Supporting Information

Direct Functionalization of Cyclic Ethers with Maleimide Iodides via Free Radial Mediated sp^3 C-H Activation

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Materials and Methods

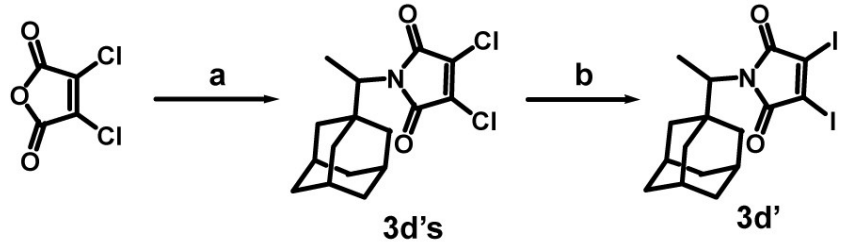
Materials

Unless otherwise noted, all reagents were purchased from commercial sources and used without further purification. Tetrahydrofuran (THF) were dried over calcium hydride (CaH_2) and distilled before use.

Methods

^1H NMR and ^{13}C NMR spectra were recorded on Bruker DRX-400 and DRX-600 instruments and calibrated using residual undeuterated solvent ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.2 ppm) as the internal reference. High-resolution mass spectra (HR-MS) were obtained on a Micromass LCTTM mass spectrometer using the ESI or EI method.

Synthesis Section



Scheme S1. Synthesis of compound 3d': (a) Rimantadine hydrochloride, potassium acetate, acetic acid, 120°C, 13 h. (b) NaI, acetonitrile, 95°C, 30 h.

Synthesis of 1-(1-((3r,5r,7r)-adamantan-1-yl)ethyl)-3,4-dichloro-1*H*-pyrrole-2,5-dione (3d's): Dichloromaleic anhydride (10.3 g, 62 mmol) was dissolved in acetic acid (50 mL) with slow addition of rimantadine hydrohloride (12 g, 56 mmol); the solution was heated to reflux at 120°C for 13 h. After removal of solvent, the crude residue was separated by column chromatography on silica gel (hexane/ ethyl acetate = 50:1) to give the product 3d's (3.92 g, 22%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.88 (q, *J* = 7.4 Hz, 1H), 1.97 (s, 3H), 1.63 (dd, *J* = 47.0, 11.9 Hz, 6H), 1.56 – 1.47 (m, 6H), 1.38 (d, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.1, 133.3, 132.2, 58.7, 39.2, 37.5, 36.7, 28.2, 11.8.

Synthesis of 1-(1-((3r,5r,7r)-adamantan-1-yl)ethyl)-3,4-diiodo-1*H*-pyrrole-2,5-dione (3d'): A solution of sodium iodide (10.8 g, 72 mmol) and 1-(1-((3r,5r,7r)-adamantan-1-yl)ethyl)-3,4-dichloro-1*H*-pyrrole-2,5-dione (3.92 g, 12 mmol) in acetonitrile (70 mL) was heated at 95°C for 30 h. After removal of solvent, the crude residue was separated by column chromatography on silica gel (hexane/ ethyl acetate = 50:1) to give the yellow product 3d (4.24 g, 70%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.84 (dd, *J* = 14.7, 7.3 Hz, 1H), 1.91 (s, 3H), 1.56 (dd, *J* = 41.2, 10.5 Hz, 5H), 1.51 – 1.42 (m, 7H), 1.32 (d, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.2, 166.5, 118.6, 116.3, 58.9, 39.1, 37.4, 36.5, 28.1, 11.5. HRMS (EI) *m/z*: $[M]^+$ calcd for $C_{16}H_{19}I_2NO_2$ 510.9505; found 510.9503.

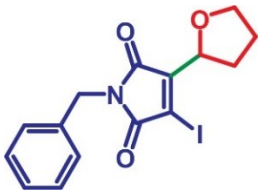
Procedure and characterization for direct C-H activation of maleimide iodides with cyclic ethers

General procedure:

1-benzyl-3,4-diiodo-1H-pyrrole-2,5-dione (**1a**, 65.85 mg, 0.15 mmol), *tert*-butyl peroxy-2-ethylhexanoate (TBPO, 0.13 mL, 0.75 mmol) and Na_2CO_3 (47.70 mg, 0.45 mmol) were added in THF (**2a**, 2.5 mL, excess, as well as solvent) in a sealed tube. The mixture was stirred in an oil bath at 70 ℃ for 24 h. After removal of the solvent under vacuum, the crude product was purified by column chromatography on silica gel (hexane/ ethyl acetate = 8:1) to give compound **3a** as a yellow oil (34.5 mg, 60 %).

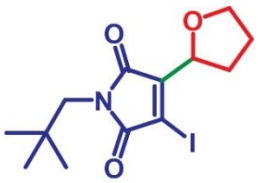
Product Characterization

1-benzyl-3-iodo-4-(tetrahydrofuran-2-yl)-1*H*-pyrrole-2,5-dione (3a):



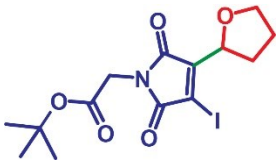
Yellow oil, 60 % (34.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.16 (m, 5H), 4.80 (t, J = 7.5 Hz, 1H), 4.62 (s, 2H), 4.05 (dd, J = 14.6, 7.5 Hz, 1H), 3.87 (td, J = 7.9, 5.1 Hz, 1H), 2.29 – 1.85 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 166.0, 150.9, 135.8, 128.7, 128.0, 102.0, 74.8, 69.6, 42.5, 31.5, 26.8. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{15}H_{15}INO_3$ 384.0097; found 384.0096.

3-iodo-1-neopentyl-4-(tetrahydrofuran-2-yl)-1*H*-pyrrole-2,5-dione (3b):



Yellow oil, 50% (27.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.90 (t, J = 7.5 Hz, 1H), 4.13 (dd, J = 14.6, 7.5 Hz, 1H), 3.95 (dd, J = 12.4, 7.4 Hz, 1H), 3.34 (s, 2H), 2.35 – 2.26 (m, 1H), 2.18 – 1.95 (m, 3H), 0.91 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.2, 167.0, 150.8, 101.9, 74.7, 69.6, 50.3, 33.5, 31.6, 27.9, 26.8. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{13}H_{18}INO_3Na$ 386.0229; found 384.0230.

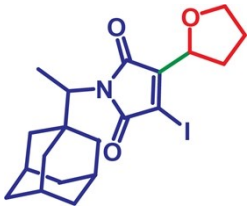
***tert*-butyl 2-(3-iodo-2,5-dioxo-4-(tetrahydrofuran-2-yl)-2,5-dihydro-1*H*-pyrrol-1-yl)acetate (3c)**:



Yellow oil, 38 % (23.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.90 (t, J = 7.3 Hz, 1H), 4.18 (s, 2H), 4.12 (dd, J = 14.5, 7.3 Hz, 1H), 3.95 (dd, J = 12.5, 7.3 Hz, 1H), 2.36 – 2.25 (m, 1H), 2.14 – 1.96 (m, 3H), 1.44 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.9, 165.8, 151.4, 101.7, 83.0, 74.8, 69.6, 40.4, 31.6, 27.9, 26.7. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{14}H_{18}INO_5Na$ 430.0127; found 430.0125.

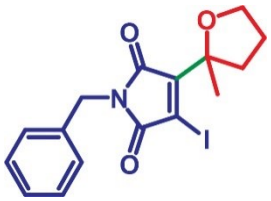
1-(1-((3r,5r,7r)-adamantan-1-yl)ethyl)-3-iodo-4-(tetrahydrofuran-2-yl)-1*H*-pyrrole-2,5-dione

(3d):



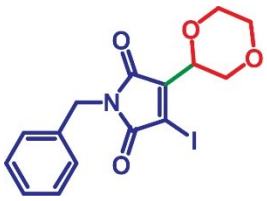
Yellow oil, 47 % (32 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.89 (s, 1H), 4.14 (d, *J* = 7.3 Hz, 1H), 3.95 (s, 1H), 3.83 (d, *J* = 52.8 Hz, 1H), 2.31 (s, 1H), 2.14 (s, 1H), 2.01 (s, 2H), 1.96 (s, 3H), 1.75 – 1.58 (m, 6H), 1.52 (q, *J* = 12.3 Hz, 6H), 1.36 (dd, *J* = 7.4, 2.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.8, 167.4, 166.9, 103.5, 74.9, 69.6, 57.5, 39.3, 37.6, 36.7, 31.6, 28.3, 26.9, 11.7. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{20}H_{26}INO_3Na$ 478.0855; found 478.0856.

1-benzyl-3-iodo-4-(2-methyltetrahydrofuran-2-yl)-1*H*-pyrrole-2,5-dione (3e):



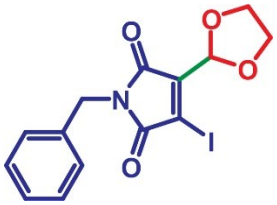
Yellow oil, 73% (43.2 mg) ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 5H), 4.68 (s, 2H), 3.99 – 3.88 (m, 2H), 2.36 – 2.26 (m, 1H), 2.08 – 1.93 (m, 2H), 1.81 (dd, *J* = 12.9, 5.7 Hz, 1H), 1.55 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.9, 166.3, 153.8 135.8, 128.7, 128.0, 81.7, 68.1, 42.6, 37.7, 26.2, 25.6. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{16}H_{16}INO_3Na$ 420.0073; found 420.0074.

1-benzyl-3-(1,4-dioxan-2-yl)-4-iodo-1*H*-pyrrole-2,5-dione (3f):



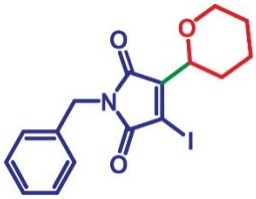
Yellow oil, 45% (27 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.23 (m, 6H), 4.72 (d, *J* = 3.7 Hz, 1H), 4.69 (s, 2H), 3.96 – 3.71 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.9, 165.7, 146.0, 135.5, 128.7, 128.1, 105.7, 72.2, 67.5, 66.7, 66.2, 42.7. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{15}H_{15}INO_4$ 400.0046; found 400.0049.

1-benzyl-3-(1,3-dioxolan-2-yl)-4-iodo-1*H*-pyrrole-2,5-dione (3g):



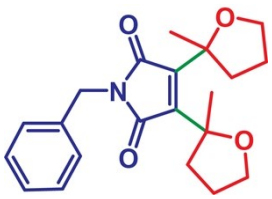
Yellow oil, 35% (21 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.26 (m, 5H), 5.87 (s, 1H), 4.70 (s, 2H), 4.28 – 4.19 (m, 2H), 4.07 – 3.99 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.3, 165.6, 145.7, 135.6, 128.7, 128.1, 106.8, 98.9, 66.2, 42.7. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{14}H_{12}INO_4Na$ 407.9709; found 407.9708.

1-benzyl-3-iodo-4-(tetrahydro-2H-pyran-2-yl)-1*H*-pyrrole-2,5-dione (3h):



Yellow oil, 50% (30 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (dt, *J* = 17.5, 8.5 Hz, 5H), 4.69 (s, 2H), 4.40 (d, *J* = 1.9 Hz, 1H), 4.11 (dd, *J* = 11.4, 3.8 Hz, 1H), 3.52 (td, *J* = 11.9, 1.7 Hz, 1H), 1.99 – 1.50 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.2, 166.1, 149.7, 135.7, 128.7, 128.0, 102.5, 73.8, 68.8, 42.6, 29.2, 25.3, 23.1. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{16}H_{16}INO_3Na$ 420.0073; found 420.0074.

1-benzyl-3,4-bis(2-methyltetrahydrofuran-2-yl)-1H-pyrrole-2,5-dione (3i):

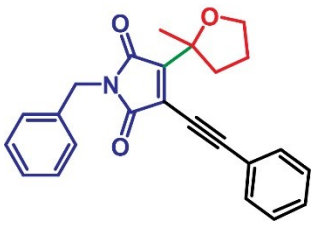


Yellow oil, 20% (21 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (dt, *J* = 12.2, 5.9 Hz, 5H), 4.60 (s, 2H), 3.92 (td, *J* = 7.9, 4.9 Hz, 2H), 3.74 (q, *J* = 7.7 Hz, 2H), 2.38 – 2.14 (m, 4H), 1.89 (ddt, *J* = 19.7, 7.5, 6.3 Hz, 4H), 1.49 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.9, 143.5, 136.6, 128.8, 128.7 127.6, 82.1, 67.3, 41.5, 39.4, 27.5, 25.2. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{21}H_{25}NO_4Na$ 378.1681; found 378.1680.

General procedure for the Sonogashira coupling reaction:

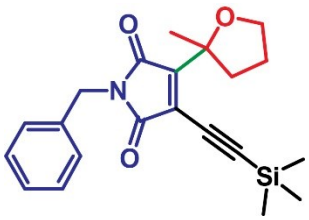
CuI (6 mg, 20 %), $(PPh_3)_2PdCl_2$ (5.3 mg, 5 %), and DIPEA (38.7 mL, 0.3 mmol) were successively added to dry THF (1.5 ml) under nitrogen. Then, compound **3e** (60 mg, 0.15 mmol) and the corresponding terminal alkyne (0.225 mmol, commercially available) in THF (1 ml) were added dropwise. The mixture was stirred at ambient temperature overnight. After the completion of the reaction as detected by TLC, the mixture was directly purified by column chromatography on silica gel (hexane/ethyl acetate = 8:1) to give the product.

1-benzyl-3-(2-methyltetrahydrofuran-2-yl)-4-(phenylethynyl)-1*H*-pyrrole-2,5-dione (5a):



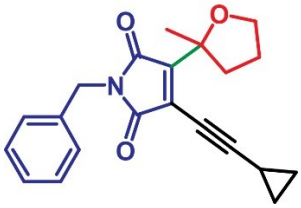
Yellow oil, 80% (44.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.23 (m, 10H), 4.68 (s, 2H), 4.04 (s, 2H), 2.33 (s, 1H), 2.00 (s, 3H), 1.64 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.8, 167.0, 150.0, 136.1, 132.2, 129.8, 128.7, 128.4, 127.9, 81.9, 79.9, 68.6, 42.0, 38.2, 26.3, 25.9, 25.6. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{24}H_{21}NO_3Na$ 394.1419; found 394.1420.

1-benzyl-3-(2-methyltetrahydrofuran-2-yl)-4-((trimethylsilyl)ethynyl)-1*H*-pyrrole-2,5-dione (5b):



Yellow oil, 50% (27 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 18.3, 7.5 Hz, 5H), 4.63 (s, 2H), 3.97 (dd, *J* = 11.1, 5.0 Hz, 2H), 2.26 (dd, *J* = 11.6, 4.1 Hz, 1H), 2.05 – 1.81 (m, 3H), 1.60 (s, 3H), 0.25 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.7, 166.8, 151.6, 136.0, 128.6, 127.9, 122.1, 114.2, 93.8, 81.7, 68.6, 42.0, 38.2, 26.1, 25.8, 1.0. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{21}H_{25}NO_3SiNa$ 390.1501; found 390.1500.

1-benzyl-3-(cyclopropylethynyl)-4-(2-methyltetrahydrofuran-2-yl)-1*H*-pyrrole-2,5-dione (5c):

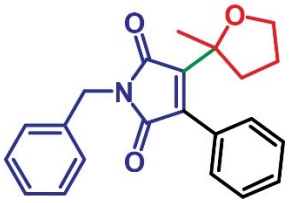


Yellow oil, 65% (31.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (dt, *J* = 10.8, 5.4 Hz, 5H), 4.62 (s, 2H), 3.94 (dd, *J* = 13.2, 6.1 Hz, 2H), 2.32 – 1.80 (m, 4H), 1.56 (s, 3H), 1.04 – 0.77 (m, 5H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.2, 167.1, 148.5, 136.1, 128.6, 127.8, 123.2, 113.3, 81.7, 68.4, 66.9, 41.9, 38.0, 26.2, 25.8, 9.8, 1.3. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{21}H_{21}NO_3Na$ 358.1419; found 358.1418.

General procedure for the Suzuki coupling reaction

A mixture of compound **3e** (58 mg, 0.146 mmol), phenboronic (0.292 mmol, commercially available), K_2CO_3 (47.88 mg, 0.292 mmol), $Pd(PPh_3)_4$ (16.87 mg, 10 %) and *N*,*N*-dimethylacetamide (DMAc, 1 ml) was added to a 10 ml sealed tube. After three freeze-pump-thaw cycles, the tube was sealed under nitrogen atmosphere and stirred at 60 ℃ for 24 h. After cooled to room temperature, the mixture was directly purified by column chromatography on silica gel (eluted with 10-25% hexane/ethyl acetate) to give the product.

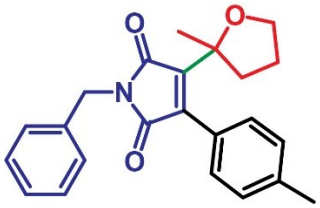
1-benzyl-3-(2-methyltetrahydrofuran-2-yl)-4-phenyl-1*H*-pyrrole-2,5-dione (7a):



Colourless oil, 88% (26.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (tt, *J* = 19.2, 12.5 Hz, 10H), 4.59 (s, 2H), 3.44 (dd, *J* = 14.8, 7.3 Hz, 1H), 2.91 (td, *J* = 8.0, 6.1 Hz, 1H), 2.17 (ddd, *J* = 12.8, 7.8, 5.3 Hz, 1H), 1.91 – 1.57 (m, 3H), 1.54 (d, *J* = 9.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.6, 144.2, 137.9, 136.4, 130.3, 129.0, 128.7, 127.8, 127.1, 82.1, 67.1, 41.9, 38.1, 27.3, 25.3. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$

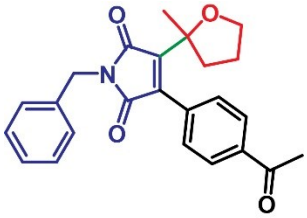
calcd for $C_{22}H_{21}NO_3Na$ 370.1419; found 370.1418.

1-benzyl-3-(2-methyltetrahydrofuran-2-yl)-4-(p-tolyl)-1*H*-pyrrole-2,5-dione (7b):



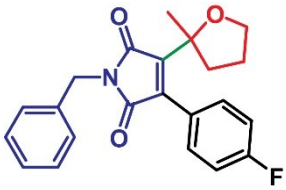
Colourless oil, 93% (50.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.26 (m, 7H), 7.18 (d, *J* = 8.0 Hz, 2H), 4.70 (s, 2H), 3.58 (dd, *J* = 14.4, 7.6 Hz, 1H), 3.07 (td, *J* = 8.0, 6.0 Hz, 1H), 2.38 (s, 3H), 2.34 – 2.23 (m, 1H), 2.00 – 1.77 (m, 2H), 1.71 (dd, *J* = 13.1, 5.4 Hz, 1H), 1.66 (s, 3H). HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calcd for $C_{23}H_{23}NO_3Na$ 384.1576; found 384.1577.

3-(4-acetylphenyl)-1-benzyl-4-(2-methyltetrahydrofuran-2-yl)-1*H*-pyrrole-2,5-dione (7c):



Colourless oil, 85% (48.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.3 Hz, 2H), 7.51 – 7.26 (m, 7H), 4.70 (s, 2H), 3.55 (dd, *J* = 14.8, 7.2 Hz, 1H), 3.02 (dd, *J* = 14.1, 7.9 Hz, 1H), 2.62 (s, 3H), 2.27 (ddd, *J* = 13.1, 7.7, 5.6 Hz, 1H), 2.05 – 1.96 (m, 1H), 1.86 (tt, *J* = 13.2, 6.6 Hz, 1H), 1.76 – 1.67 (m, 1H), 1.66 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.7, 170.2, 170.0, 145.7, 136.9, 136.6, 136.2, 133.8, 130.6, 128.7, 127.9, 127.0, 82.1, 67.1, 41.9, 38.1, 27.3, 26.6, 25.3. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calcd for $C_{24}H_{23}NO_3Na$ 412.1525; found 412.1526.

1-benzyl-3-(4-fluorophenyl)-4-(2-methyltetrahydrofuran-2-yl)-1*H*-pyrrole-2,5-dione (7d):



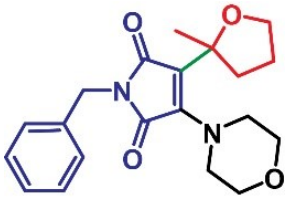
Colourless oil, 73% (38.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 – 7.27 (m, 7H), 7.06 (t, *J* = 8.7 Hz, 2H), 4.70 (s, 2H), 3.58 (dd, *J* = 14.5, 7.6 Hz, 1H), 3.02 (dd, *J* = 14.1, 8.0 Hz, 1H), 2.27 (t, *J* = 13.1 Hz, 1H), 2.05 – 1.94 (m, 1H), 1.92 – 1.80 (m, 1H), 1.69 (dd, *J* = 13.2, 6.9 Hz, 1H), 1.66 (s, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ 170.5, 164.0, 162.4, 144.2, 136.7, 136.3, 132.6, 128.7, 127.9, 124.6, 114.4, 114.2, 82.2, 67.0, 41.9, 38.1, 27.3, 25.3. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calcd for $C_{22}H_{20}FNO_3Na$ 388.1325; found 388.1326.

General procedure for the nucleophilic substitution:

Compound **3e** (60 mg, 0.15 mmol) and the secondary amine (33.3 µl, 0.30 mmol) were successively added to dichloromethane (0.45 ml). The mixture was stirred at 25 ℃ for 24 h. after the completion of the reaction as detected by TLC, the mixture was directly purified by column chromatography on

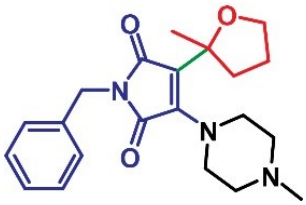
silica gel (**9a**, hexane/ethyl acetate = 8:1; **9b**, dichloromethane/methanol = 10:1) to give the product.

1-benzyl-3-(2-methyltetrahydrofuran-2-yl)-4-morpholino-1*H*-pyrrole-2,5-dione (9a):



Yellow oil, 84% (45 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.26 (m, 5H), 4.57 (s, 2H), 3.96 – 3.76 (m, 5H), 3.68 (dt, *J* = 13.9, 4.7 Hz, 3H), 3.53 – 3.44 (m, 2H), 2.46 – 2.32 (m, 1H), 2.06 – 1.74 (m, 3H), 1.49 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.0, 167.8, 143.4, 136.9, 128.5, 127.5, 112.2, 81.3, 67.4, 67.2, 51.8, 41.0, 39.1, 27.6, 25.0. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{20}H_{24}N_2O_4Na$ 379.1634; found 379.1633.

1-benzyl-3-(4-methylpiperazin-1-yl)-4-(2-methyltetrahydrofuran-2-yl)-1*H*-pyrrole-2,5-dione (9b):



Yellow oil, 94% (52 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.22 (m, 5H), 4.56 (s, 2H), 3.90 (td, *J* = 8.1, 5.2 Hz, 2H), 3.75 – 3.60 (m, 2H), 3.50 (dd, *J* = 11.5, 5.4 Hz, 2H), 2.57 – 2.37 (m, 5H), 2.30 (s, 3H), 2.04 – 1.70 (m, 3H), 1.50 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.1, 167.9, 143.8, 137.0, 128.5, 127.5, 111.7, 81.3, 67.1, 55.5, 51.3, 46.1, 41.0, 39.2, 27.6, 24.9. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{28}N_3O_3$ 370.2131; found 370.2132.

Mechanism study

Initiator *tert*-butyl peroxy-2-ethylhexanoate (TBPO) (0.13 mL, 0.75 mmol) and Na_2CO_3 (47.70 mg, 0.45 mmol) was dissolved in 2-MeTHF (2.5 mL, excess, as well as solvent) in a sealed tube. The mixture was stirred in an oil bath at 70 ℃ for 3 d. The mixture was then subjected for ESI-TOF analysis.

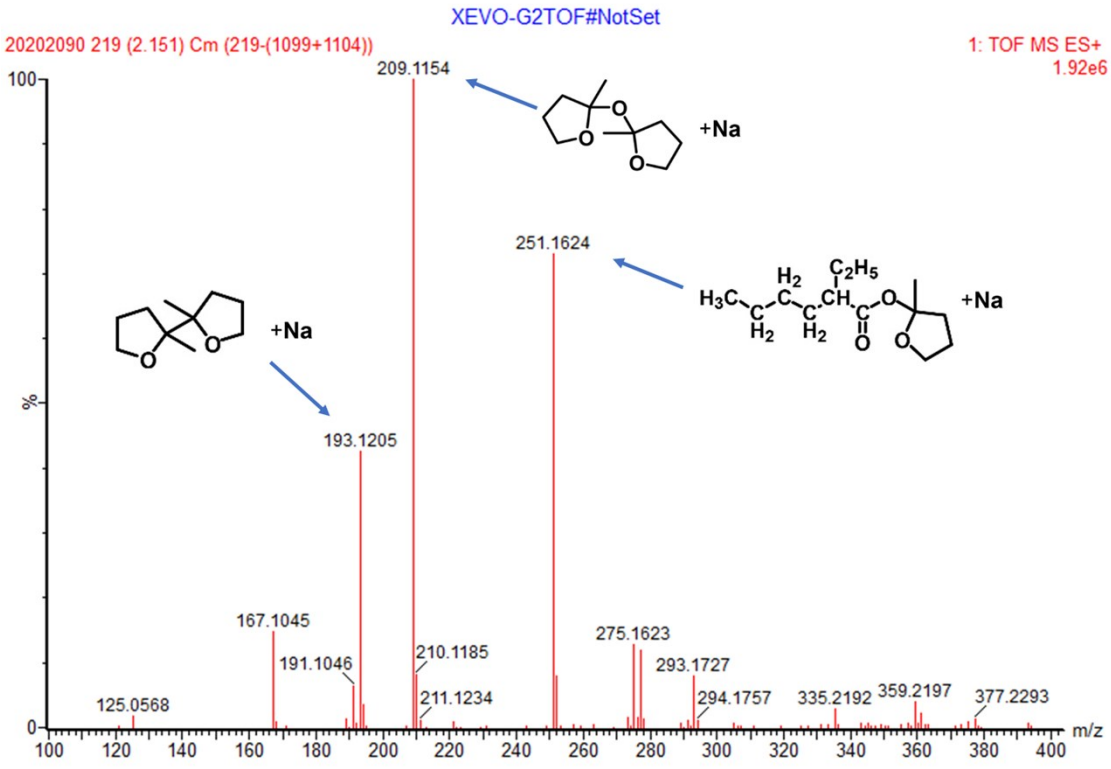
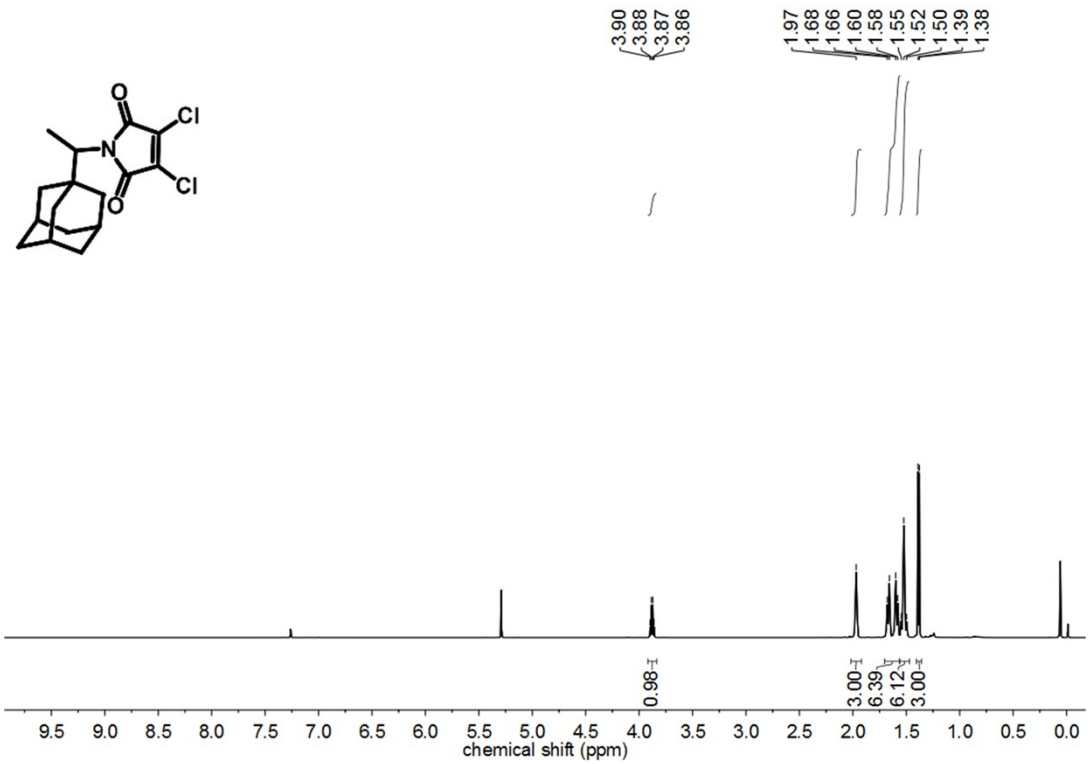


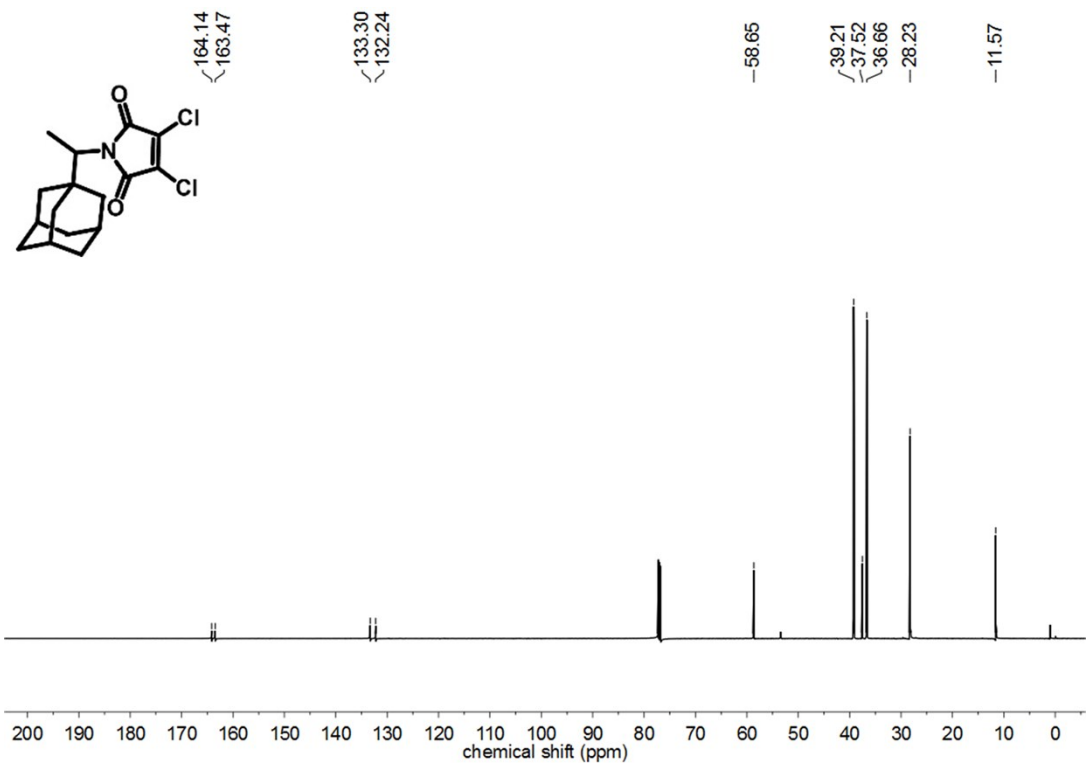
Figure S1. ESI-TOF spectrum for the mechanism study reaction.

Copies of ^{1}H and ^{13}C NMR Spectra

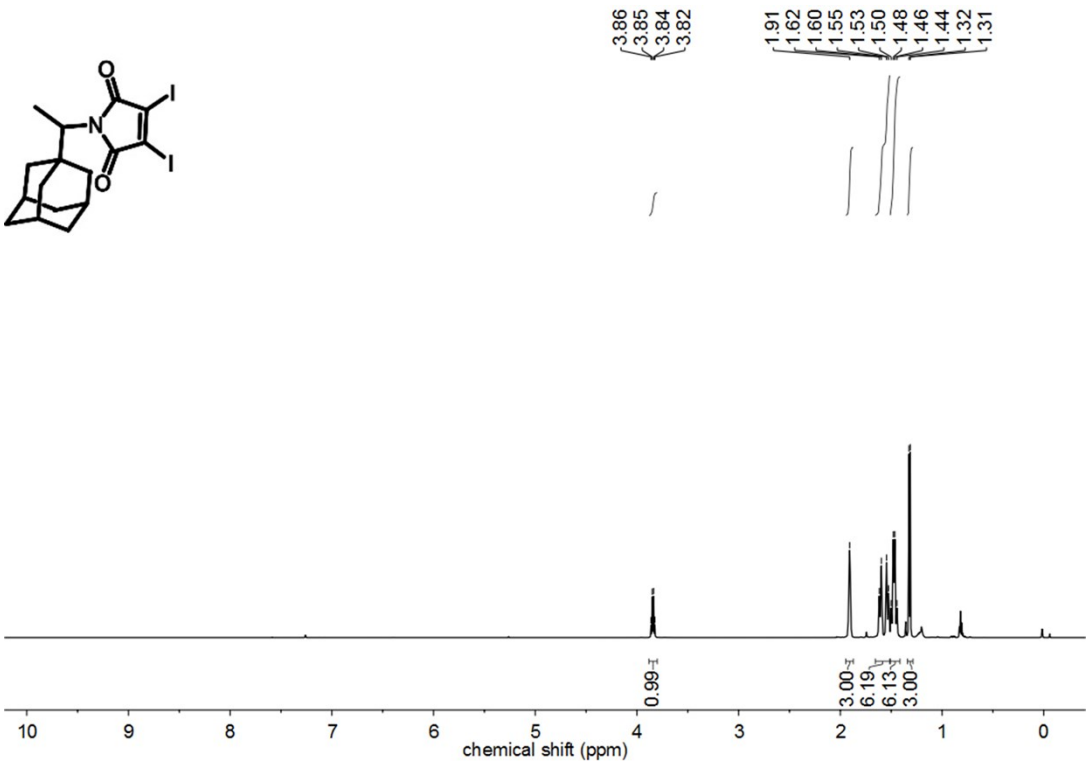
^{1}H NMR spectrum of compound **3d's** (600 MHz, $CDCl_3$)



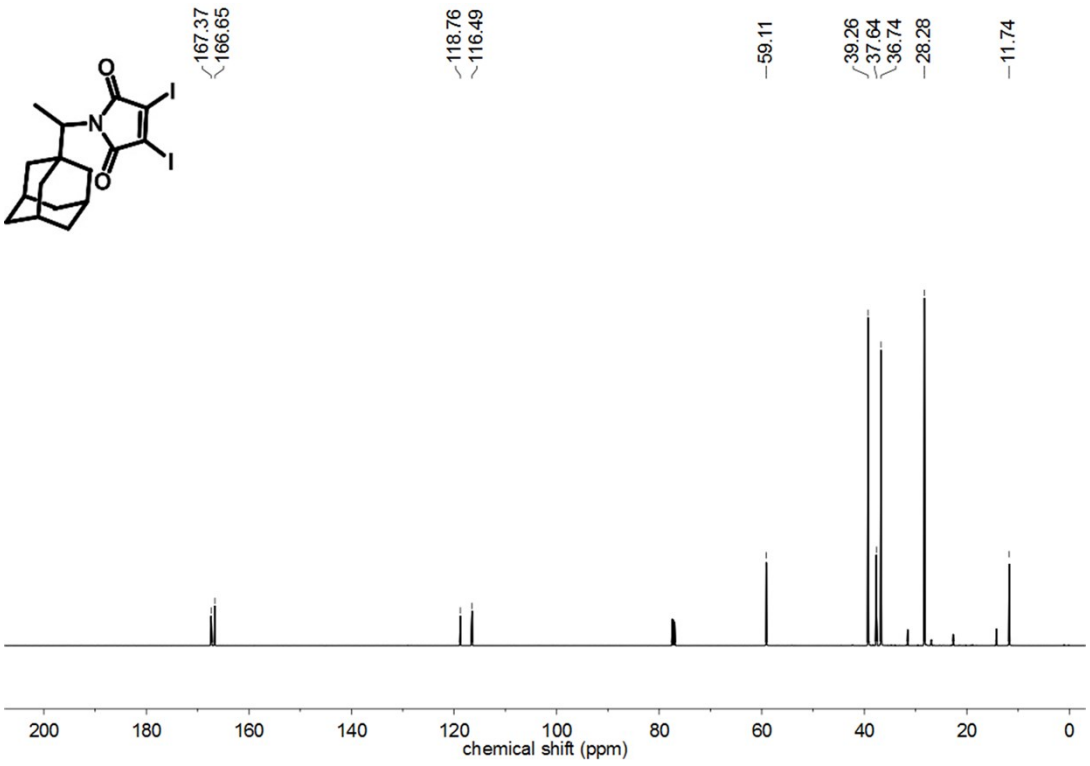
^{13}C NMR spectrum of compound **3d's** (151 MHz, $CDCl_3$)



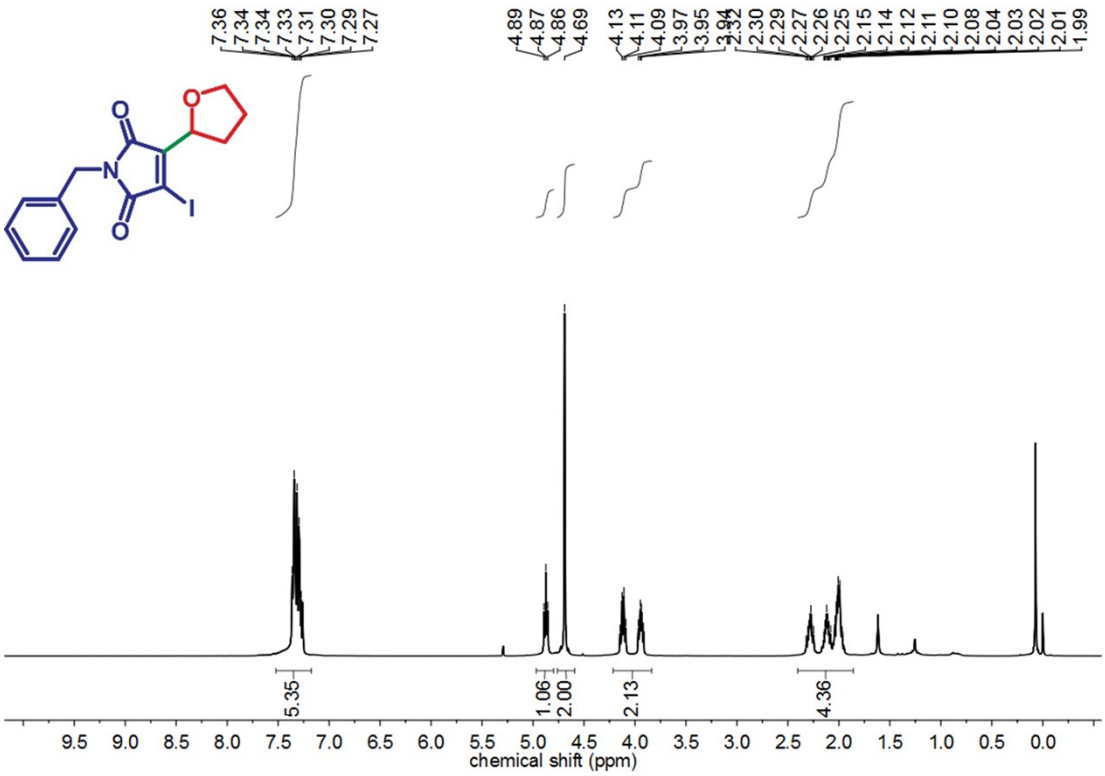
^{1}H NMR spectrum of compound **3d'** (600 MHz, $CDCl_3$)



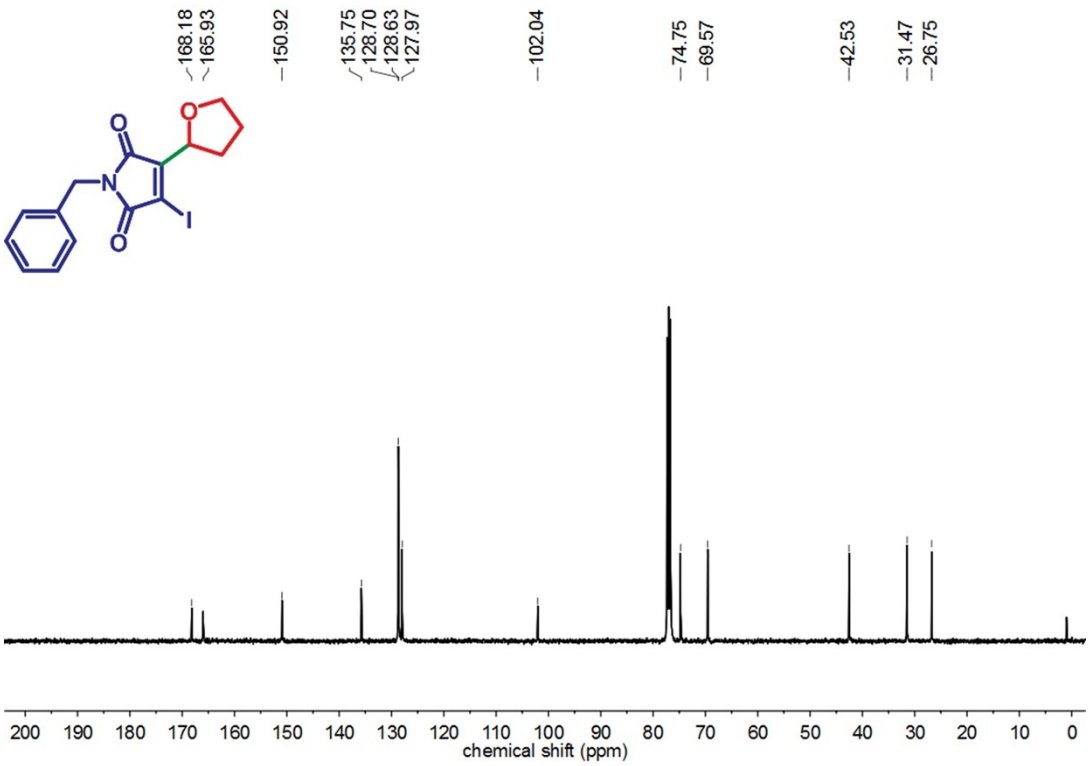
^{13}C NMR spectrum of compound **3d'** (151 MHz, $CDCl_3$)



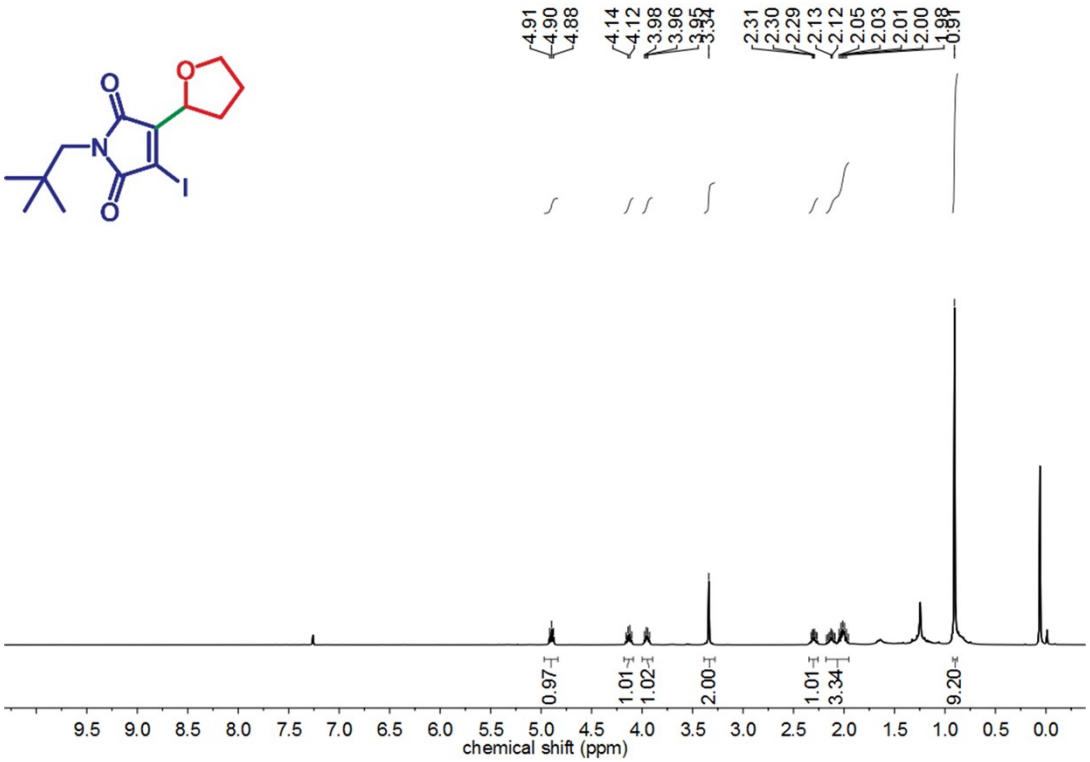
^{1}H NMR spectrum of compound **3a** (400 MHz, $CDCl_3$)



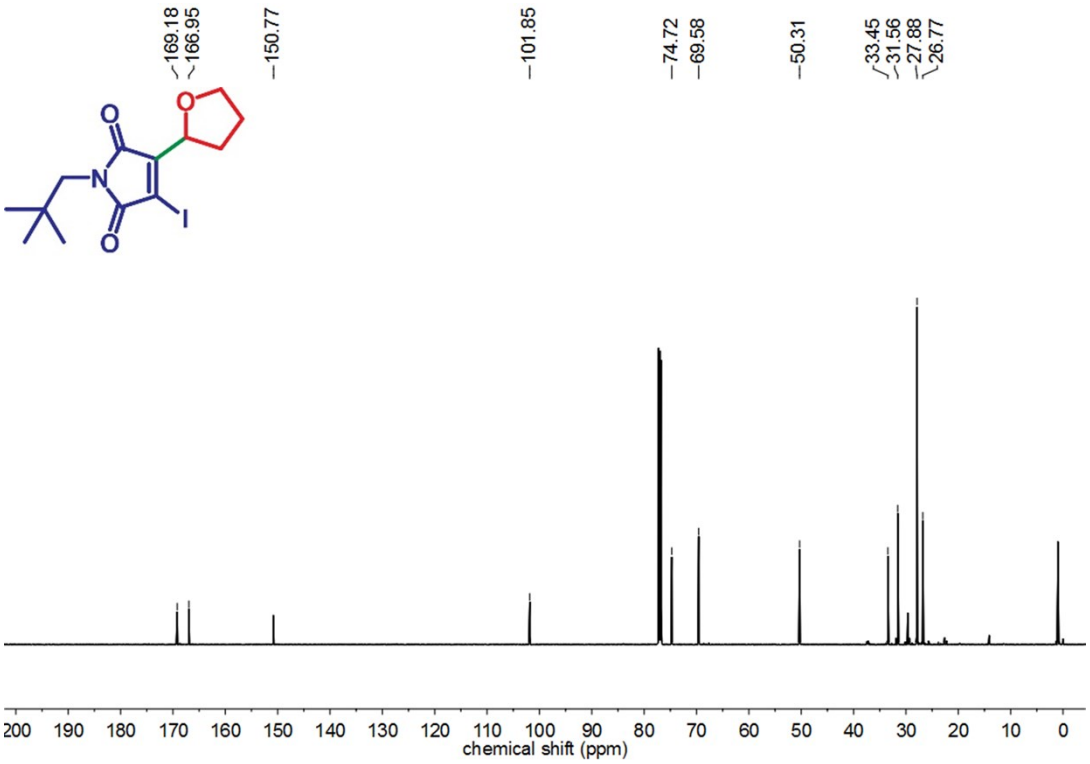
^{13}C NMR spectrum of compound **3a** (151 MHz, $CDCl_3$)



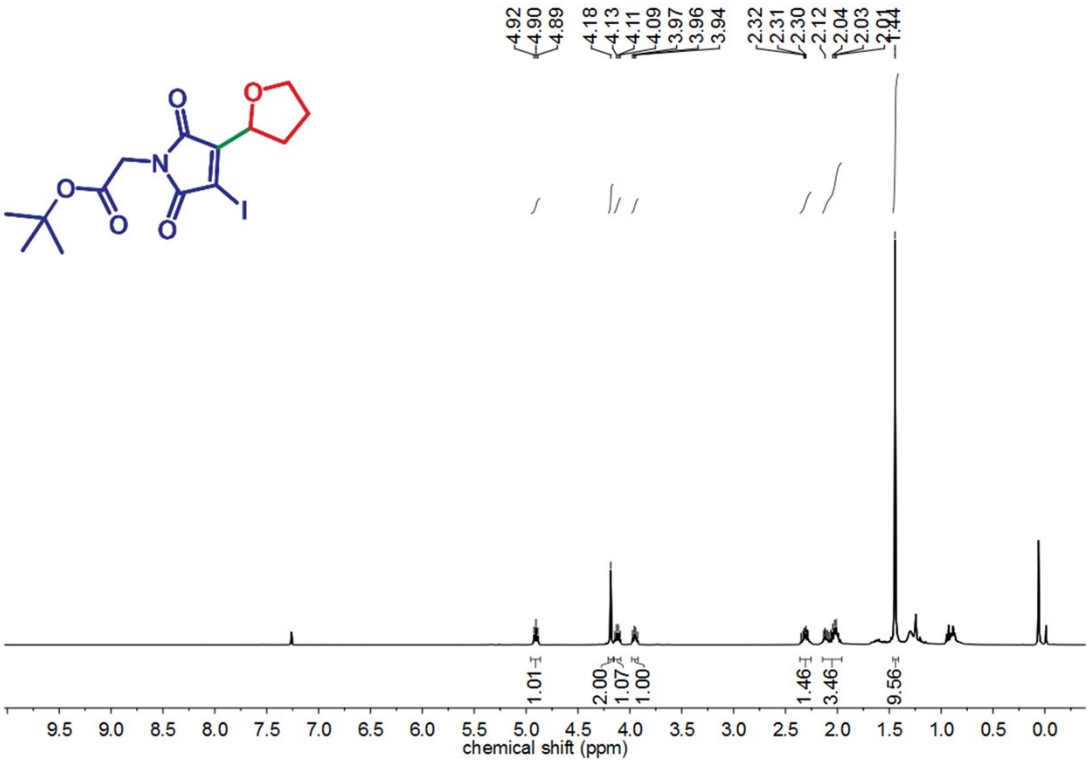
^{1}H NMR spectrum of compound **3b** (400 MHz, $CDCl_3$)



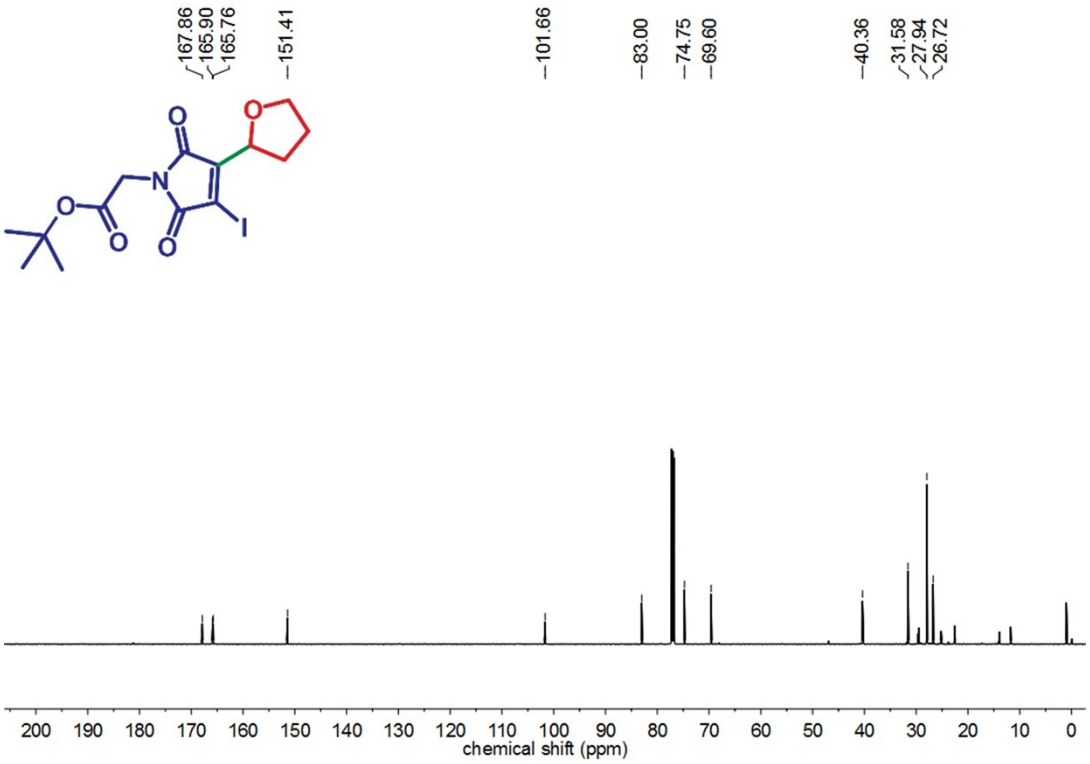
^{13}C NMR spectrum of compound **3b** (151 MHz, $CDCl_3$)



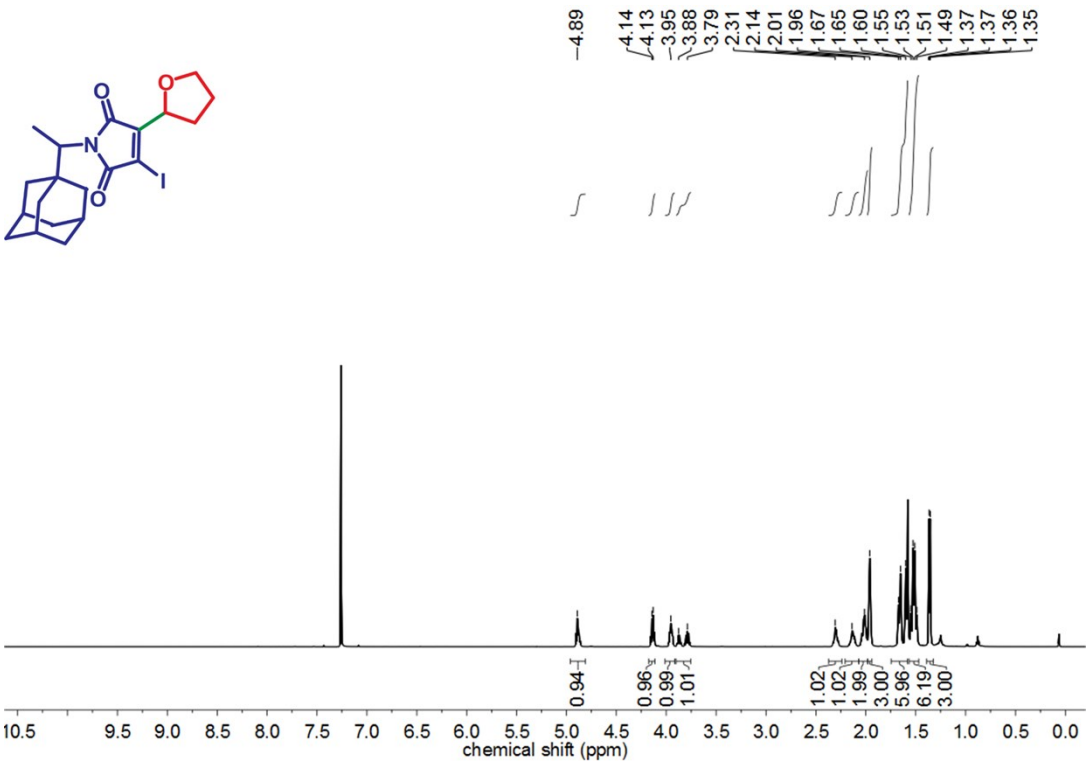
^{1}H NMR spectrum of compound **3c** (400 MHz, $CDCl_3$)



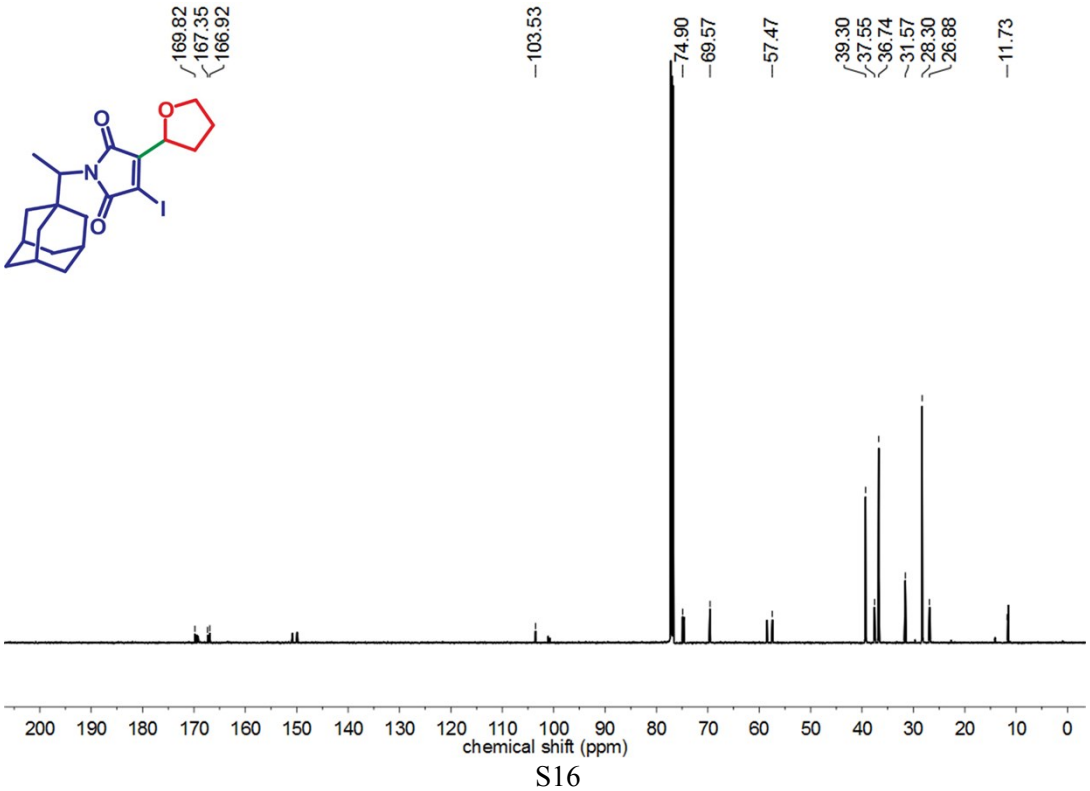
^{13}C NMR spectrum of compound **3c** (151 MHz, $CDCl_3$)



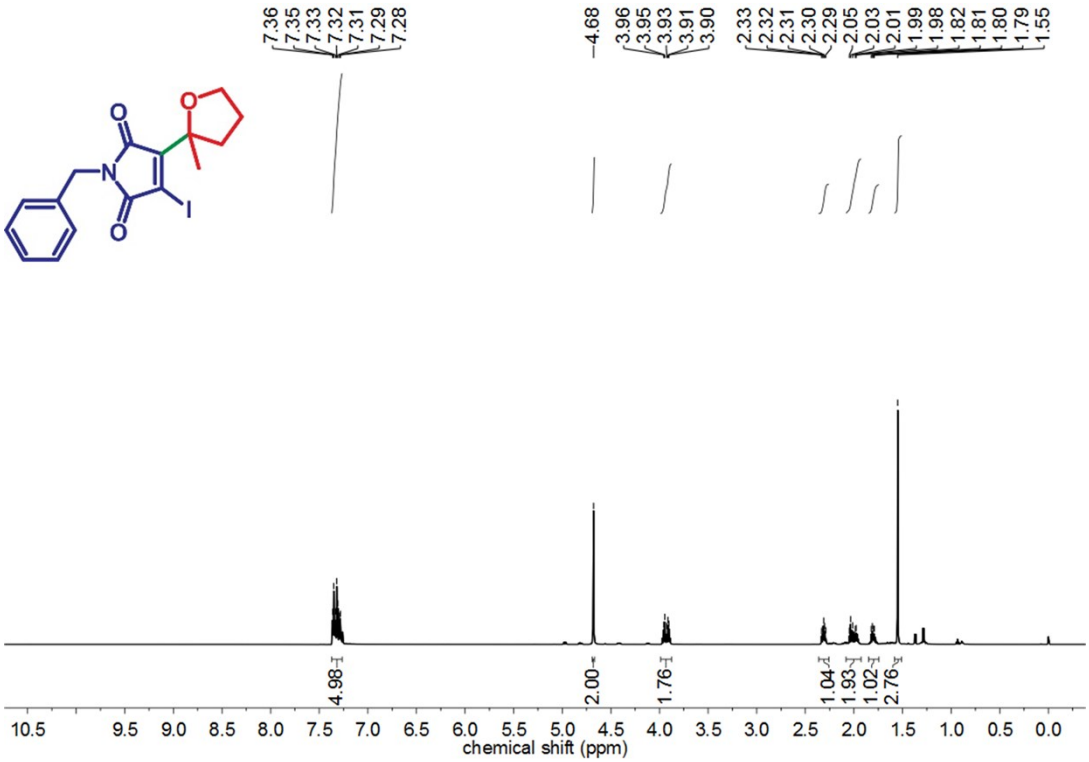
^{1}H NMR spectrum of compound **3d** (600 MHz, $CDCl_3$)



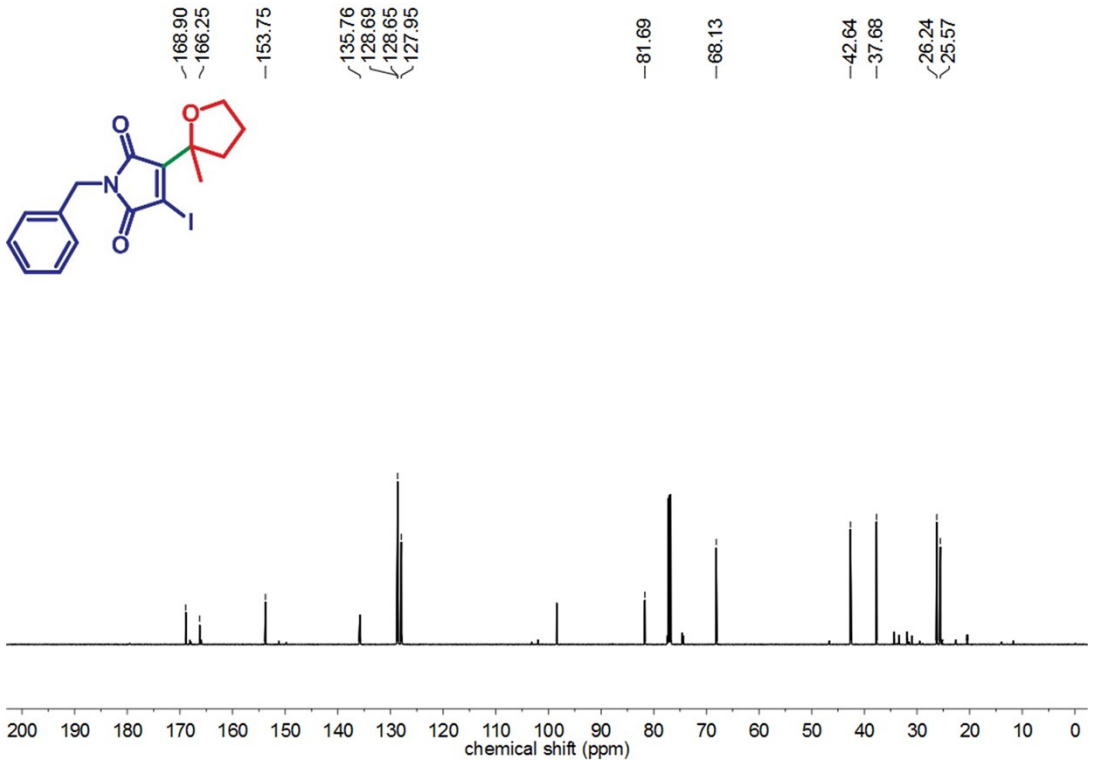
^{13}C NMR spectrum of compound **3d** (151 MHz, $CDCl_3$)



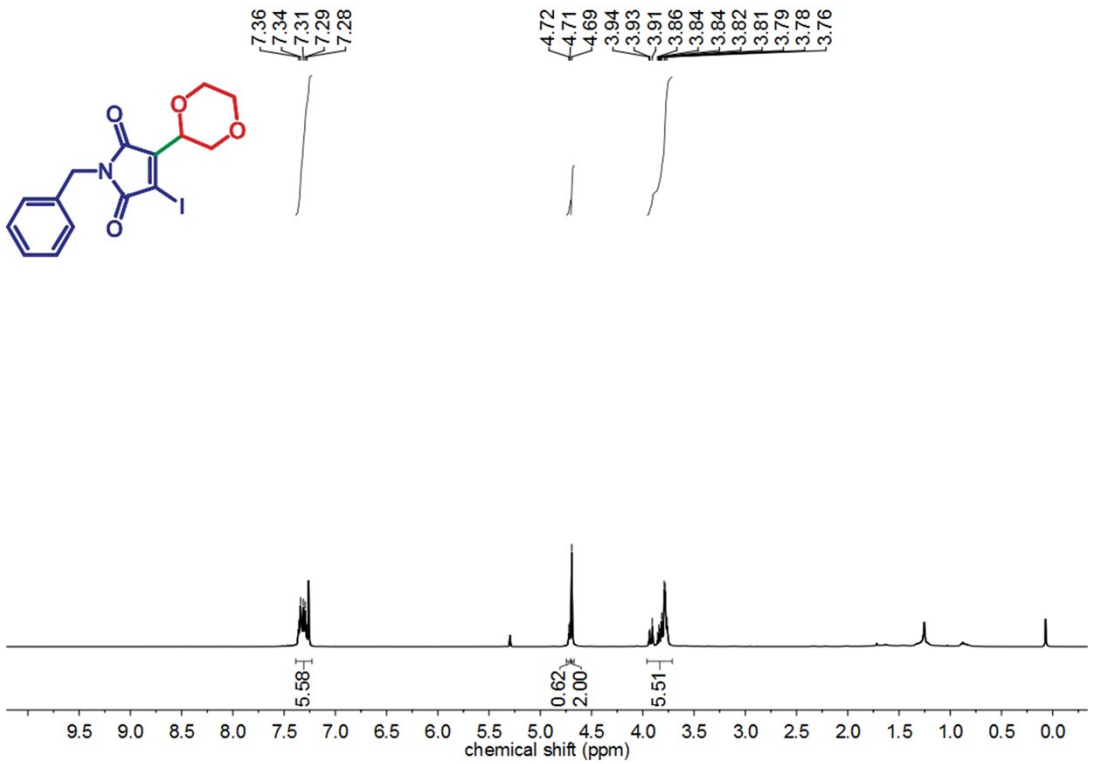
^{1}H NMR spectrum of compound **3e** (600 MHz, $CDCl_3$)



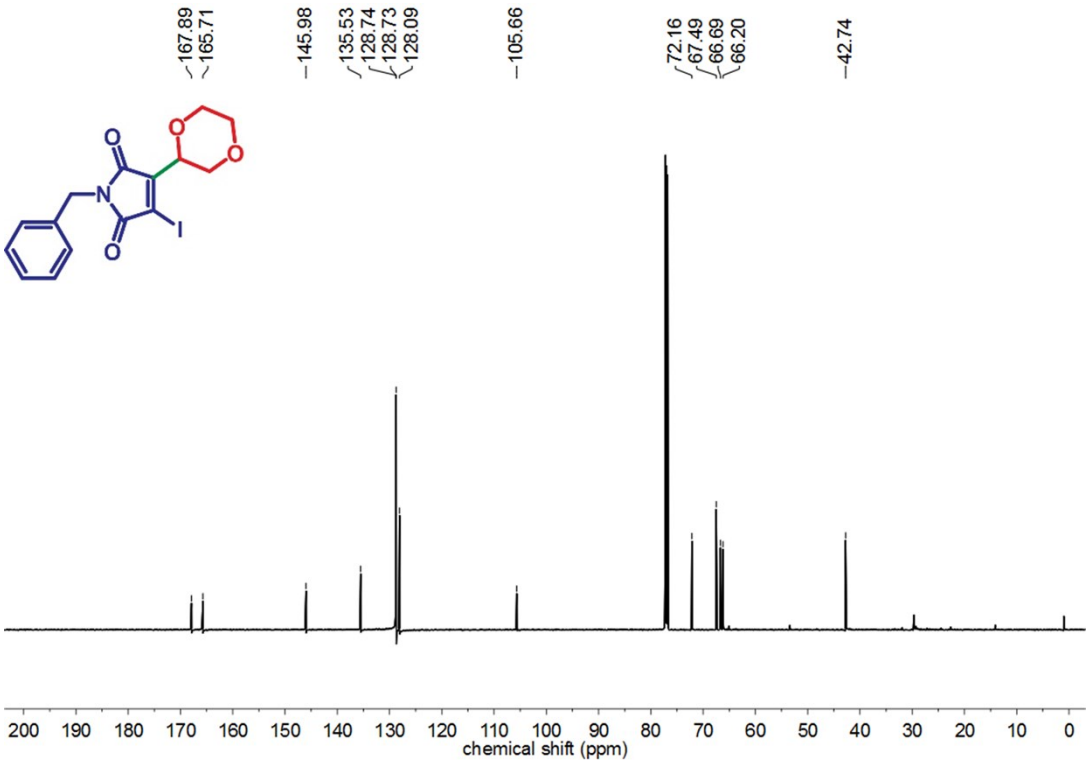
^{13}C NMR spectrum of compound **3e** (151 MHz, $CDCl_3$)



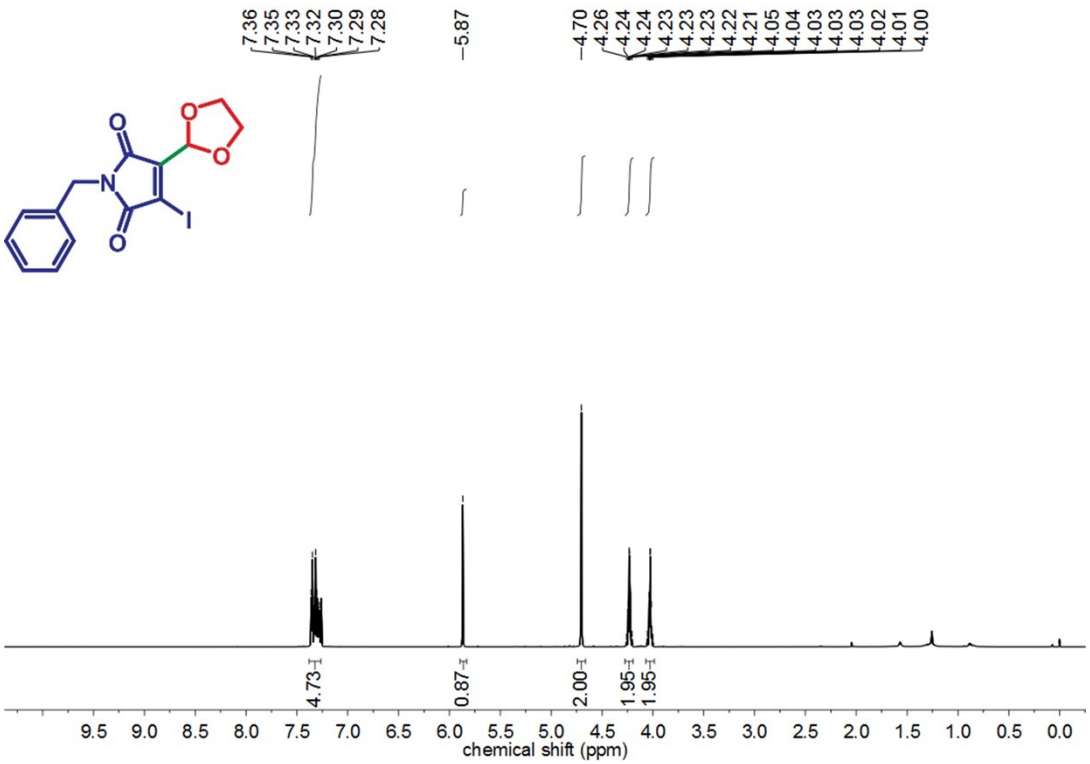
^{1}H NMR spectrum of compound **3f** (400 MHz, $CDCl_3$)



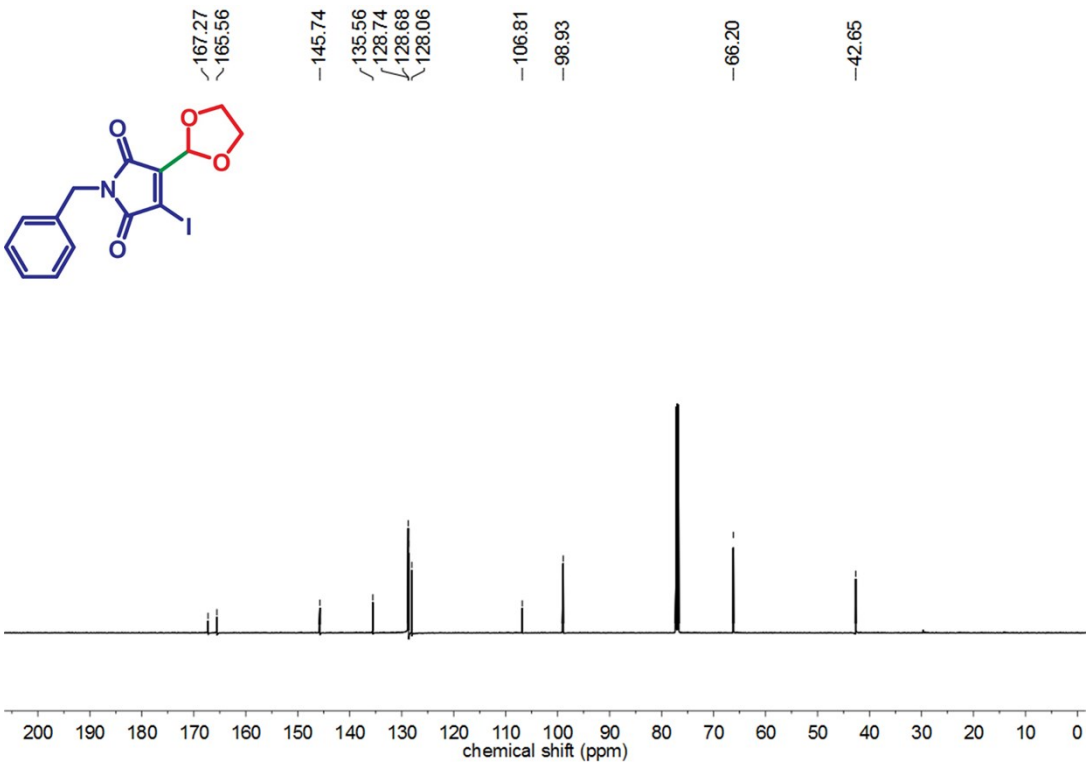
^{13}C NMR spectrum of compound **3f** (151 MHz, $CDCl_3$)



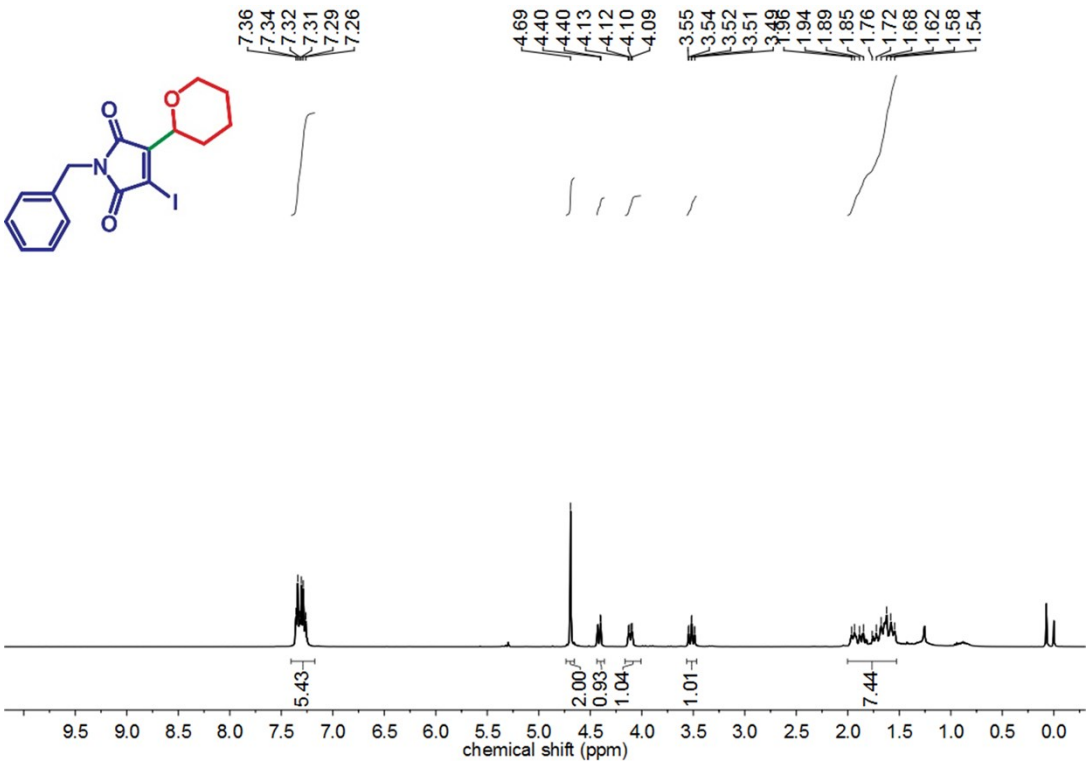
^{1}H NMR spectrum of compound **3g** (600 MHz, $CDCl_3$)



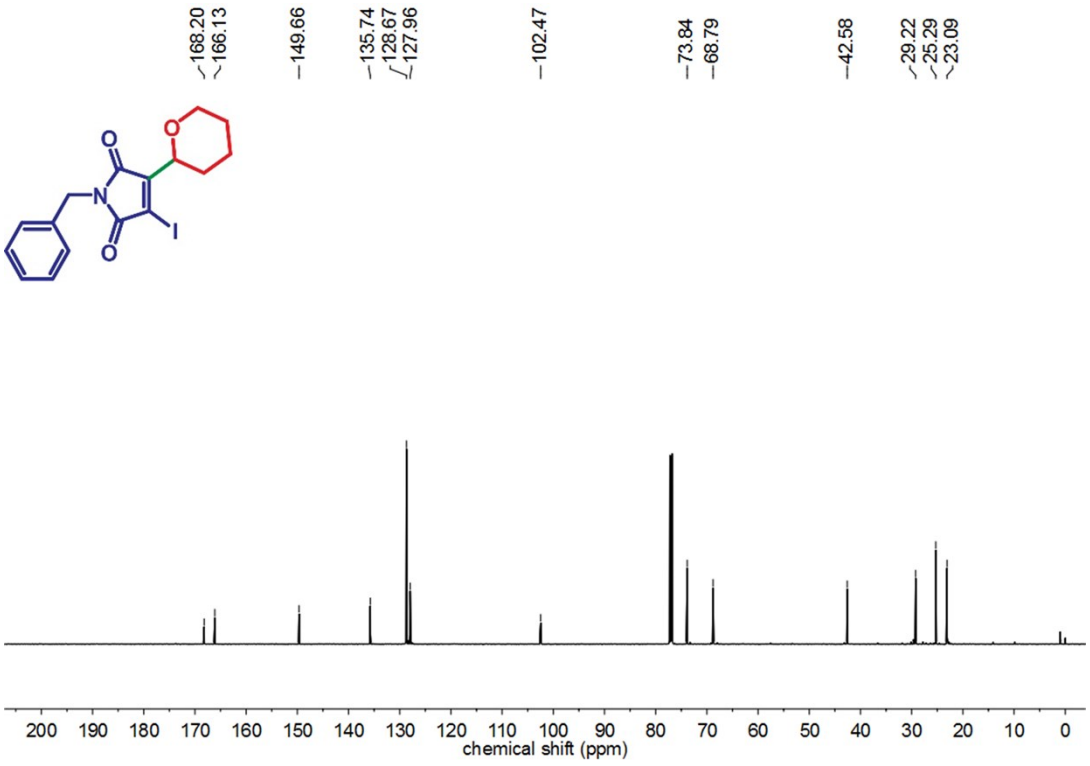
^{13}C NMR spectrum of compound **3g** (151 MHz, $CDCl_3$)



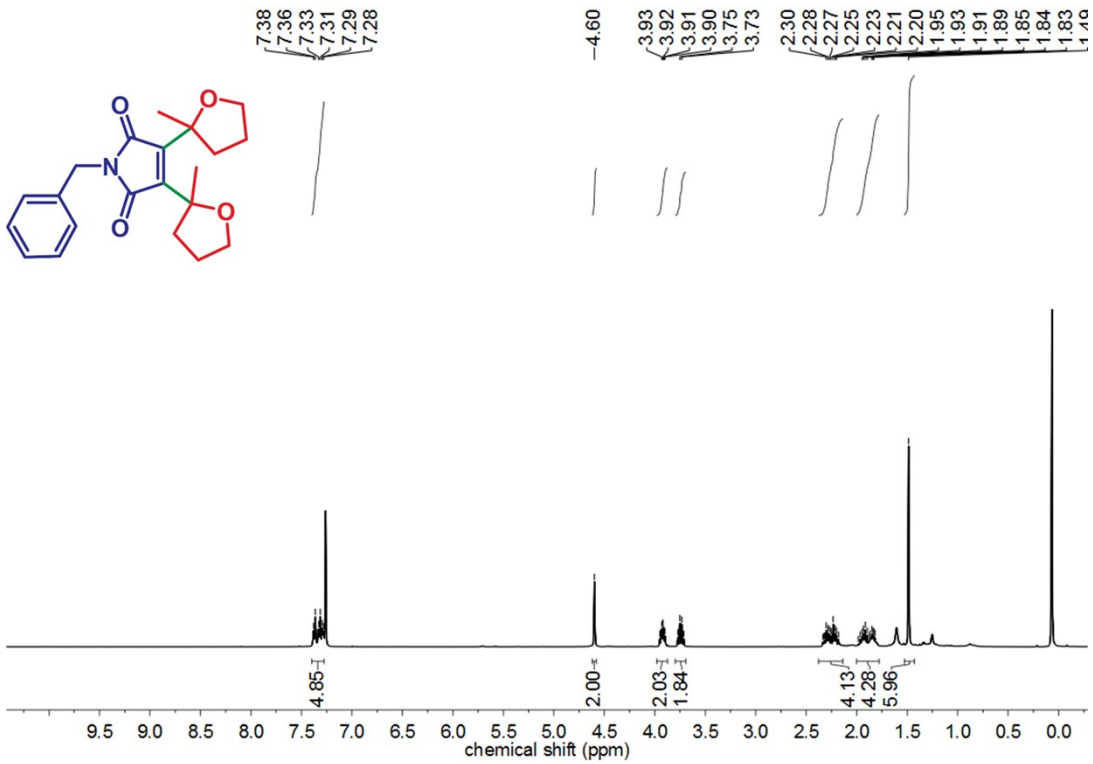
^{1}H NMR spectrum of compound **3h** (400 MHz, $CDCl_3$)



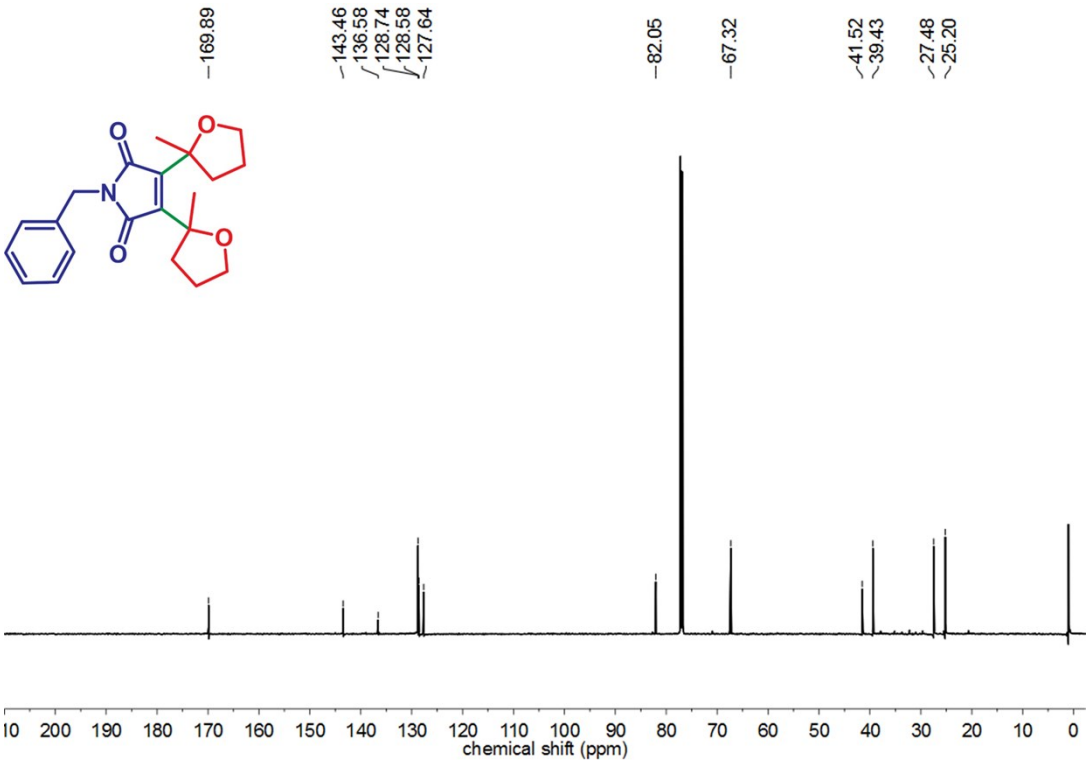
^{13}C NMR spectrum of compound **3h** (151 MHz, $CDCl_3$)



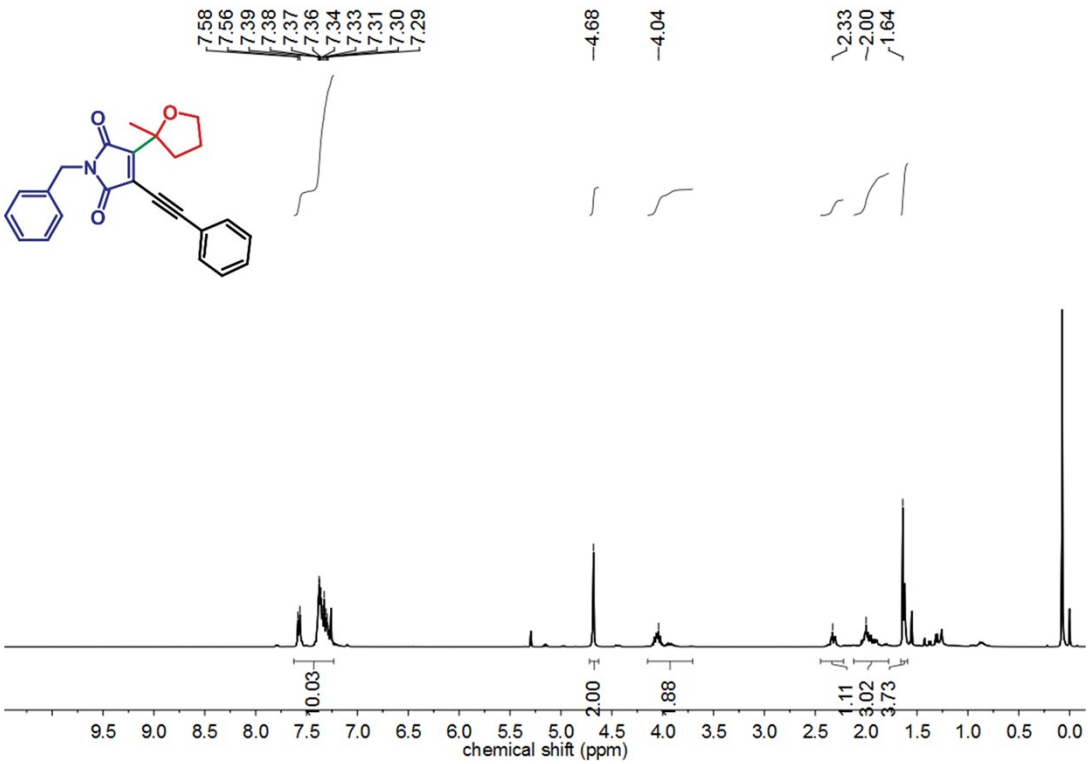
^{1}H NMR spectrum of compound **3i** (400 MHz, $CDCl_3$)



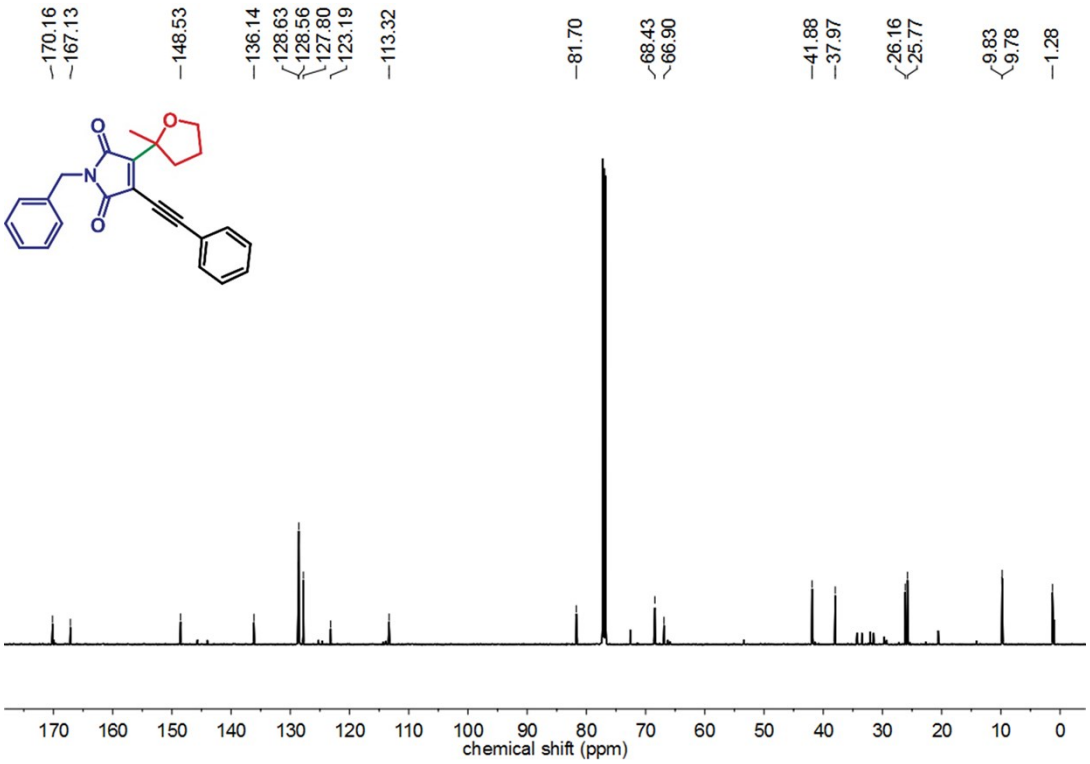
^{13}C NMR spectrum of compound **3i** (151 MHz, $CDCl_3$)



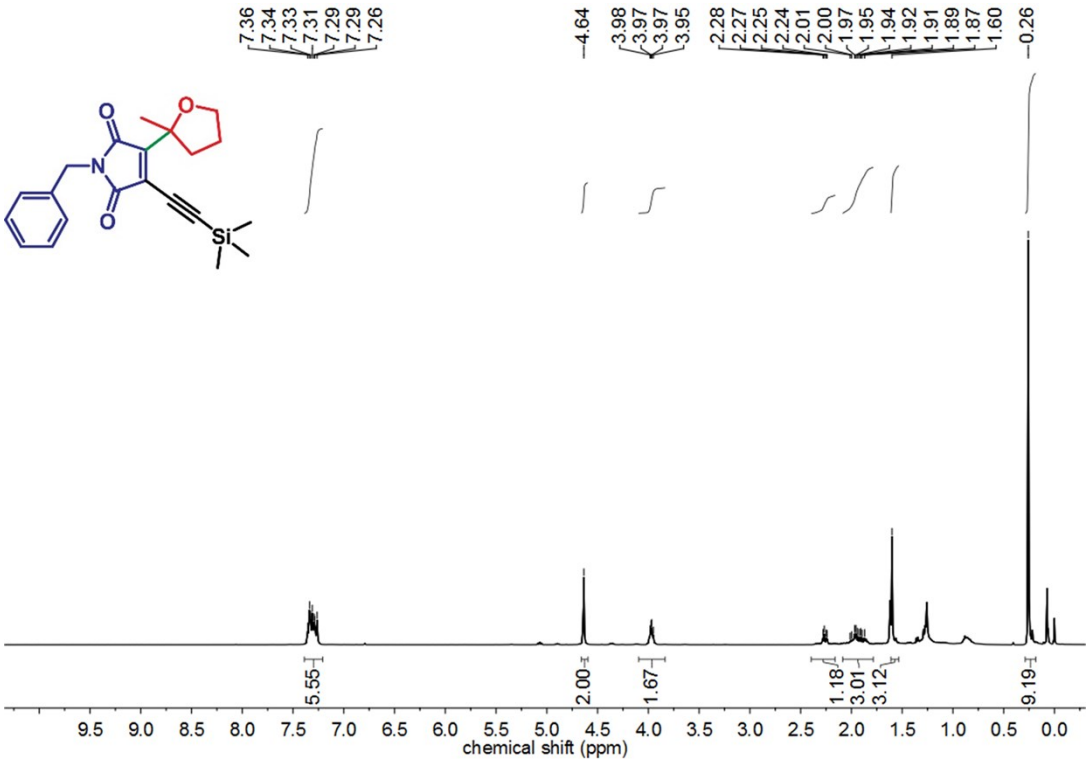
^{1}H NMR spectrum of compound **5a** (400 MHz, $CDCl_3$)



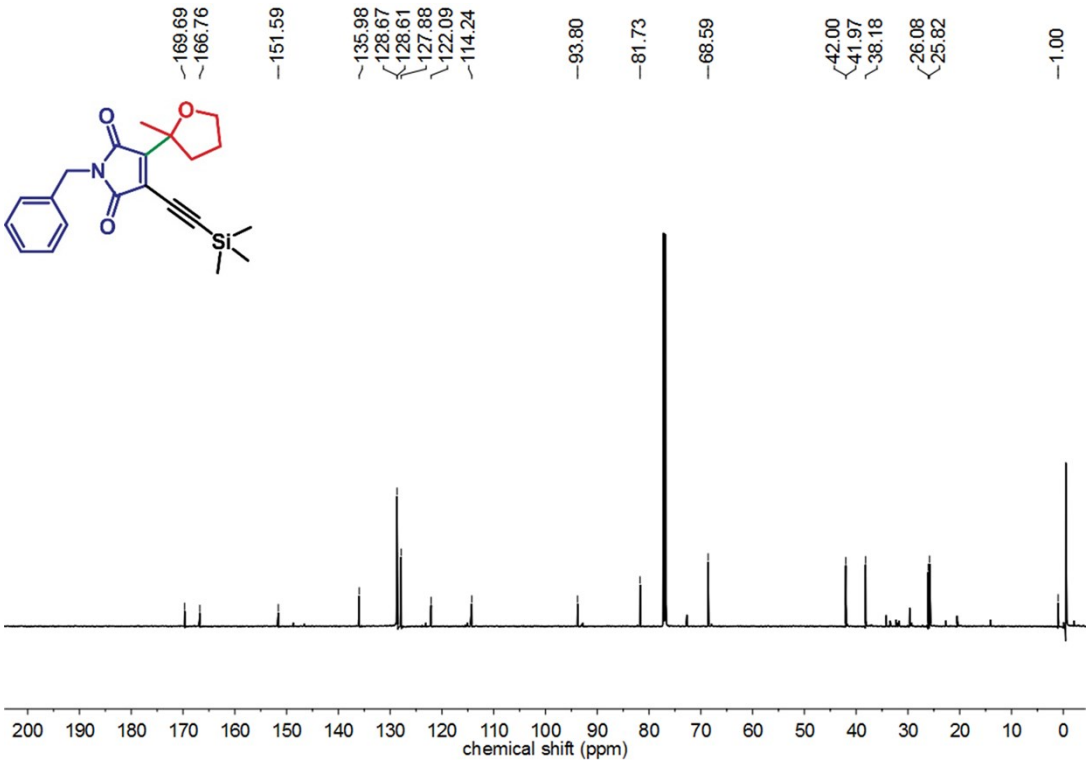
^{13}C NMR spectrum of compound **5a** (151 MHz, $CDCl_3$)



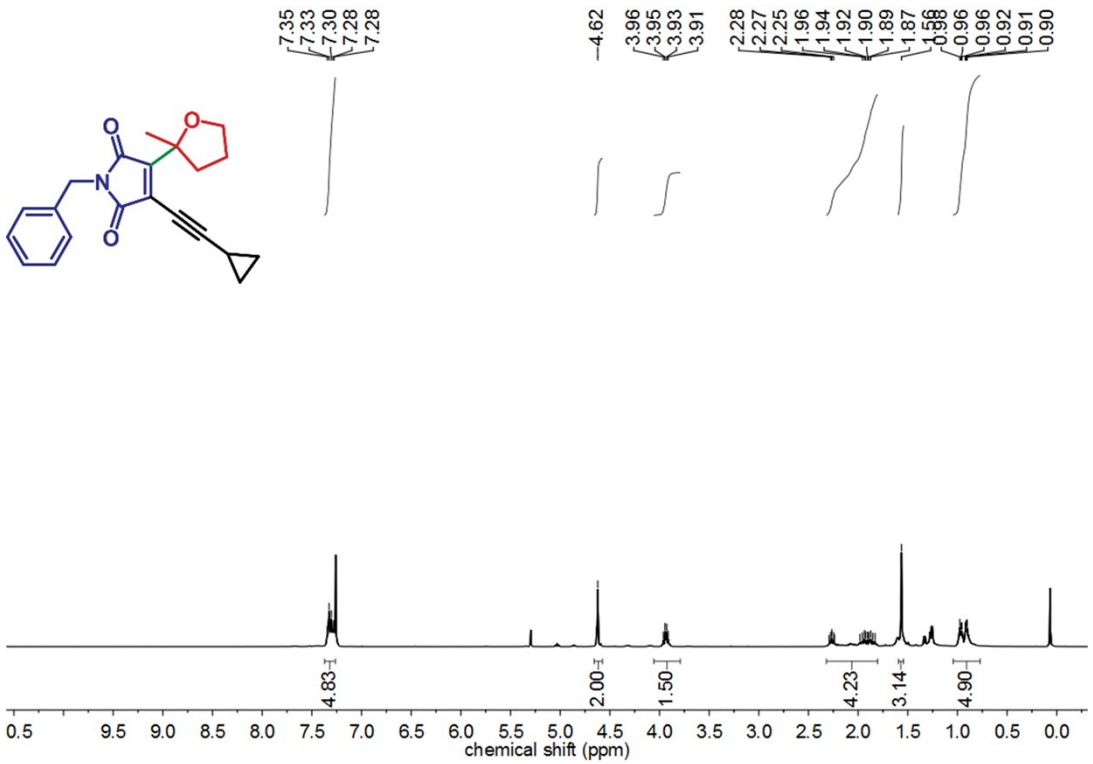
^{1}H NMR spectrum of compound **5b** (400 MHz, $CDCl_3$)



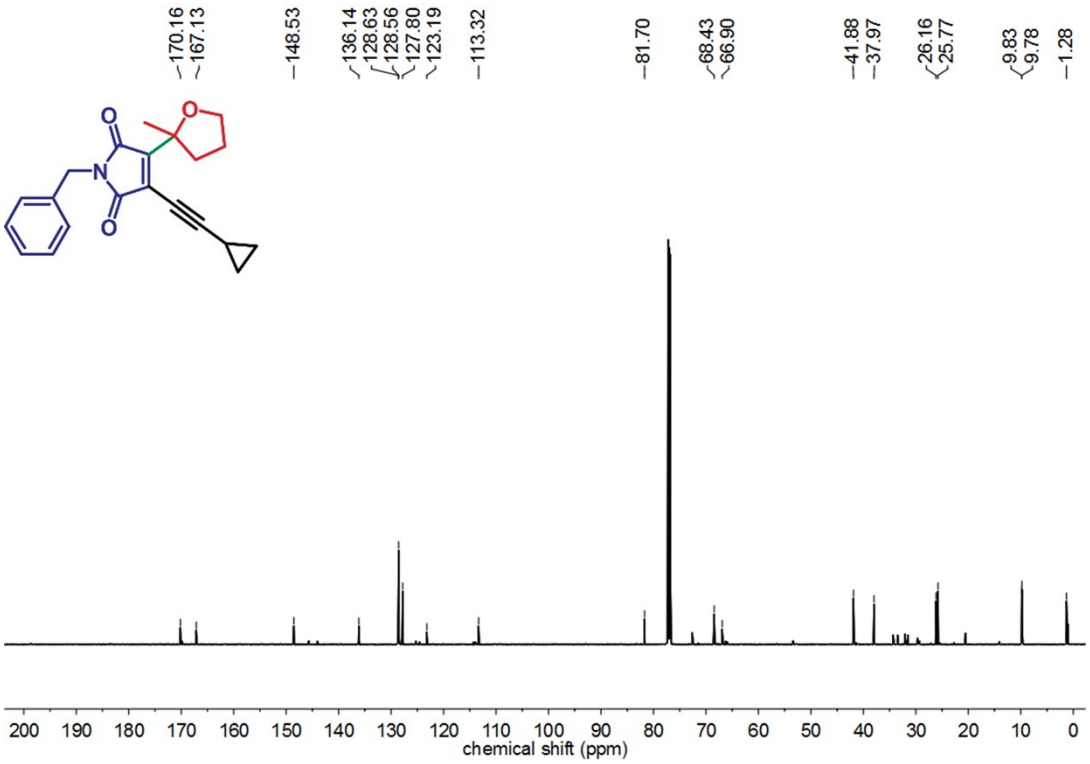
^{13}C NMR spectrum of compound **5b** (151 MHz, $CDCl_3$)



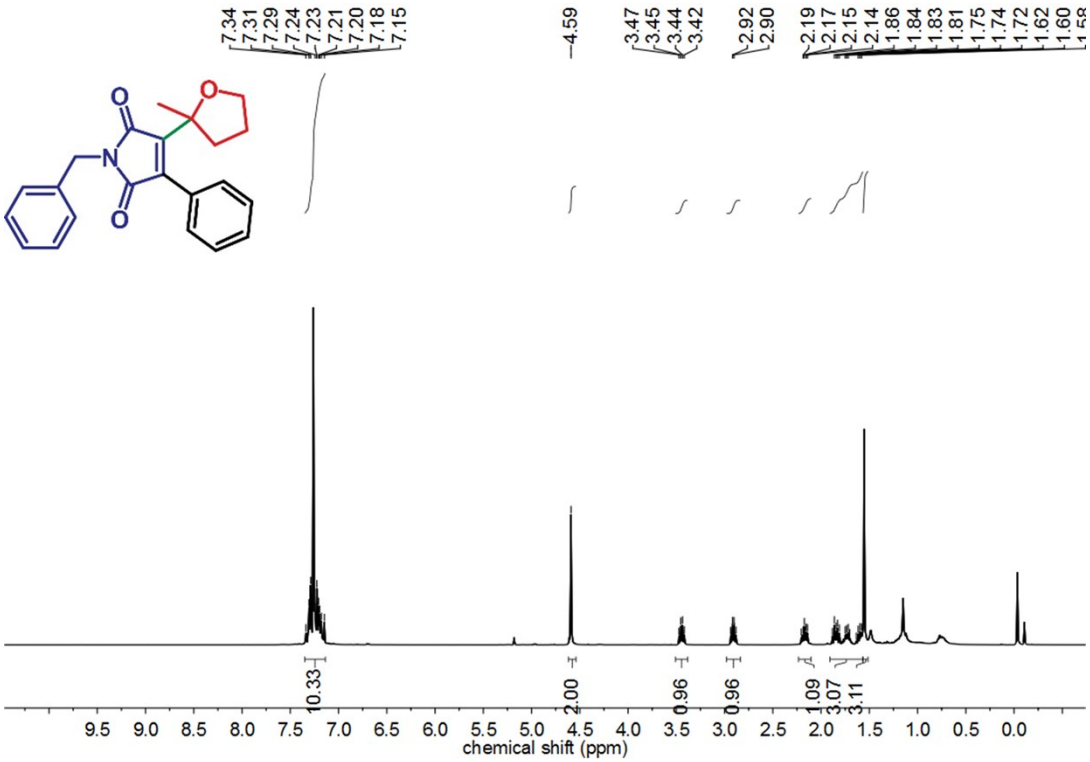
^{1}H NMR spectrum of compound **5c** (400 MHz, $CDCl_3$)



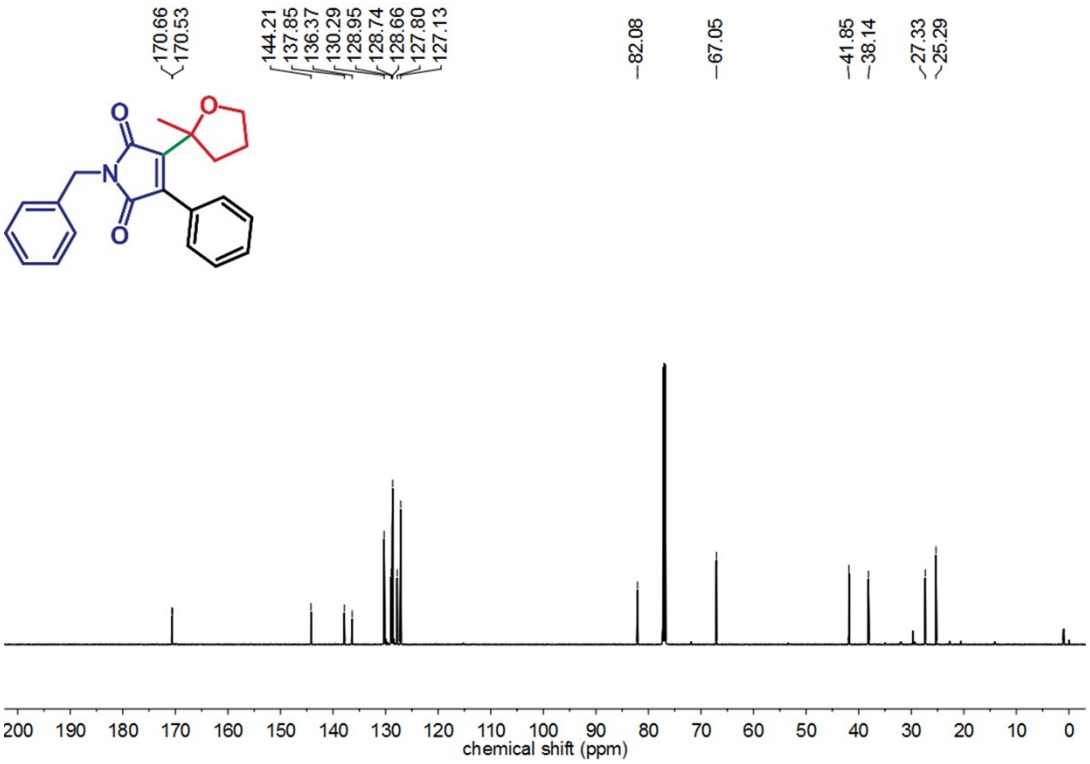
^{13}C NMR spectrum of compound **5c** (151 MHz, $CDCl_3$)



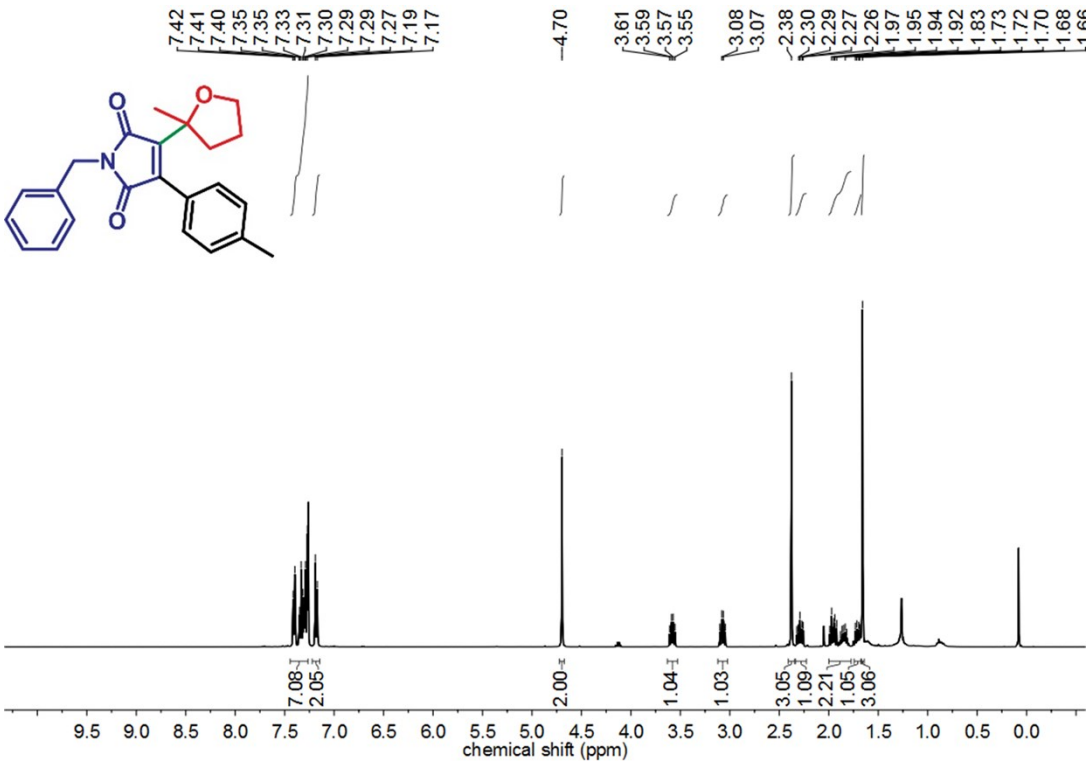
^{1}H NMR spectrum of compound **7a** (400 MHz, $CDCl_3$)



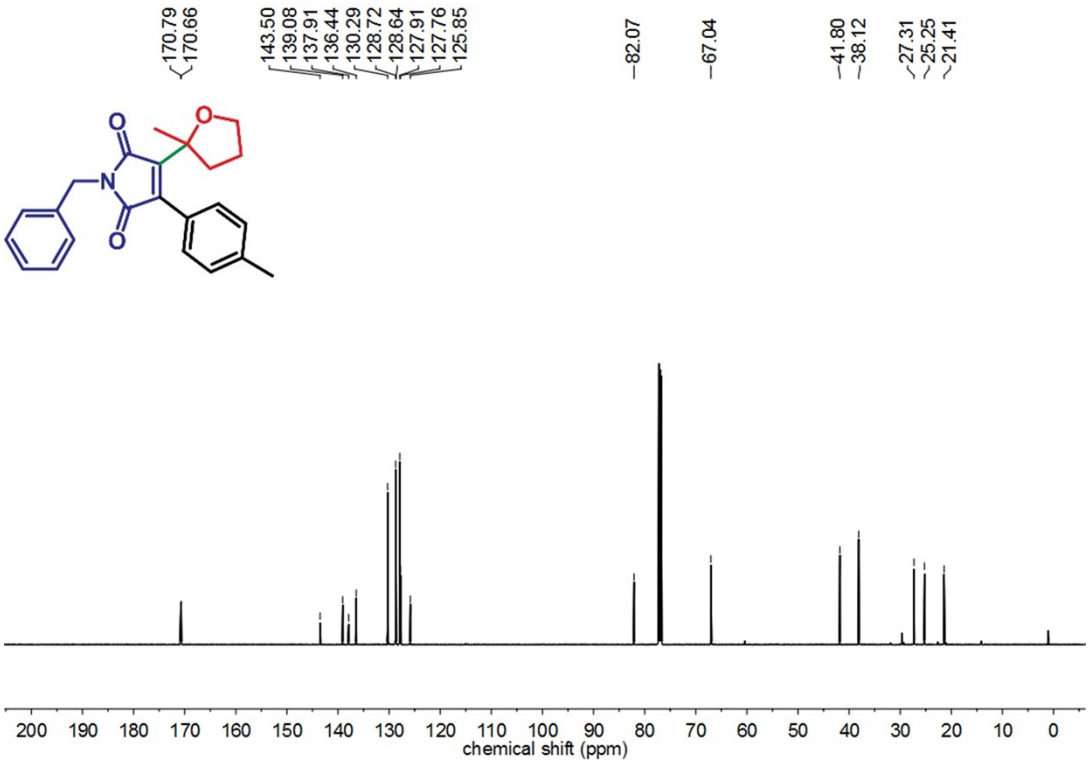
^{13}C NMR spectrum of compound **7a** (151 MHz, $CDCl_3$)



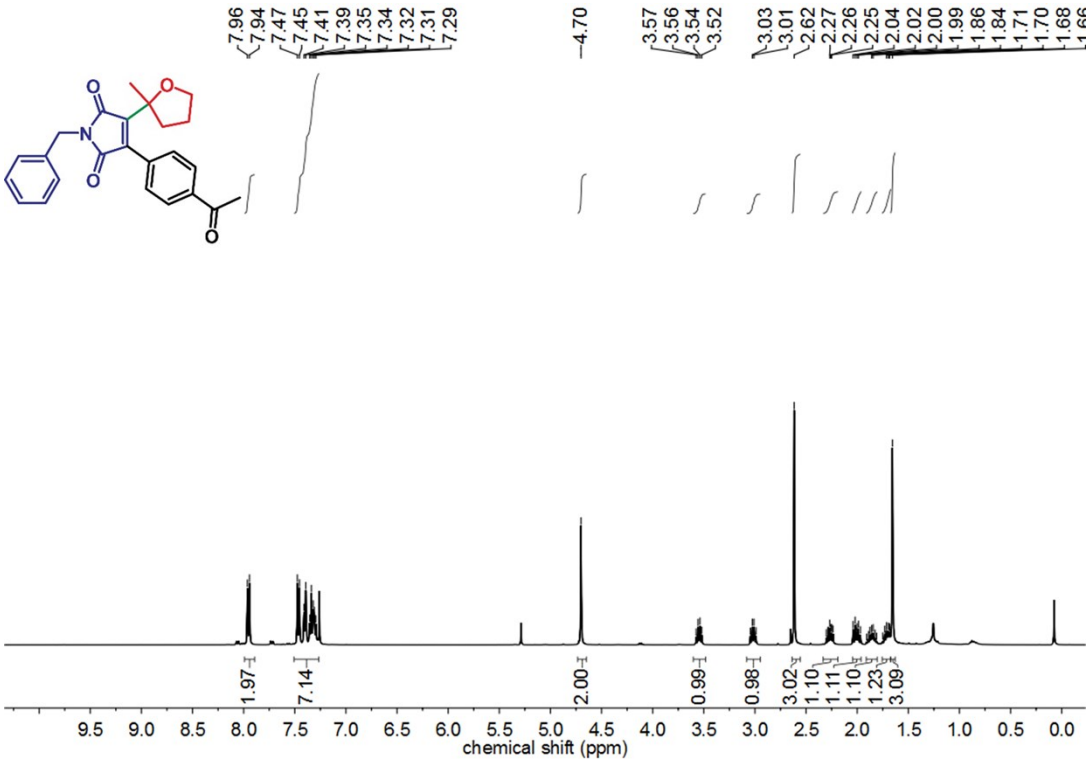
^{1}H NMR spectrum of compound **7b** (400 MHz, $CDCl_3$)



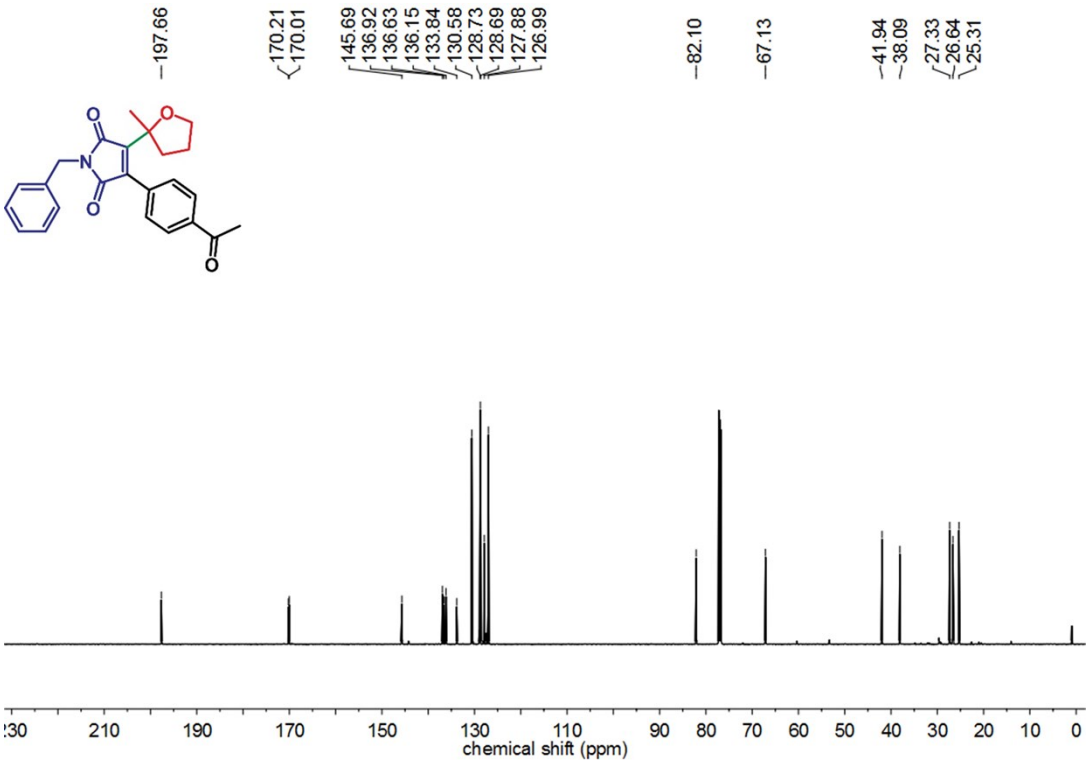
^{13}C NMR spectrum of compound **7b** (151 MHz, $CDCl_3$)



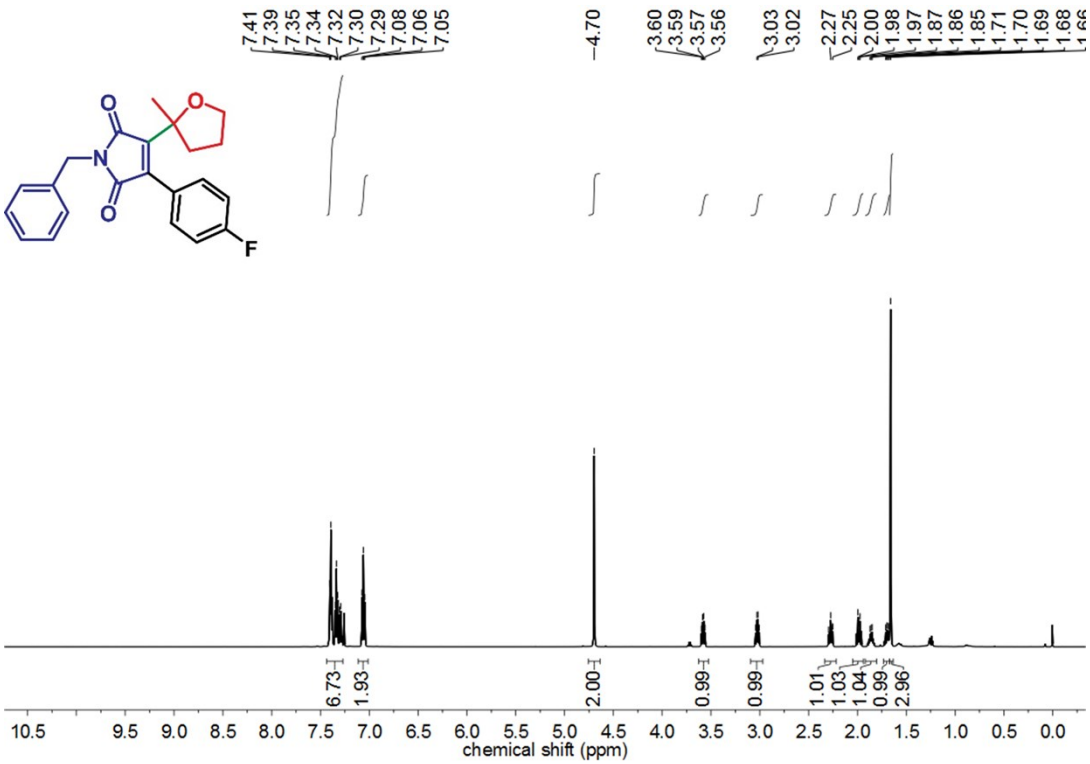
^{1}H NMR spectrum of compound **7c** (400 MHz, $CDCl_3$)



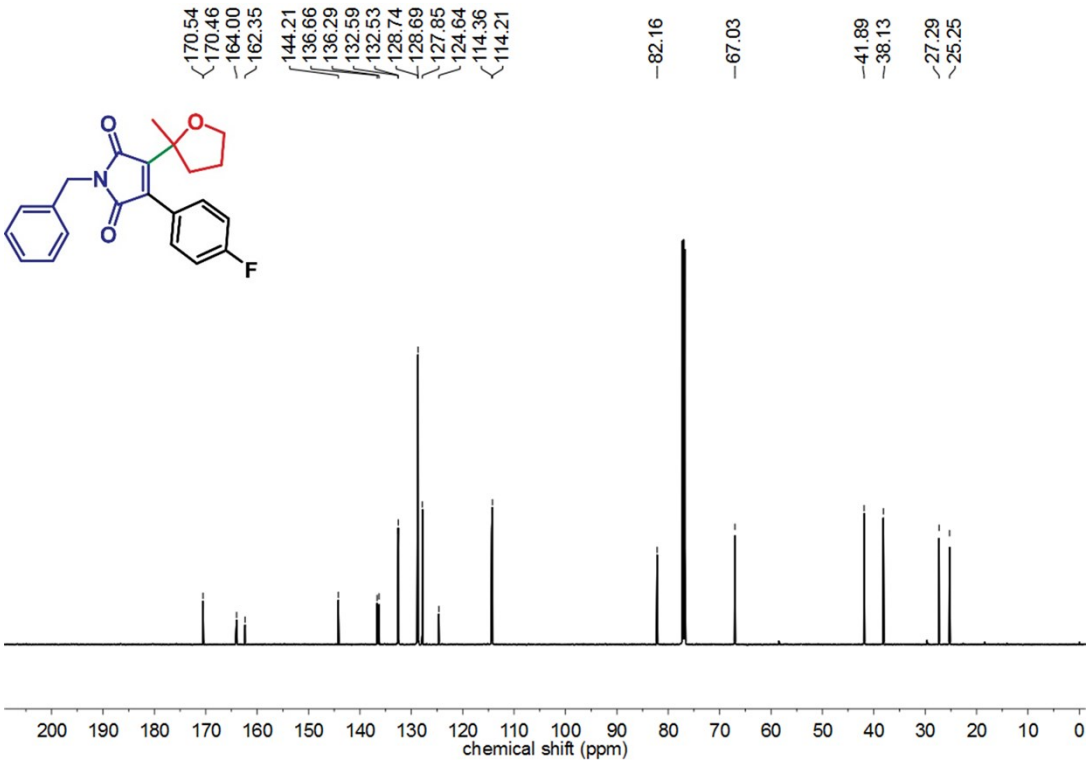
^{13}C NMR spectrum of compound **7c** (151 MHz, $CDCl_3$)



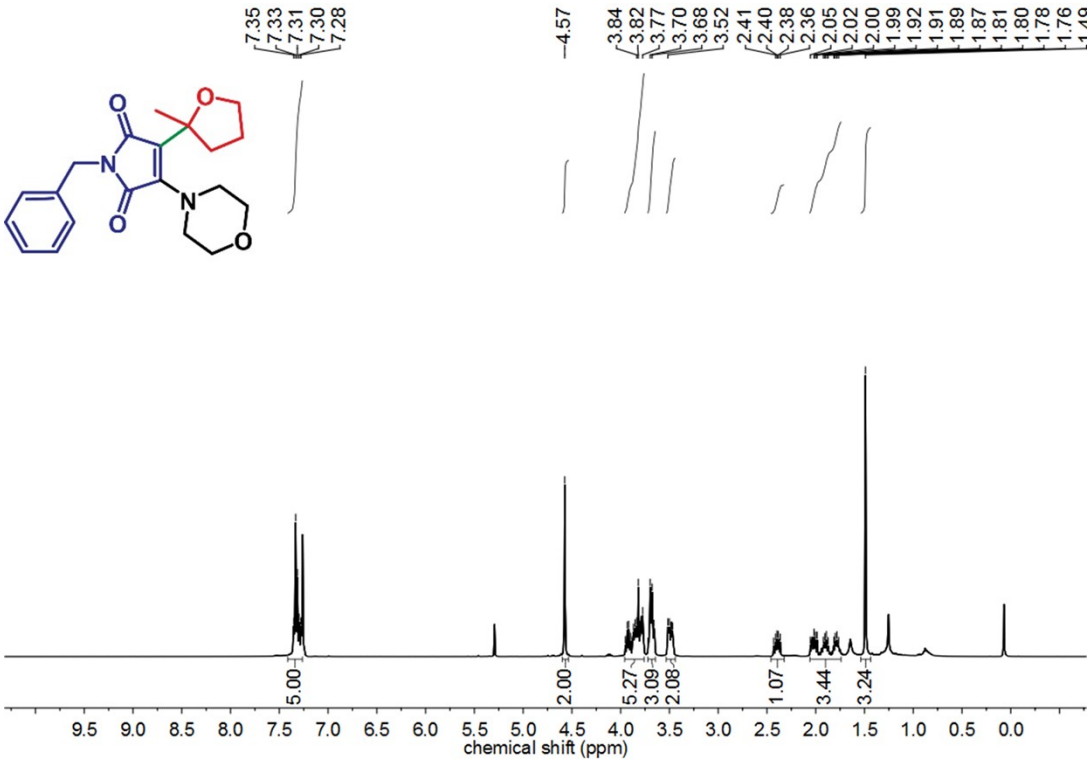
^{1}H NMR spectrum of compound **7d** (600 MHz, $CDCl_3$)



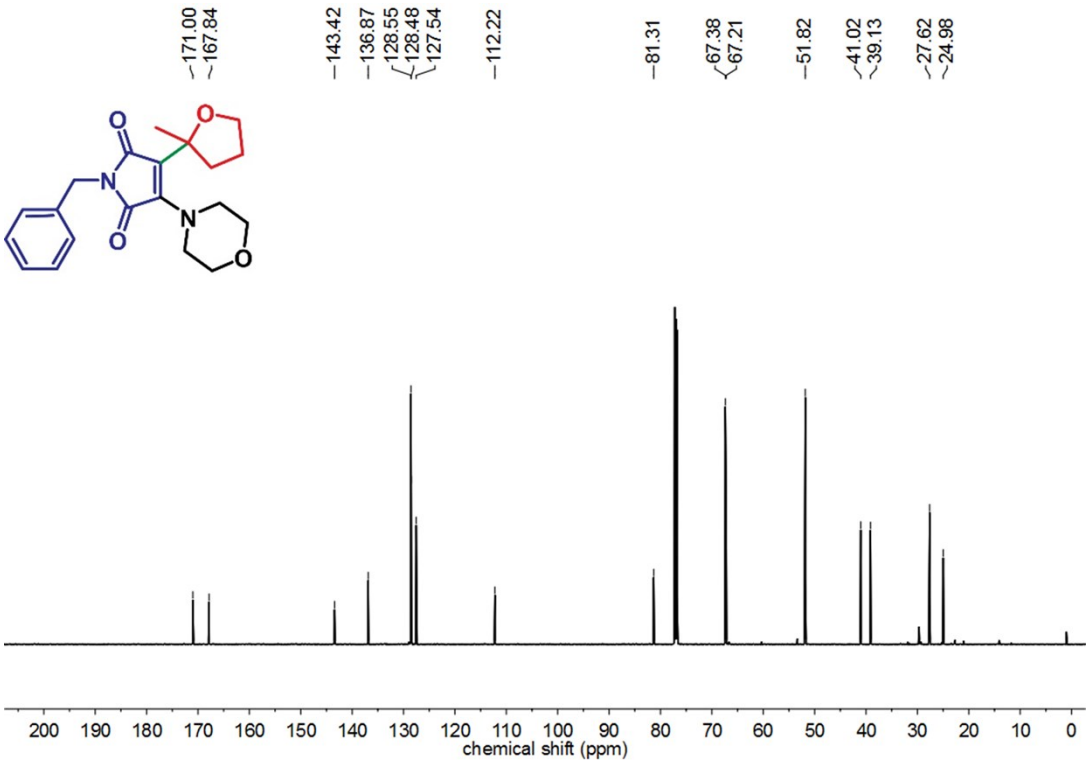
^{13}C NMR spectrum of compound **7d** (151 MHz, $CDCl_3$)



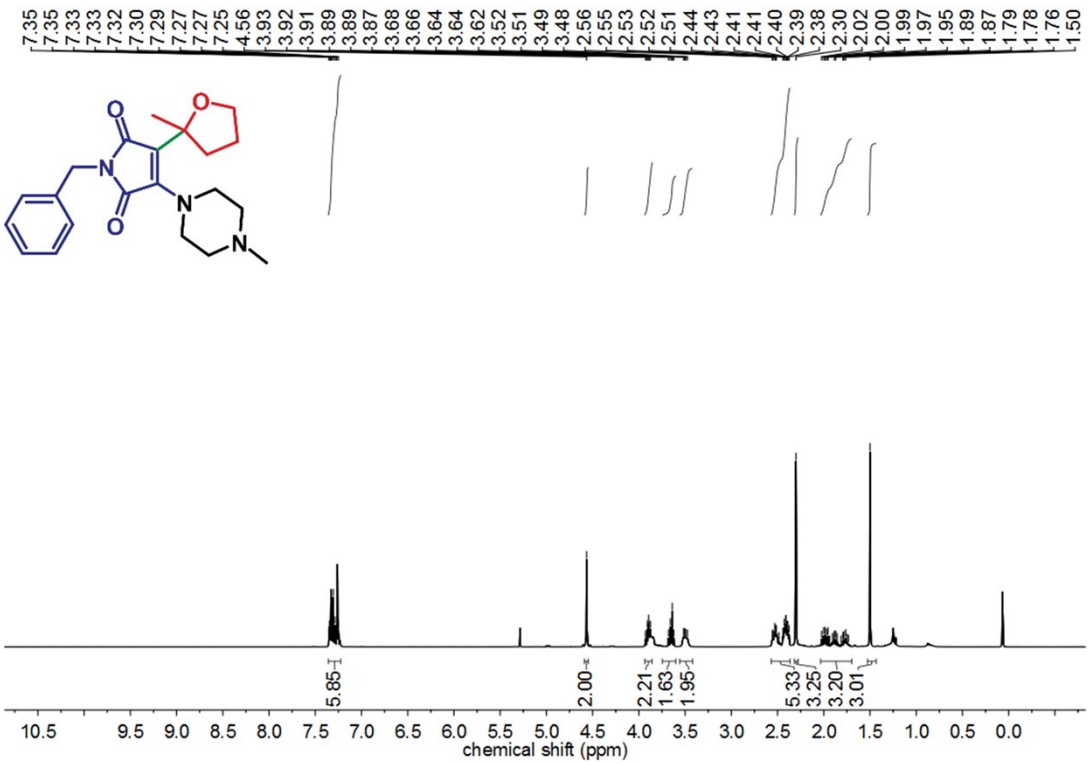
^{1}H NMR spectrum of compound **9a** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of compound **9a** (151 MHz, $CDCl_3$)



^{1}H NMR spectrum of compound **9b** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of compound **9b** (151 MHz, $CDCl_3$)