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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

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I. General experimental information

Commercial reagents were used without further purification. 1-Arylpyrazolidinones **1**,[1] allenyl acetates **2**,[2] and $[RhCp^*Cl_2]_2$[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), $[RhCp^*Cl_2]_2$ (3.1 mg, 0.005 mmol), NaOAc (8.2 mg, 0.1 mmol) and 1-phenylbuta-2,3-dien-1-yl acetate (**2a**, 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 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 (2:1) as eluent to afford **3a**. **3b-3ee** were obtained in a similar manner.

(*E*)-9-Methyl-9-styryl-2,3-dihydro-1*H*,9*H*-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 ℃. ^{1}H NMR ($CDCl_3$, 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). ^{13}C{^{1}H} NMR ($CDCl_3$, 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 $C_{19}H_{18}N_2NaO$ 313.1311; Found 313.1308.

(*E*)-7,9-Dimethyl-9-styryl-2,3-dihydro-1*H*,9*H*-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 ℃. ^{1}H NMR ($CDCl_3$, 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).

$^{13}C\{^{1}H\}$ 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*: $[M+Na]^+$ Calcd for $C_{20}H_{20}N_2NaO$ 327.1468; Found 327.1472.

(*E*)-7-Chloro-9-methyl-9-styryl-2,3-dihydro-1*H*,9*H*-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 ℃. ^{1}H 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). $^{13}C\{^{1}H\}$ 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*: $[M+Na]^+$ Calcd for $C_{19}H_{17}ClN_2NaO$ 347.0922; Found 347.0927.

(*E*)-7-Bromo-9-methyl-9-styryl-2,3-dihydro-1*H*,9*H*-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 ℃. ^{1}H 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). $^{13}C\{^{1}H\}$ 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*: $[M+Na]^+$ Calcd for $C_{19}H_{17}BrN_2NaO$ 391.0416; Found 391.0406.

(*E*)-9-Methyl-9-styryl-7-(trifluoromethyl)-2,3-dihydro-1*H*,9*H*-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 ℃. ^{1}H 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). $^{13}C\{^{1}H\}$ 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, $^{3}J_{C\text{-}F}$ = 3.0 Hz), 125.0 (q,

$^{2}J_{C\text{-}F}$ = 32.1 Hz), 124.3 (q, $^{1}J_{C\text{-}F}$ = 269.9 Hz), 119.9 (q, $^{3}J_{C\text{-}F}$ = 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-1*H*,9*H*-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 ℃. ^{1}H 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{^{1}H} 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-1*H*,9*H*-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 ℃. ^{1}H 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{^{1}H} 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-1*H*,9*H*-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 ℃. ^{1}H 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). $^{13}C\{^1H\}$ 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*: $[M+Na]^+$ Calcd for $C_{19}H_{17}BrN_2NaO$ 391.0416; Found 391.0428.

(*E*)-5-Fluoro-9-methyl-9-styryl-2,3-dihydro-1*H*,9*H*-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 ℃. ^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). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 164.9, 149.0 (d, $^1J_{C\text{-}F}$ = 244.2 Hz), 138.3 (d, $^3J_{C\text{-}F}$ = 3.5 Hz), 136.0, 134.0 (d, $^2J_{C\text{-}F}$ = 13.4 Hz), 129.8, 129.6, 128.5, 128.0, 126.9, 124.1 (d, $^3J_{C\text{-}F}$ = 5.6 Hz), 118.3 (d, $^4J_{C\text{-}F}$ = 3.3 Hz), 115.8 (d, $^2J_{C\text{-}F}$ = 18.2 Hz), 66.7, 52.1 (d, $^4J_{C\text{-}F}$ = 2.1 Hz), 35.6, 24.6. ^{19}F NMR (565 MHz, $CDCl_3$) δ: -132.78 – -132.81 (m). HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{19}H_{17}FN_2NaO$ 331.1217; Found 331.1203.

(*E*)-5-Methoxy-9-methyl-9-styryl-2,3-dihydro-1*H*,9*H*-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 ℃. ^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). $^{13}C\{^1H\}$ 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*: $[M+Na]^+$ Calcd for $C_{20}H_{20}N_2NaO_2$ 343.1417; Found 343.1420.

(*E*)-6,7,9-Trimethyl-9-styryl-2,3-dihydro-1*H*,9*H*-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 ℃. ^{1}H NMR ($CDCl_3$, 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). ^{13}C{^{1}H} NMR ($CDCl_3$, 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 $C_{21}H_{22}N_2NaO$ 341.1624; Found 341.1621.

(*E*)-2,2,9-Trimethyl-9-styryl-2,3-dihydro-1*H*,9*H*-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 ℃. ^{1}H NMR ($CDCl_3$, 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). ^{13}C{^{1}H} NMR ($CDCl_3$, 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 $C_{21}H_{22}N_2NaO^+$ 341.1624; Found 341.1619.

(*E*)-2,2,7,9-Tetramethyl-9-styryl-2,3-dihydro-1*H*,9*H*-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 ℃. ^{1}H NMR ($CDCl_3$, 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). ^{13}C{^{1}H} NMR ($CDCl_3$, 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 $C_{22}H_{24}N_2NaO^+$ 355.1781; Found 355.1787.

(*E*)-7-Methoxy-2,2,9-trimethyl-9-styryl-2,3-dihydro-1*H*,9*H*-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 ℃. ^{1}H NMR ($CDCl_3$, 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). ^{13}C{^{1}H} NMR ($CDCl_3$, 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 $C_{22}H_{24}N_2NaO_2$ 371.1730; Found 371.1734.

(*E*)-7-Fluoro-2,2,9-trimethyl-9-styryl-2,3-dihydro-1*H*,9*H*-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 ℃. ^{1}H NMR ($CDCl_3$, 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). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 170.2, 159.3 (d, $^{1}J_{C\text{-}F}$ = 239.5 Hz), 143.4 (d, $^{4}J_{C\text{-}F}$ = 2.2 Hz), 136.6 (d, $^{3}J_{C\text{-}F}$ = 8.5 Hz), 136.2, 129.8, 129.5, 128.6, 128.0, 127.0, 115.6 (d, $^{2}J_{C\text{-}F}$ = 23.9 Hz), 110.8 (d, $^{3}J_{C\text{-}F}$ = 9.2 Hz), 110.1 (d, $^{2}J_{C\text{-}F}$ = 24.7 Hz), 66.2 (d, $^{4}J_{C\text{-}F}$ = 2.2 Hz), 64.6, 46.0, 24.5, 23.2, 22.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ -120.49 (td, J_1 = 7.9 Hz, J_2 = 4.1 Hz). HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{21}H_{21}FN_2NaO^+$ 359.1530; Found 359.1540.

(*E*)-2,2,9-Trimethyl-9-styryl-7-(trifluoromethyl)-2,3-dihydro-1*H*,9*H*-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 ℃. ^{1}H NMR ($CDCl_3$, 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). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 170.0, 149.6, 136.0, 135.7, 129.7, 129.5, 128.7, 128.2, 127.0, 126.7 (q, $^{3}J_{C\text{-}F}$ = 3.3 Hz), 124.9 (q, $^{2}J_{C\text{-}F}$ = 31.8 Hz), 124.4 (q, $^{1}J_{C\text{-}F}$ =

269.5 Hz), 119.8 (q, $^{3}J_{C\text{-}F}$ = 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*: $[M+Na]^+$ Calcd for $C_{22}H_{21}F_3N_2NaO^+$ 409.1498; Found 409.1487.

(*E*)-9-Methyl-9-(4-methylstyryl)-2,3-dihydro-1*H*,9*H*-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 ℃. ^{1}H 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}C{^{1}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*: $[M+Na]^+$ Calcd for $C_{20}H_{20}N_2NaO$ 327.1468; Found 327.1470.

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

Eluent: petroleum ether/ethyl acetate (2:1). Yellow oil (42.6 mg, 67%). ^{1}H 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}C{^{1}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*: $[M+Na]^+$ Calcd for $C_{21}H_{22}N_2NaO$ 341.1624; Found 341.1632.

(*E*)-9-(2-([1,1'-Biphenyl]-4-yl)vinyl)-9-methyl-2,3-dihydro-1*H*,9*H*-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 ℃. ^{1}H 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). $^{13}C\{^{1}H\}$ 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*: $[M+Na]^+$ Calcd for $C_{25}H_{22}N_2NaO$ 389.1624; Found 389.1622.

(*E*)-9-(4-Fluorostyryl)-9-methyl-2,3-dihydro-1*H*,9*H*-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 ℃. ^{1}H 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). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150 MHz): δ 164.7, 162.6 (d, $^{1}J_{C\text{-}F}$ = 245.4 Hz), 147.2, 134.9, 132.5 (d, $^{4}J_{C\text{-}F}$ = 3.0 Hz), 130.2 (d, $^{5}J_{C\text{-}F}$ = 2.4 Hz), 129.0, 128.5 (d, $^{3}J_{C\text{-}F}$ = 7.1 Hz), 128.2, 123.0, 122.7, 115.5 (d, $^{2}J_{C\text{-}F}$ = 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*: $[M+Na]^+$ Calcd for $C_{19}H_{17}FN_2NaO$ 331.1217; Found 331.1214.

(*E*)-9-(4-Bromostyryl)-9-methyl-2,3-dihydro-1*H*,9*H*-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 ℃. ^{1}H 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). $^{13}C\{^{1}H\}$ 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*: $[M+Na]^+$ Calcd for $C_{19}H_{17}BrN_2NaO$ 391.0416; Found 391.0407.

(*E*)-9-Methyl-9-(4-(trifluoromethyl)styryl)-2,3-dihydro-1*H*,9*H*-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 ℃. ^{1}H 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_1 = 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). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 164.9, 147.2, 139.9, 134.5, 133.0, 129.7 (q, $^2J_{C-F}$ = 31.7 Hz), 129.2, 128.0, 127.1, 125.5 (q, $^3J_{C-F}$ = 3.5 Hz), 124.3 (q, $^1J_{C-F}$ = 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*: $[M+Na]^+$ Calcd for $C_{20}H_{17}F_3N_2NaO$ 381.1185; Found 381.1177.

(*E*)-9-Methyl-9-(3-methylstyryl)-2,3-dihydro-1*H*,9*H*-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). $^{13}C\{^1H\}$ 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*: $[M+Na]^+$ Calcd for $C_{20}H_{20}N_2NaO$ 327.1468; Found 327.1479.

(*E*)-9-(3-Chlorostyryl)-9-methyl-2,3-dihydro-1*H*,9*H*-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 ℃. ^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). $^{13}C\{^1H\}$ 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*: $[M+Na]^+$ Calcd for $C_{19}H_{17}ClN_2NaO$ 347.0922; Found 347.0921.

(*E*)-9-Methyl-9-(2-methylstyryl)-2,3-dihydro-1*H*,9*H*-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 ℃. ^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). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 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 $C_{20}H_{20}N_2NaO$ 327.1468; Found 327.1471.

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

Eluent: petroleum ether/ethyl acetate (2:1). Yellow oil (50.8 mg, 78%). ^{1}H NMR ($CDCl_3$, 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). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 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 $C_{19}H_{17}ClN_2NaO$ 347.0922; Found 347.0918.

(*E*)-9-Methyl-9-(2-(naphthalen-1-yl)vinyl)-2,3-dihydro-1*H*,9*H*-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 ℃. ^{1}H NMR ($CDCl_3$, 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). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 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 $C_{23}H_{20}N_2NaO$ 363.1468; Found 363.1457.

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

Eluent: petroleum ether/ethyl acetate (2:1). Yellow oil (29.0 mg, 64%). ^{1}H NMR ($CDCl_3$, 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). $^{13}C\{^1H\}$ 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*: $[M+Na]^+$ Calcd for $C_{14}H_{16}N_2NaO$ 251.1155; Found 251.1147.

(*E*)-9-(Hept-1-en-1-yl)-9-methyl-2,3-dihydro-1*H*,9*H*-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). $^{13}C\{^1H\}$ 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*: $[M+Na]^+$ Calcd for $C_{18}H_{24}N_2NaO$ 307.1781; Found 307.1788.

(*E*)-9-Methyl-9-(3-phenylprop-1-en-1-yl)-2,3-dihydro-1*H*,9*H*-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). $^{13}C\{^1H\}$ 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*: $[M+Na]^+$ Calcd for $C_{20}H_{20}N_2NaO$ 327.1468; Found 327.1473.

(*E*)-2,9-dimethyl-9-styryl-2,3-dihydro-1*H*,9*H*-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). $^{13}C\{^{1}H\}$ 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*: $[M+Na]^+$ Calcd for $C_{20}H_{20}N_2NaO$ 327.1468; Found 327.1475.

3ee-2: Eluent: petroleum ether/ethyl acetate (3:1). Yellow oil (22.6 mg, 37%), ^{1}H 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). $^{13}C\{^{1}H\}$ 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*: $[M+Na]^+$ Calcd for $C_{20}H_{20}N_2NaO$ 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), $[RhCp^*Cl_2]_2$ (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 ℃ under argon for 6 h. Upon completion, it was quenched with saturated brine and extracted with dichloromethane (10 mL × 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-1*H*,9*H*-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 ℃. ^{1}H 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). $^{13}C\{^1H\}$ 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*: $[M+Na]^+$ Calcd for $C_{29}H_{26}N_2NaO$ 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 ℃. ^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). $^{13}C\{^1H\}$ 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*: $[M+Na]^+$ Calcd for $C_{30}H_{28}N_2NaO$ 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 ℃. ^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). $^{13}C\{^1H\}$ 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 ℃. ^{1}H 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{^{1}H} 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 ℃. ^{1}H 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{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 164.6, 159.0 (d, $^1J_{C\text{-}F}$ = 249.4 Hz), 143.7, 140.6, 137.1 (d, $^3J_{C\text{-}F}$ = 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, $^3J_{C\text{-}F}$ = 7.3 Hz), 120.1, 116.8 (d, $^2J_{C\text{-}F}$ = 24.2 Hz), 109.2 (d, $^2J_{C\text{-}F}$ = 24.5 Hz), 65.6 (d, $^4J_{C\text{-}F}$ = 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-1*H*,9*H*-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 ℃. ^{1}H NMR ($CDCl_3$, 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). ^{13}C{^{1}H} NMR ($CDCl_3$, 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 $C_{29}H_{25}ClN_2NaO$ 475.1548; Found 475.1557.

7-Bromo-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 (4g)

Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid (61.7 mg, 62%), mp 99.2-99.9 ℃. ^{1}H NMR ($CDCl_3$, 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). ^{13}C{^{1}H} NMR ($CDCl_3$, 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 $C_{29}H_{25}BrN_2NaO$ 519.1042; Found 519.1050.

9-Methyl-1-oxo-5-((*E*)-4-phenylbuta-1,3-dien-2-yl)-9-((*E*)-styryl)-2,3-dihydro-1*H*,9*H*-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 ℃. ^{1}H NMR ($CDCl_3$, 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). $^{13}C\{^1H\}$ 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*: $[M+Na]^+$ Calcd for $C_{30}H_{25}N_3NaO$ 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 ℃. ^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). $^{13}C\{^1H\}$ 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, $^3J_{C\text{-}F}$ = 3.3 Hz), 127.0, 126.8, 125.0 (q, $^2J_{C\text{-}F}$ = 32.6 Hz), 124.2 (q, $^1J_{C\text{-}F}$ = 270.3 Hz), 123.2, 120.5, 118.9 (q, $^3J_{C\text{-}F}$ = 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*: $[M+Na]^+$ Calcd for $C_{30}H_{25}F_3N_2NaO$ 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 ℃. ^1H NMR ($CDCl_3$, 600 MHz, 55 ℃): 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). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 164.2, 160.3 (d, $^1J_{C\text{-}F}$ = 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, $^3J_{C\text{-}F}$ = 10.2 Hz), 121.7, 111.6 (d, $^2J_{C\text{-}F}$

= 23.1 Hz), 109.7 (d, $^{2}J_{C\text{-}F}$ = 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*: $[M+H]^+$ Calcd for $C_{29}H_{25}FN_2NaO$ 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 ℃. ^{1}H 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}C{^{1}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*: $[M+Na]^+$ Calcd for $C_{31}H_{30}N_2NaO$ 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 ℃. ^{1}H 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}C{^{1}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*: $[M+Na]^+$ Calcd for $C_{30}H_{28}N_2NaO$ 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 ℃. ^{1}H 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). $^{13}C\{^1H\}$ 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*: $[M+Na]^+$ Calcd for $C_{30}H_{28}N_2NaO$ 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 ℃. ^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). $^{13}C\{^1H\}$ 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*: $[M+Na]^+$ Calcd for $C_{31}H_{30}N_2NaO$ 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 ℃. ^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). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 164.5, 162.52 (d, $^1J_{C\text{-}F}$ = 245.3 Hz), 162.49 (d, $^1J_{C\text{-}F}$ = 245.6 Hz), 144.5, 144.2, 135.4, 133.0 (d, $^4J_{C\text{-}F}$ = 3.2 Hz), 132.5 (d, $^4J_{C\text{-}F}$ = 3.5 Hz), 131.5,

130.3, 130.2, 128.8, 128.4 (d, $^{3}J_{C\text{-}F}$ = 8.1 Hz), 128.3 (d, $^{3}J_{C\text{-}F}$ = 7.2 Hz), 127.9, 123.4, 122.9, 121.8, 119.8, 115.6 (d, $^{2}J_{C\text{-}F}$ = 21.5 Hz), 115.5 (d, $^{2}J_{C\text{-}F}$ = 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*: $[M+Na]^+$ Calcd for $C_{29}H_{24}F_2N_2NaO$ 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 ℃. ^{1}H 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}C{^{1}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*: $[M+Na]^+$ Calcd for $C_{29}H_{24}Br_2N_2NaO$ 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)benzonitrile (4p)

Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid (40.8 mg, 43%), mp 170.5-171.5 ℃. ^{1}H 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}C{^{1}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*: $[M+Na]^+$ Calcd for $C_{31}H_{24}N_4NaO$ 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-1*H*,9*H*-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 ℃. ^{1}H NMR ($CDCl_3$, 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). ^{13}C{^{1}H} NMR ($CDCl_3$, 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 $C_{31}H_{30}N_2NaO$ 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-1*H*,9*H*-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 ℃. ^{1}H NMR ($CDCl_3$, 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). ^{13}C{^{1}H} NMR ($CDCl_3$, 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 $C_{29}H_{24}Cl_2N_2NaO$ 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-1*H*,9*H*-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 ℃. ^{1}H NMR ($CDCl_3$, 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). ^{13}C{^{1}H} NMR ($CDCl_3$, 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 $C_{31}H_{30}N_2NaO$ 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 ℃. ^{1}H NMR ($CDCl_3$, 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). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 164.5, 160.5 (d, $^{1}J_{C\text{-}F}$ = 248.6 Hz), 160.4 (d, $^{1}J_{C\text{-}F}$ = 248.1 Hz), 144.8, 144.3, 135.3, 132.8 (d, $^{4}J_{C\text{-}F}$ = 3.9 Hz), 131.5, 130.3, 129.1 (d, $^{3}J_{C\text{-}F}$ = 9.5 Hz), 127.9 (d, $^{3}J_{C\text{-}F}$ = 8.1 Hz), 127.8 (d, $^{3}J_{C\text{-}F}$ = 8.7 Hz), 125.5, 124.8 (d, $^{2}J_{C\text{-}F}$ = 11.6 Hz), 124.23, 124.16 (d, $^{4}J_{C\text{-}F}$ = 3.6 Hz), 124.0 (d, $^{4}J_{C\text{-}F}$ = 3.2 Hz), 123.2, 122.9, 122.0, 121.7 (d, $^{4}J_{C\text{-}F}$ = 3.3 Hz), 120.6, 115.9 (d, $^{2}J_{C\text{-}F}$ = 21.9 Hz), 115.7 (d, $^{2}J_{C\text{-}F}$ = 22.8 Hz), 65.6, 50.9, 35.3, 24.3. ^{19}F NMR (565 MHz, $CDCl_3$): δ: -116.73 (s), -117.45 – -117.49 (m). HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{29}H_{24}F_2N_2NaO$ 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), $[RhCp^*Cl_2]_2$ (3.1 mg, 0.005 mmol), NaOAc (8.2 mg, 0.1 mmol) and 1-phenylbuta-2,3-dien-1-yl acetate (**2a**, 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 Na_2SO_4, 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 Na_2SO_4, 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-1*H*,9*H*-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. ^{1}H NMR ($CDCl_3$, 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). ^{13}C{^{1}H} NMR ($CDCl_3$, 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 $C_{19}H_{16}N_2NaO$ 311.1155; Found 311.1147.

(*E*)-7,9-Dimethyl-9-styryl-1*H*,9*H*-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. ^{1}H NMR ($CDCl_3$, 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). ^{13}C{^{1}H} NMR ($CDCl_3$, 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-1*H*,9*H*-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 ℃. ^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-1*H*,9*H*-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 ℃. ^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 ℃ 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-1*H*,9*H*-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 ℃. ^{1}H NMR ($CDCl_3$, 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). ^{13}C{^{1}H} NMR ($CDCl_3$, 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 $C_{29}H_{24}N_2NaOS$ 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 ℃. ^{1}H NMR ($CDCl_3$, 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). ^{13}C{^{1}H} NMR ($CDCl_3$, 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 $C_{30}H_{26}N_2NaOS$ 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 ℃. ^{1}H NMR ($CDCl_3$, 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). ^{13}C{^{1}H} NMR ($CDCl_3$, 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 ℃. ^{1}H 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{^{1}H} 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 ℃. ^{1}H 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{^{1}H} 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 ℃ 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-1*H*,9*H*-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). ^{1}H NMR ($CDCl_3$, 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). ^{13}C{^{1}H} NMR ($CDCl_3$, 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 $C_{35}H_{32}N_2NaO_5$ 583.2203; Found 583.2200.

Dimethyl (*E*)-5-(7,9-dimethyl-1-oxo-9-styryl-2,3-dihydro-1*H*,9*H*-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). ^{1}H NMR ($CDCl_3$, 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). ^{13}C{^{1}H} NMR ($CDCl_3$, 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-1*H*,9*H*-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). ^{1}H 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{^{1}H} 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-1*H*,9*H*-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). ^{1}H 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{^{1}H} 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). ^{1}H 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 ℃ 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 ℃. ^{1}H NMR ($CDCl_3$, 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). ^{13}C{^{1}H} NMR ($CDCl_3$, 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 $C_{34}H_{31}N_3NaO_3$ 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 ℃. ^{1}H NMR ($CDCl_3$, 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). ^{13}C{^{1}H} NMR ($CDCl_3$, 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 $C_{34}H_{31}N_3NaO_3$ 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), $Pd_2(dba)_3$ (18.3 mg, 0.02 mmol), DavePhos (11.8 mg, 0.03 mmol), ^{t}BuONa (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 ℃ 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 Na_2SO_4, 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-1*H*,9*H*-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 ℃. ^{1}H NMR ($CDCl_3$, 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). ^{13}C{^{1}H} NMR ($CDCl_3$, 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 $C_{33}H_{34}N_3O_2$ 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), $[RhCp^*Cl_2]_2$ (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 Na_2SO_4, 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

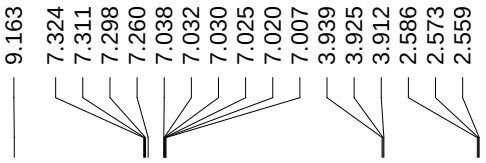
To a reaction tube equipped with a stir bar were charged with **1a** (648.3 mg, 4 mmol), DCE (20 mL), $[RhCp^*Cl_2]_2$ (61.8 mg, 0.1 mmol), NaOAc (164 mg, 2 mmol) and **2a** (2.2570 g, 12 mmol). The tube was then

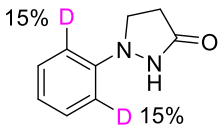
sealed, and the mixture was stirred at 50 ℃ under argon for 24 h. Upon completion, it was quenched with saturated brine and extracted with dichloromethane (30 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered through a pad of celite, and concentrated under reduced pressure. 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)

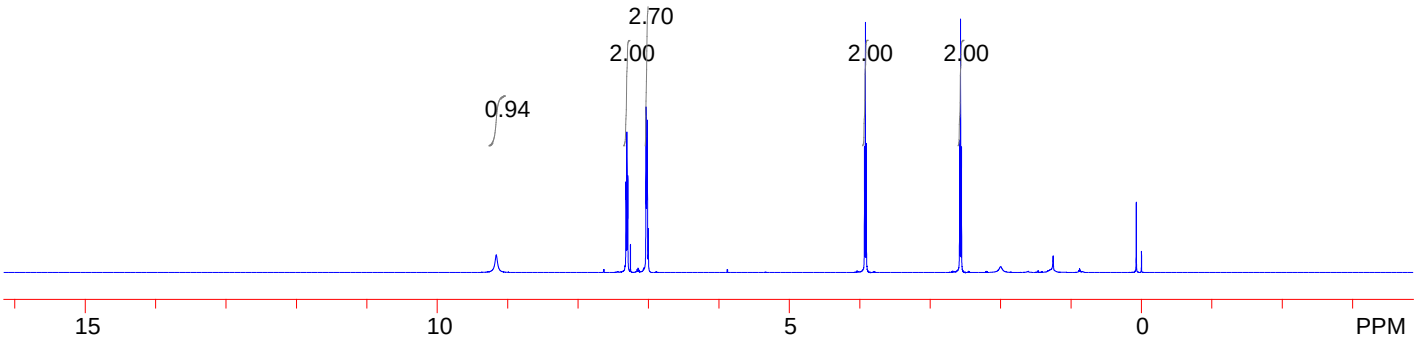
To a reaction tube equipped with a stir bar were charged with **1a** (32.4 mg, 0.2 mmol), DCE (2 mL), CD_3OD (163 μL, 4 mmol), $[RhCp^*Cl_2]_2$ (3.1 mg, 0.005 mmol) and NaOAc (8.2 mg, 0.1 mmol). The tube was then sealed, and the mixture was stirred at room temperature under argon for 0.5 h. Afterwards, it was quenched with saturated brine and extracted with dichloromethane (10 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4, 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**-d_2. Upon analyzing the ^1H NMR spectrum of the mixture, the deuteration ratio was determined to be 15%.





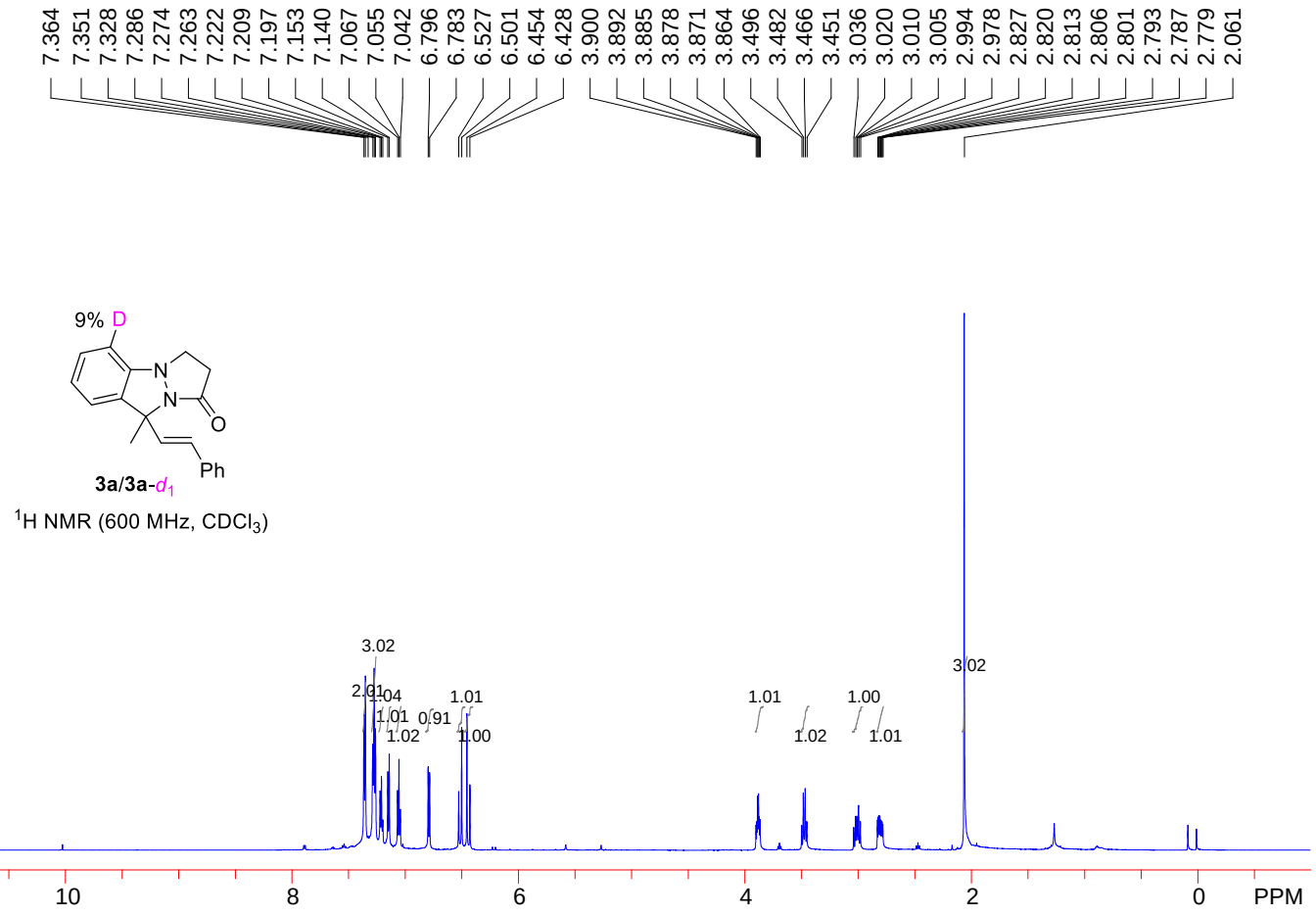
1a/1a-d_2

^1H NMR (600 MHz, $CDCl_3$)



2. H/D exchange experiment (II)

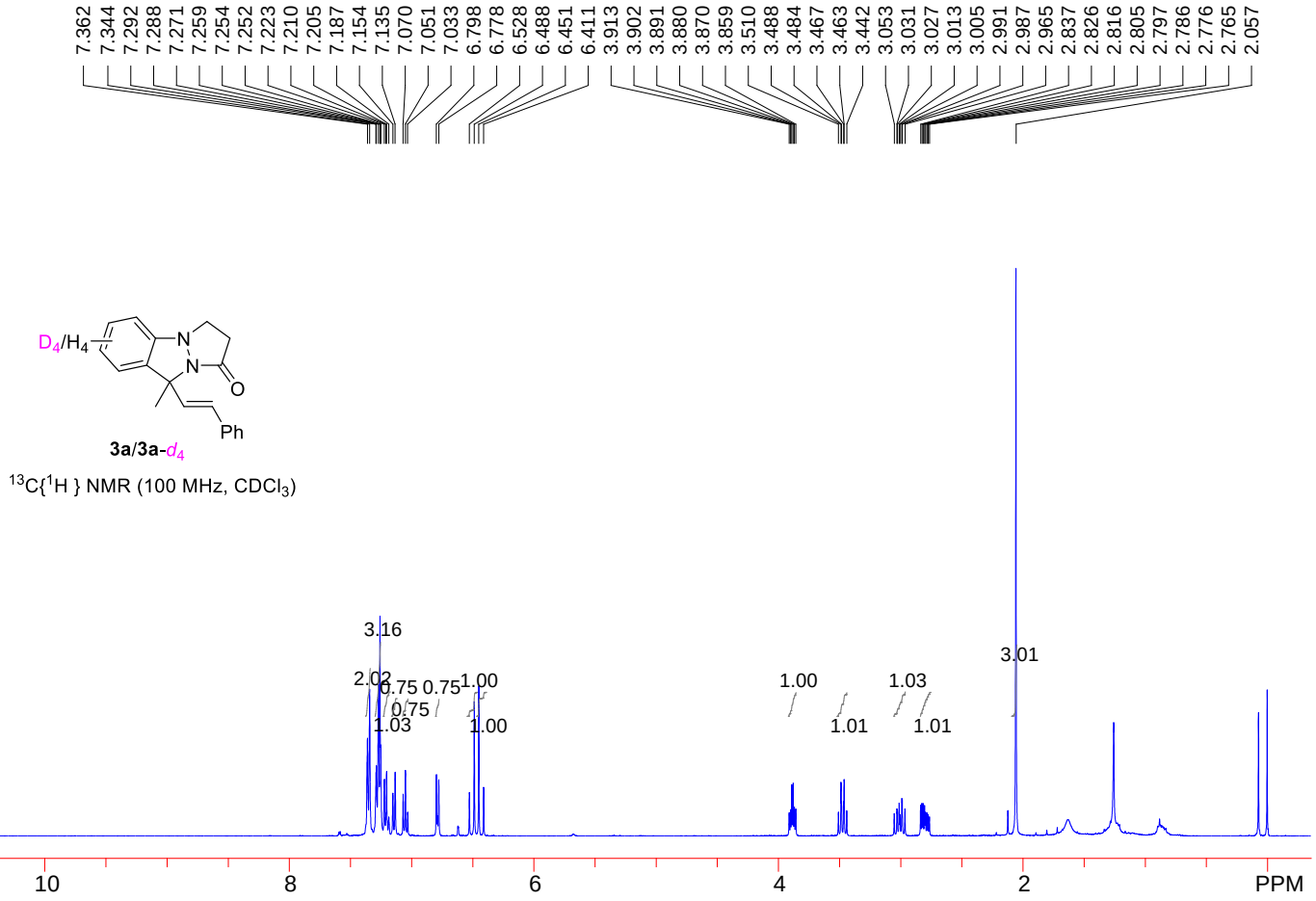
To a reaction tube equipped with a stir bar were charged with **1a** (64.8 mg, 0.4 mmol), **2a** (37.7 mg, 0.2 mmol), DCE (2 mL), CD_3OD (163 μL, 4 mmol), $[RhCp^*Cl_2]_2$ (3.1 mg, 0.005 mmol) and NaOAc (8.2 mg, 0.1 mmol). The tube was then sealed, and the mixture was stirred at room temperature under 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 Na_2SO_4, 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**-d_1. 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**-d_5 (16.2 mg, 0.1 mmol), **2a** (18.8 mg, 0.1 mmol), DCE (1 mL), $[RhCp^*Cl_2]_2$ (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 × 3). The combined organic phases were dried over anhydrous Na_2SO_4, 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**-d_4. Upon analyzing the ^{1}H NMR spectrum of the mixture, the ratio of **3a** to **3a**-d_4 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), $[RhCp^*Cl_2]_2$ (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 × 3). The combined organic phases were dried over anhydrous Na_2SO_4, 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), $[RhCp^*Cl_2]_2$ (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 ℃ under argon for 6 h. From the resulting mixture, the generation of **4a** was not observed based on TLC detection.

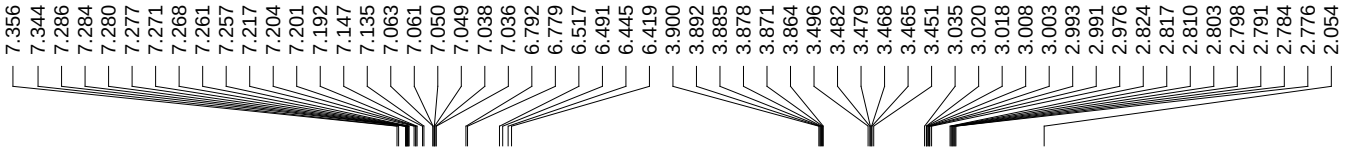
IV. References

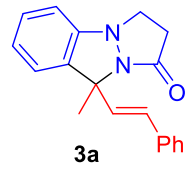
[1] N. Li, X. Zhang and X. Fan, Synthesis of pyrazolidinone fused cinnolines via the cascade reactions of 1-phenylpyrazolidinones with vinylene carbonate, *Tetrahedron Lett*., 2022, **103**, 153984.

[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.

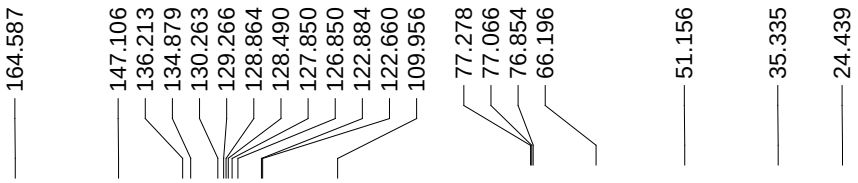
V. NMR spectra of 3a-3ee

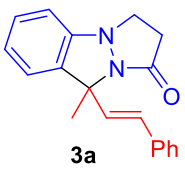




3a

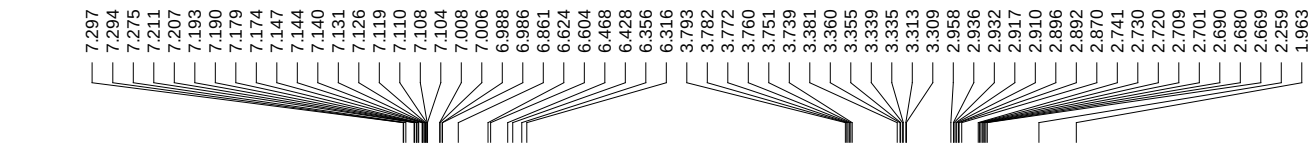
^{1}H NMR (600 MHz, $CDCl_3$)

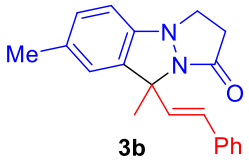




3a

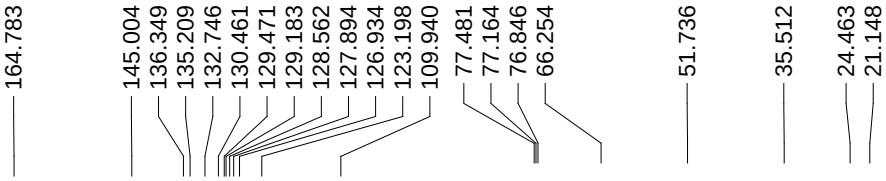
^{13}C{^{1}H } NMR (150 MHz, $CDCl_3$)

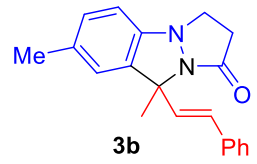




3b

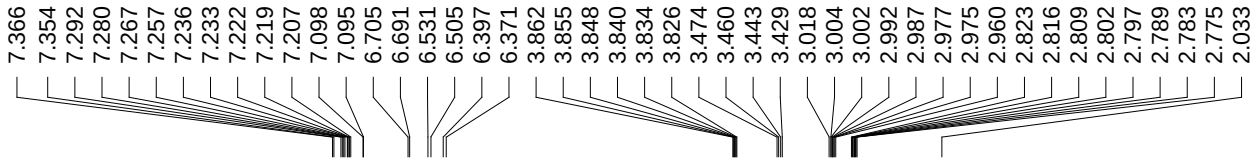
^{1}H NMR (400 MHz, $CDCl_3$)

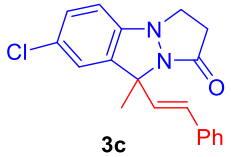




3b

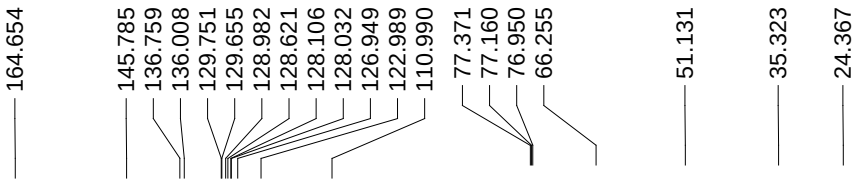
^{13}C{^{1}H } NMR (100 MHz, $CDCl_3$)

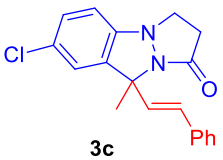




3c

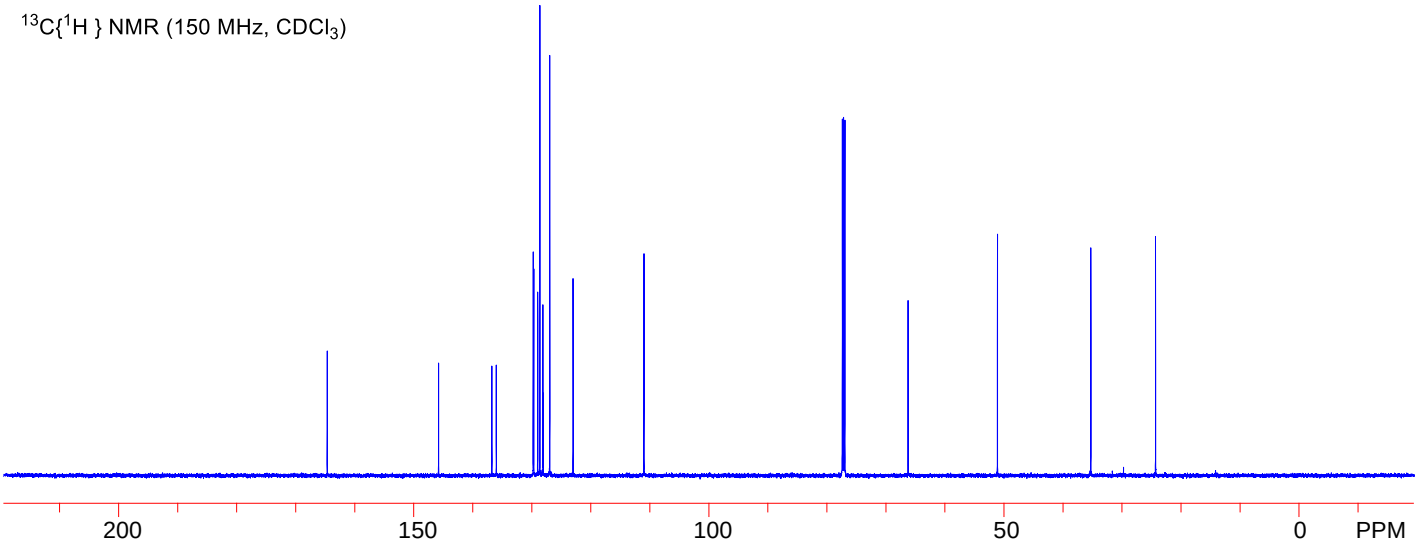
^{1}H NMR (600 MHz, $CDCl_3$)

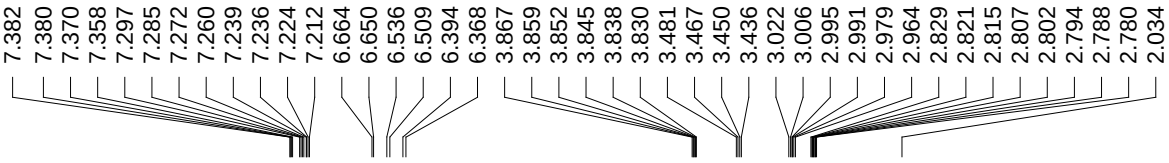


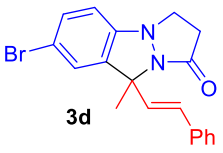


3c

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

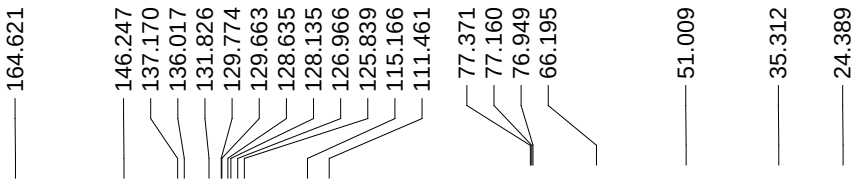


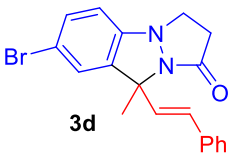




3d

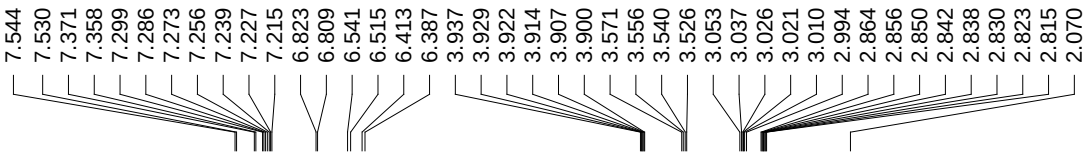
^{1}H NMR (600 MHz, $CDCl_3$)

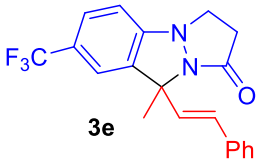




3d

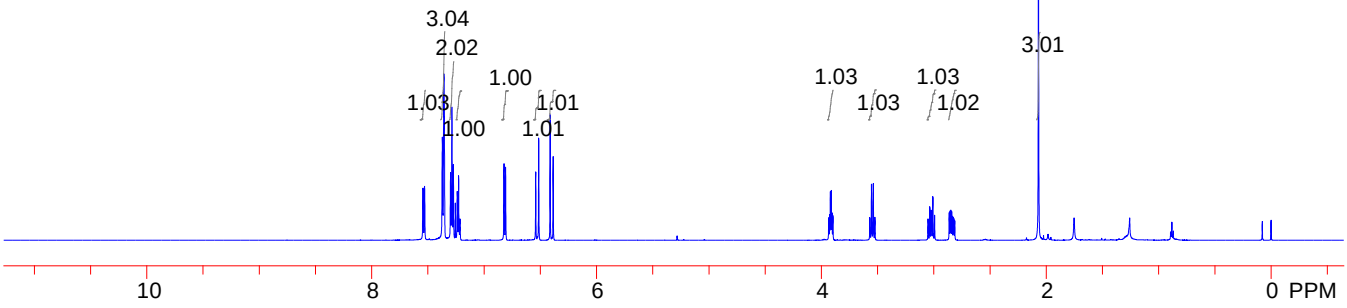
^{13}C{^{1}H } NMR (150 MHz, $CDCl_3$)

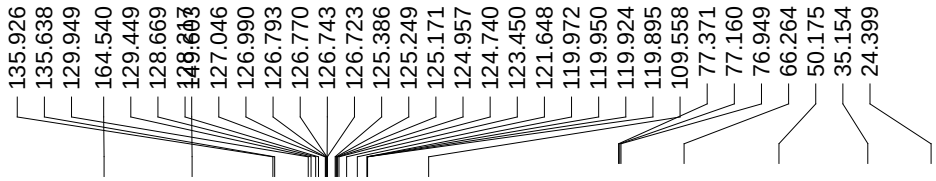


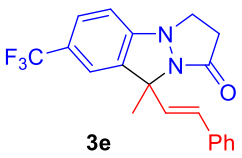


3e

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

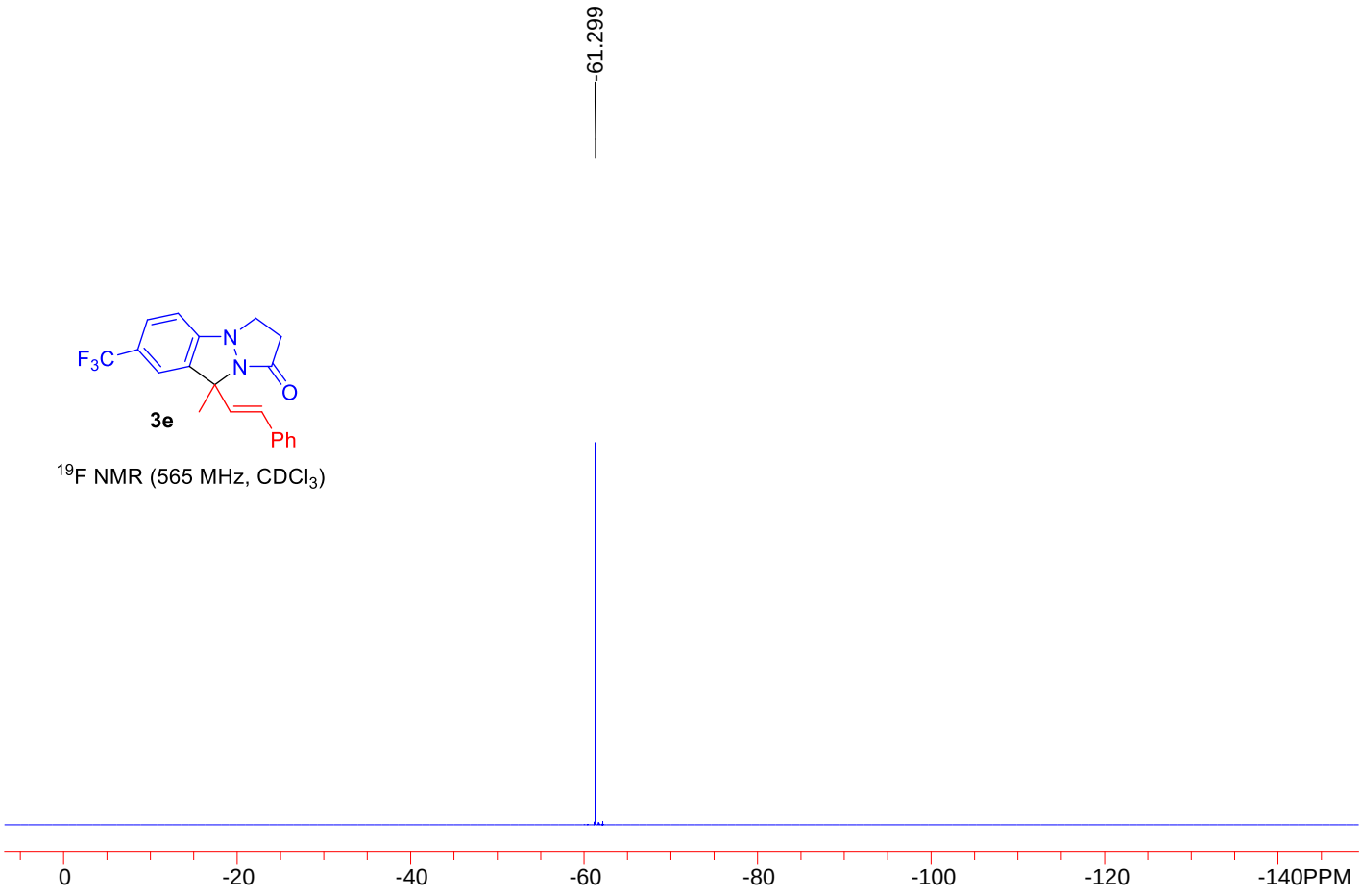






3e

^{13}C{^{1}H } NMR (150 MHz, $CDCl_3$)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O
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3e
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-40
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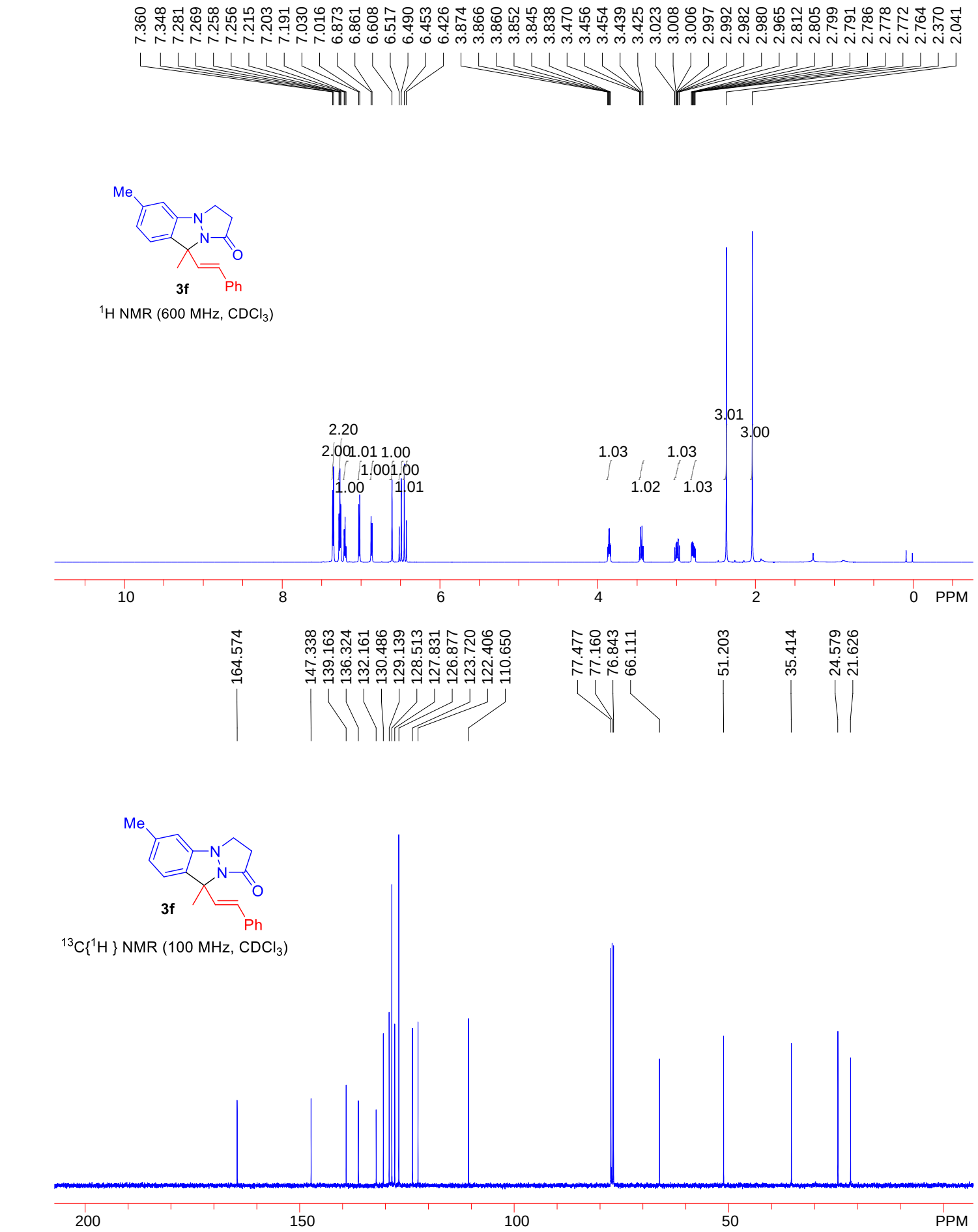
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O
Ph
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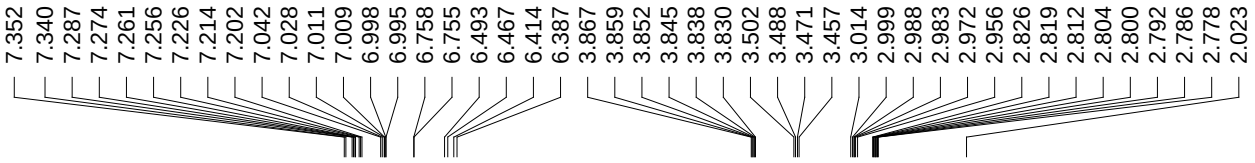
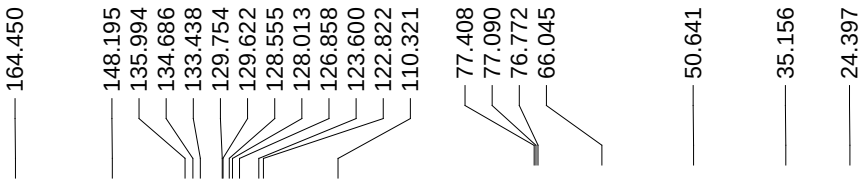
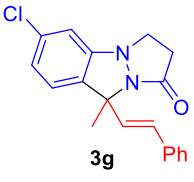
PPM



3g

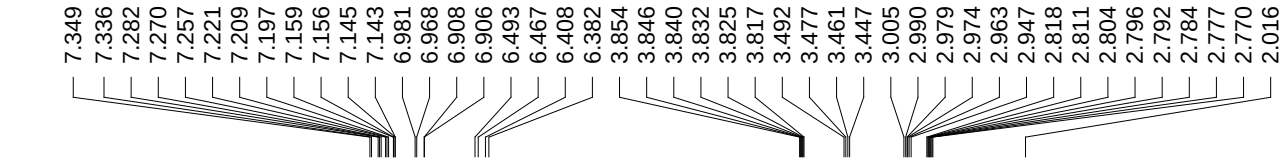
^{1}H NMR (600 MHz, $CDCl_3$)

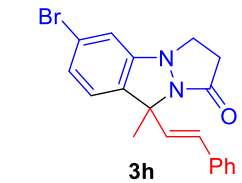




3g

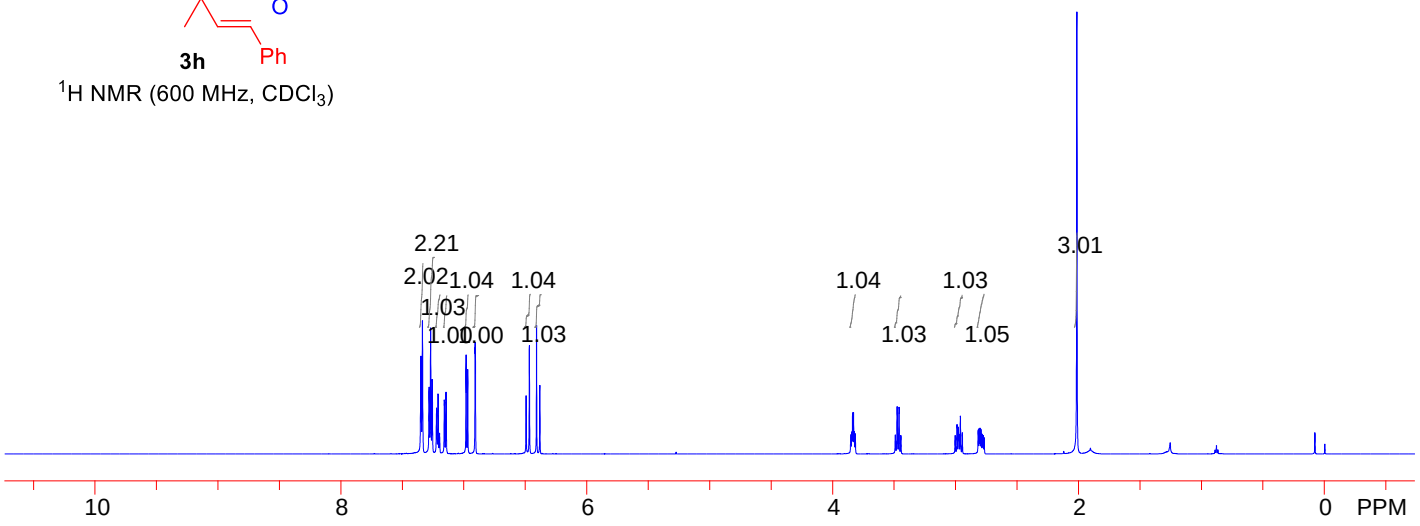
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

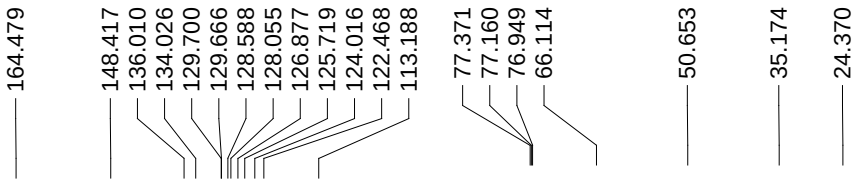


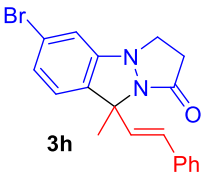


3h

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

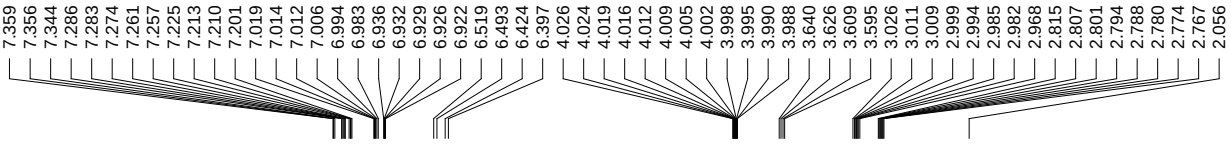






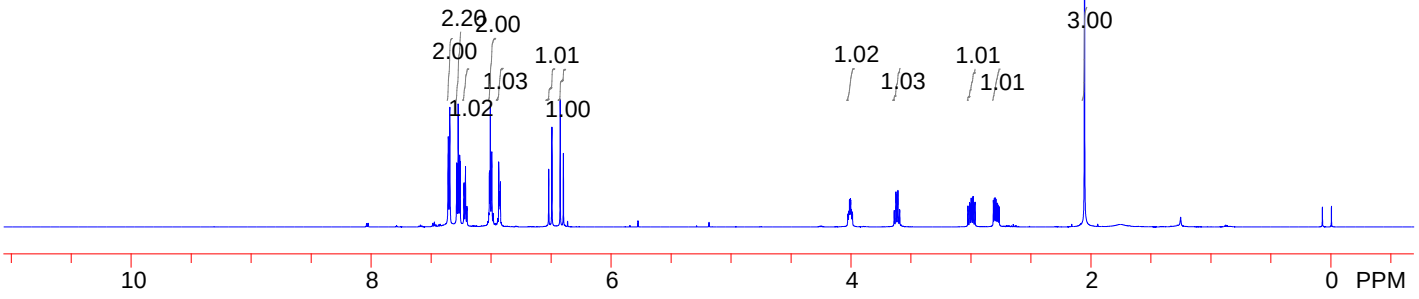
3h

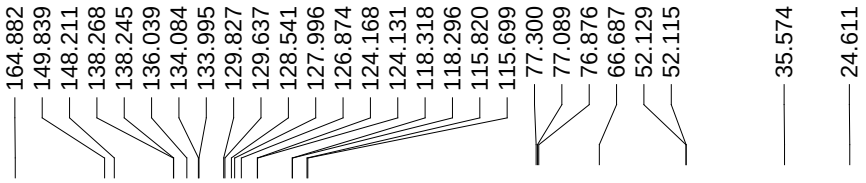
^{13}C{^{1}H } NMR (150 MHz, $CDCl_3$)

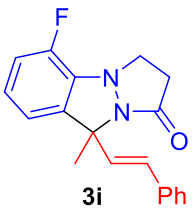


3i

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

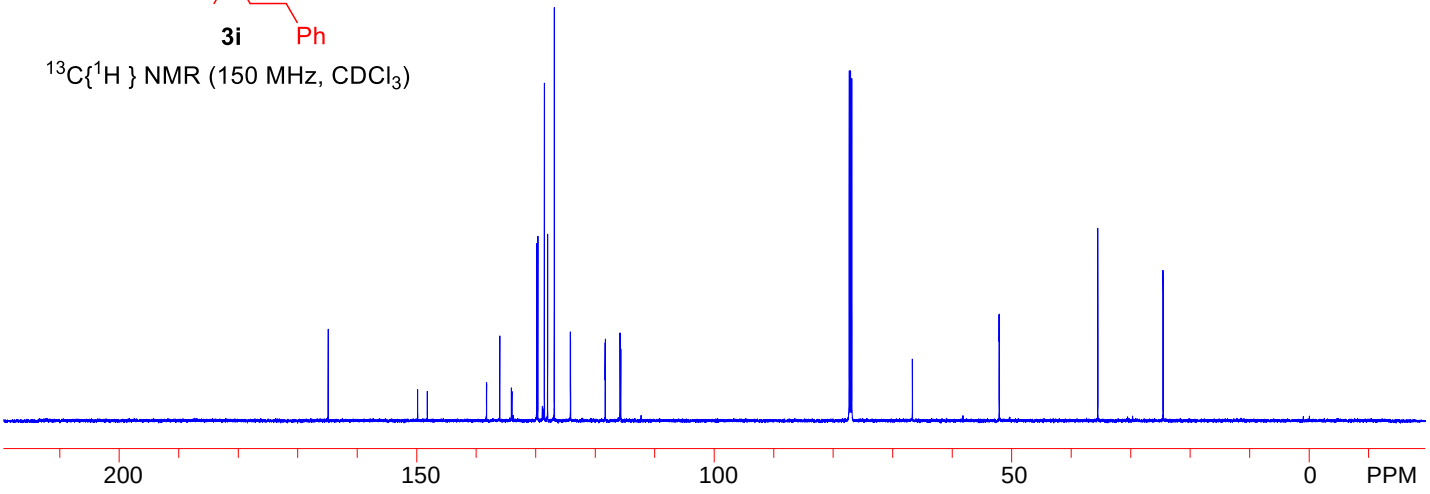


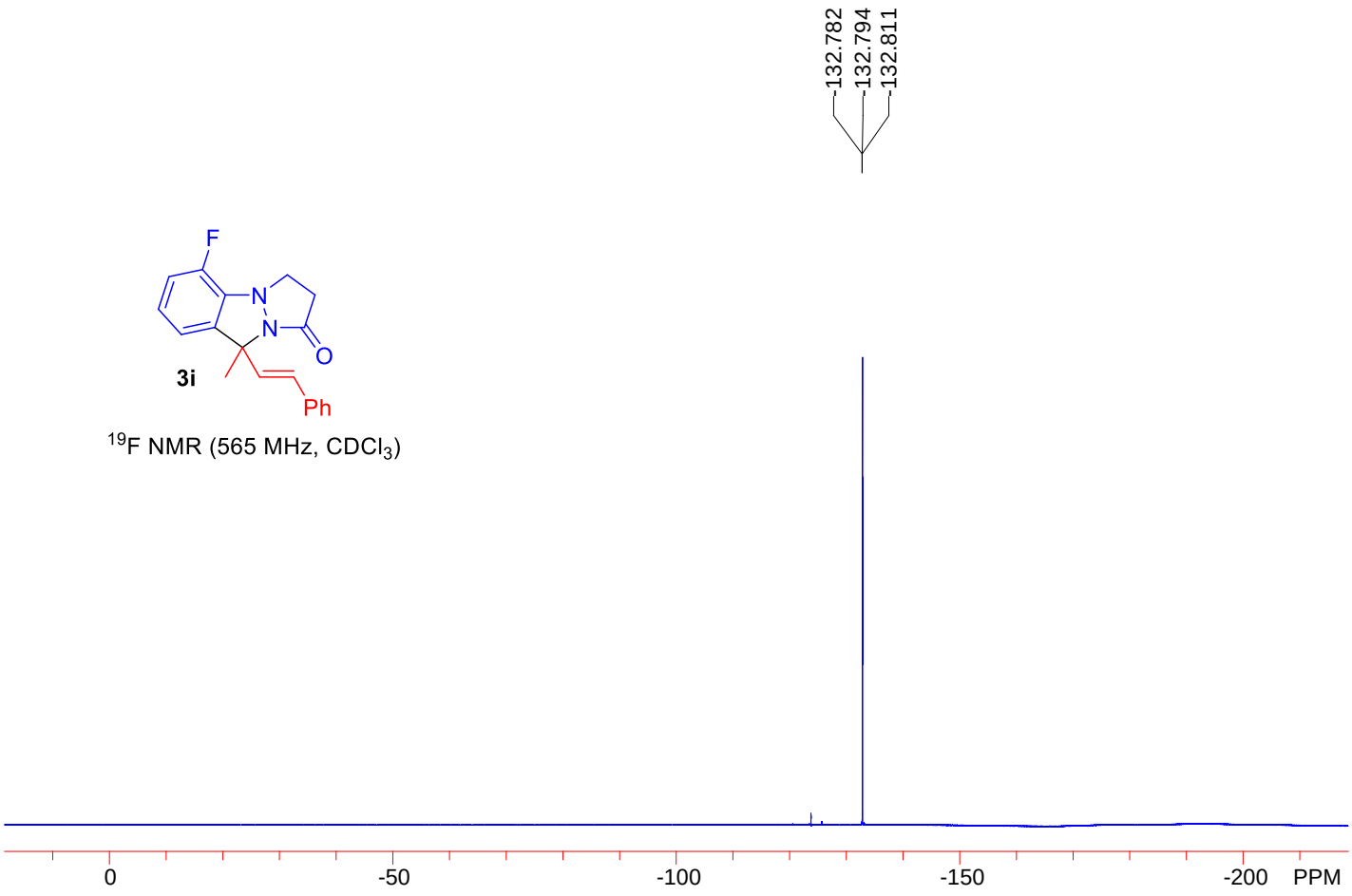




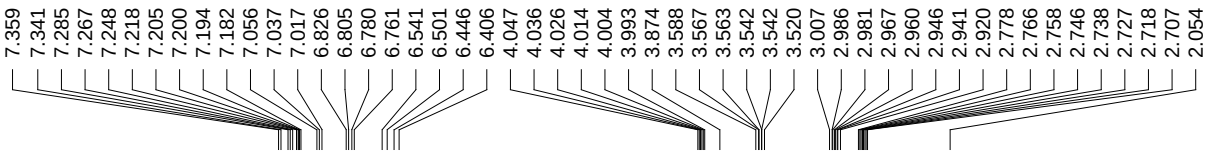
3i

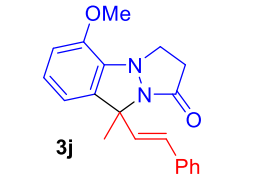
^{13}C{^{1}H } NMR (150 MHz, $CDCl_3$)





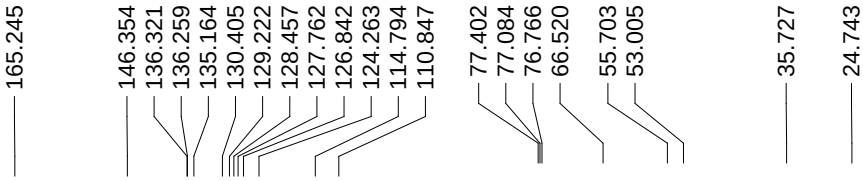
^{19}F NMR (565 MHz, $CDCl_3$)

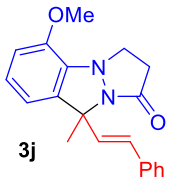




3j

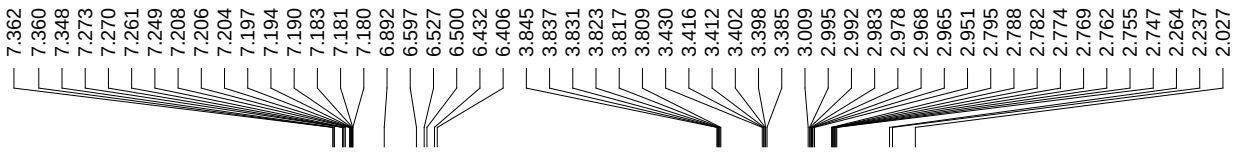
^{1}H NMR (400 MHz, $CDCl_3$)

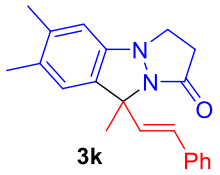




3j

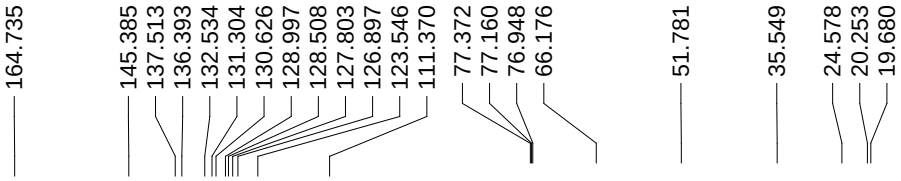
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

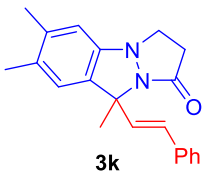




3k

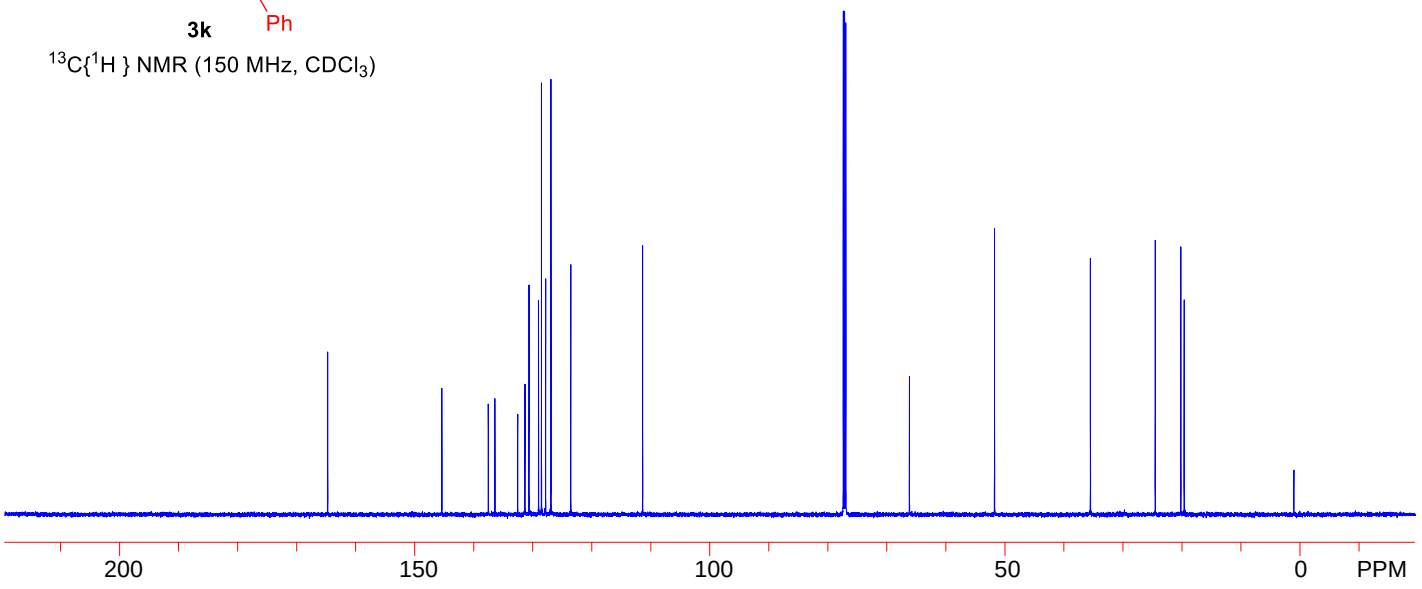
^{1}H NMR (600 MHz, $CDCl_3$)

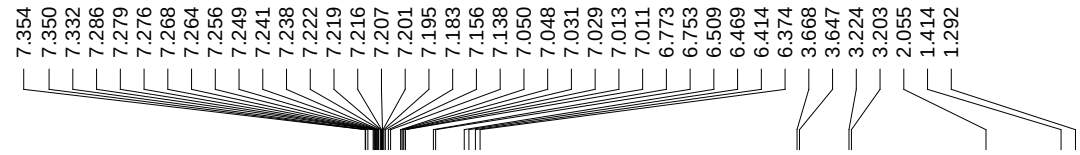


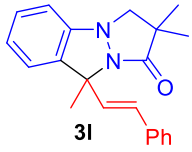


3k

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

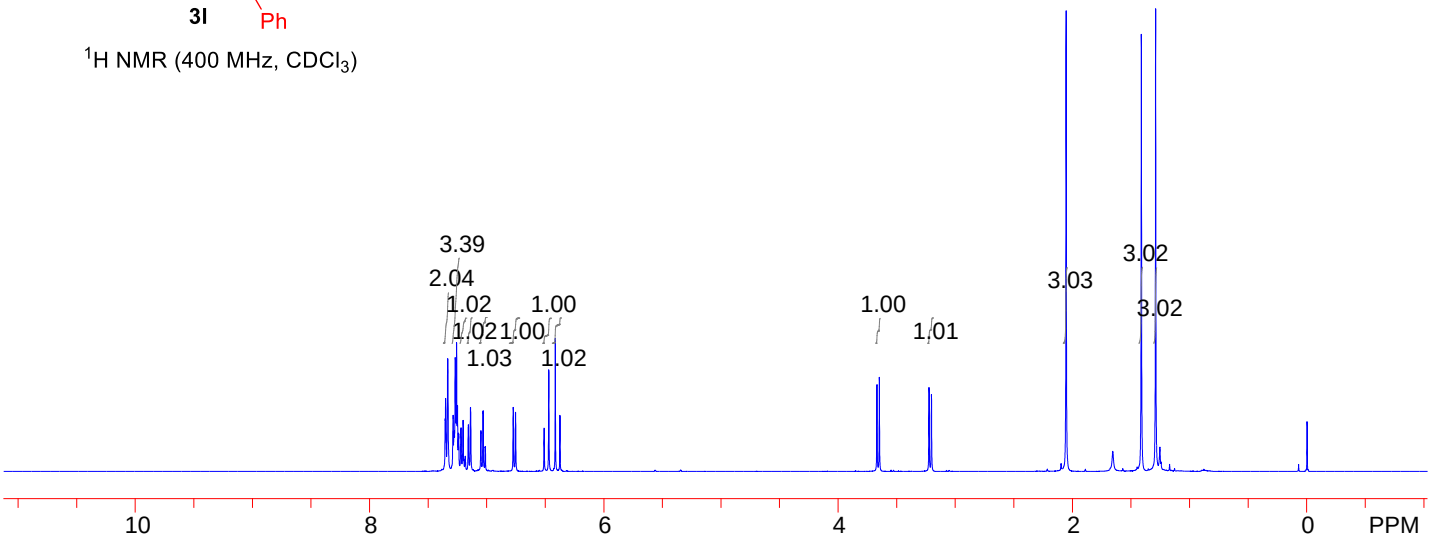


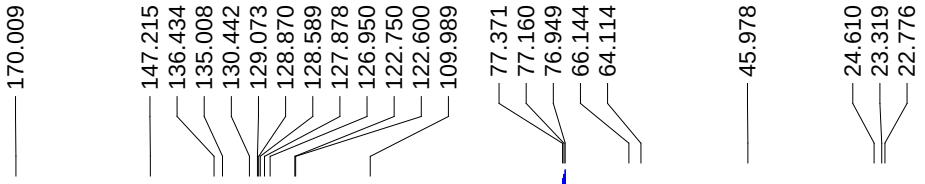


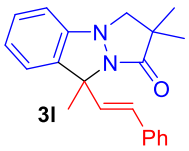


3l

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

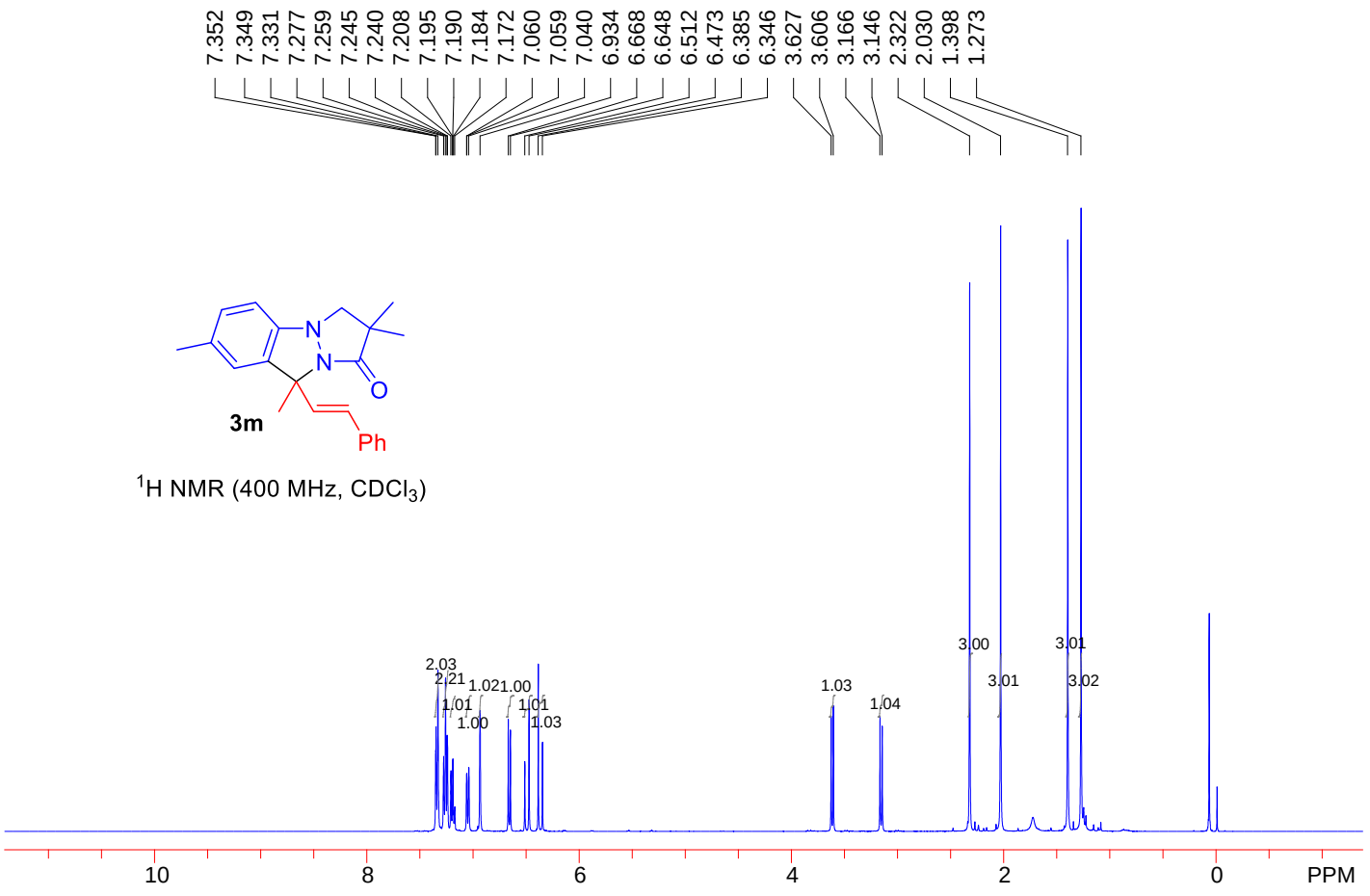


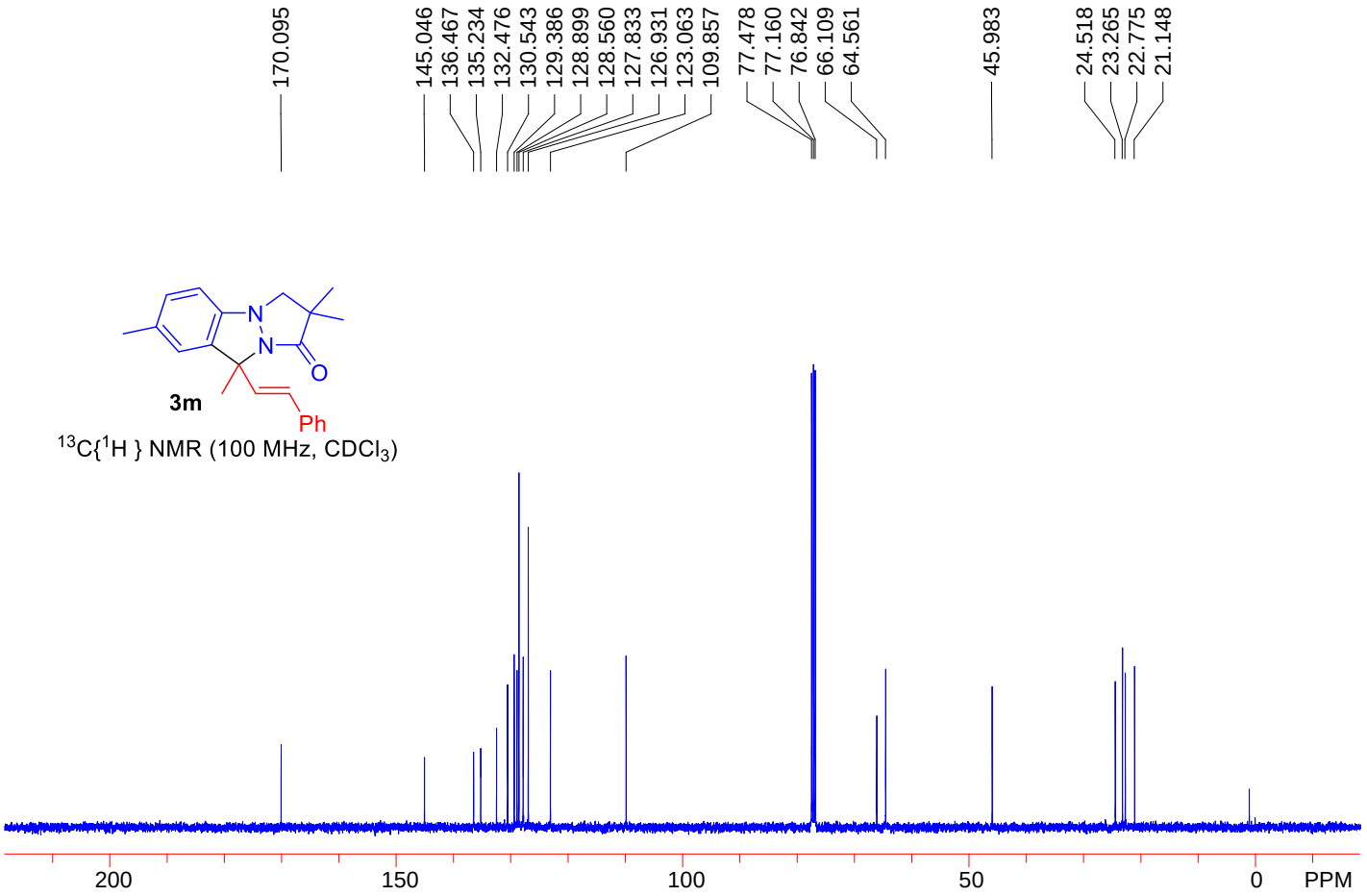


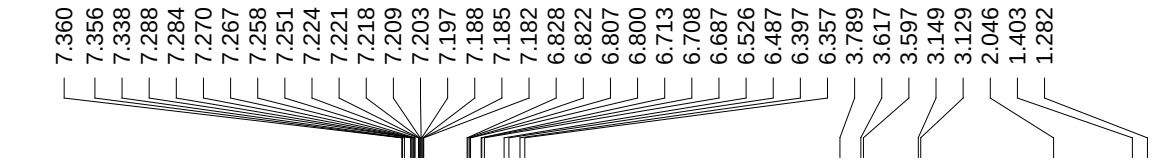


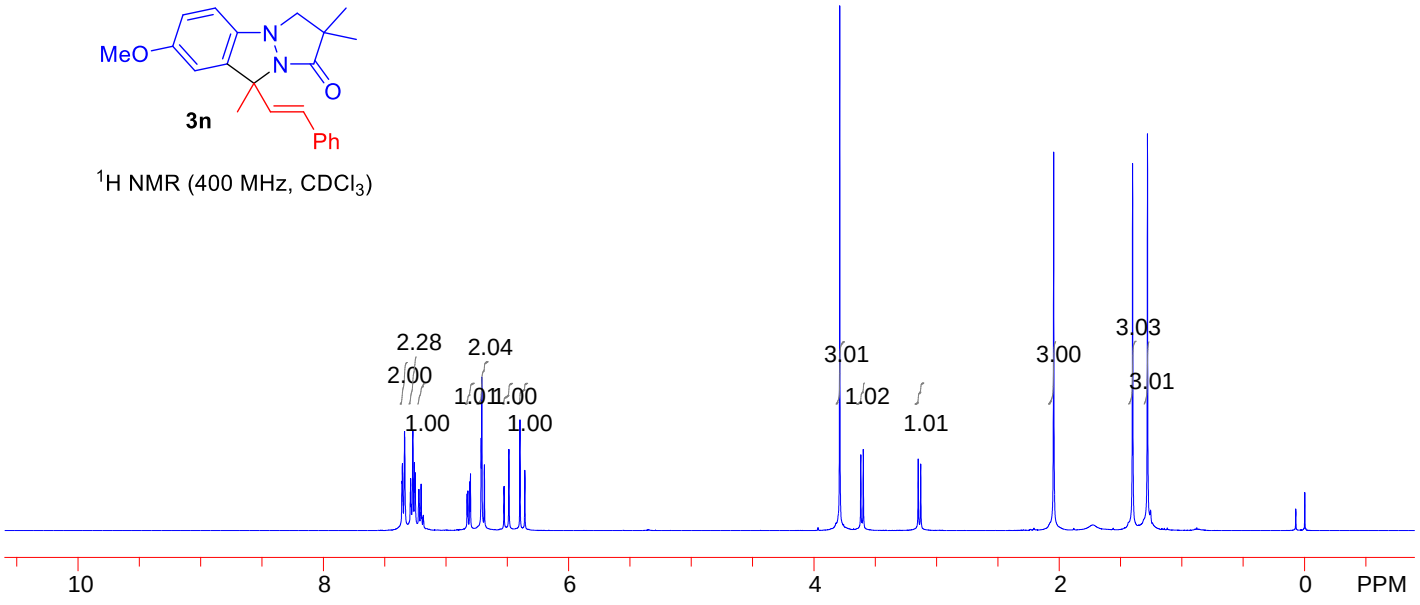
3l

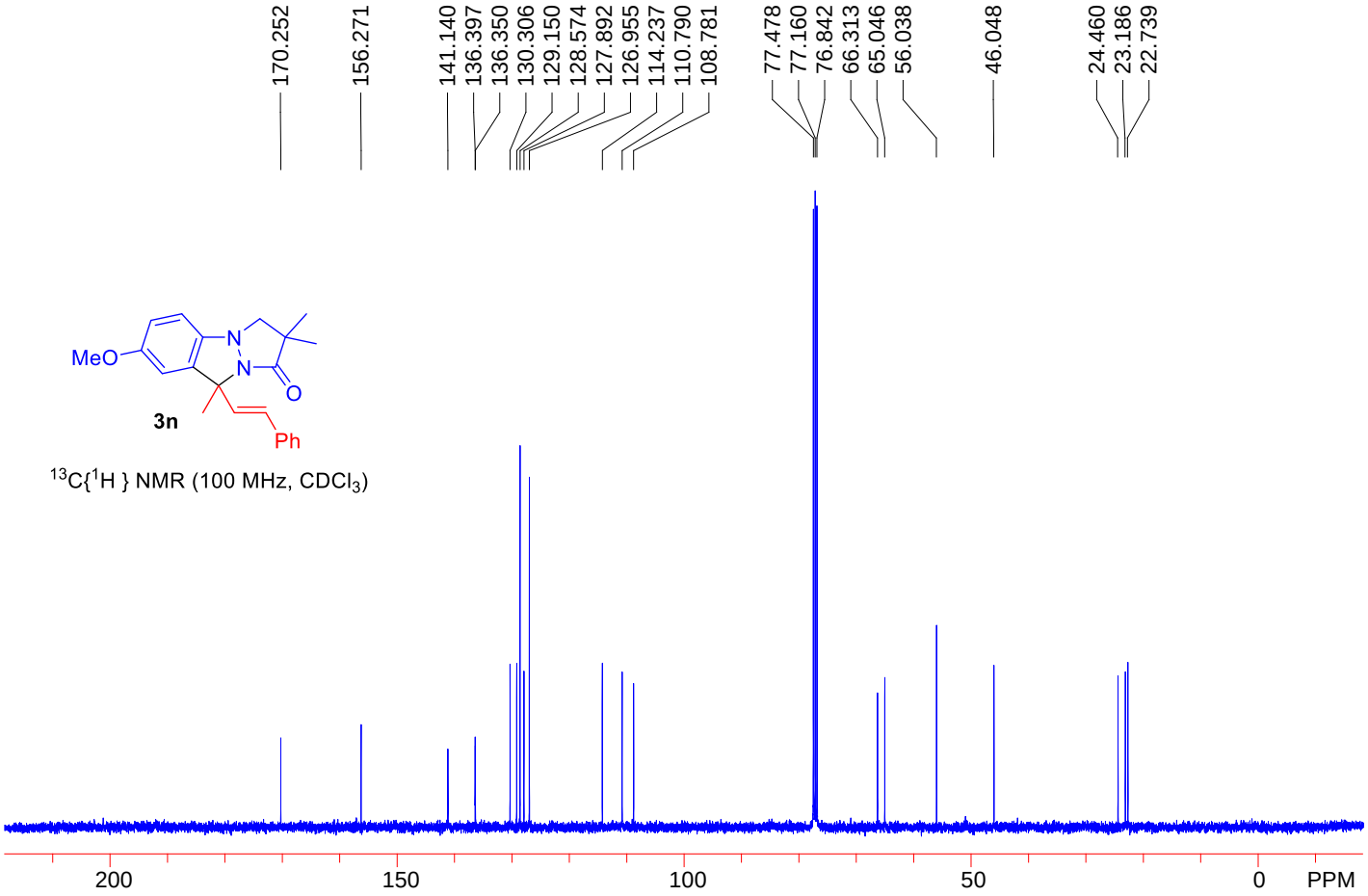
^{13}C{^{1}H } NMR (150 MHz, $CDCl_3$)

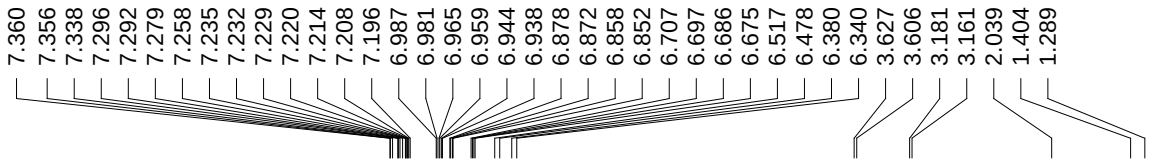

7.352
7.349
7.331
7.277
7.259
7.245
7.240
7.208
7.195
7.190
7.184
7.172
7.060
7.059
7.040
6.934
6.668
6.648
6.512
6.473
6.385
6.346
3.627
3.606
3.166
3.146
2.322
2.030
1.398
1.273
3m
Ph
1H NMR (400 MHz, CDCl3)
2.03
2.21
1.01
1.02
1.00
1.00
1.01
1.03
1.03
1.04
3.00
3.01
3.01
3.02
10
8
6
4
2
0
PPM

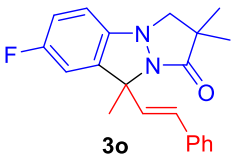

170.095
145.046
136.467
135.234
132.476
130.543
129.386
128.899
128.560
127.833
126.931
123.063
109.857
77.478
77.160
76.842
66.109
64.561
45.983
24.518
23.265
22.775
21.148
3m
Ph
13C{1H } NMR (100 MHz, CDCl3)
200
150
100
50
0
PPM


7.360
7.356
7.338
7.288
7.284
7.270
7.267
7.258
7.251
7.224
7.221
7.218
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
6.526
6.487
6.397
6.357
3.789
3.617
3.597
3.149
3.129
2.046
1.403
1.282


MeO
N
N
O
Ph
3n
^{1}H NMR (400 MHz, CDCl$_3$)
2.28
2.00
2.04
1.00
1.01
1.00
1.00
3.01
1.02
1.01
3.00
3.03
3.01
10
8
6
4
2
0
PPM

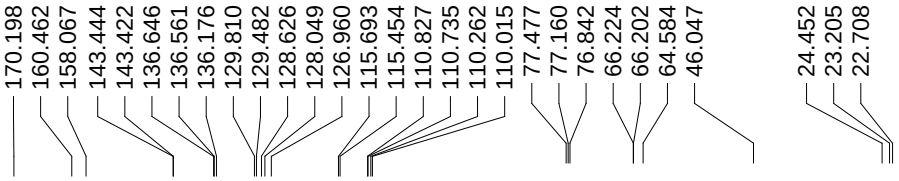

170.252
156.271
141.140
136.397
136.350
130.306
129.150
128.574
127.892
126.955
114.237
110.790
108.781
77.478
77.160
76.842
66.313
65.046
56.038
46.048
24.460
23.186
22.739
MeO
N
N
O
Ph
3n
^{13}C{^{1}H } NMR (100 MHz, CDCl$_3$)
200
150
100
50
0
PPM

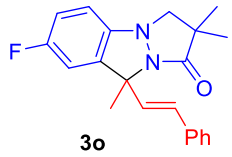




3o

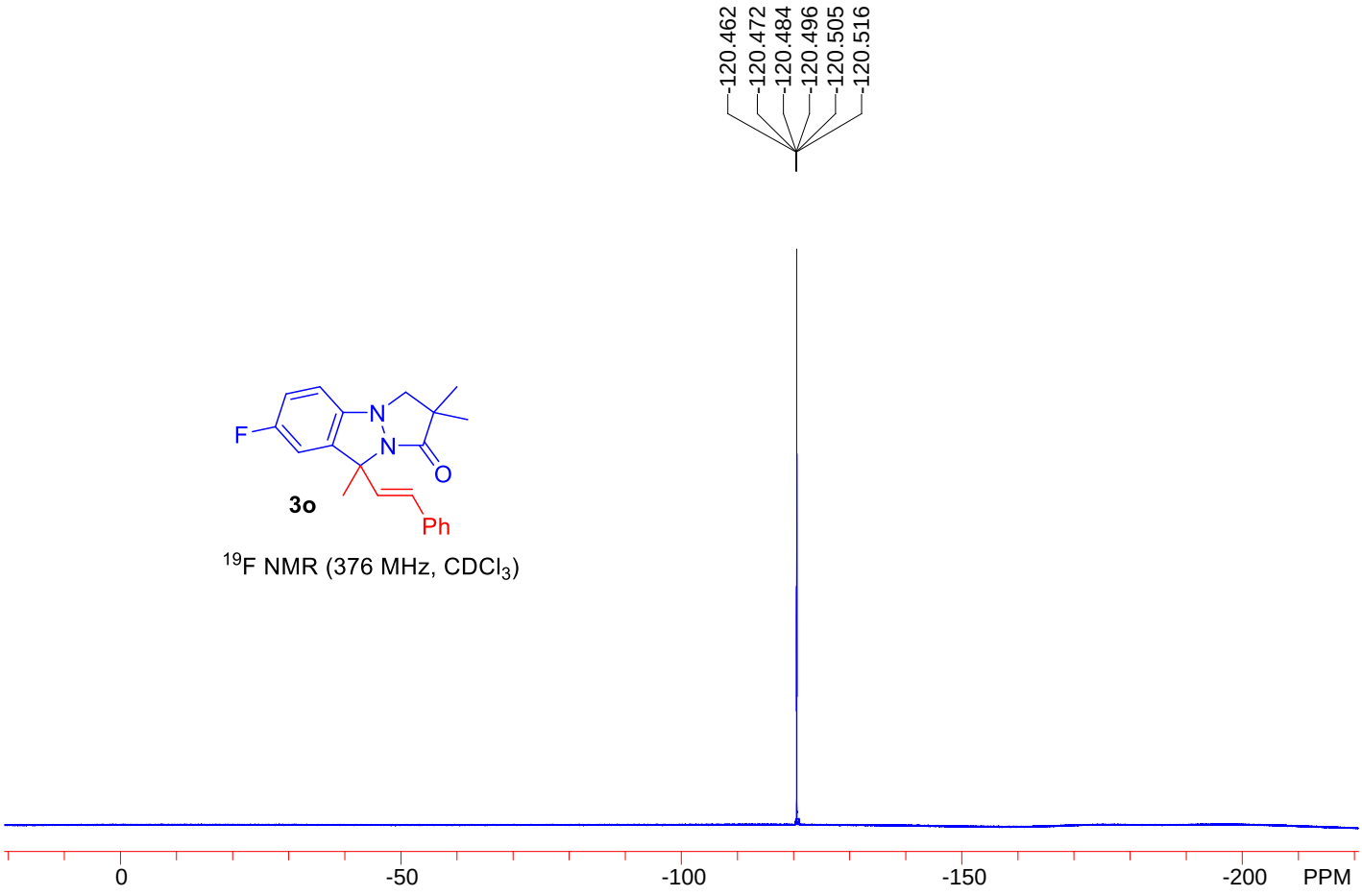
^{1}H NMR (400 MHz, $CDCl_3$)





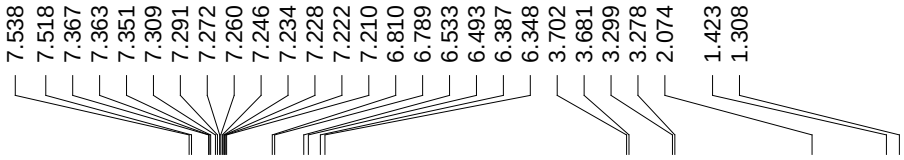
3o

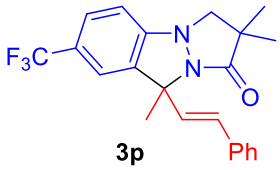
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



3o

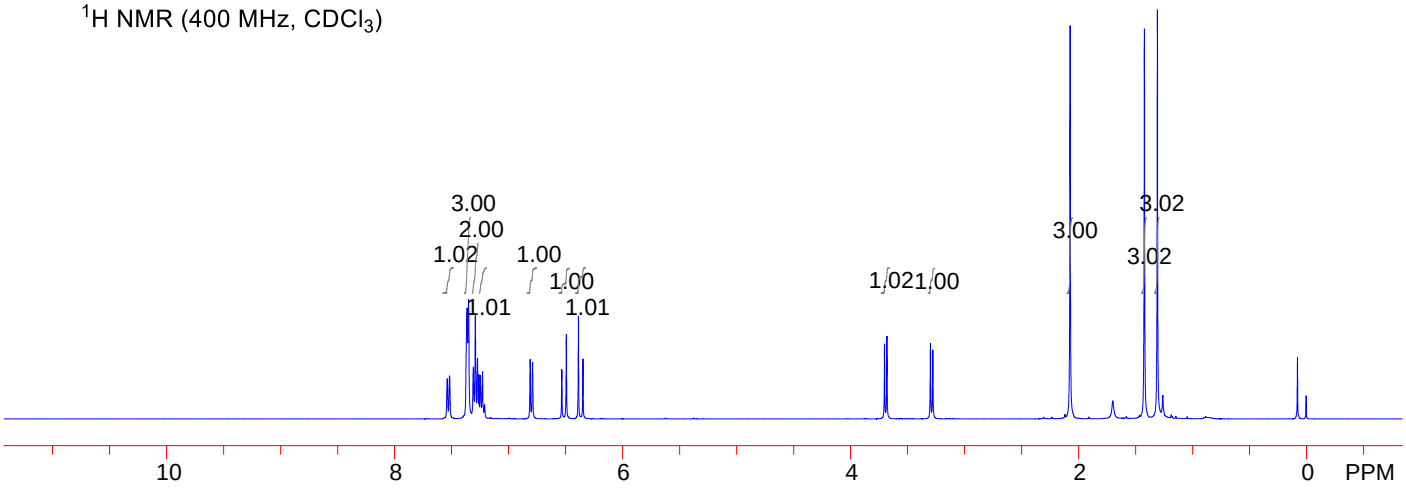
^{19}F NMR (376 MHz, $CDCl_3$)

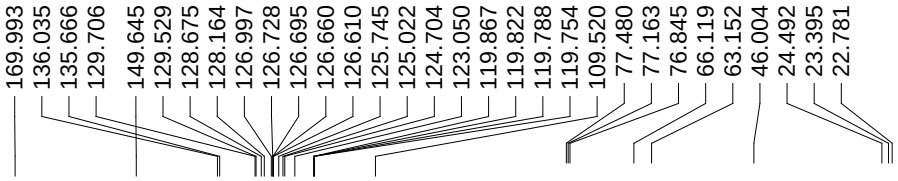


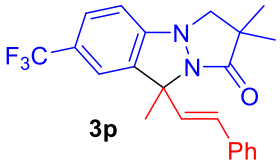


3p

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

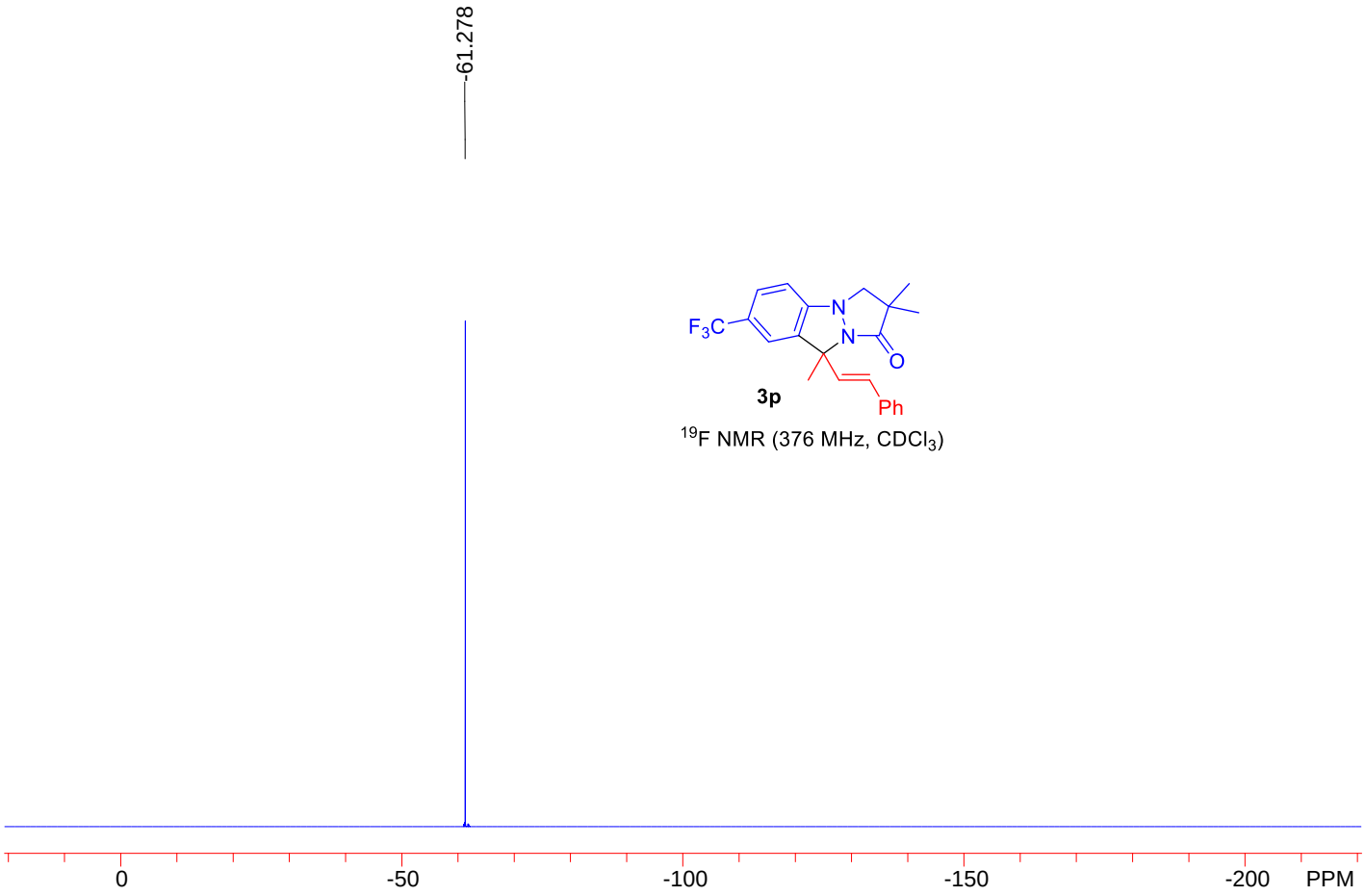






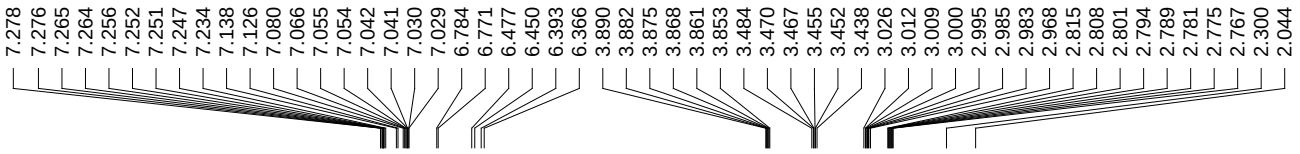
3p

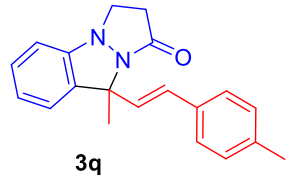
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



3p

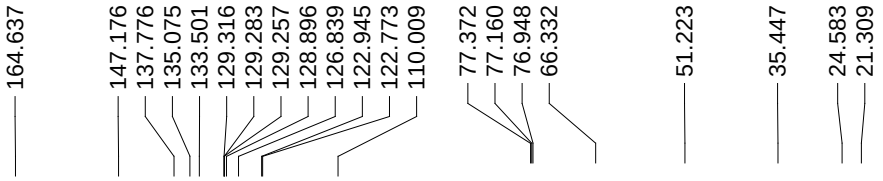
^{19}F NMR (376 MHz, $CDCl_3$)

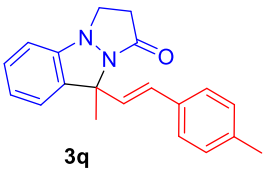




3q

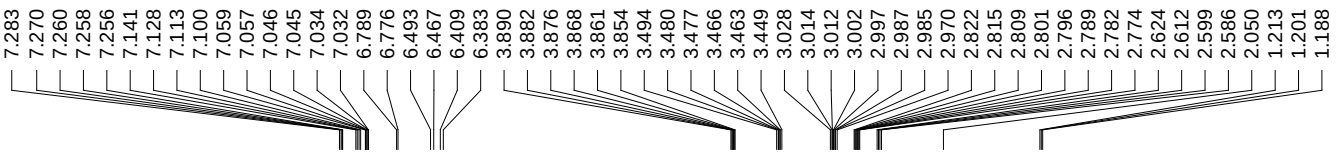
^{1}H NMR (600 MHz, $CDCl_3$)

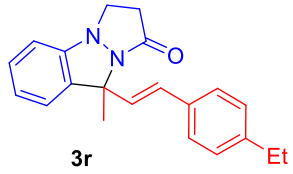




3q

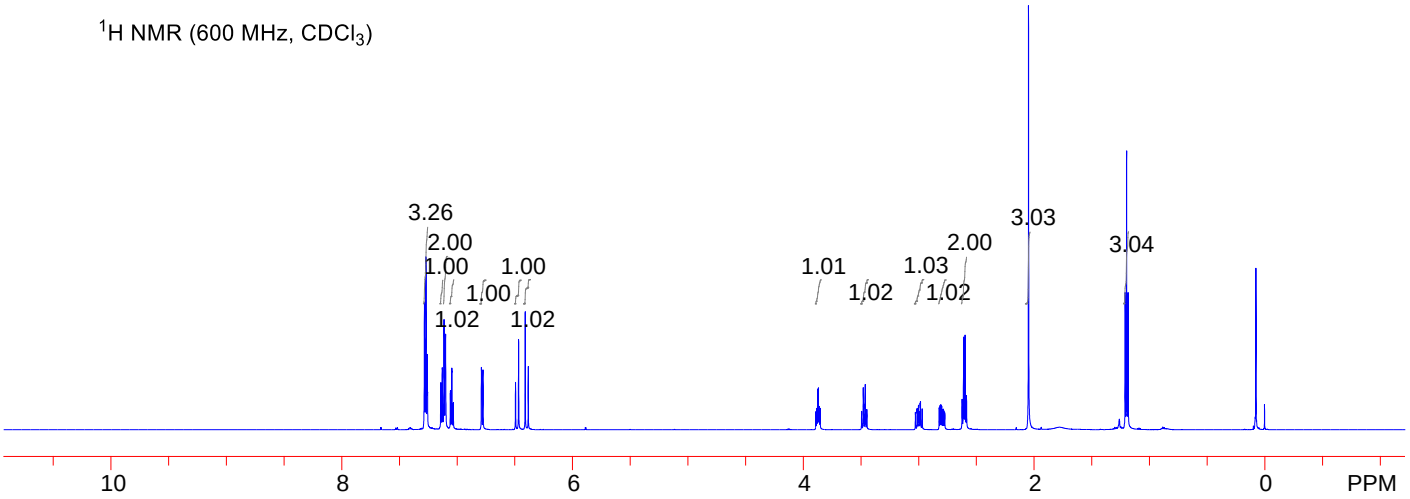
$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$)

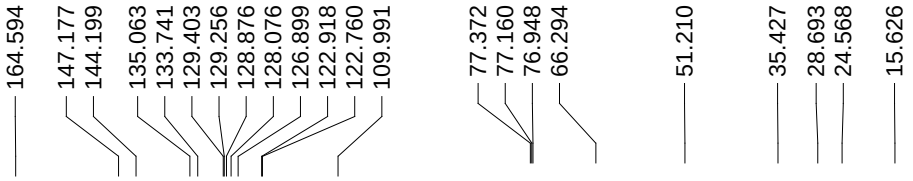


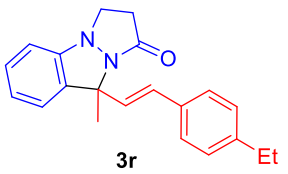


3r

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

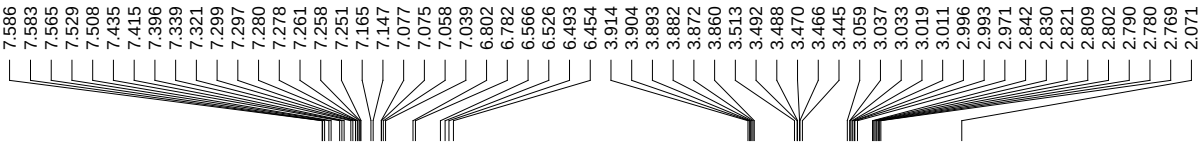


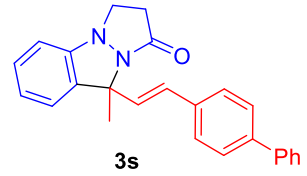




3r

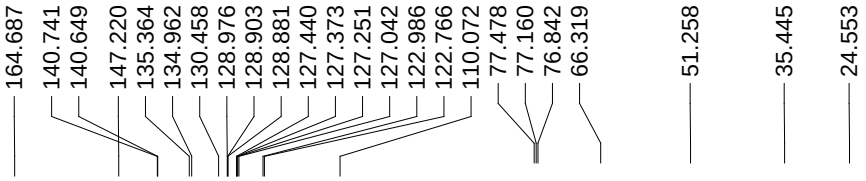
$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$)

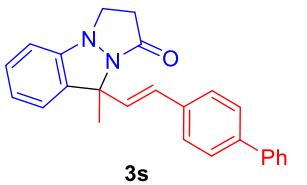




3s

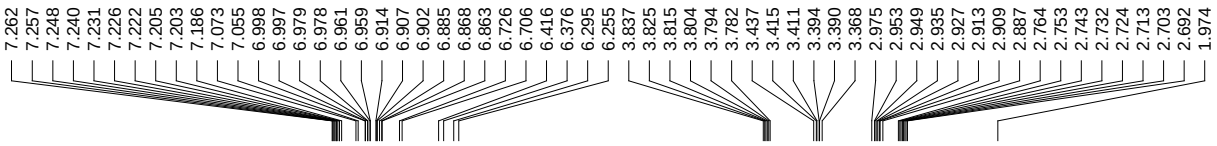
^{1}H NMR (400 MHz, $CDCl_3$)

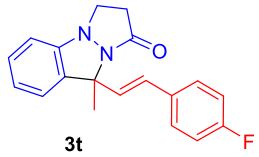




3s

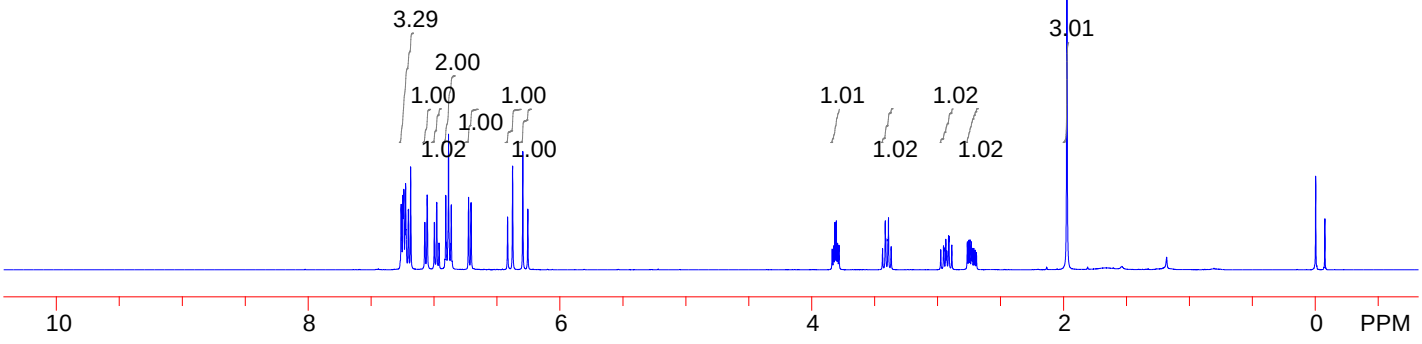
^{13}C{^{1}H } NMR (100 MHz, $CDCl_3$)

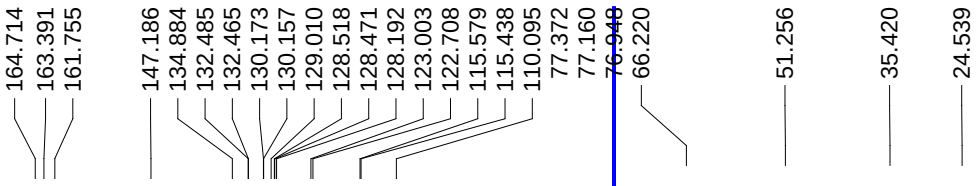


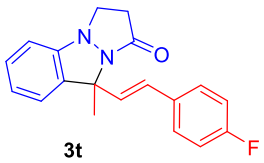


3t

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

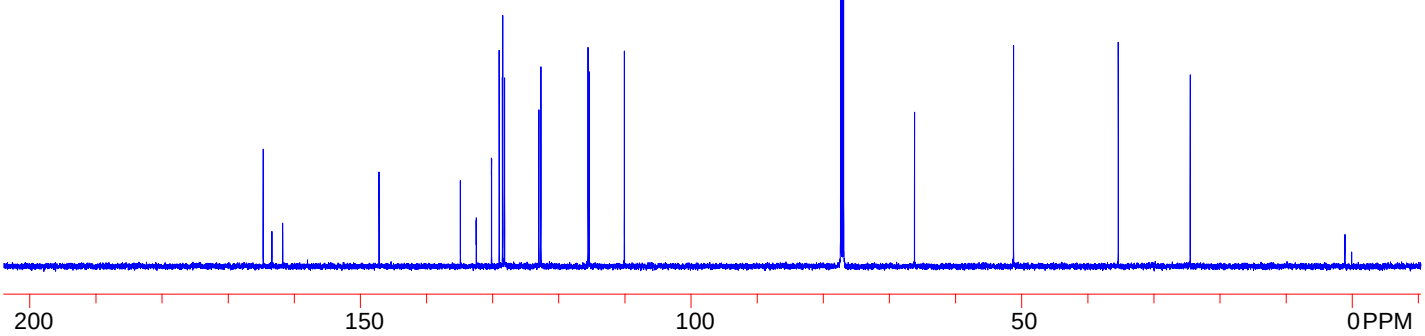


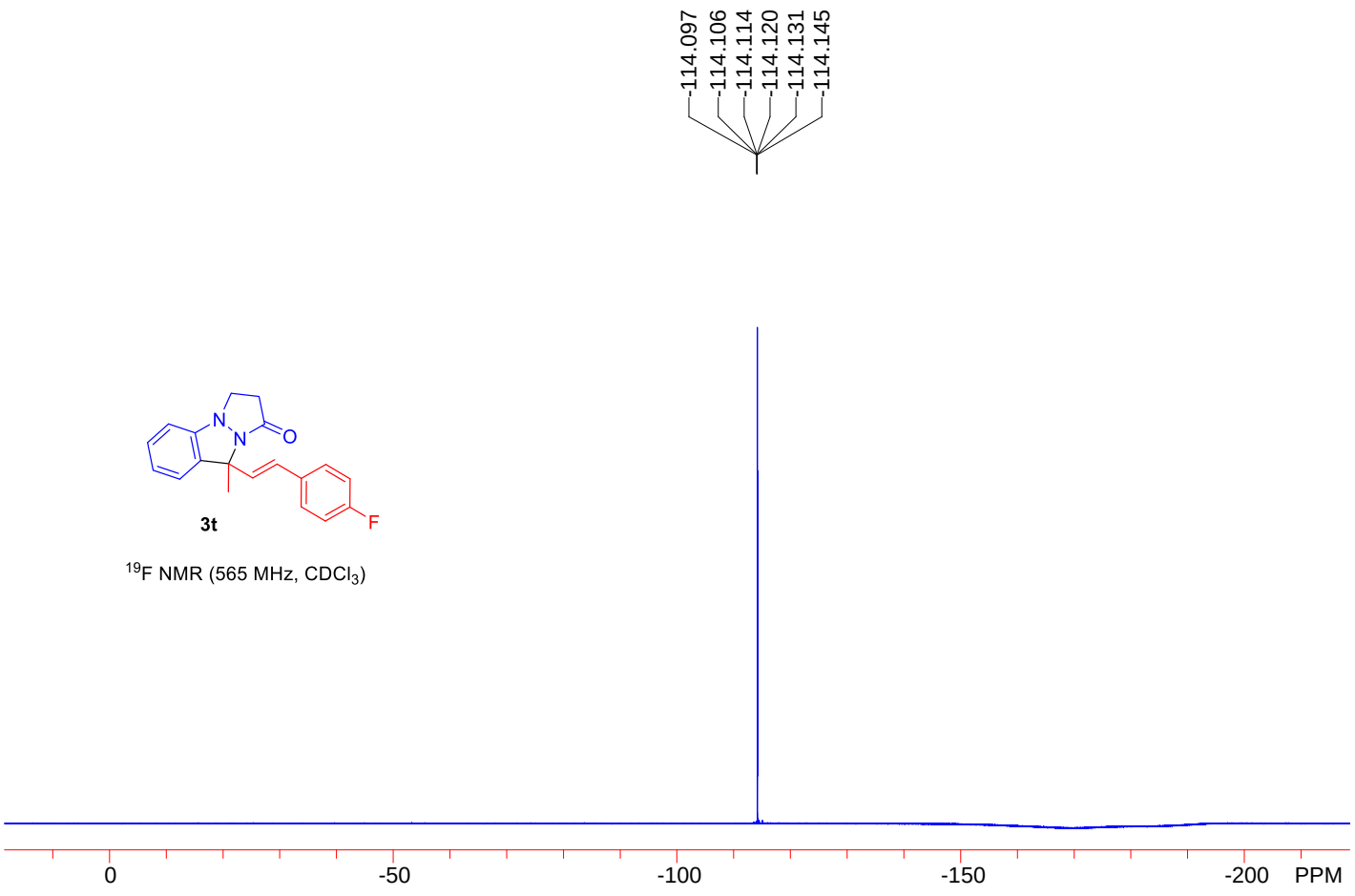




3t

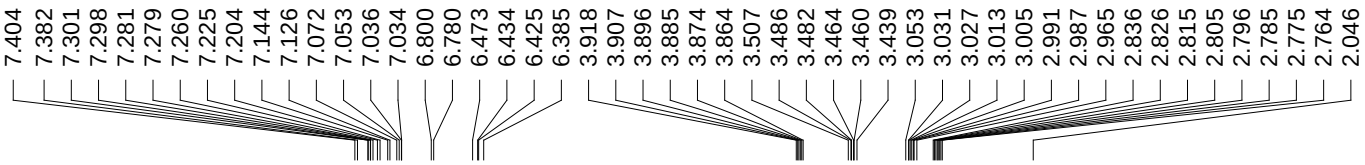
$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$)

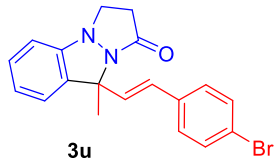




3t

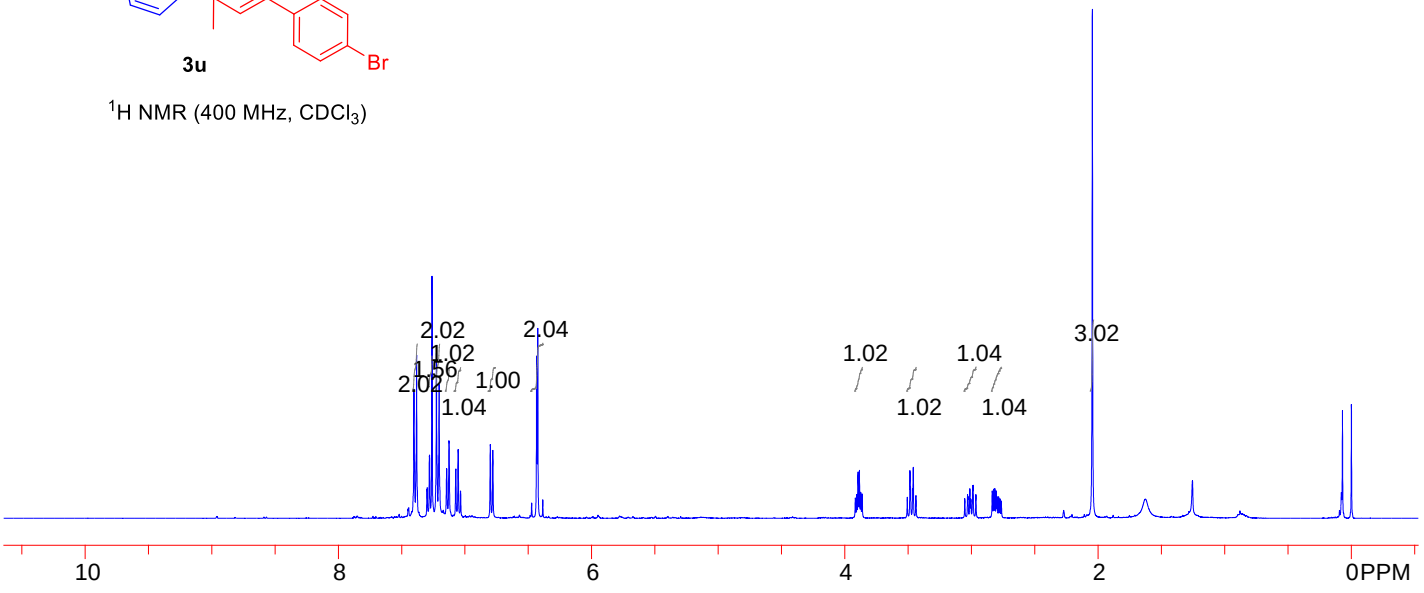
^{19}F NMR (565 MHz, $CDCl_3$)

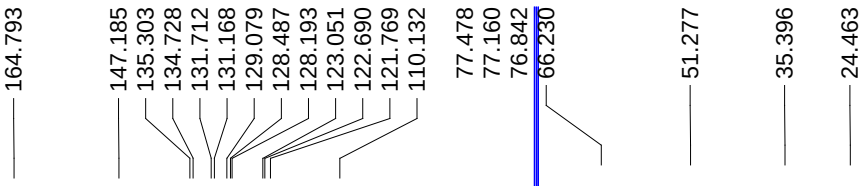


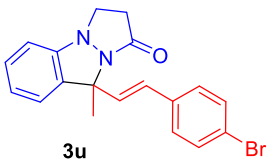


3u

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

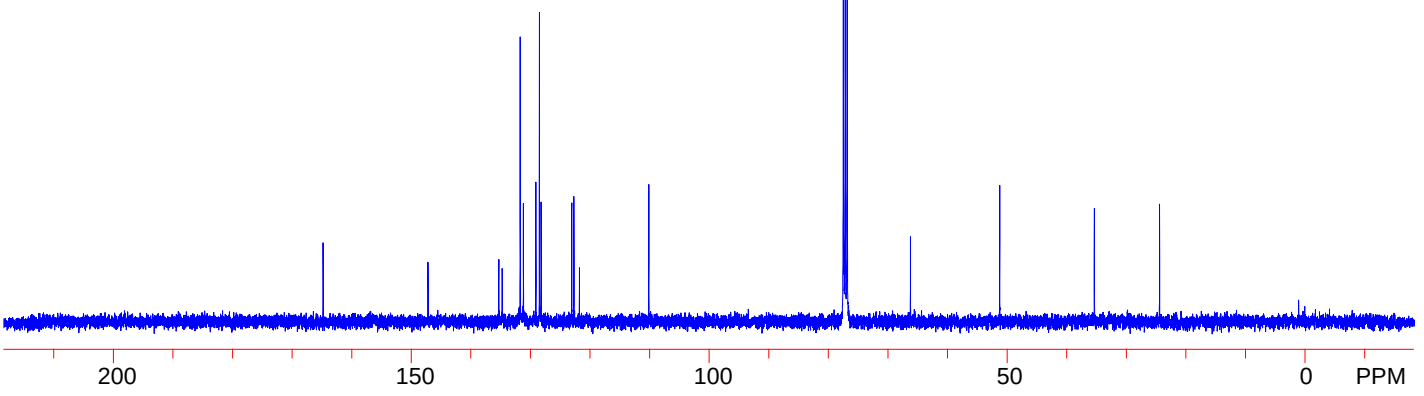


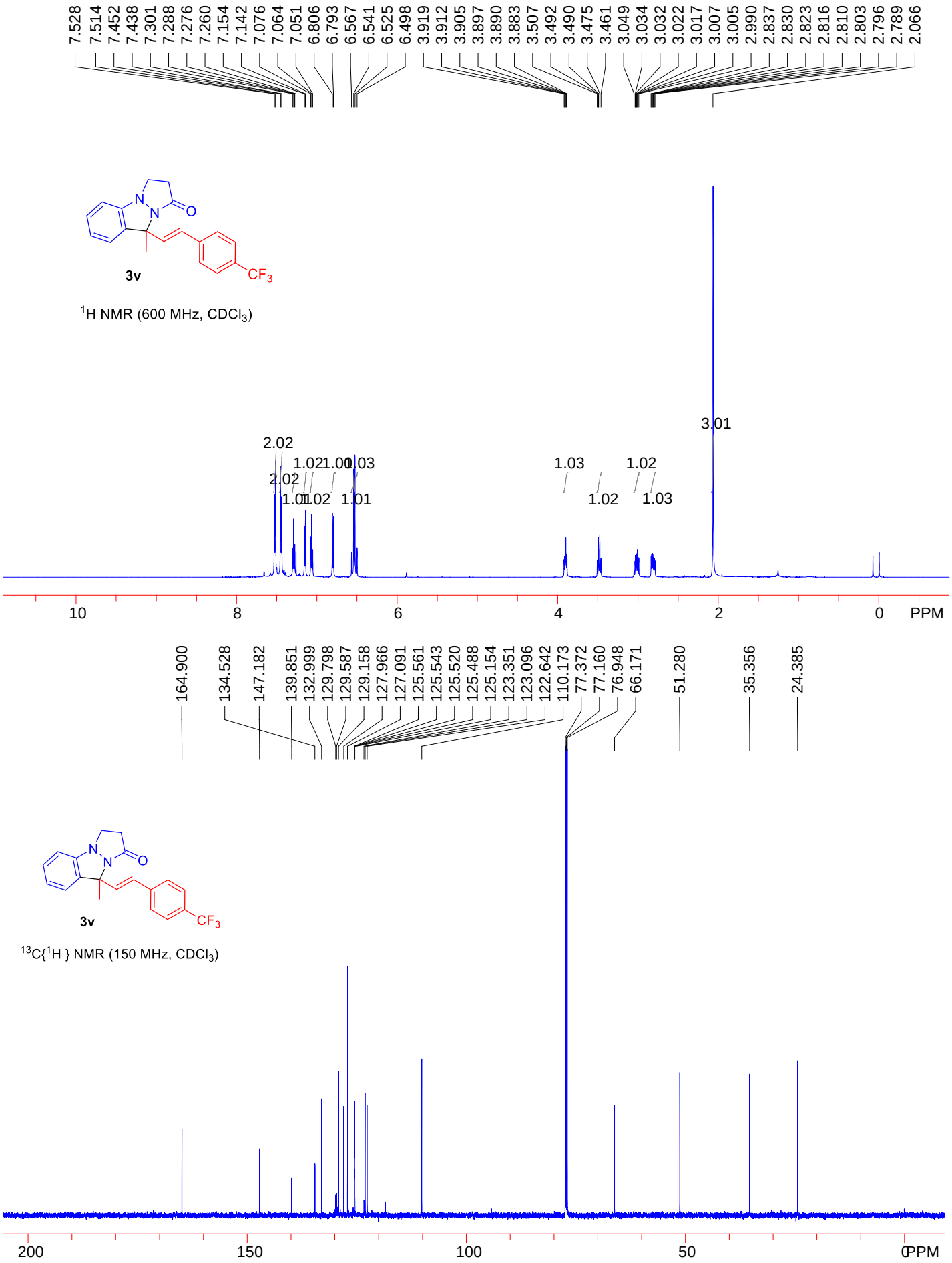


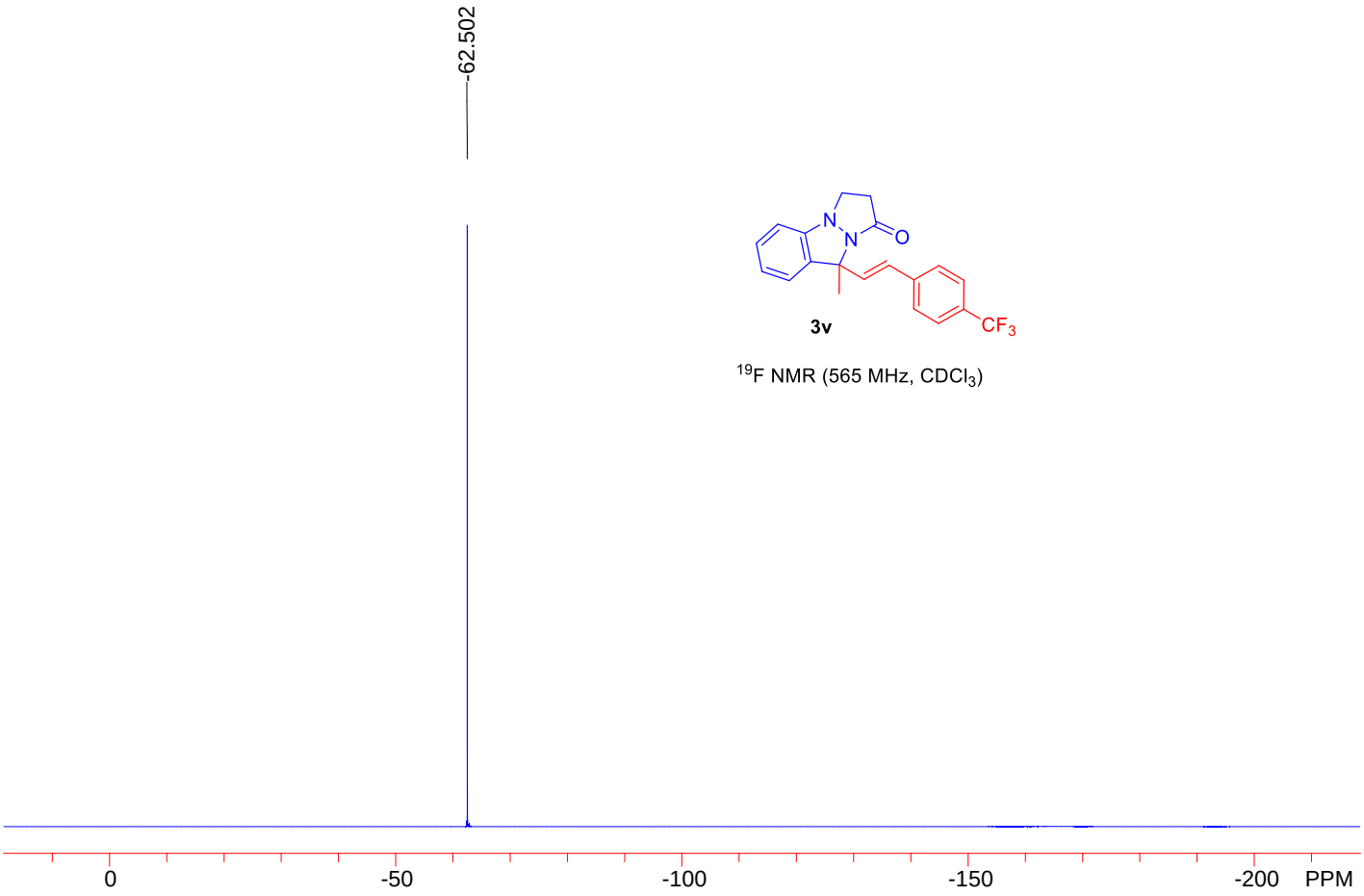


3u

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

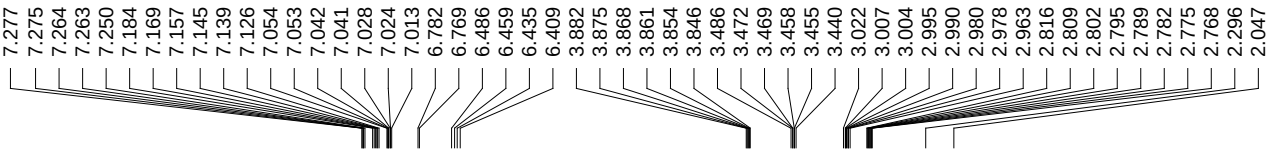


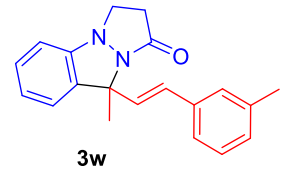

7.528
7.514
7.452
7.438
7.301
7.288
7.276
7.260
7.154
7.142
7.076
7.064
7.051
6.806
6.793
6.567
6.541
6.525
6.498
3.919
3.912
3.905
3.897
3.890
3.883
3.507
3.492
3.490
3.475
3.461
3.049
3.034
3.032
3.022
3.017
3.007
3.005
2.990
2.837
2.830
2.823
2.816
2.810
2.803
2.796
2.789
2.066
3v
1H NMR (600 MHz, CDCl3)
2.02
2.02
1.02
1.00
1.03
1.01
1.02
1.01
1.03
1.02
1.02
1.03
3.01
10
8
6
4
2
0
PPM
164.900
134.528
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
3v
13C{1H } NMR (150 MHz, CDCl3)
200
150
100
50
0
PPM



3v

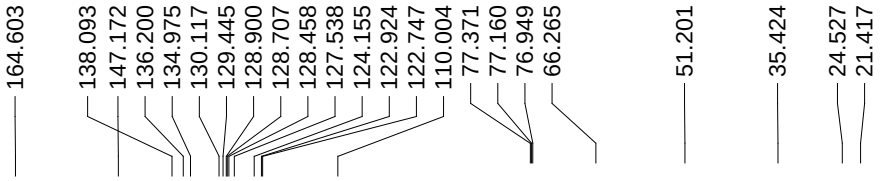
^{19}F NMR (565 MHz, $CDCl_3$)

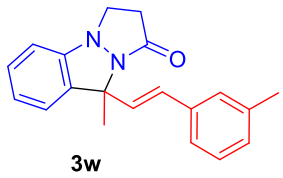




3w

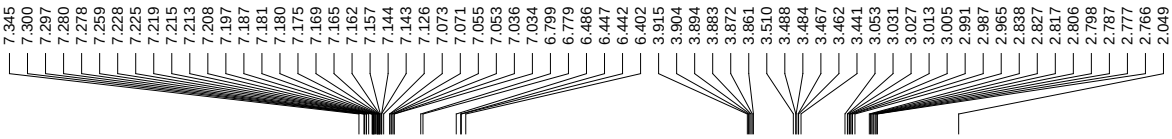
^{1}H NMR (600 MHz, $CDCl_3$)

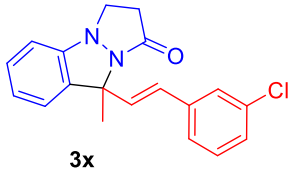




3w

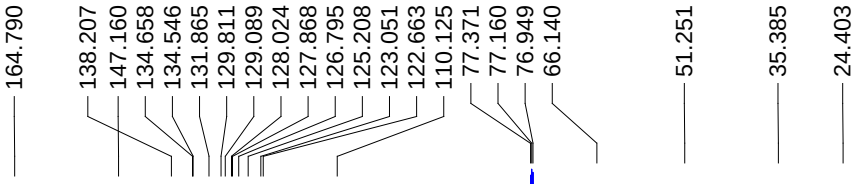
^{13}C{^{1}H } NMR (150 MHz, $CDCl_3$)

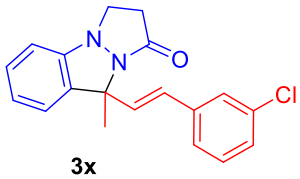




3x

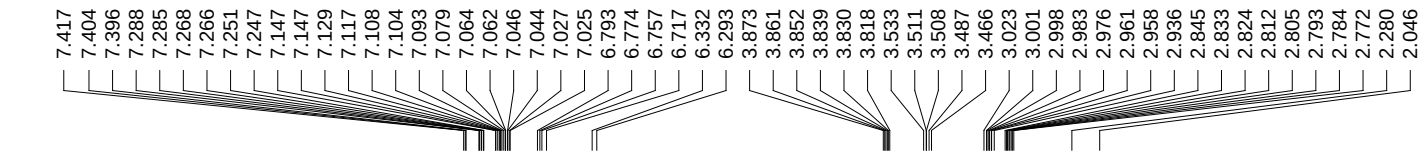
^{1}H NMR (400 MHz, $CDCl_3$)

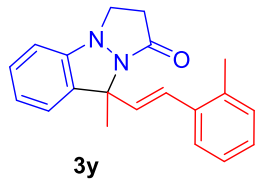




3x

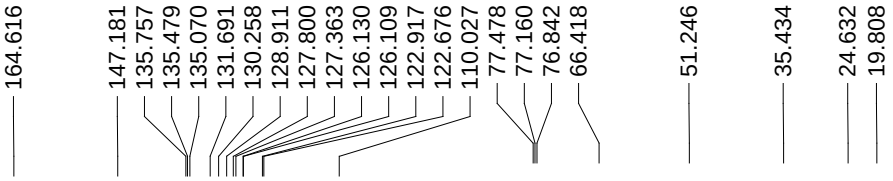
^{13}C{^{1}H } NMR (150 MHz, $CDCl_3$)

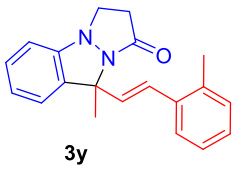




3y

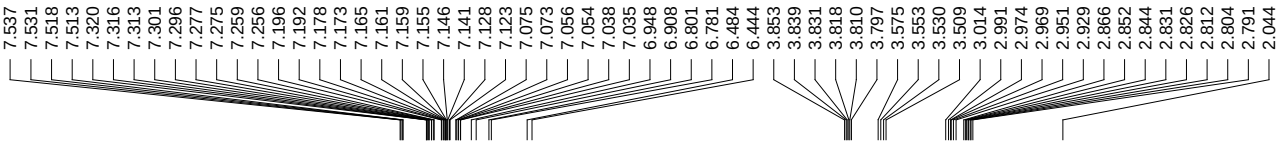
^{1}H NMR (400 MHz, $CDCl_3$)

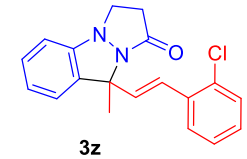




3y

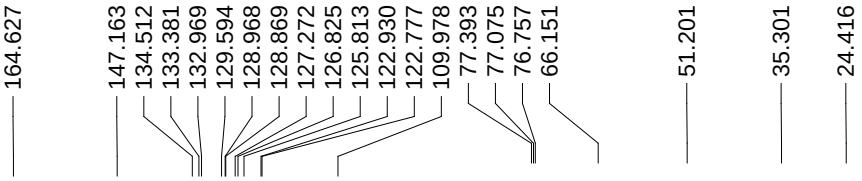
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

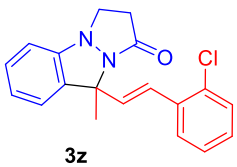




3z

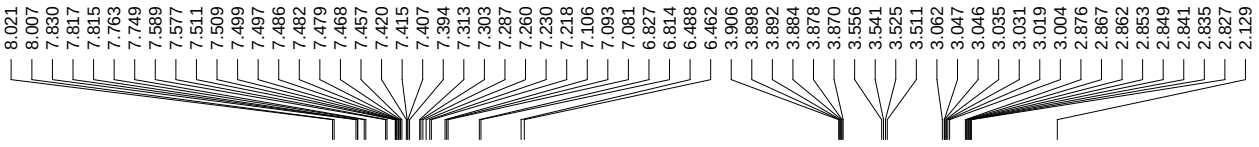
^{1}H NMR (400 MHz, $CDCl_3$)

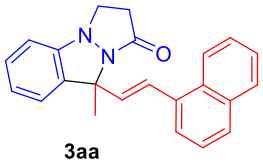




3z

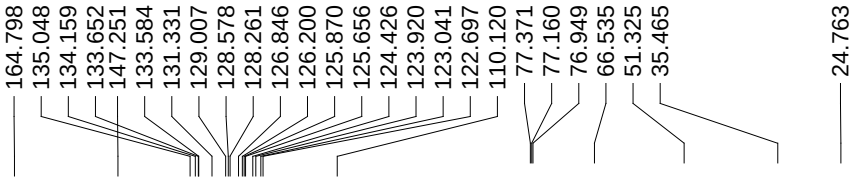
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

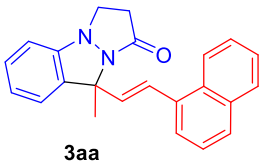




3aa

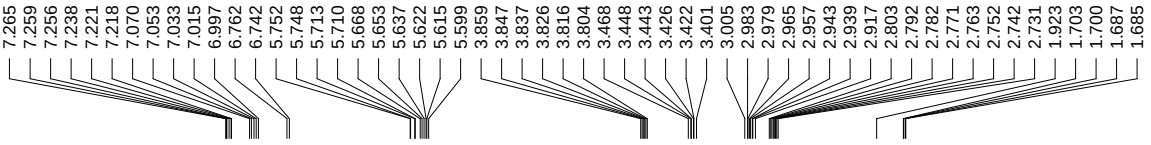
^{1}H NMR (600 MHz, $CDCl_3$)

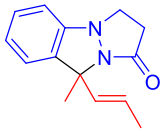




3aa

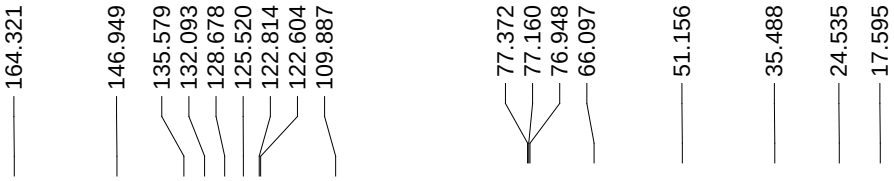
^{13}C{^{1}H } NMR (150 MHz, $CDCl_3$)

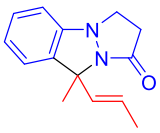




3bb

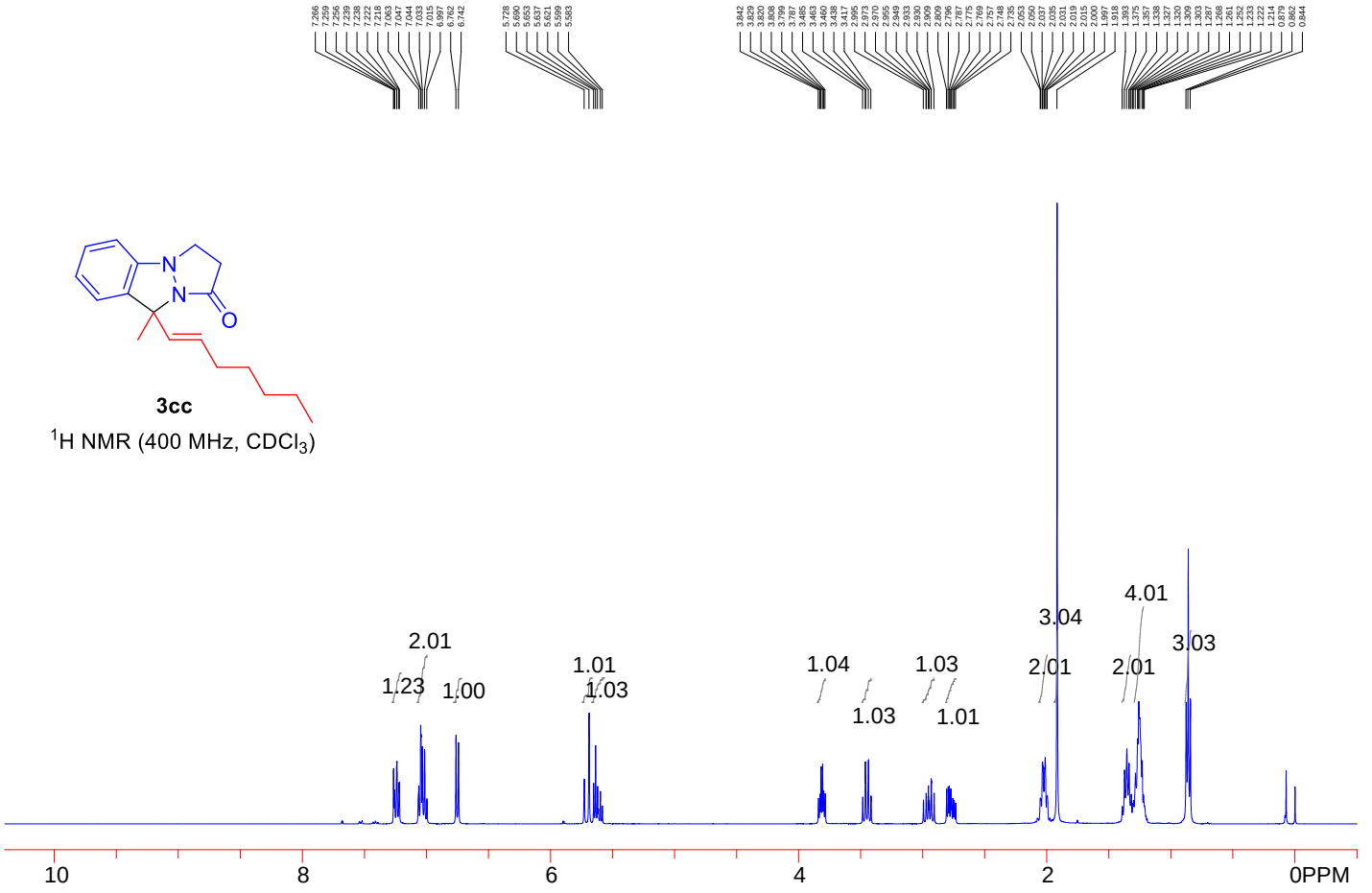
^{1}H NMR (400 MHz, $CDCl_3$)

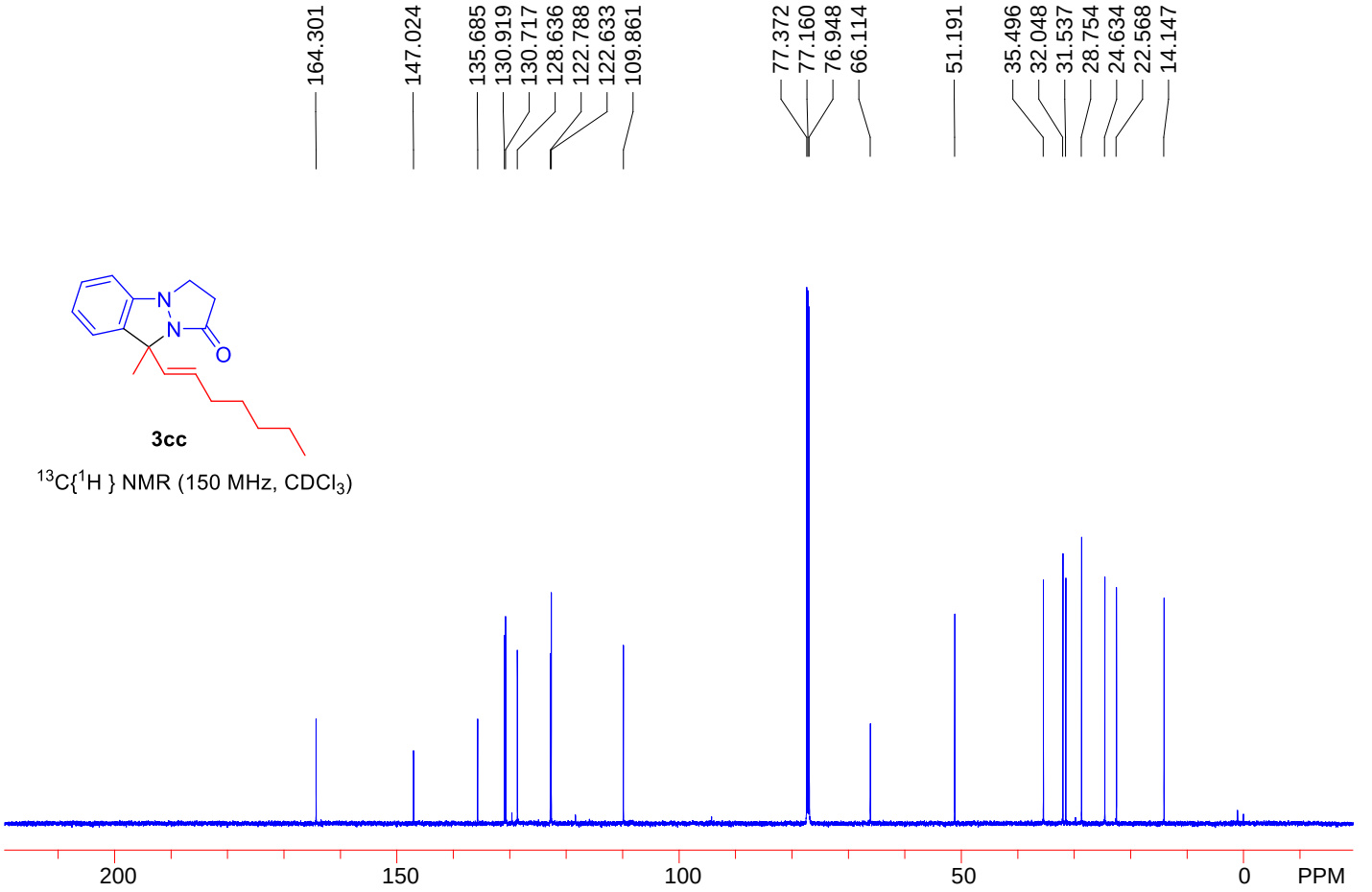


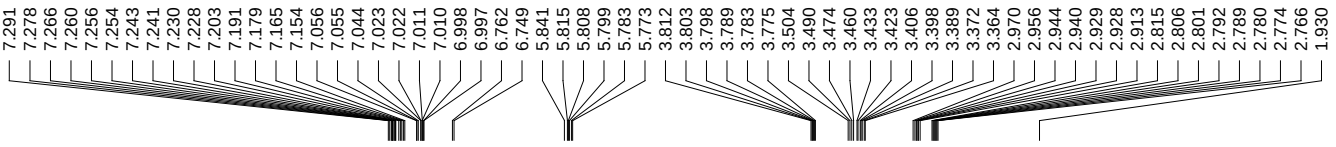


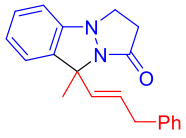
3bb

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


3cc
1H NMR (400 MHz, CDCl3)
2.01
1.23
1.00
1.01
1.03
1.04
1.03
1.03
1.01
3.04
2.01
4.01
2.01
3.03
10
8
6
4
2
0PPM

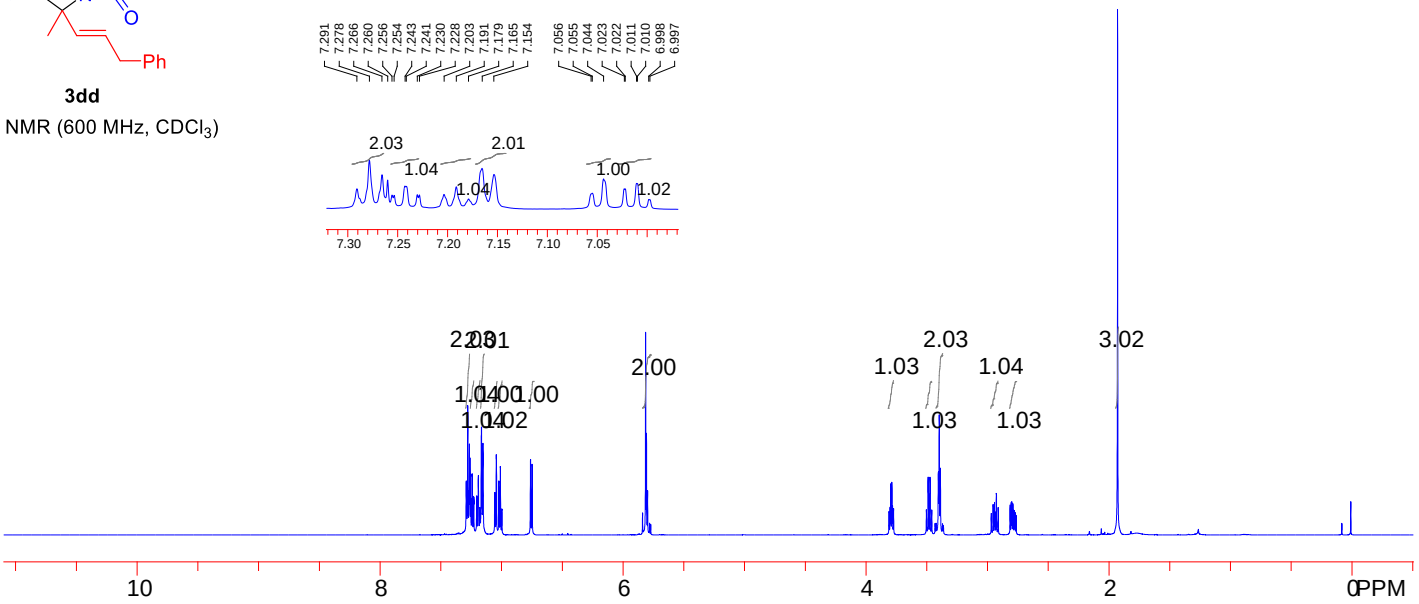

3cc
13C{1H } NMR (150 MHz, CDCl3)
200
150
100
50
0
PPM

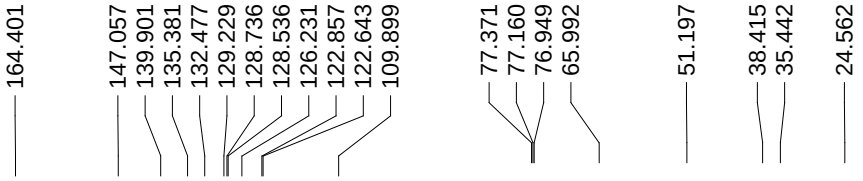


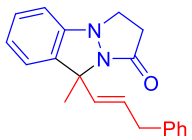


3dd

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

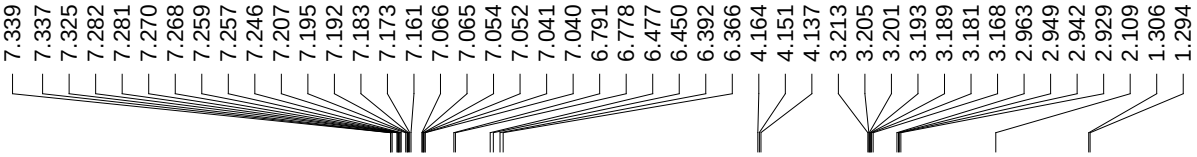


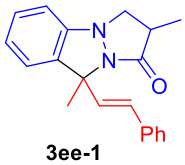




3dd

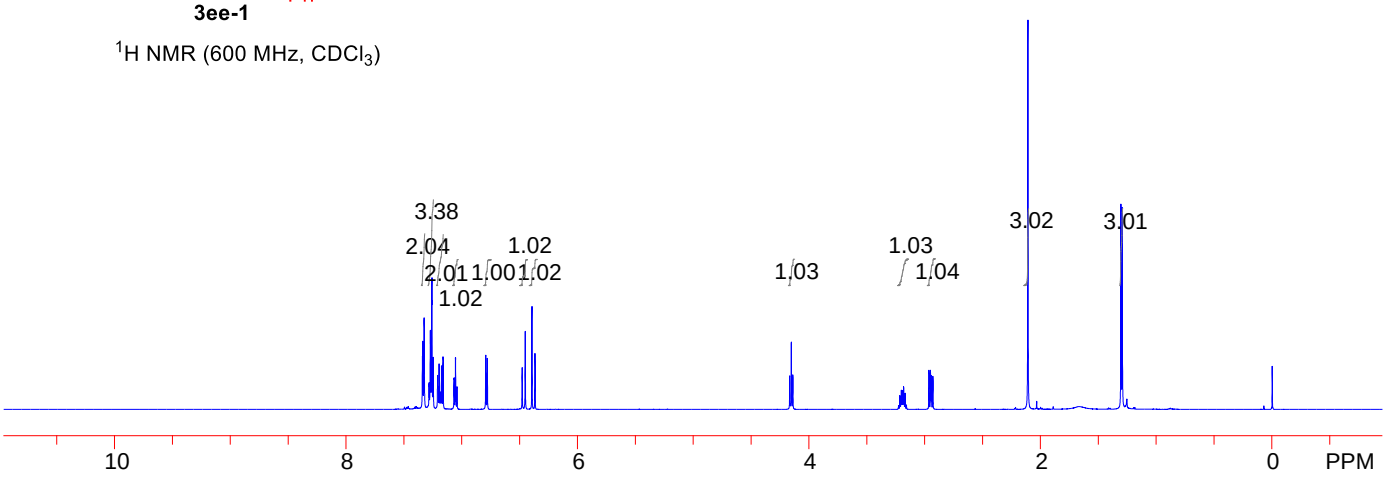
$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$)

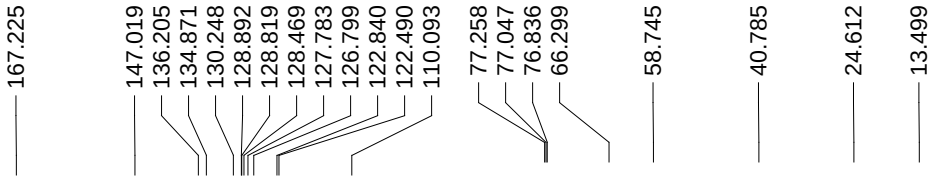


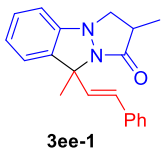


3ee-1

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

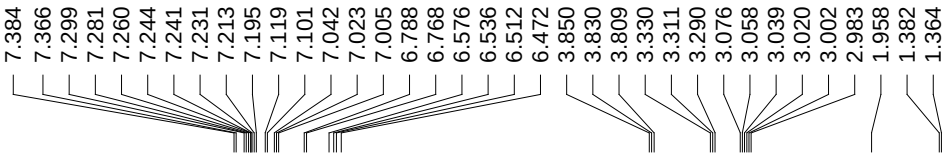


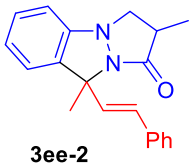




3ee-1

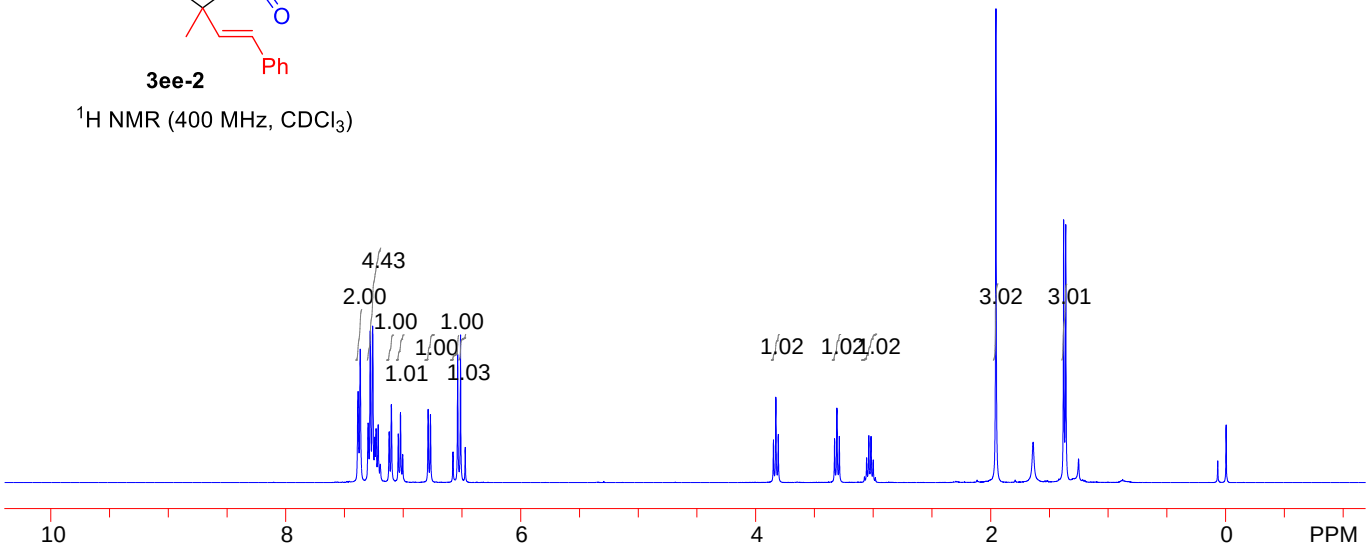
^{13}C{^{1}H } NMR (150 MHz, $CDCl_3$)

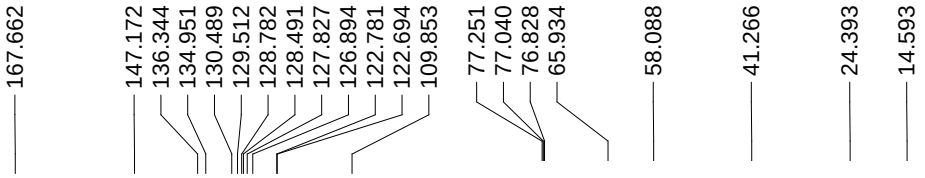


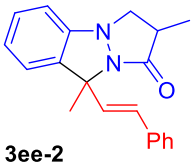


3ee-2

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



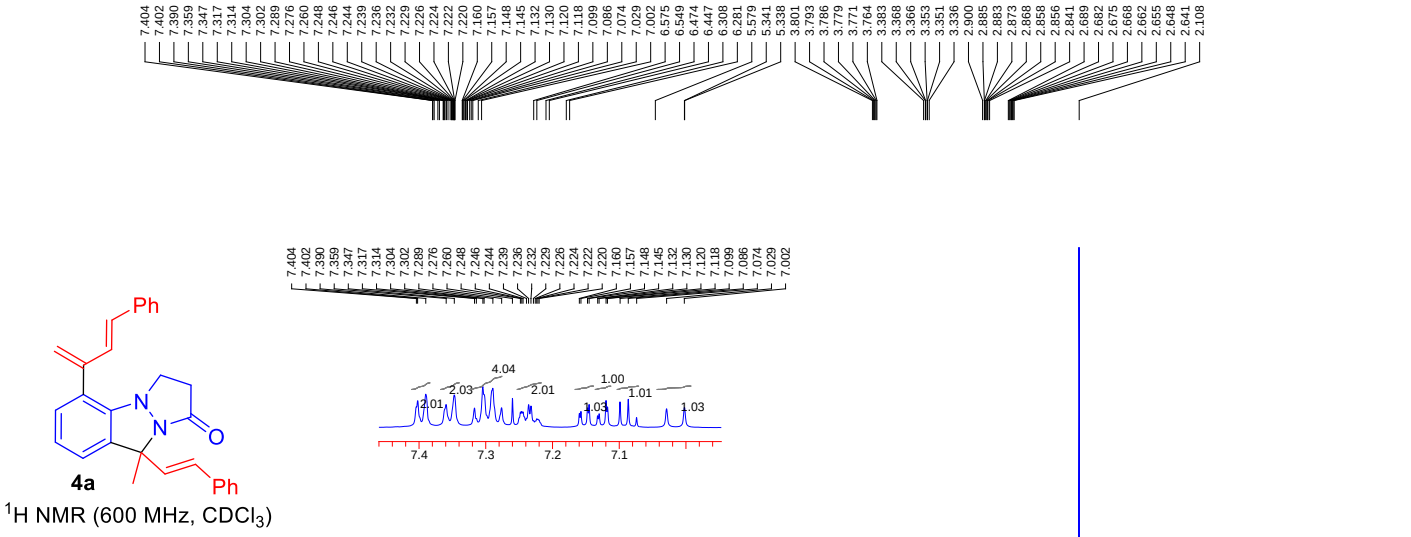




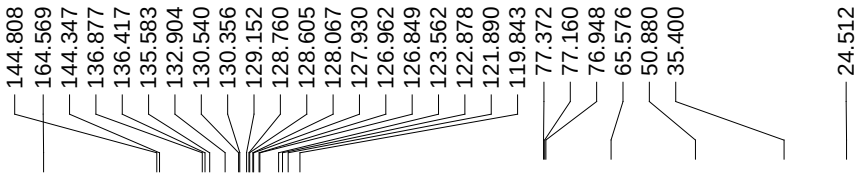
3ee-2

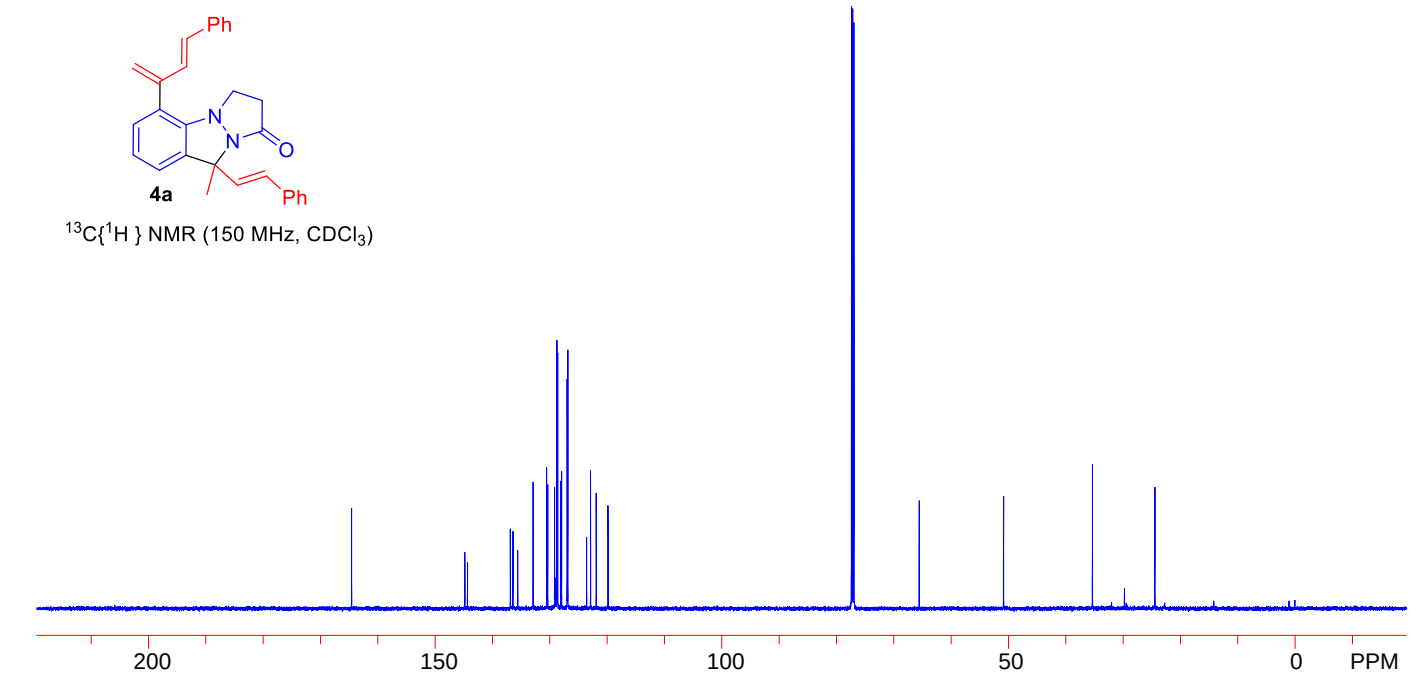
^{13}C{^{1}H } NMR (150 MHz, $CDCl_3$)

VI. NMR spectra of 4a-4t

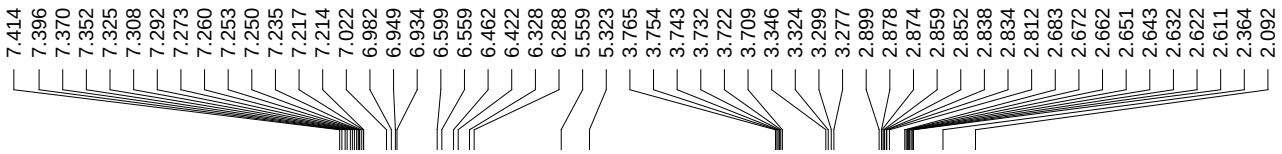


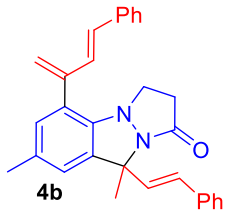
^{1}H NMR (600 MHz, $CDCl_3$)





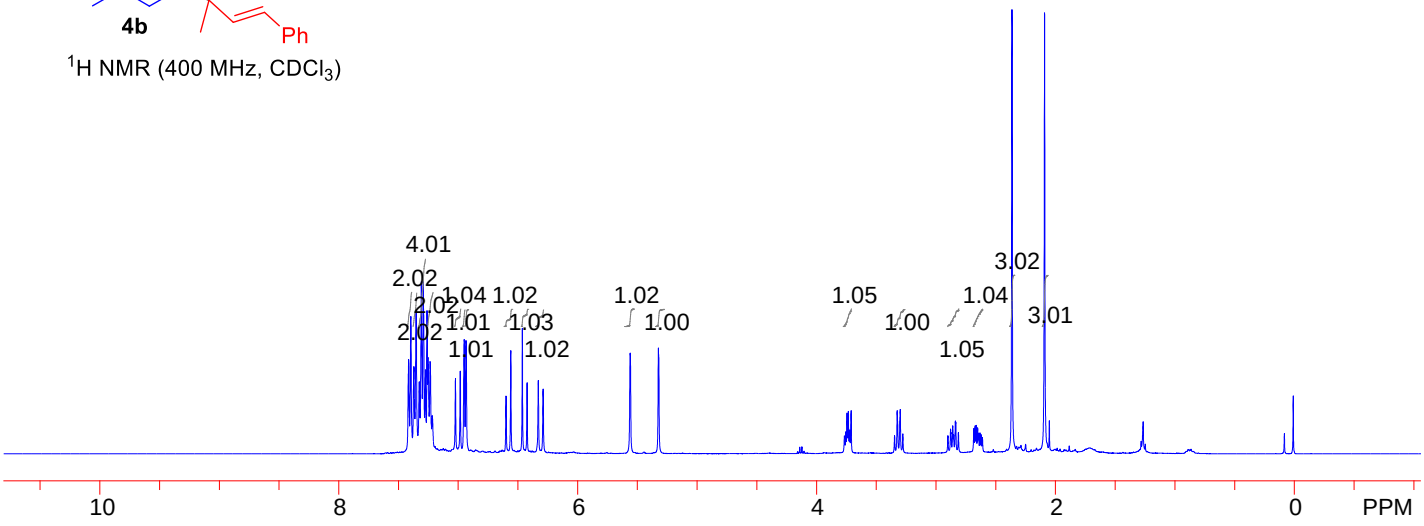
$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$)

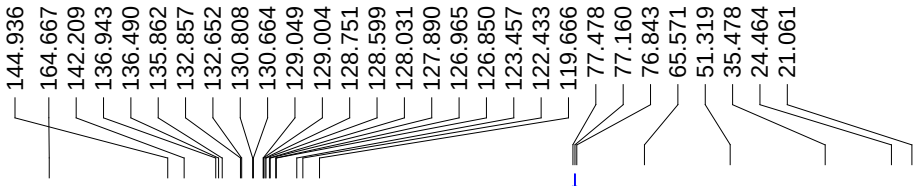


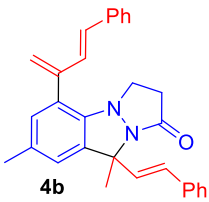


4b

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

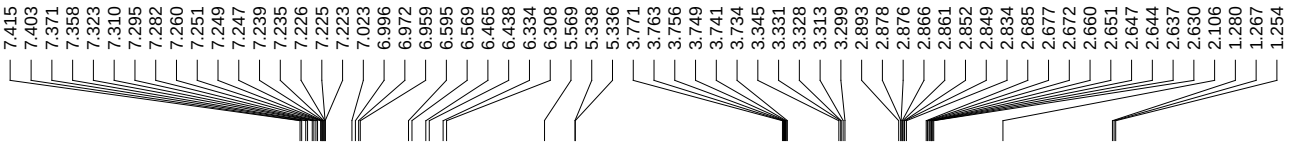


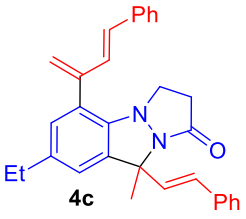




4b

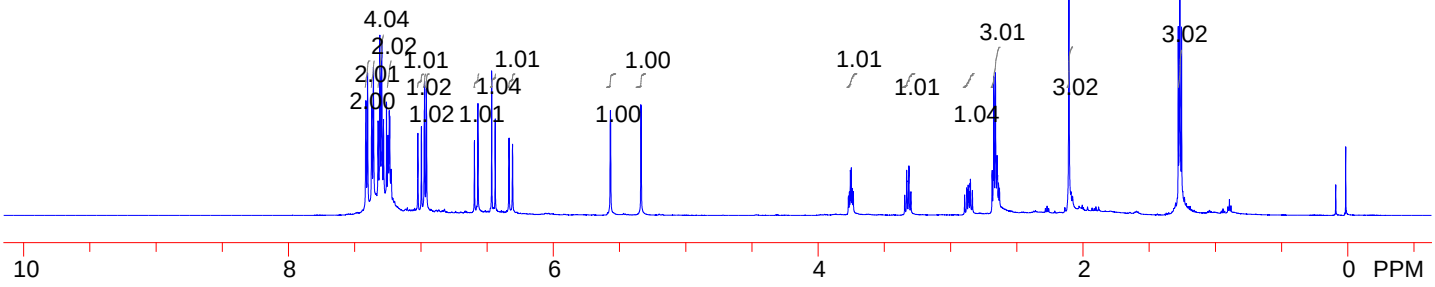
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

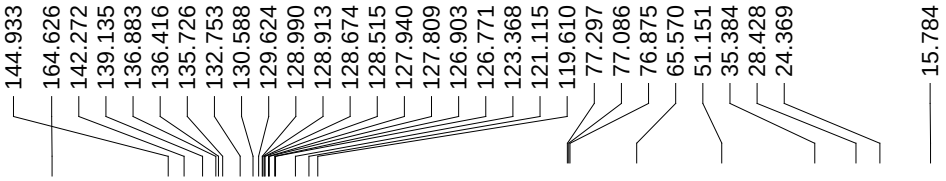


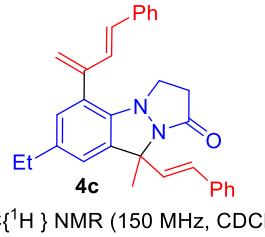


4c

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

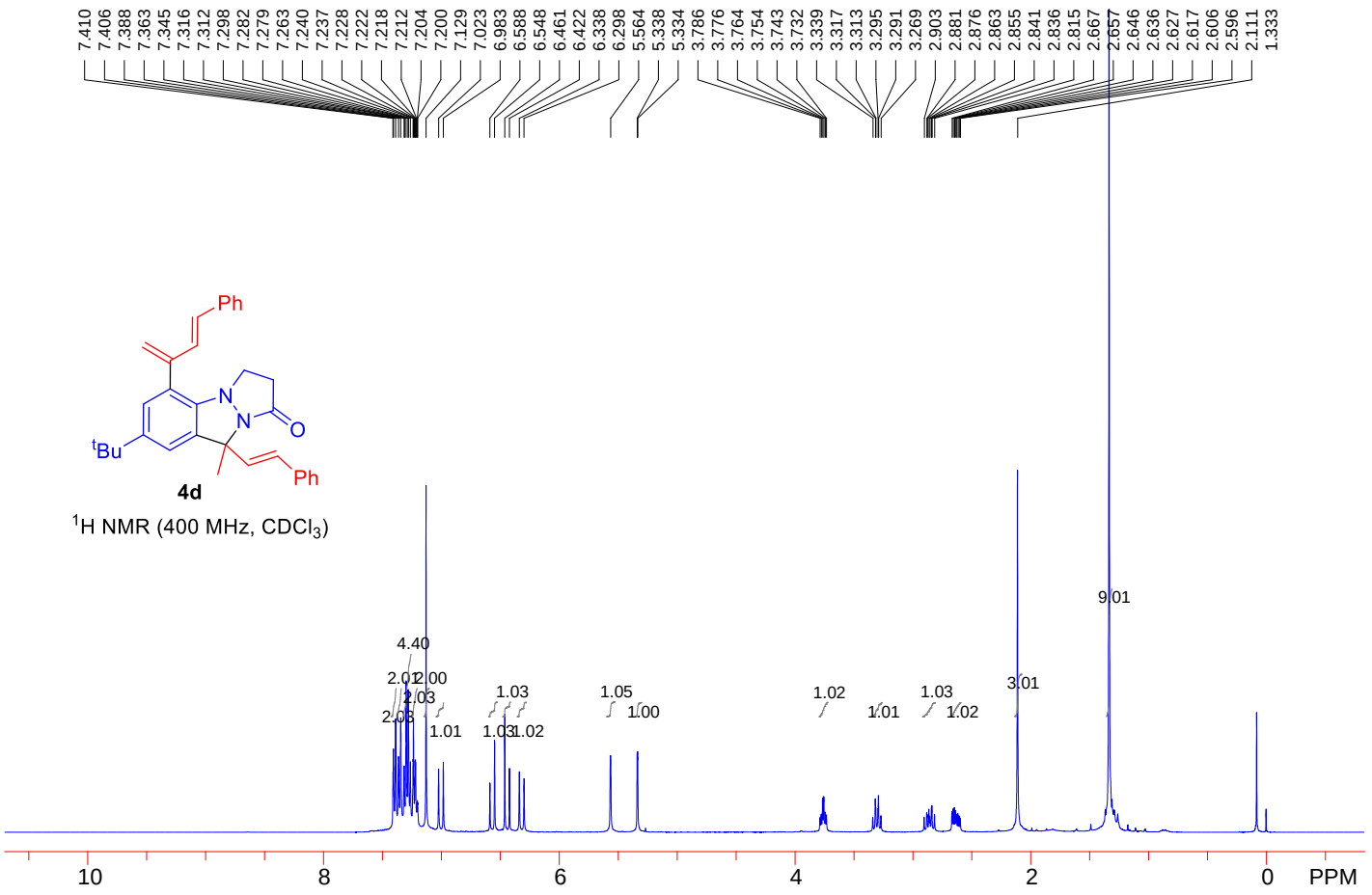






4c

^{13}C{^{1}H } NMR (150 MHz, $CDCl_3$)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7.388
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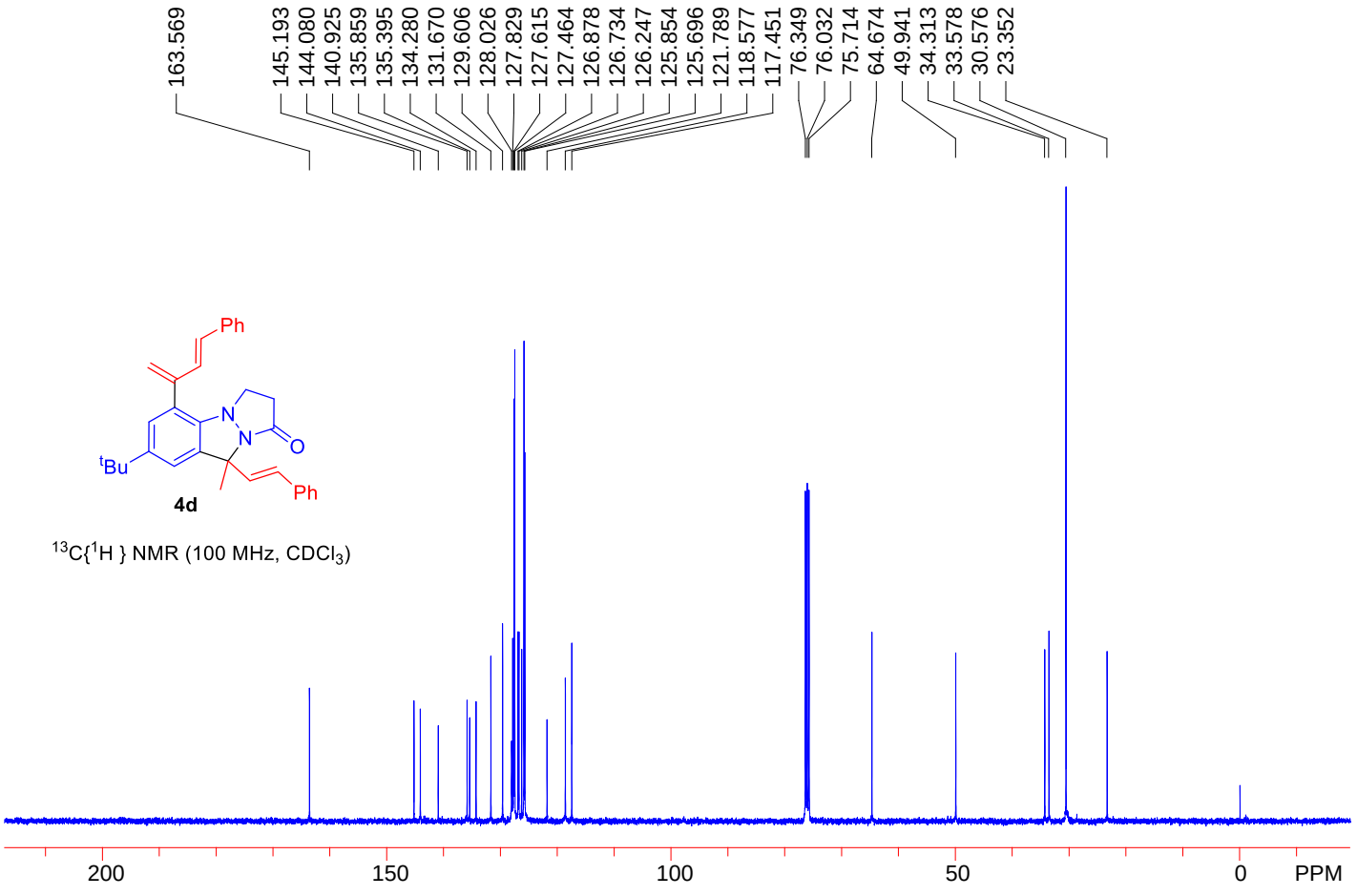
7.345
7.316
7.312
7.298
7.282
7.279
7.263
7.240
7.237
7.228
7.222
7.218
7.212
7.204
7.200
7.129
7.023
6.983
6.588
6.548
6.461
6.422
6.338
6.298
5.564
5.338
5.334
3.786
3.776
3.764
3.754
3.743
3.732
3.339
3.317
3.313
3.295
3.291
3.269
2.903
2.881
2.876
2.863
2.855
2.841
2.836
2.815
2.667
2.657
2.646
2.636
2.627
2.617
2.606
2.596
2.111
1.333
Ph
N
N
O
tBu
Ph
4d
1H NMR (400 MHz, CDCl3)
4.40
2.01
2.00
2.03
2.03
1.01
1.03
1.03
1.02
1.05
1.00
1.02
1.01
1.03
1.02
3.01
9.01
10
8
6
4
2
0
PPM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144.080
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135.859
135.395
134.280
131.670
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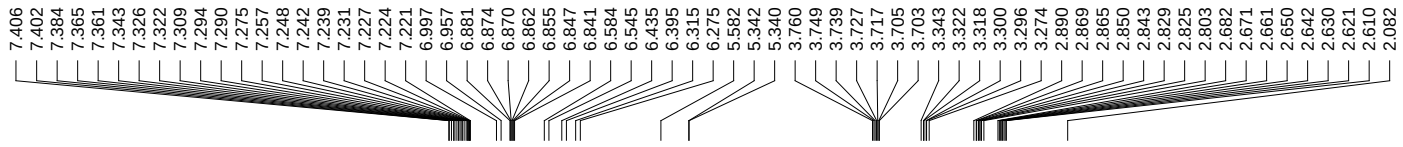
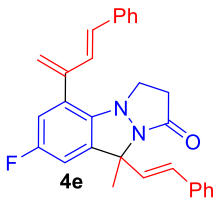
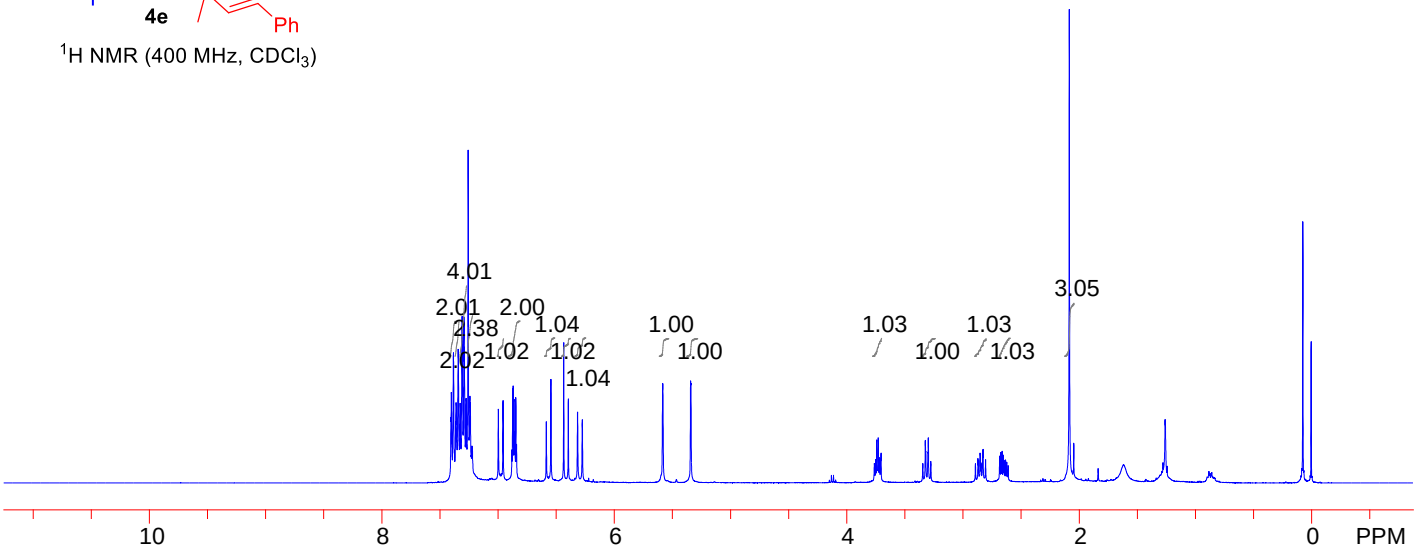
127.464
126.878
126.734
126.247
125.854
125.696
121.789
118.577
117.451
76.349
76.032
75.714
64.674
49.941
34.313
33.578
30.576
23.352
Ph
N
N
O
tBu
Ph
4d
13C{1H } NMR (100 MHz, CDCl3)
200
150
100
50
0
PPM

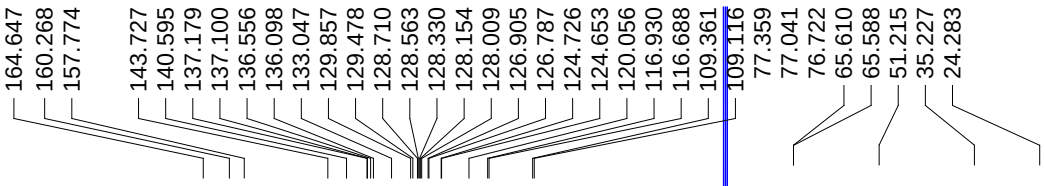


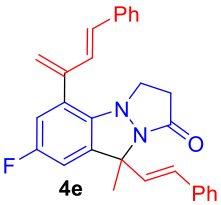


4e

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

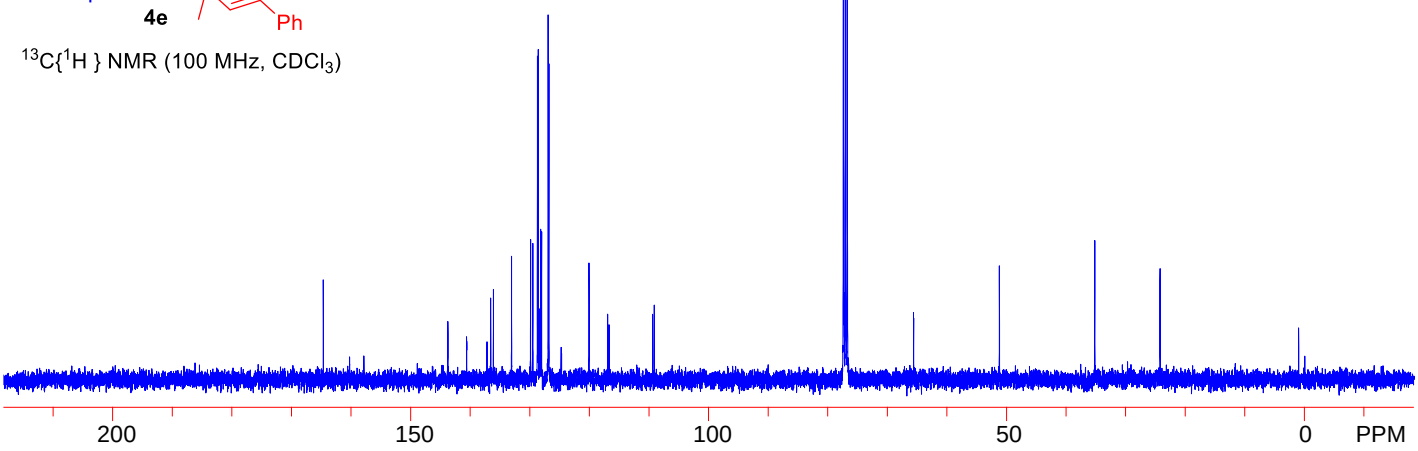


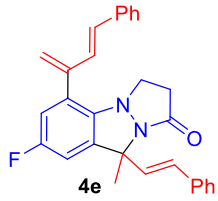




4e

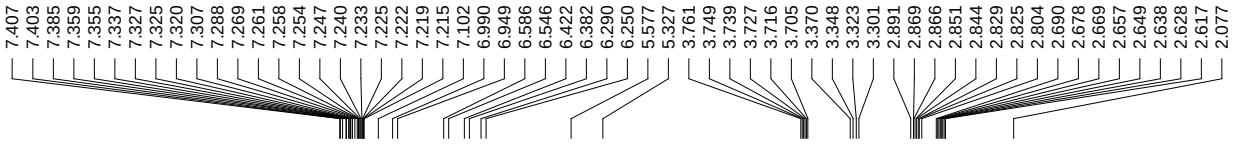
^{13}C{^{1}H } NMR (100 MHz, $CDCl_3$)

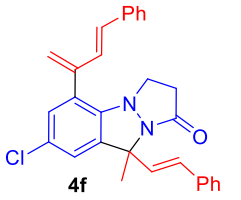




4e

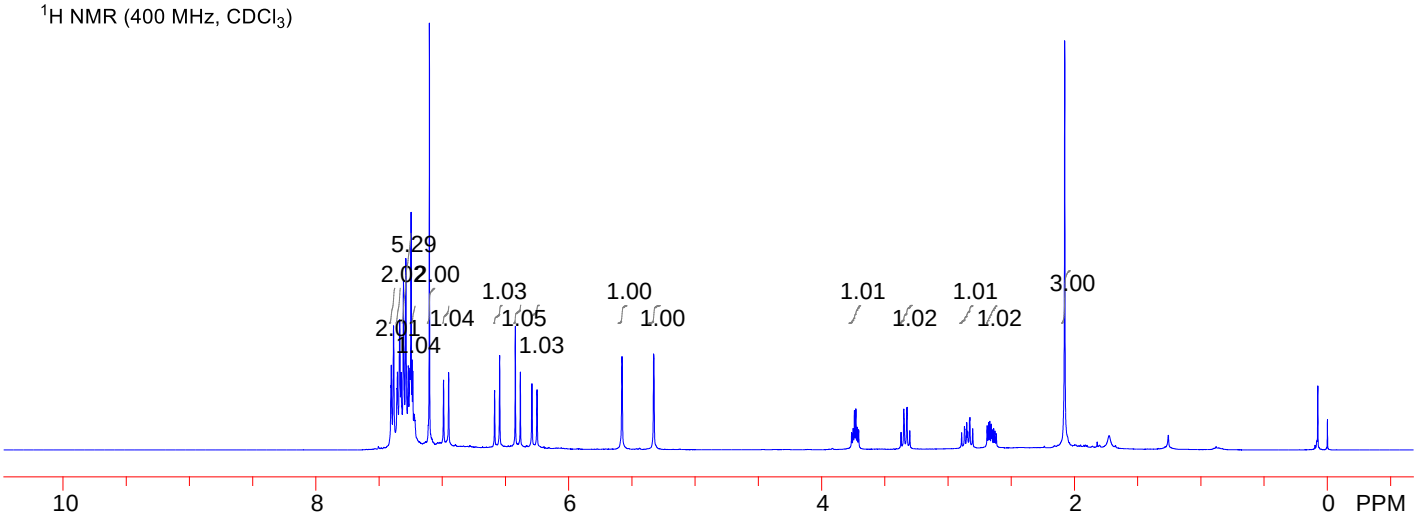
^{19}F NMR (376 MHz, $CDCl_3$)

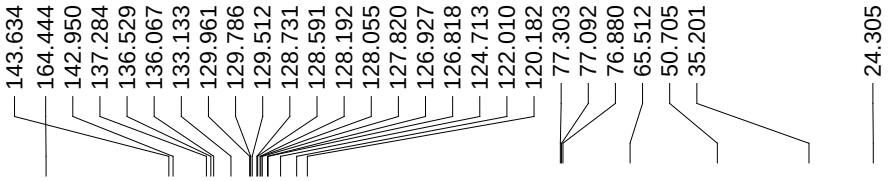


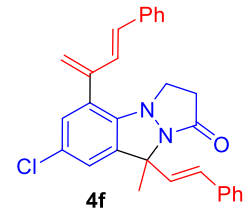


4f

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

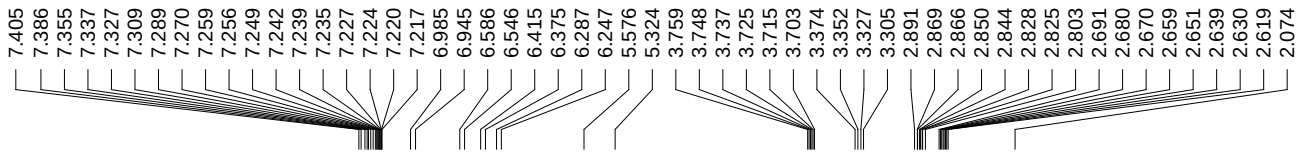


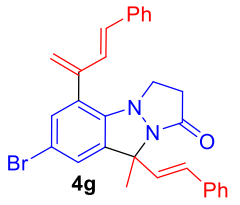




4f

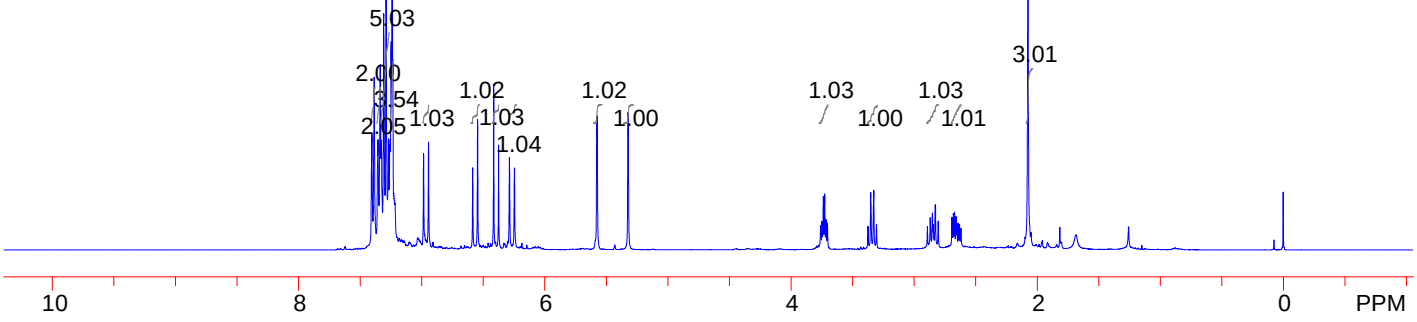
^{13}C{^{1}H } NMR (150 MHz, $CDCl_3$)

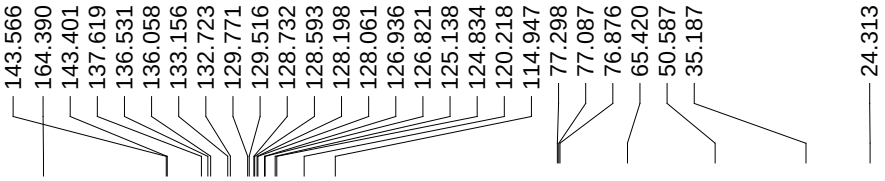


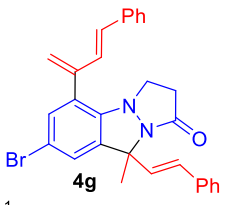


4g

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

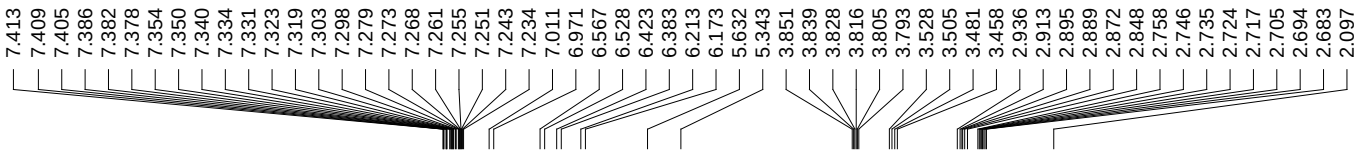


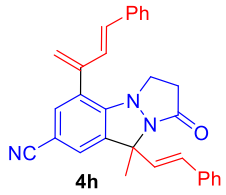




4g

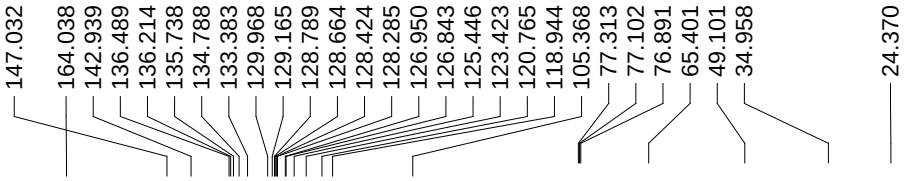
$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$)

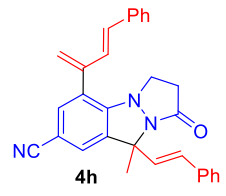




4h

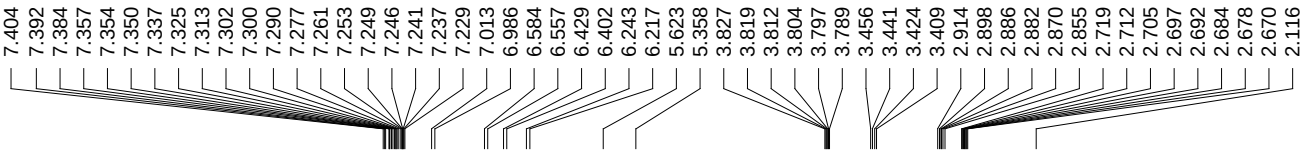
^{1}H NMR (400 MHz, $CDCl_3$)

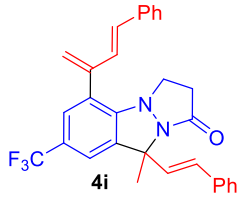




4h

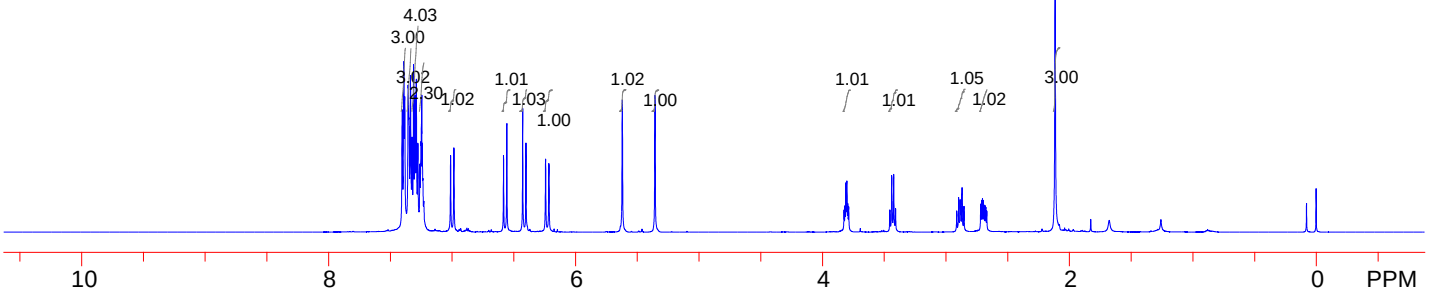
$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$)

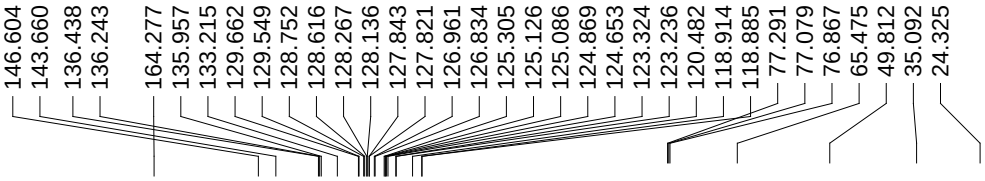


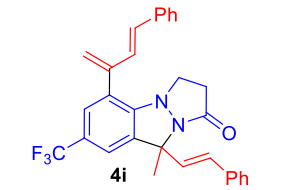


4i

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

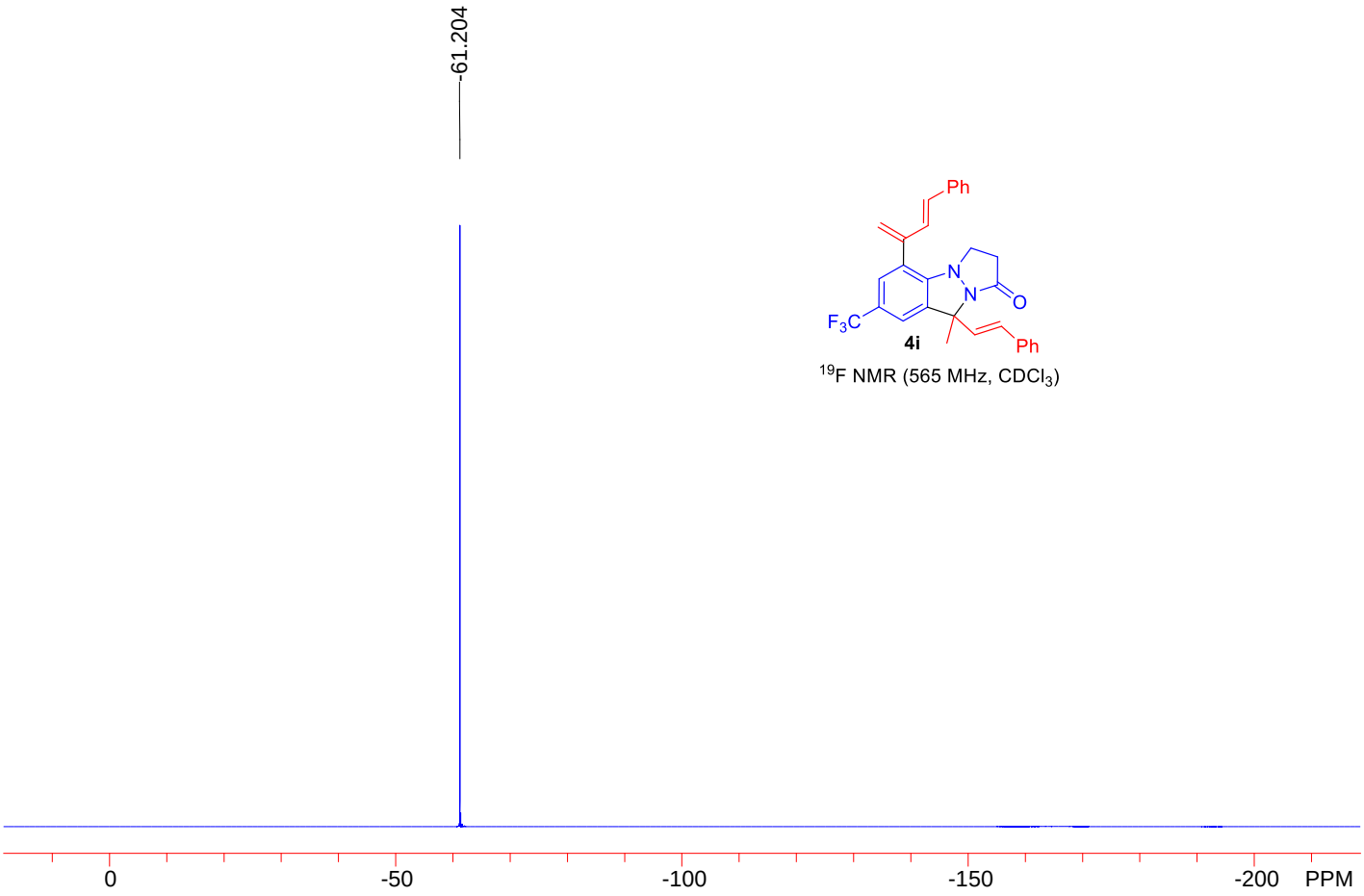






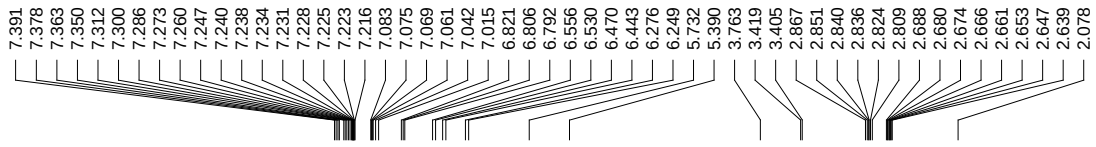
4i

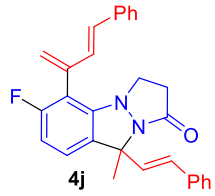
^{13}C{^{1}H } NMR (150 MHz, $CDCl_3$)



4i

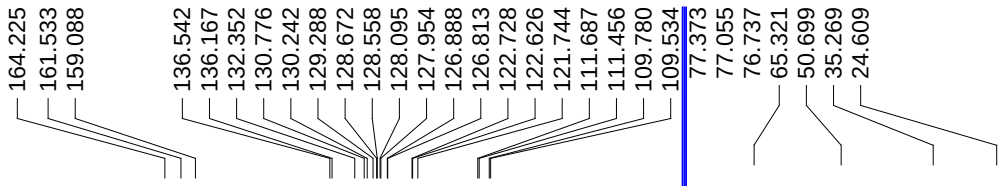
^{19}F NMR (565 MHz, $CDCl_3$)

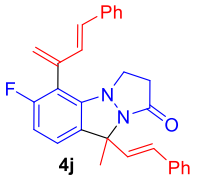




4j

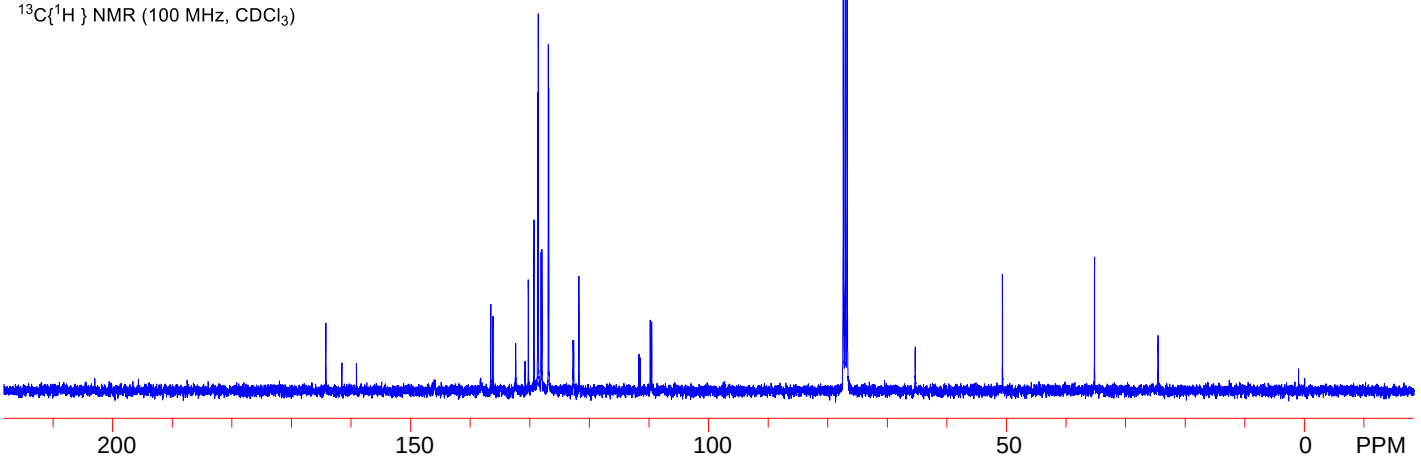
^{1}H NMR (600 MHz, $CDCl_3$, 55 ^{o}C)

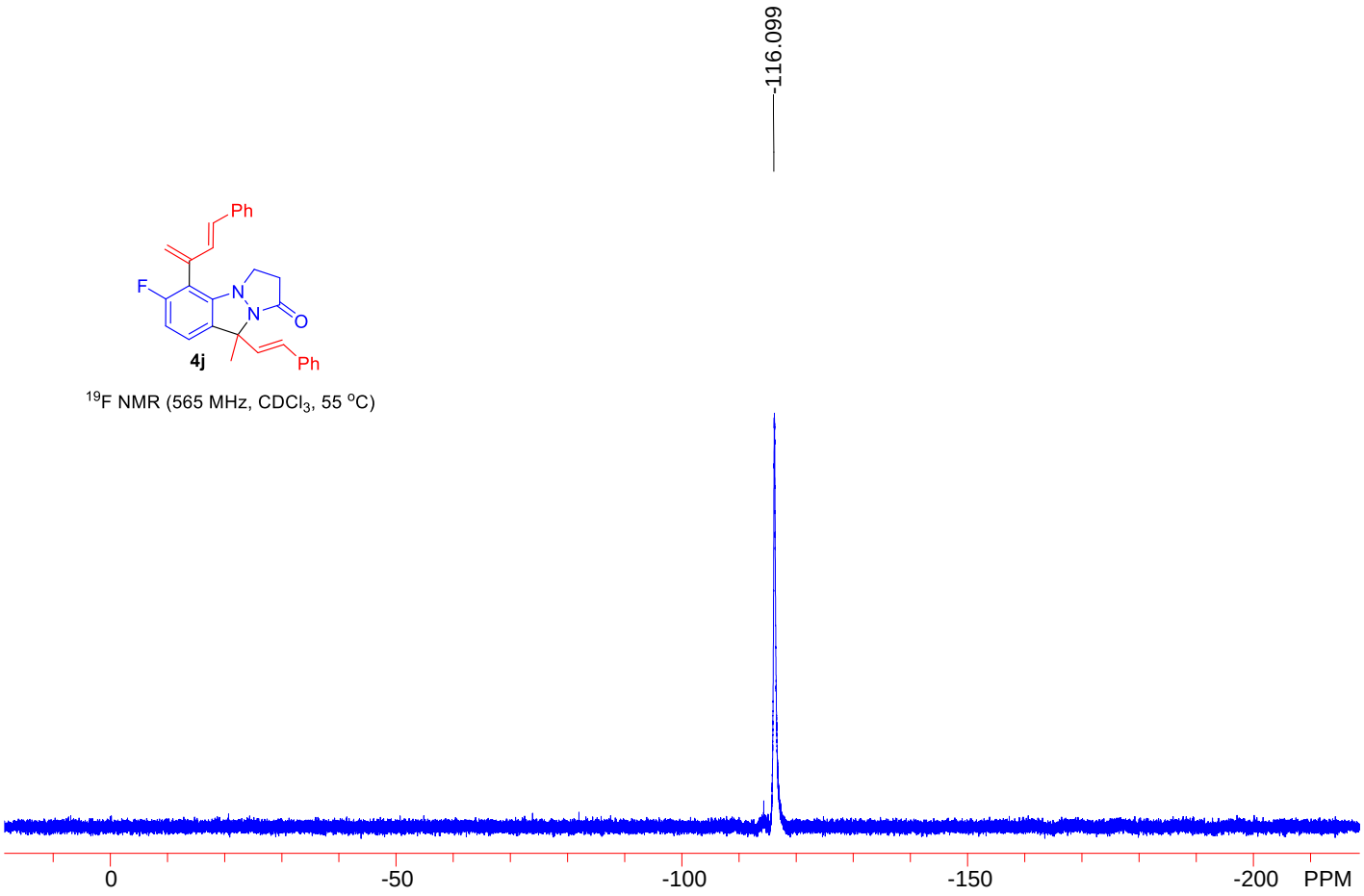




4j

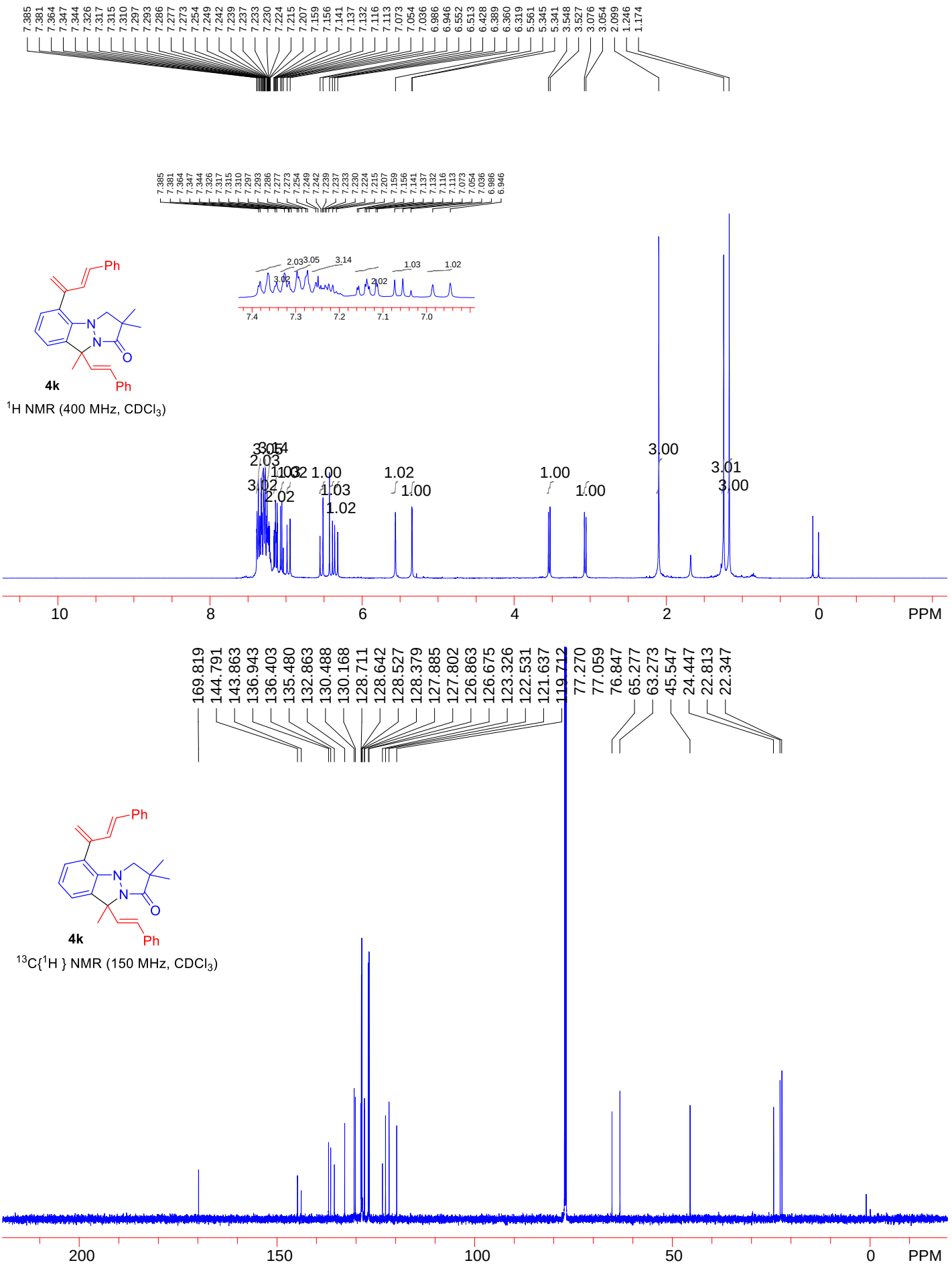
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

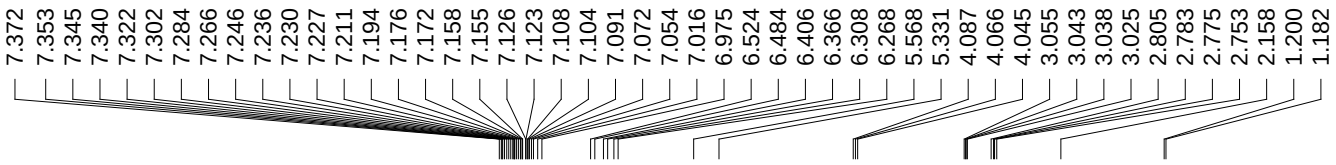


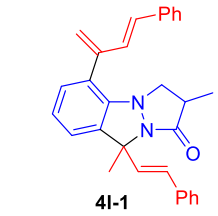


4j

^{19}F NMR (565 MHz, $CDCl_3$, 55 °C)

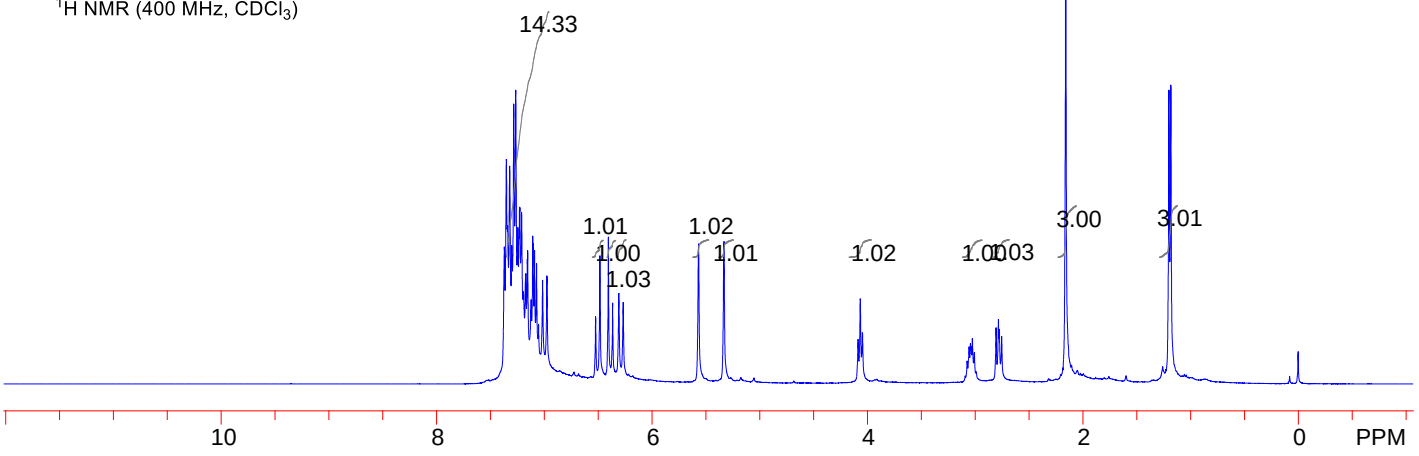

7.385 7.381 7.364 7.347 7.344 7.326 7.317 7.315 7.310 7.297 7.293 7.286 7.277 7.273 7.254 7.249 7.242 7.239 7.237 7.233 7.230 7.224 7.215 7.207 7.159 7.156 7.141 7.137 7.132 7.116 7.113 7.073 7.054 7.036 6.986 6.946 6.552 6.513 6.428 6.389 6.360 6.319 5.561 5.345 5.341 3.548 3.527 3.076 3.054 2.099 1.246 1.174
Ph
N
N
O
Ph
4k
1H NMR (400 MHz, CDCl3)
2.03 3.05 3.14 3.02 2.02 1.03 1.02
7.4 7.3 7.2 7.1 7.0
3.00 1.00 1.02 1.00 1.00 3.01 3.00
10 8 6 4 2 0 PPM
169.819 144.791 143.863 136.943 136.403 135.480 132.863 130.488 130.168 128.711 128.642 128.527 128.379 127.885 127.802 126.863 126.675 123.326 122.531 121.637 119.712 77.270 77.059 76.847 65.277 63.273 45.547 24.447 22.813 22.347
Ph
N
N
O
Ph
4k
13C{1H } NMR (150 MHz, CDCl3)
200 150 100 50 0 PPM

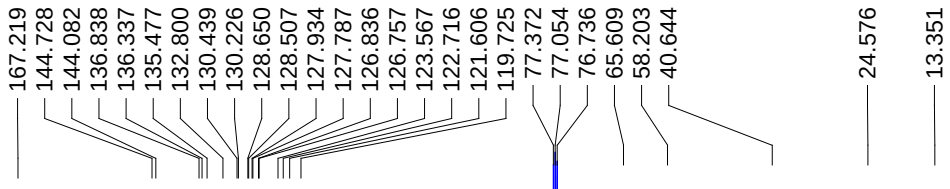


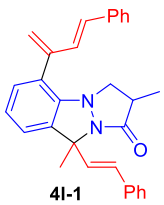


4l-1

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

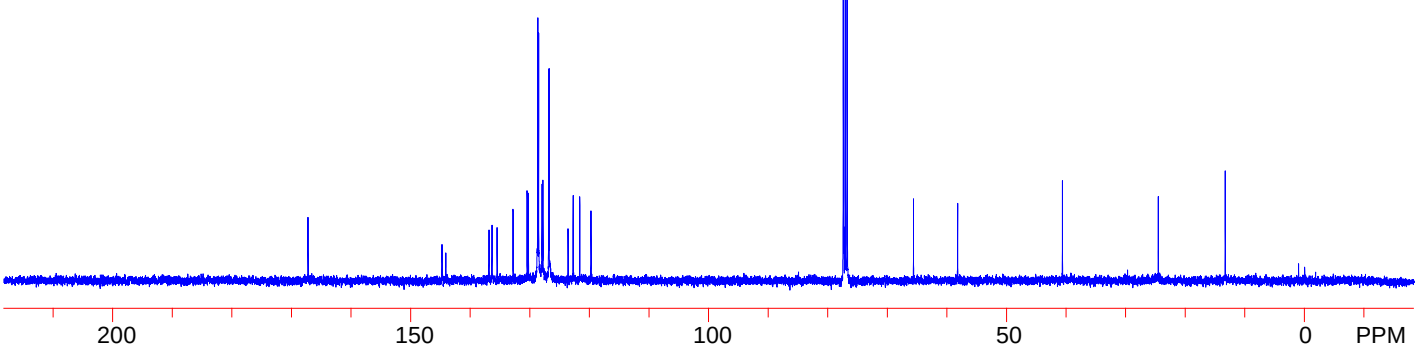


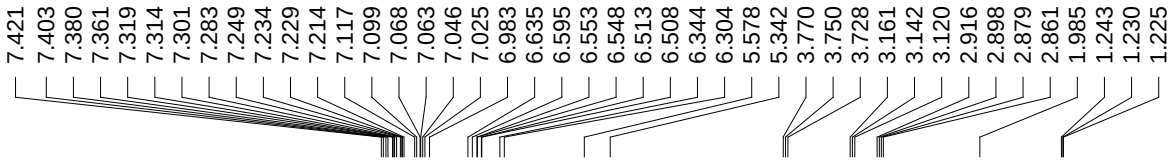


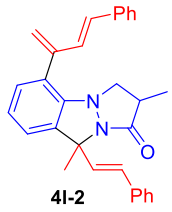


4l-1

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

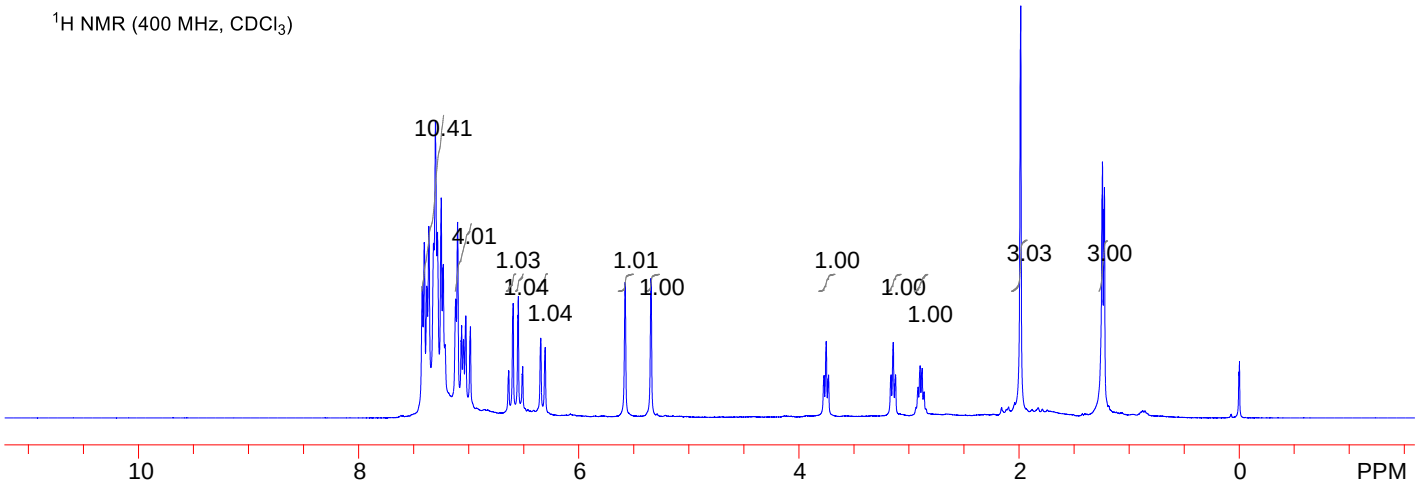


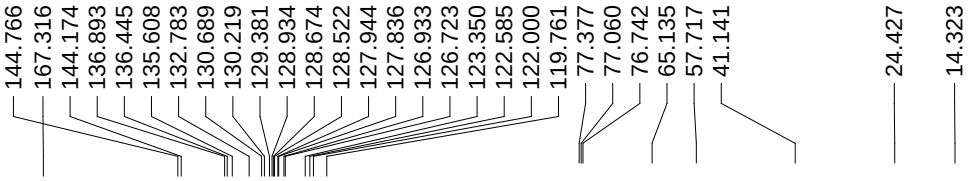


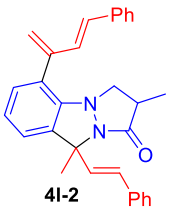


4l-2

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

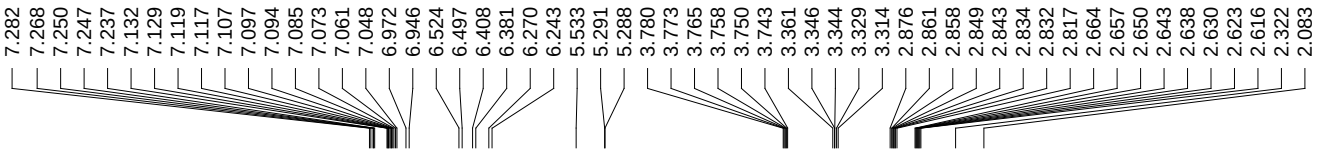


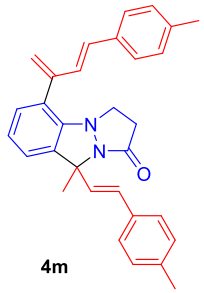




4l-2

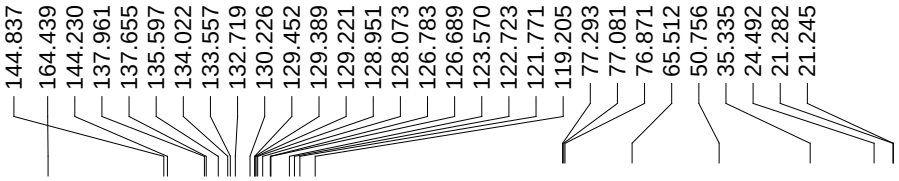
^{13}C{^{1}H } NMR (100 MHz, $CDCl_3$)

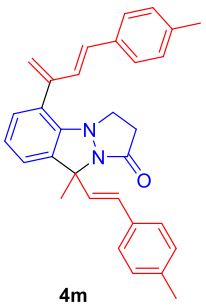




4m

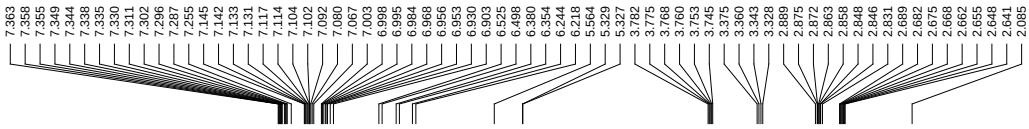
^{1}H NMR (600 MHz, $CDCl_3$)

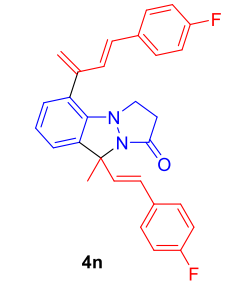




4m

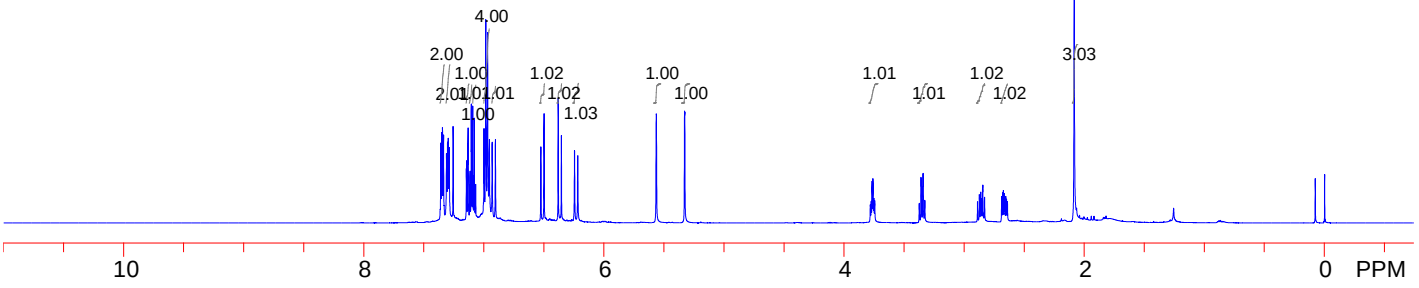
$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$)

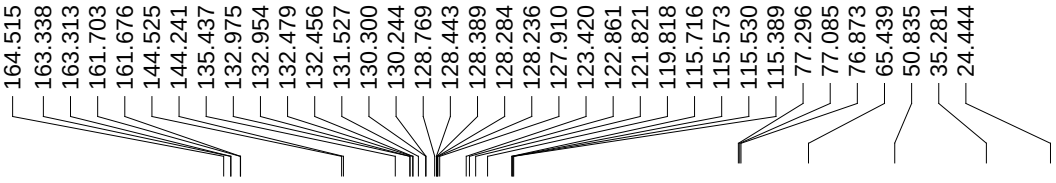


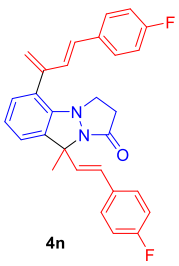


4n

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

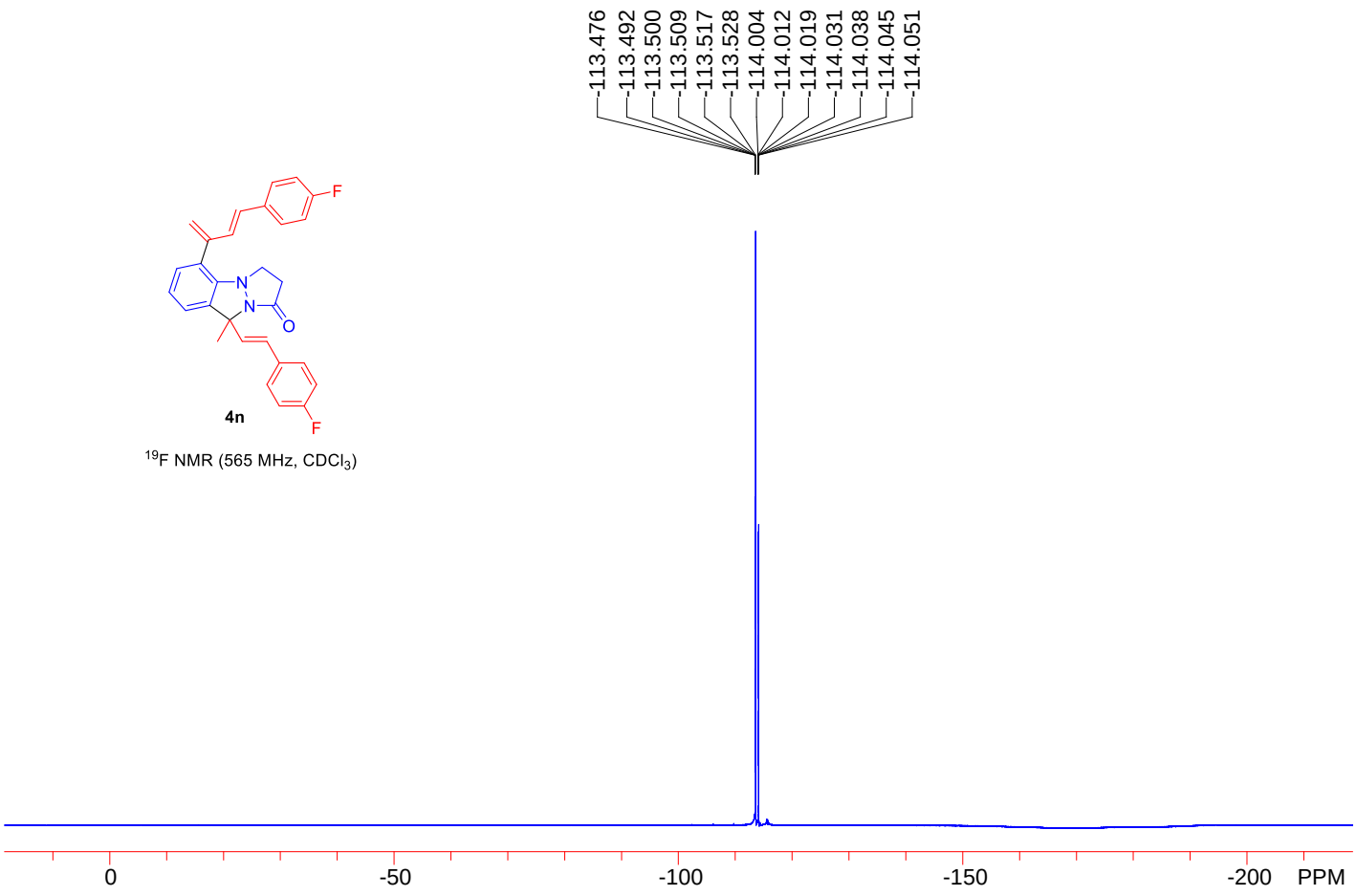






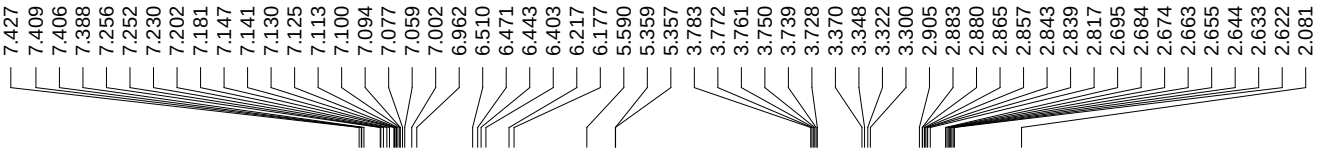
4n

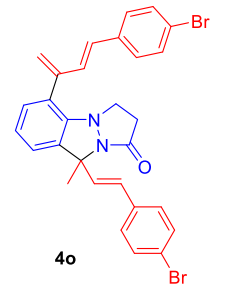
^{13}C{^{1}H } NMR (150 MHz, $CDCl_3$)



4n

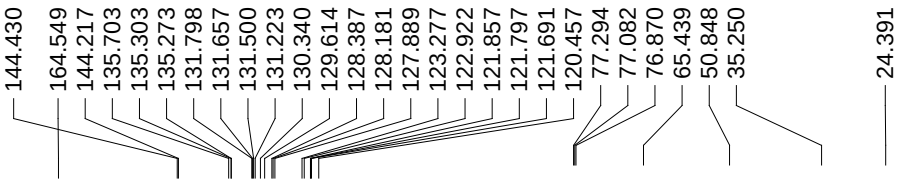
^{19}F NMR (565 MHz, $CDCl_3$)

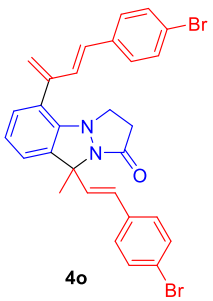




4o

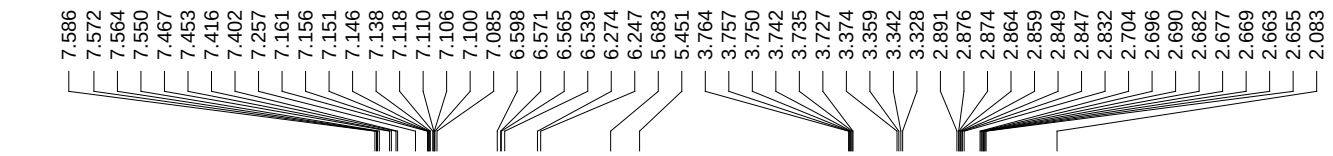
^{1}H NMR (400 MHz, $CDCl_3$)

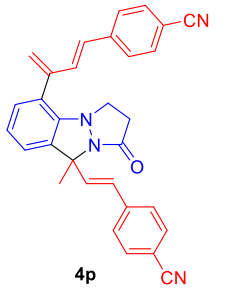




4o

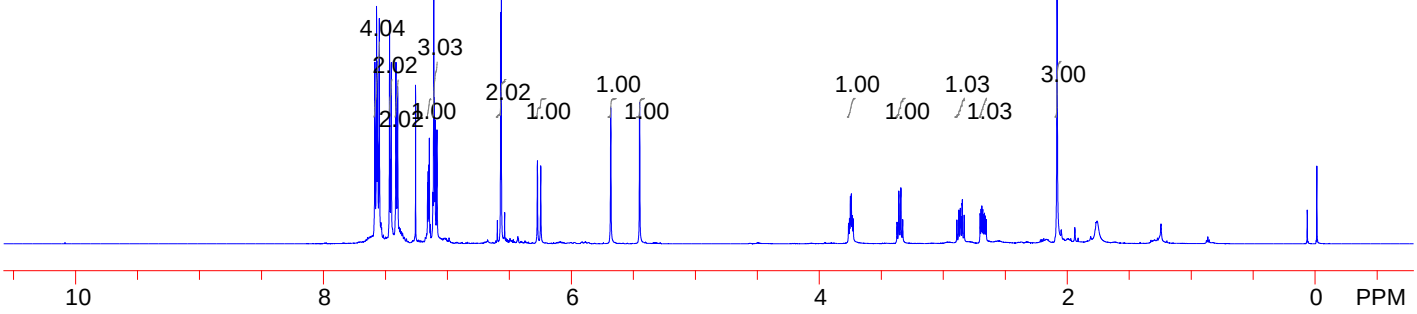
$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$)

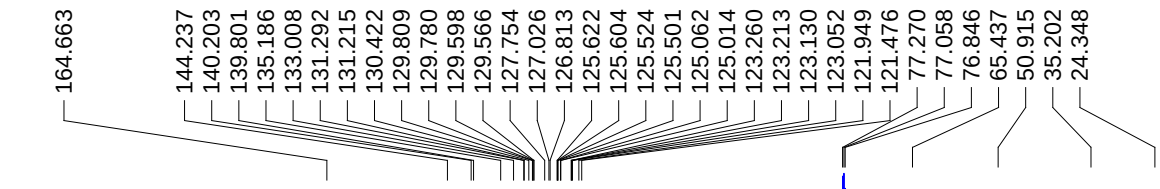


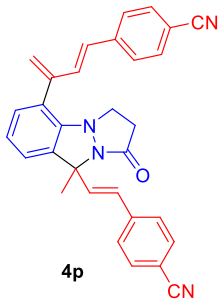


4p

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

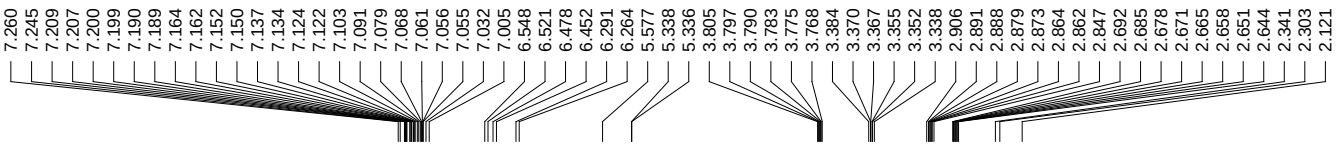


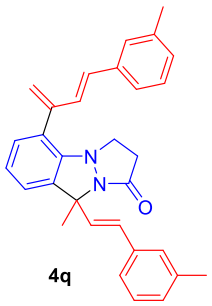




4p

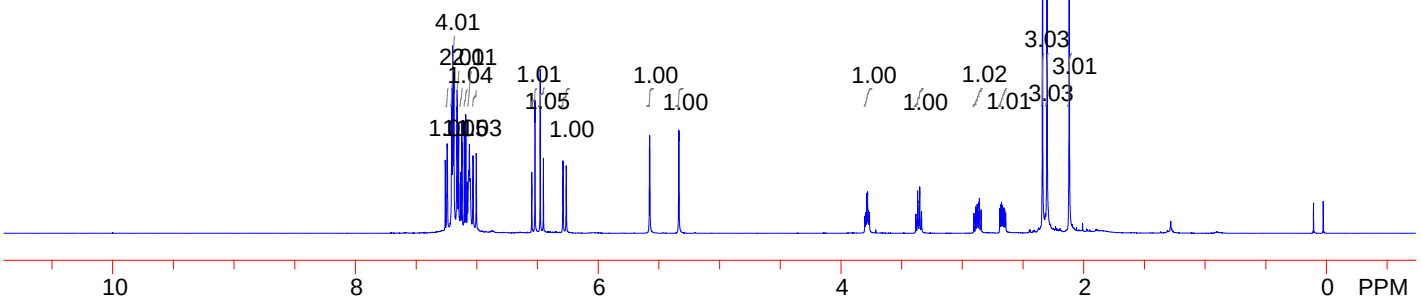
^{13}C{^{1}H } NMR (150 MHz, $CDCl_3$)

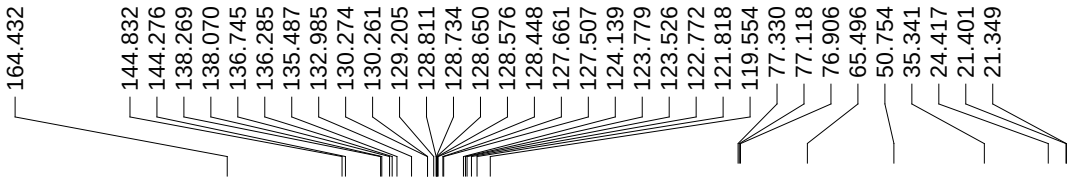


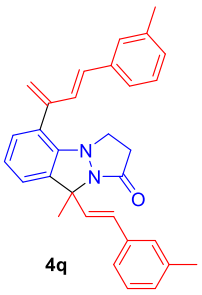


4q

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

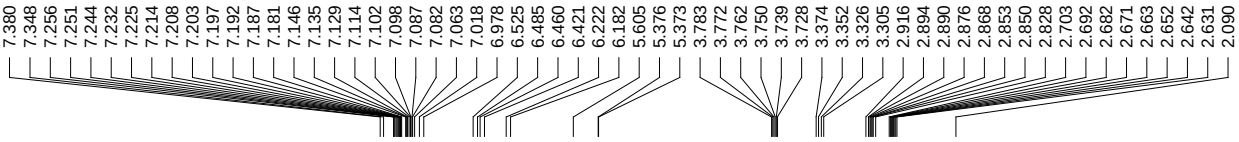


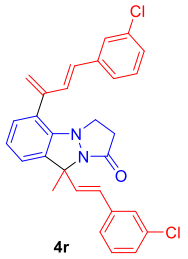




4q

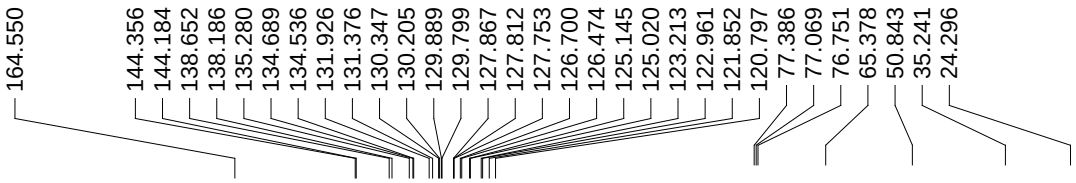
^{13}C{^{1}H } NMR (150 MHz, $CDCl_3$)

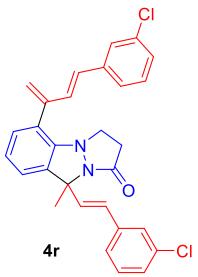




4r

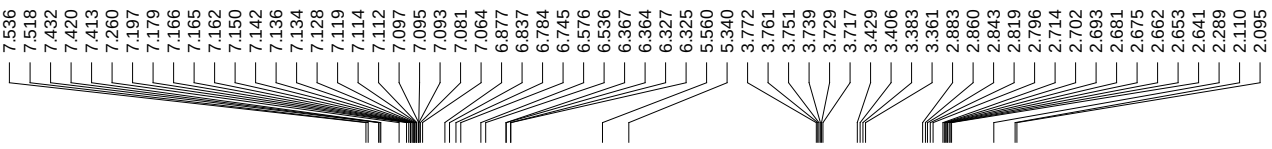
^{1}H NMR (400 MHz, $CDCl_3$)

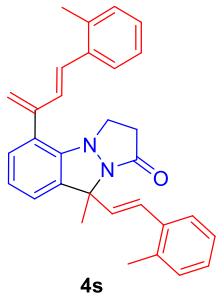




4r

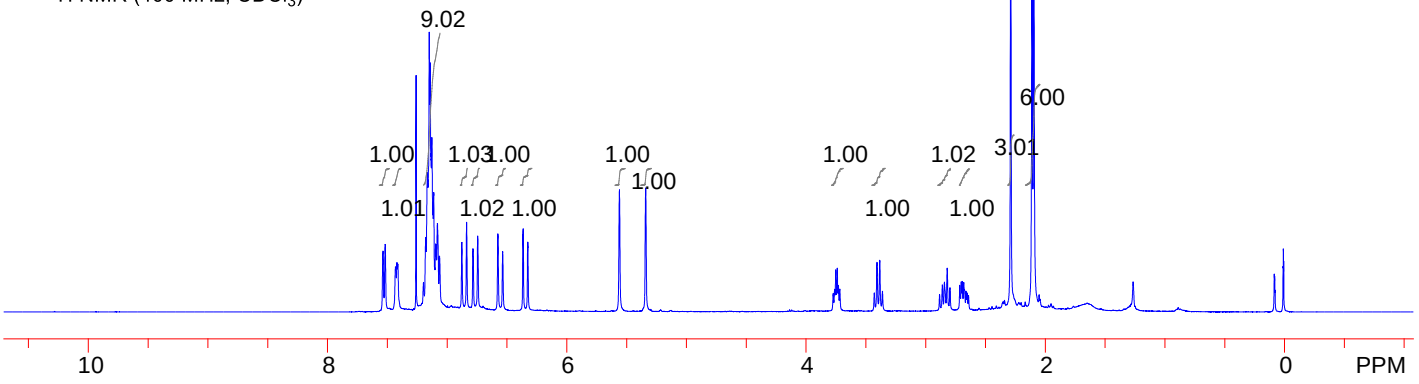
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

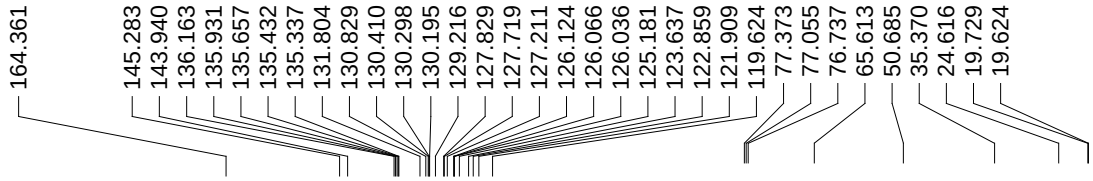


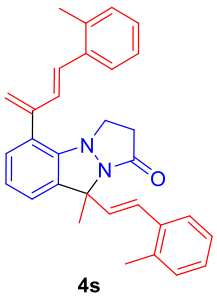


4s

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

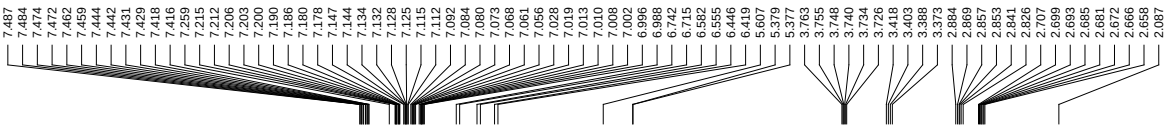


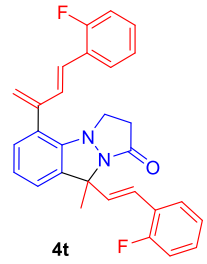




4s

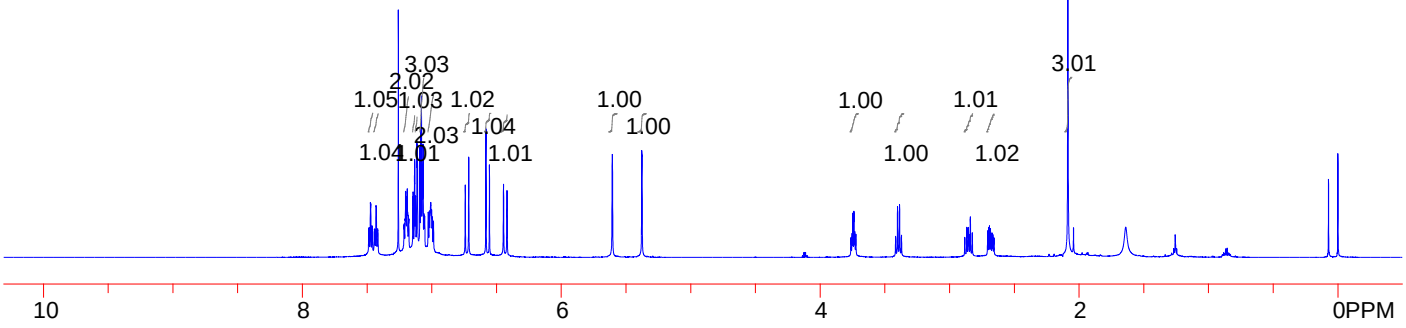
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

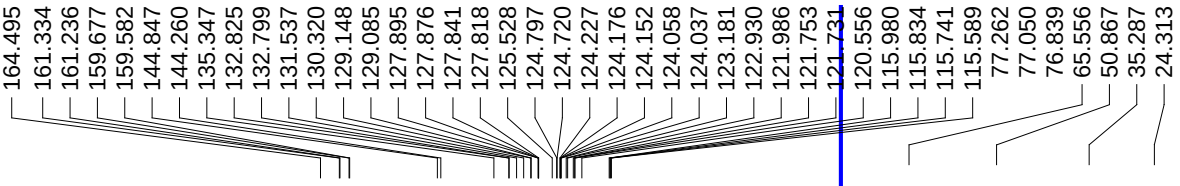


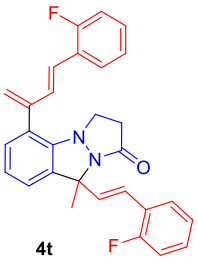


4t

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

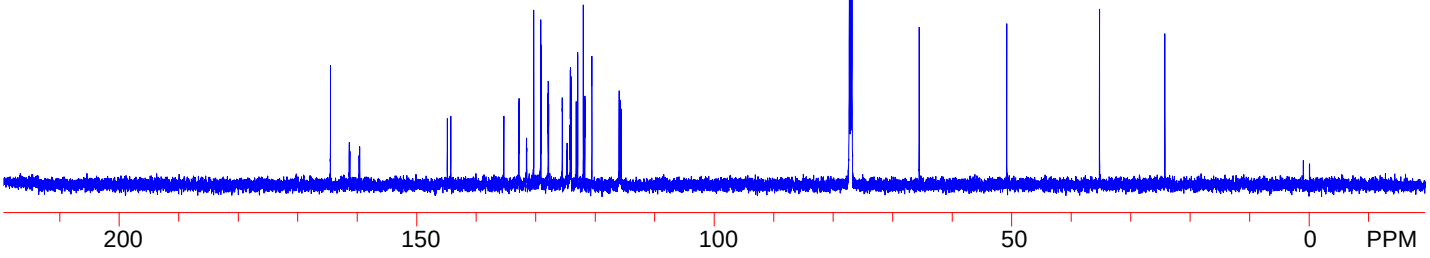


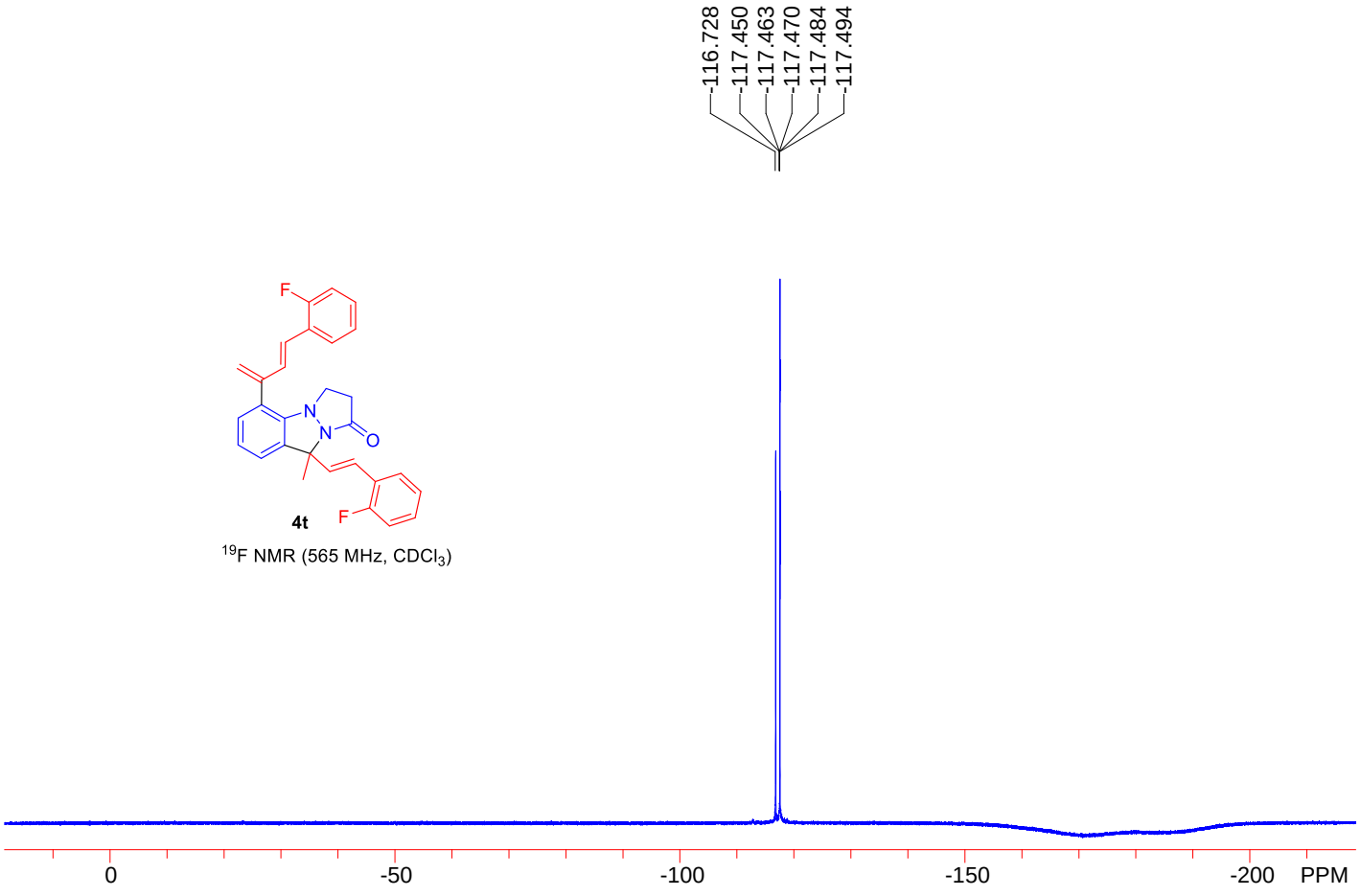




4t

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

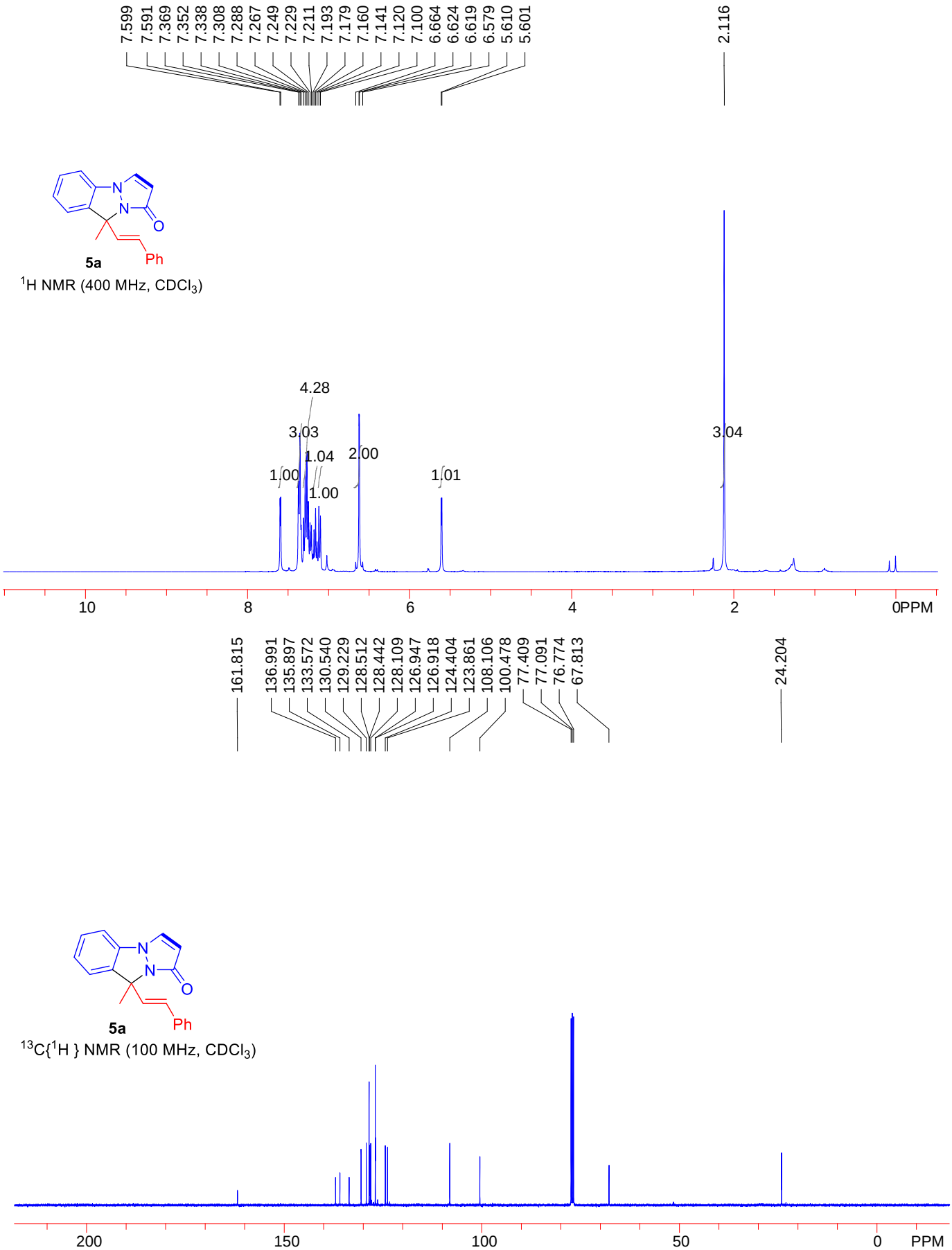


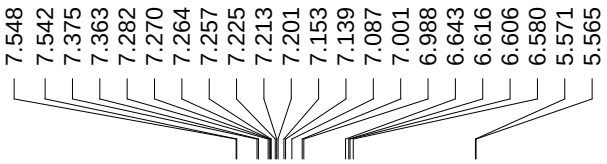


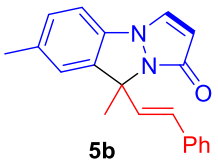
4t

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

VII. NMR spectra of 5a-5d

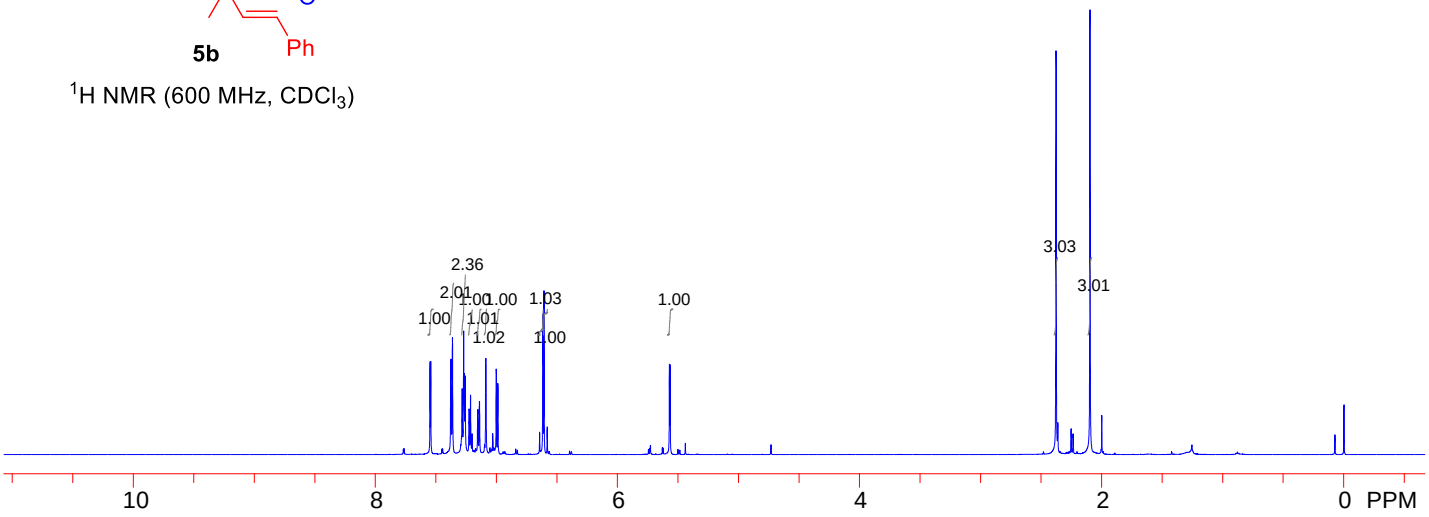


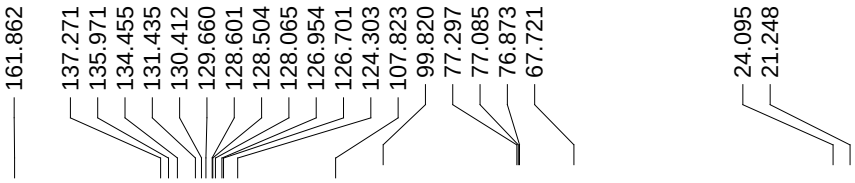


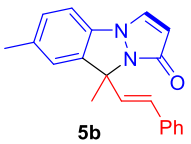


5b

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

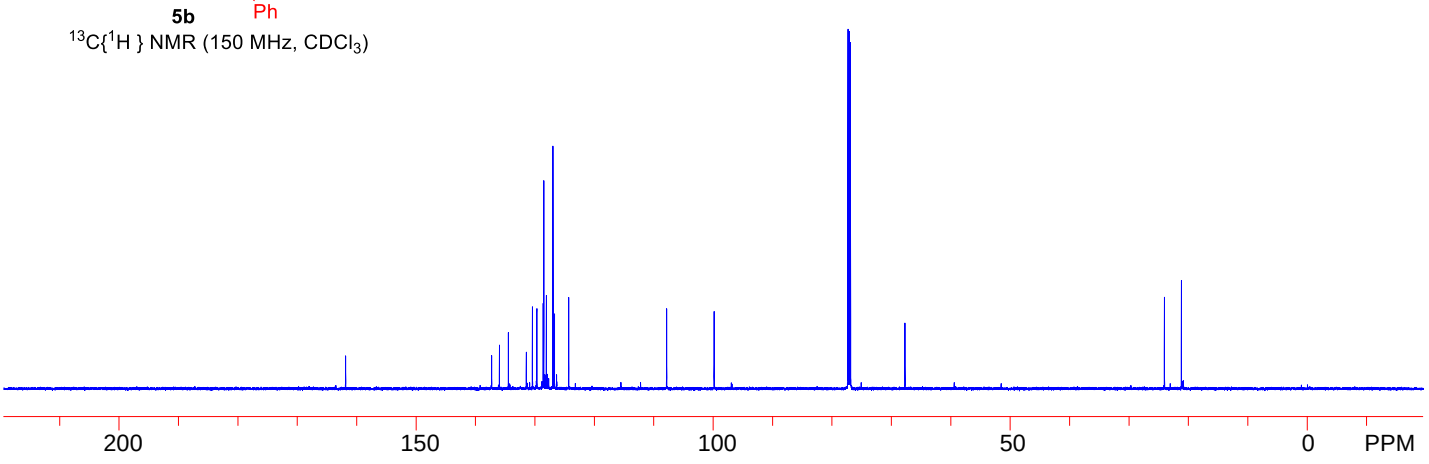


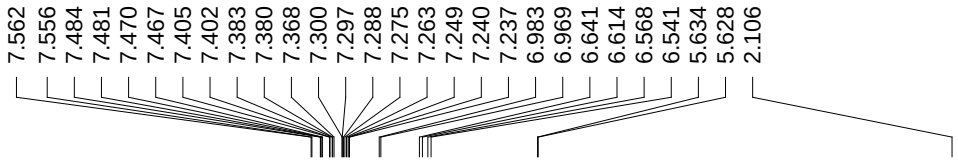


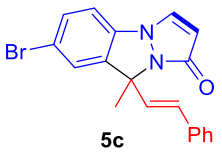


5b

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

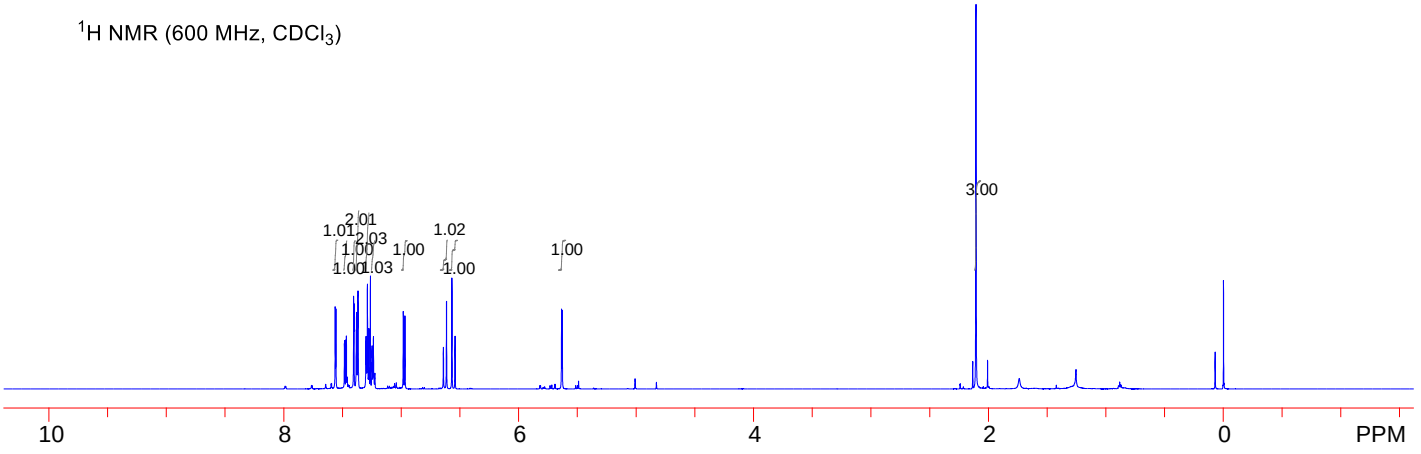


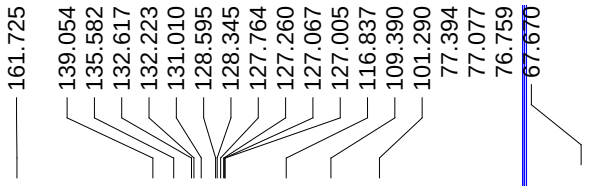


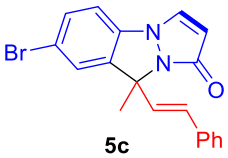


5c

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

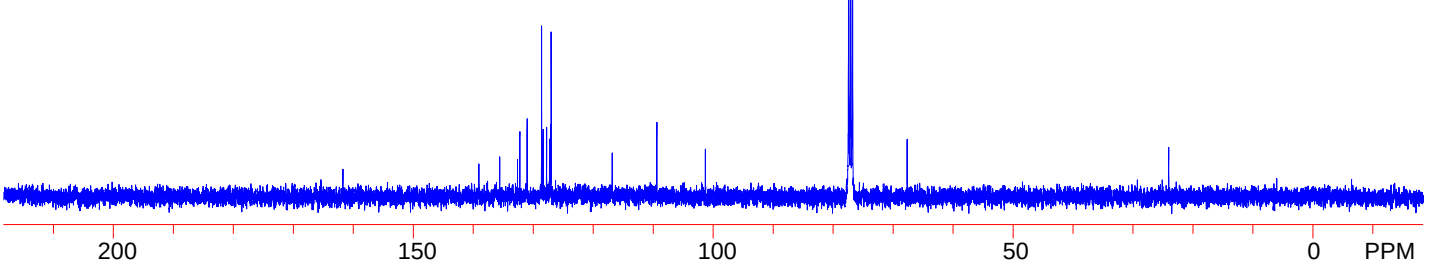


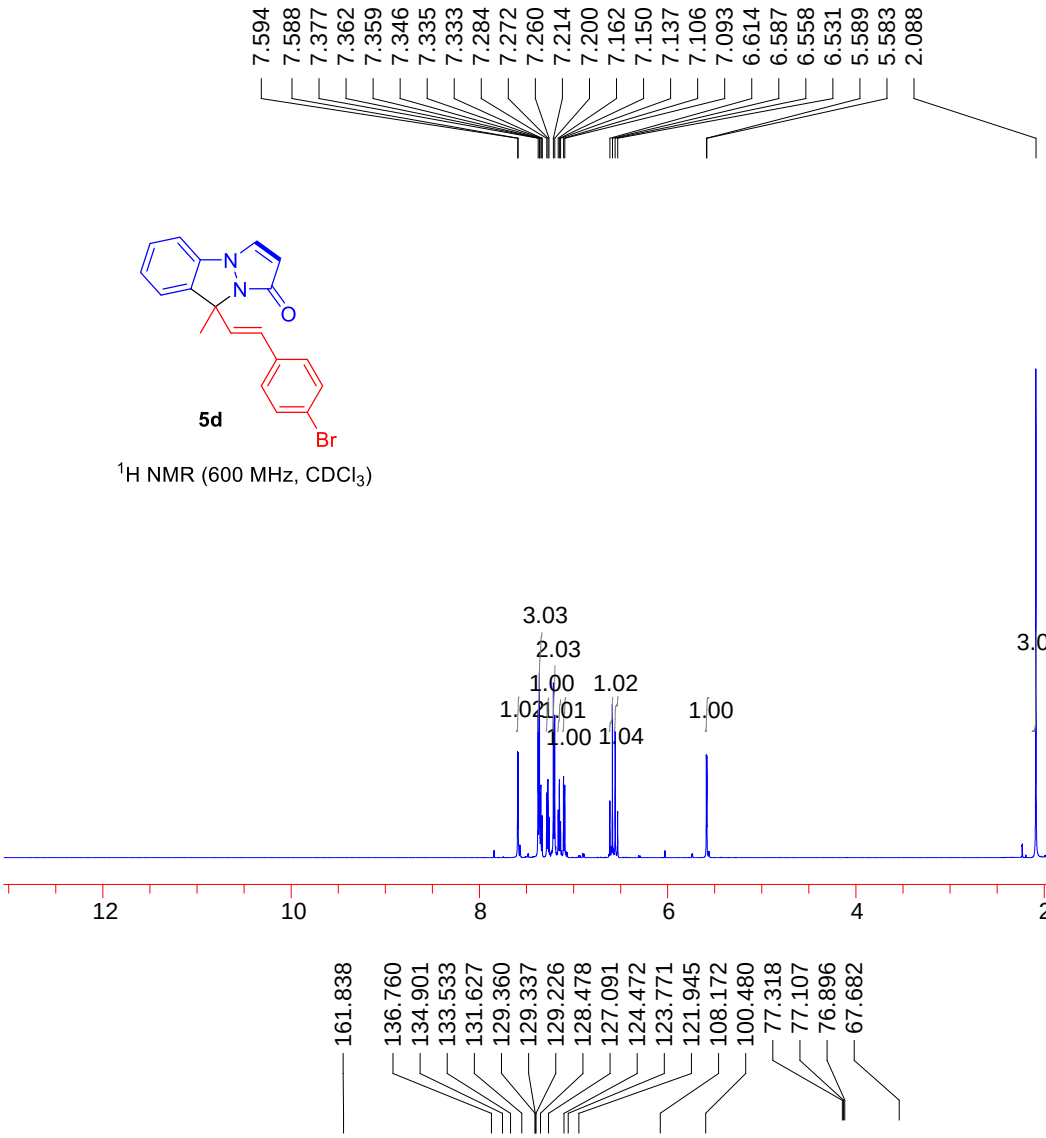


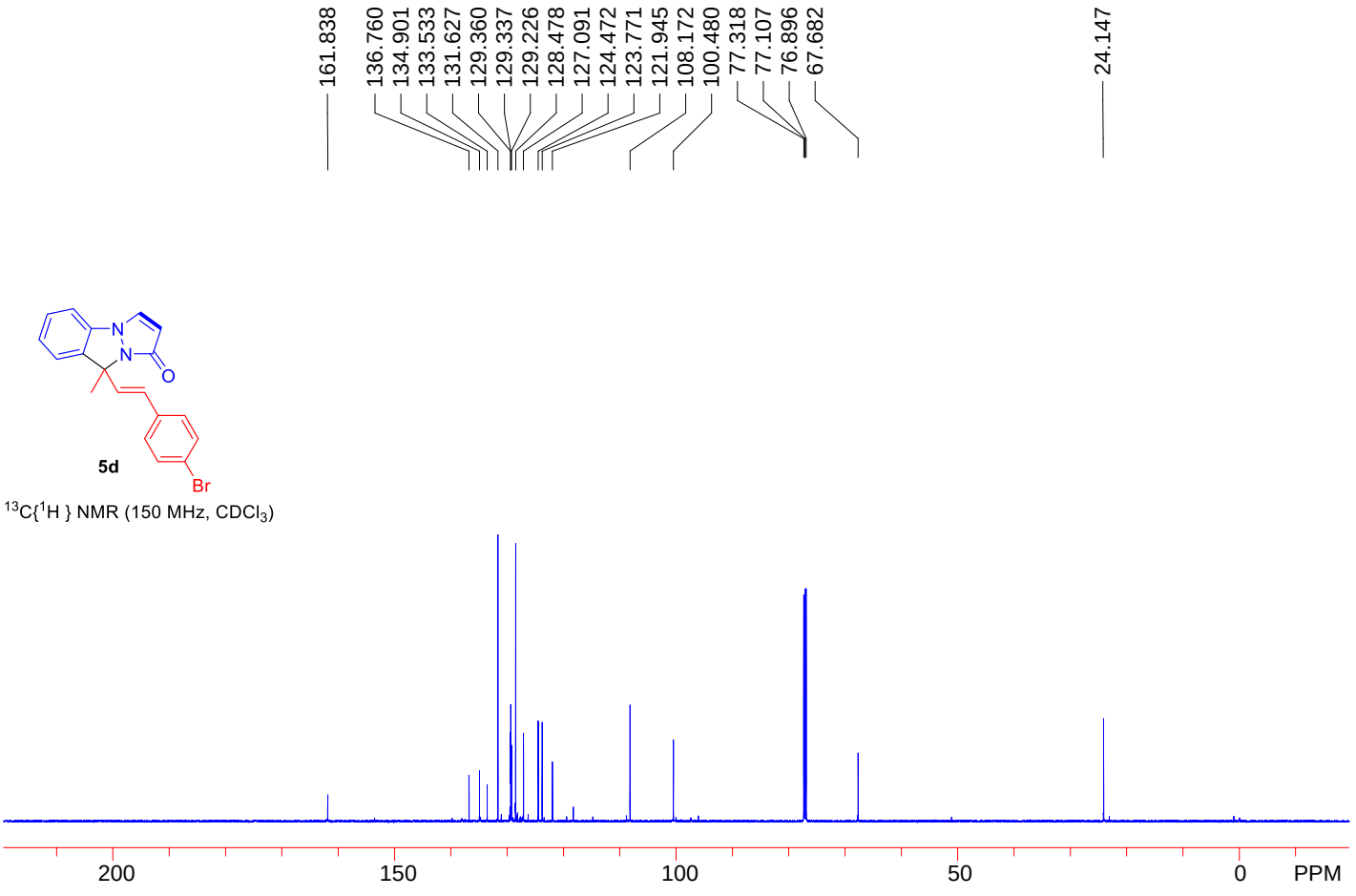


5c

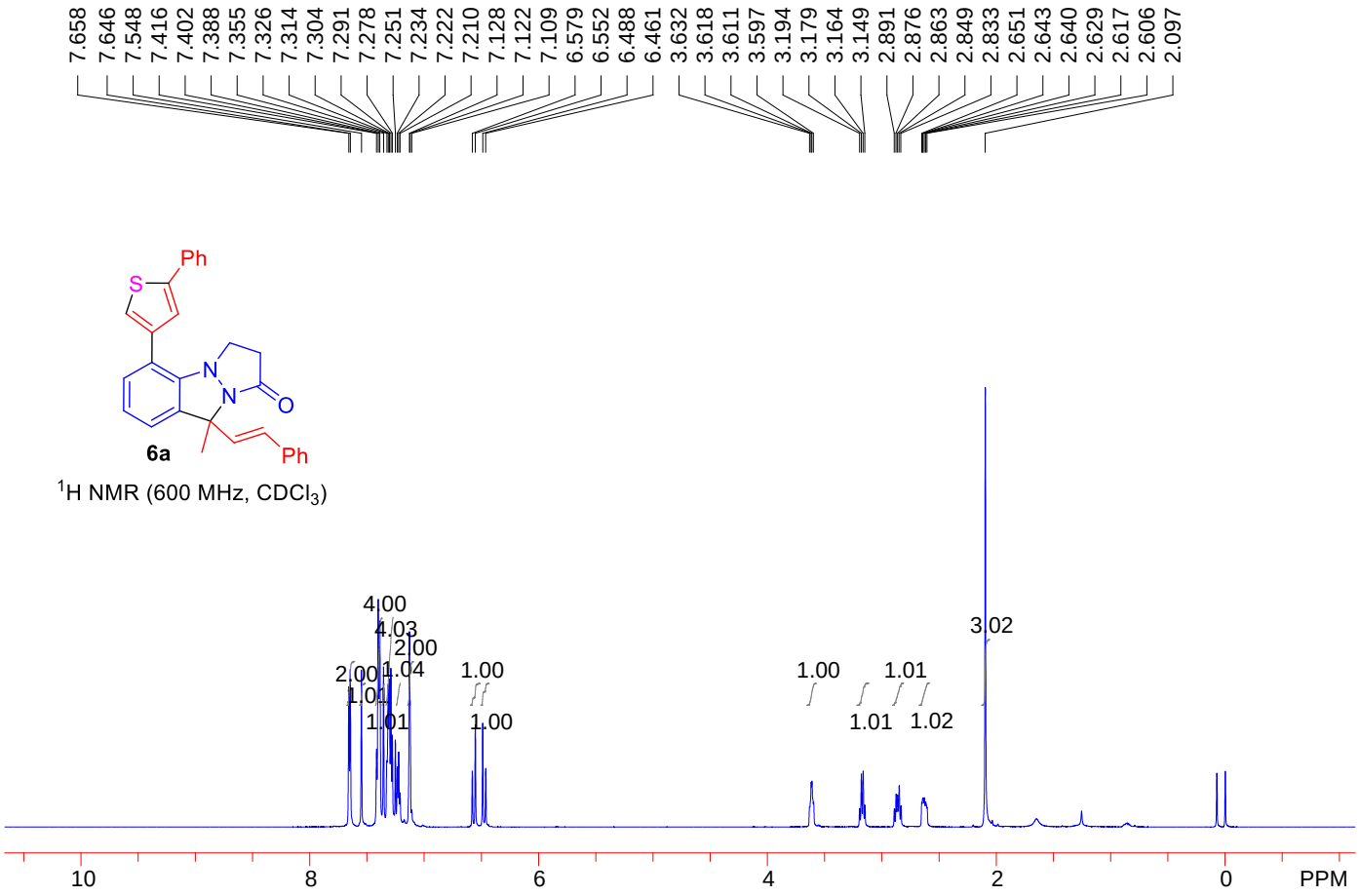
^{13}C{^{1}H } NMR (100 MHz, $CDCl_3$)

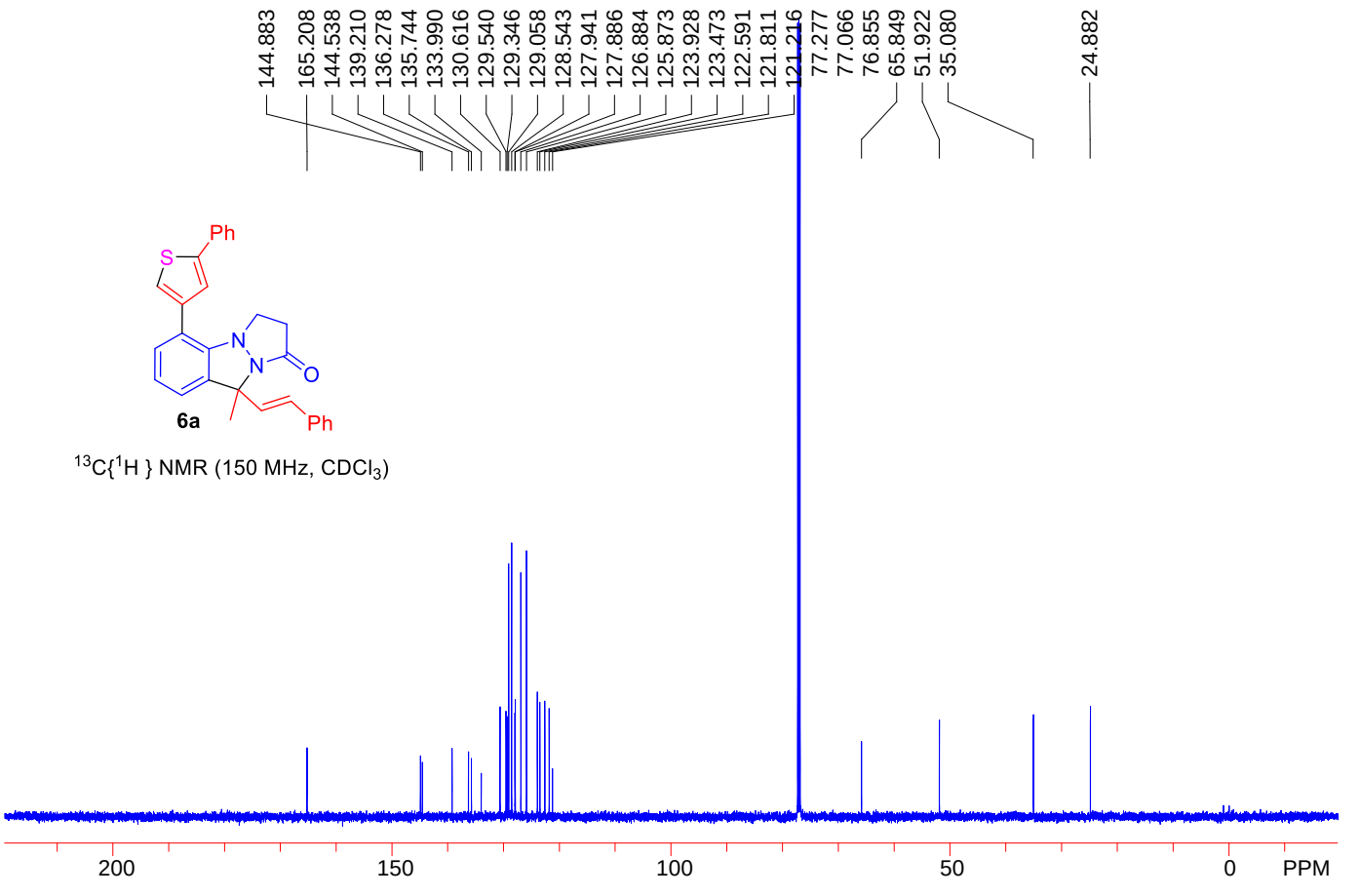


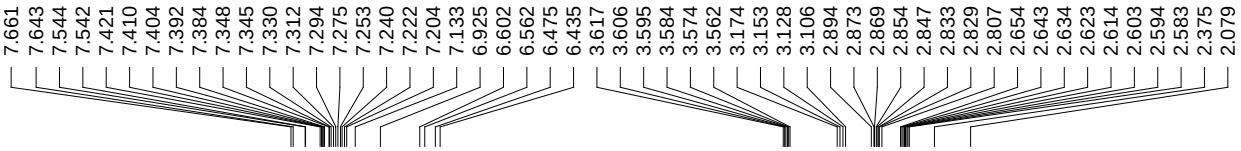

7.594
7.588
7.377
7.362
7.359
7.346
7.335
7.333
7.284
7.272
7.260
7.214
7.200
7.162
7.150
7.137
7.106
7.093
6.614
6.587
6.558
6.531
5.589
5.583
2.088
5d
Br
1H NMR (600 MHz, CDCl3)
3.03
2.03
1.00
1.02
1.02
1.01
1.00
1.04
1.00
3.02
12
10
8
6
4
2
0
PPM

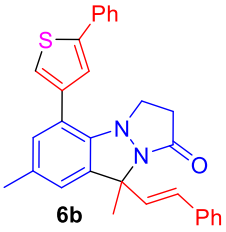

161.838
136.760
134.901
133.533
131.627
129.360
129.337
129.226
128.478
127.091
124.472
123.771
121.945
108.172
100.480
77.318
77.107
76.896
67.682
24.147
5d
Br
13C{1H } NMR (150 MHz, CDCl3)
200
150
100
50
0
PPM

VIII. NMR spectra of 6a-6e



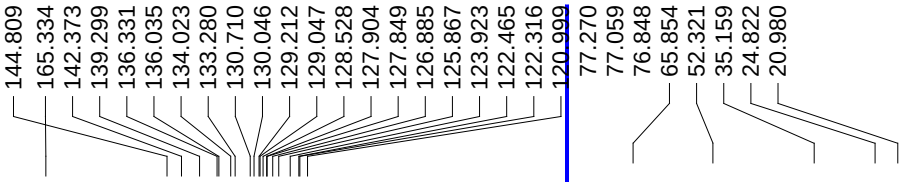


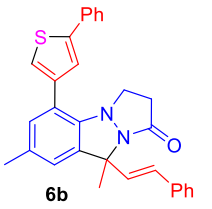




6b

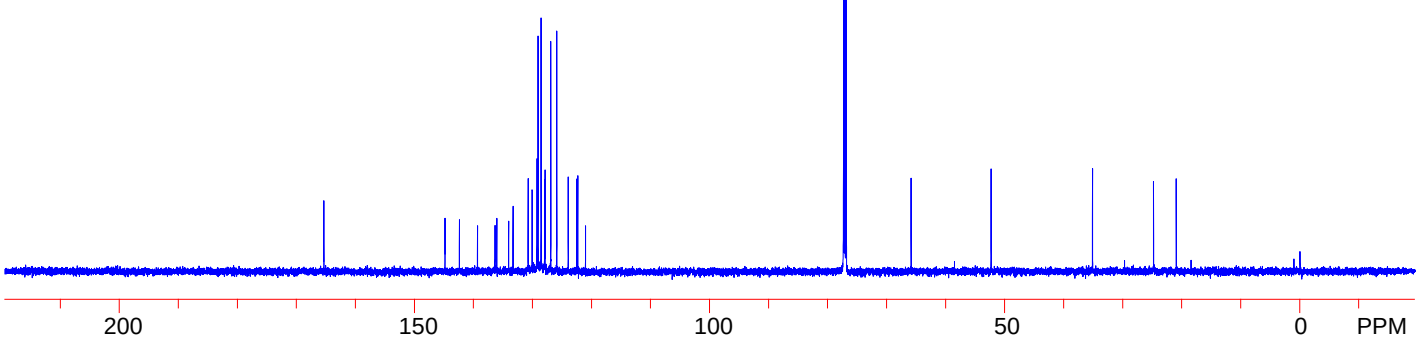
^{1}H NMR (400 MHz, $CDCl_3$)

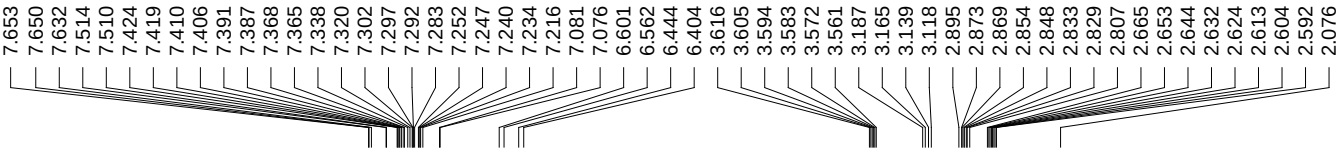


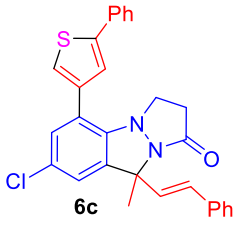


6b

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

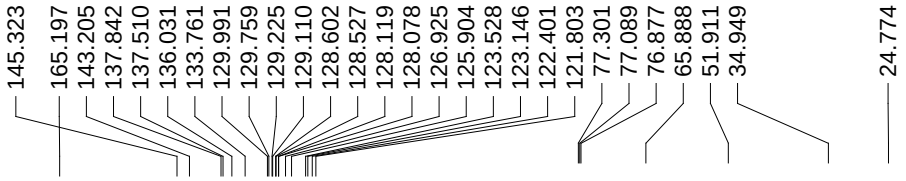


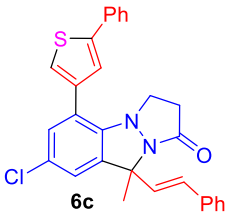




6c

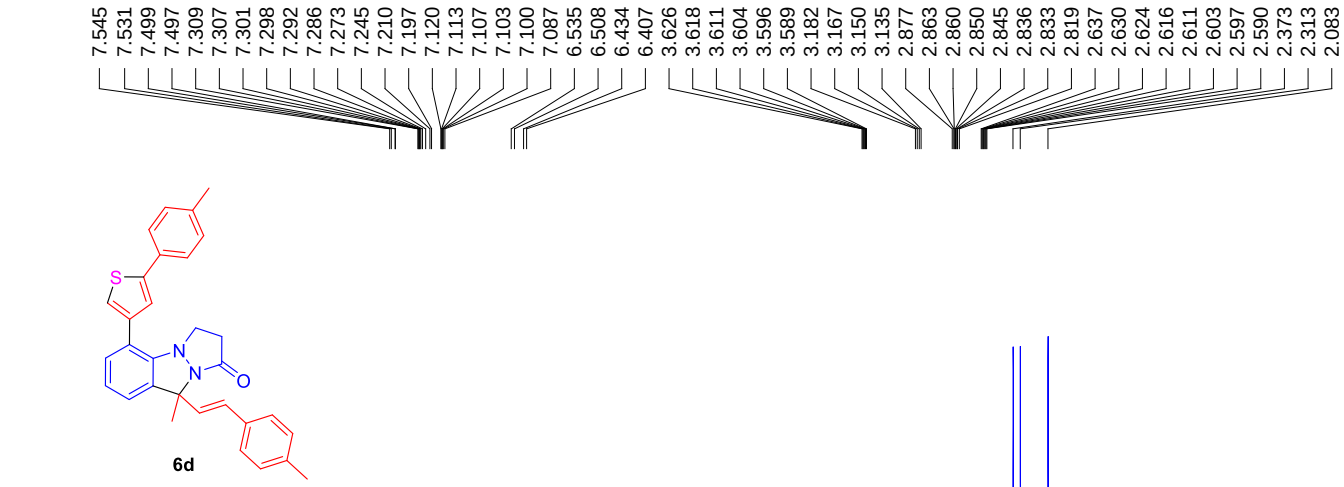
^{1}H NMR (400 MHz, $CDCl_3$)





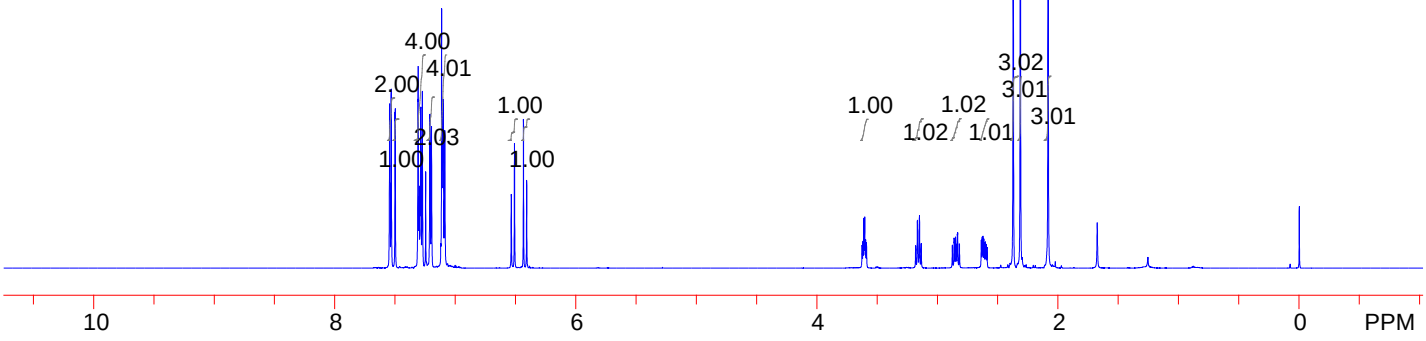
6c

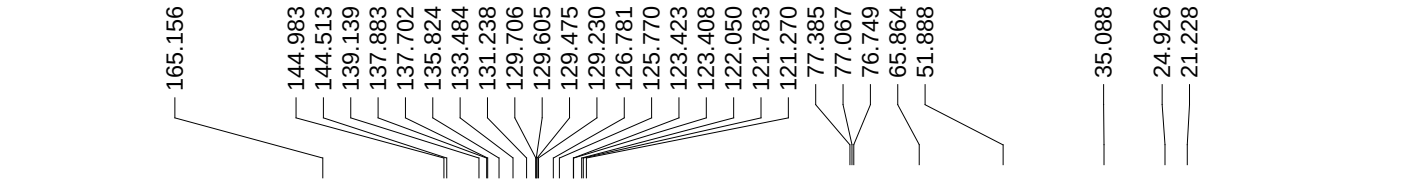
$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$)

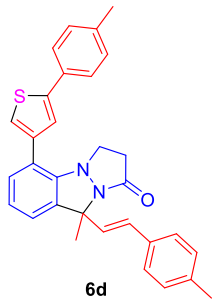


6d

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

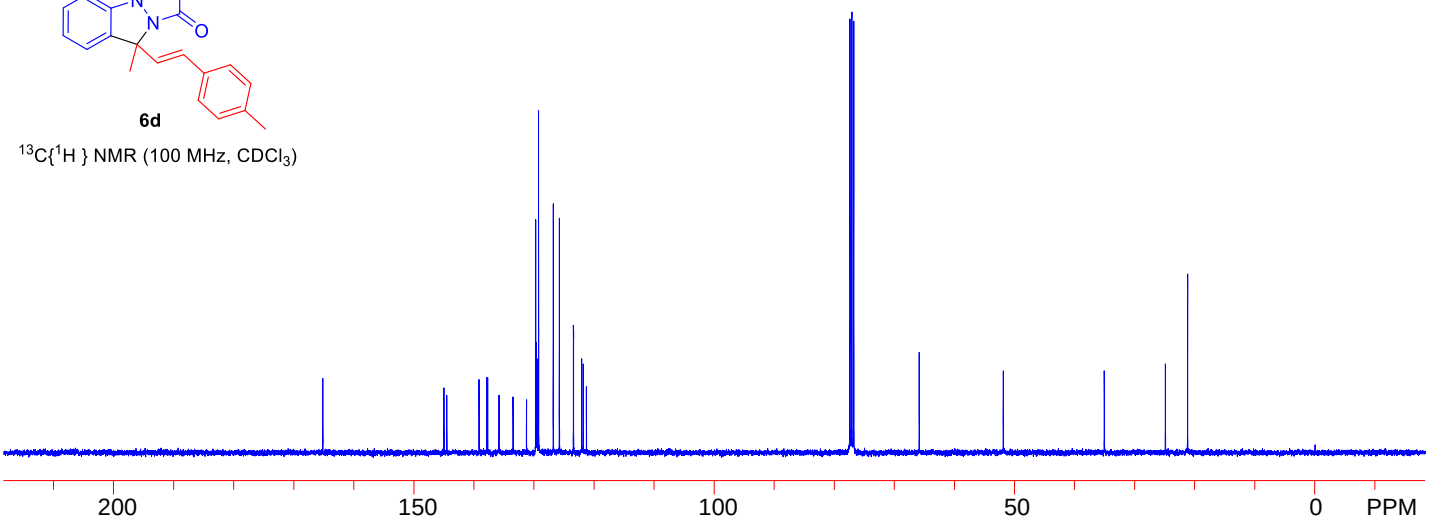


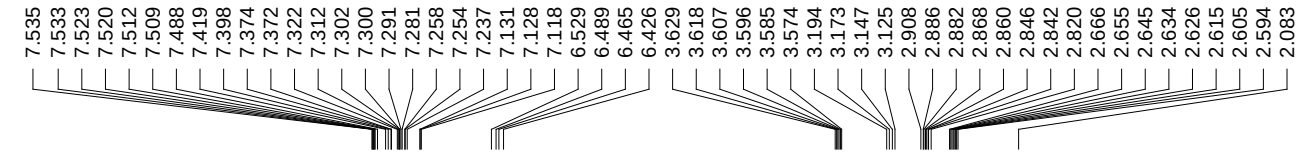


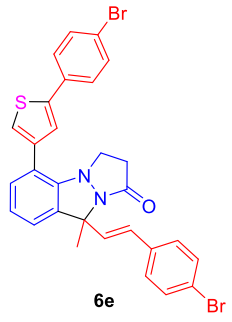


6d

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

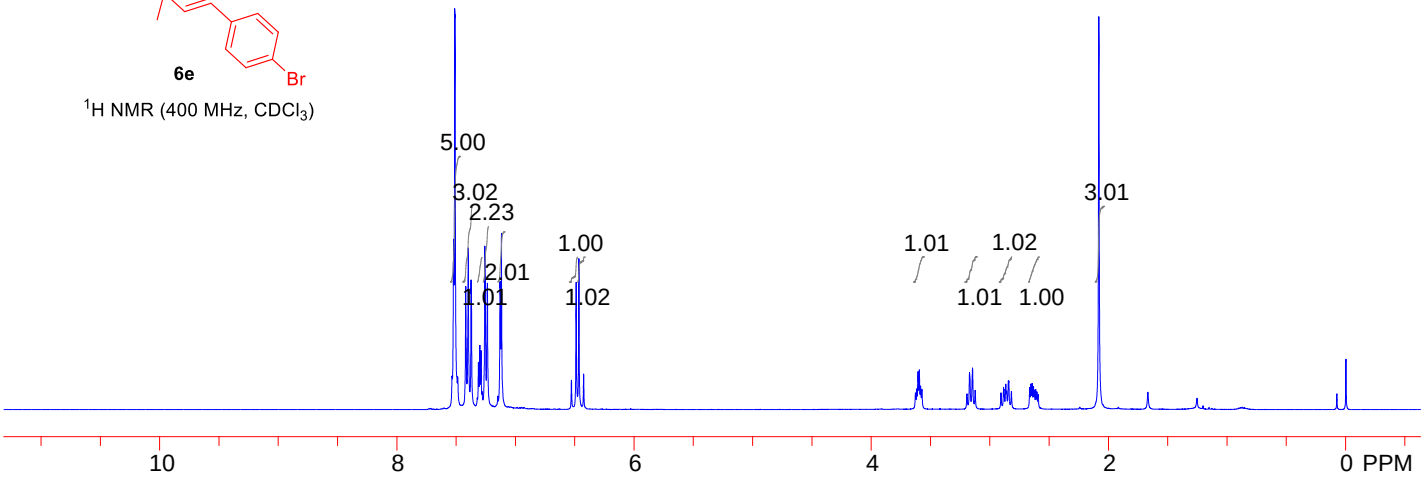


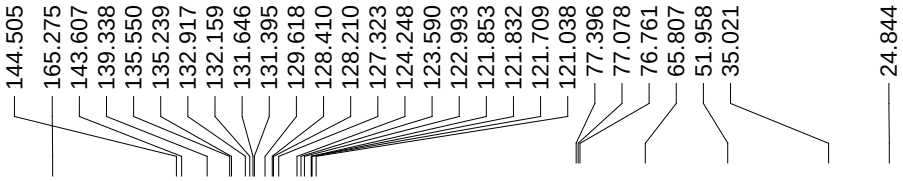


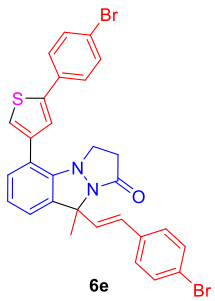


6e

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



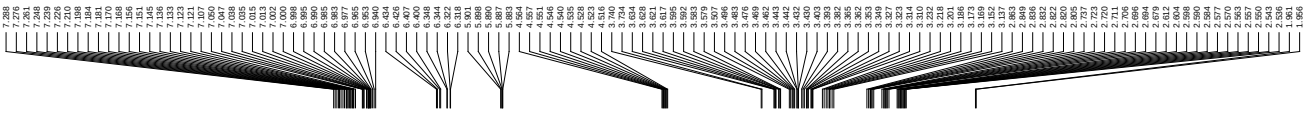


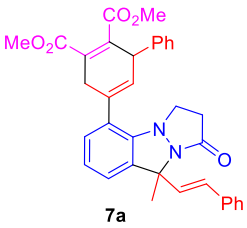


6e

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

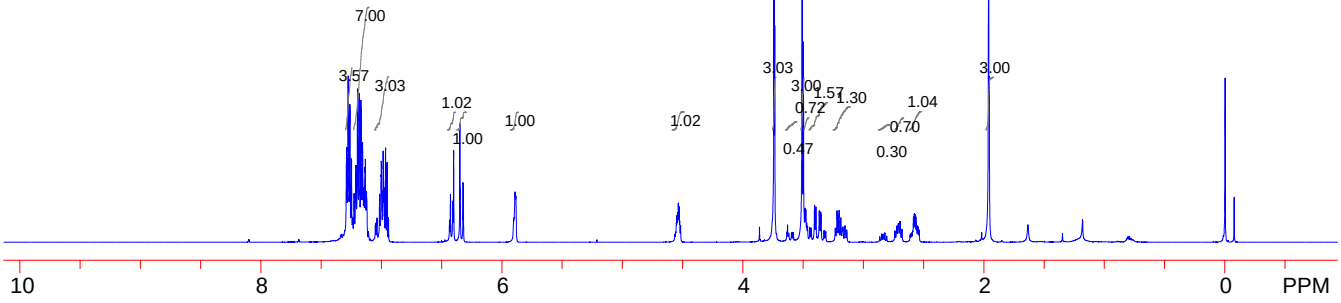
IX. NMR spectra of 7a-7e

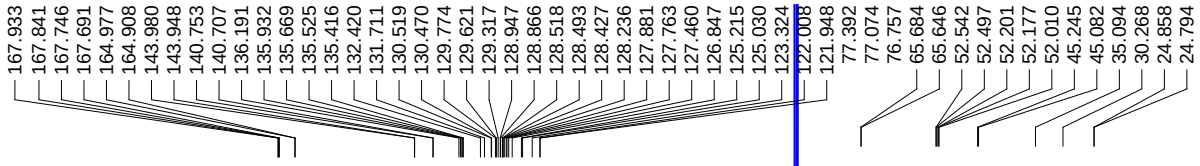


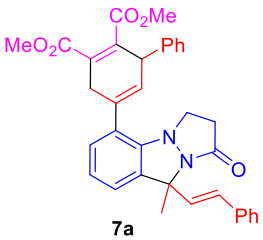


7a

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

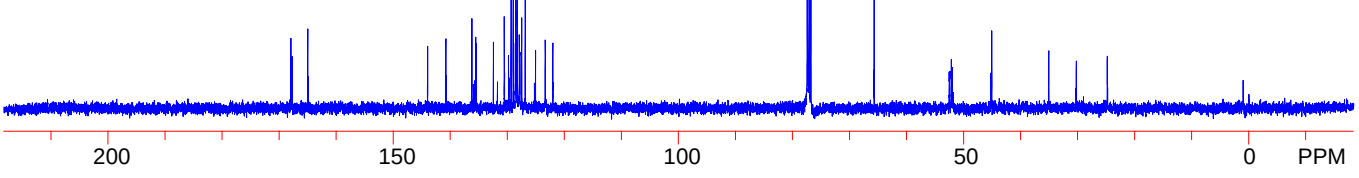


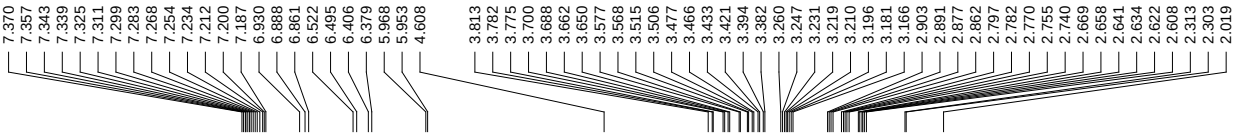


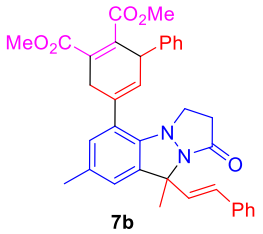


7a

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

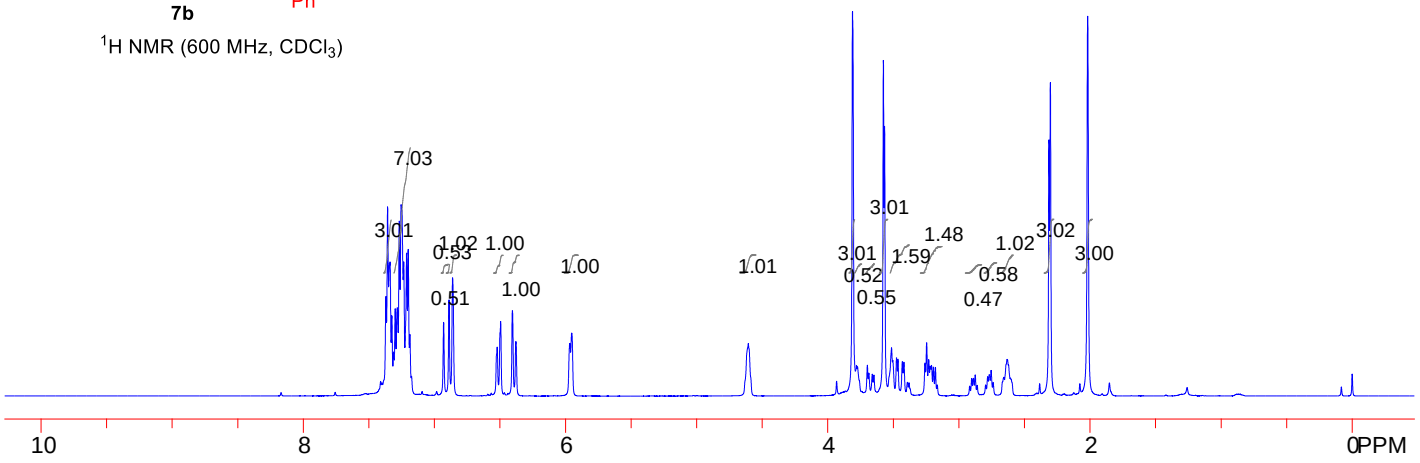


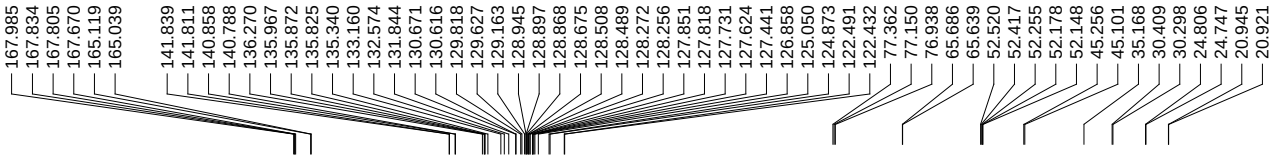


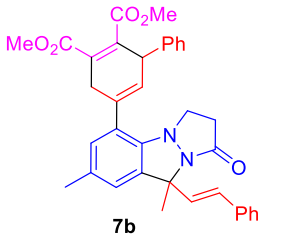


7b

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

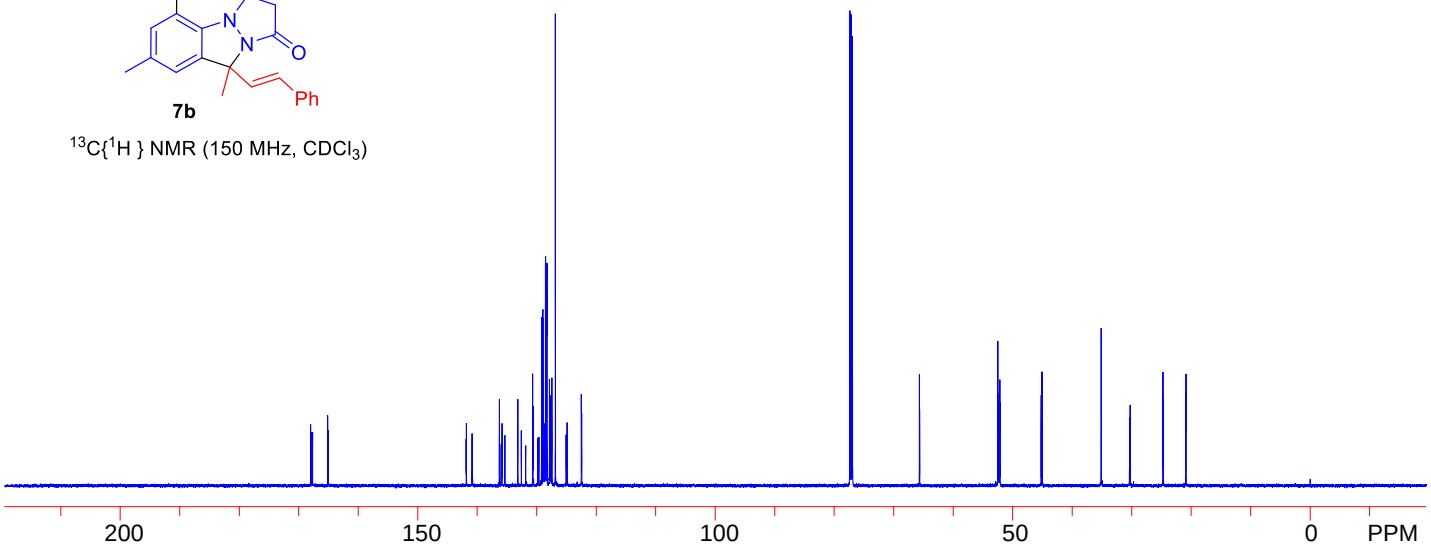


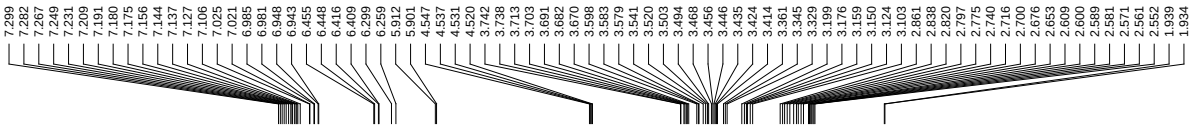


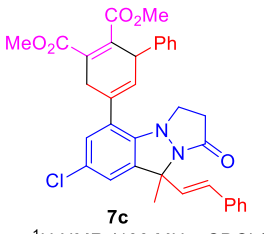


7b

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

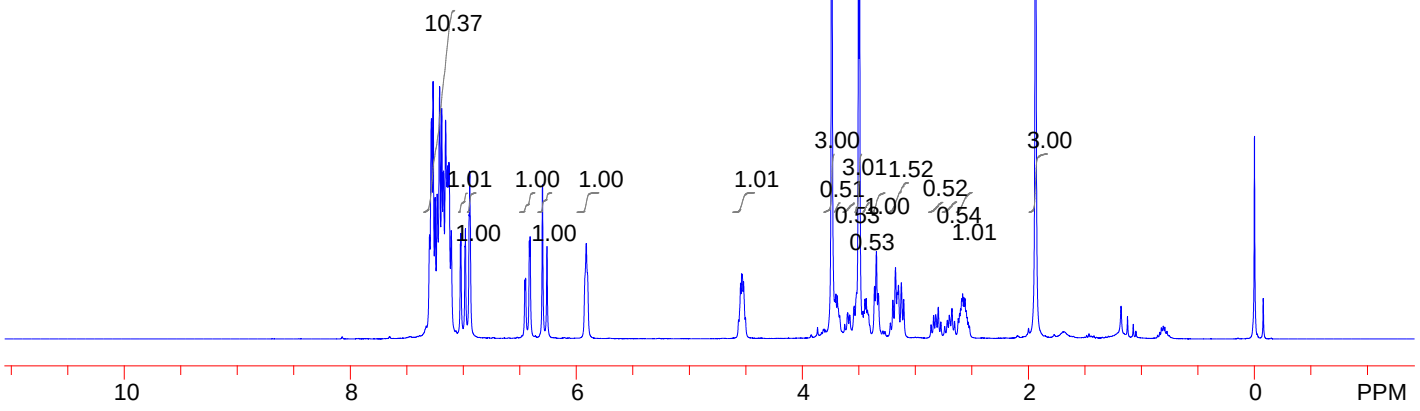


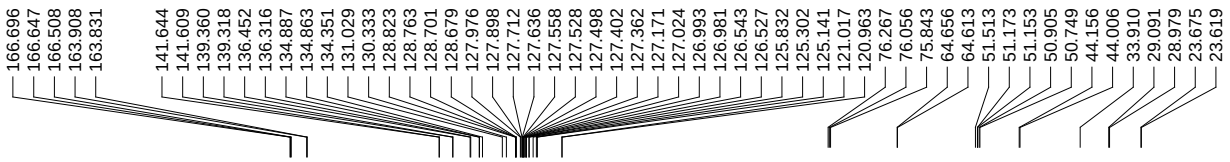


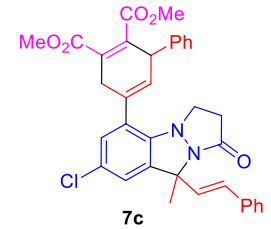


7c

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

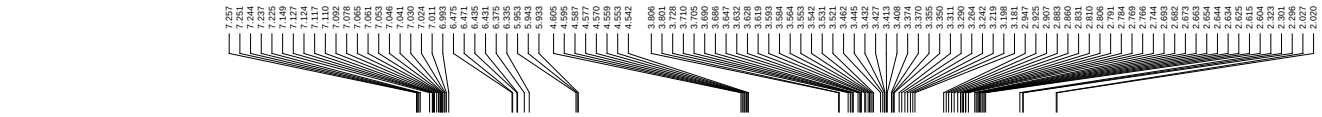


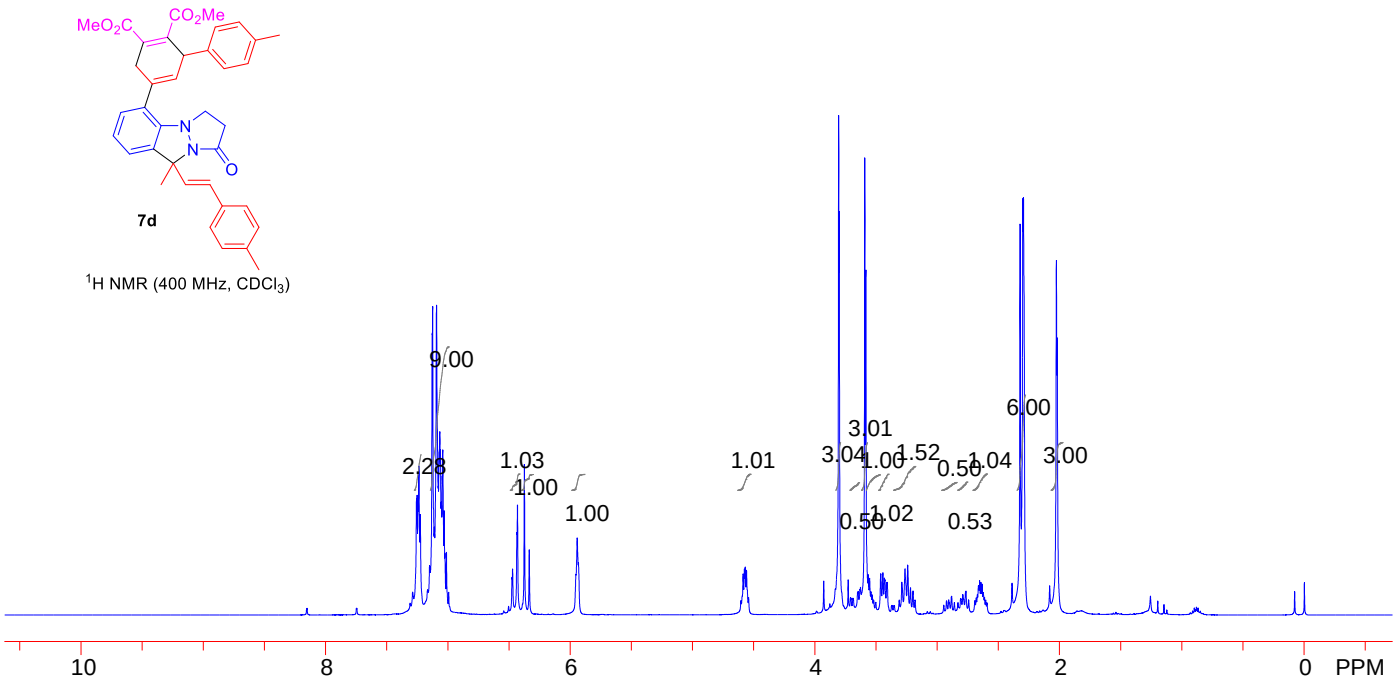


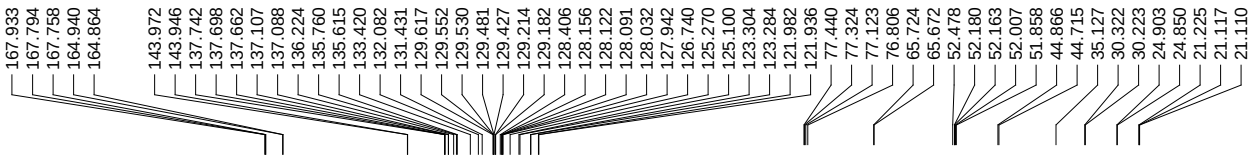


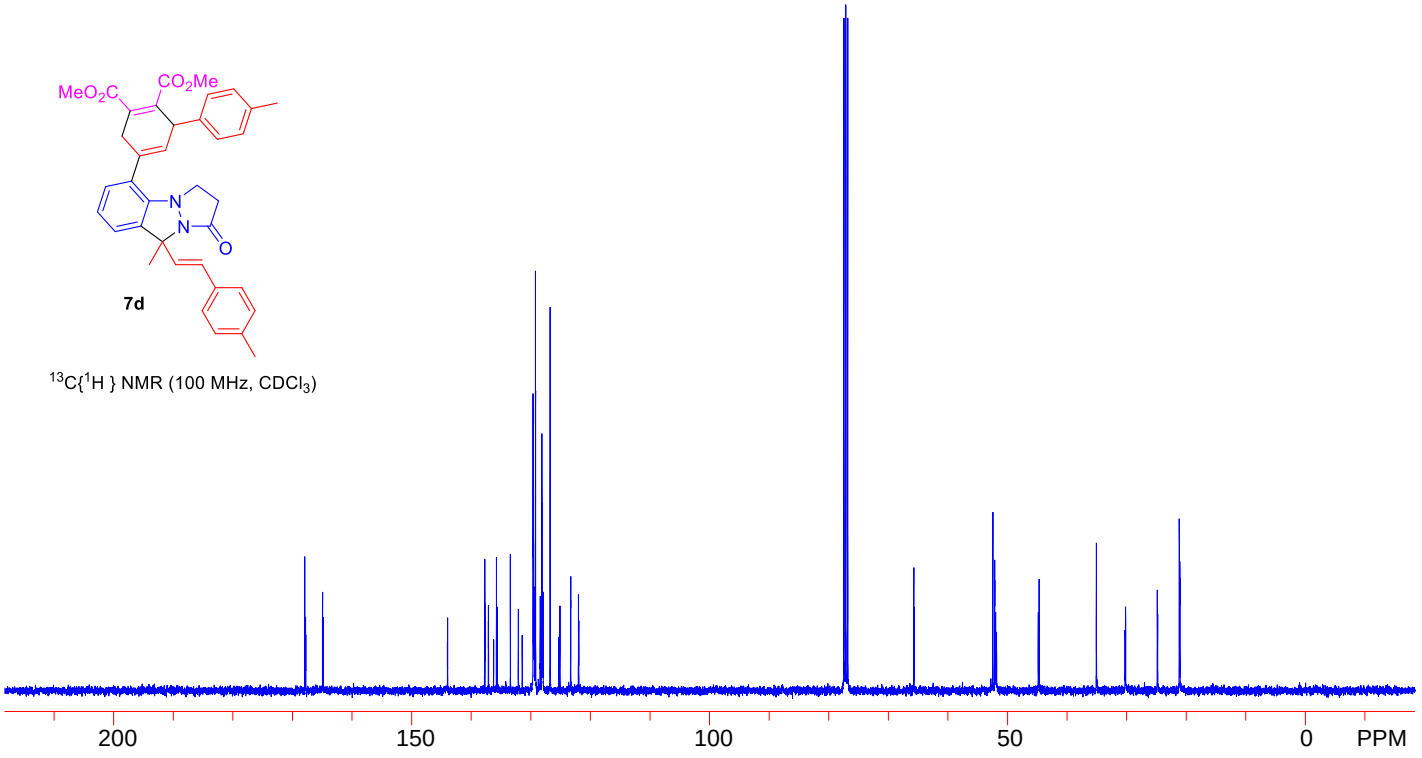
7c

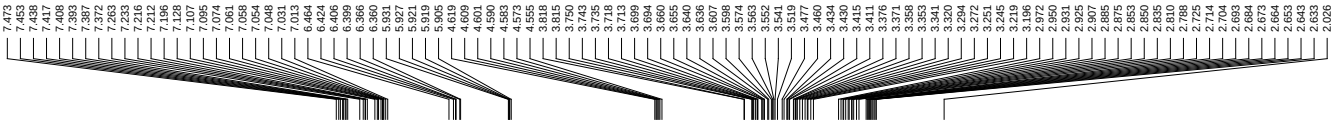
$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$)

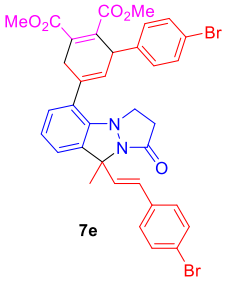



MeO2C
CO2Me
N
N
O
7d
1H NMR (400 MHz, CDCl3)
9.00
2.28
1.03
1.00
1.00
1.01
3.04
3.01
1.00
1.52
0.50
1.04
6.00
3.00
0.50
1.02
0.53
10
8
6
4
2
0
PPM



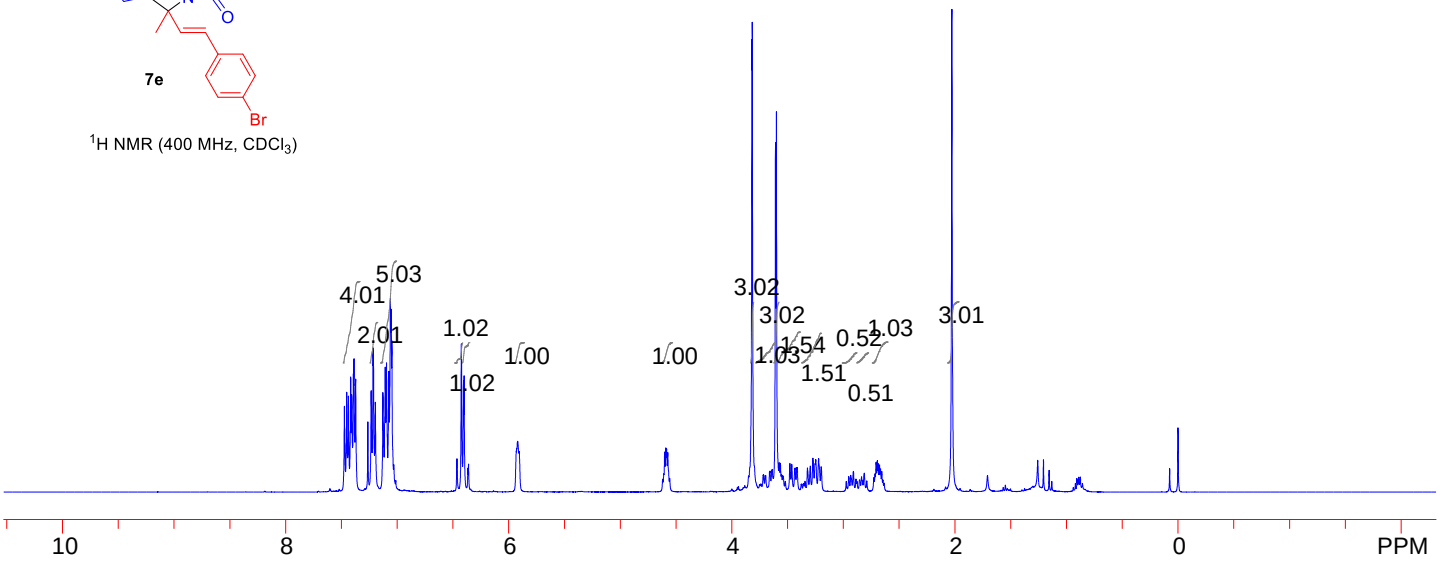

MeO2C
CO2Me
N
N
O
7d
13C{1H } NMR (100 MHz, CDCl3)
200
150
100
50
0
PPM

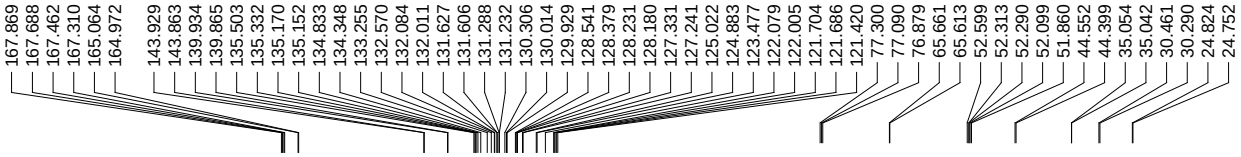


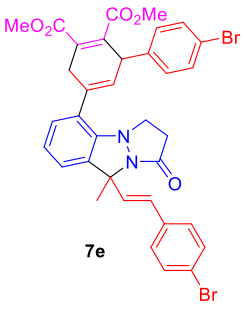


7e

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



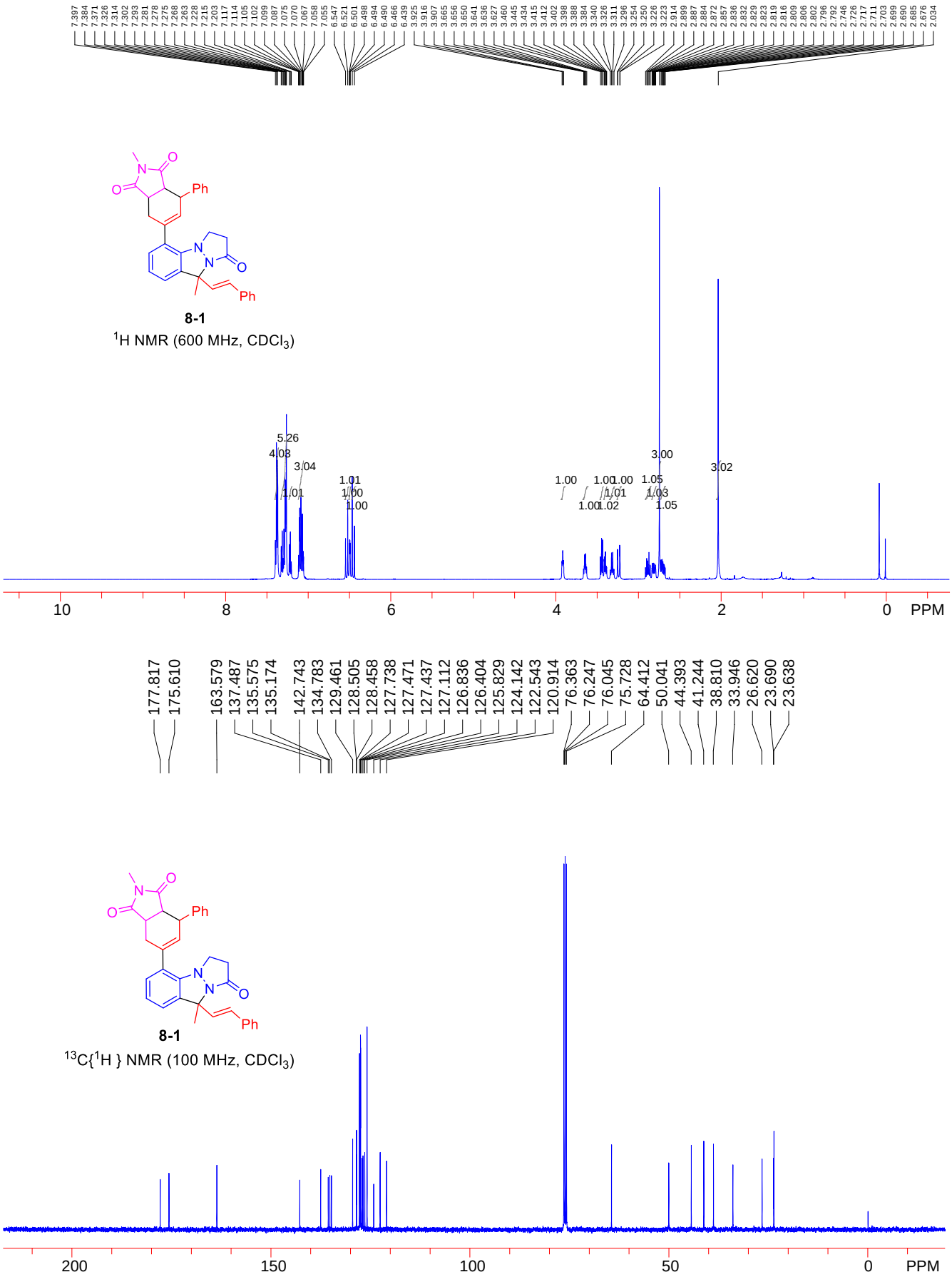


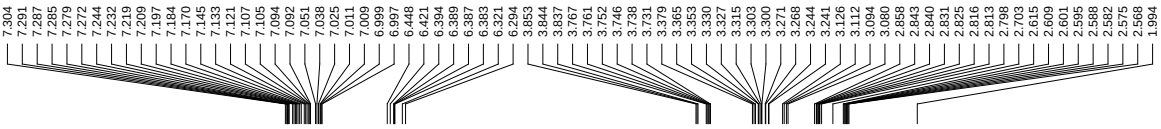


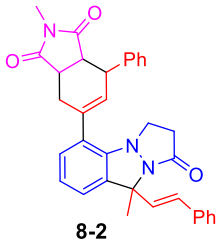
7e

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

X. NMR spectra of 8-9

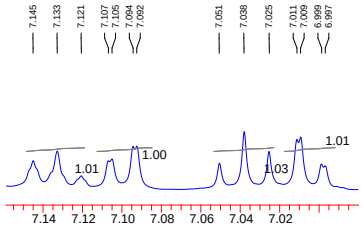


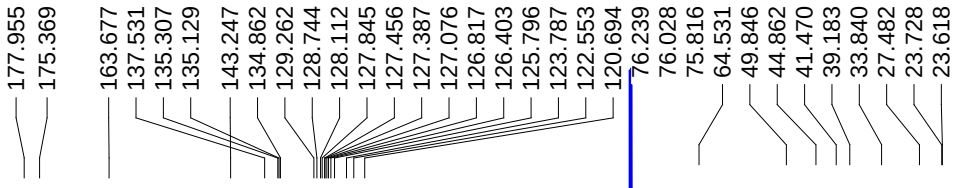


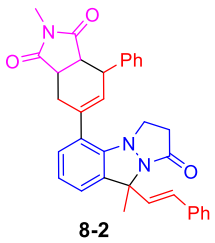


8-2

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

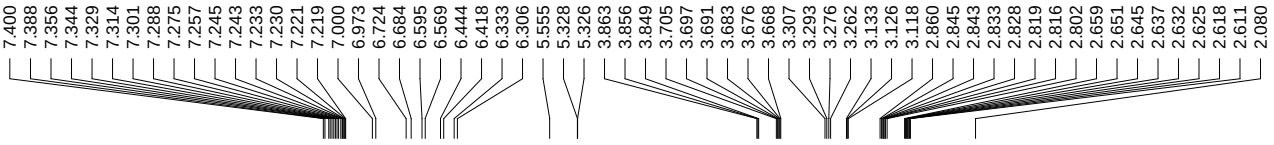


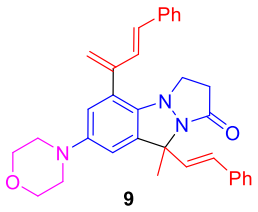




8-2

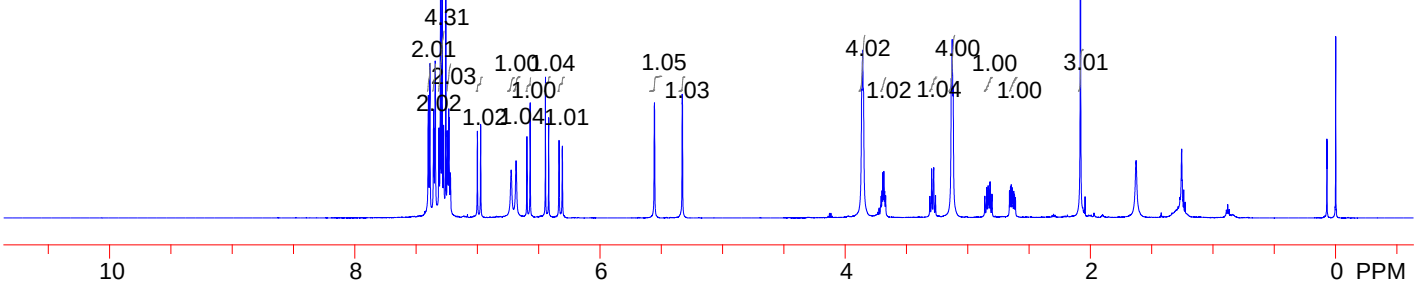
$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$)

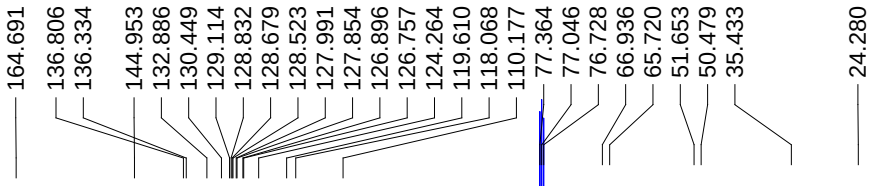


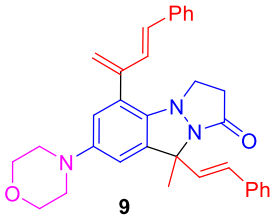


9

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

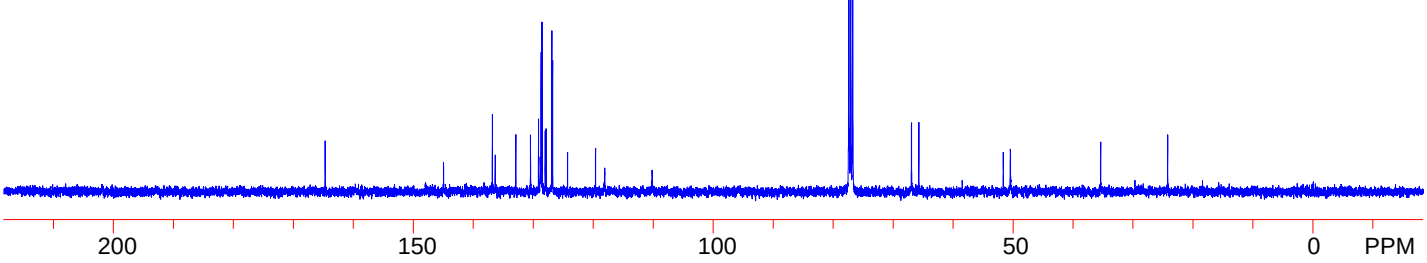






9

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



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

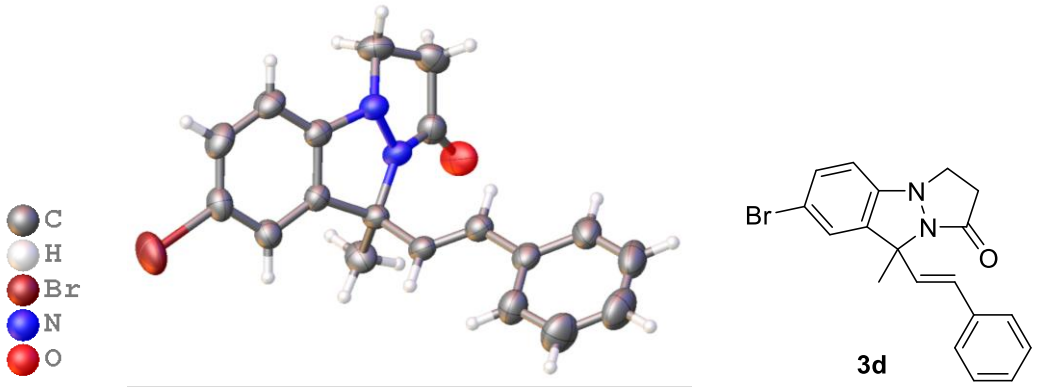


Figure S1 X-ray crystal structure of **3d** with 50% ellipsoid probability

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 Kα radiation, λ = 1.54184 Å. 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	$C_{19}H_{17}BrN_2O$
Formula weight	369.25
Temp, K	293(2)
Crystal system	monoclinic
Space group	C2/c
a, Å	31.6641(9)
b, Å	7.1775(2)
c, 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> 2σ(I))	0.0511, 0.1304
R_1, wR_2 (all data)	0.0601, 0.1361