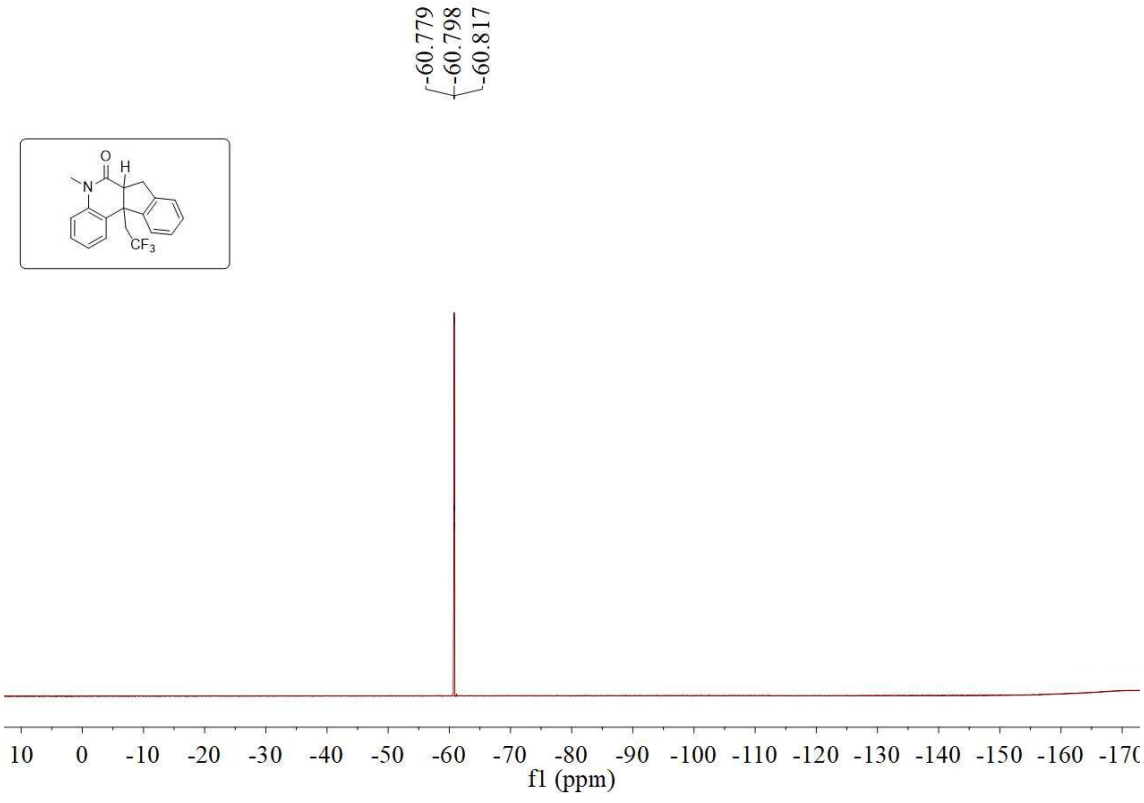
^{1}H-NMR Spectra of (+/-)-*Syn*-4o



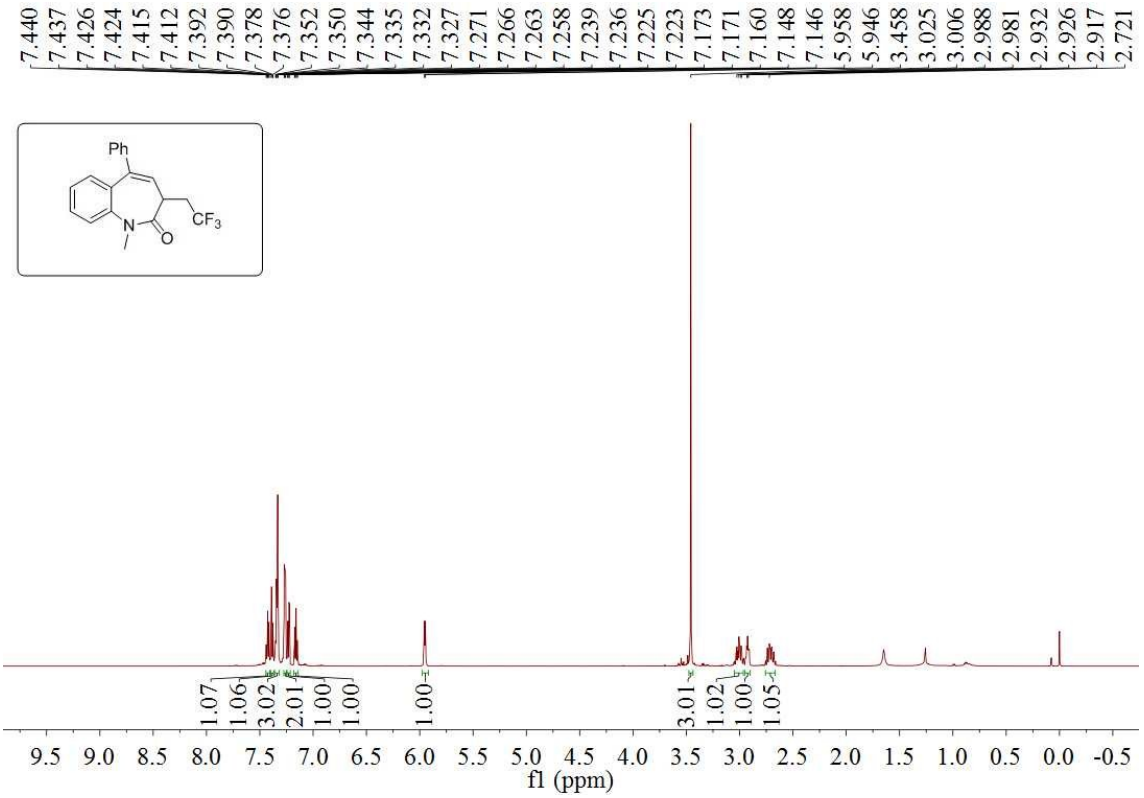
^{13}C-NMR Spectra of (+/-)-*Syn*-4o



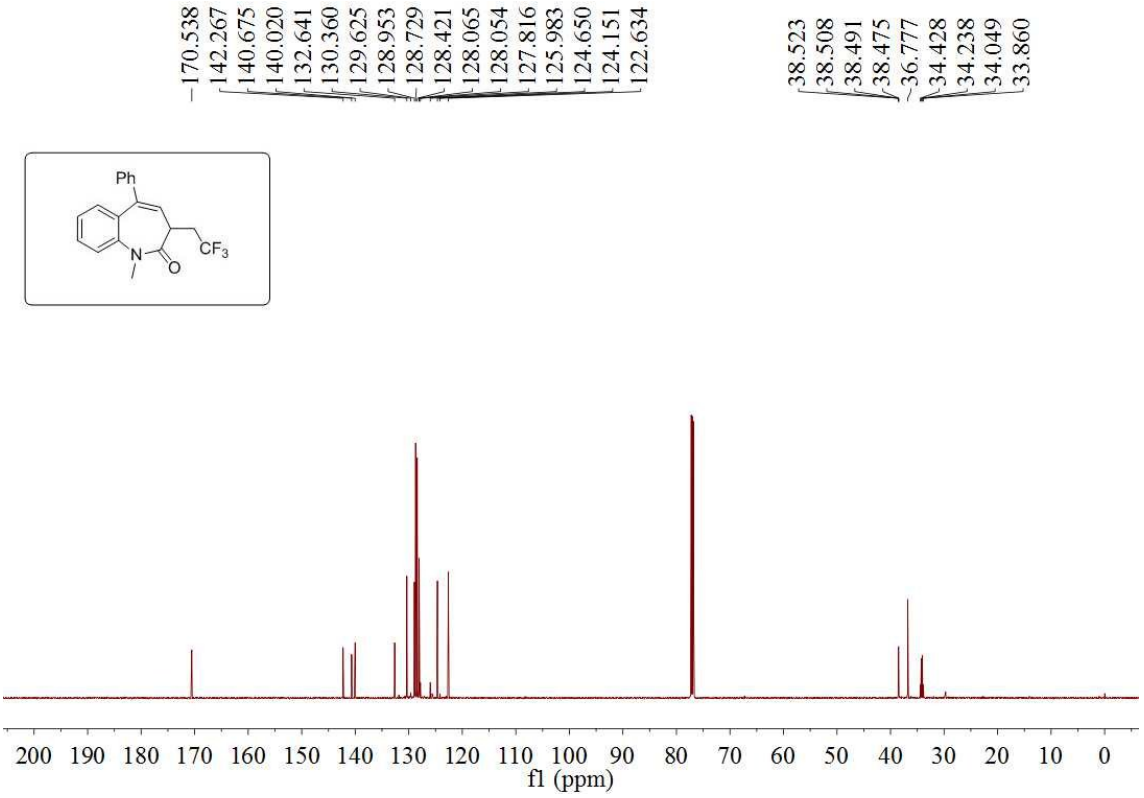
^{19}F-NMR Spectra of (+/-)-*Syn*-4o



^{1}H-NMR Spectra of 5



^{13}C-NMR Spectra of 5



^{19}F-NMR Spectra of 5