Supporting Information

Visible light-mediated [2+2] cycloaddition reaction for dihydrocyclobuta[*b*]naphthalene-3,8-diones synthesis under mild conditions

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1. General procedure for preparing DHCBNDOs

In a 15 mL tube, 1,4-naphthoquinone **1** (1.0 mmol) and alkyne **2** (1.0 mmol) were dissolved in 10 mL of acetonitrile. The reaction mixture was under irradiation of visible blue LEDs (460 nm) for 4 h. After completion (by TLC), the reaction mixture was evaporated to dryness in a vacuo. The residue was purified by medium-pressure chromatography (silica gel) using a mixed solvent of hexane and ethyl acetate (5–30% EA).

(2aS,8aS)-8a-methyl-1-phenyl-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione (3aa)*:* Yellow solid, yield 86%, m.p. 154-156 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.83 (s, 3H, CH_3), 3.78 (d, 1H, *J*=1.2 Hz, C*H*), 6.55 (d, 1H, *J*=2.0 Hz, =CH_2), 7.27-7.34 (m, 3H, Ar-*H*), 7.49-7.51 (m, 2H, Ar-*H*), 7.68-7.71 (m, 2H, Ar-*H*), 8.01-8.06 (m, 2H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 19.8, 57.2, 57.5, 125.5, 127.0, 127.6, 128.0, 128.6, 129.1, 131.6, 133.7, 133.7, 134.4, 134.5, 153.4, 196.6, 198.4; HRMS (ESI), m/z calcd 275.1067 for $C_{19}H_{15}O_2$ $[M+H]^+$, found 275.1069.

(2aS,8aS)-1-(2-methoxyphenyl)-8a-methyl-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione (3ab)*:* Faint yellow solid, yield 85%, 152-154 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.74 (s, 3H, CH_3), 3.69 (s, 3H, OCH_3), 3.72 (d, 1H, *J*=1.6 Hz, C*H*), 6.54 (d, 1H, *J*=1.6 Hz, =CH_2), 6.72 (d, 1H, *J*=8.0 Hz, Ar-*H*), 6.85-6.88 (m, 1H, Ar-H), 7.12-7.16 (m, 1H, Ar-*H*), 7.48-7.59 (m, 3H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 20.0, 55.0, 57.5, 59.0, 110.4, 120.5, 120.6, 126.9, 127.8, 127.9, 127.9, 129.8, 132.9, 133.7, 134.0, 134.2, 134.3, 149.9, 158.9, 196.9, 199.0; HRMS (ESI), m/z calcd 305.1172 for $C_{20}H_{17}O_3$ $[M+H]^+$, found 305.1176.

(2aS,8aS)-1-(3,5-dimethoxyphenyl)-8a-methyl-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione (3ac)*:* Faint yellow solid, yield 88%, 151-153 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.74 (s, 3H, C*H*$_3$), 3.68 (d, 1H, *J*=1.6 Hz, C*H*), 3.70 (s, 6H, OC*H*$_3$), 6.31 (t, 1H, *J*=2.0 Hz, Ar-*H*), 6.46 (d, 1H, *J*=1.6 Hz, =C*H*$_2$), 6.58 (t, 2H, *J*=2.0 Hz, Ar-*H*), 7.61-7.64 (m, 2H, Ar-*H*), 7.93-7.99 (m, 2H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 19.9, 55.4, 57.1, 57.4, 101.6, 103.4, 127.0, 127.6, 128.0, 128.1, 133.2, 133.6, 133.7, 134.4, 134.5, 153.3, 161.0, 196.6, 198.3; HRMS (ESI), m/z calcd 335.1278 for $C_{21}H_{19}O_4$ $[M+H]^+$, found 335.1280.

(2aS,8aS)-1-(4-ethylphenyl)-8a-methyl-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione (3ad)*:* Yellow solid, yield 93%, 155-157 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.20 (t, 3H, *J*=7.6 Hz, C*H*$_3$), 1.83 (s, 3H, C*H*$_3$), 2.61 (q, 2H, *J*=7.6 Hz, C*H*$_2$), 3.77 (d, 1H, *J*=1.6 Hz, C*H*), 6.49 (d, 1H, *J*=1.6 Hz, =C*H*$_2$), 7.16 (d, 2H, *J*=8.4 Hz, Ar-*H*), 7.42 (d, 2H, *J*=8.4 Hz, Ar-*H*), 7.69-7.72 (m, 2H, Ar-*H*), 8.02-8.06 (m, 2H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 15.4, 19.8, 28.8, 57.1, 57.5, 125.6, 126.4, 127.0, 128.0, 128.1, 129.2, 133.7, 133.8, 134.3, 134.4, 145.6, 153.5, 196.9, 198.6; HRMS (ESI), m/z calcd 303.1380 for $C_{21}H_{19}O_2$ $[M+H]^+$, found 303.1385.

(2aS,8aS)-8a-methyl-1-(4-propylphenyl)-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione (3ae)*:* Yellow solid, yield 90%, 154-156 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.84 (t, 3H, *J*=7.2 Hz, C*H*$_3$), 1.53 (q, 2H, *J*=7.6 Hz, C*H*$_2$), 1.75 (s, 3H, C*H*$_3$), 2.47 (t, 2H, C*H*$_2$), 3.70 (d, 1H, *J*=1.6 Hz, C*H*), 6.40 (d, 1H, *J*=1.6 Hz, =C*H*$_2$), 7.06 (d, 2H, *J*=8.0 Hz, Ar-*H*), 7.34 (d, 2H, *J*=8.4 Hz, Ar-*H*), 7.62-7.65 (m, 2H, Ar-*H*), 7.94-7.99 (m, 2H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 13.8, 19.8, 24.4, 37.9, 57.1, 57.5, 125.5, 126.4, 127.0, 128.0, 128.7, 129.2, 133.7, 133.8, 134.3, 134.4, 144.0, 153.5, 196.9, 198.6; HRMS (ESI), m/z calcd 317.1536 for $C_{22}H_{21}O_2$ $[M+H]^+$, found 317.1539.

(2aS,8aS)-8a-methyl-1-(4-((1s,4S)-4-propylcyclohexyl)phenyl)-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione (3af)*:*Yellow solid, yield 95%, 149-151 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.89 (t, 3H, *J*=7.2 Hz, CH_3), 1.04-1.07 (m, 2H, CH_2), 1.18-1.22 (m, 2H, CH_2), 1.28-1.42 (m, 6H, CH_2), 1.82 (s, 3H, CH_3), 1.85 (s, 3H, CH_3), 2.40-2.46 (m, 1H, C*H*), 3.76 (d, 1H, *J*=1.6 Hz, C*H*), 6.48 (d, 1H, *J*=1.6 Hz, =CH_2), 7.17 (d, 2H, *J*=8.4 Hz, Ar-*H*), 7.42 (d, 2H, *J*=8.4 Hz, Ar-*H*), 7.68-7.72 (m, 2H, Ar-*H*), 8.01-8.06 (m, 2H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.4, 19.9, 20.0, 33.5, 34.1, 37.0, 39.7, 44.6, 57.1, 57.5, 125.5, 126.4, 127.0, 128.0, 129.3, 133.7, 133.7, 134.3, 134.4, 149.2, 153.5, 196.8, 198.5; HRMS (ESI), m/z calcd 399.2319 for $C_{28}H_{31}O_2$ $[M+H]^+$, found 399.2323.

(2aS,8aS)-1-(4-bromophenyl)-8a-methyl-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione (3ag)*:* Yellow solid, yield 83%, 165-167 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.72 (s, 3H, CH_3), 3.68 (d, 1H, *J*=1.6 Hz, C*H*), 6.48 (d, 1H, *J*=2.0 Hz, =CH_2), 7.28 (d, 2H, *J*=8.8 Hz, Ar-*H*), 7.36 (d, 2H, *J*=8.8 Hz, Ar-*H*), 7.62-7.65 (m, 2H, Ar-*H*), 7.94-7.98 (m, 2H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 19.8, 57.1, 57.5, 123.3, 127.1, 127.1, 128.0, 128.3, 130.3, 131.9, 133.5, 133.6, 134.5, 134.6, 152.2, 196.2, 198.2; HRMS (ESI), m/z calcd 353.0172 for $C_{19}H_{14}BrO_2$ $[M+H]^+$, found 353.0176.

(2aS,8aS)-8a-methyl-1-(4-nitrophenyl)-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione (3ah)*:* Yellow solid, yield 80%, 173-175 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.78 (s, 3H, CH_3), 3.78 (d, 1H, *J*=1.6 Hz, C*H*), 6.72 (d, 1H, *J*=2.0 Hz, =CH_2), 7.62 (d, 2H, *J*=8.8 Hz, Ar-*H*), 7.68-7.71 (m, 2H, Ar-*H*), 7.99-8.03 (m, 2H, Ar-*H*), 8.11 (d, 2H, *J*=8.8 Hz, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 19.9, 57.2, 57.7, 124.0, 126.4, 127.2, 128.2, 133.4, 133.6, 134.8, 134.8,

137.1, 147.6, 151.1, 195.4, 197.6; HRMS (ESI), m/z calcd 320.0917 for $C_{19}H_{14}NO_4$ $[M+H]^+$, found 320.0921.

4-((2aS,8aS)-8a-methyl-3,8-dioxo-2a,3,8,8a-tetrahydrocyclobuta[b]naphthalen-1-yl)benzonitrile (3ai)*:* Yellow solid, yield 82%, 170-172 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.75 (s, 3H, C*H*$_3$), 3.75 (br s, 1H, C*H*), 6.66 (br s, 1H, =C*H*$_2$), 7.54 (br s, 4H, Ar-*H*), 7.66-7.68 (m, 2H, Ar-*H*), 7.96-8.01 (m, 2H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 19.9, 57.2, 57.6, 112.3, 118.5, 126.1, 127.2, 128.1, 131.7, 132.4, 133.4, 133.6, 134.7, 134.7, 135.3, 151.4, 195.5, 197.7; HRMS (ESI), m/z calcd 300.1019 for $C_{20}H_{14}NO_2$ $[M+H]^+$, found 300.1022.

(2aS,8aS)-8a-methyl-1-(pyridin-3-yl)-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione (3aj)*:* Yellow solid, yield 93%, 168-170 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.74 (s, 3H, C*H*$_3$), 3.74 (d, 1H, *J*=1.6 Hz, C*H*), 6.59 (d, 1H, *J*=2.0 Hz, =C*H*$_2$), 6.17 (dd, 1H, *J*=8.0 Hz, 4.8 Hz, Ar-*H*), 7.63-7.66 (m, 2H, Ar-*H*), 7.74 (dt, 1H, *J*=8.0 Hz, 2.0 Hz, Ar-*H*), 7.94-7.99 (m, 2H, Ar-*H*), 8.39 (dd, 1H, *J*=4.8 Hz, 1.6 Hz, Ar-*H*), 8.65 (d, 1H, *J*=2.0 Hz, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 19.8, 57.2, 57.7, 123.5, 127.1, 127.4, 128.0, 129.9, 132.7, 133.6, 134.6, 134.6, 147.0, 149.6, 150.5, 195.9, 197.8; HRMS (ESI), m/z calcd 276.1019 for $C_{18}H_{14}NO_2$ $[M+H]^+$, found 276.1024.

(2aS,8aS)-8a-methyl-1-(thiophen-2-yl)-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione (3ak)*:* Faint yellow solid, yield 91%, 164-166 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.72 (s, 3H, C*H*$_3$), 3.71 (d, 1H, *J*=1.6 Hz, C*H*), 6.17 (d, 1H, *J*=1.6 Hz, =C*H*$_2$), 6.90 (dd, 1H, *J*=4.8 Hz, 3.6 Hz, Ar-*H*), 7.18-7.20 (m, 2H, Ar-*H*), 7.61-7.64 (m, 2H, Ar-*H*), 7.94-7.99 (m, 2H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 19.7, 57.5, 57.8, 125.0, 126.7, 126.8, 127.2, 127.7, 128.0, 133.4,

133.8, 134.4, 134.5, 134.5, 147.6, 196.2, 197.5; HRMS (ESI), m/z calcd 281.0631 for $C_{17}H_{13}O_2S$ $[M+H]^+$, found 281.0635.

(2aS,8aS)-2a-methyl-1,2-diphenyl-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione (3al): Yellow solid, yield 83%, 160-162 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.80 (s, 3H, C*H*$_3$), 4.21 (s, 1H, C*H*), 7.28-7.37 (m, 6H, Ar-*H*), 7.51-7.55 (m, 4H, Ar-*H*), 7.68-7.77 (m, 2H, Ar-*H*), 7.93 (dd, 1H, *J*=7.6 Hz, 1.2 Hz, Ar-*H*), 8.13 (dd, 1H, *J*=7.6 Hz, 1.2 Hz, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 19.3, 55.5, 58.5, 126.9, 127.0, 127.0, 127.9, 128.5, 128.7, 128.9, 128.9, 132.8, 132.8, 133.9, 134.0, 134.3, 134.5, 140.6, 145.0, 196.7, 198.6; HRMS (ESI), m/z calcd 351.1380 for $C_{25}H_{19}O_2$ $[M+H]^+$, found 351.1385.

(2aS,8aS)-2a-methyl-3,8-dioxo-2-phenyl-2a,3,8,8a-tetrahydrocyclobuta[b]naphthalene-1-carb aldehyde (3am): Faint yellow solid, yield 85%, 173-175 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.81 (s, 3H, C*H*$_3$), 4.00 (s, 1H, C*H*), 7.33-7.39 (m, 3H, Ar-*H*), 7.63-7.68 (m, 2H, Ar-*H*), 7.84 (dd, 2H, *J*=8.0 Hz, 2.0 Hz, Ar-*H*), 7.94 (d, 1H, *J*=7.6 Hz, Ar-*H*), 9.85 (s, 1H, C*H*O); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 20.3, 56.2, 127.4, 128.0, 129.1, 129.3, 130.8, 132.0, 133.5, 133.8, 134.6, 134.9, 135.0, 161.1, 185.0, 194.4, 196.7; HRMS (ESI), m/z calcd 303.1016 for $C_{20}H_{15}O_3$ $[M+H]^+$, found 303.1020.

(2aS,8aS)-1-butyl-8a-methyl-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione (3an): Faint yellow oil, yield 95%; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.83 (t, 3H, *J*=7.2 Hz, C*H*$_3$), 1.21-1.39 (m, 4H, C*H*$_2$), 1.59 (s, 3H, C*H*$_3$), 1.92-2.08 (m, 2H, C*H*$_2$), 3.62 (d, 1H, *J*=1.2 Hz, C*H*), 6.01 (d, 1H, *J*=1.2 Hz, =C*H*$_2$), 7.74-7.76 (m, 2H, Ar-*H*), 8.03-8.10 (m, 2H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 13.7, 18.9, 22.3, 27.0, 27.5, 57.1, 58.0, 127.1, 127.6, 128.8, 133.4,

133.8, 134.3, 134.3, 159.1, 197.6, 198.1; HRMS (ESI), m/z calcd 255.1380 for $C_{17}H_{19}O_2$ $[M+H]^+$, found 255.1385.

***(2aS,8aS)-8a-methyl-1-pentyl-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione (3ao)**:* Faint yellow oil, yield 96%; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.82 (t, 3H, *J*=7.2 Hz, C*H*$_3$), 1.18-1.25 (m, 4H, C*H*$_2$), 1.36-1.40 (m, 2H, C*H*$_2$), 1.58 (s, 3H, C*H*$_3$), 1.91-2.06 (m, 2H, C*H*$_2$), 3.61 (d, 1H, *J*=1.2 Hz, C*H*), 6.01 (d, 1H, *J*=1.2 Hz, =C*H*$_2$), 7.74-7.76 (m, 2H, Ar-*H*), 8.03-8.10 (m, 2H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 13.9, 18.8, 22.3, 25.1, 27.3, 31.4, 57.1, 58.0, 127.1, 127.6, 128.8, 133.4, 133.7, 134.2, 134.3, 159.2, 197.5, 198.0; HRMS (ESI), m/z calcd 269.1536 for $C_{18}H_{21}O_2$ $[M+H]^+$, found 269.1539.

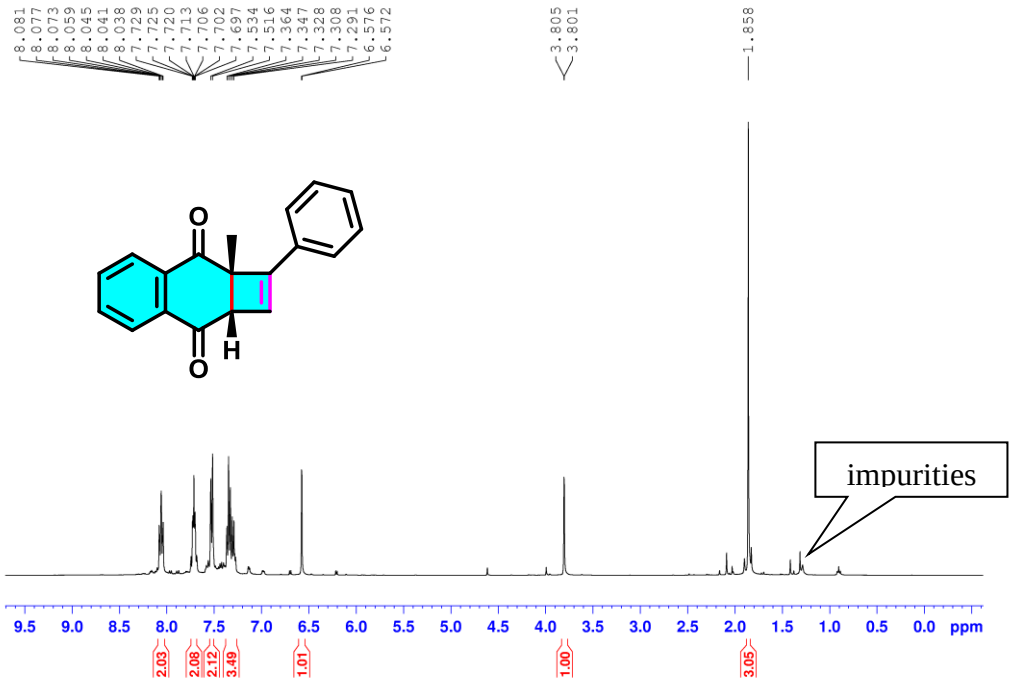
***(2aS,8aS)-1-phenyl-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione (3ba)**:* Yellow solid, yield 87%, 153-155 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.06 (dd, 1H, *J*=4.0 Hz, 1.6 Hz, C*H*), 4.45 (d, 1H, *J*=4.0 Hz, C*H*), 6.49 (d, 1H, *J*=0.8 Hz, =C*H*$_2$), 7.22-7.29 (m, 3H, Ar-*H*), 7.47-7.49 (m, 2H, Ar-*H*), 7.64-7.68 (m, 2H, Ar-*H*), 7.94-8.03 (m, 2H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 49.1, 52.2, 125.5 127.6, 127.8, 128.6, 129.2, 132.0, 133.7, 134.0, 134.6, 149.2, 195.6; HRMS (ESI), m/z calcd 261.0910 for $C_{18}H_{13}O_2$ $[M+H]^+$, found 261.0915.

***(2aR,8aR)-8a-chloro-1-phenyl-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione (3ca)**:* Faint yellow solid, yield 90%, 159-161 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.32 (d, 1H, *J*=1.6 Hz, C*H*), 6.74 (d, 1H, *J*=1.6 Hz, =C*H*$_2$), 7.35-7.40 (m, 3H, Ar-*H*), 7.64-7.67 (m, 2H, Ar-*H*), 7.74-7.82 (m, 2H, Ar-*H*), 8.06-8.14 (m, 2H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 61.6, 68.3, 126.2, 127.4, 128.7, 129.0, 129.2, 130.0, 132.3, 133.1, 135.0, 149.6, 190.0, 193.8; HRMS (ESI), m/z calcd 295.0520 for $C_{18}H_{12}ClO_2$ $[M+H]^+$, found 295.0525.

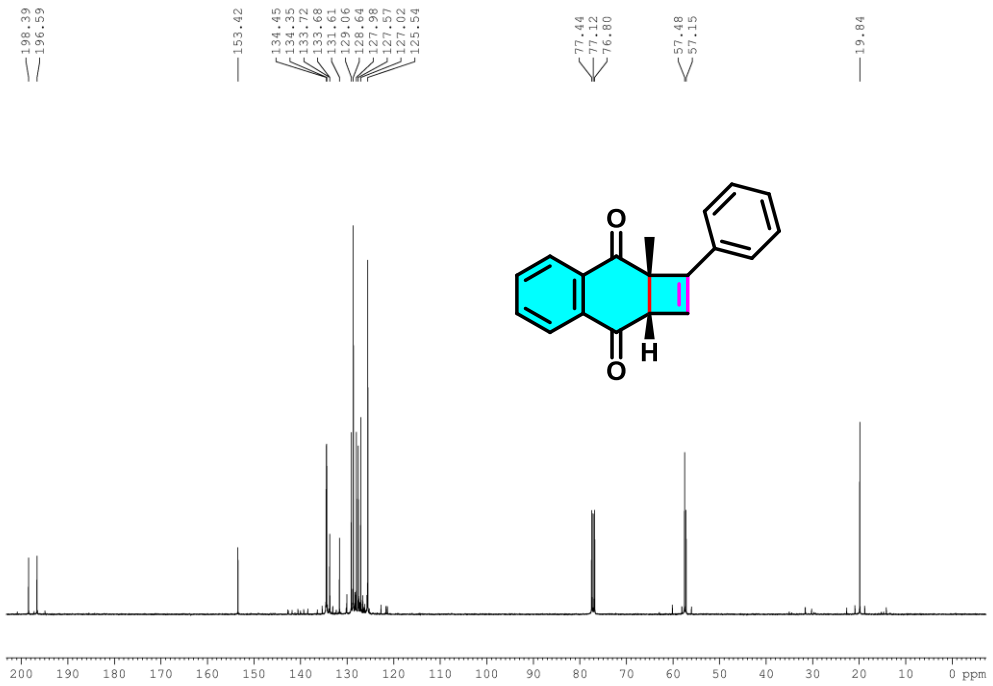
(2aS,8aR)-2a,8a-dichloro-1-phenyl-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione (3da):

Faint yellow solid, yield 92%, 163-165 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.73 (s, 1H, =CH_2), 7.39-7.41 (m, 3H, Ar-*H*), 7.65-7.67 (m, 2H, Ar-*H*), 7.79-7.83 (m, 2H, Ar-*H*), 8.09-8.18 (m, 2H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 127.2, 127.4, 128.3, 128.4, 128.7, 128.9, 128.9, 131.2, 131.4, 131.7, 131.7, 135.4, 135.5, 152.6, 188.4, 188.6; HRMS (ESI), m/z calcd 329.0131 for $C_{18}H_{11}ClO_2$ $[M+H]^+$, found 329.0131.

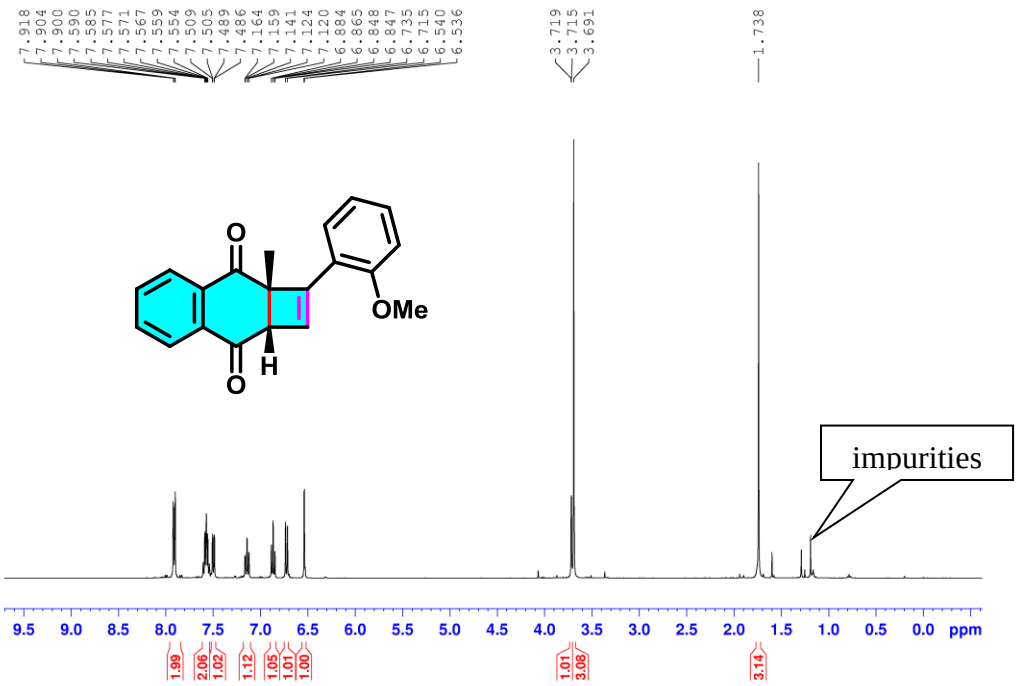
2. Structure characterization spectra of DHCBNDOs



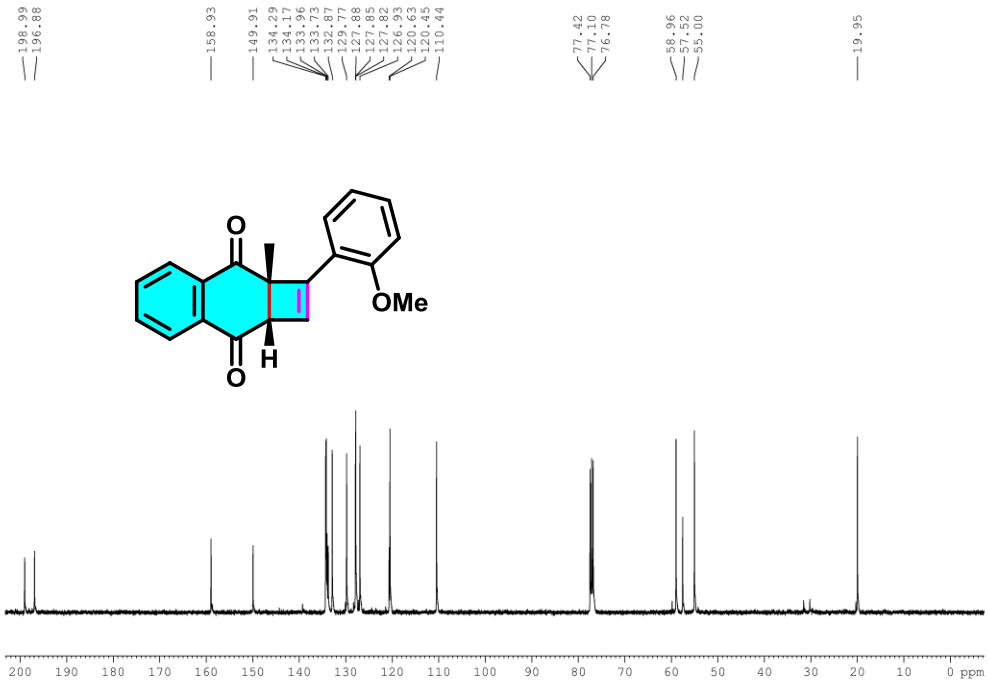
SI-Fig. 1. ^{1}H NMR spectrum of compound **3aa**.



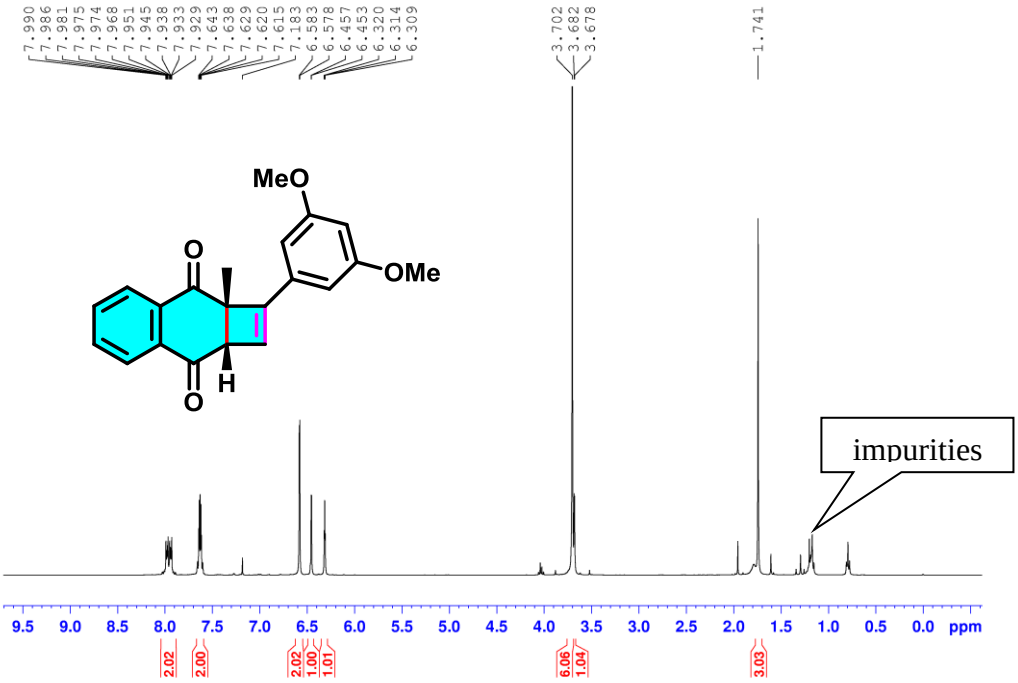
SI-Fig. 2. ^{13}C NMR spectrum of compound **3aa**.



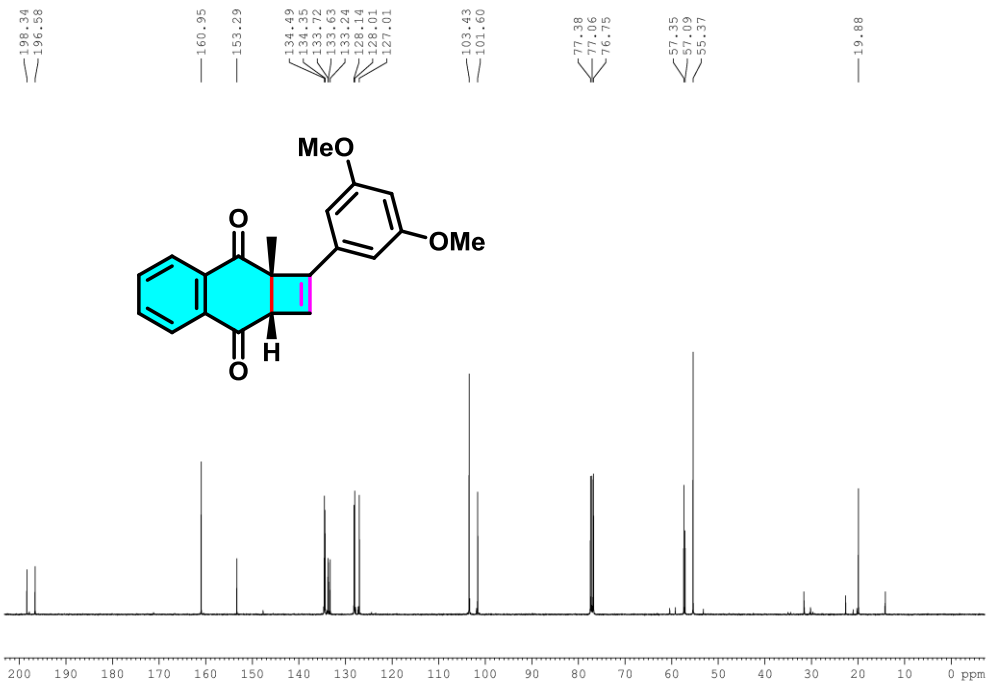
SI-Fig. 3. ^{1}H NMR spectrum of compound **3ab**.



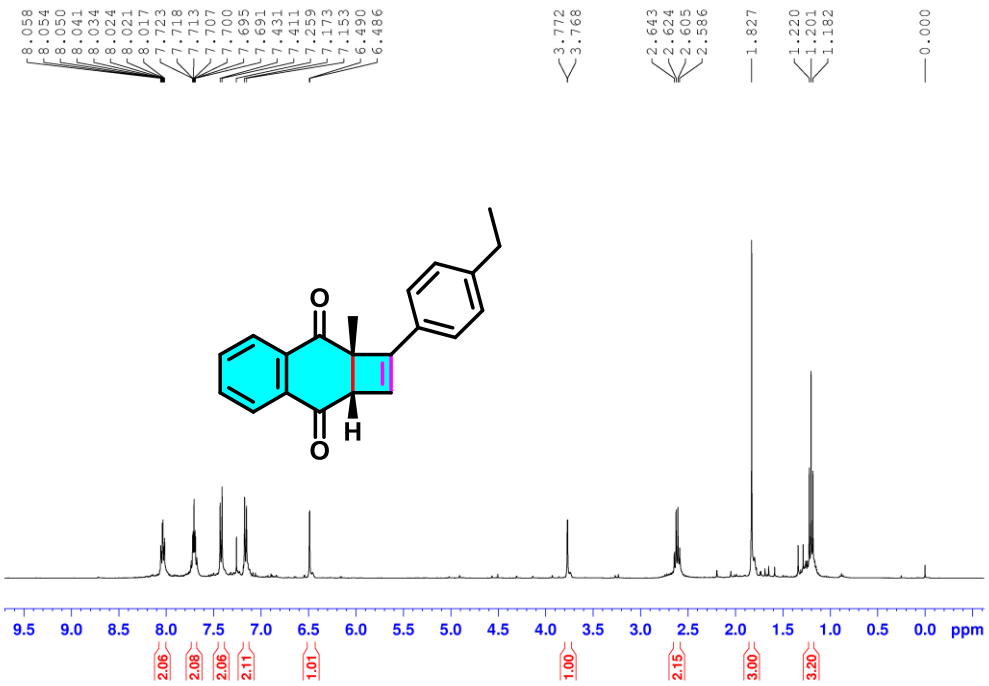
SI-Fig. 4. ^{13}C NMR spectrum of compound **3ab**.



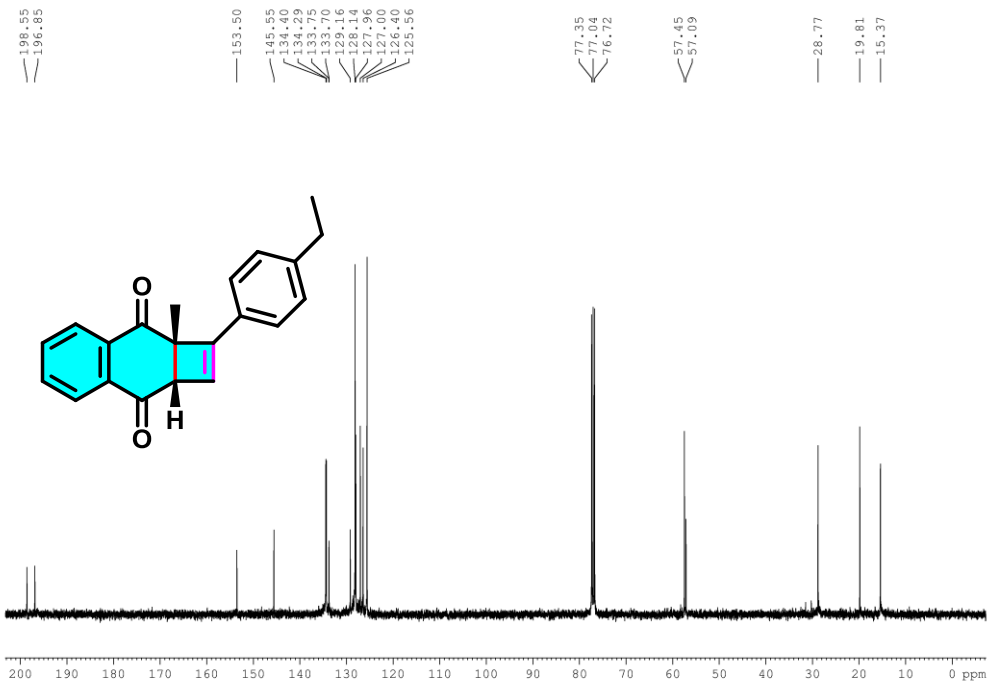
SI-Fig. 5. ^{1}H NMR spectrum of compound **3ac**.



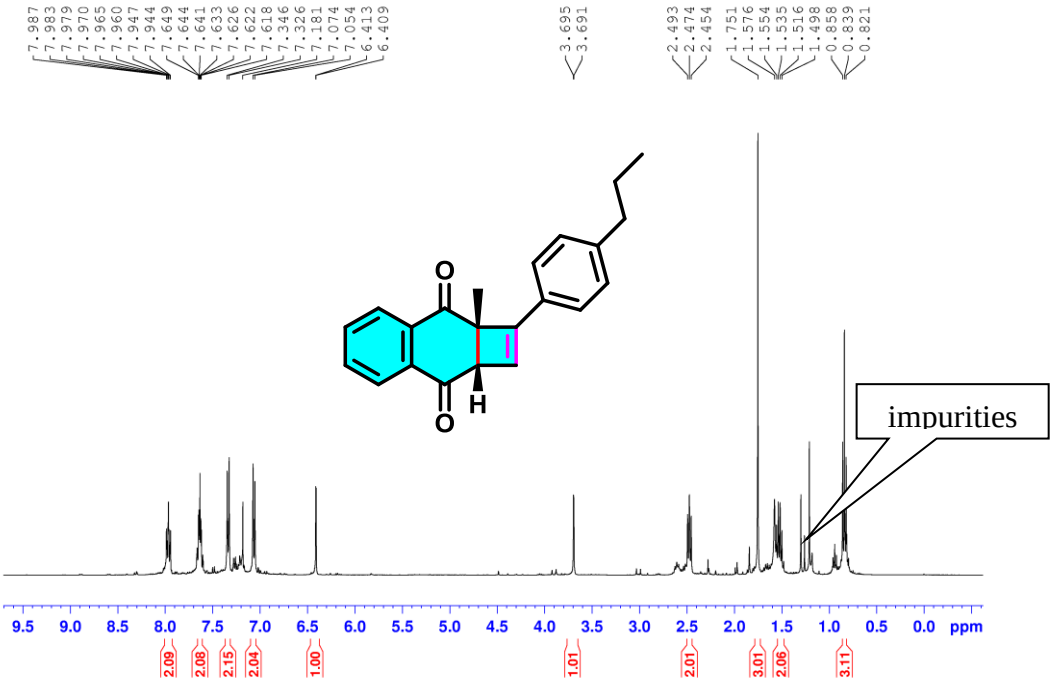
SI-Fig. 6. ^{13}C NMR spectrum of compound **3ac**.



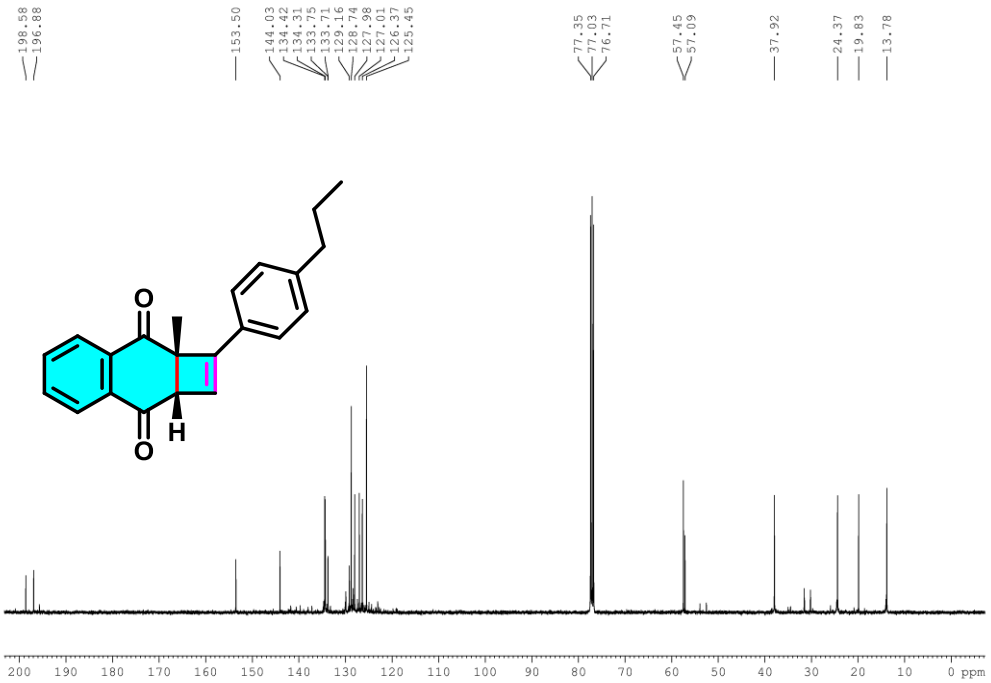
SI-Fig. 7. ^{1}H NMR spectrum of compound **3ad**.



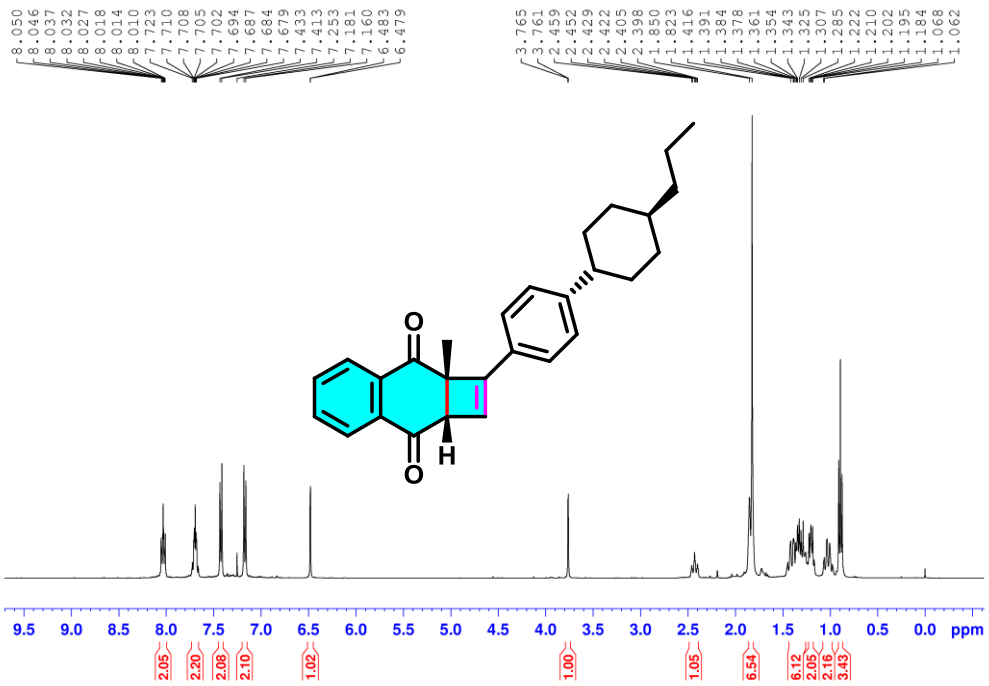
SI-Fig. 8. ^{13}C NMR spectrum of compound **3ad**.



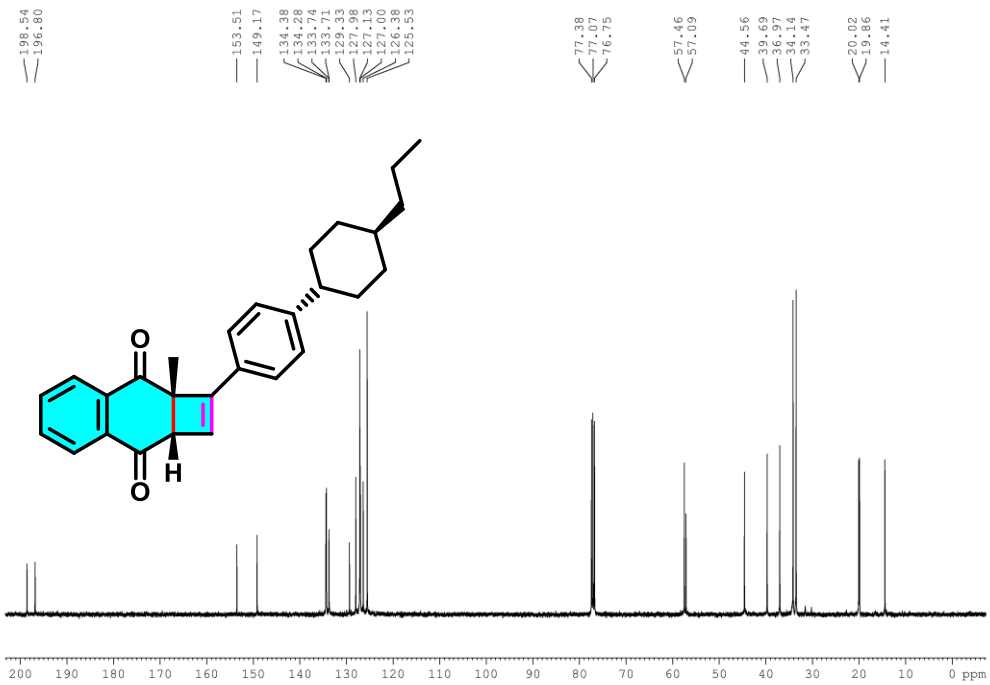
SI-Fig. 9. ^{1}H NMR spectrum of compound **3ae**.



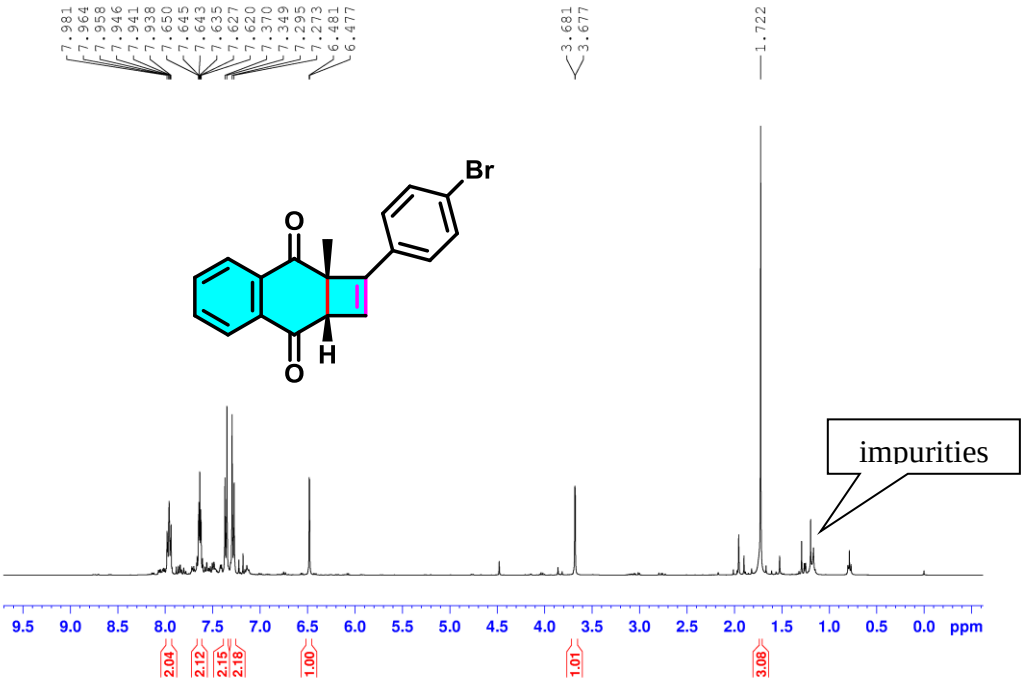
SI-Fig. 10. ^{13}C NMR spectrum of compound **3ae**.



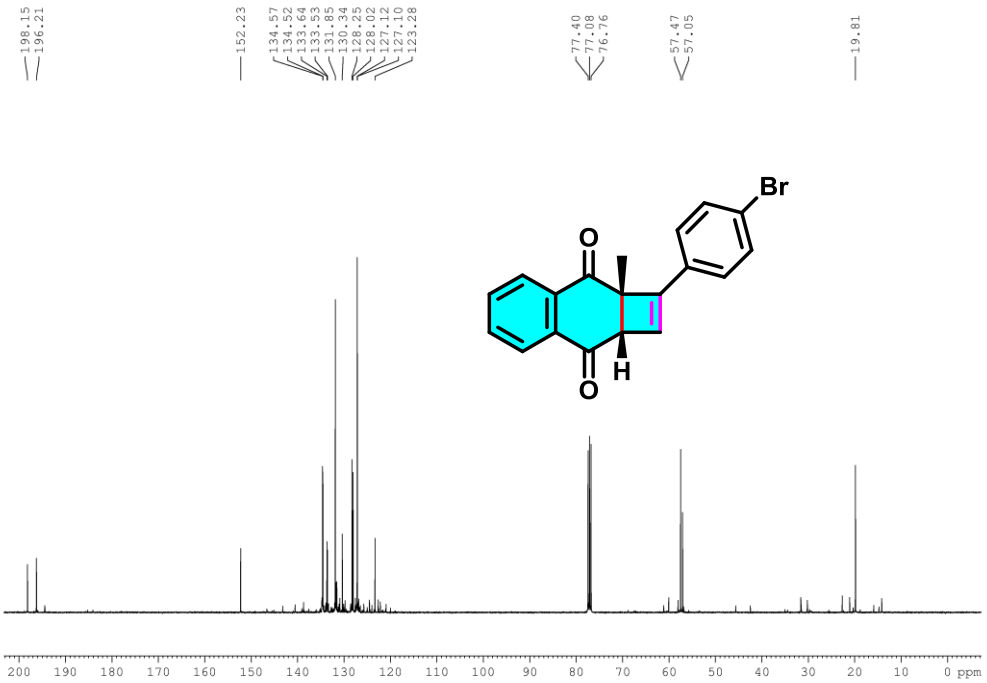
SI-Fig. 11. ^{1}H NMR spectrum of compound **3af**.



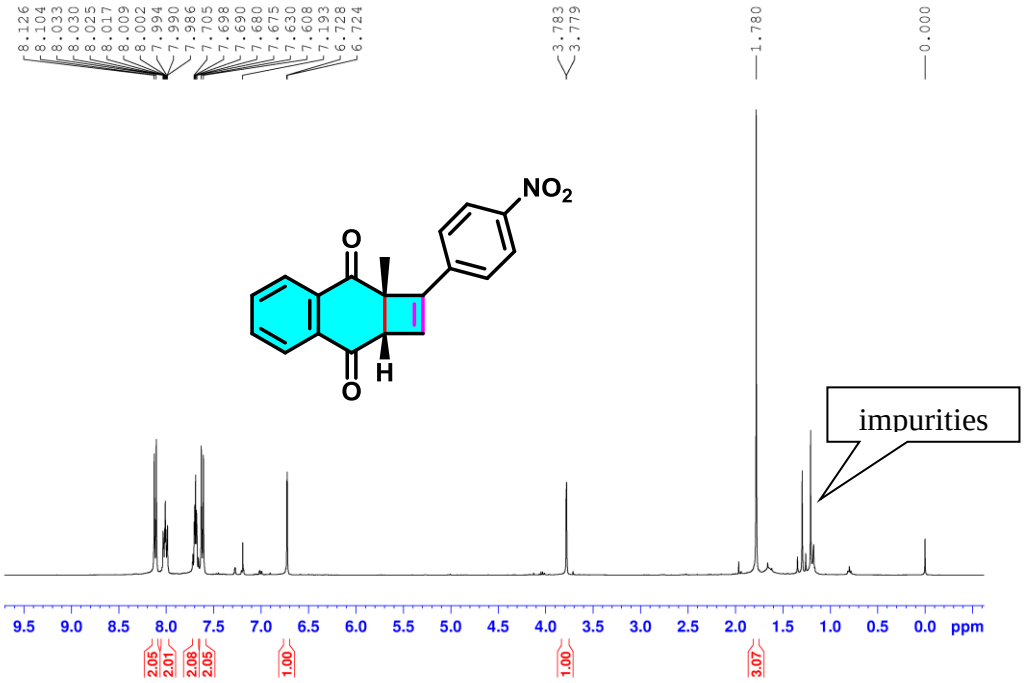
SI-Fig. 12. ^{13}C NMR spectrum of compound **3af**.



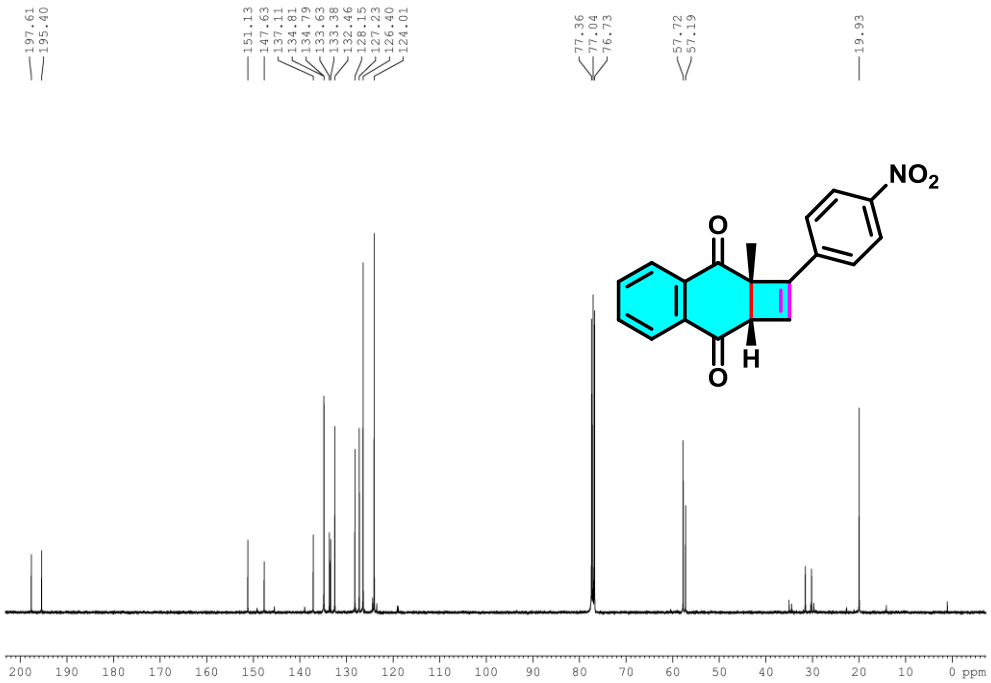
SI-Fig. 13. ^{1}H NMR spectrum of compound **3ag**.



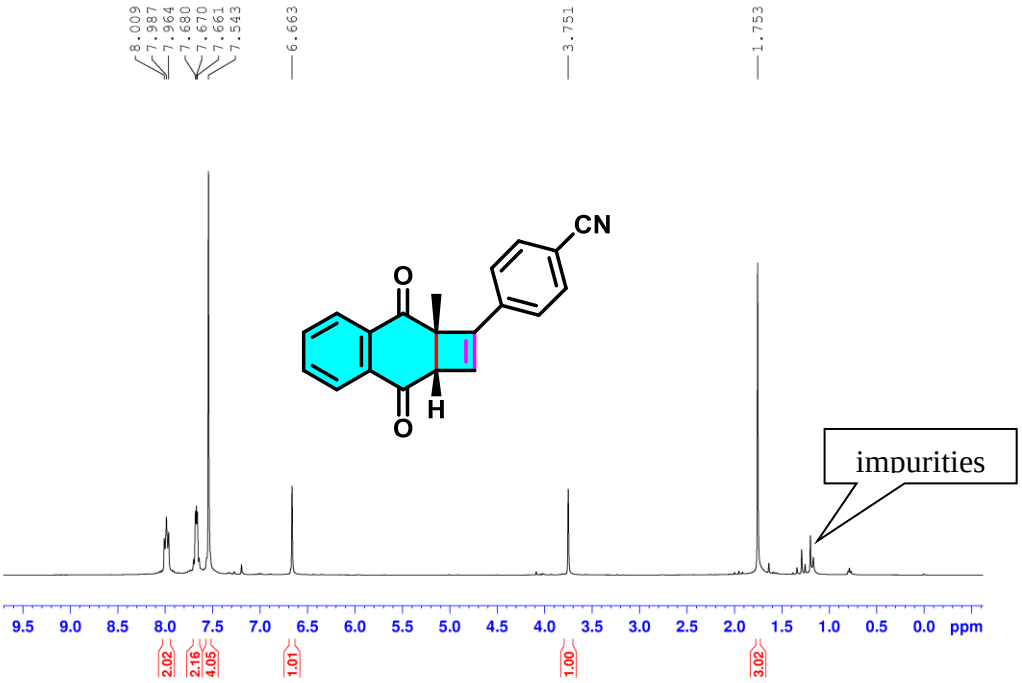
SI-Fig. 14. ^{13}C NMR spectrum of compound **3ag**.



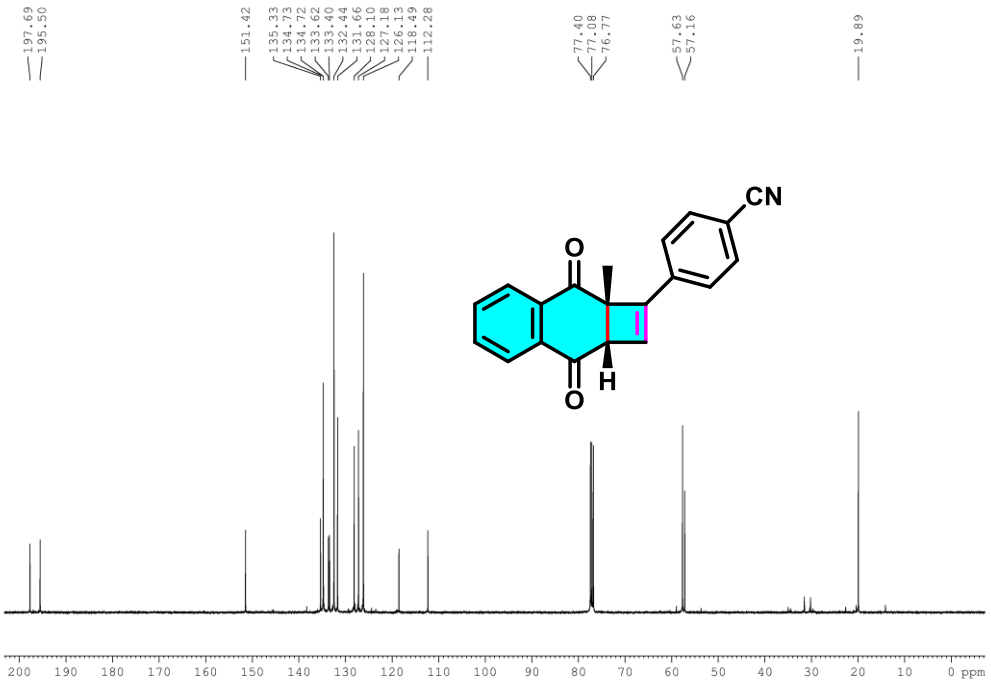
SI-Fig. 15. ^{1}H NMR spectrum of compound **3ah**.



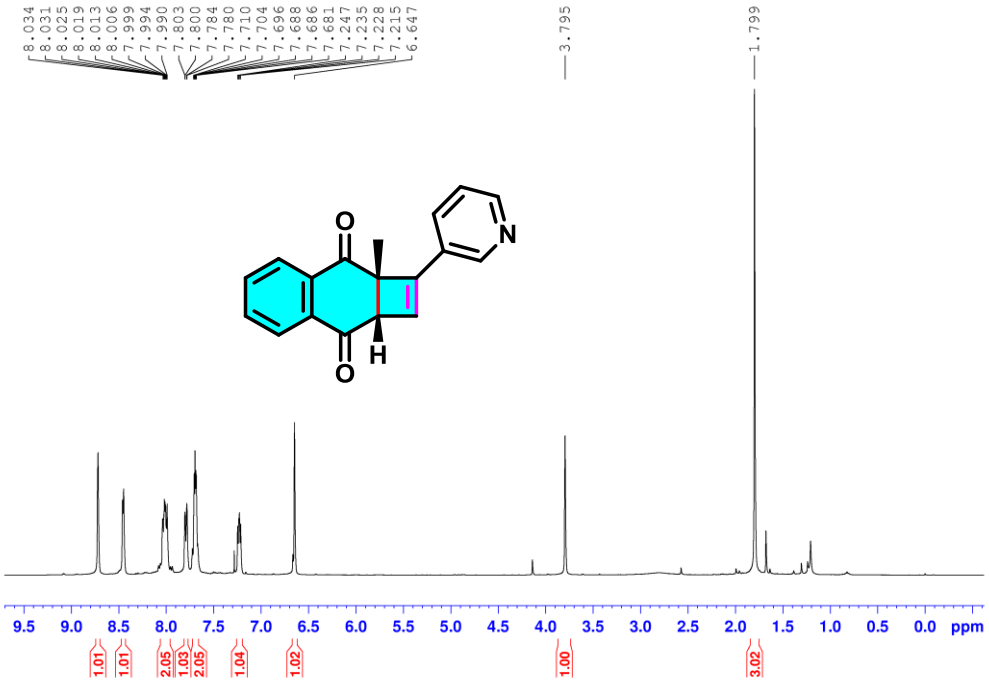
SI-Fig. 16. ^{13}C NMR spectrum of compound **3ah**.



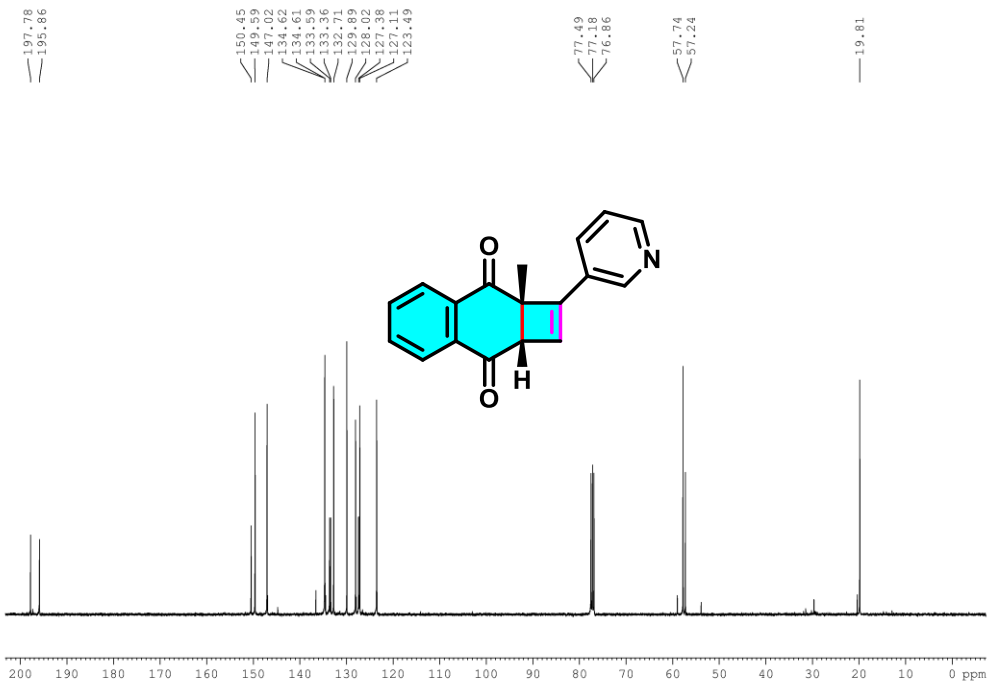
SI-Fig. 17. ^{1}H NMR spectrum of compound **3ai**.



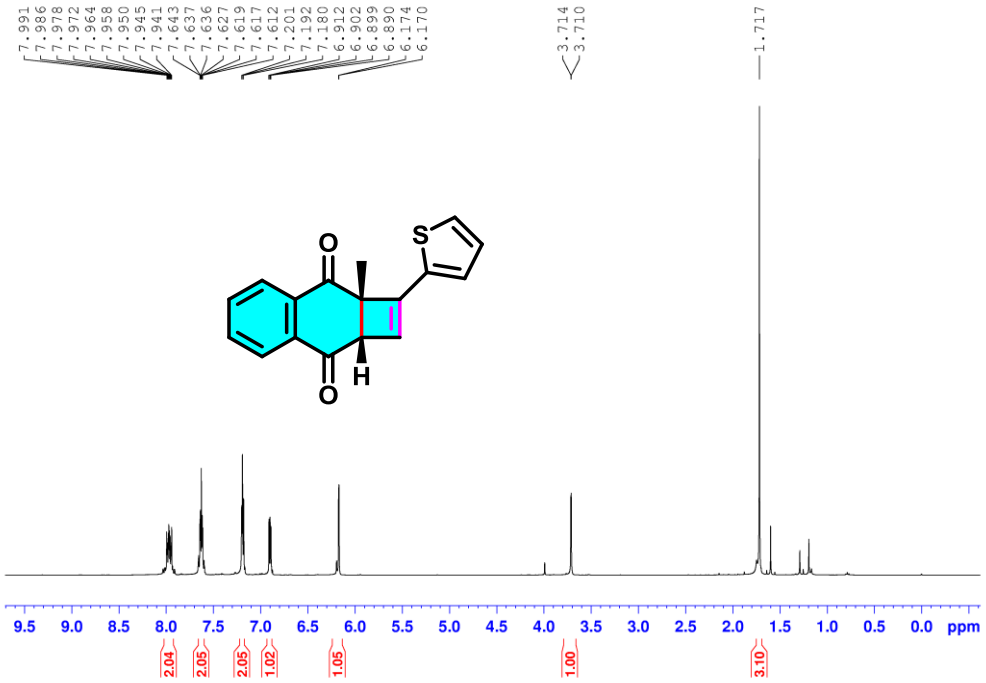
SI-Fig. 18. ^{13}C NMR spectrum of compound **3ai**.



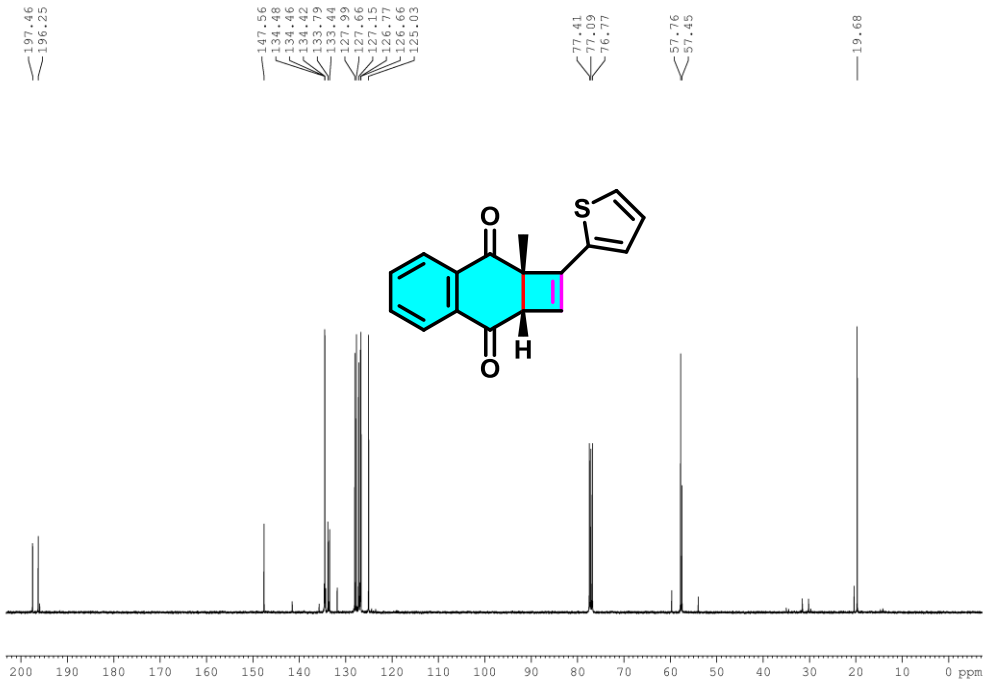
SI-Fig. 19. ^{1}H NMR spectrum of compound **3aj**.



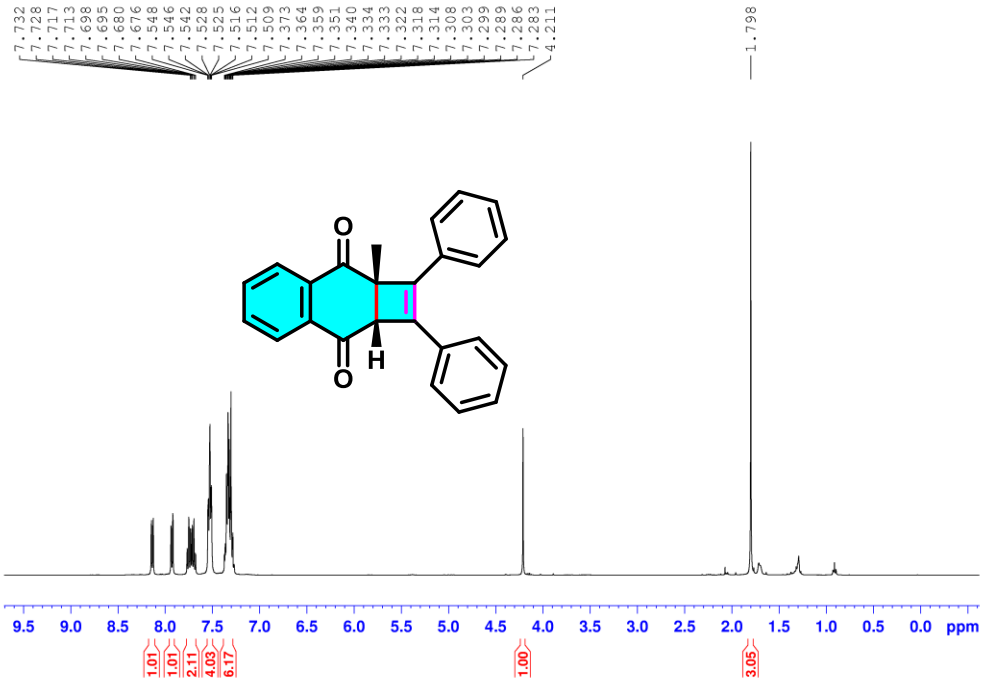
SI-Fig. 20. ^{13}C NMR spectrum of compound **3aj**.



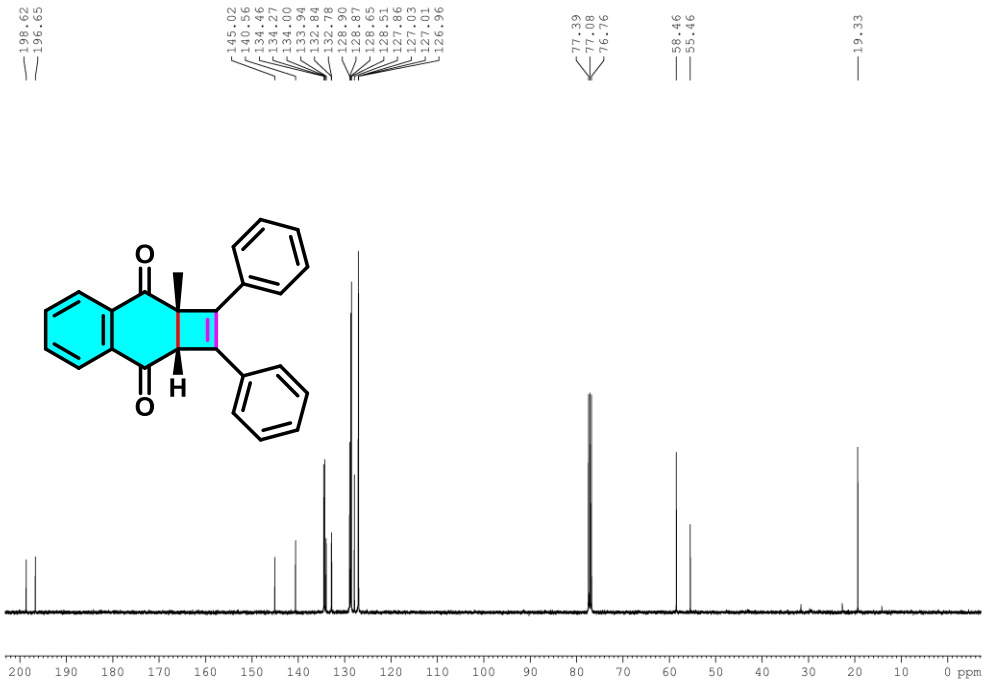
SI-Fig. 21. ^{1}H NMR spectrum of compound **3ak**.



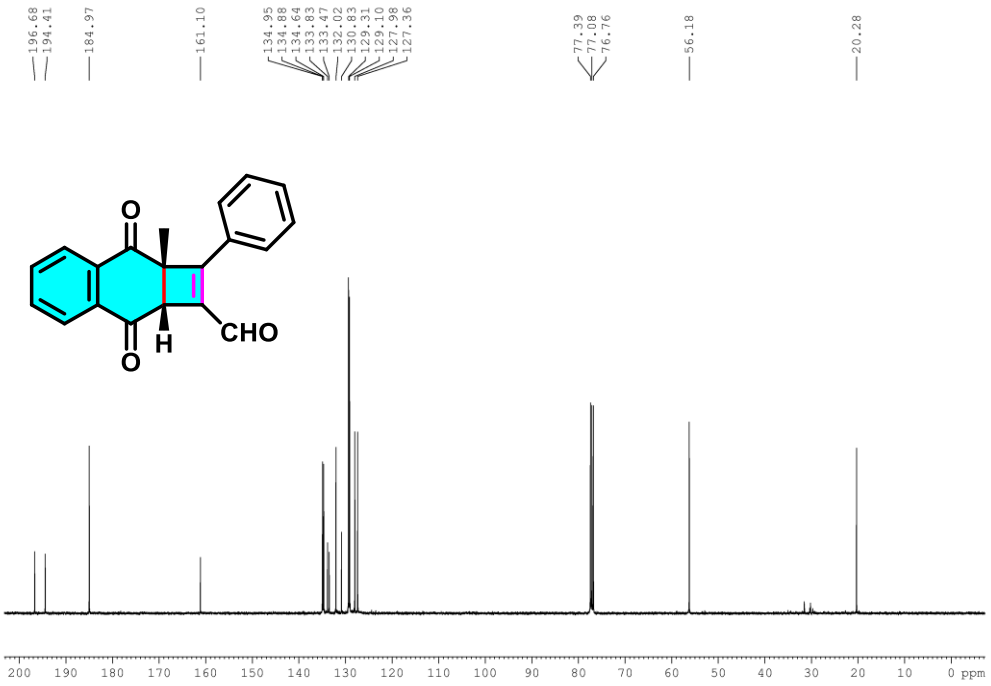
SI-Fig. 22. ^{13}C NMR spectrum of compound **3ak**.



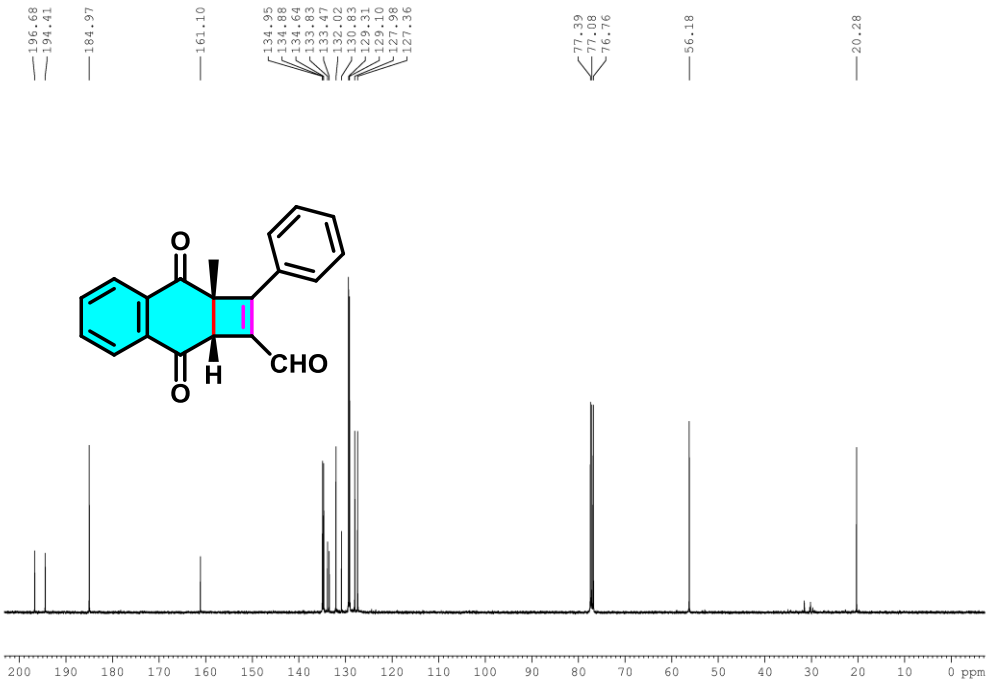
SI-Fig. 23. ^{1}H NMR spectrum of compound **3al**.



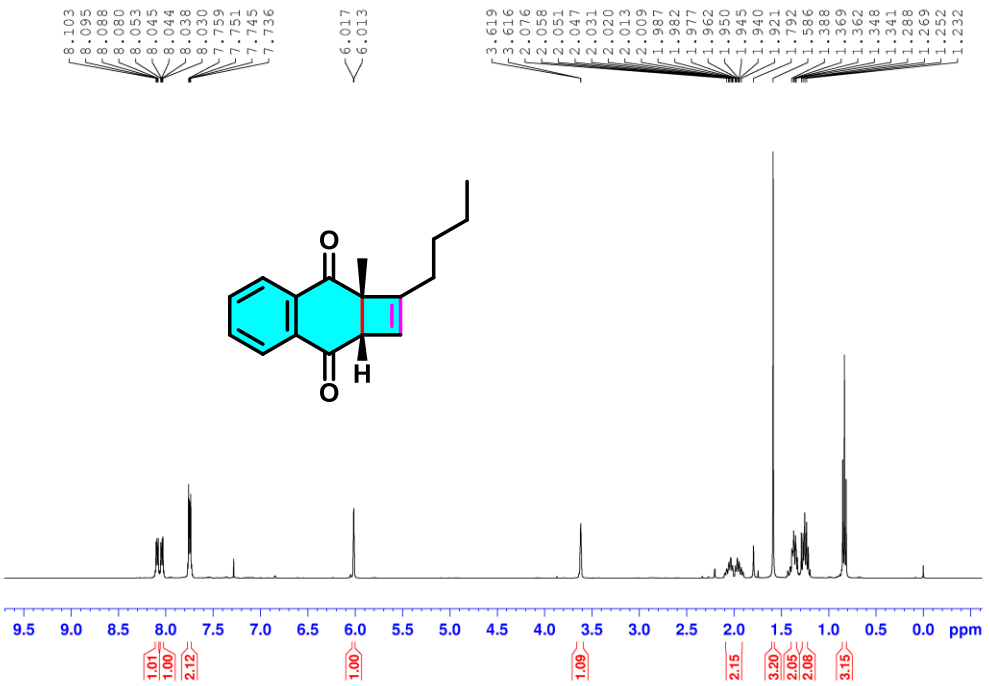
SI-Fig. 24. ^{13}C NMR spectrum of compound **3al**.



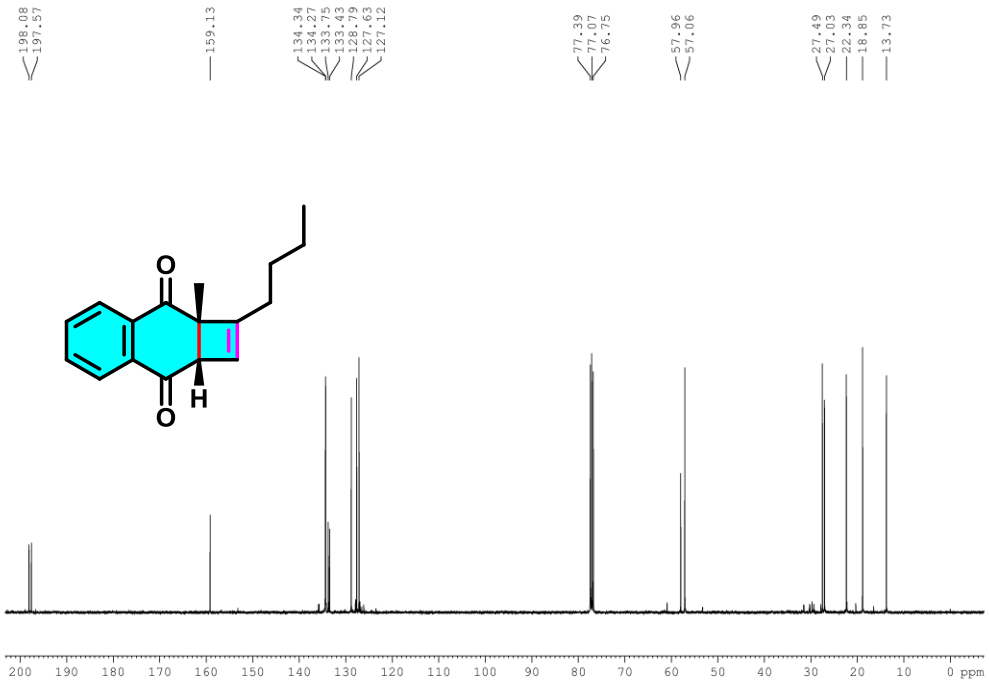
SI-Fig. 25. ^{1}H NMR spectrum of compound **3am**.



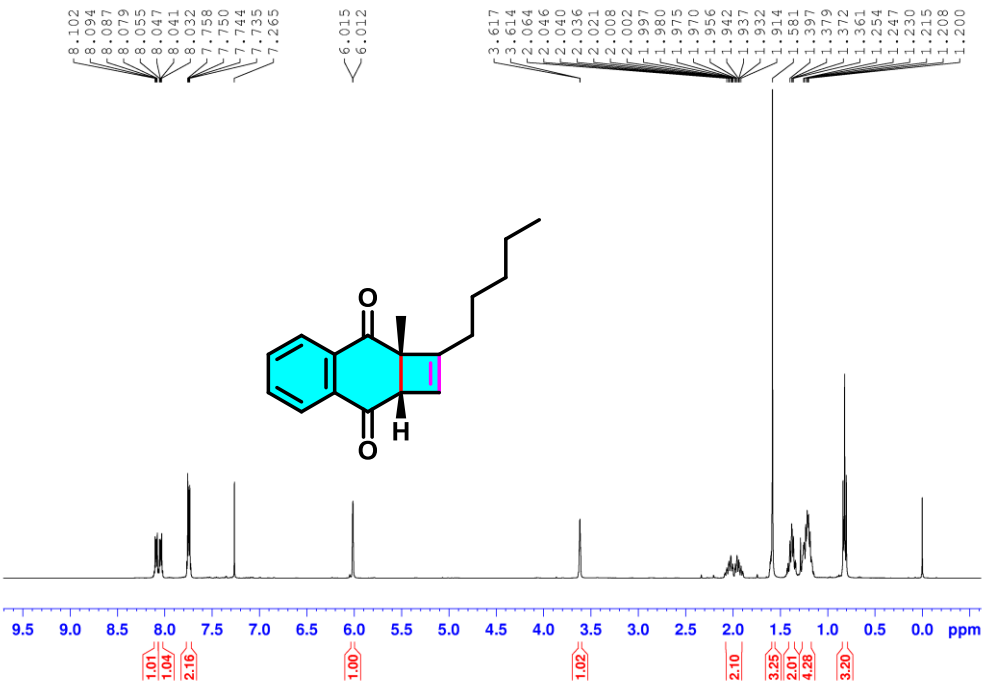
SI-Fig. 26. ^{13}C NMR spectrum of compound **3am**.



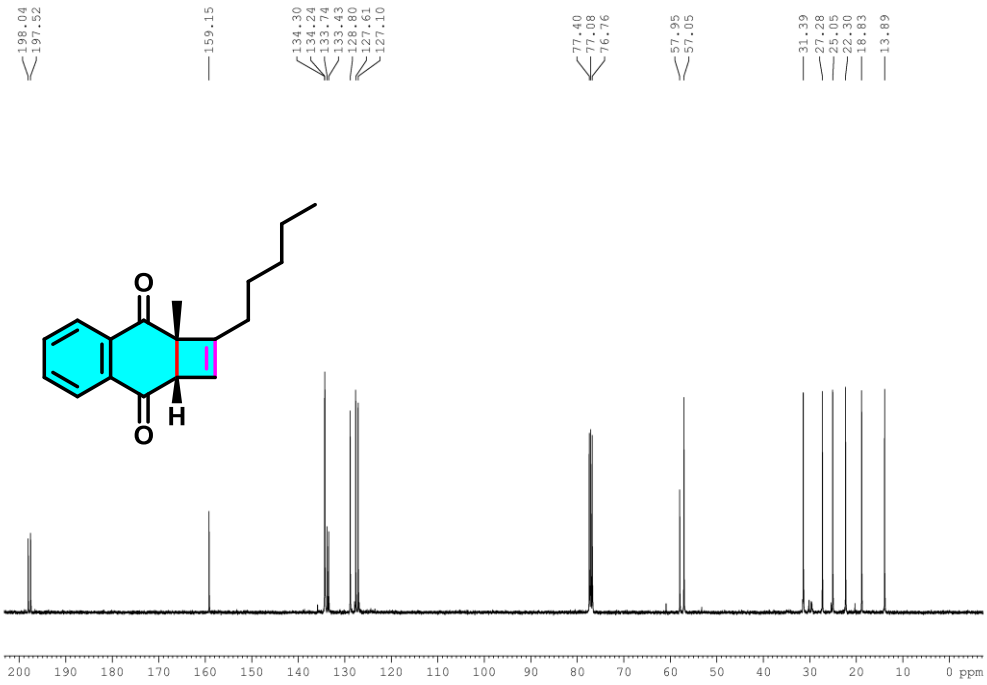
SI-Fig. 27. ^{1}H NMR spectrum of compound **3an**.



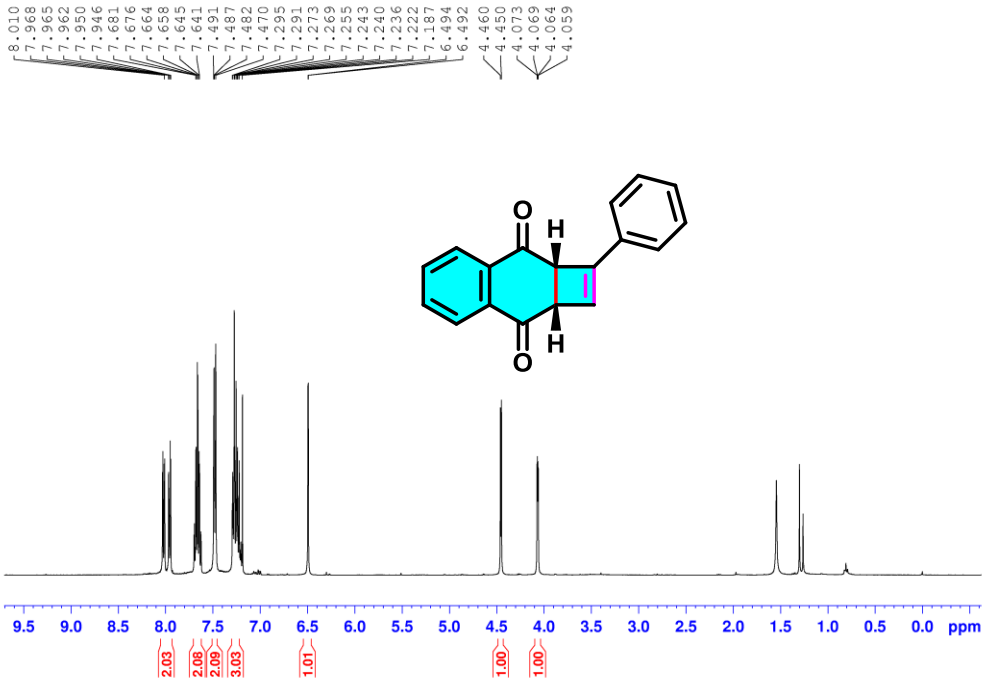
SI-Fig. 28. ^{13}C NMR spectrum of compound **3an**.



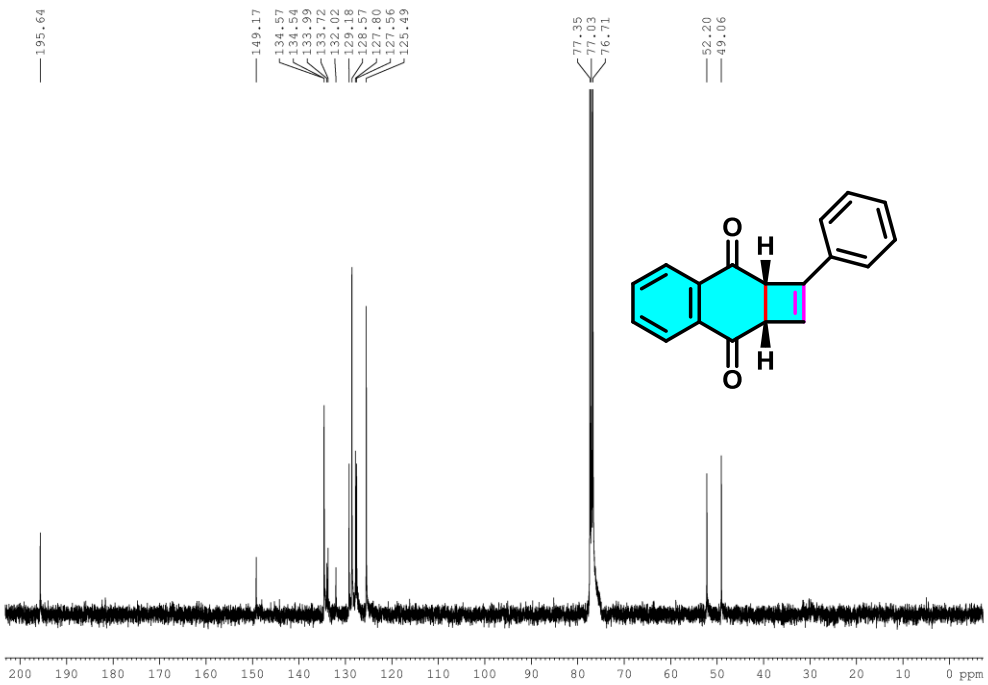
SI-Fig. 29. ^{1}H NMR spectrum of compound **3ao**.



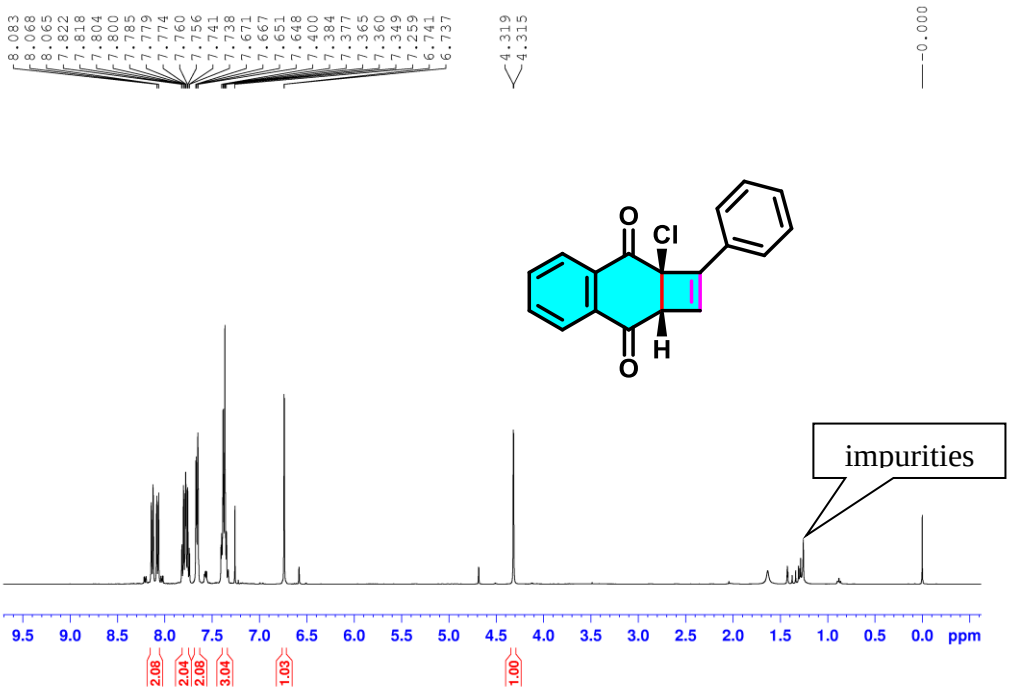
SI-Fig. 30. ^{13}C NMR spectrum of compound **3ao**.



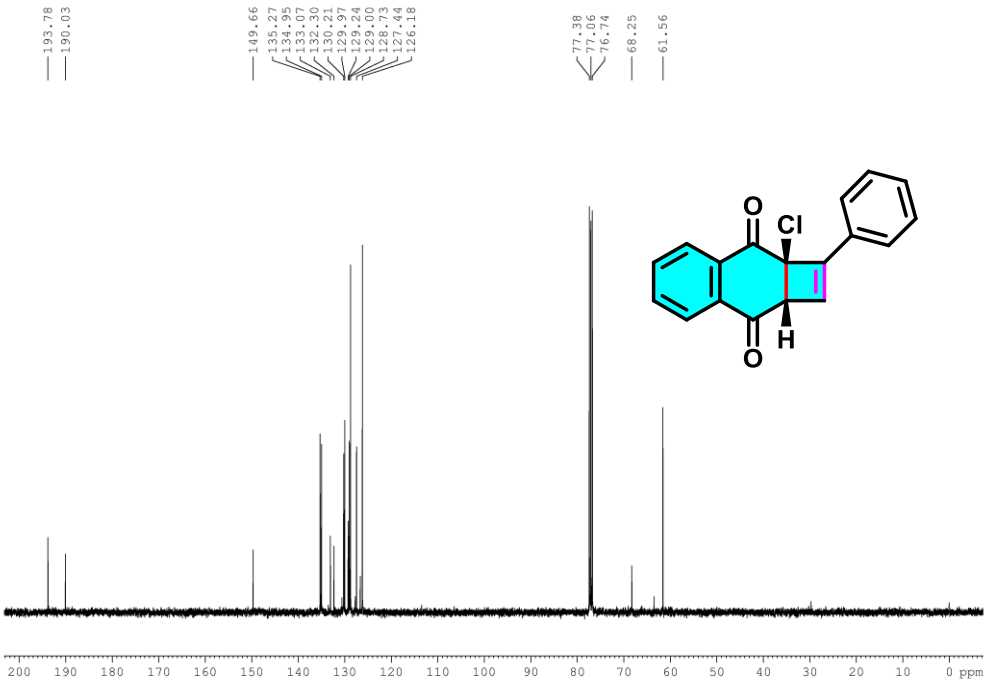
SI-Fig. 31. ^{1}H NMR spectrum of compound **3ba**.



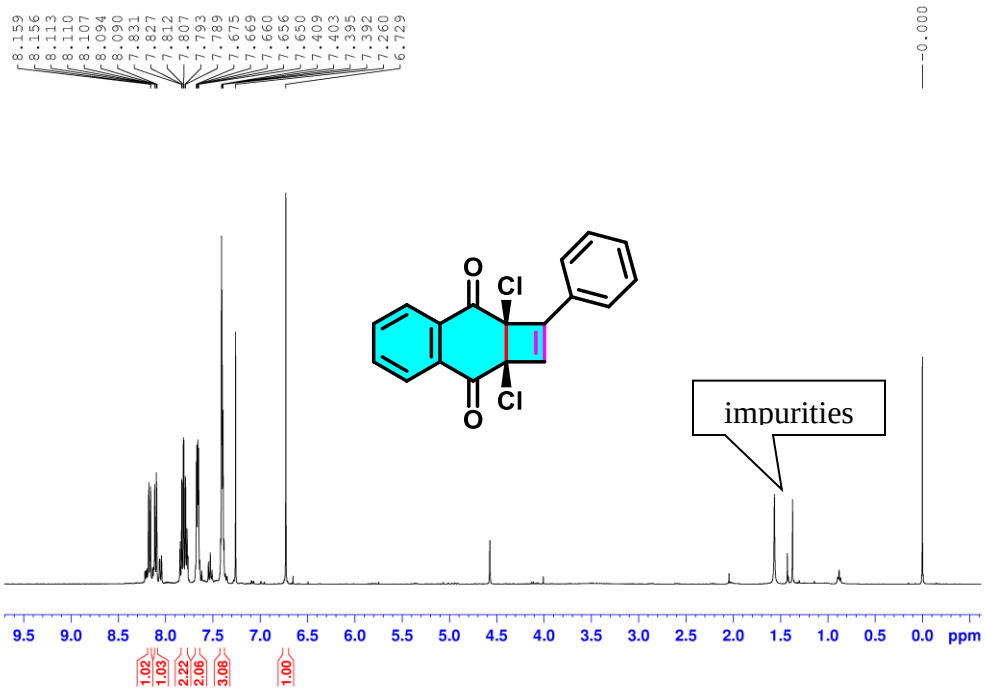
SI-Fig. 32. ^{13}C NMR spectrum of compound **3ba**.



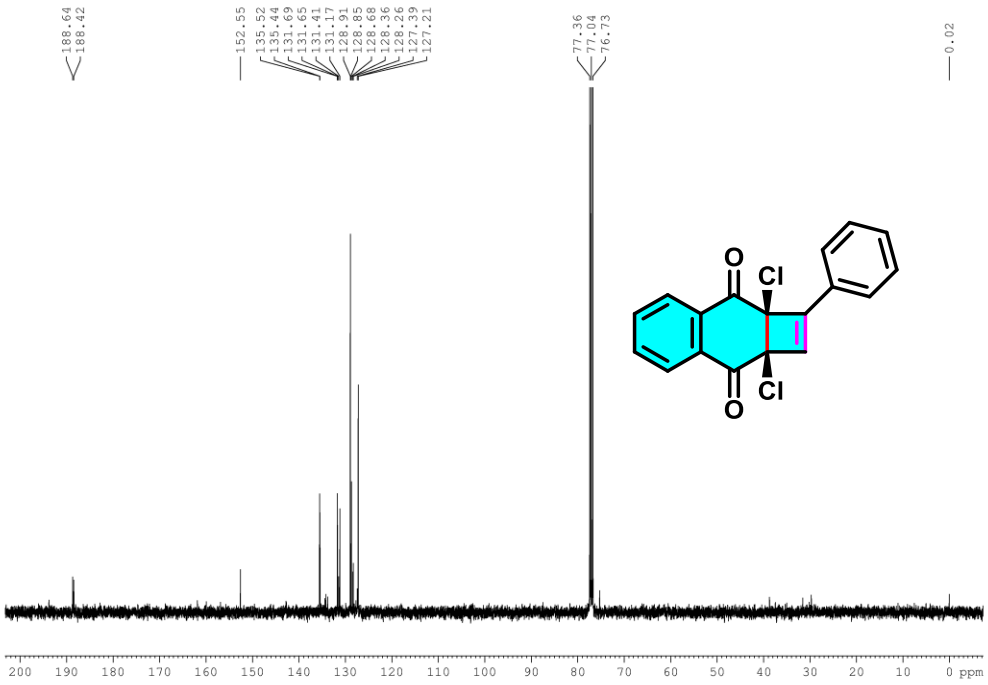
SI-Fig. 33. ^{1}H NMR spectrum of compound **3ca**.



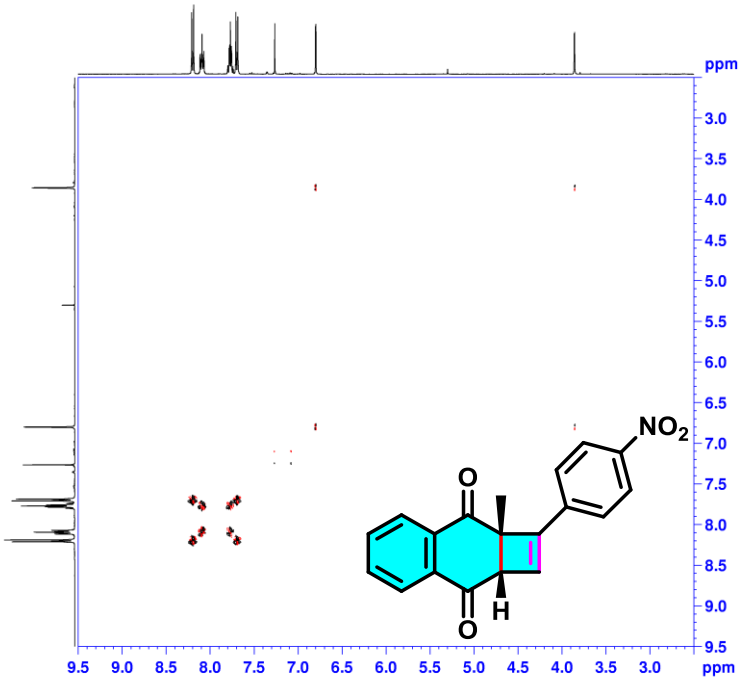
SI-Fig. 34. ^{13}C NMR spectrum of compound **3ca**.



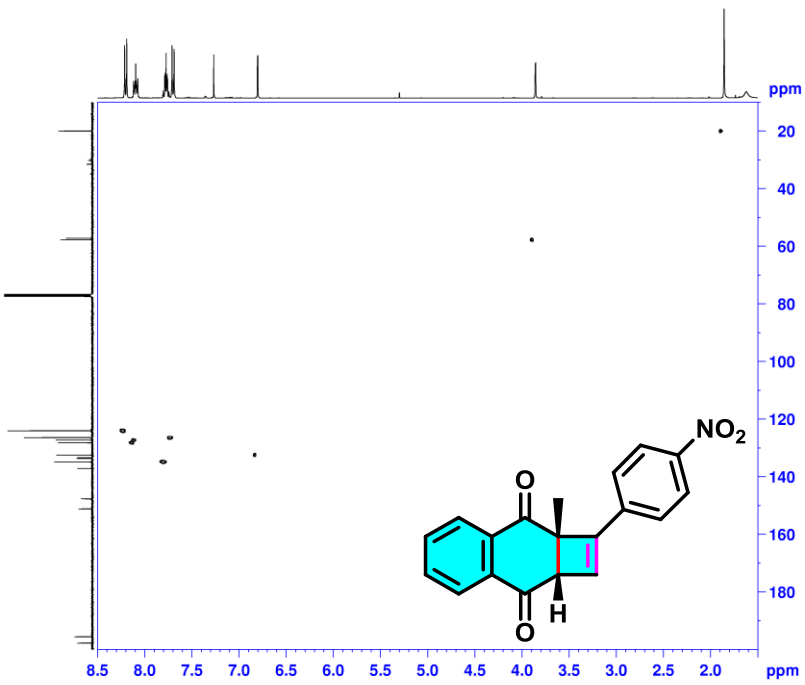
SI-Fig. 35. ^{1}H NMR spectrum of compound **3da**.



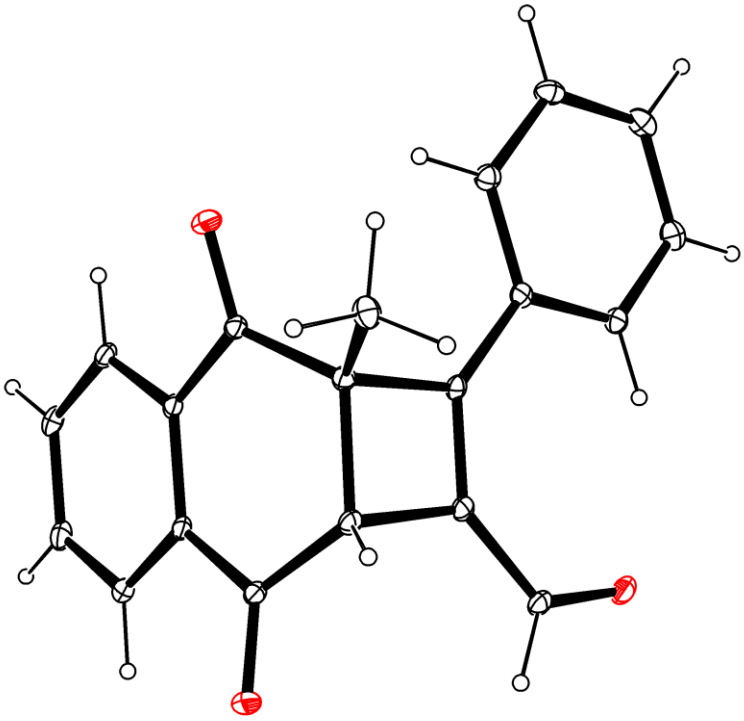
SI-Fig. 36. ^{13}C NMR spectrum of compound **3da**.



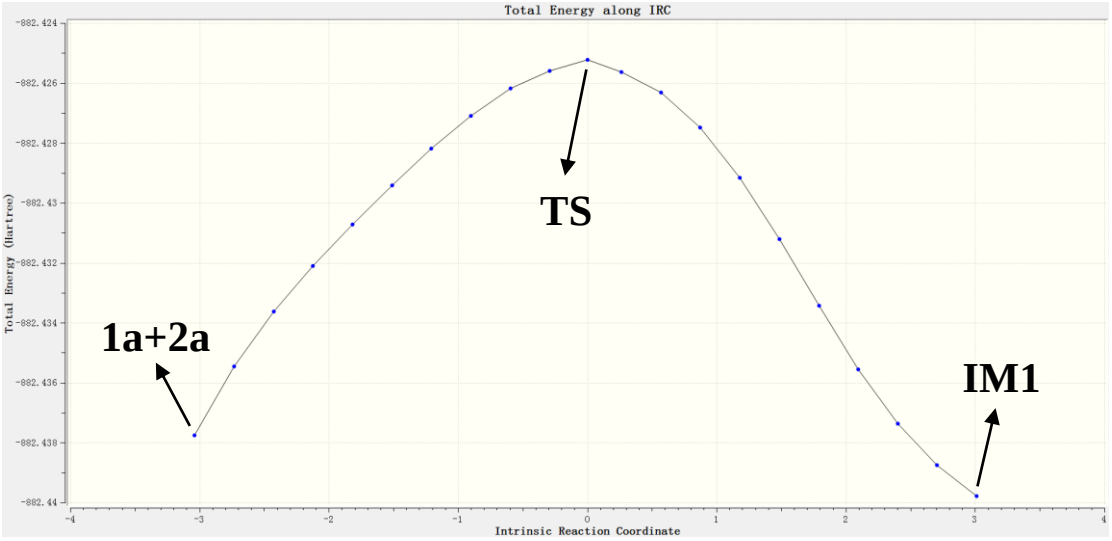
SI-Fig. 37. H-H COSY spectrum of compound **3ah**.



SI-Fig. 38. HSQC spectrum of compound **3ah**.



SI-Fig. 39. ORTEP diagram of crystal structures of **3am**. (CCDC-2288747)



SI-Fig. 40. Total energy along IRC.

3. Cartesian coordination of stationary points

Cartesian coordination of 1a

O	5.25365600	7.37913900	-0.31739300
O	3.66061000	11.14452100	3.11906300
C	3.67093100	8.83636300	2.58971100
C	5.19660000	9.65087400	0.28243500
H	5.77476300	9.87418000	-0.61028900
C	4.80917300	10.61599800	1.13006800
C	4.01217400	10.26878900	2.35182500
C	4.87838700	8.21642300	0.48122900
C	4.08616300	7.84712100	1.69128000
C	2.93166900	8.48795400	3.71859200
H	2.62230900	9.27427200	4.39896800
C	3.76230700	6.51232000	1.92195200
H	4.09789200	5.76785700	1.20769200
C	2.61006600	7.15451300	3.94616700
H	2.03478700	6.87973500	4.82416200
C	5.11921600	12.06833700	0.94917300
H	5.67575600	12.44460300	1.81191500
H	4.19314900	12.64784200	0.90285500
H	5.69913400	12.23625000	0.04099400
C	3.02458900	6.16823900	3.04937900
H	2.77023800	5.12948800	3.23292000

****

Cartesian coordination of 1a*

O	5.25570200	7.35409700	-0.32545600
O	3.64808500	11.15581800	3.14285800

C	3.68384000	8.85172700	2.57208100
C	5.18856300	9.63445600	0.29251400
H	5.76504900	9.86857700	-0.59506100
C	4.79161900	10.60268800	1.15572200
C	4.01080000	10.28218300	2.35730000
C	4.87354100	8.24074600	0.49519600
C	4.09462800	7.85646000	1.67966800
C	2.94117600	8.49260700	3.70413600
H	2.63873900	9.28977300	4.37585000
C	3.76579400	6.51009000	1.91566000
H	4.09323700	5.75240000	1.21173200
C	2.61692800	7.16806200	3.93773500
H	2.04159400	6.89681800	4.81649000
C	5.11259700	12.05375600	0.95624000
H	5.67283100	12.43143300	1.81649900
H	4.18721200	12.63495300	0.90743400
H	5.69182600	12.21604100	0.04615800
C	3.03205900	6.17549800	3.03837800
H	2.77775000	5.13663300	3.22156500

****

Cartesian coordination of 1a[3,*]

O	5.26032200	7.36701600	-0.33136200
O	3.64899800	11.14991400	3.13979600
C	3.68310400	8.84781600	2.57242900
C	5.18961300	9.63743000	0.29136100
H	5.76623400	9.87417300	-0.59603300
C	4.79342100	10.60789400	1.15402800
C	4.01143700	10.27888600	2.35552800

C	4.86751400	8.25454700	0.50787400
C	4.09541900	7.84955400	1.67687600
C	2.94114700	8.48924400	3.70338600
H	2.63894000	9.28661800	4.37466100
C	3.76423800	6.50401200	1.91707300
H	4.08613500	5.73738300	1.22049200
C	2.61537800	7.16512900	3.93962000
H	2.04006500	6.89386400	4.81825400
C	5.11487700	12.05709300	0.95349300
H	5.67520400	12.43812700	1.81220400
H	4.19149600	12.64135800	0.90334200
H	5.69463000	12.21796200	0.04316100
C	3.03019100	6.17264600	3.04100400
H	2.77520800	5.13415200	3.22551200

****

Cartesian coordination of 2a

C	3.03242800	7.19982300	5.61505000
C	3.97103600	6.21327100	5.16010300
C	3.25613300	7.88836800	6.81459900
H	4.14615200	7.66631000	7.39339900
C	1.88468300	7.48147800	4.86224100
H	1.71667200	6.94546800	3.93440600
C	0.97795000	8.43660000	5.30509900
H	0.09125800	8.64981800	4.71715000
C	2.34463300	8.84218100	7.25075600
H	2.52411200	9.37163900	8.18071700
C	1.20505700	9.11837900	6.49853800
H	0.49524000	9.86389100	6.84181800

C	4.75861400	5.38386000	4.77631100
H	5.45481500	4.65073100	4.43770100

****

Cartesian coordination of TS

O	6.02460200	4.15535100	5.42363000
O	6.26654300	6.84300400	10.06554700
C	3.04647200	8.15256900	7.73235100
C	5.21224500	5.10857100	8.83619300
C	6.65614300	6.10557500	6.55838900
H	7.21226400	6.42313900	5.68127500
C	5.44740600	7.68769600	6.90614500
C	4.25600700	7.48738400	7.40659800
C	6.66152700	6.92597400	7.72630900
C	6.05234500	6.32856400	8.98905100
C	5.96696400	4.82641900	6.44728600
C	5.19696400	4.37925200	7.63838000
C	4.47749000	4.66137100	9.93798200
H	4.52281200	5.23614700	10.85679500
C	3.01425600	9.51760200	8.09604100
H	3.94223800	10.08058000	8.09618200
C	1.84000300	7.42017600	7.74460400
H	1.87937700	6.36298400	7.50201400
C	4.43064800	3.21484700	7.54762300
H	4.43948400	2.67285100	6.60788100
C	3.71353900	3.50891900	9.83513000
H	3.13560400	3.16536000	10.68699000
C	0.64038100	8.04449600	8.05144800
H	-0.28577000	7.47967800	8.03223700

C	1.82005300	10.11851600	8.46215200
H	1.80671400	11.16263600	8.75734000
C	7.80057900	7.88357700	7.99457000
H	7.48394700	8.65319500	8.69895600
H	8.14227200	8.34485000	7.06563000
H	8.63325900	7.33375700	8.44067600
C	0.63018000	9.38917900	8.42366500
H	-0.30568300	9.86891500	8.69186400
C	3.68887200	2.78478200	8.63790900
H	3.09067000	1.88224700	8.56489500
H	5.86448800	8.35071200	6.15158100

****

Cartesian coordination of IM1

O	0.76117500	-1.75514100	-2.65642500
O	1.84518200	0.06519000	2.30103300
C	-1.62824600	1.84298300	-0.24884600
C	0.95295200	-1.67079400	0.96345600
C	1.54564100	0.03477000	-1.34514400
H	2.13826800	0.36471500	-2.19284800
C	0.66222700	1.16665400	-0.75425900
C	-0.62636500	0.79270500	-0.24787800
C	1.88382300	0.54153700	-0.00805600
C	1.55108900	-0.32073600	1.18857100
C	0.94801600	-1.32837100	-1.53631000
C	0.67153300	-2.15026300	-0.32262900
C	0.69895300	-2.47393000	2.07358300
H	0.92886000	-2.07994600	3.05762300
C	-1.35700400	3.22842700	-0.21679700

H	-0.32845700	3.57551900	-0.18326400
C	-2.97436700	1.42788600	-0.24426700
H	-3.16895300	0.36044600	-0.23098000
C	0.13949000	-3.42711300	-0.48880200
H	-0.06458600	-3.77179900	-1.49692400
C	0.16187400	-3.74491900	1.90321800
H	-0.03865900	-4.36741300	2.76917700
C	-4.00958100	2.35281800	-0.27171600
H	-5.04156700	2.01908800	-0.29695200
C	-2.39091800	4.15175900	-0.17912100
H	-2.17265800	5.21340900	-0.12537400
C	3.05896200	1.46537100	0.20596500
H	2.87810600	2.10175100	1.07359700
H	3.22874300	2.08657400	-0.67620600
H	3.96260600	0.88084700	0.39885100
C	-3.71623100	3.71470500	-0.22710600
H	-4.52287800	4.44129800	-0.21621800
C	-0.11761800	-4.22200200	0.62237800
H	-0.53546800	-5.21502500	0.49262200
H	0.89745500	2.14030100	-1.19555100

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Cartesian coordination of 3aa

O	2.35377200	-2.23870100	-2.21515900
O	0.59008000	0.65644100	1.93958700
C	0.10527200	2.80688000	-1.05852700
C	0.20076600	-1.15641800	0.48445200
C	2.24493800	-0.03629300	-1.33794200
H	3.32427200	0.02149900	-1.51202000

C	1.40604600	0.87997000	-2.20759200
C	0.96199200	1.62926800	-1.18734200
C	1.75007600	0.83694000	-0.13341400
C	0.83591000	0.14291300	0.86505200
C	1.81731200	-1.48306500	-1.43182900
C	0.66339700	-1.92555700	-0.59181800
C	-0.85921300	-1.62435700	1.26460600
H	-1.18769300	-1.01794500	2.10172900
C	-0.37857700	3.45098300	-2.20568800
H	-0.11009000	3.06763500	-3.18601400
C	-0.23644100	3.30887700	0.20258900
H	0.12085800	2.80667600	1.09640700
C	0.06482600	-3.15359800	-0.87797800
H	0.45659000	-3.73348600	-1.70689500
C	-1.46152100	-2.83853200	0.96428000
H	-2.28984700	-3.19532100	1.56763500
C	-1.04791300	4.43496300	0.30942400
H	-1.30923300	4.81622500	1.29115200
C	-1.18830400	4.57193000	-2.09411100
H	-1.55716100	5.06347200	-2.98850900
C	2.85239100	1.61596300	0.57452600
H	3.49702000	0.93887600	1.14241400
H	2.42592800	2.34000200	1.27038900
H	3.46026500	2.14755100	-0.16213300
C	-1.52446300	5.06809000	-0.83410000
H	-2.15613900	5.94620100	-0.74738200
C	-0.99857900	-3.60487300	-0.10797000
H	-1.46742600	-4.55654700	-0.33603200
H	1.25518900	0.88883700	-3.28158700

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