

Supporting Information

Synthesis of Structurally Diverse Pyrazolo[1,2-*a*]pyrazolones Based on Selective C–H Bond Alkenylation-Annulation of 1-Arylpyrazolidinones with Allenyl Acetates

Yongdi Xin^a, Qianting Zhou^a, Bin Li^a, Biao Cheng,^b Xinying Zhang^{a,*}, Xuesen Fan^{a,*}

^aState Key Laboratory of Antiviral Drugs, Pingyuan Laboratory, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang 453007, China

^bCollege of Tobacco Science, Henan Agricultural University, Zhengzhou 450046, China

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I. General experimental information

Commercial reagents were used without further purification. 1-Arylpyrazolidinones **1**,^[1] allenyl acetates **2**,^[2] and $[\text{RhCp}^*\text{Cl}_2]_2$ ^[3] were prepared based on literature procedures. Melting points were recorded with a micro melting point apparatus and uncorrected. The ^1H NMR spectra were recorded at 400 MHz or 600 MHz. The ^{13}C NMR spectra were recorded at 100 MHz or 150 MHz. The ^{19}F NMR spectra were recorded at 565 MHz or 376 MHz. Chemical shifts were expressed in parts per million (δ), and were reported as s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), td (triplet of doublets), m (multiplet), etc. The coupling constants J were given in Hz. High resolution mass spectra (HRMS) were obtained via ESI-TOF mode by using a BRUKER compact mass spectrometer. All reactions were monitored by thin layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm), and components were visualized by observation under UV light (254 and 365 nm).

II. Experimental procedures and spectroscopic data

1. Typical procedure for the synthesis of **3a** and spectroscopic data of **3a-3ee**

To a reaction tube equipped with a stir bar were charged with 1-phenylpyrazolidin-3-one (**1a**, 64.8 mg, 0.4 mmol), DCE (2 mL), [RhCp*Cl₂]₂ (3.1 mg, 0.005 mmol), NaOAc (8.2 mg, 0.1 mmol) and 1-phenylbuta-2,3-dien-1-yl acetate (**2a**, 37.6 mg, 0.2 mmol). The tube was then sealed, and the mixture was stirred at room temperature under argon for 2 h. Upon completion, it was quenched with saturated brine, and extracted with dichloromethane (10 mL × 3). The combined organic phases were dried over anhydrous Na₂SO₄, filtered through a pad of celite, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (2:1) as eluent to afford **3a**. **3b-3ee** were obtained in a similar manner.

(E)-9-Methyl-9-styryl-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-1-one (3a)

Eluent: petroleum ether/ethyl acetate (2:1). Yellow solid (45.3 mg, 78%), mp 121.6-122.5 °C. ¹H NMR (CDCl₃, 600 MHz): δ 7.35 (d, *J* = 7.2 Hz, 2H), 7.29-7.26 (m, 3H), 7.22-7.19 (m, 1H), 7.14 (d, *J* = 7.2 Hz, 1H), 7.05 (td, *J*₁ = 7.2 Hz, *J*₂ = 1.2 Hz, 1H), 6.79 (d, *J* = 7.8 Hz, 1H), 6.50 (d, *J* = 15.6 Hz, 1H), 6.43 (d, *J* = 15.6 Hz, 1H), 3.88 (td, *J*₁ = 9.0 Hz, *J*₂ = 4.8 Hz, 1H), 3.50-3.45 (m, 1H), 3.04-2.98 (m, 1H), 2.82-2.78 (m, 1H), 2.05 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 150 MHz): δ 164.6, 147.1, 136.2, 134.9, 130.3, 129.3, 128.9, 128.5, 127.9, 126.9, 122.9, 122.7, 110.0, 66.2, 51.2, 35.3, 24.4. HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₉H₁₈N₂NaO 313.1311; Found 313.1308.

(E)-7,9-Dimethyl-9-styryl-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-1-one (3b)

Eluent: petroleum ether/ethyl acetate (2:1). Yellow solid (42.0 mg, 69%), mp 82.3-89.3 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.30-7.28 (m, 2H), 7.21-7.17 (m, 2H), 7.15-7.10 (m, 1H), 7.00 (dd, *J*₁ = 8.0 Hz, *J*₂ = 0.8 Hz, 1H), 6.86 (s, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 6.45 (d, *J* = 16.0 Hz, 1H), 6.34 (d, *J* = 16.0 Hz, 1H), 3.77 (td, *J*₁ = 8.4 Hz, *J*₂ = 4.4 Hz, 1H), 3.38-3.31 (m, 1H), 2.96-2.87 (m, 1H), 2.74-2.67 (m, 1H), 2.26 (s, 3H), 1.96 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 164.8, 145.0, 136.3, 135.2, 132.7, 130.5, 129.5, 129.2, 128.6, 127.9, 126.9, 123.2, 109.9, 66.3, 51.7, 35.5, 24.5, 21.1. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{20}\text{N}_2\text{NaO}$ 327.1468; Found 327.1472.

(E)-7-Chloro-9-methyl-9-styryl-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-1-one (3c)

Eluent: petroleum ether/ethyl acetate (2:1). Yellow solid (48.7 mg, 75%), mp 124.0-124.9 °C. ^1H NMR (CDCl_3 , 600 MHz): δ 7.36 (d, $J = 7.2$ Hz, 2H), 7.28 (t, $J = 7.2$ Hz, 2H), 7.24-7.21 (m, 2H), 7.10 (d, $J = 1.8$ Hz, 1H), 6.70 (d, $J = 8.4$ Hz, 1H), 6.52 (d, $J = 15.6$ Hz, 1H), 6.38 (d, $J = 15.6$ Hz, 1H), 3.84 (td, $J_1 = 8.4$ Hz, $J_2 = 4.2$ Hz, 1H), 3.47-3.43 (m, 1H), 3.02-2.96 (m, 1H), 2.82-2.78 (m, 1H), 2.03 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150 MHz): δ 164.7, 145.8, 136.8, 136.0, 129.8, 129.7, 129.0, 128.6, 128.1, 128.0, 126.9, 123.0, 111.0, 66.3, 51.1, 35.3, 24.4. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{19}\text{H}_{17}\text{ClN}_2\text{NaO}$ 347.0922; Found 347.0927.

(E)-7-Bromo-9-methyl-9-styryl-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-1-one (3d)

Eluent: petroleum ether/ethyl acetate (2:1). Yellow solid (49.4 mg, 67%), mp 73.5-74.2 °C. ^1H NMR (CDCl_3 , 600 MHz): δ 7.38-7.36 (m, 3H), 7.29 (t, $J = 7.2$ Hz, 2H), 7.24-7.21 (m, 2H), 6.66 (d, $J = 8.4$ Hz, 1H), 6.52 (d, $J = 16.2$ Hz, 1H), 6.38 (d, $J = 15.6$ Hz, 1H), 3.85 (td, $J_1 = 9.0$ Hz, $J_2 = 4.8$ Hz, 1H), 3.48-3.44 (m, 1H), 3.02-2.96 (m, 1H), 2.83-2.78 (m, 1H), 2.03 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150 MHz): δ 164.6, 146.2, 137.2, 136.0, 131.8, 129.8, 129.7, 128.6, 128.1, 127.0, 125.8, 115.2, 111.5, 66.2, 51.0, 35.3, 24.4. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{19}\text{H}_{17}\text{BrN}_2\text{NaO}$ 391.0416; Found 391.0406.

(E)-9-Methyl-9-styryl-7-(trifluoromethyl)-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-1-one (3e)

Eluent: petroleum ether/ethyl acetate (2:1). Yellow solid (47.0 mg, 66%), mp 104.8-105.6 °C. ^1H NMR (CDCl_3 , 600 MHz): δ 7.54 (d, $J = 8.4$ Hz, 1H), 7.37-7.36 (m, 3H), 7.29 (t, $J = 7.8$ Hz, 2H), 7.23 (t, $J = 7.2$ Hz, 1H), 6.82 (d, $J = 8.4$ Hz, 1H), 6.53 (d, $J = 15.6$ Hz, 1H), 6.40 (d, $J = 15.6$ Hz, 1H), 3.92 (td, $J_1 = 9.0$ Hz, $J_2 = 4.8$ Hz, 1H), 3.57-3.53 (m, 1H), 3.05-2.99 (m, 1H), 2.86-2.82 (m, 1H), 2.07 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150 MHz): δ 164.5, 149.5, 135.8, 135.6, 129.9, 129.4, 128.6, 128.1, 126.9, 126.7 (q, $^3J_{\text{C-F}} = 3.0$ Hz), 125.0 (q,

$^2J_{C-F} = 32.1$ Hz), 124.3 (q, $^1J_{C-F} = 269.9$ Hz), 119.9 (q, $^3J_{C-F} = 3.3$ Hz), 109.5, 66.2, 50.1, 35.1, 24.3. ^{19}F NMR (565 MHz, $CDCl_3$) δ : -61.30 (s). HRMS (ESI) m/z : $[M+Na]^+$ Calcd for $C_{20}H_{17}F_3N_2NaO$ 381.1185; Found 381.1174.

(E)-6,9-Dimethyl-9-styryl-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-1-one (3f)

Eluent: petroleum ether/ethyl acetate (2:1). Yellow solid (54.8 mg, 90%), mp 42.0-43.8 °C. 1H NMR ($CDCl_3$, 600 MHz): δ 7.35 (d, $J = 7.2$ Hz, 2H), 7.28-7.26 (m, 2H), 7.20 (t, $J = 7.2$ Hz, 1H), 7.02 (d, $J = 8.4$ Hz, 1H), 6.87 (d, $J = 7.2$ Hz, 1H), 6.61 (s, 1H), 6.50 (d, $J = 16.2$ Hz, 1H), 6.44 (d, $J = 16.2$ Hz, 1H), 3.86 (td, $J_1 = 8.4$ Hz, $J_2 = 4.8$ Hz, 1H), 3.47-3.43 (m, 1H), 3.02-2.97 (m, 1H), 2.81-2.76 (m, 1H), 2.37 (s, 3H), 2.04 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 164.6, 147.3, 139.2, 136.3, 132.2, 130.5, 129.1, 128.5, 127.8, 126.9, 123.7, 122.4, 110.7, 66.1, 51.2, 35.4, 24.6, 21.6. HRMS (ESI) m/z : $[M+Na]^+$ Calcd for $C_{20}H_{20}N_2NaO$ 327.1468; Found 327.1471.

(E)-6-Chloro-9-methyl-9-styryl-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-1-one (3g)

Eluent: petroleum ether/ethyl acetate (2:1). Yellow solid (50.6 mg, 78%), mp 49.5-50.3 °C. 1H NMR ($CDCl_3$, 600 MHz): δ 7.35 (d, $J = 7.2$ Hz, 2H), 7.27 (t, $J = 7.8$ Hz, 2H), 7.21 (t, $J = 7.2$ Hz, 1H), 7.04 (d, $J = 8.4$ Hz, 1H), 7.00 (dd, $J_1 = 7.8$ Hz, $J_2 = 1.2$ Hz, 1H), 6.76 (d, $J = 1.8$ Hz, 1H), 6.48 (d, $J = 15.6$ Hz, 1H), 6.40 (d, $J = 16.2$ Hz, 1H), 3.85 (td, $J_1 = 9.0$ Hz, $J_2 = 4.8$ Hz, 1H), 3.50-3.46 (m, 1H), 3.01-2.96 (m, 1H), 2.83-2.78 (m, 1H), 2.02 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 164.5, 148.2, 136.0, 134.7, 133.4, 129.8, 129.6, 128.6, 128.0, 126.9, 123.6, 122.8, 110.3, 66.0, 50.6, 35.2, 24.4. HRMS (ESI) m/z : $[M+Na]^+$ Calcd for $C_{19}H_{17}ClN_2NaO$ 347.0922; Found 347.0909.

(E)-6-Bromo-9-methyl-9-styryl-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-1-one (3h)

Eluent: petroleum ether/ethyl acetate (2:1). Yellow solid (58.0 mg, 79%), mp 45.3-46.3 °C. 1H NMR ($CDCl_3$, 600 MHz): δ 7.34 (d, $J = 7.8$ Hz, 2H), 7.27 (t, $J = 7.2$ Hz, 2H), 7.21 (t, $J = 7.2$ Hz, 1H), 7.15 (dd, $J_1 = 8.4$ Hz, $J_2 = 1.8$ Hz, 1H), 6.97 (d, $J = 7.8$ Hz, 1H), 6.91 (d, $J = 1.2$ Hz, 1H), 6.48 (d, $J = 15.6$ Hz, 1H), 6.40 (d, $J = 15.6$

Hz, 1H), 3.84 (td, $J_1 = 8.4$ Hz, $J_2 = 4.8$ Hz, 1H), 3.49-3.45 (m, 1H), 3.01-2.95 (m, 1H), 2.82-2.77 (m, 1H), 2.02 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150 MHz): δ 164.5, 148.4, 136.0, 134.0, 129.70, 129.67, 128.6, 128.1, 126.9, 125.7, 124.0, 122.5, 113.2, 66.1, 50.7, 35.2, 24.4. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{19}\text{H}_{17}\text{BrN}_2\text{NaO}$ 391.0416; Found 391.0428.

(E)-5-Fluoro-9-methyl-9-styryl-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-1-one (3i)

Eluent: petroleum ether/ethyl acetate (2:1). Yellow solid (31.0 mg, 50%), mp 57.4-58.3 °C. ^1H NMR (CDCl_3 , 600 MHz): δ 7.36-7.34 (m, 2H), 7.29-7.26 (m, 2H), 7.23-7.20 (m, 1H), 7.02-6.98 (m, 2H), 6.94-6.92 (m, 1H), 6.51 (d, $J = 15.6$ Hz, 1H), 6.41 (d, $J = 16.2$ Hz, 1H), 4.03-3.99 (m, 1H), 3.64-3.60 (m, 1H), 3.03-2.97 (m, 1H), 2.82-2.77 (m, 1H), 2.06 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150 MHz): δ 164.9, 149.0 (d, $^1J_{\text{C-F}} = 244.2$ Hz), 138.3 (d, $^3J_{\text{C-F}} = 3.5$ Hz), 136.0, 134.0 (d, $^2J_{\text{C-F}} = 13.4$ Hz), 129.8, 129.6, 128.5, 128.0, 126.9, 124.1 (d, $^3J_{\text{C-F}} = 5.6$ Hz), 118.3 (d, $^4J_{\text{C-F}} = 3.3$ Hz), 115.8 (d, $^2J_{\text{C-F}} = 18.2$ Hz), 66.7, 52.1 (d, $^4J_{\text{C-F}} = 2.1$ Hz), 35.6, 24.6. ^{19}F NMR (565 MHz, CDCl_3) δ : -132.78 – -132.81 (m). HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{19}\text{H}_{17}\text{FN}_2\text{NaO}$ 331.1217; Found 331.1203.

(E)-5-Methoxy-9-methyl-9-styryl-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-1-one (3j)

Eluent: petroleum ether/ethyl acetate (2:1). Yellow solid (40.8 mg, 64%), mp 73.9-74.9 °C. ^1H NMR (CDCl_3 , 400 MHz): δ 7.35 (d, $J = 7.2$ Hz, 2H), 7.27 (t, $J = 7.2$ Hz, 2H), 7.22-7.18 (m, 1H), 7.04 (t, $J = 7.6$ Hz, 1H), 6.82 (d, $J = 8.4$ Hz, 1H), 6.77 (d, $J = 7.6$ Hz, 1H), 6.52 (d, $J = 16.0$ Hz, 1H), 6.43 (d, $J = 16.0$ Hz, 1H), 4.02 (td, $J_1 = 8.4$ Hz, $J_2 = 4.4$ Hz, 1H), 3.87 (s, 3H), 3.59-3.52 (m, 1H), 3.01-2.92 (m, 1H), 2.78-2.71 (m, 1H), 2.05 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 165.2, 146.4, 136.32, 136.26, 135.2, 130.4, 129.2, 128.5, 127.8, 126.8, 124.3, 114.8, 110.8, 66.5, 55.7, 53.0, 35.7, 24.7. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{20}\text{N}_2\text{NaO}_2$ 343.1417; Found 343.1420.

(E)-6,7,9-Trimethyl-9-styryl-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-1-one (3k)

Eluent: petroleum ether/ethyl acetate (2:1). Yellow solid (57.4 mg, 90%), mp 136.9-137.7 °C. ¹H NMR (CDCl₃, 600 MHz): δ 7.36-7.35 (m, 2H), 7.27-7.25 (m, 2H), 7.21-7.18 (m, 1H), 6.89 (s, 1H), 6.60 (s, 1H), 6.51 (d, *J* = 16.2 Hz, 1H), 6.42 (d, *J* = 15.6 Hz, 1H), 3.83 (td, *J*₁ = 8.4 Hz, *J*₂ = 4.8 Hz, 1H), 3.43-3.39 (m, 1H), 3.01-2.95 (m, 1H), 2.80-2.75 (m, 1H), 2.26 (s, 3H), 2.24 (s, 3H), 2.03 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 150 MHz): δ 164.7, 145.4, 137.5, 136.4, 132.5, 131.3, 130.6, 129.0, 128.5, 127.8, 126.9, 123.5, 111.4, 66.2, 51.8, 35.5, 24.6, 20.3, 19.7. HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₁H₂₂N₂NaO 341.1624; Found 341.1621.

(E)-2,2,9-Trimethyl-9-styryl-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-1-one (3l)

Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid (34.1 mg, 54%), mp 134.8-135.8 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.35-7.33 (m, 2H), 7.29-7.24 (m, 3H), 7.22-7.18 (m, 1H), 7.15 (d, *J* = 7.2 Hz, 1H), 7.03 (td, *J*₁ = 7.6 Hz, *J*₂ = 0.8 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 6.49 (d, *J* = 16.0 Hz, 1H), 6.39 (d, *J* = 16.0 Hz, 1H), 3.66 (d, *J* = 8.4 Hz, 1H), 3.21 (d, *J* = 8.4 Hz, 1H), 2.06 (s, 3H), 1.41 (s, 3H), 1.29 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 150 MHz): δ 170.0, 147.2, 136.4, 135.0, 130.4, 129.1, 128.9, 128.6, 127.9, 127.0, 122.8, 122.6, 110.0, 66.1, 64.1, 46.0, 24.6, 23.3, 22.8. HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₁H₂₂N₂NaO⁺ 341.1624; Found 341.1619.

(E)-2,2,7,9-Tetramethyl-9-styryl-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-1-one (3m)

Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid (26.6 mg, 40%), mp 137.5-138.5 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.35-7.33 (m, 2H), 7.28-7.24 (m, 2H), 7.21-7.17 (m, 1H), 7.06-7.04 (m, 1H), 6.93 (s, 1H), 6.66 (d, *J* = 8.0 Hz, 1H), 6.49 (d, *J* = 15.6 Hz, 1H), 6.37 (d, *J* = 15.6 Hz, 1H), 3.62 (d, *J* = 8.4 Hz, 1H), 3.16 (d, *J* = 8.0 Hz, 1H), 2.32 (s, 3H), 2.03 (s, 3H), 1.40 (s, 3H), 1.27 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ 170.1, 145.0, 136.5, 135.2, 132.5, 130.5, 129.4, 128.9, 128.6, 127.8, 126.9, 123.1, 109.9, 66.1, 64.6, 46.0, 24.5, 23.3, 22.8, 21.1. HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₂H₂₄N₂NaO⁺ 355.1781; Found 355.1787.

(E)-7-Methoxy-2,2,9-trimethyl-9-styryl-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-1-one (3n)

Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid (30.4 mg, 44%), mp 80.8-81.8 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.36-7.34 (m, 2H), 7.29-7.25 (m, 2H), 7.22-7.18 (m, 1H), 6.81 (dd, *J*₁ = 8.4 Hz, *J*₂ = 2.4 Hz, 1H), 6.71-6.69 (m, 2H), 6.51 (d, *J* = 15.6 Hz, 1H), 6.38 (d, *J* = 16.0 Hz, 1H), 3.79 (s, 3H), 3.61 (d, *J* = 8.0 Hz, 1H), 3.14 (d, *J* = 8.0 Hz 1H), 2.05 (s, 3H), 1.40 (s, 3H), 1.28 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ 170.3, 156.3, 141.1, 136.40, 136.35, 130.3, 129.2, 128.6, 127.9, 127.0, 114.2, 110.8, 108.8, 66.3, 65.0, 56.0, 46.0, 24.5, 23.2, 22.7. HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₂H₂₄N₂NaO₂ 371.1730; Found 371.1734.

(E)-7-Fluoro-2,2,9-trimethyl-9-styryl-2,3-dihydro-1H,9H-pyrazolo[1,2-*a*]indazol-1-one (3o)

Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid (31.5 mg, 47%), mp 118.2-119.2 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.36-7.34 (m, 2H), 7.30-7.26 (m, 2H), 7.24-7.20 (m, 1H), 6.96 (td, *J*₁ = 8.8 Hz, *J*₂ = 2.4 Hz, 1H), 6.87 (dd, *J*₁ = 8.0 Hz, *J*₂ = 2.4 Hz, 1H), 6.69 (dd, *J*₁ = 8.4 Hz, *J*₂ = 4.0 Hz, 1H), 6.50 (d, *J* = 15.6 Hz, 1H), 6.36 (d, *J* = 16.0 Hz, 1H), 3.62 (d, *J* = 8.4 Hz, 1H), 3.17 (d, *J* = 8.0 Hz, 1H), 2.04 (s, 3H), 1.40 (s, 3H), 1.29 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ 170.2, 159.3 (d, ¹*J*_{C-F} = 239.5 Hz), 143.4 (d, ⁴*J*_{C-F} = 2.2 Hz), 136.6 (d, ³*J*_{C-F} = 8.5 Hz), 136.2, 129.8, 129.5, 128.6, 128.0, 127.0, 115.6 (d, ²*J*_{C-F} = 23.9 Hz), 110.8 (d, ³*J*_{C-F} = 9.2 Hz), 110.1 (d, ²*J*_{C-F} = 24.7 Hz), 66.2 (d, ⁴*J*_{C-F} = 2.2 Hz), 64.6, 46.0, 24.5, 23.2, 22.7. ¹⁹F NMR (376 MHz, CDCl₃): δ -120.49 (td, *J*₁ = 7.9 Hz, *J*₂ = 4.1 Hz). HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₁H₂₁FN₂NaO⁺ 359.1530; Found 359.1540.

(E)-2,2,9-Trimethyl-9-styryl-7-(trifluoromethyl)-2,3-dihydro-1H,9H-pyrazolo[1,2-*a*]indazol-1-one (3p)

Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid (31.5 mg, 41%), mp 90.7-91.7 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.53 (d, *J* = 8.0 Hz, 1H), 7.37-7.35 (m, 3H), 7.29 (t, *J* = 7.2 Hz, 2H), 7.25-7.21 (m, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 6.51 (d, *J* = 16.0 Hz, 1H), 6.37 (d, *J* = 15.6 Hz, 1H), 3.69 (d, *J* = 8.4 Hz, 1H), 3.29 (d, *J* = 8.4 Hz, 1H), 2.07 (s, 3H), 1.42 (s, 3H), 1.31 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ 170.0, 149.6, 136.0, 135.7, 129.7, 129.5, 128.7, 128.2, 127.0, 126.7 (q, ³*J*_{C-F} = 3.3 Hz), 124.9 (q, ²*J*_{C-F} = 31.8 Hz), 124.4 (q, ¹*J*_{C-F} =

269.5 Hz), 119.8 (q, $^3J_{C-F} = 3.4$ Hz), 109.5, 66.1, 63.2, 46.0, 24.5, 23.4, 22.8. ^{19}F NMR (376 MHz, CDCl_3): δ -61.28 (s). HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{22}\text{H}_{21}\text{F}_3\text{N}_2\text{NaO}^+$ 409.1498; Found 409.1487.

(E)-9-Methyl-9-(4-methylstyryl)-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-1-one (3q)

Eluent: petroleum ether/ethyl acetate (2:1). Yellow solid (44.5 mg, 73%), mp 44.6-45.2 °C. ^1H NMR (CDCl_3 , 600 MHz): δ 7.28-7.23 (m, 3H), 7.13 (d, $J = 7.2$ Hz, 1H), 7.07 (d, $J = 8.4$ Hz, 2H), 7.04 (td, $J_1 = 7.8$ Hz, $J_1 = 0.6$ Hz, 1H), 6.78 (d, $J = 7.8$ Hz, 1H), 6.46 (d, $J = 16.2$ Hz, 1H), 6.38 (d, $J = 16.2$ Hz, 1H), 3.87 (td, $J_1 = 9.0$ Hz, $J_2 = 4.8$ Hz, 1H), 3.48-3.44 (m, 1H), 3.03-2.97 (m, 1H), 2.82-2.77 (m, 1H), 2.30 (s, 3H), 2.04 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150 MHz): δ 164.6, 147.2, 137.8, 135.1, 133.5, 129.3, 129.28, 129.26, 128.9, 126.8, 122.9, 122.8, 110.0, 66.3, 51.2, 35.4, 24.6, 21.3. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{20}\text{N}_2\text{NaO}$ 327.1468; Found 327.1470.

(E)-9-(4-Ethylstyryl)-9-methyl-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-1-one (3r)

Eluent: petroleum ether/ethyl acetate (2:1). Yellow oil (42.6 mg, 67%). ^1H NMR (CDCl_3 , 600 MHz): δ 7.28-7.26 (m, 3H), 7.13 (d, $J = 7.8$ Hz, 1H), 7.11 (d, $J = 7.8$ Hz, 2H), 7.05 (td, $J_1 = 7.8$ Hz, $J_2 = 1.2$ Hz, 1H), 6.78 (d, $J = 7.8$ Hz, 1H), 6.48 (d, $J = 15.6$ Hz, 1H), 6.40 (d, $J = 15.6$ Hz, 1H), 3.87 (td, $J_1 = 8.4$ Hz, $J_2 = 4.2$ Hz, 1H), 3.49-3.45 (m, 1H), 3.03-2.97 (m, 1H), 2.82-2.77 (m, 1H), 2.61 (q, $J = 7.2$ Hz, 2H), 2.05 (s, 3H), 1.20 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150 MHz): δ 164.6, 147.2, 144.2, 135.1, 133.7, 129.4, 129.3, 128.9, 128.1, 126.9, 122.9, 122.8, 110.0, 66.3, 51.2, 35.4, 28.7, 24.6, 15.6. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{21}\text{H}_{22}\text{N}_2\text{NaO}$ 341.1624; Found 341.1632.

(E)-9-(2-([1,1'-Biphenyl]-4-yl)vinyl)-9-methyl-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-1-one (3s)

Eluent: petroleum ether/ethyl acetate (2:1). Yellow solid (40.4 mg, 55%), mp 136.0-136.9 °C. ^1H NMR (CDCl_3 , 400 MHz): δ 7.59-7.57 (m, 2H), 7.52 (d, $J = 8.4$ Hz, 2H), 7.44-7.40 (m, 4H), 7.34-7.25 (m, 2H), 7.16 (d, $J = 7.2$ Hz, 1H), 7.08-7.04 (m, 1H), 6.79 (d, $J = 8.0$ Hz, 1H), 6.55 (d, $J = 16.0$ Hz, 1H), 6.47 (d, $J = 15.6$ Hz, 1H), 3.89 (td, $J_1 = 8.4$ Hz, $J_2 = 4.0$ Hz, 1H), 3.51-3.45 (m, 1H), 3.06-2.97 (m, 1H), 2.84-2.77 (m, 1H), 2.07

(s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 164.7, 147.2, 140.7, 140.6, 135.4, 135.0, 130.5, 129.0, 128.90, 128.88, 127.44, 127.37, 127.3, 127.0, 123.0, 122.8, 110.1, 66.3, 51.3, 35.4, 24.6. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{25}\text{H}_{22}\text{N}_2\text{NaO}$ 389.1624; Found 389.1622.

(E)-9-(4-Fluorostyryl)-9-methyl-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-1-one (3t)

Eluent: petroleum ether/ethyl acetate (2:1). Yellow solid (35.7 mg, 58%), mp 114.8-115.7 °C. ^1H NMR (CDCl_3 , 400 MHz): δ 7.26-7.19 (m, 3H), 7.06 (d, $J = 7.2$ Hz, 1H), 6.98 (td, $J_1 = 7.6$ Hz, $J_2 = 0.4$ Hz, 1H), 6.91-6.86 (m, 2H), 6.72 (d, $J = 8.0$ Hz, 1H), 6.40 (d, $J = 16.0$ Hz, 1H), 6.28 (d, $J = 16.0$ Hz, 1H), 3.81 (td, $J_1 = 8.8$ Hz, $J_2 = 4.8$ Hz, 1H), 3.44-3.37 (m, 1H), 2.98-2.89 (m, 1H), 2.77-2.69 (m, 1H), 1.97 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150 MHz): δ 164.7, 162.6 (d, $^1J_{\text{C-F}} = 245.4$ Hz), 147.2, 134.9, 132.5 (d, $^4J_{\text{C-F}} = 3.0$ Hz), 130.2 (d, $^5J_{\text{C-F}} = 2.4$ Hz), 129.0, 128.5 (d, $^3J_{\text{C-F}} = 7.1$ Hz), 128.2, 123.0, 122.7, 115.5 (d, $^2J_{\text{C-F}} = 21.2$ Hz), 110.1, 66.2, 51.3, 35.4, 24.5. ^{19}F NMR (565 MHz, CDCl_3): δ -114.10 – -114.15 (m). HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{19}\text{H}_{17}\text{FN}_2\text{NaO}$ 331.1217; Found 331.1214.

(E)-9-(4-Bromostyryl)-9-methyl-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-1-one (3u)

Eluent: petroleum ether/ethyl acetate (2:1). Yellow solid (55.5 mg, 75%), mp 54.3-55.3 °C. ^1H NMR (CDCl_3 , 400 MHz): δ 7.39 (d, $J = 8.8$ Hz, 2H), 7.30-7.26 (m, 1H), 7.21 (d, $J = 8.4$ Hz, 2H), 7.14 (d, $J = 7.2$ Hz, 1H), 7.07-7.03 (m, 1H), 6.79 (d, $J = 8.0$ Hz, 1H), 6.47-6.39 (m, 2H), 3.89 (td, $J_1 = 8.8$ Hz, $J_2 = 4.0$ Hz, 1H), 3.51-3.44 (m, 1H), 3.05-2.97 (m, 1H), 2.84-2.76 (m, 1H), 2.05 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 164.8, 147.2, 135.3, 134.7, 131.7, 131.2, 129.1, 128.5, 128.2, 123.1, 122.7, 121.8, 110.1, 66.2, 51.3, 35.4, 24.5. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{19}\text{H}_{17}\text{BrN}_2\text{NaO}$ 391.0416; Found 391.0407.

(E)-9-Methyl-9-(4-(trifluoromethyl)styryl)-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-1-one (3v)

Eluent: petroleum ether/ethyl acetate (2:1). Yellow solid (39.4 mg, 55%), mp 44.3-45.3 °C. ^1H NMR (CDCl_3 , 600 MHz): δ 7.52 (d, $J = 8.4$ Hz, 2H), 7.45 (d, $J = 8.4$ Hz, 2H), 7.29 (t, $J = 7.8$ Hz, 1H), 7.15 (d, $J = 7.2$ Hz, 1H), 7.06 (t, $J = 7.2$ Hz, 1H), 6.80 (d, $J = 7.8$ Hz, 1H), 6.55 (d, $J = 15.6$ Hz, 1H), 6.51 (d, $J = 16.2$ Hz, 1H),

3.90 (td, $J_1 = 8.4$ Hz, $J_2 = 4.2$ Hz, 1H), 3.51-3.46 (m, 1H), 3.05-2.99 (m, 1H), 2.84-2.79 (m, 1H), 2.07 (s, 3H).
 $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150 MHz): δ 164.9, 147.2, 139.9, 134.5, 133.0, 129.7 (q, $^2J_{\text{C-F}} = 31.7$ Hz), 129.2, 128.0, 127.1, 125.5 (q, $^3J_{\text{C-F}} = 3.5$ Hz), 124.3 (q, $^1J_{\text{C-F}} = 270.5$ Hz), 123.1, 122.6, 110.2, 66.2, 51.3, 35.4, 24.4.
 ^{19}F NMR (565 MHz, CDCl_3): δ -62.50 (s). HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{17}\text{F}_3\text{N}_2\text{NaO}$ 381.1185; Found 381.1177.

(E)-9-Methyl-9-(3-methylstyryl)-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-1-one (3w)

Eluent: petroleum ether/ethyl acetate (2:1). Yellow oil (41.4 mg, 68%). ^1H NMR (CDCl_3 , 600 MHz): δ 7.28-7.25 (m, 1H), 7.18 (s, 1H), 7.17-7.13 (m, 3H), 7.05-7.01 (m, 2H), 6.78 (d, $J = 7.8$ Hz, 1H), 6.47 (d, $J = 16.2$ Hz, 1H), 6.42 (d, $J = 15.6$ Hz, 1H), 3.86 (td, $J_1 = 8.4$ Hz, $J_2 = 4.2$ Hz, 1H), 3.49-3.44 (m, 1H), 3.02-2.96 (m, 1H), 2.82-2.77 (m, 1H), 2.30 (s, 3H), 2.05 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150 MHz): δ 164.6, 147.2, 138.1, 136.2, 135.0, 130.1, 129.4, 128.9, 128.7, 128.5, 127.5, 124.2, 122.9, 122.7, 110.0, 66.3, 51.2, 35.4, 24.5, 21.4. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{20}\text{N}_2\text{NaO}$ 327.1468; Found 327.1479.

(E)-9-(3-Chlorostyryl)-9-methyl-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-1-one (3x)

Eluent: petroleum ether/ethyl acetate (2:1). Yellow solid (45.2 mg, 70%), mp 45.6-46.2 °C. ^1H NMR (CDCl_3 , 400 MHz): δ 7.35 (s, 1H), 7.30-7.26 (m, 1H), 7.23-7.16 (m, 3H), 7.14-7.13 (m, 1H), 7.05 (td, $J_1 = 7.2$ Hz, $J_2 = 0.8$ Hz, 1H), 6.79 (d, $J = 8.0$ Hz, 1H), 6.49-6.40 (m, 2H), 3.89 (td, $J_1 = 8.4$ Hz, $J_2 = 4.4$ Hz, 1H), 3.51-3.44 (m, 1H), 3.05-2.97 (m, 1H), 2.84-2.77 (m, 1H), 2.05 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150 MHz): δ 164.8, 147.2, 138.2, 134.7, 134.5, 131.9, 129.8, 129.1, 128.0, 127.9, 126.8, 125.2, 123.1, 122.7, 110.1, 66.1, 51.3, 35.4, 24.4. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{19}\text{H}_{17}\text{ClN}_2\text{NaO}$ 347.0922; Found 347.0921.

(E)-9-Methyl-9-(2-methylstyryl)-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-1-one (3y)

Eluent: petroleum ether/ethyl acetate (2:1). Yellow solid (37.6 mg, 62%), mp 94.5-95.3 °C. ^1H NMR (CDCl_3 , 400 MHz): δ 7.42-7.40 (m, 1H), 7.29-7.25 (m, 1H), 7.15-7.08 (m, 4H), 7.05 (td, $J_1 = 7.2$ Hz, $J_2 = 0.8$ Hz, 1H), 6.78 (d, $J = 7.6$ Hz, 1H), 6.74 (d, $J = 16.0$ Hz, 1H), 6.31 (d, $J = 15.6$ Hz, 1H), 3.85 (td, $J_1 = 8.4$ Hz, $J_2 = 4.8$ Hz,

1H), 3.53-3.47 (m, 1H), 3.02-2.94 (m, 1H), 2.85-2.77 (m, 1H), 2.28 (s, 3H), 2.05 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ 164.6, 147.2, 135.8, 135.5, 135.1, 131.7, 130.3, 128.9, 127.8, 127.4, 126.13, 126.11, 122.9, 122.7, 110.0, 66.4, 51.2, 35.4, 24.6, 19.8. HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₀H₂₀N₂NaO 327.1468; Found 327.1471.

(E)-9-(2-Chlorostyryl)-9-methyl-2,3-dihydro-1H,9H-pyrazolo[1,2-*a*]indazol-1-one (3z)

Eluent: petroleum ether/ethyl acetate (2:1). Yellow oil (50.8 mg, 78%). ¹H NMR (CDCl₃, 400 MHz): 7.52 (dd, *J*₁ = 7.6 Hz, *J*₂ = 2.4 Hz, 1H), 7.32-7.26 (m, 2H), 7.20-7.12 (m, 3H), 7.06 (td, *J*₁ = 7.6 Hz, *J*₂ = 0.8 Hz, 1H), 6.93 (d, *J* = 16.0 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.46 (d, *J* = 16.0 Hz, 1H), 3.82 (td, *J*₁ = 8.8 Hz, *J*₂ = 5.6 Hz, 1H), 3.58-3.51 (m, 1H), 3.01-2.93 (m, 1H), 2.87-2.79 (m, 1H), 2.04 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ 164.6, 147.2, 134.5, 133.4, 133.0, 129.6, 129.0, 128.9, 127.3, 126.8, 125.8, 122.9, 122.8, 110.0, 66.2, 51.2, 35.3, 24.4. HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₉H₁₇ClN₂NaO 347.0922; Found 347.0918.

(E)-9-Methyl-9-(2-(naphthalen-1-yl)vinyl)-2,3-dihydro-1H,9H-pyrazolo[1,2-*a*]indazol-1-one (3aa)

Eluent: petroleum ether/ethyl acetate (2:1). Yellow solid (46.7 mg, 69%), mp 46.3-47.2 °C. ¹H NMR (CDCl₃, 600 MHz): δ 8.01 (d, *J* = 8.4 Hz, 1H), 7.83-7.82 (m, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 7.2 Hz, 1H), 7.51-7.46 (m, 2H), 7.42-7.39 (m, 1H), 7.31-7.29 (m, 2H), 7.22 (d, *J* = 7.2 Hz, 1H), 7.09 (t, *J* = 7.8 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 6.48 (d, *J* = 15.6 Hz, 1H), 3.89 (td, *J*₁ = 8.4 Hz, *J*₂ = 4.8 Hz, 1H), 3.56-3.51 (m, 1H), 3.06-3.00 (m, 1H), 2.88-2.83 (m, 1H), 2.13 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 150 MHz): δ 164.8, 147.3, 135.0, 134.2, 133.7, 133.6, 131.3, 129.0, 128.6, 128.3, 126.8, 126.2, 125.9, 125.7, 124.4, 123.9, 123.0, 122.7, 110.1, 66.5, 51.3, 35.5, 24.8. HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₃H₂₀N₂NaO 363.1468; Found 363.1457.

(E)-9-Methyl-9-(prop-1-en-1-yl)-2,3-dihydro-1H,9H-pyrazolo[1,2-*a*]indazol-1-one (3bb)

Eluent: petroleum ether/ethyl acetate (2:1). Yellow oil (29.0 mg, 64%). ¹H NMR (CDCl₃, 400 MHz): δ 7.26-7.22 (m, 1H), 7.07-7.00 (m, 2H), 6.75 (d, *J* = 8.0 Hz, 1H), 5.73 (dd, *J*₁ = 15.6 Hz, *J*₂ = 1.6 Hz, 1H), 5.67-5.60 (m, 1H), 3.83 (td, *J*₁ = 8.8 Hz, *J*₂ = 4.8 Hz, 1H), 3.47-3.40 (m, 1H), 3.01-2.92 (m, 1H), 2.80-2.73 (m,

1H), 1.92 (s, 3H), 1.69 (dd, $J_1 = 6.4$ Hz, $J_2 = 1.2$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150 MHz): δ 164.3, 146.9, 135.6, 132.1, 128.7, 125.5, 122.8, 122.6, 109.9, 66.1, 51.2, 35.5, 24.5, 17.6. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{14}\text{H}_{16}\text{N}_2\text{NaO}$ 251.1155; Found 251.1147.

(E)-9-(Hept-1-en-1-yl)-9-methyl-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-1-one (3cc)

Eluent: petroleum ether/ethyl acetate (2:1). Yellow oil (39.9 mg, 70%). ^1H NMR (CDCl_3 , 400 MHz): δ 7.26-7.22 (m, 1H), 7.06-7.00 (m, 2H), 6.75 (d, $J = 8.0$ Hz, 1H), 5.71 (d, $J = 15.2$ Hz, 1H), 5.65-5.58 (m, 1H), 3.81 (td, $J_1 = 8.8$ Hz, $J_2 = 5.2$ Hz, 1H), 3.48-3.42 (m, 1H), 3.00-2.91 (m, 1H), 2.81-2.74 (m, 1H), 2.05-2.00 (m, 2H), 1.91 (s, 3H), 1.39-1.30 (m, 2H), 1.29-1.21 (m, 4H), 0.86 (t, $J = 6.8$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150 MHz): δ 164.3, 147.0, 135.7, 130.9, 130.7, 128.6, 122.8, 122.6, 109.9, 66.1, 51.2, 35.5, 32.0, 31.5, 28.8, 24.6, 22.6, 14.1. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{18}\text{H}_{24}\text{N}_2\text{NaO}$ 307.1781; Found 307.1788.

(E)-9-Methyl-9-(3-phenylprop-1-en-1-yl)-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-1-one (3dd)

Eluent: petroleum ether/ethyl acetate (2:1). Yellow oil (36.4 mg, 60%). ^1H NMR (CDCl_3 , 600 MHz): δ 7.28 (t, $J = 7.8$ Hz, 2H), 7.24 (td, $J_1 = 7.8$ Hz, $J_2 = 1.2$ Hz, 1H), 7.19 (t, $J = 7.2$ Hz, 1H), 7.16 (d, $J = 6.6$ Hz, 2H), 7.06-7.04 (m, 1H), 7.01 (td, $J_1 = 7.2$ Hz, $J_2 = 0.6$ Hz, 1H), 6.76 (d, $J = 7.8$ Hz, 1H), 5.84-5.77 (m, 2H), 3.79 (td, $J_1 = 8.4$ Hz, $J_2 = 5.4$ Hz, 1H), 3.50-3.46 (m, 1H), 3.43-3.36 (m, 2H), 2.97-2.91 (m, 1H), 2.82-2.77 (m, 1H), 1.93 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150 MHz): δ 164.4, 147.1, 139.9, 135.4, 132.5, 129.2, 128.7, 128.5, 126.2, 122.9, 122.6, 109.9, 66.0, 51.2, 38.4, 35.4, 24.6. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{20}\text{N}_2\text{NaO}$ 327.1468; Found 327.1473.

(E)-2,9-dimethyl-9-styryl-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-1-one (3ee)

Product **3ee** was obtained as a mixture of two diastereoisomers. **3ee-1**: Eluent: petroleum ether/ethyl acetate (3:1). Yellow oil (13.6 mg, 22%), ^1H NMR (CDCl_3 , 600 MHz): δ 7.40-7.33 (m, 2H), 7.28-7.25 (m, 3H), 7.21-7.16 (m, 2H), 7.05 (td, $J_1 = 7.2$ Hz, $J_2 = 0.6$ Hz, 1H), 6.78 (d, $J = 7.8$ Hz, 1H), 6.46 (d, $J = 16.2$ Hz, 1H), 6.38 (d, $J = 15.6$ Hz, 1H), 4.15 (t, $J = 7.8$ Hz, 1H), 3.21-3.17 (m, 1H), 2.95 (dd, $J_1 = 12.6$ Hz, $J_2 = 8.4$ Hz, 1H),

2.11 (s, 3H), 1.30 (d, $J = 7.2$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150 MHz): δ 167.2, 147.0, 136.2, 134.9, 130.2, 128.9, 128.8, 128.5, 127.8, 126.8, 122.8, 122.5, 110.1, 66.3, 58.7, 40.8, 24.6, 13.5. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{20}\text{N}_2\text{NaO}$ 327.1468; Found 327.1475.

3ee-2: Eluent: petroleum ether/ethyl acetate (3:1). Yellow oil (22.6 mg, 37%), ^1H NMR (CDCl_3 , 400 MHz): δ 7.38 (d, $J = 7.2$ Hz, 2H), 7.30-7.20 (m, 4H), 7.11 (d, $J = 7.2$ Hz, 1H), 7.02 (t, $J = 7.6$ Hz, 1H), 6.78 (d, $J = 8.0$ Hz, 1H), 6.56 (d, $J = 16.0$ Hz, 1H), 6.49 (d, $J = 16.0$ Hz, 1H), 3.83 (t, $J = 8.0$ Hz, 1H), 3.31 (t, $J = 7.6$ Hz, 1H), 3.08-2.98 (m, 1H), 1.96 (s, 3H), 1.37 (d, $J = 7.2$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150 MHz): δ 167.7, 147.2, 136.3, 135.0, 130.5, 129.5, 128.8, 128.5, 127.8, 126.9, 122.8, 122.7, 109.9, 65.9, 58.1, 41.3, 24.4, 14.6. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{20}\text{N}_2\text{NaO}$ 327.1468; Found 327.1477.

2. Typical procedure for the synthesis of **4a** and spectroscopic data of **4a-4t**

To a reaction tube equipped with a stir bar were charged with 1-phenylpyrazolidin-3-one (**1a**, 32.4 mg, 0.2 mmol), DCE (2 mL), $[\text{RhCp}^*\text{Cl}_2]_2$ (3.1 mg, 0.005 mmol), NaOAc (8.2 mg, 0.1 mmol) and 1-phenylbuta-2,3-dien-1-yl acetate (**2a**, 112.8 mg, 0.6 mmol). The tube was then sealed, and the mixture was stirred at 50 °C under argon for 6 h. Upon completion, it was quenched with saturated brine and extracted with dichloromethane (10 mL \times 3). The combined organic phases were dried over anhydrous Na_2SO_4 , filtered through a pad of celite, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (3:1) as eluent to afford **4a**. **4b-4t** were obtained in a similar manner.

9-Methyl-5-((E)-4-phenylbuta-1,3-dien-2-yl)-9-((E)-styryl)-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-1-one (4a)

Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid (61.2 mg, 73%), mp 77.7-78.7 °C. ^1H NMR (CDCl_3 , 600 MHz): δ 7.40-7.39 (m, 2H), 7.35 (d, $J = 7.2$ Hz, 2H), 7.32-7.28 (m, 4H), 7.25-7.22 (m, 2H), 7.15 (dd, $J_1 = 7.2$ Hz, $J_2 = 1.8$ Hz, 1H), 7.13 (dd, $J_1 = 7.2$ Hz, $J_2 = 1.2$ Hz, 1H), 7.09 (t, $J = 7.8$ Hz, 1H), 7.02 (d, $J = 16.2$ Hz,

1H), 6.56 (d, $J = 15.6$ Hz, 1H), 6.46 (d, $J = 16.2$ Hz, 1H), 6.29 (d, $J = 16.2$ Hz, 1H), 5.58 (s, 1H), 5.34 (d, $J = 1.8$ Hz, 1H), 3.78 (td, $J_1 = 9.0$ Hz, $J_2 = 4.8$ Hz, 1H), 3.38-3.34 (m, 1H), 2.90-2.84 (m, 1H), 2.69-2.64 (m, 1H), 2.11 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150 MHz): δ 164.6, 144.8, 144.3, 136.9, 136.4, 135.6, 132.9, 130.5, 130.4, 129.2, 128.8, 128.6, 128.1, 127.9, 127.0, 126.8, 123.6, 122.9, 121.9, 119.8, 65.6, 50.9, 35.4, 24.5. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{29}\text{H}_{26}\text{N}_2\text{NaO}$ 441.1937; Found 441.1919.

7,9-Dimethyl-5-((*E*)-4-phenylbuta-1,3-dien-2-yl)-9-((*E*)-styryl)-2,3-dihydro-1*H*,9*H*-pyrazolo[1,2-*a*]indazol-1-one (4b)

Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid (47.4 mg, 55%), mp 131.7-132.5 °C. ^1H NMR (CDCl_3 , 400 MHz): δ 7.41 (d, $J = 7.2$ Hz, 2H), 7.36 (d, $J = 7.2$ Hz, 2H), 7.33-7.27 (m, 4H), 7.25-7.21 (m, 2H), 7.00 (d, $J = 16.0$ Hz, 1H), 6.95 (s, 1H), 6.93 (s, 1H), 6.58 (d, $J = 16.0$ Hz, 1H), 6.44 (d, $J = 16.0$ Hz, 1H), 6.31 (d, $J = 16.0$ Hz, 1H), 5.56 (s, 1H), 5.32 (s, 1H), 3.77-3.71 (m, 1H), 3.35-3.28 (m, 1H), 2.90-2.81 (m, 1H), 2.68-2.61 (m, 1H), 2.36 (s, 3H), 2.09 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 164.7, 144.9, 142.2, 136.9, 136.5, 135.9, 132.9, 132.7, 130.8, 130.7, 129.05, 129.00, 128.8, 128.6, 128.0, 127.9, 127.0, 126.9, 123.5, 122.4, 119.7, 65.6, 51.3, 35.5, 24.5, 21.1. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{30}\text{H}_{28}\text{N}_2\text{NaO}$ 455.2094; Found 455.2097.

7-Ethyl-9-methyl-5-((*E*)-4-phenylbuta-1,3-dien-2-yl)-9-((*E*)-styryl)-2,3-dihydro-1*H*,9*H*-pyrazolo[1,2-*a*]indazol-1-one (4c)

Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid (45.6 mg, 51%), mp 131.0-131.6 °C. ^1H NMR (CDCl_3 , 600 MHz): δ 7.41 (d, $J = 7.2$ Hz, 2H), 7.36 (d, $J = 7.8$ Hz, 2H), 7.32-7.28 (m, 4H), 7.25-7.22 (m, 2H), 7.01 (d, $J = 16.2$ Hz, 1H), 6.97 (s, 1H), 6.96 (s, 1H), 6.58 (d, $J = 15.6$ Hz, 1H), 6.45 (d, $J = 16.2$ Hz, 1H), 6.32 (d, $J = 15.6$ Hz, 1H), 5.57 (s, 1H), 5.34 (d, $J = 1.2$ Hz, 1H), 3.75 (td, $J_1 = 9.0$ Hz, $J_2 = 4.8$ Hz, 1H), 3.35-3.30 (m, 1H), 2.89-2.83 (m, 1H), 2.69-2.63 (m, 3H), 2.11 (s, 3H), 1.27 (t, $J = 7.8$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150 MHz): δ 164.6, 144.9, 142.3, 139.1, 136.9, 136.4, 135.7, 132.8, 130.6, 129.6, 129.0, 128.9, 128.7, 128.5,

127.9, 127.8, 126.9, 126.8, 123.4, 121.1, 119.6, 65.6, 51.2, 35.4, 28.4, 24.4, 15.8. HRMS (ESI) m/z : $[M+Na]^+$
Calcd for $C_{31}H_{30}N_2NaO$ 469.2250; Found 469.2247.

7-(*tert*-Butyl)-9-methyl-5-((*E*)-4-phenylbuta-1,3-dien-2-yl)-9-((*E*)-styryl)-2,3-dihydro-1*H*,9*H*-pyrazolo[1,2-*a*]indazol-1-one (4d)

Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid (57.6 mg, 61%), mp 76.5-77.5 °C. 1H NMR ($CDCl_3$, 400 MHz): δ 7.41-7.39 (m, 2H), 7.35 (d, $J = 7.2$ Hz, 2H), 7.32-7.26 (m, 4H), 7.24-7.20 (m, 2H), 7.13 (s, 2H), 7.00 (d, $J = 16.0$ Hz, 1H), 6.57 (d, $J = 16.0$ Hz, 1H), 6.44 (d, $J = 15.6$ Hz, 1H), 6.32 (d, $J = 16.0$ Hz, 1H), 5.56 (s, 1H), 5.34 (d, $J = 1.6$ Hz, 1H), 3.76 (td, $J_1 = 8.8$ Hz, $J_2 = 4.0$ Hz, 1H), 3.34-3.27 (m, 1H), 2.90-2.82 (m, 1H), 2.67-2.60 (m, 1H), 2.11 (s, 3H), 1.33 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 163.6, 145.2, 144.1, 140.9, 135.9, 135.4, 134.3, 131.7, 129.6, 128.0, 127.8, 127.6, 127.5, 126.9, 126.7, 126.2, 125.9, 125.7, 121.8, 118.6, 117.5, 64.7, 49.9, 34.3, 33.6, 30.6, 23.4. HRMS (ESI) m/z : $[M+Na]^+$ Calcd for $C_{33}H_{34}N_2NaO$ 497.2563; Found 497.2554.

7-Fluoro-9-methyl-5-((*E*)-4-phenylbuta-1,3-dien-2-yl)-9-((*E*)-styryl)-2,3-dihydro-1*H*,9*H*-pyrazolo[1,2-*a*]indazol-1-one (4e)

Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid (55.7 mg, 64%), mp 118.7-119.6 °C. 1H NMR ($CDCl_3$, 400 MHz): δ 7.41-7.38 (m, 2H), 7.37-7.34 (m, 2H), 7.33-7.28 (m, 4H), 7.26-7.22 (m, 2H), 6.98 (d, $J = 16.0$ Hz, 1H), 6.88-6.84 (m, 2H), 6.56 (d, $J = 15.6$ Hz, 1H), 6.42 (d, $J = 16.0$ Hz, 1H), 6.30 (d, $J = 16.0$ Hz, 1H), 5.58 (s, 1H), 5.34 (d, $J = 0.8$ Hz, 1H), 3.76-3.70 (m, 1H), 3.34-3.27 (m, 1H), 2.89-2.80 (m, 1H), 2.68-2.61 (m, 1H), 2.08 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 164.6, 159.0 (d, $^1J_{C-F} = 249.4$ Hz), 143.7, 140.6, 137.1 (d, $^3J_{C-F} = 7.9$ Hz), 136.6, 136.1, 133.0, 129.9, 129.5, 128.7, 128.6, 128.3, 128.2, 128.0, 126.9, 126.8, 124.7 (d, $^3J_{C-F} = 7.3$ Hz), 120.1, 116.8 (d, $^2J_{C-F} = 24.2$ Hz), 109.2 (d, $^2J_{C-F} = 24.5$ Hz), 65.6 (d, $^4J_{C-F} = 2.2$ Hz), 51.2, 35.2, 24.3. ^{19}F NMR (376 MHz, $CDCl_3$): δ -120.50 (t, $J = 9.4$ Hz). HRMS (ESI) m/z : $[M+Na]^+$
Calcd for $C_{29}H_{25}FN_2NaO$ 459.1843; Found 459.1841.

7-Chloro-9-methyl-5-((E)-4-phenylbuta-1,3-dien-2-yl)-9-((E)-styryl)-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-1-one (4f)

Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid (40.7 mg, 45%), mp 155.9-156.4 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.41-7.39 (m, 2H), 7.36-7.34 (m, 2H), 7.33-7.25 (m, 5H), 7.24-7.22 (m, 1H), 7.10 (s, 2H), 6.97 (d, *J* = 16.4 Hz, 1H), 6.57 (d, *J* = 16.0 Hz, 1H), 6.40 (d, *J* = 16.0 Hz, 1H), 6.27 (d, *J* = 16.0 Hz, 1H), 5.58 (s, 1H), 5.33 (s, 1H), 3.73 (td, *J*₁ = 8.8 Hz, *J*₂ = 4.8 Hz, 1H), 3.37-3.30 (m, 1H), 2.89-2.80 (m, 1H), 2.69-2.62 (m, 1H), 2.08 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 150 MHz): δ 164.4, 143.6, 143.0, 137.3, 136.5, 136.1, 133.1, 130.0, 129.8, 129.5, 128.7, 128.6, 128.2, 128.1, 127.8, 126.9, 126.8, 124.7, 122.0, 120.2, 65.5, 50.7, 35.2, 24.3. HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₉H₂₅ClN₂NaO 475.1548; Found 475.1557.

7-Bromo-9-methyl-5-((E)-4-phenylbuta-1,3-dien-2-yl)-9-((E)-styryl)-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-1-one (4g)

Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid (61.7 mg, 62%), mp 99.2-99.9 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.40 (d, *J* = 7.6 Hz, 2H), 7.35 (d, *J* = 7.2 Hz, 2H), 7.33-7.26 (m, 5H), 7.25-7.22 (m, 3H), 6.97 (d, *J* = 16.0 Hz, 1H), 6.57 (d, *J* = 16.0 Hz, 1H), 6.40 (d, *J* = 16.0 Hz, 1H), 6.27 (d, *J* = 16.0 Hz, 1H), 5.58 (s, 1H), 5.32 (s, 1H), 3.73 (td, *J*₁ = 8.8 Hz, *J*₂ = 4.4 Hz, 1H), 3.37-3.31 (m, 1H), 2.89-2.80 (m, 1H), 2.69-2.62 (m, 1H), 2.07 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 150 MHz): δ 164.4, 143.6, 143.4, 137.6, 136.5, 136.1, 133.2, 132.7, 129.8, 129.5, 128.7, 128.6, 128.2, 128.1, 127.0, 126.8, 125.1, 124.8, 120.2, 114.9, 65.4, 50.6, 35.2, 24.3. HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₉H₂₅BrN₂NaO 519.1042; Found 519.1050.

9-Methyl-1-oxo-5-((E)-4-phenylbuta-1,3-dien-2-yl)-9-((E)-styryl)-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazole-7-carbonitrile (4h)

Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid (46.7 mg, 53%), mp 138.1-139.0 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.41-7.38 (m, 4H), 7.35-7.32 (m, 4H), 7.30-7.23 (m, 4H), 6.99 (d, *J* = 16.0 Hz, 1H), 6.55 (d, *J* = 15.6 Hz, 1H), 6.40 (d, *J* = 16.0 Hz, 1H), 6.19 (d, *J* = 16.0 Hz, 1H), 5.63 (s, 1H), 5.34 (s, 1H), 3.82

(td, $J_1 = 9.2$ Hz, $J_2 = 4.8$ Hz, 1H), 3.53-3.46 (m, 1H), 2.94-2.85 (m, 1H), 2.76-2.68 (m, 1H), 2.10 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150 MHz): δ 164.0, 147.0, 142.9, 136.5, 136.2, 135.7, 134.8, 133.4, 130.0, 129.2, 128.8, 128.7, 128.4, 128.3, 127.0, 126.8, 125.4, 123.4, 120.8, 118.9, 105.4, 65.4, 49.1, 35.0, 24.4. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{30}\text{H}_{25}\text{N}_3\text{NaO}$ 466.1890; Found 466.1872.

9-Methyl-5-((*E*)-4-phenylbuta-1,3-dien-2-yl)-9-((*E*)-styryl)-7-(trifluoromethyl)-2,3-dihydro-1*H*,9*H*-pyrazolo[1,2-*a*]indazol-1-one (4i)

Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid (46.4 mg, 48%), mp 109.3-110.3 °C. ^1H NMR (CDCl_3 , 600 MHz): δ 7.40-7.38 (m, 3H), 7.36-7.34 (m, 3H), 7.33-7.28 (m, 4H), 7.26-7.23 (m, 2H), 7.00 (d, $J = 16.2$ Hz, 1H), 6.57 (d, $J = 16.2$ Hz, 1H), 6.42 (d, $J = 16.2$ Hz, 1H), 6.23 (d, $J = 15.6$ Hz, 1H), 5.62 (s, 1H), 5.36 (s, 1H), 3.81 (td, $J_1 = 9.0$ Hz, $J_2 = 4.8$ Hz, 1H), 3.46-3.41 (m, 1H), 2.91-2.86 (m, 1H), 2.72-2.67 (m, 1H), 2.12 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150 MHz): δ 164.3, 146.6, 143.7, 136.4, 136.2, 136.0, 133.2, 129.7, 129.5, 128.8, 128.6, 128.3, 128.1, 127.8 (q, $^3J_{\text{C-F}} = 3.3$ Hz), 127.0, 126.8, 125.0 (q, $^2J_{\text{C-F}} = 32.6$ Hz), 124.2 (q, $^1J_{\text{C-F}} = 270.3$ Hz), 123.2, 120.5, 118.9 (q, $^3J_{\text{C-F}} = 4.4$ Hz), 65.5, 49.8, 35.1, 24.3. ^{19}F NMR (565 MHz, CDCl_3): δ -61.20 (s). HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{30}\text{H}_{25}\text{F}_3\text{N}_2\text{NaO}$ 509.1811; Found 509.1803.

6-Fluoro-9-methyl-5-((*E*)-4-phenylbuta-1,3-dien-2-yl)-9-((*E*)-styryl)-2,3-dihydro-1*H*,9*H*-pyrazolo[1,2-*a*]indazol-1-one (4j)

Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid (35.7 mg, 41%), mp 91.5-92.4 °C. ^1H NMR (CDCl_3 , 600 MHz, 55 °C): δ 7.39-7.35 (m, 4H), 7.31-7.22 (m, 6H), 7.07 (dd, $J_1 = 8.4$ Hz, $J_2 = 4.8$ Hz, 1H), 7.03 (d, $J = 16.2$ Hz, 1H), 6.81 (t, $J = 9.0$ Hz, 1H), 6.54 (d, $J = 15.6$ Hz, 1H), 6.46 (d, $J = 16.2$ Hz, 1H), 6.26 (d, $J = 16.2$ Hz, 1H), 5.73 (s, 1H), 5.39 (s, 1H), 3.76 (br s, 1H), 3.42-3.41 (m, 1H), 2.87-2.81 (m, 1H), 2.69-2.64 (m, 1H), 2.08 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 164.2, 160.3 (d, $^1J_{\text{C-F}} = 244.5$ Hz), 136.5, 136.2, 132.4, 130.8, 130.2, 129.3, 128.7, 128.6, 128.1, 128.0, 126.9, 126.8, 122.7 (d, $^3J_{\text{C-F}} = 10.2$ Hz), 121.7, 111.6 (d, $^2J_{\text{C-F}}$

= 23.1 Hz), 109.7 (d, $^2J_{C-F}$ = 24.6 Hz), 65.3, 50.7, 35.3, 24.6. ^{19}F NMR (565 MHz, CDCl_3): δ -116.10 (s).

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{29}\text{H}_{25}\text{FN}_2\text{NaO}$ 459.1843; Found 459.1823.

2,2,9-Trimethyl-5-((*E*)-4-phenylbuta-1,3-dien-2-yl)-9-((*E*)-styryl)-2,3-dihydro-1*H*,9*H*-pyrazolo[1,2-*a*]indazol-1-one (4k)

Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (40.1 mg, 45%), mp 114.0-114.9 °C. ^1H NMR (CDCl_3 , 400 MHz): δ 7.39-7.34 (m, 3H), 7.33-7.31 (m, 2H), 7.30-7.27 (m, 3H), 7.25-7.21 (m, 3H), 7.16-7.11 (m, 2H), 7.05 (t, J = 7.2 Hz, 1H), 6.97 (d, J = 16.0 Hz, 1H), 6.53 (d, J = 15.6 Hz, 1H), 6.41 (d, J = 15.6 Hz, 1H), 6.34 (d, J = 16.4 Hz, 1H), 5.56 (s, 1H), 5.34 (d, J = 1.6 Hz, 1H), 3.54 (d, J = 8.4 Hz, 1H), 3.07 (d, J = 8.8 Hz, 1H), 2.10 (s, 3H), 1.25 (s, 3H), 1.17 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150 MHz): δ 169.8, 144.8, 143.9, 136.9, 136.4, 135.5, 132.9, 130.5, 130.2, 128.7, 128.6, 128.5, 128.4, 127.9, 127.8, 126.9, 126.7, 123.3, 122.5, 121.6, 119.7, 65.3, 63.3, 45.5, 24.4, 22.8, 22.3. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{31}\text{H}_{30}\text{N}_2\text{NaO}$ 469.2250; Found 469.2236.

2,9-Dimethyl-5-((*E*)-4-phenylbuta-1,3-dien-2-yl)-9-((*E*)-styryl)-2,3-dihydro-1*H*,9*H*-pyrazolo[1,2-*a*]indazol-1-one (4l, dr = 1.1:1)

4l-1: Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (19.0 mg, 22%), mp 57.2-58.2 °C. ^1H NMR (CDCl_3 , 400 MHz): δ 7.37-6.98 (m, 14H), 6.50 (d, J = 16.0 Hz, 1H), 6.39 (d, J = 16.0 Hz, 1H), 6.29 (d, J = 16.0 Hz, 1H), 5.57 (s, 1H), 5.33 (s, 1H), 4.07 (t, J = 8.4 Hz, 1H), 3.06-3.03 (m, 1H), 2.78 (dd, J_1 = 12.0 Hz, J_2 = 8.8 Hz, 1H), 2.16 (s, 3H), 1.19 (d, J = 7.2 Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 167.2, 144.7, 144.1, 136.8, 136.3, 135.5, 132.8, 130.4, 130.2, 128.7, 128.5, 127.9, 127.8, 126.84, 126.76, 123.6, 122.7, 121.6, 119.7, 65.6, 58.2, 40.6, 24.6, 13.4. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{30}\text{H}_{28}\text{N}_2\text{NaO}$ 455.2094; Found 455.2100.

4l-2: Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (17.4 mg, 20%), mp 57.7-58.7 °C. ^1H NMR (CDCl_3 , 400 MHz): δ 7.42-7.21 (m, 10H), 7.12-6.68 (m, 4H), 6.62 (d, J = 16.0 Hz, 1H), 6.53 (dd, J_1 = 16.0 Hz,

$J_2 = 2.0$ Hz, 1H), 6.32 (d, $J = 16.0$ Hz, 1H), 5.58 (s, 1H), 5.34 (s, 1H), 3.75 (t, $J = 8.0$ Hz, 1H), 3.14 (t, $J = 7.6$ Hz, 1H), 2.92-2.86 (m, 1H), 1.99 (s, 3H), 1.24-1.23 (m, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 167.3, 144.8, 144.2, 136.9, 136.4, 135.6, 132.8, 130.7, 130.2, 129.4, 128.9, 128.7, 128.5, 127.9, 127.8, 126.9, 126.7, 123.4, 122.6, 122.0, 119.8, 65.1, 57.7, 41.1, 24.4, 14.3. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{30}\text{H}_{28}\text{N}_2\text{NaO}$ 455.2094; Found 455.2090.

9-Methyl-9-((*E*)-4-methylstyryl)-5-((*E*)-4-(*p*-tolyl)buta-1,3-dien-2-yl)-2,3-dihydro-1*H*,9*H*-pyrazolo[1,2-*a*]indazol-1-one (4m)

Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid (63.9 mg, 72%), mp 48.4-49.4 °C. ^1H NMR (CDCl_3 , 600 MHz): δ 7.28 (d, $J = 8.4$ Hz, 2H), 7.25-7.24 (m, 2H), 7.13-7.05 (m, 7H), 6.96 (d, $J = 15.6$ Hz, 1H), 6.51 (d, $J = 16.2$ Hz, 1H), 6.39 (d, $J = 16.2$ Hz, 1H), 6.26 (d, $J = 16.2$ Hz, 1H), 5.53 (s, 1H), 5.29 (d, $J = 1.8$ Hz, 1H), 3.76 (td, $J_1 = 9.0$ Hz, $J_2 = 4.2$ Hz, 1H), 3.36-3.31 (m, 1H), 2.88-2.82 (m, 1H), 2.66-2.62 (m, 1H), 2.32 (s, 6H), 2.08 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150 MHz): δ 164.4, 144.8, 144.2, 138.0, 137.7, 135.6, 134.0, 133.6, 132.7, 130.2, 129.5, 129.4, 129.2, 129.0, 128.1, 126.8, 126.7, 123.6, 122.7, 121.8, 119.2, 65.5, 50.8, 35.3, 24.5, 21.3, 21.2. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{31}\text{H}_{30}\text{N}_2\text{NaO}$ 469.2250; Found 469.2243.

5-((*E*)-4-(4-Fluorophenyl)buta-1,3-dien-2-yl)-9-((*E*)-4-fluorostyryl)-9-methyl-2,3-dihydro-1*H*,9*H*-pyrazolo[1,2-*a*]indazol-1-one (4n)

Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid (54.1 mg, 60%), mp 140.2-150.2 °C. ^1H NMR (CDCl_3 , 600 MHz): δ 7.36-7.33 (m, 2H), 7.30 (dd, $J_1 = 9.0$ Hz, $J_2 = 5.4$ Hz, 2H), 7.14 (dd, $J_1 = 7.2$ Hz, $J_2 = 1.8$ Hz, 1H), 7.11 (dd, $J_1 = 7.8$ Hz, $J_2 = 1.8$ Hz, 1H), 7.08 (t, $J = 7.2$ Hz, 1H), 7.00-6.95 (m, 4H), 6.92 (d, $J = 16.2$ Hz, 1H), 6.51 (d, $J = 16.2$ Hz, 1H), 6.37 (d, $J = 15.6$ Hz, 1H), 6.23 (d, $J = 15.6$ Hz, 1H), 5.56 (s, 1H), 5.33 (d, $J = 1.2$ Hz, 1H), 3.76 (td, $J_1 = 8.4$ Hz, $J_2 = 4.2$ Hz, 1H), 3.38-3.33 (m, 1H), 2.89-2.83 (m, 1H), 2.69-2.64 (m, 1H), 2.09 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150 MHz): δ 164.5, 162.52 (d, $^1J_{\text{C-F}} = 245.3$ Hz), 162.49 (d, $^1J_{\text{C-F}} = 245.6$ Hz), 144.5, 144.2, 135.4, 133.0 (d, $^4J_{\text{C-F}} = 3.2$ Hz), 132.5 (d, $^4J_{\text{C-F}} = 3.5$ Hz), 131.5,

130.3, 130.2, 128.8, 128.4 (d, $^3J_{C-F} = 8.1$ Hz), 128.3 (d, $^3J_{C-F} = 7.2$ Hz), 127.9, 123.4, 122.9, 121.8, 119.8, 115.6 (d, $^2J_{C-F} = 21.5$ Hz), 115.5 (d, $^2J_{C-F} = 21.2$ Hz), 65.4, 50.8, 35.3, 24.4. ^{19}F NMR (565 MHz, CDCl_3): δ : -113.48 – -113.53 (m), -114.00 – -114.05 (m). HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{29}\text{H}_{24}\text{F}_2\text{N}_2\text{NaO}$ 477.1749; Found 477.1740.

5-((*E*)-4-(4-Bromophenyl)buta-1,3-dien-2-yl)-9-((*E*)-4-bromostyryl)-9-methyl-2,3-dihydro-1*H*,9*H*-pyrazolo[1,2-*a*]indazol-1-one (4o)

Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid (66.3 mg, 58%), mp 114.6-115.6 °C. ^1H NMR (CDCl_3 , 400 MHz): δ 7.43-7.39 (m, 4H), 7.26-7.23 (m, 2H), 7.19 (d, $J = 8.4$ Hz, 2H), 7.15-7.13 (m, 1H), 7.11-7.06 (m, 2H), 6.98 (d, $J = 16.0$ Hz, 1H), 6.49 (d, $J = 15.6$ Hz, 1H), 6.42 (d, $J = 16.0$ Hz, 1H), 6.20 (d, $J = 16.0$ Hz, 1H), 5.59 (s, 1H), 5.36 (d, $J = 0.8$ Hz, 1H), 3.76 (td, $J_1 = 8.8$ Hz, $J_2 = 4.4$ Hz, 1H), 3.37-3.30 (m, 1H), 2.91-2.82 (m, 1H), 2.70-2.62 (m, 1H), 2.08 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150 MHz): δ 164.5, 144.4, 144.2, 135.7, 135.30, 135.27, 131.8, 131.7, 131.5, 131.2, 130.3, 129.6, 128.4, 128.2, 127.9, 123.3, 122.9, 121.9, 121.8, 121.7, 120.5, 65.4, 50.8, 35.3, 24.4. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{29}\text{H}_{24}\text{Br}_2\text{N}_2\text{NaO}$ 597.0148; Found 597.0164.

4-((*E*)-2-(5-((*E*)-4-(4-Cyanophenyl)buta-1,3-dien-2-yl)-9-methyl-1-oxo-2,3-dihydro-1*H*,9*H*-pyrazolo[1,2-*a*]indazol-9-yl)vinyl)benzotrile (4p)

Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid (40.8 mg, 43%), mp 170.5-171.5 °C. ^1H NMR (CDCl_3 , 600 MHz): δ 7.59-7.55 (m, 4H), 7.46 (d, $J = 8.4$ Hz, 2H), 7.41 (d, $J = 8.4$ Hz, 2H), 7.16-7.14 (m, 1H), 7.12-7.09 (m, 3H), 6.60-6.54 (m, 2H), 6.26 (d, $J = 16.2$ Hz, 1H), 5.68 (s, 1H), 5.45 (s, 1H), 3.75 (td, $J_1 = 8.4$ Hz, $J_2 = 4.2$ Hz, 1H), 3.37-3.33 (m, 1H), 2.89-2.83 (m, 1H), 2.70-2.66 (m, 1H), 2.08 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150 MHz): δ 164.7, 144.2, 144.0, 141.2, 140.8, 135.0, 134.3, 132.54, 132.45, 132.4, 130.8, 130.5, 127.5, 127.4, 127.1, 123.2, 122.9, 122.4, 122.0, 118.8, 111.2, 111.1, 65.4, 51.0, 35.2, 24.4. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{31}\text{H}_{24}\text{N}_4\text{NaO}$ 491.1842; Found 491.1839.

9-Methyl-9-((E)-3-methylstyryl)-5-((E)-4-(m-tolyl)buta-1,3-dien-2-yl)-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-1-one (4q)

Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid (57.7 mg, 65%), mp 93.9-94.9 °C. ¹H NMR (CDCl₃, 600 MHz): δ 7.25 (s, 1H), 7.21-7.19 (m, 4H), 7.16-7.15 (m, 2H), 7.13 (dd, *J*₁ = 7.8 Hz, *J*₂ = 1.8 Hz, 1H), 7.09 (t, *J* = 7.2 Hz, 1H), 7.07-7.06 (m, 2H), 7.02 (d, *J* = 16.2 Hz, 1H), 6.53 (d, *J* = 16.2 Hz, 1H), 6.47 (d, *J* = 15.6 Hz, 1H), 6.28 (d, *J* = 16.2 Hz, 1H), 5.58 (s, 1H), 5.34 (d, *J* = 1.2 Hz, 1H), 3.79 (td, *J*₁ = 9.0 Hz, *J*₂ = 4.8 Hz, 1H), 3.38-3.34 (m, 1H), 2.91-2.85 (m, 1H), 2.69-2.64 (m, 1H), 2.34 (s, 3H), 2.30 (s, 3H), 2.12 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 150 MHz): δ 164.4, 144.8, 144.3, 138.3, 138.1, 136.7, 136.3, 135.5, 133.0, 130.27, 130.26, 129.2, 128.8, 128.73, 128.65, 128.6, 128.4, 127.7, 127.5, 124.1, 123.8, 123.5, 122.8, 121.8, 119.6, 65.5, 50.8, 35.3, 24.4, 21.4, 21.3. HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₃₁H₃₀N₂NaO 469.2250; Found 469.2251.

5-((E)-4-(3-Chlorophenyl)buta-1,3-dien-2-yl)-9-((E)-3-chlorostyryl)-9-methyl-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-1-one (4r)

Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid (49.5 mg, 51%), mp 138.9-139.9 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.38 (s, 1H), 7.35 (s, 1H), 7.25-7.18 (m, 6H), 7.15-7.06 (m, 3H), 7.00 (d, *J* = 16.0 Hz, 1H), 6.51 (d, *J* = 16.0 Hz, 1H), 6.44 (d, *J* = 15.6 Hz, 1H), 6.20 (d, *J* = 16.0 Hz, 1H), 5.61 (s, 1H), 5.37 (d, *J* = 1.2 Hz, 1H), 3.76 (td, *J*₁ = 8.4 Hz, *J*₂ = 4.4 Hz, 1H), 3.37-3.31 (m, 1H), 2.92-2.83 (m, 1H), 2.70-2.63 (m, 1H), 2.09 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ 164.6, 144.4, 144.2, 138.7, 138.2, 135.3, 134.7, 134.5, 131.9, 131.4, 130.3, 130.2, 129.9, 129.8, 127.9, 127.81, 127.75, 126.7, 126.5, 125.1, 125.0, 123.2, 123.0, 121.9, 120.8, 65.4, 50.8, 35.2, 24.3. HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₉H₂₄Cl₂N₂NaO 509.1158; Found 509.1164.

9-Methyl-9-((E)-2-methylstyryl)-5-((E)-4-(o-tolyl)buta-1,3-dien-2-yl)-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-1-one (4s)

Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid (53.8 mg, 60%), mp 131.7-132.7 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.53 (d, *J* = 7.2 Hz, 1H), 7.43-7.41 (m, 1H), 7.20-7.06 (m, 9H), 6.86 (d, *J* = 16.0 Hz, 1H), 6.76 (d, *J* = 15.6 Hz, 1H), 6.56 (d, *J* = 16.0 Hz, 1H), 6.35 (dd, *J*₁ = 16.0 Hz, *J*₂ = 1.2 Hz, 1H), 5.56 (s, 1H), 5.34 (s, 1H), 3.75 (td, *J*₁ = 8.4 Hz, *J*₂ = 4.4 Hz, 1H), 3.43-3.36 (m, 1H), 2.88-2.80 (m, 1H), 2.71-2.64 (m, 1H), 2.29 (s, 3H), 2.11-2.10 (m, 6H). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ 164.4, 145.3, 143.9, 136.2, 135.9, 135.7, 135.4, 135.3, 131.8, 130.8, 130.4, 130.3, 130.2, 129.2, 127.8, 127.7, 127.2, 126.12, 126.07, 126.0, 125.2, 123.6, 122.9, 121.9, 119.6, 65.6, 50.7, 35.4, 24.6, 19.7, 19.6. HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₃₁H₃₀N₂NaO 469.2250; Found 469.2253.

5-((*E*)-4-(2-Fluorophenyl)buta-1,3-dien-2-yl)-9-((*E*)-2-fluorostyryl)-9-methyl-2,3-dihydro-1*H*,9*H*-pyrazolo[1,2-*a*]indazol-1-one (4t)

Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid (38.1 mg, 42%), mp 84.6-85.6 °C. ¹H NMR (CDCl₃, 600 MHz): δ 7.47 (td, *J*₁ = 7.8 Hz, *J*₂ = 1.8 Hz, 1H), 7.43 (td, *J*₁ = 7.8 Hz, *J*₂ = 1.2 Hz, 1H), 7.22-7.18 (m, 2H), 7.14 (dd, *J*₁ = 7.8 Hz, *J*₂ = 1.8 Hz, 1H), 7.12 (dd, *J*₁ = 7.8 Hz, *J*₂ = 1.8 Hz, 1H), 7.09-7.06 (m, 4H), 7.03-6.99 (m, 2H), 6.73 (d, *J* = 16.2 Hz, 1H), 6.57 (d, *J* = 16.2 Hz, 1H), 6.43 (d, *J* = 16.2 Hz, 1H), 5.61 (s, 1H), 5.38 (d, *J* = 1.2 Hz, 1H), 3.74 (td, *J*₁ = 9.0 Hz, *J*₂ = 4.8 Hz, 1H), 3.42-3.37 (m, 1H), 2.88-2.83 (m, 1H), 2.71-2.66 (m, 1H), 2.09 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 150 MHz): δ 164.5, 160.5 (d, ¹*J*_{C-F} = 248.6 Hz), 160.4 (d, ¹*J*_{C-F} = 248.1 Hz), 144.8, 144.3, 135.3, 132.8 (d, ⁴*J*_{C-F} = 3.9 Hz), 131.5, 130.3, 129.1 (d, ³*J*_{C-F} = 9.5 Hz), 127.9 (d, ³*J*_{C-F} = 8.1 Hz), 127.8 (d, ³*J*_{C-F} = 8.7 Hz), 125.5, 124.8 (d, ²*J*_{C-F} = 11.6 Hz), 124.23, 124.16 (d, ⁴*J*_{C-F} = 3.6 Hz), 124.0 (d, ⁴*J*_{C-F} = 3.2 Hz), 123.2, 122.9, 122.0, 121.7 (d, ⁴*J*_{C-F} = 3.3 Hz), 120.6, 115.9 (d, ²*J*_{C-F} = 21.9 Hz), 115.7 (d, ²*J*_{C-F} = 22.8 Hz), 65.6, 50.9, 35.3, 24.3. ¹⁹F NMR (565 MHz, CDCl₃): δ: -116.73 (s), -117.45 – -117.49 (m). HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₉H₂₄F₂N₂NaO 477.1749; Found 477.1736.

3. Typical procedure for the synthesis of 5a and spectroscopic data of 5a-5d

To a reaction tube equipped with a stir bar were charged with 1-phenylpyrazolidin-3-one (**1a**, 64.8 mg, 0.4 mmol), DCE (2 mL), [RhCp*Cl₂]₂ (3.1 mg, 0.005 mmol), NaOAc (8.2 mg, 0.1 mmol) and 1-phenylbuta-2,3-dien-1-yl acetate (**2a**, 37.6 mg, 0.2 mmol). The tube was then sealed, and the mixture was stirred at room temperature under argon for 2 h. Upon completion, it was quenched with water and extracted with dichloromethane (10 mL × 3). The combined organic phases were dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. To the residue were added manganese dioxide (34.8 mg, 0.4 mmol) and acetic acid (2 mL). The resulting mixture was stirred at 100 °C for 12 h. Upon completion, it was cooled to room temperature, diluted with water, and extracted with dichloromethane (10 mL × 3). The organic layer was dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ethyl acetate/methanol (20:1) as eluent to afford **5a**. **5b-5d** were obtained in a similar manner.

(E)-9-Methyl-9-styryl-1H,9H-pyrazolo[1,2-a]indazol-1-one (5a)

Eluent: ethyl acetate/methanol (20:1). Yellow solid (23.1 mg, 40%), mp 50.7-51.7 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.60 (d, *J* = 3.2 Hz, 1H), 7.37-7.34 (m, 3H), 7.31-7.19 (m, 4H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 1H), 6.66-6.58 (m, 2H), 5.61 (d, *J* = 3.6 Hz, 1H), 2.12 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ 161.8, 137.0, 135.9, 133.6, 130.5, 129.2, 128.5, 128.4, 128.1, 126.94, 126.92, 124.4, 123.9, 108.1, 100.5, 67.8, 24.2. HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₉H₁₆N₂NaO 311.1155; Found 311.1147.

(E)-7,9-Dimethyl-9-styryl-1H,9H-pyrazolo[1,2-a]indazol-1-one (5b)

Eluent: ethyl acetate/methanol (20:1). Yellow solid (25.8 mg, 43%), mp 70.8-71.8 °C. ¹H NMR (CDCl₃, 600 MHz): δ 7.55 (d, *J* = 3.6 Hz, 1H), 7.37 (d, *J* = 7.2 Hz, 2H), 7.28-7.26 (m, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.15 (d, *J* = 8.4 Hz, 1H), 7.09 (s, 1H), 6.99 (d, *J* = 7.8 Hz, 1H), 6.63 (d, *J* = 16.2 Hz, 1H), 6.59 (d, *J* = 15.6 Hz, 1H), 5.57 (d, *J* = 3.6 Hz, 1H), 2.38 (s, 3H), 2.10 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 150 MHz): δ 161.9, 137.3, 136.0,

134.5, 131.4, 130.4, 129.7, 128.6, 128.5, 128.1, 127.0, 126.7, 124.3, 107.8, 99.8, 67.7, 24.1, 21.2. HRMS (ESI) m/z : $[M+Na]^+$ Calcd for $C_{20}H_{18}N_2NaO$ 325.1311; Found 325.1301.

(E)-7-Bromo-9-methyl-9-styryl-1H,9H-pyrazolo[1,2-a]indazol-1-one (5c)

Eluent: ethyl acetate/methanol (20:1). Yellow solid (23.3 mg, 32%), mp 60.9-61.9 °C. 1H NMR ($CDCl_3$, 600 MHz): δ 7.56 (d, $J = 3.6$ Hz, 1H), 7.48 (dd, $J_1 = 8.4$ Hz, $J_2 = 1.8$ Hz, 1H), 7.40 (d, $J = 1.8$ Hz, 1H), 7.38-7.37 (m, 2H), 7.30-7.28 (m, 2H), 7.25-7.24 (m, 1H), 6.98 (d, $J = 8.4$ Hz, 1H), 6.63 (d, $J = 16.2$ Hz, 1H), 6.55 (d, $J = 16.2$ Hz, 1H), 5.63 (d, $J = 3.6$ Hz, 1H), 2.11 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 161.7, 139.1, 135.6, 132.6, 132.2, 131.0, 128.6, 128.3, 127.8, 127.3, 127.1, 127.0, 116.8, 109.4, 101.3, 67.7, 24.1. HRMS (ESI) m/z : $[M+Na]^+$ Calcd for $C_{19}H_{15}BrN_2NaO$ 389.0260; Found 389.0255.

(E)-9-(4-Bromostyryl)-9-methyl-1H,9H-pyrazolo[1,2-a]indazol-1-one (5d)

Eluent: ethyl acetate/methanol (20:1). Yellow solid (35.1 mg, 48%), mp 74.7-75.7 °C. 1H NMR ($CDCl_3$, 600 MHz): δ 7.59 (d, $J = 3.6$ Hz, 1H), 7.38-7.33 (m, 3H), 7.28 (d, $J = 7.2$ Hz, 1H), 7.21 (d, $J = 8.4$ Hz, 2H), 7.15 (t, $J = 7.2$ Hz, 1H), 7.10 (d, $J = 7.8$ Hz, 1H), 6.60 (d, $J = 16.2$ Hz, 1H), 6.54 (d, $J = 16.2$ Hz, 1H), 5.59 (d, $J = 3.6$ Hz, 1H), 2.09 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 161.8, 136.8, 134.9, 133.5, 131.6, 129.4, 129.3, 129.2, 128.5, 127.1, 124.5, 123.8, 121.9, 108.2, 100.5, 67.7, 24.1. HRMS (ESI) m/z : $[M+Na]^+$ Calcd for $C_{19}H_{15}BrN_2NaO$ 389.0260; Found 389.0265.

4. Typical procedure for the synthesis of 6a and spectroscopic data of 6a-6e

To a reaction tube equipped with a stir bar were charged with **4a** (83.6 mg, 0.2 mmol), toluene (2 mL), sulfur (32.0 mg, 0.125 mmol) and 4Å molecular sieve (33.4 mg). The tube was then sealed, and the mixture was stirred at 180 °C for 18 h. Upon completion, it was cooled to room temperature and concentrated under reduced pressure. The residue was purified by silical gel column chromatography with petroleum ether/ethyl acetate (2:1) as the eluent to give **6a**. **6b-6e** were obtained in a similar manner.

(E)-9-Methyl-5-(5-phenylthiophen-3-yl)-9-styryl-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-1-one (6a)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (62.0 mg, 69%), mp 173.6-174.6 °C. ¹H NMR (CDCl₃, 600 MHz): δ 7.65 (d, *J* = 7.2 Hz, 2H), 7.55 (s, 1H), 7.42-7.39 (m, 4H), 7.36 (s, 1H), 7.33-7.28 (m, 4H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.13-7.11 (m, 2H), 6.57 (d, *J* = 16.2 Hz, 1H), 6.47 (d, *J* = 16.2 Hz, 1H), 3.63-3.60 (m, 1H), 3.19-3.15 (m, 1H), 2.89-2.83 (m, 1H), 2.65-2.61 (m, 1H), 2.10 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 150 MHz): δ 165.2, 144.9, 144.5, 139.2, 136.3, 135.7, 134.0, 130.6, 129.5, 129.3, 129.1, 128.5, 127.94, 127.89, 126.9, 125.9, 123.9, 123.5, 122.6, 121.8, 121.2, 65.8, 51.9, 35.1, 24.9. HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₉H₂₄N₂NaOS 471.1502; Found 471.1508.

(*E*)-7,9-Dimethyl-5-(5-phenylthiophen-3-yl)-9-styryl-2,3-dihydro-1*H*,9*H*-pyrazolo[1,2-*a*]indazol-1-one (6b)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (32.4 mg, 35%), mp 92.0-93.0 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.65 (d, *J* = 7.2 Hz, 2H), 7.54 (d, *J* = 0.8 Hz, 1H), 7.42-7.38 (m, 4H), 7.35-7.28 (m, 4H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.13 (s, 1H), 6.93 (s, 1H), 6.58 (d, *J* = 16.0 Hz, 1H), 6.46 (d, *J* = 16.0 Hz, 1H), 3.59 (td, *J*₁ = 8.8 Hz, *J*₂ = 4.4 Hz, 1H), 3.17-3.11 (m, 1H), 2.89-2.81 (m, 1H), 2.65-2.58 (m, 1H), 2.38 (s, 3H), 2.08 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 150 MHz): δ 165.3, 144.8, 142.4, 139.3, 136.3, 136.0, 134.0, 133.3, 130.7, 130.0, 129.2, 129.0, 128.5, 127.9, 127.8, 126.9, 125.9, 123.9, 122.5, 122.3, 121.0, 65.9, 52.3, 35.2, 24.8, 21.0. HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₃₀H₂₆N₂NaOS 485.1658; Found 485.1661.

(*E*)-7-Chloro-9-methyl-5-(5-phenylthiophen-3-yl)-9-styryl-2,3-dihydro-1*H*,9*H*-pyrazolo[1,2-*a*]indazol-1-one (6c)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (36.9 mg, 38%), mp 170.0-171.0 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.65-7.63 (m, 2H), 7.51 (d, *J* = 1.6 Hz, 1H), 7.42-7.39 (m, 4H), 7.37 (d, *J* = 1.2 Hz, 1H), 7.34-7.28 (m, 4H), 7.25-7.22 (m, 1H), 7.08 (d, *J* = 2.0 Hz, 1H), 6.58 (d, *J* = 15.6 Hz, 1H), 6.42 (d, *J* = 16.0 Hz, 1H), 3.59 (td, *J*₁ = 8.8 Hz, *J*₂ = 4.4 Hz, 1H), 3.19-3.12 (m, 1H), 2.90-2.81 (m, 1H), 2.67-2.59 (m, 1H), 2.08 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 150 MHz): δ 165.2, 145.3, 143.2, 137.8, 137.5, 136.0, 133.8, 130.0, 129.8, 129.2,

129.1, 128.6, 128.5, 128.12, 128.08, 126.9, 125.9, 123.5, 123.1, 122.4, 121.8, 65.9, 51.9, 34.9, 24.8. HRMS (ESI) m/z : $[M+Na]^+$ Calcd for $C_{29}H_{23}ClN_2NaOS$ 505.1112; Found 505.1108.

(E)-9-Methyl-9-(4-methylstyryl)-5-(5-(*p*-tolyl)thiophen-3-yl)-2,3-dihydro-1*H*,9*H*-pyrazolo[1,2-*a*]indazol-1-one (6d)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (47.8 mg, 50%), mp 149.3-150.3 °C. 1H NMR ($CDCl_3$, 600 MHz): δ 7.54 (d, $J = 8.4$ Hz, 2H), 7.50 (d, $J = 1.2$ Hz, 1H), 7.31-7.27 (m, 4H), 7.20 (d, $J = 7.8$ Hz, 2H), 7.12-7.09 (m, 4H), 6.52 (d, $J = 16.2$ Hz, 1H), 6.42 (d, $J = 16.2$ Hz, 1H), 3.61 (td, $J_1 = 9.0$ Hz, $J_2 = 4.8$ Hz, 1H), 3.18-3.14 (m, 1H), 2.88-2.82 (m, 1H), 2.64-2.59 (m, 1H), 2.37 (s, 3H), 2.31 (s, 3H), 2.08 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 165.2, 145.0, 144.5, 139.1, 137.9, 137.7, 135.8, 133.5, 131.2, 129.7, 129.6, 129.5, 129.2, 126.8, 125.8, 123.42, 123.41, 122.1, 121.8, 121.3, 65.9, 51.9, 35.1, 24.9, 21.2. HRMS (ESI) m/z : $[M+Na]^+$ Calcd for $C_{31}H_{28}N_2NaOS$ 499.1815; Found 499.1835.

(E)-5-(5-(4-Bromophenyl)thiophen-3-yl)-9-(4-bromostyryl)-9-methyl-2,3-dihydro-1*H*,9*H*-pyrazolo[1,2-*a*]indazol-1-one (6e)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (48.4 mg, 40%), mp 82.1-83.1 °C. 1H NMR ($CDCl_3$, 400 MHz): δ 7.54-7.49 (m, 5H), 7.42-7.37 (m, 3H), 7.32-7.28 (m, 1H), 7.26-7.24 (m, 2H), 7.13-7.12 (m, 2H), 6.51 (d, $J = 16.0$ Hz, 1H), 6.45 (d, $J = 15.6$ Hz, 1H), 3.60 (td, $J_1 = 8.8$ Hz, $J_2 = 4.4$ Hz, 1H), 3.19-3.13 (m, 1H), 2.91-2.82 (m, 1H), 2.67-2.59 (m, 1H), 2.08 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 165.3, 144.5, 143.6, 139.3, 135.6, 135.2, 132.9, 132.2, 131.6, 131.4, 129.6, 128.4, 128.2, 127.3, 124.2, 123.6, 123.0, 121.9, 121.8, 121.7, 121.0, 65.8, 52.0, 35.0, 24.8. HRMS (ESI) m/z : $[M+Na]^+$ Calcd for $C_{29}H_{22}Br_2N_2NaOS$ 626.9712; Found 626.9704.

5. Typical procedure for the synthesis of 7a and spectroscopic data of 7a-7e

To a reaction tube equipped with a stir bar were charged with **4a** (83.6 mg, 0.2 mmol), toluene (2 mL) and dimethyl but-2-ynedioate (56.8 mg, 0.4 mmol). The tube was then sealed, and the mixture was stirred at

120 °C for 12 h. Upon completion, it was cooled to room temperature and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) as the eluent to give **7a** as a mixture of two diastereoisomers. **7b-7e** were obtained in a similar manner.

Dimethyl (E)-5-(9-methyl-1-oxo-9-styryl-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-5-yl)-1,4-dihydro-[1,1'-biphenyl]-2,3-dicarboxylate (7a)

Eluent: petroleum ether/ethyl acetate (1:1). Yellow solid (88.6 mg, 79% , dr = 1:2.3). ¹H NMR (CDCl₃, 600 MHz): δ 7.29-7.23 (m, 3H), 7.21-7.11 (m, 7H), 7.05-6.94 (m, 3H), 6.43-6.40 (m, 1H), 6.35-6.32 (m, 1H), 5.90-5.88 (m, 1H), 4.56-4.52 (m, 1H), 3.74-3.73 (m, 3H), 3.63-3.58 (m, 0.3H), 3.51-3.50 (m, 3H), 3.48-3.46 (m, 0.7H), 3.44-3.31 (m, 1.7H), 3.23-3.14 (m, 1.3H), 2.86-2.81 (m, 0.3H), 2.74-2.68 (m, 0.7H), 2.61-2.54 (m, 1H), 1.961-1.956 (m, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ 167.9, 167.84, 167.75, 167.69, 165.0, 164.9, 144.0, 143.9, 140.8, 140.7, 136.2, 135.9, 135.7, 135.5, 135.4, 132.4, 131.7, 130.52, 130.47, 129.8, 129.6, 129.3, 128.95, 128.87, 128.52, 128.49, 128.4, 128.2, 127.9, 127.8, 127.5, 126.8, 125.2, 125.0, 123.3, 122.0, 121.9, 65.7, 65.6, 52.54, 52.50, 52.20, 52.18, 52.0, 45.2, 45.1, 35.1, 30.3, 24.9, 24.8. HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₃₅H₃₂N₂NaO₅ 583.2203; Found 583.2200.

Dimethyl (E)-5-(7,9-dimethyl-1-oxo-9-styryl-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-5-yl)-1,4-dihydro-[1,1'-biphenyl]-2,3-dicarboxylate (7b)

Eluent: petroleum ether/ethyl acetate (1:1). Yellow solid (92.9 mg, 81% , dr = 1:1). ¹H NMR (CDCl₃, 600 MHz): δ 7.37-7.31 (m, 3H), 7.30-7.19 (m, 7H), 6.93 (s, 0.5H), 6.89 (s, 0.5H), 6.86 (s, 1H), 6.51 (d, *J* = 16.2 Hz, 1H), 6.39 (d, *J* = 16.2 Hz, 1H), 5.97-5.95 (m, 1H), 4.61 (br s, 1H), 3.81 (s, 3H), 3.782-3.775 (m, 0.5H), 3.70-3.65 (m, 0.5H), 3.58-3.57 (m, 3H), 3.52-3.38 (m, 1.5H), 3.26-3.17 (m, 1.5H), 2.90-2.86 (m, 0.5H), 2.80-2.74 (m, 0.5H), 2.67-2.61 (m, 1H), 2.31-2.30 (m, 3H), 2.02 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 150 MHz): δ 168.0, 167.83, 167.81, 167.7, 165.1, 165.0, 141.84, 141.81, 140.9, 140.8, 136.3, 136.0, 135.9, 135.8, 135.3, 133.2, 132.6, 131.8, 130.7, 130.6, 129.8, 129.6, 129.2, 128.95, 128.90, 128.87, 128.7, 128.51, 128.49, 128.27,

128.26, 127.9, 127.8, 127.7, 127.6, 127.4, 126.9, 125.1, 124.9, 122.5, 122.4, 65.7, 65.6, 52.5, 52.4, 52.3, 52.2, 52.1, 45.3, 45.1, 35.2, 30.4, 30.3, 24.8, 24.7, 20.95, 20.92. HRMS (ESI) m/z : $[M+Na]^+$ Calcd for $C_{36}H_{34}N_2NaO_5$ 597.2360; Found 597.2375.

Dimethyl (E)-5-(7-chloro-9-methyl-1-oxo-9-styryl-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-5-yl)-1,4-dihydro-[1,1'-biphenyl]-2,3-dicarboxylate (7c)

Eluent: petroleum ether/ethyl acetate (1:1). Yellow solid (71.0 mg, 60%, dr = 1:1). 1H NMR ($CDCl_3$, 400 MHz): δ 7.30-7.11 (m, 10H), 7.03-6.98 (m, 1H), 6.95-6.94 (m, 1H), 6.46-6.41 (m, 1H), 6.28 (d, J = 16.0 Hz, 1H), 5.91-5.90 (m, 1H), 4.55-4.52 (m, 1H), 3.742-3.738 (m, 3H), 3.71-3.67 (m, 0.5H), 3.60-3.52 (m, 0.5H), 3.50-3.49 (m, 3H), 3.47-3.41 (m, 0.5H), 3.36-3.33 (m, 1H), 3.20-3.10 (m, 1.5H), 2.86-2.78 (m, 0.5H), 2.74-2.65 (m, 0.5H), 2.61-2.52 (m, 1H), 1.94-1.93 (m, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 166.7, 166.6, 166.5, 163.9, 163.8, 141.64, 141.61, 139.4, 139.3, 136.5, 136.3, 134.89, 134.86, 134.4, 131.0, 130.3, 128.82, 128.76, 128.70, 128.68, 128.0, 127.9, 127.7, 127.64, 127.56, 127.53, 127.50, 127.40, 127.36, 127.2, 127.02, 126.99, 126.98, 126.54, 126.53, 125.8, 125.3, 125.1, 121.02, 120.96, 64.7, 64.6, 51.5, 51.17, 51.15, 50.9, 50.7, 44.2, 44.0, 33.9, 29.1, 29.0, 23.7, 23.6. HRMS (ESI) m/z : $[M+Na]^+$ Calcd for $C_{35}H_{31}ClN_2NaO_5$ 617.1814; Found 617.1807.

Dimethyl (E)-4'-methyl-5-(9-methyl-9-(4-methylstyryl)-1-oxo-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-5-yl)-1,4-dihydro-[1,1'-biphenyl]-2,3-dicarboxylate (7d)

Eluent: petroleum ether/ethyl acetate (1:1). Yellow solid (74.5 mg, 63%, dr = 1:1). 1H NMR ($CDCl_3$, 400 MHz): δ 7.26-7.23 (m, 2H), 7.15-6.99 (m, 9H), 6.48-6.43 (m, 1H), 6.36 (d, J = 16.0 Hz, 1H), 5.95-5.93 (m, 1H), 4.61-4.54 (m, 1H), 3.81-3.80 (m, 3H), 3.73-3.62 (m, 0.5H), 3.59-3.58 (m, 3H), 3.56-3.52 (m, 1H), 3.46-3.41 (m, 1H), 3.37-3.18 (m, 1.5H), 2.95-2.86 (m, 0.5H), 2.83-2.74 (m, 0.5H), 2.69-2.60 (m, 1H), 2.32-2.30 (m, 6H), 2.03-2.02 (m, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 167.9, 167.79, 167.76, 164.94, 164.86, 143.97, 143.95, 137.74, 137.70, 137.66, 137.11, 137.09, 136.2, 135.8, 135.6, 133.4, 132.1, 131.4,

129.62, 129.55, 129.53, 129.48, 129.4, 129.21, 129.18, 128.4, 128.2, 128.12, 128.09, 128.0, 127.9, 126.7, 125.3, 125.1, 123.30, 123.28, 122.0, 121.9, 65.72, 65.67, 52.5, 52.18, 52.16, 52.0, 51.9, 44.9, 44.7, 35.1, 30.3, 30.2, 24.90, 24.85, 21.2, 21.12, 21.11. HRMS (ESI) m/z : $[M+Na]^+$ Calcd for $C_{37}H_{36}N_2NaO_5$ 611.2516; Found 611.2519.

Dimethyl (*E*)-4'-bromo-5-(9-(4-bromostyryl)-9-methyl-1-oxo-2,3-dihydro-1*H*,9*H*-pyrazolo[1,2-*a*]indazol-5-yl)-1,4-dihydro-[1,1'-biphenyl]-2,3-dicarboxylate (7e)

Eluent: petroleum ether/ethyl acetate (1:1). Yellow solid (105.9 mg, 74% , dr = 1:1). 1H NMR ($CDCl_3$, 400 MHz): δ 7.47-7.37 (m, 4H), 7.23-7.20 (m, 2H), 7.13-7.01 (m, 5H), 6.44 (d, $J = 16.0$ Hz, 1H), 6.41-6.36 (m, 1H), 5.93-5.91 (m, 1H), 4.62-4.56 (m, 1H), 3.818-3.815 (m, 3H), 3.75-3.64 (m, 1H), 3.61-3.60 (m, 3H), 3.57-3.41 (m, 1.5H), 3.38-3.20 (m, 1.5H), 2.97-2.88 (m, 0.5H), 2.85-2.79 (m, 0.5H), 2.73-2.63 (m, 1H), 2.03 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 167.9, 167.7, 167.5, 167.3, 165.1, 165.0, 143.93, 143.86, 139.93, 139.87, 135.5, 135.3, 135.17, 135.15, 134.8, 134.3, 133.3, 132.6, 132.1, 132.0, 131.63, 131.61, 131.3, 131.2, 130.3, 130.0, 129.9, 128.5, 128.4, 128.23, 128.18, 127.3, 127.2, 125.0, 124.9, 123.5, 122.1, 122.0, 121.70, 121.69, 121.4, 65.7, 65.6, 52.6, 52.31, 52.29, 52.1, 51.9, 44.6, 44.4, 35.1, 35.0, 30.5, 30.3, 24.82, 24.75. HRMS (ESI) m/z : $[M+Na]^+$ Calcd for $C_{35}H_{30}Br_2N_2NaO_5$ 739.0414; Found 739.0406.

6. Synthesis of 8 and its spectroscopic data

To a reaction tube equipped with a stir bar were charged with **4a** (41.8 mg, 0.1 mmol), toluene (2 mL) and *N*-methylmaleimide (22.2 mg, 0.2 mmol). The tube was then sealed, and the mixture was stirred at 120 °C for 12 h. Upon completion, it was cooled to room temperature and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:2) as the eluent to give product **8** as a mixture of two diastereoisomers.

(*E*)-2-Methyl-6-(9-methyl-1-oxo-9-styryl-2,3-dihydro-1*H*,9*H*-pyrazolo[1,2-*a*]indazol-5-yl)-4-phenyl-3a,4,7,7a-tetrahydro-1*H*-isoindole-1,3(2*H*)-dione (8)

8-1: Eluent: petroleum ether/ethyl acetate (1:2). White solid (18.7 mg, 35%), mp 106.3-107.0 °C. ¹H NMR (CDCl₃, 600 MHz): δ 7.40-7.37 (m, 4H), 7.33-7.26 (m, 5H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.12-7.06 (m, 3H), 6.53 (d, *J* = 15.6 Hz, 1H), 6.50-6.49 (m, 1H), 6.45 (d, *J* = 16.2 Hz, 1H), 3.92 (t, *J* = 5.4 Hz, 1H), 3.65 (td, *J*₁ = 9.0 Hz, *J*₂ = 5.4 Hz, 1H), 3.46-3.43 (m, 1H), 3.40 (td, *J*₁ = 7.8 Hz, *J*₂ = 1.8 Hz, 1H), 3.34-3.30 (m, 1H), 3.24 (dd, *J*₁ = 16.8 Hz, *J*₂ = 2.4 Hz, 1H), 2.91-2.86 (m, 1H), 2.84-2.79 (m, 1H), 2.75 (s, 3H), 2.73-2.68 (m, 1H), 2.03 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ 177.8, 175.6, 163.6, 142.7, 137.5, 135.6, 135.2, 134.8, 129.5, 128.51, 128.46, 127.7, 127.5, 127.44, 127.1, 126.8, 126.4, 125.8, 124.1, 122.5, 120.9, 64.4, 50.0, 44.4, 41.2, 38.8, 33.9, 26.6, 23.7, 23.6. HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₃₄H₃₁N₃NaO₃ 552.2258; Found 552.2269.

8-2: Eluent: petroleum ether/ethyl acetate (1:2). White solid (18.6 mg, 35%), mp 117.1-118.1 °C. ¹H NMR (CDCl₃, 600 MHz): δ 7.30-7.27 (m, 4H), 7.24-7.17 (m, 5H), 7.13 (t, *J* = 7.2 Hz, 1H), 7.10 (dd, *J*₁ = 7.8 Hz, *J*₂ = 1.2 Hz, 1H), 7.04 (t, *J* = 7.8 Hz, 1H), 7.00 (dd, *J*₁ = 7.2 Hz, *J*₂ = 1.2 Hz, 1H), 6.43 (d, *J* = 16.2 Hz, 1H), 6.39-6.38 (m, 1H), 6.31 (d, *J* = 16.2 Hz, 1H), 3.84 (t, *J* = 5.4 Hz, 1H), 3.75 (td, *J*₁ = 8.4 Hz, *J*₂ = 3.6 Hz, 1H), 3.38-3.35 (m, 1H), 3.33-3.30 (m, 1H), 3.26 (dd, *J*₁ = 16.2 Hz, *J*₂ = 1.8 Hz, 1H), 3.13-3.08 (m, 1H), 2.86-2.80 (m, 1H), 2.70 (s, 3H), 2.62-2.57 (m, 2H), 1.99 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 150 MHz): δ 178.0, 175.4, 163.7, 143.2, 137.5, 135.3, 135.1, 134.9, 129.3, 128.7, 128.1, 127.8, 127.5, 127.4, 127.1, 126.8, 126.4, 125.8, 123.8, 122.6, 120.7, 64.5, 49.8, 44.9, 41.5, 39.2, 33.8, 27.5, 23.7, 23.6. HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₃₄H₃₁N₃NaO₃ 552.2258; Found 552.2265.

7. Synthesis of 9 and its spectroscopic data

To a reaction tube equipped with a stir bar was charged with **4g** (99.2 mg, 0.2 mmol), dioxane (2 mL), Pd₂(dba)₃ (18.3 mg, 0.02 mmol), DavePhos (11.8 mg, 0.03 mmol), ^tBuONa (38.4 mg, 0.4 mmol) and morpholine (52.3 mg, 0.6 mmol). The tube was then sealed, and the mixture was stirred at 100 °C under argon for 12 h. Upon completion, it was cooled to room temperature, diluted with dichloromethane (20 mL) and washed with water and brine. The organic layer was dried over anhydrous Na₂SO₄, filtered, and concentrated

under reduced pressure. The residue was purified by silica gel column chromatography with petroleum ether/ethyl acetate (2:1) as eluent to afford **9**.

9-Methyl-7-morpholino-5-((E)-4-phenylbuta-1,3-dien-2-yl)-9-((E)-styryl)-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-1-one (9)

Eluent: petroleum ether/ethyl acetate (2:1). Yellow solid (46.4 mg, 46%), mp 112.2-113.2 °C. ¹H NMR (CDCl₃, 600 MHz): δ 7.39 (d, *J* = 7.2 Hz, 2H), 7.35 (d, *J* = 7.2 Hz, 2H), 7.33-7.28 (m, 4H), 7.23 (td, *J*₁ = 7.2 Hz, *J*₂ = 1.2 Hz, 2H), 6.99 (d, *J* = 16.2 Hz, 1H), 6.72 (s, 1H), 6.68 (s, 1H), 6.58 (d, *J* = 15.6 Hz, 1H), 6.43 (d, *J* = 15.6 Hz, 1H), 6.32 (d, *J* = 16.2 Hz, 1H), 5.56 (s, 1H), 5.33 (d, *J* = 1.2 Hz, 1H), 3.86 (t, *J* = 4.2 Hz, 4H), 3.69 (td, *J*₁ = 8.4 Hz, *J*₂ = 4.8 Hz, 1H), 3.31-3.26 (m, 1H), 3.13 (t, *J* = 4.2 Hz, 4H), 2.86-2.80 (m, 1H), 2.66-2.61 (m, 1H), 2.08 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ 164.7, 145.0, 136.8, 136.3, 132.9, 130.4, 129.1, 128.8, 128.7, 128.5, 128.0, 127.9, 126.9, 126.8, 124.3, 119.6, 118.1, 110.2, 66.9, 65.7, 51.7, 50.5, 35.4, 24.3. HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₃₃H₃₄N₃O₂ 504.2646; Found 504.2637.

8. Gram-scale synthesis of **3a**

To a reaction tube equipped with a stir bar were charged with **1a** (1.6208 g, 10 mmol), DCE (20 mL), [RhCp*Cl₂]₂ (77.3 mg, 0.125 mmol), NaOAc (205 mg, 2.5 mmol) and **2a** (940.4 mg, 5 mmol). The tube was then sealed, and the mixture was stirred at room temperature under argon for 12 h. Upon completion, it was quenched with saturated brine and extracted with dichloromethane (30 mL × 3). The combined organic phases were dried over anhydrous Na₂SO₄, filtered through a pad of celite, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography with petroleum ether/ethyl acetate (2:1) as eluent to afford **3a** (1.059 g, 73%).

9. Gram-scale synthesis of **4a**

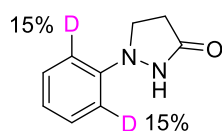
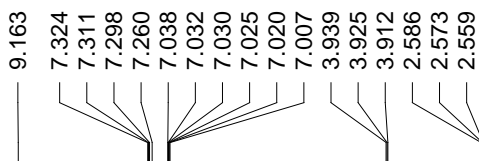
To a reaction tube equipped with a stir bar were charged with **1a** (648.3 mg, 4 mmol), DCE (20 mL), [RhCp*Cl₂]₂ (61.8 mg, 0.1 mmol), NaOAc (164 mg, 2 mmol) and **2a** (2.2570 g, 12 mmol). The tube was then

sealed, and the mixture was stirred at 50 °C under argon for 24 h. Upon completion, it was quenched with saturated brine and extracted with dichloromethane (30 mL × 3). The combined organic phases were dried over anhydrous Na₂SO₄, filtered through a pad of celite, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1) as eluent to afford **4a** (932.2 mg, 55%).

III. Mechanistic studies

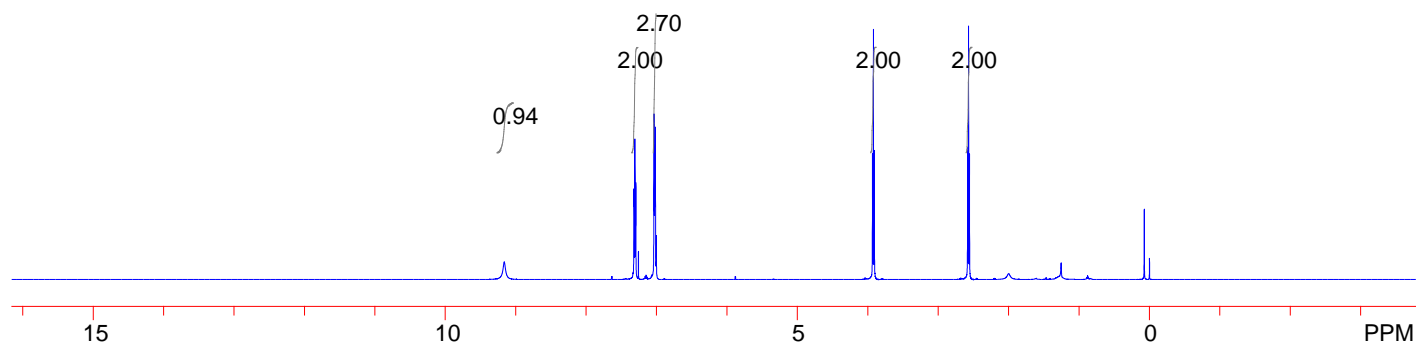
1. H/D exchange experiment (I)

To a reaction tube equipped with a stir bar were charged with **1a** (32.4 mg, 0.2 mmol), DCE (2 mL), CD₃OD (163 μL, 4 mmol), [RhCp*Cl₂]₂ (3.1 mg, 0.005 mmol) and NaOAc (8.2 mg, 0.1 mmol). The tube was then sealed, and the mixture was stirred at room temperature under argon for 0.5 h. Afterwards, it was quenched with saturated brine and extracted with dichloromethane (10 mL × 3). The combined organic phases were dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (2:1) as eluent to give a mixture of **1a** and **1a-d₂**. Upon analyzing the ¹H NMR spectrum of the mixture, the deuteration ratio was determined to be 15%.



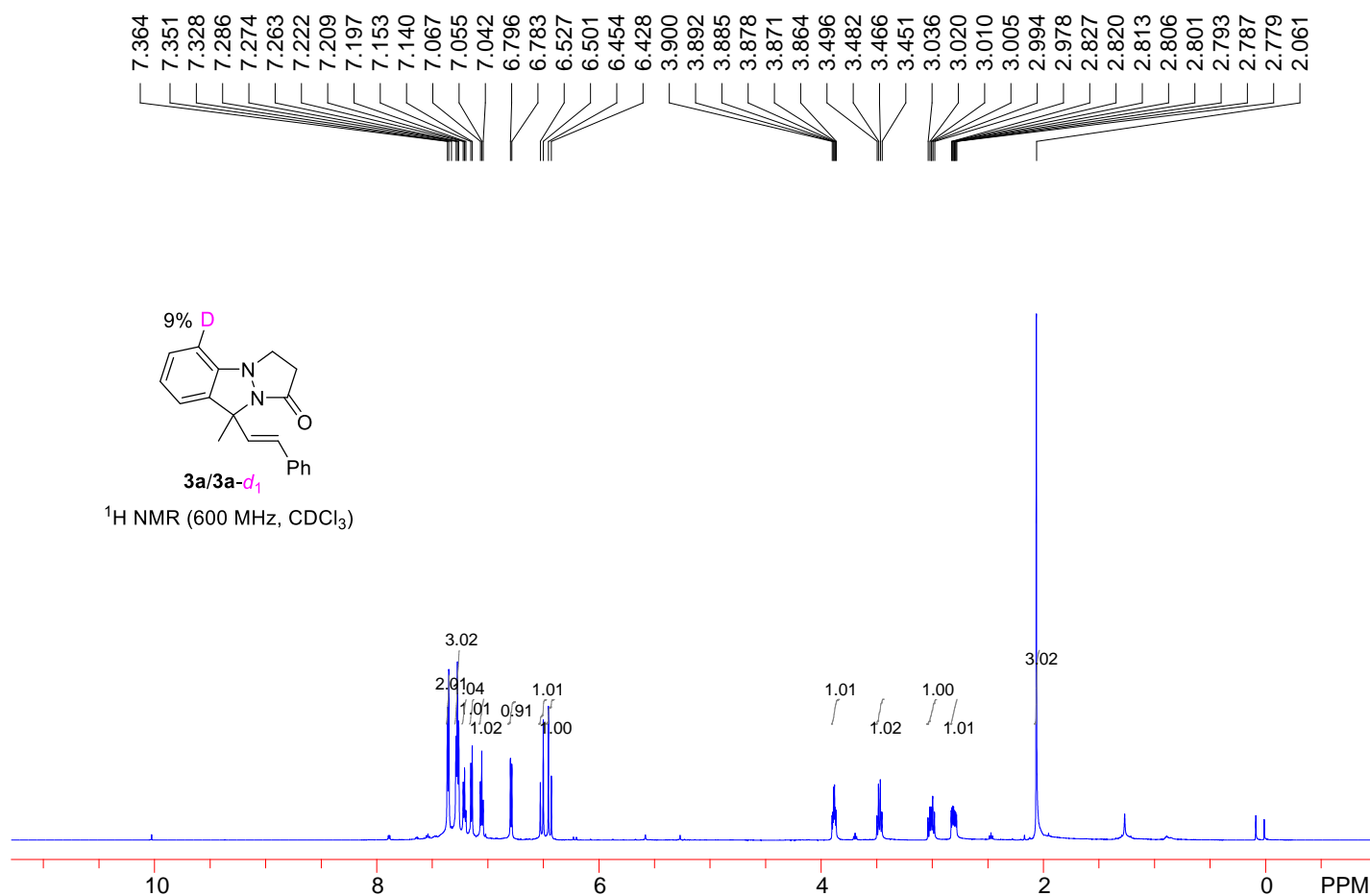
1a/1a-d₂

¹H NMR (600 MHz, CDCl₃)



2. H/D exchange experiment (II)

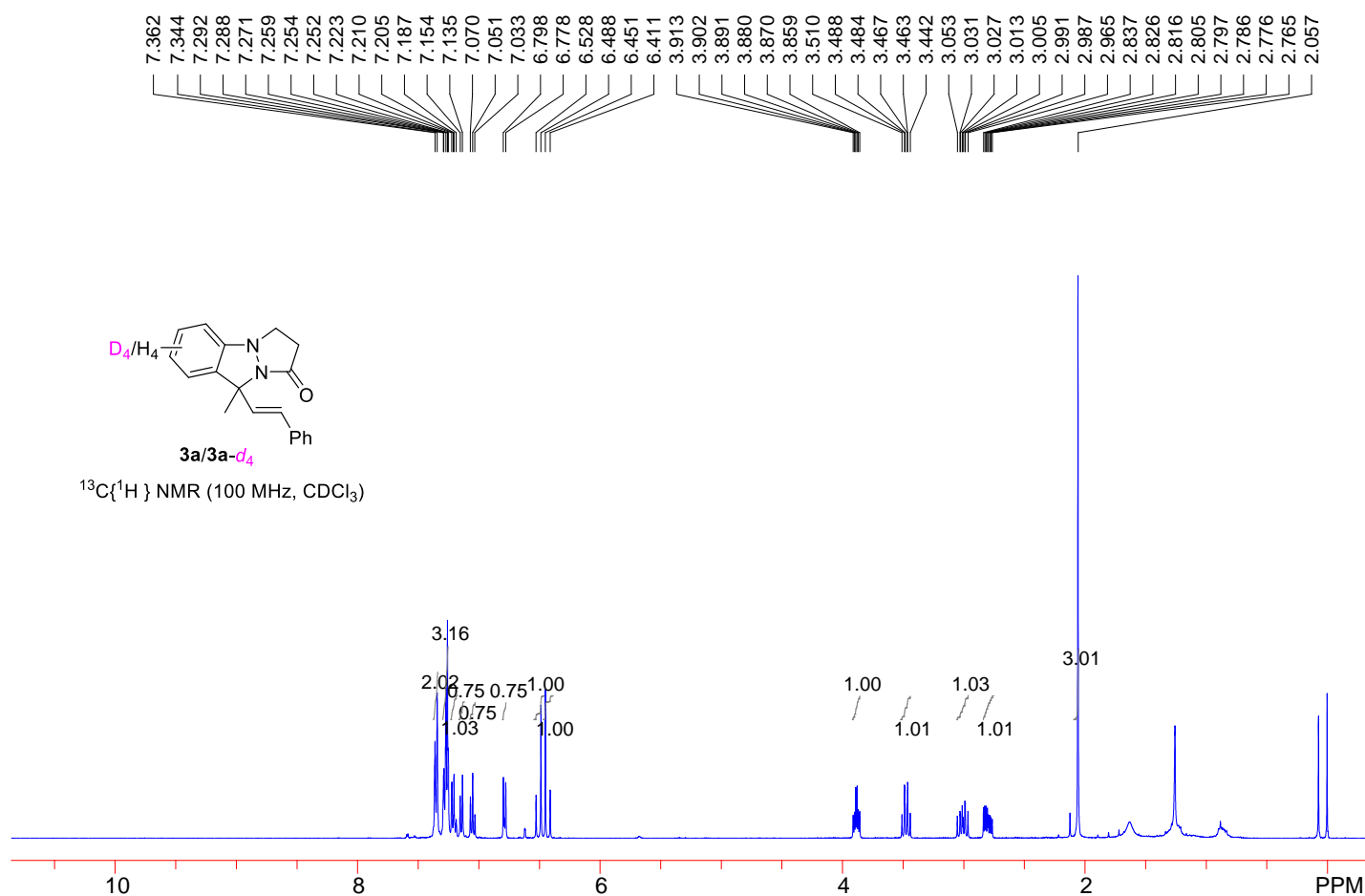
To a reaction tube equipped with a stir bar were charged with **1a** (64.8 mg, 0.4 mmol), **2a** (37.7 mg, 0.2 mmol), DCE (2 mL), CD₃OD (163 μL, 4 mmol), [RhCp*Cl₂]₂ (3.1 mg, 0.005 mmol) and NaOAc (8.2 mg, 0.1 mmol). The tube was then sealed, and the mixture was stirred at room temperature under argon for 0.5 h. Afterwards, it was quenched with saturated brine and extracted with dichloromethane (10 mL × 3). The combined organic phases were dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (2:1) as eluent to give a mixture of **3a** and **3a-d₁**. Upon analyzing the ¹H NMR spectrum of the mixture, the deuteration ratio was determined to be about 9%.



3. Kinetic isotope effect study

To a reaction tube equipped with a stir bar were charged with **1a** (16.7 mg, 0.1 mmol), **1a-d₅** (16.2 mg, 0.1 mmol), **2a** (18.8 mg, 0.1 mmol), DCE (1 mL), [RhCp*Cl₂]₂ (1.6 mg, 0.0025 mmol) and NaOAc (4.1 mg, 0.05 mmol). The tube was then sealed, and the mixture was stirred at room temperature under argon for 0.5 h.

Afterwards, it was quenched with saturated brine and extracted with dichloromethane (10 mL \times 3). The combined organic phases were dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (2:1) as eluent to give a mixture of **3a** and **3a-d₄**. Upon analyzing the ¹H NMR spectrum of the mixture, the ratio of **3a** to **3a-d₄** was determined to be about 0.75:0.25. Accordingly, the intermolecular KIE (k_H/k_D) was calculated to be about 3.0.



4. Electronic competition experiment

To a reaction tube equipped with a stir bar were added **1b** (35.2 mg, 0.2 mmol), **1e** (46.0 mg, 0.2 mmol), **2a** (37.7 mg, 0.2 mmol), [RhCp*Cl₂]₂ (3.1 mg, 0.005 mmol), NaOAc (8.2 mg, 0.1 mmol) and DCE (2 mL). The tube was then sealed, and the mixture was stirred at room temperature for 0.5 h. Afterwards, it was quenched with saturated brine and extracted with dichloromethane (10 mL \times 3). The combined organic phases were dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified by

silica gel column chromatography using petroleum ether/ethyl acetate (2:1) as eluent to give **3e** (36.5 mg, 51%). Meanwhile, product **3b** was formed in trace amount.

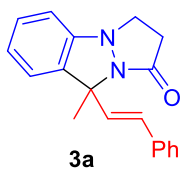
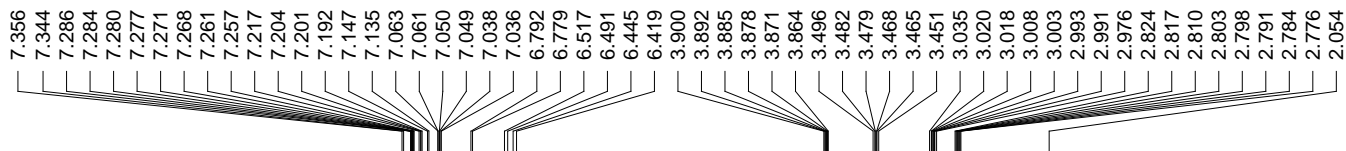
5. Controle experiment

To a reaction tube equipped with a stir bar were added **3a** (29.0 mg, 0.1 mmol), **2a** (41.8 mg, 0.1 mmol), $[\text{RhCp}^*\text{Cl}_2]_2$ (1.6 mg, 0.0025 mmol), NaOAc (4.1 mg, 0.05 mmol) and DCE (1 mL). The tube was then sealed, and the mixture was stirred at 50 °C under argon for 6 h. From the resulting mixture, the generation of **4a** was not observed based on TLC detection.

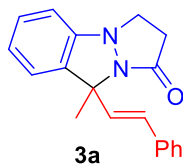
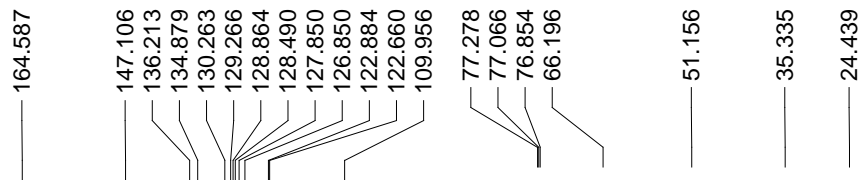
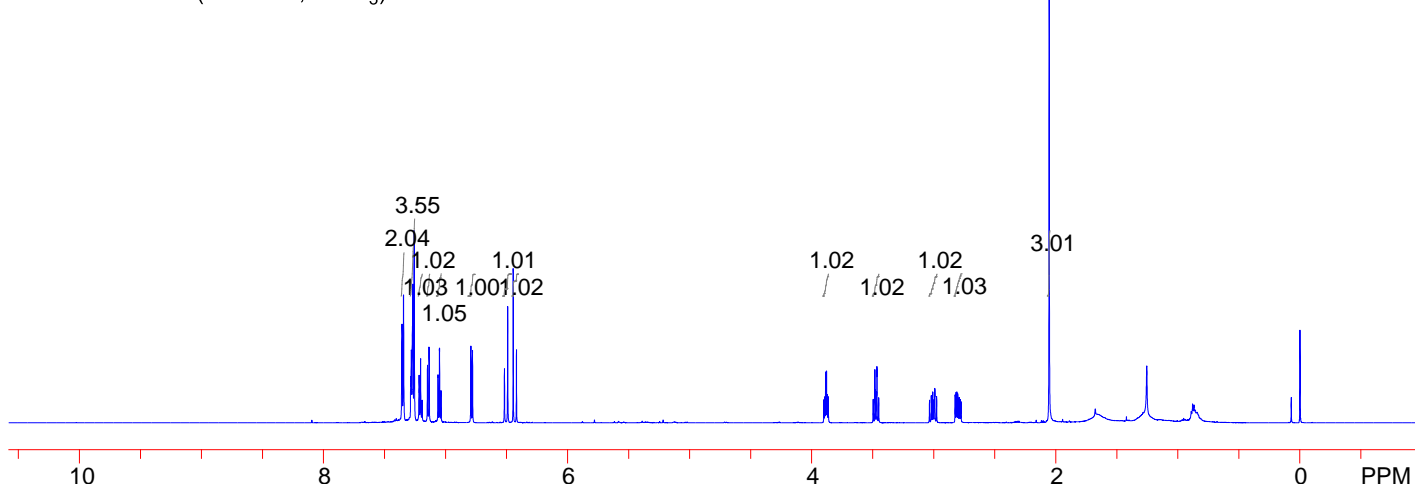
IV. References

- [1] N. Li, X. Zhang and X. Fan, Synthesis of pyrazolidinone fused cinnolines via the cascade reactions of 1-phenylpyrazolidinones with vinylene carbonate, *Tetrahedron Lett.*, 2022, **103**, 153984.
- [2] A. Singh, R. K. Shukla and C. M. R. Volla, Rh(III)-Catalyzed [5+1] annulation of 2-alkenylanilides and 2-alkenylphenols with allenyl acetates, *Chem. Sci.*, 2022, **13**, 2043–2049.
- [3] K.-I. Fujita, Y. Takahashi, M. Owaki, K. Yamamoto and R. Yamaguchi, Synthesis of five-, six-, and seven-membered ring lactams by Cp*Rh complex-catalyzed oxidative *N*-heterocyclization of amino alcohols, *Org. Lett.*, 2004, **6**, 2785–2788.

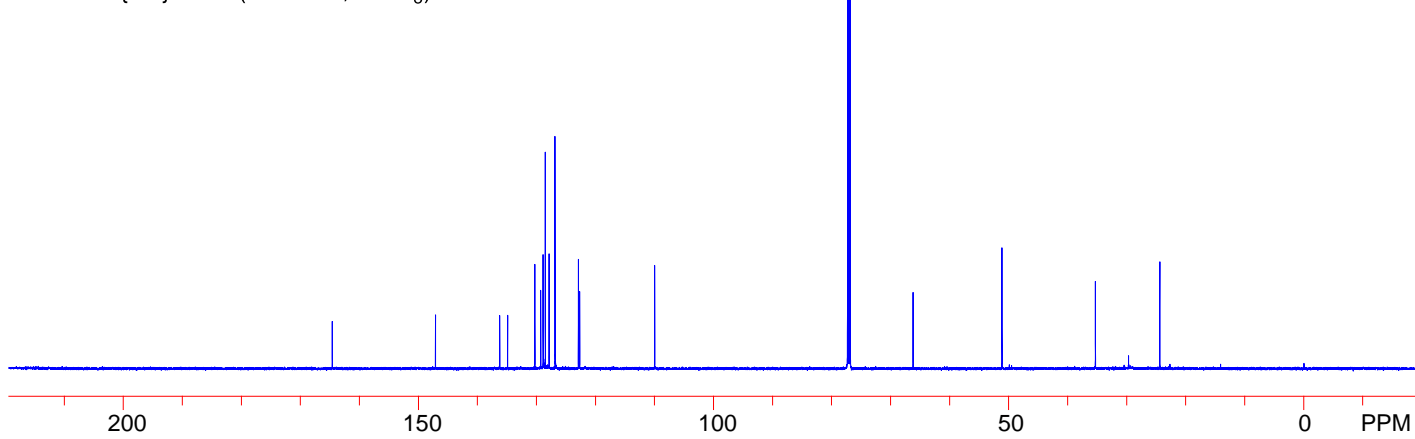
V. NMR spectra of 3a-3ee

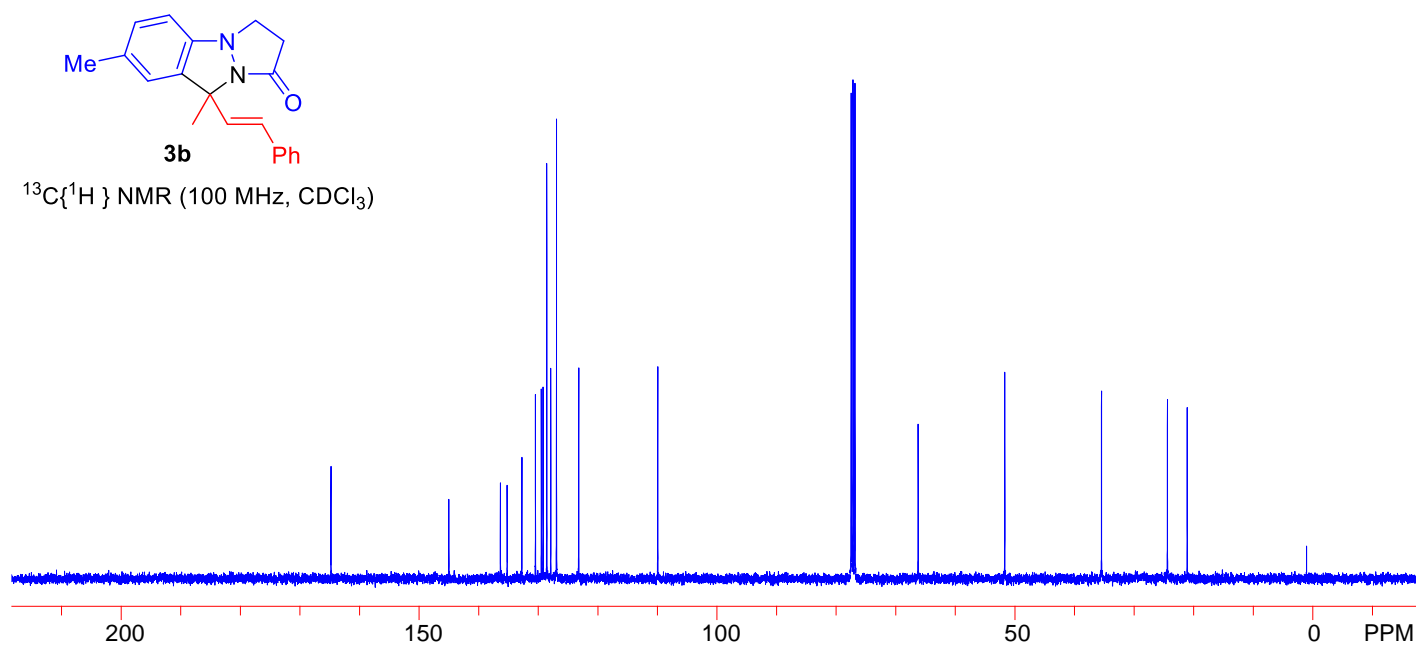
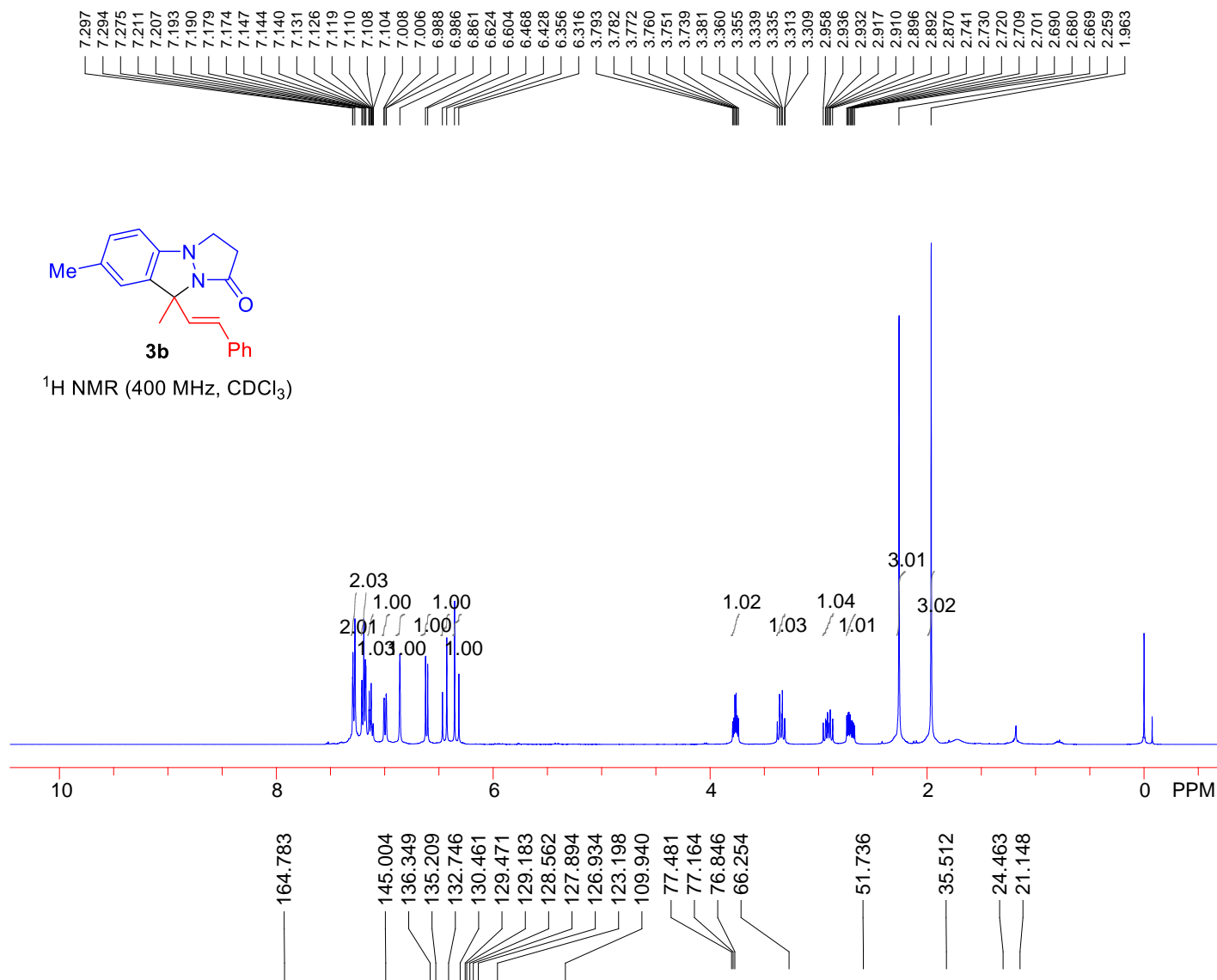


¹H NMR (600 MHz, CDCl₃)

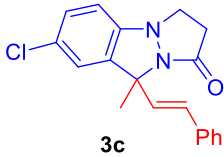


¹³C{¹H} NMR (150 MHz, CDCl₃)

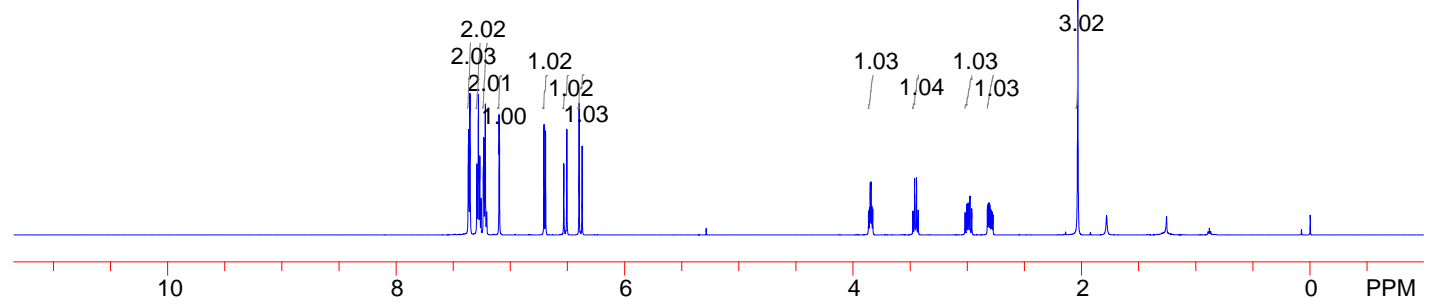




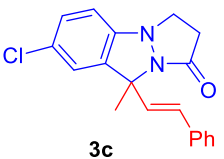
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6.705
6.691
6.531
6.505
6.397
6.371
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3.848
3.840
3.834
3.826
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2.033



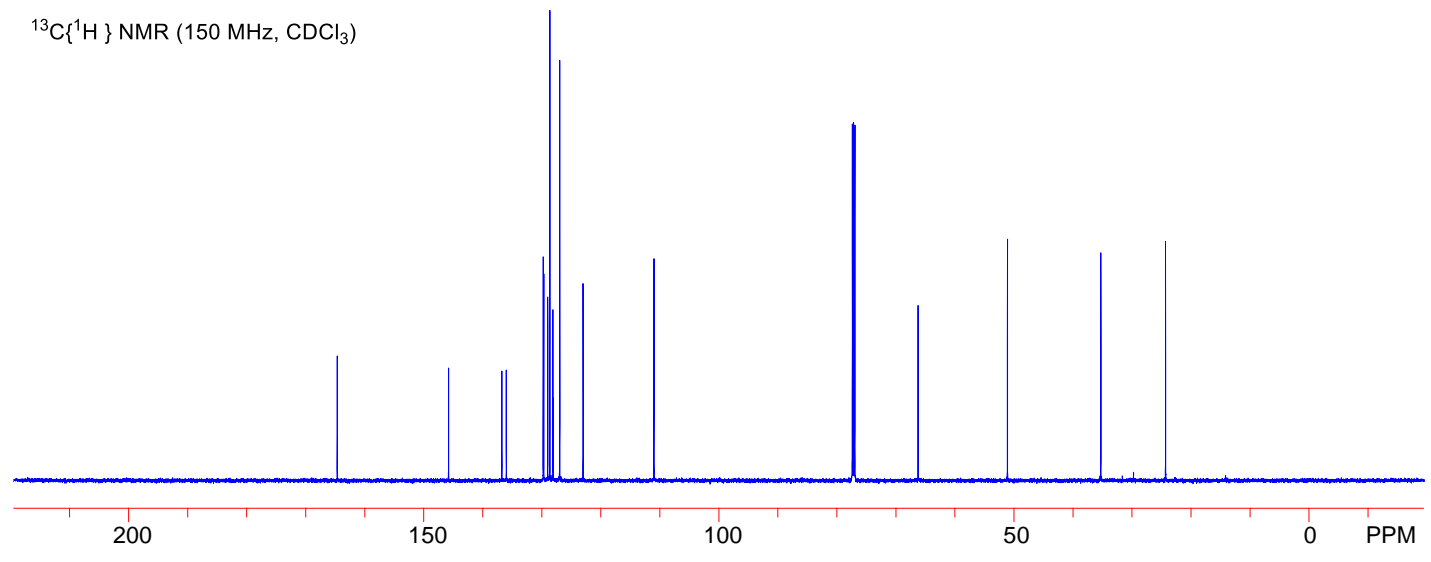
¹H NMR (600 MHz, CDCl₃)

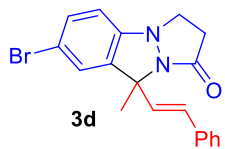
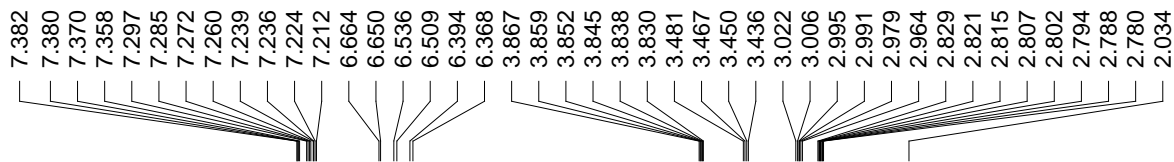


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76.950
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51.131
35.323
24.367

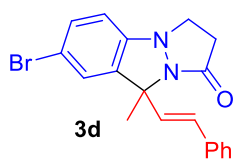
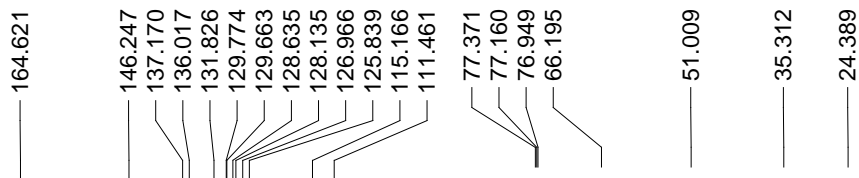
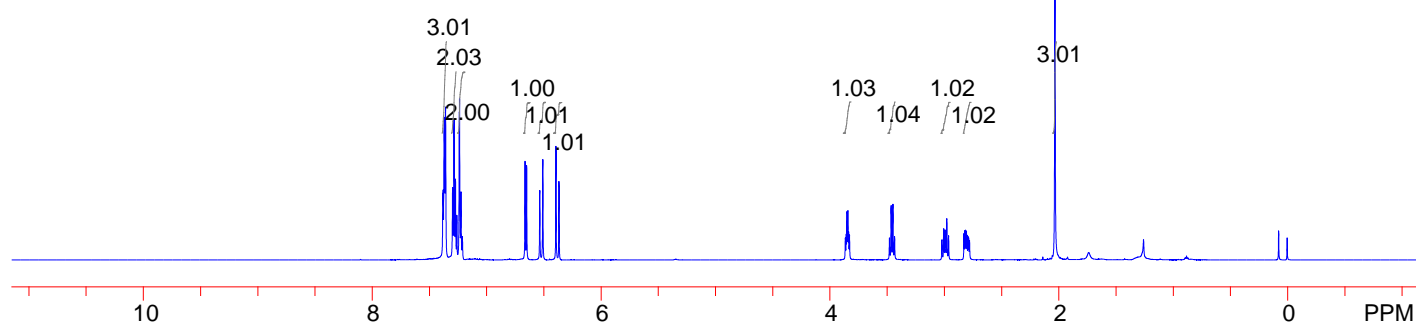


¹³C{¹H} NMR (150 MHz, CDCl₃)

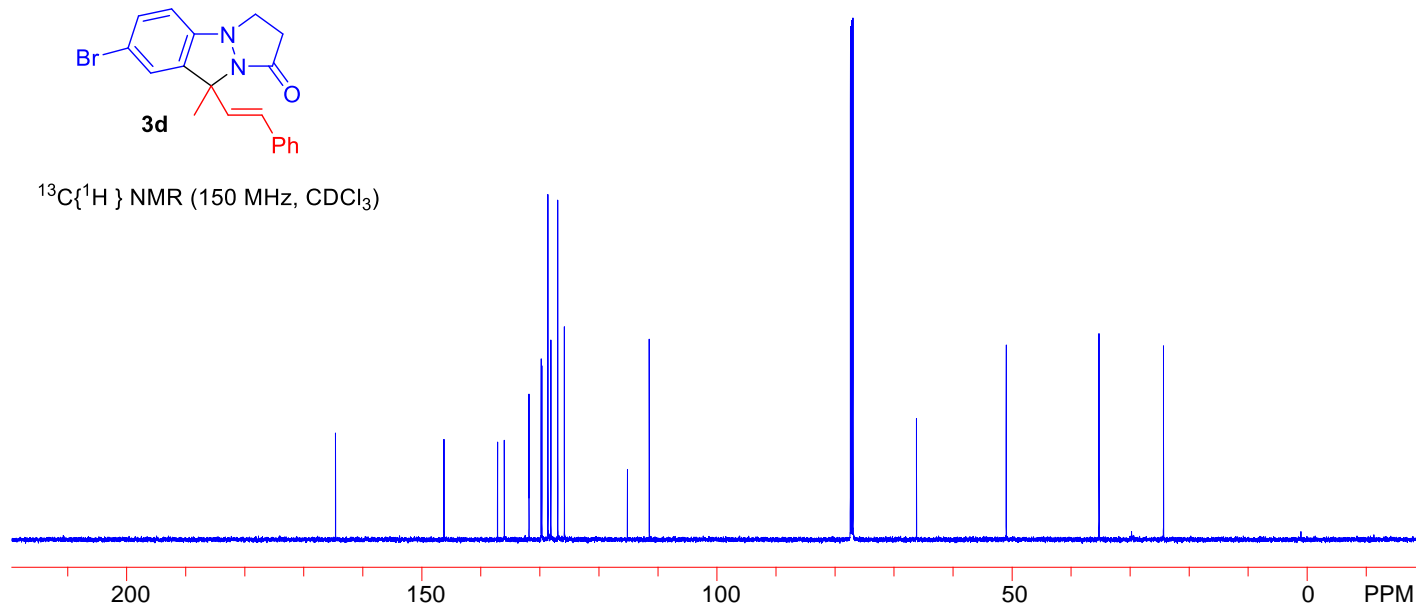




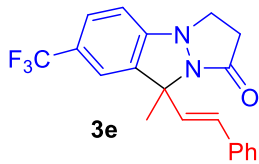
^1H NMR (600 MHz, CDCl_3)



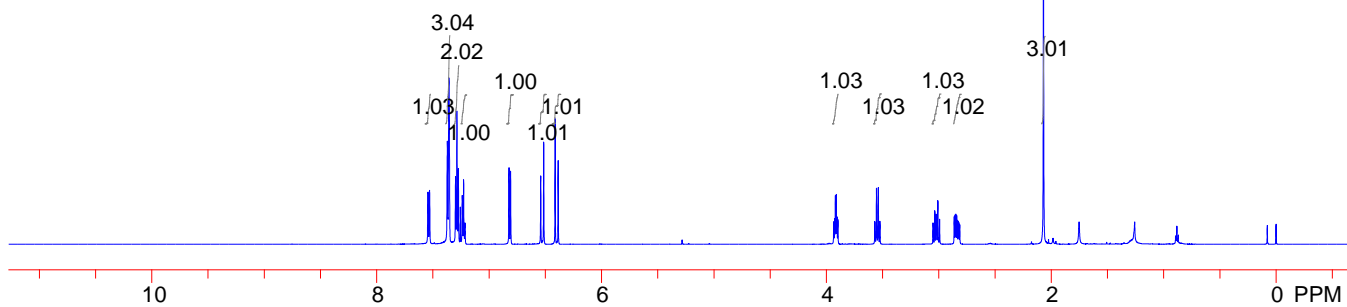
$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)



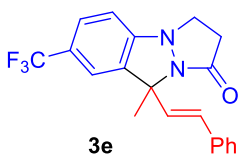
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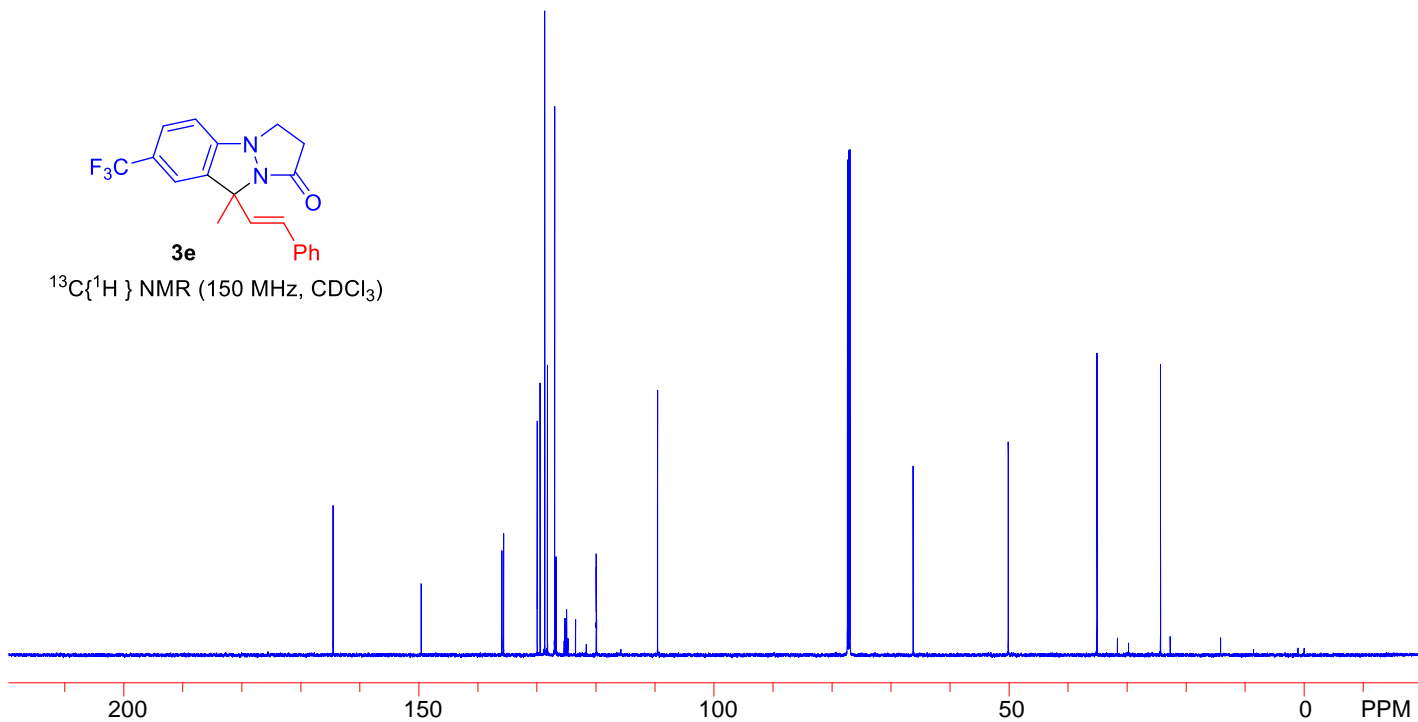
$^1\text{H NMR}$ (600 MHz, CDCl_3)



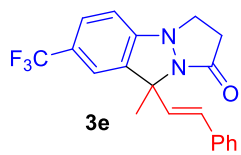
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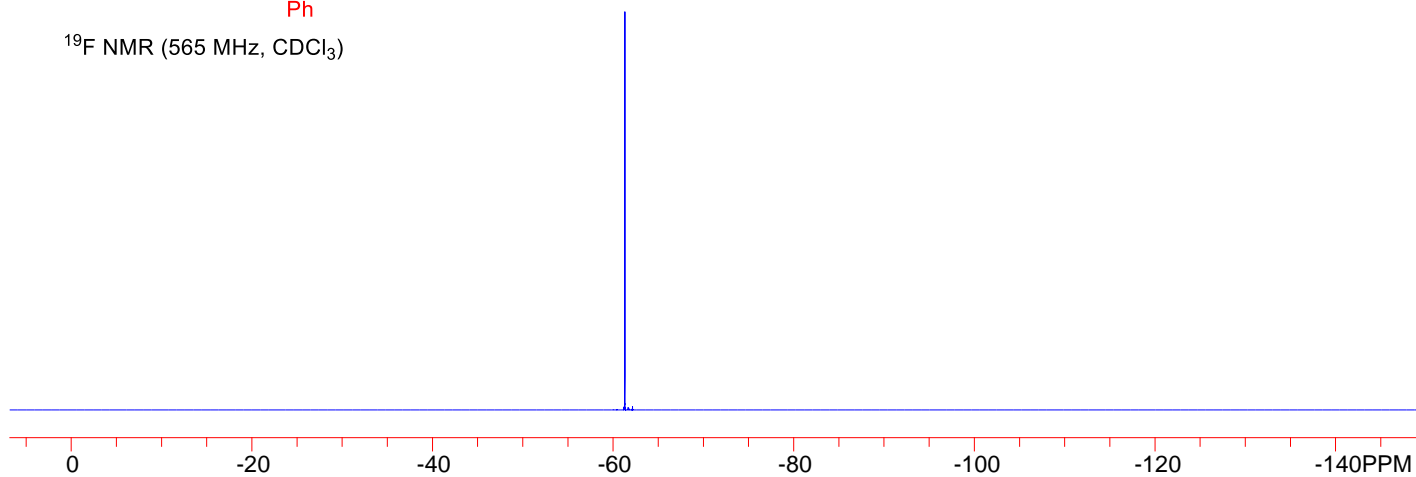
$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)



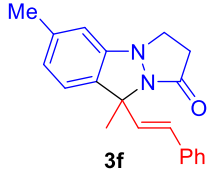
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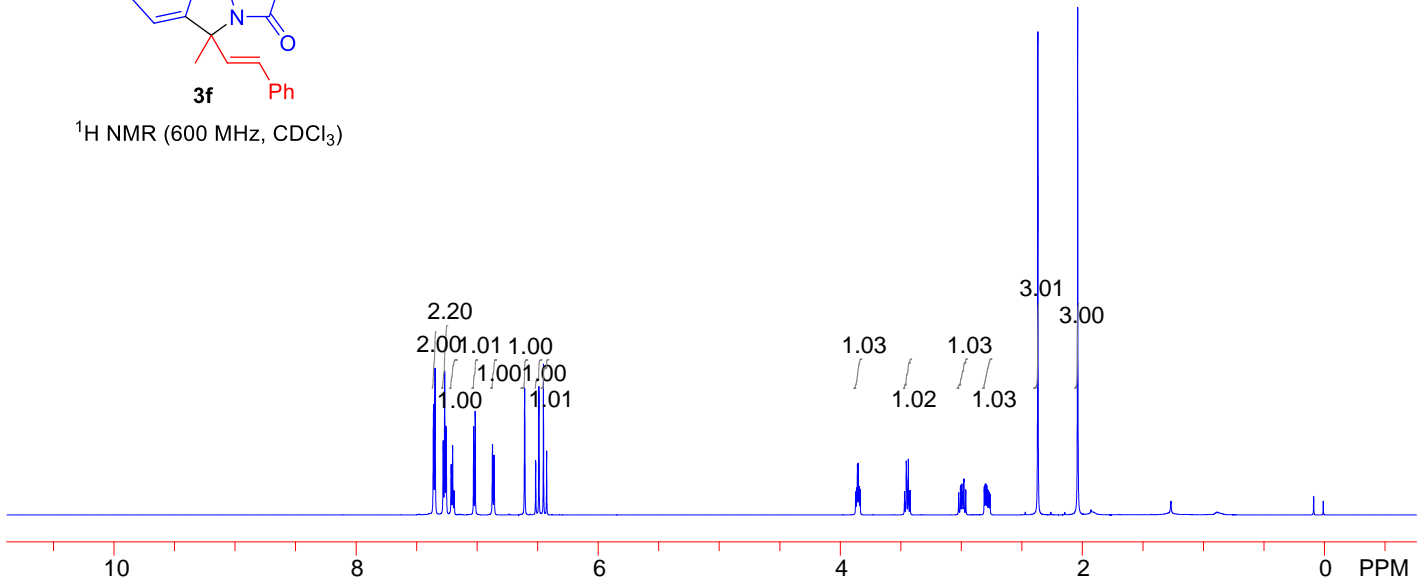
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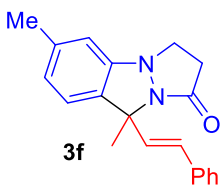
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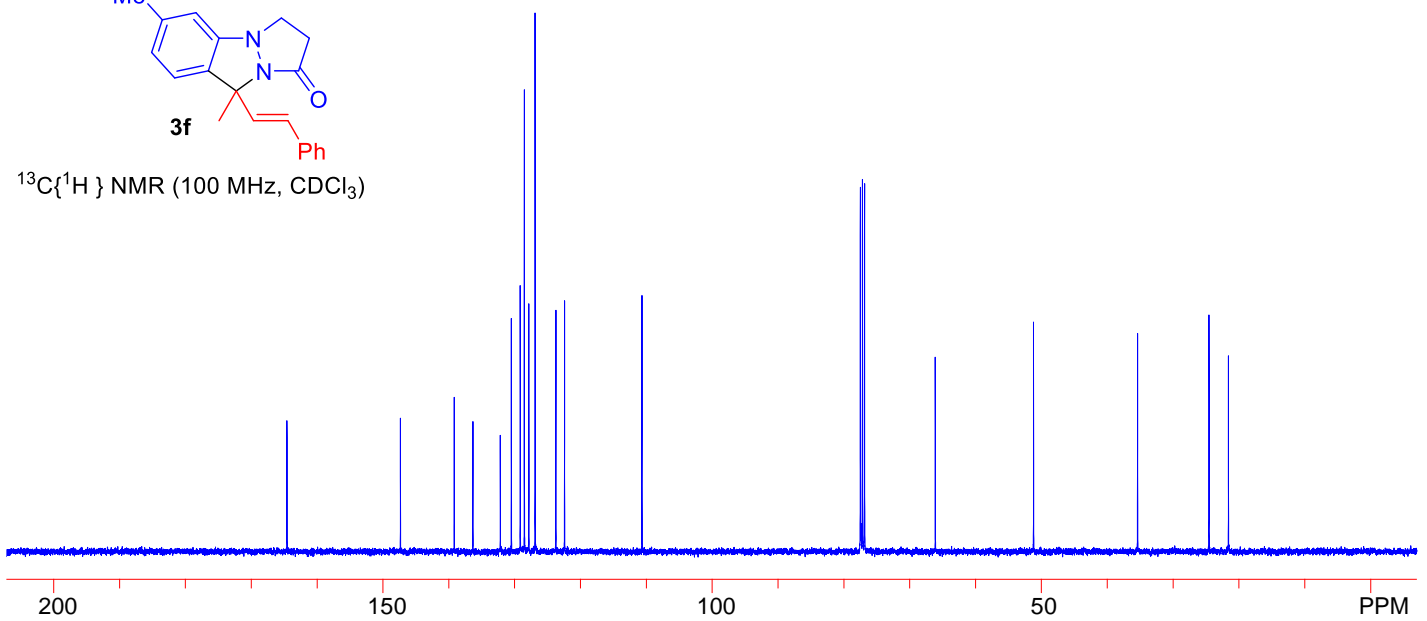
$^1\text{H NMR}$ (600 MHz, CDCl_3)



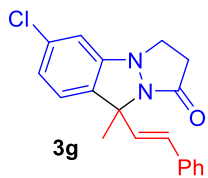
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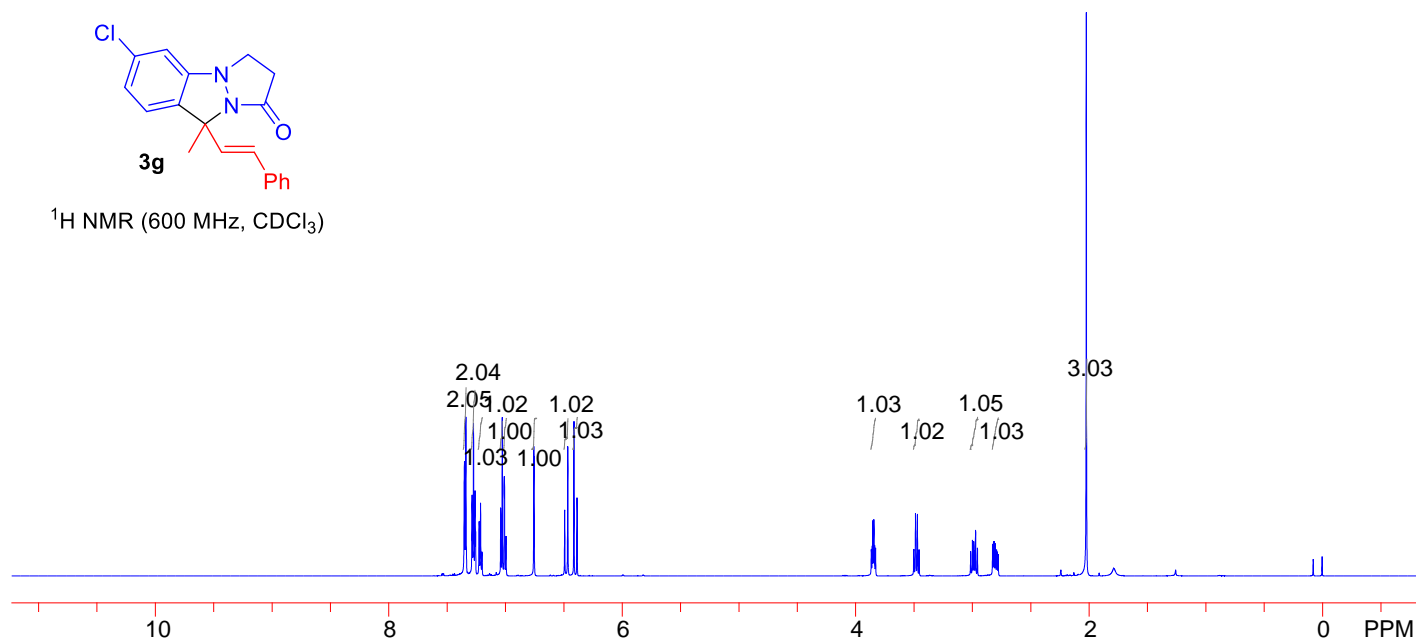
$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)



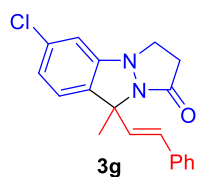
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7.009
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6.995
6.758
6.755
6.493
6.467
6.414
6.387
3.867
3.859
3.852
3.845
3.838
3.830
3.502
3.488
3.471
3.457
3.014
2.999
2.988
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2.023



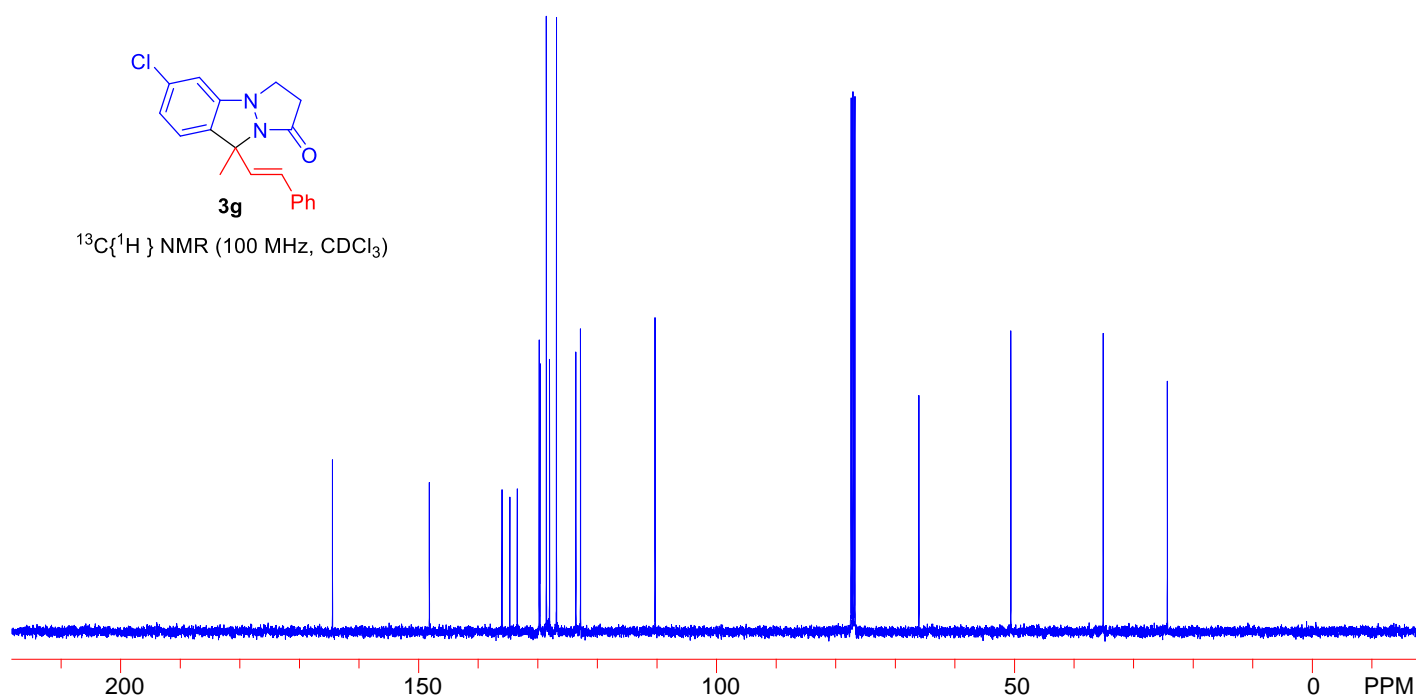
$^1\text{H NMR}$ (600 MHz, CDCl_3)



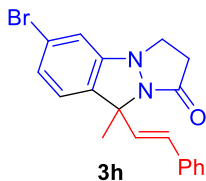
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129.754
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128.555
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77.408
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76.772
66.045
50.641
35.156
24.397



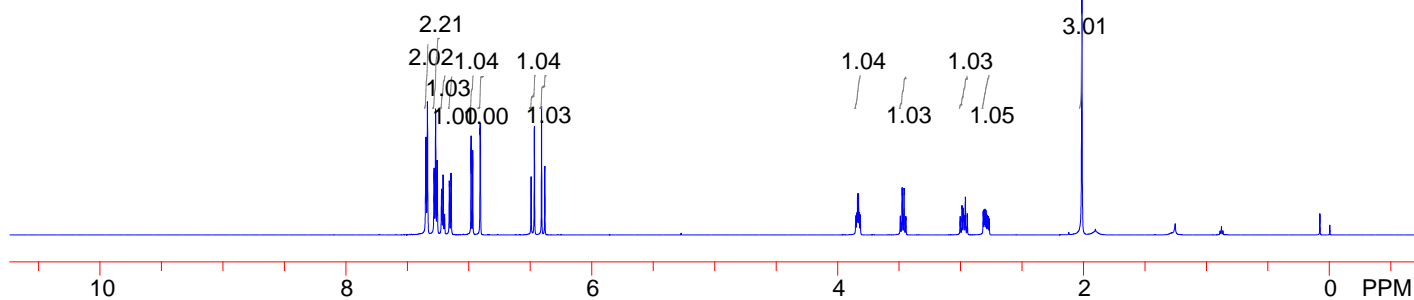
$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)



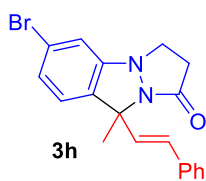
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6.908
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6.467
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6.382
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3.825
3.817
3.492
3.477
3.461
3.447
3.005
2.990
2.979
2.974
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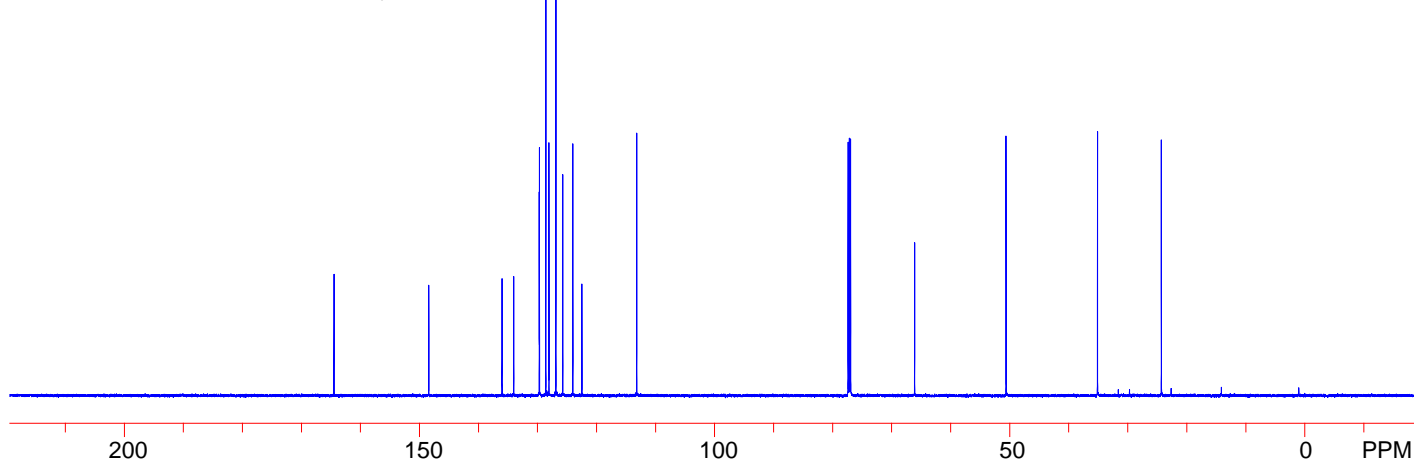
$^1\text{H NMR}$ (600 MHz, CDCl_3)

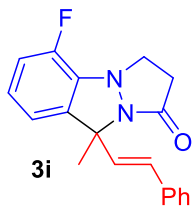
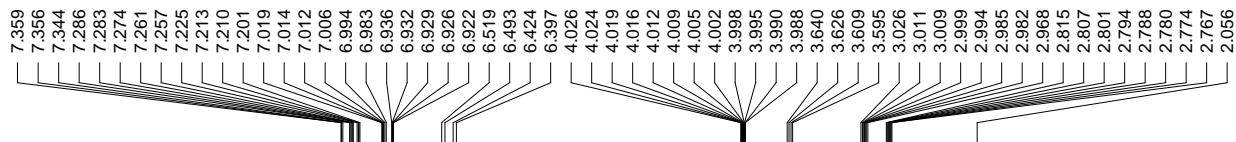


164.479
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136.010
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129.700
129.666
128.588
128.055
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122.468
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77.371
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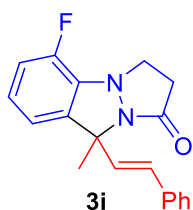
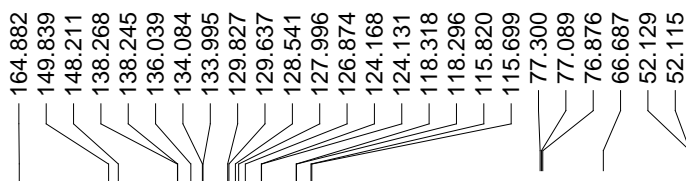
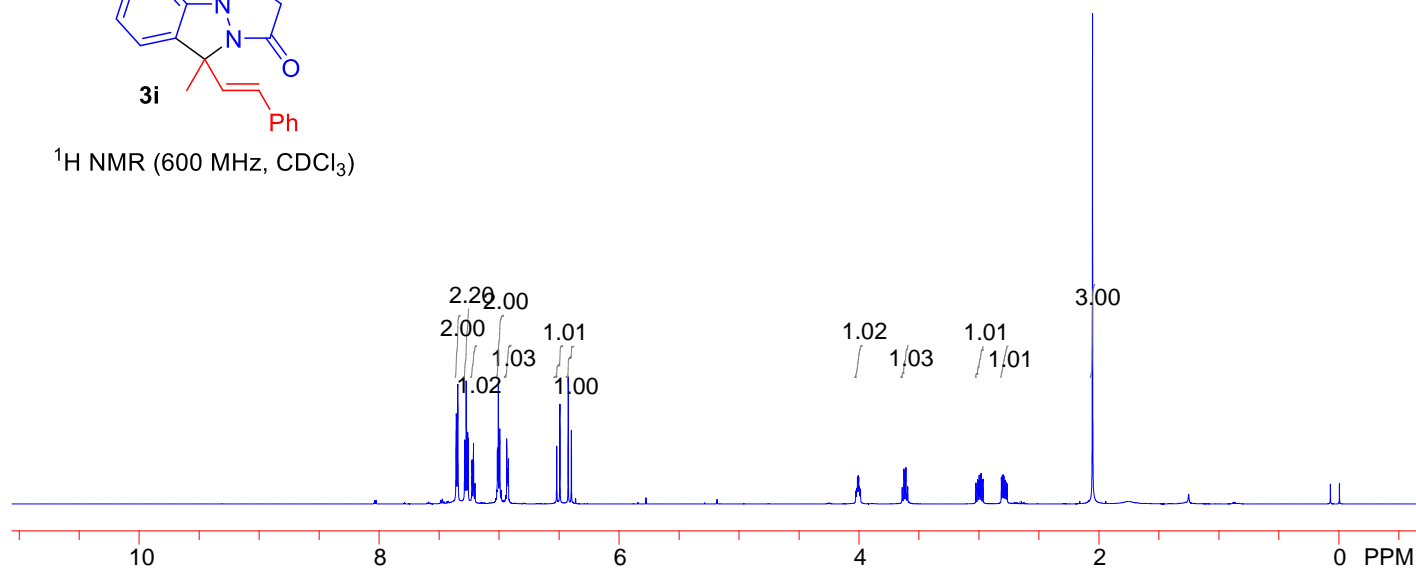


$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)

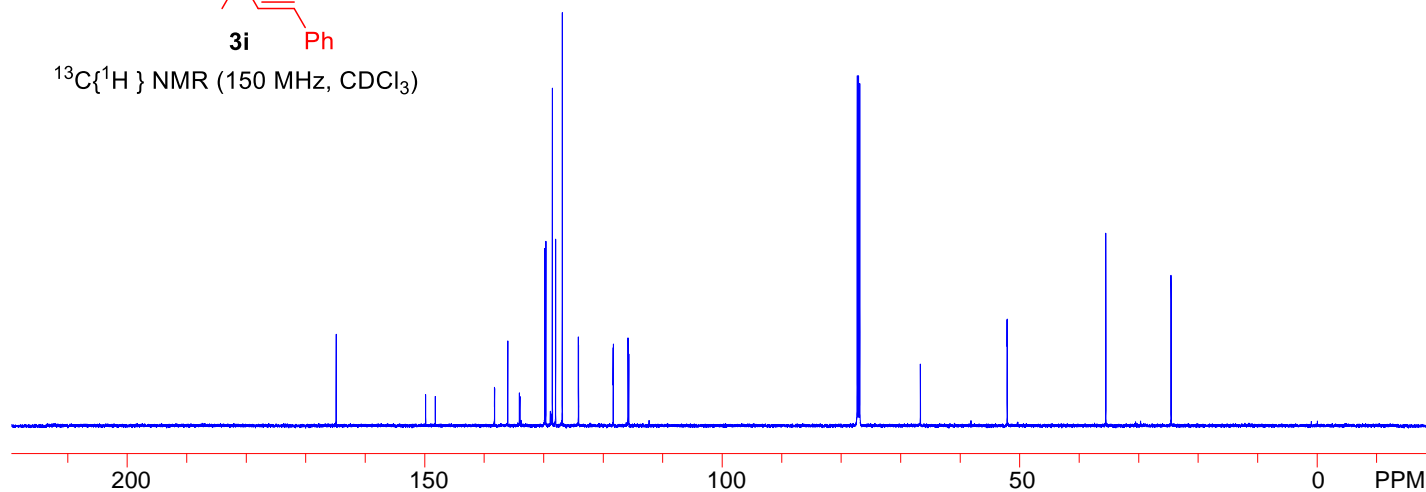


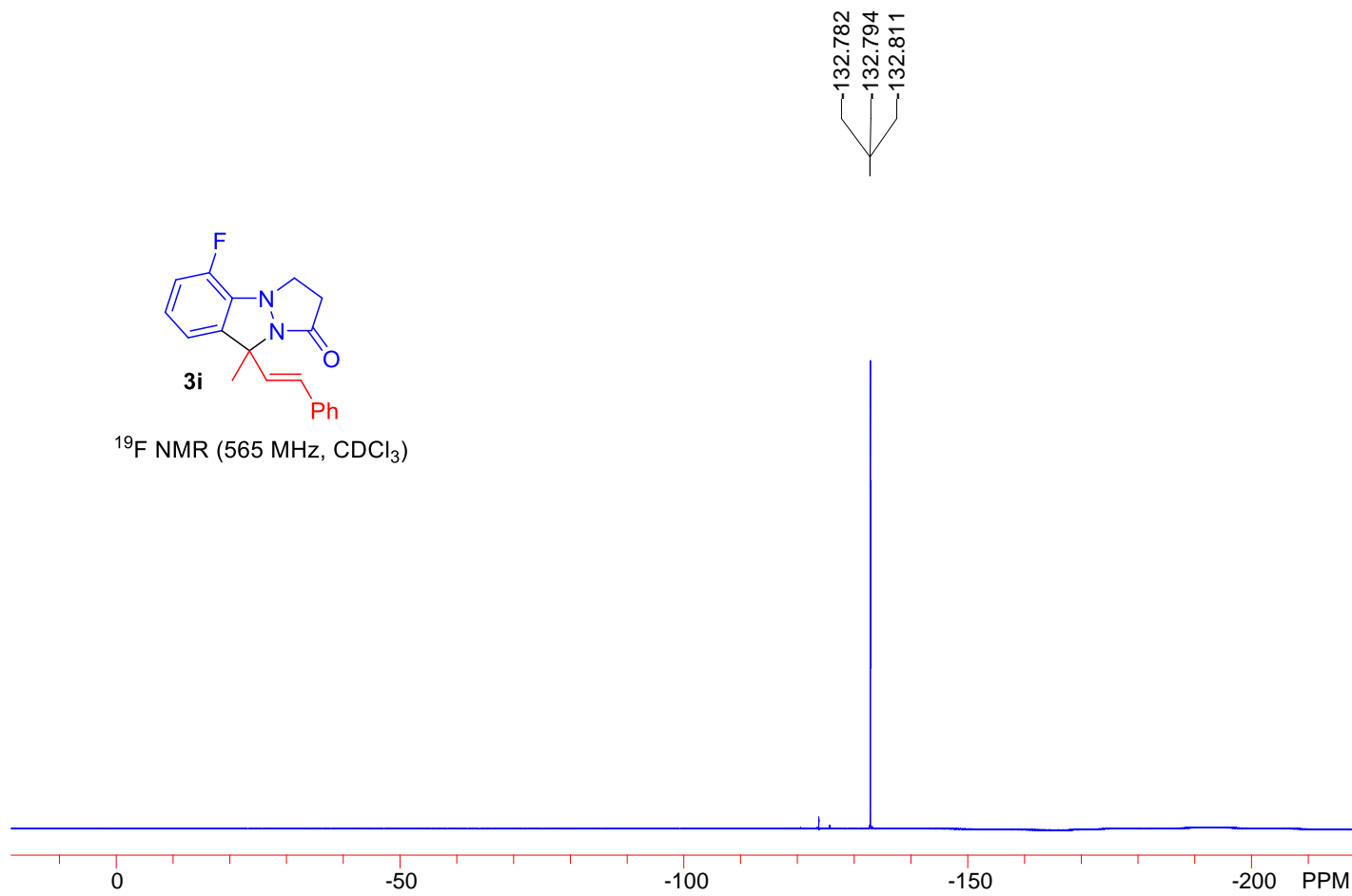
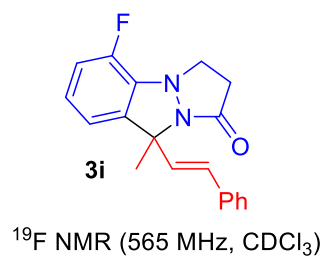


^1H NMR (600 MHz, CDCl_3)

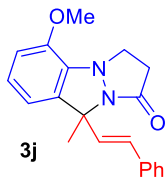


$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)

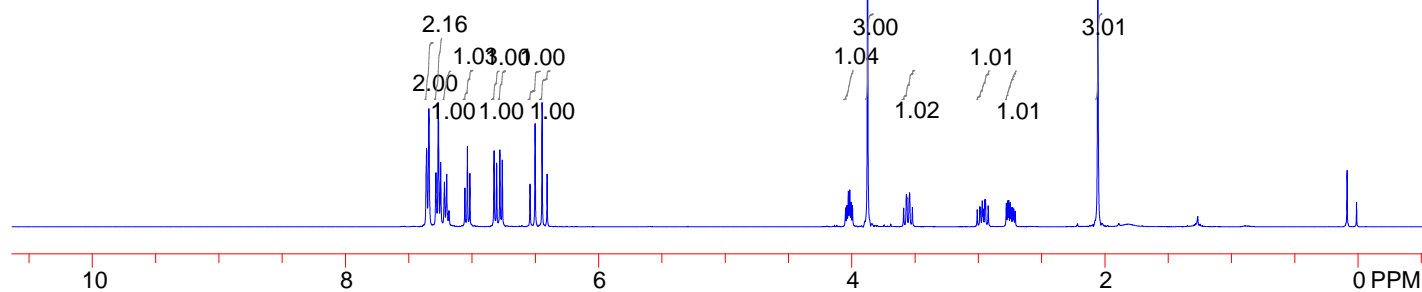
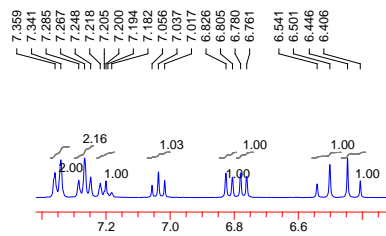




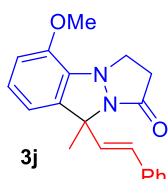
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7.200
7.194
7.182
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6.805
6.780
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6.501
6.446
6.406
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4.026
4.014
4.004
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3.874
3.588
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3.563
3.542
3.542
3.520
3.007
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2.707
2.054



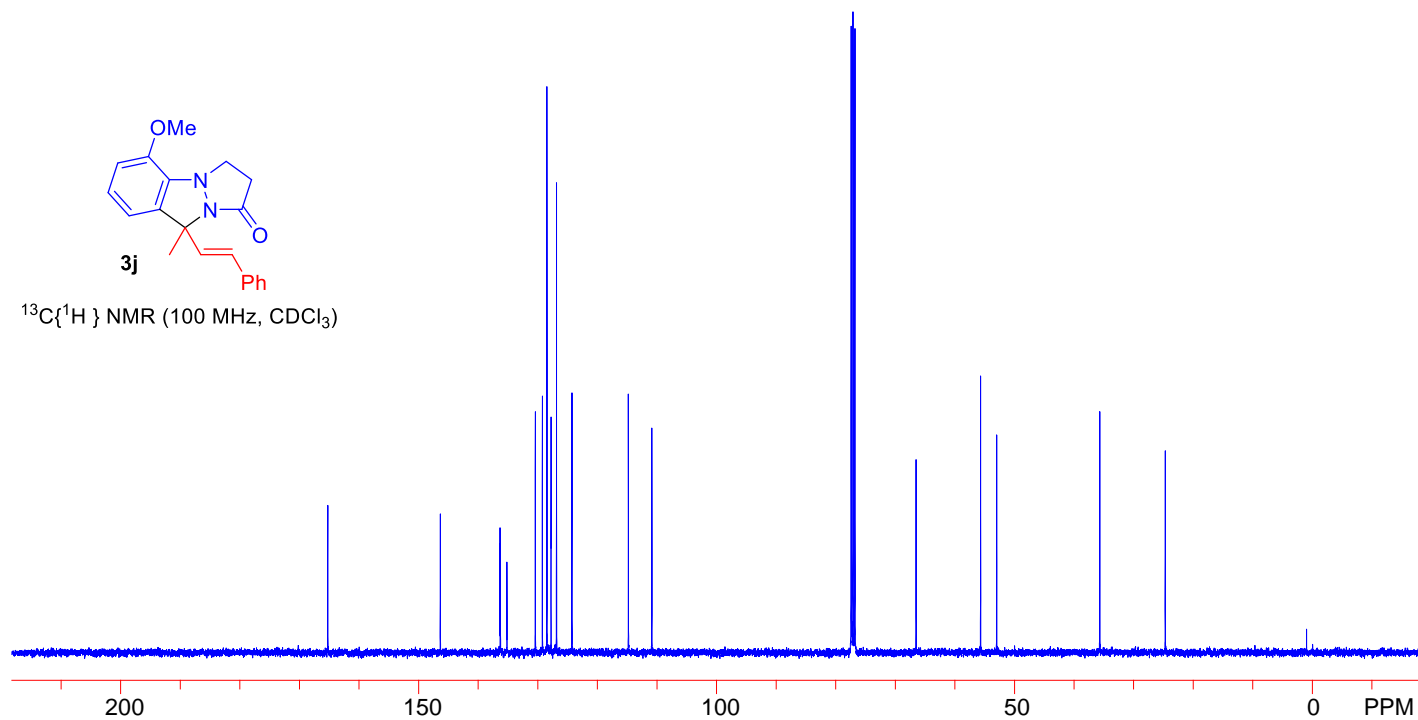
$^1\text{H NMR}$ (400 MHz, CDCl_3)



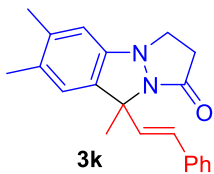
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136.321
136.259
135.164
130.405
129.222
128.457
127.762
126.842
124.263
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55.703
53.005
35.727
24.743



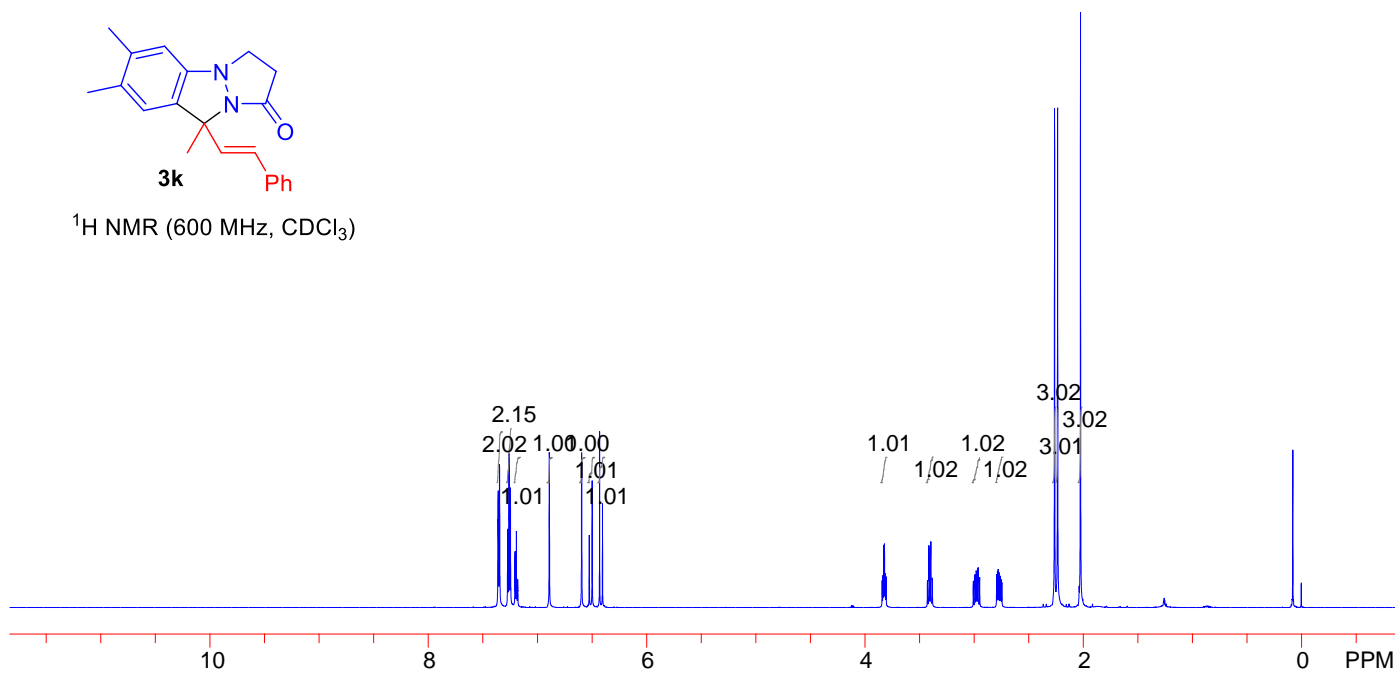
$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)



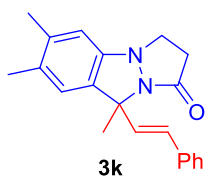
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7.208
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7.204
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7.194
7.190
7.183
7.181
7.180
6.892
6.597
6.527
6.500
6.432
6.406
3.845
3.837
3.831
3.823
3.817
3.809
3.430
3.416
3.412
3.402
3.398
3.385
3.009
2.995
2.992
2.983
2.978
2.968
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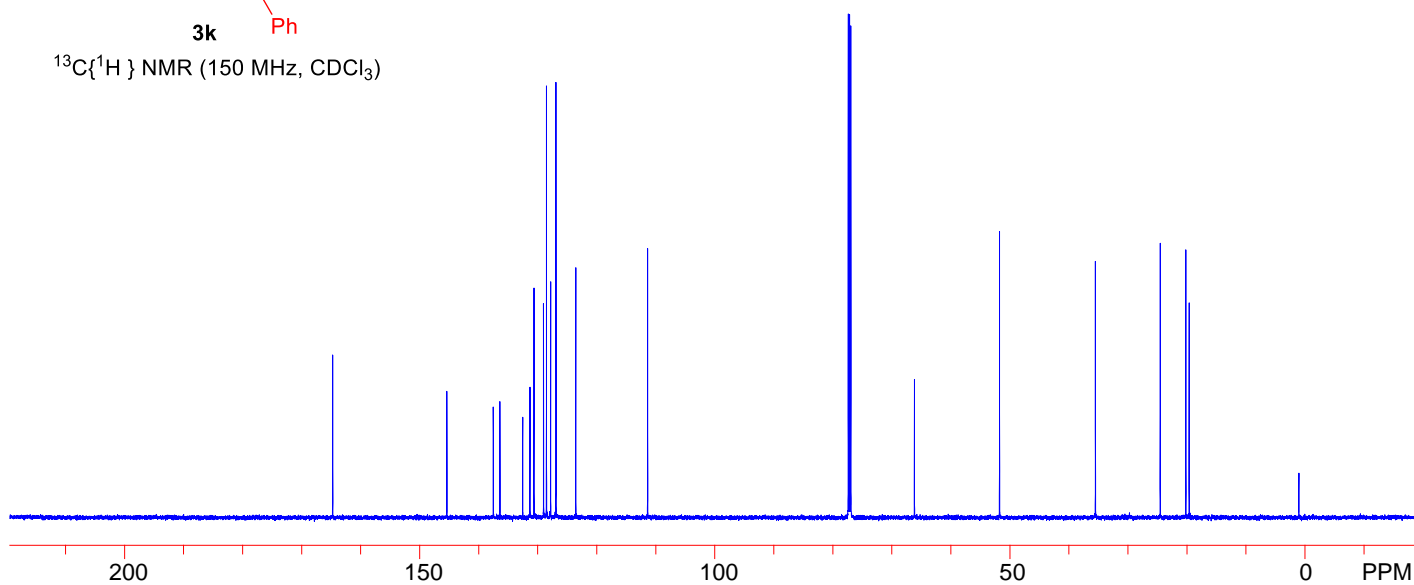
^1H NMR (600 MHz, CDCl_3)



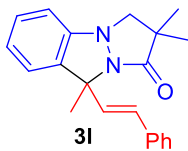
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127.803
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51.781
35.549
24.578
20.253
19.680



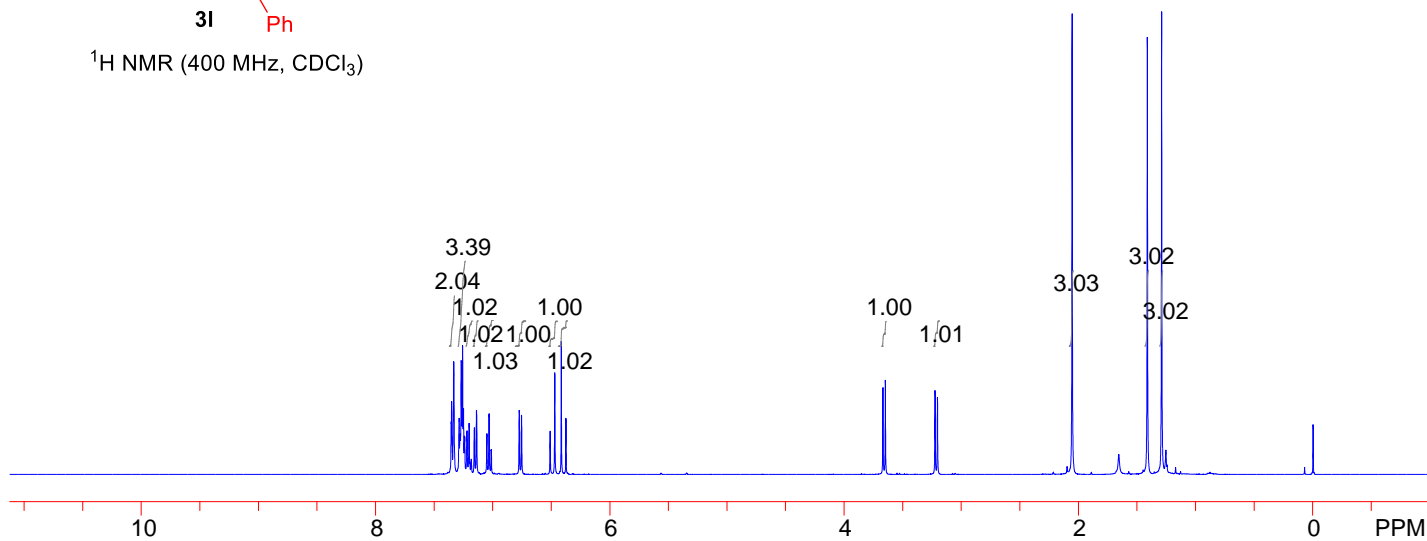
$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)



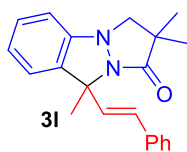
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7.286
7.279
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7.268
7.264
7.256
7.249
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7.238
7.222
7.219
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7.201
7.195
7.183
7.156
7.138
7.050
7.048
7.031
7.029
7.013
7.011
6.773
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1.292



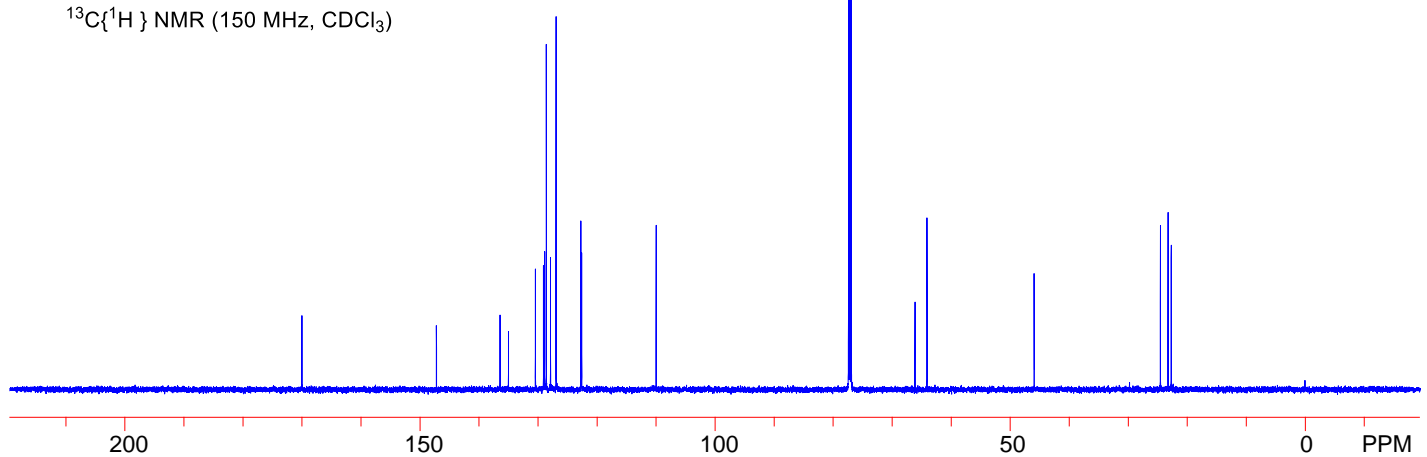
^1H NMR (400 MHz, CDCl_3)



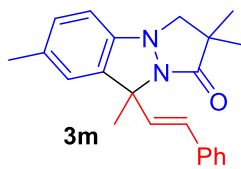
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127.878
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22.776



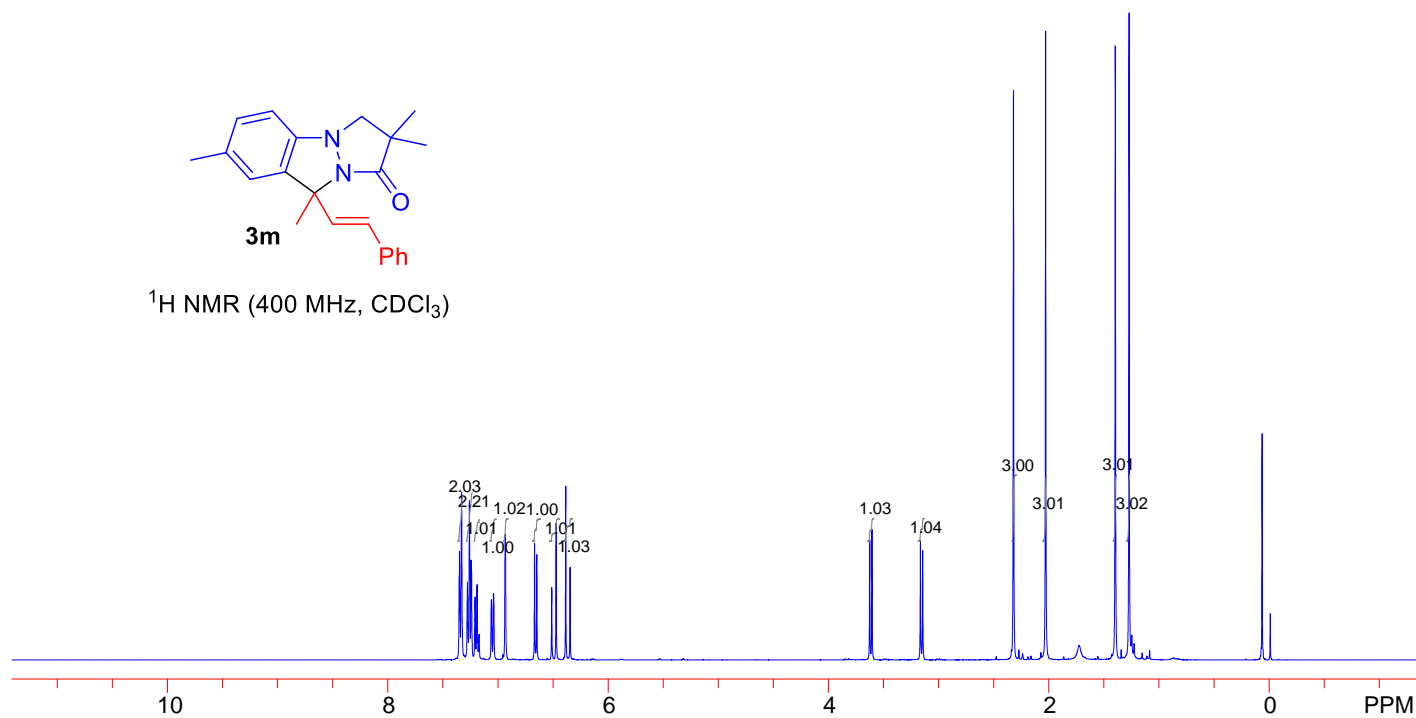
$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)



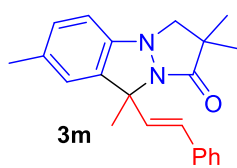
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7.190
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7.060
7.059
7.040
6.934
6.668
6.648
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2.030
1.398
1.273



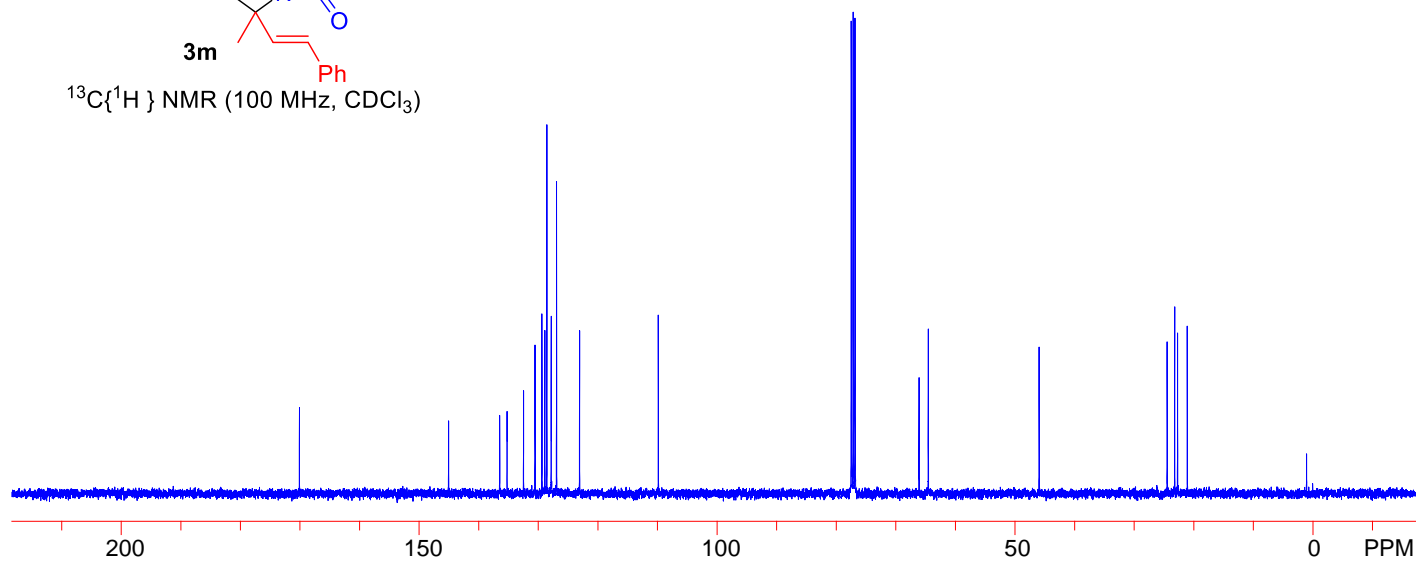
^1H NMR (400 MHz, CDCl_3)



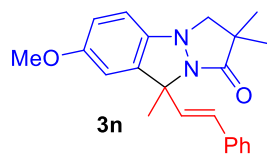
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132.476
130.543
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127.833
126.931
123.063
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77.160
76.842
66.109
64.561
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24.518
23.265
22.775
21.148



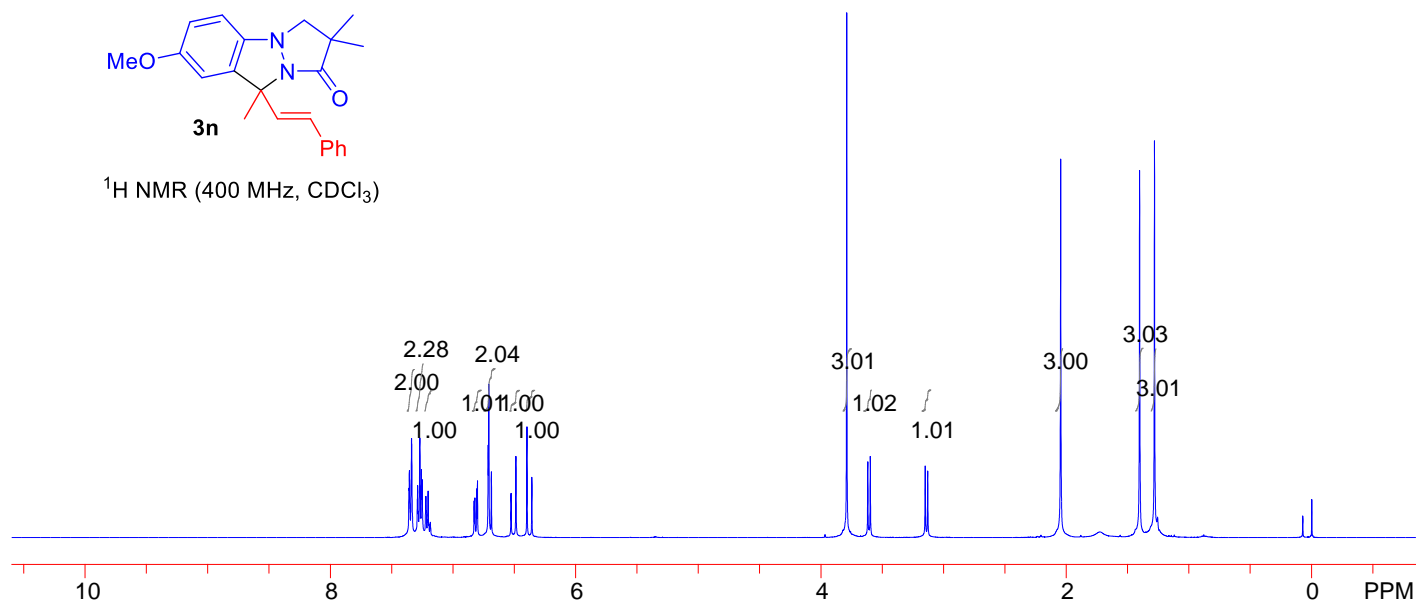
$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)



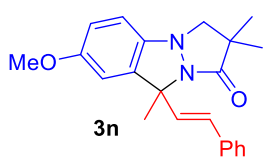
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7.224
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7.209
7.203
7.197
7.188
7.185
7.182
6.828
6.822
6.807
6.800
6.713
6.708
6.687
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1.282



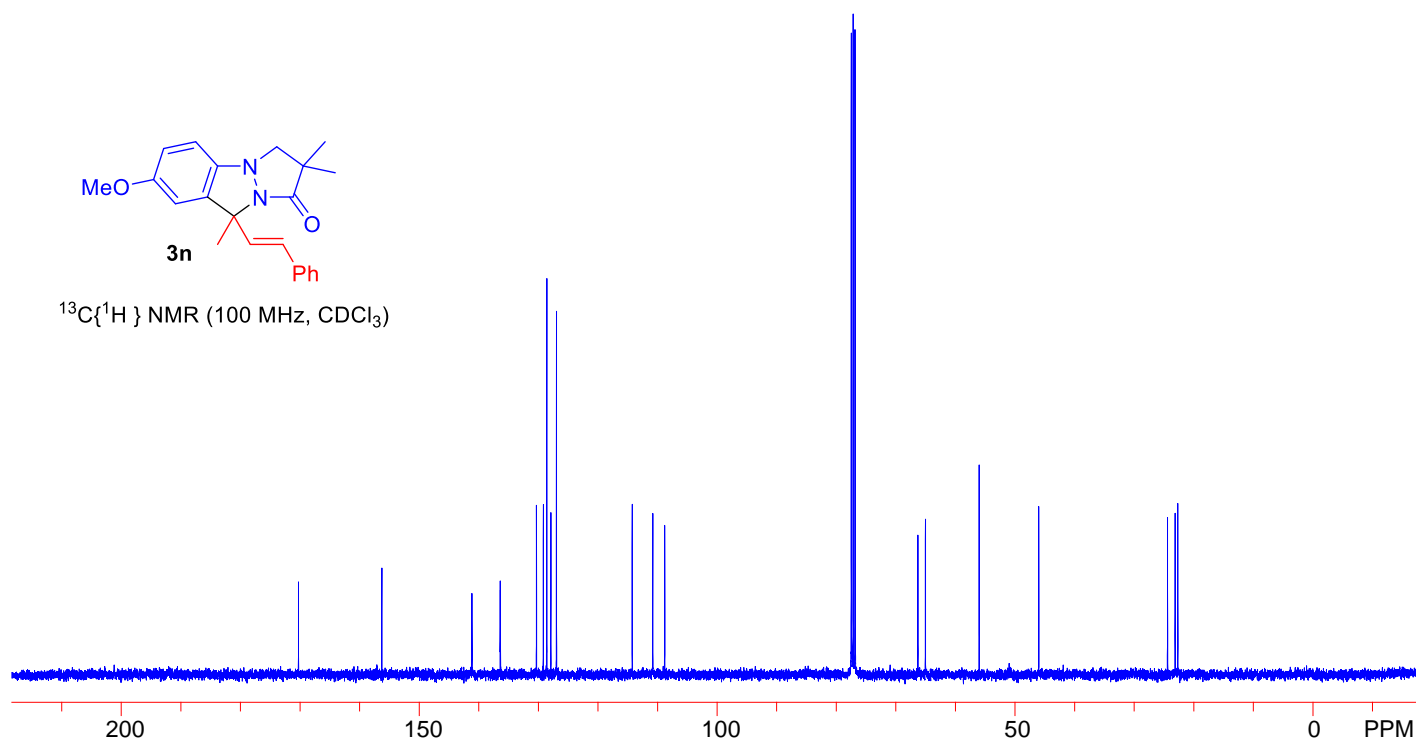
^1H NMR (400 MHz, CDCl_3)

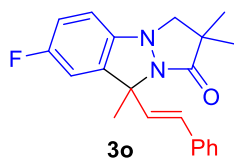
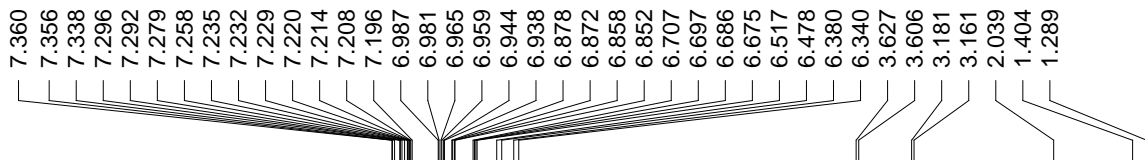


170.252
156.271
141.140
136.397
136.350
130.306
129.150
128.574
127.892
126.955
114.237
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66.313
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46.048
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23.186
22.739

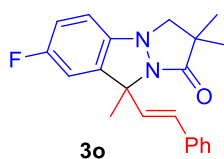
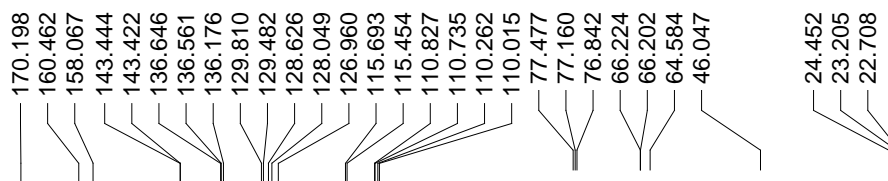
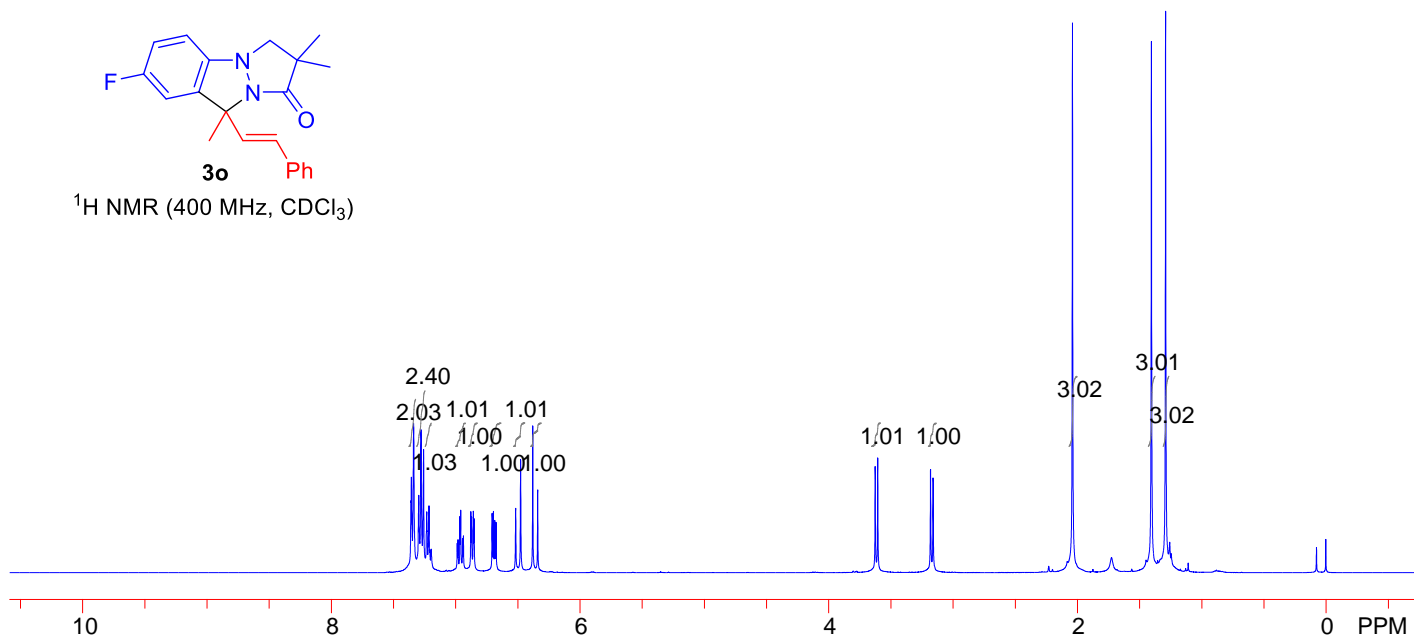


$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)

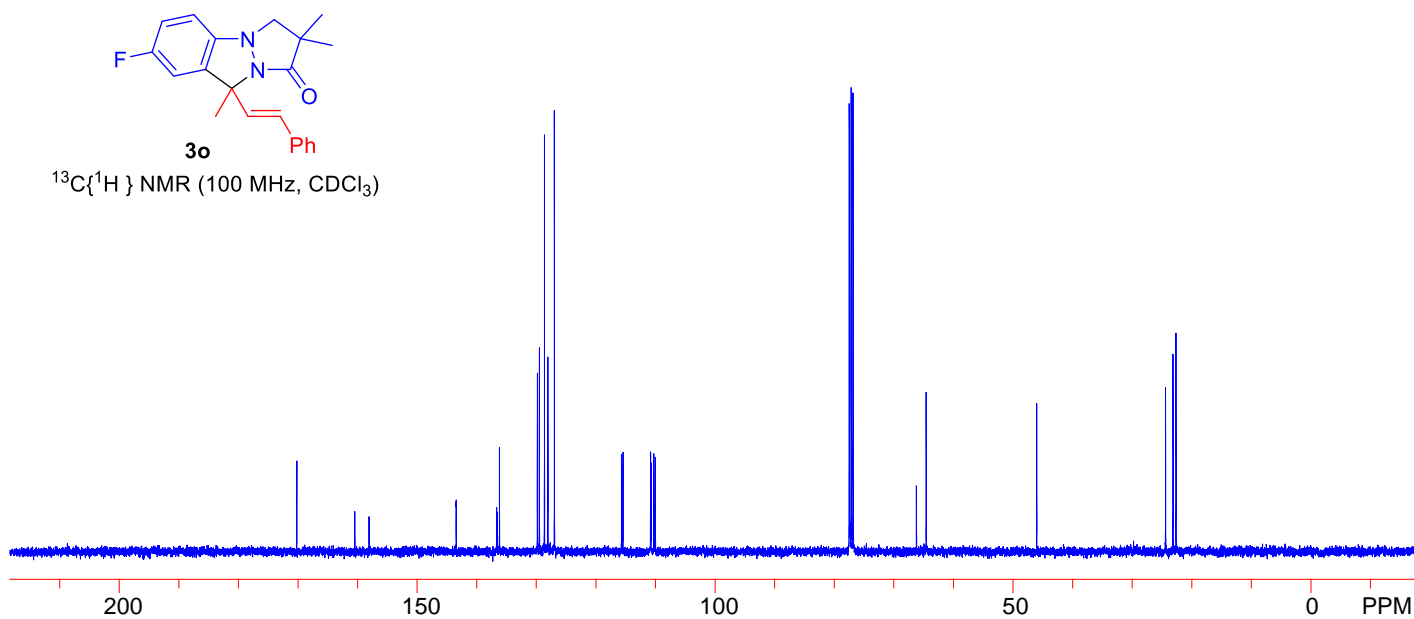


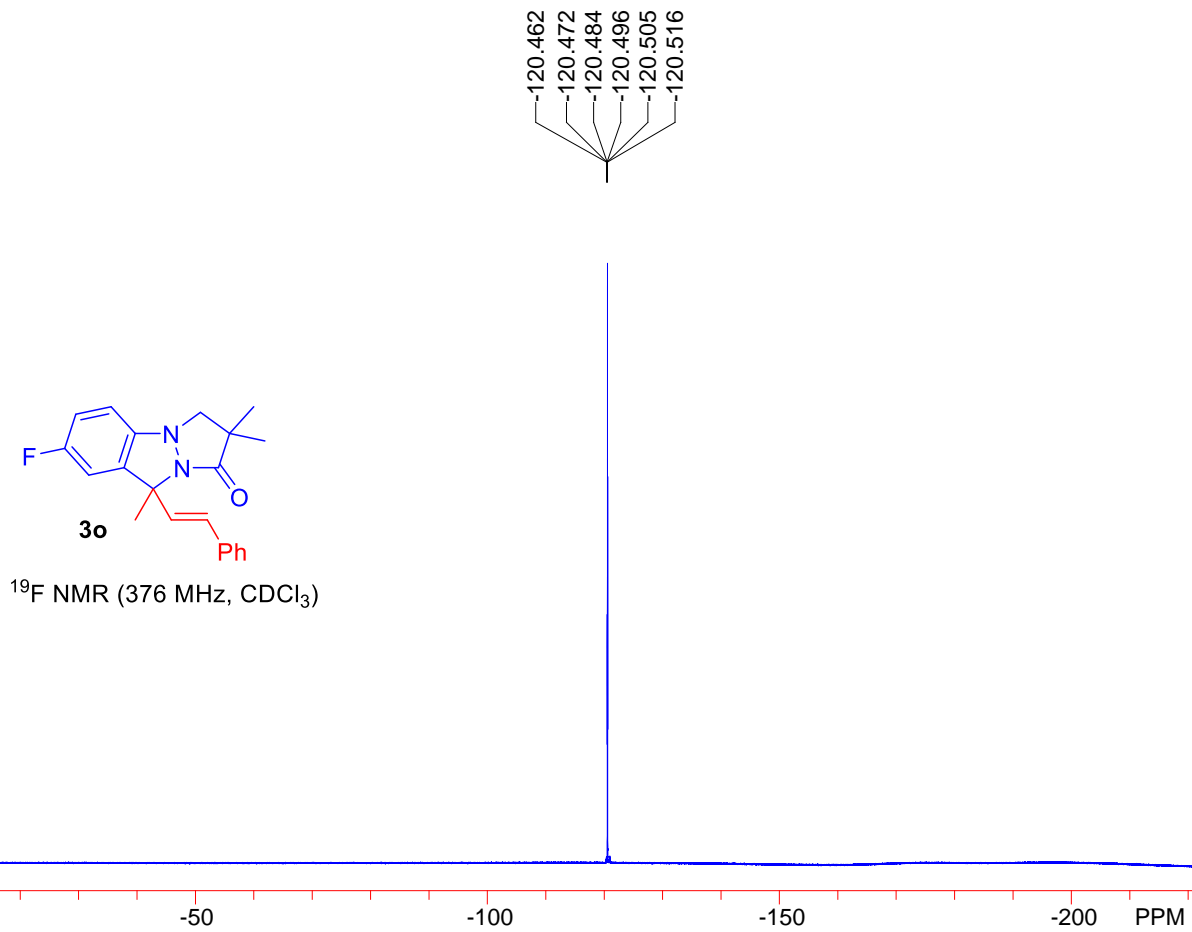


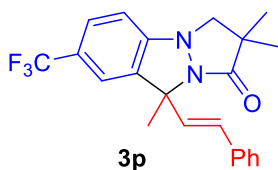
^1H NMR (400 MHz, CDCl_3)



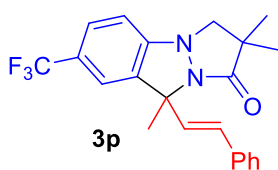
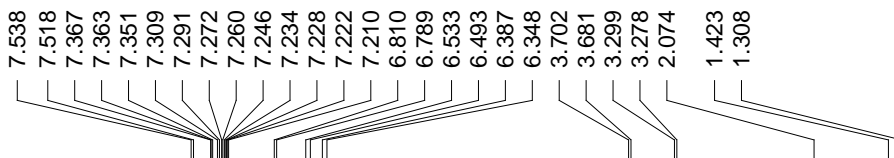
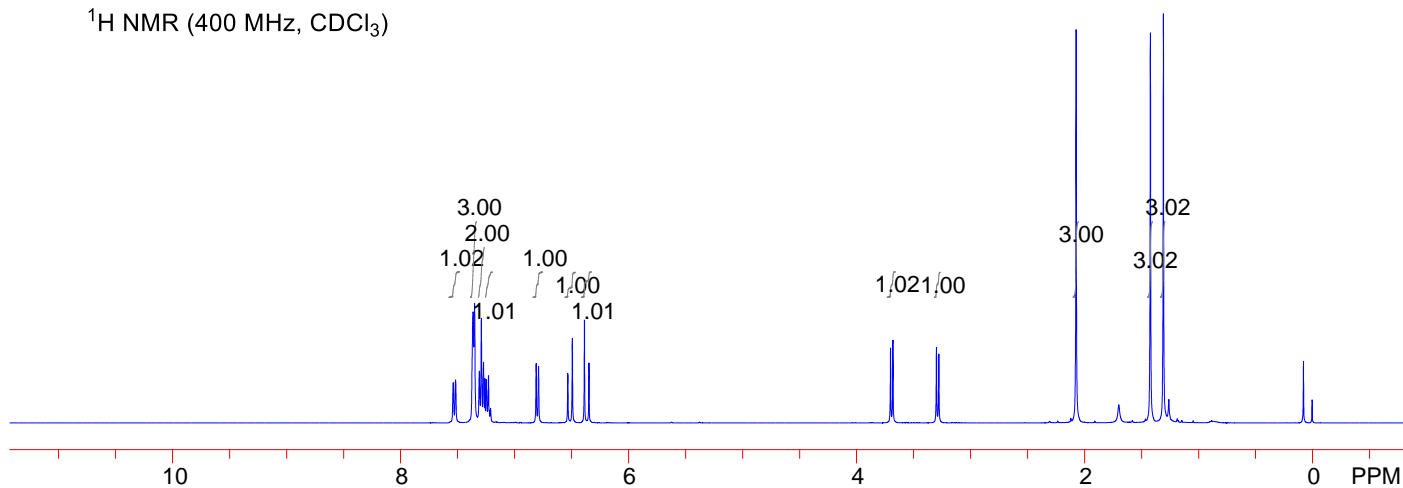
$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)



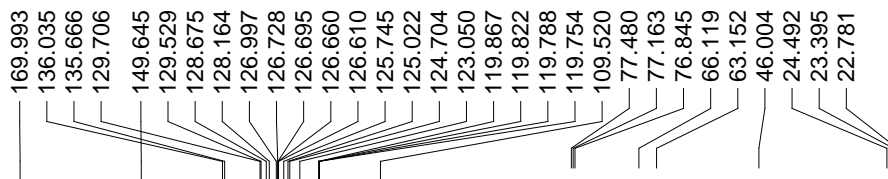
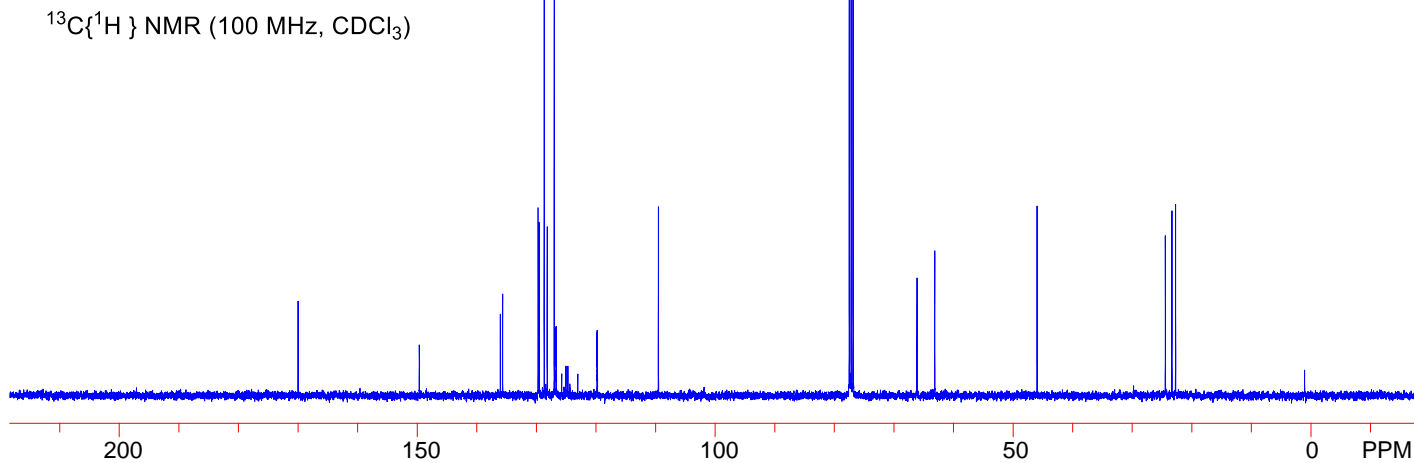


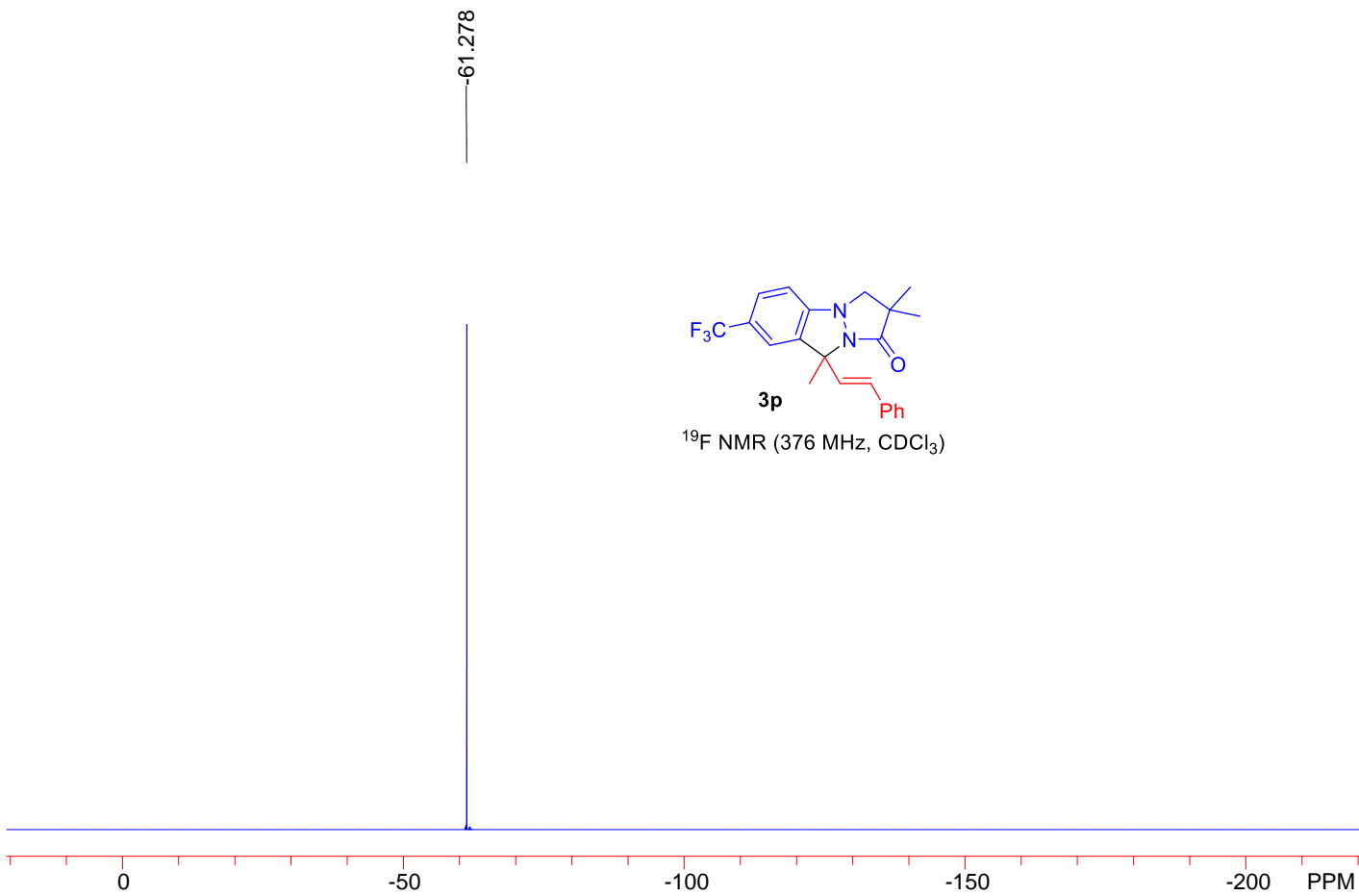


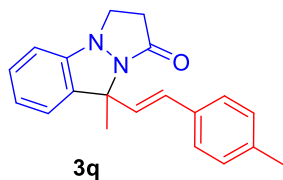
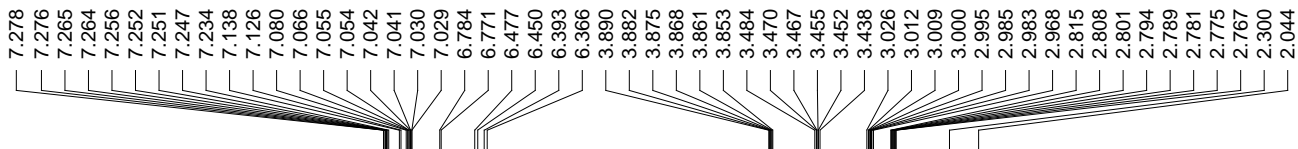
^1H NMR (400 MHz, CDCl_3)



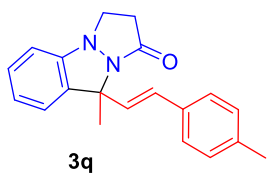
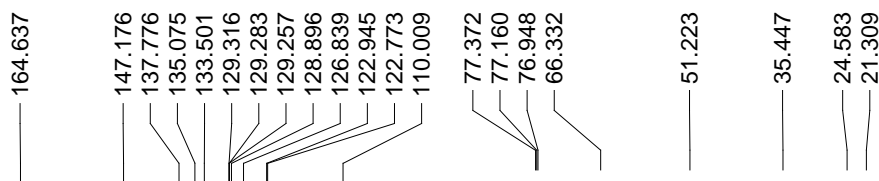
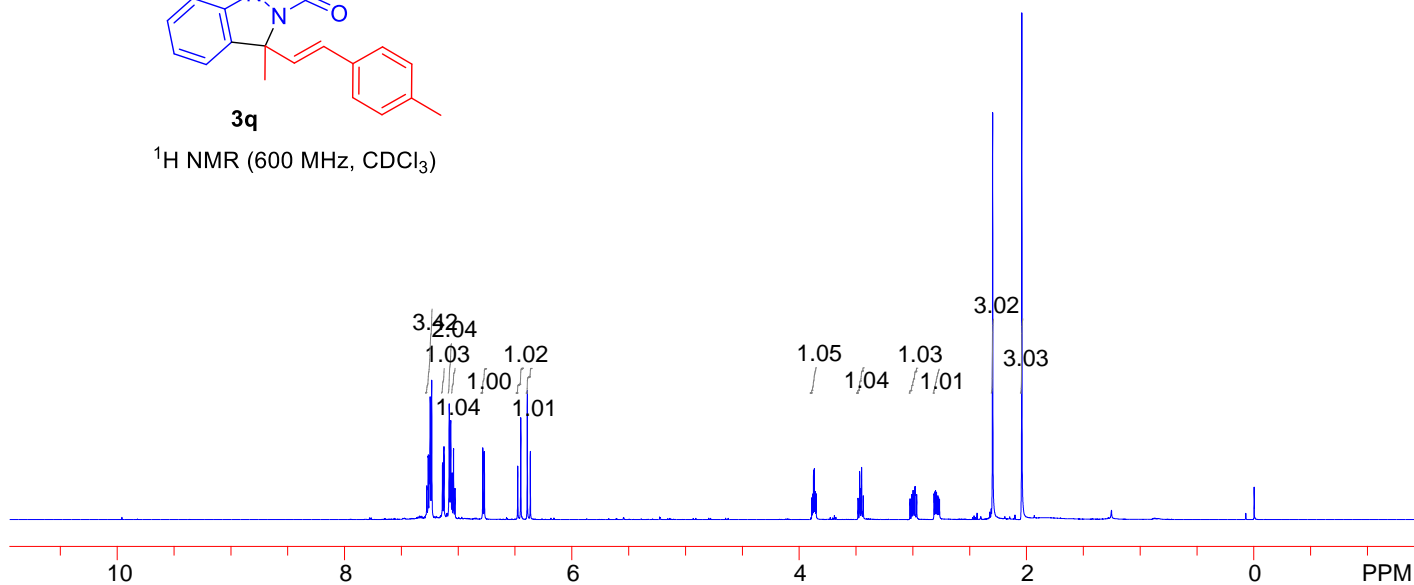
$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)



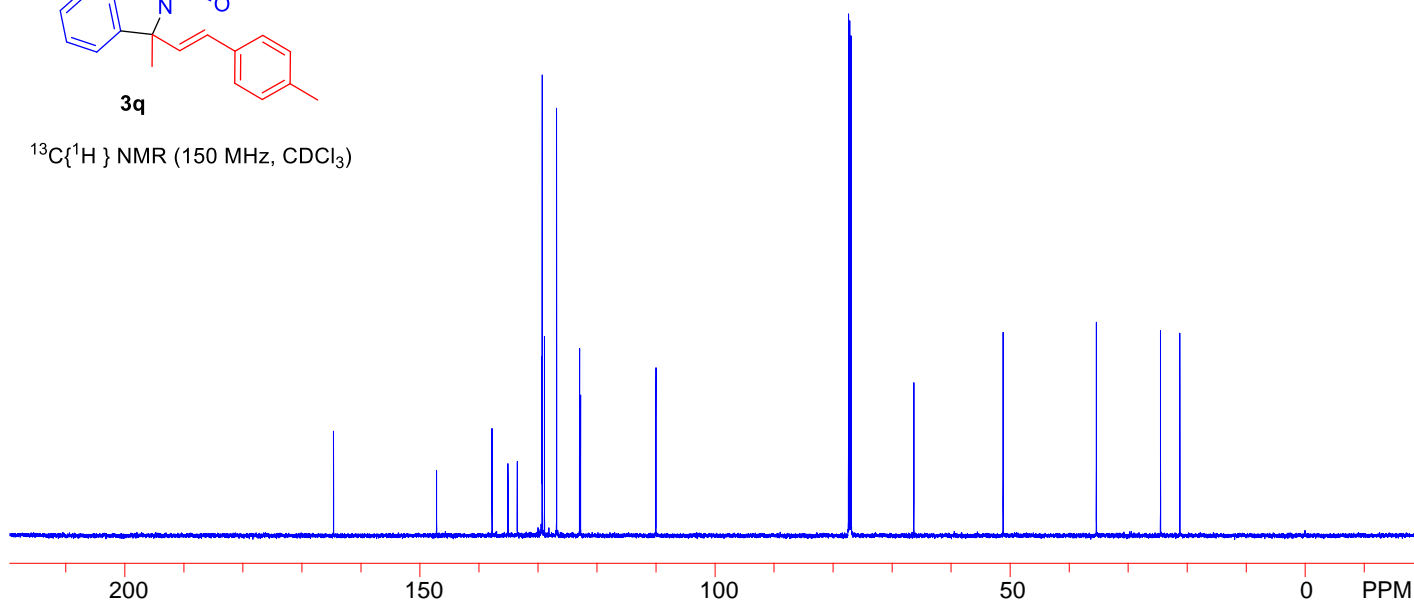




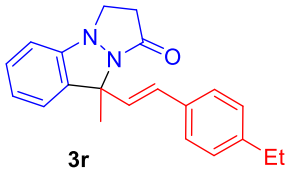
$^1\text{H NMR}$ (600 MHz, CDCl_3)



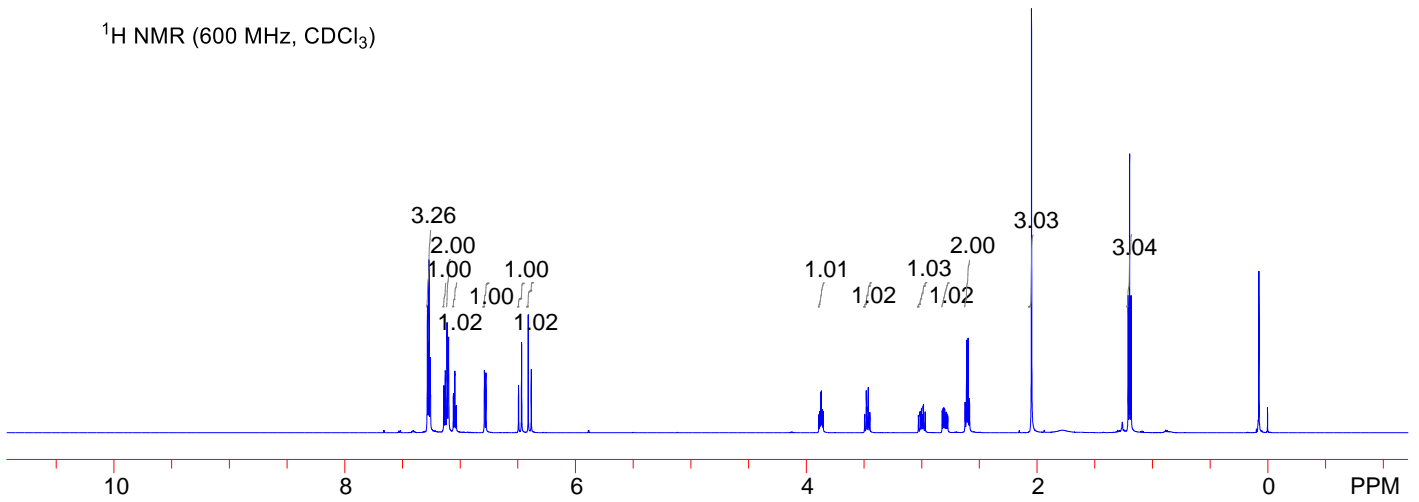
$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)



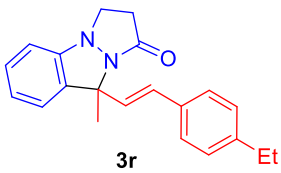
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1.201
1.188



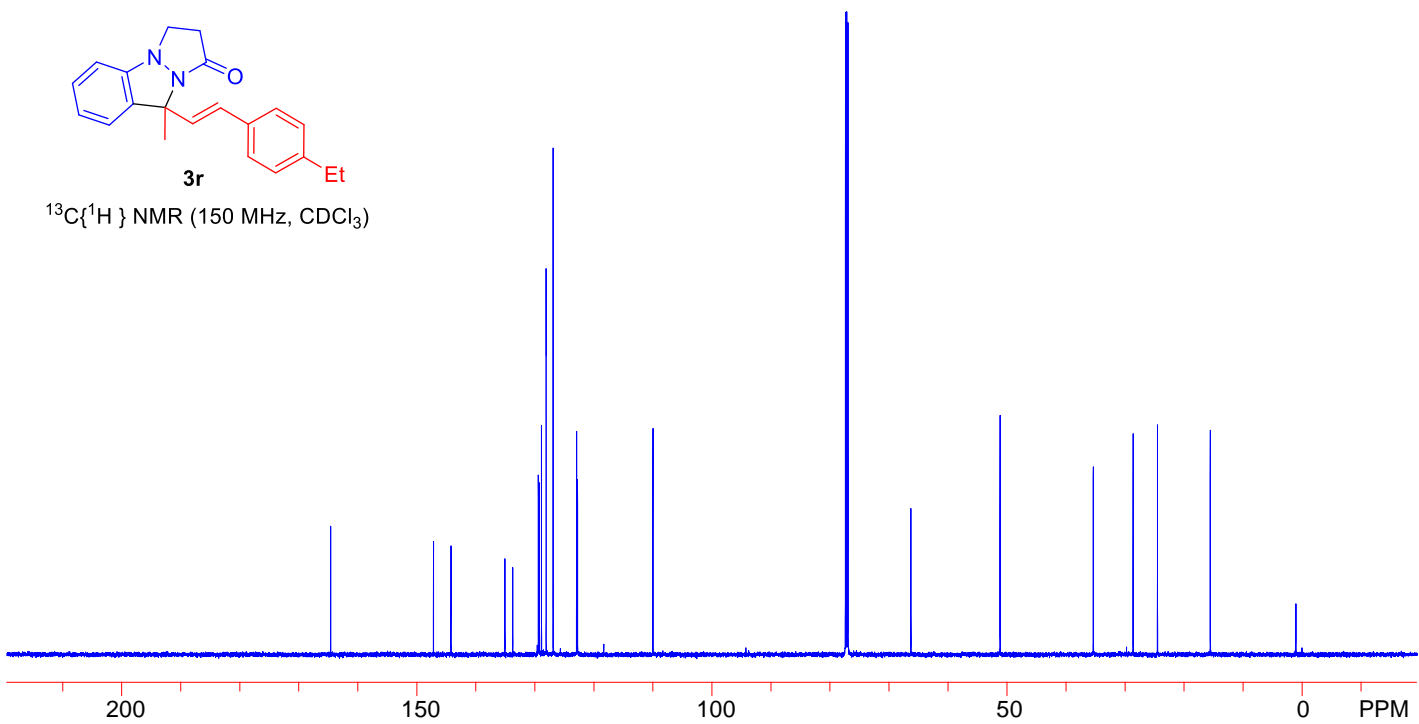
$^1\text{H NMR}$ (600 MHz, CDCl_3)



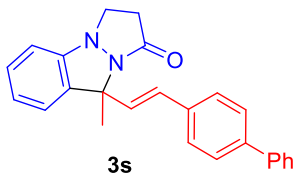
164.594
147.177
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135.063
133.741
129.403
129.256
128.876
128.076
126.899
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77.372
77.160
76.948
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51.210
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24.568
15.626



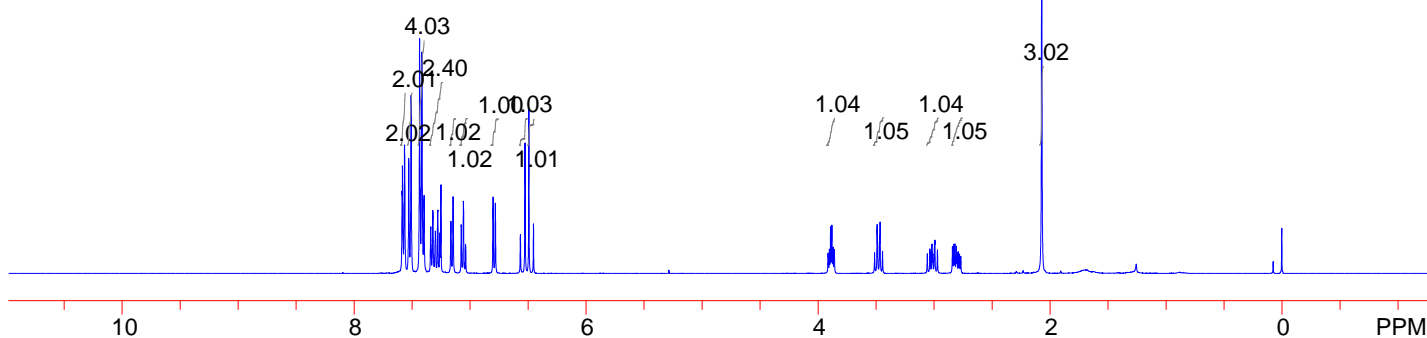
$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)



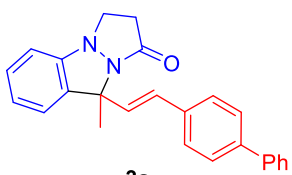
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7.396
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7.321
7.299
7.297
7.280
7.278
7.261
7.258
7.251
7.165
7.147
7.077
7.075
7.058
7.039
6.802
6.782
6.566
6.526
6.493
6.454
3.914
3.904
3.893
3.882
3.872
3.860
3.513
3.482
3.488
3.470
3.466
3.445
3.059
3.037
3.033
3.019
3.011
2.996
2.993
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2.830
2.821
2.809
2.802
2.790
2.780
2.769
2.071



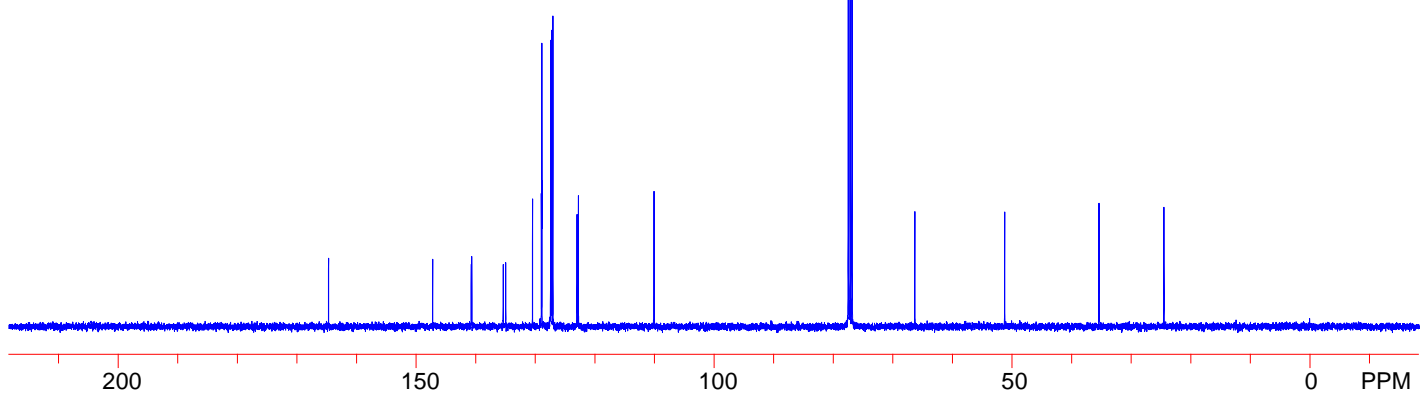
$^1\text{H NMR}$ (400 MHz, CDCl_3)



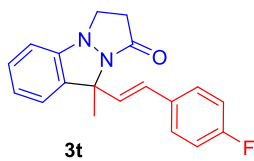
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140.741
140.649
147.220
135.364
134.962
130.458
128.976
128.903
128.881
127.440
127.373
127.251
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122.766
110.072
77.478
77.160
76.842
66.319
51.258
35.445
24.553



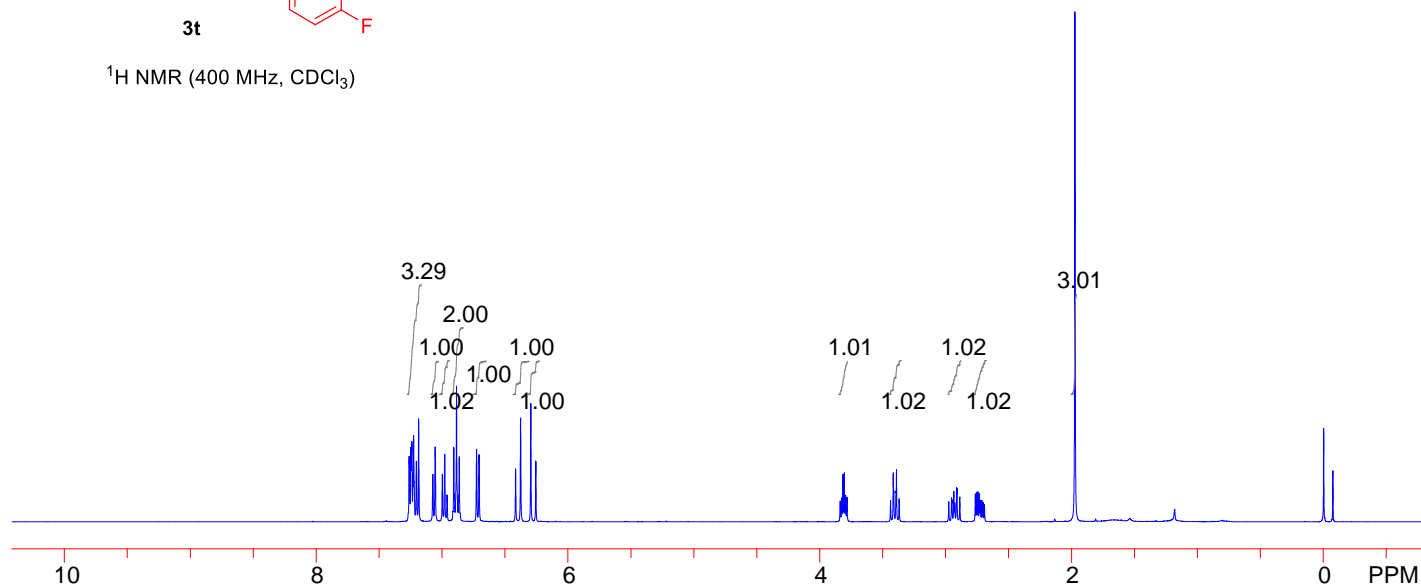
$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)



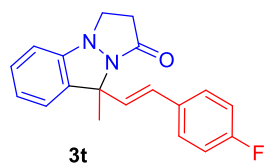
7.262
7.257
7.248
7.240
7.231
7.226
7.222
7.205
7.203
7.186
7.073
7.055
6.998
6.997
6.979
6.978
6.961
6.959
6.914
6.907
6.902
6.885
6.868
6.863
6.726
6.706
6.416
6.376
6.295
6.255
3.837
3.825
3.815
3.804
3.794
3.782
3.782
3.437
3.415
3.411
3.394
3.390
3.368
2.975
2.953
2.949
2.935
2.927
2.913
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2.753
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2.732
2.724
2.713
2.703
2.692
1.974



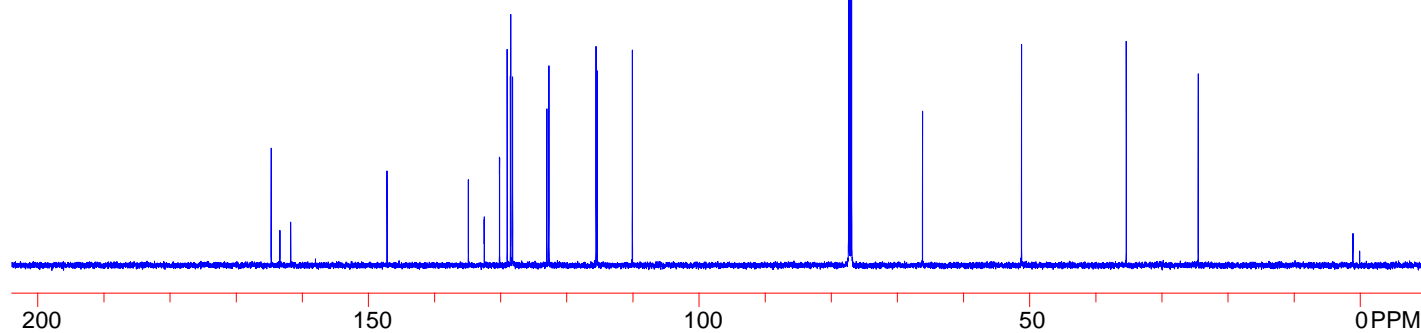
$^1\text{H NMR}$ (400 MHz, CDCl_3)



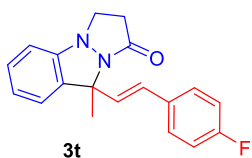
164.714
163.391
161.755
147.186
134.884
132.485
132.465
130.173
130.157
129.010
128.518
128.471
128.192
123.003
122.708
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115.438
110.095
77.372
77.160
76.948
66.220
51.256
35.420
24.539



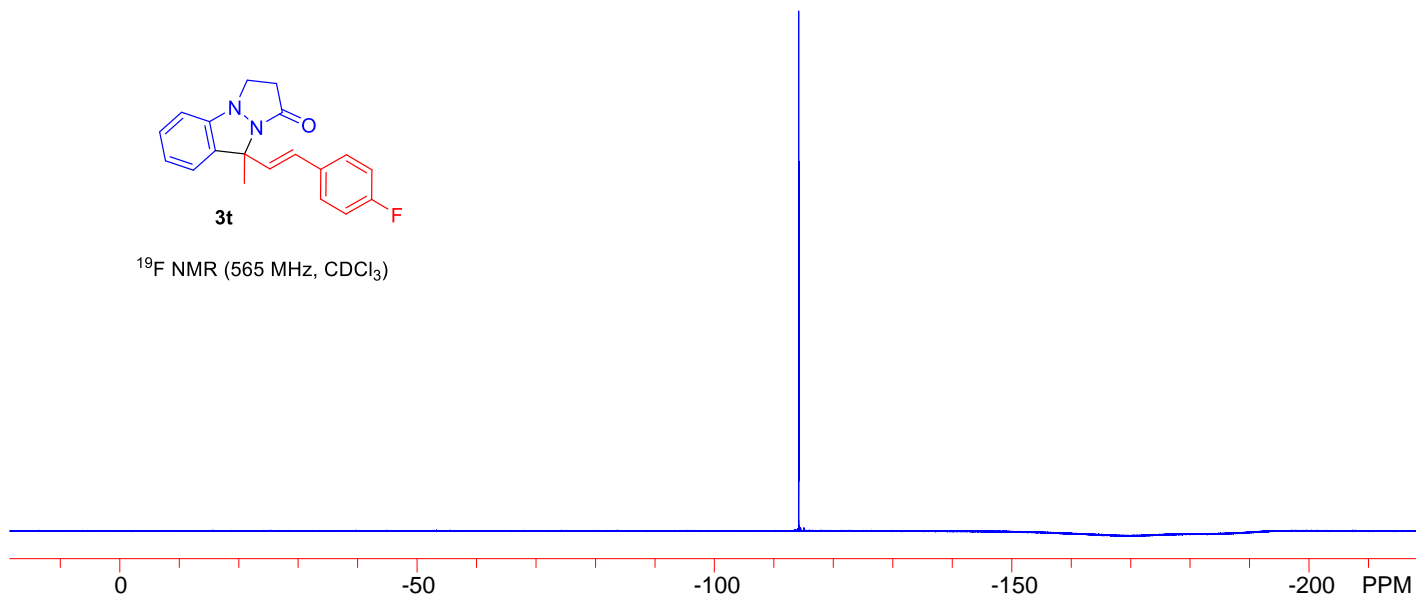
$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)



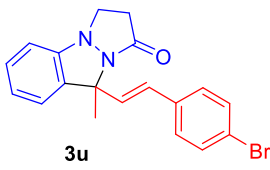
-114.097
-114.106
-114.114
-114.120
-114.131
-114.145



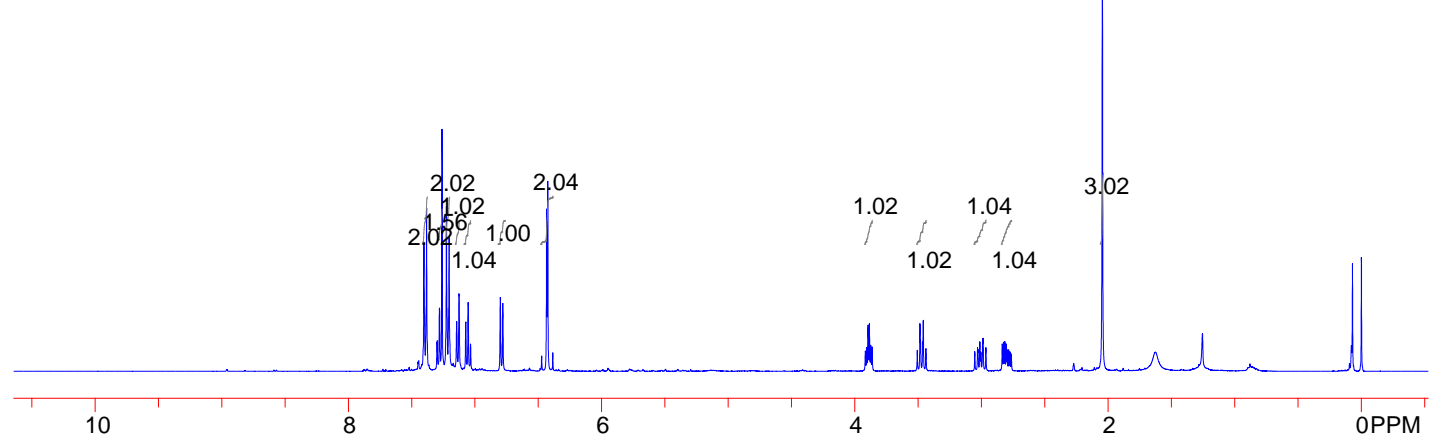
^{19}F NMR (565 MHz, CDCl_3)



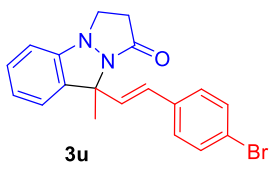
7.404
7.382
7.301
7.298
7.281
7.279
7.260
7.225
7.204
7.144
7.126
7.072
7.053
7.036
7.034
6.800
6.780
6.473
6.434
6.425
6.385
3.918
3.907
3.896
3.885
3.874
3.864
3.507
3.486
3.482
3.464
3.460
3.439
3.053
3.031
3.027
3.013
3.005
2.991
2.987
2.965
2.836
2.826
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2.805
2.796
2.785
2.775
2.764
2.046



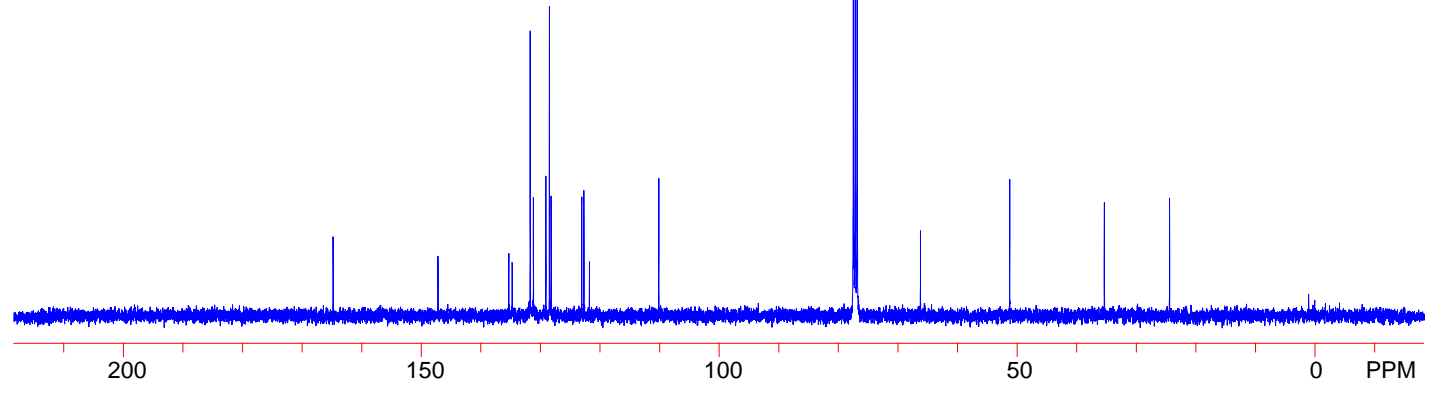
¹H NMR (400 MHz, CDCl₃)



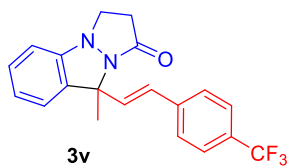
164.793
147.185
135.303
134.728
131.712
131.168
129.079
128.487
128.193
123.051
122.690
121.769
110.132
77.478
77.160
76.842
66.230
51.277
35.396
24.463



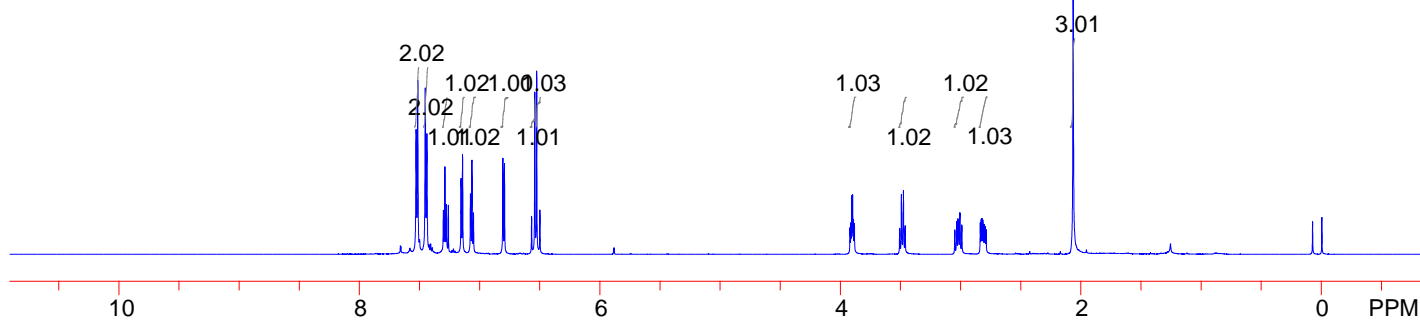
¹³C{¹H} NMR (100 MHz, CDCl₃)



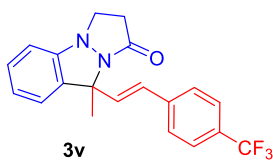
7.528
7.514
7.452
7.438
7.301
7.288
7.276
7.260
7.154
7.142
7.076
7.064
7.051
6.806
6.793
6.567
6.541
6.525
6.498
3.919
3.912
3.905
3.897
3.890
3.883
3.507
3.492
3.490
3.475
3.461
3.049
3.034
3.032
3.022
3.017
3.007
3.005
2.990
2.837
2.830
2.823
2.816
2.810
2.803
2.796
2.789
2.066



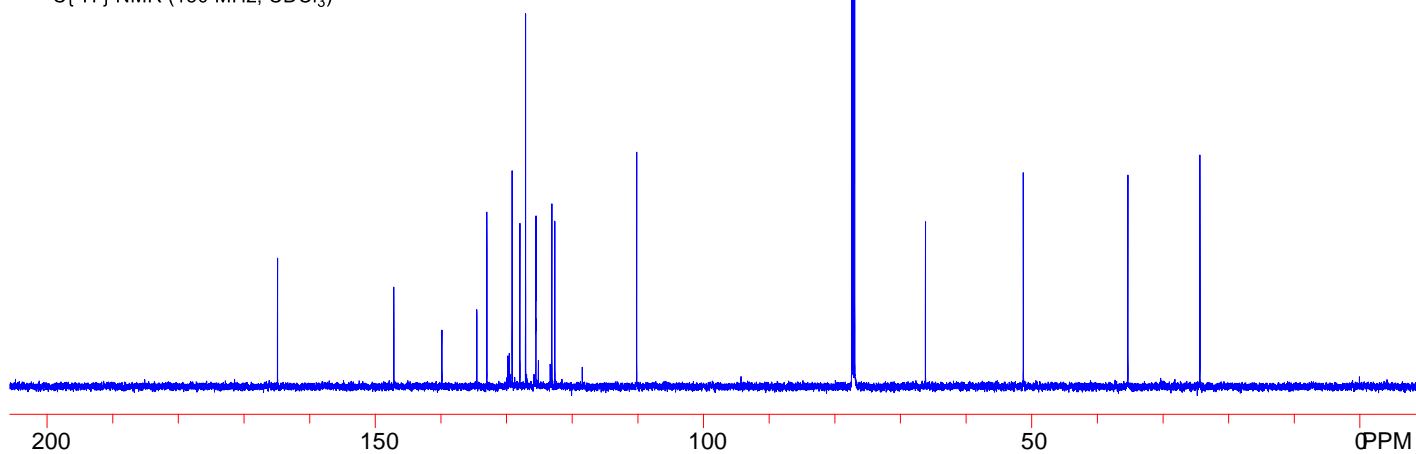
$^1\text{H NMR}$ (600 MHz, CDCl_3)

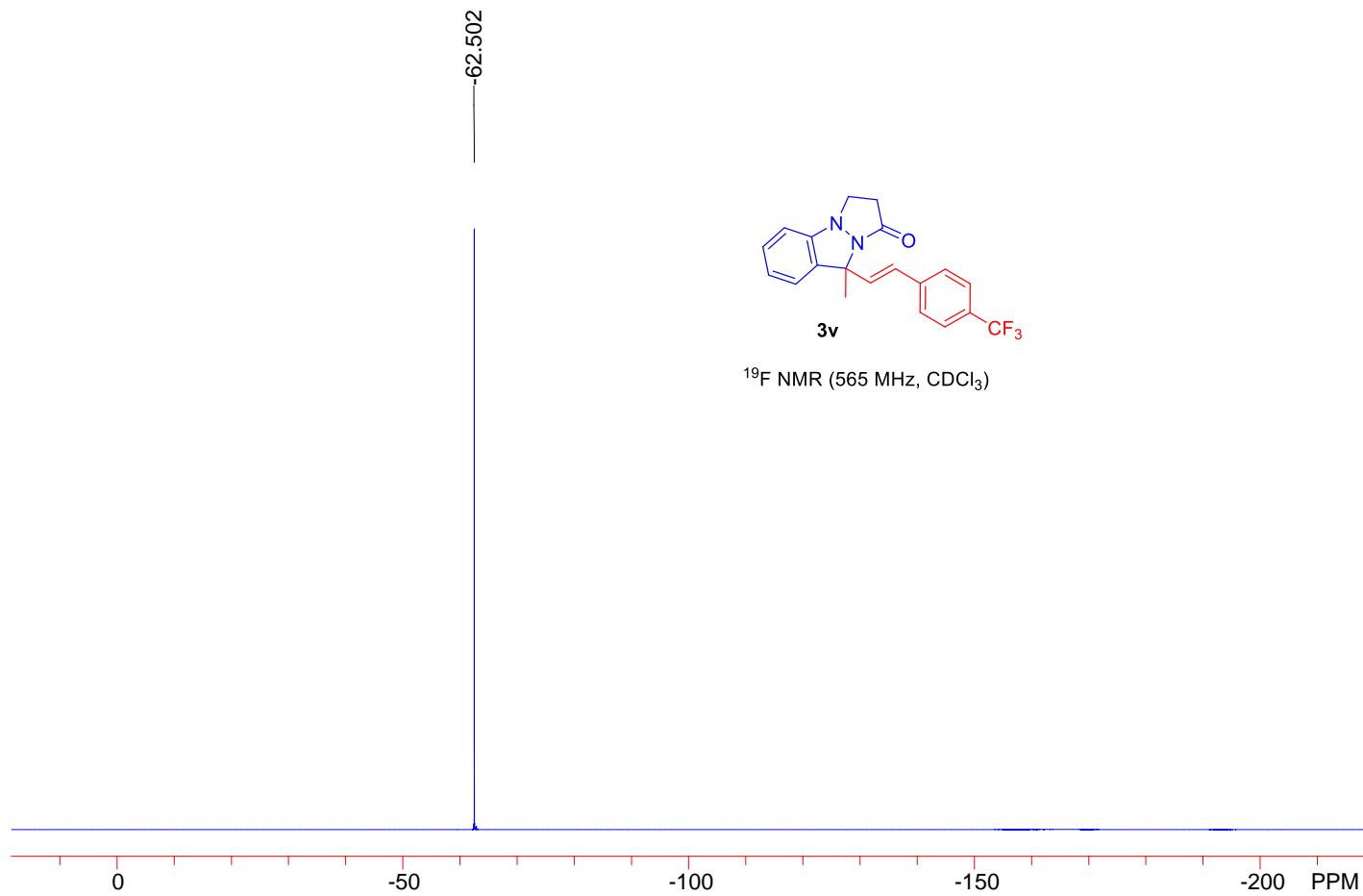


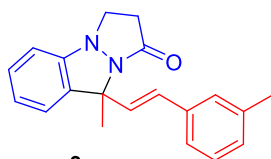
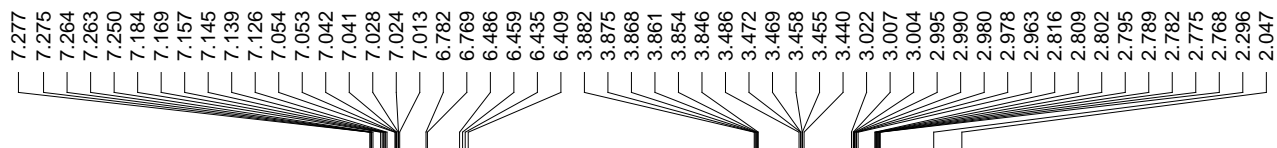
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147.182
139.851
132.999
129.798
129.587
129.158
127.966
127.091
125.561
125.543
125.520
125.488
125.154
123.351
123.096
122.642
110.173
77.372
77.160
76.948
66.171
51.280
35.356
24.385



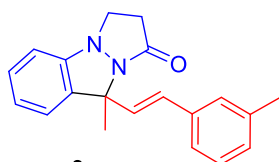
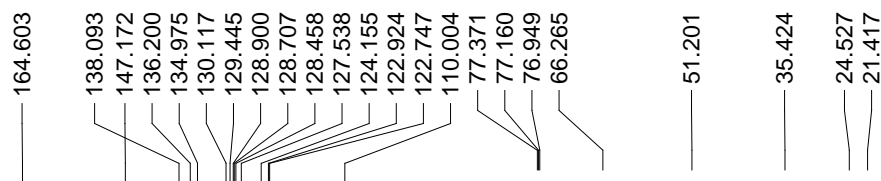
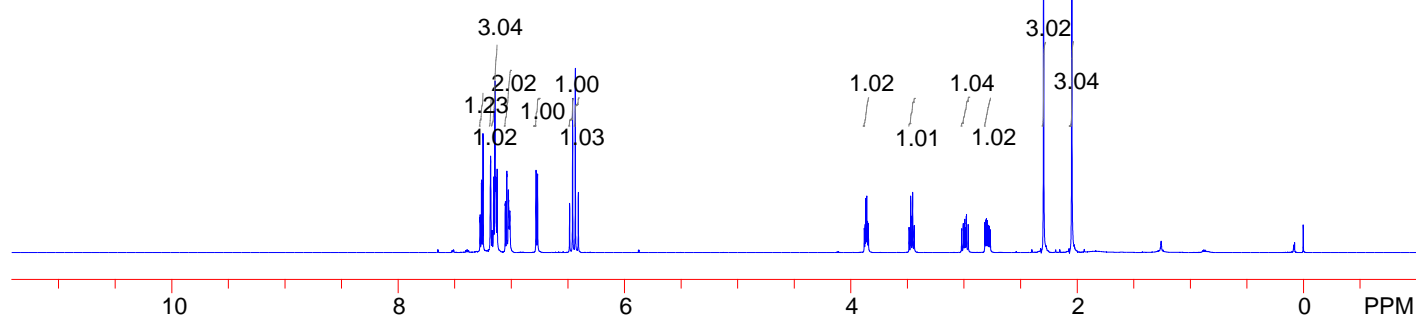
$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)



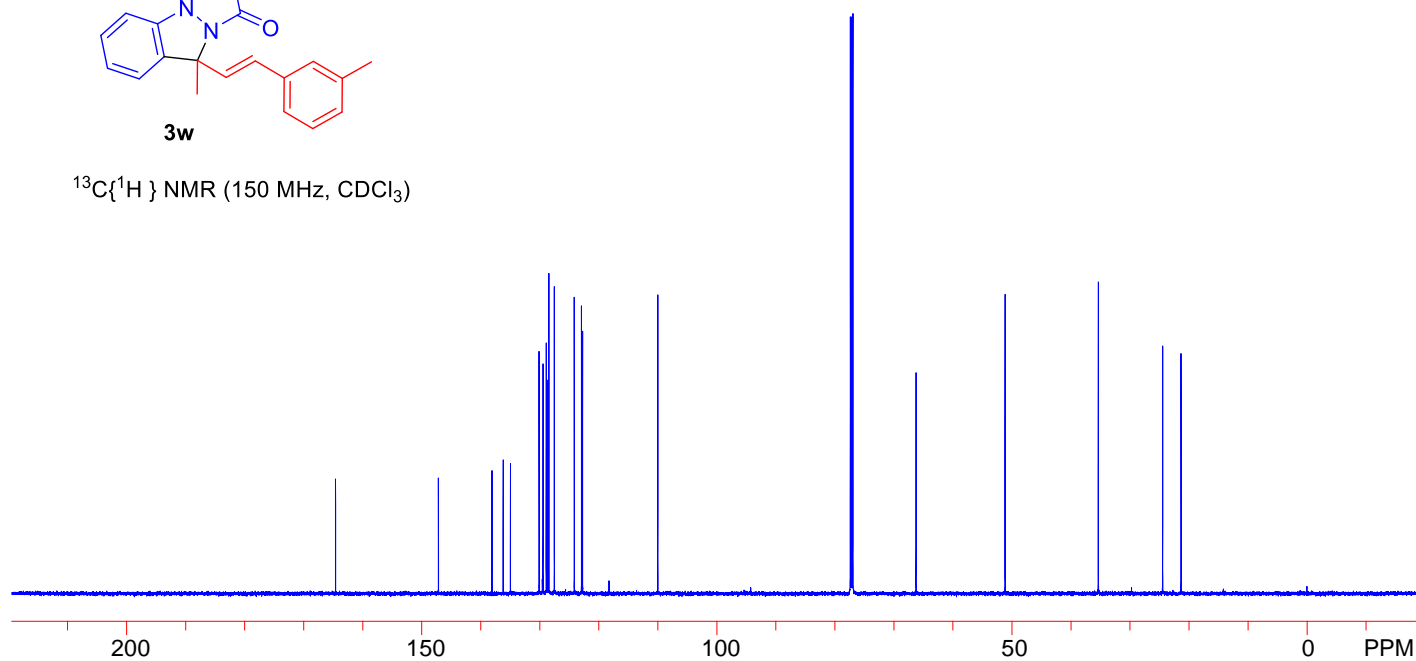


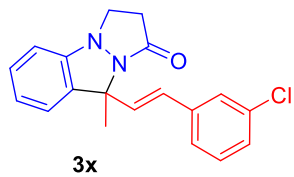


^1H NMR (600 MHz, CDCl_3)

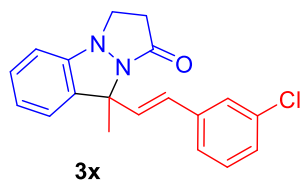
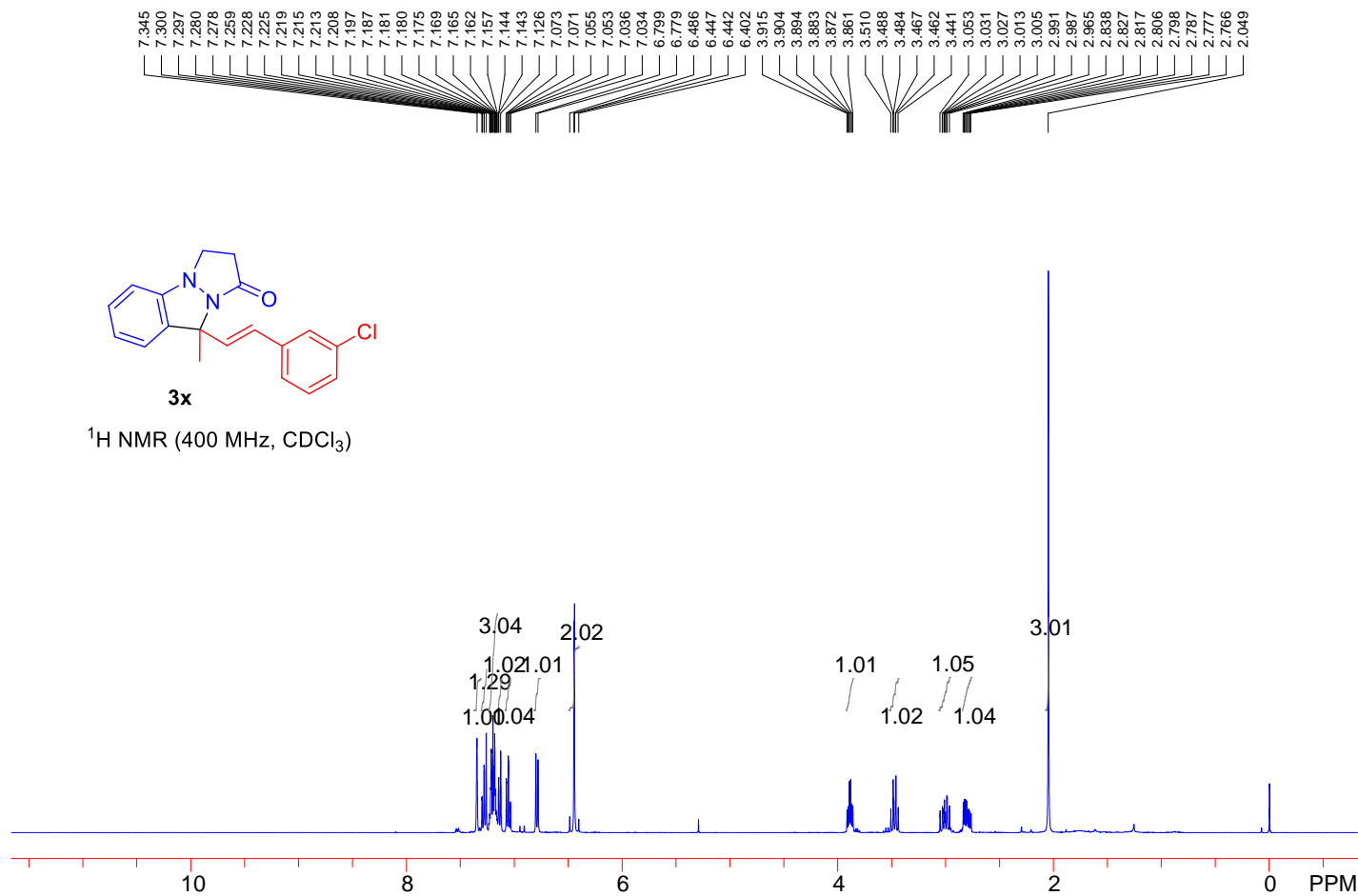


$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)

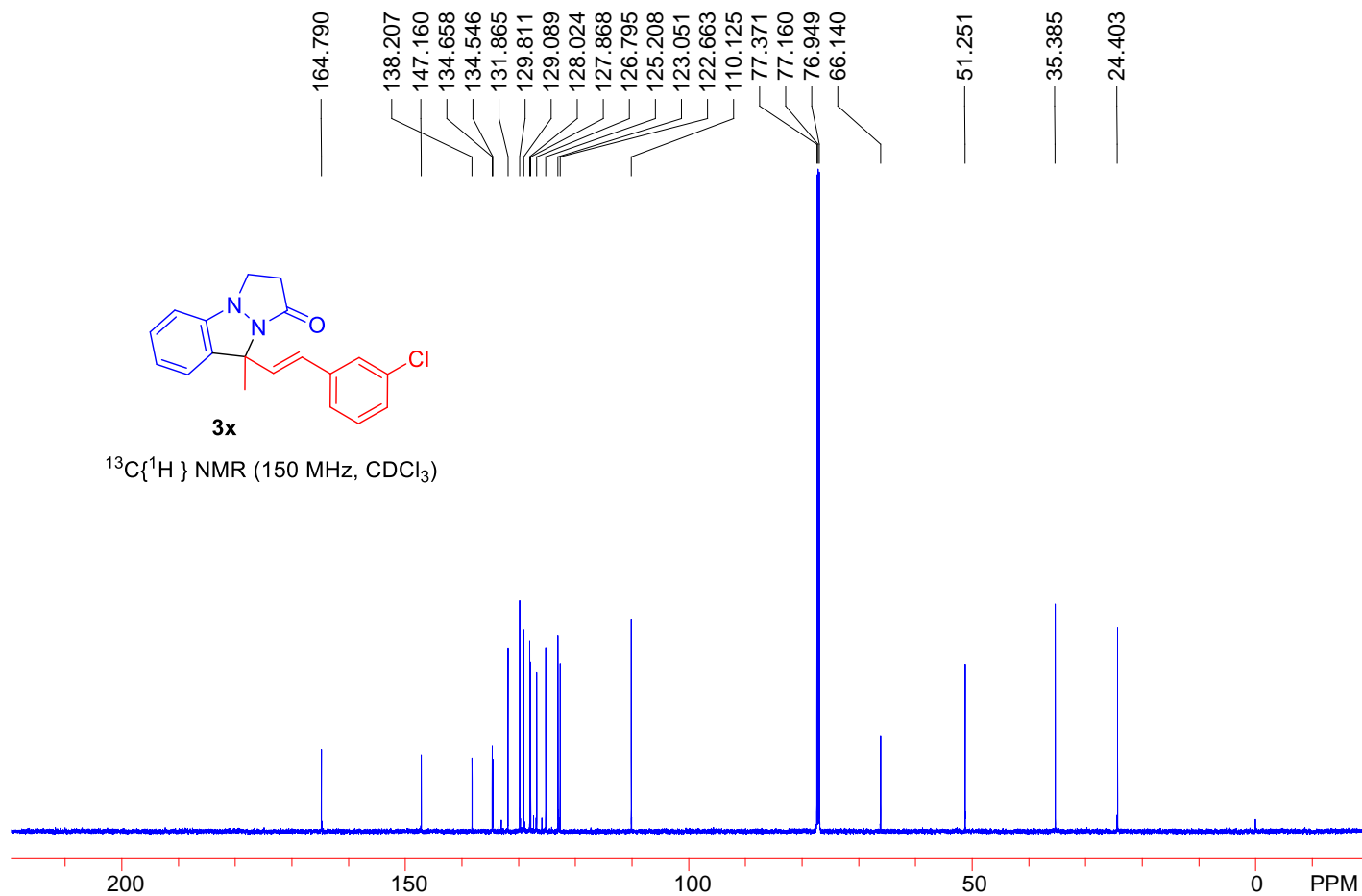




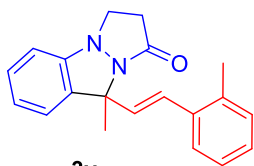
$^1\text{H NMR}$ (400 MHz, CDCl_3)



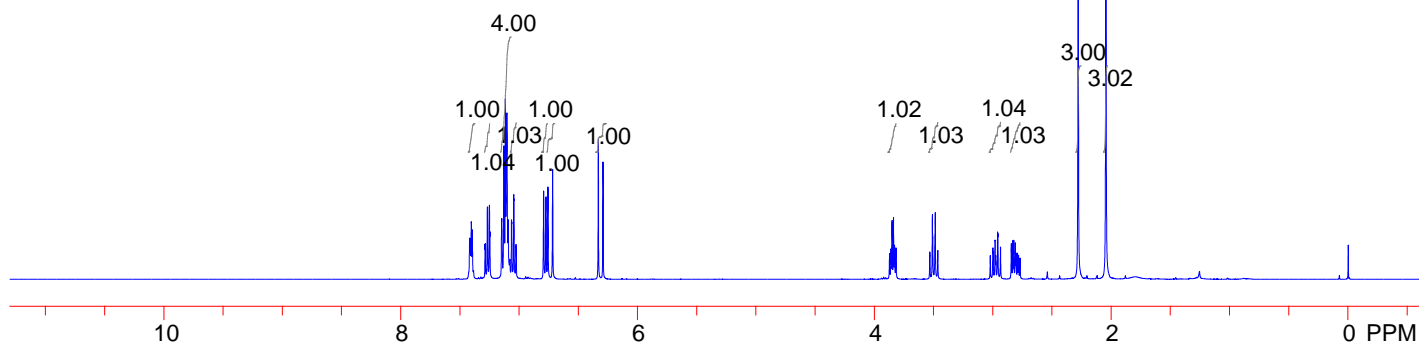
$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)



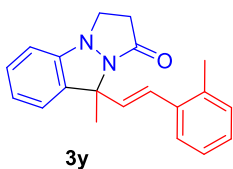
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7.288
7.285
7.268
7.266
7.251
7.247
7.147
7.147
7.129
7.117
7.108
7.104
7.093
7.079
7.064
7.062
7.046
7.044
7.027
7.025
6.793
6.774
6.757
6.717
6.332
6.293
3.873
3.861
3.852
3.839
3.830
3.818
3.533
3.511
3.508
3.487
3.466
3.023
3.001
2.998
2.983
2.976
2.961
2.958
2.936
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2.833
2.824
2.812
2.805
2.793
2.784
2.772
2.280
2.046



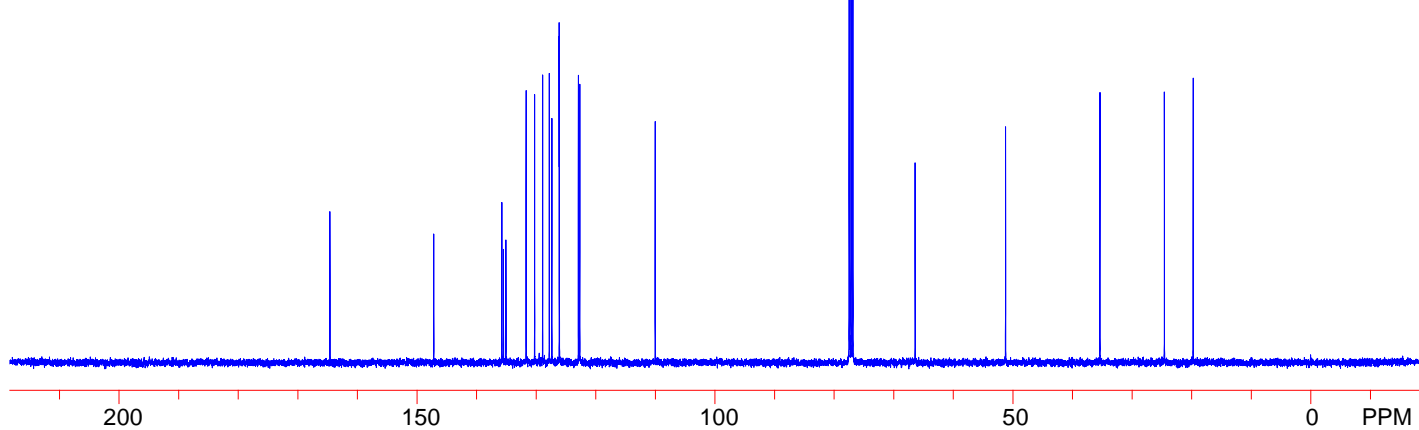
$^1\text{H NMR}$ (400 MHz, CDCl_3)



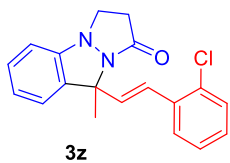
164.616
147.181
135.757
135.479
135.070
131.691
130.258
128.911
127.800
127.363
126.130
126.109
122.917
122.676
110.027
77.478
77.160
76.842
66.418
51.246
35.434
24.632
19.808



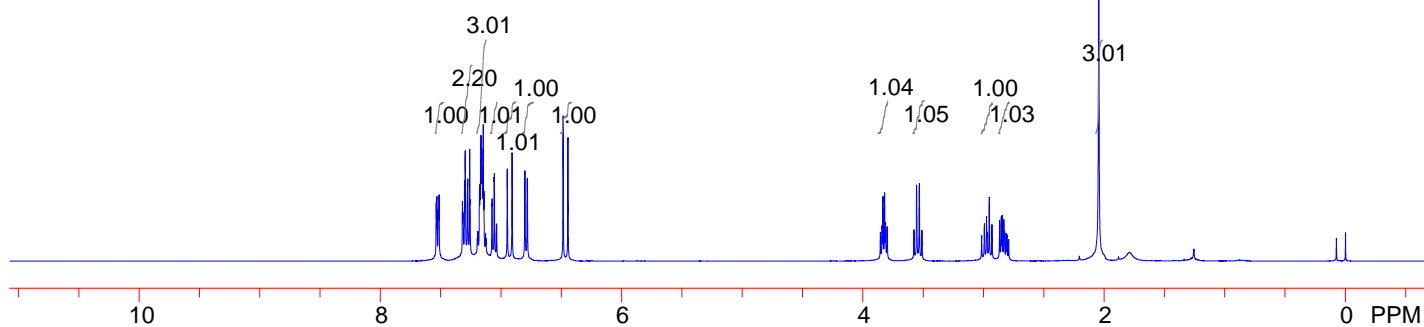
$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)



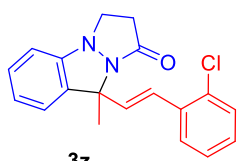
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7.531
7.518
7.513
7.320
7.316
7.313
7.301
7.296
7.277
7.275
7.259
7.256
7.196
7.192
7.178
7.173
7.165
7.161
7.159
7.155
7.146
7.141
7.128
7.123
7.075
7.073
7.056
7.054
7.038
7.035
6.948
6.908
6.801
6.781
6.484
6.444
3.853
3.839
3.831
3.818
3.810
3.797
3.575
3.553
3.530
3.509
3.014
2.991
2.974
2.969
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2.866
2.852
2.844
2.831
2.826
2.812
2.804
2.791
2.044



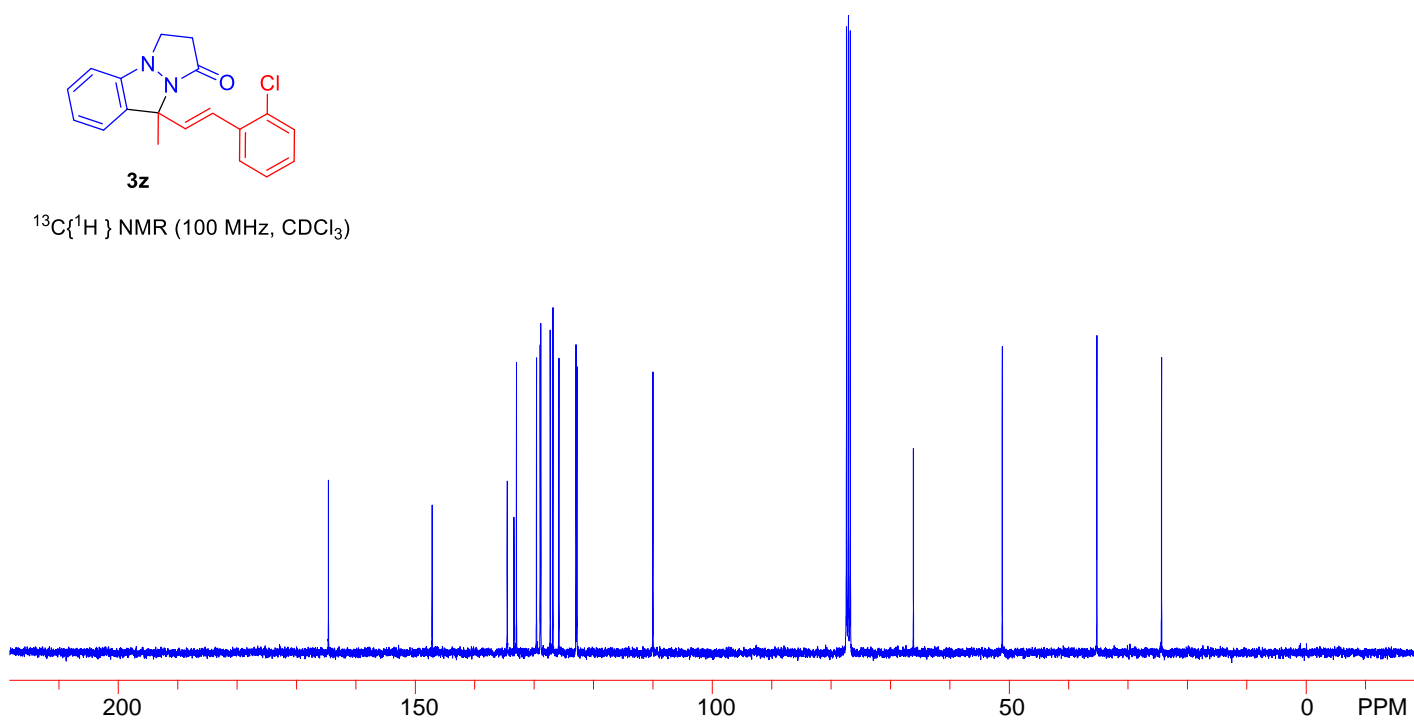
$^1\text{H NMR}$ (400 MHz, CDCl_3)



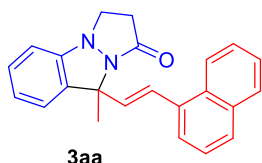
164.627
147.163
134.512
133.381
132.969
129.594
128.968
128.869
127.272
126.825
125.813
122.930
122.777
109.978
77.393
77.075
76.757
66.151
51.201
35.301
24.416



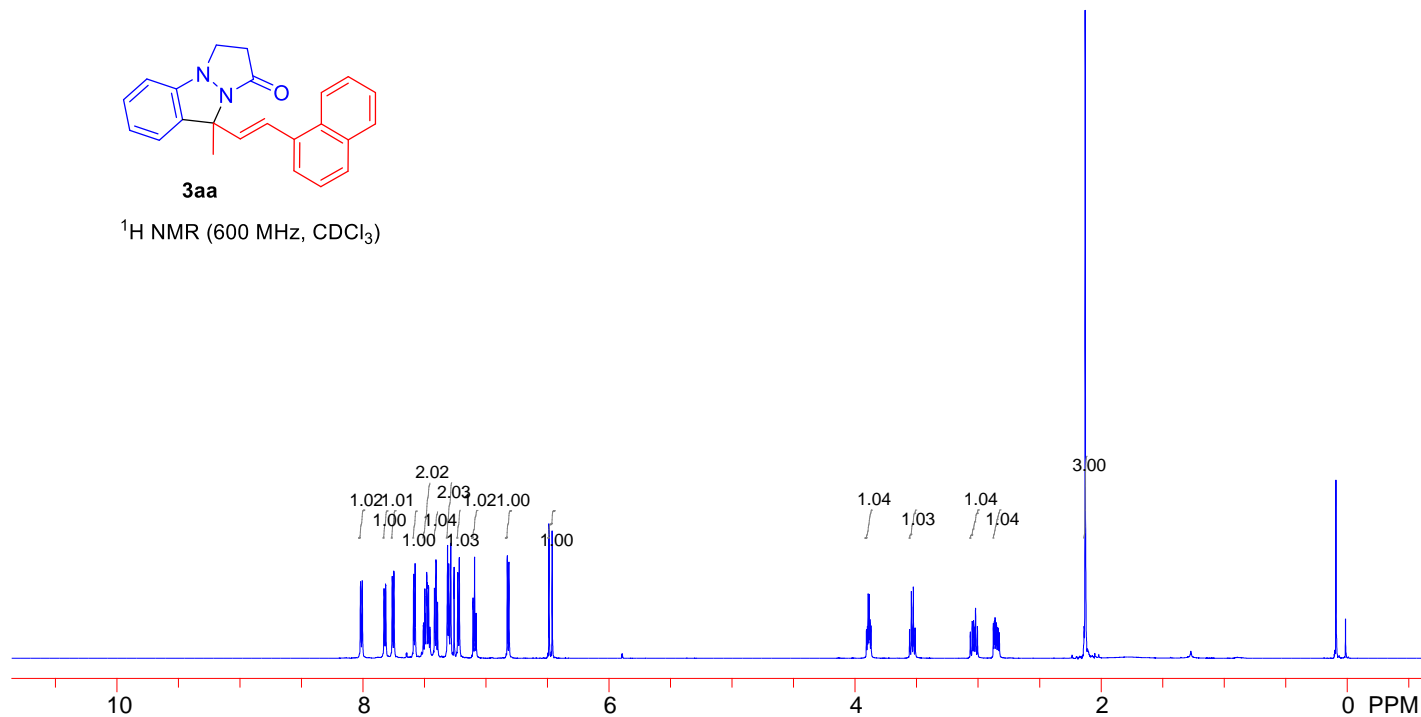
$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)



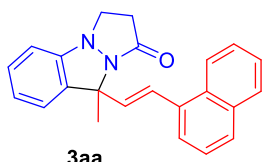
8.021
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7.815
7.763
7.749
7.589
7.577
7.511
7.509
7.499
7.497
7.486
7.482
7.479
7.468
7.457
7.420
7.415
7.407
7.394
7.313
7.303
7.287
7.260
7.230
7.218
7.106
7.093
7.081
6.827
6.814
6.488
6.462
3.906
3.898
3.892
3.884
3.878
3.870
3.556
3.541
3.525
3.511
3.062
3.047
3.046
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2.129



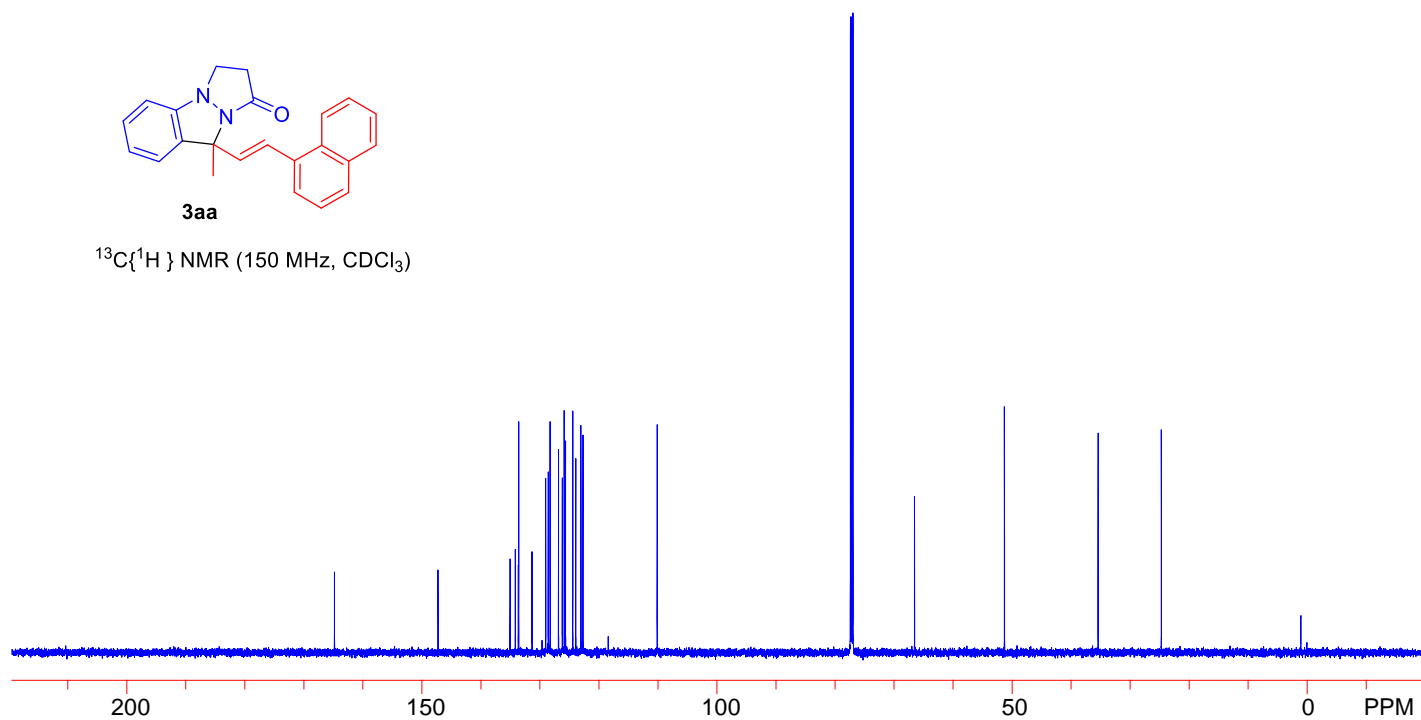
$^1\text{H NMR}$ (600 MHz, CDCl_3)



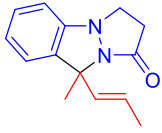
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134.159
133.652
147.251
133.584
131.331
129.007
128.578
128.261
126.846
126.200
125.870
125.656
124.426
123.920
123.041
122.697
110.120
77.371
77.160
76.949
66.535
51.325
35.465
24.763



$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)

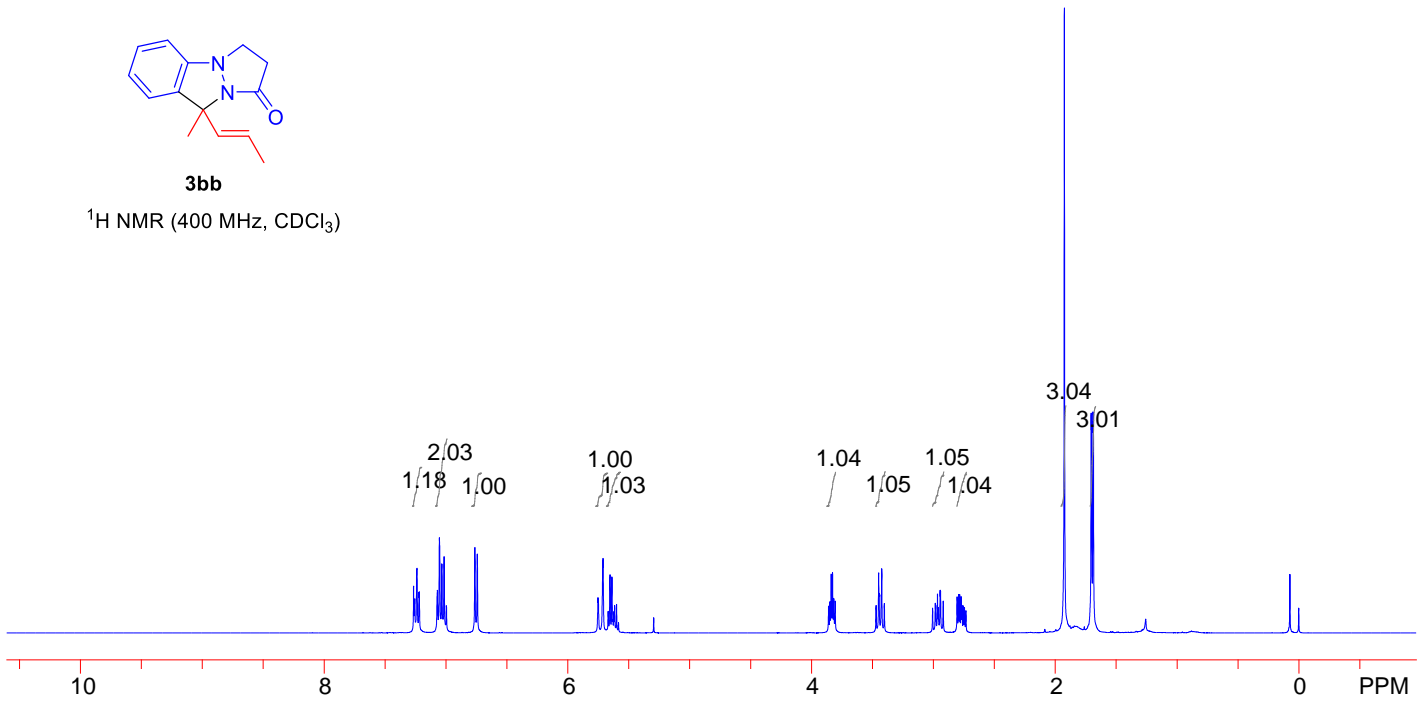


7.265
7.259
7.256
7.238
7.221
7.218
7.070
7.053
7.033
7.015
6.997
6.762
6.742
5.752
5.748
5.713
5.710
5.668
5.653
5.637
5.622
5.615
5.599
3.859
3.847
3.837
3.826
3.816
3.804
3.468
3.448
3.443
3.426
3.422
3.401
3.005
2.983
2.979
2.965
2.957
2.943
2.939
2.917
2.803
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1.687
1.685

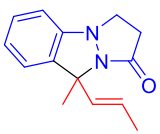


3bb

^1H NMR (400 MHz, CDCl_3)

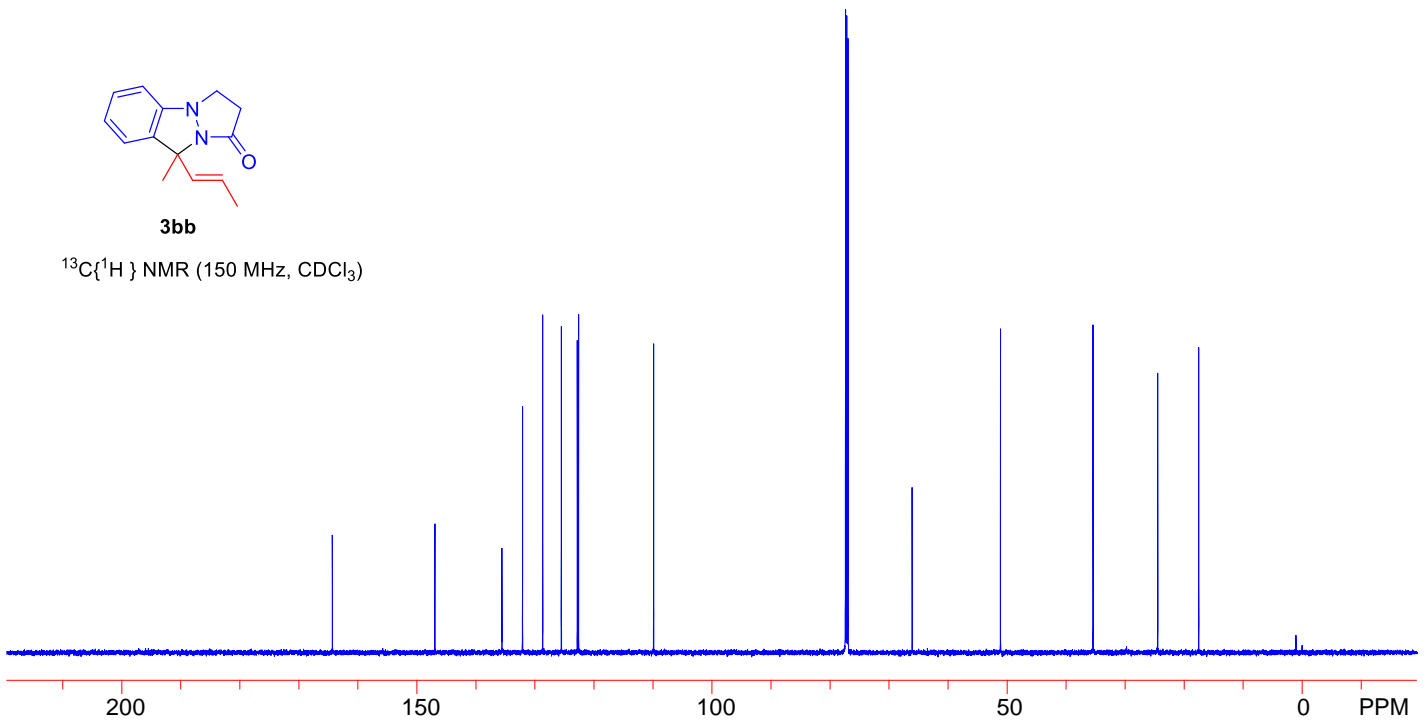


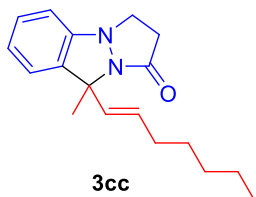
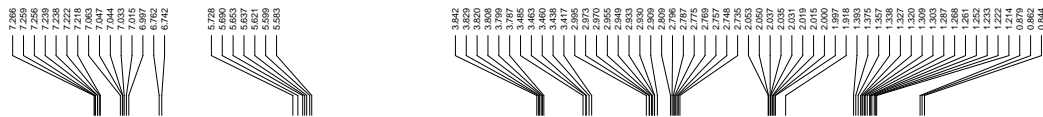
164.321
146.949
135.579
132.093
128.678
125.520
122.814
122.604
109.887
77.372
77.160
76.948
66.097
51.156
35.488
24.535
17.595



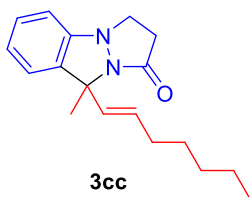
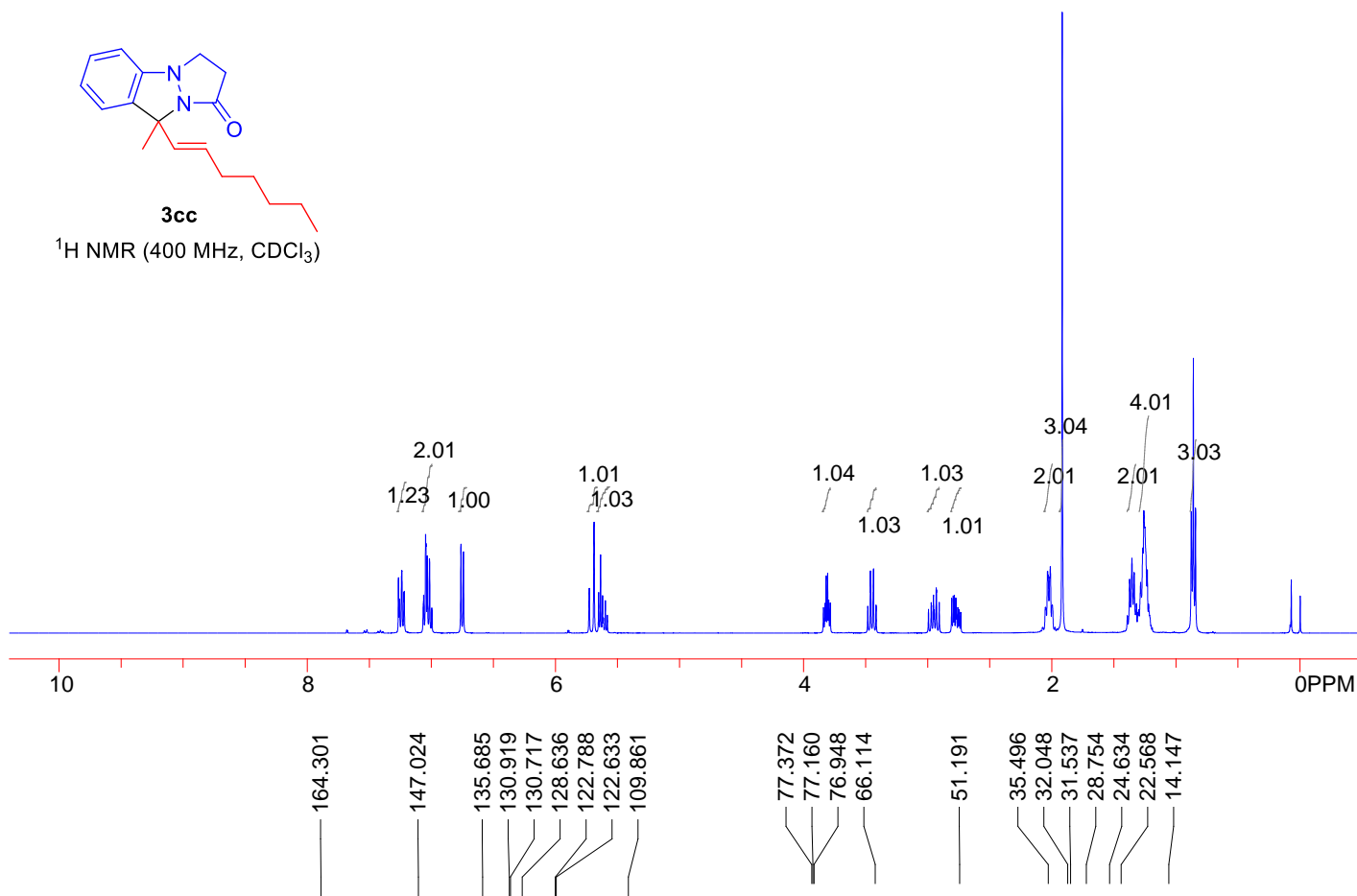
3bb

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)

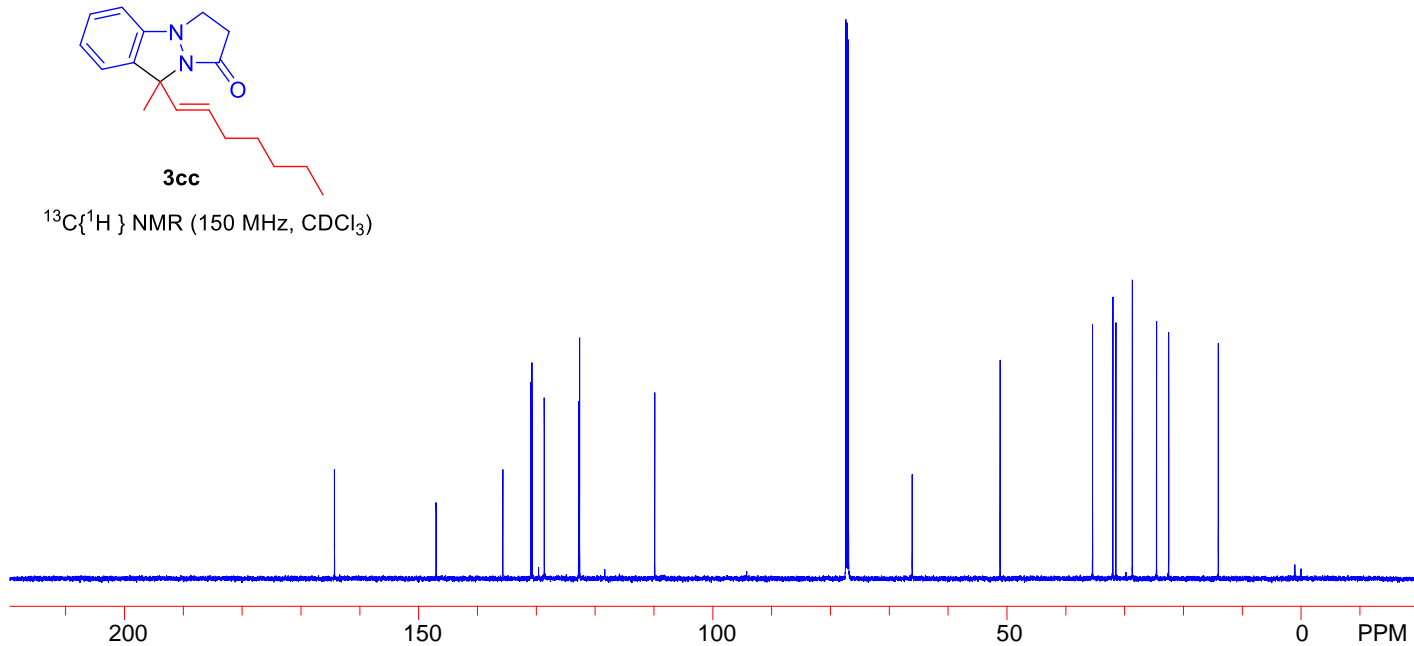




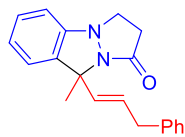
^1H NMR (400 MHz, CDCl_3)



$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)

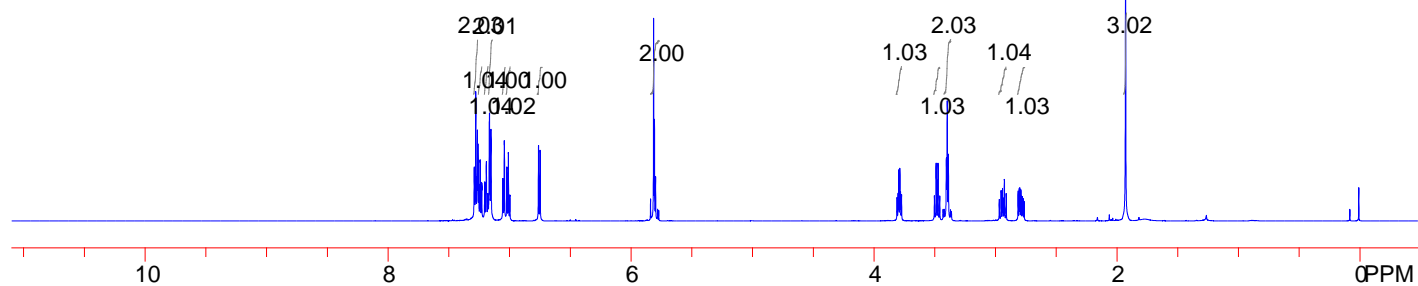
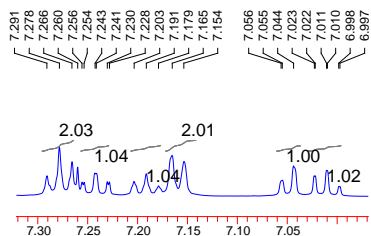


7.291
7.278
7.266
7.260
7.256
7.254
7.243
7.241
7.230
7.228
7.203
7.191
7.179
7.165
7.154
7.056
7.055
7.044
7.023
7.022
7.011
7.010
6.998
6.997
6.762
6.749
5.841
5.815
5.808
5.799
5.783
5.773
3.812
3.803
3.798
3.789
3.783
3.775
3.504
3.490
3.474
3.460
3.433
3.423
3.406
3.398
3.389
3.372
3.364
2.970
2.956
2.944
2.940
2.929
2.928
2.913
2.815
2.806
2.801
2.792
2.789
2.780
2.774
2.766
1.930

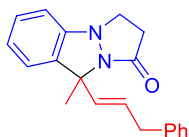


3dd

^1H NMR (600 MHz, CDCl_3)

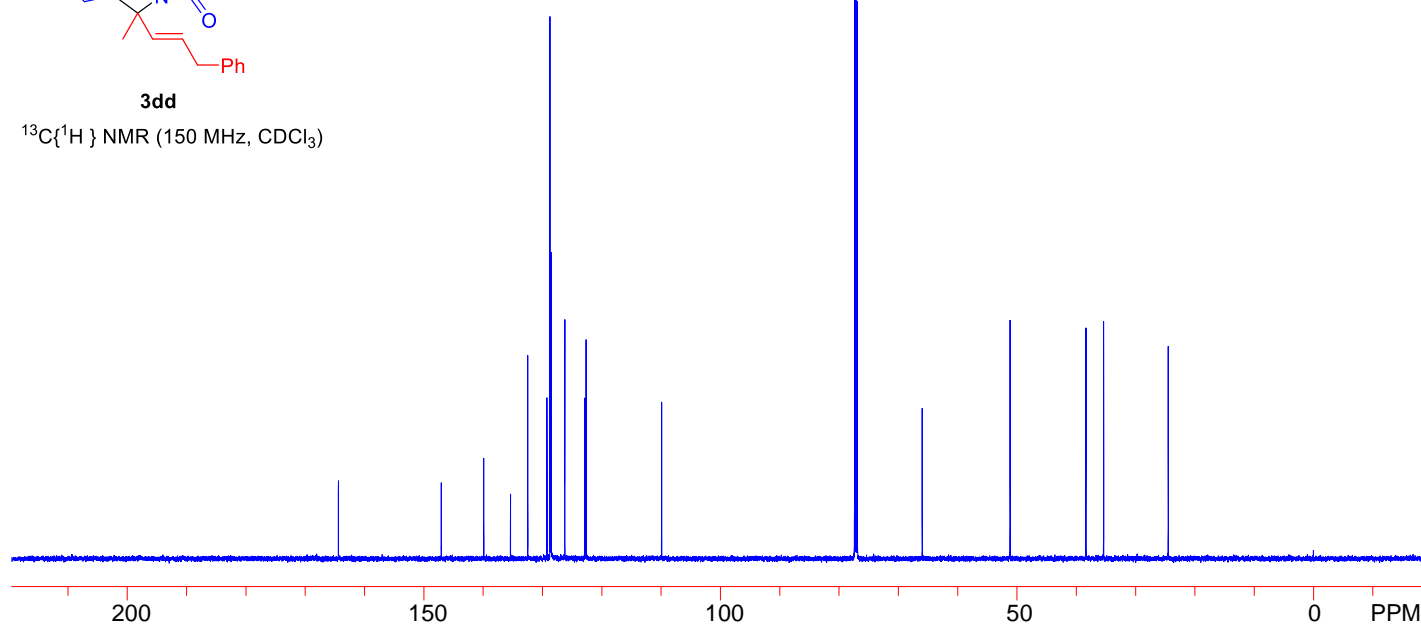


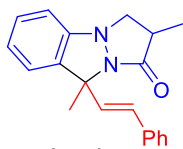
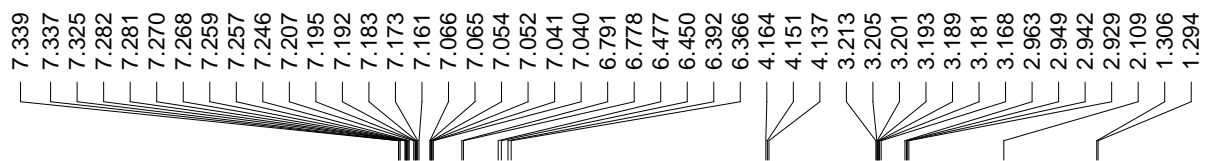
164.401
147.057
139.901
135.381
132.477
129.229
128.736
128.536
126.231
122.857
122.643
109.899
77.371
77.160
76.949
65.992
51.197
38.415
35.442
24.562



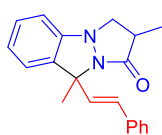
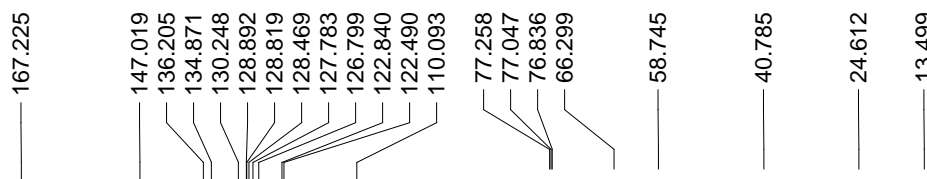
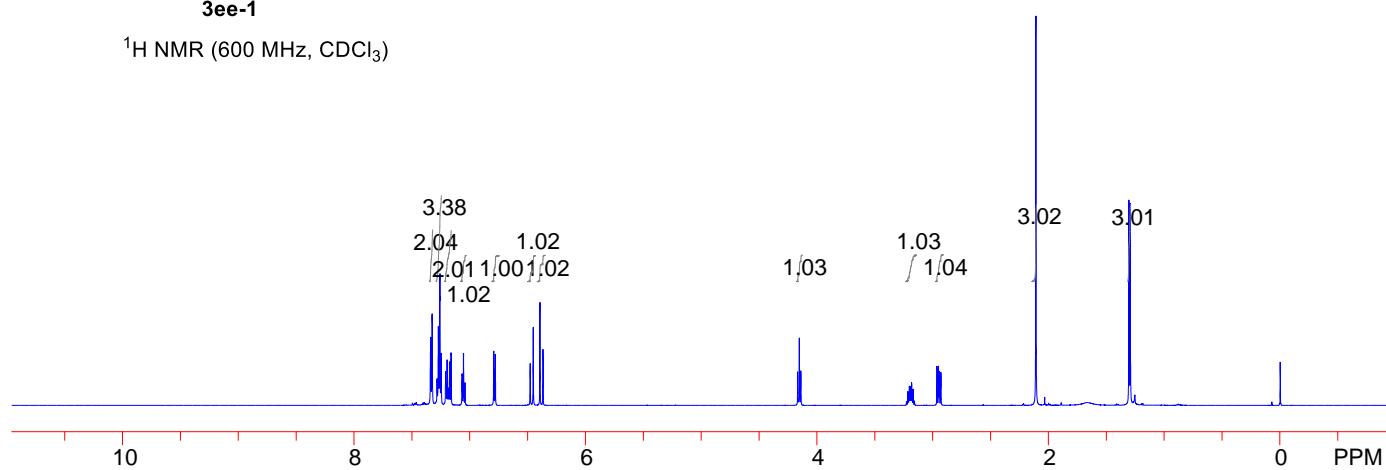
3dd

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)

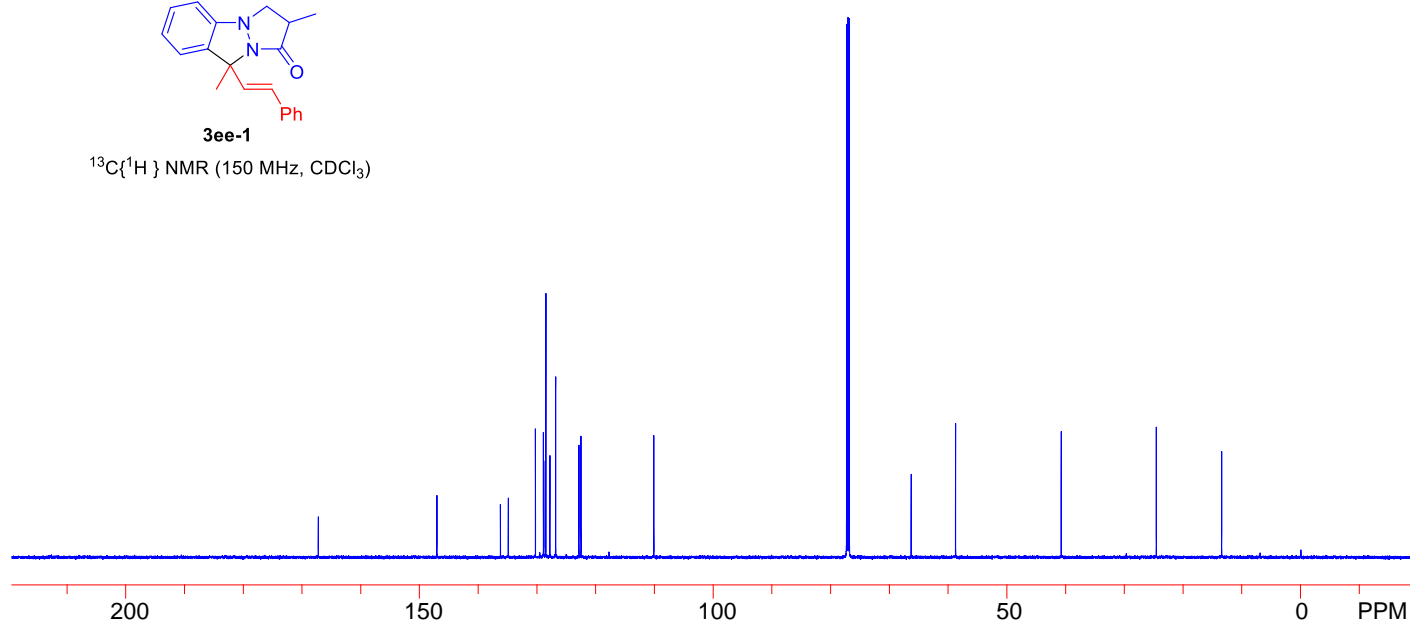




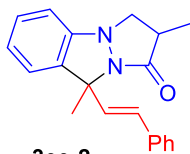
^1H NMR (600 MHz, CDCl_3)



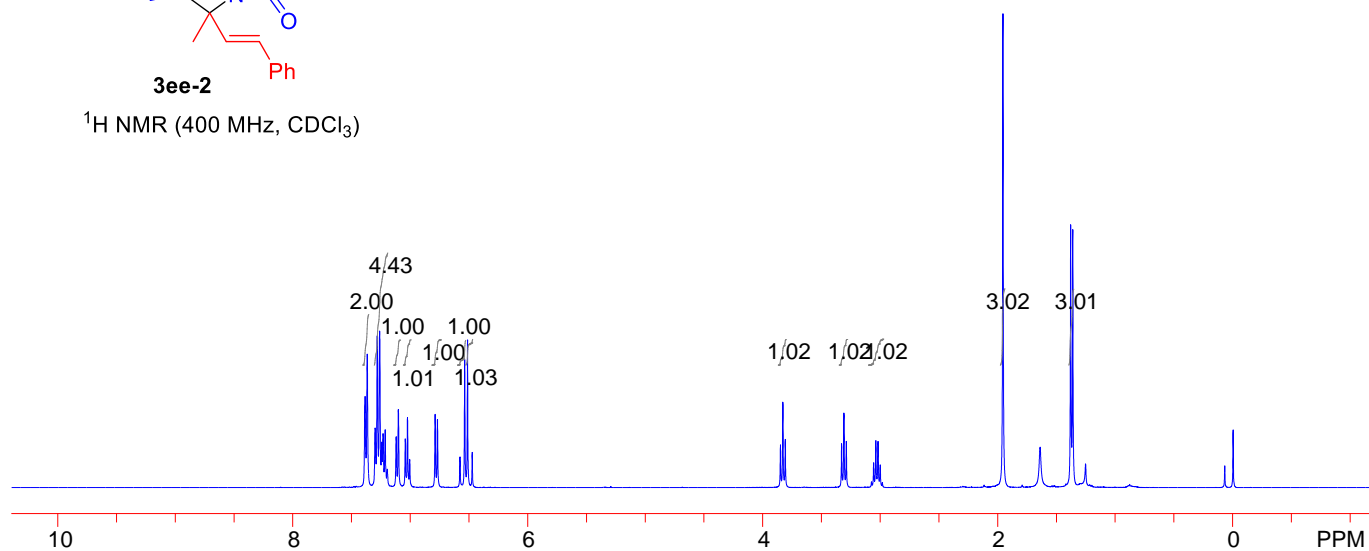
$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)



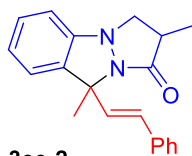
7.384
7.366
7.299
7.281
7.260
7.244
7.241
7.231
7.213
7.195
7.119
7.101
7.042
7.023
7.005
6.788
6.768
6.576
6.536
6.512
6.472
3.850
3.830
3.809
3.330
3.311
3.290
3.076
3.058
3.039
3.020
3.002
2.983
1.958
1.382
1.364



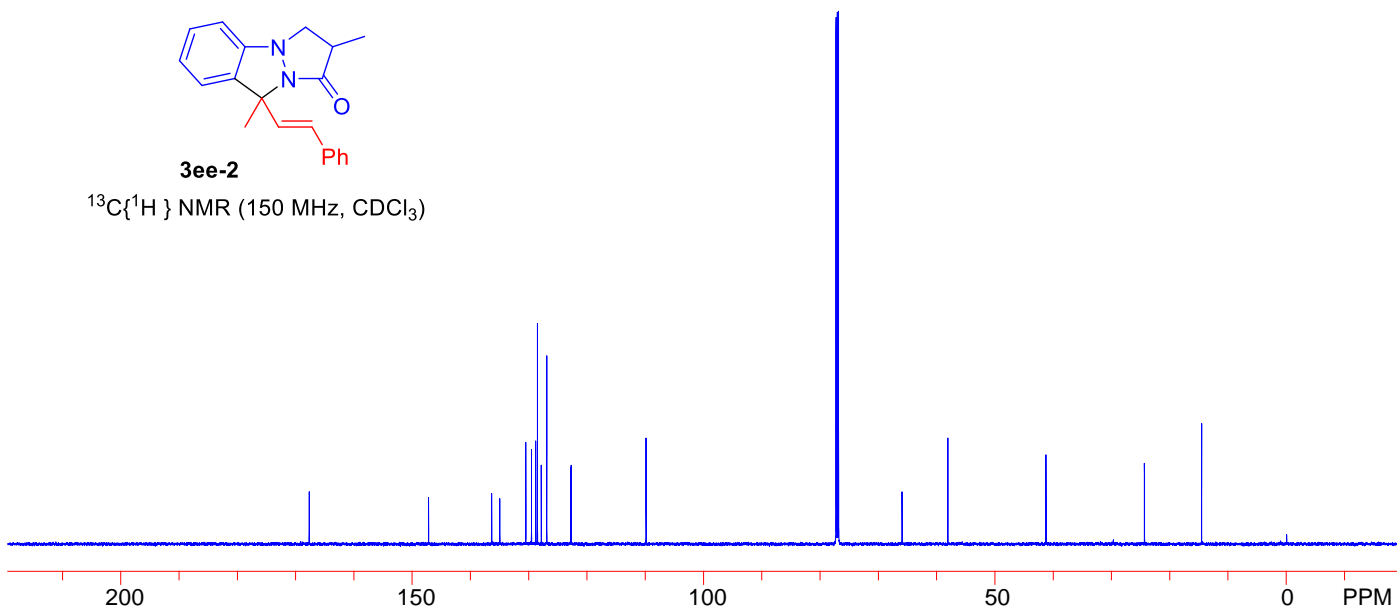
^1H NMR (400 MHz, CDCl_3)



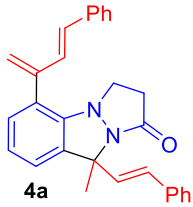
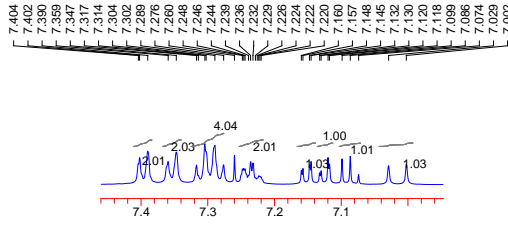
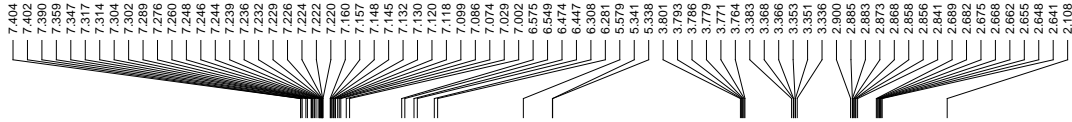
167.662
147.172
136.344
134.951
130.489
129.512
128.782
128.491
127.827
126.894
122.781
122.694
109.853
77.251
77.040
76.828
65.934
58.088
41.266
24.393
14.593



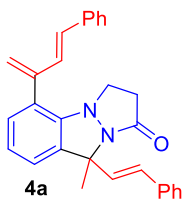
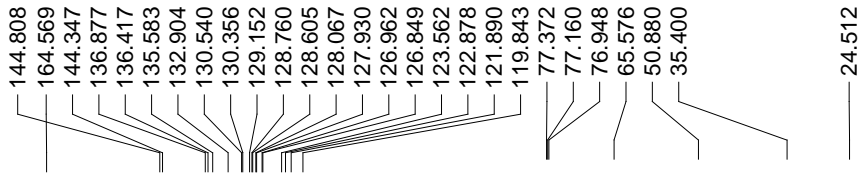
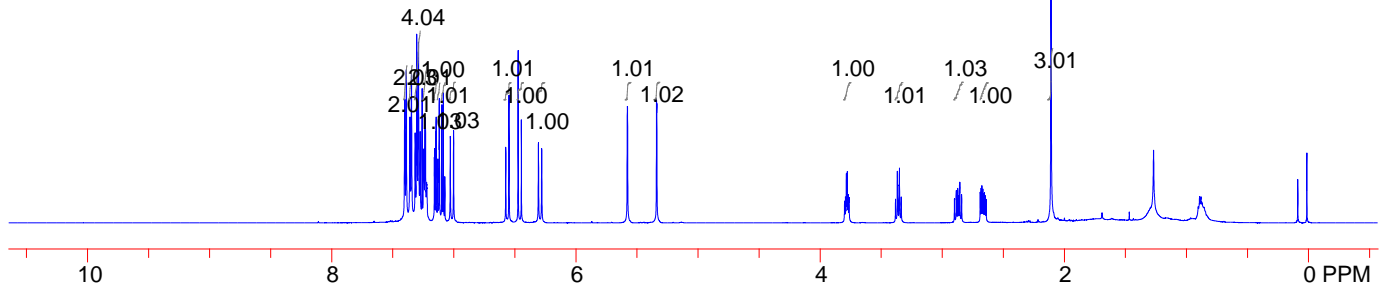
$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)



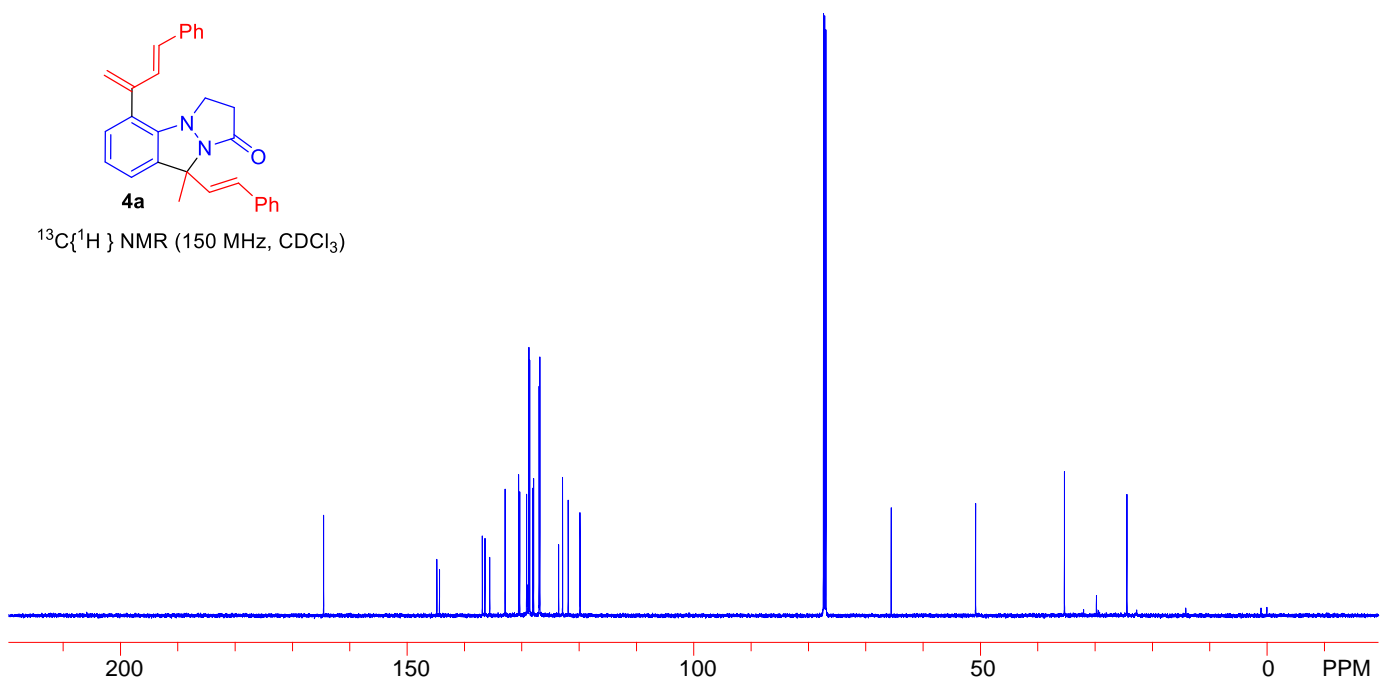
VI. NMR spectra of 4a-4t



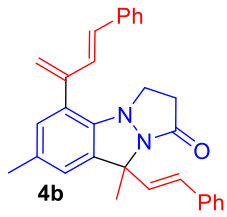
^1H NMR (600 MHz, CDCl_3)



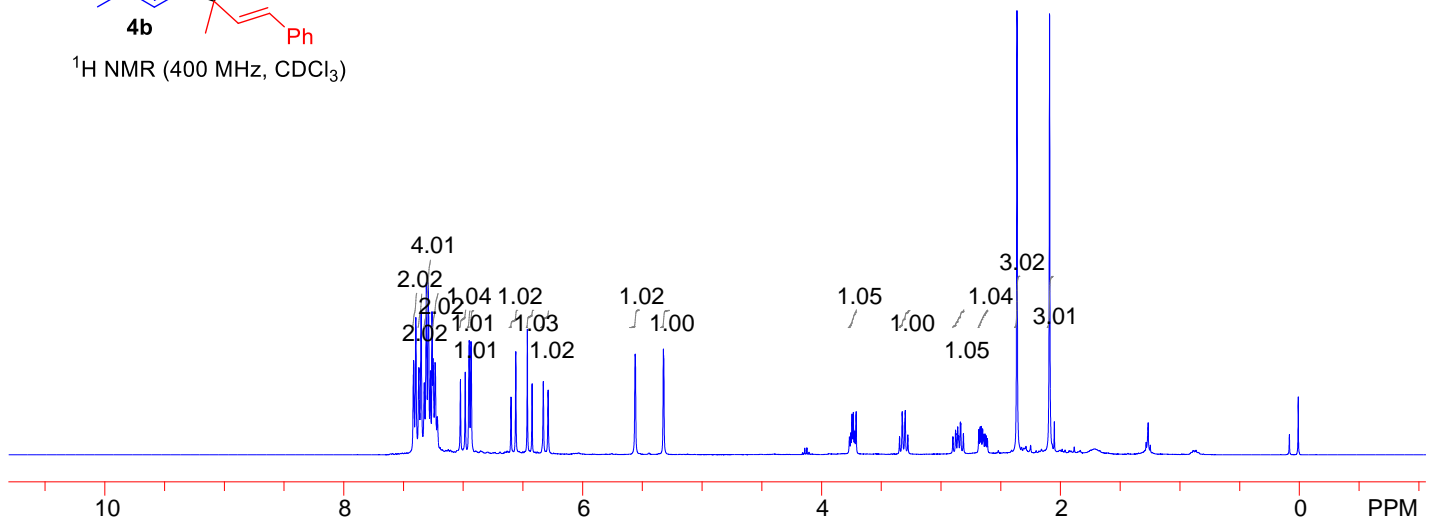
$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)



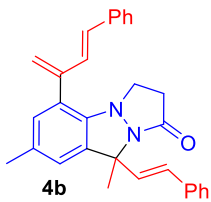
7.414
7.396
7.370
7.352
7.325
7.308
7.292
7.273
7.260
7.253
7.250
7.235
7.217
7.214
7.022
6.982
6.949
6.934
6.599
6.559
6.462
6.422
6.328
6.288
5.559
5.323
3.765
3.754
3.743
3.732
3.722
3.709
3.346
3.324
3.299
3.277
2.899
2.878
2.874
2.859
2.852
2.838
2.834
2.812
2.683
2.672
2.662
2.651
2.643
2.632
2.622
2.611
2.364
2.092



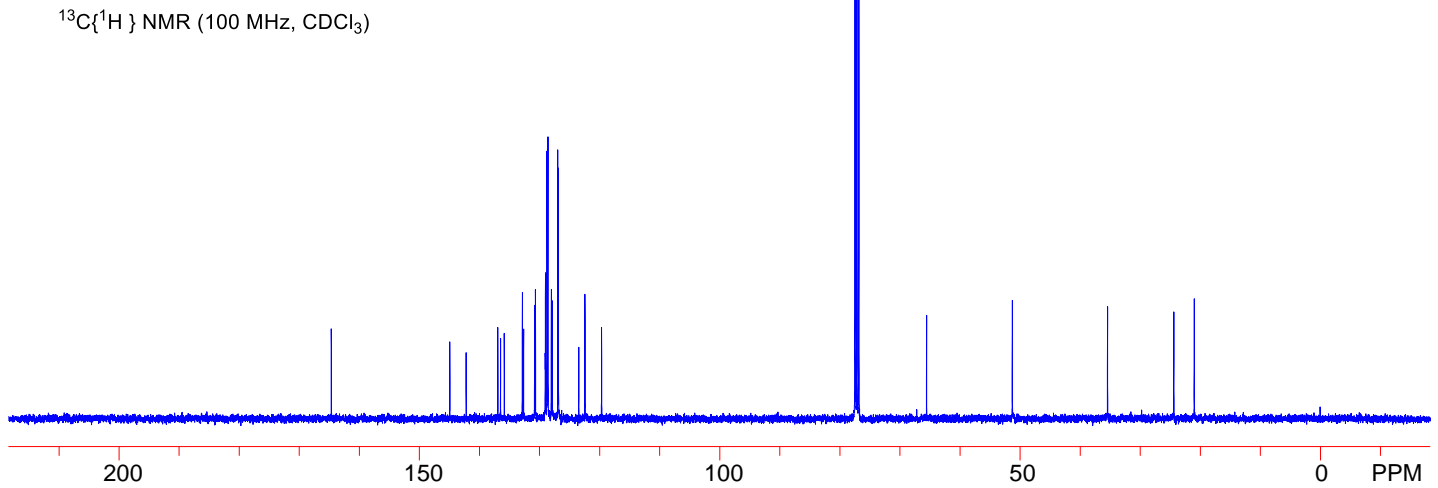
$^1\text{H NMR}$ (400 MHz, CDCl_3)



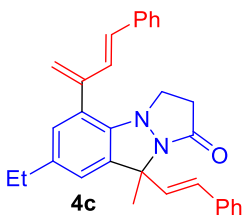
144.936
164.667
142.209
136.943
136.490
135.862
132.857
132.652
130.808
130.664
129.049
129.004
128.751
128.599
128.031
127.890
126.965
126.850
123.457
122.433
119.666
77.478
77.160
76.843
65.571
51.319
35.478
24.464
21.061



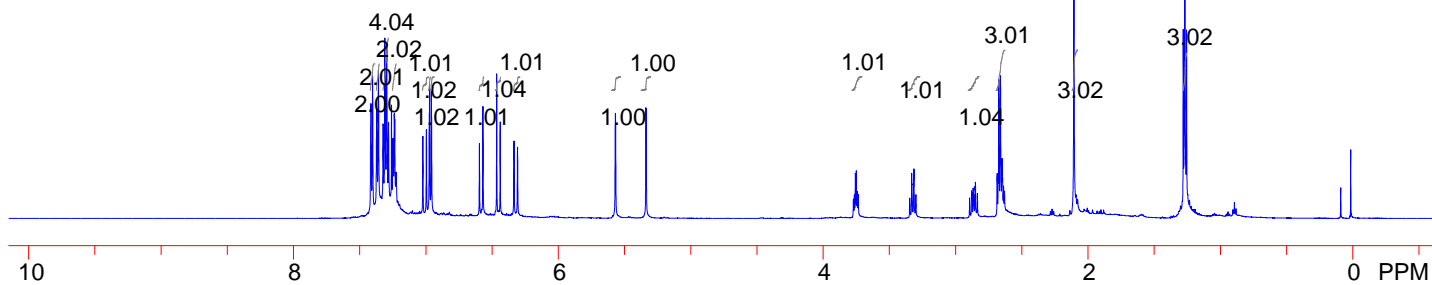
$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)



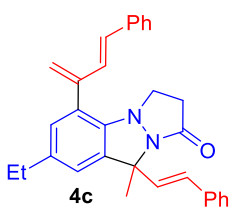
7.415
7.403
7.371
7.358
7.323
7.310
7.295
7.282
7.260
7.251
7.249
7.247
7.239
7.235
7.226
7.225
7.223
7.023
6.996
6.972
6.959
6.959
6.569
6.465
6.438
6.334
6.308
5.569
5.338
5.336
3.771
3.763
3.756
3.749
3.741
3.734
3.345
3.331
3.328
3.313
3.299
2.893
2.878
2.876
2.866
2.861
2.852
2.849
2.834
2.685
2.677
2.672
2.660
2.651
2.647
2.644
2.637
2.630
2.106
1.280
1.267
1.254



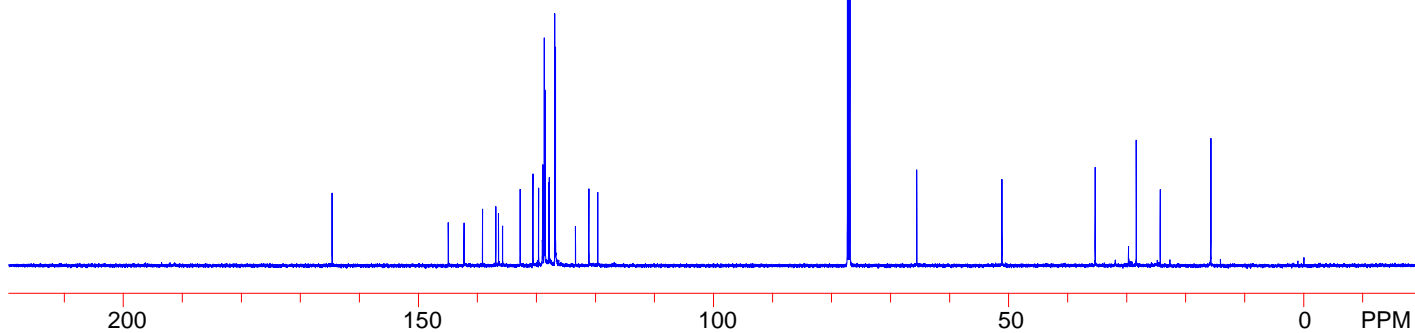
$^1\text{H NMR}$ (600 MHz, CDCl_3)



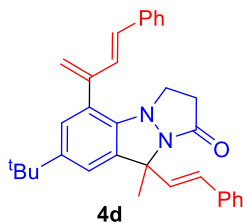
144.933
164.626
142.272
139.135
136.883
136.416
135.726
132.753
130.588
129.624
128.990
128.913
128.674
128.515
127.940
127.809
126.903
126.771
123.368
121.115
119.610
77.297
77.086
76.875
65.570
51.151
35.384
28.428
24.369
15.784



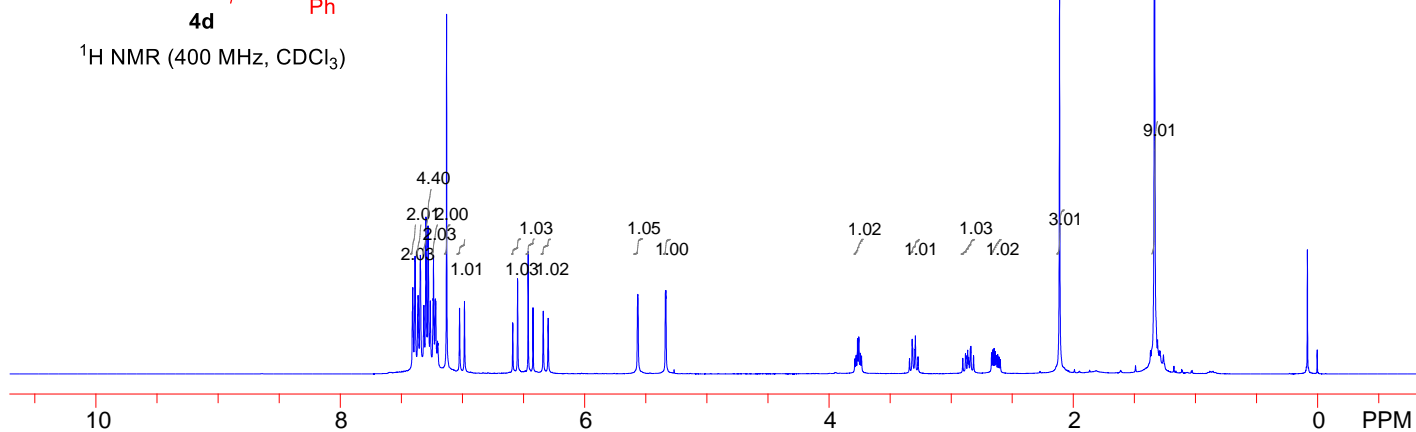
$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)



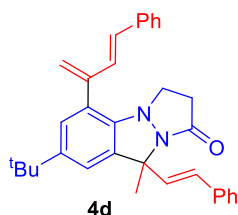
7.410
7.406
7.388
7.388
7.363
7.345
7.316
7.312
7.298
7.282
7.279
7.263
7.240
7.237
7.228
7.222
7.218
7.212
7.204
7.200
7.129
7.023
6.983
6.588
6.548
6.461
6.422
6.338
6.298
5.564
5.338
5.334
3.786
3.776
3.764
3.754
3.743
3.732
3.339
3.317
3.313
3.295
3.291
3.269
2.903
2.881
2.876
2.863
2.855
2.841
2.836
2.815
2.667
2.657
2.646
2.636
2.627
2.617
2.606
2.596
2.111
1.333



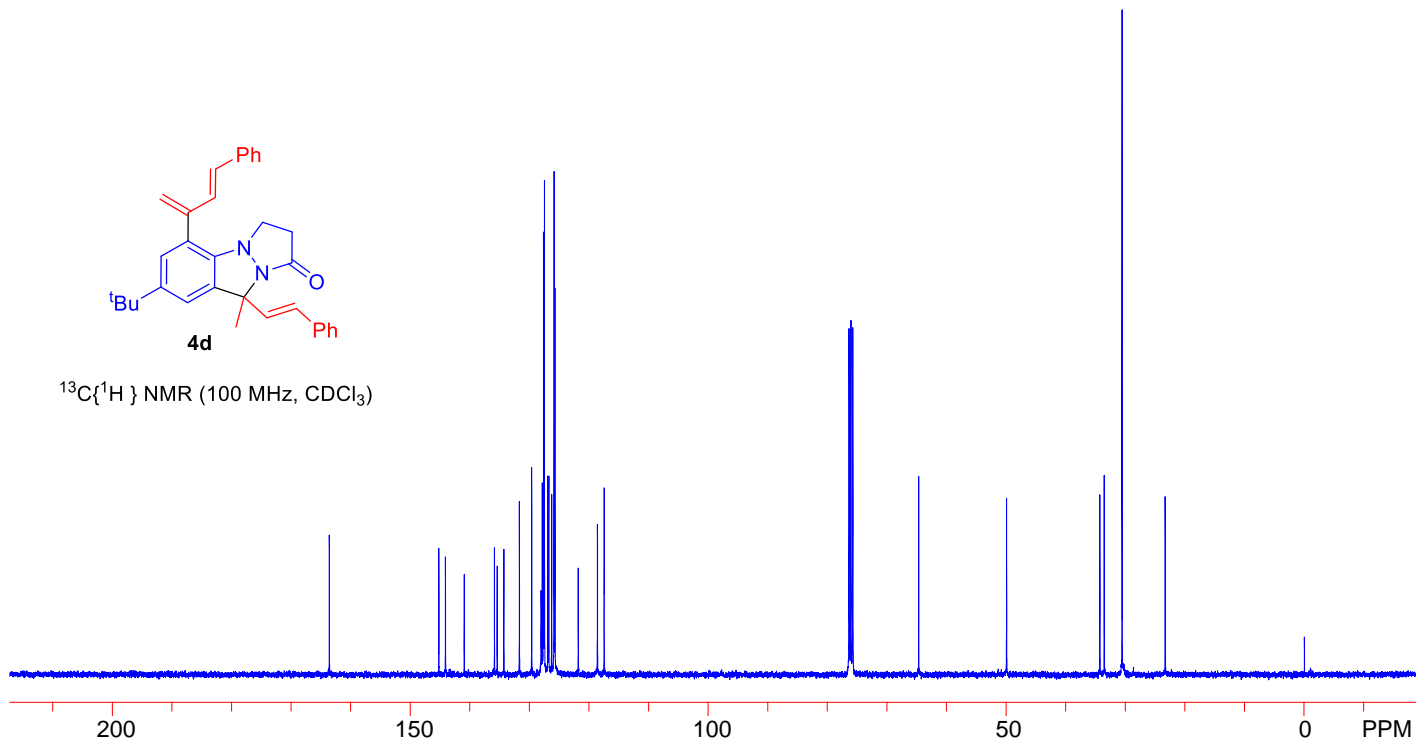
$^1\text{H NMR}$ (400 MHz, CDCl_3)



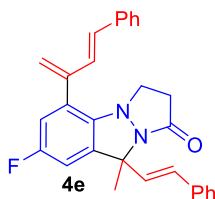
163.569
145.193
144.080
140.925
135.859
135.395
134.280
131.670
129.606
128.026
127.829
127.615
127.464
126.878
126.734
126.247
125.854
125.696
121.789
118.577
117.451
76.349
76.032
75.714
64.674
49.941
34.313
33.578
30.576
23.352



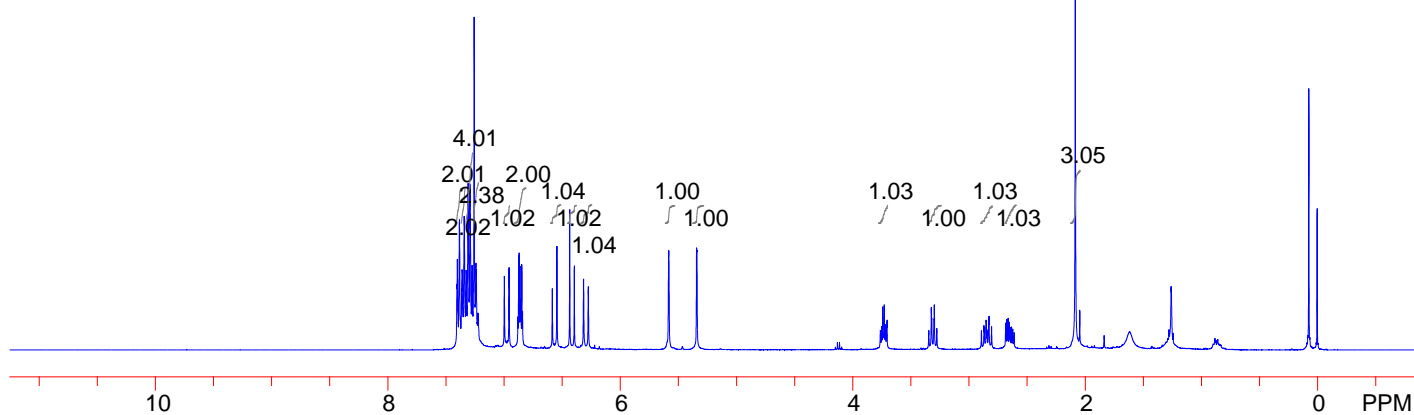
$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)



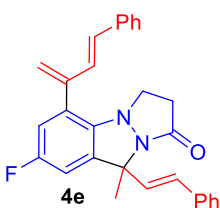
7.406
7.402
7.384
7.365
7.361
7.343
7.326
7.322
7.309
7.294
7.290
7.275
7.257
7.248
7.242
7.239
7.231
7.227
7.224
7.221
7.221
6.997
6.957
6.881
6.874
6.870
6.862
6.855
6.847
6.841
6.584
6.545
6.435
6.395
6.315
6.275
5.582
5.342
5.340
3.760
3.749
3.739
3.727
3.717
3.705
3.703
3.343
3.322
3.318
3.300
3.296
3.274
2.890
2.869
2.865
2.850
2.843
2.829
2.825
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2.682
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2.661
2.650
2.642
2.630
2.621
2.610
2.082



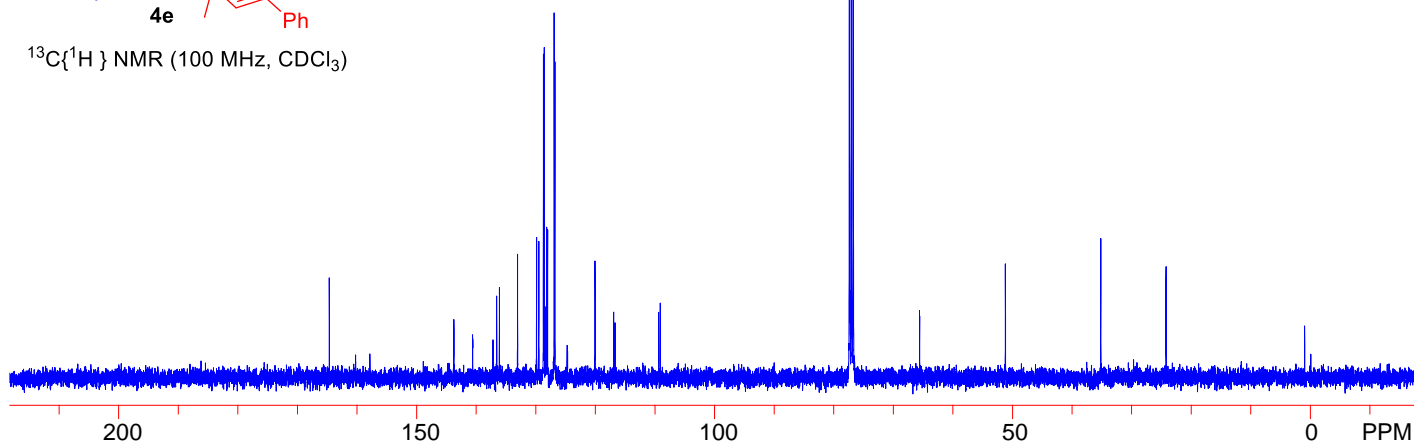
^1H NMR (400 MHz, CDCl_3)

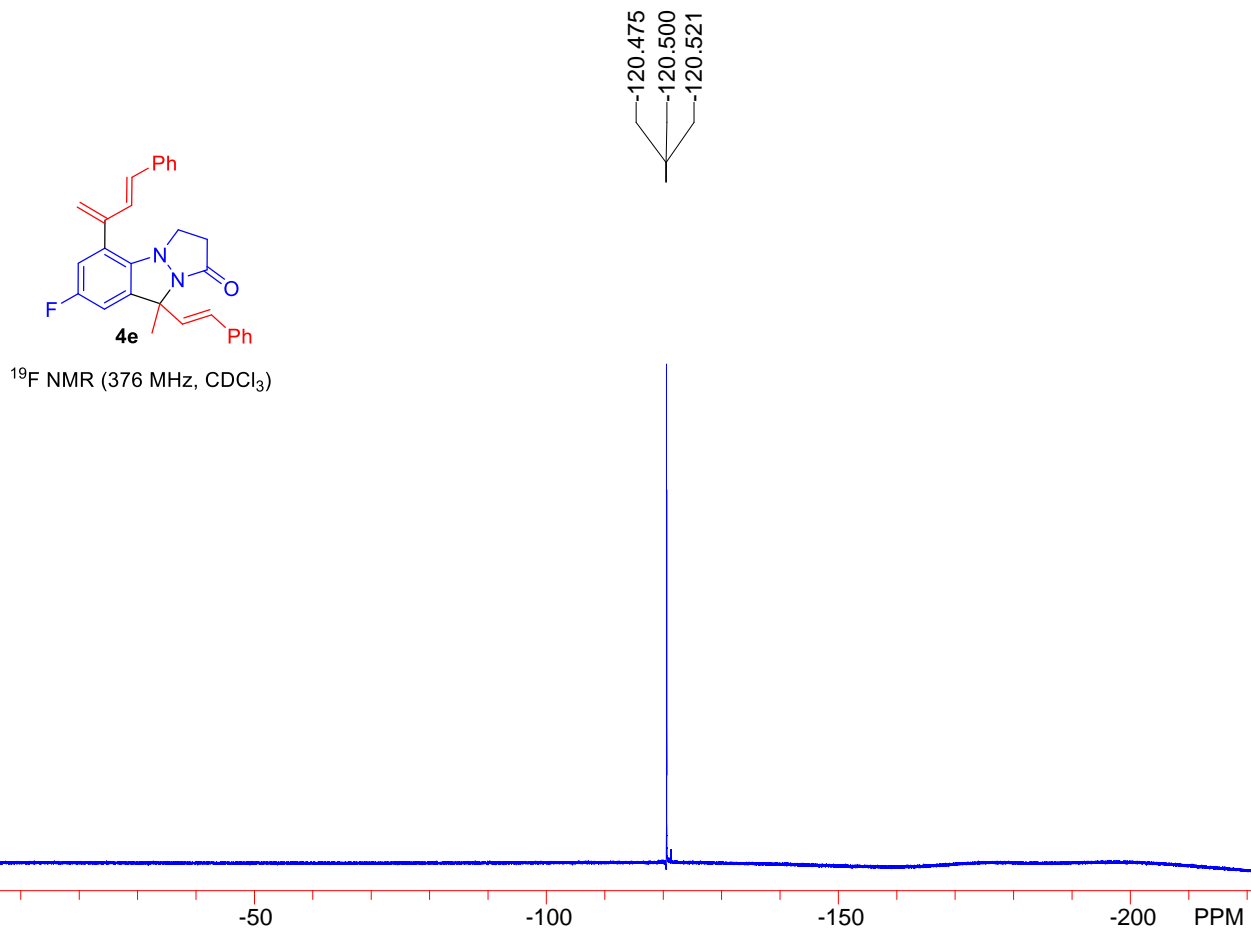


164.647
160.268
157.774
143.727
140.595
137.179
137.100
136.556
136.098
133.047
129.857
129.478
128.710
128.563
128.330
128.154
128.009
126.905
126.787
124.726
124.653
120.056
116.930
116.688
109.361
109.116
77.359
77.041
76.722
65.610
65.588
51.215
35.227
24.283

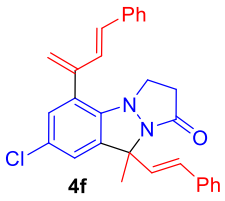


$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)

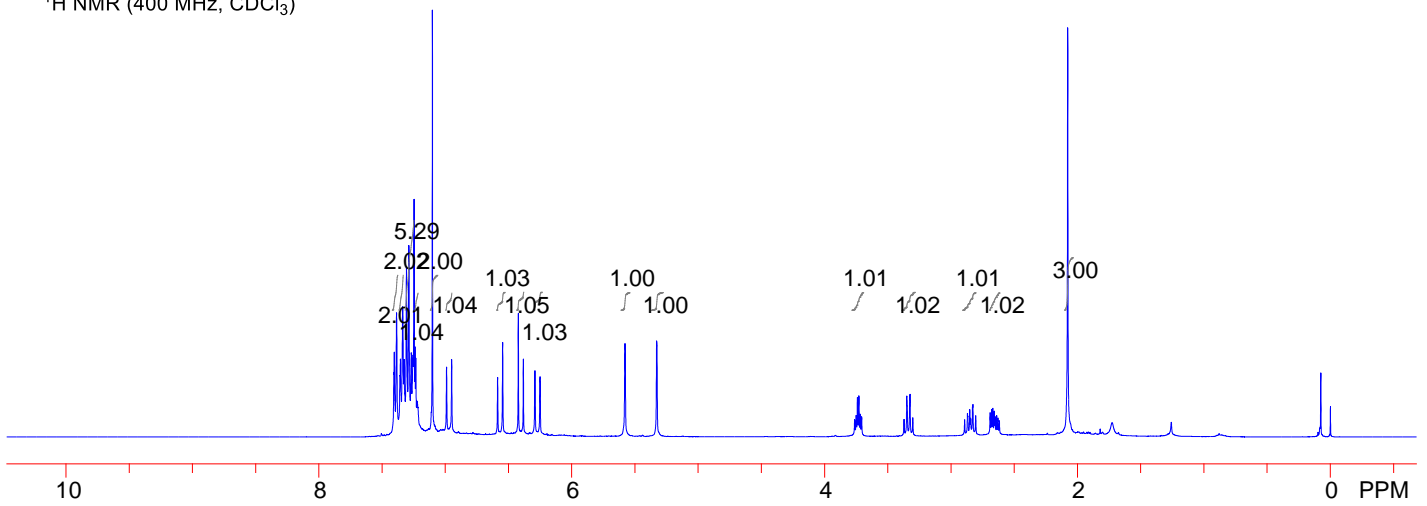




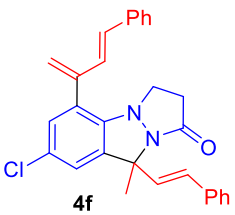
7.407
7.403
7.385
7.359
7.355
7.337
7.327
7.325
7.320
7.307
7.288
7.269
7.261
7.258
7.254
7.247
7.240
7.233
7.225
7.222
7.219
7.215
7.102
6.990
6.949
6.586
6.546
6.422
6.382
6.290
6.250
5.577
5.327
3.761
3.749
3.739
3.727
3.716
3.705
3.370
3.348
3.323
3.301
2.891
2.869
2.866
2.851
2.844
2.829
2.825
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2.690
2.678
2.669
2.657
2.649
2.638
2.628
2.617
2.077



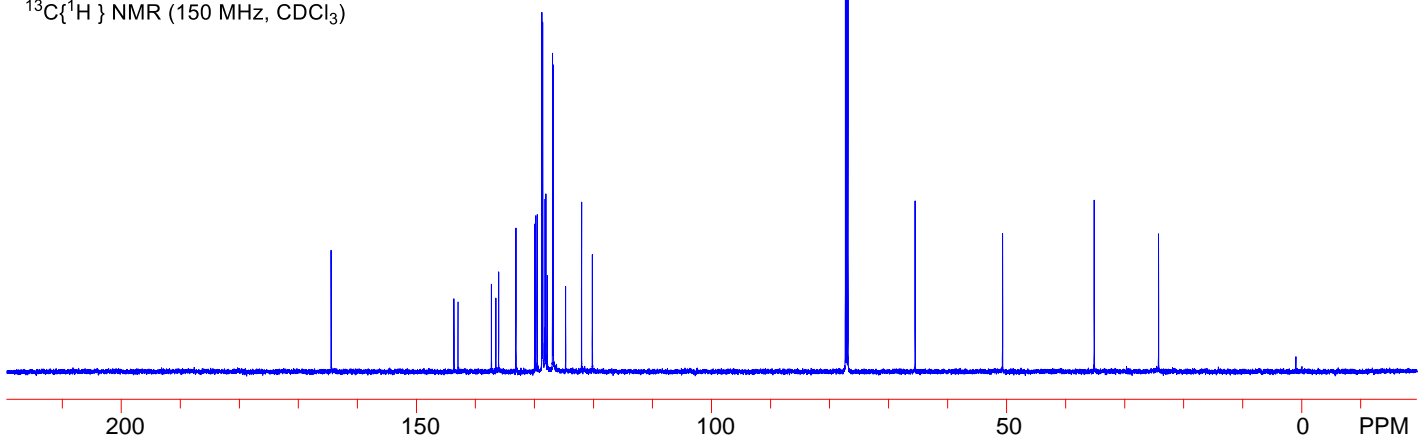
$^1\text{H NMR}$ (400 MHz, CDCl_3)



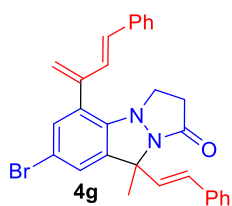
143.634
164.444
142.950
137.284
136.529
136.067
133.133
129.961
129.786
129.512
128.731
128.591
128.192
128.055
127.820
126.927
126.818
124.713
122.010
120.182
77.303
77.092
76.880
65.512
50.705
35.201
24.305



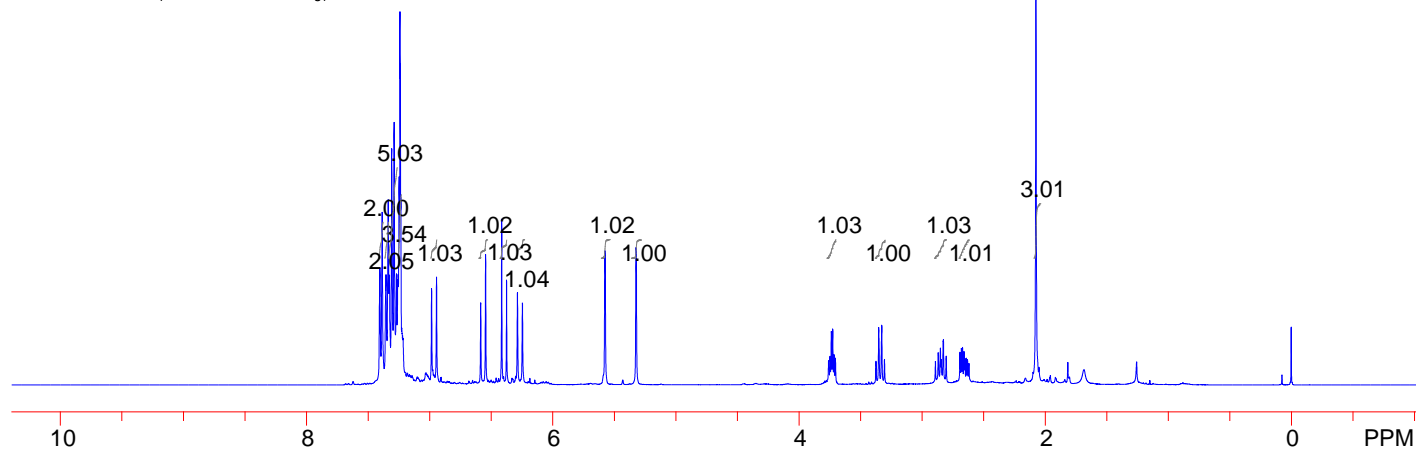
$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)



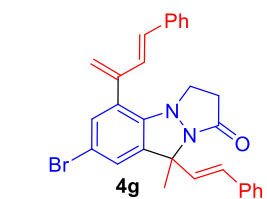
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7.386
7.355
7.337
7.327
7.309
7.289
7.270
7.259
7.256
7.249
7.242
7.239
7.235
7.227
7.224
7.220
7.217
6.985
6.945
6.586
6.546
6.415
6.375
6.287
6.247
5.576
5.324
3.759
3.748
3.737
3.725
3.715
3.703
3.374
3.352
3.327
3.305
2.891
2.869
2.866
2.850
2.844
2.828
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2.659
2.651
2.639
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2.619
2.074



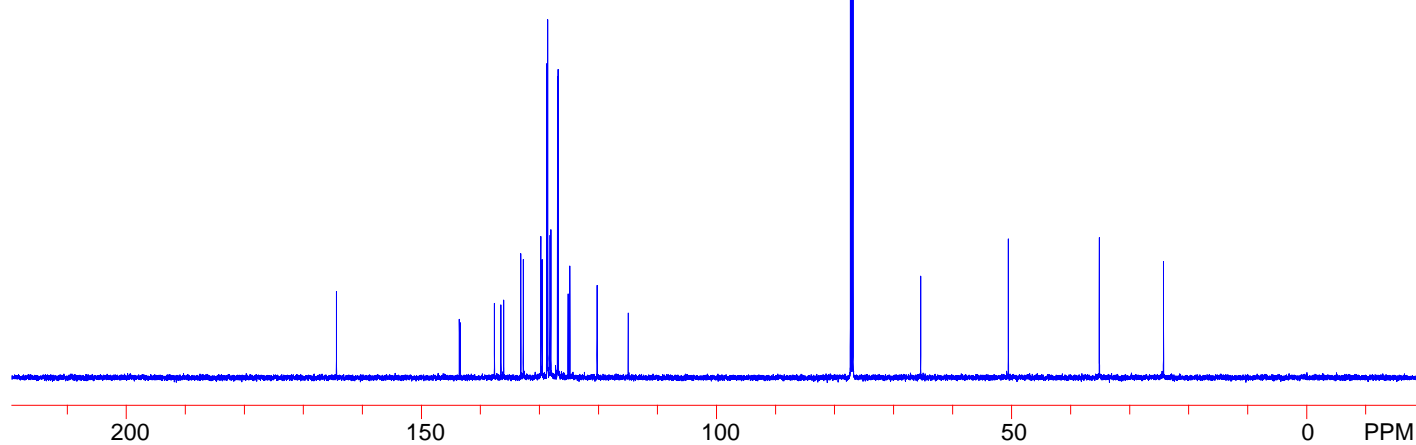
$^1\text{H NMR}$ (400 MHz, CDCl_3)



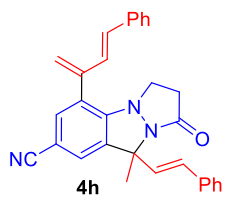
143.566
164.390
143.401
137.619
136.531
136.058
133.156
132.723
129.771
129.516
128.732
128.593
128.198
128.061
126.936
126.821
125.138
124.834
120.218
114.947
77.298
77.087
76.876
65.420
50.587
35.187
24.313



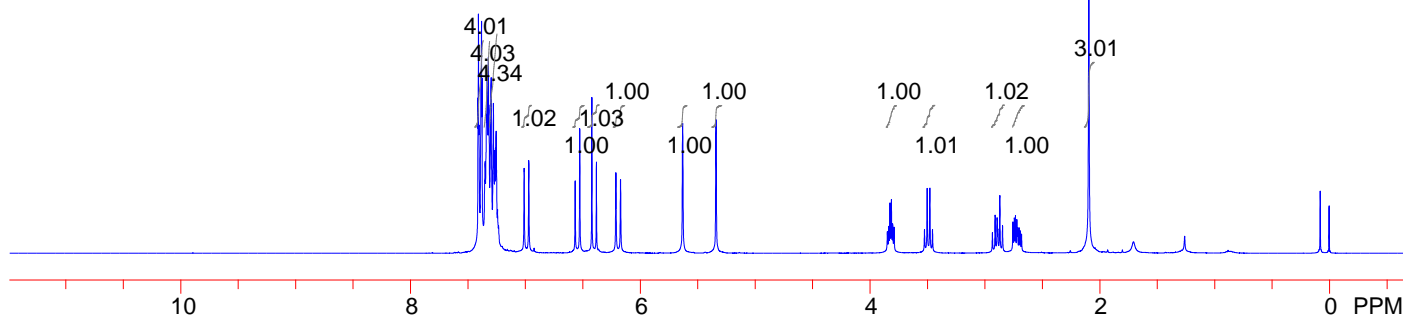
$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)



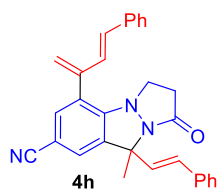
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7.405
7.386
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7.378
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7.350
7.340
7.334
7.331
7.323
7.319
7.303
7.298
7.279
7.273
7.268
7.261
7.255
7.251
7.243
7.234
7.011
6.971
6.567
6.528
6.423
6.383
6.213
6.173
5.632
5.343
3.851
3.839
3.828
3.816
3.805
3.793
3.528
3.505
3.481
3.458
2.936
2.913
2.895
2.889
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2.746
2.735
2.724
2.717
2.705
2.694
2.683
2.097



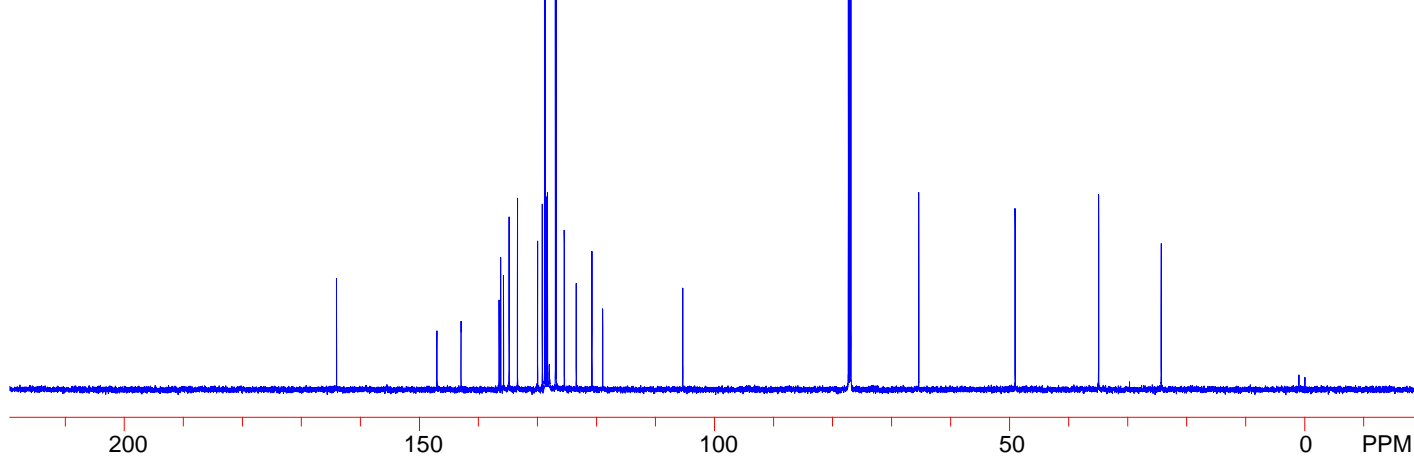
$^1\text{H NMR}$ (400 MHz, CDCl_3)



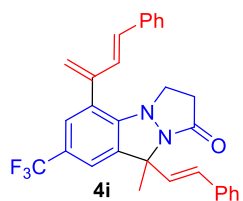
147.032
164.038
142.939
136.489
136.214
135.738
134.788
133.383
129.968
129.165
128.789
128.664
128.424
128.285
126.950
126.843
125.446
123.423
120.765
118.944
105.368
77.313
77.102
76.891
65.401
49.101
34.958
24.370



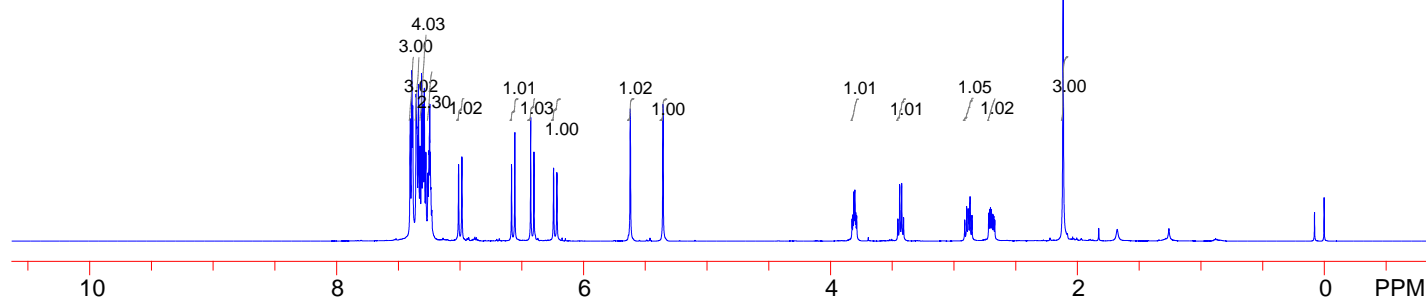
$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)



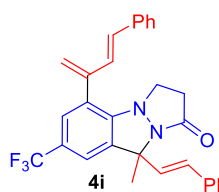
7.404
7.392
7.384
7.384
7.357
7.354
7.350
7.337
7.325
7.313
7.302
7.300
7.290
7.277
7.261
7.253
7.249
7.246
7.241
7.237
7.229
7.013
6.986
6.584
6.557
6.429
6.402
6.243
6.217
5.623
5.358
3.827
3.819
3.812
3.804
3.797
3.789
3.456
3.441
3.424
3.409
2.914
2.898
2.886
2.882
2.870
2.855
2.719
2.712
2.705
2.697
2.692
2.684
2.678
2.670
2.116



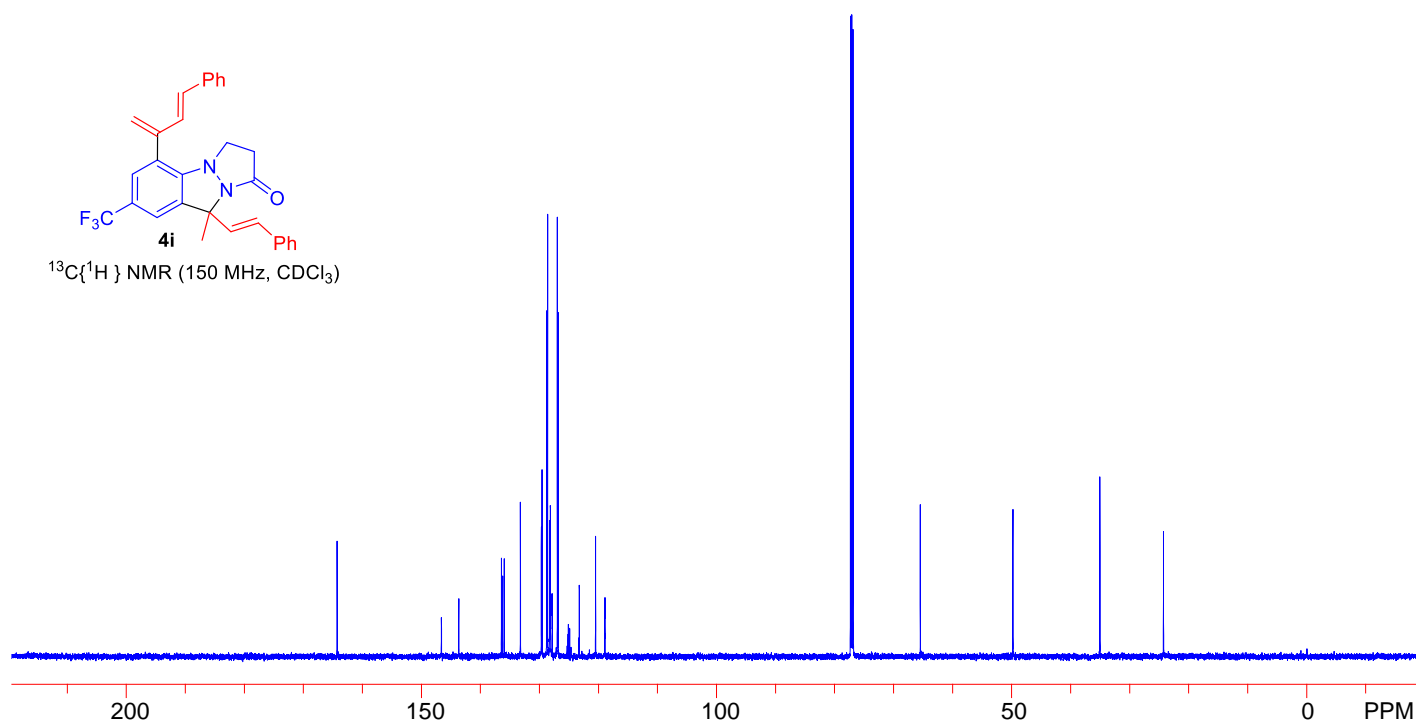
$^1\text{H NMR}$ (600 MHz, CDCl_3)



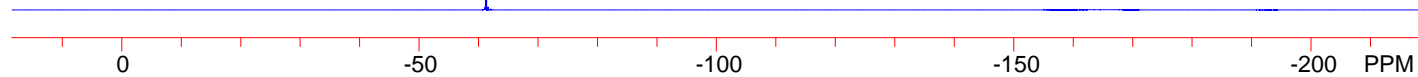
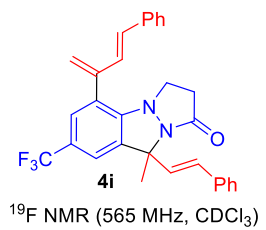
146.604
143.660
136.438
136.243
164.277
135.957
133.215
129.662
129.549
128.752
128.616
128.267
128.136
127.843
127.821
126.961
126.834
125.305
125.126
125.086
124.869
124.653
123.324
123.236
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35.092
24.325



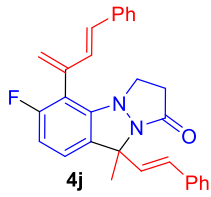
$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)



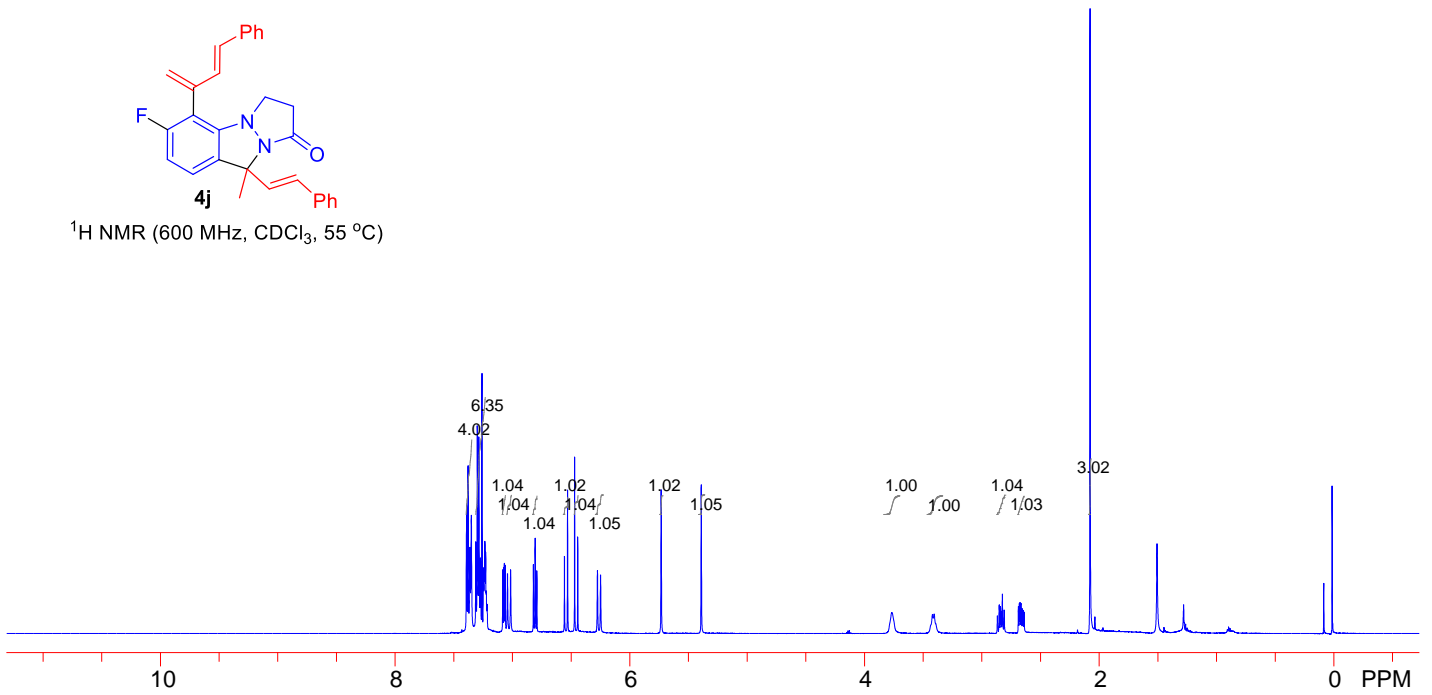
-61.204



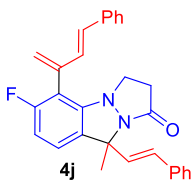
7.391
7.378
7.363
7.350
7.312
7.300
7.286
7.273
7.260
7.247
7.240
7.238
7.234
7.231
7.228
7.225
7.223
7.216
7.083
7.075
7.069
7.061
7.042
7.015
6.821
6.806
6.792
6.556
6.530
6.470
6.443
6.276
6.249
5.732
5.390
3.763
3.419
3.405
2.867
2.851
2.840
2.836
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2.688
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2.674
2.666
2.661
2.653
2.647
2.639
2.078



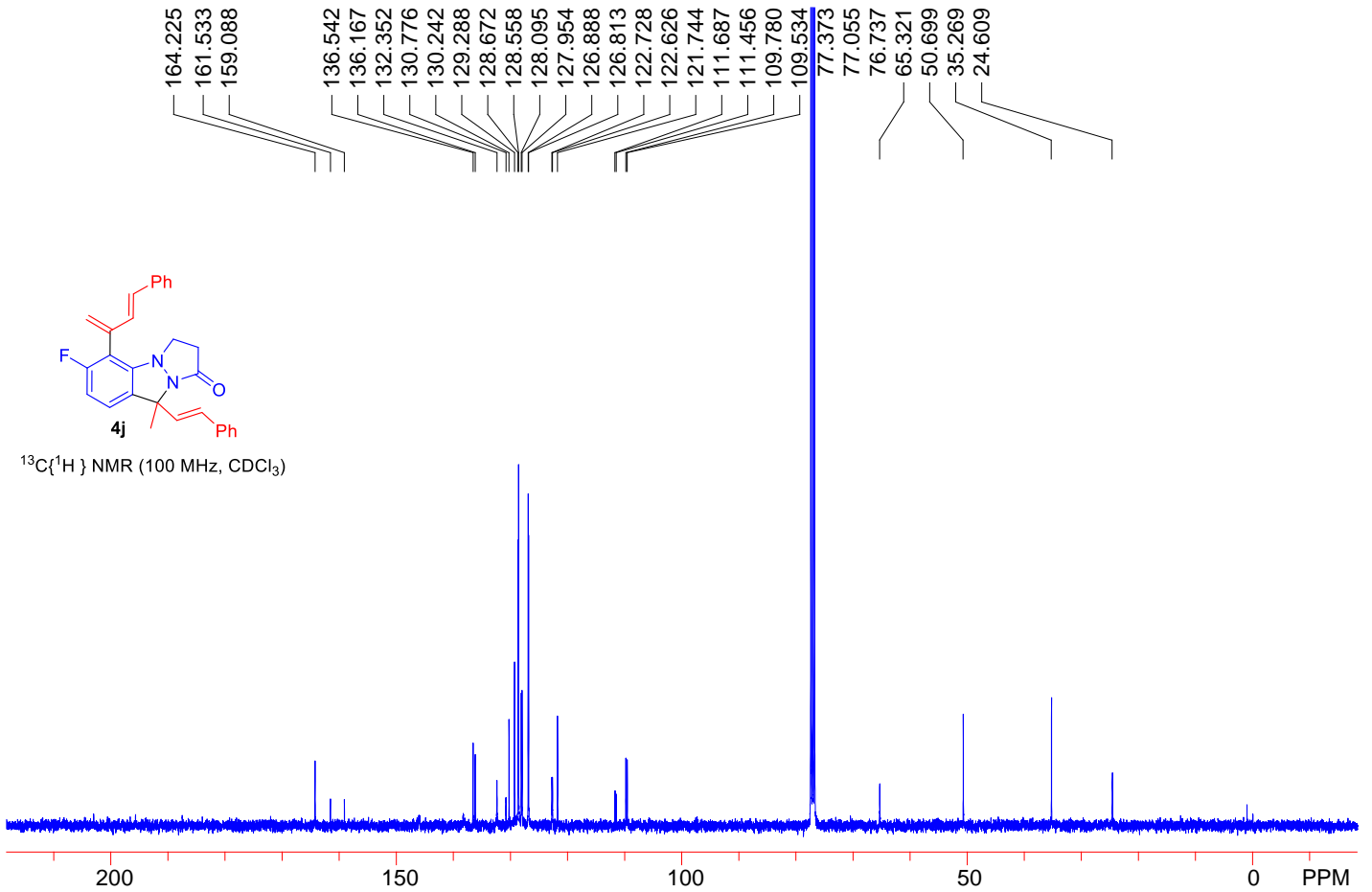
$^1\text{H NMR}$ (600 MHz, CDCl_3 , 55 $^\circ\text{C}$)

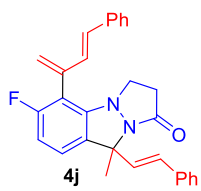


164.225
161.533
159.088
136.542
136.167
132.352
130.776
130.242
129.288
128.672
128.558
128.095
127.954
126.888
126.813
122.728
122.626
121.744
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111.456
109.780
109.534
77.373
77.055
76.737
65.321
50.699
35.269
24.609

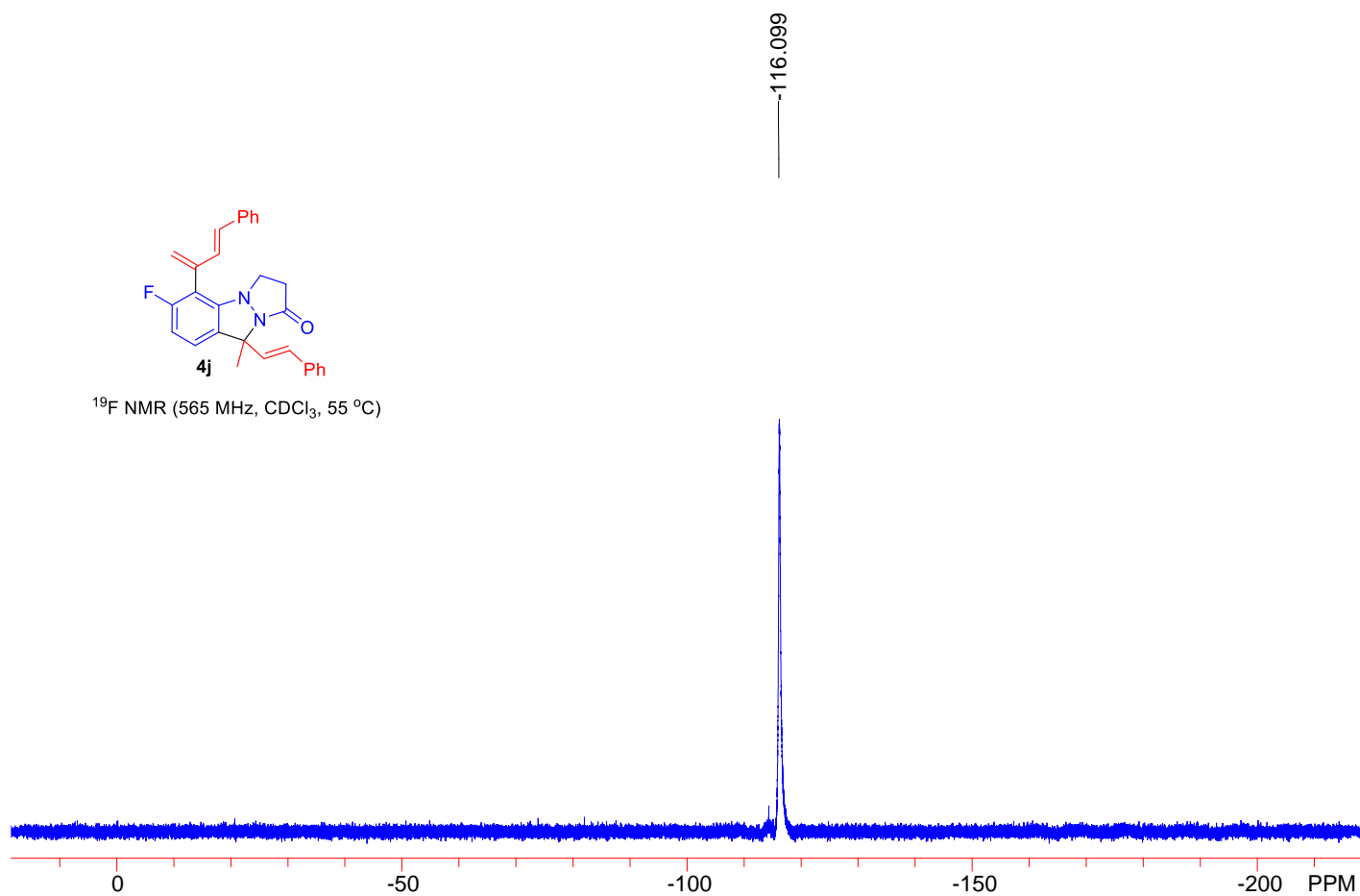


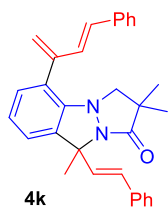
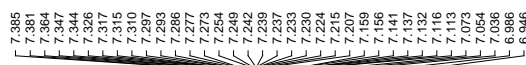
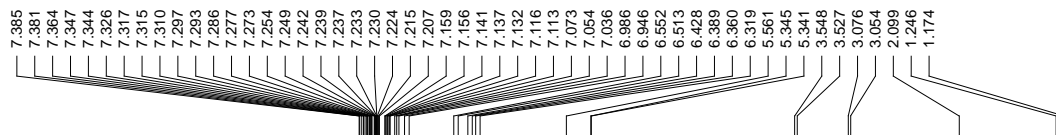
$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)





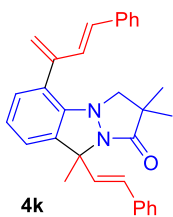
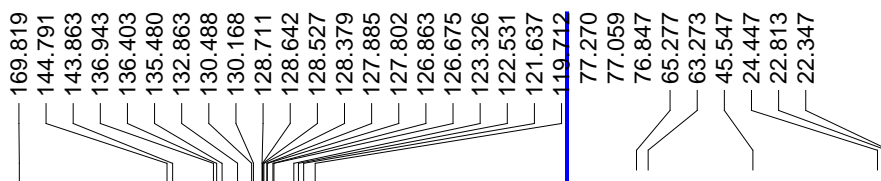
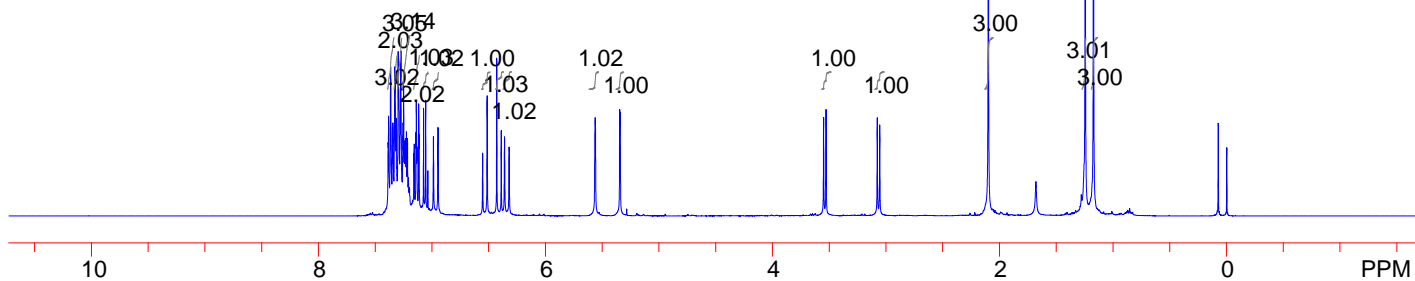
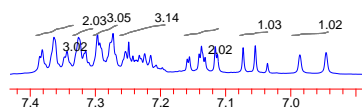
^{19}F NMR (565 MHz, CDCl_3 , 55 °C)





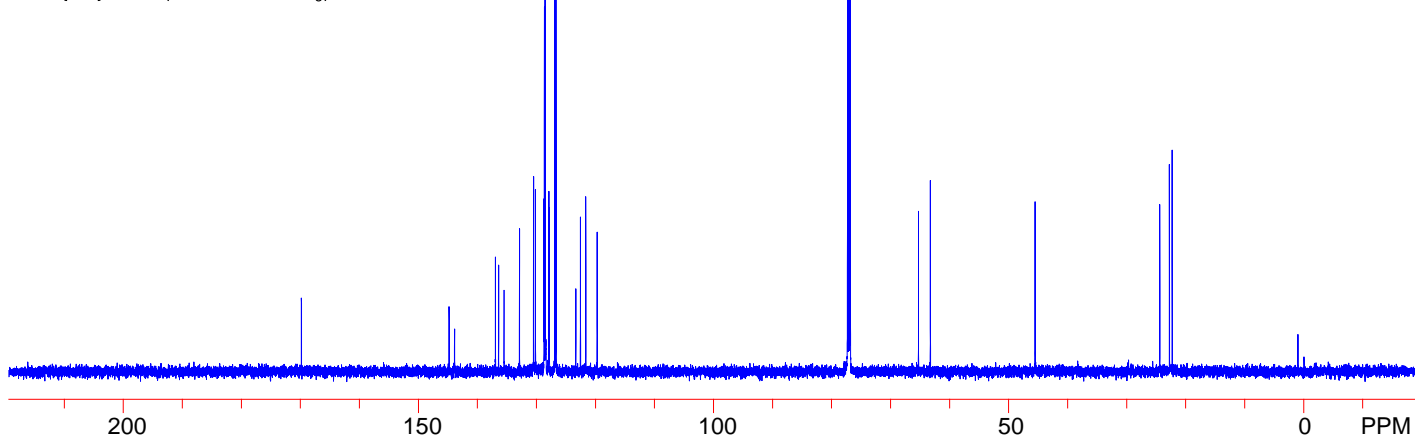
4k

^1H NMR (400 MHz, CDCl_3)

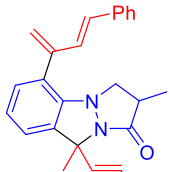


4k

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)

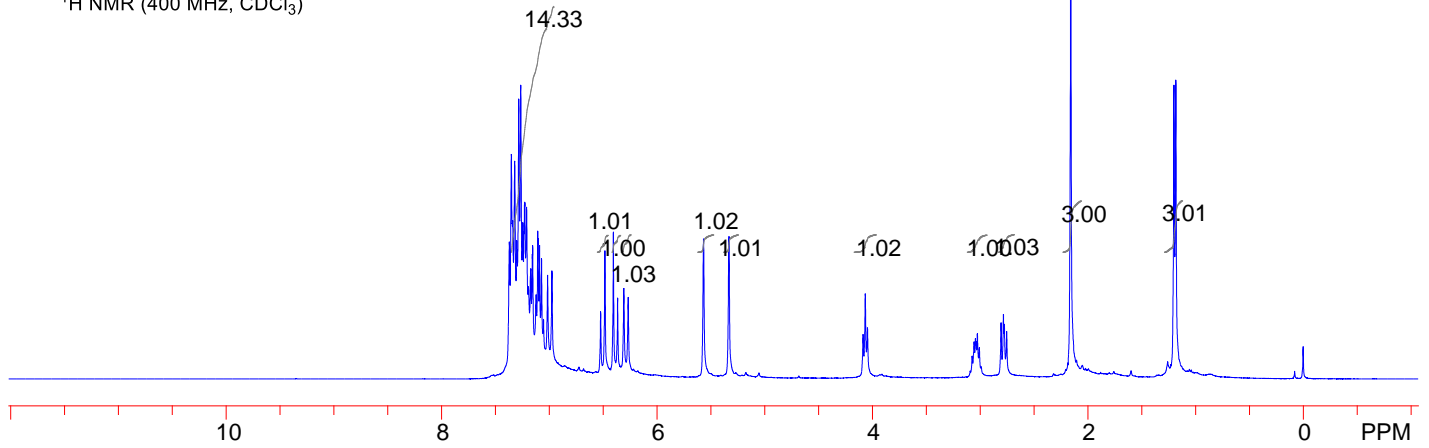


7.372
7.353
7.345
7.340
7.322
7.302
7.284
7.266
7.246
7.236
7.230
7.227
7.211
7.194
7.176
7.172
7.158
7.155
7.126
7.123
7.108
7.104
7.091
7.072
7.054
7.016
6.975
6.524
6.484
6.406
6.366
6.308
6.268
5.568
5.331
4.087
4.066
4.045
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3.043
3.038
3.025
2.805
2.783
2.775
2.753
2.158
1.200
1.182

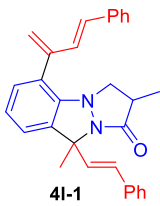


4I-1

^1H NMR (400 MHz, CDCl_3)

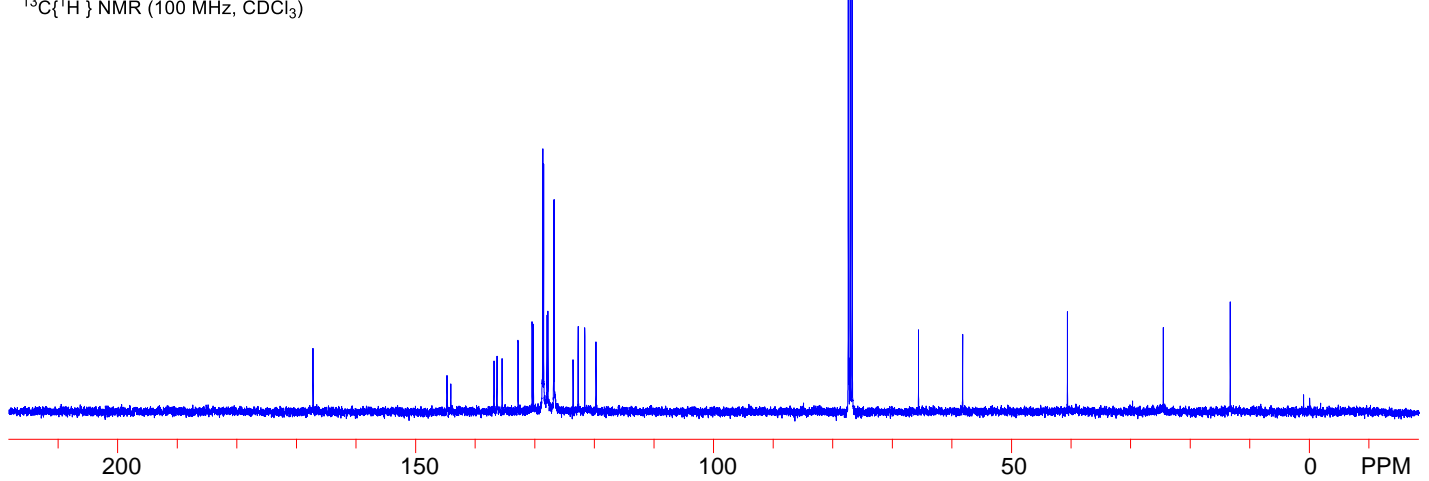


167.219
144.728
144.082
136.838
136.337
135.477
132.800
130.439
130.226
128.650
128.507
127.934
127.787
126.836
126.757
123.567
122.716
121.606
119.725
77.372
77.054
76.736
65.609
58.203
40.644
24.576
13.351

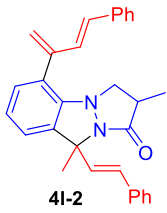


4I-1

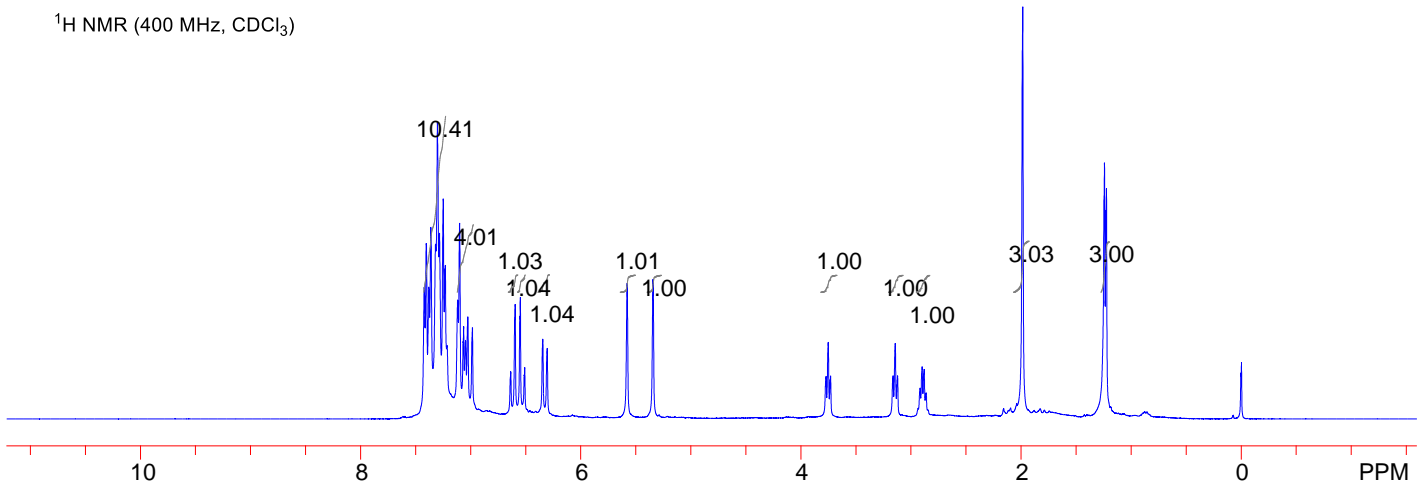
$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)



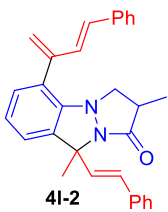
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7.380
7.361
7.319
7.314
7.301
7.283
7.249
7.234
7.229
7.214
7.117
7.099
7.068
7.063
7.046
7.025
6.983
6.635
6.595
6.553
6.548
6.513
6.508
6.344
6.304
5.578
5.342
3.770
3.750
3.728
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2.916
2.898
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2.861
1.985
1.243
1.230
1.225



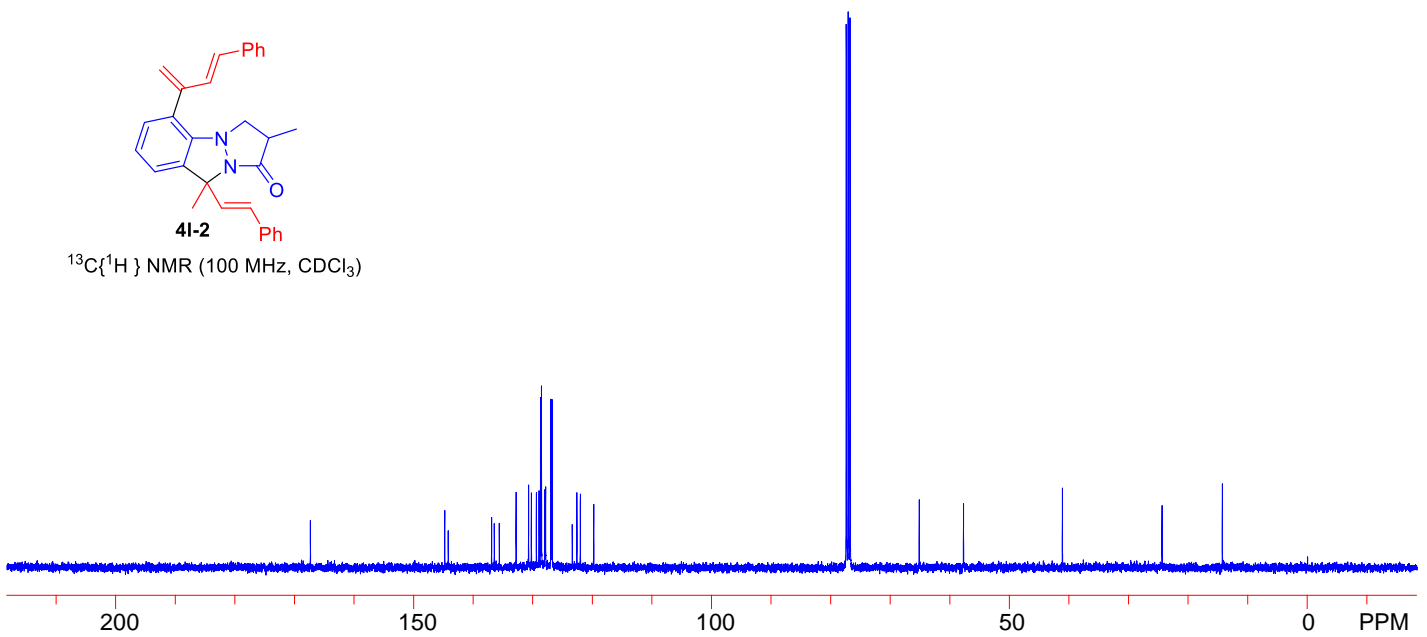
$^1\text{H NMR}$ (400 MHz, CDCl_3)



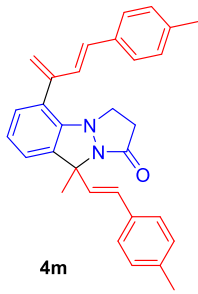
144.766
167.316
144.174
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136.445
135.608
132.783
130.689
130.219
129.381
128.934
128.674
128.522
127.944
127.836
126.933
126.723
123.350
122.585
122.000
119.761
77.377
77.060
76.742
65.135
57.717
41.141
24.427
14.323



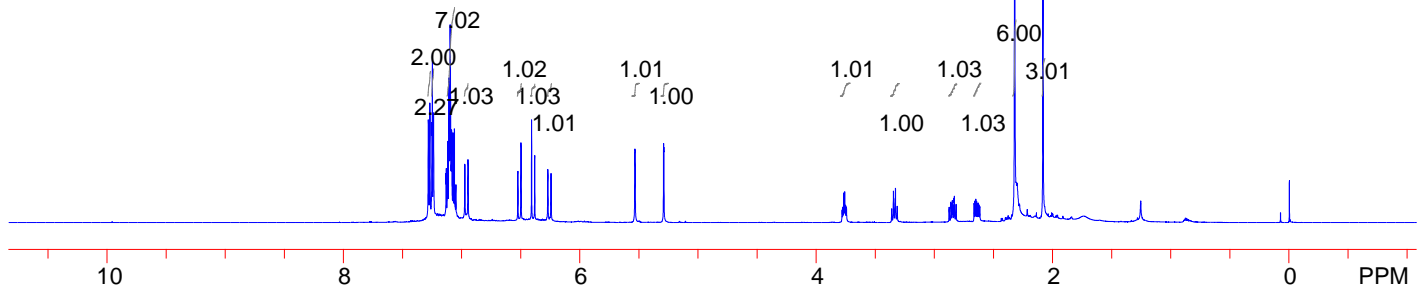
$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)



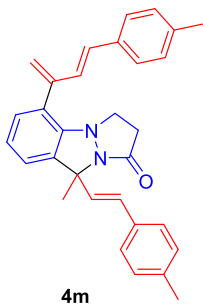
7.282
7.268
7.250
7.247
7.237
7.132
7.129
7.119
7.117
7.107
7.097
7.094
7.085
7.073
7.061
7.048
6.972
6.946
6.524
6.497
6.408
6.381
6.270
6.243
5.533
5.291
5.288
3.780
3.773
3.765
3.758
3.750
3.743
3.361
3.346
3.344
3.329
3.314
2.876
2.861
2.858
2.849
2.843
2.834
2.832
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2.643
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2.616
2.322
2.083



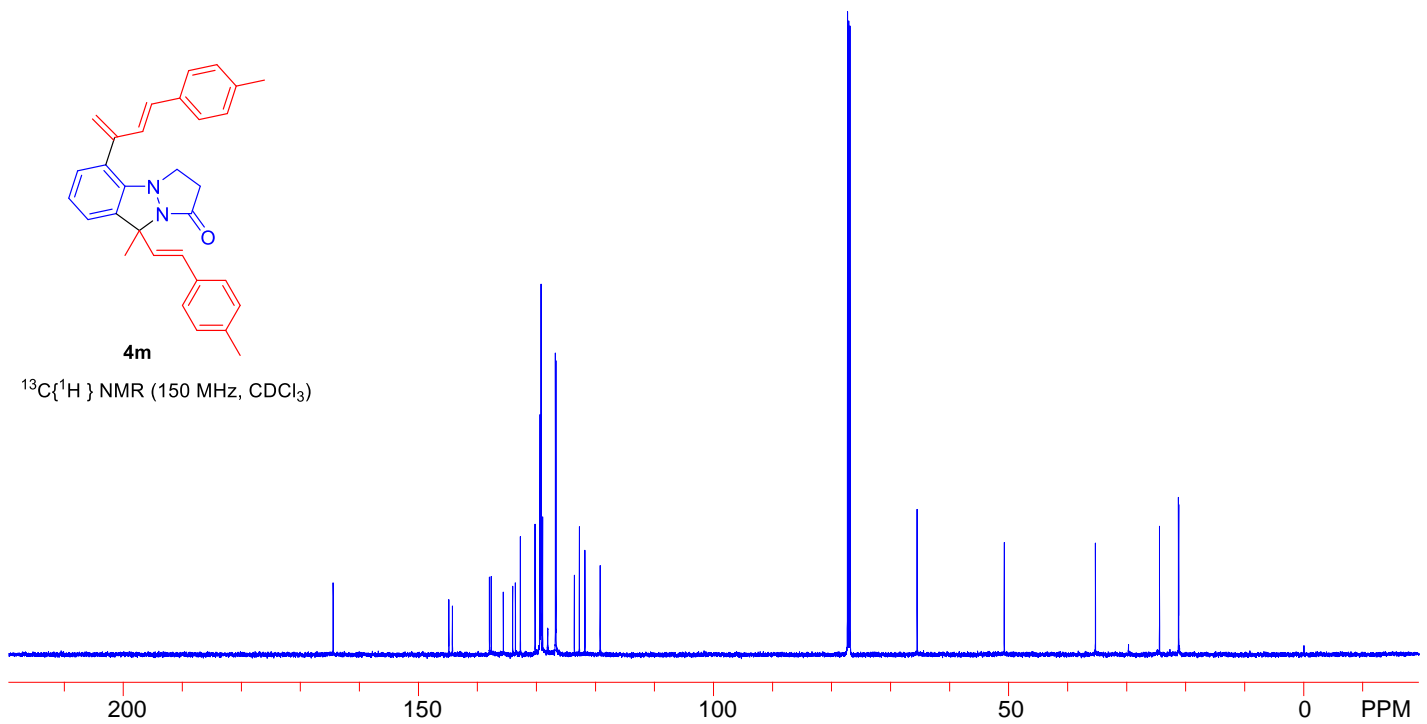
$^1\text{H NMR}$ (600 MHz, CDCl_3)

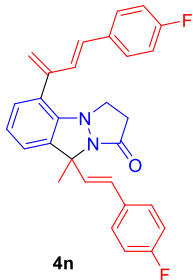
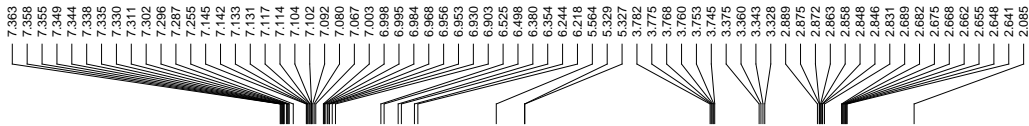


144.837
164.439
144.230
137.961
137.655
135.597
134.022
133.557
132.719
130.226
129.452
129.389
129.221
128.951
128.073
126.783
126.689
123.570
122.723
121.771
119.205
77.293
77.081
76.871
65.512
50.756
35.335
24.492
21.282
21.245

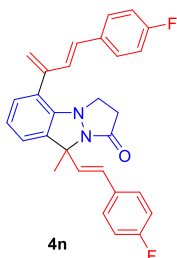
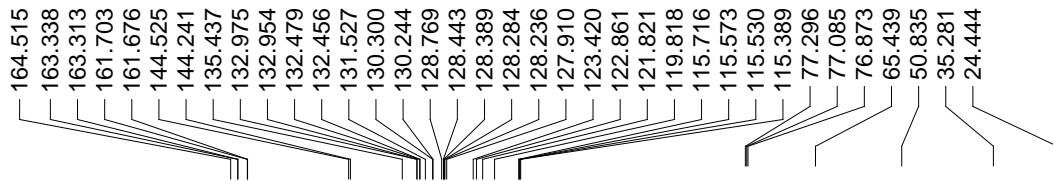
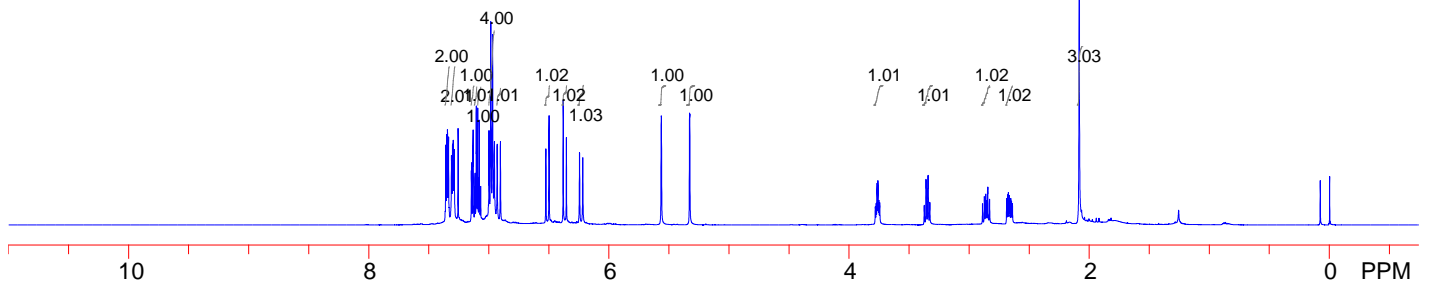


$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)

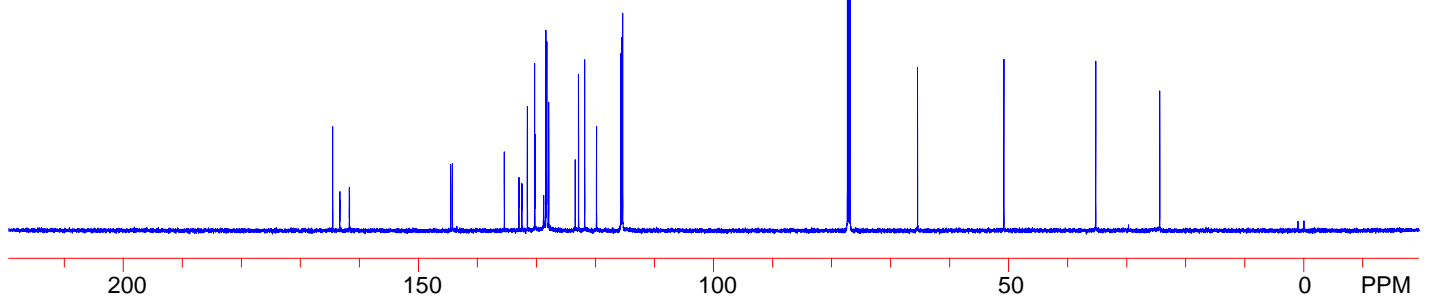


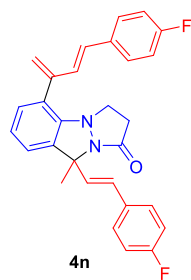


$^1\text{H NMR}$ (600 MHz, CDCl_3)



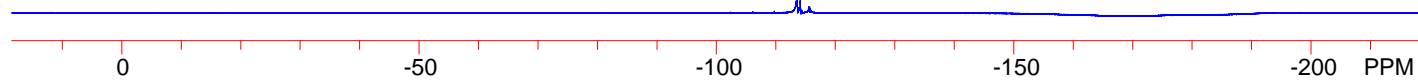
$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)



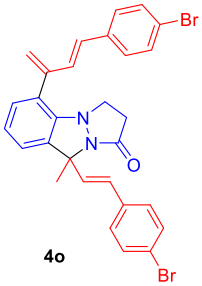


^{19}F NMR (565 MHz, CDCl_3)

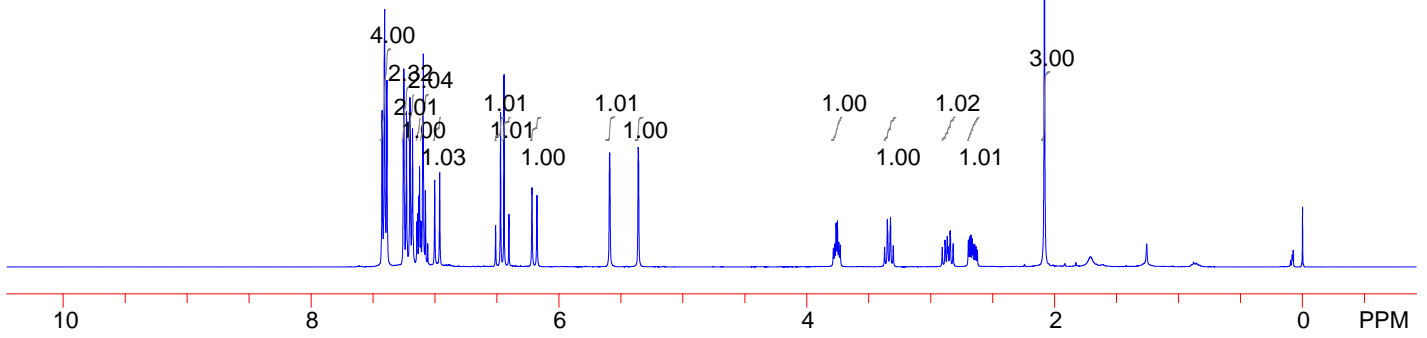
-113.476
-113.492
-113.500
-113.509
-113.517
-113.528
-114.004
-114.012
-114.019
-114.031
-114.038
-114.045
-114.051



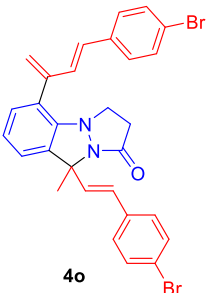
7.427
7.409
7.406
7.388
7.256
7.252
7.230
7.202
7.181
7.147
7.141
7.130
7.125
7.113
7.100
7.094
7.077
7.059
7.002
6.962
6.510
6.471
6.443
6.403
6.217
6.177
5.590
5.359
5.357
3.783
3.772
3.761
3.750
3.739
3.728
3.370
3.348
3.322
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2.905
2.883
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2.865
2.857
2.843
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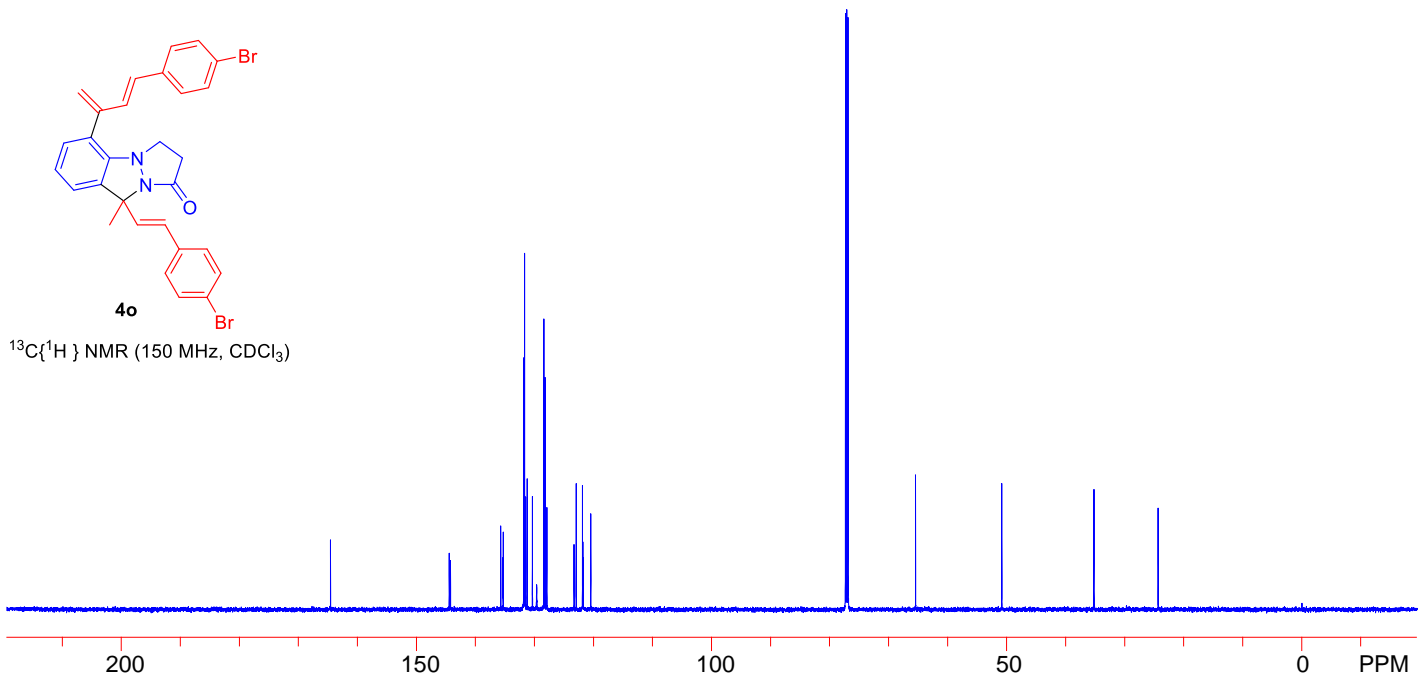
$^1\text{H NMR}$ (400 MHz, CDCl_3)



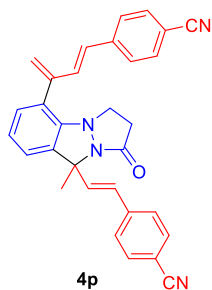
144.430
164.549
144.217
135.703
135.303
135.273
131.798
131.657
131.500
131.223
130.340
129.614
128.387
128.181
127.889
123.277
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121.691
120.457
77.294
77.082
76.870
65.439
50.848
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24.391



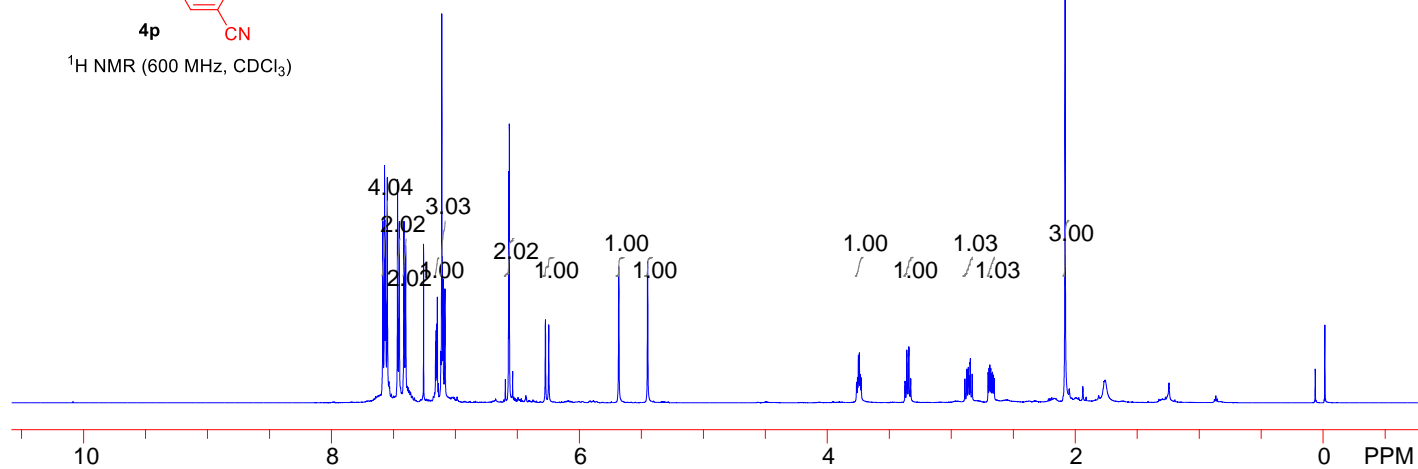
$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)



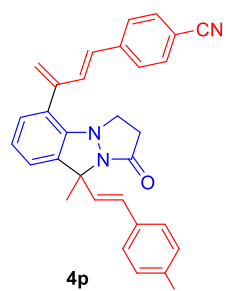
7.586
7.572
7.564
7.550
7.467
7.453
7.416
7.402
7.257
7.161
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7.151
7.146
7.138
7.118
7.110
7.106
7.100
7.085
6.598
6.571
6.565
6.539
6.274
6.247
5.683
5.451
3.764
3.757
3.750
3.742
3.735
3.727
3.374
3.359
3.342
3.328
2.891
2.876
2.874
2.864
2.859
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2.083



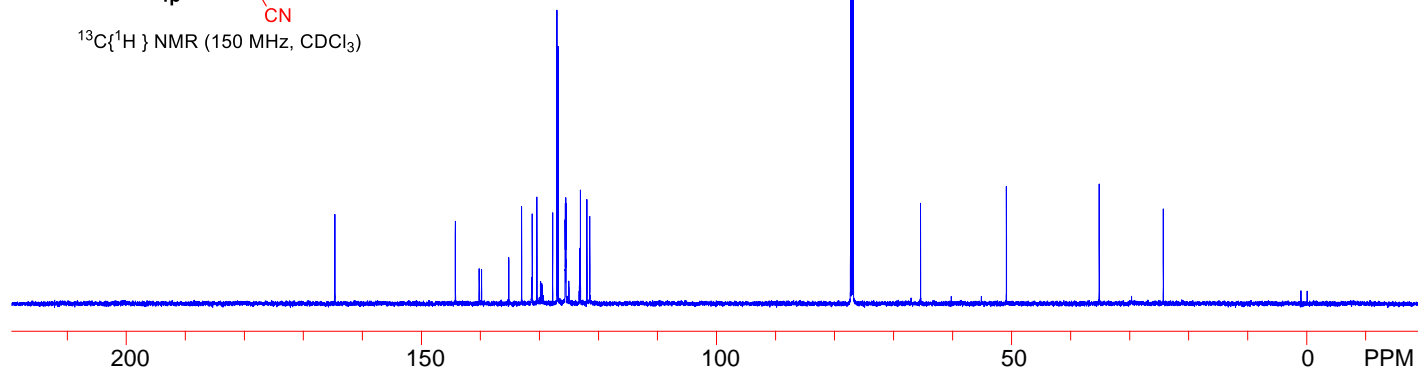
^1H NMR (600 MHz, CDCl_3)

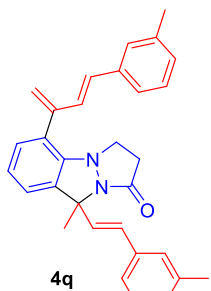
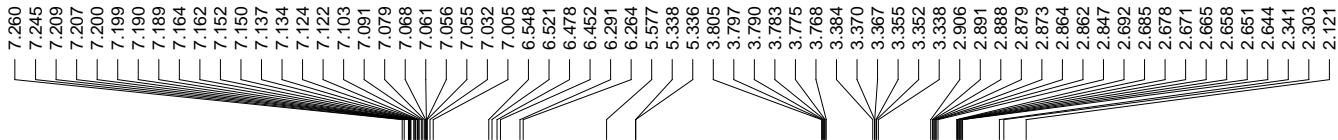


164.663
144.237
140.203
139.801
135.186
133.008
131.292
131.215
130.422
129.809
129.780
129.598
129.566
127.754
127.026
126.813
125.622
125.604
125.524
125.501
125.062
125.014
123.260
123.213
123.130
123.052
121.949
121.476
77.270
77.058
76.846
65.437
50.915
35.202
24.348



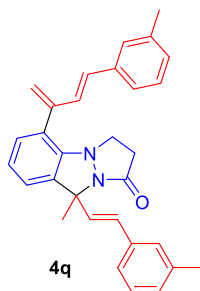
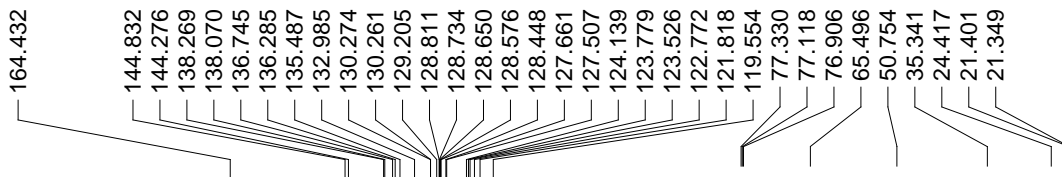
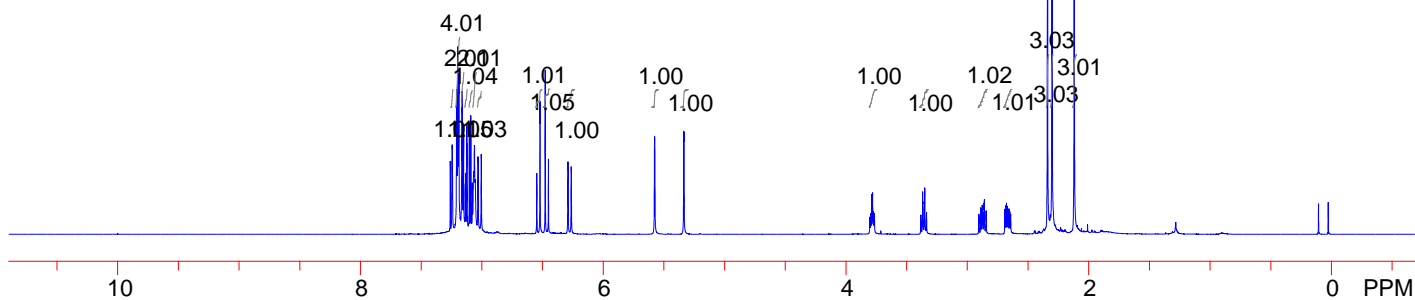
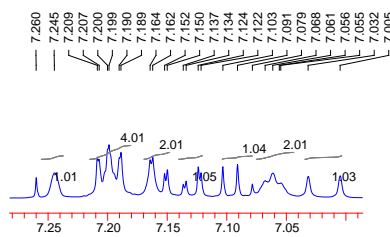
$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)





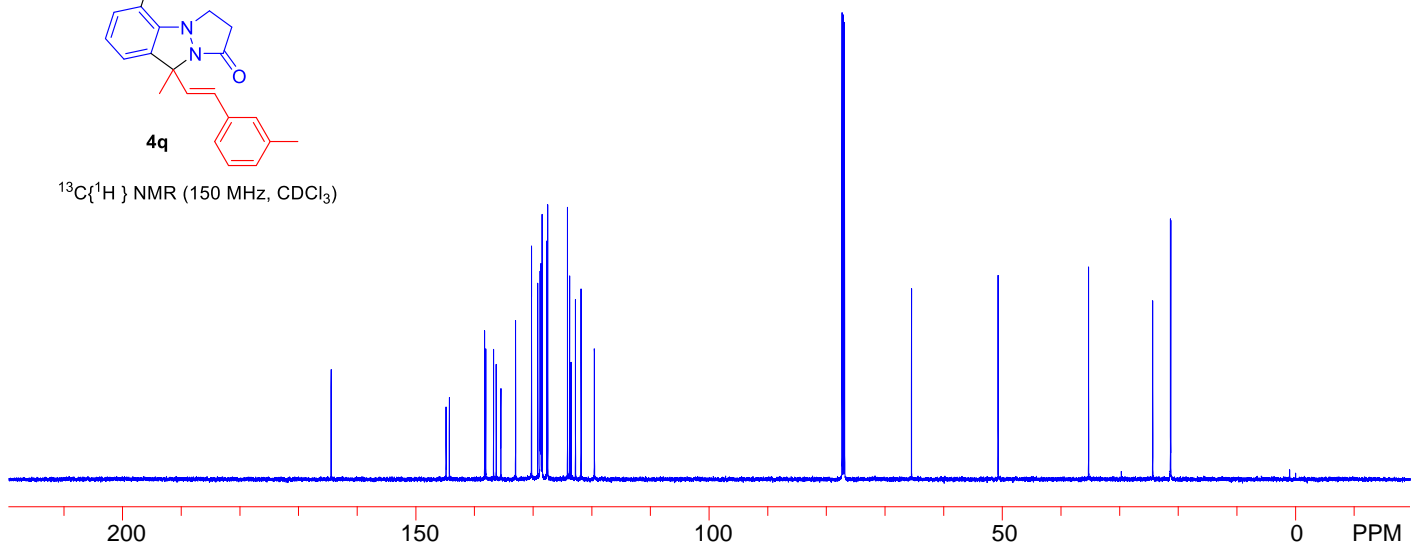
4q

¹H NMR (600 MHz, CDCl₃)

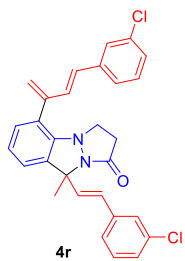


4q

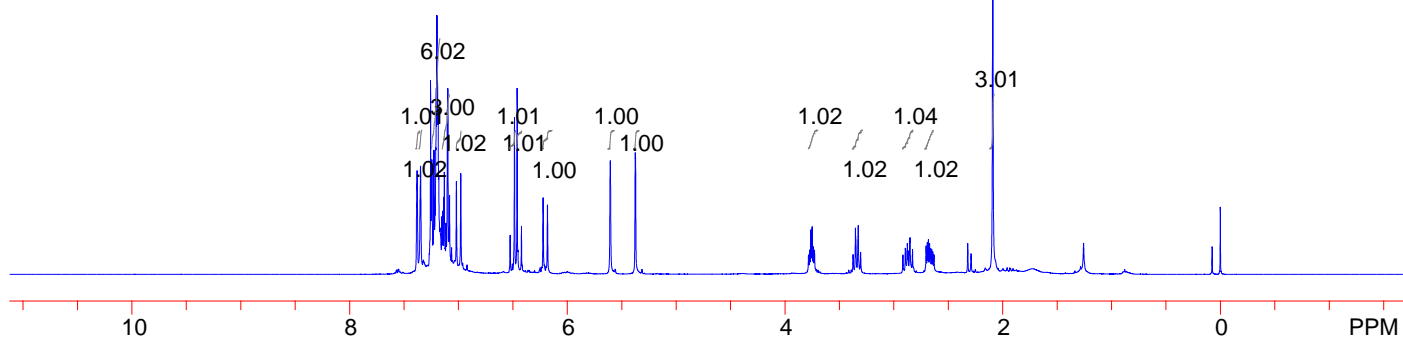
¹³C{¹H} NMR (150 MHz, CDCl₃)



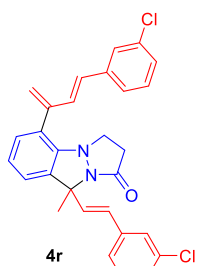
7.380
7.348
7.256
7.251
7.244
7.232
7.225
7.214
7.208
7.203
7.197
7.192
7.187
7.181
7.146
7.135
7.129
7.114
7.102
7.098
7.087
7.082
7.063
7.018
6.978
6.525
6.485
6.460
6.421
6.222
6.182
5.605
5.376
5.373
5.373
3.783
3.772
3.762
3.750
3.739
3.728
3.728
3.374
3.352
3.326
3.305
3.305
2.916
2.894
2.890
2.876
2.868
2.853
2.850
2.828
2.703
2.692
2.682
2.671
2.663
2.652
2.642
2.631
2.090



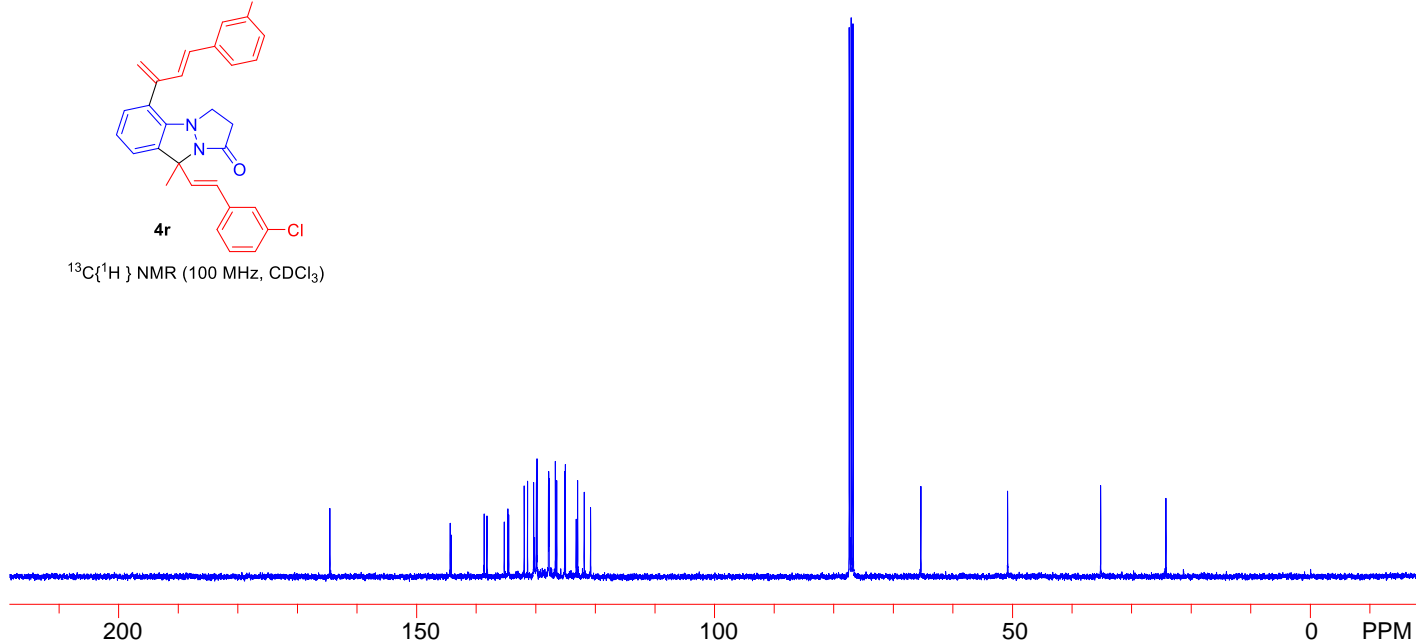
$^1\text{H NMR}$ (400 MHz, CDCl_3)

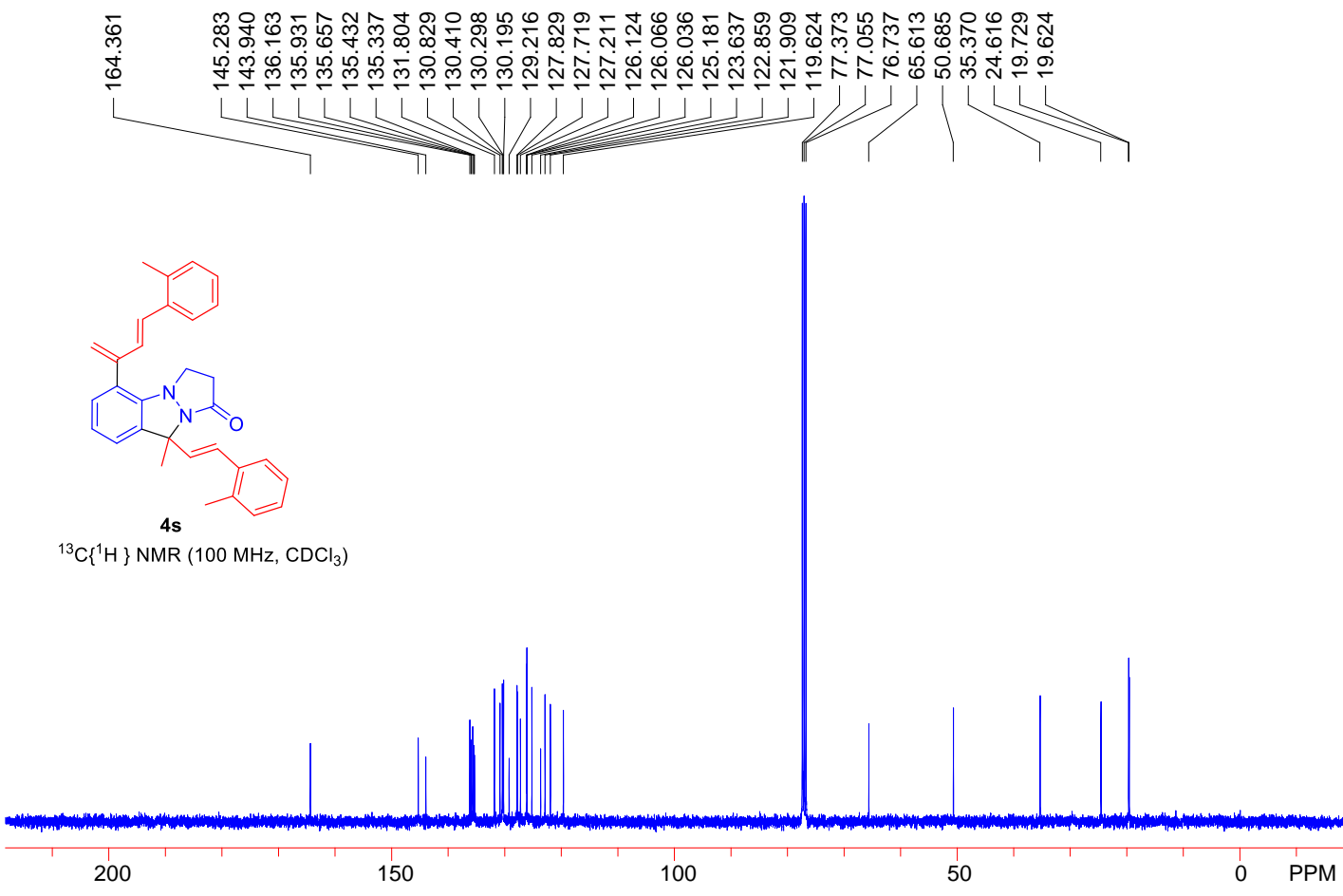
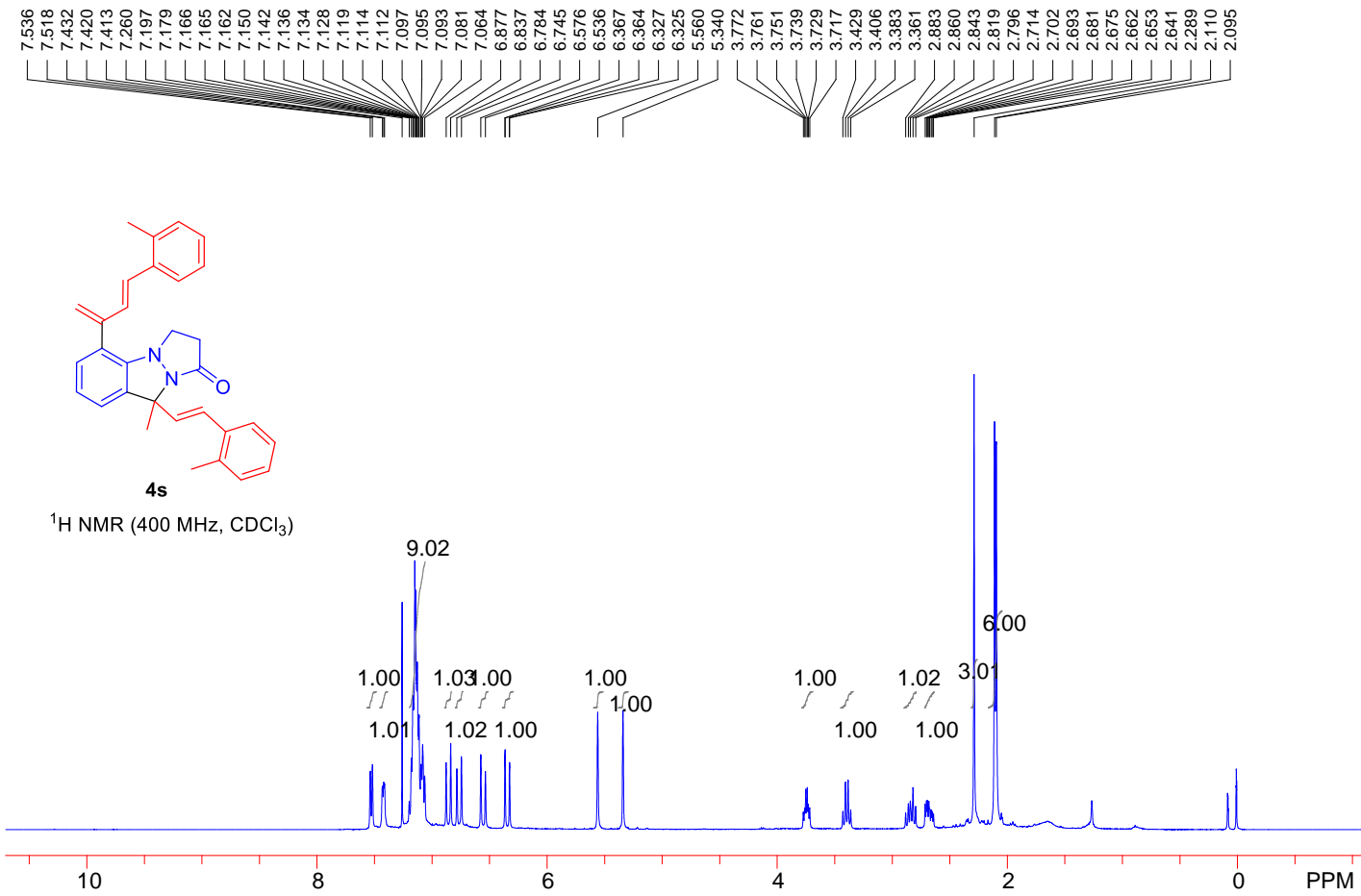


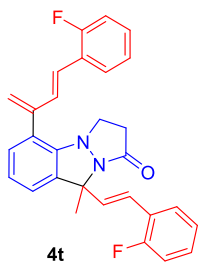
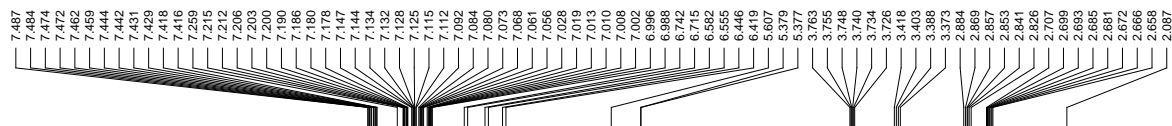
164.550
144.356
144.184
138.652
138.186
135.280
134.689
134.536
131.926
131.376
130.347
130.205
129.889
129.799
127.867
127.812
127.753
126.700
126.474
125.145
125.020
123.213
122.961
121.852
120.797
77.386
77.069
76.751
65.378
50.843
35.241
24.296



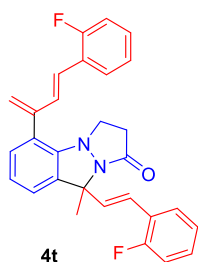
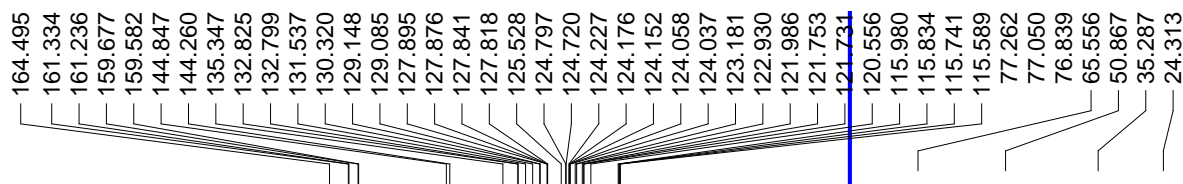
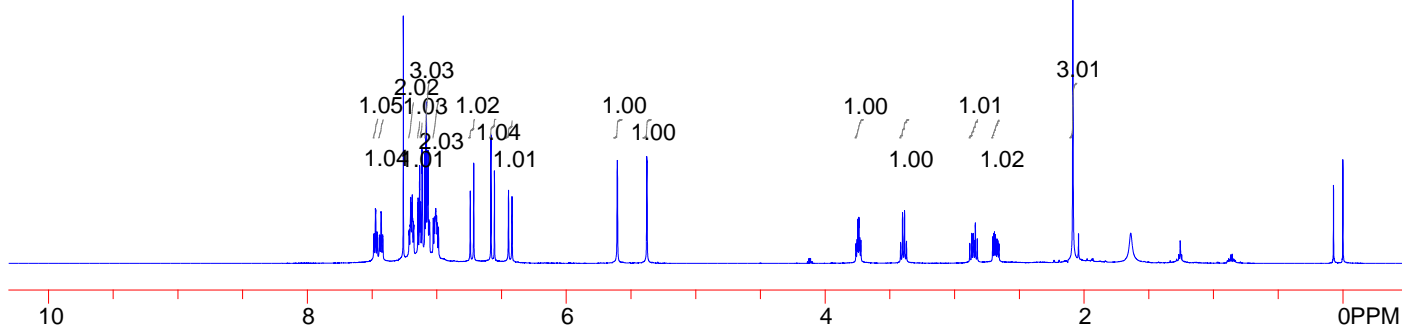
$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)



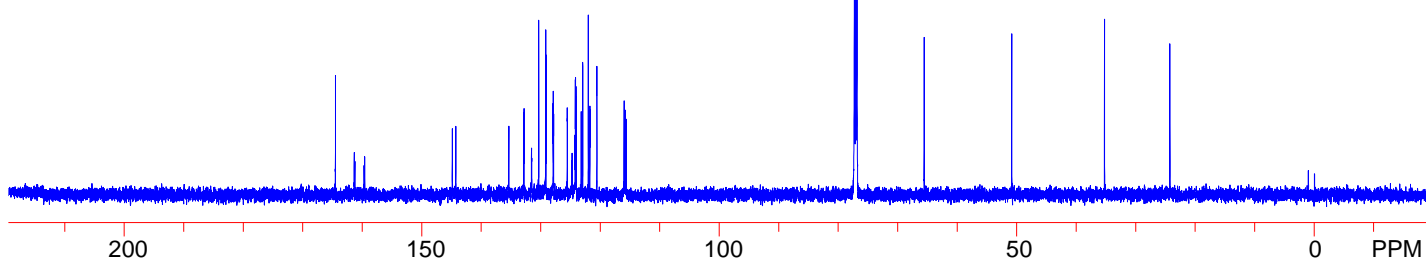


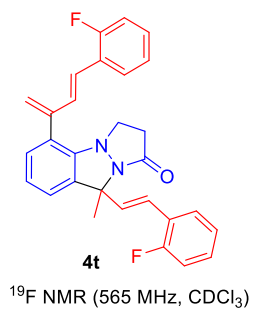


$^1\text{H NMR}$ (600 MHz, CDCl_3)

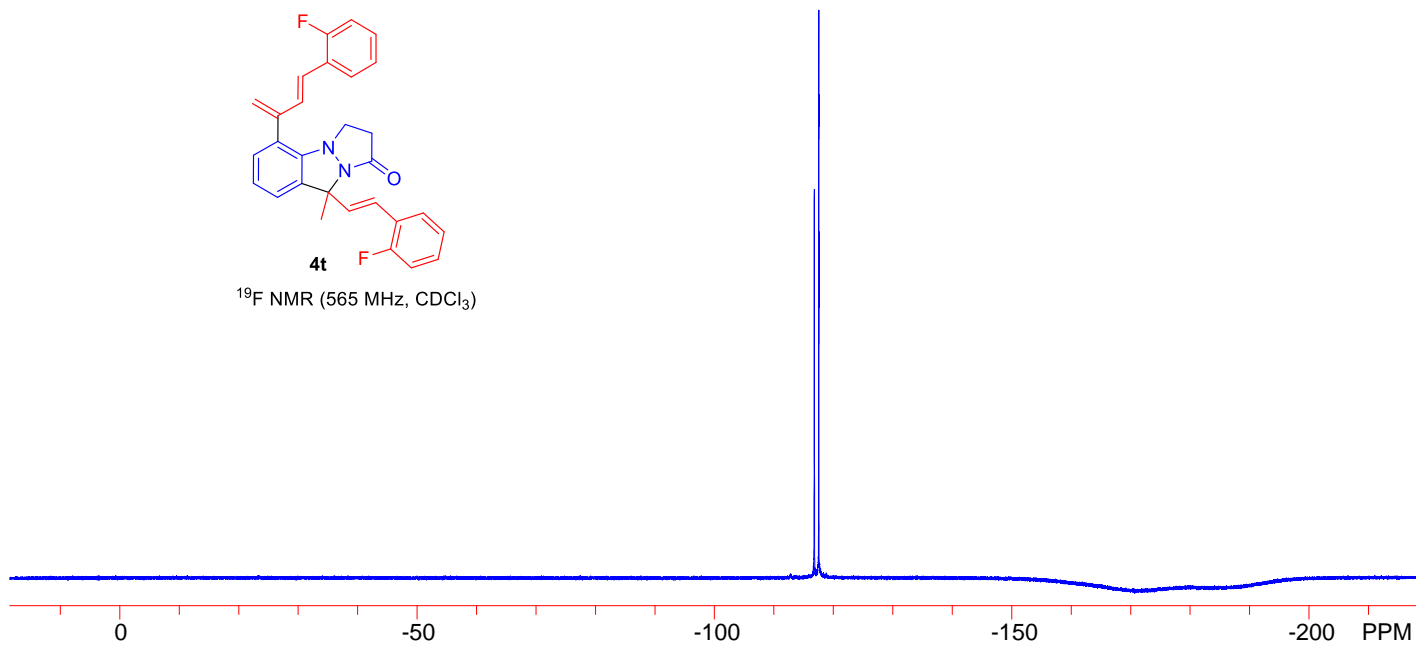


$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)

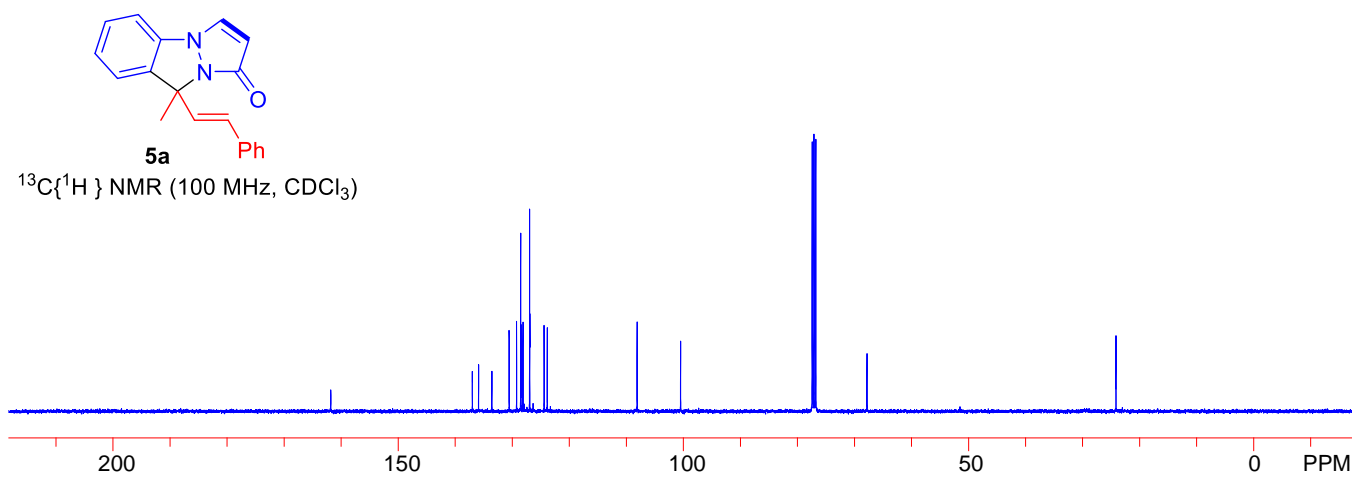
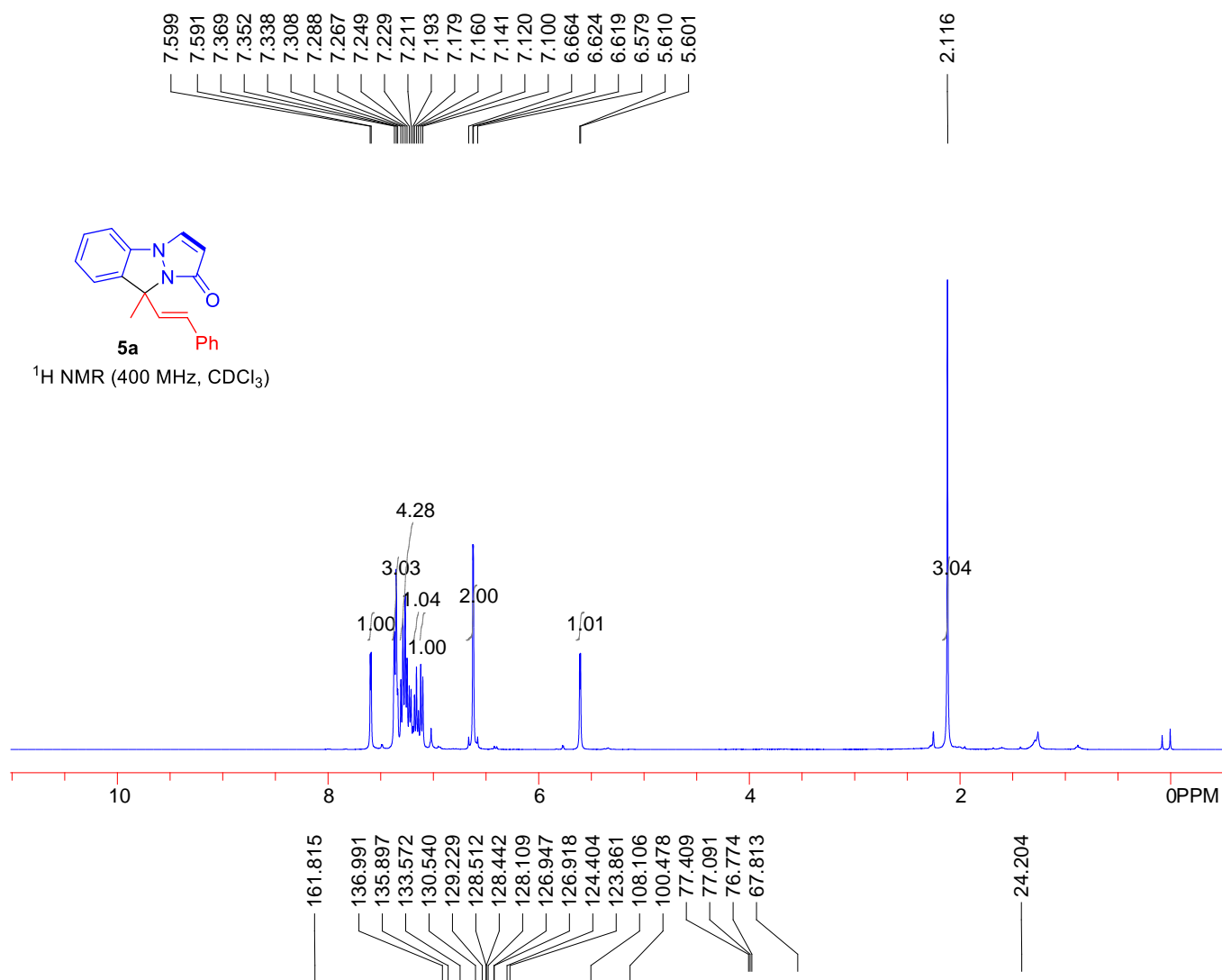




116.728
117.450
117.463
117.470
117.484
117.494

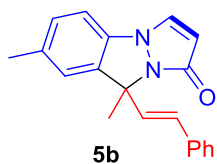


VII. NMR spectra of 5a-5d

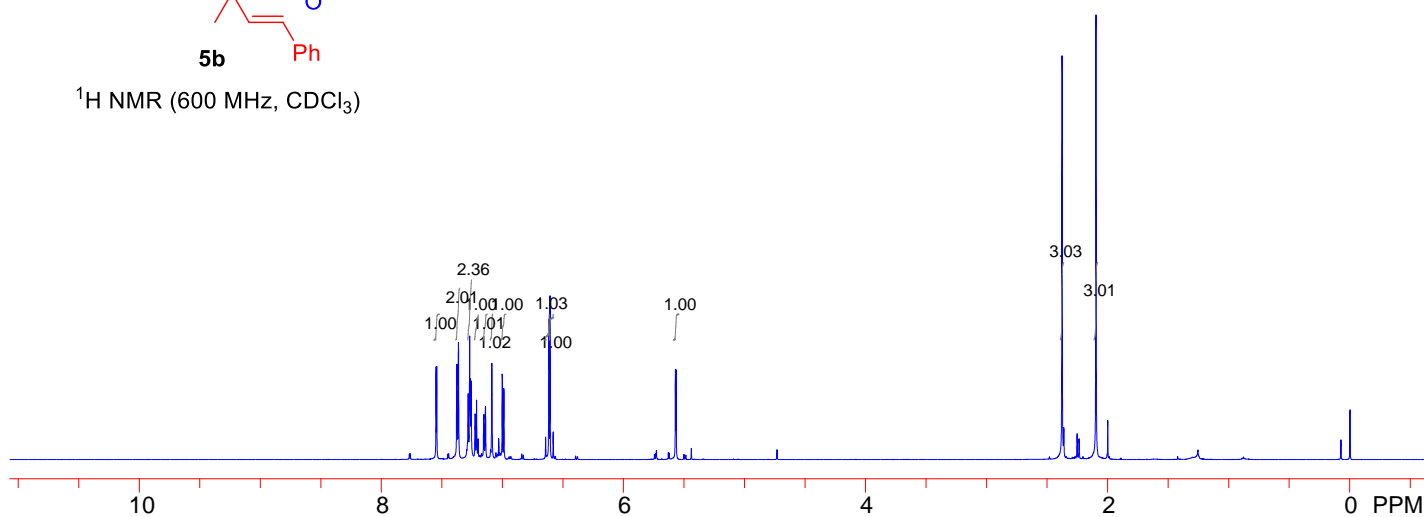


7.548
7.542
7.375
7.363
7.282
7.270
7.264
7.257
7.225
7.213
7.201
7.153
7.139
7.087
7.001
6.988
6.643
6.616
6.606
6.580
5.571
5.565

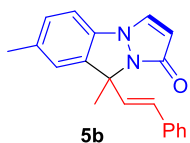
2.378
2.098



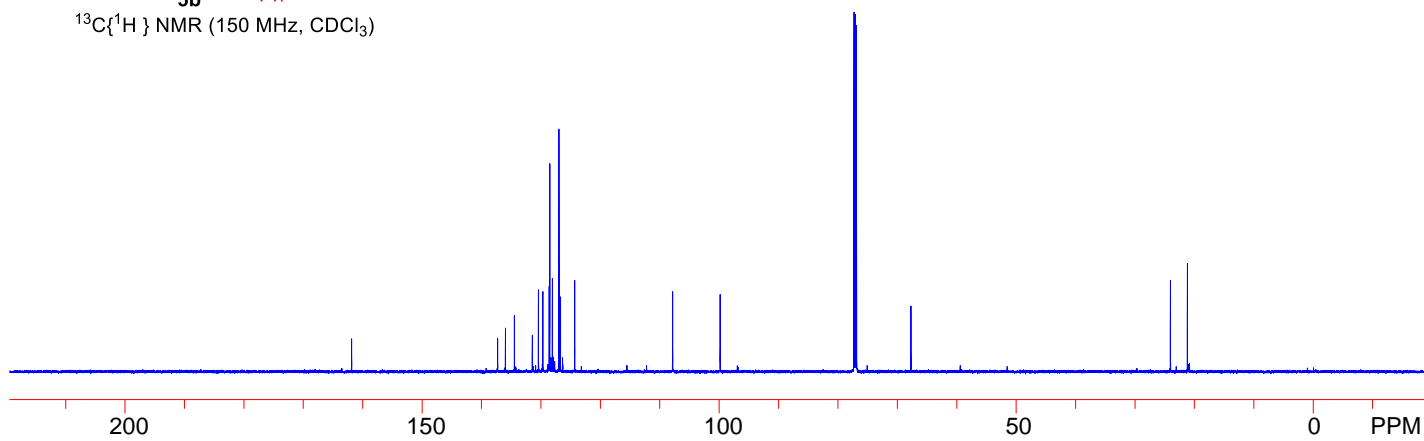
^1H NMR (600 MHz, CDCl_3)

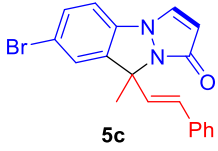
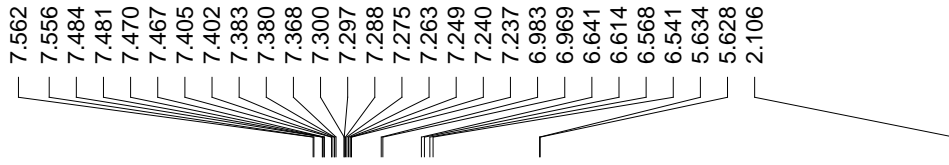


161.862
137.271
135.971
134.455
131.435
130.412
129.660
128.601
128.504
128.065
126.954
126.701
124.303
107.823
99.820
77.297
77.085
76.873
67.721
24.095
21.248

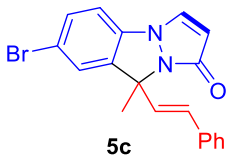
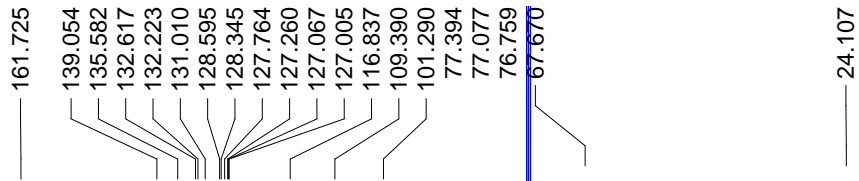
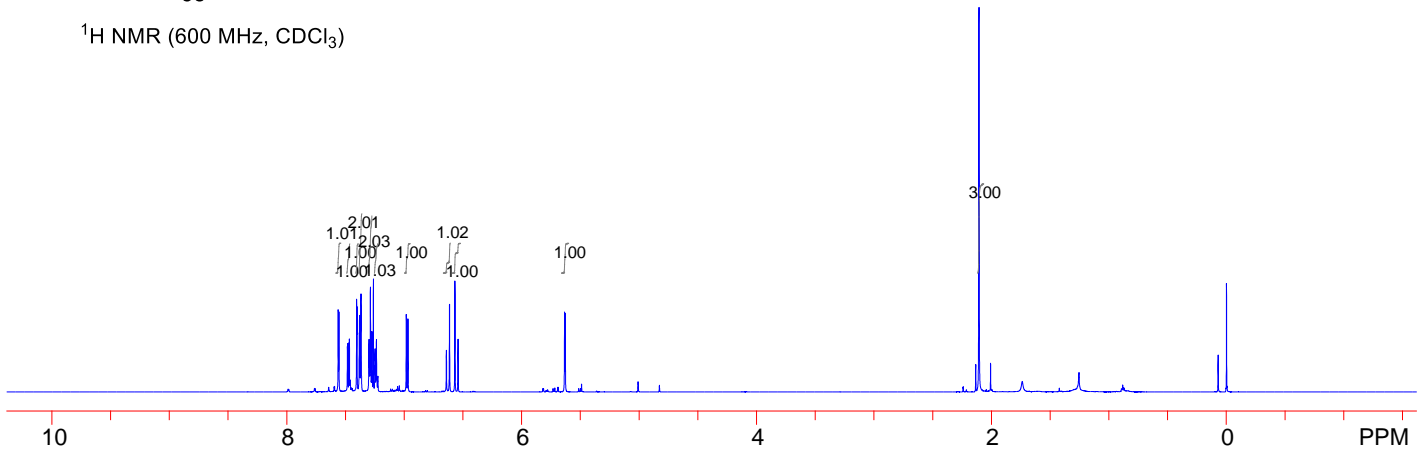


$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)

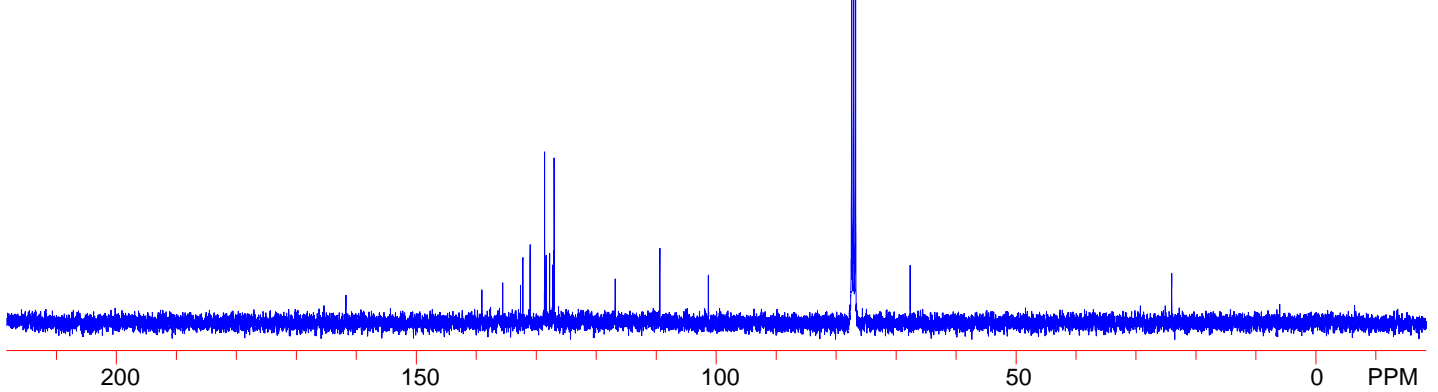


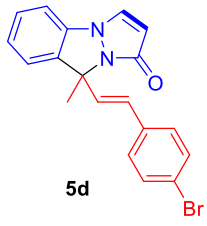


^1H NMR (600 MHz, CDCl_3)



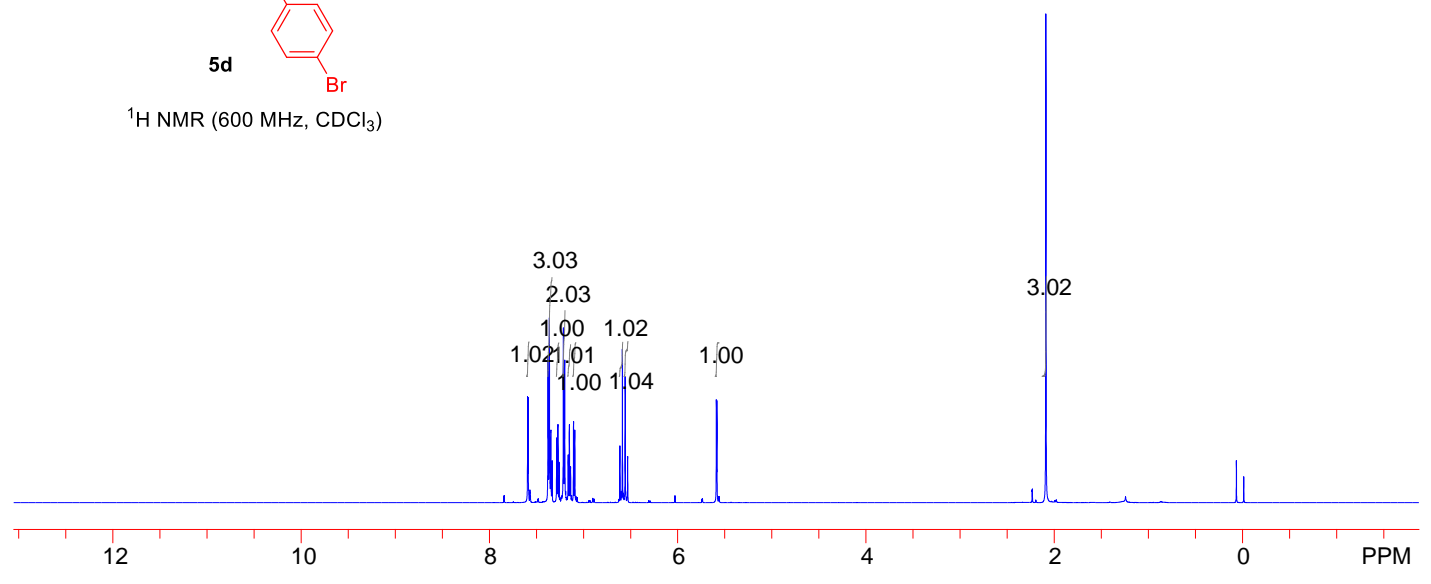
$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)



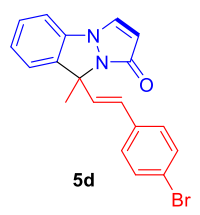


¹H NMR (600 MHz, CDCl₃)

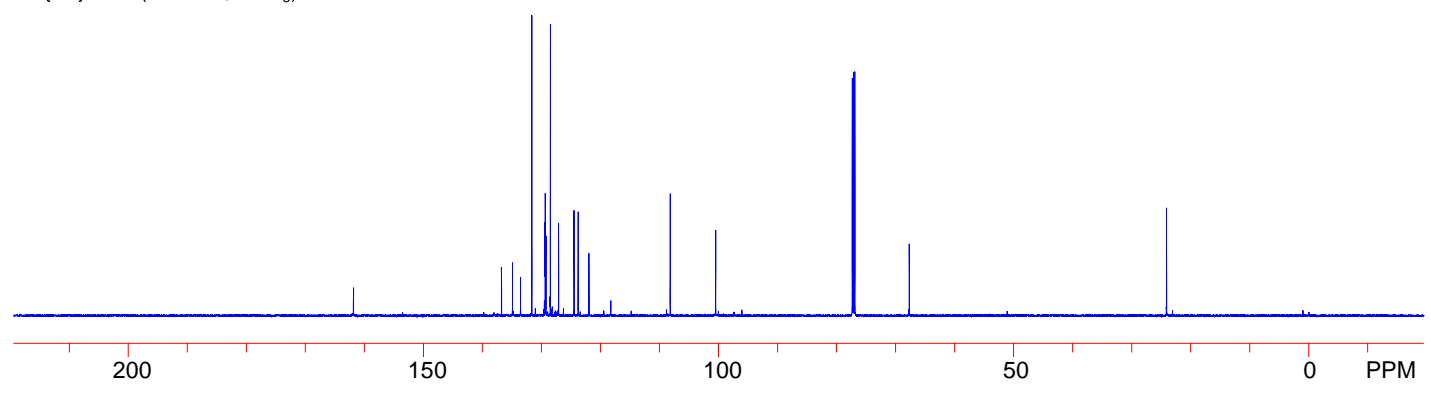
7.594
7.588
7.377
7.362
7.359
7.346
7.335
7.333
7.284
7.272
7.260
7.214
7.200
7.162
7.150
7.137
7.106
7.093
6.614
6.587
6.558
6.531
5.589
5.583
2.088



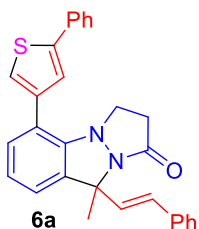
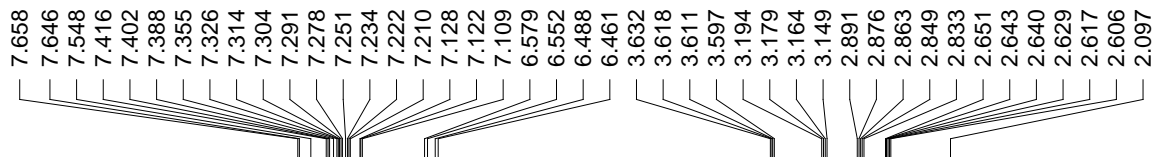
161.838
136.760
134.901
133.533
131.627
129.360
129.337
129.226
128.478
127.091
124.472
123.771
121.945
108.172
100.480
77.318
77.107
76.896
67.682
24.147



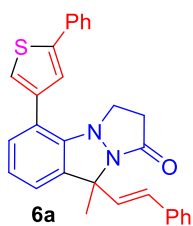
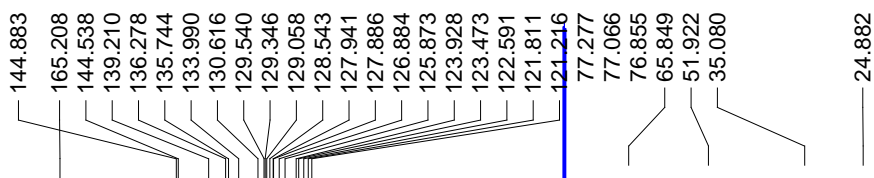
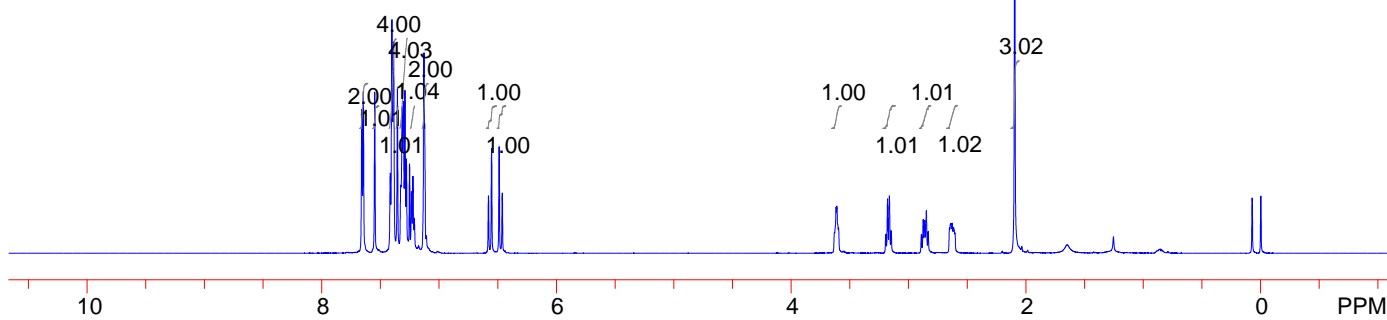
¹³C{¹H} NMR (150 MHz, CDCl₃)



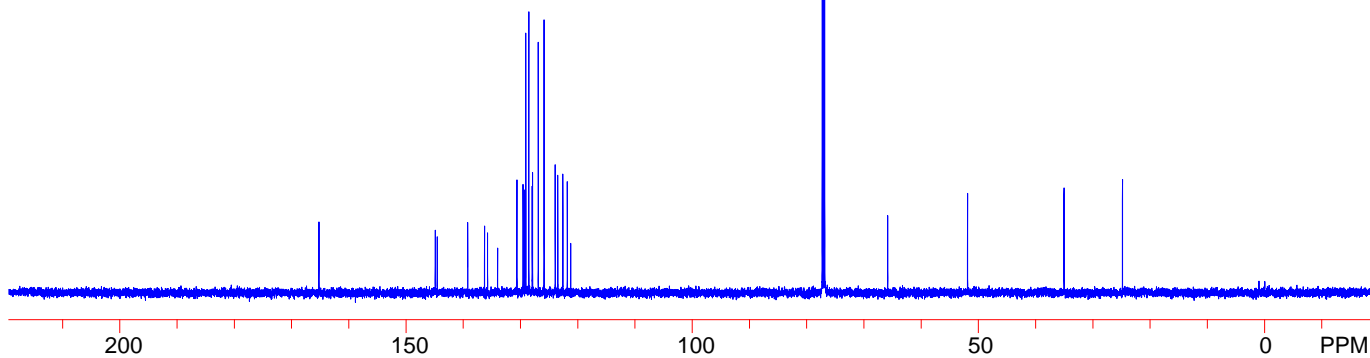
VIII. NMR spectra of 6a-6e



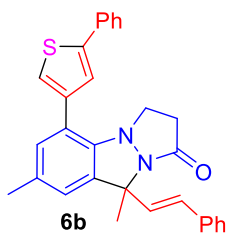
¹H NMR (600 MHz, CDCl₃)



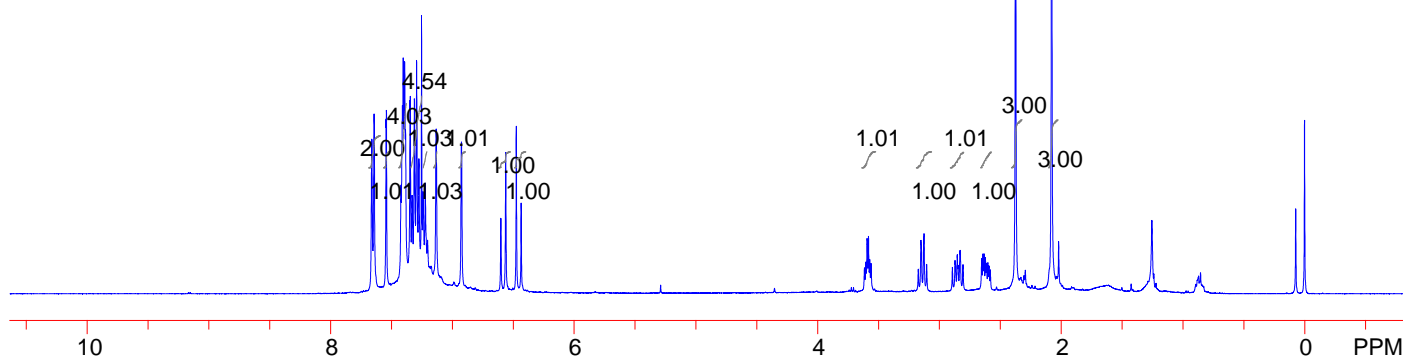
¹³C{¹H} NMR (150 MHz, CDCl₃)



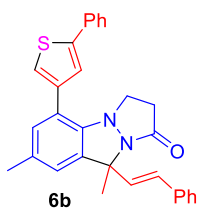
7.661
7.643
7.544
7.542
7.421
7.410
7.404
7.392
7.384
7.348
7.345
7.330
7.312
7.294
7.275
7.253
7.240
7.222
7.204
7.133
6.925
6.602
6.562
6.475
6.435
3.617
3.606
3.595
3.584
3.574
3.562
3.174
3.153
3.128
3.106
2.894
2.873
2.869
2.854
2.847
2.833
2.829
2.807
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2.643
2.634
2.623
2.614
2.603
2.594
2.583
2.375
2.079



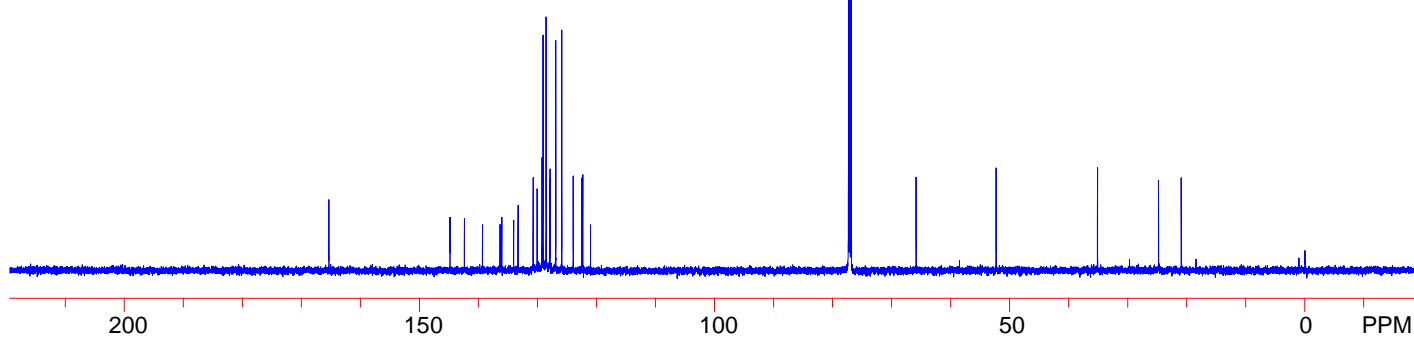
$^1\text{H NMR}$ (400 MHz, CDCl_3)

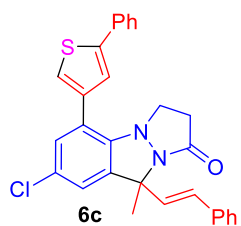
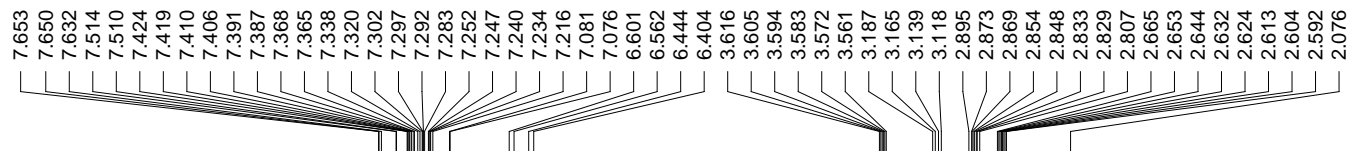


144.809
165.334
142.373
139.299
136.331
136.035
134.023
133.280
130.710
130.046
129.212
129.047
128.528
127.904
127.849
126.885
125.867
123.923
122.465
122.316
120.999
77.270
77.059
76.848
65.854
52.321
35.159
24.822
20.980

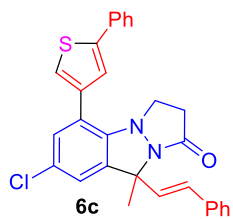
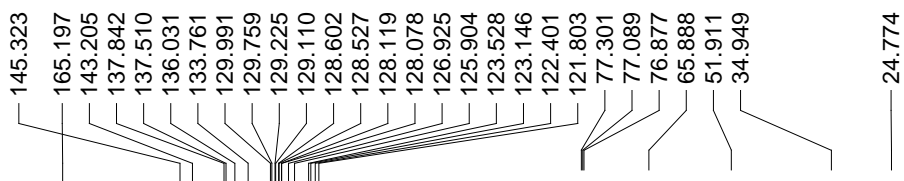
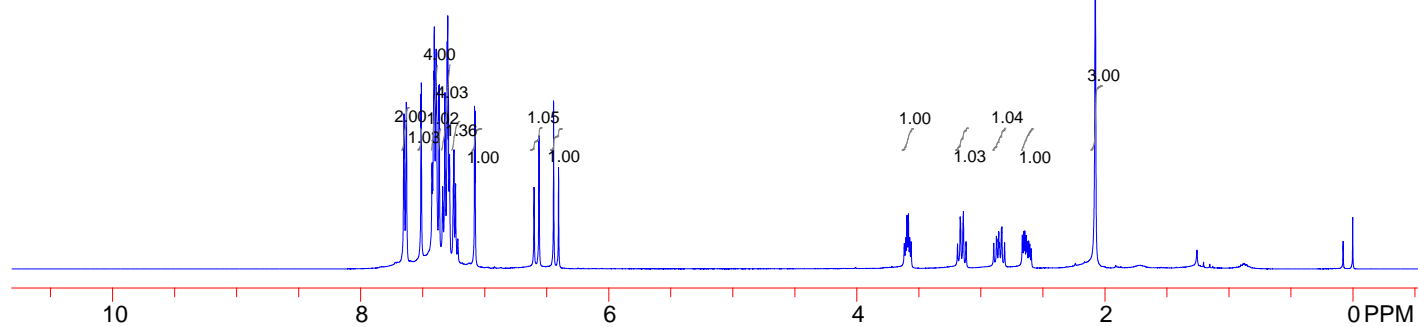


$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)

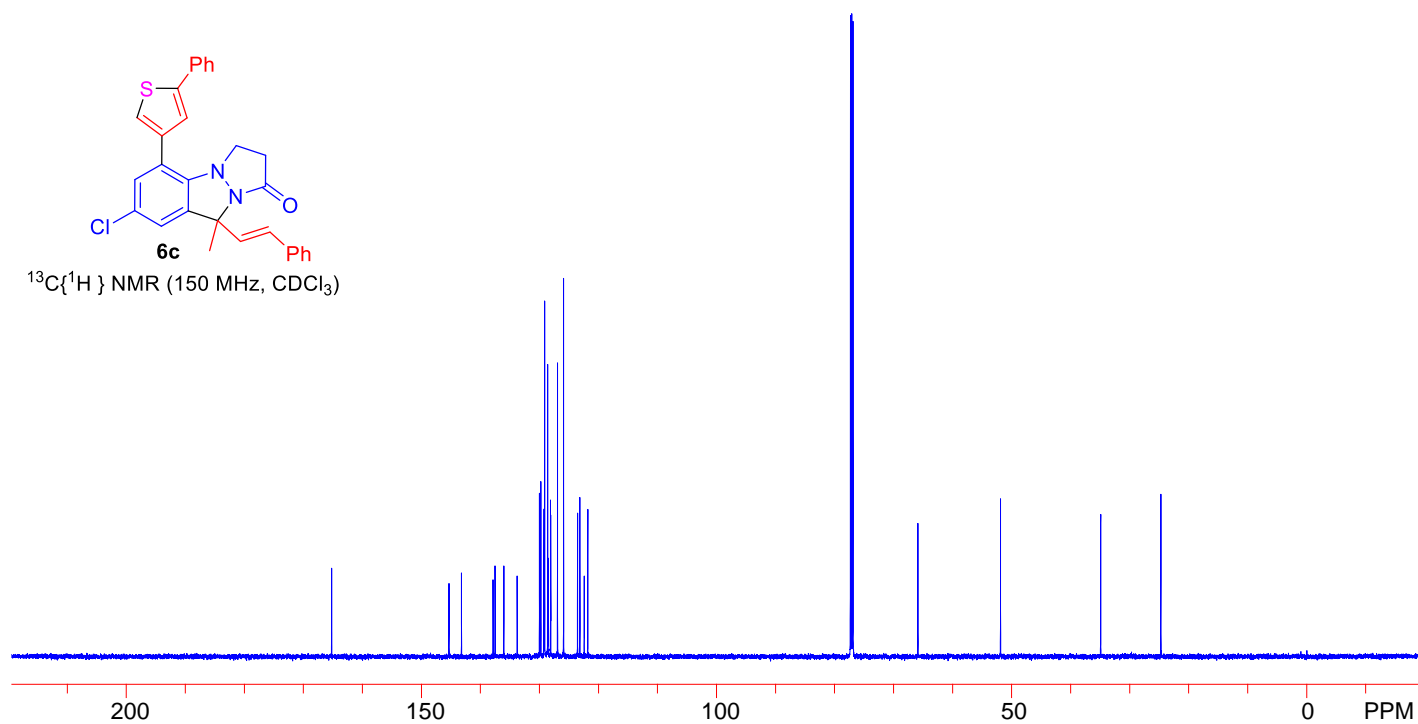




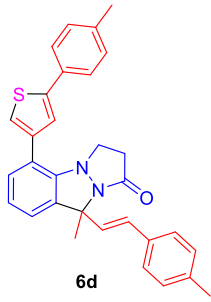
^1H NMR (400 MHz, CDCl_3)



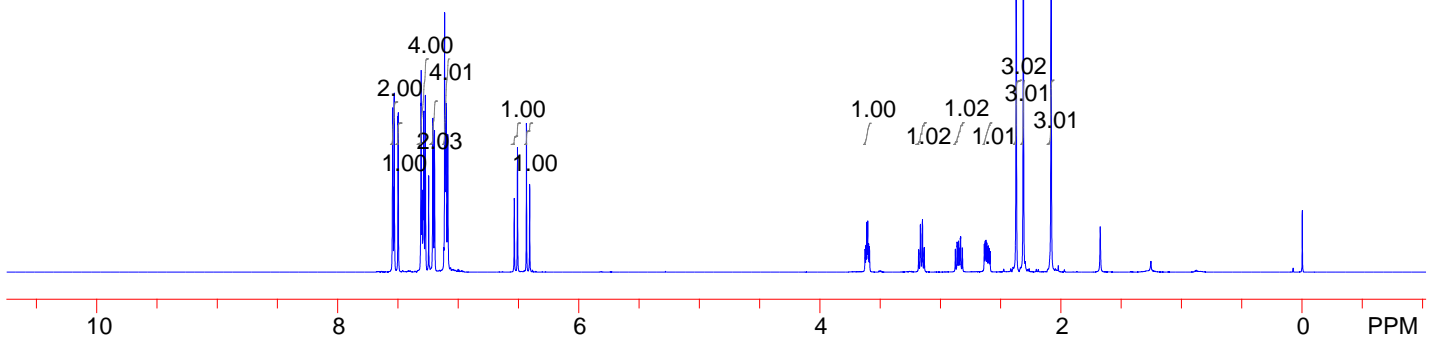
$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)



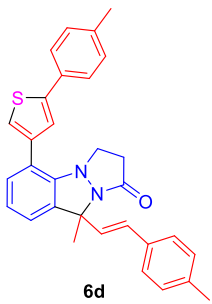
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7.531
7.499
7.497
7.309
7.307
7.301
7.298
7.292
7.286
7.273
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7.210
7.197
7.120
7.113
7.107
7.103
7.100
7.087
6.535
6.508
6.434
6.407
3.626
3.618
3.611
3.604
3.596
3.589
3.182
3.167
3.150
3.135
2.877
2.863
2.860
2.850
2.845
2.836
2.833
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2.597
2.590
2.373
2.313
2.083



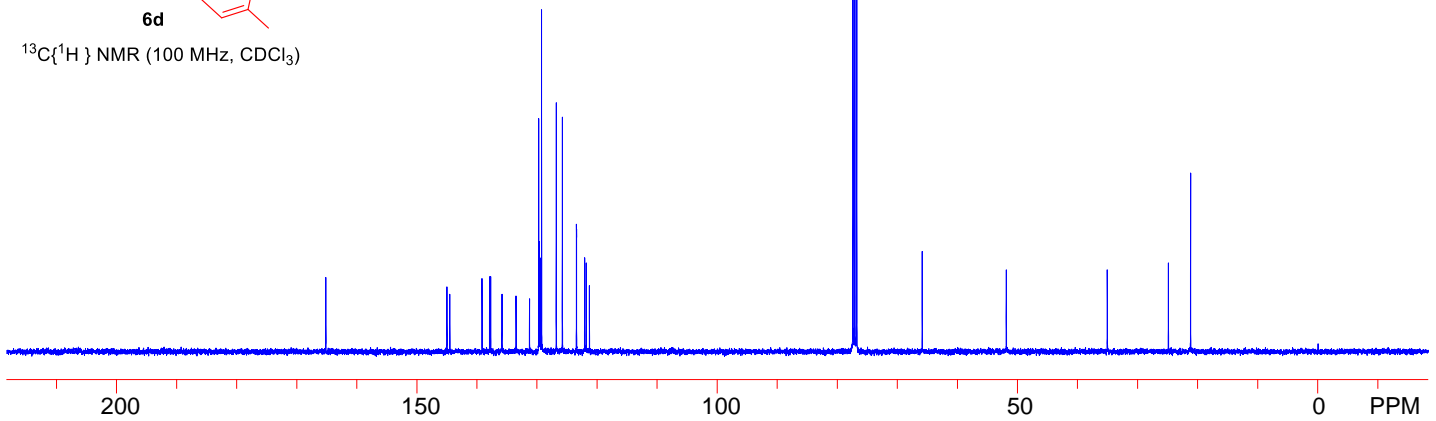
$^1\text{H NMR}$ (600 MHz, CDCl_3)



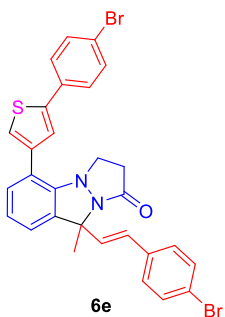
165.156
144.983
144.513
139.139
137.883
137.702
135.824
133.484
131.238
129.706
129.605
129.475
129.230
126.781
125.770
123.423
123.408
122.050
121.783
121.270
77.385
77.067
76.749
65.864
51.888
35.088
24.926
21.228



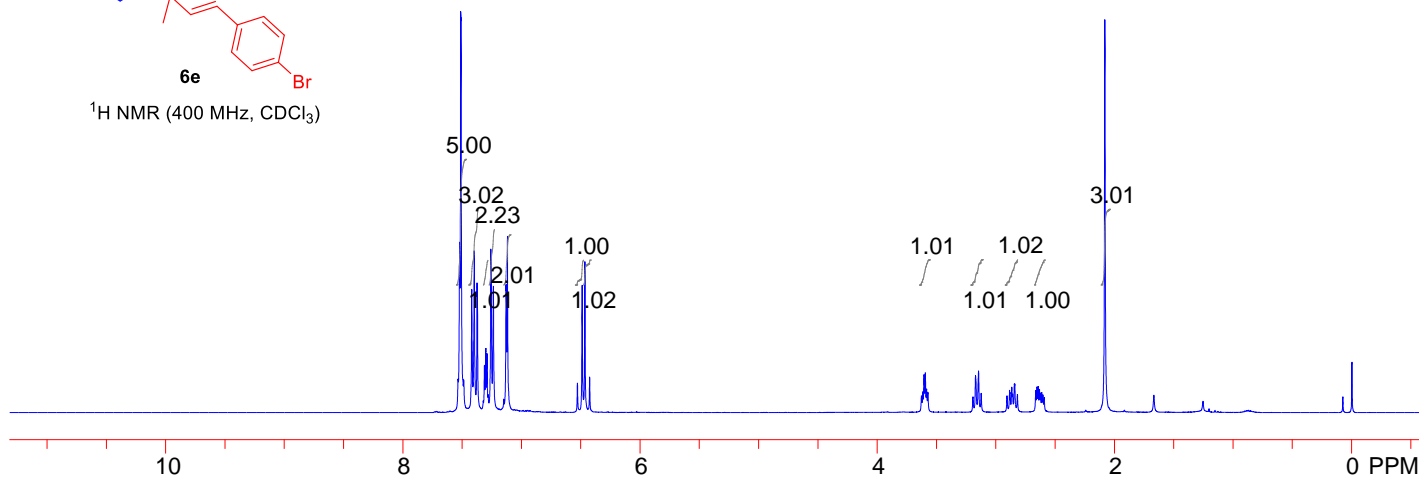
$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)



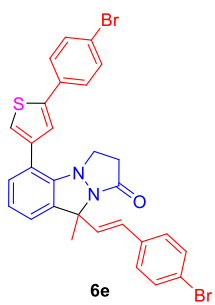
7.535
7.533
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7.520
7.512
7.509
7.488
7.419
7.398
7.374
7.372
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7.312
7.302
7.300
7.291
7.281
7.258
7.254
7.237
7.131
7.128
7.118
6.529
6.489
6.465
6.426
3.629
3.618
3.607
3.596
3.585
3.574
3.194
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3.147
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2.908
2.886
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2.868
2.860
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2.083



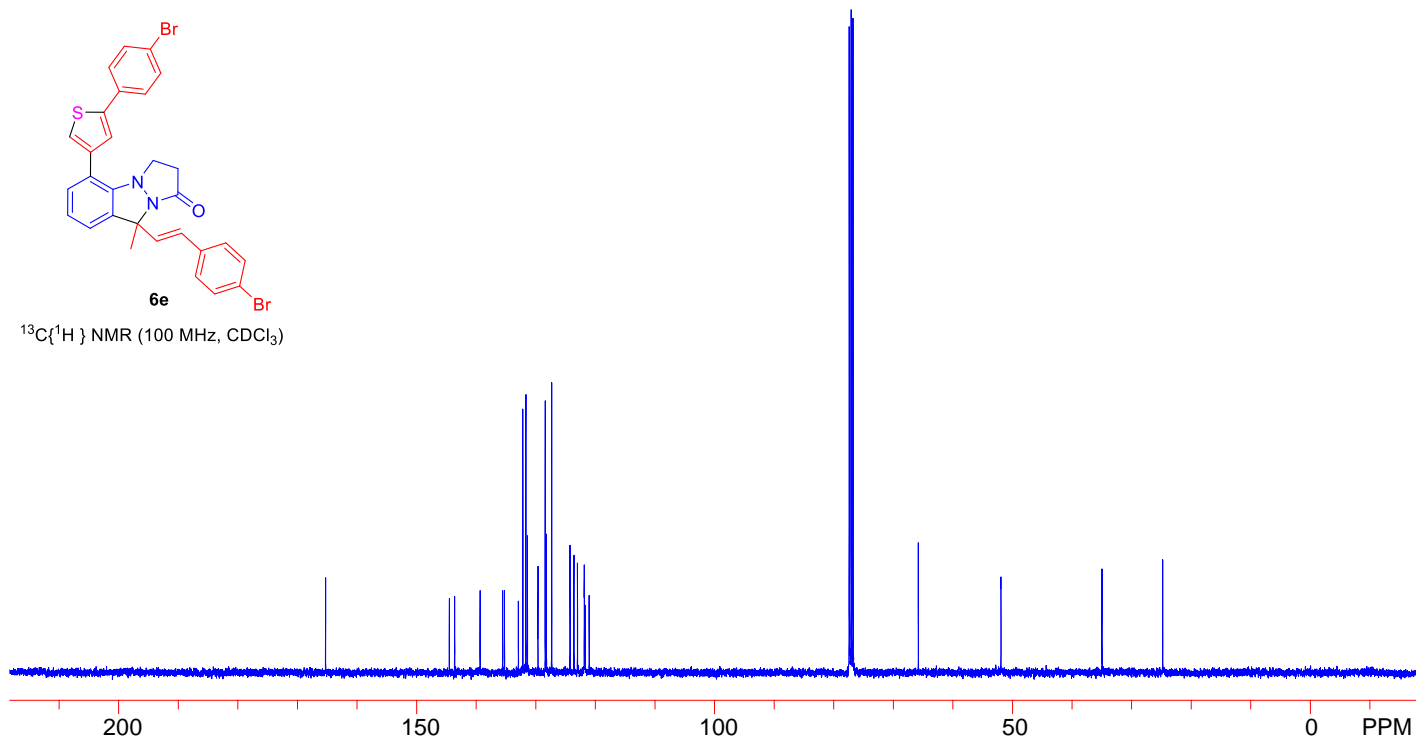
$^1\text{H NMR}$ (400 MHz, CDCl_3)



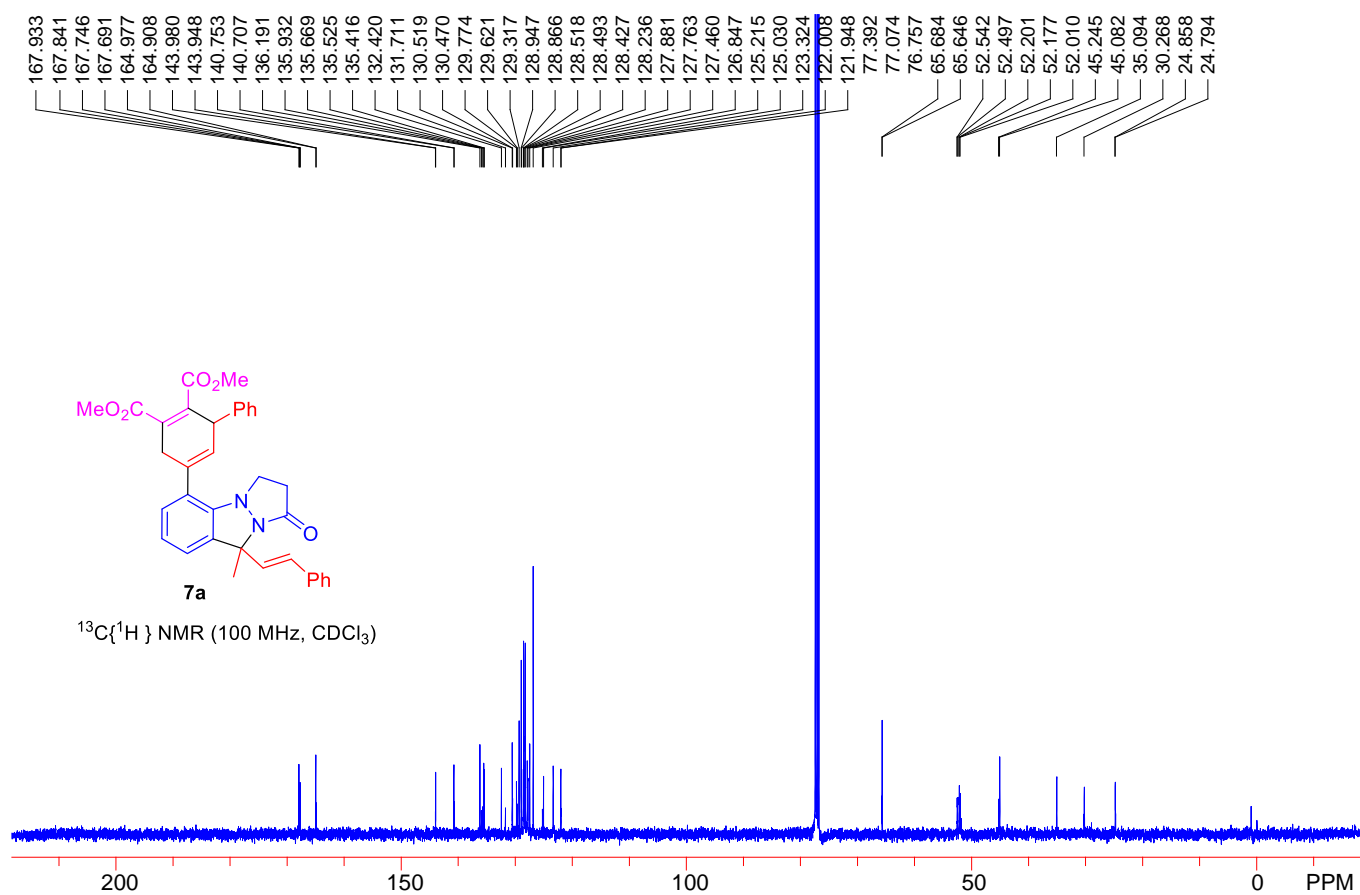
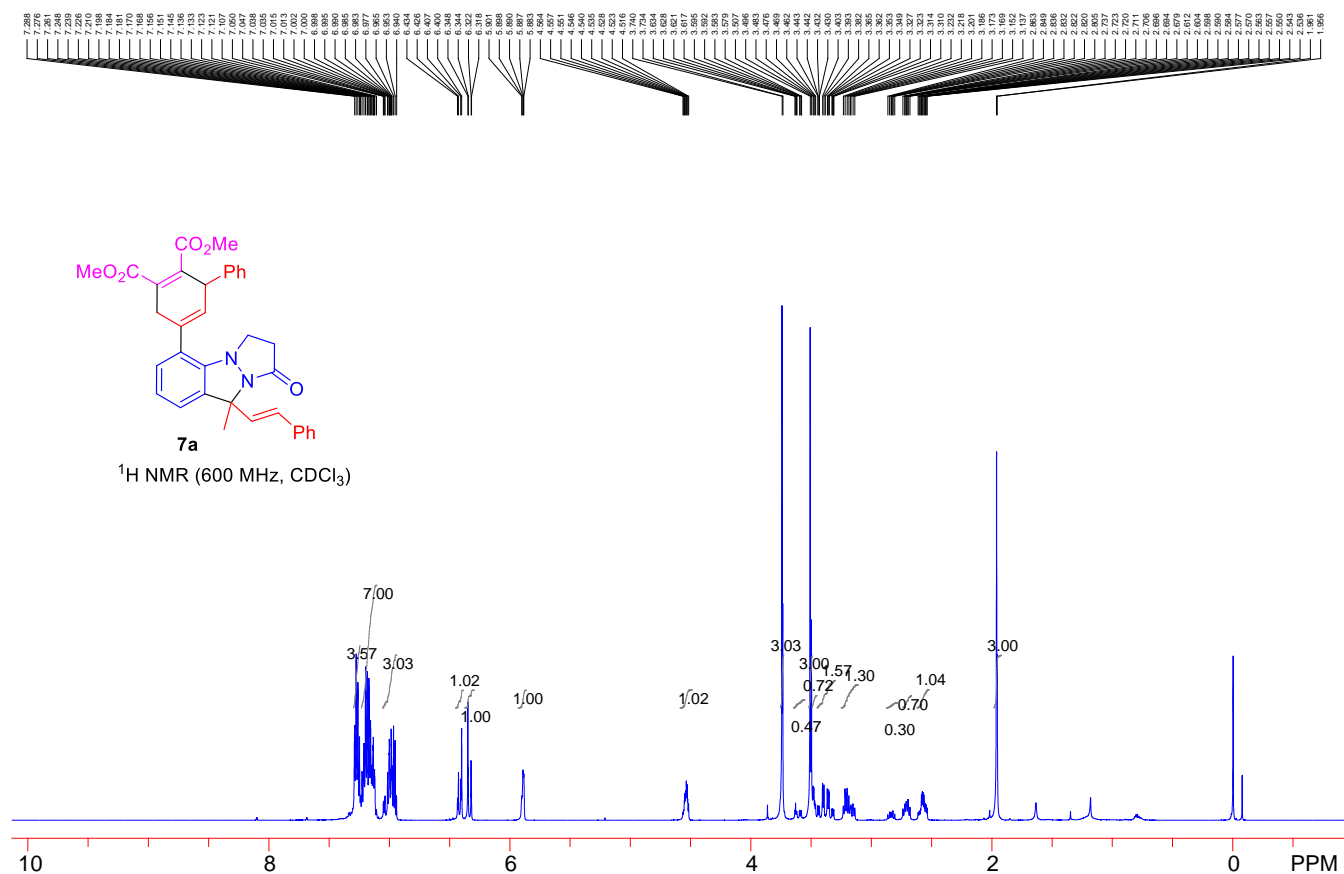
144.505
165.275
143.607
139.338
135.550
135.239
132.917
132.159
131.646
131.395
129.618
128.410
128.210
127.323
124.248
123.590
122.993
121.853
121.832
121.709
121.038
77.396
77.078
76.761
65.807
51.958
35.021
24.844

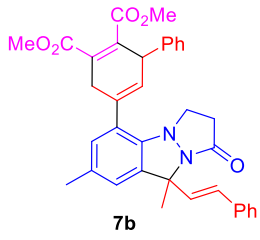
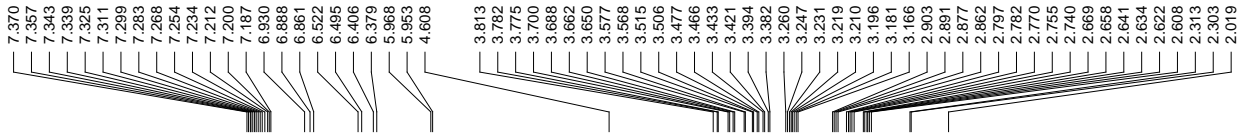


$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)

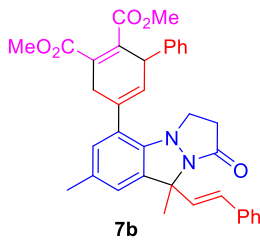
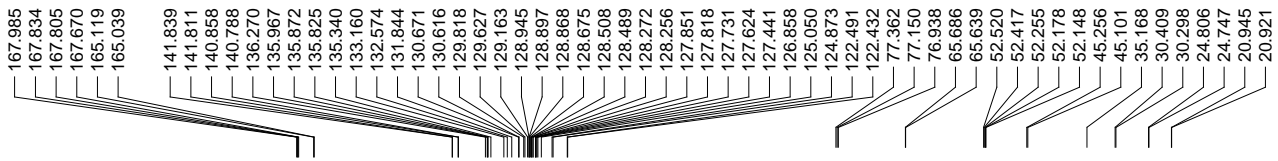
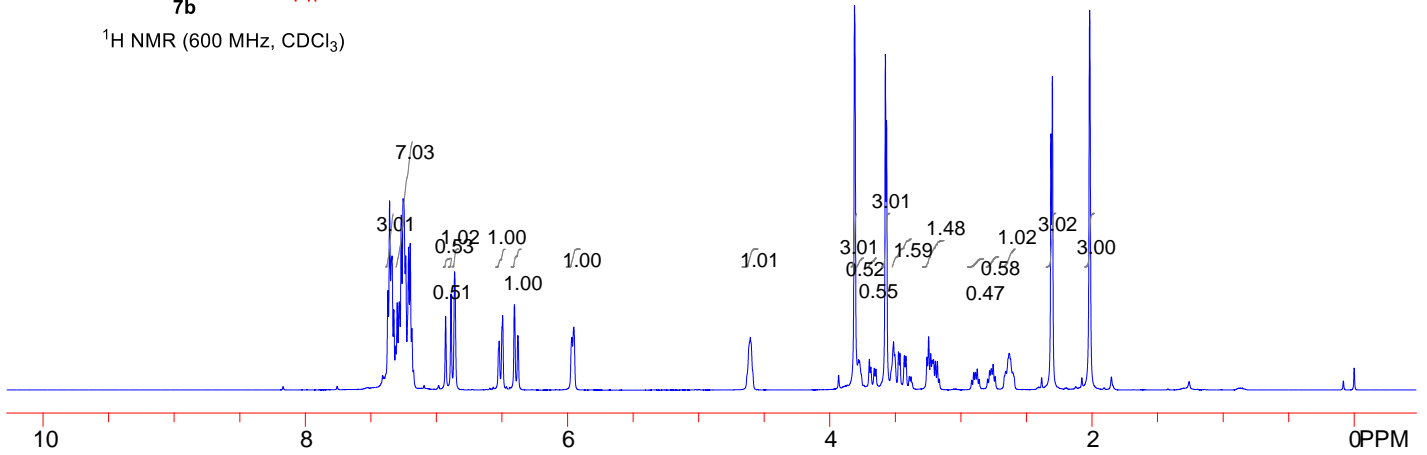


IX. NMR spectra of 7a-7e

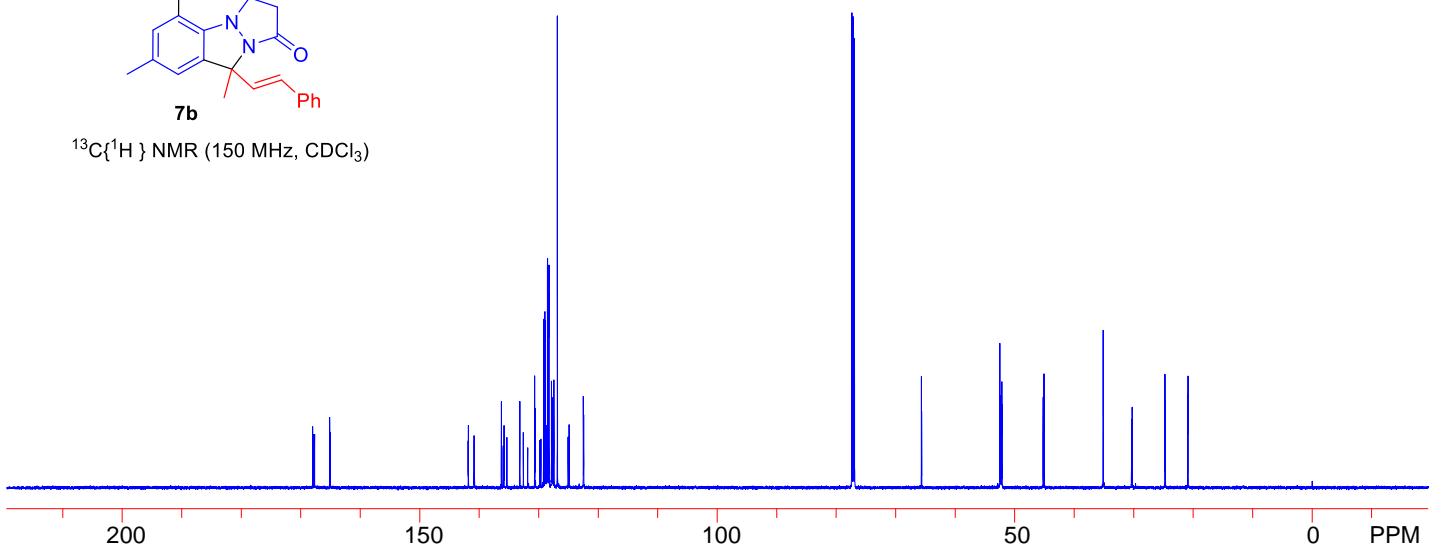


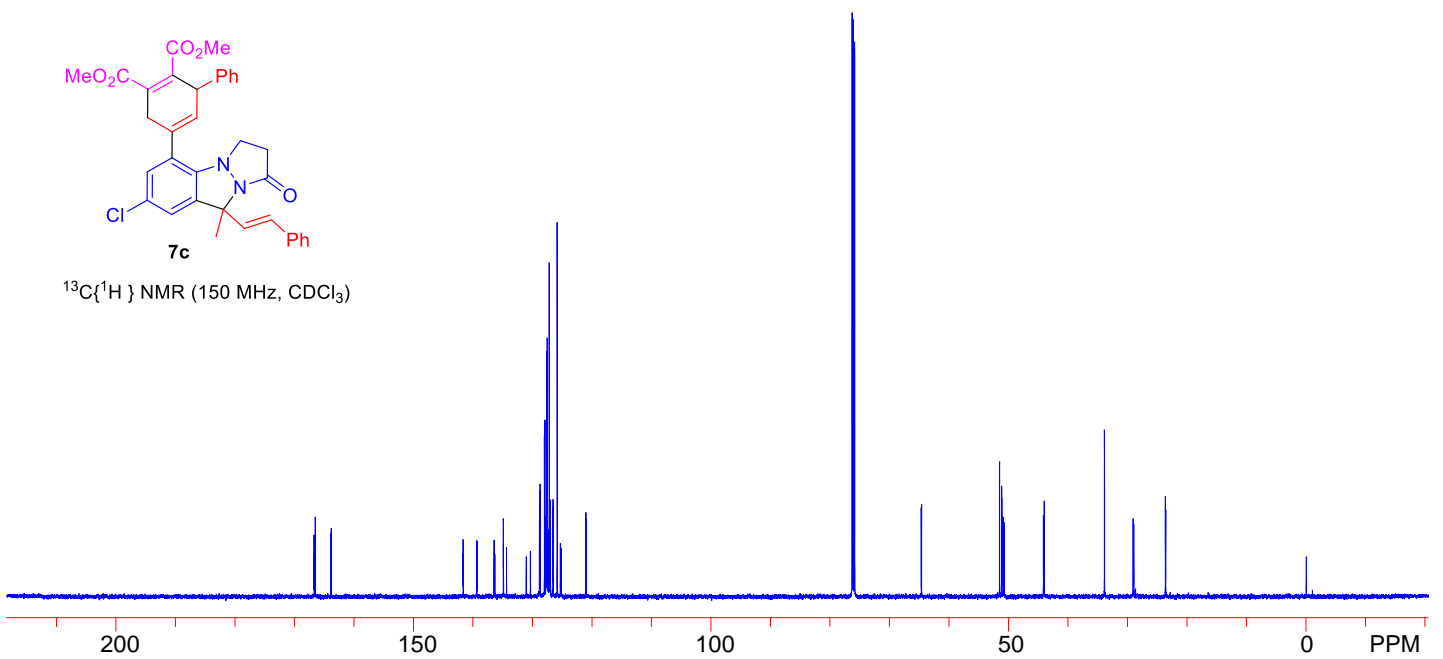
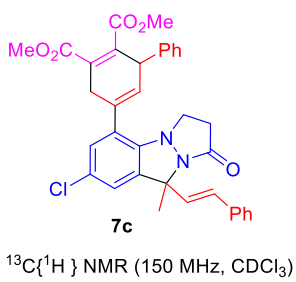
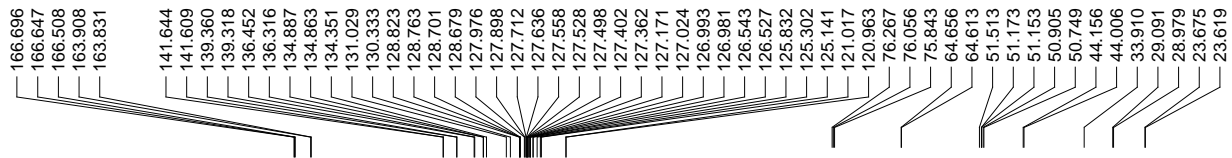
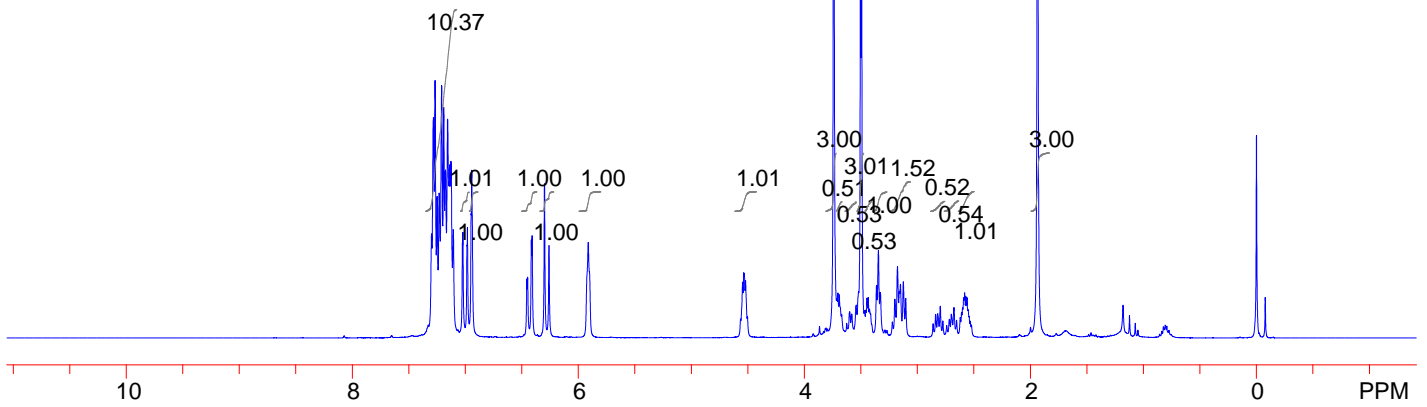
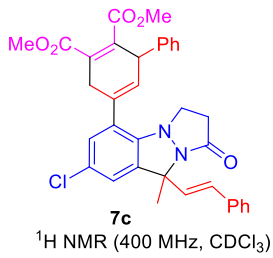
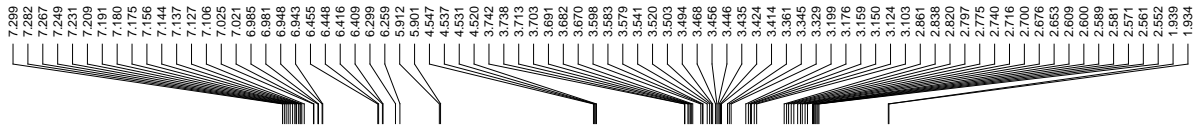


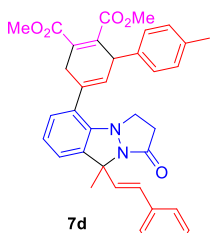
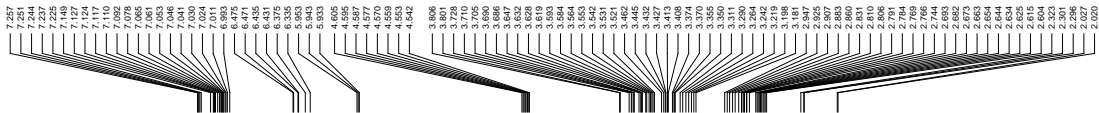
7b
¹H NMR (600 MHz, CDCl₃)



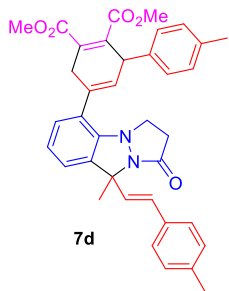
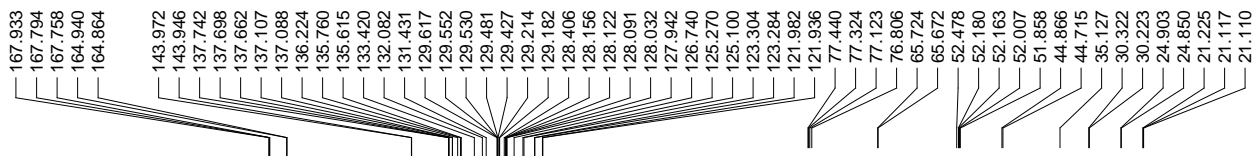
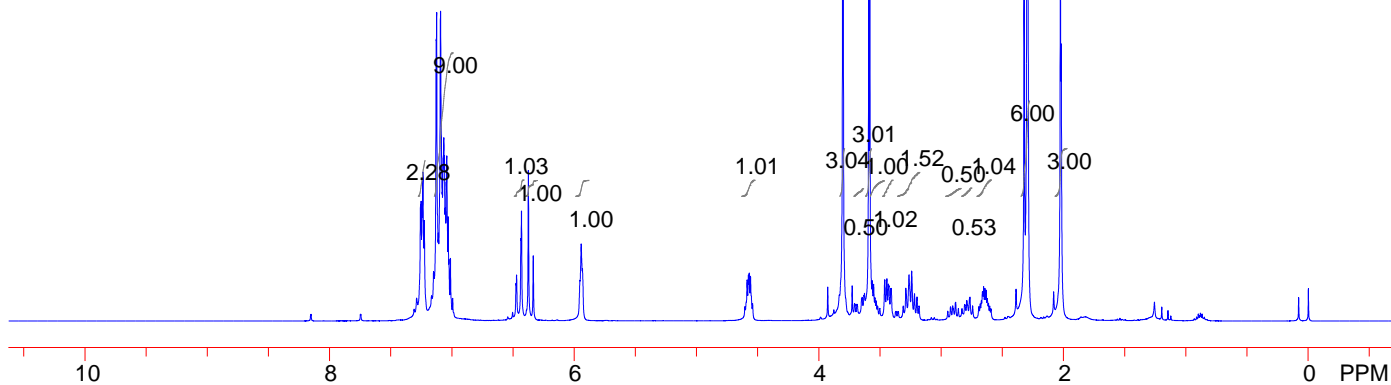
7b
¹³C{¹H} NMR (150 MHz, CDCl₃)



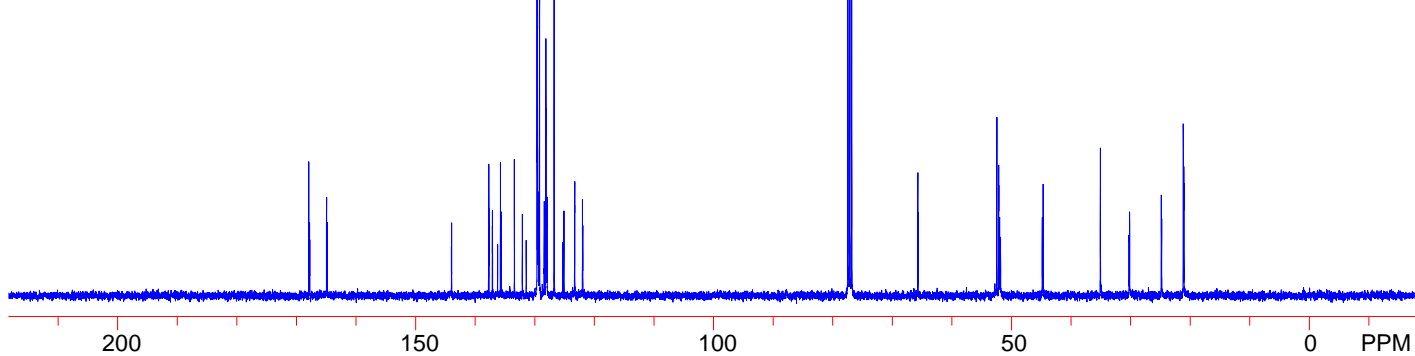


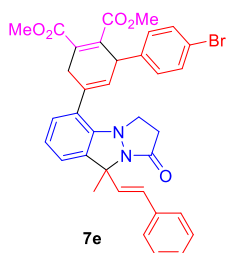
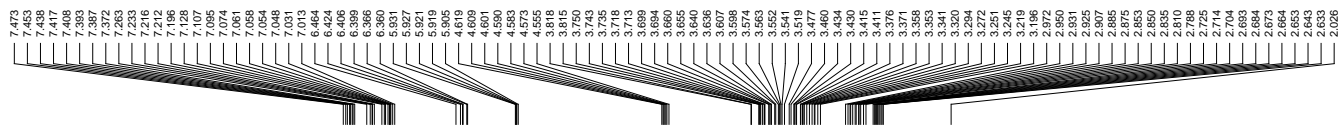


¹H NMR (400 MHz, CDCl₃)

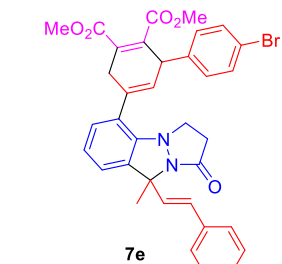
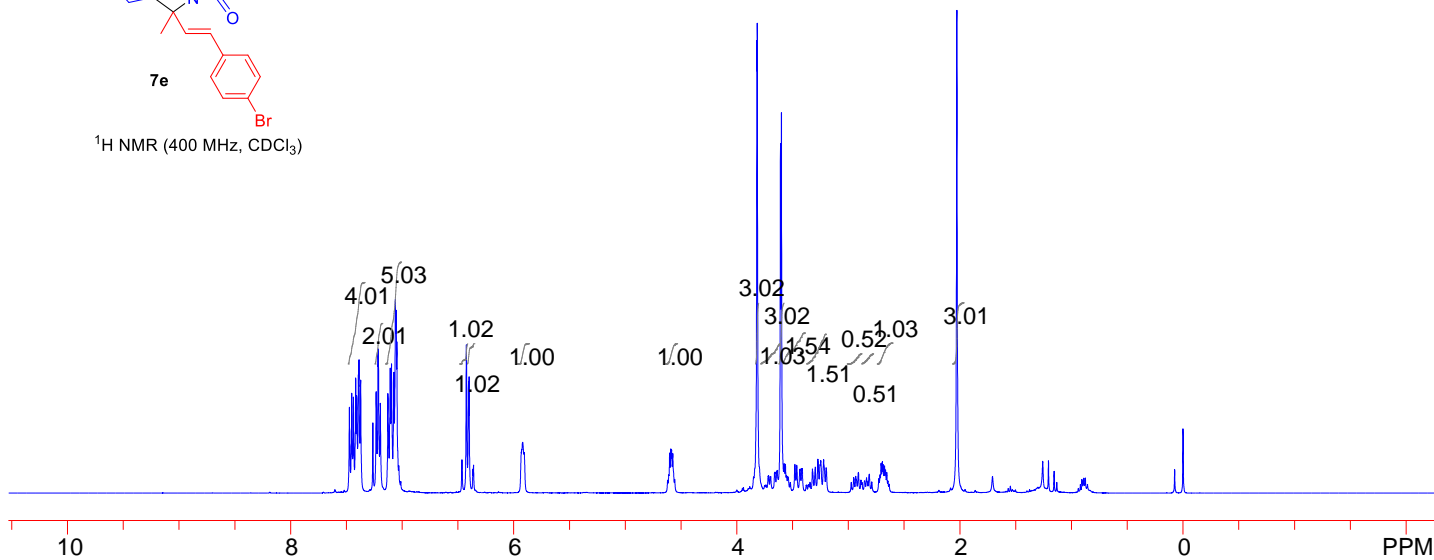


¹³C{¹H} NMR (100 MHz, CDCl₃)

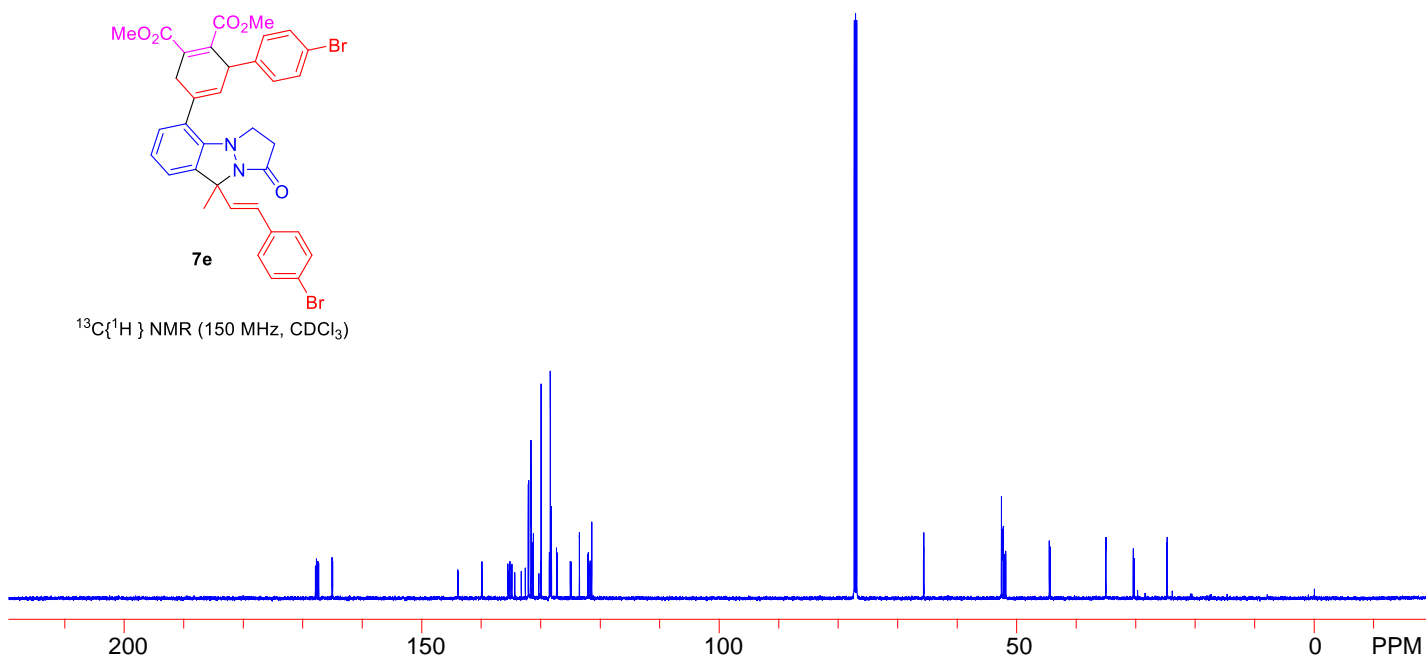




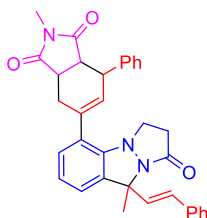
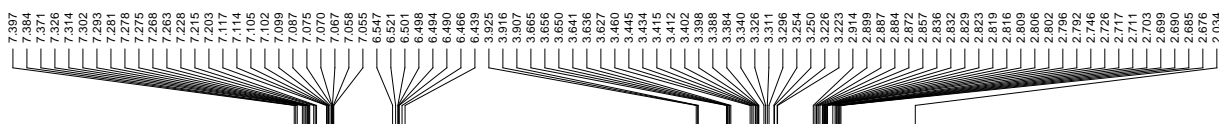
$^1\text{H NMR}$ (400 MHz, CDCl_3)



$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)

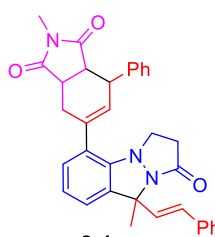
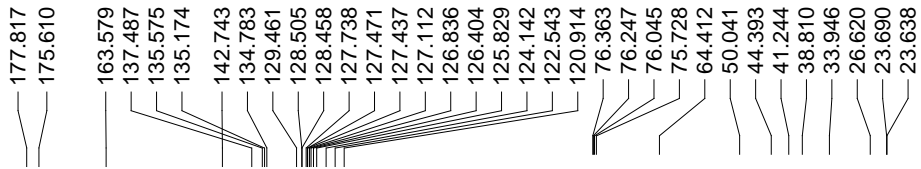
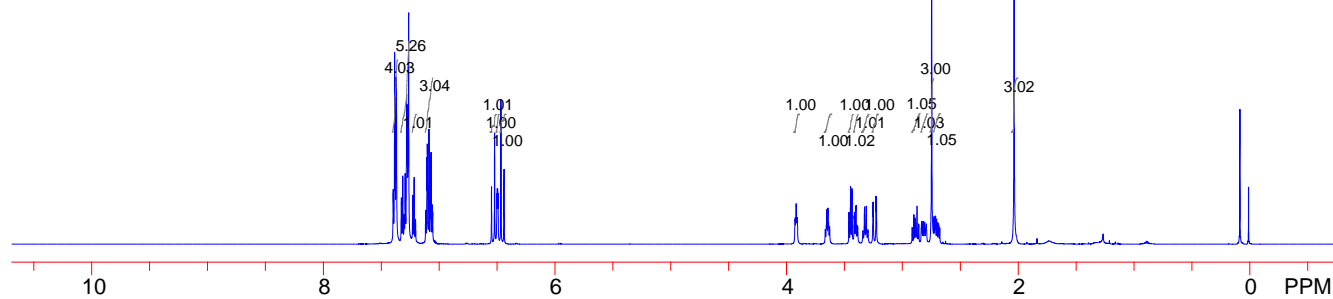


X. NMR spectra of 8-9



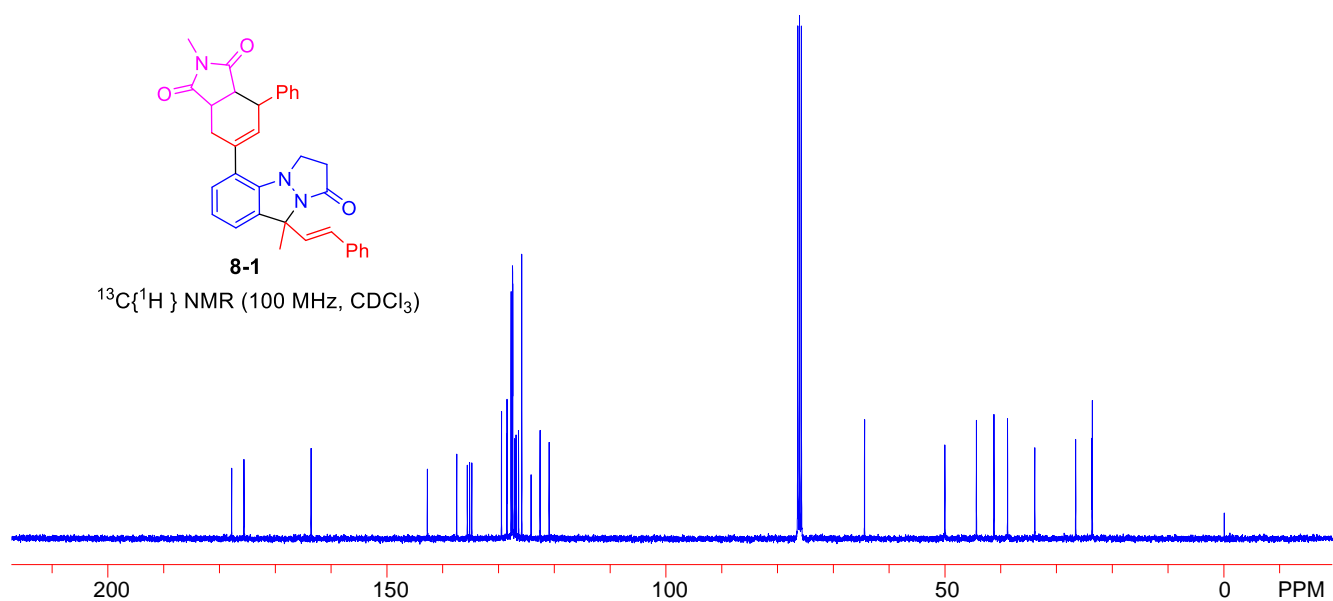
8-1

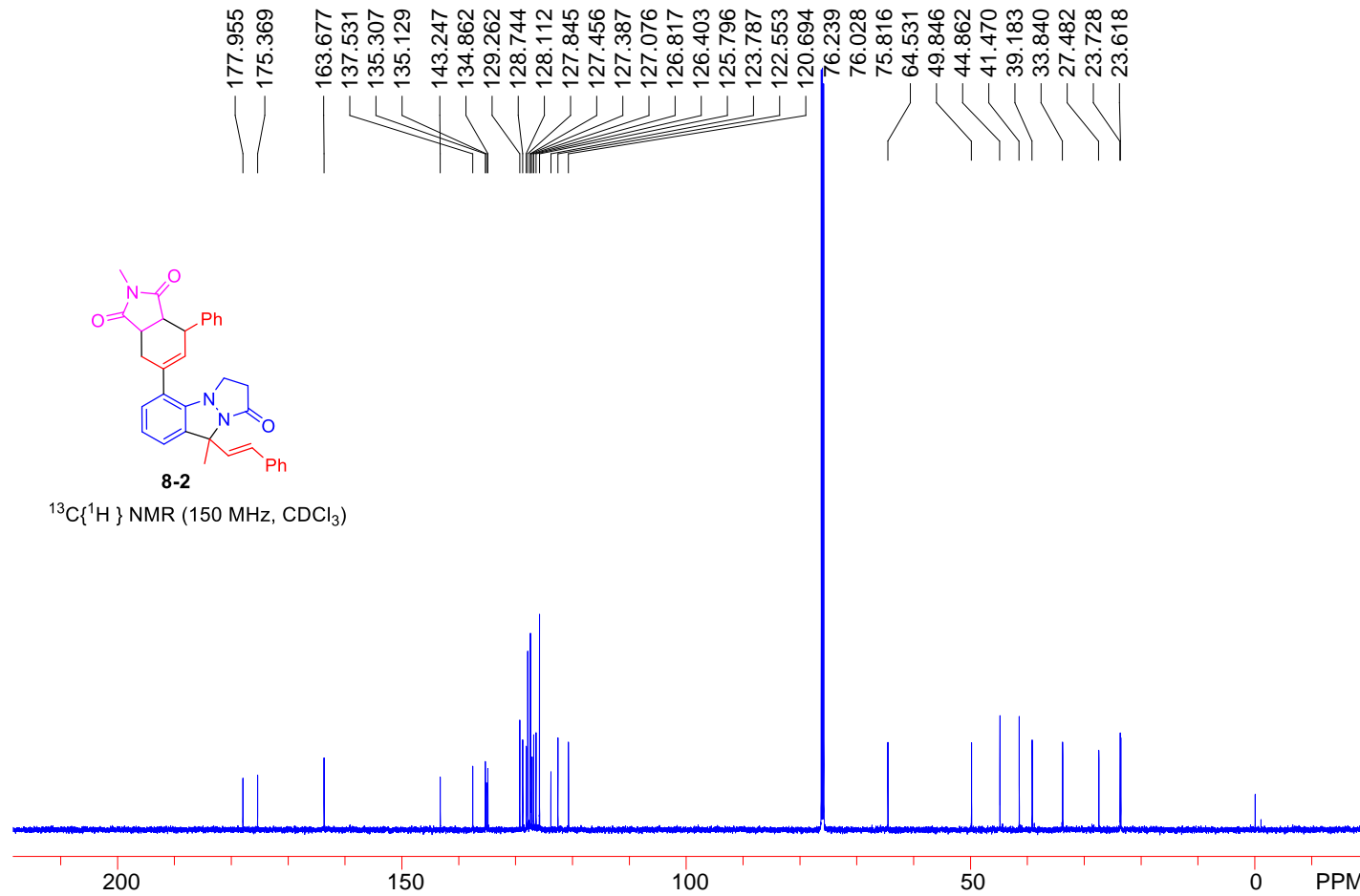
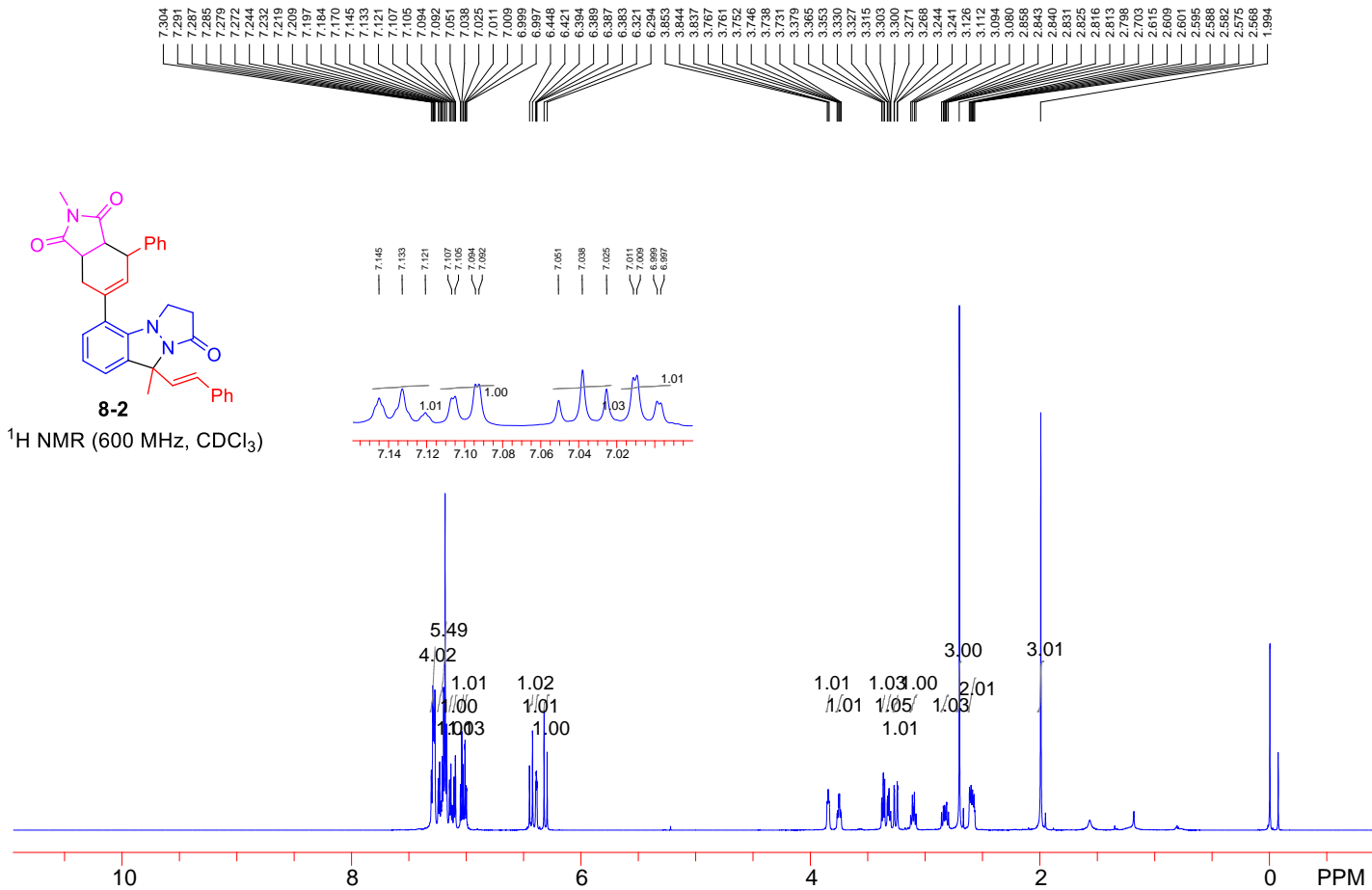
^1H NMR (600 MHz, CDCl_3)

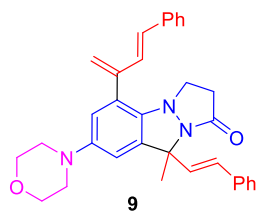
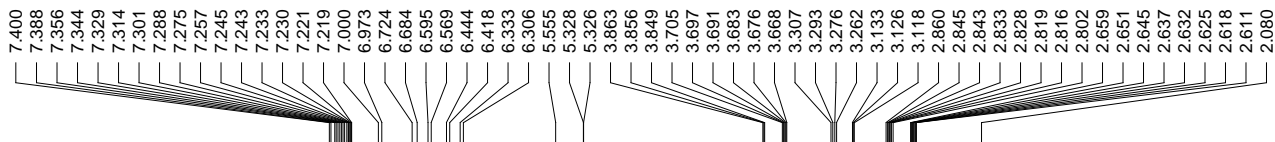


8-1

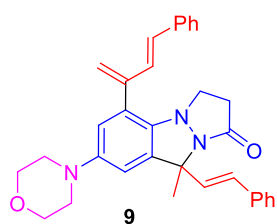
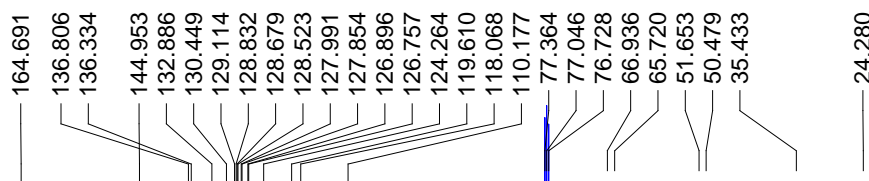
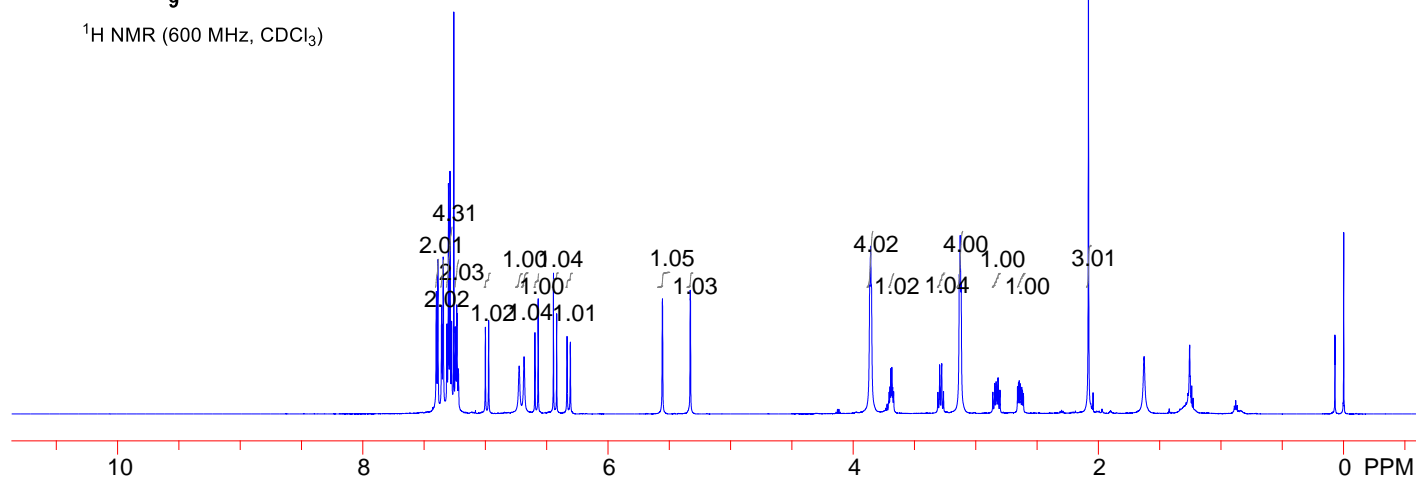
$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)



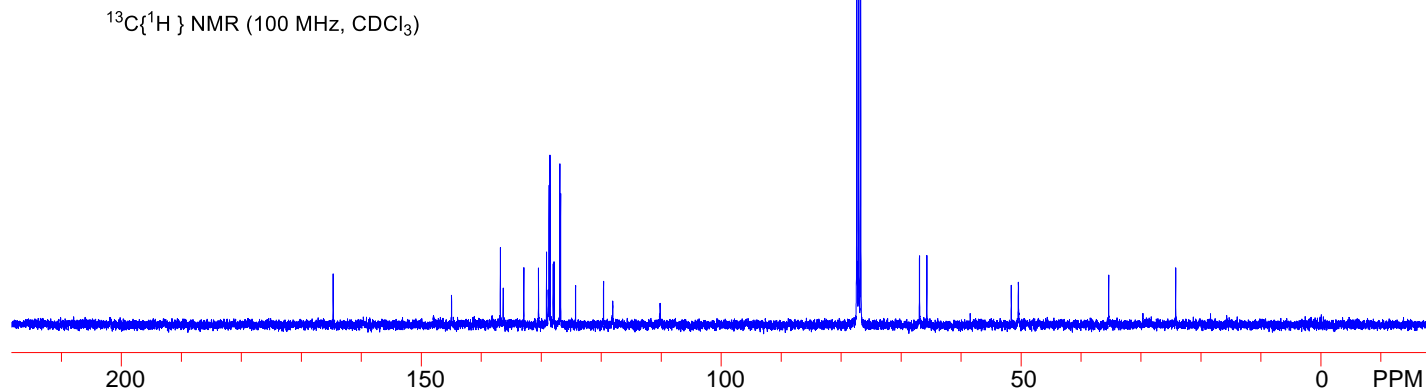




$^1\text{H NMR}$ (600 MHz, CDCl_3)



$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)



XI. X-ray crystal structure and data of 3d

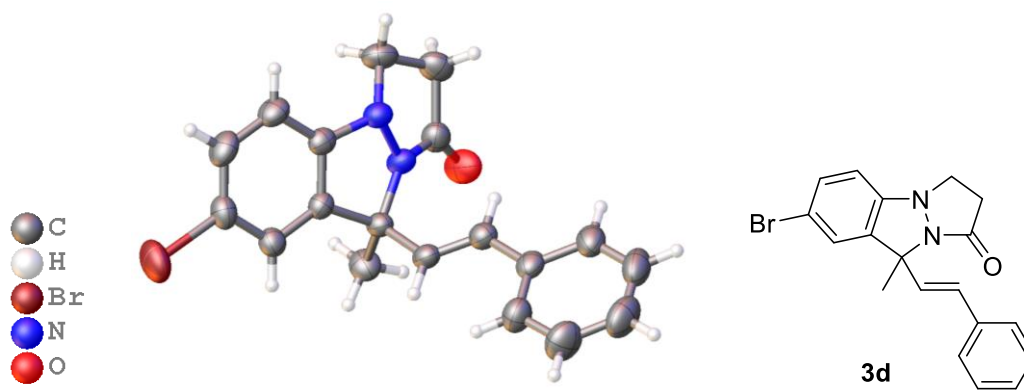


Figure S1 X-ray crystal structure of **3d** with 50% ellipsoid probability

X-ray structure determination. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent from a dichloromethane solution of **3d**. Crystal data collection and refinement parameters of **3d** are summarized in Table S1. Intensity data were collected at 293 K on a SuperNova Dual diffractometer using mirror-monochromated Cu K α radiation, $\lambda = 1.54184 \text{ \AA}$. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multi-scan technique. Using Olex2, the structure was solved with the SHELXS structure solution program using Direct Methods and refined with the SHELXL refinement package using Least Squares minimisation. Nonhydrogen atoms were refined with anisotropic displacement parameters. The H-atoms were either located or calculated and subsequently treated with a riding model.

Table S1 Crystallographic data and structure refinement results of **3d**

Empirical formula	C ₁₉ H ₁₇ BrN ₂ O
Formula weight	369.25
Temp, K	293(2)
Crystal system	monoclinic
Space group	C2/c
<i>a</i> , Å	31.6641(9)
<i>b</i> , Å	7.1775(2)
<i>c</i> , Å	15.5658(4)
α (°)	90
β (°)	102.601(3)
γ (°)	90
Volume, Å ³	3452.41(17)

Z	8
ρ_{calc} , g cm ⁻³	1.421
λ , Å	1.54184
μ , mm ⁻¹	3.283
No. of data collected	7106
No. of unique data	3291
R_{int}	0.0233
Goodness-of-fit on F^2	1.127
R_1 , wR_2 ($I > 2\sigma(I)$)	0.0511, 0.1304
R_1 , wR_2 (all data)	0.0601, 0.1361