Electronic Supplementary Information

Pd-Catalyzed Carboannulation of γ,δ-Alkenyl Oximes: Efficient Access to 5-Membered Cyclic Nitrone and Dihydroazines

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1. General information.

Instrumentation and software

^{1}H and ^{13}C spectra were recorded at 25 ºC on a Varian 400 or on a Bruker 600 MHz spectrometer. The chemical shifts (δ) are given in parts per million (ppm) relative to internal standards (TMS, 0 ppm for ^{1}H, $CDCl_3$, 77.0 ppm for ^{13}C). High resolution mass spectra were recorded on Bruker microTOF spectrometer. Flash chromatography was performed on silica gel 60 (particle size 300-400 mesh ASTM, purchased from Taizhou, China). Copies of NMR were processed with MestReNova Software.

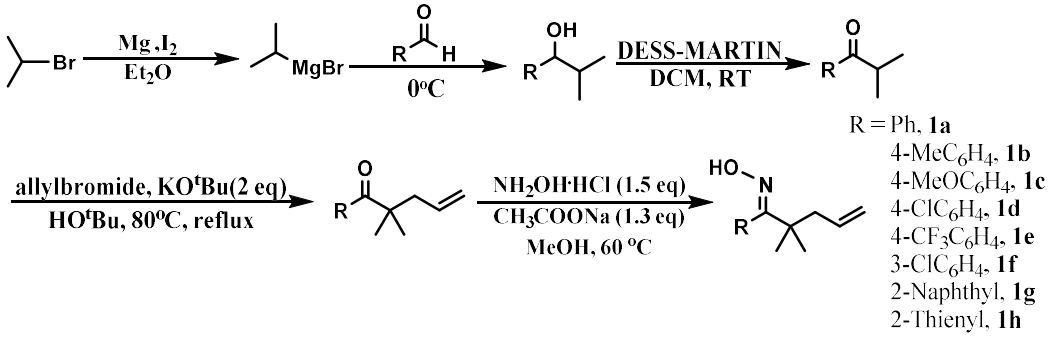
Solvents and reagents

Tetrahydrofuran was distilled from sodium with benzophenone as indicator. Unless otherwise noted, all reactions were conducted under a nitrogen atmosphere and commercial chemicals were used without further purification. All Palladium salts, ligands, NaO*t*−Bu, $NH_2OH{\cdot}HCl$ and iodobenzene were purchased from commierical sources. Oximes were synthesized according to literature.[1-6]

2. Experimental procedures

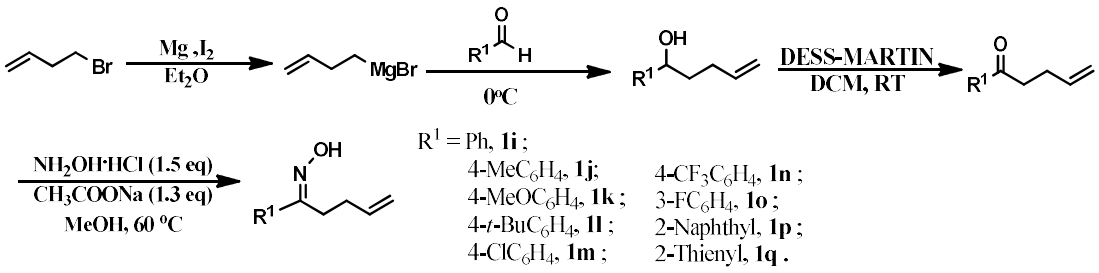
2.1 Synthesis of starting materials

General procedure (I) for synthesis of oximes.[1-2,4]



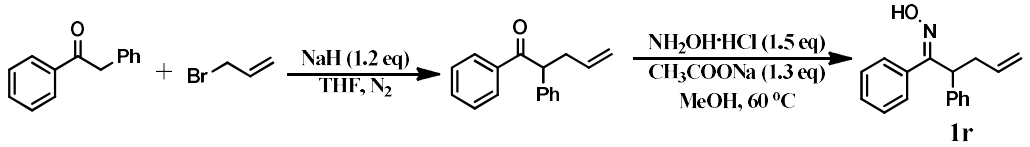
Scheme S1.

General procedure (II) for synthesis of oximes.[3,4]



Scheme S2.

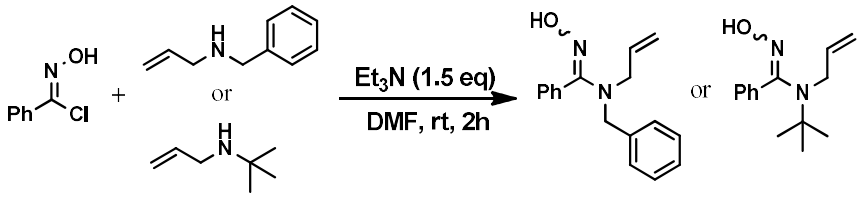
General procedure (III) for synthesis of (Z/E)-1,2-diphenylpent-4-en-1-one oxime.[5]



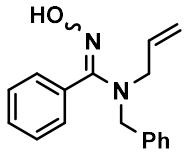
1r

Scheme S3.

General procedure for synthesis of (Z/E)-N-allyl-N-benzyl-N'-hydroxybenzimidamide or (Z/E)-N-allyl-N-(tert-butyl)-N'-hydroxybenzimidamide[6] (as represented by the synthesis of **1t**).

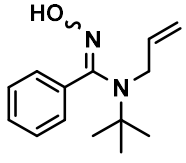


To a 100 mL round bottom flask were charged *N*-Allylbenzylamine or *N*-allyl(tert-butyl)amine (10 mmol), triethylamine (15 mmol) and DMF (15 mL). *N*-hydroxybenzimidoyl chloride (12 mmol) in DMF (6 mL) was added dropwise to the mixture while stirring. After the addition was complete, the mixture was stirred at room temperature for 2 h. The reaction was quenched with water, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated. The resulting residue was purified by flash column chromatography (hexane/ethyl acetate = 25:1) to afford (*Z*/*E*)-*N*-allyl-N-benzyl-*N*'-hydroxybenzimidamide **1s** (2.0 g, 7.5 mmol, *E*/*Z* mixture, *E*/*Z* not determined, ratio 4.3:1) in 75% yield as a partial solidified yellow oil or afford *(Z/E)-N-allyl-N-(tert-butyl)-N'-hydroxybenzimidamide* **1t** (1.8 g, 8.0 mmol) in 80% yield as a yellow solid.



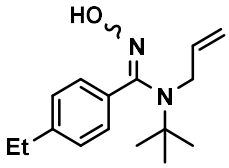
1s

Yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (m, 2H), 7.38 – 7.20 (m, 8H), 6.01 – 5.76 (m, 1H), 5.25 – 5.08 (m, 2H), 4.44 (s, 1H), 3.79 (s, 1H), 3.74 (d, *J* = 6.1 Hz, 1H), 3.27 (d, *J* = 5.9 Hz, 1H). **^{13}C NMR** was not assigned due to the complexity caused by *E*/*Z* isomerism; **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{17}H_{19}N_2O$ ($[M+H]^+$), 267.1492; found 267.1499.



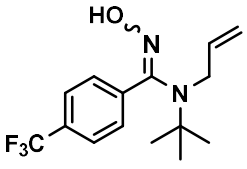
1t

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (m, 2H), 7.35 (m, 3H), 5.77 (m, 1H), 5.04 (m, 2H), 3.77 (d, *J* = 6.6 Hz, 2H), 1.24 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 155.5, 136.6, 135.5, 129.2, 128.2, 127.9, 117.4, 55.8, 48.8, 28.9. **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{14}H_{21}N_2O$ ($[M + H]^+$), 233.1654; found 233.1651. m.p. = 57 - 58 °C.



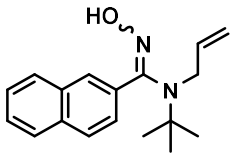
1u

Yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (m, 2H), 7.17 (m, 2H), 5.86 – 5.69 (m, 1H), 5.16 – 4.94 (m, 2H), 3.76 (d, *J* = 6.6 Hz, 2H), 2.66 (q, *J* = 7.6 Hz, 2H), 1.25 – 1.21 (m, 12H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 155.4, 145.5, 135.7, 134.0, 127.9, 127.7, 117.3, 55.7, 48.7, 28.9, 28.6, 15.3. **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{16}H_{24}N_2NaO$ ($[M+Na]^+$), 283.1786; found 283.1781. m.p. = 61 - 62 °C.



1v

Yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (m, 2H), 7.60 (m, 2H), 5.75 (m, 1H), 5.15 – 4.94 (m, 2H), 3.80 (d, *J* = 6.7 Hz, 2H), 1.22 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 154.3, 141.1, 135.3, 131.0 (q, *J* = 33 Hz), 128.1, 125.1 (q, *J* = 3.7 Hz), 124.1 (q, *J* = 270 Hz), 117.5, 56.1, 48.5, 29.1. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -62.6 (s, 3F). **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{15}H_{19}F_3N_2NaO$ ($[M + Na]^+$), 323.1347; found 323.1347. m.p. = 75 - 76 °C.

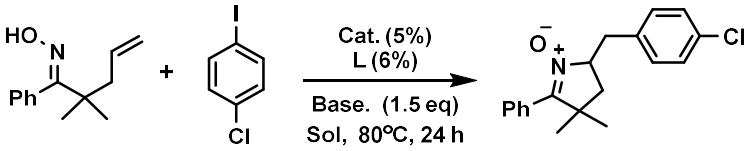


1w

Yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (m, 1H), 7.90 – 7.80 (m, 4H), 7.49 (m, 2H), 5.82 (m, 1H), 5.04 (m, 2H), 3.85 (d, *J* = 6.7 Hz, 2H), 1.28 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 155.6, 135.4, 134.0, 133.8, 133.0, 128.5, 127.9, 127.6, 127.5, 126.6, 126.2, 125.2, 117.6, 55.9, 48.9, 29.0. **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{18}H_{23}N_2O$ ($[M+H]^+$), 283.1810; found 283.1789. m.p. = 83 - 84 °C.

2.2 Optimization data

Table S1. Optimization of Pd-catalyzed carbonitronylation reaction.

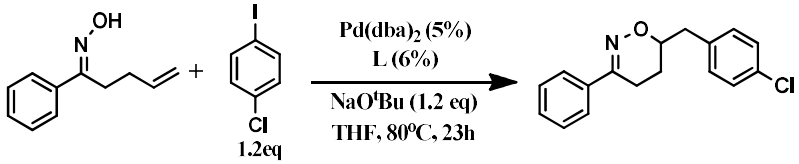


entry	solvent	catalyst	ligand	base	yield(%)[a]
1	THF	$Pd(dba)_2$	Xantphos	NaO^{t}Bu	72
2	DMF	$Pd(dba)_2$	Xantphos	NaO^{t}Bu	NR
3	CH_3CN	$Pd(dba)_2$	Xantphos	NaO^{t}Bu	37
4	CH_2Cl_2	$Pd(dba)_2$	Xantphos	NaO^{t}Bu	52
5	Tol	$Pd(dba)_2$	Xantphos	NaO^{t}Bu	65
6	DCE	$Pd(dba)_2$	Xantphos	NaO^{t}Bu	25
7	THF	$Pd(dba)_2$	Dppbz	NaO^{t}Bu	NR
8	THF	$Pd(dba)_2$	Dpe-phos	NaO^{t}Bu	64
9	THF	$Pd(dba)_2$	P(p-MePh)$_3$	NaO^{t}Bu	41
10	THF	$Pd(dba)_2$	P(p-CF_3Ph)$_3$	NaO^{t}Bu	71
11	THF	$Pd(dba)_2$	P(p-ClPh)$_3$	NaO^{t}Bu	67
12	THF	$Pd(dba)_2$	Dppe	NaO^{t}Bu	16

13	THF	$Pd(dba)_2$	Binap	NaO^tBu	65
14	THF	$Pd(dba)_2$	Biphep	NaO^tBu	77
15	THF	$Pd(dba)_2$	Xantphos	Na_2CO_3	Trace
16	THF	$Pd(dba)_2$	Xantphos	K_3PO_4	34
17	THF	$Pd(dba)_2$	Xantphos	Et_3N	20
18	THF	$Pd(dba)_2$	Xantphos	KO^tBu	25
19	THF	$Pd(PPh)_4$	Xantphos	NaO^tBu	43
20	THF	$Pd(OAc)_2$	Xantphos	NaO^tBu	65
21	THF	$Pd(cod)Cl_2$	Xantphos	NaO^tBu	50
22	THF	$Pd(dppf)Cl_2$	Xantphos	NaO^tBu	32
23	THF	$PdCl_2$	Xantphos	NaO^tBu	70
24	THF	$Pd(dba)_2$	Xantphos	NaO^tBu (0.8 equiv.)	68
25	THF	$Pd(dba)_2$	Xantphos	NaO^tBu (1.0 equiv.)	83
26	THF	$Pd(dba)_2$	Xantphos	NaO^tBu (1.2 equiv.)	89 (81)

[a] Yield of crude reaction mixture versus an internal standard.

Table S2. Optimization Pd-catalyzed carboetherification reaction.

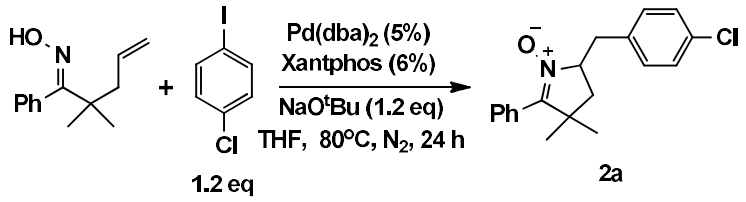


entry	solvent	catalyst	ligand	T	Yield(%)[a]
1	THF	$Pd(dba)_2$	Xantphos	80°C	98 (92)
2	THF	$Pd(dba)_2$	dppbz	80°C	NR
3	THF	$Pd(dba)_2$	SPhos	80°C	10
4	THF	$Pd(dba)_2$	PPh_3	80°C	NR
5	THF	$Pd(dba)_2$	dppe	80°C	NR
6	THF	$Pd(dba)_2$	DPEPhos	80°C	NR
7	THF	$Pd(dba)_2$	Binap	80°C	NR
8	THF	$Pd(dba)_2$	Biphep	80°C	NR
9	THF	$Pd(dba)_2$	dppf	80°C	Trace
10	THF	$Pd(dba)_2$	Xantphos	60 °C	68
11	THF	$Pd(dba)_2$	Xantphos	100 °C	98

[a] Yield of crude reaction mixture versus an internal standard. Isolated yields in parenthesis.

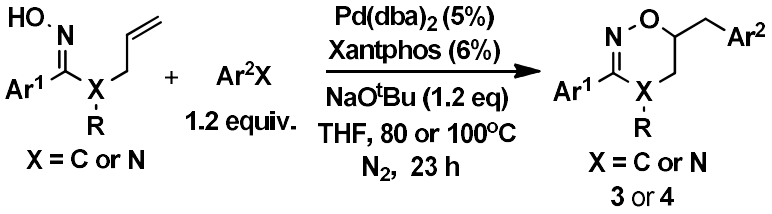
2.3 General procedures for palladium-catalyzed the reaction of γ,δ–unsaturated oxime with iodobenzene or bromobenzene.

General procedure (I) for the synthesis of nitrone:



A flame-dried vial containing $Pd(dba)_2$ (6.0 mg, 0.01 mmol, 0.05 eq) and Xantphos (7.0 mg, 0.012 mmol, 0.06 eq) were dissolved in THF (2 mL) under an atmosphere of N_2. The mixture was stirred at room tempeture for ca. 3 min, before 1-chloro-4-iodobenzene (57.2 mg, 0.24 mmol, 1.2 eq), 2,2-dimethyl-1-phenylpent-4-en-1-one oxime (41 mg, 0.20 mmol) and NaO^tBu (24 mg, 0.24 mmol) were sequentially added. The mixture was stirred at 80 ^{0}C until full conversion as monitored by TLC. After complete conversion of starting material, as judged by TLC, The solvent was removed in vacuo, and the residue was purified by column chromatography (petroleum: EtOAc = 1:1) or (CH_2Cl_2:MeOH = 200:3) to afford the corresponding nitrones.

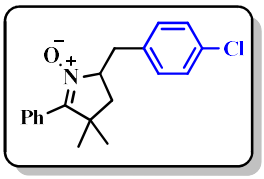
*General procedure (II) for the synthesis of oxazine **3** and oxadiazine **4**:*



A flamed-dried vial containing $Pd(dba)_2$ (6.0 mg, 0.01 mmol, 0.05 eq) and Xantphos (7.0 mg, 0.012 mmol, 0.06 eq) were dissolved in THF (2 mL) under an atmosphere of N_2. The mixture was stirred at room tempeture for ca. 3 min, before halides (0.24 mmol, 1.2 eq), oxime (0.20 mmol) and NaO^tBu (24 mg, 0.24 mmol) were sequentially added. The mixture was stirred at 80 ^{0}C (for oxazines) or 100^{o}C (for oxadiazines) until full conversion as monitored by TLC. After complete conversion of starting material, as judged by TLC, the solvent was removed *in vacuo*, and the residue was purified by column chromatography (eluent: petroleum/EtOAc) to afford the corresponding oxazines or oxadiazines.

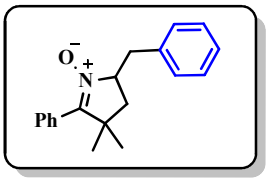
3. Compound characterization

3.1 Characterization of new oximes and products.



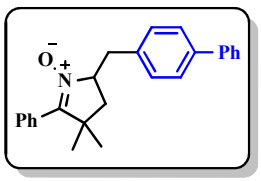
2-(4-chlorobenzyl)-4,4-dimethyl-5-phenyl-3,4-dihydro- 2*H*-pyrrole oxide: Following the general procedure (I), the reaction of (*Z/E*)-2,2-dimethyl-1-phenylpent- 4-en-1-one oxime (0.2 mmol, 41 mg) and 1-chloro-4-iodobenzene (0.24 mmol, 57.2 mg) afforded **2a** (52.7 mg, 84% yield) as a yellow solid. m.p. = 101 - 102 ºC.

^{1}H NMR (400 MHz, $CHCl_3$) δ 7.80 (m, 2H), 7.49 – 7.37 (m, 3H), 7.30 (m, 2H), 7.23 (m, 2H), 4.42 (m, 1H), 3.40 (dd, *J* = 13.8, 3.9 Hz, 1H), 3.22 (dd, *J* = 13.7, 7.8 Hz, 1H), 2.04 (dd, *J* = 12.8, 8.0 Hz, 1H), 1.75 (m, 1H), 1.32 (s, 3H), 1.09 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 148.8, 135.1, 132.7, 131.2, 129.5, 129.0, 128.7, 128.4, 128.3, 71.2, 43.0, 39.9, 37.1, 27.9, 27.3. **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{19}H_{20}ClNNaO$ ($[M+Na]^+$), 336.1126; found 336.1138.



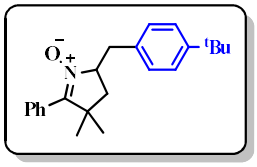
2-benzyl-4,4-dimethyl-5-phenyl-3,4-dihydro-2*H*-pyrrole oxide: Following the general procedure (I), the reaction of (*Z/E*)-2,2-dimethyl-1-phenylpent-4-en-1-one oxime (0.2 mmol, 41 mg) and iodobenzene (0.24 mmol, 49.0 mg) afforded **2b** (36.9 mg, 66% yield) as a yellow solid, m.p. = 102 - 103 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (m, 2H), 7.48 – 7.38 (m, 3H), 7.36 – 7.23 (m, 5H), 4.44 (m, 1H), 3.52 (dd, *J* = 13.6, 3.7 Hz, 1H), 3.16 (dd, *J* = 13.6, 8.4 Hz, 1H), 2.04 (dd, *J* = 12.8, 8.1 Hz, 1H), 1.80 (dd, *J* = 12.8, 8.5 Hz, 1H), 1.31 (s, 3H), 1.08 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 148.6, 136.7, 129.7, 129.4, 129.1, 128.5, 128.32, 128.28, 126.8, 71.6, 43.0, 40.1, 38.0, 27.9, 27.4. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{19}H_{21}NNaO$ ($[M+Na]^+$), 302.1515; found 302.1526.



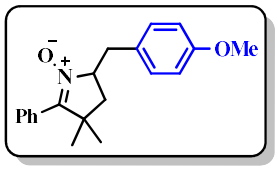
2-([1,1'- biphenyl]-4-ylmethyl)-4,4-dimethyl-5-phenyl-3,4-dihydro-2*H*-pyrrole oxide: Following the general procedure (I), the reaction of (*Z/E*)-2,2-dimethyl-1-phenylpent-4-en-1-one oxime (0.2 mmol, 41 mg) and 4-iodo-1,1'-biphenyl (0.24 mmol, 67.2 mg) afforded **2c** (49.8 mg, 70% yield) as a white solid, m.p. = 108 - 109 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (m, 2H), 7.58 (m, 4H), 7.48 – 7.38 (m, 5H), 7.38 – 7.30 (m, 3H), 4.47 (m, 1H), 3.56 (dd, *J* = 13.6, 3.6 Hz, 1H), 3.20 (dd, *J* = 13.5, 8.4 Hz, 1H), 2.09 (dd, *J* = 12.8, 8.0 Hz, 1H), 1.84 (dd, *J* = 12.8, 8.5 Hz, 1H), 1.32 (s, 3H), 1.11 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 148.9, 140.8, 139.8, 135.9, 130.2, 129.8, 129.5, 129.1, 128.8, 128.41, 128.36, 127.3, 127.0, 71.6, 43.1, 40.2, 37.8, 28.0, 27.4. **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{25}H_{25}NNaO$ ($[M+Na]^+$), 378.1834; found 378.1838.



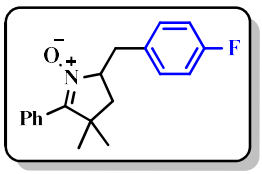
2-(4-(tert-butyl)benzyl)-4,4-dimethyl-5-phenyl-3,4-dihydro-2*H*-pyrrole-1-oxide: Following the general procedure (I), the reaction of (*Z/E*)-2,2-dimethyl-1-phenylpent-4-en-1-one oxime (0.2 mmol, 41 mg) and 1-bromo-4-(*tert*-butyl)benzene (0.24 mmol, 51.1 mg) afforded **2d** (43.6 mg, 65% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (m, 2H), 7.43 (m, 3H), 7.34 (m, 2H), 7.21 (m, 2H), 4.41 (m, 1H), 3.56 (dd, *J* = 13.5, 3.7 Hz, 1H), 3.04 (dd, *J* = 13.5, 8.9 Hz, 1H), 2.05 (dd, *J* = 12.9, 8.0 Hz, 1H), 1.83 – 1.77 (m, 1H), 1.31 (s, 12H), 1.11 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 149.7, 148.5, 133.7, 129.4, 129.3, 129.2, 128.3, 125.4, 71.8, 43.0, 40.4, 37.8, 34.4, 31.3, 27.9, 27.4. **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{23}H_{29}NNaO$ ($[M+Na]^+$), 358.2141; found 356.2150.



2-(4-methoxybenzyl)-4,4-dimethyl-5-phenyl-3,4-dihydro-2*H*-pyrrole oxide: Following the general procedure (I), the reaction of (*Z/E*)-2,2-dimethyl-1-phenylpent-4-en-1-one oxime (0.2 mmol, 41 mg) and 1-iodo-4-methoxybenzene (0.24 mmol, 56.2 mg) afforded **2e** (46.4 mg, 75% yield) as a yellow solid, m.p. = 117 - 119 ºC.

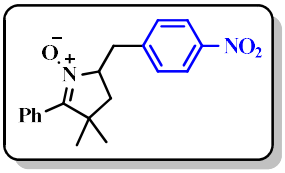
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.77 (m, 2H), 7.48 – 7.38 (m, 3H), 7.35 – 7.27 (m, 1H), 7.20 (d, *J* = 8.5 Hz, 1H), 6.86 (d, *J* = 8.6 Hz, 2H), 4.40 (m, 1H), 3.80 (s, 3H), 3.40 (dd, *J* = 13.8, 3.8 Hz, 1H), 3.15 (dd, *J* = 13.7, 8.1 Hz, 1H), 2.03 (dd, *J* = 12.8, 8.1 Hz, 1H), 1.80 (dd, *J* = 12.8, 8.4 Hz, 1H), 1.31 (s, 3H), 1.07 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 158.5, 148.7, 130.7, 129.4, 129.2, 128.6, 128.3, 128.2, 114.0, 71.7, 55.2, 43.0, 40.0, 37.0, 27.9, 27.4. **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{20}H_{23}NNaO_2$ ($[M+Na]^+$), 332.1621; found 332.1631.



2-(4-fluorobenzyl)-4,4-dimethyl-5-phenyl-3,4-dihydro-2*H*-pyrrole oxide: Following the general procedure (I), the reaction of (*Z/E*)-2,2-dimethyl-1-phenylpent-4-en-1-one oxime (0.2 mmol, 41 mg) and 1-fluoro-4-iodobenzene (0.24 mmol, 53.3 mg) afforded **2f** (38.1 mg, 64% yield) as a white solid, m.p. = 98 - 99 ºC.

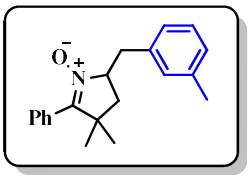
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (m, 2H), 7.49 – 7.38 (m, 3H), 7.27 – 7.22 (m, 2H), 7.01 (m, 2H), 4.42 (m, 1H), 3.38 (dd, *J* = 13.8, 3.8 Hz, 1H), 3.24 (dd, *J* = 13.9, 7.7 Hz, 1H), 2.05 (dd, *J* = 12.9, 8.1 Hz, 1H), 1.80 – 1.75 (m, 1H), 1.32 (s, 3H), 1.06 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ161.9 (d, *J* = 243 Hz), 148.9, 132.2(d, *J* = 3.3 Hz), 131.3 (d, *J* = 7.8 Hz), 129.5, 129.0, 128.4, 128.3, 115.4 (d, *J* = 21 Hz), 71.4, 43.0, 39.7, 36.9, 27.9, 27.4. ^{19}F NMR (470 MHz, $CDCl_3$) δ [(-116.1) - (-116.2), m, 1F]. **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{19}H_{21}FNO$ ($[M+H]^+$), 298.1602; found 298.1610.



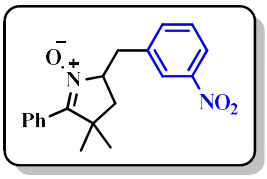
4,4-dimethyl-2- (4-nitrobenzyl)-5-phenyl-3,4-dihydro-2*H*-pyrrole oxide: Following the general procedure (I), the reaction of (*Z/E*)-2,2-dimethyl-1-phenylpent-4-en-1-one oxime (0.2 mmol, 41 mg) and 1-iodo-4-nitrobenzene (0.24 mmol, 59.8 mg) afforded **2g** (20.1 mg, 31% yield) as a yellow solid, m.p. = 143 - 144 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (m, 2H), 7.68 (m, 2H), 7.36 (m, 5H), 4.39 (m, 1H), 3.47 – 3.35 (m, 1H), 3.30 (dd, *J* = 13.3, 7.4 Hz, 1H), 1.98 (dd, *J* = 12.9, 8.0 Hz, 1H), 1.63 (m, 1H), 1.24 (s, 3H), 0.99 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 149.6, 147.1, 144.6, 130.7, 129.8, 128.7, 128.5, 128.2, 123.7, 70.8, 43.1, 40.0, 37.5, 28.0, 27.1. **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{19}H_{21}N_2O_3$ ($[M+H]^+$), 325.1547; found 325.1539.



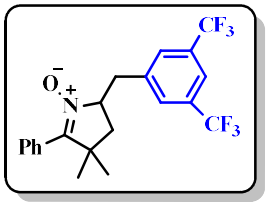
4,4-dimethyl-2-(3- methylbenzyl)-5-phenyl-3,4-dihydro-2*H*-pyrrole oxide: Following the general procedure (I), the reaction of (*Z/E*)-2,2-dimethyl-1-phenylpent-4-en-1-one oxime (0.2 mmol, 41 mg) and 1-iodo-3-methylbenzene (0.24 mmol, 52.3 mg) afforded **2h** (42.8 mg, 73% yield) as a yellow solid, m.p. = 101 - 102 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.77 (m, 2H), 7.48 – 7.37 (m, 3H), 7.21 (m, 1H), 7.11 (s, 1H), 7.07 (m, 2H), 4.42 (m, 1H), 3.50 (dd, *J* = 13.5, 3.9 Hz, 1H), 3.09 (dd, *J* = 13.5, 8.5 Hz, 1H), 2.34 (s, 3H), 2.04 (dd, *J* = 12.9, 8.1 Hz, 1H), 1.81 (dd, *J* = 12.9, 8.4 Hz, 1H), 1.31 (s, 3H), 1.09 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 148.6, 138.2, 136.7, 130.4, 129.4, 129.1, 128.4, 128.29, 128.28, 127.5, 126.7, 71.7, 43.0, 40.1, 38.1, 27.8, 27.4, 21.3. **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{20}H_{23}NNaO$ ($[M+Na]^+$), 316.1672; found 316.1695.



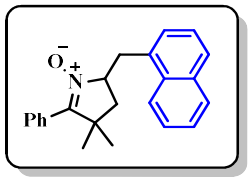
4,4-dimethyl-2-(3-nitrobenzyl)-5-phenyl-3,4-dihydro-2*H*-pyrrole oxide: Following the general procedure (I), the reaction of (*Z/E*)-2,2-dimethyl-1-phenylpent-4-en-1-one oxime (0.2 mmol, 41 mg) and 1-iodo-3-nitrobenzene (0.24 mmol, 59.8 mg) afforded **2i** (48.0 mg, 74% yield) as a yellow solid, m.p. = 102 - 103 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 8.06 (m, 1H), 7.73 (m, 2H), 7.62 (m, 1H), 7.44 (m, 1H), 7.41 – 7.32 (m, 3H), 4.44 (m, 1H), 3.45 (dd, *J* = 13.9, 4.0 Hz, 1H), 3.34 (dd, *J* = 13.9, 7.4 Hz, 1H), 2.03 (dd, *J* = 12.8, 7.9 Hz, 1H), 1.67 (dd, *J* = 12.8, 9.0 Hz, 1H), 1.28 (s, 3H), 1.02 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 149.4, 148.3, 138.8, 136.1, 129.7, 129.5, 128.7, 128.4, 128.2, 124.5, 122.0, 70.8, 43.0, 39.9, 37.3, 27.9, 27.1. **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{19}H_{20}N_2NaO_3$ ($[M+Na]^+$), 347.1366; found 347.1368.



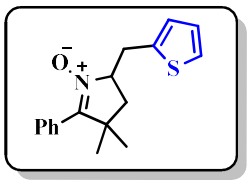
3-(3,5-bis(trifluoromethyl)benzyl)-4,4-dimethyl-5-phenyl-3,4-dihydro-2*H*-pyrrole oxide: Following the general procedure (I), the reaction of (*Z/E*)-2,2-dimethyl-1-phenylpent-4-en-1-one oxime (0.2 mmol, 41 mg) and 1-iodo-3,5-bis(trifluoromethyl)-benzene (0.24 mmol, 81.6 mg) afforded **2j** (64.8 mg, 78% yield) as a white solid, m.p. = 106 - 107 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.69 (m, 5H), 7.41 – 7.29 (m, 3H), 4.51 – 4.32 (m, 1H), 3.42 (m, 2H), 2.04 (dd, *J* = 12.8, 8.0 Hz, 1H), 1.61 (dd, *J* = 12.7, 9.2 Hz, 1H), 1.29 (s, 3H), 0.98 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 149.3, 139.3, 131.8 (q, *J* = 33 Hz), 130.1, 129.7, 128.6, 128.4, 128.2, 123.7 (q, *J* = 270 Hz), 120.9 (hept, $^3J_{C\text{-}F}$ = 3.7 Hz), 70.6, 43.0, 39.7, 37.1, 27.8, 27.2. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -62.8 (s, 6F).**HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{21}H_{19}F_6NNaO$ ($[M+Na]^+$), 438.1263; found 438.1267.



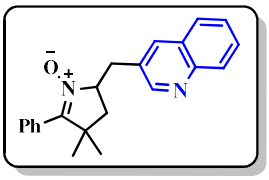
4,4-dimethyl-2-(naphthalen-1- ylmethyl)-5-phenyl-3,4-dihydro-2*H*-pyrrole oxide: Following the general procedure (I), the reaction of (*Z/E*)-2,2-dimethyl-1-phenylpent-4-en-1-one oxime (0.2 mmol, 41 mg) and 1-iodonaphthalene (0.24 mmol, 61.0 mg) afforded **2k** (30.3 mg, 46 % yield) as a yellow solid, m.p. = 112 - 113 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.3 Hz, 1H), 7.93 (m, 2H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.79 (m, 1H), 7.57 (m, 1H), 7.51- 7.39 (m, 6H), 4.55 (m, 2H), 3.14 (dd, *J* = 13.4, 9.8 Hz, 1H), 1.98 (dd, *J* = 12.8, 7.7 Hz, 1H), 1.87 (dd, *J* = 12.7, 8.5 Hz, 1H), 1.28 (s, 3H), 1.27 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 148.1, 133.9, 133.5, 132.0, 129.5, 129.0, 128.8, 128.32, 128.29, 127.6, 127.4, 126.4, 125.8, 125.4, 123.9, 71.1, 43.1, 41.7, 36.1, 28.2, 27.0. **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{23}H_{24}NO$ ($[M+H]^+$), 330.1852; found 330.1862.



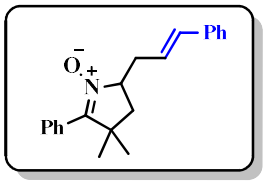
4,4-dimethyl-5-phenyl-2-(thiophen-2- ylmethyl)-3,4-dihydro-2*H*-pyrrole oxide: Following the general procedure (I), the reaction of (*Z/E*)-2,2-dimethyl-1-phenylpent-4-en-1-one oxime (0.2 mmol, 41 mg) and 2-iodothiophene (0.24 mmol, 50.4 mg) afforded **2l** (29.1 mg, 51% yield) as a yellow solid, m.p. = 78 - 79 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (m, 2H), 7.44 (m, 3H), 7.20 (d, *J* = 5.1 Hz, 1H), 7.00 – 6.95 (m, 1H), 6.93 (m, 1H), 4.51 – 4.38 (m, 1H), 3.59 (dd, *J* = 14.8, 3.9 Hz, 1H), 3.52 (dd, *J* = 14.8, 7.2 Hz, 1H), 2.13 (dd, *J* = 12.8, 8.0 Hz, 1H), 1.85 (dd, *J* = 12.8, 8.8 Hz, 1H), 1.37 (s, 3H), 1.12 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 148.9, 137.9, 129.5, 129.0, 128.33, 128.30, 126.91, 129.90, 124.7, 71.0, 43.0, 39.9, 32.0, 27.9, 27.4. **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{17}H_{19}NNaOS$ ($[M+Na]^+$), 308.1080; found 308.1086.



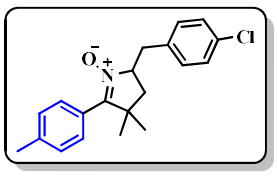
4,4-dimethyl-5-phenyl-2-(quinolin-3-ylmethyl)-3,4-dihydro-2*H*- pyrrole-1-oxide: Following the general procedure (I), the reaction of (*Z/E*)-2,2-dimethyl-1-phenylpent-4-en-1-one oxime (0.2 mmol, 41 mg) and 3-bromoquinoline (0.24 mmol, 49.9 mg) afforded **2m** (41.6 mg, 63% yield) as a yellow solid, m.p. = 142 - 143 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (d, *J* = 1.8 Hz, 1H), 8.18 – 8.06 (m, 2H), 7.80 (m, 3H), 7.69 (m, 1H), 7.56 (m, 1H), 7.49 – 7.38 (m, 3H), 4.56 (m, 1H), 3.63 (dd, *J* = 14.1, 3.8 Hz, 1H), 3.47 (dd, *J* = 14.0, 7.6 Hz, 1H), 2.11 (m, 1H), 1.81 (m, 1H), 1.33 (s, 3H), 1.05 (s, 3H).**^{13}C NMR** (150 MHz, $CDCl_3$) δ 152.2, 149.1, 147.3, 136.4, 129.6, 129.5, 129.21, 129.17, 128.8, 128.4, 128.2, 128.0, 127.5, 126.8, 71.1, 43.0, 40.1, 35.0, 27.9, 27.1. **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{22}H_{23}N_2O$ ($[M+H]^+$), 331.1810; found 331.2060.



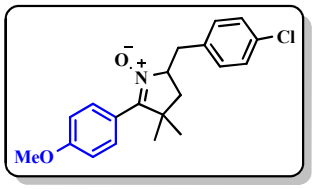
2-cinnamyl-4,4-dimethyl-5-phenyl-3,4-dihydro-2*H*-pyrrole oxide: Following the general procedure (I), the reaction of (*Z/E*)-2,2-dimethyl-1-phenylpent-4-en-1-one oxime (0.2 mmol, 41 mg) and beta-bromostyrene (0.24 mmol, 43.9 mg) afforded **2n** (39.1 mg, 64% yield) as a yellow solid, m.p. = 111 - 113 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (m, 2H), 7.34 (m, 3H), 7.29 (m, 2H), 7.21 (m, 2H), 7.17 – 7.12 (m, 1H), 6.46 (m, 1H), 6.15 – 6.04 (m, 1H), 4.22 (m, 1H), 3.10 – 2.98 (m, 1H), 2.69 – 2.57 (m, 1H), 2.10 (dd, *J* = 12.8, 7.8 Hz, 1H), 1.79 (dd, *J* = 12.8, 8.8 Hz, 1H), 1.29 (s, 3H), 1.23 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 148.3, 137.1, 133.8, 129.5, 128.5, 128.33, 128.30, 127.4, 126.1, 124.5, 70.2, 43.1, 40.9, 36.0, 28.2, 27. **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{21}H_{22}ClNNaO$ ($[M+Na]^+$), 328.1677; found 328.1870.



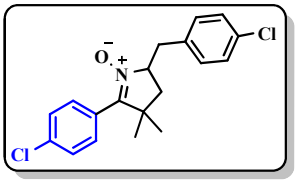
2-(4-chlorobenzyl)-4,4-dimethyl-5-(p-tolyl)-3,4-dihydro-2*H*-pyrrole oxide: Following the general procedure (I), the reaction of (*Z/E*)-2,2-dimethyl-1-(p-tolyl)pent-4-en-1-one oxime (0.2 mmol, 43.5 mg) and 1-chloro-4-iodobenzene (0.24 mmol, 57.2 mg) afforded **2o** (54.4 mg, 83% yield) as a yellow solid, m.p. = 106 - 107ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (m, 2H), 7.28 (m, 3H), 7.23 (m, 3H), 4.40 (m, 1H), 3.40 (dd, *J* = 13.8, 3.9 Hz, 1H), 3.21 (dd, *J* = 13.8, 7.9 Hz, 1H), 2.38 (s, 3H), 2.02 (dd, *J* = 12.8, 8.0 Hz, 1H), 1.72 (dd, *J* = 12.8, 8.7 Hz, 1H), 1.32 (s, 3H), 1.09 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 148.9, 139.7, 135.2, 132.6, 131.1, 129.0, 128.6, 128.1, 126.0, 71.1, 42.9, 39.9, 37.1, 27.9, 27.3, 21.4. **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{20}H_{22}ClNNaO$ ($[M+Na]^+$), 350.1282; found 350.1293.



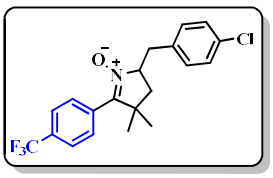
2-(4-chlorobenzyl)-5-(4-methoxyphenyl)-4,4-dimethyl-3,4-dihydro-2*H*-pyrrole oxide: Following the general procedure (I), the reaction of (*Z/E*)-1-(4-methoxyphenyl)-2,2-dimethylpent-4-en-1-one oxime (0.2 mmol, 46.7 mg) and 1-chloro-4-iodobenzene (0.24 mmol, 57.2 mg) afforded **2p** (56.4 mg, 82 % yield) as a yellow solid, m.p. = 110 - 111 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.8 Hz, 2H), 7.28 (m, 2H), 7.22 (m, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 4.38 (m, 1H), 3.84 (s, 3H), 3.42 (dd, *J* = 13.8, 3.6 Hz, 1H), 3.18 (dd, *J* = 13.7, 8.0 Hz, 1H), 2.00 (dd, *J* = 12.7, 7.9 Hz, 1H), 1.71 (dd, *J* = 12.7, 8.8 Hz, 1H), 1.34 (s, 3H), 1.14 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 160.3, 148.2, 135.3, 132.6, 131.1, 129.9, 128.6, 121.3, 113.7, 70.9, 55.2, 42.9, 40.2, 37.2, 28.1, 27.4. **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{20}H_{22}ClNNaO_2$ ($[M+Na]^+$), 366.1231; found 366.1221.



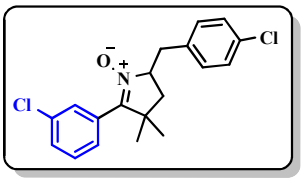
2-(4-chlorobenzyl)-5-(4-chlorophenyl)-4,4-dimethyl-3,4-dihydro-2*H*-pyrrole oxide: Following the general procedure (I), the reaction of (*Z/E*)-1-(4-chlorophenyl)-2,2-dimethyl pent-4-en-1-one oxime (0.2 mmol, 47.5 mg) and 1-chloro-4-iodobenzene (0.24 mmol, 57.2 mg) afforded compound **2q** (50.9 mg, 73% yield) as a yellow solid, m.p. = 109 - 110 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (m, 2H), 7.43 (m, 2H), 7.30 (m, 2H), 7.23 (m, 2H), 4.42 (m, 1H), 3.42 (dd, *J* = 13.8, 3.9 Hz, 1H), 3.20 (dd, *J* = 13.8, 8.0 Hz, 1H), 2.06 (dd, *J* = 12.8, 8.0 Hz, 1H), 1.76 (dd, *J* = 12.8, 8.7 Hz, 1H), 1.34 (s, 3H), 1.12 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 147.7, 135.5, 135.0, 132.8, 131.1, 129.6, 128.8, 128.7, 127.3, 71.4, 42.9, 40.1, 37.2, 28.0, 27.3. **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{19}H_{19}Cl_2NNaO$ ($[M+Na]^+$), 370.0736; found 370.0743.



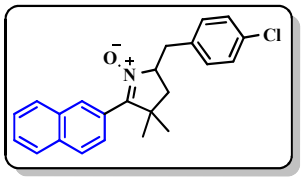
3-(4-chlorobenzyl)-4,4-dimethyl-5-(4-(trifluoro-methyl)phenyl)-3,4- dihydro-2*H*-pyrrole oxide: Following the general procedure (I), the reaction of (*Z/E*)-2,2-dimethyl-1-(4-(trifluoromethyl)phenyl)pent-4-en-1-one oxime (0.2 mmol, 54.3 mg) and 1-chloro-4-iodobenzene (0.24 mmol, 57.2 mg) afforded **2r** (57.3 mg, 75% yield) as a yellow solid, m.p. = 128 - 129ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.2 Hz, 2H), 7.70 (m, 2H), 7.30 (m, 2H), 7.22 (m, 2H), 4.44 (m, 1H), 3.39 (dd, *J* = 13.8, 3.7 Hz, 1H), 3.22 (dd, *J* = 13.8, 7.8 Hz, 1H), 2.08 (dd, *J* = 12.8, 8.0 Hz, 1H), 1.78 (dd, *J* = 12.8, 8.9 Hz, 1H), 1.34 (s, 3H), 1.11 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 147.3, 134.8, 132.9, 132.5, 131.2 (q, *J* = 33 Hz), 131.1, 128.8, 128.6, 125.4 (q, *J* = 3.7 Hz), 123.7(q, *J* = 270 Hz), 71.6, 42.9, 40.0, 37.1, 27.9, 27.3. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -63.0 (s, 3F). **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{20}H_{19}ClF_3NNaO$ ($[M+Na]^+$), 404.0999; found 404.1005.



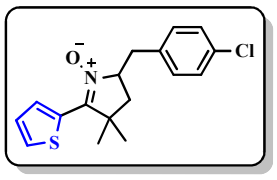
3-(4-chlorobenzyl)-5-(3- chlorophenyl)-4,4-dimethyl-3,4-dihydro-2*H*-pyrrole oxide: Following the general procedure (I), the reaction of (*Z/E*)-1-(3-chlorophenyl)-2,2-dimethylpent-4-en-1-one oxime (0.2 mmol, 47.5 mg) and 1-chloro-4-iodobenzene (0.24 mmol, 57.2 mg) afforded **2s** (53.6 mg, 77% yield) as a yellow solid, m.p. = 85 - 86 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (m, 1H), 7.73 – 7.65 (m, 1H), 7.38 (m, 2H), 7.30 (m, 2H), 7.21 (m, 2H), 4.41 (m, 1H), 3.40 (dd, *J* = 13.8, 3.9 Hz, 1H), 3.19 (dd, *J* = 13.8, 7.8 Hz, 1H), 2.12 – 1.97 (m, 1H), 1.79 – 1.73 (m, 1H), 1.32 (s, 3H), 1.10 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 147.3, 134.9, 134.5, 132.8, 131.1, 130.6, 129.6, 128.7, 128.3, 126.3, 71.5, 42.9, 40.0, 37.1, 27.9, 27.2. **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{19}H_{19}Cl_2NNaO$ ($[M+Na]^+$), 370.0736; found 370.0727.



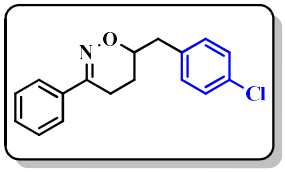
2-(4-chlorobenzyl)-4,4-dimethyl-5-(naphthalen-2-yl)-3,4-dihydro-2*H*-pyrrole oxide: Following the general procedure (I), the reaction of (*Z/E*)-2,2-dimethyl-1-(naphth alen-2-yl)pent-4-en-1-one oxime (0.2 mmol, 50.7 mg) and 1-chloro-4-iodobenzene (0.24 mmol, 57.2 mg) afforded **2t** (62.6 mg, 86% yield) as a yellow solid, m.p. = 141 - 142 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.92 – 7.80 (m, 4H), 7.56 – 7.47 (m, 2H), 7.31 (m, 2H), 7.25 (m, 2H), 4.46 (m, 1H), 3.47 (dd, *J* = 13.7, 3.9 Hz, 1H), 3.23 (dd, *J* = 13.8, 8.0 Hz, 1H), 2.08 (dd, *J* = 12.8, 8.0 Hz, 1H), 1.79 (dd, *J* = 12.8, 8.8 Hz, 1H), 1.40 (s, 3H), 1.17 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 148.8, 135.2, 133.5, 132.9, 132.7, 131.1, 129.7, 128.7, 128.5, 127.9, 127.5, 127.1, 126.4, 126.3, 125.0, 71.3, 43.1, 40.2, 37.2, 28.1, 27.4. **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{23}H_{22}ClNNaO$ ($[M+Na]^+$), 386.1288; found 386.1282.



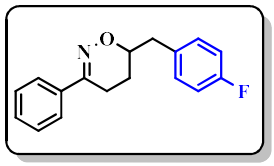
5-(4-chlorobenzyl)-4,4-dimethyl-5-(thiophen-2-yl)-3,4-dihydro-2*H*-pyrrole oxide: Following the general procedure (I), the reaction of (*Z/E*)-2,2-dimethyl-1-(thiophen-2-yl)pent-4-en -1-one oxime (0.2 mmol, 41.9 mg) and 1-chloro-4-iodobenzene (0.24 mmol, 57.2 mg) afforded **2u** (48.6 mg, 76% yield) as a yellow solid, m.p. = 99 - 100 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 3.9 Hz, 1H), 7.50 (m, 1H), 7.23 (m, 2H), 7.19 – 7.09 (m, 3H), 4.39 (m, 1H), 3.42 (dd, *J* = 13.8, 3.8 Hz, 1H), 3.13 (dd, *J* = 13.8, 8.0 Hz, 1H), 2.07 (dd, *J* = 13.0, 8.4 Hz, 1H), 1.76 (dd, *J* = 13.0, 8.3 Hz, 1H), 1.41 (s, 3H), 1.30 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 145.0, 135.0, 132.6, 130.9, 129.6, 128.7, 128.5, 126.9, 126.1, 70.0, 42.5, 40.4, 37.3, 28.4, 27.3. **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{17}H_{18}ClNNaOS$ ($[M+Na]^+$), 342.0690; found 324.0682.



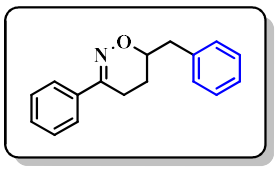
6-(4-chlorobenzyl)-3-phenyl-5,6-dihydro-4*H*-1,2-oxazin: Following the general procedure (II), the reaction of (*Z/E*)-1-phenylpent-4-en-1-one oxime (0.2 mmol, 35 mg) and 1-chloro-4-iodobenzene (0.24 mmol, 57.2 mg) afforded **3a** (52.6 mg, 92% yield) as a white solid, m.p. = 115 - 116 ºC.

^{1}H NMR (400 MHz, $CHCl_3$) δ 7.67 (m, 2H), 7.41 – 7.32 (m, 3H), 7.28 (m, 2H), 7.22 (m, 2H), 3.94 (m, 1H), 3.07 (dd, *J* = 14.0, 6.4 Hz, 1H), 2.86 (dd, *J* = 14.0, 6.1 Hz, 1H), 2.68 (m, 1H), 2.59 (m, 1H), 2.11 – 1.97 (m, 1H), 1.84 – 1.68 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 154.6, 135.7, 135.6, 132.4, 130.9, 129.5, 128.5, 128.4, 125.3, 75.5 , 39.8 , 23.8 , 21.9. **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{17}H_{16}ClNNaO$ ($[M+Na]^+$), 308.0813; found 308.0815.



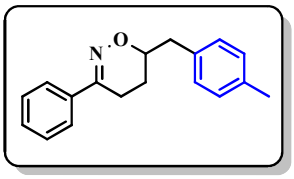
6-(4-fluorobenzyl)-3-phenyl-5,6-dihydro-4*H*-1,2-oxazine: Following the general procedure (II), the reaction of (*Z/E*)-1-phenylpent-4-en-1-one oxime (0.2 mmol, 35 mg) and 1-fluoro-4-iodobenzene (0.24 mmol, 53.3 mg) afforded **3b** (44.7 mg, 83% yield) as a white solid, m.p. = 85 - 86ºC.

^{1}H NMR (400 MHz, $CHCl_3$) δ 7.60 (m, 2H), 7.31 – 7.27 (m, 3H), 7.21 – 7.14 (m, 2H), 6.92 (m, 2H), 3.97 – 3.77 (m, 1H), 3.01 (dd, *J* = 14.0, 6.3 Hz, 1H), 2.78 (dd, *J* = 14.0, 6.2 Hz, 1H), 2.61 (m, 1H), 2.49 (m, 1H), 2.07 – 1.87 (m, 1H), 1.81 – 1.59 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 162.8 (d, *J* = 243 Hz), 154.6, 135.7, 132.8 (d, *J* = 3.2 Hz), 131.0 (d, *J* = 7.9 Hz), 129.4, 128.4, 125.3, 115.2 (d, *J* = 21 Hz), 75.6, 39.6, 23.8, 21.9. **^{19}F NMR** (470 MHz, $CDCl_3$) δ [(-116.6) - (-116.7), m, 1F].**HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{17}H_{17}FNO$ ($[M + H]^+$), 270.1289; found 270.1293.



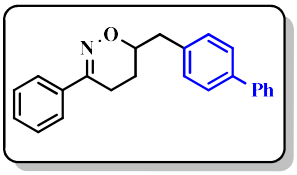
6-benzyl-3-phenyl-5,6-dihydro-4*H*-1,2-oxazine: Following the general procedure (II), the reaction of (*Z/E*)-1-phenylpent-4-en-1-one oxime (0.2 mmol, 35 mg) and iodobenzene (0.24 mmol, 49.0 mg) afforded **3c** (41.7 mg, 83% yield) as a white solid, m.p. = 87 - 88 ºC.

^{1}H NMR (400 MHz, $CHCl_3$) δ 7.72 – 7.64 (m, 2H), 7.39 – 7.33 (m, 3H), 7.29 (m, 4H), 7.24 (s, 1H), 4.03 – 3.91 (m, 1H), 3.15 (dd, *J* = 13.8, 5.9 Hz, 1H), 2.85 (dd, *J* = 13.8, 6.9 Hz, 1H), 2.66 (m, 1H), 2.53 (m, 1H), 2.09 – 1.97 (m, 1H), 1.83 – 1.67 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 154.5, 137.1, 135.8, 129.58, 129.4, 128.41, 128.36, 126.5, 125.3, 75.8, 40.4, 23.7, 21.9. **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{17}H_{17}NNaO$ ($[M+Na]^+$), 274.1202; found 274.1202.



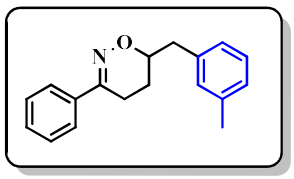
6-(4-methylbenzyl)-3-phenyl-5,6- dihydro-4*H*-1,2-oxazine : Following the general procedure (II), the reaction of (*Z/E*)-1-phenylpent-4-en-1-one oxime (0.2 mmol, 35 mg) and 1-iodo-4-methylbenzene (0.24 mmol, 52.3 mg) afforded **3d** (37.1 mg, 70% yield) as a white solid, m.p. = 93 - 94°C.

^{1}H NMR (400 MHz, $CHCl_3$) δ 7.73 – 7.63 (m, 2H), 7.41 – 7.32 (m, 3H), 7.15 (m, 4H), 4.01 – 3.88 (m, 1H), 3.12 (dd, *J* = 13.8, 5.8 Hz, 1H), 2.81 (dd, *J* = 13.7, 7.1 Hz, 1H), 2.67 (m, 1H), 2.53 (m, 1H), 2.33 (s, 3H), 2.10 – 1.97 (m, 1H), 1.83 – 1.67 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 154.5, 136.1, 135.9, 133.9, 129.44, 129.36, 129.1, 128.4, 125.3, 76.0, 40.0, 23.6, 21.9, 21.0. **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{18}H_{19}NNO$ ($[M+H]^+$), 288.1359; found 288.1367.



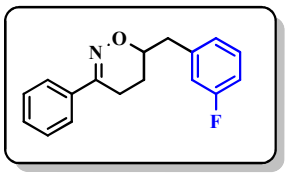
6-([1,1'-biphenyl]-4-ylmethyl)-3-phenyl-5,6-dihydro-4*H*-1,2-oxazine: Following the general procedure (II), the reaction of (*Z/E*)-1-phenylpent-4-en-1-one oxime (0.2 mmol, 35 mg) and 4-iodo-1,1'-biphenyl (0.24 mmol, 67.2 mg) afforded **3e** (60.8 mg, 93 % yield) as a yellow solid, m.p. = 114 - 115°C.

^{1}H NMR (400 MHz, $CHCl_3$) δ 7.71 – 7.65 (m, 2H), 7.61 – 7.53 (m, 4H), 7.42 (m, 2H), 7.35 (m, 6H), 4.08 – 3.89 (m, 1H), 3.16 (dd, *J* = 13.8, 6.1 Hz, 1H), 2.90 (dd, *J* = 13.8, 6.6 Hz, 1H), 2.67 (m, 1H), 2.60 – 2.48 (m, 1H), 2.13 – 2.00 (m, 1H), 1.78 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 154.5, 140.9, 139.5, 136.2, 135.8, 130.0, 129.4, 128.7, 128.4, 127.13, 127.11, 127.0, 125.3, 75.7, 40.1, 23.8, 21.9. **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{23}H_{21}NNaO$ ($[M+Na]^+$), 350.1515; found 350.1525.

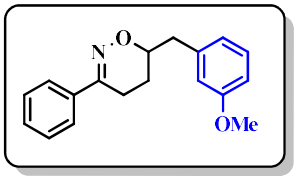


6-(3-methylbenzyl)-3-phenyl-5,6-dihydro-4*H*-1,2-oxazine: Following the general procedure (II), the reaction of (*Z/E*)-1-phenylpent-4-en-1-one oxime (0.2 mmol, 35 mg) and 1-iodo-3-methylbenzene (0.24 mmol, 52.3 mg) afforded **3f** (21.2 mg, 40% yield) as a white solid, m.p. = 60 - 61 °C.

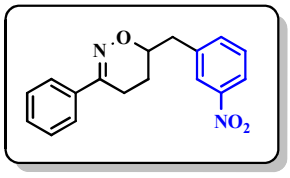
^{1}H NMR (400 MHz, $CHCl_3$) δ 7.72 – 7.63 (m, 2H), 7.41 – 7.27 (m, 4H), 7.23 – 7.01 (m, 3H), 4.02 – 3.90 (m, 1H), 3.12 (dd, *J* = 13.5, 5.8 Hz, 1H), 2.81 (dd, *J* = 13.7, 7.0 Hz, 1H), 2.67 (m, 1H), 2.54 (m, 1H), 2.34 (s, 3H), 2.09 – 1.97 (m, 1H), 1.82 – 1.67 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 154.5, 138.0, 137.0, 135.8, 130.3, 129.4, 128.4, 128.3, 127.3, 126.5, 125.7, 75.9, 40.4, 23.7, 21.9, 21.4. **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{18}H_{19}NNaO$ ($[M+Na]^+$), 288.1359; found 288.1358.



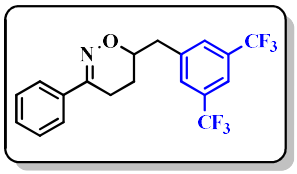
6-(3-fluorobenzyl)-3-phenyl-5,6-dihydro-4*H*-1,2-oxazine: Following the general procedure (II), the reaction of (*Z/E*)-1-phenylpent-4-en-1-one oxime (0.2 mmol, 35 mg) and 1-fluoro-3-iodobenzene (0.24 mmol, 53.3 mg) afforded **3g** (45.7 mg, 85% yield) as a white solid, m.p. = 67 - 68 ºC. **^{1}H NMR** (400 MHz, $CHCl_3$) δ 7.72 – 7.64 (m, 2H), 7.36 (m, 3H), 7.31 – 7.24 (m, 1H), 7.06 (m, 1H), 7.00 (m, 1H), 6.93 (m, 1H), 4.03 – 3.92 (m, 1H), 3.11 (dd, *J* = 13.9, 6.4 Hz, 1H), 2.87 (dd, *J* = 14.0, 6.2 Hz, 1H), 2.69 (m, 1H), 2.59 (m, 1H), 2.11 – 1.98 (m, 1H), 1.84 – 1.68 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 162.8 (d, *J* = 243 Hz), 154.6, 139.6 (d, *J* = 7.5 Hz), 135.7, 129.8 (d, *J* = 8.3 Hz), 129.5, 128.4, 125.3, 125.2 (d, *J* = 2.7 Hz), 116.4 (d, *J* = 21 Hz), 113.5 (d, *J* = 21 Hz), 75.4, 40.2 (d, *J* = 1.2 Hz), 23.9, 21.9. **^{19}F NMR** (470 MHz, $CDCl_3$) δ [(-113.4) - (-113.6), m, 1F]. **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{17}H_{16}FNNaO$ ($[M+Na]^+$), 292.1108; found 292.1112.



6-(3-methoxybenzyl)-3-phenyl-5,6-dihydro-4*H*-1,2-oxazine: Following the general procedure (II), the reaction of (*Z/E*)-1-phenylpent-4-en-1-one oxime (0.2 mmol, 35mg) and 1-iodo-3-methoxybenzene (0.24 mmol, 56.2 mg) afforded **3h** (31.5 mg, 56% yield) as a white solid, m.p. = 69 - 70 ºC. **^{1}H NMR** (400 MHz, $CHCl_3$) δ 7.68 (m, 2H), 7.42 – 7.32 (m, 3H), 7.29 – 7.18 (m, 1H), 6.92 – 6.75 (m, 3H), 4.03 – 3.92 (m, 1H), 3.80 (s, 3H), 3.13 (dd, *J* = 13.7, 5.8 Hz, 1H), 2.82 (dd, *J* = 13.7, 7.0 Hz, 1H), 2.73 – 2.61 (m, 1H), 2.55 (m, 1H), 2.10 – 1.99 (m, 1H), 1.82 – 1.69 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.6, 154.5, 138.6, 135.8, 129.4, 128.4, 125.3, 121.9, 115.3, 111.9, 75.8, 55.2, 40.5, 23.7, 21.9. **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{18}H_{19}NNaO_2$ ($[M+Na]^+$), 304.1308; found 304.1311.

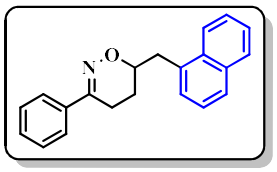


6-(3-nitrobenzyl)-3-phenyl-5,6-dihydro-4*H*-1,2-oxazine: Following the general procedure (II), the reaction of (*Z/E*)-1-phenylpent-4-en-1-one oxime (0.2 mmol, 35 mg) and 1-iodo-3-nitrobenzene (0.24 mmol, 59.8 mg) afforded **3i** (52.1 mg, 88% yield) as a white solid, m.p. = 90 - 91 ºC. **^{1}H NMR** (400 MHz, $CHCl_3$) δ 8.09 – 7.96 (m, 2H), 7.57 (m, 3H), 7.38 (m, 1H), 7.32 – 7.22 (m, 3H), 3.98 – 3.86 (m, 1H), 3.03 (dd, *J* = 14.2, 7.3 Hz, 1H), 2.94 (dd, *J* = 14.2, 5.0 Hz, 1H), 2.62 (m, 1H), 2.52 (m, 1H), 2.07 – 1.94 (m, 1H), 1.80 – 1.63 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 154.7, 148.3, 139.3, 135.9, 135.5, 129.6, 129.3, 128.4, 125.3, 124.3, 121.8, 74.9, 40.1, 24.1, 21.9. **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{17}H_{17}N_2O_3$ ($[M+H]^+$), 297.1234; found 297.1242.



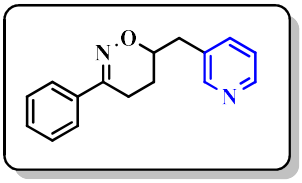
6-(3,5-bis(trifluoro- methyl)benzyl)-3-phenyl-5,6-dihydro -4*H*-1,2-oxazine: Following the general procedure (II), the reaction of (*Z/E*)-1-phenylpent-4-en-1-one oxime (0.2 mmol, 35 mg) and 1-iodo-3,5-bis(trifluoromethyl)benzene (0.24 mmol, 81.6 mg) afforded **3j** (61.9 mg, 80% yield) as a white solid, m.p. = 122 - 123 ºC.

^{1}H NMR (400 MHz, $CHCl_3$) δ 7.76 (m, 3H), 7.67 (m, 2H), 7.40 – 7.36 (m, 3H), 4.14 – 3.93 (m, 1H), 3.16 (dd, *J* = 14.3, 7.3 Hz, 1H), 3.07 (dd, *J* = 14.3, 4.8 Hz, 1H), 2.74 (m, 1H), 2.66 (m, 1H), 2.21 – 2.01 (m, 1H), 1.96 – 1.73 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 154.8, 139.8, 135.4, 131.6 (q, *J* = 33 Hz), 129.68, 129.65, 128.5, 125.3, 123.3 (q, *J* = 270 Hz), 120.7 (hept, $^3J_{C\text{-}F}$ = 3.7 Hz), 74.8, 40.3, 24.2, 21.9. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -62.7 (s, 6F). **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{19}H_{15}F_6NNaO$ ($[M+Na]^+$),410.0950; found 410.0963.



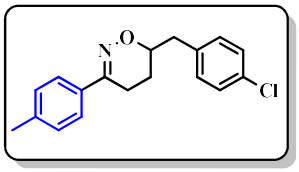
6-(naphthalen-1-ylmethyl)-3-phenyl-5,6- dihydro-4*H*-1,2-oxazine: Following the general procedure (II), the reaction of (*Z/E*)-1-phenylpent-4-en-1-one oxime (0.2 mmol, 35 mg) and 1-iodonaphthalene (0.24 mmol, 61 mg) afforded **3k** (57.8 mg, 96% yield) as a white solid, m.p. = 148 - 149 ºC.

^{1}H NMR (400 MHz, $CHCl_3$) δ 8.11 (d, *J* = 8.4 Hz, 1H), 7.87 (m, 1H), 7.81 – 7.74 (m, 1H), 7.67 (m, 2H), 7.57 – 7.46 (m, 2H), 7.45 – 7.41 (m, 2H), 7.37 – 7.34 (m, 3H), 4.26 – 4.03 (m, 1H), 3.73 (dd, *J* = 13.9, 5.3 Hz, 1H), 3.22 (dd, *J* = 13.9, 8.0 Hz, 1H), 2.66 (m, 1H), 2.47 (m, 1H), 2.09 – 1.95 (m, 1H), 1.94 – 1.75 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 154.7, 135.8, 133.9, 133.0, 132.2, 129.4, 128.8, 128.4, 128.0, 127.5, 126.1, 125.6, 125.5, 125.3, 123.8, 75.1, 37.6, 24.2, 22.0. **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{21}H_{19}NNaO$ ($[M+Na]^+$), 324.1359; found 324.1366.

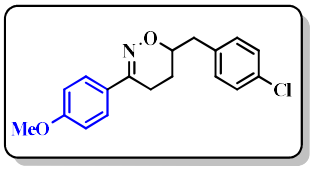


3-phenyl-6-(pyridin-3-ylmethyl)-5,6-dihydro-4*H*-1,2-oxazine: Following the general procedure (II), the reaction of (*Z/E*)-1-phenylpent-4-en-1-one oxime (0.2 mmol, 35 mg) and 3-bromopyridine (0.24 mmol, 37.9 mg) afforded **3l** (43.4 mg, 86% yield) as a yellow solid, m.p. = 82 - 83 ºC.

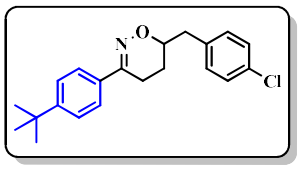
^{1}H NMR (400 MHz, $CHCl_3$) δ 8.57 – 8.44 (m, 2H), 7.72 – 7.60 (m, 3H), 7.41 – 7.31 (m, 3H), 7.25 (m, 1H), 3.98 (m, 1H), 3.06 (dd, *J* = 14.2, 6.7 Hz, 1H), 2.92 (dd, *J* = 14.2, 5.5 Hz, 1H), 2.70 (m, 1H), 2.59 (m, 1H), 2.14 – 1.98 (m, 1H), 1.87 – 1.68 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 154.7, 150.5, 148.0, 137.2, 135.6, 132.7, 129.5, 128.4, 125.3, 123.3, 75.1, 37.6, 23.9, 21.8. **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{16}H_{17}N_2O$ ($[M+H]^+$), 253.1341; found 253.1407.



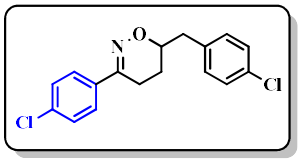
6-(4-chlorobenzyl)- 3-(p-tolyl)-5,6-dihydro-4*H*-1,2-oxazine: Following the general procedure (II), the reaction of (*Z/E*)-1-(p-tolyl)pent-4-en-1-one oxime (0.2 mmol, 37.8 mg) and 1-chloro-4-iodobenzene (0.24 mmol, 57.2 mg) afforded **3m** (42.6 mg, 71% yield) as a white solid, m.p. = 94 - 95 ºC. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.6 Hz, 2H), 7.38 – 7.10 (m, 6H), 4.01 – 3.86 (m, 1H), 3.06 (dd, *J* = 13.8, 6.1 Hz, 1H), 2.85 (dd, *J* = 13.8, 5.8 Hz, 1H), 2.67 (m, 1H), 2.55 (m, 1H), 2.35 (s, 3H), 2.10 – 1.96 (m, 1H), 1.84 – 1.65 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 154.5, 139.5, 135.7, 132.9, 132.4, 130.9, 129.1, 128.5, 125.2, 75.4, 39.8, 23.9, 21.9, 21.3. **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{18}H_{19}ClNO$ ($[M+H]^+$), 300.1150; found 300.1159.



6-(4-chlorobenzyl)-3-(4- methoxyphenyl)-5,6-dihydro-4*H*-1,2-oxazine: Following the general procedure (II), the reaction of (*Z/E*)-1-(4-methoxyphenyl)pent-4-en-1-one oxime (0.2 mmol, 41.0 mg) and 1-chloro-4-iodobenzene (0.24 mmol, 57.2 mg) afforded **3n** (41.7 mg, 66% yield) as a white solid, m.p. = 115 - 116 ºC.
^{1}H NMR (400 MHz, $CHCl_3$) δ 7.63 (m, 2H), 7.27 (m, 2H), 7.22 (m, 2H), 6.89 (m, 2H), 3.98 – 3.87 (m, 1H), 3.82 (s, 3H), 3.06 (dd, *J* = 14.0, 6.4 Hz, 1H), 2.85 (dd, *J* = 14.0, 6.1 Hz, 1H), 2.67 (m, 1H), 2.54 (m, 1H), 2.08 – 1.97 (m, 1H), 1.84 – 1.65 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 160.6, 154.2, 135.7, 132.4, 130.9, 128.5, 128.2, 126.6, 113.7, 75.3, 55.3, 39.8, 23.9, 21.8. **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{18}H_{18}ClNNaO_2$ ($[M+Na]^+$), 338.0918; found 338.0921.

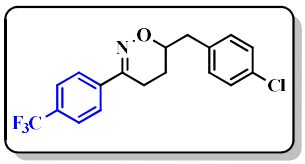


3-(4-(tert-butyl)phenyl)-6-(4-chlorobenzyl)-5,6-dihydro-4*H*-1,2-oxazine: Following the general procedure (II), the reaction of (*Z/E*)-1-(4-(tert-butyl)phenyl)pent-4-en-1-one oxime (0.2 mmol, 46.2 mg) and 1-chloro-4-iodobenzene (0.24 mmol, 57.2 mg) afforded **3o** (56.1 mg, 82% yield) as a white solid, m.p. = 131 - 132 ºC.
^{1}H NMR (400 MHz, $CHCl_3$) δ 7.61 (m, 2H), 7.39 (m, 2H), 7.28 (m, 2H), 7.21 (m, 2H), 3.92 (m, 1H), 3.07 (dd, *J* = 14.0, 6.4 Hz, 1H), 2.84 (dd, *J* = 13.9, 6.1 Hz, 1H), 2.66 (m, 1H), 2.57 (m, 1H), 2.14 – 1.94 (m, 1H), 1.75 (m, 1H), 1.32 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 154.5, 152.7, 135.7, 132.8, 132.4, 130.9, 128.5, 125.3, 125.0, 75.4, 39.8, 34.7, 31.2, 23.9, 21.8. **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{21}H_{24}ClNNaO$ ($[M+Na]^+$), 364.1439; found 364.1439.



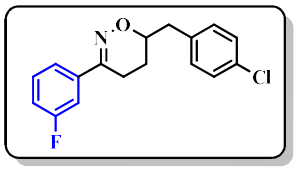
6-(4-chlorobenzyl)-3-(4-chlorophenyl)-5,6-dihydro-4*H*-1,2-oxazine: Following the general procedure (II), the reaction of(Z/E)-1-(4-chlorophenyl)pent-4-en-1-one oxime (0.2 mmol, 41.9 mg) and 1-chloro-4-iodobenzene (0.24 mmol, 57.2 mg) afforded **3p** (51.2 mg, 80% yield) as a white solid, m.p. = 111 - 112 ºC.

^{1}H NMR (400 MHz, $CHCl_3$) δ 7.61 (m, 2H), 7.33 (m, 2H), 7.28 (m, 2H), 7.21 (m, 2H), 4.05 – 3.85 (m, 1H), 3.06 (dd, *J* = 14.0, 6.4 Hz, 1H), 2.86 (dd, *J* = 14.0, 6.1 Hz, 1H), 2.61 (m, 1H), 2.55 (m, 1H), 2.04 (m, 1H), 1.87 – 1.65 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 153.5, 135.4, 134.1, 132.5, 130.9, 128.6, 128.5, 126.5, 75.6, 39.7, 23.6, 21.8. **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{17}H_{15}Cl_2NNaO$ ($[M+Na]^+$), 342.0423; found 342.0413.



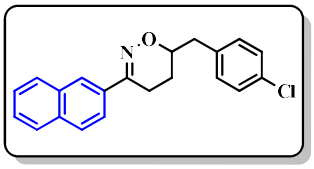
6-(4-chlorobenzyl)-3-(4-(trifluoromethyl)phenyl)-5,6-dihydro-4*H*-1,2-oxazine: Following the general procedure (II), the reaction of (*Z/E*)-1-(4-(trifluoromethyl)phenyl)pent-4-en-1-one oxime (0.2 mmol, 48.6 mg) and 1-chloro-4-iodobenzene (0.24 mmol, 57.2 mg) afforded **3q** (56.6 mg, 80% yield) as a white solid, m.p. = 92 - 93ºC.

^{1}H NMR (400 MHz, $CHCl_3$) δ 7.79 (m, 2H), 7.62 (m, 2H), 7.29 (m, 2H), 7.22 (m, 2H), 4.09 – 3.88 (m, 1H), 3.08 (dd, *J* = 14.0, 6.4 Hz, 1H), 2.88 (dd, *J* = 14.0, 6.1 Hz, 1H), 2.68 (m, 1H), 2.60 (m, 1H), 2.19 – 1.95 (m, 1H), 1.90 – 1.66 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 153.3, 139.0, 135.4, 132.6, 131.3 (q, *J* = 33 Hz), 130.9, 128.6, 125.5, 125.4 (q, *J* = 3.7 Hz), 124.0 (q, *J* = 270 Hz), 75.8, 39.7, 23.5, 21.9. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -62.8 (s ,3F). **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{18}H_{16}ClF_3NO$ ($[M+H]^+$), 354.0867; found 354.0877.



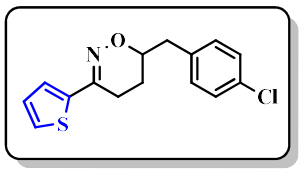
6-(4-chlorobenzyl)-3-(3-fluorophenyl)-5,6-dihydro-4*H*-1,2-oxazine: Following the general procedure (II), the reaction of (*Z/E*)-1-(3-fluorophenyl)pent-4-en-1-one oxime (0.2 mmol, 38.6 mg) and 1-chloro-4-iodobenzene (0.24 mmol, 57.2 mg) afforded **3r** (51.7 mg, 85% yield) as a white solid, m.p. = 81 - 82ºC.

^{1}H NMR (400 MHz, $CHCl_3$) δ 7.43 (m, 2H), 7.38 – 7.26 (m, 3H), 7.22 (m, 2H), 7.07 (m, 1H), 4.05 – 3.88 (m, 1H), 3.08 (dd, *J* = 14.0, 6.4 Hz, 1H), 2.88 (dd, *J* = 14.0, 6.1 Hz, 1H), 2.65 (m, 1H), 2.55 (m, 1H), 2.16 – 1.96 (m, 1H), 1.89 – 1.66 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 162.8 (d, *J* = 243 Hz), 153.4(d, *J* = 2.6 Hz), 137.9 (d, *J* = 7.7 Hz), 135.4, 132.5, 130.9, 129.9(d, *J* = 8.1 Hz), 128.6, 120.9 (d, *J* = 2.9 Hz), 116.4 (d, *J* = 21.2 Hz), 112.3 (d, *J* = 23.1 Hz), 75.7, 39.7, 23.6, 21.9. **^{19}F NMR** (470 MHz, $CDCl_3$) δ [(-112.6) - (-112.8), m, 1F). **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{17}H_{16}ClNO$ ($[M+H]^+$), 304.0899; found 304.0899.



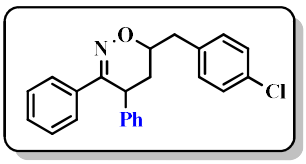
6-(4-chlorobenzyl)-3-(naphthalen-2-yl)-5,6-dihydro-4*H*-1,2-oxazine: Following the general procedure (II), the reaction of (*Z/E*)-1-(naphthalen-2-yl)pent-4-en-1-one oxime (0.2 mmol, 45.1 mg) and 1-chloro-4-iodobenzene (0.24 mmol, 57.2 mg) afforded **3s** (49.1 mg, 73% yield) as a white solid, m.p. = 116 - 117 ºC.

^{1}H NMR (400 MHz, $CHCl_3$) δ 8.01 – 7.94 (m, 2H), 7.85 – 7.77 (m, 3H), 7.52 – 7.43 (m, 2H), 7.32 – 7.26 (m, 2H), 7.22 (m, 2H), 4.05 – 3.90 (m, 1H), 3.07 (dd, *J* = 14.0, 6.5 Hz, 1H), 2.86 (dd, *J* = 14.0, 6.0 Hz, 1H), 2.80 (m, 1H), 2.74 – 2.57 (m, 1H), 2.15 – 1.97 (m, 1H), 1.77 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 154.3, 135.6, 133.8, 133.1, 132.9, 132.4, 130.9, 128.5, 128.4, 128.1, 127.6, 126.7, 126.3, 124.8, 122.8, 75.6, 39.8, 23.8, 21.8. **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{21}H_{18}ClNNaO$ ($[M+Na]^+$), 358.0969; found 358.0966.



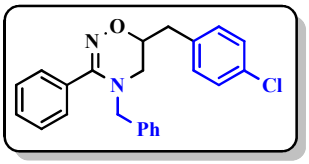
6-(4-chlorobenzyl)-3-(thiophen-2-yl)-5,6-dihydro-4*H*-1,2-oxazine: Following the general procedure (II), the reaction of (*Z/E*)-1-(thiophen-2-yl)pent-4-en-1-one oxime (0.2 mmol, 36.2 mg) and 1-chloro-4-iodobenzene (0.24 mmol, 57.2 mg) afforded **3t** (30.0 mg, 52% yield) as a white solid, m.p. = 82 - 83 ºC.

^{1}H NMR (400 MHz, $CHCl_3$) δ 7.32 – 7.25 (m, 4H), 7.20 (m, 3H), 7.01 (m, 1H), 4.06 – 3.85 (m, 1H), 3.05 (dd, *J* = 14.0, 6.5 Hz, 1H), 2.86 (dd, *J* = 14.0, 6.0 Hz, 1H), 2.72 (m, 1H), 2.67 – 2.54 (m, 1H), 2.12 – 1.93 (m, 1H), 1.88 – 1.67 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 151.4, 139.8, 135.5, 132.5, 130.9, 128.5, 127.2, 126.9, 125.3, 76.0, 39.8, 23.5, 22.2. **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{15}H_{14}ClNNaOS$ ($[M+Na]^+$), 314.0377; found 314.0369.



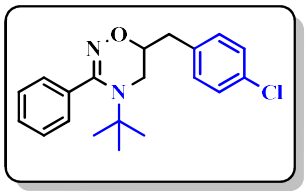
6-(4-chlorobenzyl)-3,4-diphenyl-5,6-dihydro-4*H*-1,2-oxazine: Following the general procedure (II), the reaction of (*Z/E*)-1,2-diphenylpent-4-en-1-one oxime (0.2 mmol, 47.1 mg) and 1-chloro-4-iodobenzene (0.24 mmol, 57.2 mg) afforded **3u** (39.0 mg, 54% yield, 2.0/1 d.r.) as a white solid, m.p. = 160-161ºC.

^{1}H NMR (400 MHz, $CHCl_3$) δ 7.59 (m, 2H), 7.31 – 7.21 (m, 8H), 7.16 (m, 4H), 4.16 (m, 1H), 4.13 – 4.02 (m, 1H), 2.93 (dd, *J* = 14.3, 6.7 Hz, 1H), 2.86 (dd, *J* = 14.3, 4.8 Hz, 1H), 2.10 – 2.00 (m, 1H), 1.99 – 1.91 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 153.3, 142.1, 135.4, 135.0, 132.4, 130.9, 129.1, 128.9, 128.31, 128.28, 127.0, 126.0, 70.9, 39.8, 37.2, 32.6. **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{23}H_{20}ClNNaO$ ($[M+Na]^+$), 384.1126; found 384.1126.



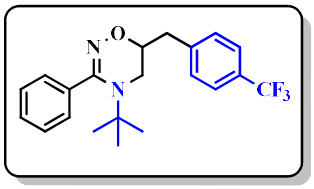
4-benzyl-6-(4- chlorobenzyl)-3-phenyl-5,6-dihydro-4*H*-1,2,4-oxadiazine: Following the general procedure (II), the reaction of (*Z/E*)-*N*-allyl-*N*-benzyl-*N*′-hydroxybenzimidamide (0.2 mmol, 50.0 mg) and 1-chloro-4-iodobenzene (0.24 mmol, 57.2 mg) afforded **4a** (38.4 mg, 51% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CHCl_3$) δ 7.55 – 7.47 (m, 2H), 7.38 (m, 3H), 7.30 (m, 3H), 7.26 – 7.21 (m, 2H), 7.16 – 7.08 (m, 4H), 4.27 (d, *J* = 15.7 Hz, 1H), 4.13 (d, *J* = 15.6 Hz, 1H), 3.98 – 3.85 (m, 1H), 3.21 – 3.07 (m, 2H), 3.00 (dd, *J* = 14.2, 6.6 Hz, 1H), 2.72 (dd, *J* = 14.2, 6.2 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 156.3, 136.3, 135.3, 132.4, 132.2, 130.6, 129.7, 128.79, 128.75, 128.5, 127.7, 127.3, 73.0, 55.3, 49.2, 37.7. **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{23}H_{22}ClN_2O$ ($[M+H]^+$); 377.1415; found 377.1410.



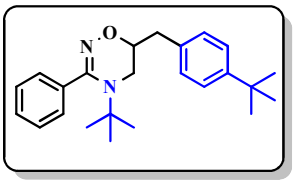
4-(tert-butyl)-6-(4-chlorobenzyl)-3-phenyl-5,6-dihydro-4*H*-1,2,4-oxadiazine: Following the general procedure (II), the reaction of (*Z/E*)-*N*-allyl-*N*-(tert-butyl)-*N*′-hydroxybenzimidamide (0.2 mmol, 46 mg) and 4-Bromochlorobenzene (0.24 mmol, 46 mg) afforded **4a'** (55 mg, 81% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CHCl_3$) δ 7.44 – 7.39 (m, 2H), 7.30 (m, 5H), 7.23 (m, 2H), 4.05 – 3.93 (m, 1H), 3.54 – 3.41 (m, 1H), 3.04 (dd, *J* = 14.1, 6.3 Hz, 1H), 2.93 (m, 1H), 2.79 (dd, *J* = 14.1, 6.3 Hz, 1H), 1.03 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 155.8, 137.3, 135.4, 132.4, 130.7, 128.9, 128.8, 128.5, 127.8, 75.6, 58.2, 46.4, 38.1, 30.0. **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{20}H_{23}ClN_2NaO$ ($[M+Na]^+$); 365.1397; found 365.1396.



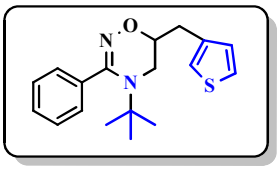
4-(tert-butyl)- 3-phenyl-6-(4-(trifluoromethyl)benzyl)-5,6-dihydro-4*H*-1,2,4-oxadiazine: Following the general procedure (II), the reaction of (*Z/E*)-*N*-allyl-*N*-(tert-butyl)-*N*′-hydroxybenzimidamide (0.2 mmol, 46 mg) and 4-Bromobenzotrifluoride (0.24 mmol, 54 mg) afforded **4b** (50 mg, 66% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CHCl_3$) δ 7.57 (m, 2H), 7.41 (m, 4H), 7.33 (m, 3H), 4.09 – 4.00 (m, 1H), 3.51 (dd, *J* = 12.5, 2.5 Hz, 1H), 3.10 (dd, *J* = 14.1, 6.7 Hz, 1H), 2.94 (m, 2H), 1.05 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 156.0, 141.1, 137.2, 129.7, 128.95, 128.93 (q, *J* = 33 Hz), 128.91, 127.8, 125.3(q, *J* = 3.7 Hz), 124.2 (q, *J* = 270 Hz), 75.4, 58.3, 46.6, 38.6, 30.0. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -62.4 (s, 3F). **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{21}H_{23}F_3N_2NaO$ ($[M+Na]^+$); 399.1660; found 399.1656.



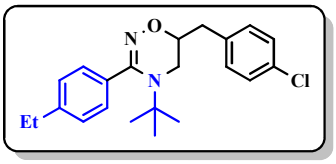
4-(tert-butyl)- 6-(4-(tert-butyl)benzyl)-3-phenyl-5,6-dihydro-4*H*-1,2,4- oxadiazine: Following the general procedure (II), the reaction of (*Z/E*)-*N*-allyl-*N*-(tert-butyl)-*N*′-hydroxy benzimidamide (0.2 mmol, 46 mg) and 1-Bromo-4-tert-butylbenzene (0.24 mmol, 51 mg) afforded **4c** (50 mg, 68% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CHCl_3$) δ 7.44 – 7.39 (m, 2H), 7.32 (m, 5H), 7.22 (m, 2H), 4.07 – 3.94 (m, 1H), 3.49 (dd, *J* = 12.5, 2.3 Hz, 1H), 3.07 (dd, *J* = 14.0, 6.0 Hz, 1H), 2.95 (m, 1H), 2.77 (dd, *J* = 14.0, 6.8 Hz, 1H), 1.31 (s, 9H), 1.03 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 155.8, 149.4, 137.5, 133.8, 128.98, 128.96, 128.8, 127.8, 125.4, 76.0, 58.1, 46.7, 38.3, 34.4, 31.3, 30.1. **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{24}H_{32}N_2NaO$ ($[M+Na]^+$); 387.2412; found 387.2413.



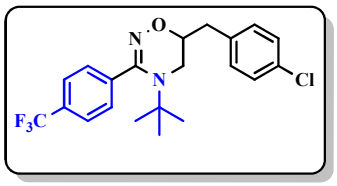
4-(tert-butyl)-3-phenyl-6-(thiophen- 3-ylmethyl)-5,6-dihydro-4*H*-1,2,4-oxadiazine: Following the general procedure (II), the reaction of (*Z/E*)-*N*-allyl-*N*-(tert-butyl)-*N*′-hydroxy benzimidamide (0.2 mmol, 46 mg) and 3-Bromothiophene (0.24 mmol, 39 mg) afforded **4d** (33 mg, 53% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CHCl_3$) δ 7.45 – 7.40 (m, 2H), 7.33 (m, 3H), 7.28 (m, 1H), 7.12 (s, 1H), 7.05 (m, 1H), 4.02 (m, 1H), 3.49 (dd, *J* = 12.6, 2.4 Hz, 1H), 3.09 (dd, *J* = 14.5, 5.8 Hz, 1H), 2.97 – 2.81 (m, 2H), 1.09 – 0.98 (m, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 155.7, 137.5, 137.0, 129.0, 128.8, 128.7, 127.8, 125.6, 122.1, 75.4, 58.2, 46.5, 33.2, 30.1. **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{18}H_{22}N_2NaOS$ ($[M+Na]^+$); 337.1351; found 337.1345.



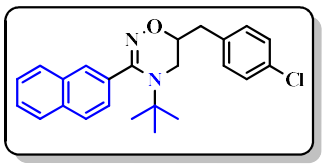
4-(tert-butyl)-6-(4-chlorobenzyl)-3-(4-ethylphenyl)-5,6-dihydro-4*H*-1,2,4-oxadiazine: Following the general procedure (II), the reaction of (*Z/E*)-*N*-allyl-*N*-(*tert*-butyl)-4-ethyl-*N*′-hydroxybenzimid amide (0.2 mmol, 52 mg) and 4-Bromochlorobenzene (0.24 mmol, 46 mg) afforded **4e** (55 mg, 74% yield) as a yellow solid, m.p. = 111 - 112 °C.

^{1}H NMR (400 MHz, $CHCl_3$) δ 7.29 (m, 4H), 7.23 (m, 2H), 7.14 (m, 2H), 4.04 – 3.93 (m, 1H), 3.46 (dd, *J* = 12.5, 2.4 Hz, 1H), 3.04 (dd, *J* = 14.1, 6.2 Hz, 1H), 2.93 (m, 1H), 2.79 (dd, *J* = 14.1, 6.3 Hz, 1H), 2.64 (q, *J* = 7.6 Hz, 2H), 1.21 (t, *J* = 7.6 Hz, 3H), 1.04 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 156.0, 145.2, 135.5, 134.5, 132.4, 130.7, 128.9, 128.6, 127.3, 75.6, 58.2, 46.5, 38.1, 30.1, 28.6, 15.4. **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{22}H_{28}ClN_2O$ ($[M+H]^+$); 371.1890; found 371.1885.



4-(tert-butyl)-6-(4-chlorobenzyl)-3-(4-(trifluoromethyl)phenyl)-5,6-dihydro-4*H*-1,2,4-oxadiazine: Following the general procedure (II), the reaction of (*Z/E*)-*N*-allyl-*N*-(*tert*-butyl)-*N*′-hydroxy-4-(trifluoromethyl)benzimidamide (0.2 mmol, 60 mg) and 4-Bromochlorobenzene (0.24 mmol, 46 mg) afforded **4f** (62 mg, 76% yield) as a yellow solid, m.p. = 156 - 157 ºC.

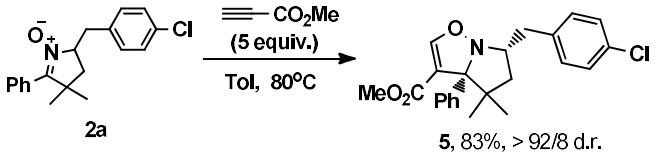
^{1}H NMR (400 MHz, $CHCl_3$) δ 7.57 (m, 4H), 7.29 (m, 2H), 7.23 (m, 2H), 4.08 – 3.91 (m, 1H), 3.49 (dd, *J* = 12.8, 2.4 Hz, 1H), 3.05 (dd, *J* = 14.1, 6.2 Hz, 1H), 2.95 – 2.75 (m, 2H), 1.03 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 154.1, 141.3, 135.1, 132.6, 130.9 (q, *J* = 33 Hz), 130.6, 129.1, 128.6, 124.8 (bs, 1C), 123.9 (q, *J* = 270 Hz), 75.9, 58.5, 46.0, 38.0, 30.0. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -62.6 (s, 3F). **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{21}H_{22}ClF_3N_2NaO$ ($[M+Na]^+$); 433.1270; found 433.1265.



4-(tert-butyl)-6-(4-chlorobenzyl)-3-(naphthalen-2-yl)-5,6-dihydro-4*H*-1,2,4-oxadiazine: Following the general procedure (II), the reaction of (*Z/E*)-*N*-allyl-*N*-(tert-butyl)-*N*′-hydroxy-2-naphthimidamide (0.2 mmol, 56 mg) and 4-Bromochlorobenzene (0.24 mmol, 46 mg) afforded **4g** (48 mg, 61% yield) as a yellow solid, m.p. = 137 - 138 ºC.

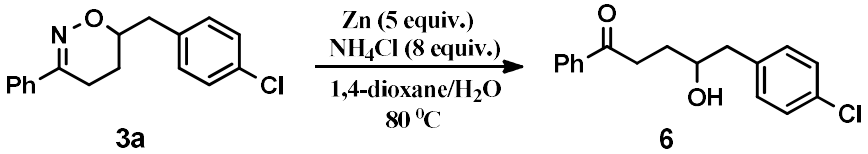
^{1}H NMR (400 MHz, $CHCl_3$) δ 7.91 (s, 1H), 7.86 – 7.76 (m, 4H), 7.55 – 7.45 (m, 3H), 7.30 (m, 2H), 7.24 (m, 1H), 4.11 – 3.98 (m, 1H), 3.52 (dd, *J* = 12.6, 2.4 Hz, 1H), 3.08 (dd, *J* = 14.1, 6.2 Hz, 1H), 3.02 – 2.88 (m, 1H), 2.82 (dd, *J* = 14.1, 6.3 Hz, 1H), 1.05 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 135.4, 134.8, 133.5, 132.8, 132.5, 130.70, 128.6, 128.3, 128.2, 127.6, 127.4, 126.7, 126.5, 126.2, 75.8, 58.4, 46.4, 38.2, 30.1. **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{24}H_{25}ClN_2NaO$ ($[M+Na]^+$); 415.1553; found 415.1550.

3.2 Synthetic elaboration of products and characterization data.



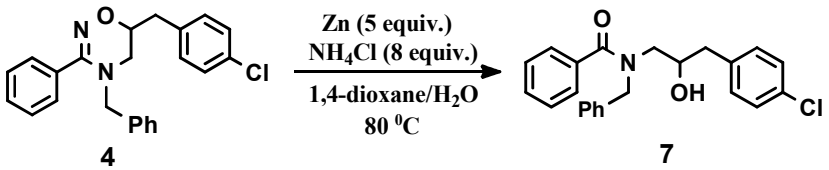
(3*R,6*R**)-Methyl 6-(4-chlorobenzyl)-4,4-dimethyl-3a-phenyl-3a,4,5,6-tetrahydro pyrrolo[1,2-*b*]isoxazole-3-carboxylate:** nitrone **2a** (31 mg, 0.1 mmol) and methyl propiolate (42 mg, 0.5 mmol, 5 equiv.) were dissolved in toluene (2 mL) in a vial. The mixture was stirred at 80^0C until full conversion was reached, as monitored by TLC. The solvent was removed *in vacuo*, and the residue was purified by column chromatography (petroleum: EtOAc = 45:1) to afford the corresponding cycloadduct **5** (33 mg, 83% yield, > 92/8 d.r.) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (m, 2H), 7.36 (s, 1H), 7.26-7.15 (m, 4H), 7.15-7.06 (m, 3H), 3.68 (s, 3H), 3.57-3.42 (m, 1H), 3.11 (dd, *J* = 13.4, 4.6 Hz, 1H), 2.85 (dd, *J* = 13.4, 7.7 Hz, 1H), 1.48 – 1.34 (m, 2H), 1.18 (s, 3H), 0.67 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.1, 155.8, 144.9, 137.0, 132.2, 131.0, 128.4, 127.7, 127.0, 126.7, 111.6, 83.8, 67.9, 51.4, 44.7, 43.8, 39.3, 27.7, 27.3. **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{23}H_{24}ClNNaO_3$ ($[M+Na]^+$), 420.1337; found 420.1337.



5-(4-Chlorophenyl)-4-hydroxy-1-phenylpentan-1-one: Dihydroazine **3a** (28.6 mg, 0.10 mmol), Zn powder (32.7 mg, 0.50 mmol, 5 equiv.), and NH_4Cl (42.8 mg, 0.80 mmol, 8 equiv.) were dissolved in dioxane/H_2O (2 mL, 1:1 v/v) in a vial. The mixture was stirred at 80^0C until full conversion was reached, as monitored by TLC. The solvent was removed *in vacuo*, and the residue was purified by column chromatography (petroleum: EtOAc = 15:1) to afford γ-hydroxyketone **6** (18.2 mg, 63% yield) as a white solid, m.p. = 66 - 67 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.6 Hz, 2H), 7.60-7.54 (m, 1H), 7.50-7.42 (m, 2H), 7.31-7.24 (m, 2H), 7.20-7.13 (m, 2H), 3.89 (m, 1H), 3.17 (t, *J* = 6.9 Hz, 2H), 2.83 (dd, *J* = 13.6, 4.6 Hz, 1H), 2.73 (dd, *J* = 13.6, 8.1 Hz, 1H), 2.10 – 1.94 (m, 2H), 1.92 – 1.78 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 200.6, 136.9, 136.8, 133.2, 132.4, 130.8, 128.8, 128.6, 128.1, 72.0, 43.7, 34.9, 30.8. **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{17}H_{17}ClNNaO_2$ ($[M+Na]^+$), 311.0809; found 311.0805.



***N*-Benzyl-*N*-(3-(4-chlorophenyl)-2-hydroxypropyl)benzamide:** diazine **4** (37.7 mg, 0.10 mmol), Zn powder (32.7 mg, 0.50 mmol, 5 equiv.), and NH_4Cl (42.8 mg, 0.80

mmol, 8 equiv.) were dissolved in dioxane/H_2O (2 mL, 1:1 v/v). The mixture was stirred at 80ºC until full conversion was reached, as monitored by TLC. The solvent was removed *in vacuo*, and the residue was purified by column chromatography (petroleum: EtOAc = 4:1) to afford the corresponding β-amino alcohol derivative **7** (24.5 mg, 67% yield) as a yellow solid, m.p. = 93 - 94 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (m, 1H), 7.37 (m, 2H), 7.30 (m, 2H), 7.20 (m, 1H), 7.06 (m, 4H), 4.50 (m, 2H), 4.01 (d, *J* = 9.2 Hz, 2H), 3.81 – 3.63 (m, 1H), 3.29 (d, *J* = 14.0 Hz, 1H), 2.81 – 2.55 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 174.2, 136.4, 136.1, 135.5, 132.2, 130.6, 130.0, 128.8, 128.5, 127.8, 127.1 126.8, 72.2, 54.5, 51.9, 41.4. **HRMS** (ESI-TOF) (*m/z*): Calcd for $C_{23}H_{22}ClNNaO_2$ ($[M+Na]^+$), 402.1231; found 402.1241.

References

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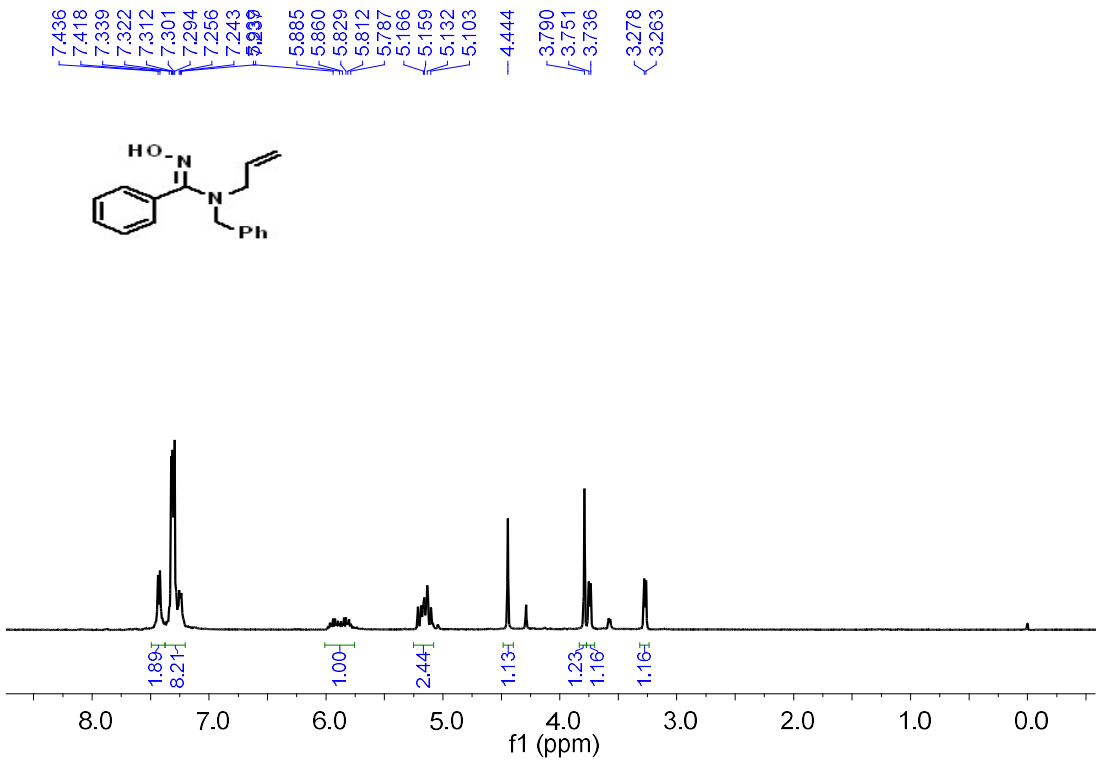
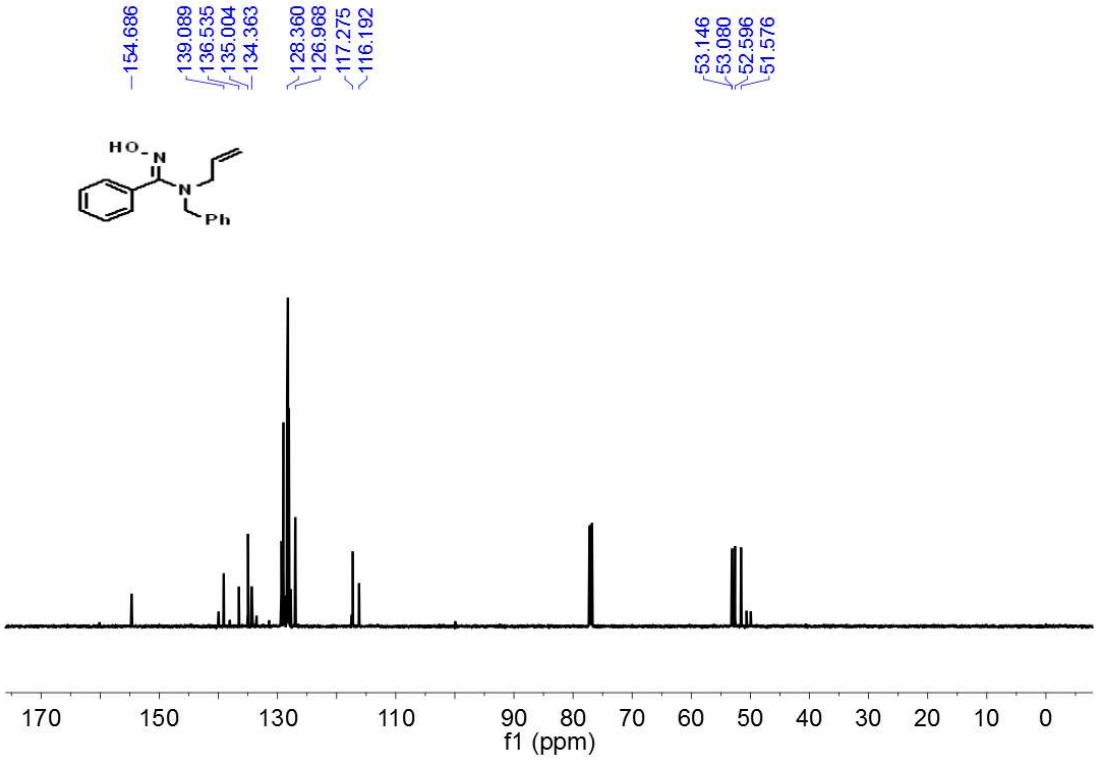
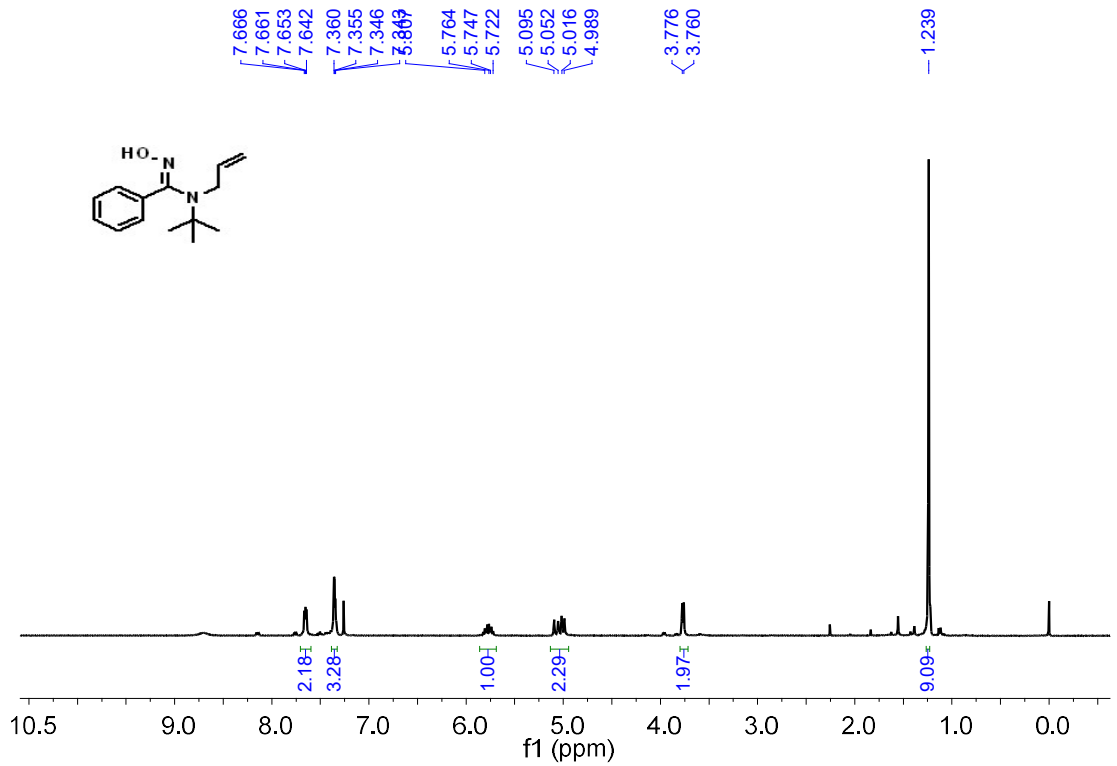
4. NMR spectra of all new compounds



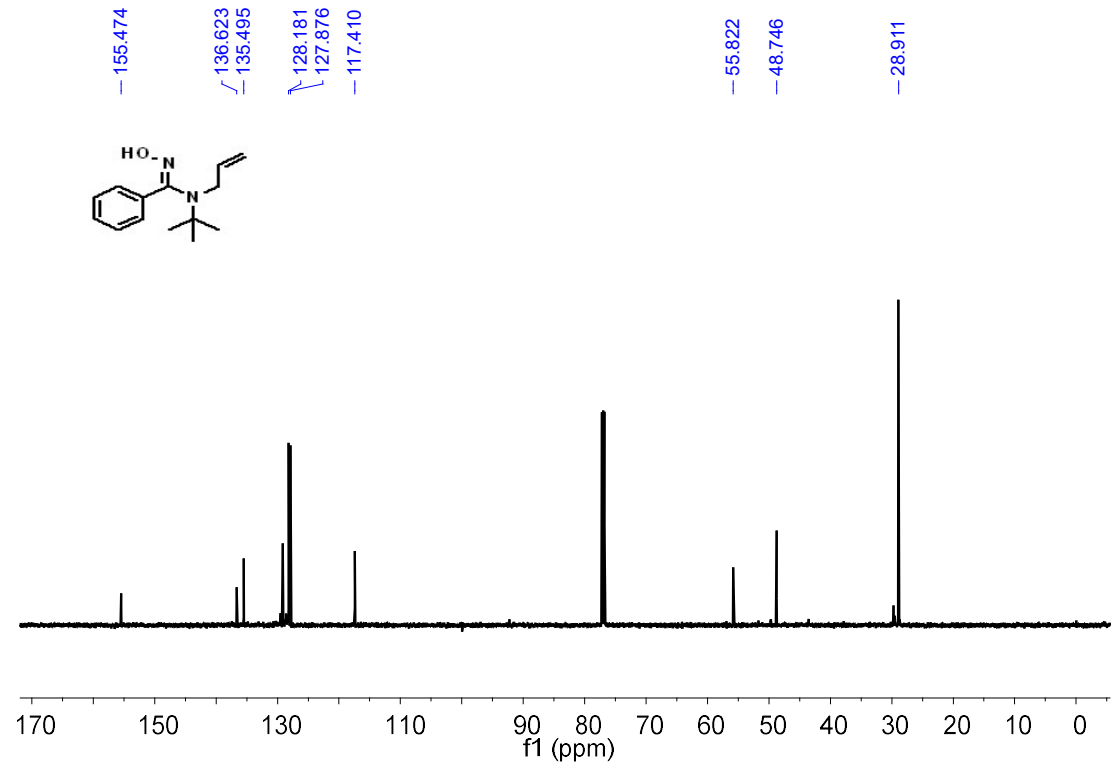
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for substrate 1s.



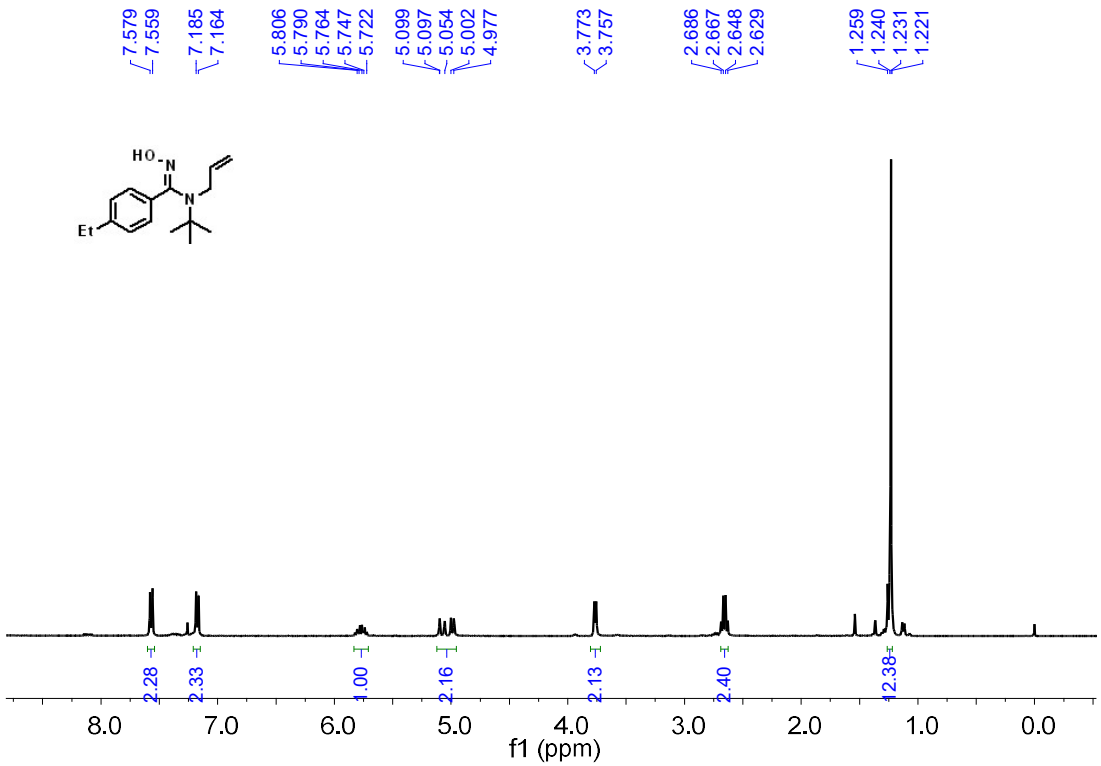
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 1s.



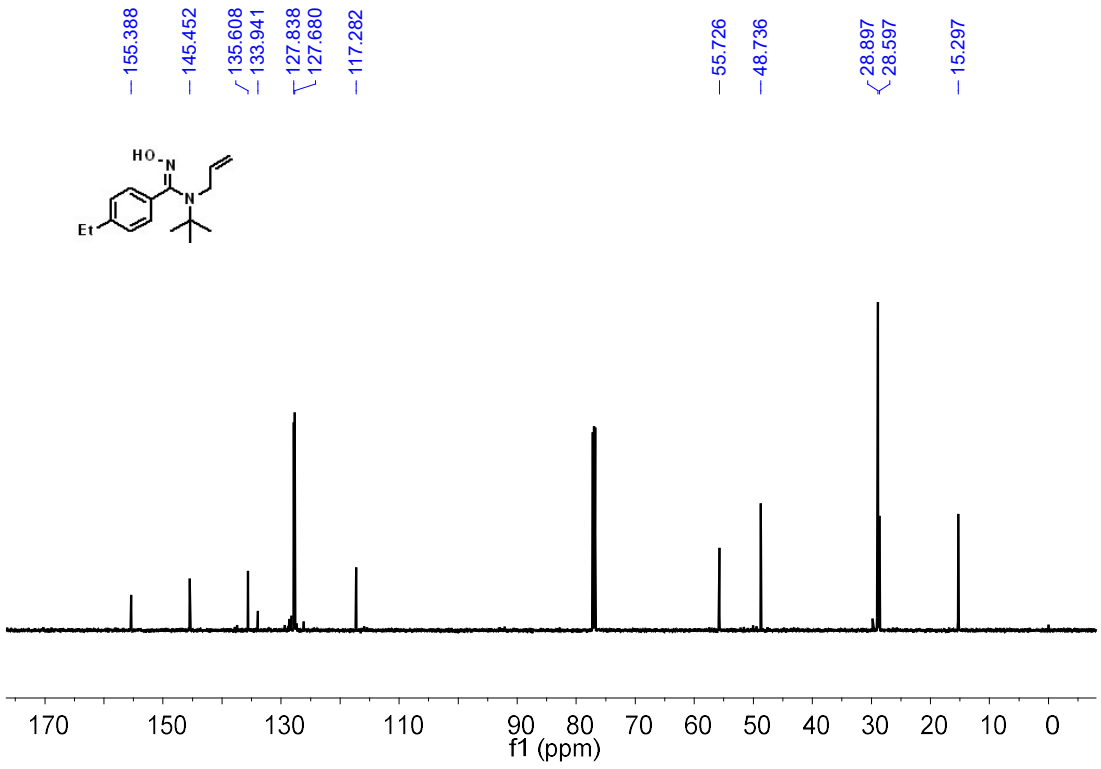
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for substrate 1t.



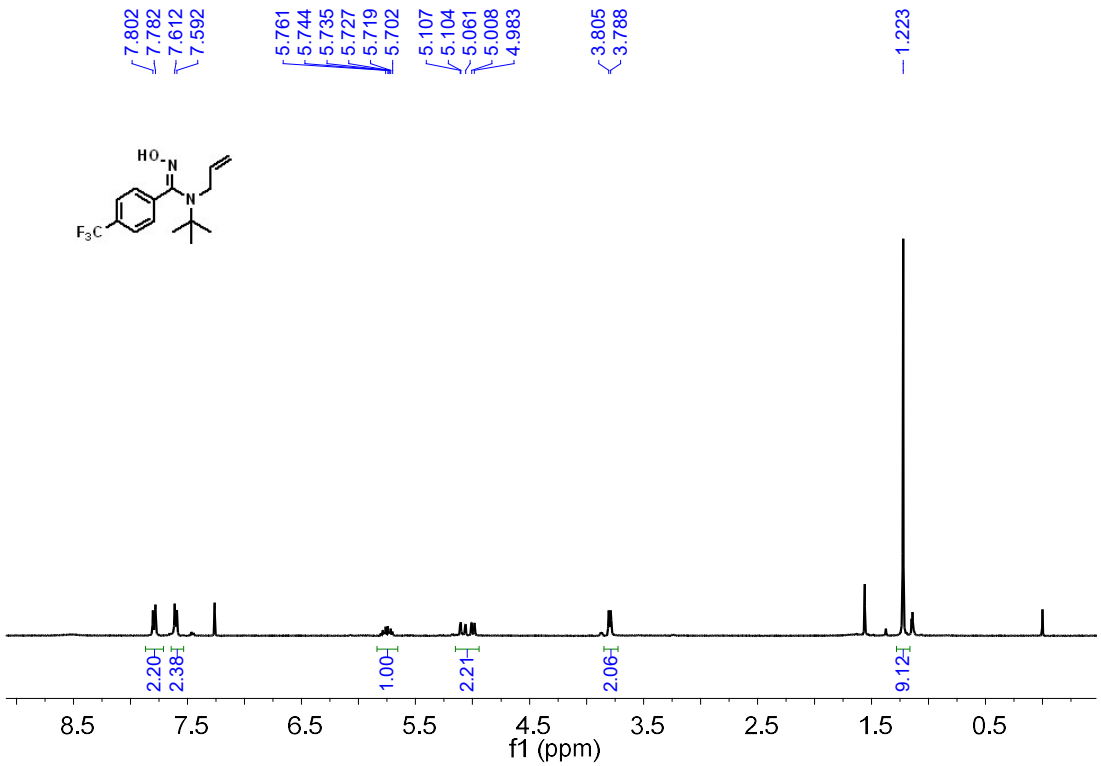
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for substrate 1t.



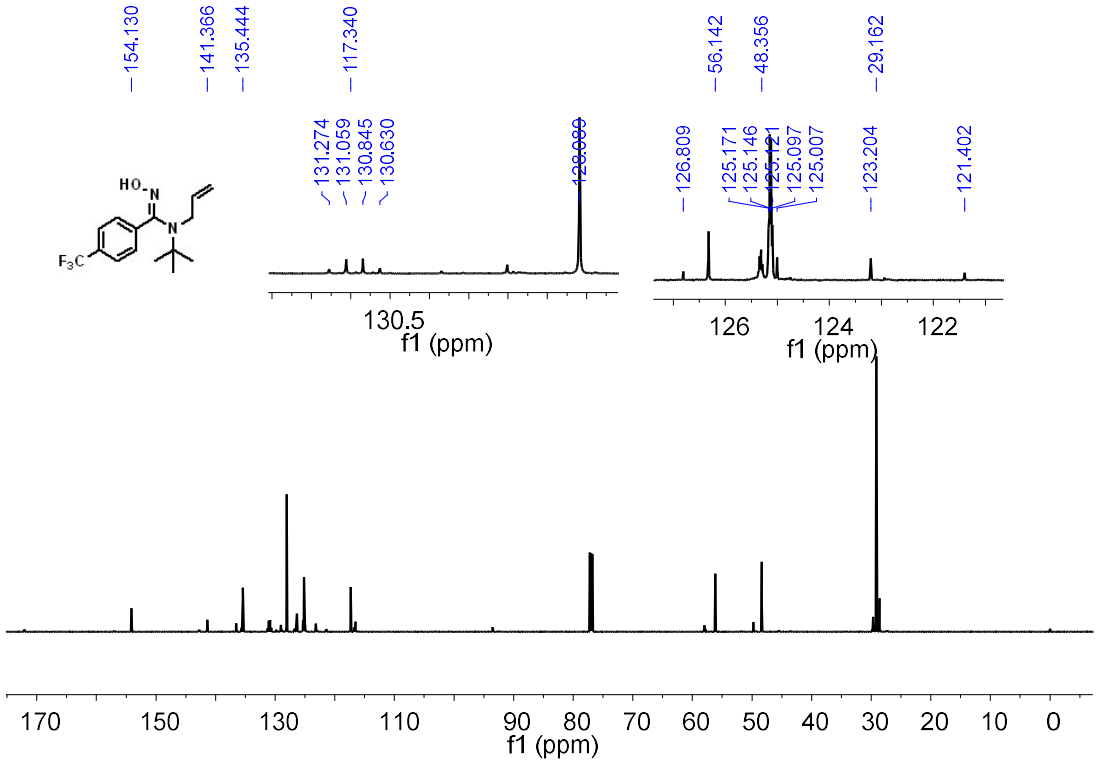
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for substrate 1u.



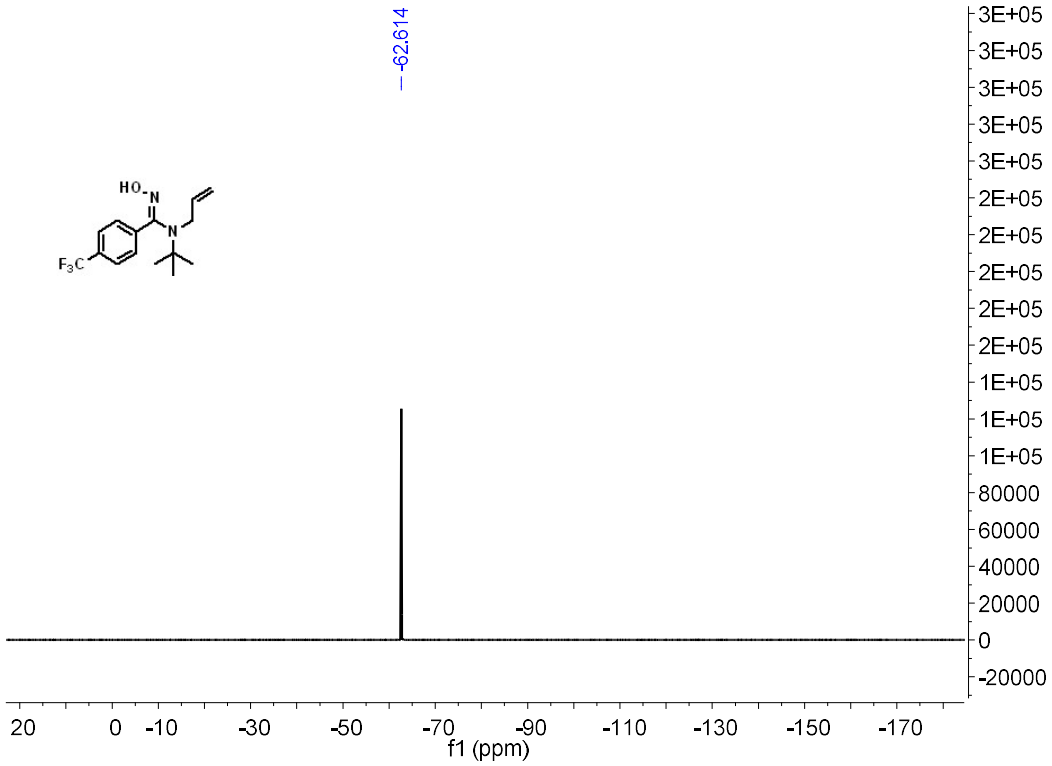
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for substrate 1u.



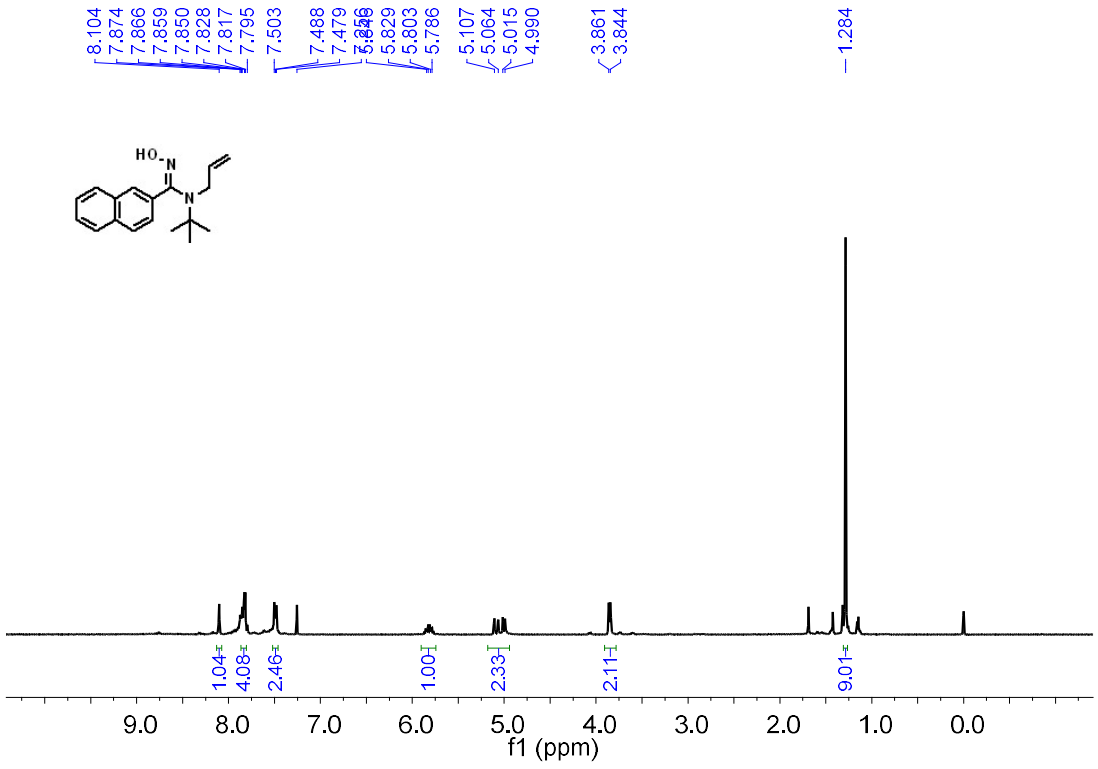
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for substrate 1v.



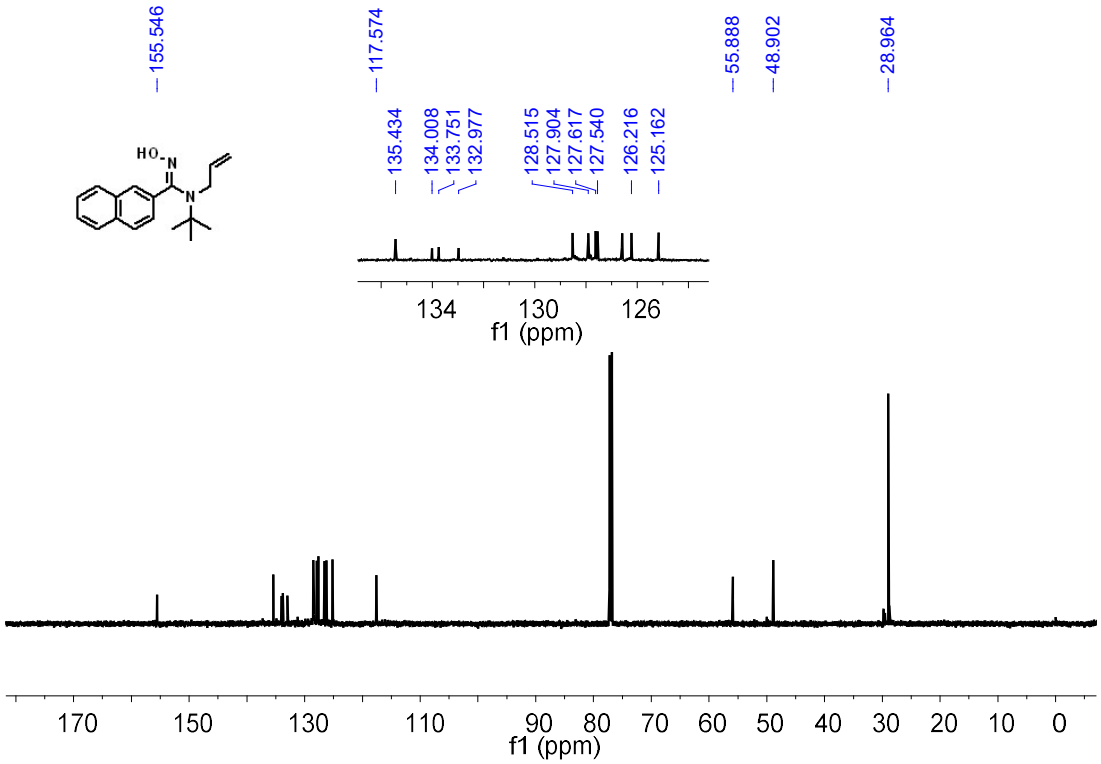
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for substrate 1v.



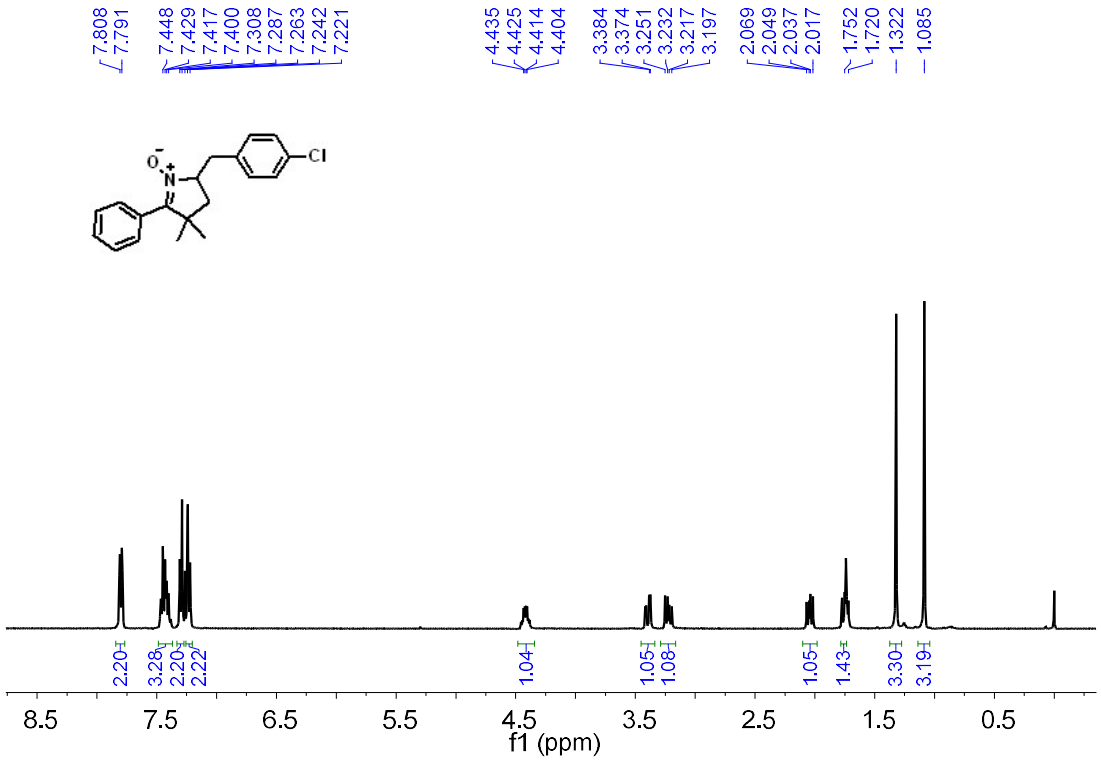
^{19}F NMR (470 MHz, $CDCl_3$) spectrum for substrate 1v



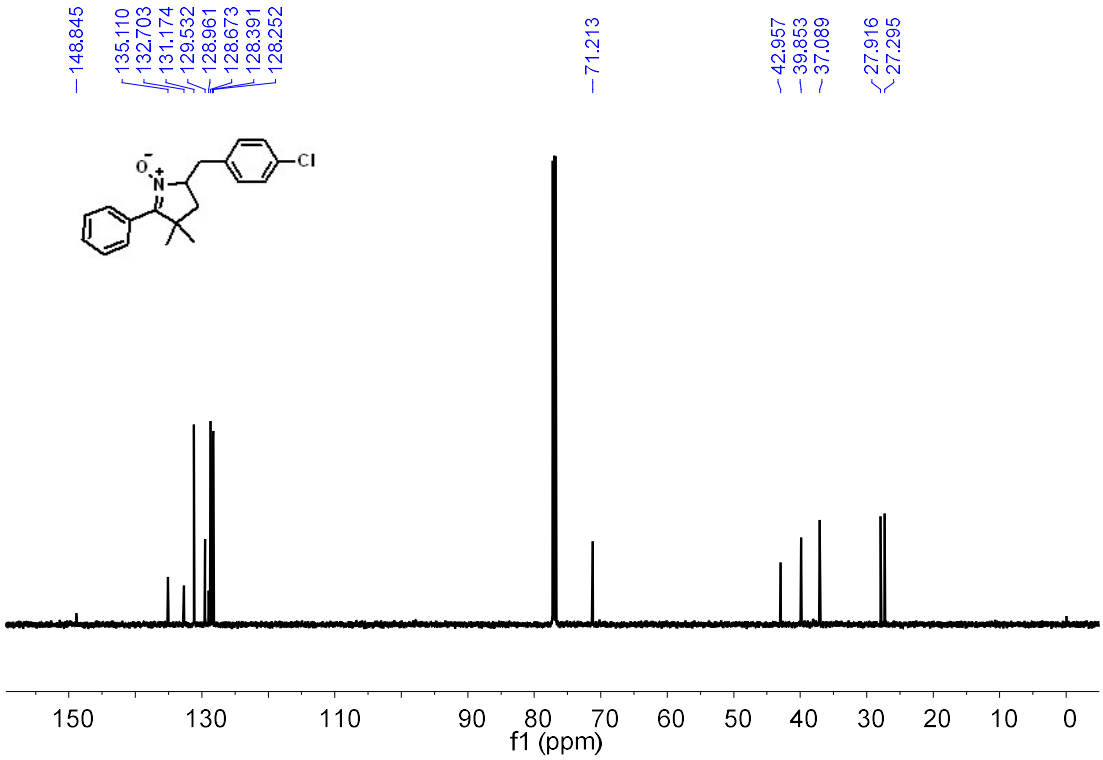
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for substrate 1w.



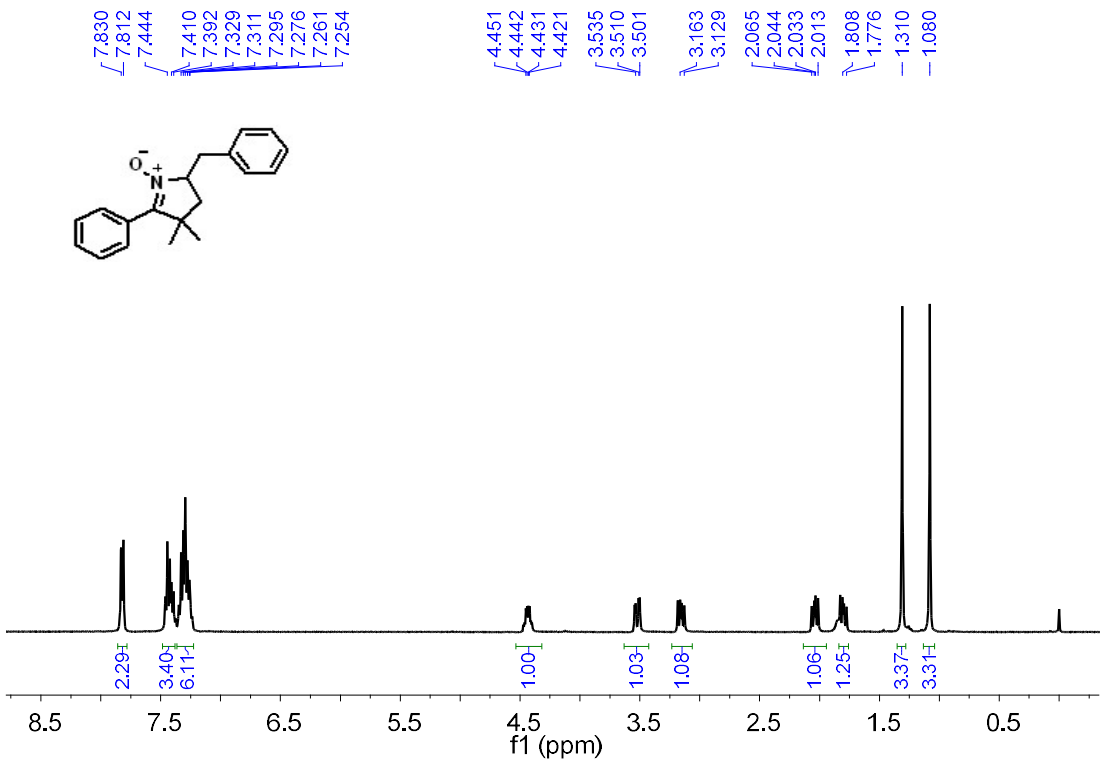
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 1w.



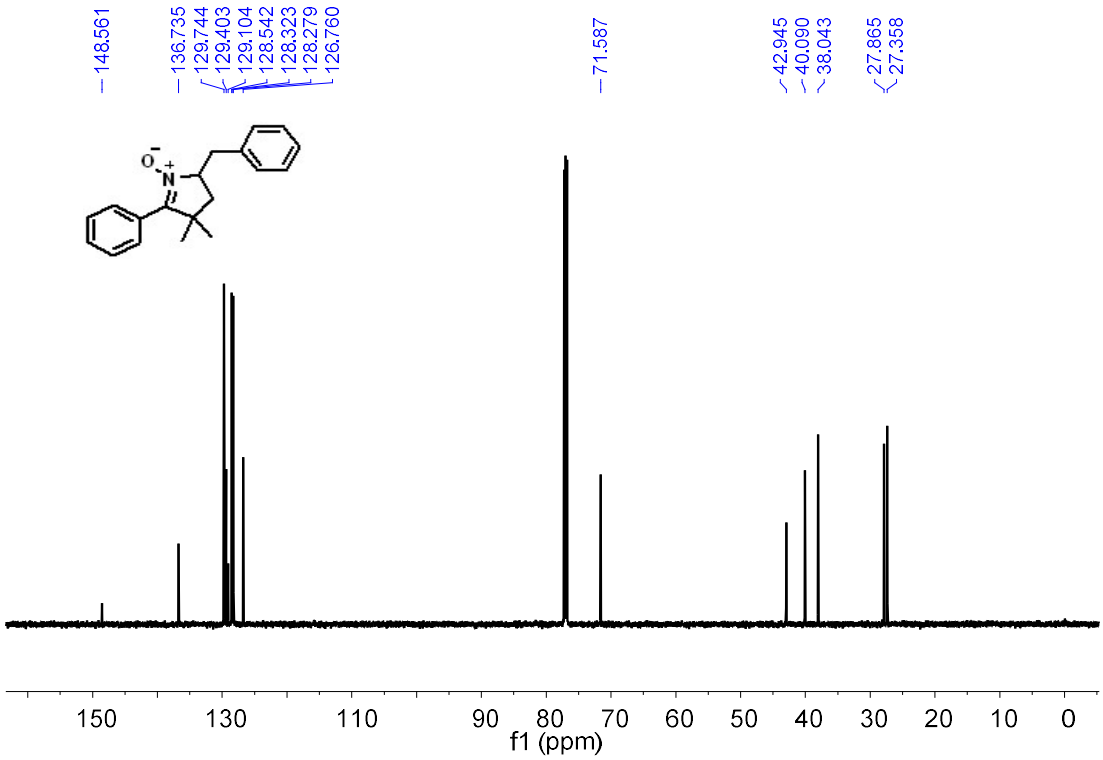
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 2a.



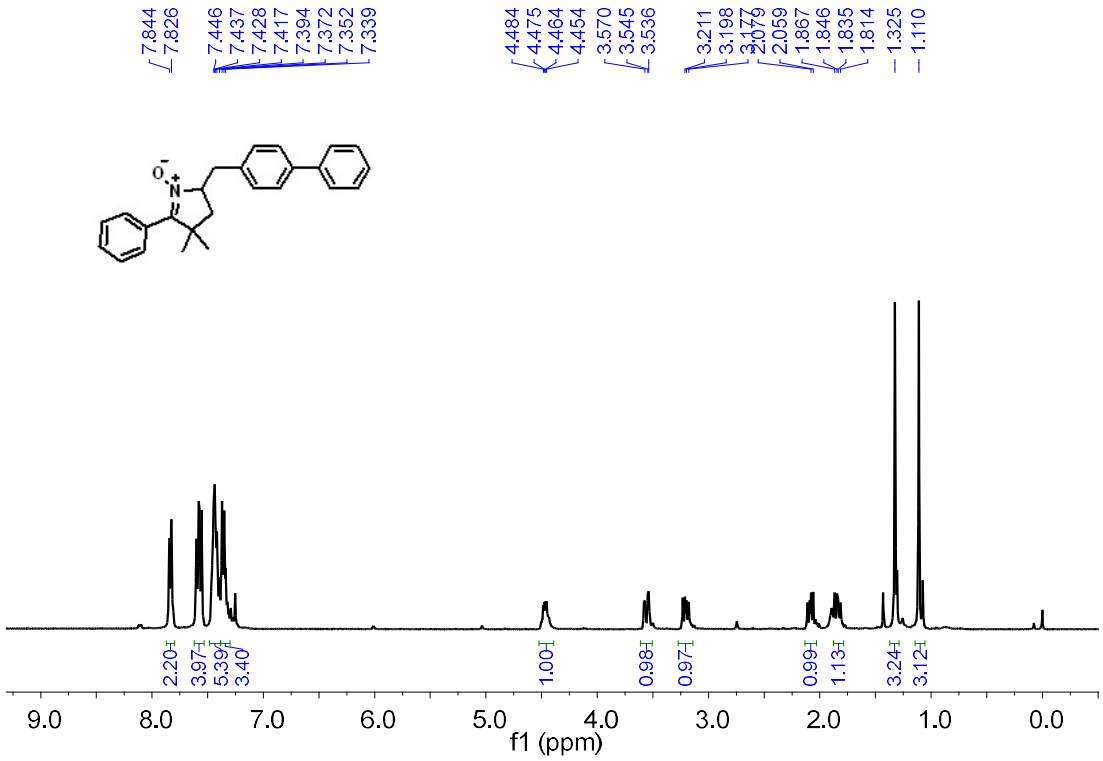
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 2a.



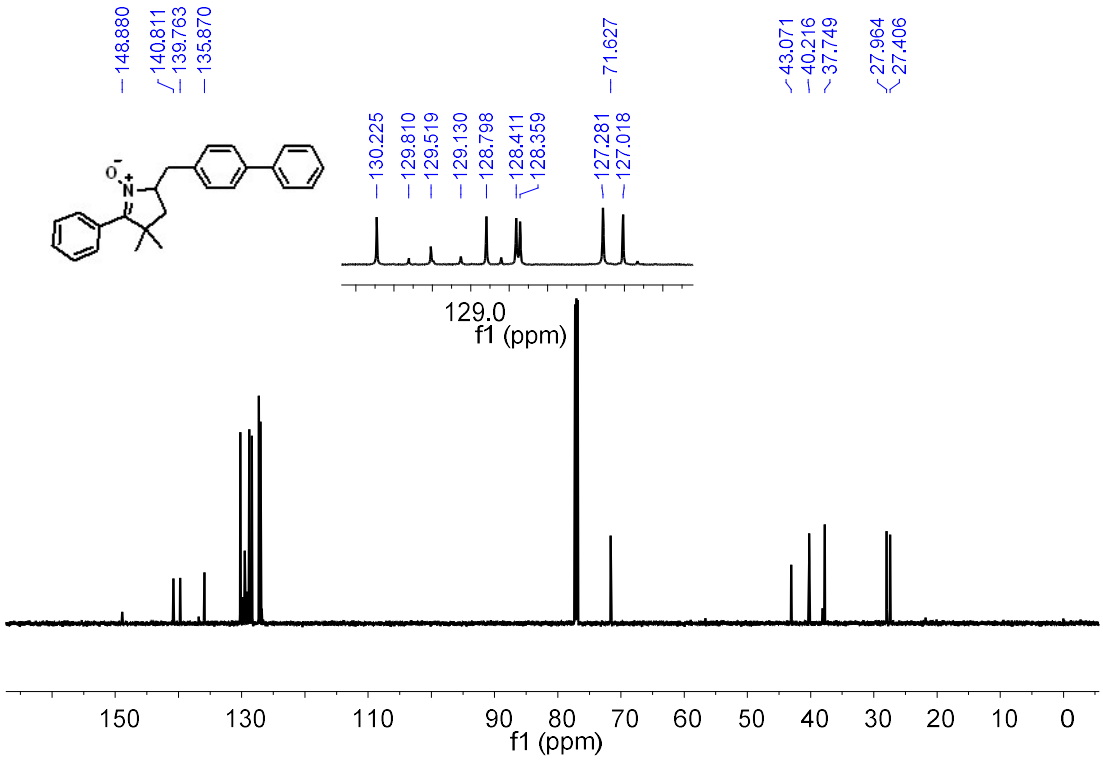
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 2b.



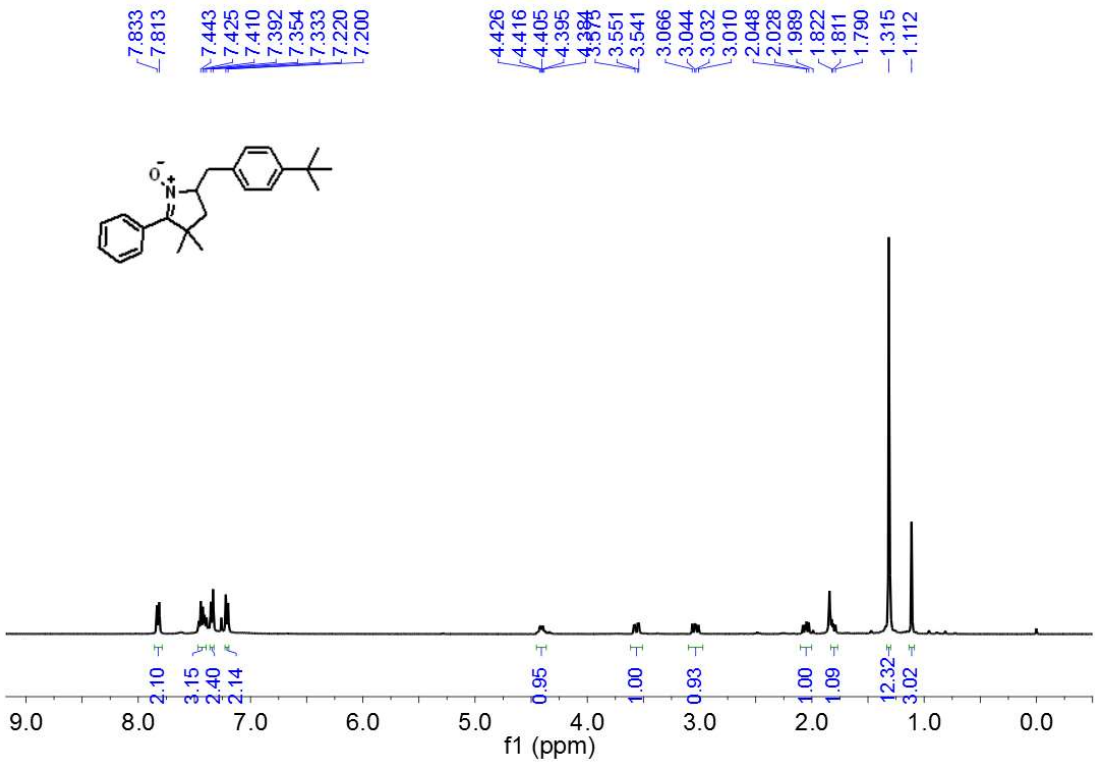
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 2b.



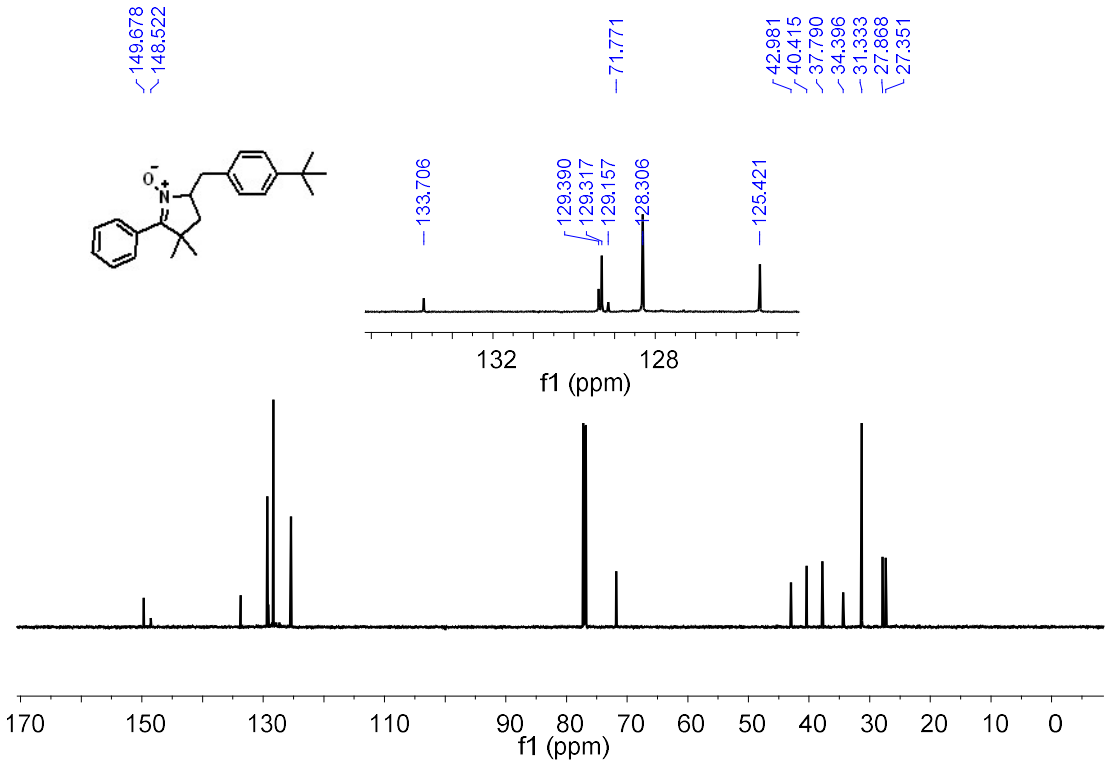
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 2c.



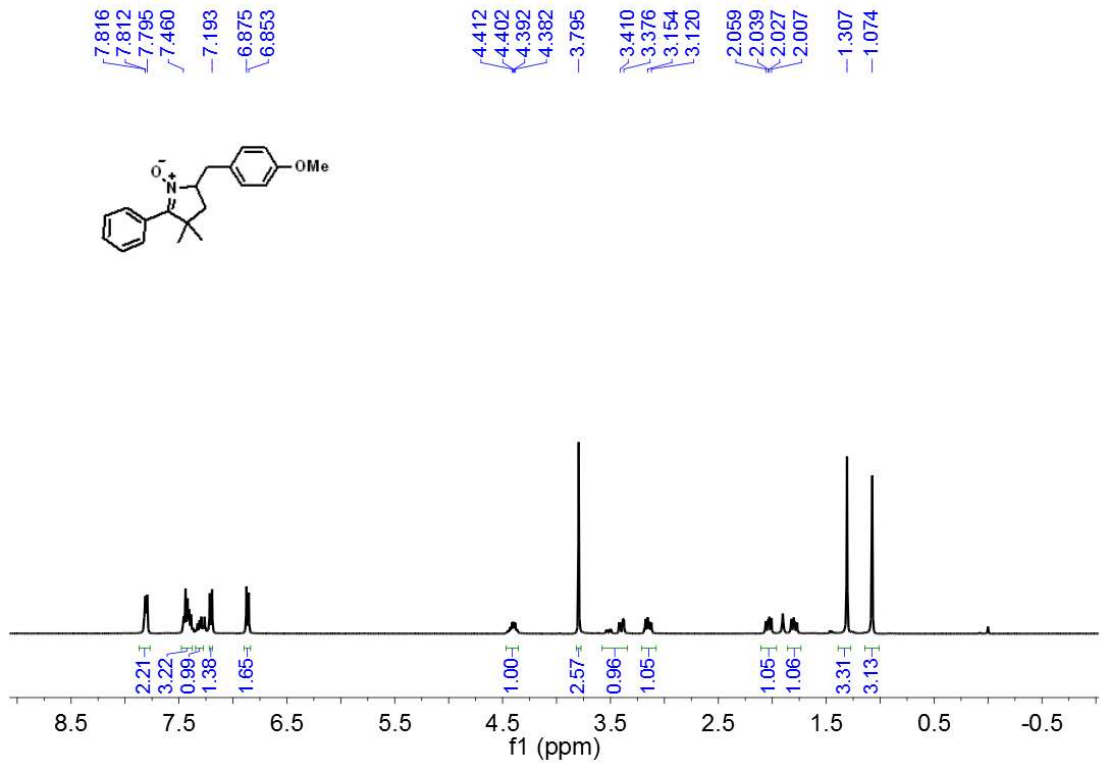
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 2c.



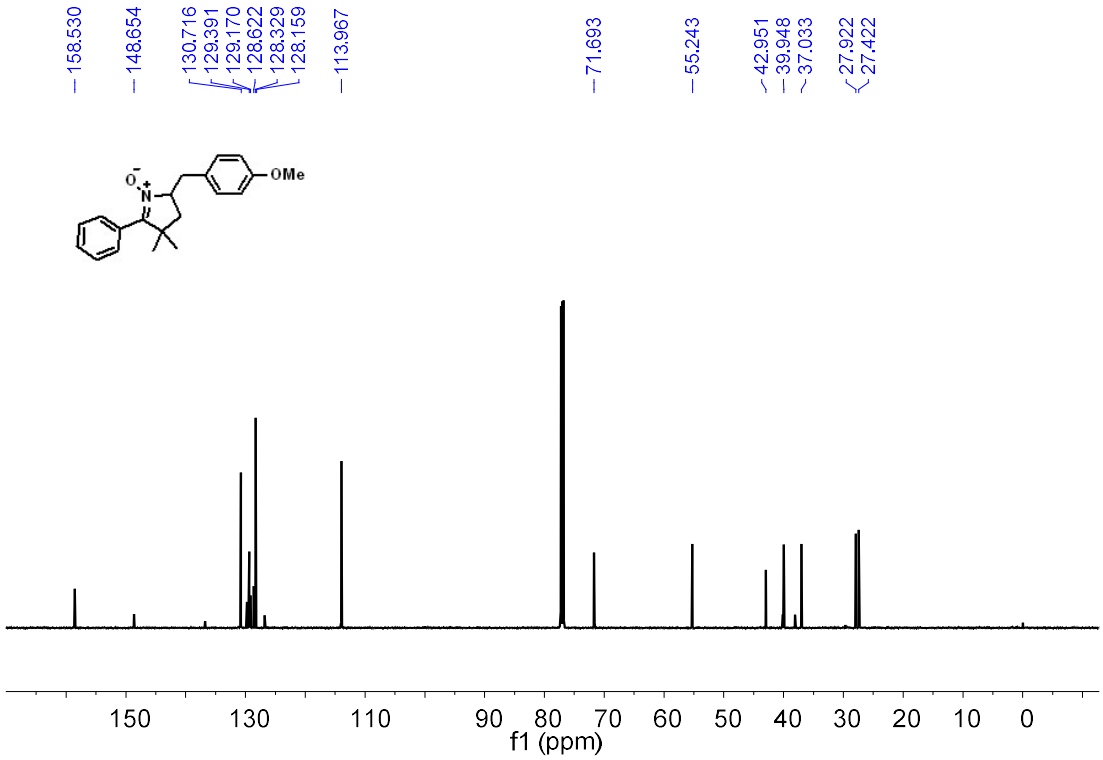
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 2d.



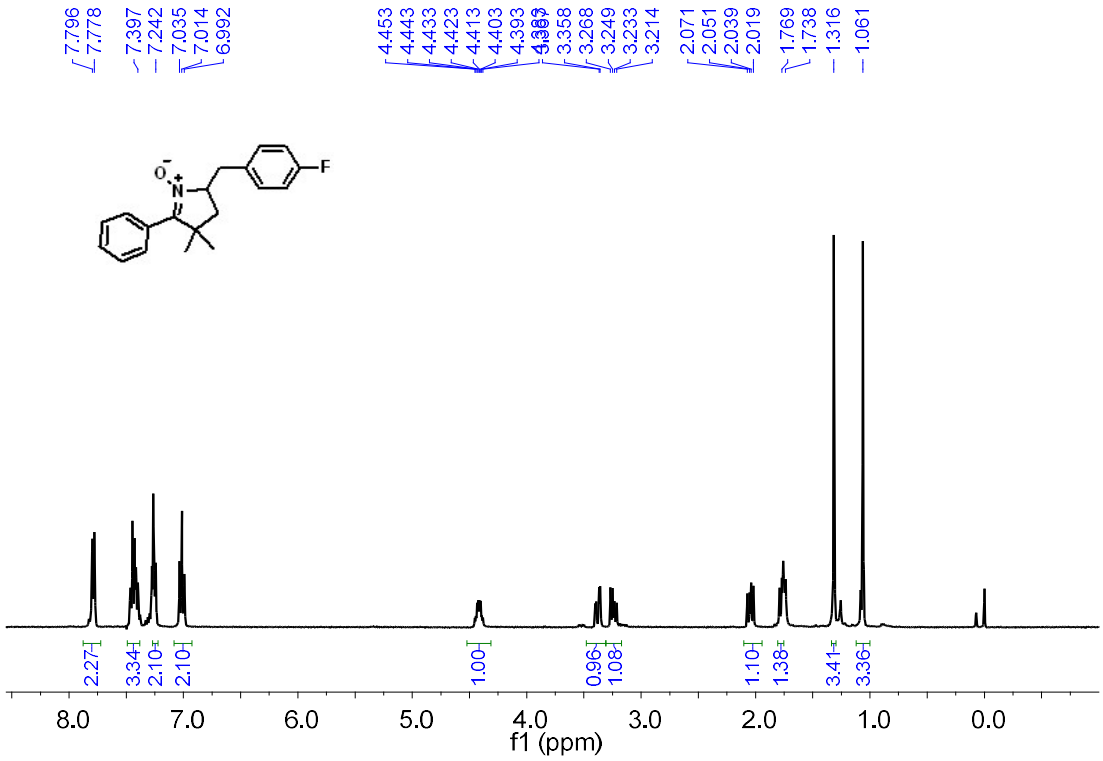
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 2d.



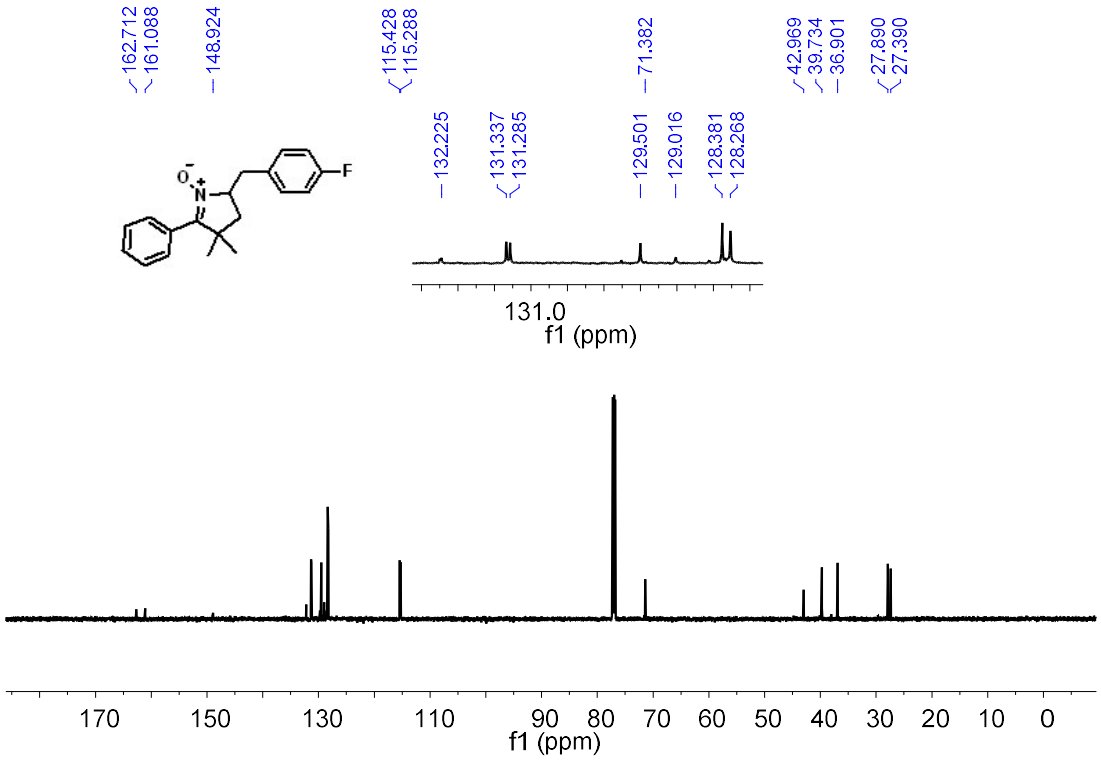
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 2e.



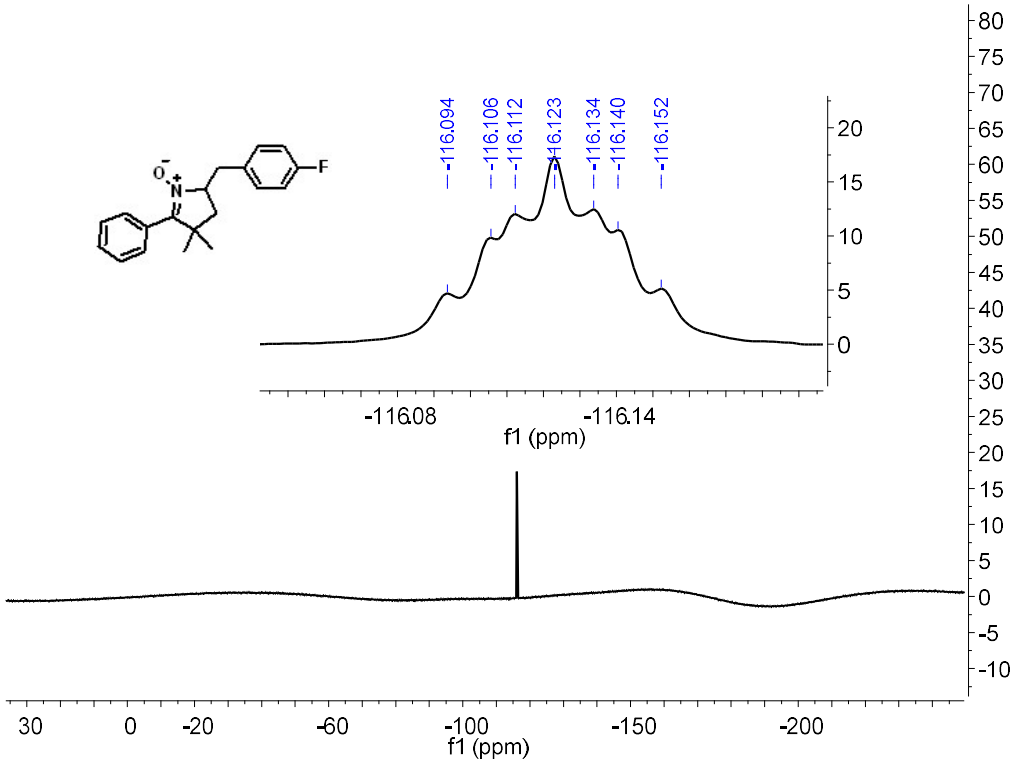
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 2e.



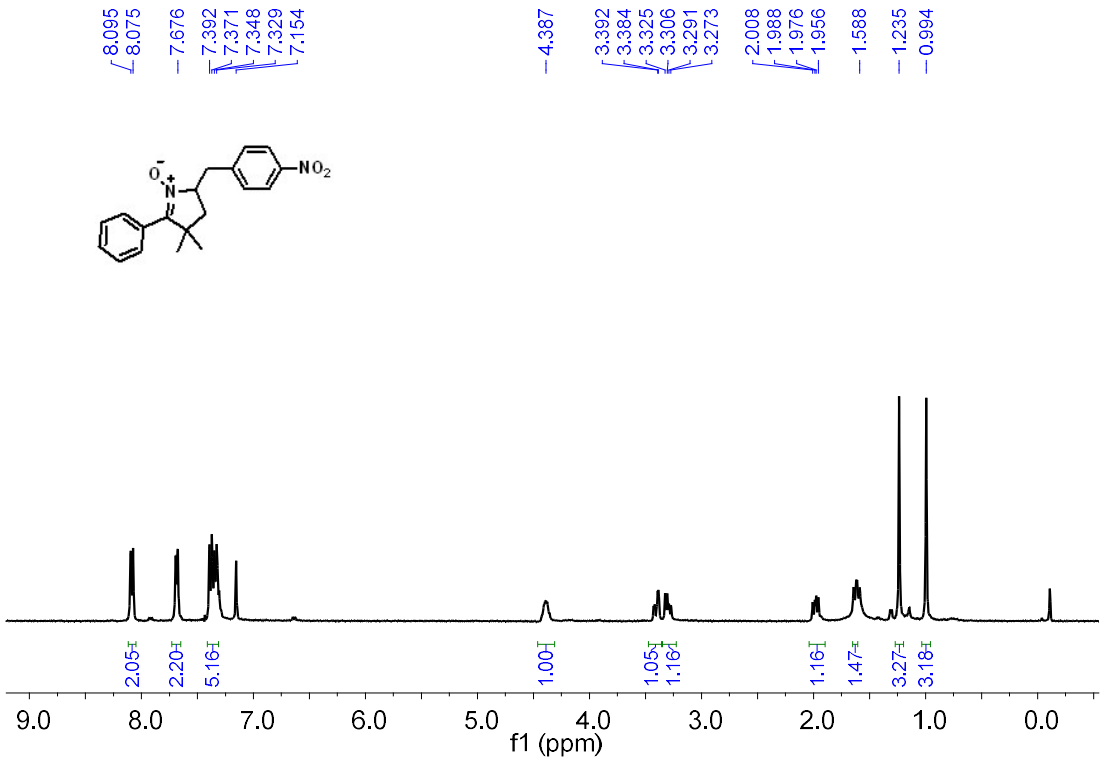
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 2f.



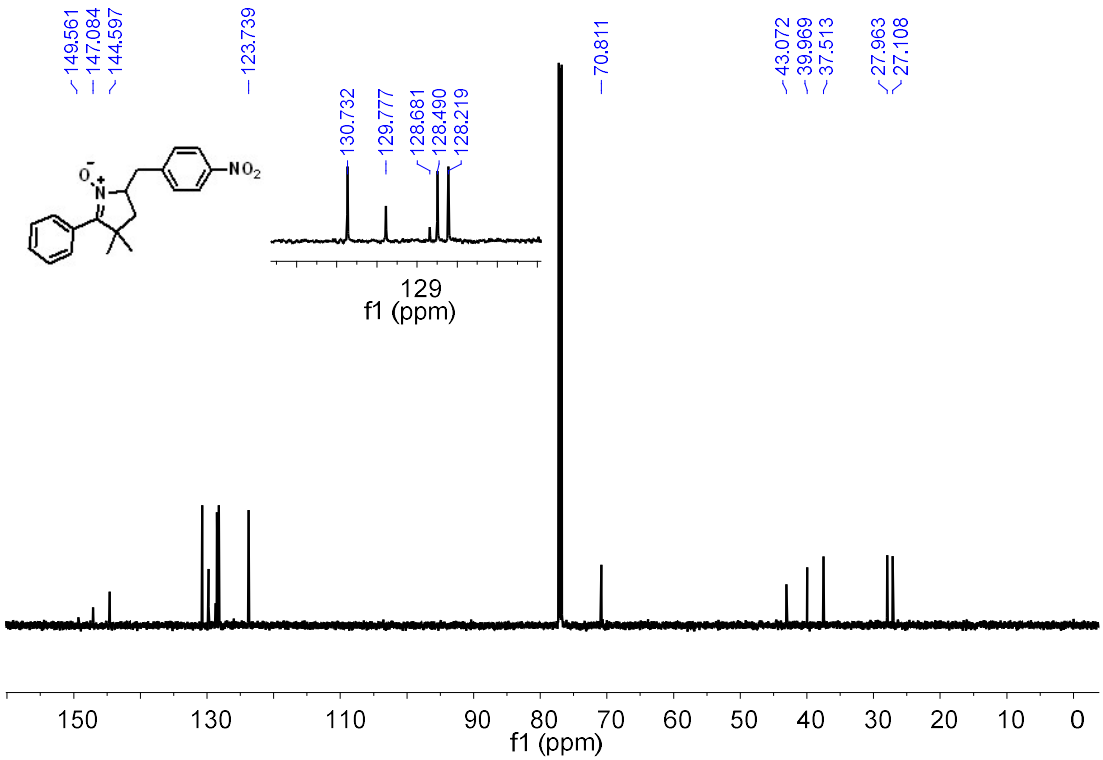
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 2f.



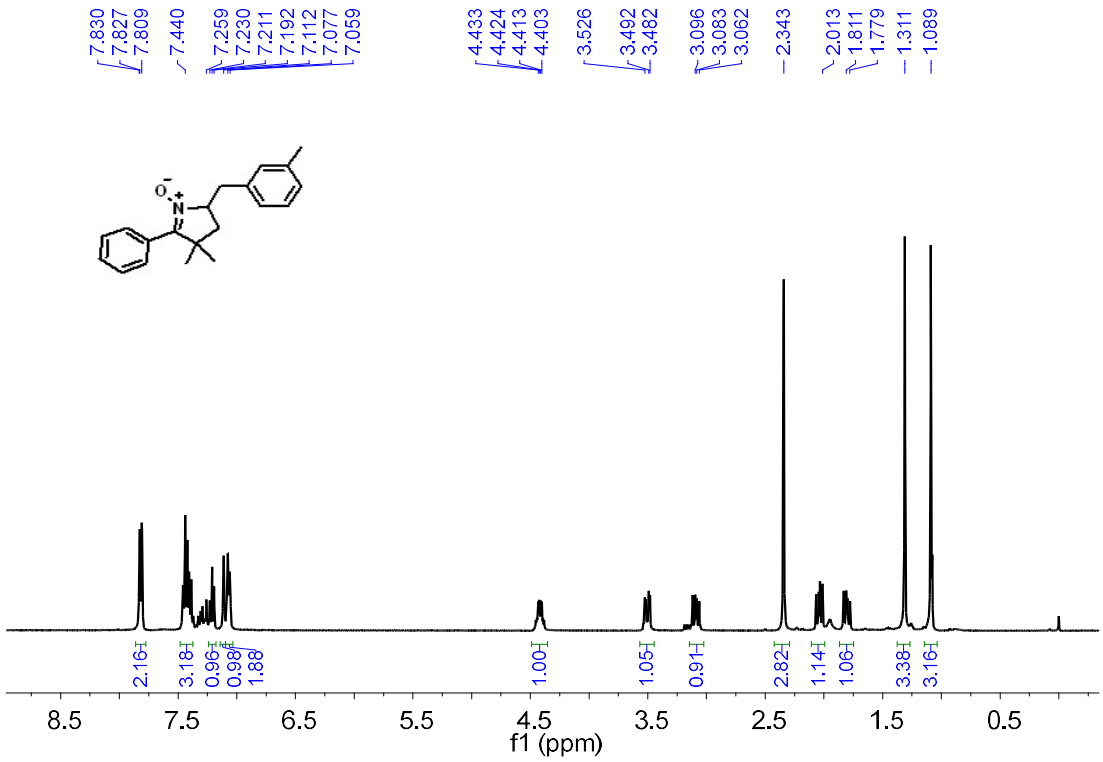
^{19}F NMR (470 MHz, $CDCl_3$) spectrum for 2f.



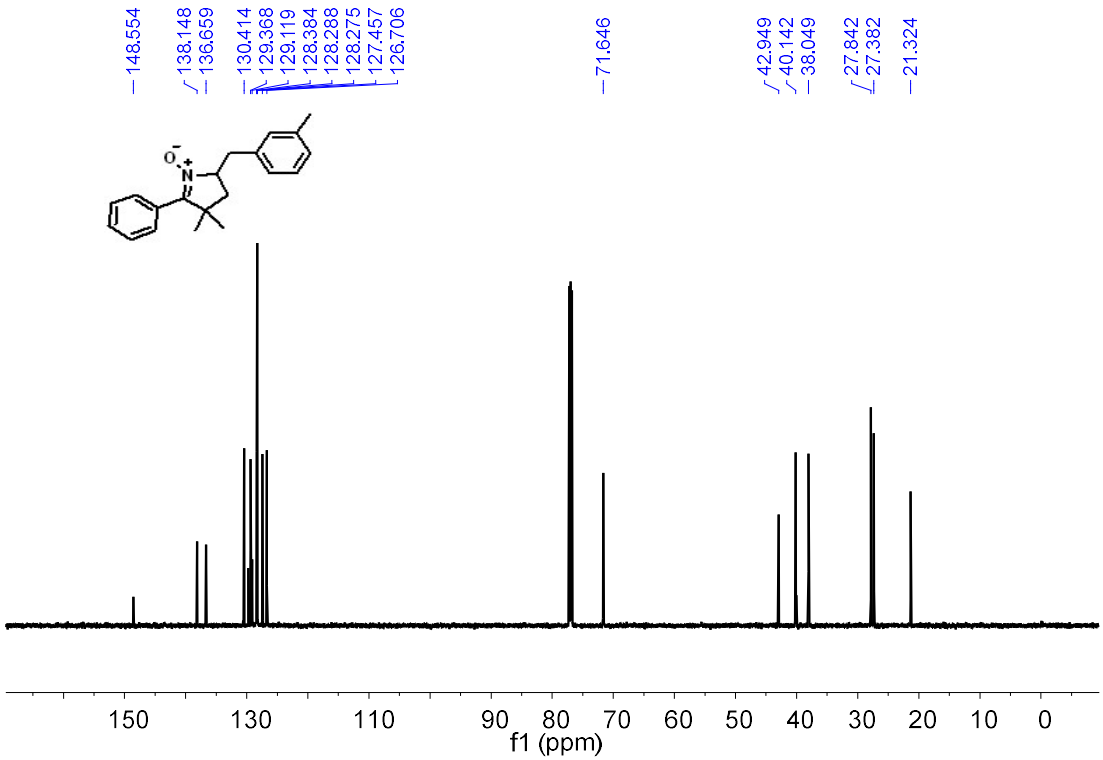
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 2g.



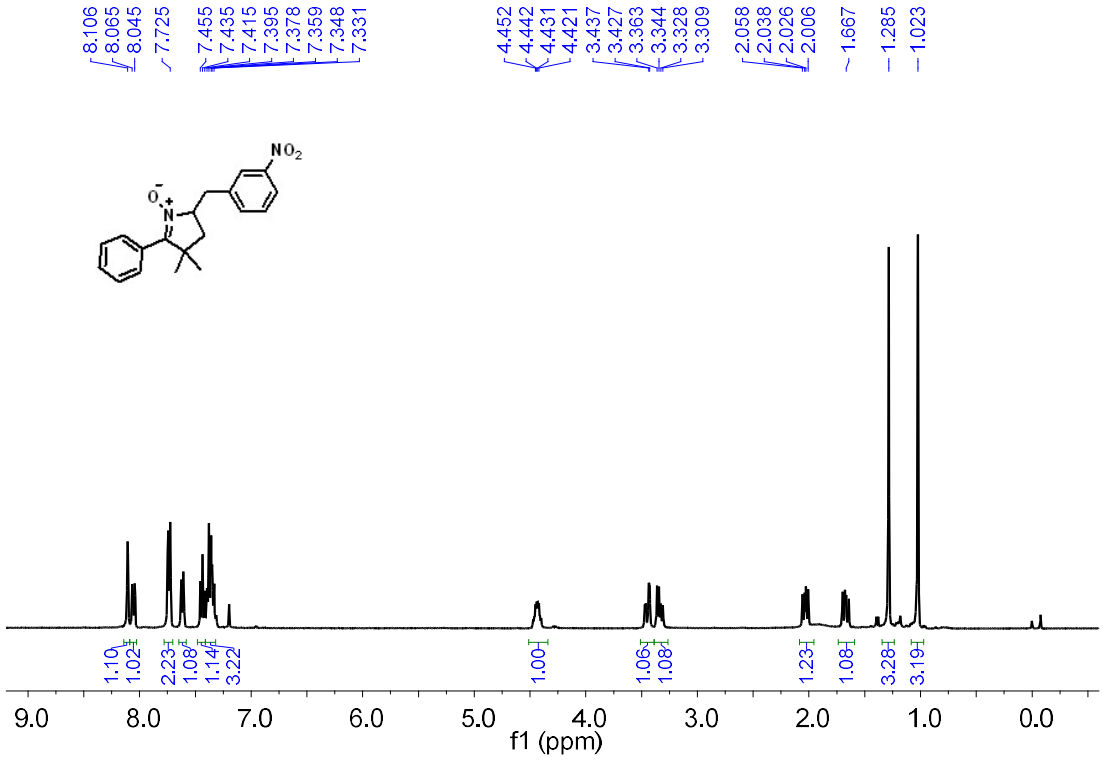
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 2g.



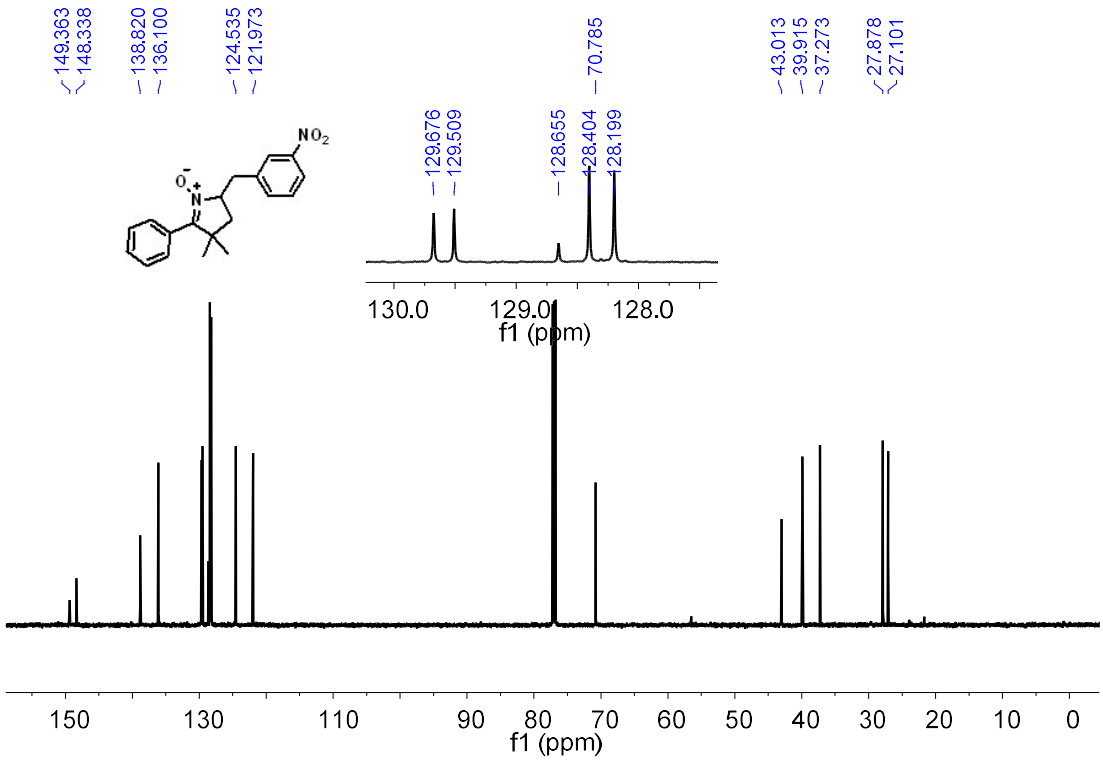
[1]H NMR (400 MHz, CDCl3) spectrum for 2h.



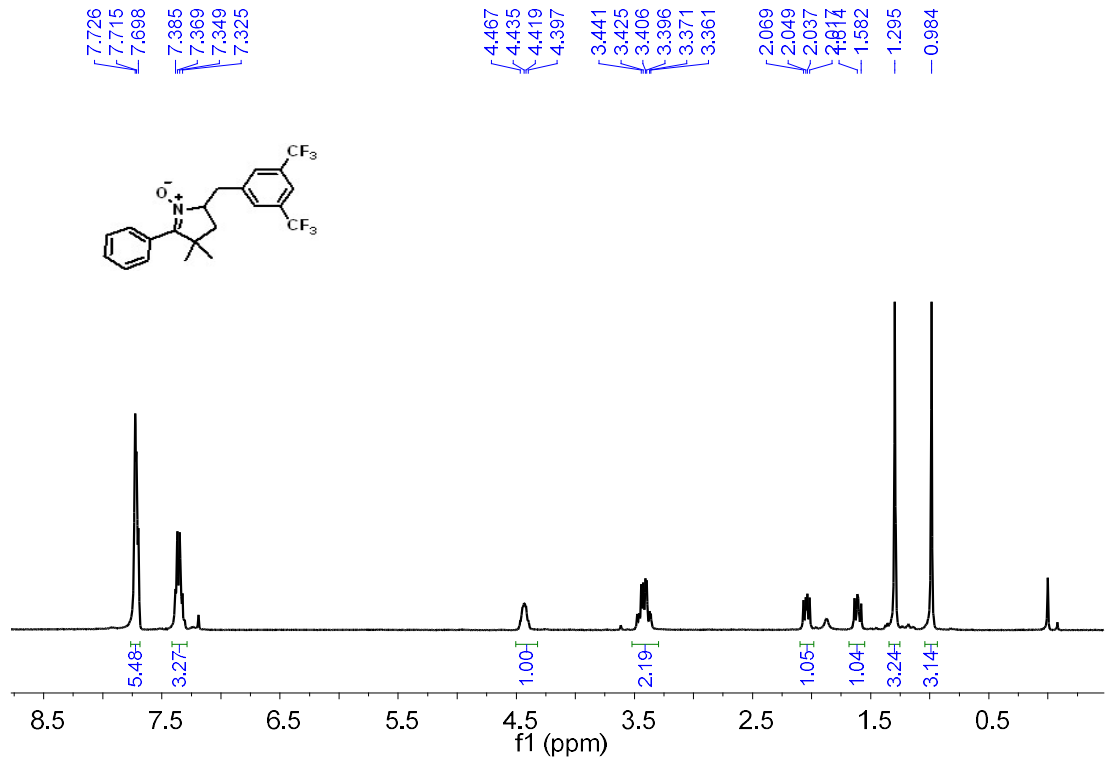
[13]C NMR (150 MHz, CDCl3) spectrum for 2h.



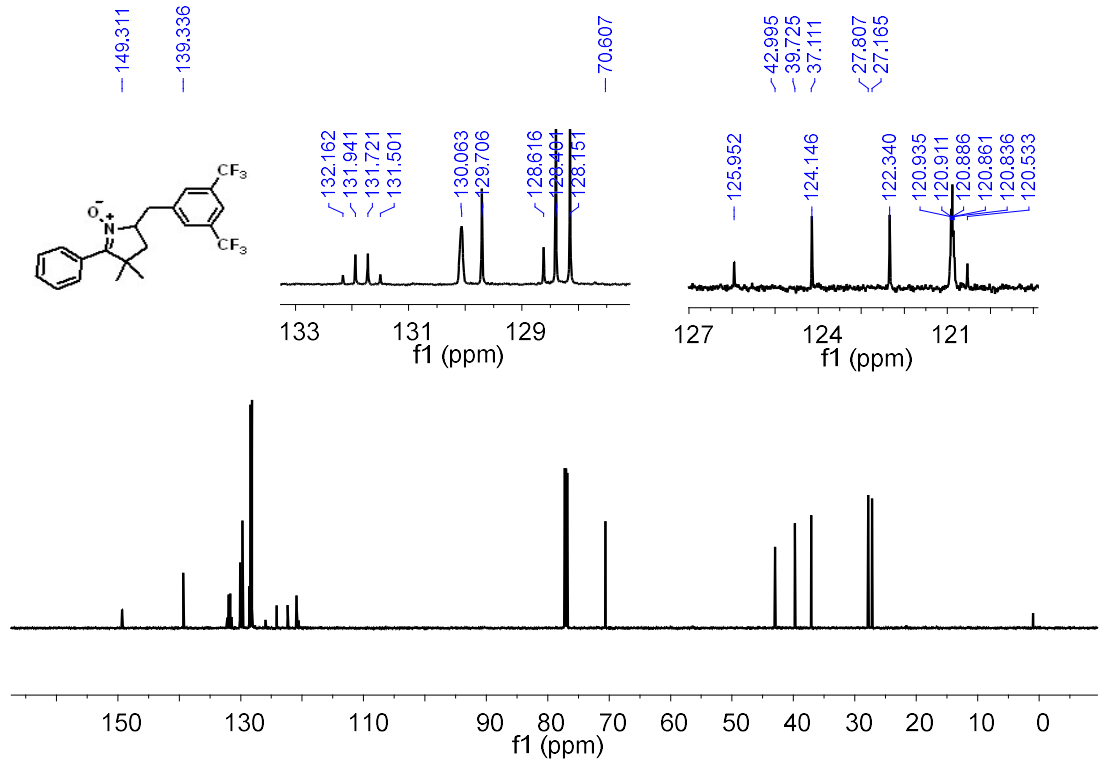
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 2i.



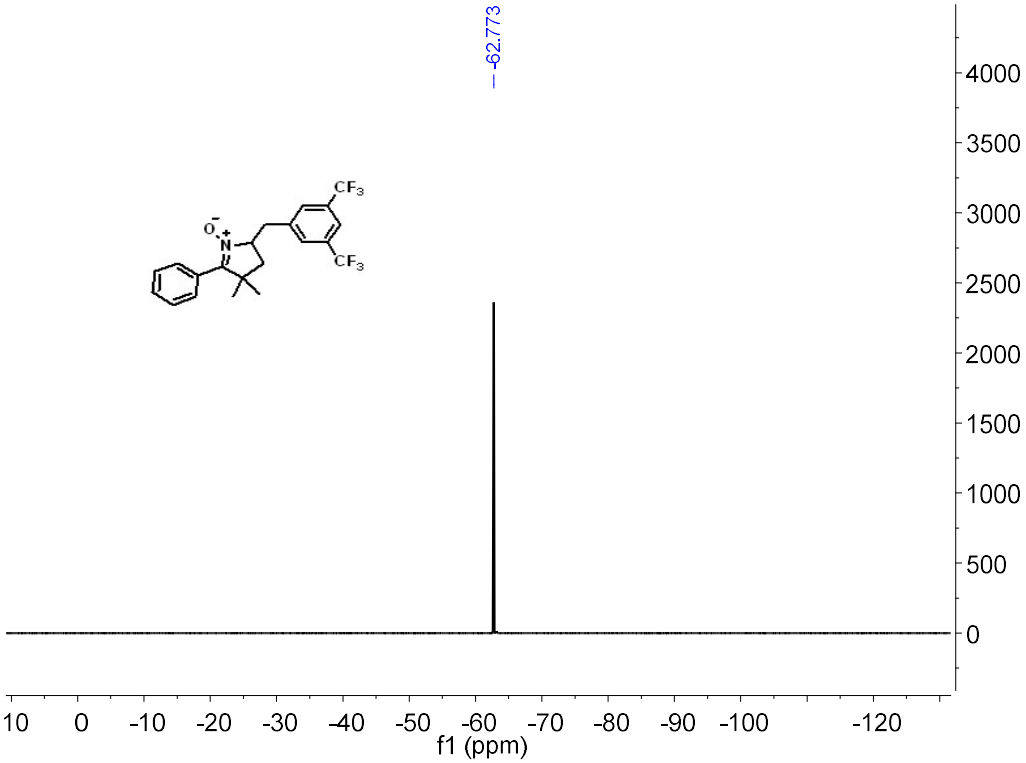
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 2i.



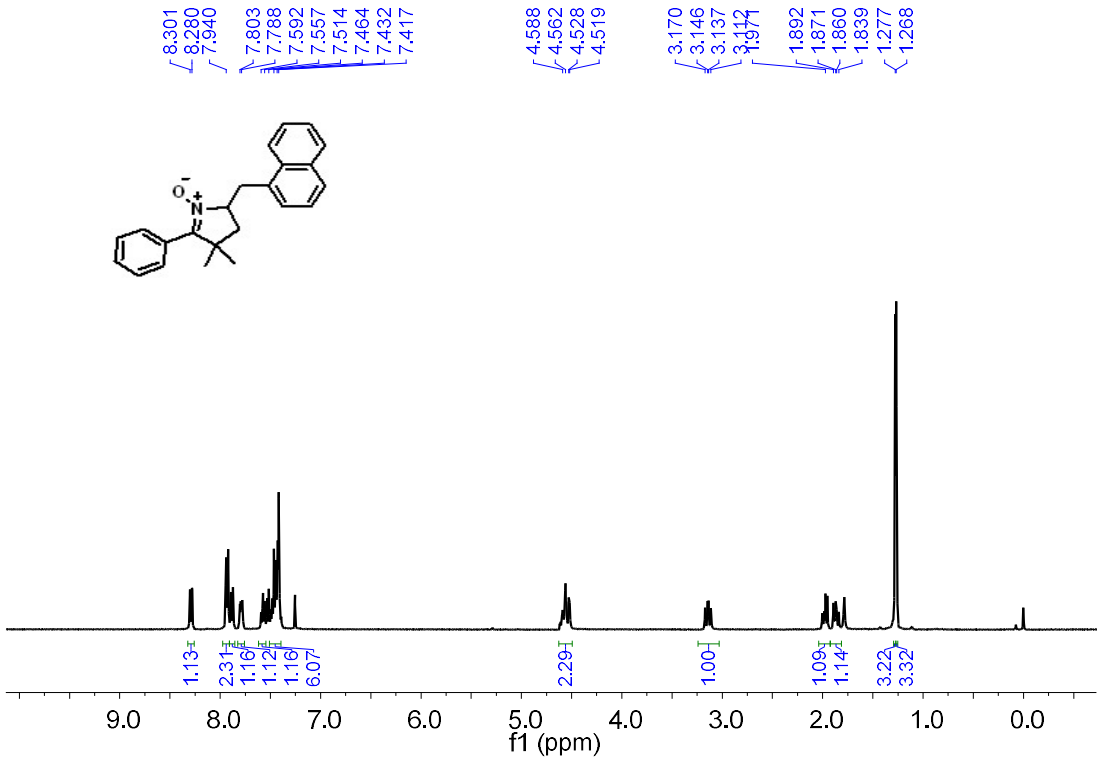
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 2j.



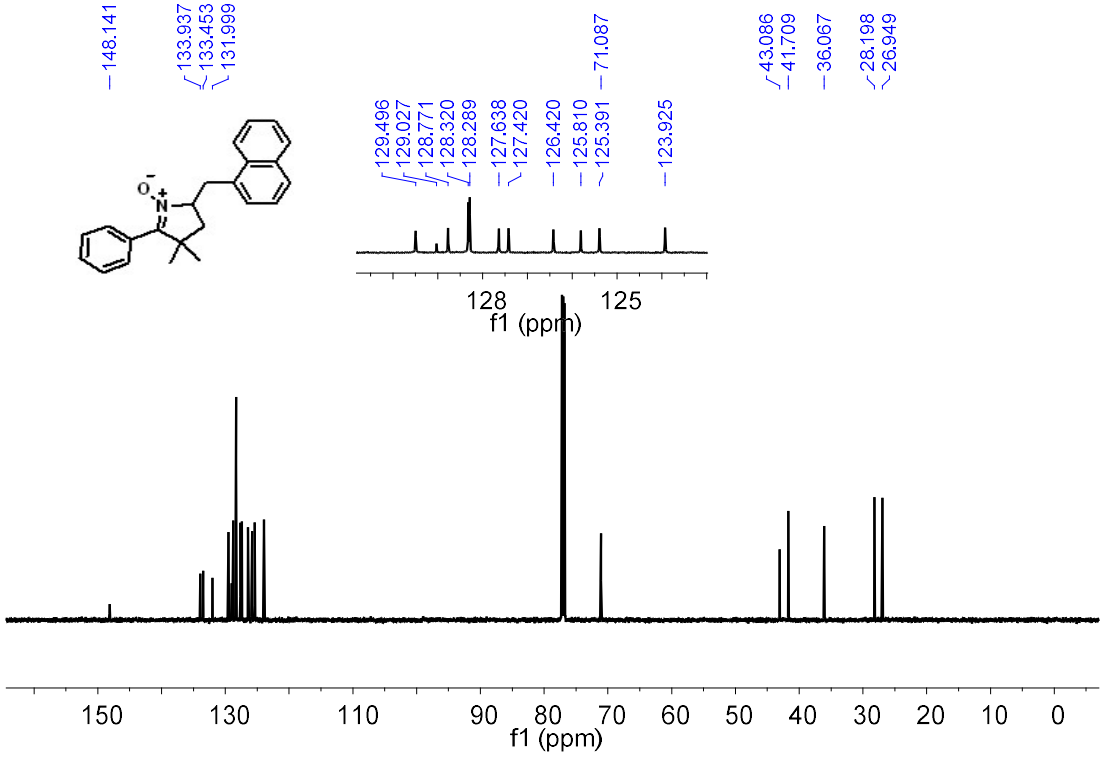
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 2j.



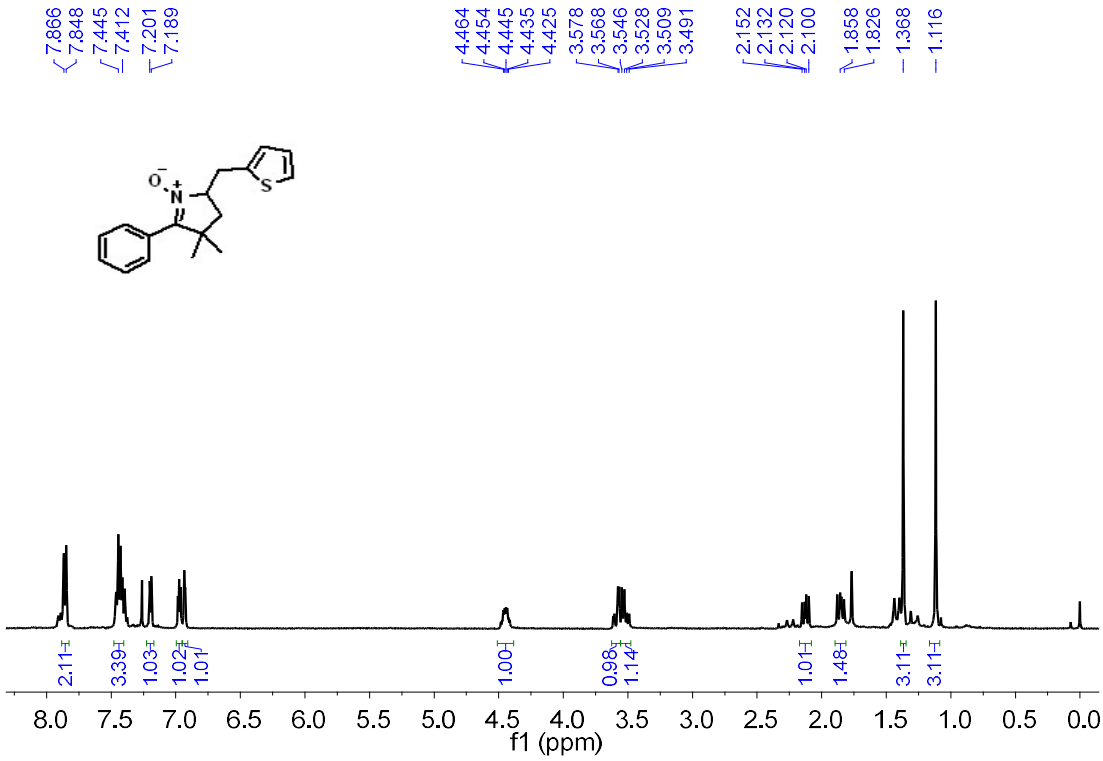
^{19}F NMR (470 MHz, $CDCl_3$) spectrum for 2j.



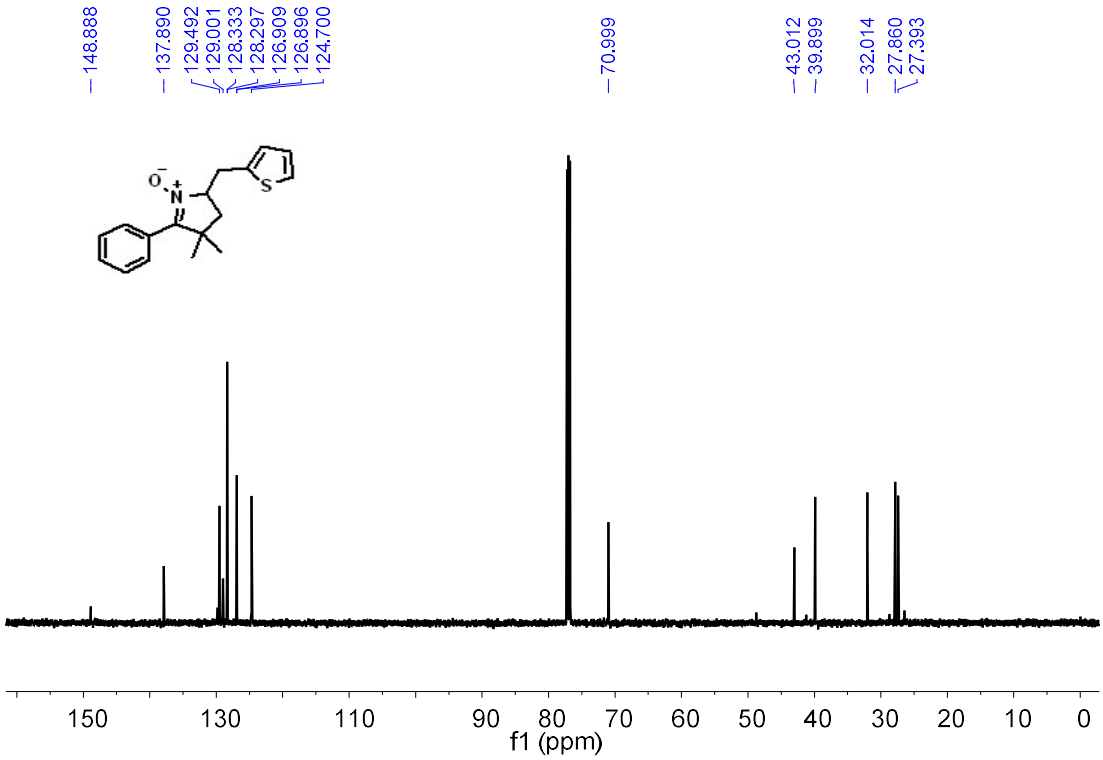
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 2k.



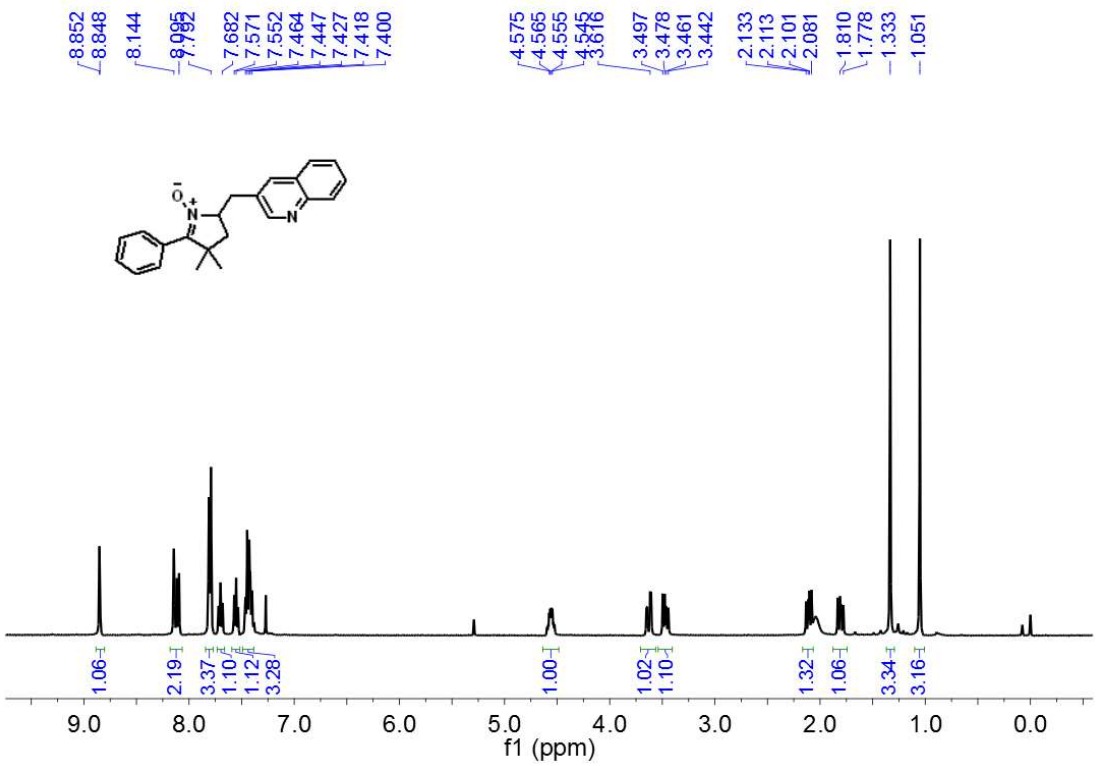
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 2k.



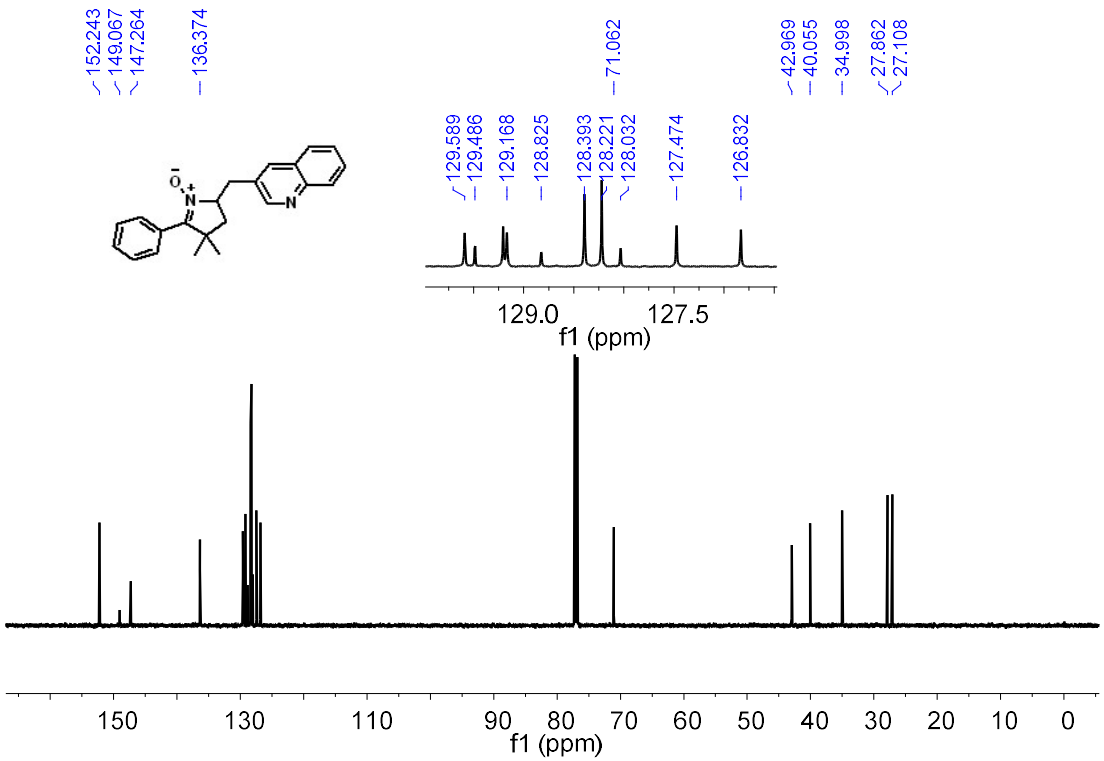
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 2l.



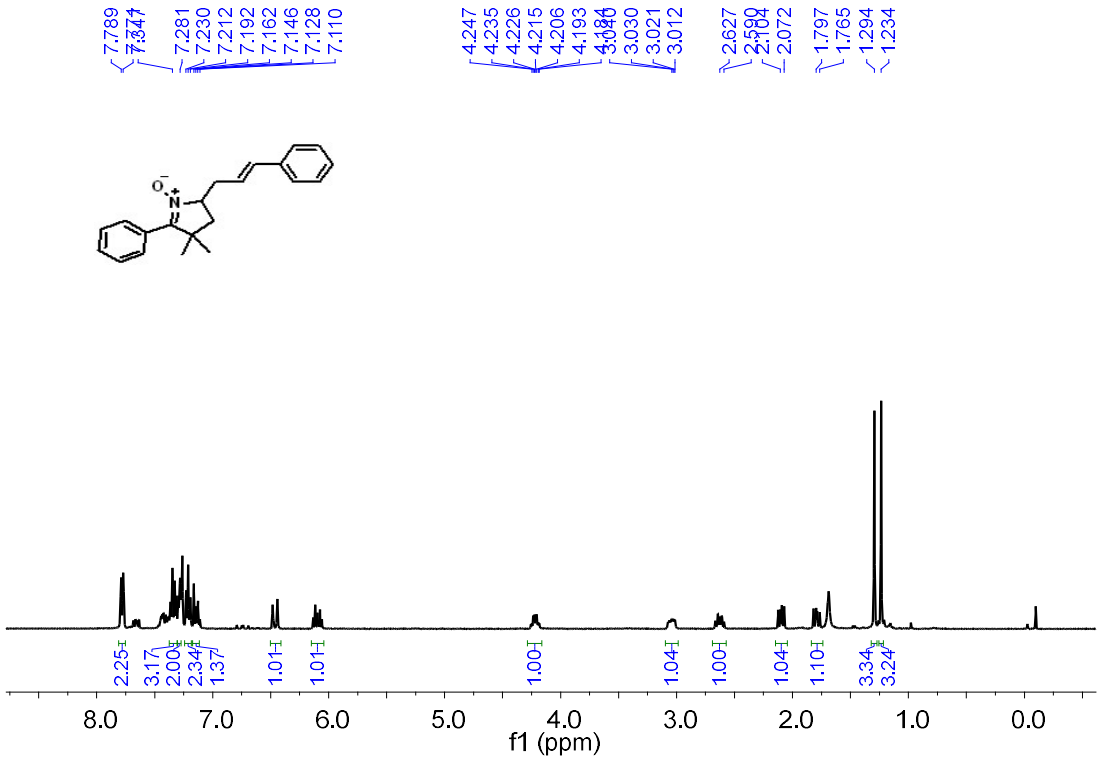
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 2l.



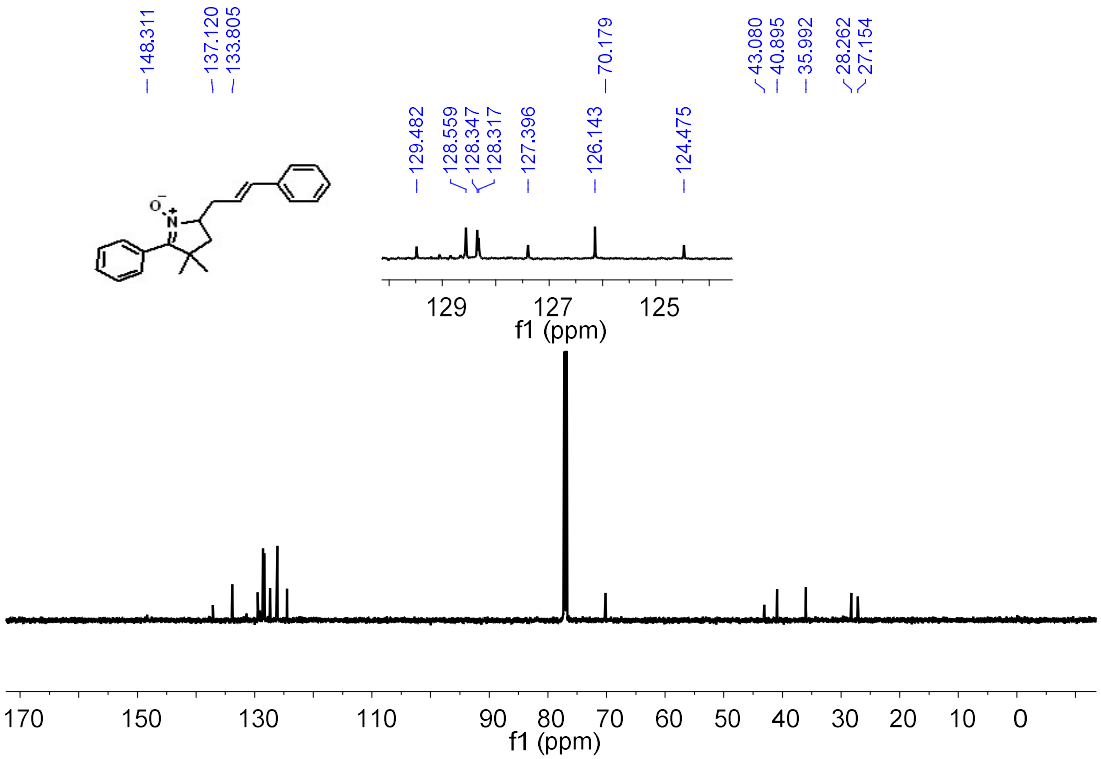
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 2m.



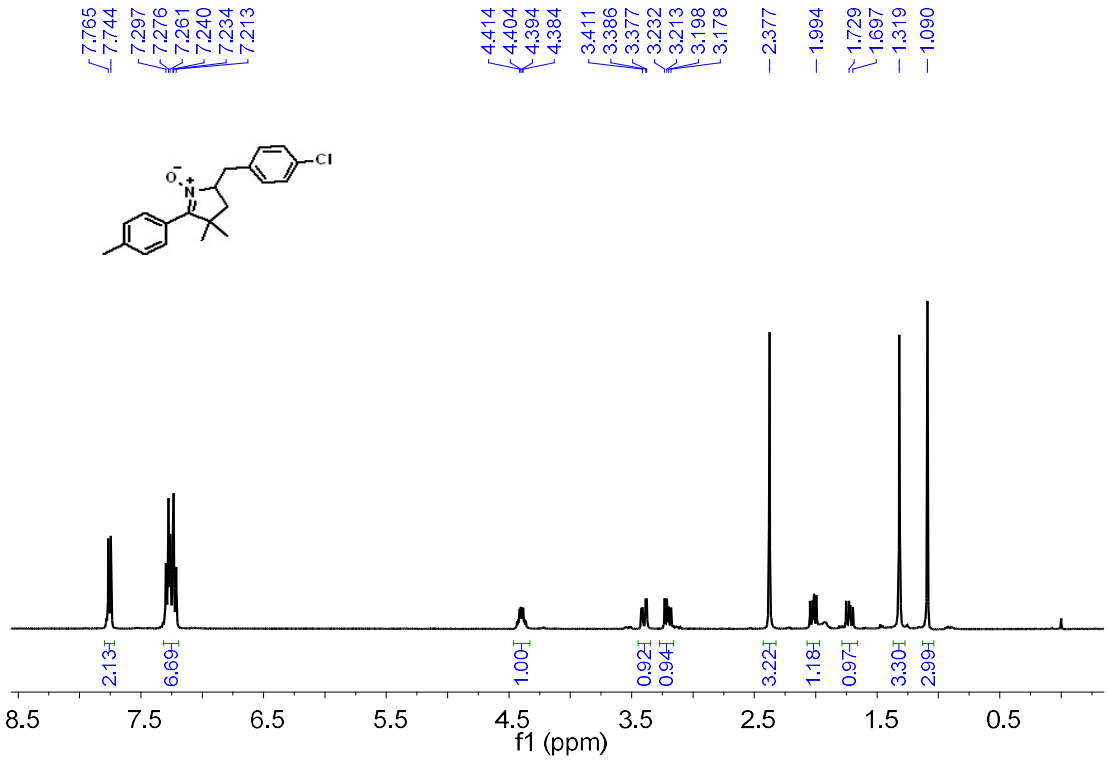
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 2m.



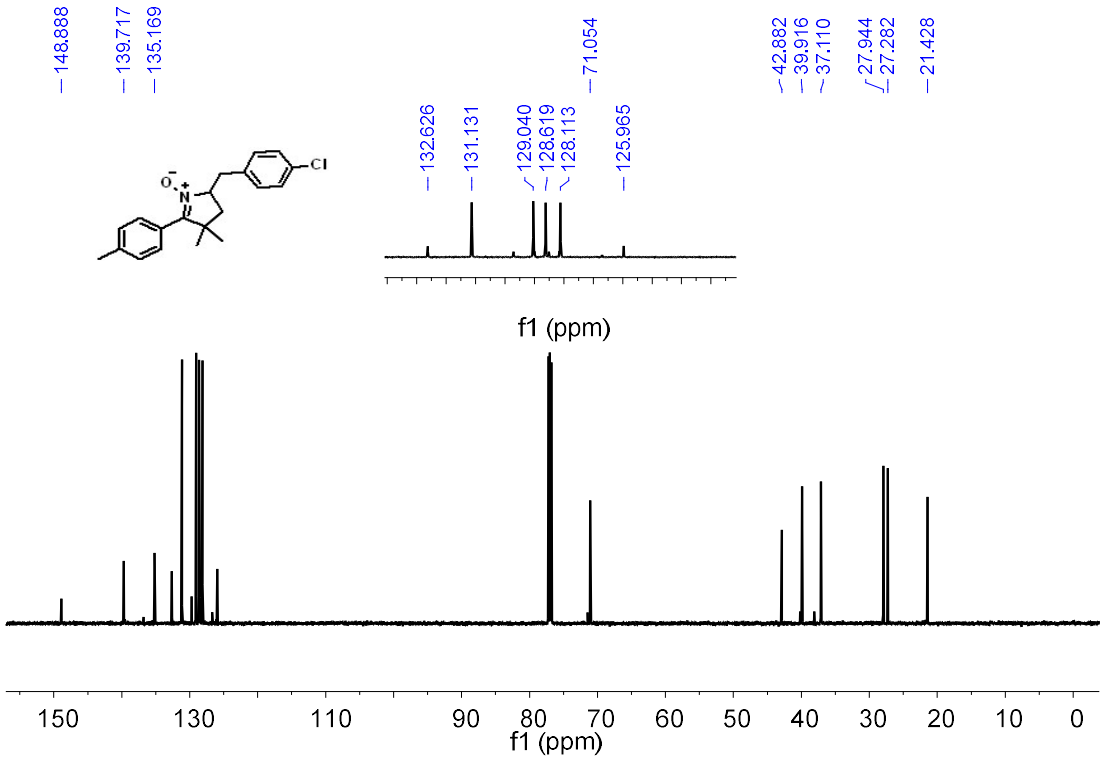
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 2n.



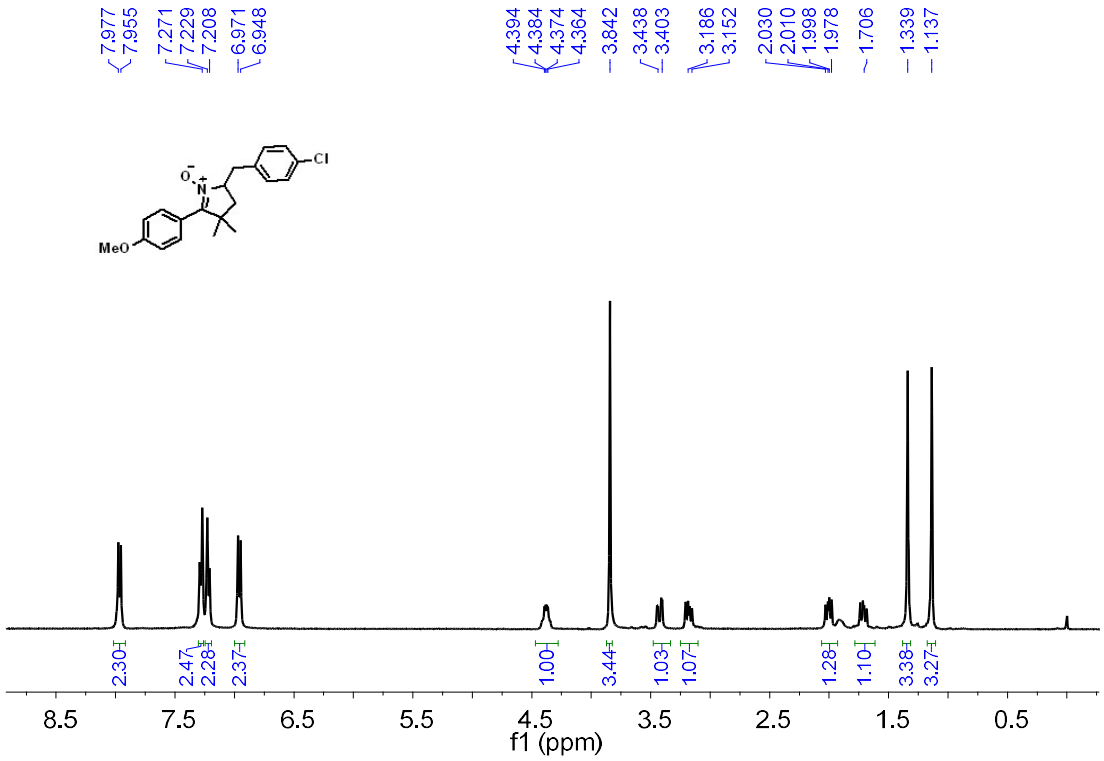
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 2n.



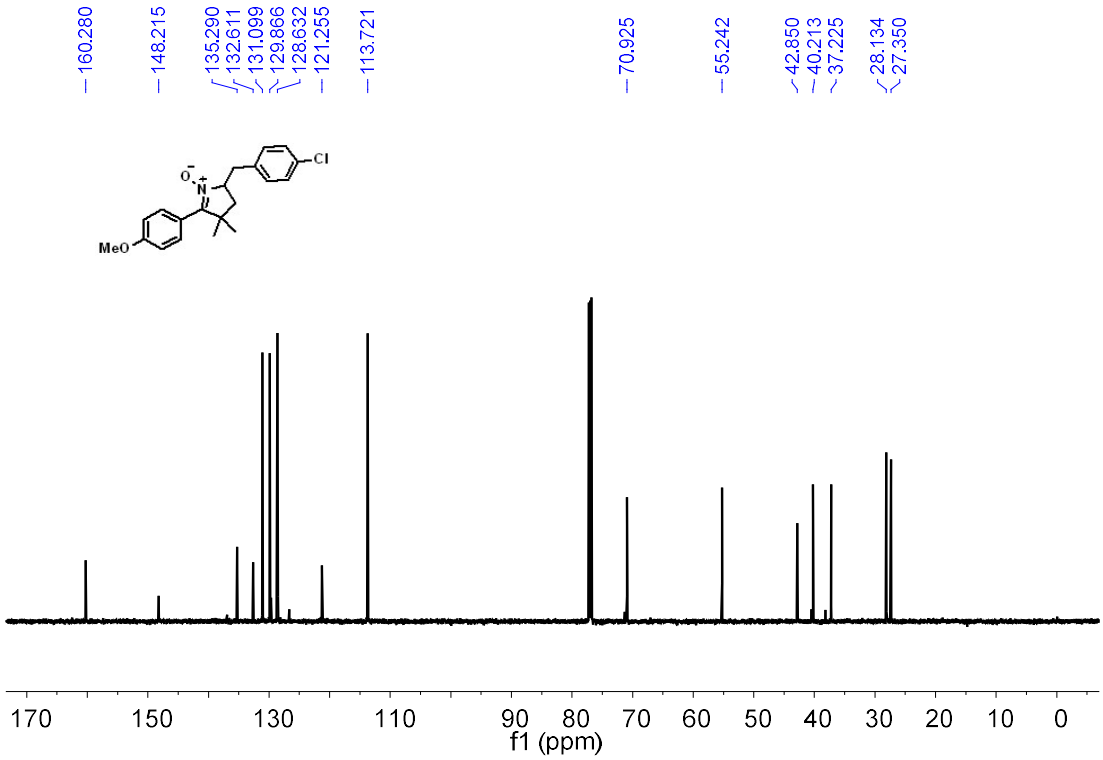
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 2o.



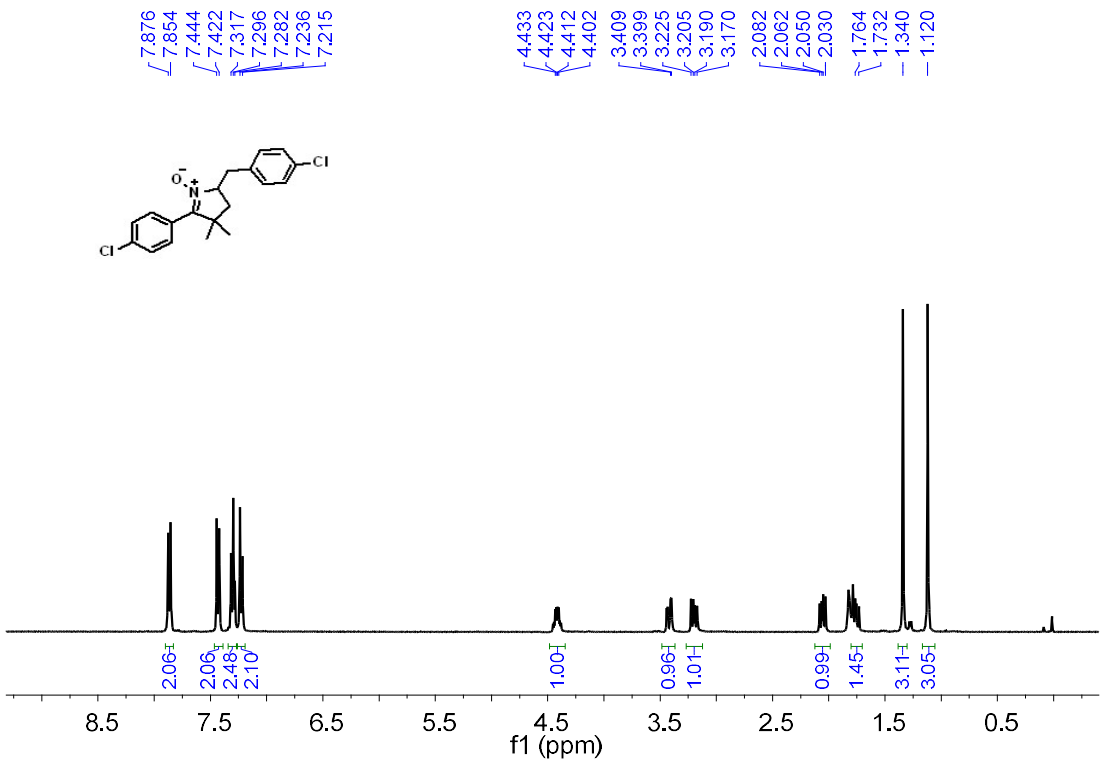
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 2o.



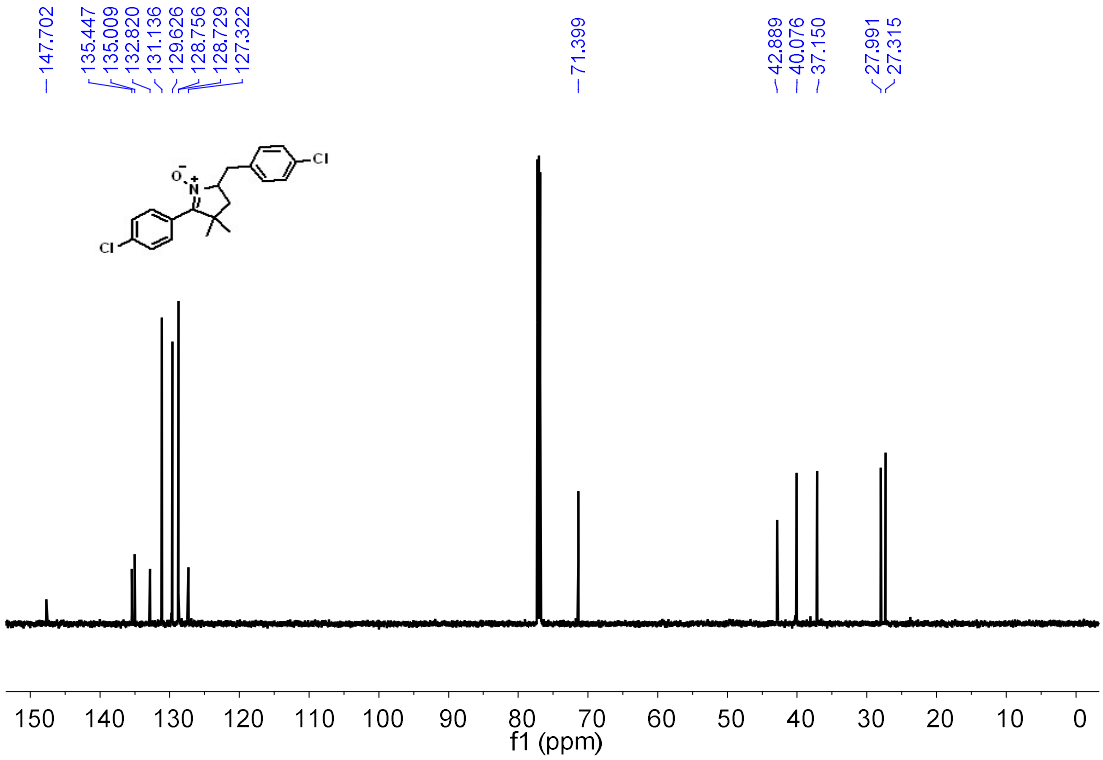
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 2p.



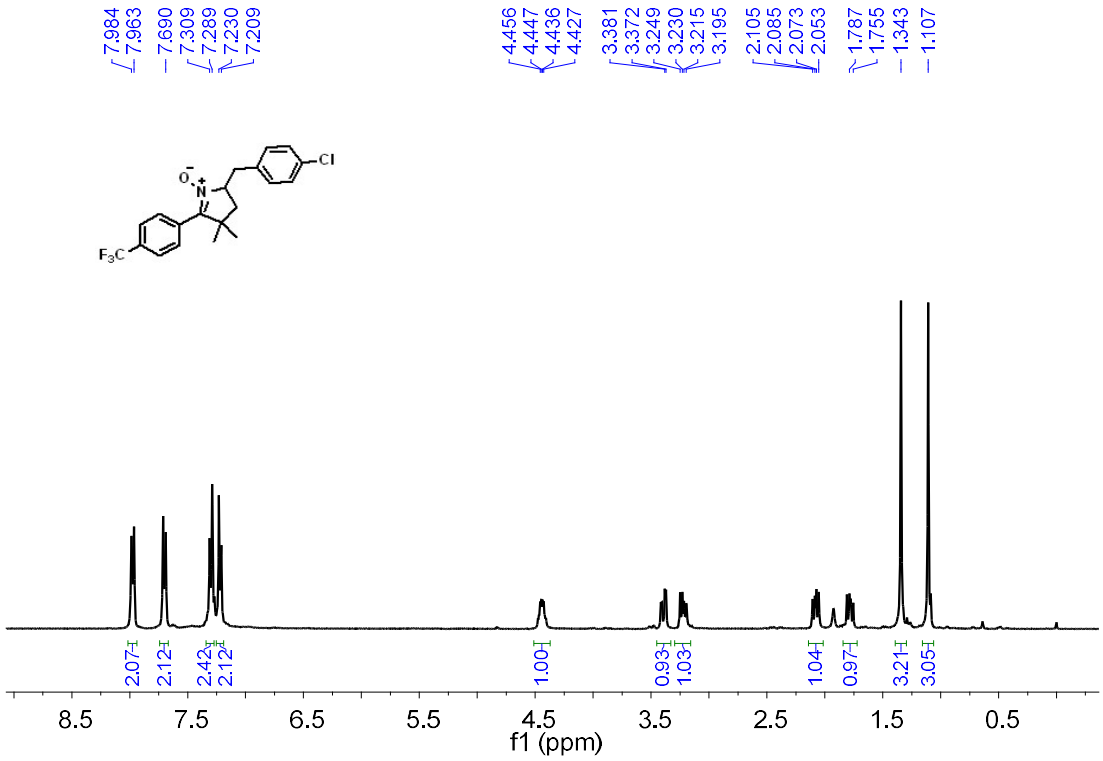
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 2p.



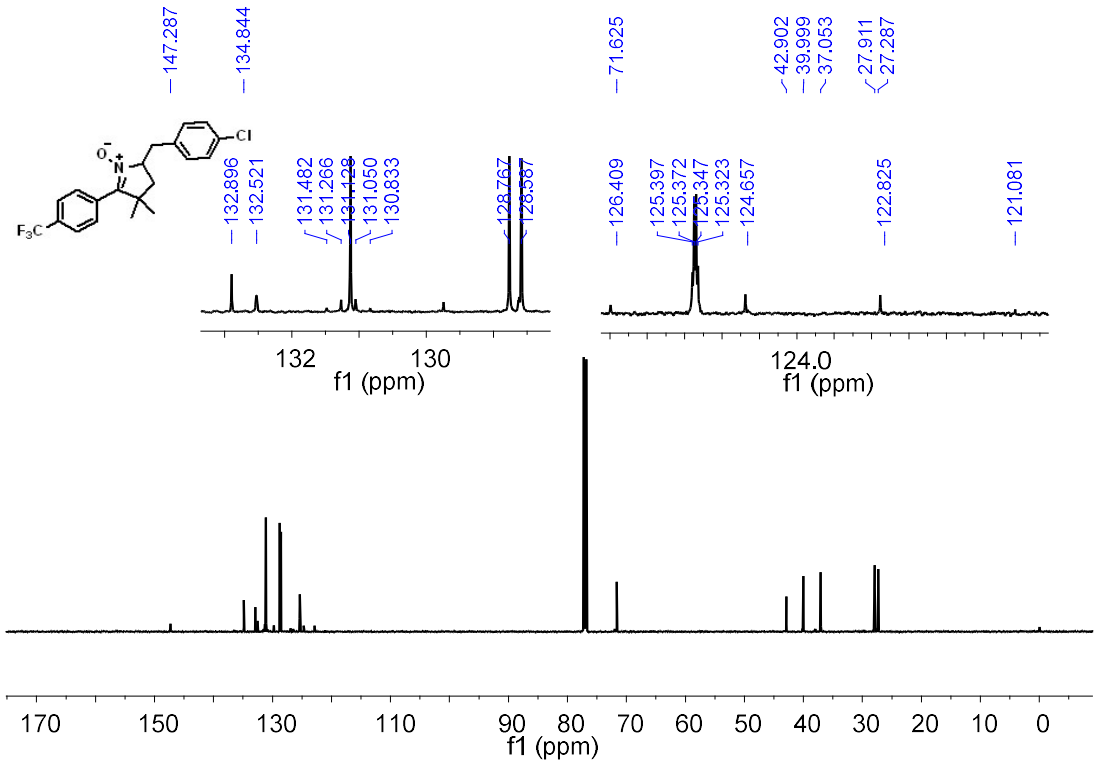
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 2q.



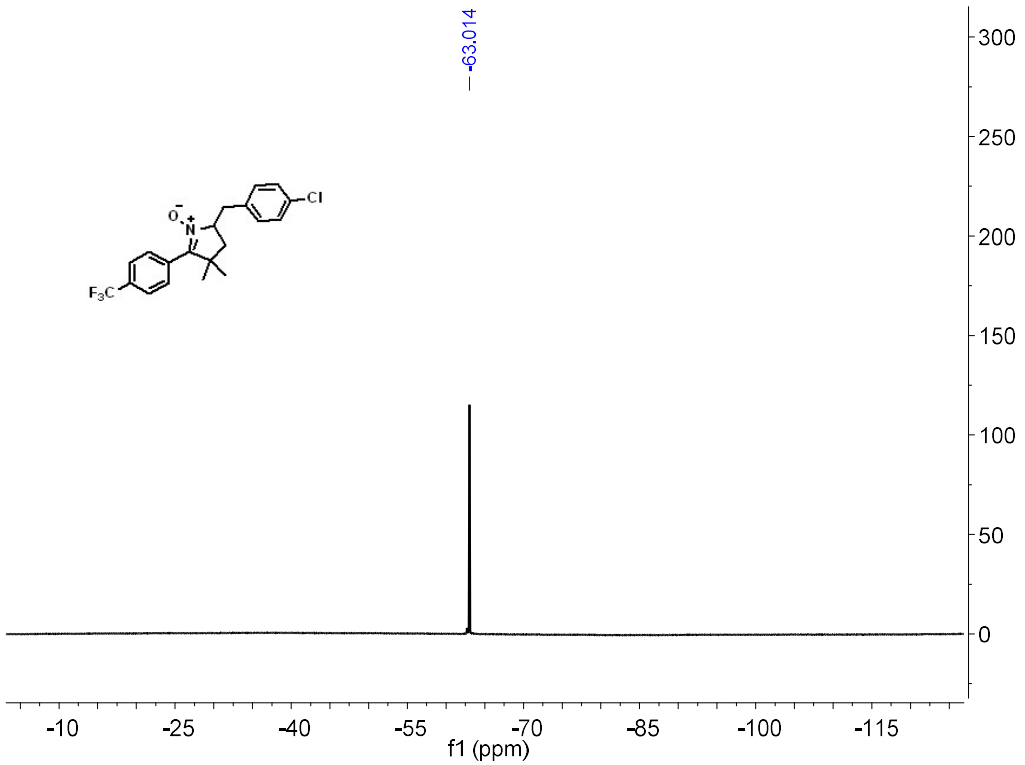
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 2q.



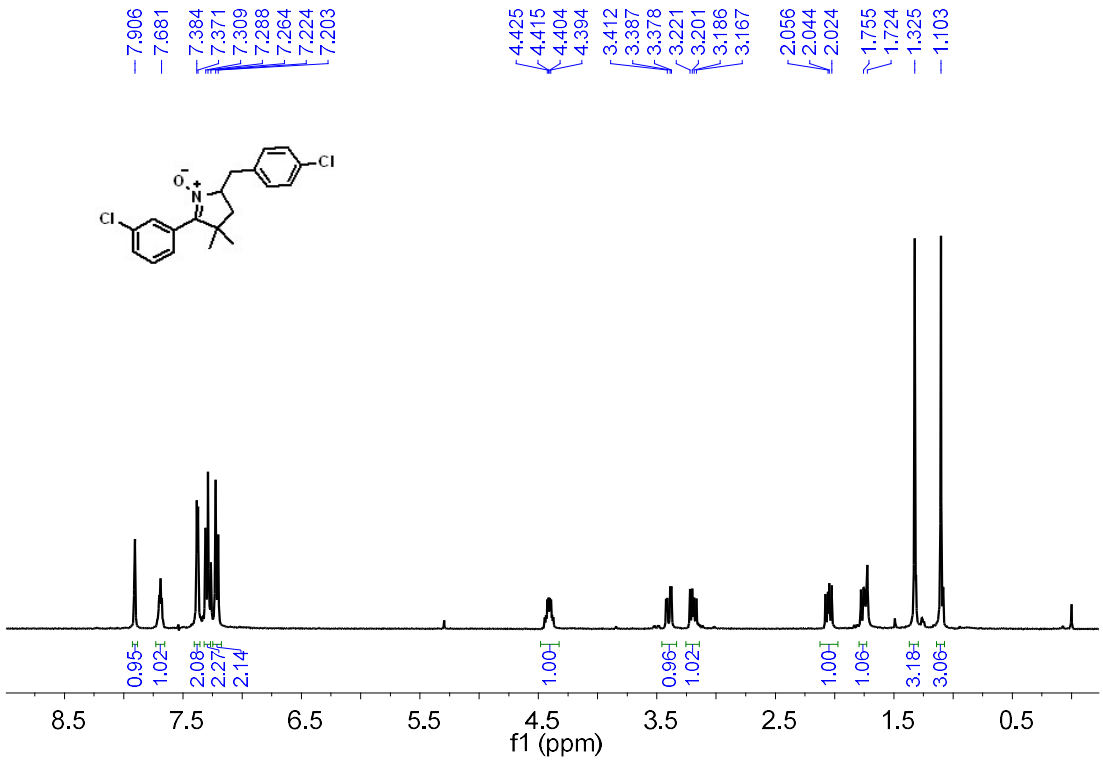
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 2r.



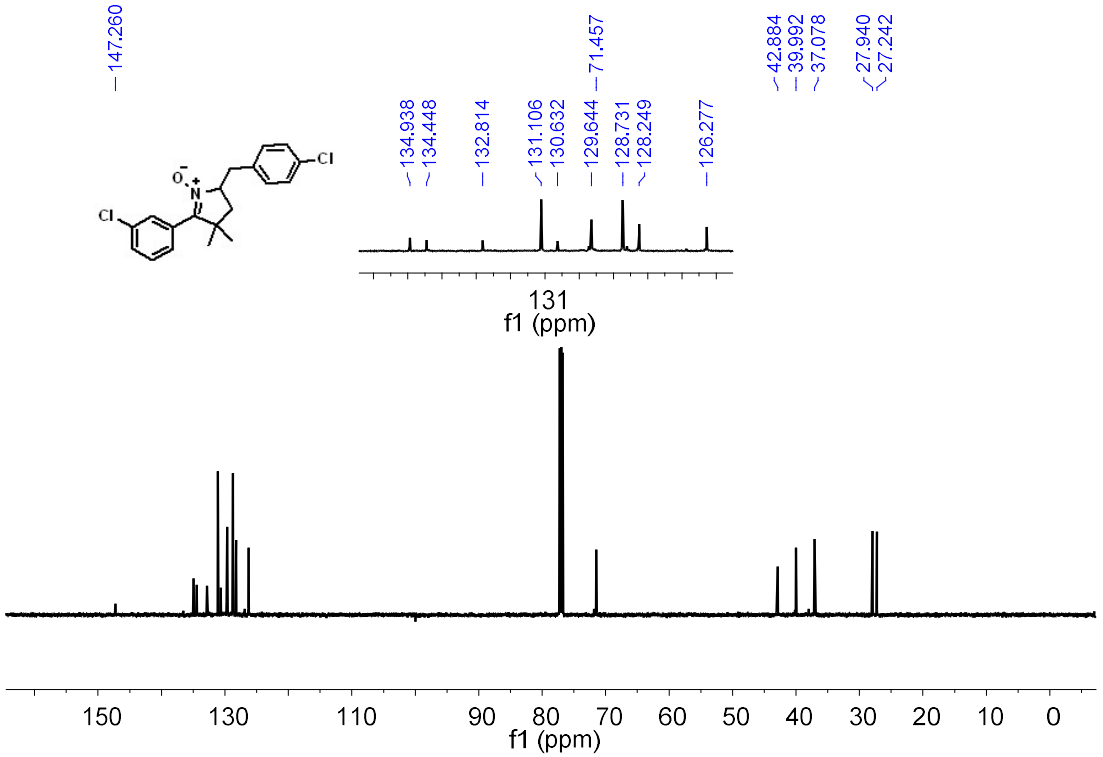
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 2r.



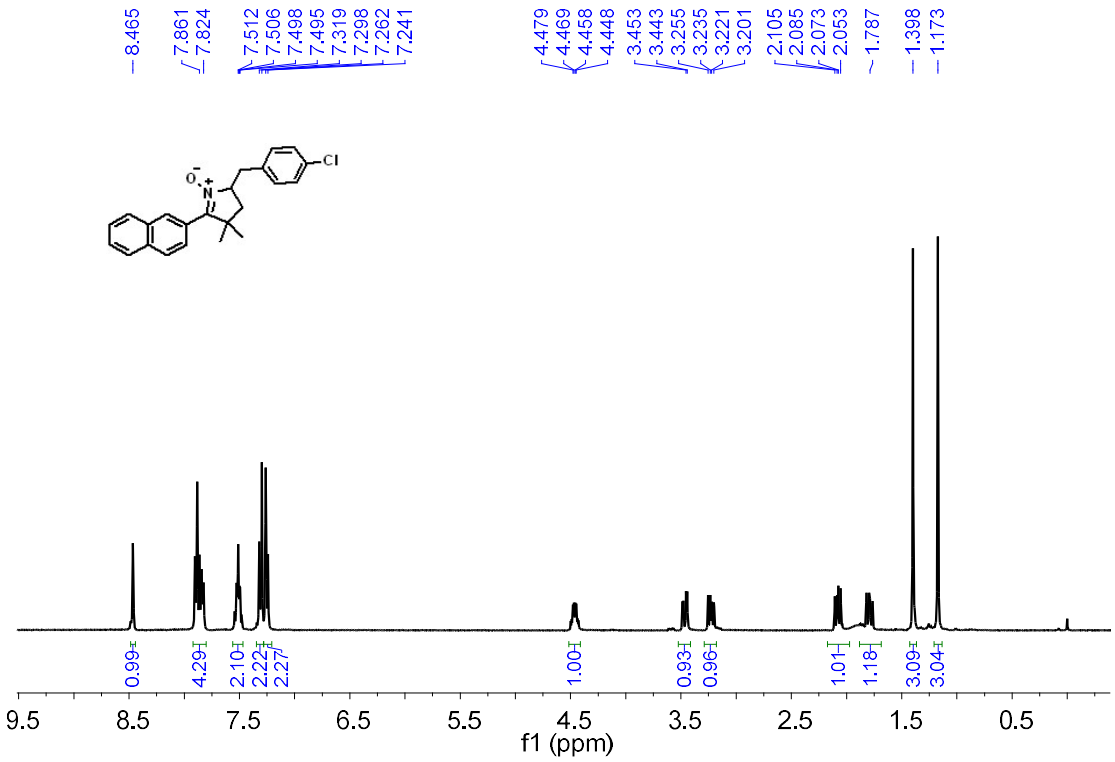
^{19}F NMR (470 MHz, $CDCl_3$) spectrum for 2r



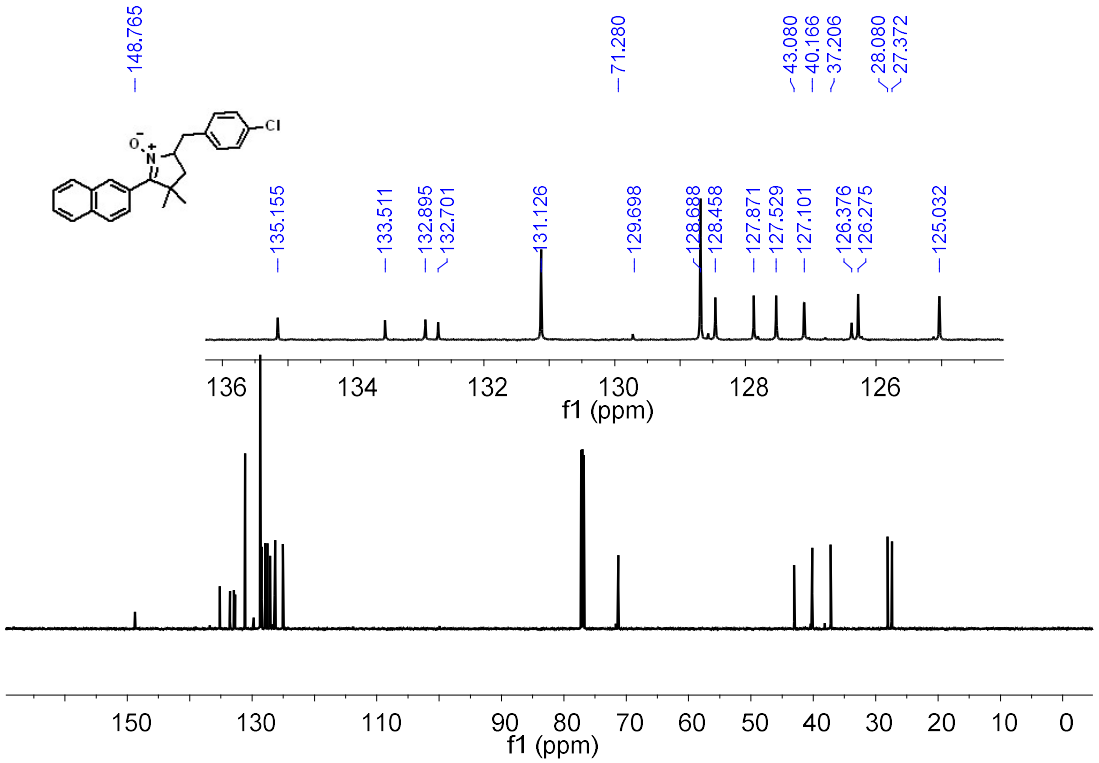
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 2s.



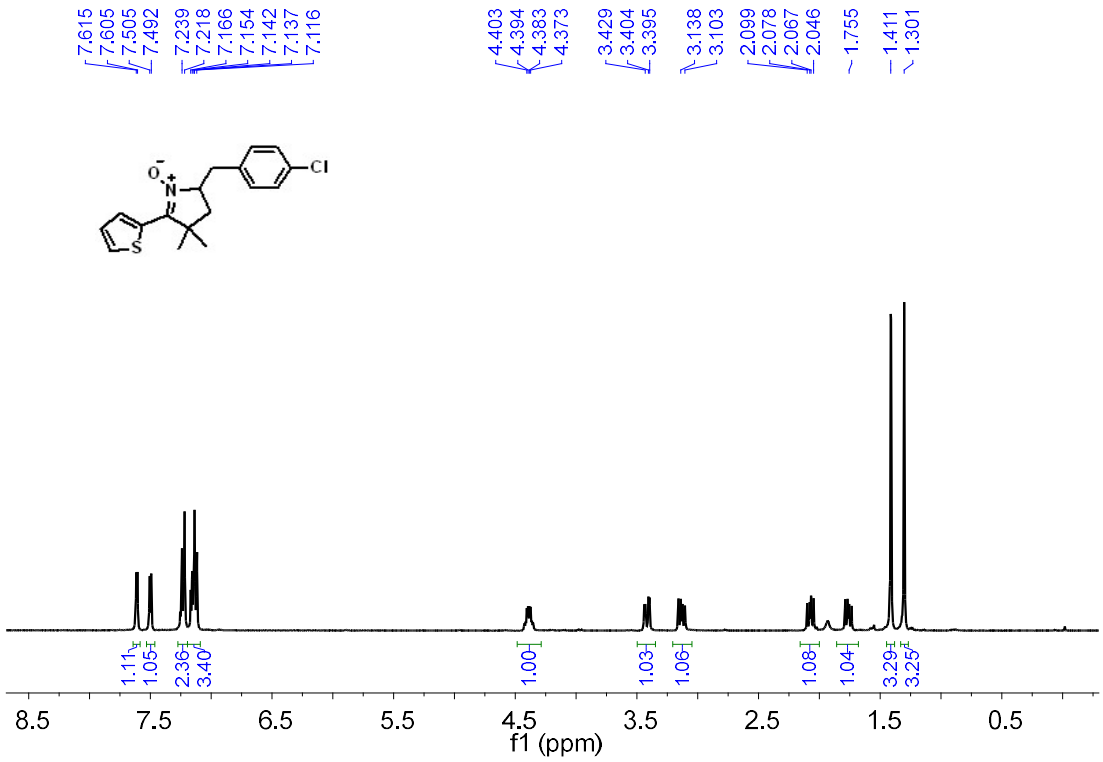
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 2s.



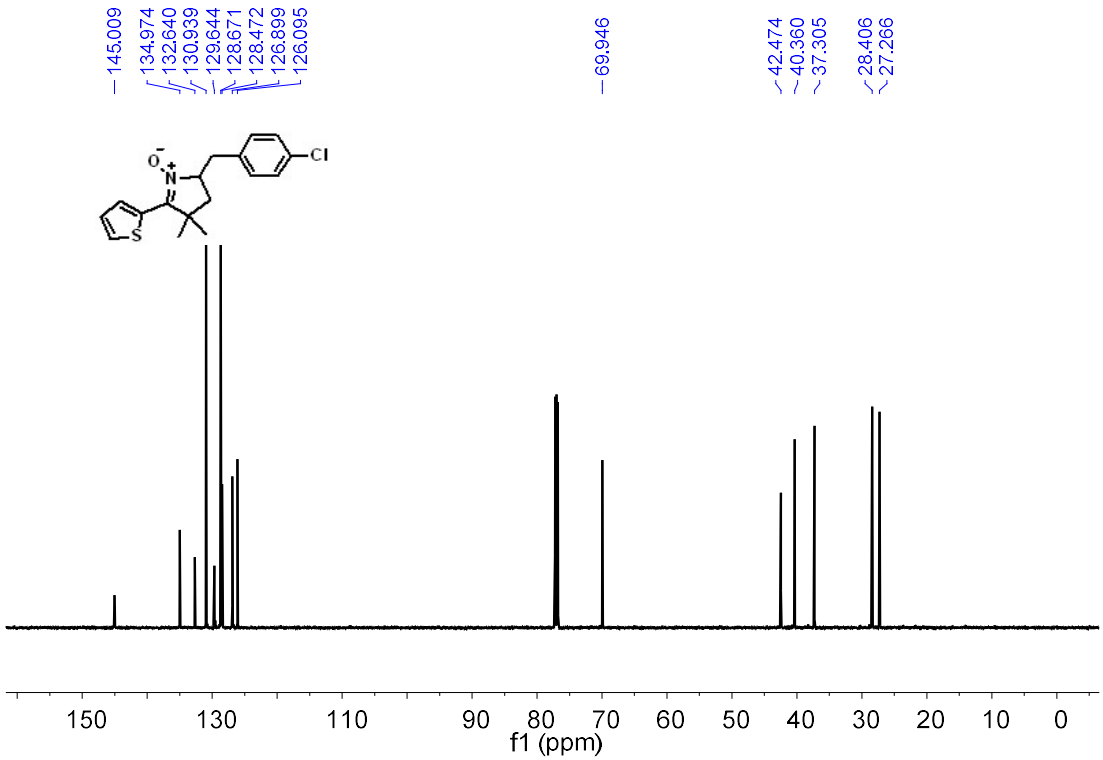
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 2t.



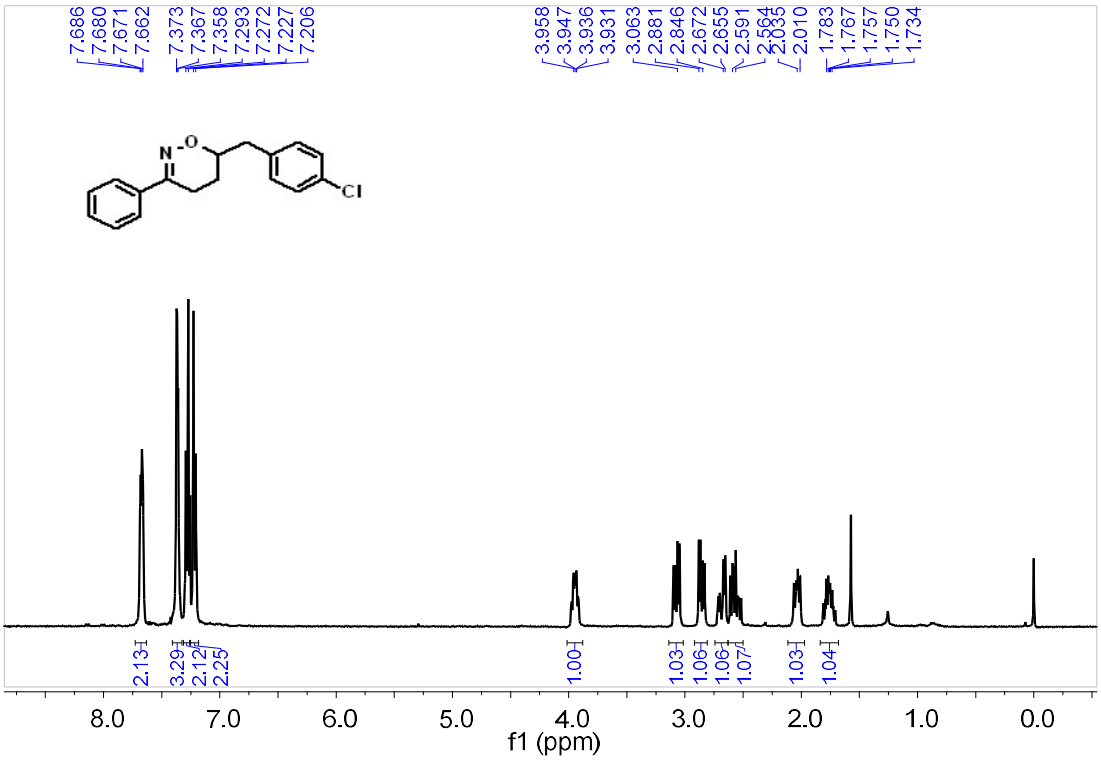
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 2t.



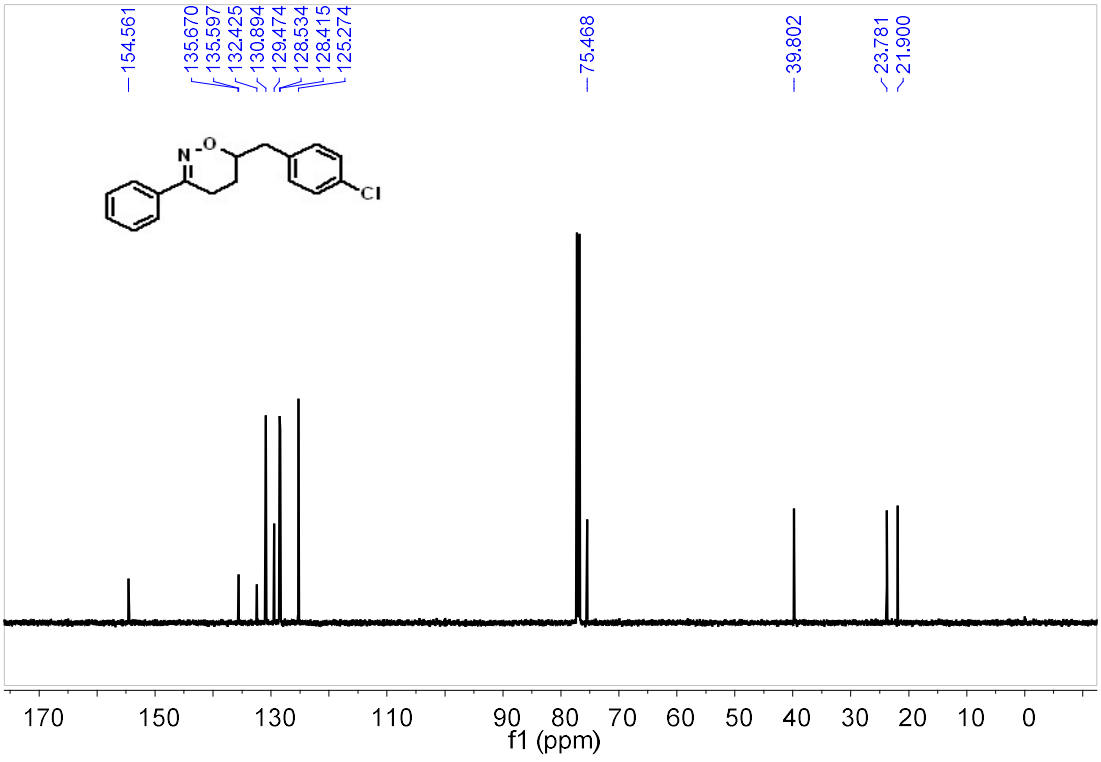
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 2u.



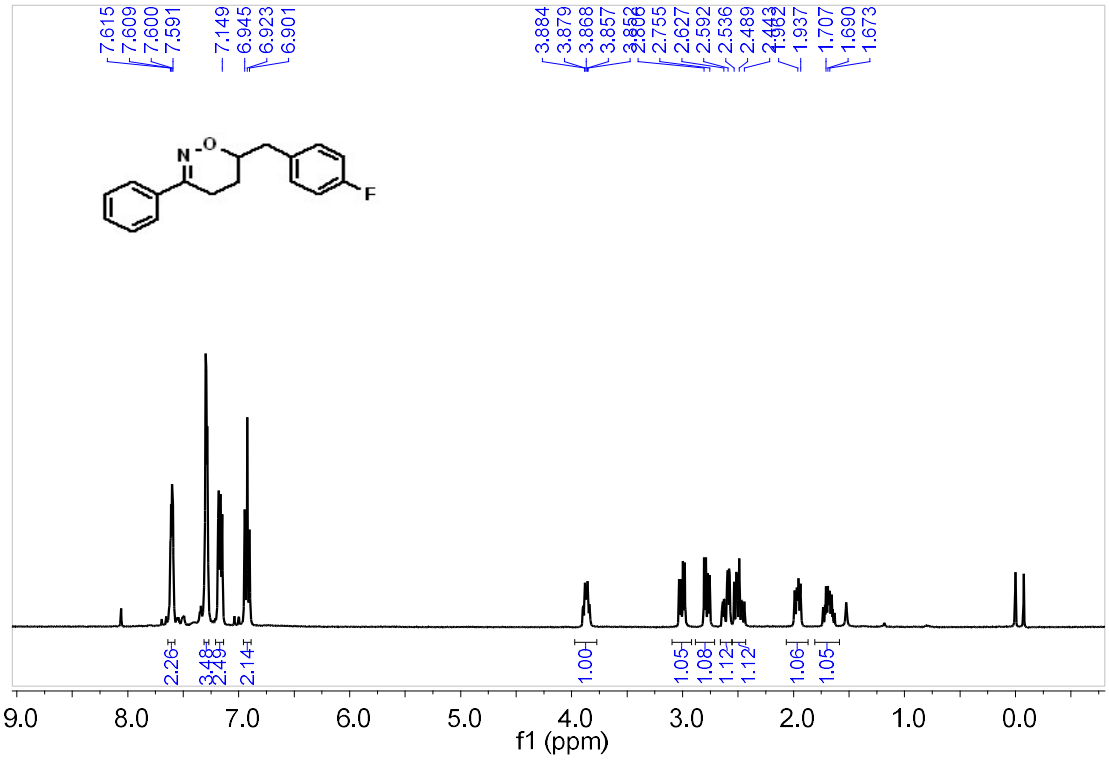
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 2u.



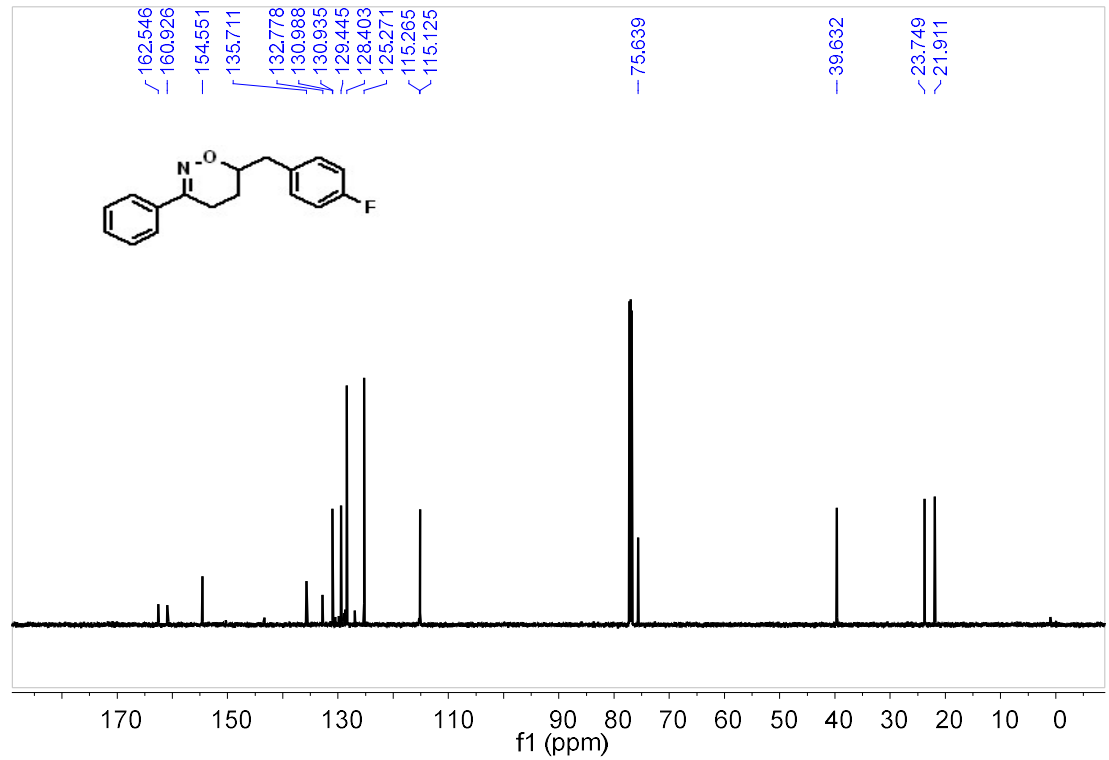
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3a.



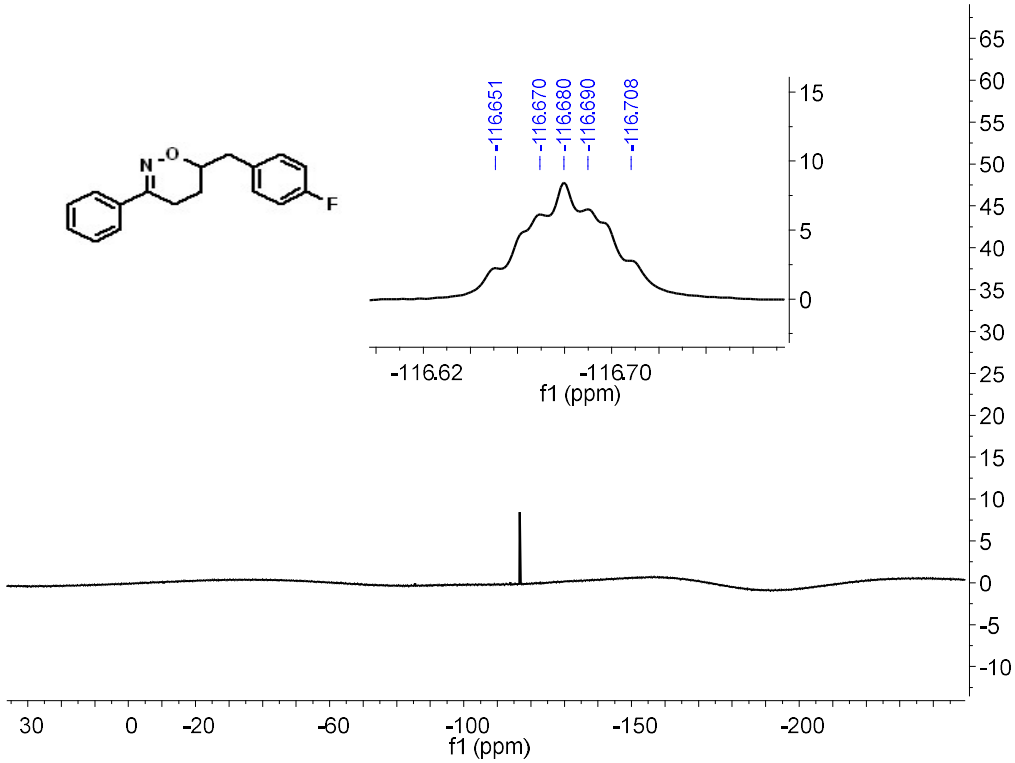
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3a.



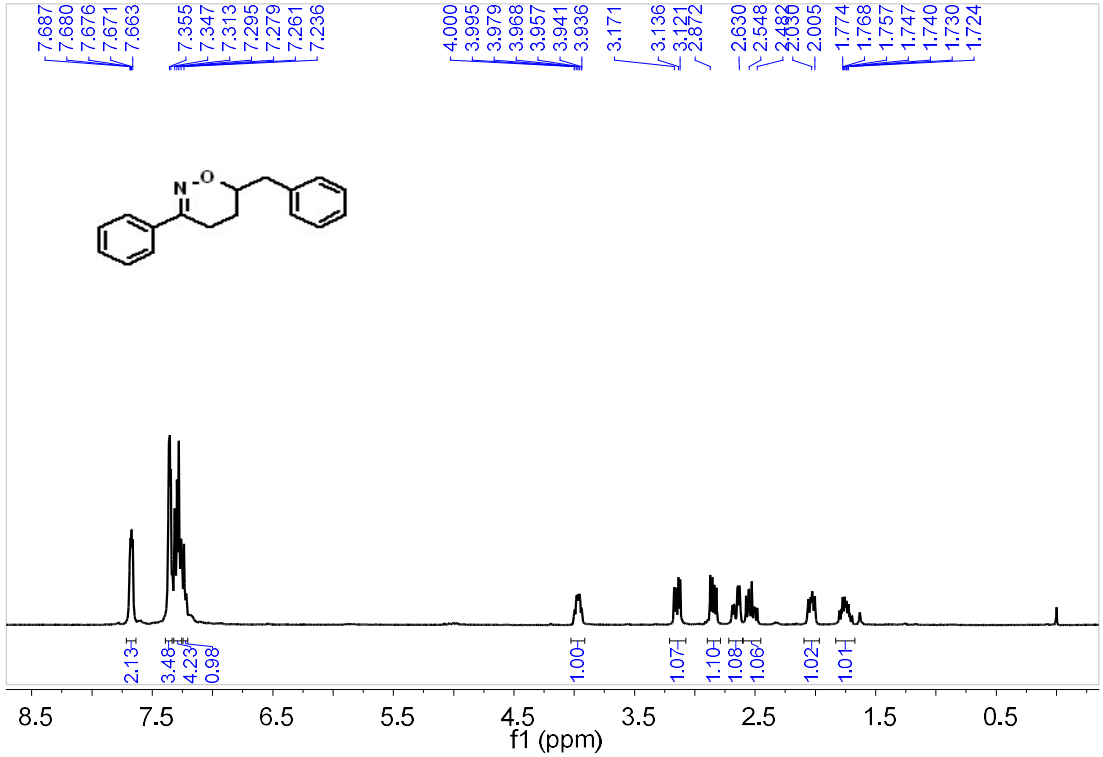
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3b.



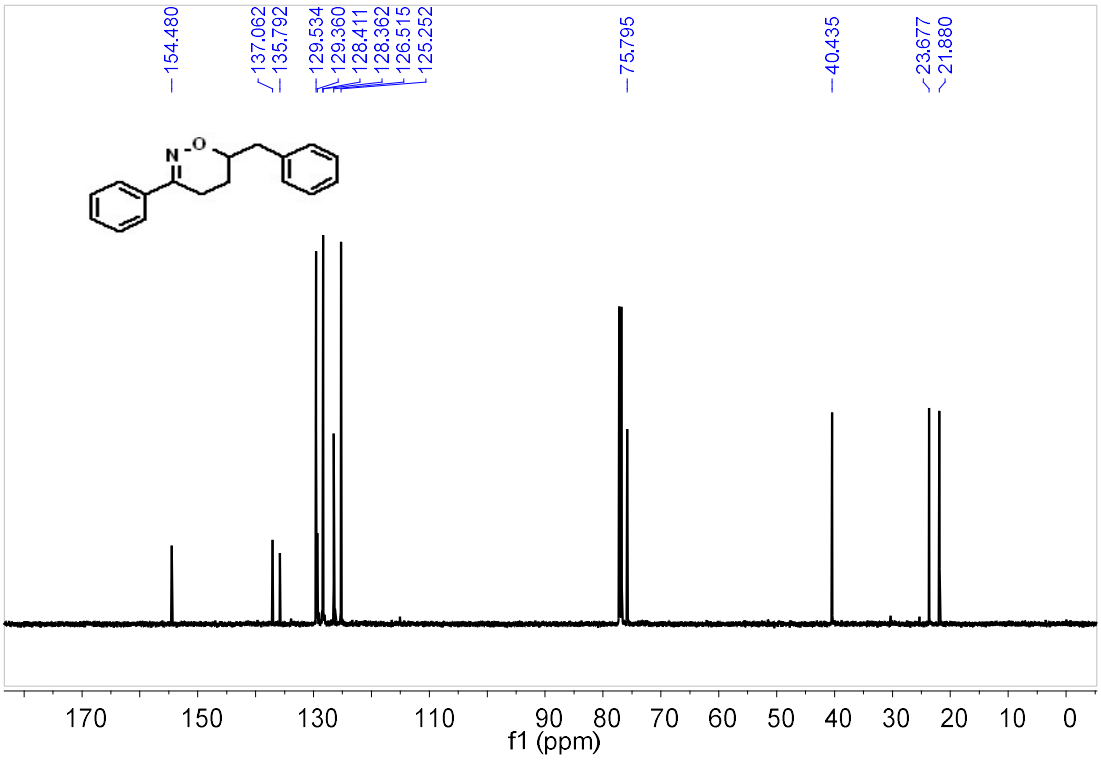
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3b.



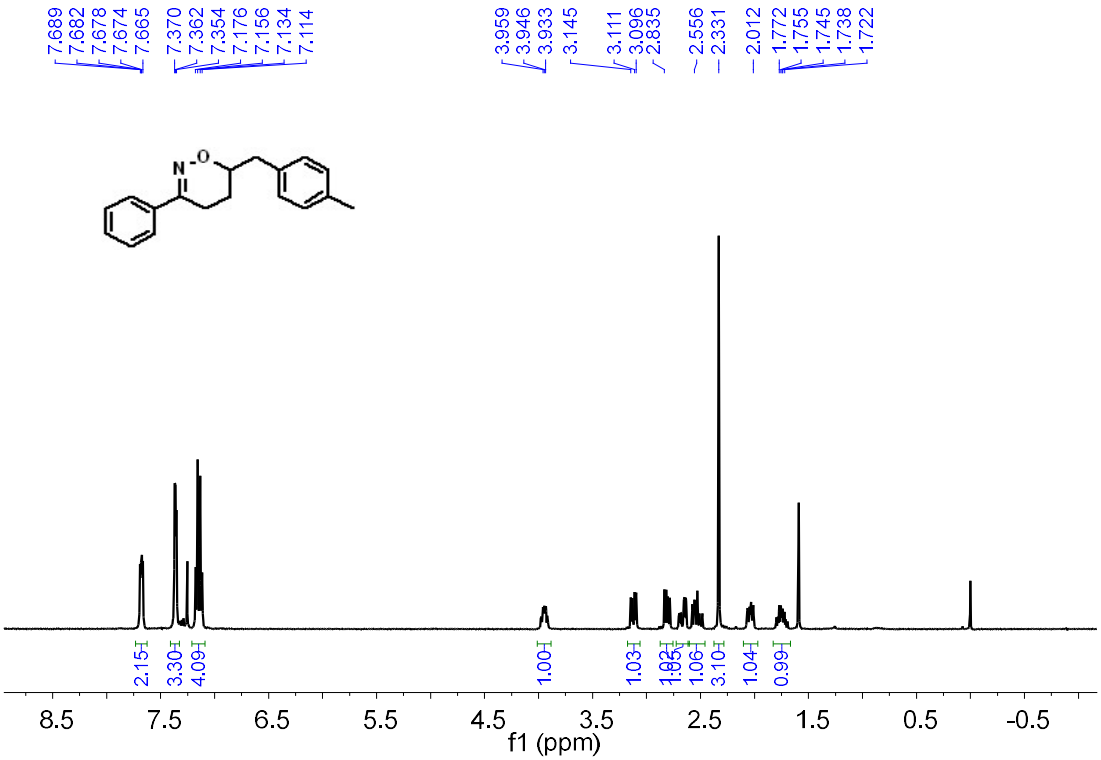
^{19}F NMR (470 MHz, $CDCl_3$) spectrum for 3b



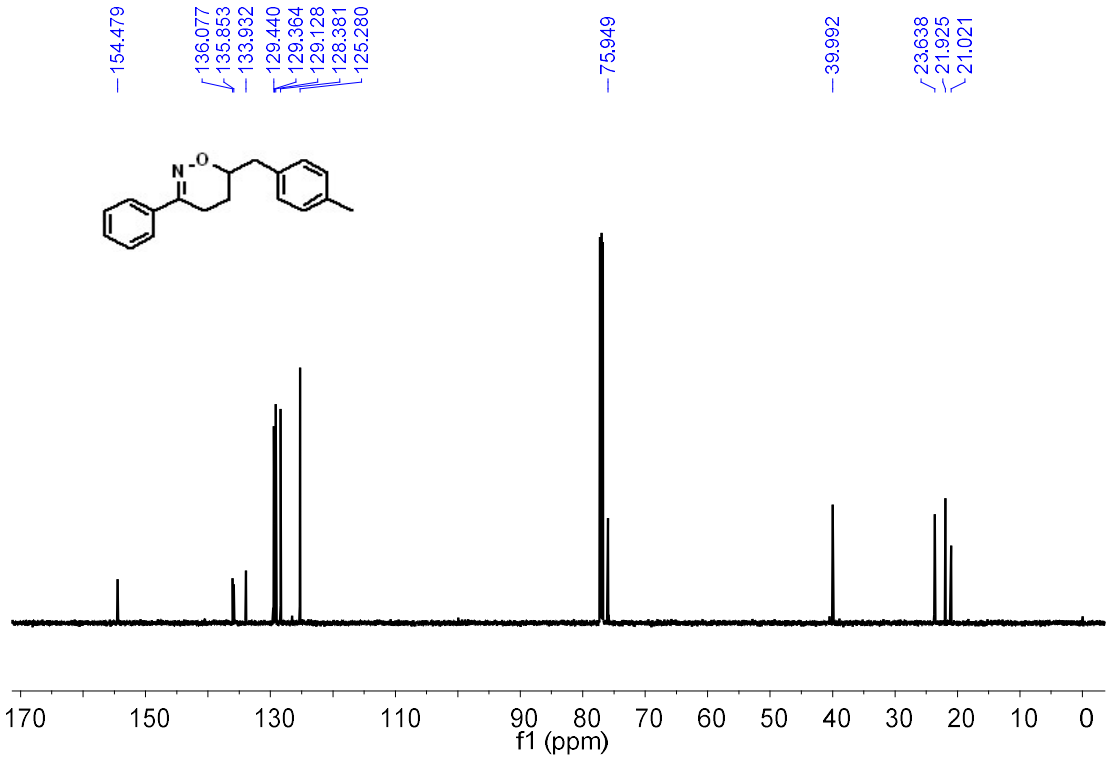
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3c.



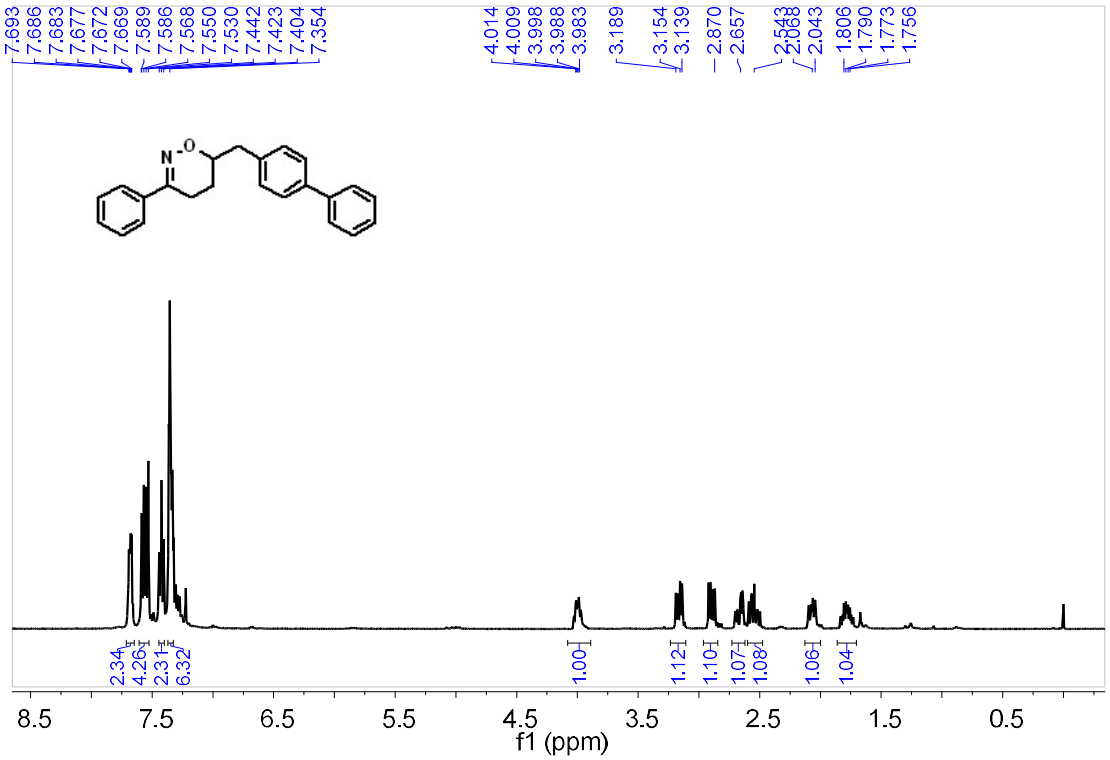
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3c.



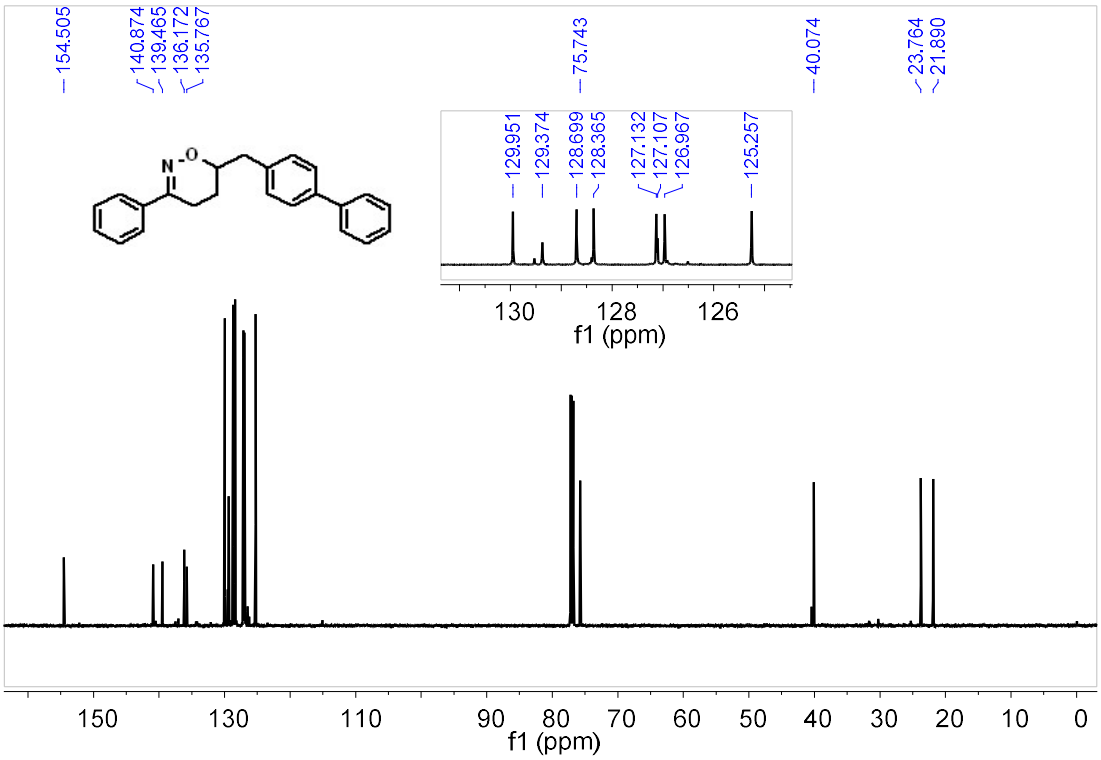
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3d.



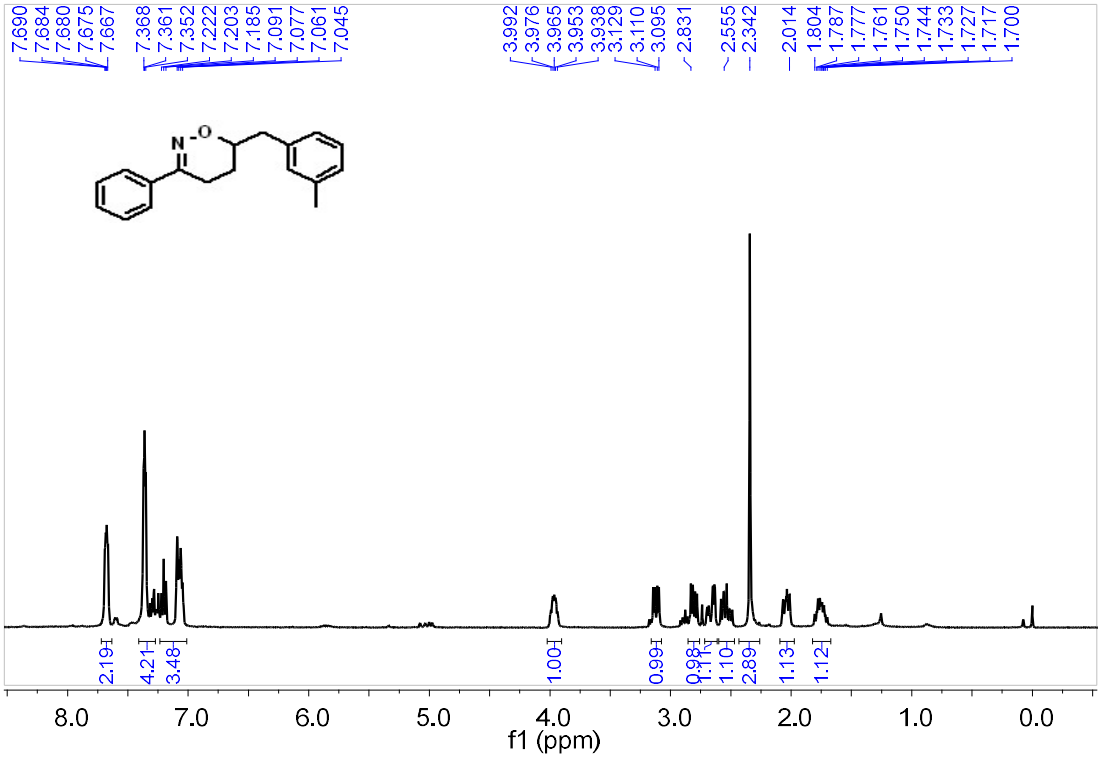
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3d.



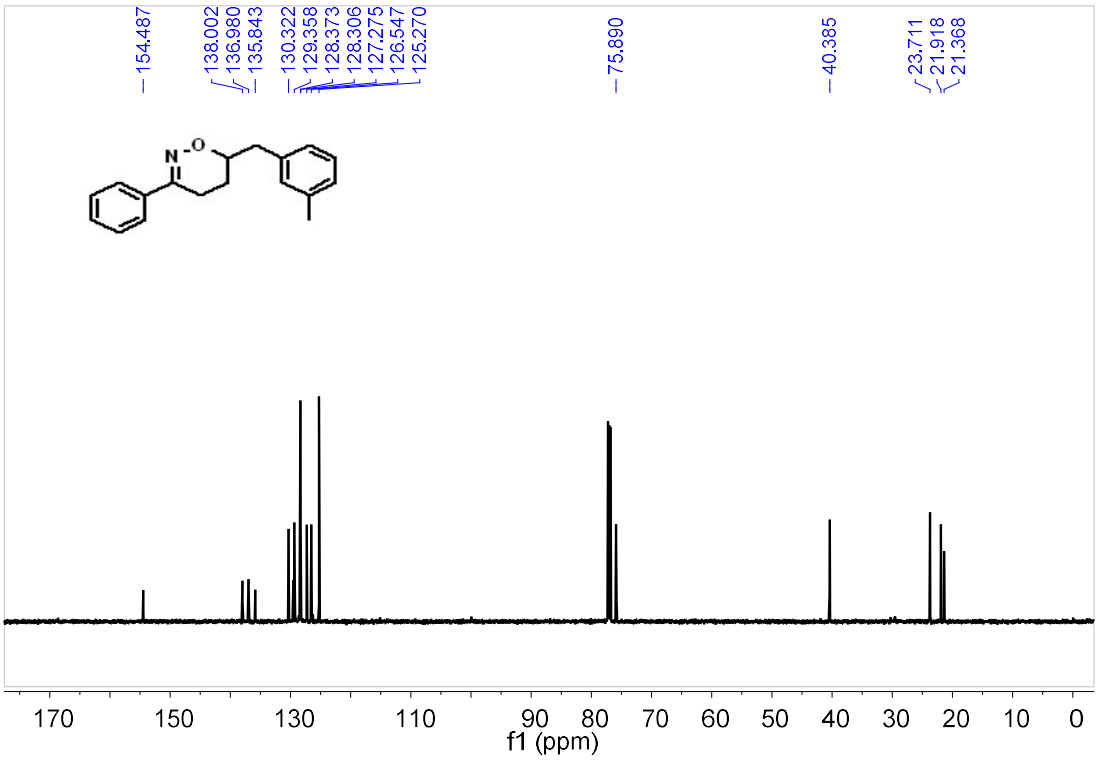
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3e.



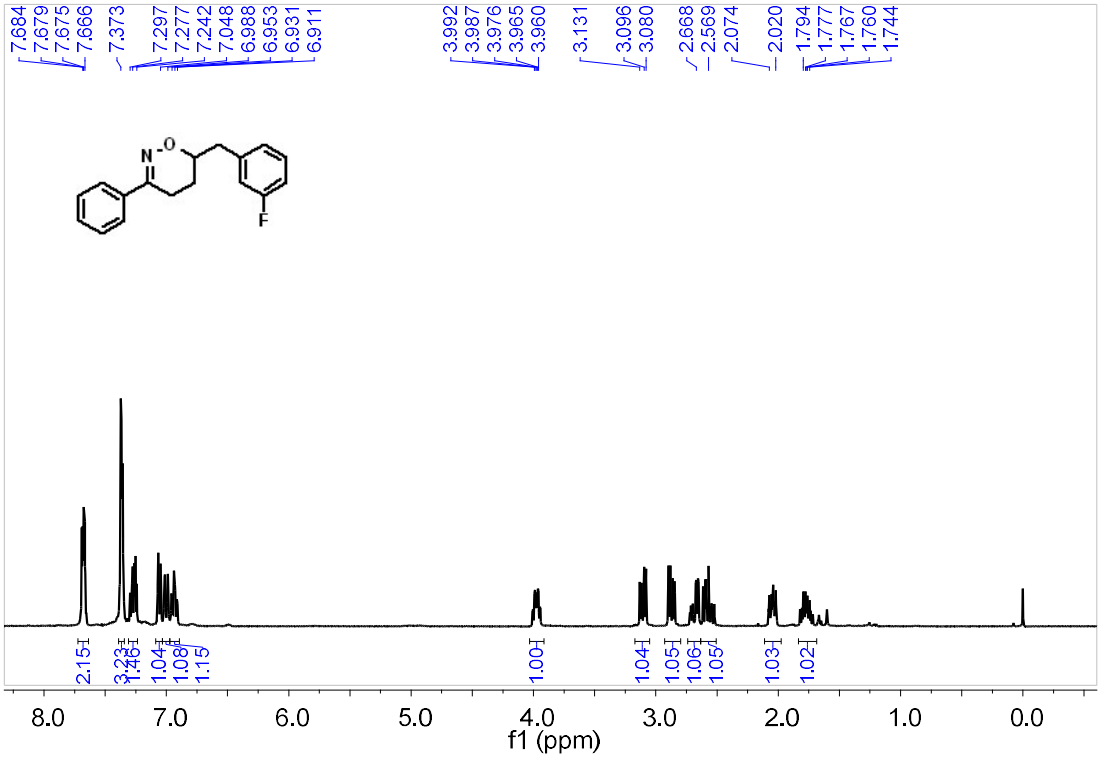
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3e.



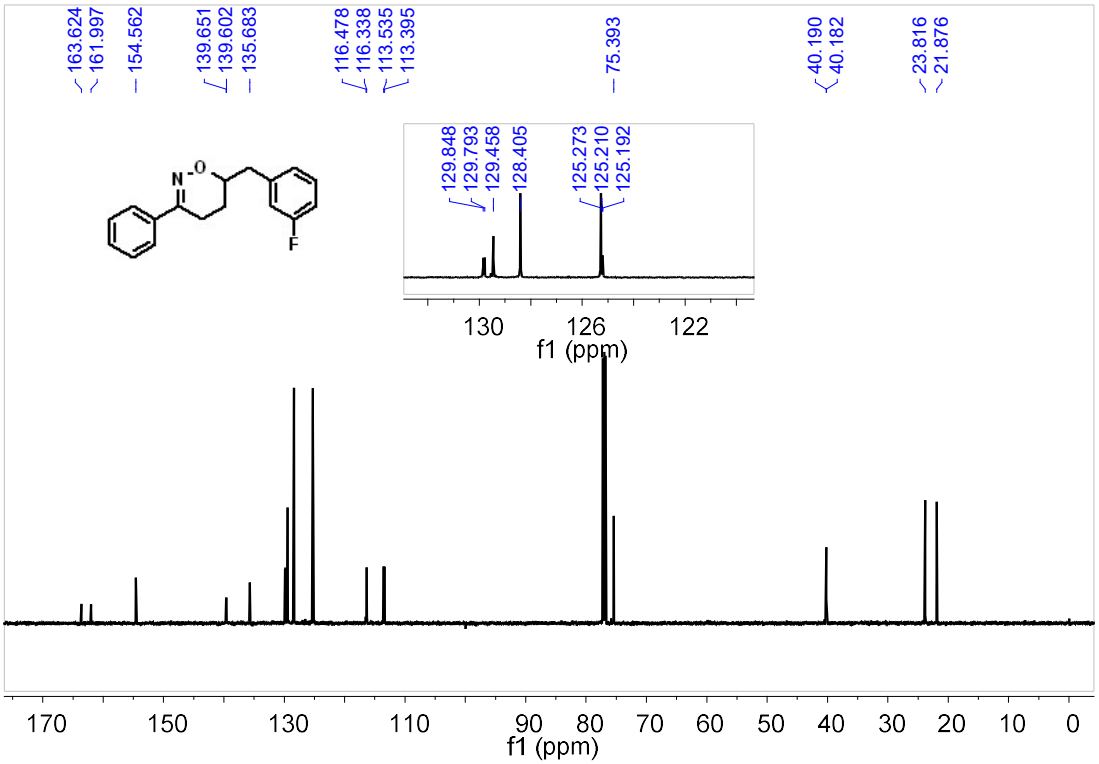
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3f.



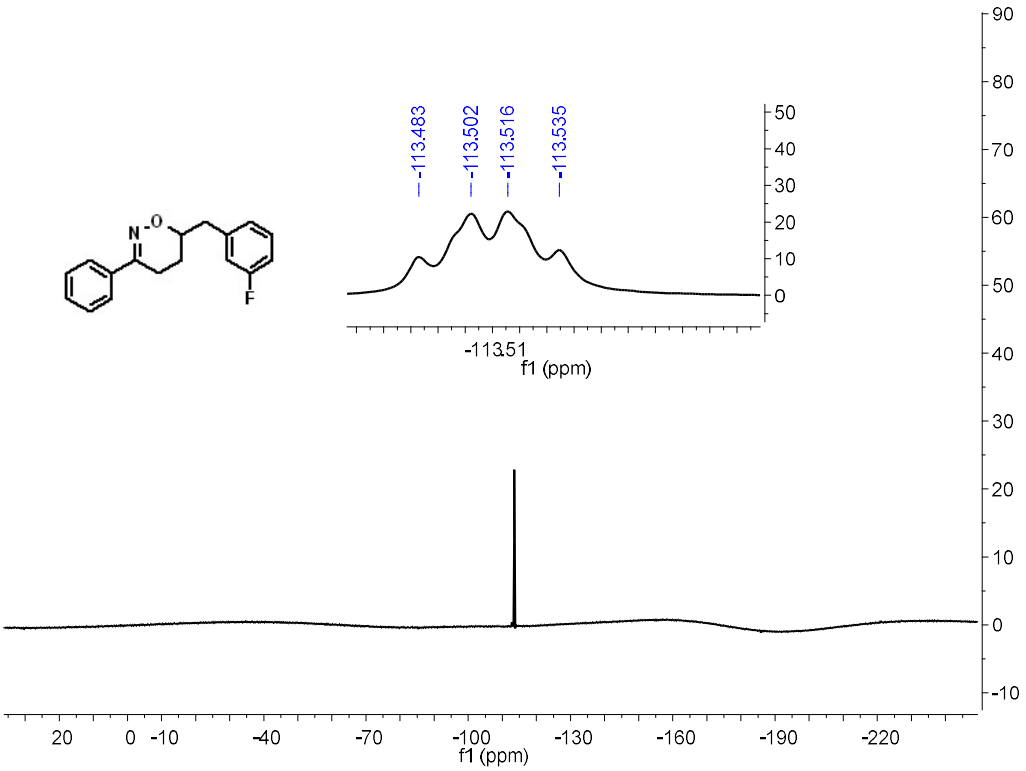
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3f.



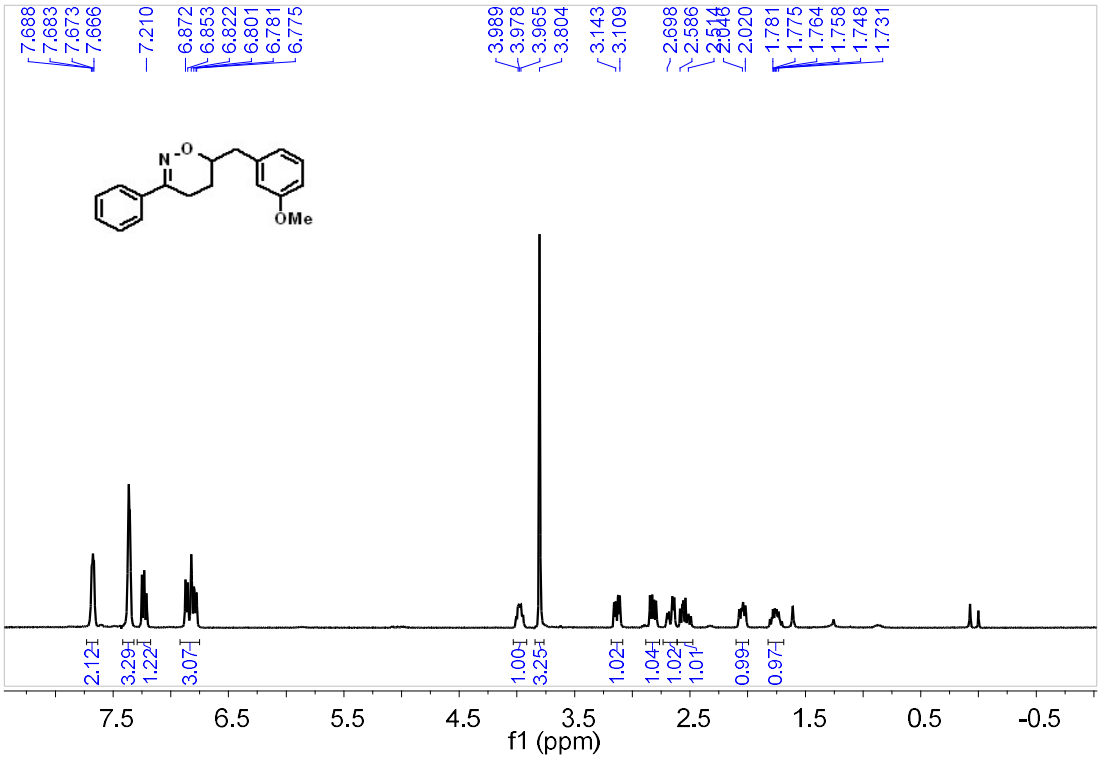
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3g.



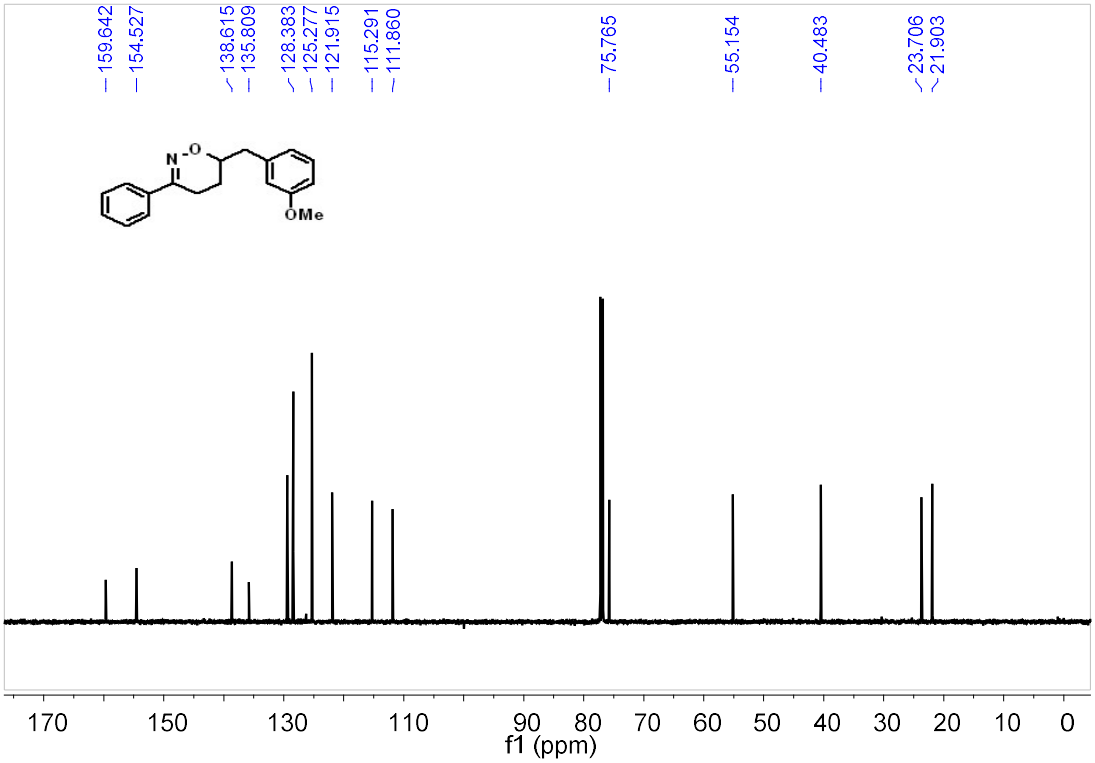
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3g.



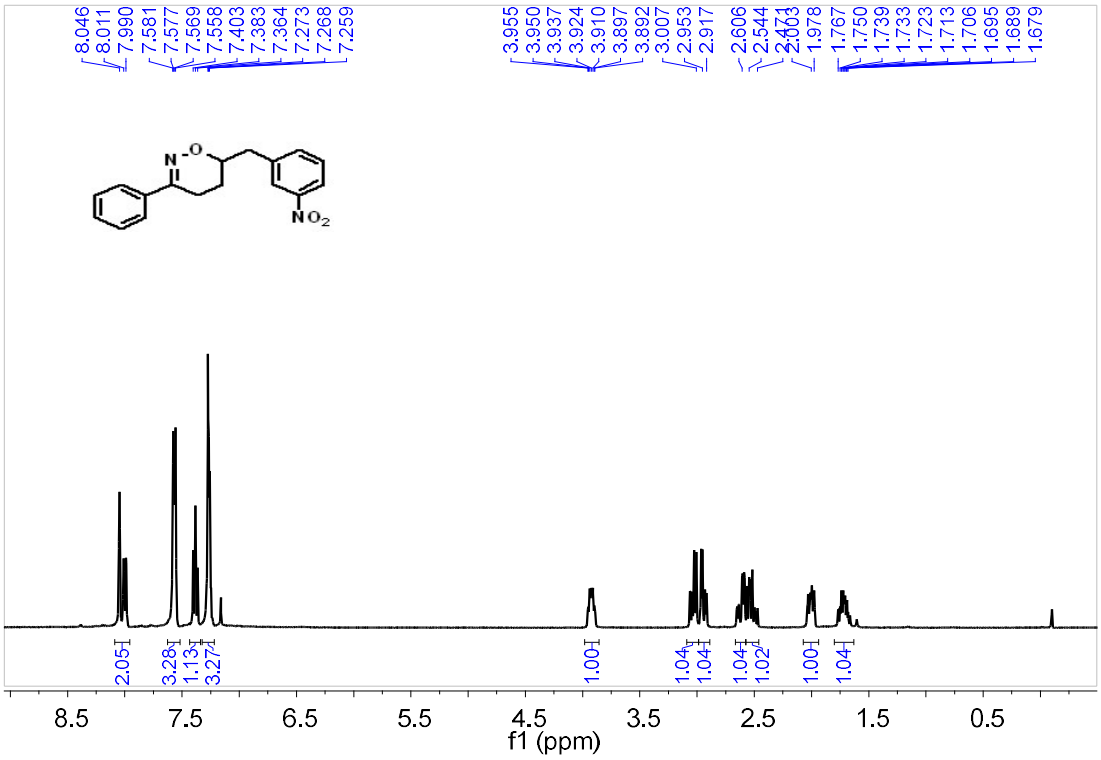
^{19}F NMR (470 MHz, $CDCl_3$) spectrum for 3g



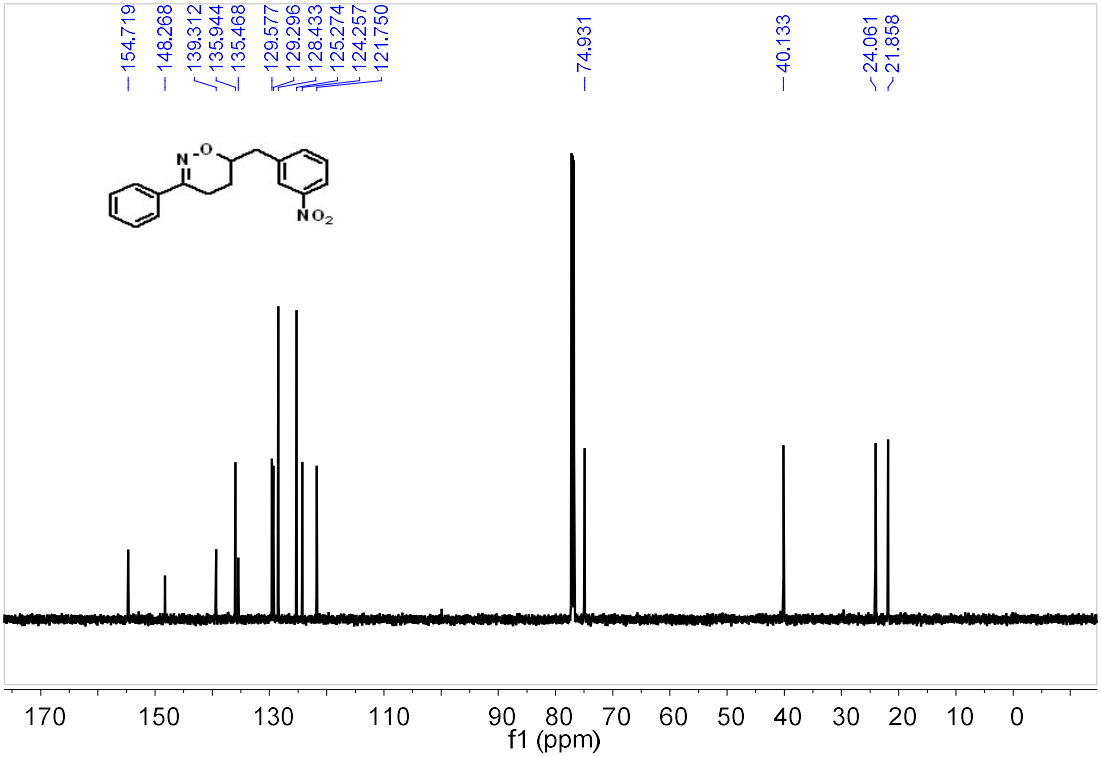
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3h.



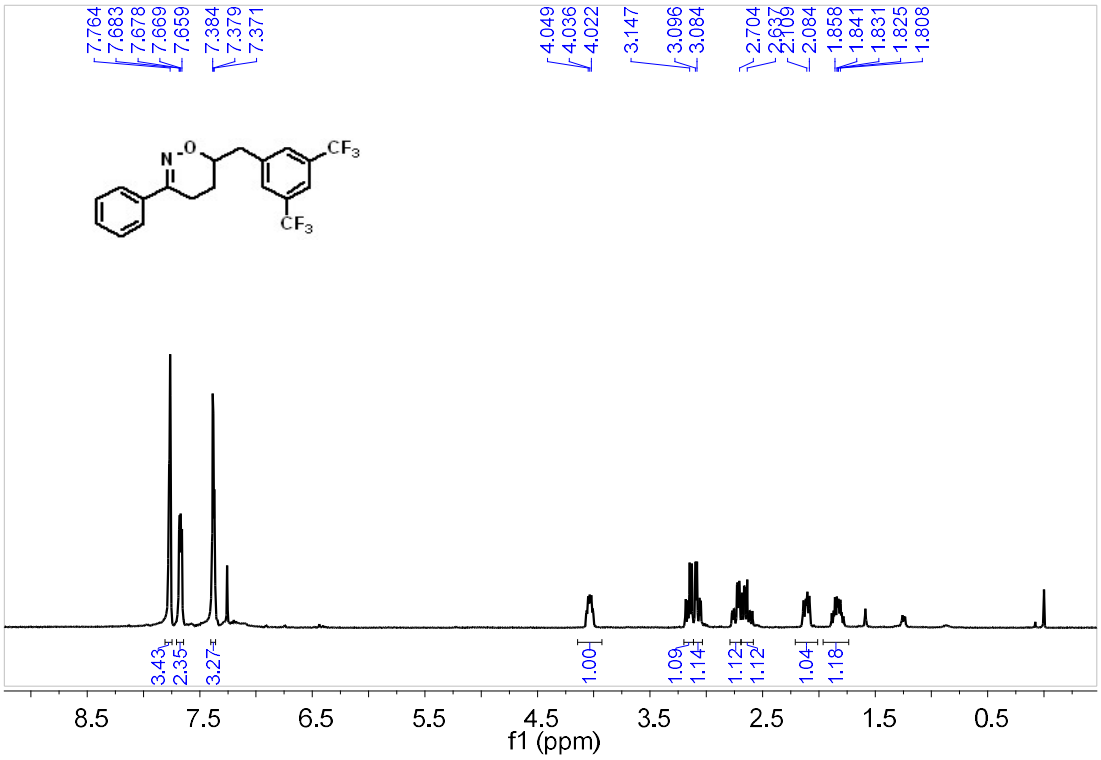
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3h.



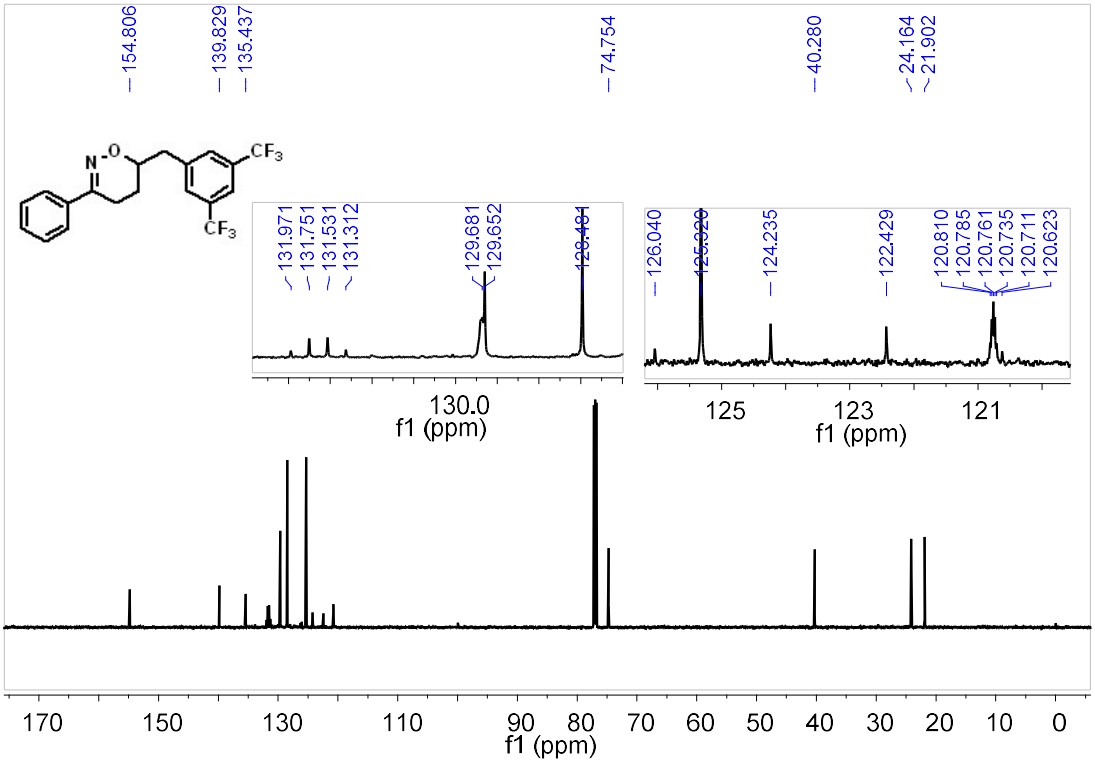
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3i.



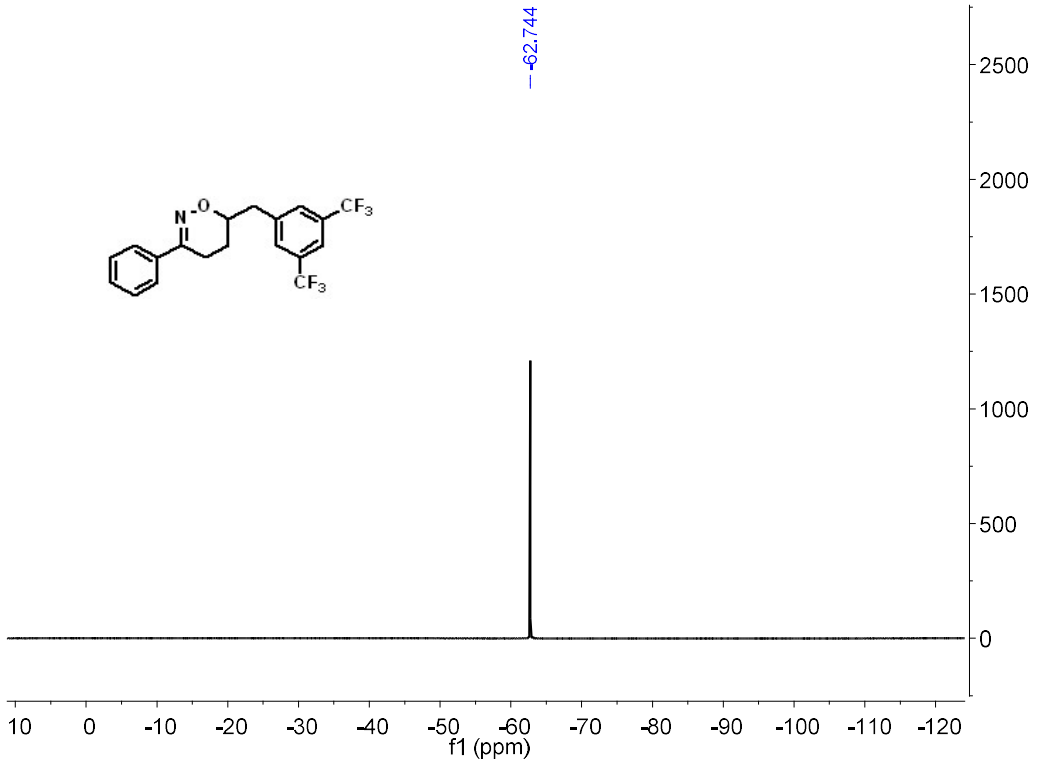
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3i.



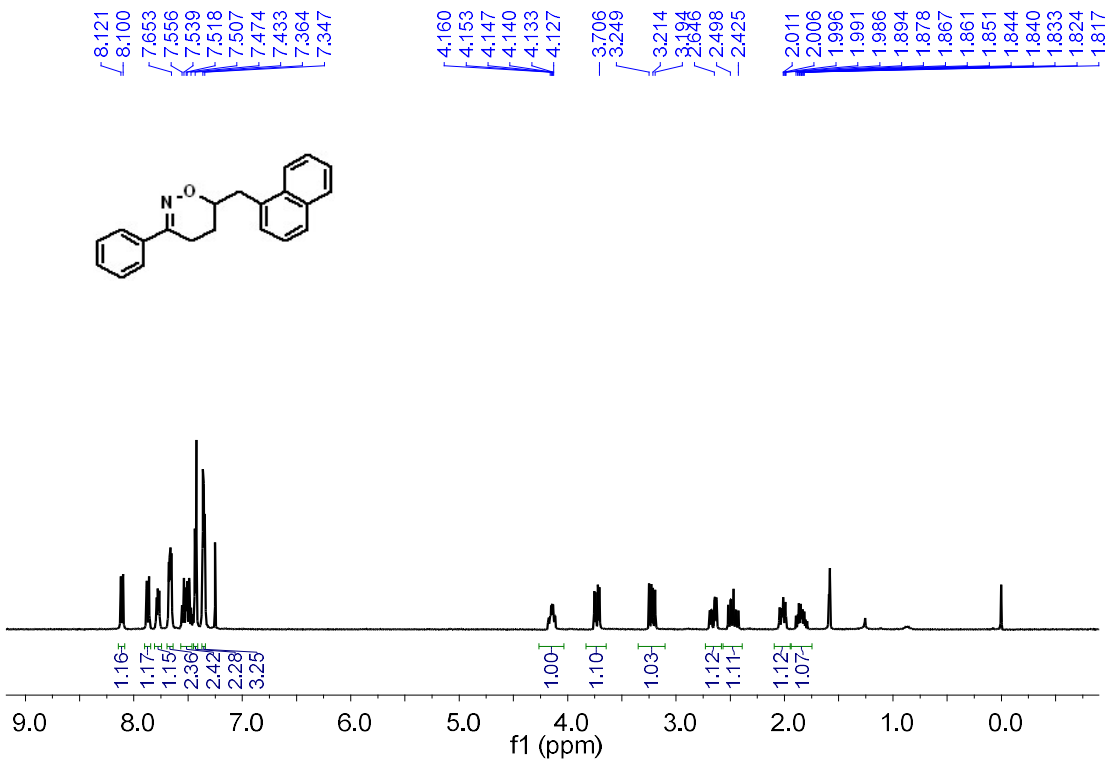
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3j.



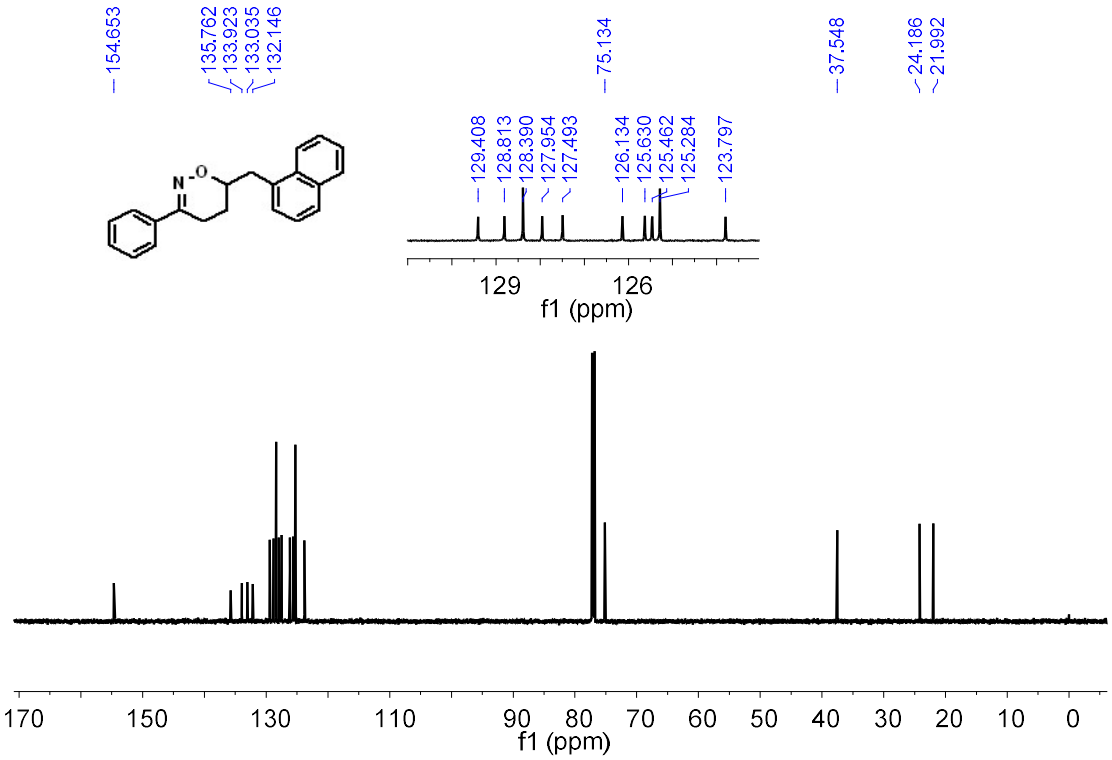
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3j.



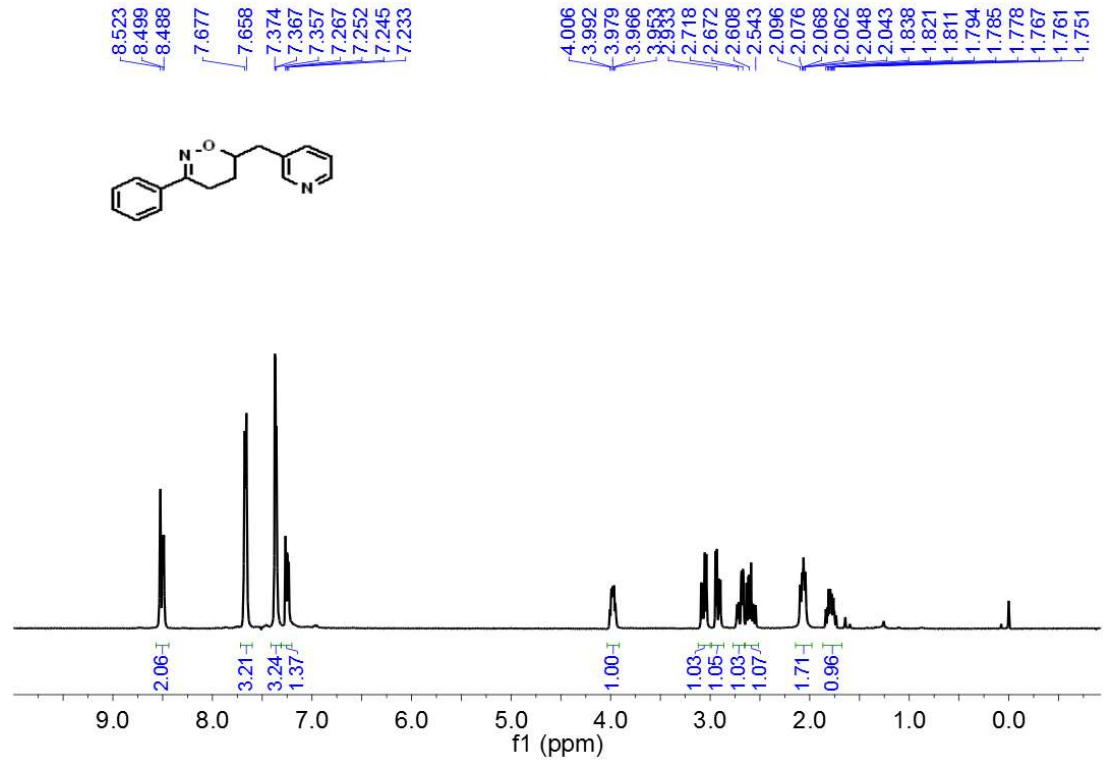
^{19}F NMR (470 MHz, $CDCl_3$) spectrum for 3j



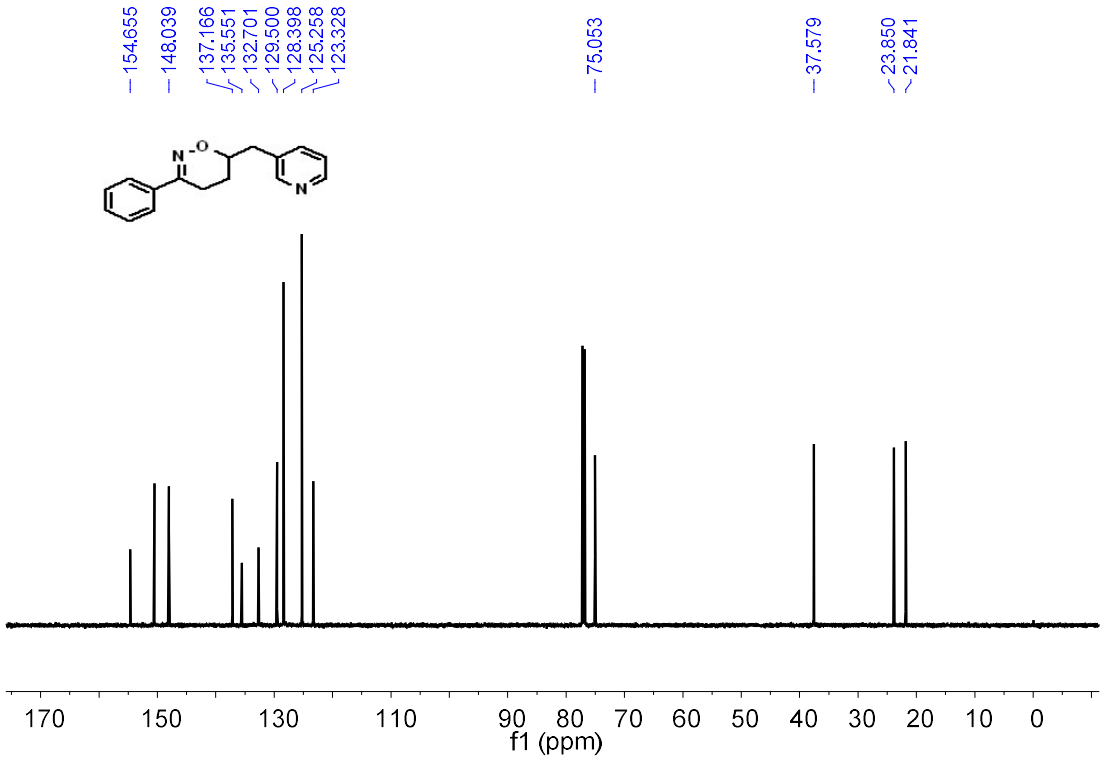
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3k.



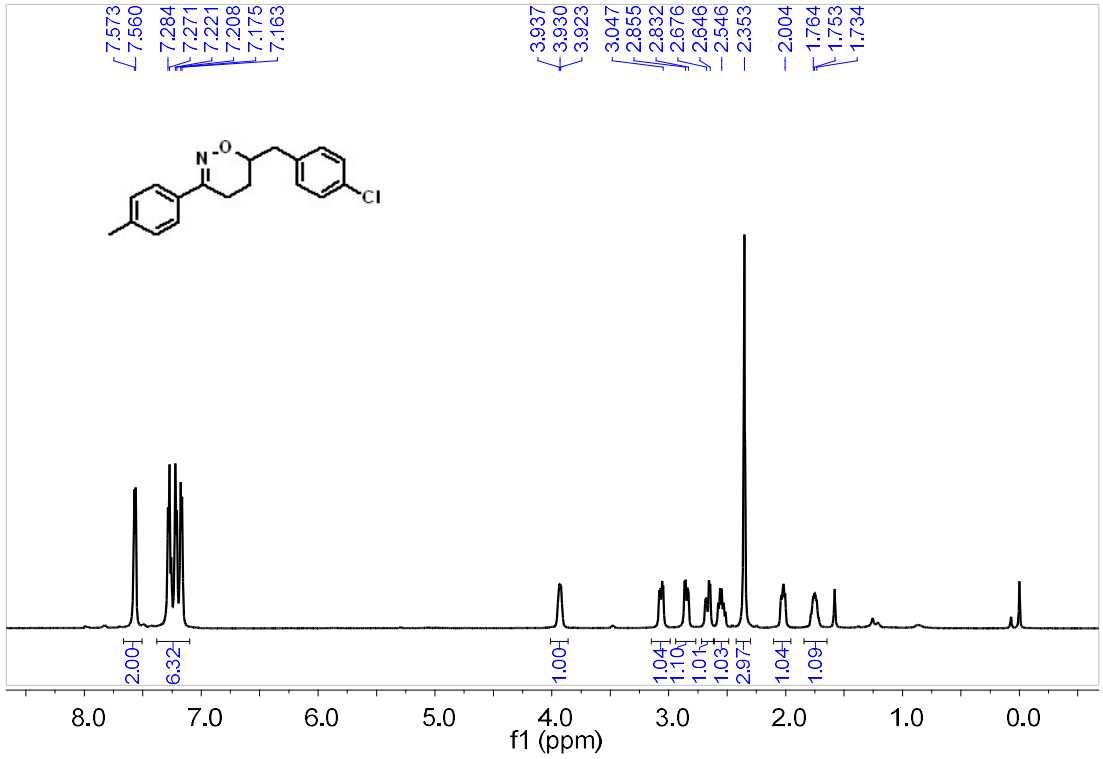
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3k



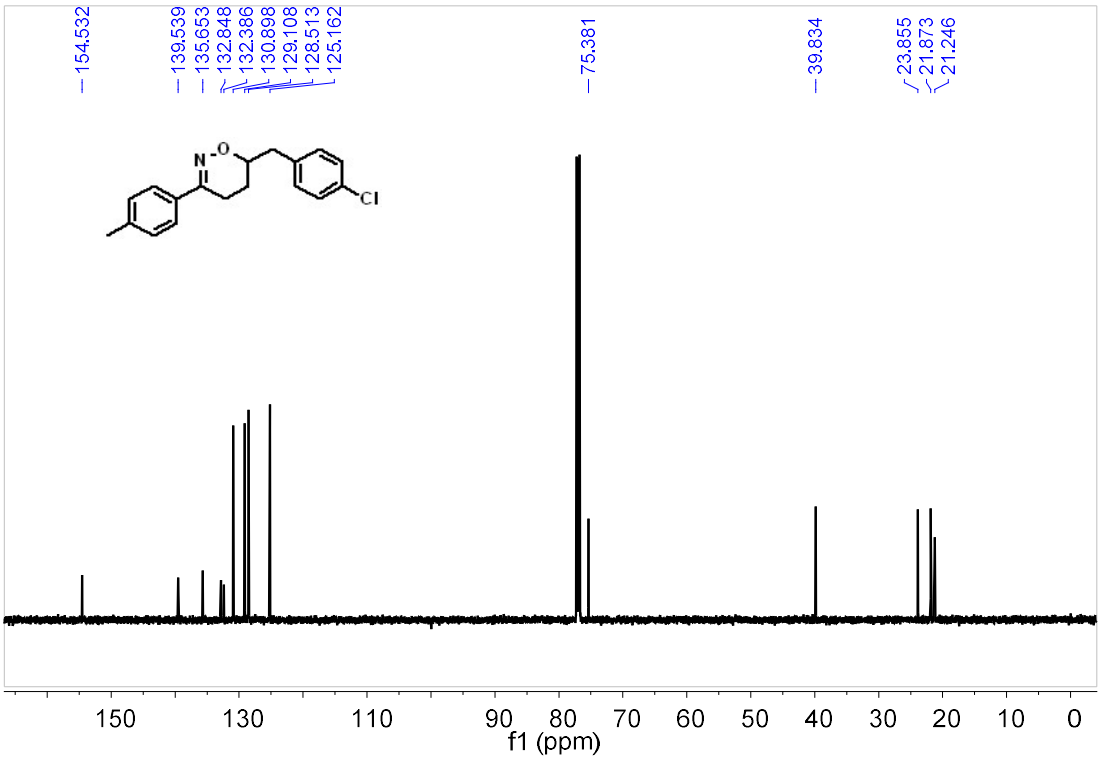
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3l.



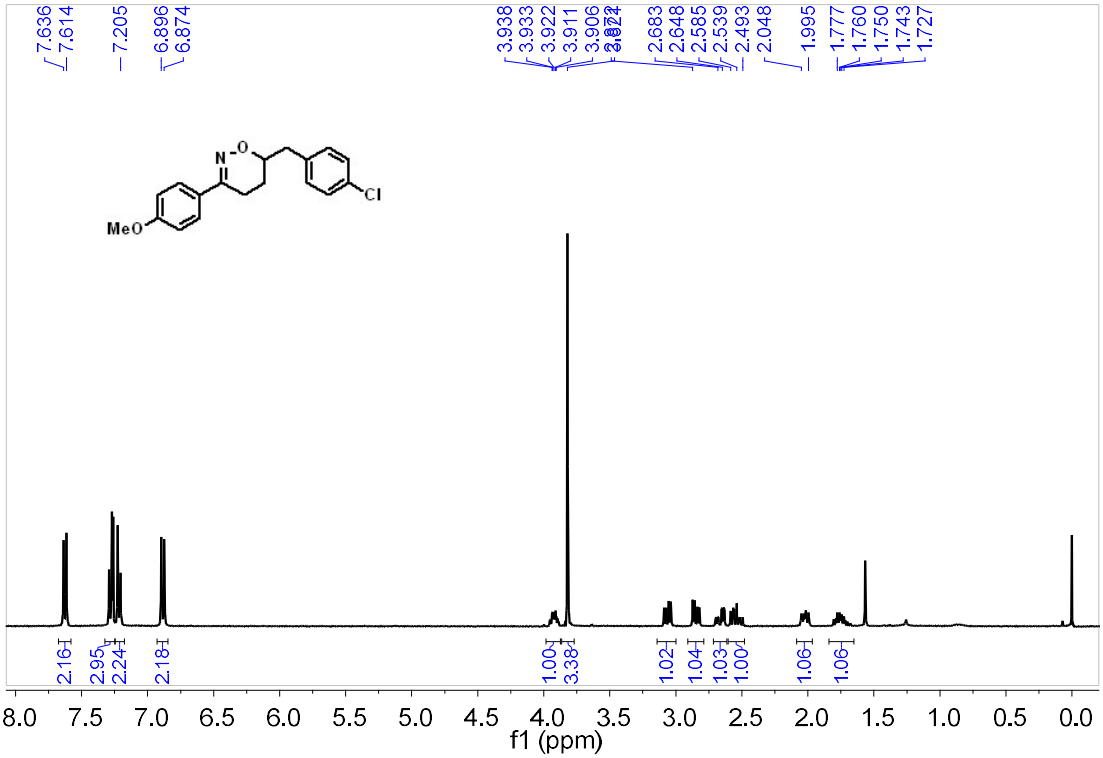
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3l.



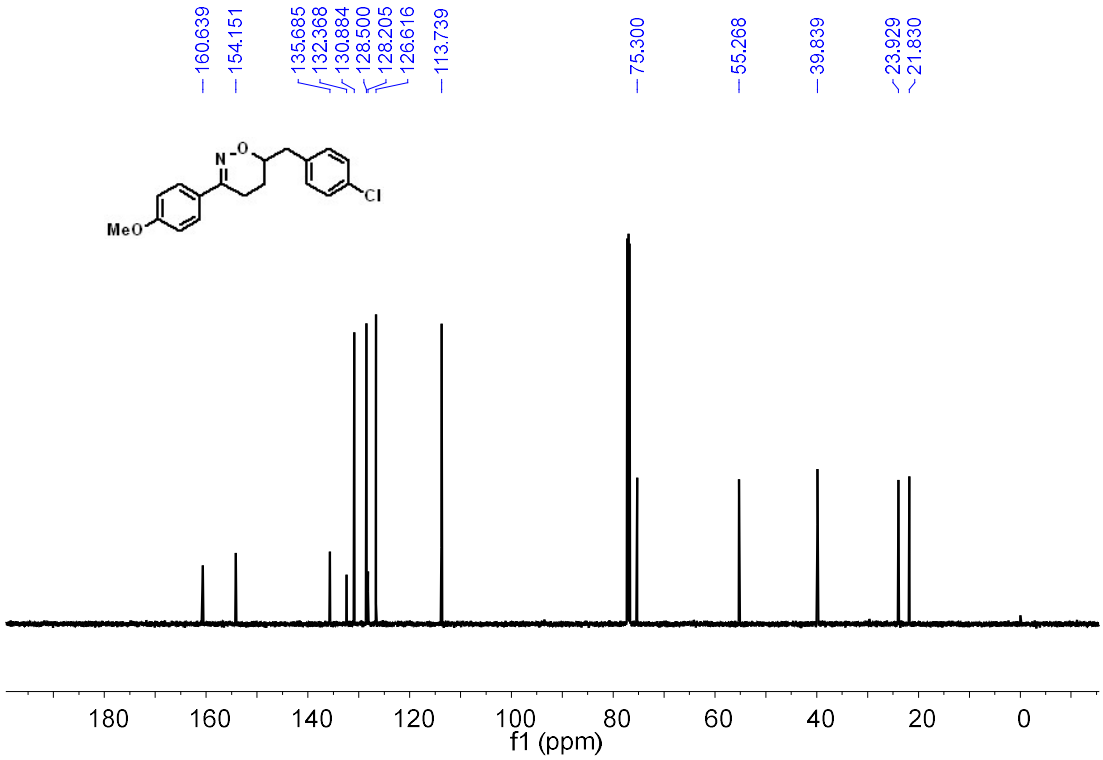
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for 3m.



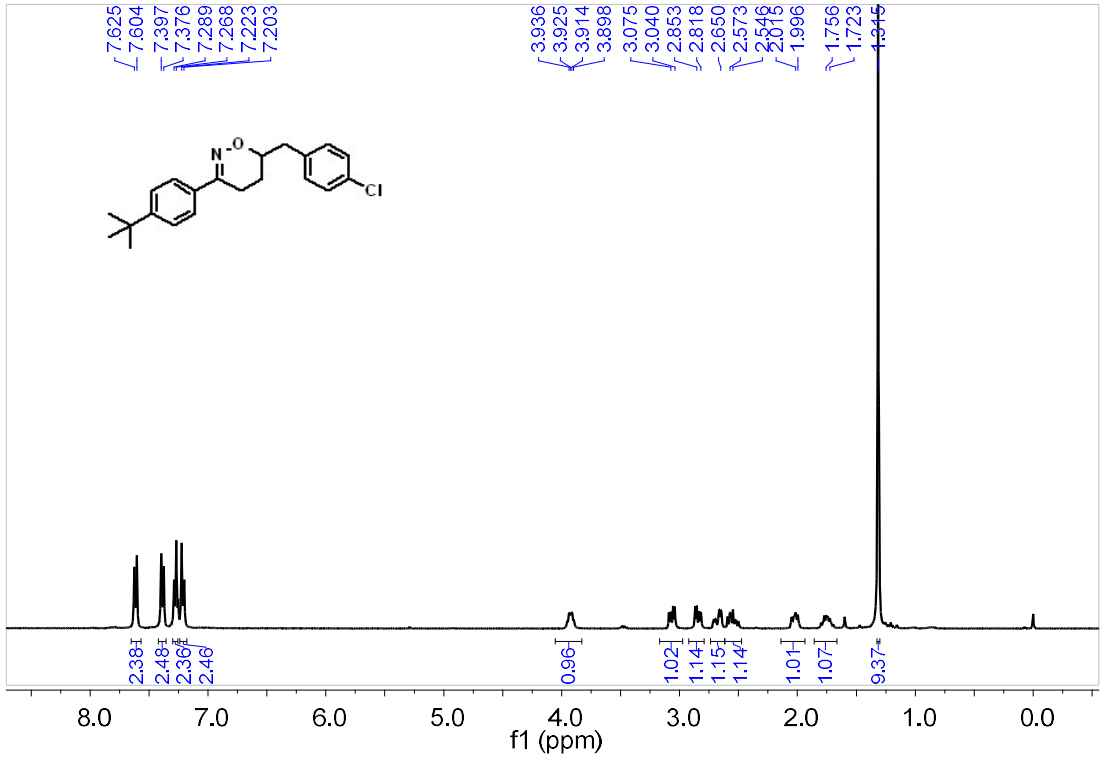
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3m.



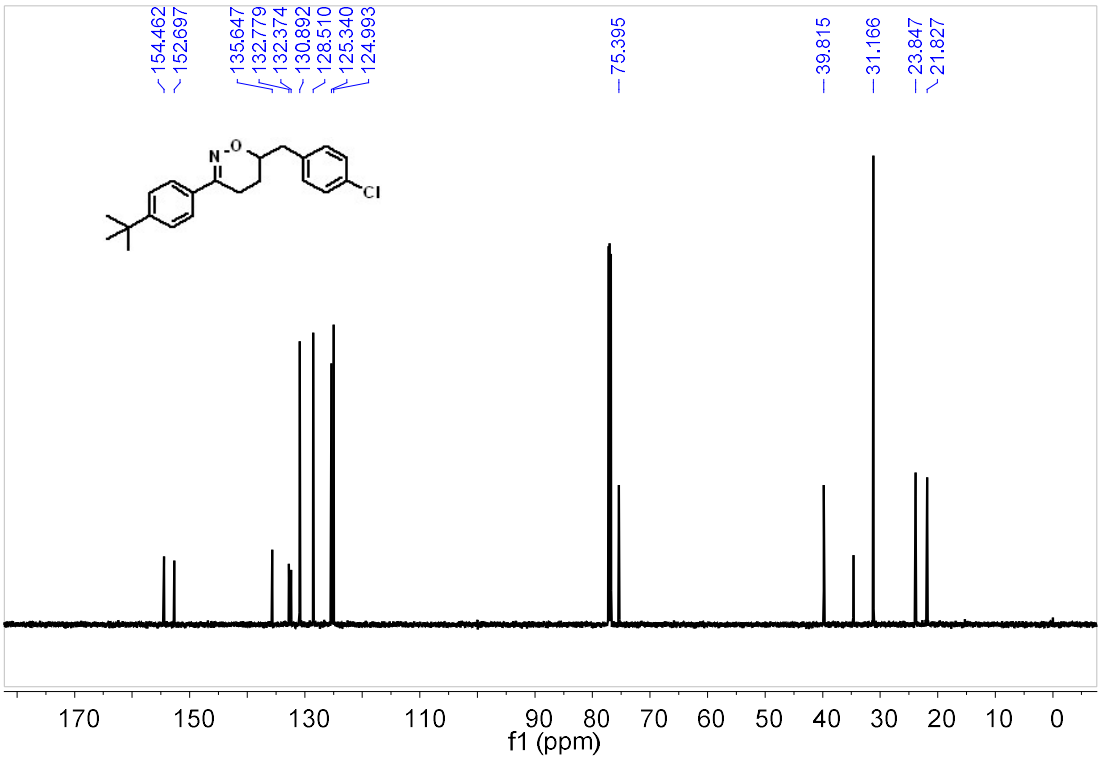
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3n.



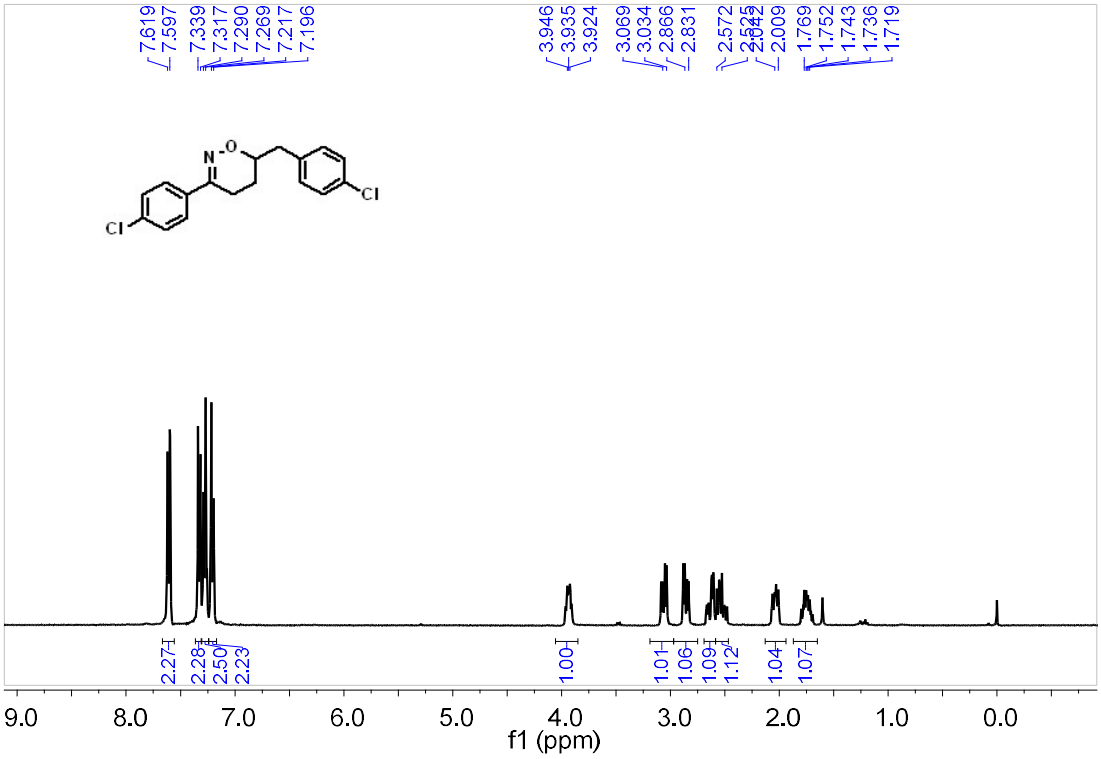
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3n.



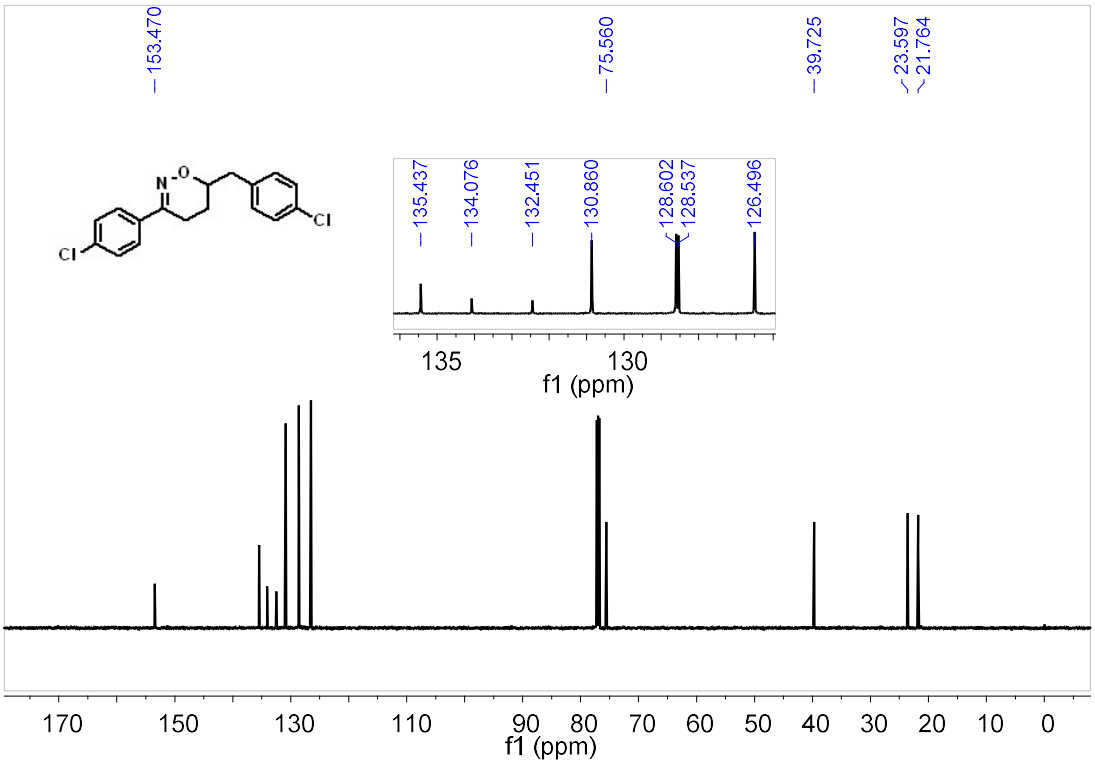
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3o.



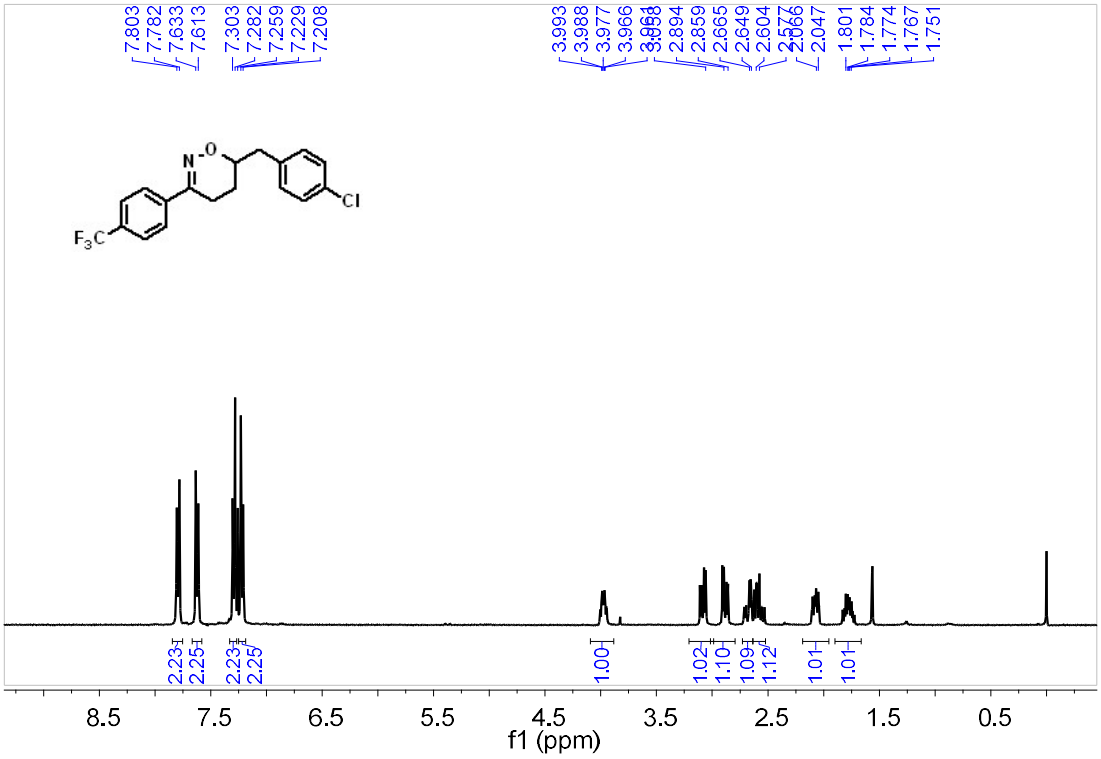
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3o.



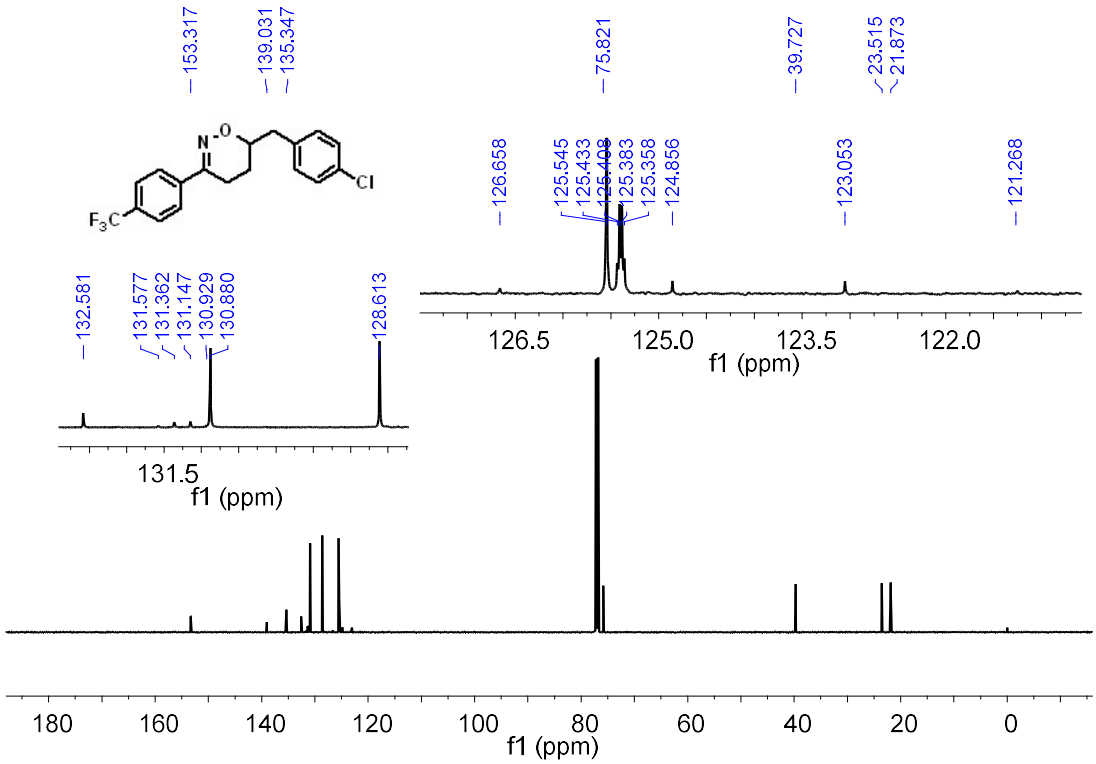
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3p.



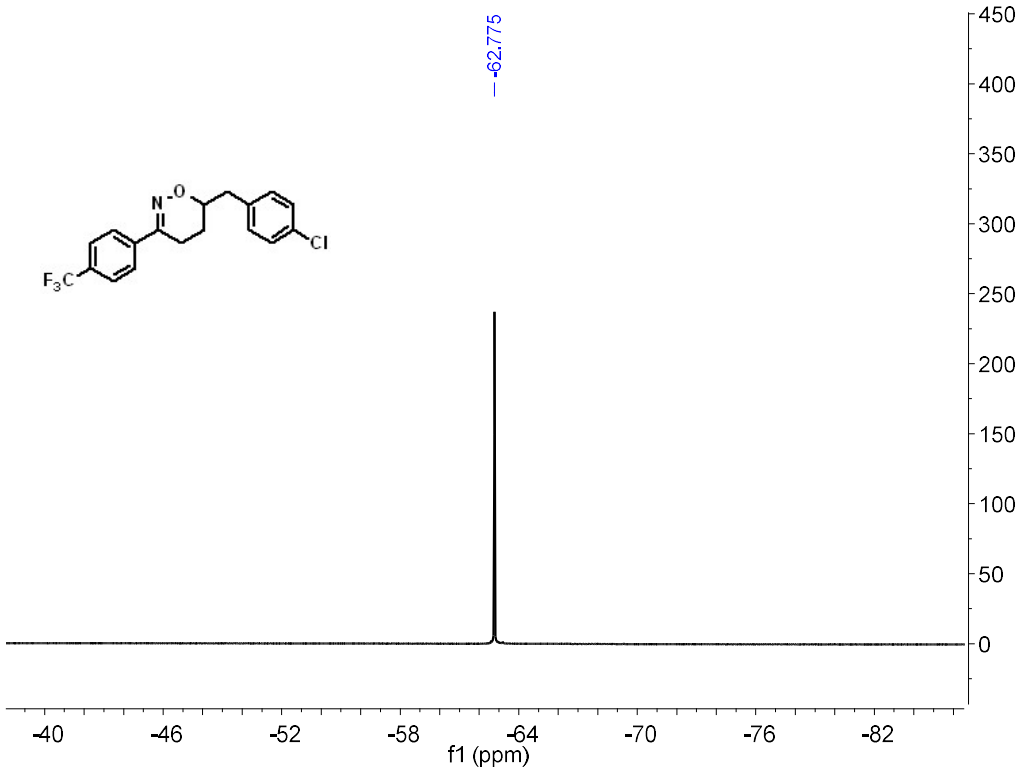
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3p.



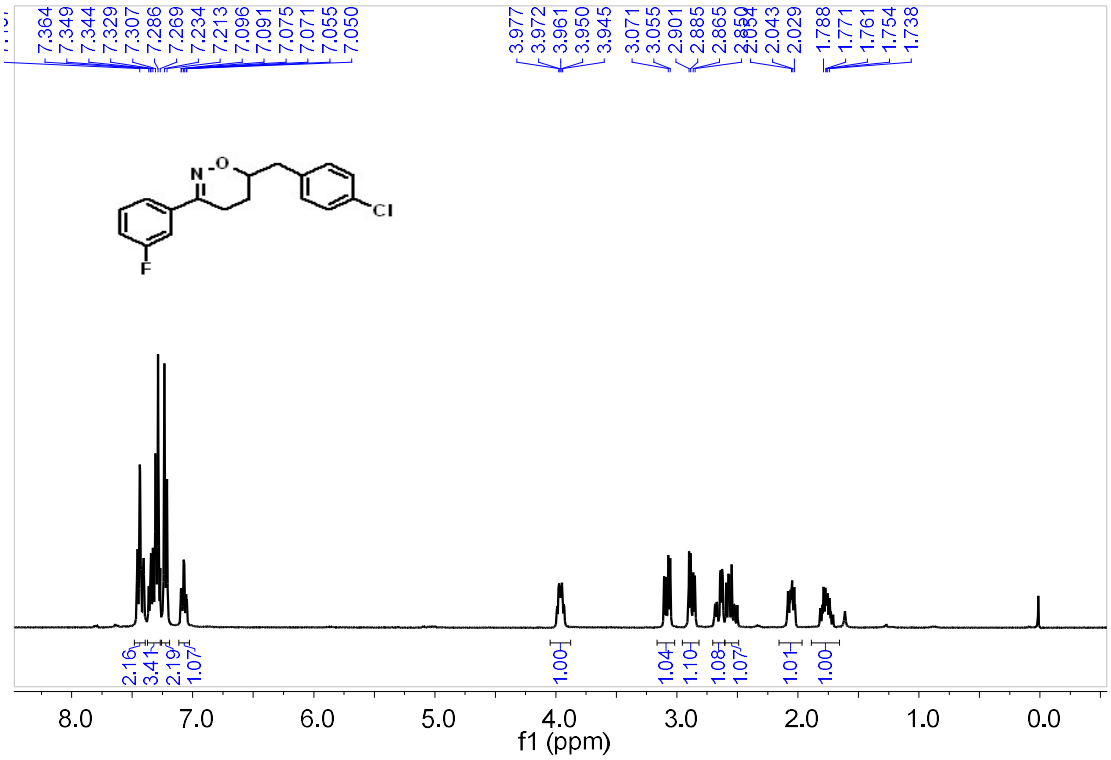
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3q.



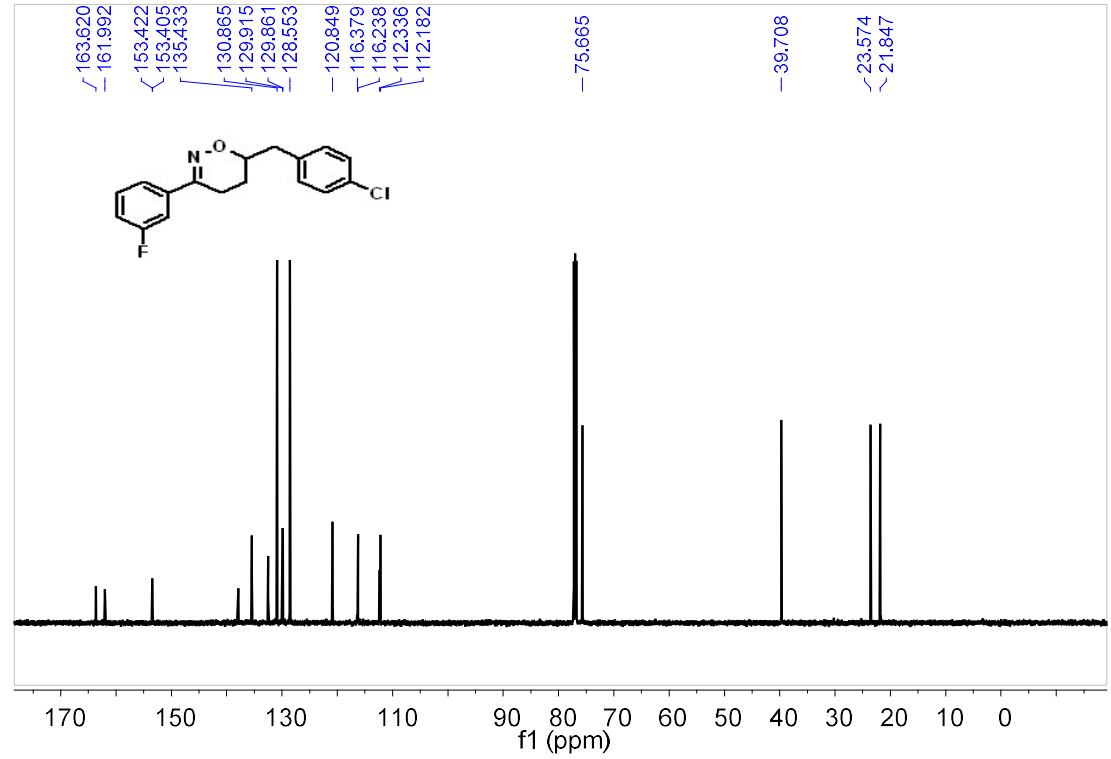
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3q.



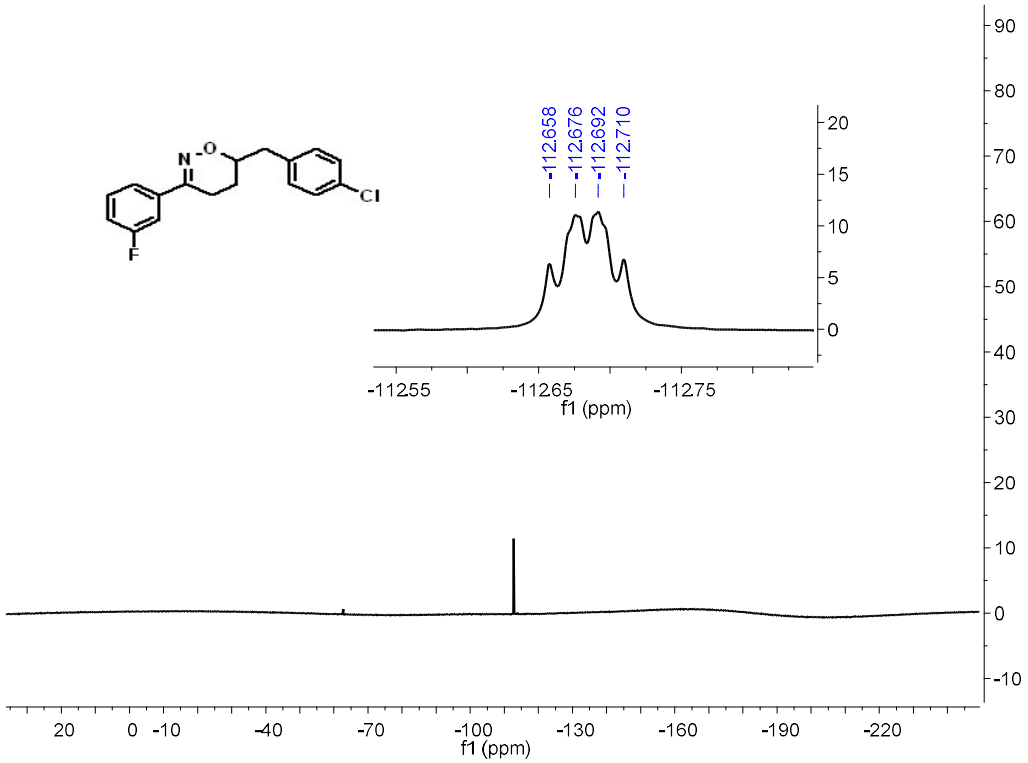
^{19}F NMR (470 MHz, $CDCl_3$) spectrum for 3q



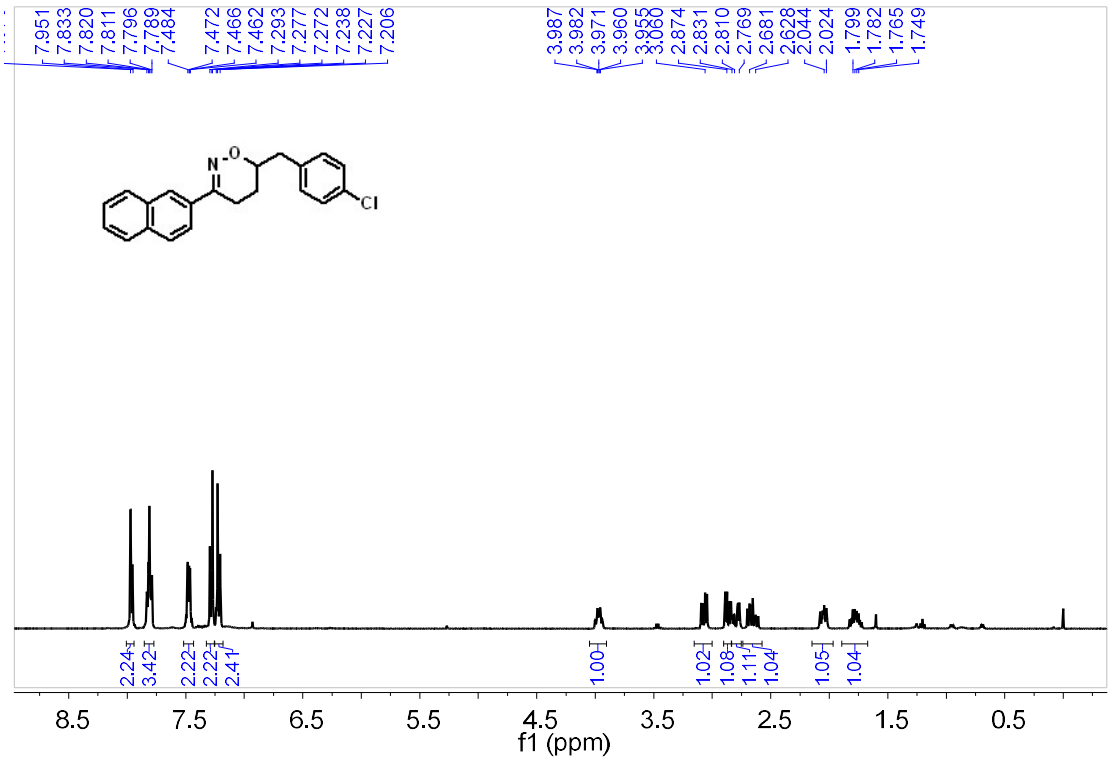
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3r.



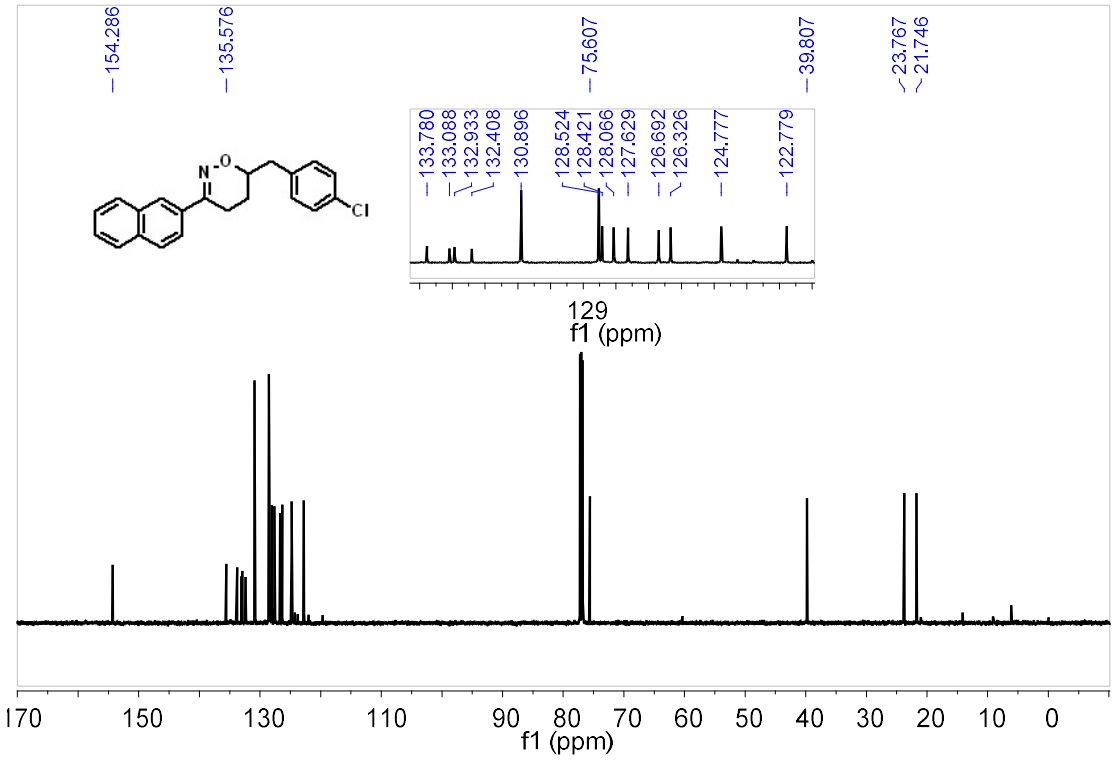
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3r.



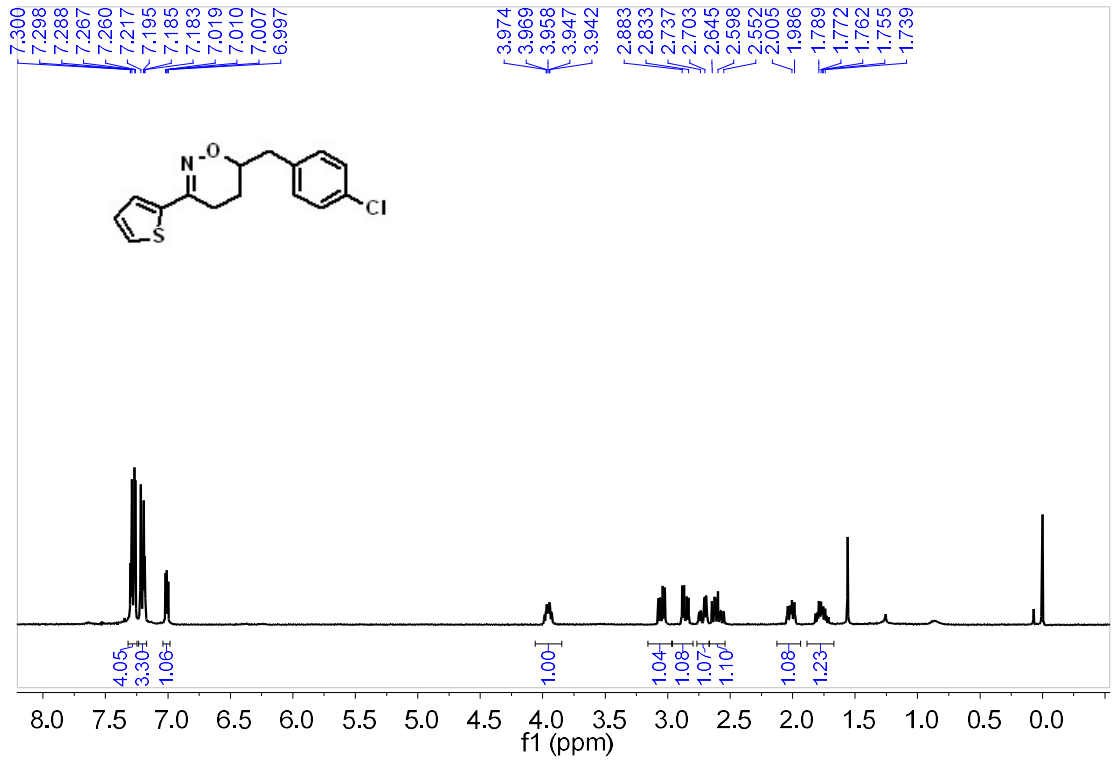
^{19}F NMR (470 MHz, $CDCl_3$) spectrum for 3r



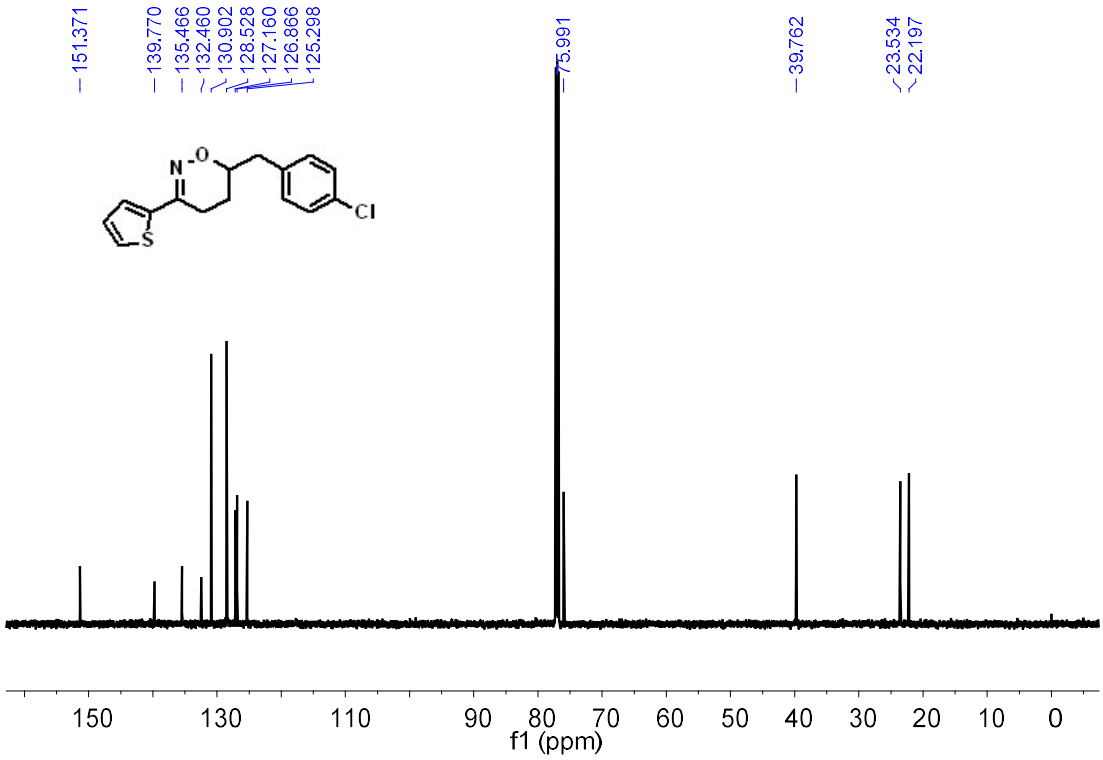
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3s.



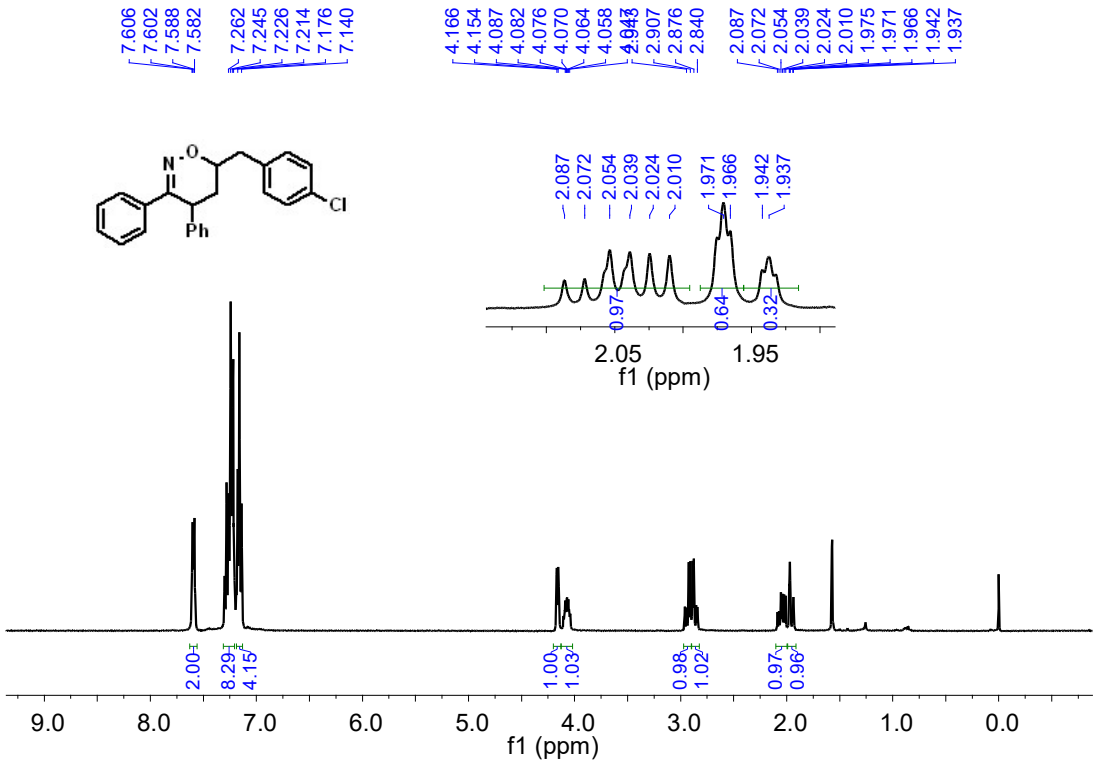
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3s.



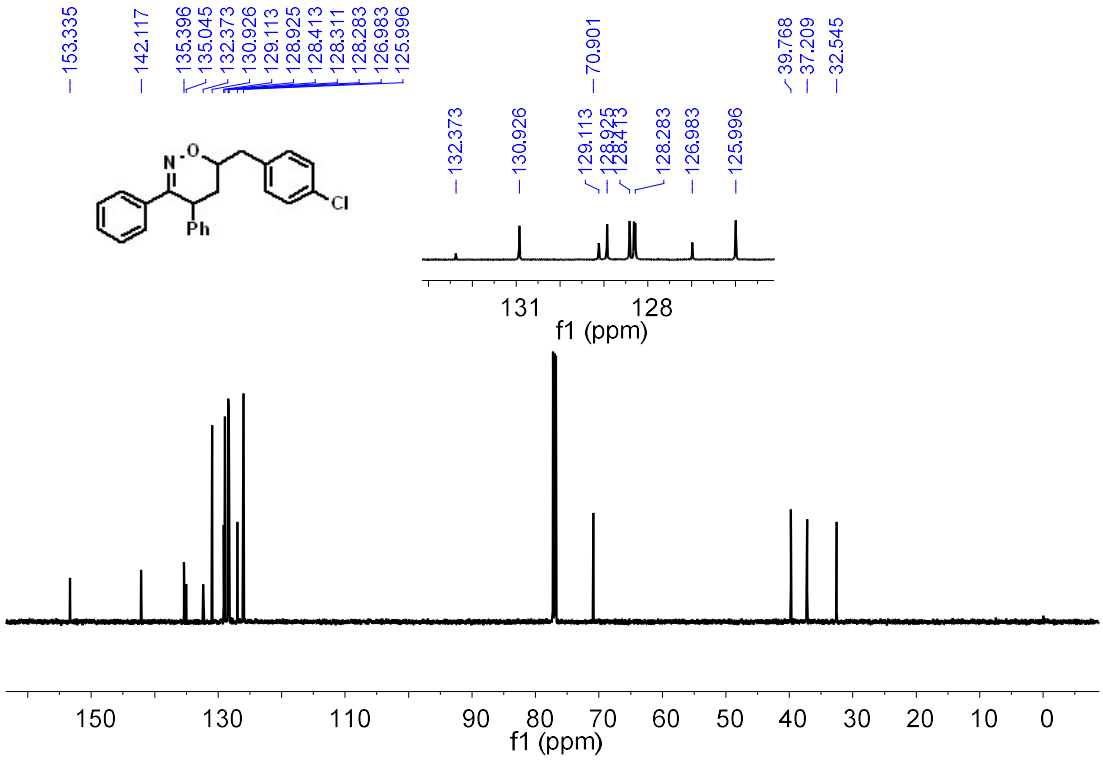
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3t.



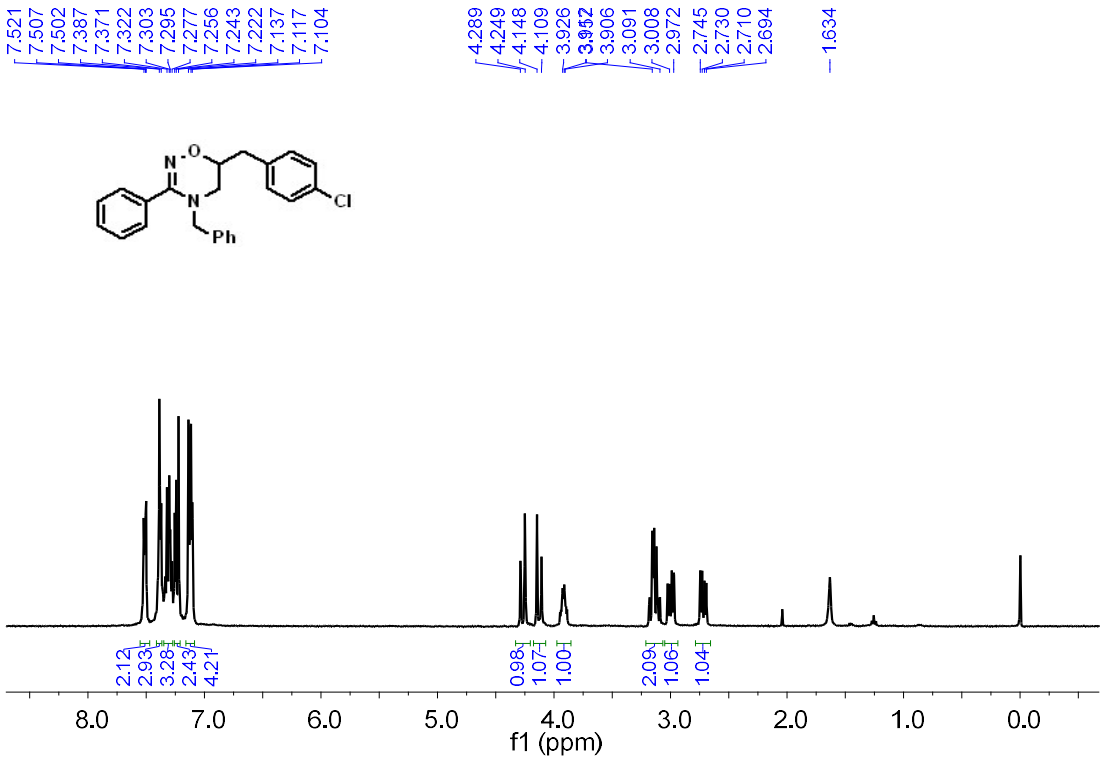
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3t.



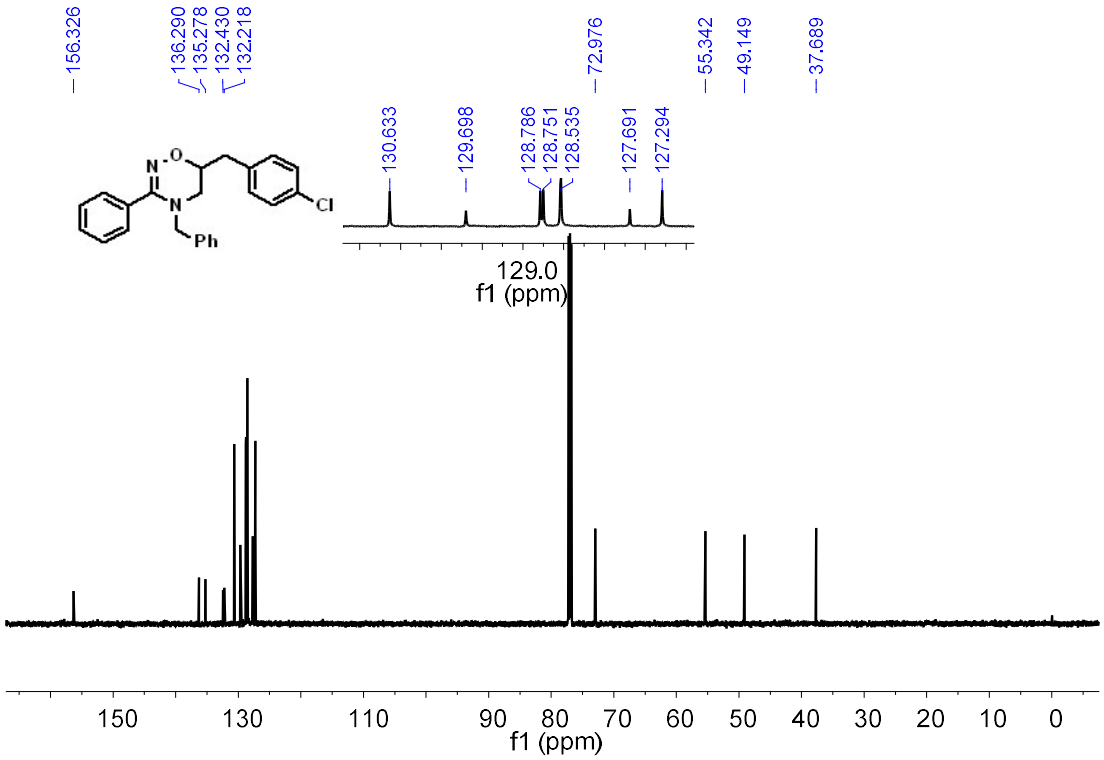
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3u.



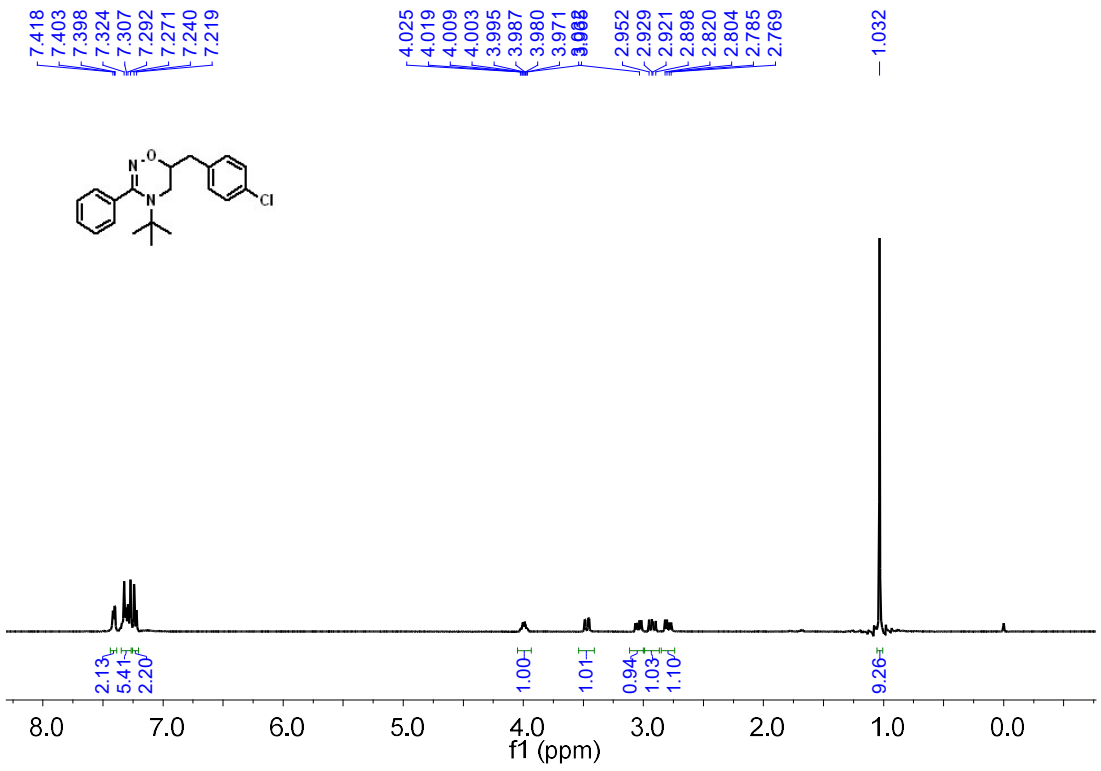
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3u.



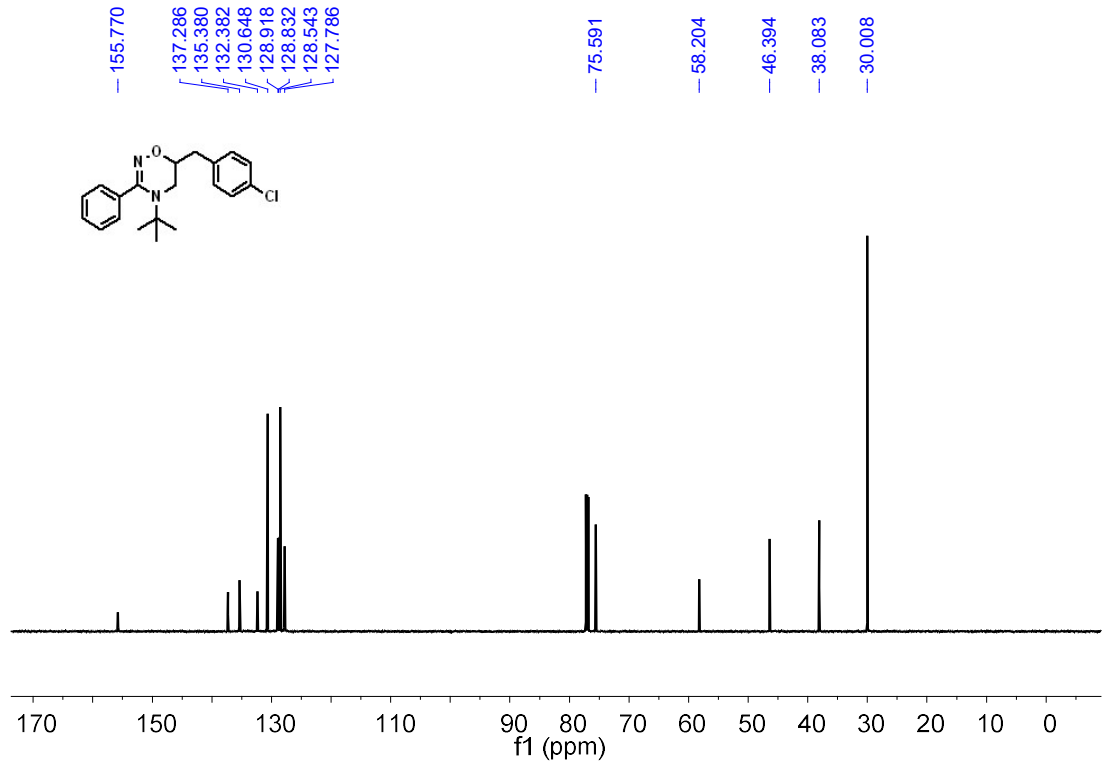
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 4a.



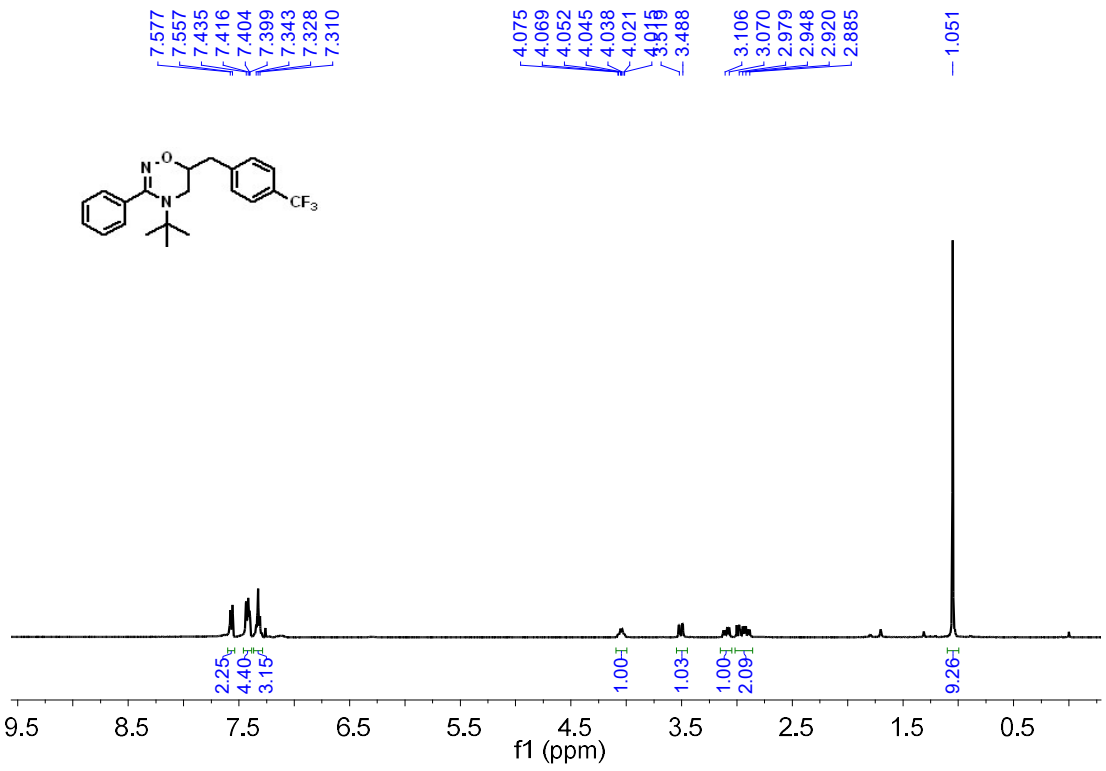
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 4a



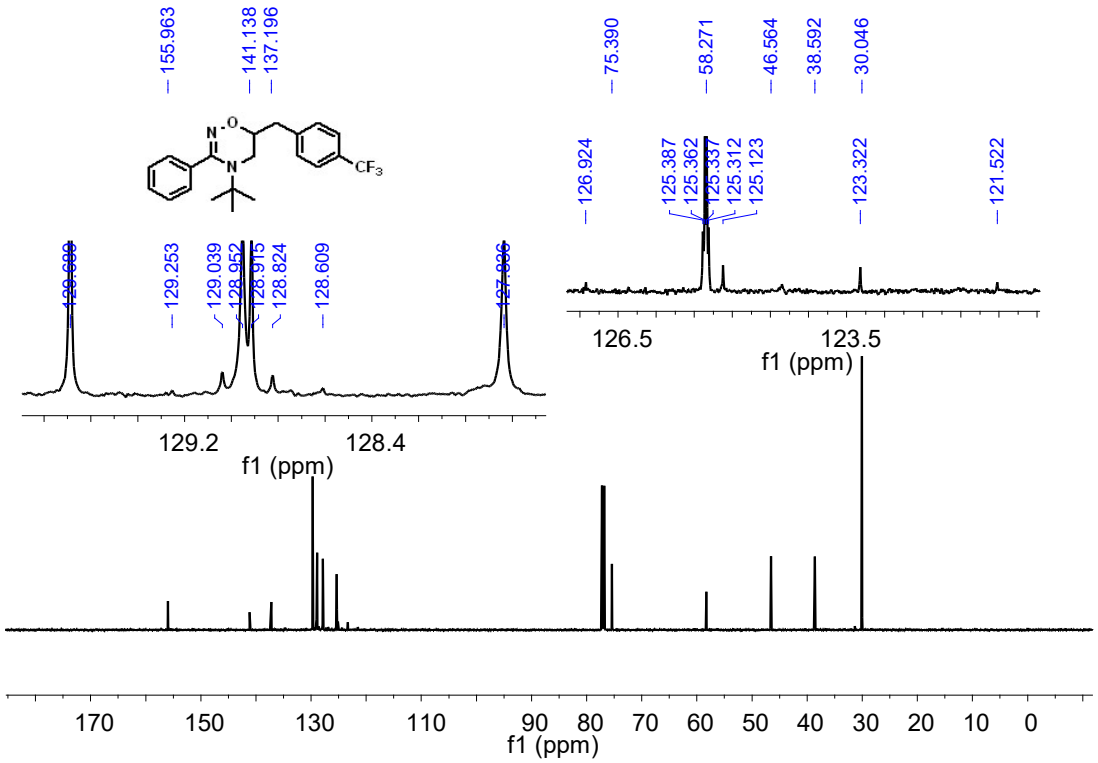
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 4a'.



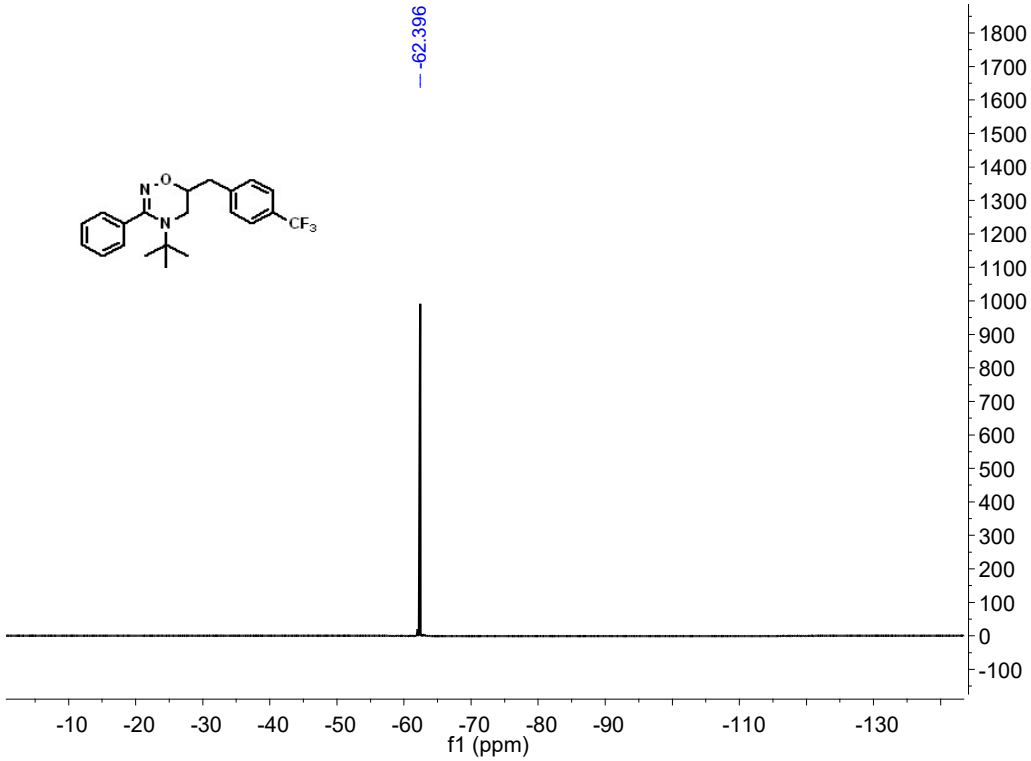
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 4a'.



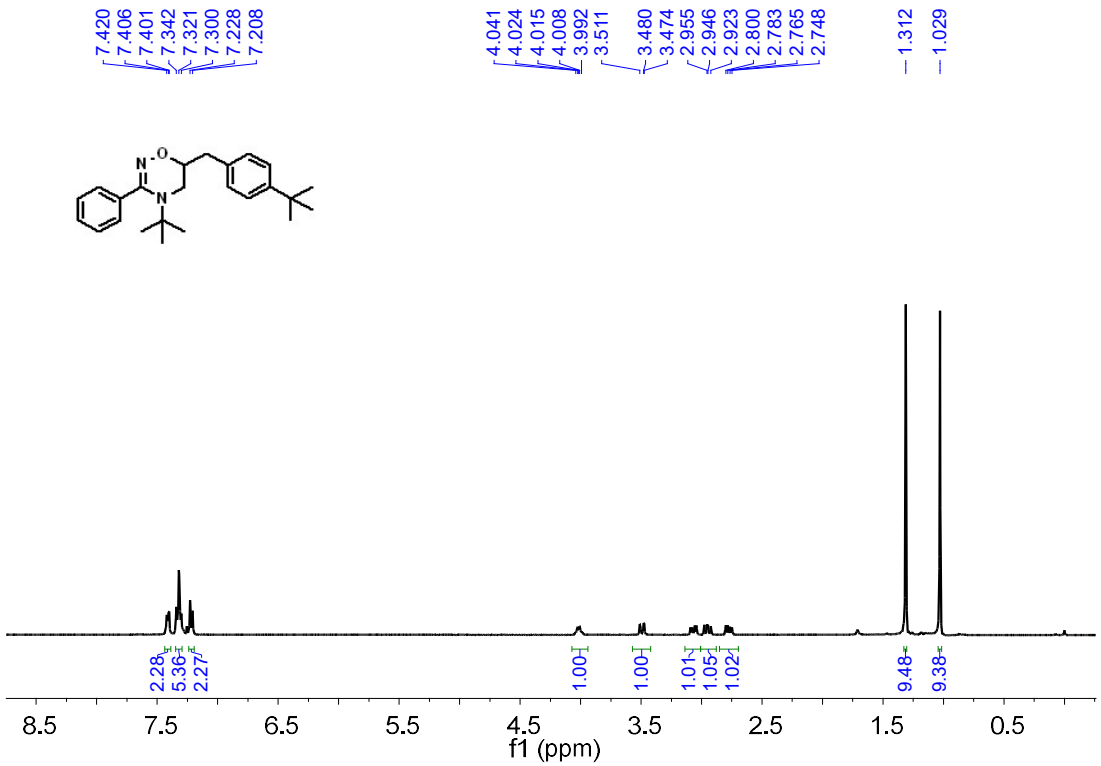
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 4b.



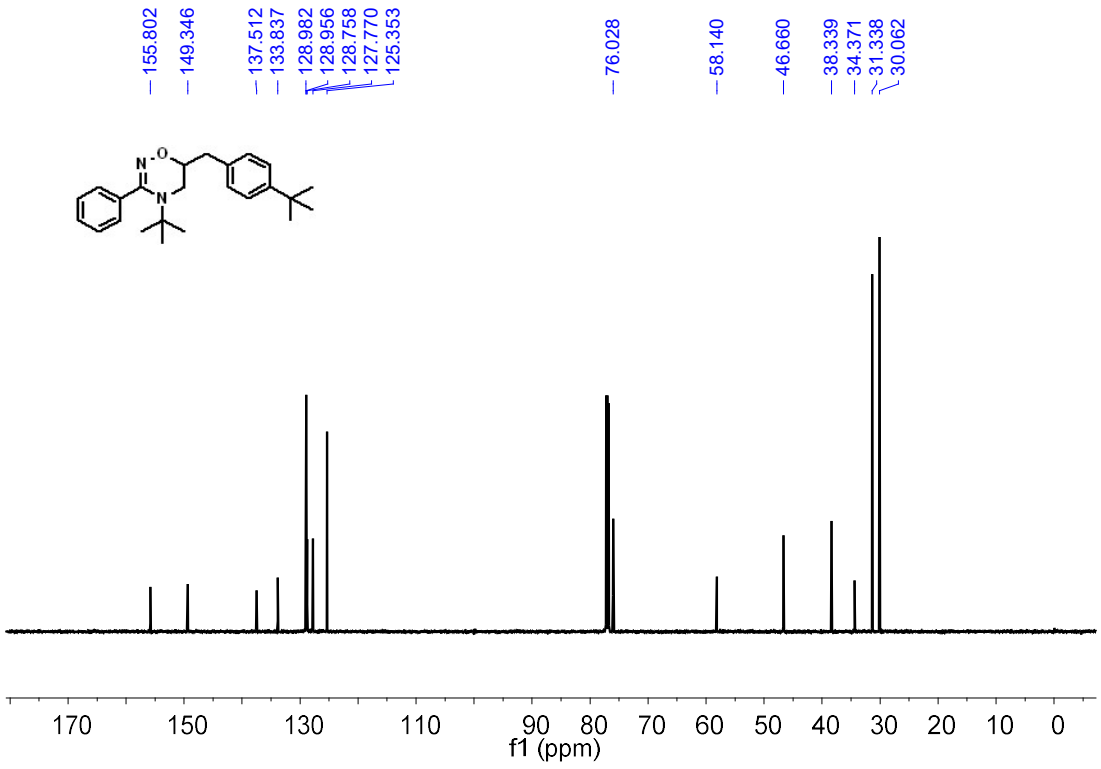
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 4b



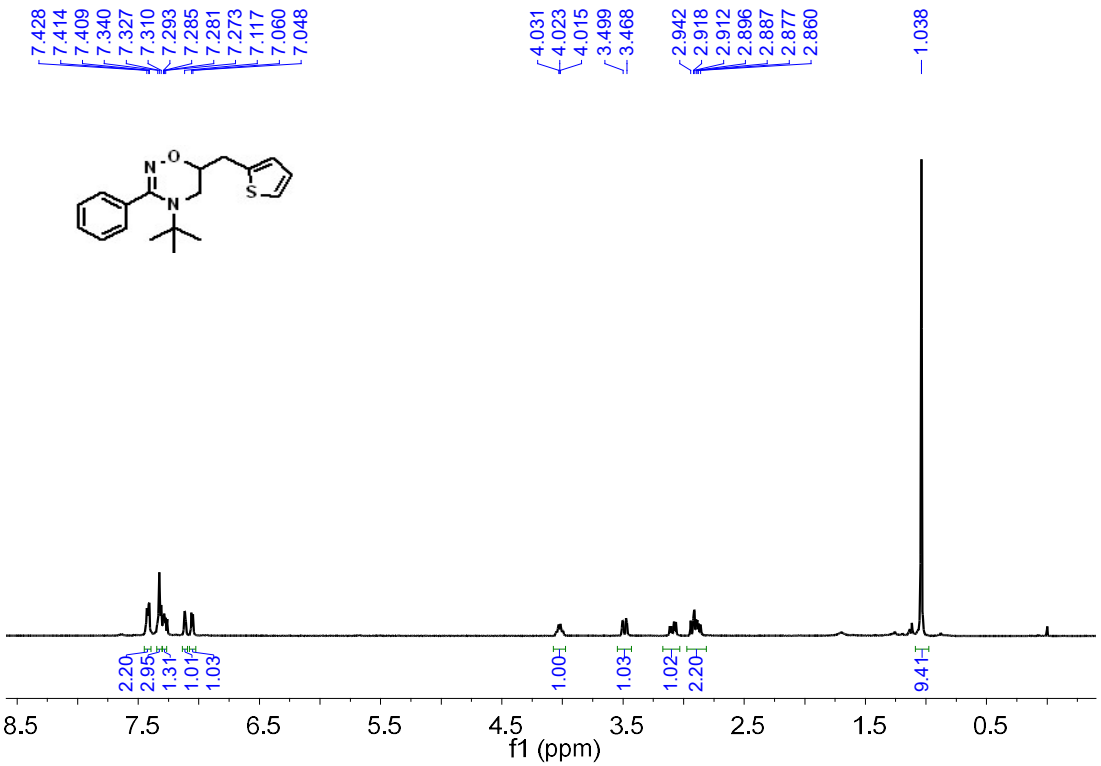
^{19}F NMR (470 MHz, $CDCl_3$) spectrum for 4b



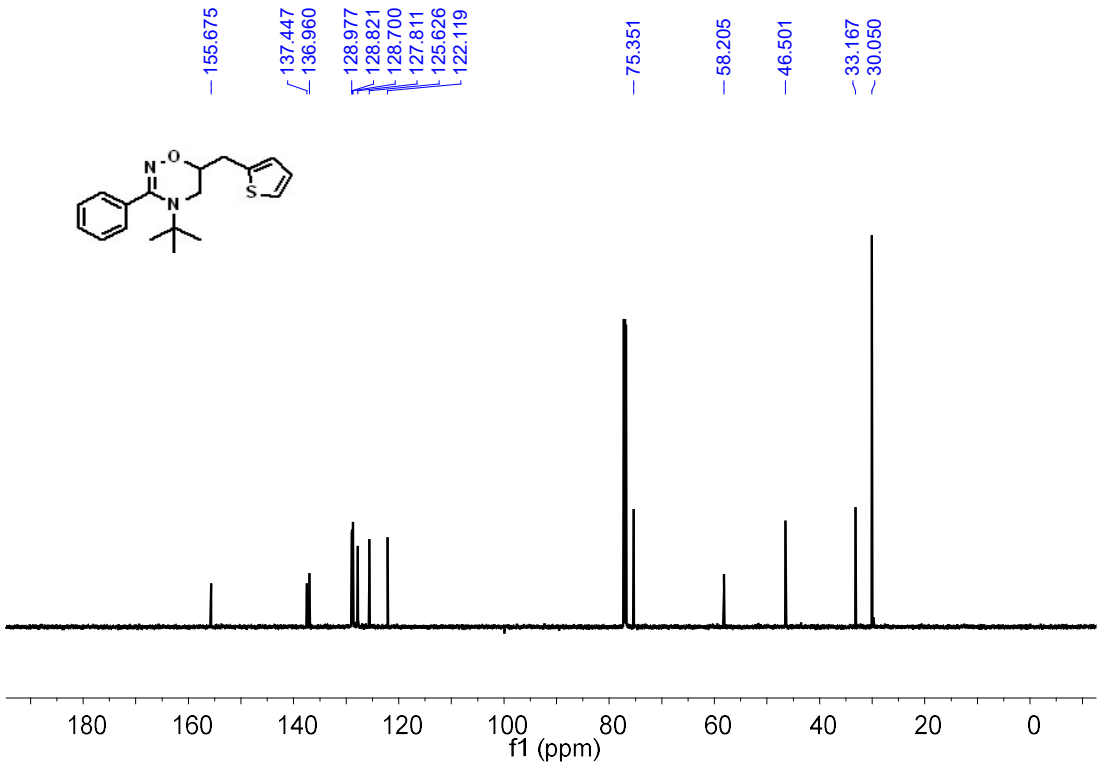
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 4c.



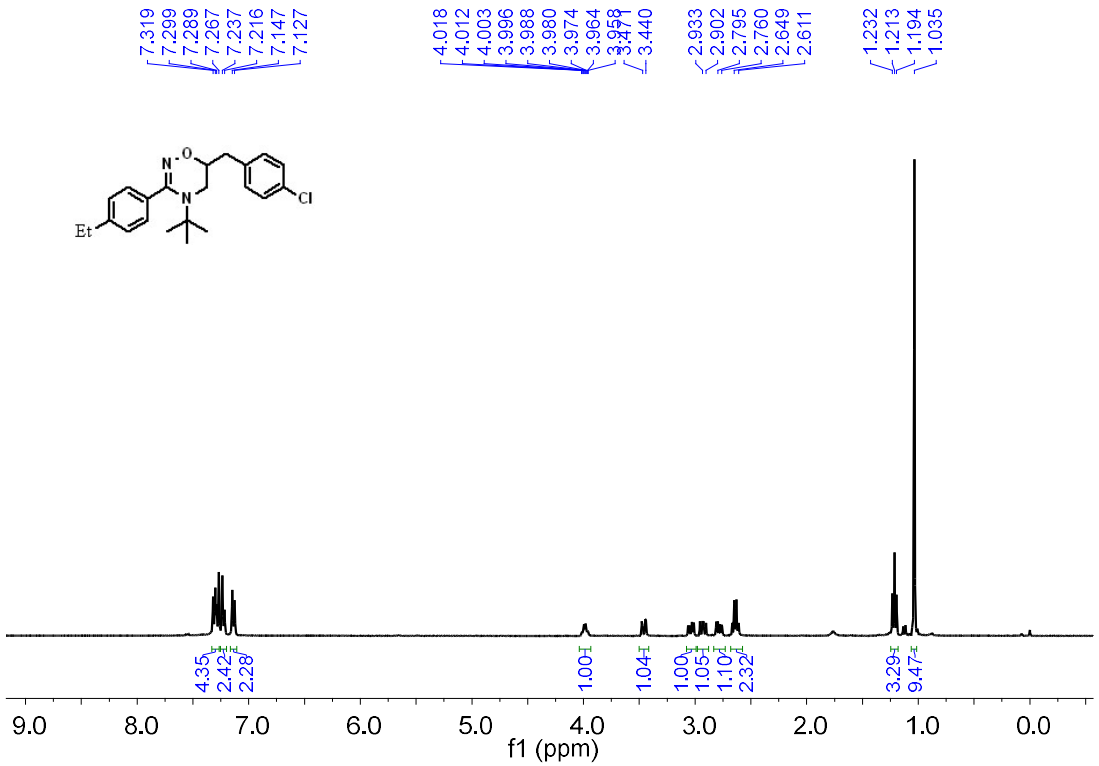
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 4c



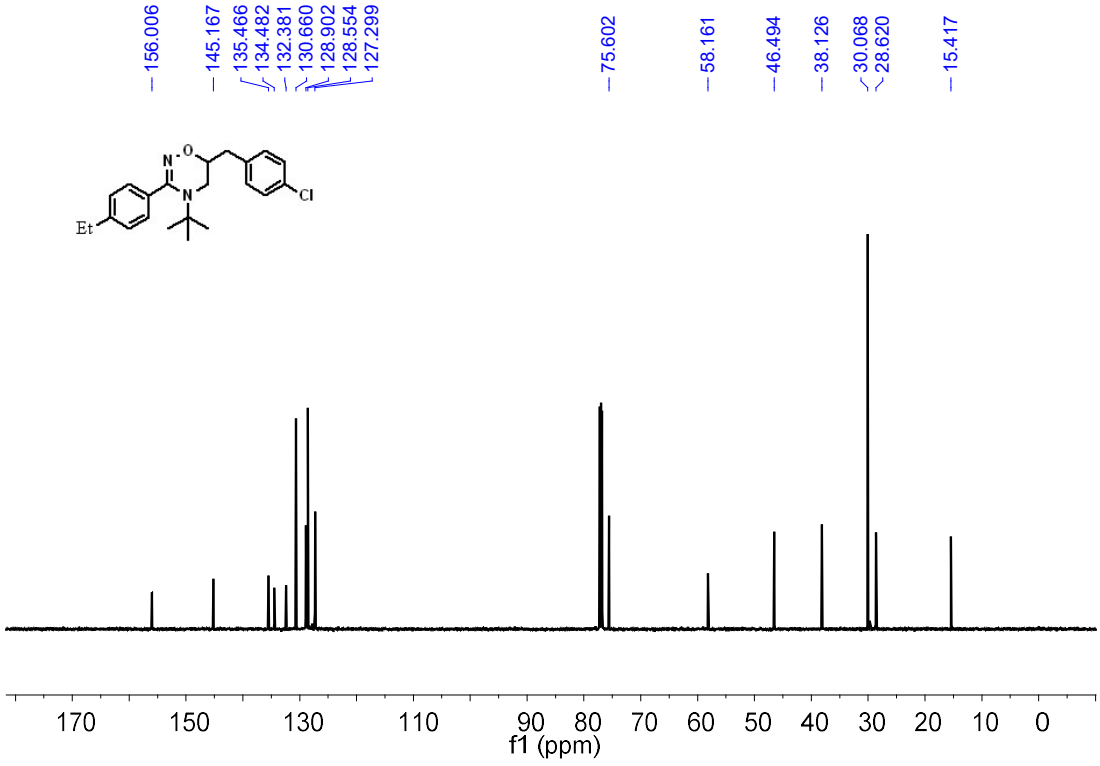
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 4d.



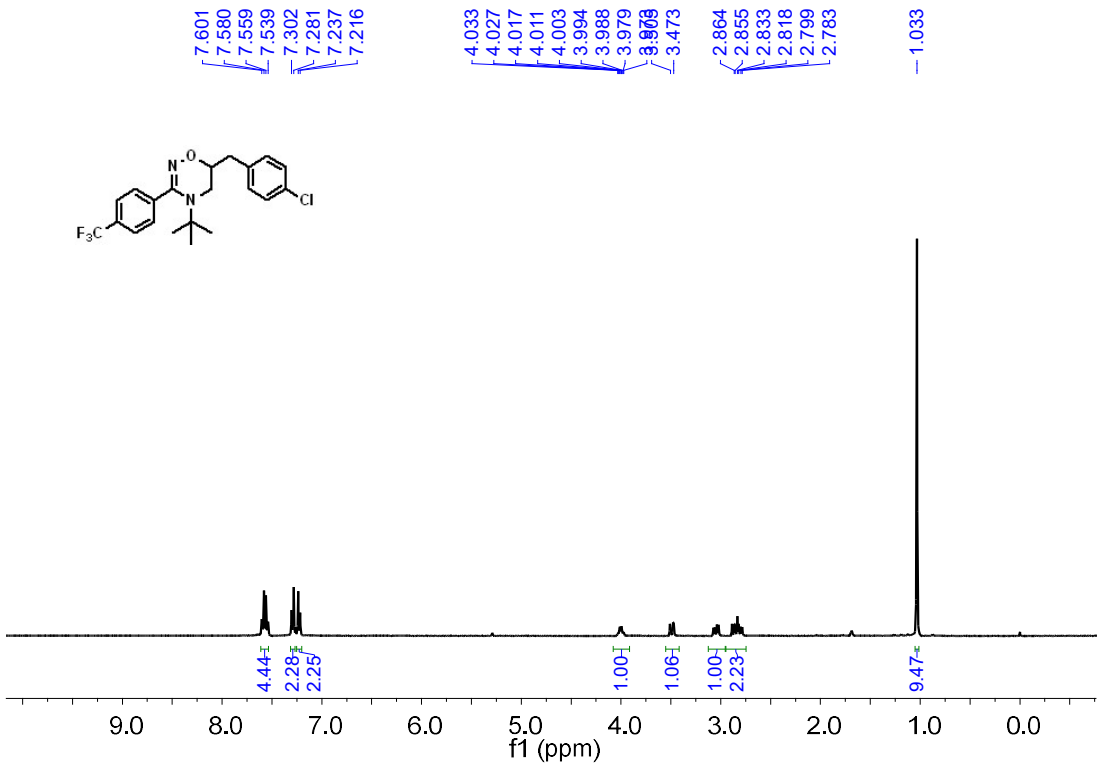
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 4d



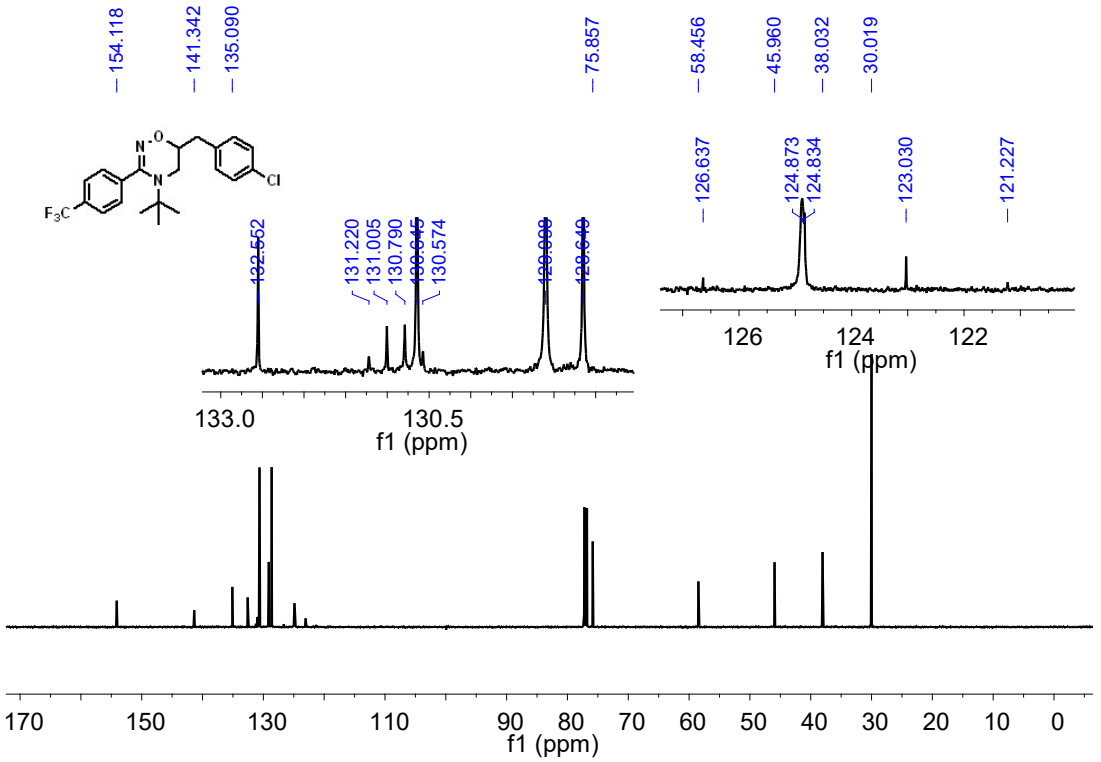
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 4e.



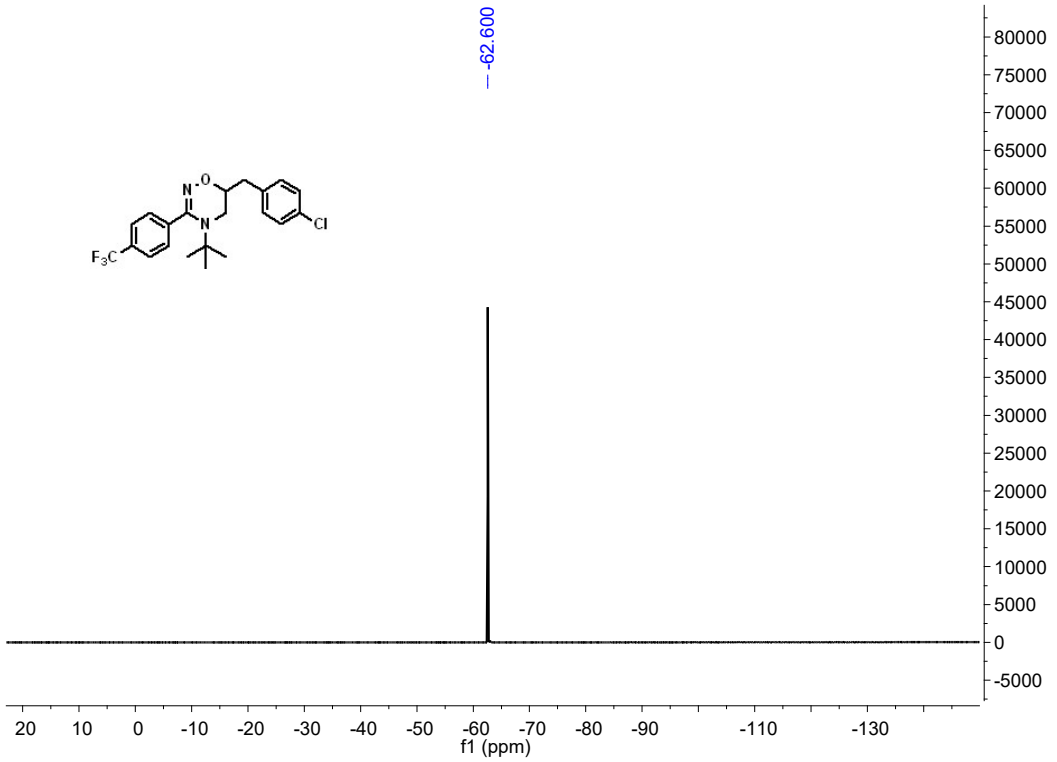
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 4e



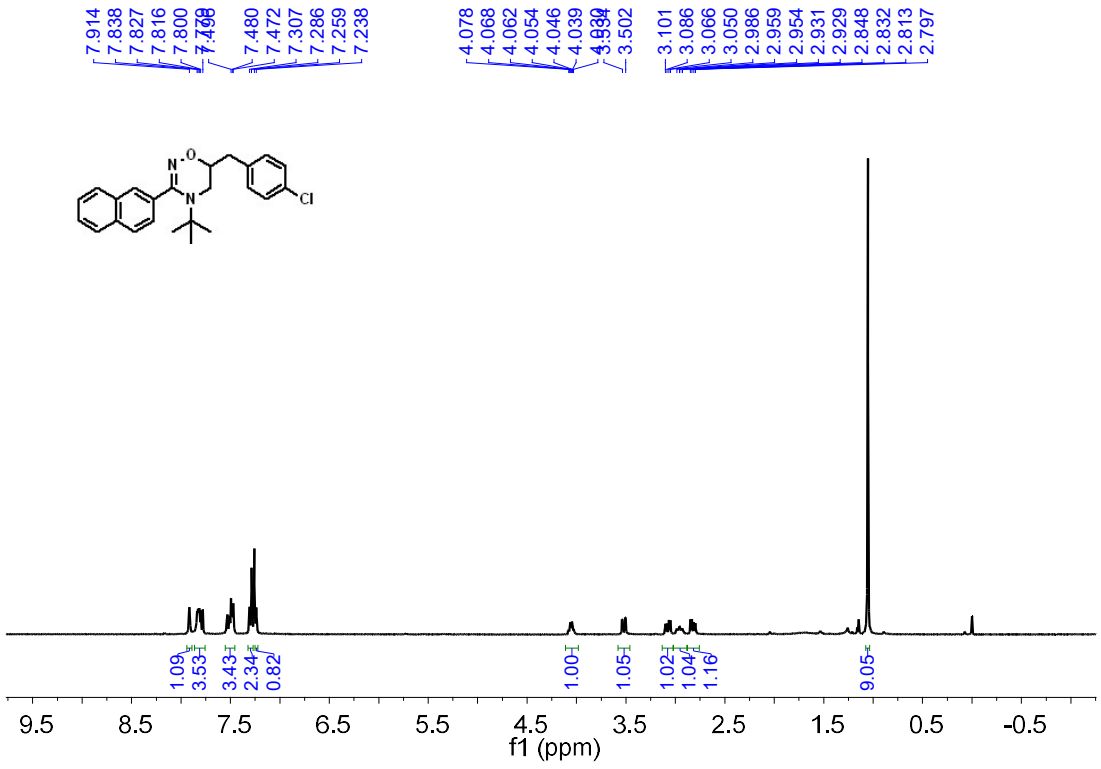
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 4f.



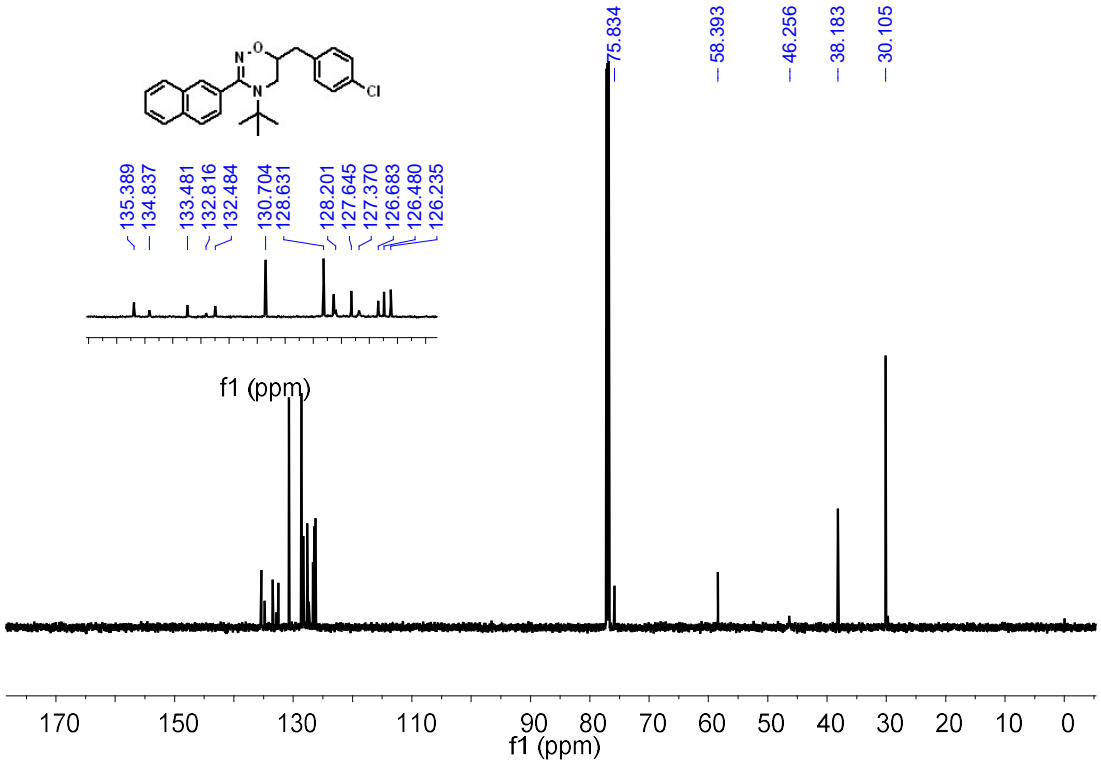
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 4f



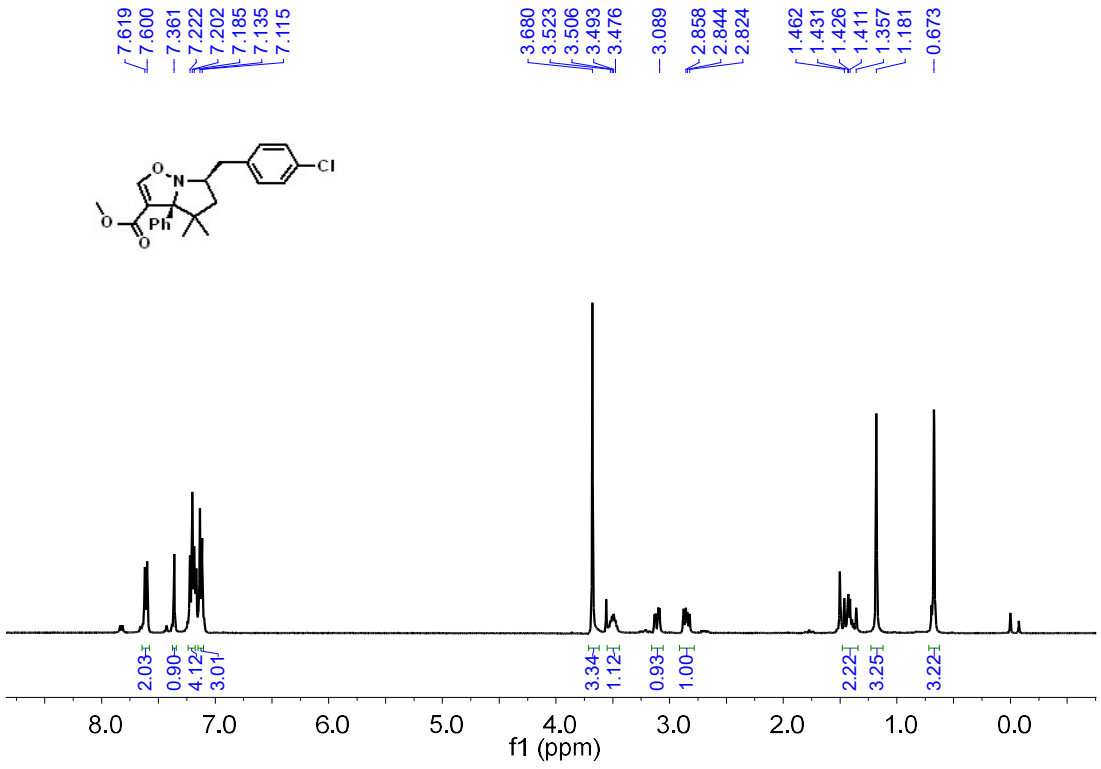
^{19}F NMR (470 MHz, $CDCl_3$) spectrum for 4f



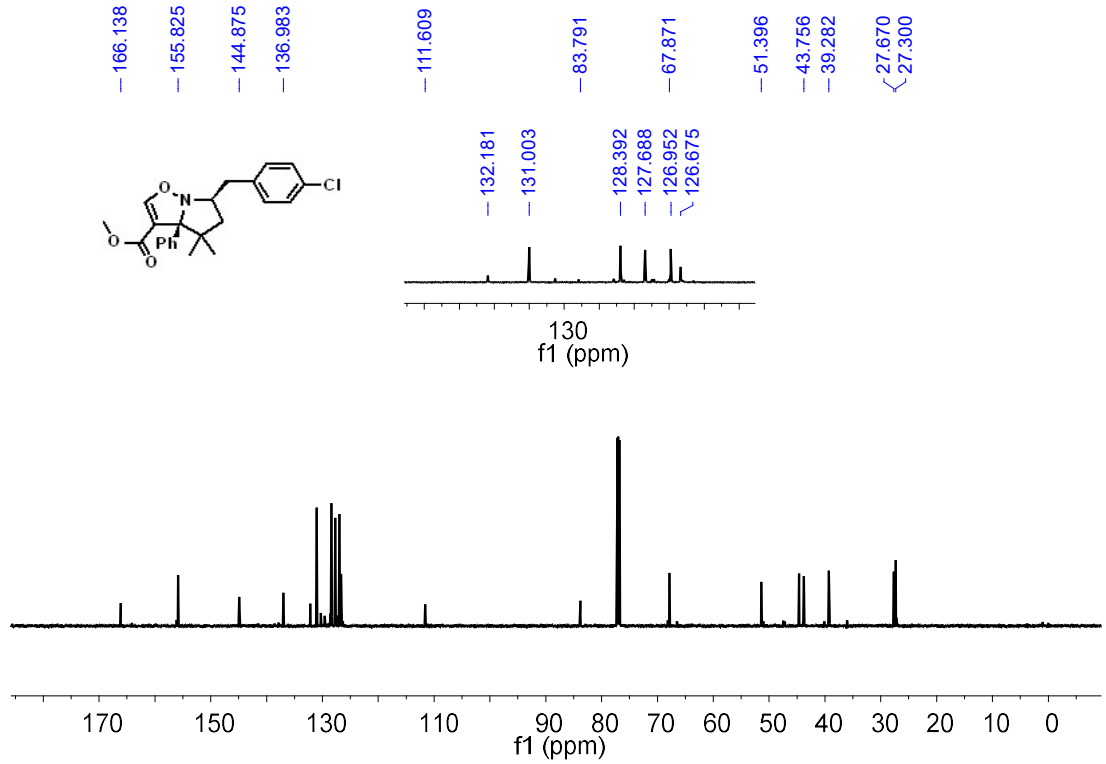
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 4g.



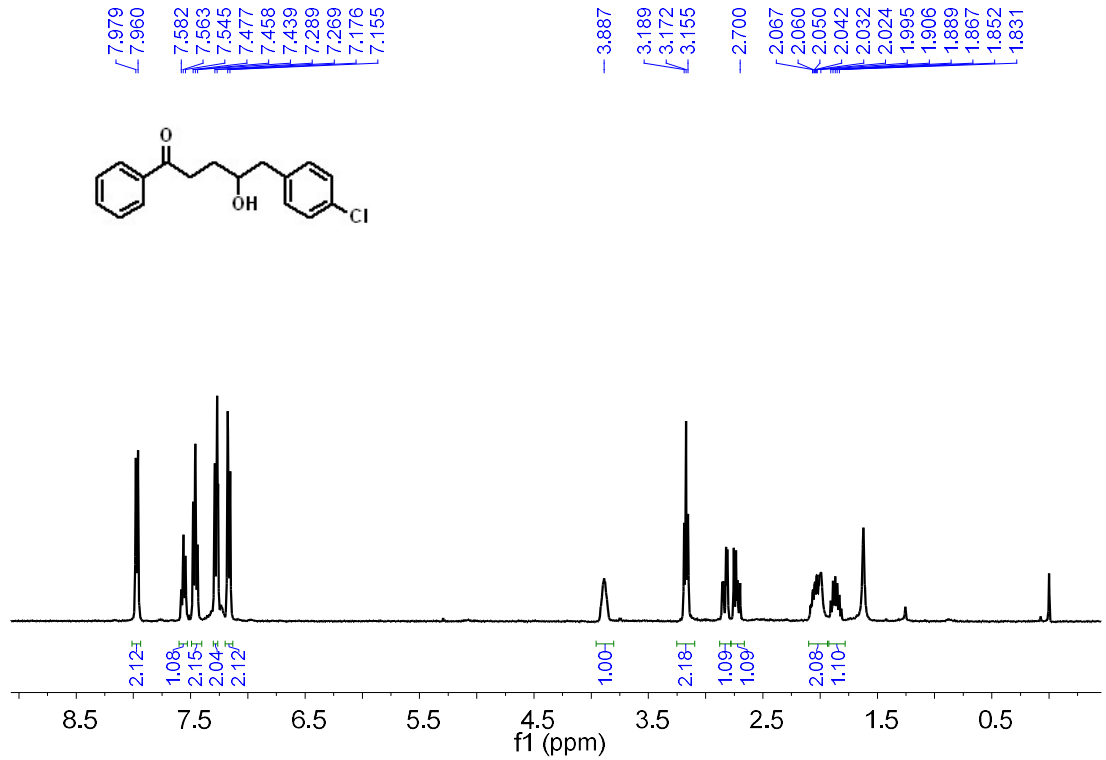
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 4g



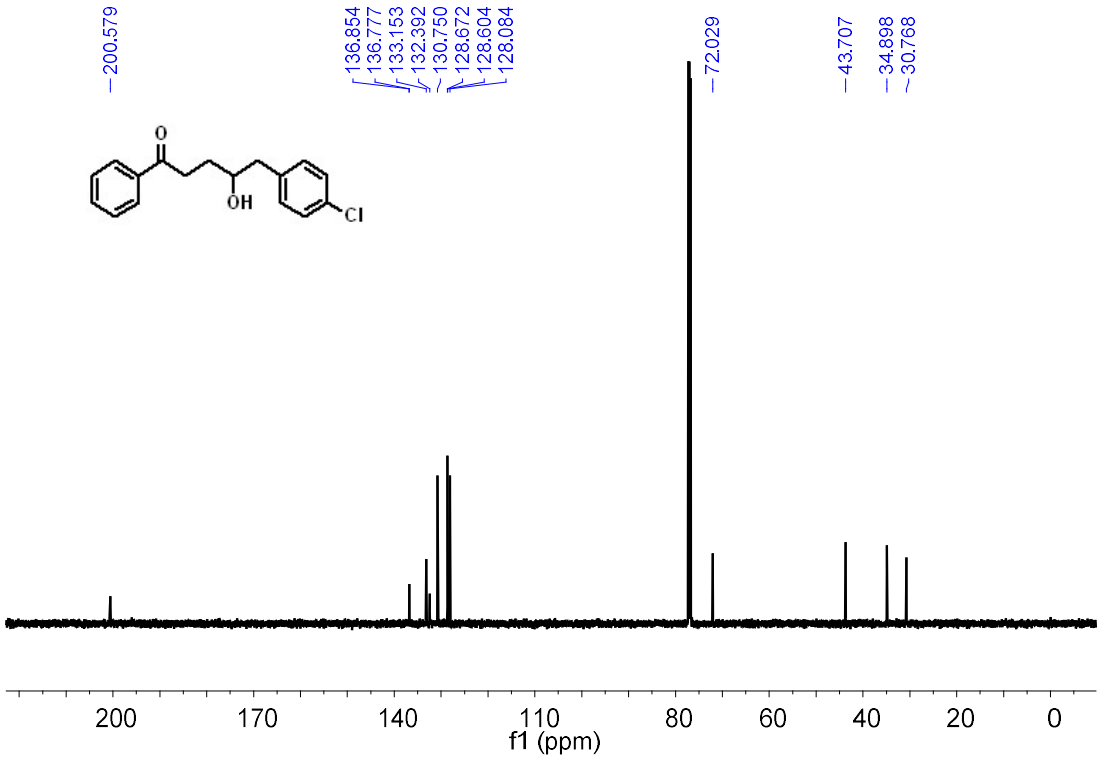
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5.



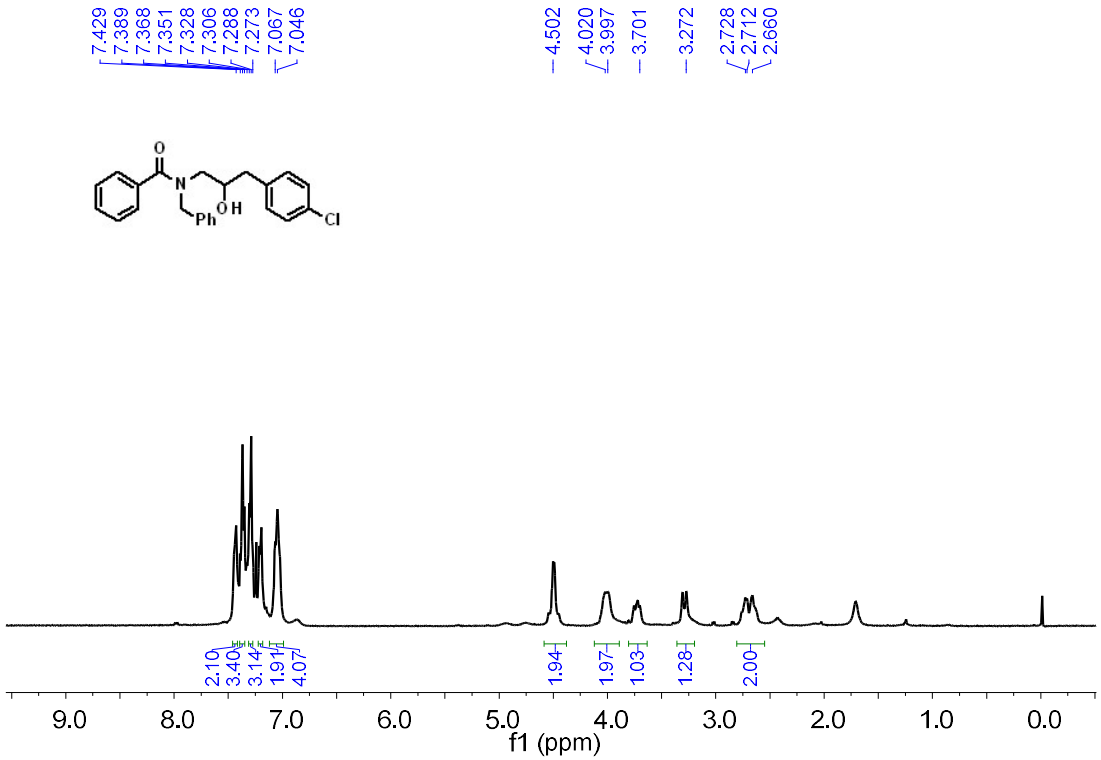
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 5.



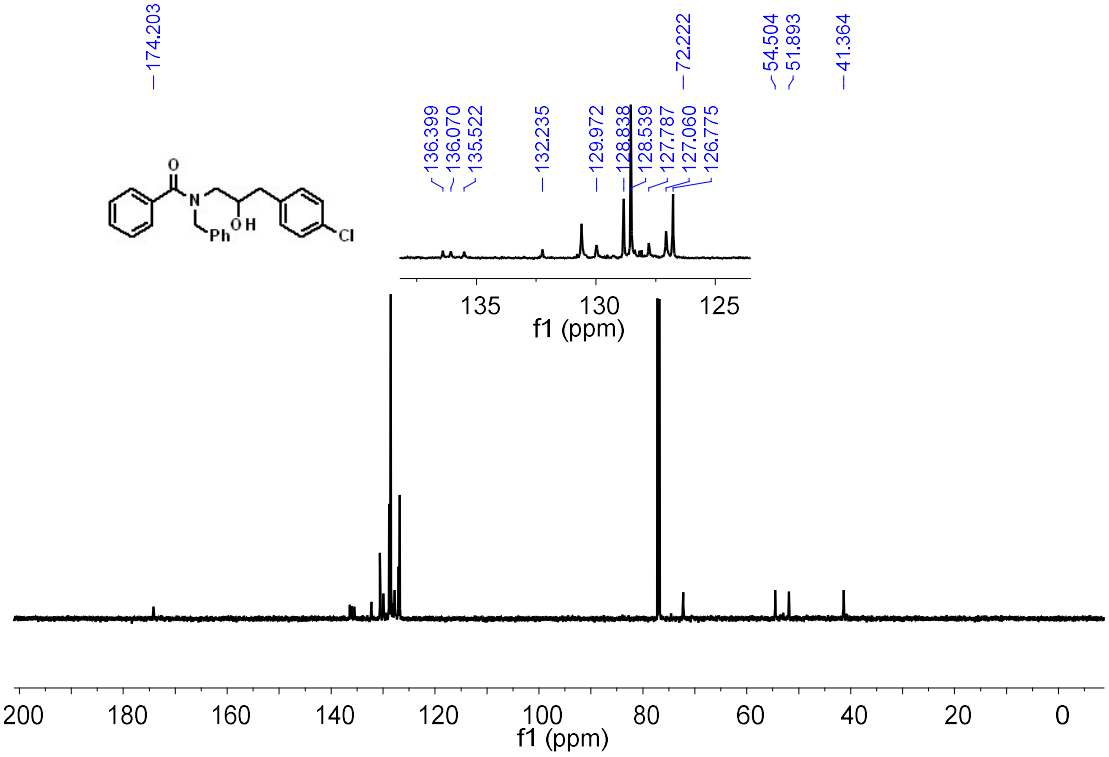
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 6.



^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 6.



^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 7.



^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 7.