Supporting Information

$Fe(NO_3)_3·9H_2O$-Mediated Visible-Light Photocatalysis for the Nitration of Cyclobutanols: Access to Functionalized Nitrocyclobutenes

Dongfang Jiang*[ac], Can Yang[a], Xinying Man[b], Xin Li[c], Haifei Wang*[a], Yunlin Song*[d] and Zhenjie Qi*[b]

[a] School of Biological Science and Medical Engineering, Hunan University of Technology, Zhuzhou 412007, P. R. China.

[b] School of Resource & Environment and Safety Engineering, Jining University, Qufu, Shandong, 273155, P. R. China.

[c] Hunan Provincial Key Laboratory of the Research and Development of Novel Pharmaceutical Preparations, Changsha

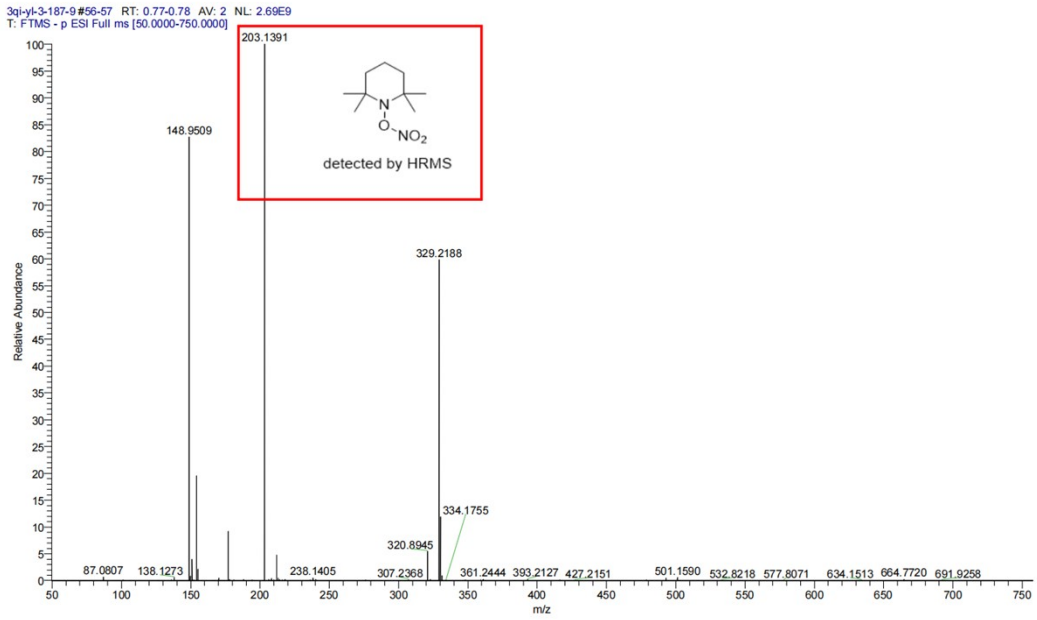
[d] Ministry of Agriculture, Nanjing Agricultural University, Nanjing 210095, China.

Table of contents

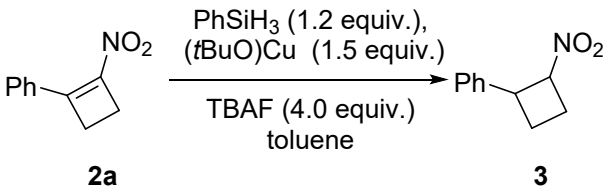
1 General remark

^{1}H NMR and ^{13}C NMR spectra were recorded on 400MHz and 100MHz in $CDCl_3$ (BRUKER 400M or JNM-ECS 400M). All chemical shifts were given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. All compounds were further characterized by HRMS; copies of their ^{1}H NMR and ^{13}C NMR spectra are provided. Products were purified by flash chromatography on 200-300 mesh silica gels. All melting points were determined without correction. Unless otherwise noted, commercially available reagents and solvents were used without further purification. Cyclobutanols were prepared according to the literature procedures.[1-2]

2 Figure S1. TEMPO adduct derived from the nitro radical radical was detected by HRMS



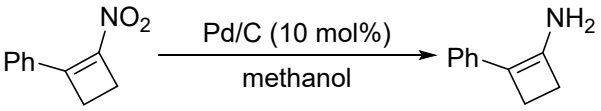
3 Derivatization of 2a



2a **3**

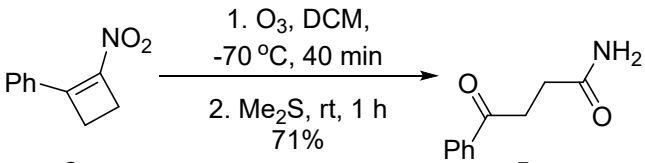
In a 10 mL Schlenk-flask, copper(I)-t-butoxide (6.8 mg, 50 micromol) was dissolved in toluene (5 mL). Phenyl silane (150 microL, 1.20 mmol) was added at room temperature. After stirring for 5 min the nitroolefin (1.00 mmol) was added with vigorous stirring. After stirring for 24 h, TBAF solution (4 mL, 1.0 M in THF, 4.0 mmol) was added and stirring was continued for 1

hr. Water (20 mL) was added and the mixture extracted with ether (2 x 30 mL). After drying over sodium sulfate, the solvent was evaporated. Flash chromatography (PE:EtOAc) provided the product **3** as a colorless oil in 76% yield.



2a **4**

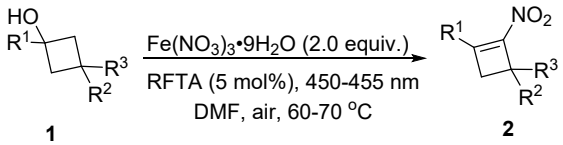
The compound of **2a** (0.5 mmol, 1.0 equiv.) was dissolved in a mixture of 5 mL of methanol and after addition of Pd/C (10%), hydrogenated with hydrogen gas at normal pressure for 4 hours. The mixture was filtrated, the solvent was evaporated, and the compound was purified with cyclohexane/ethyl acetate gradient mixtures over a silica gel column provided the product **4** as a yellow oil in 68% yield.



2a **5**

At -78 °C, ozone was bubbled through a solution of **2a** (1 mmol, 1.0 equiv.) in DCM (30 mL) for 40 min until a faint blue color persisted. Then, the ozone was replaced by a stream of dry nitrogen. After treatment with Me_2S (0.1 mL), the solution was allowed to come to room temperature over 1 h. The solution was washed with saturated aqueous NaCl (75 mL), dried over Na_2SO_4. After filtration, the filtrate was concentrated under vacuum. The residue was rescrystallized with PE to give **5** as a yellow oil in 71% yield

4 General procedure for the synthesis of nitro-cyclobutenes

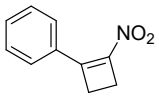


1 **2**

In a sealed tube, 25 mL over-dried Schlenk tube charged with a stir bar, cyclobutanols **1** (0.2 mmol, 1.0 equiv.), $Fe(NO_3)_3 \cdot 9H_2O$ (2.0 equiv.) and RFTA (5 mol%) was added DMF (3.0 mL). The resulting mixture was allowed to stir at 60-70°C for 24 hours under irradiation with blue

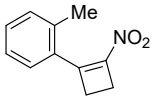
LEDs (450-455 nm) under air atmosphere. After completion, saturated aqueous NH_4Cl solution was added and the resulting mixture was diluted with EA. The organic layer was separated and the aqueous layer was extracted with EtOAc. The combined extracts were washed with brine, dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated under vacuum and the obtained residue was purified by flash column chromatography on silica gel (PE/EA as eluent, the ratio varies from 10:1 to 4:1) to afford nitro-cyclobutene derivatives **2**.

5 The data of products



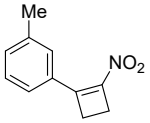
(2-nitrocyclobut-1-en-1-yl)benzene (2a)

White solid (76% yield). melting point: 62-64 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.07 (dd, J = 5.6, 3.2 Hz, 2H), 7.48 (ddd, J = 9.5, 6.8, 2.6 Hz, 3H), 3.02 (t, J = 7.1 Hz, 2H), 2.67 (t, J = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 147.8, 135.5, 132.5, 130.6, 129.8, 128.8, 26.3, 22.4; HRMS calcd for $C_{10}H_{10}NO_2$ $[M+H]^+$ 176.0706; found: 176.0702.



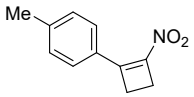
1-methyl-2-(2-nitrocyclobut-1-en-1-yl)benzene (2b)

White solid (68% yield). melting point: 77-79 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.92 – 7.82 (m, 1H), 7.45 – 7.32 (m, 3H), 3.09 (t, J = 7.1 Hz, 2H), 2.69 (t, J = 7.1 Hz, 2H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 144.6, 144.5, 130.9, 130.2, 129.4, 127.7, 125.9, 125.7, 27.8, 22.2, 19.9; HRMS calcd for $C_{11}H_{12}NO_2S$ $[M+H]^+$ 190.0863; found: 190.0866.



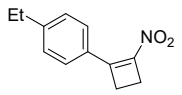
1-methyl-3-(2-nitrocyclobut-1-en-1-yl)benzene (2c)

White solid (73% yield). melting point: 79-81 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.05 – 7.88 (m, 2H), 7.32 (dd, J = 16.2, 7.4 Hz, 2H), 3.05 (t, J = 7.1 Hz, 2H), 2.64 (t, J = 7.1 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 148.4, 139.4, 132.3, 130.4, 129.4, 127.8, 126.4, 125.6, 26.5, 23.8, 21.2; HRMS calcd for $C_{11}H_{12}NO_2S$ $[M+H]^+$ 190.0863; found: 190.0867.



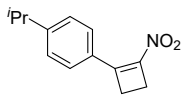
1-methyl-4-(2-nitrocyclobut-1-en-1-yl)benzene (2d)

White solid (75% yield). melting point: 81-83 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.03 – 7.85 (m, 2H), 7.15 (d, J = 7.1 Hz, 2H), 3.04 (t, J = 7.1 Hz, 2H), 2.57 (t, J = 7.1 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 150.0, 136.7, 135.5, 132.9, 129.2, 127.7, 28.9, 22.7, 21.4; HRMS calcd for $C_{11}H_{12}NO_2S$ $[M+H]^+$ 190.0863; found: 190.0867.



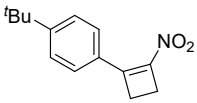
1-ethyl-4-(2-nitrocyclobut-1-en-1-yl)benzene (2e)

White solid (75% yield). melting point: 168-170 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.92 (d, J = 7.5 Hz, 2H), 7.09 (d, J = 7.3 Hz, 2H), 3.14 (t, J = 7.1 Hz, 2H), 2.63 – 2.44 (m, 4H), 1.19 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$ ppm): δ 150.7, 144.5, 136.7, 135.4, 131.0, 127.8, 28.6, 27.8, 23.1, 15.5; HRMS calcd for $C_{12}H_{14}NO_2$ $[M+H]^+$ 204.1019; found: 204.1023.



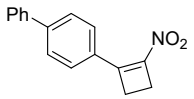
1-isopropyl-4-(2-nitrocyclobut-1-en-1-yl)benzene (2f)

White solid (70% yield). melting point: 89-91 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.95 (dd, J = 11.5, 7.5 Hz, 2H), 7.29 (d, J = 7.0 Hz, 2H), 3.17 (t, J = 7.1 Hz, 2H), 2.99 – 2.90 (m, 1H), 2.57 (t, J = 7.1 Hz, 2H), 1.20 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 150.1, 148.0, 135.2, 134.5, 128.1, 126.6, 33.9, 27.8, 26.0, 24.0; HRMS calcd for $C_{13}H_{16}NO_2$ $[M+H]^+$ 218.1176; found: 218.1172.



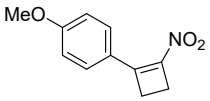
1-(tert-butyl)-4-(2-nitrocyclobut-1-en-1-yl)benzene (2g)

White solid (71% yield). melting point: 73-75 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.90 – 7.77 (m, 2H), 7.46 – 7.29 (m, 2H), 3.11 (t, J = 7.1 Hz, 2H), 2.57 (t, J = 7.1 Hz, 2H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 155.6, 152.1, 136.7, 135.4, 127.5, 126.0, 35.0, 29.7, 27.8, 24.5; HRMS calcd for $C_{14}H_{18}NO_2$ $[M+H]^+$ 232.1332; found: 232.1335.



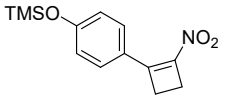
4-(2-nitrocyclobut-1-en-1-yl)-1,1'-biphenyl (2h)

White solid (69% yield). melting point: 107-109 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.77 – 7.57 (m, 4H), 7.49 (dt, J = 7.3, 3.5 Hz, 4H), 7.39 (t, J = 7.4 Hz, 1H), 3.07 (t, J = 7.1 Hz, 2H), 2.57 (t, J = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 148.9, 142.9, 139.2, 136.7, 136.3, 128.9, 127.7, 127.5, 127.0, 126.8, 27.8, 23.2; HRMS calcd for $C_{16}H_{14}NO_2$ $[M+H]^+$ 252.1019; found: 252.1015.



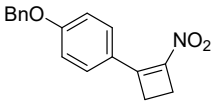
1-methoxy-4-(2-nitrocyclobut-1-en-1-yl)benzene (2i)

White solid (72% yield). melting point: 118-120 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.02 (dd, J = 14.2, 6.9 Hz, 2H), 7.30 (d, J = 7.4 Hz, 1H), 3.79 (s, 2H), 3.09 (t, J = 7.1 Hz, 1H), 2.75 (t, J = 7.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 159.0, 151.2, 136.7, 133.6, 127.4, 113.5, 55.3, 27.8, 23.01; HRMS calcd for $C_{11}H_{12}NO_3$ $[M+H]^+$ 206.0812; found: 206.0817.



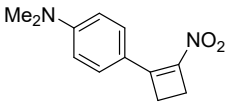
trimethyl(4-(2-nitrocyclobut-1-en-1-yl)phenoxy)silane (2j)

White solid (61% yield). melting point: 104-106 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.03 – 7.89 (m, 2H), 7.50 – 7.35 (m, 2H), 3.09 (t, J = 7.1 Hz, 2H), 2.57 (t, J = 7.1 Hz, 2H), 0.21 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 152.9, 148.4, 136.7, 133.2, 126.2, 115.9, 27.8, 22.4, 0.2; HRMS calcd for $C_{13}H_{18}NO_3Si$ $[M+H]^+$ 264.1050; found: 264.1053.



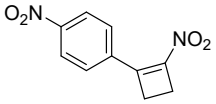
1-(benzyloxy)-4-(2-nitrocyclobut-1-en-1-yl)benzene (2k)

White solid (68% yield). melting point: 131-133 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.09 (dd, J = 7.9, 6.5 Hz, 2H), 7.47 (d, J = 7.0 Hz, 2H), 7.34 (dt, J = 14.0, 7.3 Hz, 5H), 5.14 (s, 2H), 3.05 (t, J = 7.1 Hz, 2H), 2.57 (t, J = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 158.7, 151.2, 136.7, 135.7, 133.8, 128.3, 128.0, 127.9, 127.0, 69.6, 27.8; HRMS calcd for $C_{17}H_{16}NO_3$ $[M+H]^+$ 282.1125; found: 282.1129.



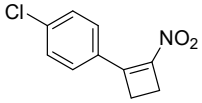
N,N-dimethyl-4-(2-nitrocyclobut-1-en-1-yl)aniline (2l)

White solid (67% yield). melting point: 117-119 °C.^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.99 – 7.93 (m, 2H), 7.12 (d, J = 7.4 Hz, 2H), 3.08 (t, J = 7.1 Hz, 2H), 3.02 (s, 6H), 2.57 (t, J = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 151.0, 148.9, 136.7, 131.5, 128.4, 111.2, 40.4, 27.8, 22.9; HRMS calcd for $C_{12}H_{15}N_2O_4$ $[M+H]^+$ 219.1128; found: 219.1126.



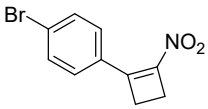
1-nitro-4-(2-nitrocyclobut-1-en-1-yl)benzene (2m)

White solid (55% yield). melting point: 82-84 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.14 (d, J = 7.4 Hz, 2H), 7.96 (dd, J = 11.6, 7.4 Hz, 2H), 3.11 (t, J = 7.1 Hz, 2H), 2.57 (t, J = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 147.4, 145.2, 140.8, 136.7, 127.4, 123.4, 27.8, 22.5; HRMS calcd for $C_{10}H_9N_2O_4$ $[M+H]^+$ 221.0557; found: 221.0554.



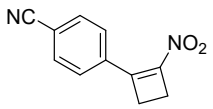
1-chloro-4-(2-nitrocyclobut-1-en-1-yl)benzene (2n)

White solid (68% yield). melting point: 96-98 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.03 (d, J = 7.5 Hz, 2H), 7.40 (d, J = 7.4 Hz, 2H), 3.06 (t, J = 7.1 Hz, 2H), 2.57 (t, J = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 148.7, 136.7, 135.4, 128.8, 127.7, 27.8, 22.4; HRMS calcd for $C_{10}H_9ClNO_2$ $[M+H]^+$ 210.0316; found: 210.0313.



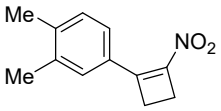
1-bromo-4-(2-nitrocyclobut-1-en-1-yl)benzene (2o)

White solid (73% yield). melting point: 106-108 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.11 – 7.97 (m, 2H), 7.57 (d, J = 7.4 Hz, 2H), 3.01 (t, J = 7.1 Hz, 2H), 2.57 (t, J = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 148.6, 136.7, 136.2, 130.4, 127.8, 118.7, 27.8, 23.7; HRMS calcd for $C_{10}H_9BrNO_2$ $[M+H]^+$ 253.9811; found: 253.9814.



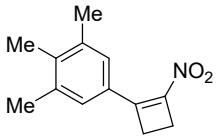
4-(2-nitrocyclobut-1-en-1-yl)benzonitrile (2p)

White solid (53% yield). melting point: 113-115 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.87 (d, J = 7.6 Hz, 2H), 7.72 (dd, J = 8.0, 6.6 Hz, 2H), 3.11 (t, J = 7.1 Hz, 2H), 2.57 (t, J = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 148.7, 137.2, 136.7, 131.0, 128.4, 117.5, 112.0, 27.8, 22.9; HRMS calcd for $C_{13}H_{16}NO_2$ $[M+H]^+$ 201.0659; found: 201.0656.



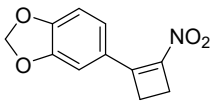
1,2-dimethyl-4-(2-nitrocyclobut-1-en-1-yl)benzene (2q)

White solid (70% yield). melting point: 117-119 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm):δ 7.90 – 7.75 (m, 2H), 6.99 (dd, J = 7.5, 1.8 Hz, 1H), 3.05 (t, J = 7.1 Hz, 2H), 2.57 (t, J = 7.1 Hz, 2H), 2.32 (d, J = 12.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 144.6, 140.4, 138.3, 137.2, 132.1, 130.3, 127.3, 126.4, 27.8, 23.1, 20.0, 19.8; HRMS calcd for $C_{12}H_{14}NO_2$ $[M+H]^+$ 204.1019; found: 204.1013.



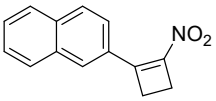
1,2,3-trimethyl-5-(2-nitrocyclobut-1-en-1-yl)benzene (2r)

White solid (64% yield). melting point: 101-103 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.79 (d, J = 11.9 Hz, 2H), 3.02 (t, J = 7.1 Hz, 2H), 2.57 (t, J = 7.1 Hz, 2H), 2.40 (s, 6H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 150.2, 136.6, 136.5, 136.2, 133.3, 126.5, 27.8, 22.7, 20.7, 15.5.; HRMS calcd for $C_{13}H_{16}NO_2$ $[M+H]^+$ 218.1176; found: 218.1172.



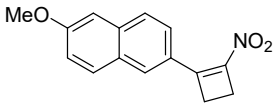
5-(2-nitrocyclobut-1-en-1-yl)benzo[d][1,3]dioxole (2s)

White solid (68% yield). melting point: 105-107 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.81 (d, J = 1.8 Hz, 1H), 7.60 (dd, J = 7.5, 1.9 Hz, 1H), 7.18 (d, J = 7.6 Hz, 1H), 3.04 (t, J = 7.1 Hz, 2H), 2.57 (t, J = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 149.3, 148.3, 143.5, 138.3, 131.1, 124.1, 109.0, 108.3, 101.5, 27.8, 22.2; HRMS calcd for $C_{11}H_{10}NO_4$ $[M+H]^+$ 220.0604; found: 220.0601.



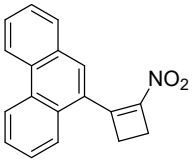
2-(2-nitrocyclobut-1-en-1-yl)naphthalene (2t)

White solid (54% yield). melting point: 104-106 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.04 – 7.91 (m, 2H), 7.91 – 7.70 (m, 3H), 7.55 (p, J = 5.7 Hz, 2H), 3.12 (t, J = 7.1 Hz, 2H), 2.67 (t, J = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 147.5, 138.1, 134.2, 133.8, 133.7, 129.1, 128.6, 127.8, 127.0, 127.0, 126.1, 125.8, 27.8, 22.7; HRMS calcd for $C_{14}H_{12}NO_2$ $[M+H]^+$ 226.0863; found: 226.0866.



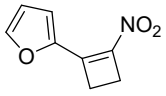
2-methoxy-6-(2-nitrocyclobut-1-en-1-yl)naphthalene (2u)

White solid (54% yield). melting point: 148-150 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.87 – 7.61 (m, 4H), 7.42 (d, J = 7.4 Hz, 1H), 3.02 (t, J = 7.1 Hz, 2H), 2.57 (t, J = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 157.7, 147.2, 137.7, 134.5, 133.3, 130.2, 128.1, 127.5, 127.4, 127.3, 118.4, 106.2, 55.6, 27.8, 23.7; HRMS calcd for $C_{15}H_{14}NO_3$ $[M+H]^+$ 256.0968; found: 256.0964.



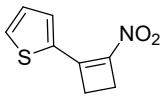
9-(2-nitrocyclobut-1-en-1-yl)phenanthrene (2v)

White solid (46% yield). melting point: 181-183 °C.^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.72 (d, J = 7.1 Hz, 1H), 8.54 (d, J = 7.3 Hz, 1H), 8.10 (dd, J = 17.4, 7.3 Hz, 2H), 7.82 – 7.53 (m, 5H), 3.09 (t, J = 7.1 Hz, 2H), 2.57 (t, J = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 146.9, 145.3, 136.2, 131.7, 130.9, 130.6, 129.4, 129.1, 128.0, 127.1, 127.1, 127.0, 126.1, 125.4, 123.2, 122.8, 27.8, 24.0; HRMS calcd for $C_{18}H_{14}NO_2$ $[M+H]^+$ 276.1019; found: 276.1015.



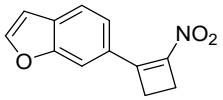
2-(2-nitrocyclobut-1-en-1-yl)furan (2w)

White solid (69% yield). melting point: 119-121 °C.^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.71 (dd, J = 7.5, 1.2 Hz, 1H), 7.17 (dd, J = 7.4, 1.2 Hz, 1H), 7.02 (t, J = 7.5 Hz, 1H), 3.11 (t, J = 7.1 Hz, 2H), 2.57 (t, J = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 149.8, 146.0, 143.3, 134.9, 111.9, 110.5, 27.4, 22.4; HRMS calcd for $C_8H_8NO_3$ $[M+H]^+$ 166.0499; found: 166.0497.



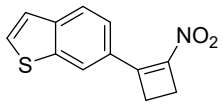
2-(2-nitrocyclobut-1-en-1-yl)thiophene (2x)

White solid (69% yield). melting point: 118-120 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.74 (dd, J = 7.3, 1.4 Hz, 1H), 7.12 – 6.95 (m, 2H), 2.91 (t, J = 7.1 Hz, 2H), 2.57 (t, J = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 150.9, 135.6, 133.6, 129.7, 127.5, 122.0, 27.4, 23.2; HRMS calcd for $C_8H_8NO_2S$ $[M+H]^+$ 182.0270; found: 182.0273.



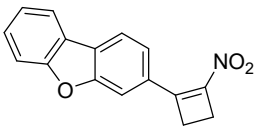
6-(2-nitrocyclobut-1-en-1-yl)benzofuran (2y)

White solid (63% yield). melting point: 130-132 °C.^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.15 (d, J = 7.5 Hz, 1H), 7.63 – 7.46 (m, 2H), 7.35 (d, J = 7.6 Hz, 2H), 3.05 (t, J = 7.1 Hz, 2H), 2.57 (t, J = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 154.1, 145.5, 143.5, 138.3, 134.2, 130.4, 124.4, 121.2, 108.4, 108.1, 27.8, 22.0; HRMS calcd for $C_{12}H_{10}NO_3$ $[M+H]^+$ 216.0655; found: 216.0658.



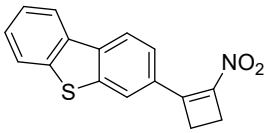
6-(2-nitrocyclobut-1-en-1-yl)benzo[b]thiophene (2z)

White solid (60% yield). melting point: 133-135 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.97 (d, J = 7.5 Hz, 1H), 7.90 (s, 1H), 7.46 (dt, J = 16.0, 7.4 Hz, 3H), 3.05 (t, J = 7.1 Hz, 2H), 2.57 (t, J = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 146.4, 139.0, 138.3, 136.0, 134.9, 126.1, 125.5, 123.7, 123.1, 118.8, 27.8, 22.5; HRMS calcd for $C_{12}H_{10}NO_2S$ $[M+H]^+$ 232.0427; found: 232.0422.



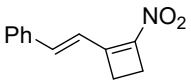
3-(2-nitrocyclobut-1-en-1-yl)dibenzo[b,d]furan (2aa)

White solid (54% yield). melting point: 182-184 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.04 (d, J = 7.4 Hz, 1H), 7.95 – 7.79 (m, 2H), 7.74 (d, J = 7.5 Hz, 1H), 7.55 (d, J = 10.4 Hz, 2H), 7.44 (dt, J = 7.4, 3.8 Hz, 1H), 3.04 (t, J = 7.1 Hz, 2H), 2.57 (t, J = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 156.1, 155.5, 151.5, 138.3, 136.0, 127.1, 123.8, 122.8, 122.1, 121.3, 120.0, 119.7, 112.1, 108.7, 27.8, 21.5; HRMS calcd for $C_{16}H_{12}NO_3$ $[M+H]^+$ 266.0812; found: 266.0815.



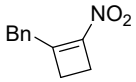
3-(2-nitrocyclobut-1-en-1-yl)dibenzo[b,d]thiophene (2ab)

White solid (51% yield). melting point: 177-179 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.51 – 8.40 (m, 1H), 8.31 – 8.13 (m, 2H), 8.03 – 7.83 (m, 3H), 7.37 (dd, J = 7.5, 1.0 Hz, 1H), 3.02 (t, J = 7.1 Hz, 2H), 2.57 (t, J = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 143.5, 138.9, 138.5, 138.3, 135.4, 134.6, 132.4, 124.3, 124.2, 124.2, 123.0, 122.9, 121.4, 119.5, 27.8, 22.4; HRMS calcd for $C_{16}H_{12}NO_2S$ $[M+H]^+$ 282.0583; found: 282.0588.



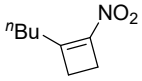
(E)-(2-(2-nitrocyclobut-1-en-1-yl)vinyl)benzene (2ac)

White solid (63% yield). melting point: 109-111 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.54 (d, J = 6.5 Hz, 2H), 7.46 – 7.29 (m, 3H), 6.85 (d, J = 15.1 Hz, 1H), 6.49 (d, J = 15.2 Hz, 1H), 2.93 (t, J = 7.1 Hz, 2H), 2.57 (t, J = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 148.9, 137.9, 137.0, 130.9, 129.8, 129.0, 126.7, 126.1, 27.2, 23.7; HRMS calcd for $C_{12}H_{12}NO_2$ $[M+H]^+$ 202.0863; found: 202.0865.



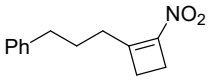
((2-nitrocyclobut-1-en-1-yl)methyl)benzene (2ad)

White solid (40% yield). melting point: 111-113 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.28 (s, 1H), 7.26 – 7.16 (m, 4H), 3.22 (s, 2H), 3.03 (t, J = 7.1 Hz, 2H), 2.57 (t, J = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 154.8, 148.7, 137.7, 129.2, 128.1, 127.1, 36.8, 26.6, 22.4; HRMS calcd for $C_{11}H_{12}NO_2$ $[M+H]^+$ 190.0863; found: 190.0867.



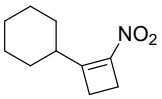
1-butyl-2-nitrocyclobut-1-ene (2ae)

White solid (37% yield). melting point: 108-110 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 3.18 (t, J = 7.1 Hz, 2H), 2.57 (t, J = 7.1 Hz, 2H), 2.13 (t, J = 7.1 Hz, 2H), 1.33 (ddd, J = 20.9, 14.5, 7.3 Hz, 2H), 0.93 (t, J = 7.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 145.8, 141.2, 31.0, 29.7, 29.0, 26.6, 22.7, 14.0; HRMS calcd for $C_8H_{14}NO_2$ $[M+H]^+$ 156.1019; found: 156.1014.



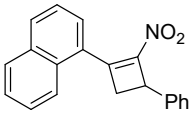
(3-(2-nitrocyclobut-1-en-1-yl)propyl)benzene (2af)

White solid (41% yield). melting point: 109-111 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.28 (s, 1H), 7.24 (s, 1H), 7.23 – 7.12 (m, 3H), 2.92 (t, J = 7.1 Hz, 2H), 2.72 – 2.47 (m, 4H), 2.13 (t, J = 7.1 Hz, 2H), 1.51 (p, J = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 152.5, 141.9, 140.0, 128.4, 128.4, 126.2, 33.8, 31.0, 29.2, 27.5, 26.6; HRMS calcd for $C_{13}H_{16}NO_2$ $[M+H]^+$ 218.1176; found: 218.1174.



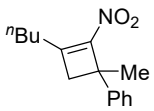
(2-nitrocyclobut-1-en-1-yl)cyclohexane (2ag)

White solid (38% yield). melting point: 93-95 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 2.98 (t, J = 7.1 Hz, 2H), 2.57 (t, J = 7.1 Hz, 2H), 2.12 (p, J = 6.9 Hz, 1H), 1.77 – 1.39 (m, 7H), 1.39 – 1.07 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 164.3, 145.1, 39.5, 32.5, 30.0, 26.7, 25.7, 25.7; HRMS calcd for $C_{10}H_{16}NO_2$ $[M+H]^+$ 182.1176; found: 182.1172.



1-(2-nitro-3-phenylcyclobut-1-en-1-yl)naphthalene (2ah)

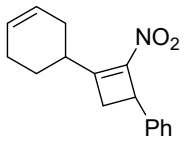
White solid (54% yield). melting point: 157-159 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.05 (d, J = 7.4 Hz, 1H), 7.98 (d, J = 7.5 Hz, 1H), 7.90 (dd, J = 11.4, 7.5 Hz, 2H), 7.71 (dt, J = 14.9, 6.9 Hz, 2H), 7.52 (t, J = 7.4 Hz, 1H), 7.41 – 7.27 (m, 4H), 7.23 (d, J = 7.1 Hz, 1H), 3.85 (t, J = 7.0 Hz, 1H), 2.98 (dd, J = 12.4, 7.0 Hz, 1H), 2.73 (dd, J = 12.4, 7.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 153.2, 148.5, 146.4, 133.7, 132.6, 131.3, 128.6, 128.3, 127.7, 127.1, 126.8, 126.7, 126.4, 125.9, 124.7, 44.5, 36.1; HRMS calcd for $C_{20}H_{16}NO_2$ $[M+H]^+$ 302.1176; found: 302.1173.



(3-butyl-1-methyl-2-nitrocyclobut-2-en-1-yl)benzene (2ai)

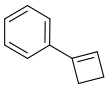
White solid (19% yield). melting point: 128-130 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.55 (d, J = 5.8 Hz, 2H), 7.37 – 7.29 (m, 1H), 7.28 (s, 1H), 7.24 (s, 1H), 2.92 (d, J = 12.4 Hz, 1H), 2.67 (d, J = 12.4 Hz, 1H), 2.02 – 1.86 (m, 2H), 1.51 – 1.20 (m, 7H), 0.93 (t, J = 7.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 165.9, 143.9, 143.01, 128.5, 126.9, 125.2, 50.4, 49.3, 30.3, 29.7, 25.2,

22.7, 14.90; HRMS calcd for $C_{15}H_{20}NO_2$ $[M+H]^+$ 246.1489; found: 246.1484.



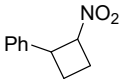
(3-butyl-1-methyl-2-nitrocyclobut-2-en-1-yl)benzene (2aj)

White solid (43% yield). melting point: 145-147 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.41 – 7.27 (m, 5H), 5.75 – 5.61 (m, 2H), 3.85 (t, J = 9.1 Hz, 1H), 2.98 (dd, J = 12.4, 9.0 Hz, 1H), 2.73 (dd, J = 12.4, 9.1 Hz, 1H), 2.34 (dd, J = 14.5, 7.8 Hz, 2H), 2.25 – 2.15 (m, 3H), 1.87 (dd, J = 12.6, 6.5 Hz, 1H), 1.66 (dd, J = 12.7, 6.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 158.4, 147.3, 141.3, 128.5, 127.9, 126.9, 126.4, 124.5, 40.2, 36.7, 32.0, 31.0, 24.0; HRMS calcd for $C_{16}H_{18}NO_2$ $[M+H]^+$ 256.1332; found: 256.1337.



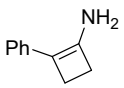
cyclobut-1-en-1-ylbenzene (3)

White solid (42% yield). melting point: 64-66 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.25 – 7.15 (m, 3H), 7.05 (dd, J = 7.1, 2.2 Hz, 2H), 6.31 (t, J = 6.2 Hz, 1H), 2.77 (t, J = 7.1 Hz, 2H), 2.57 (dd, J = 13.5, 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 144.1, 139.7, 128.2, 128.0, 126.2, 124.9, 26.9, 26.0; HRMS calcd for $C_{10}H_{11}$ $[M+H]^+$ 131.0855; found: 131.0852.



(2-nitrocyclobutyl)benzene (4)

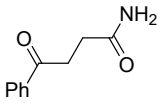
White solid (76% yield). melting point: 55-57 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.28 (d, J = 2.0 Hz, 1H), 7.24 (d, J = 2.4 Hz, 1H), 7.19 (d, J = 6.5 Hz, 3H), 5.02 (q, J = 6.9 Hz, 1H), 4.06 (q, J = 6.9 Hz, 1H), 2.83 (dd, J = 12.8, 6.9 Hz, 1H), 2.61 – 2.43 (m, 2H), 2.31 (dd, J = 12.8, 6.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 140.5, 128.5, 126.5, 125.2, 97.3, 45.7, 21.9, 19.0; HRMS calcd for $C_{10}H_{12}NO_2$ $[M+H]^+$ 178.0863; found: 178.0861.



2-phenylcyclobut-1-en-1-amine (5)

White solid (68% yield). melting point: 101-103 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 77.37 – 7.29 (m, 2H), 7.19 (d, J = 6.2 Hz, 3H), 4.55 (s, 2H), 2.74 (t, J = 7.1 Hz, 2H), 2.49 (t, J = 7.1 Hz,

2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 139.7, 136.1, 128.3, 128.0, 126.3, 107.5, 33.3, 28.8; HRMS calcd for $C_{10}H_{12}N$ $[M+H]^+$ 146.0964; found: 146.0968.



4-oxo-4-phenylbutanamide (6)

White solid (71% yield). melting point: 78-80 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.02 – 7.91 (m, 2H), 7.65 – 7.54 (m, 1H), 7.48 (t, J = 7.4 Hz, 2H), 7.20 (s, 2H), 2.83 (t, J = 5.2 Hz, 2H), 2.37 (t, J = 5.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 199.3, 174.2, 138.1, 133.2, 128.8, 125.8, 39.3, 33.1; HRMS calcd for $C_{10}H_{12}NO_2$ $[M+H]^+$ 178.0863; found: 178.0866.

6 X-ray of 2a Crystallography details

Compound **2a** was dissolved in MeOH and cold *n*-hexane was added, leaving to slow evaporation overnight to yield colorless needle. A suitable crystal was selected and mounted on a X-ray with Mo radiation (7.1171(2), 17.9923(6), 7.2098(2)) for cell determination and subsequent data collection at 296 K. Using SHELXL-2014, the structure was solved with the ShelXT11[1]

structure solution program using Intrinsic Phasing and refined with the ShelXL12[2] refinement package using Least Squares minimisation. The solved structure of **2a** has been deposited in The Cambridge Crystallographic Data Centre (CCDC: 2478060)

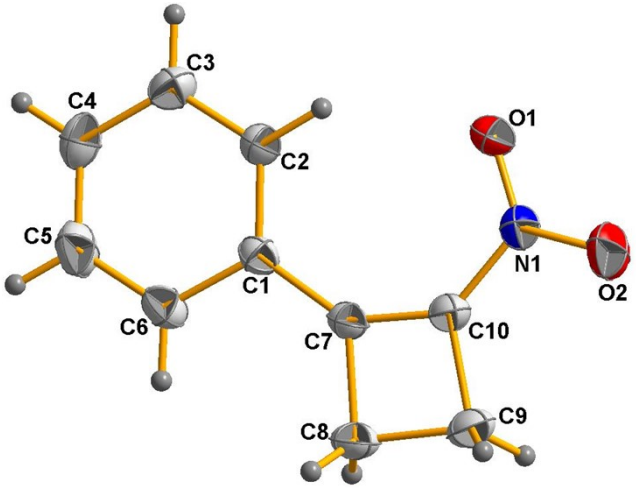


Figure S2. ORTEP diagram of compound **2a** with ellipsoid shown at the 50% contour percent probability level

Table S1. Crystal Data and Structure Refinement for **2a**

Identification code	**2a**
Empirical formula	$C_{10}H_9NO_2$
Formula weight	175.18
Temperature/K	290.89(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	7.1171(2)
b/Å	17.9923(6)
c/Å	7.2098(2)
α/°	90.00
β/°	106.534(4)
γ/°	90.00
Volume/Å^3	885.05(5)
Z	4
ρ_{calc}g/cm^3	1.315
μ/mm^{-1}	0.762
F(000)	368.0
Crystal size/mm^3	0.21 × 0.15 × 0.14
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	13.88 to 138.7
Index ranges	$-6 \le h \le 8$, $-21 \le k \le 21$, $-8 \le l \le 6$
Reflections collected	3211
Independent reflections	1580 [R_{int} = 0.0206, R_{sigma} = 0.0254]
Data/restraints/parameters	1580/0/126

Goodness-of-fit on F^2	1.024
Final R indexes [I>=2σ (I)]	R_1 = 0.0450, wR_2 = 0.1201
Final R indexes [all data]	R_1 = 0.0483, wR_2 = 0.1242
Largest diff. peak/hole / e $Å^{-3}$	0.16/-0.19

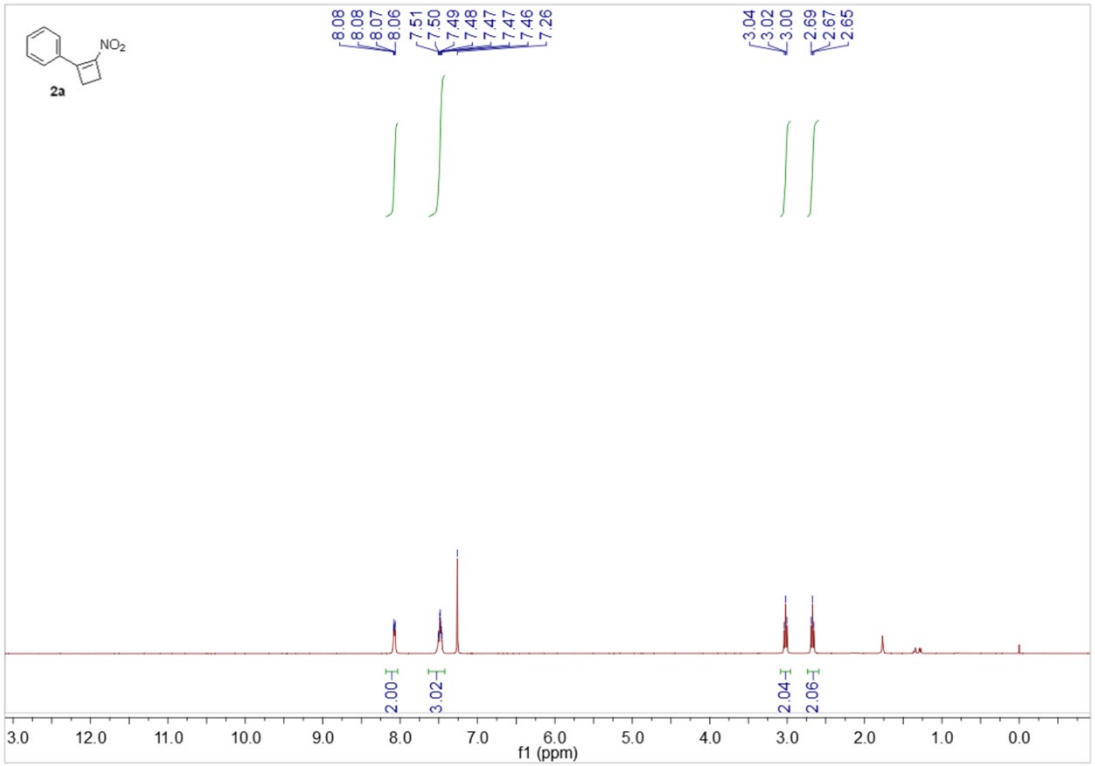
7 Refrence

1. D. Wang, R. Ren, C. Zhu. Manganese-Promoted Ring-Opening Hydrazination of Cyclobutanols: Synthesis of Alkyl Hydrazines. *J. Org. Chem*. **2016**, *81*, 8043–8049.

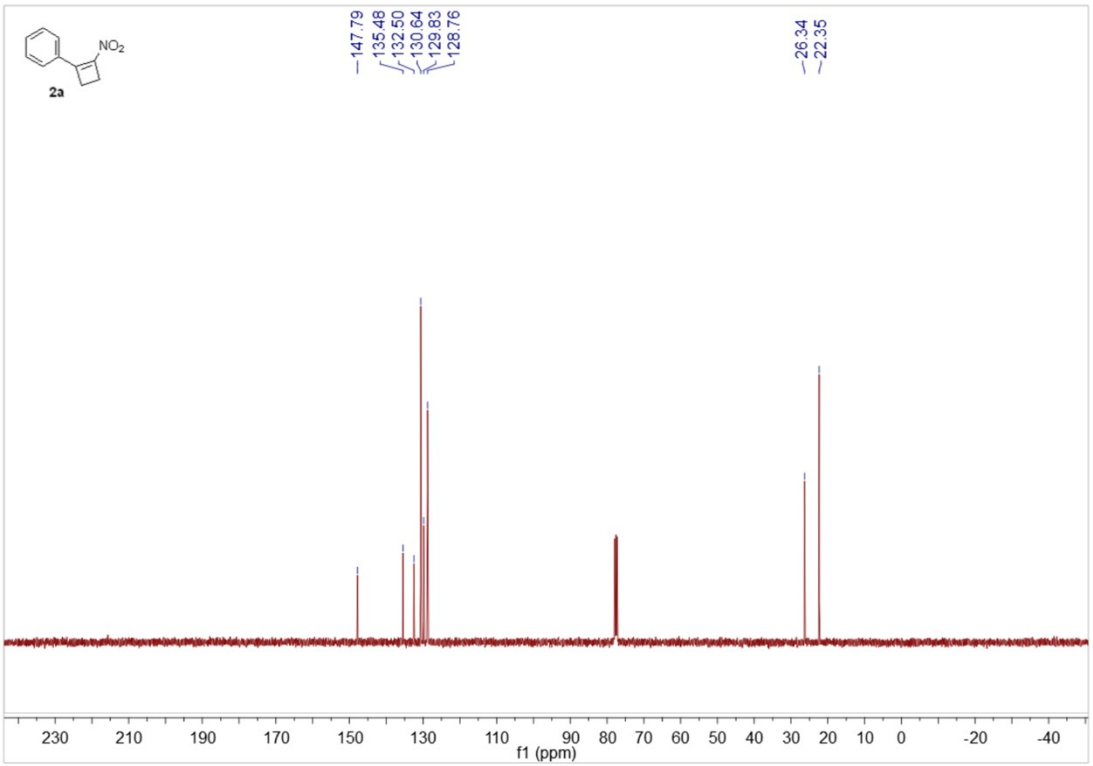
2. W.-J. Yan, H.-Y. Tu, Z. Liao, X.-Q. Shen, X.-G. Zhang. Palladium-Catalyzed Ring-Opening Diarylation of Cyclobutanols for the Synthesis of Acylindanes. *Adv. Synth. Catal.* **2023**, *365*, 2147-2151.

8 Copies of NMR Spectra

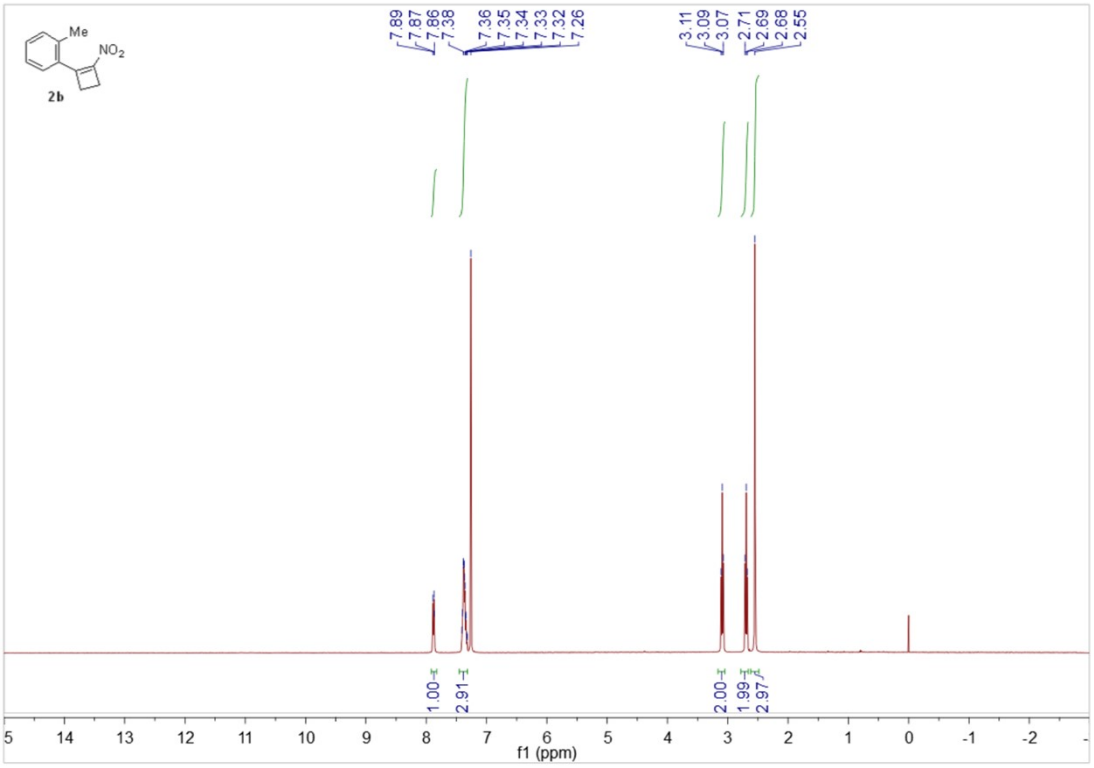
^{1}H NMR of **2a** (400 MHz, $CDCl_3$):



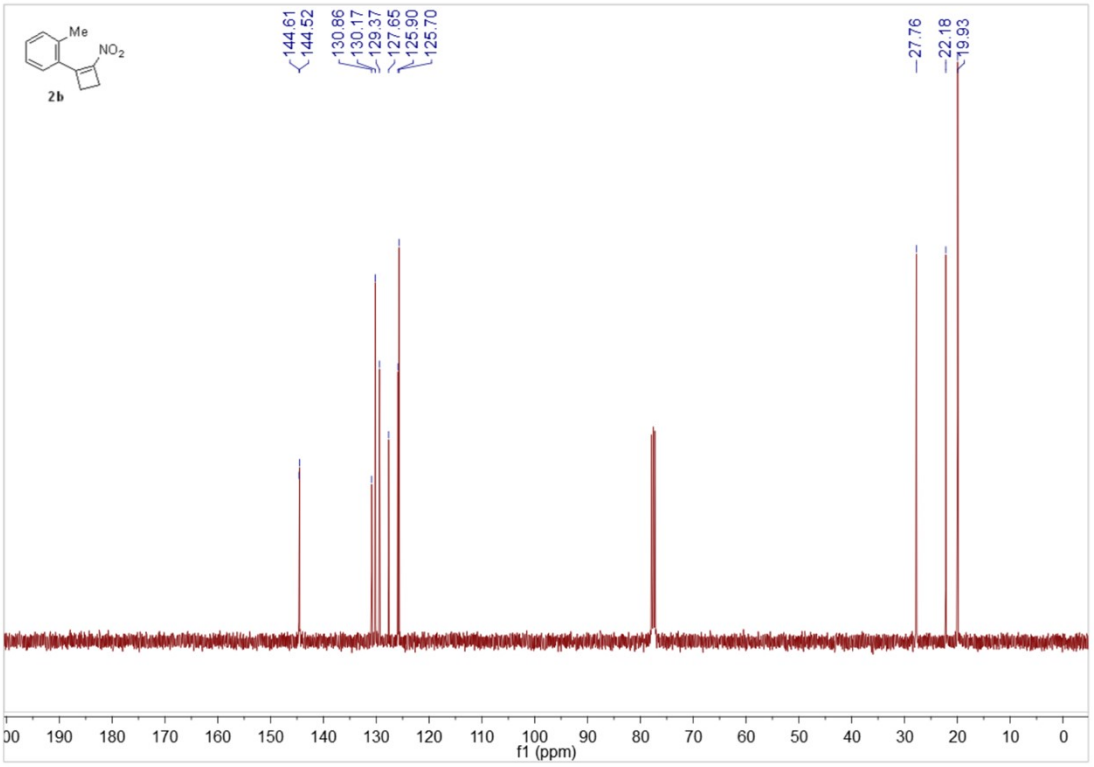
^{13}C NMR of **2a** (100 MHz, $CDCl_3$):



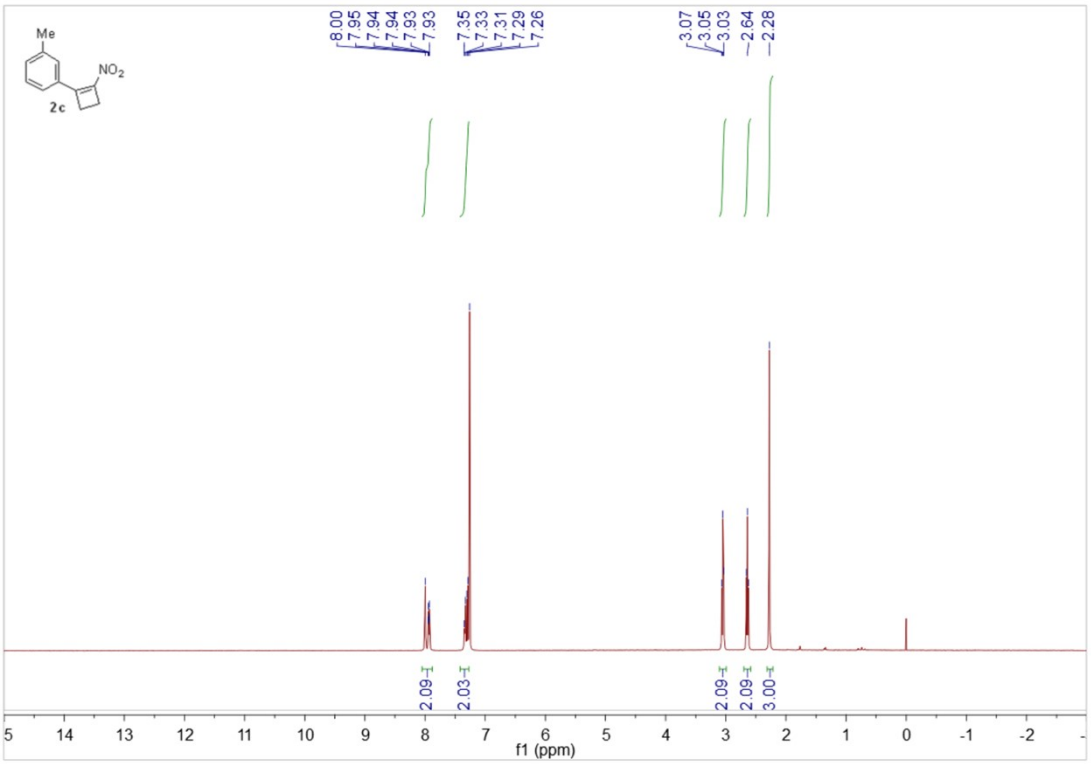
^{1}H NMR of **2b** (400 MHz, $CDCl_3$):



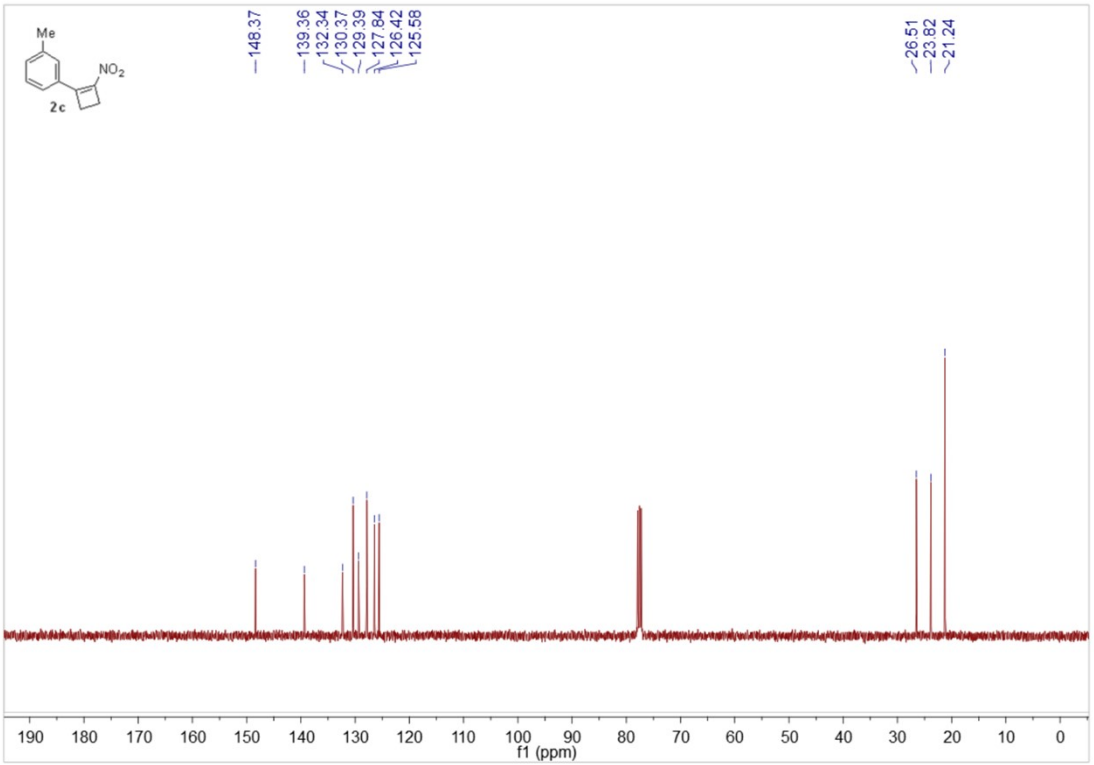
^{13}C NMR of **2b** (100 MHz, $CDCl_3$):



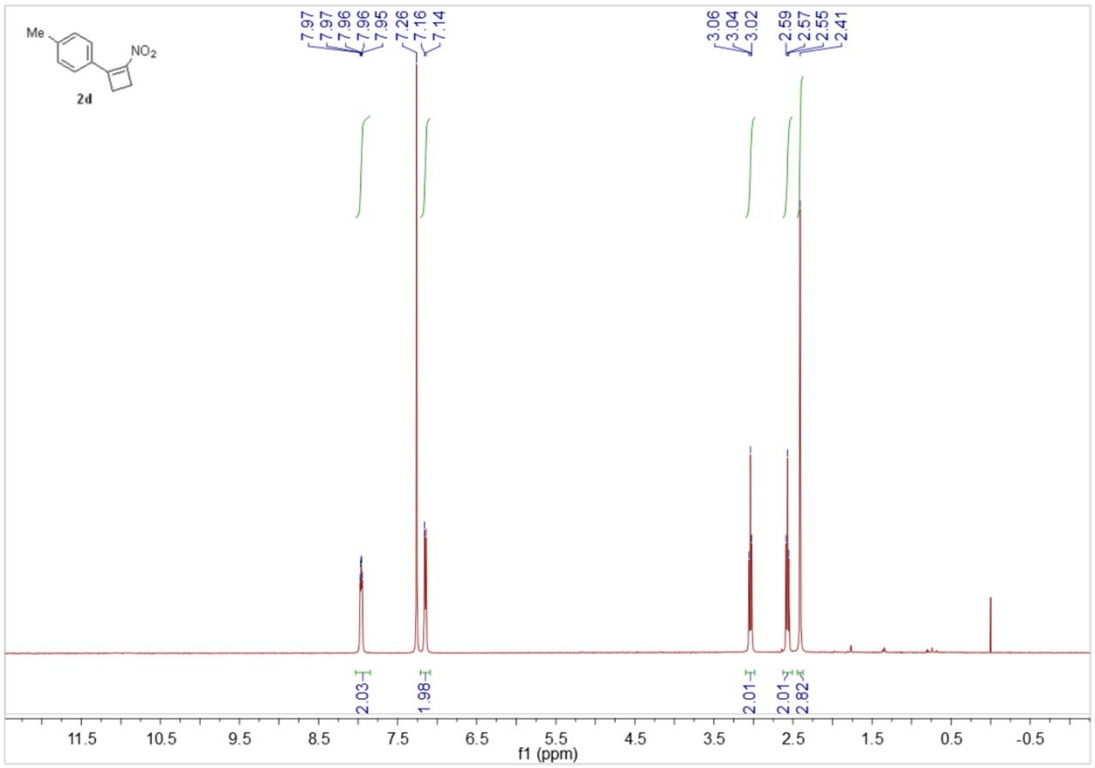
^{1}H NMR of **2c** (400 MHz, $CDCl_3$):



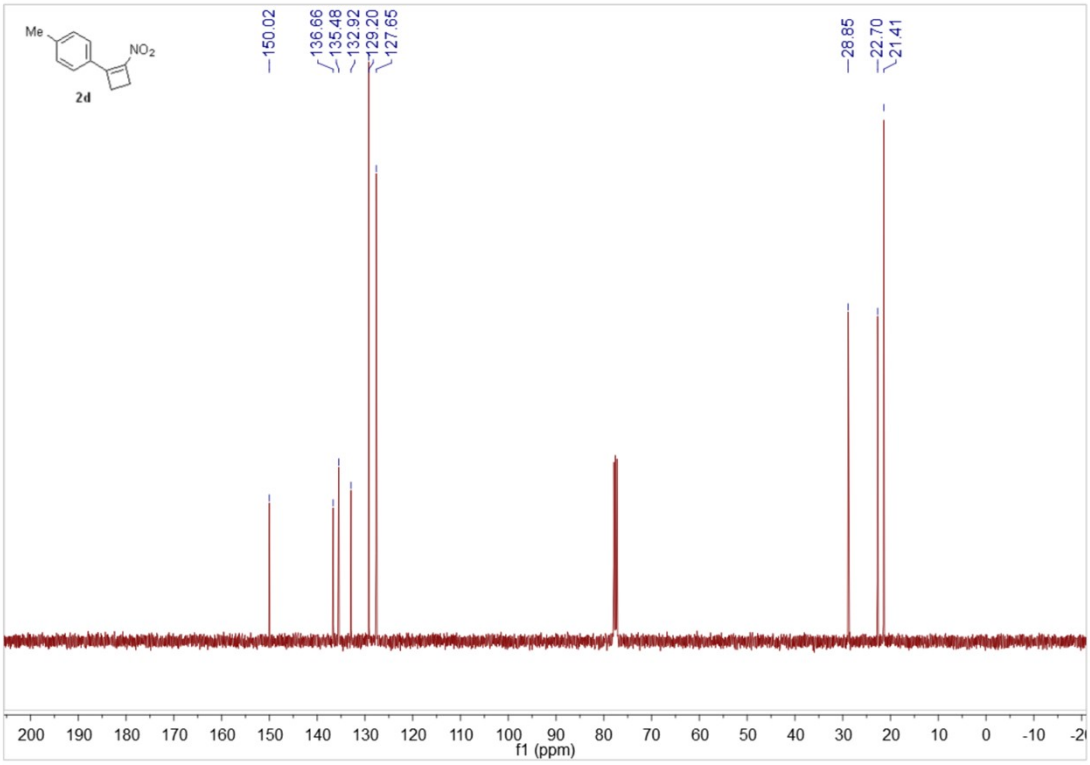
^{13}C NMR of **2c** (100 MHz, $CDCl_3$):



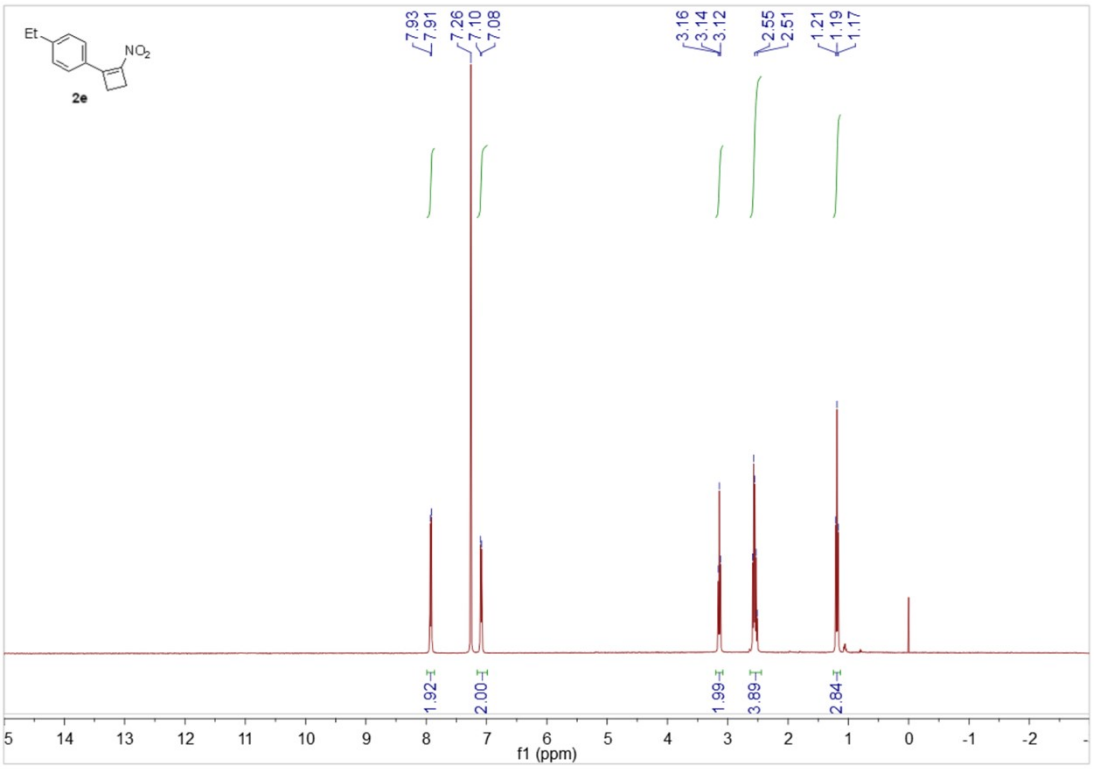
^{1}H NMR of **2d** (400 MHz, $CDCl_3$):



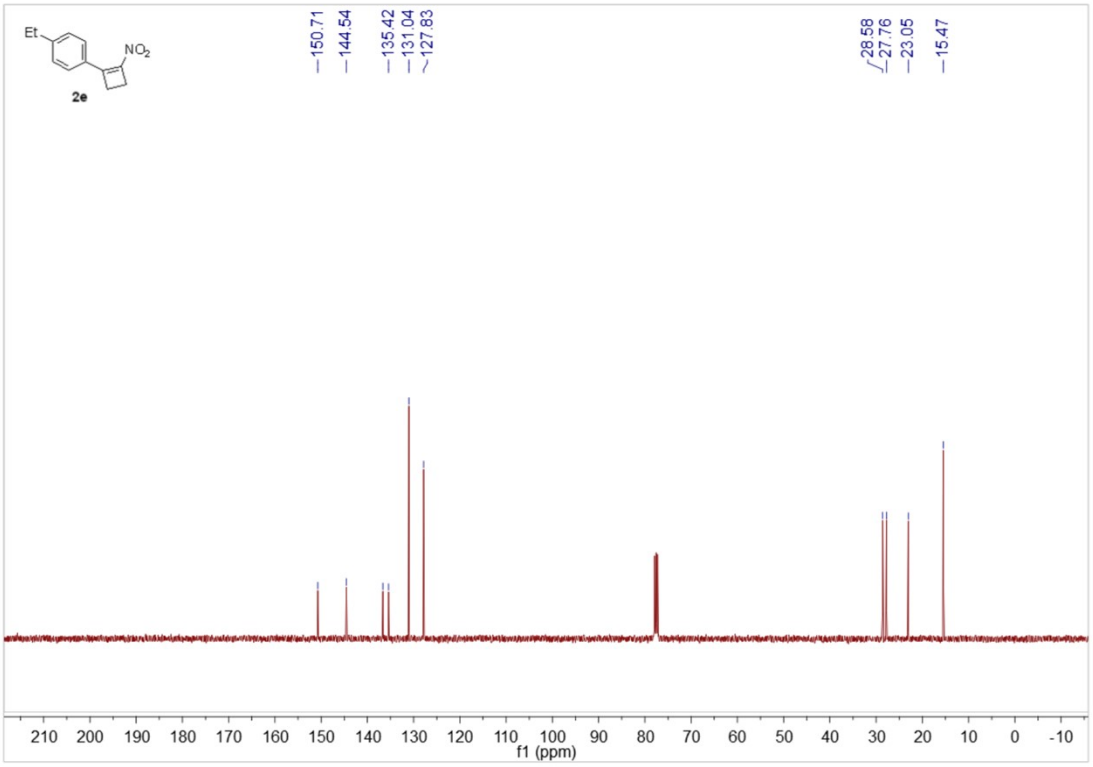
^{13}C NMR of **2d** (100 MHz, $CDCl_3$):



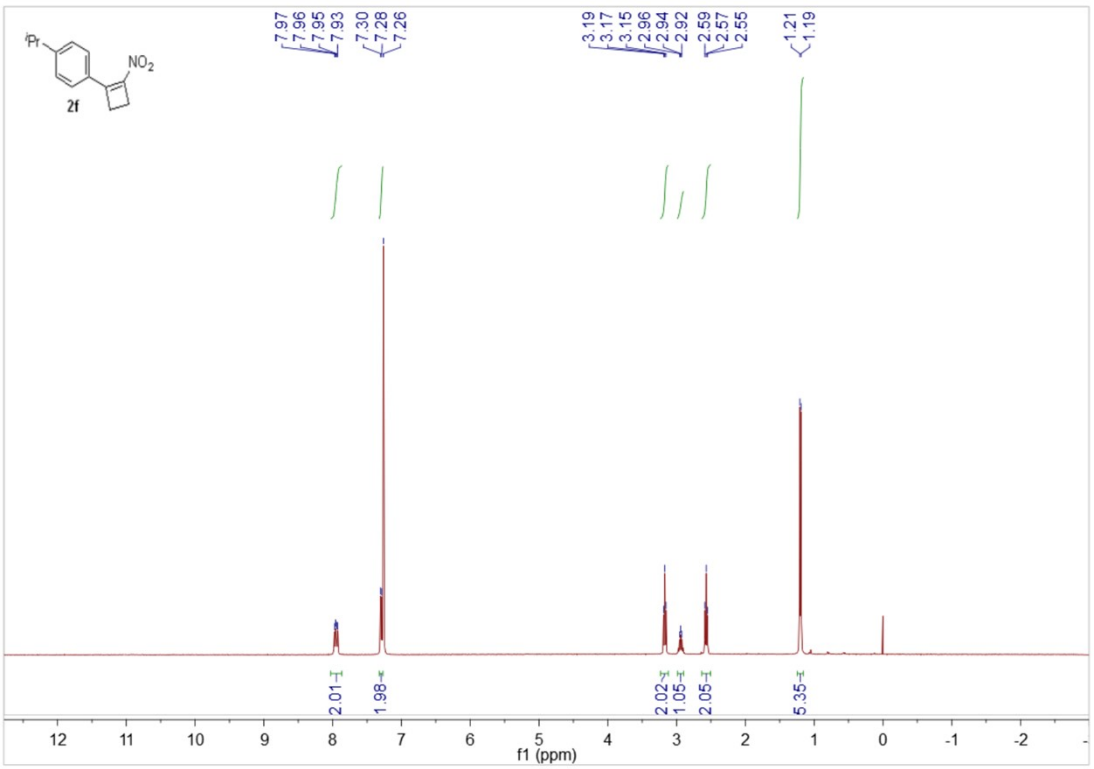
^{1}H NMR of **2e** (400 MHz, $CDCl_3$):



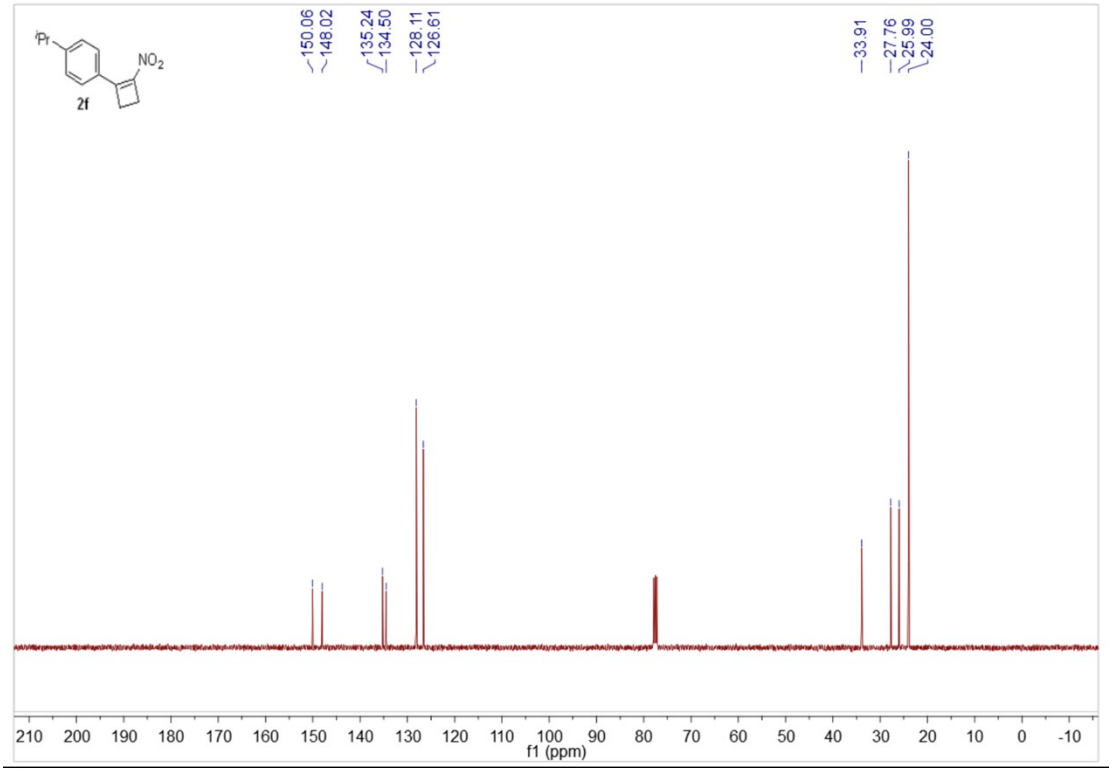
^{13}C NMR of **2e** (100 MHz, $CDCl_3$):



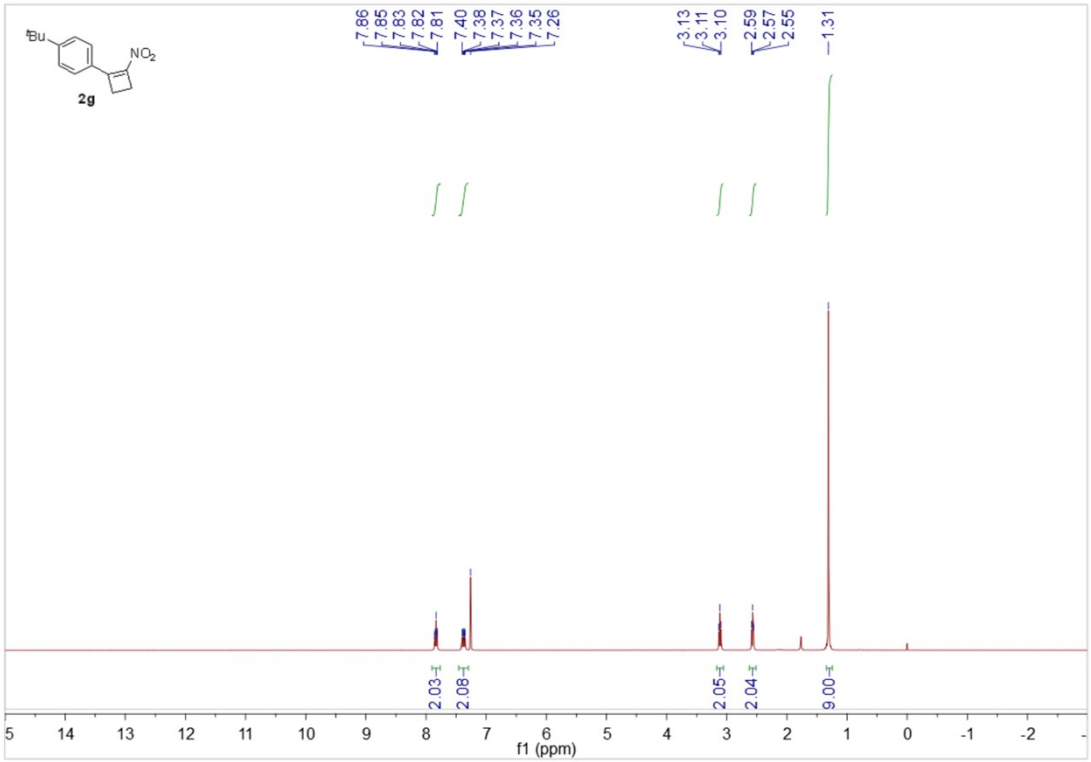
^{1}H NMR of **2f** (400 MHz, $CDCl_3$):



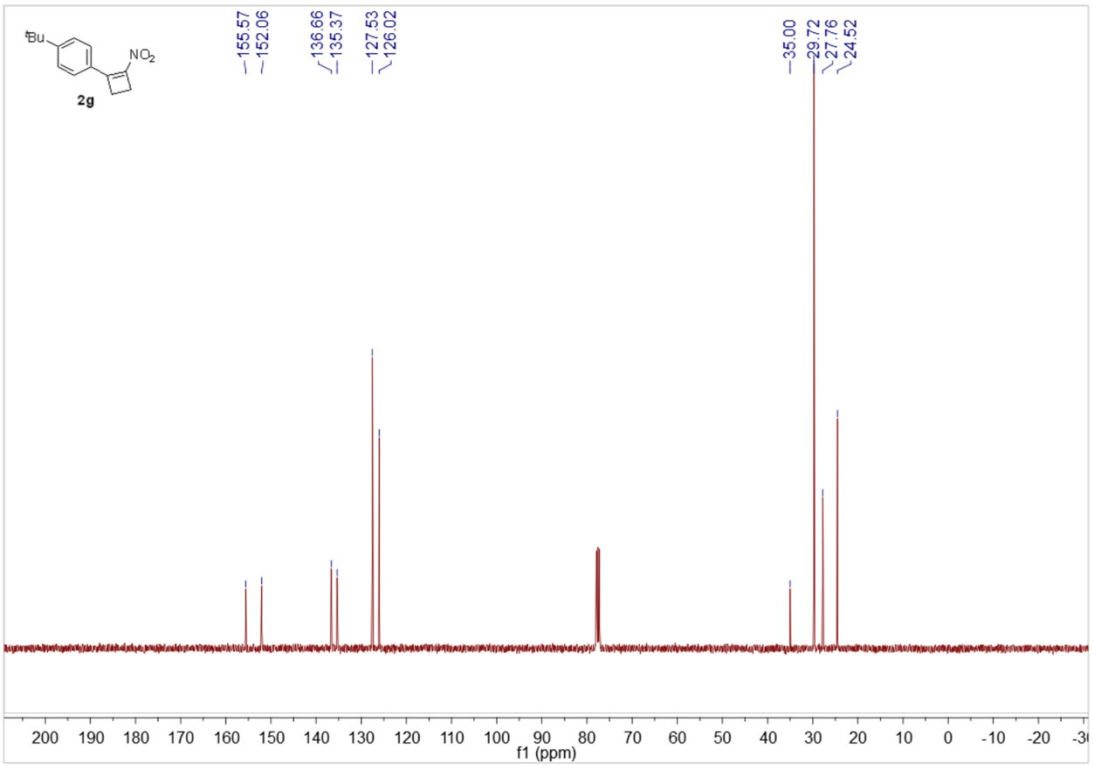
^{13}C NMR of **2f** (100 MHz, $CDCl_3$):



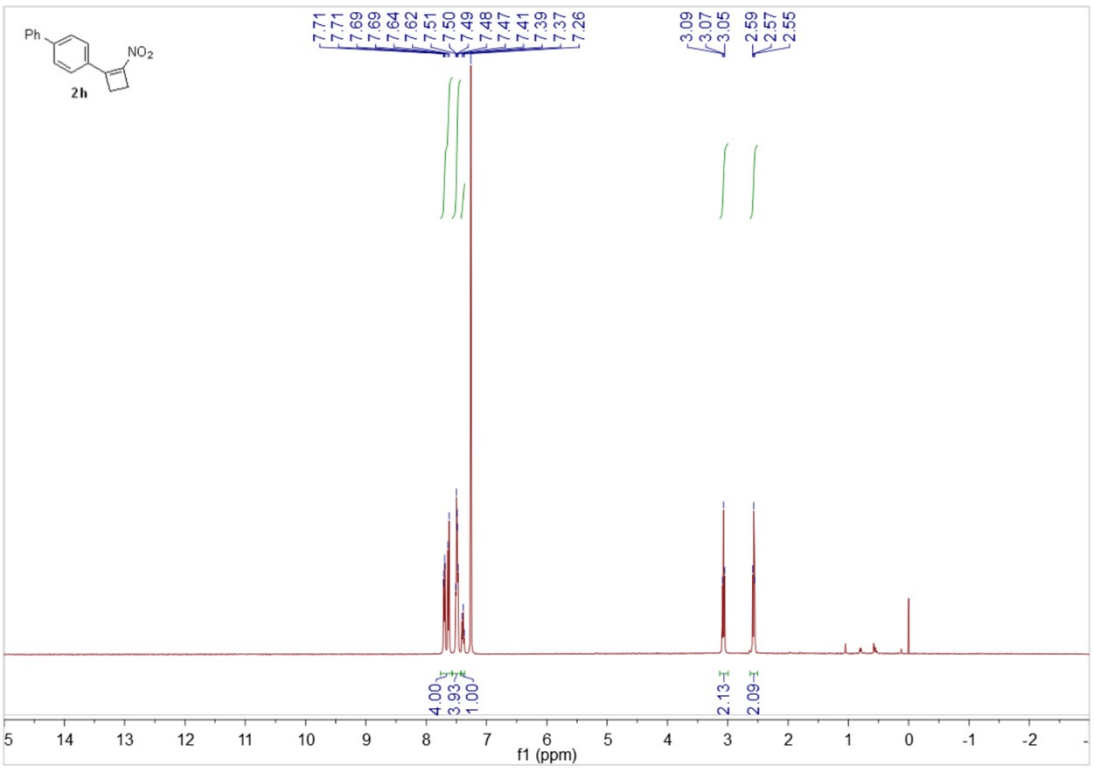
^{1}H NMR of **2g** (400 MHz, $CDCl_3$):



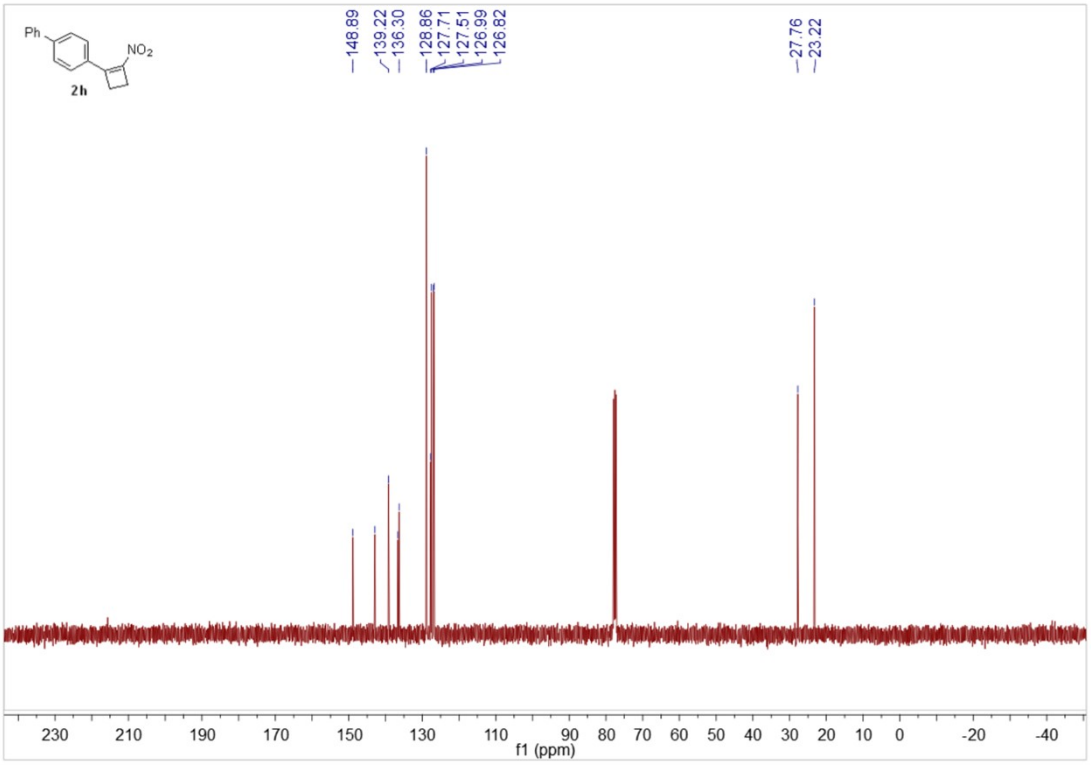
^{13}C NMR of **2g** (100 MHz, $CDCl_3$):



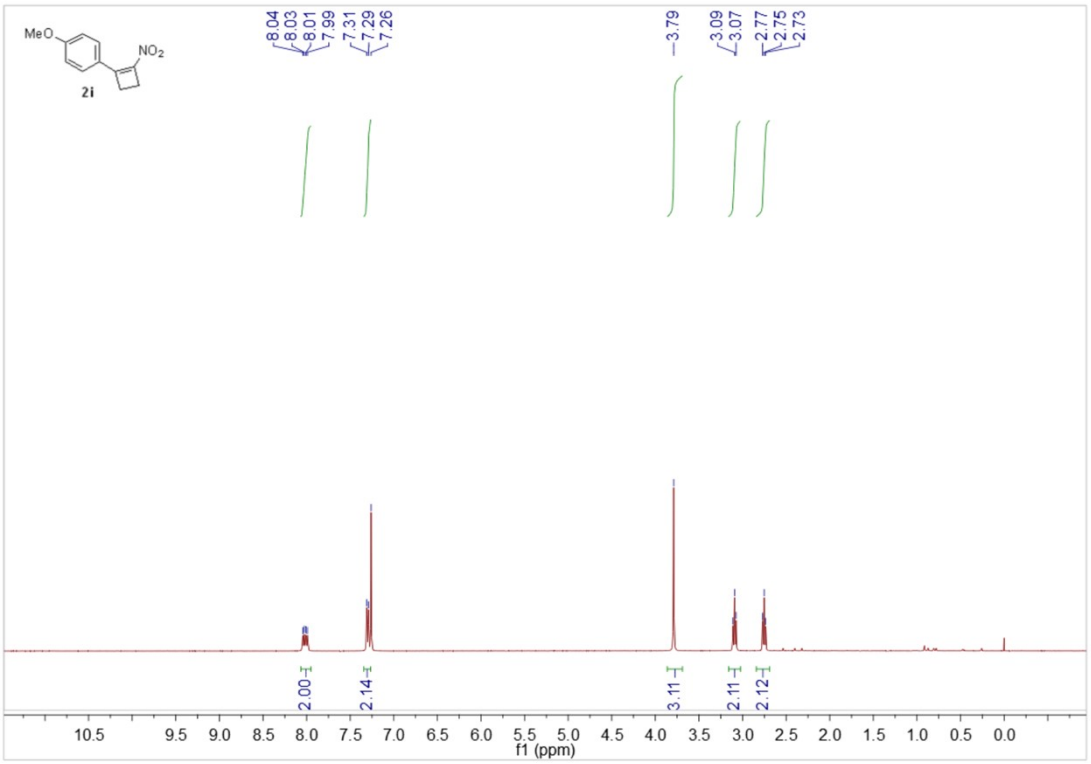
^{1}H NMR of **2h** (400 MHz, $CDCl_3$):



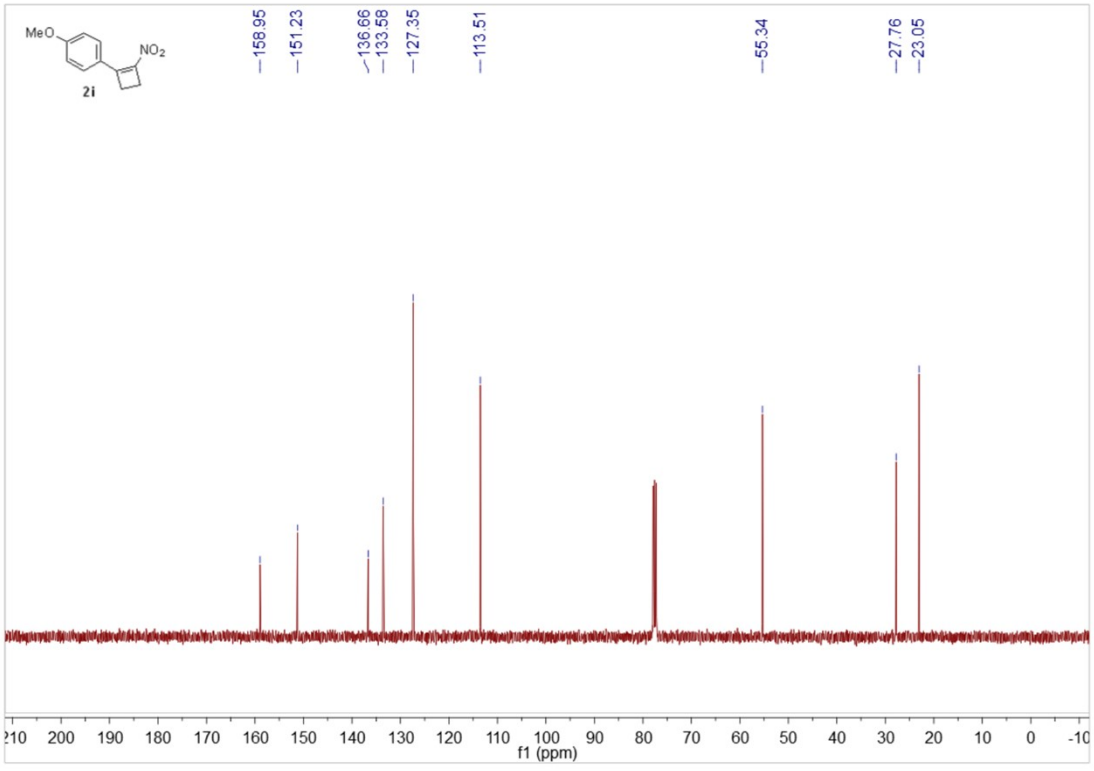
^{13}C NMR of **2h** (100 MHz, $CDCl_3$):



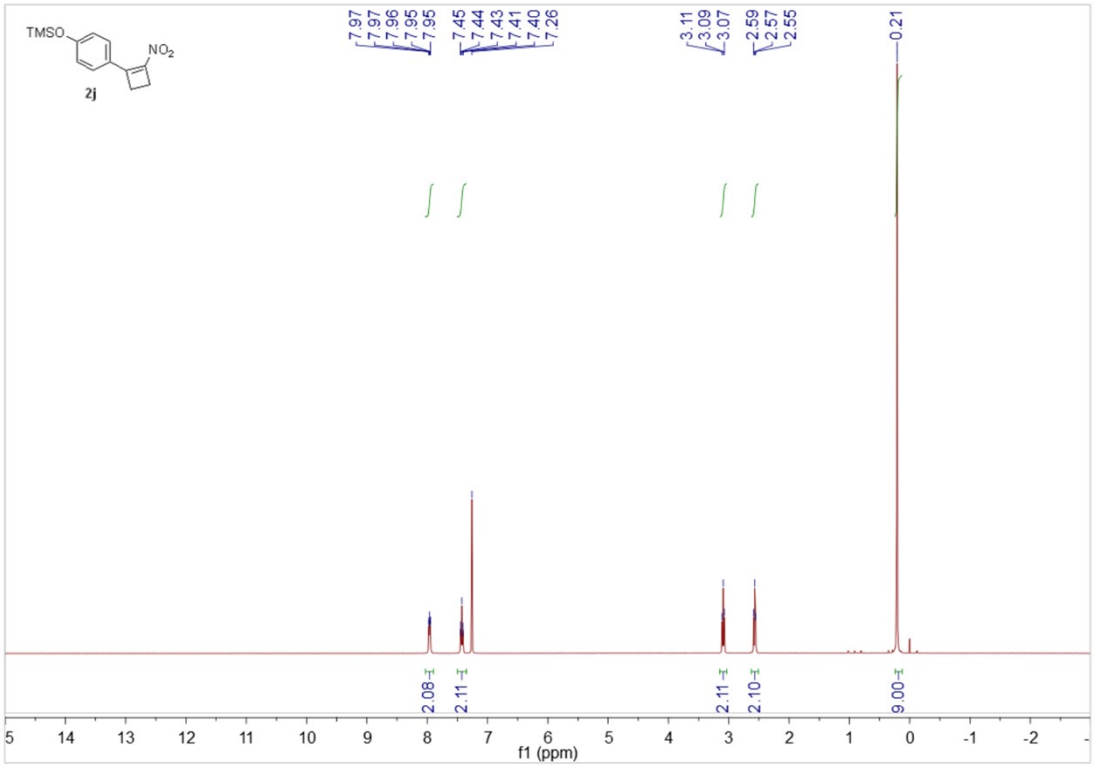
^{1}H NMR of **2i** (400 MHz, $CDCl_3$):



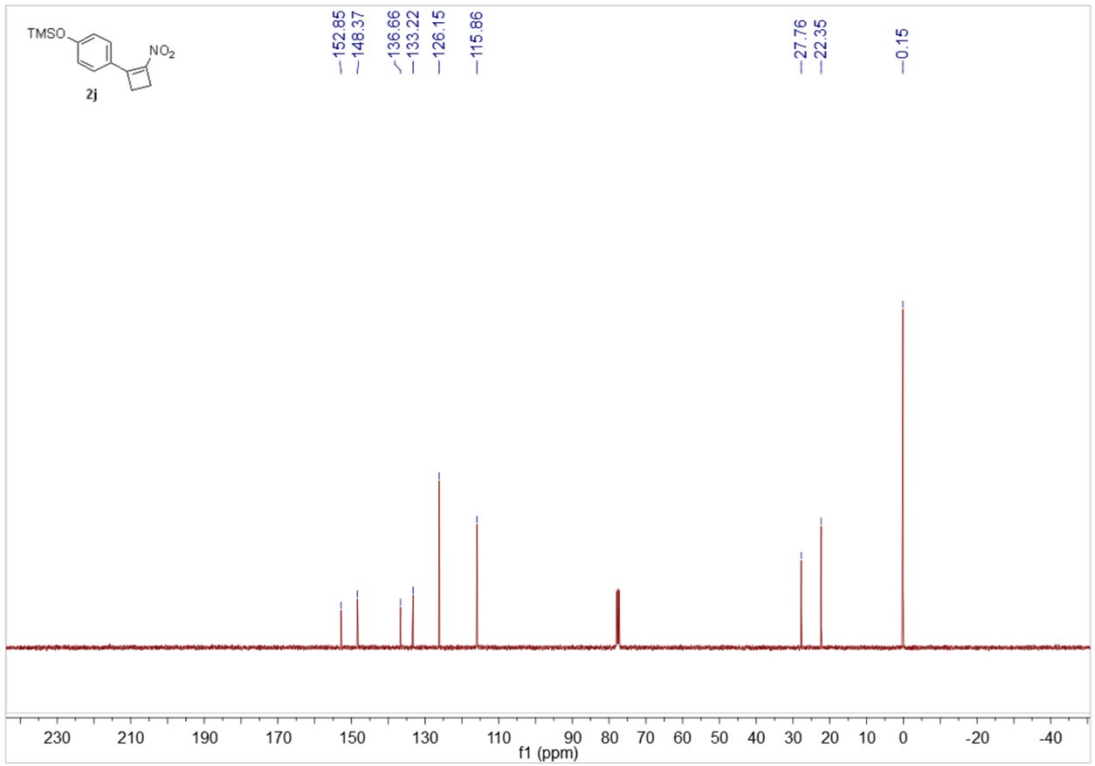
^{13}C NMR of **2i** (100 MHz, $CDCl_3$):



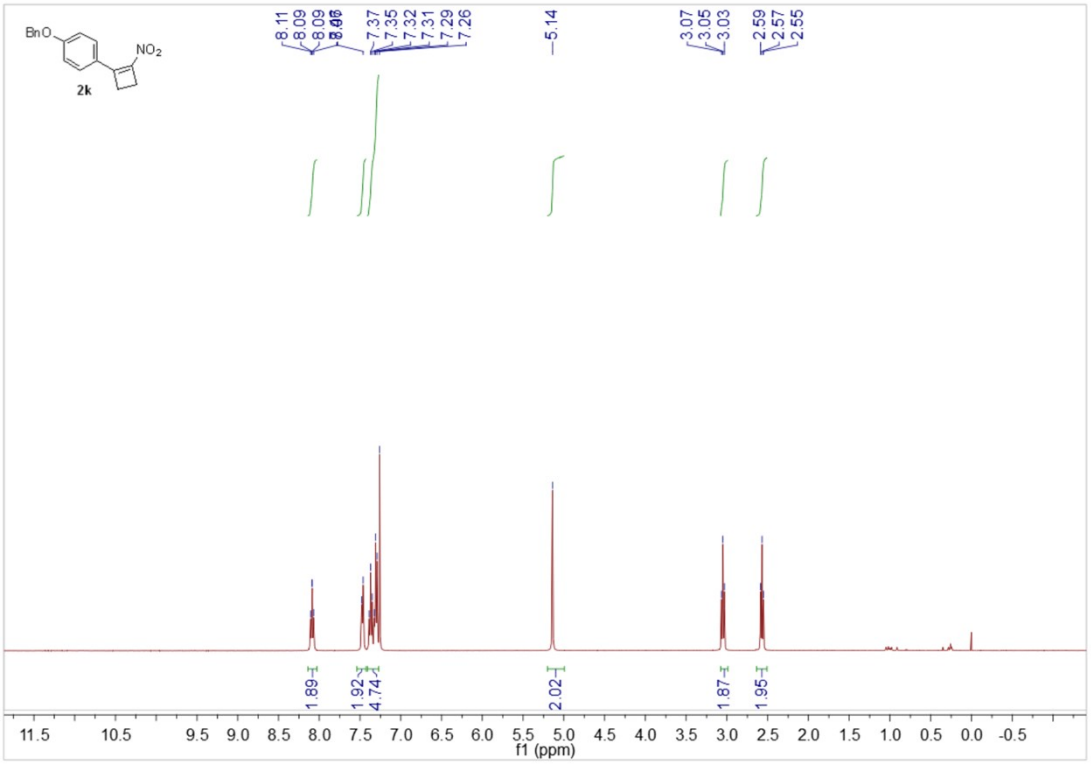
^{1}H NMR of **2j** (400 MHz, $CDCl_3$):



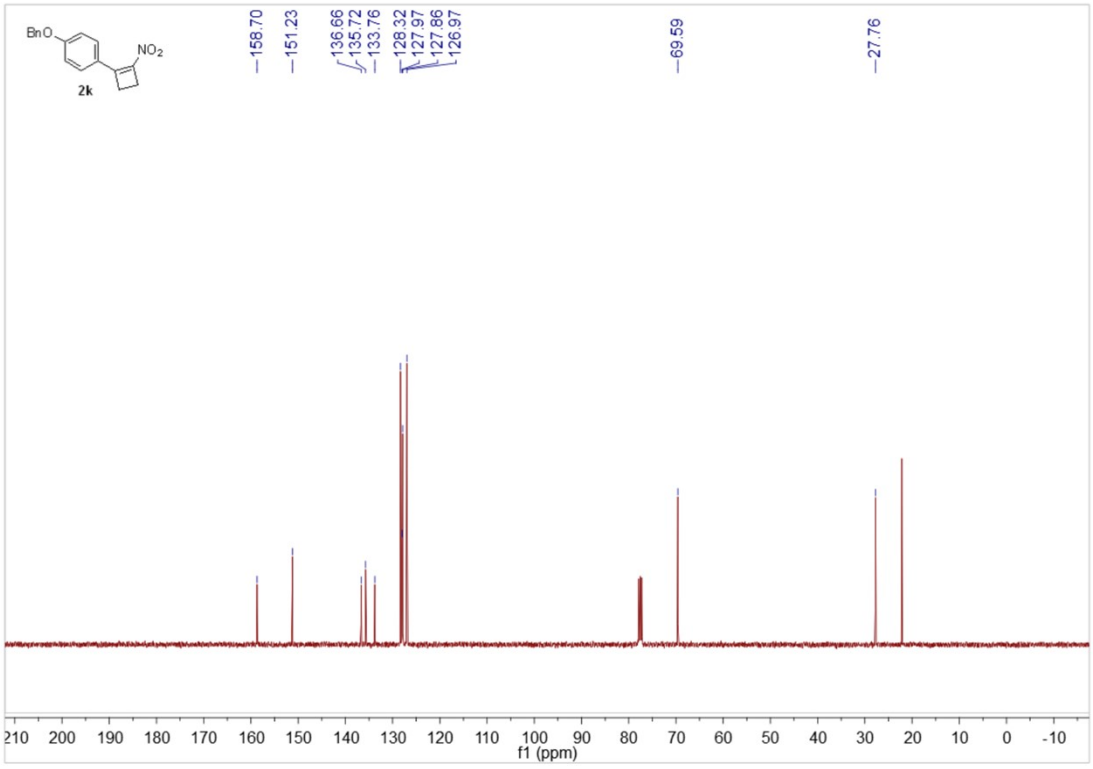
^{13}C NMR of **2j** (100 MHz, $CDCl_3$):



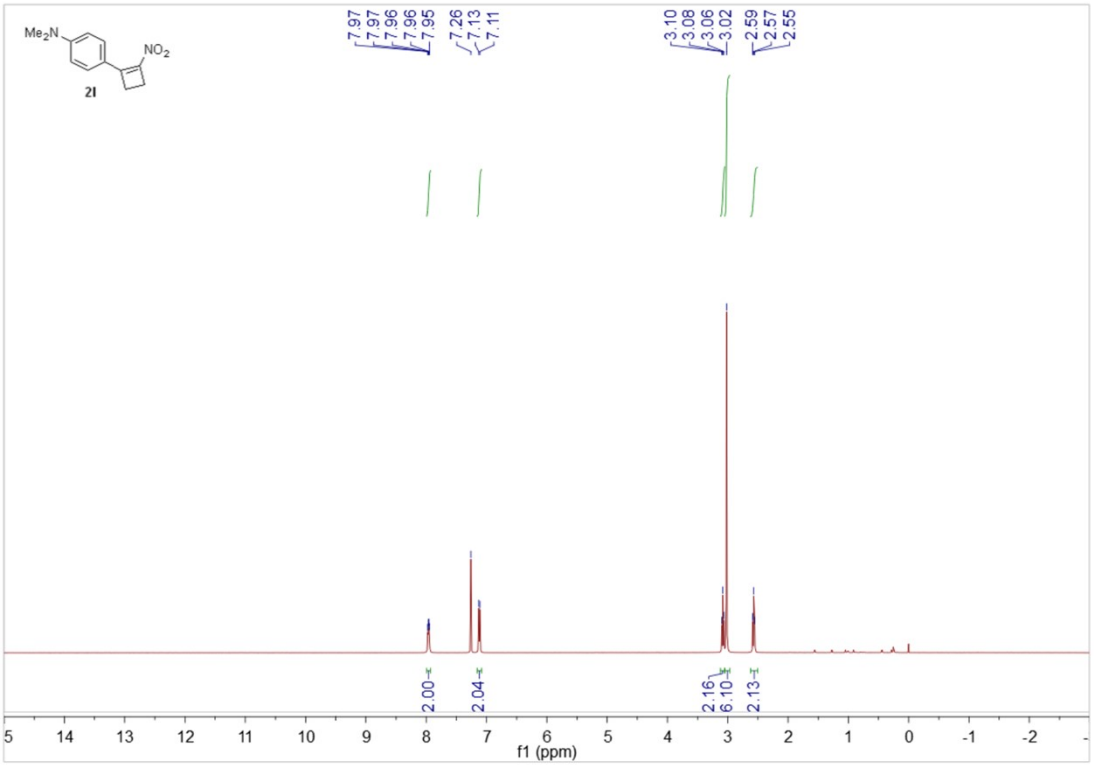
^{1}H NMR of **2k** (400 MHz, $CDCl_3$):



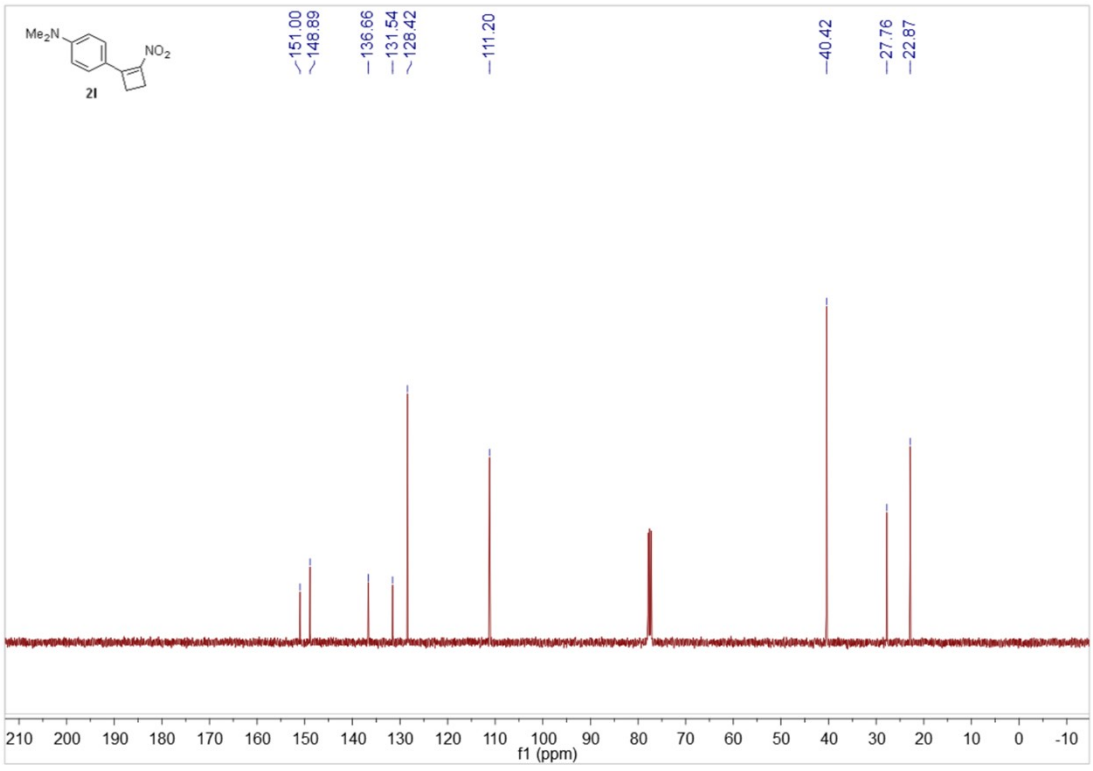
^{13}C NMR of **2k** (100 MHz, $CDCl_3$):



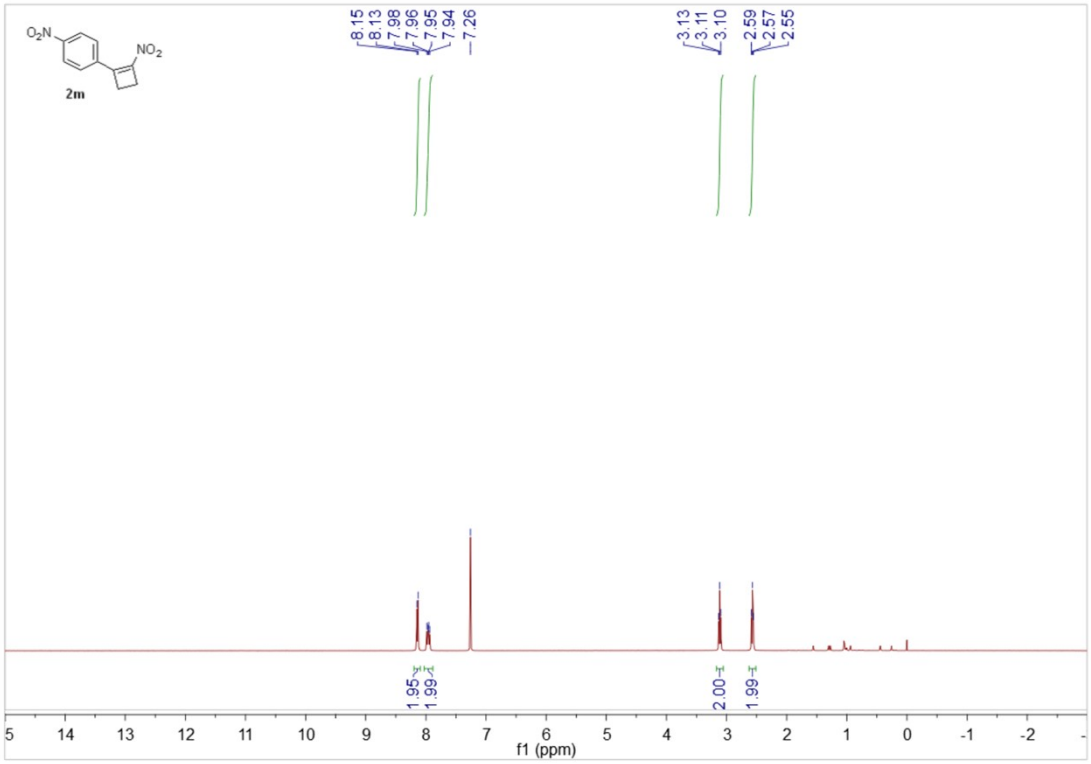
^{1}H NMR of **2l** (400 MHz, $CDCl_3$):



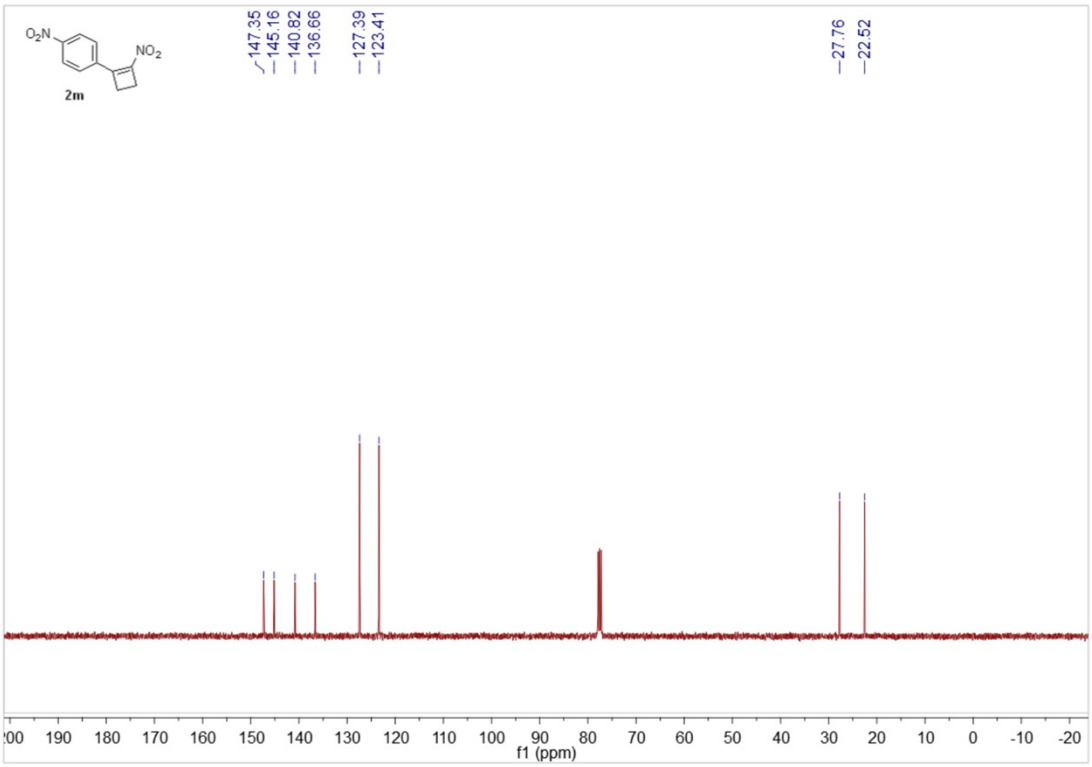
^{13}C NMR of **2l** (100 MHz, $CDCl_3$):



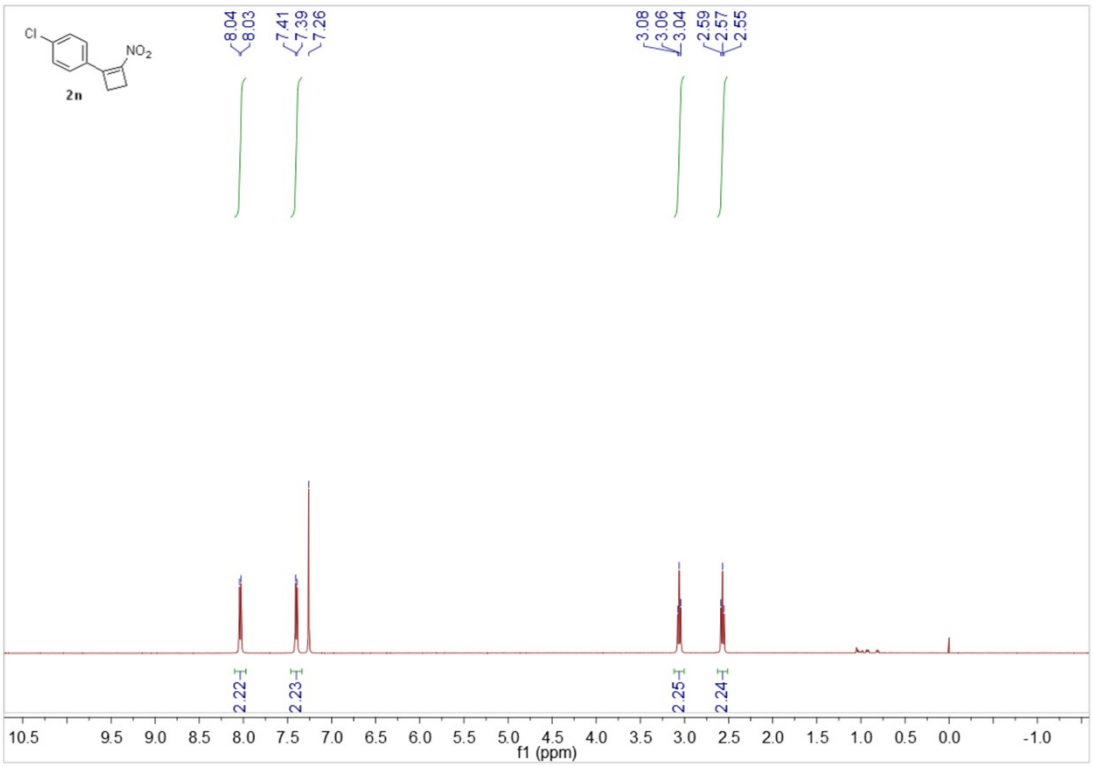
^{1}H NMR of **2m** (400 MHz, $CDCl_3$):



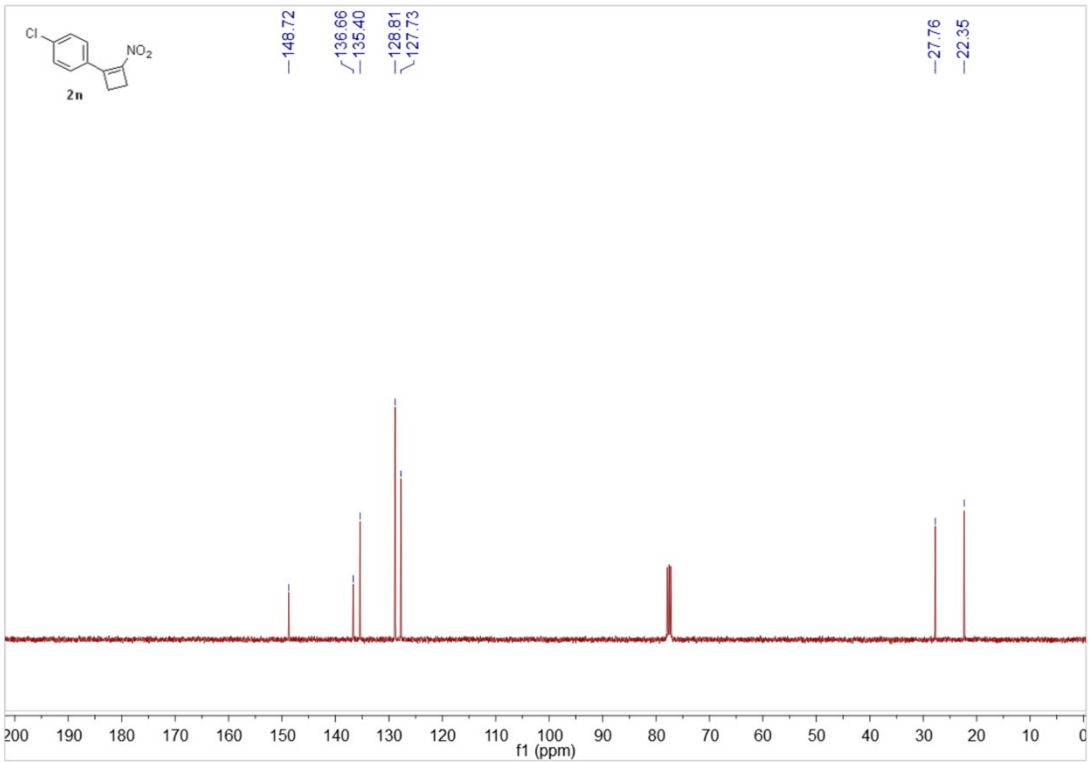
^{13}C NMR of **2m** (100 MHz, $CDCl_3$):



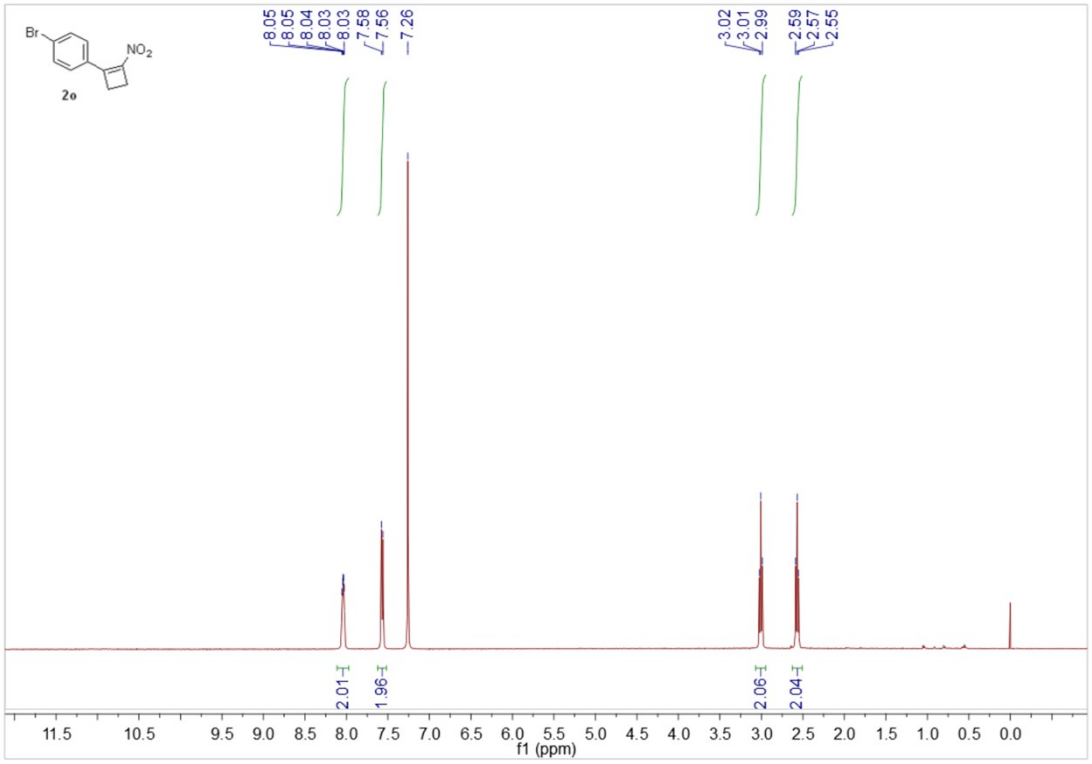
^{1}H NMR of **2n** (400 MHz, $CDCl_3$):



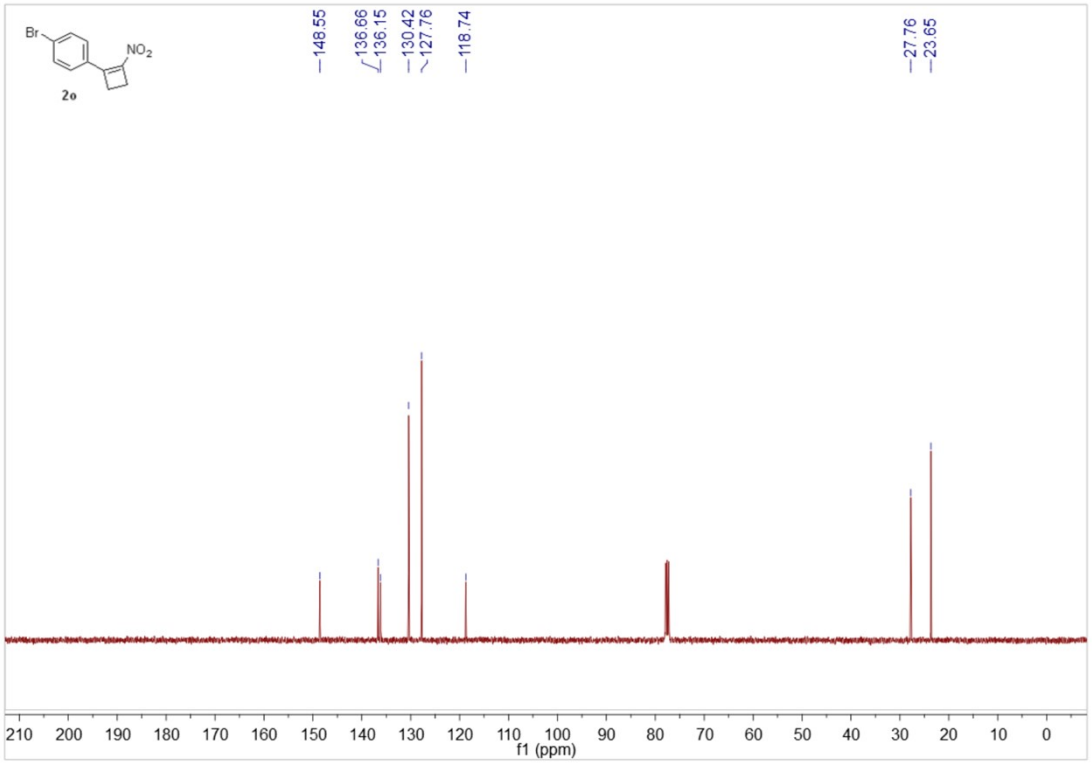
^{13}C NMR of **2n** (100 MHz, $CDCl_3$):



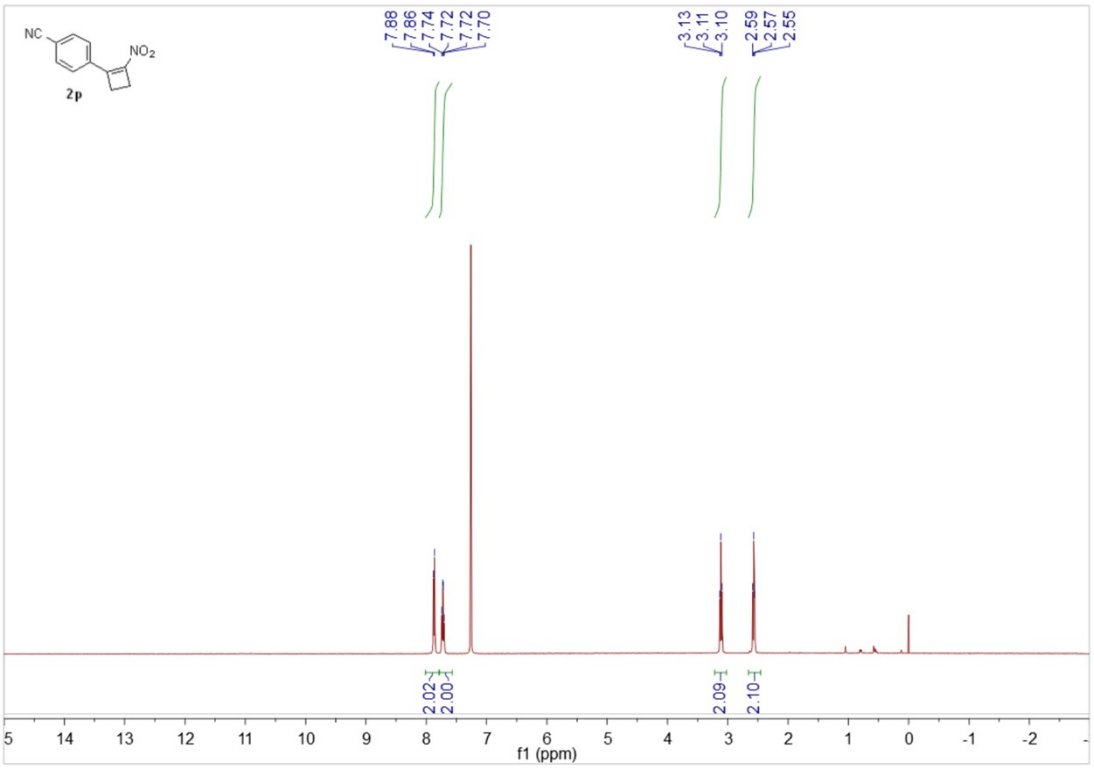
^{1}H NMR of **2o** (400 MHz, $CDCl_3$):



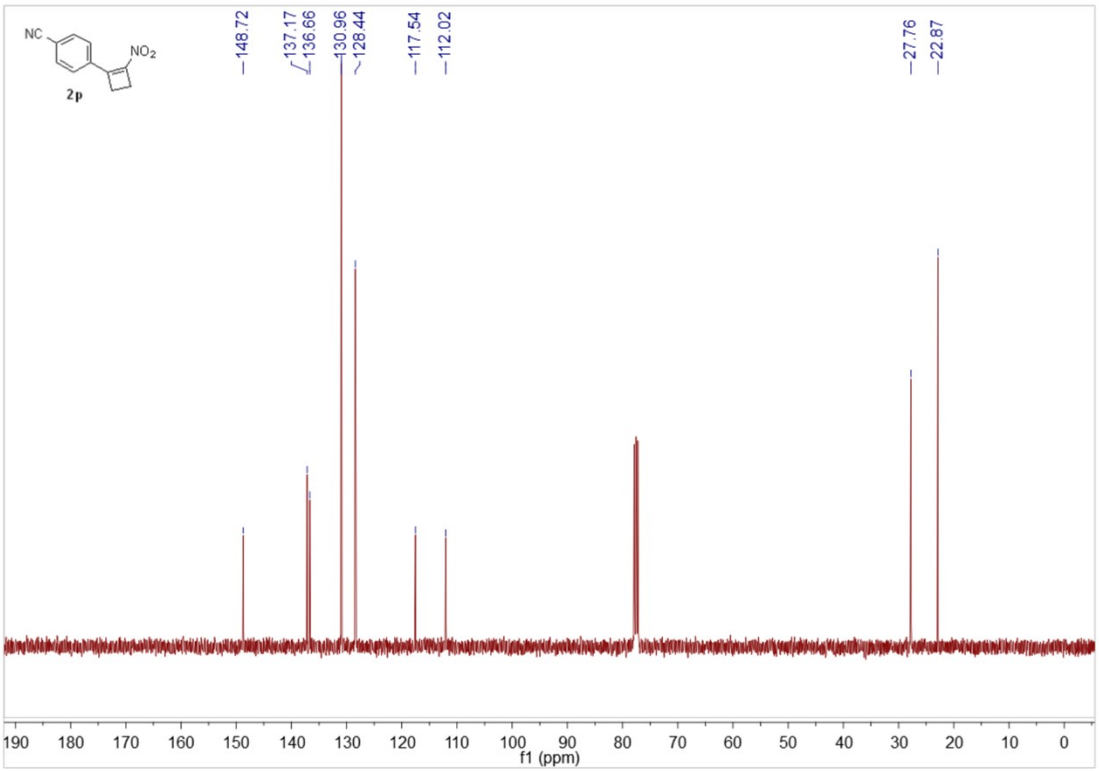
^{13}C NMR of **3o** (100 MHz, $CDCl_3$):



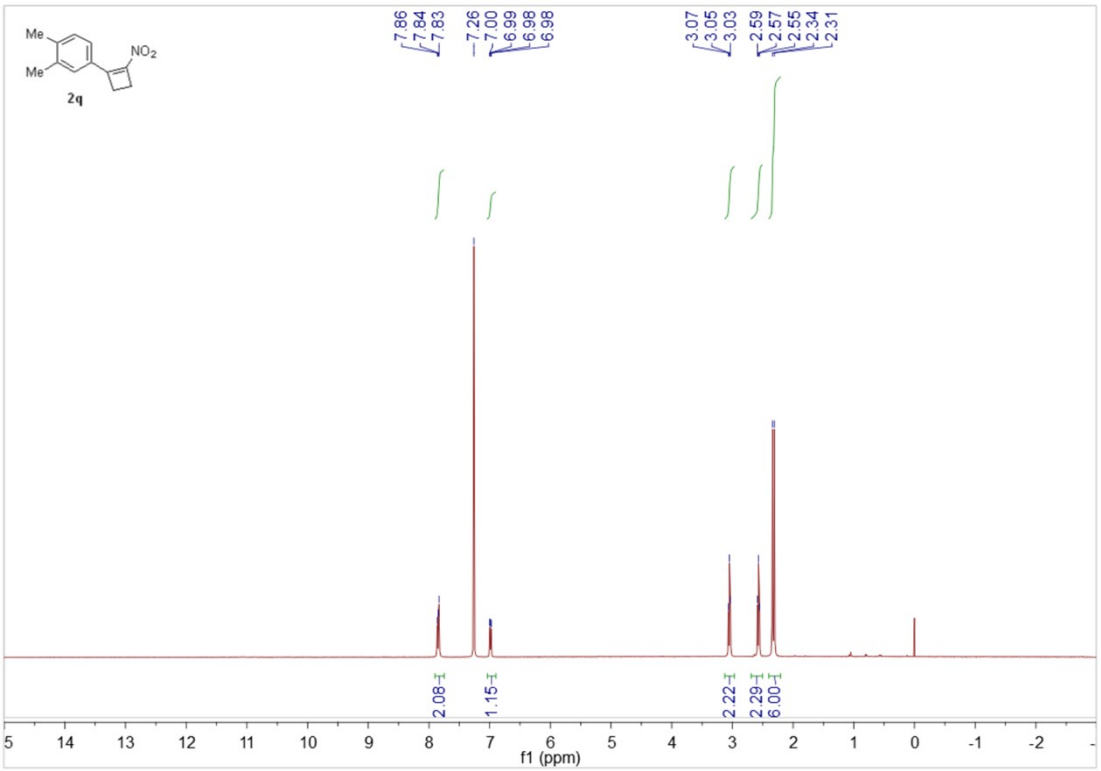
^{1}H NMR of **2p** (400 MHz, $CDCl_3$):



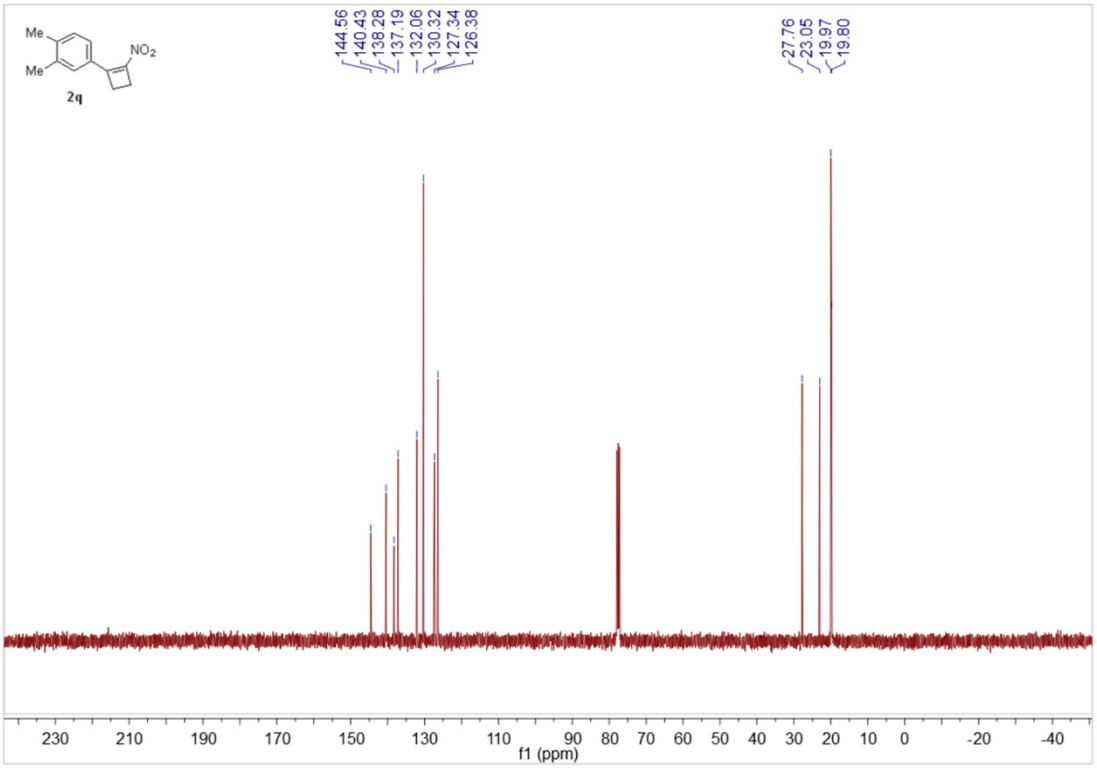
^{13}C NMR of **2p** (100 MHz, $CDCl_3$):



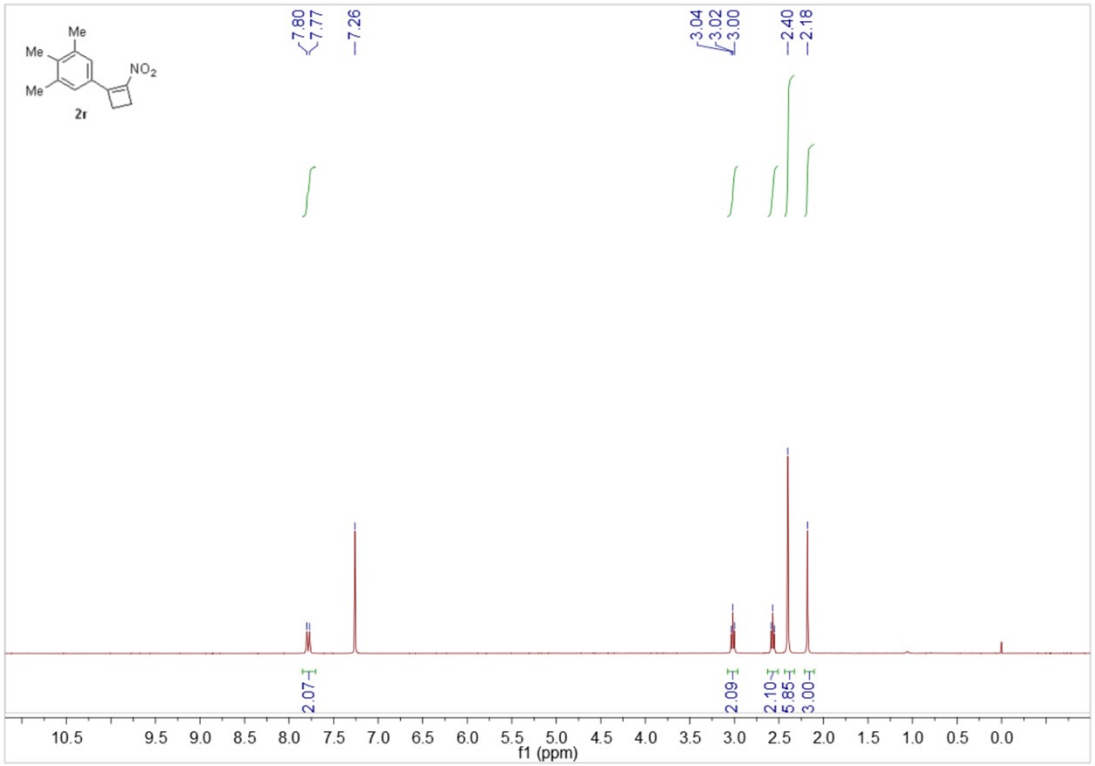
^{1}H NMR of **2q** (400 MHz, $CDCl_3$):



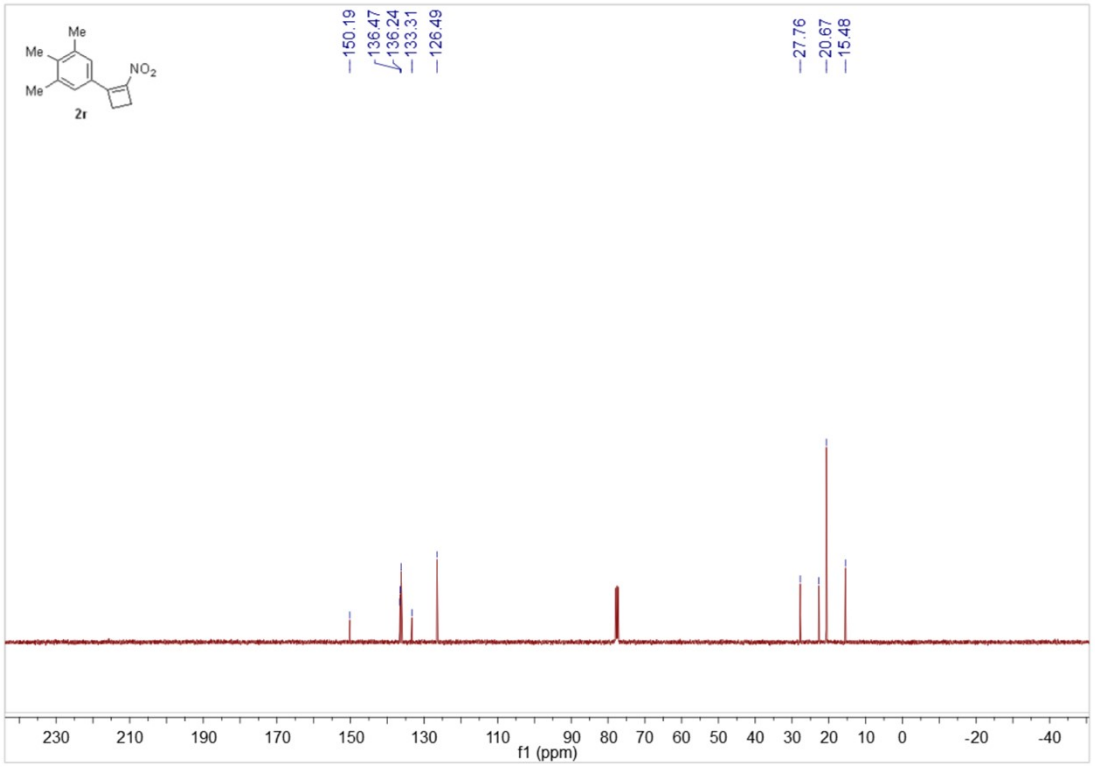
^{13}C NMR of **2q** (100 MHz, $CDCl_3$):



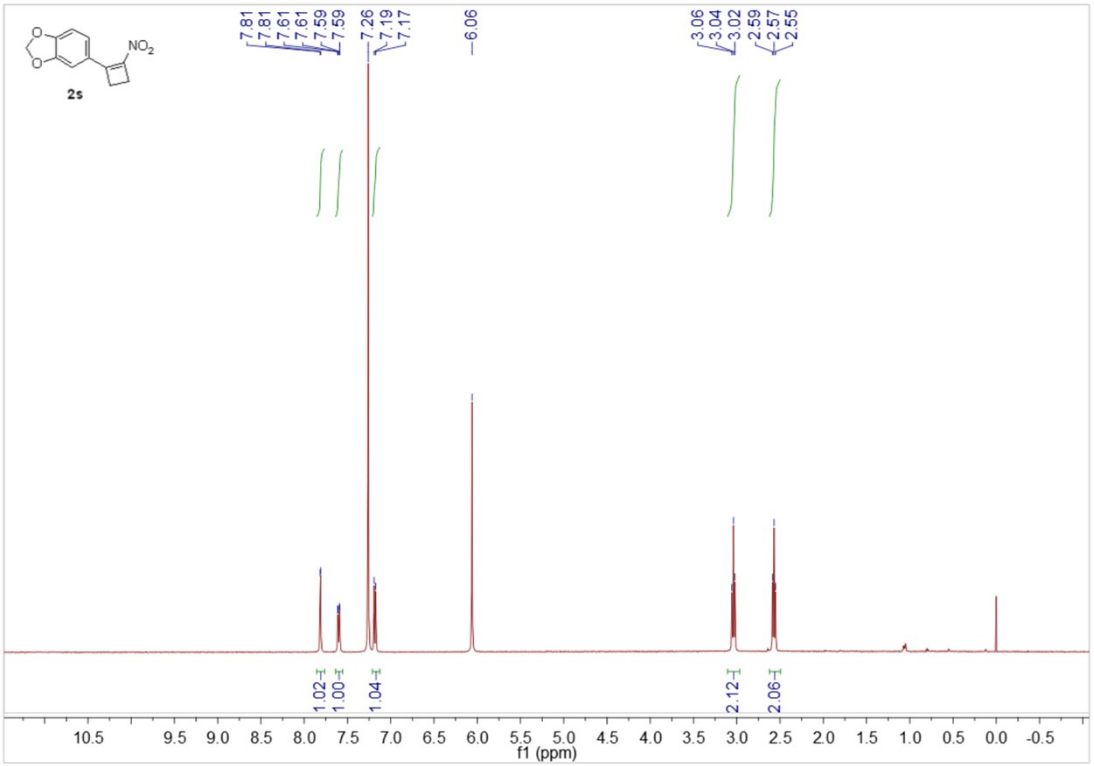
^{1}H NMR of **2r** (400 MHz, $CDCl_3$):



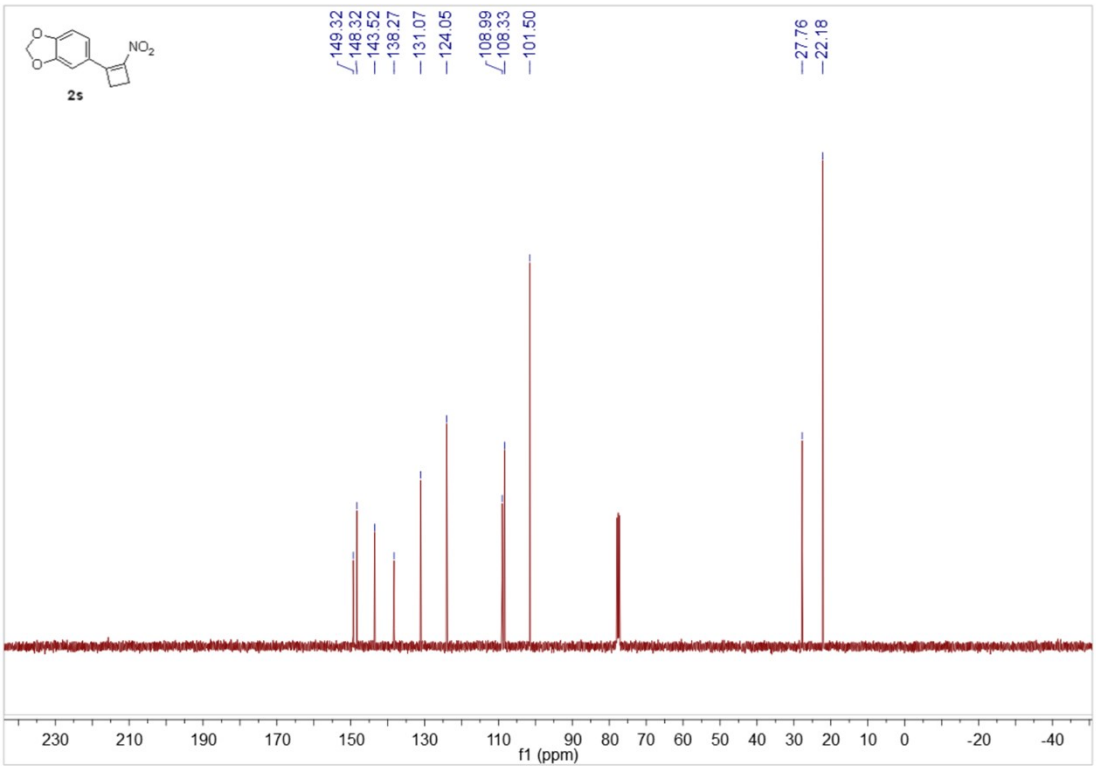
^{13}C NMR of **2r** (100 MHz, $CDCl_3$):



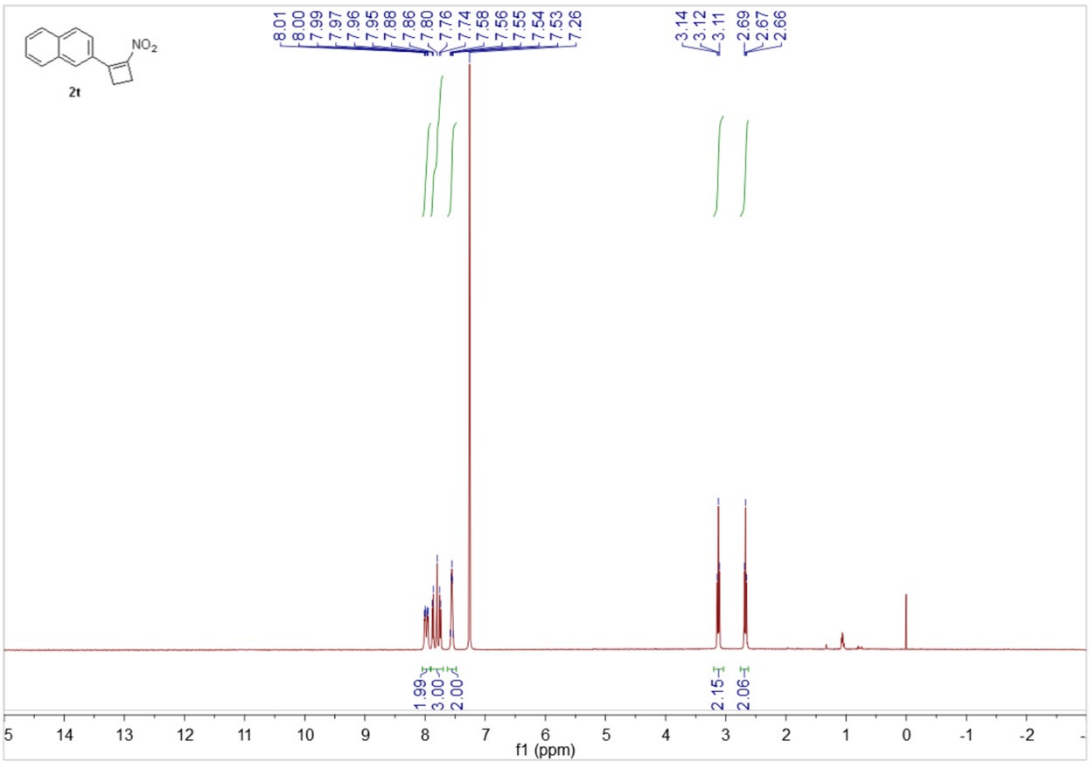
^{1}H NMR of **2s** (400 MHz, $CDCl_3$):



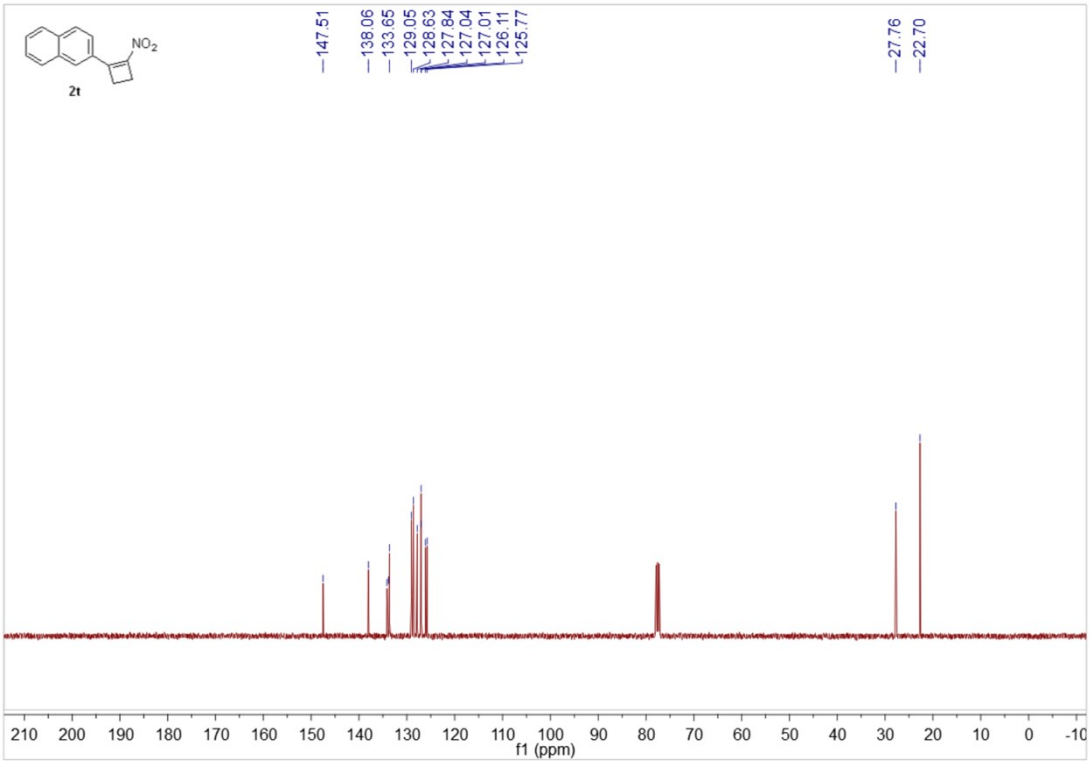
^{13}C NMR of **2s** (100 MHz, $CDCl_3$):



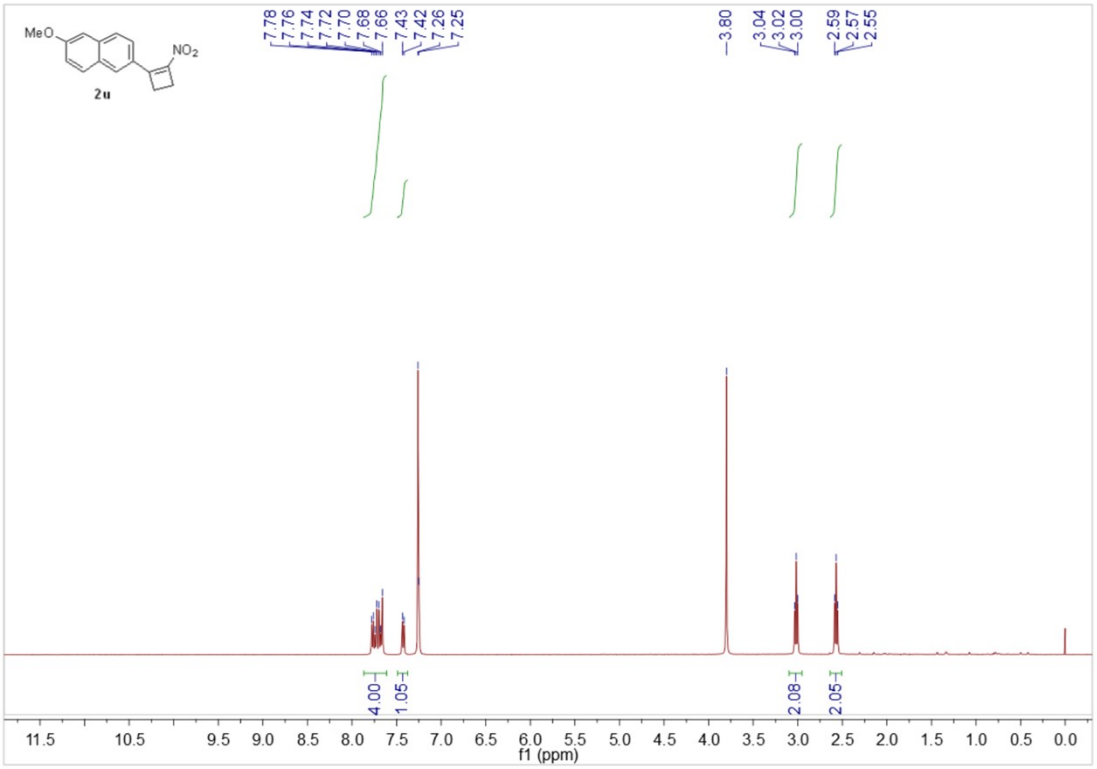
^{1}H NMR of **2t** (400 MHz, $CDCl_3$):



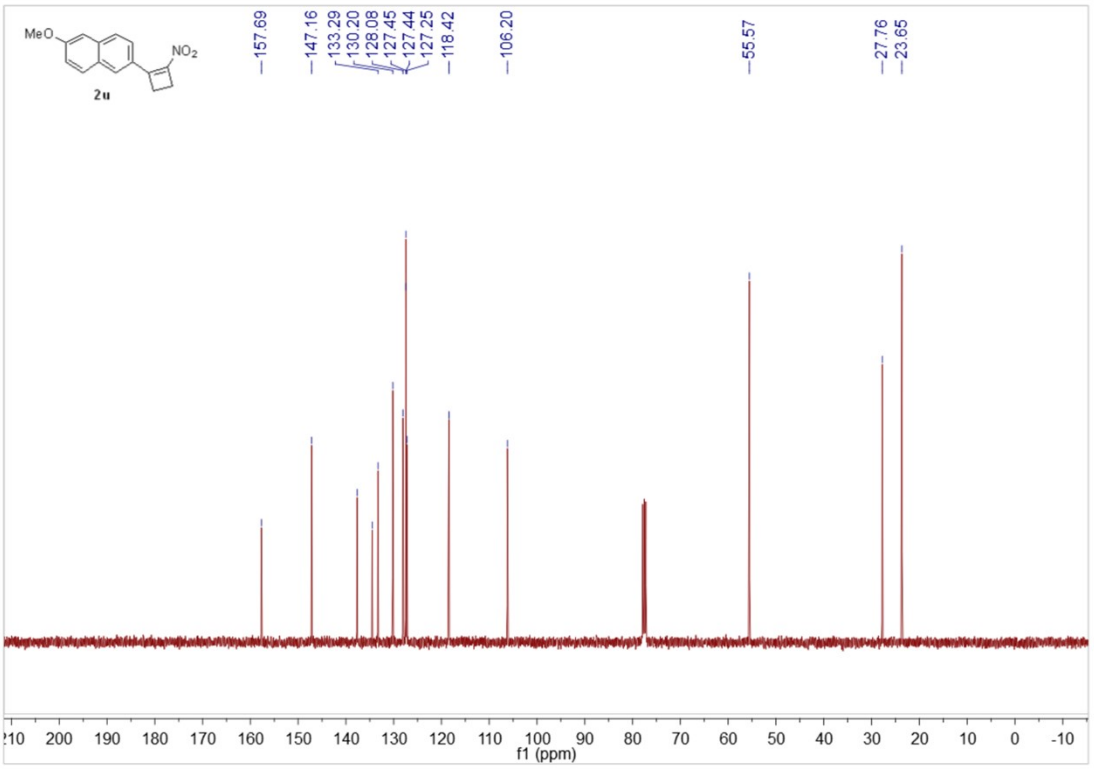
^{13}C NMR of **2t** (100 MHz, $CDCl_3$):



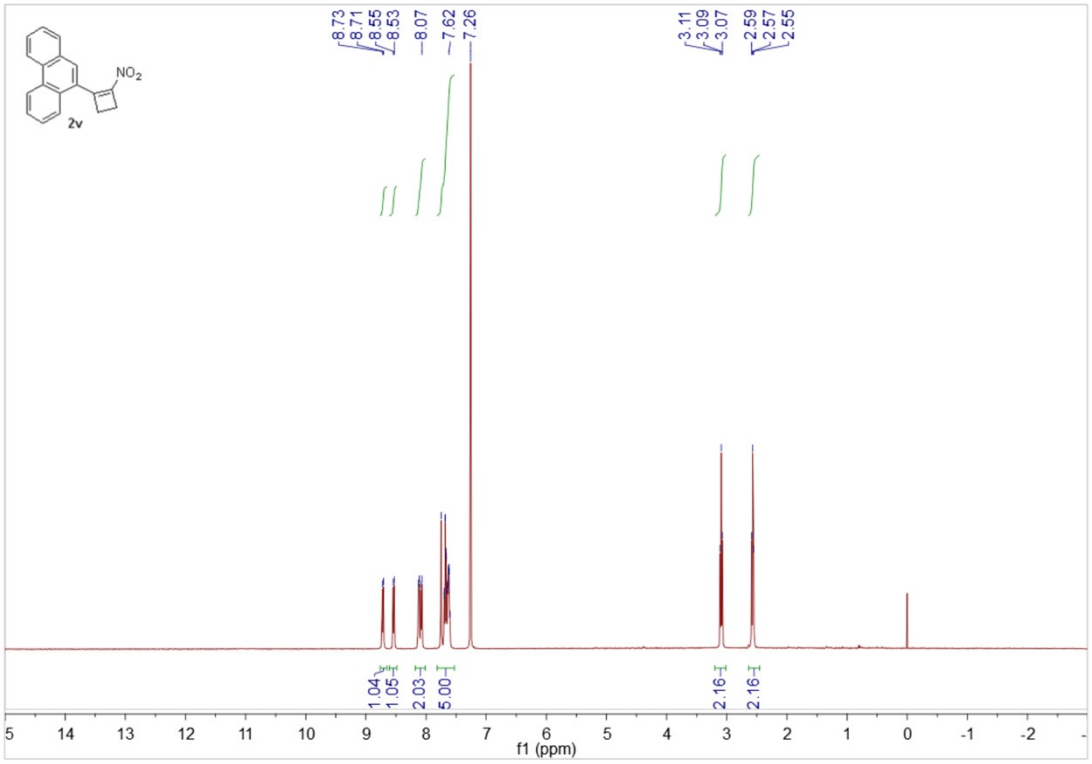
^{1}H NMR of **2u** (400 MHz, $CDCl_3$):



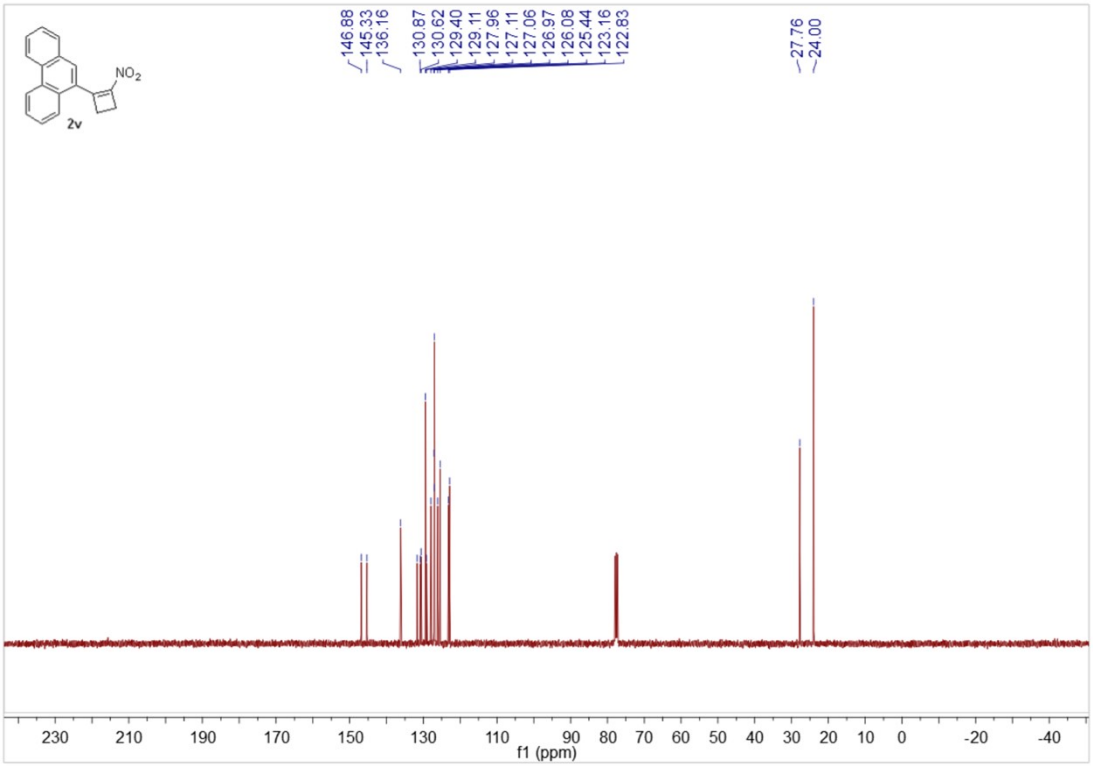
^{13}C NMR of **2u** (100 MHz, $CDCl_3$):



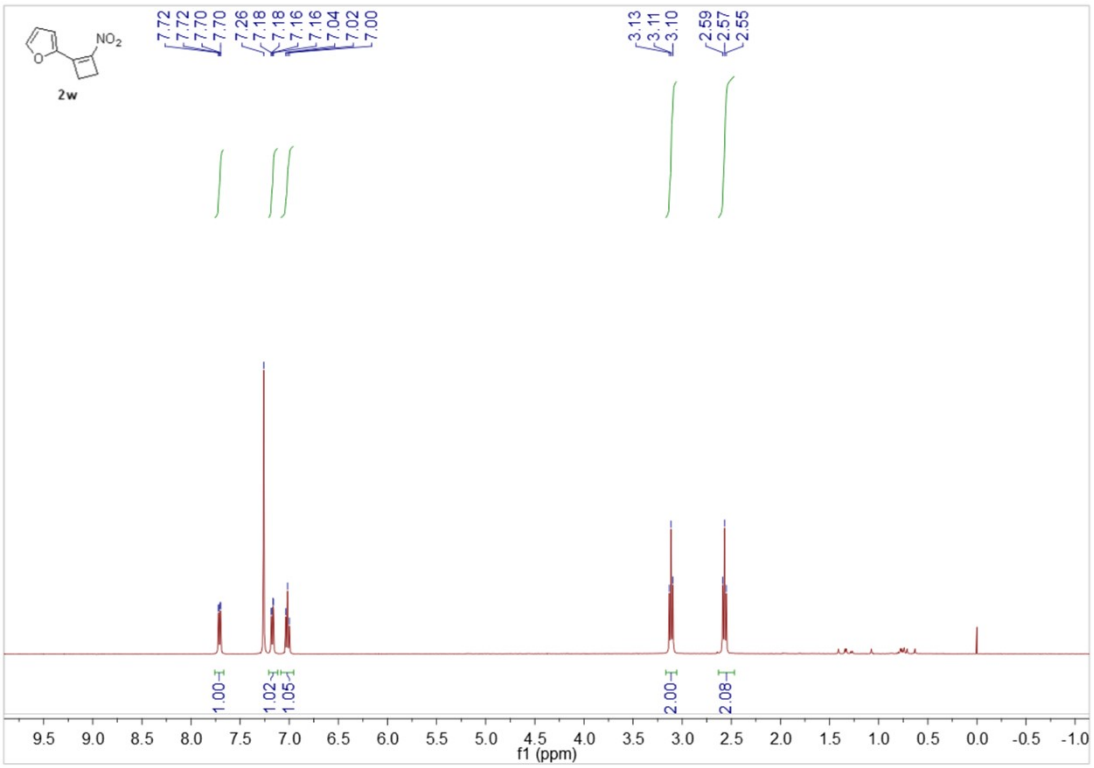
^{1}H NMR of **2v** (400 MHz, $CDCl_3$):



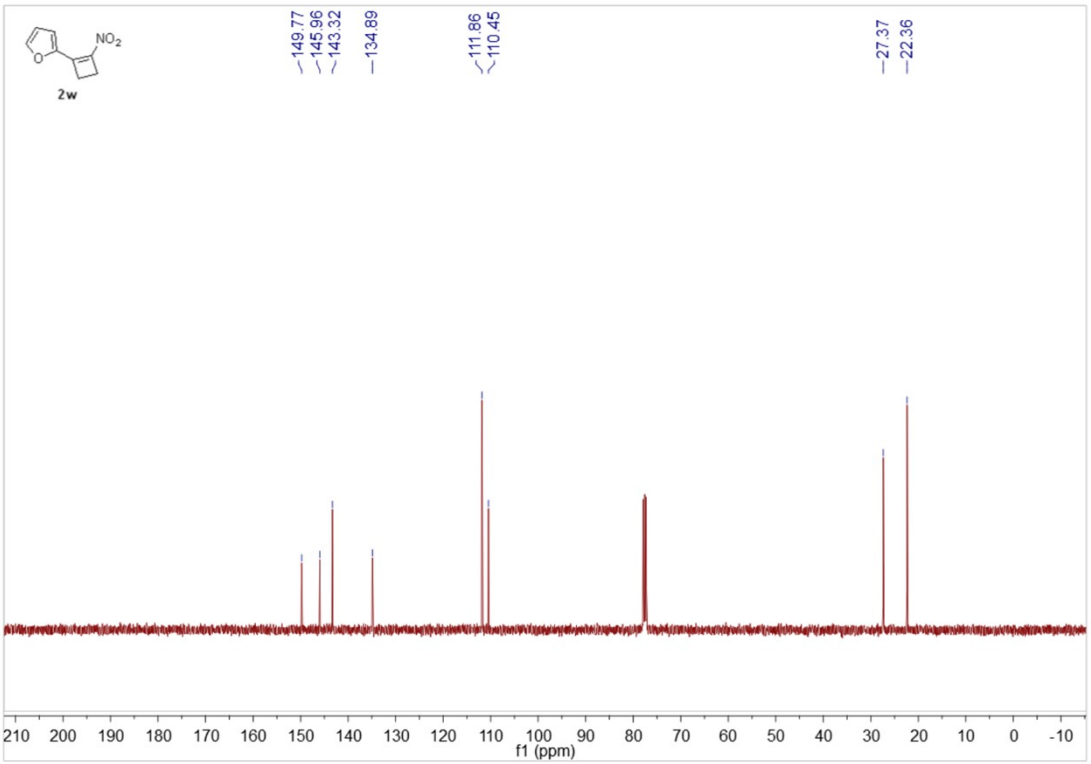
^{13}C NMR of **3v** (100 MHz, $CDCl_3$):



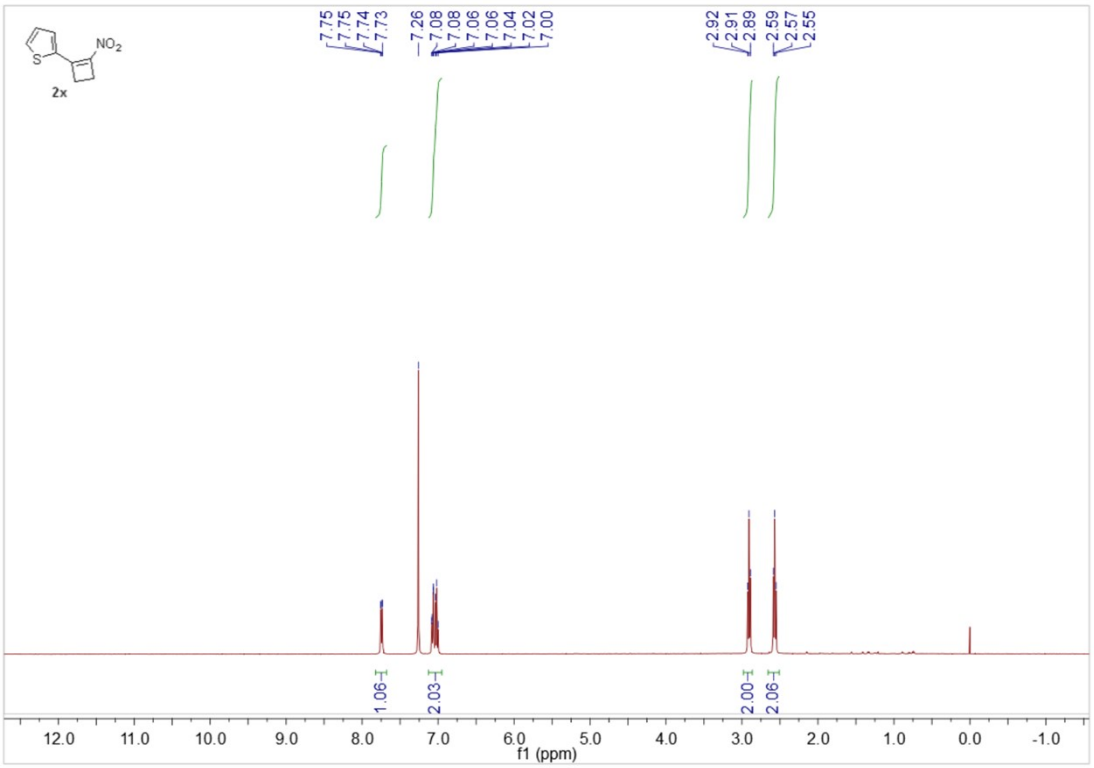
^{1}H NMR of **2w** (400 MHz, $CDCl_3$):



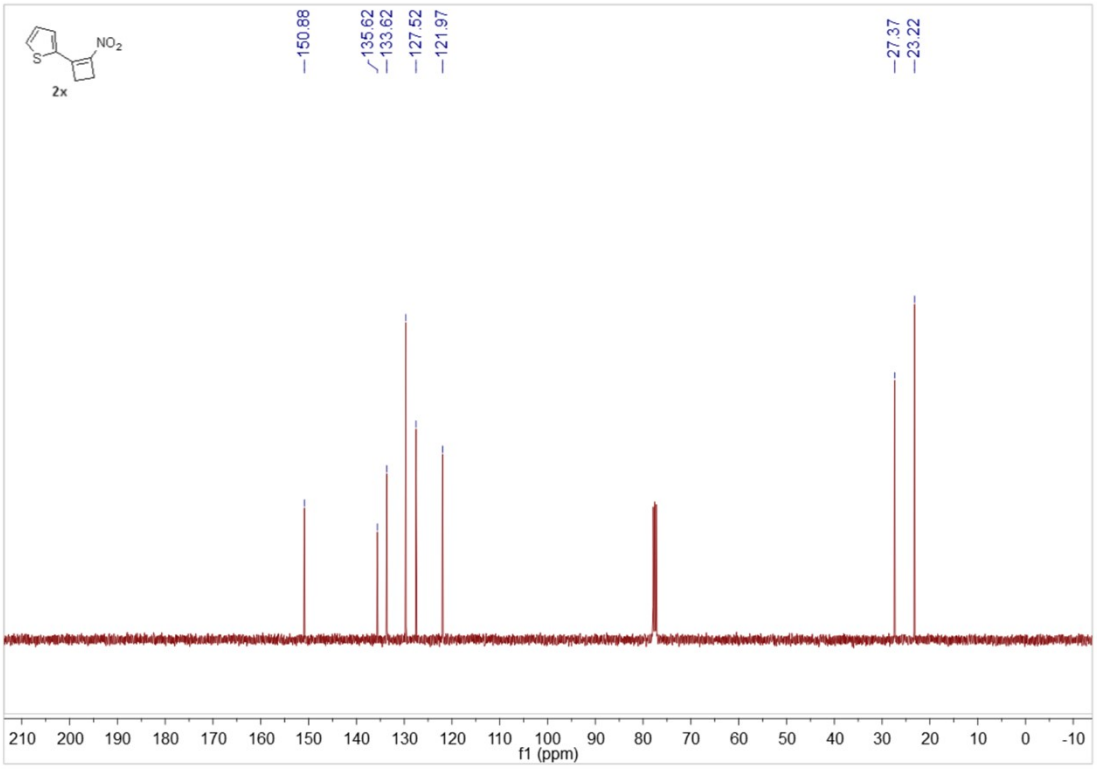
^{13}C NMR of **2w** (100 MHz, $CDCl_3$):



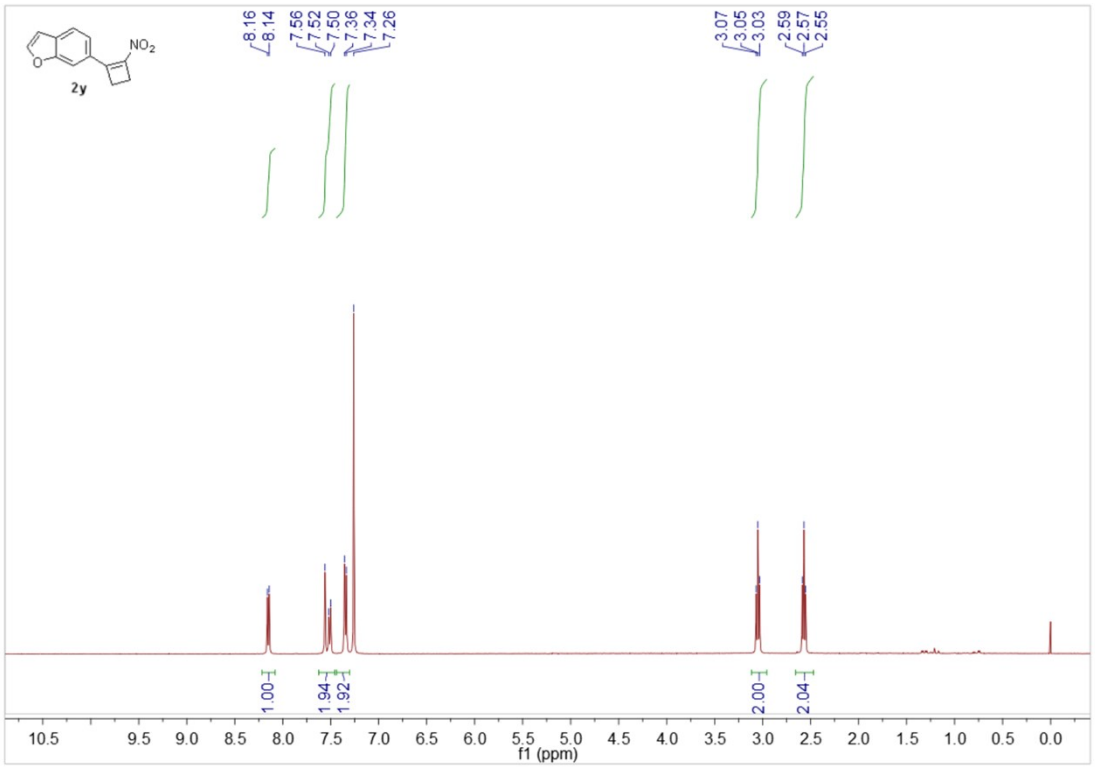
^{1}H NMR of **2x** (400 MHz, $CDCl_3$):



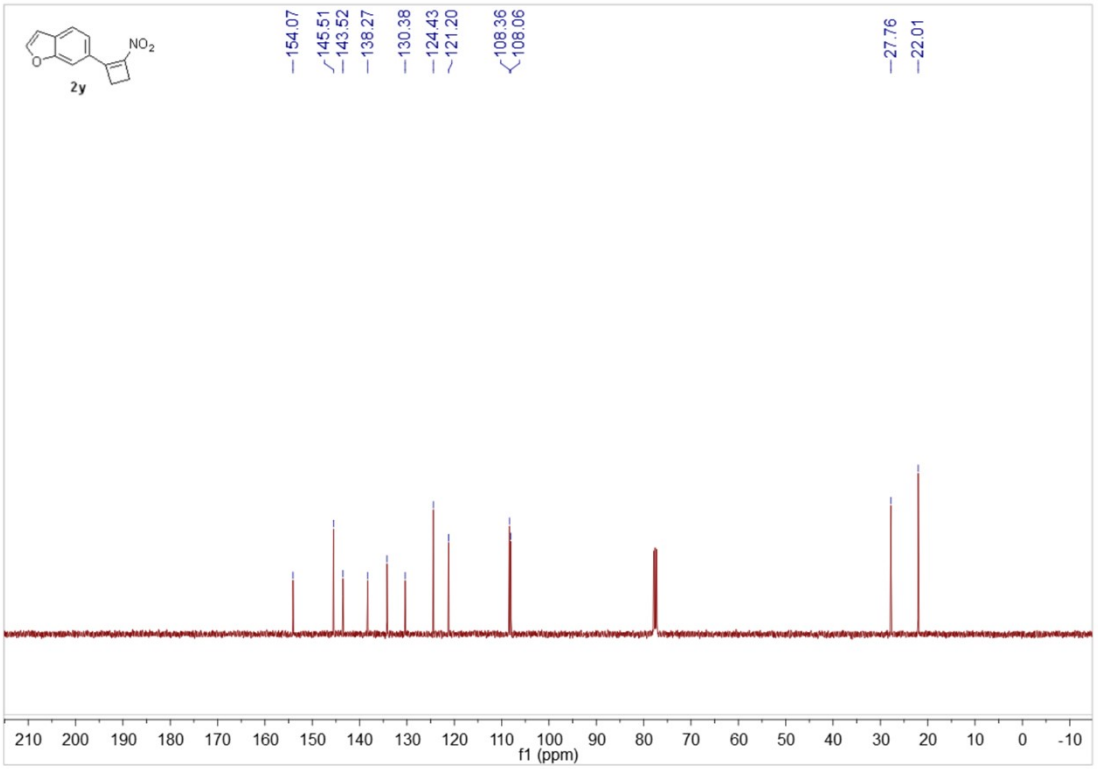
^{13}C NMR of **3x** (100 MHz, $CDCl_3$):



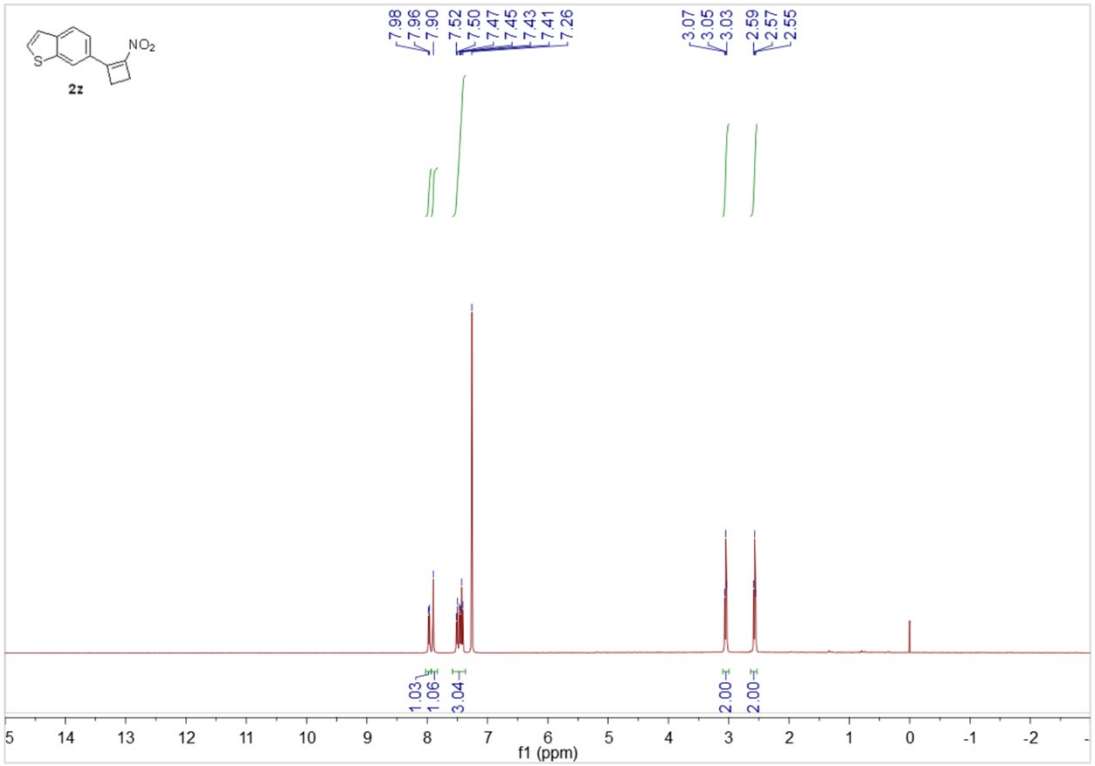
^{1}H NMR of **2y** (400 MHz, $CDCl_3$):



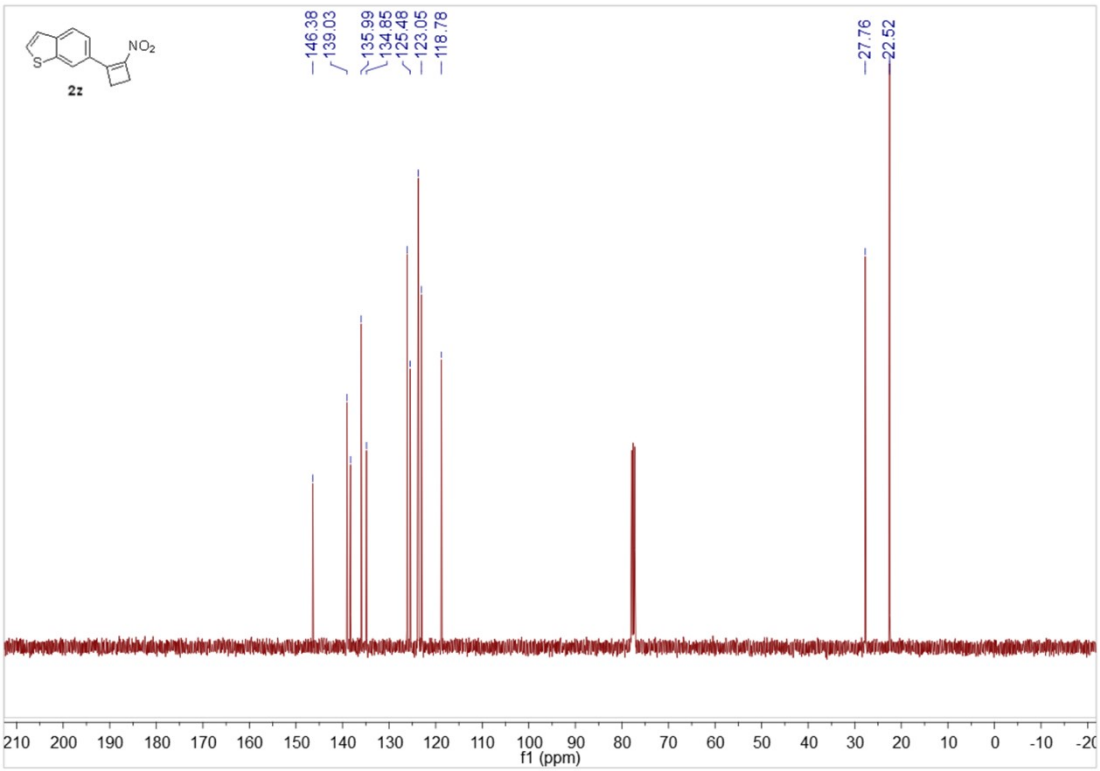
^{13}C NMR of **2y** (100 MHz, $CDCl_3$):



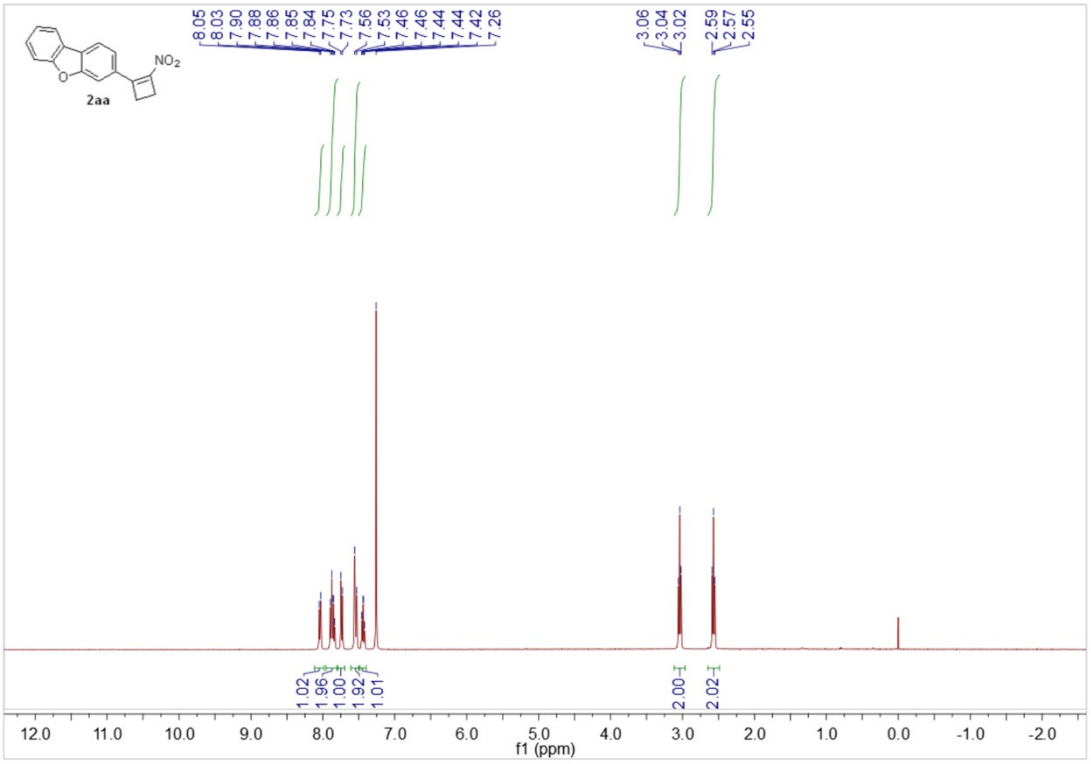
^{1}H NMR of **2z** (400 MHz, $CDCl_3$):



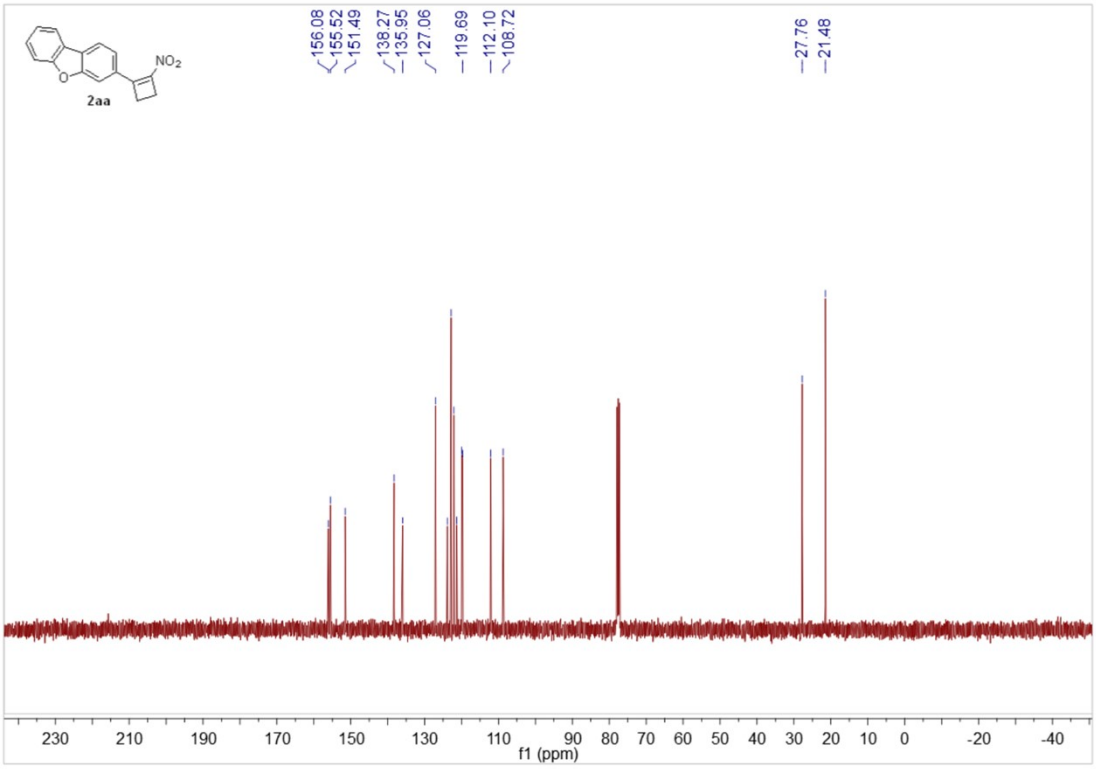
^{13}C NMR of **2z** (100 MHz, $CDCl_3$):



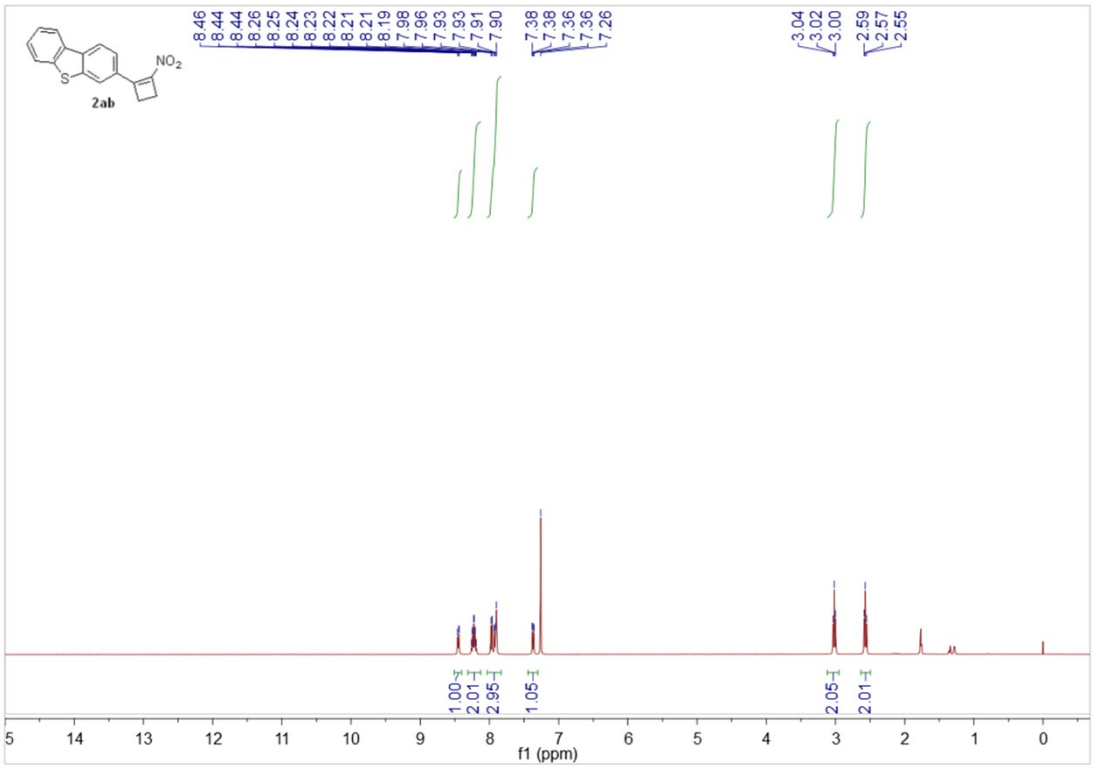
^{1}H NMR of **2aa** (400 MHz, $CDCl_3$):



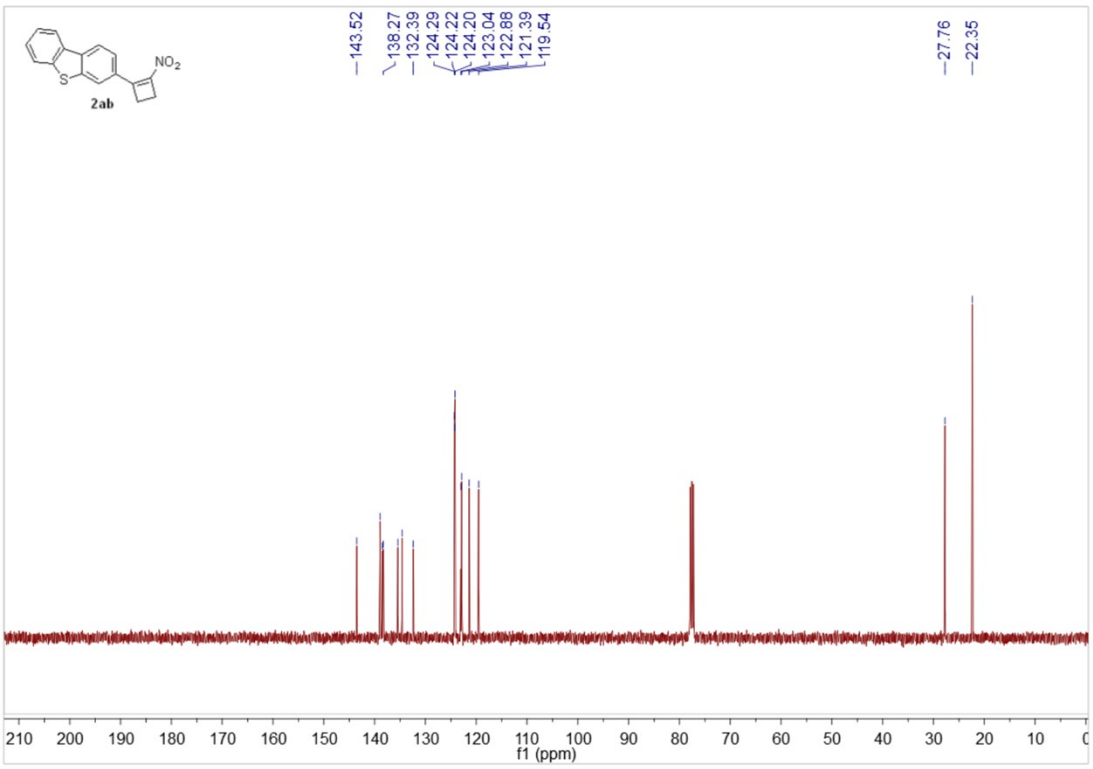
^{13}C NMR of **2aa** (100 MHz, $CDCl_3$):



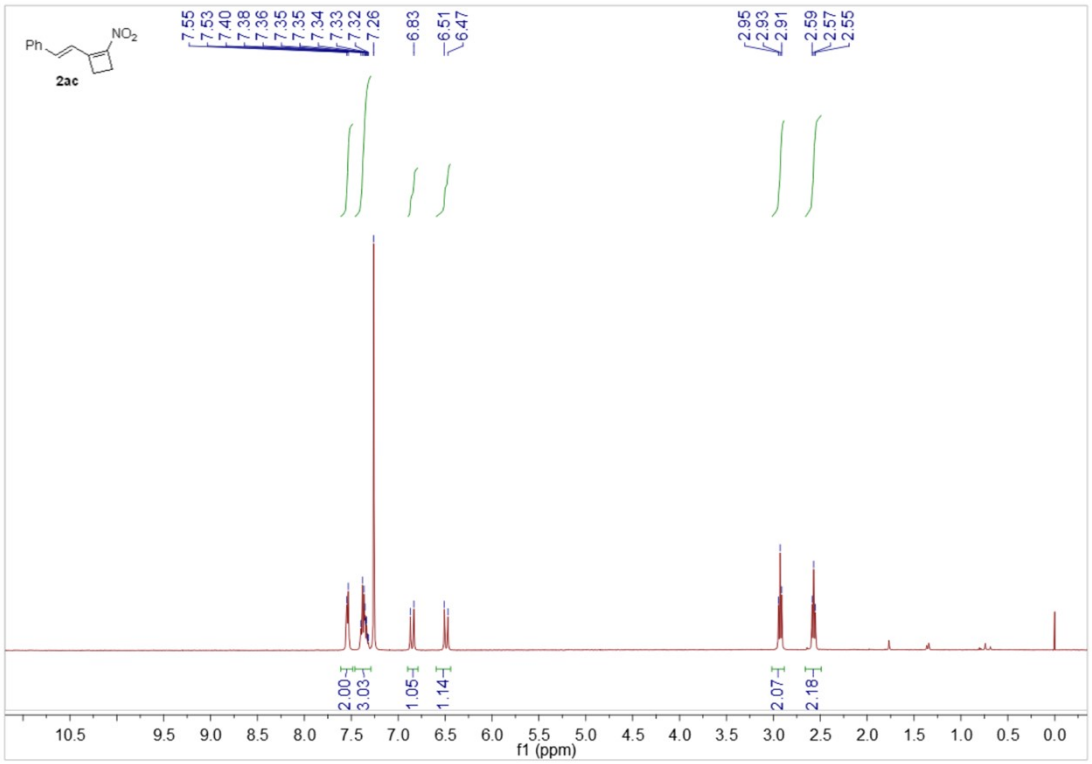
^{1}H NMR of **2ab** (400 MHz, $CDCl_3$):



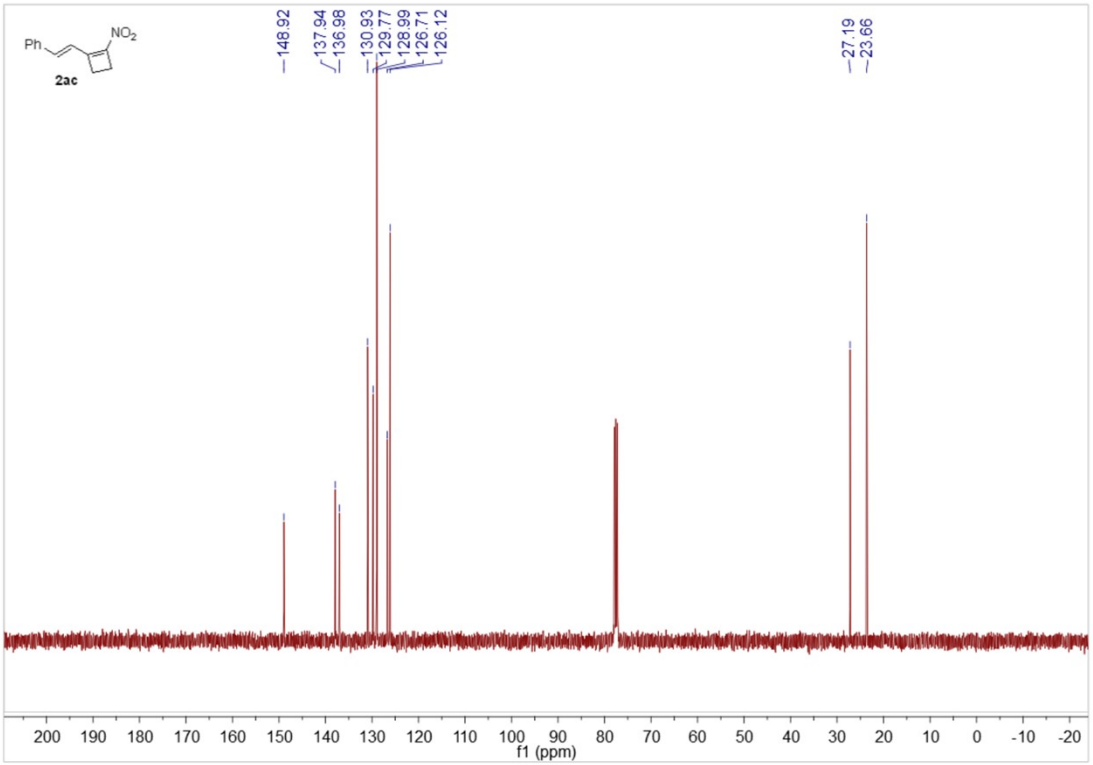
^{13}C NMR of **2ab** (100 MHz, $CDCl_3$):



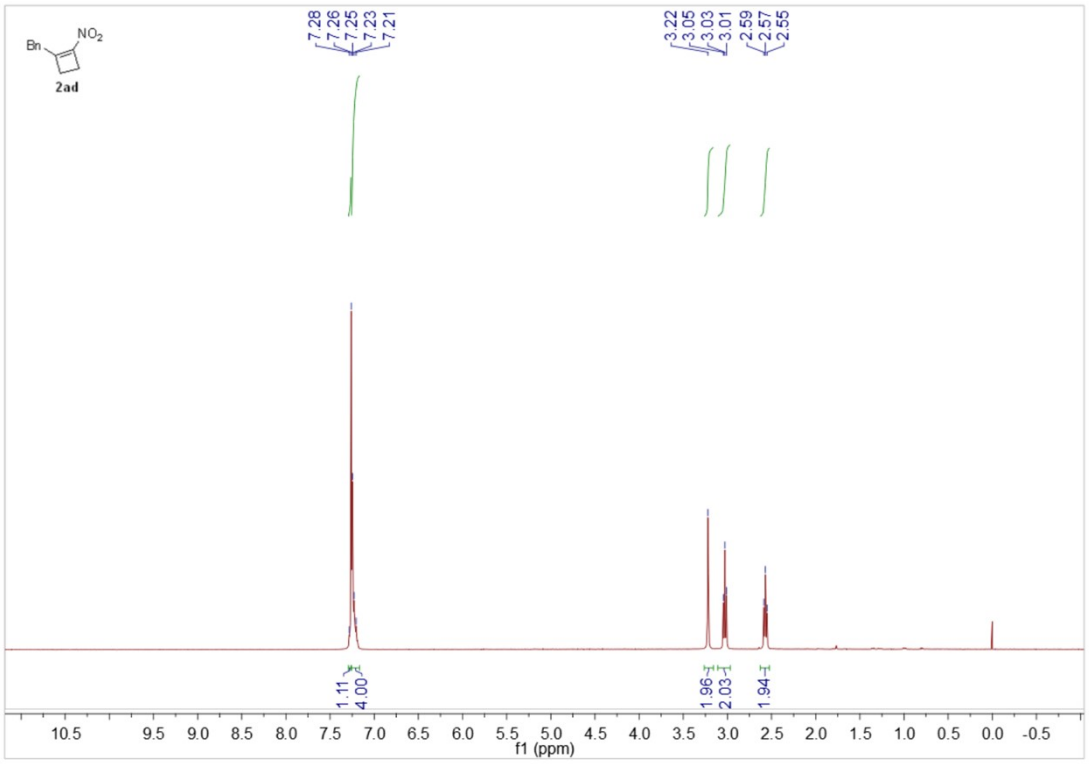
^{1}H NMR of **2ac** (400 MHz, $CDCl_3$):



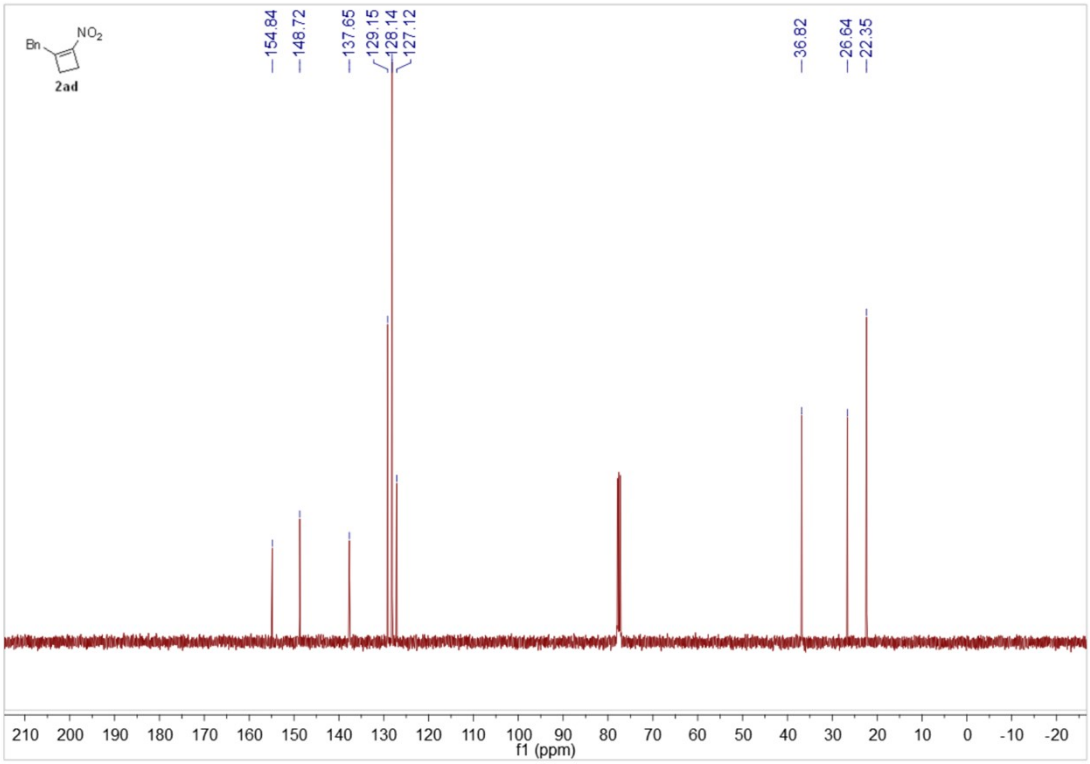
^{13}C NMR of **2ac** (100 MHz, $CDCl_3$):



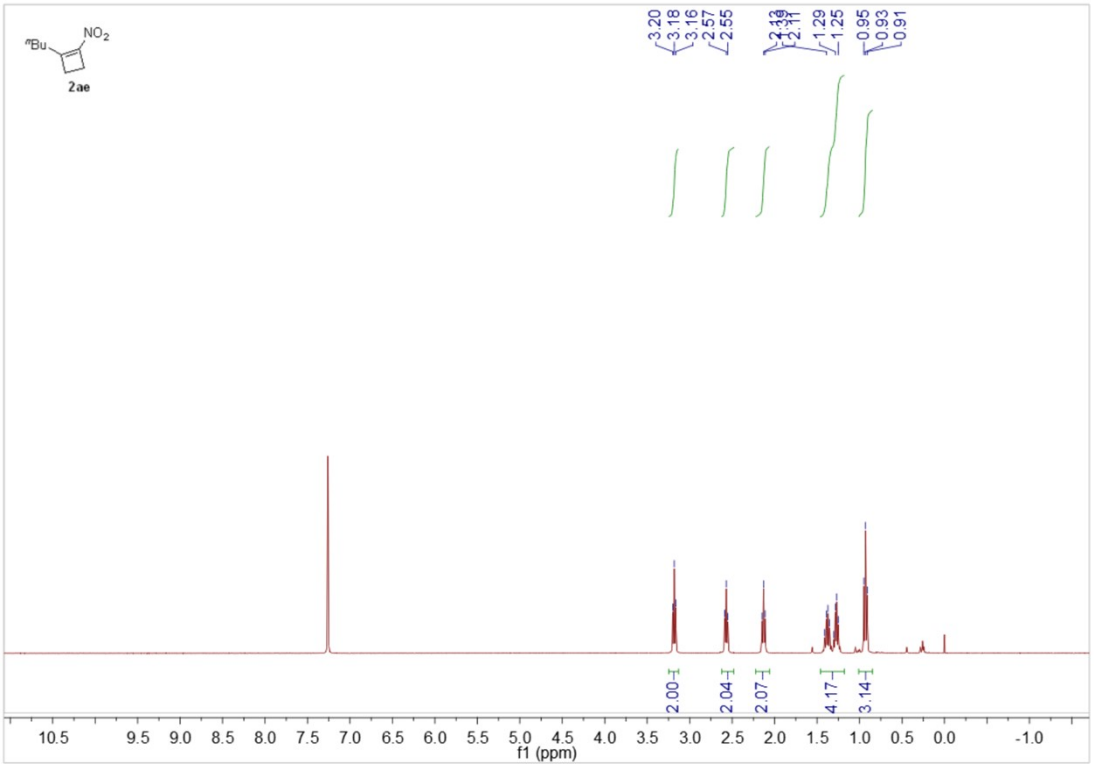
^{1}H NMR of **2ad** (400 MHz, $CDCl_3$):



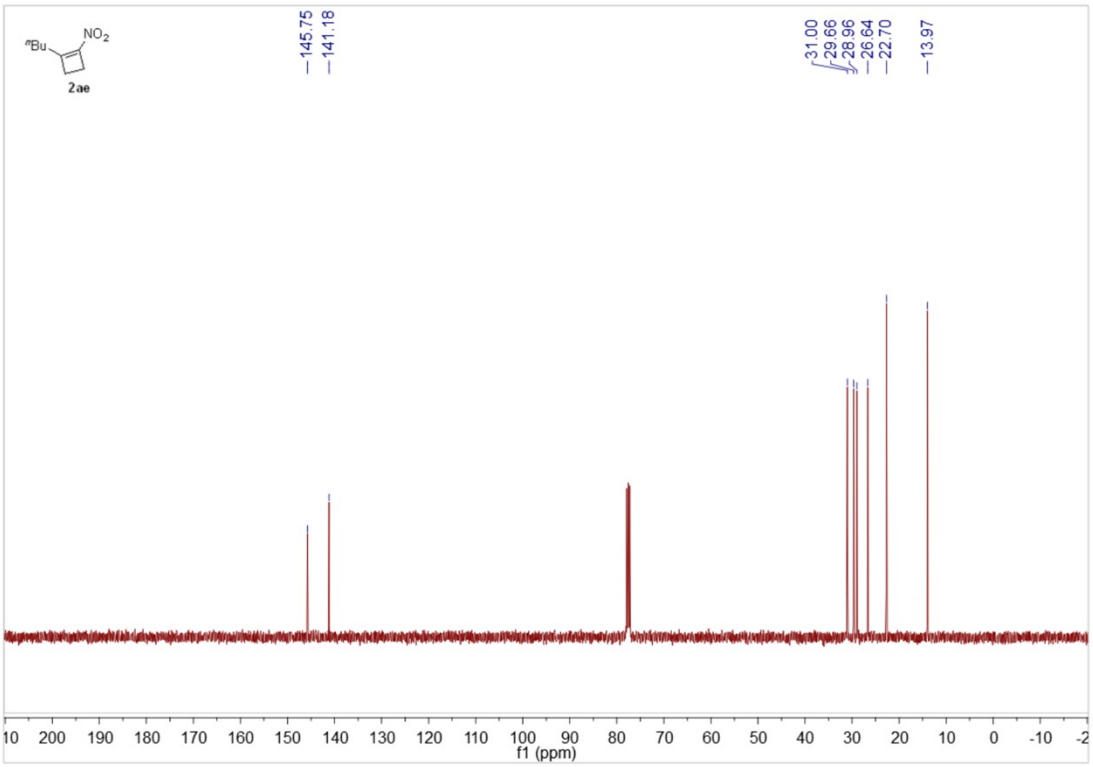
^{13}C NMR of **2ad** (100 MHz, $CDCl_3$):



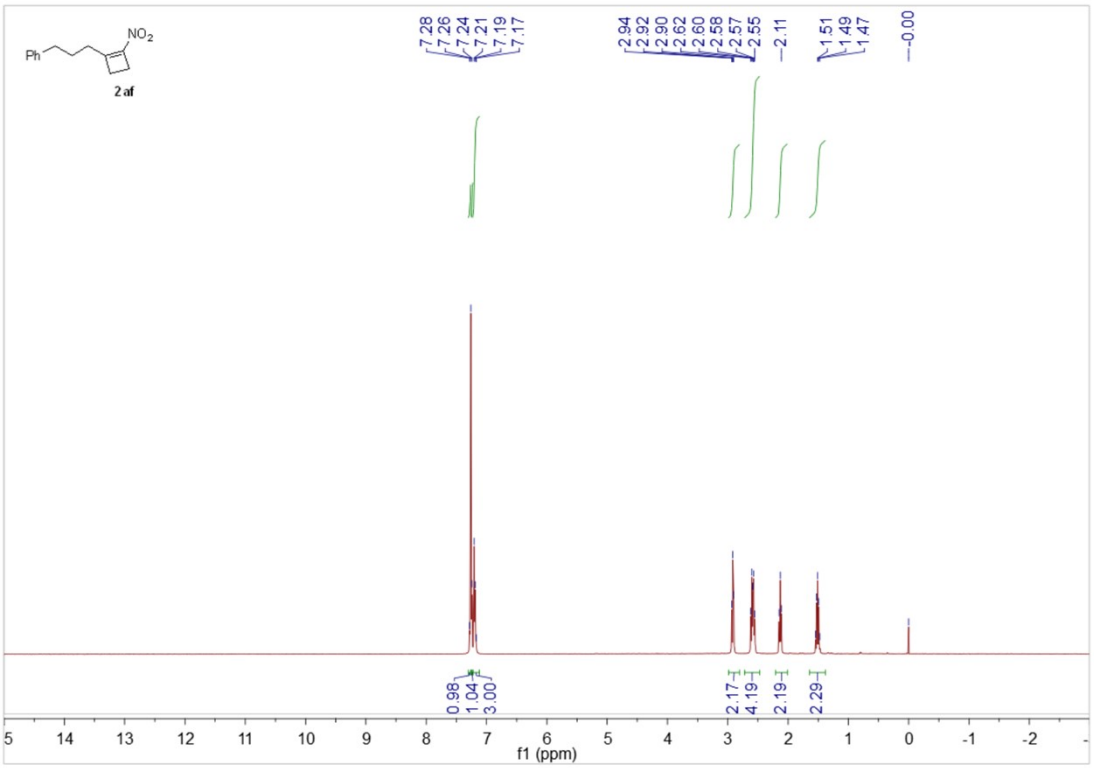
^{1}H NMR of **2ae** (400 MHz, $CDCl_3$):



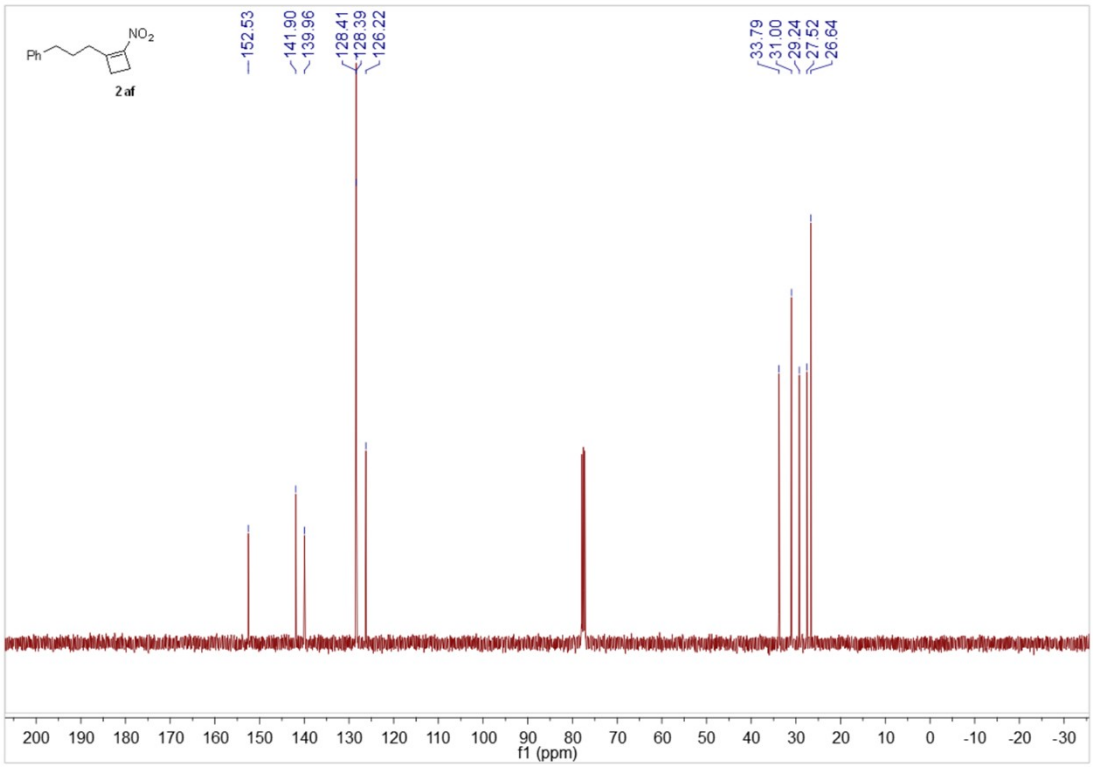
^{13}C NMR of **2ae** (100 MHz, $CDCl_3$):



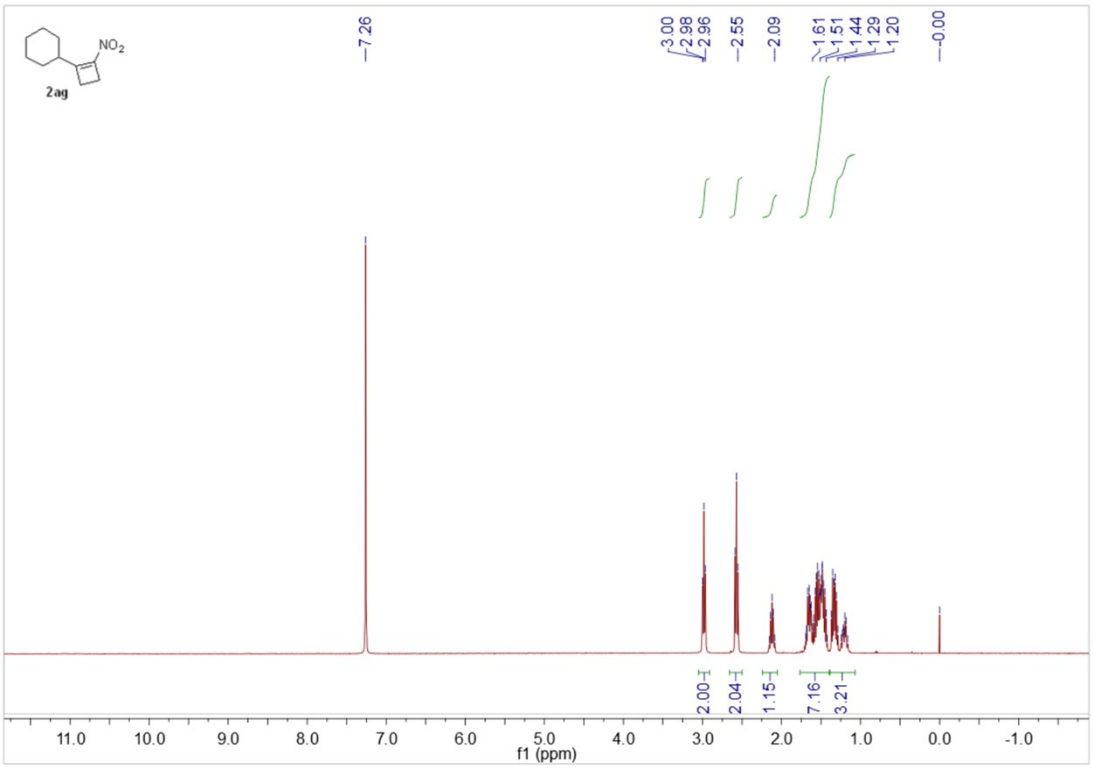
^{1}H NMR of **2af** (400 MHz, $CDCl_3$):



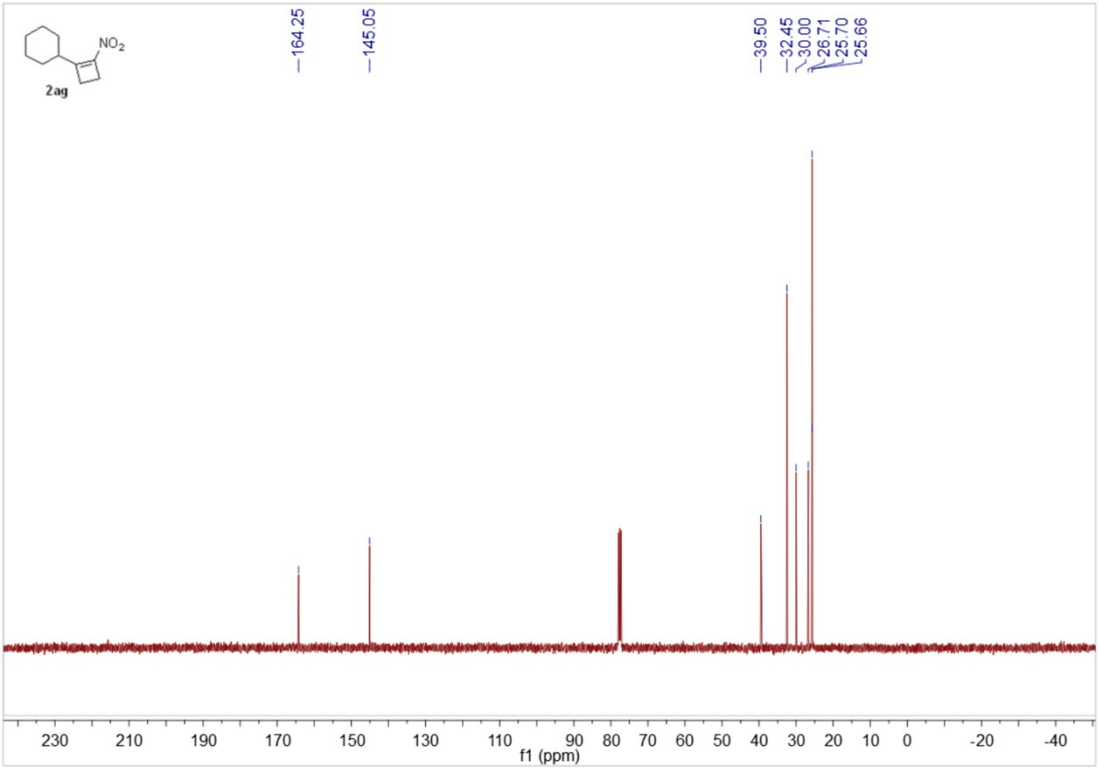
^{13}C NMR of **2af** (100 MHz, $CDCl_3$):



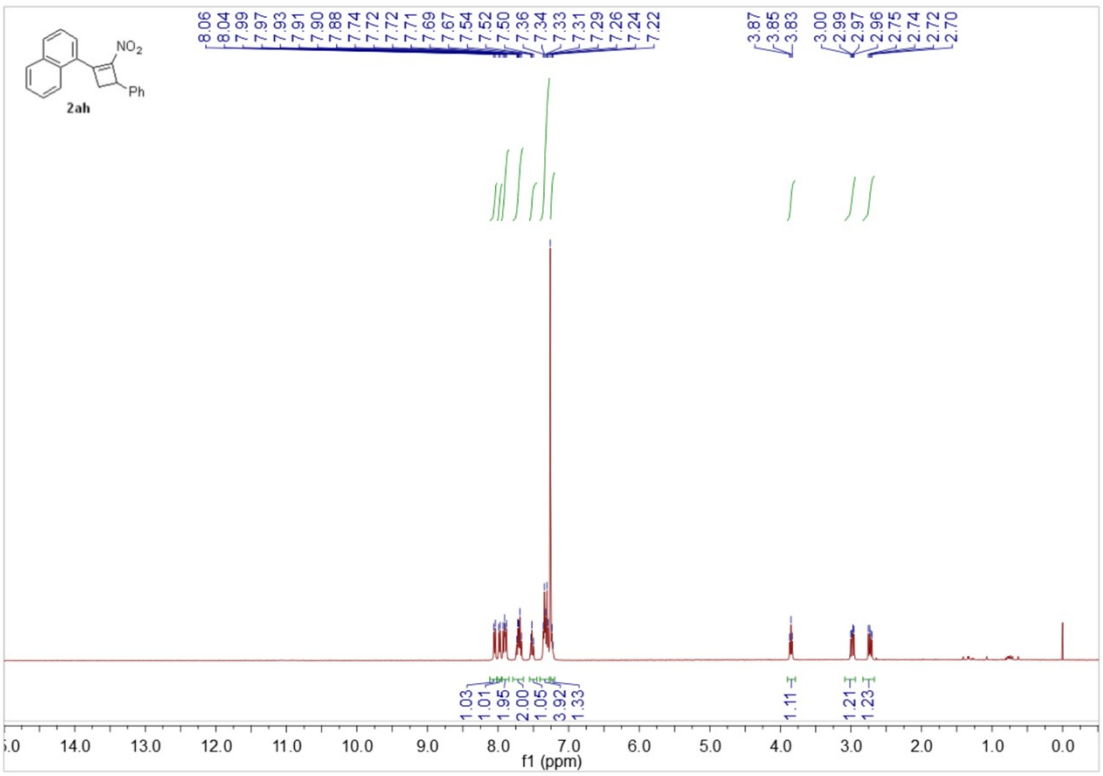
^{1}H NMR of **2ag** (400 MHz, $CDCl_3$):



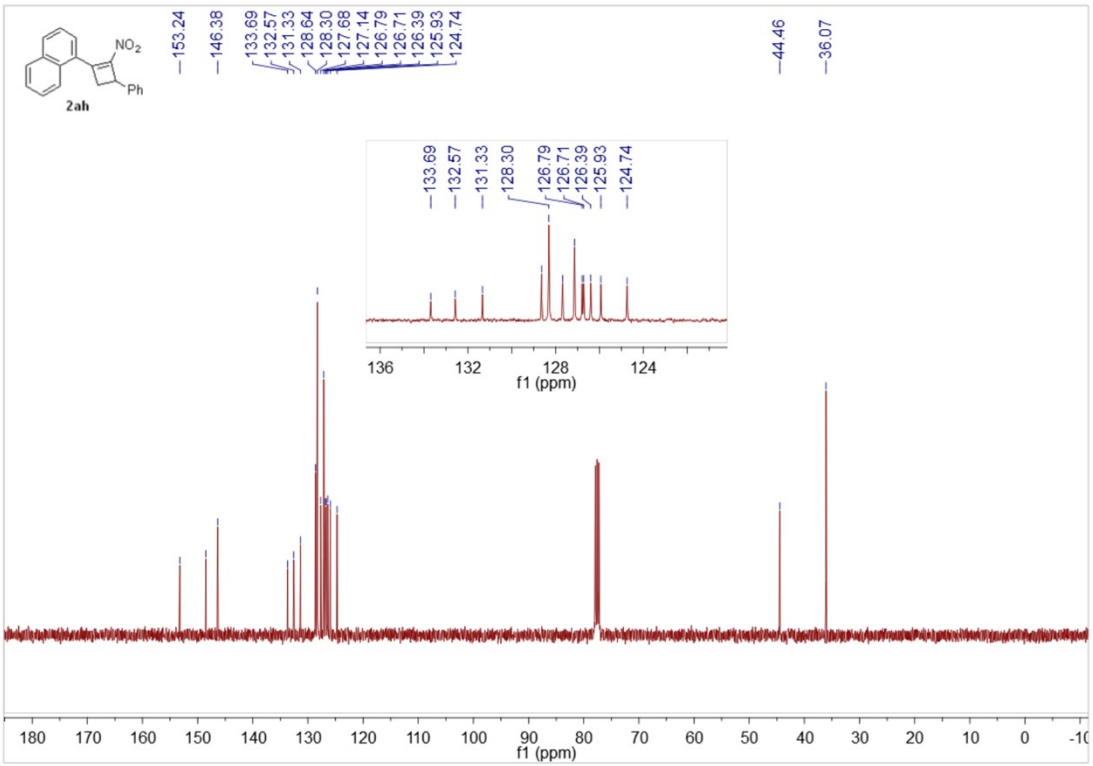
^{13}C NMR of **2ag** (100 MHz, $CDCl_3$):



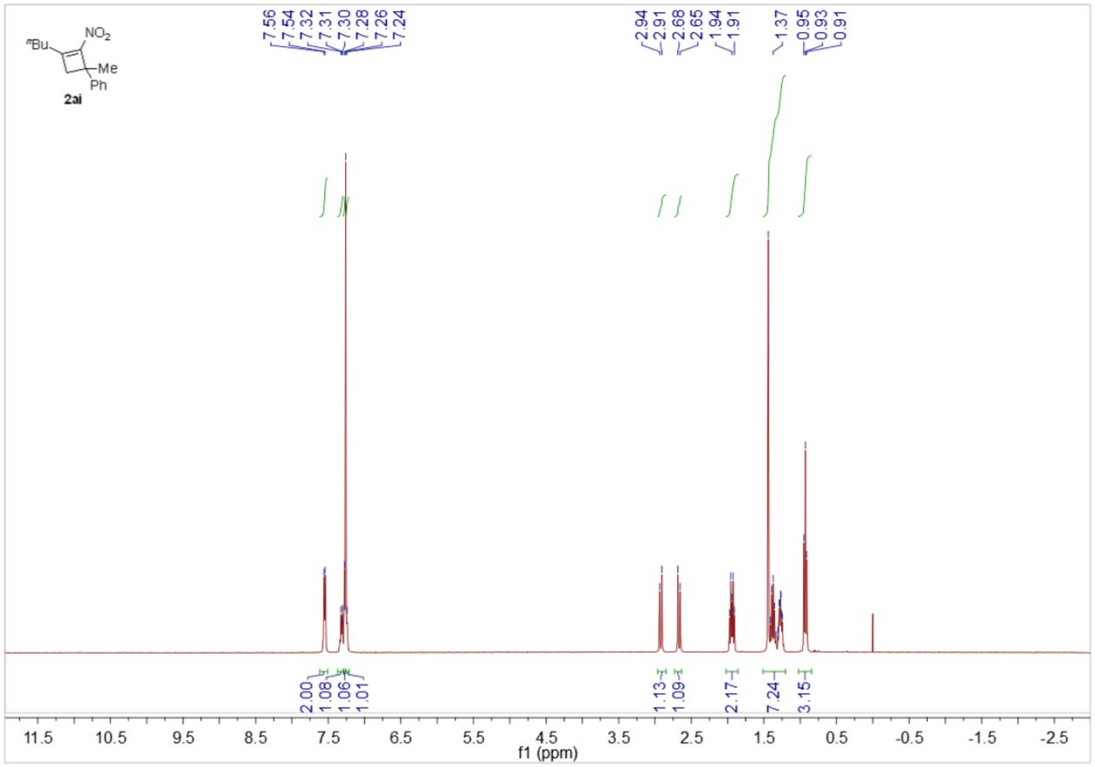
^{1}H NMR of **2ah** (400 MHz, $CDCl_3$):



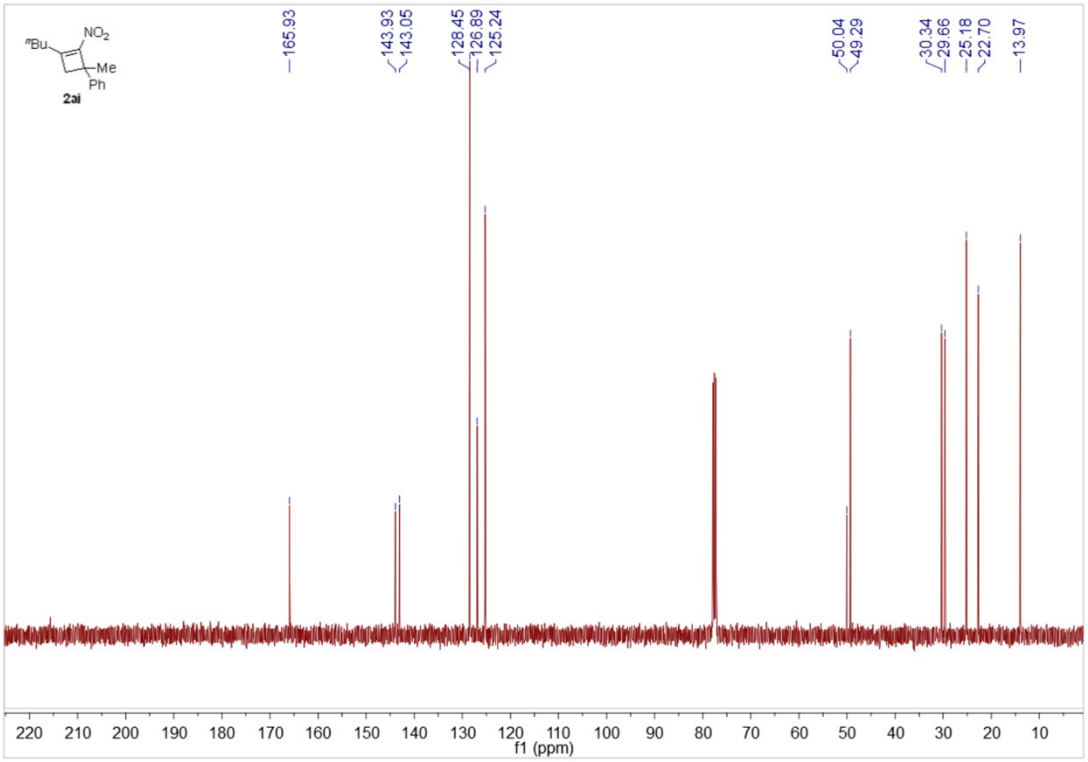
^{13}C NMR of **2ah** (100 MHz, $CDCl_3$):



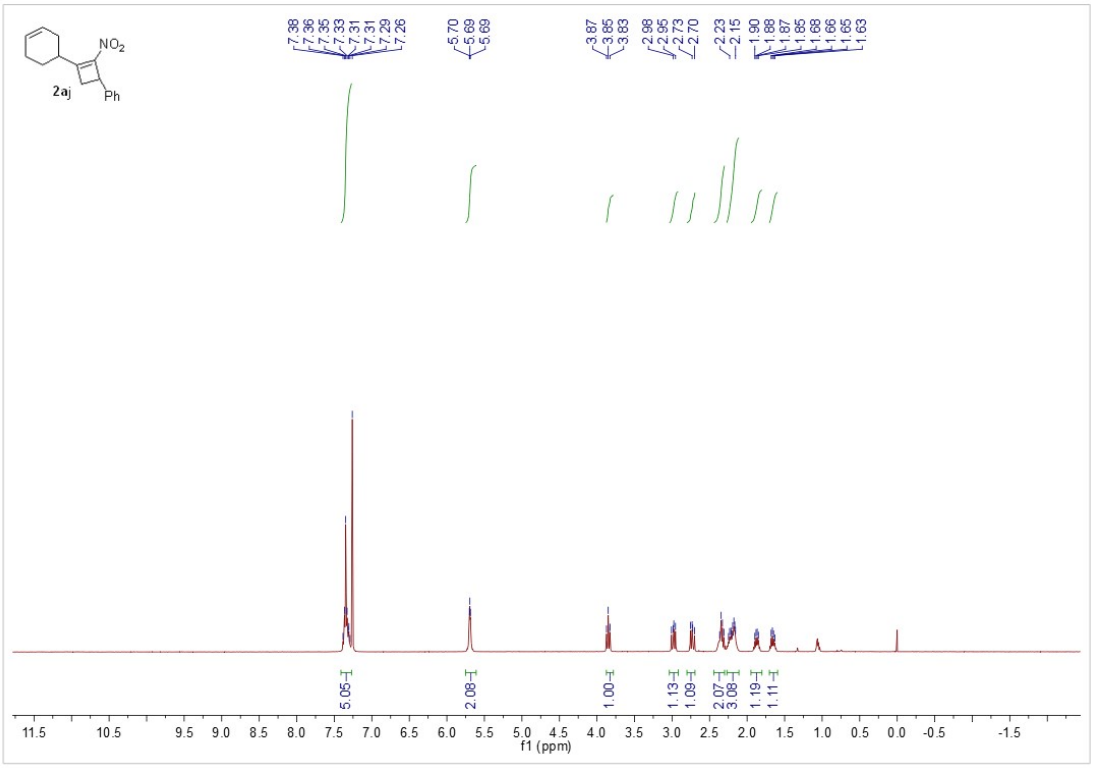
^{1}H NMR of **2ai** (400 MHz, $CDCl_3$):



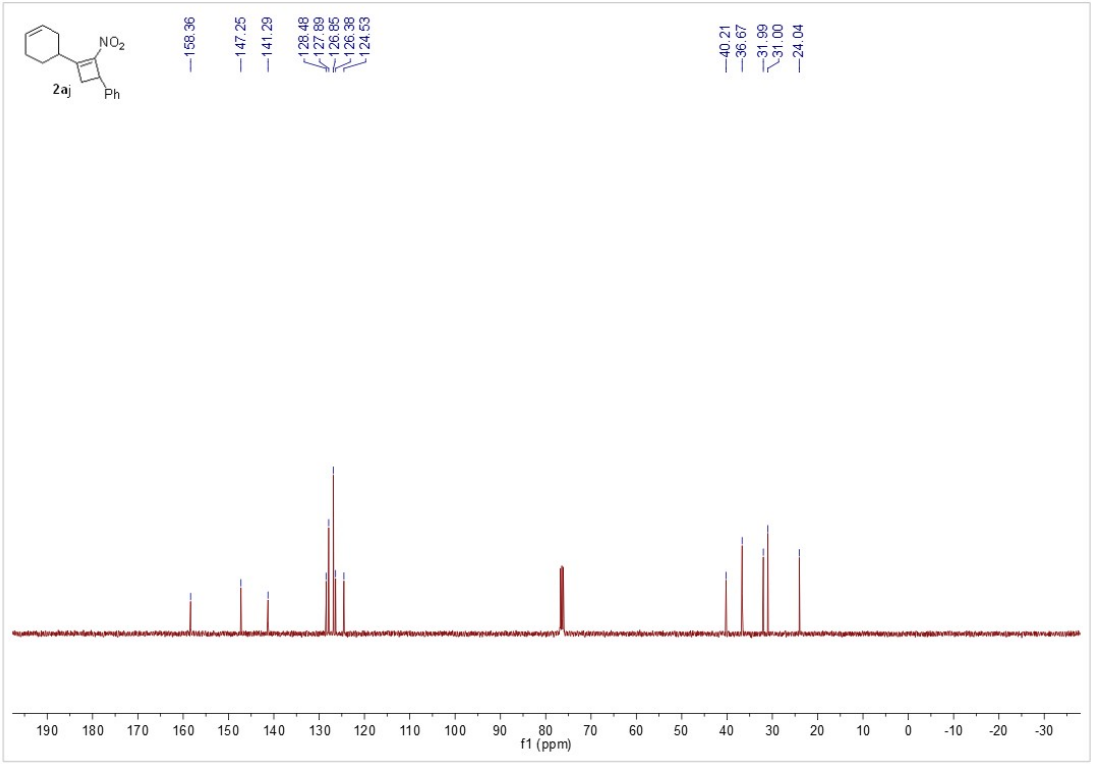
^{13}C NMR of **2ai** (100 MHz, $CDCl_3$):



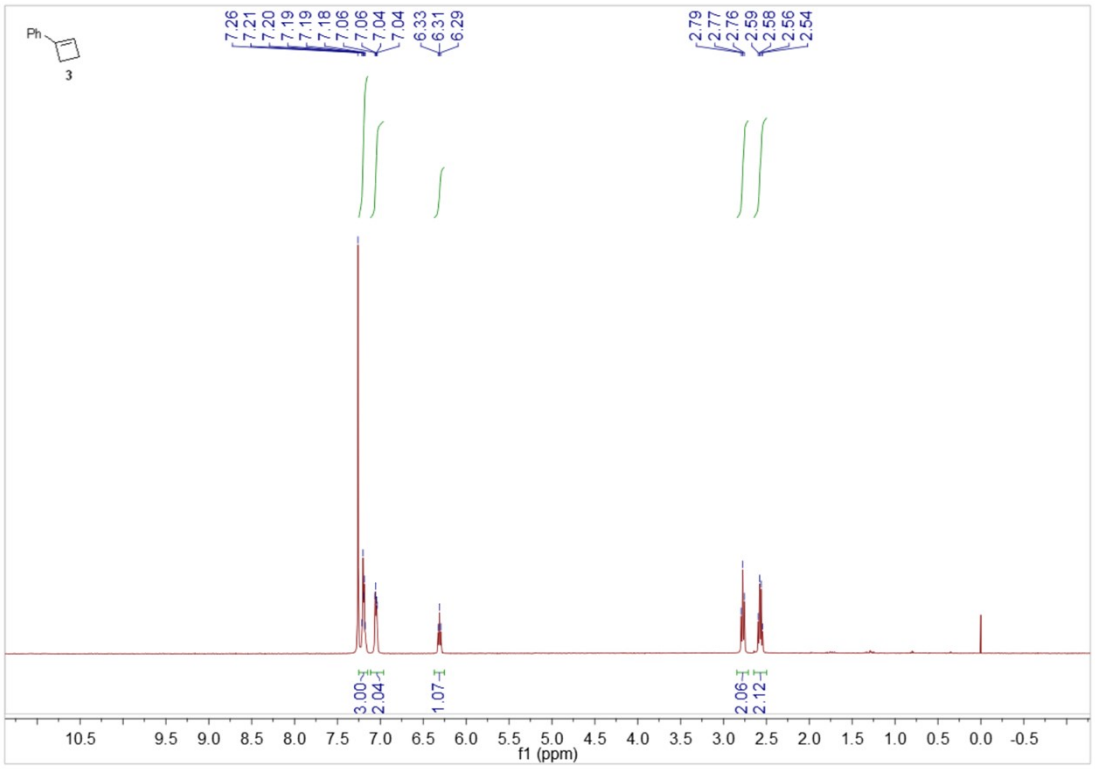
^{1}H NMR of **2aj** (400 MHz, $CDCl_3$):



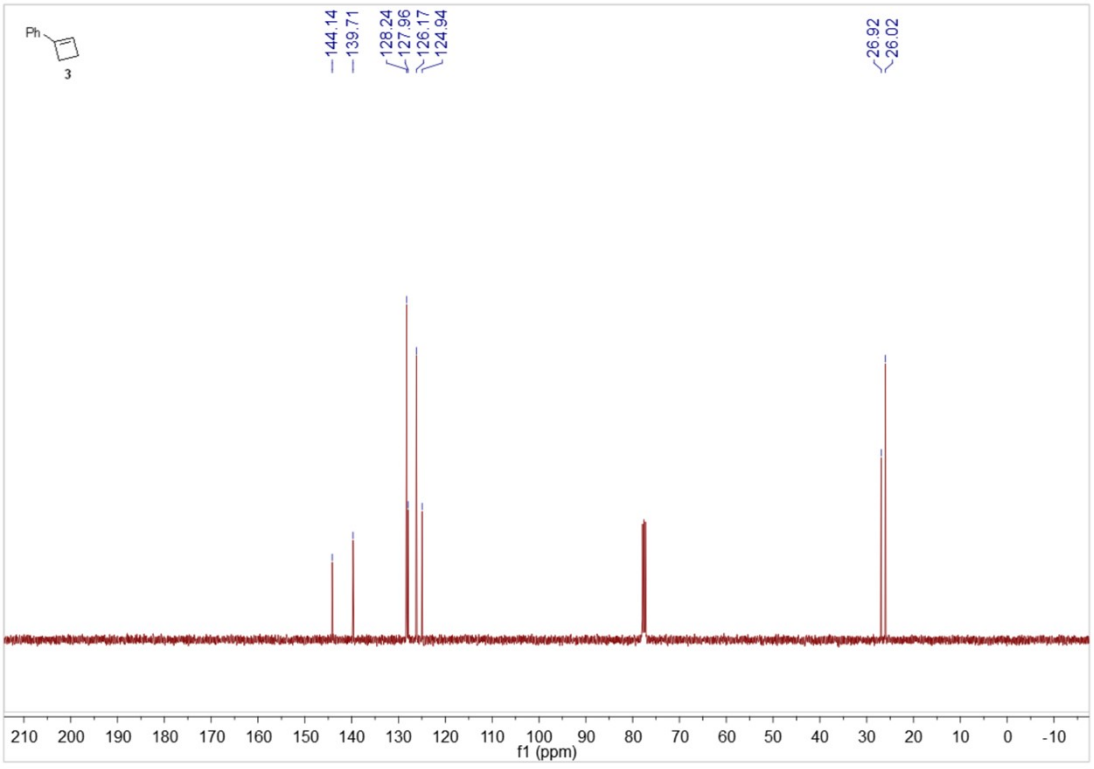
^{13}C NMR of **2aj** (100 MHz, $CDCl_3$):



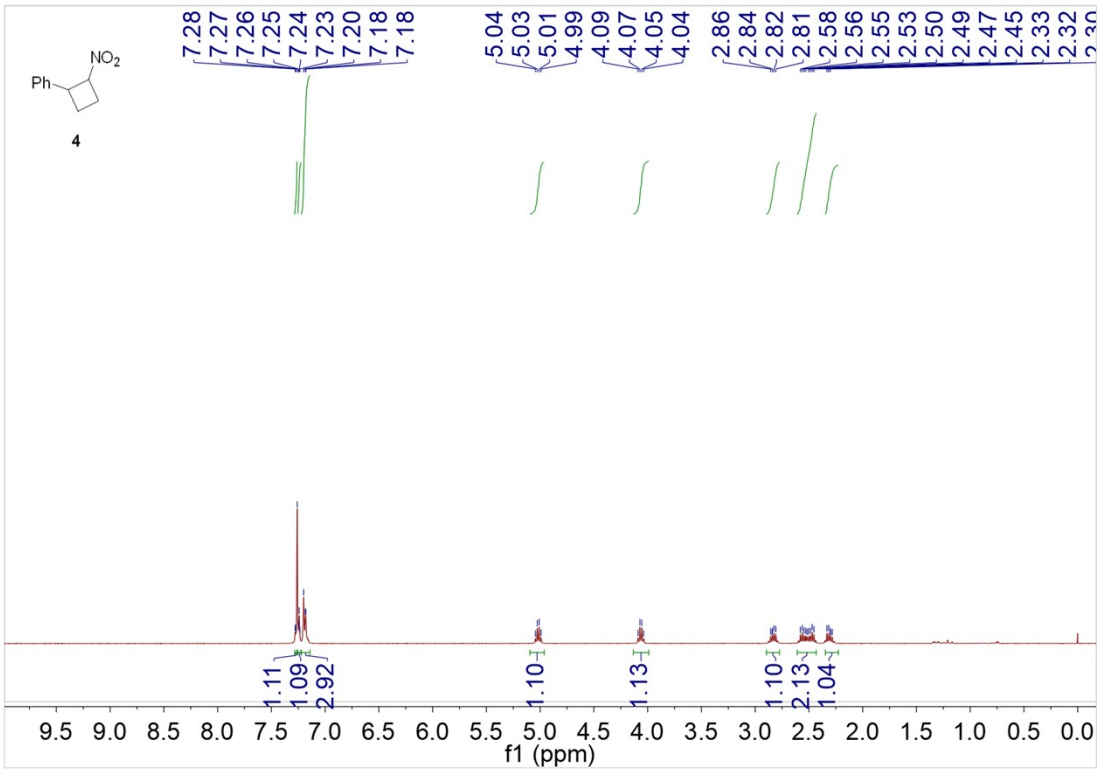
^{1}H NMR of **3** (400 MHz, $CDCl_3$):



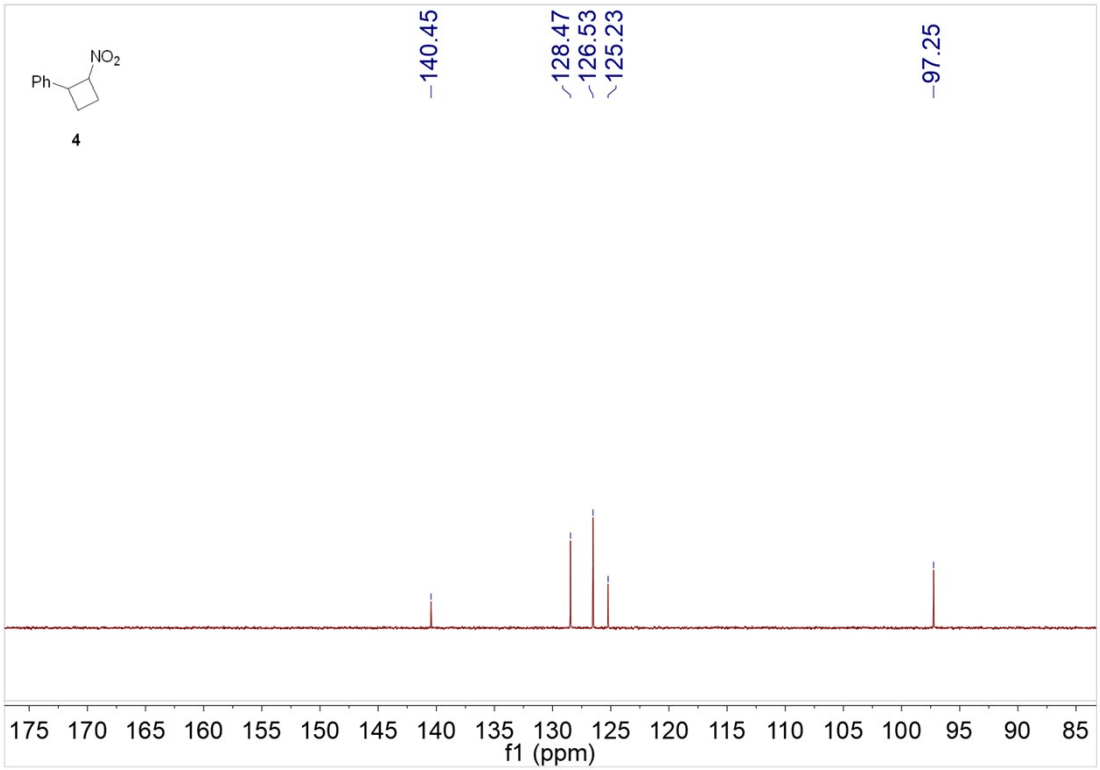
^{13}C NMR of **3** (100 MHz, $CDCl_3$):



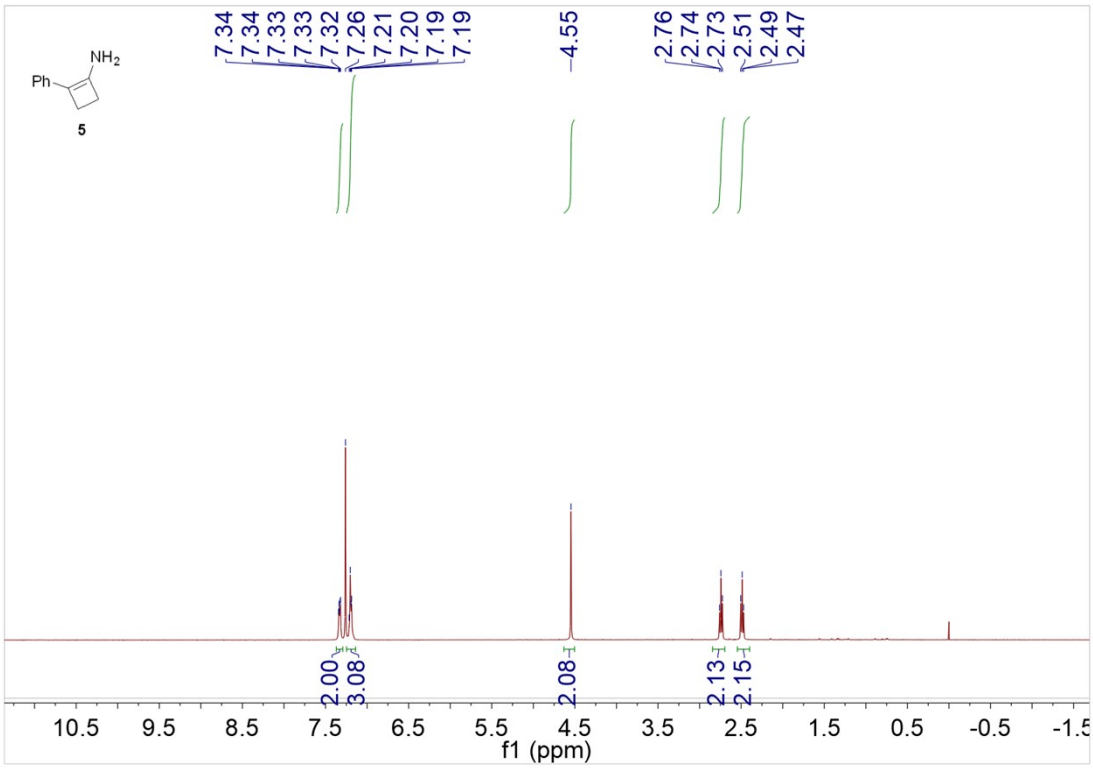
^{1}H NMR of **4** (400 MHz, $CDCl_3$):



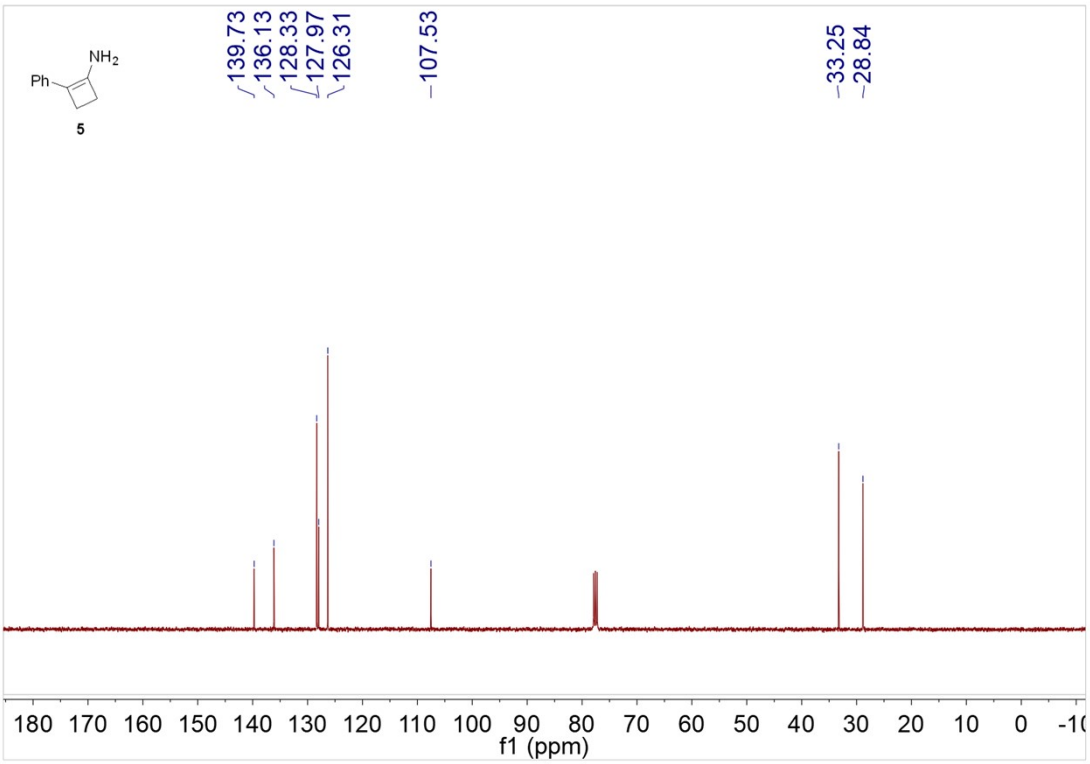
^{13}C NMR of **4** (100 MHz, $CDCl_3$):



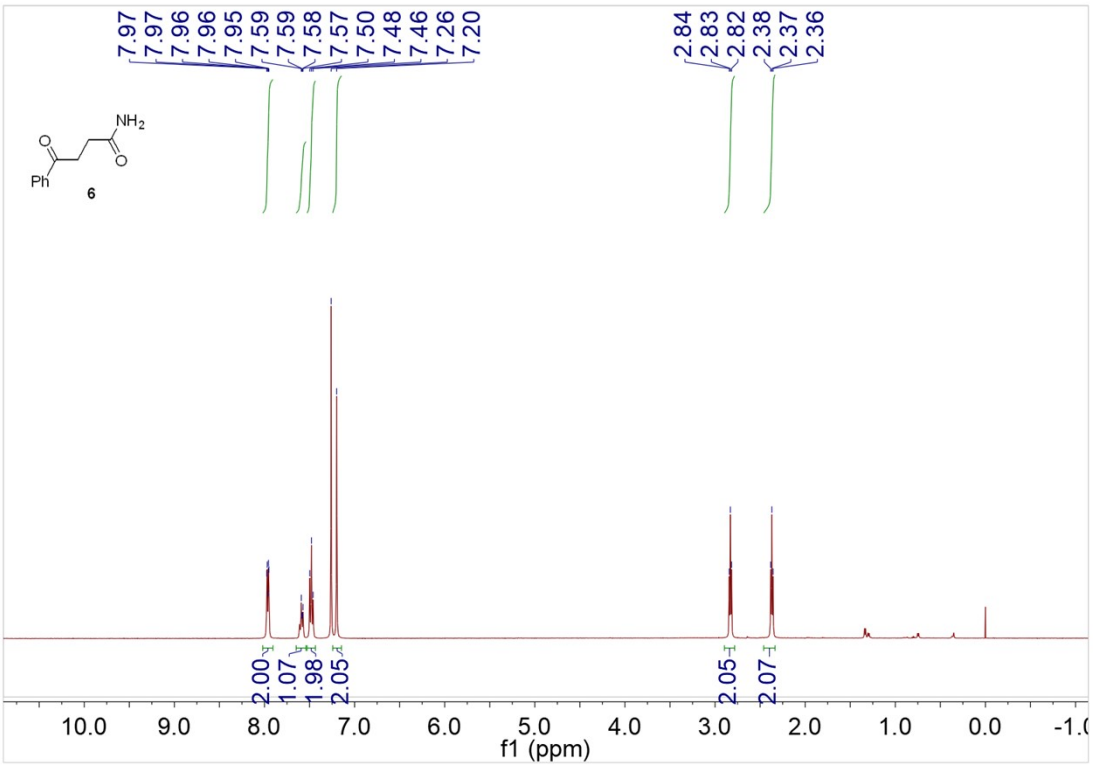
^{1}H NMR of **5** (400 MHz, $CDCl_3$):



^{13}C NMR of **5** (100 MHz, $CDCl_3$):



^{1}H NMR of **6** (400 MHz, $CDCl_3$):



^{13}C NMR of **6** (100 MHz, $CDCl_3$):