

Supporting Information

Synthesis of Homophthalimide Spiroanthalones through [5 + 1] Spiroannulation of Aryl/Alkenyl Enaminones with Diazo Homophthalimides

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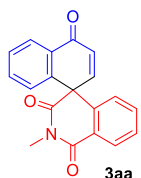
I. General experimental information

All reagents were purchased from commercial sources and were used without further purification. Aryl/alkenyl enaminones (**1**)^{1,2}, diazo homophthalimides (**2**)^{3,4} and [RhCp*Cl₂]₂ were prepared based on literature procedures. Melting points were recorded with a micro melting point apparatus and uncorrected. The ¹H NMR spectra were recorded at 400 MHz or 600 MHz. The ¹³C NMR spectra were recorded at 100 MHz or 150 MHz. The ¹⁹F NMR spectra were recorded at 376 MHz. Chemical shifts were expressed in parts per million (δ), and were reported as s (singlet), d (doublet), t (triplet), dd (doublet of doublets), 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

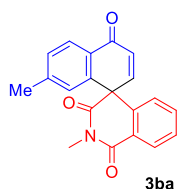
1. Typical procedure for the synthesis of 3aa and spectroscopic data of 3aa-3ap

To a reaction tube equipped with a stir bar were added (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one (**1a**, 35.0 mg, 0.2 mmol), [RhCp*Cl₂]₂ (5.0 mg, 0.008 mmol), AgNTf₂ (31.1 mg, 0.08 mmol), 4-diazo-2-methylisoquinoline-1,3(2*H*,4*H*)-dione (**2a**, 80.4 mg, 0.4 mmol) and DCE (2 mL). The tube was then sealed, and the mixture was stirred at 60 °C (oil bath) under air for 12 h. Upon completion, it was cooled to room temperature, filtered through a pad of celite and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (8:1) as eluent to afford **3aa**. Other products **3ba-3ap** were obtained in a similar manner.



2-Methyl-1*H*,4'*H*-spiro[isoquinoline-4,1'-naphthalene]-1,3,4'(2*H*)-trione (**3aa**)

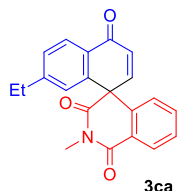
Eluent: petroleum ether/ethyl acetate (8:1). White solid (49.1 mg, 81%), mp 215.1-216.6 °C. ¹H NMR (600 MHz, CDCl₃): δ 8.38-8.36 (m, 1H), 8.27-8.26 (m, 1H), 7.54-7.51 (m, 2H), 7.48-7.43 (m, 2H), 6.93-6.91 (m, 1H), 6.86-6.85 (m, 1H), 6.83 (d, *J* = 9.6 Hz, 1H), 6.69 (d, *J* = 9.6 Hz, 1H), 3.43 (s, 3H). ¹³C{¹H} NMR (150 MHz, CDCl₃): δ 184.0, 169.8, 164.0, 145.2, 142.8, 138.7, 134.7, 133.4, 131.5, 129.7, 129.4, 128.9, 128.7, 128.3, 127.9, 127.3, 124.4, 54.3, 28.0. HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₉H₁₃NNaO₃ 326.0788; Found 326.0786.



2,7'-Dimethyl-1*H*,4'*H*-spiro[isoquinoline-4,1'-naphthalene]-1,3,4'(2*H*)-trione (**3ba**)

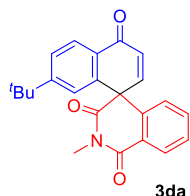
Eluent: petroleum ether/ethyl acetate (9:1). Yellow solid (50.1 mg, 79%), mp 227.9-229.6 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.39-8.36 (m, 1H), 8.17 (d, *J* = 8.0 Hz, 1H), 7.53-7.51 (m, 2H), 7.28-7.26 (m, 1H),

6.91-6.89 (m, 1H), 6.76 (d, $J = 10.0$ Hz, 1H), 6.65 (d, $J = 10.0$ Hz, 1H), 6.60 (s, 1H), 3.45 (s, 3H), 2.26 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 183.9, 170.0, 164.0, 144.9, 144.5, 143.0, 138.9, 134.7, 129.9, 129.6, 129.4, 129.3, 128.8, 128.3, 128.1, 127.3, 124.3, 54.2, 28.0, 21.8. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{15}\text{NNaO}_3$ 340.0944; Found 340.0944.



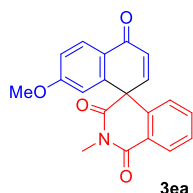
7'-Ethyl-2-methyl-1*H*,4'*H*-spiro[isoquinoline-4,1'-naphthalene]-1,3,4'(2*H*)-trione (3ca)

Eluent: petroleum ether/ethyl acetate (8:1). Yellow solid (50.3 mg, 76%), mp 185.4-187.2 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.39-8.36 (m, 1H), 8.19 (d, $J = 8.4$ Hz, 1H), 7.54-7.50 (m, 2H), 7.31 (d, $J = 8.0$ Hz, 1H), 6.91-6.89 (m, 1H), 6.77 (d, $J = 10.0$ Hz, 1H), 6.65 (d, $J = 10.0$ Hz, 1H), 6.60 (s, 1H), 3.45 (s, 3H), 2.55 (q, $J = 7.6$ Hz, 2H), 1.10 (t, $J = 7.6$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 183.9, 170.0, 164.1, 150.5, 144.9, 143.0, 139.0, 134.7, 129.7, 129.5, 129.4, 128.8, 128.5, 128.3, 127.4, 127.0, 124.4, 54.3, 28.9, 28.0, 14.9. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{21}\text{H}_{17}\text{NNaO}_3$ 354.1101; Found 354.1101.



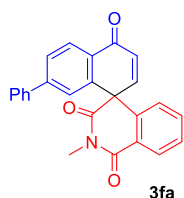
7'-(*tert*-Butyl)-2-methyl-1*H*,4'*H*-spiro[isoquinoline-4,1'-naphthalene]-1,3,4'(2*H*)-trione (3da)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (41.6 mg, 58%), mp 164.2-165.8 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.39-8.37 (m, 1H), 8.19 (d, $J = 8.4$ Hz, 1H), 7.54-7.49 (m, 3H), 6.92-6.90 (m, 1H), 6.80-6.78 (m, 2H), 6.67 (d, $J = 10.0$ Hz, 1H), 3.45 (s, 3H), 1.15 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 183.9, 170.1, 164.1, 157.3, 145.0, 142.5, 139.0, 134.6, 129.9, 129.4, 129.2, 128.8, 128.1, 127.1, 126.1, 124.4, 124.3, 54.5, 35.1, 30.9, 28.0. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{23}\text{H}_{21}\text{NNaO}_3$ 382.1414; Found 382.1414.



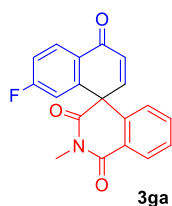
7'-Methoxy-2-methyl-1*H*,4'*H*-spiro[isoquinoline-4,1'-naphthalene]-1,3,4'(2*H*)-trione (3ea)

Eluent: petroleum ether/ethyl acetate (6:1). Yellow solid (48.0 mg, 72%), mp 182.8-184.6 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.37-8.35 (m, 1H), 8.25 (d, *J* = 8.8 Hz, 1H), 7.53-7.51 (m, 2H), 6.99 (dd, *J*₁ = 8.8 Hz, *J*₂ = 2.4 Hz, 1H), 6.93-6.91 (m, 1H), 6.74 (d, *J* = 10.0 Hz, 1H), 6.63 (d, *J* = 10.0 Hz, 1H), 6.26 (d, *J* = 2.4 Hz, 1H), 3.72 (s, 3H), 3.44 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 183.2, 169.9, 164.0, 163.3, 144.9, 144.4, 138.9, 134.7, 129.8, 129.7, 129.4, 128.9, 128.2, 125.1, 124.3, 114.2, 113.2, 55.5, 54.3, 28.0. HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₀H₁₅NNaO₄ 356.0893; Found 356.0893.



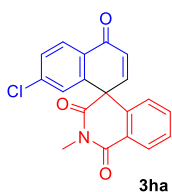
2-Methyl-7'-phenyl-1*H*,4'*H*-spiro[isoquinoline-4,1'-naphthalene]-1,3,4'(2*H*)-trione (3fa)

Eluent: petroleum ether/ethyl acetate (4:1). Yellow solid (54.6 mg, 72%), mp 196.2-197.5 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.40-8.37 (m, 1H), 8.34 (d, *J* = 8.4 Hz, 1H), 7.70 (dd, *J*₁ = 8.4 Hz, *J*₂ = 1.6 Hz, 1H), 7.56-7.52 (m, 2H), 7.39-7.35 (m, 5H), 6.98-6.95 (m, 2H), 6.82 (d, *J* = 10.0 Hz, 1H), 6.70 (d, *J* = 10.0 Hz, 1H), 3.46 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 183.8, 169.9, 164.0, 146.3, 145.2, 143.4, 139.2, 138.8, 134.8, 130.4, 129.7, 129.5, 129.0, 128.9, 128.6, 128.3, 127.9, 127.6, 127.3, 126.4, 124.4, 54.5, 28.1. HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₅H₁₇NNaO₃ 402.1101; Found 402.1099.



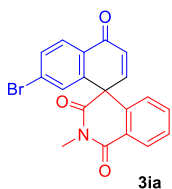
7'-Fluoro-2-methyl-1*H*,4'*H*-spiro[isoquinoline-4,1'-naphthalene]-1,3,4'(2*H*)-trione (3ga)

Eluent: petroleum ether/ethyl acetate (8:1). Yellow solid (39.8 mg, 62%), mp 203.3-204.7 °C. ¹H NMR (600 MHz, CDCl₃): δ 8.39-8.38 (m, 1H), 8.31 (dd, *J*₁ = 8.4 Hz, *J*₂ = 5.4 Hz, 1H), 7.56-7.55 (m, 2H), 7.17 (td, *J*₁ = 8.4 Hz, *J*₂ = 2.4 Hz, 1H), 6.92-6.90 (m, 1H), 6.80 (d, *J* = 10.2 Hz, 1H), 6.67 (d, *J* = 10.2 Hz, 1H), 6.51 (dd, *J*₁ = 9.0 Hz, *J*₂ = 2.4 Hz, 1H), 3.44 (s, 3H). ¹³C{¹H} NMR (150 MHz, CDCl₃): δ 182.7, 169.3, 165.4 (d, ¹*J*_{C-F} = 254.9 Hz), 163.7, 145.4 (d, ³*J*_{C-F} = 8.7 Hz), 145.0, 138.1, 134.9, 130.4 (d, ³*J*_{C-F} = 9.8 Hz), 129.7, 129.5, 129.2, 128.3 (d, ⁴*J*_{C-F} = 3.3 Hz), 128.2, 124.3, 116.7 (d, ²*J*_{C-F} = 21.9 Hz), 114.6 (d, ²*J*_{C-F} = 23.0 Hz), 54.4 (d, ⁴*J*_{C-F} = 2.1 Hz), 28.1. ¹⁹F NMR (376 MHz, CDCl₃): δ -103.07 - -103.13 (m). HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₉H₁₂FNNaO₃ 344.0693; Found 344.0693.



7'-Chloro-2-methyl-1*H*,4'*H*-spiro[isoquinoline-4,1'-naphthalene]-1,3,4'(2*H*)-trione (3ha)

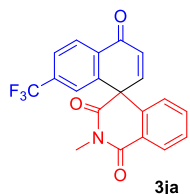
Eluent: petroleum ether/ethyl acetate (6:1). Yellow solid (36.4 mg, 54%), mp 223.4-224.9 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.40-8.38 (m, 1H), 8.22 (d, *J* = 8.4 Hz, 1H), 7.57-7.55 (m, 2H), 7.45 (dd, *J*₁ = 8.4 Hz, *J*₂ = 1.6 Hz, 1H), 6.90-6.88 (m, 1H), 6.80-6.76 (m, 2H), 6.66 (d, *J* = 10.0 Hz, 1H), 3.45 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 183.0, 169.3, 163.7, 145.1, 144.3, 139.9, 138.0, 134.9, 130.1, 129.7, 129.4, 129.2, 128.9, 128.2, 127.9, 124.4, 54.2, 28.2. HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₉H₁₂ClNNaO₃ 360.0398; Found 360.0399.



7'-Bromo-2-methyl-1*H*,4'*H*-spiro[isoquinoline-4,1'-naphthalene]-1,3,4'(2*H*)-trione (3ia)

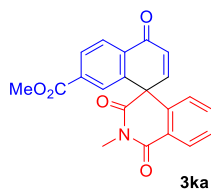
Eluent: petroleum ether/ethyl acetate (8:1). Yellow solid (51.8 mg, 68%), mp 242.5-244.3 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.40-8.38 (m, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.61 (dd, *J*₁ = 8.4 Hz, *J*₂ = 1.6 Hz, 1H), 7.57-7.55 (m, 2H), 6.96 (d, *J* = 2.0 Hz, 1H), 6.90-6.88 (m, 1H), 6.76 (d, *J* = 10.0 Hz, 1H), 6.65 (d, *J* = 10.0

Hz, 1H), 3.45 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 183.1, 169.3, 163.7, 145.1, 144.4, 138.0, 134.9, 132.3, 130.9, 130.6, 129.7, 129.3, 129.2, 128.9, 128.6, 128.3, 124.4, 54.2, 28.2. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{19}\text{H}_{12}\text{BrNNaO}_3$ 403.9893; Found 403.9893.



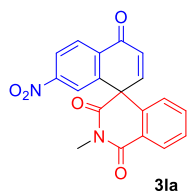
2-Methyl-7'-(trifluoromethyl)-1H,4'H-spiro[isoquinoline-4,1'-naphthalene]-1,3,4'(2H)-trione (3ja)

Eluent: petroleum ether/ethyl acetate (9:1). Yellow solid (48.2 mg, 65%), mp 172.1-173.8 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.42-8.40 (m, 2H), 7.74 (d, $J = 8.4$ Hz, 1H), 7.58-7.55 (m, 2H), 7.07 (s, 1H), 6.86-6.83 (m, 2H), 6.69 (d, $J = 10.0$ Hz, 1H), 3.45 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 182.8, 169.2, 163.6, 145.9, 143.3, 137.7, 135.0, 134.5 (q, $^2J_{\text{C-F}} = 26.7$ Hz), 129.9, 129.4, 129.2, 128.2, 128.1, 125.6 (q, $^3J_{\text{C-F}} = 3.6$ Hz), 125.1 (q, $^3J_{\text{C-F}} = 3.6$ Hz), 124.5, 123.1 (q, $^1J_{\text{C-F}} = 271.6$ Hz), 54.6, 28.2. ^{19}F NMR (376 MHz, CDCl_3): δ -63.06 (s). HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{12}\text{F}_3\text{NNaO}_3$ 394.0661; Found 394.0661.



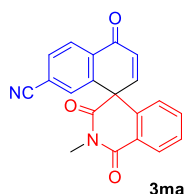
Methyl 2-methyl-1,3,4'-trioxo-2,3-dihydro-1H,4'H-spiro[isoquinoline-4,1'-naphthalene]-7'-carboxylate (3ka)

Eluent: petroleum ether/ethyl acetate (7:1). White solid (36.8 mg, 51%), mp 213.3-215.1 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.41-8.39 (m, 1H), 8.35 (d, $J = 8.4$ Hz, 1H), 8.12 (dd, $J_1 = 8.4$ Hz, $J_2 = 1.6$ Hz, 1H), 7.55-7.52 (m, 2H), 7.49 (d, $J = 1.6$ Hz, 1H), 6.85-6.81 (m, 2H), 6.68 (d, $J = 10.0$ Hz, 1H), 3.85 (s, 3H), 3.45 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 183.3, 169.5, 165.5, 163.7, 145.9, 142.9, 138.1, 134.8, 134.7, 134.3, 129.7, 129.5, 129.4, 129.3, 129.2, 128.2, 127.5, 124.5, 54.6, 52.6, 28.2. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{21}\text{H}_{15}\text{NNaO}_5$ 384.0842; Found 384.0837.



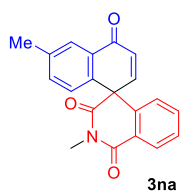
2-Methyl-7'-nitro-1*H*,4'*H*-spiro[isoquinoline-4,1'-naphthalene]-1,3,4'(2*H*)-trione (3la)

Eluent: petroleum ether/ethyl acetate (5:1). Brown solid (31.3 mg, 45%), mp 197.2-198.7 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.48-8.42 (m, 2H), 8.31 (dd, *J*₁ = 8.4 Hz, *J*₂ = 2.0 Hz, 1H), 7.69 (d, *J* = 2.0 Hz, 1H), 7.62-7.55 (m, 2H), 6.89 (d, *J* = 10.0 Hz, 1H), 6.86-6.84 (m, 1H), 6.71 (d, *J* = 10.0 Hz, 1H), 3.46 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 182.2, 168.9, 163.3, 150.3, 146.3, 144.1, 137.2, 135.9, 135.0, 130.1, 129.6, 129.2, 129.0, 128.1, 124.6, 123.6, 123.5, 54.8, 28.3. HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₉H₁₂N₂NaO₅ 371.0638; Found 371.0637.



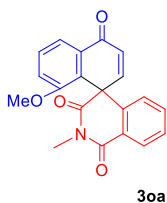
2-Methyl-1,3,4'-trioxo-2,3-dihydro-1*H*,4'*H*-spiro[isoquinoline-4,1'-naphthalene]-7'-carbonitrile (3ma)

Eluent: petroleum ether/ethyl acetate (5:1). White solid (38.7 mg, 59%), mp 237.6-239.2 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.44-8.41 (m, 1H), 8.38 (d, *J* = 8.4 Hz, 1H), 7.75 (dd, *J*₁ = 8.4 Hz, *J*₂ = 0.8 Hz, 1H), 7.60-7.57 (m, 2H), 7.14 (s, 1H), 6.87-6.85 (m, 2H), 6.72 (d, *J* = 10.0 Hz, 1H), 3.45 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 182.4, 168.8, 163.3, 145.7, 143.6, 137.3, 135.1, 134.5, 132.2, 131.8, 130.0, 129.6, 129.4, 128.1, 128.0, 124.5, 117.3, 116.8, 54.2, 28.3. HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₀H₁₂N₂NaO₃ 351.0740; Found 351.0740.



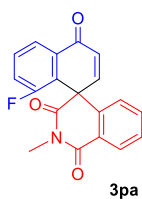
2,6'-Dimethyl-1*H*,4'*H*-spiro[isoquinoline-4,1'-naphthalene]-1,3,4'(2*H*)-trione (3na)

Eluent: petroleum ether/ethyl acetate (7:1). White solid (31.1 mg, 49%), mp 248.6-250.2 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.37-8.35 (m, 1H), 8.08 (s, 1H), 7.52-7.50 (m, 2H), 7.27-7.25 (m, 1H), 6.92-6.90 (m, 1H), 6.80 (d, $J = 10.0$ Hz, 1H), 6.73 (d, $J = 8.0$ Hz, 1H), 6.68 (d, $J = 10.0$ Hz, 1H), 3.43 (s, 3H), 2.40 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 184.2, 170.0, 164.0, 145.1, 140.1, 138.9, 138.8, 134.6, 134.4, 131.2, 129.9, 129.4, 128.8, 128.2, 127.7, 127.4, 124.4, 54.1, 28.0, 21.1. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{15}\text{NNaO}_3$ 340.0944; Found 340.0945.



8'-Methoxy-2-methyl-1*H*,4'*H*-spiro[isoquinoline-4,1'-naphthalene]-1,3,4'(2*H*)-trione (3oa)

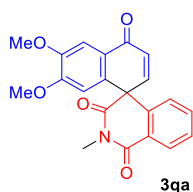
Eluent: petroleum ether/ethyl acetate (5:1). White solid (30.6 mg, 46%), mp 204.6-206.3 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.31 (dd, $J_1 = 7.6$ Hz, $J_2 = 2.0$ Hz, 1H), 7.93 (d, $J = 8.0$ Hz, 1H), 7.51 (t, $J = 8.0$ Hz, 1H), 7.46-7.39 (m, 2H), 7.03 (d, $J = 8.0$ Hz, 1H), 6.76-6.72 (m, 1H), 6.69 (d, $J = 10.0$ Hz, 1H), 6.52 (d, $J = 10.0$ Hz, 1H), 3.48 (s, 3H), 3.47 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 184.1, 170.8, 164.4, 155.4, 145.6, 138.4, 134.0, 133.0, 132.3, 129.7, 129.1, 128.1, 127.8, 126.4, 124.8, 119.1, 116.0, 56.0, 52.3, 27.7. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{15}\text{NNaO}_4$ 356.0893; Found 356.0894.



8'-Fluoro-2-methyl-1*H*,4'*H*-spiro[isoquinoline-4,1'-naphthalene]-1,3,4'(2*H*)-trione (3pa)

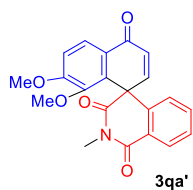
Eluent: petroleum ether/ethyl acetate (7:1). Yellow solid (27.0 mg, 42%), mp 221.3-222.7 °C. ^1H NMR (600 MHz, CDCl_3): δ 8.35-8.34 (m, 1H), 8.13 (d, $J = 7.8$ Hz, 1H), 7.55 (td, $J_1 = 8.4$ Hz, $J_2 = 5.4$ Hz, 1H), 7.52-7.47 (m, 2H), 7.23 (t, $J = 9.0$ Hz, 1H), 6.80-6.78 (m, 1H), 6.72 (d, $J = 10.2$ Hz, 1H), 6.55 (d, $J = 10.2$ Hz, 1H), 3.48 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 182.7 (d, $^4J_{\text{C-F}} = 3.3$ Hz), 169.7, 163.8, 159.0 (d, $^1J_{\text{C-F}} = 249.3$ Hz), 145.2, 137.2, 134.4, 133.4 (d, $^4J_{\text{C-F}} = 2.3$ Hz), 130.6 (d, $^2J_{\text{C-F}} = 13.1$ Hz), 130.3 (d, $^3J_{\text{C-F}} =$

8.9 Hz), 129.7, 128.8, 128.0, 126.8, 124.4, 122.8 (d, $^4J_{C-F} = 3.3$ Hz), 120.4 (d, $^2J_{C-F} = 20.7$ Hz), 51.7, 28.0. ^{19}F NMR (376 MHz, CDCl_3): δ -112.90 (dd, $J_1 = 9.8$ Hz, $J_2 = 5.6$ Hz). HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{19}\text{H}_{12}\text{FNNaO}_3$ 344.0693; Found 344.0693.



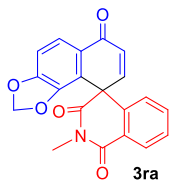
6',7'-Dimethoxy-2-methyl-1*H*,4'*H*-spiro[isoquinoline-4,1'-naphthalene]-1,3,4'(2*H*)-trione (3qa)

Eluent: petroleum ether/ethyl acetate (6:1). White solid (37.1 mg, 51%), mp 231.6-233.5 °C. ^1H NMR (600 MHz, CDCl_3): δ 8.37-8.36 (m, 1H), 7.72 (s, 1H), 7.54-7.52 (m, 2H), 6.90-6.89 (m, 1H), 6.74 (d, $J = 9.6$ Hz, 1H), 6.61 (d, $J = 9.6$ Hz, 1H), 6.15 (s, 1H), 3.98 (s, 3H), 3.68 (s, 3H), 3.46 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 183.3, 170.1, 164.0, 153.6, 149.6, 144.8, 138.9, 137.0, 134.8, 129.5, 129.2, 128.9, 128.1, 125.7, 124.4, 109.1, 108.0, 56.2, 56.1, 54.4, 28.1. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{21}\text{H}_{17}\text{NNaO}_5$ 386.0999; Found 386.0996.



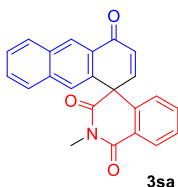
7',8'-Dimethoxy-2-methyl-1*H*,4'*H*-spiro[isoquinoline-4,1'-naphthalene]-1,3,4'(2*H*)-trione (3qa')

Eluent: petroleum ether/ethyl acetate (6:1). White solid (13.1 mg, 18%), mp 231.6-233.5 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.35-8.33 (m, 1H), 8.08 (d, $J = 8.8$ Hz, 1H), 7.45-7.43 (m, 2H), 7.11 (d, $J = 8.8$ Hz, 1H), 6.79-6.77 (m, 1H), 6.64 (d, $J = 10.0$ Hz, 1H), 6.47 (d, $J = 10.0$ Hz, 1H), 3.88 (s, 3H), 3.49 (s, 3H), 3.18 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 183.4, 170.7, 164.3, 156.6, 150.0, 144.2, 139.1, 137.4, 134.0, 129.3, 128.3, 127.9, 126.9, 125.5, 124.6, 123.6, 112.9, 59.4, 55.8, 52.5, 27.8. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{21}\text{H}_{17}\text{NNaO}_5$ 386.0999; Found 386.0996.



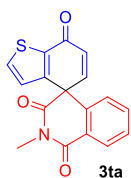
2-Methyl-1*H*,6'*H*-spiro[isoquinoline-4,9'-naphtho[1,2-*d*][1,3]dioxole]-1,3,6'(2*H*)-trione (3ra)

Eluent: petroleum ether/ethyl acetate (6:1). Yellow solid (36.1 mg, 52%), mp 214.3-215.9 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.32-8.30 (m, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.52-7.47 (m, 2H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.94-6.91 (m, 1H), 6.65 (d, *J* = 10.0 Hz, 1H), 6.54 (d, *J* = 10.0 Hz, 1H), 5.88 (d, *J* = 1.2 Hz, 1H), 5.72 (d, *J* = 1.2 Hz, 1H), 3.46 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 182.4, 169.7, 164.1, 151.8, 144.0, 143.9, 137.0, 134.3, 129.2, 129.0, 128.7, 127.4, 125.7, 124.7, 124.3, 123.2, 109.4, 102.6, 51.4, 27.9. HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₀H₁₃NNaO₅ 370.0686; Found 370.0685.



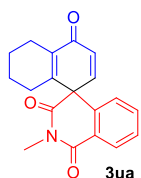
2'-Methyl-1'*H*,4'*H*-spiro[anthracene-1,4'-isoquinoline]-1',3',4'(2'*H*)-trione (3sa)

Eluent: petroleum ether/ethyl acetate (6:1). Yellow solid (53.0 mg, 75%), mp 239.6-241.1 °C. ¹H NMR (600 MHz, CDCl₃): δ 8.50 (s, 1H), 8.43-8.41 (m, 1H), 8.02-8.01 (m, 1H), 7.65-7.64 (m, 1H), 7.55-7.51 (m, 4H), 7.26 (s, 1H), 6.99-6.97 (m, 1H), 6.87 (d, *J* = 10.2 Hz, 1H), 6.79 (d, *J* = 10.2 Hz, 1H), 3.44 (s, 3H). ¹³C{¹H} NMR (150 MHz, CDCl₃): δ 184.3, 170.3, 164.1, 145.2, 139.8, 138.5, 135.1, 134.8, 132.3, 130.3, 129.8, 129.4, 129.1, 129.0, 128.9, 128.6, 128.5, 127.7, 127.6, 127.4, 124.4, 54.0, 28.1. HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₃H₁₅NNaO₃ 376.0944; Found 376.0944.



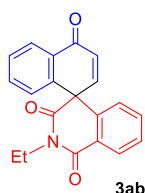
2'-Methyl-1'*H*,7'*H*-spiro[benzo[*b*]thiophene-4,4'-isoquinoline]-1',3',7'(2'*H*)-trione (3ta)

Eluent: petroleum ether/ethyl acetate (5:1). Brown solid (26.0 mg, 42%), mp 202.8-204.6 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.37-8.34 (m, 1H), 7.63 (d, $J = 5.2$ Hz, 1H), 7.54-7.52 (m, 2H), 6.93-6.91 (m, 1H), 6.83 (d, $J = 9.6$ Hz, 1H), 6.65-6.63 (m, 2H), 3.44 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 179.1, 168.6, 163.9, 148.5, 145.1, 137.5, 136.6, 134.7, 134.2, 129.8, 129.2, 127.3, 126.2, 124.2, 54.4, 28.1. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{17}\text{H}_{11}\text{NNaO}_3\text{S}$ 332.0352; Found 332.0350.



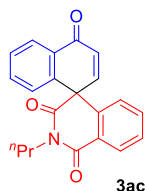
2-Methyl-5',6',7',8'-tetrahydro-1H,4'H-spiro[isoquinoline-4,1'-naphthalene]-1,3,4'(2H)-trione (3ua)

Eluent: petroleum ether/ethyl acetate (4:1). White solid (29.5 mg, 48%), mp 183.2-184.6 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.32 (d, $J = 7.2$ Hz, 1H), 7.61 (t, $J = 7.2$ Hz, 1H), 7.53 (t, $J = 7.2$ Hz, 1H), 7.08 (d, $J = 8.0$ Hz, 1H), 6.62 (d, $J = 9.6$ Hz, 1H), 6.42 (d, $J = 9.6$ Hz, 1H), 3.44 (s, 3H), 2.50 (br, 2H), 1.94-1.87 (m, 1H), 1.77-1.67 (m, 2H), 1.65-1.60 (m, 2H), 1.54-1.45 (m, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 185.4, 169.3, 163.8, 151.3, 145.1, 136.4, 136.1, 134.8, 129.7, 129.0, 128.7, 126.6, 124.9, 56.7, 27.8, 27.5, 22.3, 21.7, 21.5. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{19}\text{H}_{17}\text{NNaO}_3$ 330.1101; Found 330.1101.



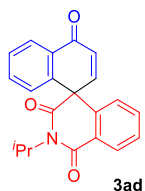
2-Ethyl-1H,4'H-spiro[isoquinoline-4,1'-naphthalene]-1,3,4'(2H)-trione (3ab)

Eluent: petroleum ether/ethyl acetate (8:1). White solid (49.5 mg, 78%), mp 163.3-164.5 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.38-8.36 (m, 1H), 8.30-8.26 (m, 1H), 7.54-7.49 (m, 2H), 7.48-7.43 (m, 2H), 6.92-6.90 (m, 1H), 6.86-6.82 (m, 2H), 6.71 (d, $J = 10.0$ Hz, 1H), 4.10 (q, $J = 7.2$ Hz, 2H), 1.23 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 184.0, 169.3, 163.5, 145.2, 142.8, 138.7, 134.6, 133.4, 131.4, 129.8, 129.5, 128.8, 128.6, 128.2, 127.7, 127.4, 124.6, 54.2, 36.5, 13.1. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{15}\text{NNaO}_3$ 340.0944; Found 340.0944.



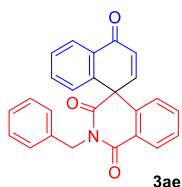
2-Propyl-1*H*,4'*H*-spiro[isoquinoline-4,1'-naphthalene]-1,3,4'(2*H*)-trione (3ac)

Eluent: petroleum ether/ethyl acetate (6:1). Yellow solid (48.3 mg, 73%), mp 128.1-129.8 °C. ^1H NMR (600 MHz, CDCl_3): δ 8.37-8.36 (m, 1H), 8.28-8.27 (m, 1H), 7.52-7.51 (m, 2H), 7.48-7.43 (m, 2H), 6.91-6.90 (m, 1H), 6.85-6.82 (m, 2H), 6.70 (d, $J = 9.6$ Hz, 1H), 4.00 (t, $J = 7.2$ Hz, 2H), 1.68-1.61 (m, 2H), 0.93 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 184.0, 169.5, 163.7, 145.2, 142.9, 138.7, 134.6, 133.4, 131.5, 129.8, 129.5, 128.8, 128.6, 128.2, 127.7, 127.3, 124.6, 54.3, 42.8, 21.2, 11.3. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{21}\text{H}_{17}\text{NNaO}_3$ 354.1101; Found 354.1101.



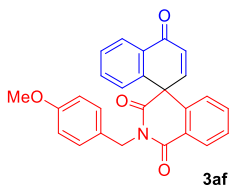
2-Isopropyl-1*H*,4'*H*-spiro[isoquinoline-4,1'-naphthalene]-1,3,4'(2*H*)-trione (3ad)

Eluent: petroleum ether/ethyl acetate (6:1). White solid (51.0 mg, 77%), mp 201.6-203.1 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.36-8.34 (m, 1H), 8.28-8.26 (m, 1H), 7.52-7.44 (m, 4H), 6.90-6.88 (m, 2H), 6.85 (d, $J = 10.4$ Hz, 1H), 6.71 (d, $J = 10.0$ Hz, 1H), 5.24-5.17 (m, 1H), 1.48 (d, $J = 6.8$ Hz, 3H), 1.42 (d, $J = 6.8$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 184.0, 169.8, 164.0, 145.4, 142.7, 138.6, 134.4, 133.3, 131.4, 129.8, 129.6, 128.8, 128.6, 127.9, 127.6, 127.4, 125.1, 54.8, 46.6, 19.7, 19.3. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{21}\text{H}_{17}\text{NNaO}_3$ 354.1101; Found 354.1101.



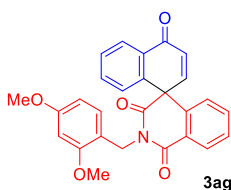
2-Benzyl-1*H*,4'*H*-spiro[isoquinoline-4,1'-naphthalene]-1,3,4'(2*H*)-trione (3ae)

Eluent: petroleum ether/ethyl acetate (6:1). White solid (56.9 mg, 75%), mp 176.3-177.6 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.37-8.35 (m, 1H), 8.27-8.25 (m, 1H), 7.52-7.35 (m, 6H), 7.29-7.22 (m, 3H), 6.92-6.89 (m, 1H), 6.81-6.75 (m, 2H), 6.69 (d, $J = 10.0$ Hz, 1H), 5.25 (d, $J = 14.0$ Hz, 1H), 5.17 (d, $J = 13.6$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 183.9, 169.7, 163.6, 145.0, 142.6, 138.7, 136.5, 134.7, 133.3, 131.4, 129.9, 129.6, 129.0, 128.9, 128.7, 128.6, 128.2, 127.8, 127.7, 127.4, 124.5, 54.3, 44.4. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{25}\text{H}_{17}\text{NNaO}_3$ 402.1101; Found 402.1097.



2-(4-Methoxybenzyl)-1*H*,4'*H*-spiro[isoquinoline-4,1'-naphthalene]-1,3,4'(2*H*)-trione (3af)

Eluent: petroleum ether/ethyl acetate (6:1). White solid (55.6 mg, 68%), mp 186.4-187.9 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.37-8.33 (m, 1H), 8.26 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.2$ Hz, 1H), 7.52-7.43 (m, 3H), 7.39-7.34 (m, 3H), 6.91-6.87 (m, 1H), 6.81-6.73 (m, 4H), 6.69 (d, $J = 10.0$ Hz, 1H), 5.19 (d, $J = 13.6$ Hz, 1H), 5.10 (d, $J = 13.2$ Hz, 1H), 3.76 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 183.9, 169.7, 163.6, 159.2, 145.1, 142.7, 138.6, 134.7, 133.3, 131.4, 130.7, 129.9, 129.6, 128.8, 128.7, 128.6, 128.2, 127.8, 127.3, 124.6, 113.8, 55.2, 54.3, 43.9. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{26}\text{H}_{19}\text{NNaO}_4$ 432.1206; Found 432.1206.

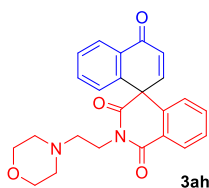


2-(2,4-Dimethoxybenzyl)-1*H*,4'*H*-spiro[isoquinoline-4,1'-naphthalene]-1,3,4'(2*H*)-trione (3ag)

Eluent: petroleum ether/ethyl acetate (5:1). White solid (63.2 mg, 72%), mp 195.3-196.9 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.36-8.32 (m, 1H), 8.25 (dd, $J_1 = 7.6$ Hz, $J_2 = 1.6$ Hz, 1H), 7.51-7.38 (m, 4H), 7.15-7.13 (m, 1H), 6.90-6.82 (m, 3H), 6.67 (d, $J = 10.0$ Hz, 1H), 6.41-6.38 (m, 2H), 5.18 (s, 2H), 3.76 (s, 3H), 3.65 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 184.1, 169.2, 163.7, 160.4, 158.4, 145.5, 142.8, 138.8, 134.5, 133.2,

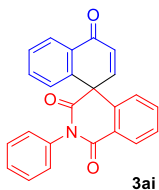
131.5, 130.4, 129.6, 129.5, 128.8, 128.5, 128.2, 128.1, 127.2, 124.8, 116.8, 104.0, 98.4, 55.4, 55.3, 54.6,

40.1. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{21}NNaO_5$ 462.1312; Found 462.1312.



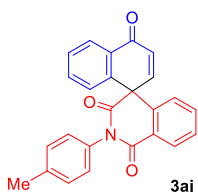
2-(2-Morpholinoethyl)-1*H*,4'*H*-spiro[isoquinoline-4,1'-naphthalene]-1,3,4'(2*H*)-trione (3ah)

Eluent: petroleum ether/ethyl acetate (2:1). Brown oil (37.0 mg, 46%), mp 180.5-182.4 °C. 1H NMR (400 MHz, $CDCl_3$): 8.37-8.34 (m, 1H), 8.28 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.6$ Hz, 1H), 7.54-7.42 (m, 4H), 6.96-6.94 (m, 1H), 6.91-6.86 (m, 2H), 6.70 (d, $J = 10.0$ Hz, 1H), 4.29-4.17 (m, 2H), 3.58 (br s, 4H), 2.63 (t, $J = 6.0$ Hz, 2H), 2.54 (s, 2H), 2.48 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 184.0, 169.8, 163.7, 145.4, 142.9, 138.7, 134.7, 133.3, 131.5, 129.6, 129.5, 128.8, 128.7, 128.2, 128.1, 127.3, 124.4, 66.9, 55.8, 54.3, 53.8, 37.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{23}N_2O_4$ 403.1652; Found 403.1651.



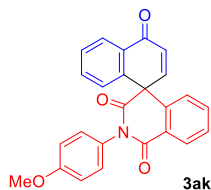
2-Phenyl-1*H*,4'*H*-spiro[isoquinoline-4,1'-naphthalene]-1,3,4'(2*H*)-trione (3ai)

Eluent: petroleum ether/ethyl acetate (8:1). White solid (46.7 mg, 64%), mp 208.1-209.6 °C. 1H NMR (600 MHz, $CDCl_3$): 8.41 (dd, $J_1 = 7.8$ Hz, $J_2 = 1.8$ Hz, 1H), 8.28 (dd, $J_1 = 7.2$ Hz, $J_2 = 1.2$ Hz, 1H), 7.60-7.46 (m, 6H), 7.44-7.43 (m, 1H), 7.17 (d, $J = 7.2$ Hz, 2H), 7.08-7.07 (m, 1H), 7.02 (dd, $J_1 = 7.8$ Hz, $J_2 = 1.2$ Hz, 1H), 6.99 (d, $J = 9.6$ Hz, 1H), 6.75 (d, $J = 10.2$ Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 183.8, 169.5, 163.9, 144.8, 142.5, 138.9, 135.1, 134.7, 133.5, 131.4, 130.3, 129.9, 129.4, 129.1, 128.9, 128.8, 128.3, 128.2, 127.6, 124.8, 54.7. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{15}NNaO_3$ 388.0944; Found 388.0944.



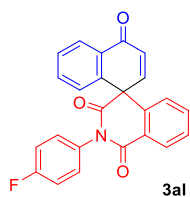
2-(*p*-Tolyl)-1*H*,4'*H*-spiro[isoquinoline-4,1'-naphthalene]-1,3,4'(2*H*)-trione (3aj)

Eluent: petroleum ether/ethyl acetate (7:1). White solid (57.6 mg, 76%), mp 234.4-235.9 °C. ¹H NMR (400 MHz, CDCl₃): 8.41- 8.39 (m, 1H), 8.29-8.26 (m, 1H), 7.58-7.48 (m, 4H), 7.28-7.26 (m, 2H), 7.08-6.97 (m, 5H), 6.75 (d, *J* = 10.0 Hz, 1H), 2.39 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 183.9, 169.5, 164.0, 144.9, 142.6, 139.0, 138.9, 135.0, 133.5, 132.0, 131.4, 130.2, 130.1, 129.9, 129.0, 128.8, 128.2, 127.8, 127.6, 127.5, 124.8, 54.7, 21.3. HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₅H₁₇NNaO₃ 402.1101; Found 402.1099.



2-(4-Methoxyphenyl)-1*H*,4'*H*-spiro[isoquinoline-4,1'-naphthalene]-1,3,4'(2*H*)-trione (3ak)

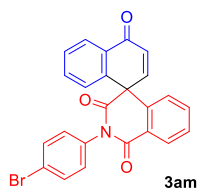
Eluent: petroleum ether/ethyl acetate (7:1). White solid (61.6 mg, 78%), mp 193.2-194.6 °C. ¹H NMR (400 MHz, CDCl₃): 8.41-8.39 (m, 1H), 8.29-8.26 (m, 1H), 7.60-7.47 (m, 4H), 7.09-7.05 (m, 3H), 7.02-6.97 (m, 4H), 6.75 (d, *J* = 10.0 Hz, 1H), 3.82 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 183.9, 169.7, 164.1, 159.7, 144.9, 142.6, 138.8, 135.0, 133.4, 131.4, 130.2, 129.9, 129.1, 129.0, 128.7, 128.2, 127.6, 127.5, 127.2, 124.8, 114.7, 55.5, 54.8. HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₅H₁₇NNaO₄ 418.1050; Found 418.1050.



2-(4-Fluorophenyl)-1*H*,4'*H*-spiro[isoquinoline-4,1'-naphthalene]-1,3,4'(2*H*)-trione (3al)

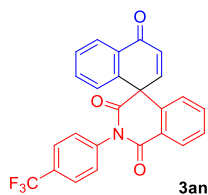
Eluent: petroleum ether/ethyl acetate (10:1). White solid (61.3 mg, 80%), mp 253.2-254.8 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.41-8.39 (m, 1H), 8.29-8.27 (m, 1H), 7.62-7.48 (m, 4H), 7.16-7.14 (m, 4H), 7.06-7.01 (m, 2H), 6.97 (d, *J* = 10.0 Hz, 1H), 6.75 (d, *J* = 10.0 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 183.7, 169.6, 163.9, 162.6 (d, ¹*J*_{C-F} = 247.7 Hz), 144.6, 142.4, 138.9, 135.2, 133.5, 131.4, 130.5 (d, ⁴*J*_{C-F} = 3.7 Hz), 130.3, 130.0 (d, ³*J*_{C-F} = 8.7 Hz), 129.9, 129.1, 128.9, 128.3, 127.6, 127.5, 124.6, 116.5 (d, ²*J*_{C-F} = 23.1 Hz), 54.7.

^{19}F NMR (376 MHz, CDCl_3): δ -112.19 - -112.26 (m). HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{24}\text{H}_{14}\text{FNNaO}_3$ 406.0850; Found 406.0846.



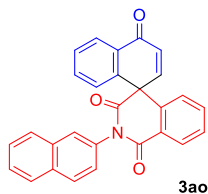
2-(4-Bromophenyl)-1*H*,4'*H*-spiro[isoquinoline-4,1'-naphthalene]-1,3,4'(2*H*)-trione (3am)

Eluent: petroleum ether/ethyl acetate (9:1). White solid (71.8 mg, 81%), mp 226.6-228.1 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.39 (dd, $J_1 = 7.6$ Hz, $J_2 = 1.6$ Hz, 1H), 8.29-8.27 (m, 1H), 7.61-7.56 (m, 4H), 7.52-7.49 (m, 2H), 7.07-7.00 (m, 4H), 6.96 (d, $J = 10.0$ Hz, 1H), 6.75 (d, $J = 10.0$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 183.7, 169.4, 163.7, 144.6, 142.4, 138.9, 135.2, 133.7, 133.5, 132.6, 131.4, 130.3, 130.0, 129.9, 129.1, 128.9, 128.3, 127.6, 127.5, 124.5, 123.1, 54.7. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{24}\text{H}_{14}\text{BrNNaO}_3$ 466.0049; Found 466.0049.



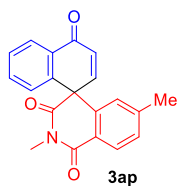
2-(4-(Trifluoromethyl)phenyl)-1*H*,4'*H*-spiro[isoquinoline-4,1'-naphthalene]-1,3,4'(2*H*)-trione (3an)

Eluent: petroleum ether/ethyl acetate (9:1). White solid (65.8 mg, 76%), mp 241.6-243.1 °C. ^1H NMR (600 MHz, CDCl_3): δ 8.40 (d, $J = 7.2$ Hz, 1H), 8.29-8.28 (m, 1H), 7.74 (d, $J = 8.4$ Hz, 2H), 7.62-7.56 (m, 2H), 7.54-7.49 (m, 2H), 7.32 (d, $J = 8.4$ Hz, 2H), 7.06 (d, $J = 7.2$ Hz, 1H), 7.04 (d, $J = 7.8$ Hz, 1H), 6.98 (d, $J = 9.6$ Hz, 1H), 6.76 (d, $J = 10.2$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 183.7, 169.4, 163.7, 144.4, 142.3, 138.9, 137.9, 135.4, 133.6, 131.4, 131.2 (q, $^2J_{\text{C-F}} = 32.1$ Hz), 130.4, 129.9, 129.2, 129.0, 128.9, 128.4, 127.7, 127.5, 126.5 (q, $^3J_{\text{C-F}} = 3.3$ Hz), 124.4, 123.7 (q, $^1J_{\text{C-F}} = 270.1$ Hz), 54.7. ^{19}F NMR (376 MHz, CDCl_3): δ -62.72 (s). HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{25}\text{H}_{14}\text{F}_3\text{NNaO}_3$ 456.0818; Found 456.0819.



2-(Naphthalen-2-yl)-1*H*,4'*H*-spiro[isoquinoline-4,1'-naphthalene]-1,3,4'(2*H*)-trione (3ao)

Eluent: petroleum ether/ethyl acetate (9:1). White solid (53.9 mg, 65%), mp 283.6-285.1 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.42 (d, *J* = 7.2 Hz, 1H), 8.29 (d, *J* = 7.6 Hz, 1H), 7.93 (d, *J* = 8.8 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 7.2 Hz, 1H), 7.69 (s, 1H), 7.60-7.48 (m, 6H), 7.25-7.22 (m, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.04-7.01 (m, 2H), 6.76 (d, *J* = 10.0 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 183.8, 169.7, 164.1, 144.8, 142.6, 139.0, 135.1, 133.5, 133.4, 133.2, 132.1, 131.4, 130.3, 129.9, 129.4, 129.1, 128.8, 128.3, 128.2, 127.9, 127.7, 127.6, 127.4, 127.0, 126.6, 125.5, 124.8, 54.8. HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₈H₁₇NNaO₃ 438.1101; Found 438.1101.

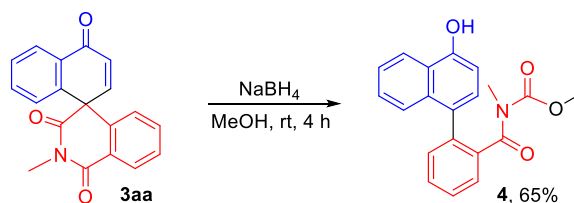


2,6-Dimethyl-1*H*,4'*H*-spiro[isoquinoline-4,1'-naphthalene]-1,3,4'(2*H*)-trione (3ap)

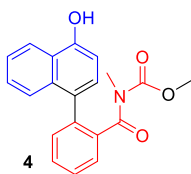
Eluent: petroleum ether/ethyl acetate (10:1). White solid (32.3 mg, 51%), mp 176.8-178.6 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.28-8.25 (m, 1H), 8.17 (d, *J* = 0.8 Hz, 1H), 7.47-7.43 (m, 2H), 7.33 (dd, *J*₁ = 8.0 Hz, *J*₂ = 1.6 Hz, 1H), 6.85-6.78 (m, 3H), 6.68 (d, *J* = 10.0 Hz, 1H), 3.42 (s, 3H), 2.44 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 184.0, 170.0, 164.2, 145.4, 143.0, 139.1, 135.8, 135.7, 133.4, 131.5, 129.6, 129.5, 128.6, 128.1, 127.8, 127.3, 124.2, 54.1, 28.0, 21.1. HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₀H₁₅NNaO₃ 340.0944; Found 340.0944.

III. Structural elaborations

1. Synthesis of 4



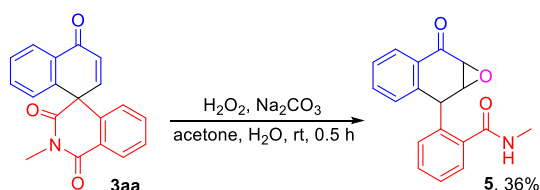
To a flask containing a solution of **3aa** (30.3 mg, 0.1 mmol) in MeOH (1.5 mL) was charged with NaBH₄ (3.0 mg, 0.08 mmol) at 0 °C. The resulting mixture was stirred at 0 °C for 10 min, and then at rt for 4 h. Upon completion, it was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (5:1) as the eluent to give **4**.



Methyl (2-(4-hydroxynaphthalen-1-yl)benzoyl)(methyl)carbamate (**4**)

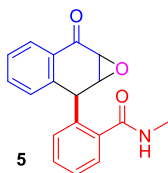
Eluent: petroleum ether/ethyl acetate (5:1). White solid (21.8 mg, 65%), mp 202.5-203.9 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.25 (d, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.59 (dd, *J*₁ = 7.2 Hz, *J*₂ = 1.2 Hz, 1H), 7.55-7.38 (m, 5H), 7.12 (d, *J* = 7.6 Hz, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 6.23 (s, 1H), 3.23 (s, 3H), 2.63 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 173.5, 154.4, 151.6, 138.5, 137.0, 132.7, 131.2, 129.9, 129.6, 127.6, 127.5, 127.1, 126.5, 126.1, 125.2, 124.4, 121.9, 107.7, 53.2, 31.4. HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₀H₁₇NNaO₄ 358.1050; Found 358.1050.

2. Synthesis of 5⁵



To a flask containing a solution of Na₂CO₃ (31 mg, 0.3 mmol) in H₂O (1.5 mL) were charged with 30% H₂O₂ (31 μL, 0.3 mmol) and a solution of **3aa** (30.3 mg, 0.1 mmol) in acetone (1 mL) in a dropwise manner at 0 °C. After being stirred at room temperature for 0.5 h, it was quenched with saturated Na₂S₂O₃ solution

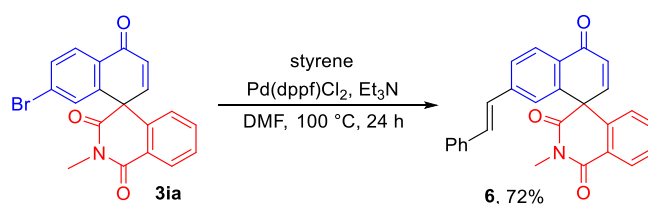
and extracted with dichloromethane (10 mL × 3). The combined organic layers were washed with water and brine, dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The crude product thus obtained was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (1:1) as eluent to afford **5**.



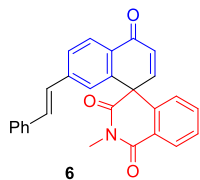
N-Methyl-2-(7-oxo-1a,2,7,7a-tetrahydronaphtho[2,3-*b*]oxiren-2-yl)benzamide (**5**)

Eluent: petroleum ether/ethyl acetate (1:1). White solid (10.6 mg, 36%), mp 250.1-251.9 °C. ¹H NMR (600 MHz, CDCl₃): δ 8.31-8.30 (m, 1H), 8.08 (d, *J* = 7.8 Hz, 1H), 7.90 (d, *J* = 7.2 Hz, 1H), 7.85 (t, *J* = 7.8 Hz, 1H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.31 (t, *J* = 7.2 Hz, 1H), 6.84 (d, *J* = 6.6 Hz, 1H), 6.04 (br s, 1H), 4.11 (dd, *J*₁ = 13.2 Hz, *J*₂ = 4.8 Hz, 1H), 3.07 (dd, *J*₁ = 17.4 Hz, *J*₂ = 4.2 Hz, 1H), 2.95 (s, 3H), 2.36 (dd, *J*₁ = 17.4 Hz, *J*₂ = 12.6 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 194.2, 163.2, 143.6, 138.5, 134.4, 132.7, 130.9, 129.1, 129.0, 128.7, 128.3, 128.1, 127.4, 127.3, 71.5, 65.1, 40.9, 34.0. HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₈H₁₅NNaO₃ 316.0944; Found 316.0943.

3. Synthesis of **6**⁶



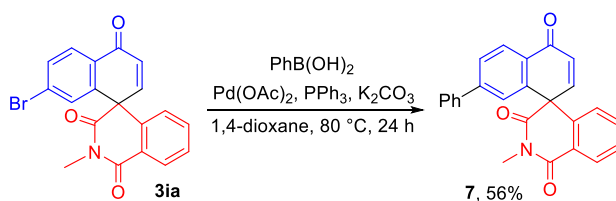
To a reaction tube equipped with a stir bar were charged with **3ia** (38.1 mg, 0.1 mmol), styrene (11.5 μL, 0.1 mmol), Pd(dppf)Cl₂ (7.3 mg, 0.01 mmol), Et₃N (20.2 mg, 0.2 mmol) and DMF (0.5 mL). The tube was then sealed and the resulting mixture was stirred at 100 °C (oil bath) under argon for 24 h. Upon completion, it was diluted with water and extracted with ethyl acetate (10 mL × 3). The combined organic layers were dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (5:1) as the eluent to give **6**.



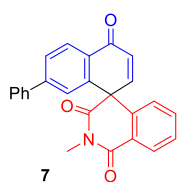
(E)-2-Methyl-7'-styryl-1H,4'H-spiro[isoquinoline-4,1'-naphthalene]-1,3,4'(2H)-trione (6)

Eluent: petroleum ether/ethyl acetate (5:1). White solid (29.2 mg, 72%), mp 187.9-189.6 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.41-8.39 (m, 1H), 8.26 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J*₁ = 8.0 Hz, *J*₂ = 1.2 Hz, 1H), 7.56-7.51 (m, 2H), 7.45 (d, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.28-7.25 (m, 1H), 7.07 (d, *J* = 16.4 Hz, 1H), 6.96-6.91 (m, 2H), 6.82 (d, *J* = 1.2 Hz, 1H), 6.78 (d, *J* = 10.0 Hz, 1H), 6.67 (d, *J* = 10.0 Hz, 1H), 3.47 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 183.5, 169.9, 164.0, 144.9, 143.4, 142.5, 138.8, 136.3, 134.8, 132.3, 130.5, 129.7, 129.5, 128.9, 128.8, 128.6, 128.3, 127.8, 126.9, 126.8, 126.5, 125.8, 124.4, 54.4, 28.1. HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₇H₁₉NNaO₃ 428.1257; Found 428.1256.

4. Synthesis of 7⁷



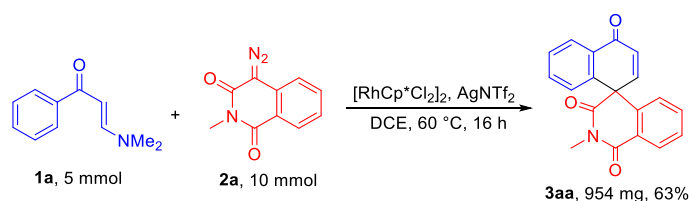
To a reaction tube equipped with a stir bar were added with **3ia** (38.1 mg, 0.1 mmol), phenylboronic acid (18.3 mg, 0.15 mmol), PPh₃ (15.7 mg, 0.06 mmol), K₂CO₃ (55.3 mg, 0.4 mmol), Pd(OAc)₂ (2.2 mg, 0.01 mmol) and dioxane (1 mL). The tube was then sealed, and the mixture was stirred at 80 °C (oil bath) under argon for 24 h. Upon completion, it was diluted with water and extracted with ethyl acetate (10 mL × 3). The organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1) as eluent to give **7**.



2-Methyl-7'-phenyl-1H,4'H-spiro[isoquinoline-4,1'-naphthalene]-1,3,4'(2H)-trione (7)

Eluent: petroleum ether/ethyl acetate (4:1). Yellow solid (21.2 mg, 56%), mp 196.2-197.9 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.40-8.37 (m, 1H), 8.34 (d, $J = 8.4$ Hz, 1H), 7.70 (dd, $J_1 = 8.4$ Hz, $J_2 = 1.6$ Hz, 1H), 7.56-7.52 (m, 2H), 7.39-7.35 (m, 5H), 6.98-6.95 (m, 2H), 6.82 (d, $J = 10.0$ Hz, 1H), 6.70 (d, $J = 10.0$ Hz, 1H), 3.46 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 183.8, 169.9, 164.0, 146.3, 145.2, 143.4, 139.2, 138.8, 134.8, 130.4, 129.7, 129.5, 129.0, 128.9, 128.6, 128.3, 127.9, 127.6, 127.3, 126.4, 124.4, 54.5, 28.1. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{25}\text{H}_{17}\text{NNaO}_3$ 402.1101; Found 402.1099.

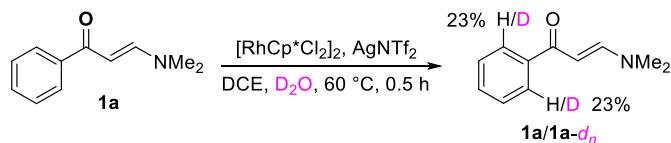
5. Gram-scale synthesis of **3aa**



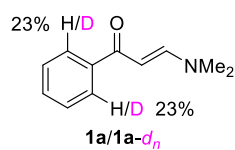
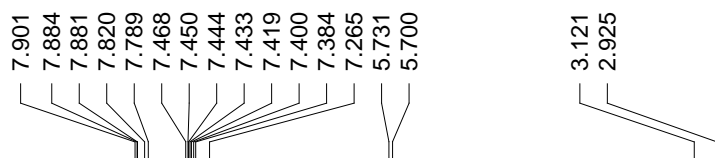
To a reaction tube equipped with a stir bar were added **1a** (875.0 mg, 5 mmol), $[\text{RhCp}^*\text{Cl}_2]_2$ (124 mg, 0.2 mmol), AgNTf_2 (776 mg, 2 mmol), **2a** (2010 mg, 10 mmol) and DCE (20 mL). The tube was then sealed, and the mixture was stirred at 60 °C (oil bath) under air for 16 h. Upon completion, it was cooled to room temperature, filtered through a pad of celite and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (8:1) as eluent to afford **3aa** (954 mg, 63%).

IV. Mechanism studies

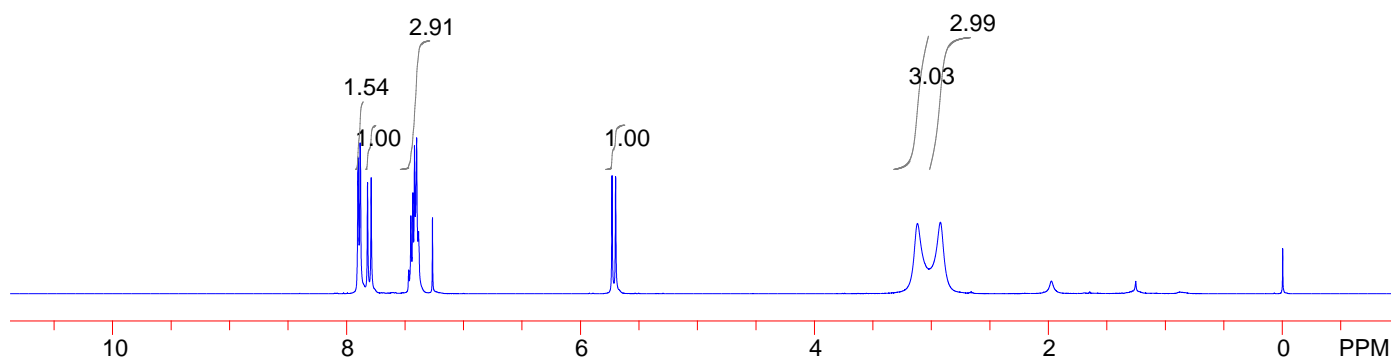
1. Studies on the reversibility of C–H bond activation

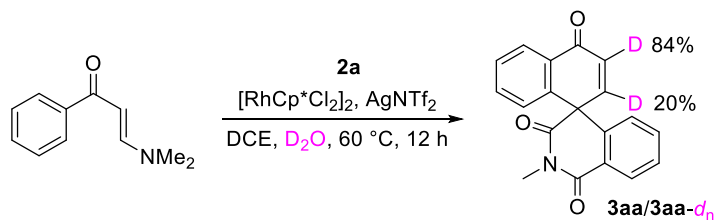


To a reaction tube equipped with a stir bar were charged with **1a** (35.0 mg, 0.2 mmol), $[\text{RhCp}^*\text{Cl}_2]_2$ (5.0 mg, 0.008 mmol), AgNTf_2 (31.1 mg, 0.08 mmol), DCE (2 mL) and D_2O (36.2 uL, 2 mmol). The tube was then sealed, and the resulting mixture was stirred at 60 °C (oil bath) under air for 0.5 h. Afterwards, it was cooled to room temperature, filtered through a pad of celite and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (2:1) as eluent to give a mixture of **1a** and **1a-d_n**. Upon analyzing the ^1H NMR spectrum of the mixture, the deuteration ratio on the *ortho*-positions of **1a** was determined to be 23%.

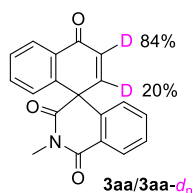
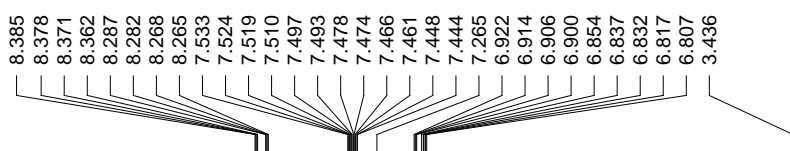


^1H NMR (400MHz, CDCl_3)

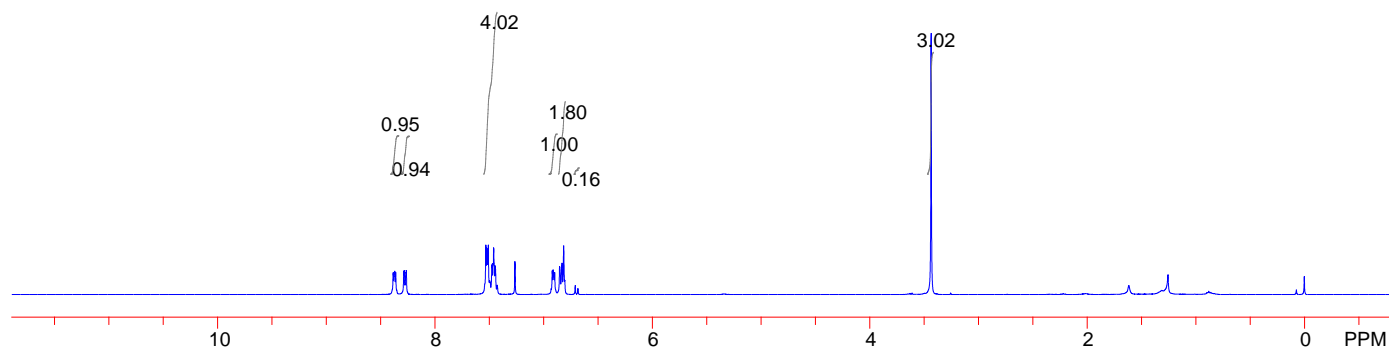




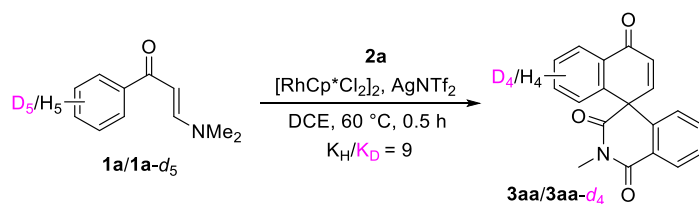
To a reaction tube equipped with a stir bar were charged with **1a** (35.0 mg, 0.2 mmol), $[\text{RhCp}^*\text{Cl}_2]_2$ (5.0 mg, 0.008 mmol), AgNTf_2 (31.1 mg, 0.08 mmol), **2a** (80.1 mg, 0.4 mmol), DCE (2 mL) and D_2O (36.2 μL , 2 mmol). The resulting mixture was stirred at 60 °C (oil bath) under air for 12 h. Afterwards, it was cooled to room temperature, filtered through a pad of celite, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (8:1) as eluent to give a mixture of **3aa** and **3aa- d_n** (33.9 mg, 56%). Upon analyzing the ^1H NMR spectrum of the mixture, the deuteration percentages at different positions were determined as 84% and 20%.



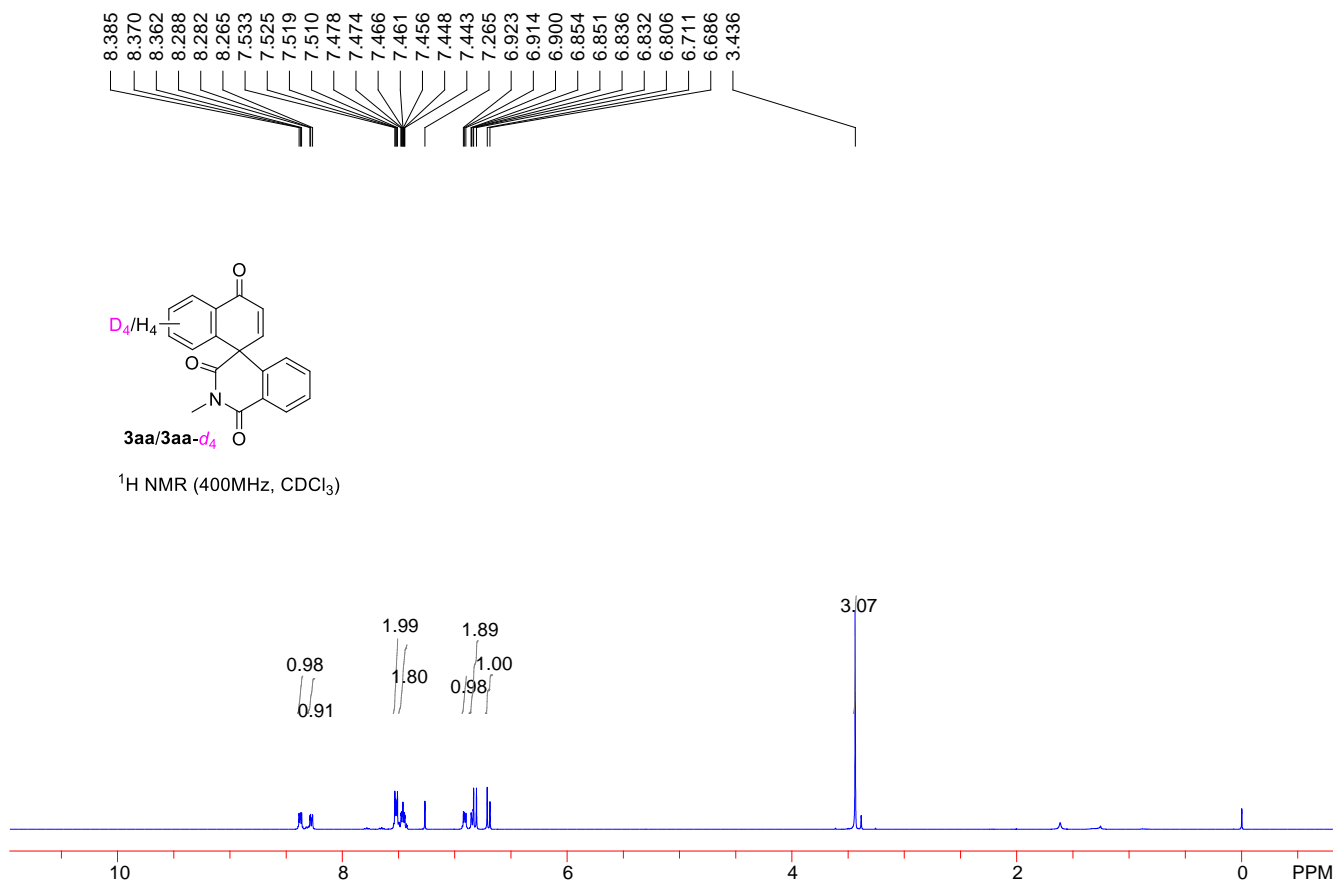
^1H NMR (400MHz, CDCl_3)



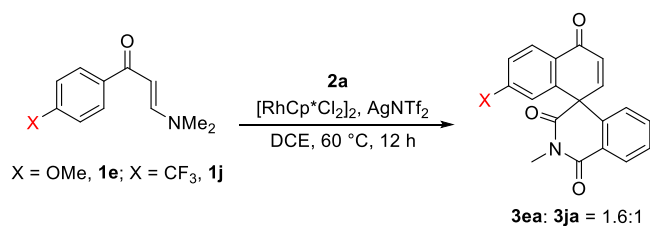
2. Kinetic isotope effect experiments



To a reaction tube equipped with a stir bar were charged with **1a** (35.0 mg, 0.2 mmol), **1a-d₅** (36.0 mg, 0.2 mmol), [RhCp*Cl₂]₂ (5.0 mg, 0.008 mmol), AgNTf₂ (31.1 mg, 0.08 mmol), **2a** (80.1 mg, 0.4 mmol) and DCE (2 mL). The resulting mixture was stirred at 60 °C (oil bath) under argon for 0.5 h. 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 Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (8:1) as eluent to give a mixture of **3aa** and **3aa-d₄**. Upon analyzing the ¹H NMR spectrum of the mixture, the ratio of **3aa** to **3aa-d₄** was determined to be about 0.9:0.1. Accordingly, the intermolecular KIE (k_H/k_D) was calculated to be 9.

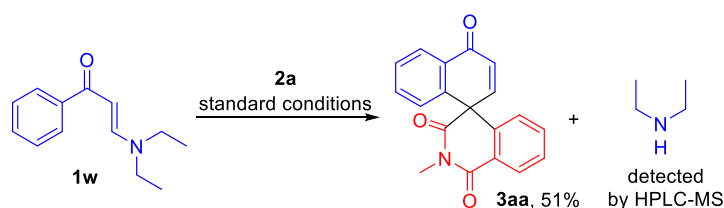


3. Electronic competition experiment



To a reaction tube equipped with a stir bar were added (*E*)-3-(dimethylamino)-1-(4-methoxyphenyl)prop-2-en-1-one (**1e**, 41.0 mg, 0.2 mmol), (*E*)-3-(dimethylamino)-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (**1j**, 48.6 mg, 0.2 mmol), [RhCp*Cl₂]₂ (5.0 mg, 0.008 mmol), AgNTf₂ (31.1 mg, 0.08 mmol), **2a** (40.2 mg, 0.2 mmol) and DCE (2 mL). The tube was then sealed, and the mixture was stirred at 60 °C (oil bath) under air for 12 h. Upon completion, it was cooled to room temperature, filtered through a pad of celite and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (8:1) as eluent to afford **3ea** (16.1 mg, 24%) and **3ja** (11.9 mg, 15%).

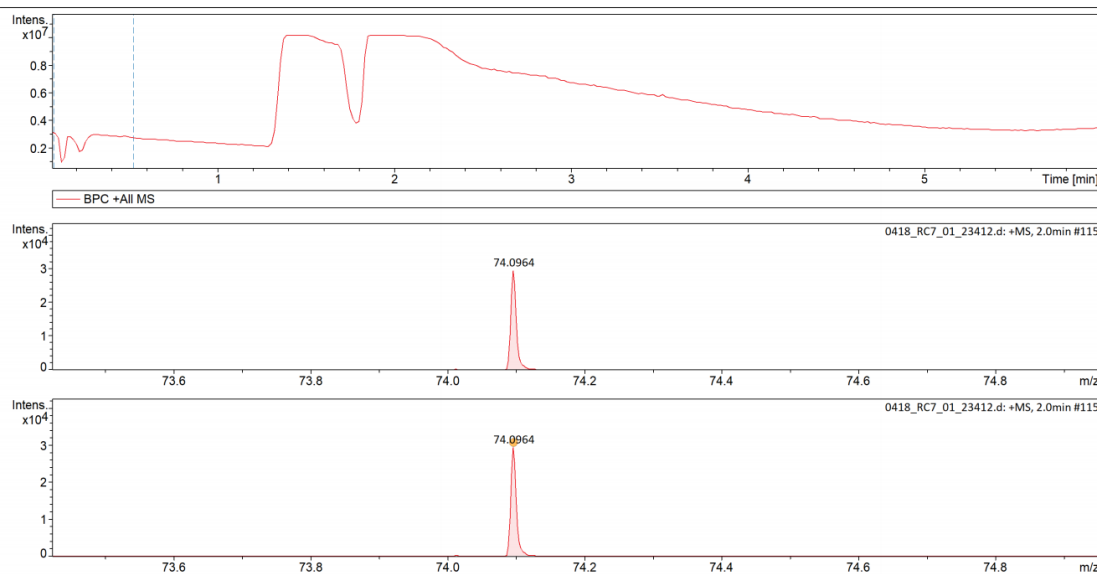
4. Control Experiments



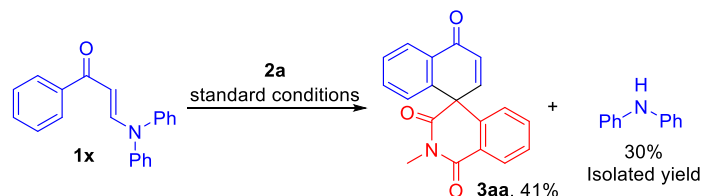
4.1. To a reaction tube equipped with a stir bar were charged with (*E*)-3-(diethylamino)-1-phenylprop-2-en-1-one (**1w**, 40.6 mg, 0.2 mmol), [RhCp*Cl₂]₂ (5.0 mg, 0.008 mmol), AgNTf₂ (31.1 mg, 0.08 mmol), **2a** (80.1 mg, 0.4 mmol) and DCE (2 mL). The resulting mixture was stirred at 60 °C under argon for 12 h. From the resulting mixture, the formation of diethylamine was detected by HPLC-MS, and **3aa** was isolated in 51% yield.

Generic Display Report

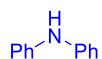
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Analysis Name	E:\S-Ota\ky\0418_RC7_01_23412.d	Operator	Demo User
Method	LC_NO UV_P50-1500_6MIN.m	Instrument	compact
Sample Name	0418		
Comment			



Bruker Compass DataAnalysis 4.4 printed: 2018/4/19 18:22:59 by: 111111 Page 1 of 1



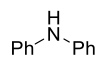
4.2. To a reaction tube equipped with a stir bar were charged with (*E*)-3-(diphenylamino)-1-phenylprop-2-en-1-one (**1x**, 59.8 mg, 0.2 mmol), [RhCp*Cl₂]₂ (5.0 mg, 0.008 mmol), AgNTf₂ (31.1 mg, 0.08 mmol), **2a** (80.1 mg, 0.4 mmol) and DCE (2 mL). The resulting mixture was stirred at 60 °C (oil bath) under air for 12 h. From the resulting mixture, diphenylamine was isolated in 30% yield, and **3aa** was isolated in 41% yield.



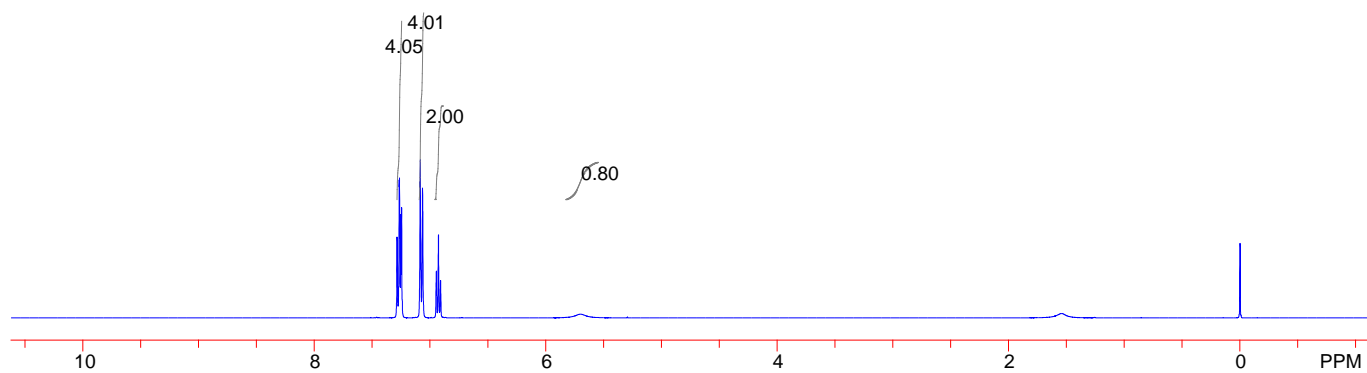
Diphenylamine

Eluent: petroleum ether/ethyl acetate (20:1). White solid (10.2 mg, 30%), ¹H NMR (400 MHz, CDCl₃): δ 7.28-7.24 (m, 4H), 7.09-7.06 (m, 4H), 6.94-6.91 (m, 2H), 5.70 (s, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 143.1, 129.4, 121.0, 117.8. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₂H₁₂N 170.0964; Found 170.0966.

7.284
7.279
7.265
7.263
7.253
7.249
7.244
7.239
7.085
7.082
7.063
6.944
6.926
6.908
5.698



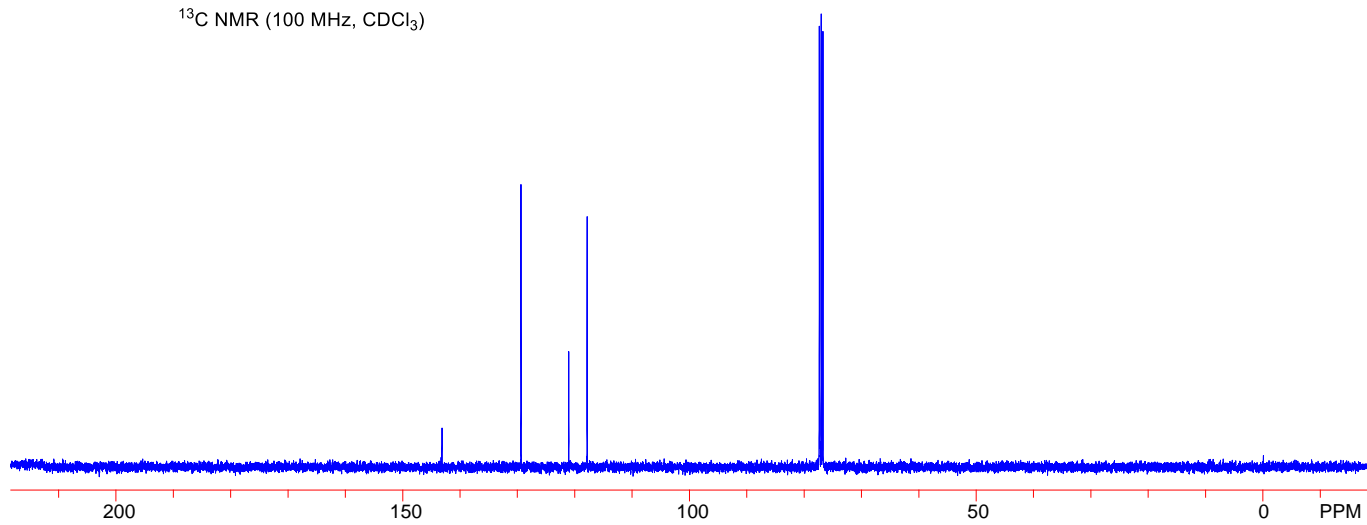
¹H NMR (400 MHz, CDCl₃)



143.141
129.367
121.039
117.847
77.349
77.031
76.713



¹³C NMR (100 MHz, CDCl₃)



V. X-Ray crystal structure and data for 3aa

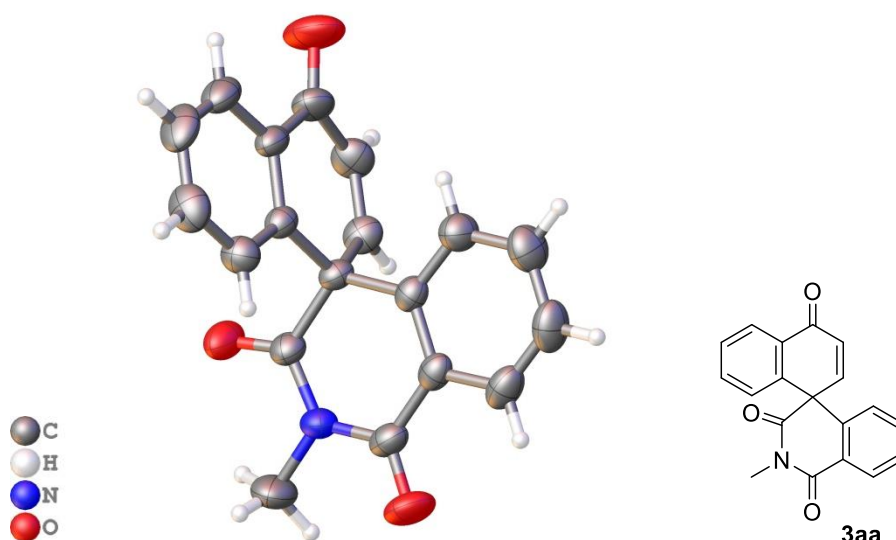


Fig. S1. X-ray crystal structure of **3aa** with 50% ellipsoid probability

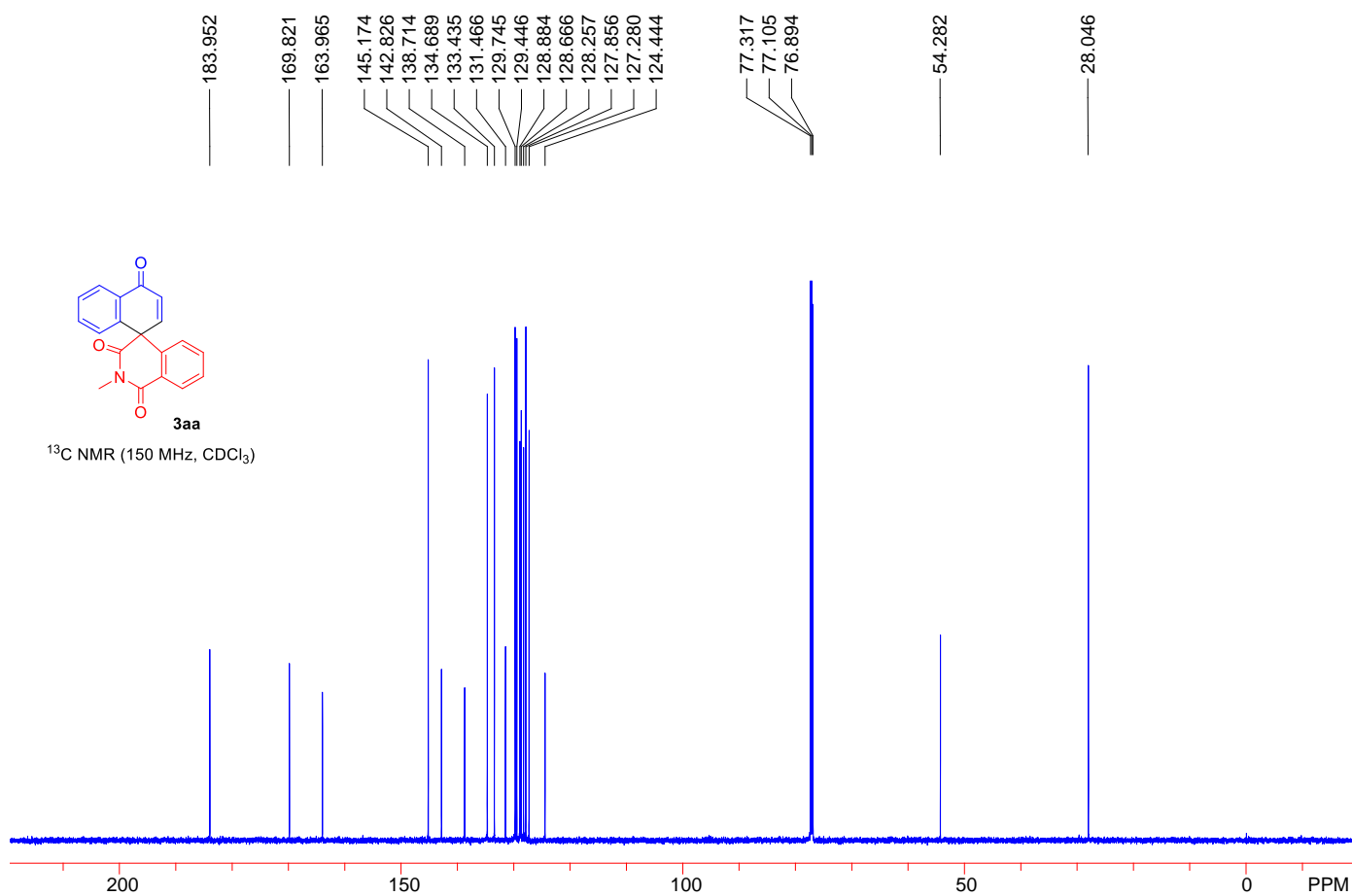
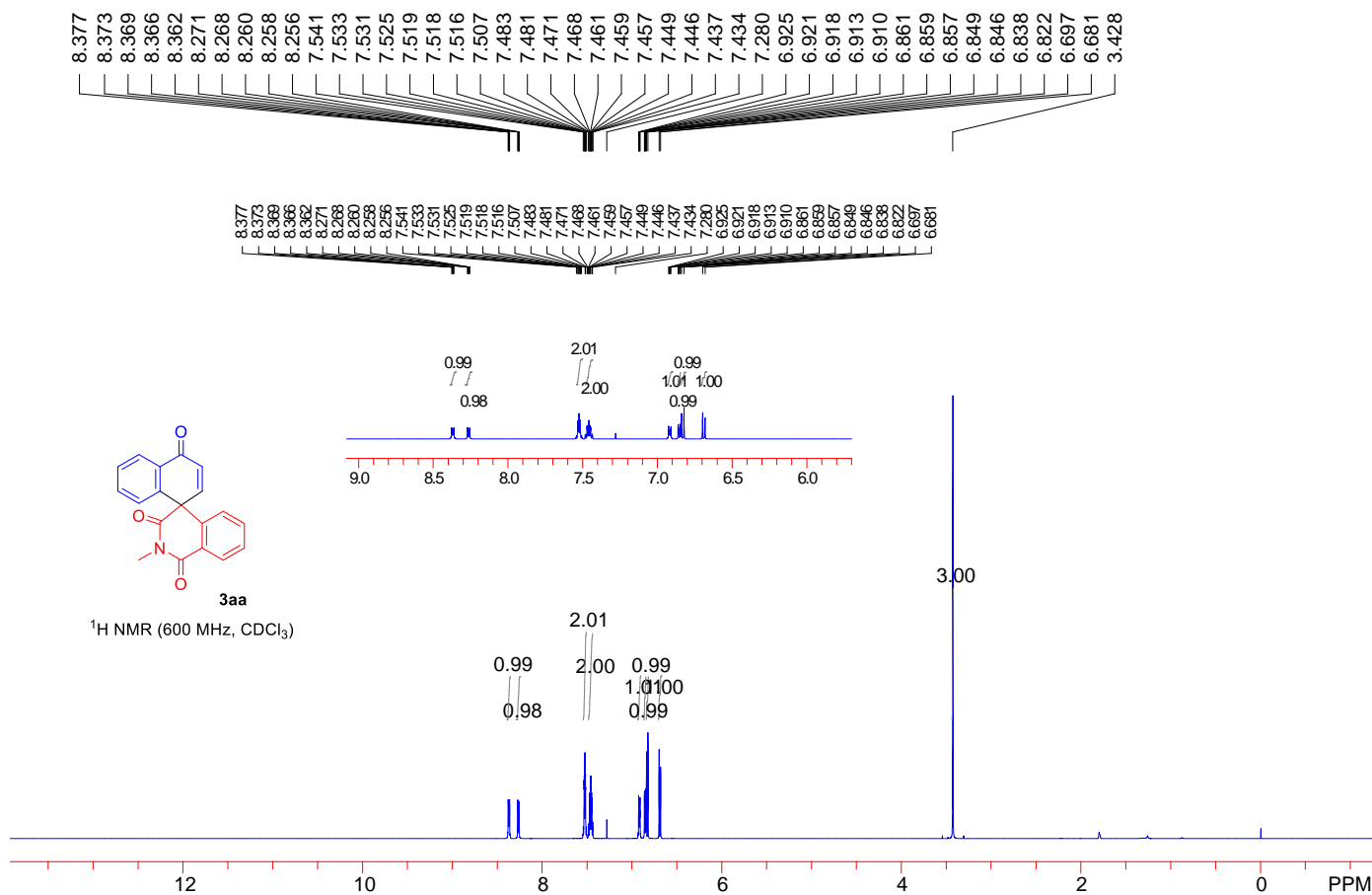
X-Ray structure determination. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent from a petroleum ether/dichloromethane (3:1) solution of **3aa**. Crystal data collection and refinement parameters of **3aa** are summarized in Table S1. Intensity data were collected at 293 K on a SuperNova Dual diffractometer using mirror-monochromated Cu K α radiation, $\lambda = 1.54184$ 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.

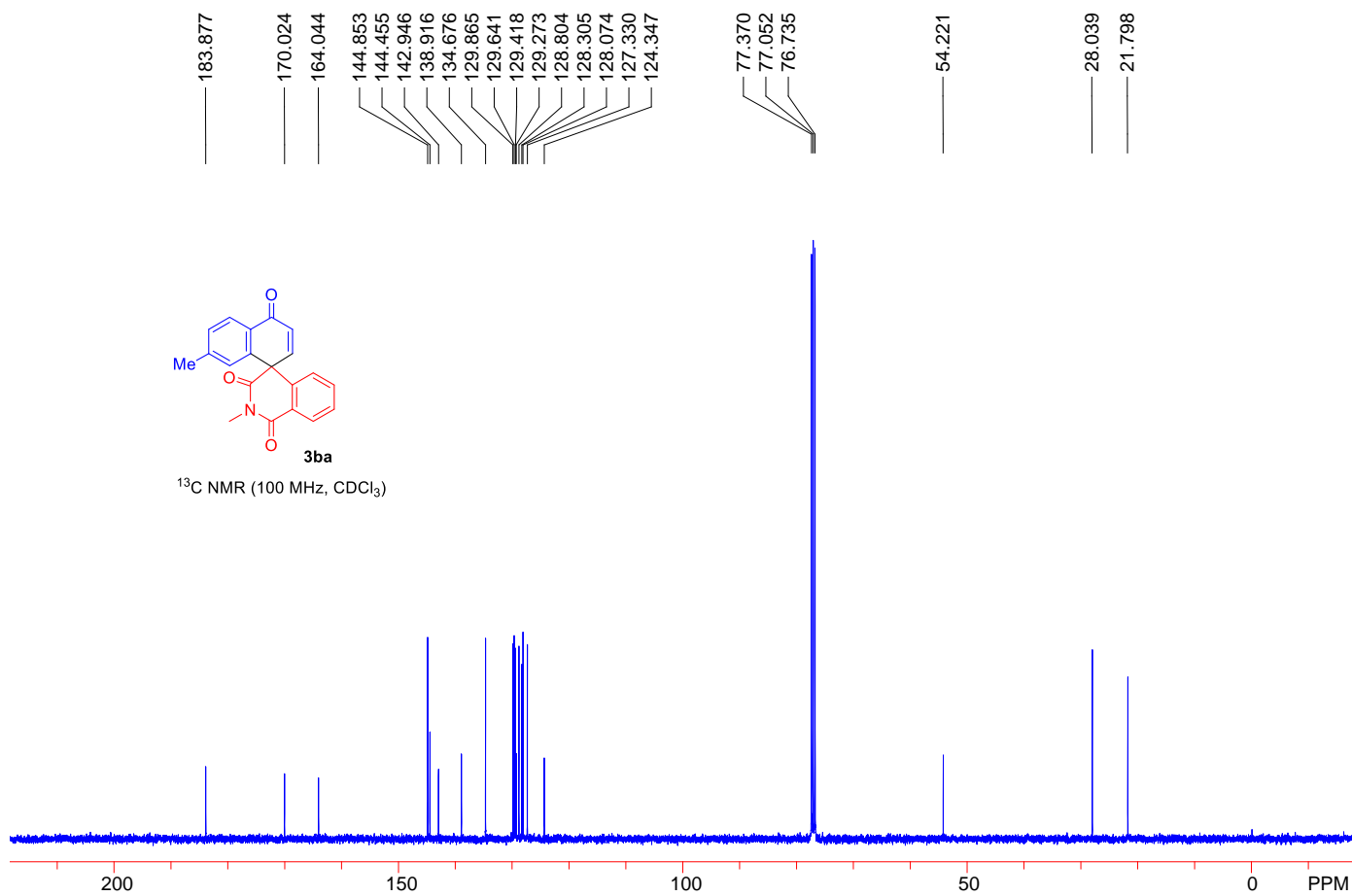
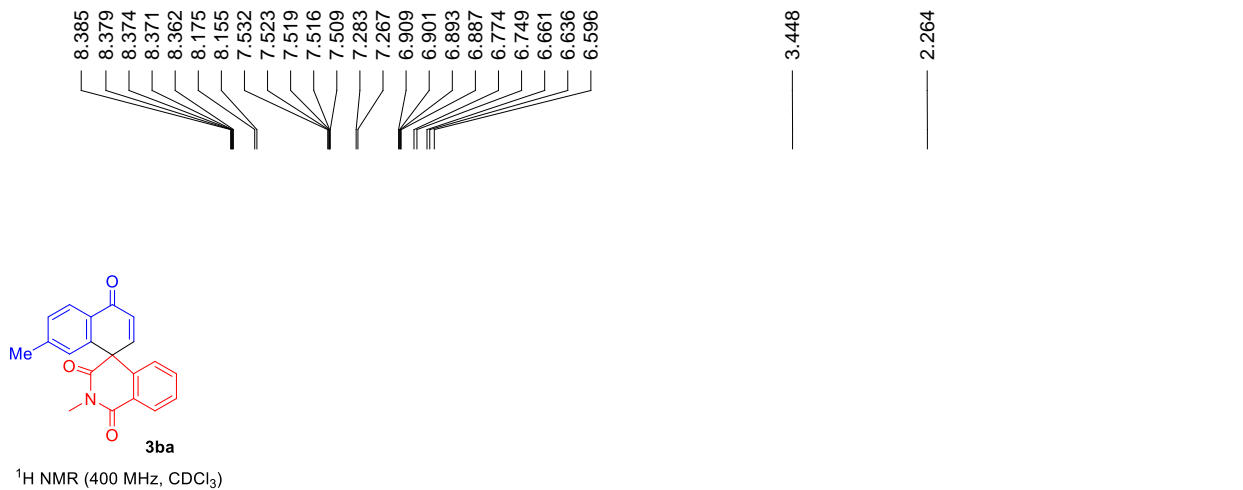
Table S1. Crystallographic data and structure refinement results of **3aa**

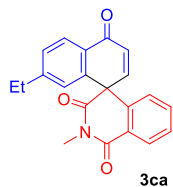
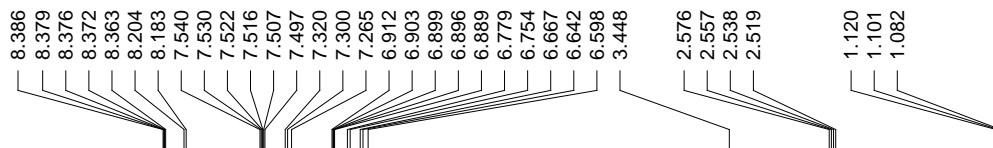
Empirical formula	C ₁₉ H ₁₃ NO ₃
Formula weight	303.30
Temperature/K	293(2)
Crystal system	monoclinic
Space group	Ia
a/Å	8.4176(2)
b/Å	11.4940(3)

c/Å	15.1975(4)
α /°	90
β /°	94.974(2)
γ /°	90
Volume/Å ³	1464.85(6)
Z	4
ρ_{calc} /cm ³	1.375
μ /mm ⁻¹	0.765
F(000)	632.0
Crystal size/mm ³	0.2 × 0.18 × 0.1
Radiation	Cu K α (λ = 1.54184)
2 Θ range for data collection/°	9.662 to 143.04
Index ranges	-10 ≤ h ≤ 9, -14 ≤ k ≤ 11, -17 ≤ l ≤ 18
Reflections collected	6526
Independent reflections	2600 [R_{int} = 0.0236, R_{sigma} = 0.0255]
Data/restraints/parameters	2600/2/209
Goodness-of-fit on F ²	1.093
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0323, wR_2 = 0.0831
Final R indexes [all data]	R_1 = 0.0339, wR_2 = 0.0846
Largest diff. peak/hole / e Å ⁻³	0.13/-0.12
Flack parameter	0.06(17)

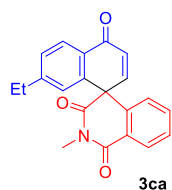
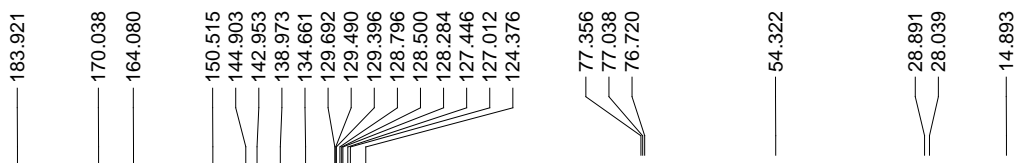
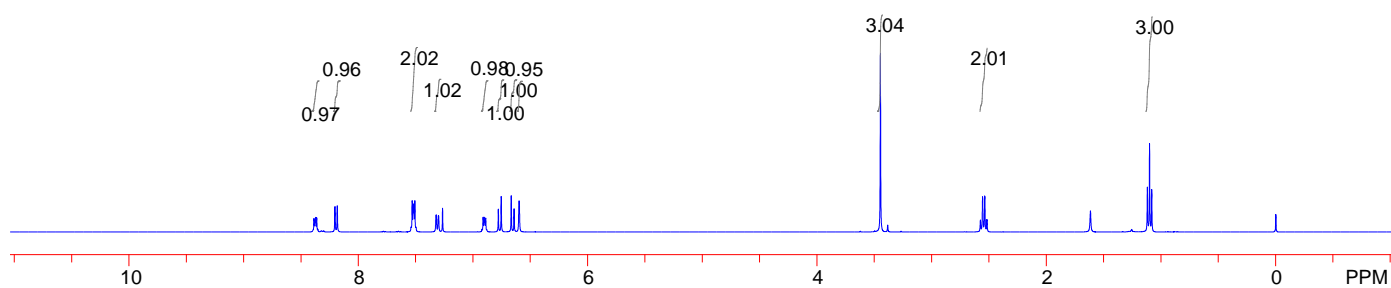
VI. Copies of NMR spectra of 3aa-3ap



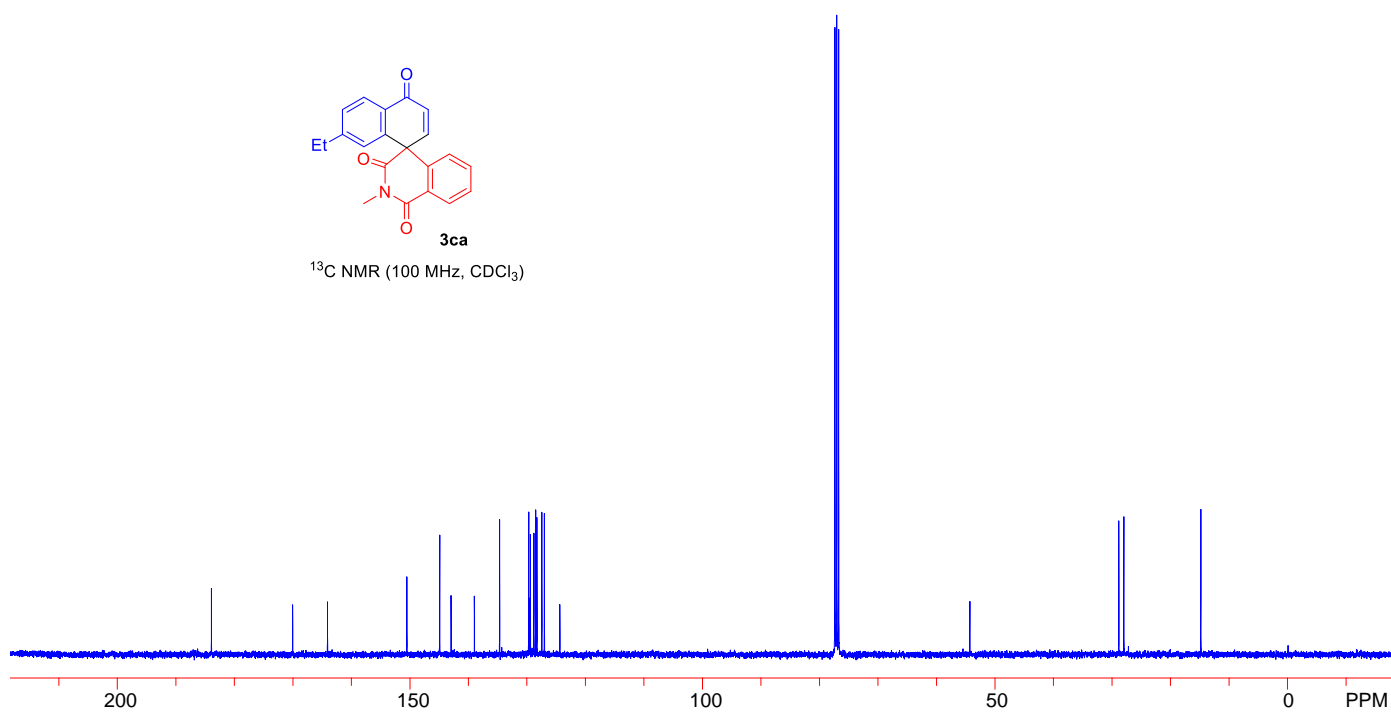


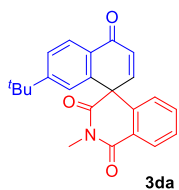
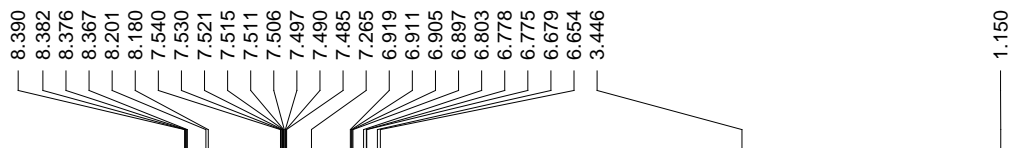


¹H NMR (400 MHz, CDCl₃)

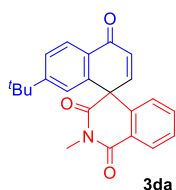
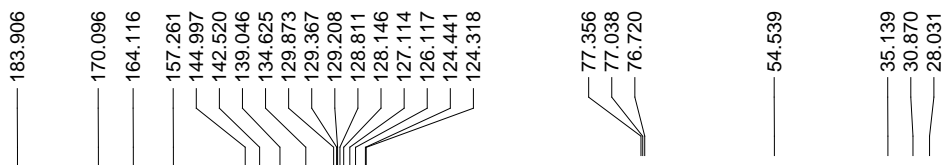
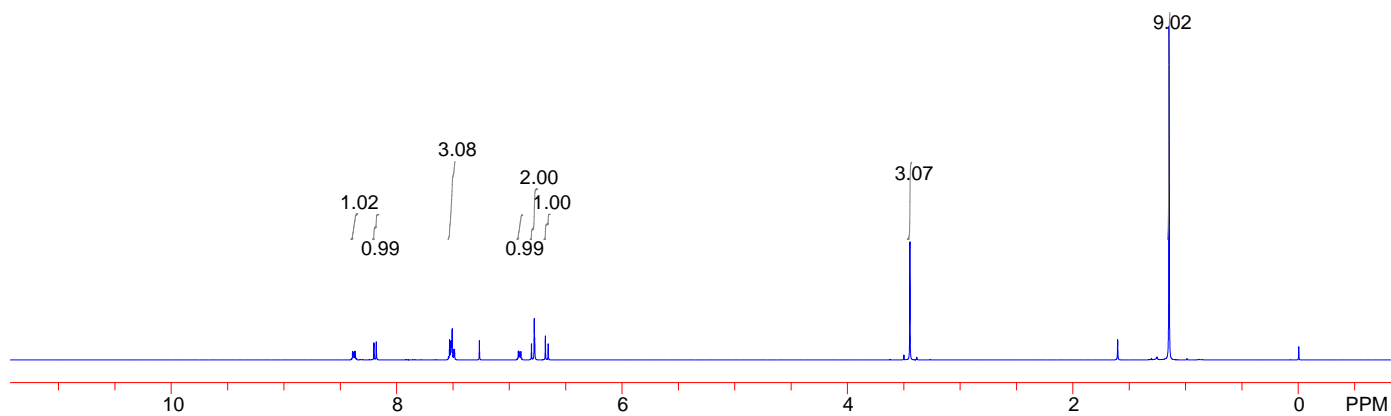


¹³C NMR (100 MHz, CDCl₃)

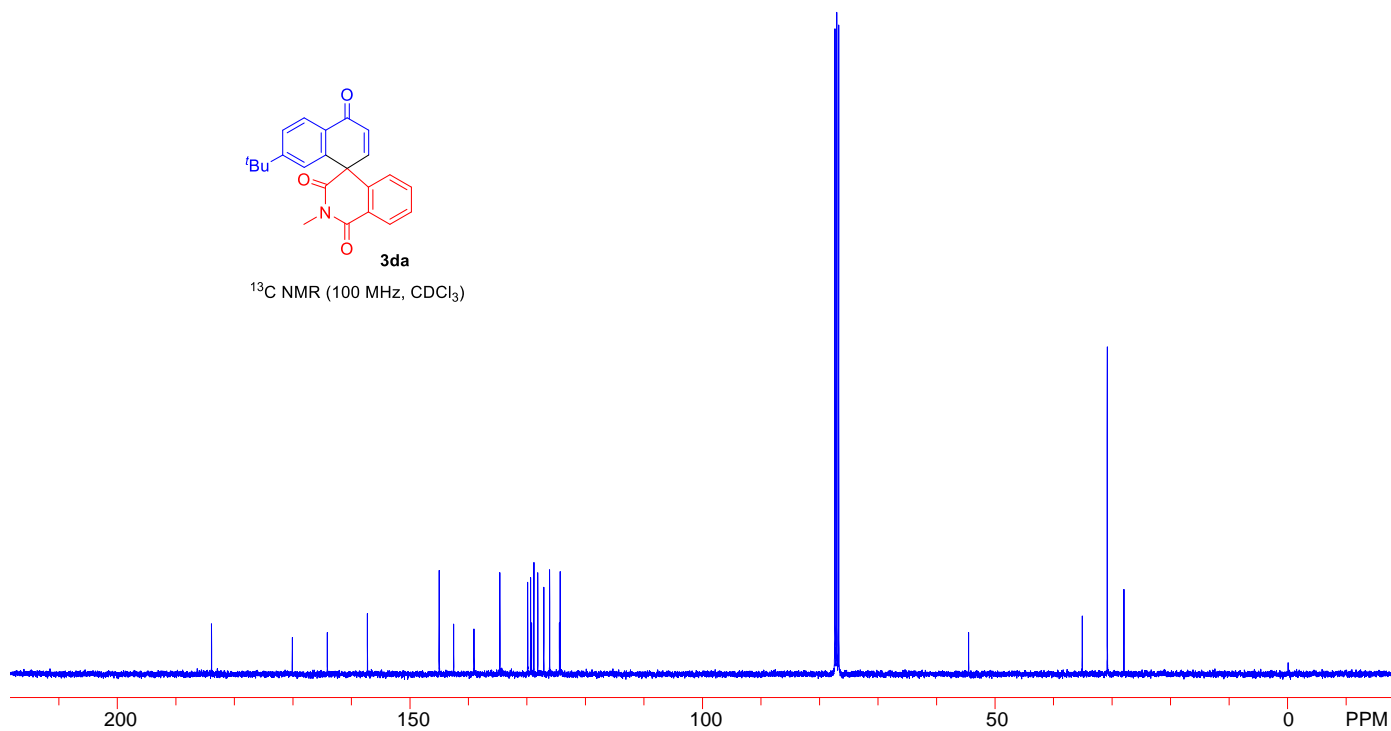


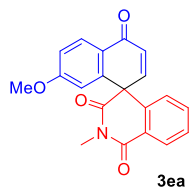
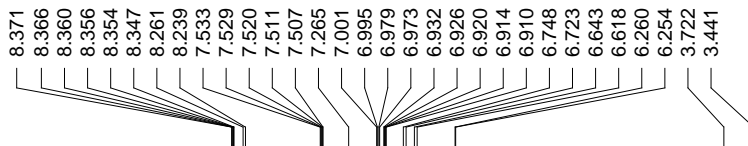


¹H NMR (400 MHz, CDCl₃)

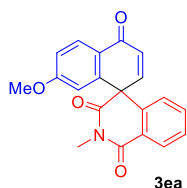
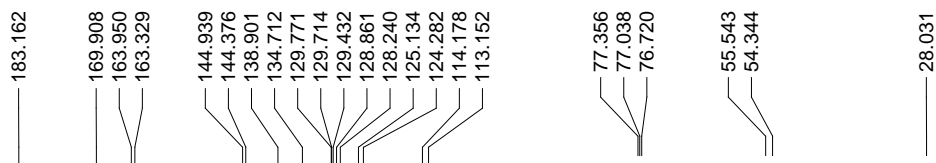
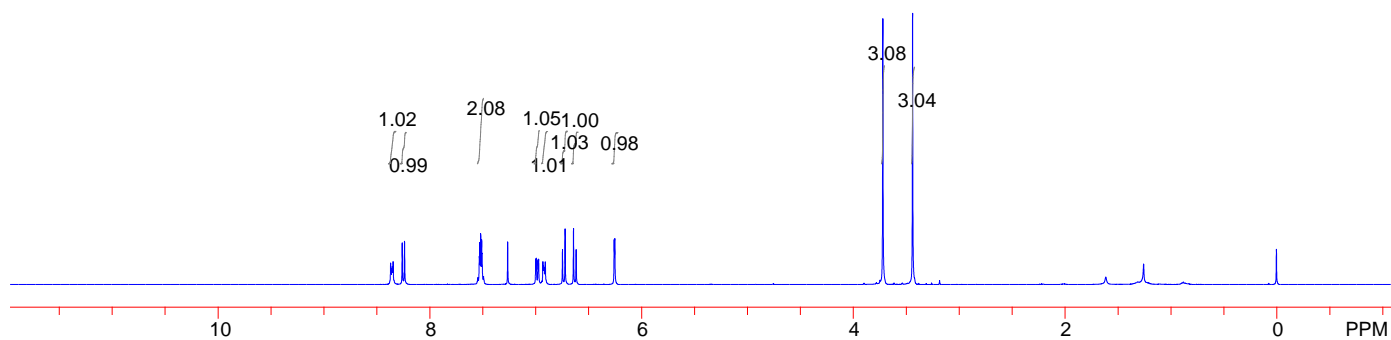


¹³C NMR (100 MHz, CDCl₃)

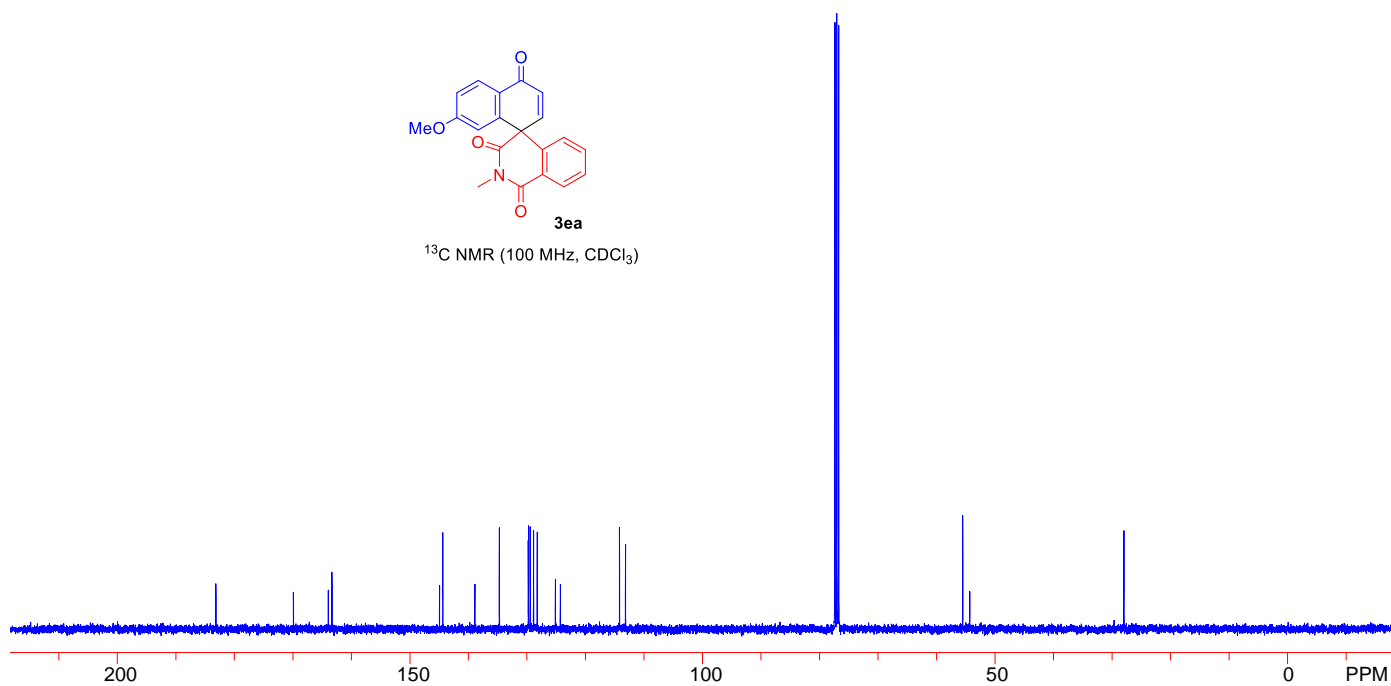


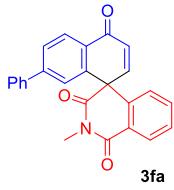
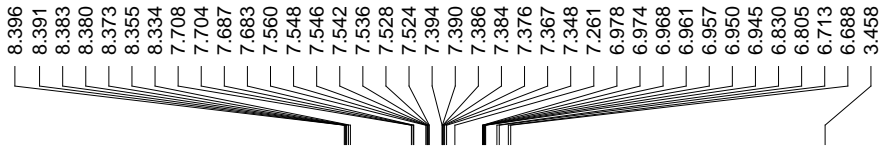


¹H NMR (400 MHz, CDCl₃)

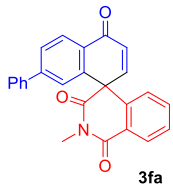
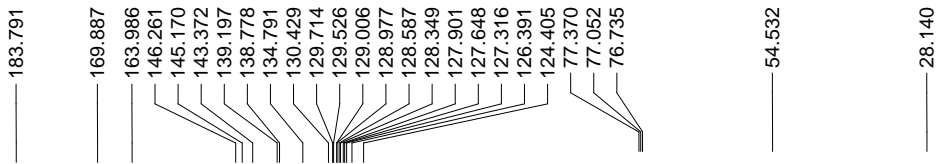
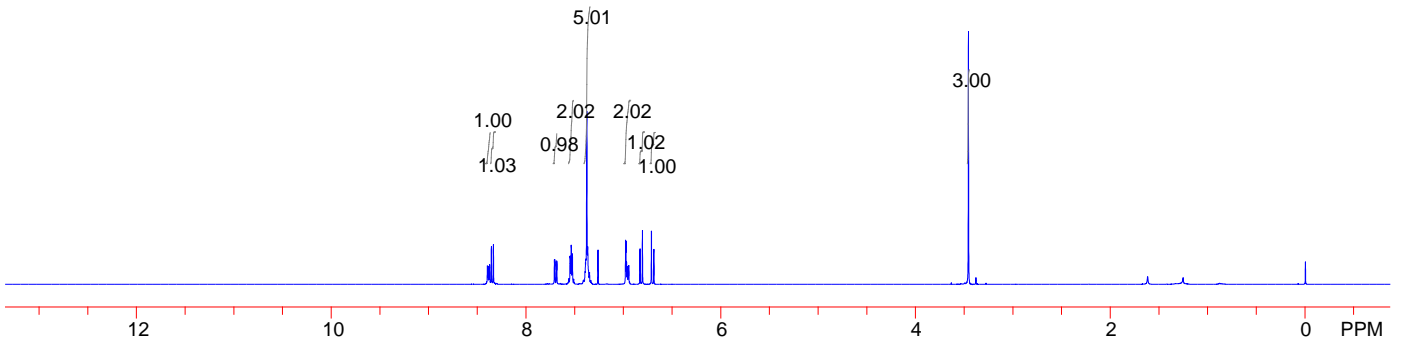


¹³C NMR (100 MHz, CDCl₃)

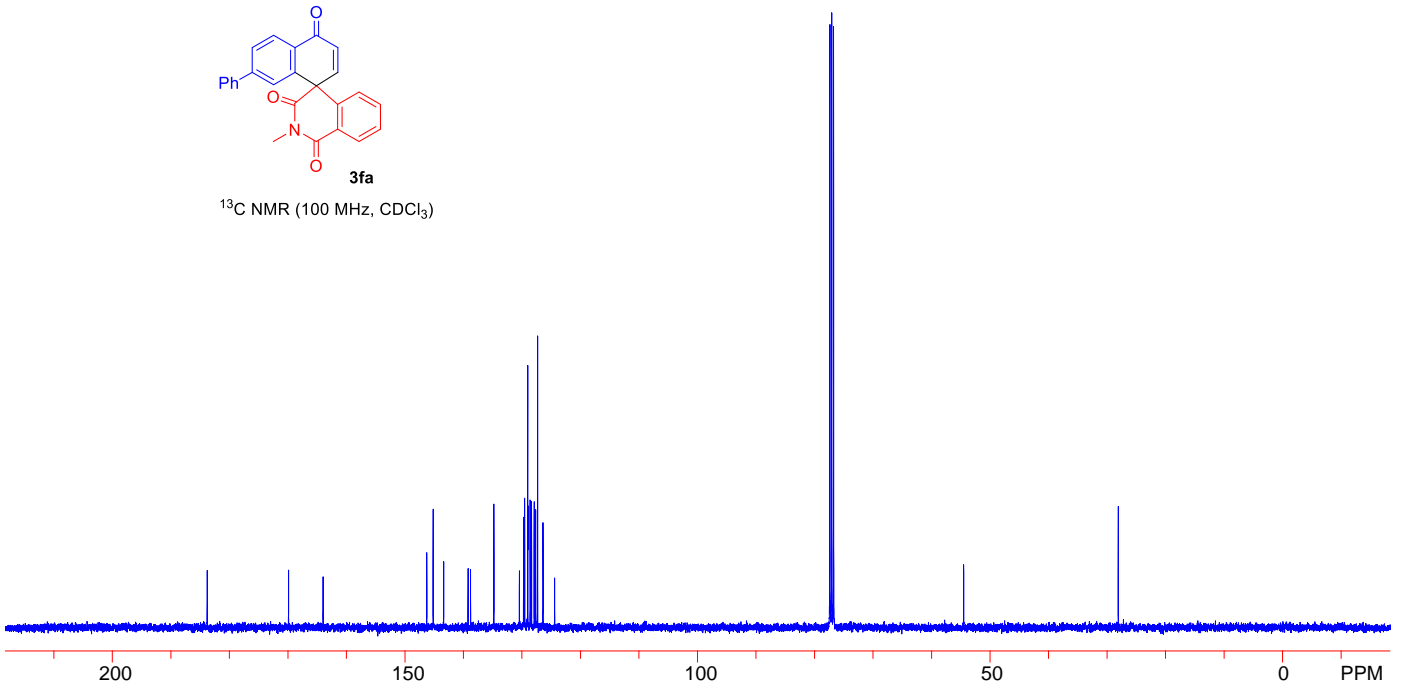




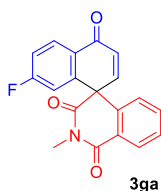
¹H NMR (400 MHz, CDCl₃)



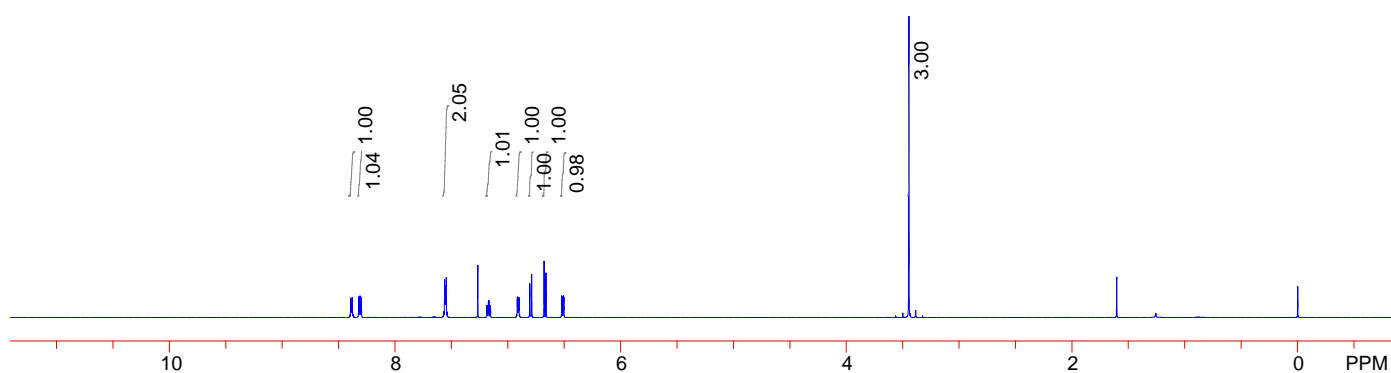
¹³C NMR (100 MHz, CDCl₃)



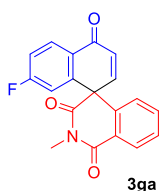
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8.389
8.384
8.382
8.377
8.322
8.313
8.308
8.298
7.560
7.556
7.554
7.552
7.548
7.545
7.266
7.185
7.181
7.171
7.167
7.157
7.153
6.916
6.911
6.909
6.904
6.901
6.805
6.788
6.678
6.661
6.521
6.517
6.506
6.502
3.444



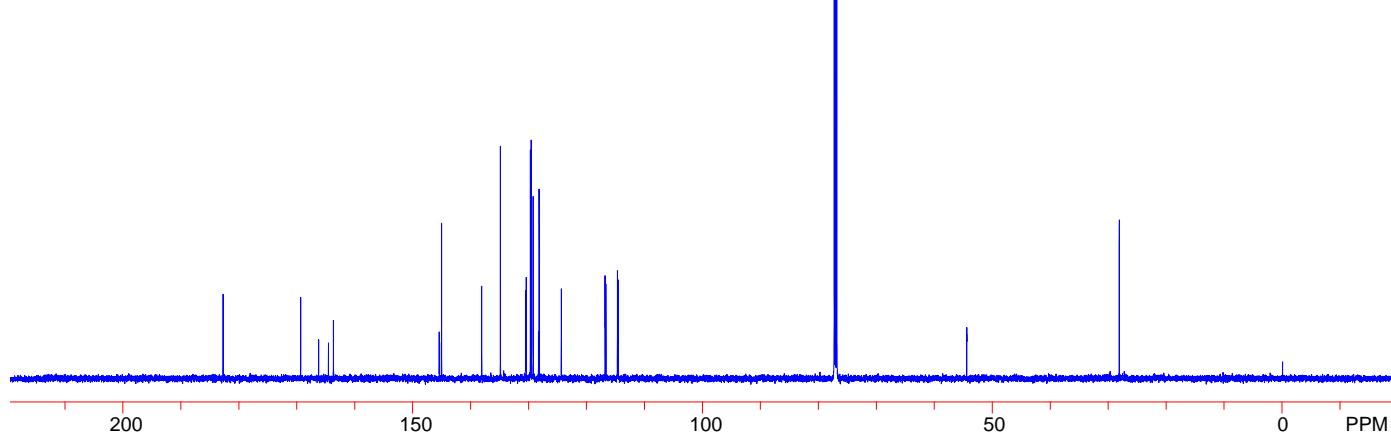
¹H NMR (600 MHz, CDCl₃)



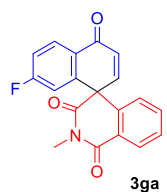
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169.325
166.233
164.534
163.674
145.415
145.357
145.007
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134.856
130.452
130.387
129.679
129.541
129.205
128.294
128.272
128.170
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116.656
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114.512
77.251
77.040
76.828
54.435
54.421
28.134



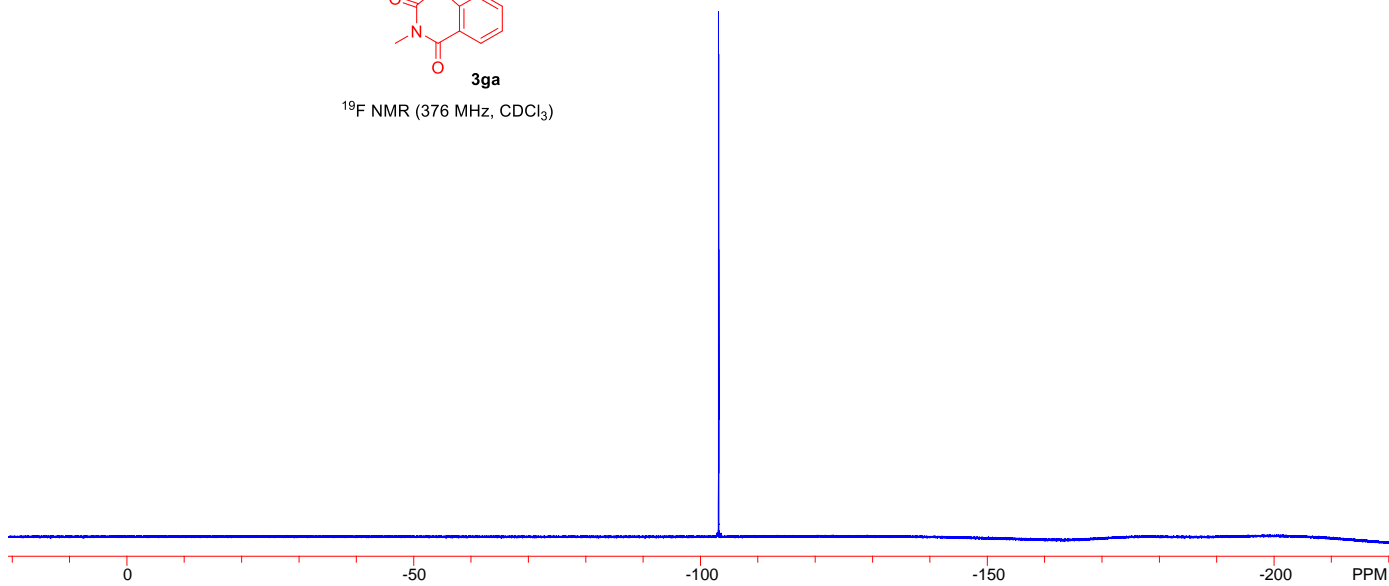
¹³C NMR (150 MHz, CDCl₃)

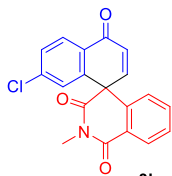
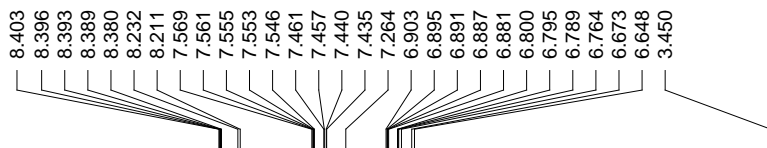


103.068
103.090
103.109
103.131

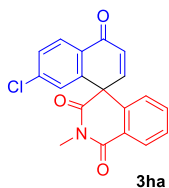
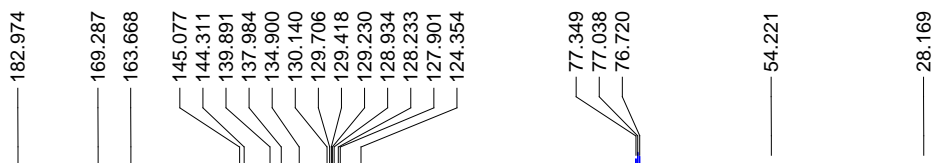
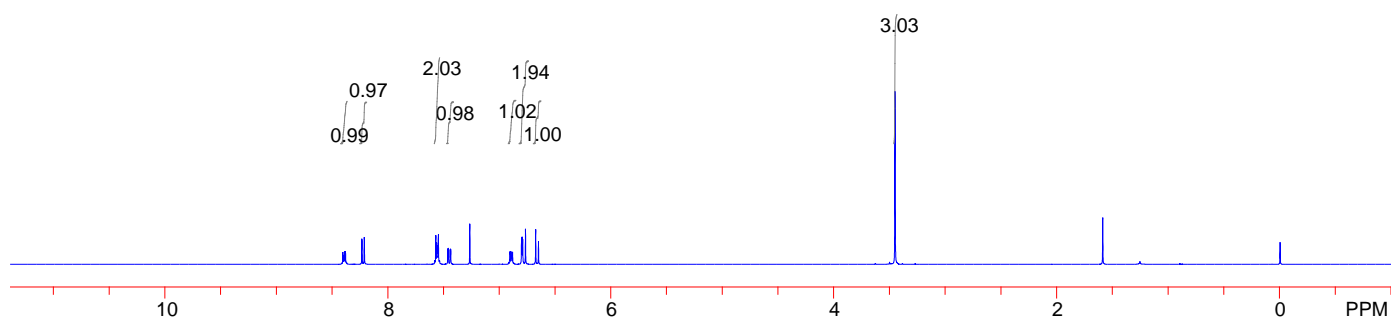


¹⁹F NMR (376 MHz, CDCl₃)

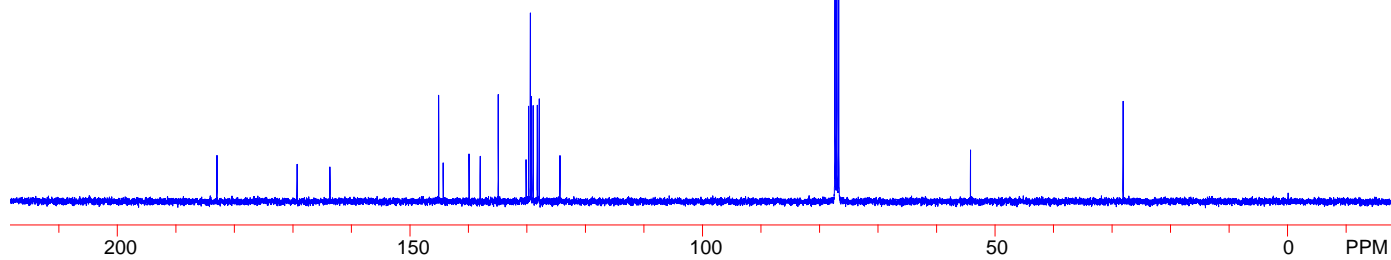




¹H NMR (400 MHz, CDCl₃)

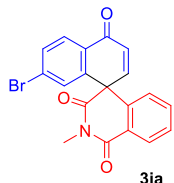


¹³C NMR (100 MHz, CDCl₃)

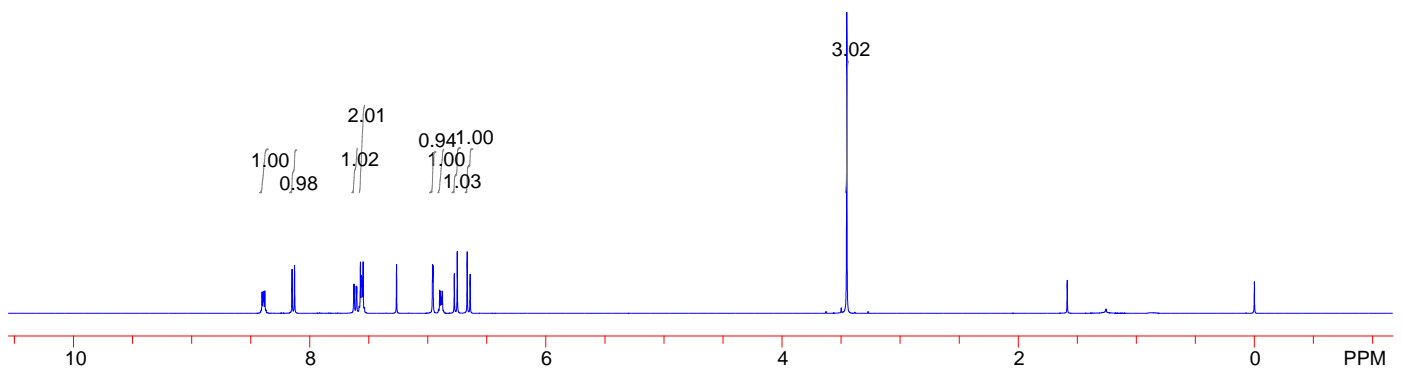


8.403
8.389
8.380
8.149
8.128
7.627
7.623
7.606
7.602
7.571
7.562
7.557
7.554
7.547
7.264
6.960
6.955
6.899
6.890
6.876
6.775
6.750
6.666
6.641

3.451



¹H NMR (400 MHz, CDCl₃)



183.126

169.280

163.654

145.105

144.390

137.962

134.907

132.343

130.877

130.552

129.706

129.324

129.230

128.941

128.565

128.255

124.354

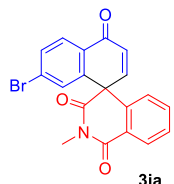
77.377

77.060

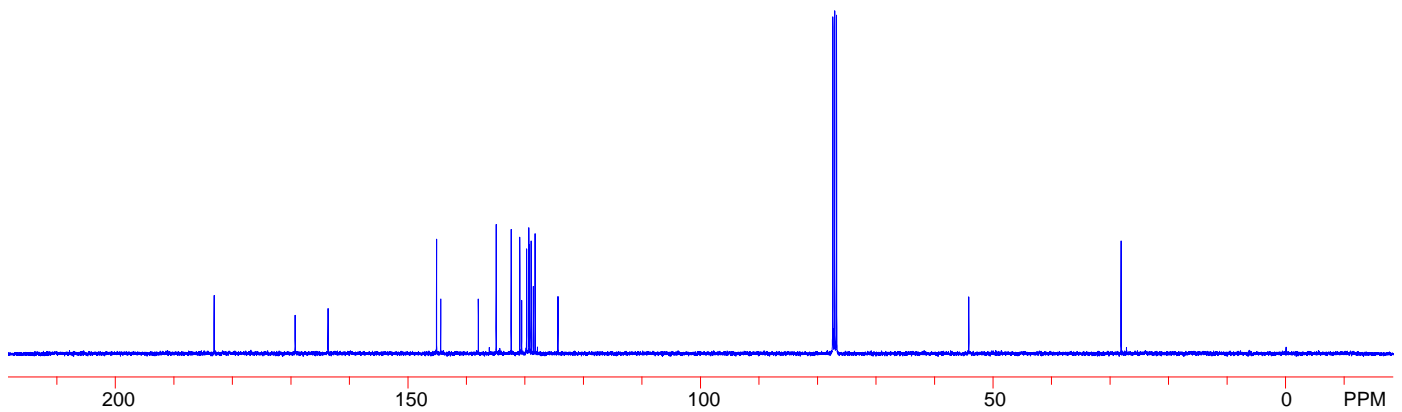
76.742

54.171

28.176

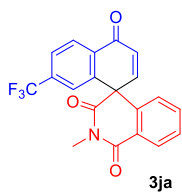


¹³C NMR (100 MHz, CDCl₃)

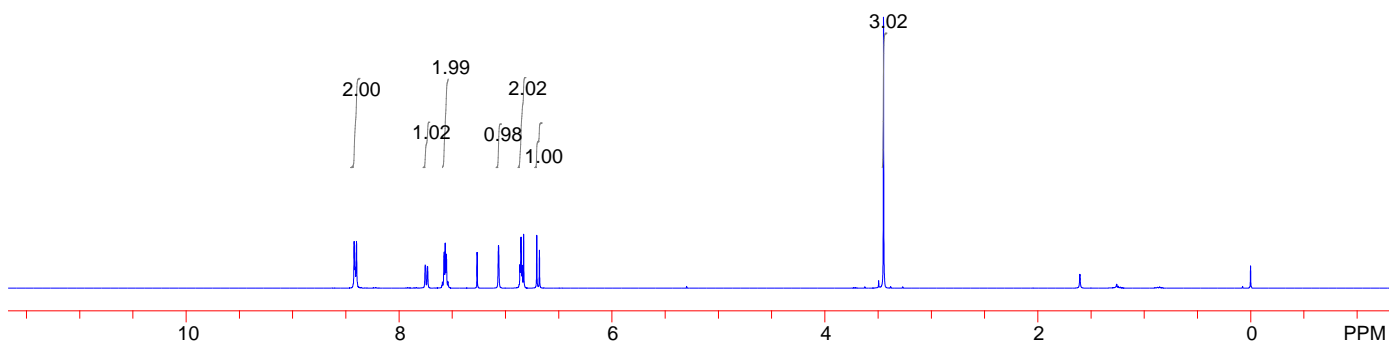


8.421
8.416
8.411
8.399
7.753
7.732
7.576
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7.266
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6.864
6.860
6.855
6.842
6.829
6.707
6.682

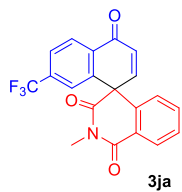
3.450



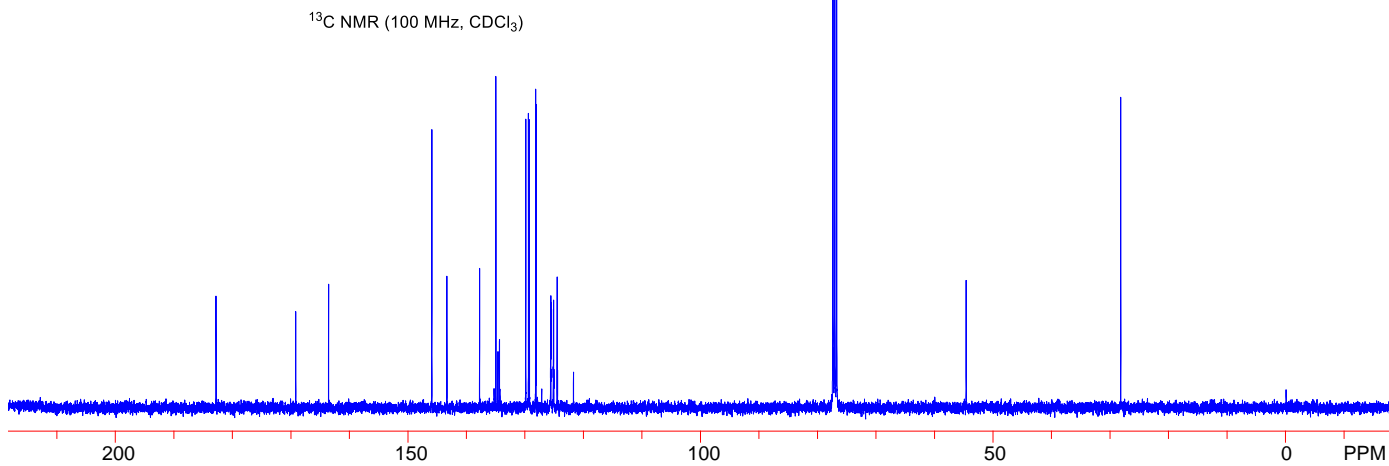
¹H NMR (400 MHz, CDCl₃)

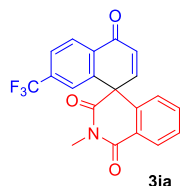


182.801
169.179
163.560
145.900
143.329
137.745
134.957
134.611
134.344
129.851
129.389
129.230
128.154
128.081
125.626
125.597
125.561
125.524
125.163
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125.048
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76.720
54.611
28.226

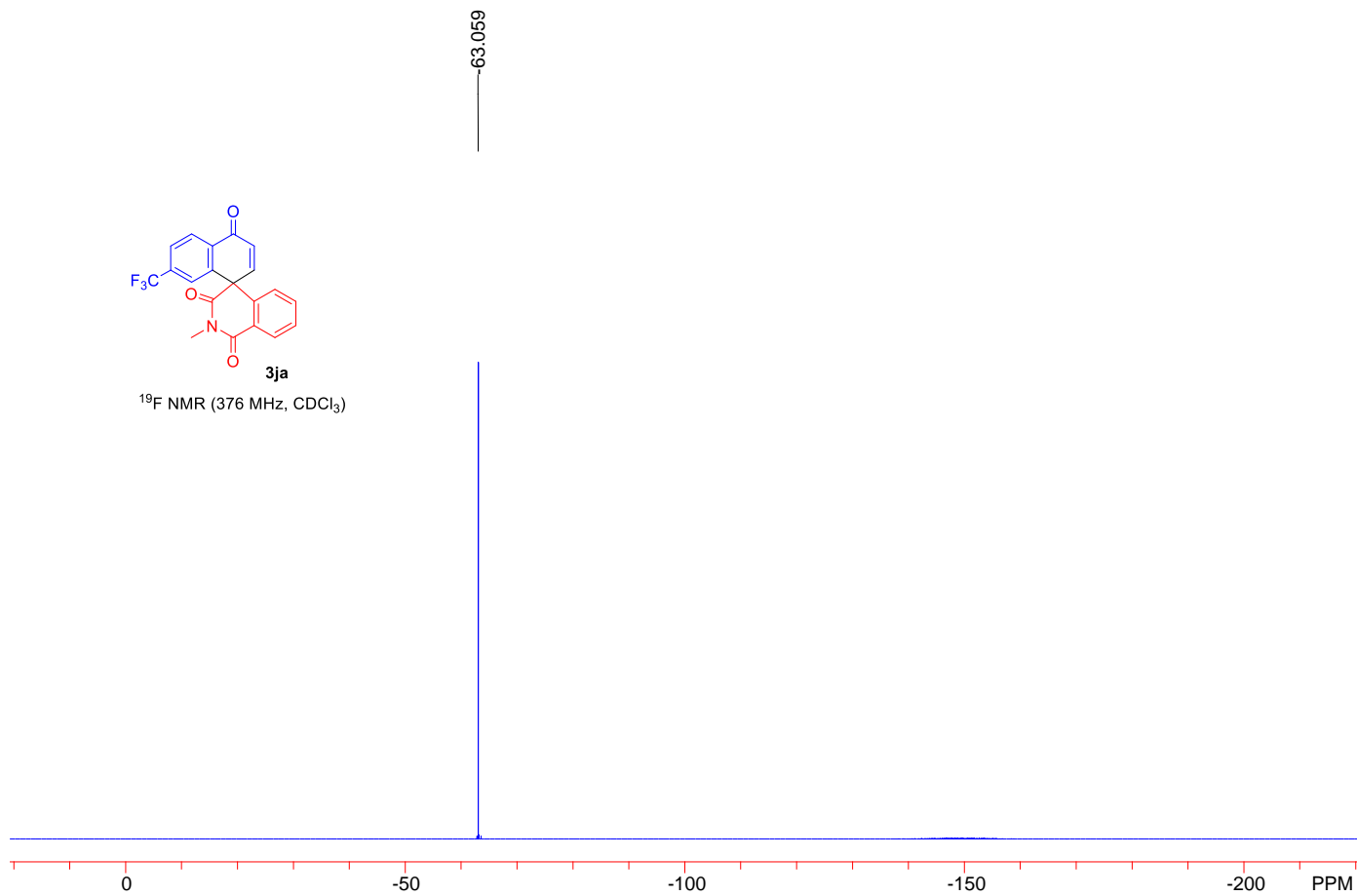


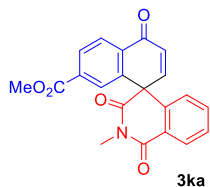
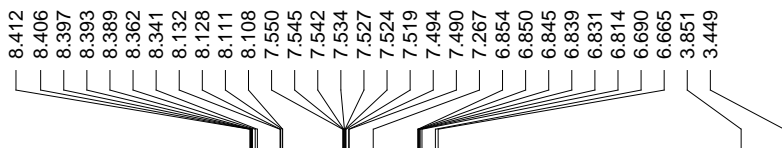
¹³C NMR (100 MHz, CDCl₃)



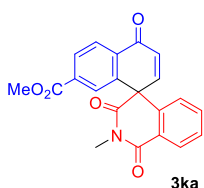
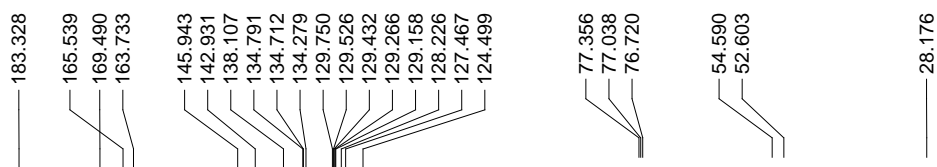
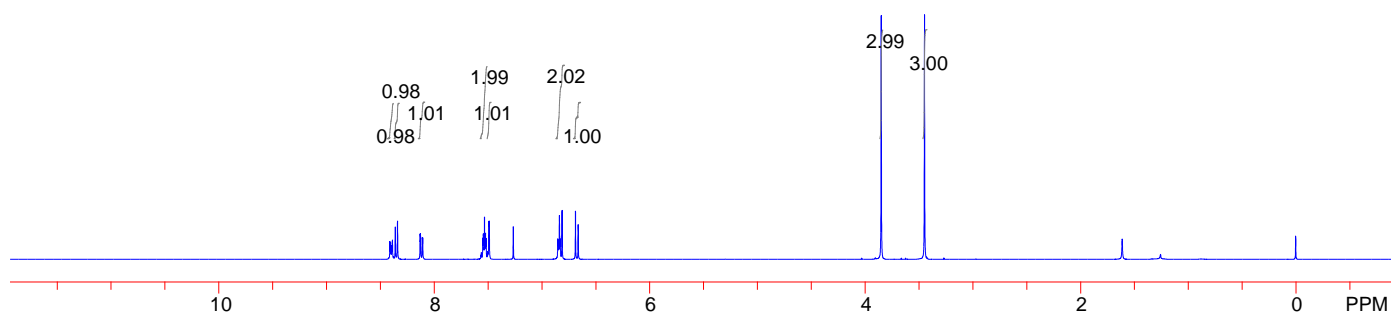


^{19}F NMR (376 MHz, CDCl_3)

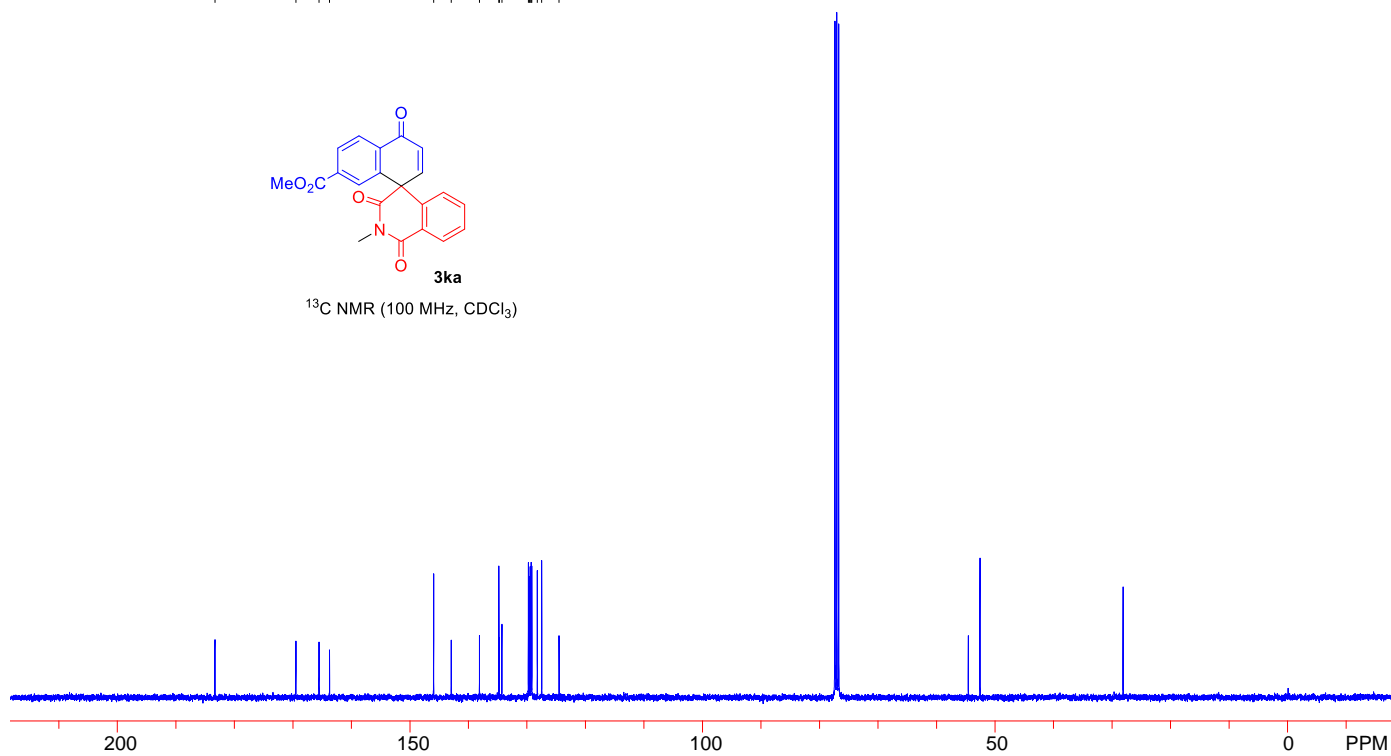




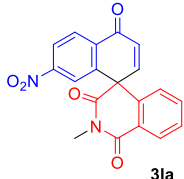
¹H NMR (400 MHz, CDCl₃)



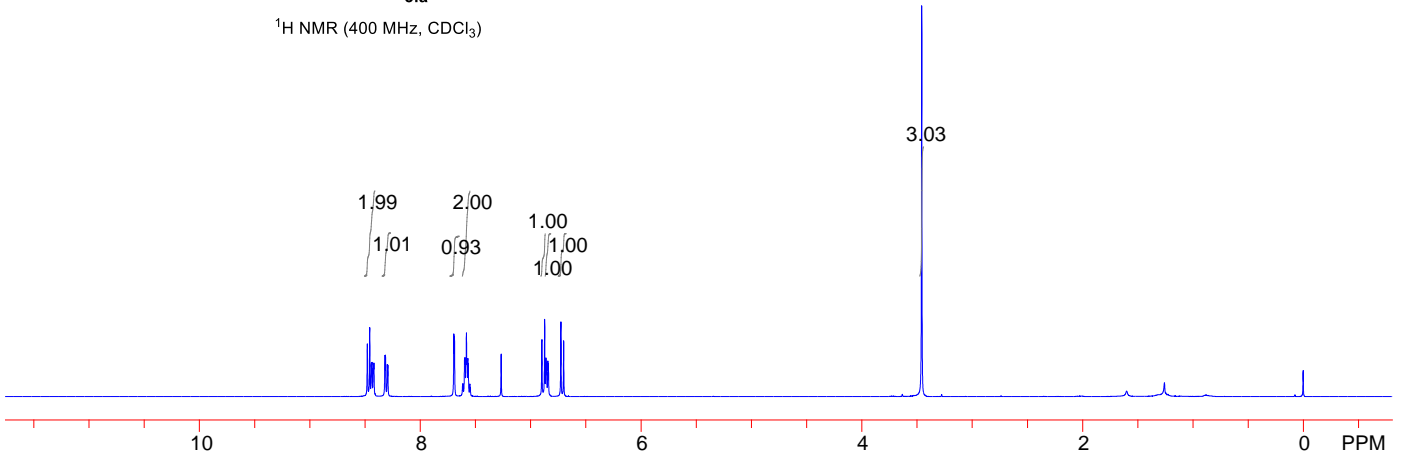
¹³C NMR (100 MHz, CDCl₃)



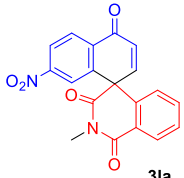
8.480
8.458
8.443
8.438
8.427
8.424
8.420
8.320
8.315
8.299
8.294
7.696
7.691
7.617
7.614
7.599
7.595
7.587
7.582
7.577
7.569
7.565
7.551
7.546
7.267
6.898
6.873
6.861
6.843
6.839
6.726
6.701
3.456



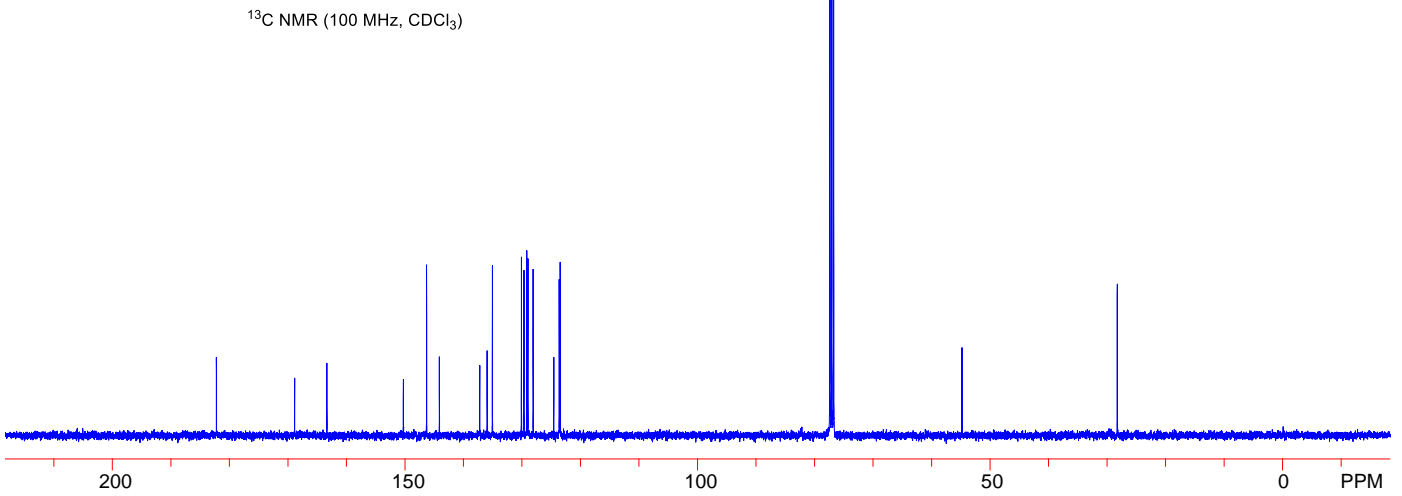
¹H NMR (400 MHz, CDCl₃)

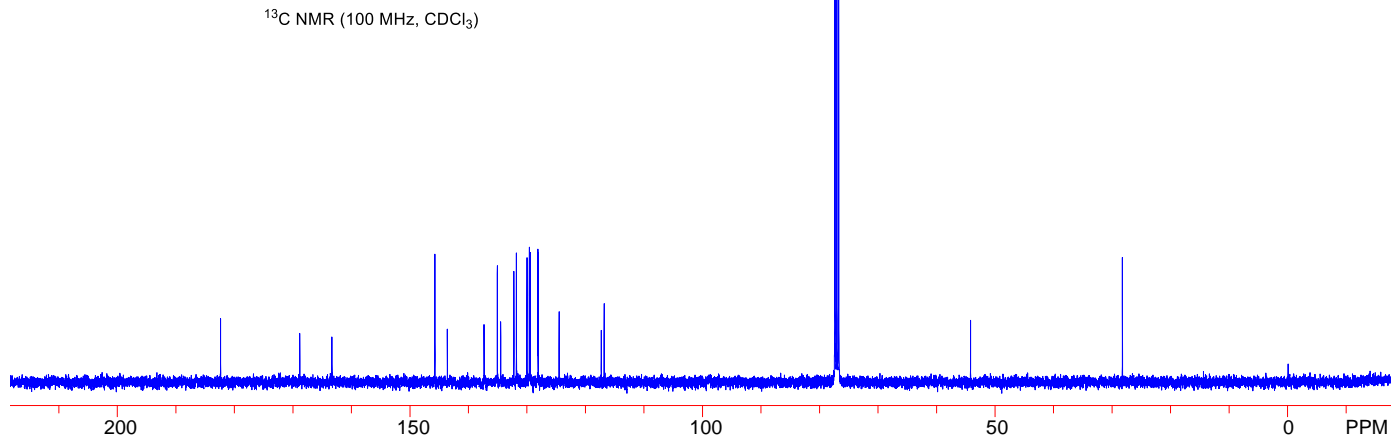
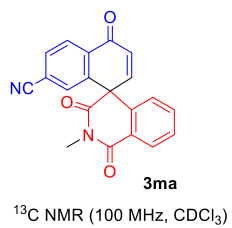
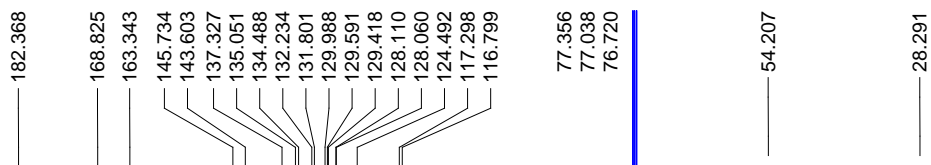
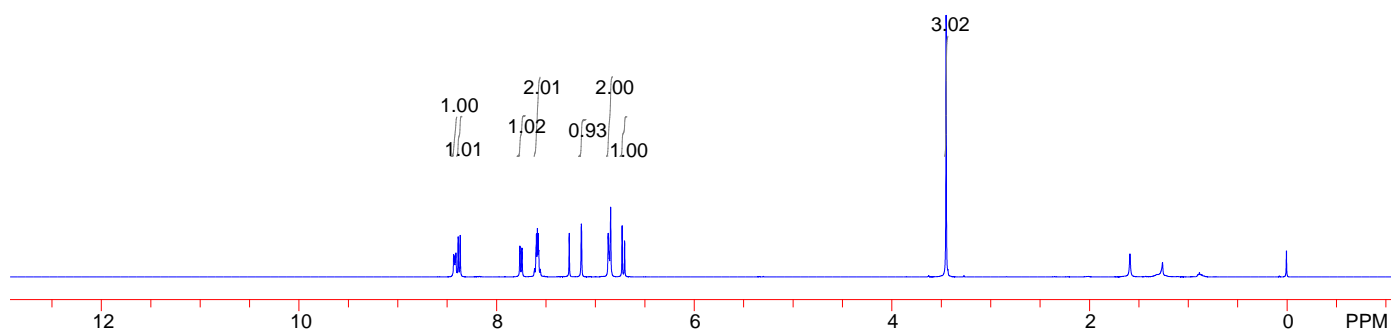
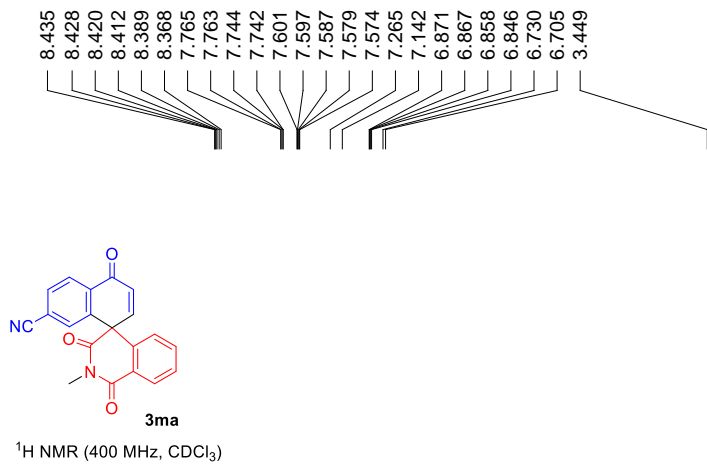


182.216
168.854
163.336
146.290
150.270
144.109
137.211
135.947
135.044
130.089
129.641
129.172
128.970
128.081
124.557
123.625
123.452
77.356
77.038
76.727
54.813
28.313



¹³C NMR (100 MHz, CDCl₃)

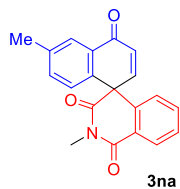




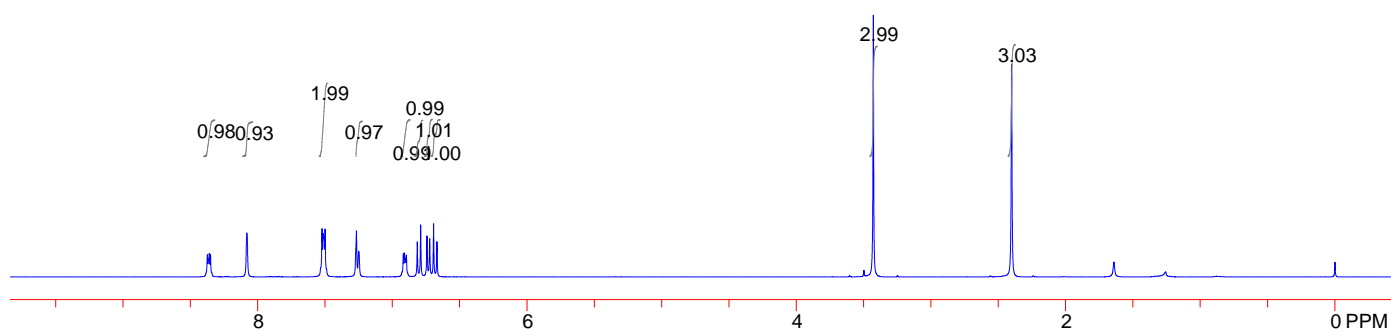
8.374
8.367
8.359
8.351
8.080
7.522
7.514
7.509
7.499
7.267
7.250
6.918
6.910
6.902
6.896
6.815
6.790
6.742
6.722
6.693
6.668

3.427

2.400



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



184.224

169.973

164.029

140.086

138.901

145.098

138.836

134.625

134.445

131.194

129.880

129.410

128.796

128.182

127.706

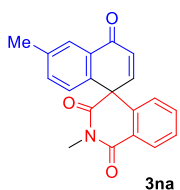
127.410

124.434

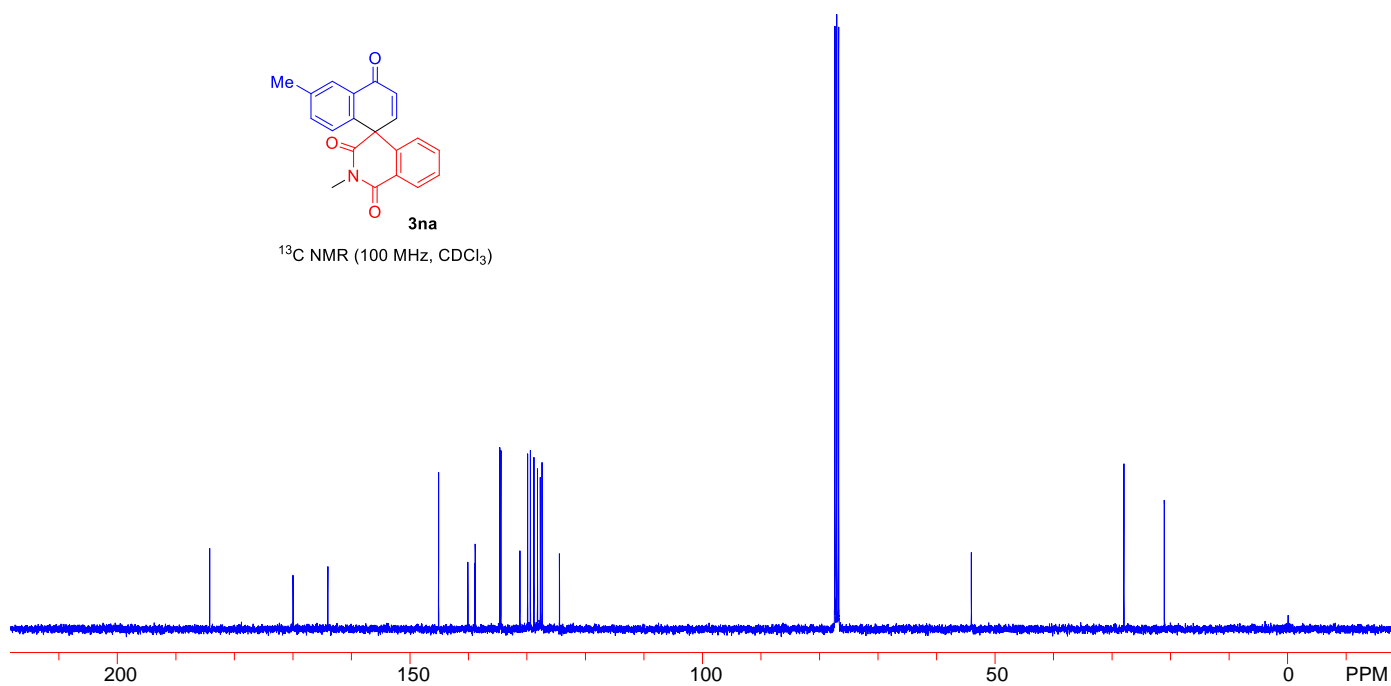
54.070

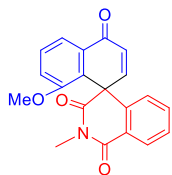
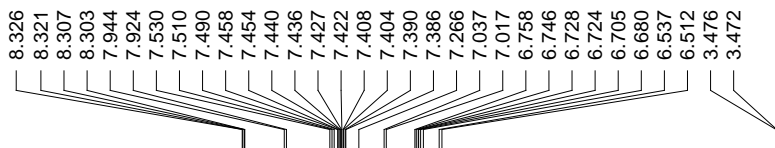
28.031

21.141

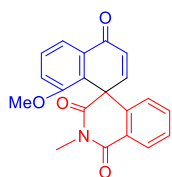
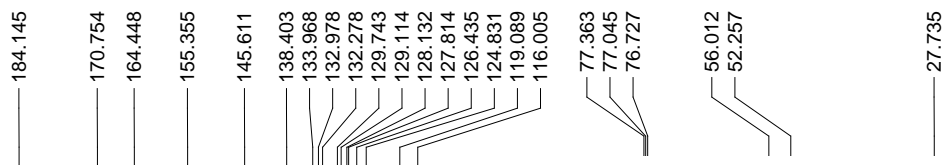
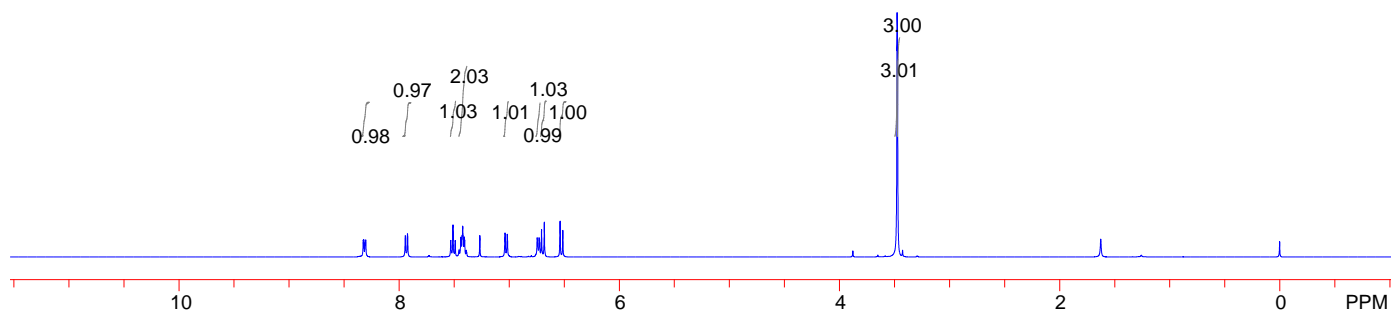


$^{13}\text{C NMR}$ (100 MHz, CDCl_3)

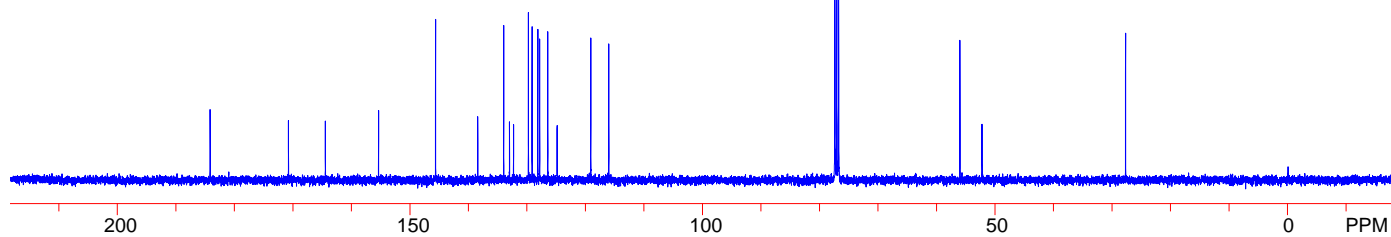


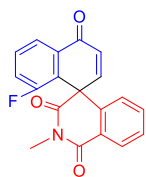
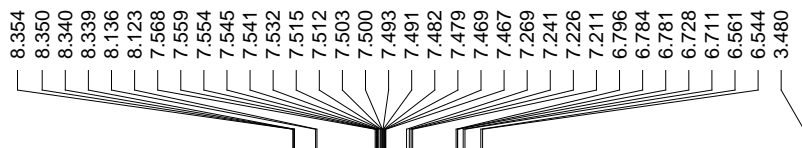


¹H NMR (400 MHz, CDCl₃)



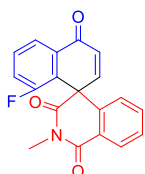
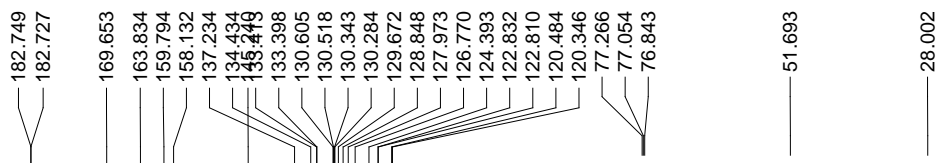
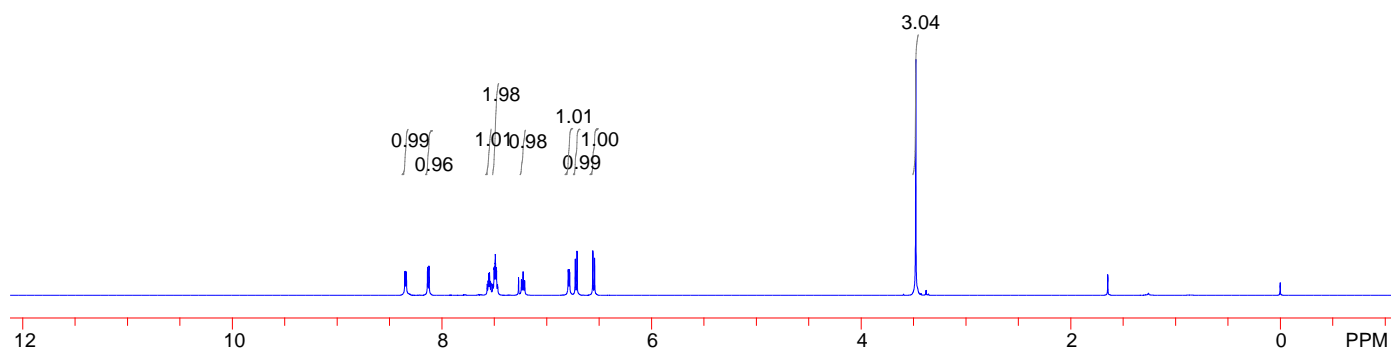
¹³C NMR (100 MHz, CDCl₃)





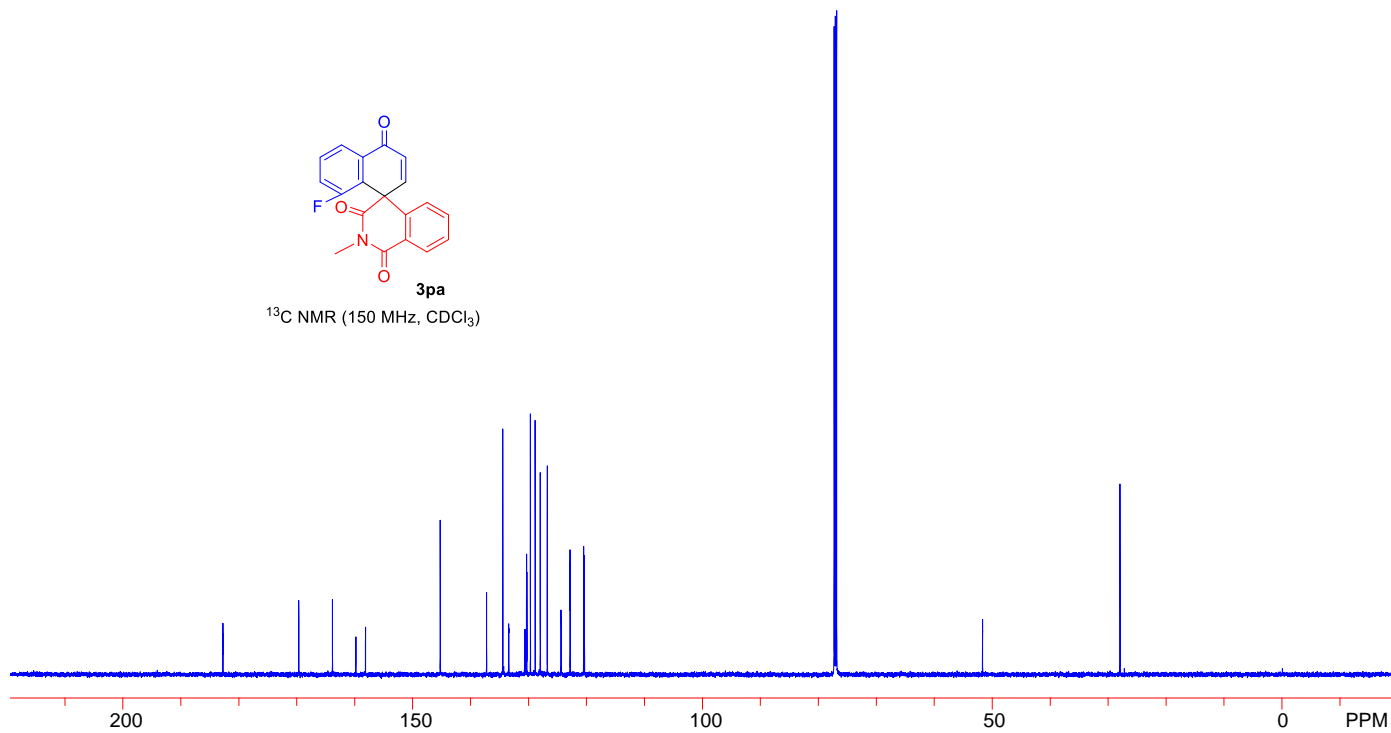
3pa

¹H NMR (600 MHz, CDCl₃)

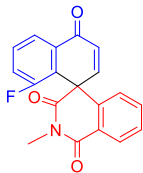


3pa

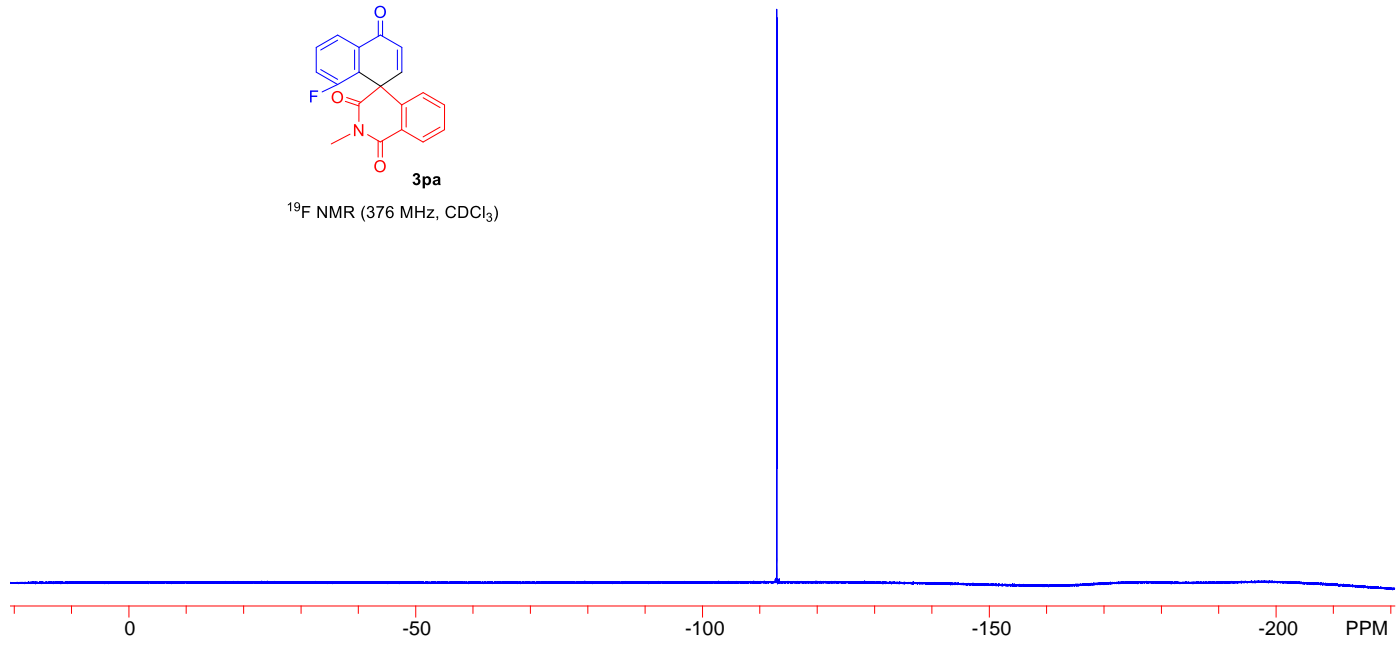
¹³C NMR (150 MHz, CDCl₃)

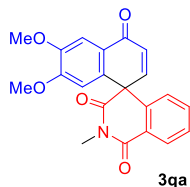
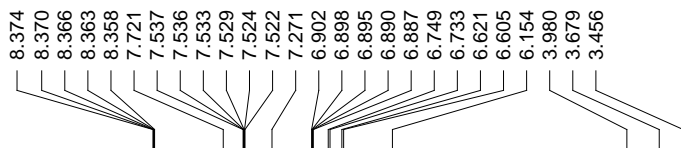


112.875
112.890
112.901
112.916

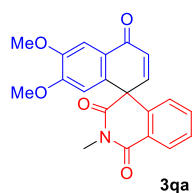
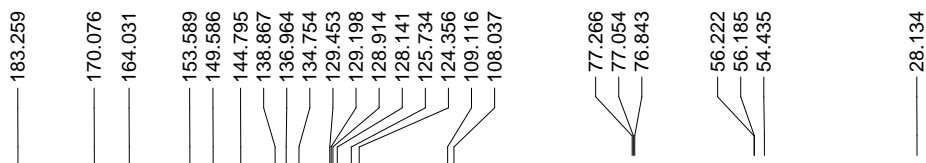
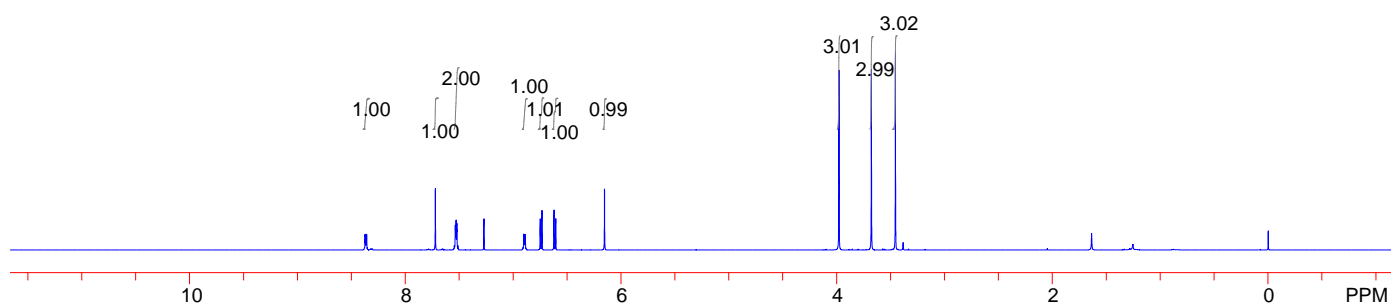


¹⁹F NMR (376 MHz, CDCl₃)

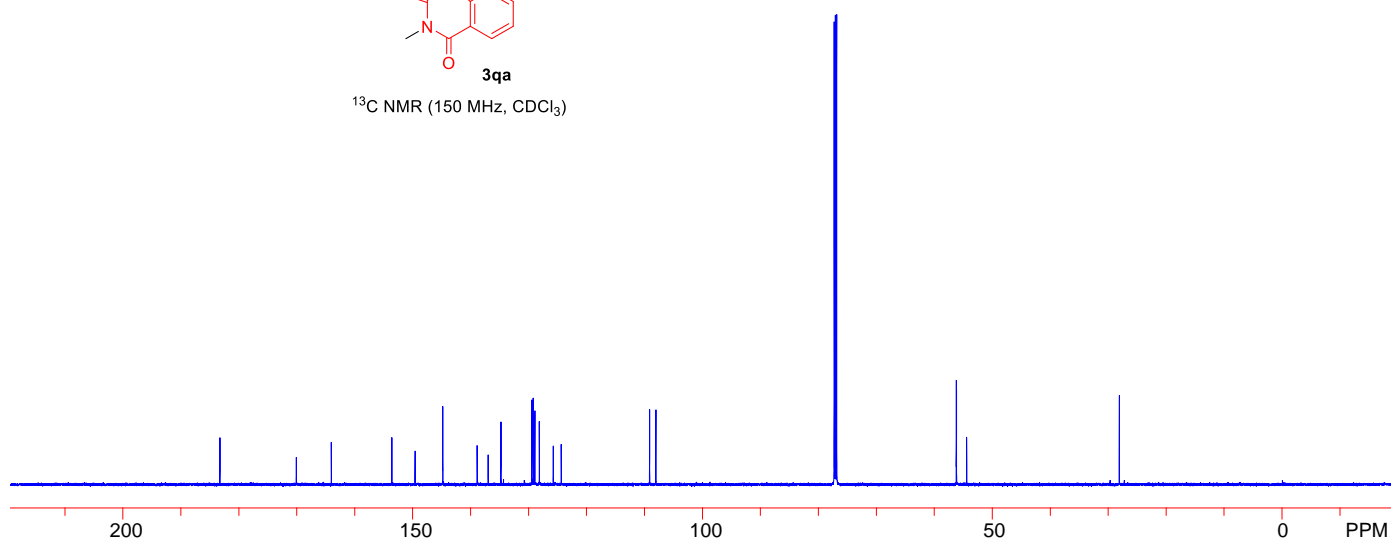




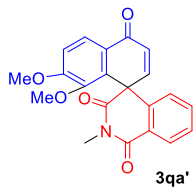
¹H NMR (600 MHz, CDCl₃)



¹³C NMR (150 MHz, CDCl₃)

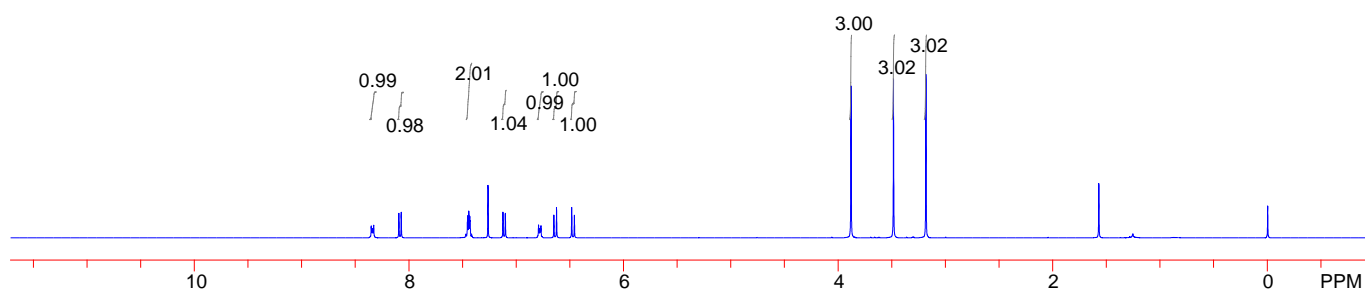


8.351
8.345
8.342
8.340
8.333
8.328
8.093
8.071
7.450
7.442
7.442
7.433
7.429
7.263
7.123
7.101
7.101
6.792
6.788
6.781
6.779
6.776
6.769
6.649
6.624
6.483
6.458
3.881
3.486
3.183

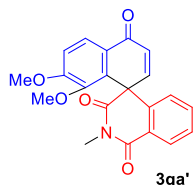


3qa:3qa' = 2.8:1

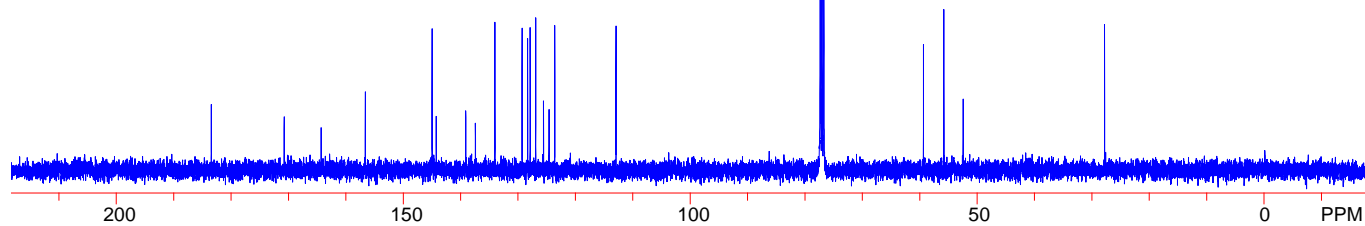
¹H NMR (400 MHz, CDCl₃)



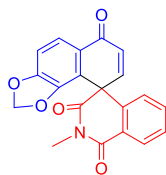
183.444
170.739
164.304
156.611
144.968
144.246
139.111
137.420
134.018
129.280
128.320
127.872
126.911
125.546
124.586
123.589
112.921
77.341
77.031
76.773
59.371
55.817
52.466
27.844



¹³C NMR (100 MHz, CDCl₃)

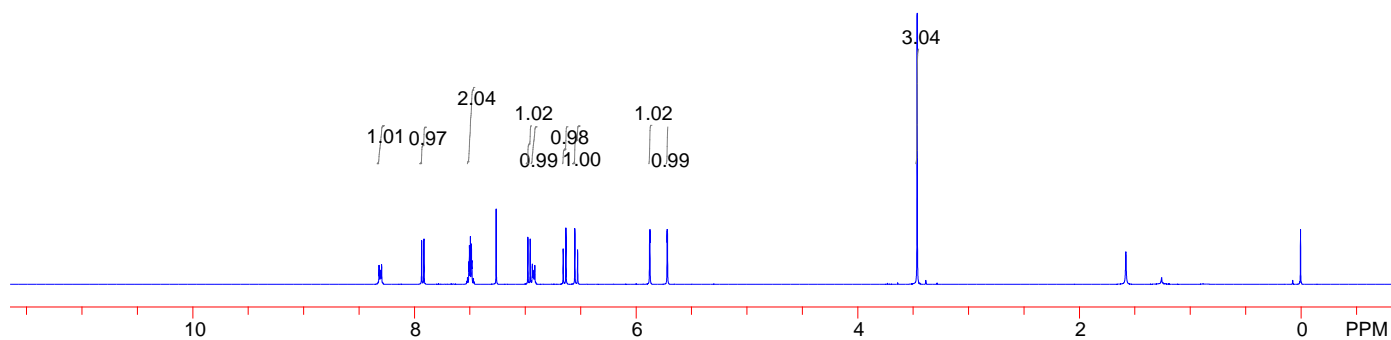


8.320
8.315
8.310
8.305
8.303
8.297
7.935
7.915
7.522
7.509
7.504
7.496
7.486
7.482
7.468
7.263
6.977
6.956
6.937
6.931
6.929
6.924
6.919
6.914
6.658
6.633
6.553
6.528
5.879
5.876
5.721
5.718
3.463

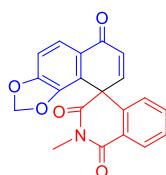


3ra

¹H NMR (400 MHz, CDCl₃)

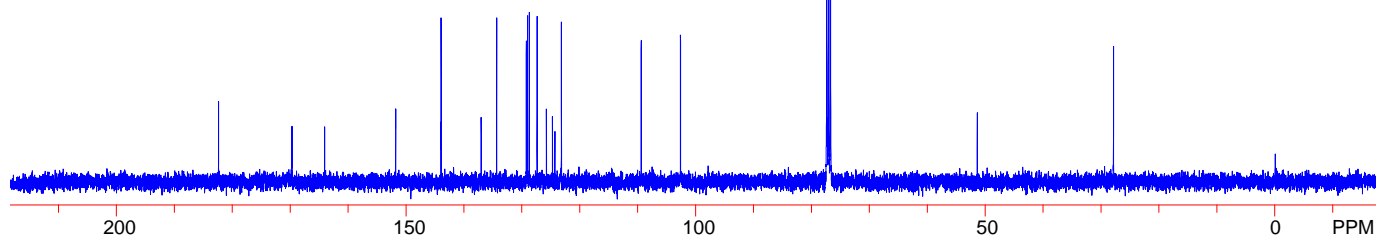


182.368
169.685
164.058
151.779
143.957
143.928
137.016
134.344
129.215
129.013
128.703
127.352
125.748
124.701
124.289
123.155
109.382
102.607
77.349
77.031
76.713
51.390
27.901

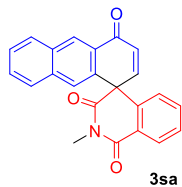


3ra

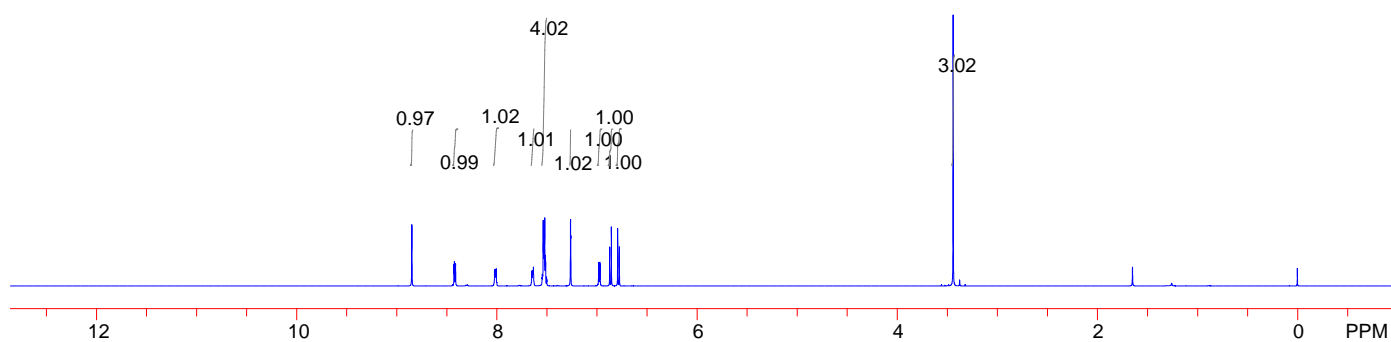
¹³C NMR (100 MHz, CDCl₃)



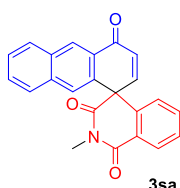
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8.414
8.024
8.017
8.013
8.008
7.652
7.646
7.642
7.640
7.636
7.547
7.546
7.544
7.538
7.535
7.529
7.527
7.523
7.517
7.514
7.265
7.263
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6.983
6.981
6.974
6.970
6.875
6.858
6.795
6.778
3.443



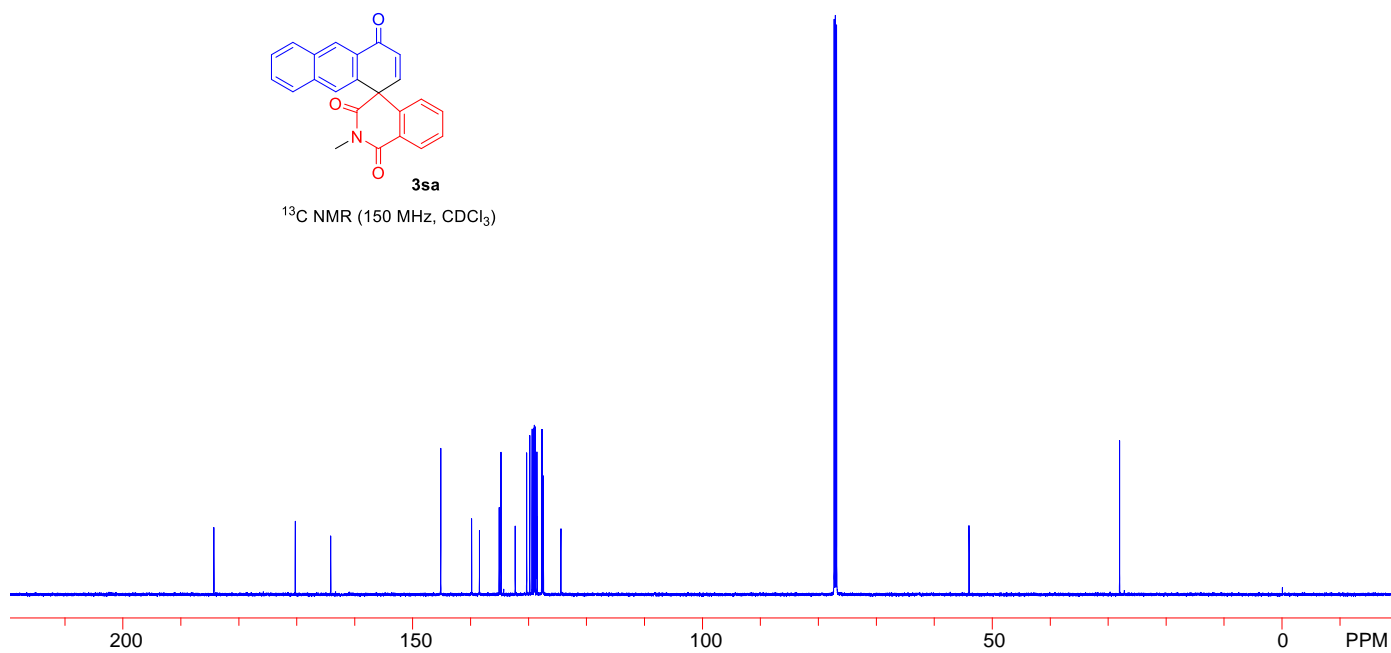
¹H NMR (600 MHz, CDCl₃)



184.302
170.258
164.140
139.815
138.473
135.068
145.152
134.754
132.297
130.321
129.789
129.388
129.103
128.994
128.855
128.542
128.505
127.725
127.594
127.426
124.415
77.273
77.062
76.850
54.027
28.083

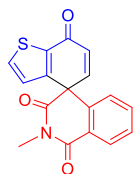


¹³C NMR (150 MHz, CDCl₃)



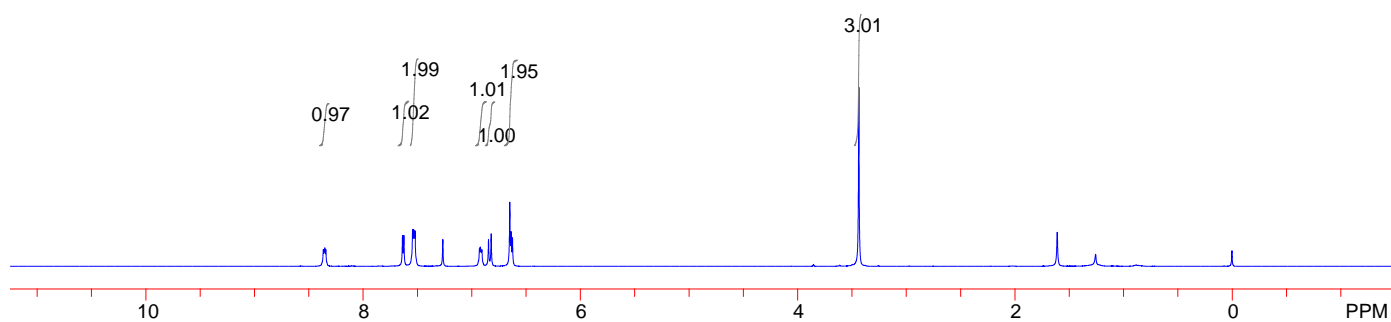
8.366
8.352
8.343
7.637
7.624
7.544
7.535
7.531
7.521
7.266
6.928
6.920
6.907
6.845
6.821
6.650
6.637
6.625

3.437



3ta

¹H NMR (400 MHz, CDCl₃)

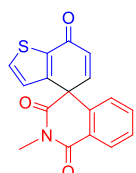


179.139
168.551
163.870
148.471
145.113
137.457
136.611
134.719
134.214
129.800
129.186
127.287
126.189
124.232

77.356
77.038
76.720

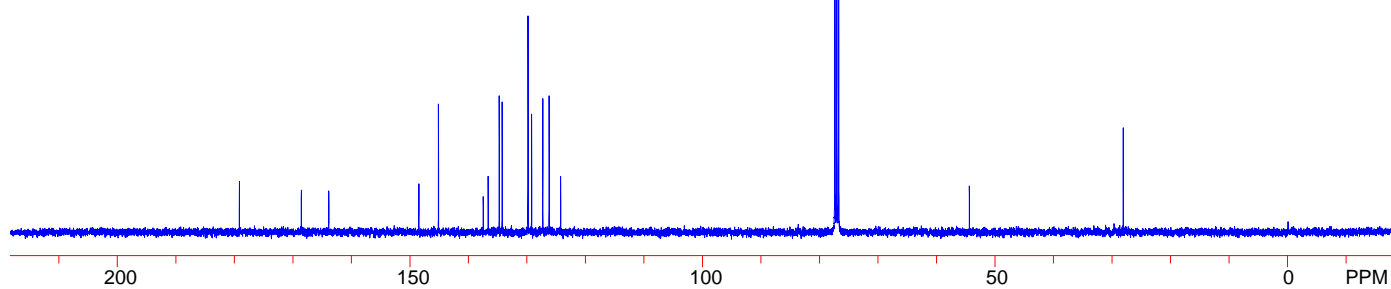
54.395

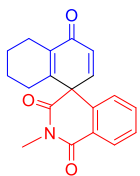
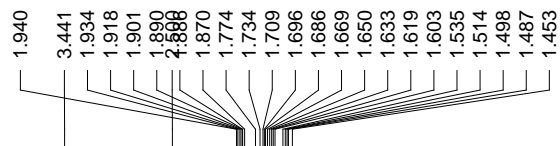
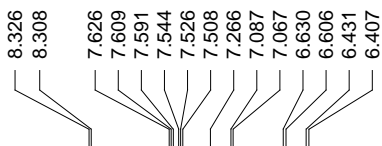
28.125



3ta

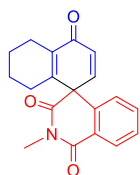
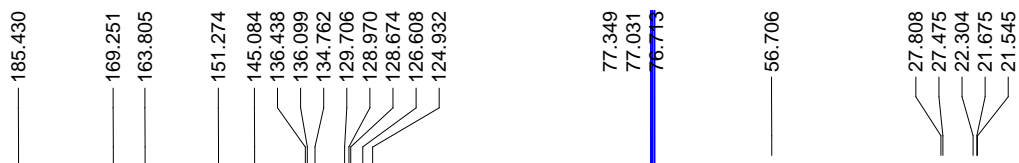
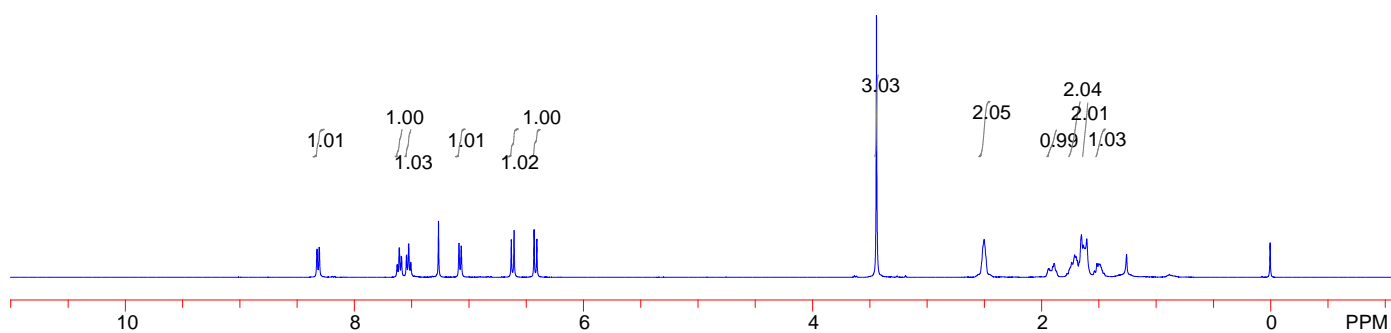
¹³C NMR (100 MHz, CDCl₃)





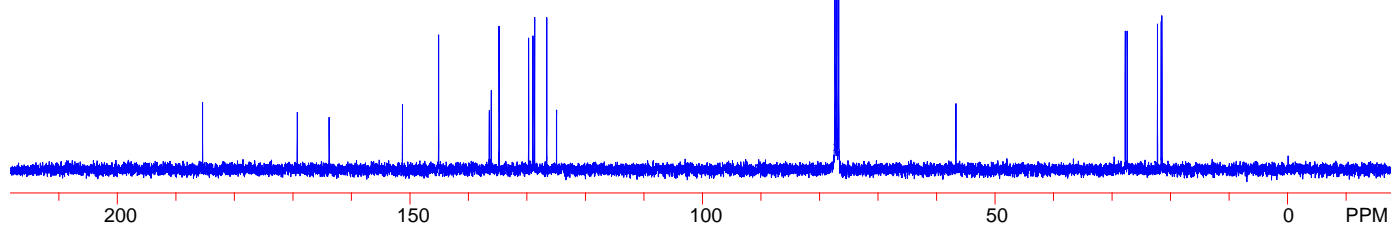
3ua

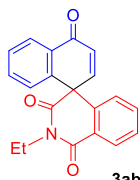
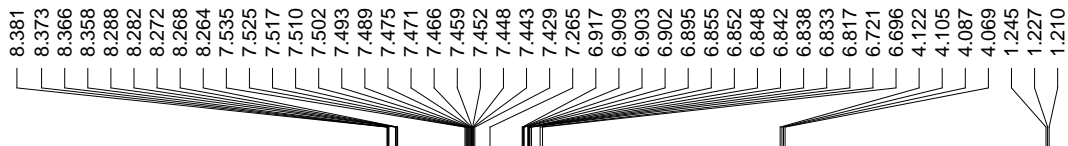
¹H NMR (400 MHz, CDCl₃)



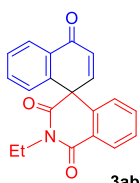
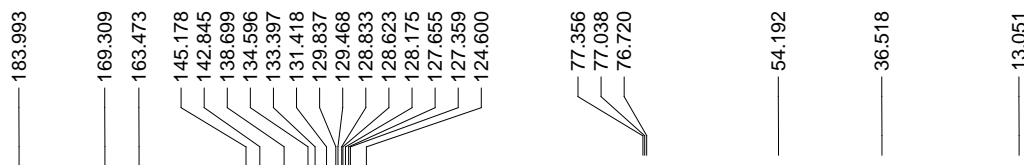
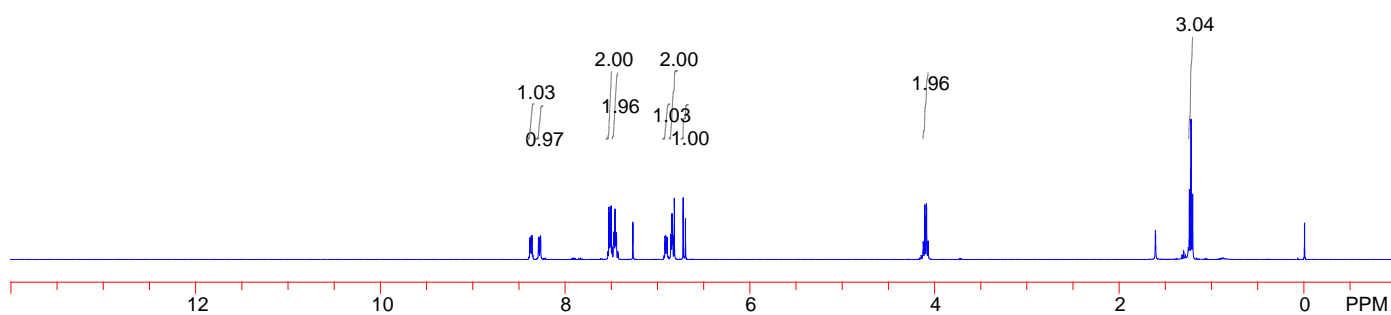
3ua

¹³C NMR (100 MHz, CDCl₃)

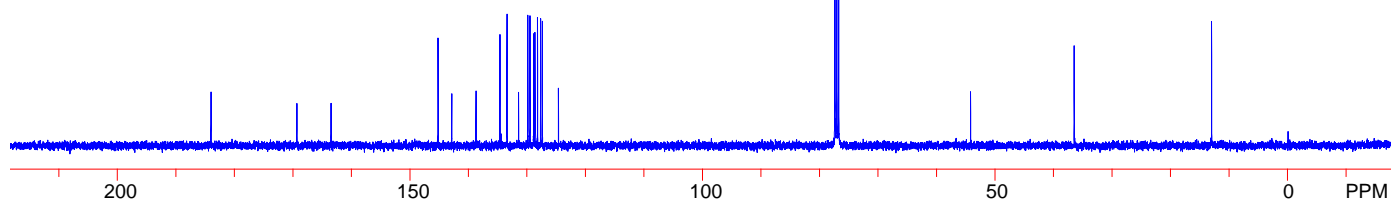




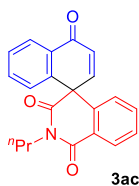
¹H NMR (400 MHz, CDCl₃)



¹³C NMR (100 MHz, CDCl₃)

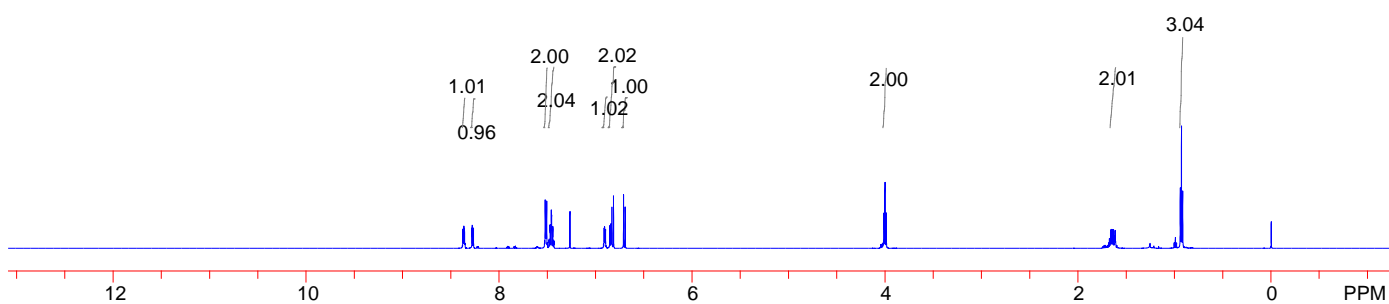


8.374
8.369
8.368
8.364
8.358
8.281
8.278
8.270
8.268
8.266
7.529
7.522
7.517
7.512
7.507
7.483
7.481
7.471
7.469
7.459
7.456
7.446
7.443
7.434
7.431
7.266
6.912
6.907
6.903
6.902
6.897
6.897
6.853
6.852
6.850
6.841
6.839
6.831
6.815
6.710
6.694
4.014
4.002
3.989
1.677
1.674
1.664
1.659
1.652
1.646
1.639
1.634
1.624
1.622
1.617
1.612
0.942
0.930
0.918

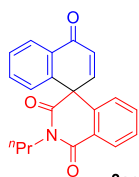


3ac

¹H NMR (600 MHz, CDCl₃)

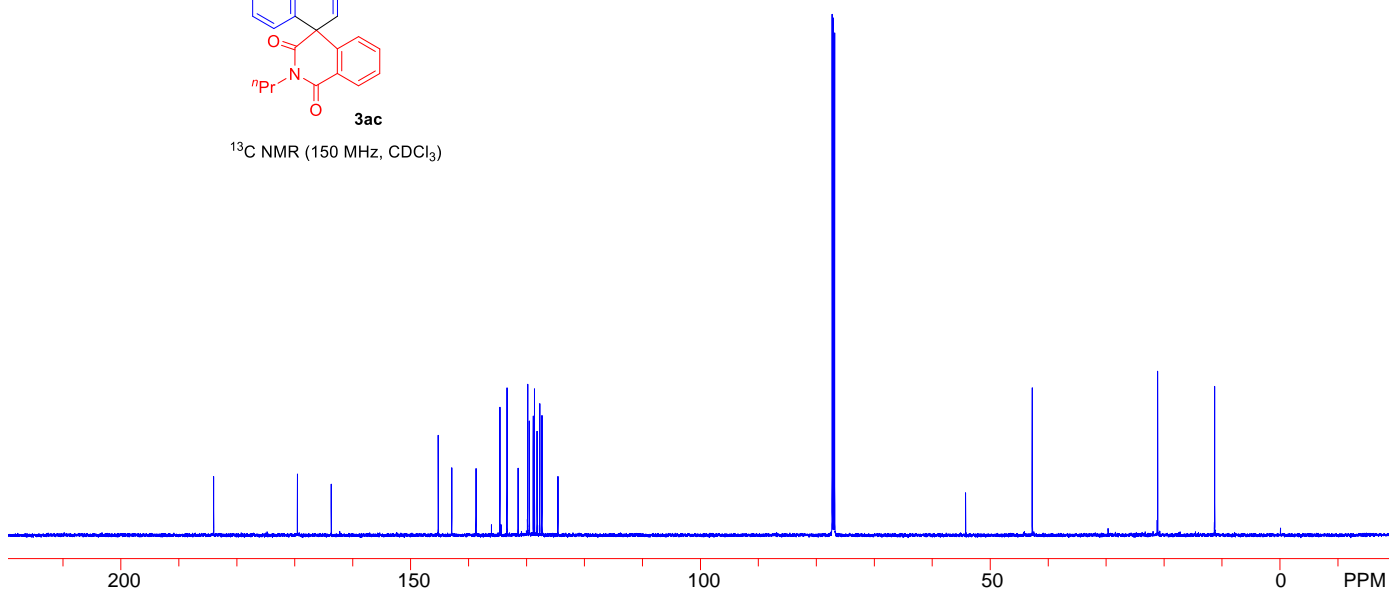


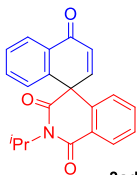
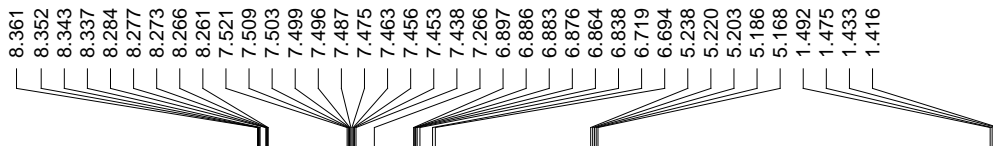
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169.544
163.696
145.233
142.899
138.714
134.594
133.369
131.451
129.796
129.504
128.841
128.622
128.177
127.710
127.331
124.582
77.266
77.054
76.843
54.267
42.790
21.163
11.341



3ac

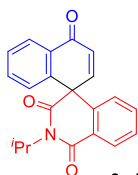
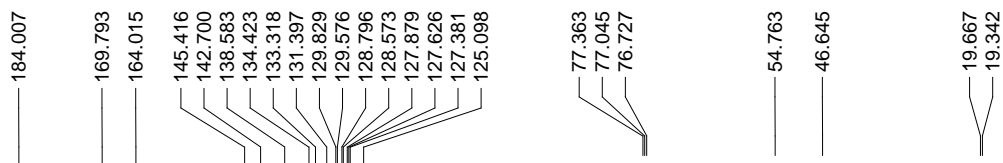
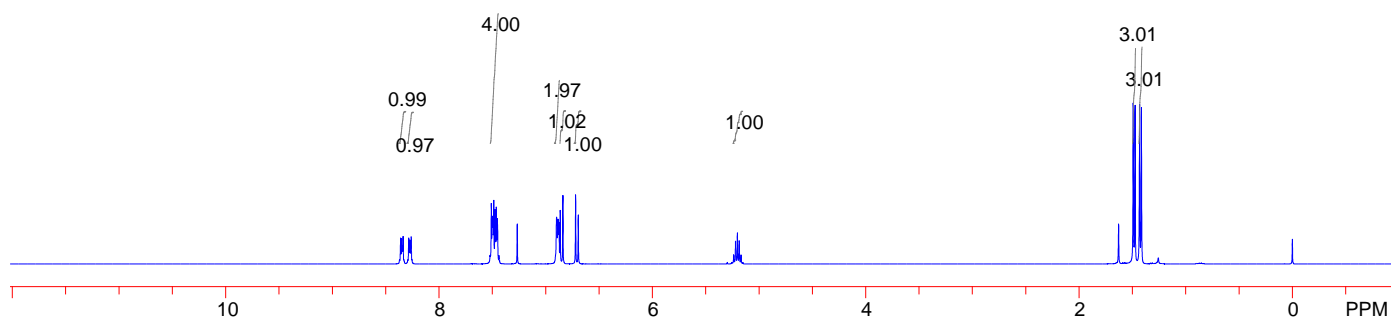
¹³C NMR (150 MHz, CDCl₃)





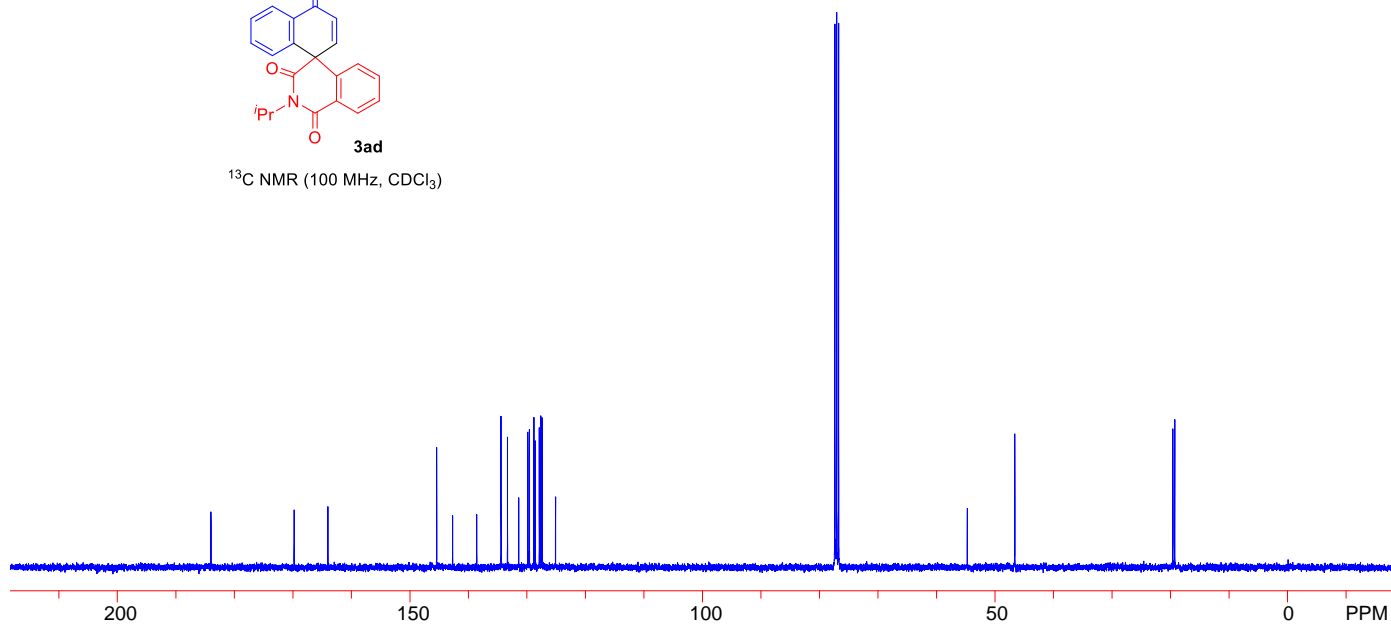
3ad

¹H NMR (400 MHz, CDCl₃)

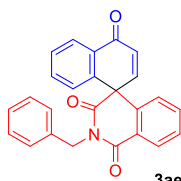


3ad

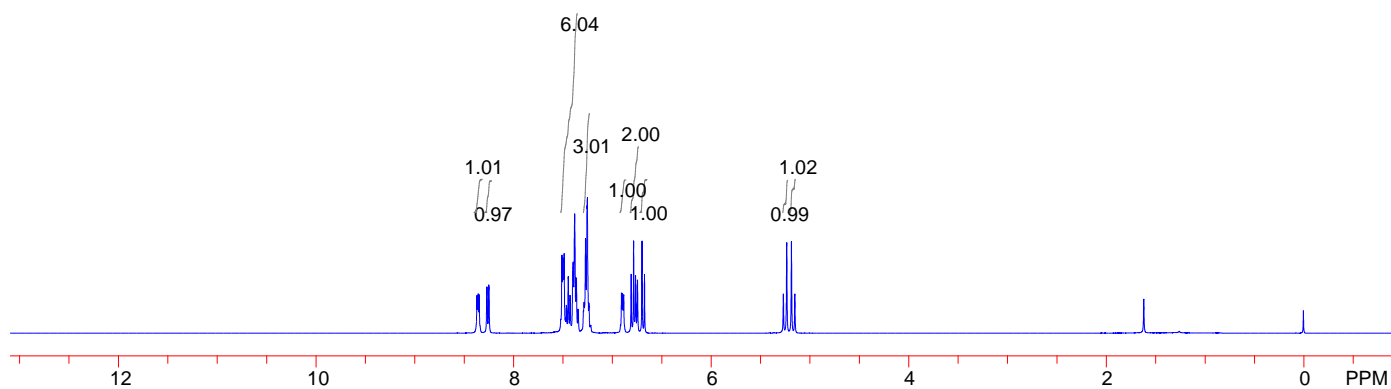
¹³C NMR (100 MHz, CDCl₃)



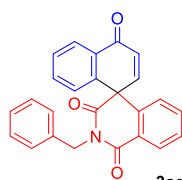
8.372
8.365
8.359
8.348
8.271
8.269
8.251
7.523
7.511
7.505
7.501
7.494
7.489
7.476
7.466
7.447
7.429
7.398
7.367
7.348
7.345
7.294
7.287
7.273
7.258
7.254
7.238
7.223
7.219
6.918
6.909
6.898
6.891
6.886
6.811
6.786
6.767
6.747
6.701
6.676
5.271
5.236
5.189
5.155



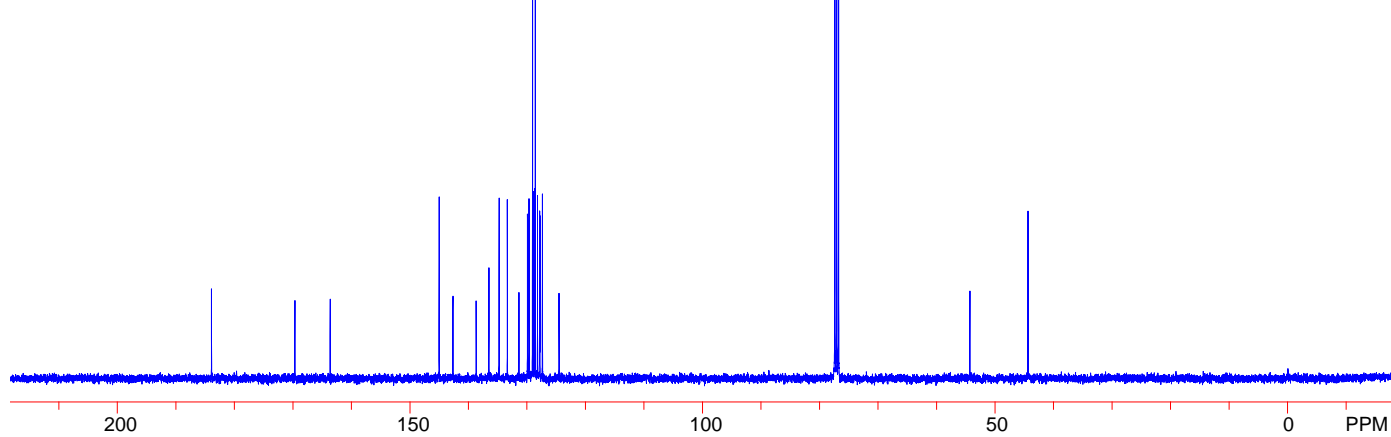
¹H NMR (400 MHz, CDCl₃)



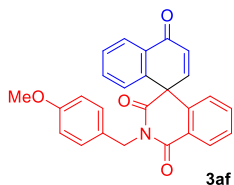
183.913
169.663
163.625
144.997
142.642
138.670
136.496
134.748
133.340
131.361
129.902
129.634
129.042
128.883
128.659
128.558
128.190
127.829
127.771
127.352
124.506
77.370
77.060
76.742
54.322
44.405



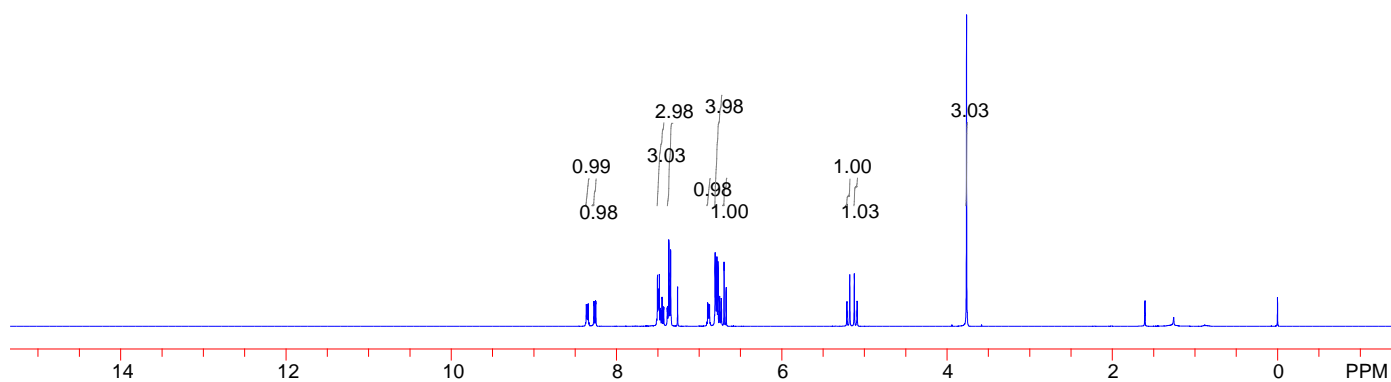
¹³C NMR (100 MHz, CDCl₃)



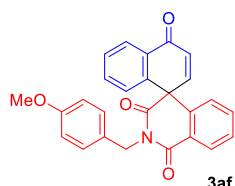
8.373
8.365
8.358
8.354
8.350
8.341
8.332
8.273
8.270
8.253
8.250
7.515
7.504
7.495
7.491
7.488
7.481
7.469
7.466
7.449
7.447
7.430
7.428
7.386
7.382
7.366
7.344
7.261
6.907
6.896
6.888
6.884
6.880
6.874
6.865
6.813
6.806
6.801
6.796
6.789
6.784
6.771
6.751
6.750
6.732
6.731
6.698
6.673
6.673
5.211
5.177
5.121
5.088
3.763



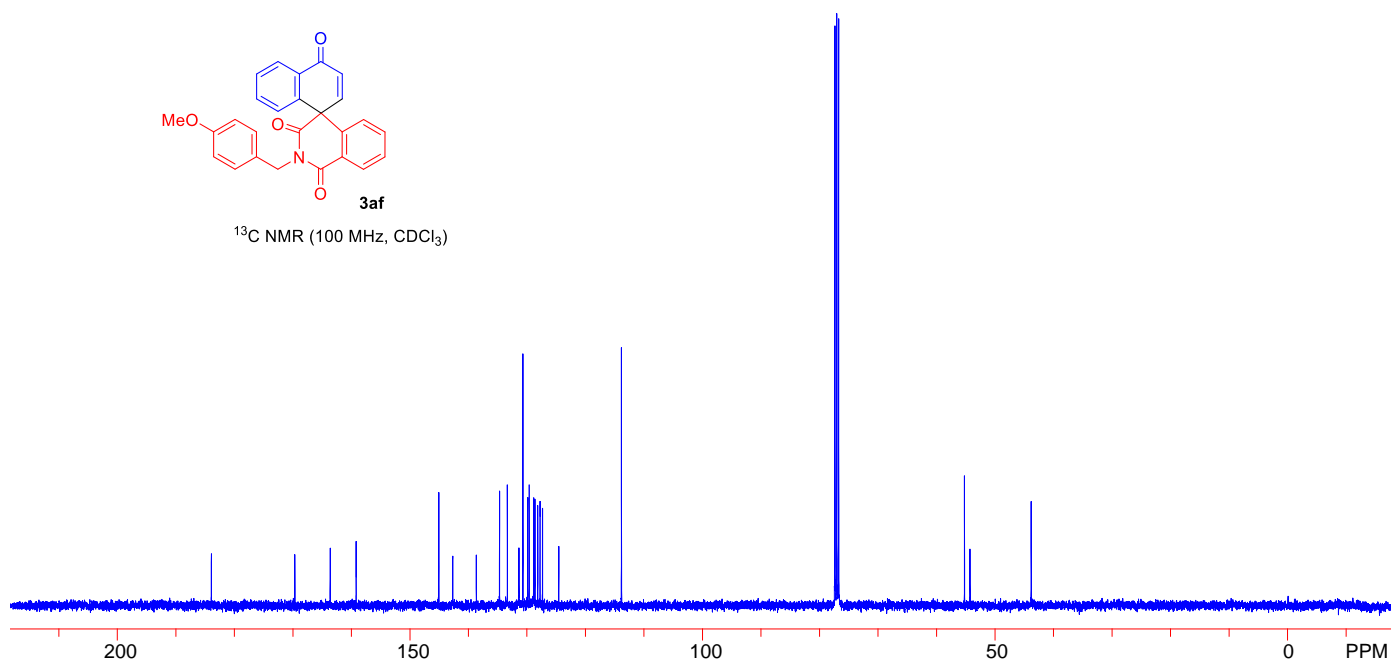
¹H NMR (400 MHz, CDCl₃)



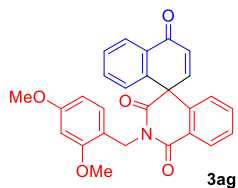
183.935
169.670
163.617
159.190
145.055
142.679
138.641
134.676
133.340
131.353
130.682
129.858
129.598
128.840
128.768
128.623
128.154
127.756
127.330
124.557
113.845
77.363
77.045
76.727
55.247
54.308
43.857



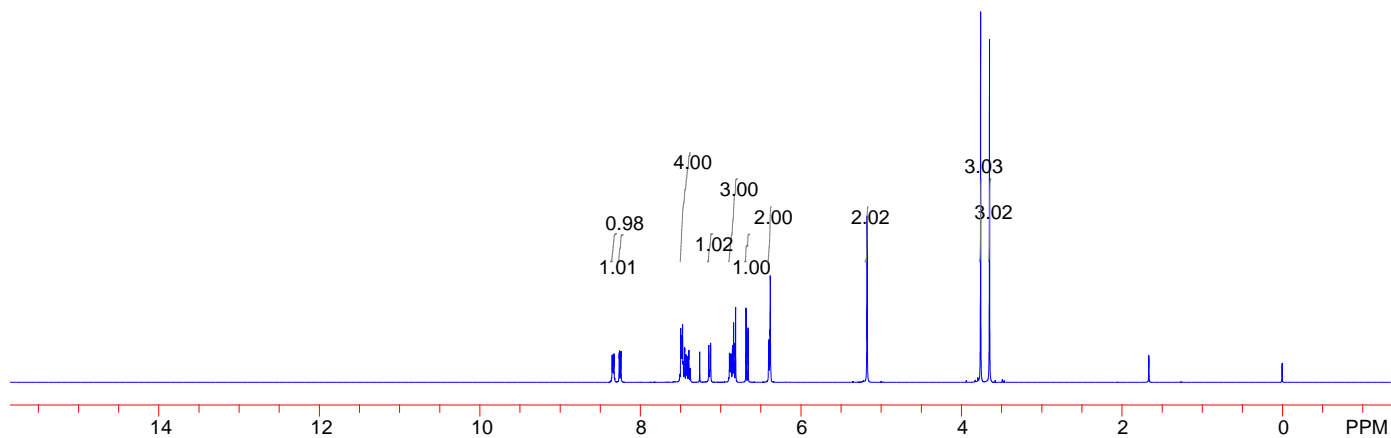
¹³C NMR (100 MHz, CDCl₃)



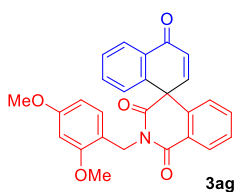
8.361
8.353
8.347
8.341
8.338
8.330
8.321
8.265
8.261
8.246
8.243
7.511
7.507
7.499
7.493
7.489
7.487
7.481
7.476
7.471
7.468
7.463
7.452
7.449
7.434
7.430
7.421
7.417
7.402
7.398
7.383
7.379
7.263
7.149
7.133
7.127
6.902
6.892
6.886
6.882
6.875
6.870
6.861
6.854
6.852
6.841
6.836
6.833
6.816
6.686
6.661
6.406
6.400
6.390
6.384
5.178
3.762
3.651



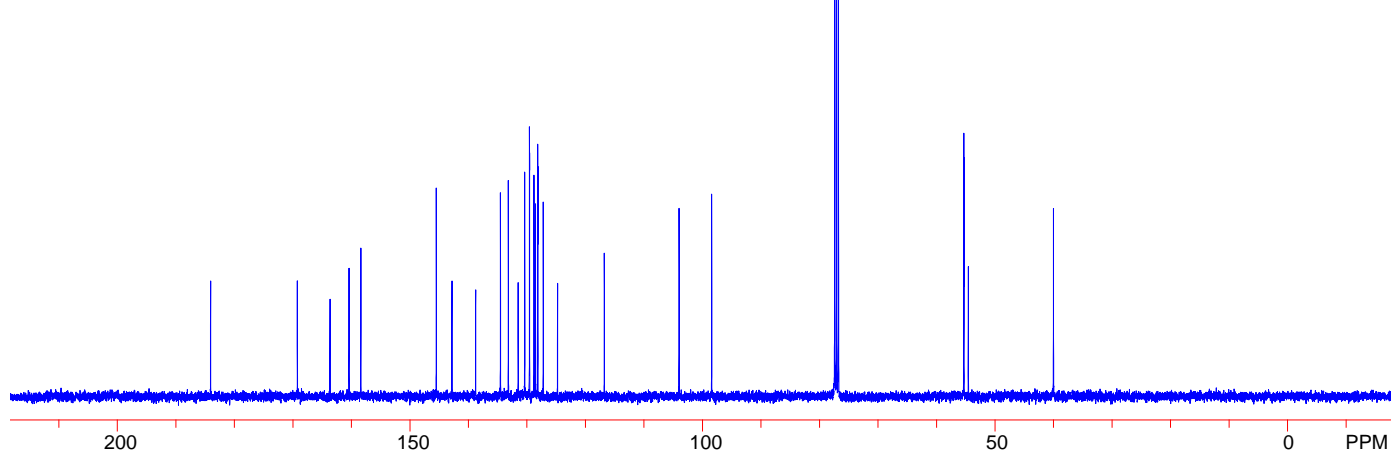
¹H NMR (400 MHz, CDCl₃)



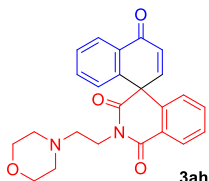
184.065
163.654
169.237
160.411
158.388
145.481
142.809
138.764
134.517
133.173
131.491
130.378
129.562
129.548
128.782
128.529
128.146
128.125
127.200
124.766
116.778
103.993
98.425
77.392
77.074
76.756
55.355
55.326
54.582
40.057



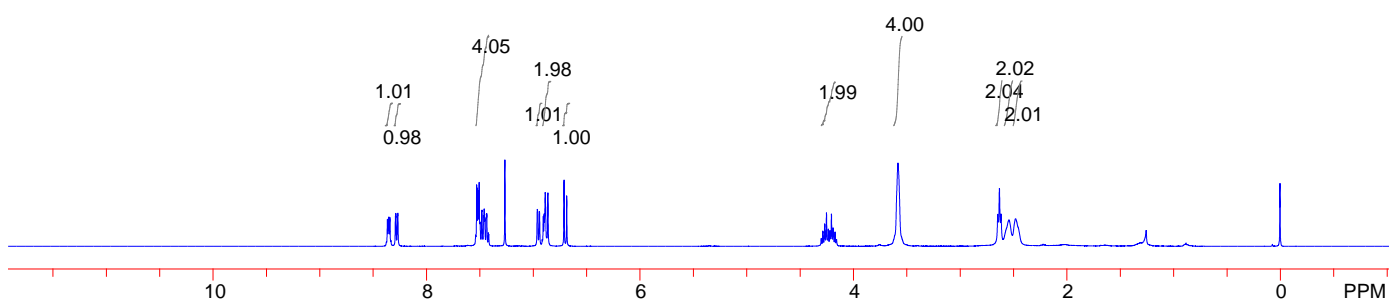
¹³C NMR (100 MHz, CDCl₃)



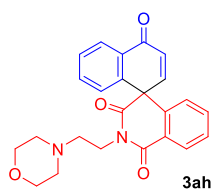
8.367
8.359
8.352
8.344
8.292
8.288
8.272
8.269
7.540
7.530
7.522
7.515
7.507
7.498
7.483
7.480
7.465
7.460
7.454
7.439
7.435
7.420
7.417
7.265
6.962
6.943
6.941
6.906
6.898
6.887
6.862
6.711
6.686
4.285
4.267
4.251
4.235
4.219
4.205
4.190
4.171
3.581
2.645
2.630
2.615
2.540
2.479



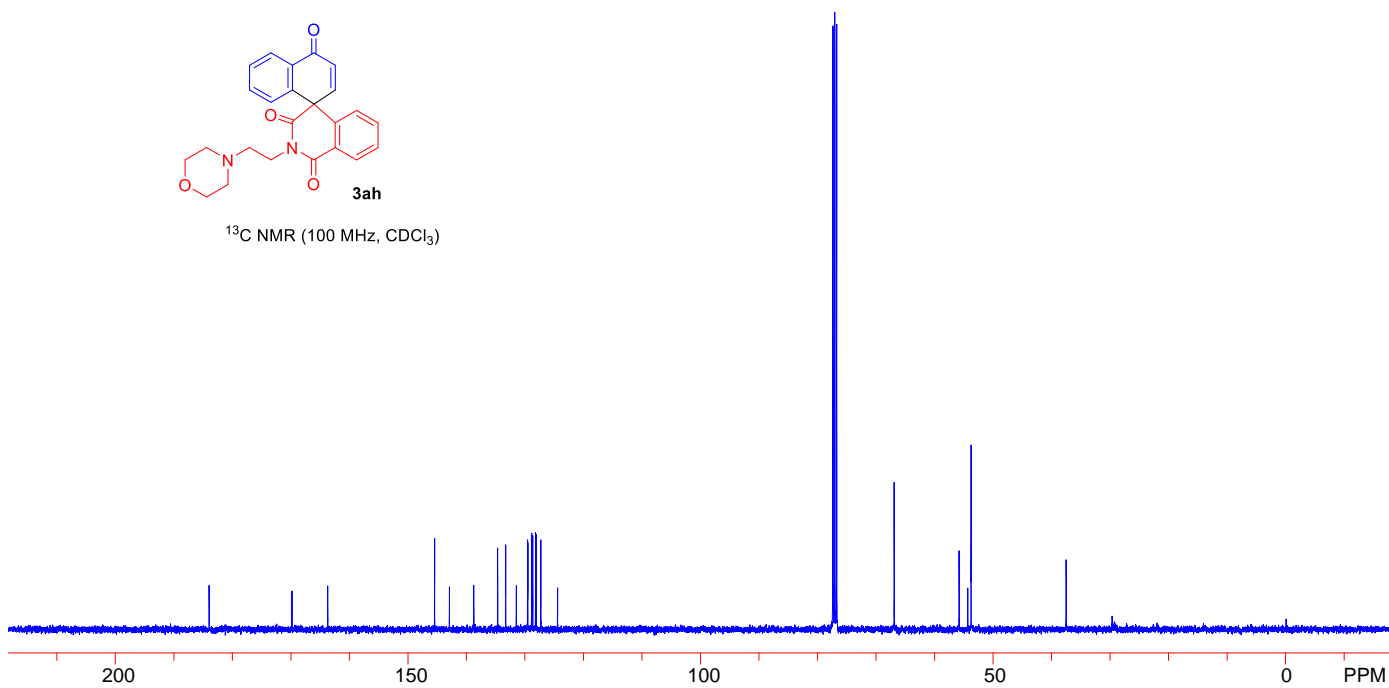
¹H NMR (400 MHz, CDCl₃)

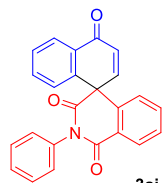
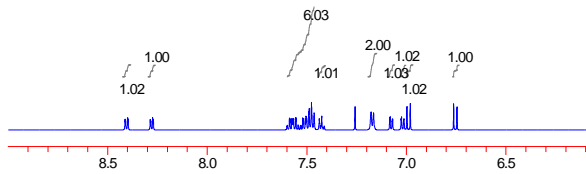
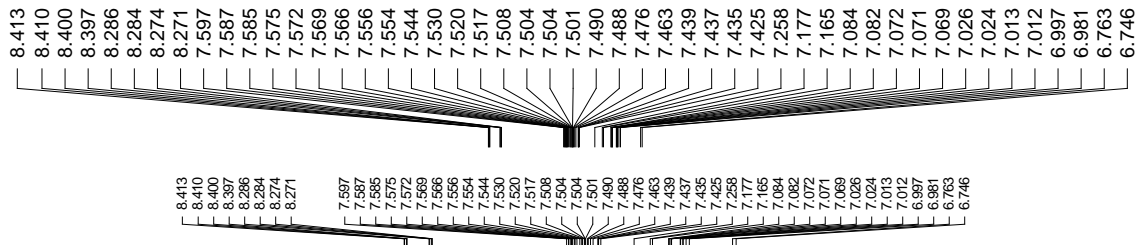


183.971
169.815
163.704
145.438
142.903
138.742
134.661
133.289
131.469
129.548
129.504
128.847
128.659
128.190
128.089
127.280
124.419
77.356
77.038
76.720
66.904
55.817
54.344
53.773
37.551

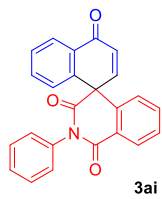
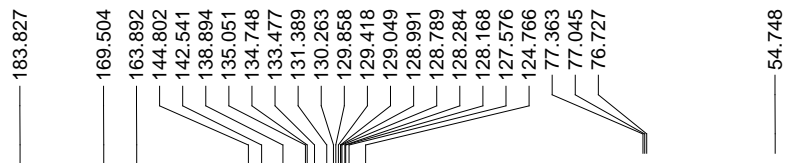
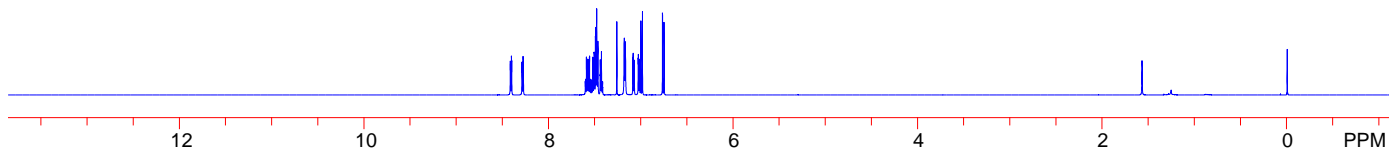
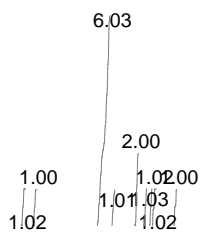


¹³C NMR (100 MHz, CDCl₃)

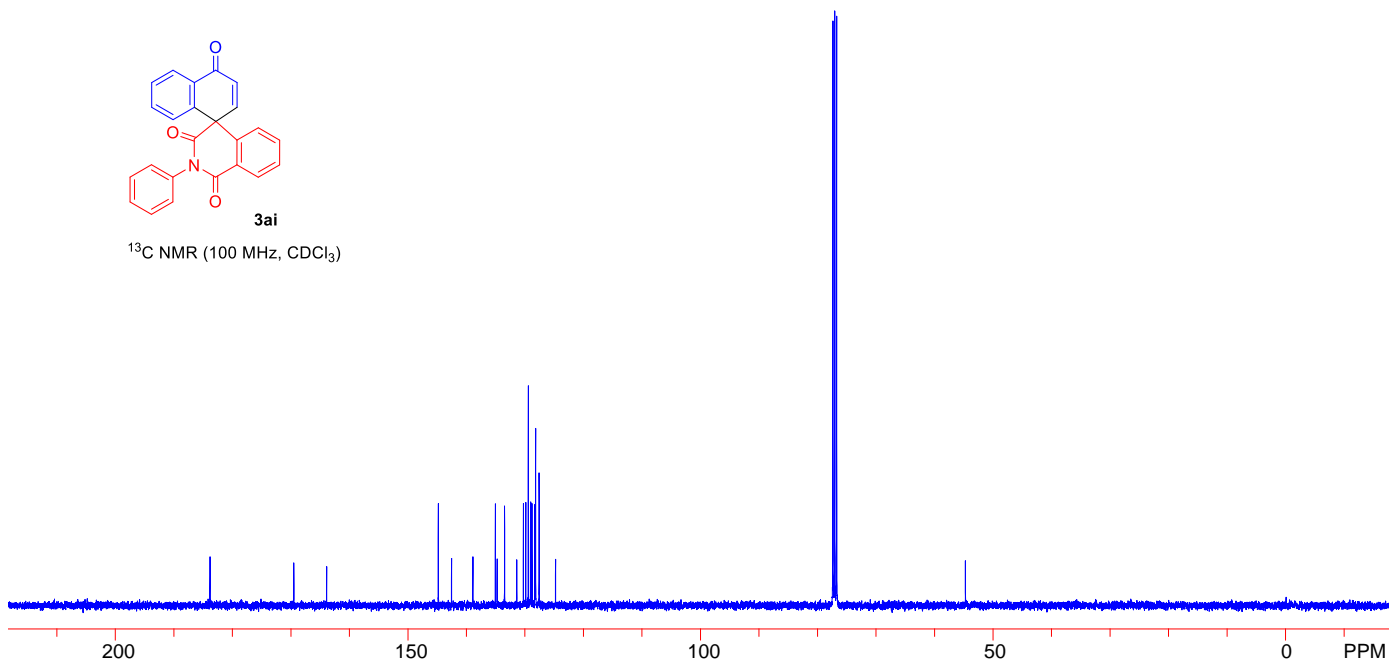




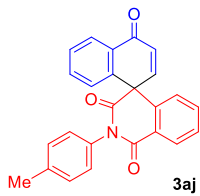
¹H NMR (600 MHz, CDCl₃)



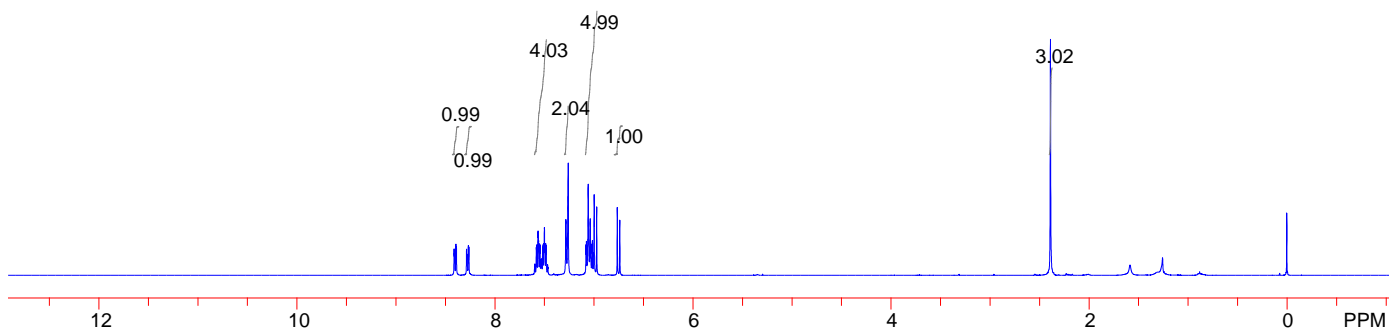
¹³C NMR (100 MHz, CDCl₃)



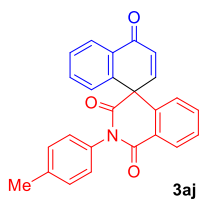
8.413
8.409
8.407
8.395
8.390
8.287
8.283
8.280
8.269
8.264
7.582
7.577
7.565
7.562
7.559
7.549
7.545
7.530
7.519
7.514
7.505
7.501
7.495
7.487
7.483
7.283
7.260
7.080
7.076
7.058
7.038
7.021
7.017
7.004
6.998
6.973
6.764
6.739
2.388



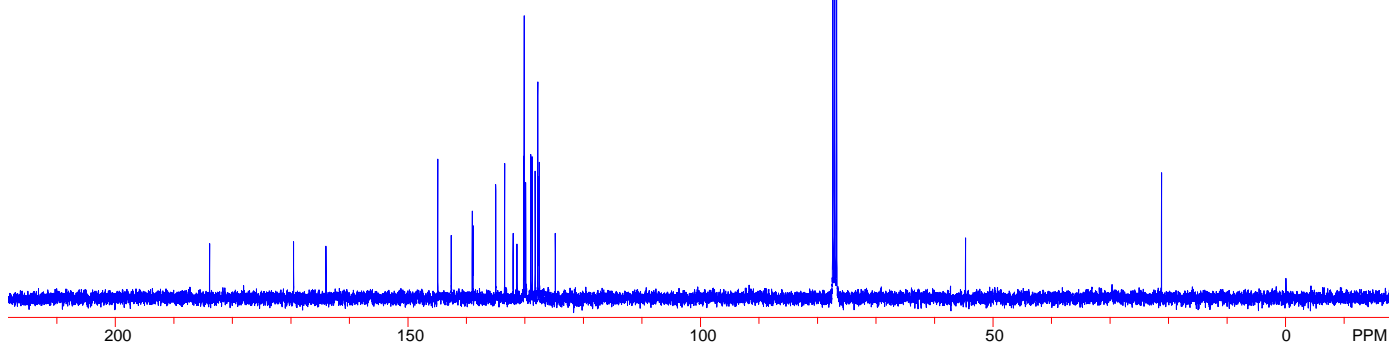
3aj
¹H NMR (400 MHz, CDCl₃)



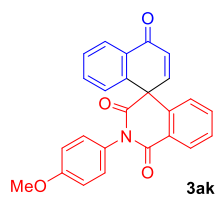
183.899
169.540
164.000
144.903
142.599
139.002
138.858
134.994
133.470
132.018
131.361
130.212
130.125
129.873
129.006
128.753
128.247
127.800
127.583
127.540
124.802
77.370
77.052
76.735
54.727
21.271



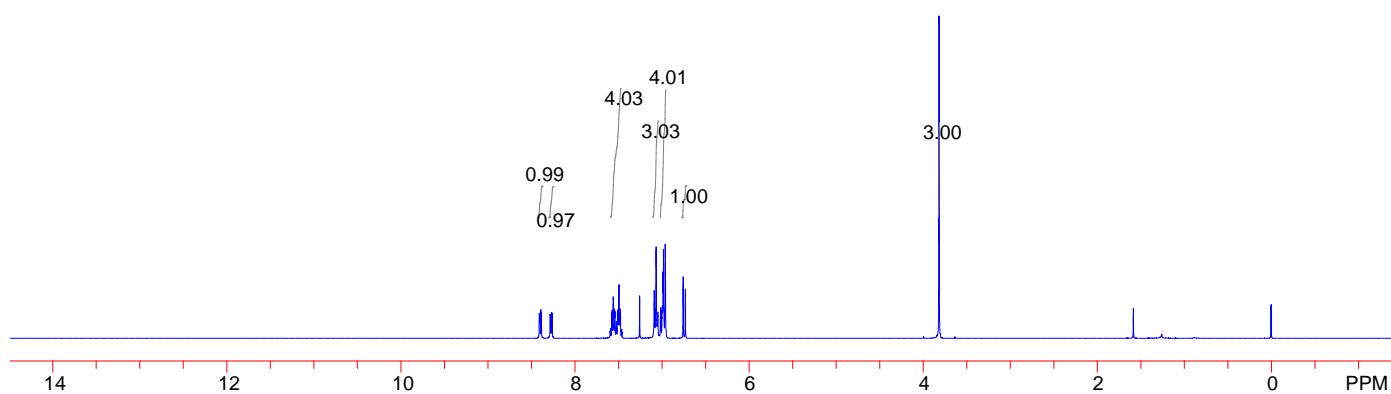
3aj
¹³C NMR (100 MHz, CDCl₃)



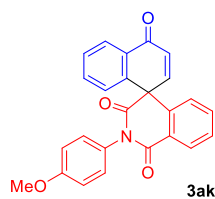
8.410
8.407
8.404
8.392
8.387
8.286
8.282
8.278
8.268
8.262
7.598
7.593
7.579
7.574
7.564
7.562
7.560
7.556
7.546
7.542
7.527
7.513
7.508
7.502
7.496
7.489
7.483
7.479
7.465
7.258
7.091
7.070
7.055
7.052
7.049
7.019
7.014
7.002
6.997
6.990
6.985
6.965
6.759
6.734
3.818



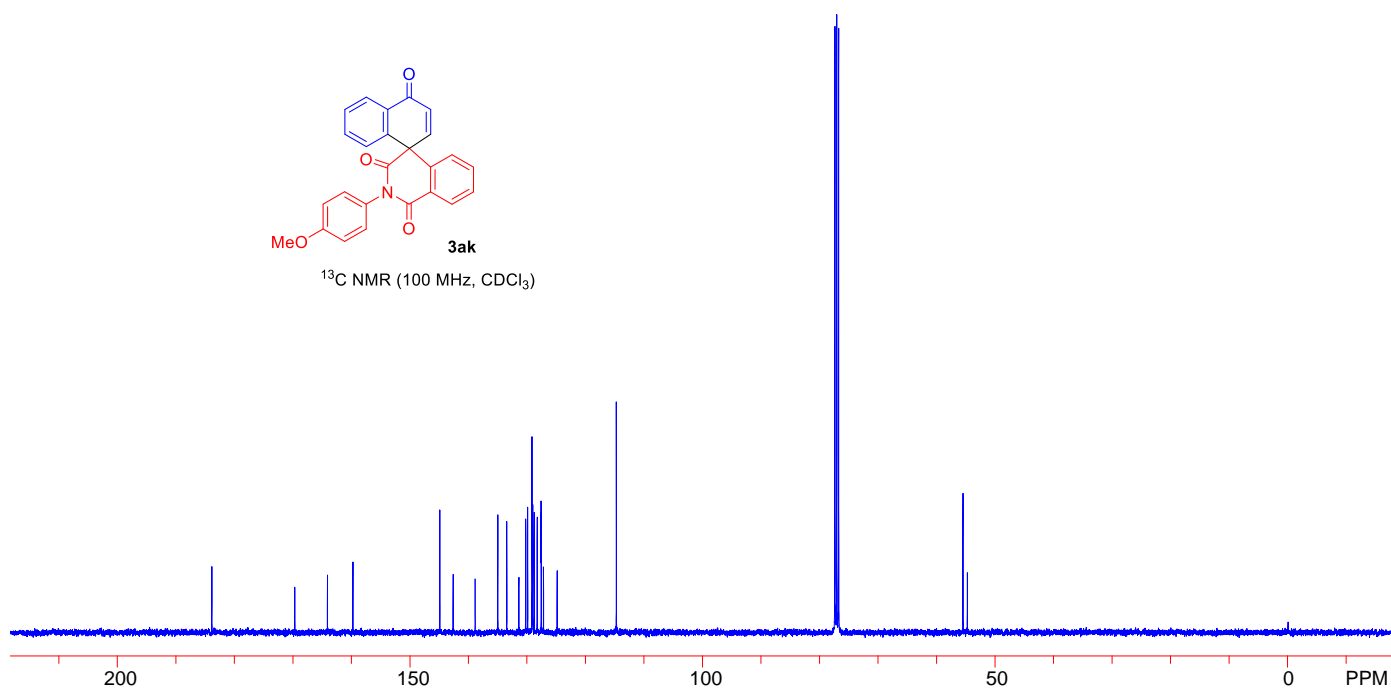
¹H NMR (400 MHz, CDCl₃)



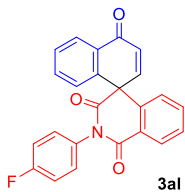
183.856
169.685
164.094
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144.889
142.606
138.843
134.979
133.448
131.375
130.205
129.873
129.136
129.006
128.746
128.240
127.569
127.540
127.164
124.831
114.719
77.363
77.045
76.727
55.500
54.756



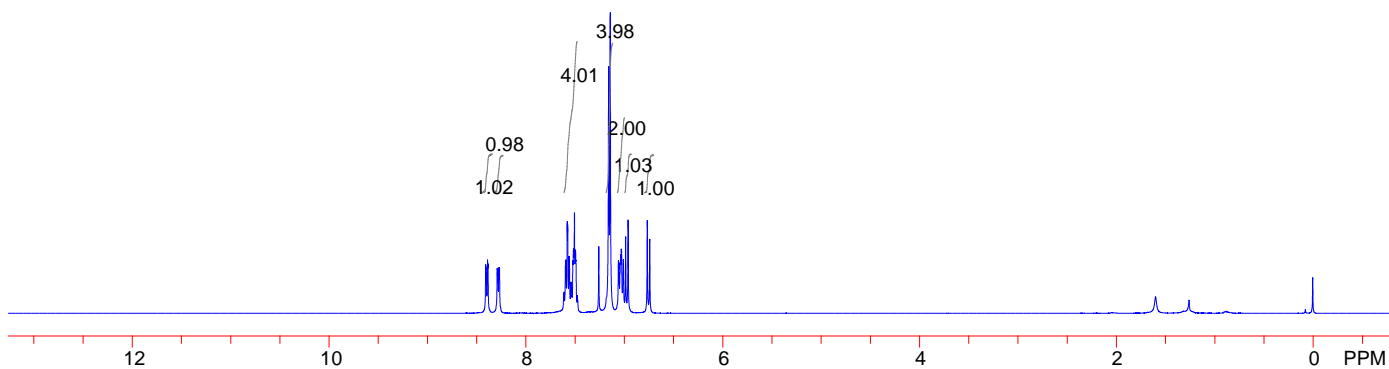
¹³C NMR (100 MHz, CDCl₃)



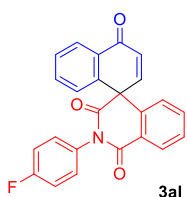
8.408
8.405
8.390
8.385
8.291
8.287
8.284
8.274
8.268
7.615
7.612
7.597
7.593
7.579
7.575
7.560
7.557
7.541
7.522
7.517
7.513
7.506
7.498
7.494
7.491
7.476
7.259
7.159
7.142
7.059
7.054
7.037
7.031
7.027
7.009
6.986
6.961
6.766
6.741



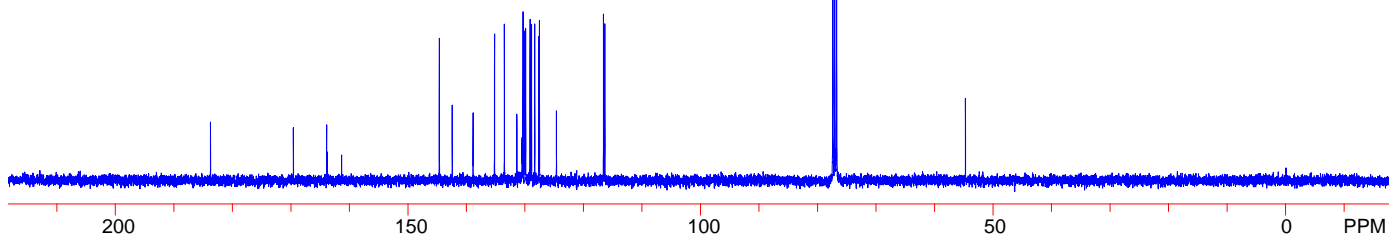
¹H NMR (400 MHz, CDCl₃)

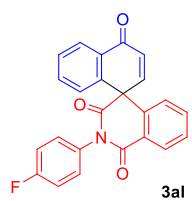


183.740
163.892
163.805
161.328
160.576
144.629
142.419
138.858
135.189
133.506
131.382
130.487
130.450
130.320
130.075
129.988
129.873
129.114
128.861
128.320
127.619
127.511
124.607
116.575
116.344
77.370
77.052
76.735
54.734



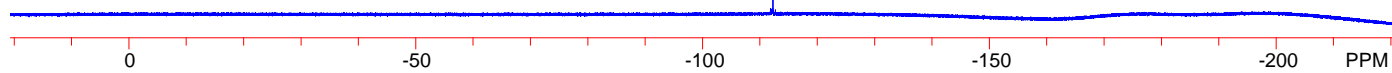
¹³C NMR (100 MHz, CDCl₃)

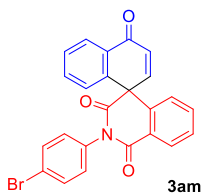
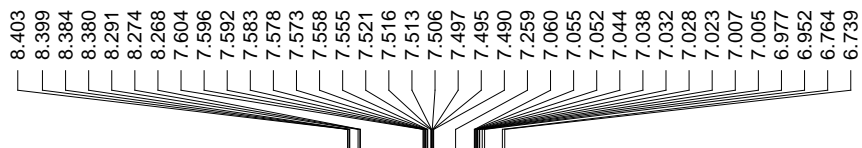




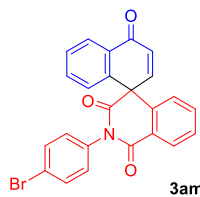
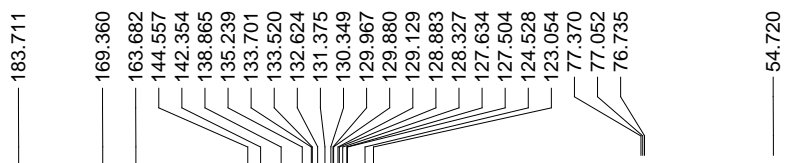
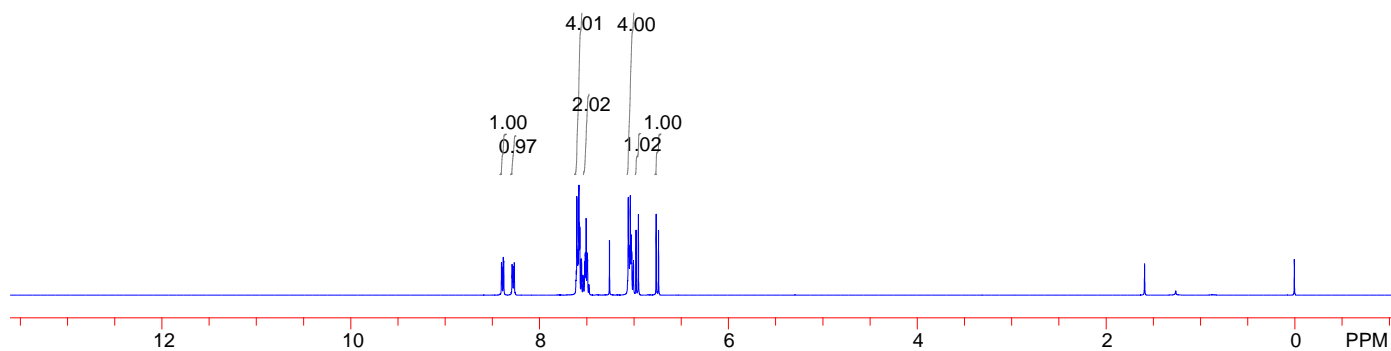
¹⁹F NMR (376 MHz, CDCl₃)

-112.186
-112.205
-112.219
-112.238
-112.256

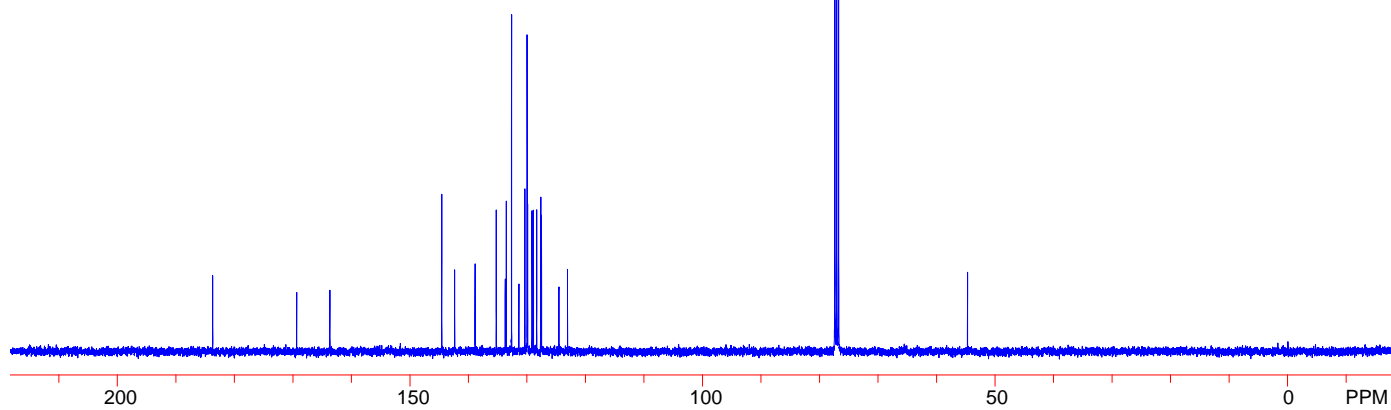


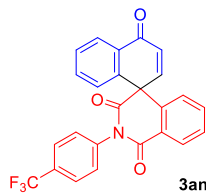
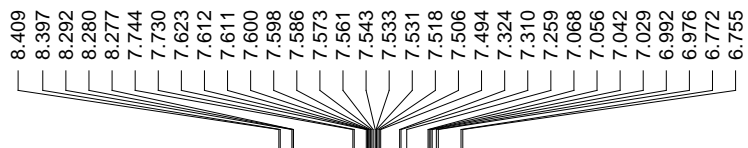


¹H NMR (400 MHz, CDCl₃)

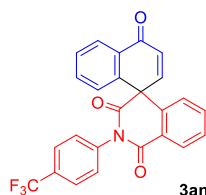
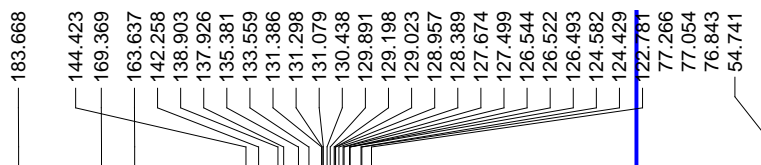
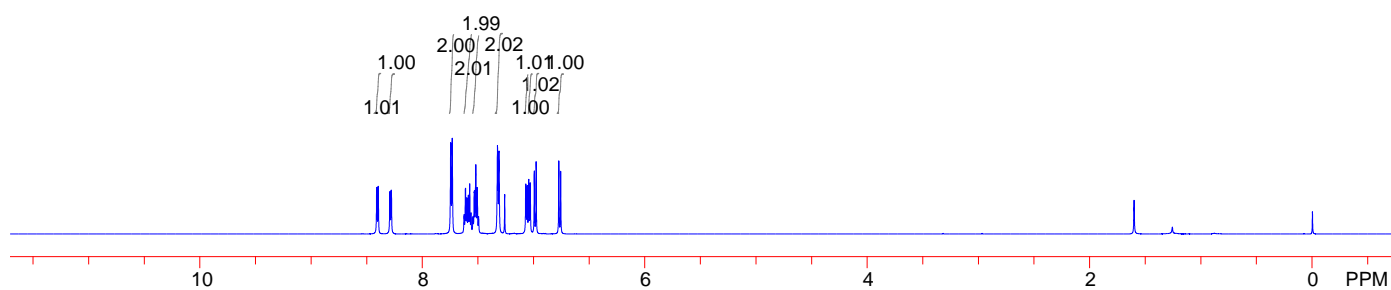


¹³C NMR (100 MHz, CDCl₃)

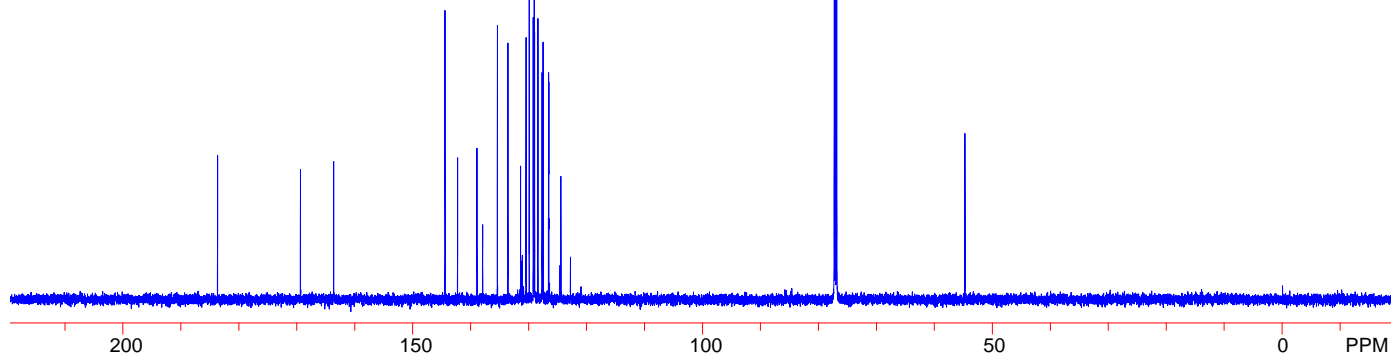


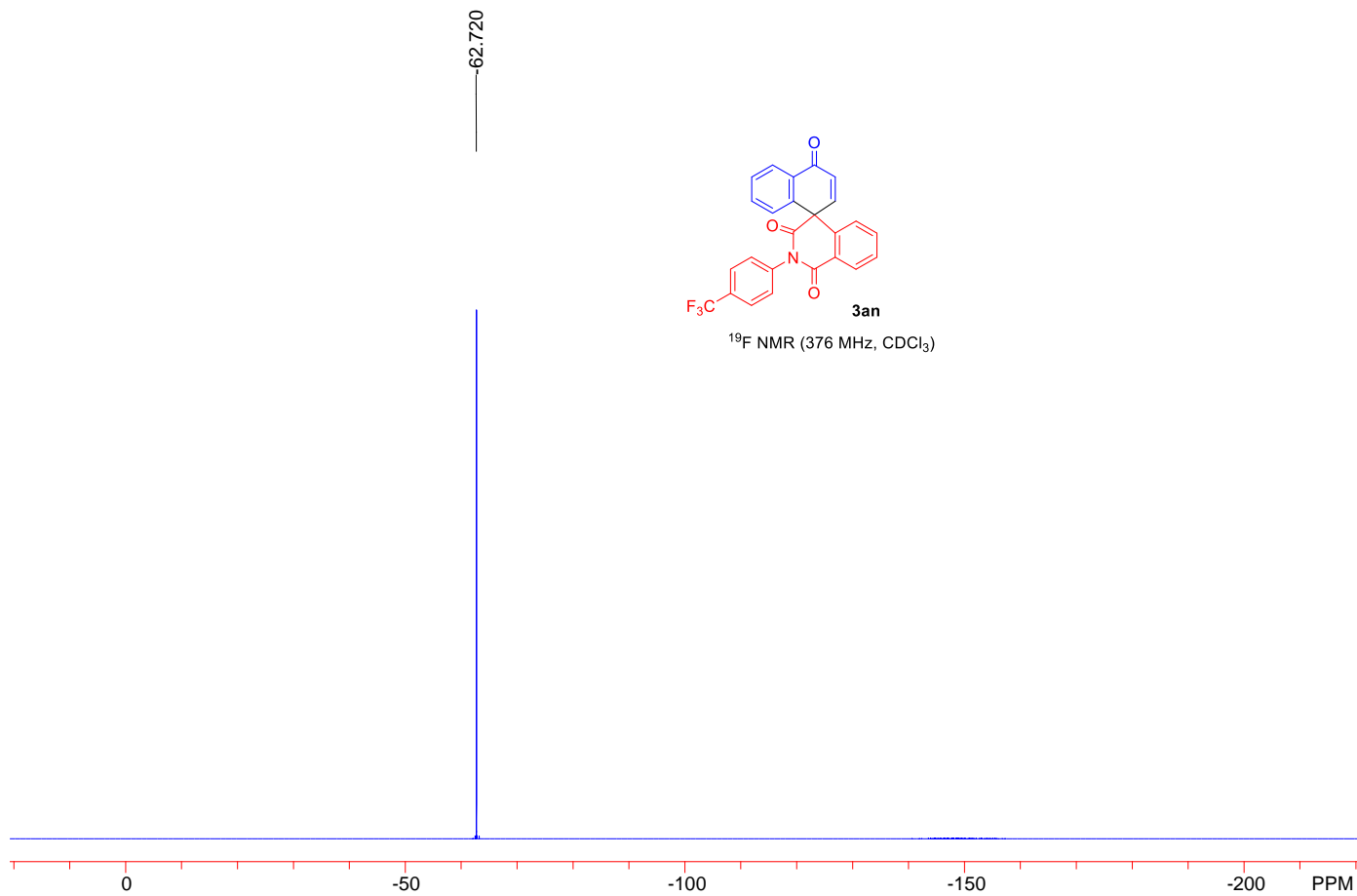


¹H NMR (600 MHz, CDCl₃)

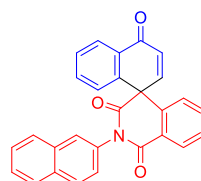


¹³C NMR (150 MHz, CDCl₃)

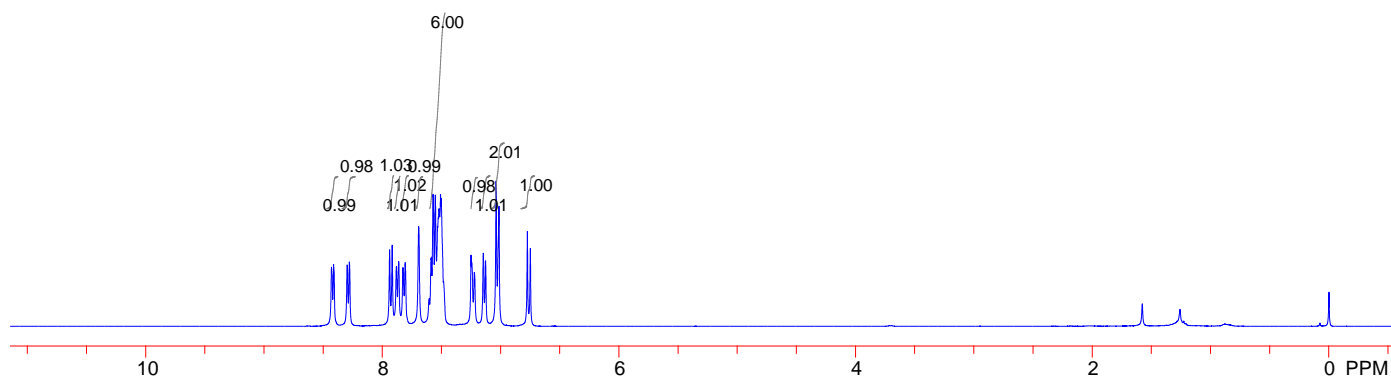




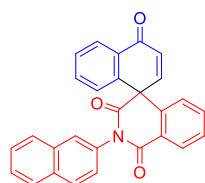
8.430
8.412
8.297
8.278
7.938
7.916
7.881
7.861
7.825
7.807
7.692
7.603
7.589
7.585
7.571
7.552
7.533
7.526
7.520
7.516
7.508
7.502
7.482
7.250
7.244
7.222
7.146
7.127
7.038
7.013
6.773
6.748



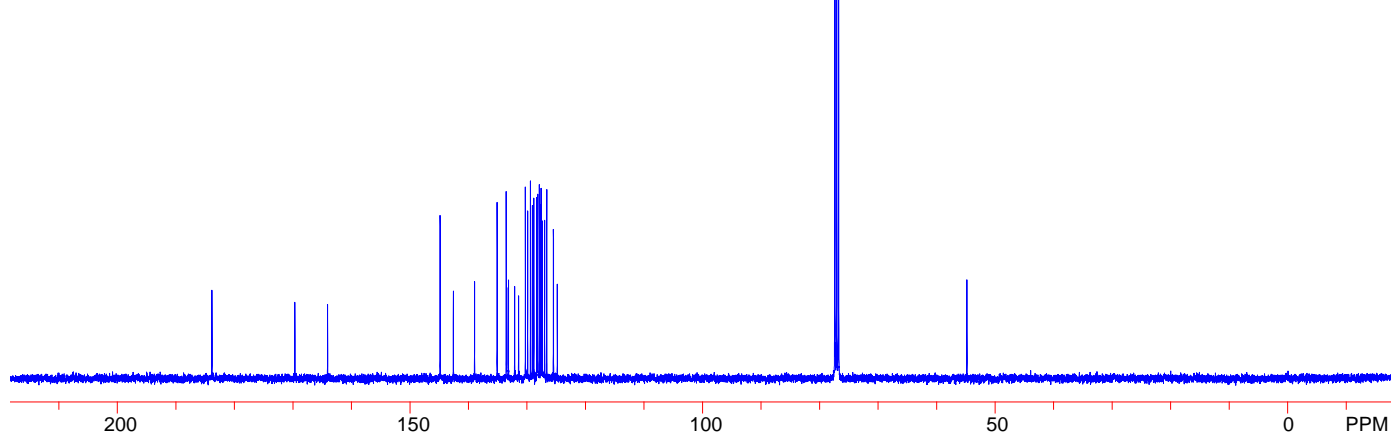
¹H NMR (400 MHz, CDCl₃)

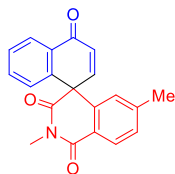
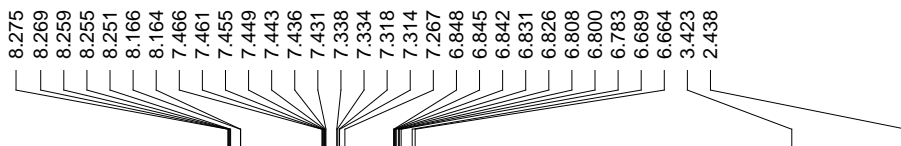


183.841
144.845
169.670
164.080
142.577
138.952
135.095
133.542
133.448
133.159
132.104
131.426
130.270
129.880
129.403
129.071
128.825
128.320
128.161
127.872
127.662
127.590
127.410
126.984
126.622
125.481
124.809
77.377
77.060
76.742
54.842

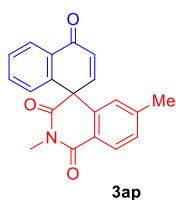
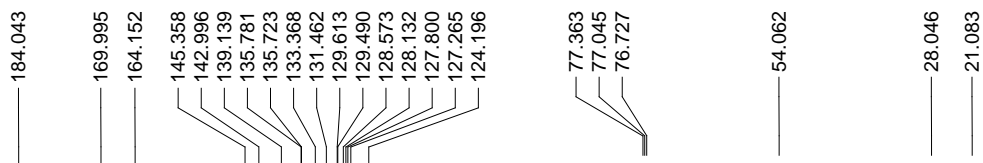
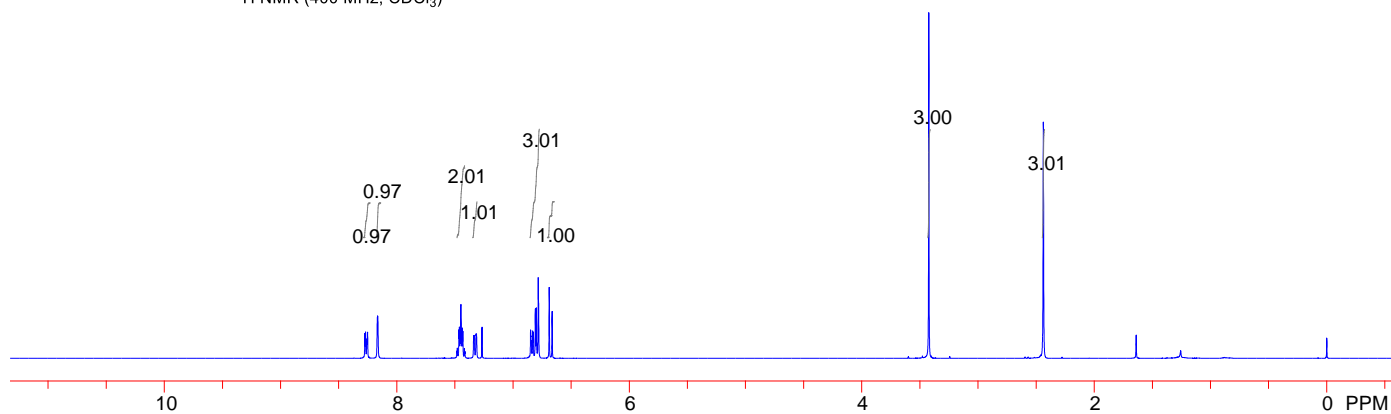


¹³C NMR (100 MHz, CDCl₃)

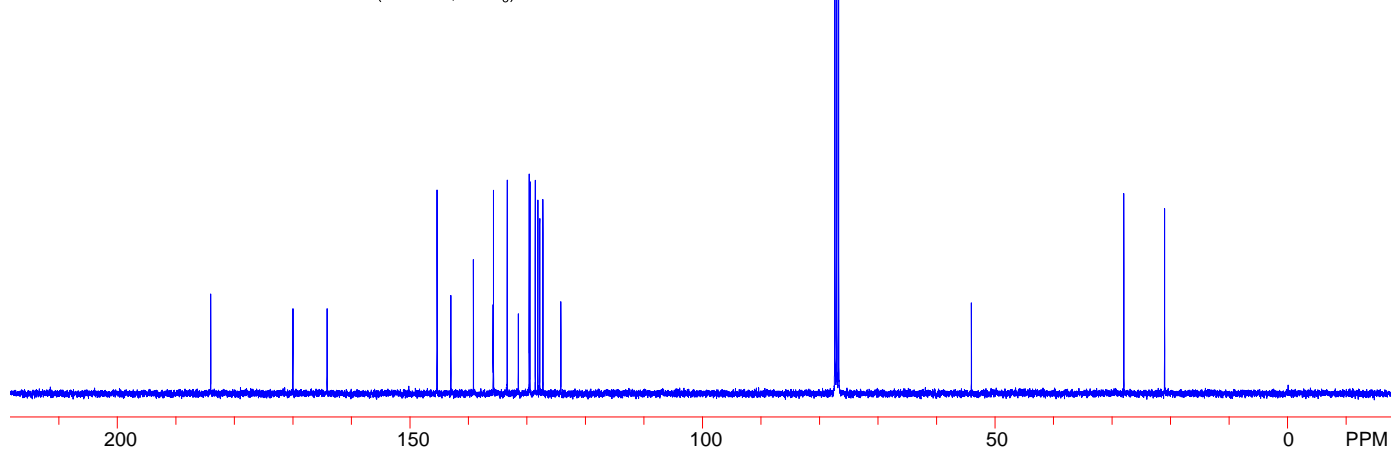




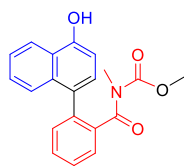
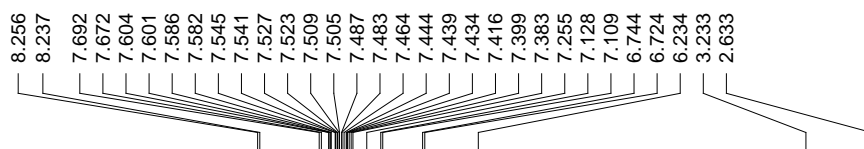
¹H NMR (400 MHz, CDCl₃)



¹³C NMR (100 MHz, CDCl₃)

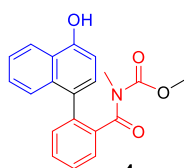
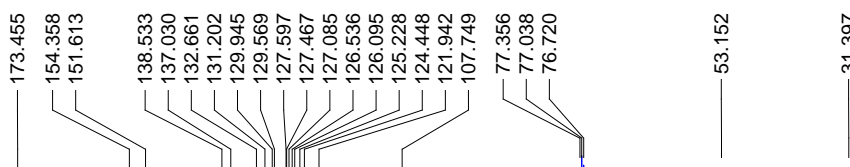
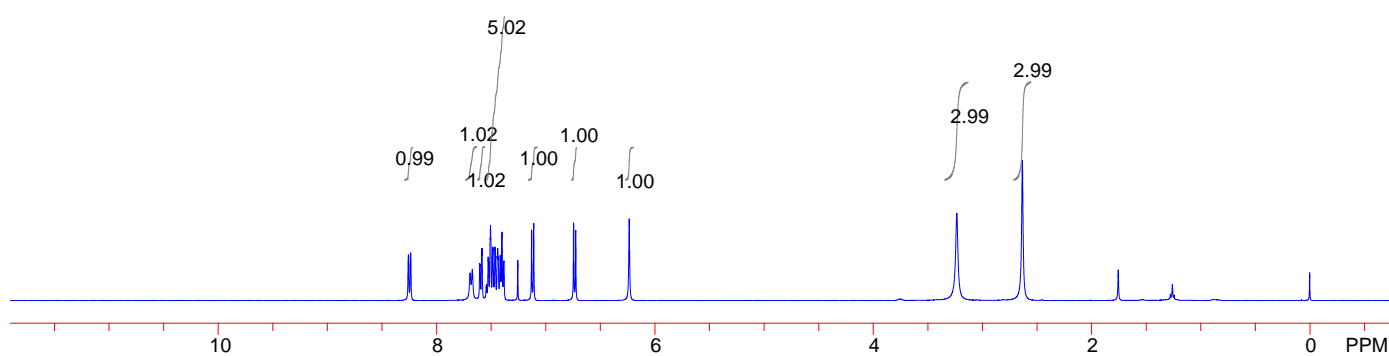


VII. Copies of NMR spectra of 4-7



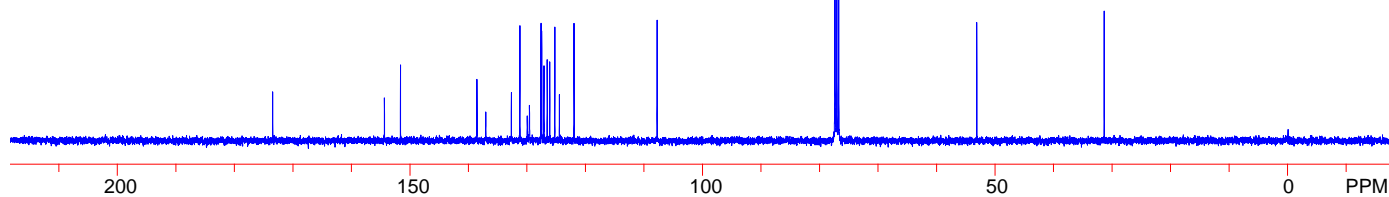
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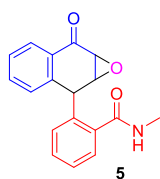
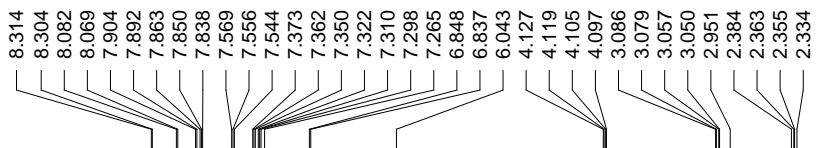
¹H NMR (400 MHz, CDCl₃)



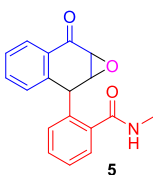
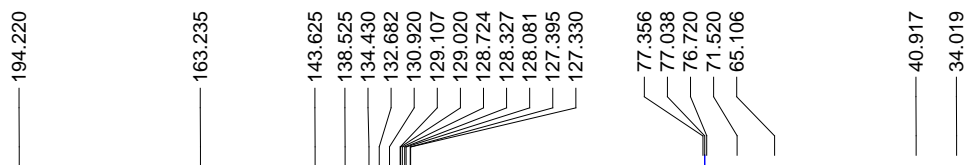
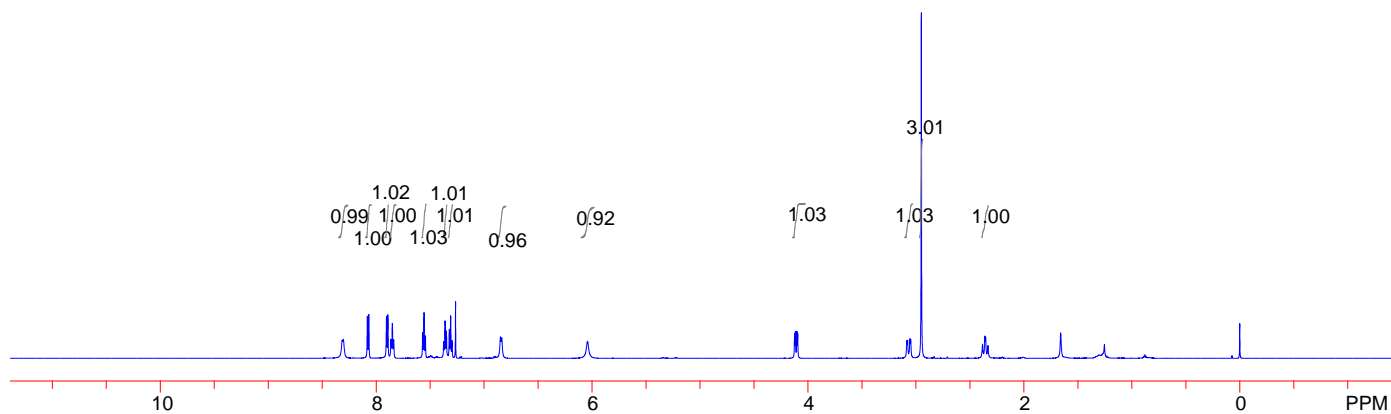
4

¹³C NMR (100 MHz, CDCl₃)

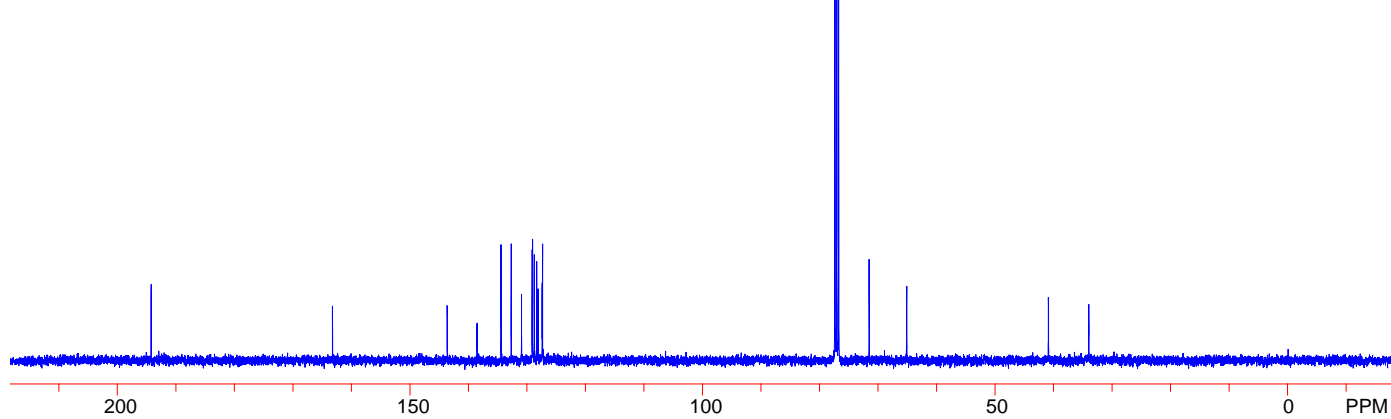




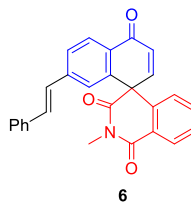
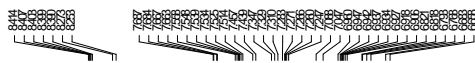
^1H NMR (600 MHz, CDCl_3)



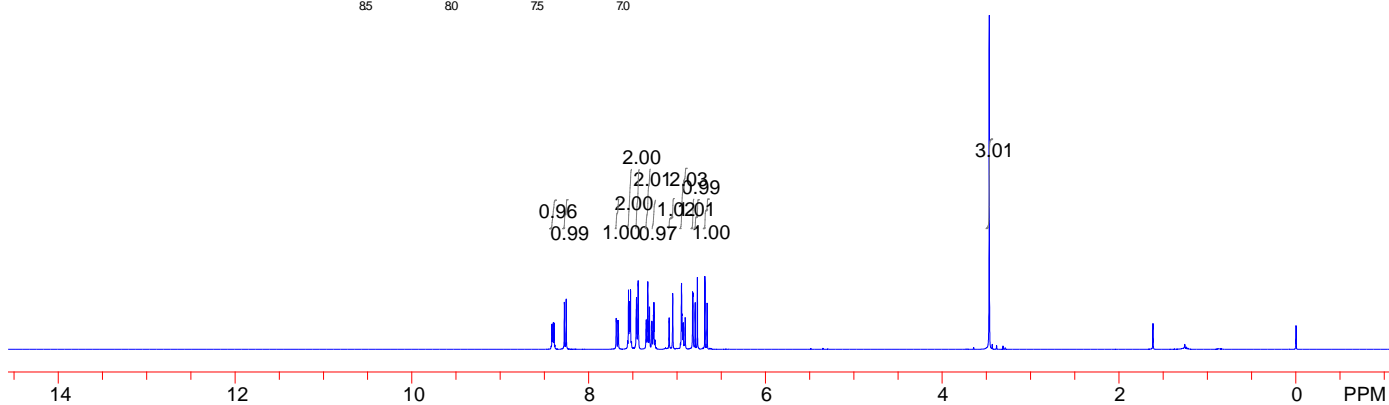
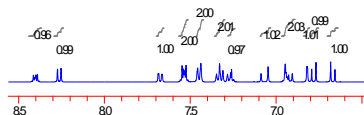
^{13}C NMR (100 MHz, CDCl_3)



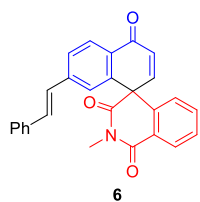
8.414
8.407
8.403
8.399
8.390
8.273
8.253
7.687
7.684
7.667
7.663
7.558
7.548
7.539
7.534
7.525
7.514
7.457
7.439
7.347
7.329
7.310
7.283
7.271
7.266
7.260
7.247
7.088
7.047
6.960
6.947
6.942
6.937
6.934
6.927
6.918
6.906
6.821
6.818
6.793
6.768
6.683
6.658
3.467



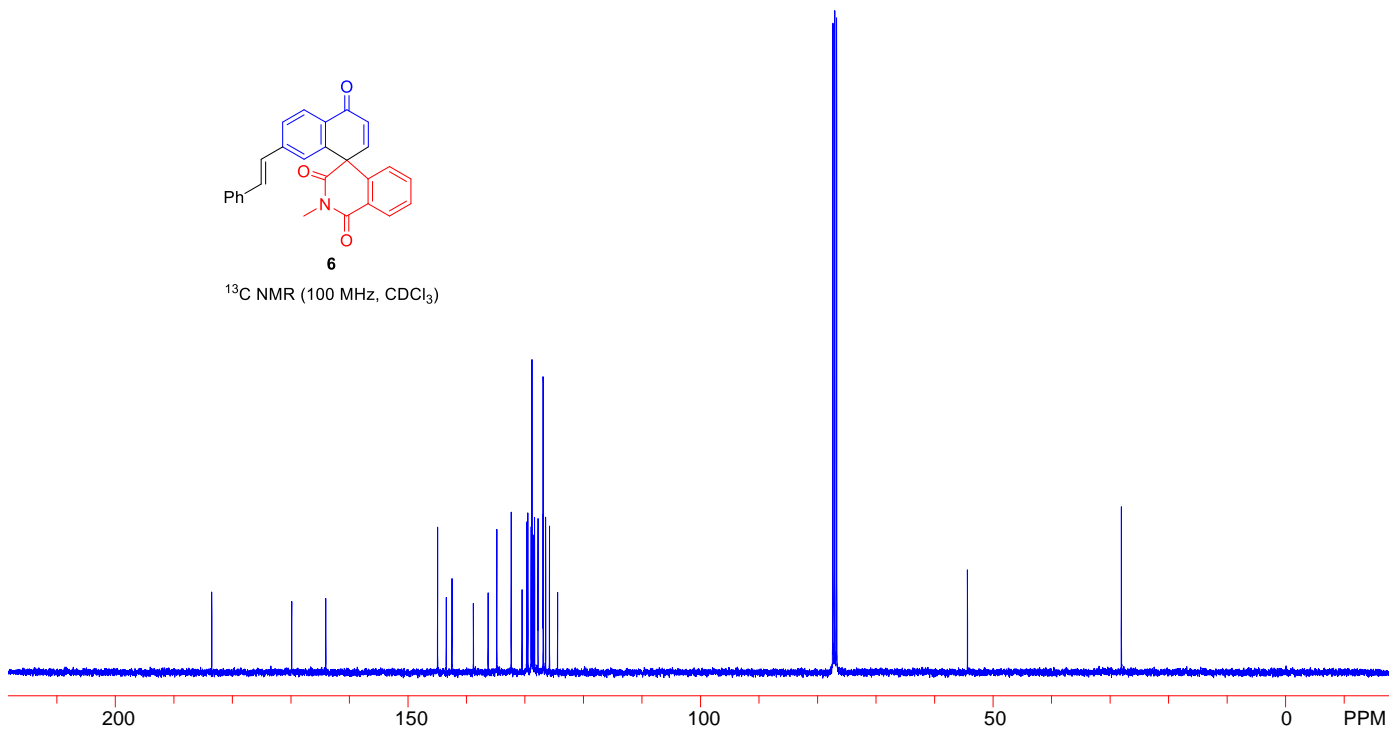
¹H NMR (400 MHz, CDCl₃)

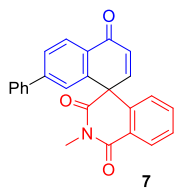
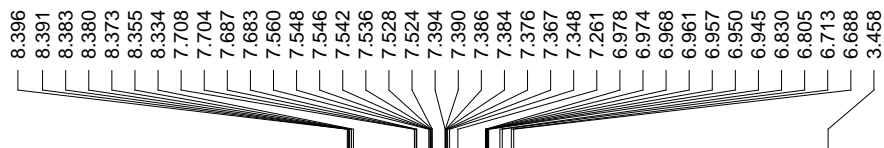


183.538
169.865
164.044
144.932
143.444
142.469
138.807
136.286
134.806
132.343
130.494
129.706
129.504
128.948
128.796
128.580
128.349
127.764
126.897
126.846
126.456
125.806
124.419
77.370
77.052
76.735
54.395
28.133

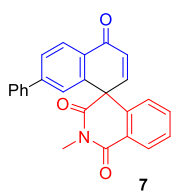
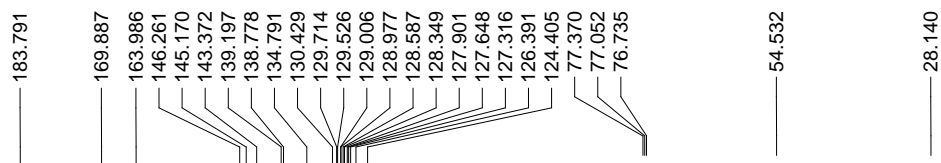
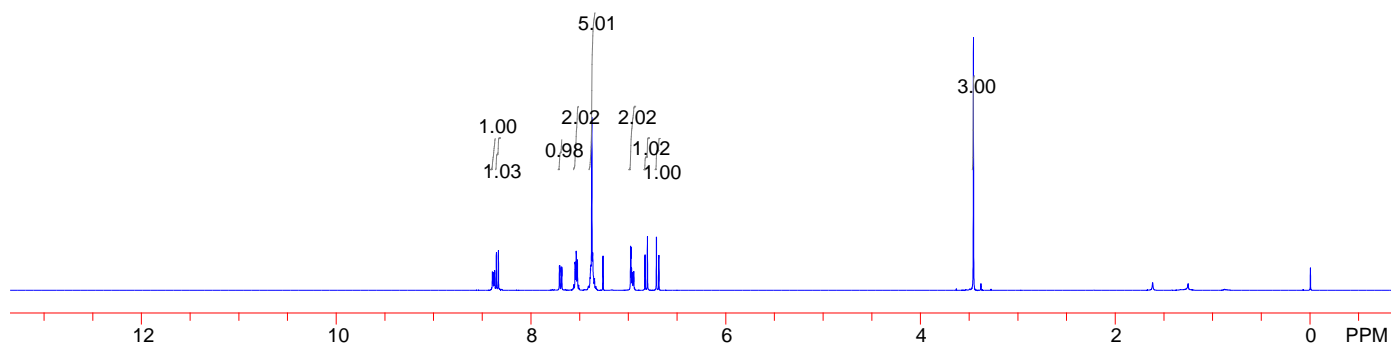


¹³C NMR (100 MHz, CDCl₃)

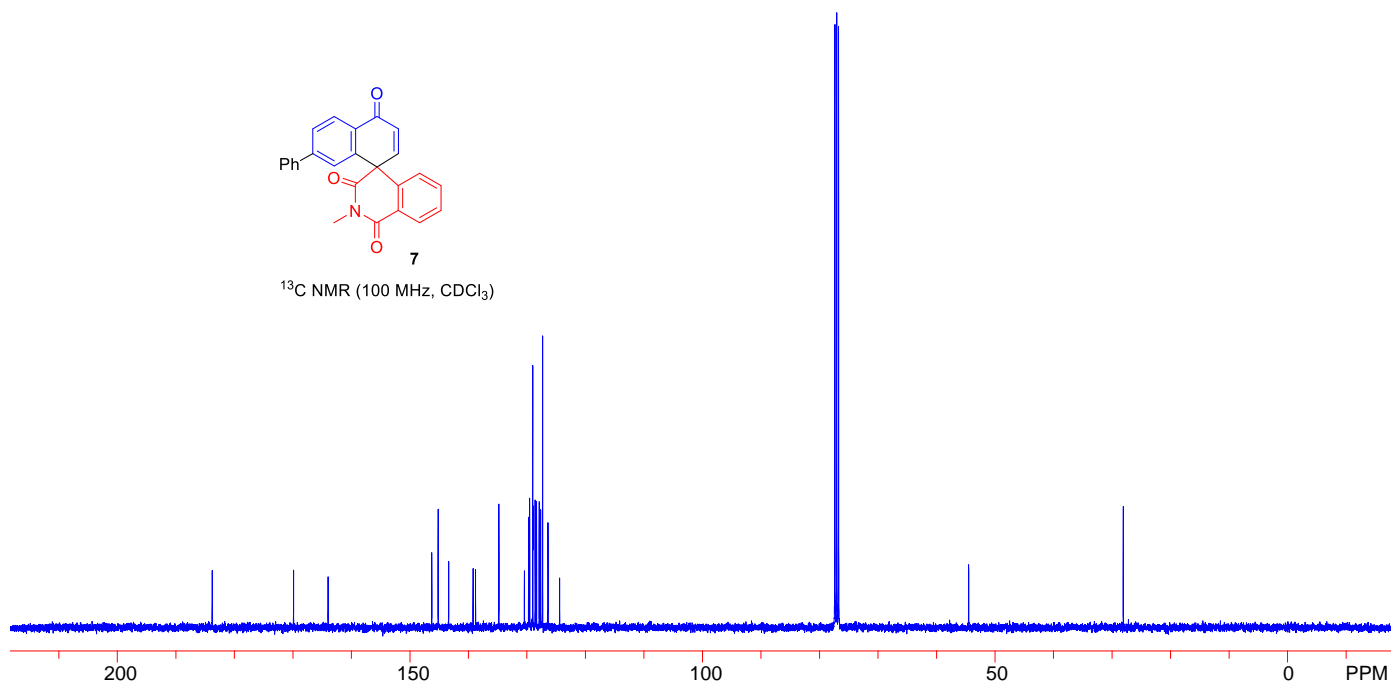




¹H NMR (400 MHz, CDCl₃)



¹³C NMR (100 MHz, CDCl₃)



VIII. References

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