Visible-Light-Mediated Substituent-Controlled Regiodivergent (2 + 2)/(3 + 2) Cycloadditions for the Synthesis of Aza-analogs of β-Lactam and γ-fused Lactam Derivatives

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Supporting Information

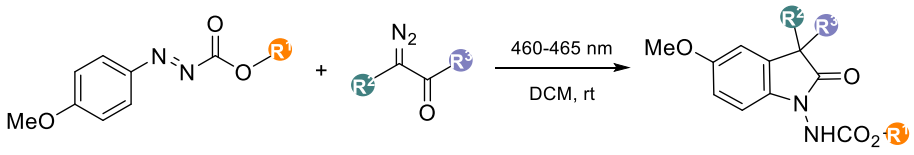
1. General methods

Nuclear magnetic resonance (NMR) spectra were recorded in $CDCl_3$ and DMSO-d_6 on Bruker 600 MHz (at 600 MHz for ^1H, and at 150 MHz for ^{13}C). The ^1H NMR chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as standard. The ^{13}C NMR chemical shifts were given using $CDCl_3$ as the internal standard ($CDCl_3$: δ = 77.2 ppm and DMSO-d_6: δ = 39.5 ppm). High-resolution mass spectra (HRMS) were obtained using Agilent P/N G1969-90010. High-resolution mass spectra were reported for the molecular ion $[M+H]^+$ or $[M+Na]^+$. Melting points were recorded on BUCHI Melting Point M-565 instrument. X-ray diffraction experiment was carried out on an Agilent D8 QUEST and the data obtained were deposited at the Cambridge Crystallographic Data Centre. UV detection was performed at 254 nm. TLC was performed on glass-backed silica plates; products were visualized using UV light. All reagents and solvents were obtained from commercial sources and used without further purification. azo esters **1**[1], α-diazo ketones **2**[2] and azonaphthalenes **4**[1] were prepared according to the literature procedures.

Reference

1. L.-W. Qi, J.-H. Mao, J. Zhang and B. Tan, *Nature Chem.*, 2018, **10**, 58-64.
2. J. R. Denton and H. M. L. Davies, *Org. Lett.*, 2009, **11**, 787-790.

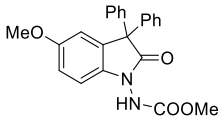
2. General procedure for synthesis of product 3



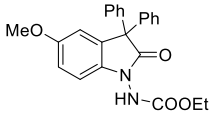
1, 0.15 mmol **2**, 0.225 mmol **3**

A mixture of 4-methoxyazobenzenes **1** (0.15 mmol) and α-diazo ketones **2** (0.225 mmol) was stirred in CH_2Cl_2 (1.0 mL) at room temperature and then irradiated under blue LEDs for hours. After the reaction completed (monitored by TLC), the reaction mixture was purified by column chromatography to afford the desired products **3** as white solids.

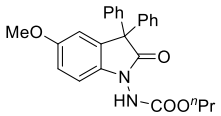
Analytical data of compounds 3



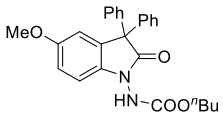
3a ***Methyl (5-methoxy-2-oxo-3,3-diphenylindolin-1-yl)carbamate (3a):*** The residue was purified by flash chromatography (PE/EA = 5/1) giving the product **3a** as a white solid in 74% yield (43.0 mg), m. p. 199.1-200.7 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.35 – 7.27 (m, 10H), 7.03 (s, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 6.86 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.83 (d, *J* = 3.0 Hz, 1H), 3.84 (s, 3H), 3.77 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.7, 134.8, 131.6, 128.54, 128.52, 127.5, 113.6, 112.9, 109.1, 61.5, 55.8, 53.6. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{23}H_{20}N_2O_4Na$ 411.1315; found 411.1310.



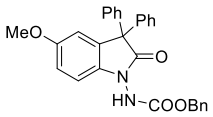
3b ***Ethyl (5-methoxy-2-oxo-3,3-diphenylindolin-1-yl)carbamate (3b):*** The residue was purified by flash chromatography (PE/EA = 5/1) giving the product **3b** as a white solid in 62% yield (37.4 mg), m. p. 157.6-159.1 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.34 – 7.24 (m, 10H), 7.00 – 6.87 (m, 2H), 6.83 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.80 (d, *J* = 2.4 Hz, 1H), 4.26 (s, 2H), 3.74 (s, 3H), 1.40 – 1.08 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.6, 134.9, 131.6, 128.53, 128.50, 127.5, 113.6, 112.9, 109.1, 62.9, 61.5, 55.8, 14.3. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{24}H_{22}N_2O_4Na$ 425.1472; found 425.1472.



3c ***Propyl (5-methoxy-2-oxo-3,3-diphenylindolin-1-yl)carbamate (3c):*** The residue was purified by flash chromatography (PE/EA = 5/1) giving the product **3c** as a white solid in 64% yield (40.0 mg), m. p. 75.2-77.1 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.32 – 7.30 (m, 2H), 7.28 – 7.23 (m, 9H), 6.91 (d, *J* = 8.4 Hz, 1H), 6.82 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.79 (d, *J* = 2.4 Hz, 1H), 4.14 (s, 2H), 3.73 (s, 3H), 1.75 – 1.43 (m, 2H), 0.98 – 0.65 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.5, 156.7, 138.3, 134.9, 131.6, 128.7, 128.6, 128.5, 128.54, 127.53, 127.4, 113.5, 112.9, 109.2, 68.4, 61.6, 55.8, 22.1, 10.1. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{25}H_{24}N_2O_4Na$ 439.1628; found 439.1624.

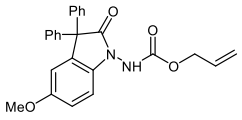


3d ***Butyl (5-methoxy-2-oxo-3,3-diphenylindolin-1-yl)carbamate (3d):*** The residue was purified by flash chromatography (PE/EA = 5/1) giving the product **3d** as a white solid in 62% yield (40.0 mg), m. p. 82.4-84.2 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.33 – 7.22 (m, 10H), 7.17 (s, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.82 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.79 (d, *J* = 2.4 Hz, 1H), 4.19 (s, 2H), 3.73 (s, 3H), 1.68 – 1.22 (m, 4H), 0.96 – 0.81 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.4, 132.7, 129.3, 126.3, 126.2, 125.2, 111.3, 110.6, 106.9, 64.4, 59.3, 53.5, 28.4, 16.6, 11.4. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{26}H_{26}N_2O_4Na$ 453.1785; found 453.1782.



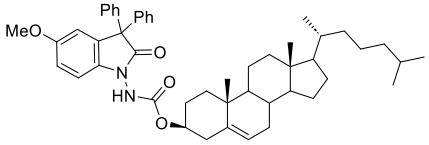
3e

Benzyl (5-methoxy-2-oxo-3,3-diphenylindolin-1-yl)carbamate (3e): The residue was purified by flash chromatography (PE/EA = 5/1) giving the product **3e** as a white solid in 56% yield (39.0 mg), m. p. 84.0-85.9 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.39 – 7.09 (m, 15H), 6.96 (s, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.75 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.72 (d, *J* = 2.4 Hz, 1H), 5.16 (s, 2H), 3.66 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.7, 134.8, 131.6, 128.7, 128.5, 127.5, 113.6, 112.9, 109.1, 68.5, 61.5, 55.8. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{29}H_{24}N_2O_4Na$ 487.1628; found 487.1623.



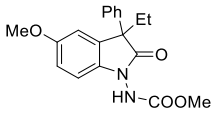
3f

Allyl (5-methoxy-2-oxo-3,3-diphenylindolin-1-yl)carbamate (3f): The residue was purified by flash chromatography (PE/EA = 5/1) giving the product **3f** as a white solid in 70% yield (43.5 mg), m. p. 84.2-86.0 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.26 – 7.15 (m, 10H), 6.96 (s, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.76 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.73 (d, *J* = 2.4 Hz, 1H), 5.87 (s, 1H), 5.36 – 5.09 (m, 2H), 4.63 (s, 2H), 3.67 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.7, 134.8, 131.6, 128.5, 127.5, 118.8, 113.6, 112.9, 109.1, 67.3, 61.5, 55.8. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{25}H_{22}N_2O_4Na$ 437.1472; found 437.1471.



3g

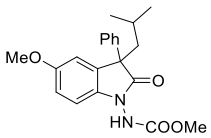
(3S,10R,13R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl (5-methoxy-2-oxo-3,3-diphenylindolin-1-yl)carbamate (3g): The residue was purified by flash chromatography (PE/EA = 5/1) giving the product **3g** as a white solid in 60% yield (67.3 mg), m. p. 206.9-208.8 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.27 – 7.24 (m, 5H), 7.23 – 7.21 (m, 4H), 7.20 – 7.19 (m, 1H), 6.99 (s, 1H), 6.86 (d, *J* = 9.0 Hz, 1H), 6.76 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.73 (d, *J* = 2.4 Hz, 1H), 5.29 (s, 1H), 4.98 (s, 1H), 4.55 (s, 1H), 3.68 (s, 3H), 2.40 – 2.08 (m, 2H), 1.97 – 1.72 (m, 5H), 1.55 – 1.15 (m, 12H), 1.11 – 0.96 (m, 7H), 0.95 – 0.88 (m, 4H), 0.84 (d, *J* = 6.6 Hz, 3H), 0.80 – 0.76 (m, 6H), 0.60 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.4, 156.6, 139.2, 138.0, 134.9, 128.70, 128.68, 128.6, 128.5, 127.5, 123.0, 113.5, 112.9, 109.1, 61.6, 56.9, 56.7, 56.1, 55.8, 50.0, 42.3, 39.7, 39.5, 36.9, 36.5, 36.2, 35.8, 31.9, 31.8, 28.2, 28.0, 24.3, 23.8, 22.8, 22.6, 21.0, 19.4, 18.7, 11.9. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{49}H_{62}N_2O_4Na$ 765.4602; found 765.4601.



3h

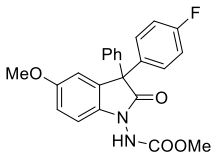
Methyl (3-ethyl-5-methoxy-2-oxo-3-phenylindolin-1-yl)carbamate (3h): The residue was purified by flash chromatography (PE/EA = 5/1) giving the product **3h** as a white solid in 51% yield (26.0 mg), m. p. 141.6-142.5 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 7.8 Hz,

2H), 7.34 – 7.17 (m, 4H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.87 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.82 (s, 1H), 3.81 (s, 6H), 2.52 (dq, *J* = 14.4, 7.2 Hz, 1H), 2.25 (dq, *J* = 14.4, 7.2 Hz, 1H), 0.78 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.7, 139.6, 135.8, 128.6, 127.5, 126.9, 112.7, 112.0, 108.8, 56.5, 55.8, 53.5, 9.0. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{19}H_{20}N_2O_4Na$ 363.1315; found 363.1313.



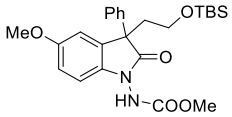
3i

Methyl (3-isobutyl-5-methoxy-2-oxo-3-phenylindolin-1-yl)carbamate (3i): The residue was purified by flash chromatography (PE/EA = 5/1) giving the product **3i** as a white solid in 57% yield (31.5 mg), m. p. 124.4-125.3 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 7.2 Hz, 2H), 7.30 – 7.28 (m, 2H), 7.25 – 7.22 (m, 1H), 7.07 (s, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.88 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.86 (s, 1H), 3.82 (s, 6H), 2.49 (dd, *J* = 13.8, 6.6 Hz, 1H), 2.19 (dd, *J* = 14.4, 6.0 Hz, 1H), 1.58 (s, 1H), 0.85 (d, *J* = 6.6 Hz, 3H), 0.71 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.5, 140.9, 135.7, 128.6, 127.4, 126.7, 112.7, 108.8, 55.9, 55.5, 53.4, 25.4, 24.3, 23.5. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{21}H_{24}N_2O_4Na$ 391.1628; found 391.1627.



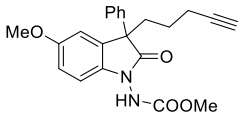
3j

Methyl (3-(4-fluorophenyl)-5-methoxy-2-oxo-3-phenylindolin-1-yl)carbamate (3j): The residue was purified by flash chromatography (PE/EA = 5/1) giving the product **3j** as a white solid in 67% yield (40.8 mg), m. p. 142.0-143.4 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.33 – 7.27 (m, 7H), 7.09 (s, 1H), 7.02 – 6.97 (m, 2H), 6.95 (d, *J* = 8.4 Hz, 1H), 6.87 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.80 (d, *J* = 2.4 Hz, 1H), 3.84 (s, 3H), 3.78 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.2(d, $J_{C,F}$ = 244.5 Hz),156.8, 155.5, 134.7, 131.5, 130.3(d, $J_{C,F}$ = 30.0 Hz), 128.7, 128.3, 127.7, 115.5, 115.3, 113.5, 113.0, 109.2, 60.9, 55.8, 53.7. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{23}H_{19}FN_2O_4Na$ 429.1221; found 429.1220.



3k

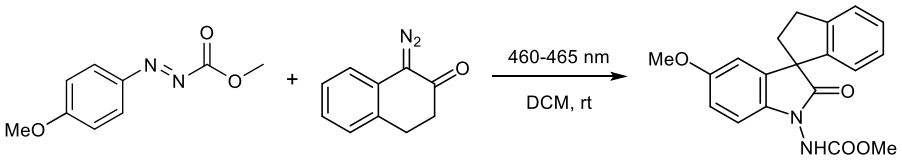
Methyl (3-(2-((tert-butyldimethylsilyl)oxy)ethyl)-5-methoxy-2-oxo-3-phenylindolin-1-yl)carbamate (3k): The residue was purified by flash chromatography (PE/EA = 5/1) giving the product **3k** as a colorless oil in 36% yield (25.2 mg). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 7.8 Hz, 2H), 7.36 – 7.32 (m, 2H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.20 (s, 1H), 6.94 (d, *J* = 9.0 Hz, 1H), 6.91 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.88 (s, 1H), 3.84 (s, 6H), 3.65 (s, 1H), 3.47 (s, 1H), 2.87 – 2.79 (m, 1H), 2.55 – 2.50 (m, 1H), 0.87 (s, 9H), 0.01 (s, 3H), 0.00 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.1, 141.0, 134.1, 133.0, 132.1, 130.7, 118.5, 117.4, 114.3, 64.9, 61.3, 59.2, 58.9, 31.3, 23.6, 0.0. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{25}H_{34}N_2O_5SiNa$ 493.2129; found 493.2127.



3l

Methyl (5-methoxy-2-oxo-3-(pent-4-yn-1-yl)-3-phenylindolin-1-yl)carbamate (3l): The residue was purified by flash chromatography (PE/EA = 5/1) giving the product **3l** as a colorless oil in 32% yield (18.4 mg). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 7.8 Hz, 2H), 7.23 (t, *J* = 7.8 Hz, 2H), 7.18 (t, *J* = 7.2 Hz, 1H), 6.97 – 6.83 (m, 2H), 6.79 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.75 (s, 1H), 3.72 (s, 6H), 2.46 (td, *J* = 13.2, 4.8 Hz, 1H), 2.29 (s, 1H), 2.14 – 2.04 (m, 2H), 1.86 (t, *J* = 2.4 Hz, 1H), 1.47 – 1.42 (m, 1H), 1.21 – 1.12 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.7, 138.3, 134.5, 127.6, 126.5, 125.7, 111.7, 111.0, 107.7, 82.6, 67.7, 54.7, 54.4, 52.4, 22.2, 17.4. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{22}H_{22}N_2O_4Na$ 401.1472; found 401.1468.

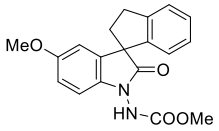
3. General procedure for synthesis of product 3m



1a, 0.15 mmol **2m**, 0.225 mmol **3m**

A mixture of 4-methoxyazobenzenes **1a** (0.15 mmol) and α-diazo ketones **2m** (0.225 mmol) was stirred in CH_2Cl_2 (1.0 mL) at room temperature and then irradiated under blue LEDs for hours. After the reaction completed (monitored by TLC), the reaction mixture was purified by column chromatography (PE/EtOAc = 5:1, v/v) to afford the desired products **3m** as white solids.

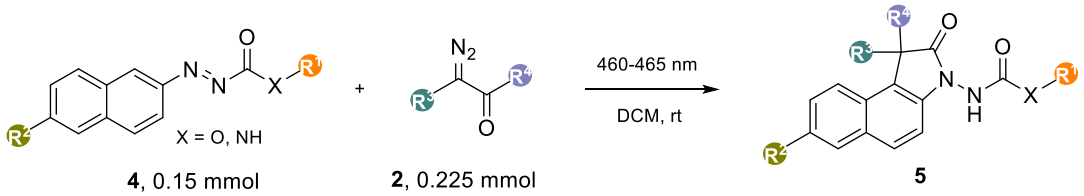
Analytical data of compounds 3m



3m

Methyl (5'-methoxy-2'-oxo-2,3-dihydrospiro[indene-1,3'-indolin]-1'-yl)carbamate (3m): The residue was purified by flash chromatography (PE/EA = 3/1) giving the product **3m** as a white solid in 15% yield (7.5 mg), m. p. 87.5-89.0 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 7.8 Hz, 1H), 7.17 (t, *J* = 7.8 Hz, 1H), 7.03 (t, *J* = 7.2 Hz, 1H), 6.90 (s, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.75 (dd, *J* = 8.4, 2.4 Hz, 2H), 6.58 (d, *J* = 3.0 Hz, 1H), 3.74 (s, 3H), 3.66 (s, 3H), 3.38 – 3.32 (m, 1H), 3.17 – 3.12 (m, 1H), 2.69 – 2.64 (m, 1H), 2.39 – 2.35 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.0, 144.8, 143.5, 135.2, 133.2, 128.2, 127.2, 125.0, 123.7, 113.0, 110.7, 108.6, 59.2, 55.8, 53.6, 37.8, 31.7. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{19}H_{18}N_2O_4Na$ 361.1159; found 361.1162.

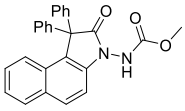
4. General procedure for synthesis of product 5



4, 0.15 mmol **2**, 0.225 mmol **5**

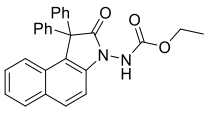
A mixture of azonaphthalenes **4** (0.15 mmol) and α-diazo ketones **2** (0.225 mmol) was stirred in CH_2Cl_2 (1.0 mL) at room temperature and then irradiated under blue LEDs for hours. After the reaction completed (monitored by TLC), the reaction mixture was purified by column chromatography to afford the desired products **5** as white solids.

Analytical data of compounds 5



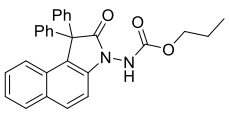
5a

Methyl (2-oxo-1,1-diphenyl-1,2-dihydro-3H-benzo[e]indol-3-yl)carbamate (5a): The residue was purified by flash chromatography (PE/EA = 8/1) giving the product **5a** as a white solid in 91% yield (55.6 mg), m. p. 192.7-193.9 °C. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.82 (d, *J* = 9.0 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.32 – 7.28 (m, 4H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.21 – 7.11 (m, 9H), 3.71 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.0, 154.7, 138.5, 137.3, 130.2, 129.6, 128.9, 128.4, 128.3, 127.7, 127.6, 127.3, 126.6, 126.1, 122.9, 122.4, 121.8, 108.6, 61.0, 52.6. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{26}H_{20}N_2O_3Na$ 431.1366; found 431.1369.



5b

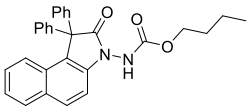
***Ethyl (2-oxo-1,1-diphenyl-1,2-dihydro-3H-benzo[e]indol-3-yl)carbamate (5b)*:** The residue was purified by flash chromatography (PE/EA = 8/1) giving the product **5b** as a white solid in 88% yield (55.8 mg), m. p. 166.3-167.8 °C. ^{1}H NMR (700 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 9.1 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.42 – 7.41 (m, 3H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.29 (t, *J* = 7.7 Hz, 1H), 7.26 – 7.17 (m, 8H), 7.09 (s, 1H), 4.28 – 4.10 (m, 2H), 1.32 – 1.10 (m, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 178.9, 155.3, 139.7, 131.3, 130.6, 130.0, 129.5, 129.4, 128.4, 127.6, 127.1, 123.9, 123.5, 122.8, 109.6, 63.0, 62.0, 14.3. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{27}H_{22}N_2O_3Na$ 445.1523; found 445.1526.



5c

***Propyl (2-oxo-1,1-diphenyl-1,2-dihydro-3H-benzo[e]indol-3-yl)carbamate (5c)*:** The residue was purified by flash chromatography (PE/EA = 8/1) giving the product **5c** as a white solid

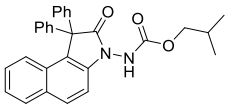
in 82% yield (53.6 mg), m. p. 192.4-194.1 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.46 – 7.33 (m, 5H), 7.32 – 7.26 (m, 5H), 7.25 – 7.21 (m, 3H), 7.01 (s, 1H), 4.21 (s, 2H), 1.76 – 1.56 (m, 2H), 1.06 – 0.60 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.0, 155.4, 139.7, 131.3, 130.6, 130.0, 129.5, 129.3, 128.4, 127.7, 127.2, 124.0, 123.5, 122.9, 109.5, 68.6, 62.1, 22.1, 10.2. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{28}H_{24}N_2O_3Na$ 459.1679; found 459.1678.



5d

***Butyl (2-oxo-1,1-diphenyl-1,2-dihydro-3H-benzo[e]indol-3-yl)carbamate (5d)*:**

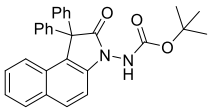
The residue was purified by flash chromatography (PE/EA = 8/1) giving the product **5d** as a white solid in 87% yield (58.5 mg), m. p. 146.5-147.7 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 9.0 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.46 – 7.35 (m, 5H), 7.32 – 7.27 (m, 5H), 7.25 – 7.22 (m, 3H), 6.95 (s, 1H), 4.24 (s, 2H), 1.69 (s, 2H), 1.43 (s, 2H), 0.96 – 0.80 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.5, 155.4, 139.7, 131.3, 130.6, 130.0, 129.5, 129.4, 128.4, 127.7, 127.2, 124.0, 123.5, 122.9, 109.5, 66.9, 62.1, 30.7, 18.9, 13.7. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{29}H_{26}N_2O_3Na$ 473.1836; found 473.1838.



5e

***Isobutyl (2-oxo-1,1-diphenyl-1,2-dihydro-3H-benzo[e]indol-3-yl)carbamate (5e)*:**

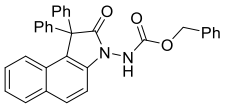
The residue was purified by flash chromatography (PE/EA = 8/1) giving the product **5e** as a white solid in 80% yield (54.3 mg), m. p. 149.2-151.0 °C. ^{1}H NMR (700 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 7.7 Hz, 1H), 7.40 (d, *J* = 9.1 Hz, 1H), 7.36 – 7.33 (m, 3H), 7.31 – 7.30 (m, 1H), 7.23 (t, *J* = 7.7 Hz, 1H), 7.20 – 7.16 (m, 8H), 6.91 (s, 1H), 3.96 (s, 2H), 1.31 – 1.15 (m, 1H), 0.91 – 0.58 (m, 6H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 177.8, 154.4, 138.6, 130.2, 129.6, 129.0, 128.4, 127.4, 126.6, 126.1, 122.9, 122.5, 121.8, 108.5, 71.9, 61.0, 26.8, 17.8. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{29}H_{26}N_2O_3Na$ 473.1836; found 473.1836.



5f

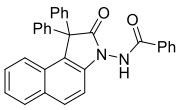
***Tert-butyl (2-oxo-1,1-diphenyl-1,2-dihydro-3H-benzo[e]indol-3-yl)carbamate (5f)*:**

The residue was purified by flash chromatography (PE/EA = 8/1) giving the product **5f** as a white solid in 82% yield (55.5 mg), m. p. 129.1-130.5 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 9.0 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.36 – 7.31 (m, 3H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.25 – 7.11 (m, 9H), 6.76 (s, 1H), 1.56 – 1.25 (m, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.5, 154.1, 139.9, 138.4, 131.2, 130.6, 130.0, 129.5, 129.3, 128.7, 128.6, 128.4, 127.6, 127.4, 127.1, 123.9, 123.5, 122.8, 109.6, 83.0, 62.1, 56.8, 28.1. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{29}H_{26}N_2O_3Na$ 473.1836; found 473.1845.



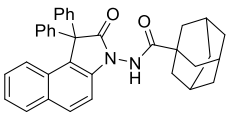
5g

***EBenzyl (2-oxo-1,1-diphenyl-1,2-dihydro-3H-benzo[e]indol-3-yl)carbamate (5g)*:** The residue was purified by flash chromatography (PE/EA = 8/1) giving the product **5g** as a white solid in 83% yield (60.3 mg), m. p. 117.4-119.3 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.54 – 7.41 (m, 7H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.34 – 7.19 (m, 10H), 7.15 (s, 1H), 5.30 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.9, 155.1, 139.6, 131.3, 130.7, 130.0, 129.5, 128.7, 128.4, 127.7, 127.2, 124.0, 123.5, 122.9, 68.6, 62.1. HRMS (ESI-TOF) m/z $[M + Na]^+$ Calcd for $C_{32}H_{24}N_2O_3Na$ 507.1679; found 507.1679.



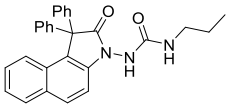
5h

***N-(2-oxo-1,1-diphenyl-1,2-dihydro-3H-benzo[e]indol-3-yl)benzamide (5h)*:** The residue was purified by flash chromatography (PE/EA = 8/1) giving the product **5h** as a white solid in 80% yield (54.6 mg), m. p. 259.1-261.0 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 9.19 – 9.06 (m, 1H), 7.95 (d, *J* = 7.8 Hz, 2H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.48 – 7.39 (m, 7H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.28 – 7.24 (m, 2H), 7.23 – 7.15 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.8, 166.2, 139.6, 132.8, 131.3, 130.8, 130.5, 130.0, 129.4, 129.3, 128.8, 128.4, 127.7, 127.6, 127.1, 123.9, 123.5, 123.2, 109.9, 62.5. HRMS (ESI-TOF) m/z $[M + Na]^+$ Calcd for $C_{31}H_{22}N_2O_2Na$ 477.1573; found 477.1575.



5i

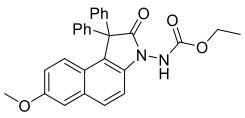
***N-(2-oxo-1,1-diphenyl-1,2-dihydro-3H-benzo[e]indol-3-yl)adamantane-1-carboxamide (5i)*:** The residue was purified by flash chromatography (PE/EA = 25/1) giving the product **5i** as a white solid in 65% yield (49.8 mg), m. p. 295.5-297.5 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 9.0 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.80 (s, 1H), 7.49 – 7.42 (m, 5H), 7.30 – 7.25 (m, 4H), 7.25 – 7.20 (m, 4H), 7.15 (d, *J* = 9.0 Hz, 1H), 2.13 – 2.10 (m, 3H), 2.09 – 2.06 (m, 6H), 1.82 – 1.75 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.6, 176.9, 139.7, 131.2, 130.4, 130.0, 129.41, 129.39, 128.4, 127.6, 127.1, 123.8, 123.4, 123.1, 109.4, 62.3, 40.8, 39.0, 36.3, 27.9. HRMS (ESI-TOF) m/z $[M + Na]^+$ Calcd for $C_{35}H_{32}N_2O_2Na$ 535.2356; found 535.2357.



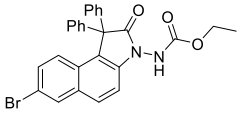
5j

***1-(2-oxo-1,1-diphenyl-1,2-dihydro-3H-benzo[e]indol-3-yl)-3-propylurea (5j)*:** The residue was purified by flash chromatography (PE/EA = 6/1) giving the product **5j** as a white solid in 86% yield (56.1 mg), m. p. 269.7-271.7 ℃. ^{1}H NMR (700 MHz, DMSO-d_6) δ 8.97 (s, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.94 (dd, *J* = 7.0, 2.1 Hz, 1H), 7.49 – 7.43 (m, 2H), 7.38 (dd, *J* = 7.0, 2.1 Hz, 1H), 7.34 – 7.27 (m, 9H), 7.24 (s, 1H), 6.91 (t, *J* = 5.6 Hz, 1H), 3.07 (p, *J* = 6.3 Hz, 2H), 1.48 (m, 2H), 0.88 (t, *J* =

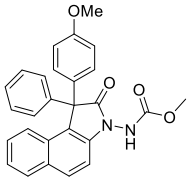
7.7 Hz, 3H). ^{13}C NMR (176 MHz, DMSO) δ 178.0, 156.2, 141.3, 140.8, 137.6, 130.4, 130.3, 129.5, 129.1, 129.0, 128.8, 128.2, 127.6, 127.1, 127.0, 123.4, 122.4, 121.8, 110.2, 61.4, 41.3, 22.8, 11.2. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{28}H_{25}N_3O_2Na$ 458.1839; found 458.1842.



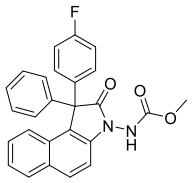
5k ***Ethyl (7-methoxy-2-oxo-1,1-diphenyl-1,2-dihydro-3H-benzo[e]indol-3-yl)carbamate (5k)*****:** The residue was purified by flash chromatography (PE/EA = 8/1) giving the product **5k** as a white solid in 82% yield (55.7 mg), m. p. 192.1-194.0 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 8.4 Hz, 1H), 7.47 – 7.36 (m, 5H), 7.33 (d, *J* = 9.0 Hz, 1H), 7.29 – 7.23 (m, 6H), 7.15 (d, *J* = 3.0 Hz, 1H), 7.00 (s, 1H), 6.94 (dd, *J* = 9.0, 2.4 Hz, 1H), 4.30 (s, 2H), 3.86 (s, 3H), 1.38 – 1.08 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.0, 156.1, 155.3, 137.8, 132.5, 129.4, 129.1, 128.4, 127.6, 125.5, 124.9, 123.3, 120.1, 109.9, 107.3, 63.0, 62.1, 55.3, 14.3. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{28}H_{24}N_2O_4Na$ 475.1628; found 475.1627.



5l ***Ethyl (7-bromo-2-oxo-1,1-diphenyl-1,2-dihydro-3H-benzo[e]indol-3-yl)carbamate (5l)*****:** The residue was purified by flash chromatography (PE/EA = 8/1) giving the product **5l** as a white solid in 78% yield (58.4 mg), m. p. 202.8-204.1 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.03 (s, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.45 – 7.38 (m, 5H), 7.37 – 7.27 (m, 8H), 7.03 (s, 1H), 4.32 (s, 2H), 1.49 – 1.09 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.7, 155.2, 140.1, 132.4, 131.3, 130.6, 129.8, 129.3, 128.5, 128.4, 127.9, 125.1, 123.2, 117.8, 110.7, 63.2, 61.9, 14.3. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{27}H_{21}BrN_2O_3Na$ 523.0628; found 523.0626.

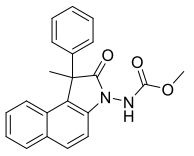


5m ***Methyl (1-(4-methoxyphenyl)-2-oxo-1-phenyl-1,2-dihydro-3H-benzo[e]indol-3-yl)carbamate (5m)*****:** The residue was purified by flash chromatography (PE/EA = 6/1) giving the product **5m** as a white solid in 71% yield (46.8 mg), m. p. 234.8-236.7 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.45 – 7.39 (m, 2H), 7.36 (d, *J* = 9.0 Hz, 1H), 7.36 – 7.25 (m, 5H), 7.26 – 7.22 (m, 2H), 7.07 (s, 1H), 6.83 – 6.78 (m, 2H), 3.85 (s, 3H), 3.74 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.0, 159.0, 155.7, 139.5, 131.3, 130.6, 130.0, 129.5, 129.2, 128.4, 127.6, 127.2, 124.0, 123.5, 123.1, 113.8, 109.5, 61.4, 55.2, 53.7. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{27}H_{22}N_2O_4Na$ 461.1472; found 461.1478.



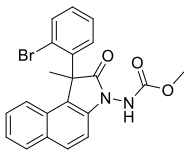
5n

***Methyl (1-(4-fluorophenyl)-2-oxo-1-phenyl-1,2-dihydro-3H-benzo[e]indol-3-yl)carbamate (5n)*:** The residue was purified by flash chromatography (PE/EA = 6/1) giving the product **5n** as a white solid in 70% yield (45.0 mg), m. p. 217.9-219.7 ℃. ^{1}H NMR (700 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.39 – 7.36 (m, 4H), 7.33 (d, *J* = 9.1 Hz, 1H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.26 – 7.21 (m, 5H), 6.93 (t, *J* = 8.4 Hz, 2H), 3.82 (s, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 179.0, 162.1 (d, $J_{C,F}$ = 248.5 Hz), 155.7, 139.6, 131.3, 131.1, 130.8, 129.8, 129.6, 129.2, 128.5, 127.8, 127.3, 124.1, 123.2, 122.6, 115.2(d, $J_{C,F}$ = 21.1 Hz), 109.6, 61.4, 53.7. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{26}H_{19}FN_2O_3Na$ 449.1272; found 449.1274.



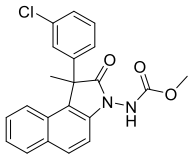
5o

***Methyl (1-methyl-2-oxo-1-phenyl-1,2-dihydro-3H-benzo[e]indol-3-yl)carbamate (5o)*:** The residue was purified by flash chromatography (PE/EA = 6/1) giving the product **5o** as a white solid in 79% yield (41.2 mg), m. p. 107.2-108.9 ℃. ^{1}H NMR (700 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 9.1 Hz, 1H), 7.89 – 7.85 (m, 1H), 7.42 – 7.38 (m, 1H), 7.36 – 7.26 (m, 8H), 7.27 – 7.22 (m, 1H), 3.81 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 179.2, 155.6, 139.5, 139.2, 131.4, 129.9, 129.6, 129.0, 128.8, 127.6, 127.2, 127.0, 124.0, 122.8, 109.4, 53.6, 52.0, 22.4. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{21}H_{18}N_2O_3Na$ 369.1210; found 369.1218.



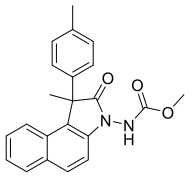
5p

***Methyl (1-(2-bromophenyl)-1-methyl-2-oxo-1,2-dihydro-3H-benzo[e]indol-3-yl)carbamate (5p)*:** The residue was purified by flash chromatography (PE/EA = 6/1) giving the product **5p** as a white solid in 73% yield (45.0 mg), m. p. 145.2-146.7 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.99 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.56 (td, *J* = 7.8, 1.2 Hz, 1H), 7.47 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.32 – 7.27 (m, 2H), 7.26 – 7.22 (m, 2H), 7.21 (d, *J* = 8.4 Hz, 1H), 3.88 (s, 3H), 2.07 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.2, 155.9, 139.8, 138.8, 134.5, 131.2, 130.1, 129.7, 129.6, 128.5, 127.8, 127.1, 124.1, 123.8, 122.9, 121.2, 109.4, 60.4, 53.5, 21.1. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{21}H_{17}BrN_2O_3Na$ 447.0315; found 447.0319.



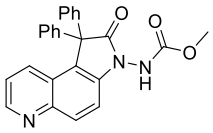
5q

***Methyl (1-(3-chlorophenyl)-1-methyl-2-oxo-1,2-dihydro-3H-benzo[e]indol-3-yl)carbamate (5q)*:** The residue was purified by flash chromatography (PE/EA = 6/1) giving the product **5q** as a white solid in 63% yield (36.0 mg), m. p. 165.8-167.1 ℃. ^{1}H NMR (700 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 8.4 Hz, 1H), 7.80 – 7.77 (m, 1H)., 7.51 (s, 1H), 7.31 – 7.22 (m, 5H), 7.14 – 6.98 (m, 3H), 3.71 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 178.8, 155.7, 141.3, 139.6, 134.7, 131.4, 130.3, 130.1, 130.0, 129.7, 128.8, 127.9, 127.4, 127.3, 125.4, 124.2, 123.5, 122.5, 109.5, 53.7, 51.7, 22.3. HRMS (ESI-TOF) m/z [M + Na]$^{+}$ Calcd for $C_{21}H_{17}ClN_2O_3Na$ 403.0820; found 403.0828.



5r

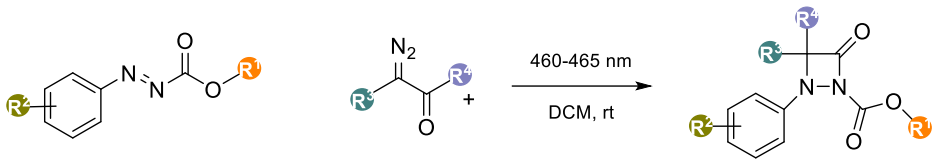
***Methyl (1-methyl-2-oxo-1-(p-tolyl)-1,2-dihydro-3H-benzo[e]indol-3-yl)carbamate (5r)*:** The residue was purified by flash chromatography (PE/EA = 6/1) giving the product **5r** as a white solid in 87% yield (47.0 mg), m. p. 103.1-104.9 ℃. ^{1}H NMR (700 MHz, Chloroform-*d*) δ 7.94 – 7.91 (m, 1H), 7.90 – 7.87 (m, 1H), 7.59 (s, 1H), 7.45 – 7.43 (m, 1H), 7.37 – 7.33 (m, 3H), 7.20 (d, *J* = 7.7 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 3.83 (s, 3H), 2.29 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 179.4, 155.7, 139.5, 137.2, 136.2, 131.3, 129.8, 129.54, 129.49, 129.0, 127.1, 126.9, 124.3, 124.0, 122.9, 109.5, 53.6, 51.7, 22.4, 21.0. HRMS (ESI-TOF) m/z [M + Na]$^{+}$ Calcd for $C_{22}H_{20}N_2O_3Na$ 383.1366; found 383.1370.



5s

***Methyl (2-oxo-1,1-diphenyl-1,2-dihydro-3H-pyrrolo[3,2-f]quinolin-3-yl)carbamate (5s)*:** The residue was purified by flash chromatography (PE/EA = 20/1) giving the product **5s** as a white solid in 75% yield (46.1 mg), m. p. 240.9-241.8 ℃. ^{1}H NMR (700 MHz, Chloroform-*d*) δ 8.75 (d, *J* = 4.2 Hz, 1H), 8.23 (d, *J* = 9.1 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.70 (s, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.45 – 7.35 (m, 4H), 7.31 – 7.27 (m, 6H), 7.17 (dd, *J* = 8.4, 4.2 Hz, 1H), 3.89 (s, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 178.7, 155.7, 148.4, 145.8, 140.1, 131.9, 131.6, 129.2, 128.6, 127.9, 125.5, 122.8, 121.8, 113.0, 62.0, 53.8. HRMS (ESI-TOF) m/z [M + Na]$^{+}$ Calcd for $C_{25}H_{19}N_3O_3Na$ 432.1319; found 432.1320.

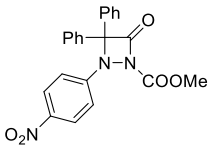
5. General procedure for synthesis of product 7



6, 0.15 mmol **2**, 0.225 mmol **7**

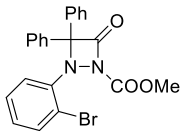
A mixture of non-electron-donating substituted azobenzenes **6** (0.15 mmol) and α-diazo ketones **2** (0.225 mmol) was stirred in CH_2Cl_2 (1.0 mL) at room temperature and then irradiated under blue LEDs for hours. After the reaction completed (monitored by TLC), the reaction mixture was purified by column chromatography to afford the desired products **7** as white solids.

Analytical data of compounds 7



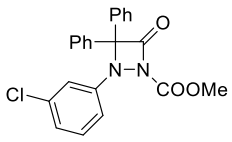
7a

***Methyl 2-(4-nitrophenyl)-4-oxo-3,3-diphenyl-1,2-diazetidine-1-carboxylate (7a)*:** The residue was purified by flash chromatography (PE/EA = 50/1) giving the product **7a** as a white solid in 91% yield (46.5 mg), m. p. 149.3-151.6 °C.^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.18 – 8.15 (m, 2H), 7.45 – 7.42 (m, 2H), 7.41 – 7.37 (m, 4H), 7.36 – 7.32 (m, 6H), 3.26 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.3, 158.6, 144.1, 142.6, 134.3, 129.7, 128.8, 128.1, 124.9, 116.2, 93.0, 53.7. HRMS (ESI-TOF) m/z $[M + Na]^+$ Calcd for $C_{22}H_{17}N_3O_5Na$ 426.1060; 426.1065.



7b

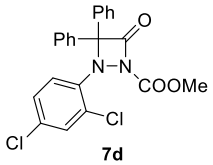
***Methyl 2-(2-bromophenyl)-4-oxo-3,3-diphenyl-1,2-diazetidine-1-carboxylate (7b)*:** The residue was purified by flash chromatography (PE/EA = 20/1) giving the product **7b** as a white solid in 91% yield (60.0 mg), m. p. 159.1-161.0 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.93 – 7.86 (m, 2H), 7.46 – 7.37 (m, 3H), 7.31 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.23 – 7.20 (m, 2H), 7.18 – 7.10 (m, 3H), 7.08 – 7.02 (m, 2H), 6.81 (td, *J* = 7.8, 1.8 Hz, 1H), 3.91 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.3, 148.7, 143.8, 135.8, 133.3, 132.6, 130.0, 129.4, 128.8, 128.6, 128.5, 128.1, 127.4, 126.9, 122.2, 118.6, 95.5, 54.3. HRMS (ESI-TOF) m/z $[M + Na]^+$ Calcd for $C_{22}H_{17}BrN_2O_3Na$ 459.0315; found 459.0317.



7c

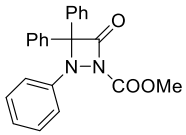
***Methyl 2-(3-chlorophenyl)-4-oxo-3,3-diphenyl-1,2-diazetidine-1-carboxylate (7c)*:** The residue was purified by flash chromatography (PE/EA = 25/1) giving the product **7c** as a white solid in 65% yield (38.3 mg), m. p. 118.2-120.1 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.51 – 7.46

(m, 4H), 7.43 – 7.39 (m, 7H), 7.33 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.29 (t, *J* = 7.8 Hz, 1H), 7.12 (dt, *J* = 7.8, 1.8 Hz, 1H), 3.33 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.4, 158.9, 138.9, 134.74, 134.66, 130.0, 129.4, 128.7, 128.1, 125.0, 116.5, 114.7, 92.4, 53.4. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{22}H_{17}ClN_2O_3Na$ 415.0820; found 415.0825.



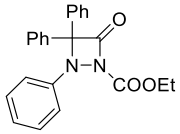
7d

***Methyl 2-(2,4-dichlorophenyl)-4-oxo-3,3-diphenyl-1,2-diazetidine-1-carboxylate (7d)*:** The residue was purified by flash chromatography (PE/EA = 30/1) giving the product **7d** as a white solid in 77% yield (49.5 mg), m. p. 171.6-173.0 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.87 (dd, *J* = 7.2, 2.4 Hz, 2H), 7.45 – 7.29 (m, 3H), 7.22 – 7.19 (m, 1H), 7.20 – 7.14 (m, 4H), 7.13 (d, *J* = 2.4 Hz, 1H), 7.04 – 6.97 (m, 2H), 3.91 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.0, 148.7, 141.5, 135.5, 132.5, 131.1, 129.8, 128.9, 128.8, 128.6, 128.3, 127.0, 122.3, 95.6, 54.5. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{22}H_{16}Cl_2N_2O_3Na$ 449.0430; found 449.0432.



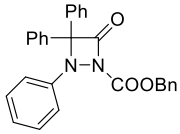
7e

***Methyl 4-oxo-2,3,3-triphenyl-1,2-diazetidine-1-carboxylate (7e)*:** The residue was purified by flash chromatography (PE/EA = 60/1) giving the product **7e** as a white solid in 61% yield (33.0 mg), m. p. 124.5-125.5 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.52 – 7.48 (m, 4H), 7.43 – 7.39 (m, 8H), 7.38 – 7.35 (m, 2H), 7.17 – 7.14 (m, 1H), 3.32 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.3, 159.0, 138.0, 134.9, 129.2, 128.8, 128.6, 128.1, 124.9, 116.5, 92.0, 53.3. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{22}H_{18}N_2O_3Na$ 381.1210; found 381.1216.



7f

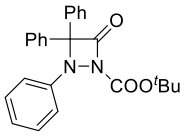
***Ethyl 4-oxo-2,3,3-triphenyl-1,2-diazetidine-1-carboxylate (7f)*:** The residue was purified by flash chromatography (PE/EA = 50/1) giving the product **7f** as a white solid in 47% yield (26.4 mg), m. p. 130.1-132.0 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.53 – 7.48 (m, 4H), 7.43 – 7.38 (m, 8H), 7.38 – 7.34 (m, 2H), 7.14 (tt, *J* = 7.2, 1.2 Hz, 1H), 3.82 (q, *J* = 7.2 Hz, 2H), 0.80 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.6, 158.4, 138.1, 135.1, 129.2, 128.8, 128.6, 128.3, 124.9, 116.6, 91.7, 63.0, 13.6. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{23}H_{20}N_2O_3Na$ 395.1366; found 395.1374.



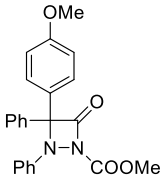
7g

***Benzyl 4-oxo-2,3,3-triphenyl-1,2-diazetidine-1-carboxylate (7g)*:** The residue was

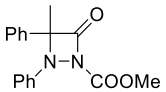
purified by flash chromatography (PE/EA = 40/1) giving the product **7g** as a white solid in 71% yield (46.5 mg), m. p. 127.5-129.0 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.43 – 7.37 (m, 4H), 7.34 (d, *J* = 7.8 Hz, 2H), 7.31 – 7.25 (m, 7H), 7.22 – 7.15 (m, 4H), 7.08 (t, *J* = 7.2 Hz, 1H), 6.91 (d, *J* = 7.2 Hz, 2H), 4.69 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.5, 157.2, 137.0, 133.8, 133.5, 128.2, 127.8, 127.6, 127.4, 127.3, 127.1, 123.9, 115.6, 90.9, 67.6. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{28}H_{22}N_2O_3Na$ 457.1523; found 457.1526.



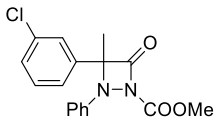
7h ***Tert-butyl 4-oxo-2,3,3-triphenyl-1,2-diazetidine-1-carboxylate (7h)*****:** The residue was purified by flash chromatography (PE/EA = 40/1) giving the product **7h** as a white solid in 63% yield (38.1 mg), m. p. 123.2-125.1 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.54 – 7.48 (m, 4H), 7.44 – 7.38 (m, 8H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.13 (t, *J* = 7.2 Hz, 1H), 1.08 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.7, 156.9, 138.2, 135.5, 129.1, 128.8, 128.6, 128.5, 124.8, 116.6, 91.1, 83.2, 27.4. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{25}H_{24}N_2O_3Na$ 423.1679; found 423.1680.



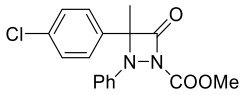
7i ***Methyl 3-(4-methoxyphenyl)-4-oxo-2,3-diphenyl-1,2-diazetidine-1-carboxylate (7i)*****:** The residue was purified by flash chromatography (PE/EA = 60/1) giving the product **7i** as a white solid in 88% yield (51.2 mg), m. p. 125.0-126.7 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.56 – 7.53 (m, 2H), 7.43 – 7.38 (m, 5H), 7.37 – 7.35 (m, 4H), 7.15 (tt, *J* = 7.2, 1.2 Hz, 1H), 6.92 – 6.89 (m, 2H), 3.82 (s, 3H), 3.36 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.6, 160.3, 159.1, 138.1, 135.2, 129.8, 129.0, 128.8, 128.5, 127.9, 127.0, 124.9, 116.5, 113.9, 92.0, 55.3, 53.3. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{23}H_{20}N_2O_4Na$ 411.1315; found 411.1312.



7j ***Methyl 3-methyl-4-oxo-2,3-diphenyl-1,2-diazetidine-1-carboxylate (7j)*****:** The residue was purified by flash chromatography (PE/EA = 50/1) giving the product **7j** as a white solid in 71% yield (31.5 mg), m. p. 120.7-122.5 ℃.^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.63 – 7.58 (m, 2H), 7.40 (t, *J* = 7.2 Hz, 2H), 7.39 – 7.32 (m, 5H), 7.15 (tt, *J* = 6.6, 1.8 Hz, 1H), 3.80 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.1, 159.1, 137.9, 136.1, 128.84, 128.78, 125.8, 124.8, 116.5, 85.8, 53.8, 21.8. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{17}H_{16}N_2O_3Na$ 319.1053; found 319.1056.

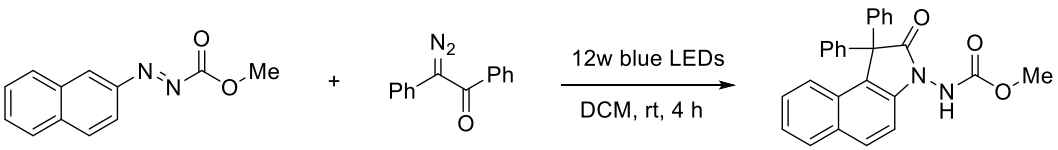


7k ***Methyl 3-(3-chlorophenyl)-3-methyl-4-oxo-2-phenyl-1,2-diazetidine-1-carboxylate (7k)*****:** The residue was purified by flash chromatography (PE/EA = 50/1) giving the product **7k** as colorless oil in 90% yield (44.6 mg). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.63 – 7.61 (m, 1H), 7.51 – 7.47 (m, 1H), 7.40 – 7.31 (m, 6H), 7.16 (tt, *J* = 7.2, 1.2 Hz, 1H), 3.86 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.1, 157.6, 137.1, 136.5, 133.6, 128.9, 127.72, 127.70, 124.9, 123.8, 122.7, 115.4, 83.8, 52.8, 20.8. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{17}H_{15}ClN_2O_3Na$ 353.0663; found 353.0667.



7l ***Methyl 3-(4-chlorophenyl)-3-methyl-4-oxo-2-phenyl-1,2-diazetidine-1-carboxylate (7l)*****:** The residue was purified by flash chromatography (PE/EA = 50/1) giving the product **7l** as a white solid in 77% yield (38.1 mg), m. p. 129.7-131.2 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.56 – 7.52 (m, 2H), 7.38 – 7.34 (m, 4H), 7.33 – 7.30 (m, 2H), 7.16 (tt, *J* = 7.2, 1.2 Hz, 1H), 3.83 (s, 3H), 1.99 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.6, 158.9, 137.7, 134.83, 134.78, 129.0, 128.9, 127.2, 125.0, 116.6, 85.1, 53.9, 21.9. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{17}H_{15}ClN_2O_3Na$ 353.0663; found 353.0665.

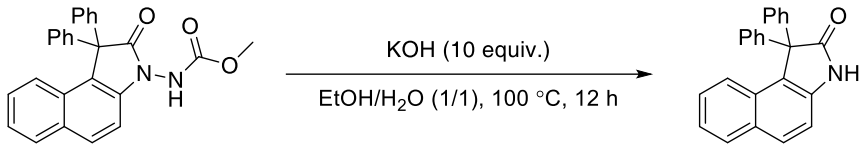
6. Gram-scale synthesis of compound 5a



4a, 3.5 mmol **2a**, 5.25 mmol **5a**, 75%

A mixture of azonaphthalenes **1a** (3.5 mmol, 750 mg) and α-diazo ketones **2a** (5.25 mmol, 1.17 g) was stirred in CH_2Cl_2 (10.0 mL) at room temperature and then irradiated under blue LEDs for 4 hours. Until the reaction completed (monitored by TLC), the reaction mixture was purified by flash chromatography on silica gel (PE/EA = 5/1) to give compound **5a** as a white solid in 75% yield (1.07 g).

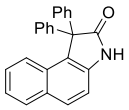
7. Synthesis of product 8



5a, 0.15 mmol **8**, 76%

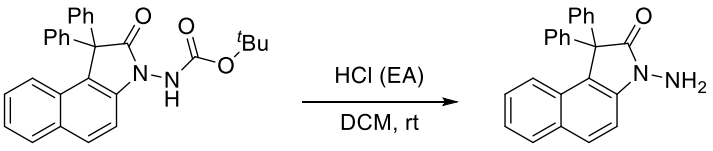
To the solution of KOH (1.5 mmol, 84.16 mg) in H_2O (0.5 mL) was added the solution of **5a** (0.15 mmol, 61.27 mg). Then, the reaction mixture was stirred at 100 ℃ for 12 hours. Until the reaction completed (monitored by TLC), the reaction mixture was concentrated purified by flash chromatography on silica gel (PE/EA = 8/1) to give compound **8** as a white solid in 76% yield (38 mg).

Analytical data of compounds 8



8 ***1,1-diphenyl-1,3-dihydro-2H-benzo[e]indol-2-one (8)*****:** The residue was purified by filtration (washing) to give the product **8** as a white solid in 76% yield (38.0 mg), m. p. 310.1-311.7 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.82 (s, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.33 (d, *J* = 7.2 Hz, 4H), 7.22 – 7.18 (m, 8H), 7.17 – 7.14 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 181.1, 138.2, 137.2, 129.6, 129.3, 129.2, 128.3, 128.2, 127.4, 126.5, 126.0, 124.9, 122.6, 122.3, 110.6, 63.0. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{24}H_{17}NONa$ 358.1202; found 358.1199.

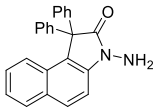
8. Synthesis of product 9



5f, 0.3 mmol **9**, 65%

To the solution of **5f** (0.3 mmol, 135 mg) in CH_2Cl_2 (2 mL) was added hydrogen chloride ethyl acetate solution (0.1 mL, 4.0 M in ethyl acetate) dropwise and the reaction was stirred at room temperature for 20 hours. Until the reaction completed (monitored by TLC), the reaction mixture was purified by flash chromatography on silica gel (PE/EA = 6/1) to give compound **9** as a white solid in 65% yield (68 mg).

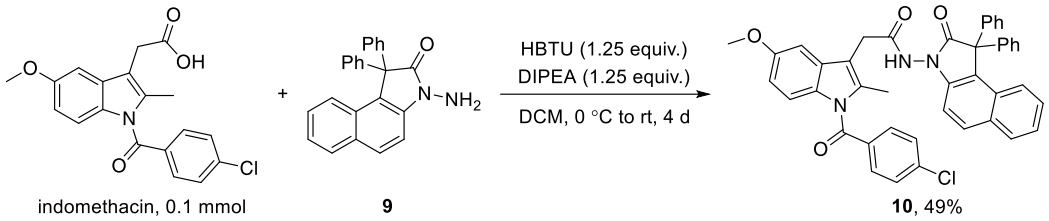
Analytical data of compounds 9



9

***3-amino-1,1-diphenyl-1,3-dihydro-2H-benzo[e]indol-2-one (9)*:** The residue was purified by flash chromatography (PE/EA = 3/1) giving the product **9** as a white solid in 65% yield (68.0 mg), m. p. 228.5-229.7 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 7.2 Hz, 1H), 7.77 (d, *J* = 7.2 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.37 (d, *J* =7.2 Hz, 1H), 7.31 – 7.25 (m, 4H), 7.23 – 7.17 (m, 6H), 7.19 – 7.13 (m, 2H), 3.21 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.3, 141.0, 139.0, 131.0, 130.5, 129.8, 129.5, 129.3, 128.4, 127.6, 127.0, 123.7, 123.4, 123.1, 110.5, 62.4. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{24}H_{18}N_2ONa$ 373.1311; found 373.1306.

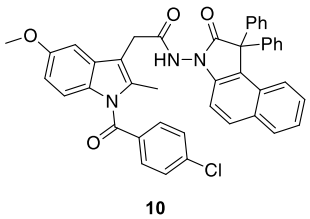
9. Synthesis of product 10



indomethacin, 0.1 mmol **9** **10**, 49%

To the solution of indomethacin (0.1 mmol, 35.78 mg) in CH_2Cl_2 (2 mL) was added HBTU (0.125 mmol, 47.41 mg) at 0 °C. This solution was stirred for 30 min, followed by addition of **9** (0.1 mmol, 35.04 mg) and DIPEA (0.125 mmol, 16.16 mg). Then, the solution was warmed to RT and stirred for 4 days. Until the reaction completed (monitored by TLC), the reaction mixture was quenched with 50 mL of H_2O and extracted with DCM (3×50 mL). The organic layers were collected and dried with Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (PE/EA = 8/1) to give compound **10** as a white solid in 49% yield (33.5 mg).

Analytical data of compounds 10

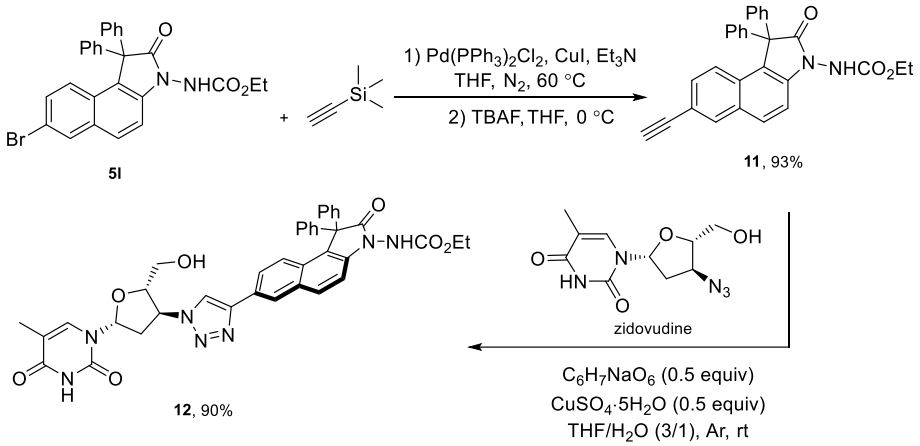


10

***2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)-N-(2-oxo-1,1-diphenyl-1,2-dihydro-3H-benzo[e]indol-3-yl)acetamide (10)*:** The residue was purified by flash chromatography (PE/EA = 8/1) giving the product **10** as a white solid in 49% yield (33.5 mg), m. p. 158.9-160.4 °C. ^{1}H NMR (700 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.68 (s, 1H), 7.59 (d, *J* = 7.7 Hz, 2H), 7.38 (t, *J* = 7.7 Hz, 3H), 7.35 (d, *J* = 7.7 Hz, 4H), 7.22 – 7.17 (m, 6H), 7.16 – 7.13 (m, 2H), 7.05 (s, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.83 (d, *J* = 9.1 Hz, 1H), 6.65 (d, *J* = 8.4 Hz, 1H), 3.84 (s, 2H), 3.79 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 178.4, 169.2, 168.3, 156.5, 139.7, 139.4, 136.8, 133.4, 131.3, 131.2, 130.9, 130.5, 130.0, 129.9, 129.44, 129.38, 129.3, 128.4,

127.7, 127.2, 124.0, 123.4, 123.1, 115.3, 112.9, 111.1, 109.3, 100.6, 62.2, 55.9, 30.7, 13.5. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{43}H_{32}ClN_3O_4Na$ 712.1974; found 712.1973.

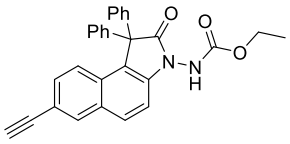
10. Synthesis of product 12



Compound **11** were prepared according to the improved literature procedures.[3] Then, under argon atmosphere, a flame-dried 10 mL schlenk tube was charged with compound **11** (20.09 mg, 0.045 mmol), zidovudine (14.43 mg, 0.054 mmol) and a stir bar was added a freshly prepared solution of $CuSO_4{\cdot}5H_2O$ (5.62 mg. 0.0225 mmol.), THF (1.5 mL) and sodium ascorbate (4.46 mg. 0.0225 mmol.) in H_2O (0.5 mL). the reaction mixture was concentrated purified by flash chromatography on silica gel (DCM/MeOH = 20/1) to give compound **12** as a white solid in 90% yield (29 mg).

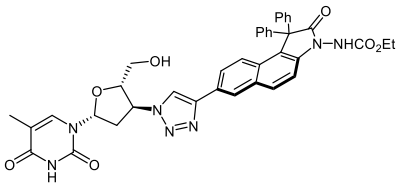
3. X. Fan, C. He, M. Ji, X. Sun, H. Luo, C. Li, H. Tong, W. Zhang, Z. Sun and W. Chu, *Chem. Commun.*, 2022, **58**, 6348-6351.

Analytical data of compounds 11 and 12



11

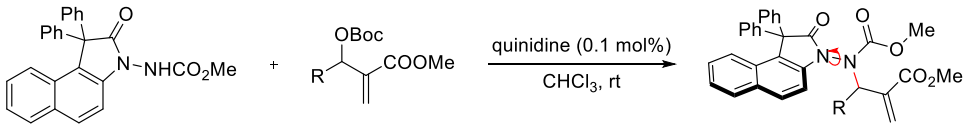
***Ethyl (7-ethynyl-2-oxo-1,1-diphenyl-1,2-dihydro-3H-benzo[e]indol-3-yl)carbamate (11)*:** The residue was purified by flash chromatography (PE/EA = 25/1) giving the product **11** as a white solid in 93% yield (41.6 mg), m. p. 230.5-232.3 ℃. ^{1}H NMR (700 MHz, Chloroform-*d*) δ 8.05 (s, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.47 – 7.38 (m, 6H), 7.33 – 7.26 (m, 7H), 7.15 (s, 1H), 4.32 (s, 2H), 3.12 (s, 1H), 1.37 – 1.13 (m, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 178.8, 155.3, 140.7, 133.8, 130.7, 130.6, 129.9, 129.6, 129.3, 128.5, 127.8, 123.6, 123.1, 117.6, 110.4, 83.6, 77.5, 63.1, 61.9, 14.3. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{29}H_{22}N_2O_3Na$ 469.1523; found 469.1532.



12

***Ethyl (7-(1-((2S,3S,5R)-2-(hydroxymethyl)-5-(5-methyl-2,4-dioxo-3,4-dihydropyrimidin-1(2H)-yl)tetrahydrofuran-3-yl)-1H-1,2,3-triazol-4-yl)-2-oxo-1,1-diphenyl-1,2-dihydro-3H-benzo[e]indol-3-yl)carbamate (12)*:** The residue was purified by flash chromatography (DCM/MeOH = 20/1) giving the product **12** as a white solid in 90% yield (29 mg), m. p. 198.1-200.0 °C. ^{1}H NMR (700 MHz, Chloroform-*d*) δ 8.29 (s, 1H), 8.17 (s, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.79 (s, 1H), 7.63 – 7.54 (m, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.43 – 7.32 (m, 5H), 7.29 (s, 1H), 7.26 – 7.21 (m, 5H), 6.92 (s, 1H), 6.77 (s, 1H), 6.14 (t, *J* = 7.0 Hz, 1H), 5.42 – 5.39 (m, 1H), 4.41 (t, *J* = 2.8 Hz, 1H), 4.25 (s, 2H), 3.98 (dd, *J* = 13.6, 2.1 Hz, 1H), 3.73 (dd, *J* = 13.6, 2.1 Hz, 1H), 3.14 – 2.86 (m, 3H), 1.88 (s, 3H), 1.38 – 1.25 (m, 3H). ^{13}C NMR (176 MHz, MeOD) δ 179.0, 165.0, 156.1, 150.9, 140.5, 136.9, 131.4, 130.8, 129.4, 129.3, 128.9, 128.1, 127.7, 127.3, 125.71, 125.68, 124.5, 123.8, 123.1, 120.7, 110.3, 110.0, 85.3, 85.0, 62.2, 60.8, 59.8, 37.7, 13.4, 11.1. HRMS (ESI-TOF) m/z [M + Na]$^{+}$ Calcd for $C_{39}H_{35}N_7O_7Na$ 736.2490; found 736.2493.

11. Synthesis of product 13



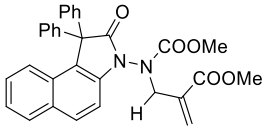
5a

13a, R = H, 12%, 32% ee

13b, R = Ph, 82%, 94% ee, >20:1 dr

To the solution of **5a** (0.05 mmol, 20.42 mg) in $CHCl_3$ (1.0 mL) was added MBH-adducts (0.06 mmol). Then, quinidine (10 mol%) was added and the reaction mixture was stirred at room temperature for 3 hours. Until the reaction completed (monitored by TLC), the reaction mixture was purified by flash chromatography on silica gel (PE/EA = 8/1) to give compounds **13** as white solids.

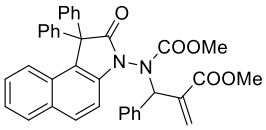
Analytical data of compounds 13a and 13b



13a

***Methyl 2-(((methoxycarbonyl)(2-oxo-1,1-diphenyl-1,2-dihydro-3H-benzo[e]indol-3-yl)amino)methyl)acrylate (13a)*:** The residue was purified by flash chromatography (PE/EA = 8/1) giving the product **13a** as a white solid in 12% yield (3.0 mg), m. p. 166.3-168.1 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.83 – 7.72 (m, 2H), 7.38 – 7.33 (m, 3H), 7.32 – 7.08 (m, 10H), 7.07 – 7.02 (m, 1H), 5.92 (s, 1H), 5.37 (s, 1H), 4.78 (d, *J* = 14.4 Hz, 1H), 4.29 (d, *J* = 14.4 Hz, 1H), 3.64 (s, 3H), 3.52 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.3, 166.0, 155.7, 140.5, 139.5, 137.2, 133.8, 132.0,

131.2, 130.5, 130.0, 129.7, 129.4, 129.0, 128.39, 128.35, 127.9, 127.4, 127.2, 124.0, 123.4, 122.8, 109.3, 62.1, 54.0, 52.0, 49.7. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{31}H_{26}N_2O_5Na$ 529.1734; found 529.1731. The *ee* value was determined by the chiral HPLC analysis (OD-H column, *n*-hexane/*i*-propanol = 90:10, v = 1 mL/min, λ= 254.0 nm; t_{minor}= 12.88 min, t_{major} = 18.7 min).

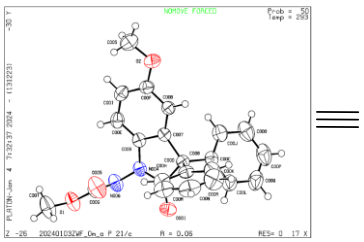


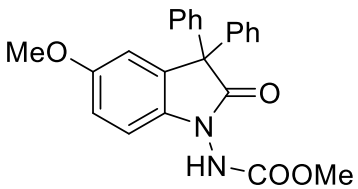
13b

***Methyl 2-(((methoxycarbonyl)(2-oxo-1,1-diphenyl-1,2-dihydro-3H-benzo[e]indol-3-yl)amino)(phenyl)methyl)acrylate (13b)*:** The residue was purified by flash chromatography (PE/EA = 8/1) giving the product **13b** as a white solid in 82% yield (24.0 mg), m. p. 180.5-182.1 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.46 (d, *J* = 9.0 Hz, 1H), 7.36 (d, *J* = 7.8 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.31 – 7.26 (m, 4H), 7.25 – 7.22 (m, 3H), 7.21 – 7.17 (m, 4H), 6.98 (t, *J* = 7.2 Hz, 2H), 6.92 (t, *J* = 7.2 Hz, 2H), 6.38 (s, 1H), 6.35 (s, 1H), 6.02 (s, 1H), 3.65 (s, 3H), 3.58 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.4, 165.9, 156.0, 140.2, 139.0, 136.9, 131.0, 130.2, 129.9, 129.6, 129.3, 129.1, 128.8, 128.22, 128.16, 128.0, 127.4, 127.3, 127.1, 123.9, 123.5, 122.9, 109.9, 64.7, 61.4, 53.9, 52.0. HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{37}H_{30}N_2O_5Na$ 605.2047; found 605.2050. The *ee* value was determined by the chiral HPLC analysis (OD-H column, *n*-hexane/*i*-propanol = 90:10, v = 1 mL/min, λ= 254.0 nm; t_{major}= 12.6 min, t_{minor} = 15.6 min).

12. X-ray crystal structures of 3a, 5b and 7a

To a 10 mL tube containing **3a** (30.0 mg) was added a mixture solvent (methylene chloride /ethyl acetate = 10:1, v/v) (4 mL). A clear solution was obtained through ultrasound treatment and was kept at room temperature and the crystals were obtained after the solvent evaporated, which were characterized by single crystal X-ray diffraction. X-ray diffraction experiment was carried out on an Agilent D8 QUEST and the data obtained were deposited at the Cambridge Crystallographic Data Centre.





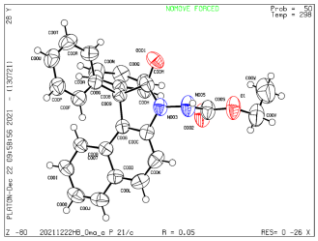
3a, CCDC 2325419

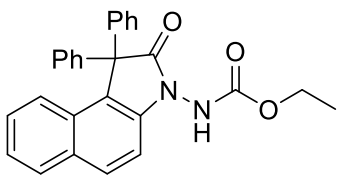
(Ellipsoid contour probability 50%)

Identification code	**3a**
Chemical formula	$C_{23}H_{20}N_2O_4$
Formula weight	388.41 g/mol
Temperature	293(2) K
Wavelength	1.54178 Å

Crystal system	monoclinic
Space group	P 1 21/c 1
Unit cell dimensions	a = 10.4537(3) Å α = 90°
	b = 14.6776(4) Å β = 108.6830(10)°
	c = 13.2849(4) Å γ = 90°
Volume	1930.96(10) $Å^3$
Z	4
Density (calculated)	1.336 g/cm^3
Absorption coefficient	0.755 mm^{-1}
F (000)	816
Theta range for data collection	4.46 to 68.58°
Index ranges	-12<=h<=12, -17<=k<=17, -16<=l<=15
Reflections collected	27665
Independent reflections	3547 [R(int) = 0.0649]
Coverage of independent reflections	99.7%
Absorption correction	Multi-Scan
Structure solution technique	direct methods
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2016/6 (Sheldrick, 2016)
Function minimized	$\Sigma w (F_o^2 - F_c^2)^2$
Data / restraints / parameters	3547 / 0 / 264
Goodness-of-fit on F^2	1.068
Final R indices	2832 data; I>2σ(I) $R_1 = 0.0630$, $wR_2 = 0.1469$
	all data $R_1 = 0.0750$, $wR_2 = 0.1614$
Weighting scheme	$w=1/[\sigma^2(F_o^2) + (0.0953P)^2 + 0.3648P]$
	where $P= (F_o^2 + 2F_c^2)/3$
Largest diff. peak and hole	0.241 and -0.472 $eÅ^{-3}$
R.M.S. deviation from mean	0.102 $eÅ^{-3}$

To a 10 mL tube containing **5b** (30.0 mg) was added a mixture of solvent (ethyl acetate /petroleum ether = 1:15, v/v) (4.0 mL). A clear solution was obtained through ultrasound treatment and was kept at room temperature and the crystals were obtained after the solvent evaporated, which were characterized by X-ray single crystal diffraction. X-ray diffraction experiment was carried out on an Agilent D8 QUEST and the data obtained were deposited at the Cambridge Crystallographic Data Centre.



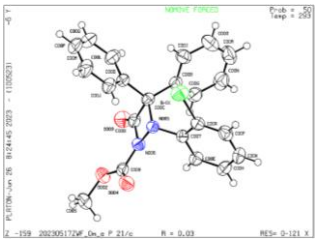


5b, CCDC 2253535

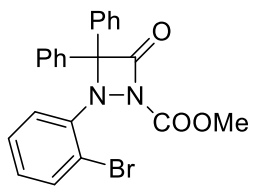
(Ellipsoid contour probability 50%)

Identification code	**5b**
Chemical formula	$C_{27}H_{22}N_2O_3$
Formula weight	422.46 g/mol
Temperature	298(2) K
Wavelength	1.54184 Å
Crystal system	monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 11.2636(3) Å α = 90°
	b = 14.7245(4) Å β = 106.7092(10)°
	c = 13.7242(3) Å γ = 90°
Volume	2180.06(12) $Å^3$
Z	44
Density (calculated)	1.287 g/cm^3
Absorption coefficient	0.679 mm^{-1}
F (000)	888
Radiation	CuKα (λ = 1.54178)
Theta range for data collection	6.724 to 137.472°
Index ranges	-16<=h<=16, -17<=k<=17, -13<=l<=13
Reflections collected	35458
Independent reflections	4018 [R(int) = 0.0567, R(sigma) = 0.0294]
Absorption correction	Multi-Scan
Structure solution technique	direct methods
Structure solution program	XT, VERSION 2014/5
Data / restraints / parameters	4018 / 0 / 290
Goodness-of-fit on F^2	1.026
Final R indices	I>2σ(I) R_1 = 0.0489, wR_2 = 0.1308
	all data R_1 = 0.0597, wR_2 = 0.1457
Largest diff. peak and hole	0.15 and -0.20 $eÅ^{-3}$

To a 10 mL tube containing **7b** (20.0 mg) was added a mixture solvent (methylene chloride /ethyl acetate = 20:1, v/v) (4 mL). A clear solution was obtained through ultrasound treatment and was kept at room temperature and the crystals were obtained after the solvent evaporated, which were characterized by single crystal X-ray diffraction. X-ray diffraction experiment was carried out on an Agilent D8 QUEST and the data obtained were deposited at the Cambridge Crystallographic Data Centre.



≡

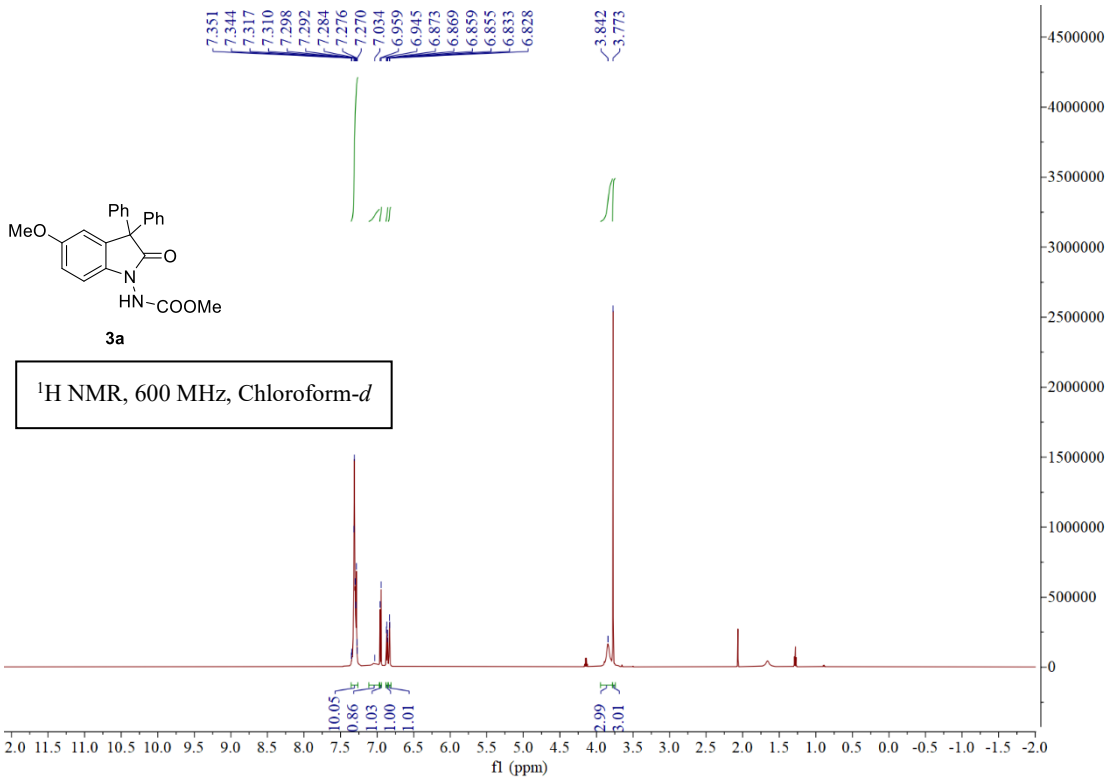


7b, CCDC 2267724

(Ellipsoid contour probability 50%)

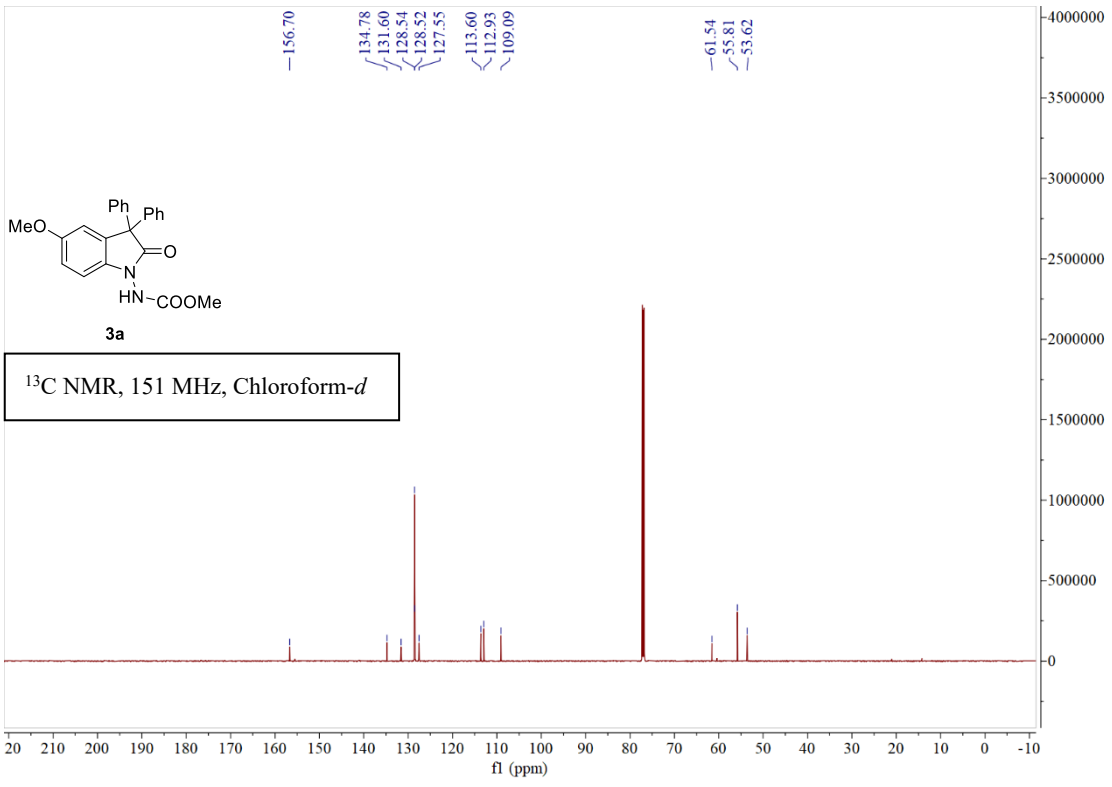
Identification code	**7b**
Chemical formula	$C_{22}H_{17}BrN_2O_3$
Formula weight	437.28 g/mol
Temperature	293(2) K
Wavelength	1.54178 Å
Crystal system	monoclinic
Space group	P 1 21/c 1
Unit cell dimensions	a = 12.1826(4) Å α = 90°
	b = 7.4970(2) Å β = 92.662(2)°
	c = 21.2926(7) Å γ = 90°
Volume	1942.62(10) $Å^3$
Z	4
Density (calculated)	1.495 g/cm^3
Absorption coefficient	3.098 mm^{-1}
F (000)	888
Theta range for data collection	3.63 to 68.55°
Index ranges	-14<=h<=14, -9<=k<=9, -25<=l<=25
Reflections collected	24905
Independent reflections	3561 [R(int) = 0.0633]
Coverage of independent reflections	99.6%
Absorption correction	Multi-Scan
Structure solution technique	direct methods
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2016/6 (Sheldrick, 2016)
Function minimized	$\Sigma w (F_o^2 - F_c^2)^2$
Data / restraints / parameters	3561 / 0 / 254
Goodness-of-fit on F^2	1.051
Δ/σmax	0.001
Final R indices	3129 data; I>2σ(I) R_1 = 0.0331, wR_2 = 0.0858
	all data R_1 = 0.0384, wR_2 = 0.0899
Weighting scheme	$w=1/[\sigma^2(F_o^2) + (0.0424P)^2 + 0.8764P]$
	where $P= (F_o^2 + 2F_c^2)/3$
Absolute structure parameter	0.00(5)
Largest diff. peak and hole	0.476 and -0.262 $eÅ^{-3}$
R.M.S. deviation from mean	0.051 $eÅ^{-3}$

13. ^{1}H NMR, ^{13}C NMR and HPLC Spectra



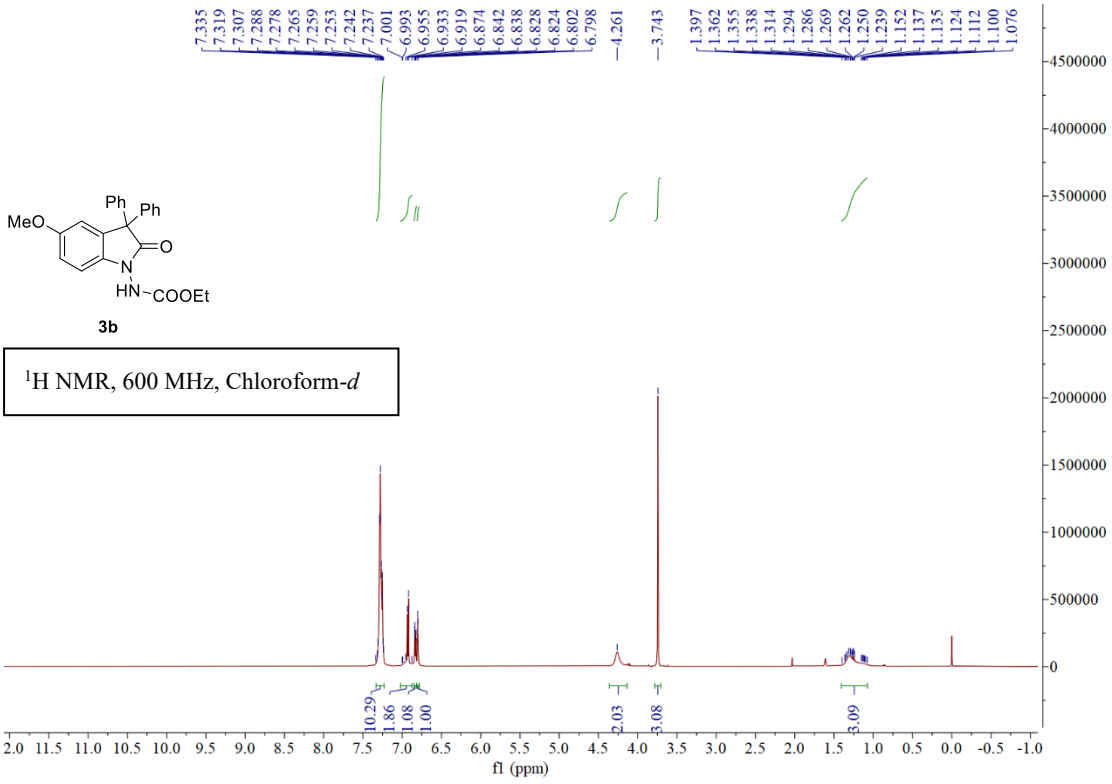
3a

^{1}H NMR, 600 MHz, Chloroform-*d*



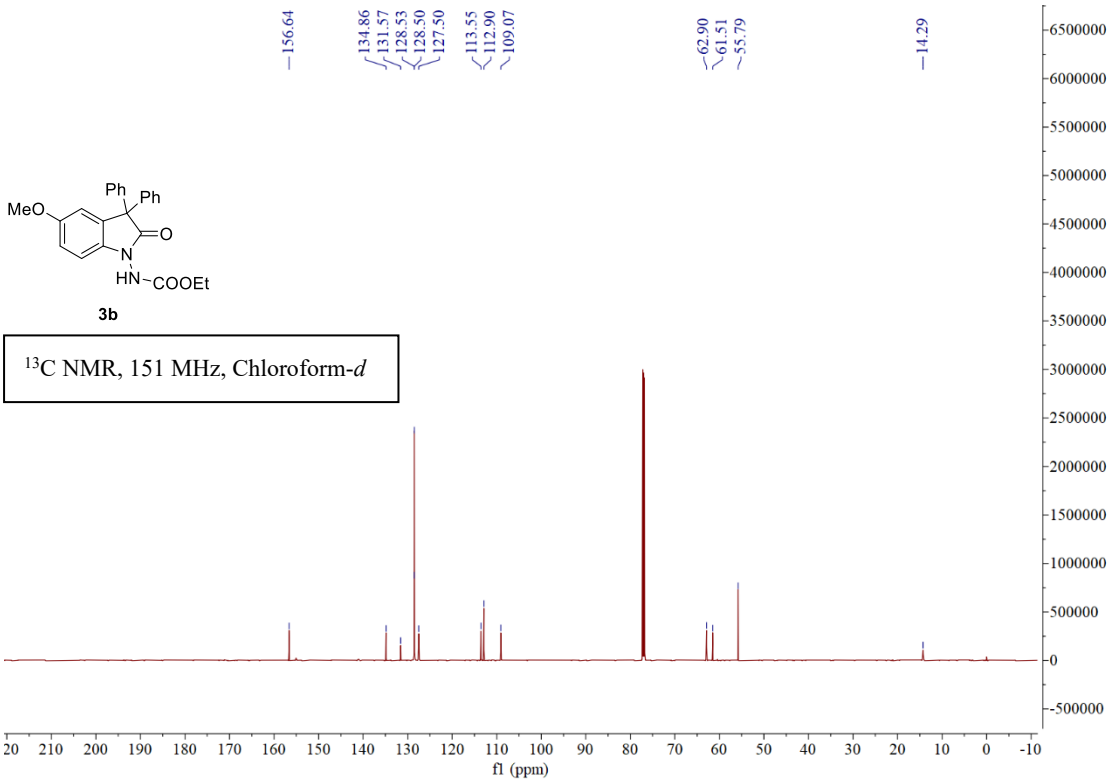
3a

^{13}C NMR, 151 MHz, Chloroform-*d*



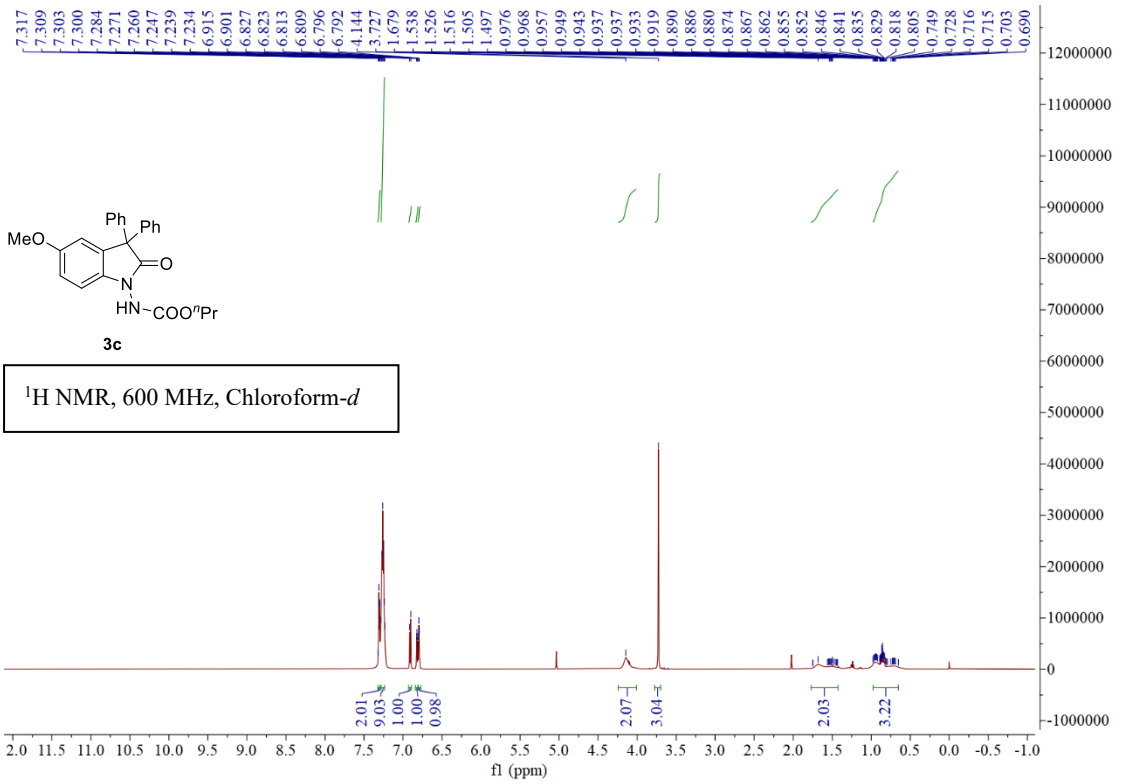
3b

^{1}H NMR, 600 MHz, Chloroform-*d*



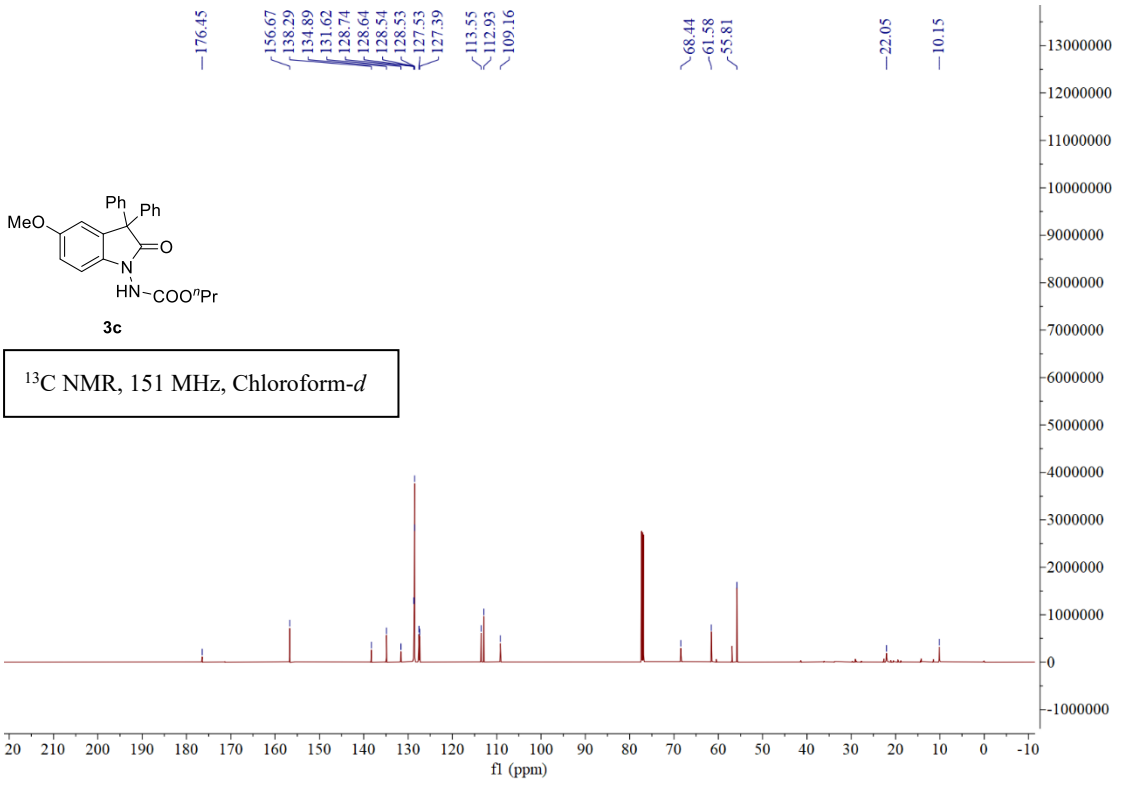
3b

^{13}C NMR, 151 MHz, Chloroform-*d*



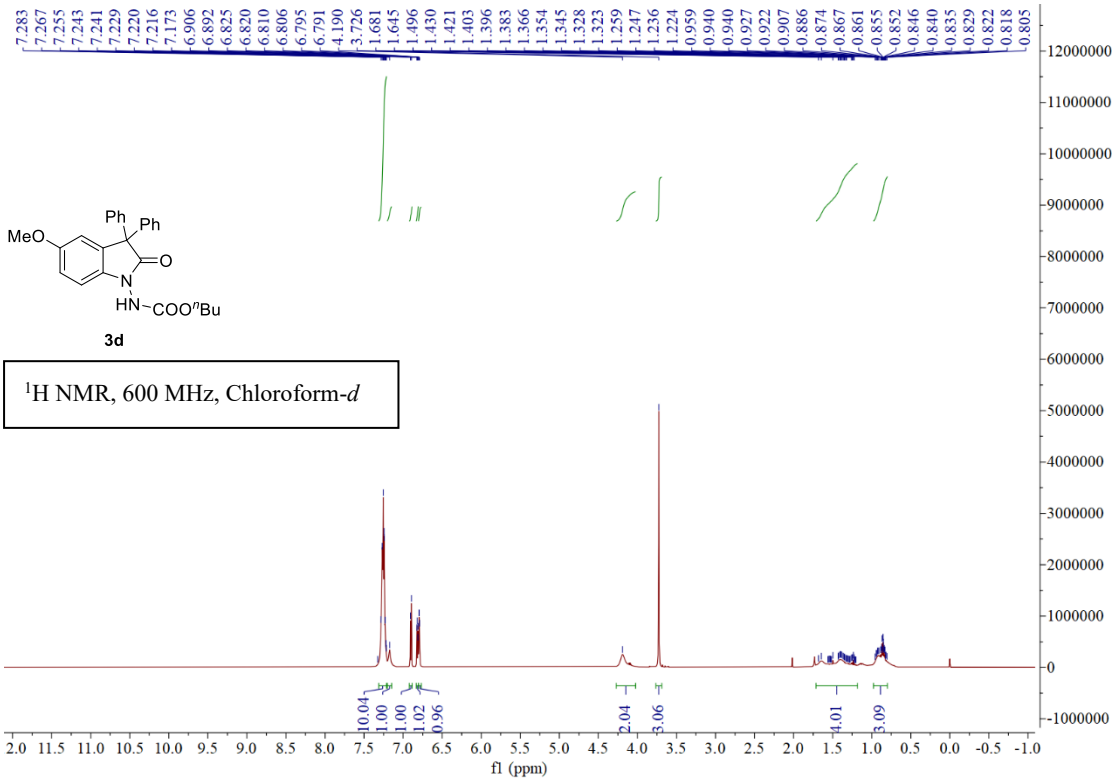
3c

^{1}H NMR, 600 MHz, Chloroform-*d*



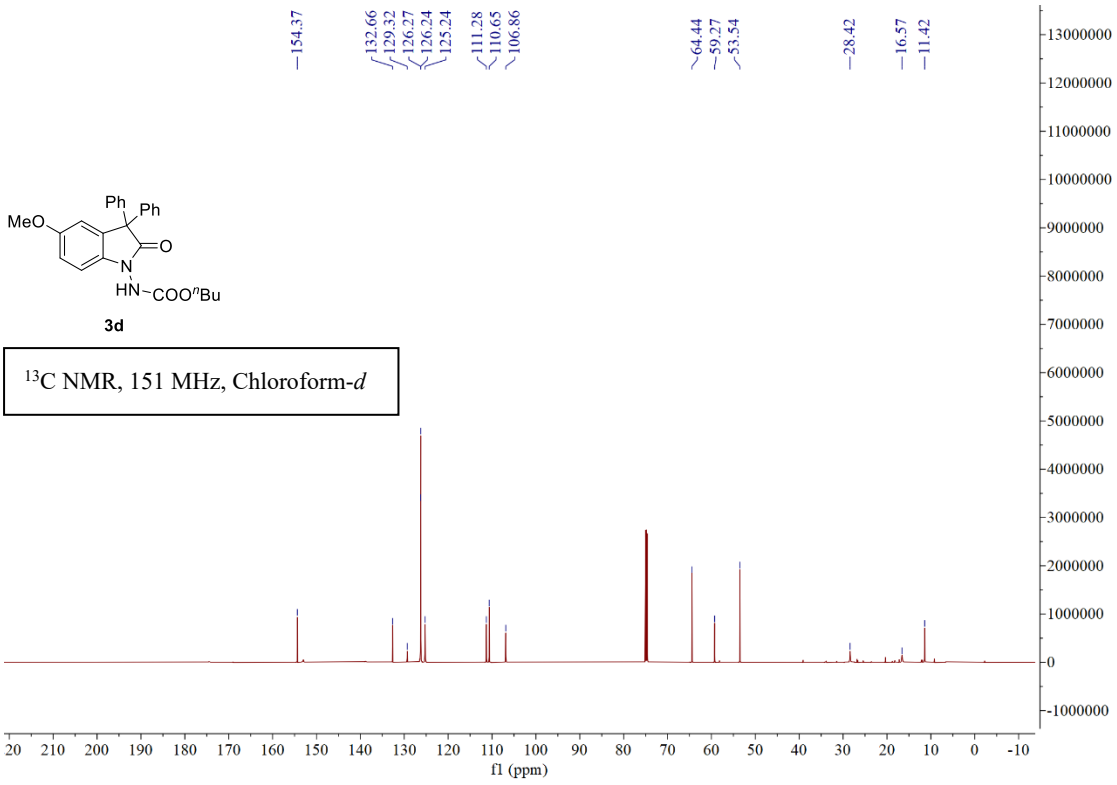
3c

^{13}C NMR, 151 MHz, Chloroform-*d*



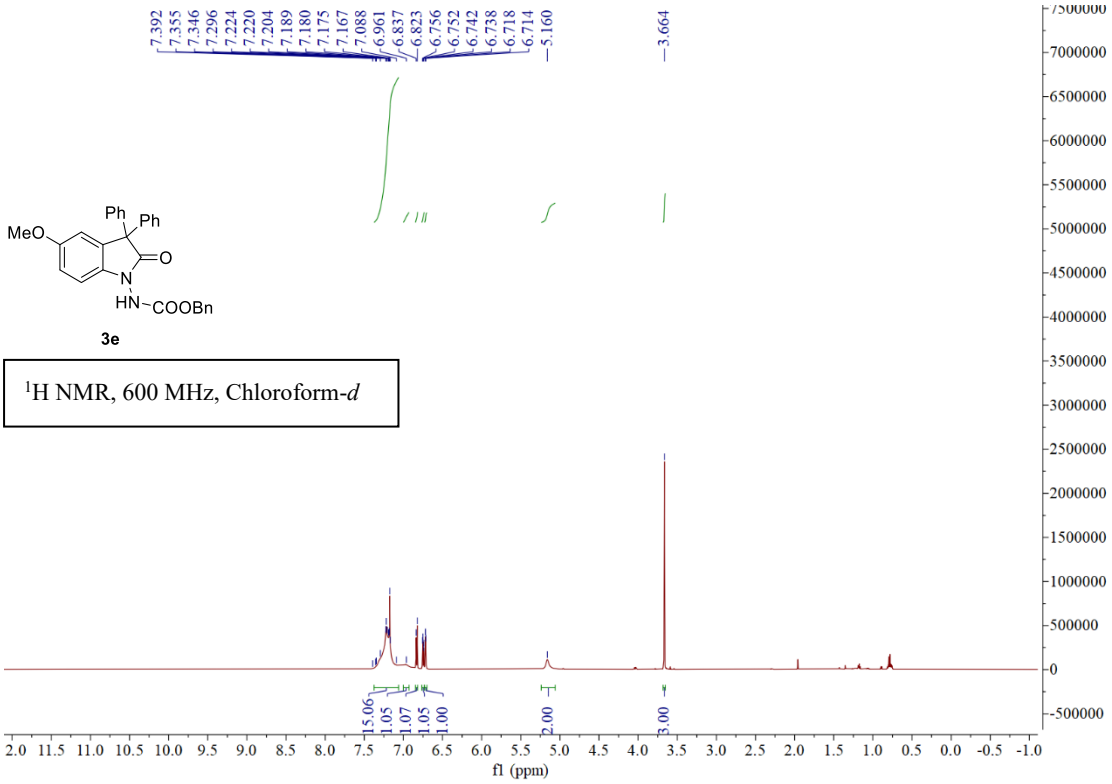
3d

^{1}H NMR, 600 MHz, Chloroform-*d*



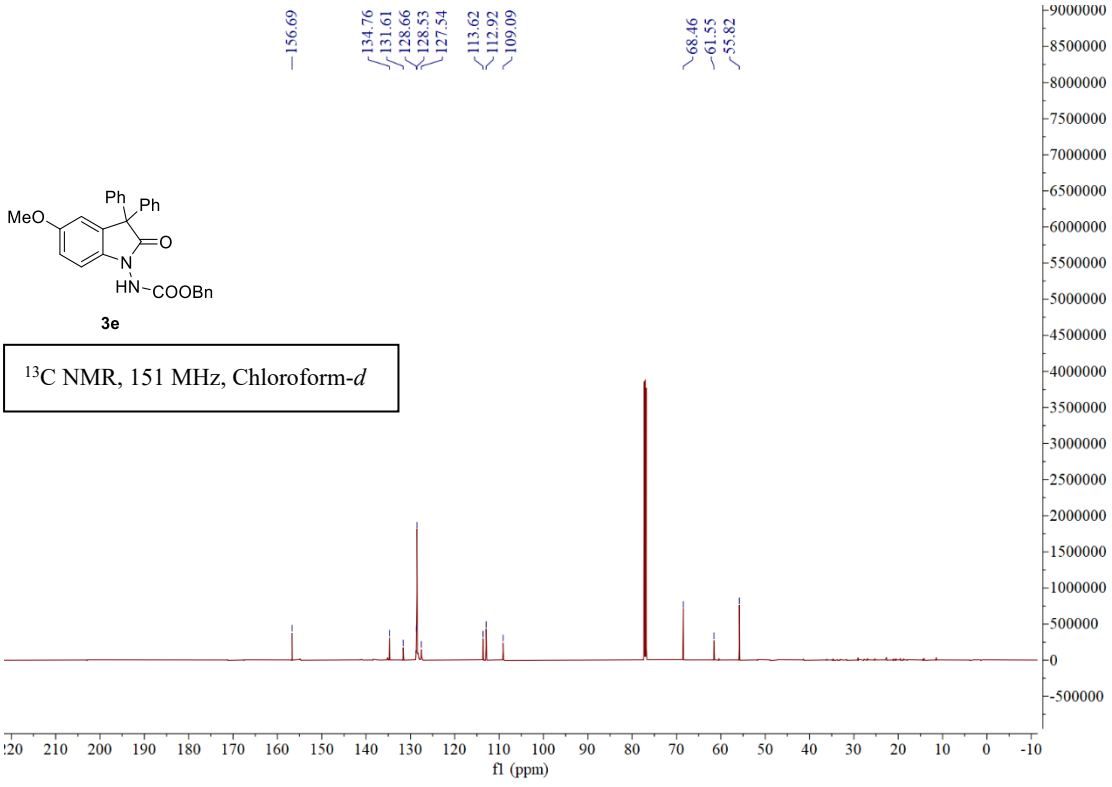
3d

^{13}C NMR, 151 MHz, Chloroform-*d*



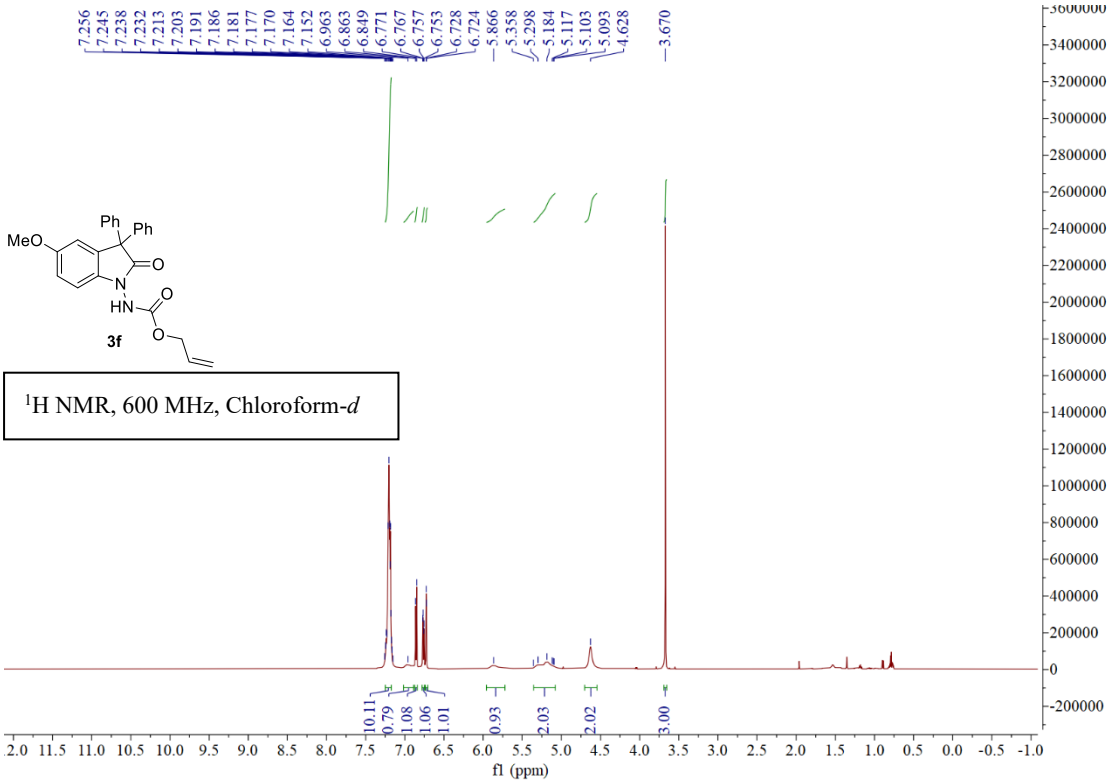
3e

^{1}H NMR, 600 MHz, Chloroform-*d*

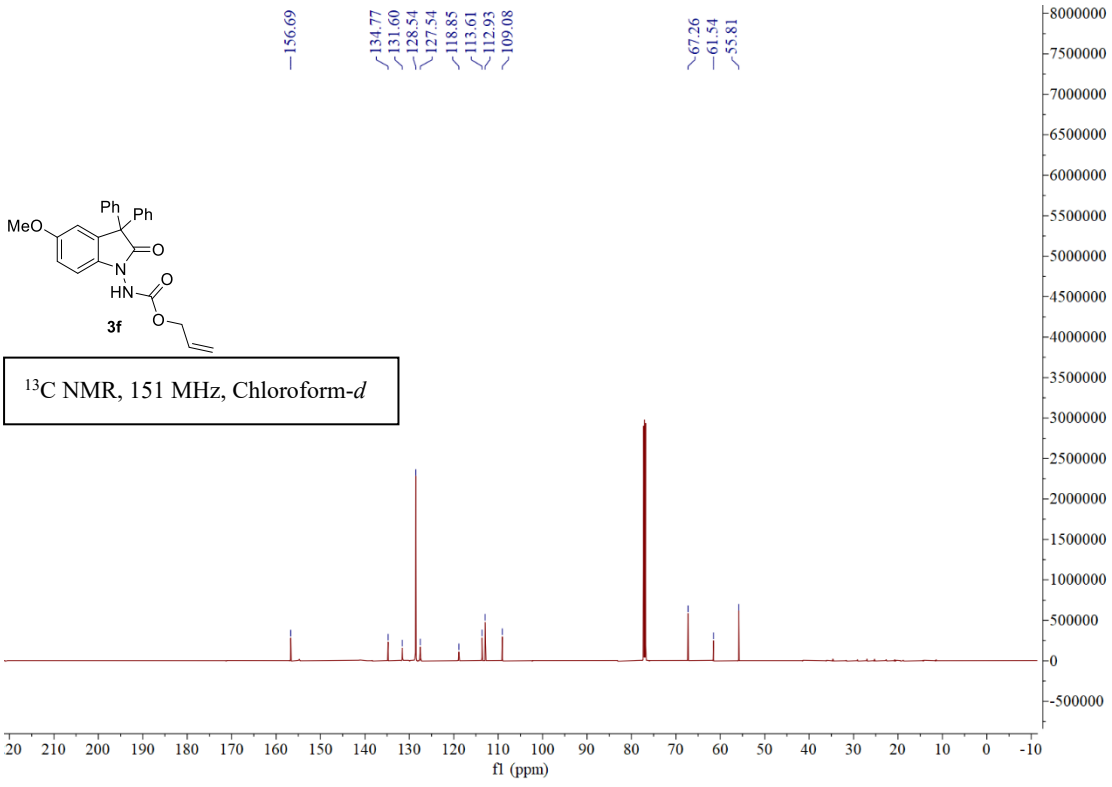


3e

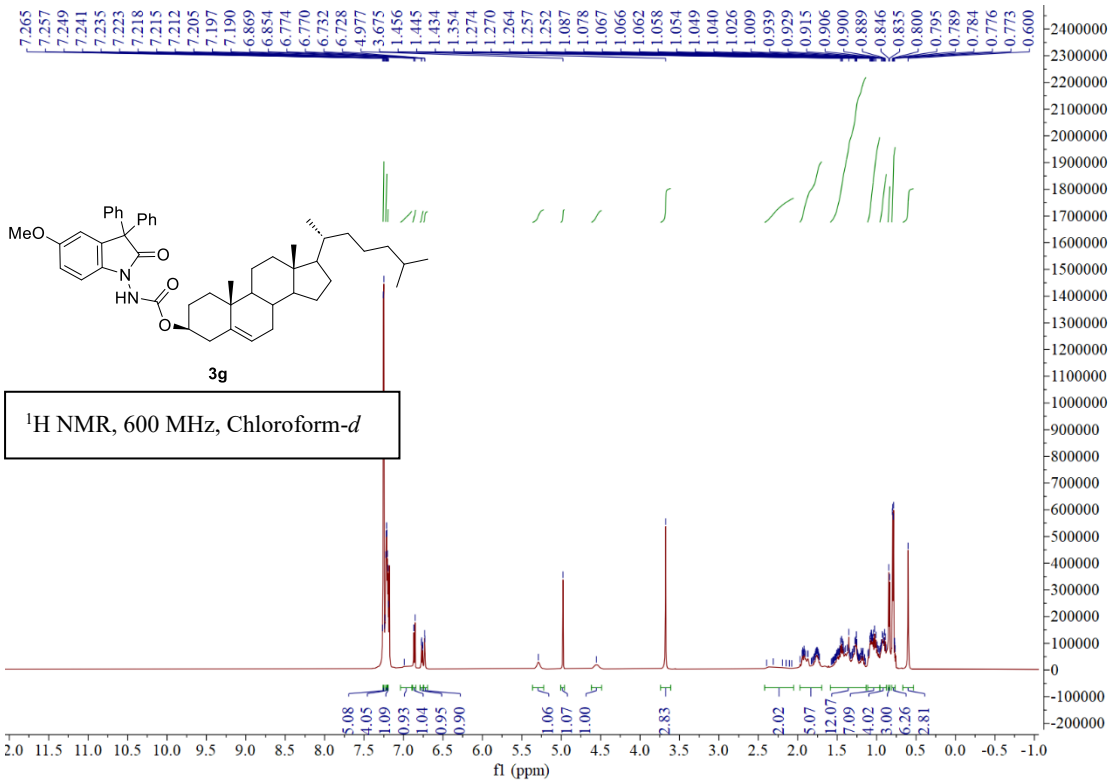
^{13}C NMR, 151 MHz, Chloroform-*d*



^{1}H NMR, 600 MHz, Chloroform-*d*



^{13}C NMR, 151 MHz, Chloroform-*d*

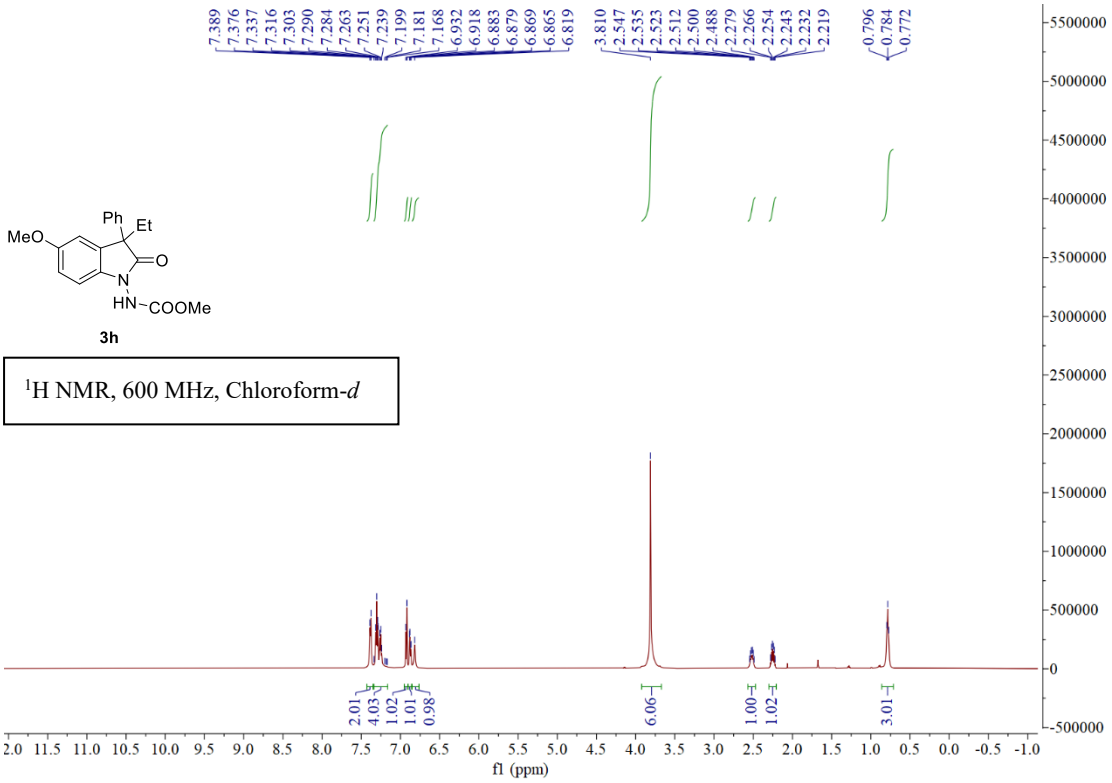


3g

^{1}H NMR, 600 MHz, Chloroform-*d*

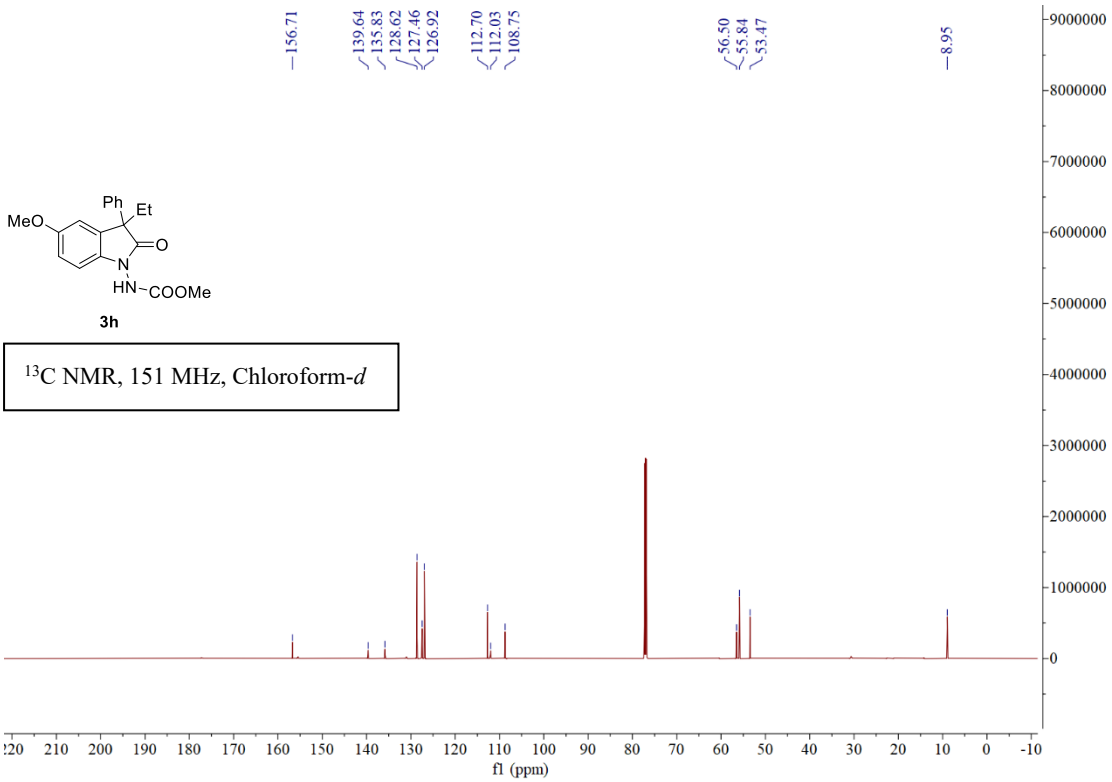
3g

^{13}C NMR, 151 MHz, Chloroform-*d*



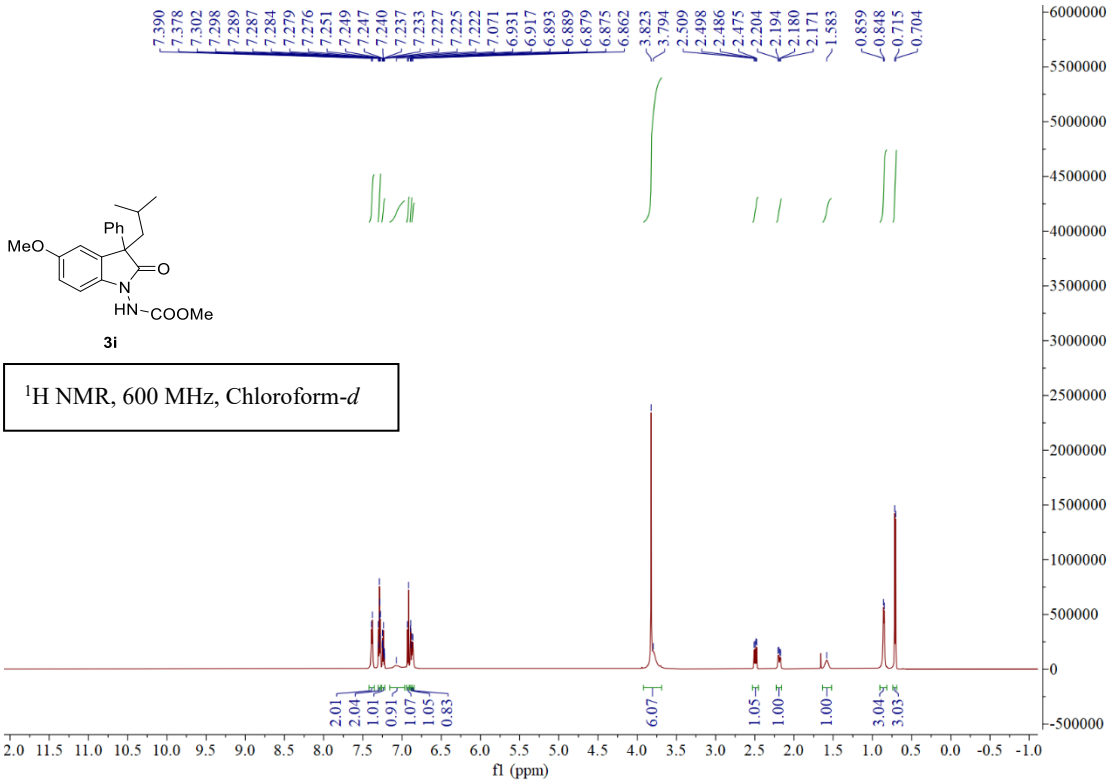
3h

^{1}H NMR, 600 MHz, Chloroform-*d*



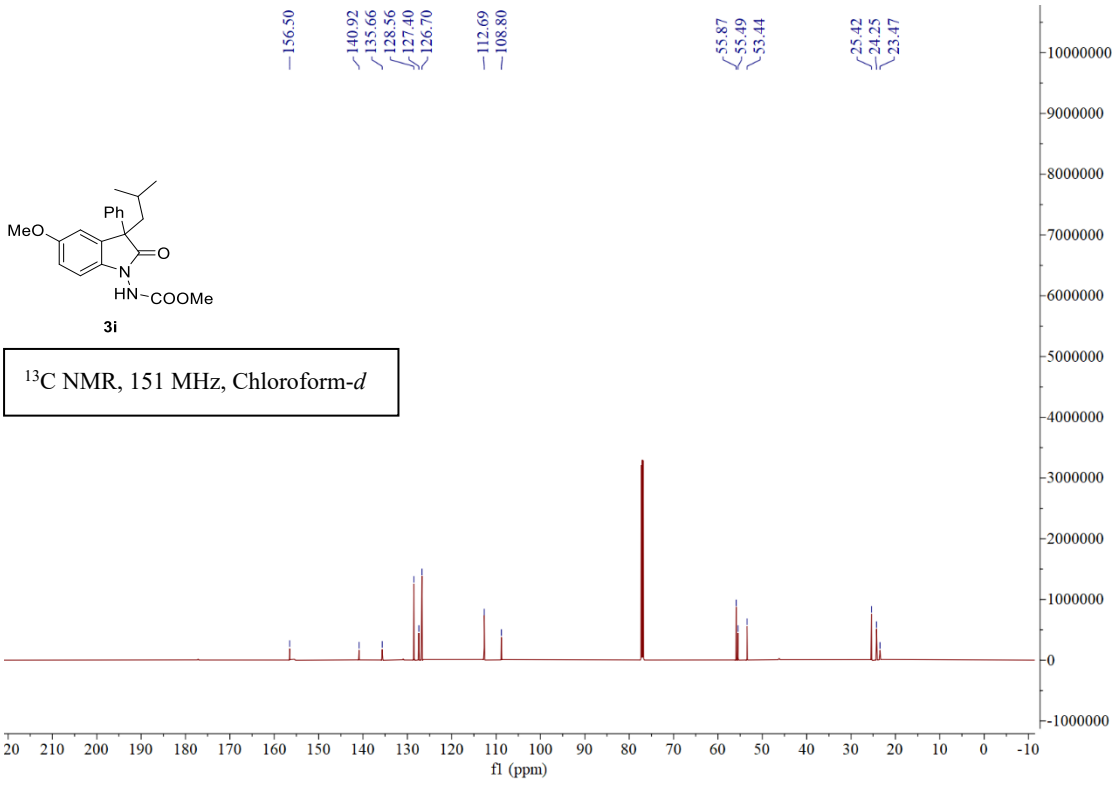
3h

^{13}C NMR, 151 MHz, Chloroform-*d*



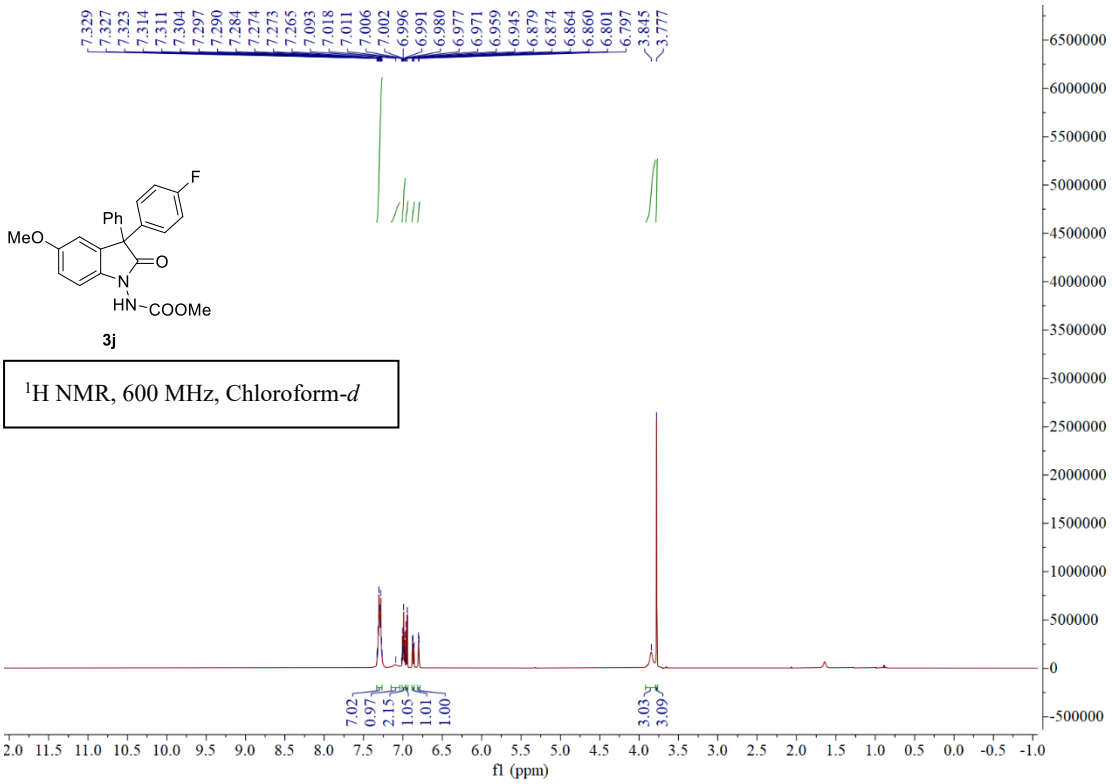
3i

^{1}H NMR, 600 MHz, Chloroform-*d*



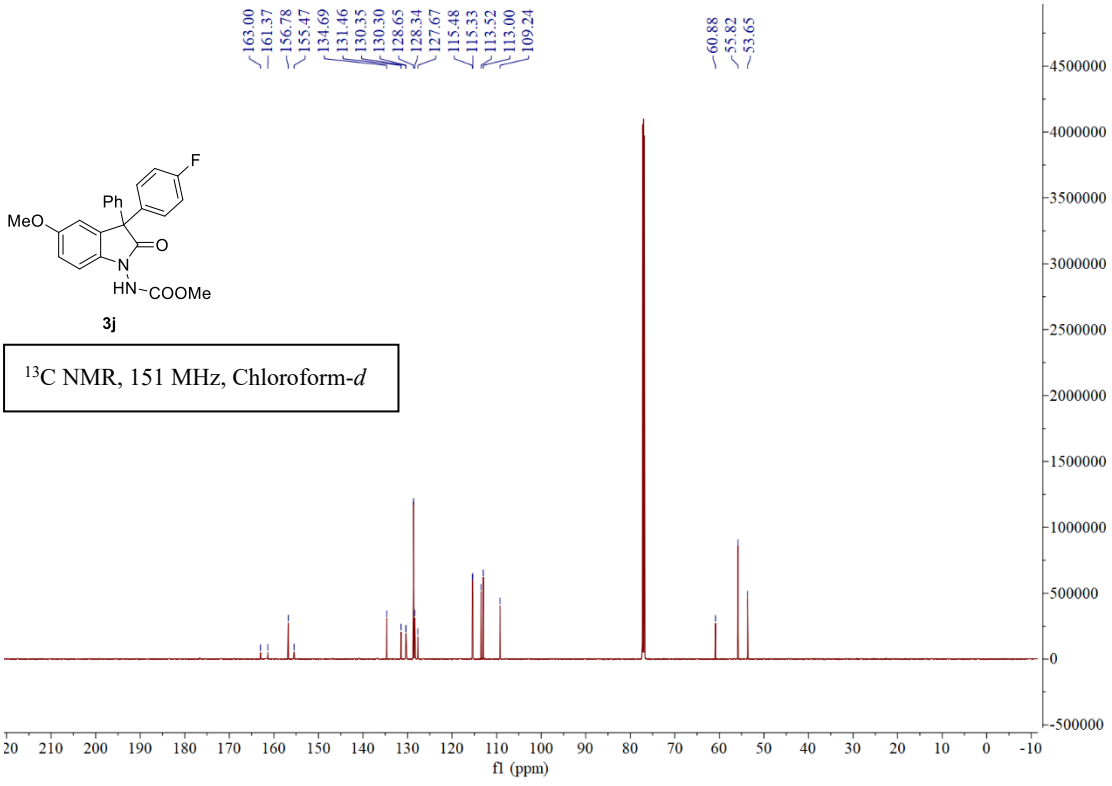
3i

^{13}C NMR, 151 MHz, Chloroform-*d*



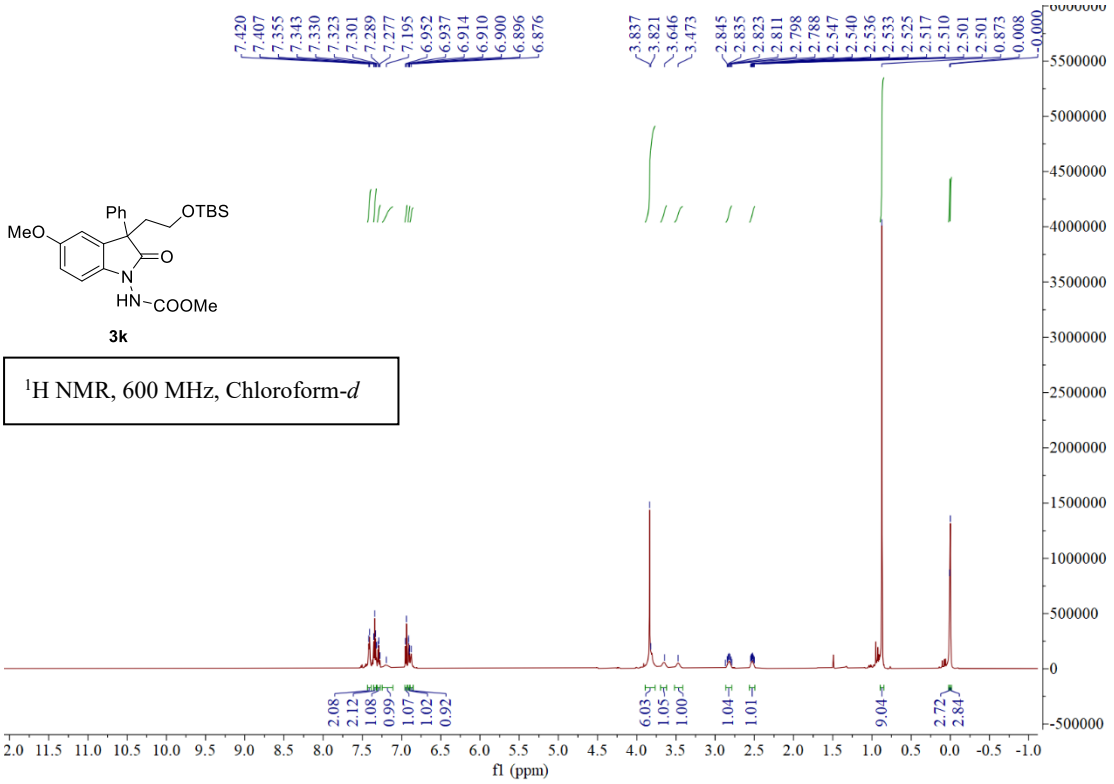
3j

^{1}H NMR, 600 MHz, Chloroform-*d*



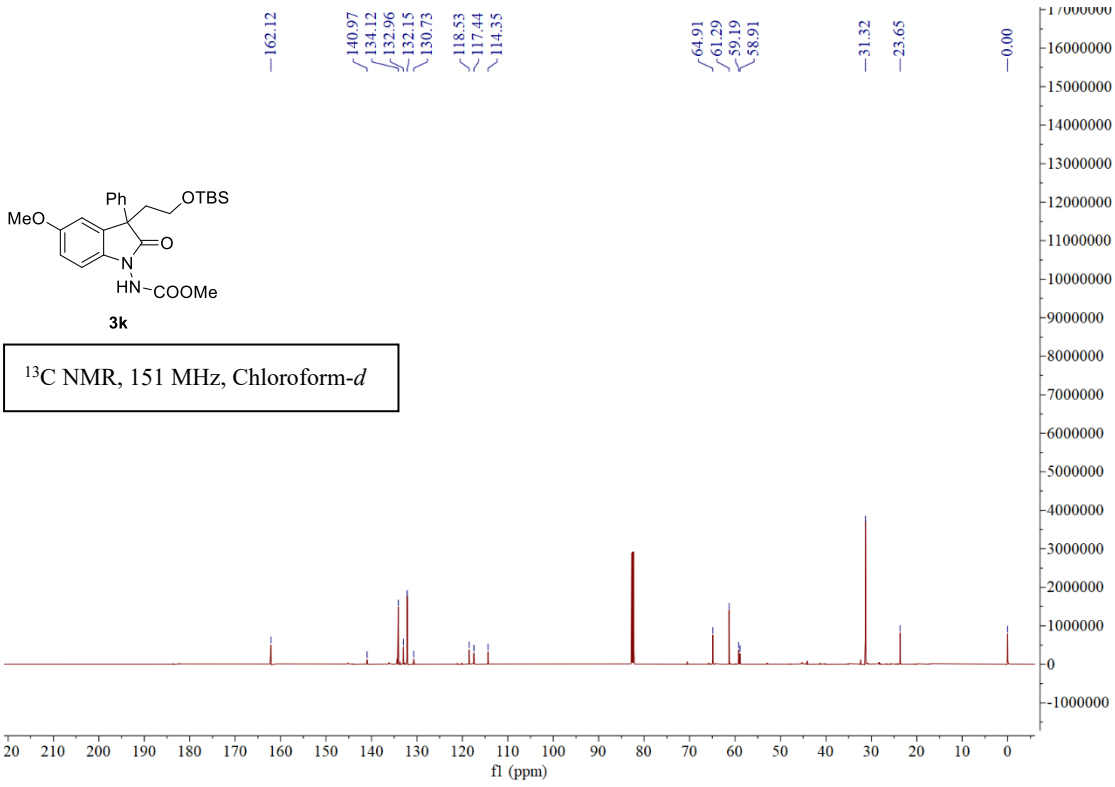
3j

^{13}C NMR, 151 MHz, Chloroform-*d*



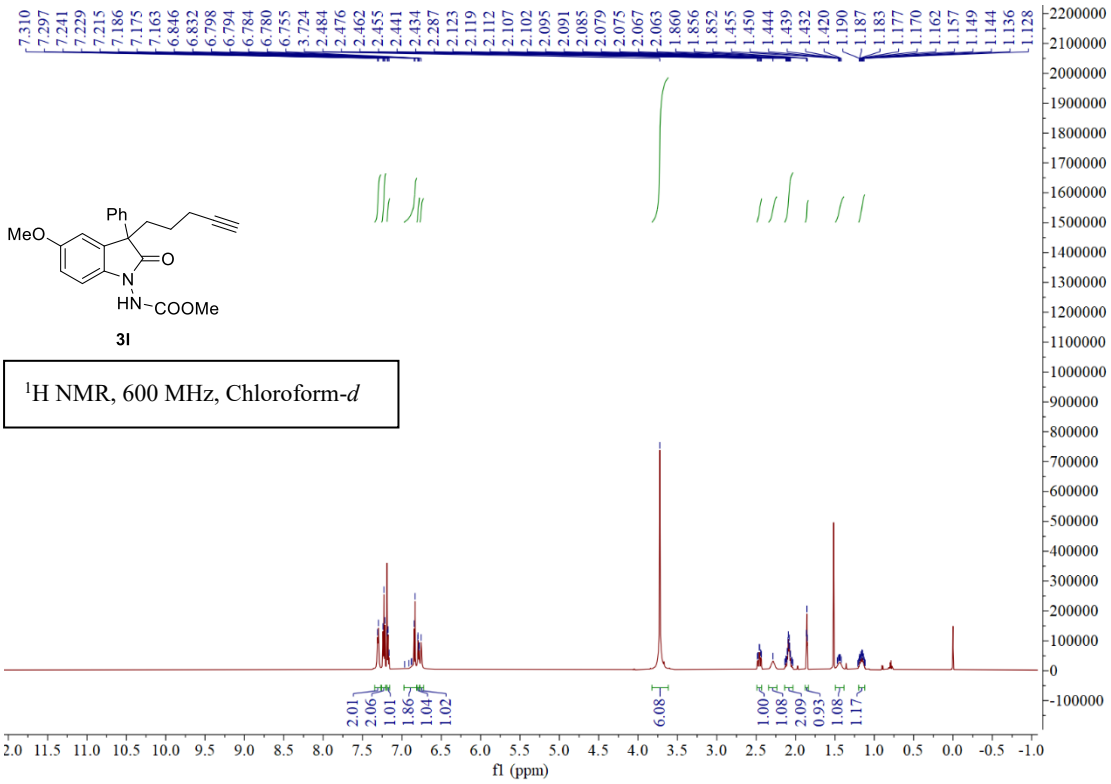
3k

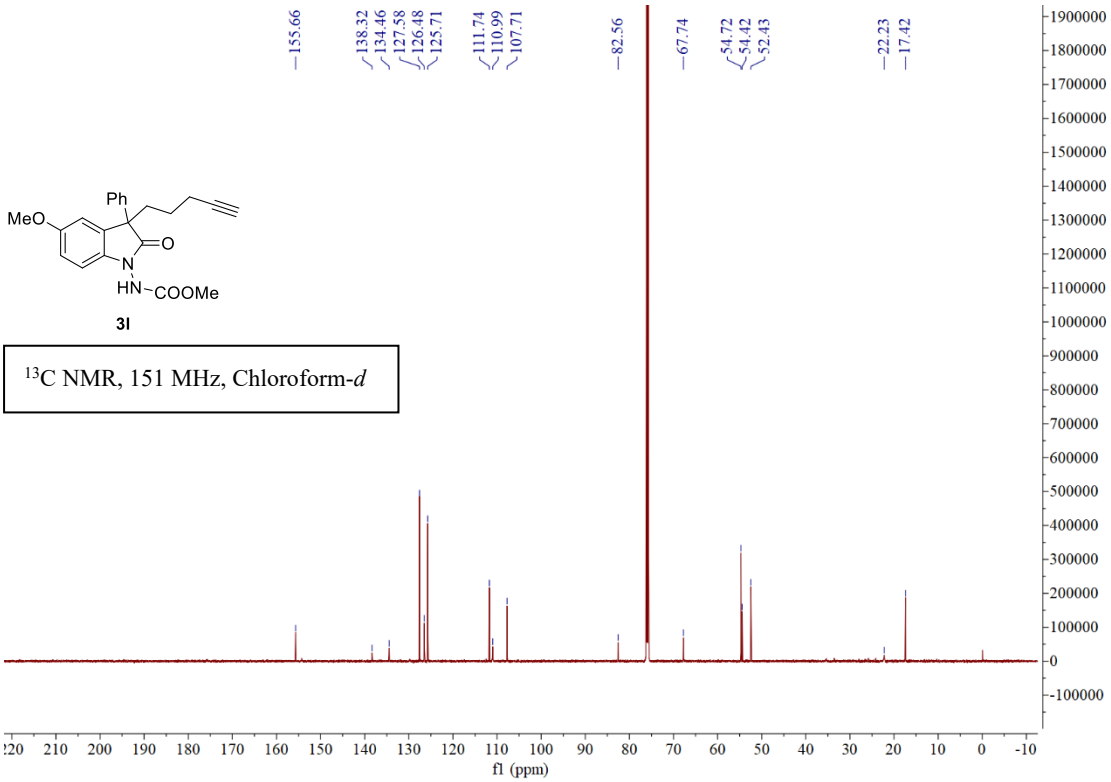
^{1}H NMR, 600 MHz, Chloroform-*d*

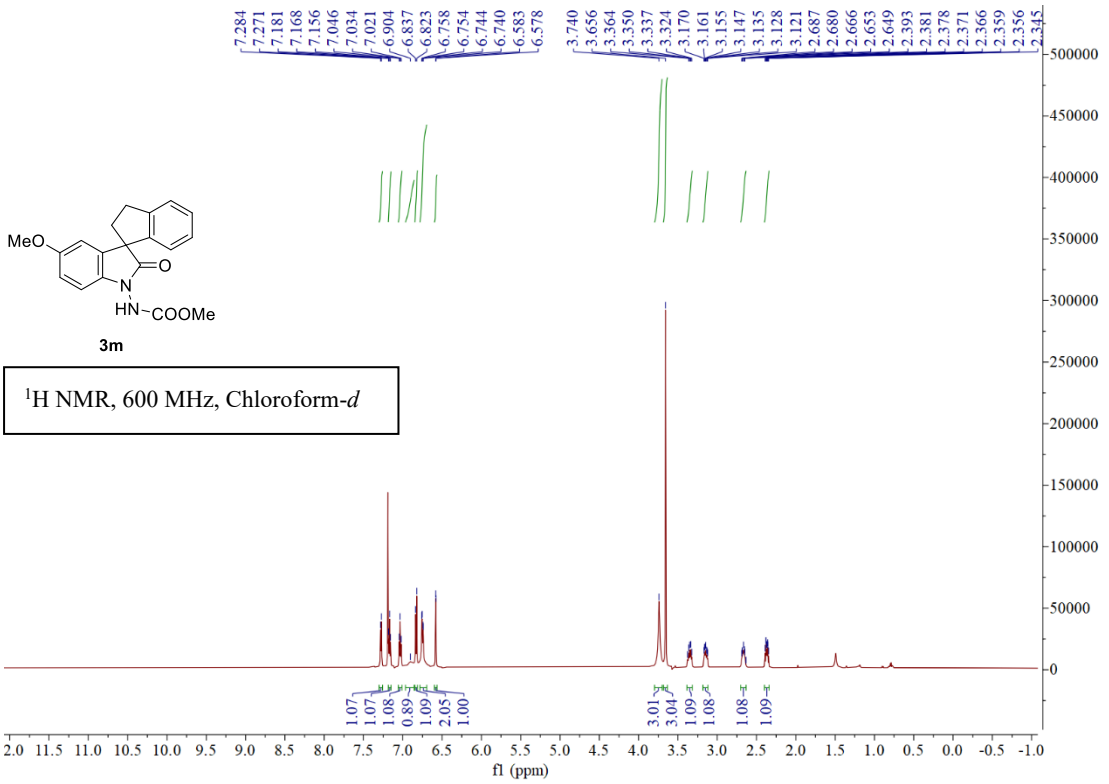


3k

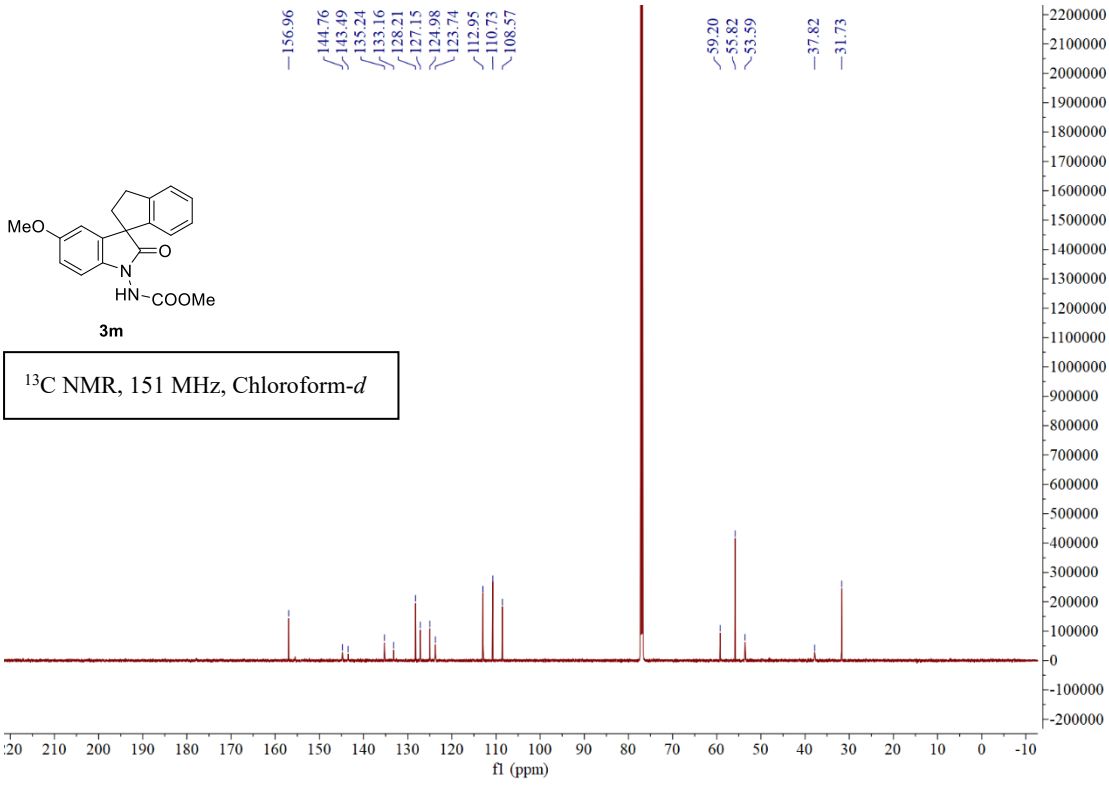
^{13}C NMR, 151 MHz, Chloroform-*d*


Ph
MeO
O
N
HN
COOMe
3l
1H NMR, 600 MHz, Chloroform-d
f1 (ppm)

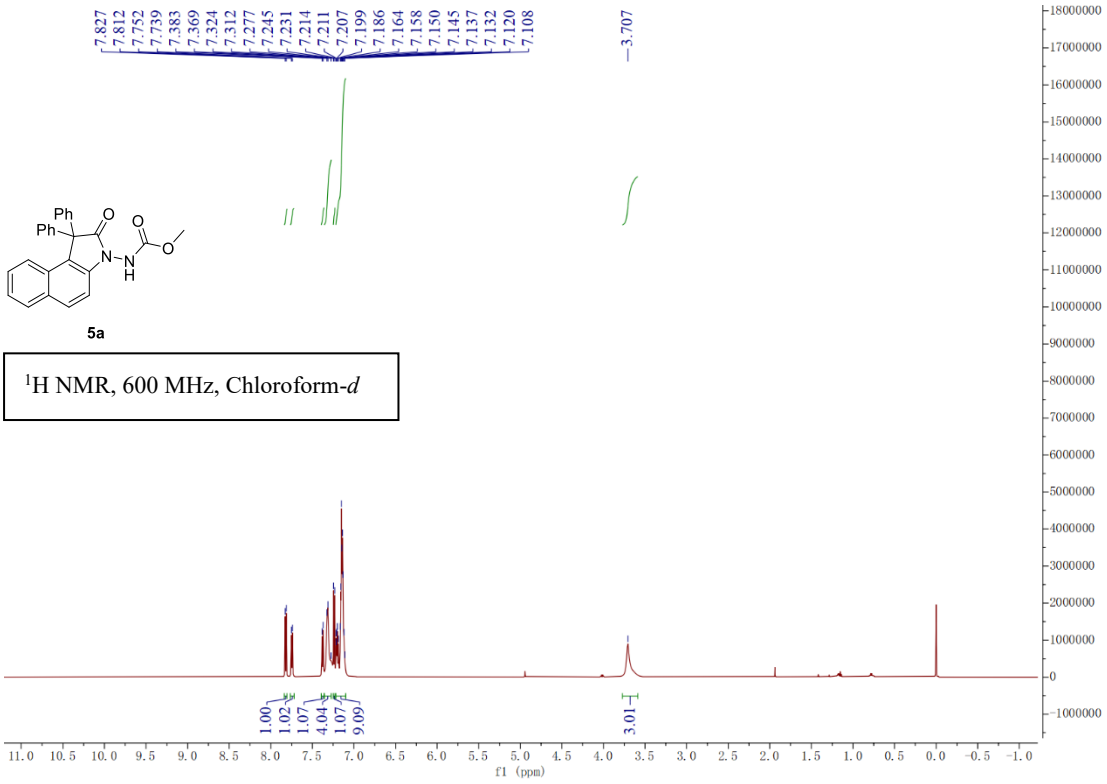

Ph
MeO
O
N
HN
COOMe
3l
13C NMR, 151 MHz, Chloroform-d
f1 (ppm)



^{1}H NMR, 600 MHz, Chloroform-*d*

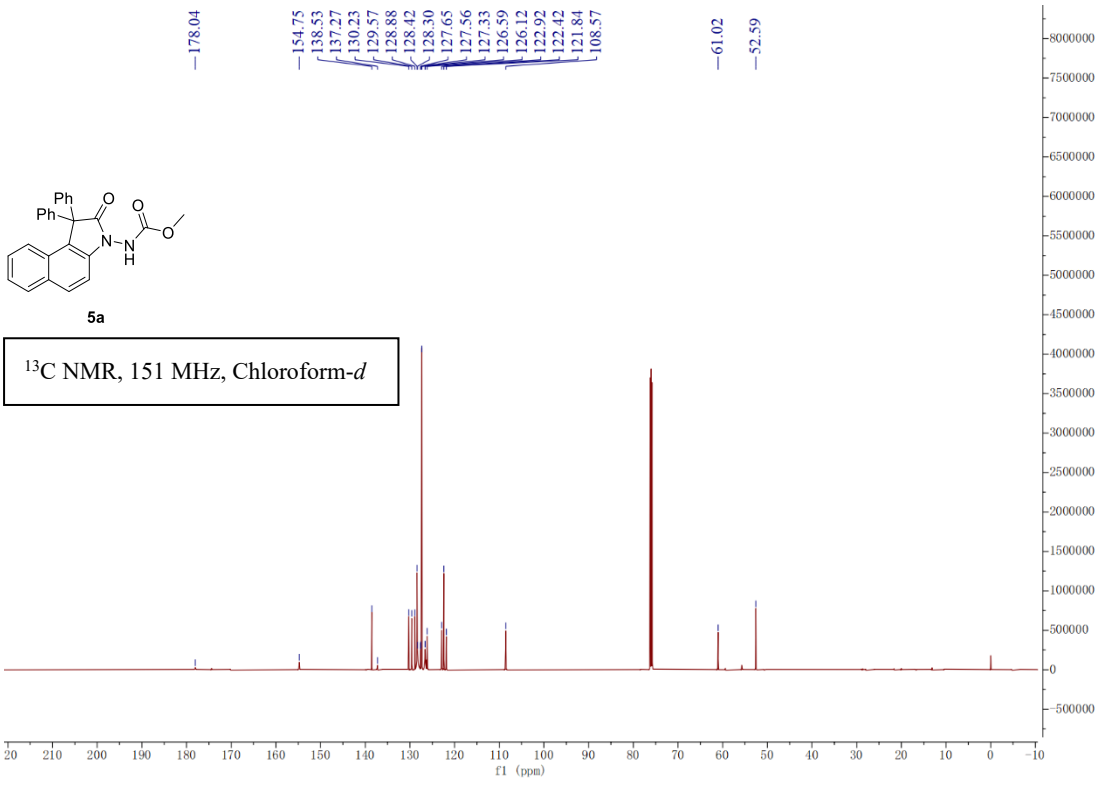


^{13}C NMR, 151 MHz, Chloroform-*d*



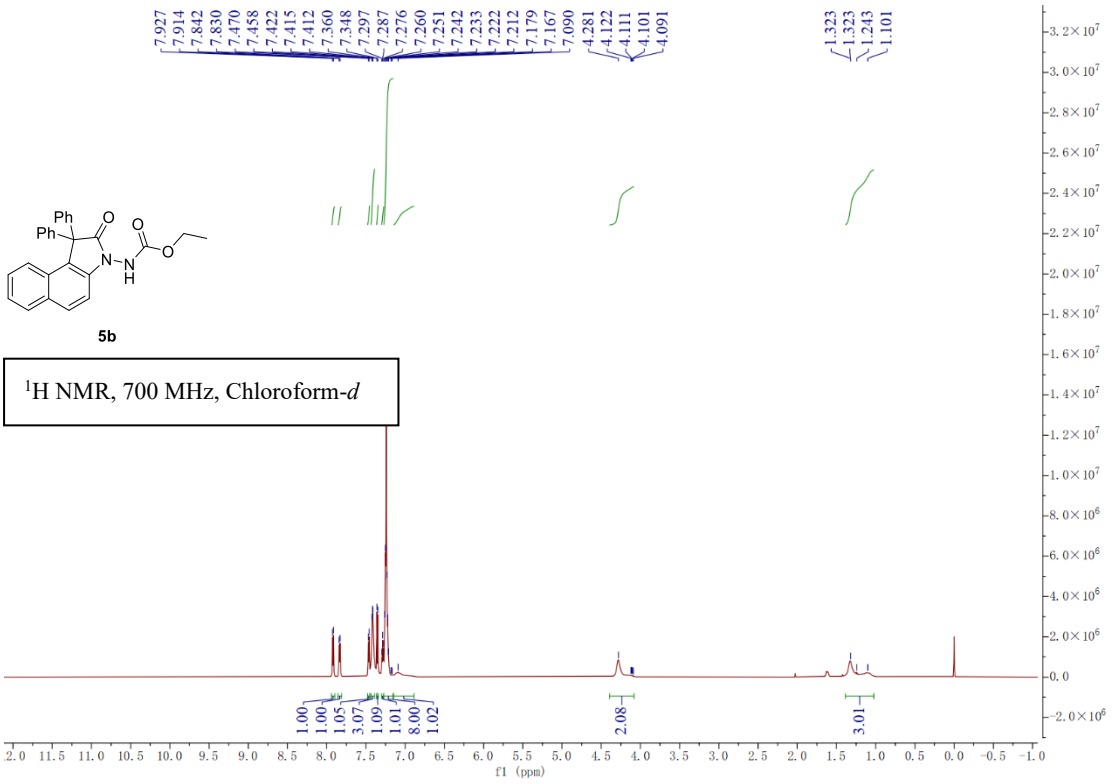
5a

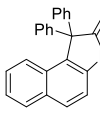
^{1}H NMR, 600 MHz, Chloroform-*d*



5a

^{13}C NMR, 151 MHz, Chloroform-*d*



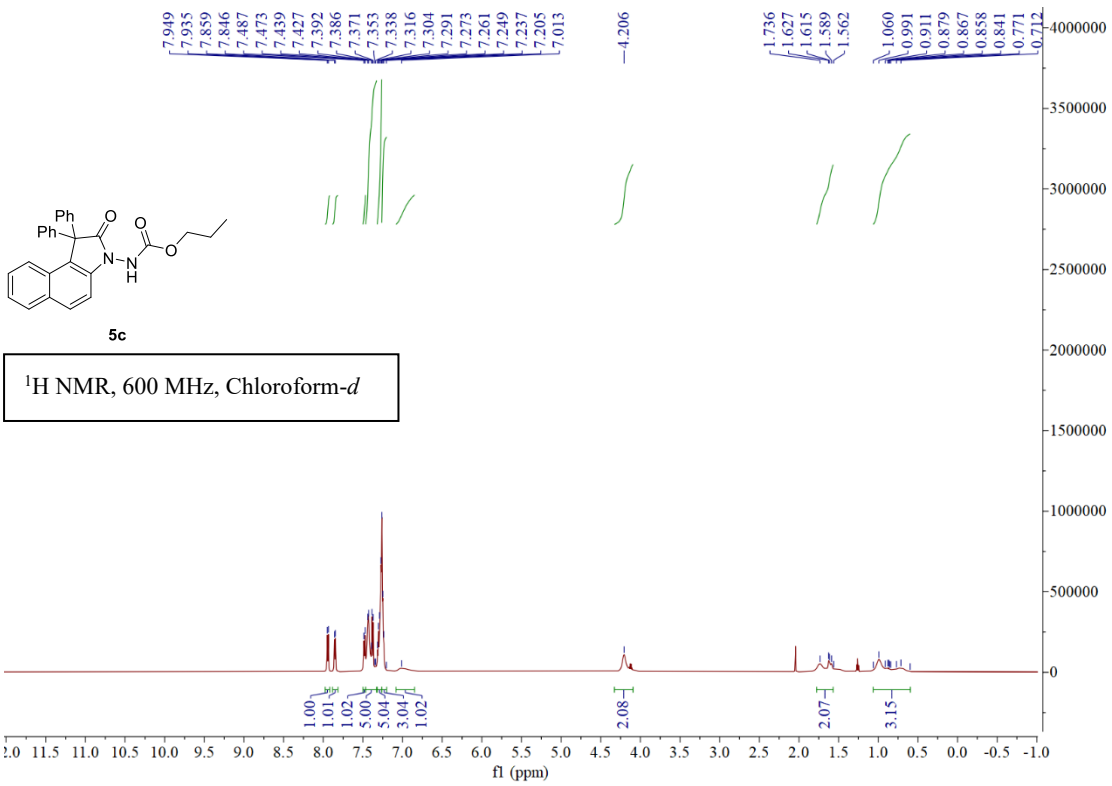


5b

^{1}H NMR, 700 MHz, Chloroform-*d*

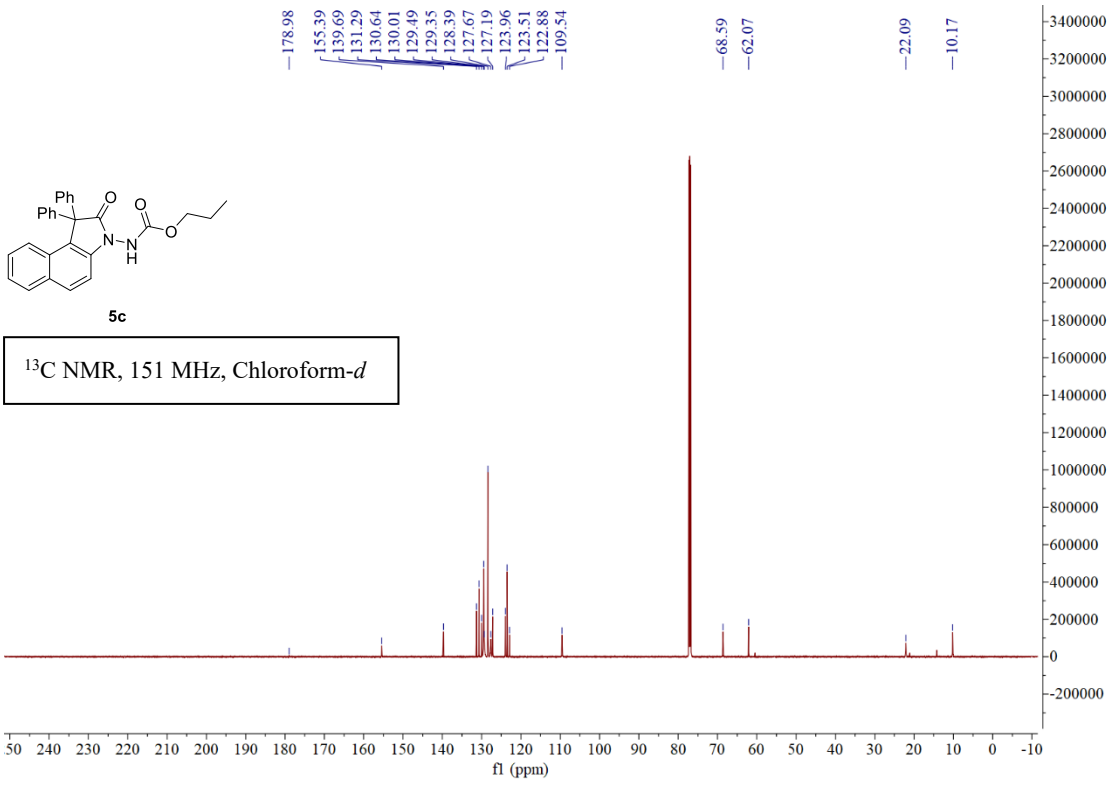
5b

^{13}C NMR, 176 MHz, Chloroform-*d*



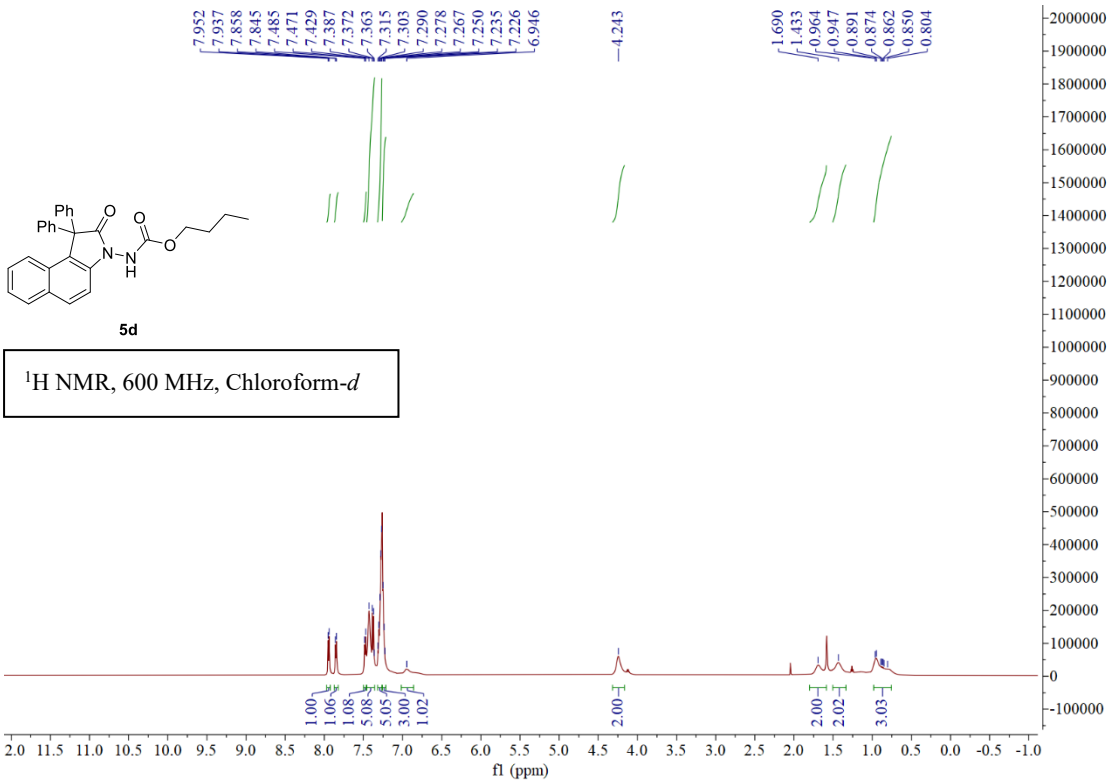
5c

^{1}H NMR, 600 MHz, Chloroform-*d*



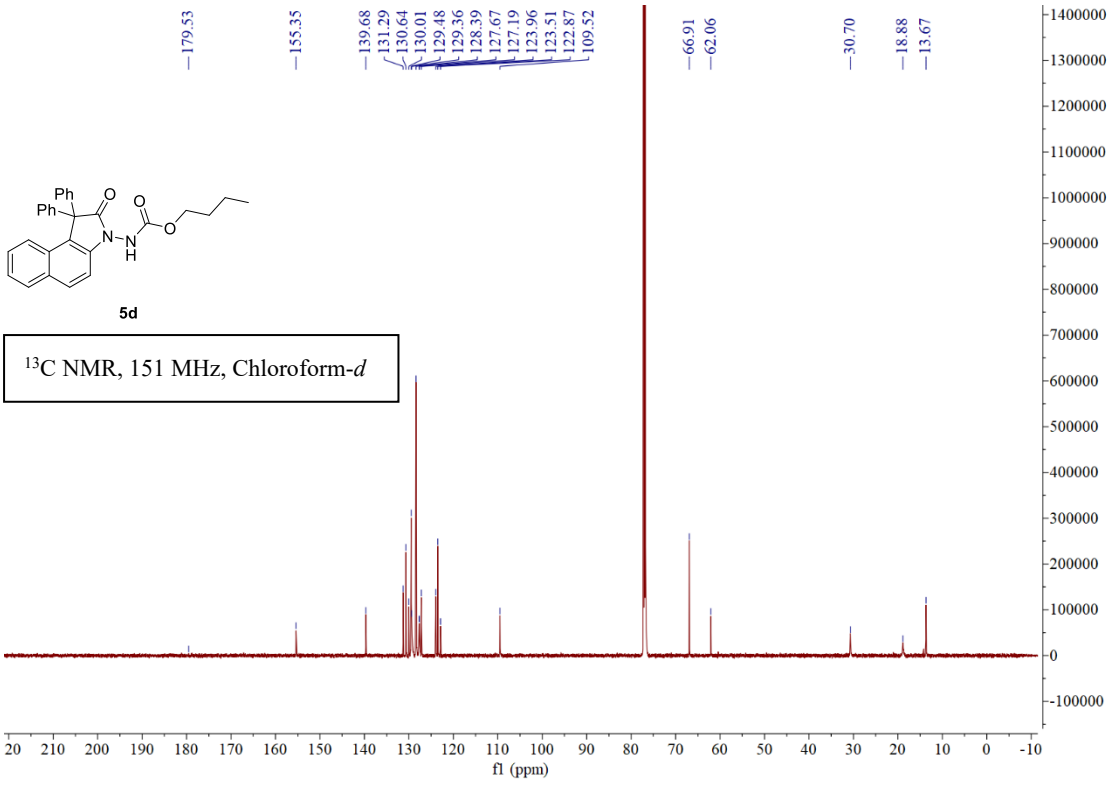
5c

^{13}C NMR, 151 MHz, Chloroform-*d*



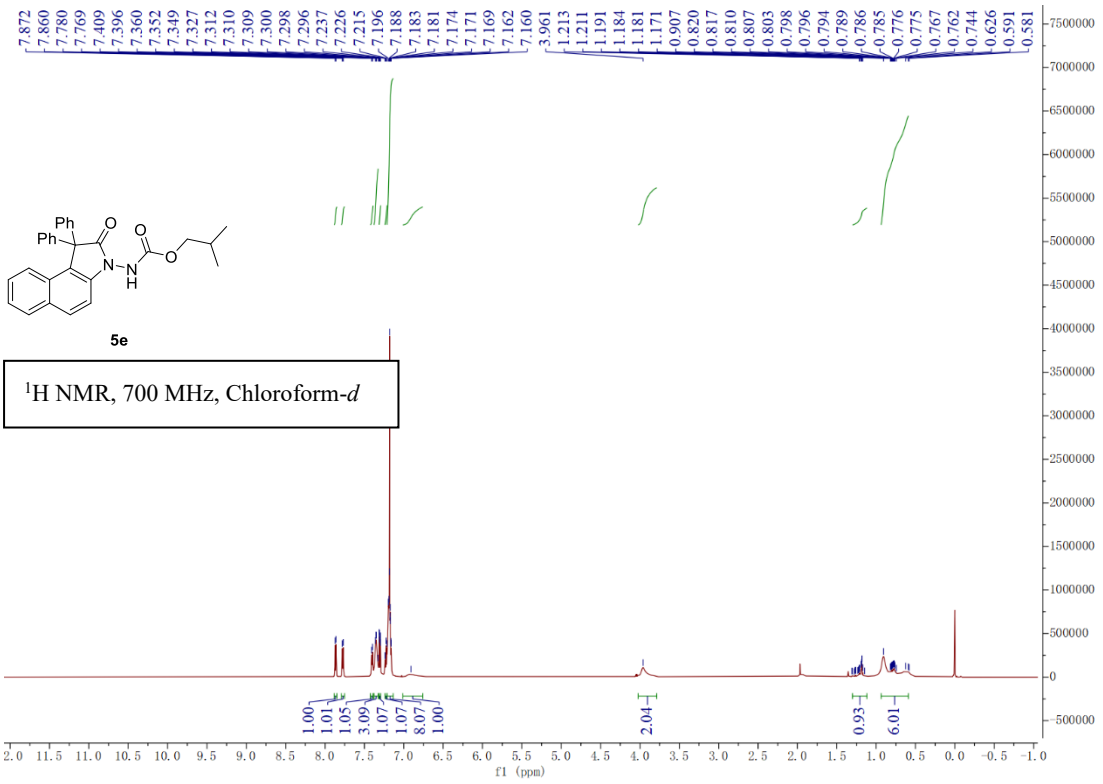
5d

^{1}H NMR, 600 MHz, Chloroform-*d*



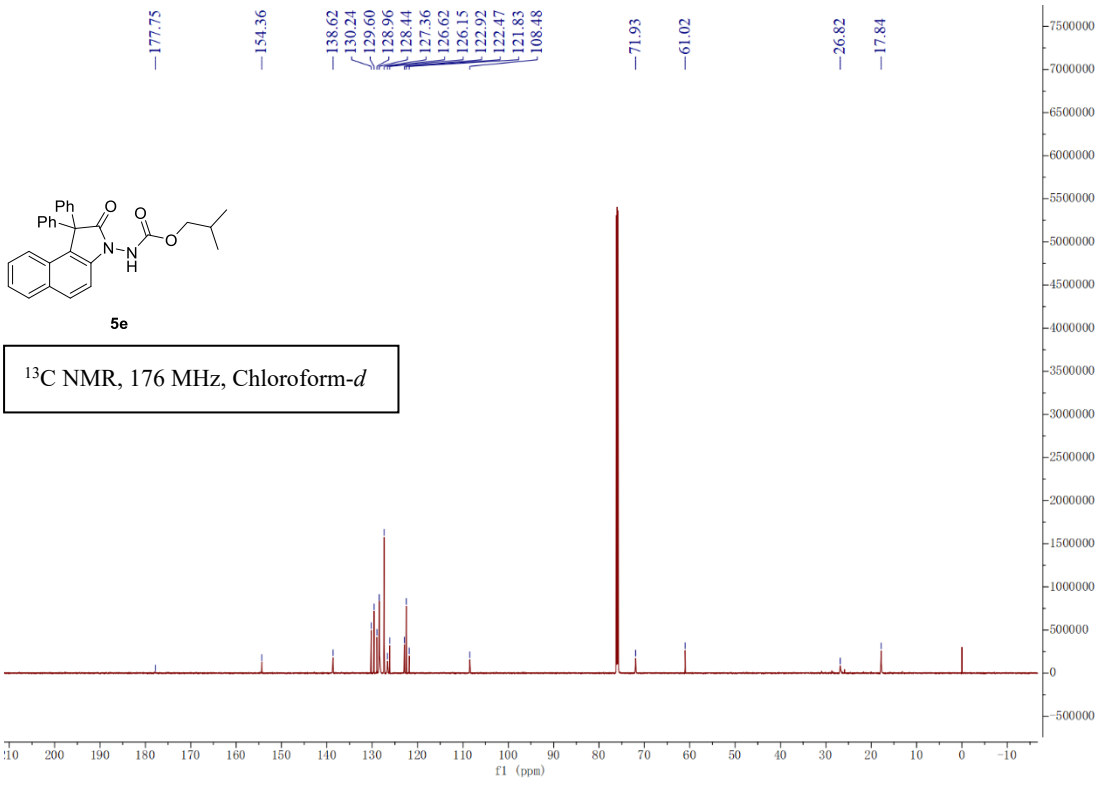
5d

^{13}C NMR, 151 MHz, Chloroform-*d*



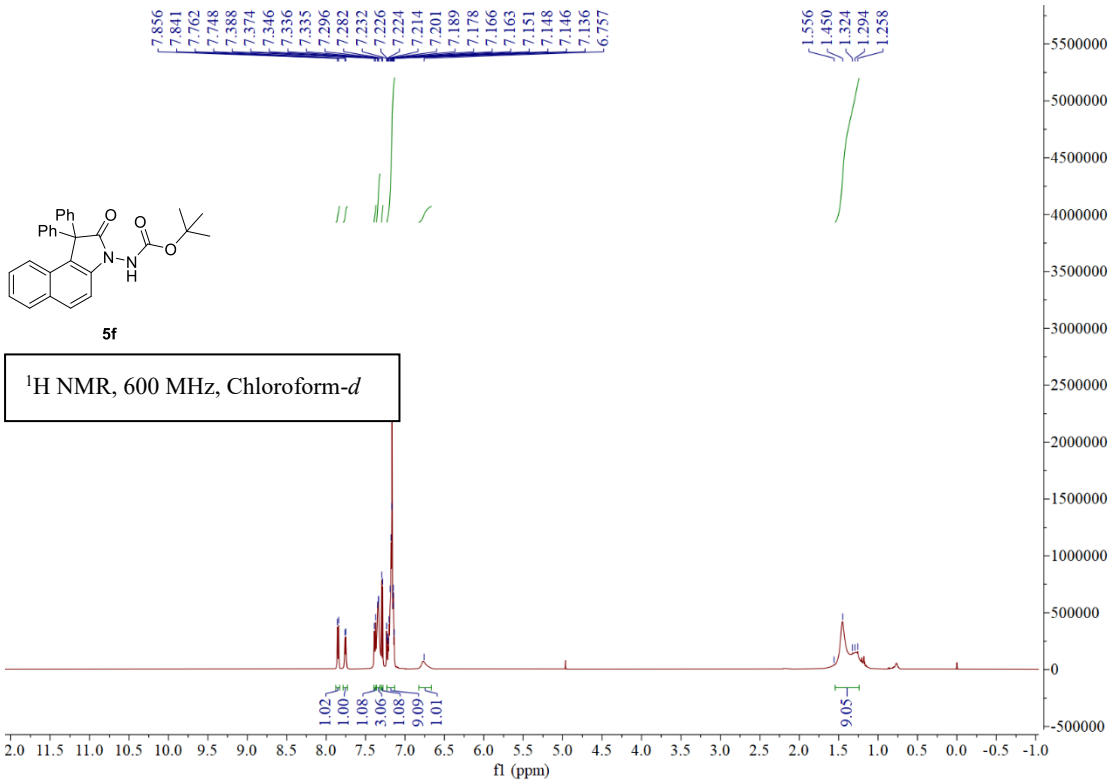
5e

^{1}H NMR, 700 MHz, Chloroform-*d*



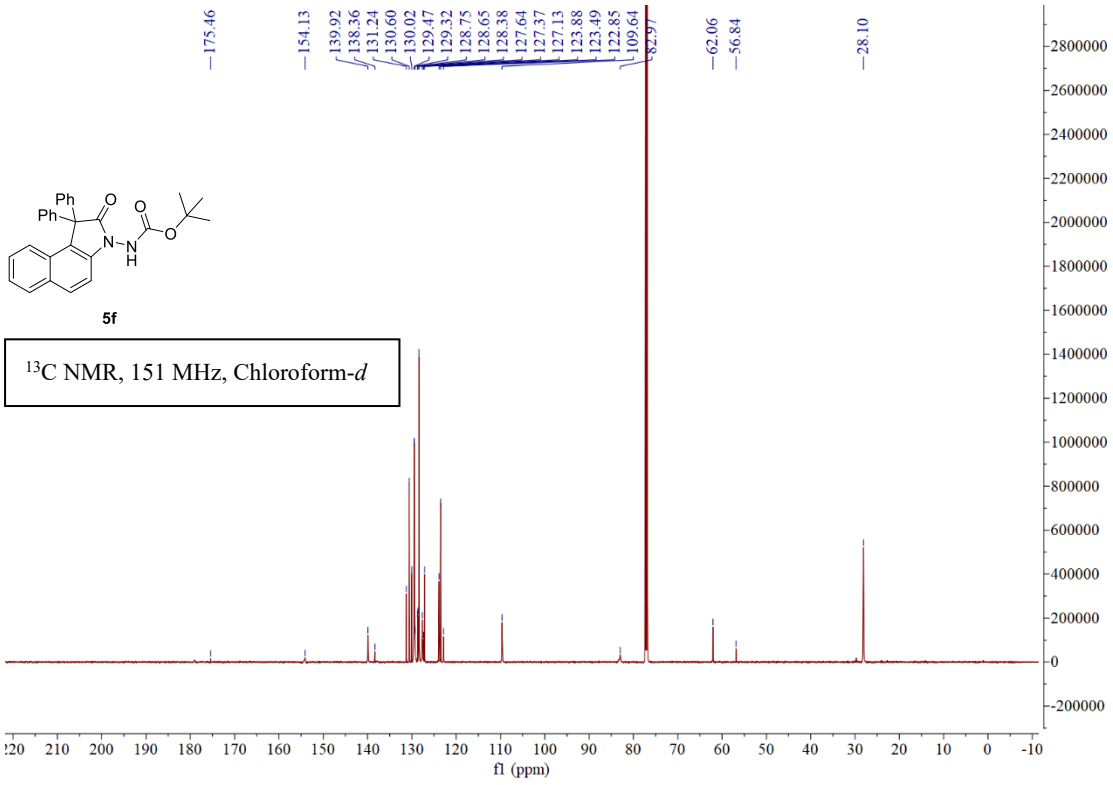
5e

^{13}C NMR, 176 MHz, Chloroform-*d*



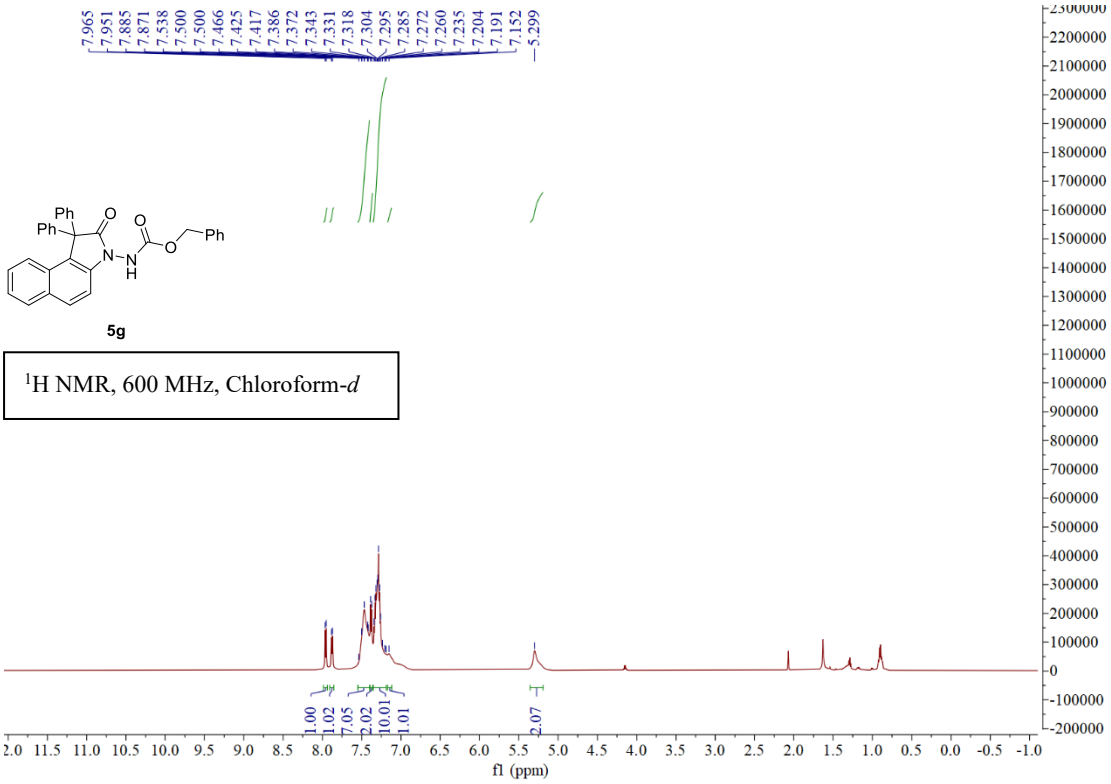
5f

^{1}H NMR, 600 MHz, Chloroform-*d*



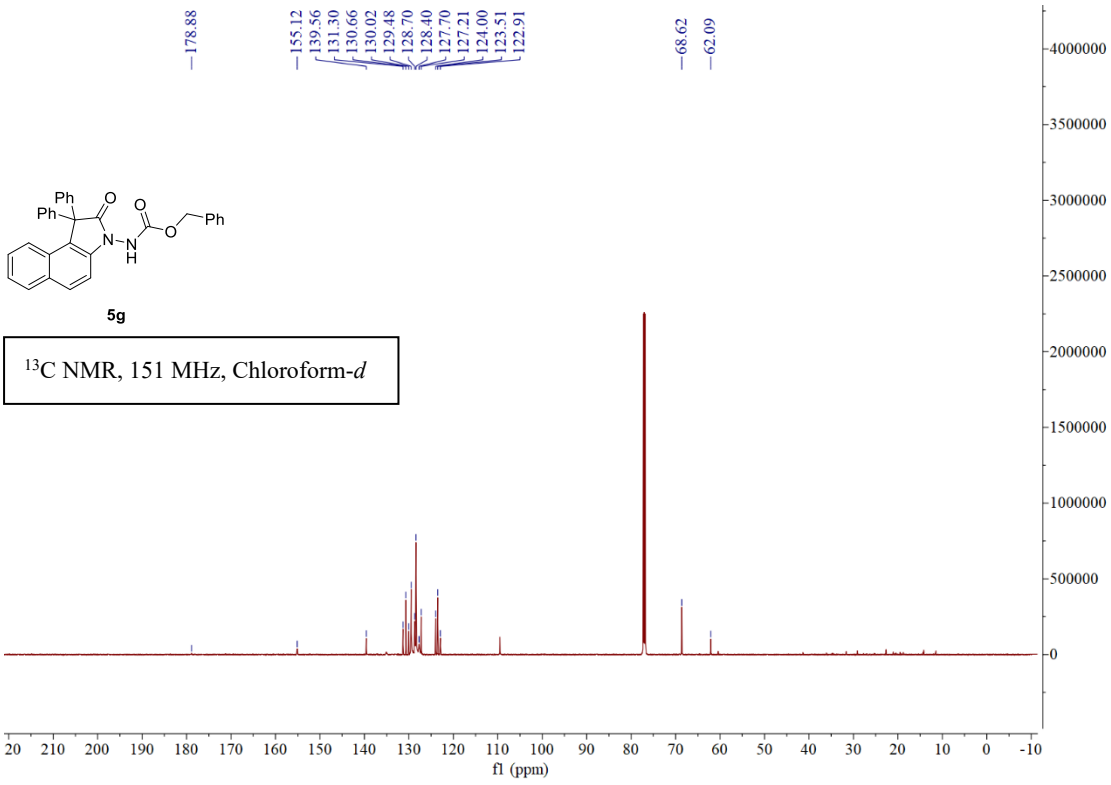
5f

^{13}C NMR, 151 MHz, Chloroform-*d*



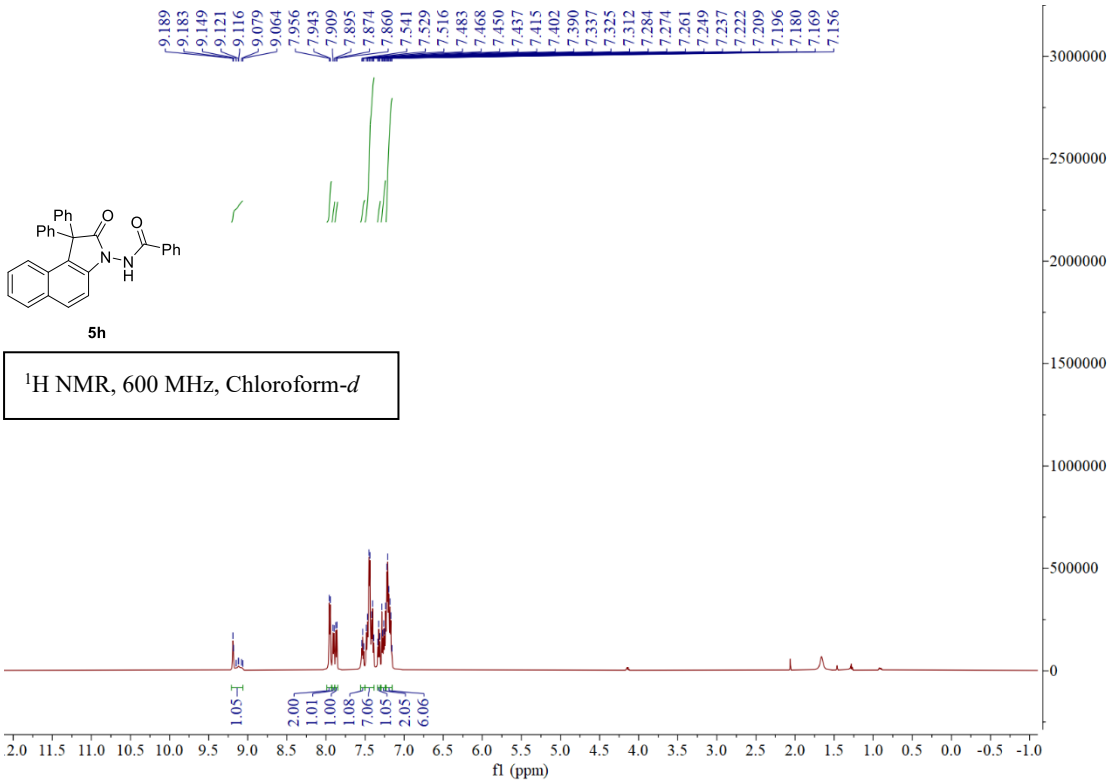
5g

^{1}H NMR, 600 MHz, Chloroform-*d*



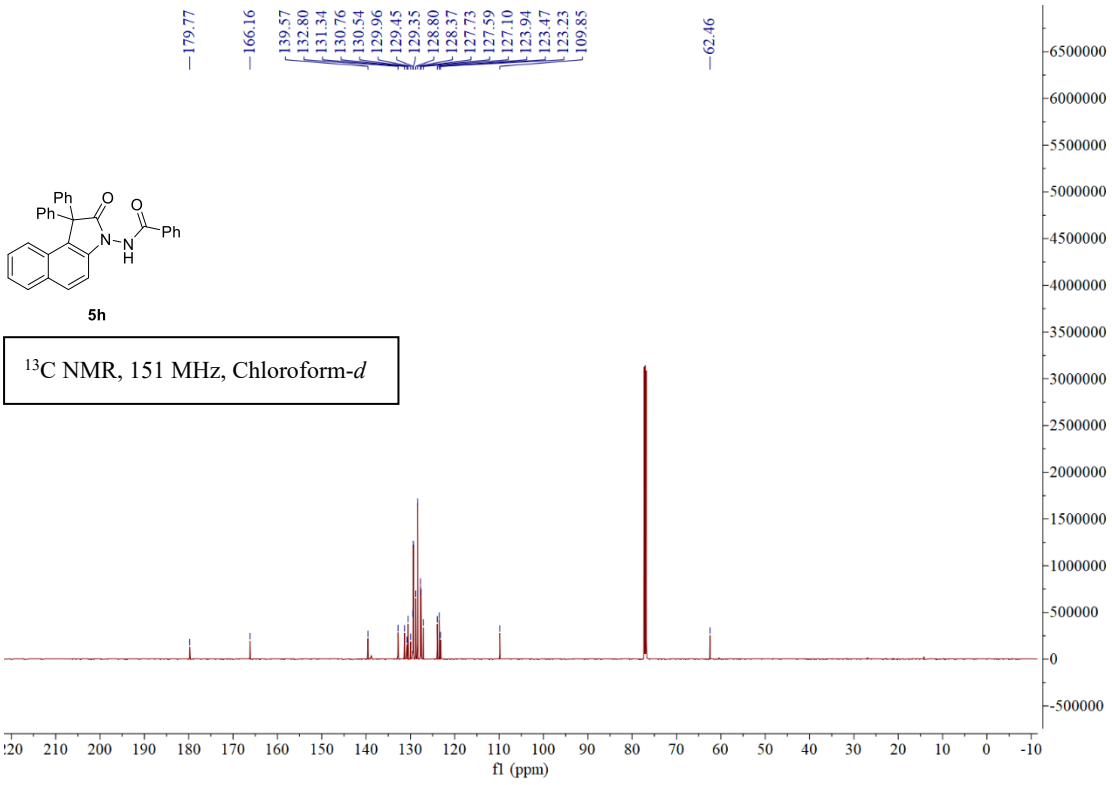
5g

^{13}C NMR, 151 MHz, Chloroform-*d*



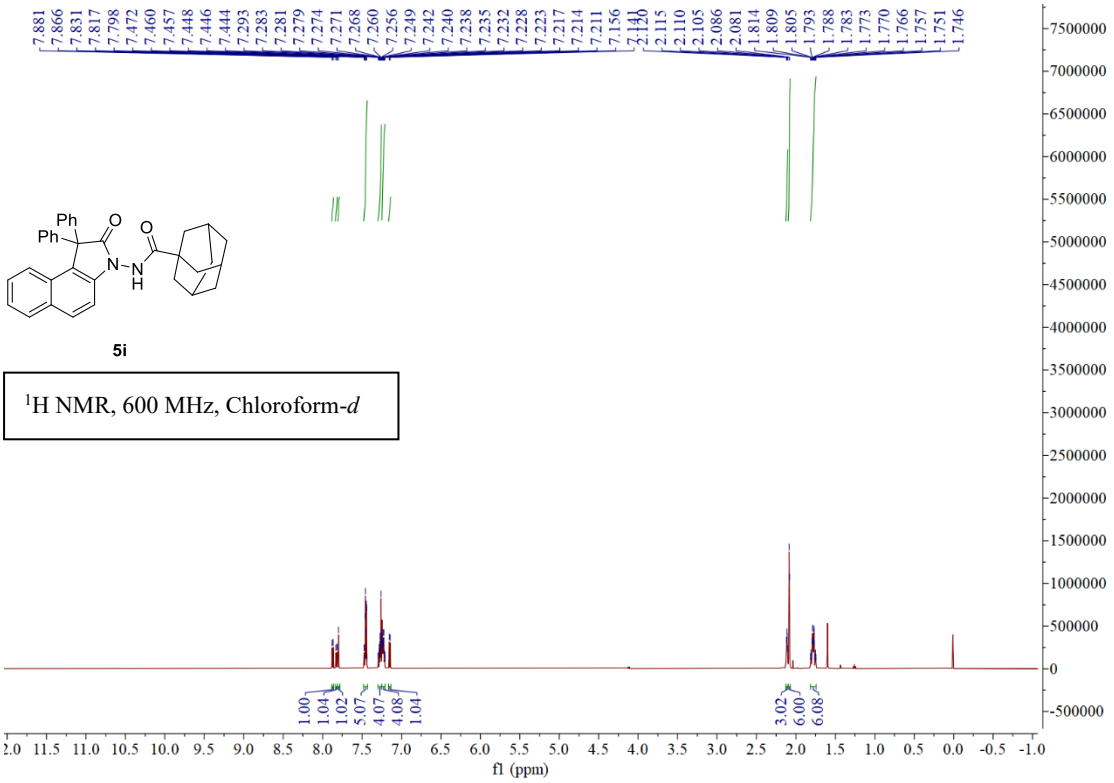
5h

^{1}H NMR, 600 MHz, Chloroform-*d*



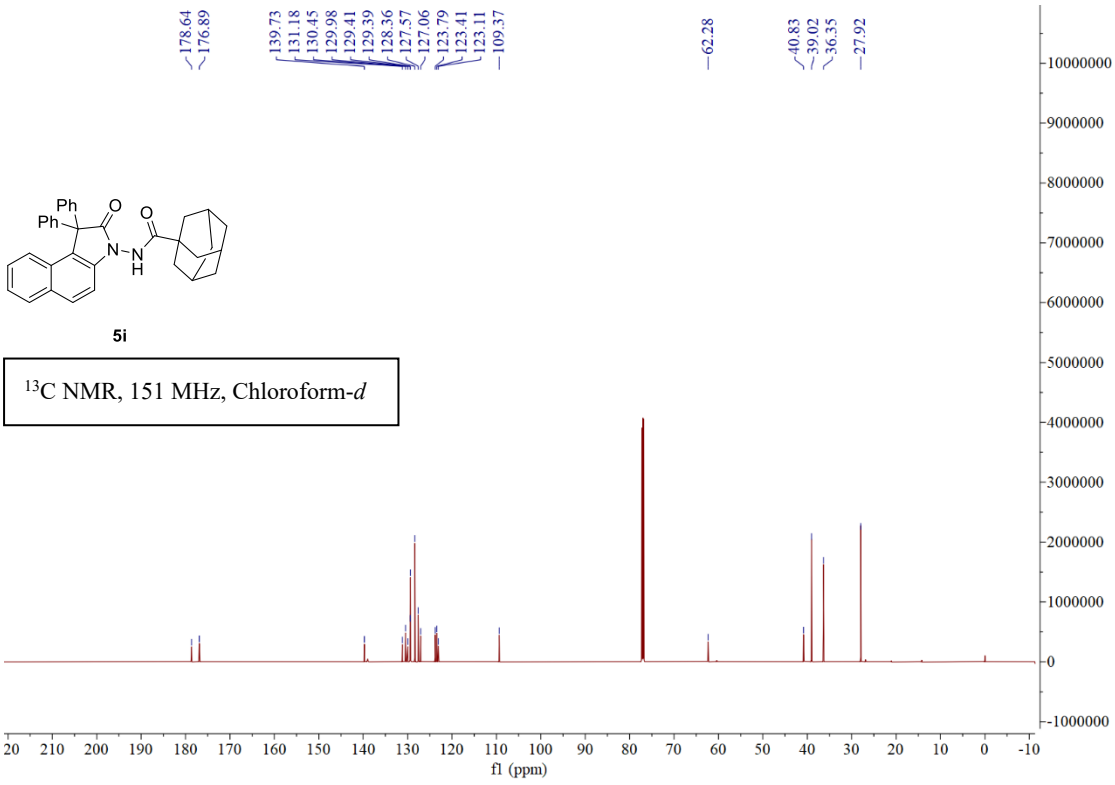
5h

^{13}C NMR, 151 MHz, Chloroform-*d*



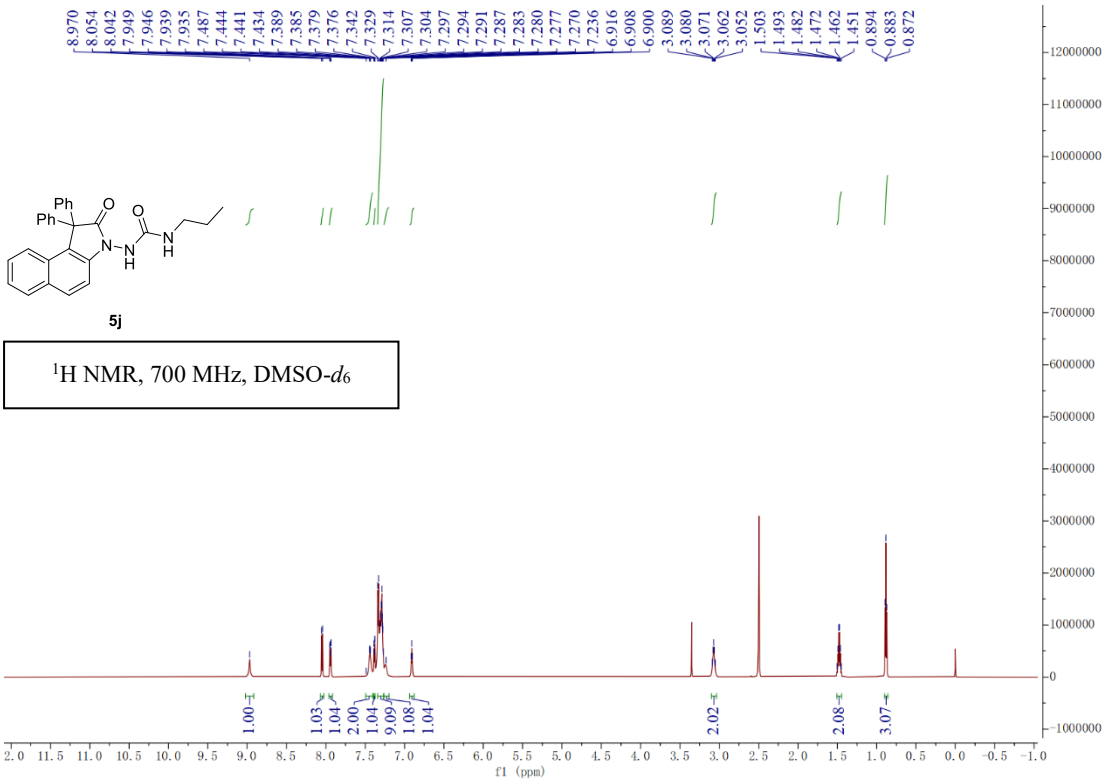
5i

^{1}H NMR, 600 MHz, Chloroform-*d*



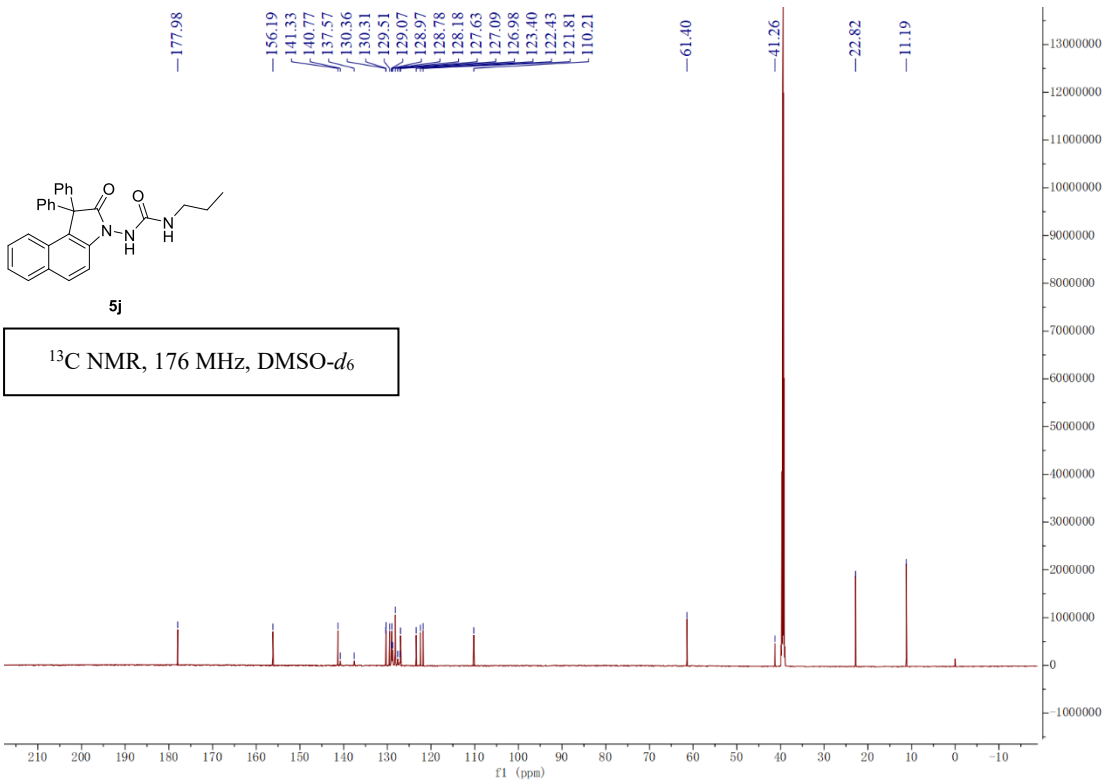
5i

^{13}C NMR, 151 MHz, Chloroform-*d*



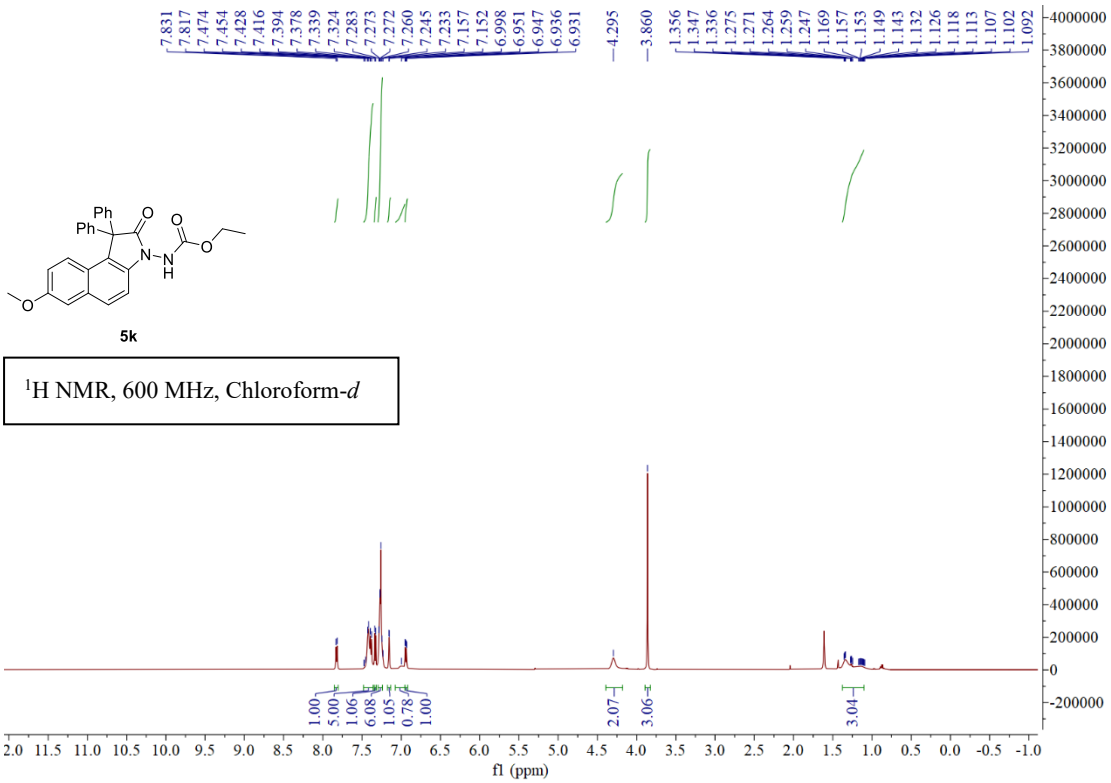
5j

^{1}H NMR, 700 MHz, DMSO-d_6



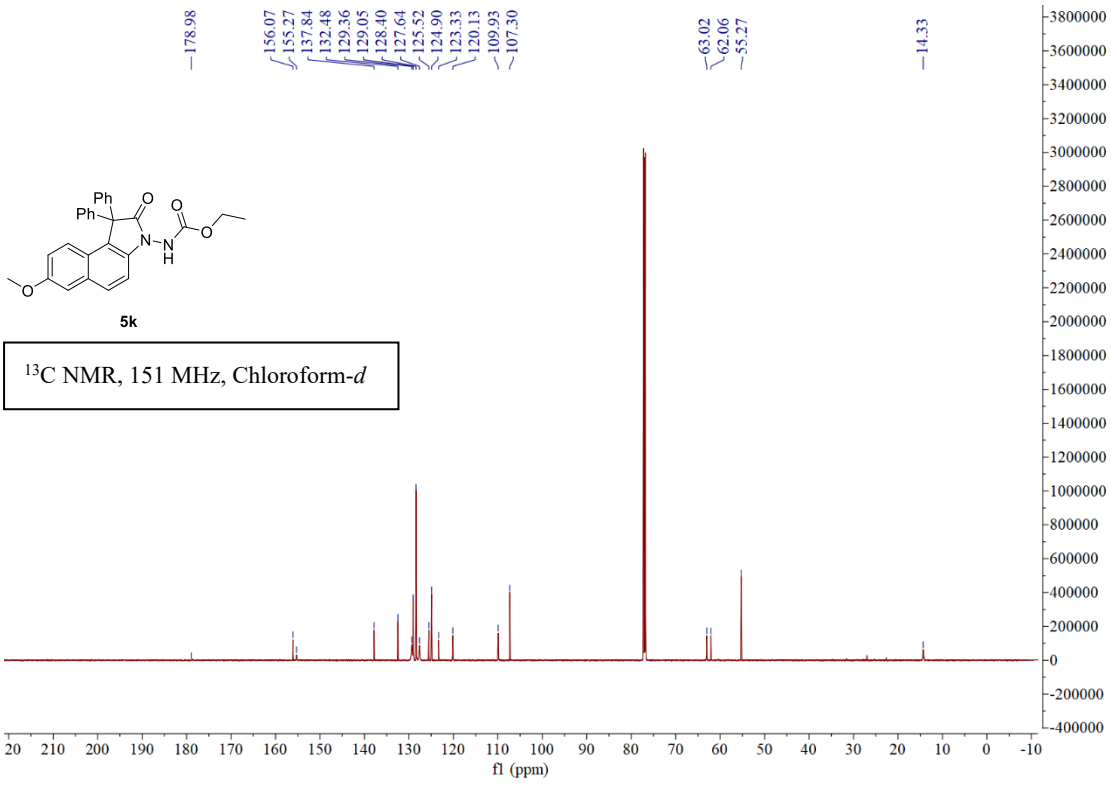
5j

^{13}C NMR, 176 MHz, DMSO-d_6



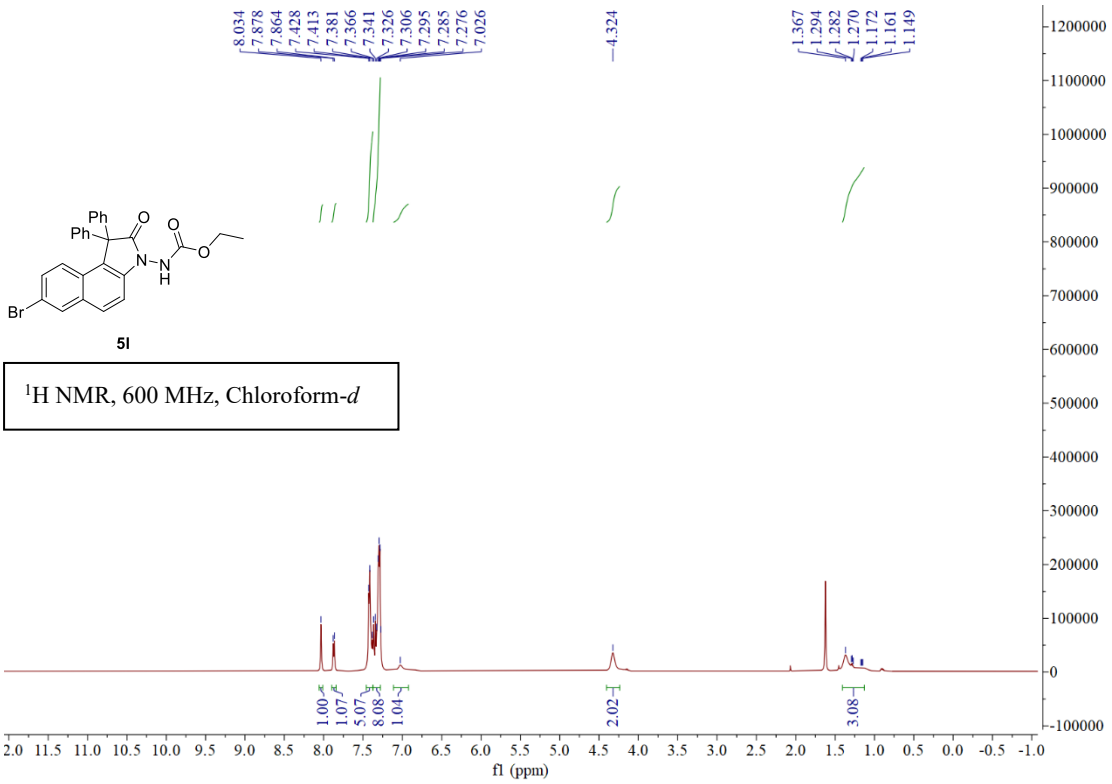
5k

^{1}H NMR, 600 MHz, Chloroform-*d*



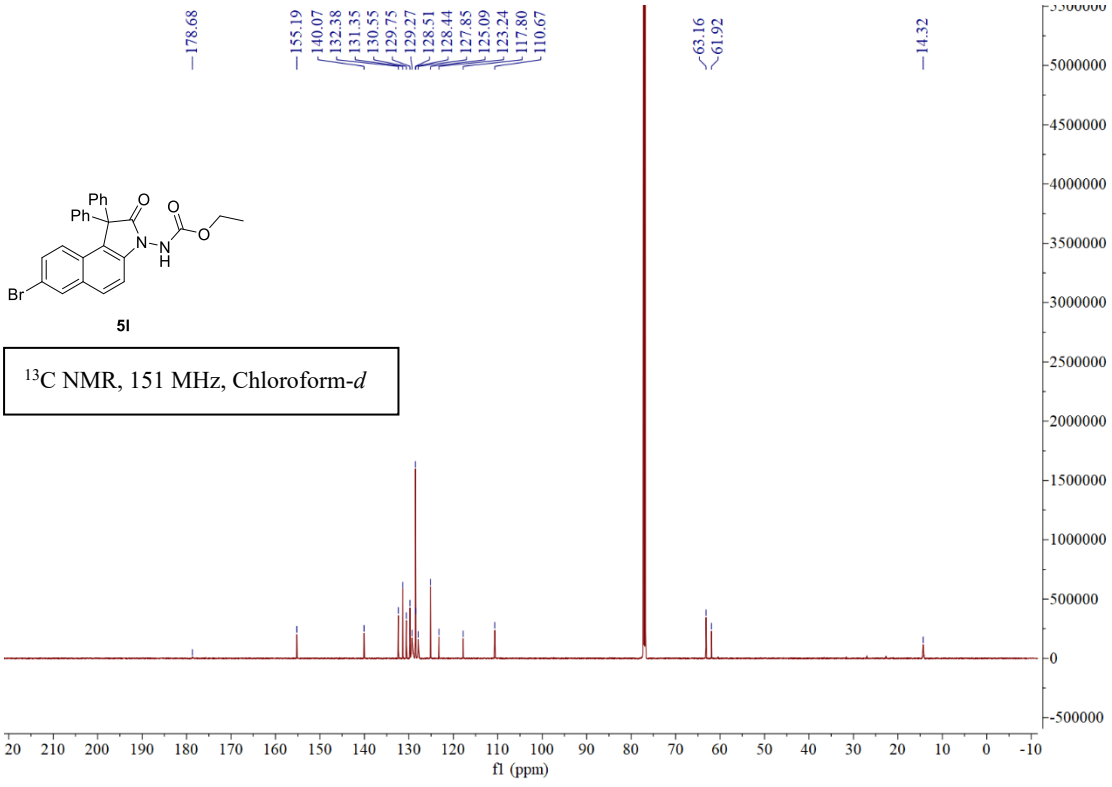
5k

^{13}C NMR, 151 MHz, Chloroform-*d*



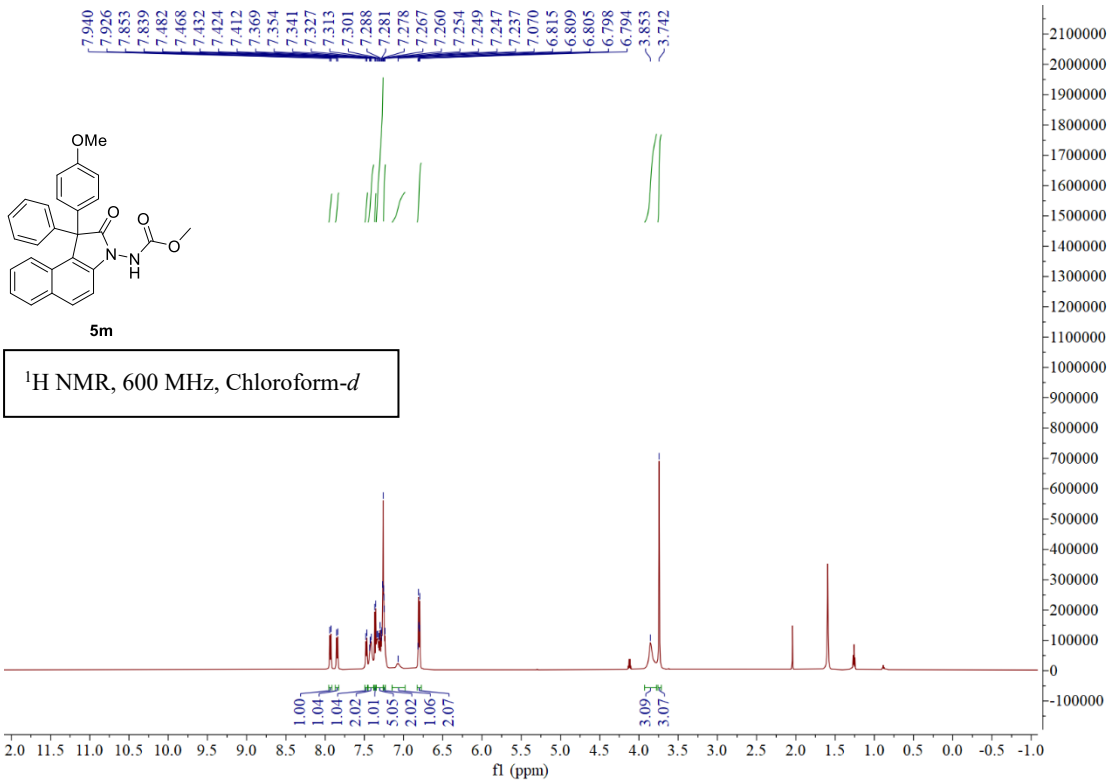
5l

^{1}H NMR, 600 MHz, Chloroform-*d*



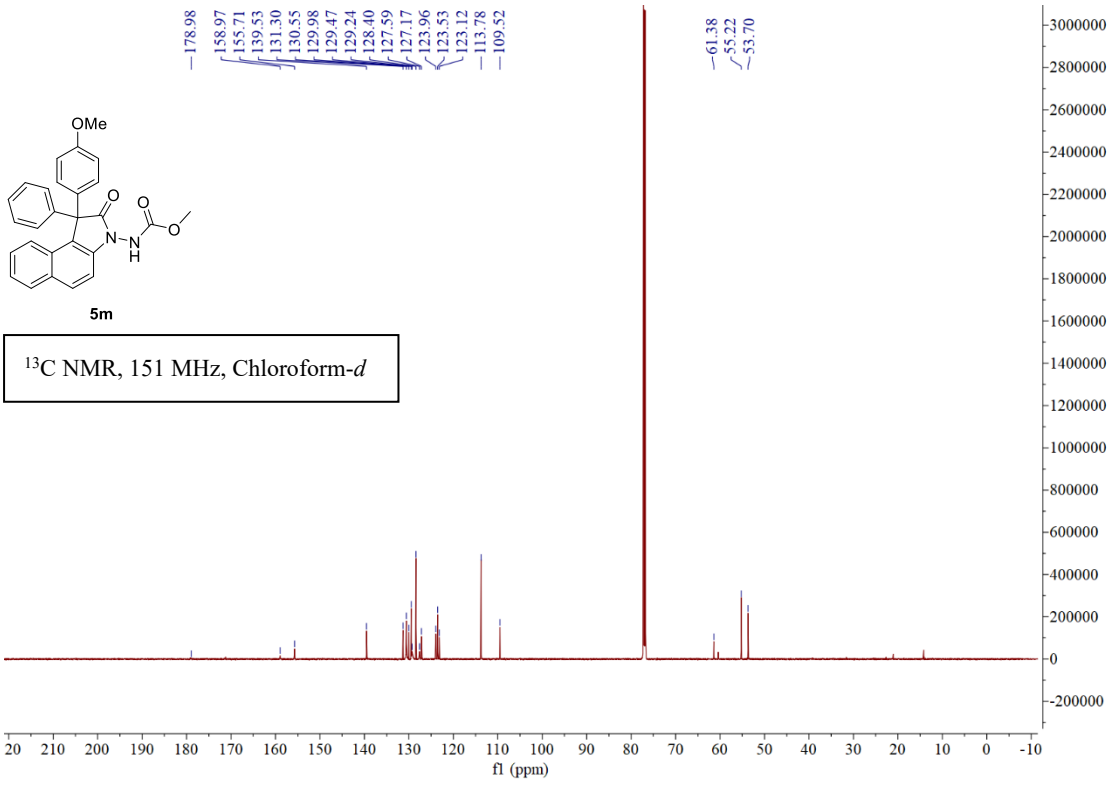
5l

^{13}C NMR, 151 MHz, Chloroform-*d*



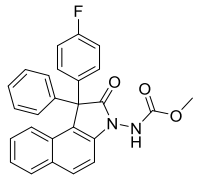
5m

^{1}H NMR, 600 MHz, Chloroform-*d*



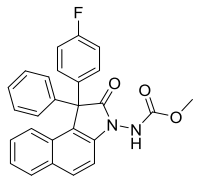
5m

^{13}C NMR, 151 MHz, Chloroform-*d*



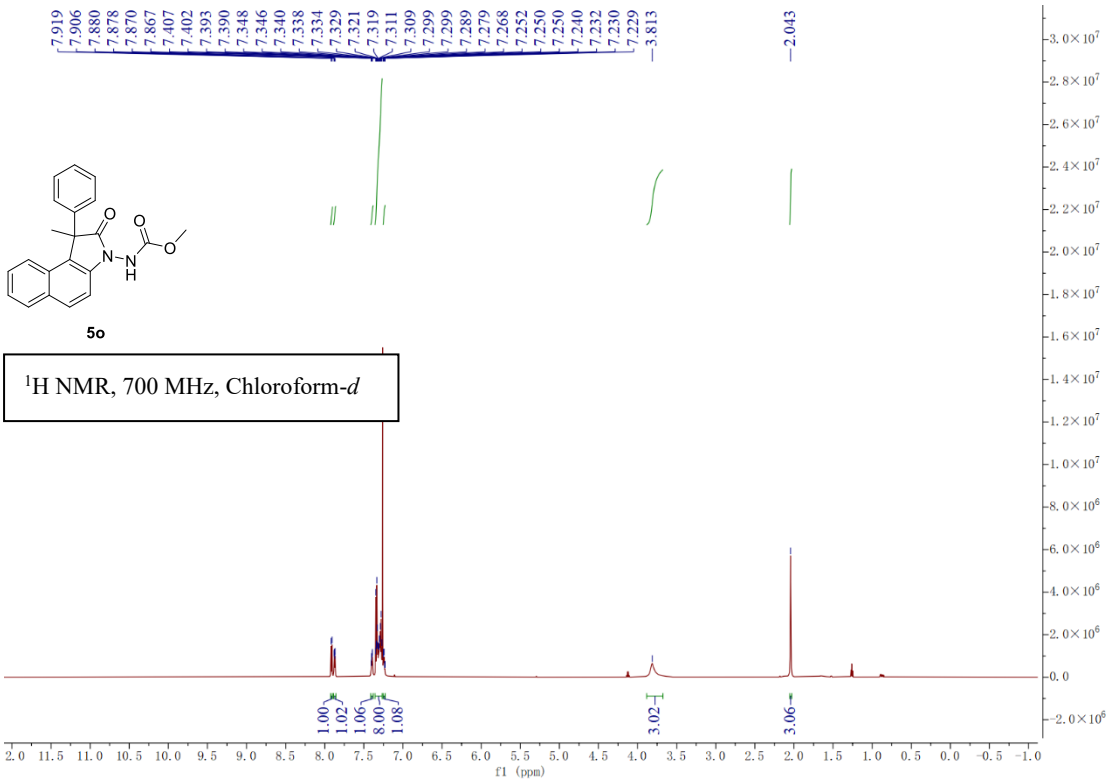
5n

^{1}H NMR, 700 MHz, Chloroform-*d*



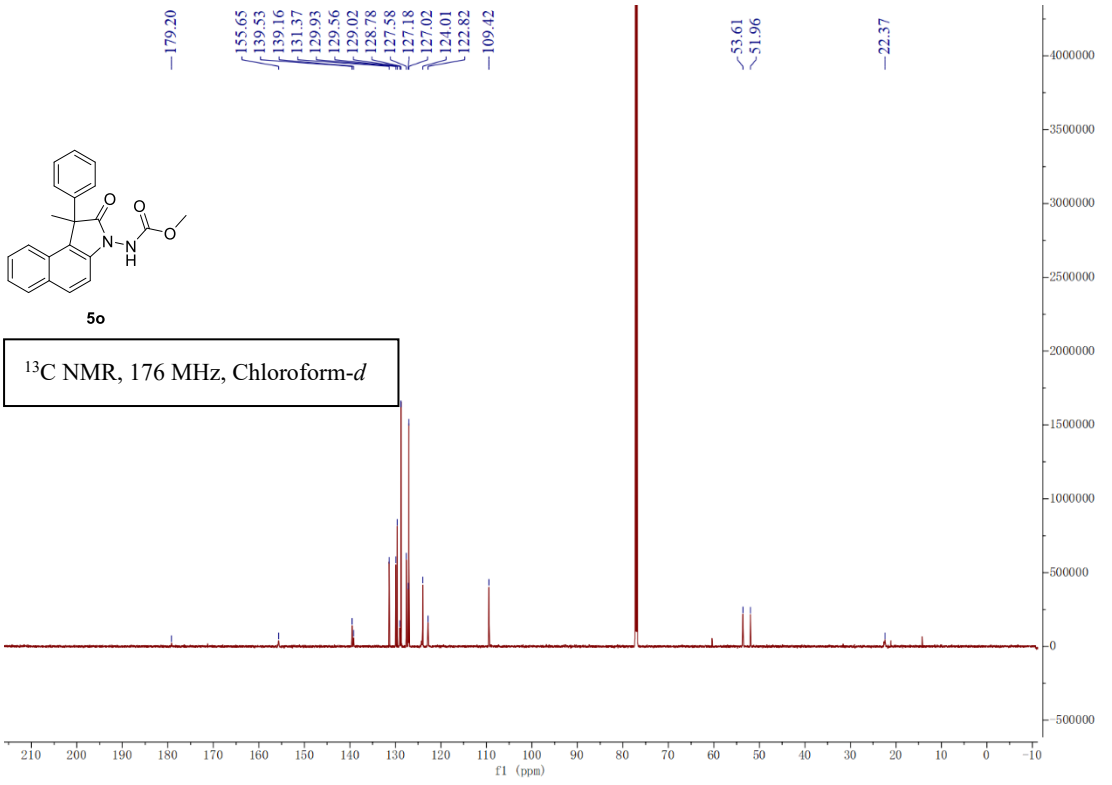
5n

^{13}C NMR, 176 MHz, Chloroform-*d*



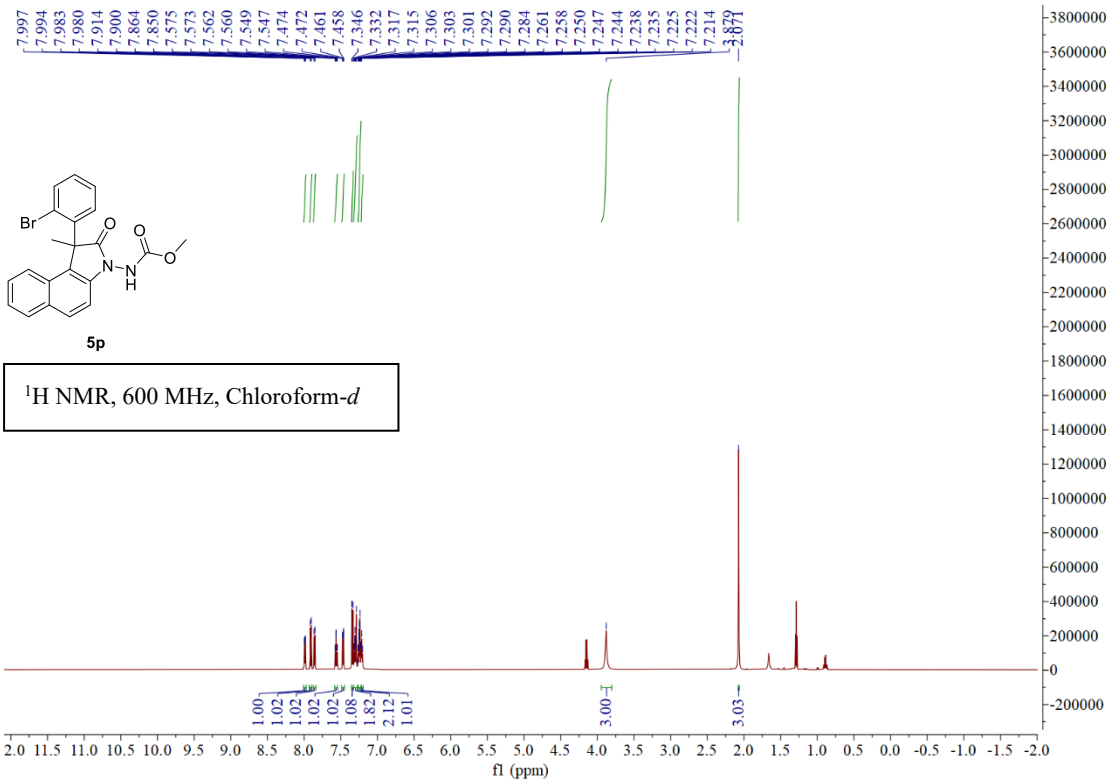
5o

^{1}H NMR, 700 MHz, Chloroform-*d*

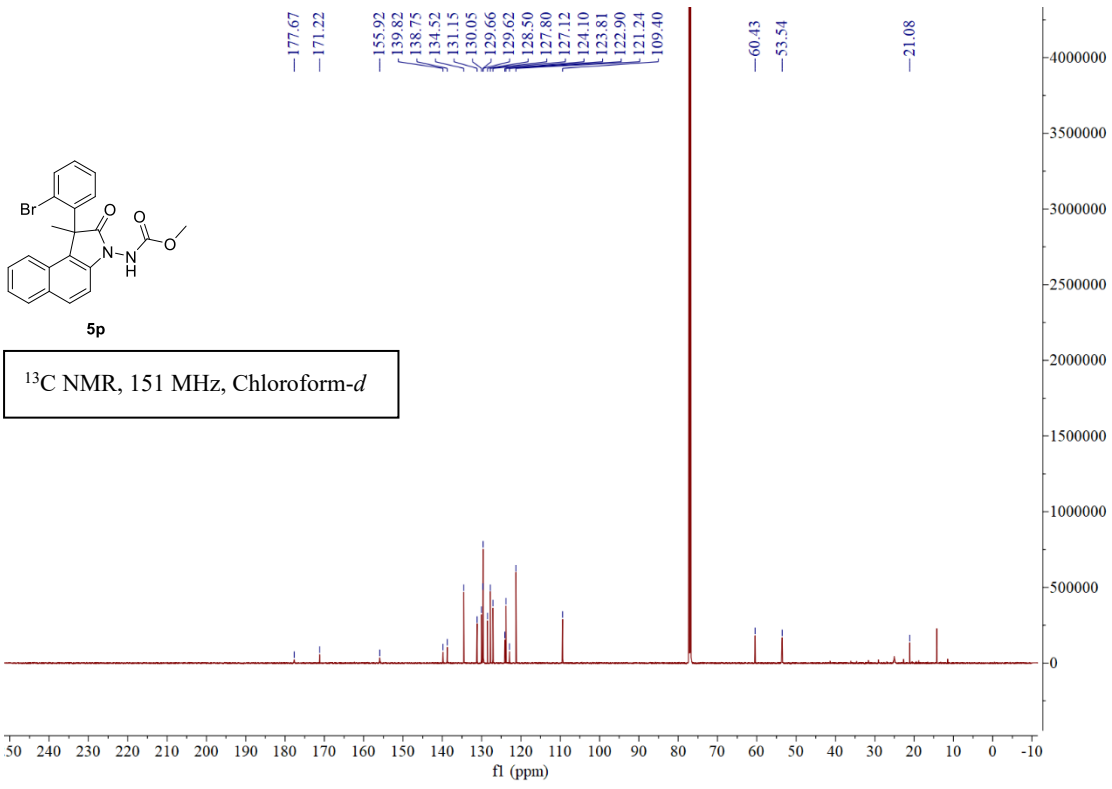


5o

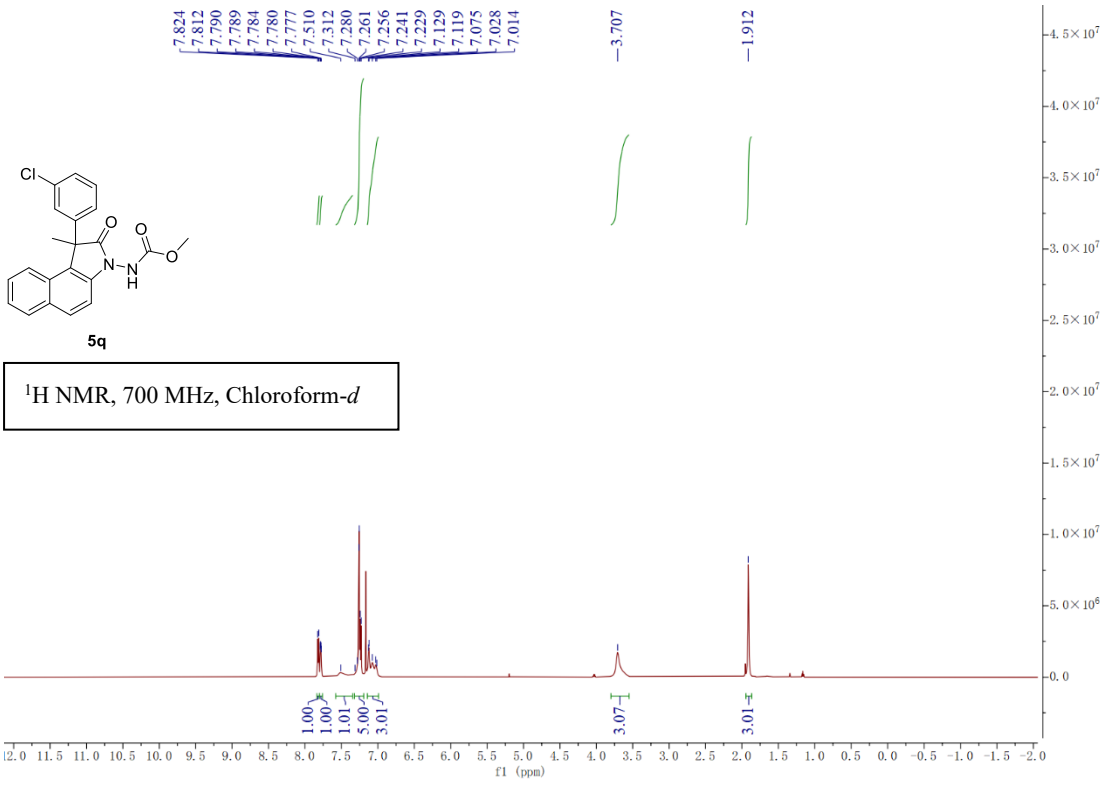
^{13}C NMR, 176 MHz, Chloroform-*d*



^{1}H NMR, 600 MHz, Chloroform-*d*

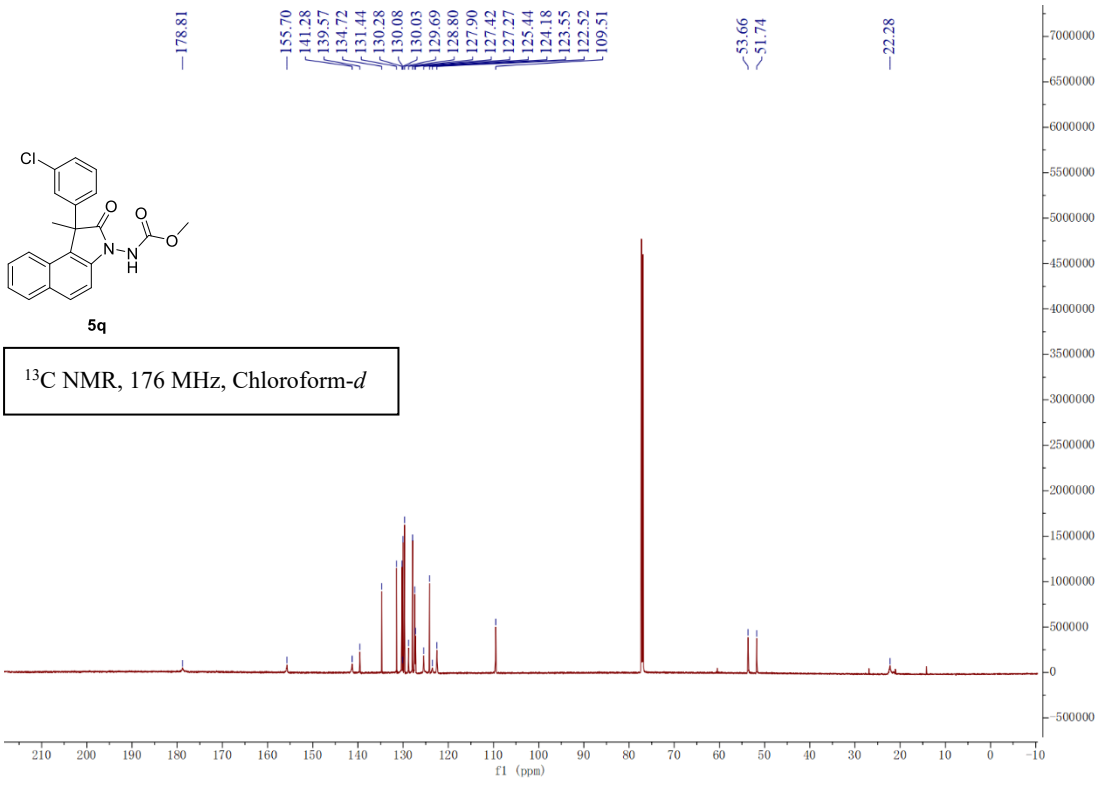


^{13}C NMR, 151 MHz, Chloroform-*d*



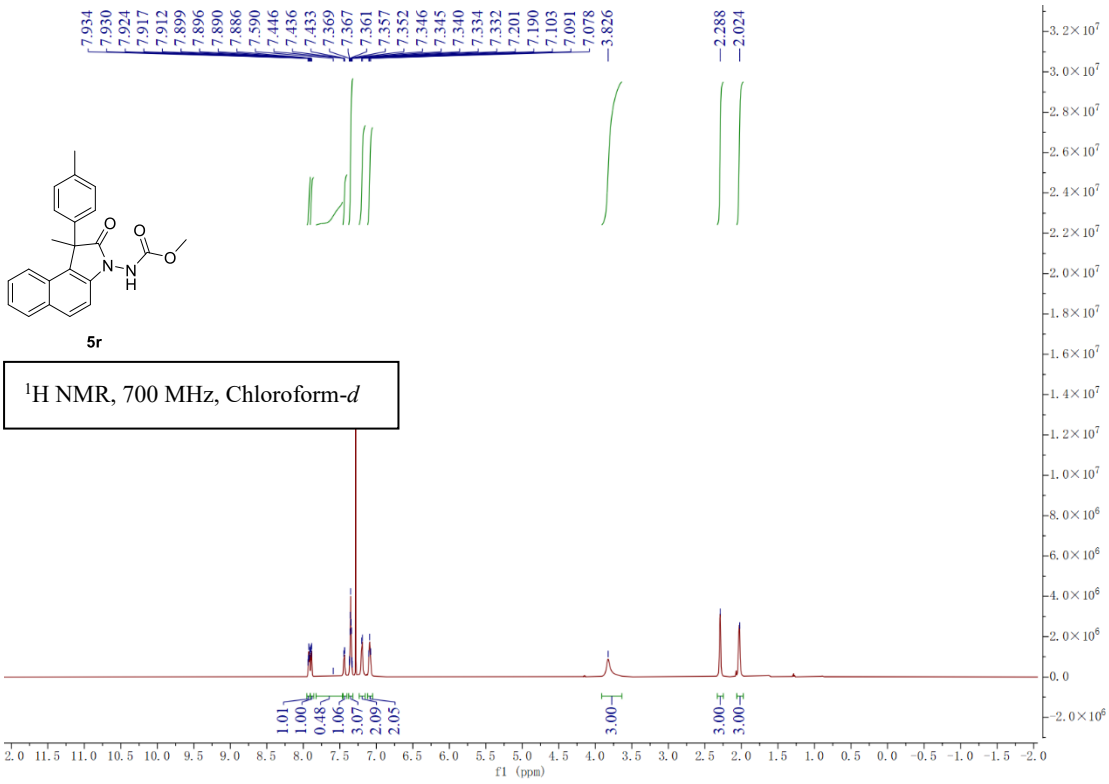
5q

^{1}H NMR, 700 MHz, Chloroform-*d*



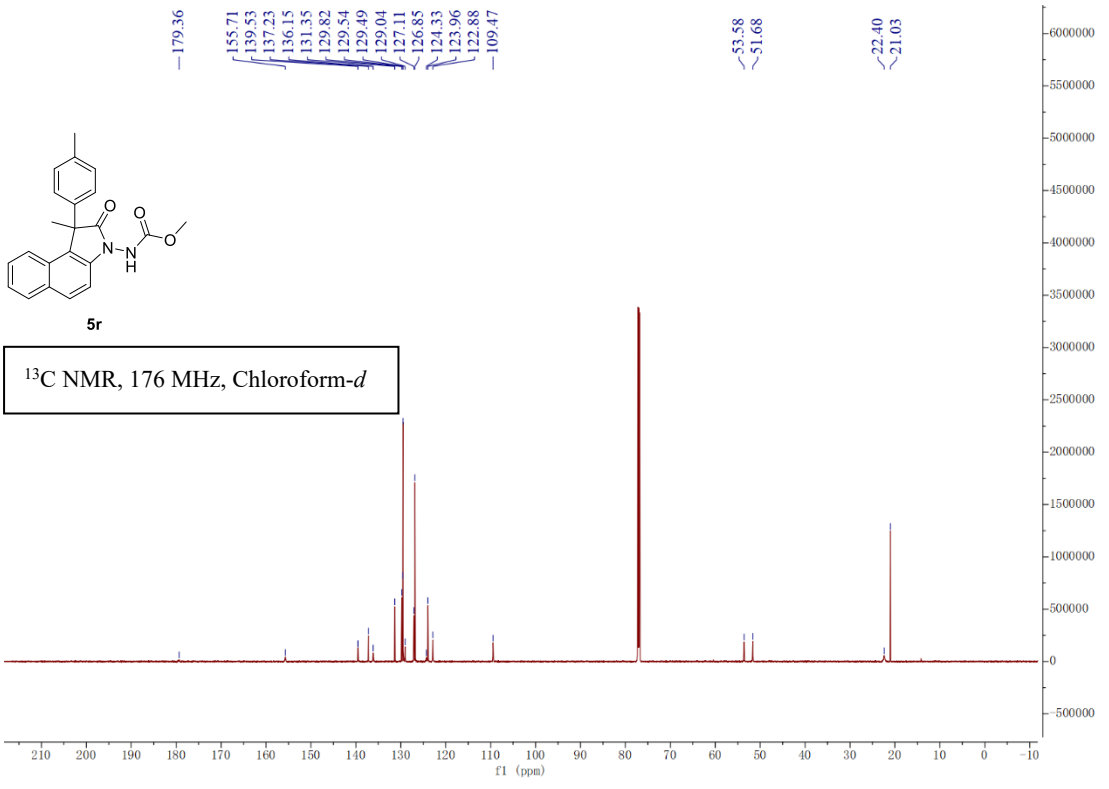
5q

^{13}C NMR, 176 MHz, Chloroform-*d*



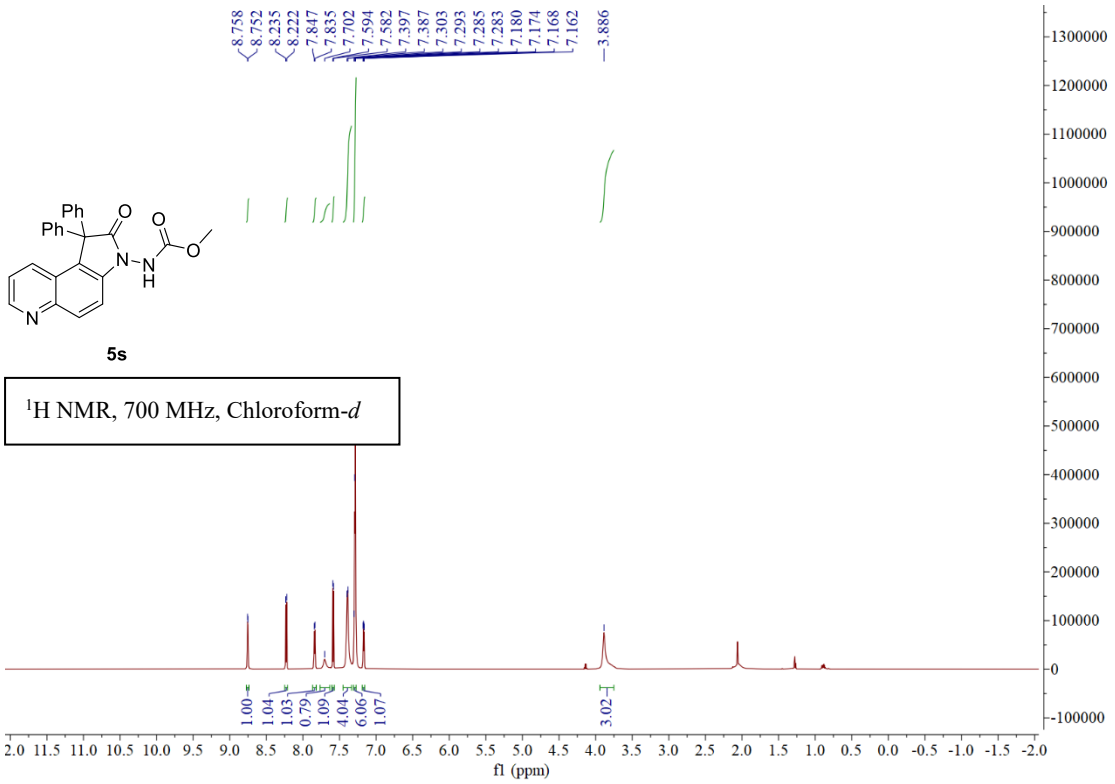
5r

^{1}H NMR, 700 MHz, Chloroform-*d*



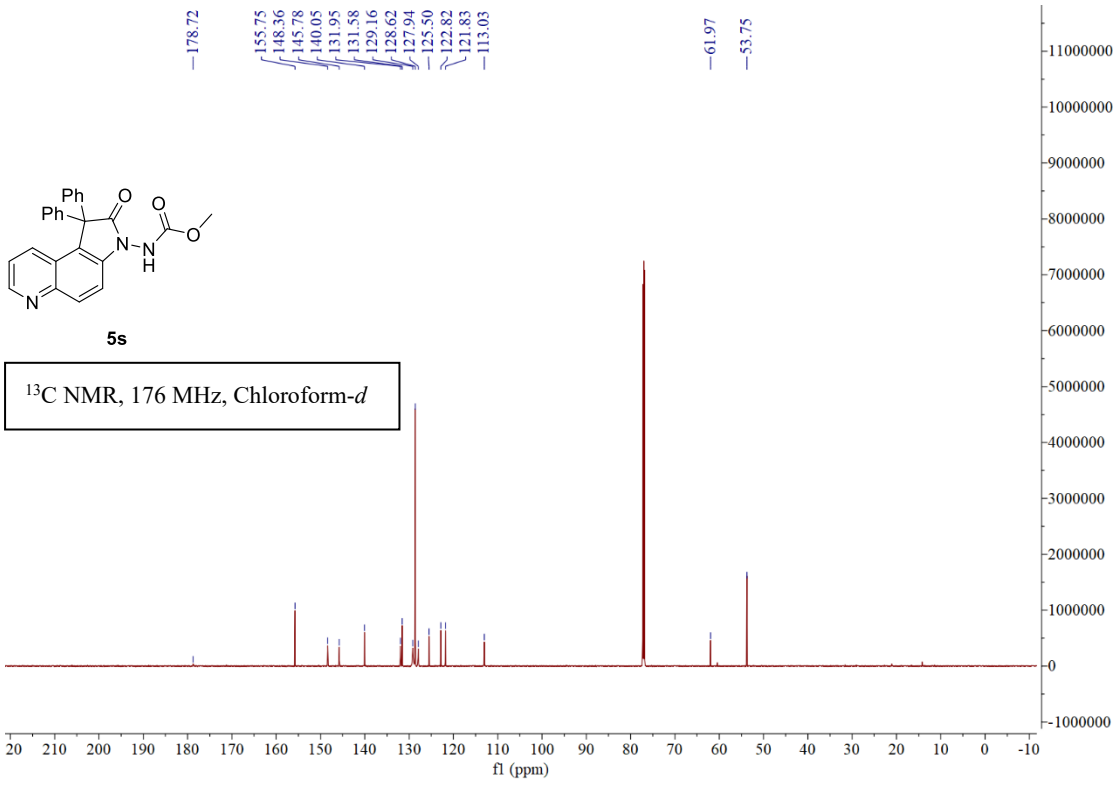
5r

^{13}C NMR, 176 MHz, Chloroform-*d*



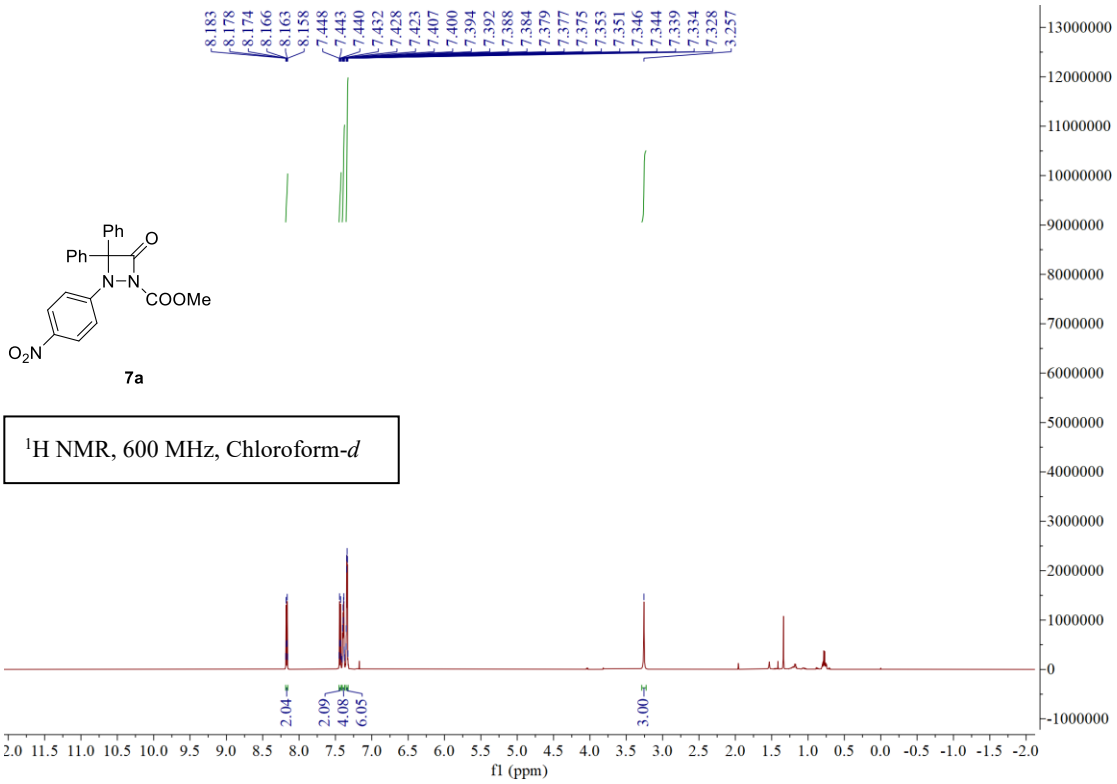
5s

^{1}H NMR, 700 MHz, Chloroform-*d*



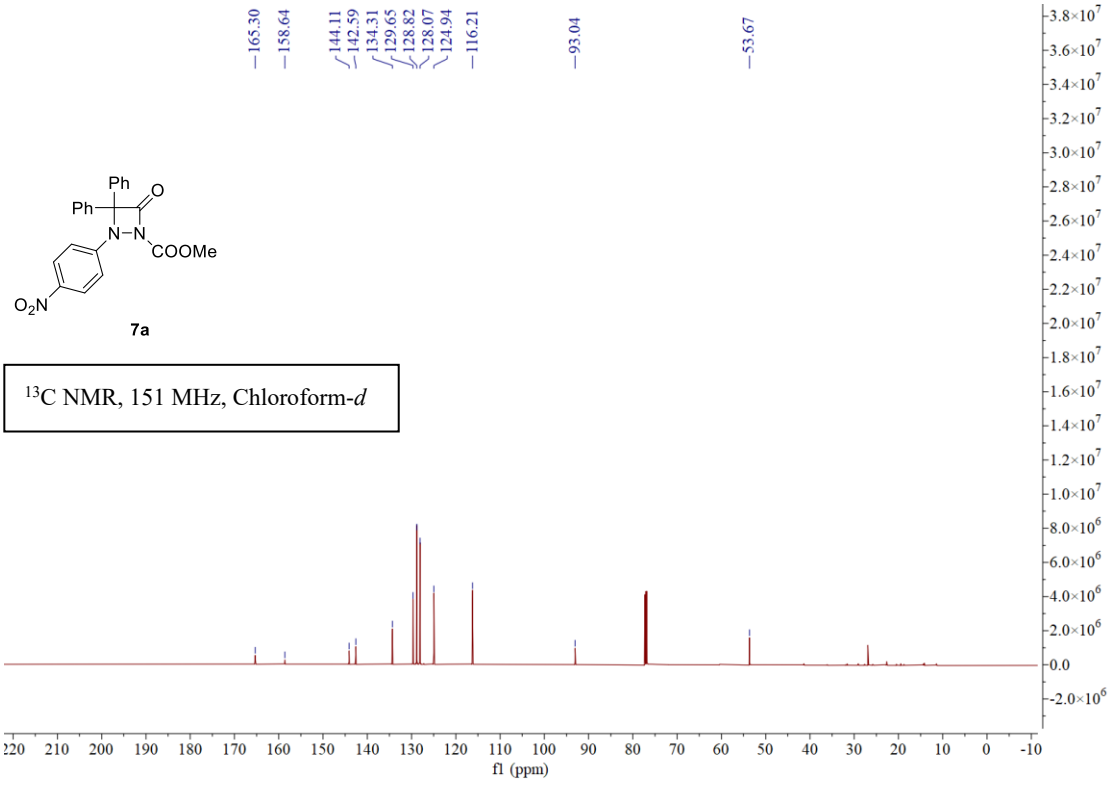
5s

^{13}C NMR, 176 MHz, Chloroform-*d*



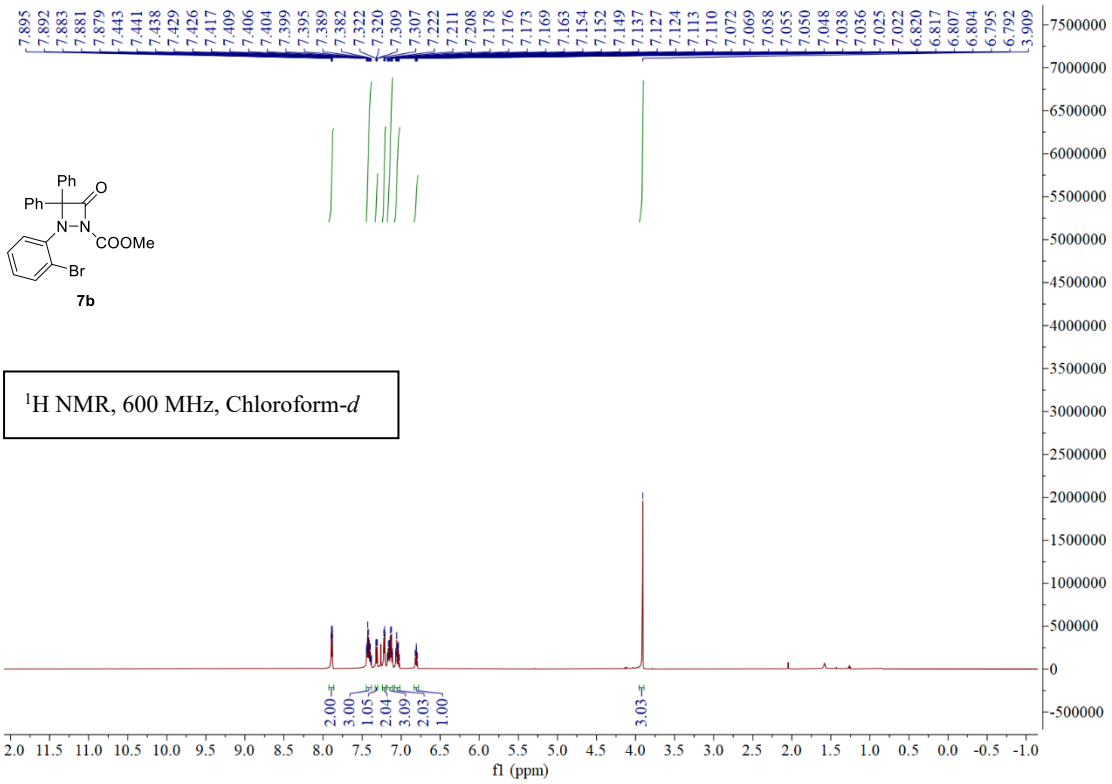
7a

^{1}H NMR, 600 MHz, Chloroform-*d*

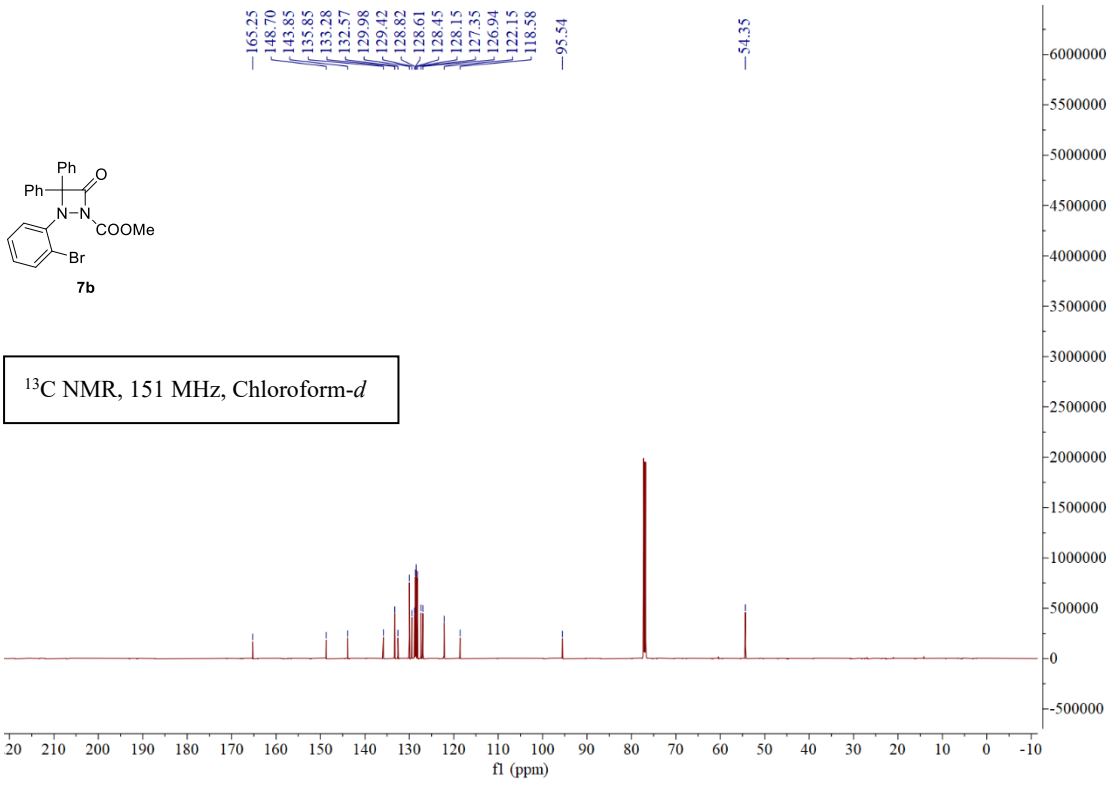


7a

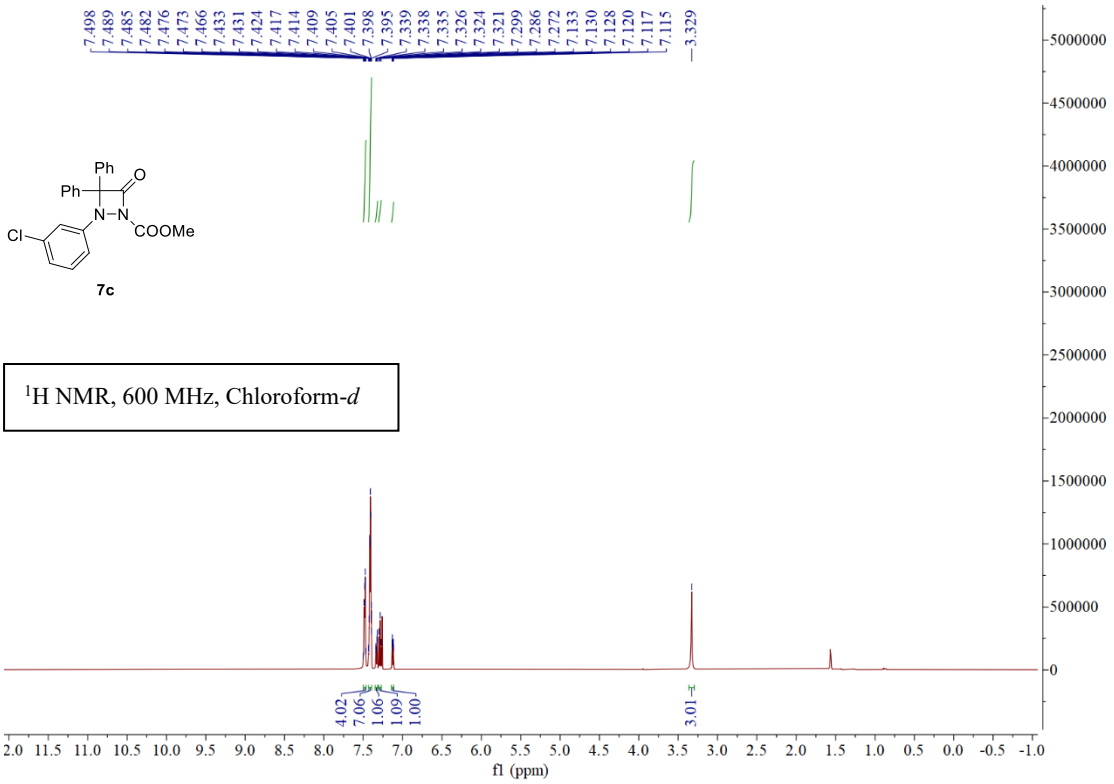
^{13}C NMR, 151 MHz, Chloroform-*d*



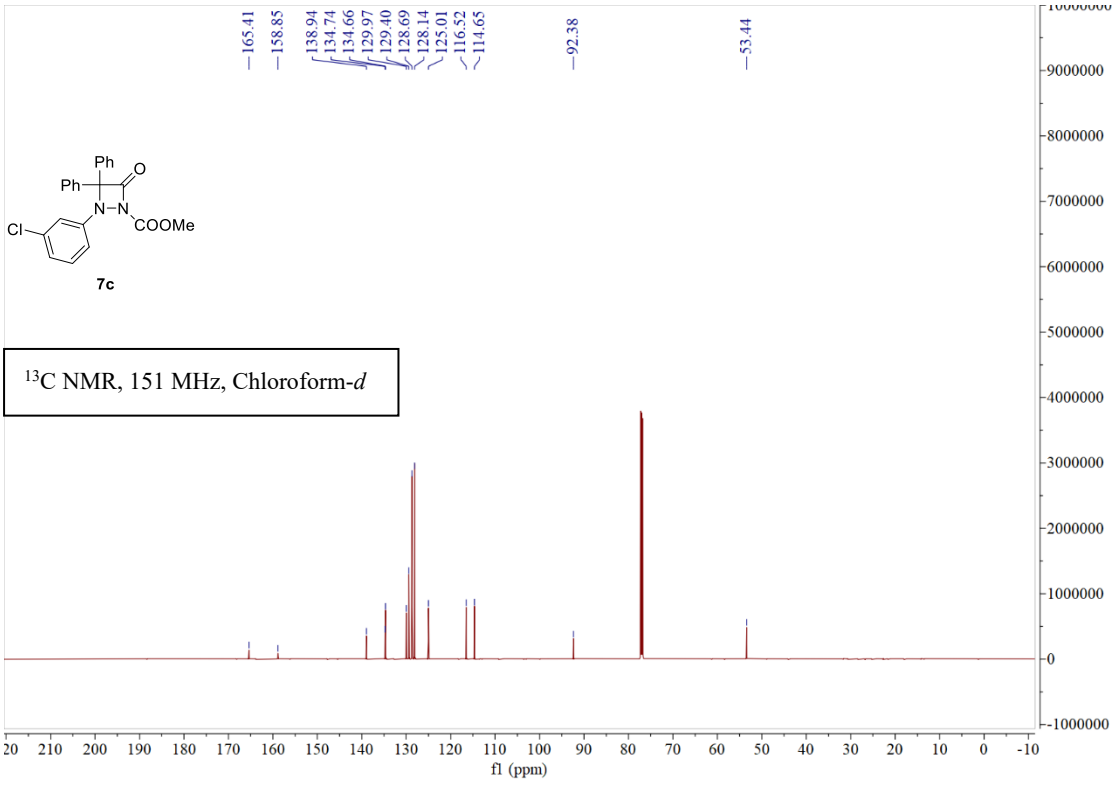
^{1}H NMR, 600 MHz, Chloroform-*d*



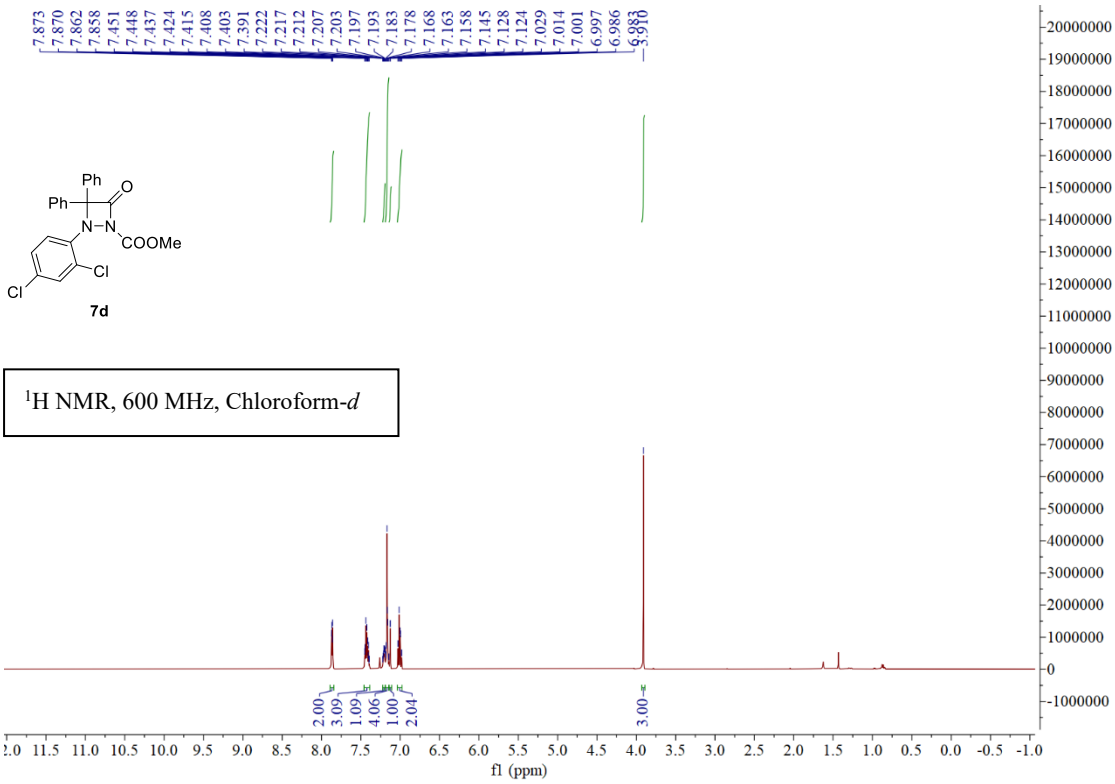
^{13}C NMR, 151 MHz, Chloroform-*d*



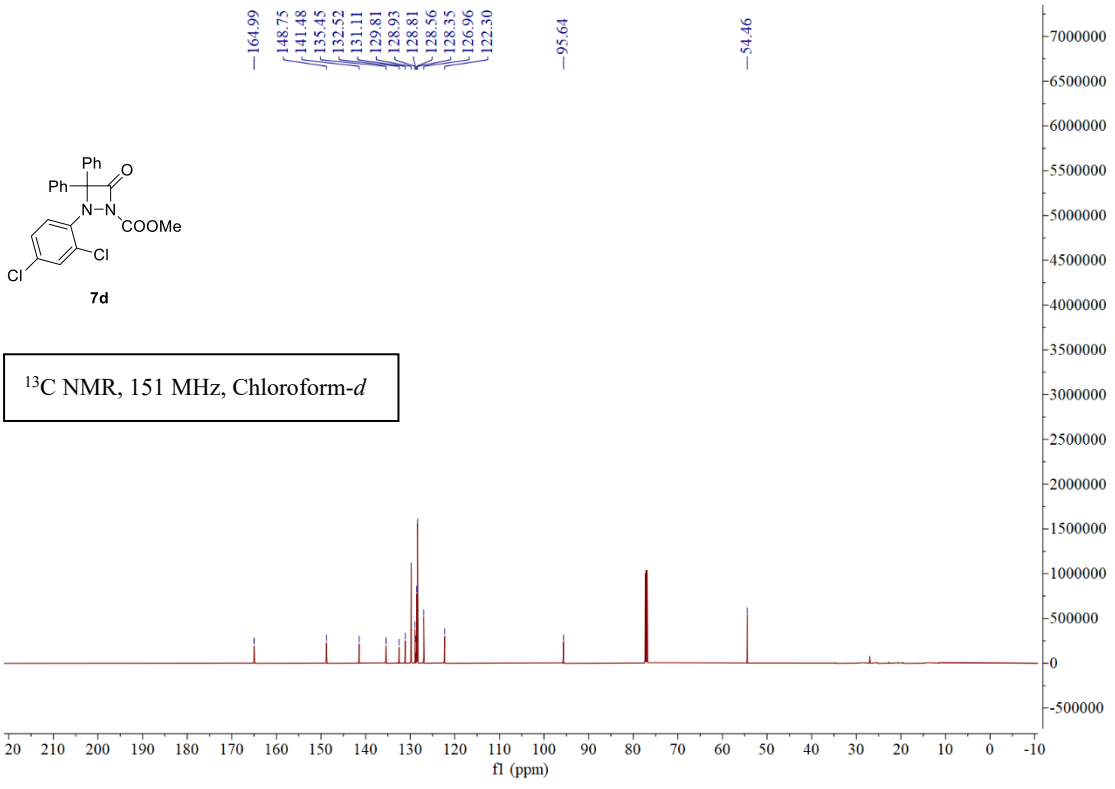
^{1}H NMR, 600 MHz, Chloroform-*d*



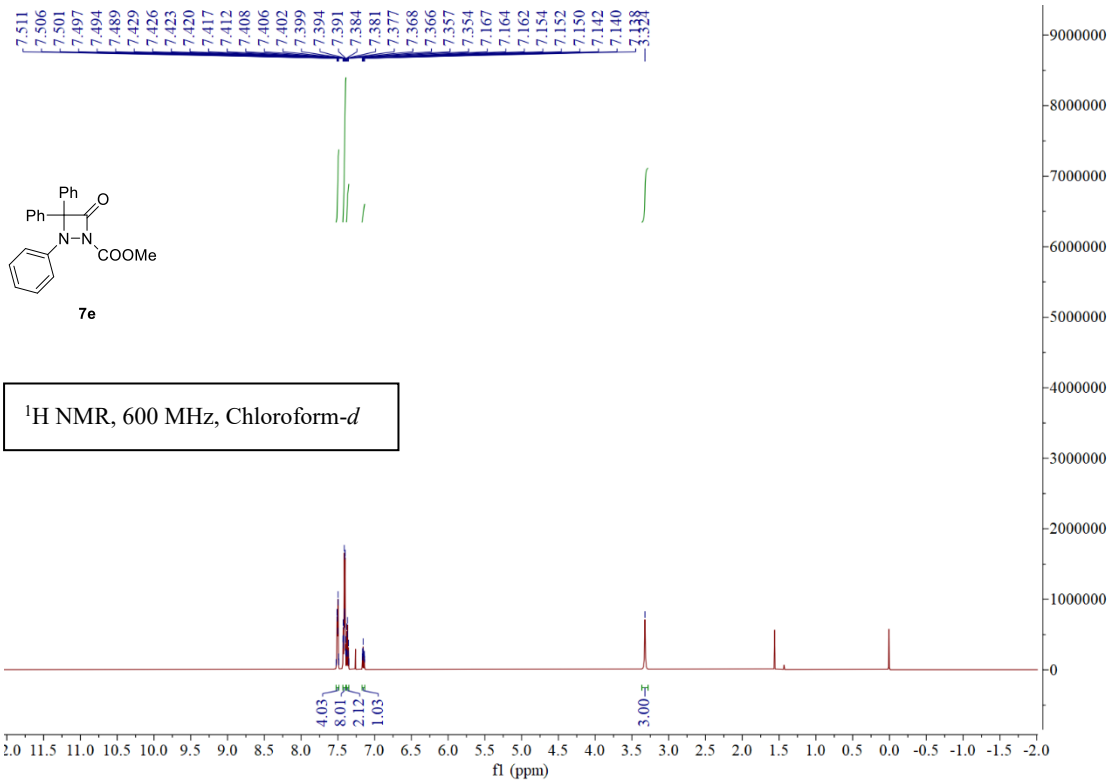
^{13}C NMR, 151 MHz, Chloroform-*d*



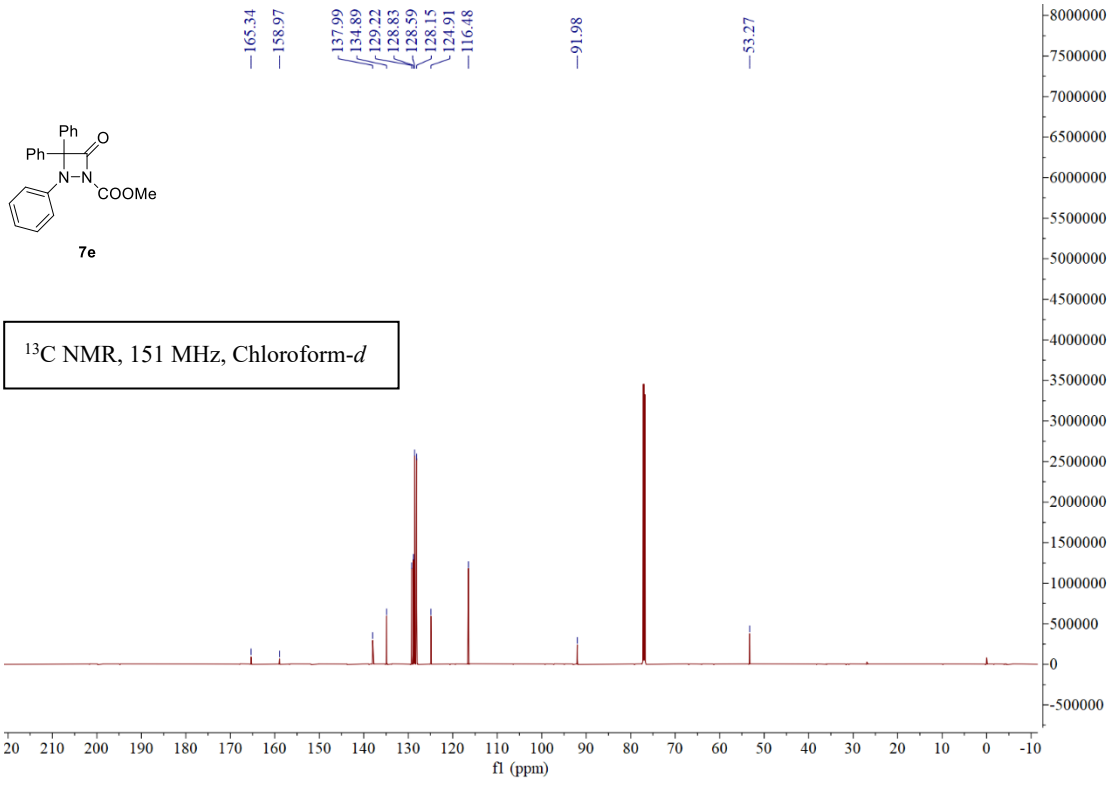
^{1}H NMR, 600 MHz, Chloroform-*d*



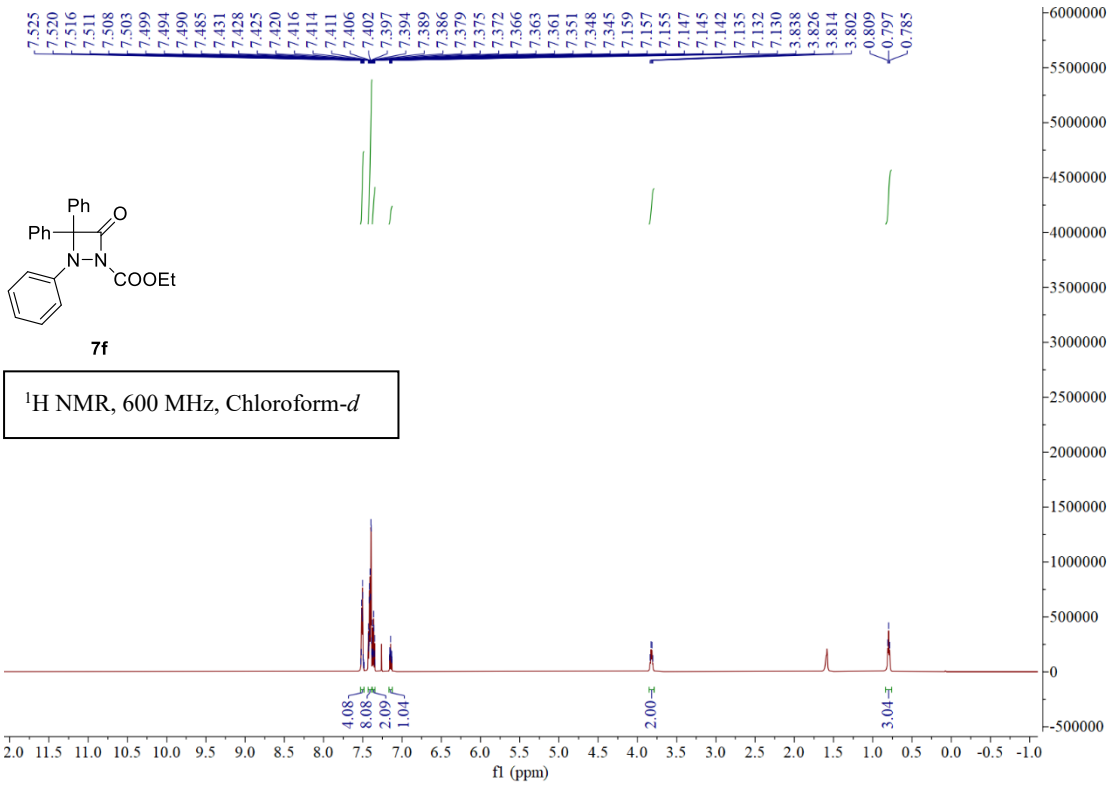
^{13}C NMR, 151 MHz, Chloroform-*d*



^{1}H NMR, 600 MHz, Chloroform-*d*

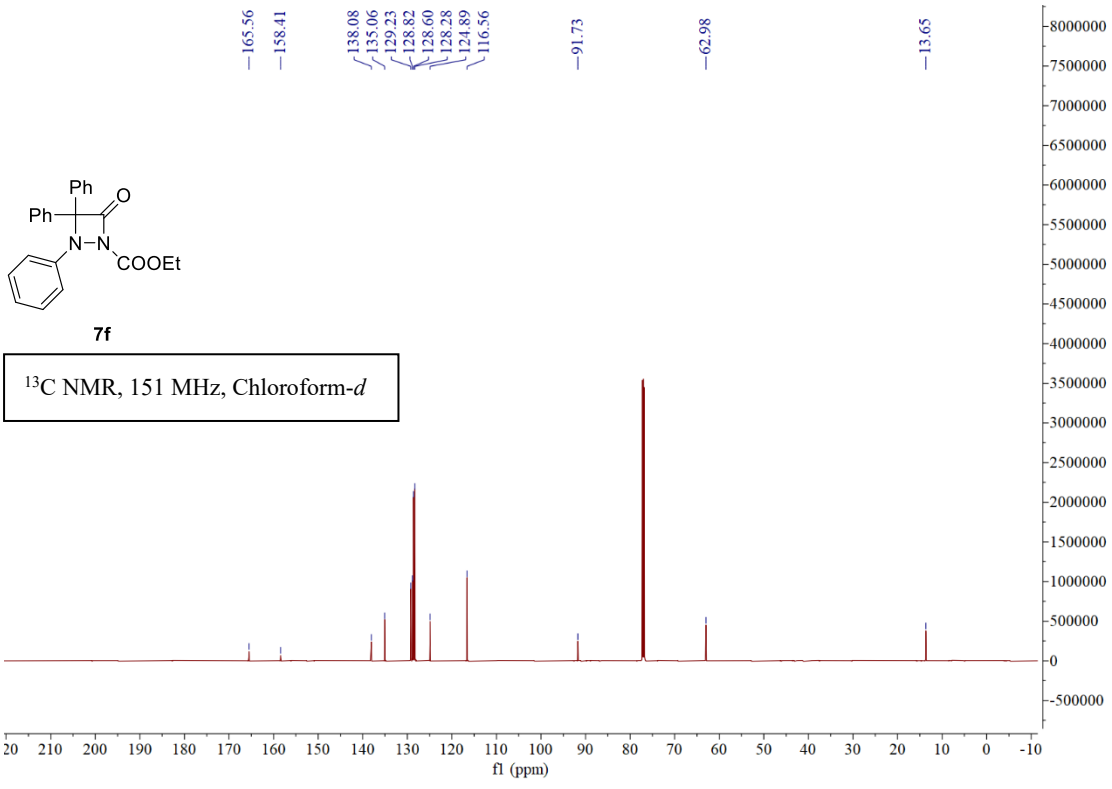


^{13}C NMR, 151 MHz, Chloroform-*d*



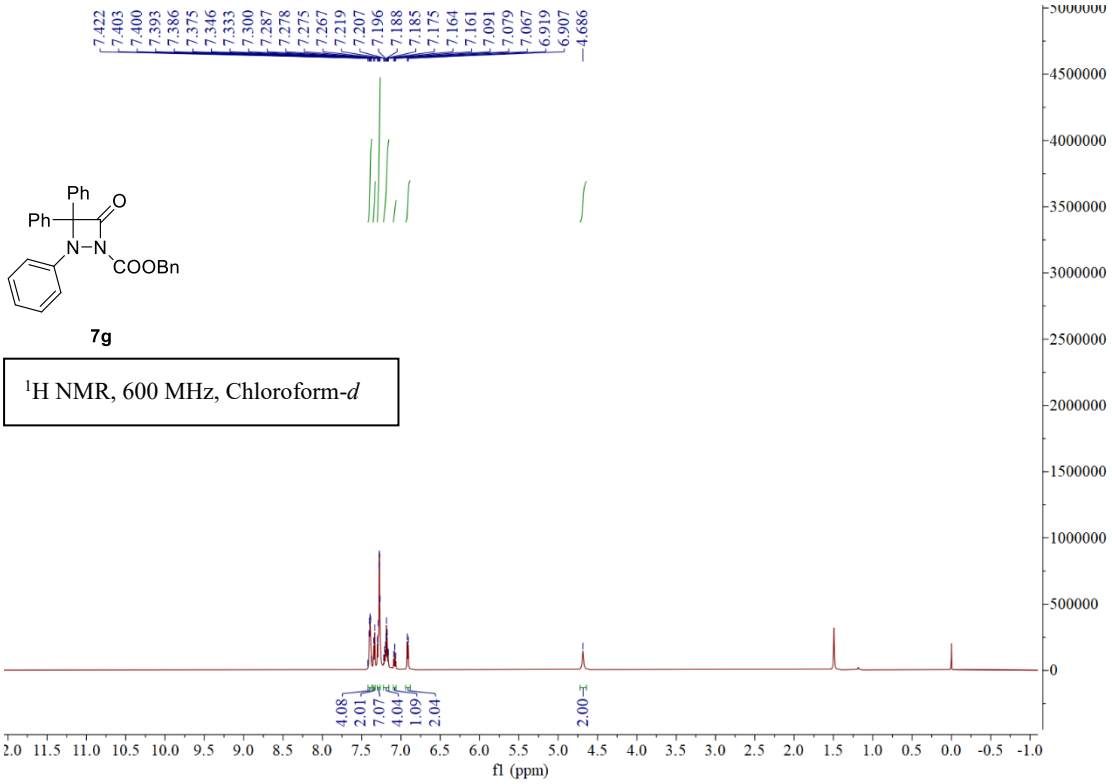
7f

^{1}H NMR, 600 MHz, Chloroform-*d*



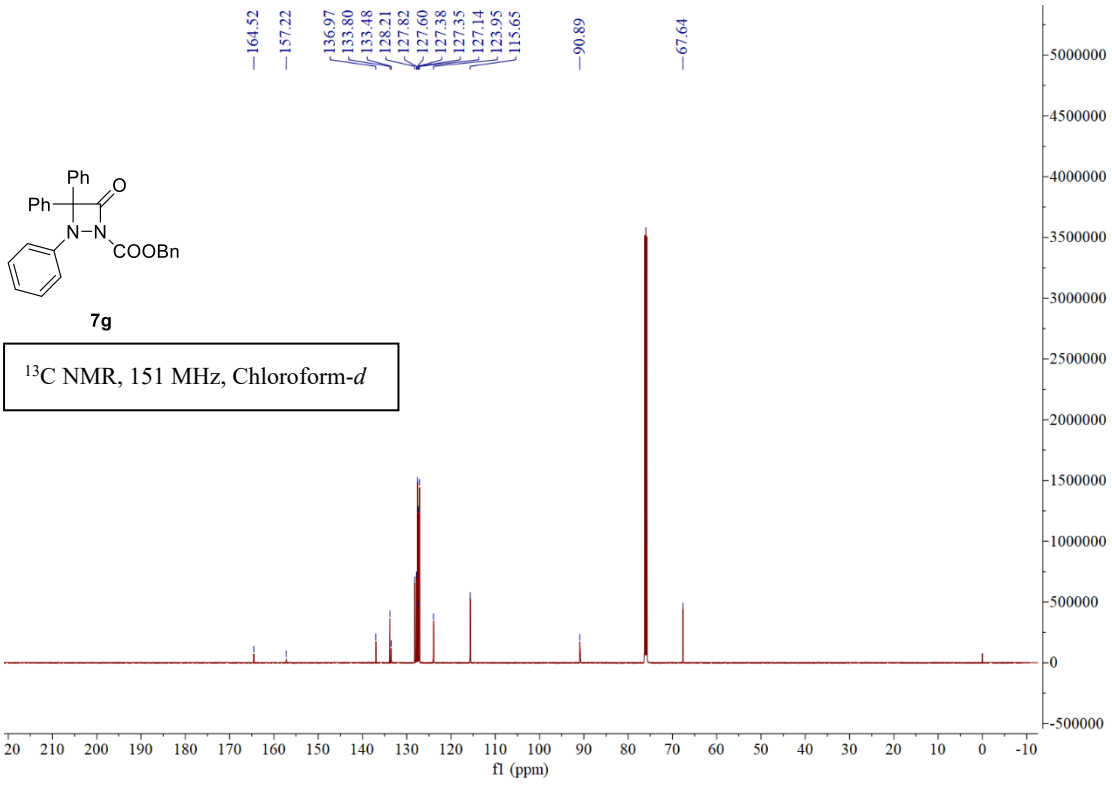
7f

^{13}C NMR, 151 MHz, Chloroform-*d*



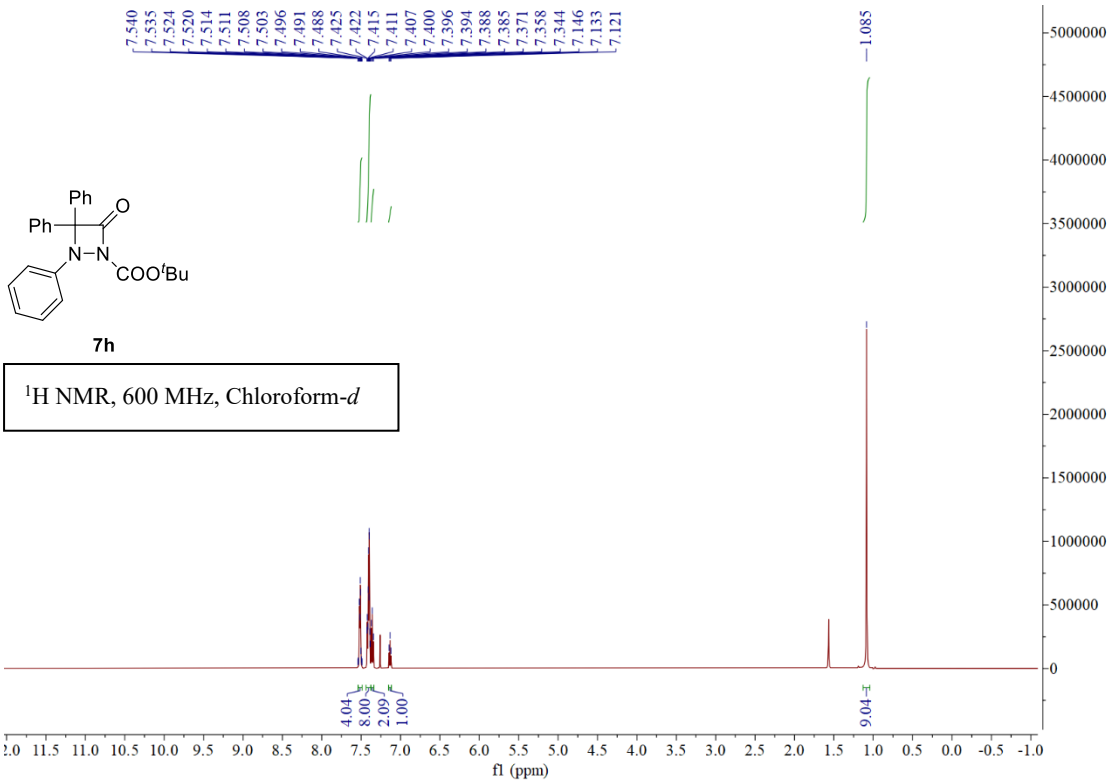
7g

^{1}H NMR, 600 MHz, Chloroform-*d*



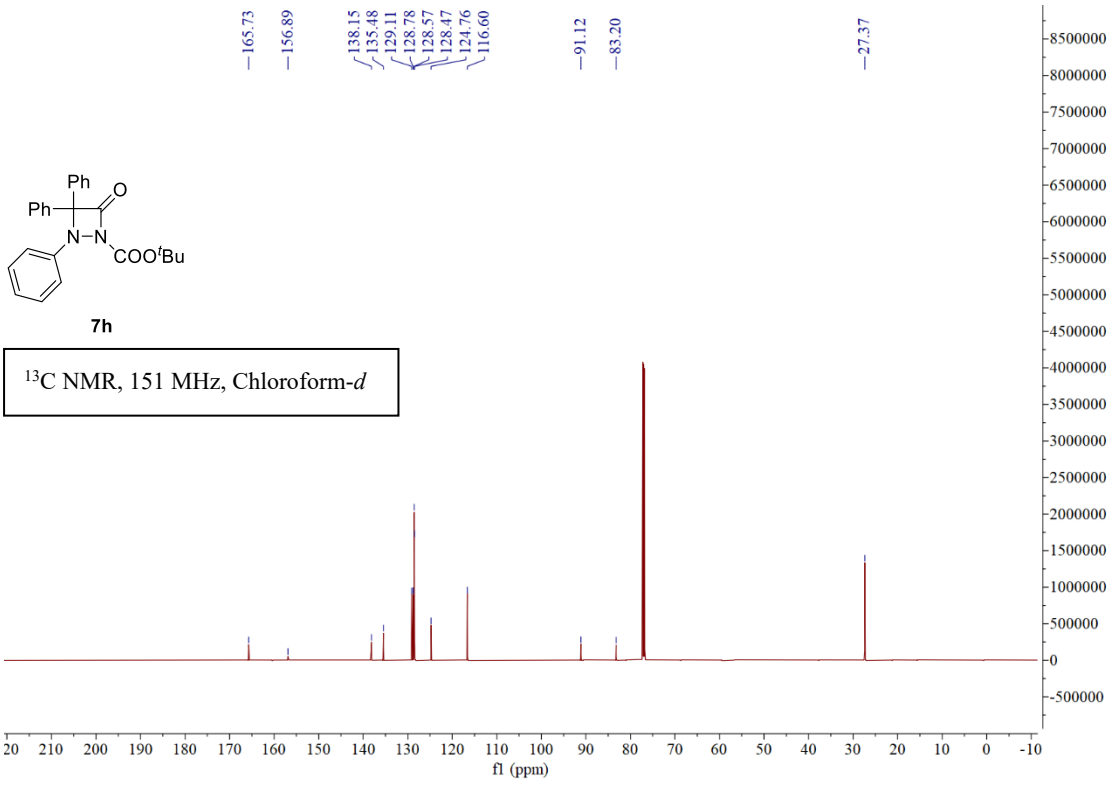
7g

^{13}C NMR, 151 MHz, Chloroform-*d*



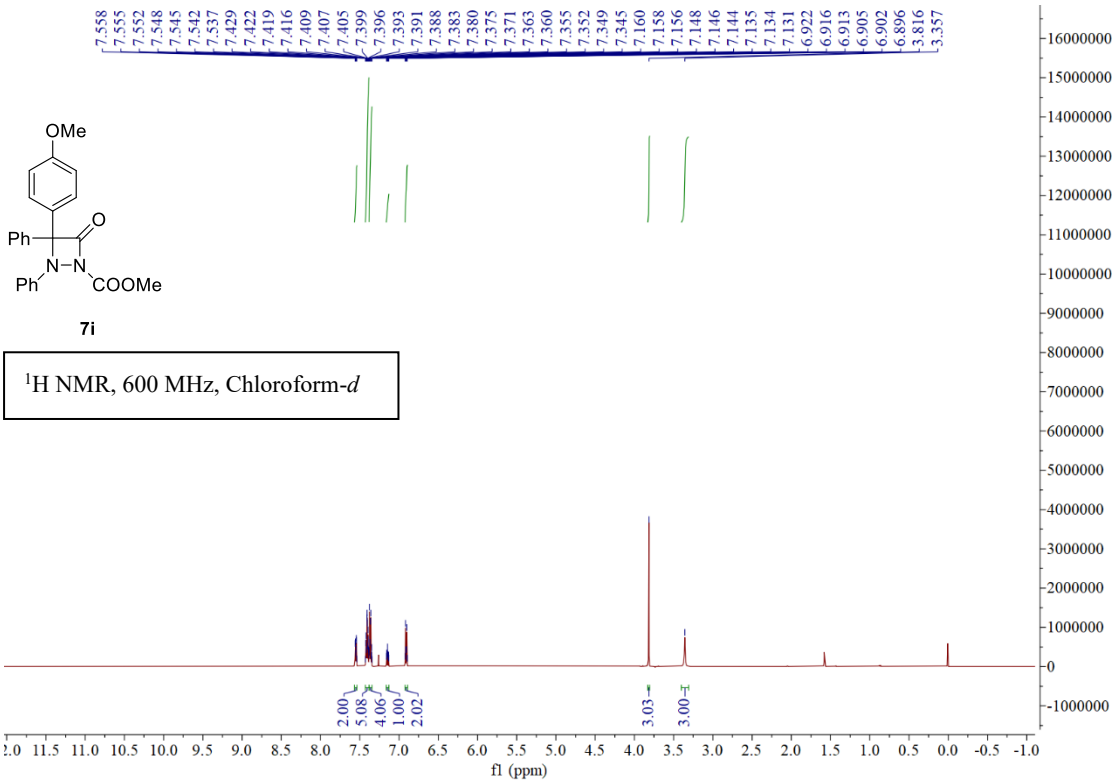
7h

^{1}H NMR, 600 MHz, Chloroform-*d*



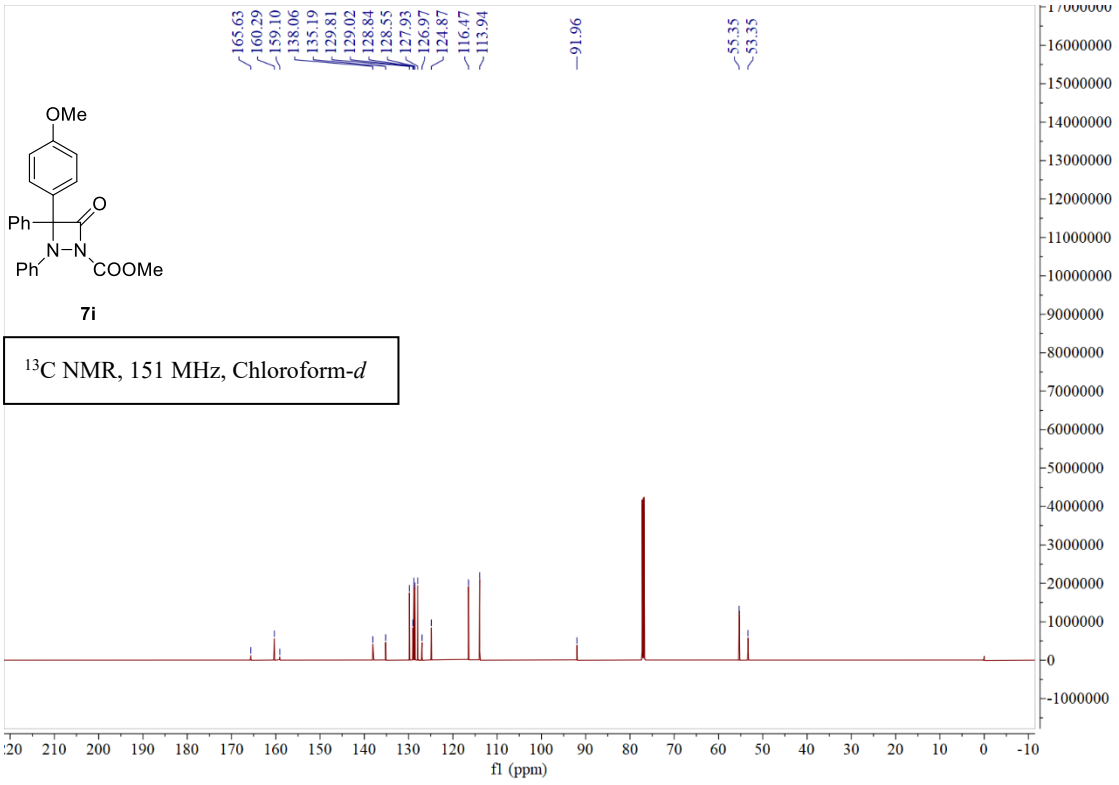
7h

^{13}C NMR, 151 MHz, Chloroform-*d*



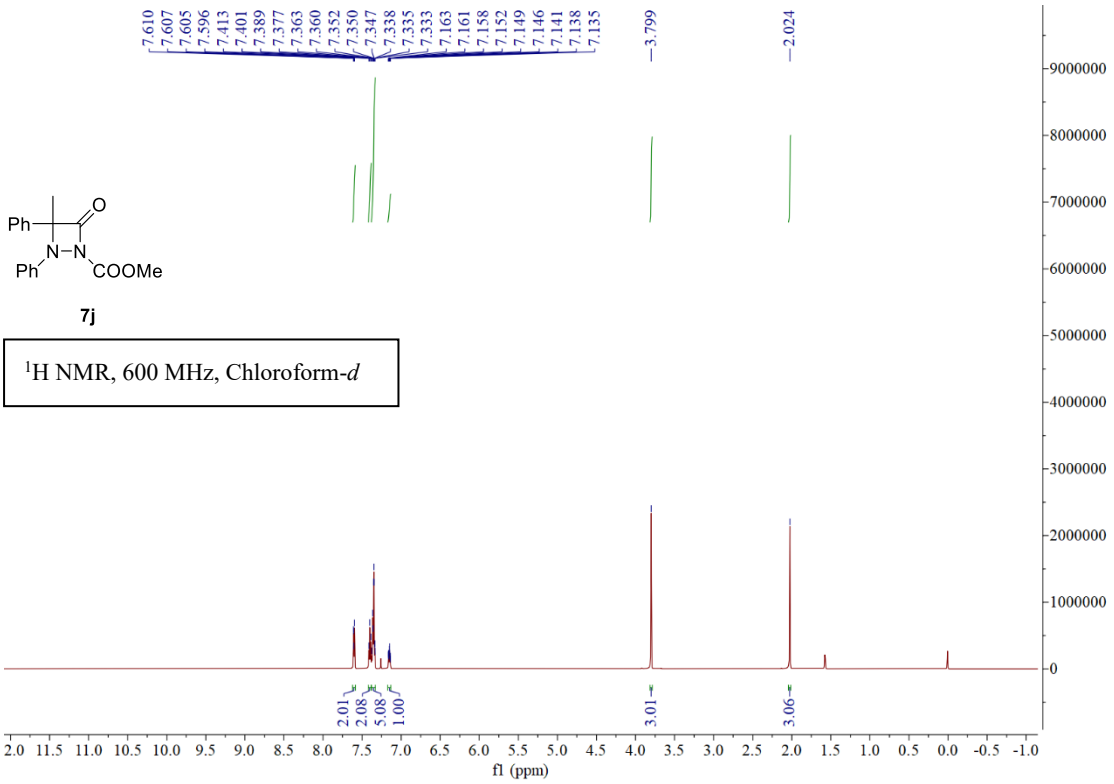
7i

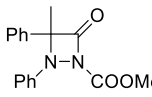
^{1}H NMR, 600 MHz, Chloroform-*d*



7i

^{13}C NMR, 151 MHz, Chloroform-*d*



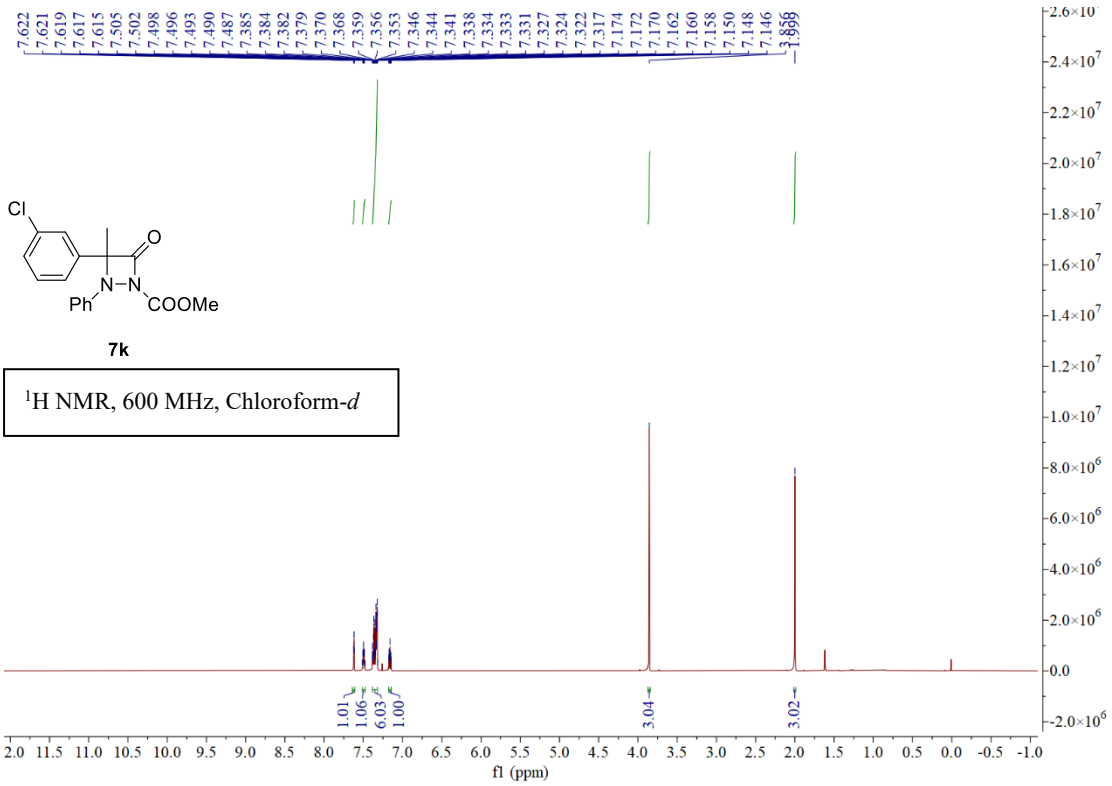


7j

^{1}H NMR, 600 MHz, Chloroform-*d*

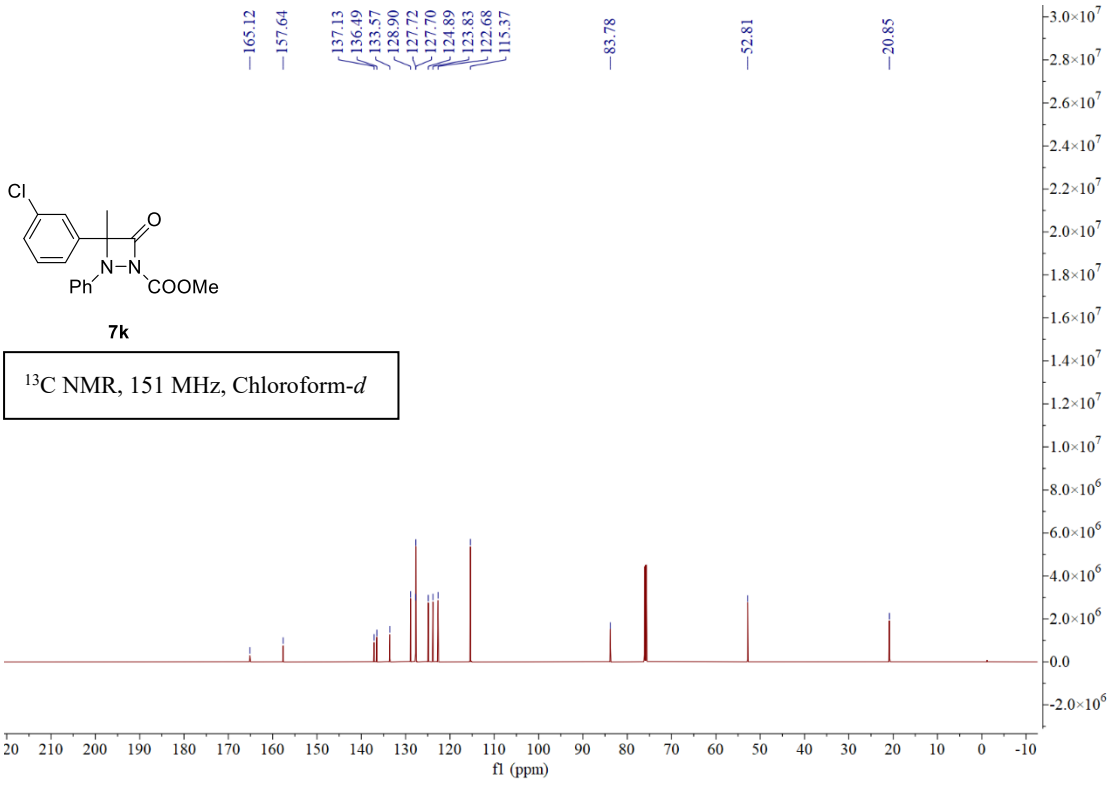
7j

^{13}C NMR, 151 MHz, Chloroform-*d*



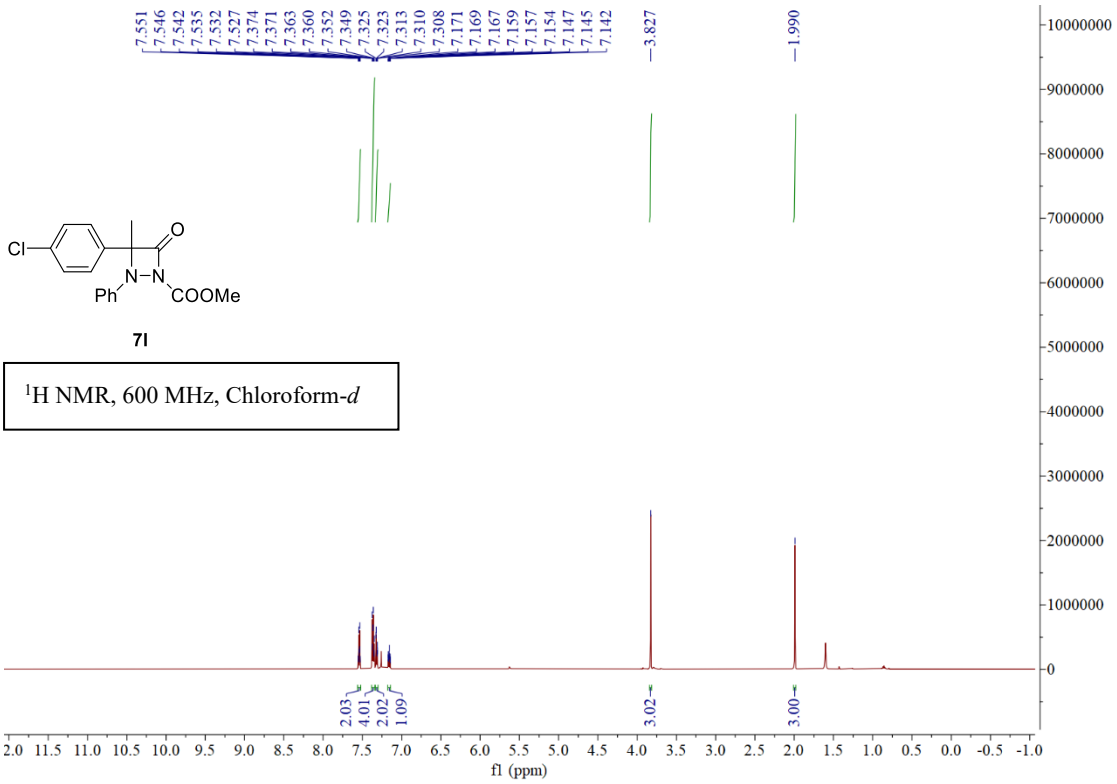
7k

^{1}H NMR, 600 MHz, Chloroform-*d*



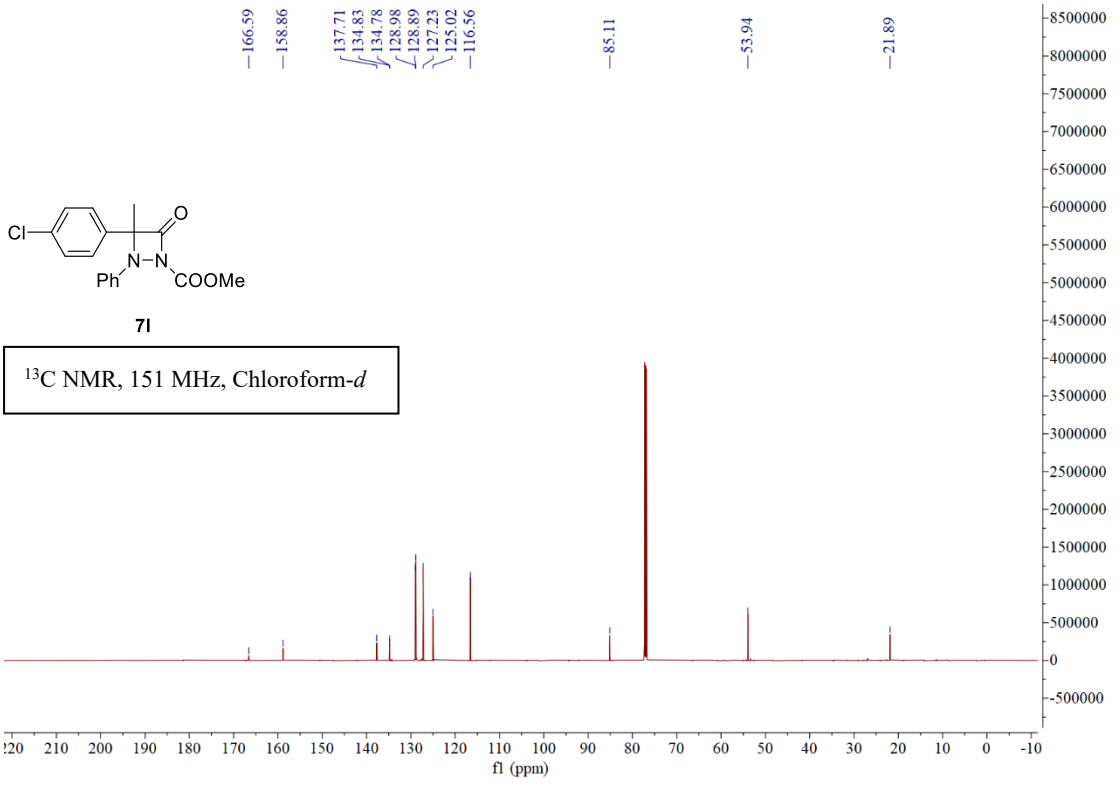
7k

^{13}C NMR, 151 MHz, Chloroform-*d*



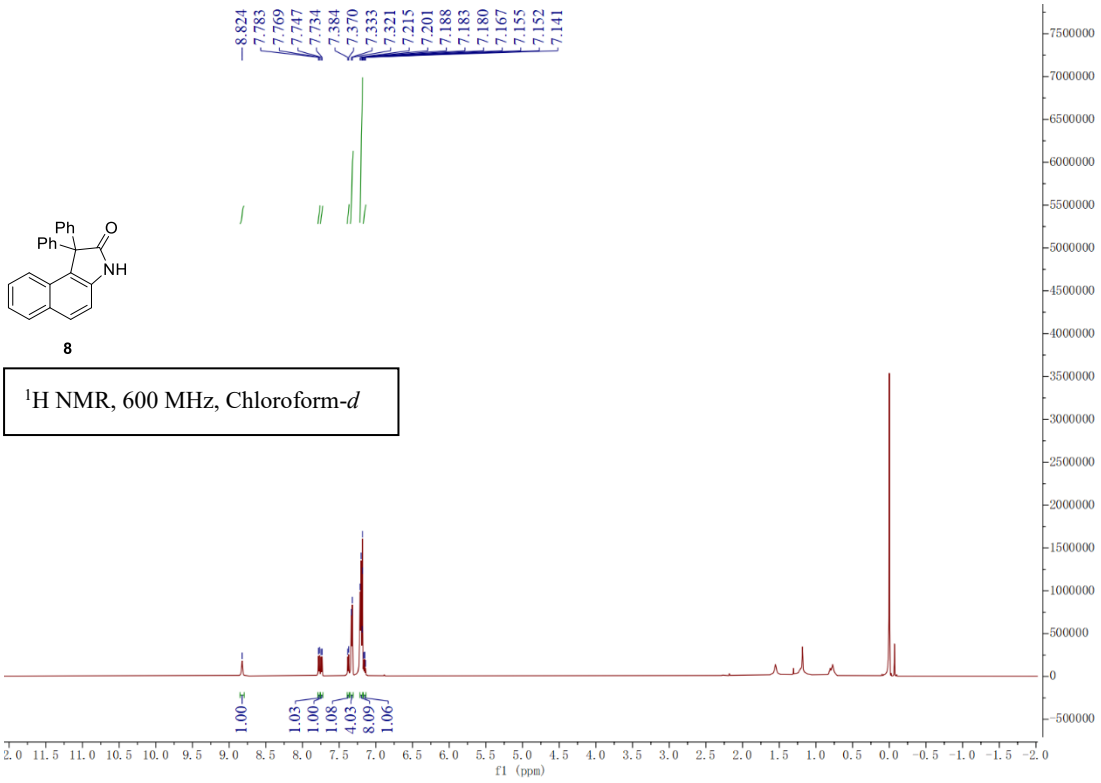
7l

^{1}H NMR, 600 MHz, Chloroform-*d*



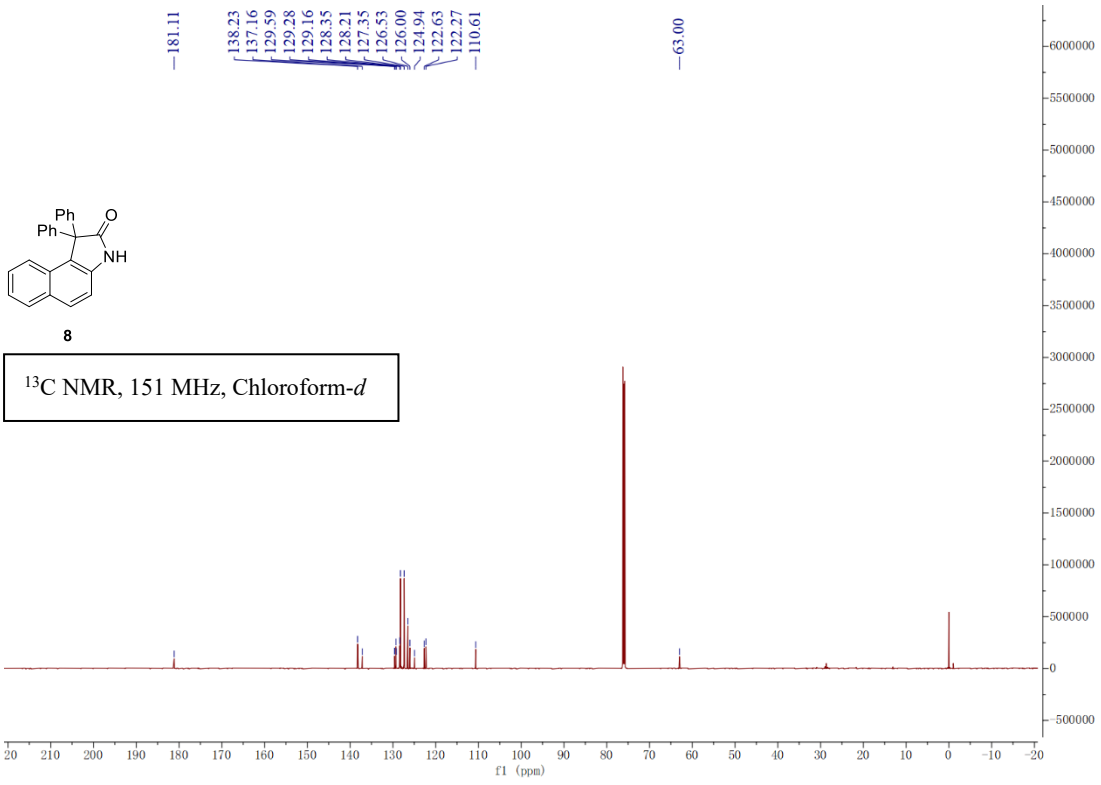
7l

^{13}C NMR, 151 MHz, Chloroform-*d*



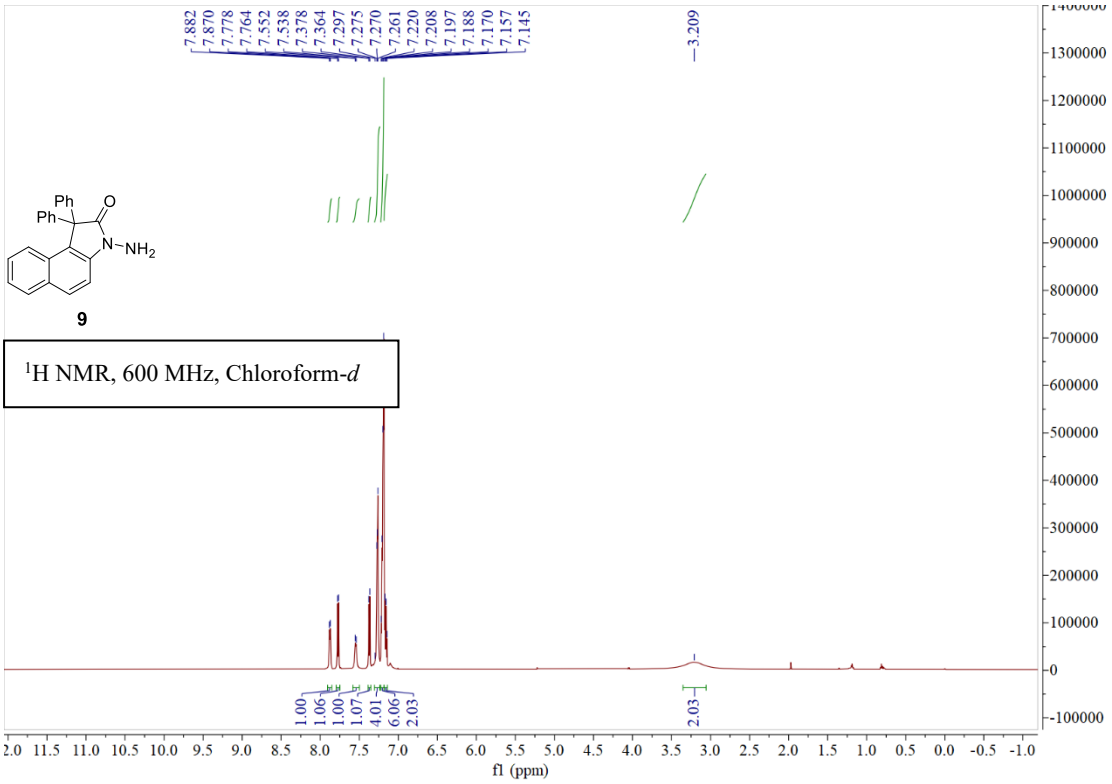
8

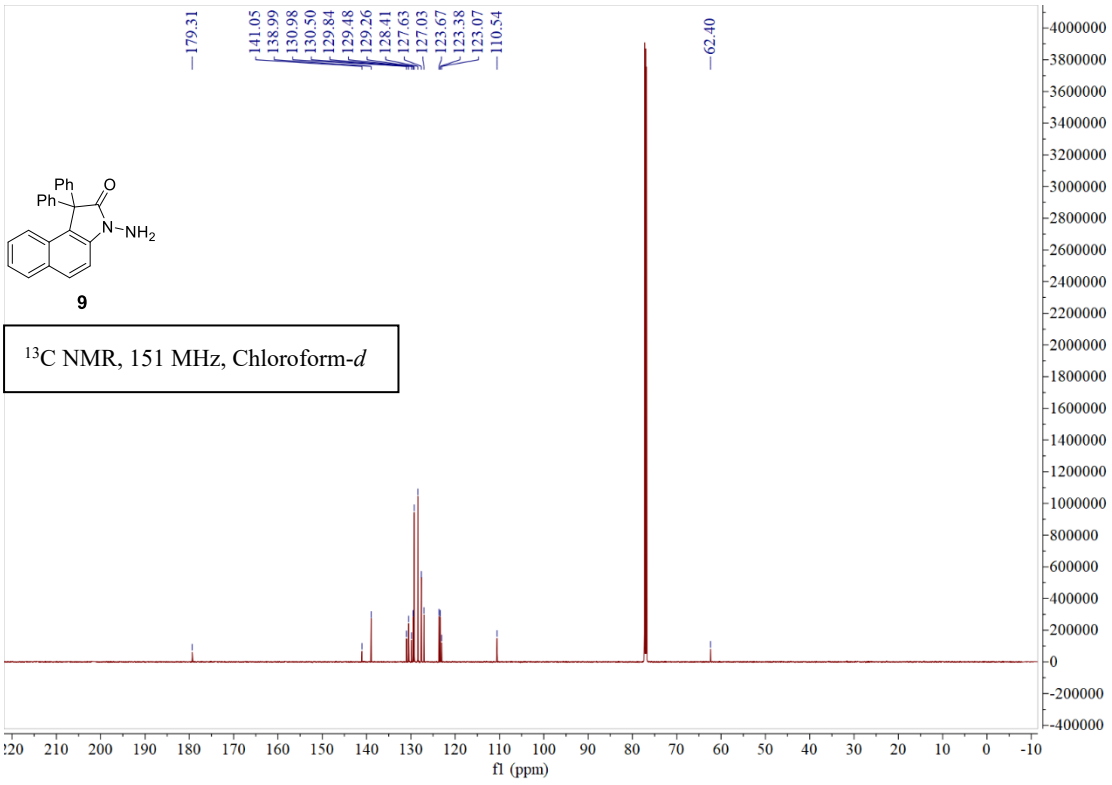
^{1}H NMR, 600 MHz, Chloroform-*d*

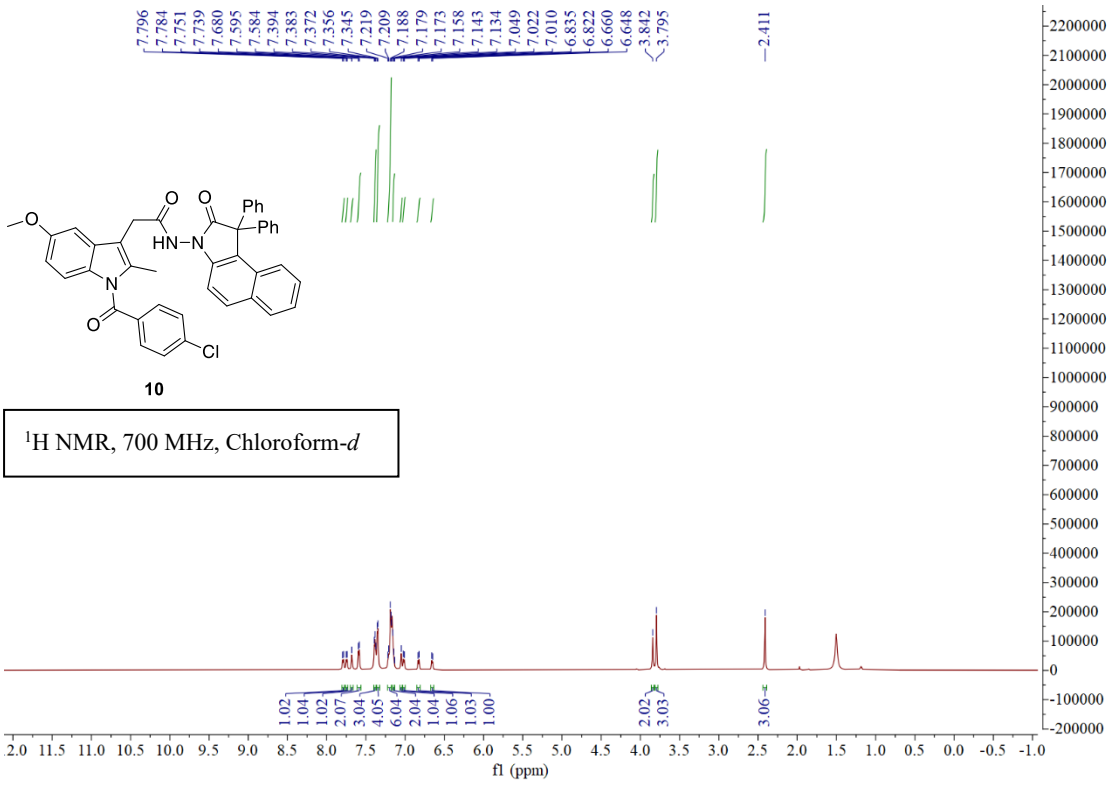


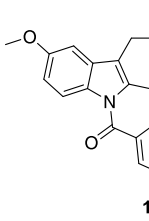
8

^{13}C NMR, 151 MHz, Chloroform-*d*


7.882
7.870
7.778
7.764
7.552
7.538
7.378
7.364
7.297
7.275
7.270
7.261
7.220
7.208
7.197
7.188
7.170
7.157
7.145
3.209
Ph
Ph
O
N
NH2
9
1H NMR, 600 MHz, Chloroform-d
1.00
1.06
1.00
1.07
4.01
6.06
2.03
2.03
f1 (ppm)


179.31
141.05
138.99
130.98
130.50
129.84
129.48
129.26
128.41
127.63
127.03
123.67
123.38
123.07
110.54
62.40
Ph
Ph
O
N
NH2
9
13C NMR, 151 MHz, Chloroform-d
f1 (ppm)



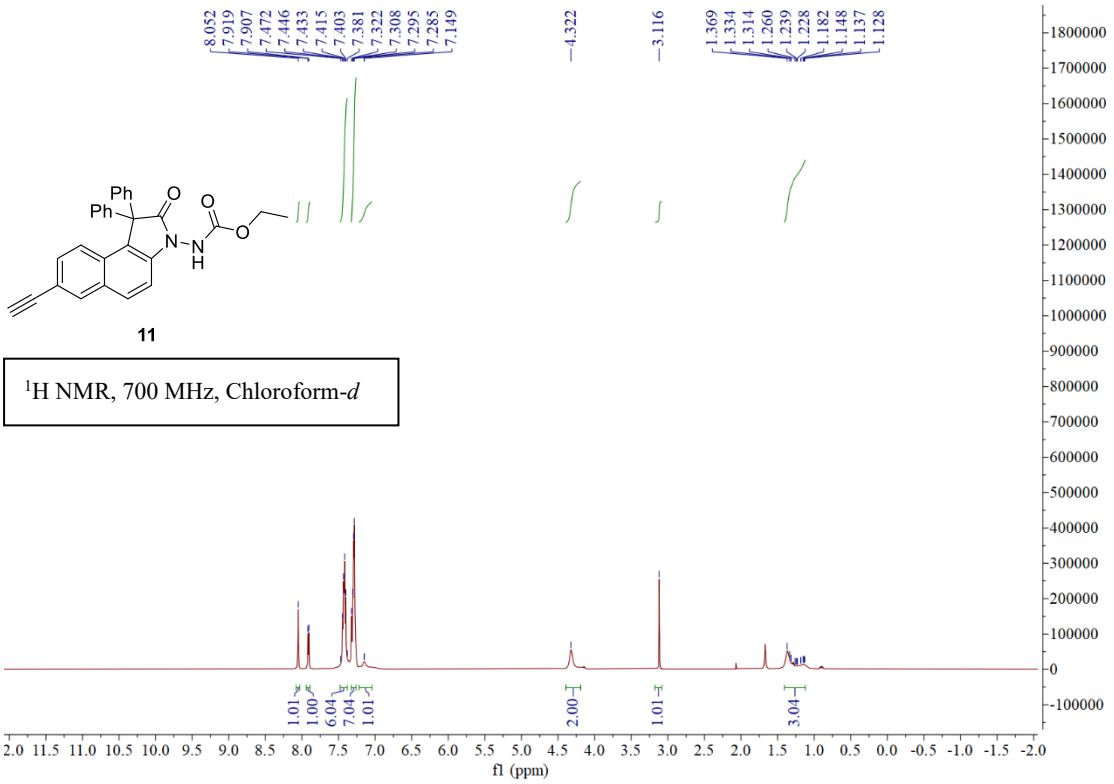


10

^{1}H NMR, 700 MHz, Chloroform-*d*

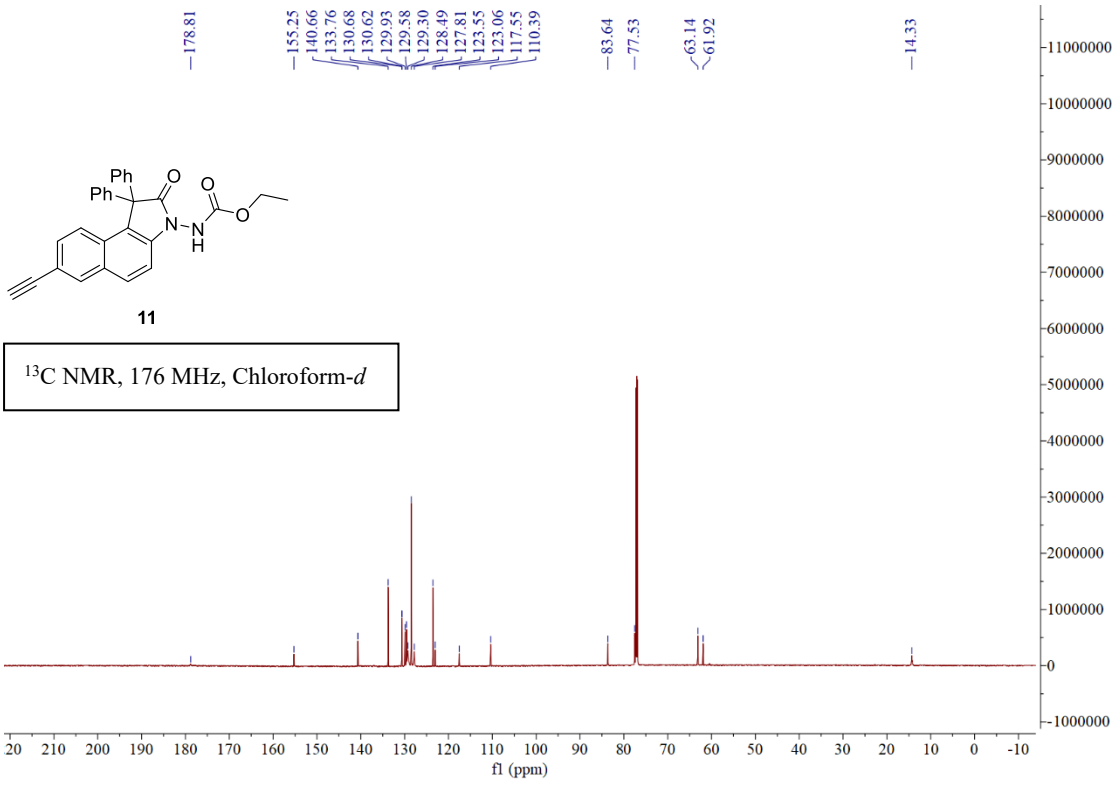
10

^{13}C NMR, 176 MHz, Chloroform-*d*



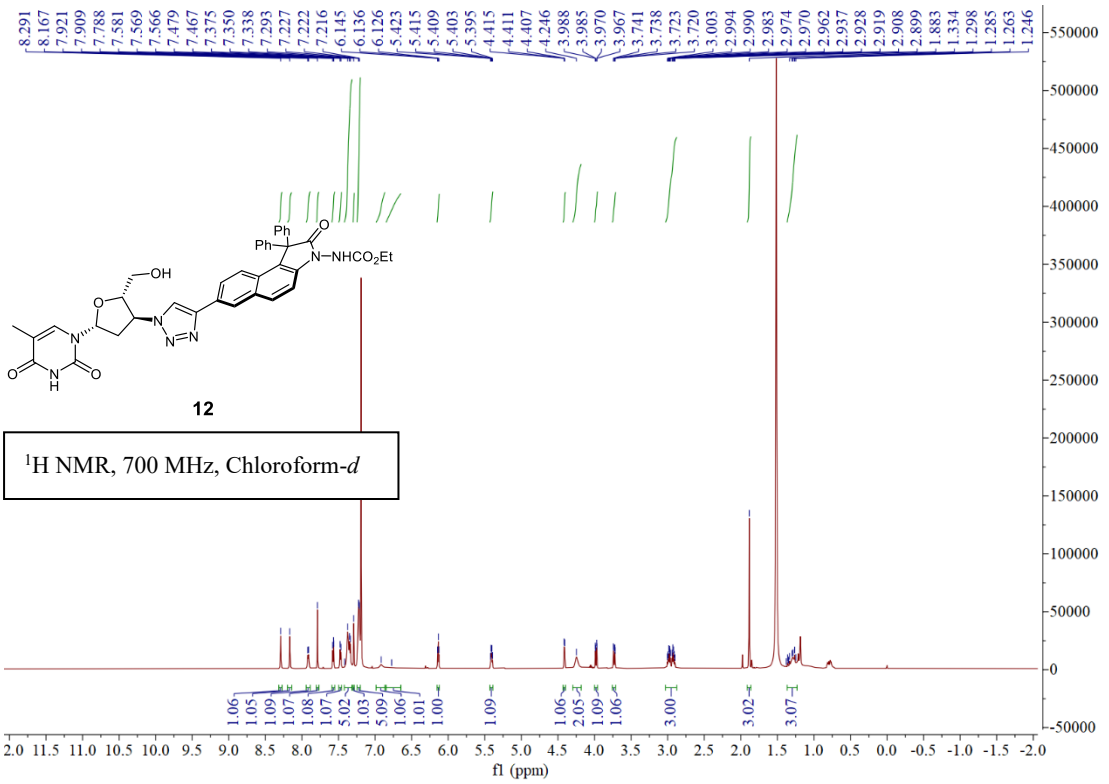
11

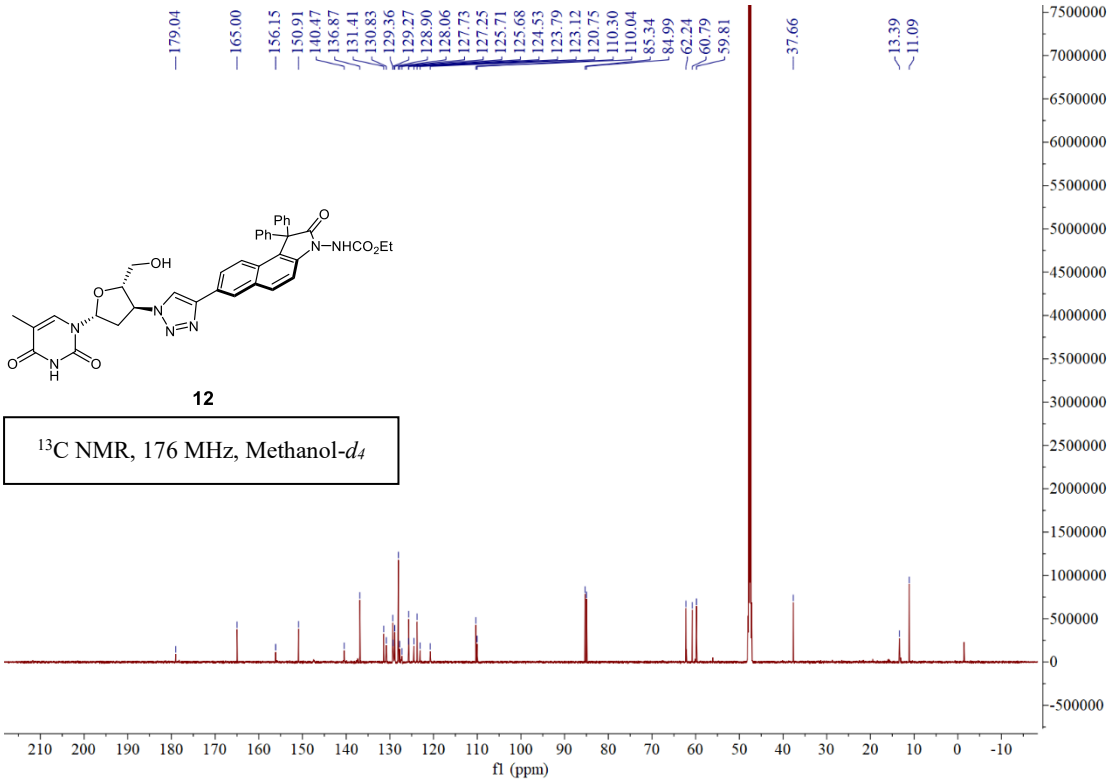
^{1}H NMR, 700 MHz, Chloroform-*d*

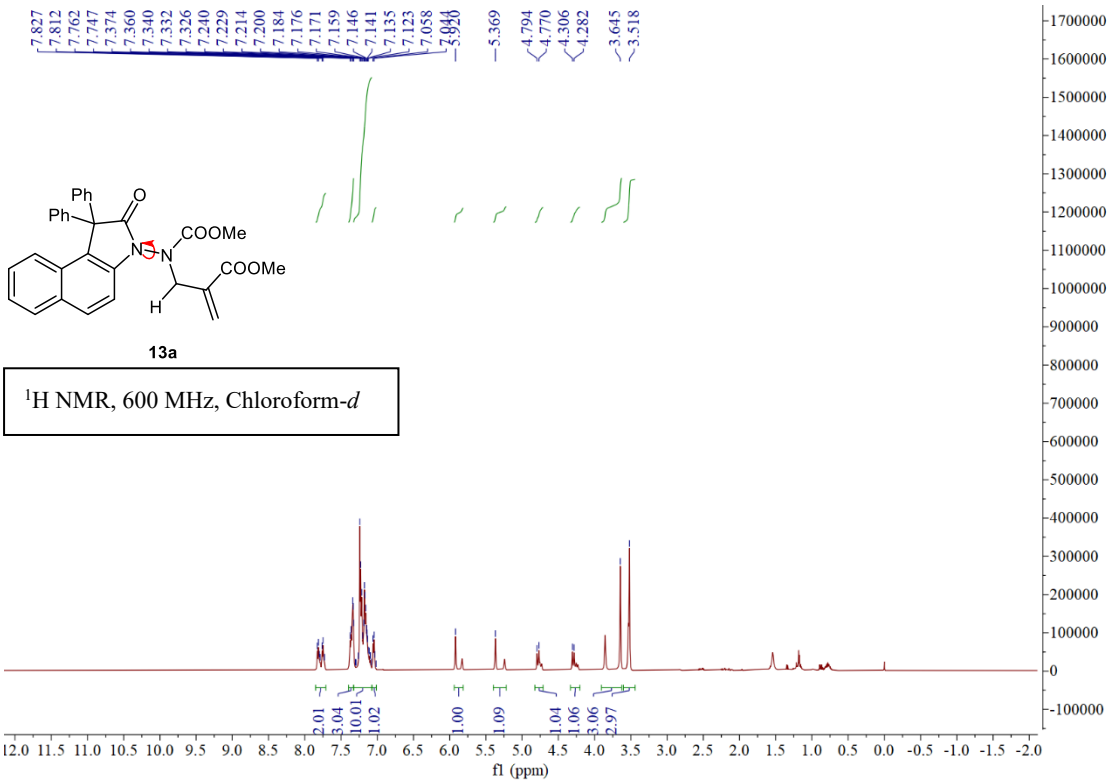


11

^{13}C NMR, 176 MHz, Chloroform-*d*

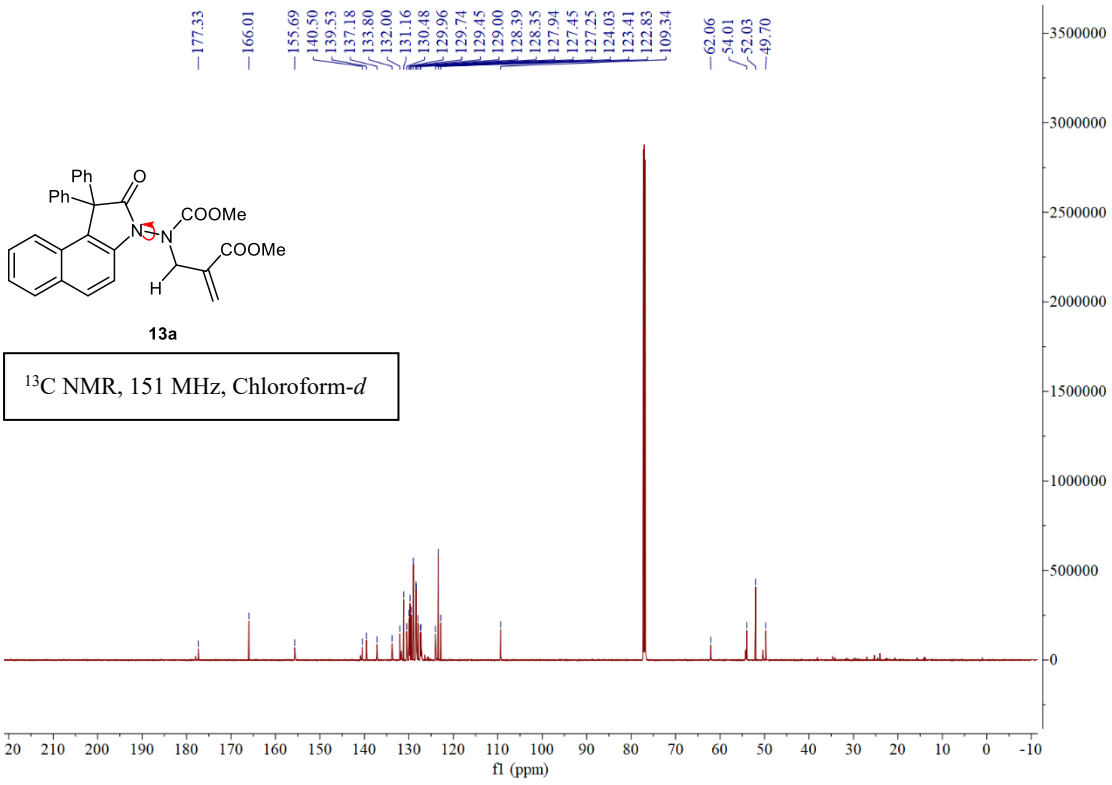

8.291
8.167
7.921
7.909
7.788
7.581
7.569
7.566
7.479
7.467
7.375
7.350
7.338
7.293
7.227
7.222
7.216
6.145
6.136
6.126
5.423
5.415
5.409
5.403
5.395
4.415
4.411
4.407
4.246
3.988
3.985
3.970
3.967
3.741
3.738
3.723
3.720
3.003
2.994
2.990
2.983
2.974
2.970
2.962
2.937
2.928
2.919
2.908
2.899
1.883
1.334
1.298
1.285
1.263
1.246
Ph
Ph
O
N–NHCO2Et
OH
O
N
N
N
O
N
H
O
12
1H NMR, 700 MHz, Chloroform-d
1.06
1.05
1.09
1.07
1.08
1.07
5.02
1.03
5.09
1.06
1.01
1.00
1.09
1.06
2.05
1.09
1.06
3.00
3.02
3.07
fl (ppm)


179.04
165.00
156.15
150.91
140.47
136.87
131.41
130.83
129.36
129.27
128.90
128.06
127.73
127.25
125.71
125.68
124.53
123.79
123.12
120.75
110.30
110.04
85.34
84.99
62.24
60.79
59.81
37.66
13.39
11.09
Ph
Ph
O
N–NHCO2Et
OH
O
N
N
N
O
N
H
O
12
13C NMR, 176 MHz, Methanol-d4
fl (ppm)



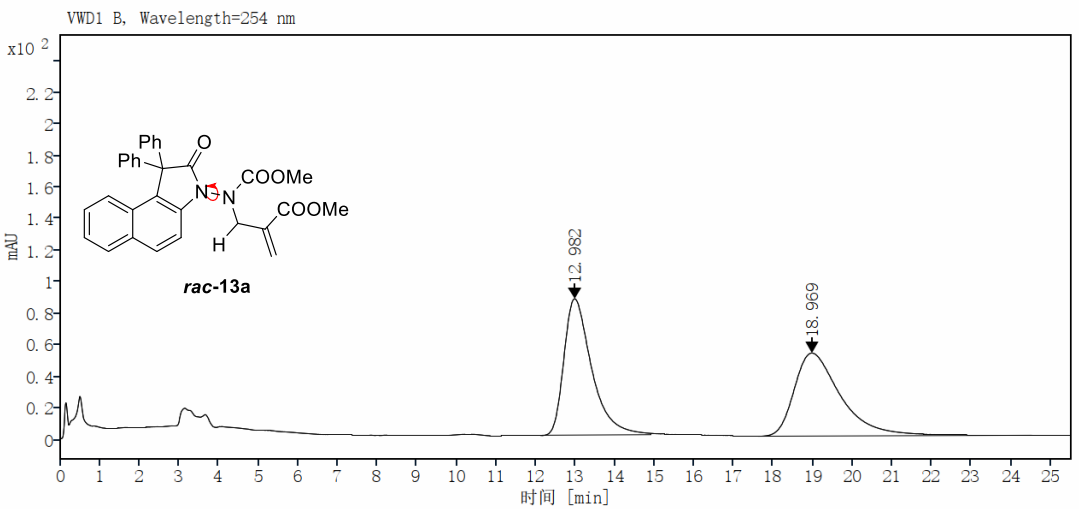
13a

^{1}H NMR, 600 MHz, Chloroform-*d*



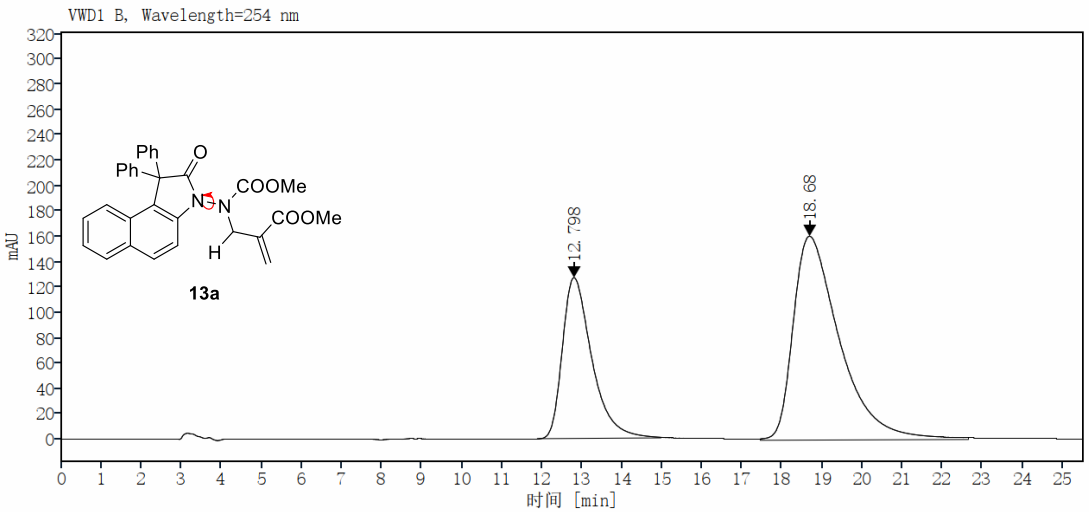
13a

^{13}C NMR, 151 MHz, Chloroform-*d*



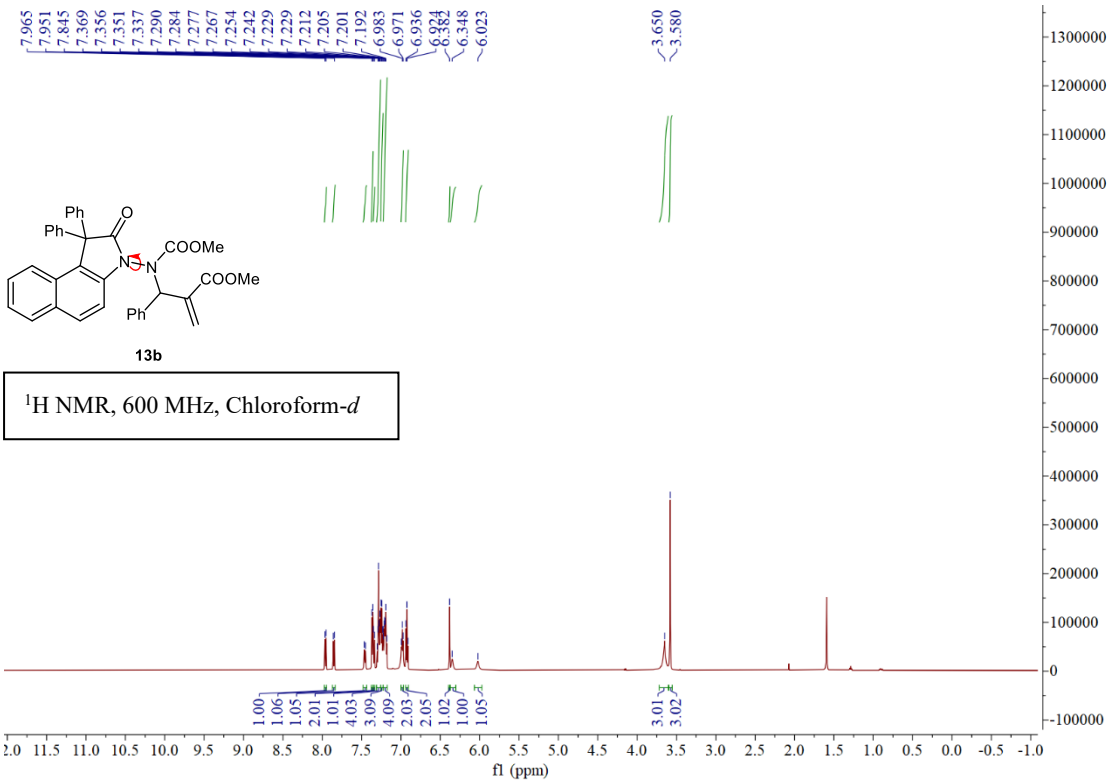
VWD1 B, Wavelength=254 nm

No.	RT [min]	Area	Width [min]	Area %
1	12.982	4197.8672	0.720	49.4699
2	18.969	4287.8369	1.193	50.5301
Total		8485.7041		



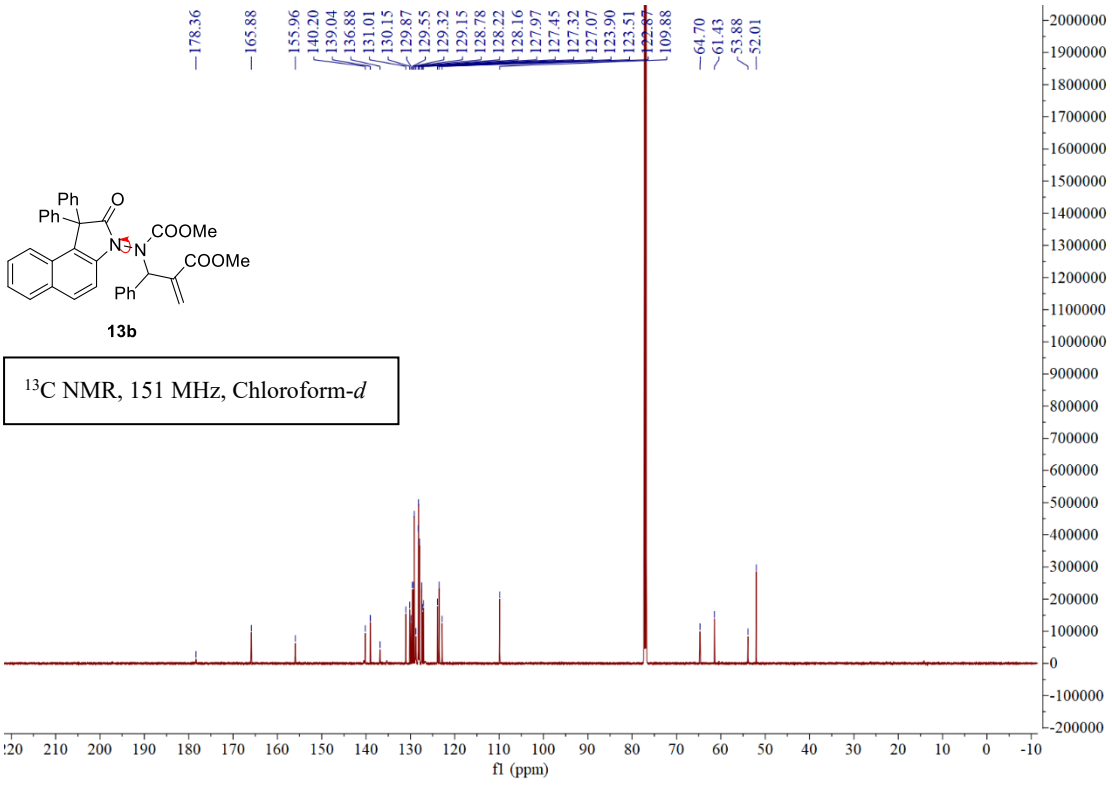
VWD1 B, Wavelength=254 nm

No.	RT [min]	Area	Width [min]	Area %
1	12.798	6492.1860	0.766	33.2986
2	18.680	13004.6670	1.177	66.7014
Total		19496.8530		



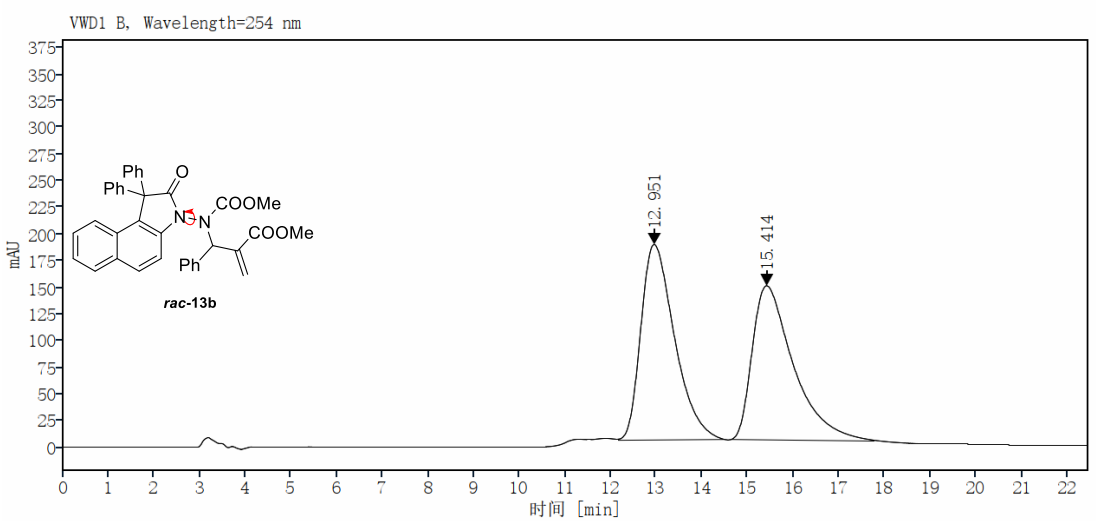
13b

^{1}H NMR, 600 MHz, Chloroform-*d*



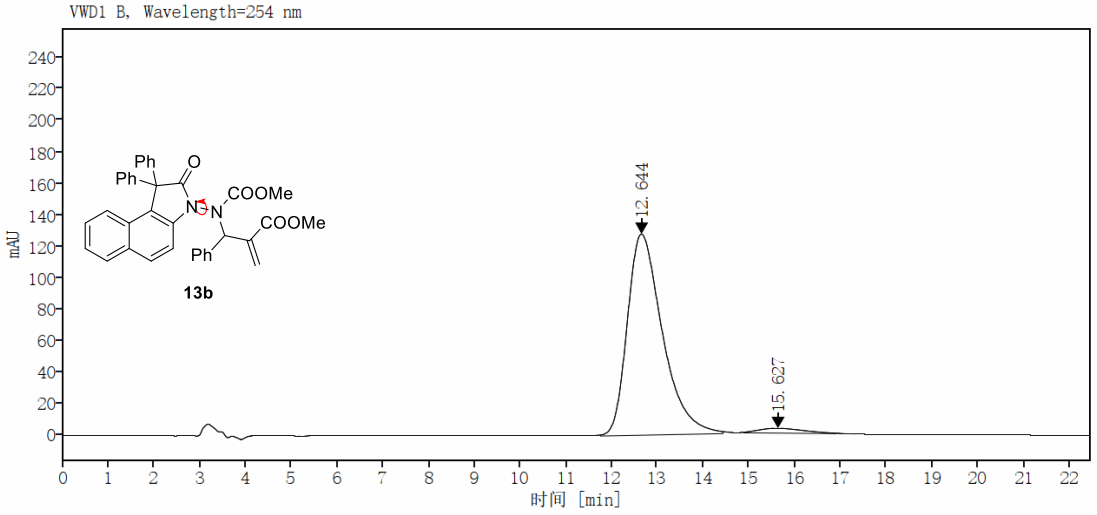
13b

^{13}C NMR, 151 MHz, Chloroform-*d*



VWD1 B, Wavelength=254 nm

No.	RT [min]	Area	Width [min]	Area %
1	12.951	9412.3945	0.793	50.8764
2	15.414	9088.0996	0.933	49.1236
Total		18500.4941		



VWD1 B, Wavelength=254 nm

No.	RT [min]	Area	Width [min]	Area %
1	12.644	6829.2905	0.802	97.0019
2	15.627	211.0752	1.087	2.9981
Total		7040.3658		