Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Unsymmetrical Relay C–H Alkenylation and [2 + 2] Cycloaddition of *N*-Arylsydnones with Allenyl Acetates Leading to Quinoline Fused Cyclobutanes

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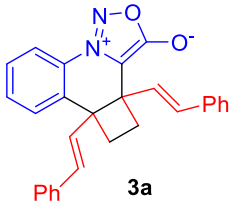
I. General experimental information

Commercial reagents were used without further purification. *N*-Arylsydnones (**1**),[1, 2] allenyl acetates (**2**),[3] and $[Cp^*RhCl_2]_2$ [4] 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 600 MHz and 400 MHz. The ^{13}C NMR spectra were recorded at 150 MHz and 100 MHz. The ^{19}F NMR spectra were recorded at 565 MHz. Chemical shifts were expressed in parts per million (δ), and were reported as s (singlet), d (doublet), t (triplet), dd (doublet of doublet), m (multiplet), etc. The coupling constants *J* were given in Hz. High resolution mass spectra (HRMS) were obtained *via* ESI mode by using a MicrOTOF 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-3nn

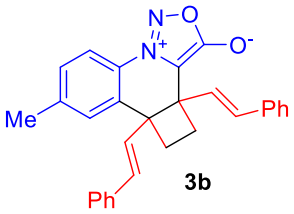
To a reaction tube equipped with a stir bar were charged with 3-phenyl-1,2,3-oxadiazol-3-ium-5-olate (**1a**, 32.4 mg, 0.2 mmol), DCE (2 mL), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), AgOAc (6.7 mg, 0.04 mmol), TEMPO (31.3 mg, 0.2 mmol) and 1-phenylbuta-2,3-dien-1-yl acetate (**2a**, 94.1 mg, 0.5 mmol). The tube was then sealed, and the resulting mixture was stirred at 50 ℃ under argon for 24 h. Upon completion, it was cooled to room temperature, quenched with water and extracted with dichloromethane for three times. 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 (5:1) as eluent to afford **3a**. Other products **3b-3nn** were obtained in a similar manner.



3a

3b,5a-Di((*E*)-styryl)-3b,4,5,5a-tetrahydrocyclobuta[*c*][1,2,3]oxadiazolo[3,4-*a*]quinolin-10-ium-3-olate (3a)

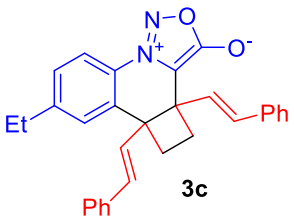
Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (70.3 mg, 84%), mp 190.0-191.3 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.15 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 7.51-7.46 (m, 2H), 7.43 (d, J = 7.8 Hz, 2H), 7.35-7.27 (m, 6H), 7.24 (t, J = 7.8 Hz, 2H), 7.19 (t, J = 7.8 Hz, 1H), 6.79 (d, J = 16.2 Hz, 1H), 6.42 (d, J = 16.2 Hz, 1H), 6.33 (d, J = 16.8 Hz, 1H), 6.22 (d, J = 15.6 Hz, 1H), 2.79-2.72 (m, 2H), 2.59-2.54 (m, 1H), 2.36-2.31 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 166.9, 136.4, 136.3, 134.2, 132.8, 132.3, 132.1, 129.6, 129.4, 129.0, 128.9, 128.62, 128.56, 128.2, 127.9, 127.3, 126.7, 126.6, 117.4, 104.5, 50.2, 45.4, 31.3, 31.1. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{28}H_{22}N_2NaO_2$ 441.1573; Found 441.1557.



3b

7-Methyl-3b,5a-di((*E*)-styryl)-3b,4,5,5a-tetrahydrocyclobuta[*c*][1,2,3]oxadiazolo[3,4-*a*]quinolin-10-ium-3-olate (3b)

Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (64.9 mg, 75%), mp 164.6-165.9 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.03 (d, *J* = 8.4 Hz, 1H), 7.44 (d, *J* = 7.2 Hz, 2H), 7.34 (t, *J* = 7.8 Hz, 2H), 7.31-7.28 (m, 3H), 7.27-7.21 (m, 3H), 7.18 (d, *J* = 7.2 Hz, 1H), 7.09 (s, 1H), 6.79 (d, *J* = 16.2 Hz, 1H), 6.41 (d, *J* = 16.2 Hz, 1H), 6.33 (d, *J* = 16.2 Hz, 1H), 6.22 (d, *J* = 15.6 Hz, 1H), 2.77-2.69 (m, 2H), 2.57-2.52 (m, 1H), 2.36 (s, 3H), 2.32-2.29 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 167.0, 142.9, 136.42, 136.37, 134.0, 132.7, 132.1, 129.6, 129.3, 129.1, 128.9, 128.5, 128.2, 127.9, 127.4, 127.3, 126.73, 126.68, 117.2, 104.2, 50.3, 45.4, 31.2, 31.0, 21.6. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{29}H_{24}N_2NaO_2$ 455.1730; Found 455.1721.

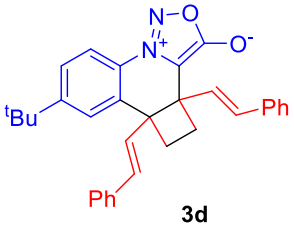


3c

7-Ethyl-3b,5a-di((*E*)-styryl)-3b,4,5,5a-tetrahydrocyclobuta[*c*][1,2,3]oxadiazolo[3,4-*a*]quinolin-10-ium-3-olate (3c)

Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (69.7 mg, 78%), mp 177.4-178.3 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.06 (d, *J* = 8.4 Hz, 1H), 7.44 (d, *J* = 7.8 Hz, 2H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.31-7.28 (m, 4H), 7.24 (t, *J* = 7.8 Hz, 2H), 7.20-7.17 (m, 1H), 7.11 (d, *J* = 1.2 Hz, 1H), 6.80 (d, *J* = 16.2 Hz, 1H), 6.41 (d, *J* = 16.2 Hz, 1H), 6.34 (d, *J* = 16.8 Hz, 1H), 6.22 (d, *J* = 15.6 Hz, 1H), 2.78-2.71 (m, 2H), 2.65 (q, *J* = 7.8 Hz, 2H), 2.58-2.53 (m, 1H), 2.36-2.30 (m, 1H), 1.21 (t, *J* = 7.8 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 167.0, 149.1, 136.4, 134.1, 132.7, 132.1, 129.2, 128.9, 128.53, 128.48, 128.2, 128.1, 127.9, 127.5, 127.4,

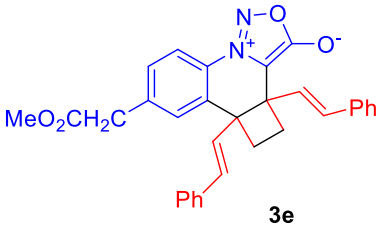
126.73, 126.67, 117.3, 104.2, 50.3, 45.5, 31.2, 31.0, 28.9, 15.3. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{30}H_{26}N_2NaO_2$ 469.1886; Found 469.1889.



3d

7-(*tert*-Butyl)-3b,5a-di((*E*)-styryl)-3b,4,5,5a-tetrahydrocyclobuta[*c*][1,2,3]oxadiazolo[3,4-*a*]quinolin-10-ium-3-olate (3d)

Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (68.3 mg, 72%), mp 106.3-107.3 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.07 (d, *J* = 8.4 Hz, 1H), 7.50 (dd, J_1 = 9.0 Hz, J_2 = 2.4 Hz, 1H), 7.43 (d, *J* = 7.2 Hz, 2H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.31-7.28 (m, 4H), 7.26-7.23 (m, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 6.78 (d, *J* = 16.2 Hz, 1H), 6.41 (d, *J* = 15.6 Hz, 1H), 6.34 (d, *J* = 16.2 Hz, 1H), 6.22 (d, *J* = 15.6 Hz, 1H), 2.78-2.72 (m, 2H), 2.59-2.56 (m, 1H), 2.37-2.32 (m, 1H), 1.29 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 167.0, 155.9, 136.44, 136.37, 133.7, 132.7, 132.2, 129.3, 128.9, 128.5, 128.1, 127.8, 127.4, 127.2, 126.7, 126.6, 125.9, 125.8, 117.0, 104.2, 50.5, 45.5, 35.3, 31.21, 31.17, 31.08. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{32}H_{30}N_2NaO_2$ 497.2199; Found 497.2194.

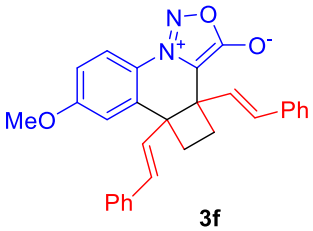


3e

7-(2-Methoxy-2-oxoethyl)-3b,5a-di((*E*)-styryl)-3b,4,5,5a-tetrahydrocyclobuta[*c*][1,2,3]oxadiazolo[3,4-*a*]quinolin-10-ium-3-olate (3e)

Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (64.8 mg, 66%), mp 80.6-81.7 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.12 (d, *J* = 8.4 Hz, 1H), 7.44-7.41 (m, 3H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.31-7.28 (m, 3H), 7.26-7.23 (m, 2H), 7.21-7.18 (m, 2H), 6.80 (d, *J* = 16.2 Hz, 1H), 6.41 (d, *J* = 16.2 Hz, 1H), 6.32 (d, *J* = 16.2

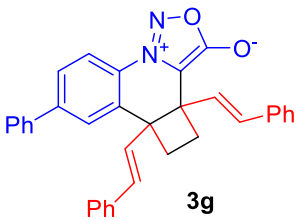
Hz, 1H), 6.21 (d, *J* = 15.6 Hz, 1H), 3.67 (s, 3H), 3.64 (s, 2H), 2.79-2.71 (m, 2H), 2.58-2.54 (m, 1H), 2.37-2.31 (m, 1H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150 MHz): δ 170.9, 166.9, 138.5, 136.3, 136.2, 134.4, 132.9, 132.4, 130.2, 129.7, 128.9, 128.8, 128.64, 128.56, 128.3, 127.9, 127.2, 126.74, 126.70, 117.6, 104.4, 52.4, 50.2, 45.5, 40.8, 31.3, 31.0. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{31}H_{26}N_2NaO_4$ 513.1785; Found 513.1776.



3f

7-Methoxy-3b,5a-di((*E*)-styryl)-3b,4,5,5a-tetrahydrocyclobuta[*c*][1,2,3]oxadiazolo[3,4-*a*]quinolin-10-ium-3-olate (3f)

Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (78.9 mg, 88%), mp 150.1-150.8 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.09 (d, *J* = 8.4 Hz, 1H), 7.43 (d, *J* = 7.8 Hz, 2H), 7.35-7.27 (m, 5H), 7.25-7.22 (m, 2H), 7.18 (t, *J* = 7.2 Hz, 1H), 6.96 (dd, J_1 = 9.0 Hz, J_2 = 2.4 Hz, 1H), 6.81-6.78 (m, 2H), 6.41 (d, *J* = 15.6 Hz, 1H), 6.33 (d, *J* = 16.2 Hz, 1H), 6.21 (d, *J* = 15.6 Hz, 1H), 3.79 (s, 3H), 2.76-2.71 (m, 2H), 2.57-2.53 (m, 1H), 2.36-2.31 (m, 1H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150 MHz): δ 166.9, 162.2, 136.4, 136.3, 136.2, 132.7, 132.3, 128.90, 128.86, 128.5, 128.2, 127.9, 127.4, 126.73, 126.65, 122.9, 119.1, 114.2, 113.7, 103.7, 55.8, 50.5, 45.4, 31.1, 31.0. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{29}H_{24}N_2NaO_3$ 471.1679; Found 471.1672.

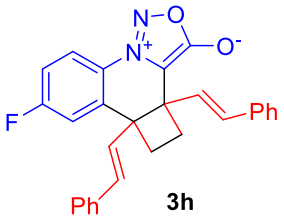


3g

7-Phenyl-3b,5a-di((*E*)-styryl)-3b,4,5,5a-tetrahydrocyclobuta[*c*][1,2,3]oxadiazolo[3,4-*a*]quinolin-10-ium-3-olate (3g)

Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (82.1 mg, 83%), mp 120.2-121.7 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.22 (d, *J* = 8.4 Hz, 1H), 7.68 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 7.52-7.51 (m, 3H),

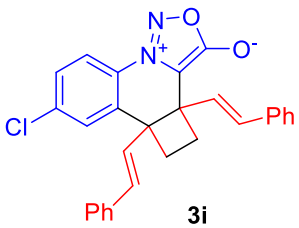
7.44-7.40 (m, 4H), 7.38-7.35 (m, 1H), 7.34-7.31 (m, 4H), 7.28-7.21 (m, 3H), 7.18 (t, *J* = 7.2 Hz, 1H), 6.83 (d, *J* = 16.2 Hz, 1H), 6.46 (d, *J* = 16.2 Hz, 1H), 6.39 (d, *J* = 16.2 Hz, 1H), 6.24 (d, *J* = 16.2 Hz, 1H), 2.81-2.76 (m, 2H), 2.60-2.57 (m, 1H), 2.42-2.35 (m, 1H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150 MHz): δ 166.9, 145.3, 139.1, 136.4, 136.3, 134.8, 132.9, 132.5, 129.2, 129.0, 128.9, 128.7, 128.62, 128.59, 128.3, 127.9, 127.7, 127.33, 127.30, 127.2, 126.8, 126.7, 117.9, 104.4, 50.5, 45.6, 31.3, 31.2. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{34}H_{26}N_2NaO_2$ 517.1886; Found 517.1887.



3h

7-Fluoro-3b,5a-di((*E*)-styryl)-3b,4,5,5a-tetrahydrocyclobuta[*c*][1,2,3]oxadiazolo[3,4-*a*]quinolin-10-ium-3-olate (3h)

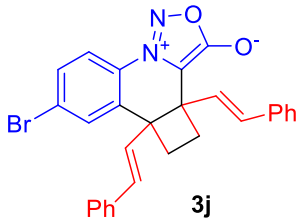
Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (59.4 mg, 68%), mp 101.9-102.5 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.17 (dd, J_1 = 9.0 Hz, J_2 = 3.0 Hz, 1H), 7.43 (d, *J* = 7.2 Hz, 2H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.32-7.29 (m, 3H), 7.26-7.24 (m, 2H), 7.22-7.16 (m, 2H), 7.03 (dd, J_1 = 9.0 Hz, J_2 = 3.0 Hz, 1H), 6.82 (d, *J* = 16.2 Hz, 1H), 6.41 (d, *J* = 16.2 Hz, 1H), 6.31 (d, *J* = 16.8 Hz, 1H), 6.20 (d, *J* = 15.6 Hz, 1H), 2.79-2.72 (m, 2H), 2.59-2.55 (m, 1H), 2.37-2.32 (m, 1H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150 MHz): δ 166.7, 164.3 (d, $^{1}J_{C\text{-}F}$ = 253.8 Hz), 137.2 (d, $^{3}J_{C\text{-}F}$ = 7.7 Hz), 136.1 (d, $^{2}J_{C\text{-}F}$ = 33.9 Hz), 133.0 (d, $^{2}J_{C\text{-}F}$ = 31.8 Hz), 129.0, 128.6, 128.5, 128.02, 128.00, 126.9, 126.74, 126.69, 125.8 (d, $^{4}J_{C\text{-}F}$ = 3.3 Hz), 119.8 (d, $^{3}J_{C\text{-}F}$ = 9.9 Hz), 116.3, 116.1, 115.9, 104.3, 50.3, 45.4, 31.3, 31.0. ^{19}F NMR (565 MHz, $CDCl_3$) δ: -105.18 – -105.22 (m). HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{28}H_{21}FN_2NaO_2$ 459.1479; Found 459.1474.



3i

7-Chloro-3b,5a-di((*E*)-styryl)-3b,4,5,5a-tetrahydrocyclobuta[*c*][1,2,3]oxadiazolo[3,4-*a*]quinolin-10-ium-3-olate (3i)

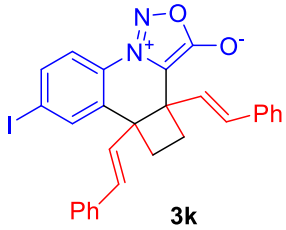
Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (59.8 mg, 66%), mp 167.4-168.5 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.10 (d, *J* = 9.0 Hz, 1H), 7.46-7.44 (m, 3H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.31-7.30 (m, 4H), 7.26-7.24 (m, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 6.82 (d, *J* = 16.2 Hz, 1H), 6.41 (d, *J* = 16.2 Hz, 1H), 6.30 (d, *J* = 16.2 Hz, 1H), 6.19 (d, *J* = 15.6 Hz, 1H), 2.79-7.72 (m, 2H), 2.58-2.54 (m, 1H), 2.36-2.30 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 166.6, 138.2, 136.2, 136.05, 136.00, 133.2, 132.9, 129.3, 129.0, 128.9, 128.6, 128.5, 128.1, 128.0, 127.9, 126.8, 126.7, 118.9, 104.5, 50.2, 45.5, 31.3, 31.0. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{28}H_{21}ClN_2NaO_2$ 475.1184; Found 475.1176.



3j

7-Bromo-3b,5a-di((*E*)-styryl)-3b,4,5,5a-tetrahydrocyclobuta[*c*][1,2,3]oxadiazolo[3,4-*a*]quinolin-10-ium-3-olate (3j)

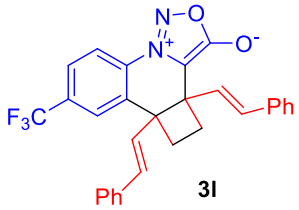
Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (75.6 mg, 76%), mp 117.7-118.1 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.03 (d, *J* = 9.0 Hz, 1H), 7.61 (dd, J_1 = 9.0 Hz, J_2 = 2.4 Hz, 1H), 7.45-7.44 (m, 3H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.32-7.30 (m, 3H), 7.26-7.24 (m, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 6.82 (d, *J* = 16.2 Hz, 1H), 6.41 (d, *J* = 16.2 Hz, 1H), 6.30 (d, *J* = 16.2 Hz, 1H), 6.18 (d, *J* = 16.2 Hz, 1H), 2.79-2.72 (m, 2H), 2.58-2.54 (m, 1H), 2.36-2.30 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 166.6, 136.2, 136.1, 136.0, 133.2, 132.9, 132.3, 131.9, 129.0, 128.58, 128.56, 128.45, 128.0, 127.9, 126.8, 126.7, 126.4, 119.0, 104.5, 50.1, 45.5, 31.4, 31.0. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{28}H_{21}BrN_2NaO_2$ 519.0679; Found 519.0672.



3k

7-Iodo-3b,5a-di((*E*)-styryl)-3b,4,5,5a-tetrahydrocyclobuta[*c*][1,2,3]oxadiazolo[3,4-*a*]quinolin-10-ium-3-olate (3k)

Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (50.1 mg, 46%), mp 146.3-146.8 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.87 (d, J = 8.4 Hz, 1H), 7.81 (dd, J_1 = 9.0 Hz, J_2 = 1.8 Hz, 1H), 7.64 (d, J = 1.8 Hz, 1H), 7.44 (d, J = 7.2 Hz, 2H), 7.36 (t, J = 7.2 Hz, 2H), 7.32-7.29 (m, 3H), 7.26-7.23 (m, 2H), 7.21-7.19 (m, 1H), 6.80 (d, J = 16.2 Hz, 1H), 6.40 (d, J = 16.2 Hz, 1H), 6.29 (d, J = 16.2 Hz, 1H), 6.18 (d, J = 16.2 Hz, 1H), 2.79-2.72 (m, 2H), 2.57-2.53 (m, 1H), 2.35-2.27 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 166.6, 138.2, 137.8, 136.2, 136.04, 135.99, 133.1, 132.9, 129.2, 129.0, 128.6, 128.4, 128.03, 128.01, 126.9, 126.8, 126.7, 118.8, 104.5, 98.4, 49.9, 45.5, 31.4, 31.0. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{28}H_{21}IN_2NaO_2$ 567.0540; Found 567.0536.

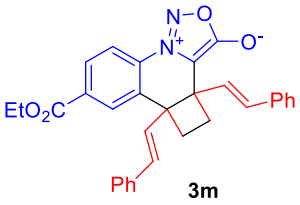


3l

3b,5a-Di((*E*)-styryl)-7-(trifluoromethyl)-3b,4,5,5a-tetrahydrocyclobuta[*c*][1,2,3]oxadiazolo[3,4-*a*]quinolin-10-ium-3-olate (3l)

Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (59.4 mg, 61%), mp 122.4-123.9 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.30 (d, J = 9.0 Hz, 1H), 7.75 (dd, J_1 = 9.0 Hz, J_2 = 1.8 Hz, 1H), 7.59 (s, 1H), 7.44 (d, J = 7.8 Hz, 2H), 7.36 (t, J = 7.8 Hz, 2H), 7.32-7.30 (m, 3H), 7.26-7.24 (m, 2H), 7.22-7.19 (m, 1H), 6.85 (d, J = 16.2 Hz, 1H), 6.43 (d, J = 16.2 Hz, 1H), 6.32 (d, J = 16.2 Hz, 1H), 6.20 (d, J = 16.2 Hz, 1H), 2.84-2.77 (m, 2H), 2.61-2.56 (m, 1H), 2.38-2.33 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 166.6, 136.1, 135.9, 135.3, 134.0 (q, $^{2}J_{C\text{-}F}$ = 34.1 Hz), 133.38, 133.35, 131.9, 129.0, 128.6, 128.5, 128.1, 127.7, 126.8, 126.7, 126.62,

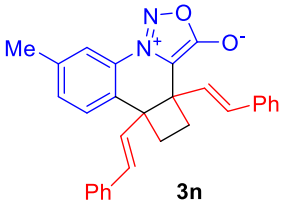
126.57, 125.7 (q, $^{3}J_{C\text{-}F}$ = 3.3 Hz), 123.0 (q, $^{1}J_{C\text{-}F}$ = 271.4 Hz), 118.2, 105.1, 50.2, 45.5, 31.4, 31.1. ^{19}F NMR (565 MHz, $CDCl_3$) δ: -62.9 (s). HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{29}H_{21}F_3N_2NaO_2$ 509.1447; Found 509.1447.



3m

7-(Ethoxycarbonyl)-3b,5a-di((*E*)-styryl)-3b,4,5,5a-tetrahydrocyclobuta[*c*][1,2,3]oxadiazolo[3,4-*a*]quinolin-10-ium-3-olate (3m)

Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (83.4 mg, 85%), mp 92.9-93.8 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.23 (d, *J* = 8.4 Hz, 1H), 8.14 (dd, J_1 = 9.0 Hz, J_2 = 1.8 Hz, 1H), 8.01 (d, *J* = 1.8 Hz, 1H), 7.43-7.42 (m, 2H), 7.34-7.31 (m, 4H), 7.29-7.27 (m, 1H), 7.25-7.23 (m, 2H), 7.20-7.18 (m, 1H), 6.80 (d, *J* = 16.2 Hz, 1H), 6.46 (d, *J* = 16.2 Hz, 1H), 6.33 (d, *J* = 16.2 Hz, 1H), 6.22 (d, *J* = 16.2 Hz, 1H), 4.39-4.33 (m, 2H), 2.82-2.77 (m, 2H), 2.58-2.55 (m, 1H), 2.38-2.32 (m, 1H), 1.35 (t, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 166.6, 164.8, 136.3, 136.2, 134.7, 133.9, 133.1, 133.0, 132.4, 130.9, 129.7, 128.9, 128.6, 128.5, 128.3, 128.0, 126.9, 126.8, 117.5, 105.0, 61.9, 50.2, 45.4, 31.33, 31.25, 14.3. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{31}H_{26}N_2NaO_4$ 513.1785; Found 513.1765.

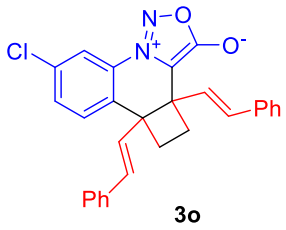


3n

8-Methyl-3b,5a-di((*E*)-styryl)-3b,4,5,5a-tetrahydrocyclobuta[*c*][1,2,3]oxadiazolo[3,4-*a*]quinolin-10-ium-3-olate (3n)

Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (58.8 mg, 68%), mp 190.9-191.4 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.97 (s, 1H), 7.42 (d, *J* = 7.2 Hz, 2H), 7.35-7.29 (m, 6H), 7.28-7.23 (m, 2H), 7.21-7.18 (m, 2H), 6.76 (d, *J* = 16.2 Hz, 1H), 6.41 (d, *J* = 16.2 Hz, 1H), 6.32 (d, *J* = 16.2 Hz, 1H), 6.22 (d, *J* = 16.2 Hz,

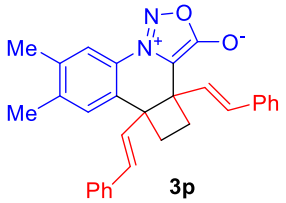
1H), 2.77-2.70 (m, 2H), 2.57-2.53 (m, 1H), 2.45 (s, 3H), 2.33-2.28 (m, 1H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150 MHz): δ 167.0, 139.1, 136.4, 136.3, 132.9, 132.7, 132.1, 131.2, 129.5, 129.23, 129.18, 128.9, 128.5, 128.2, 127.9, 127.3, 126.7, 126.6, 117.6, 104.6, 50.1, 45.4, 31.2, 31.1, 21.2. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{29}H_{24}N_2NaO_2$ 455.1730; Found 455.1726.



3o

8-Chloro-3b,5a-di((*E*)-styryl)-3b,4,5,5a-tetrahydrocyclobuta[*c*][1,2,3]oxadiazolo[3,4-*a*]quinolin-10-ium-3-olate (3o)

Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (59.8 mg, 66%), mp 111.1-112.2 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.17 (d, J = 2.4 H, 1H), 7.47 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 7.42 (d, J = 7.2 Hz, 2H), 7.35 (t, J = 7.2 Hz, 2H), 7.32-7.29 (m, 4H), 7.28-7.24 (m, 2H), 7.21 (t, J = 7.2 Hz, 1H), 6.78 (d, J = 16.2 Hz, 1H), 6.41 (d, J = 16.2 Hz, 1H), 6.29 (d, J = 16.2 Hz, 1H), 6.19 (d, J = 16.2 Hz, 1H), 2.79-2.72 (m, 2H), 2.59-2.54 (m, 1H), 2.35-2.29 (m, 1H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150 MHz): δ 166.6, 136.2, 136.0, 134.7, 133.1, 132.8, 132.6, 132.1, 130.7, 130.3, 128.9, 128.6, 128.4, 128.3, 128.0, 126.8, 126.7, 126.6, 117.7, 104.8, 50.0, 45.4, 31.3, 31.1. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{28}H_{21}ClN_2NaO_2$ 475.1184; Found 475.1174.

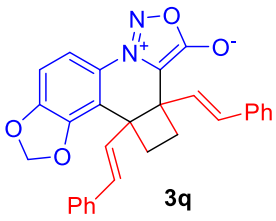


3p

7,8-Dimethyl-3b,5a-di((*E*)-styryl)-3b,4,5,5a-tetrahydrocyclobuta[*c*][1,2,3]oxadiazolo[3,4-*a*]quinolin-10-ium-3-olate (3p)

Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (67.9 mg, 76%), mp 99.1-99.7 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.92 (s, 1H), 7.44-7.43 (m, 2H), 7.34 (t, J = 7.8 Hz, 2H), 7.31-7.27 (m, 3H), 7.25-7.22 (m, 2H), 7.19-7.17 (m, 1H), 7.03 (s, 1H), 6.76 (d, J = 16.2 Hz, 1H), 6.40 (d, J = 16.2 Hz, 1H), 6.32 (d, J = 16.2 Hz, 1H),

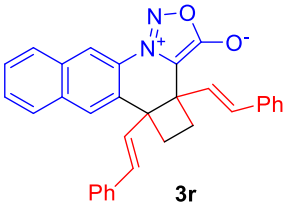
6.21 (d, *J* = 16.2 Hz, 1H), 2.76-2.69 (m, 2H), 2.56-2.51 (m, 1H), 2.34 (s, 3H), 2.32-2.27 (m, 1H), 2.26 (s, 3H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150 MHz): δ 167.0, 141.7, 137.7, 136.5, 136.4, 132.6, 131.9, 131.4, 129.9, 129.4, 128.9, 128.5, 128.1, 127.8, 127.5, 127.4, 126.7, 126.6, 117.9, 104.2, 50.0, 45.5, 31.14, 31.08, 20.0, 19.7. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{30}H_{26}N_2NaO_2$ 469.1886; Found 469.1875.



3q

9c,11a-Di((*E*)-styryl)-9c,10,11,11a-tetrahydrocyclobuta[*c*][1,3]dioxolo[4,5-*f*][1,2,3]oxadiazolo[3,4-*a*]quinolin-4-ium-1-olate (3q)

Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (64.8 mg, 70%), mp 198.5-199.4 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.75 (d, *J* = 9.0 Hz, 1H), 7.38 (d, *J* = 7.2 Hz, 2H), 7.30-7.25 (m, 6H), 7.22-7.20 (m, 2H), 6.94 (d, *J* = 8.4 Hz, 1H), 6.74 (d, *J* = 16.2 Hz, 1H), 6.31-6.23 (m, 3H), 6.03 (d, *J* = 30.0 Hz, 2H), 2.87-2.81 (m, 1H), 2.72-2.68 (m, 1H), 2.46-2.41 (m, 2H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150 MHz): δ 166.4, 150.6, 146.2, 136.6, 136.5, 132.7, 131.8, 129.1, 128.7, 128.6, 127.9, 127.8, 126.9, 126.5, 126.1, 124.3, 117.6, 111.7, 108.1, 103.3, 102.8, 48.1, 45.2, 31.2, 29.9. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{29}H_{22}N_2NaO_4$ 485.1472; Found 485.1463.

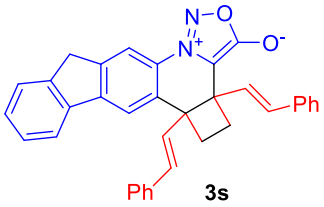


3r

3b,5a-Di((*E*)-styryl)-3b,4,5,5a-tetrahydrobenzo[*g*]cyclobuta[*c*][1,2,3]oxadiazolo[3,4-*a*]quinolin-12-ium-3-olate (3r)

Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (70.3 mg, 75%), mp 116.1-116.7 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.70 (s, 1H), 7.97-7.96 (m, 1H), 7.79-7.77 (m, 1H), 7.74 (s, 1H), 7.59-7.55 (m, 2H), 7.51 (d, *J* = 7.8 Hz, 2H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.33-7.29 (m, 3H),7.24-7.22 (m, 2H), 7.18 (t, *J* = 7.2 Hz,

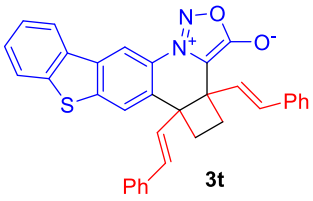
1H), 6.95 (d, *J* = 16.2 Hz, 1H), 6.46 (d, *J* = 16.2 Hz, 1H), 6.40 (d, *J* = 16.2 Hz, 1H), 6.25 (d, *J* = 16.2 Hz, 1H), 2.83-2.73 (m, 2H), 2.60-2.57 (m, 1H), 2.38-2.33 (m, 1H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150 MHz): δ 167.1, 136.4, 136.3, 134.5, 132.9, 132.2, 131.8, 131.0, 129.0, 128.88, 128.86, 128.8, 128.7, 128.6, 128.3, 128.2, 128.0, 127.9, 127.44, 127.36, 126.75, 126.73, 117.0, 105.7, 50.4, 45.9, 31.1, 30.8. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{32}H_{24}N_2NaO_2$ 491.1730; Found 491.1727.



3s

3b,5a-Di((*E*)-styryl)-3b,4,5a,11-tetrahydro-5*H*-cyclobuta[*c*]indeno[1,2-*g*][1,2,3]oxadiazolo[3,4-*a*]quinolin-13-ium-3-olate (3s)

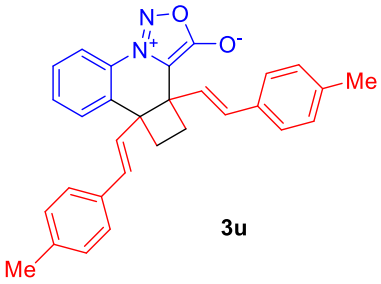
Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (70.9 mg, 70%), mp 141.1-142.5 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.33 (s, 1H), 7.74-7.73 (m, 1H), 7.65 (s, 1H), 7.59-7.57 (m, 1H), 7.47 (d, *J* = 7.2 Hz, 2H), 7.37-7.35 (m, 4H), 7.33-7.30 (m, 3H), 7.26-7.23 (m, 2H), 7.20-7.18 (m, 1H), 6.85 (d, *J* = 16.2 Hz, 1H), 6.46-6.41 (m, 2H), 6.25 (d, *J* = 16.2 Hz, 1H), 4.01 (s, 2H), 2.82-2.76 (m, 2H), 2.62-2.58 (m, 1H), 2.41-2.36 (m, 1H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150 MHz): δ 167.0, 145.7, 144.0, 143.5, 139.7, 136.41, 136.40, 133.4, 132.8, 132.2, 129.4, 128.9, 128.54, 128.51, 128.2, 128.0, 127.9, 127.4, 127.3, 126.7, 125.4, 121.0, 120.0, 114.1, 104.4, 50.7, 45.5, 36.9, 31.3, 31.2. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{35}H_{26}N_2NaO_2$ 529.1886; Found 529.1885.



3t

3b,5a-Di((*E*)-styryl)-3b,4,5,5a-tetrahydrobenzo[4,5]thieno[2,3-*g*]cyclobuta[*c*][1,2,3]oxadiazolo[3,4-*a*]quinolin-13-ium-3-olate (3t)

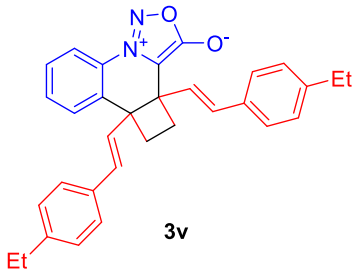
Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (75.5 mg, 72%), mp 154.2-155.8 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.91 (s, 1H), 8.24-8.21 (m, 1H), 7.87-7.84 (m, 1H), 7.76 (s, 1H), 7.55-7.53 (m, 2H), 7.49 (d, *J* = 7.2 Hz, 2H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.33-7.31 (m, 3H), 7.26-7.23 (m, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 6.91 (d, *J* = 16.8 Hz, 1H), 6.45-6.42 (m, 2H), 6.25 (d, *J* = 16.2 Hz, 1H), 2.83-2.76 (m, 2H), 2.63-2.59 (m, 1H), 2.43-2.37 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 167.0, 143.2, 140.3, 136.3, 136.2, 135.5, 134.4, 133.0, 132.5, 132.3, 129.0, 128.7, 128.6, 128.4, 128.2, 128.0, 127.2, 126.8, 126.7, 125.3, 123.10, 123.08, 122.3, 110.5, 105.0, 50.7, 45.8, 31.3, 31.0. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{34}H_{24}N_2NaO_2S$ 547.1451; Found 547.1444.



3u

3b,5a-Bis((*E*)-4-methylstyryl)-3b,4,5,5a-tetrahydrocyclobuta[*c*][1,2,3]oxadiazolo[3,4-*a*]quinolin-10-ium-3-olate (3u)

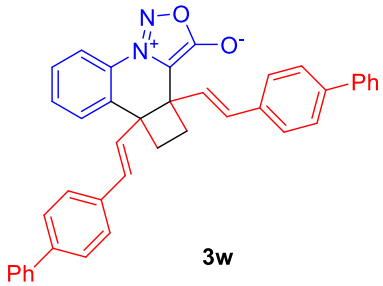
Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (72.3 mg, 81%), mp 187.2-187.7 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.15 (dd, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 7.50-7.45 (m, 2H), 7.33-7.32 (m, 3H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 7.8 Hz, 2H), 7.05 (d, *J* = 7.8 Hz, 2H), 6.75 (d, *J* = 16.2 Hz, 1H), 6.36 (d, *J* = 15.6 Hz, 1H), 6.27 (d, *J* = 16.2 Hz, 1H), 6.16 (d, *J* = 15.6 Hz, 1H), 2.77-2.69 (m, 2H), 2.57-2.54 (m, 1H), 2.35 (s, 3H), 2.33-2.30 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 167.0, 138.2, 137.7, 134.3, 133.6, 133.5, 132.6, 132.1, 132.0, 129.7, 129.6, 129.4, 129.2, 128.5, 127.9, 126.6, 126.5, 126.3, 117.3, 104,7, 50.2, 45.4, 31.4, 31.0, 21.22, 21.21. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{30}H_{26}N_2NaO_2$ 469.1886; Found 469.1880.



3v

3b,5a-Bis((*E*)-4-ethylstyryl)-3b,4,5,5a-tetrahydrocyclobuta[*c*][1,2,3]oxadiazolo[3,4-*a*]quinolin-10-ium-3-olate (3v)

Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (78.8 mg, 83%), mp 155.5-156.9 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.15-8.14 (m, 1H), 7.49-7.45 (m, 2H), 7.36 (d, J = 7.8 Hz, 2H), 7.33 (dd, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 7.24-7.23 (m, 2H), 7.18 (d, J = 7.8 Hz, 2H), 7.08 (d, J = 8.4 Hz, 2H), 6.76 (d, J = 16.2 Hz, 1H), 6.38 (d, J = 16.2 Hz, 1H), 6.29 (d, J = 16.2 Hz, 1H), 6.18 (d, J = 16.2 Hz, 1H), 2.77-2.70 (m, 2H), 2.65 (q, J = 7.8 Hz, 2H), 2.61-2.54 (m, 3H), 2.34-2.28 (m, 1H), 1.24 (t, J = 7.8 Hz, 3H), 1.19 (t, J = 7.8 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 167.0, 144.6, 144.1, 134.3, 133.9, 133.8, 132.7, 132.1, 132.0, 129.7, 129.4, 128.5, 128.4, 128.1, 128.0, 126.74, 126.65, 126.3, 117.3, 104.7, 50.3, 45.4, 31.4, 31.0, 28.7, 28.6, 15.6, 15.5. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{32}H_{30}N_2NaO_2$ 497.2199; Found 497.2190.

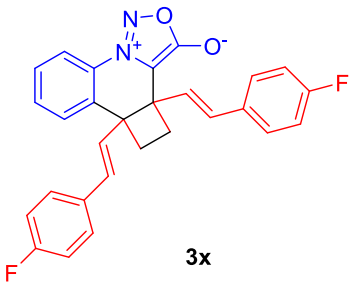


3w

3b,5a-Bis((*E*)-2-([1,1'-biphenyl]-4-yl)vinyl)-3b,4,5,5a-tetrahydrocyclobuta[*c*][1,2,3]oxadiazolo[3,4-*a*]quinolin-10-ium-3-olate (3w)

Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (77.6 mg, 68%), mp 239.8-240.3 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.17 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 7.59-7.54 (m, 6H), 7.52-7.47 (m, 6H), 7.44-7.38 (m, 6H), 7.36-7.29 (m, 3H), 6.82 (d, J = 16.2 Hz, 1H), 6.48 (d, J = 16.2 Hz, 1H), 6.39 (d, J = 16.2 Hz, 1H), 6.28 (d, J = 16.2 Hz, 1H), 2.82-2.74 (m, 2H), 2.61-2.58 (m, 1H), 2.38-2.33 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$,

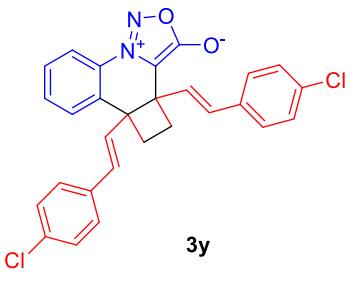
150 MHz): δ 166.9, 141.1, 140.65, 140.60, 140.5, 135.4, 135.3, 134.2, 132.4, 132.1, 131.9, 129.7, 129.4, 129.1, 128.9, 128.8, 128.7, 127.59, 127.57, 127.4, 127.3, 127.24, 127.19, 127.1, 127.00, 126.95, 117.4, 104.5, 50.4, 45.5, 31.3, 31.1. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{40}H_{30}N_2NaO_2$ 593.2199; Found 593.2192.



3x

3b,5a-Bis((*E*)-4-fluorostyryl)-3b,4,5,5a-tetrahydrocyclobuta[*c*][1,2,3]oxadiazolo[3,4-*a*]quinolin-10-ium-3-olate (3x)

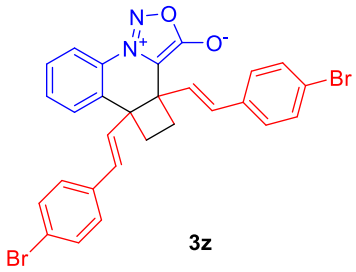
Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (64.5 mg, 71%), mp 220.1-220.9 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.17 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 7.54-7.48 (m, 2H), 7.39-7.36 (m, 2H), 7.33 (dd, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 7.29-7.26 (m, 2H), 7.05-7.01 (m, 2H), 6.96-6.93 (m, 2H), 6.72 (d, J = 16.2 Hz, 1H), 6.40 (d, J = 16.2 Hz, 1H), 6.23 (d, J = 16.2 Hz, 1H), 6.12 (d, J = 15.6 Hz, 1H), 2.77-2.71 (m, 2H), 2.58-2.54 (m, 1H), 2.37-2.32 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 166.8, 162.7 (d, $^1J_{C\text{-}F}$ = 247.2 Hz), 162.5 (d, $^1J_{C\text{-}F}$ = 246.2 Hz), 134.1, 132.47 (d, $^4J_{C\text{-}F}$ = 3.3 Hz), 132.37 (d, $^4J_{C\text{-}F}$ = 3.3 Hz), 132.1, 131.7, 131.2, 129.6, 129.3, 128.8, 128.7, 128.2 (d, $^3J_{C\text{-}F}$ = 7.7 Hz), 128.1 (d, $^3J_{C\text{-}F}$ = 7.7 Hz), 126.9 (d, $^5J_{C\text{-}F}$ = 2.3 Hz), 117.4, 115.8 (d, $^2J_{C\text{-}F}$ = 21.9 Hz), 115.5 (d, $^2J_{C\text{-}F}$ = 20.9 Hz), 104.3, 50.1, 45.3, 31.15, 31.12. ^{19}F NMR (565 MHz, $CDCl_3$) δ: -113.25 – -113.30, -113.78 – -113.83 (m). HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{28}H_{20}F_2N_2NaO_2$ 477.1385; Found 477.1379.



3y

3b,5a-Bis((*E*)-4-chlorostyryl)-3b,4,5,5a-tetrahydrocyclobuta[*c*][1,2,3]oxadiazolo[3,4-*a*]quinolin-10-ium-3-olate (3y)

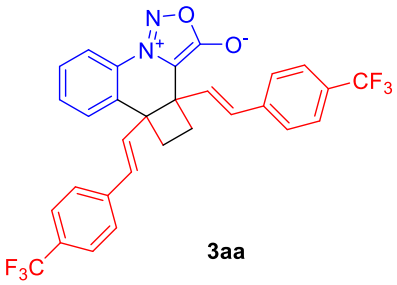
Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (74.1 mg, 76%), mp 204.5-205.3 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): 8.16 (d, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 7.54-7.48 (m, 2H), 7.33-7.29 (m, 5H), 7.24-7.21 (m, 4H), 6.71 (d, J = 15.6 Hz, 1H), 6.40 (d, J = 15.6 Hz, 1H), 6.28 (d, J = 16.2 Hz, 1H), 6.17 (d, J = 16.2 Hz, 1H), 2.76-2.71 (m, 2H), 2.58-2.53 (m, 1H), 2.38-2.31 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 166.8, 134.8, 134.6, 134.0, 133.9, 133.7, 132.2, 131.7, 131.2, 129.7, 129.6, 129.3, 129.1, 128.8, 128.7, 127.9, 127.74, 127.71, 117.4, 104.1, 50.2, 45.3, 31.2, 31.0. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{28}H_{20}Cl_2N_2NaO_2$ 509.0794; Found 509.0788.



3z

3b,5a-Bis((*E*)-4-bromostyryl)-3b,4,5,5a-tetrahydrocyclobuta[*c*][1,2,3]oxadiazolo[3,4-*a*]quinolin-10-ium-3-olate (3z)

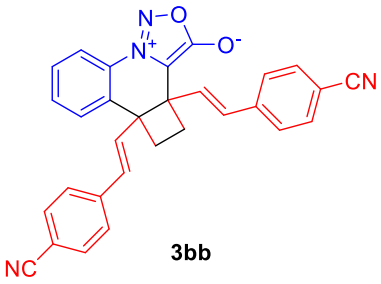
Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (76.1 mg, 66%), mp 204.5-205.3 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.16 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 7.54-7.48 (m, 2H), 7.45 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 7.31 (dd, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 7.27-7.25 (m, 2H), 7.16 (d, J = 8.4 Hz, 2H), 6.69 (d, J = 16.2 Hz, 1H), 6.38 (d, J = 16.2 Hz, 1H), 6.29 (d, J = 16.2 Hz, 1H), 6.18 (d, J = 16.2 Hz, 1H), 2.76-2.71 (m, 2H), 2.57-2.53 (m, 1H), 2.38-2.31 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 166.8, 135.2, 135.1, 133.9, 132.2, 132.0, 131.8, 131.7, 131.3, 129.8, 129.6, 129.3, 128.8, 128.2, 128.0, 127.8, 122.2, 121.8, 117.4, 104.0, 50.2, 45.3, 31.2, 31.0. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{28}H_{20}Br_2N_2NaO_2$ 596.9784; Found 596.9782.



3aa

3b,5a-Bis((*E*)-4-(trifluoromethyl)styryl)-3b,4,5,5a-tetrahydrocyclobuta[*c*][1,2,3]oxadiazolo[3,4-*a*]quinoli n-10-ium-3-olate (3aa)

Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (58.8 mg, 53%), mp 96.9-97.5 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.20-8.18 (m, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.56-7.49 (m, 6H), 7.41 (d, *J* = 7.8 Hz, 2H), 7.33-7.31 (m, 1H), 6.80 (d, *J* = 16.2 Hz, 1H), 6.52 (d, *J* = 16.2 Hz, 1H), 6.42 (d, *J* = 16.2 Hz, 1H), 6.30 (d, *J* = 16.2 Hz, 1H), 2.81-2.75 (m, 2H), 2.62-2.58 (m, 1H), 2.42-2.37 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 166.7, 139.6, 139.5, 133.6, 132.3, 131.74, 131.68, 131.2, 130.2 (q, $^{2}J_{C\text{-}F}$ = 32.9), 129.8 (q, $^{2}J_{C\text{-}F}$ = 31.8 Hz), 129.5, 129.4, 129.3, 128.9, 126.8, 126.7, 125.9 (q, $^{3}J_{C\text{-}F}$ = 4.4 Hz), 125.6 (q, $^{3}J_{C\text{-}F}$ = 4.4 Hz), 124.1 (q, $^{1}J_{C\text{-}F}$ = 270.2 Hz), 124.0 (q, $^{1}J_{C\text{-}F}$ = 270.2 Hz), 117.5, 103.7, 50.2, 45.4, 31.2, 30.9. ^{19}F NMR (565 MHz, $CDCl_3$) δ: -62.56 (s), -62.60 (s). HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{30}H_{20}F_6N_2NaO_2$ 577.1321; Found 577.1317.

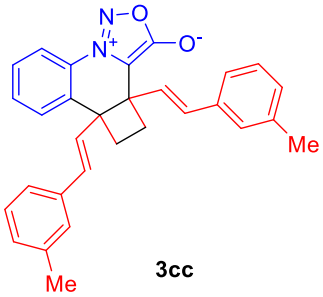


3bb

3b,5a-Bis((*E*)-4-cyanostyryl)-3b,4,5,5a-tetrahydrocyclobuta[*c*][1,2,3]oxadiazolo[3,4-*a*]quinolin-10-ium-3 -olate (3bb)

Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (57.2 mg, 61%), mp 145.4-146.2 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.19 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.58-7.53 (m, 4H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.31 (dd, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 6.76 (d, *J* = 16.2 Hz, 1H), 6.53 (d, *J* = 16.2 Hz, 1H), 6.44 (d, *J* = 16.2 Hz, 1H), 6.34 (d, *J* = 16.2 Hz, 1H), 2.82-2.74 (m, 2H), 2.61-2.57

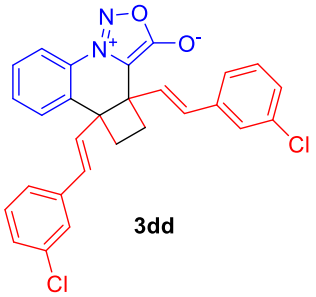
(m, 1H), 2.44-2.40 (m, 1H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150 MHz): δ 166.6, 140.5, 140.3, 133.4, 133.0, 132.7, 132.5, 132.4, 131.5, 131.1, 130.5, 129.5, 129.3, 129.1, 127.1, 127.0, 118.7, 118.6, 117.5, 111.7, 111.3, 103.3, 50.3, 45.4, 31.4, 30.8. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{30}H_{20}N_4NaO_2$ 491.1478; Found 491.1472.



3cc

3b,5a-Bis((*E*)-3-methylstyryl)-3b,4,5,5a-tetrahydrocyclobuta[*c*][1,2,3]oxadiazolo[3,4-*a*]quinolin-10-ium-3-olate (3cc)

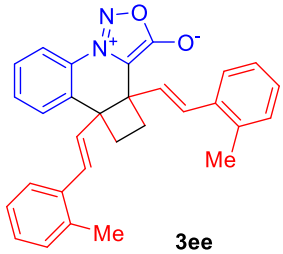
Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (69.7 mg, 78%), mp 175.2-176.9 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.15-8.14 (m, 1H), 7.51-7.45 (m, 2H), 7.33 (dd, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 7.25-7.21 (m, 3H), 7.15-7.10 (m, 4H), 7.01 (d, *J* = 6.6 Hz, 1H), 6.76 (d, *J* = 16.2 Hz, 1H), 6.39 (d, *J* = 16.2 Hz, 1H), 6.32 (d, *J* = 15.6 Hz, 1H), 6.21 (d, *J* = 15.6 Hz, 1H), 2.78-2.71 (m, 2H), 2.58-2.54 (m, 1H), 2.35-2.30 (m, 4H), 2.27 (s, 3H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150 MHz): δ 166.9, 138.5, 138.1, 136.4, 136.3, 134.2, 132.9, 132.3, 132.1, 129.7, 129.4, 129.01, 128.96, 128.8, 128.7, 128.6, 128.4, 127.5, 127.4, 127.2, 123.92, 123.87, 117.3, 104.6, 50.3, 45.4, 31.2, 31.0, 21.40, 21.35. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{30}H_{26}N_2NaO_2$ 469.1886; Found 469.1877.



3dd

3b,5a-Bis((*E*)-3-chlorostyryl)-3b,4,5,5a-tetrahydrocyclobuta[*c*][1,2,3]oxadiazolo[3,4-*a*]quinolin-10-ium-3-olate (3dd)

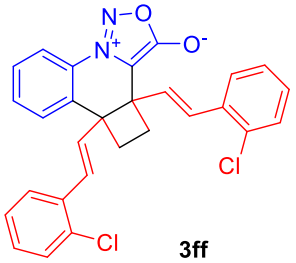
Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (69.2 mg, 71%), mp 184.2-185.3 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.16 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 7.55-7.49 (m, 2H), 7.39 (s, 1H), 7.32-7.30 (m, 2H), 7.28-7.24 (m, 3H), 7.19-7.17 (m, 3H), 6.71 (d, J = 16.2 Hz, 1H), 6.41 (d, J = 16.2 Hz, 1H), 6.32 (d, J = 16.2 Hz, 1H), 6.21 (d, J = 16.2 Hz, 1H), 2.77-2.72 (m, 2H), 2.58-2.55 (m, 1H), 2.39-2.33 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 166.7, 138.1, 138.0, 134.9, 134.5, 133.8, 132.2, 131.7, 131.2, 130.6, 130.1, 129.8, 129.5, 129.3, 128.8, 128.5, 128.2, 127.9, 126.7, 126.6, 124.9, 124.7, 117.4, 103.9, 50.2, 45.3, 31.2, 30.9. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{28}H_{20}Cl_2N_2NaO_2$ 509.0794; Found 509.0788.



3ee

3b,5a-Bis((*E*)-2-methylstyryl)-3b,4,5,5a-tetrahydrocyclobuta[*c*][1,2,3]oxadiazolo[3,4-*a*]quinolin-10-ium-3-olate (3ee)

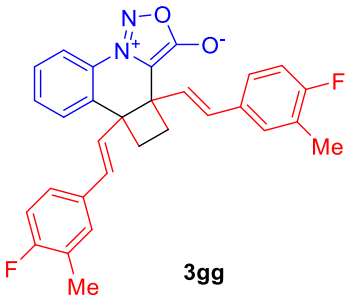
Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (62.5 mg, 70%), mp 180.2-181.5 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.16 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 7.53 (td, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 7.48 (td, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 7.43 (d, J = 7.2 Hz, 1H), 7.38 (dd, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 7.33 (d, J = 7.8 Hz, 1H), 7.20-7.18 (m. 2H), 7.16-7.06 (m, 4H), 6.99 (d, J = 16.2 Hz, 1H), 6.70 (d, J = 16.2 Hz, 1H), 6.21 (d, J = 16.2 Hz, 1H), 6.07 (d, J = 15.6 Hz, 1H), 2.81-2.76 (m, 2H), 2.60-2.57 (m, 1H), 2.39 (s, 3H), 2.38-2.34 (m, 1H), 2.27 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 166.8, 135.9, 135.61, 135.58, 134.3, 132.1, 131.2, 130.8, 130.5, 130.3, 130.2, 129.7, 129.4, 128.6, 128.4, 128.1, 127.8, 126.4, 126.06, 126.03, 125.98, 117.3, 104.4, 50.2, 45.5, 31.4, 31.1, 19.9, 19.8. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{30}H_{26}N_2NaO_2$ 469.1886; Found 469.1884.



3ff

3b,5a-Bis((*E*)-2-chlorostyryl)-3b,4,5,5a-tetrahydrocyclobuta[*c*][1,2,3]oxadiazolo[3,4-*a*]quinolin-10-ium-3-olate (3ff)

Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (74.1 mg, 76%), mp 170.3-171.4 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.17 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 7.55 (td, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 7.51-7.49 (m, 1H), 7.47-7.45 (m, 2H), 7.38 (td, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 2H), 7.30-7.29 (m, 1H), 7.22-7.17 (m, 2H), 7.16-7.11 (m, 3H), 6.90 (d, J = 16.2 Hz, 1H), 6.27 (d, J = 16.2 Hz, 1H), 6.21 (d, J = 15.6 Hz, 1H), 2.87-2.80 (m, 2H), 2.59-2.55 (m, 1H), 2.41-2.37 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 166.8, 134.8, 134.7, 134.0, 133.3, 132.3, 132.2, 129.9, 129.8, 129.63, 129.58, 129.5, 129.2, 129.0, 128.9, 128.7, 127.5, 127.2, 127.1, 126.9, 117.3, 104.0, 50.4, 45.4, 31.6, 30.7. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{28}H_{20}Cl_2N_2NaO_2$ 509.0794; Found 509.0795.

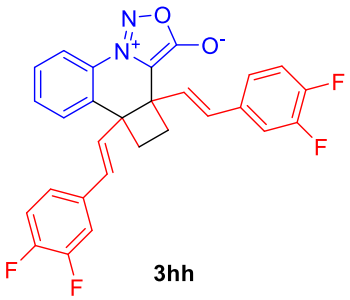


3gg

3b,5a-Bis((*E*)-4-fluoro-3-methylstyryl)-3b,4,5,5a-tetrahydrocyclobuta[*c*][1,2,3]oxadiazolo[3,4-*a*]quinolin-10-ium-3-olate (3gg)

Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (70.4 mg, 73%), mp 209.1-210.0 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.15-8.14 (m, 1H), 7.53-7.47 (m, 2H), 7.34 (d, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 7.25-7.19 (m, 2H), 7.14 (d, J = 7.2 Hz, 1H), 7.11-7.09 (m, 1H), 6.96 (t, J = 9.0 Hz, 1H), 6.87 (t, J = 9.0 Hz, 1H), 6.70 (d, J = 16.2 Hz, 1H), 6.37 (d, J = 16.2 Hz, 1H), 6.22 (d, J = 16.2 Hz, 1H), 6.11 (d, J = 16.2 Hz, 1H), 2.77-2.71 (m,

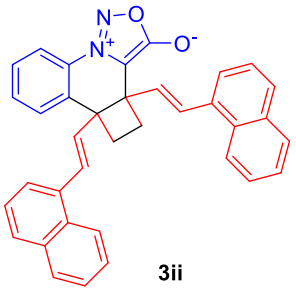
2H), 2.57-2.52 (m, 1H), 2.36-2.31 (m, 1H), 2.23 (s, 3H), 2.19 (s, 3H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150 MHz): δ 166.9, 161.3 (d, $^{1}J_{C\text{-}F}$ = 245.1 Hz), 161.1 (d, $^{1}J_{C\text{-}F}$ = 245.1 Hz), 134.2, 132.3 (d, $^{4}J_{C\text{-}F}$ = 3.3 Hz), 132.2 (d, $^{4}J_{C\text{-}F}$ = 4.4 Hz), 132.1, 131.8, 131.3, 129.8 (d, $^{3}J_{C\text{-}F}$ = 5.4 Hz), 129.7 (d, $^{3}J_{C\text{-}F}$ = 5.6 Hz), 129.6, 129.4, 128.7, 128.6, 126.8, 125.6 (d, $^{3}J_{C\text{-}F}$ = 7.7 Hz), 125.5 (d, $^{3}J_{C\text{-}F}$ = 7.7 Hz), 125.3 (d, $^{2}J_{C\text{-}F}$ = 17.4 Hz), 124.8 (d, $^{2}J_{C\text{-}F}$ = 17.6 Hz), 117.3, 115.4 (d, $^{2}J_{C\text{-}F}$ = 23.1 Hz), 115.1 (d, $^{2}J_{C\text{-}F}$ = 23.0 Hz), 104.4, 50.2, 45.3, 31.12, 31.05, 14.6 (d, $^{3}J_{C\text{-}F}$ = 3.3 Hz), 14.5 (d, $^{3}J_{C\text{-}F}$ = 3.3 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ: -117.59 – -117.60 (m), -118.12 – -118.16 (m). HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{30}H_{24}F_2N_2NaO_2$ 505.1698; Found 505.1697.



3hh

3b,5a-Bis((*E*)-3,4-difluorostyryl)-3b,4,5,5a-tetrahydrocyclobuta[*c*][1,2,3]oxadiazolo[3,4-*a*]quinolin-10-ium-3-olate (3hh)

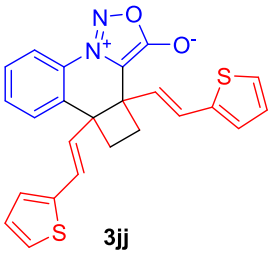
Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (54.0 mg, 55%), mp 224.2-225.9 ℃. ^{1}H NMR (DMSO-d_6, 600 MHz): δ 8.16-8.14 (m, 1H), 7.67-7.64 (m, 1H), 7.62-7.58 (m, 2H), 7.54-7.50 (m, 1H), 7.40-7.32 (m, 4H), 7.25 (br s, 1H), 6.86 (d, *J* = 16.2 Hz, 1H), 6.54-6.49 (m, 2H), 6.44 (d, *J* = 16.2 Hz, 1H), 2.76-2.69 (m, 2H), 2.42-2.37 (m, 2H). $^{13}C\{^{1}H\}$ NMR (DMSO-d_6, 150 MHz): δ 166.3, 150.2 (dd, $^{1}J_{C\text{-}F}$ = 243.9 Hz, $^{2}J_{C\text{-}F}$ = 21.9 Hz), 150.1 (d, $^{1}J_{C\text{-}F}$ = 240.6 Hz), 149.34 (d, $^{1}J_{C\text{-}F}$ = 243.9 Hz), 149.27 (d, $^{1}J_{C\text{-}F}$ = 245.1 Hz), 134.9, 134.3, 132.9, 131.5, 129.9, 129.8, 129.72, 129.69, 129.5, 129.2, 124.01, 123.98, 118.1 (d, $^{2}J_{C\text{-}F}$ = 17.6 Hz), 118.0 (d, $^{2}J_{C\text{-}F}$ = 17.6 Hz), 117.4, 115.4 (d, $^{2}J_{C\text{-}F}$ = 21.9 Hz), 115.3 (d, $^{2}J_{C\text{-}F}$ = 21.9 Hz), 104.4, 50.0, 45.0, 30.8, 29.8. ^{19}F NMR (565 MHz, DMSO-d_6) δ: -138.63 – -138.70 (m), -138.76 – -138.84 (m), -139.70 – -139.78(m), -139.84 – -139.92 (m). HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{28}H_{18}F_4N_2NaO_2$ 513.1197; Found 513.1195.



3ii

3b,5a-Bis((*E*)-2-(naphthalen-1-yl)vinyl)-3b,4,5,5a-tetrahydrocyclobuta[*c*][1,2,3]oxadiazolo[3,4-*a*]quinoli n-10-ium-3-olate (3ii)

Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (98.5 mg, 95%), mp 169.3-170.9 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.16 (d, *J* = 7.8 Hz, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.77-7.75 (m, 2H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.56-7.44 (m, 7H), 7.41-7.38 (m, 2H), 7.34-7.27 (m, 4H), 6.39 (d, *J* = 15.6 Hz, 1H), 6.26 (d, *J* = 15.6 Hz, 1H), 2.96-2.90 (m, 2H), 2.69-2.64 (m, 1H), 2.46-2.41 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 167.0, 134.7, 134.4, 134.2, 133.7, 133.5, 132.9, 132.2, 131.3, 131.2, 130.9, 130.4, 130.0, 129.7, 129.5, 128.8, 128.7, 128.6, 128.4, 128.3, 126.5, 126.3, 126.1, 125.9, 125.7, 125.5, 124.5, 124.4, 124.3, 123.7, 117.4, 104.3, 50.5, 45.7, 31.7, 31.2. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{36}H_{26}N_2NaO_2$ 541.1886; Found 541.1873.

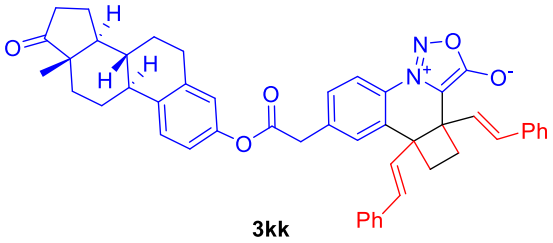


3jj

3b,5a-Bis((*E*)-2-(thiophen-2-yl)vinyl)-3b,4,5,5a-tetrahydrocyclobuta[*c*][1,2,3]oxadiazolo[3,4-*a*]quinolin-1 0- ium-3-olate (3jj)

Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (41.3 mg, 48%), mp 110.0-111.9 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.15 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 7.53-7.47 (m, 2H), 7.34 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 7.21 (d, *J* = 4.8 Hz, 1H), 7.12 (dd, J_1 = 5.4 Hz, J_2 = 1.2 Hz, 1H), 7.06 (d, *J* = 3.6 Hz, 1H), 7.02-7.01 (m, 1H), 6.92-6.89 (m, 3H), 6.52 (d, *J* = 15.6 Hz, 1H), 6.17 (d, *J* = 16.2 Hz, 1H), 6.05 (d, *J* = 16.2 Hz, 1H), 2.74-2.69 (m, 1H), 2.67-2.63 (m, 1H), 2.57-2.53 (m, 1H), 2.34-2.29 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$,

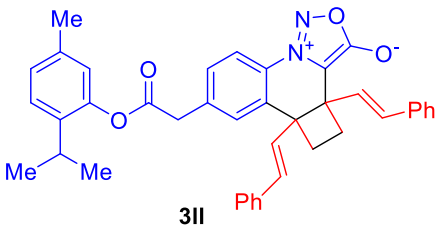
150 MHz): δ 166.9, 141.4, 133.8, 132.1, 129.6, 129.3, 128.7, 128.4, 127.7, 127.4, 126.7, 126.4, 126.0, 125.7, 125.1, 124.8, 117.4, 104.1, 50.3, 45.4, 31.3, 30.9. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{24}H_{18}N_2NaO_2S_2$ 453.0702; Found 453.0699.



3kk

7-(2-(((8*R*,9*S*,13*S*,14*S*)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)-2-oxoethyl)-3b,5a-di((*E*)-styryl)-3b,4,5,5a-tetrahydrocyclobuta[*c*][1,2,3]oxadiazolo[3,4-*a*]quinolin-10-ium-3-olate (3kk)

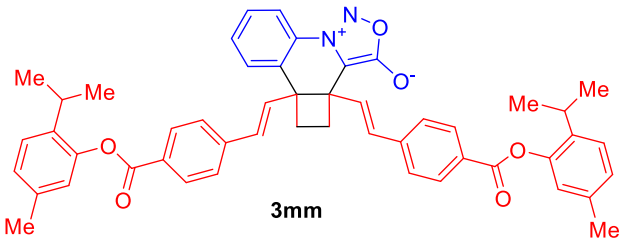
Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid (99.1 mg, 68%), mp 141.6-142.4 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.16 (d, *J* = 8.4 Hz, 1H), 7.51 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 7.42 (d, *J* = 7.2 Hz, 2H), 7.34-7.28 (m, 6H), 7.26-7.23 (m, 2H), 7.21-7.18 (m, 2H), 6.79 (d, *J* = 16.2 Hz, 1H), 6.75-6.72 (m, 2H), 6.42 (d, *J* = 16.2 Hz, 1H), 6.34 (d, *J* = 16.2 Hz, 1H), 6.21 (d, *J* = 16.2 Hz, 1H), 3.87 (s, 2H), 3.72 (t, *J* = 8.4 Hz, 1H), 2.81-2.73 (m, 3H), 2.59-2.54 (m, 1H), 2.38-2.26 (m, 2H), 2.20-2.07 (m, 2H), 1.96-1.93 (m, 1H), 1.87-1.83 (m, 1H), 1.71-1.66 (m, 1H), 1.52-1.44 (m, 2H), 1.42-1.39 (m, 1H), 1.36-1.33 (m, 1H), 1.30-1.26 (m, 2H), 1.19-1.14 (m, 1H), 0.76 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 169.2, 166.9, 148.2, 138.42, 138.39, 138.1, 136.3, 136.2, 134.5, 132.9, 132.5, 130.3, 129.7, 128.9, 128.8, 128.5, 128.3, 127.9, 127.1, 126.73, 126.72, 126.5, 121.2, 118.2, 117.7, 104.5, 81.8, 50.3, 50.1, 45.5, 44.1, 43.2, 41.0, 38.5, 36.7, 31.2, 31.1, 30.6, 29.5, 27.0, 26.2, 23.1, 11.0. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{48}H_{44}N_2NaO_5$ 751.3142; Found 751.3169.



3ll

7-(2-(2-Isopropyl-5-methylphenoxy)-2-oxoethyl)-3b,5a-di((*E*)-styryl)-3b,4,5,5a-tetrahydrocyclobuta[*c*][1,2,3]oxadiazolo[3,4-*a*]quinolin-10-ium-3-olate (3ll)

Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (74.3 mg, 61%), mp 86.4-87.1 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.17 (d, *J* = 8.4 Hz, 1H), 7.53 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 7.42-7.40 (m, 2H), 7.33-7.30 (m, 5H), 7.29-7.23 (m, 3H), 7.20-7.18 (m, 1H), 7.14 (d, *J* = 7.8 Hz, 1H), 7.00 (d, *J* = 7.8 Hz, 1H), 6.80 (d, *J* = 16.2 Hz, 1H), 6.74 (d, *J* = 0.6 Hz, 1H), 6.42 (d, *J* = 15.6 Hz, 1H), 6.33 (d, *J* = 16.2 Hz, 1H), 6.22 (d, *J* = 16.2 Hz, 1H), 3.90 (s, 2H), 2.80-2.73 (m, 3H), 2.59-2.56 (m, 1H), 2.37-2.32 (m, 1H), 2.26 (s, 3H), 1.05 (t, *J* = 7.2 Hz, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 169.1, 166.9, 147.7, 138.1, 136.8, 136.7, 136.3, 136.2, 134.6, 133.0, 132.6, 130.4, 129.7, 128.9, 128.8, 128.7, 128.6, 128.3, 128.0, 127.5, 127.1, 126.75, 126.71, 126.5, 122.5, 117.7, 104.5, 50.3, 45.5, 41.1, 31.3, 31.1, 27.1, 22.9, 20.8. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{40}H_{36}N_2NaO_4$ 631.2567; Found 631.2562.

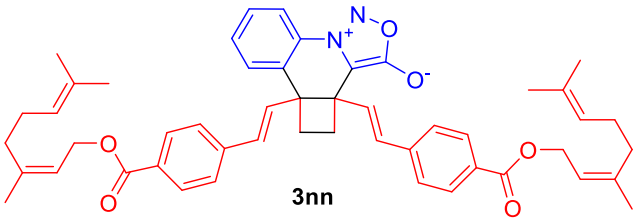


3mm

3b,5a-Bis((*E*)-4-((2-isopropyl-5-methylphenoxy)carbonyl)styryl)-3b,4,5,5a-tetrahydrocyclobuta[*c*][1,2,3]oxadiazolo[3,4-*a*]quinolin-10-ium-3-olate (3mm)

Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (100.2 mg, 65%), mp 128.5-129.9 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.20-8.18 (m, 3H), 8.12 (d, *J* = 7.8 Hz, 2H), 7.57-7.51 (m, 4H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.35 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 7.24-7.21 (m, 2H), 7.07-7.04 (m, 2H), 6.92 (d, *J* = 9.0 Hz, 2H), 6.87 (d, *J* = 16.2 Hz, 1H), 6.60 (d, *J* = 16.2 Hz, 1H), 6.52 (d, *J* = 16.2 Hz, 1H), 6.41 (d, *J* = 16.2 Hz, 1H), 3.06-3.00 (m, 2H), 2.85-2.80 (m, 2H), 2.64-2.61 (m, 1H), 2.44-2.40 (m, 1H), 2.33 (s, 3H), 2.32 (s, 3H), 1.21-1.18 (m, 12H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 166.8, 165.1, 165.0, 148.2, 148.1, 141.3, 141.1, 137.23, 137.18, 136.75, 136.67, 133.7, 132.4, 132.2, 132.1, 131.6, 130.8, 130.6, 130.0, 129.6, 129.3, 129.2, 129.0, 128.9, 137.3, 127.2,

126.9, 126.8, 126.6, 126.5, 122.93, 122.89, 117.5, 103.8, 50.4, 45.5, 31.3, 31.0, 27.4, 27.3, 23.1, 20.92, 20.91. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{50}H_{47}N_2O_6$ 771.3429; Found 771.3419.



3nn

3b,5a-Bis((*E*)-4-((((*Z*)-3,7-dimethylocta-2,6-dien-1-yl)oxy)carbonyl)styryl)-3b,4,5,5a-tetrahydrocyclobuta[*c*][1,2,3]oxadiazolo[3,4-*a*]quinolin-10-ium-3-olate (3nn)

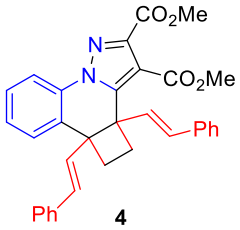
Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (93.5 mg, 60%), mp 55.3-56.2 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.17 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 8.01 (d, J = 8.4 Hz, 2H), 7.93 (d, J = 8.4 Hz, 2H), 7.55-7.49 (m, 2H), 7.45 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 9.0 Hz, 2H), 7.33 (dd, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 6.81 (d, J = 16.2 Hz, 1H), 6.51 (d, J = 16.2 Hz, 1H), 6.44 (d, J = 15.6 Hz, 1H), 6.33 (d, J = 15.6 Hz, 1H), 5.50-5.46 (m, 2H), 5.13-5.09 (m, 2H), 4.82-4.78 (m, 4H), 2.81-2.76 (m, 2H), 2.60-2.57 (m, 1H), 2.42-2.37 (m, 1H), 2.20-2.16 (m, 4H), 2.13-2.09 (m, 4H), 1.80 (s, 3H), 1.79 (s, 3H), 1.67 (s, 3H), 1.66 (s, 3H), 1.60 (s, 3H), 1.59 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 166.8, 166.3, 166.2, 142.8, 142.7, 140.5, 140.3, 133.7, 132.3, 132.22, 132.20, 132.1, 131.7, 131.6, 130.2, 130.1, 130.0, 129.8, 129.53, 129.50, 129.3, 128.8, 126.5, 126.4, 123.6, 119.3, 119.2, 117.4, 103.9, 61.7, 61.6, 50.3, 45.4, 32.25, 32.23, 31.17, 31.0, 26.7, 25.7, 23.6, 23.5, 17.7. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{50}H_{55}N_2O_6$ 779.4055; Found 779.4057.

2. Structural elaborations of 3a

2.1 Synthesis of 4[5]

To a reaction tube equipped with a stir bar were charged with **3a** (41.8 mg, 0.1 mmol), toluene (1 mL) and dimethyl but-2-ynedioate (14.8 μL, 0.12 mmol). The tube was then sealed, and the resulting mixture was stirred at 115 ℃ for 12 h. Upon completion, it was quenched with saturated brine and extracted with ethyl acetate for three times. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and

concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) as the eluent to give **4** (42.9 mg, 83%).



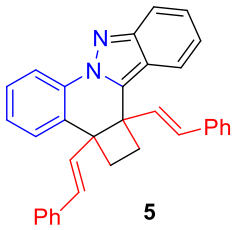
4

Dimethyl 3b,5a-di((*E*)-styryl)-3b,4,5,5a-tetrahydrocyclobuta[*c*]pyrazolo[1,5-*a*]quinoline-2,3-dicarboxylate (4)

Eluent: petroleum ether/ethyl acetate (10:1). Yellow solid (42.9 mg, 83%), mp 61.1-62.5 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.26 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 7.39-7.37 (m, 3H), 7.31 (t, J = 7.8 Hz, 2H), 7.28-7.23 (m, 6H), 7.22-7.18 (m, 2H), 6.67 (d, J = 16.2 Hz, 1H), 6.34 (d, J = 16.2 Hz, 1H), 6.30-6.27 (m, 2H), 3.99 (s, 3H), 3.60 (s, 3H), 2.89-2.84 (m, 1H), 2.71-2.67 (m, 2H), 2.36-2.31 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 163.1, 162.7, 144.1, 144.0, 136.6, 136.5, 133.4, 131.6, 131.2, 130.8, 130.7, 129.4, 128.8, 128.61, 128.58, 128.3, 127.9, 127.8, 127.4, 126.54, 126.48, 117.2, 114.4, 52.7, 52.0, 50.2, 48.4, 32.8, 30.8. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{33}H_{28}N_2NaO_4$ 539.1941; Found 539.1932.

2.2 Synthesis of 5[5]

To a reaction tube equipped with a stir bar were charged with **3a** (41.8 mg, 0.1 mmol), THF (1 mL), aryne precursor (35.8 mg, 0.12 mmol) and TBAF (0.16 mL, 1 mol/L in THF). The tube was then sealed, and the resulting mixture was stirred at room temperature under argon for 12 h. Upon completion, the reaction mixture was poured into saturated aqueous $NaHCO_3$ and extracted with EtOAc for three times. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (30:1) as the eluent to give **5** (29.1 mg, 64%).



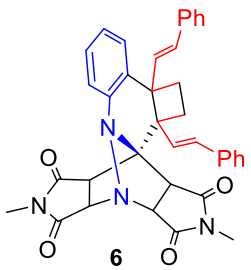
5

2a,12c-Di((*E*)-styryl)-1,2,2a,12c-tetrahydrocyclobuta[*c*]indazolo[2,3-*a*]quinoline (5)

Eluent: petroleum ether/ethyl acetate (30:1). White solid (29.1 mg, 64%), mp 211.7-212.1 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.46 (d, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 9.0 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.44-7.41 (m, 1H), 7.38 (d, *J* = 7.2 Hz, 2H), 7.34-7.20 (m, 11H), 6.93 (t, *J* = 7.8 Hz, 1H), 6.63 (d, *J* = 15.6 Hz, 1H), 6.57-6.50 (m, 2H), 6.41 (d, *J* = 16.8 Hz, 1H), 2.90-2.86 (m, 1H), 2.80-2.76 (m, 1H), 2.62-2.57 (m, 1H), 2.42-2.38 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 149.5, 136.8, 136.7, 135.0, 133.3, 132.0, 131.5, 131.4, 131.3, 130.1, 129.0, 128.8, 128.7, 128.3, 127.80, 127.78, 127.22, 127.19, 126.6, 126.5, 121.7, 121.0, 120.5, 118.0, 117.8, 50.6, 48.6, 31.6, 31.4. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{33}H_{27}N_2$ 451.2169; Found 451.2172.

2.3 Synthesis of 6[5]

To a reaction tube equipped with a stir bar were charged with **3a** (41.8 mg, 0.1 mmol), toluene (1 mL) and *N*-methylmaleimide (22.2 mg, 0.2 mmol). The tube was then sealed, and the resulting mixture was stirred at 115 ℃ for 12 h. Upon completion, it was quenched with saturated brine and extracted with ethyl acetate for three times. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (20:1) as the eluent to give **6** (30.4 mg, 51%).



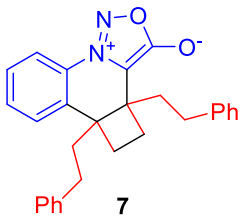
6

10,14-Dimethyl-2a,11c-di((*E*)-styryl)-1,2,2a,8a,11a,11c-hexahydro-9*H*-8,11b-[3,4]epipyrrolocyclobuta[*c*]pyrrolo[3',4':3,4]pyrazolo[1,5-*a*]quinoline-9,11,13,15(10*H*)-tetraone (6)

Eluent: petroleum ether/ethyl acetate (20:1). Yellow solid (30.4 mg, 51%), mp 197.6-198.1 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.52-7.50 (m, 4H), 7.47 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 7.35 (t, J = 7.8 Hz, 2H), 7.29-7.23 (m, 3H), 7.22-7.16 (m, 3H), 7.11-7.09 (m, 1H), 6.97 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 6.81-6.78 (m, 1H), 6.51-6.45 (m, 2H), 4.10 (d, J = 7.2 Hz, 1H), 4.07 (d, J = 6.0 Hz, 1H), 3.15 (d, J = 6.6 Hz, 1H), 2.99-2.97 (m, 4H), 2.81-2.75 (m, 1H), 2.54-2.50 (m, 1H), 2.30 (s, 3H), 2.07-2.02 (m, 1H), 1.61-1.58 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 173.63, 173.56, 172.5, 172.1, 138.7, 137.8, 137.5, 134.4, 132.7, 132.0, 130.1, 129.1, 128.68, 128.67, 128.3, 127.6, 127.5, 127.3, 126.7, 126.5, 123.4, 117.9, 82.2, 71.1, 69.7, 54.1, 51.7, 51.5, 50.1, 30.3, 26.1, 25.3, 24.4. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{37}H_{32}N_4NaO_4$ 619.2316; Found 619.2320.

2.4 Synthesis of 7[6]

To a reaction tube equipped with a stir bar were charged with **3a** (41.8 mg, 0.1 mmol), ethyl acetate (2 mL) and Pd/C (42.6 mg, 0.04mmol). The tube was then sealed, and the resulting mixture was stirred at rt under H_2 (balloon) for 24 h. Upon completion, the mixture was filtered over celite. The filtrate was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1) as eluent to afford **7** (32.1 mg, 76%).



7

3b,5a-Diphenethyl-3b,4,5,5a-tetrahydrocyclobuta[*c*][1,2,3]oxadiazolo[3,4-*a*]quinolin-10-ium-3-olate (7)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (32.1 mg, 76%), mp 147.6-148.3 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.14 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 7.65-7.62 (m, 1H), 7.55-7.54 (m, 1H), 7.50-7.47 (m, 1H), 7.29-7.27 (m, 4H), 7.25-7.22 (m, 2H), 7.20-7.15 (m, 2H), 7.03 (d, J = 7.2 Hz, 2H), 2.87-2.77 (m, 2H),

2.69-2.63 (m, 1H), 2.56-2.50 (m, 1H), 2.46-2.35 (m, 3H), 2.27-2.14 (m, 4H), 2.11-2.07 (m, 1H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150 MHz): δ 166.5, 141.9, 141.0, 136.6, 132.3, 130.6, 128.6, 128.5, 128.3, 128.1, 127.9, 126.3, 126.1, 117.1, 105.7, 47.1, 41.8, 38.7, 35.6, 35.0, 32.2, 32.0, 31.4. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{28}H_{26}N_2NaO_2$ 445.1886; Found 445.1882.

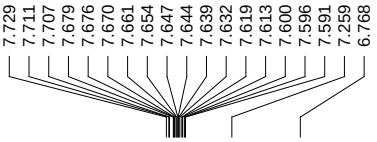
3. Gram-scale synthesis of 3a

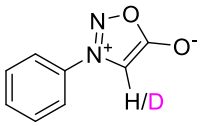
To a reaction tube equipped with a stir bar were charged with 3-phenyl-1,2,3-oxadiazol-3-ium-5-olate (**1a**, 648.6 mg, 4 mmol), DCE (40 mL), $[Cp^*RhCl_2]_2$ (61.8 mg, 0.1 mmol), AgOAc (133.5 mg, 0.8 mmol), TEMPO (625 mg, 4 mmol) and 1-phenylbuta-2,3-dien-1-yl acetate (**2a**, 1882.3 mg, 10 mmol). The tube was then sealed, and the resulting mixture was stirred at 50 ℃ under argon for 24 h. Upon completion, it was cooled to room temperature, quenched with water and extracted with dichloromethane for three times. 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 with petroleum ether/ethyl acetate (5:1) as eluent to afford **3a** (1039.4 mg, 62%).

III. Mechanistic studies

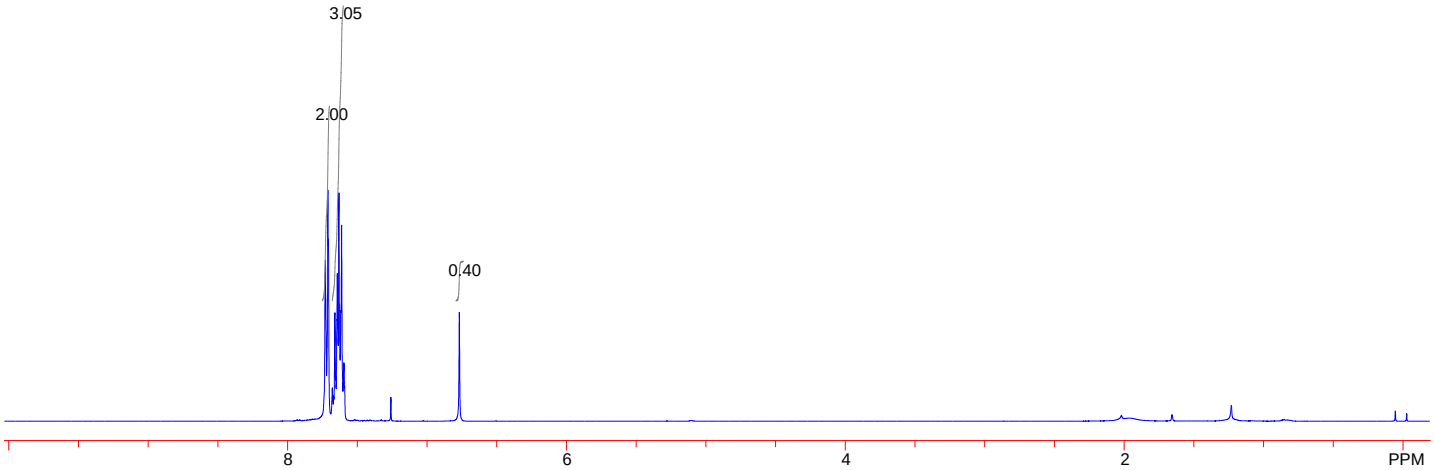
1. H/D exchange experiment (I)

To a reaction tube equipped with a stir bar were charged with **1a** (32.4 mg, 0.2 mmol), DCE (2 mL), D_2O (36 μL, 2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), AgOAc (6.7 mg, 0.02 mmol) and TEMPO (31.3 mg, 0.2 mmol). The resulting mixture was stirred at 50 ℃ under argon for 5 h. Afterwards, it was cooled to room temperature, quenched with water and extracted with dichloromethane for three times. 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 (3:1) as eluent to give a mixture of **1a** and **1a**-d_n. Upon analyzing the ^{1}H NMR spectrum of the mixture, the deuteration ratio at the 4-position of the sydnone moiety of **1a** was determined to be about 60%. Meanwhile, H/D exchange at the *ortho*-positions of the phenyl ring of **1a** was not observed.



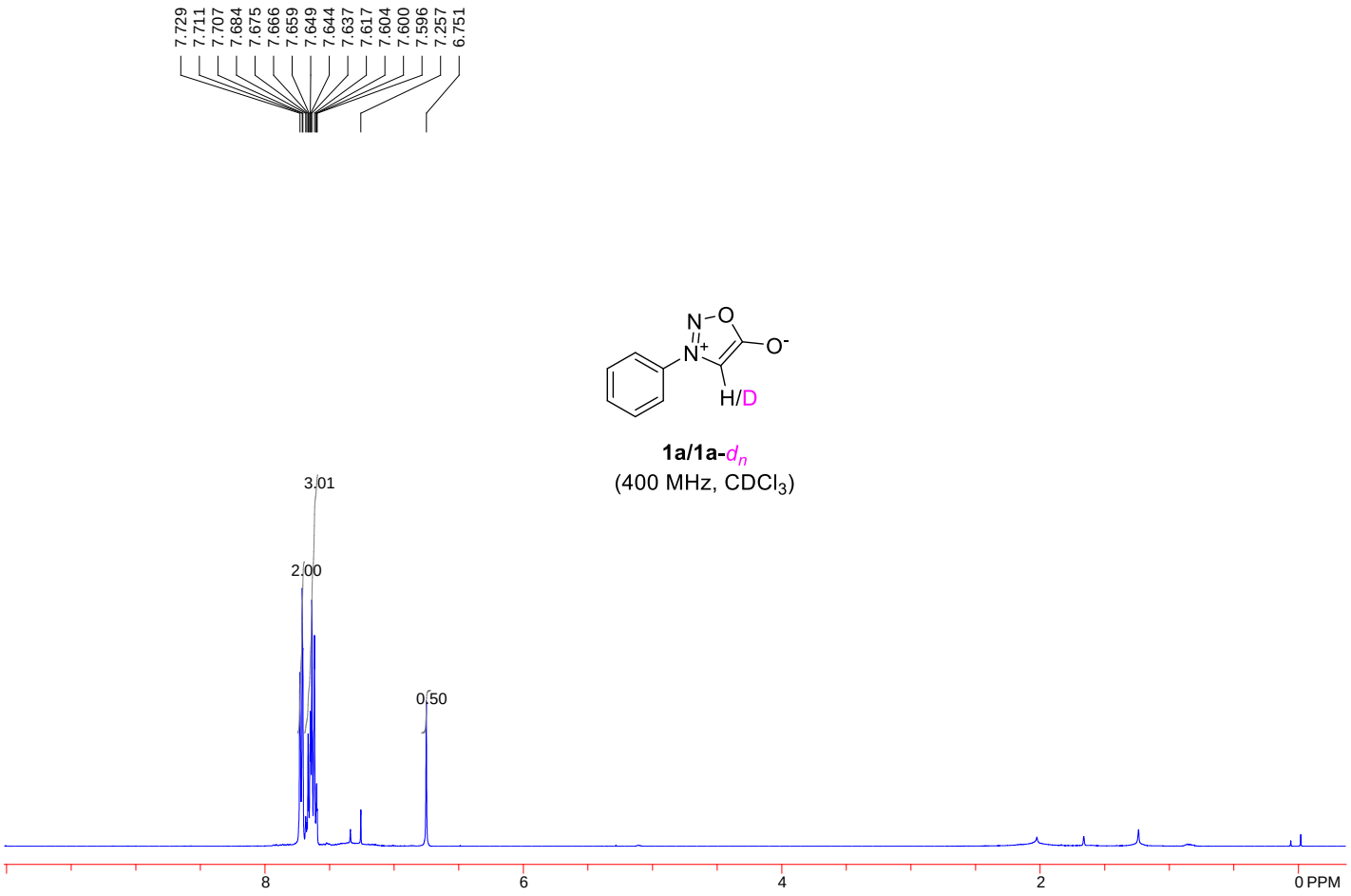


1a/1a-d_n
(400 MHz, $CDCl_3$)



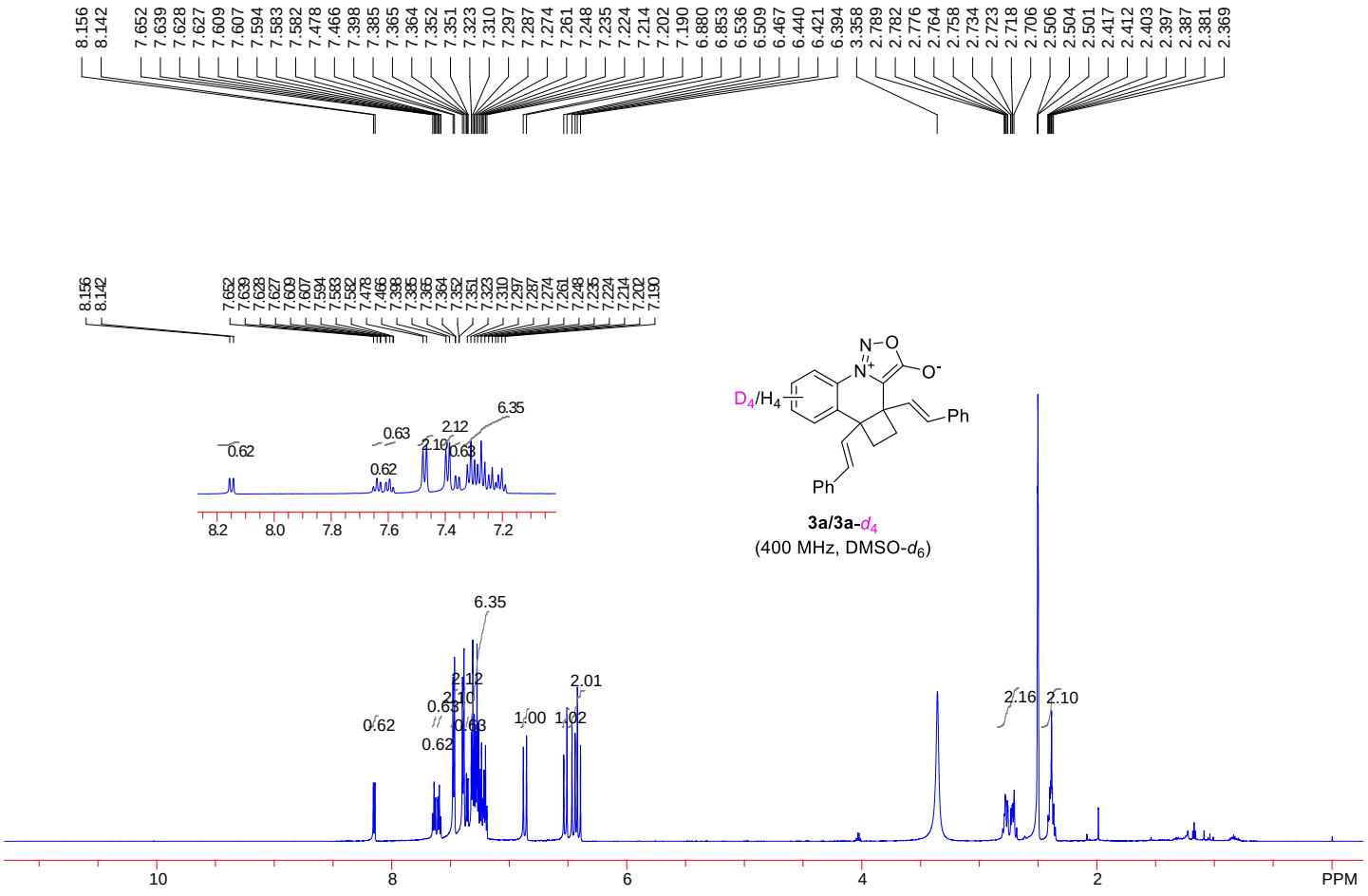
2. H/D exchange experiment (II)

To a reaction tube equipped with a stir bar were charged with **1a** (32.4 mg, 0.2 mmol), **2a** (94.1 mg, 0.5 mmol), DCE (2 mL), D_2O (36 μL, 2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), AgOAc (6.7 mg, 0.02 mmol), and TEMPO (31.3 mg, 0.2 mmol). The resulting mixture was stirred at 50 °C under argon for 5 h. Afterwards, it was cooled to room temperature, quenched with water and extracted with dichloromethane for three times. 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 (3:1) as eluent to give **3a** and a mixture of **1a** with **1a**-d_n. Upon analyzing the ^{1}H NMR spectrum of the mixture of **1a** and **1a**-d_n, the deuteration ratio at the 4-position of the sydnone moiety of **1a** was determined to be about 50%. Meanwhile, H/D exchange at the unreacted phenyl *ortho*-position of product **3a** was not observed.



3. Kinetic isotope effect study

To a reaction tube equipped with a stir bar were charged with **1a** (32.4 mg, 0.2 mmol), **1a**-d_5 (33.4 mg, 0.2 mmol), **2a** (75.3 mg, 0.4 mmol), DCE (2 mL), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), AgOAc (6.7 mg, 0.04 mmol) and TEMPO (31.3 mg, 0.2 mmol). The resulting mixture was stirred at 50 ℃ under argon for 30 min. Afterwards, it was cooled to room temperature, 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. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (5:1) 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 0.63:0.37. Accordingly, the intermolecular KIE (k_H/k_D) was calculated to be about 1.7.



IV. X-ray crystal structure and data for 3a

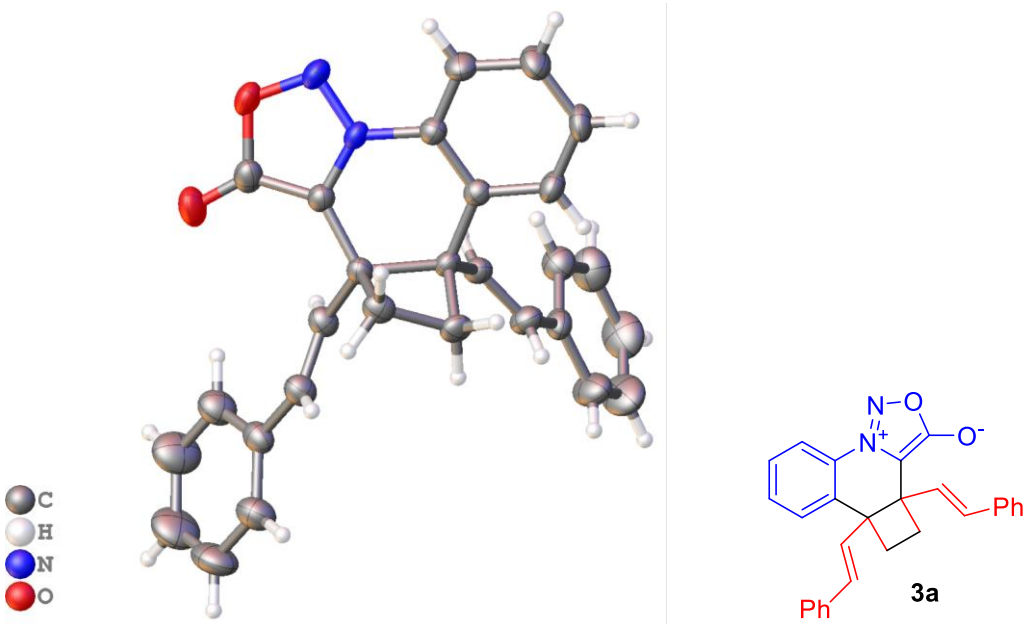


Figure S1. X-ray crystal structure of **3a** with 50% ellipsoid probability

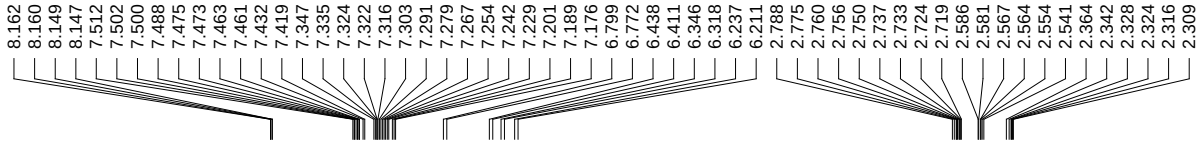
X-ray structure determination. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent from an ethyl acetate/dichloromethane (10:1) solution of **3a**. Crystal data collection and refinement parameters of **3a** are summarized in Table S1. Intensity data were collected 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.

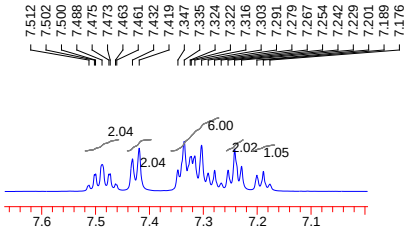
Table S1. Crystallographic data and structure refinement results of **3a**

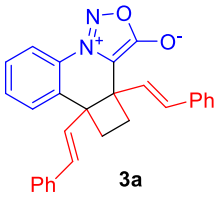
Empirical formula	$C_{28}H_{22}N_2O_2$
Formula weight	418.47
Temp, K	293 (2)
Crystal system	monoclinic
Space group	$P2_1/c$
a, Å	9.1597(2)

b, Å	20.6723(4)
c, Å	11.5149(2)
α (°)	90
β (°)	100.930(2)
γ (°)	90
Volume, Å^3	2140.82(7)
Z	4
ρ_{calc}, g cm^{-3}	1.298
λ, Å	1.54184
μ, mm^{-1}	0.651
No. of data collected	9658
No. of unique data	4041
R_{int}	0.0285
Goodness-of-fit on F^2	1.070
R_1, wR_2 (I> 2σ(I))	0.0543, 0.1318
R_1, wR_2 (all data)	0.0706, 0.1384

V. NMR spectra of 3a-3nn

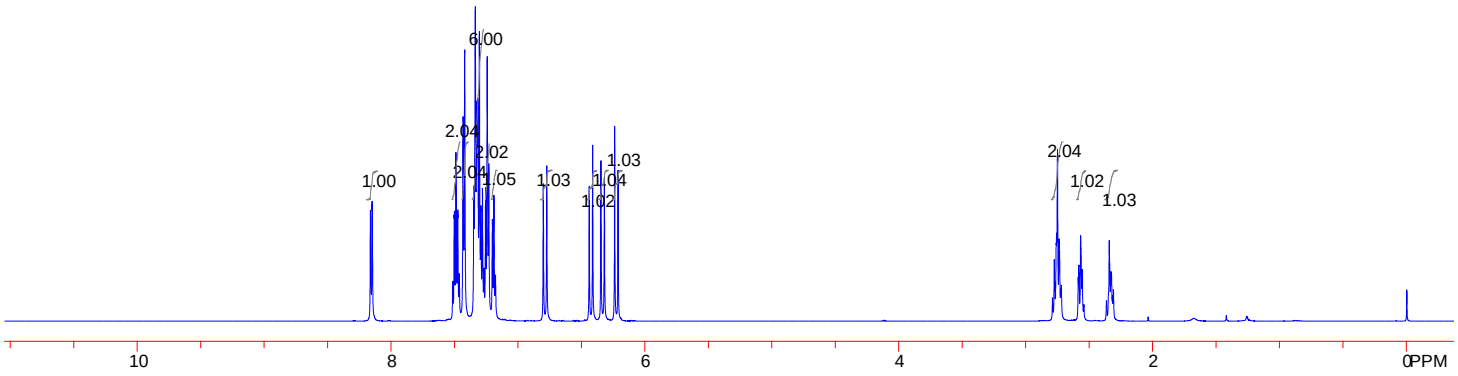


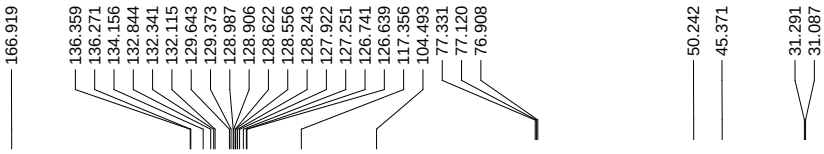


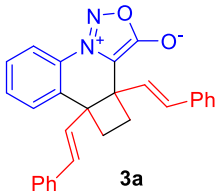


3a

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

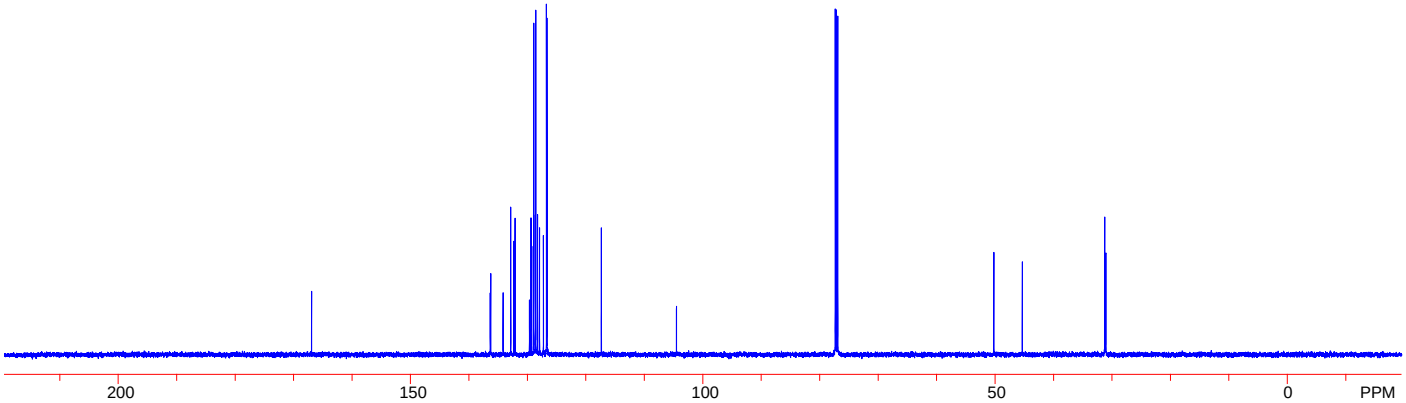


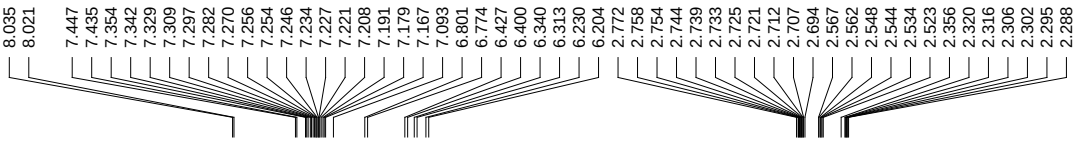


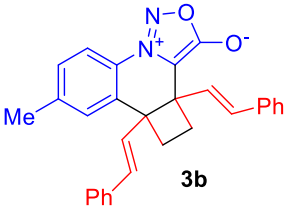


3a

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

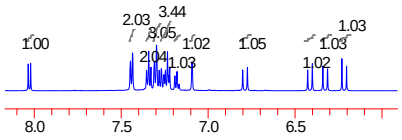


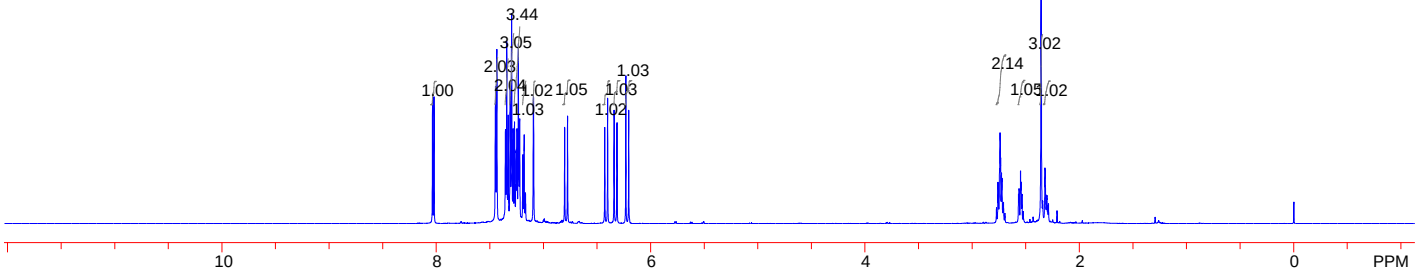


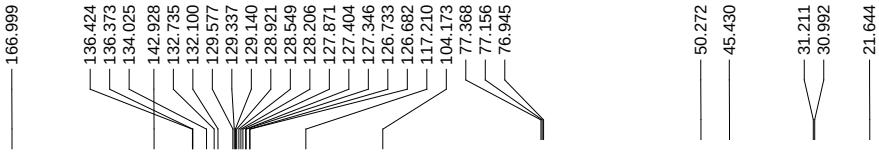


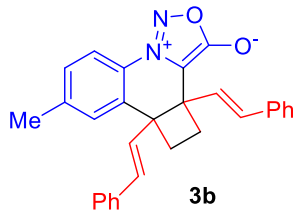
3b

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



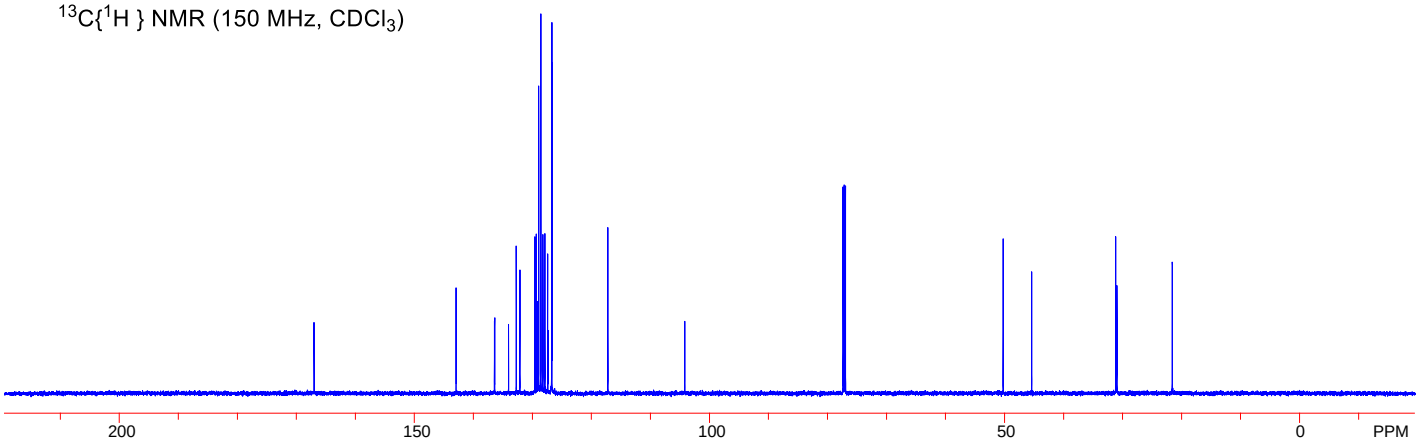


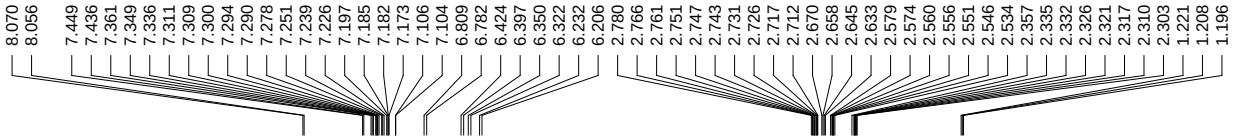


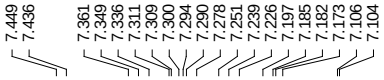


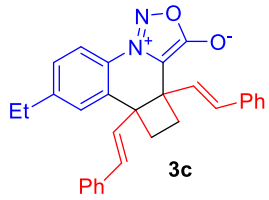
3b

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

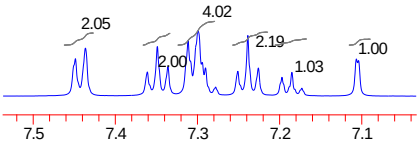




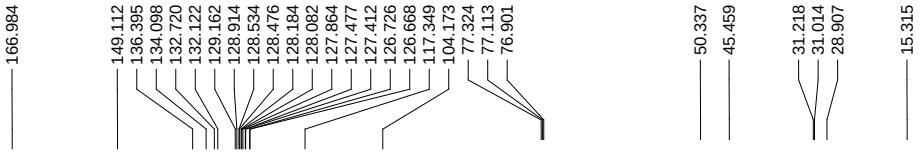


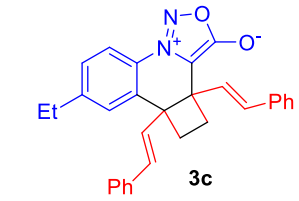


3c



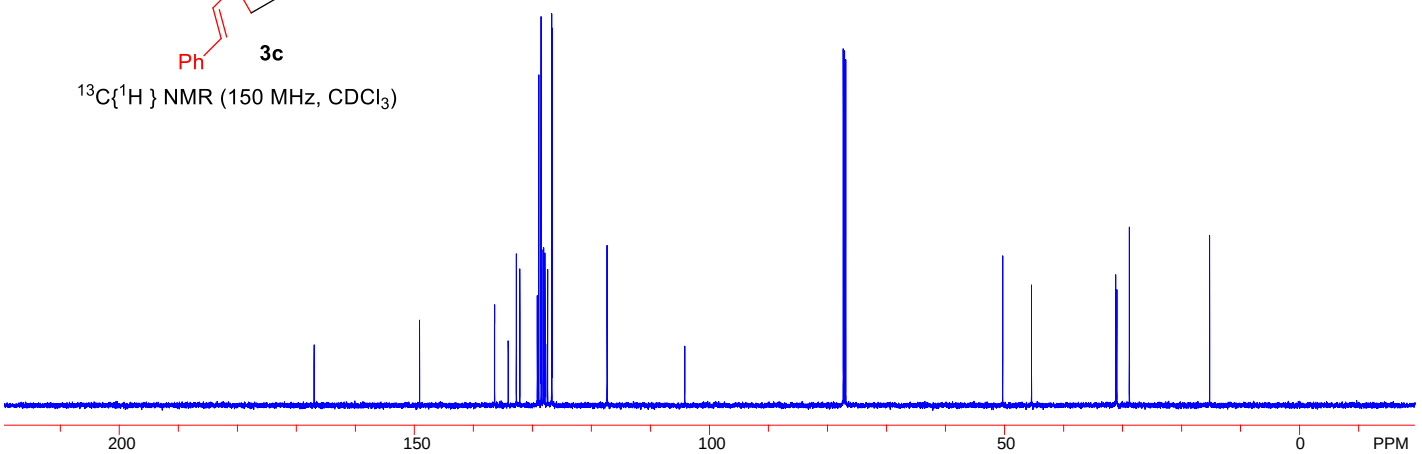
^{1}H NMR (600 MHz, $CDCl_3$)

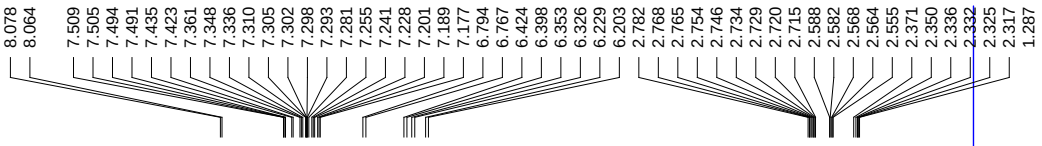


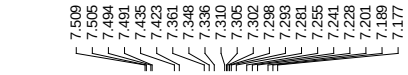


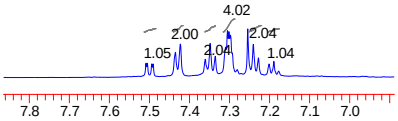
3c

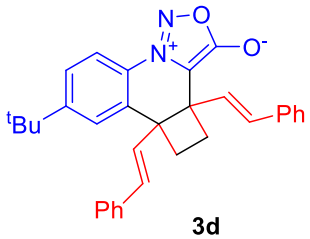
^{13}C{^{1}H } NMR (150 MHz, $CDCl_3$)





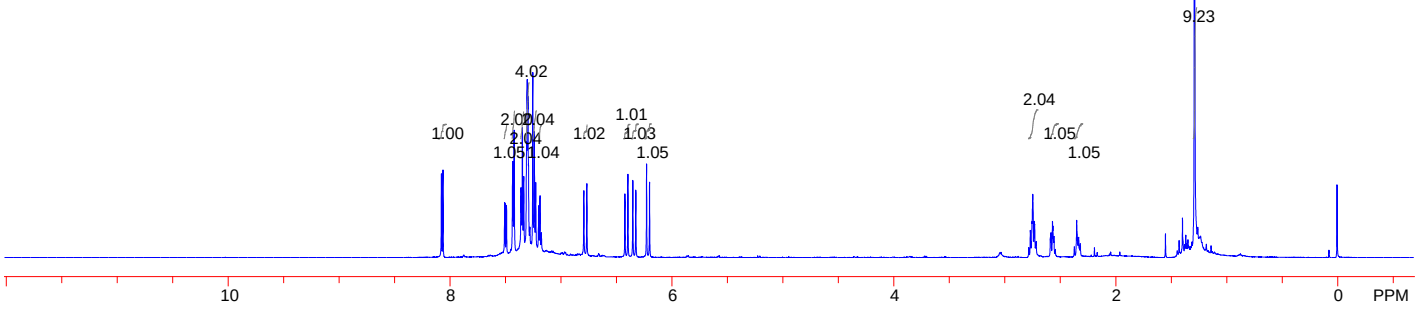


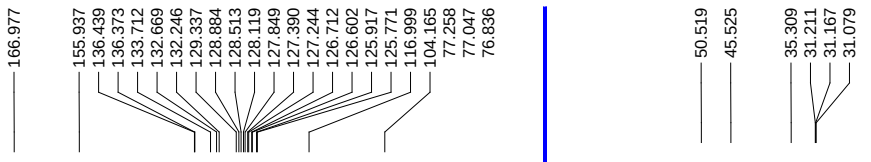


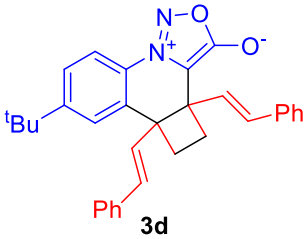


3d

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

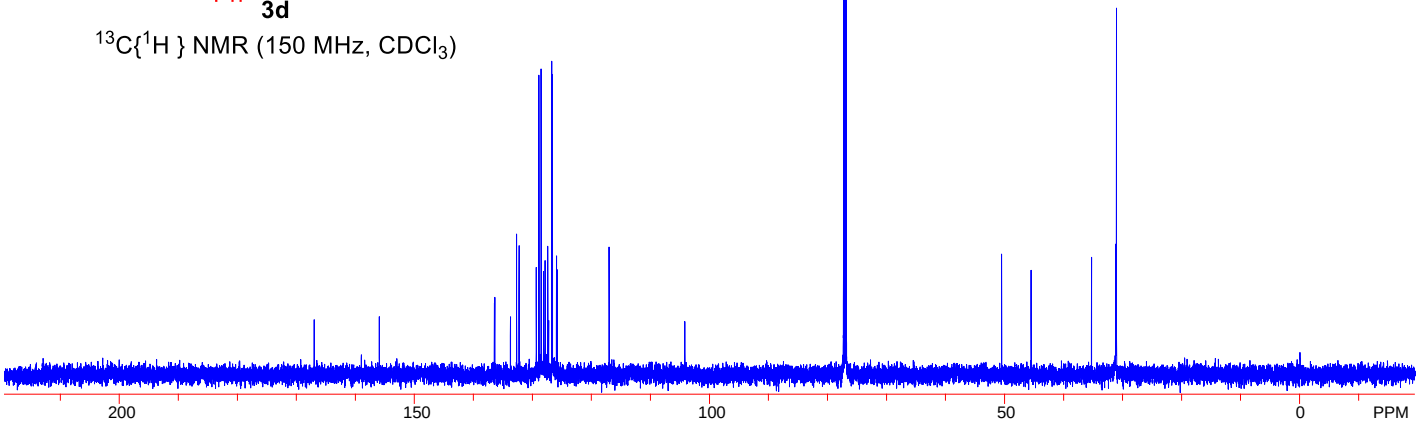


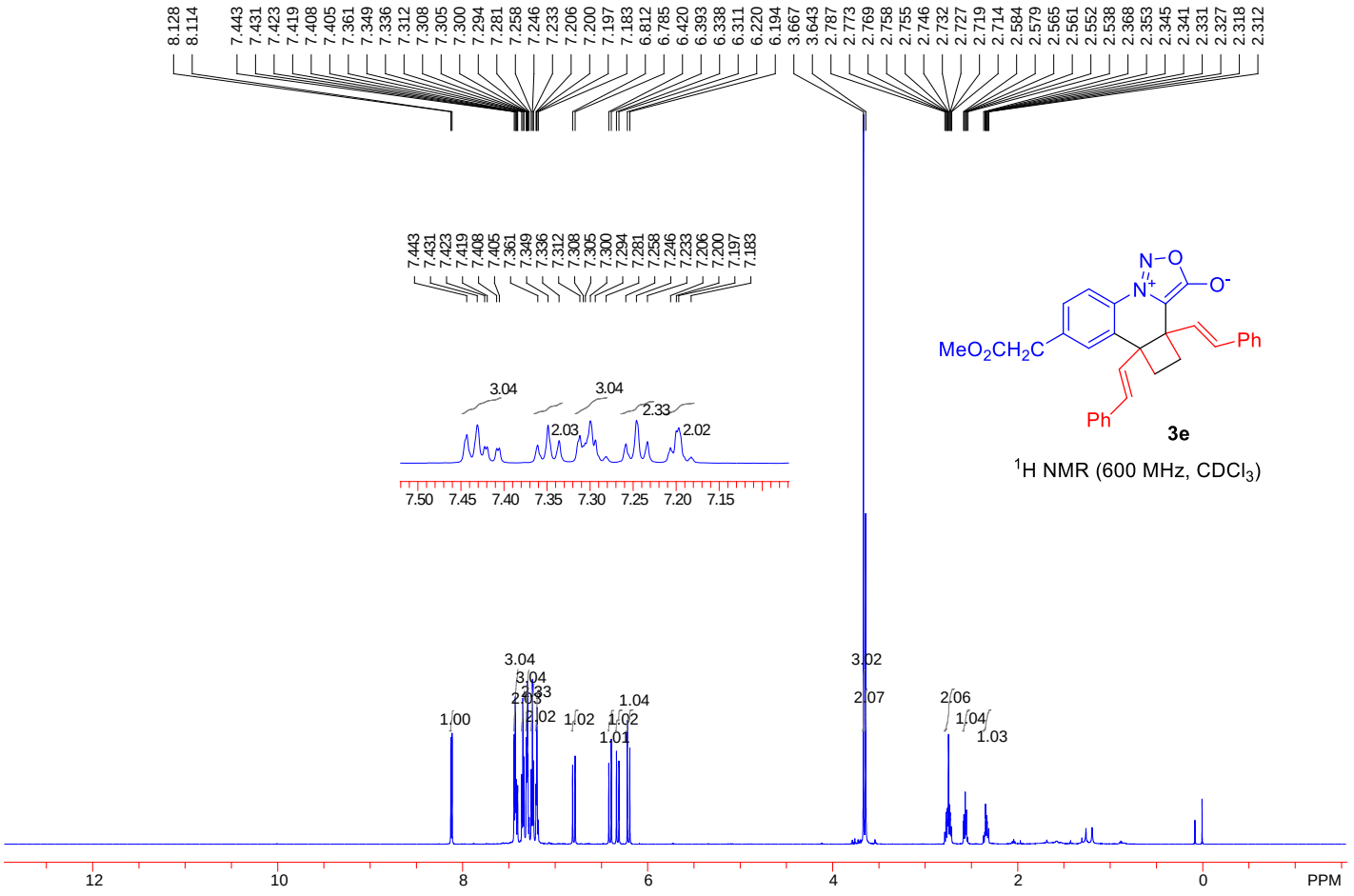




3d

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

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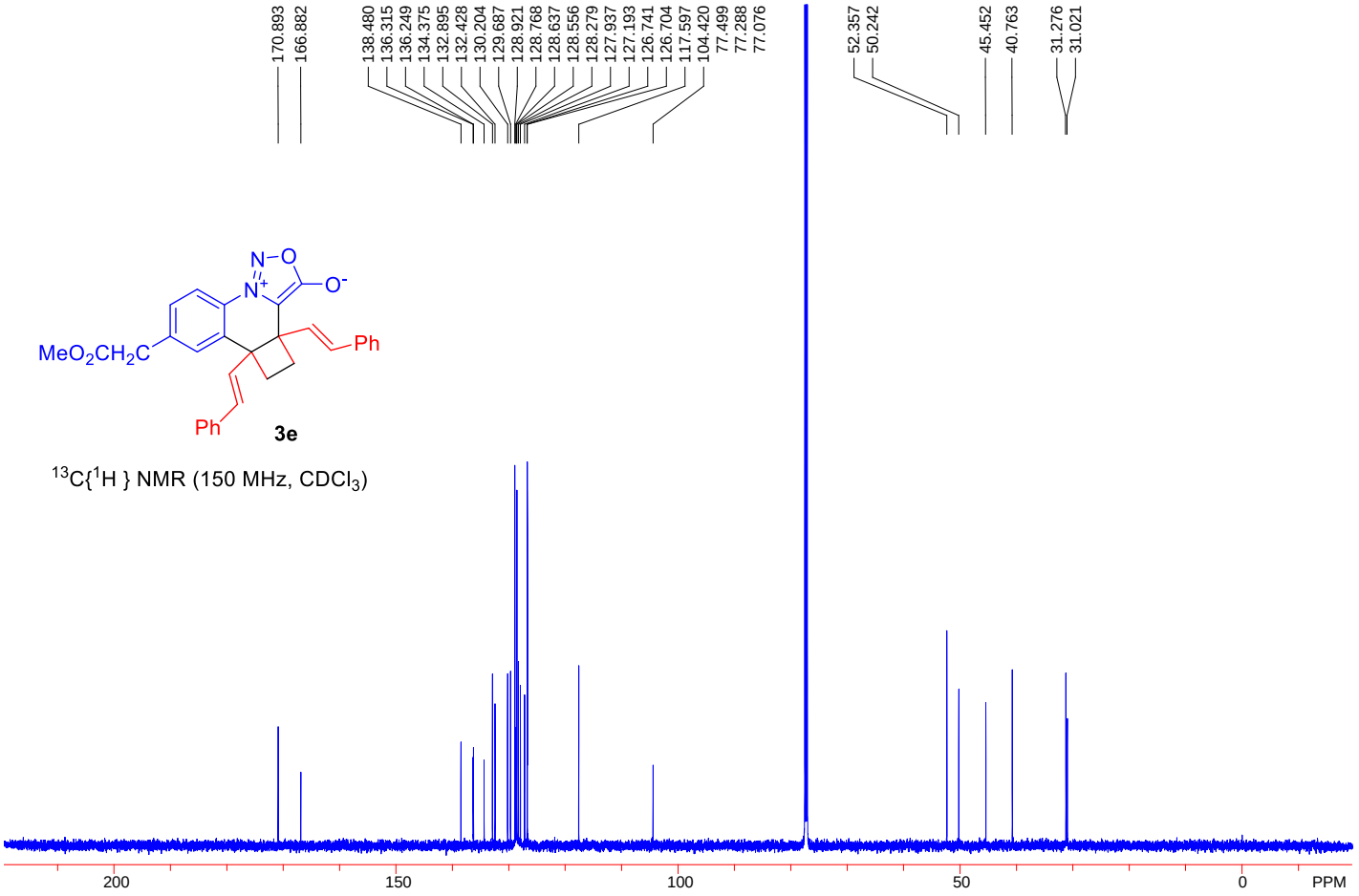
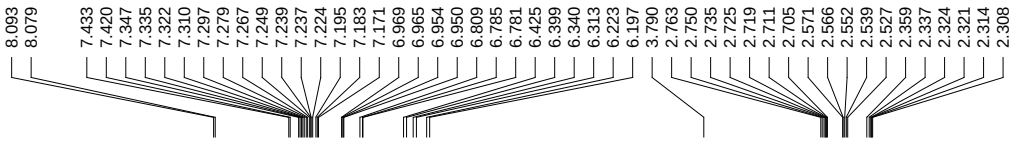
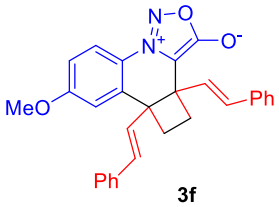
3.04 3.04 2.33 2.03 2.02
7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15
MeO2CH2C
Ph
Ph
3e
1H NMR (600 MHz, CDCl3)
1.00 3.04 3.04 2.33 2.03 2.02 1.02 1.04 1.02 1.01 3.02 2.07 2.06 1.04 1.03
12 10 8 6 4 2 0 PPM

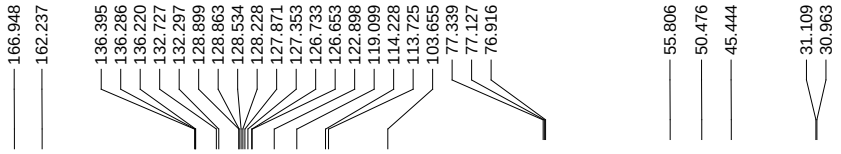

170.893 166.882 138.480 136.315 136.249 134.375 132.895 132.428 130.204 129.687 128.921 128.768 128.637 128.556 128.279 127.937 127.193 126.741 126.704 117.597 104.420 77.499 77.288 77.076 52.357 50.242 45.452 40.763 31.276 31.021
MeO2CH2C
Ph
Ph
3e
13C{1H } NMR (150 MHz, CDCl3)
200 150 100 50 0 PPM

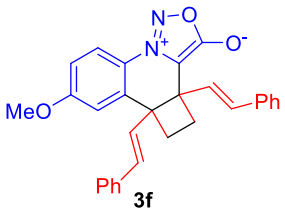




3f

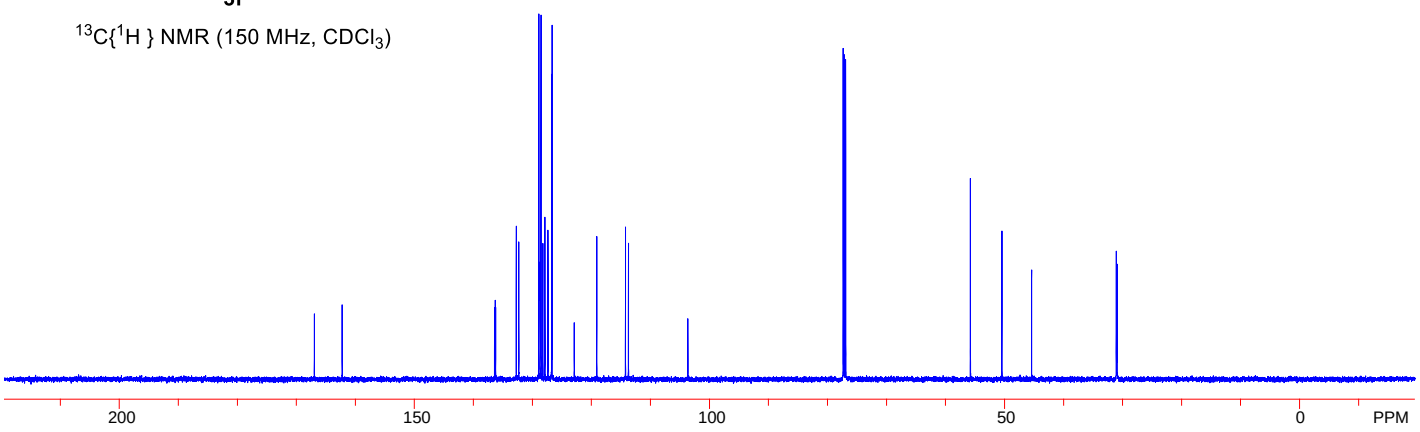
^{1}H NMR (600 MHz, $CDCl_3$)

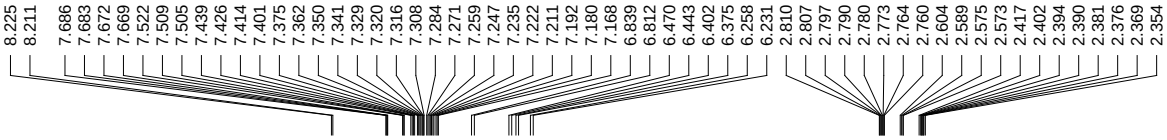


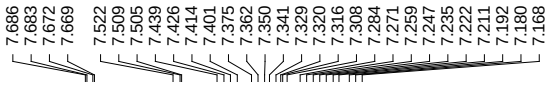


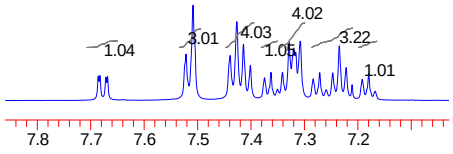
3f

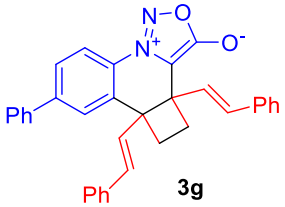
^{13}C{^{1}H } NMR (150 MHz, $CDCl_3$)





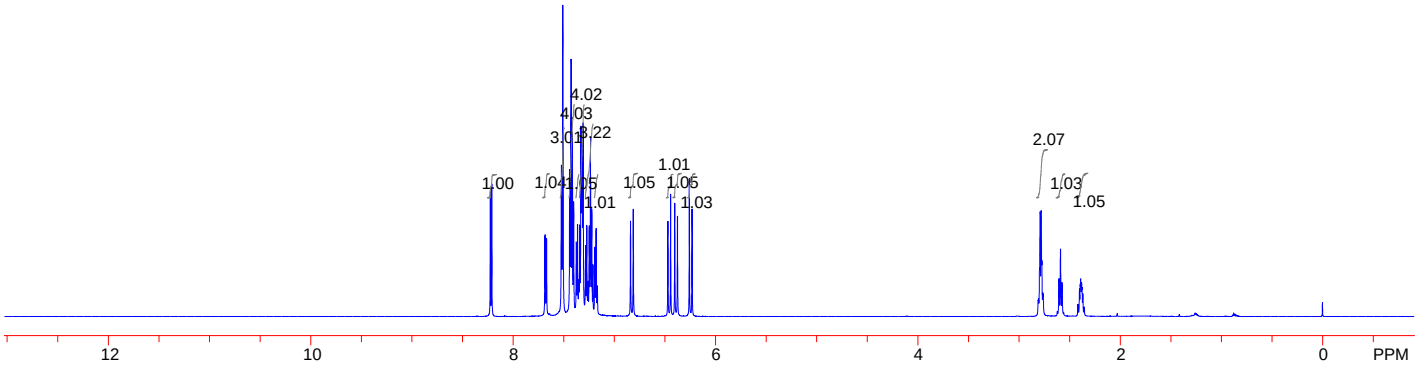


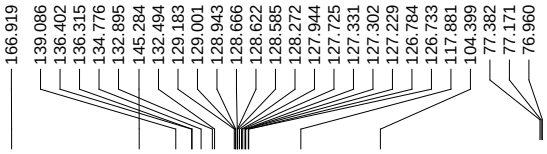


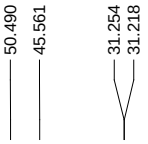


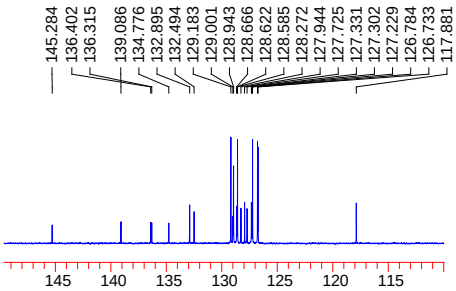
3g

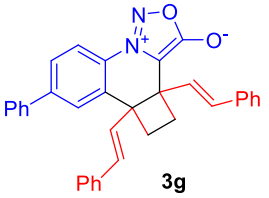
^{1}H NMR (600 MHz, $CDCl_3$)





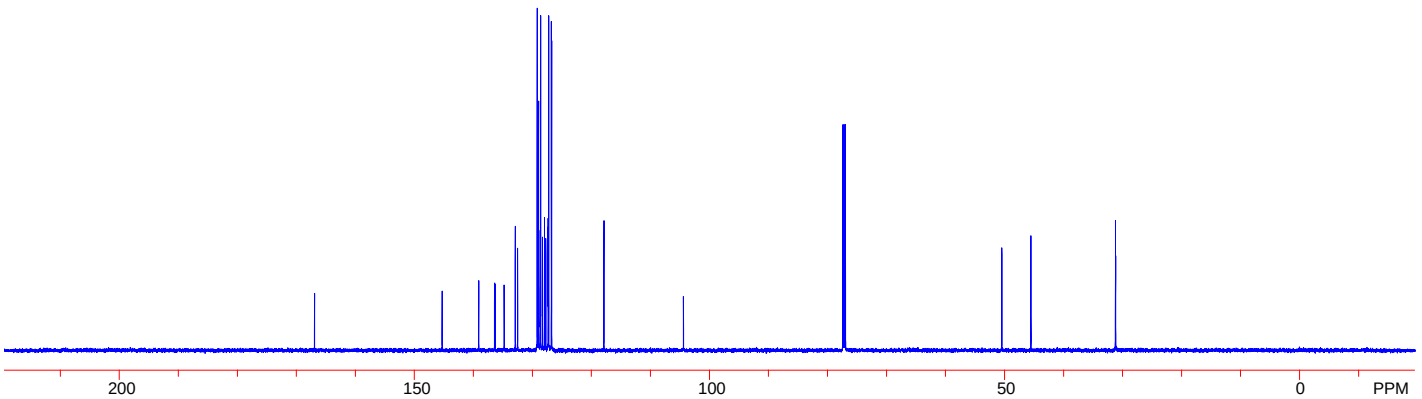


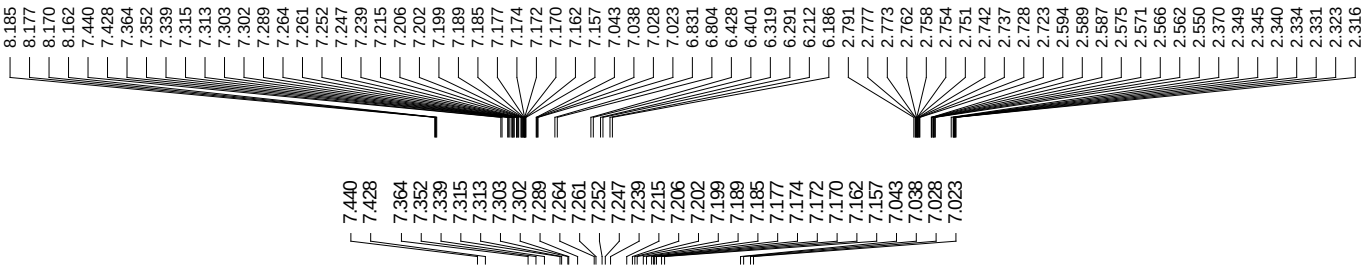


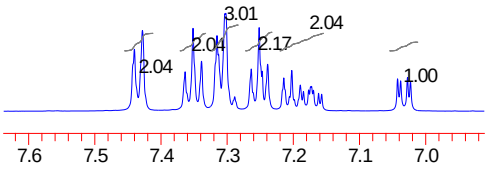


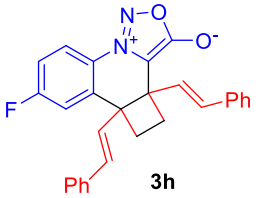
3g

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



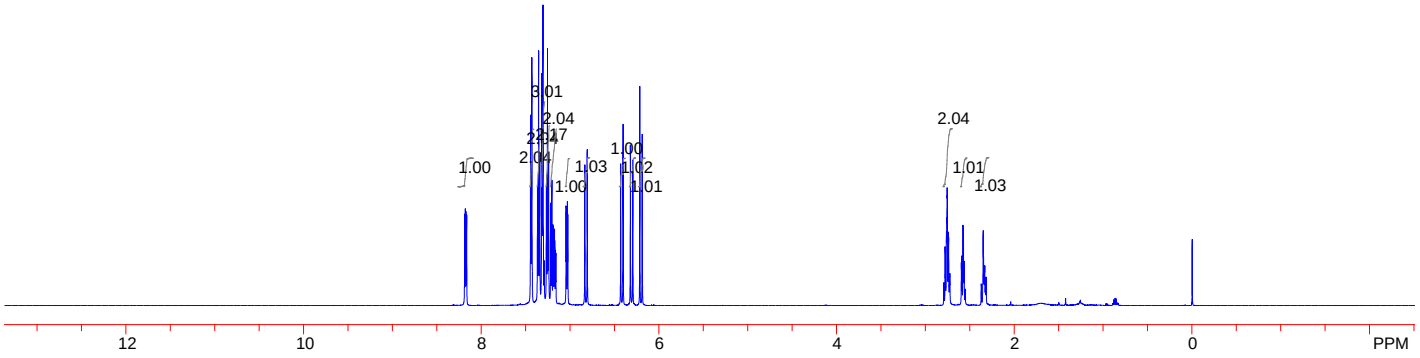


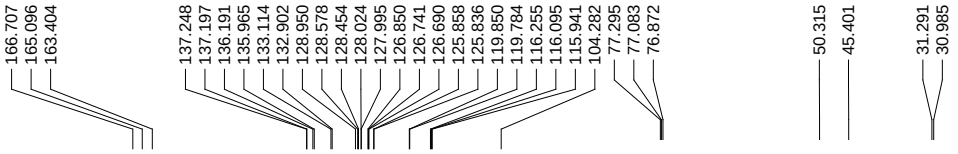


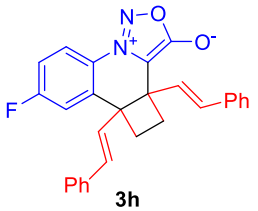


3h

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

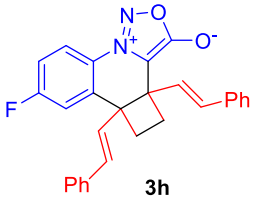






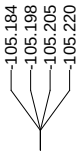
3h

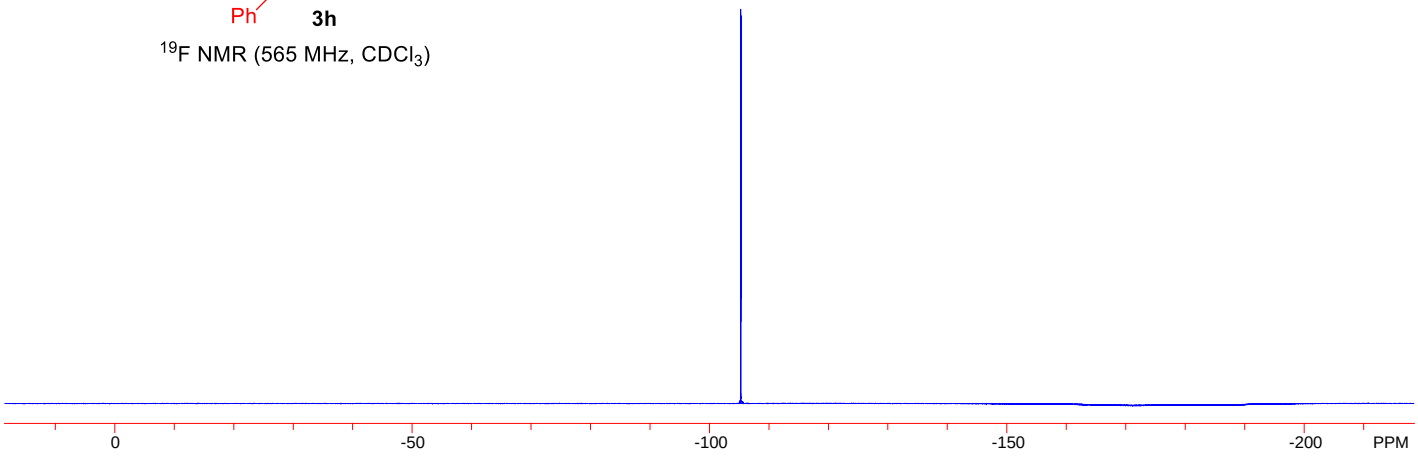
^{13}C{^{1}H } NMR (150 MHz, $CDCl_3$)

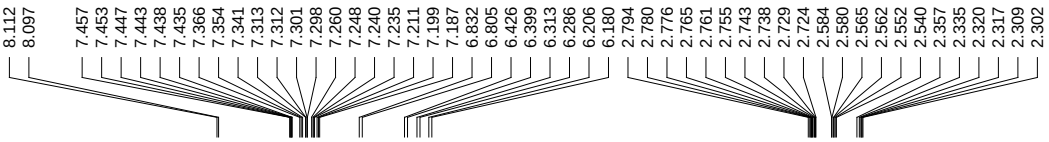


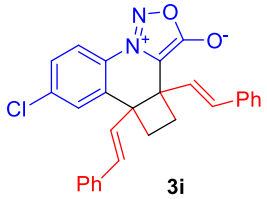
3h

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



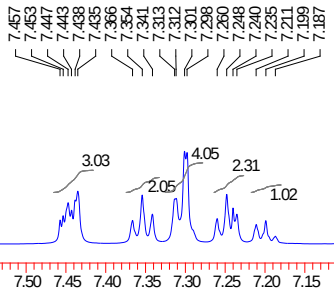


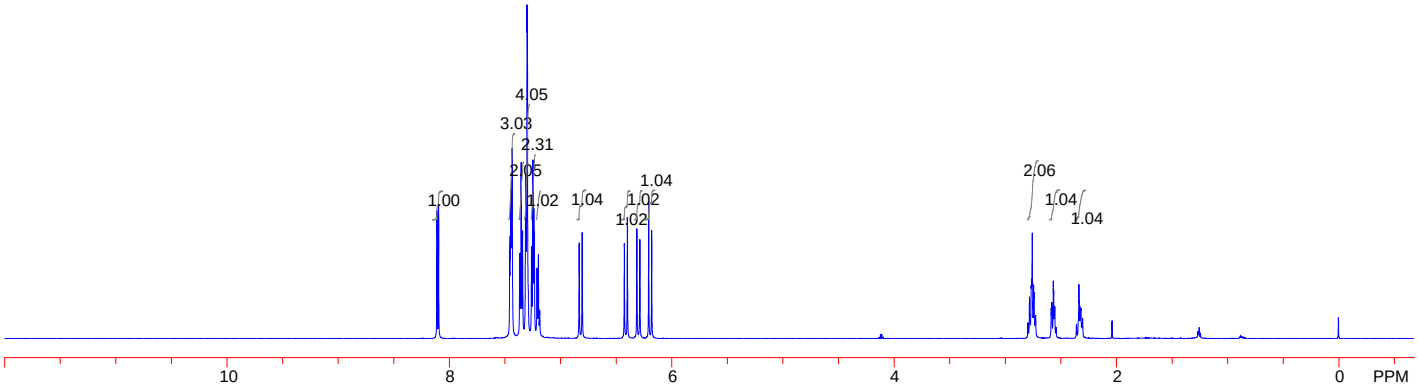


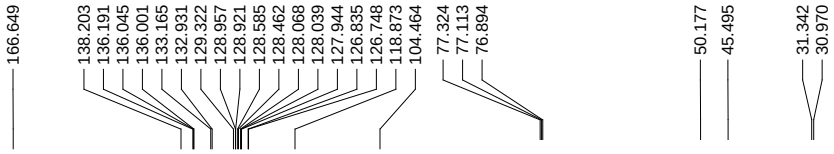


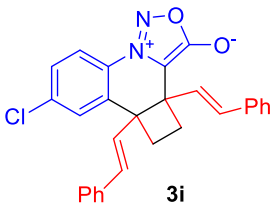
3i

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



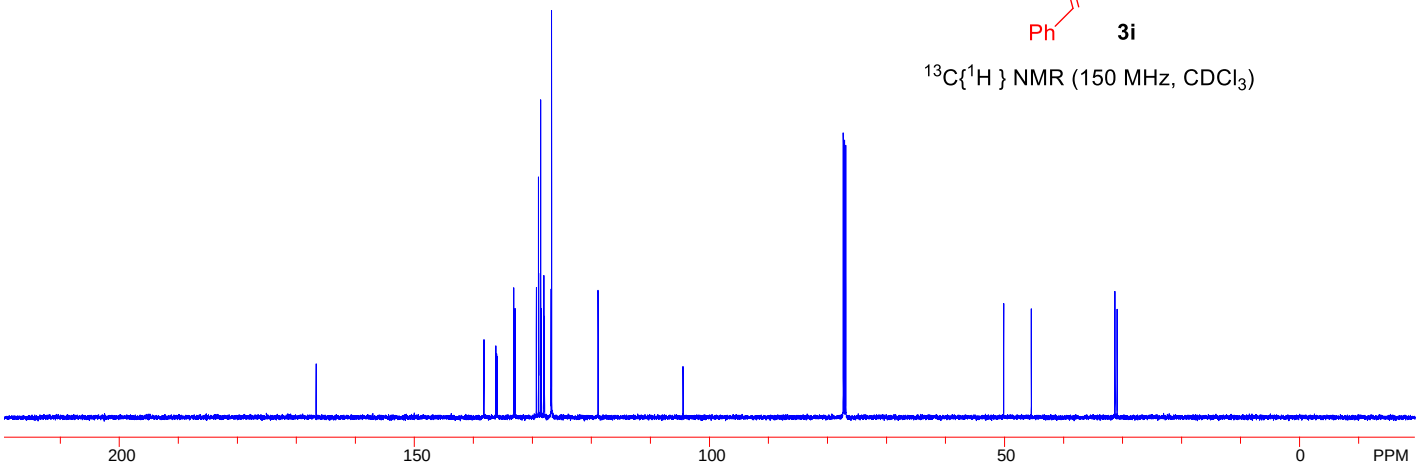


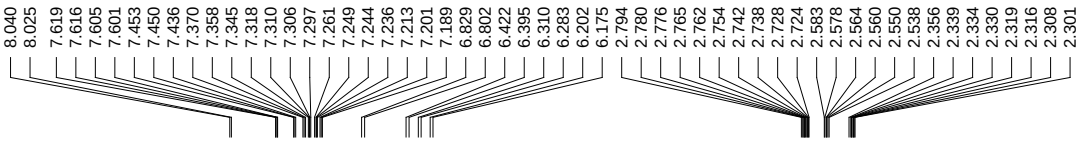


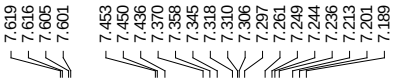


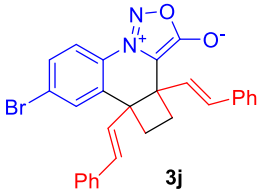
3i

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

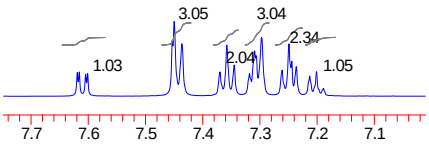




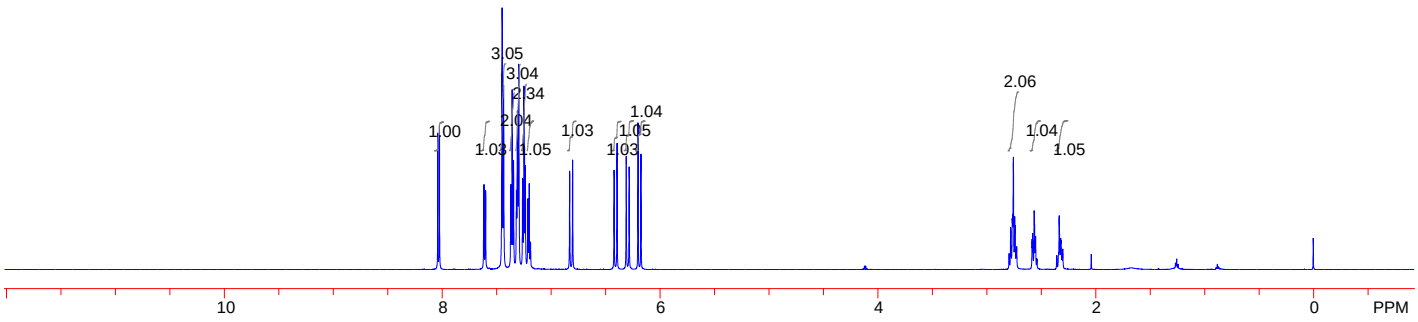


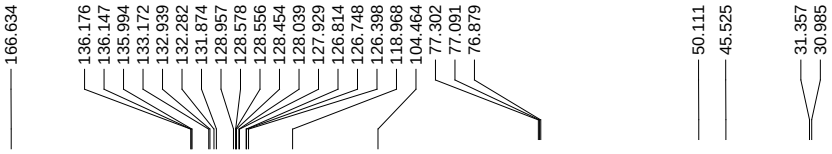


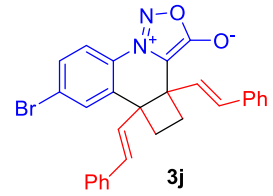
3j



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

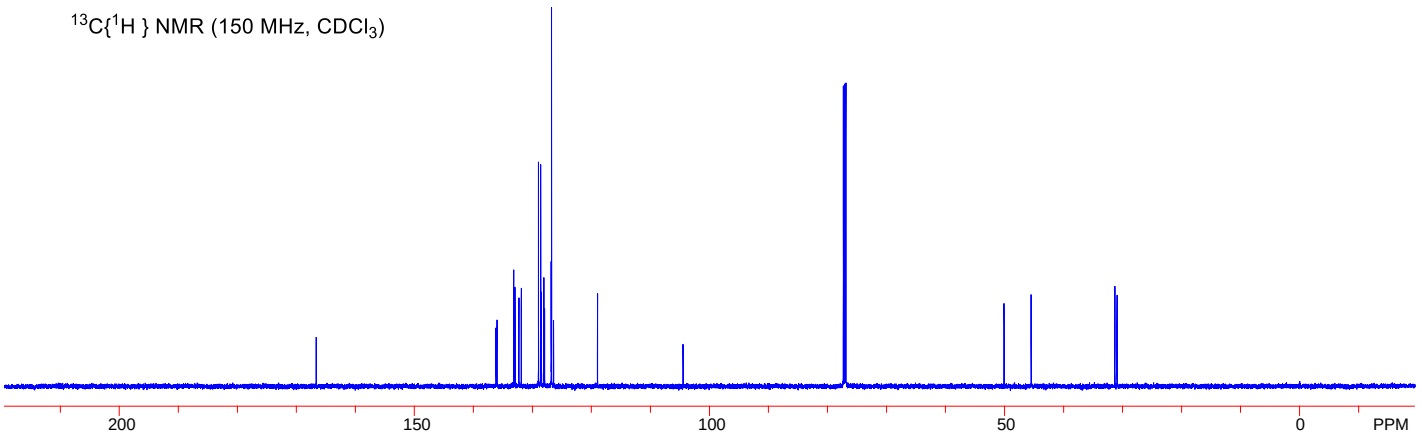


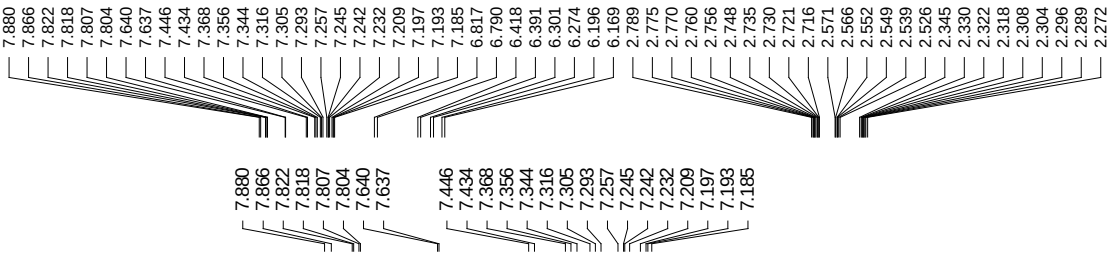


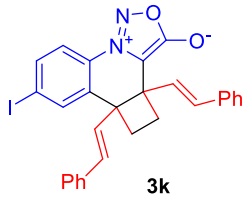


3j

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

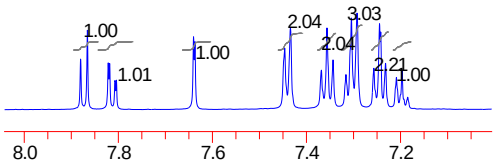


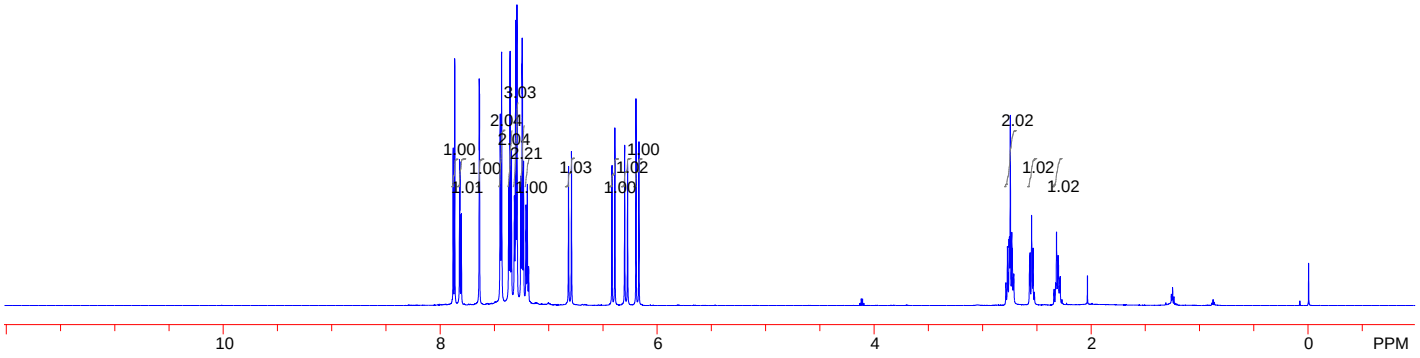


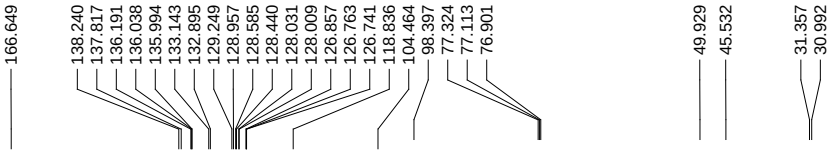


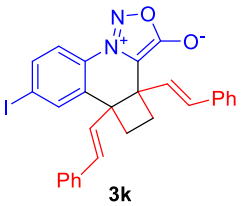
3k

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



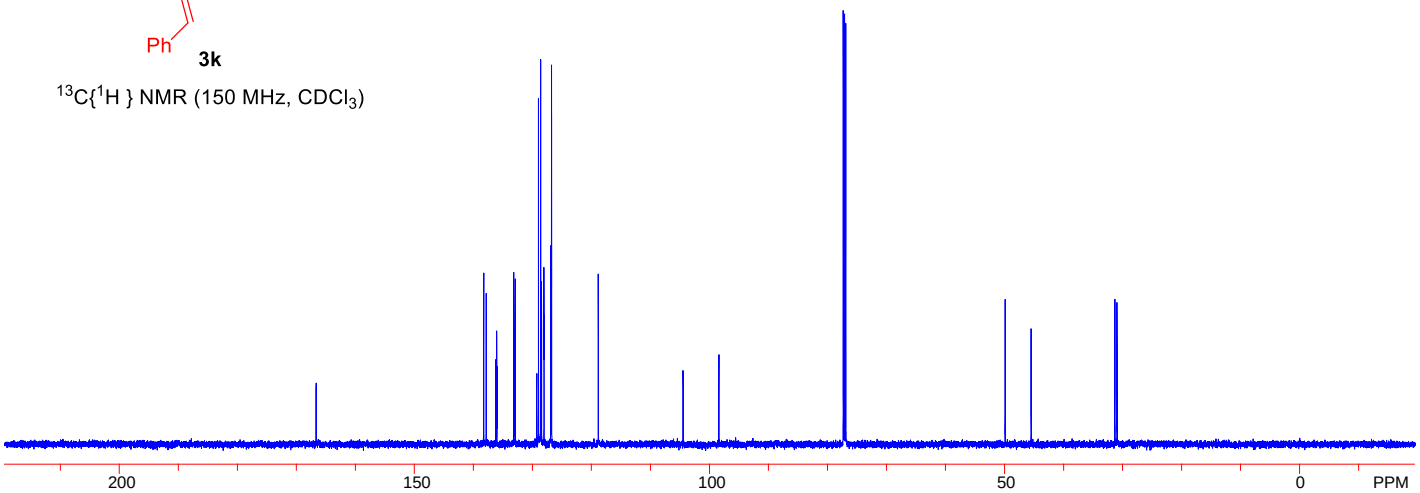


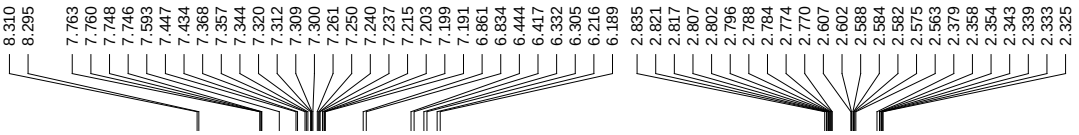


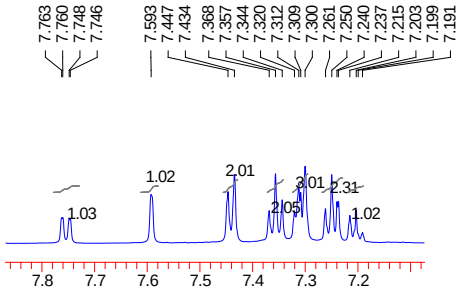


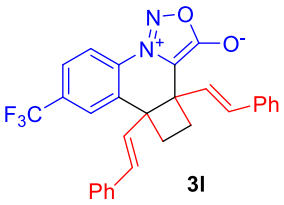
3k

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



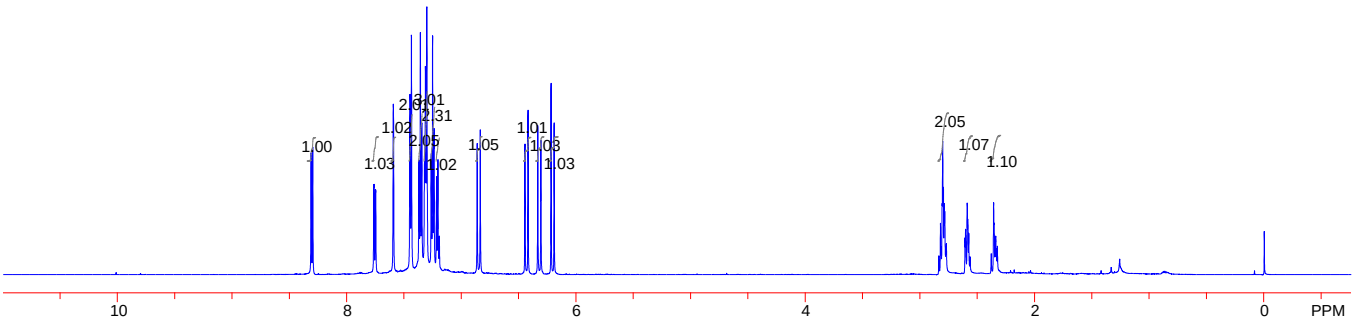


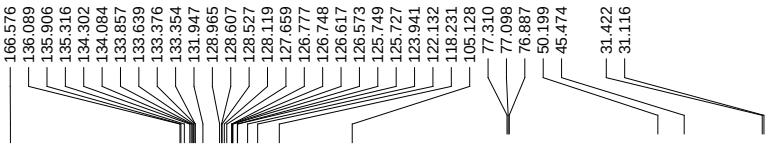


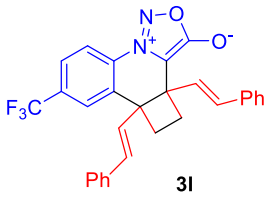


3l

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

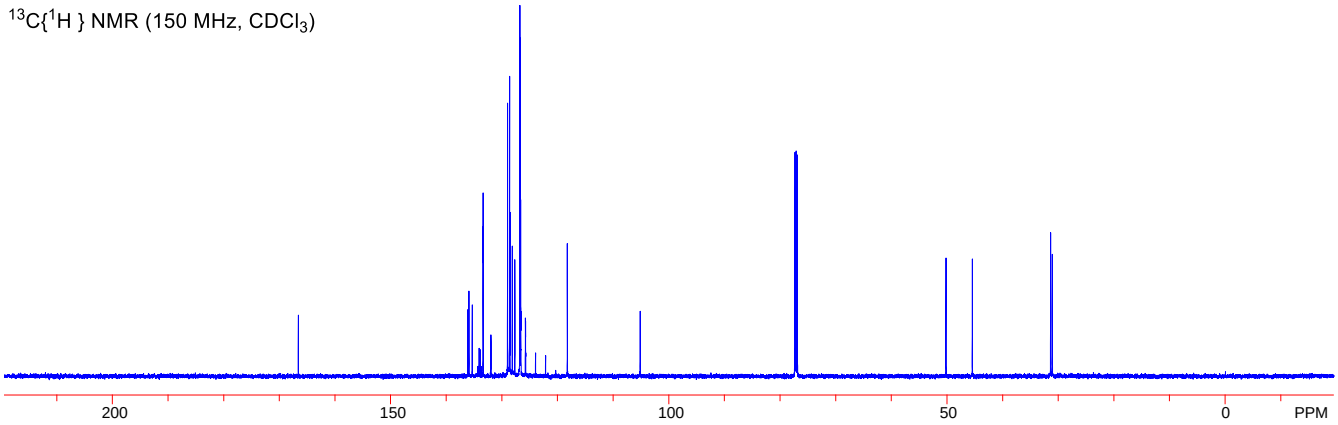


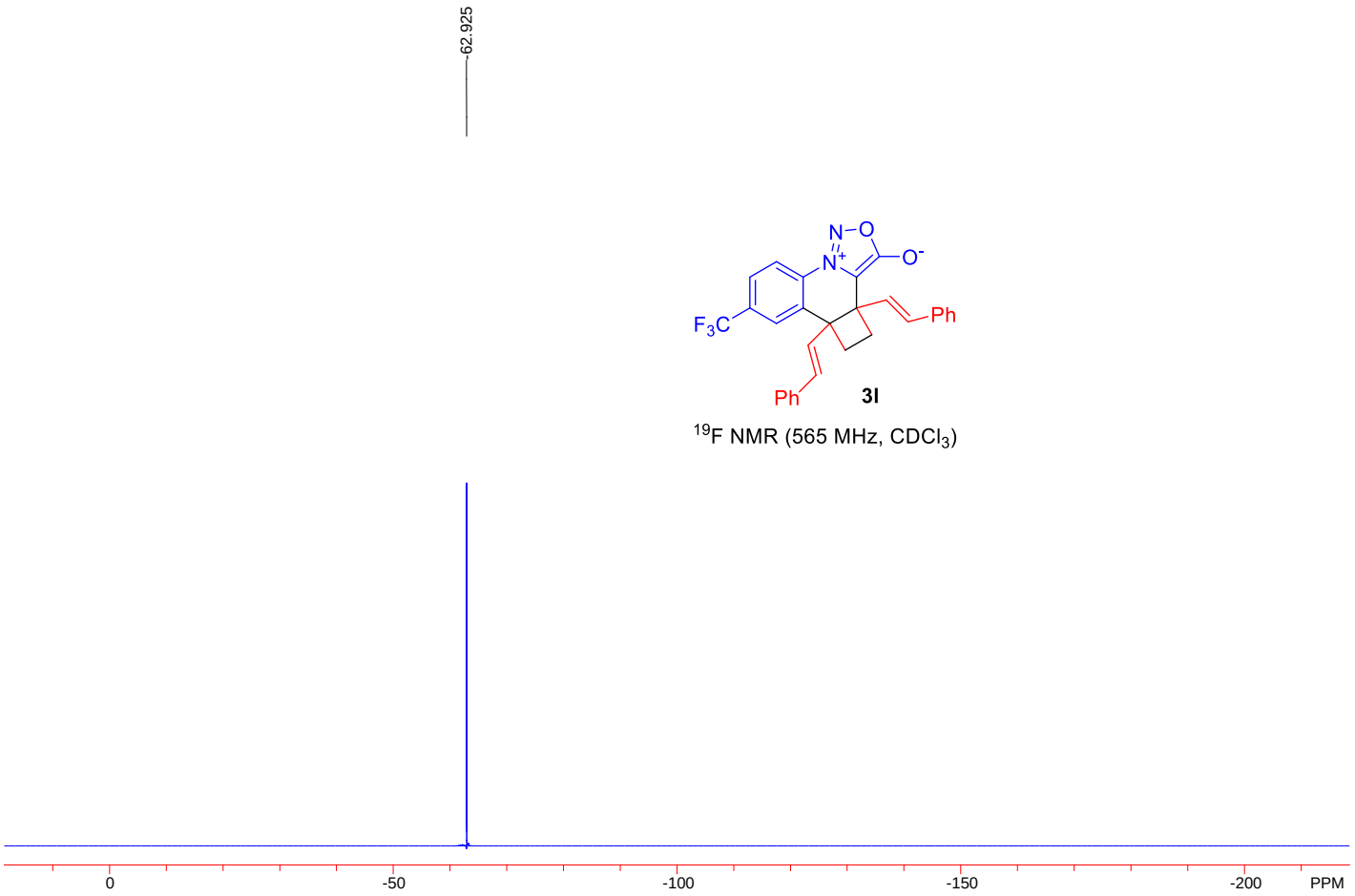




3l

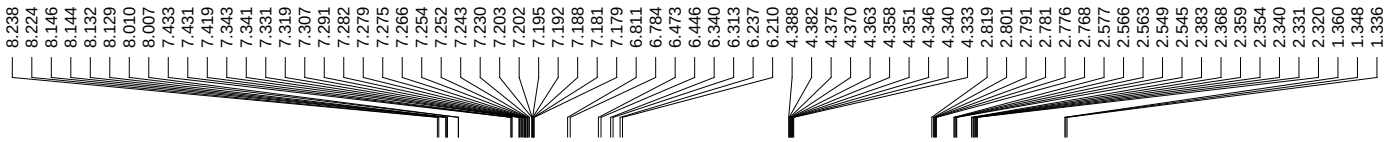
$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$)

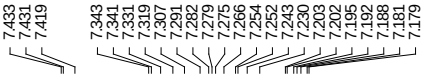


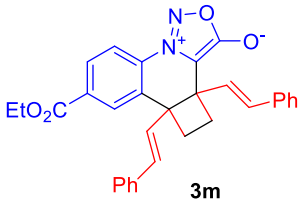


3l

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

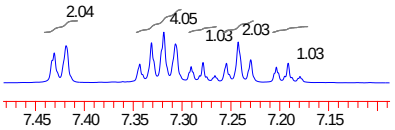


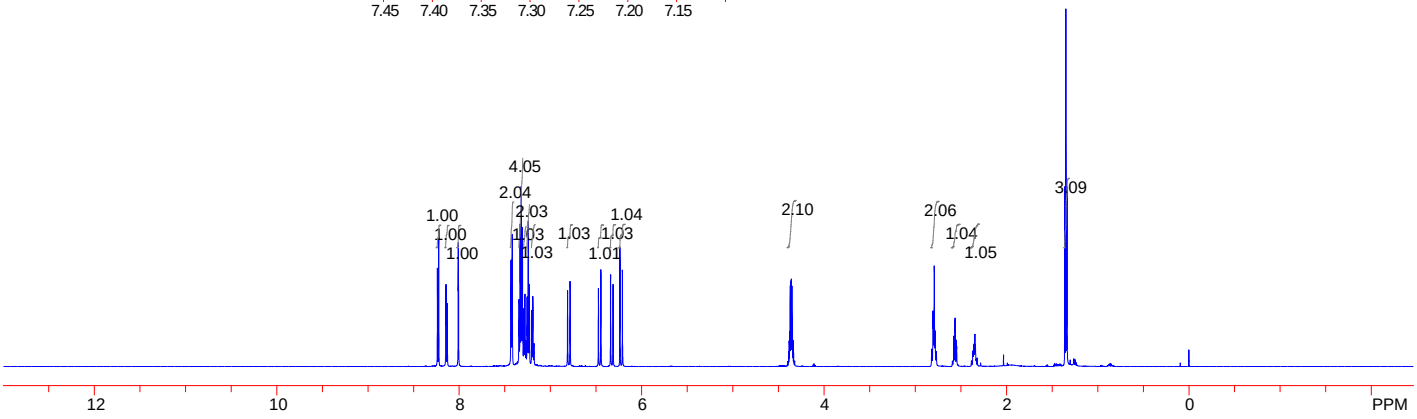


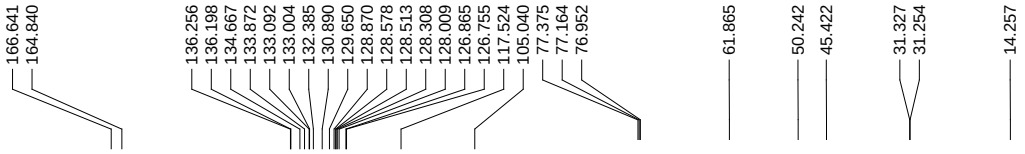


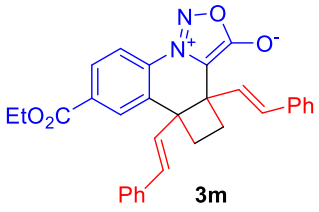
3m

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



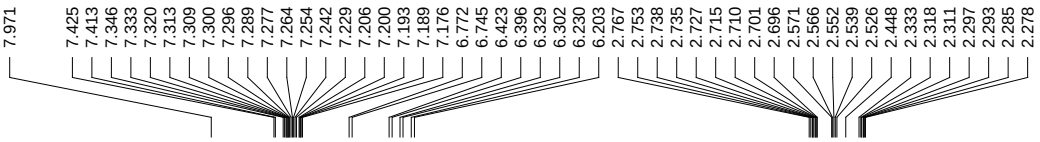


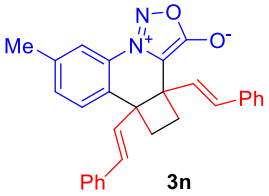




3m

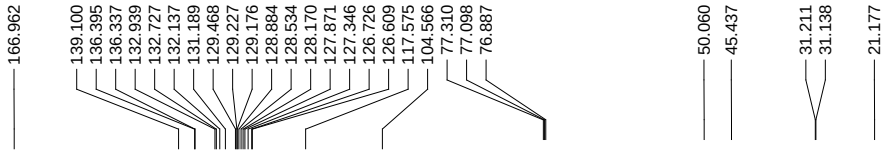
^{13}C{^{1}H } NMR (150 MHz, $CDCl_3$)

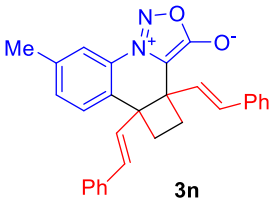




3n

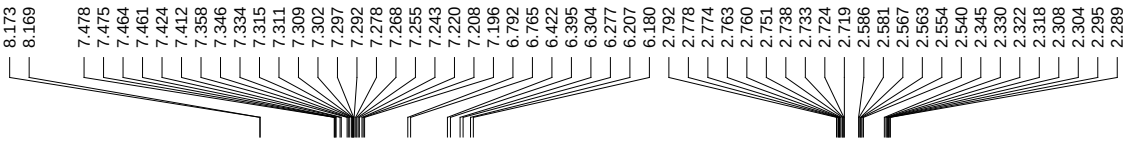
^{1}H NMR (600 MHz, $CDCl_3$)

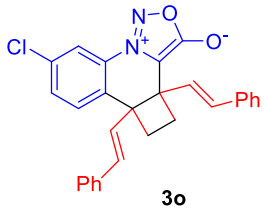




3n

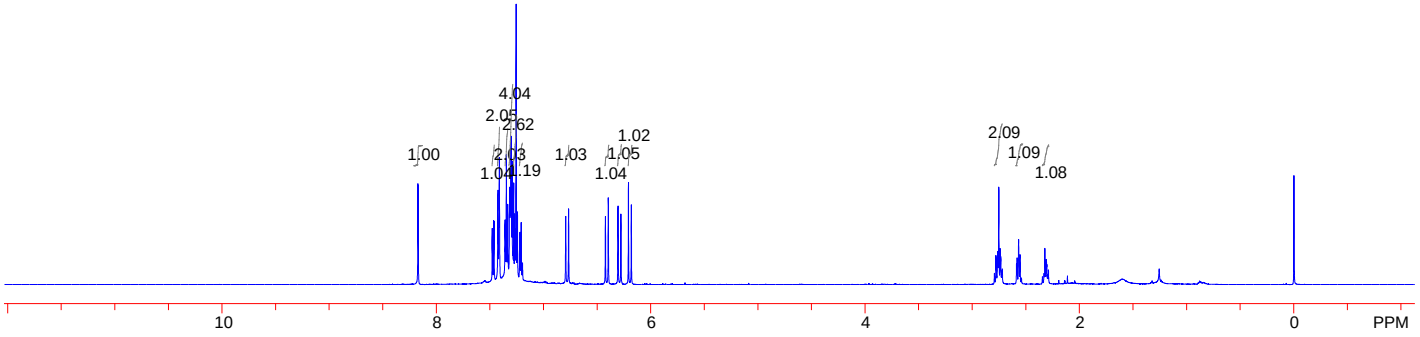
^{13}C{^{1}H } NMR (150 MHz, $CDCl_3$)

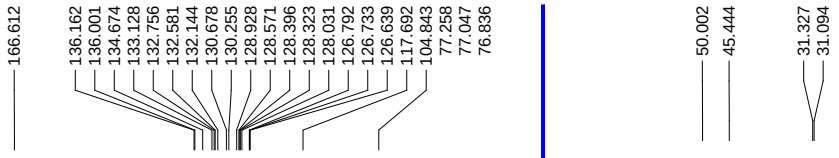


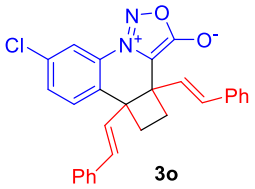


3o

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

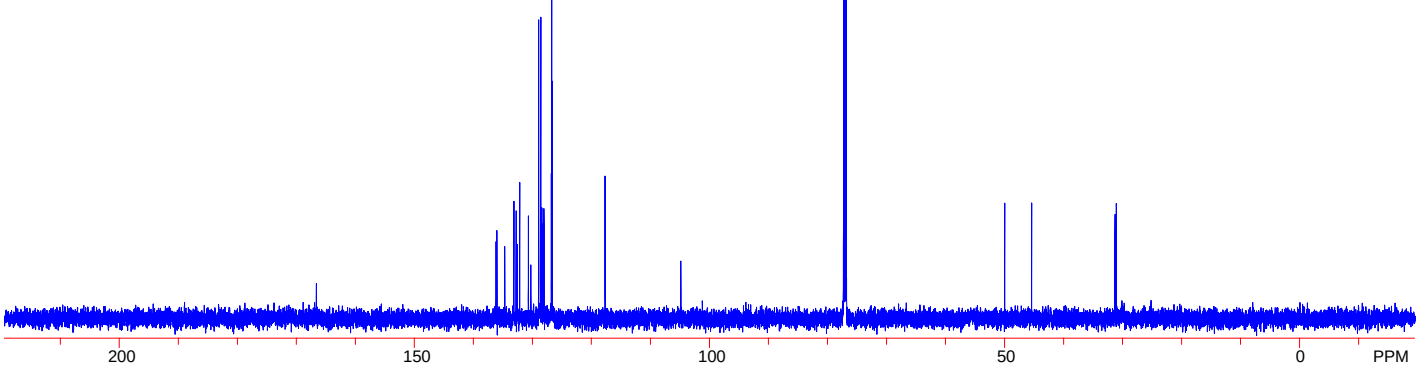


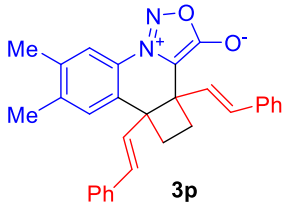




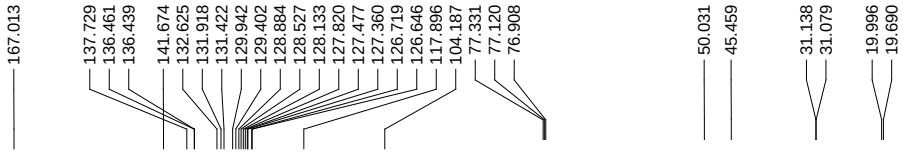
3o

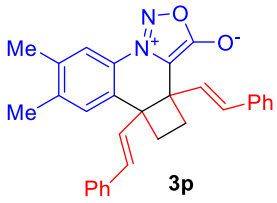
^{13}C{^{1}H } NMR (150 MHz, $CDCl_3$)



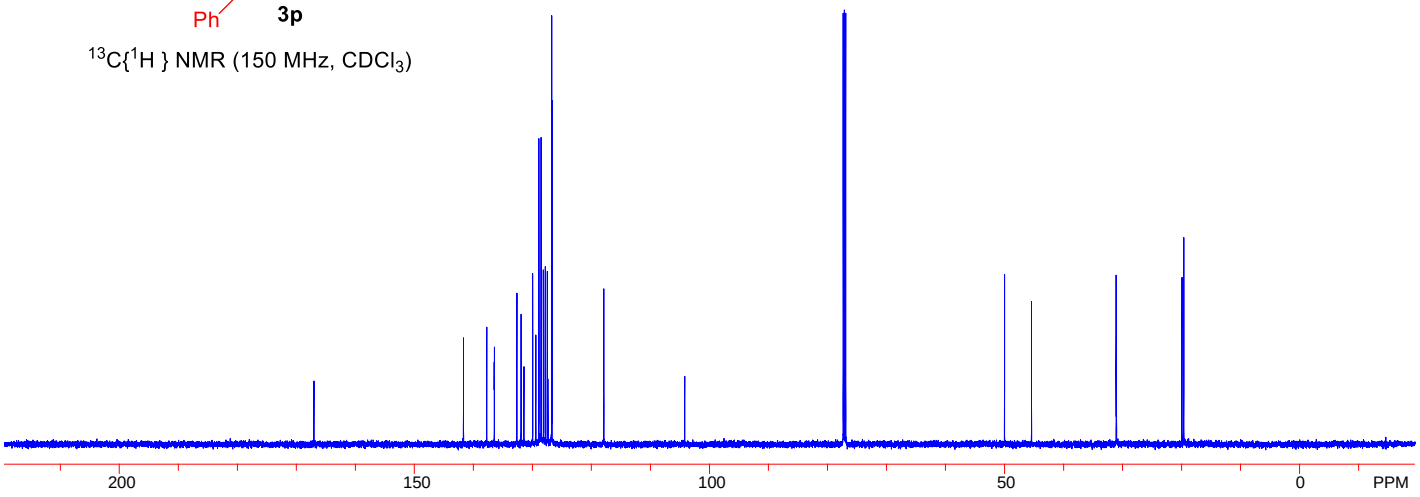


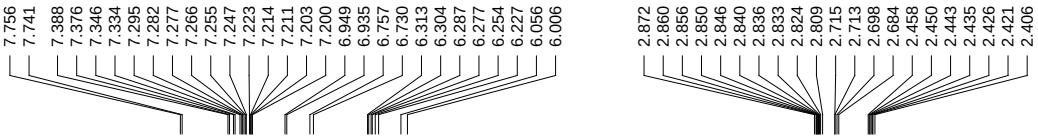
^{1}H NMR (600 MHz, $CDCl_3$)

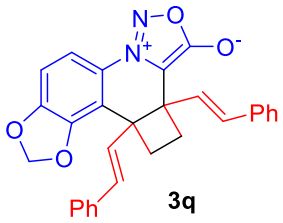




^{13}C{^{1}H } NMR (150 MHz, $CDCl_3$)

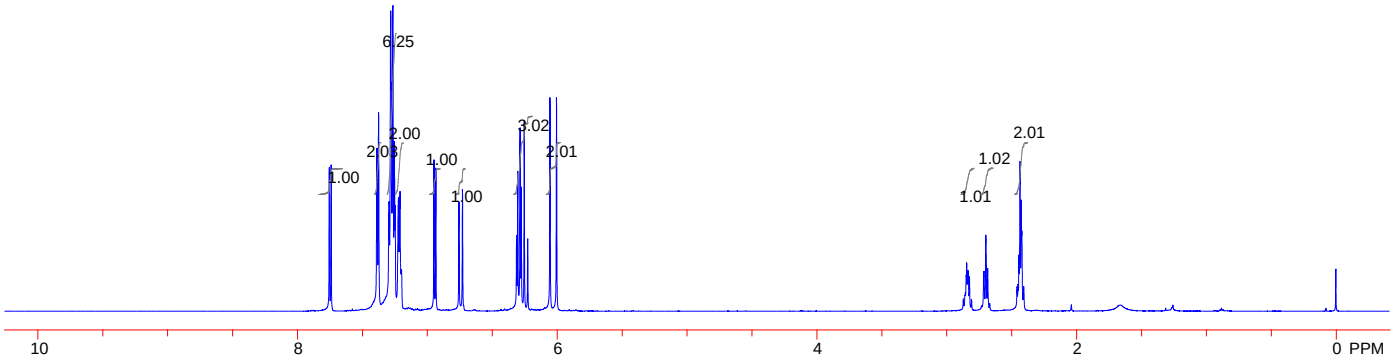


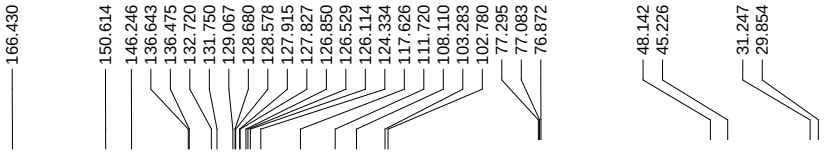


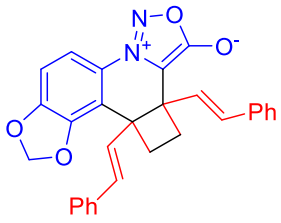


3q

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

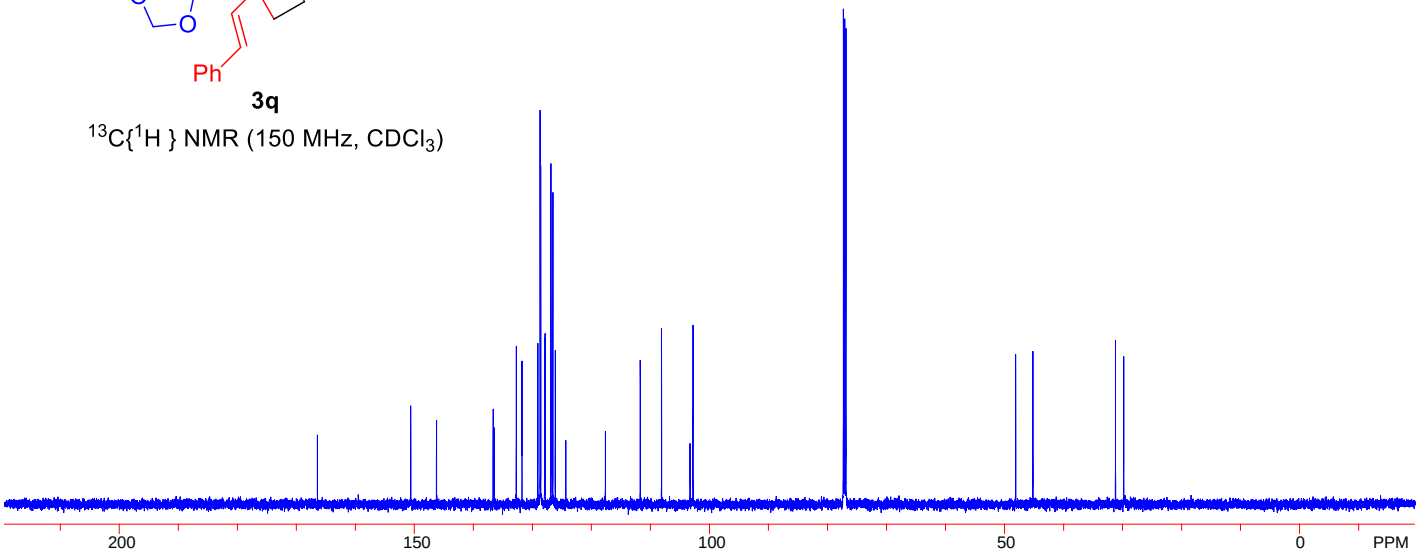


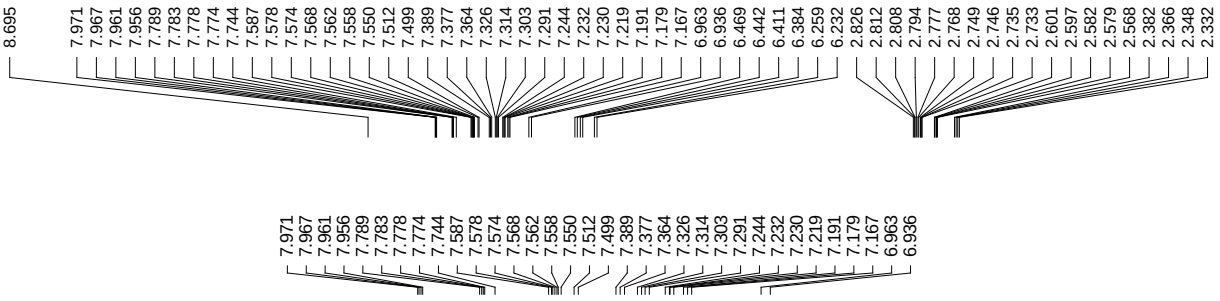


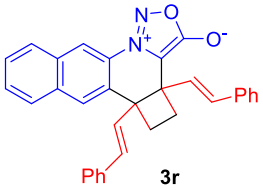


3q

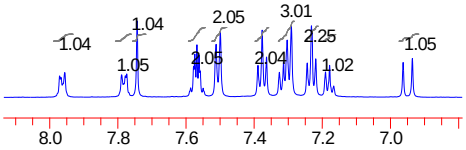
^{13}C{^{1}H } NMR (150 MHz, $CDCl_3$)



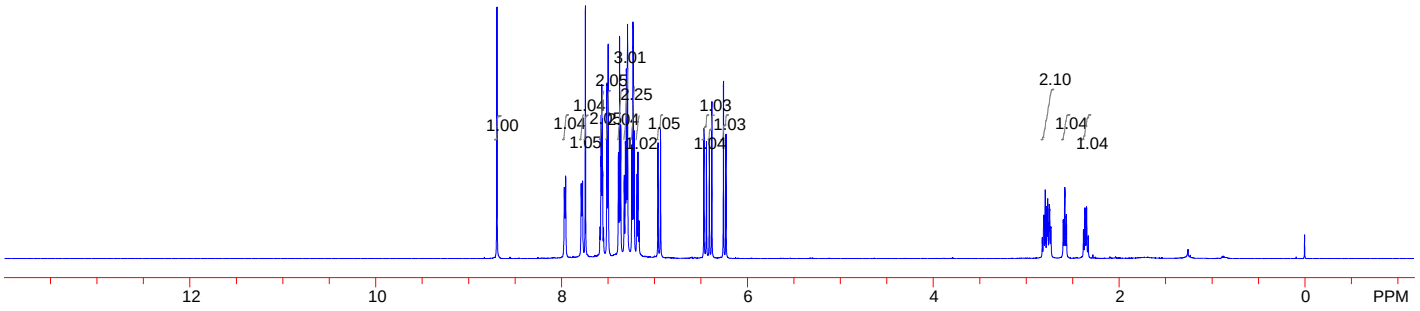


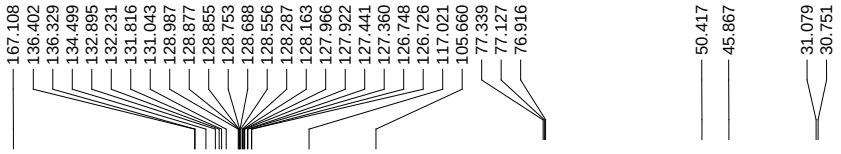


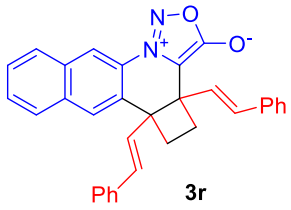
3r



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

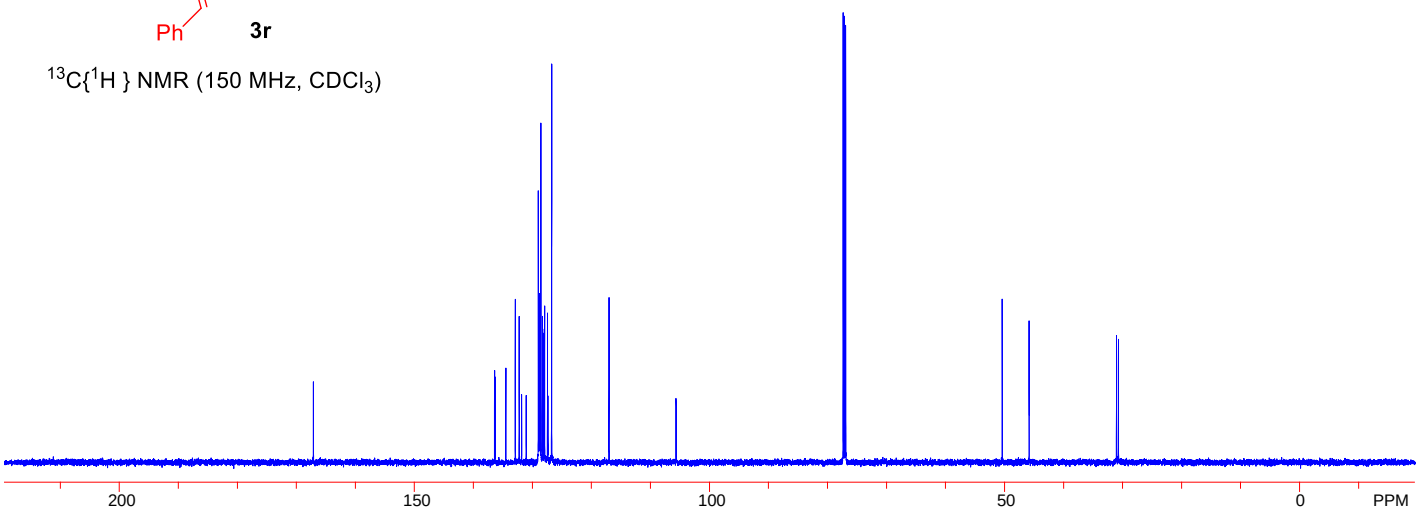


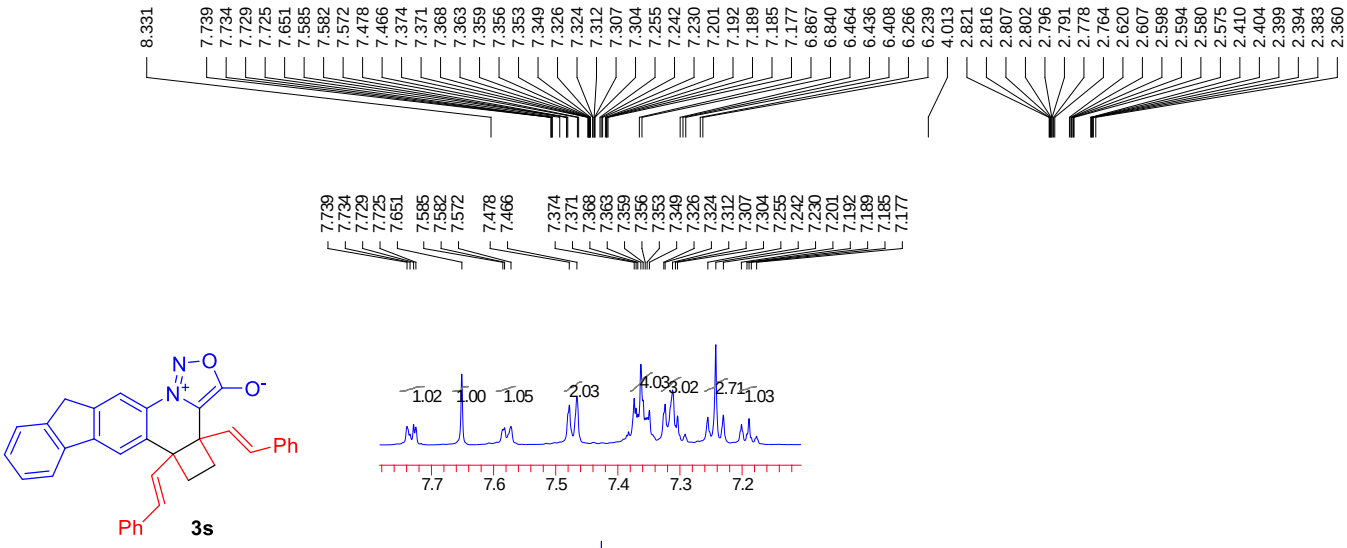




3r

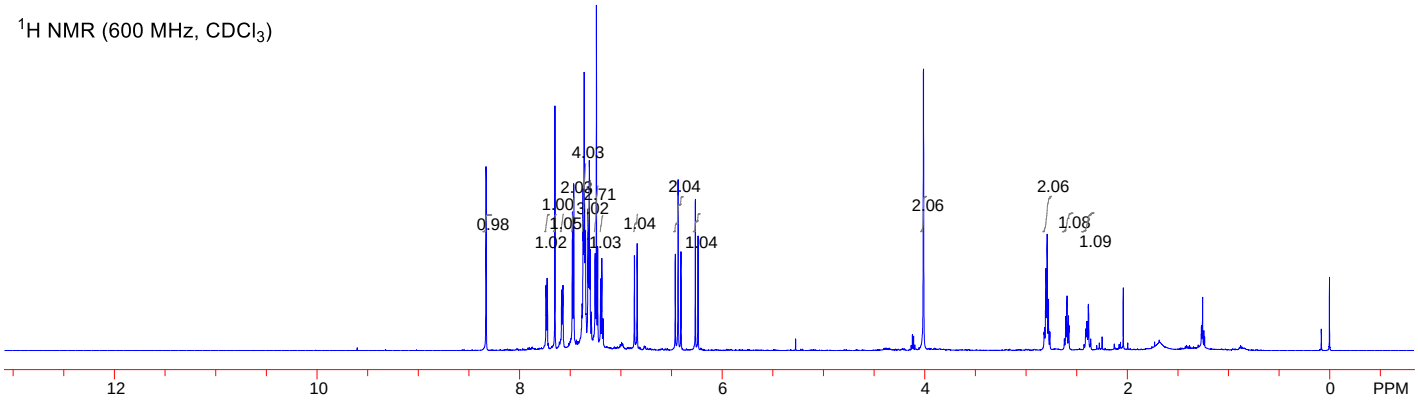
^{13}C{^{1}H } NMR (150 MHz, $CDCl_3$)

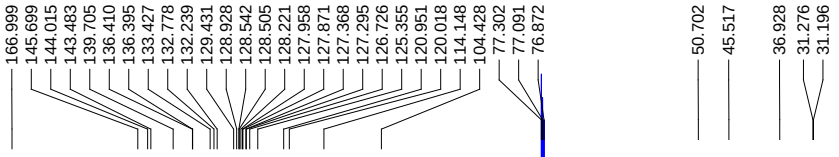


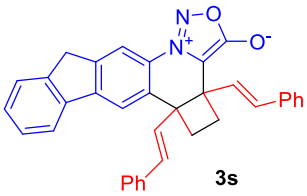


3s

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

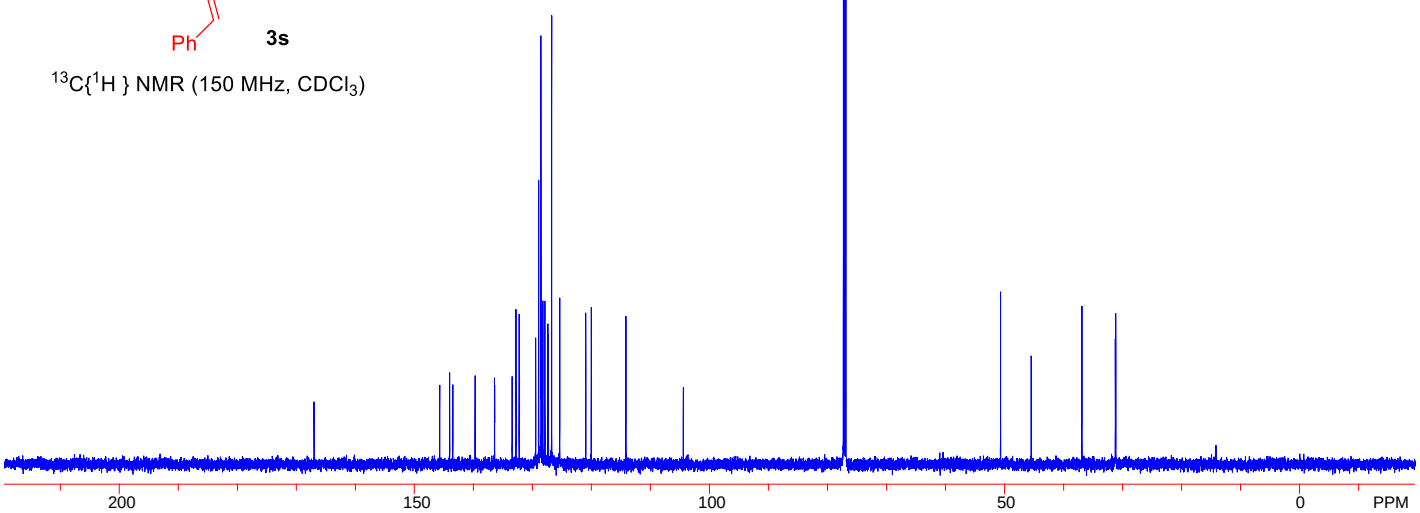


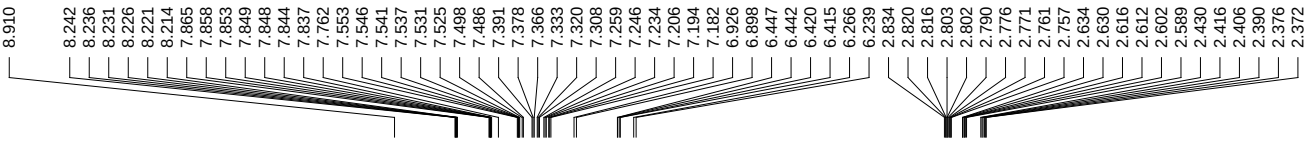


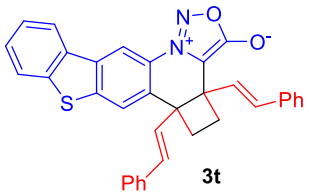


3s

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

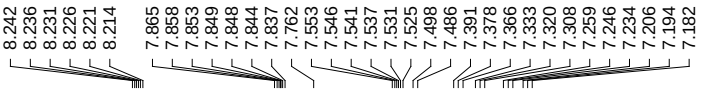


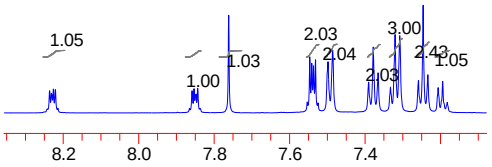


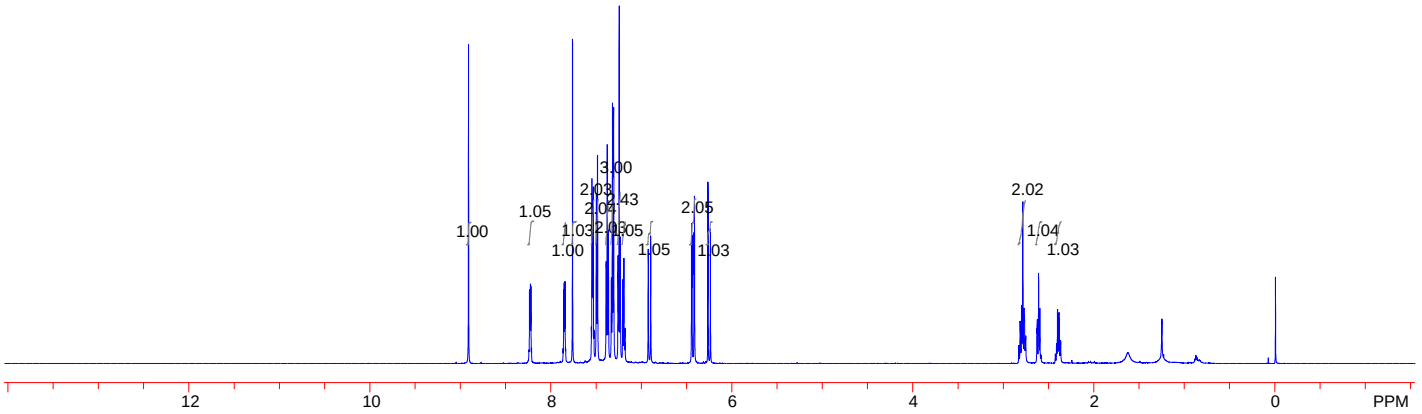


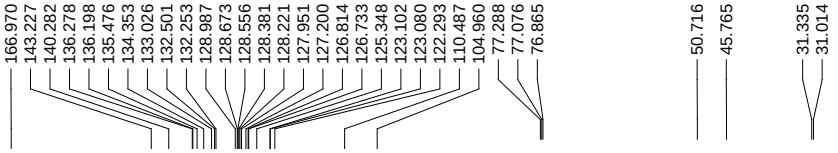
3t

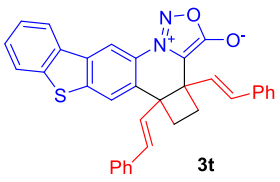
^{1}H NMR (600 MHz, $CDCl_3$)





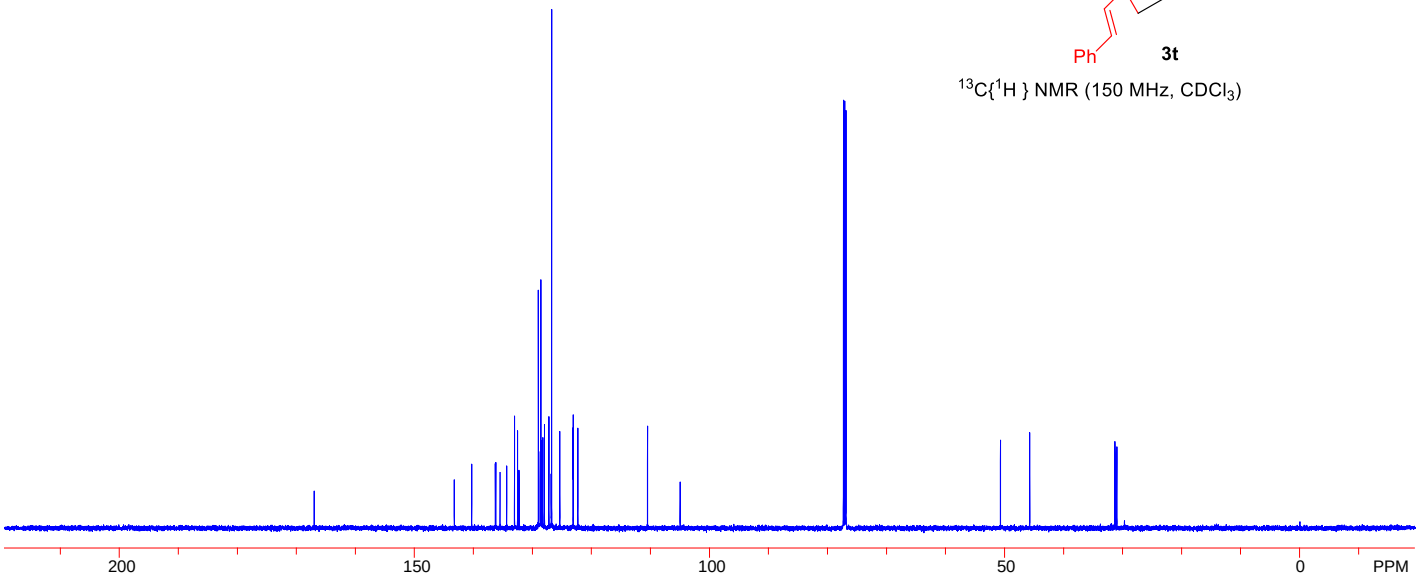


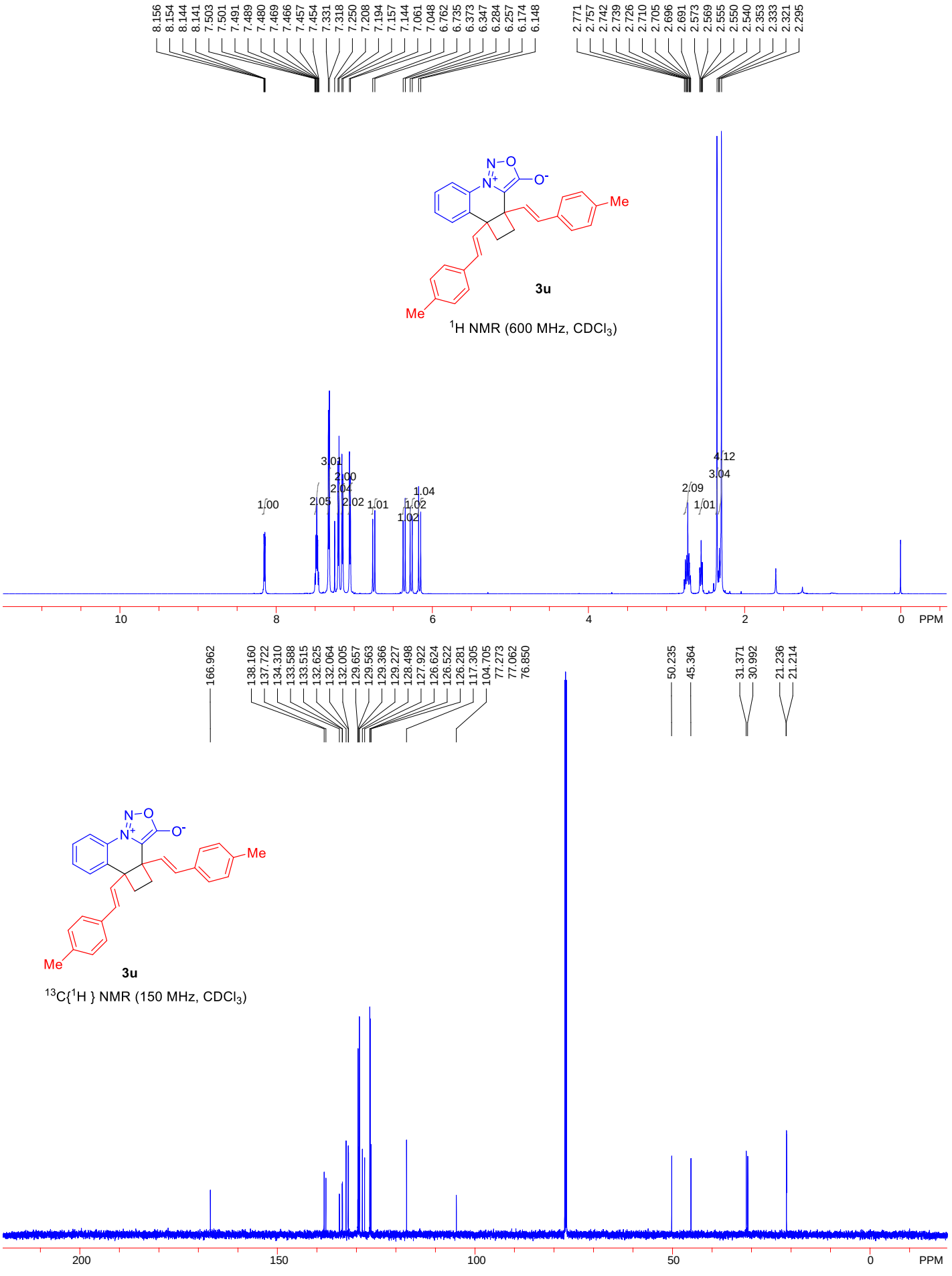




3t

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




8.156
8.154
8.144
8.141
7.503
7.501
7.491
7.489
7.480
7.469
7.466
7.457
7.454
7.331
7.318
7.250
7.208
7.194
7.157
7.144
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7.048
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6.735
6.373
6.347
6.284
6.257
6.174
6.148
2.771
2.757
2.742
2.739
2.726
2.710
2.705
2.696
2.691
2.573
2.569
2.555
2.550
2.540
2.353
2.333
2.321
2.295
N
O
N+
O-
Me
Me
3u
1H NMR (600 MHz, CDCl3)
1.00
3.01
2.00
2.04
2.05
2.02
1.01
1.04
1.02
1.02
2.09
4.12
3.04
1.01
10
8
6
4
2
0
PPM
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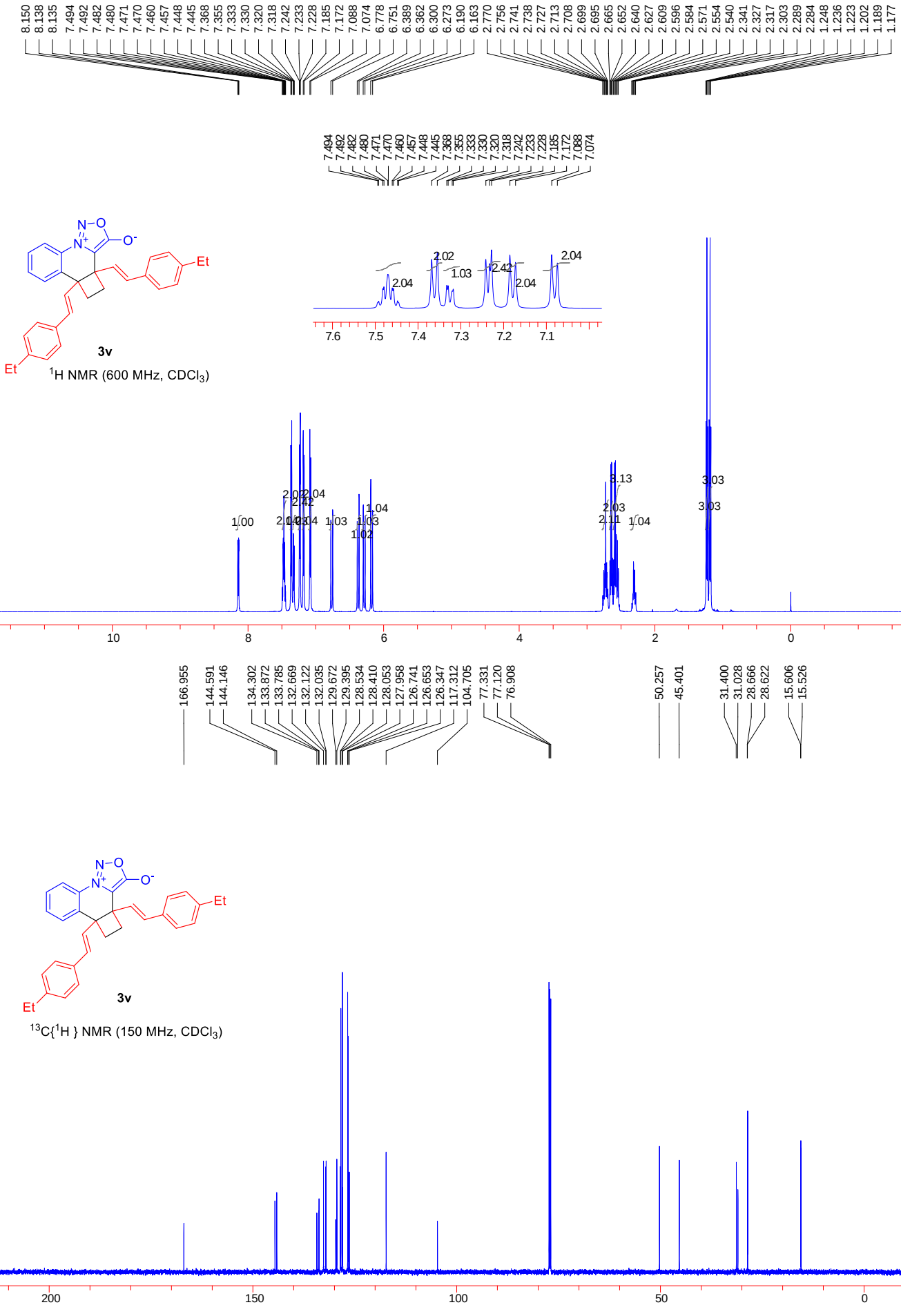
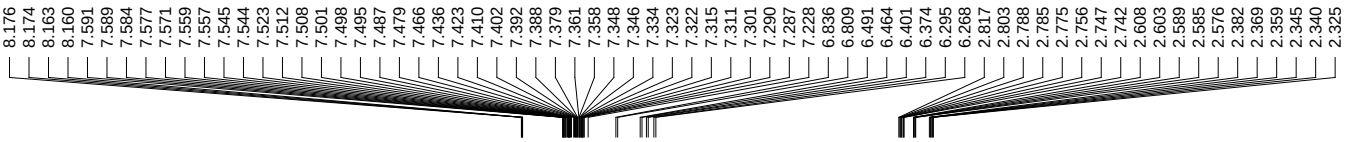
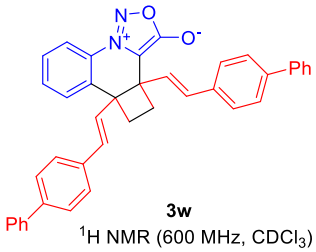
138.160
137.722
134.310
133.588
133.515
132.625
132.064
132.005
129.657
129.563
129.366
129.227
128.498
127.922
126.624
126.522
126.281
117.305
104.705
77.273
77.062
76.850
50.235
45.364
31.371
30.992
21.236
21.214
N
O
N+
O-
Me
Me
3u
13C{1H } NMR (150 MHz, CDCl3)
200
150
100
50
0
PPM

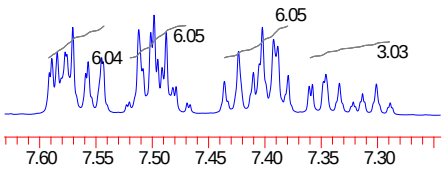

3v
1H NMR (600 MHz, CDCl3)
PPM
3v
13C{1H } NMR (150 MHz, CDCl3)
PPM

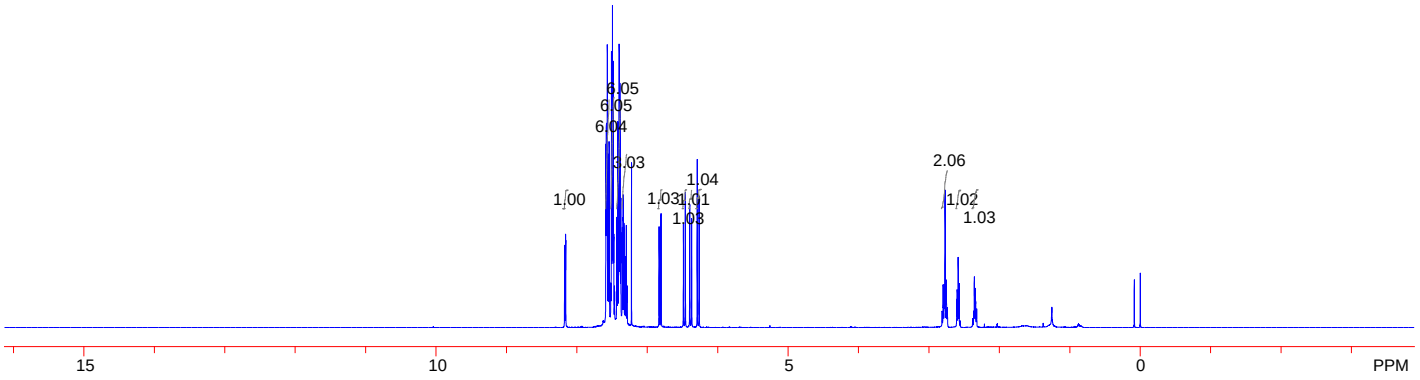


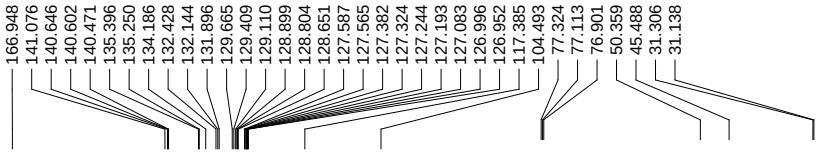


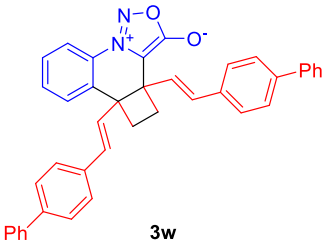
3w

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



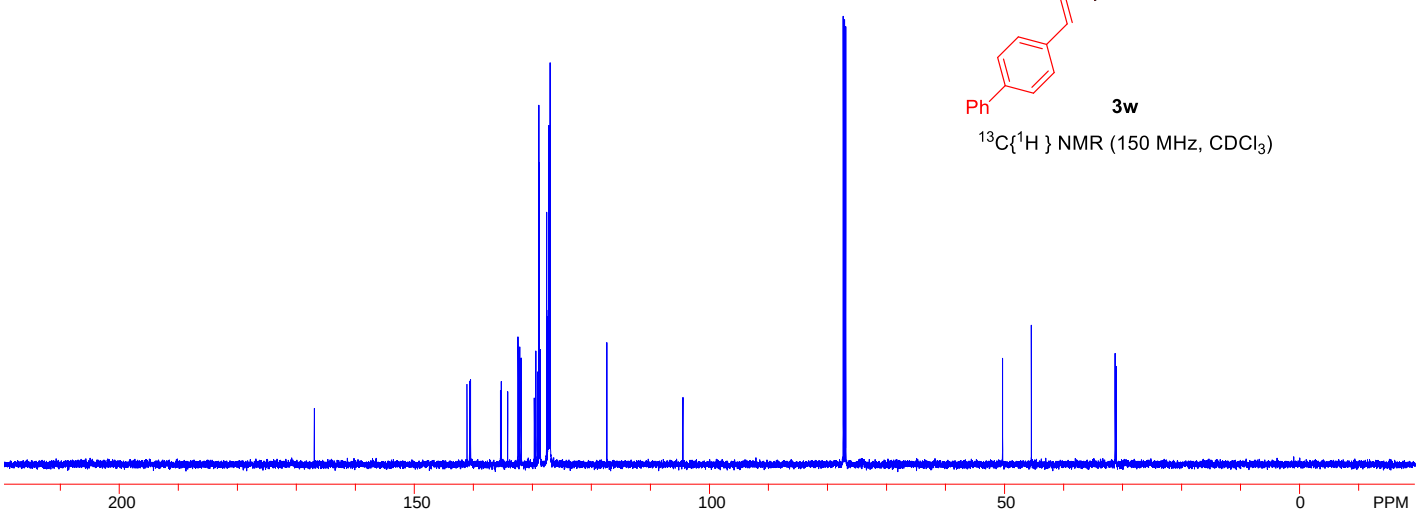


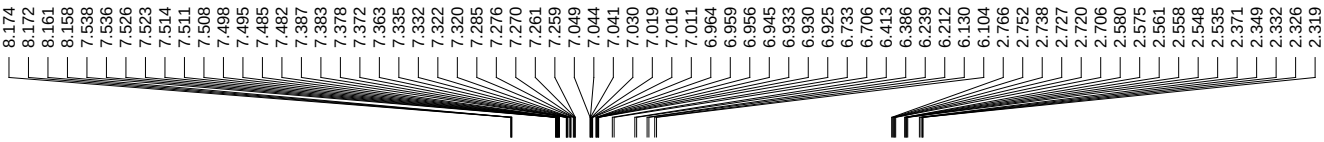


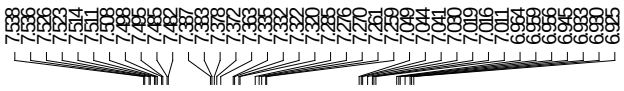


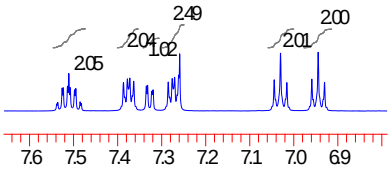
3w

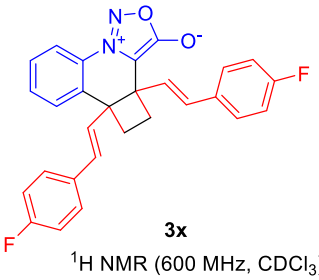
^{13}C{^{1}H } NMR (150 MHz, $CDCl_3$)





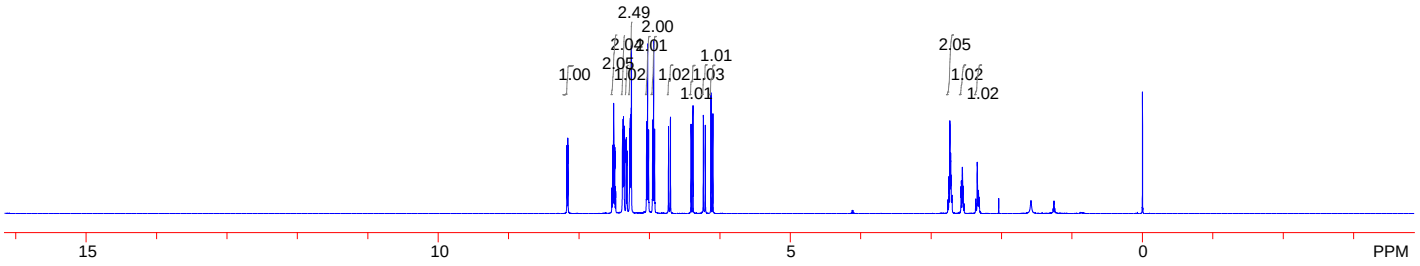


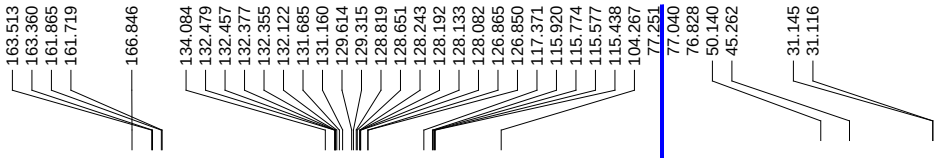


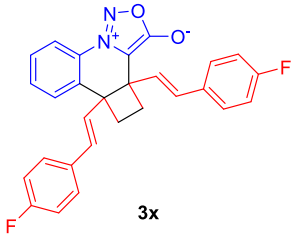


3x

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

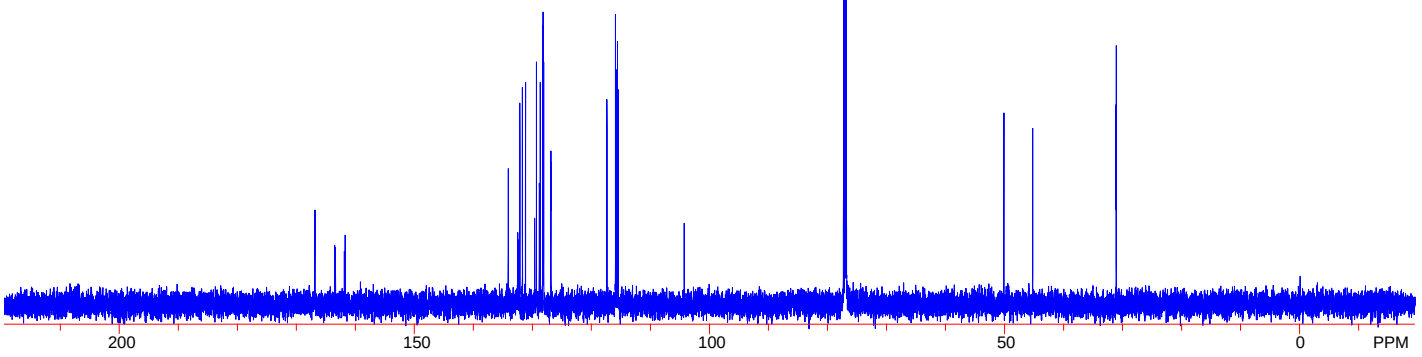


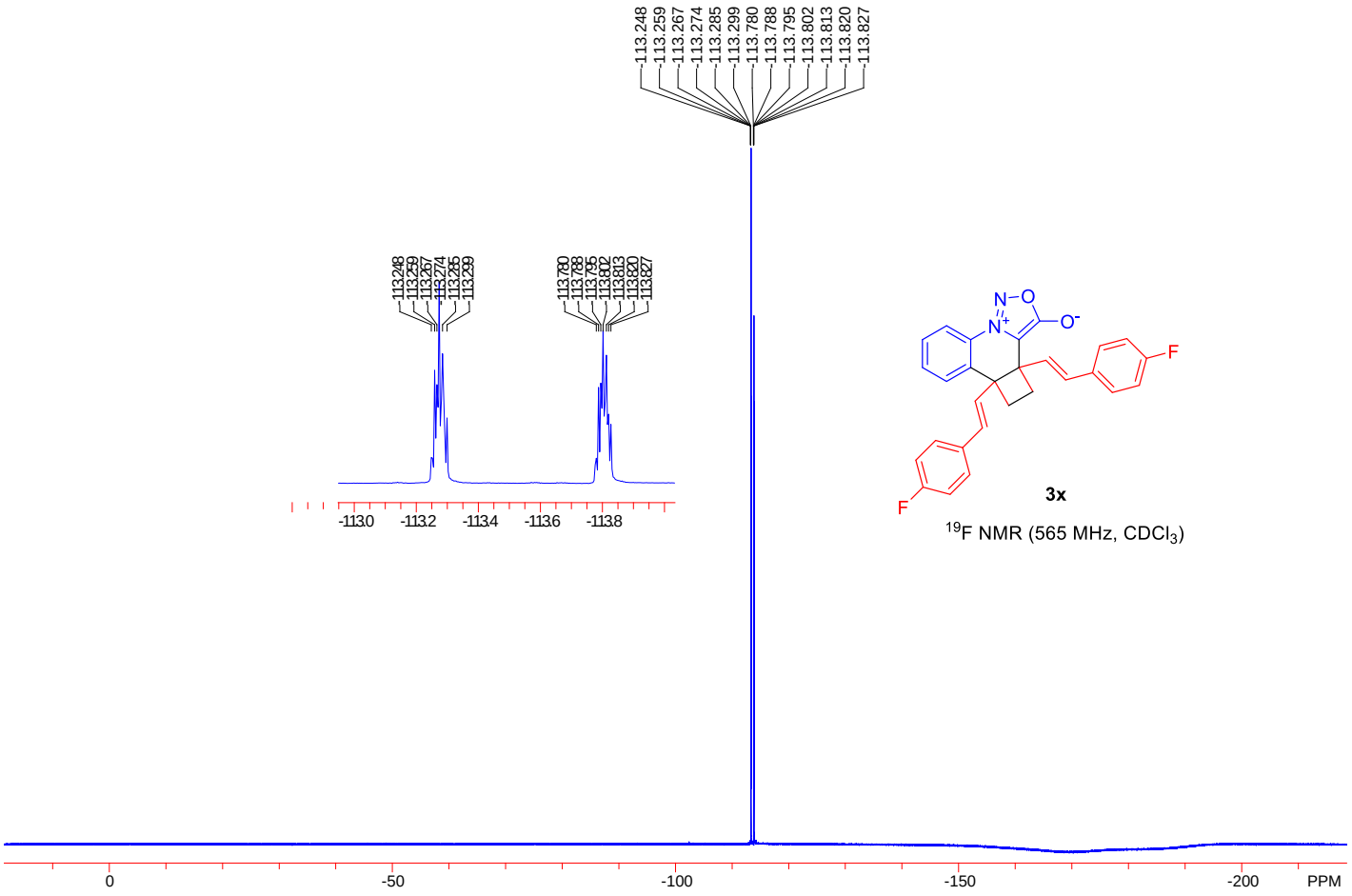


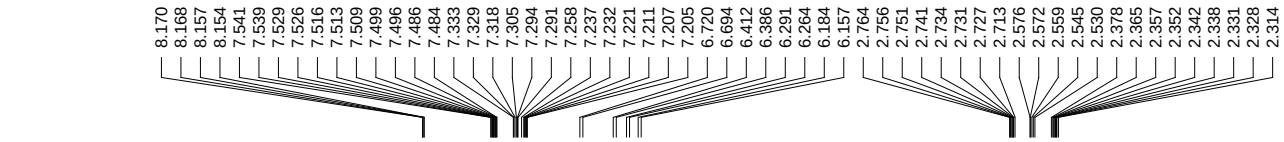


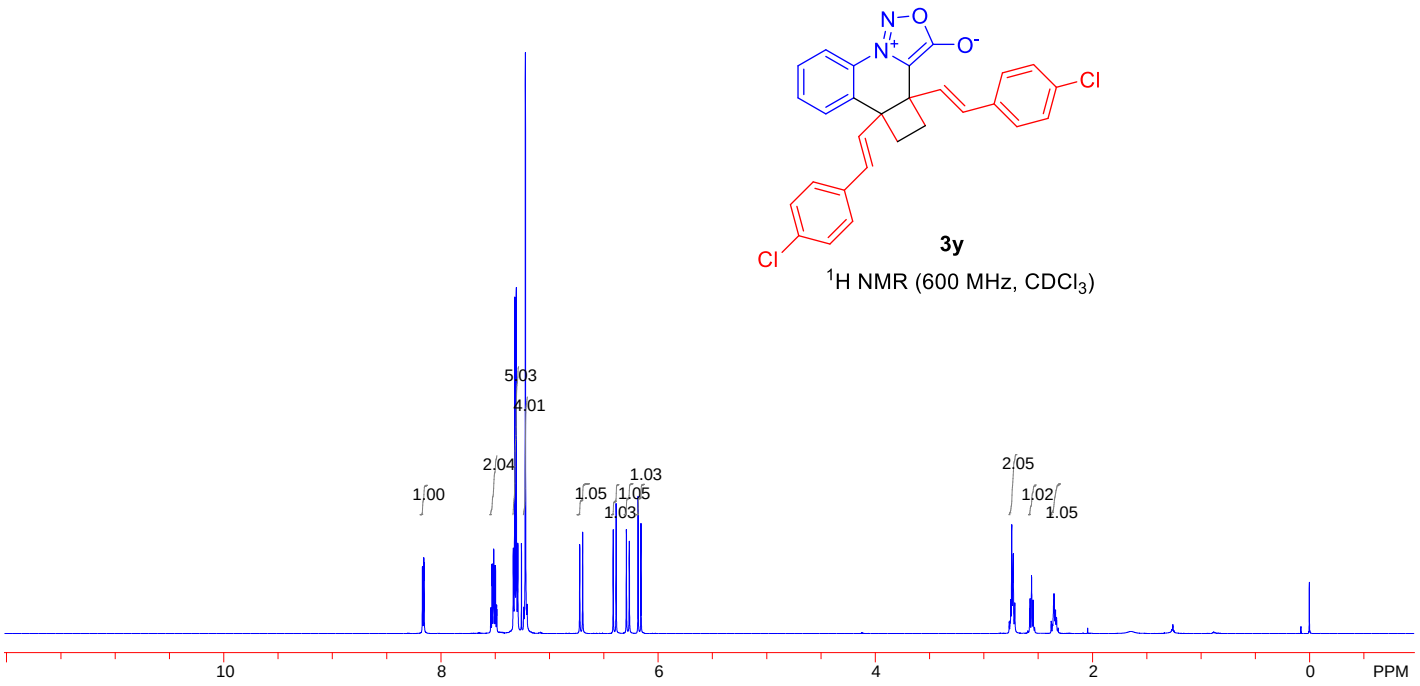
3x

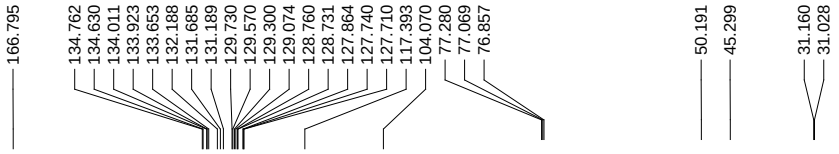
$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$)

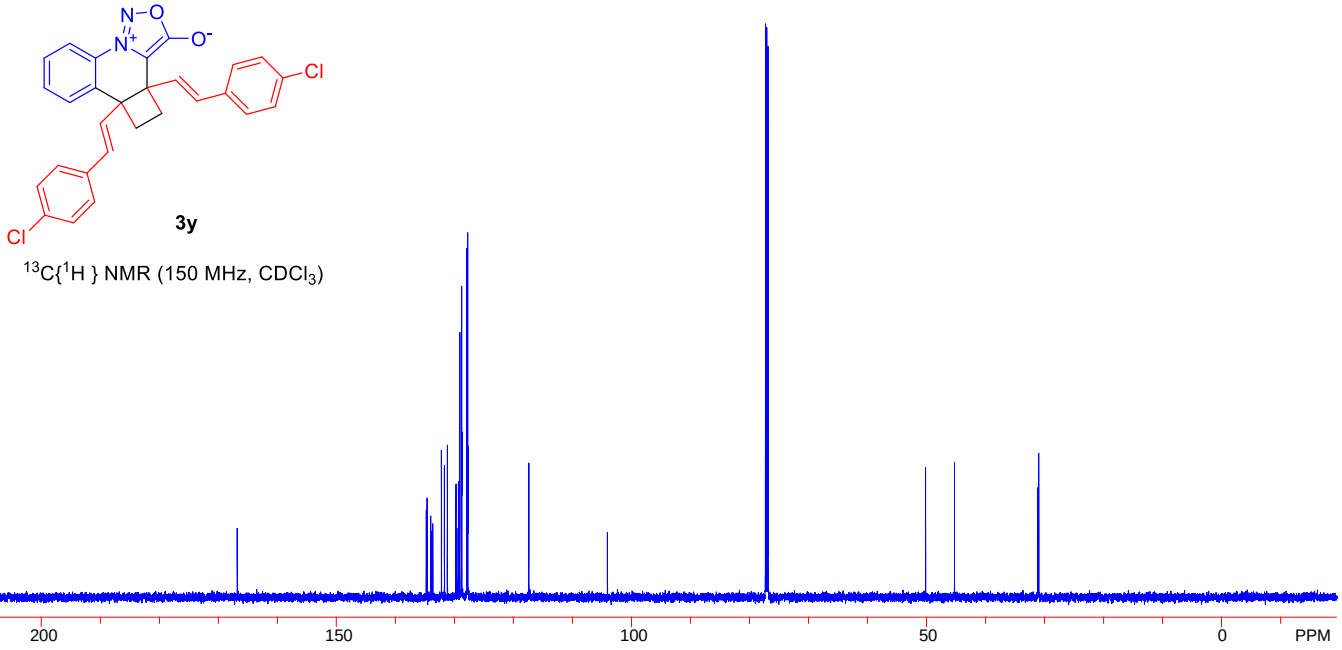


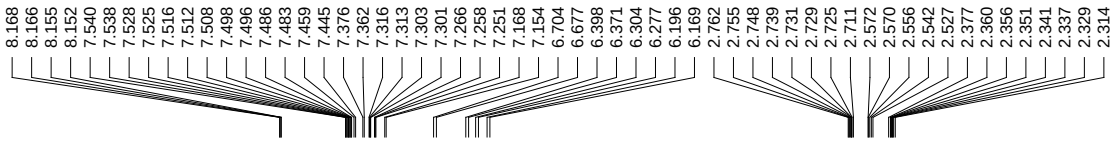

-113.248
-113.259
-113.267
-113.274
-113.285
-113.299
-113.780
-113.788
-113.795
-113.802
-113.813
-113.820
-113.827
-113.0
-113.2
-113.4
-113.6
-113.8
N–O
N+
O-
F
F
3x
19F NMR (565 MHz, CDCl3)
0
-50
-100
-150
-200
PPM

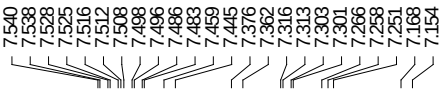

8.170
8.168
8.157
8.154
7.541
7.539
7.529
7.526
7.516
7.513
7.509
7.499
7.496
7.486
7.484
7.333
7.329
7.318
7.305
7.294
7.291
7.258
7.237
7.232
7.221
7.211
7.207
7.205
6.720
6.694
6.412
6.386
6.291
6.264
6.184
6.157
2.764
2.756
2.751
2.741
2.734
2.731
2.727
2.713
2.576
2.572
2.559
2.545
2.530
2.378
2.365
2.357
2.352
2.342
2.338
2.331
2.328
2.314

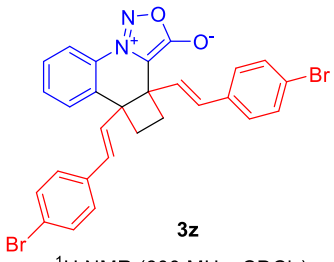

N
O
N+
O-
Cl
Cl
3y
1H NMR (600 MHz, CDCl3)
5.03
4.01
2.04
1.00
1.05
1.05
1.03
1.03
2.05
1.02
1.05
10
8
6
4
2
0
PPM


166.795
134.762
134.630
134.011
133.923
133.653
132.188
131.685
131.189
129.730
129.570
129.300
129.074
128.760
128.731
127.864
127.740
127.710
117.393
104.070
77.280
77.069
76.857
50.191
45.299
31.160
31.028


N
O
N+
O-
Cl
Cl
3y
13C{1H} NMR (150 MHz, CDCl3)
200
150
100
50
0
PPM

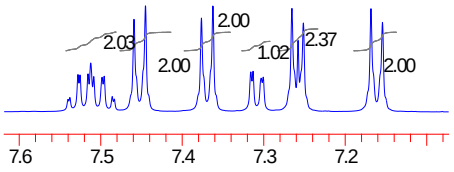


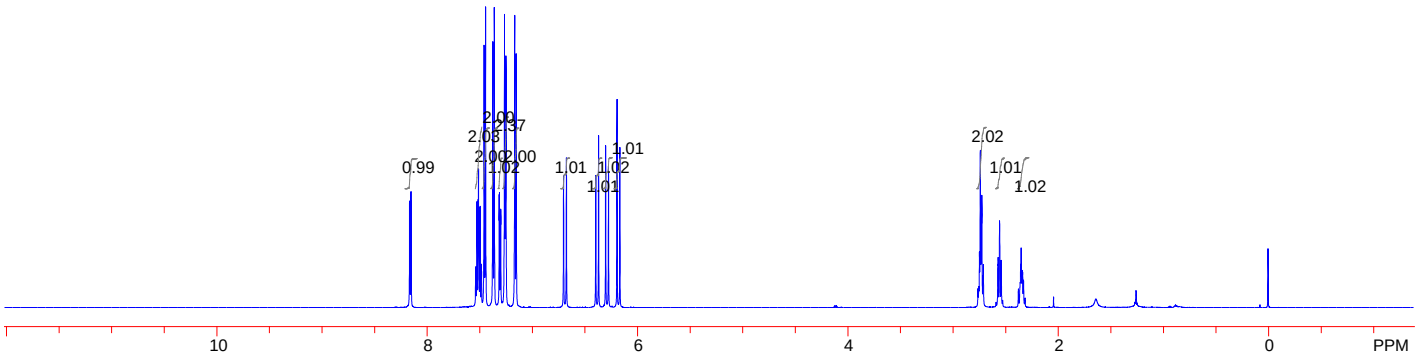


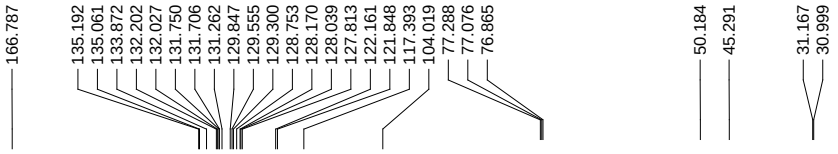


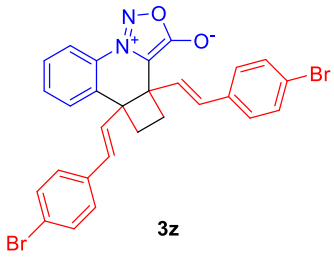
3z

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



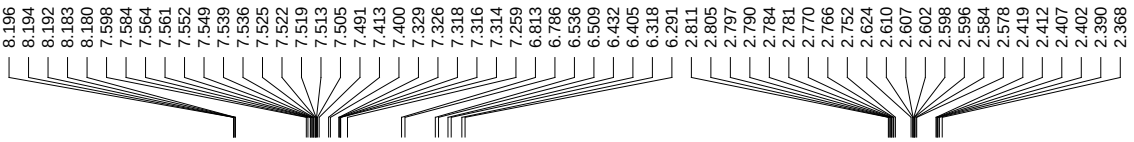


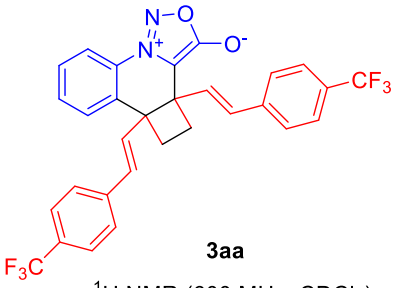




3z

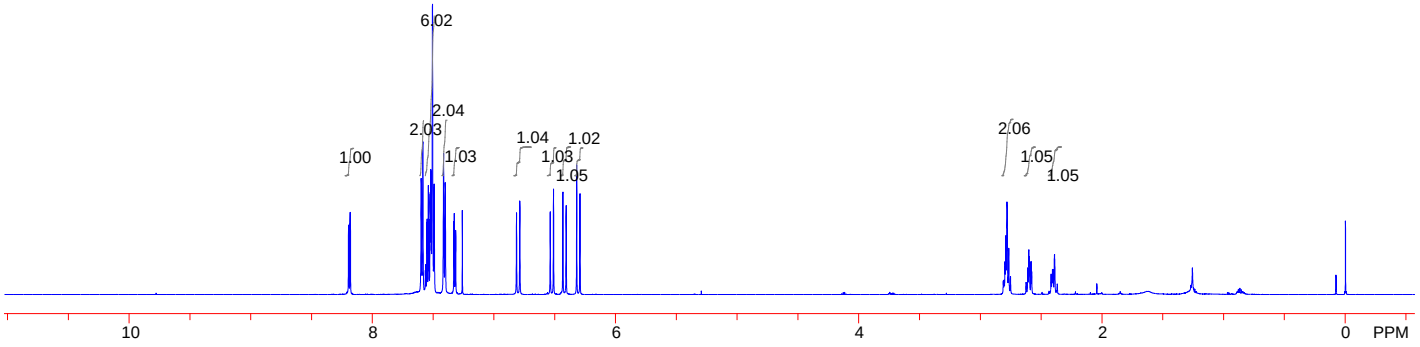
^{13}C{^{1}H } NMR (150 MHz, $CDCl_3$)

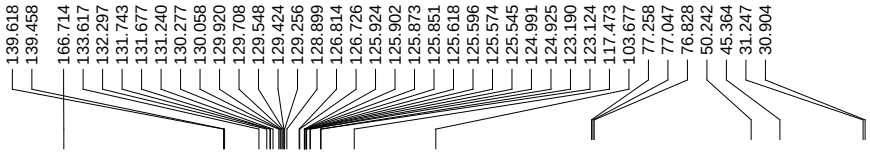


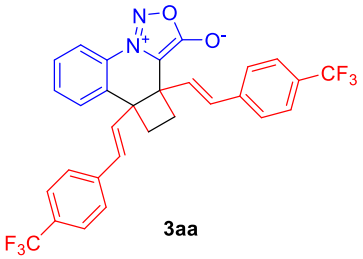


3aa

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

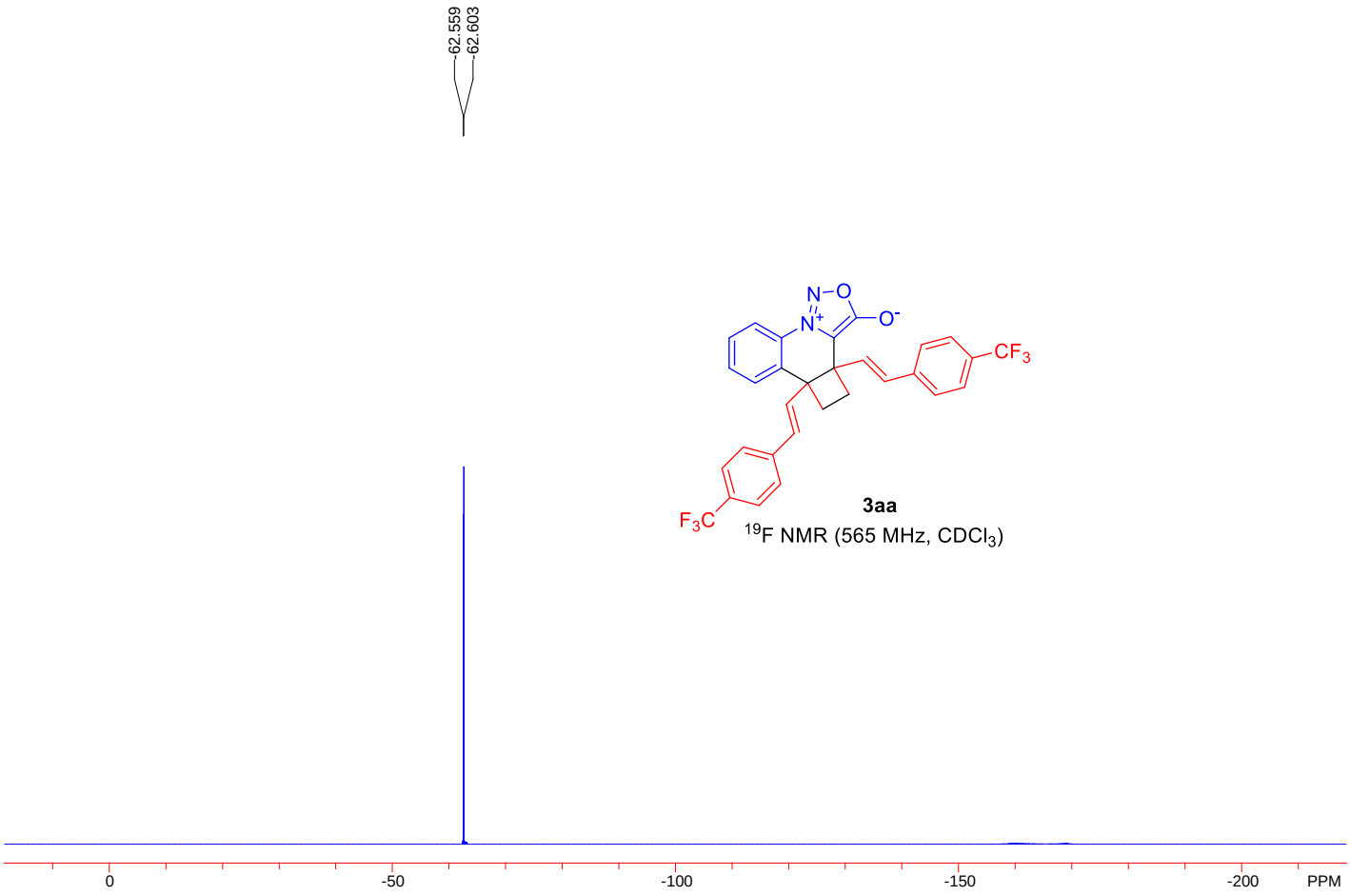






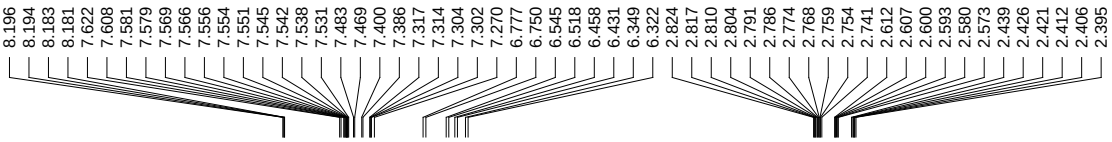
3aa

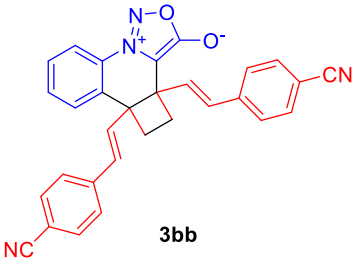
^{13}C{^{1}H } NMR (150 MHz, $CDCl_3$)



3aa

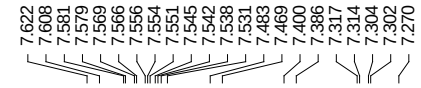
^{19}F NMR (565 MHz, $CDCl_3$)

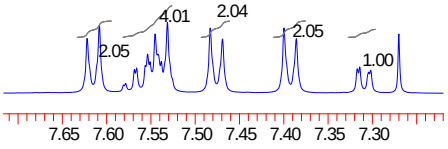


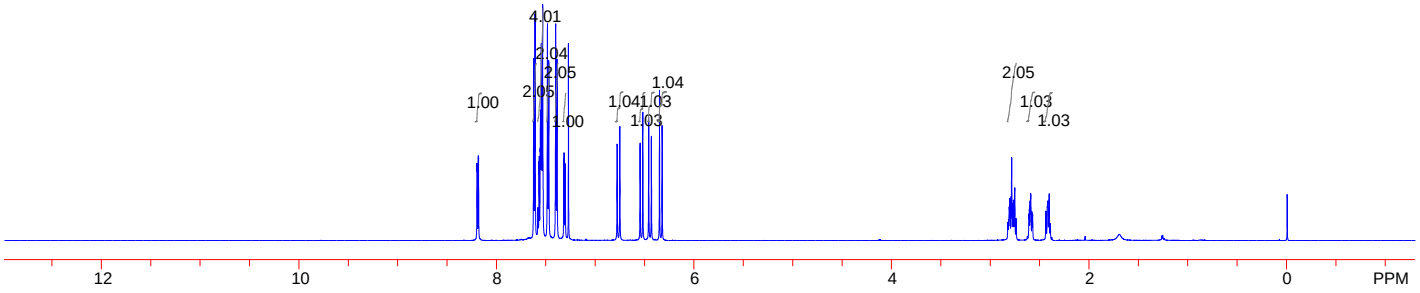


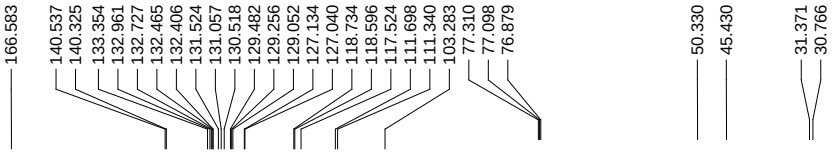
3bb

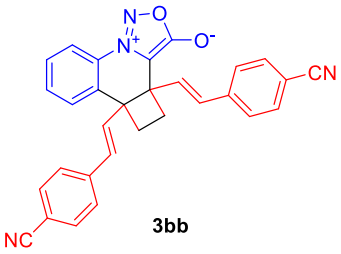
^{1}H NMR (600 MHz, $CDCl_3$)





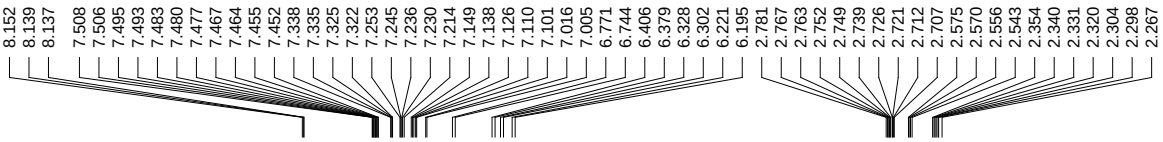


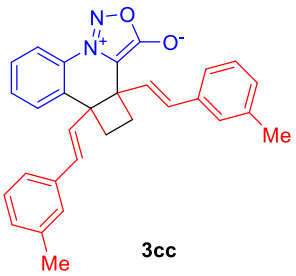




3bb

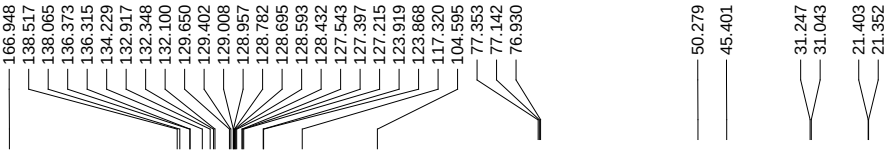
^{13}C{^{1}H } NMR (150 MHz, $CDCl_3$)

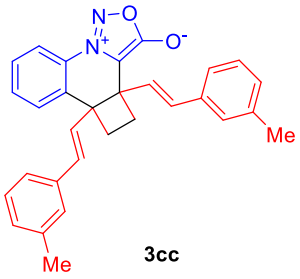




3cc

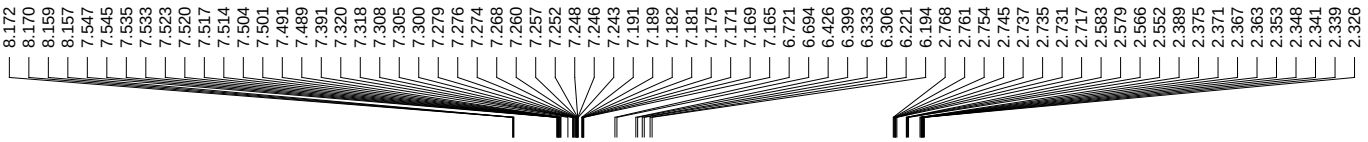
^{1}H NMR (600 MHz, $CDCl_3$)

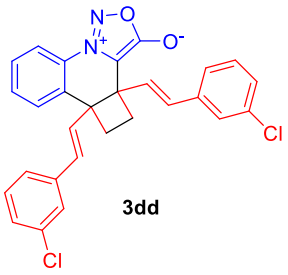




3cc

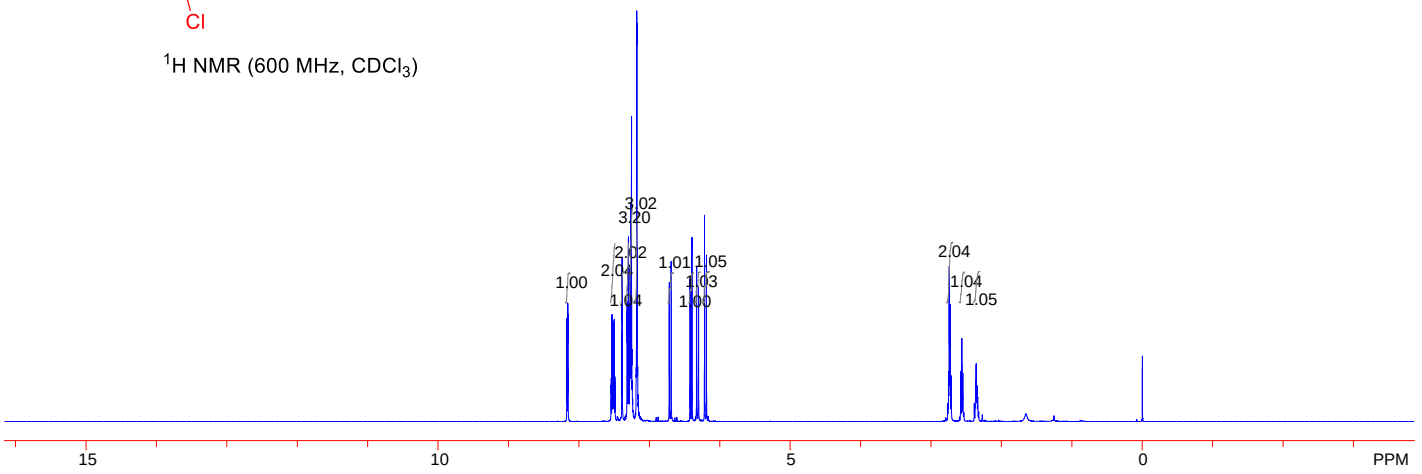
^{13}C{^{1}H } NMR (150 MHz, $CDCl_3$)

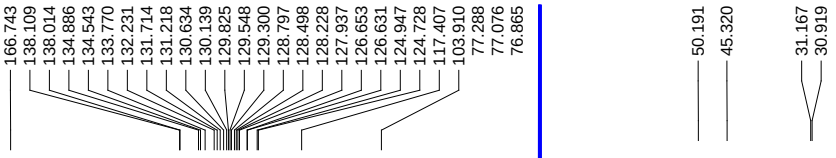


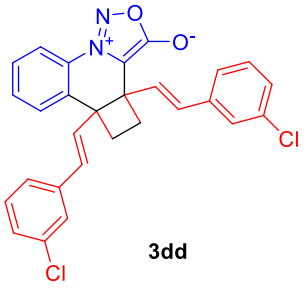


3dd

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

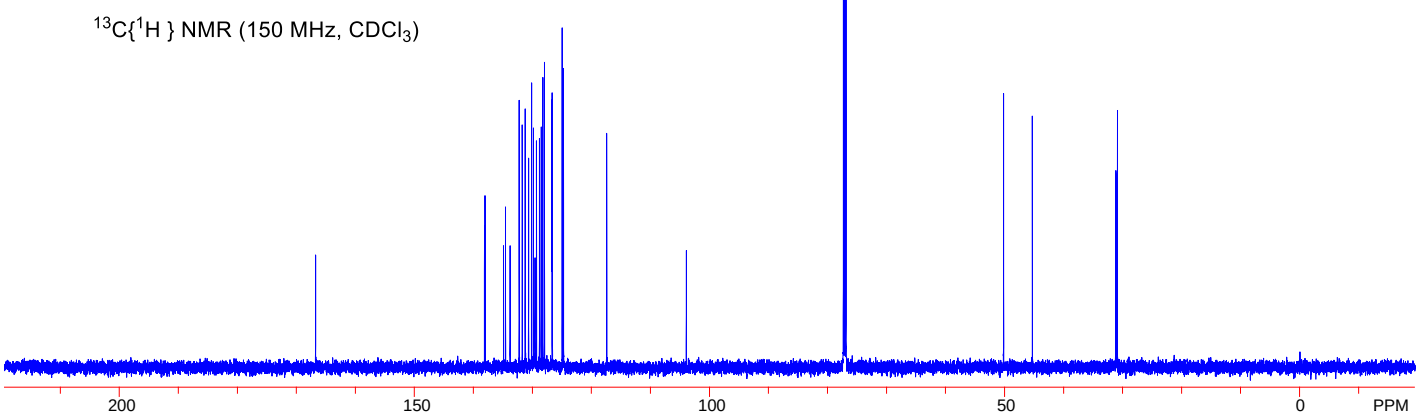


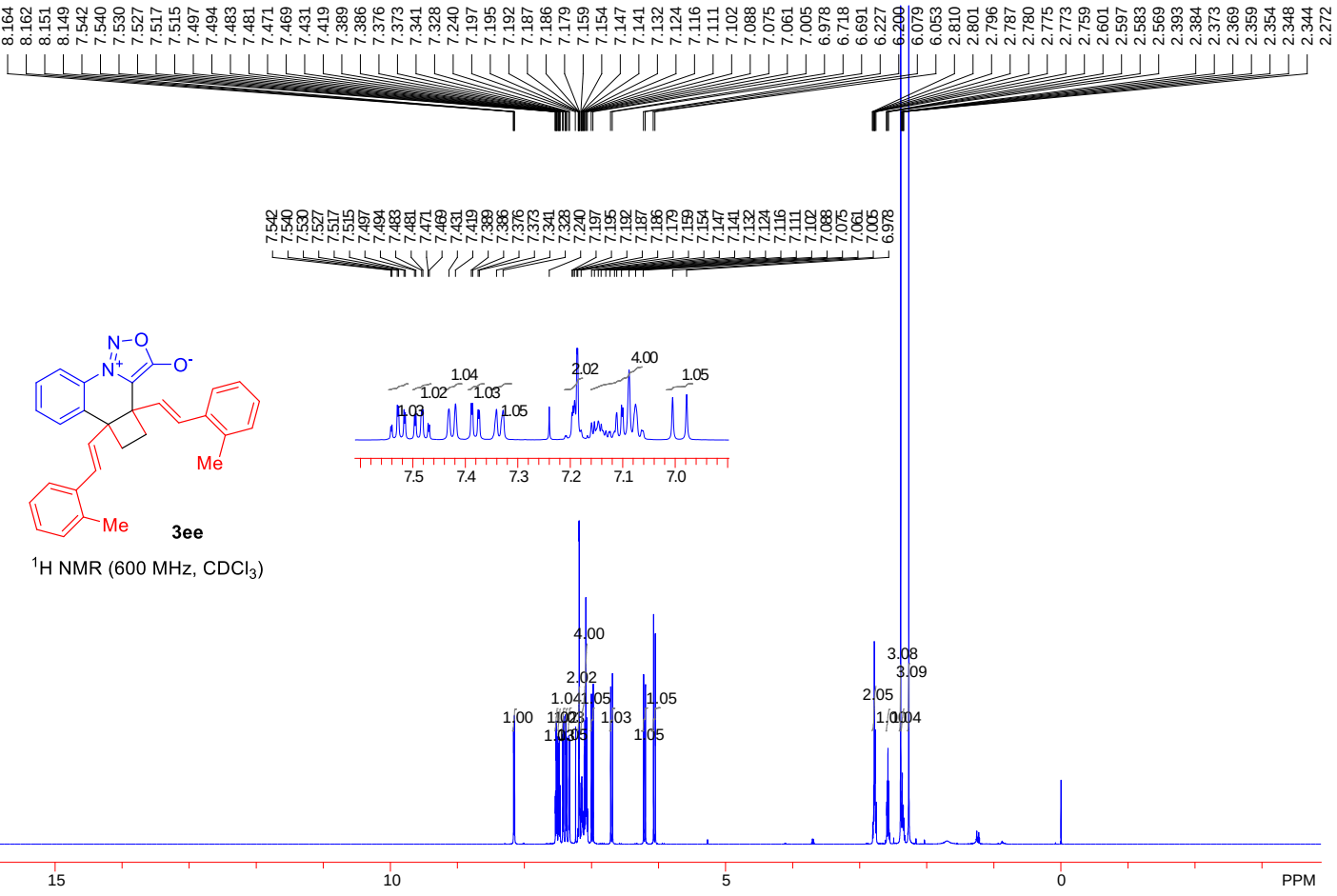


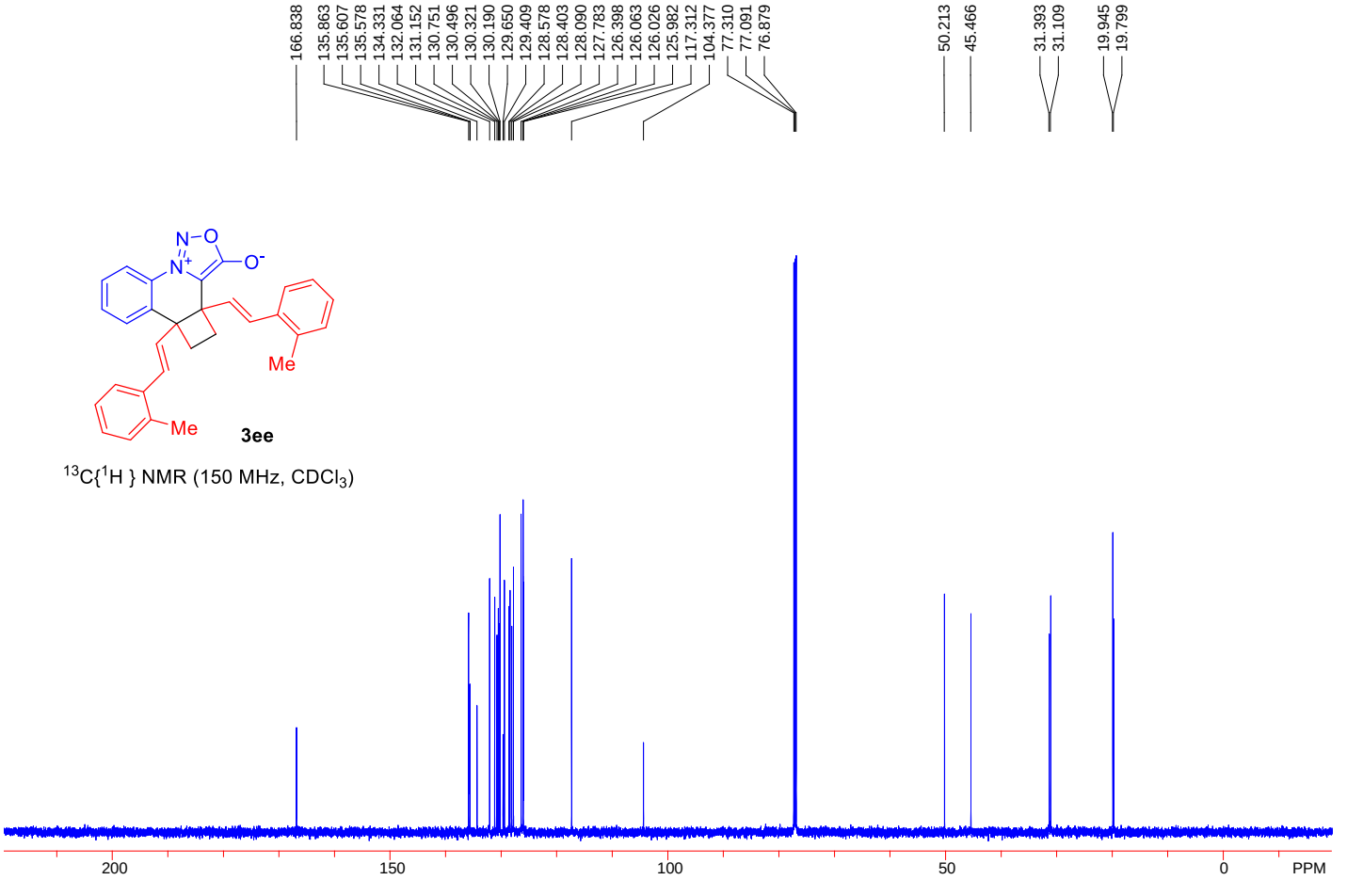


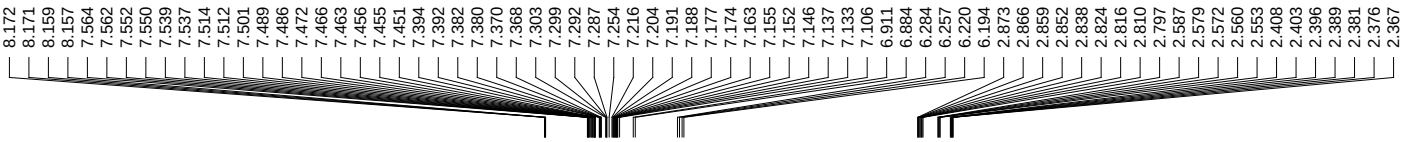
3dd

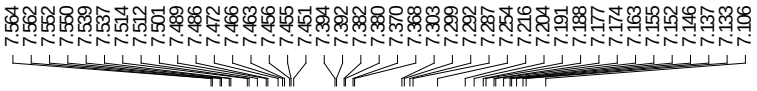
^{13}C{^{1}H } NMR (150 MHz, $CDCl_3$)

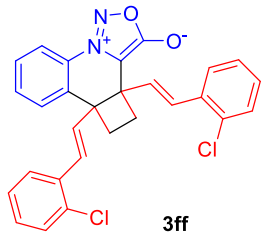



Me
Me
3ee
1H NMR (600 MHz, CDCl3)
PPM

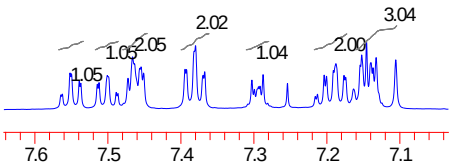

Me
Me
3ee
13C{1H } NMR (150 MHz, CDCl3)
PPM



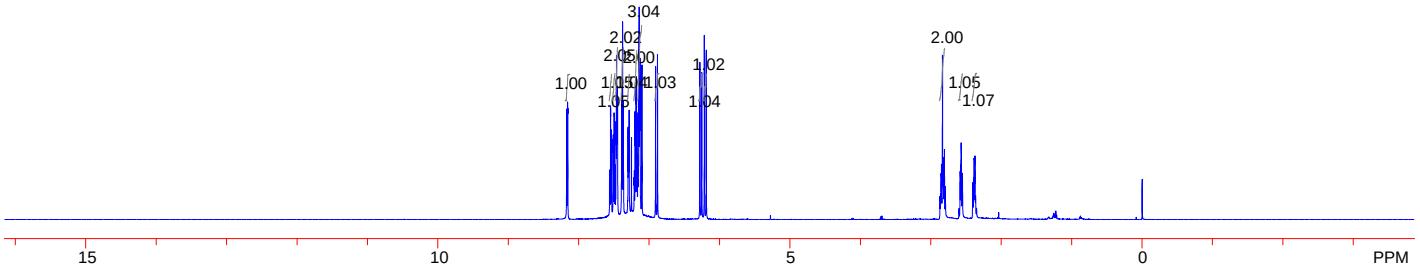


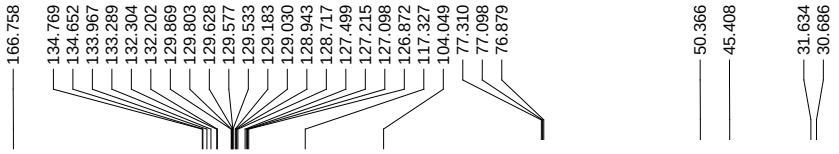


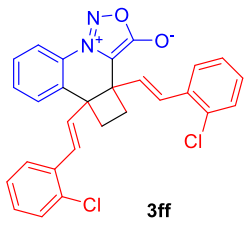
3ff



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

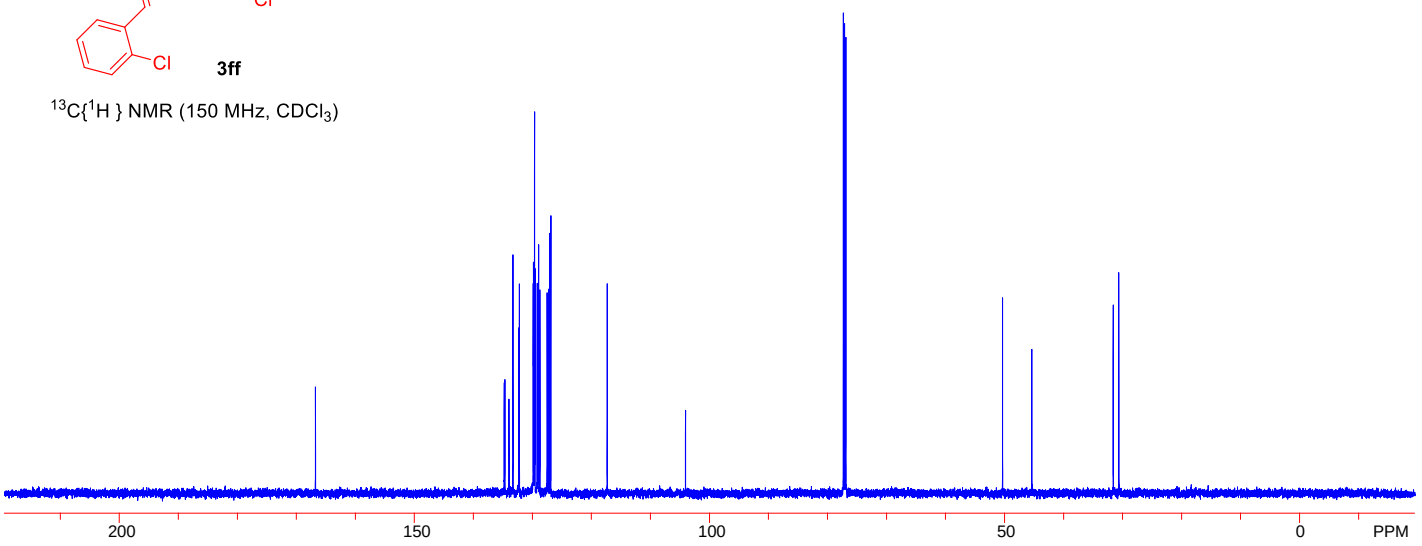


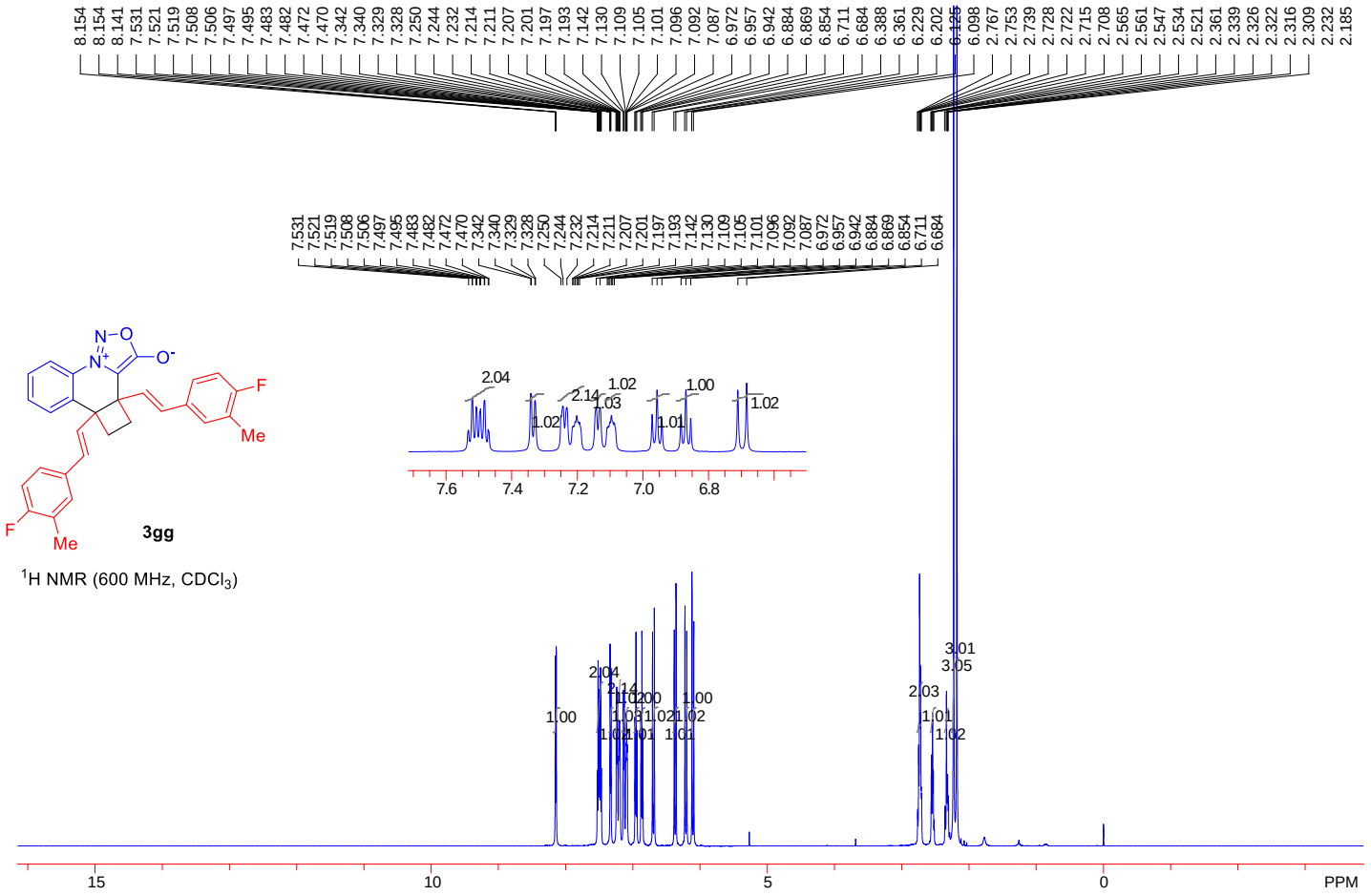


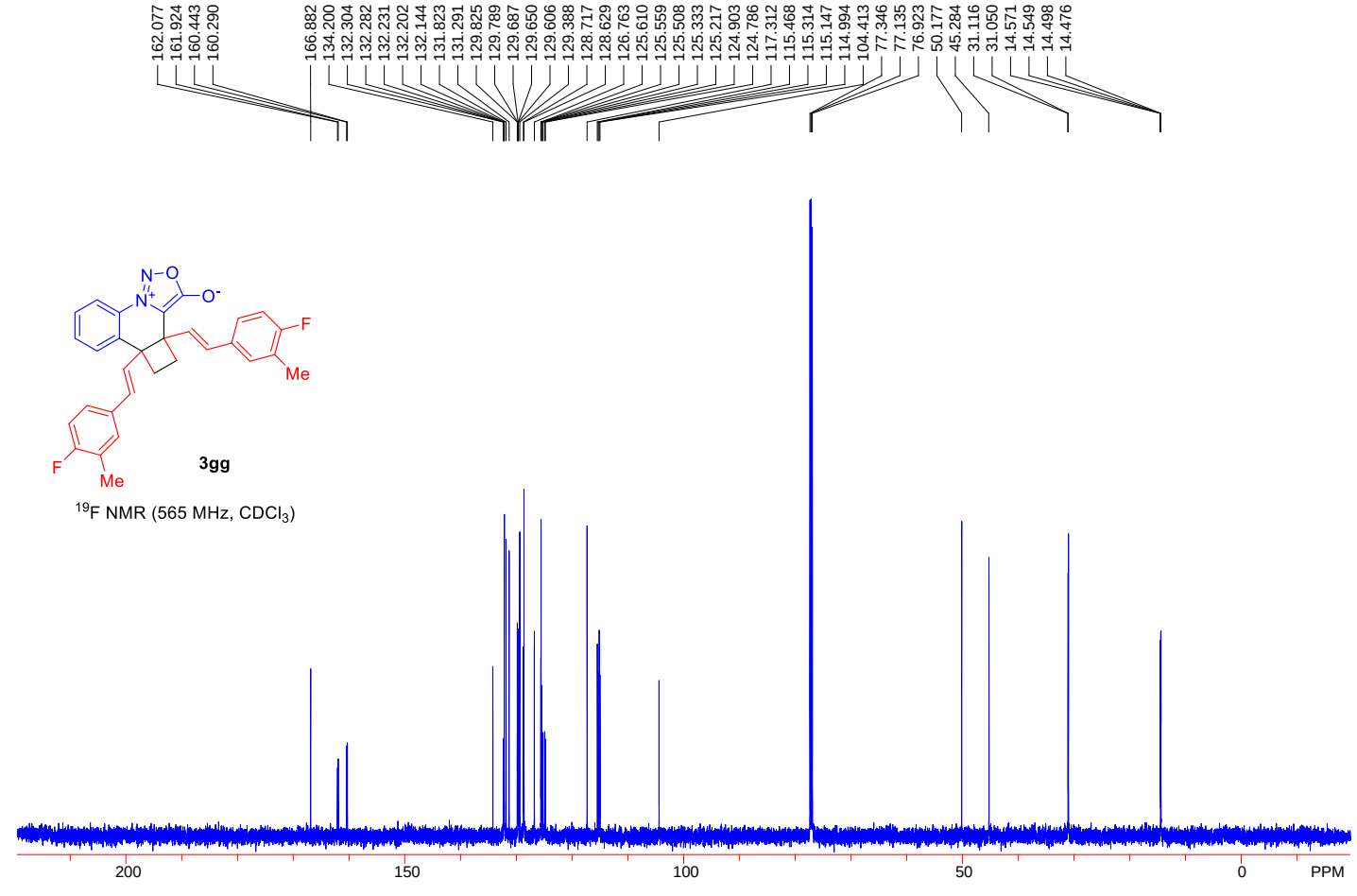


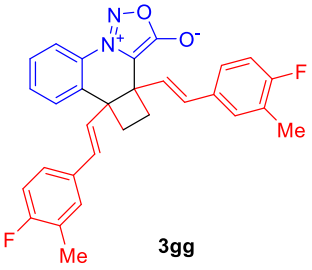
3ff

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



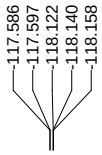

3gg
^{1}H NMR (600 MHz, CDCl$_3$)
PPM

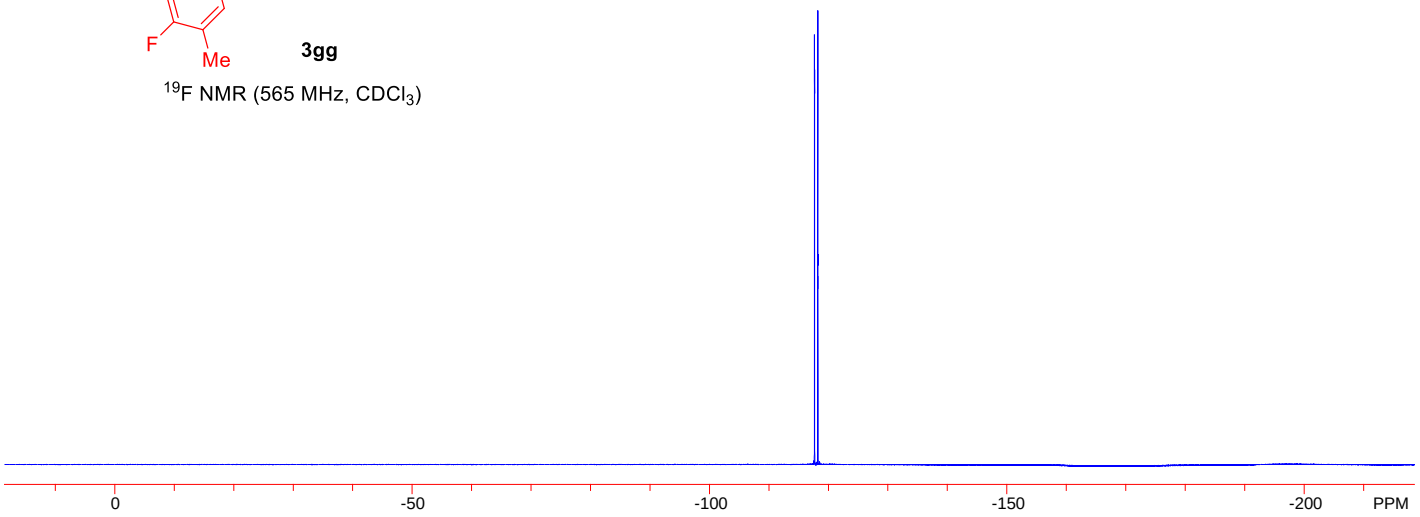

3gg
^{19}F NMR (565 MHz, CDCl$_3$)
PPM

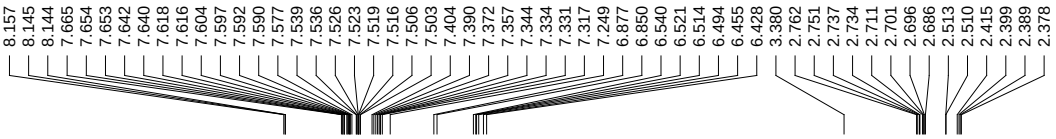


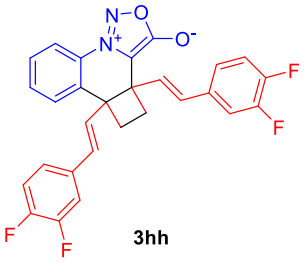
3gg

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



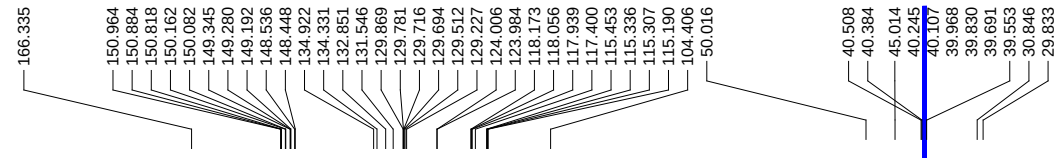


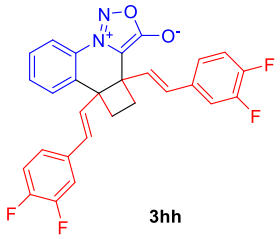




3hh

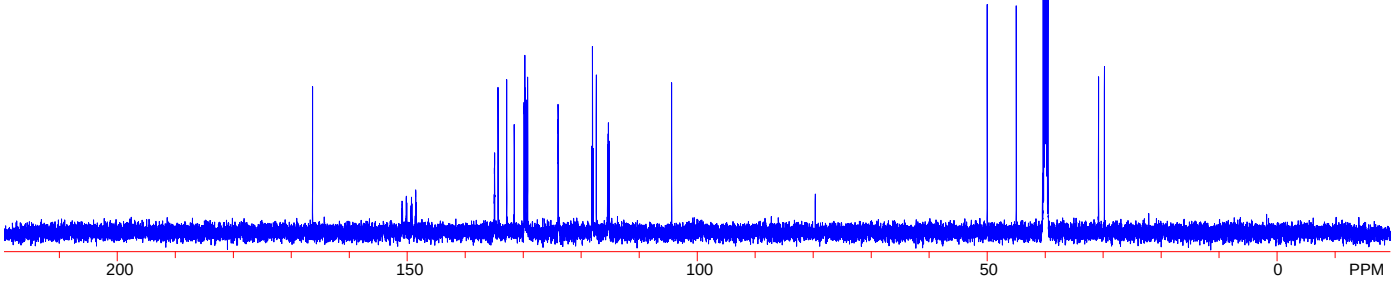
^{1}H NMR (600 MHz, DMSO-d_6)

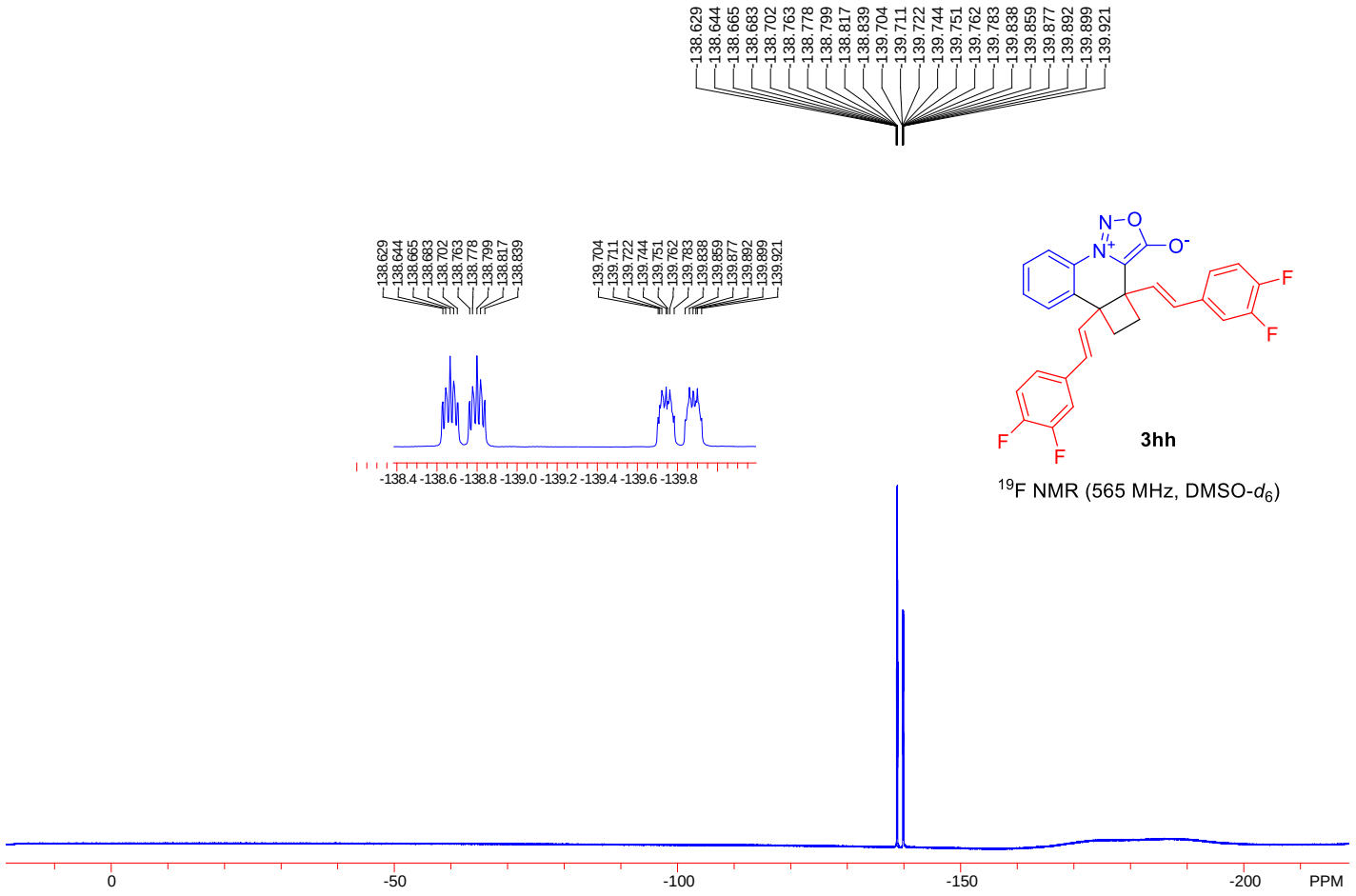


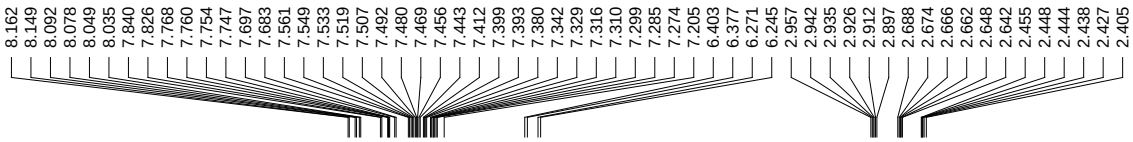


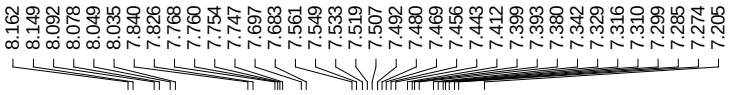
3hh

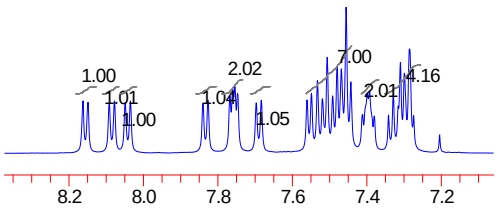
^{13}C{^{1}H } NMR (150 MHz, DMSO-d_6)

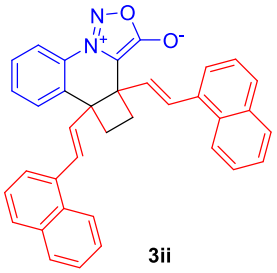



138.629
138.644
138.665
138.683
138.702
138.763
138.778
138.799
138.817
138.839
139.704
139.711
139.722
139.744
139.751
139.762
139.783
139.838
139.859
139.877
139.892
139.899
139.921
-138.4 -138.6 -138.8 -139.0 -139.2 -139.4 -139.6 -139.8
N
O
O
F
F
F
F
3hh
^{19}F NMR (565 MHz, DMSO-d_6)
0
-50
-100
-150
-200
PPM



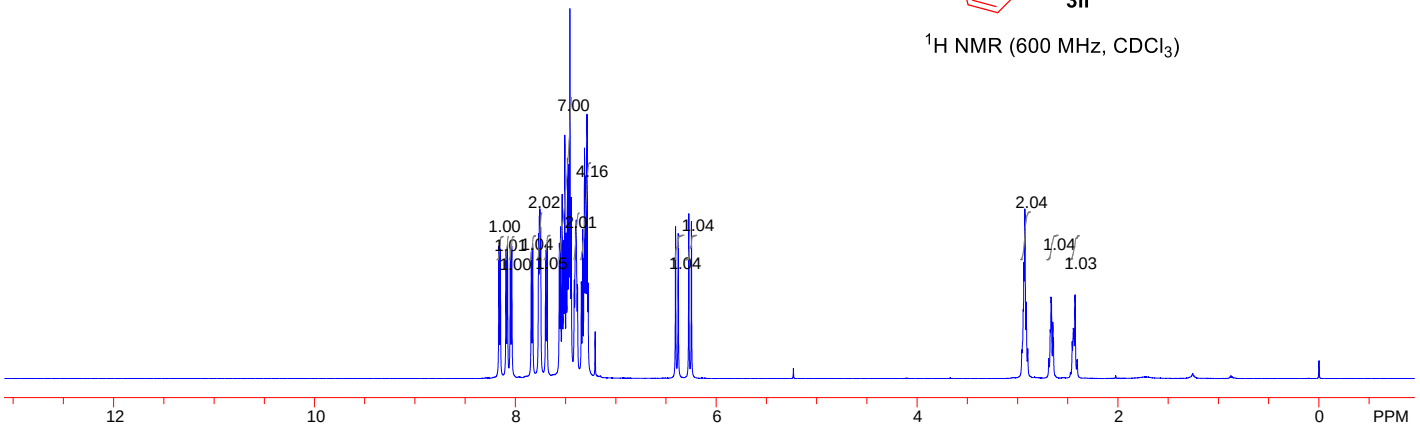


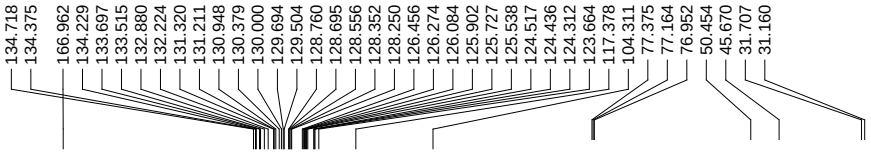


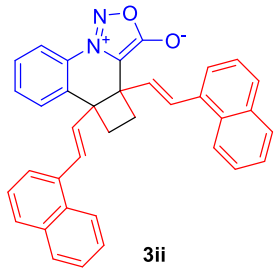


3ii

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

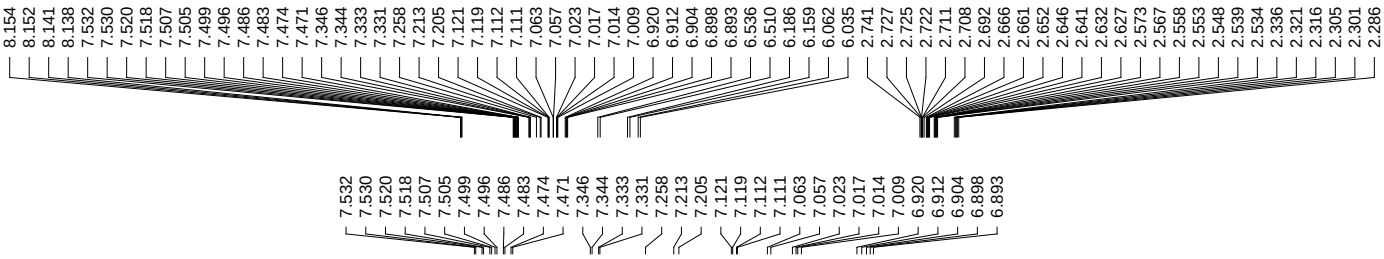


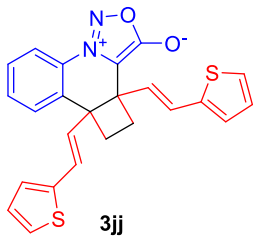




3ii

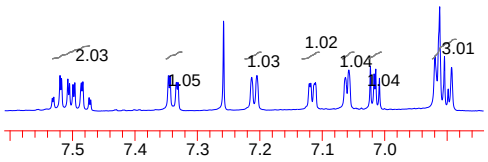
$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$)

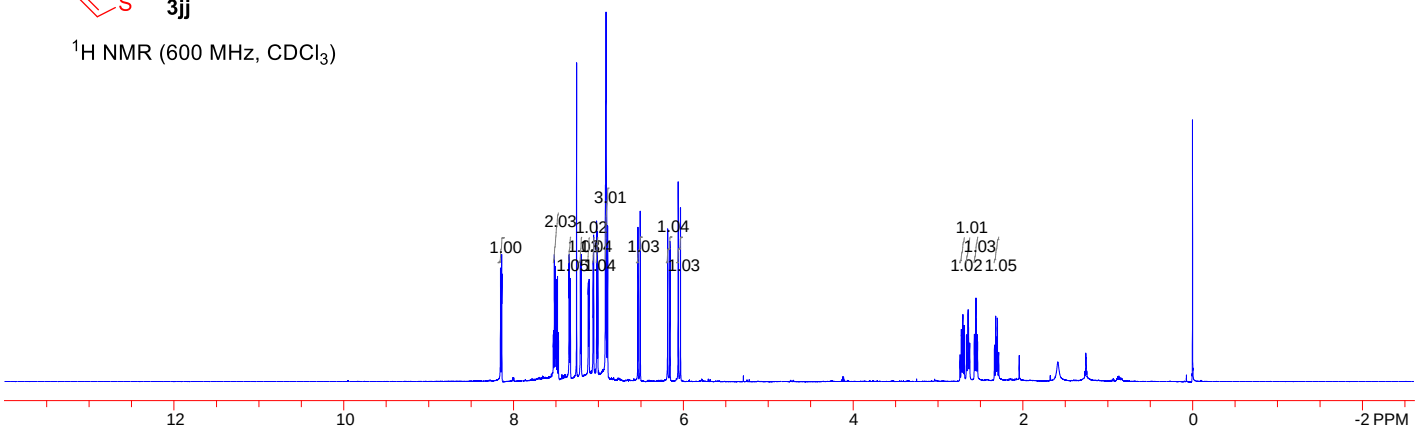


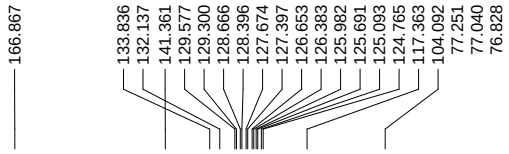


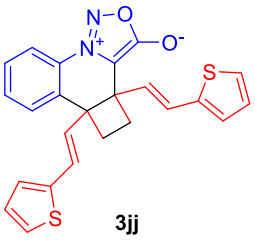
3jj

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



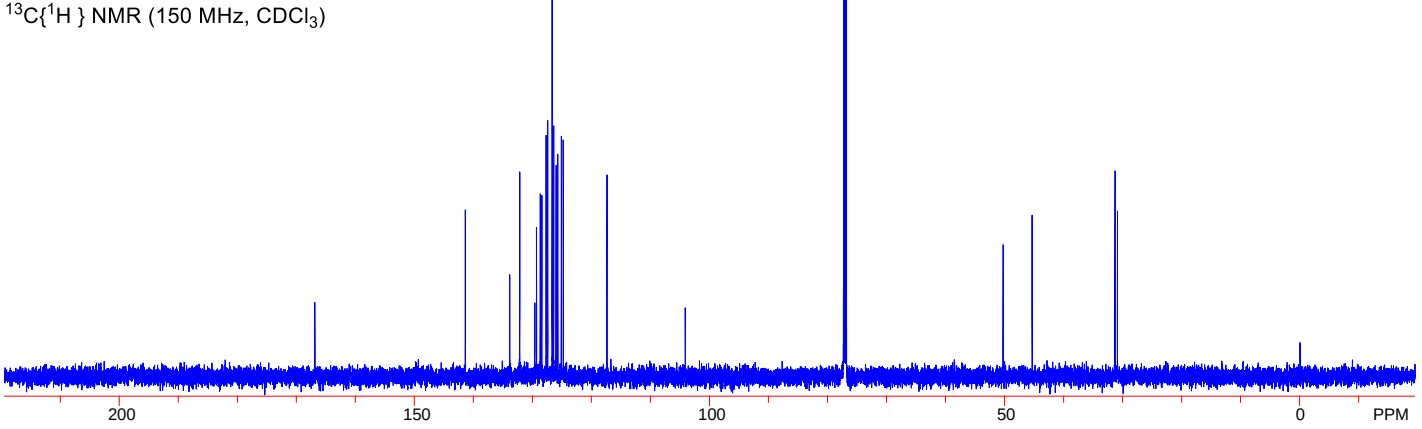


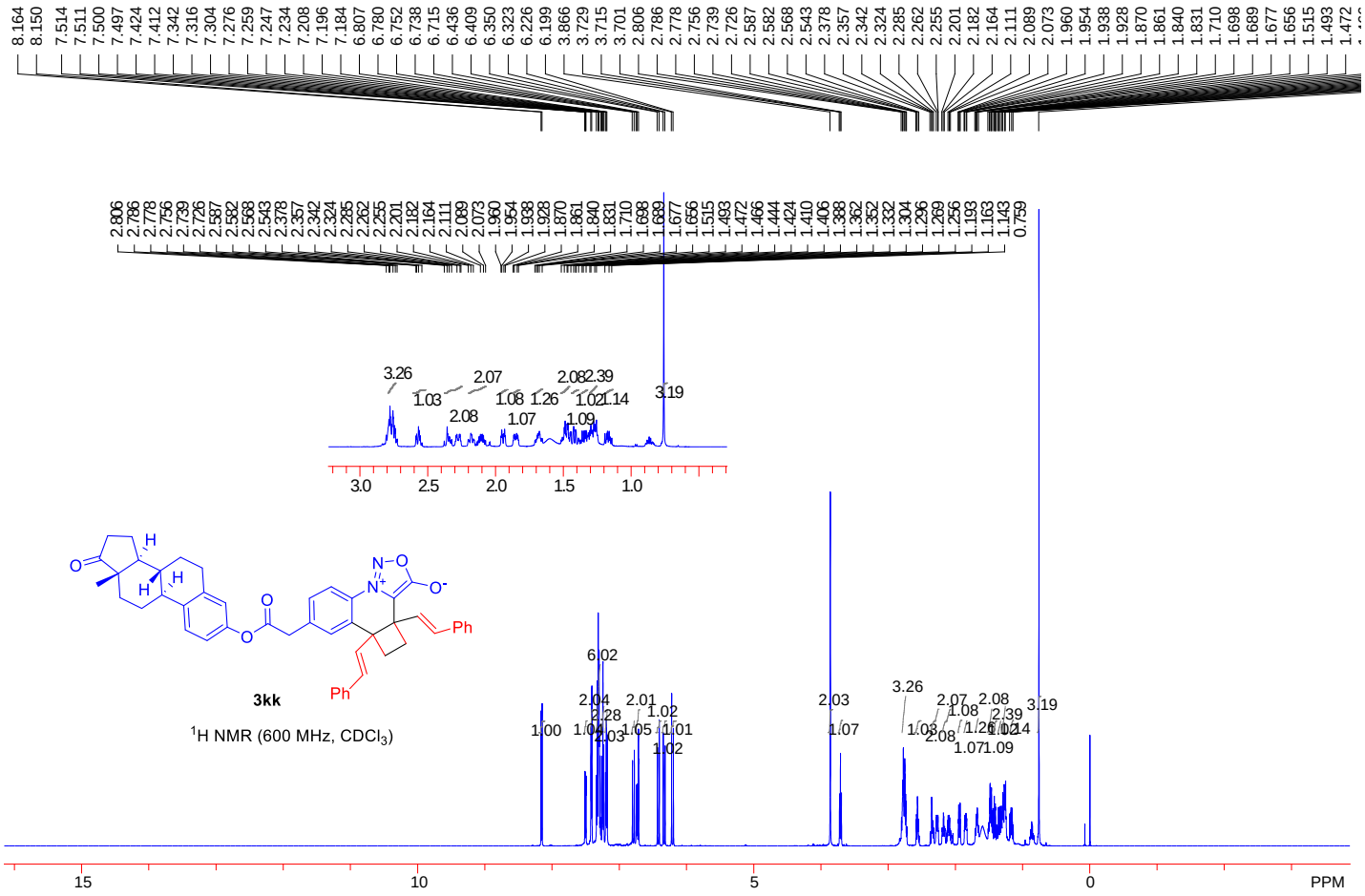


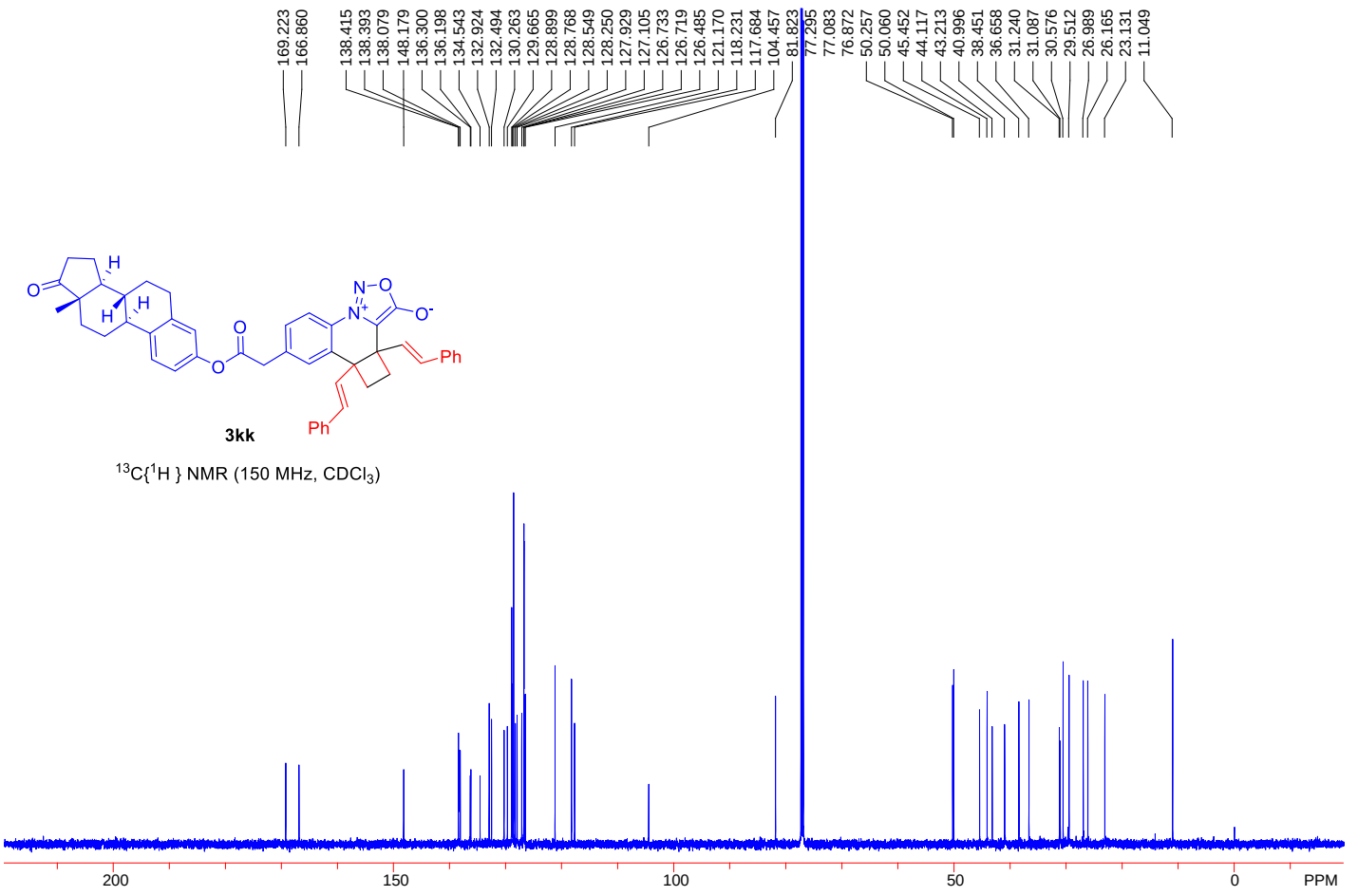


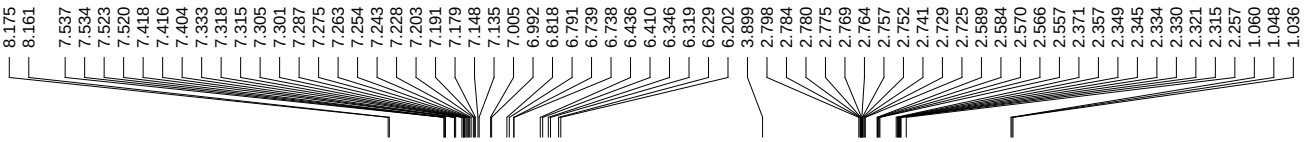
3jj

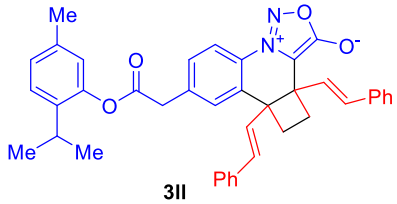
^{13}C{^{1}H } NMR (150 MHz, $CDCl_3$)




3kk
^{1}H NMR (600 MHz, CDCl$_3$)
PPM

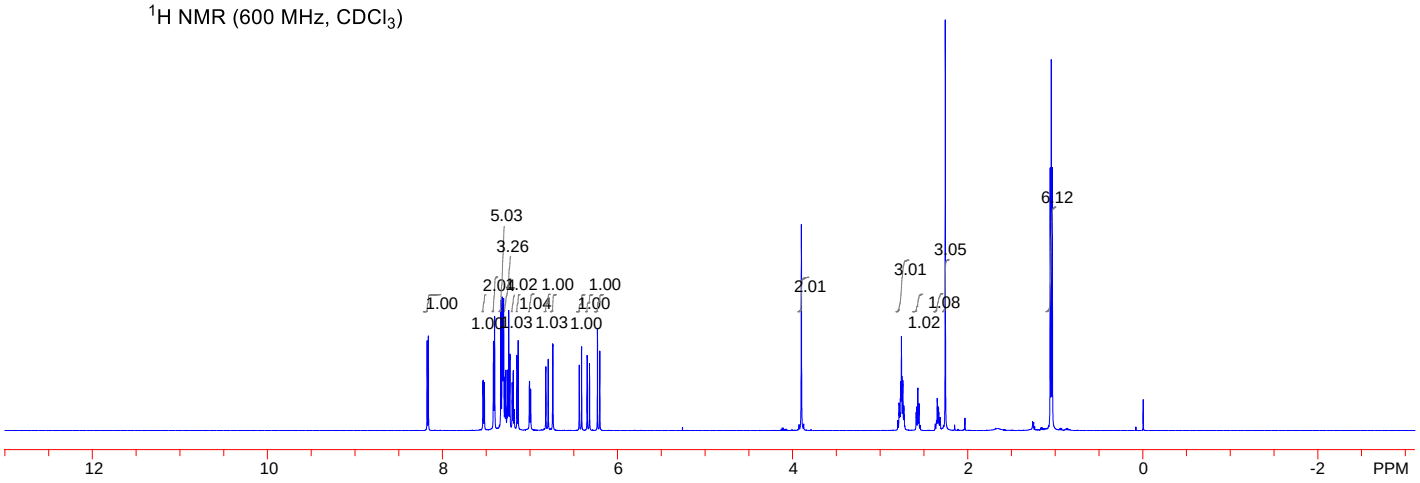

3kk
^{13}C{^{1}H } NMR (150 MHz, CDCl$_3$)
PPM

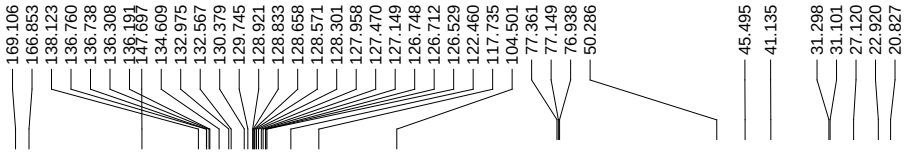


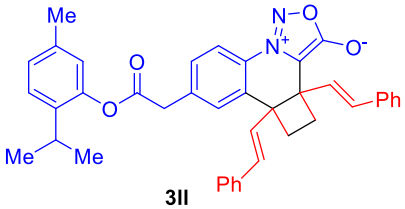


3ll

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

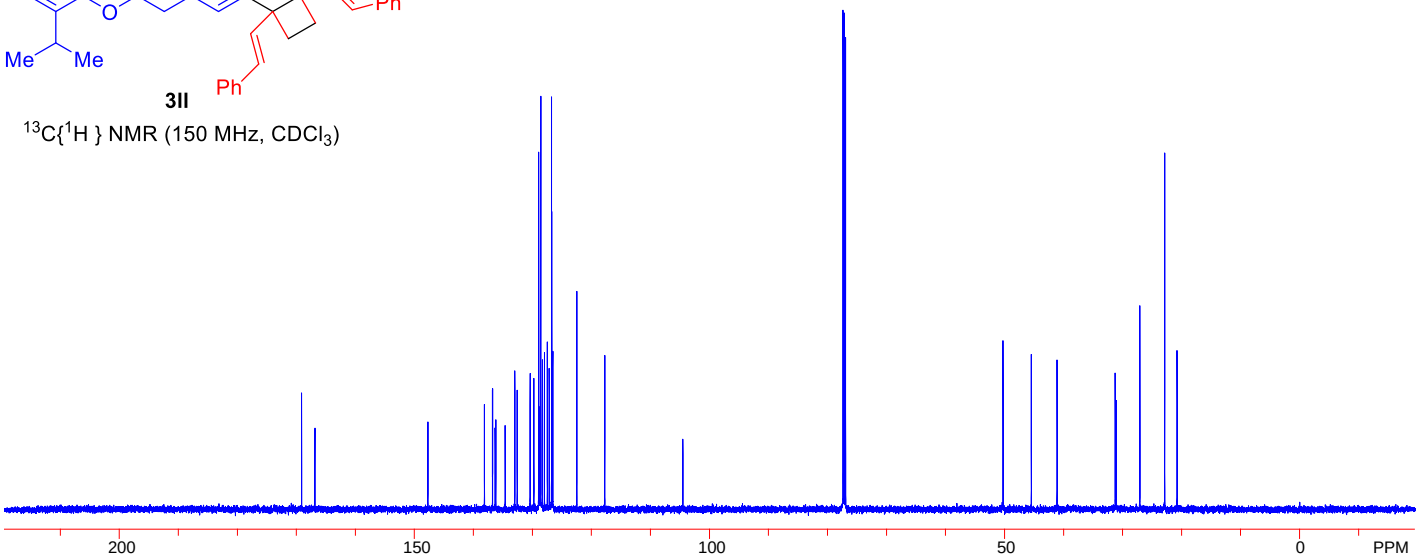


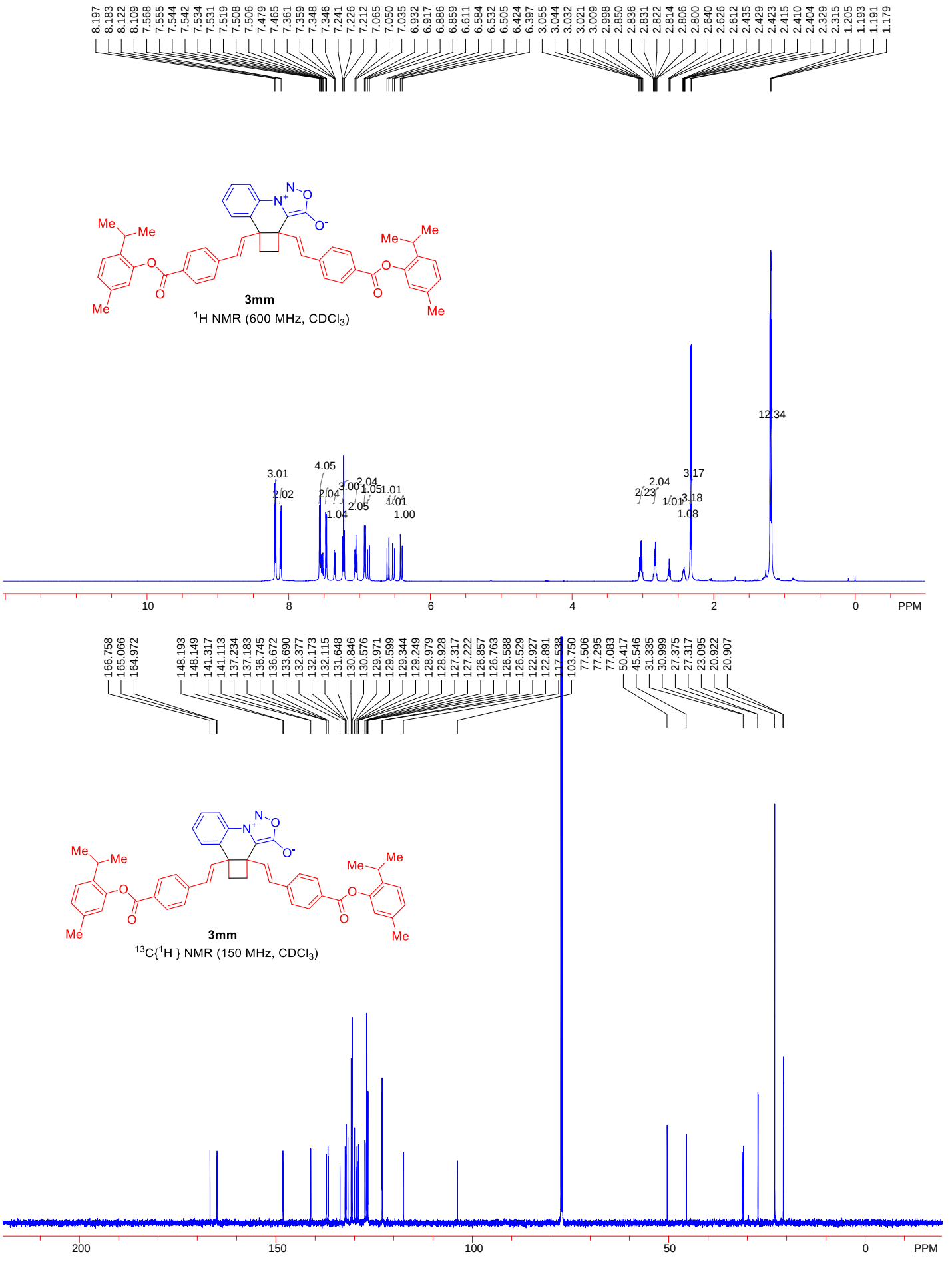


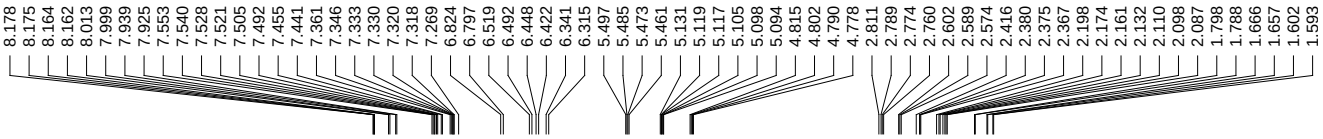


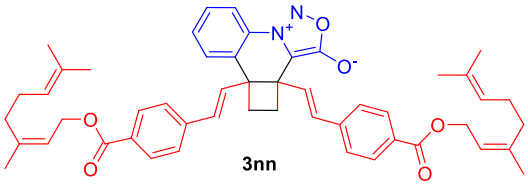
3ll

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



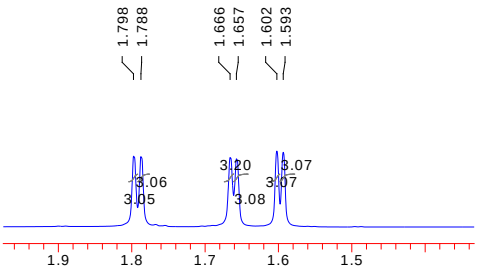

8.197 8.183 8.122 8.109 7.568 7.555 7.544 7.542 7.534 7.531 7.519 7.508 7.506 7.479 7.465 7.361 7.359 7.348 7.346 7.241 7.226 7.212 7.065 7.050 7.035 6.932 6.917 6.886 6.859 6.611 6.584 6.532 6.505 6.424 6.397 3.055 3.044 3.032 3.021 3.009 2.998 2.850 2.836 2.831 2.822 2.814 2.806 2.800 2.640 2.626 2.612 2.435 2.429 2.423 2.415 2.410 2.404 2.329 2.315 1.205 1.193 1.191 1.179
3mm
1H NMR (600 MHz, CDCl3)
3.01 2.02 4.05 2.04 3.00 2.04 1.05 1.01 2.05 1.01 1.04 1.00 2.04 2.23 3.17 1.01 3.18 1.08 12.34
10 8 6 4 2 0 PPM
166.758 165.066 164.972 148.193 148.149 141.317 141.113 137.234 137.183 136.745 136.672 133.690 132.377 132.173 132.115 131.648 130.846 130.576 129.971 129.599 129.344 129.249 128.979 128.928 127.317 127.222 126.857 126.763 126.588 126.529 122.927 122.891 117.538 103.750 77.506 77.295 77.083 50.417 45.546 31.335 30.999 27.375 27.317 23.095 20.922 20.907
3mm
13C{1H } NMR (150 MHz, CDCl3)
200 150 100 50 0 PPM

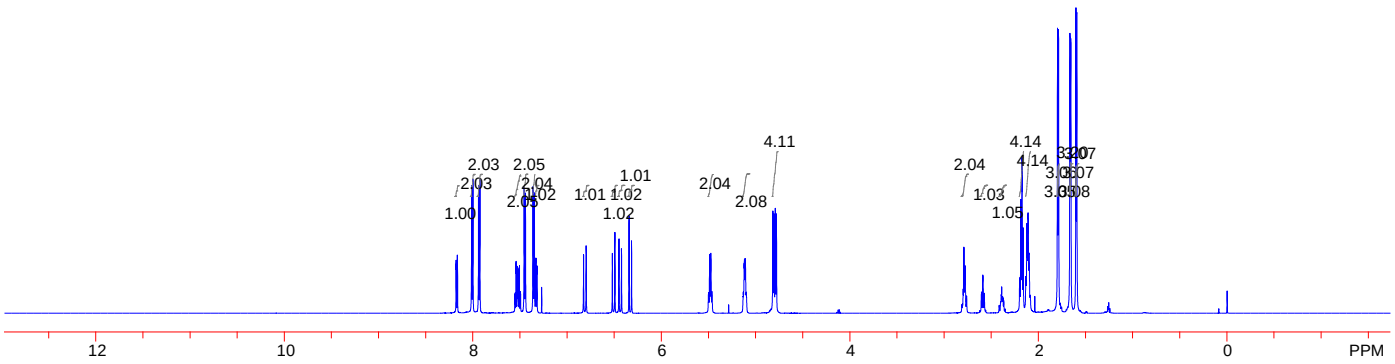


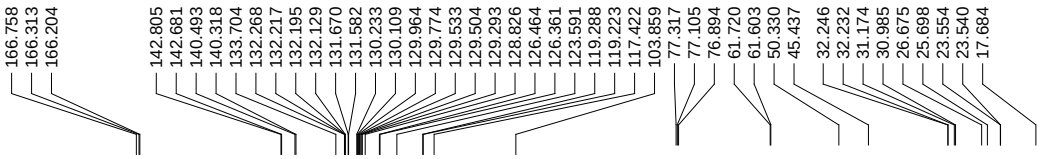


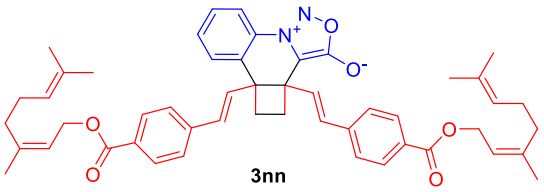
3nn

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



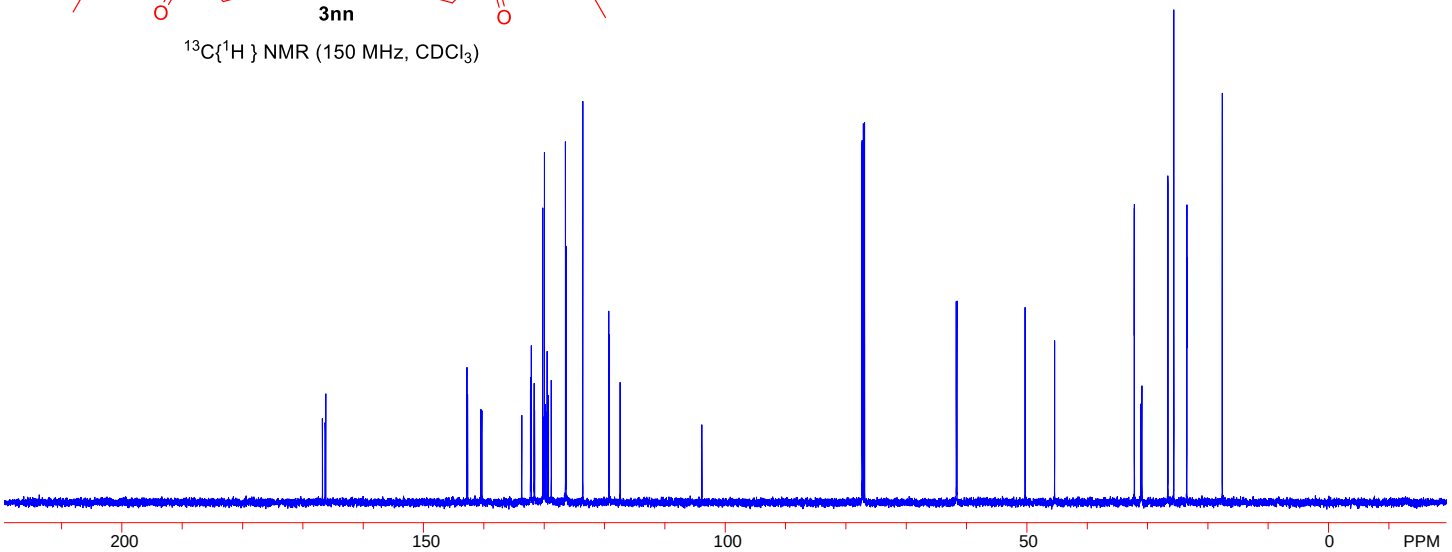




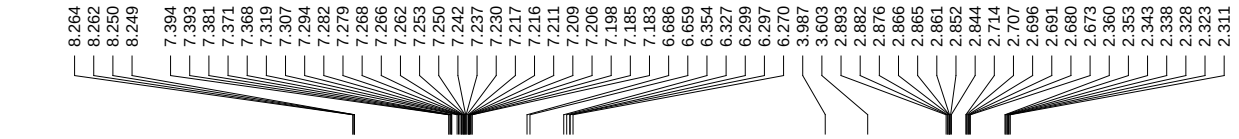


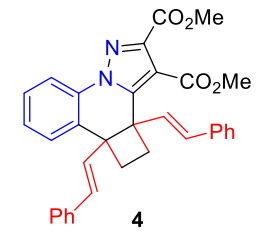
3nn

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



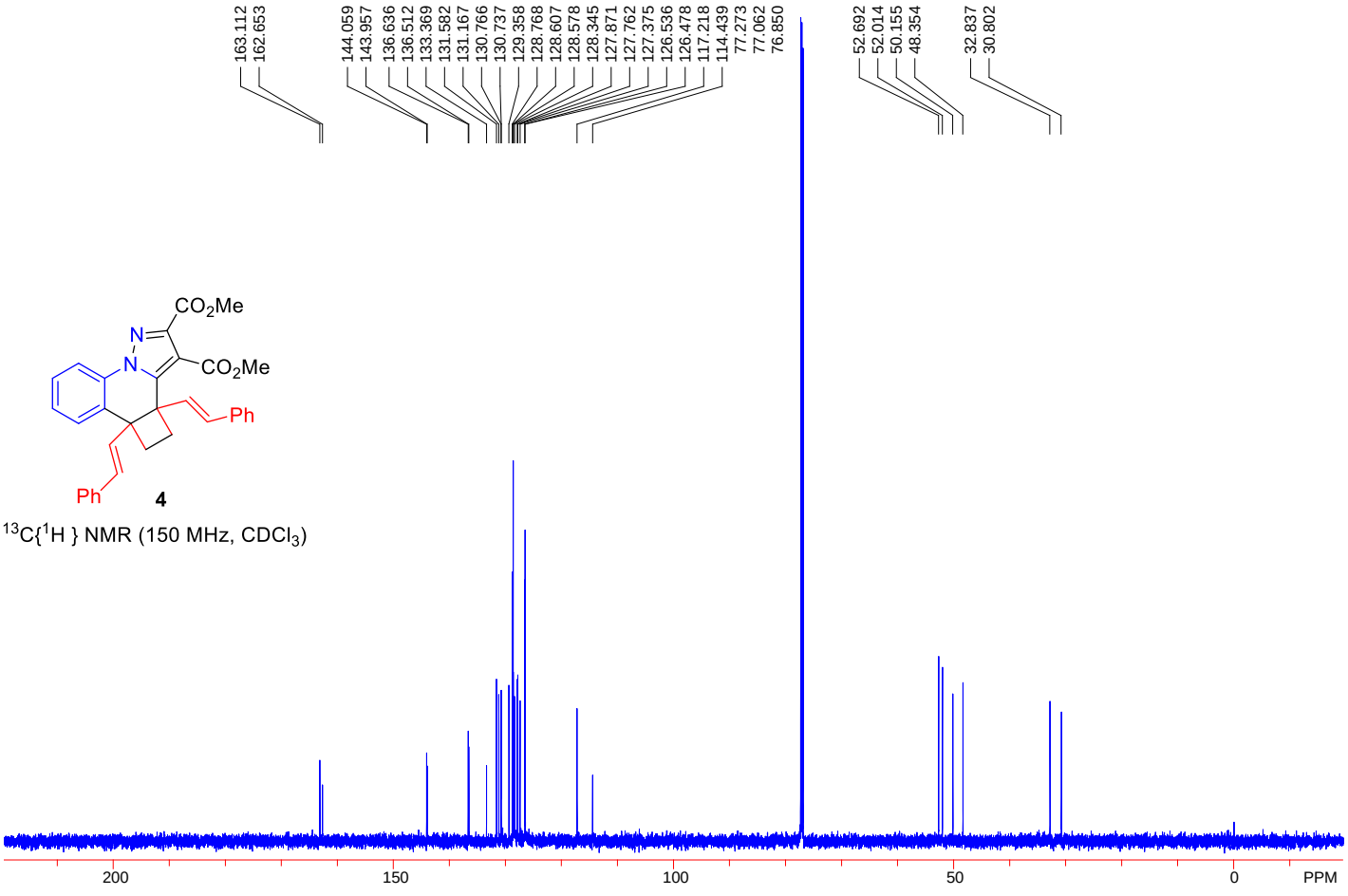
VI. NMR spectra of 4-7





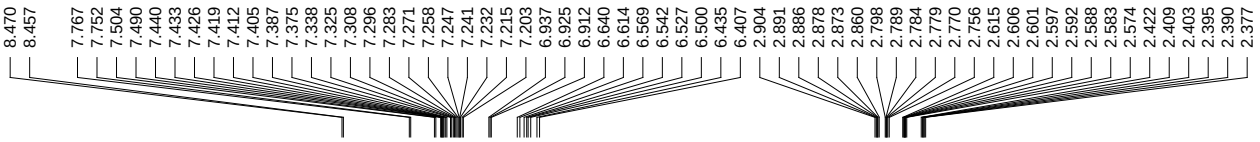
4

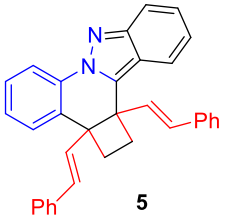
^{1}H NMR (600 MHz, $CDCl_3$)



4

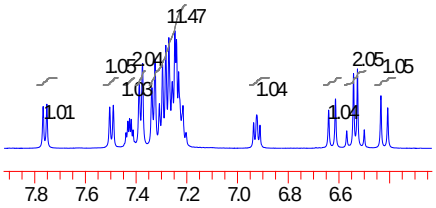
^{13}C{^{1}H } NMR (150 MHz, $CDCl_3$)

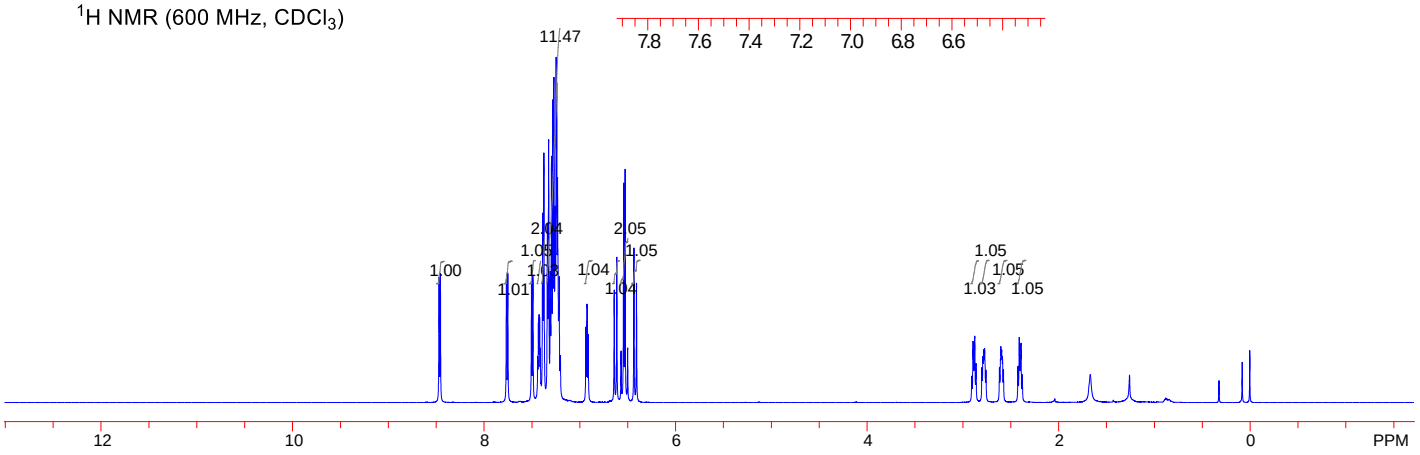


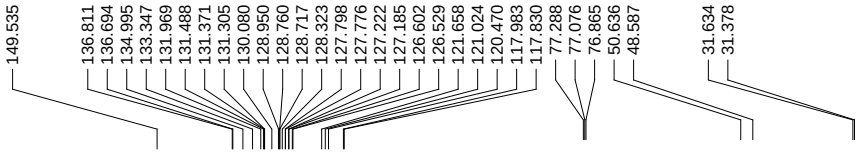


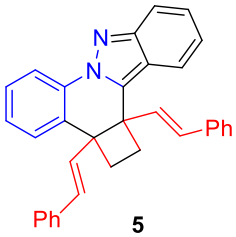
5

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



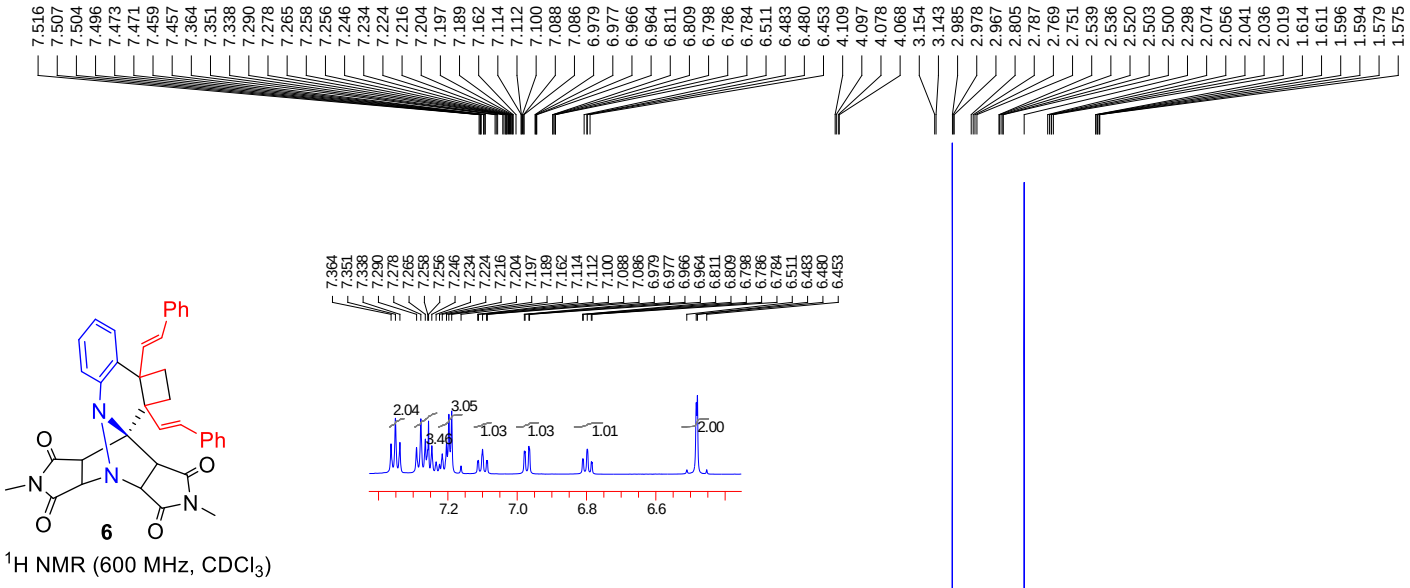


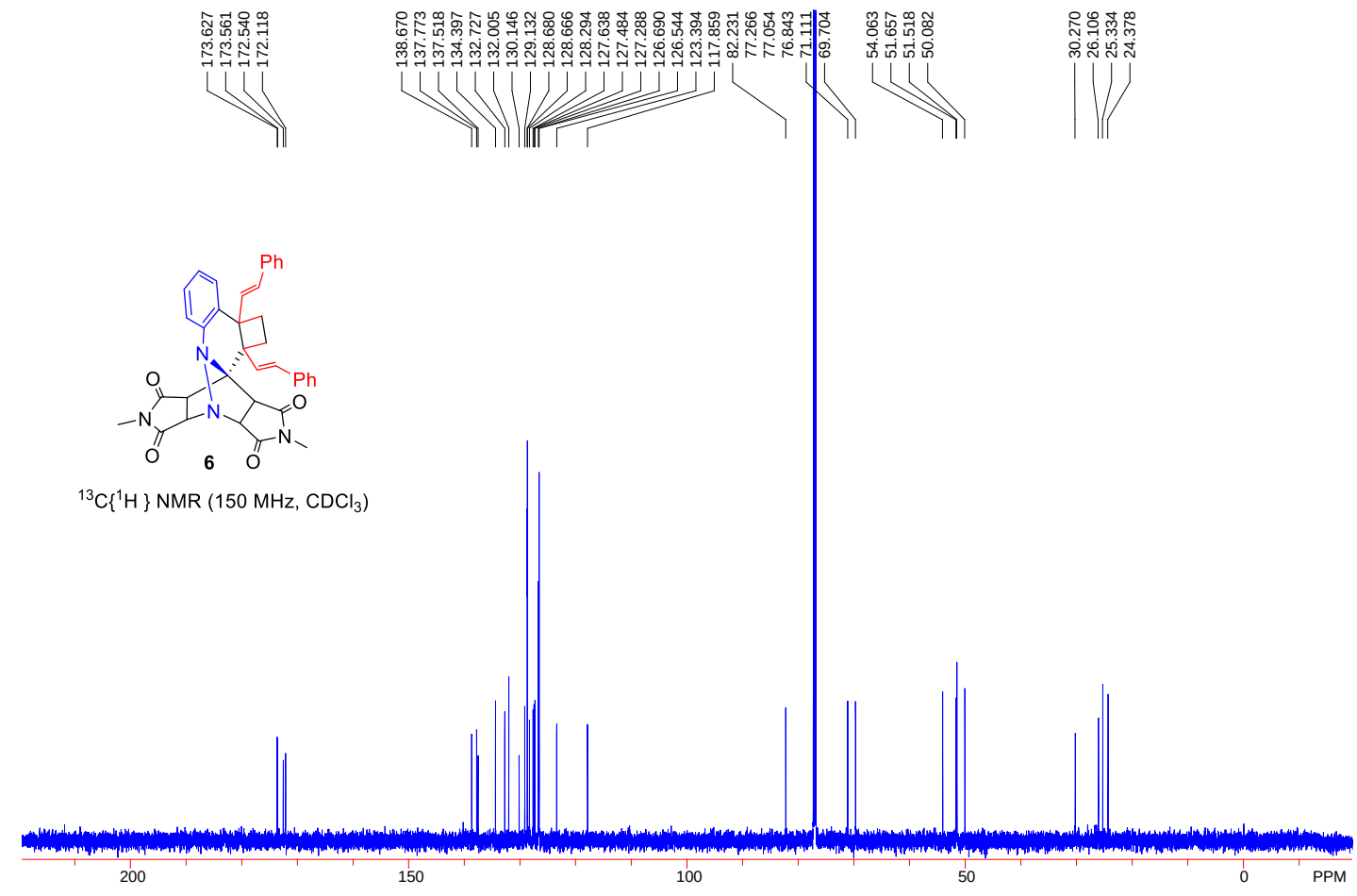


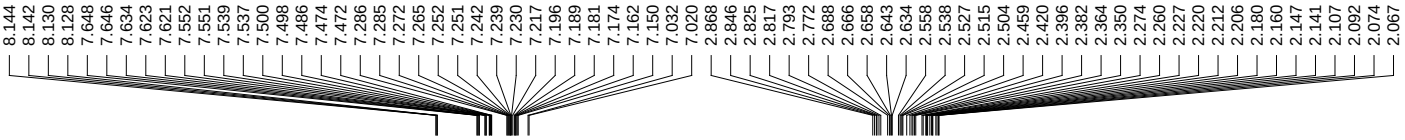


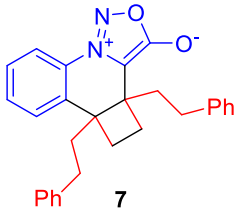
5

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


7.516 7.507 7.504 7.496 7.473 7.471 7.459 7.457 7.364 7.351 7.338 7.290 7.278 7.265 7.258 7.256 7.246 7.234 7.224 7.216 7.204 7.197 7.189 7.162 7.114 7.112 7.100 7.088 7.086 6.979 6.977 6.966 6.964 6.811 6.809 6.798 6.786 6.784 6.511 6.483 6.480 6.453 4.109 4.097 4.078 4.068 3.154 3.143 2.985 2.978 2.967 2.805 2.787 2.769 2.751 2.539 2.536 2.520 2.503 2.500 2.298 2.074 2.056 2.041 2.036 2.019 1.614 1.611 1.596 1.594 1.579 1.575
Ph
Ph
N
N
O
O
N
O
N
O
O
6
^{1}H NMR (600 MHz, CDCl$_3$)
7.364 7.351 7.338 7.290 7.278 7.265 7.258 7.256 7.246 7.234 7.224 7.216 7.204 7.197 7.189 7.162 7.114 7.112 7.100 7.088 7.086 6.979 6.977 6.966 6.964 6.811 6.809 6.798 6.786 6.784 6.511 6.483 6.480 6.453
2.04 3.05 3.46 1.03 1.03 1.01 2.00
7.2 7.0 6.8 6.6
4.03 3.05 3.46 2.04 1.03 1.03 1.03 2.00 1.01 2.05 4.02 1.00 1.03 1.02 3.04 1.03 1.02
10 8 6 4 2 0 PPM

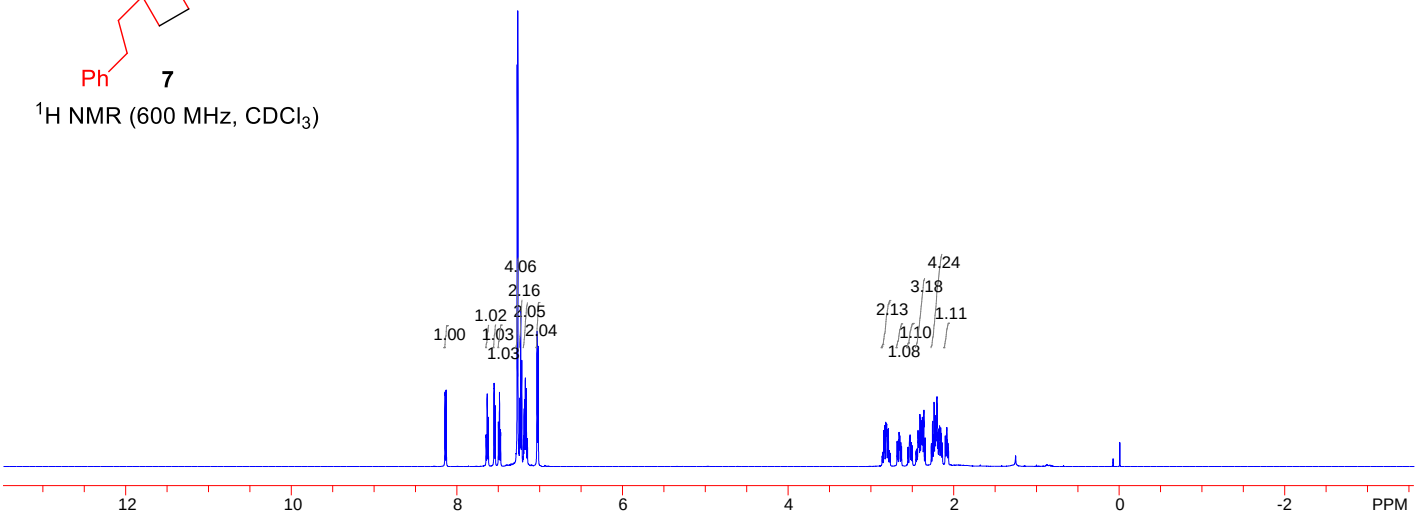

173.627 173.561 172.540 172.118 138.670 137.773 137.518 134.397 132.727 132.005 130.146 129.132 128.680 128.666 128.294 127.638 127.484 127.288 126.690 126.544 123.394 117.859 82.231 77.266 77.054 76.843 71.111 69.704 54.063 51.657 51.518 50.082 30.270 26.106 25.334 24.378
Ph
Ph
N
N
O
O
N
O
N
O
O
6
^{13}C{^{1}H } NMR (150 MHz, CDCl$_3$)
200 150 100 50 0 PPM

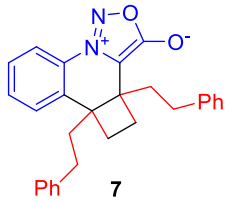




7

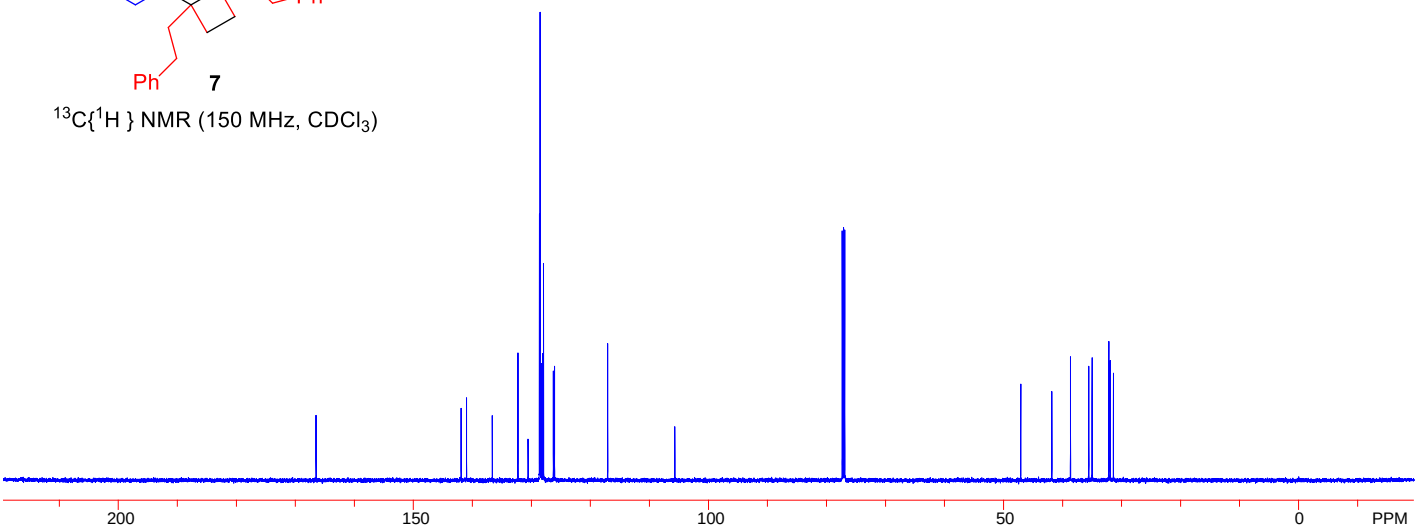
^{1}H NMR (600 MHz, $CDCl_3$)





7

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



VII. References

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