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Dehydrogenative 6π Heterocyclization under Visible Light Irradiation and Mechanistic Insights

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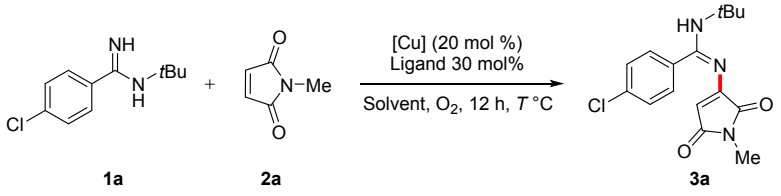
Contents

General Remarks

Catalytic reactions were carried out in Schlenk tubes under an oxygen atmosphere using pre-dried glassware. The following starting materials were synthesized according to previously described methods: Aryl amidines **1a**–**1l**,[1] maleimides **2e**–**2p**,[2] Other chemicals were obtained from commercial sources and were used without further purification. Yields refer to isolated compounds, estimated to be > 95% pure as determined by ^{1}H-NMR. Chromatography: Merck silica gel 60 (40-63 μm). NMR: Spectra were recorded on Bruker Avance III 400 in the solvent indicated; chemical shifts (δ) are given in ppm. All IR spectra were recorded on a Shimadzu IRTracer-100. HRMS was recorded on a Waters Xevo G2 (qTOF MS + c ESI). M. p.: Stuart melting point apparatus SMP3, Barlworld Scientific, values are uncorrected.

Optimizations

***Table S1*. Optimization of copper-catalyzed oxidative amination of maleimide (2a) with arylamidine 1a.**[a]



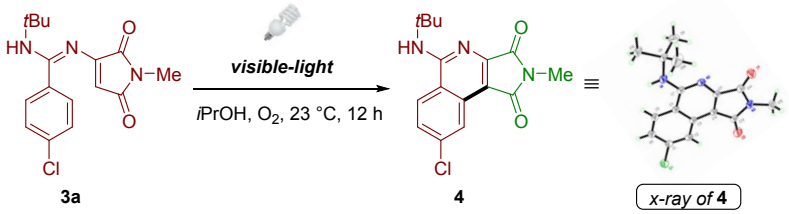
1a **2a** **3a**

Entry	[Cu]	*T*/°C	Solvent	Ligand	Yield (%)[b]
1	--	100	DCE	--	0
2	$Cu(OAc)_2$	100	DCE	--	20%
3	$Cu(OAc)_2$	100	DMF	--	Trace
4	$Cu(OAc)_2$	100	*i*-propanol	--	16%
5	$Cu(OAc)_2$	100	toluene	--	18%
6	$Cu(OAc)_2$	120	DCE	--	47%
7	$Cu(OAc)_2$	140	DCE	--	9%
8	$Cu(OAc)_2$	100	DCE	--	21%[c]

9	$Cu(OAc)_2$	100	DCE	--	32%[c, d]
10	$Cu(OAc)_2$	100	DCE	--	24%[e]
11	$Cu(OAc)_2$	120	DCE	dmbbpy	69%
12	***$Cu(OAc)_2$***	***120***	***DCE***	***bpy***	***72%***
13	$Cu(OAc)_2$	120	DCE	dtbbpy	62%
14	$Cu(OAc)_2$	120	DCE	phen	53%
15	$Cu(OAc)_2$	120	DCE	3,4,7,8-tetramethyl phen	Trace
16	$Cu(OAc)_2$	120	DCE	4,7-diphenyl phen	49%
17	$Cu(OAc)_2$	120	DCE	TMEDA	Trace
18	$Cu(OAc)_2$	120	DCE	pyridine	Trace
19	$Cu(OAc)_2$	120	DCE	*L*-Ala	9%
20	$Cu(OAc)_2$	120	DCE	bpy	63%[f]
21	$Cu(OTf)_2$	120	DCE	bpy	47%
22	CuBr	120	DCE	bpy	69%
23	Cu	120	DCE	bpy	51%
24	$CuBr_2$	120	DCE	dmbbpy	39%
25	$Cu(OAc)_2$	120	DCE	bpy	48%[g]

[a] General reaction conditions: **1a** (0.25 mmol), **2a** (0.50 mmol), [Cu] (20.0 mol %), anhydrous DCE (1.0 mL), under O_2, 100 °C, 12 h. [b] Isolated yield. [c] Under Ar. [d] $Cu(OAc)_2$ (2.0 equiv). [e] $Cu(OAc)_2$ (0.5 equiv). [f] **2a** (3.0 equiv). [g] Ligand (40 mol %). (DCE = 1,2-dichloroethane; dmbbpy = dtbbpy = 4,4'-di-methyl-2,2'-bipyridine; dtbbpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine; bpy = 2,2'-bipyridine; phen = 1,10-phenanthroline; TMEDA = tetramethylethylenediamine; DMF = *N,N*-dimethylformamide).

***Table S2*. Optimization for oxidative 6π cyclization of amidine 3a.[a]**

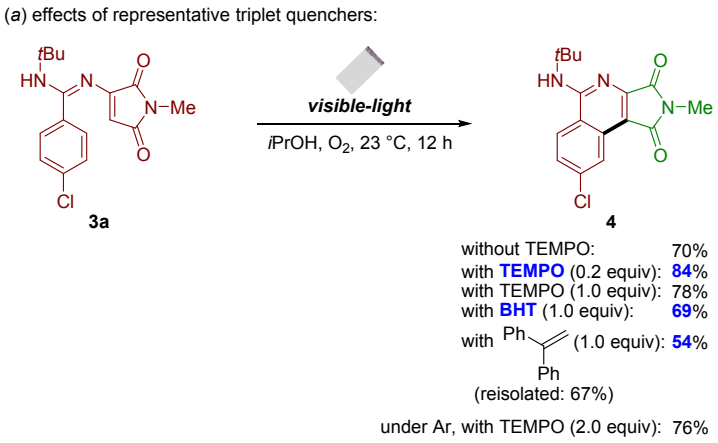


Entry	Modified conditions	Yield (%)[b]
1	with $[Ru(bpy)_3]Cl_2$ as the PC	52[c]
2	with *fac*-$Ir(ppy)_3$ as the PC	66[c]
3	with $Ir(Fppy)_3$ as the PC	69[c]
4	with Eosin Y as the PC	47[c]
5	with Mes-Are-OMe^+ ClO_4^- as the PC	0[c]
6	**none**	**70**
7	Ethylene glycol instead of *i*PrOH	57
8	TFE instead of *i*PrOH	66
9	MeOH instead of *i*PrOH	66
10	*t*BuOH instead of *i*PrOH	66
11	$(CF_3)_2CHOH$ instead of *i*PrOH	41
12	MeCN instead of *i*PrOH	60
13	PhMe instead of *i*PrOH	54
14	Acetone instead of *i*PrOH	trace
15	H_2O instead of *i*PrOH	trace

16	CH_2Cl_2 instead of *i*PrOH	trace
11	$CHCl_3$ instead of *i*PrOH	trace
17	under sunshine	65[d]
18	under air	50
19	In the dark	0
20	***TEMPO* (20 mol %)**	**84**
21	under N_2	41

[a] Reaction conditions: **3a** (0.15 mmol), *i*PrOH (2.0 mL), O_2, 23 °C, 12 h. [b] isolated yield. [c] PC (2 mol %) was used. [d] 24 h. PC = Photoredox catalyst. TFE = 2,2,2-Trifluoroethanol.

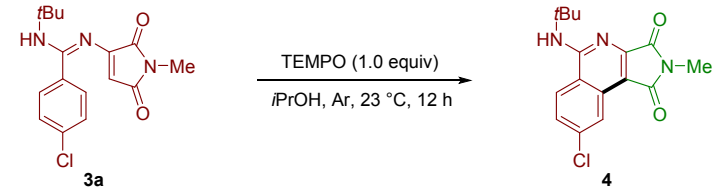
Additional Experiments:



A suspension of **3a** (48 mg, 0.15 mmol), or TEMPO (0.03 mmol, 20 mol %; or 0.15 mmol, 1.0 equiv), or BHT (33 mg, 1.0 equiv), or ethene-1,1-diyldibenzene (27 mg, 1.0 equiv) in isopropanol (3.0 mL) was stirred at 23 °C for 12 h under an atmosphere of O_2 with visible light (20W). At ambient temperature, the solvent was evaporated *in vacuo* and the remaining

residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc) to yield product **4**.

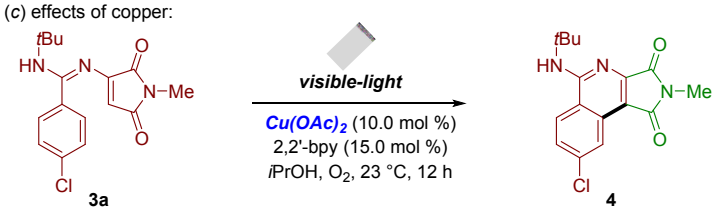
(*b*) effects of visible light:



without light: 0%
with light: 79%
without light & TEMPO/under 120 °C: 0%

A suspension of **3a** (48 mg, 0.15 mmol), TEMPO (0.15 mmol, 1.0 equiv), in isopropanol (3.0 mL) was stirred at 23 °C for 12 h under an atmosphere of O_2 with visible light (20W) or in the dark. At ambient temperature, the solvent was evaporated *in vacuo* and the remaining residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc) to yield product **4**. These results demonstrated the importance of visible light for this oxidative 6π heterocyclization.

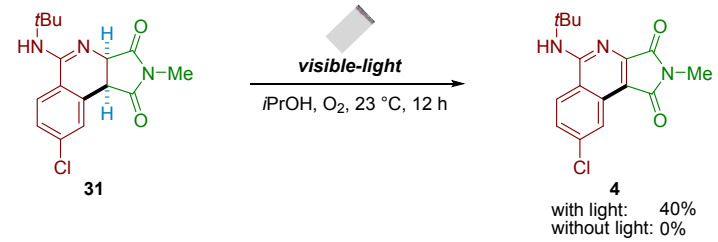
(*c*) effects of copper:



with light: 41%
without light: 0%

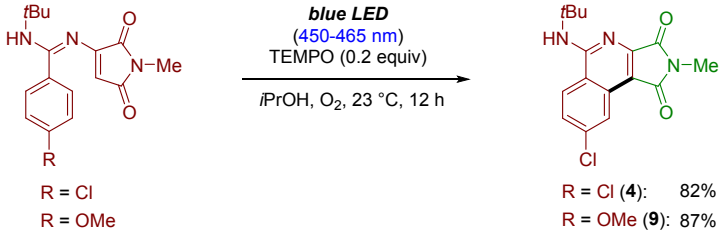
A suspension of **3a** (48 mg, 0.15 mmol), $Cu(OAc)_2$ (2.7 mg, 10 mol %), 2,2'-dipyridyl (3.5 mg, 15 mol %), in isopropanol (3.0 mL) was stirred at 23 °C for 12 h under an atmosphere of O_2 with visible light (20W) or in the dark. At ambient temperature, the solvent was evaporated *in vacuo* and the remaining residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc) to yield product **4**. These results demonstrated the copper salts will inhibit this envisioned oxidative 6π heterocyclization. Again, the reaction was completely stopped in the dark.

(*d*):



A suspension of **31** (48 mg, 0.15 mmol) in isopropanol (3.0 mL) was stirred at 23 °C for 12 h under an atmosphere of O_2 with visible light (20W) or in the dark. At ambient temperature, the solvent was evaporated *in vacuo* and the remaining residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc) to yield product **4**. These results demonstrated the compound **31** is sensitive under visible light, leading to the oxidative polycyclic isoquinoline **4**. Again, the reaction was completely stopped in the dark.

(e)



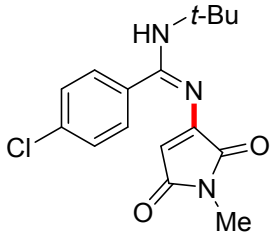
A suspension of **3a or 3f** (0.15 mmol) in isopropanol (2.0 mL) was stirred at 23 °C for 12 h under an atmosphere of O_2 with blue LED (450-465 nm, 15 W). At ambient temperature, the solvent was evaporated *in vacuo* and the remaining residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc) to yield product **4 or 9** in 82% or 87% yields, respectively.

Representative Procedures:

Representative Procedure for the Synthesis of Starting Materials 3 (A): A suspension of amidines **1** (0.25 mmol, 1.00 equiv), maleimides **2** (0.50 mmol, 2.00 equiv), $Cu(OAc)_2$ (9.0 mg, 20.0 mol %), and 2,2'-dipyridyl (11.7 mg, 30.0 mol %), in anhydrous DCE (1.0 mL) was stirred at 120 °C for 12 h under an atmosphere of O_2. At ambient temperature, the solvent was evaporated *in vacuo* and the remaining residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc) to yield products **3**.

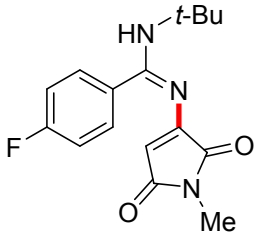
Representative Procedure for the Synthesis of π-Conjugated Polycyclic Isoquinolines (B): A suspension of **3** (0.15 mmol, 1.00 equiv), TEMPO (0.03 mmol, 20 mol %) in isopropanol

(3.0 mL) was stirred at 23 °C for 12 h under an atmosphere of O_2 with white light (distance from the light source to glassware: 5–10 cm; 20 W; 400-780 nm; commercially available from Alibaba). At ambient temperature, the solvent was evaporated *in vacuo* and the remaining residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc) to yield products **4**–**30**.



***N*-(*tert*-Butyl)-4-chloro-*N′*-(1-methyl-2,5-dioxo-2,5-dihydro-1*H*-pyrrol-3-yl)benzimidamide (3a)**

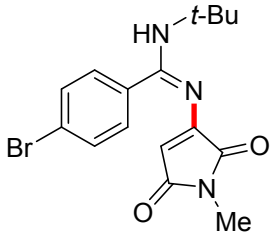
The general procedure **A** was followed using **1a** (53.0 mg, 0.25 mmol) and **2a** (56.0 mg, 0.50 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 8:1) yielded **3a** (54 mg, 68%) as a yellow solid. M. p. = 161 − 163 °C. ^{1}H-NMR (DMSO, 400 MHz): δ = 7.98 (s, 1H), 7.48 (d, J = 8.5 Hz, 2H), 7.34 (d, J = 8.5 Hz, 2H), 5.03 (s, 1H), 2.70 (s, 3H), 1.43 (s, 9H). ^{13}C-NMR (DMSO, 100 MHz): δ = 172.4, 168.8, 161.3, 154.4, 135.3, 133.9, 130.7, 128.8, 102.6, 53.2, 28.5, 23.5. IR (ATR): 3343, 2922, 1699, 1536, 1382, 1204 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{16}H_{19}ClN_3O_2$ 320.1160; found 320.1168.



***N*-(*tert*-Butyl)-4-fluoro-*N′*-(1-methyl-2,5-dioxo-2,5-dihydro-1*H*-pyrrol-3-yl)benzimidamide (3b)**

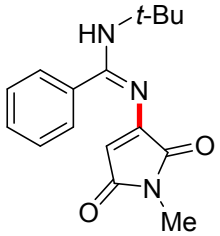
The general procedure **A** was followed using **1b** (49.0 mg, 0.25 mmol) and **2a** (56.0 mg, 0.50 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded **3b** (39 mg, 51%) as a yellow solid. M. p. = 186 − 189 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.37

– 7.30 (m, 2H), 7.05 (t, J = 8.6 Hz, 2H), 5.22 (s, 1H), 5.16 (s, 1H), 2.84 (s, 3H), 1.52 (s, 9H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 172.81, 168.83, 163.73 (d, $^{1}J_{C\text{-}F}$ = 251.7 Hz), 160.11, 153.50, 131.78 (d, $^{4}J_{C\text{-}F}$ = 3.4 Hz), 129.78 (d, $^{3}J_{C\text{-}F}$ = 8.6 Hz), 116.01 (d, $^{2}J_{C\text{-}F}$ = 21.9 Hz), 104.61, 53.54, 28.51, 23.38. ^{19}F-NMR (CDCl3, 376 MHz): δ = -108.51 (s). IR (ATR): 3318, 2960, 1749, 1538, 1382, 1211 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{16}H_{19}FN_3O_2$ 304.1456; found 304.1451.



4-Bromo-*N*-(*tert*-butyl)-*N'*-(1-methyl-2,5-dioxo-2,5-dihydro-1*H*-pyrrol-3-yl)benzimidamide (3c)

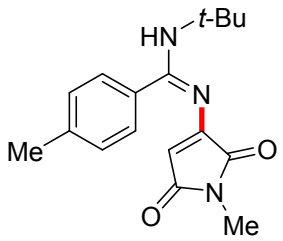
The general procedure **A** was followed using **1c** (64.0 mg, 0.25 mmol) and **2a** (56.0 mg, 0.50 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 8:1) yielded **3c** (40 mg, 44%) as a yellow solid. M. p. = 162 − 164 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.50 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H), 5.23 (s, 1H), 5.15 (s, 1H), 2.84 (s, 3H), 1.51 (s, 9H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 172.7, 168.8, 159.9, 153.3, 134.4, 132.1, 129.2, 125.0, 104.8, 53.6, 28.4, 23.4. IR (ATR): 3344, 2918, 1699, 1534, 1382, 1204, 1112 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{16}H_{19}BrN_3O_2$ 364.0655, 366.0640; found 364.0663, 366.0651.



***N*-(*tert*-Butyl)-*N'*-(1-methyl-2,5-dioxo-2,5-dihydro-1*H*-pyrrol-3-yl)benzimidamide (3d)**

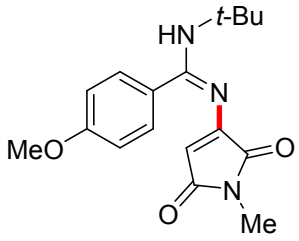
The general procedure **A** was followed using **1d** (44.0 mg, 0.25 mmol) and **2a** (56.0 mg, 0.50 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded **3d** (32 mg, 44%) as a yellow solid. M. p. = 100 − 102 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): 7.46 – 7.29 (m, 5H), 5.21 (s, 1H), 5.13 (s, 1H), 2.84 (s, 3H), 1.52 (s, 9H). ^{13}C-NMR ($CDCl_3$, 100

MHz): δ = 172.9, 169.1, 161.3, 153.7, 135.5, 130.6, 128.8, 127.6, 104.3, 53.5, 28.5, 23.3. IR (ATR): 3350, 2974, 1698, 1523, 1379, 1286, 1112 cm^{-1}. HRMS (ESI) m/z: [M+H^+] calcd for $C_{16}H_{20}N_3O_2$ 286.1550; found 286.1557.



***N*-(*tert*-Butyl)-4-methyl-*N'*-(1-methyl-2,5-dioxo-2,5-dihydro-1*H*-pyrrol-3-yl)benzimidamide (3e)**

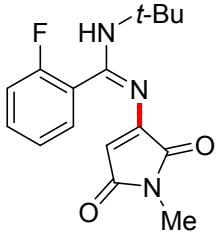
The general procedure **A** was followed using **1e** (48.0 mg, 0.25 mmol) and **2a** (56.0 mg, 0.50 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded **3e** (24 mg, 36%) as a yellow solid. M. p. = 142 − 144 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.22 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 5.21 (s, 1H), 5.11 (s, 1H), 2.84 (s, 3H), 2.35 (s, 3H), 1.51 (s, 9H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 173.1, 169.2, 161.6, 154.0, 141.0, 132.6, 129.5, 127.5, 103.9, 53.4, 28.6, 23.3, 21.4. IR (ATR): 3348, 2976, 1701, 1535, 1381, 1203, 1111 cm^{-1}. HRMS (ESI) m/z: [M+H^+] calcd for $C_{17}H_{22}N_3O_2$ 300.1707; found 300.1703.



***N*-(*tert*-Butyl)-4-methoxy-*N'*-(1-methyl-2,5-dioxo-2,5-dihydro-1*H*-pyrrol-3-yl)benzimidamide (3f)**

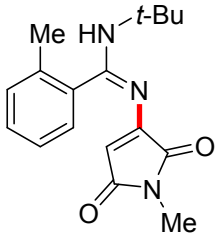
The general procedure **A** was followed using **1f** (49.0 mg, 0.25 mmol) and **2a** (56.0 mg, 0.50 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 7:1) yielded **3f** (45 mg, 57%) as a yellow solid. M. p. = 155 − 157 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.29 (d, J = 8.7 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 5.20 (s, 1H), 5.16 (s, 1H), 3.81 (s, 3H), 2.85 (s, 3H), 1.51 (s, 9H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 173.1, 169.0, 161.4, 161.3, 154.1, 129.2,

127.9, 114.1, 103.6, 55.3, 53.3, 28.5, 23.3. IR (ATR): 3352, 2976, 1698, 1505, 1381, 1257, 1173 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{17}H_{22}N_3O_3$ 316.1656; found 316.1657.



***N*-(*tert*-Butyl)-2-fluoro-*N′*-(1-methyl-2,5-dioxo-2,5-dihydro-1*H*-pyrrol-3-yl)benzimidamide (3g)**

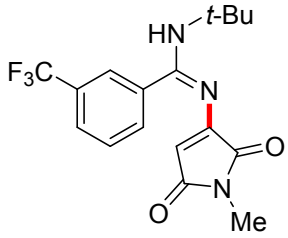
The general procedure **A** was followed using **1g** (49.0 mg, 0.25 mmol) and **2a** (56.0 mg, 0.50 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded **3g** (44 mg, 57%) as a yellow solid. M. p. = 144 − 146 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.42 - 7.35 (m, 1H), 7.24 (td, J = 7.0, 1.4 Hz, 1H), 7.14 (t, J = 7.3 Hz, 1H), 7.08 (t, J = 9.0 Hz, 1H), 5.19 (s, 1H), 5.08 (s, 1H), 2.84 (s, 3H), 1.53 (s, 9H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 172.7, 169.3, 158.7 (d, $^1J_{C\text{-}F}$ = 250.3 Hz), 155.4, 153.2, 132.1 (d, $^3J_{C\text{-}F}$ = 8.2 Hz), 129.5 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 124.5 (d, $^4J_{C\text{-}F}$ = 3.6 Hz), 122.7 (d, $^2J_{C\text{-}F}$ = 16.1 Hz), 116.3 (d, $^2J_{C\text{-}F}$ = 21.5 Hz), 104.8, 53.8, 28.5, 23.3. ^{19}F-NMR (CDCl3, 376 MHz): δ = -114.35 (s). IR (ATR): 3347, 2960, 1693, 1537, 1435, 1206, 1116 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{16}H_{19}FN_3O_2$ 304.1456; found 304.1459.



***N*-(*tert*-Butyl)-2-methyl-*N′*-(1-methyl-2,5-dioxo-2,5-dihydro-1*H*-pyrrol-3-yl)benzimidamide (3h)**

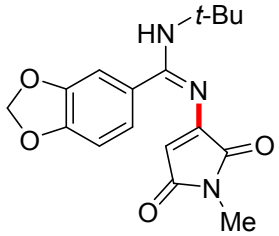
The general procedure **A** was followed using **1a** (48.0 mg, 0.25 mmol) and **2a** (56.0 mg, 0.50 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 8:1) yielded **3ha** (27 mg, 36%) as a yellow solid. M. p. = 184 − 186 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.26 – 7.18 (m, 2H), 7.11 (d, J = 9.6 Hz, 2H), 5.20 (s, 1H), 5.09 (s, 1H), 2.85 (s, 3H), 2.34 (s, 3H),

1.52 (s, 9H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 173.0, 169.2, 161.6, 153.8, 138.7, 135.4, 131.3, 128.7, 127.9, 124.7, 104.0, 53.4, 28.5, 23.3, 21.4. IR (ATR): 3347, 2930, 1698, 1526, 1363, 1235, 1112 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{17}H_{22}N_3O_2$ 300.1707; found 300.1713.



***N*-(*tert*-Butyl)-*N'*-(1-methyl-2,5-dioxo-2,5-dihydro-1*H*-pyrrol-3-yl)-3-(trifluoromethyl)benzimidamide (3i)**

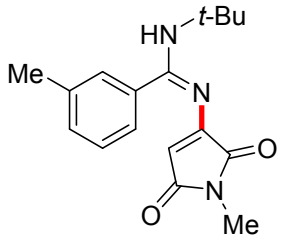
The general procedure **A** was followed using **1i** (61.0 mg, 0.25 mmol) and **2a** (56.0 mg, 0.50 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded **3i** (45 mg, 51%) as a yellow solid. M. p. = 155 − 156 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.70 – 7.64 (m, 1H), 7.59 (s, 1H), 7.53 – 7.49 (m, 2H), 5.21 (s, 1H), 5.18 (s, 1H), 2.83 (s, 3H), 1.54 (s, 9H).^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 172.5, 168.7, 159.2, 153.0, 136.2, 131.4 (q, $^2J_{C\text{-}F}$ = 32.9 Hz), 131.0, 129.5, 127.2 (q, $^3J_{C\text{-}F}$ = 3.7 Hz), 124.4 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 123.5 (q, $^1J_{C\text{-}F}$ = 272.0 Hz), 105.2, 53.8, 28.5, 23.4. ^{19}F-NMR (CDCl3, 376 MHz): δ = -62.76 (s). IR (ATR): 3320, 2964, 1702, 1513, 1389, 1286, 1110 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{17}H_{19}F_3N_3O_2$ 354.1424; found 354.1422.



***N*-(*tert*-Butyl)-*N'*-(1-methyl-2,5-dioxo-2,5-dihydro-1*H*-pyrrol-3-yl)benzo[*d*][1,3]dioxole-5-carboximidamide (3j)**

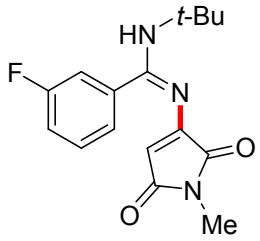
The general procedure **A** was followed using **1j** (55.0 mg, 0.25 mmol) and **2a** (56.0 mg, 0.50 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 8:1) yielded **3j** (35 mg, 43%) as a yellow solid. M. p. = 186 − 188 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 6.85 (dd,

J = 8.0, 1.6 Hz, 1H), 6.79 (d, J = 1.6 Hz, 1H), 6.76 (d, J = 8.0 Hz, 1H), 6.00 (s, 2H), 5.19 (s, 1H), 2.87 (s, 3H), 1.50 (s, 9H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 173.1, 169.1, 160.9, 153.8, 149.6, 148.0, 129.5, 122.2, 108.5, 108.0, 103.9, 101.7, 53.4, 28.5, 23.4. IR (ATR): 3349, 2958, 1694, 1535, 1377, 1250, 1112 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{17}H_{20}N_3O_4$ 330.1448; found 330.1454.



_N_-(_tert_-Butyl)-3-methyl-_N′_-(1-methyl-2,5-dioxo-2,5-dihydro-1_H_-pyrrol-3-yl)benzimidamide (3k)

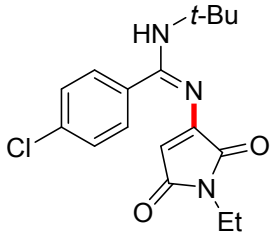
The general procedure **A** was followed using **1k** (49.0 mg, 0.25 mmol) and **2a** (56.0 mg, 0.50 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 12:1) yielded **3k** (36 mg, 48%) as a yellow solid. M. p. = 188−190 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.25 – 7.19 (m, 2H), 7.15 – 7.09 (m, 2H), 5.19 (s, 1H), 5.09 (s, 1H), 2.85 (s, 3H), 2.34 (s, 3H), 1.52 (s, 9H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 173.1, 169.3, 161.6, 153.8, 138.8, 135.4, 131.3, 128.7, 127.9, 124.7, 104.0, 53.4, 28.5, 23.3, 21.4. IR (ATR): 3352, 2971, 1698, 1522, 1374, 1085 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{17}H_{22}N_3O_2$ 300.1707; found 300.1703.



_N_-(_tert_-Butyl)-3-fluoro-_N′_-(1-methyl-2,5-dioxo-2,5-dihydro-1_H_-pyrrol-3-yl)benzimidamide (3l)

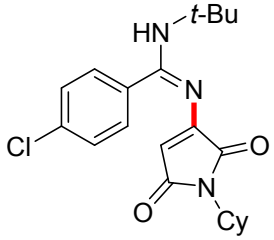
The general procedure **A** was followed using **1l** (49.0 mg, 0.25 mmol) and **2a** (56.0 mg, 0.50 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded **3l** (32 mg, 42%) as a yellow solid. M. p. = 165 − 167 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.34 (td, J = 8.0, 5.7 Hz, 1H), 7.15 – 7.08 (m, 2H), 7.08 – 7.02 (m, 1H), 5.22 (s, 1H), 5.18 (s, 1H),

2.85 (s, 3H), 1.52 (s, 9H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 172.73, 168.85, 162.53 (d, $^{1}J_{C\text{-}F}$ = 249.3 Hz), 159.43, 153.22, 137.46 (d, $^{3}J_{C\text{-}F}$ = 7.1 Hz), 130.66 (d, $^{3}J_{C\text{-}F}$ = 8.2 Hz), 123.40 (d, $^{4}J_{C\text{-}F}$ = 3.2 Hz), 117.67 (d, $^{2}J_{C\text{-}F}$ = 21.1 Hz), 114.84 (d, $^{2}J_{C\text{-}F}$ = 22.8 Hz), 104.83, 53.63, 28.47, 23.39. ^{19}F-NMR ($CDCl_3$, 376 MHz): δ = -110.69 (s). IR (ATR): 3341, 2964, 1695, 1540, 1362, 1287, 1187 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{16}H_{19}FN_3O_2$ 304.1456; found 304.1458.



***N*-(*tert*-Butyl)-4-chloro-*N′*-(1-ethyl-2,5-dioxo-2,5-dihydro-1*H*-pyrrol-3-yl)benzimidamide (3m)**

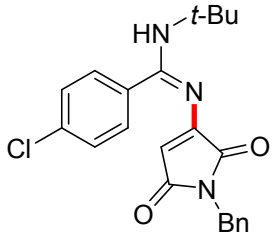
The general procedure **A** was followed using **1a** (53.0 mg, 0.25 mmol) and **2b** (53.0 mg, 0.50 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded **3m** (30 mg, 35%) as a yellow solid. M. p. = 165 − 167 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.37 – 7.31 (m, 2H), 7.29 – 7.25 (m, 2H), 5.21 (s, 1H), 5.14 (s, 1H), 3.39 (q, J = 7.2 Hz, 2H), 1.52 (s, 9H), 1.04 (t, J = 7.2 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 172.5, 168.6, 159.9, 153.3, 136.7, 134.1, 129.1, 129.0, 105.0, 53.6, 32.4, 28.5, 13.9. IR (ATR): 3343, 2974, 1693, 1533, 1397, 1202 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{17}H_{21}ClN_3O_2$ 334.1317; found 334.1319.



***N*-(*tert*-Butyl)-4-chloro-*N′*-(1-cyclohexyl-2,5-dioxo-2,5-dihydro-1*H*-pyrrol-3-yl)benzimidamide (3n)**

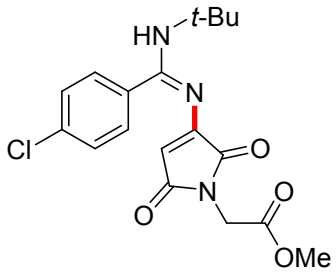
The general procedure **A** was followed using **1a** (53.0 mg, 0.25 mmol) and **2c** (89 mg, 0.50 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded **3n**

(24 mg, 25%) as a yellow solid. M. p. = 160 − 162 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.33 (d, J = 8.5 Hz, 2H), 7.26 (d, J = 8.5 Hz, 2H), 5.20 (s, 1H), 5.12 (s, 1H), 3.73 (tt, J = 12.3, 3.8 Hz, 1H), 1.95 – 1.81 (m, 2H), 1.74 (d, J = 13.1 Hz, 2H), 1.51 (s, 9H), 1.51 – 1.38 (m, 2H), 1.33 – 1.06 (m, 4H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 172.6, 168.6, 159.8, 152.9, 136.6, 134.2, 129.0, 129.0, 105.0, 53.5, 50.1, 30.0 28.5, 26.0, 25.1. IR (ATR): 3336, 2932, 1698, 1576, 1363, 1206, 1090 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{21}H_{26}ClN_3O_2$ 387.1714; found 387.1721.



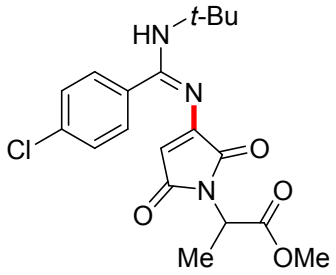
***N'*-(1-Benzyl-2,5-dioxo-2,5-dihydro-1*H*-pyrrol-3-yl)-*N*-(*tert*-butyl)-4-chlorobenzimidamide (3o)**

The general procedure **A** was followed using **1a** (53.0 mg, 0.25 mmol) and **2d** (93 mg, 0.50 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 12:1) yielded **3o** (43 mg, 53%) as a yellow solid. M. p. = 176 − 178 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.34 – 7.26 (m, 4H), 7.25 – 7.18 (m, 3H), 7.09 – 7.03 (m, 2H), 5.34 (s, 1H), 5.18 (s, 1H), 4.49 (s, 2H), 1.50 (s, 9H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 172.0, 168.2, 160.02 153.5, 136.9, 136.6, 134.3, 129.1, 129.0, 128.4, 127.8, 127.3, 105.3, 53.6, 40.9, 28.5. IR (ATR): 3346, 2919, 1695, 1530, 1385, 1204, 1090 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{22}H_{23}ClN_3O_2$ 396.1479; found 396.1483.



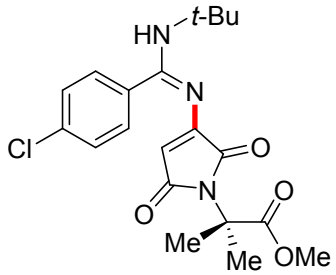
Methyl 2-(3-{[(*tert*-butylamino)(4-chlorophenyl)methylene]amino}-2,5-dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)acetate (3p)

The general procedure **A** was followed using **1a** (53.0 mg, 0.25 mmol) and **2e** (85.0 mg, 0.50 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 8:1) yielded **3p** (40 mg, 42%) as a yellow solid. M. p. = 135 − 137 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.35 (d, J = 8.5 Hz, 2H), 7.29 (d, J = 8.5 Hz, 2H), 5.30 (s, 1H), 5.23 (s, 1H), 4.10 (s, 2H), 3.65 (s, 3H), 1.52 (s, 9H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 171.3, 168.0, 167.9, 160.1, 153.6, 136.8, 133.8, 129.1, 129.0, 105.1, 53.7, 52.3, 38.3, 28.5. IR (ATR): 3344, 2975, 1694, 1533, 1397, 1283, 1202 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{18}H_{21}ClN_3O_4$ 378.1221; found 378.1230.



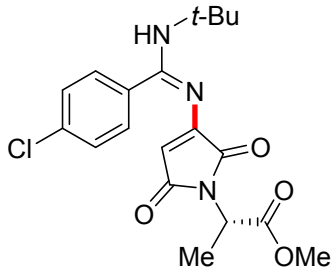
Methyl 2-(3-{[(tert-butylamino)(4-chlorophenyl)methylene]amino}-2,5-dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)propanoate (3q)

The general procedure **A** was followed using **1a** (53.0 mg, 0.25 mmol) and **2f** (91.0 mg, 0.50 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 8:1) yielded **3q** (63 mg, 64%) as a yellow solid. M. p. = 223 − 224 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.35 (d, J = 8.5 Hz, 2H), 7.29 (d, J = 8.5 Hz, 2H), 5.31 (s, 1H), 5.19 (s, 1H), 4.61 (q, J = 7.3 Hz, 1H), 3.59 (s, 3H), 1.52 (s, 9H), 1.46 (d, J = 7.3 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 171.4, 170.6, 167.7, 160.1, 153.4, 136.7, 134.0, 129.1, 129.0, 105.2, 53.7, 52.5, 46.8, 28.5, 15.2. IR (ATR): 3342, 2967, 1698, 1521, 1388, 1082 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{19}H_{23}ClN_3O_4$ 392.1377; found 392.1369.



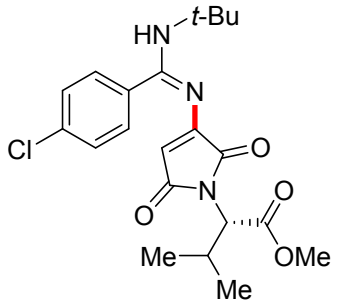
Methyl 2-(3-{[(*tert*-butylamino)(4-chlorophenyl)methylene]amino}-2,5-dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)-2-methylpropanoate (3r)

The general procedure **A** was followed using **1a** (53.0 mg, 0.25 mmol) and **2g** (98.0 mg, 0.50 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 8:1) yielded **3r** (40 mg, 25%) as a yellow solid. M. p. = 126 − 128 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.35 (d, J = 8.5 Hz, 2H), 7.27 (d, J = 8.5 Hz, 2H), 5.23 (s, 1H), 5.13 (s, 1H), 3.58 (s, 3H), 1.58 (s, 6H), 1.51 (s, 9H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 173.7, 172.3, 168.3, 159.9, 152.8, 136.6, 134.2, 129.1, 129.0, 105.4, 59.4, 53.6, 52.4, 28.5, 24.3. IR (ATR): 3360, 2963, 1747, 1615, 1417, 1267, 1089 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{20}H_{25}ClN_3O_4$ 406.1534; found 406.1537.



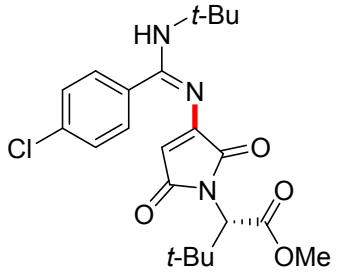
Methyl 2-(3-{[(*tert*-butylamino)(4-chlorophenyl)methylene]amino}-2,5-dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)propanoate (3s)

The general procedure **A** was followed using **1a** (53.0 mg, 0.25 mmol) and **2h** (91.0 mg, 0.50 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 8:1) yielded **3s** (57 mg, 58%) as a yellow solid. M. p. = 225 − 227 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.35 (d, J = 8.5 Hz, 2H), 7.29 (d, J = 8.5 Hz, 2H), 5.31 (s, 1H), 5.19 (s, 1H), 4.61 (q, J = 7.3 Hz, 1H), 3.59 (s, 3H), 1.52 (s, 9H), 1.46 (d, J = 7.3 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 171.4, 170.6, 167.7, 160.0, 153.4, 136.7, 134.0, 129.1, 129.0, 105.2, 53.7, 52.5, 46.8, 28.5, 15.2. IR (ATR): 3335, 2931, 1697, 1531, 1345, 1205, 1090 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{19}H_{23}ClN_3O_4$ 392.1377; found 392.1378.



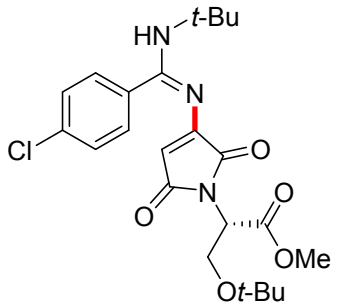
Methyl 2-(3-{[(*tert*-butylamino)(4-chlorophenyl)methylene]amino}-2,5-dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)-3-methylbutanoate (3t)

The general procedure **A** was followed using **1a** (53.0 mg, 0.25 mmol) and **2i** (106.0 mg, 0.50 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 8:1) yielded **3t** (36 mg, 35%) as a yellow solid. M. p. = 144 − 147 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.35 – 7.27 (m, 4H), 5.46 (s, 1H), 5.17 (s, 1H), 4.24 (d, J = 8.6 Hz, 1H), 3.57 (s, 3H), 2.34 – 2.17 (m, 1H), 1.52 (s, 9H), 0.90 (d, J = 6.0 Hz, 3H), 0.73 (d, J = 6.0 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 171.6, 169.7, 167.5, 160.0, 153.3, 136.6, 134.6, 129.3, 128.9, 105.5, 56.3, 53.6, 52.0, 34.2, 28.5, 25.4, 16.6. IR (ATR): 3340, 2969, 1698, 1522, 1385, 1086 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{21}H_{27}ClN_3O_4$ 420.1690; found 420.1693.



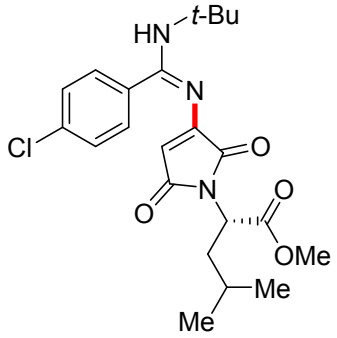
Methyl 2-(3-{[(*tert*-butylamino)(4-chlorophenyl)methylene]amino}-2,5-dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)-3,3-dimethylbutanoate (3u)

The general procedure **A** was followed using **1a** (53.0 mg, 0.25 mmol) and **2j** (112.0 mg, 0.50 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 8:1) yielded **3u** (35 mg, 32%) as a yellow solid. M. p. = 80 − 81 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.35 – 7.27 (m, 4H), 5.49 (s, 1H), 5.17 (s, 1H), 4.23 (s, 1H), 3.50 (s, 3H), 1.52 (s, 9H), 0.91 (s, 9H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 171.7, 168.6, 167.7, 159.9, 153.3, 136.7, 134.6, 129.3, 128.9, 105.6, 58.8, 53.6, 51.7, 35.4, 28.5, 27.4. IR (ATR): 3351, 2962, 1749, 1525, 1382, 1207 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{22}H_{29}ClN_3O_4$ 434.1847; found 434.1849.



Methyl 3-(*tert*-butoxy)-2-(3-{[(*tert*-butylamino)(4-chlorophenyl)methylene]amino}-2,5-dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)propanoate (3v)

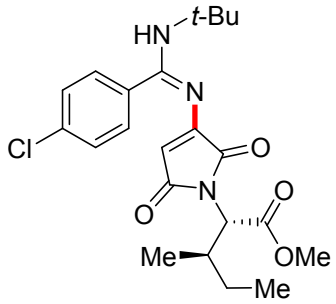
The general procedure **A** was followed using **1a** (53.0 mg, 0.25 mmol) and **2k** (128.0 mg, 0.50 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 8:1) yielded **3v** (69 mg, 59%) as a yellow solid. M. p. = 92 − 94 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.35 – 7.27 (m, 4H), 5.36 (s, 1H), 5.14 (s, 1H), 4.67 (dd, J = 9.7, 5.0 Hz, 1H), 3.86 (dd, J = 9.7, 5.0 Hz, 1H), 3.77 (t, J = 9.7 Hz, 1H), 3.61 (s, 3H), 1.51 (s, 9H), 1.04 (s, 9H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 171.5, 168.7, 167.7, 159.8, 153.0, 136.6, 134.1, 129.1, 129.0, 105.2, 73.3, 59.0, 53.6, 52.3, 52.2, 28.5, 27.3. IR (ATR): 3348, 2988, 1708, 1573, 1379, 1276 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{23}H_{31}ClN_3O_5$ 464.1952; found 464.1953.



Methyl 2-(3-{[(*tert*-butylamino)(4-chlorophenyl)methylene]amino}-2,5-dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)-4-methylpentanoate (3w)

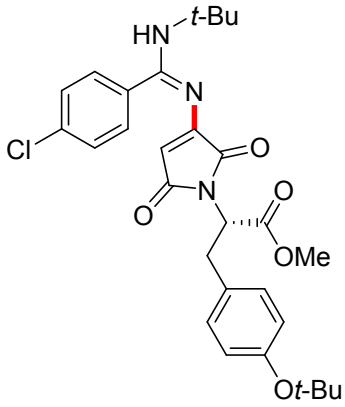
The general procedure **A** was followed using **1a** (53.0 mg, 0.25 mmol) and **2l** (113.0 mg, 0.50 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 8:1) yielded **3w** (45 mg, 42%) as a yellow solid. M. p. = 172 − 174 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.34 – 7.27 (m, 4H), 5.44 (s, 1H), 5.16 (s, 1H), 4.54 (dd, J = 11.9, 4.2 Hz, 1H), 3.60 (s, 3H), 2.03

(ddd, J = 14.2, 11.0, 4.0 Hz, 1H), 1.68 (ddd, J = 14.2, 11.0, 4.0 Hz, 1H), 1.52 (s, 9H), 1.14 – 1.01 (m, 1H), 0.81 (d, J = 6.5 Hz, 3H), 0.75 (d, J = 6.5 Hz, 3H).^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 171.6, 170.7, 167.6, 159.9, 153.4, 136.6, 134.5, 129.2, 128.9, 105.7, 53.6, 52.4, 49.9, 37.1, 28.5, 24.9, 23.1, 20.8. IR (ATR): 3347, 2963, 1698, 1522, 1394, 1207 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{22}H_{29}ClN_3O_4$ 434.1847; found 434.1845.



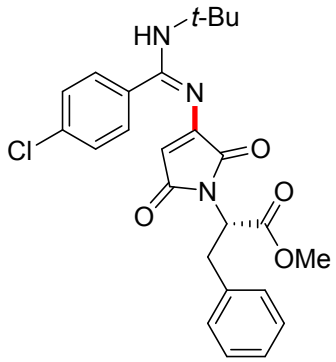
Methyl 2-(3-{[(*tert*-butylamino)(4-chlorophenyl)methylene]amino}-2,5-dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)-3-methylpentanoate (3x)

The general procedure **A** was followed using **1a** (53.0 mg, 0.25 mmol) and **2m** (113.0 mg, 0.50 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 8:1) yielded **3x** (43 mg, 40%) as a yellow solid. M. p. = 122 − 125 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.34 – 7.27 (m, 4H), 5.45 (d, J = 12.5 Hz, 1H), 5.16 (s, 1H), 4.24 (d, J = 8.6 Hz, 1H), 3.57 (s, 3H), 2.32 – 2.20 (m, 1H), 1.63 – 1.58 (m, 2H), 1.52 (s, 9H), 0.90 (d, J = 6.7 Hz, 3H), 0.73 (t, J = 6.3 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 171.6, 169.7, 167.4, 160.0, 153.3, 136.6, 134.5, 129.2, 128.9, 105.5, 56.3, 53.6, 52.0, 34.1, 28.5, 25.3, 16.5, 10.8. IR (ATR): 3355, 2968, 1697, 1522, 1386, 1285, 1199 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{22}H_{29}ClN_3O_4$ 434.1841; found 434.1844.



Methyl 3-[4-(*tert*-butoxy)phenyl]-2-(3-{[(*tert*-butylamino)(4-chlorophenyl)methylene]amino}-2,5-dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)propanoate (3y)

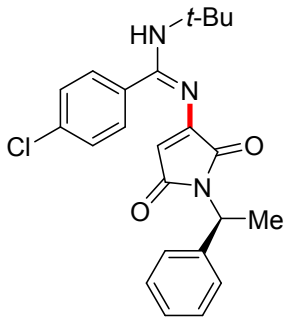
The general procedure **A** was followed using **1a** (53.0 mg, 0.25 mmol) and **2n** (166.0 mg, 0.50 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 8:1) yielded **3y** (60 mg, 44%) as a yellow solid. M. p. = 161 − 164 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.39 – 7.31 (m, 2H), 7.20 – 7.14 (m, 2H), 6.91 – 6.79 (m, 4H), 5.12 (s, 1H), 5.10 (s, 1H), 4.77 (dd, J = 11.4, 5.1 Hz, 1H), 3.65 (s, 3H), 3.33 (dd, J = 14.3, 5.1 Hz, 1H), 3.23 (dd, J = 14.2, 11.5 Hz, 1H), 1.49 (s, 9H), 1.31 (s, 9H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 171.1, 169.8, 167.7, 159.9, 154.0, 153.0, 136.6, 133.7, 131.9, 129.3, 129.1, 129.0, 124.1, 104.8, 78.2, 53.6, 52.6, 52.5, 33.9, 28.8, 28.5. IR (ATR): 3336, 2984, 1684, 1522, 1361, 1236 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{29}H_{35}ClN_3O_5$ 540.2265; found 540.2269.



Methyl 2-(3-{[(*tert*-butylamino)(4-chlorophenyl)methylene]amino}-2,5-dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)-3-phenylpropanoate (3z)

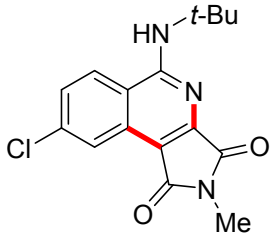
The general procedure **A** was followed using **1a** (53.0 mg, 0.25 mmol) and **2o** (130 mg, 0.50 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 8:1) yielded **3z** (32 mg, 27%) as a yellow solid. M. p. = 85 − 87 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.31 – 7.26

(m, 2H), 7.23 – 7.14 (m, 5H), 7.01 – 6.96 (m, 2H), 5.20 (s, 1H), 5.11 (s, 1H), 4.80 (dd, J = 11.5, 5.0 Hz, 1H), 3.66 (s, 3H), 3.43 – 3.27 (m, 2H), 1.49 (s, 9H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 171.3, 169.8, 167.7, 159.8, 153.0, 137.1, 136.6, 133.9, 129.0, 128.8, 128.4, 128.3, 126.6, 105.0, 53.6, 52.7, 52.6, 34.6, 28.5. IR (ATR): 3350, 2971, 1704, 1521, 1388, 1205, 1088 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{25}H_{27}ClN_3O_4$ 468.1690; found 468.1692.



_N_-(*tert*-Butyl)-4-chloro-_N'_-[2,5-dioxo-1-(1-phenylethyl)-2,5-dihydro-1*H*-pyrrol-3-yl]benzimidamide (3aa)

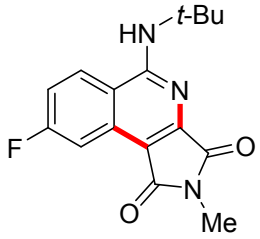
The general procedure **A** was followed using 1a (53.0 mg, 0.25 mmol) and **2p** (100.0 mg, 0.50 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded **3aa** (65 mg, 63%) as a yellow solid. M. p. = 291 − 293 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.29 – 7.09 (m, 7H), 7.12 (d, J = 6.5 Hz, 2H), 5.32 (s, 1H), 5.18 (dd, J = 14.7, 7.4 Hz, 1H), 5.14 (s, 1H), 1.66 (d, J = 7.4 Hz, 3H), 1.50 (s, 9H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 172.1, 168.1, 159.9, 153.2, 141.0, 136.5, 134.4, 129.0, 128.9, 128.2, 127.1, 126.7, 105.3, 53.5, 48.8, 28.5, 17.7. IR (ATR): 3344, 2973, 1690, 1578, 1352, 1205 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{23}H_{25}ClN_3O_2$ 410.1635; found 410.1637.



5-(*tert*-Butylamino)-8-chloro-2-methyl-1*H*-pyrrolo[3,4-*c*]isoquinoline-1,3(2*H*)-dione (4)

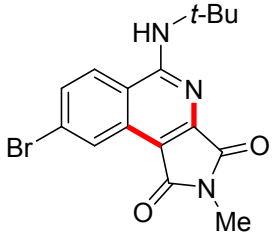
The general procedure **B** was followed using **3a** (48.0 mg, 0.15 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 5:1) yielded **4** (40 mg, 84%; without TEMPO:

33 mg, 70%) as a yellow solid. M. p. = 222 − 224 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 8.60 (d, J = 2.1 Hz, 1H), 7.67 (d, J = 9.0 Hz, 1H), 7.50 (dd, J = 9.0, 2.1 Hz, 1H), 5.83 (s, 1H), 3.17 (s, 3H), 1.65 (s, 9H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 169.0, 168.1, 159.2, 149.6, 138.6, 132.6, 128.4, 123.9, 123.7, 116.8, 109.2, 53.8, 28.9, 23.5. IR (ATR): 3428, 2973, 1696, 1538, 1434, 1205 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{16}H_{17}ClN_3O_2$ 318.1009; found 318.1014.



5-(*tert*-Butylamino)-8-fluoro-2-methyl-1*H*-pyrrolo[3,4-*c*]isoquinoline-1,3(2*H*)-dione (5)

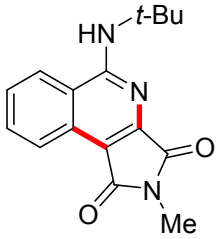
The general procedure **B** was followed using **3b** (45.5 mg, 0.15 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 5:1) yielded **5** (38 mg, 85%; without TEMPO: 31 mg, 68%) as a yellow solid. M. p. = 243 − 244 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 8.23 (dd, J = 9.3, 2.6 Hz, 1H), 7.78 (dd, J = 9.2, 5.0 Hz, 1H), 7.30 (dd, J = 8.6, 2.2 Hz, 1H), 5.84 (s, 1H), 3.17 (s, 3H), 1.65 (s, 9H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ =169.1, 168.2, 164.4 (d, $^{1}J_{C\text{-}F}$ = 254.5 Hz), 159.2, 149.7, 133.6 (d, $^{3}J_{C\text{-}F}$ = 11.6 Hz), 125.0 (d, $^{3}J_{C\text{-}F}$ = 9.8 Hz), 117.2 (d, $^{2}J_{C\text{-}F}$ = 24.8 Hz), 115.5 (d, $^{4}J_{C\text{-}F}$ = 1.7 Hz), 109.8 (d, $^{3}J_{C\text{-}F}$ = 4.5 Hz), 109.3 (d, $^{2}J_{C\text{-}F}$ = 22.3 Hz), 53.8, 29.0, 23.5. ^{19}F-NMR ($CDCl_3$, 376 MHz): δ = -105.05 (s). IR (ATR): 3360, 2971, 1698, 1522, 1347, 1199 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{16}H_{17}FN_3O_2$ 302.1305; found 302.1311.



8-Bromo-5-(*tert*-butylamino)-2-methyl-1*H*-pyrrolo[3,4-*c*]isoquinoline-1,3(2*H*)-dione (6)

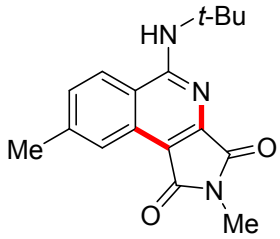
The general procedure **B** was followed using **3c** (726 mg, 2.0 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 5:1) yielded **6** [643 mg, 89%; 0.15 mmol scale:

(without TEMPO) 40 mg, 72%] as a yellow solid. M. p. = 250 − 251 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 8.75 (d, J = 2.1 Hz, 1H), 7.64 – 7.58 (m, 2H), 5.87 (s, 1H), 3.16 (s, 3H), 1.64 (s, 9H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 168.9, 168.0, 159.3, 149.5, 132.8, 132.7, 131.0, 127.1, 123.7, 117.1, 109.0, 53.8, 28.9, 23.5. IR (ATR): 3456, 2987, 1706, 1539, 1429, 1215 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{16}H_{17}BrN_3O_2$ 362.0504; found 362.0501.



5-(*tert*-Butylamino)-2-methyl-1*H*-pyrrolo[3,4-*c*]isoquinoline-1,3(2*H*)-dione (7)

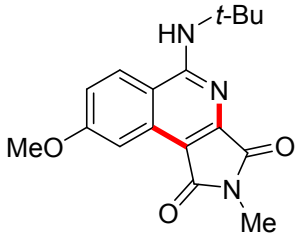
The general procedure **B** was followed using **3d** (43.0 mg, 0.15 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 6:1) yielded **7** (30 mg, 71%; without TEMPO: 18.2 mg, 43%) as a yellow solid. M. p. = 220 − 222 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 8.61 (d, J = 8.0 Hz, 1H), 7.74 (t, J = 8.0 Hz, 2H), 7.56 (td, J = 8.0, 1.5Hz, 1H), 5.90 (s, 1H), 3.17 (s, 3H), 1.65 (s, 9H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 169.5, 168.5, 159.3, 148.6, 131.8, 131.6, 127.8, 124.9, 122.0, 118.8, 110.2, 53.5, 29.0, 23.4. IR (ATR): 3467, 2918, 1684, 1521, 1363, 1211 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{16}H_{18}N_3O_2$ 284.1399; found 284.1403.



5-(*tert*-Butylamino)-2,8-dimethyl-1*H*-pyrrolo[3,4-*c*]isoquinoline-1,3(2*H*)-dione (8)

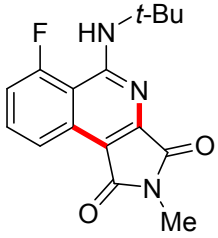
The general procedure **B** was followed using **3e** (45.0 mg, 0.15 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 6:1) yielded **8** (33.4 mg, 75%; without TEMPO: 26.2 mg, 59%) as a yellow solid. M. p. = 288 − 290 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 8.40 (s, 1H), 7.62 (d, J = 8.6 Hz, 1H), 7.38 (dd, J = 8.6, 1.3 Hz, 1H), 5.79 (s, 1H), 3.16 (s, 3H), 2.54 (s, 3H), 1.64 (s, 9H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 169.7, 168.6, 159.2, 148.7, 142.6, 131.8, 129.6, 124.1, 121.8, 116.8, 109.9, 53.4, 29.0, 23.4, 21.8. IR (ATR): 3608, 2919, 1685,

1508, 1430, 1361, 1059 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{17}H_{20}N_3O_2$ 298.1556; found 298.1553.



5-(*tert*-Butylamino)-8-methoxy-2-methyl-1*H*-pyrrolo[3,4-*c*]isoquinoline-1,3(2*H*)-dione (9)

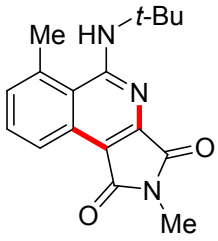
The general procedure **B** was followed using **3f** (48.0 mg, 0.15 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 4:1) yielded **9** (36.2 mg, 77%; without TEMPO: 33.8 mg, 72%) as a yellow solid. M. p. = 230 − 232 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.92 (d, J = 2.6 Hz, 1H), 7.64 (d, J = 9.3 Hz, 1H), 7.13 (dd, J = 9.3, 2.6 Hz, 1H), 5.73 (s, 1H), 3.97 (s, 3H), 3.16 (s, 3H), 1.63 (s, 9H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 169.8, 168.5, 162.2, 159.2, 149.4, 133.9, 123.8, 119.4, 113.1, 109.6, 103.3, 55.7, 53.4, 29.1, 23.4. IR (ATR): 3426, 2920, 1704, 1538, 1433, 1229 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{17}H_{20}N_3O_3$ 314.1505; found 314.1506.



5-(*tert*-Butylamino)-6-fluoro-2-methyl-1*H*-pyrrolo[3,4-*c*]isoquinoline-1,3(2*H*)-dione (10)

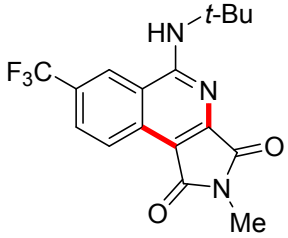
The general procedure **B** was followed using **3g** (45.0 mg, 0.15 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 5:1) yielded **10** (31.6 mg, 70%; without TEMPO: 11 mg, 24%;) as a yellow solid. M. p. = 196 − 198 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 8.40 (d, J = 8.1 Hz, 1H), 7.65 (td, J = 8.1, 5.5 Hz, 1H), 7.19 (dd, J = 14.7, 8.0 Hz, 1H), 7.09 (s, 1H), 3.16 (s, 3H), 1.63 (s, 9H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 169.1, 168.0, 160.1 (d, $^1J_{C\text{-}F}$ = 248.7 Hz), 158.5 (d, $^3J_{C\text{-}F}$ = 6.0 Hz), 149.8, 134.2 (d, $^3J_{C\text{-}F}$ = 2.5 Hz), 132.6 (d, $^3J_{C\text{-}F}$ = 10.9 Hz), 120.7 (d, $^3J_{C\text{-}F}$ = 4.1 Hz), 113.2 (d, $^2J_{C\text{-}F}$ = 25.6 Hz), 108.9 (d, $^3J_{C\text{-}F}$ = 8.9 Hz), 108.4 (d, $^3J_{C\text{-}F}$ = 3.5 Hz), 53.8, 28.9, 23.5. ^{19}F-NMR (CDCl3, 376 MHz): δ = -111.17 (s). IR

(ATR): 2918, 1698, 1540, 1497, 1448 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{16}H_{17}FN_3O_2$ 302.1305; found 302.1309.



5-(*tert*-Butylamino)-2,6-dimethyl-1*H*-pyrrolo[3,4-*c*]isoquinoline-1,3(2*H*)-dione (11)

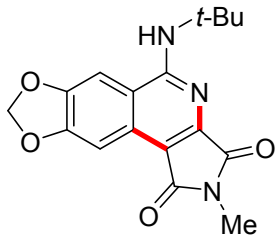
The general procedure **B** was followed using **3h** (45.0 mg, 0.15 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded **11** (24 mg, 54%; without TEMPO: 14.3 mg, 32%) as a yellow solid. M. p. = 204 − 206 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 8.51 (d, J = 7.7 Hz, 1H), 7.55 (t, J = 7.7 Hz, 1H), 7.30 (d, J = 7.7 Hz, 1H), 6.31 (s, 1H), 3.15 (s, 3H), 2.91 (s, 3H), 1.64 (s, 9H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 169.5, 168.4, 160.8, 148.3, 133.7, 133.6, 131.6, 131.2, 122.8, 119.5, 109.8, 54.0, 29.0, 24.9, 23.4. IR (ATR): 3453, 2918, 1674, 1531, 1363, cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{17}H_{20}N_3O_2$ 298.1556; found 298.1563.



5-(*tert*-Butylamino)-2-methyl-7-(trifluoromethyl)-1*H*-pyrrolo[3,4-*c*]isoquinoline-1,3(2*H*)-dione (12)

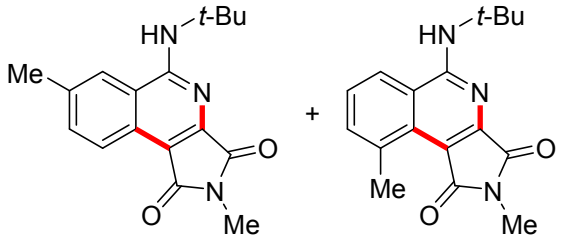
The general procedure **B** was followed using **3i** (53.0 mg, 0.15 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 5:1) yielded **12** (37.4 mg, 71%; 29 mg, 55%) as a yellow solid. M. p. = 233 − 235 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 8.75 (d, J = 8.6 Hz, 1H), 7.98 (s, 1H), 7.94 (d, J = 8.6 Hz, 1H), 5.94 (s, 1H), 3.19 (s, 3H), 1.68 (s, 9H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 168.8, 167.8, 159.5, 150.4, 133.7, 129.3 (q, $^2J_{C\text{-}F}$ = 32.8 Hz), 127.8 (q, $^3J_{C\text{-}F}$ = 3.2 Hz), 125.9, 123.7 (q, $^1J_{C\text{-}F}$ = 272.7 Hz), 119.7 (q, $^3J_{C\text{-}F}$ = 4.1 Hz), 117.8, 109.5, 54.1, 28.9, 23.6. ^{19}F-NMR (CDCl3, 376 MHz): δ = -62.37 (s). IR (ATR): 3393, 2921, 1705, 1543,

1434, 1298, 1121 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{17}H_{17}F_3N_3O_2$ 352.1273; found 352.1279.



5-(*tert*-Butylamino)-2-methyl-1*H*-[1,3]dioxolo[4,5-*g*]pyrrolo[3,4-*c*]isoquinoline-1,3(2*H*)-dione (13)

The general procedure **B** was followed using **4j** (49.4 mg, 0.15 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 3:1) yielded **13** (32.9 mg, 67%; without TEMPO: 21.6 mg, 44%) as a yellow solid. M. p. = 267 − 269 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.97 (s, 1H), 7.01 (s, 1H), 6.12 (s, 2H), 5.37 (s, 1H), 3.14 (s, 3H), 1.62 (s, 9H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 169.6, 168.6, 158.4, 151.8, 149.1, 129.6, 114.8, 110.7, 102.2, 101.9, 99.5, 53.3, 29.7, 29.2, 23.4. IR (ATR): 3433, 2920, 1694, 1511, 1363, 1245 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{17}H_{18}N_3O_4$ 328.1297; found 328.1303.



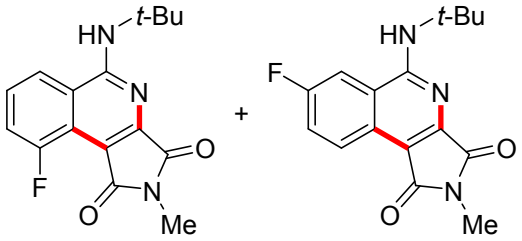
14 **14'**

ratio of **14**:**14'** = 5:4

5-(*tert*-Butylamino)-2,9-dimethyl-1*H*-pyrrolo[3,4-*c*]isoquinoline-1,3(2*H*)-dione (14) & 5-(*tert*-butylamino)-2,7-dimethyl-1*H*-pyrrolo[3,4-*c*]isoquinoline-1,3(2*H*)-dione (14')

The general procedure **B** was followed using **3k** (45.0 mg, 0.15 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 5:2) yielded mixture products **14** & **14'** (4:5) (28.5 mg, 64%; without TEMPO: 22 mg, 49%) as a yellow solid. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 8.49 (d, J = 8.4 Hz, 1.4 H), 7.62 -7.53 (m , 3.4 H), 7.50 (s, 1.4 H), 7.48 – 7.42 (m, 1H), 5.90 (s, 1H), 5.81 (s, 1.4 H), 3.17 (s, 3H), 3.15 (s, 4.2 H), 3.00 (s, 3H), 2.54 (s, 4.2H),

1.65 (s, 21.7H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 169.6, 168.8, 168.7, 167.9, 159.8, 158.8, 149.9, 147.7, 138.1, 136.5, 134.3, 133.7, 132.4, 129.5, 127.6, 124.6, 121.4, 119.8, 119.7, 118.9, 110.8, 110.4, 53.5, 53.3, 29.0, 29.0, 25.0, 23.8, 23.4, 22.1. IR (ATR): 3338, 2920, 1684, 1523, 1355, 1206 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{17}H_{20}N_3O_2$ 298.1556; found 298.1557.



15 **15'**

ratio of **15**:**15'** = 9:8

total yield: 83%
51% (without TEMPO)

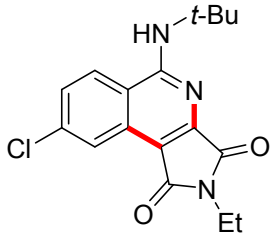
5-(*tert*-Butylamino)-9-fluoro-2-methyl-1*H*-pyrrolo[3,4-*c*]isoquinoline-1,3(2*H*)-dione (15)

The general procedure **B** was followed using **3l** (45.5 mg, 0.15 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 3:1) yielded **15** (19.9 mg, without TEMPO: 12.2 mg) & **15'** (15.6 mg, without TEMPO: 10.8 mg) as yellow solids, respectively. M. p. = 253 − 256 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 8.66 (dd, J = 9.0, 5.8 Hz, 1H), 7.53 (td, J = 9.0, 2.4 Hz, 1H), 7.38 (dd, J = 9.0, 2.3 Hz, 1H), 5.65 (s, 1H), 3.17 (s, 3H), 1.65 (s, 9H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ =169.2, 168.3, 161.7 (d, $^1J_{C\text{-}F}$ = 250.9 Hz), 158.6, 147.8 (d, $^3J_{C\text{-}F}$ = 2.3 Hz), 128.4, 127.6 (d, $^3J_{C\text{-}F}$ = 8.5 Hz), 121.4 (d, $^2J_{C\text{-}F}$ = 23.6 Hz), 120.0 (d, $^3J_{C\text{-}F}$ = 7.3 Hz), 110.3, 107.2 (d, $^2J_{C\text{-}F}$ = 22.7 Hz), 53.67, 28.92, 23.47. ^{19}F-NMR ($CDCl_3$, 376 MHz): δ = -109.11 (s). IR (ATR): 3491, 2919, 1698, 1522, 1362, 1207 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{16}H_{17}FN_3O_2$ 302.1305; found 302.1308.

5-(*tert*-Butylamino)-7-fluoro-2-methyl-1*H*-pyrrolo[3,4-*c*]isoquinoline-1,3(2*H*)-dione (15')

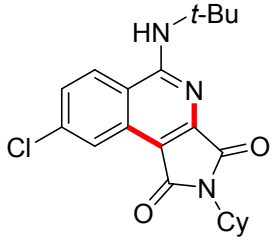
M. p. = 265 − 267 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.55 (dd, J = 5.5, 3.2 Hz, 2H), 7.51 – 7.43 (m, 1H), 5.91 (s, 1H), 3.20 (s, 3H), 1.66 (s, 9H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 167.6, 166.6, 158.7, 158.3 (d, $^1J_{C\text{-}F}$ = 260.1 Hz), 150.0, 128.32 (d, $^3J_{C\text{-}F}$ = 7.5 Hz), 121.81 (d, $^2J_{C\text{-}F}$ = 22.2 Hz), 120.62 (d, $^3J_{C\text{-}F}$ = 6.7 Hz), 117.91 (d, $^3J_{C\text{-}F}$ = 4.2 Hz), 117.45 (d, $^2J_{C\text{-}F}$ = 20.4 Hz), 108.14 (d, $^3J_{C\text{-}F}$ = 6.0 Hz), 53.8, 28.9, 23.8. ^{19}F-NMR ($CDCl_3$, 376 MHz): δ = -102.84 (s). IR

(ATR): 3483, 2918, 1698, 1498, 1362, 1206 cm^{-1}. HRMS (ESI) m/z: $[M+H^+]$ calcd for $C_{16}H_{17}FN_3O_2$ 302.1305; found 302.1311.



5-(*tert*-Butylamino)-8-chloro-2-ethyl-1*H*-pyrrolo[3,4-*c*]isoquinoline-1,3(2*H*)-dione (16)

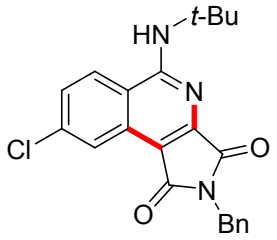
The general procedure **B** was followed using **3m** (50.0 mg, 0.15 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 5:1) yielded **16** (42 mg, 85%; without TEMPO: 34 mg, 68%) as a yellow solid. M. p. = 204 − 206 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 8.59 (d, J = 2.0 Hz, 1H), 7.70 (d, J = 9.0 Hz, 1H), 7.48 (dd, J = 9.0, 2.0 Hz, 1H), 5.89 (s, 1H), 3.73 (q, J = 7.2 Hz, 2H), 1.64 (s, 9H), 1.28 (t, J = 7.2 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 168.8, 167.8, 159.3, 149.5, 138.6, 132.6, 128.4, 123.9, 123.8, 116.9, 109.1, 53.7, 32.5, 28.9, 14.2. IR (ATR): 3407, 2973, 1701, 1537, 1434, 1206 cm^{-1}. HRMS (ESI) m/z: $[M+H^+]$ calcd for $C_{17}H_{19}ClN_3O_2$ 332.1166; found 332.1170.



5-(*tert*-Butylamino)-8-chloro-2-cyclohexyl-1*H*-pyrrolo[3,4-*c*]isoquinoline-1,3(2*H*)-dione (17)

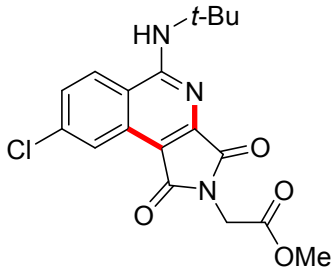
The general procedure **B** was followed using **3n** (58.0 mg, 0.15 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 7:1) yielded **17** (41 mg, 71%; without TEMPO: 34 mg, 59%) as a yellow solid. M. p. = 240 − 242 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 8.61 (d, J = 2.1 Hz, 1H), 7.68 (d, J = 9.0 Hz, 1H), 7.48 (dd, J = 9.0, 2.1 Hz, 1H), 5.83 (s, 1H), 4.10 (tt, J = 12.4, 3.5 Hz, 1H), 2.21 (td, J = 12.4, 3.5 Hz, 2H), 1.87 (d, J = 13.3 Hz, 2H), 1.75 (d, J = 10.9 Hz, 2H), 1.64 (s, 9H), 1.45 – 1.17 (m, 4H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 169.1, 168.0, 159.2, 149.1, 138.6, 132.6, 128.3, 123.9, 123.7, 117.0, 108.8, 53.7, 50.5, 30.2, 28.9,

26.1, 25.3. ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 169.08, 167.95, 159.24, 149.10, 138.55, 132.65, 128.27, 123.92, 123.70, 116.98, 108.83, 53.72, 50.45, 30.21, 28.96, 26.14, 25.27. IR (ATR): 2919, 1700, 1507, 1363, 1176 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{21}H_{25}ClN_3O_2$ 386.1635; found 386.1632.



2-Benzyl-5-(*tert*-butylamino)-8-chloro-1*H*-pyrrolo[3,4-*c*]isoquinoline-1,3(2*H*)-dione (18)

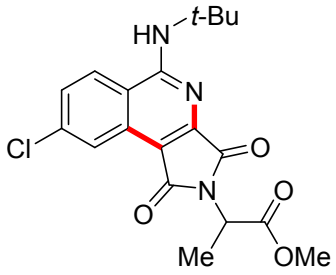
The general procedure **B** was followed using **3o** (59.0 mg, 0.15 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 7:1) yielded **18** (48.3 mg, 82%; without TEMPO: 36 mg, 61%) as a yellow solid. M. p. = 228 − 230 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 8.58 (d, J = 2.0 Hz, 1H), 7.63 (d, J = 9.0 Hz, 1H), 7.46 (dd, J = 9.0, 2.0 Hz, 3H), 7.31 (t, J = 7.5 Hz, 2H), 7.24 (d, J = 7.5 Hz, 1H), 5.83 (s, 1H), 4.84 (s, 2H), 1.63 (s, 9H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 168.5, 167.6, 159.2, 149.4, 138.7, 136.9, 132.6, 128.6, 128.6, 128.4, 127.7, 124.0, 123.7, 116.9, 109.1, 53.8, 41.2, 28.9. IR (ATR): 2972, 1704, 1539, 1392, 1208 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{22}H_{21}ClN_3O_2$ 394.1322; found 394.1324.



Methyl 2-[5-(*tert*-butylamino)-8-chloro-1,3-dioxo-1,3-dihydro-2*H*-pyrrolo[3,4-*c*]isoquinolin-2-yl]acetate (19)

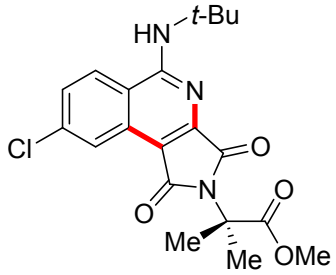
The general procedure **B** was followed using **3p** (57.0 mg, 0.15 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 3:1) yielded **19** (45.6 mg, 81%; without TEMPO: 30 mg, 53%) as a yellow solid. M. p. = 222 − 225 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 8.37 (d, J = 2.0 Hz, 1H), 7.72 (d, J = 9.0 Hz, 1H), 7.46 (dd, J = 9.0, 2.0 Hz, 1H), 6.08 (s,

1H), 4.45 (s, 2H), 3.81 (s, 3H), 1.61 (s, 9H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 168.6, 167.7, 167.1, 159.4, 149.3, 138.7, 132.3, 128.7, 123.9, 123.7, 116.8, 109.0, 54.00 52.7, 38.4, 28.9. IR (ATR): 3416, 2919, 1706, 1539, 1435, 1206 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{18}H_{19}ClN_3O_4$ 376.1064; found 376.1067.



Methyl 2-[5-(*tert*-butylamino)-8-chloro-1,3-dioxo-1,3-dihydro-2*H*-pyrrolo[3,4-*c*]isoquinolin-2-yl]propanoate (20)

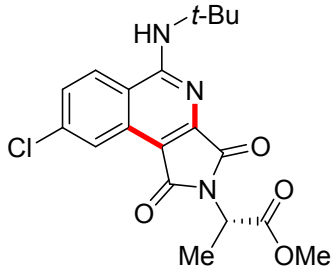
The general procedure **B** was followed using **3q** (58.5 mg, 0.15 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 3:1) yielded **20** (43.8 mg, 75%; without TEMPO: 31.5 mg, 54%) as a yellow solid. M. p. = 292 − 294 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 8.48 (d, J = 2.0 Hz, 1H), 7.71 (d, J = 9.0 Hz, 1H), 7.48 (dd, J = 9.0, 2.0 Hz, 1H), 5.97 (s, 1H), 4.98 (q, J = 7.3 Hz, 1H), 3.77 (s, 3H), 1.72 (d, J = 7.3 Hz, 3H), 1.63 (s, 9H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 170.8, 167.9, 167.0, 159.4, 149.2, 138.7, 132.4, 128.6, 123.9, 123.8, 117.0, 109.0, 53.9, 52.7, 47.1, 28.9, 15.5. IR (ATR): 3430, 2918, 1694, 1551, 1333, 1271 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{19}H_{21}ClN_3O_4$ 390.1221; found 390.1227.



Methyl 2-[5-(*tert*-butylamino)-8-chloro-1,3-dioxo-1,3-dihydro-2*H*-pyrrolo[3,4-*c*]isoquinolin-2-yl]-2-methylpropanoate (21)

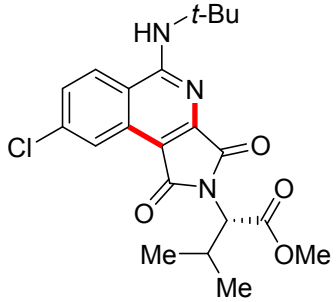
The general procedure **B** was followed using **3r** (61.0 mg, 0.15 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 3:1) yielded **21** (49 mg, 81%; without TEMPO:

40.5 mg, 67%) as a yellow solid. M. p. = 192 − 194 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 8.52 (d, J = 2.0 Hz, 1H), 7.70 (d, J = 9.0 Hz, 1H), 7.48 (dd, J = 9.0, 2.0 Hz, 1H), 5.92 (s, 1H), 3.79 (s, 3H), 1.85 (s, 6H), 1.63 (s, 9H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 173.8, 168.9, 167.7, 159.4, 148.9, 138.7, 132.4, 128.5, 123.9, 123.8, 117.1, 108.5, 59.9, 53.8, 52.7, 28.9, 24.7. IR (ATR): 3429, 2921, 1698, 1542, 1334, 1267, 1149 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{20}H_{23}ClN_3O_4$ 404.1377; found 404.1381.



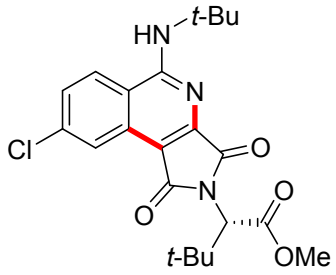
Methyl (*S*)-2-[5-(*tert*-butylamino)-8-chloro-1,3-dioxo-1,3-dihydro-2*H*-pyrrolo[3,4-*c*]isoquinolin-2-yl]propanoate (22)

The general procedure **B** was followed using **3s** (59.0 mg, 0.15 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 3:1) yielded **21** (42.6 mg, 73%; without TEMPO: 36 mg, 62%) as a yellow solid. M. p. = 292 − 294 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 8.52 (d, J = 2.0 Hz, 1H), 7.69 (d, J = 9.0 Hz, 1H), 7.49 (dd, J = 9.0, 2.0 Hz, 1H), 5.93 (s, 1H), 4.98 (q, J = 7.3 Hz, 1H), 3.77 (s, 3H), 1.72 (d, J = 7.3 Hz, 3H), 1.64 (s, 9H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 170.7, 167.9, 167.0, 159.3, 149.2, 138.7, 132.5, 128.6, 123.9, 123.7, 117.0, 109.0, 53.9, 52.7, 47.1, 28.9, 15.5. IR (ATR): 3430, 2918, 1694, 1551, 1333, 1271 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{19}H_{21}ClN_3O_4$ 390.1221; found 390.1228.



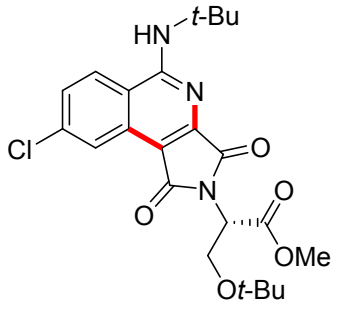
Methyl (*S*)-2-[5-(*tert*-butylamino)-8-chloro-1,3-dioxo-1,3-dihydro-2*H*-pyrrolo[3,4-*c*]isoquinolin-2-yl]-3-methylbutanoate (23)

The general procedure **B** was followed using **3t** (63.0 mg, 0.15 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 3:1) yielded **23** (48.8 mg, 78%; without TEMPO: 39 mg, 62%) as a yellow solid. M. p. = 175 − 177 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 8.57 (d, J = 2.2 Hz, 1H), 7.70 (d, J = 9.0 Hz, 1H), 7.49 (dd, J = 9.0, 2.2 Hz, 1H), 5.94 (s, 1H), 4.66 (d, J = 8.2 Hz, 1H), 3.73 (s, 3H), 2.65 – 2.47 (m, 1H), 1.65 (s, 9H), 1.13 (d, J = 7.0 Hz, 3H), 0.90 (d, J = 7.0 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 169.8, 168.2, 167.3, 159.4, 149.0, 138.7, 132.5, 128.6, 124.1, 123.7, 117.1, 108.9, 56.7, 53.9, 52.3, 34.7, 29.0, 25.9, 16.9. IR (ATR): 3467, 2901, 1704, 1540, 1436, 1248 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{21}H_{25}ClN_3O_4$ 418.1534; found 418.1531.



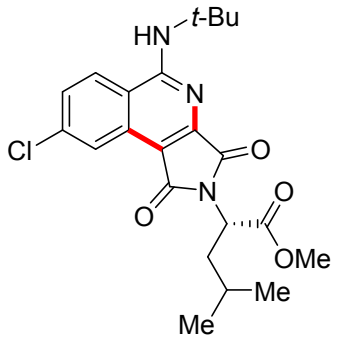
Methyl (*S*)-2-[5-(*tert*-butylamino)-8-chloro-1,3-dioxo-1,3-dihydro-2*H*-pyrrolo[3,4-*c*]isoquinolin-2-yl]-3,3-dimethylbutanoate (24)

The general procedure **B** was followed using **3u** (65.0 mg, 0.15 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 4:1) yielded **24** (56.2 mg, 87%; without TEMPO: 48 mg, 74%) as a yellow solid. M. p. = 93 − 95 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 8.59 (d, J = 2.1 Hz, 1H), 7.71 (d, J = 9.0 Hz, 1H), 7.49 (dd, J = 9.0, 2.1 Hz, 1H), 5.94 (s, 1H), 4.63 (s, 1H), 3.68 (s, 3H), 1.65 (s, 9H), 1.20 (s, 9H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 168.7, 168.4, 167.6, 159.5, 149.0, 138.7, 132.6, 128.6, 124.1, 123.7, 117.1, 108.9, 59.4, 53.9, 51.9, 35.7, 28.9, 27.9. IR (ATR): 3447, 2966, 1699, 1540, 1339, 1207 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{22}H_{27}ClN_3O_4$ 432.1690; found 432.1694.



Methyl (*S*)-3-(*tert*-butoxy)-2-[5-(*tert*-butylamino)-8-chloro-1,3-dioxo-1,3-dihydro-2*H*-pyrrolo[3,4-*c*]isoquinolin-2-yl]propanoate (25)

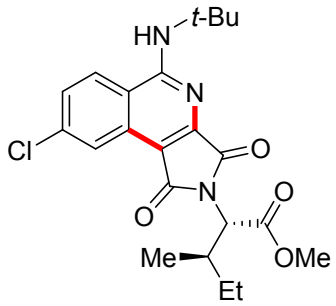
The general procedure **B** was followed using **3v** (69.5 mg, 0.15 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 2:1) yielded **25** (57 mg, 82%; without TEMPO: 42 mg, 61%) as a yellow solid. M. p. = 173 − 175 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 8.52 (d, J = 2.1 Hz, 1H), 7.71 (d, J = 9.0 Hz, 1H), 7.47 (dd, J = 9.0, 2.1 Hz, 1H), 5.95 (s, 1H), 5.04 (dd, J = 8.4, 6.5 Hz, 1H), 4.10 (s, 1H), 4.08 (d, J = 1.9 Hz, 1H), 3.77 (s, 3H), 1.64 (s, 9H), 1.14 (s, 9H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 168.9, 168.0, 167.1, 159.4, 149.1, 138.6, 132.5, 128.5, 123.9, 123.8, 117.0, 109.0, 73.7, 59.2, 53.6, 52.7, 52.6, 28.9, 27.5.IR (ATR): 3412, 2920, 1705, 1539, 1392, 1208 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{23}H_{29}ClN_3O_5$ 462.1796; found 462.1794.



Methyl (*S*)-2-[5-(*tert*-butylamino)-8-chloro-1,3-dioxo-1,3-dihydro-2*H*-pyrrolo[3,4-*c*]isoquinolin-2-yl]-4-methylpentanoate (26)

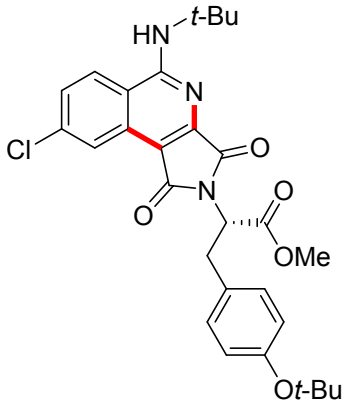
The general procedure **B** was followed using **3w** (65.0 mg, 0.15 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 3:1) yielded **26** (51 mg, 79%; without TEMPO: 36 mg, 56%) as a yellow solid. M. p. = 97 − 99 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 8.50 (d, J = 2.1 Hz, 1H), 7.71 (d, J = 9.0 Hz, 1H), 7.47 (dd, J = 9.0, 2.1 Hz, 1H), 5.98 (s, 1H), 4.95 (dd,

J = 11.7, 4.3 Hz, 1H), 3.76 (s, 3H), 2.37 (ddd, J = 14.3, 11.7, 4.3 Hz, 1H), 1.96 (ddd, J = 14.3, 11.7, 4.3 Hz, 1H), 1.63 (s, 9H), 1.53 (dd, J = 6.7, 2.7 Hz, 1H), 0.97 (d, J = 6.7 Hz, 3H), 0.94 (d, J = 6.7 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 170.9, 168.2, 167.3, 159.4, 149.1, 138.7, 132.4, 128.6, 123.9, 123.8, 117.0, 108.9, 53.9, 52.6, 50.3, 37.5, 28.9, 25.1, 23.2, 21.0. IR (ATR): 3411, 2958, 1707, 1539, 1435, 1207 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{22}H_{27}ClN_3O_4$ 432.1690; found 432.1697.



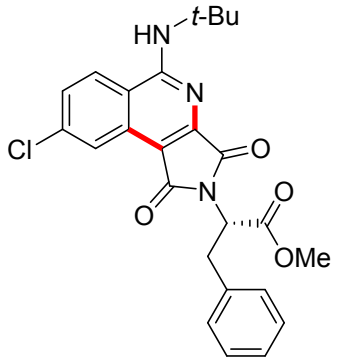
Methyl (2*S*,3*R*)-2-[5-(*tert*-butylamino)-8-chloro-1,3-dioxo-1,3-dihydro-2*H*-pyrrolo[3,4-*c*]isoquinolin-2-yl]-3-methylpentanoate (27)

The general procedure **B** was followed using **3x** (65.0 mg, 0.15 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 3:1) yielded **27** (52.4 mg, 81%; without TEMPO: 41 mg, 63%) as a yellow solid. M. p. = 116 − 118 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 8.55 (d, J = 1.8 Hz, 1H), 7.71 (d, J = 9.0 Hz, 1H), 7.48 (dd, J = 9.0, 1.8 Hz, 1H), 5.97 (s, 1H), 4.66 (d, J = 8.2 Hz, 1H), 3.73 (s, 3H), 2.65 – 2.47 (m, 1H), 1.64 (s, 9H), 1.62 – 1.51 (m, 2H), 1.13 (d, J = 7.0 Hz, 3H), 0.90 (d, J = 7.0 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 169.9, 168.2, 167.3, 159.5, 149.0, 138.7, 132.5, 128.6, 124.0, 123.8, 117.1, 108.9, 56.7, 53.9, 52.3, 34.7, 28.9, 25.9, 16.8, 11.0. IR (ATR): 3420, 2968, 1706, 1540, 1373, 1207 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{22}H_{27}ClN_3O_4$ 432.1690; found 432.1694.



Methyl (*S*)-3-[4-(*tert*-butoxy)phenyl]-2-[5-(*tert*-butylamino)-8-chloro-1,3-dioxo-1,3-dihydro-2*H*-pyrrolo[3,4-*c*]isoquinolin-2-yl]propanoate (28)

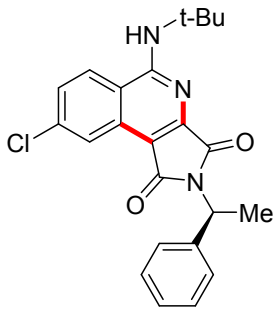
The general procedure **B** was followed using **3y** (81.0 mg, 0.15 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 2:1) yielded **28** (59 mg, 73%; without TEMPO: 41 mg, 50%) as a yellow solid. M. p. = 114 − 116 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 8.43 (d, J = 2.2 Hz, 1H), 7.64 (d, J = 9.0 Hz, 1H), 7.44 (dd, J = 9.0, 2.2 Hz, 1H), 7.08 (d, J = 8.4 Hz, 2H), 6.80 (d, J = 8.4 Hz, 2H), 5.88 (s, 1H), 5.11 (dd, J = 10.8, 5.8 Hz, 1H), 3.79 (s, 3H), 3.59 – 3.46 (m, 2H), 1.60 (s, 9H), 1.20 (s, 9H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 169.9, 167.8, 166.9, 159.3, 154.0, 148.8, 138.6, 132.4, 131.9, 129.4, 128.5, 124.3, 123.9, 123.7, 116.9, 108.7, 78.2, 53.8, 52.9, 52.7, 34.2, 28.9, 28.7. IR (ATR): 3407, 2923, 1705, 1540, 1435, 1206 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{29}H_{33}ClN_3O_5$ 538.2109; found 538.2116.



Methyl (*S*)-2-[5-(*tert*-butylamino)-8-chloro-1,3-dioxo-1,3-dihydro-2*H*-pyrrolo[3,4-*c*]isoquinolin-2-yl]-3-phenylpropanoate (29)

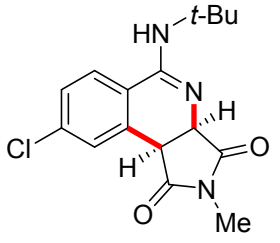
The general procedure **B** was followed using **3z** (70.0 mg, 0.15 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 4:1) yielded **29** (51.6 mg, 74%; without

TEMPO: 36 mg, 52%) as a yellow solid. M. p. = 183 − 185 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 8.46 (d, J = 1.1 Hz, 1H), 7.63 (d, J = 9.0 Hz, 1H), 7.44 (dd, J = 9.0, 1.4 Hz, 1H), 7.26 (s, 1H), 7.22 (s, 1H), 7.22 –7.18 (m, 2H), 7.17 –7.10(m, 1H), 5.88 (s, 1H), 5.17 (dd, J = 10.4, 5.9 Hz, 1H), 3.79 (s, 3H), 3.65 – 3.44 (m, 2H), 1.61 (s, 9H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 169.9, 167.9, 167.1, 159.3, 149.0, 138.6, 137.1, 132.5, 129.0, 128.9, 128.6, 126.7, 124.0, 123.7, 117.0, 108.9, 53.9, 52.9, 52.8, 34.9, 28.9. IR (ATR): 3427, 2918, 1702, 1541, 1363, 1208 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{25}H_{25}ClN_3O_4$ 466.1534; found 466.1538.



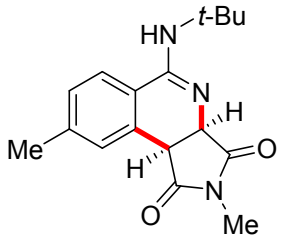
(*S*)-5-(*Tert*-butylamino)-8-chloro-2-(1-phenylethyl)-1*H*-pyrrolo[3,4-*c*]isoquinoline-1,3(2*H*)-dione (30)

The general procedure **B** was followed using **3aa** (61.5 mg, 0.15 mmol) for 12 h. Purification by column chromatography (*n*-hexane/EtOAc 5:1) yielded **30** (57 mg, 93%; without TEMPO: 43.5 mg, 70%) as a yellow solid. M. p. = 181 − 183 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 8.60 (d, J = 2.1 Hz, 1H), 7.63 (d, J = 9.0 Hz, 1H), 7.54 (d, J = 7.5 Hz, 2H), 7.47 (dd, J = 9.0, 2.1 Hz, 1H), 7.33 (t, J = 7.5 Hz, 2H), 7.25 – 7.18 (m, 1H), 5.80 (s, 1H), 5.56 (q, J = 7.3 Hz, 1H), 1.94 (d, J = 7.3 Hz, 3H), 1.63 (s, 9H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 168.7, 167.7, 159.2, 149.1, 149.0, 140.8, 138.6, 132.6, 128.4, 128.4, 127.5, 124.0, 123.6, 117.0, 108.9, 53.8, 49.2, 29.0, 17.7. IR (ATR): 3417, 2973, 1697, 1533, 1337, 1222 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{23}H_{23}ClN_3O_2$ 408.1479; found 408.1482.



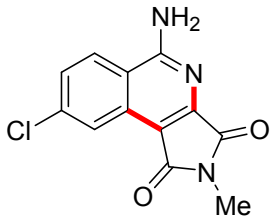
5-(*Tert*-butylamino)-8-chloro-2-methyl-3a,9b-dihydro-1*H*-pyrrolo[3,4-*c*]isoquinoline-1,3(2*H*)-dione (31)

A suspension of **3a** (48.0 mg, 0.15 mmol) with Trifluoroacetic acid (35.0 mg, 0.30 mmol) in HFIP (1,1,1,3,3,3-hexafluoro-2-propanol) (3.0 mL) was stirred at 23 °C for 12 h with visible light (20 W).The solvent was diluted with EtOAc and washed with $NaHCO_3$ (2 x 10mL), The combined organic layers were concentrated in vacuum and the remaining residue was purified by column chromatography (*n*-hexane/EtOAc 3:1) yielded **31** (42 mg, 88%) as a white solid. M. p. = 135 − 137 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.65 (s, 1H), 7.38 – 7.28 (m, 2H), 4.92 (d, J = 8.7 Hz, 1H), 4.64 (s, 1H), 3.90 (d, J = 8.7 Hz, 1H), 3.02 (s, 3H), 1.45 (s, 9H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 177.0, 175.8, 150.1, 136.8, 131.7, 130.2, 128.3, 123.6, 122.5, 58.1, 51.8, 39.9, 28.8, 25.1. IR (ATR): 3404, 2929, 1698, 1530, 1431, 1271, 1117 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{16}H_{19}ClN_3O_2$ 320.1166; found 320.1172.



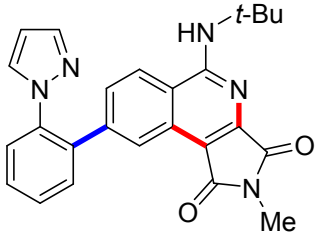
5-(*Tert*-butylamino)-2,8-dimethyl-3a,9b-dihydro-1*H*-pyrrolo[3,4-*c*]isoquinoline-1,3(2*H*)-dione (32)

A suspension of **3e** (45.0 mg, 0.15 mmol) with Trifluoroacetic acid (35.0 mg, 0.30 mmol) in HFIP (3.0 mL) was stirred at 23 °C for 12 h with visible light (20 W).The solvent was diluted with EtOAc and washed with $NaHCO_3$ (2 x 10mL), The combined organic layers were concentrated in vacuum and the remaining residue was purified by column chromatography (*n*-hexane/EtOAc 3:1) yielded **32** (21 mg, 47%) as a white solid. M. p. = 130 − 133 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.45 (s, 1H), 7.25 (d, J = 8.0 Hz, 1H), 7.15 (d, J = 8.0 Hz, 1H), 4.90 (d, J = 8.7 Hz, 1H), 4.69 (s, 1H), 3.89 (d, J = 8.7 Hz, 1H), 3.00 (s, 3H), 2.41 (s, 3H), 1.45 (s, 9H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 177.6, 176.6, 151.1, 141.3, 130.7, 129.7, 128.9, 122.2, 121.6, 58.2, 51.6, 40.3, 28.9, 25.1, 21.4. IR (ATR): 3398, 2924, 1698, 1533, 1449, 1266, 1115 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{17}H_{22}N_3O_2$ 300.1712; found 300.1715.



5-Amino-8-chloro-2-methyl-1*H*-pyrrolo[3,4-*c*]isoquinoline-1,3(2*H*)-dione (33)

A suspension of **4** (96.0 mg, 0.30 mmol) and TBDMSOTf (79.0 mg, 0.30 mmol) in DCM (10mL) was stirred at 23 °C for 12 h.[3] Purification by column chromatography (*n*-hexane/EtOAc 1:2, 5% Et_3N) yielded **33** (72 mg, 92%) as a yellow solid. M. p. > 300 °C. ^{1}H-NMR (DMSO, 400 MHz): δ = 8.39 (s, 1H), 8.37 (s, 2H), 8.27 (d, J = 2.2 Hz, 1H), 7.68 (dd, J = 9.0, 2.2 Hz, 1H), 2.99 (s, 3H). ^{13}C-NMR (DMSO, 100 MHz): δ = 168.8, 167.9, 163.1, 151.2, 138.3, 132.8, 128.2, 128.0, 122.0, 116.2, 108.4, 23.7. IR (ATR): 3344, 2973, 1689, 1521, 1362, 1205 cm^{-1}. HRMS (ESI) m/z: [M+H$^+$] calcd for $C_{12}H_9ClN_3O_2$ 262.0383; found 262.0391.



8-[2-(1*H*-Pyrazol-1-yl)phenyl]-5-(*tert*-butylamino)-2-methyl-1*H*-pyrrolo[3,4-*c*]isoquinoline-1,3(2*H*)-dione (35)

A suspension of **4** (48 mg, 0.15 mmol), *N*-phenylpyrazole (14.0 mg, 0.10 mmol) $[RuCl_2(p\text{-cymene})]_2$ (3.0 mg, 5 mmol %) and K_2CO_3 (28.0 mg, 0.20 mmol) in toluene (2 mL) was stirred at 120 °C for 12 h under an atmosphere of Ar. At ambient temperature, the solvent was evaporated *in vacuo* and the remaining residue was purified column chromatography (*n*-hexane/EtOAc 4:1) yielded **35** (17 mg, 40%) as a yellow solid. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 8.61 (d, J = 1.8 Hz, 1H), 7.65 – 7.50 (m, 6H), 7.20 (d, J = 2.3 Hz, 1H), 7.03 (dd, J = 8.7, 1.8 Hz, 1H), 6.22 (t, J = 2.3 Hz, 1H), 5.81 (s, 1H), 3.17 (s, 3H), 1.63 (s, 9H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 169.3, 168.4, 159.1, 149.0, 142.7, 140.5, 138.7, 135.3, 131.9, 131.4, 131.3, 129.4, 128.7, 128.2, 126.8, 124.2, 121.8, 117.6, 110.1, 106.8, 53.6, 28.9, 23.5. IR

(ATR): 3438, 2971, 1682, 1543, 1205 cm^{-1}. HRMS (ESI) m/z: $[M+H^+]$ calcd for $C_{25}H_{24}N_5O_2$ 426.1930; found 426.1937.

Optical Data

UV-VIS-NIR spectra were recorded using a Perkin-Elmer Lambda 1050 spectrometer equipped with a 150 mm integrating sphere and photomultiplier tube (PMT) and InGaAs detectors.

Steady-state photoluminescence (PL) measurements and t**ime-correlated single photon counting** (TCSPC) measurements were performed using a PicoQuant FluoTime 300 spectrometer equipped with a 378 nm picosecond diode laser (pulse power 0.99 nJ cm^{-2}, pulse rate 40 MHz). Quantum yields were measured with the same setup but equipped with an integrating sphere.

UV-Vis and PL spectroscopy

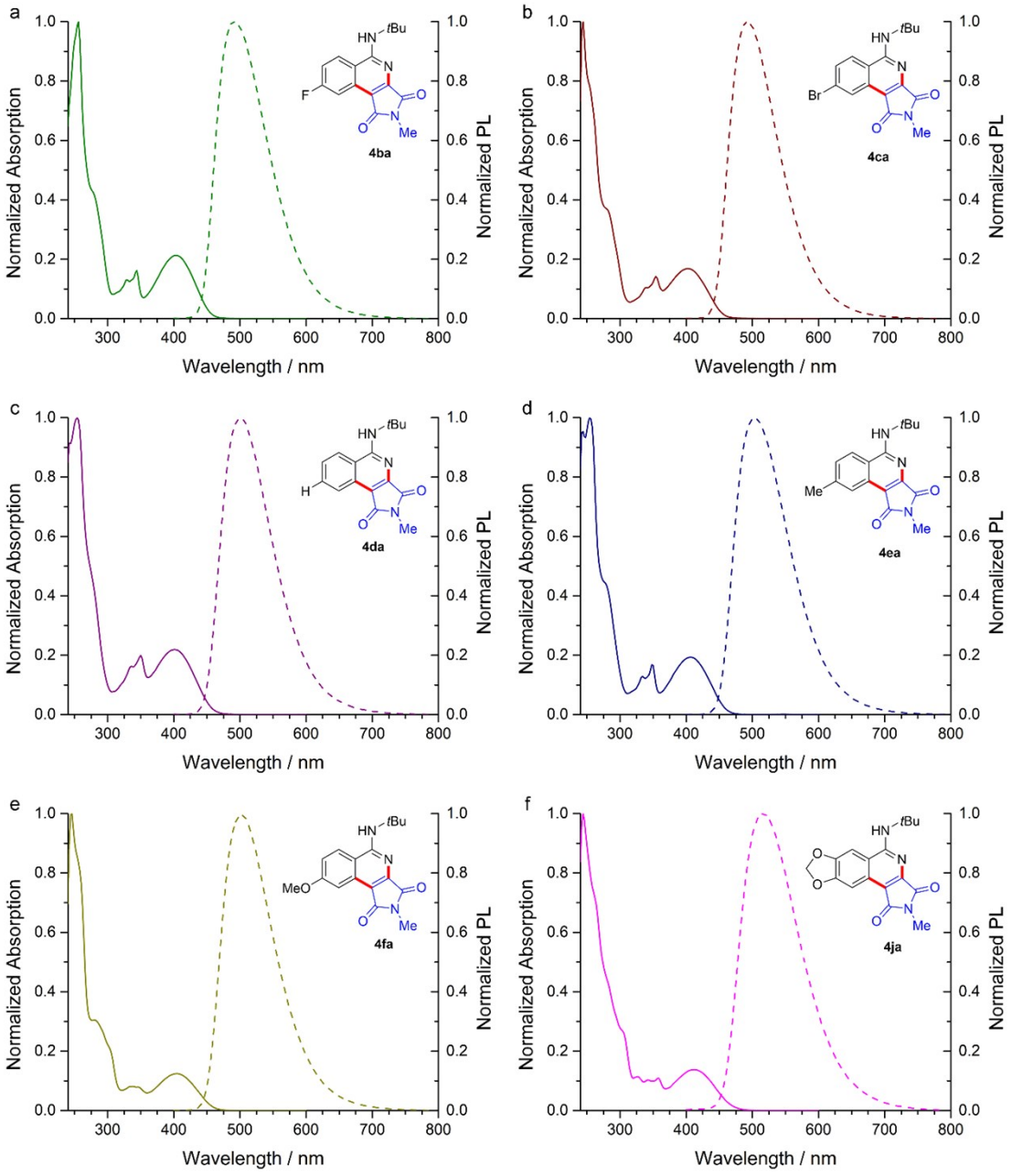


Figure S1: Normalized absorption and photoluminescence spectra of compound **4ba**, **4ca**, **4da**, **4ea**, **4fa** and **4ja** in solution (50 µM in CHCl3).

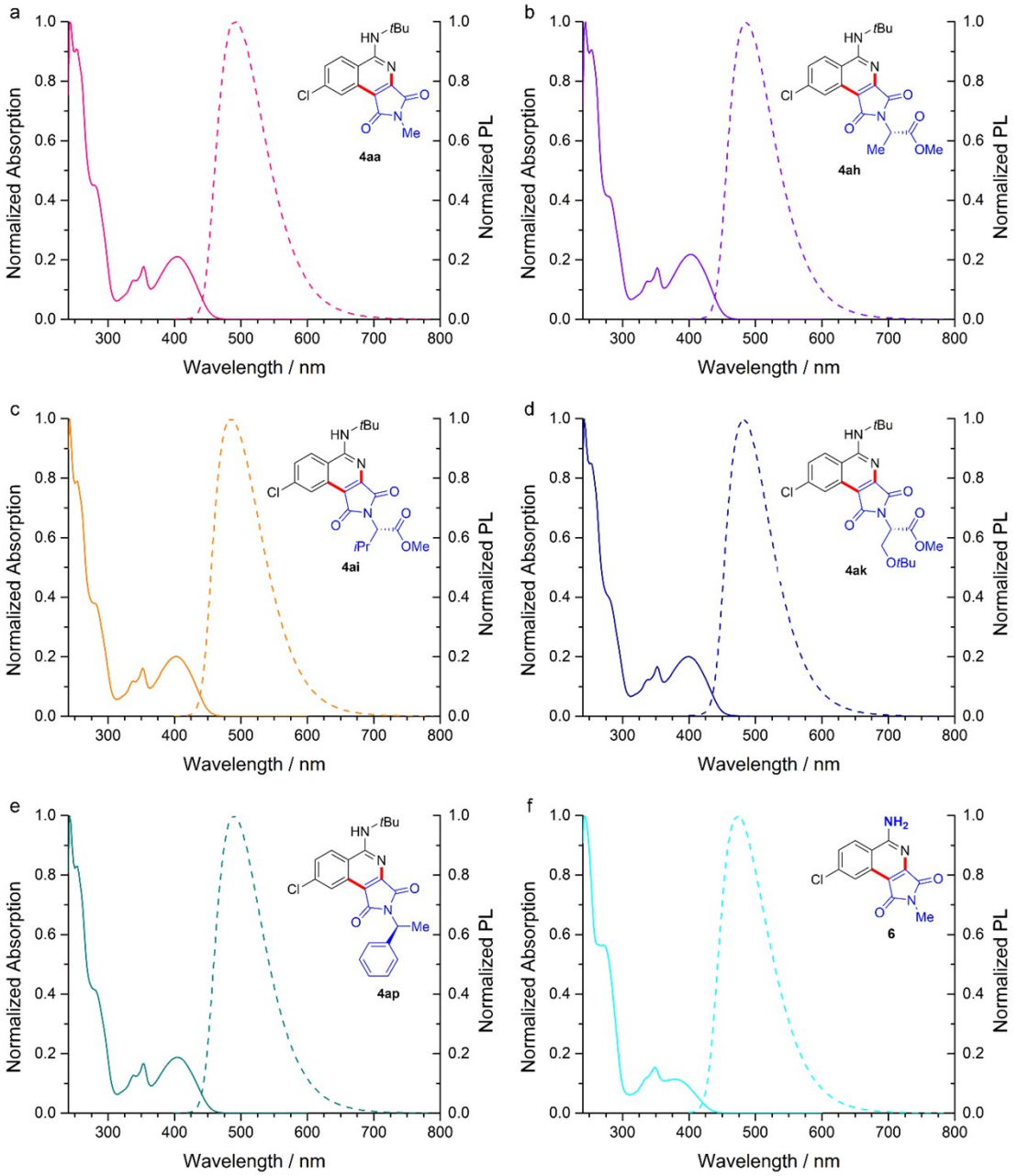


Figure S2: Normalized absorption and photoluminescence spectra of compound **4aa**, **4ah**, **4ai**, **4ak**, **4ap** and **6** in solution (50 µM in CHCl3).

PL quantum yield

Table S3: We measured the photoluminescence quantum yield PLQY using a PicoQuant FluoTime 300 spectrometer and the software *easytau*.

Compound	PLQY / %
4ap	69.54
4ah	66.62
4aa	66.06
4ai	65.5
4ak	64.87
4ba	59.52
4ca	47.87
4da	40.72
4ea	55.62
4fa	43.82
4ja	59.19
6	60.79

Time-correlated single photon counting

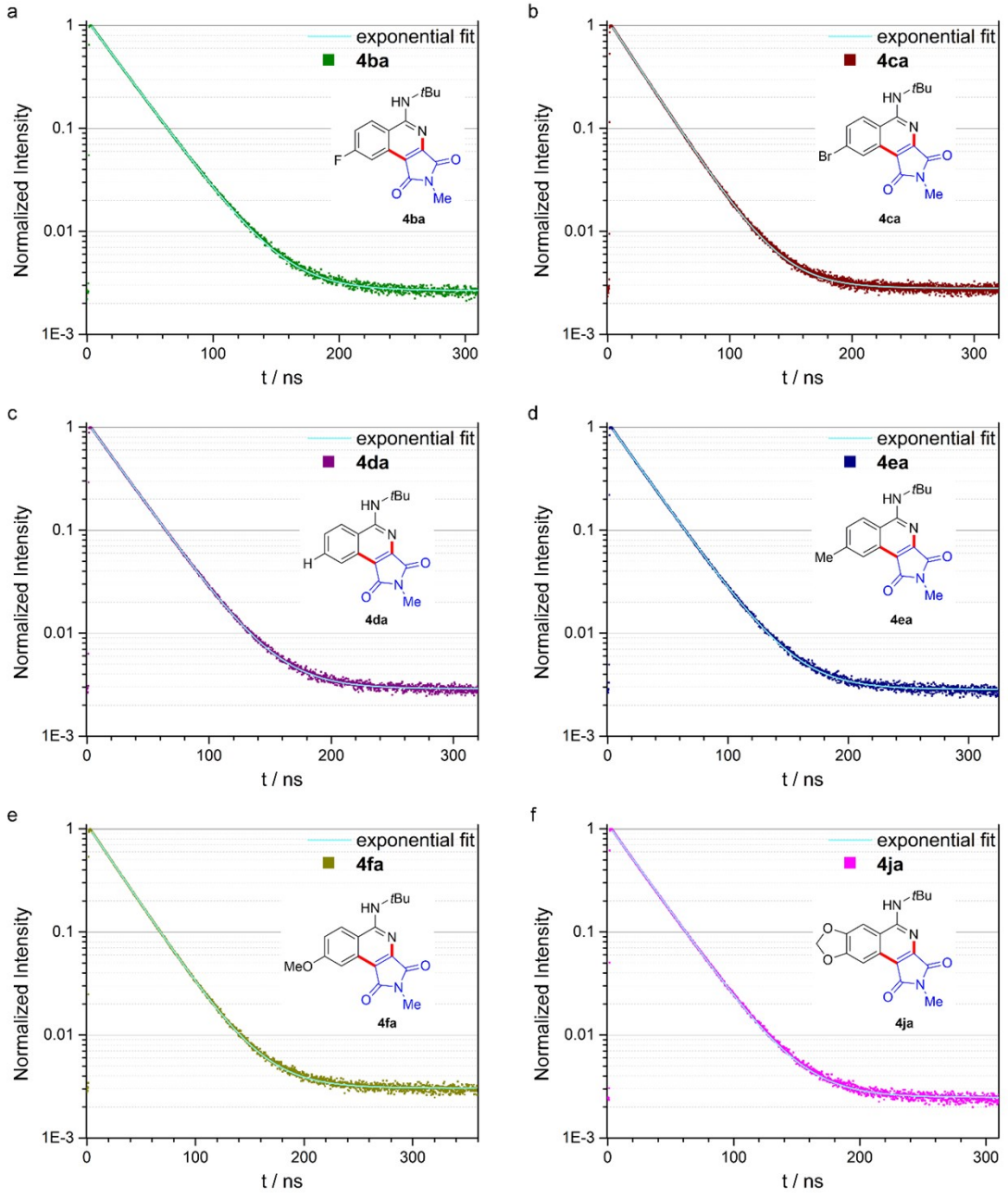


Figure S3: PL decay of compounds **4ba**, **4ca**, **4da**, **4ea**, **4fa** and **4ja** excited at 378 nm and measured at the corresponding maxima of the PL emissions. All samples were measured in solution (50 µM in $CHCl_3$). Experimental decay is shown in dots and the corresponding mono-exponential fit of the decay as light cyan line.

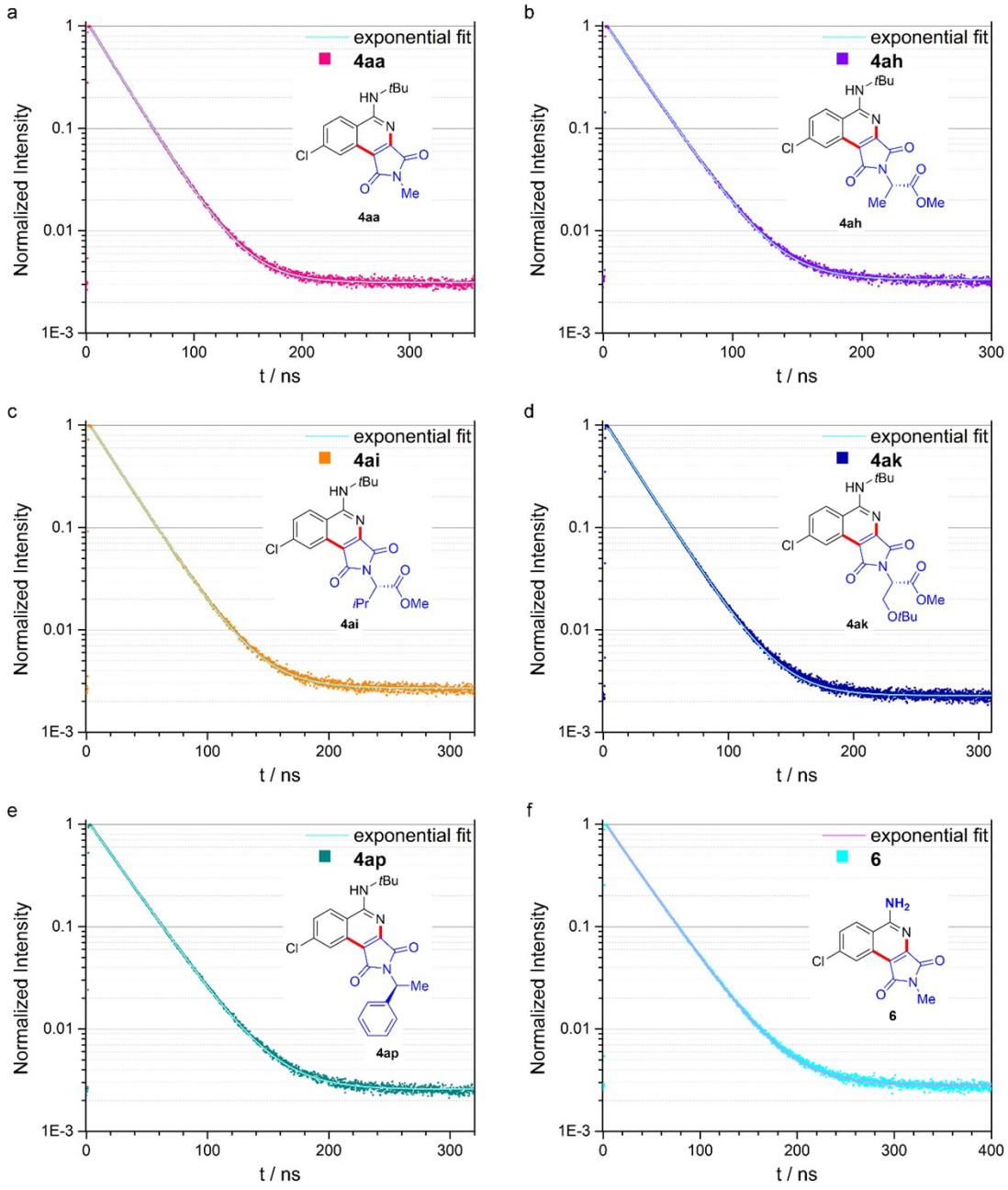


Figure S4: PL decay of compounds **4aa**, **4ah**, **4ai**, **4ak**, **4ap** and **6** excited at 378 nm and measured at the corresponding maxima of the PL emissions. All samples were measured in solution (50 µM in $CHCl_3$). Experimental decay is shown in dots and the corresponding mono-exponential fit of the decay as light cyan line.

Table S4: PL decay times of compounds shown above. The given errors are uncertainties from the fit and hence do not reflect the real time-resolution of the setup. The latter is limited by the laser pulse duration of around 100 ps.

	τ / ns	error / ns
4aa	25.52	±0.04
4ah	23.43	±0.04
4ai	23.96	±0.04
4ak	22.85	±0.06
4ap	25.88	±0.04
4ba	26.16	±0.04
4ca	23.99	±0.04
4da	26.44	±0.04
4ea	26.43	±0.04
4fa	27.83	±0.04
4ja	25.46	±0.04
6	32.20	±0.05

DFT Calculation

Complete Reference for Gaussian 09

Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2013**.

Computational Methods

All the DFT calculations were carried out with the GAUSSIAN 09 series of programs. DFT method B3-LYP[4] with a standard 6–31G(d) basis set was used for geometry optimizations. Harmonic vibrational frequency calculations were performed for all of the stationary points to confirm them as local minima or transition structures, and to derive the thermochemical corrections for the enthalpies and free energies. The M06-2x functional in combination with the 6-311+G(d,p) basis set was used to calculate the solvation single point energies to give more accurate energy information. The solvent effects were considered by single-point calculations on the gas-phase stationary points with an SMD[5] solvation model in the methanol solvent. In order to evaluate accurately the entropy of the multi-component system, the solution translational entropy correction has been calculated with the THERMO program developed by Fang et al., [6] which is based on the free volume that a solute molecule could move along three axes within the cavity. The TDDFT/B3LYP/6-31G(d) method was applied to optimize the geometry of the lowest singlet excited state.

The equation of thermal correction to Gibbs free energy with Fang's THERMO program:

$G_{(corr\text{-}THERMO)} = E_{(elec\text{-}THERMO)} - E_{(elec\text{-}B3LYP)}$

The equation of Gibbs free energy with Fang's THERMO program:

$G_{(solv\text{-}M062x)} = E_{(solv\text{-}M062x)} + G_{(corr\text{-}THERMO)}$

Calculated free energy profiles for the competitive hydrogen shift pathways of dihydroisoquinoline derivative IM-3^{S}.

The calculated competitive hydrogen shift pathways of dihydroisoquinoline derivative **IM-3^S** are shown in Figure S5. The calculated relative free energy of intramolecular 1,5-hydrogen shift via transition state **ts-14^S** is 31.1 kcal/mol, which is 4.4 kcal/mol higher than that of the arylamidine reactant **IM-1** and TFA assisted deprotonation process via transition state **ts-4^S**. Therefore, the intramolecular 1,5-hydrogen shift pathway is unfavorable.

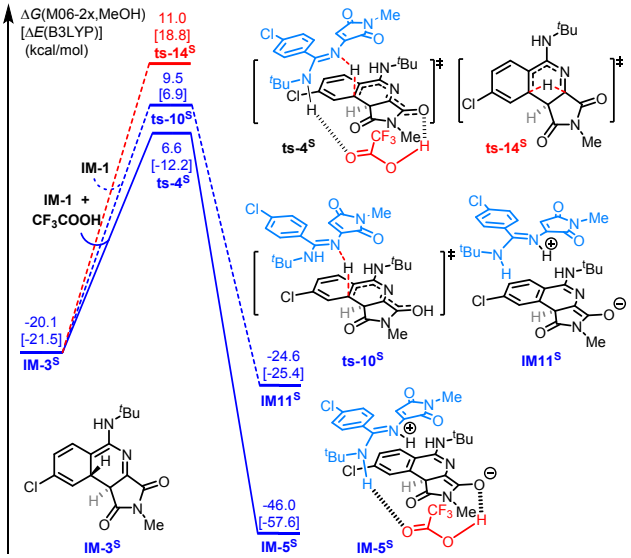


Figure S5. Calculated free energy profiles for the competitive hydrogen shift pathways of dihydroisoquinoline derivative **IM-3^S**. The values given in kcal/mol are the relative free energies calculated by the M06-2x/6-311+G(d,p)//B3LYP/6-31G(d) method in Methanol solvent with the Fang's THERMO correction. The values in square brackets are the electronic energy calculated at B3LYP/6-31G(d) level of theory without the Fang's THERMO correction.

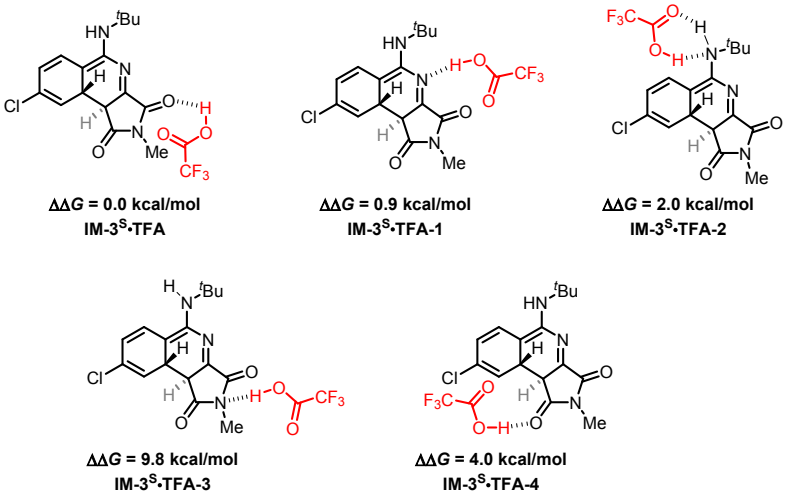


Figure S6: Possible hydrogen-bond adducts between **TFA** and intermediate **IM-3^s**.

Absolute Calculation Energies, Enthalpies, and Free Energies

Geometry	$E_{(elec\text{-}B3LYP)}$[1]	$E_{(elec\text{-}THERMO)}$[2]	$G_{(corr\text{-}B3LYP)}$[3]	$H_{(corr\text{-}B3LYP)}$[4]	$E_{(solv\text{-}M062x)}$[5]	IF[6]
IM-1	-1395.444497	-1395.16174	0.267064	0.343071	-1395.36408	-
1M-1*	-1395.371020	-	-	-	-	-
IM-1^{T}	-1395.371737	-1395.09207	0.264559	0.339368	-1395.290808	-
ts-2^{T}	-1395.359008	-1395.07801	0.26673	0.339781	-1395.277103	-373.20
IM-3^{T}	-1395.385393	-1395.10269	0.268409	0.341539	-1395.306226	-
MECP	-1395.385254	-	-	-	-	-
IM-3^{S}	-1395.406029	-1395.12117	0.270037	0.342862	-1395.328086	-
IM-3^{S}·TFA	-1922.203156	-1921.88583	0.298911	0.391429	-1922.139968	-
IM-3^{S}·TFA-1	-1922.195516	-1921.87917	0.296541	0.391485	-1922.137576	-
IM-3^{S}·TFA-2	-1922.200238	-1921.87955	0.296231	0.391628	-1922.140179	-
IM-3^{S}·TFA-3	-1922.18475	-1921.86541	0.294975	0.391033	-1922.126378	-
IM-3^{S}·TFA-4	-1922.199546	-1921.87904	0.296589	0.391331	-1922.136831	-
ts-4^{S}	-3317.610926	-3316.99812	0.58836	0.729796	-3317.470463	-1690.52
ts-4^{T}	-3317.599255	-3316.98818	0.586776	0.729333	-3317.455601	-2020.31
IM-5^{S}	-3317.683324	-3317.0655	0.590681	0.737601	-3317.559349	-
IM-5^{T}	-3317.671889	-3317.05826	0.585113	0.736715	-3317.52425	-
ts-6	-3317.667285	-3317.05254	0.589592	0.732332	-3317.537808	-302.60
IM-7	-1395.464661	-1395.17721	0.272904	0.344686	-1395.392829	-
ts-8	-3317.655109	-3317.04136	0.588029	0.731663	-3317.530184	-1139.10
IM-9	-1395.457172	-1395.16936	0.273993	0.344574	-1395.383707	-
ts-10^{S}	-2790.805181	-2790.22554	0.558574	0.681569	-2790.656926	-1777.88
IM-11^{S}	-2790.856645	-2790.2718	0.562971	0.688248	-2790.71645	-
ts-12	-1395.380252	-1395.0965	0.269174	0.341209	-1395.296954	-412.51
IM-13	-1395.393821	-1395.10873	0.270277	0.342898	-1395.316407	-
ts-14^{S}	-1395.341714	-1395.07132	0.265926	0.337636	-1395.264063	-1674.10
TFA	-526.775232	-526.75382	0.009672	0.045406	-526.797115	-

[1]The electronic energy calculated by B3LYP in gas phase without the Fang's

THERMO correction. [2] The electronic energy calculated by B3LYP in gas phase with the Fang's THERMO correction. [3]The thermal correction to Gibbs free energy calculated by B3LYP in gas phase without the Fang's THERMO correction. [4]The thermal correction to enthalpy calculated by B3LYP in gas phase without the Fang's THERMO correction. [5]The electronic energy calculated by M06-2x in Methanol without the Fang's THERMO correction. [6]The B3LYP calculated imaginary frequencies for the transition states.

B3LYP Geometries for All the Optimized Compounds and Transition State

IM-1

C	3.74473000	0.47501500	-0.18592800
C	2.75061300	0.92496200	-1.05735600
C	1.47358800	0.37691200	-0.97348200
C	1.18349900	-0.62241100	-0.03375400
C	2.19901800	-1.06299300	0.82681800
C	3.47963200	-0.51437900	0.76006800
H	2.97656400	1.69147000	-1.79061400
H	0.69790400	0.71689900	-1.65237600
H	1.98235300	-1.82465600	1.57045000
H	4.26098400	-0.84637900	1.43513700
Cl	5.35416400	1.16468800	-0.28432500
C	-0.18910500	-1.22486300	0.02826000
N	-0.19951100	-2.58468100	0.07122200
H	0.67732600	-3.02471500	-0.17316800
C	-1.38756500	-3.47929900	0.06358400
C	-0.82844500	-4.91051300	0.12680200
H	-0.23785500	-5.06625600	1.03748700
H	-1.64936900	-5.63376200	0.12784900
H	-0.19522400	-5.12983700	-0.74265800
C	-2.25849200	-3.21057500	1.30363700
H	-1.67194500	-3.33106800	2.22140900
H	-2.67155700	-2.20051800	1.28083100
H	-3.08899600	-3.92486400	1.33124200
C	-2.19846500	-3.28595600	-1.23288600
H	-2.55778900	-2.25813700	-1.31924400
H	-1.58310100	-3.51690300	-2.11039700
H	-3.06171800	-3.96136900	-1.23694600
N	-1.29936800	-0.55507600	0.00024200
C	-1.61978200	2.93599800	1.02656000
C	-1.00078600	1.60936900	1.21291500
C	-1.44307100	0.77527400	0.23755100
C	-2.41570300	1.56075300	-0.64028400
H	-0.32311100	1.39809800	2.02842400
O	-1.47234000	3.95360100	1.67792300
O	-3.01611000	1.16540000	-1.62063900
N	-2.46352800	2.83681400	-0.10742300
C	-3.25318000	3.92809100	-0.64105800
H	-3.05948500	4.80312500	-0.01812500
H	-2.97007600	4.14084500	-1.67696200
H	-4.32014900	3.68462100	-0.61404700

IM-1*

C	-4.06110300	-0.98567500	-0.08133300
C	-2.97602300	-1.59712700	-0.72700400
C	-1.73772200	-0.98650600	-0.72919300
C	-1.51748400	0.27688700	-0.08169200
C	-2.66803300	0.88636200	0.52915500
C	-3.90015200	0.26404300	0.53586000
H	-3.11478600	-2.54941800	-1.22834800
H	-0.91878700	-1.46882900	-1.24861000
H	-2.60004600	1.87343400	0.97730600
H	-4.75150700	0.74574100	1.00585000
Cl	-5.62822900	-1.77367800	-0.06145000
C	-0.24396300	0.87287000	-0.05493900
N	0.05213000	2.01666700	0.64953300
H	-0.72392900	2.31597500	1.22552800
C	0.82453100	3.19171400	0.12103300
C	0.56357700	4.32888900	1.12284500
H	0.90052900	4.05140100	2.12826500
H	1.10326900	5.23074400	0.81924600

H	-0.50348100	4.58250000	1.17029100
C	2.33321400	2.89246000	0.07957900
H	2.67923000	2.51537900	1.04809300
H	2.57785500	2.16188800	-0.69423800
H	2.88199500	3.81417500	-0.14432700
C	0.31486400	3.58172400	-1.27838200
H	0.46923000	2.76262900	-1.98701200
H	-0.75385100	3.82372400	-1.25356300
H	0.85486700	4.46093700	-1.64794100
N	0.84931400	0.34188600	-0.82142800
C	2.70437400	-2.04699900	1.18453100
C	1.57180200	-1.13463200	1.06672800
C	1.59705800	-0.51386800	-0.22680300
C	2.83436100	-1.07893600	-0.94243900
H	0.84281700	-1.00092300	1.85029600
O	3.03292400	-2.75498600	2.12035700
O	3.25085800	-0.80977700	-2.04645700
N	3.40975200	-1.96894500	-0.04622000
C	4.61689000	-2.72403900	-0.32736500
H	4.79964200	-3.38210500	0.52277300
H	4.48596700	-3.31027600	-1.24107100
H	5.46510500	-2.04660300	-0.46576000

IM-1^{T}

C	3.85659100	0.61043500	-0.15738700
C	2.83628700	1.14369400	-0.94773000
C	1.56799900	0.57302300	-0.90502200
C	1.29538400	-0.53440000	-0.07556300
C	2.34826000	-1.05412900	0.70562300
C	3.61858500	-0.48690400	0.67284500
H	3.03700800	1.98968500	-1.59619200
H	0.78757700	0.97082600	-1.54478400
H	2.15835300	-1.88414500	1.37997600
H	4.41532100	-0.88071000	1.29490100
Cl	5.45552400	1.32685200	-0.20620100
C	-0.03579600	-1.17375400	-0.08176000
N	-0.05095700	-2.53289200	0.05753500
H	0.83912000	-2.99023800	-0.09054600
C	-1.22746100	-3.43909800	0.11202500
C	-0.65184200	-4.84400200	0.36073100
H	-0.09761200	-4.88486500	1.30605900
H	-1.46240500	-5.57684000	0.41108900
H	0.01969300	-5.14917200	-0.45225600
C	-2.15005800	-3.04525300	1.27980100
H	-1.59680100	-3.03357500	2.22564400
H	-2.59361100	-2.06112800	1.11601900
H	-2.96216100	-3.77550700	1.36663500
C	-1.99883800	-3.41485600	-1.22377900
H	-2.41153800	-2.42261500	-1.41653600
H	-1.34032300	-3.69285000	-2.05493900
H	-2.82209300	-4.13762500	-1.18652500
N	-1.20342600	-0.55625000	-0.28946200
C	-1.62677000	2.95181600	0.71171500
C	-0.79470300	1.75905900	0.71478200
C	-1.50179900	0.69906300	-0.02494000
C	-2.79652300	1.26560300	-0.45375100
H	0.14665100	1.69501900	1.23901000
O	-1.41539300	4.04935800	1.21874500
O	-3.71397300	0.74948800	-1.07662700
N	-2.79293000	2.60005800	-0.00071900
C	-3.89988500	3.50700000	-0.21823500
H	-3.64231800	4.46045100	0.24507300
H	-4.07475000	3.64184800	-1.29061800
H	-4.81449500	3.10398700	0.22884700

ts-2^{T}

C	2.79017900	-2.12044100	0.16113900
C	2.50166900	-0.90913600	0.76123300
C	1.17053700	-0.41338200	0.74599500
C	0.11986700	-1.22768100	0.18444900
C	0.45925800	-2.45925700	-0.39012100
C	1.77687400	-2.91276500	-0.41186300
H	3.28649700	-0.32667200	1.23072500
H	-0.30815400	-3.05196100	-0.88003000
H	2.02973500	-3.85715600	-0.88084200
Cl	4.44096200	-2.71122000	0.13406900
C	-1.23806000	-0.66752600	0.08908700
N	-2.28372700	-1.54534100	0.09322200
H	-2.06939100	-2.46123800	0.46458300
C	-3.73213700	-1.23510100	-0.01828800
C	-4.44656600	-2.59744400	-0.01842600
H	-4.25352900	-3.14915400	0.91105300
H	-5.52833700	-2.45415100	-0.09729400
H	-4.12284100	-3.21500400	-0.86460000
C	-4.20321500	-0.39283900	1.18426200
H	-4.01264800	-0.92180500	2.12557000
H	-3.68408000	0.56746800	1.20887300
H	-5.28118800	-0.20806300	1.11094500

C	-4.01699900	-0.50333200	-1.34196700
H	-3.52686300	0.47178100	-1.36302700
H	-3.66620100	-1.09557300	-2.19463000
H	-5.09650100	-0.35083000	-1.45088600
N	-1.47157800	0.64348000	0.01478700
C	1.69689800	2.39444800	-0.50814700
C	0.89347200	1.16264100	-0.70307800
C	-0.47865500	1.48159300	-0.28138200
C	-0.52327100	2.90656500	0.09573800
O	2.88546000	2.58098500	-0.72163400
O	-1.45277800	3.58912400	0.49390400
N	0.81194600	3.36907000	-0.03402200
C	1.21459000	4.73185900	0.25021800
H	0.33476000	5.26267500	0.61713800
H	2.00660600	4.74464200	1.00528500
H	1.59402600	5.21688800	-0.65520300
H	0.90835200	0.32321800	1.49965200
H	1.12881500	0.53513100	-1.55565000

IM-3^{T}

C	-2.79773000	-2.08628200	-0.06185700
C	-2.58086100	-0.77813000	-0.38442600
C	-1.19113100	-0.21917600	-0.45964700
C	-0.09934800	-1.20600300	-0.09235900
C	-0.41239200	-2.50229900	0.24211600
C	-1.74315700	-2.98214100	0.23981500
H	-3.40065600	-0.09816400	-0.58689300
H	0.36980000	-3.18436700	0.56703400
H	-1.96064600	-4.01097000	0.50012400
Cl	-4.44340500	-2.70876300	0.00214400
C	1.27000600	-0.64747400	-0.01894100
N	2.31029300	-1.52100700	-0.11039900
H	2.07319600	-2.43416800	-0.47323500
C	3.76451500	-1.21891700	-0.06055100
C	4.47205200	-2.58029600	-0.17000800
H	4.23147200	-3.08057100	-1.11727800
H	5.55676800	-2.44247800	-0.13611300
H	4.18862500	-3.24210600	0.65706100
C	4.17215900	-0.31610000	-1.24179500
H	3.92527200	-0.79285100	-2.19773700
H	3.66015800	0.64636000	-1.18427100
H	5.25390100	-0.14134000	-1.21853700
C	4.12177200	-0.55584200	1.28202100
H	3.62995200	0.41346100	1.38062300
H	3.82096700	-1.19422100	2.12034300
H	5.20559100	-0.40474400	1.33782100
N	1.51075100	0.65219400	0.11330400
C	-1.74993600	2.29992200	0.11699400
C	-0.96095800	1.03007200	0.45079300
C	0.46849300	1.46843800	0.31371800
C	0.52299800	2.91456300	0.13996400
O	-2.95400900	2.40227800	-0.05031100
O	1.47116000	3.67591400	0.03995200
N	-0.84362300	3.33910000	0.06224200
C	-1.22593300	4.71753500	-0.18229300
H	-0.30724000	5.30418500	-0.23092900
H	-1.77591700	4.80031900	-1.12479800
H	-1.86468200	5.08644100	0.62613000
H	-1.01981200	0.13640100	-1.49305400
H	-1.21132700	0.74300600	1.48283600

MECP

C	2.79140000	-2.09563400	0.06450400
C	2.57906700	-0.78594600	0.38306900
C	1.19017700	-0.22468100	0.46328300
C	0.09364900	-1.20749000	0.09578900
C	0.40278200	-2.50542300	-0.23724700
C	1.73245500	-2.98903800	-0.23168100
H	3.40127300	-0.10707200	0.58020400
H	-0.38098300	-3.18436800	-0.56571400
H	1.94660400	-4.01968200	-0.48575100
Cl	4.43585700	-2.72268700	-0.00019700
C	-1.27389000	-0.64453700	0.02867700
N	-2.31778300	-1.51672000	0.09156200
H	-2.08726100	-2.43611200	0.44314900
C	-3.77139800	-1.20922700	0.04894400
C	-4.47855000	-2.57572400	0.04862300
H	-4.23447100	-3.15614200	0.94796300
H	-5.56362800	-2.43758900	0.03092000
H	-4.19713900	-3.16464900	-0.83257700
C	-4.18105100	-0.39019700	1.28881100
H	-3.96046500	-0.94052400	2.21111400
H	-3.64534000	0.56130800	1.30795900
H	-5.25744800	-0.18487200	1.26493900
C	-4.12349400	-0.44955800	-1.24280700
H	-3.66935500	0.54230500	-1.24874400
H	-3.77783100	-1.00250200	-2.12295400
H	-5.21146600	-0.33925700	-1.31237000

N	-1.51079200	0.65904600	-0.07573200
C	1.75820300	2.29361100	-0.12916700
C	0.95633800	1.02670500	-0.44186400
C	-0.46794700	1.47254600	-0.27896300
C	-0.51201700	2.91908300	-0.10836000
O	2.96581400	2.39100800	0.01415200
O	-1.45397900	3.68581600	0.00789300
N	0.85790800	3.33749700	-0.06475200
C	1.25176300	4.71870500	0.14108200
H	0.33819700	5.29892300	0.27829900
H	1.89229000	4.80392900	1.02339100
H	1.80318400	5.09498900	-0.72677200
H	1.02374300	0.12751400	1.49848100
H	1.18561100	0.73695900	-1.47825700

IM-3^{S}

C	2.82983700	-2.02700000	0.09134800
C	2.62284700	-0.70277800	0.02305500
C	1.25315000	-0.14031800	0.35106300
C	0.12935300	-1.16603700	0.16518700
C	0.47185100	-2.54800900	0.35834700
C	1.76289900	-2.97679600	0.36209400
H	3.42194700	0.00028100	-0.18494200
H	-0.32112400	-3.27844200	0.50771300
H	2.01350200	-4.01930900	0.52094400
Cl	4.43390200	-2.70222100	-0.19040300
C	-1.16349600	-0.72271400	-0.07273500
N	-2.22077200	-1.55218900	-0.36648300
H	-1.96574200	-2.52262600	-0.47924400
C	-3.66144800	-1.32613800	-0.07103900
C	-4.34686600	-2.68100800	-0.32051700
H	-3.96564800	-3.45213000	0.36118600
H	-5.42502400	-2.59423100	-0.15582100
H	-4.18856800	-3.01719300	-1.35230000
C	-3.87345200	-0.90116200	1.39492700
H	-3.46262400	-1.65180700	2.08032800
H	-3.39266200	0.05911100	1.59712300
H	-4.94406800	-0.79744000	1.60575800
C	-4.25126100	-0.27553100	-1.03207100
H	-3.79050700	0.70133400	-0.87298400
H	-4.08727100	-0.57536800	-2.07305200
H	-5.33107100	-0.18215200	-0.86658200
N	-1.48356800	0.64012800	0.00592900
C	1.65110400	2.40114300	-0.18602100
C	0.90160100	1.10267300	-0.46994100
C	-0.52622300	1.46958400	-0.17108700
C	-0.63028300	2.94986400	0.02362400
O	2.85153200	2.57963700	-0.14112500
O	-1.60959800	3.64350100	0.19785000
N	0.70068600	3.40883900	-0.00336600
C	1.06501500	4.79994700	0.21385100
H	0.14557100	5.35370400	0.40783700
H	1.74437900	4.87916000	1.06684900
H	1.56622300	5.20333200	-0.67085400
H	1.26706800	0.16521300	1.42000400
H	1.02161700	0.86944700	-1.54197900

IM-3^{S}·TFA

C	4.73949100	-0.98518100	0.61242300
C	4.11503400	0.17805800	0.37032800
C	2.60008100	0.22203500	0.34619900
C	1.96461400	-1.13541100	0.03160900
C	2.70223800	-2.30157200	0.43112700
C	4.02458500	-2.24368100	0.74705500
H	4.65162700	1.11489000	0.26777300
H	2.19377400	-3.26182400	0.48402600
H	4.56997400	-3.12692500	1.05927200
Cl	6.49395700	-1.05511600	0.74361400
C	0.68803800	-1.18725200	-0.51346500
N	0.09075700	-2.34634800	-0.95665600
H	0.71254600	-3.14305200	-0.94250500
C	-1.34978100	-2.71915700	-0.83255900
C	-1.85739200	-2.48006600	0.60143200
H	-1.76591600	-1.42898800	0.88743100
H	-2.91341100	-2.75799400	0.68249300
H	-1.28851400	-3.08297500	1.31928900
C	-2.19841300	-1.94964000	-1.86162000
H	-2.20788900	-0.87948300	-1.65235600
H	-1.80219800	-2.10502300	-2.87116500
H	-3.23264500	-2.30929600	-1.83449600
C	-1.40950700	-4.22139300	-1.16054000
H	-1.02528000	-4.41916100	-2.16823700
H	-0.82678600	-4.81166200	-0.44123600
H	-2.44413400	-4.57415900	-1.11767000
N	-0.08786700	-0.02583600	-0.62631800
C	2.22668200	2.72605000	-0.35349300
C	2.04012200	1.24276800	-0.64590800
C	0.54356800	1.08727600	-0.67194600

C	-0.08202700	2.43736000	-0.63850200
O	3.25140700	3.32028000	-0.09878500
O	-1.25672900	2.77540000	-0.72717900
N	0.96199300	3.33618100	-0.45838600
C	0.74922500	4.76970000	-0.31427000
H	0.34565900	5.18525000	-1.24181200
H	0.03882100	4.95828700	0.49483300
H	1.71375100	5.22366600	-0.08604300
H	2.26104900	0.52686800	1.36011700
H	2.46408300	1.04005100	-1.64458800
C	-4.99039900	0.04813900	0.79301300
F	-6.02773000	0.76807100	0.33446900
F	-5.23125700	-0.28728800	2.06315100
F	-4.91806100	-1.08832900	0.06260600
C	-3.66580200	0.83535300	0.67880300
O	-2.90828800	0.96075700	1.61186100
O	-3.51215600	1.29304300	-0.55440500
H	-2.63852400	1.77226900	-0.61912700

IM-3^{S}·TFA-1

C	4.41800900	-0.10709500	0.98079100
C	3.56001100	-1.00742700	0.47781000
C	2.36518000	-0.53591500	-0.32417600
C	1.95617100	0.91279600	-0.02657300
C	3.00509000	1.79695200	0.41600000
C	4.19526700	1.32637800	0.87222200
H	3.72322300	-2.07657100	0.55797500
H	2.83959000	2.87087700	0.39615700
H	4.97818500	2.00193900	1.19821500
Cl	5.86523100	-0.61782200	1.84155900
C	0.66345000	1.33184800	-0.27170100
N	0.16988100	2.59447700	0.06237300
H	0.78191300	3.04849800	0.73079400
C	-0.31773800	3.59518800	-0.94461100
C	0.71636500	3.79259800	-2.06987900
H	0.89057500	2.85633400	-2.61116400
H	0.36247100	4.53695100	-2.79229000
H	1.67692000	4.14073800	-1.67132500
C	-1.67178100	3.17714600	-1.54042500
H	-1.58236200	2.28344100	-2.16213000
H	-2.40050000	2.97793600	-0.74937800
H	-2.05838500	3.98814300	-2.16808100
C	-0.49998000	4.90328000	-0.15711000
H	-1.21548800	4.76628100	0.66068900
H	0.45080700	5.25081500	0.26899800
H	-0.87507800	5.69397100	-0.81431600
N	-0.27858800	0.47428500	-0.87239500
C	1.13829900	-2.83240600	-0.73218700
C	1.13477700	-1.42233800	-0.14785600
C	-0.03107500	-0.78200300	-0.83378400
C	-0.83977200	-1.83652900	-1.51979600
O	1.99814500	-3.68153900	-0.62469700
O	-1.90408000	-1.73726900	-2.09374300
N	-0.07160800	-3.00329800	-1.41799800
C	-0.48035100	-4.26501500	-2.01676600
H	-1.23237500	-4.75786000	-1.39253300
H	-0.91146800	-4.07005000	-3.00113100
H	0.40220800	-4.90032800	-2.09929100
H	2.65685300	-0.57596600	-1.39534400
H	0.89651400	-1.51297500	0.92681600
C	-4.52479400	-0.42744400	1.52571800
F	-4.75927300	0.75966400	2.11566700
F	-4.58899200	-1.38429900	2.45548200
F	-5.49142900	-0.64437000	0.61761000
C	-3.13572400	-0.42509600	0.84911700
O	-2.26315800	-1.20268800	1.16288100
O	-3.08034300	0.52675300	-0.07079400
H	-2.18601800	0.53205700	-0.50180300

IM-3^{S}·TFA-2

C	-1.23934100	-3.27904100	-0.98667000
C	-2.12462400	-2.45075400	-0.41383800
C	-1.97032600	-0.95371900	-0.57090800
C	-0.55552300	-0.50703600	-0.97147300
C	0.26797700	-1.47740600	-1.65097500
C	-0.05820200	-2.79512800	-1.68421800
H	-3.00381800	-2.80905600	0.11018500
H	1.19968800	-1.17058200	-2.11623300
H	0.57935500	-3.51291100	-2.18790500
Cl	-1.44120000	-5.02353700	-0.89255800
C	-0.18674400	0.80118900	-0.73871400
N	1.10039400	1.32178100	-1.00813000
H	1.67750100	0.61962100	-1.46640400
C	1.30154300	2.66141500	-1.68547700
C	0.32119000	2.84351400	-2.85648700
H	-0.71335700	2.88237800	-2.50495700
H	0.53467900	3.78239300	-3.37938000
H	0.41535900	2.02597500	-3.58147900

C	1.15501600	3.79968300	-0.66166800
H	0.14057100	3.84873100	-0.26350400
H	1.85244100	3.65950500	0.17221200
H	1.39115200	4.75644100	-1.14133100
C	2.74675900	2.63612900	-2.21334700
H	3.46393400	2.47476500	-1.40138300
H	2.89127000	1.84619600	-2.96078400
H	2.98510000	3.59283700	-2.68822700
N	-1.07772700	1.73508200	-0.20443200
C	-3.85653100	-0.15681400	1.07797100
C	-2.38258300	-0.17291900	0.67809200
C	-2.08630000	1.28191700	0.43910400
C	-3.22494500	2.10888400	0.94597300
O	-4.60152500	-1.10657800	1.20920100
O	-3.34244700	3.31307300	1.02140700
N	-4.21600200	1.17587500	1.30180900
C	-5.52807100	1.57877400	1.78485400
H	-5.48116100	1.84850200	2.84486000
H	-5.86599400	2.44774800	1.21601400
H	-6.20991600	0.73822100	1.65106300
H	-2.65134800	-0.64444200	-1.39206400
H	-1.80759800	-0.54393700	1.54438700
C	4.52955200	-0.65082700	1.63443700
F	5.35889700	0.34130400	2.00655400
F	5.25679800	-1.64302700	1.11530600
F	3.89914100	-1.10731400	2.73084500
C	3.50521800	-0.13007800	0.60198000
O	3.44919100	-0.56883900	-0.52858300
O	2.75110100	0.81956800	1.12648000
H	2.08743700	1.12543600	0.41948800

IM-3^{S}·TFA-3

C	2.11467200	3.53209500	-0.13292100
C	1.14026000	2.79994300	0.42939800
C	1.40225500	1.34811300	0.77990300
C	2.52478300	0.72584100	-0.05638000
C	3.55604700	1.61253600	-0.51753800
C	3.39213800	2.96338500	-0.52978700
H	0.18846800	3.22815600	0.72336200
H	4.49830100	1.19802300	-0.87032300
H	4.17979300	3.62578200	-0.86986200
Cl	1.87764000	5.24625500	-0.46140100
C	2.56123900	-0.65053300	-0.23559100
N	3.45959500	-1.29677900	-1.05172000
H	4.04720300	-0.67844800	-1.59192900
C	3.99465300	-2.67752300	-0.90190000
C	4.49664900	-2.93043700	0.53263200
H	3.67540100	-2.87128100	1.25118400
H	4.94110900	-3.92967800	0.60479100
H	5.26170200	-2.19638100	0.81152400
C	2.92712500	-3.71641200	-1.29659700
H	2.08074600	-3.68915400	-0.60752500
H	2.55990800	-3.52094000	-2.31012400
H	3.36019100	-4.72330800	-1.27535600
C	5.17468900	-2.76613800	-1.88564100
H	4.84633300	-2.56552000	-2.91252900
H	5.96554700	-2.05116000	-1.62492200
H	5.61119300	-3.76901500	-1.86149500
N	1.67610100	-1.48740900	0.45439900
C	-0.96157600	0.64022700	1.66484900
C	0.16144300	0.46333600	0.64817000
C	0.58133600	-0.96616800	0.86368600
C	-0.41110200	-1.65487500	1.74234900
O	-1.48087400	1.66742300	2.04366900
O	-0.45827200	-2.80636400	2.11406200
N	-1.34025600	-0.64287200	2.10636800
C	-2.34860900	-0.84048800	3.14937100
H	-3.35244500	-0.67496900	2.74953100
H	-2.25273900	-1.86814000	3.50273600
H	-2.16911200	-0.13593700	3.96545700
H	1.71538800	1.31766300	1.84662200
H	-0.26916000	0.58867000	-0.36091700
C	-5.15332200	-0.24995700	-1.60248200
F	-4.62914900	0.83747500	-2.19236000
F	-6.44861800	-0.03561400	-1.37287100
F	-5.02629000	-1.29181000	-2.44166400
C	-4.41796800	-0.54111200	-0.27701300
O	-4.96368700	-0.56483300	0.79654700
O	-3.11718900	-0.75745600	-0.50804200
H	-2.68736800	-0.93288200	0.35539700

IM-3^{S}·TFA-4

C	-0.30541100	-3.42840000	-0.44070900
C	0.16706300	-2.25315300	-0.88428100
C	-0.45452700	-0.95974000	-0.39363500
C	-1.89848700	-1.14196600	0.08813400
C	-2.24533600	-2.42770800	0.62706400
C	-1.47644100	-3.52960500	0.41475700

H	1.03711000	-2.18661200	-1.52788500
H	-3.14933600	-2.52915200	1.22418600
H	-1.73906300	-4.49326800	0.83572100
Cl	0.45920600	-4.94301500	-0.91570000
C	-2.76264300	-0.05624000	0.08548700
N	-4.10463000	-0.13504100	0.38261100
H	-4.43655400	-1.07796400	0.52742900
C	-4.94715200	0.91100700	1.02698500
C	-4.26317000	1.48389400	2.28283900
H	-3.33116000	1.99183600	2.02276600
H	-4.92157700	2.20991600	2.77339900
H	-4.03896700	0.68723800	3.00189100
C	-5.27131500	2.03414100	0.02322600
H	-4.36608100	2.56891400	-0.27073400
H	-5.74032000	1.61934000	-0.87580600
H	-5.96714700	2.75042000	0.47574500
C	-6.25029500	0.19638900	1.42517700
H	-6.74044200	-0.24371800	0.54848700
H	-6.06142600	-0.59990000	2.15662500
H	-6.94698100	0.90702900	1.87964400
N	-2.29102700	1.23152000	-0.19744200
C	0.88805800	0.78662000	-1.81142500
C	-0.44513500	0.15277600	-1.44786100
C	-1.22070800	1.31790000	-0.89209200
C	-0.46607600	2.58001400	-1.14385300
O	1.90252900	0.20437800	-2.18612800
O	-0.76652500	3.73338600	-0.93577900
N	0.77289300	2.15389800	-1.69022600
C	1.85277900	3.08153000	-1.99193000
H	2.30954700	2.81445600	-2.94734000
H	1.42444900	4.08343700	-2.03787700
H	2.61140000	3.04629900	-1.20422500
H	0.15471500	-0.60153800	0.46216400
H	-0.91440000	-0.22169300	-2.37362800
C	4.82865900	0.46105100	1.59393100
F	5.41423300	-0.74805400	1.58354000
F	4.35738300	0.69885900	2.82035000
F	5.76326100	1.38580400	1.30553900
C	3.68669300	0.52116200	0.55515500
O	2.54791700	0.80172000	0.85766400
O	4.14921800	0.24566600	-0.65517500
H	3.39072900	0.26487200	-1.29959900

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C	-4.51669300	-1.88721800	-0.14194400
C	-3.27598900	-2.25510900	-0.57548600
C	-2.36757900	-1.26528200	-1.12028500
C	-2.92298900	0.05598200	-1.46717000
C	-4.24491200	0.35633300	-1.03197300
C	-5.01562300	-0.57090500	-0.37451400
H	-2.94161300	-3.28354100	-0.50535700
H	-4.66558500	1.32489000	-1.27595400
H	-6.02878600	-0.32965800	-0.06933500
Cl	-5.58425500	-3.06132200	0.62006800
C	-2.09797900	1.01794300	-2.11952800
N	-2.58719300	2.32331900	-2.27889000
H	-2.90072700	2.70579600	-1.39096300
C	-1.94424400	3.35872300	-3.11704600
C	-0.59910400	3.84809000	-2.53336200
H	0.12547200	3.03182900	-2.50114800
H	-0.18666100	4.66241800	-3.14205900
H	-0.74577200	4.23377500	-1.51544700
C	-1.74809900	2.83002600	-4.54796800
H	-1.01553300	2.02015300	-4.57763200
H	-2.69755700	2.46143200	-4.95237800
H	-1.38861200	3.63762900	-5.19571200
C	-2.93941300	4.53437600	-3.14676100
H	-3.89907800	4.22039800	-3.57105300
H	-3.12280300	4.92094200	-2.13527600
H	-2.54380300	5.35941800	-3.74909500
N	-0.82766600	0.72497600	-2.47065000
C	-0.43918800	-2.87122200	-2.04919800
C	-1.38485600	-1.69203400	-2.19972600
C	-0.45332400	-0.53623500	-2.46966700
C	0.87310500	-1.04162600	-2.69915100
O	-0.69290800	-4.00608400	-1.67027500
O	1.92744400	-0.45852100	-3.00718200
N	0.80246000	-2.44345500	-2.50104500
C	1.93673500	-3.32962700	-2.70073200
H	2.44487900	-3.05342000	-3.62833100
H	2.64410900	-3.25331300	-1.87045900
H	1.55835200	-4.35080500	-2.76708900
H	-1.62374600	-0.92318400	0.10555000
H	-1.96701500	-1.92638000	-3.11650800
C	2.92710300	2.78209600	1.35911300
C	1.69342600	2.86794400	0.70917100
C	0.86087900	1.75450700	0.67809200
C	1.25081600	0.55053600	1.29414800

C	2.50261900	0.48721400	1.93343500
C	3.34167600	1.59622200	1.97028900
H	1.39925700	3.78764300	0.21587800
H	-0.08261500	1.80856500	0.14693100
H	2.82559400	-0.43070100	2.41273600
H	4.30694900	1.54239200	2.46045700
Cl	3.97835800	4.17890600	1.39855200
C	0.36598800	-0.63582900	1.22529200
N	0.94506600	-1.83581300	1.05528200
H	1.91712900	-1.78346000	0.74921100
C	0.64723900	-3.13957600	1.75995200
C	1.43496500	-4.23033300	1.01698200
H	2.49552500	-3.96730500	0.92906100
H	1.36815000	-5.16825800	1.57798800
H	1.02131400	-4.40099200	0.02019100
C	1.18786400	-2.99843400	3.19940200
H	2.26330100	-2.78677200	3.20190600
H	0.67619800	-2.19403500	3.73920000
H	1.02910700	-3.93097700	3.75164100
C	-0.83913600	-3.50130400	1.78489500
H	-1.44543200	-2.75895200	2.30806900
H	-1.21954500	-3.63037200	0.77154100
H	-0.95018300	-4.45788800	2.30738400
N	-0.97178700	-0.49537400	1.20342500
C	-2.44598900	1.22502800	4.08774500
C	-1.59099400	0.18378500	3.48286000
C	-1.59742300	0.31981200	2.13429100
C	-2.43812800	1.55237000	1.81324000
H	-1.08820300	-0.56469700	4.07956200
O	-2.69660500	1.43119500	5.25826200
O	-2.58129000	2.11115500	0.73966300
N	-2.95505700	1.99278900	3.01302600
C	-3.77260000	3.18191400	3.16996300
H	-4.73052800	3.06160700	2.65541400
H	-3.94480000	3.31650800	4.23894400
H	-3.25958100	4.05838300	2.76239000
C	5.68521600	-0.43331200	-0.04339800
F	6.72312300	-1.08343900	-0.59751400
F	5.62899200	-0.75888600	1.25916000
F	5.90749300	0.88531800	-0.13679400
C	4.36944100	-0.83694700	-0.74972200
O	3.60431000	-1.62948700	-0.22526100
O	4.25046100	-0.25135300	-1.90773400
H	3.34771900	-0.45272300	-2.34571600

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C	-6.48712000	-1.89497800	0.27134500
C	-5.26142900	-2.49055700	-0.02226000
C	-4.21891200	-1.69649000	-0.49962300
C	-4.39777100	-0.31069500	-0.69887500
C	-5.63955500	0.25853000	-0.37306800
C	-6.68727200	-0.52451200	0.10604000
H	-5.10297100	-3.55375600	0.11976500
H	-5.78512100	1.33152200	-0.45211800
H	-7.64297100	-0.07767800	0.35806500
Cl	-7.80716700	-2.88858300	0.87014300
C	-3.23844100	0.50895000	-1.16455700
N	-3.57519800	1.74588600	-1.68641100
H	-4.51437500	1.76854900	-2.05952900
C	-2.66666200	2.70582500	-2.34958900
C	-1.70174300	3.29866000	-1.30952500
H	-1.09983800	2.50925000	-0.85733800
H	-1.03612500	4.03144300	-1.77991700
H	-2.26465200	3.80509600	-0.51765800
C	-1.89153800	2.04735400	-3.50954700
H	-1.28703400	1.21491100	-3.14217300
H	-2.58337500	1.66069200	-4.26720800
H	-1.23664000	2.78153500	-3.99425500
C	-3.56510900	3.82590900	-2.90199700
H	-4.26093700	3.44161000	-3.65943200
H	-4.14856600	4.29193500	-2.09951400
H	-2.95585500	4.60215800	-3.37543900
N	-1.99584400	0.13239500	-1.01639100
C	-2.32629400	-3.46990700	-0.12872900
C	-2.85849800	-2.23674100	-0.86295500
C	-1.80857500	-1.18006100	-0.61243400
C	-0.76557900	-1.76917600	0.02084500
O	-2.88586200	-4.54397700	0.04320700
O	0.37549300	-1.22831200	0.48765700
N	-1.04870600	-3.14544600	0.27475900
C	-0.20642100	-4.05787400	1.02935800
H	0.76929400	-4.16884100	0.55018600
H	-0.06651500	-3.70377100	2.05814000
H	-0.72677600	-5.01690500	1.05051400
H	1.06183800	0.93892100	2.68851000
H	-2.86526300	-2.51209800	-1.93355800
C	3.34501600	1.83109500	-2.81229600
C	2.02496300	1.57027100	-2.43372200

C	1.74274500	1.25636800	-1.10841100
C	2.78515200	1.19733500	-0.16710400
C	4.10889700	1.43254900	-0.57016900
C	4.39259200	1.76160400	-1.89193900
H	1.22942500	1.60126200	-3.16945200
H	0.72716300	1.00420400	-0.81932200
H	4.91555000	1.36762500	0.15257900
H	5.41147100	1.95401300	-2.20824000
Cl	3.69356300	2.24492500	-4.47510000
C	2.49970000	0.82752300	1.23374800
N	3.23232000	-0.09447600	1.80491100
H	3.77076500	-0.72716800	1.11758600
C	3.26388500	-0.57352100	3.22638300
C	4.63331600	-1.26486800	3.38302300
H	5.44952000	-0.54073900	3.28373400
H	4.69796200	-1.72011800	4.37593500
H	4.77660500	-2.04269200	2.62897100
C	3.18380000	0.58446300	4.24146800
H	3.87395100	1.39176600	3.97333700
H	2.18366100	1.00746500	4.36913200
H	3.48802900	0.19889100	5.21955900
C	2.13317700	-1.59938900	3.43457900
H	1.13943700	-1.16258600	3.29041100
H	2.23458700	-2.42611800	2.72629700
H	2.18497600	-1.99782600	4.45338100
N	1.47918400	1.43588400	1.90485700
C	0.19962100	4.82612000	1.40876500
C	1.13542000	3.76325200	0.95603800
C	0.94439600	2.69409500	1.75101400
C	-0.10827800	3.02894200	2.78820100
H	1.79874500	3.90426600	0.11697200
O	0.04492800	5.94033900	0.95944200
O	-0.46278300	2.28059300	3.68344200
N	-0.52350700	4.30516800	2.51776500
C	-1.53131100	5.03955300	3.26391200
H	-1.23168700	5.14685800	4.31044000
H	-1.62029600	6.02409600	2.80221300
H	-2.49301500	4.52079400	3.21930700
C	4.34909900	-3.74672500	-1.15506500
F	3.77455400	-4.94432900	-0.93330900
F	5.66367200	-3.86946600	-0.90357900
F	4.20587500	-3.45773900	-2.46759600
C	3.68310800	-2.63586300	-0.29845900
O	4.46355000	-1.76401100	0.16553100
O	2.44012700	-2.73197000	-0.18964000
H	1.17576700	-1.78199500	0.23479900

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C	-6.79905600	-0.66779300	-0.88583200
C	-6.18894600	0.49699900	-0.42008800
C	-5.05576600	0.39635400	0.38525700
C	-4.53715400	-0.86894100	0.74516000
C	-5.16402800	-2.02073100	0.24171000
C	-6.29296400	-1.92900300	-0.56617700
H	-6.57772800	1.47369400	-0.68475700
H	-4.75056100	-3.00572000	0.43853700
H	-6.76869800	-2.82239700	-0.95517100
Cl	-8.22129700	-0.54531000	-1.89927100
C	-3.30461500	-0.92410800	1.57383300
N	-3.01232100	-2.07281900	2.22123200
H	-3.72987700	-2.78288700	2.20481000
C	-1.83887300	-2.37465900	3.09018700
C	-0.53360400	-2.27249300	2.28151000
H	-0.37879800	-1.25476500	1.91727200
H	0.31068000	-2.54004700	2.92716900
H	-0.54731000	-2.96381200	1.43254700
C	-1.81747800	-1.42237600	4.30073600
H	-1.68155200	-0.38735400	3.97955600
H	-2.74888500	-1.49683600	4.87385800
H	-0.98670000	-1.68984200	4.96270700
C	-2.04296300	-3.82319400	3.56418800
H	-2.97473800	-3.93048100	4.13466300
H	-2.06365300	-4.51732200	2.71581500
H	-1.21804400	-4.11961500	4.21829100
N	-2.45541300	0.10054400	1.62279100
C	-4.28198900	2.90161300	0.14657400
C	-4.34585800	1.60329500	0.95875000
C	-2.89909000	1.27949500	1.19405300
C	-2.08126200	2.38559100	0.76003600
O	-5.19811500	3.49189700	-0.39134800
O	-0.85109500	2.52174900	0.81067100
N	-2.95753900	3.33145100	0.18322200
C	-2.50650800	4.56630100	-0.43901200
H	-1.95361800	5.17492800	0.28132800
H	-1.85566500	4.35262400	-1.29301700
H	-3.39192400	5.10336000	-0.78083800
H	0.76565200	-2.05751200	-0.55705200
H	-4.83840500	1.87973600	1.90975600

C	6.19906700	0.07164500	0.93717900
C	5.51150700	-1.06955800	1.36131800
C	4.26393000	-1.35819400	0.82632300
C	3.67108900	-0.52037200	-0.15577600
C	4.39545200	0.63284900	-0.55589700
C	5.64005500	0.92660100	-0.01757900
H	5.94900200	-1.71770700	2.11348700
H	3.72862900	-2.23033300	1.18320900
H	3.97572100	1.30154800	-1.29832300
H	6.18058800	1.81068100	-0.33877100
Cl	7.77706700	0.43861900	1.61650800
C	2.36016500	-0.78672900	-0.68890300
N	1.54758200	0.21470000	-1.15999100
H	1.77029100	1.14894000	-0.82903600
C	0.72275400	0.17543600	-2.40439300
C	0.41508000	1.64143000	-2.75612200
H	1.33468900	2.20822800	-2.93385400
H	-0.19846600	1.68808200	-3.66152500
H	-0.13189400	2.12611700	-1.94006800
C	1.50946100	-0.47984600	-3.55478500
H	2.43446400	0.07145400	-3.75583500
H	1.77290400	-1.51707200	-3.32558100
H	0.90635200	-0.48291900	-4.46994500
C	-0.61560700	-0.56256600	-2.17728200
H	-0.49089500	-1.64691100	-2.08698700
H	-1.10476300	-0.19080100	-1.27068300
H	-1.28697300	-0.39224800	-3.02715400
N	1.78043400	-2.04193400	-0.63296100
C	3.38276900	-5.24809300	-1.27525900
C	3.53332000	-3.80341900	-1.12263200
C	2.29619200	-3.28545400	-0.84427500
C	1.29180500	-4.39656200	-0.81681700
H	4.48158400	-3.29990500	-1.22588700
O	4.20714000	-6.11078800	-1.52765800
O	0.08131700	-4.27475600	-0.62284500
N	1.98880100	-5.54532500	-1.07211300
C	1.42082200	-6.87332500	-1.16224200
H	0.66031900	-6.92005700	-1.94875900
H	2.23944700	-7.55504100	-1.40077900
H	0.96140000	-7.16836900	-0.21279400
C	2.84896200	5.49704800	-0.16647200
F	2.25615300	6.43805700	-0.92622100
F	4.01873000	5.17486800	-0.72527900
F	3.08115700	6.02080900	1.04841400
C	1.93655000	4.25430700	-0.06094000
O	2.27524800	3.17737200	-0.50400100
O	0.80515800	4.56253100	0.53779600
H	0.19766000	3.76106600	0.60439500

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C	-5.86636200	-2.42712100	-0.75850800
C	-4.69797100	-2.46982100	-0.00192900
C	-3.72680500	-1.48157000	-0.17818000
C	-3.92540600	-0.43821700	-1.10370400
C	-5.10031400	-0.44768600	-1.87506400
C	-6.07578900	-1.42604000	-1.70528100
H	-4.52806900	-3.26964100	0.71001600
H	-5.24593800	0.29290800	-2.65402000
H	-6.97860100	-1.41936200	-2.30629100
Cl	-7.09160400	-3.66493600	-0.52666100
C	-2.85565600	0.58777400	-1.29665800
N	-3.21589100	1.65106800	-2.10653700
H	-4.19186400	1.90347400	-2.04136300
C	-2.35444100	2.73158000	-2.62607300
C	-1.78755600	3.61093700	-1.49424900
H	-1.16046500	3.02210500	-0.82379100
H	-1.18641800	4.42990800	-1.90711100
H	-2.60194300	4.05341800	-0.90801400
C	-1.22483000	2.12561300	-3.47952800
H	-0.61649900	1.43331500	-2.89428900
H	-1.64416500	1.57552700	-4.32908800
H	-0.58359700	2.92379300	-3.87206400
C	-3.25995700	3.58980700	-3.52784900
H	-3.69580000	2.98647900	-4.33220100
H	-4.07706000	4.04529700	-2.95248500
H	-2.68391800	4.40228200	-3.98202000
N	-1.64775200	0.45842800	-0.83688000
C	-1.79530800	-2.86518100	0.78750200
C	-2.44627400	-1.48453500	0.63621800
C	-1.35953000	-0.64821500	-0.01922400
C	-0.26050000	-1.50690500	-0.31736100
O	-2.25154200	-3.85234800	1.33933000
O	0.82850400	-1.22471400	-0.87875800
N	-0.53194500	-2.78784200	0.21831100
C	0.39021400	-3.90658800	0.17695500
H	0.68369100	-4.12899000	-0.85309300
H	1.29384000	-3.69355800	0.75993600
H	-0.12546600	-4.76633500	0.60781300

H	-0.41679000	0.12024100	1.19589500
H	-2.68555400	-1.12594800	1.64820300
C	3.93504900	2.63105700	-1.54026600
C	2.56384300	2.44463000	-1.74391200
C	1.81931600	1.75979500	-0.79278200
C	2.43957600	1.25429600	0.36643200
C	3.82206800	1.44625500	0.54646300
C	4.57226700	2.13609100	-0.40078400
H	2.09231700	2.82010000	-2.64530400
H	0.76430000	1.56870000	-0.95708300
H	4.30929600	1.07509900	1.44263100
H	5.63558200	2.29405800	-0.25821300
Cl	4.87144900	3.49870600	-2.73762100
C	1.64851500	0.53459900	1.37221300
N	2.19941500	-0.48833300	2.02372500
H	2.98639400	-0.93415600	1.54266200
C	1.88301500	-1.01549100	3.39274300
C	2.99348900	-2.03643900	3.69644700
H	3.98443200	-1.56974100	3.66585400
H	2.84574300	-2.45420100	4.69655400
H	2.98357200	-2.86175700	2.97674900
C	1.95342600	0.14811200	4.39957000
H	2.93864600	0.62660400	4.37658300
H	1.19219700	0.90554300	4.19418900
H	1.78374700	-0.23350500	5.41189700
C	0.51166200	-1.70722600	3.46628400
H	-0.30682300	-1.00250200	3.30554300
H	0.43330700	-2.51318500	2.73247500
H	0.38751400	-2.14788700	4.46157200
N	0.34110700	0.84313000	1.64126900
C	-0.58407000	4.32680800	2.27092500
C	0.45831000	3.33003800	1.94955600
C	-0.13183700	2.11831400	1.82528400
C	-1.61438700	2.27722800	2.13978300
H	1.49703500	3.60329000	1.83676400
O	-0.47175800	5.52301600	2.44961800
O	-2.44787800	1.39564900	2.23340900
N	-1.81384000	3.62375600	2.35011300
C	-3.08395100	4.22688200	2.70597200
H	-3.47723000	3.78510400	3.62674300
H	-2.90480400	5.29313300	2.85374200
H	-3.81651100	4.08280500	1.90599600
C	5.15640900	-3.20529500	-1.37830700
F	4.86540700	-4.50474100	-1.57367300
F	6.21798400	-3.12569000	-0.56891700
F	5.47991600	-2.66142500	-2.56315000
C	3.93961900	-2.47657600	-0.76007700
O	4.01829300	-1.98182900	0.35333000
O	2.92136900	-2.50610000	-1.57259400
H	2.08021500	-2.02208900	-1.21127000

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C	3.45434900	-1.00896900	-0.04555900
C	2.79390600	0.18638000	-0.31959800
C	1.40102400	0.20005000	-0.41334400
C	0.66479500	-0.97866500	-0.20786600
C	1.35800000	-2.17566900	0.02682900
C	2.74743100	-2.20045100	0.11442100
H	3.35798900	1.10245700	-0.45645100
H	0.81777300	-3.11308500	0.10986300
H	3.27592800	-3.13019700	0.29469500
Cl	5.20437500	-1.02025200	0.07214200
C	-0.82778500	-0.90031200	-0.27121800
N	-1.49534000	-2.01591200	0.18243300
H	-0.97933300	-2.55856200	0.86067300
C	-2.96653100	-2.18087300	0.28656000
C	-3.17996900	-3.58462200	0.87934100
H	-2.73821400	-3.66607100	1.88174100
H	-4.24950600	-3.79646600	0.97290600
H	-2.73320200	-4.35411900	0.23910100
C	-3.59120500	-1.12256300	1.21767500
H	-3.14559400	-1.17479600	2.21869200
H	-3.43903000	-0.11883500	0.81629300
H	-4.66861000	-1.29901100	1.31763100
C	-3.60327000	-2.11731600	-1.11346400
H	-3.46123800	-1.13214300	-1.56062400
H	-3.15734900	-2.87191400	-1.77112300
H	-4.67817000	-2.31804600	-1.03843600
N	-1.48328800	0.10528400	-0.74495300
C	0.54612400	2.46840600	0.41094700
C	0.67260400	1.47126800	-0.75611100
C	-0.77876300	1.26823500	-1.24727100
C	-1.51810000	2.49857000	-0.67814000
O	1.39079200	2.75641000	1.23264800
O	-2.61364800	2.90986600	-0.98552400
N	-0.70747000	3.05563900	0.31704500
C	-1.13199800	4.15197100	1.17401600
H	-0.38344400	4.94821100	1.15687400

H	-2.08609200	4.51606000	0.79069800
H	-1.25162300	3.80496400	2.20474300
H	-0.85754400	1.29816400	-2.34161400
H	1.24475200	2.00974200	-1.52402900

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C	5.19737400	-0.22151500	3.24805700
C	3.92763400	0.24214900	2.91106000
C	3.37909900	-0.09589900	1.67239900
C	4.10352200	-0.88707800	0.75997800
C	5.36785400	-1.36356700	1.14551400
C	5.92464000	-1.03173700	2.37778500
H	3.36251800	0.85823400	3.60183800
H	5.91292400	-2.03911000	0.49477100
H	6.90201300	-1.40500600	2.66374000
Cl	5.89120900	0.21513400	4.80313200
C	3.46868300	-1.27626700	-0.53401000
N	4.33324000	-1.85075600	-1.45244600
H	5.27447100	-1.48626300	-1.39296900
C	3.98870900	-2.35959400	-2.79624700
C	3.04393600	-3.56731500	-2.66059000
H	2.12142400	-3.28603900	-2.15071700
H	2.79500100	-3.96324400	-3.65234700
H	3.52782300	-4.36322000	-2.08374300
C	3.36638100	-1.25932800	-3.67993200
H	2.45320300	-0.87544600	-3.22229800
H	4.06652700	-0.42461200	-3.80509800
H	3.12819300	-1.65602300	-4.67430200
C	5.31563600	-2.82613200	-3.42059600
H	6.01680800	-1.98903500	-3.53828800
H	5.79213500	-3.59316100	-2.79940900
H	5.13892800	-3.25099800	-4.41394100
N	2.19175100	-1.19377500	-0.75207700
C	0.97221400	0.43595800	2.35259500
C	2.01300100	0.40524000	1.23763400
C	1.39413800	-0.51995100	0.19108200
C	0.27249700	-1.16619500	0.81362000
O	0.93487300	1.17253400	3.32622500
O	-0.45271500	-2.10391200	0.40466600
N	0.00856300	-0.50996700	2.03953700
C	-1.11963400	-0.80459400	2.90396200
H	-2.06324900	-0.48897000	2.44553400
H	-1.16946800	-1.87609200	3.11436100
H	-0.96952800	-0.24961000	3.83124800
H	0.44295700	0.55312700	-0.77935700
H	2.14060200	1.43012600	0.86769400
C	-4.51014700	2.56948100	1.48513600
C	-3.14879700	2.67272000	1.78795000
C	-2.21567000	2.10385800	0.93030700
C	-2.62505900	1.42394100	-0.23432200
C	-4.00285000	1.33401500	-0.51465000
C	-4.94367200	1.90188800	0.33760400
H	-2.82743000	3.18525100	2.68786200
H	-1.16255200	2.17076000	1.17938000
H	-4.34130100	0.83446400	-1.41633100
H	-6.00254300	1.83542200	0.11352600
Cl	-5.68674900	3.28761500	2.55918400
C	-1.63500100	0.81064800	-1.13619700
N	-1.98274500	-0.27686000	-1.81220900
H	-2.74891500	-0.82314800	-1.40258300
C	-1.46805300	-0.86969600	-3.08966000
C	-2.74644700	-1.22099200	-3.88306000
H	-3.31357600	-0.31952700	-4.14209400
H	-2.47036800	-1.73016100	-4.81195000
H	-3.39670300	-1.89152800	-3.31076400
C	-0.62742000	0.12694900	-3.89704800
H	-1.14241100	1.08666400	-4.01801300
H	0.34996900	0.30671100	-3.44758700
H	-0.46673600	-0.29484700	-4.89459200
C	-0.67228800	-2.14804900	-2.78459100
H	0.21408800	-1.93324400	-2.18476100
H	-1.28476700	-2.86928100	-2.23583600
H	-0.36179400	-2.60816400	-3.72955600
N	-0.34648300	1.27002500	-1.20250600
C	0.06914900	4.80593600	-2.03643400
C	-0.80475900	3.63519000	-1.83177700
C	-0.04195800	2.58724000	-1.43415500
C	1.41022400	3.04666100	-1.41127200
H	-1.87216600	3.68303100	-1.99119500
O	-0.22434800	5.93392400	-2.37789900
O	2.39604900	2.37886700	-1.15634900
N	1.39325700	4.37809400	-1.75906300
C	2.57074200	5.21948800	-1.86601500
H	3.26715400	4.81547300	-2.60696400
H	2.23209200	6.20895100	-2.17732700
H	3.08301600	5.29000700	-0.90177200
C	-4.92068000	-3.69062100	0.87663100
F	-4.70087000	-5.00193100	0.67864000

F	-6.01761700	-3.33608600	0.19856600
F	-5.14641200	-3.49194600	2.18702000
C	-3.69599400	-2.86817700	0.40954400
O	-3.80607400	-2.07278700	-0.51186600
O	-2.64383200	-3.16389600	1.11569100
H	-1.77678900	-2.66166100	0.83219000

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C	-2.67408900	-2.23523100	-0.06830000
C	-2.48640600	-0.88469100	0.23237200
C	-1.19488900	-0.36460200	0.20566800
C	-0.08387200	-1.18809100	-0.09650800
C	-0.31182500	-2.53345700	-0.41044500
C	-1.60175600	-3.06422200	-0.39594800
H	-3.32527700	-0.24010600	0.46880000
H	0.51667300	-3.17220600	-0.70174300
H	-1.77476500	-4.10576800	-0.64385700
Cl	-4.29777700	-2.89948500	-0.04945200
C	1.28975800	-0.56922800	-0.09007900
N	2.32819100	-1.45322900	0.07037200
H	2.07371700	-2.31476200	0.53369300
C	3.76909800	-1.11133400	0.16851300
C	4.49988700	-2.45120400	0.35844600
H	4.30717600	-3.12732500	-0.48263700
H	5.57972000	-2.28603000	0.42324900
H	4.18516800	-2.94941300	1.28529300
C	4.24040500	-0.45029900	-1.13928800
H	4.04596900	-1.10941700	-1.99289600
H	3.72544800	0.49789800	-1.30287800
H	5.31893200	-0.26183400	-1.08910100
C	4.04182000	-0.19035500	1.37441200
H	3.49996400	0.75166700	1.26766700
H	3.73087600	-0.67317200	2.30902200
H	5.11347300	0.02878600	1.44681900
N	1.50055700	0.70167200	-0.25535300
C	-1.79398200	2.23490100	0.36323400
C	-0.83141700	1.06454700	0.47883700
C	0.29711300	1.45299400	-0.48241900
C	0.32043000	2.97618500	-0.36022200
O	-2.98720000	2.28650300	0.58893000
O	1.20587500	3.76800200	-0.58404400
N	-1.00241500	3.32654600	-0.00224200
C	-1.50128300	4.69292200	-0.02296200
H	-0.65514500	5.34637200	-0.24031400
H	-2.27098000	4.80732800	-0.79225500
H	-1.93530700	4.95026200	0.94704300
H	-0.41030500	1.13342800	1.49709000
H	-0.07081700	1.28156200	-1.51270000

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C	2.65617100	3.07776100	-0.92525900
C	1.53628500	2.46050600	-1.39535300
C	1.38141100	1.02222700	-1.27245100
C	2.58231400	0.24119200	-0.93336200
C	3.72460600	0.95187500	-0.46135700
C	3.76559600	2.32185300	-0.43701800
H	0.72927900	3.02001800	-1.85361800
H	4.60623700	0.39073400	-0.17288300
H	4.65520700	2.84380800	-0.10050900
Cl	2.80724000	4.83318100	-0.99014200
C	2.54234600	-1.17593400	-0.98827000
N	3.59032000	-1.90488400	-0.42212300
H	3.81190900	-1.56686600	0.50967100
C	3.76792100	-3.36972700	-0.52924600
C	2.67748100	-4.15316500	0.23521800
H	1.69502400	-3.97718100	-0.20700500
H	2.88768300	-5.22958500	0.20910500
H	2.64927600	-3.84178800	1.28740100
C	3.79910200	-3.79177300	-2.00794600
H	2.82903800	-3.63905100	-2.48599300
H	4.55653900	-3.21803100	-2.55384300
H	4.05284300	-4.85530100	-2.08360000
C	5.14123600	-3.65899500	0.10613200
H	5.93586300	-3.12204600	-0.42307300
H	5.16200200	-3.35049200	1.15999900
H	5.36190900	-4.73112000	0.07195200
N	1.46472700	-1.84027800	-1.48681100
C	-0.86231700	0.65826100	-2.71241100
C	0.58702100	0.32477800	-2.36662600
C	0.53767400	-1.15865800	-2.10180200
C	-0.72279400	-1.69820000	-2.61547000
O	-1.39423700	1.75779300	-2.80584800
O	-1.13791200	-2.84036400	-2.72231700
N	-1.48596900	-0.54310200	-2.98678000
C	-2.84860400	-0.63617000	-3.47610000
H	-3.03670900	-1.68300400	-3.71882500
H	-3.55919600	-0.30588400	-2.71034500
H	-2.97104900	-0.00870800	-4.36288500

H	0.57883500	0.97123400	-0.01970700
H	1.12354000	0.49540900	-3.32516100
C	-4.33786500	-2.12688500	0.13939500
C	-2.96425500	-2.37933700	0.15094100
C	-2.07827000	-1.31959400	0.30625100
C	-2.54459700	0.00698900	0.42407700
C	-3.93880000	0.23023500	0.40635300
C	-4.83266600	-0.82576100	0.27178500
H	-2.59171400	-3.38859600	0.01964200
H	-1.01331600	-1.52034800	0.30361700
H	-4.32954400	1.23489000	0.53806600
H	-5.90285400	-0.64911600	0.27694600
Cl	-5.46140700	-3.45613800	-0.03995000
C	-1.60020900	1.12647400	0.53967400
N	-1.96800800	2.32349900	0.03927100
H	-2.71794100	2.27788100	-0.64299600
C	-1.74658400	3.71611400	0.54220500
C	-3.00800700	4.09035600	1.35386600
H	-3.12485800	3.42970400	2.21979300
H	-2.93131000	5.12097300	1.71741900
H	-3.91323800	4.02092900	0.73820700
C	-0.50903600	3.84373400	1.43589600
H	-0.59368200	3.23393600	2.34002600
H	0.40512900	3.56445400	0.91041700
H	-0.42016000	4.89081300	1.74492300
C	-1.63259800	4.63798300	-0.68276300
H	-0.72808300	4.43040500	-1.25697800
H	-2.49242300	4.51973700	-1.35278600
H	-1.60129000	5.68250700	-0.35621600
N	-0.32115600	0.93459100	0.95872900
C	-0.17740400	-0.46867200	4.33069500
C	-0.90955500	0.19128200	3.24296300
C	-0.09145500	0.32076800	2.16133900
C	1.26590100	-0.25585200	2.54937100
H	-1.94111600	0.49502500	3.34718100
O	-0.54987600	-0.77318100	5.44746100
O	2.28100100	-0.31350100	1.87822900
N	1.13364400	-0.71346200	3.84039100
C	2.19132400	-1.34698300	4.60228800
H	3.03922900	-0.66674500	4.73096600
H	1.77473600	-1.60496600	5.57736500
H	2.54006400	-2.25396000	4.09826100

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C	-5.42749600	-0.83858900	0.43857400
C	-4.50564100	-1.39098700	-0.44971700
C	-3.46239100	-0.59701500	-0.92413500
C	-3.33959000	0.75435900	-0.52318200
C	-4.27786800	1.27080700	0.38579200
C	-5.32328600	0.48593900	0.86452300
H	-4.58839500	-2.42077600	-0.77878800
H	-4.16840200	2.28136500	0.76755500
H	-6.04130100	0.89007300	1.56997900
Cl	-6.75081900	-1.83182100	1.03618500
C	-2.17297800	1.53552600	-1.00396500
N	-2.25639600	2.91506300	-0.91466100
H	-3.21491500	3.23365800	-0.85523800
C	-1.39682600	3.87821800	-1.65193000
C	0.03655000	3.85723300	-1.09491600
H	0.48761200	2.87354400	-1.23404900
H	0.64738300	4.60583700	-1.61301700
H	0.03717400	4.09710800	-0.02641600
C	-1.39014300	3.57616300	-3.16475400
H	-0.96398900	2.58918500	-3.35981300
H	-2.40839300	3.60400700	-3.57143000
H	-0.79140200	4.32355200	-3.69816200
C	-2.01796500	5.26343000	-1.40292900
H	-3.03580600	5.32471900	-1.81085600
H	-2.06089200	5.48658300	-0.33060700
H	-1.41982000	6.04018500	-1.88944900
N	-1.06534200	0.95235800	-1.40874800
C	-2.05189200	-2.55216500	-2.00806400
C	-2.43498300	-1.07269200	-1.92310700
C	-1.12609200	-0.37714100	-1.66263500
C	-0.06249300	-1.29185700	-1.81351600
O	-2.79731300	-3.52118200	-2.06819600
O	1.18016200	-1.17794200	-1.74152900
N	-0.67765400	-2.58207200	-2.06550200
C	0.09253500	-3.78502300	-2.27705600
H	0.88458600	-3.59264400	-3.00581700
H	0.56341600	-4.13148100	-1.34621900
H	-0.58403900	-4.56058500	-2.64071000
H	0.18433600	-0.65551200	0.91398500
H	-2.80091500	-0.81600100	-2.93737200
C	5.88595400	-0.07391400	-0.94809500
C	4.73806300	0.63610700	-1.31626900
C	3.50223600	0.24876000	-0.81614300
C	3.39911700	-0.84796700	0.06591700

C	4.56955800	-1.55124500	0.41454300
C	5.81013200	-1.16956200	-0.08659100
H	4.81534900	1.47099000	-2.00424700
H	2.59791900	0.74478700	-1.14476100
H	4.51195400	-2.38347900	1.10981200
H	6.71028700	-1.70518400	0.19478800
Cl	7.44431500	0.41645200	-1.58229300
C	2.10450200	-1.27271700	0.59273600
N	1.87928500	-2.58306000	0.84744400
H	2.40934100	-3.21151600	0.25775100
C	1.07174800	-3.23803400	1.92408000
C	1.43748000	-4.73076600	1.84284000
H	2.51451200	-4.88350000	1.98089900
H	0.91571100	-5.28590300	2.62734900
H	1.14192600	-5.15935600	0.87788600
C	1.48642700	-2.67778300	3.29740100
H	2.55508800	-2.83685800	3.47819700
H	1.27678800	-1.60790000	3.37913700
H	0.92527800	-3.18789100	4.08761300
C	-0.44873800	-3.08028100	1.71150000
H	-0.80166500	-2.06575100	1.92153100
H	-0.73861900	-3.34795200	0.69164500
H	-0.98114900	-3.74586300	2.39987100
N	1.16462800	-0.38392200	1.02405500
C	1.73867200	2.91843900	2.46850800
C	2.32148700	1.71310400	1.84847800
C	1.29855200	0.87987400	1.53420700
C	0.00064900	1.50182400	1.98056400
H	3.38295800	1.60111700	1.69285100
O	2.29262900	3.91850200	2.88297200
O	-1.10141800	0.97916600	1.90070900
N	0.32682100	2.72175000	2.51595400
C	-0.62029200	3.67299000	3.06324000
H	-1.12753100	3.25810800	3.94029400
H	-0.05543200	4.56101400	3.35230500
H	-1.37018500	3.93419600	2.31048900

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C	2.30778800	-2.24174600	0.14914900
C	2.23036400	-1.31264100	-0.84633200
C	0.93928400	-0.75905200	-1.24061600
C	-0.24247200	-1.23566900	-0.49930300
C	-0.08149400	-2.24394500	0.47907600
C	1.15744000	-2.74945900	0.81397700
H	3.11985200	-0.97621900	-1.36730000
H	0.79901400	-0.78297600	-2.31933600
H	-0.95170100	-2.56604700	1.04540300
H	1.26911600	-3.48549500	1.60135200
Cl	3.87678300	-2.89182700	0.61741500
C	-1.44960000	-0.44392100	-0.48655400
N	-2.66698000	-1.04488900	-0.43061100
H	-2.65414800	-2.03981300	-0.60543900
C	-3.95537100	-0.47733400	0.04888600
C	-4.96827000	-1.63226700	-0.02097700
H	-4.67195000	-2.46162900	0.63358900
H	-5.95394800	-1.28702000	0.30467200
H	-5.06597800	-2.01265000	-1.04517400
C	-3.82374500	0.01864000	1.50157700
H	-3.52512600	-0.80188600	2.16437800
H	-3.08345800	0.81815800	1.57697000
H	-4.78839600	0.40386900	1.85120500
C	-4.41109200	0.66507400	-0.87882600
H	-3.70582000	1.49824000	-0.84568900
H	-4.49237800	0.31316000	-1.91341200
H	-5.39431200	1.03101700	-0.56181600
N	-1.35759000	0.87694600	-0.24864800
C	2.04991600	1.94977400	-0.79453400
C	0.85867400	1.15307500	-1.27759400
C	-0.22375700	1.51901200	-0.41400100
C	0.24945100	2.55754000	0.55751300
H	0.71253400	1.22403500	-2.34998900
O	3.18101100	1.93828200	-1.24009600
O	-0.36262700	3.14139700	1.42894100
N	1.61725400	2.72649200	0.28548600
C	2.47838800	3.60851900	1.05174400
H	2.11492100	4.63868900	0.99177100
H	2.49699600	3.30573600	2.10316400
H	3.48057800	3.54101600	0.62615100

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C	-2.18237300	-2.42340400	-0.12440800
C	-2.26989000	-1.13353200	0.24918800
C	-1.11623100	-0.54127200	1.02860400
C	0.22764500	-1.17651200	0.65710000
C	0.18714200	-2.58707100	0.39146400
C	-0.97628900	-3.20882600	0.04134100
H	-3.18028500	-0.55915600	0.12837000
H	1.11005200	-3.15929500	0.33909600

H	-0.99127700	-4.25872400	-0.22771200
Cl	-3.55067000	-3.22948500	-0.89226600
C	1.37274900	-0.40313600	0.50783700
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H	2.69060600	-1.86345400	0.89934500
C	3.85202300	-0.45486500	-0.15986700
C	4.92410300	-1.52584800	0.10658500
H	4.61171700	-2.50639400	-0.27568000
H	5.85929300	-1.25707200	-0.39379700
H	5.12865500	-1.61833800	1.17985500
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H	2.01346800	-3.91395600	-0.67705700
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ts-14^{S}

C	2.81978600	-2.01368500	0.07135600
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C	0.47689400	-2.46398800	-0.42564300
C	1.75077800	-2.91078800	-0.36006700
H	3.40985000	-0.11341600	0.80809600
H	-0.28737600	-3.11129900	-0.84808600

TFA

C	0.60064200	0.02019200	-0.00000600
F	1.10371400	-0.58086500	-1.08895300
F	1.10365700	-0.57990700	1.08950500
F	0.98777700	1.30121800	-0.00055500
C	-0.93597600	-0.14007900	0.00004000
O	-1.46652000	-1.22013200	-0.00001200
O	-1.56149700	1.04505500	-0.00001000
H	-2.52018700	0.85592100	0.00000000

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[1] J. Li, M. John and L. Ackermann, *Chem. – Eur. J.* **2014**, *20*, 5403.

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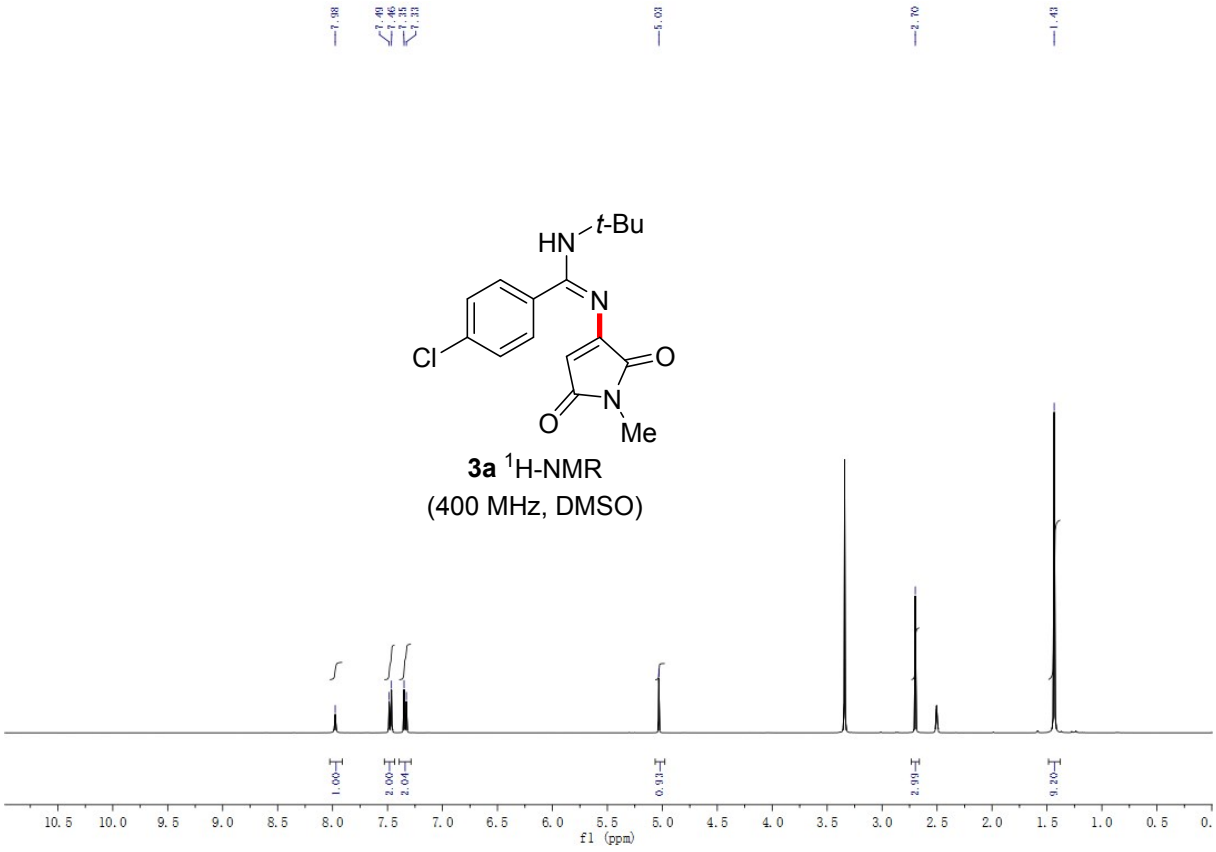
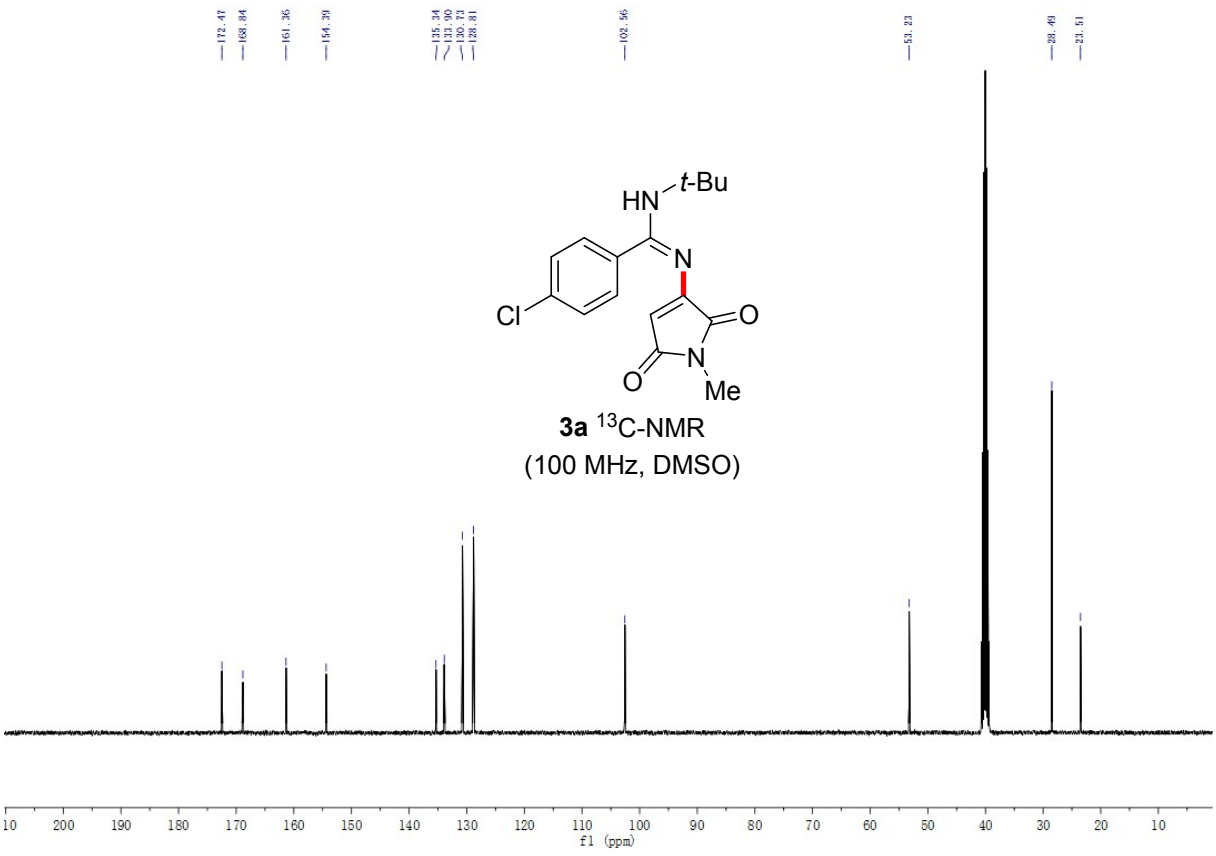
[6] D.-C. Fang, THERMO; Beijing Normal University, Beijing, People's Republic of China, **2013**.



3a ^{1}H-NMR
(400 MHz, DMSO)



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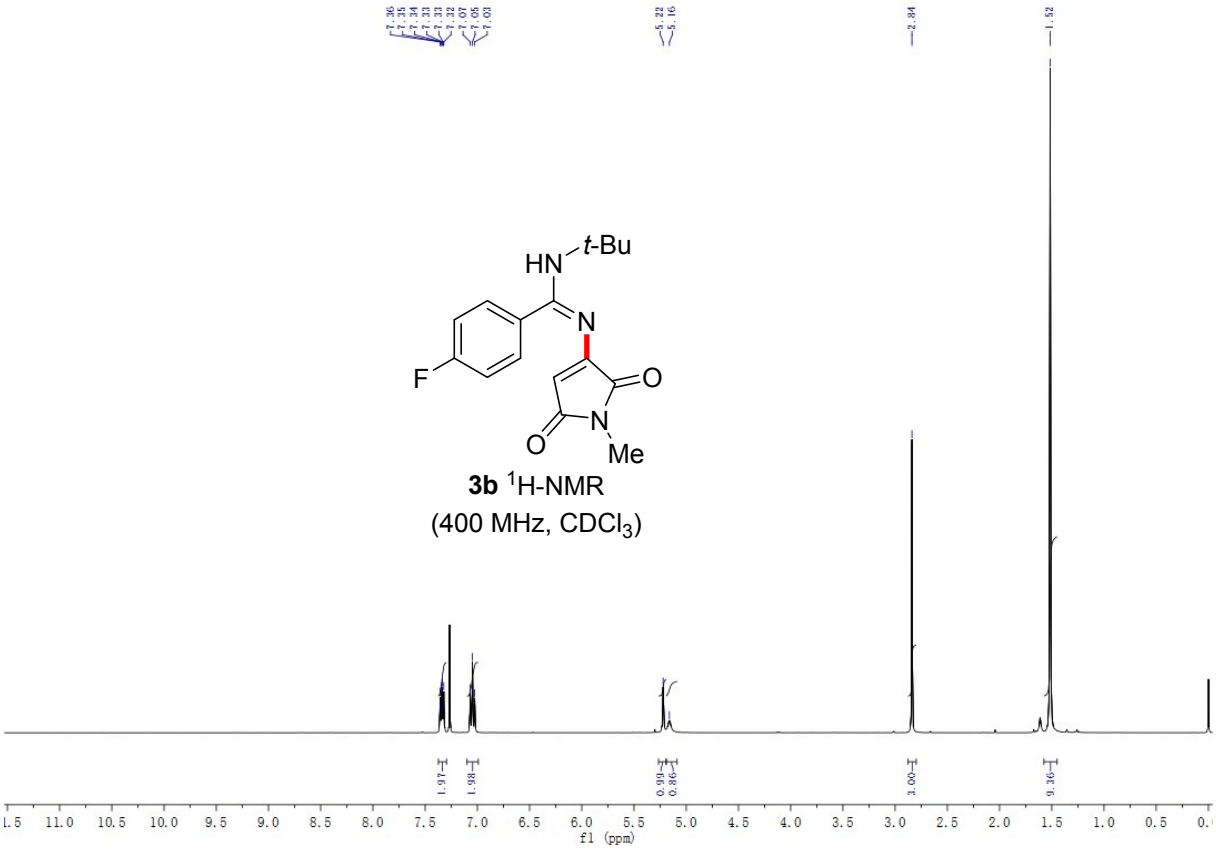
(100 MHz, DMSO)



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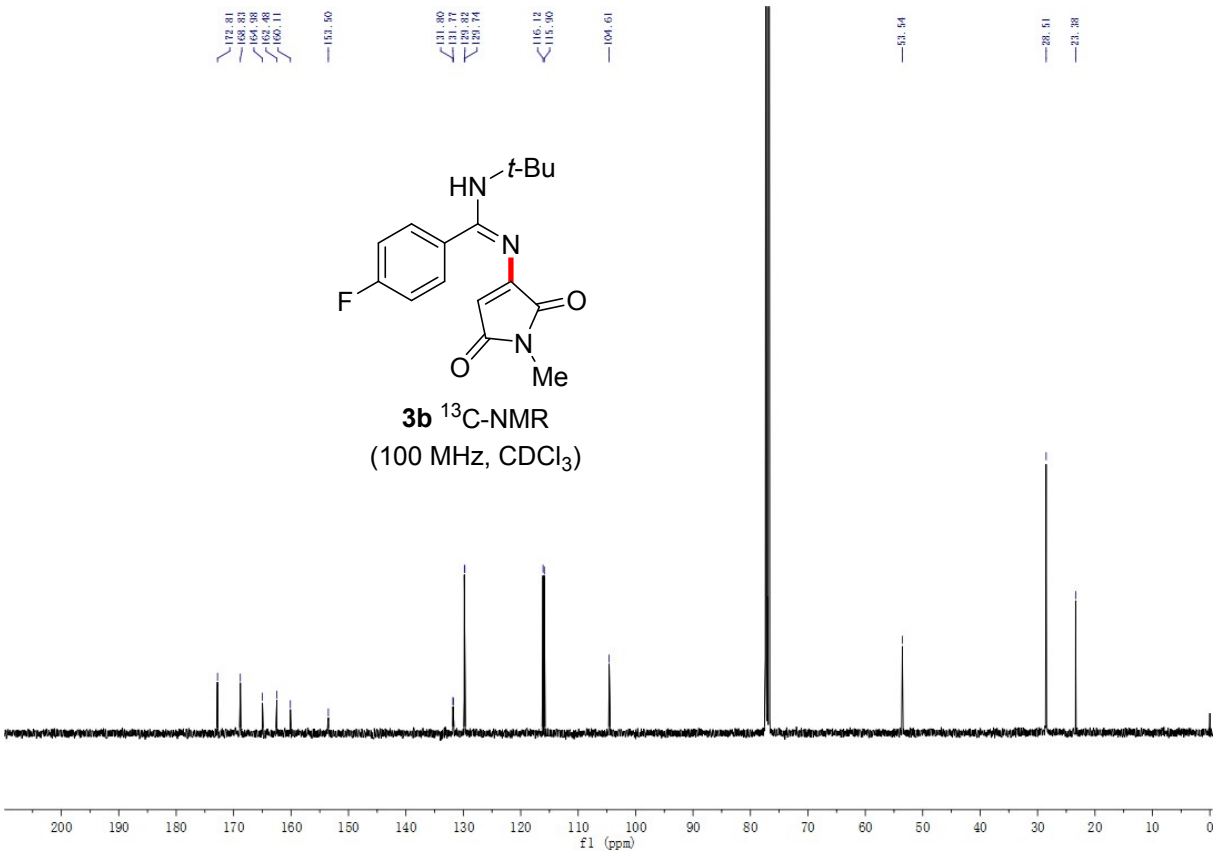

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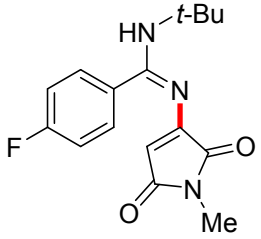
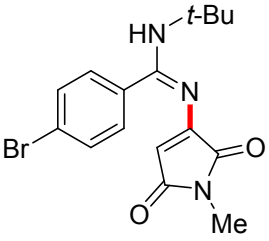


3b ^{19}F-NMR
(376 MHz, $CDCl_3$)



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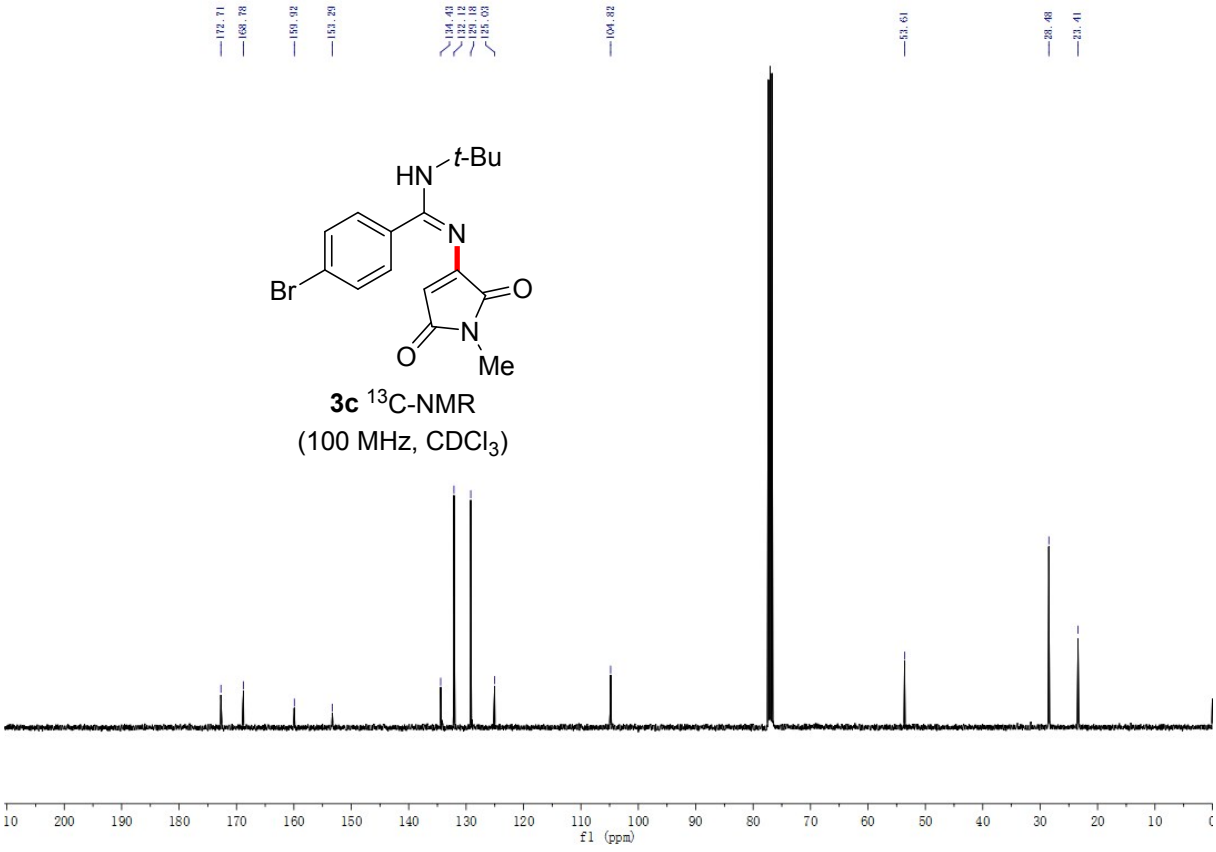

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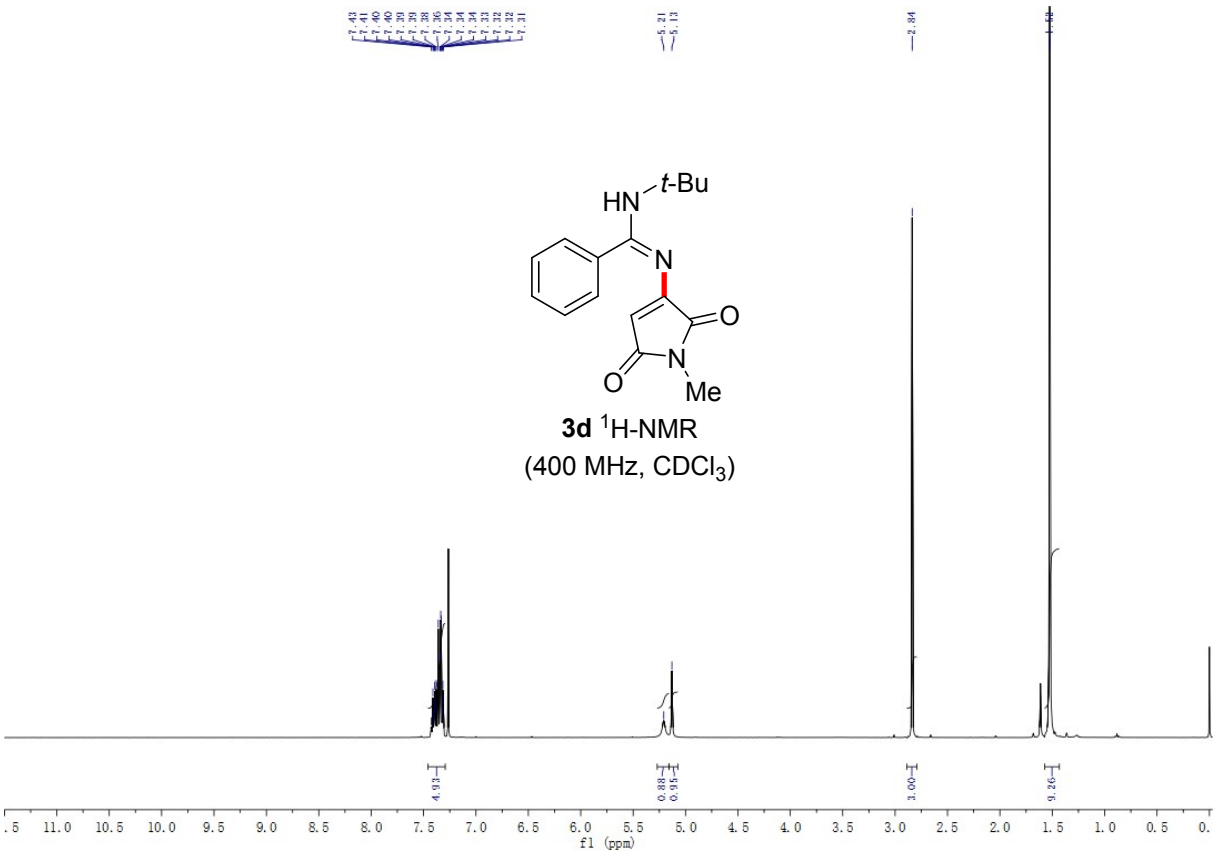

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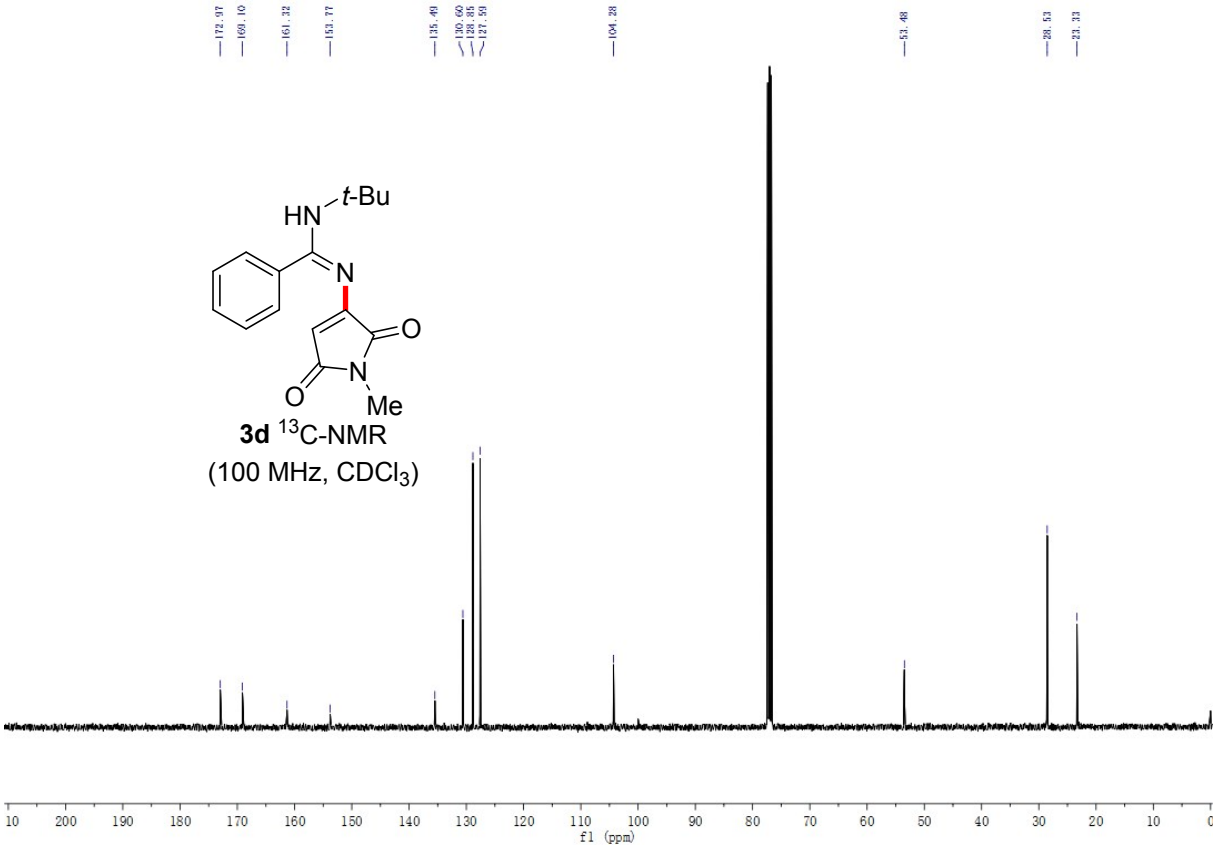

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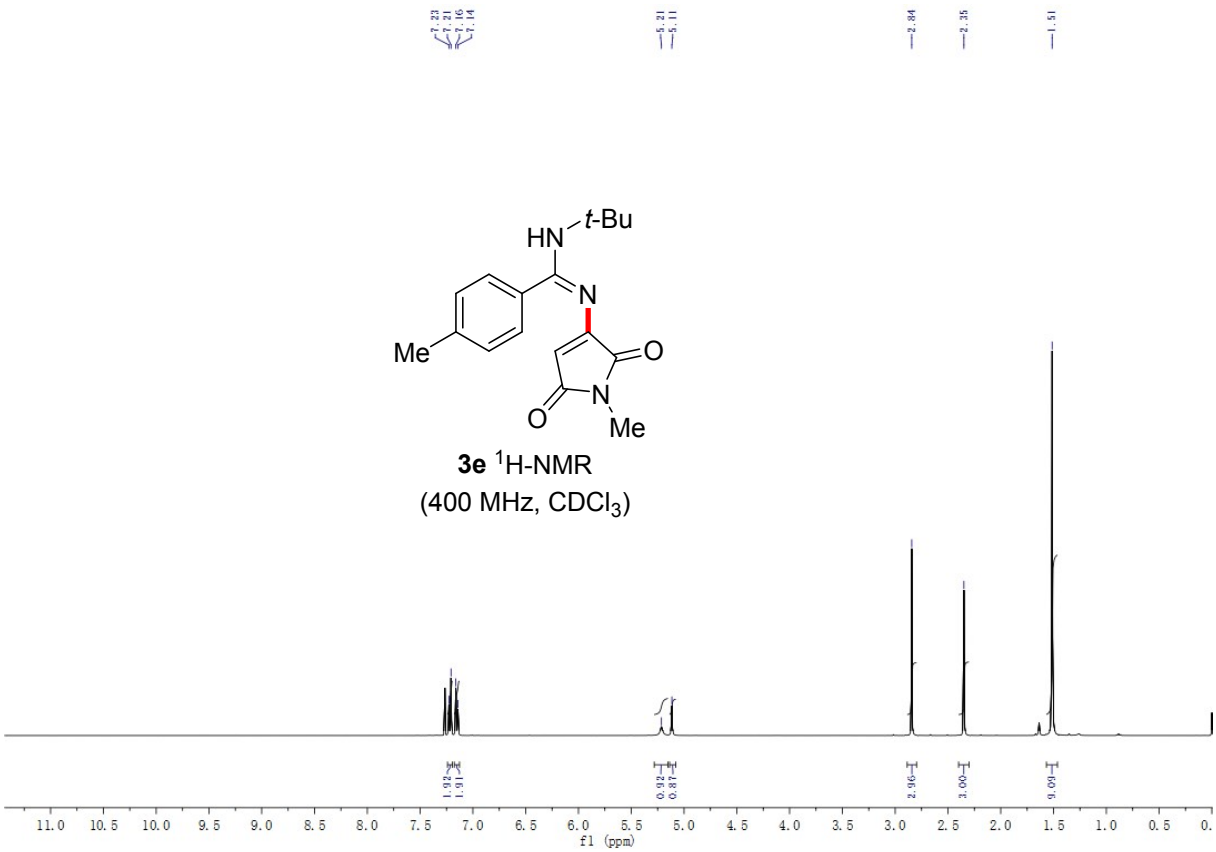

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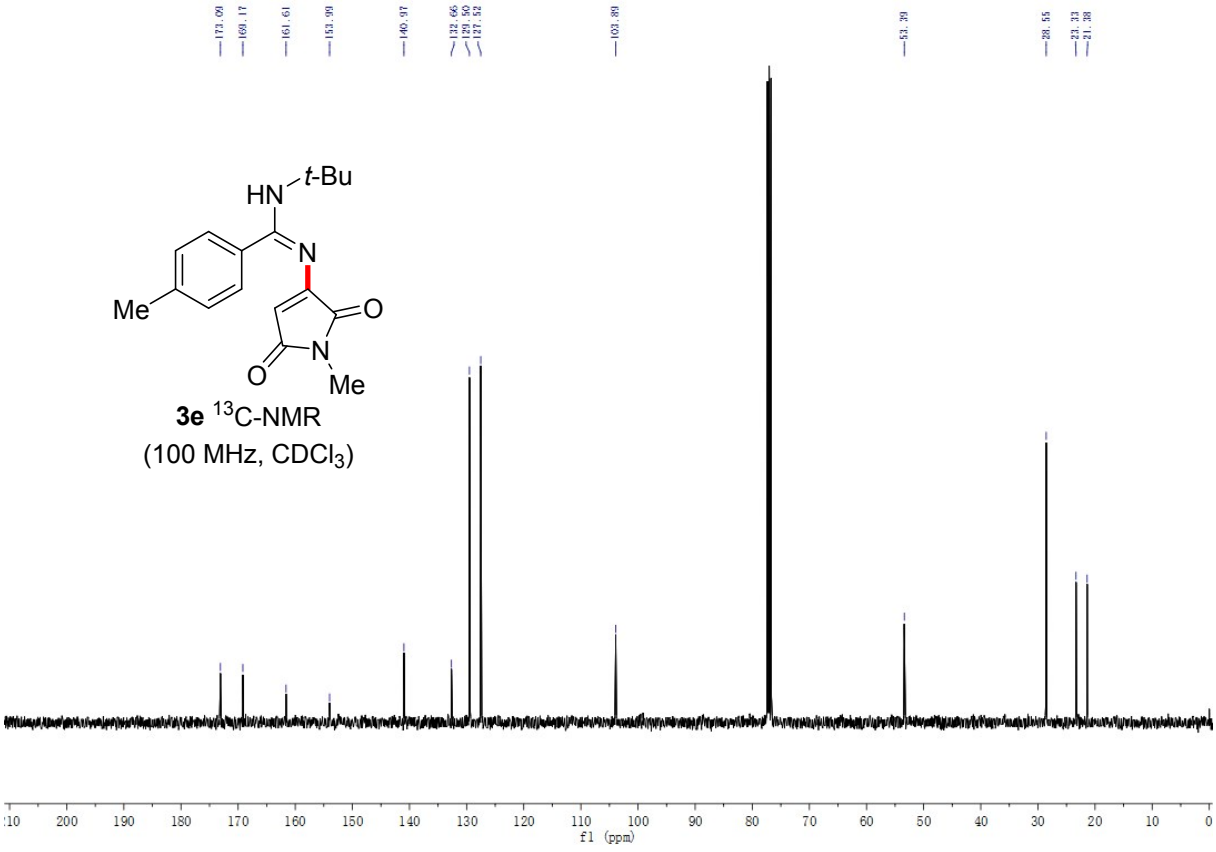

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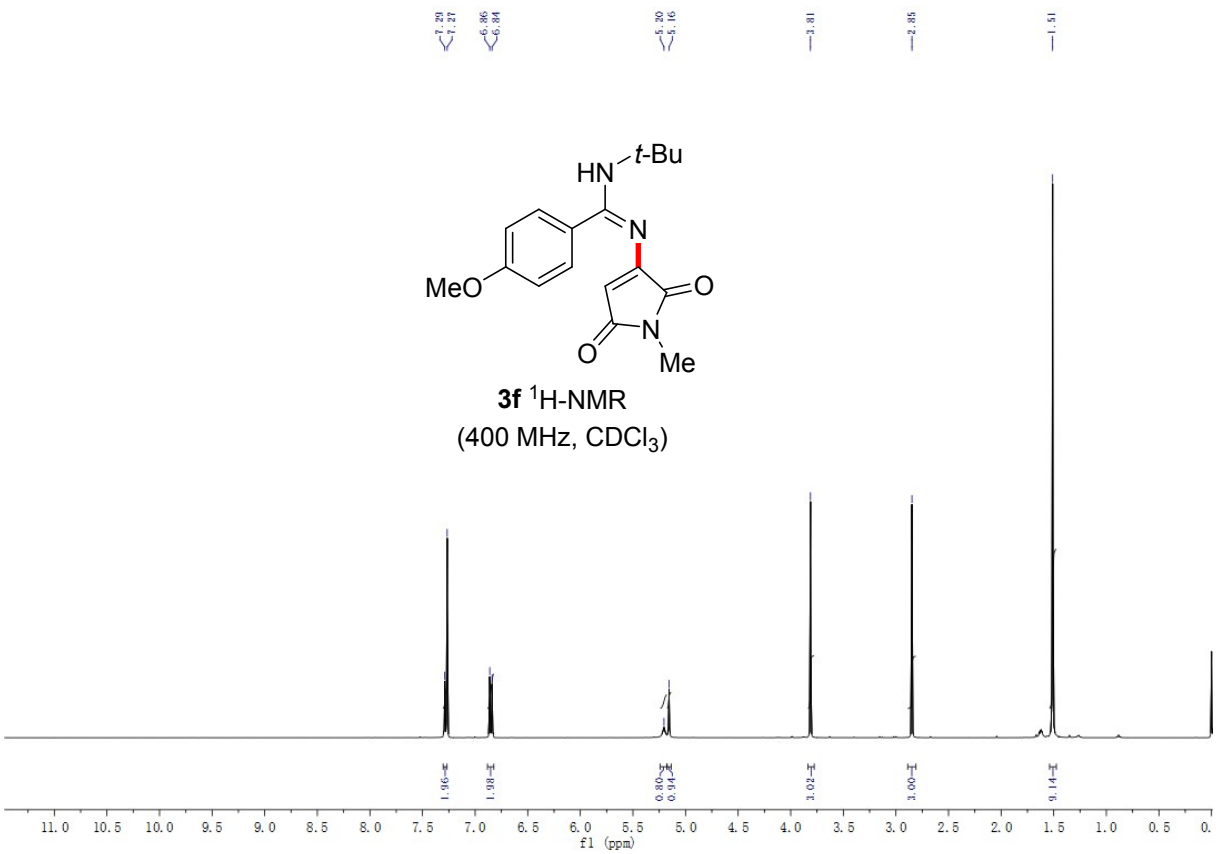

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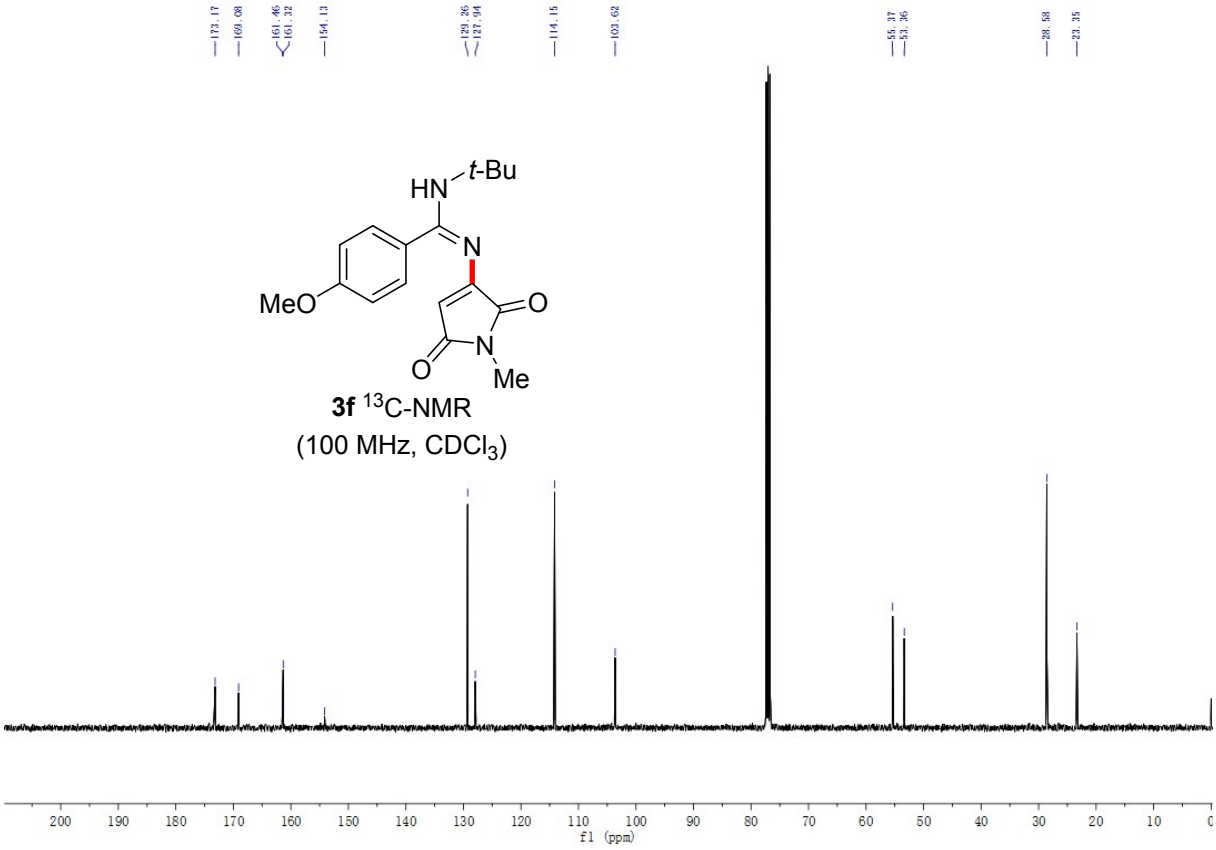

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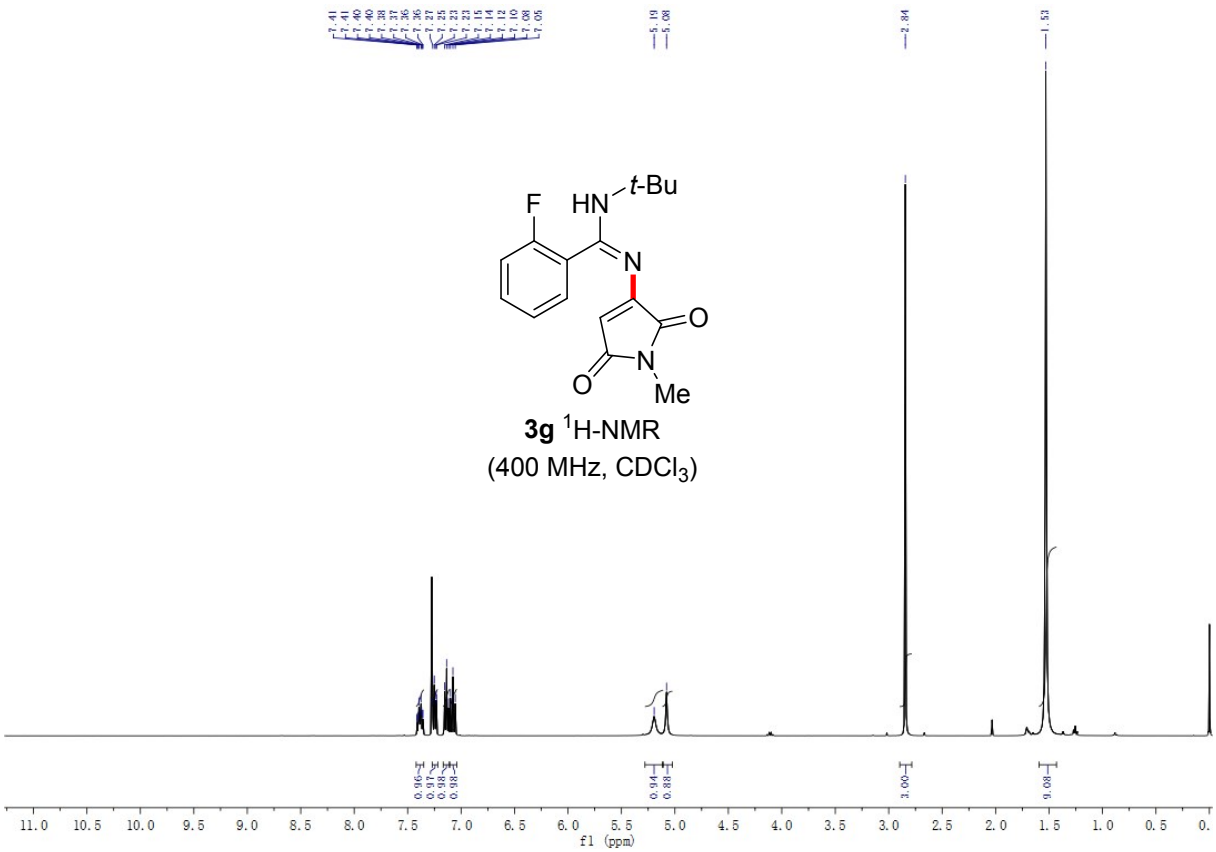

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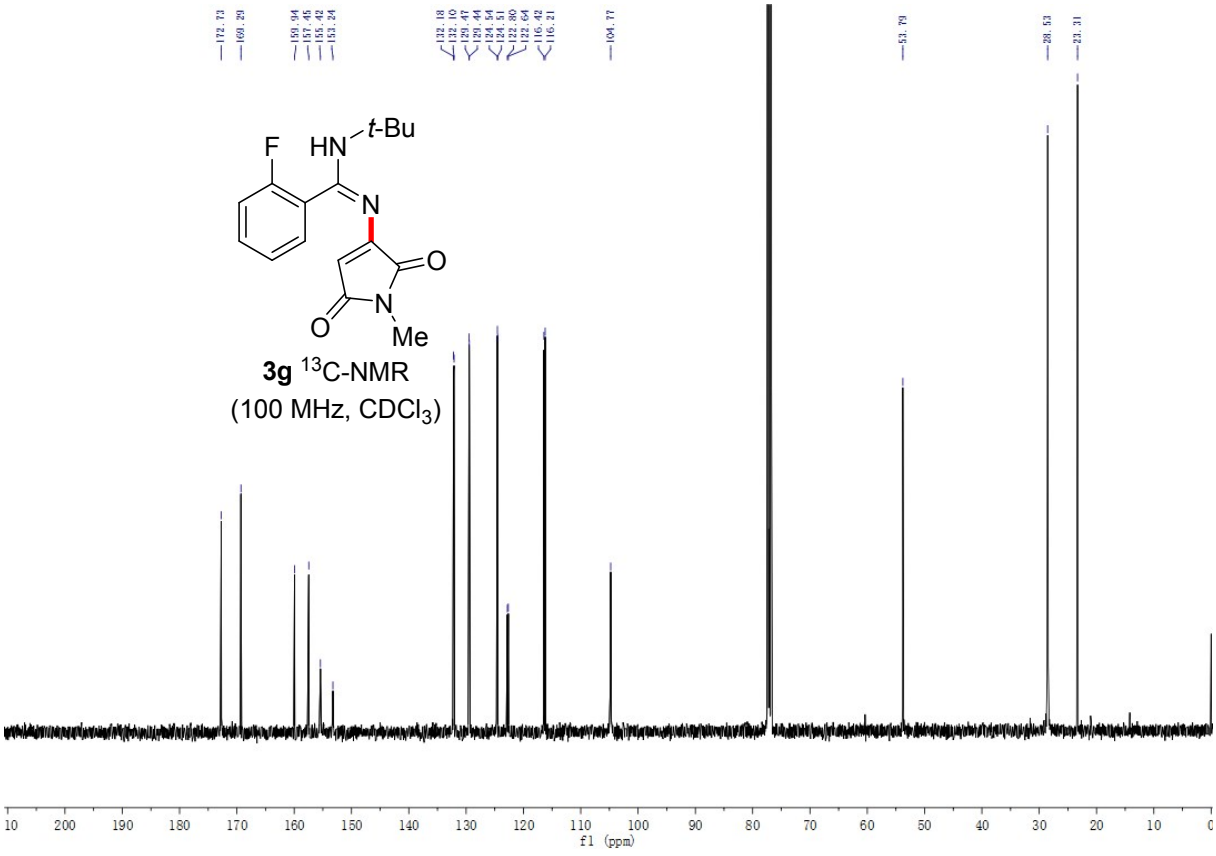

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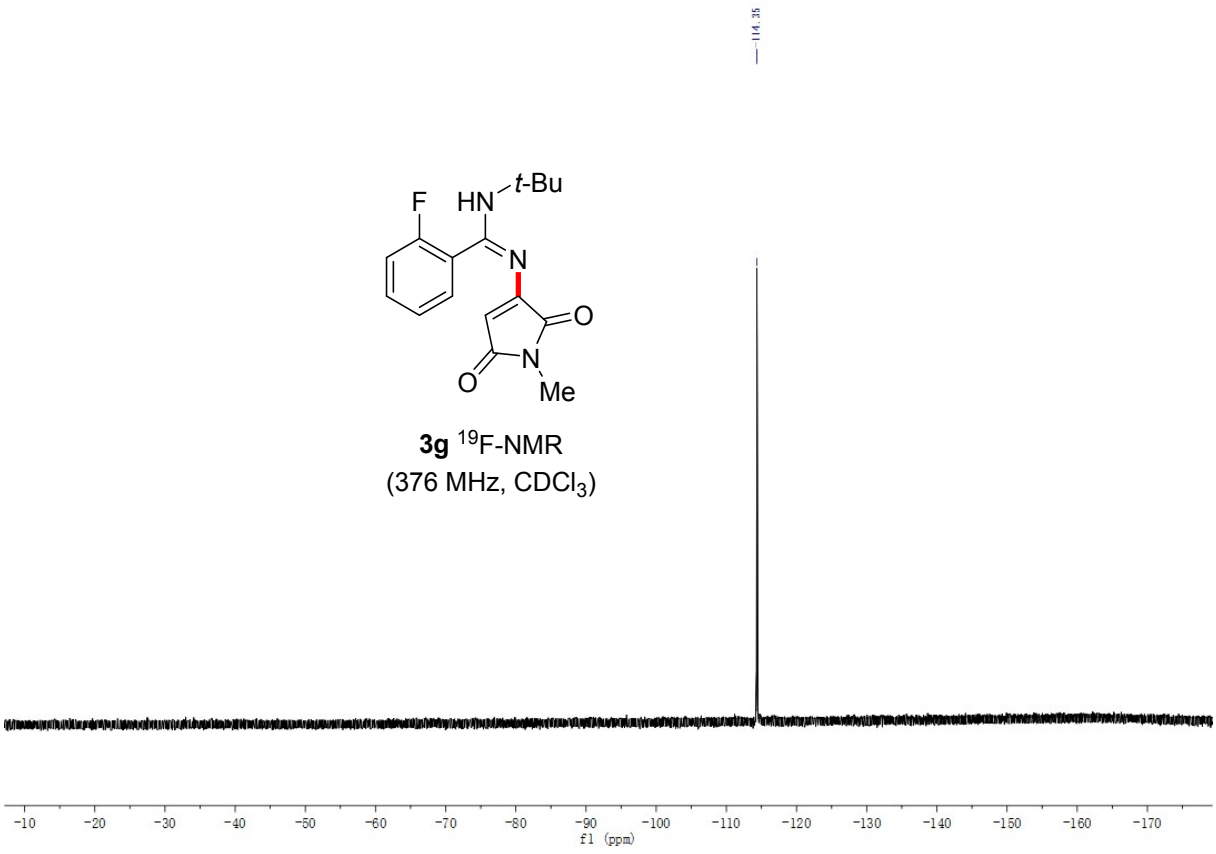
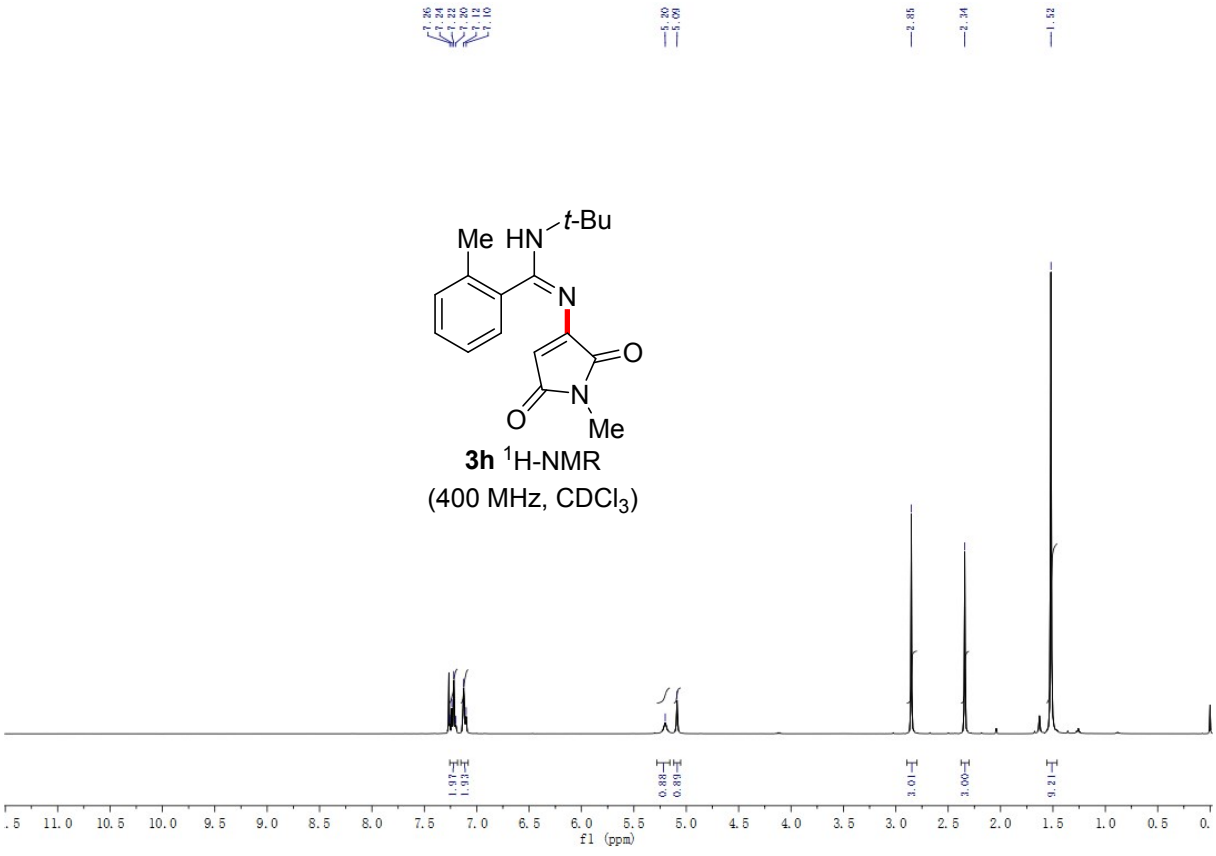
(100 MHz, $CDCl_3$)



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



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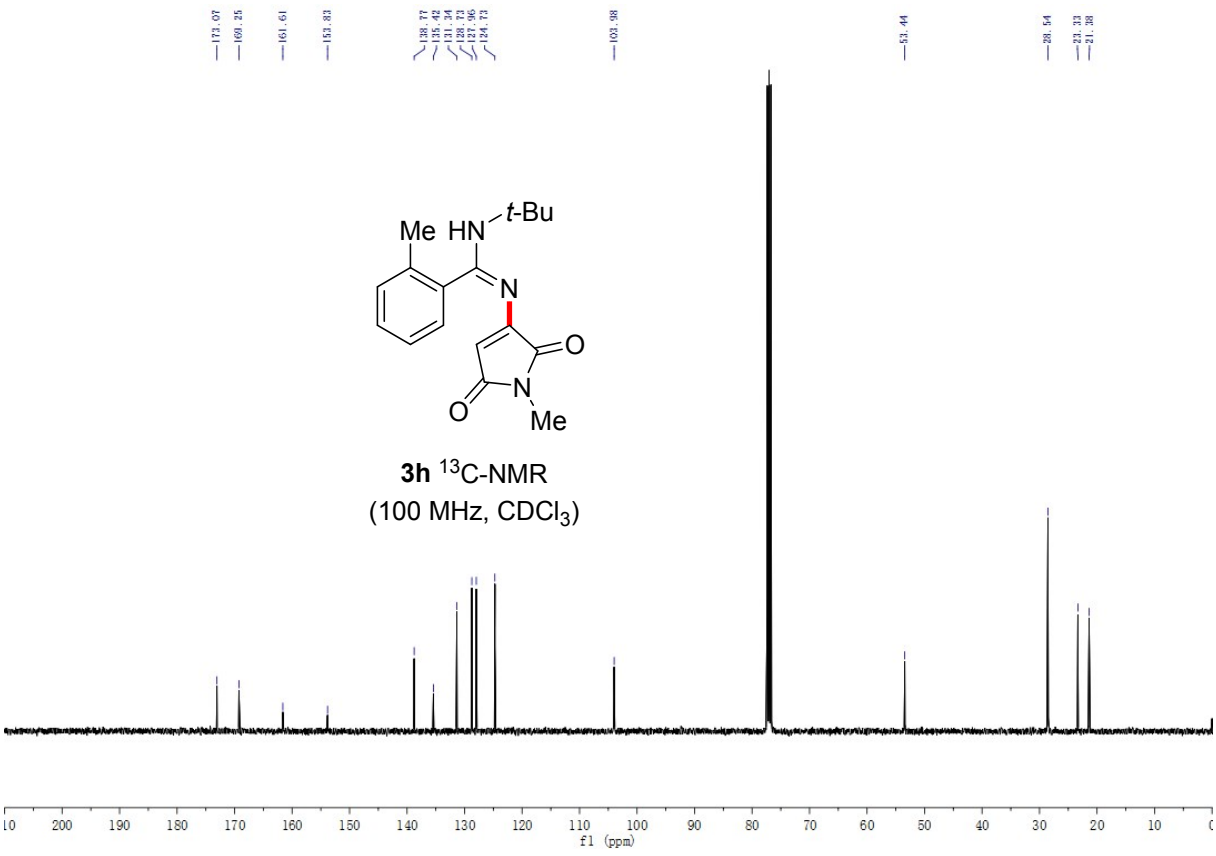

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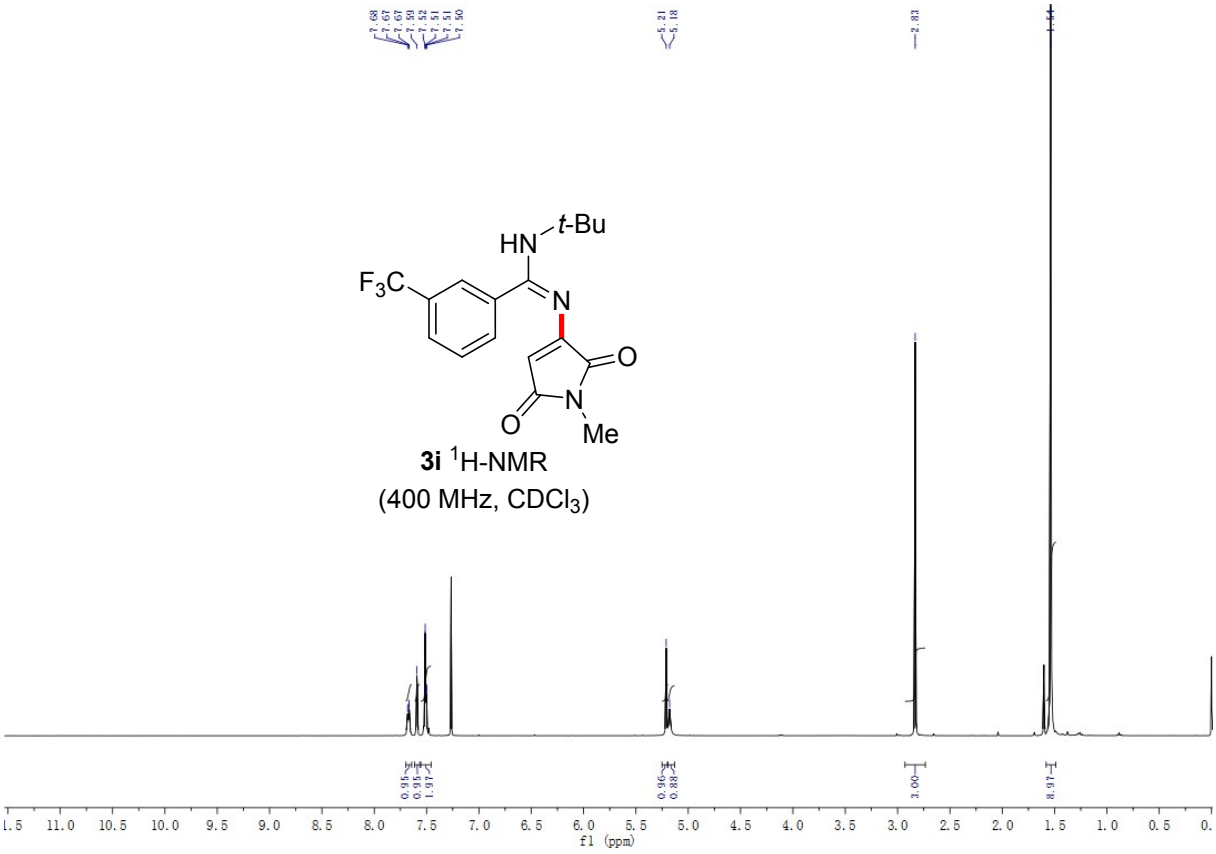
(100 MHz, $CDCl_3$)



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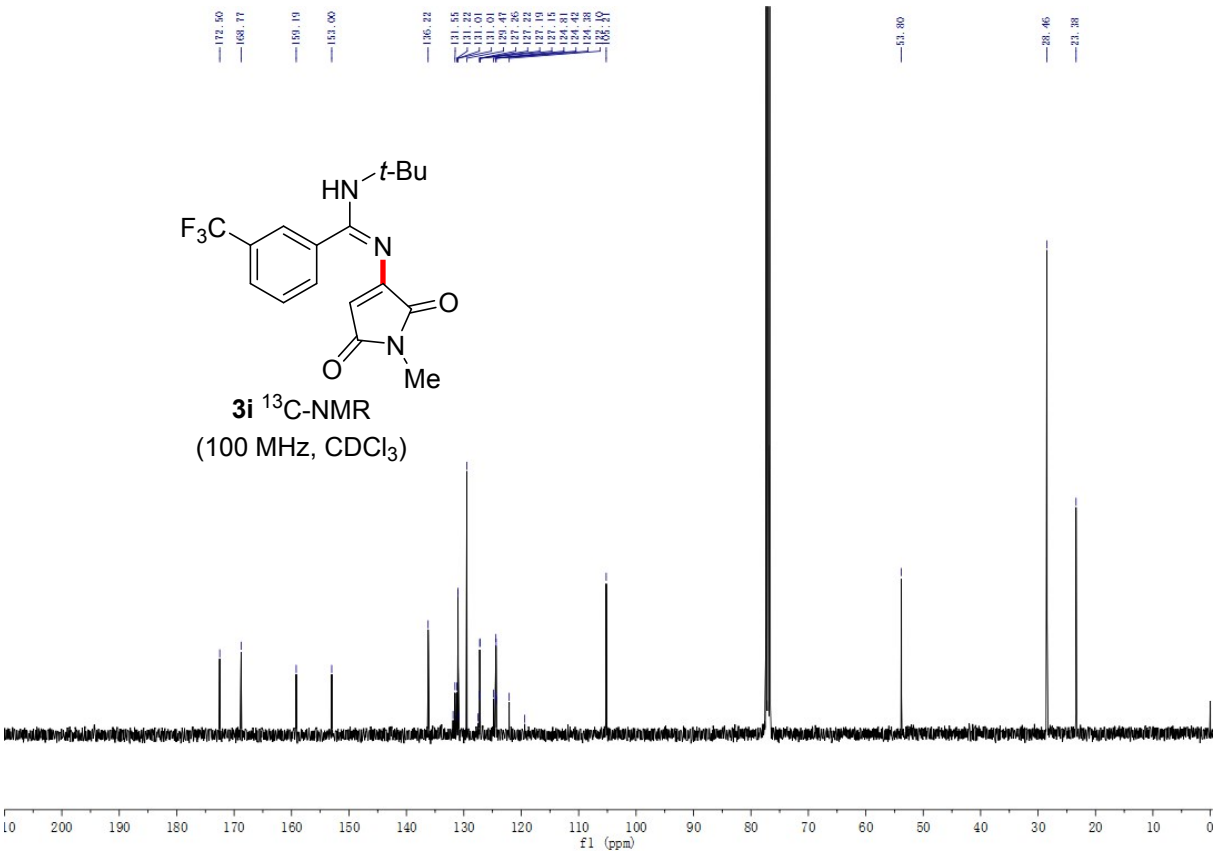

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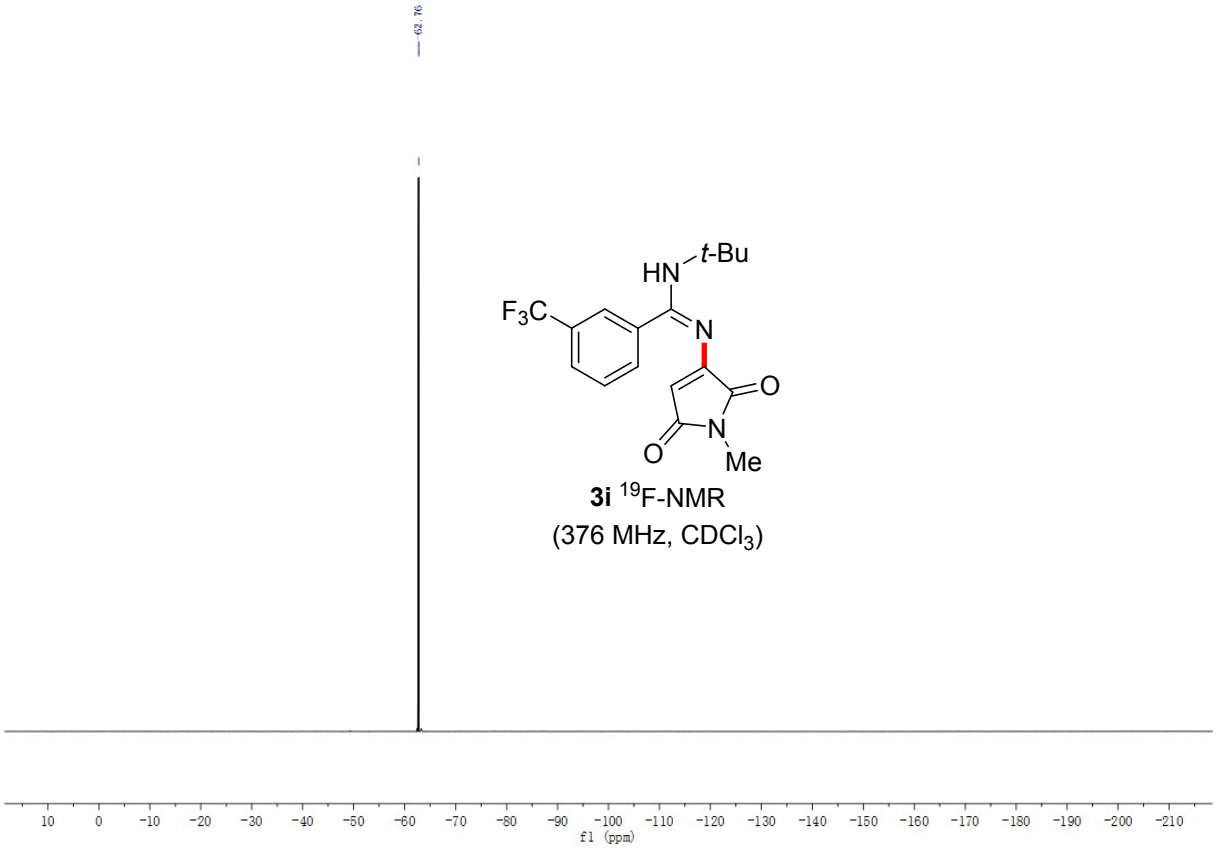

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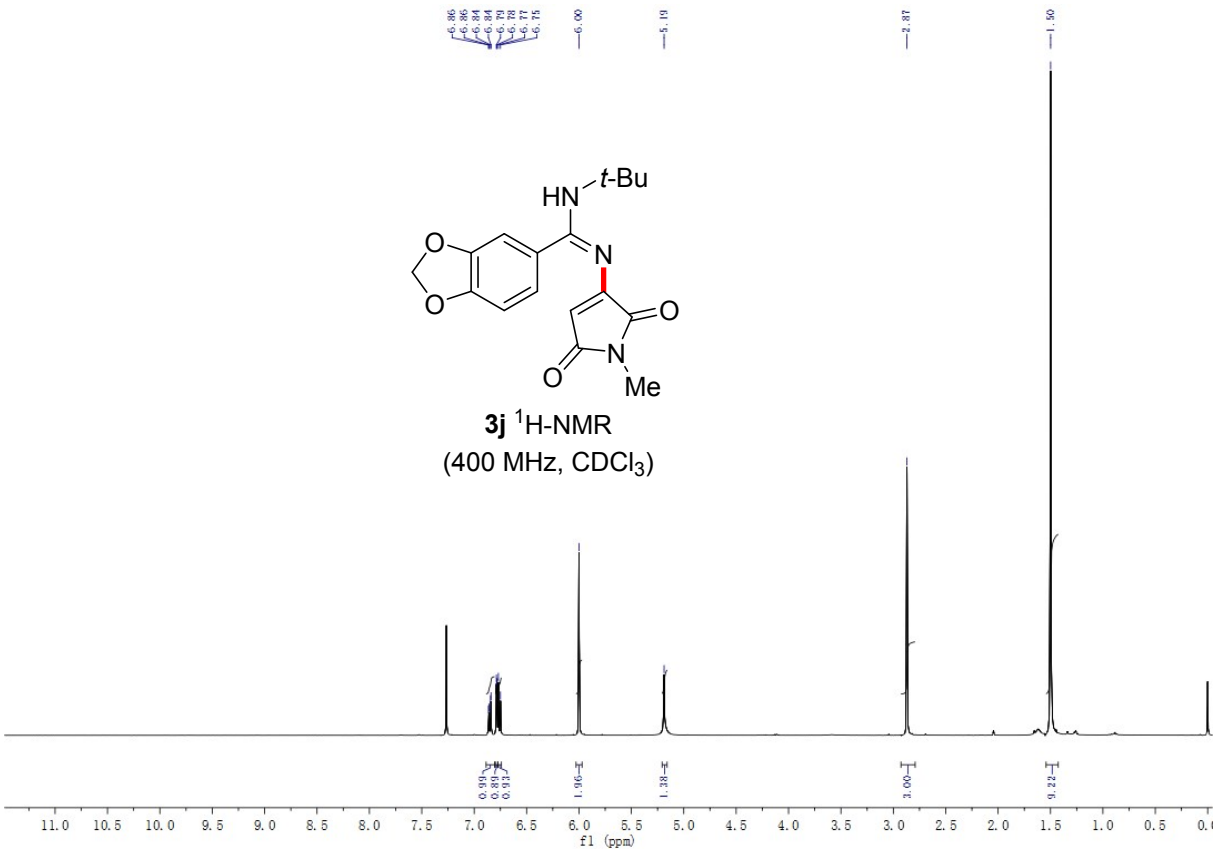

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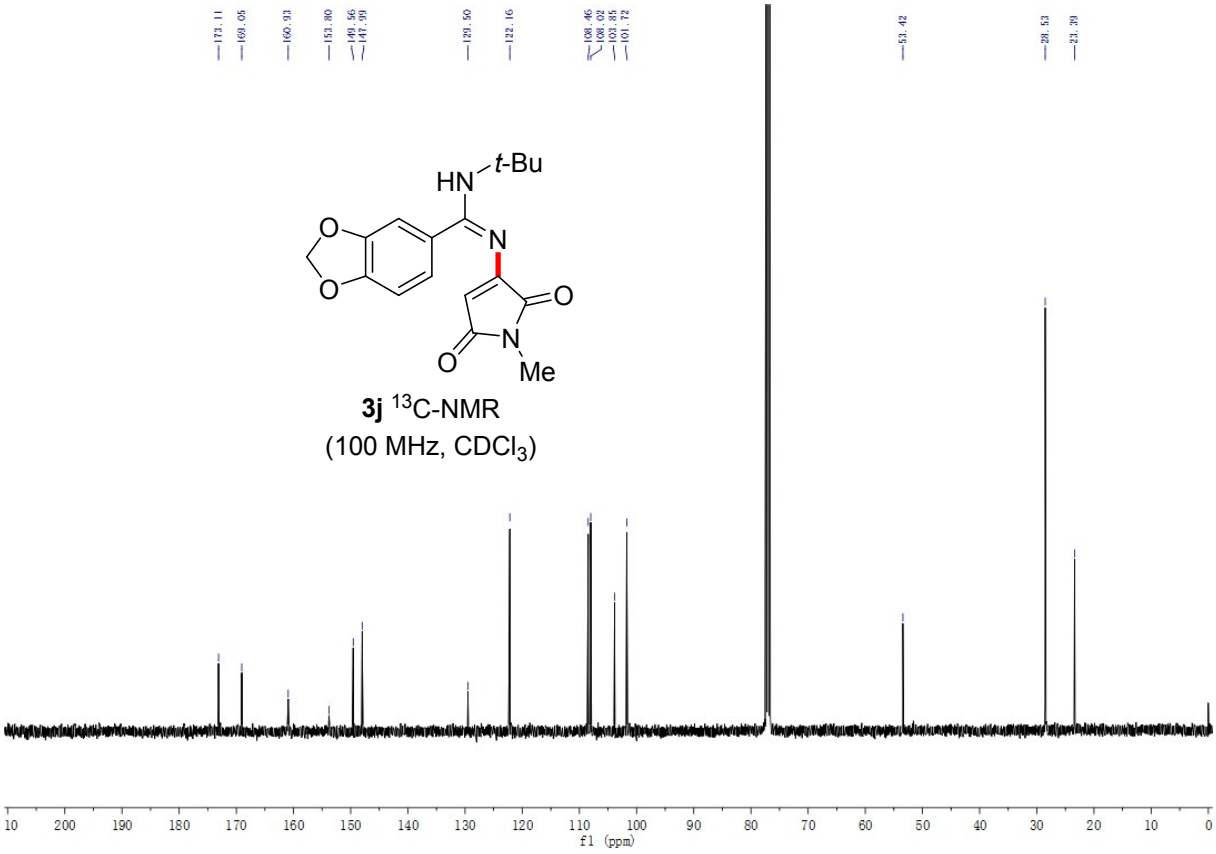

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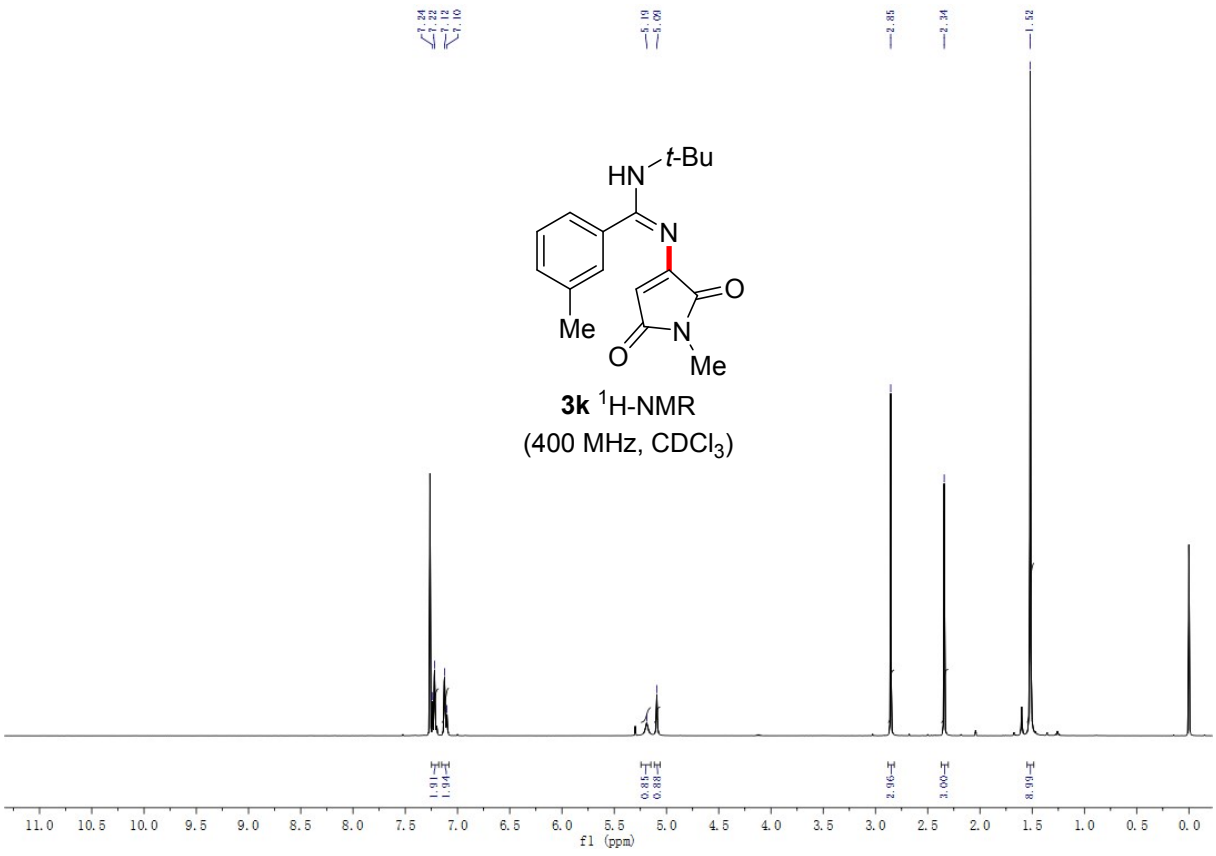

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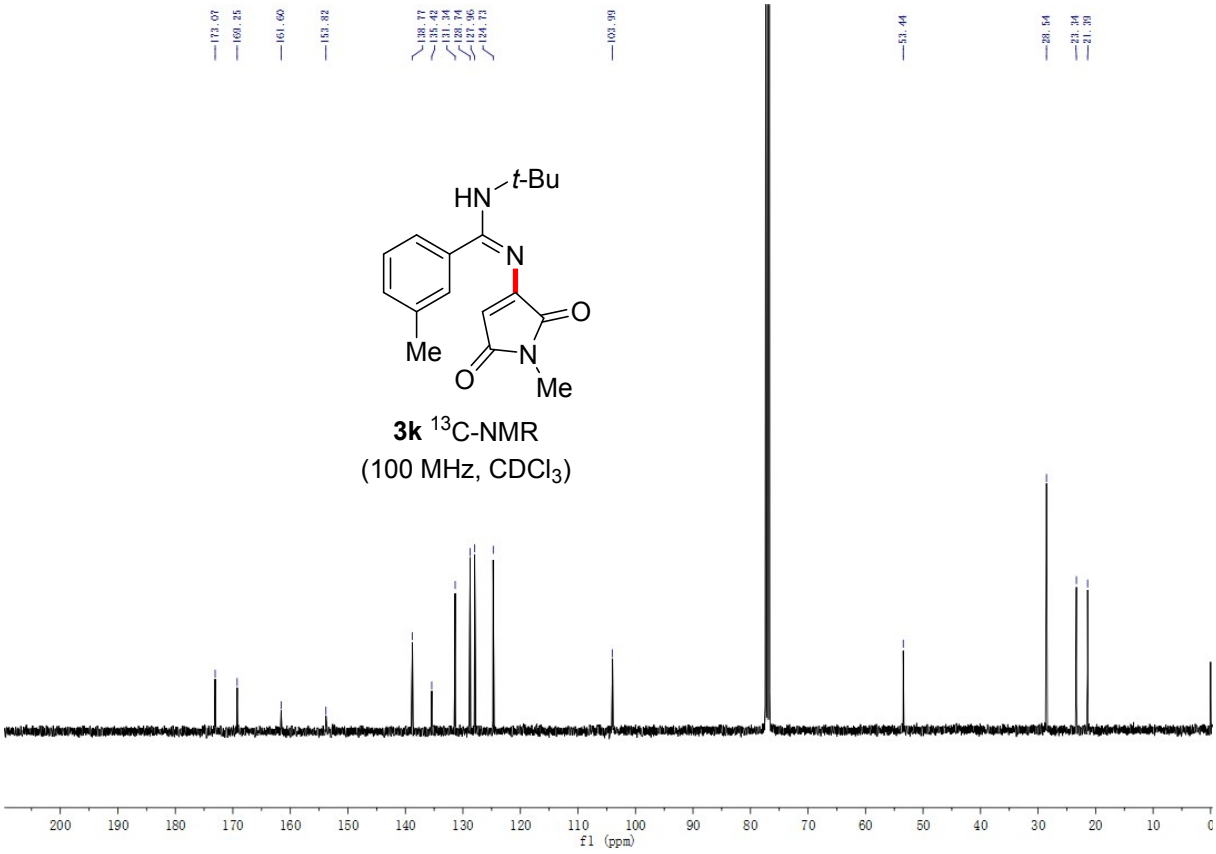

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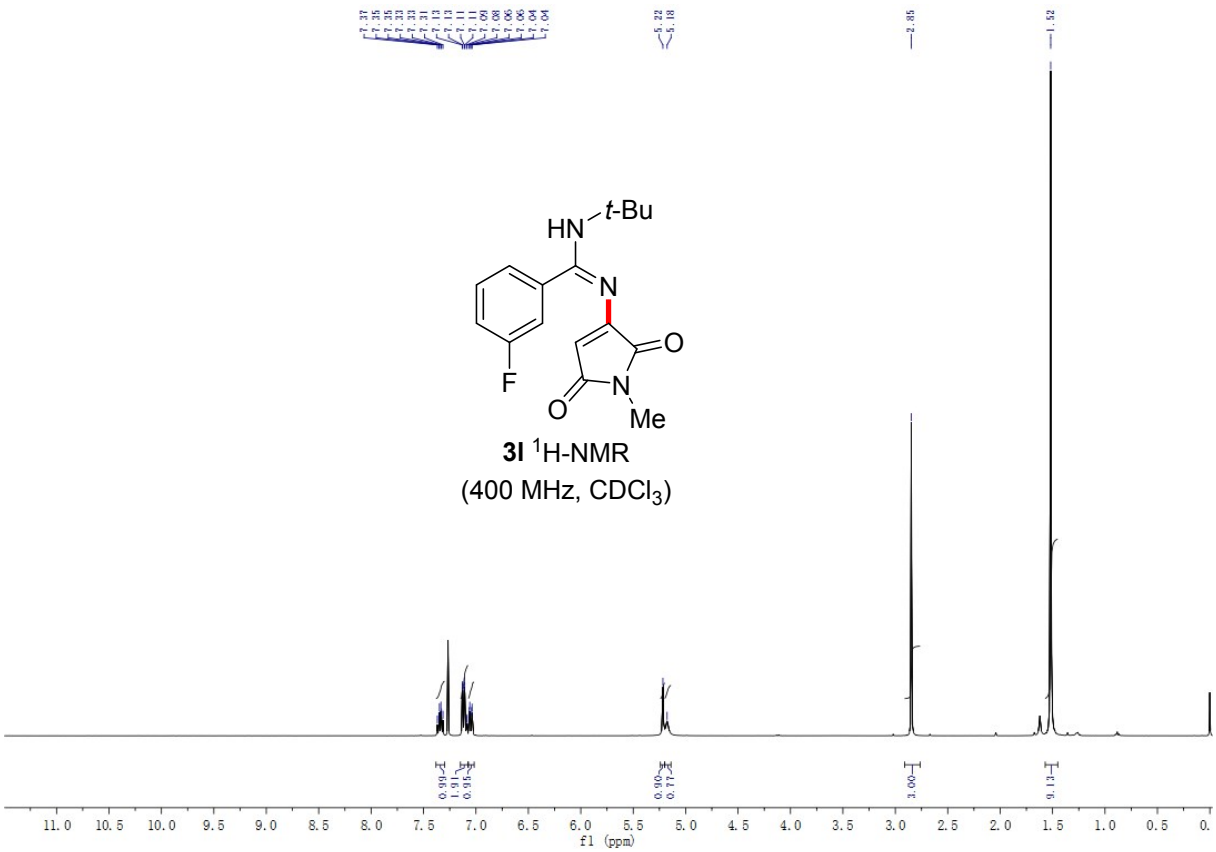

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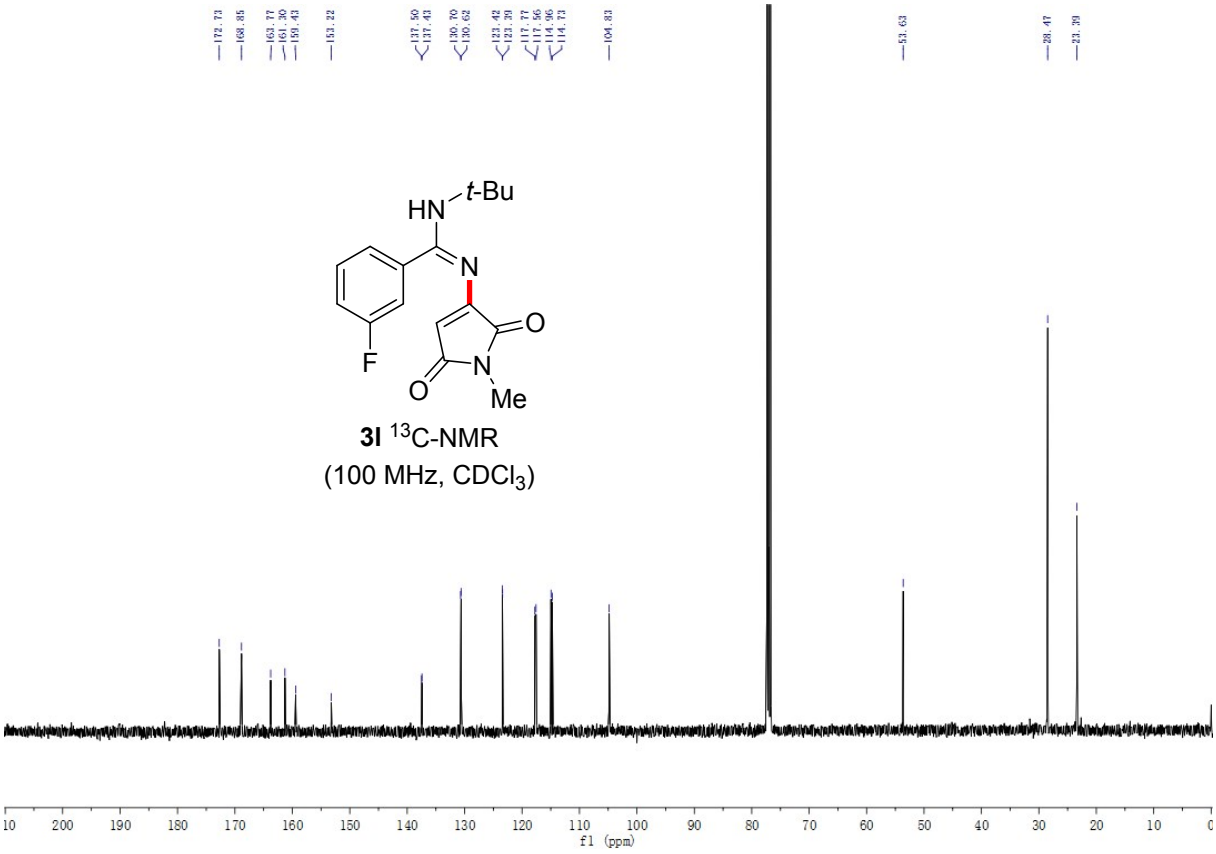

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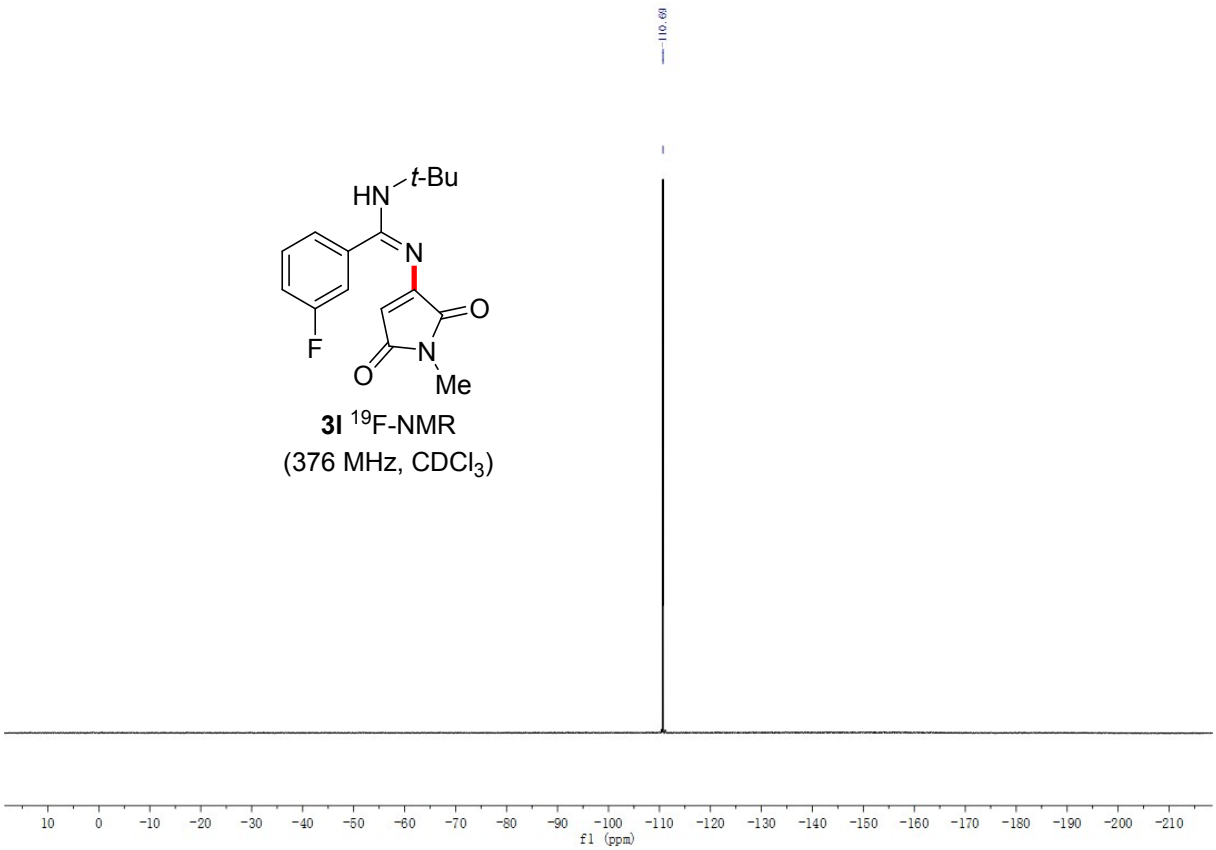

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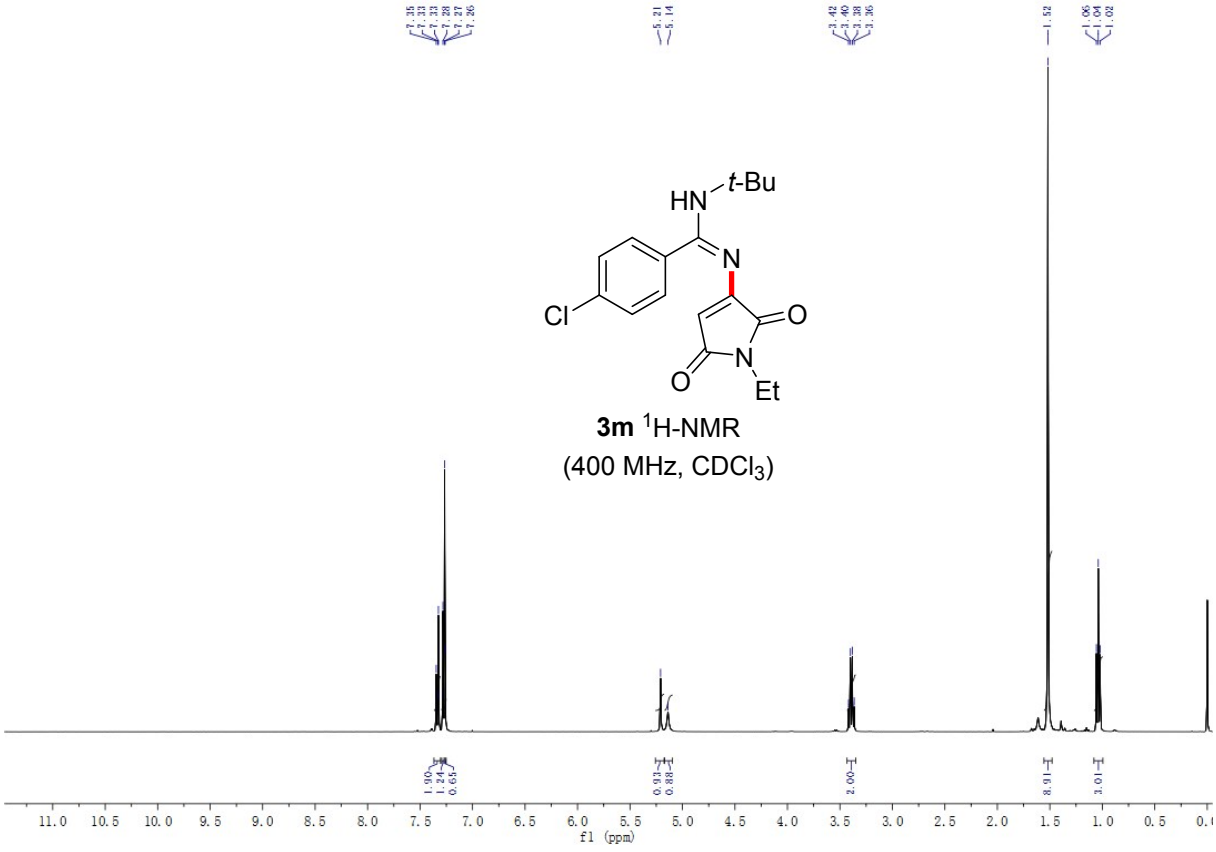

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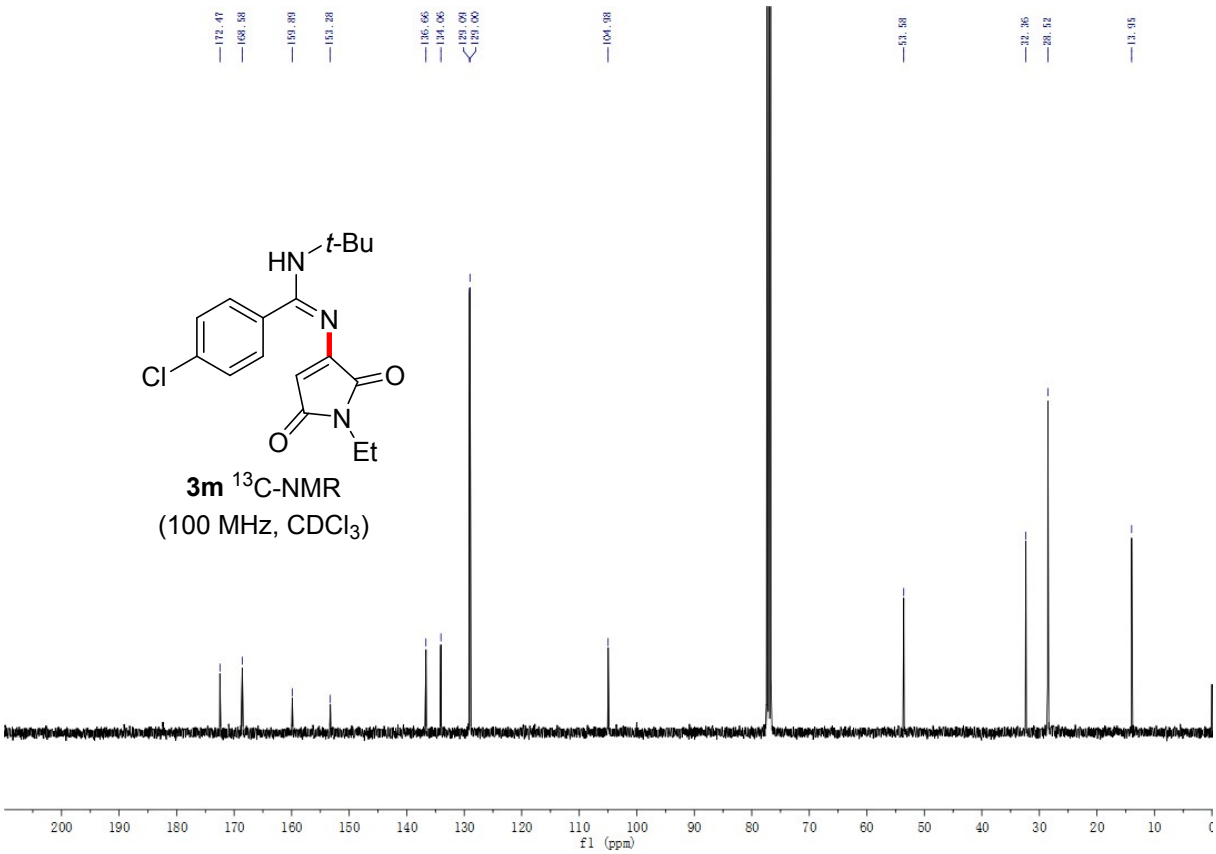

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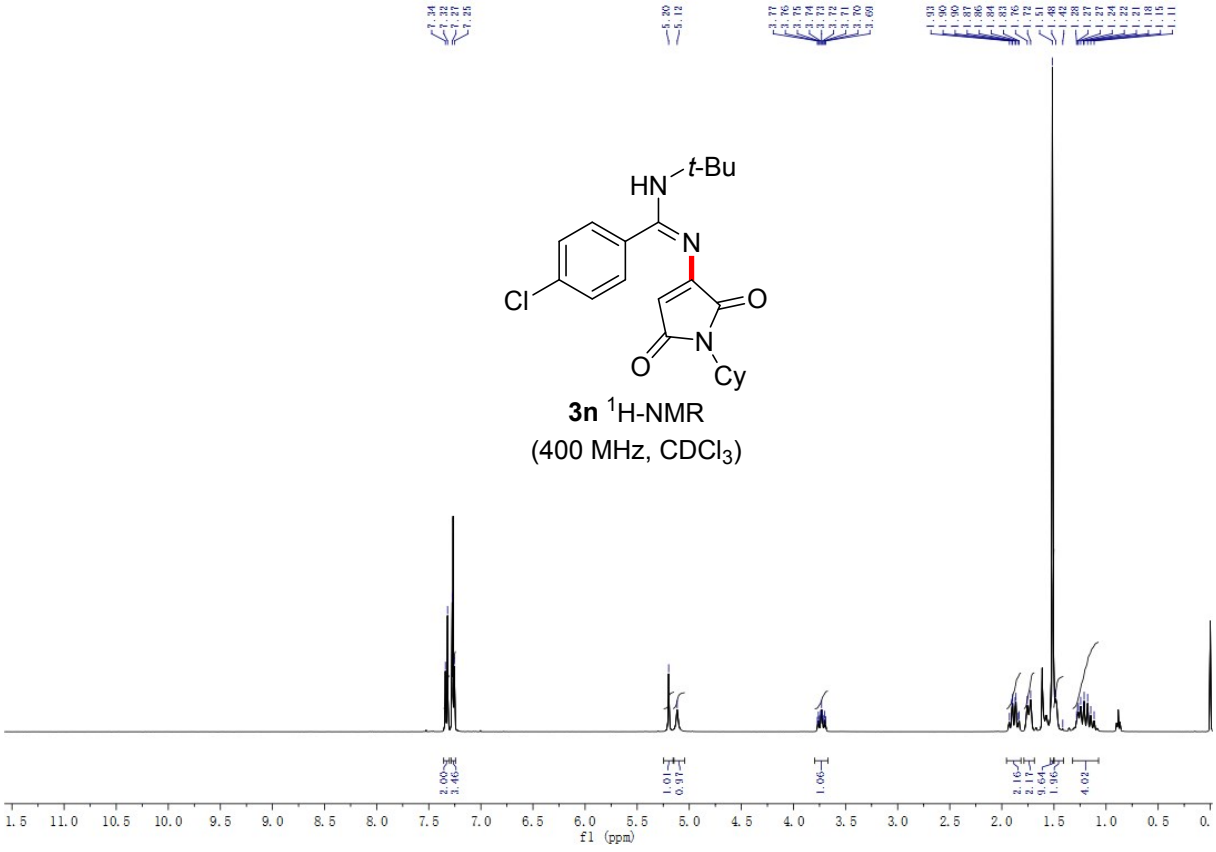

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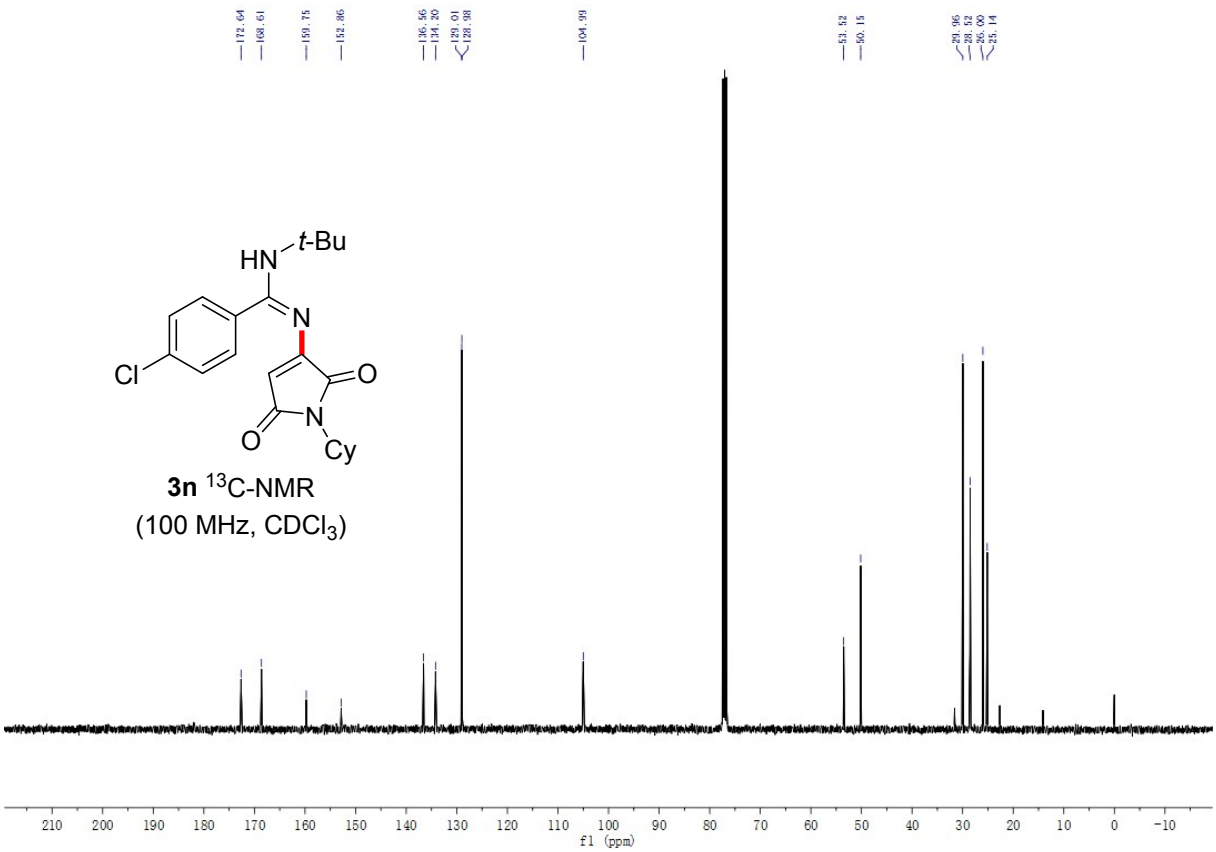

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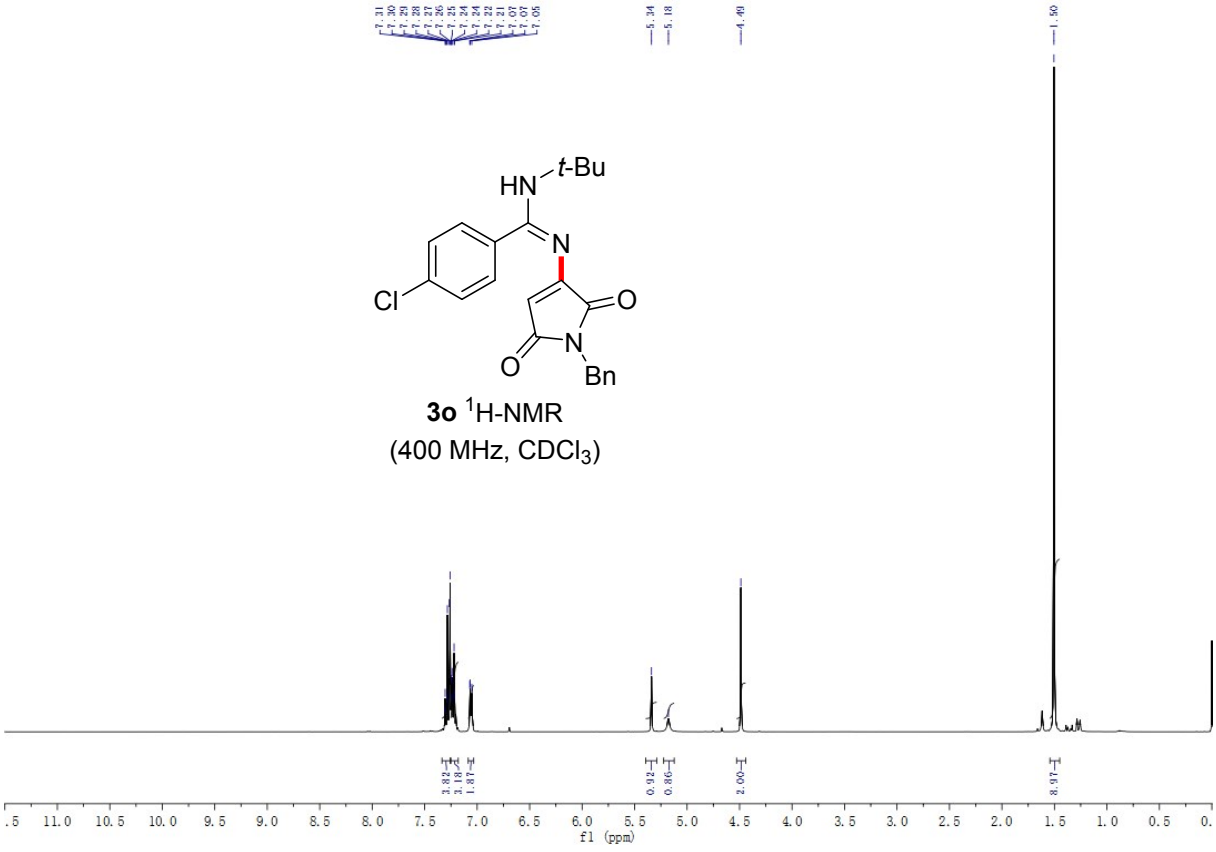

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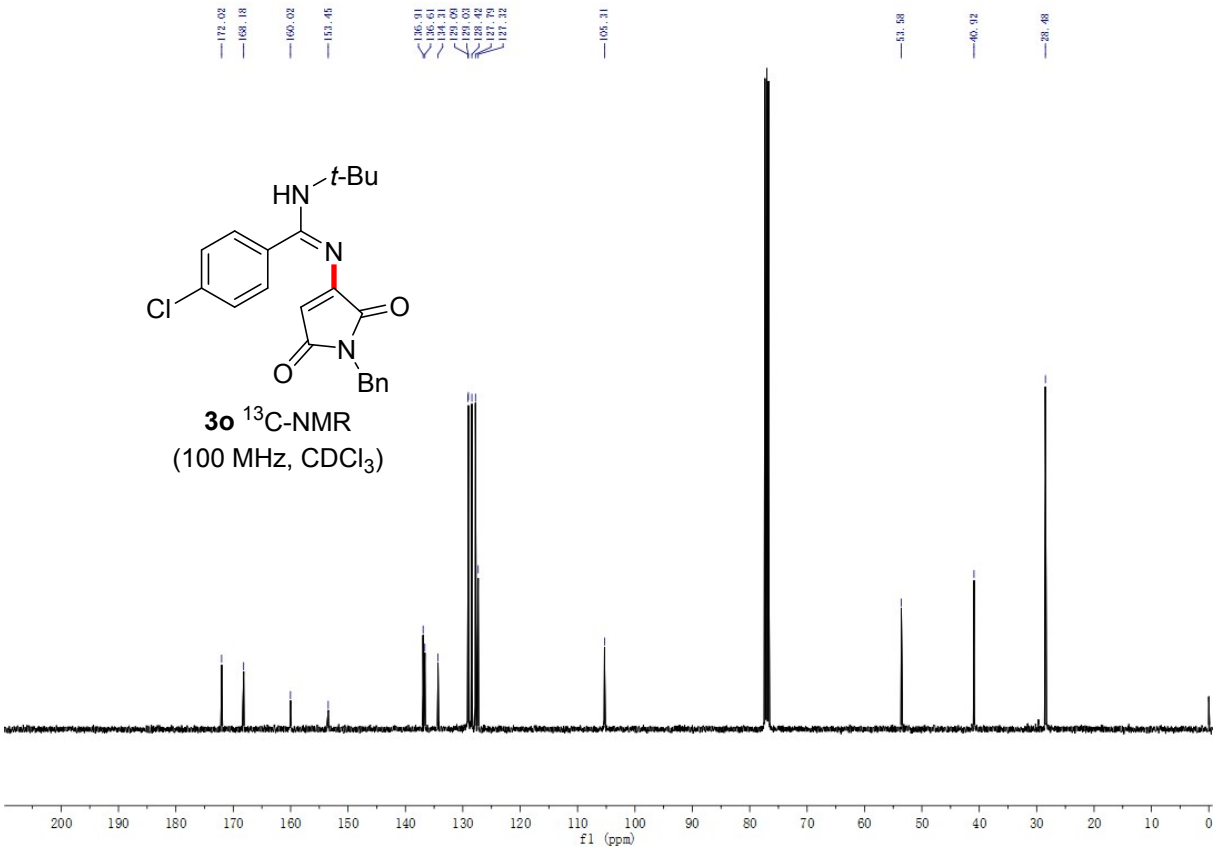

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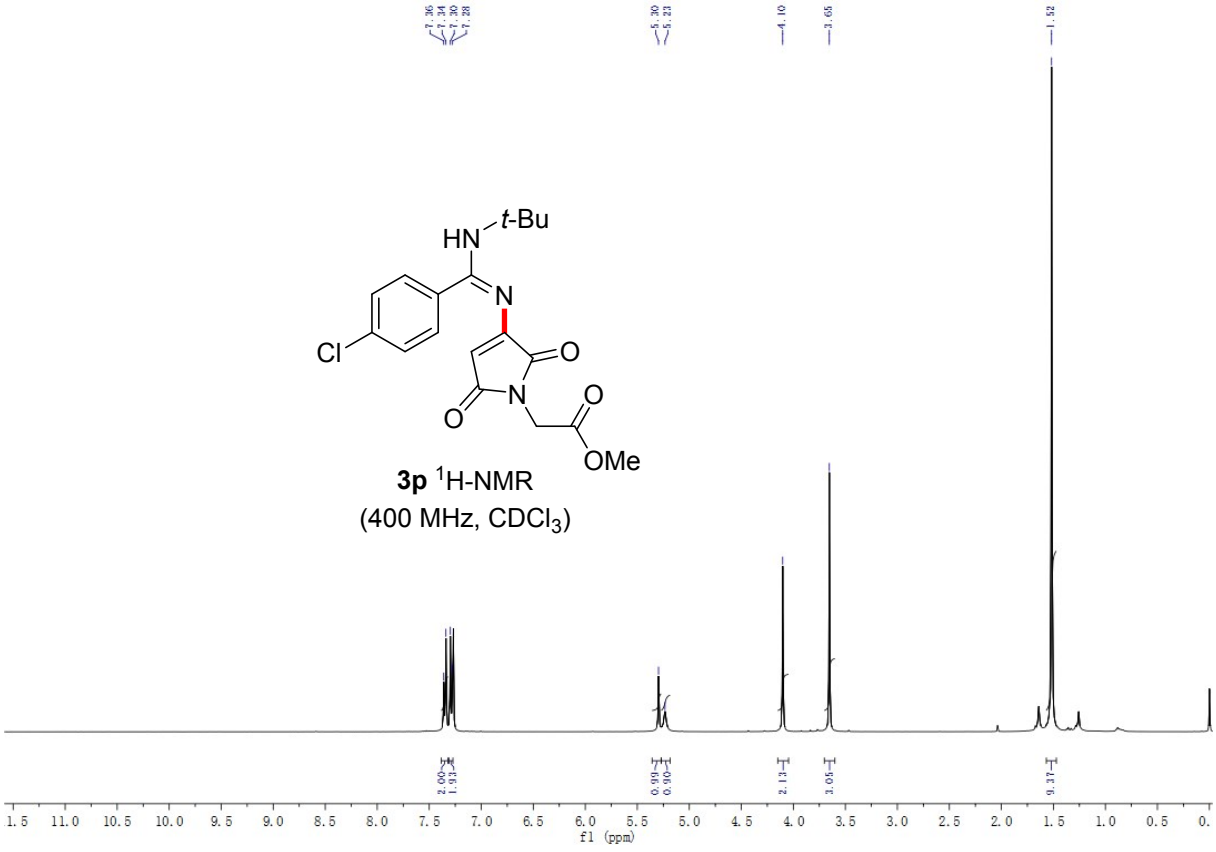
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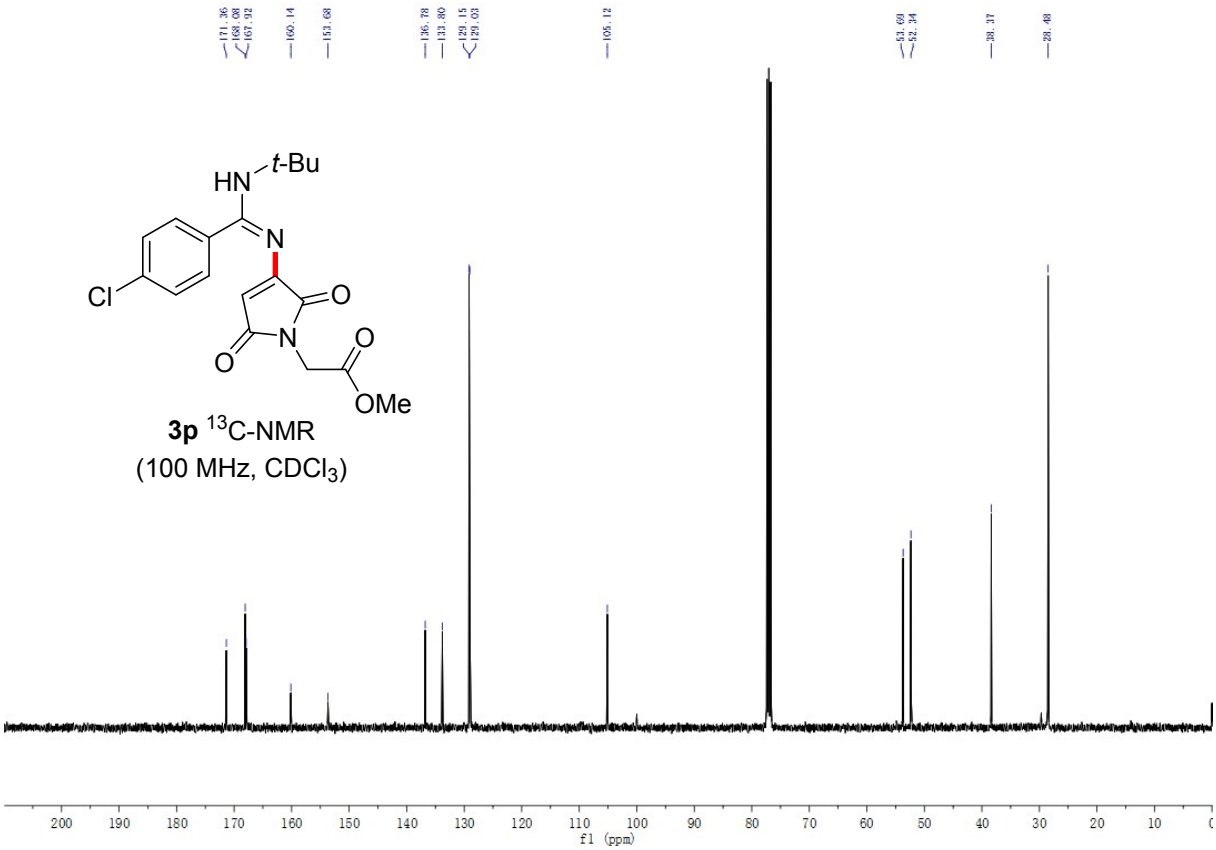
t-Bu
N
Cl
O
O
N
O
O
OMe
3p 1H-NMR
(400 MHz, CDCl3)
f1 (ppm)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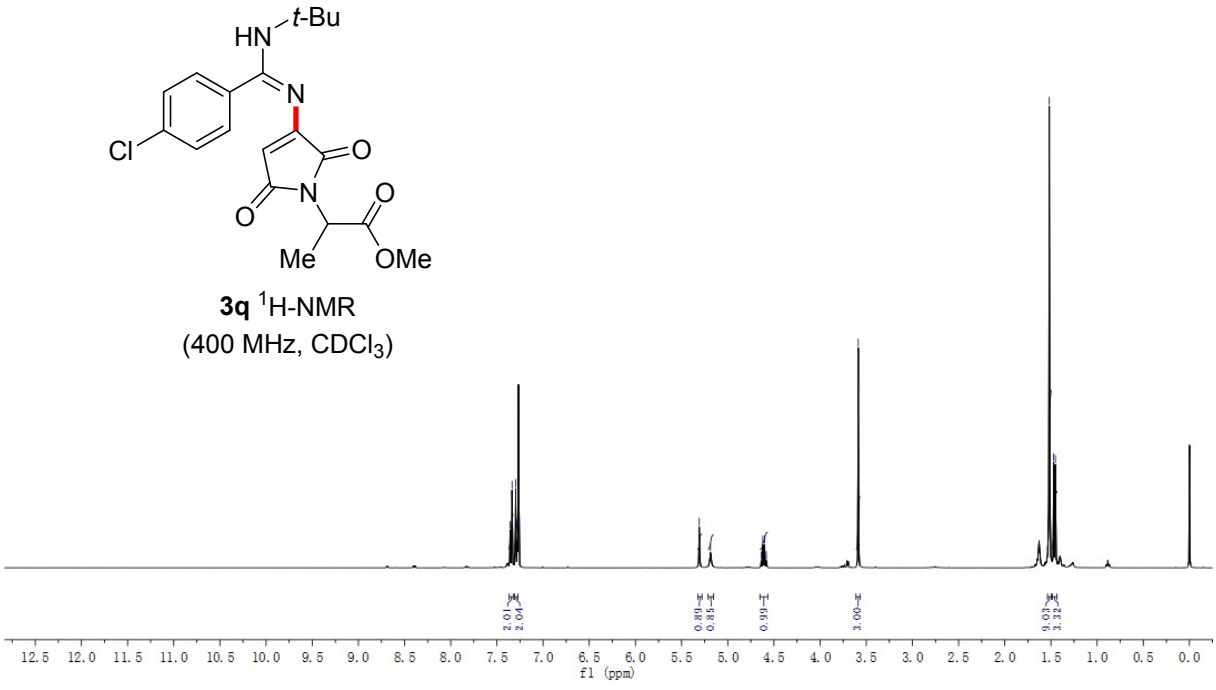
f1 (ppm)



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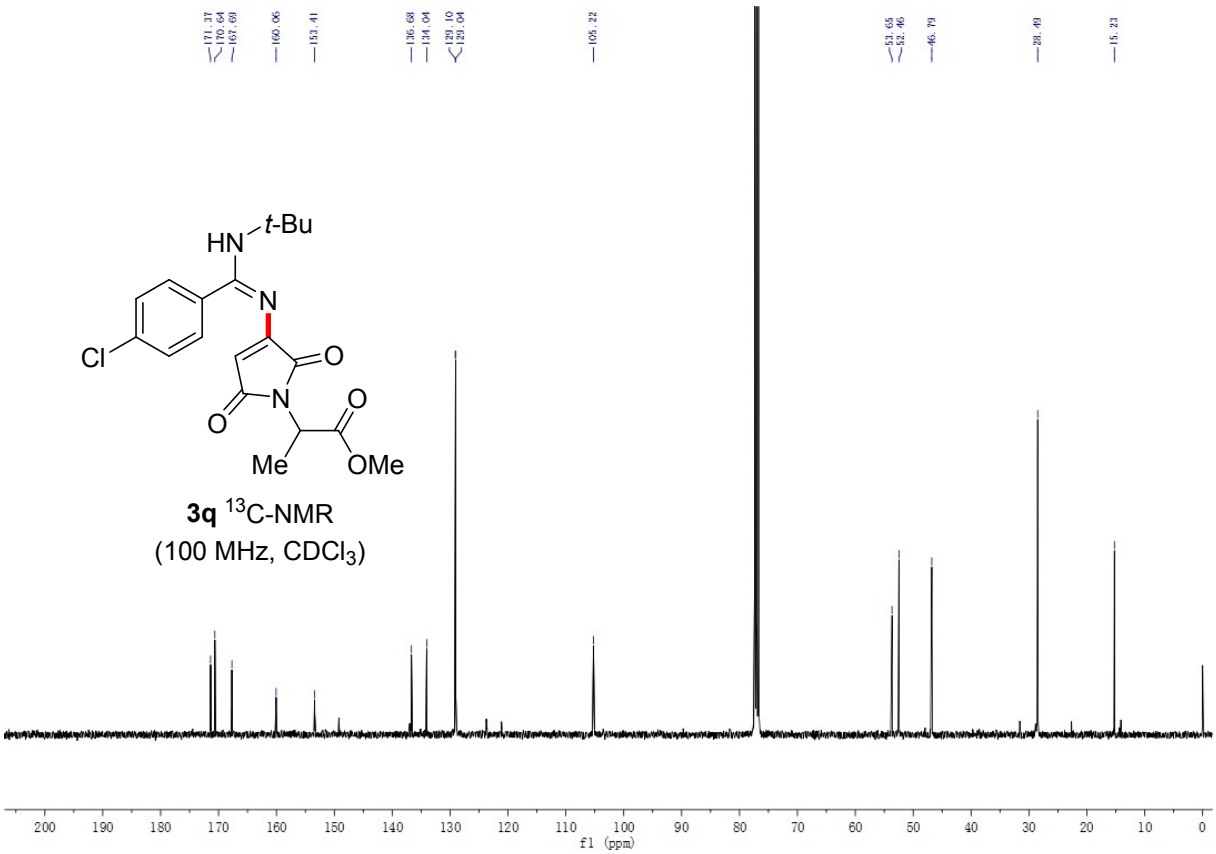

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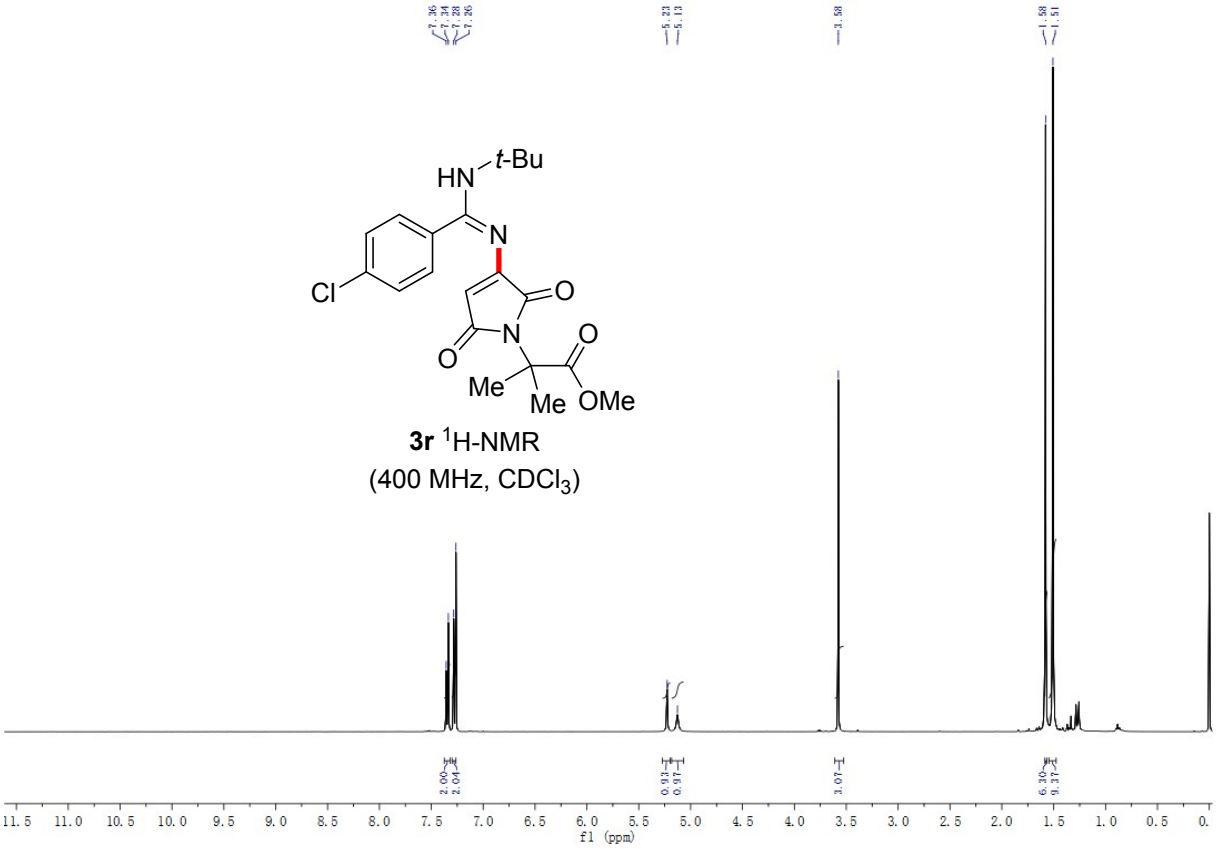
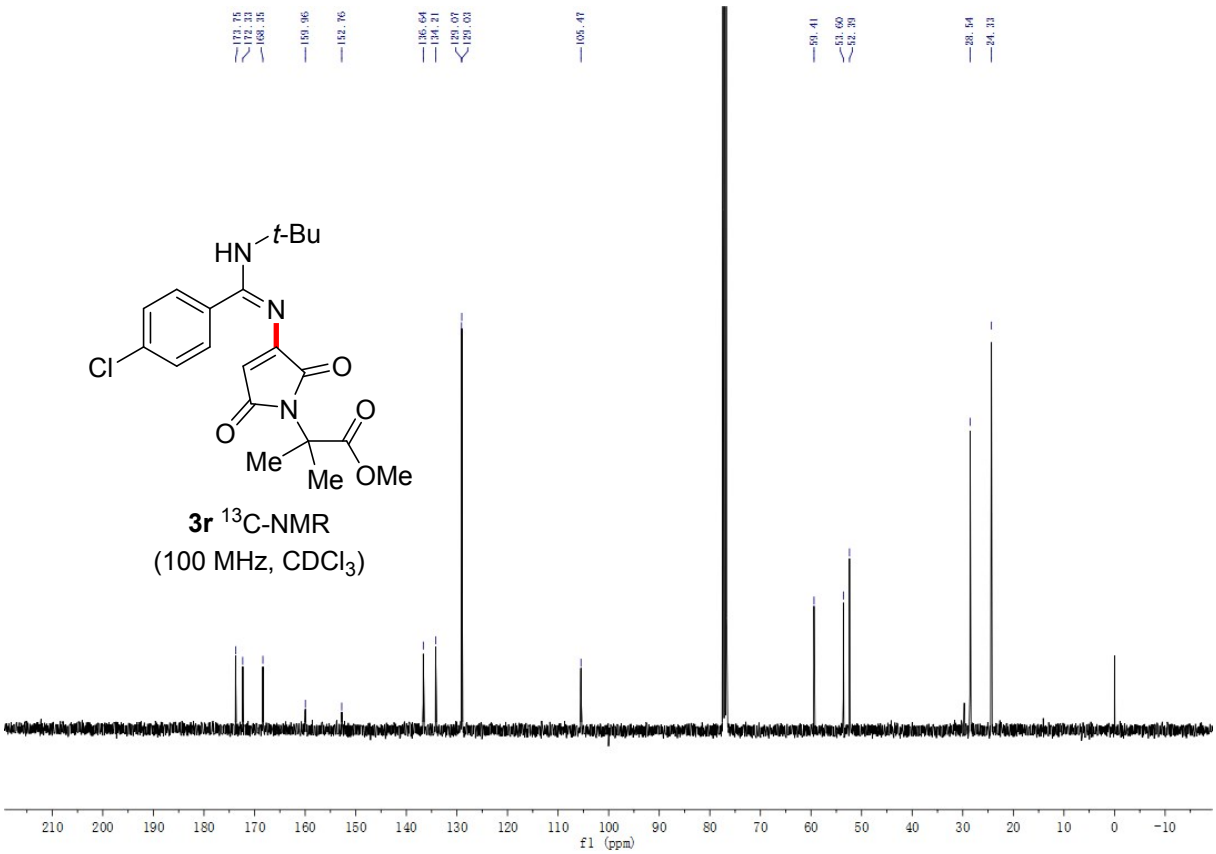
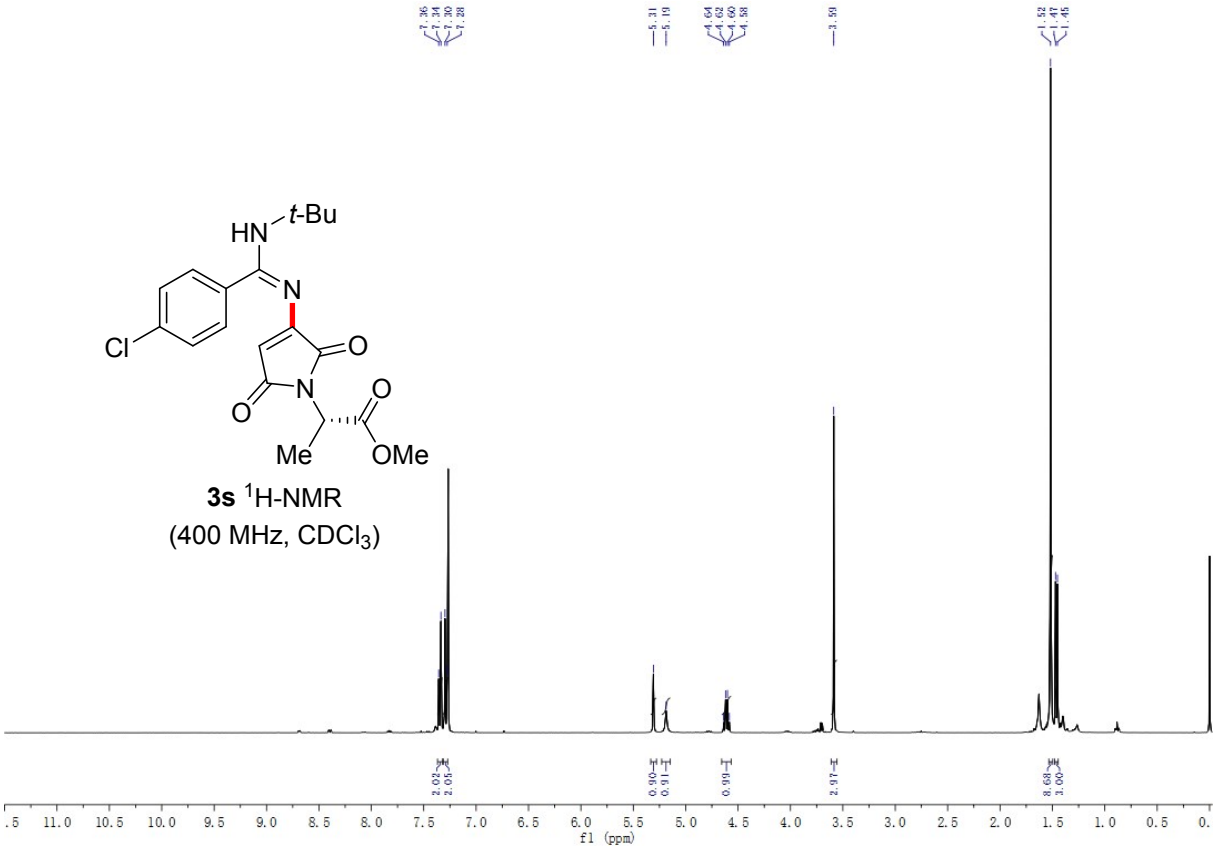
(100 MHz, $CDCl_3$)



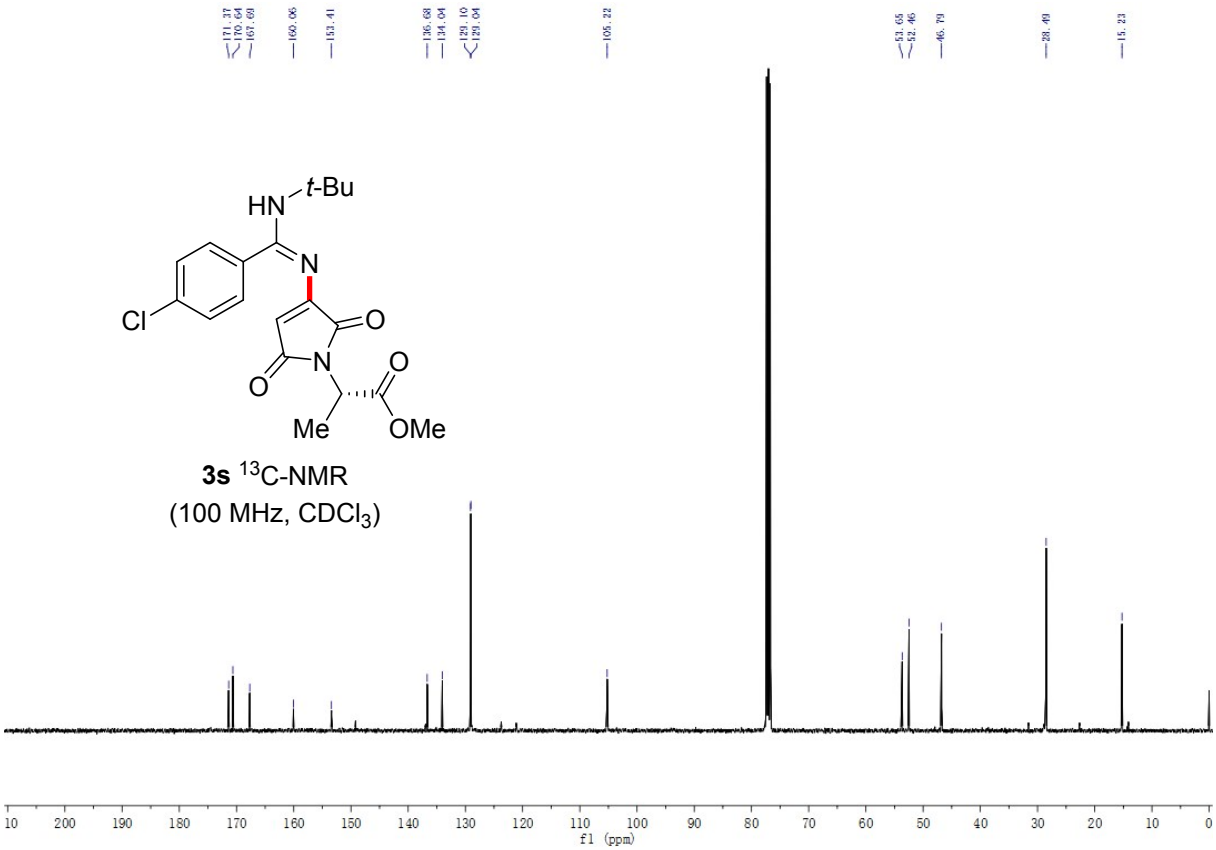
3r ^{1}H-NMR
(400 MHz, $CDCl_3$)



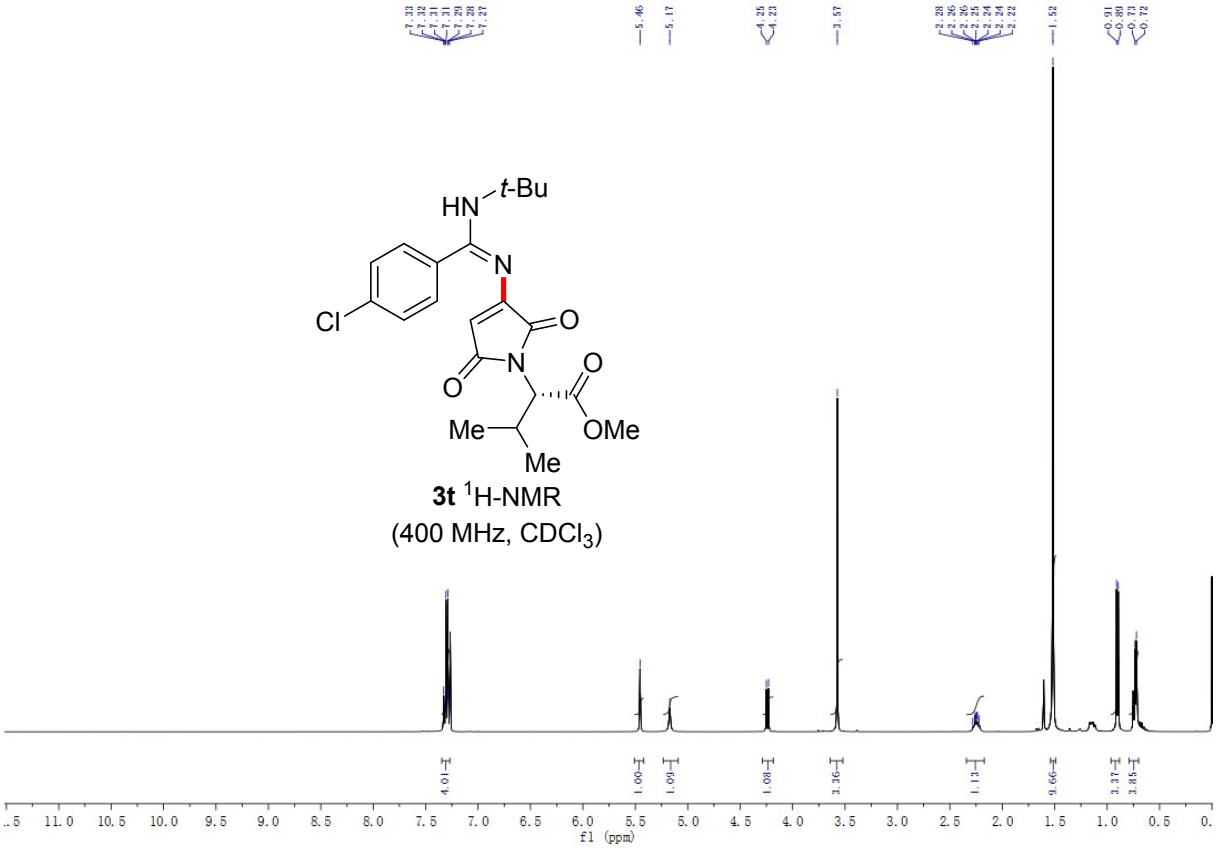
3r ^{13}C-NMR
(100 MHz, $CDCl_3$)



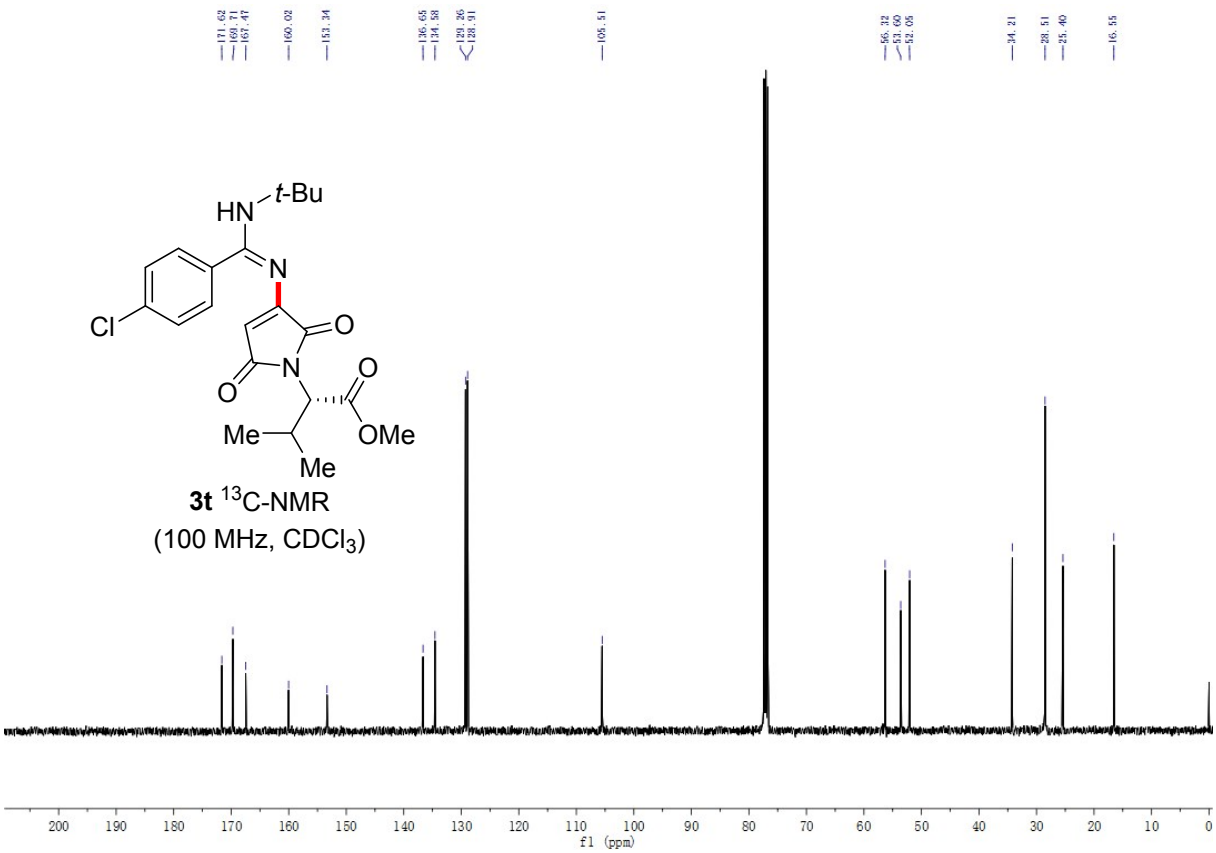
3s ^{1}H-NMR
(400 MHz, $CDCl_3$)



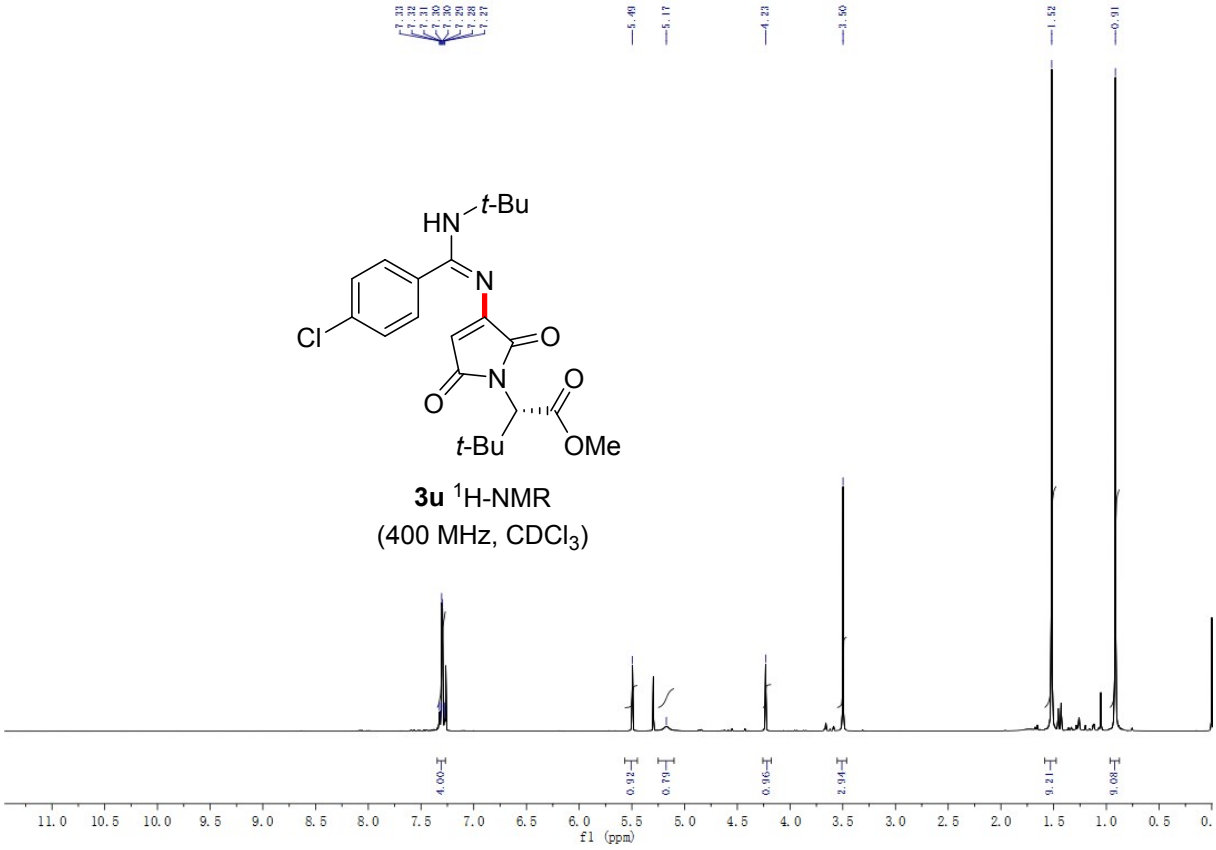
3s ^{13}C-NMR
(100 MHz, $CDCl_3$)



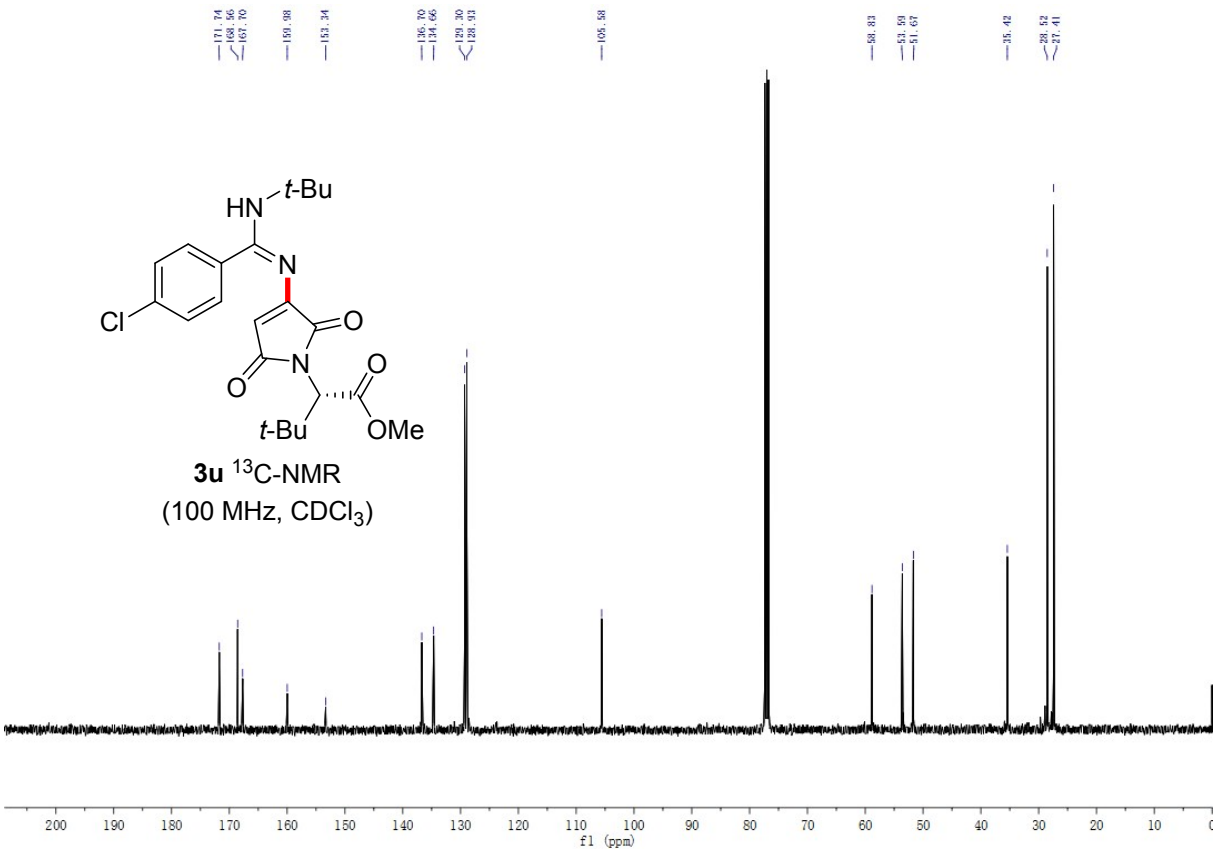
3t ^{1}H-NMR
(400 MHz, $CDCl_3$)



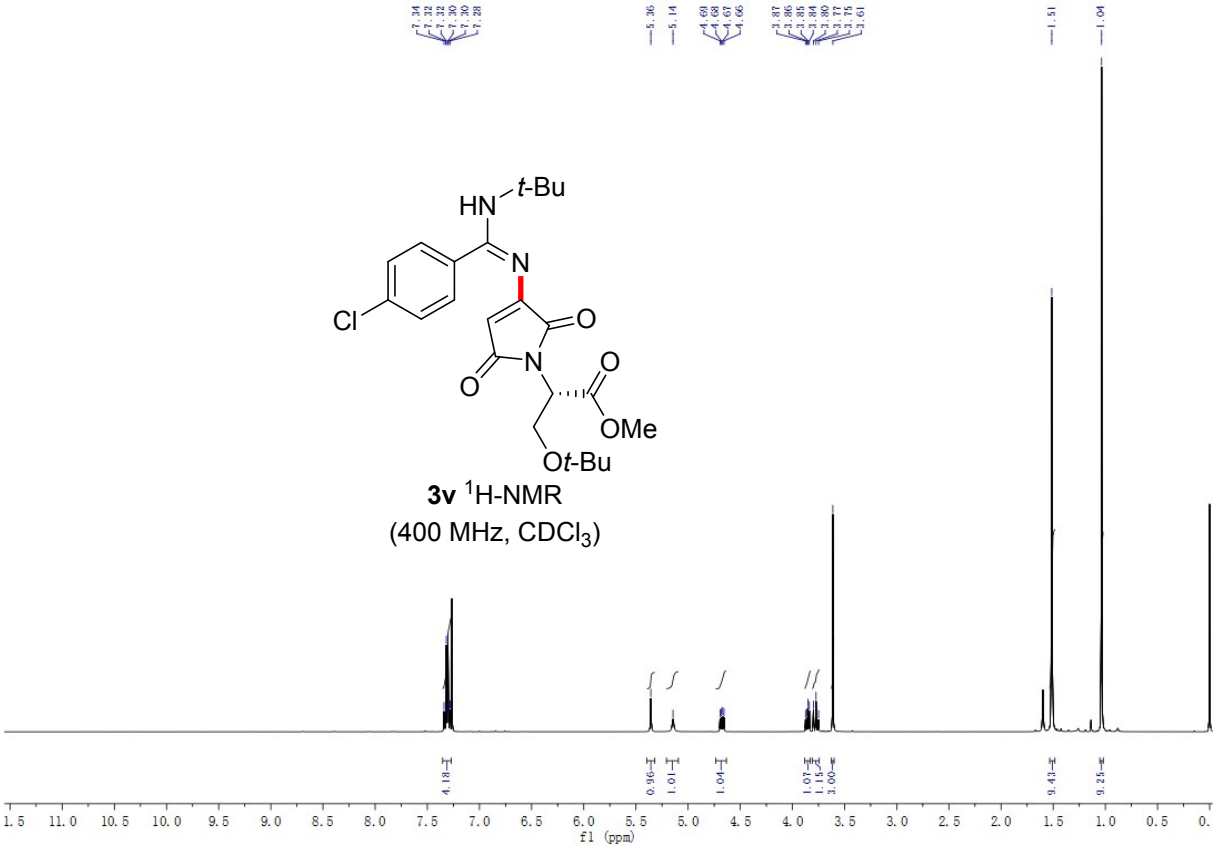
3t ^{13}C-NMR
(100 MHz, $CDCl_3$)



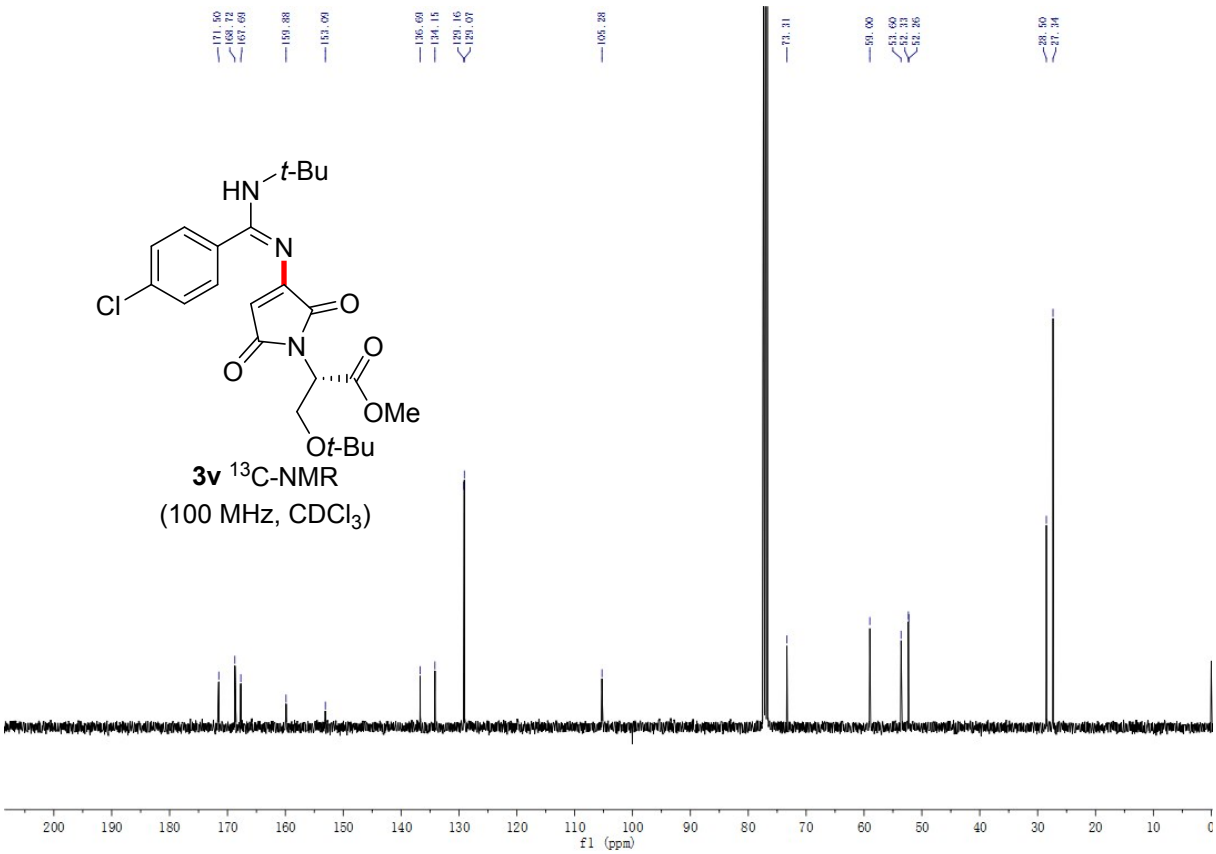
3u ^{1}H-NMR
(400 MHz, $CDCl_3$)



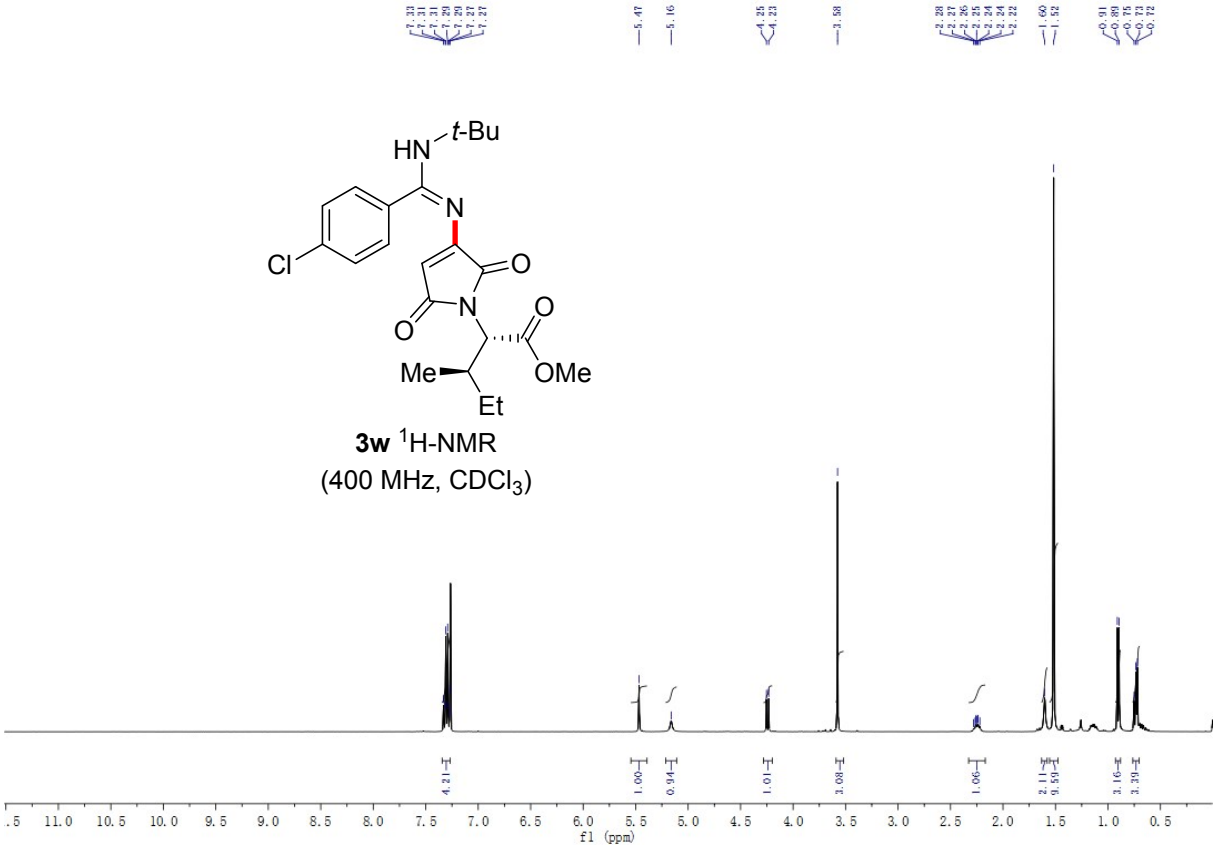
3u ^{13}C-NMR
(100 MHz, $CDCl_3$)



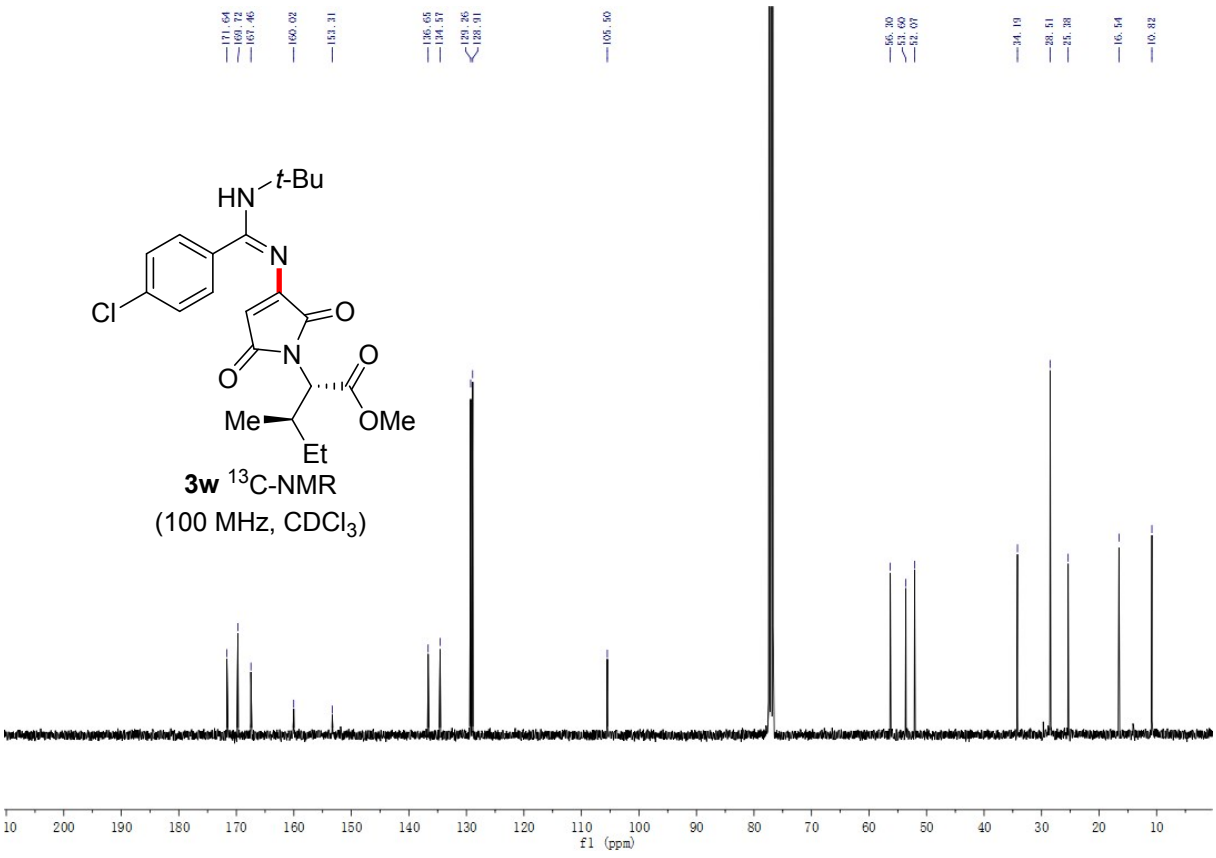
3v ^{1}H-NMR
(400 MHz, $CDCl_3$)



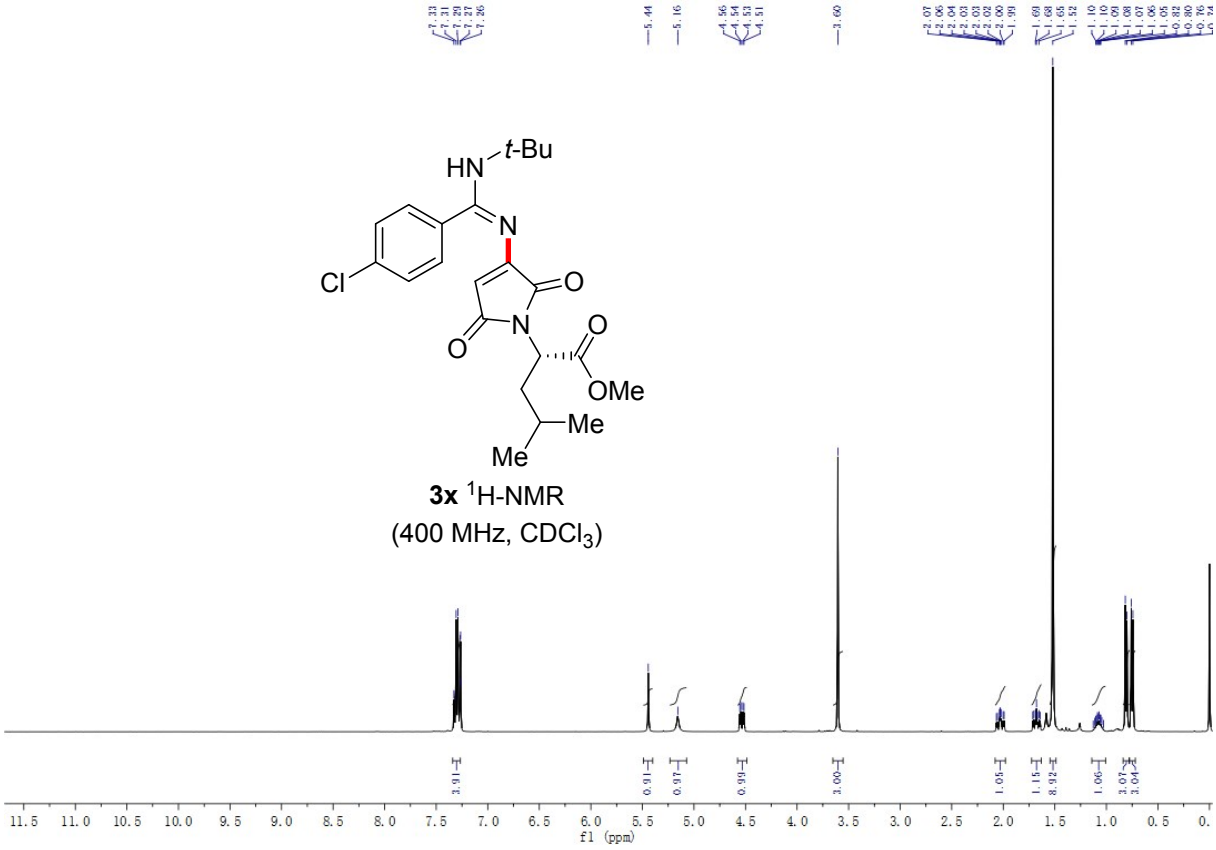
3v ^{13}C-NMR
(100 MHz, $CDCl_3$)



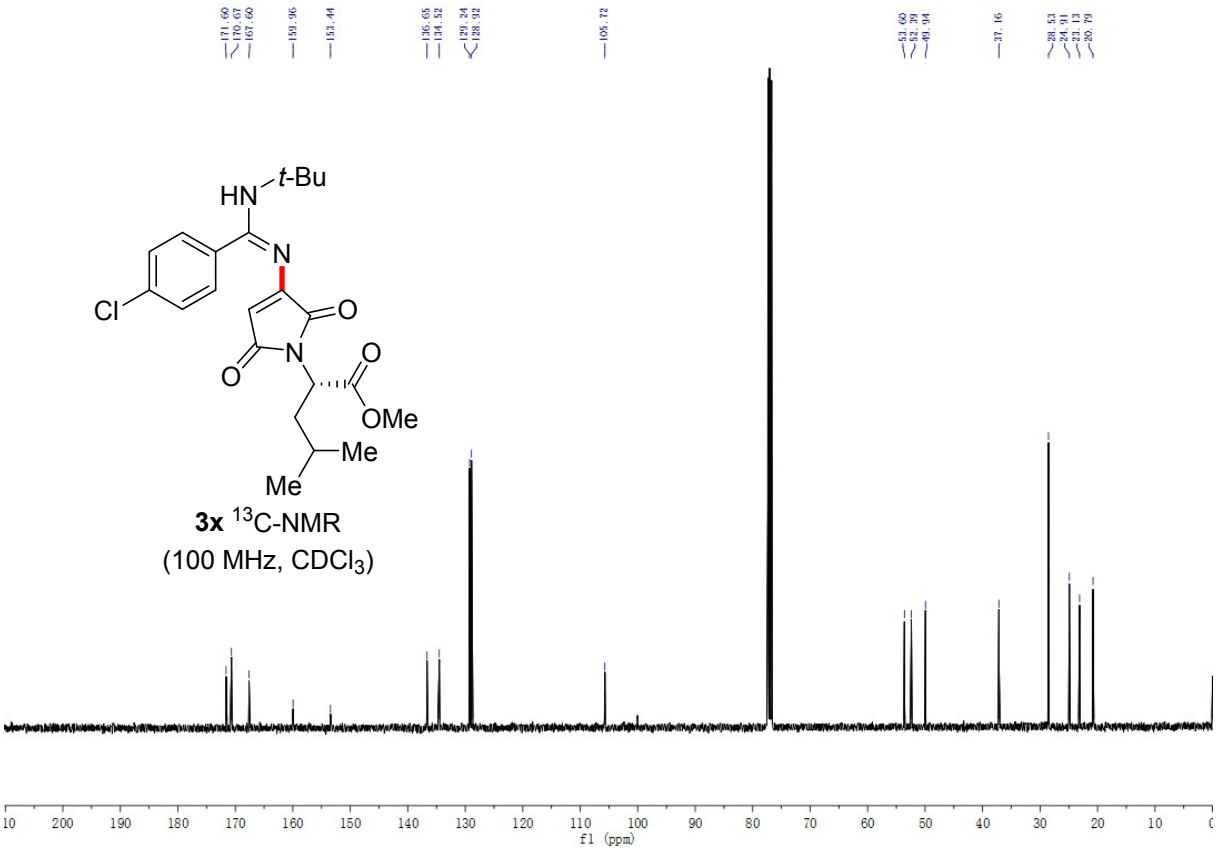
3w ^{1}H-NMR
(400 MHz, $CDCl_3$)



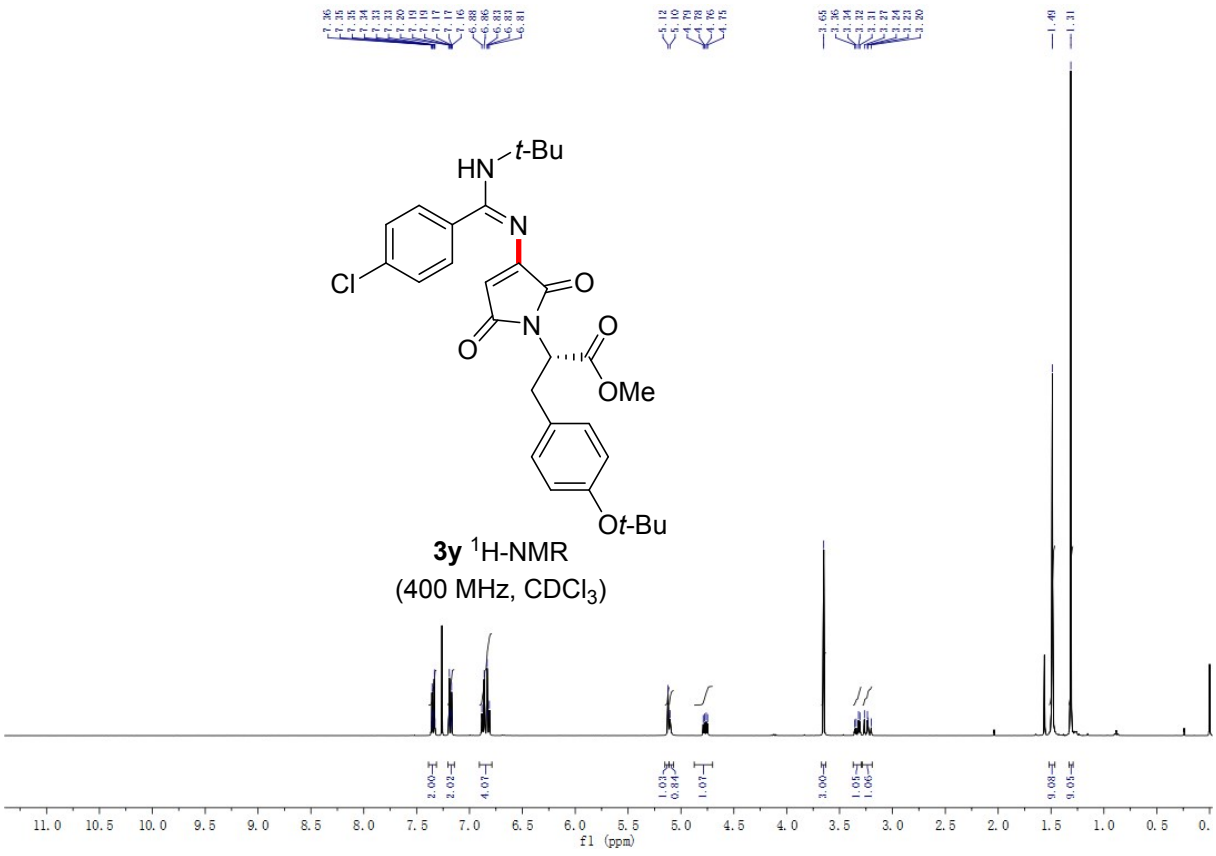
3w ^{13}C-NMR
(100 MHz, $CDCl_3$)



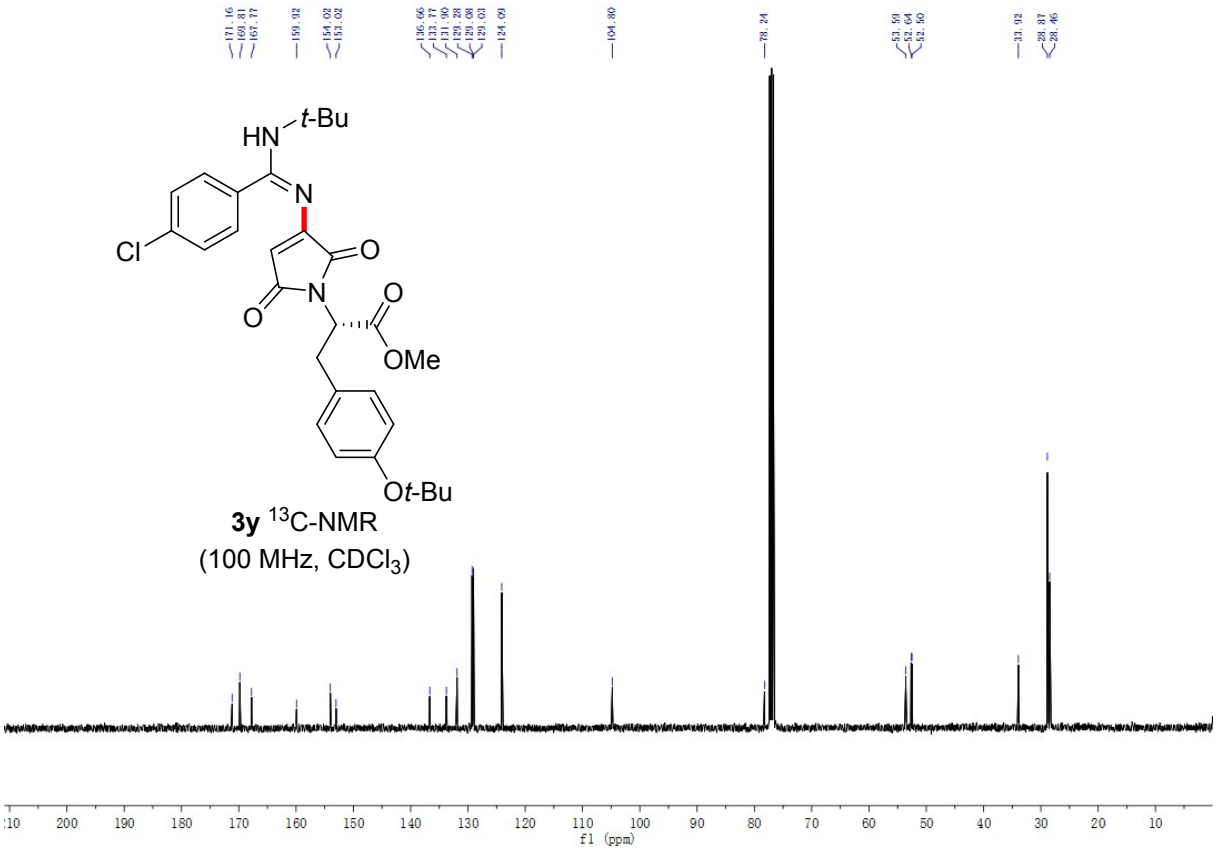
3x ^{1}H-NMR
(400 MHz, $CDCl_3$)



3x ^{13}C-NMR
(100 MHz, $CDCl_3$)



3y ^{1}H-NMR
(400 MHz, $CDCl_3$)



3y ^{13}C-NMR
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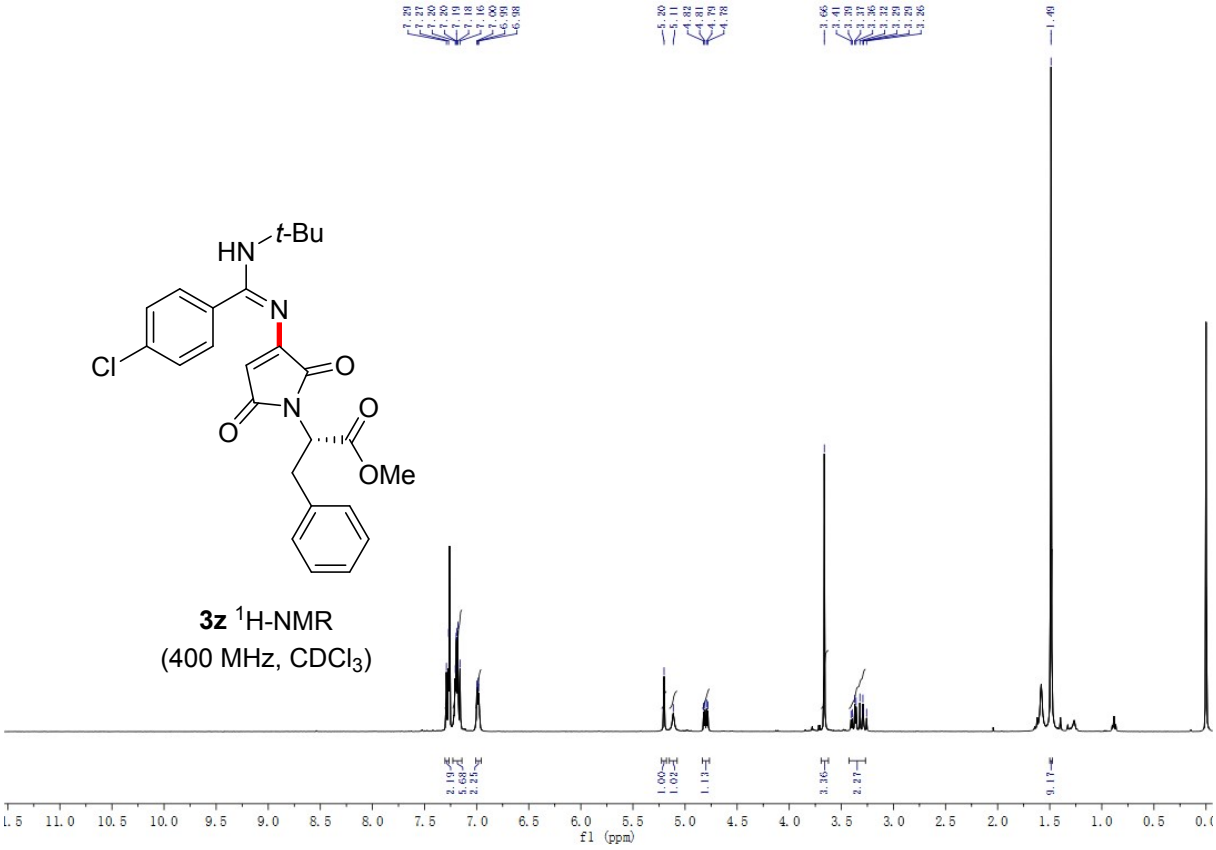

3z ^{1}H-NMR
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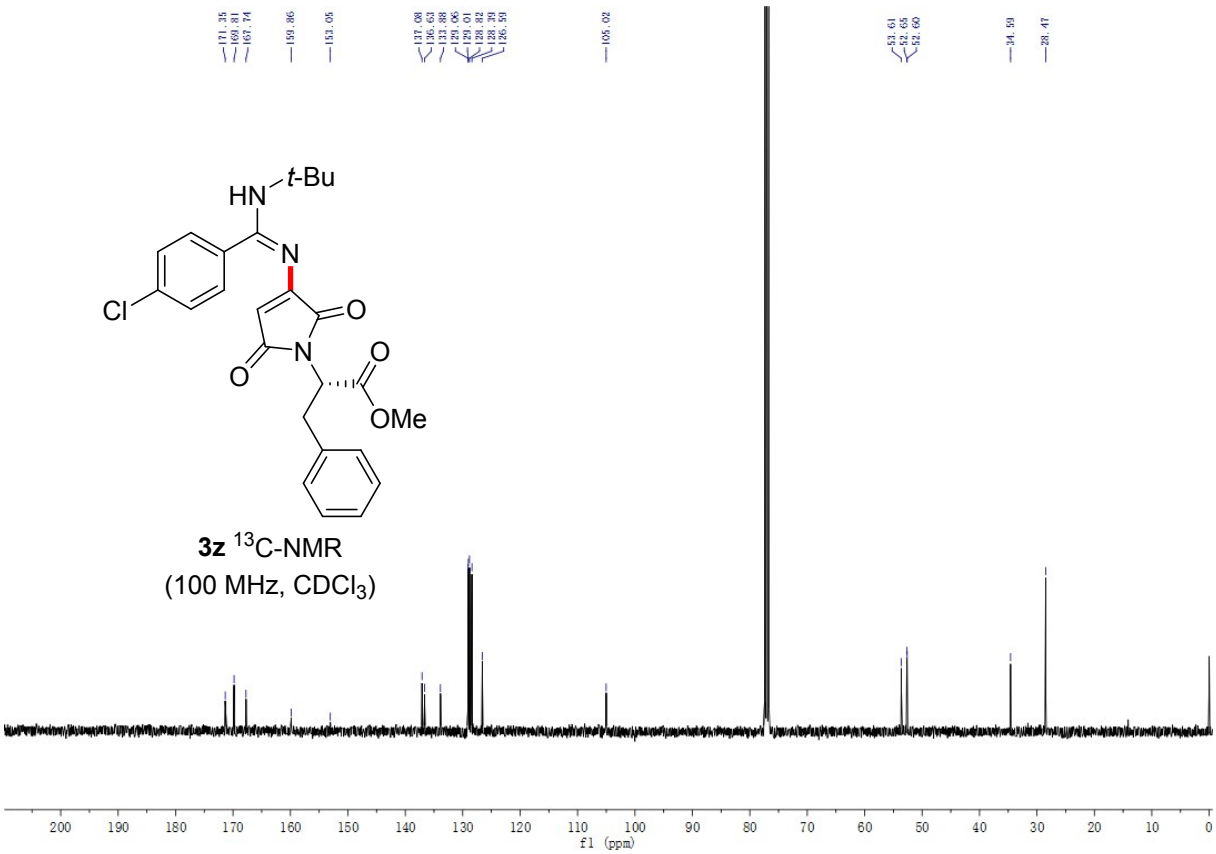
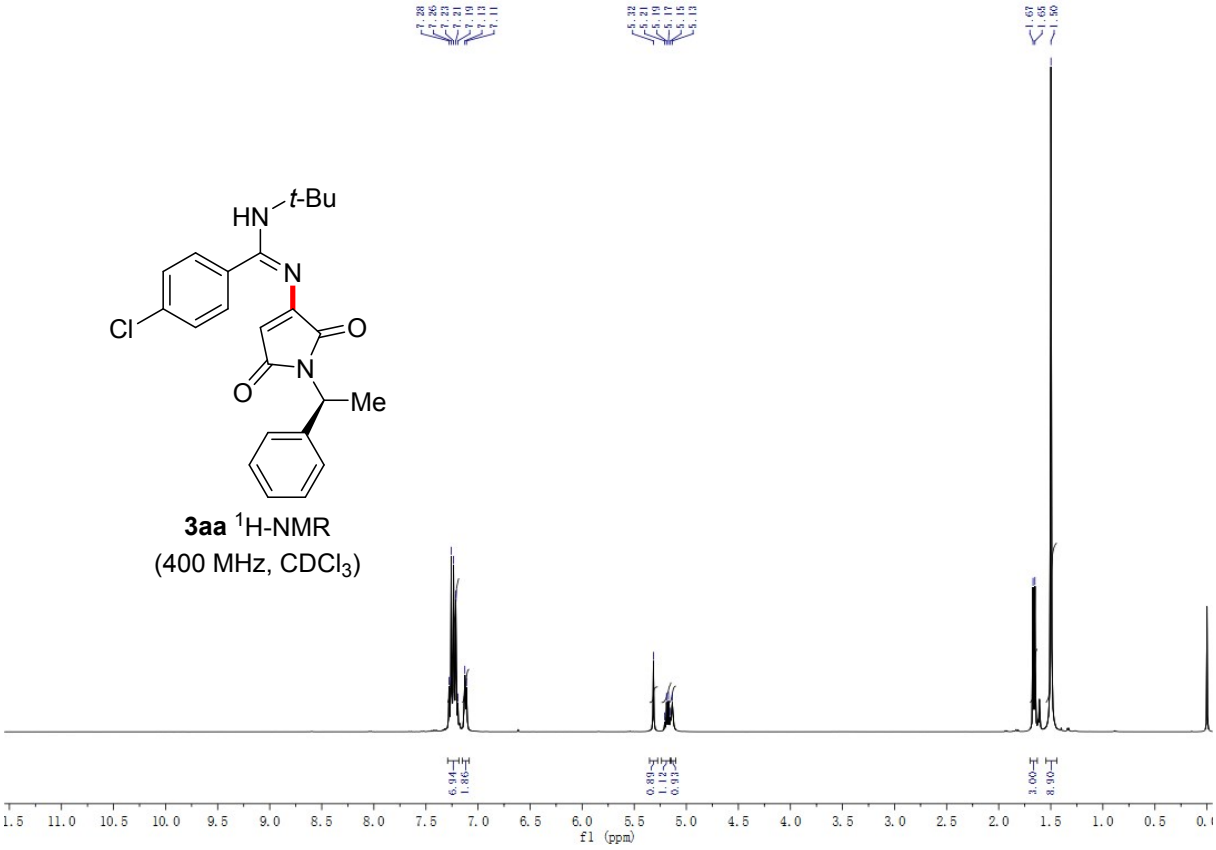
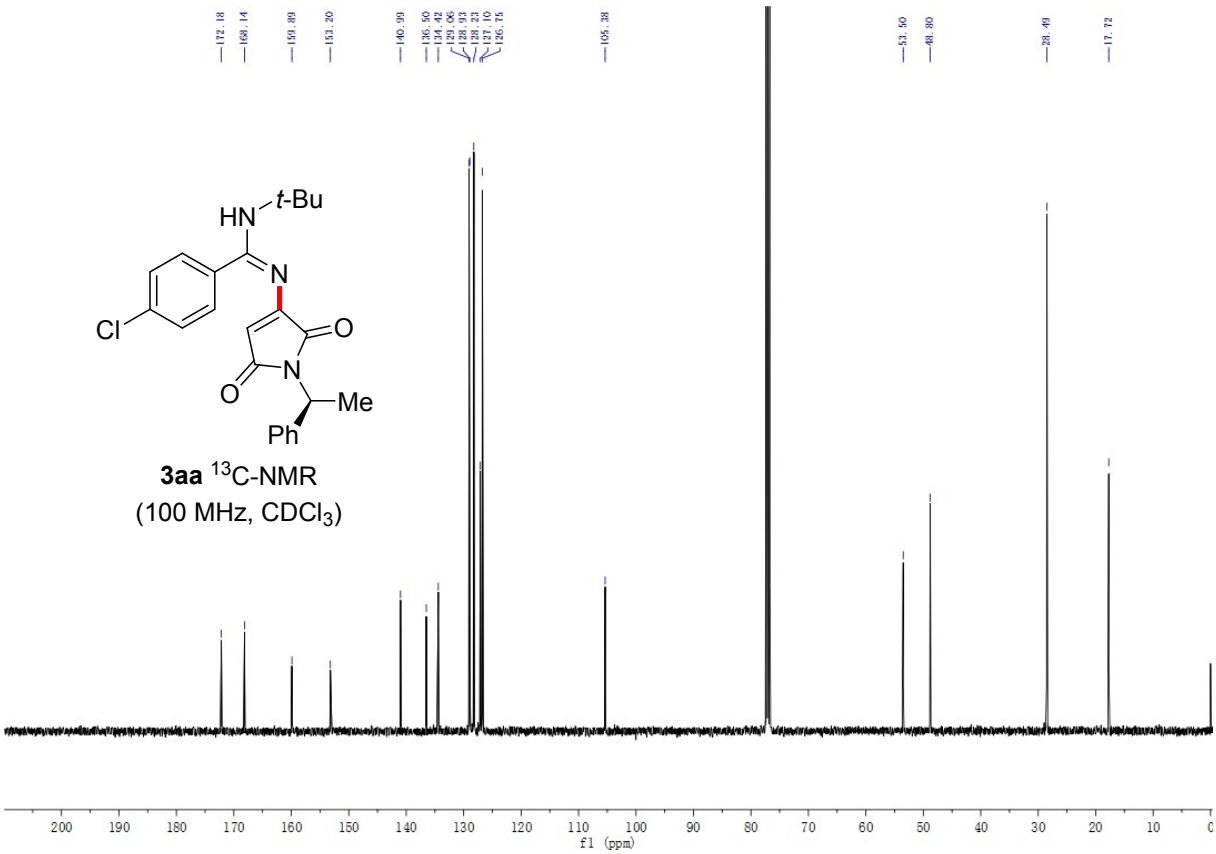


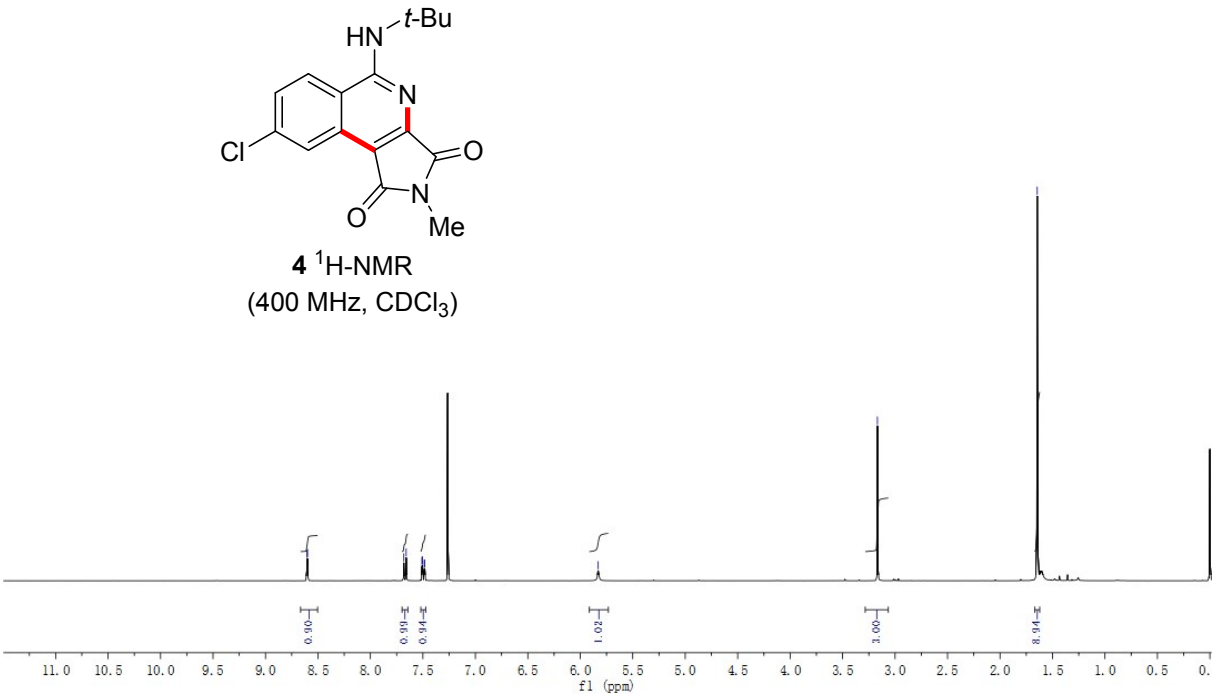
3z ^{13}C-NMR
(100 MHz, $CDCl_3$)



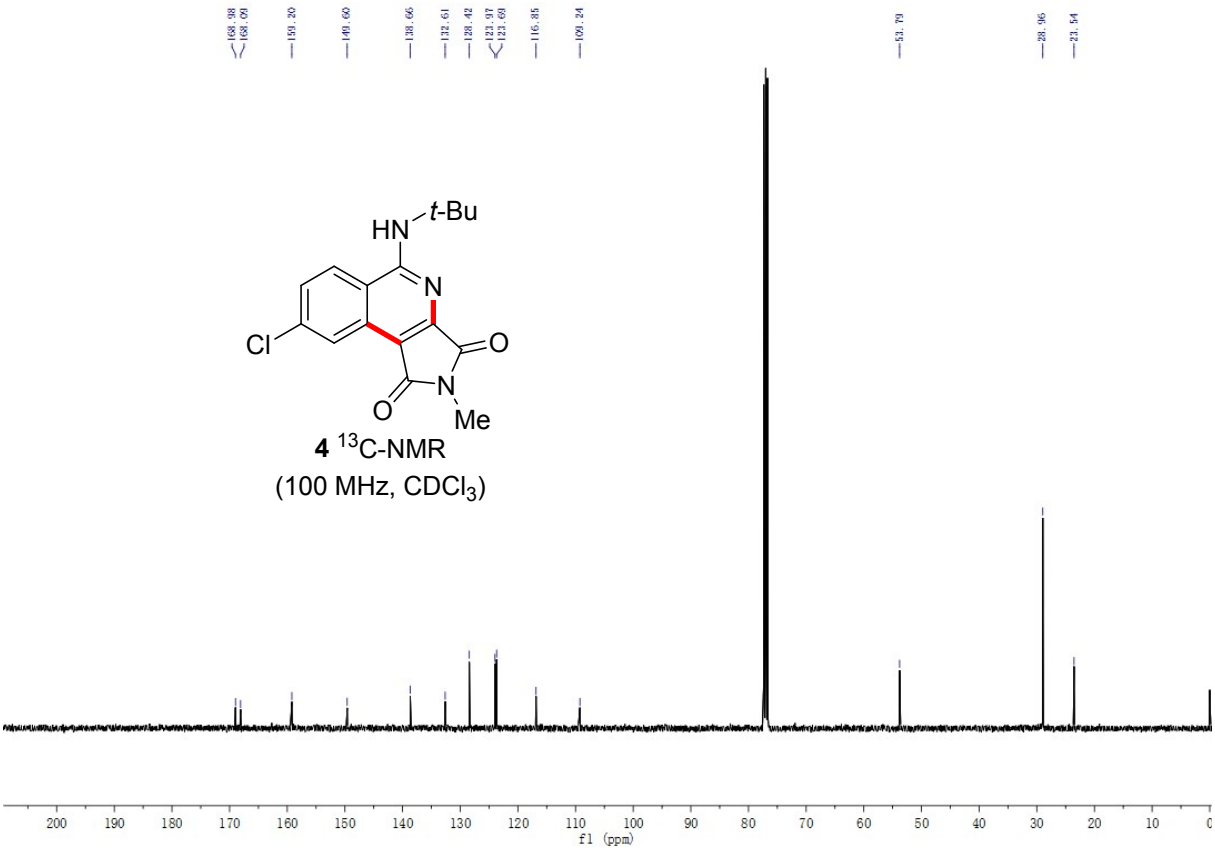
3aa ^{1}H-NMR
(400 MHz, $CDCl_3$)



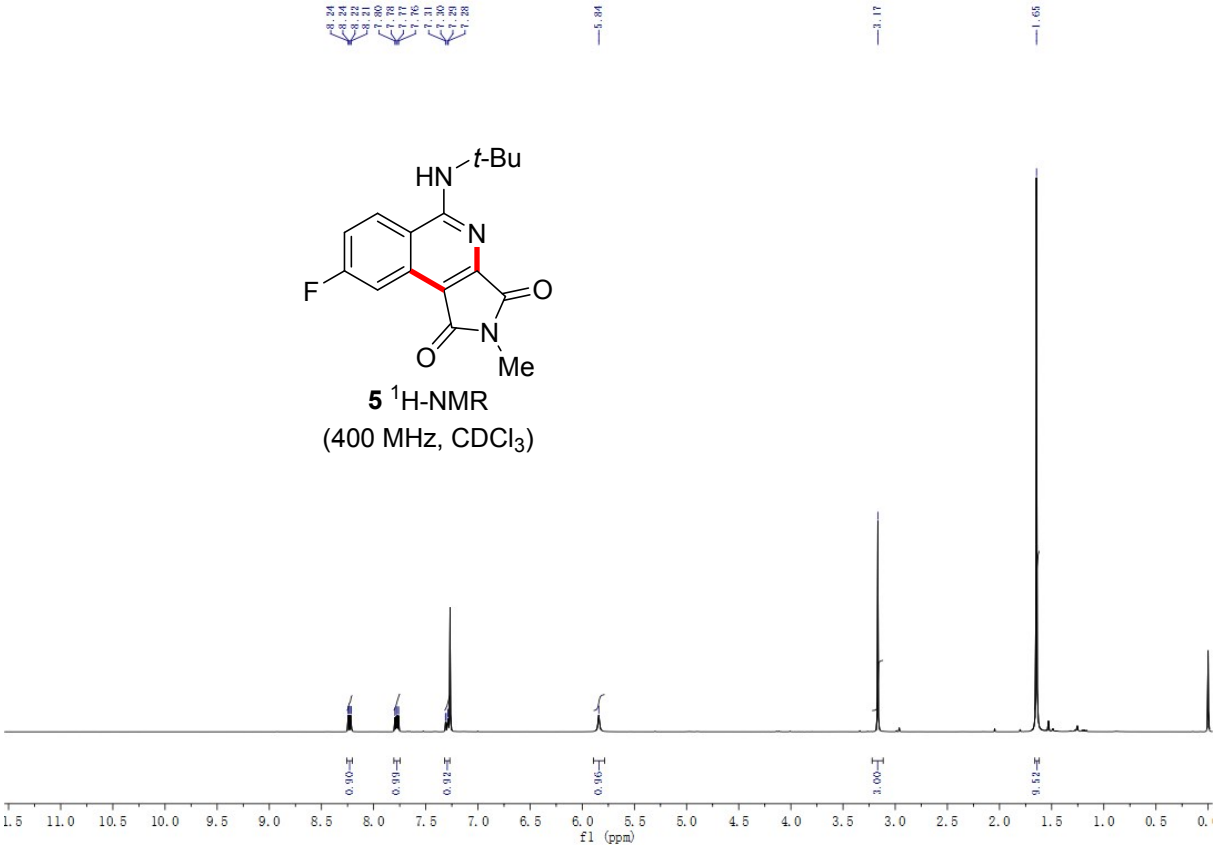
3aa ^{13}C-NMR
(100 MHz, $CDCl_3$)



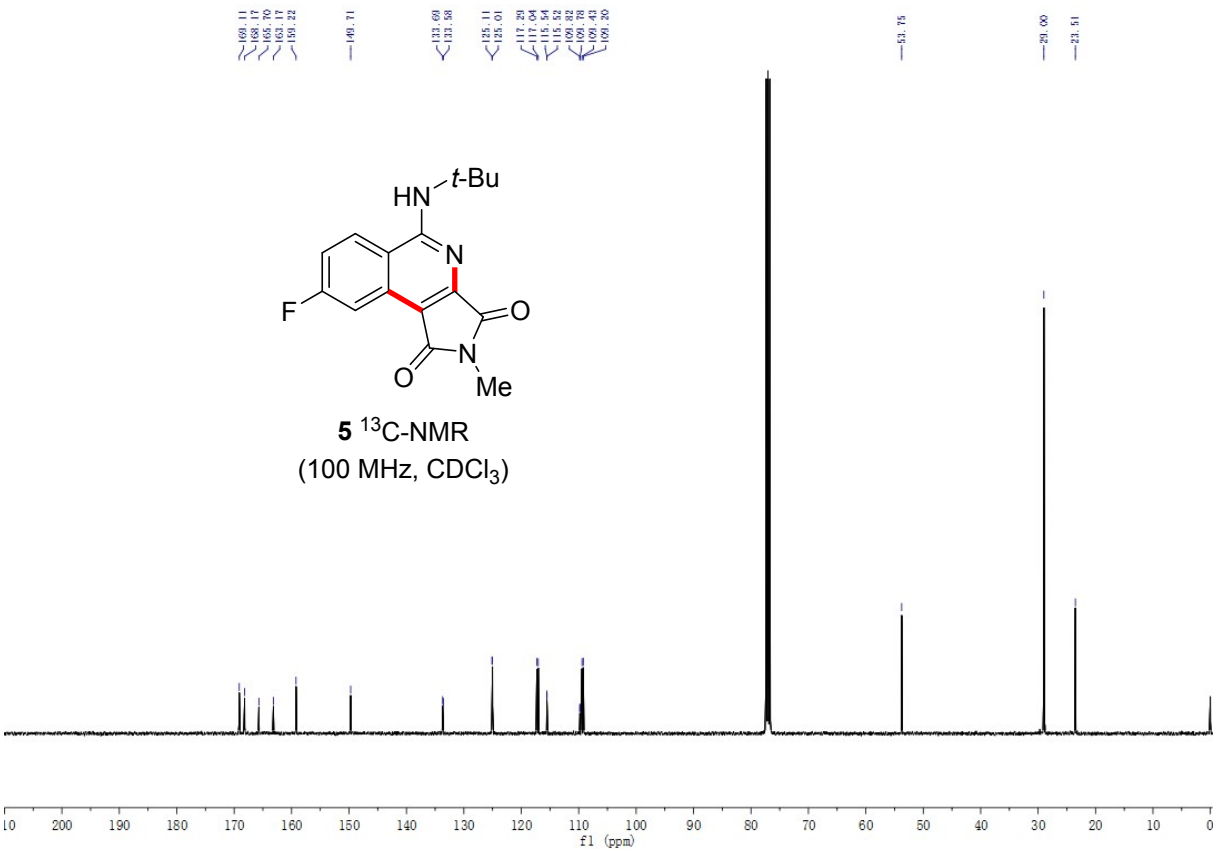
4 ^{1}H-NMR
(400 MHz, $CDCl_3$)



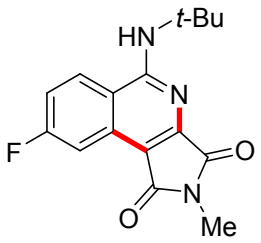
4 ^{13}C-NMR
(100 MHz, $CDCl_3$)



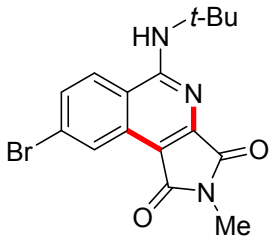
5 ^{1}H-NMR
(400 MHz, $CDCl_3$)



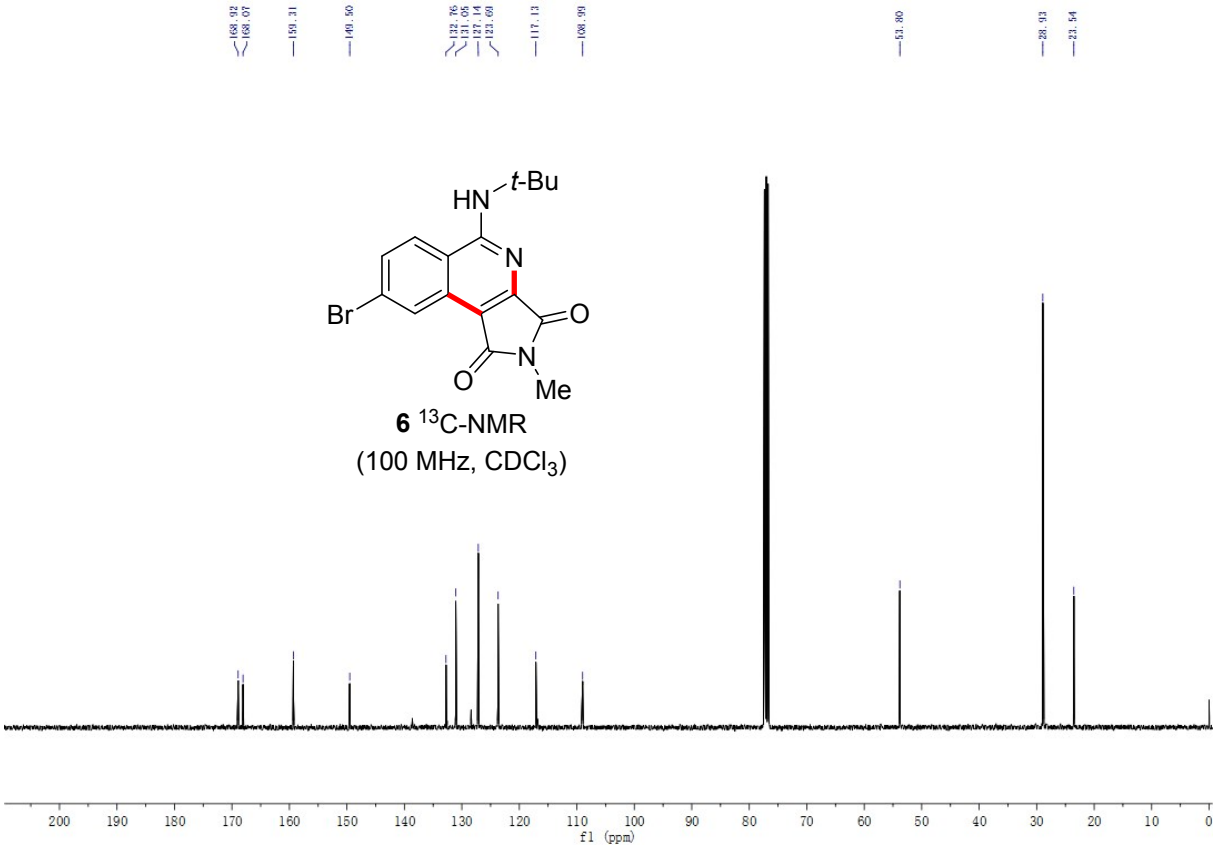
5 ^{13}C-NMR
(100 MHz, $CDCl_3$)



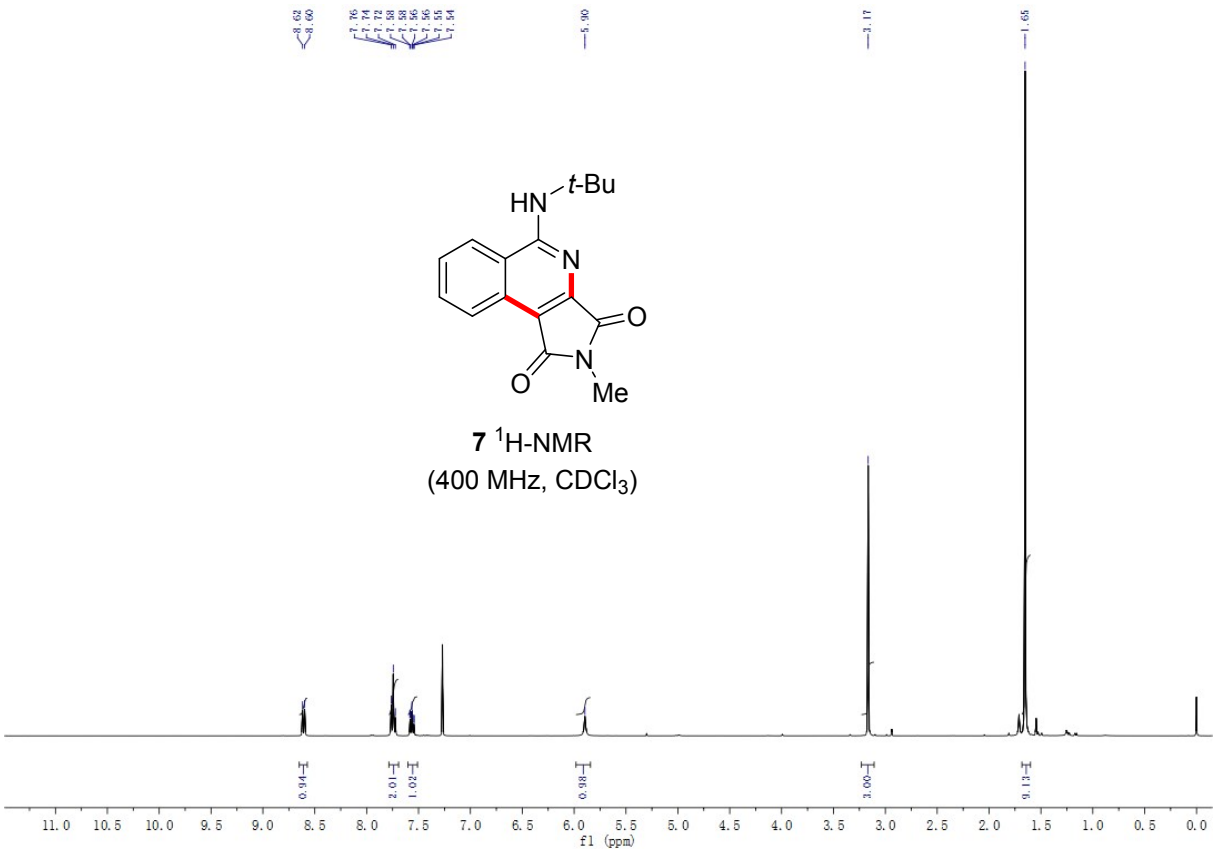
5 ^{19}F-NMR
(376 MHz, $CDCl_3$)



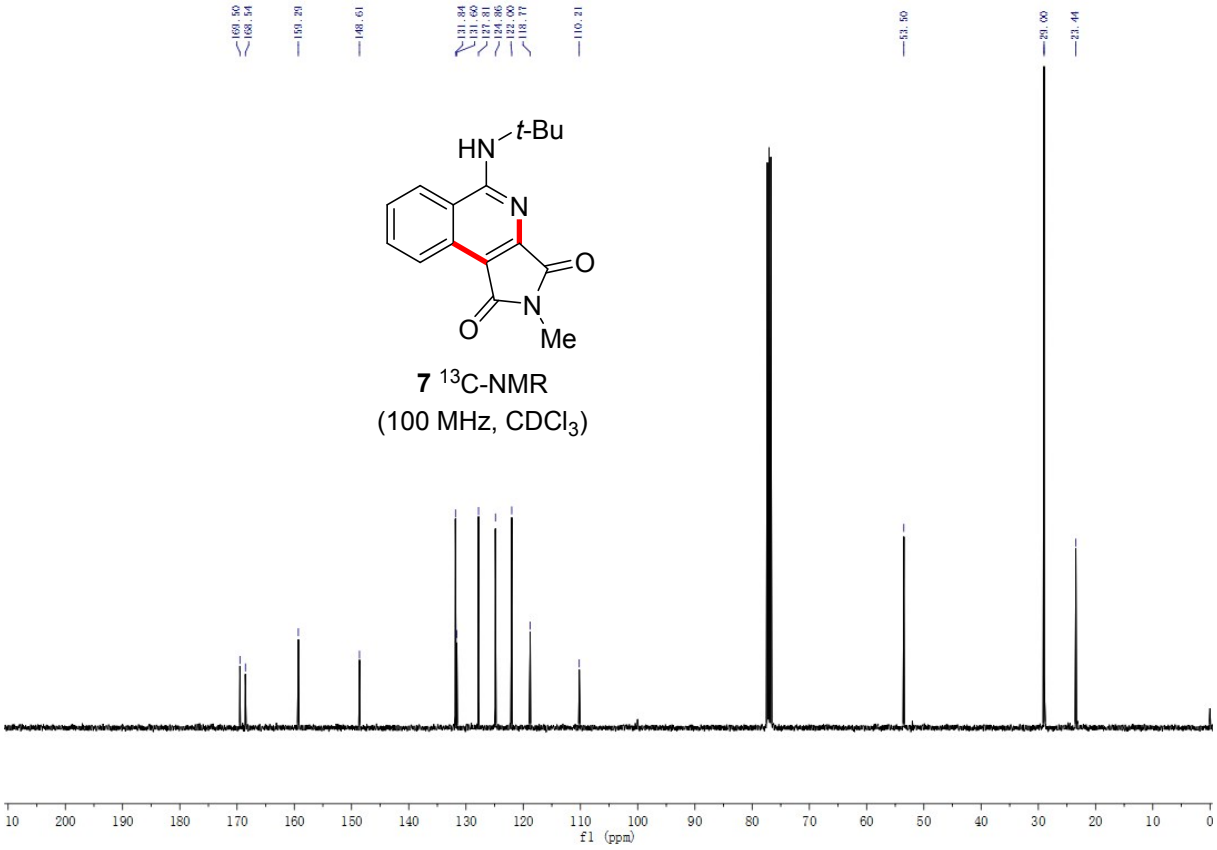
6 ^{1}H-NMR
(400 MHz, $CDCl_3$)



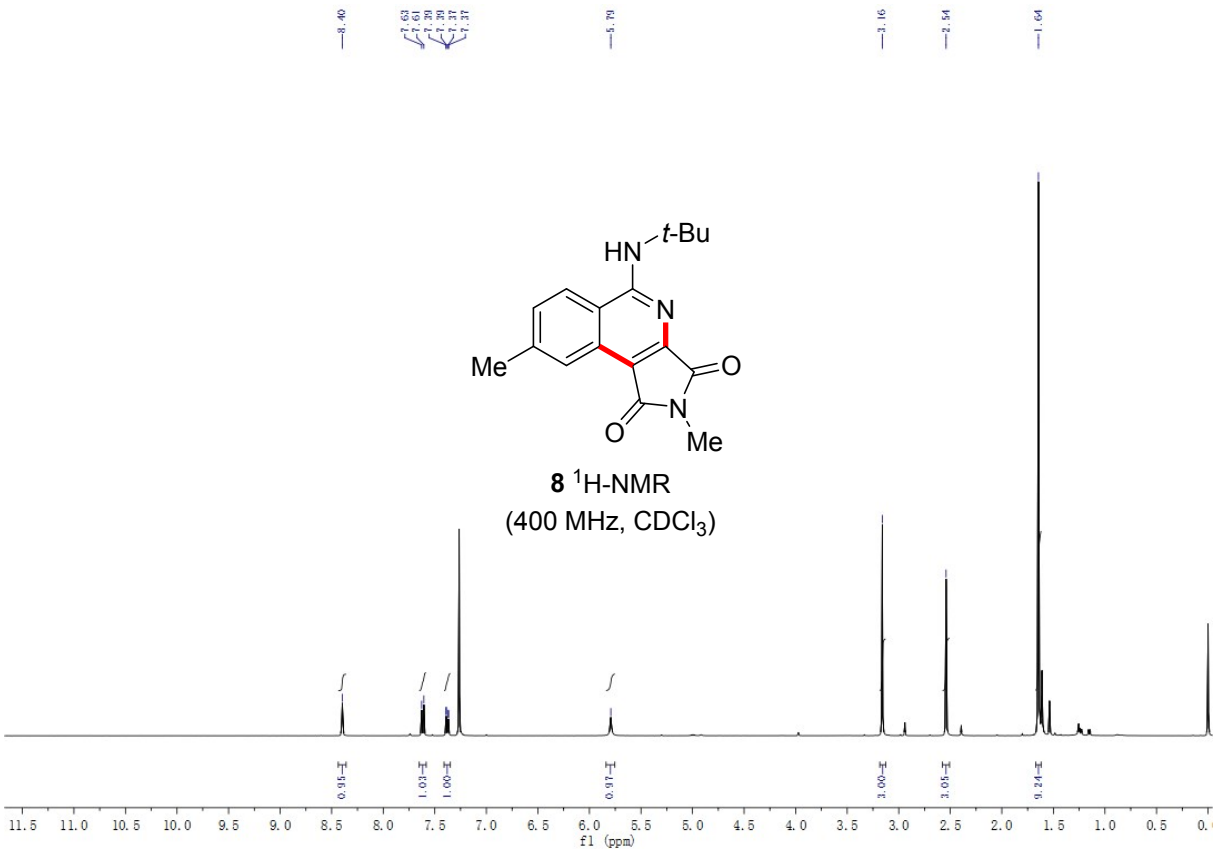
6 ^{13}C-NMR
(100 MHz, $CDCl_3$)



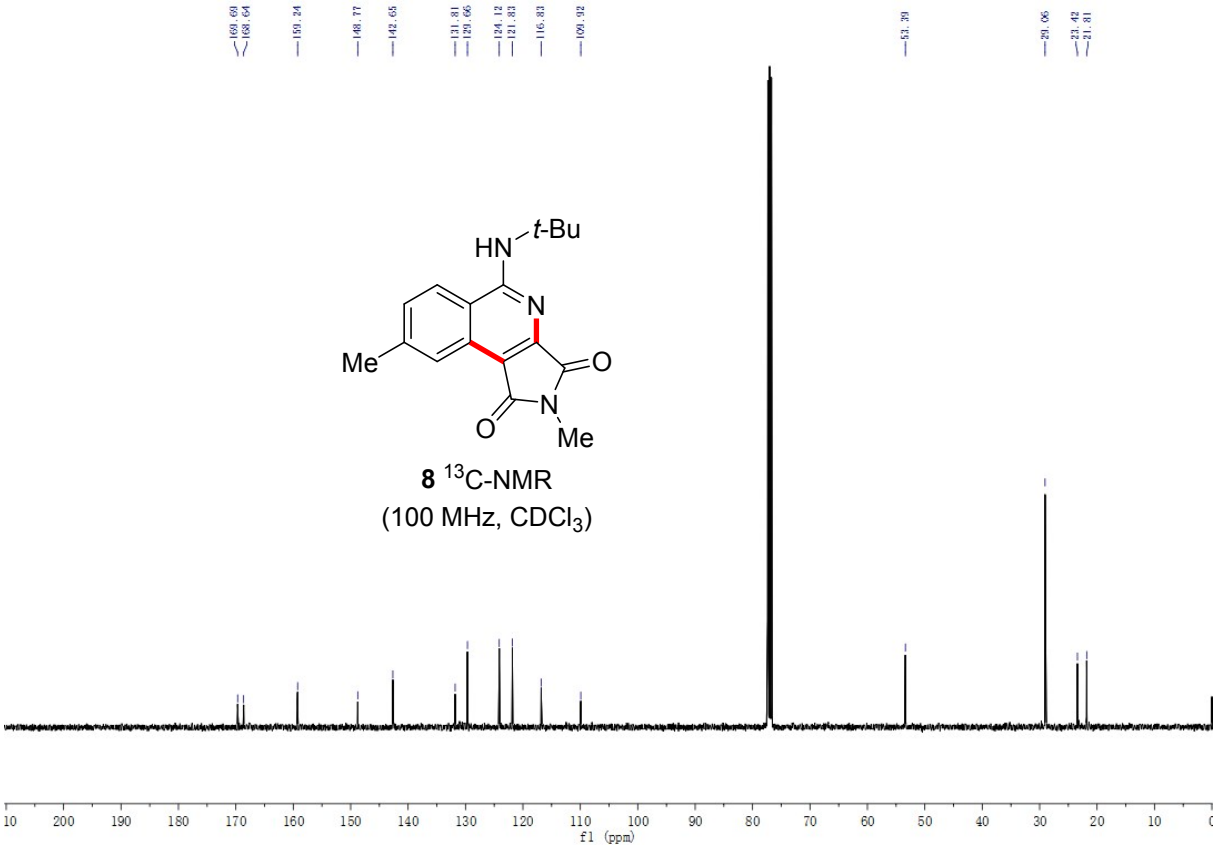
7 ^{1}H-NMR
(400 MHz, $CDCl_3$)



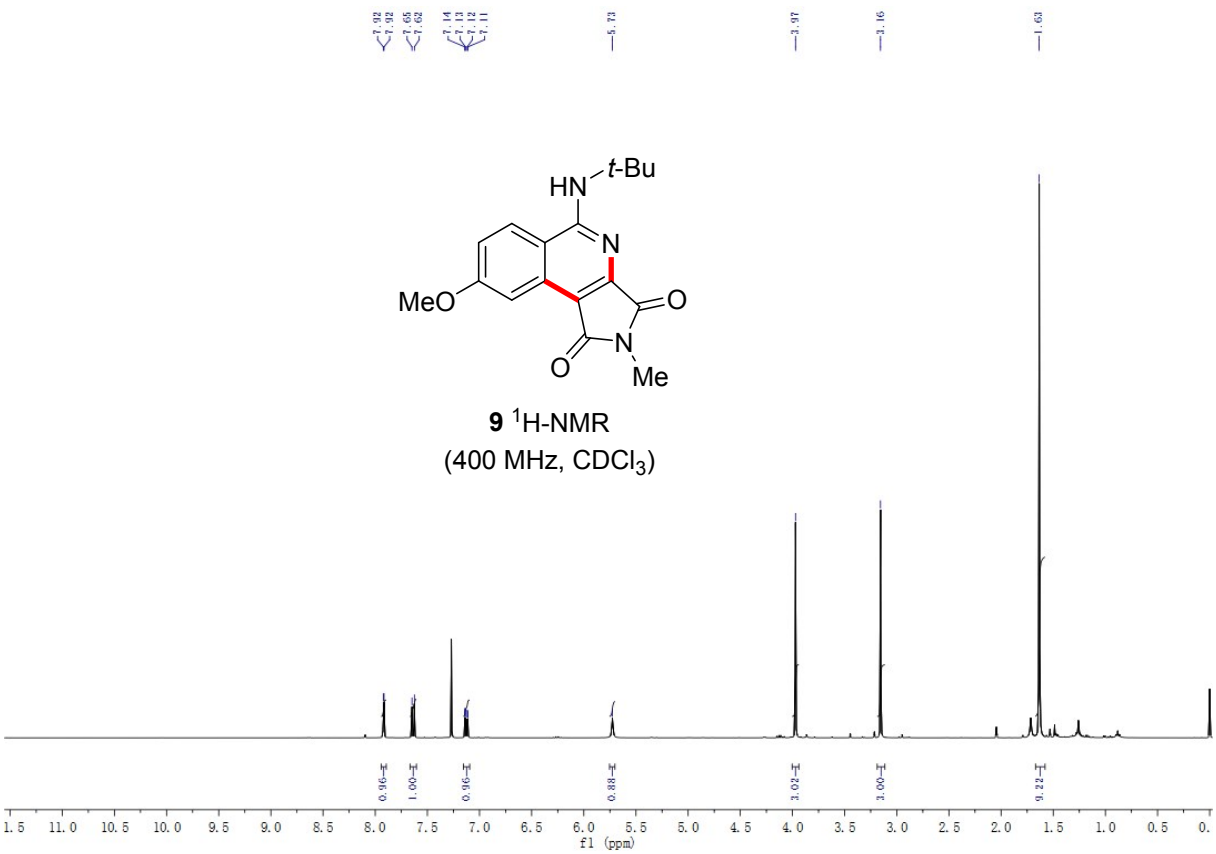
7 ^{13}C-NMR
(100 MHz, $CDCl_3$)



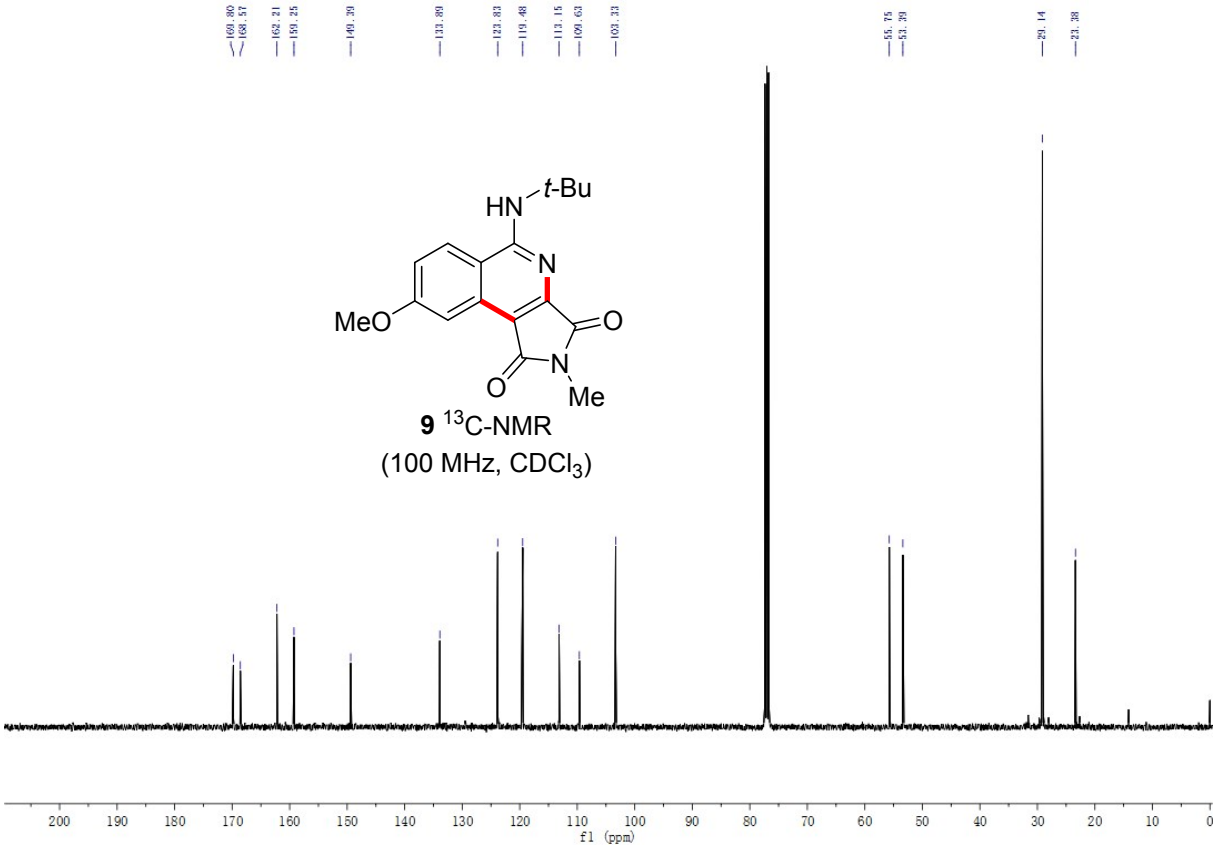
8 ^{1}H-NMR
(400 MHz, $CDCl_3$)



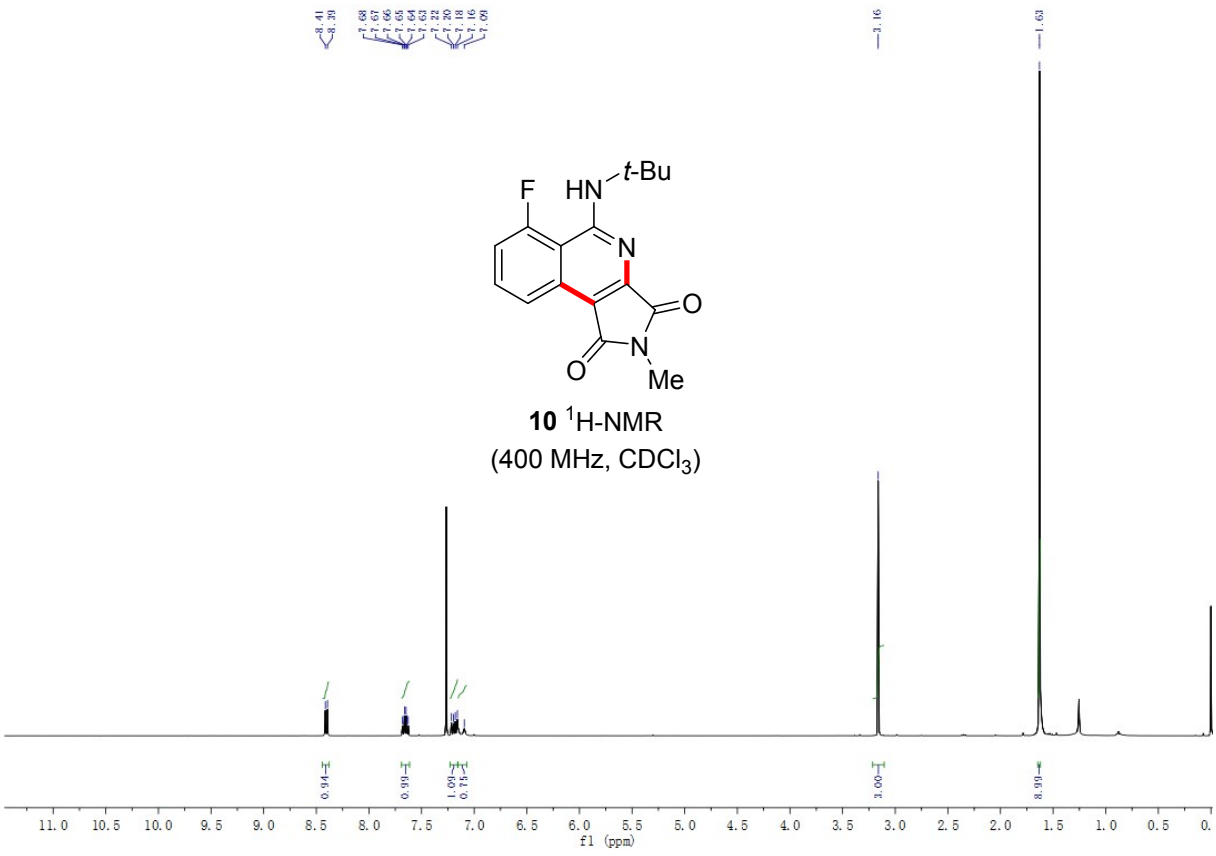
8 ^{13}C-NMR
(100 MHz, $CDCl_3$)



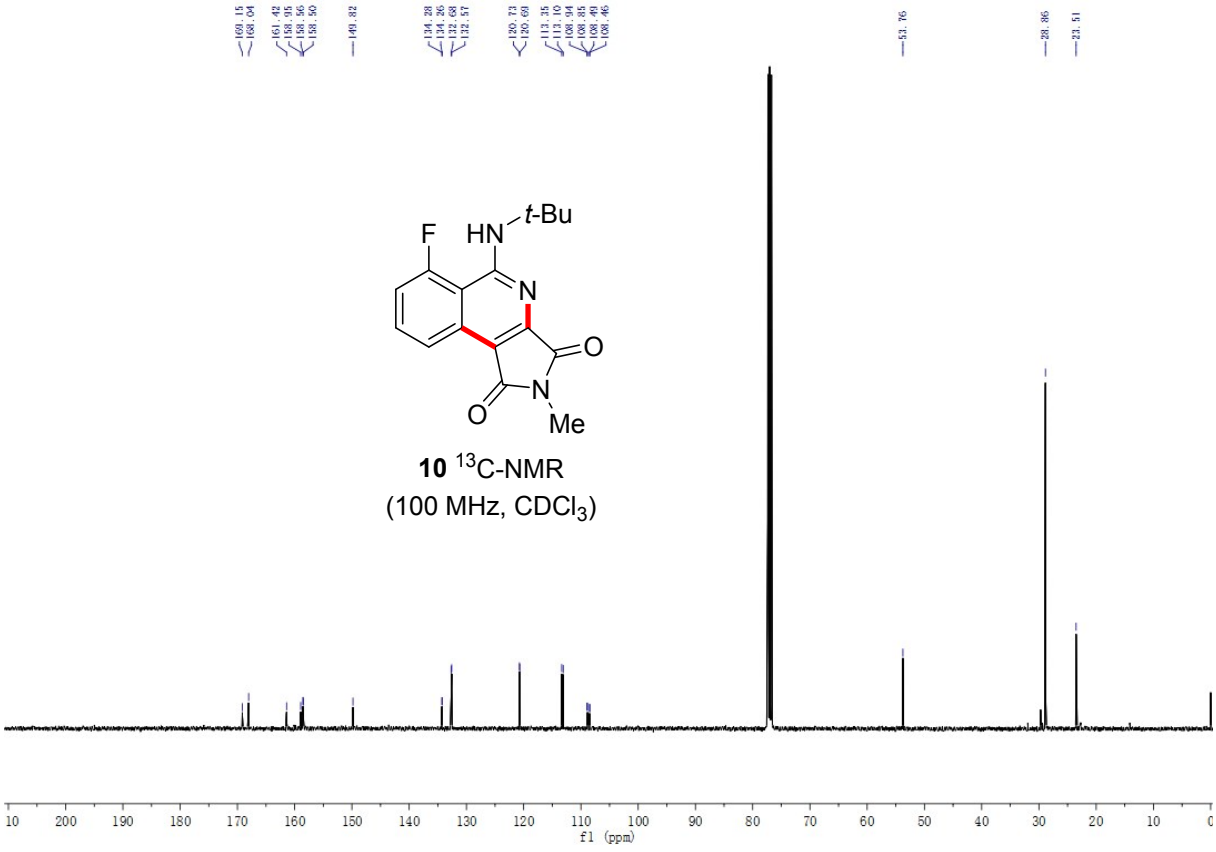
9 ^{1}H-NMR
(400 MHz, $CDCl_3$)



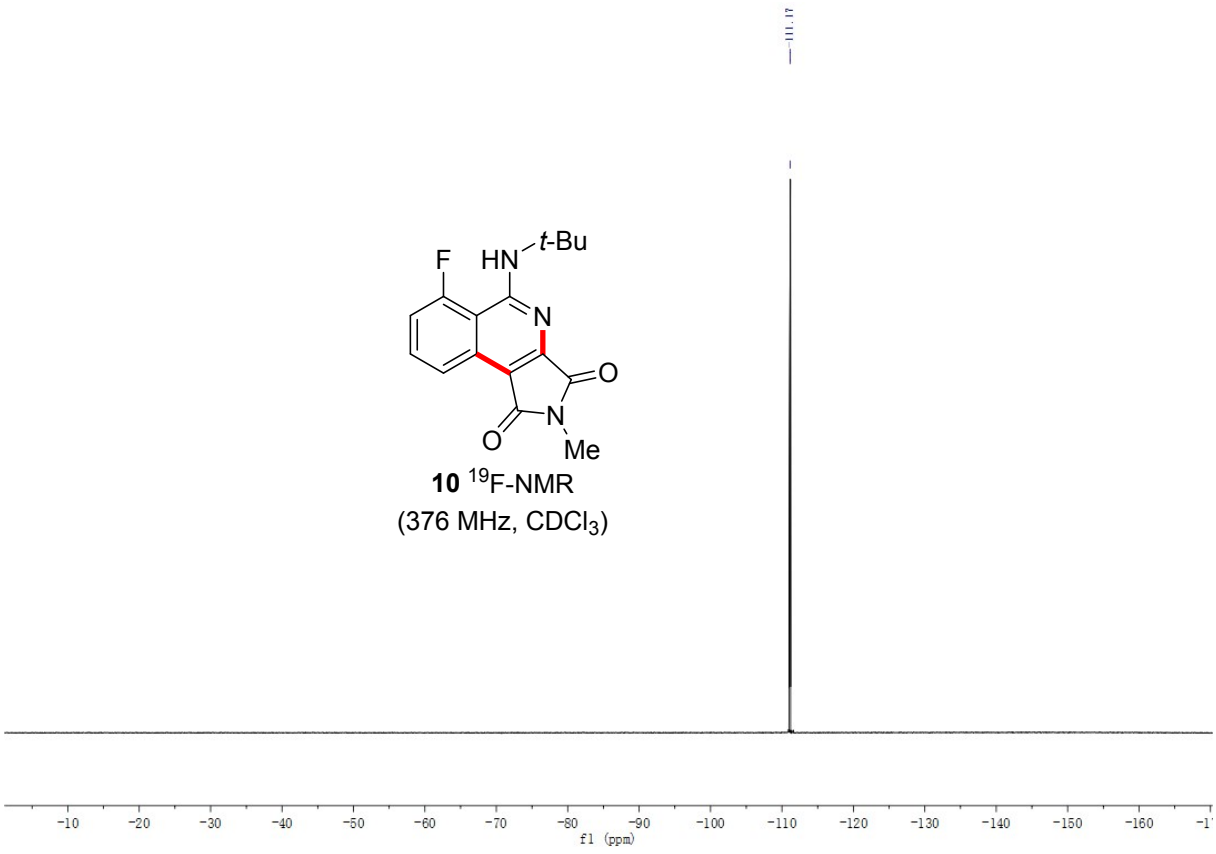
9 ^{13}C-NMR
(100 MHz, $CDCl_3$)



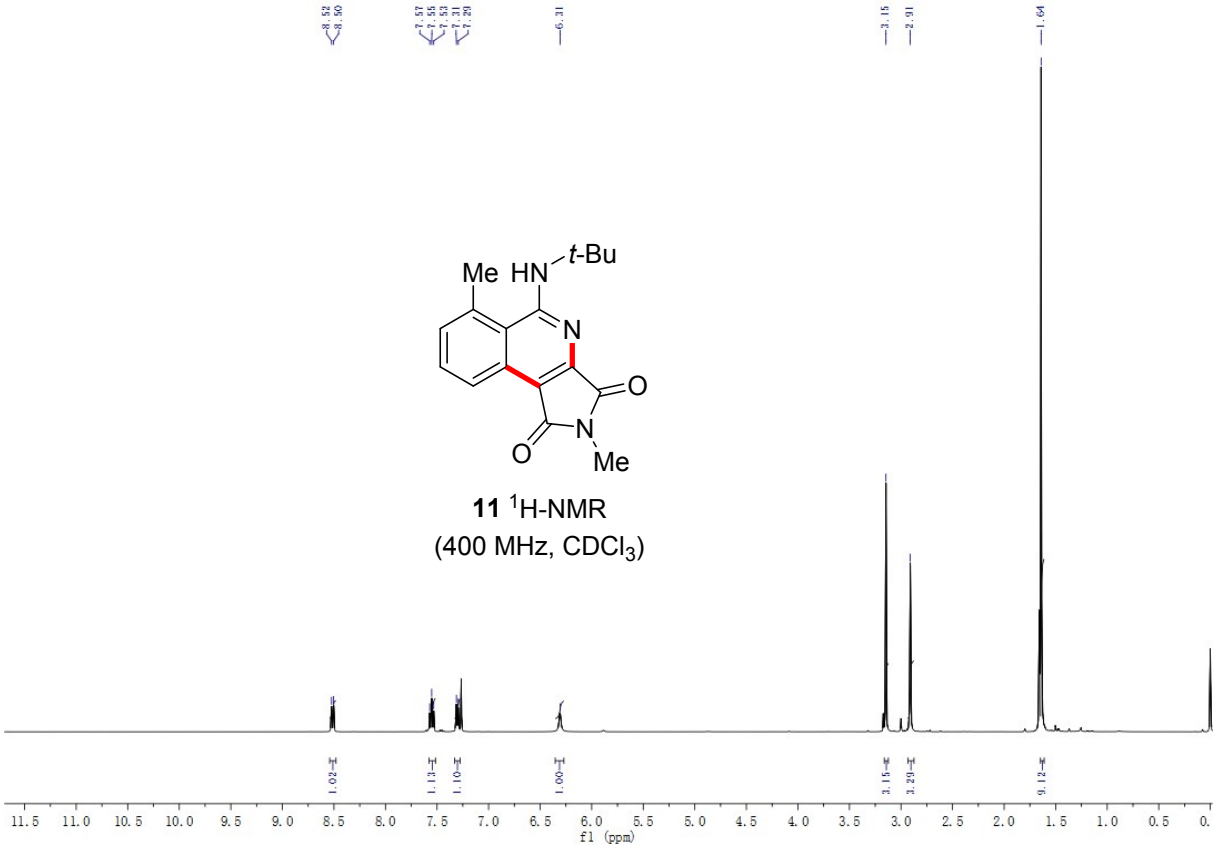
10 ^{1}H-NMR
(400 MHz, $CDCl_3$)



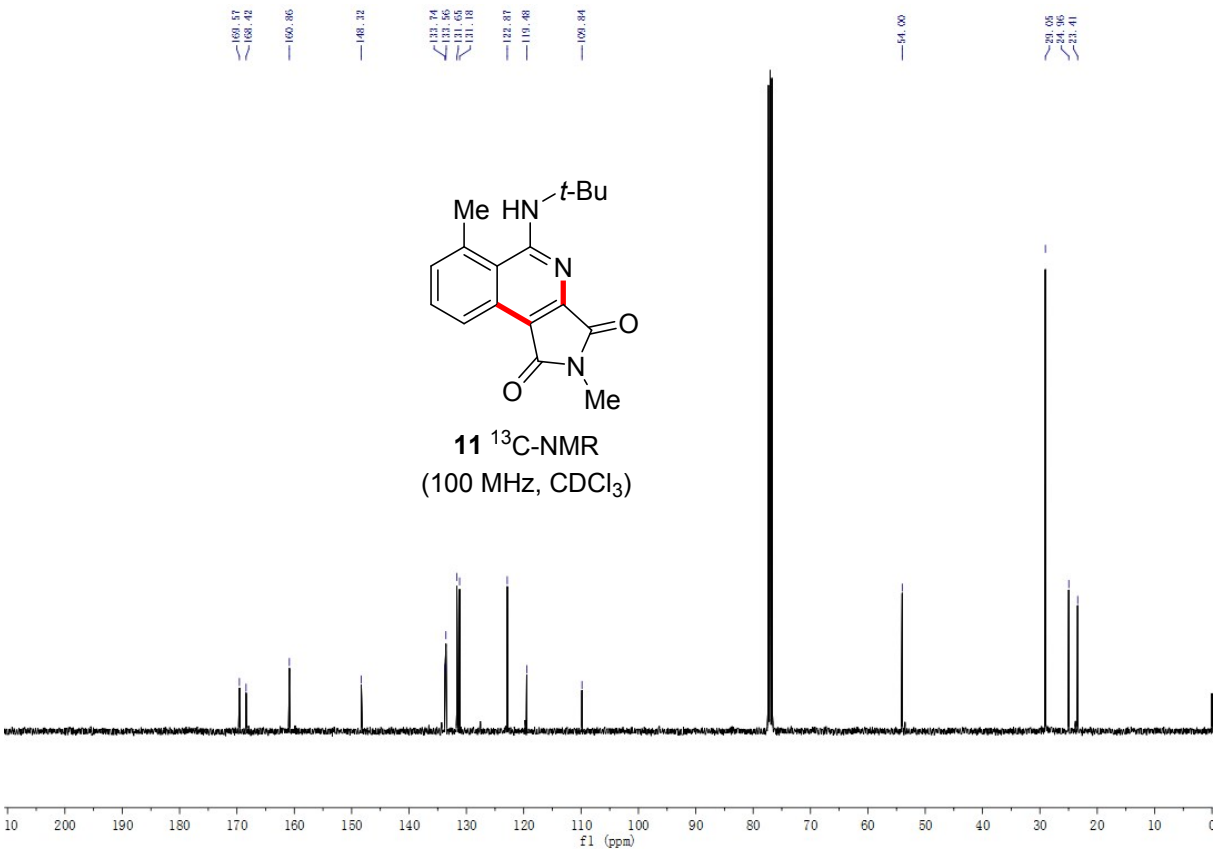
10 ^{13}C-NMR
(100 MHz, $CDCl_3$)



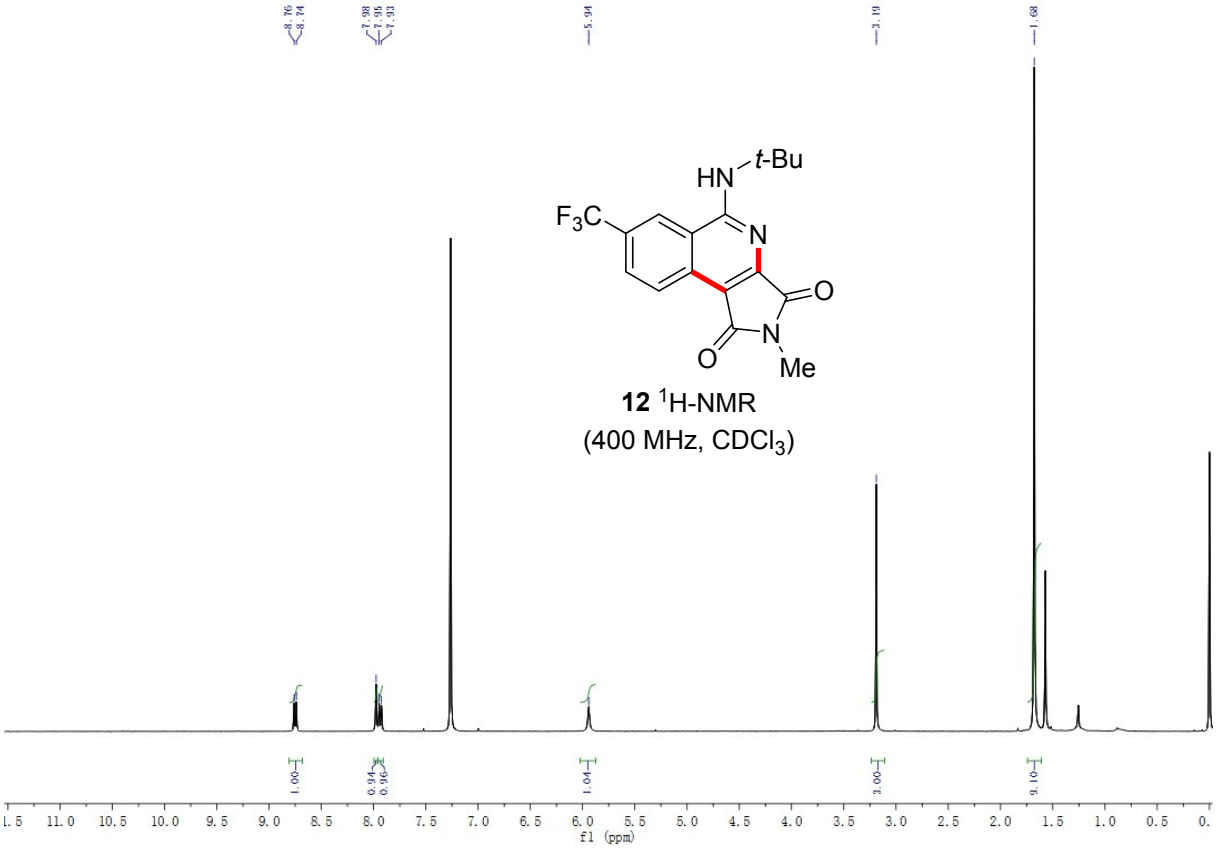
10 ^{19}F-NMR
(376 MHz, $CDCl_3$)



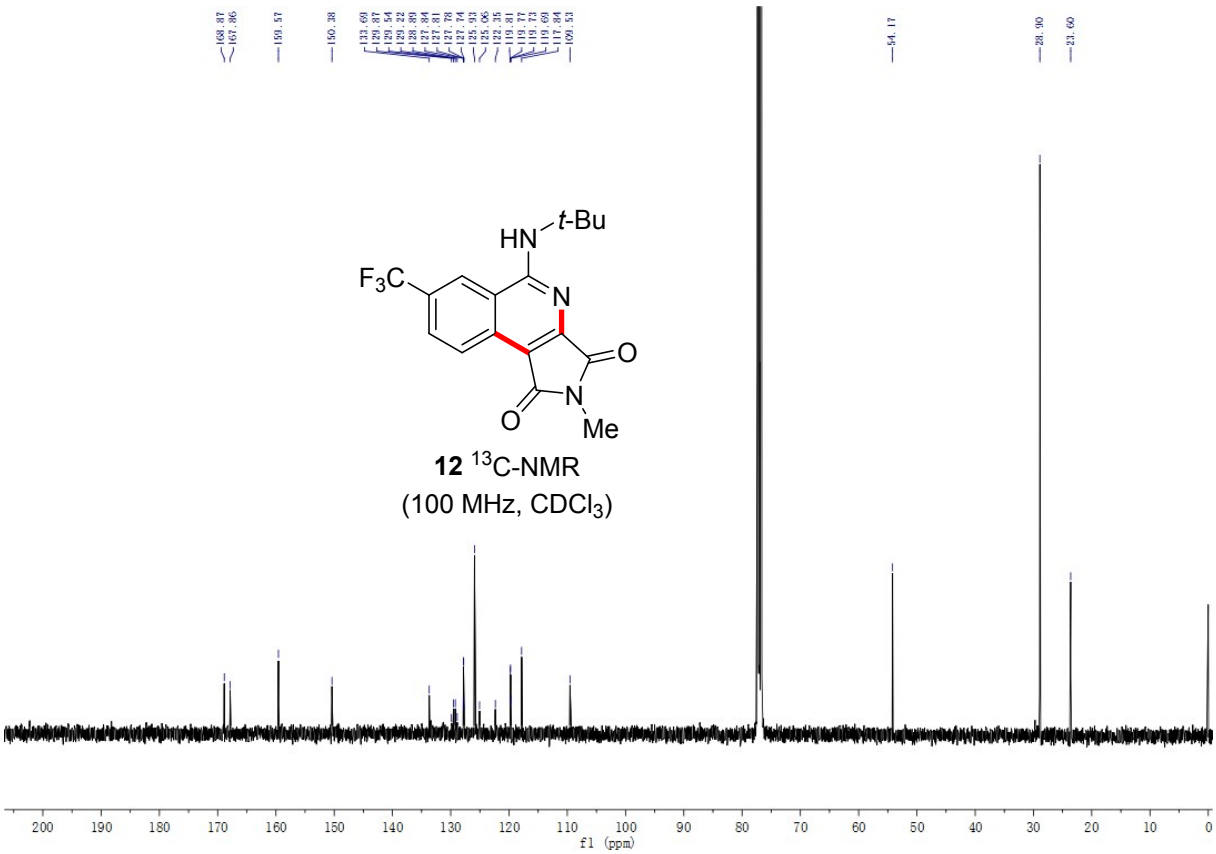
11 ^{1}H-NMR
(400 MHz, $CDCl_3$)



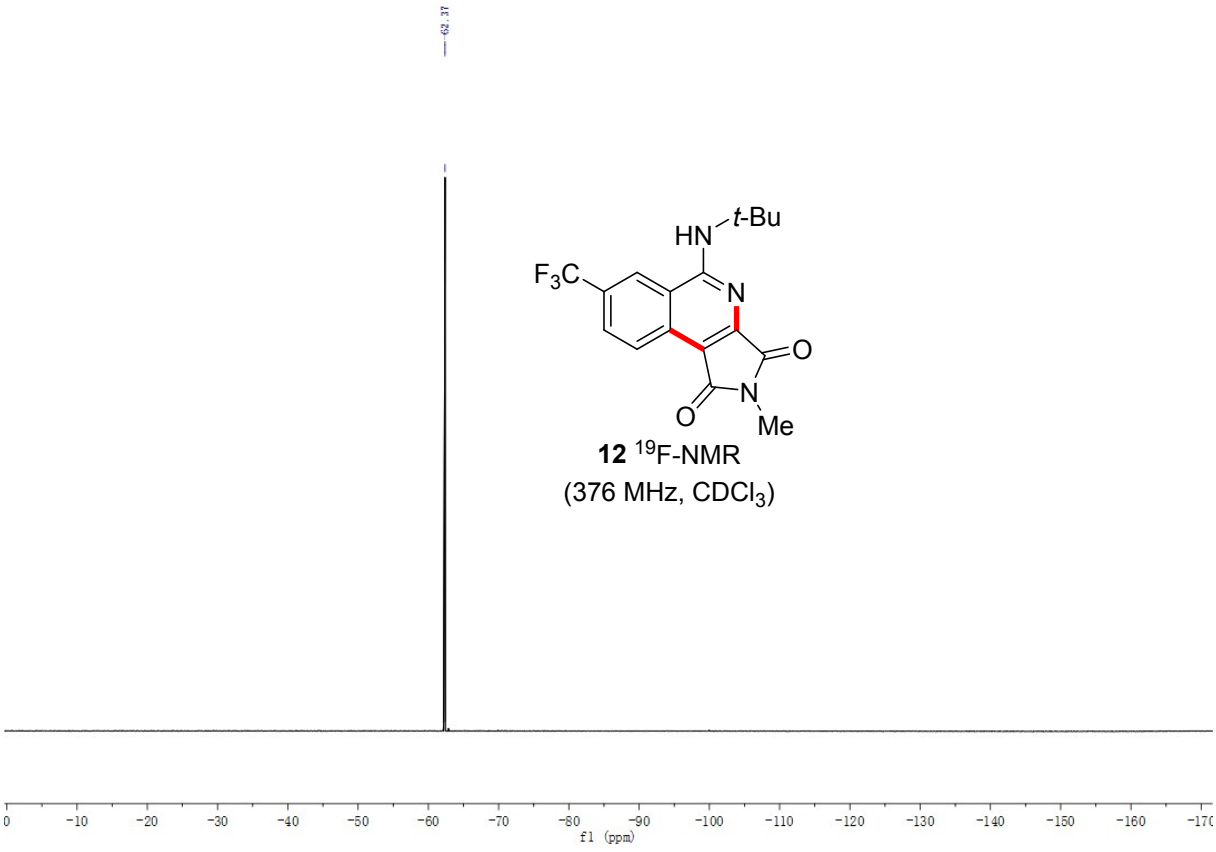
11 ^{13}C-NMR
(100 MHz, $CDCl_3$)



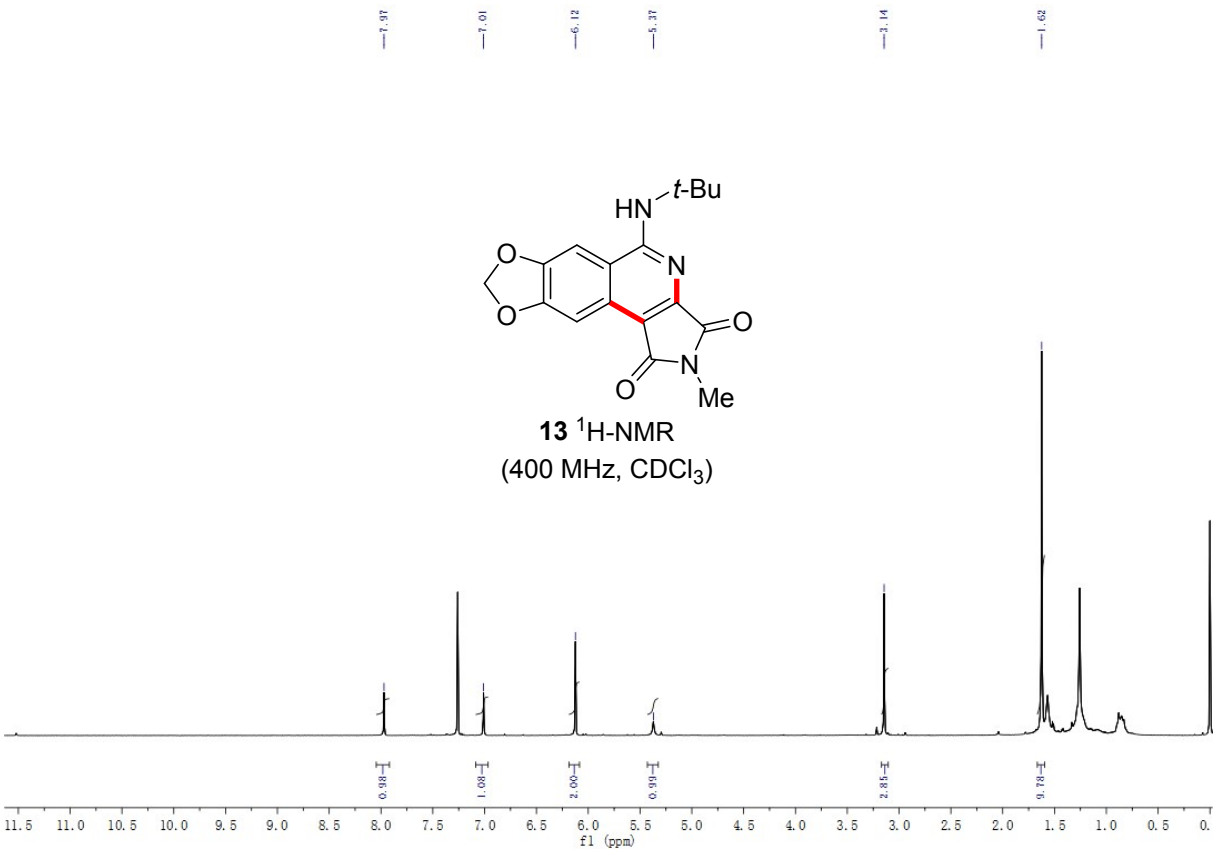
12 ^{1}H-NMR
(400 MHz, $CDCl_3$)



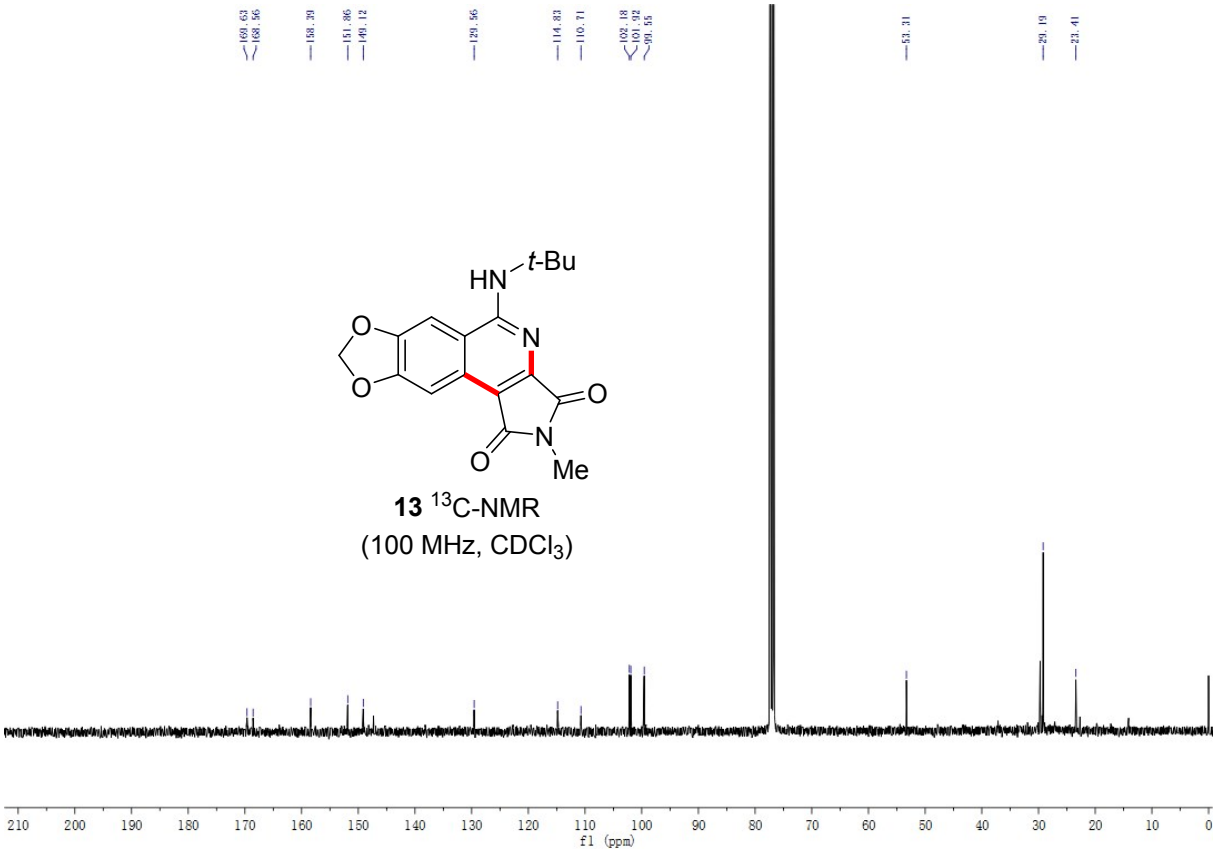
12 ^{13}C-NMR
(100 MHz, $CDCl_3$)



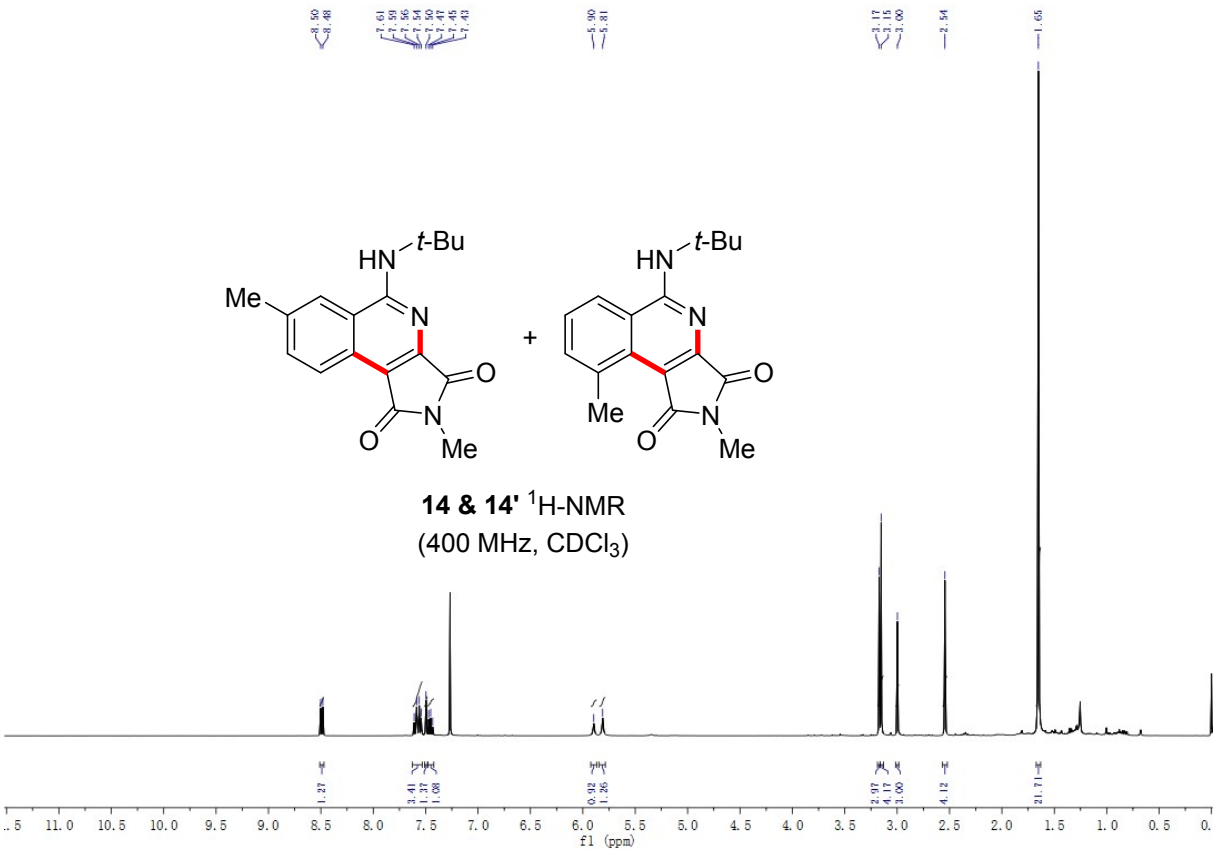
12 ^{19}F-NMR
(376 MHz, $CDCl_3$)



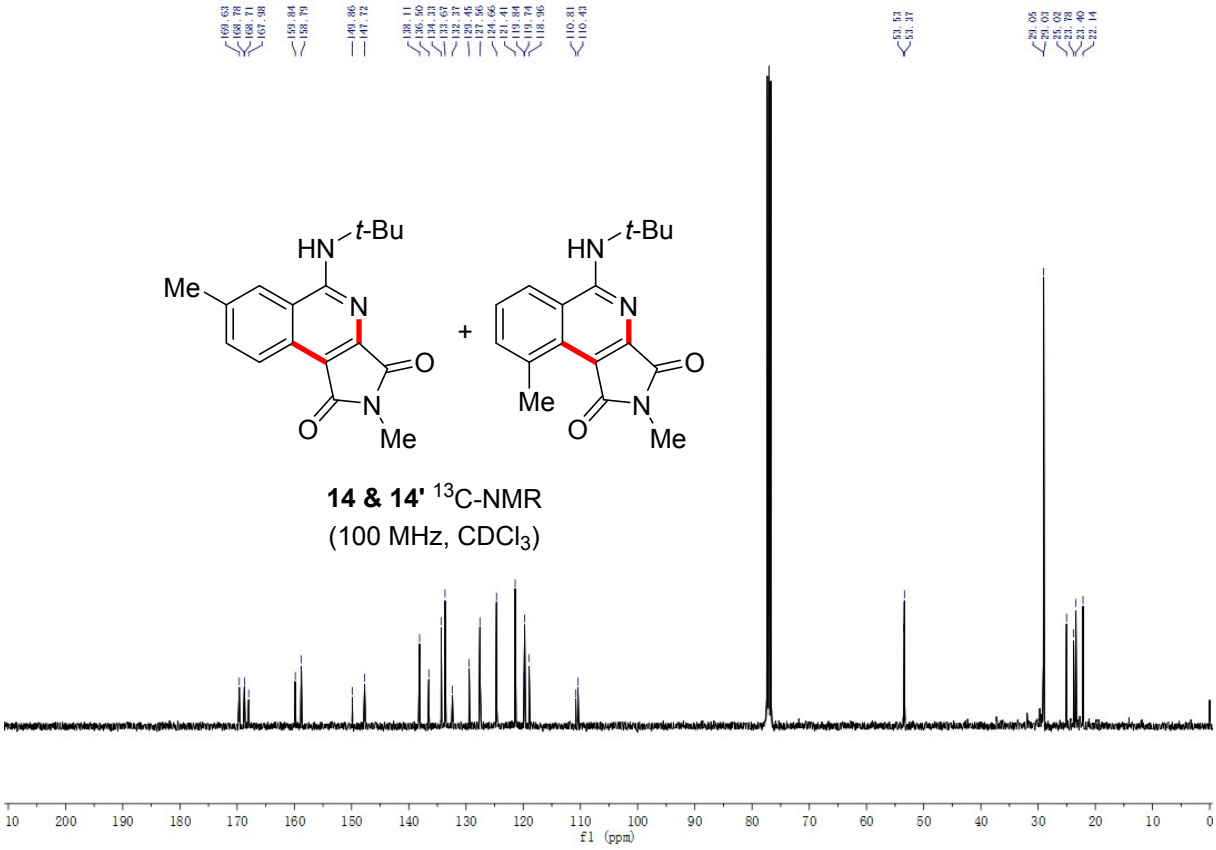
13 ^{1}H-NMR
(400 MHz, $CDCl_3$)



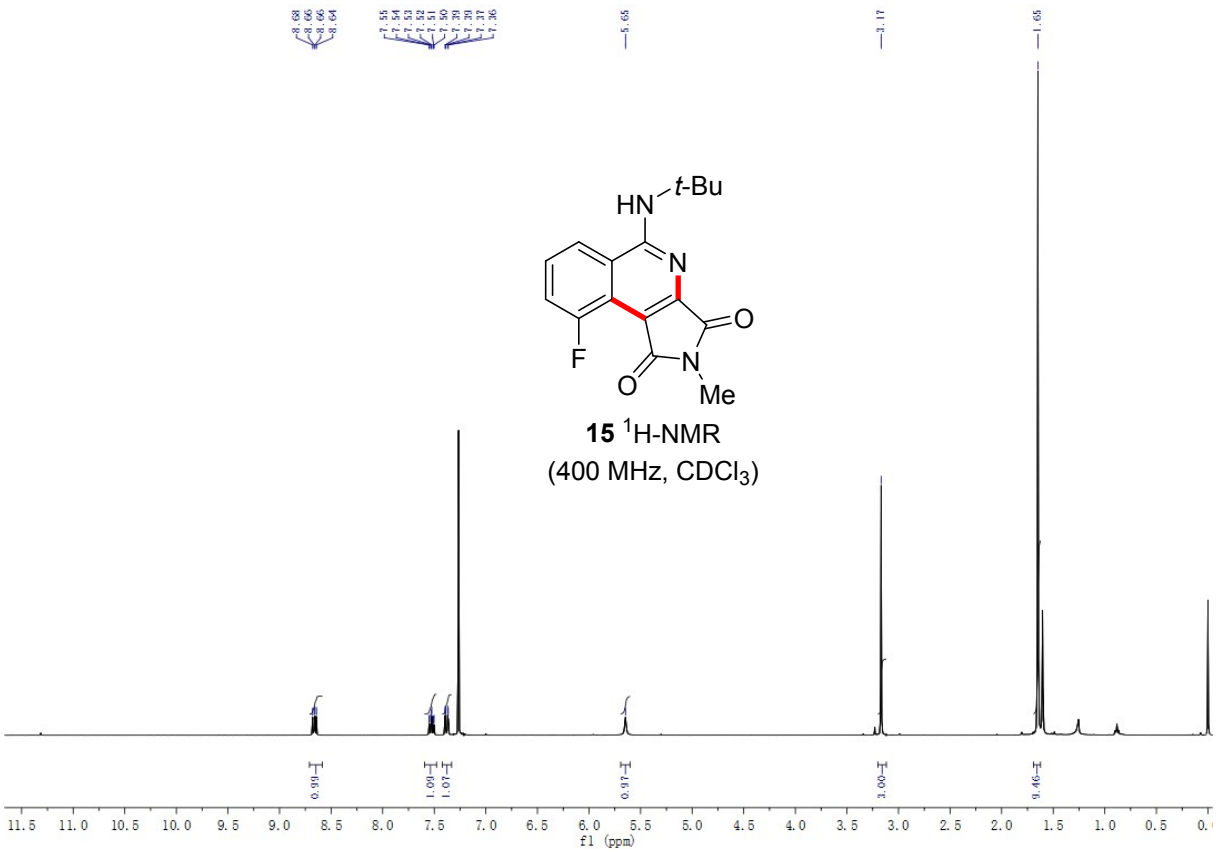
13 ^{13}C-NMR
(100 MHz, $CDCl_3$)



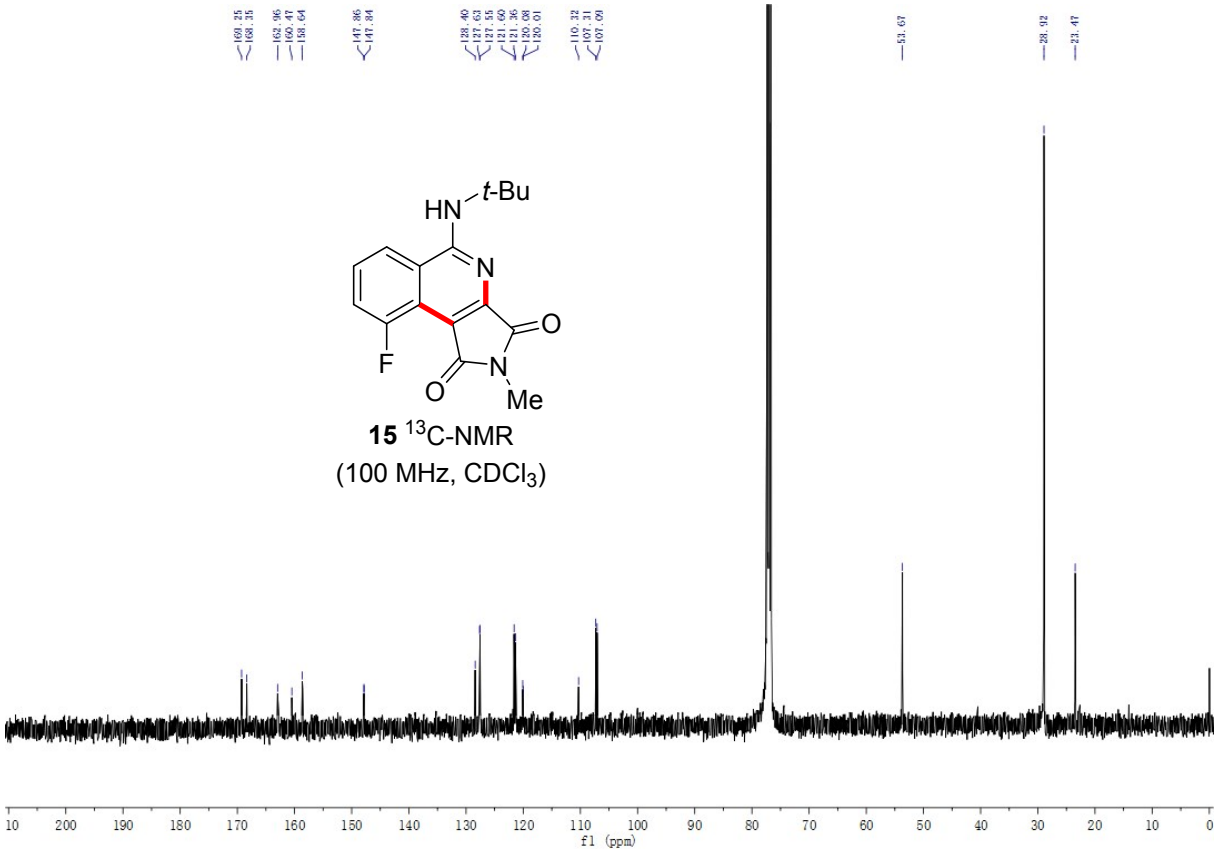
14 & 14' ^{1}H-NMR
(400 MHz, $CDCl_3$)



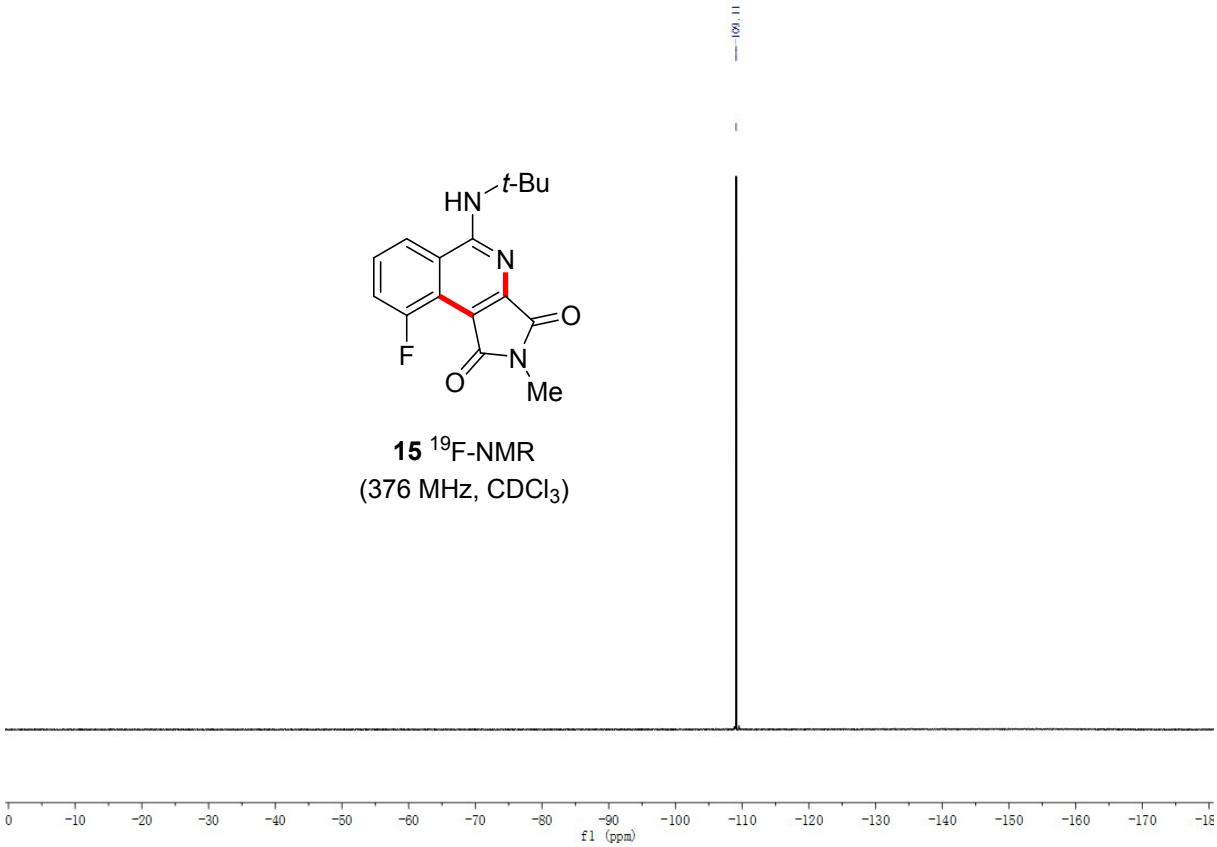
14 & 14' ^{13}C-NMR
(100 MHz, $CDCl_3$)



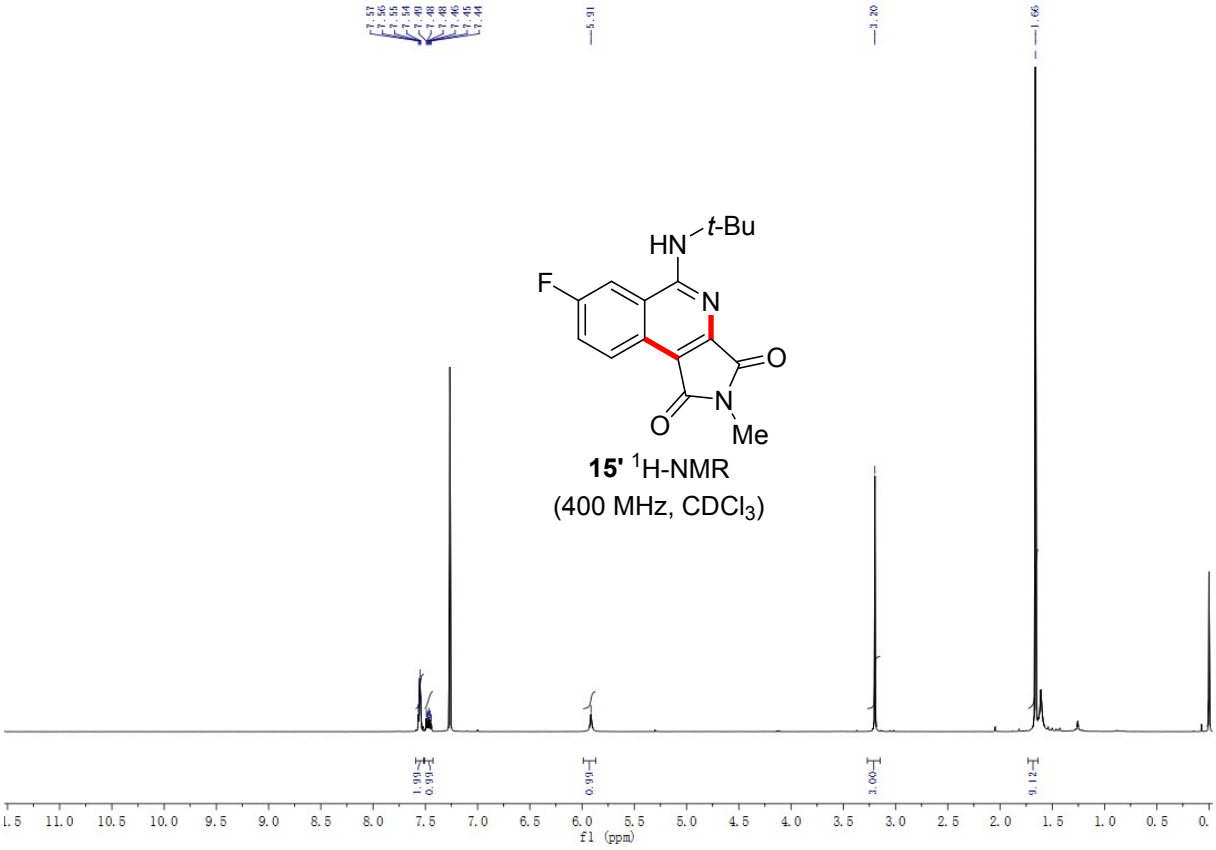
15 ^{1}H-NMR
(400 MHz, $CDCl_3$)



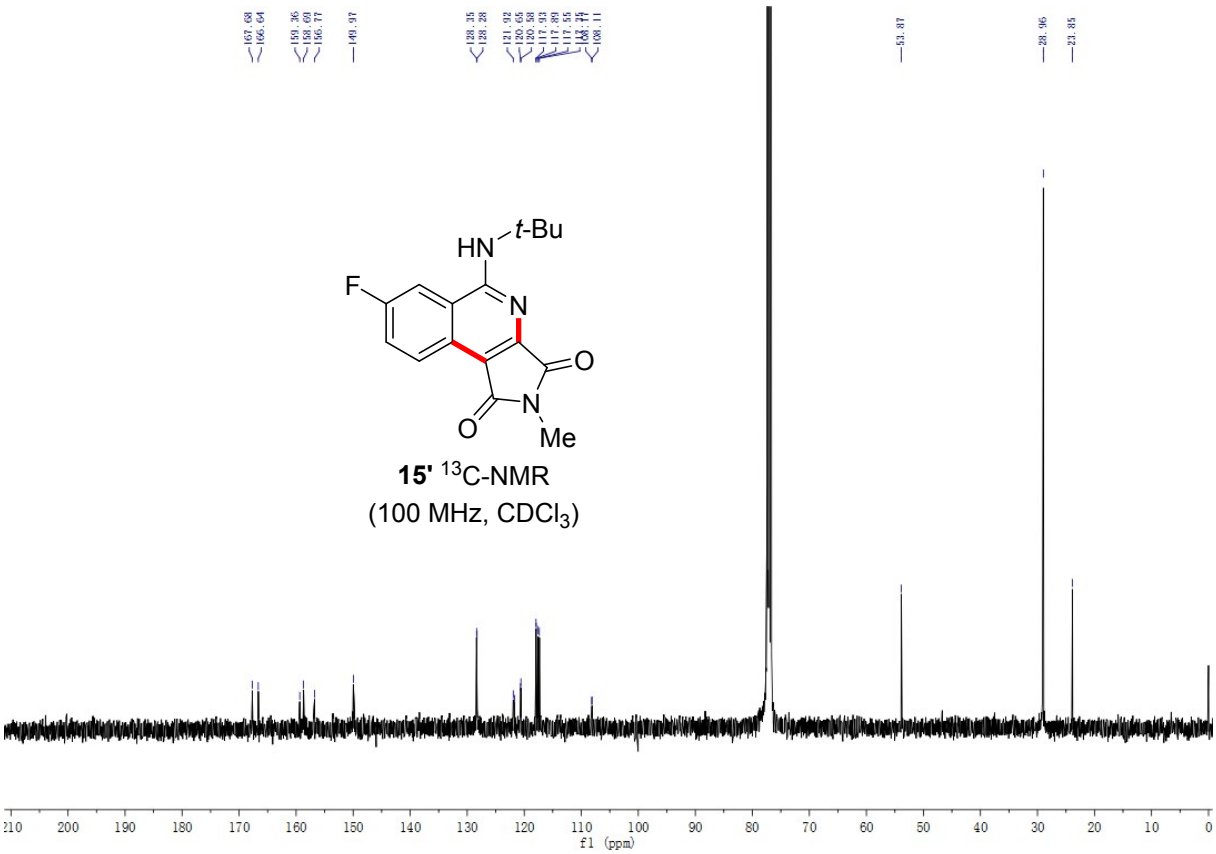
15 ^{13}C-NMR
(100 MHz, $CDCl_3$)



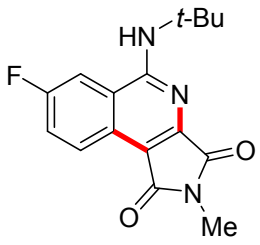
15 ^{19}F-NMR
(376 MHz, $CDCl_3$)



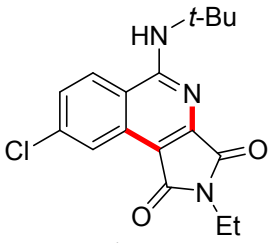
15' ^{1}H-NMR
(400 MHz, $CDCl_3$)



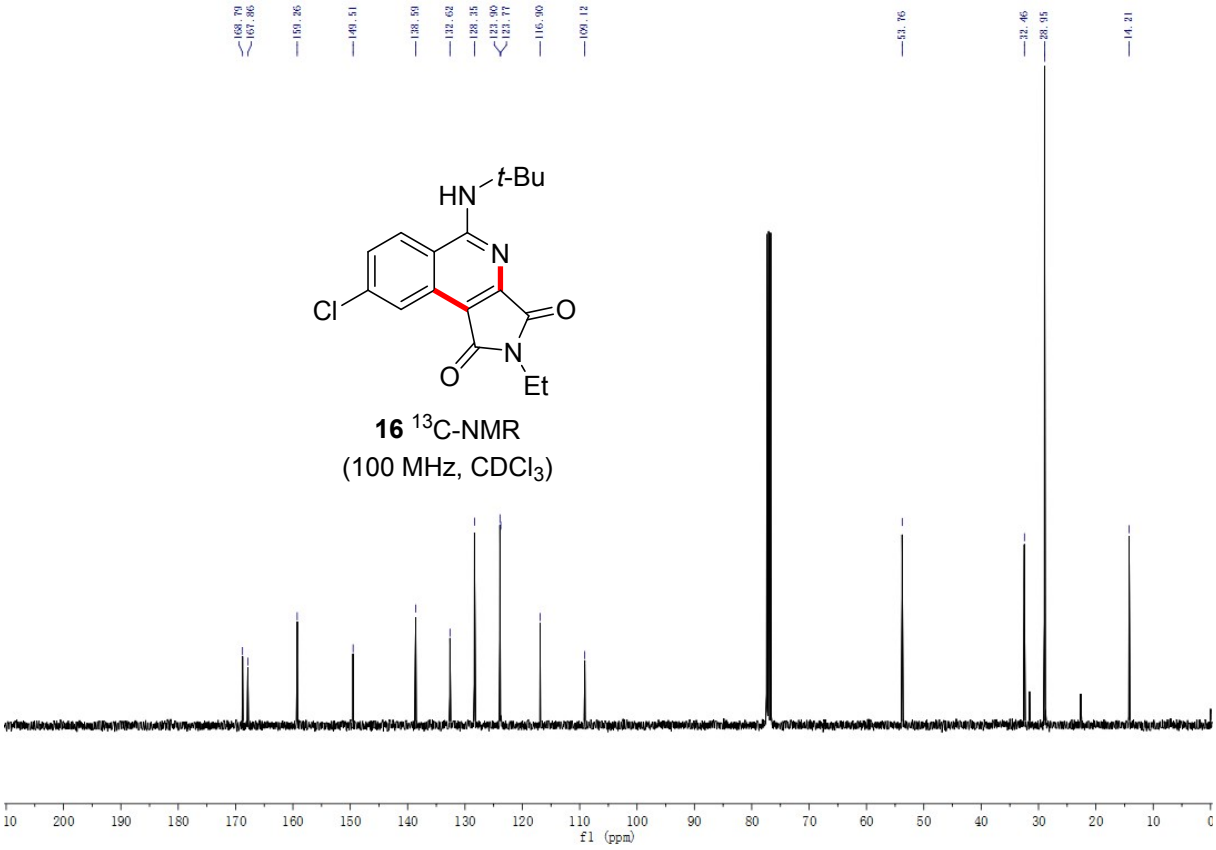
15' ^{13}C-NMR
(100 MHz, $CDCl_3$)



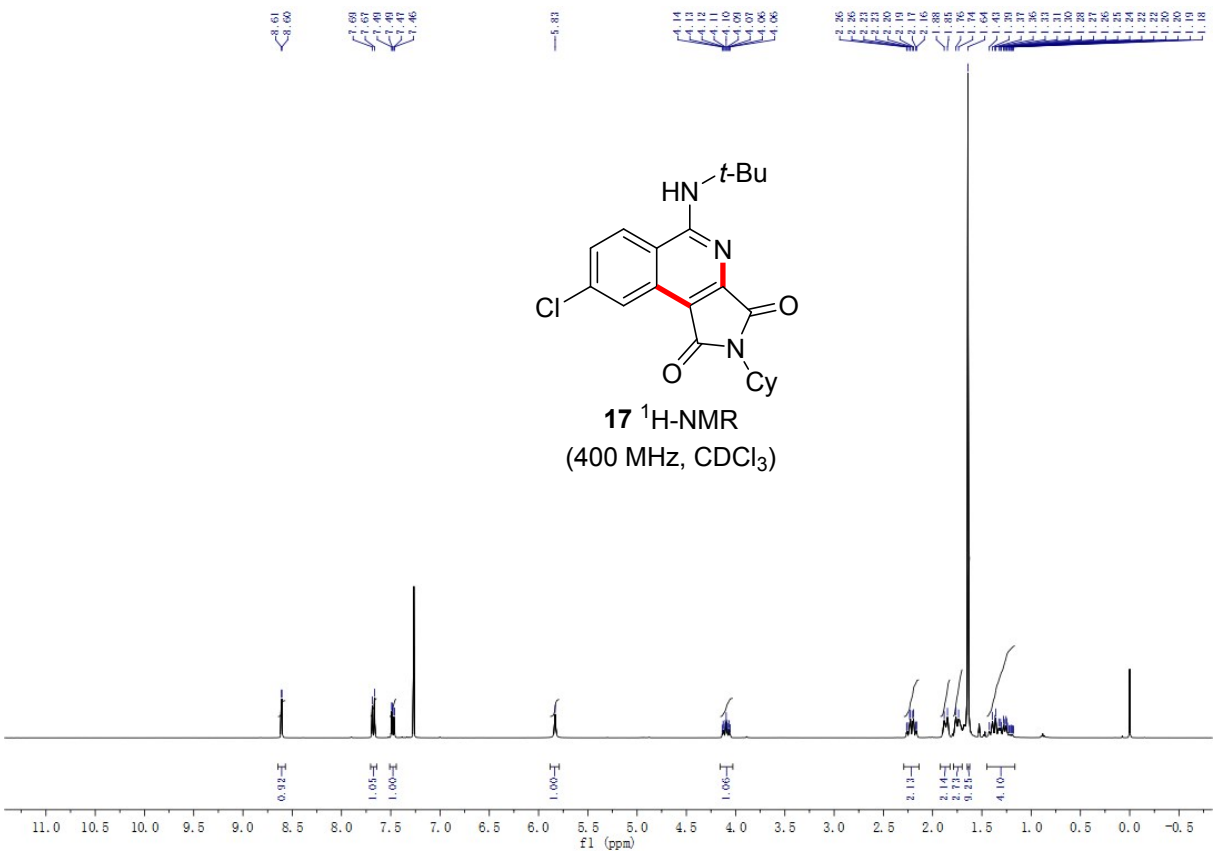
15' ^{19}F-NMR
(376 MHz, $CDCl_3$)



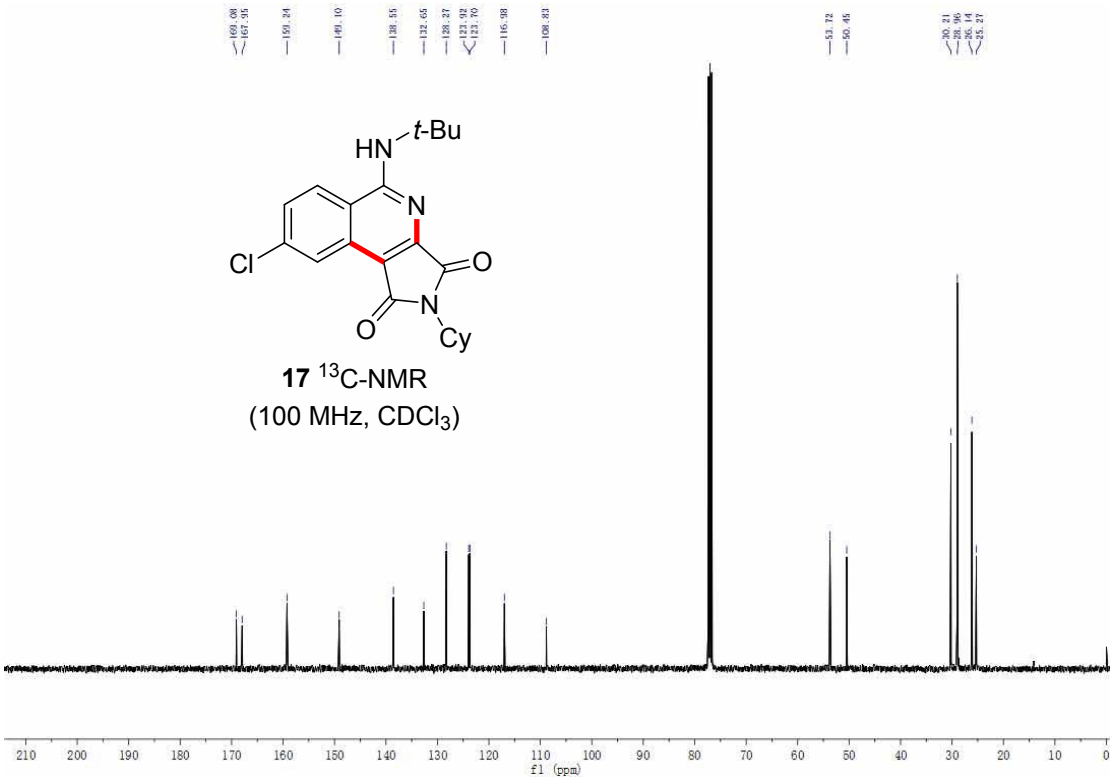
16 ^{1}H-NMR
(400 MHz, $CDCl_3$)



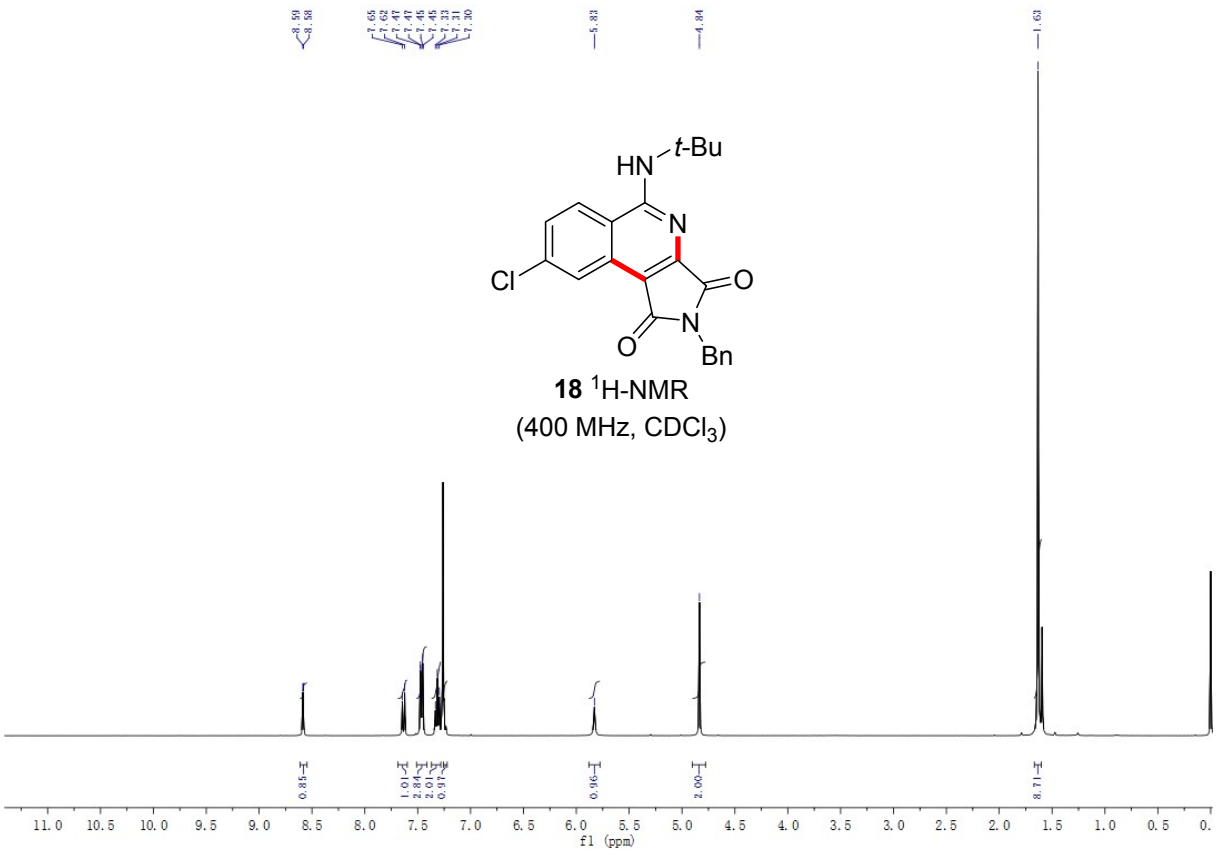
16 ^{13}C-NMR
(100 MHz, $CDCl_3$)



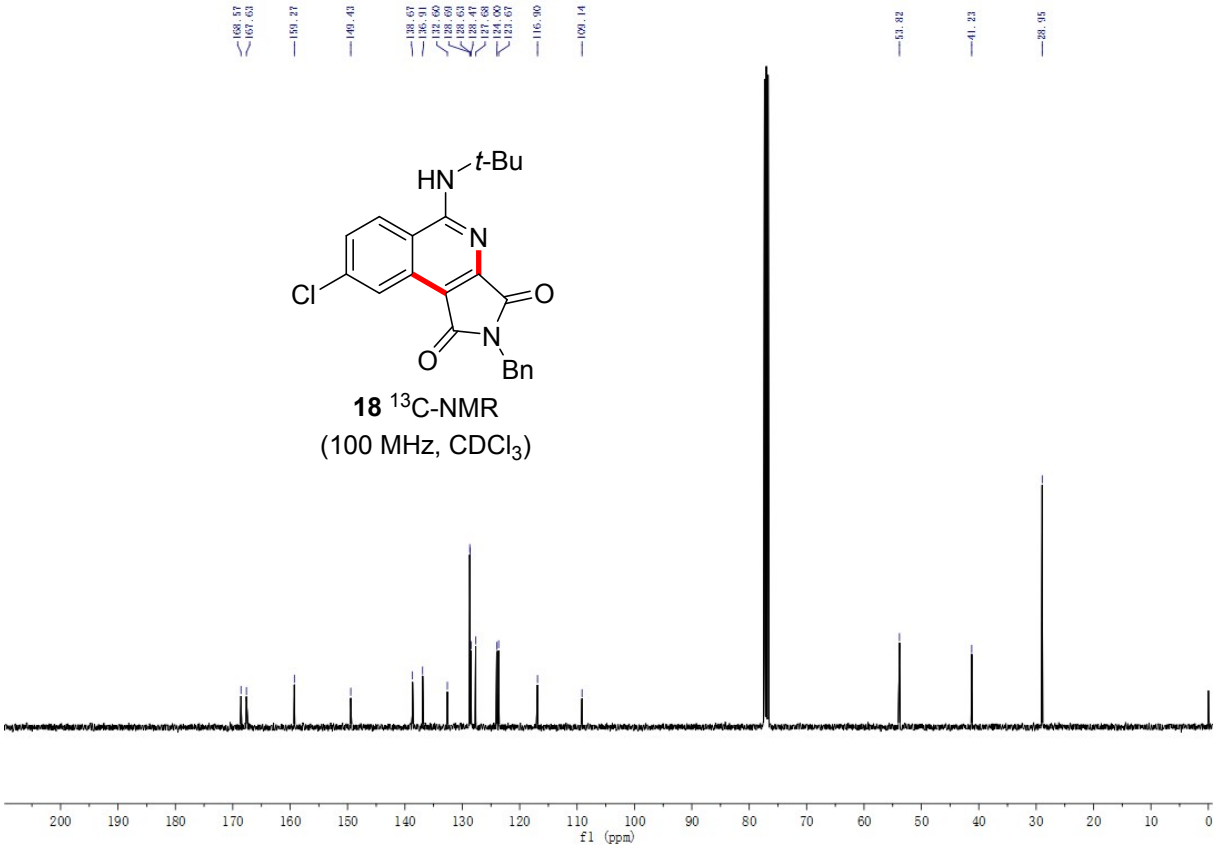
17 ^{1}H-NMR
(400 MHz, $CDCl_3$)



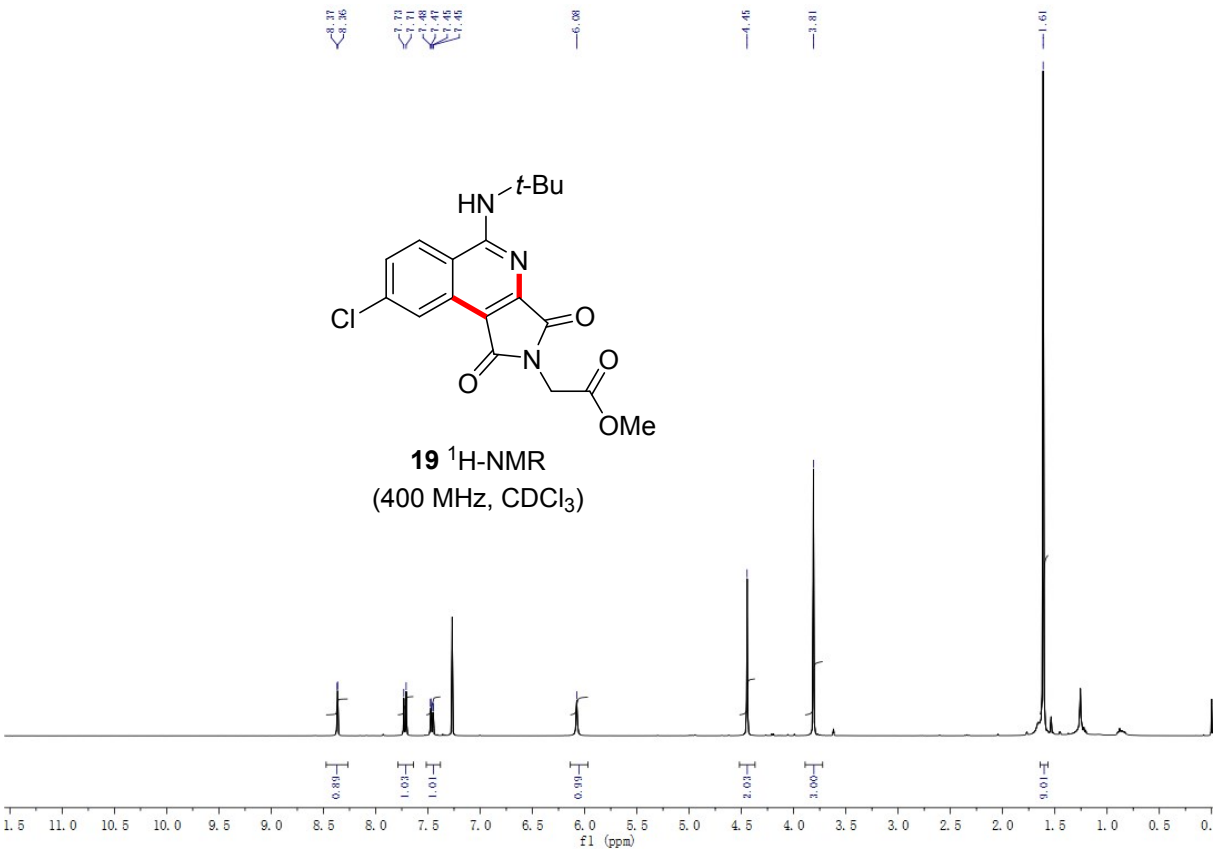
17 ^{13}C-NMR
(100 MHz, $CDCl_3$)



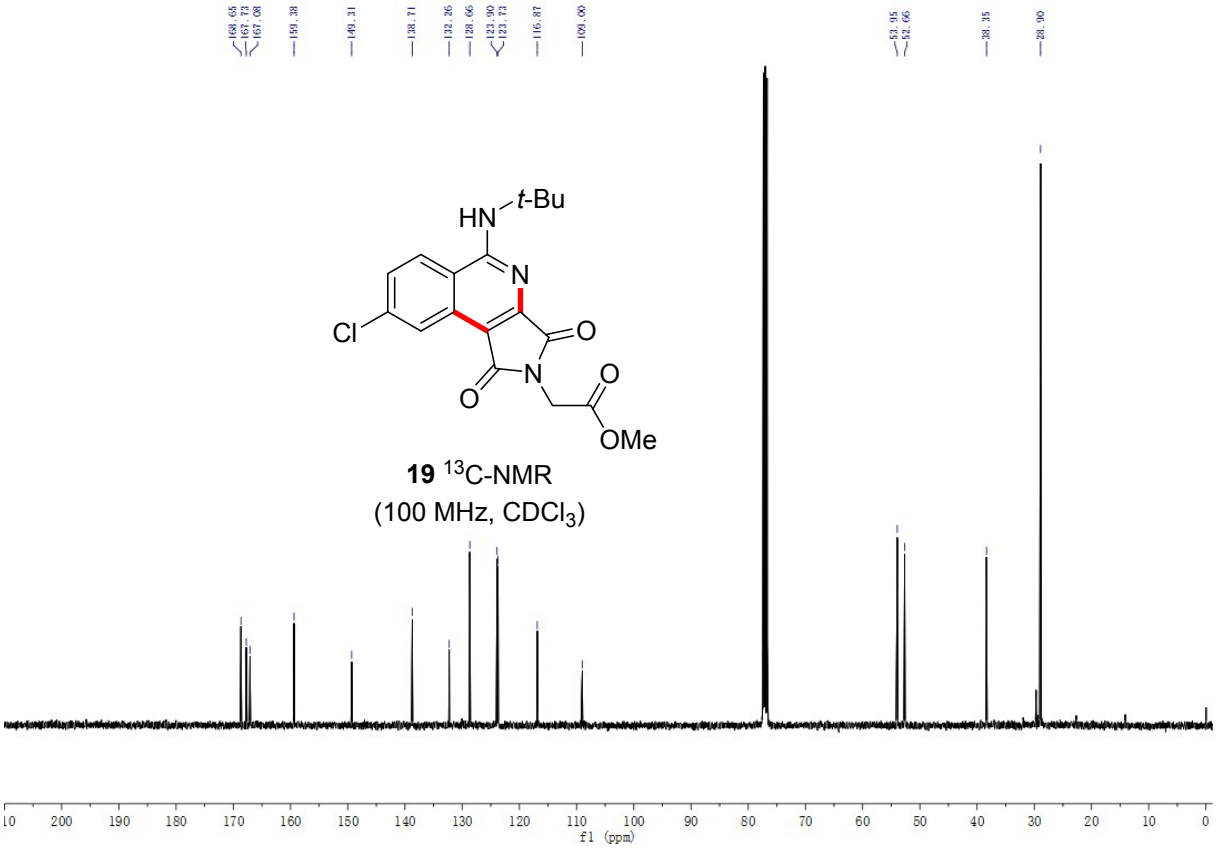
18 ^{1}H-NMR
(400 MHz, $CDCl_3$)



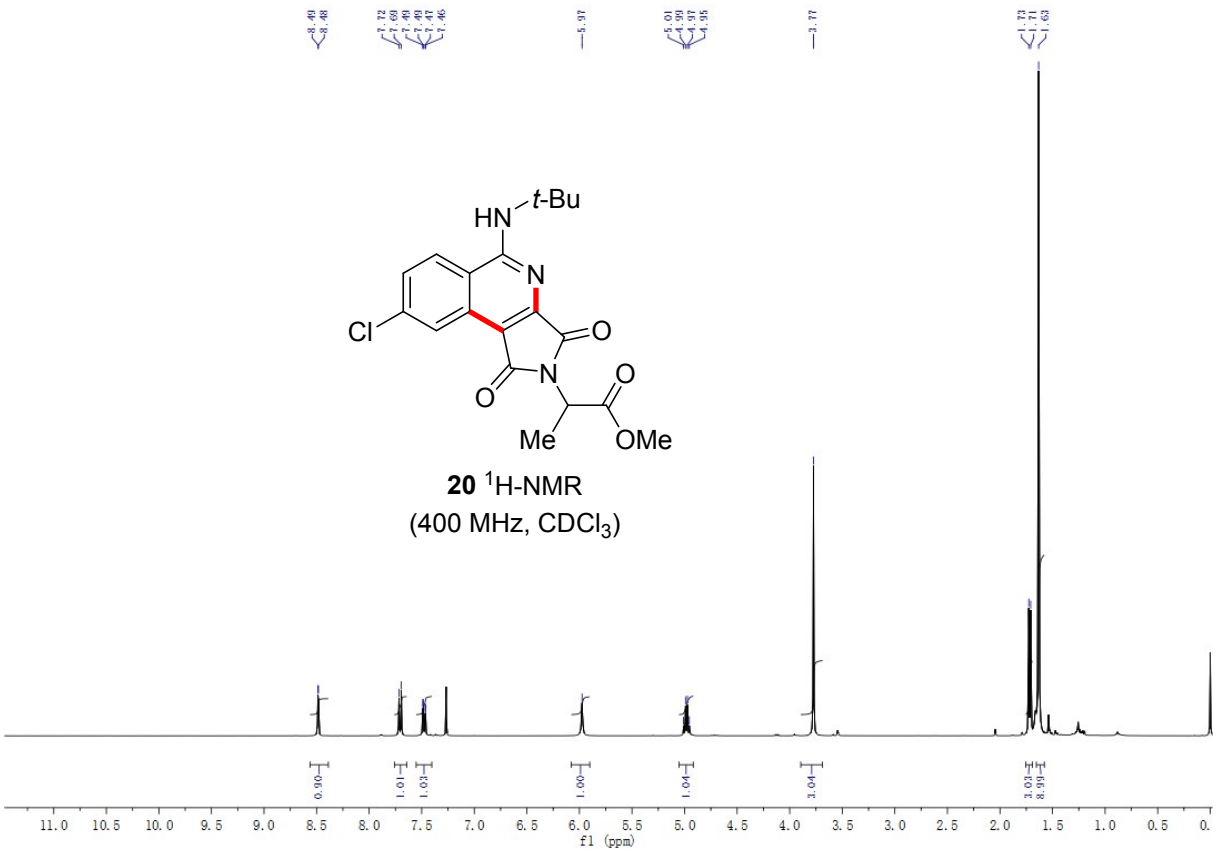
18 ^{13}C-NMR
(100 MHz, $CDCl_3$)



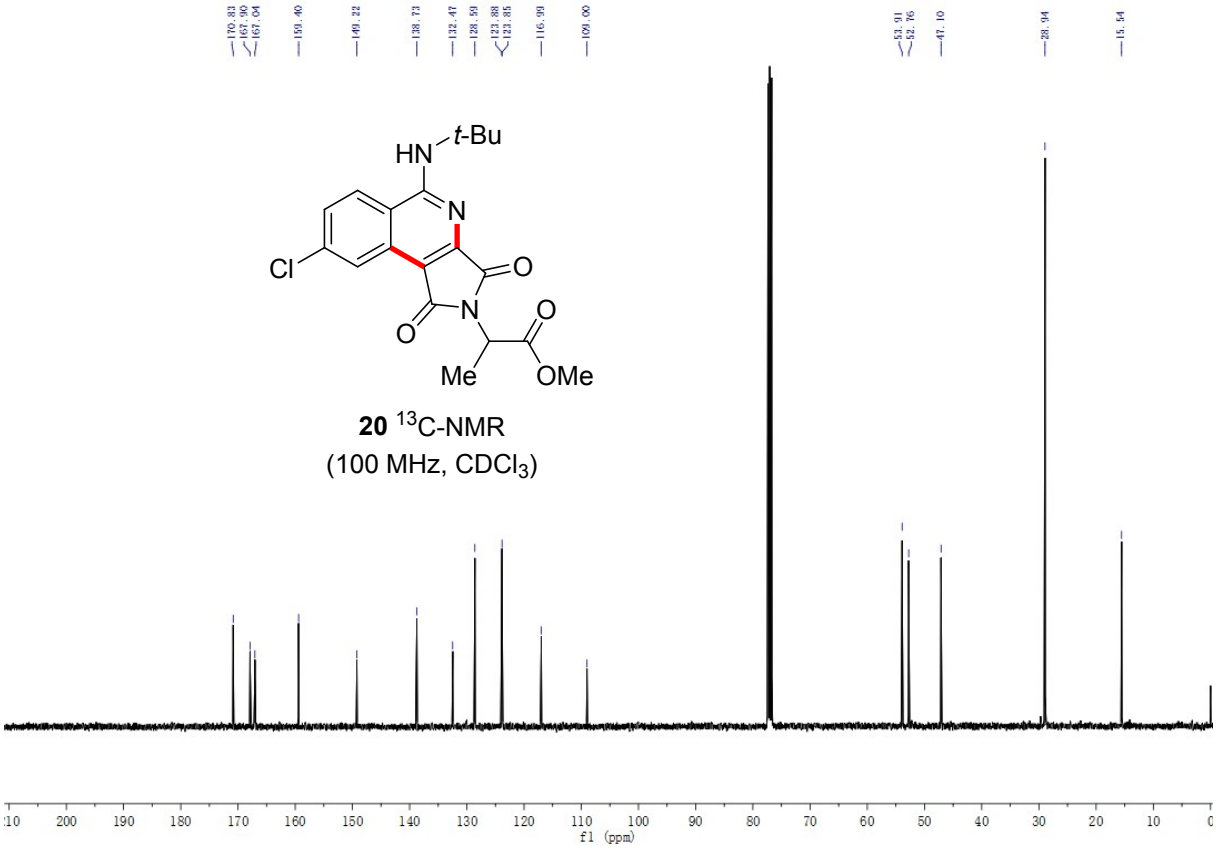
19 ^{1}H-NMR
(400 MHz, $CDCl_3$)



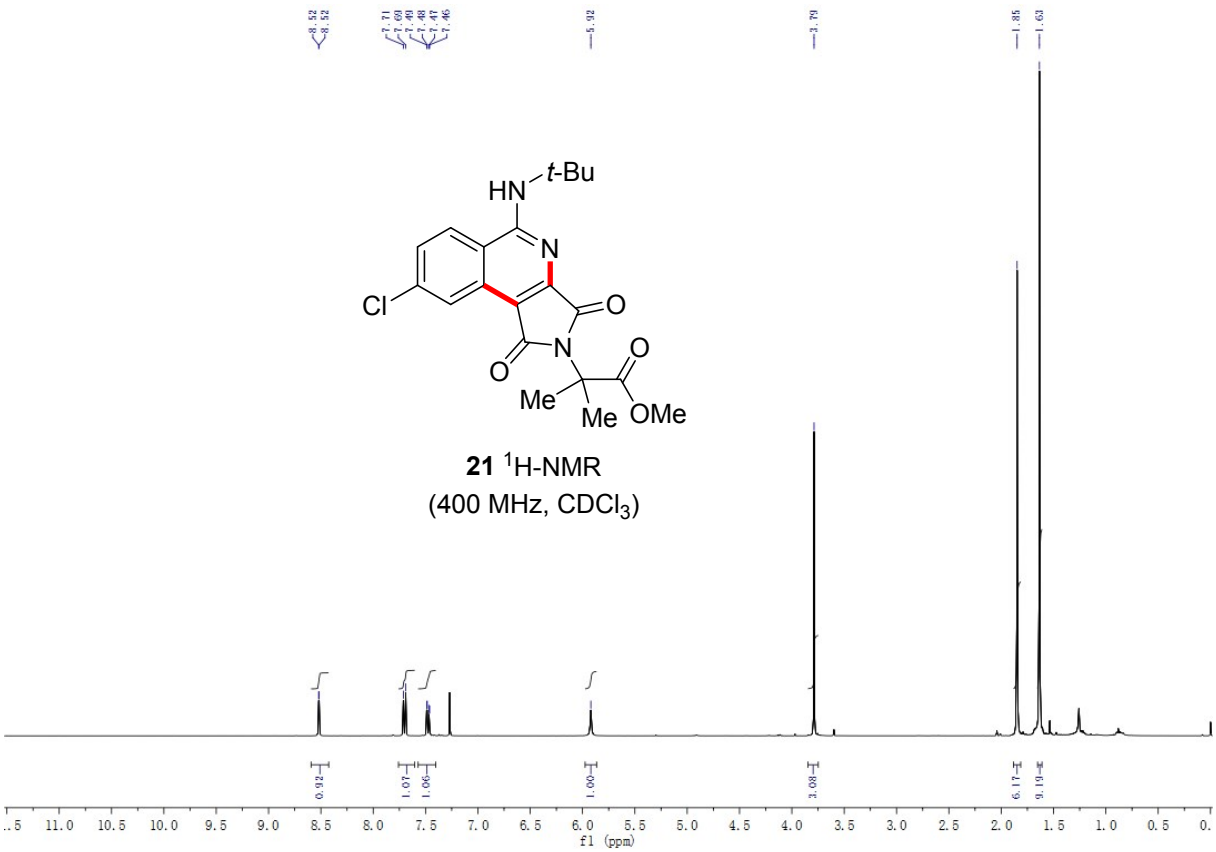
19 ^{13}C-NMR
(100 MHz, $CDCl_3$)



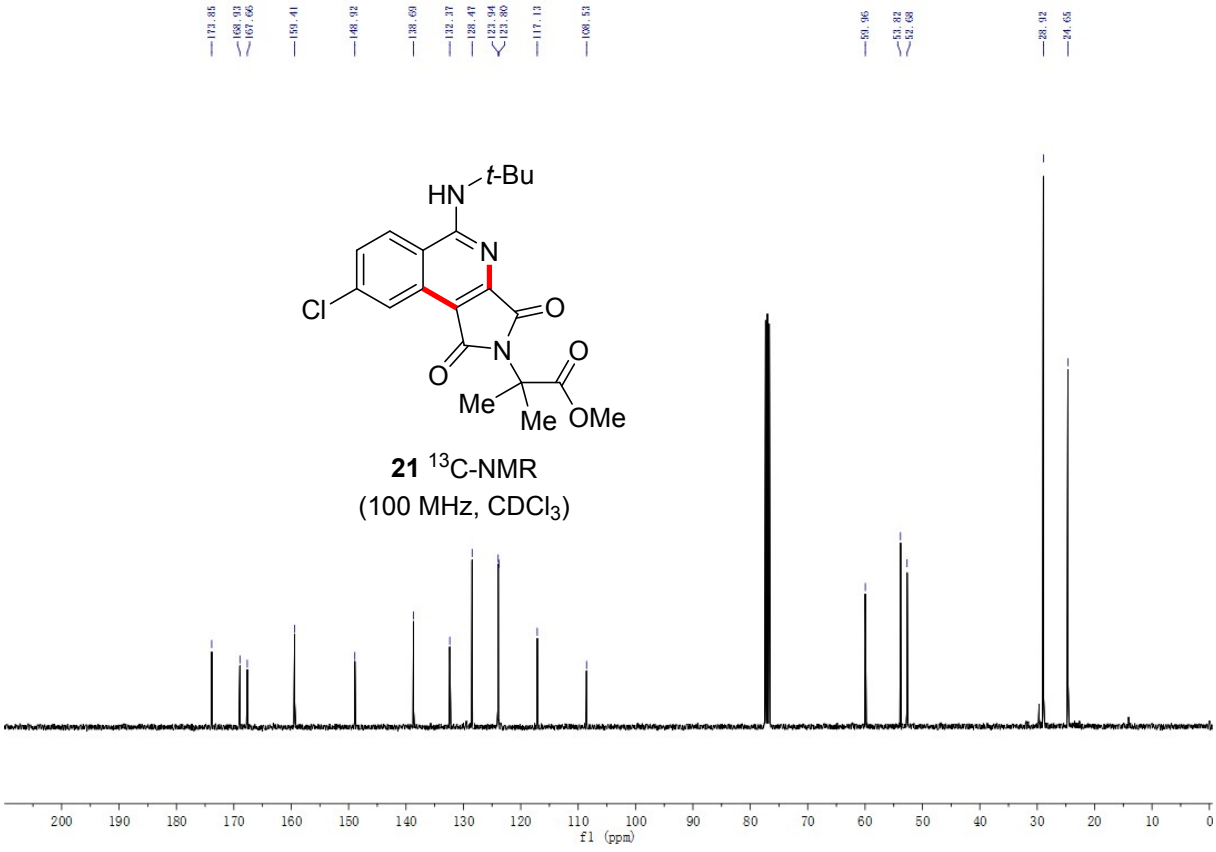
20 ^{1}H-NMR
(400 MHz, $CDCl_3$)



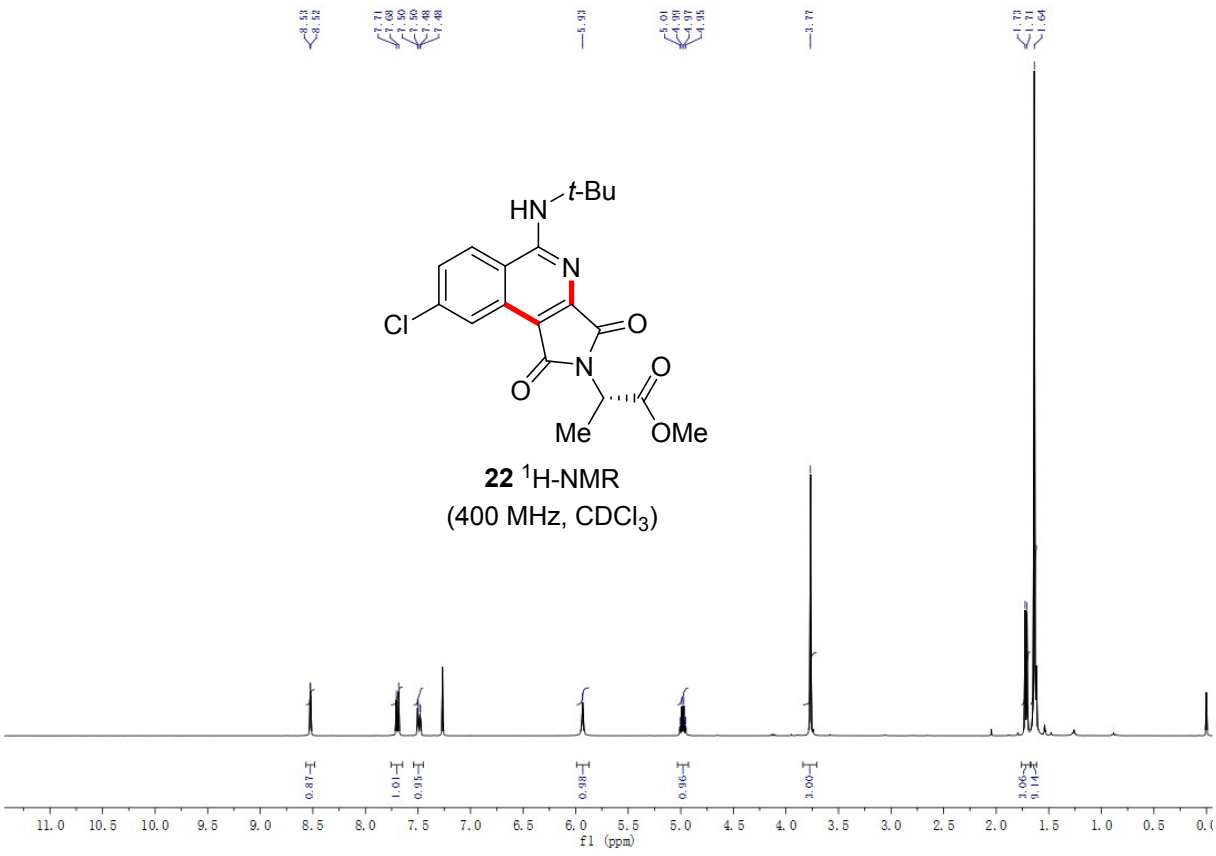
20 ^{13}C-NMR
(100 MHz, $CDCl_3$)



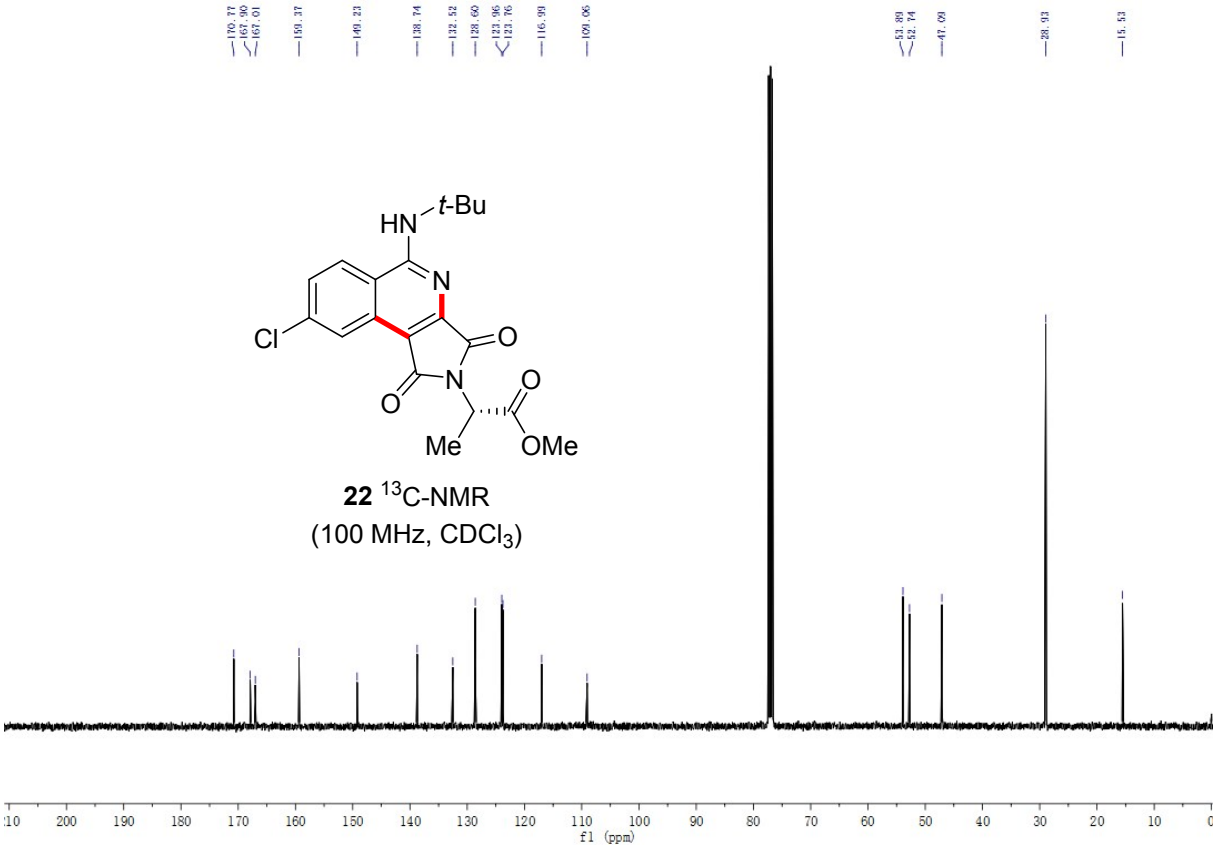
21 ^{1}H-NMR
(400 MHz, $CDCl_3$)



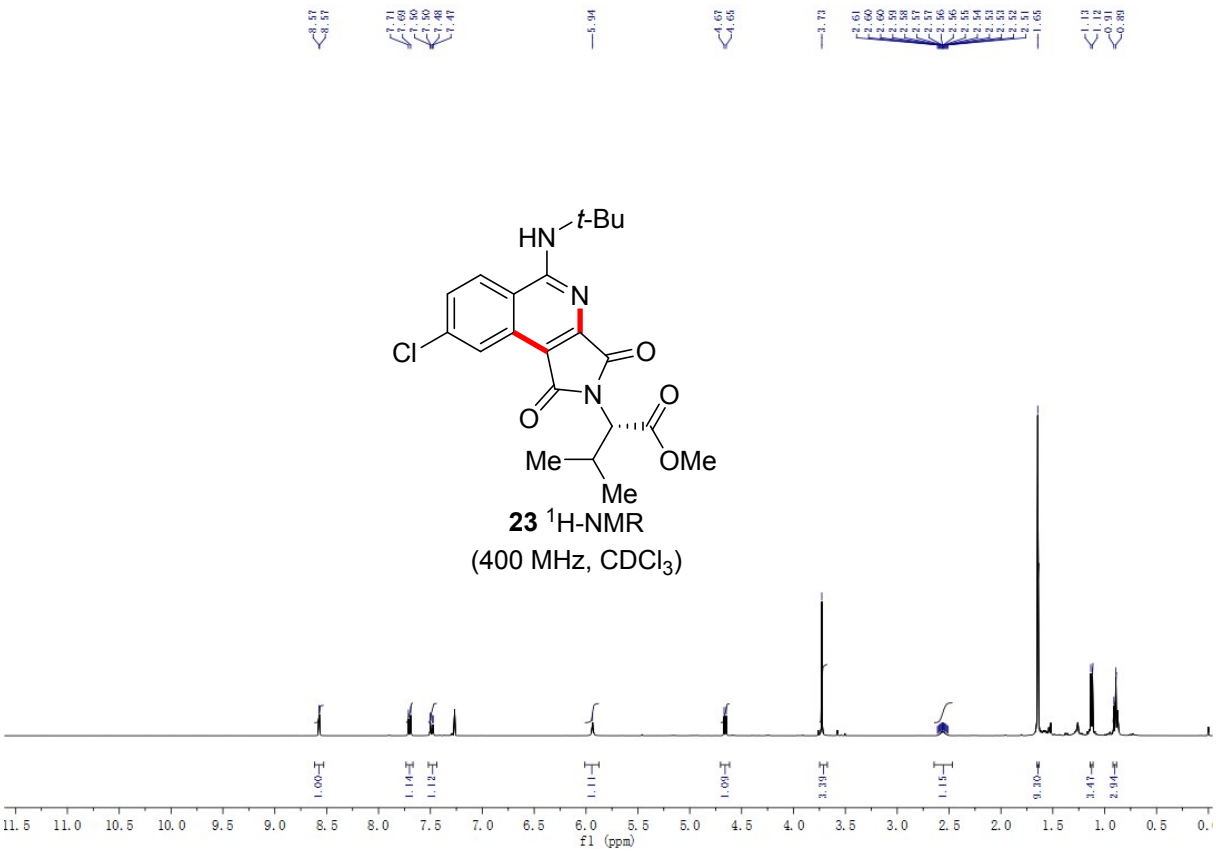
21 ^{13}C-NMR
(100 MHz, $CDCl_3$)



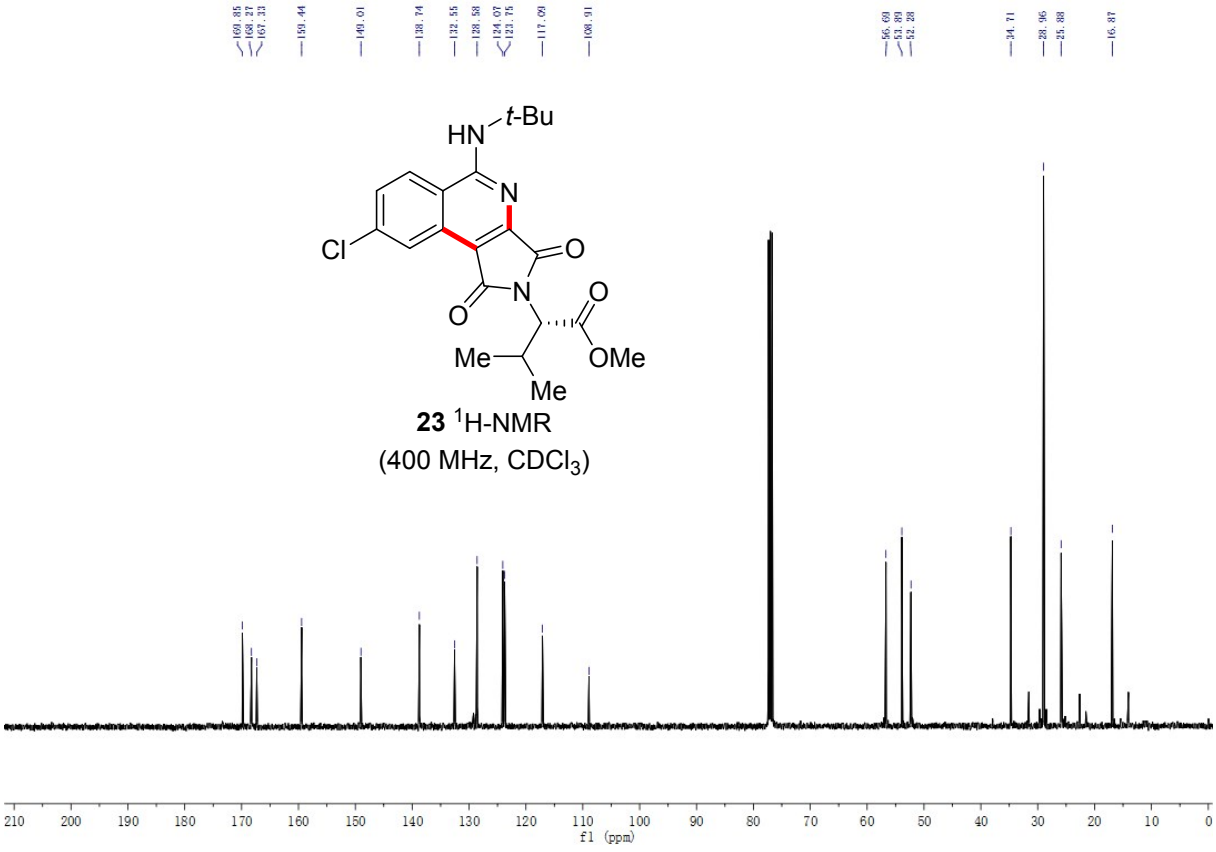
22 ^{1}H-NMR
(400 MHz, $CDCl_3$)



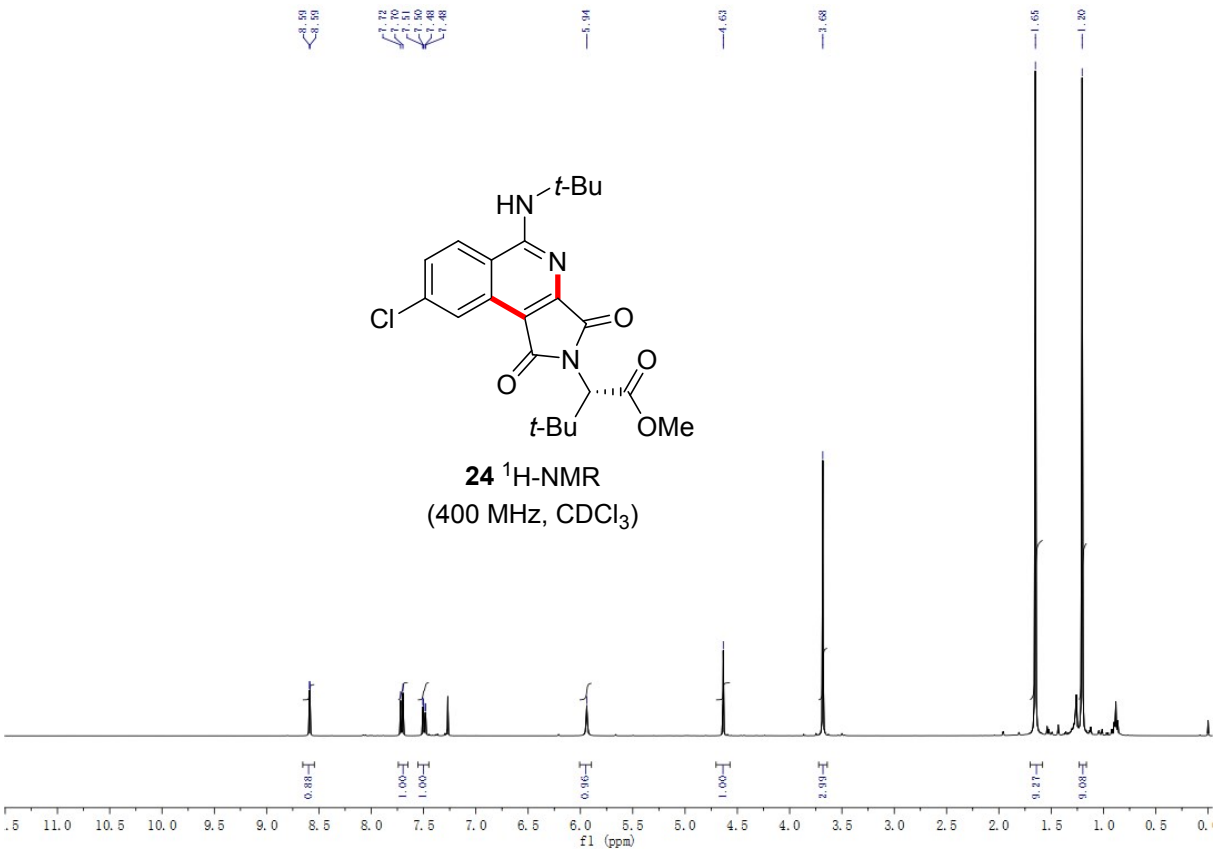
22 ^{13}C-NMR
(100 MHz, $CDCl_3$)



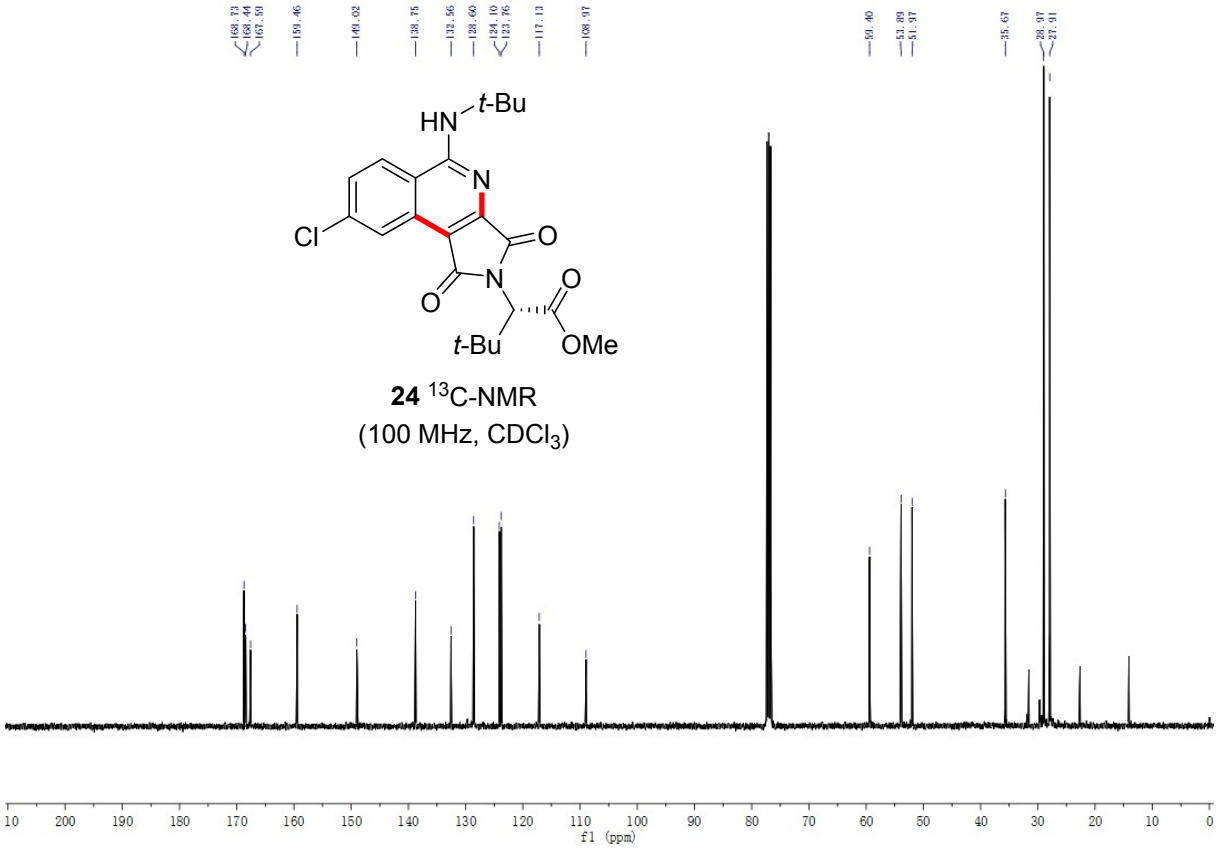
23 ^{1}H-NMR
(400 MHz, $CDCl_3$)



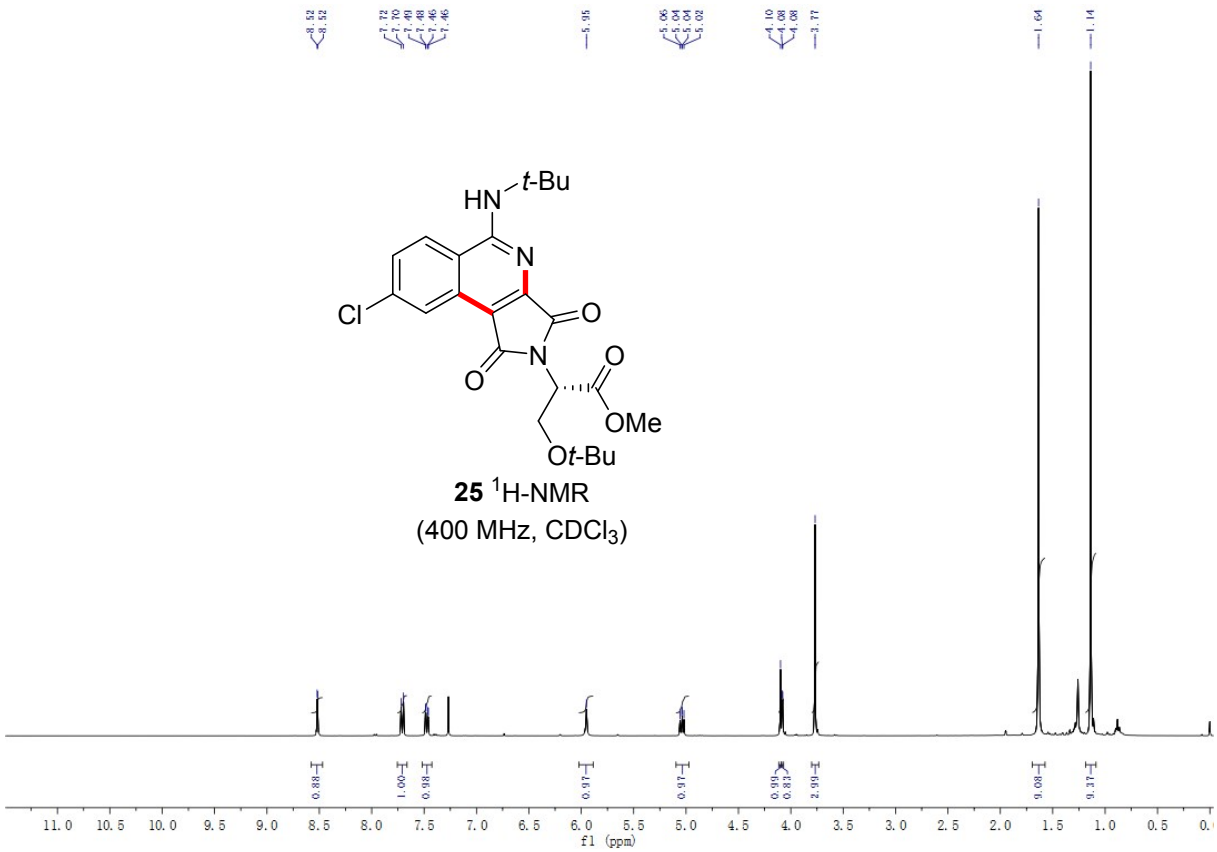
23 ^{1}H-NMR
(400 MHz, $CDCl_3$)



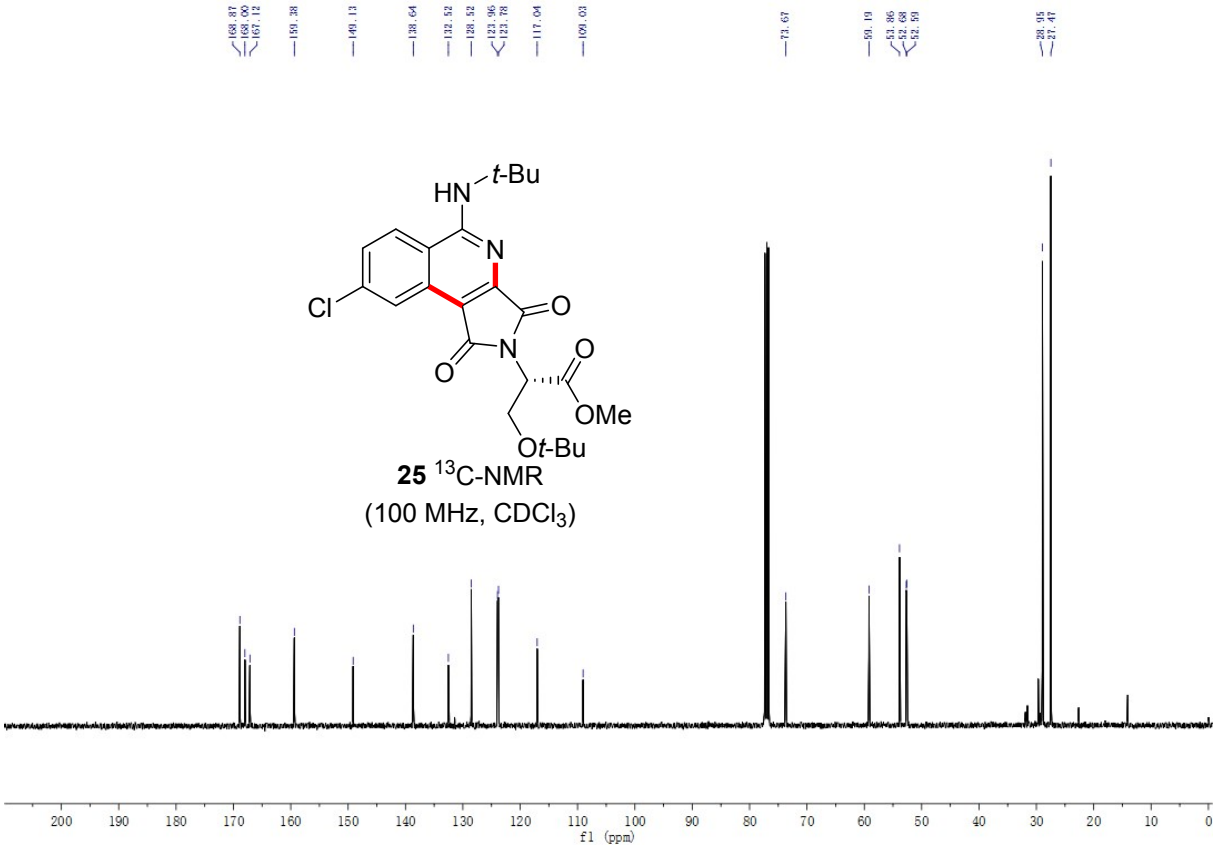
24 ^{1}H-NMR
(400 MHz, $CDCl_3$)



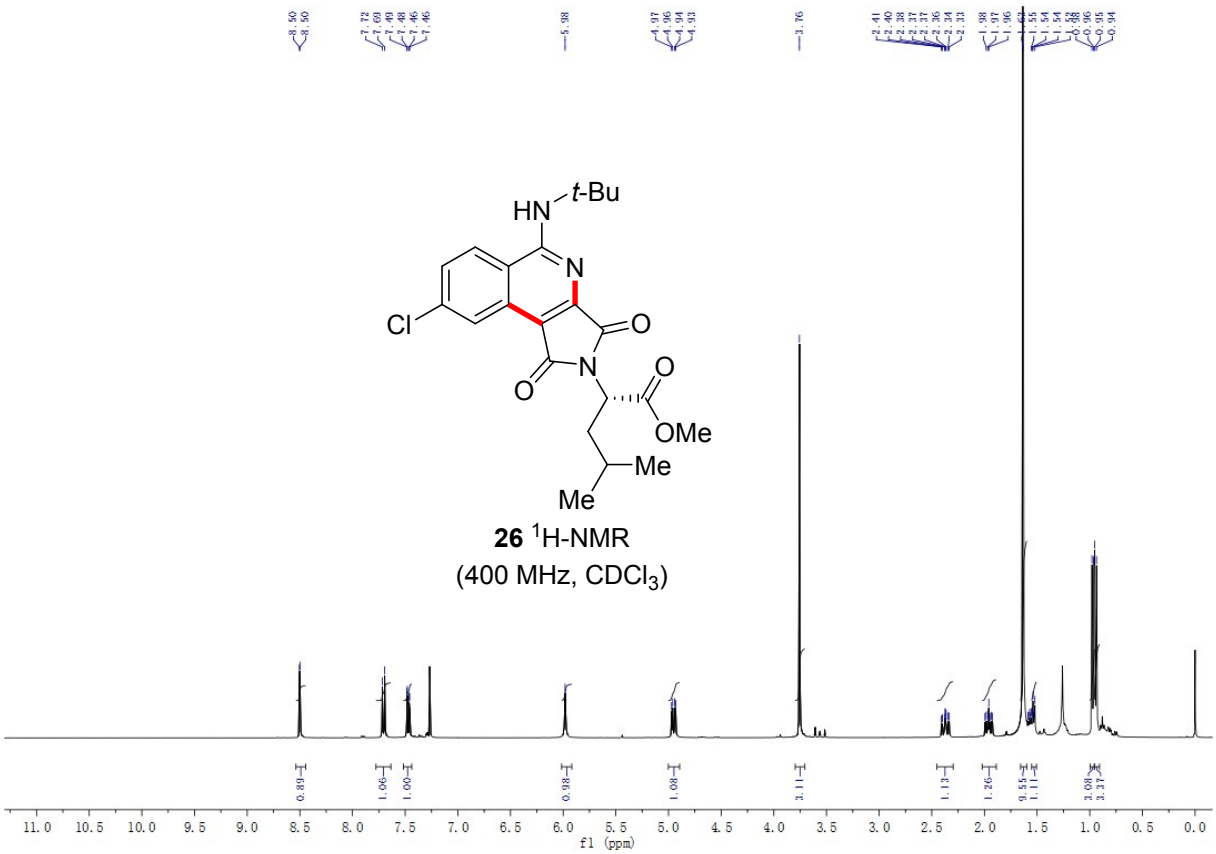
24 ^{13}C-NMR
(100 MHz, $CDCl_3$)



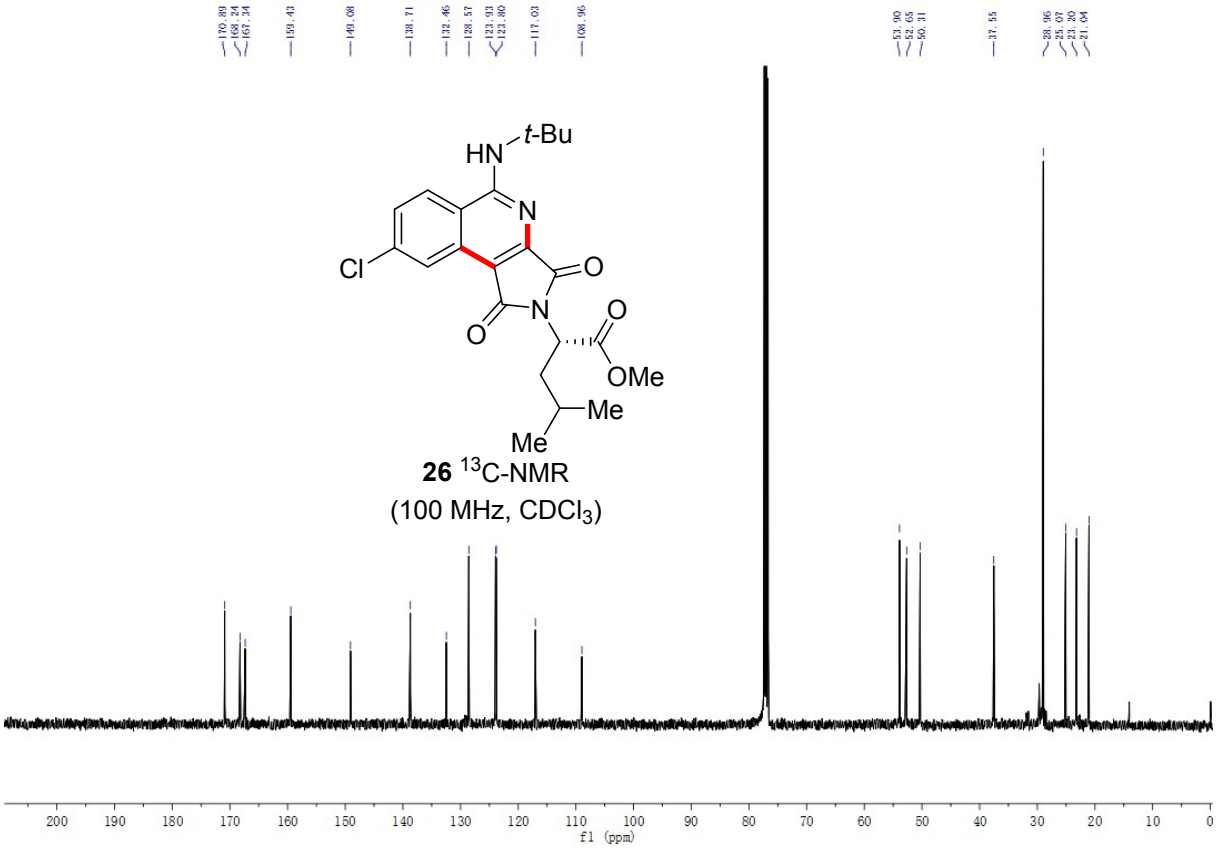
25 ^{1}H-NMR
(400 MHz, $CDCl_3$)



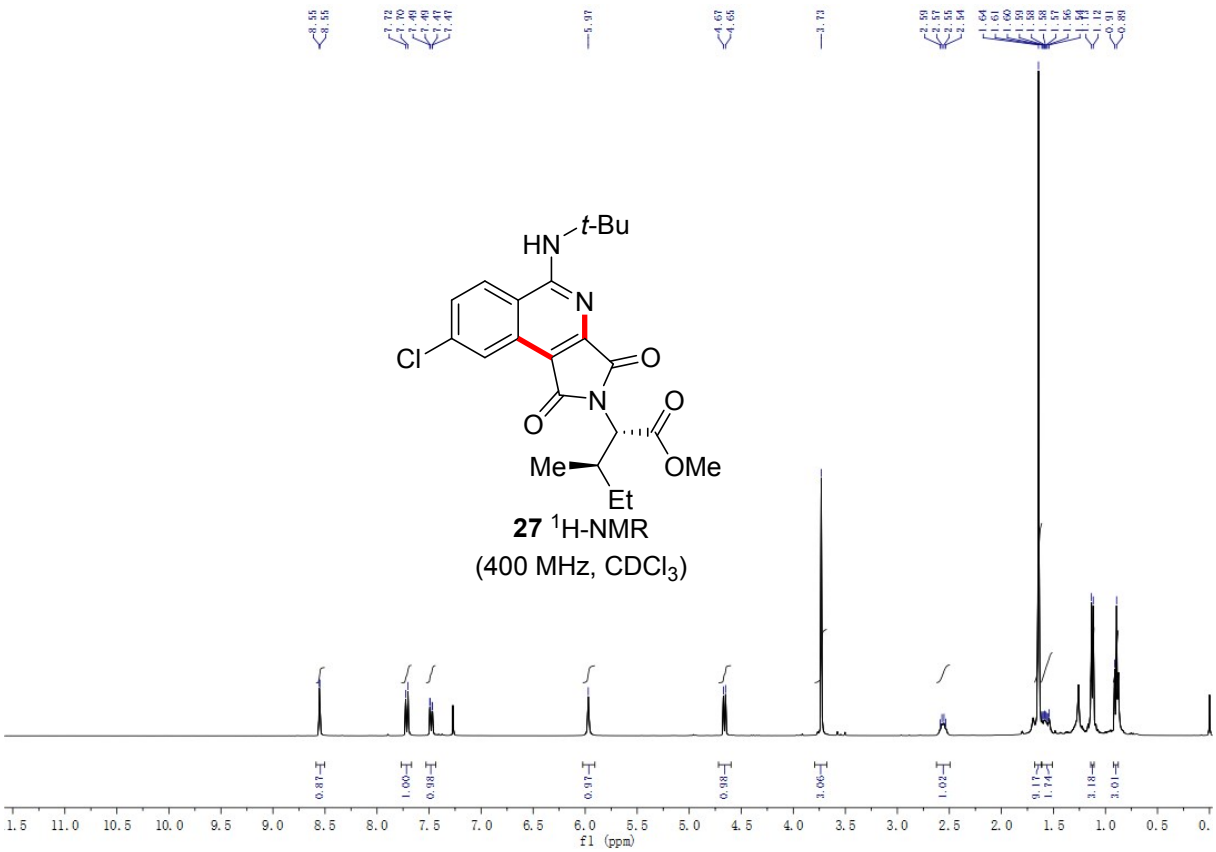
25 ^{13}C-NMR
(100 MHz, $CDCl_3$)



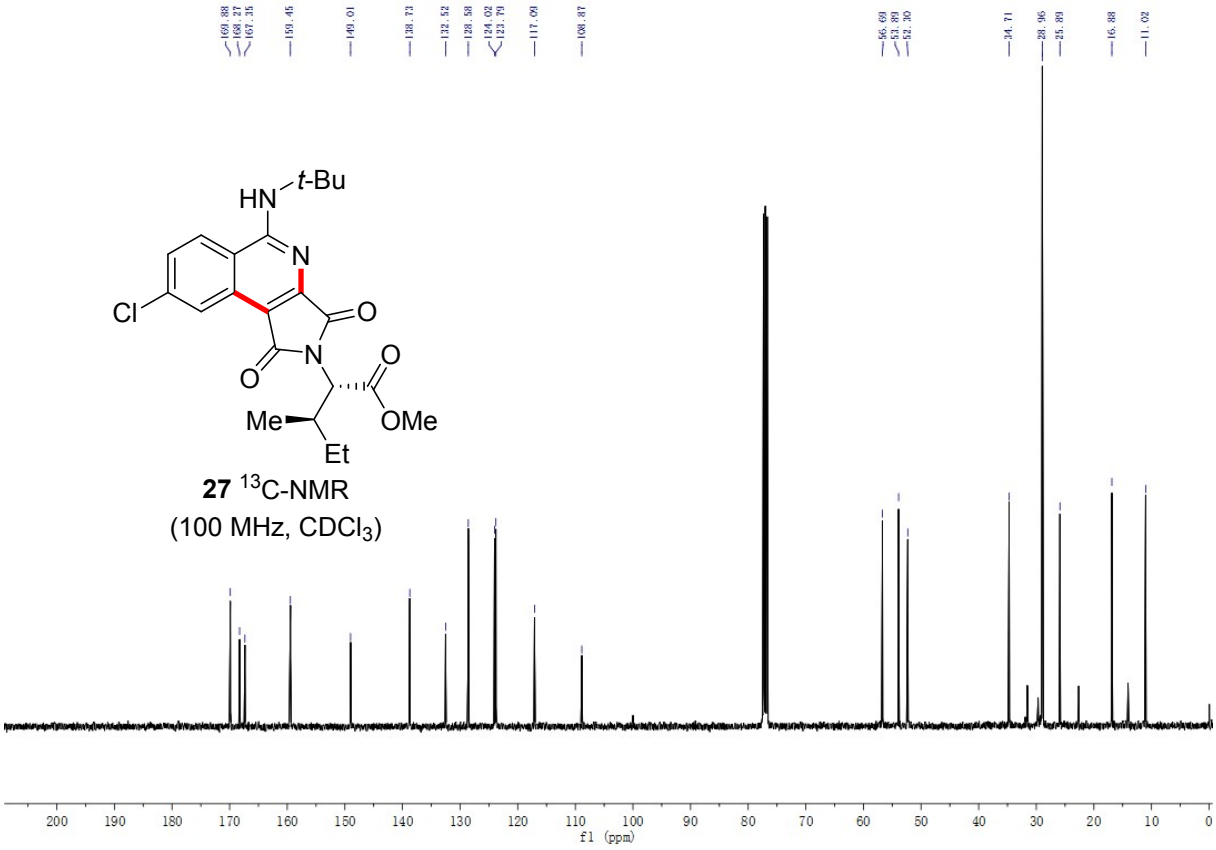
26 ^{1}H-NMR
(400 MHz, $CDCl_3$)



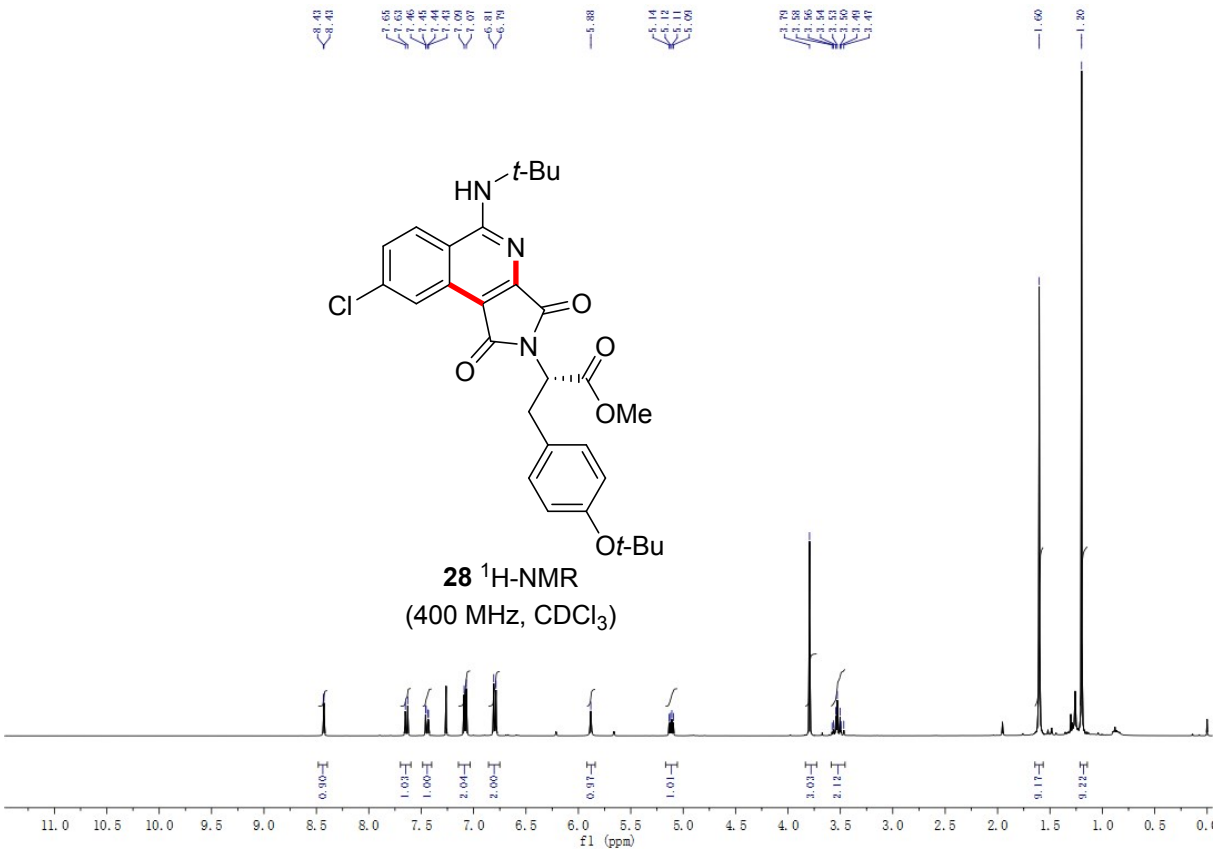
26 ^{13}C-NMR
(100 MHz, $CDCl_3$)



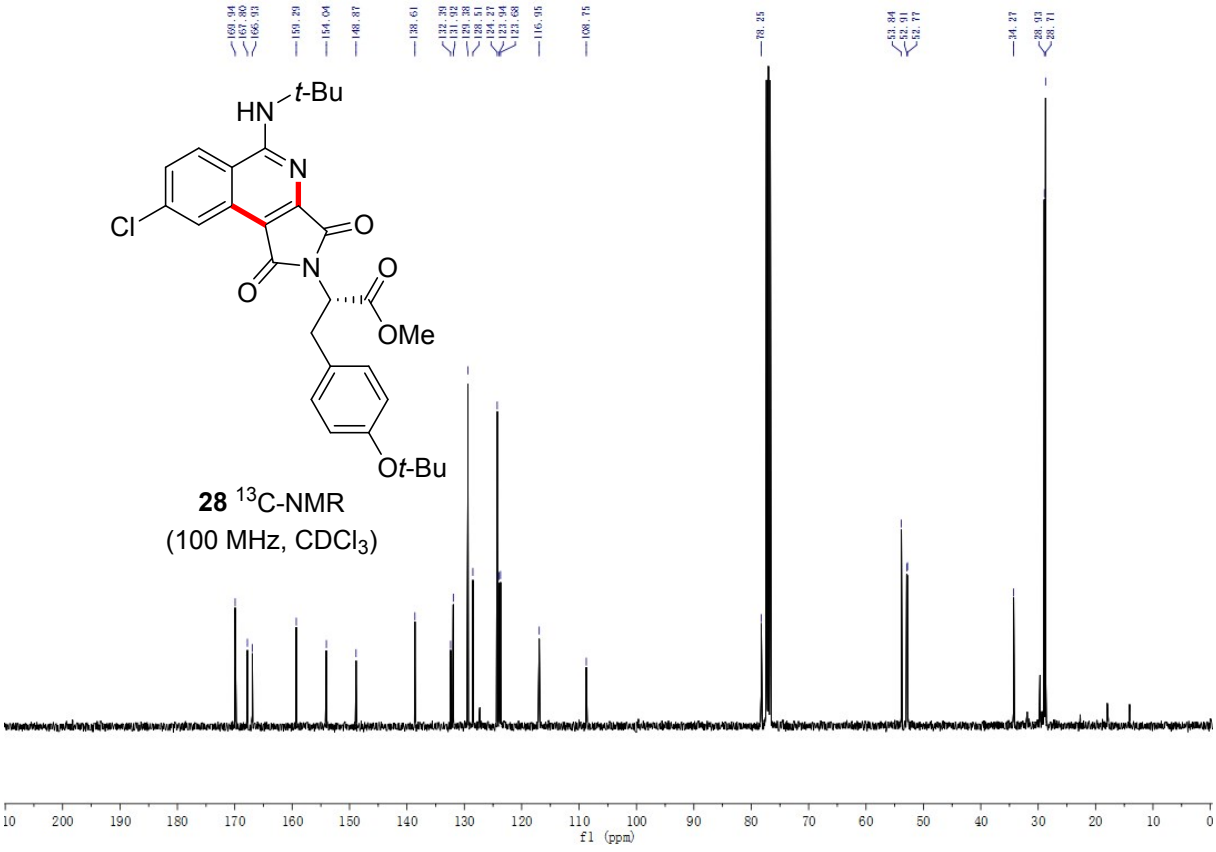
27 ^{1}H-NMR
(400 MHz, $CDCl_3$)



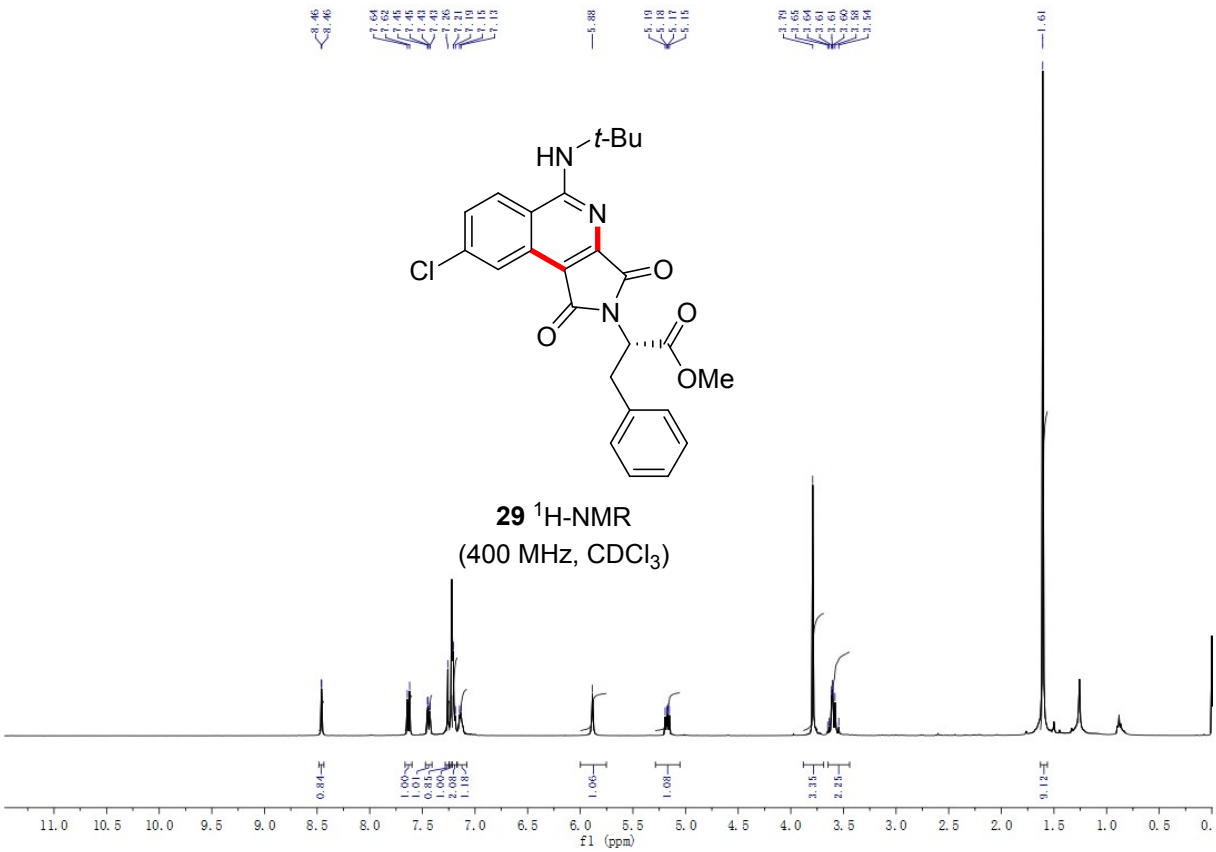
27 ^{13}C-NMR
(100 MHz, $CDCl_3$)



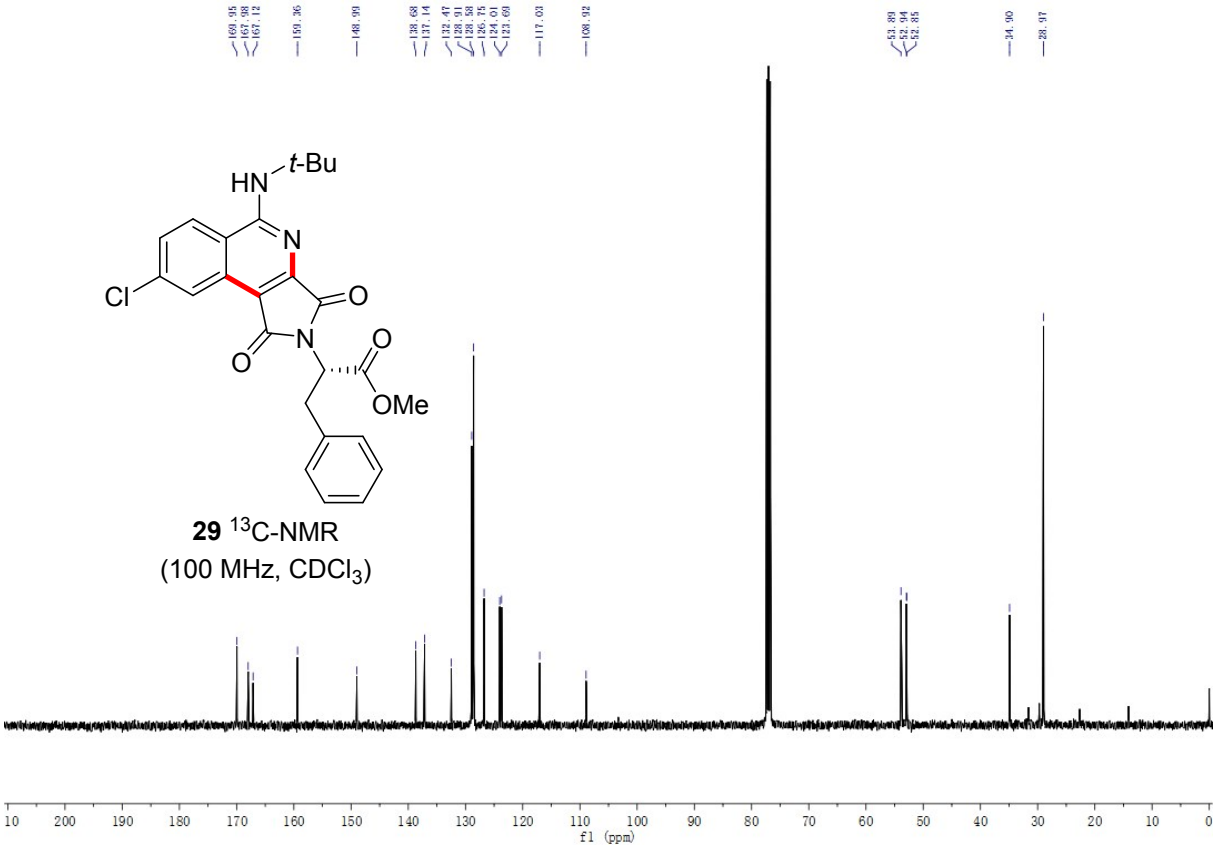
28 ^{1}H-NMR
(400 MHz, $CDCl_3$)



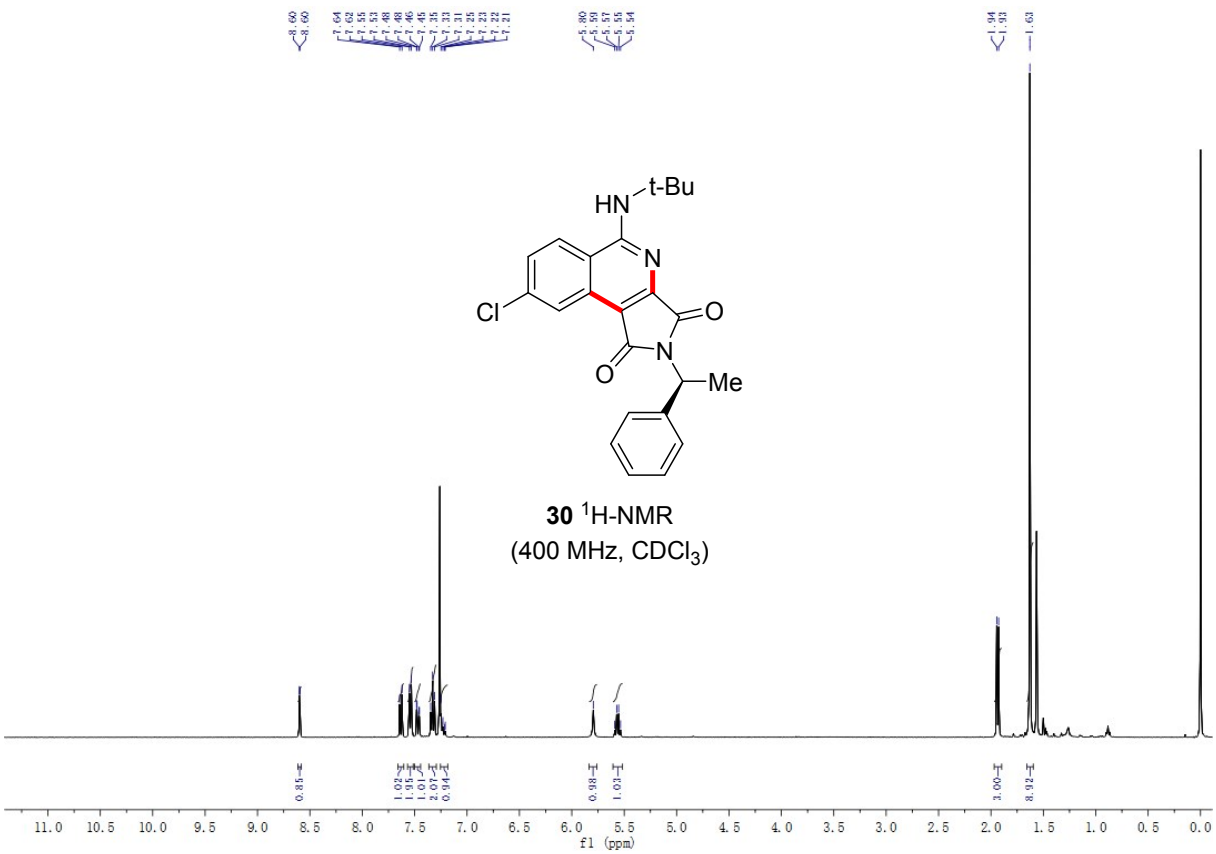
28 ^{13}C-NMR
(100 MHz, $CDCl_3$)



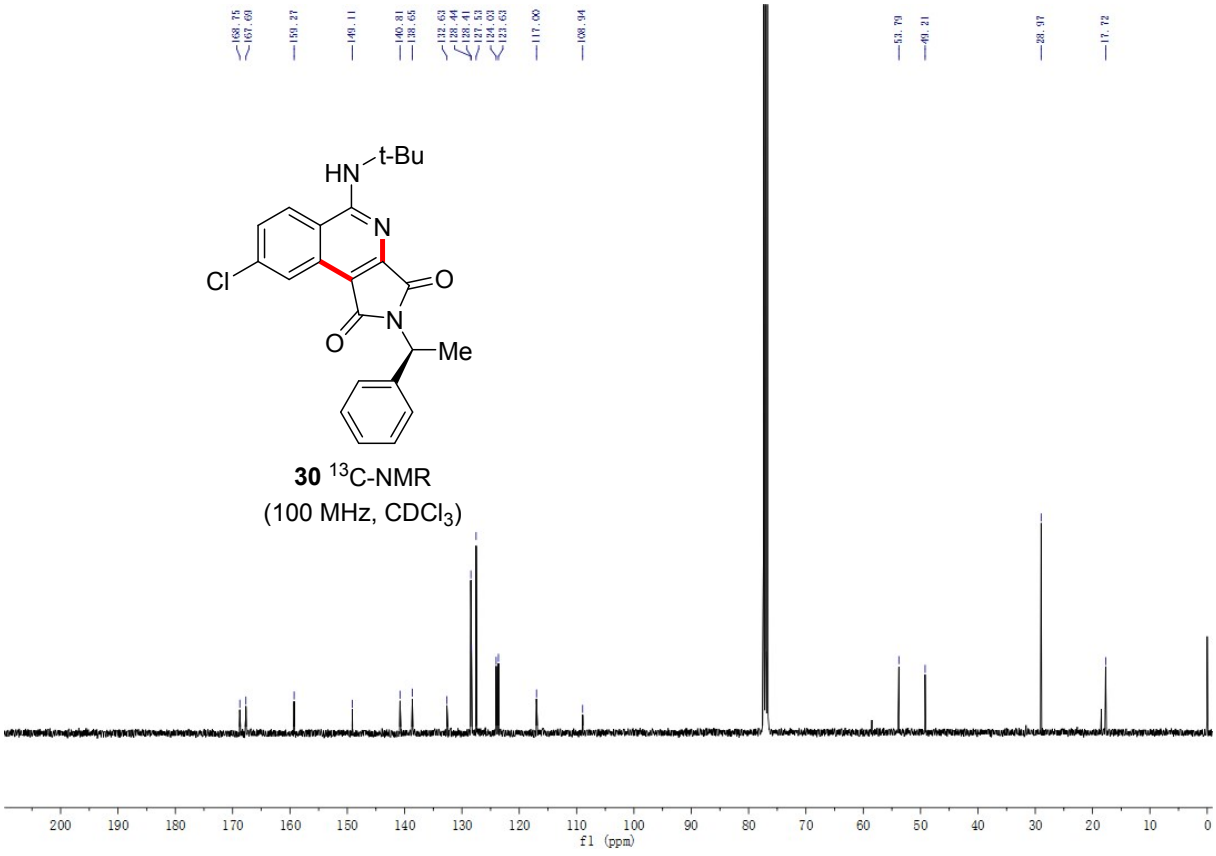
29 ^{1}H-NMR
(400 MHz, $CDCl_3$)



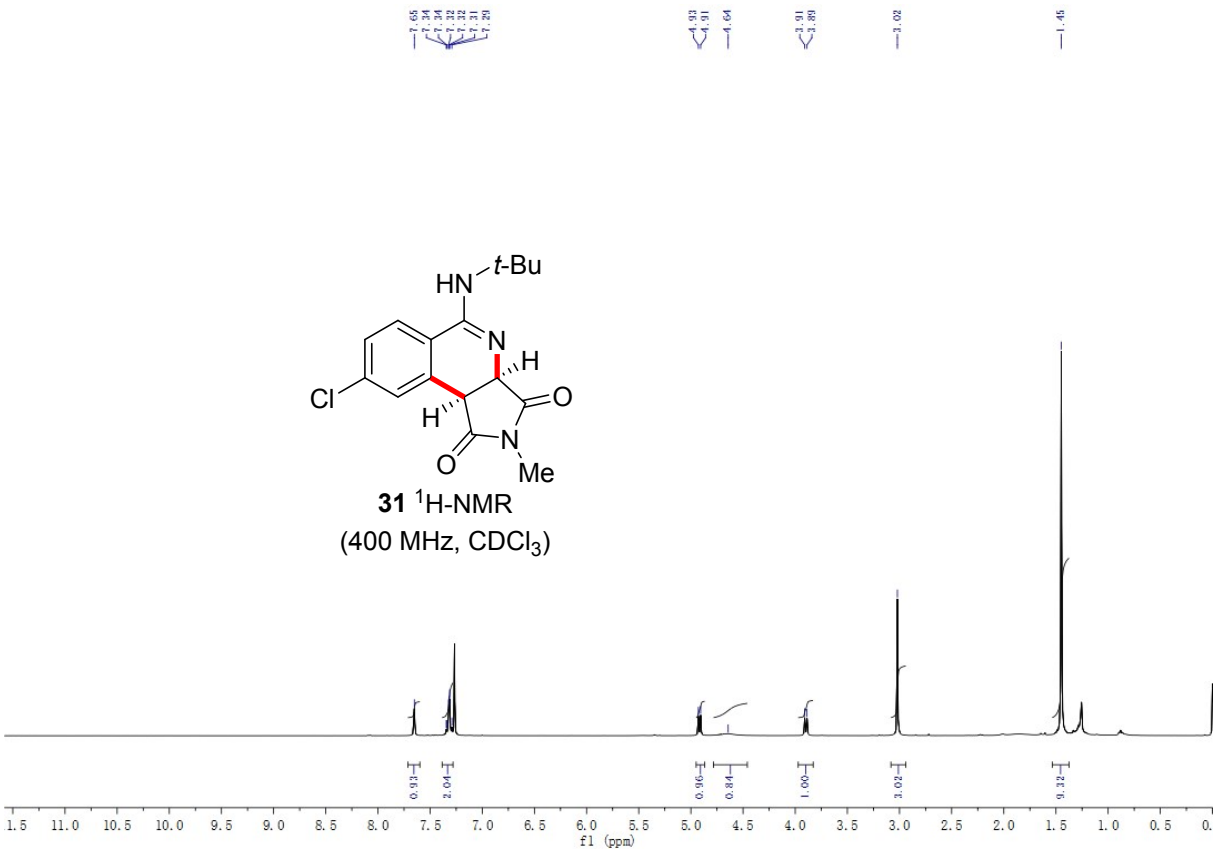
29 ^{13}C-NMR
(100 MHz, $CDCl_3$)



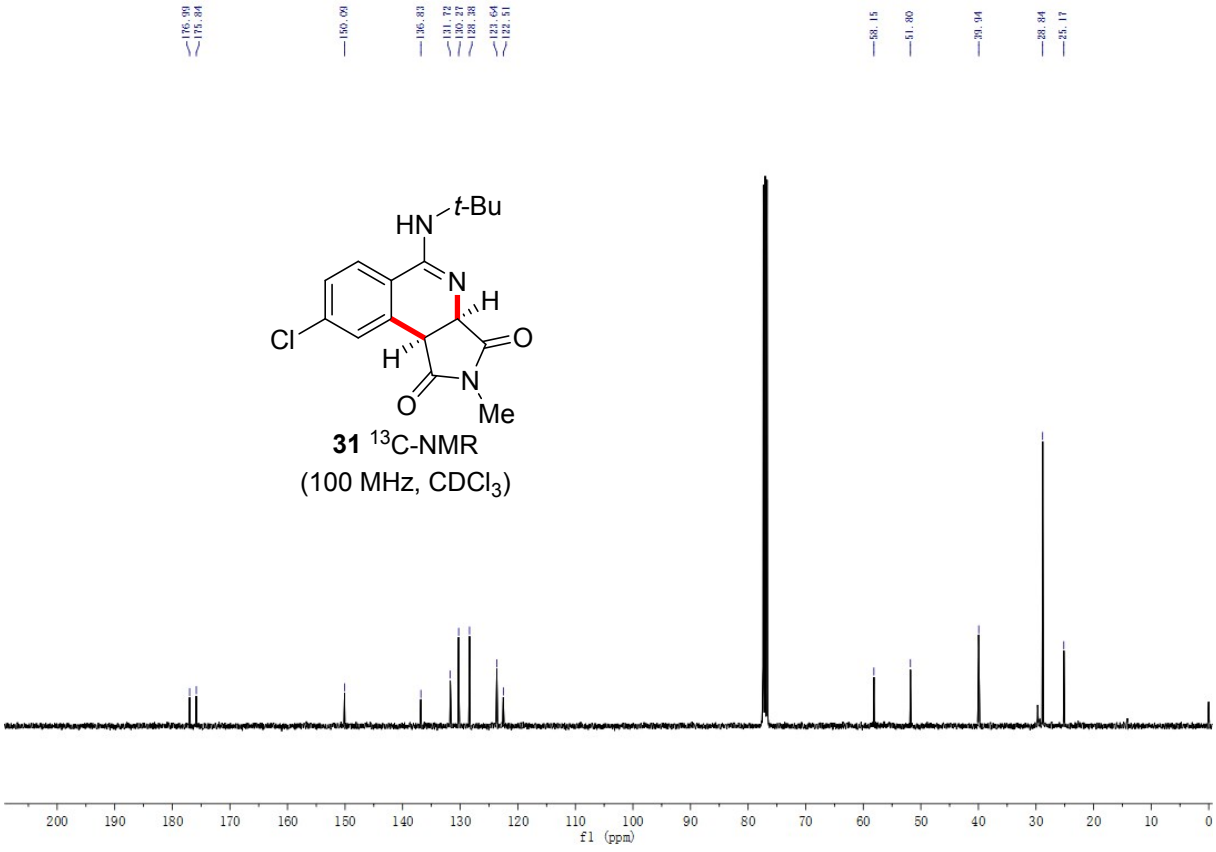
30 ^{1}H-NMR
(400 MHz, $CDCl_3$)



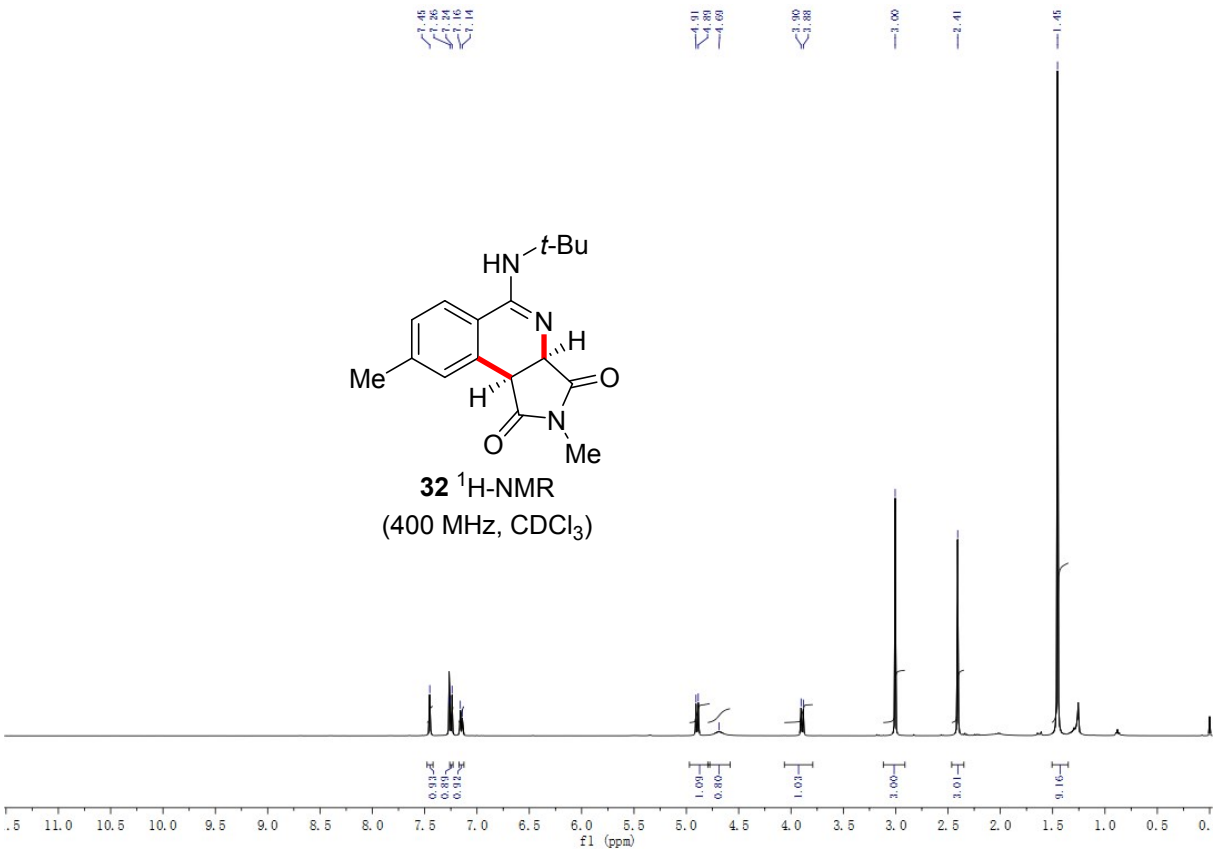
30 ^{13}C-NMR
(100 MHz, $CDCl_3$)



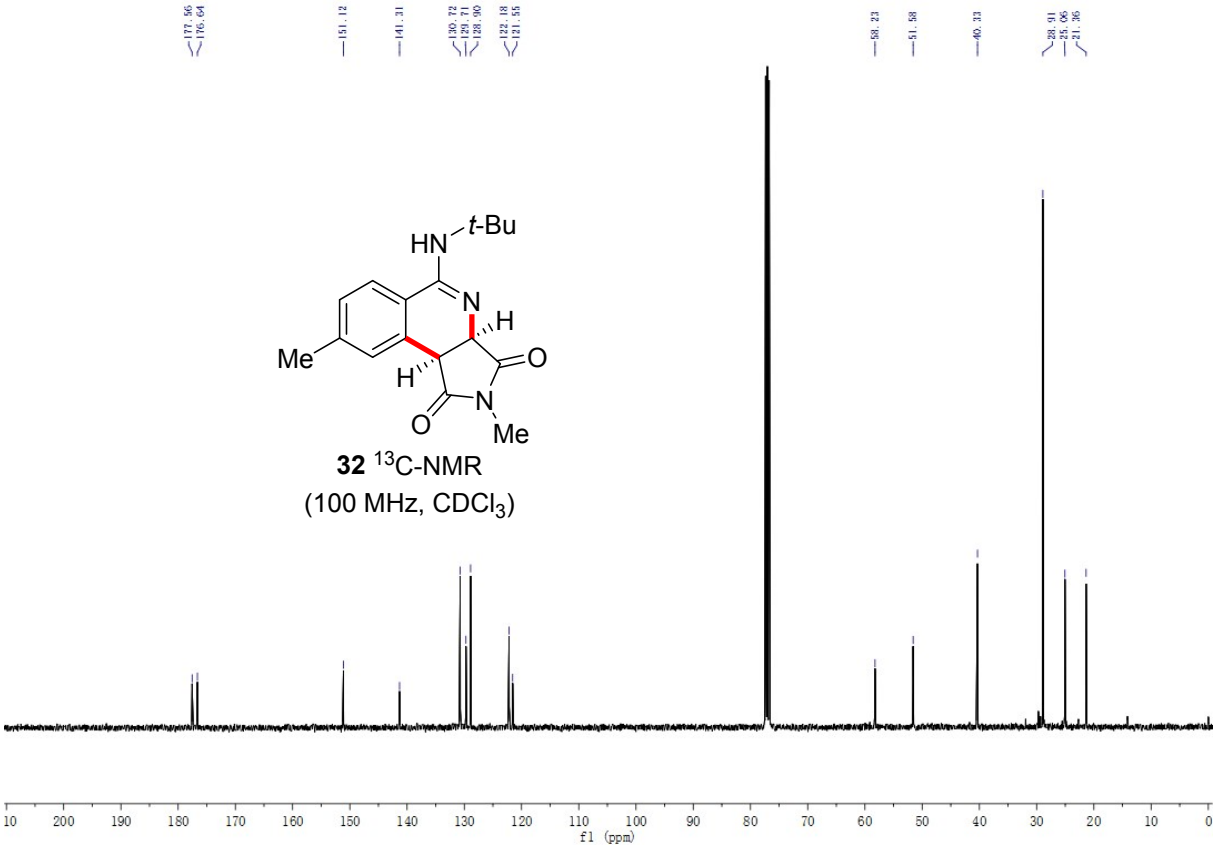
31 ^{1}H-NMR
(400 MHz, $CDCl_3$)



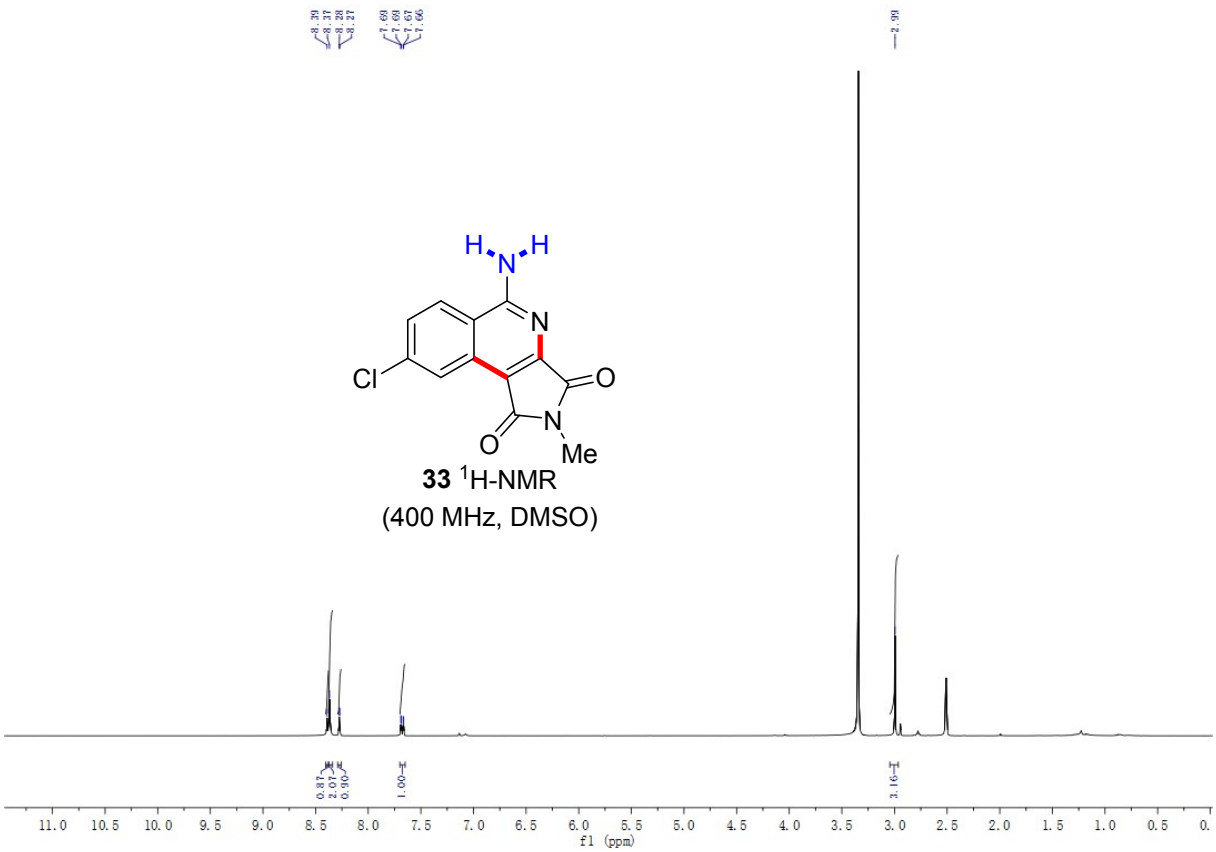
31 ^{13}C-NMR
(100 MHz, $CDCl_3$)



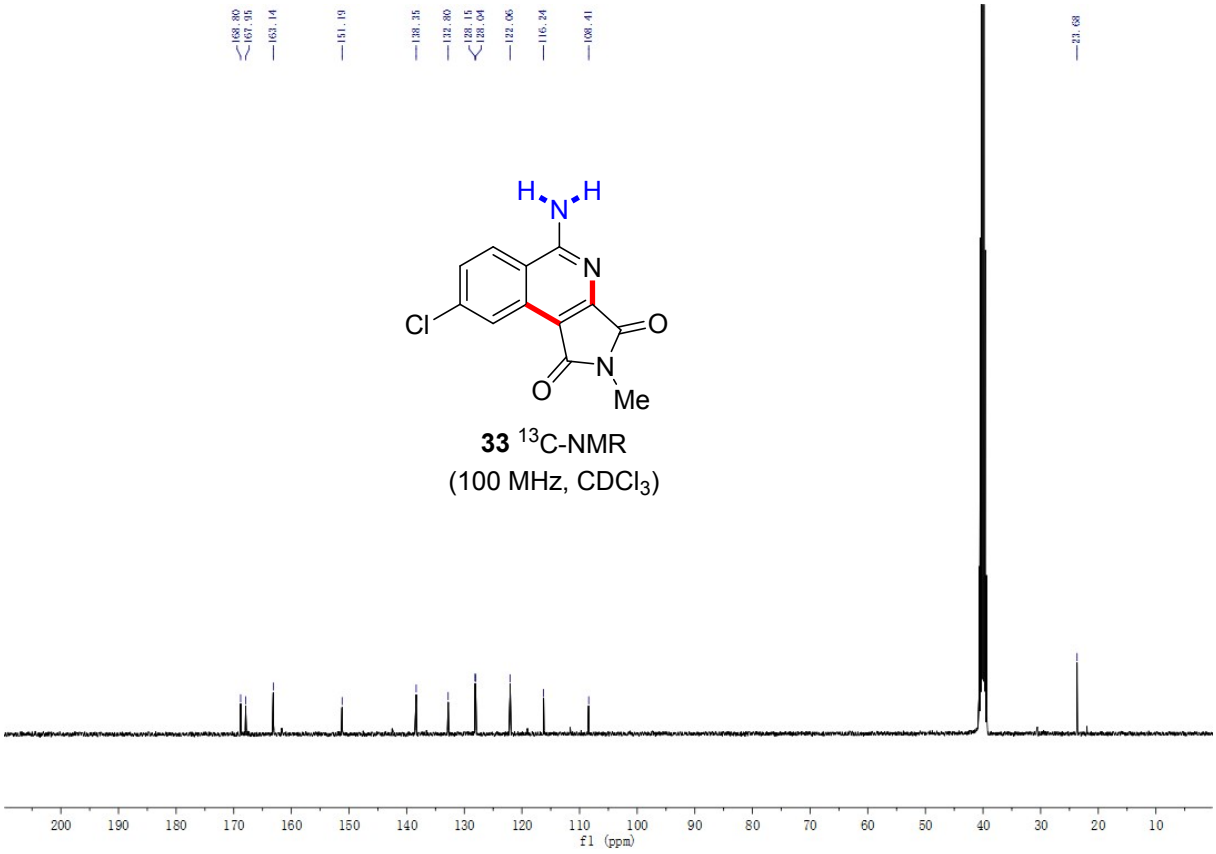
32 ^{1}H-NMR
(400 MHz, $CDCl_3$)



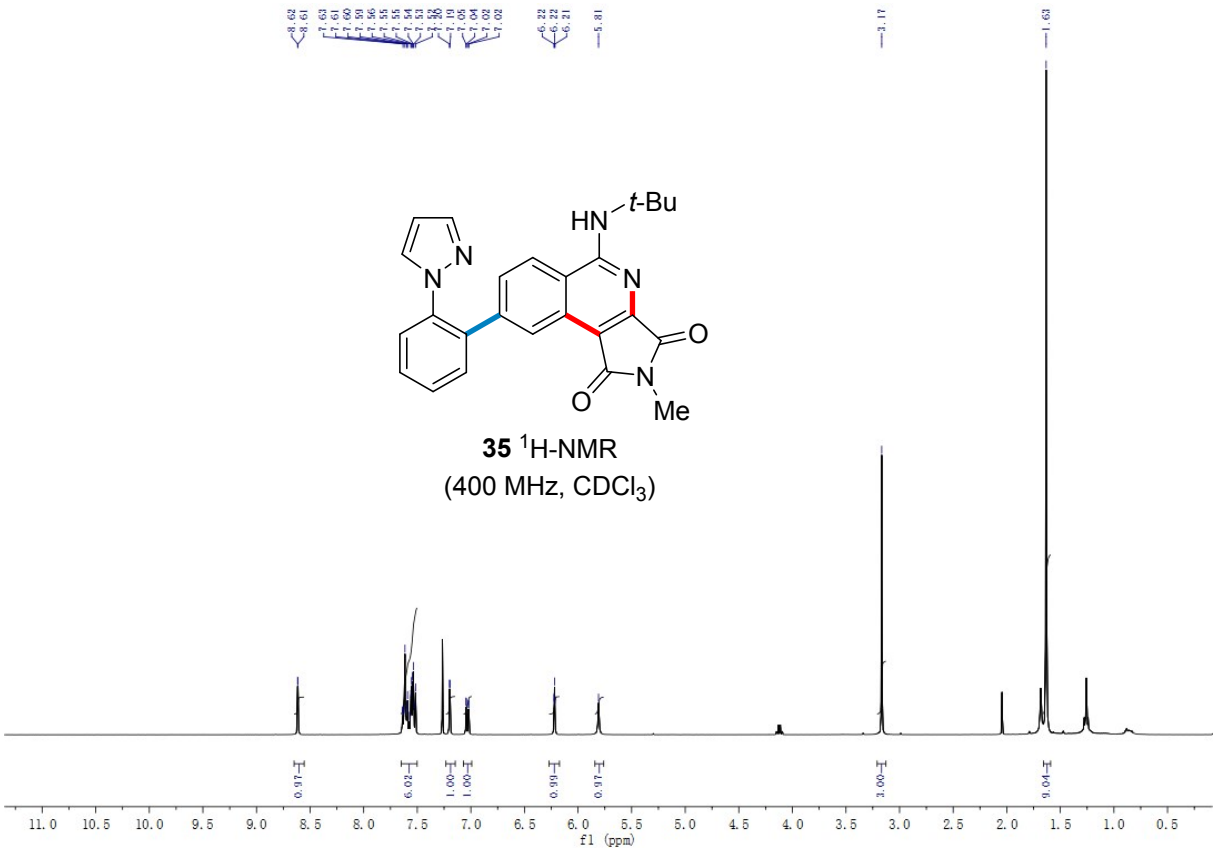
32 ^{13}C-NMR
(100 MHz, $CDCl_3$)



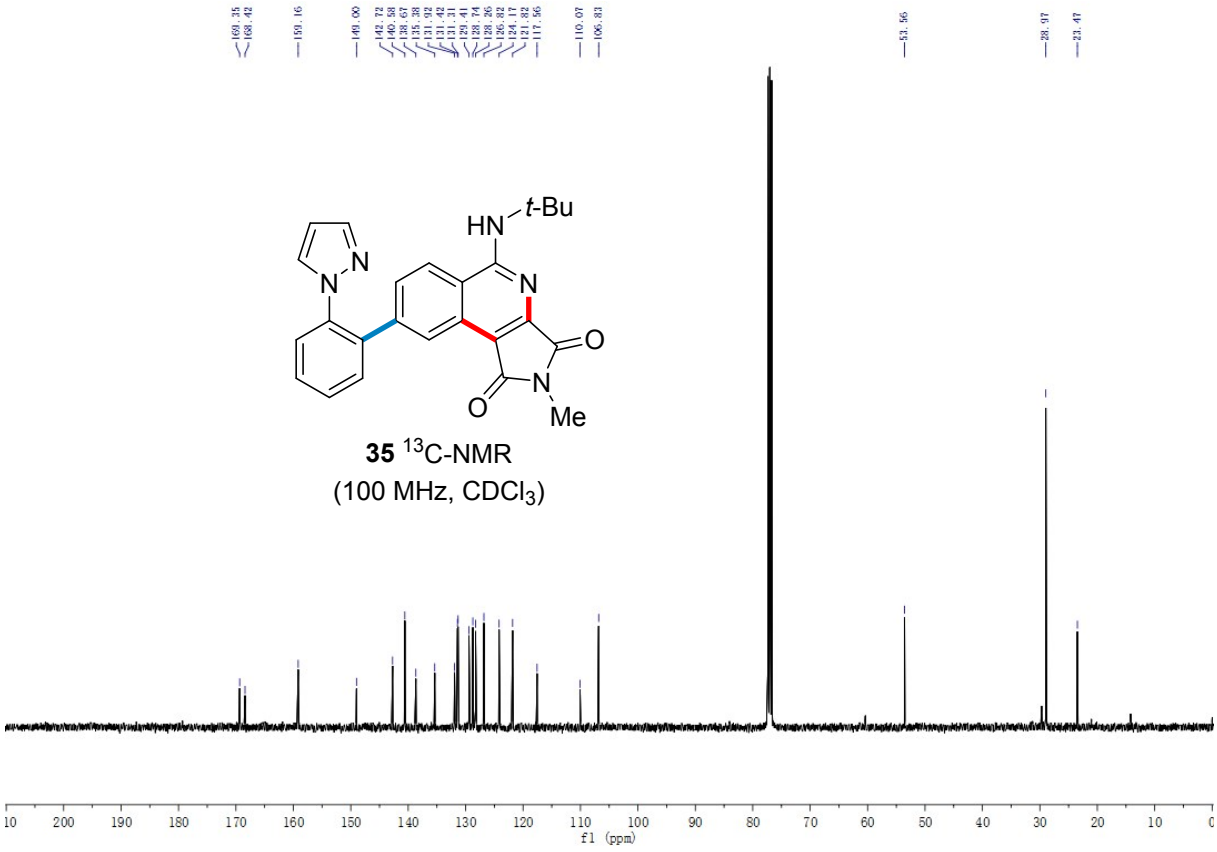
33 ^{1}H-NMR
(400 MHz, DMSO)



33 ^{13}C-NMR
(100 MHz, $CDCl_3$)



35 ^{1}H-NMR
(400 MHz, $CDCl_3$)



35 ^{13}C-NMR
(100 MHz, $CDCl_3$)