

Supporting Information

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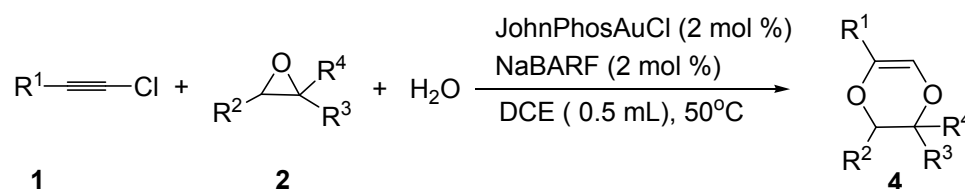
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General Information

^1H and ^{13}C NMR Spectra were recorded on a Bruker AC-500 FT spectrometer (500 MHz and 100 MHz, respectively) using tetramethylsilane as internal reference. Chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. IR spectra were recorded on a Perkin-Elmer 2000 FTIR spectrometer. High resolution mass spectra were recorded on a LC-TOF spectrometer (Micromass). The UV detection was monitored at 254 nm. Melting points were uncorrected.

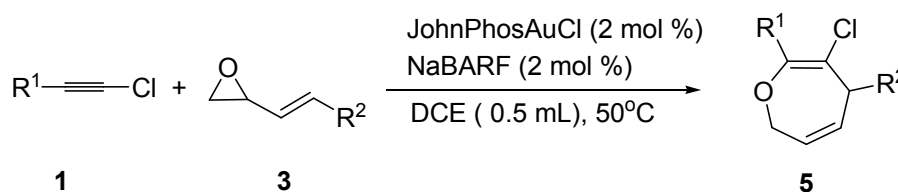
Analytical grade solvents for the column chromatography were used as received. 1,2-Dichloroethane, acetonitrile were dried over CaH_2 and distilled prior to use. All the gold complexes ^[1] and the substrates ^[2] were prepared following the literature reports. The rest of chemicals were purchased from the Sinopharm Chemical Reagent Co., Meryer, Acros, and Alfa Aesar, and used as received.

General procedure for the gold catalyzed (3+2+1) cycloaddition between chloroalkynes, water and epoxides (Tables 2 and 3)



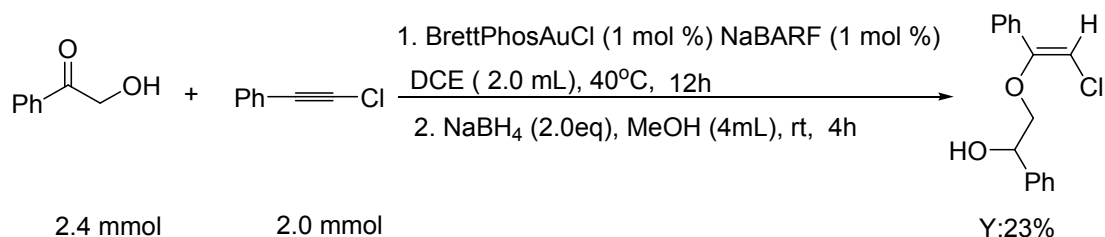
To a solution of chloroalkyne **1** (0.40 mmol) in DCE (0.15 mL) were added epoxide (0.6 mmol), JohnPhosAuCl (5.58 mg, 0.0080 mmol) and NaBARF (7.08 mg, 0.0080 mmol) subsequently. The mixture was stirred at 50 °C for 10min. DCE/ H_2O (0.35 mL, 50:1) was then added dropwise over 20 minutes. The resulting mixture was stirred at 50 °C for 23.5h. The mixture was cooled to room temperature, and purified by silica gel column chromatography, eluting with petroleum ether/ethyl acetate (20:1 to 5:1), to give 1,4-dioxenes **4**.

General procedure for the gold catalyzed (5+2) cycloaddition between phenylethynyl chloride and 1,3-butadiene monoepoxide (Tables 4)



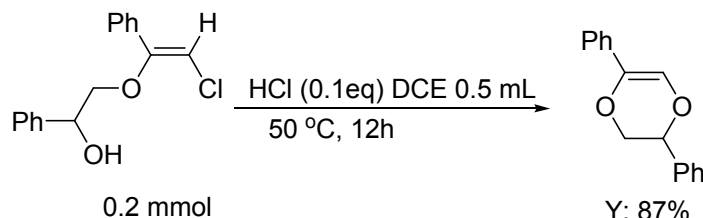
To a solution of phenylethynyl chloride **1a** (0.40 mmol) in dry DCE (0.50 mL) were added 1,3-butadiene monoepoxide (49.7 mg, 0.6 mmol) JohnPhosAuCl (5.58 mg, 0.0080 mmol) and NaBARF (7.08 mg, 0.0080 mmol) subsequently. The resulting mixture was stirred at 50 °C until no further transformation was detected by TLC analysis. The mixture was cooled to room temperature, and purified by silica gel column chromatography, eluting with petroleum ether/ethyl acetate (50:1), to give 4,7-dihydrooxepines **5**.

Procedure for the preparation of **8**



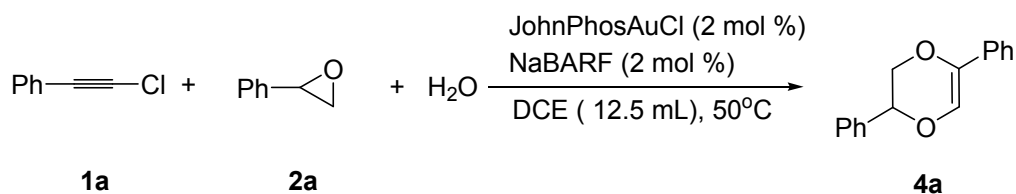
To a solution of phenylethynyl chloride **1a** (272 mg, 2 mmol) in DCE (2.0 mL) were added 2-hydroxy-1-phenylethanone (408 mg, 2.4 mmol), BrettPhosAuCl (15.6 mg, 0.02 mmol) and NaBARF (17.8 mg, 0.02 mmol) subsequently. The mixture was stirred at 40 °C for 12 h. Then the mixture was cooled to room temperature, NaBH₄ (152 mg, 4 mmol) and MeOH (8 mL) were added. The resulting mixture was stirred at room temperature for 4h. The solvent is evaporated under reduced pressure. The mixture was purified by silica gel column chromatography, eluting with petroleum ether/ethyl acetate (5:1), to give **8** (126 mg) in 23% yield.

Procedure for the preparation of **4a** from **8**



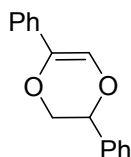
To a solution of **8** (54.2 mg, 0.2 mmol) in DCE (0.5 mL) was added concentrated hydrochloric acid (1.8 uL, 12 mmol/mL). The mixture was stirred at 50 °C for 12 h. The mixture was cooled to room temperature, and purified by silica gel column chromatography, eluting with petroleum ether/ethyl acetate (20:1), to give dioxene **4a** (83.5 mg) in 87% yield.

A 10 mmol Scale Reaction

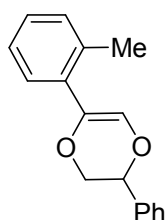


To a solution of phenylethynyl chloride **1a** (1.36 g, 10 mmol) in DCE (3.7 mL) were added Styrene oxide (1.20g ,15 mmol) JohnPhosAuCl (0.140 g, 0.20 mmol) and NaBARF (0.177 g, 0.20 mmol) subsequently. The mixture was stirred at 50 °C for 10min. DCE/H₂O (8.8 mL, 50:1) was then added dropwise over 20 minutes. The resulting mixture was stirred at 50 °C for 23.5h. The mixture was cooled to room temperature, and purified by silica gel column chromatography, eluting with petroleum ether/ethyl acetate (20:1), to give dioxene **4a** (1.93 g) in 81% yield.

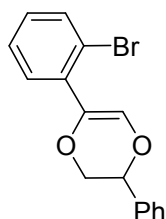
Analytical Data for The Products Shown in Tables 2, 3 and 4



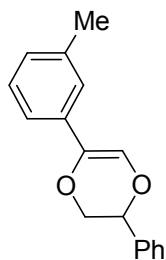
2,5-diphenyl-2,3-dihydro-1,4-dioxene (**4a**), white solid (79.1 mg), m.p. 103-105 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.42-7.32 (m, 10H), 5.85 (s, 1H), 5.14 (t, *J* = 6.8 Hz, 1H), 4.25-4.22 (m, 1H), 4.19-4.14 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): 154.8, 137.9, 133.1, 129.2, 128.8, 128.7, 128.6, 127.6, 126.4, 102.9, 74.4, 60.6; IR (film): ν 3060, 3020, 2920, 1600, 1581, 1495, 1453 cm⁻¹; HRMS (EI) Calcd for C₁₆H₁₄O₂ (M): 238.0994. Found: 238.0981.



2-phenyl-5-o-tolyl-2,3-dihydro-1,4-dioxene (**4b**), white solid (70.6 mg), m.p. 100-102 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.41-7.37 (m, 8H), 7.33-7.31 (m, 1H), 6.00 (s, 1H), 5.19 (t, *J* = 5.5 Hz, 1H), 4.33-4.25 (m, 1H), 4.23-4.20 (m, 1H), 2.17 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): 154.7, 137.9, 135.8, 132.9, 130.9, 129.7, 129.0, 128.7, 127.8, 127.0, 124.3, 102.6, 74.2, 60.1, 19.7; IR (film): ν 3059, 3022, 2923, 1599, 1580, 1490, 1449 cm⁻¹; HRMS (EI) Calcd for C₁₇H₁₆O₂ (M): 252.1150. Found: 252.1163.

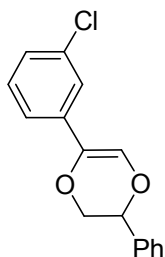


5-(2-bromophenyl)-2-phenyl-2,3-dihydro-1,4-dioxene (**4c**), white solid (82.1 mg), m.p. 127-129 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.37-7.23 (m, 8H), 7.20-7.17 (m, 1H), 5.53 (s, 1H), 5.08 (t, *J* = 6.0 Hz, 1H), 4.10-4.05 (m, 1H), 4.02-3.98 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): 153.3, 138.0, 133.5, 132.1, 131.8, 131.2, 130.9, 130.3, 128.7, 127.7, 127.1, 102.8, 73.4, 60.6; IR (film): ν 3062, 3024, 2918, 1605, 1573, 1490, 1461 cm⁻¹; HRMS (EI) Calcd for C₁₆H₁₃BrO₂ (M): 316.0099. Found: 316.0087.

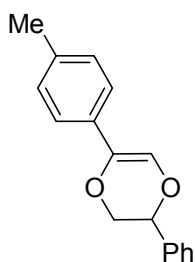


2-phenyl-5-m-tolyl-2,3-dihydro-1,4-dioxene (**4d**), white solid (81.6 mg), m.p. 110-112 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.46-7.36 (m, 9H), 5.92 (s, 1H), 5.18 (t, *J* = 6.8 Hz, 1H), 4.30-4.25 (m, 1H), 4.23-4.19 (m, 1H), 2.17 (s, 3H); ¹³C NMR (100 MHz,

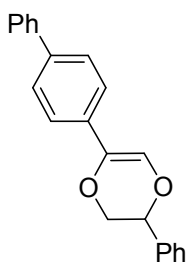
CDCl₃): 154.9, 138.8, 134.2, 133.4, 129.6, 129.5, 129.2, 128.4, 127.4, 126.2, 125.7, 74.1, 60.6, 21.5; IR (film): ν 3057, 3019, 2922, 1600, 1581, 1489, 1451 cm⁻¹; HRMS (EI) Calcd for C₁₇H₁₆O₂ (M): 252.1150. Found: 252.1146.



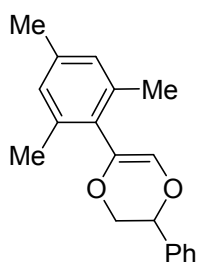
5-(3-chlorophenyl)-2-phenyl-2,3-dihydro-1,4-dioxene (**4e**), m.p. 119-121°C; ¹H NMR (500 MHz, CDCl₃) δ 7.42-7.29 (m, 9H), 5.52 (s, 1H), 5.08 (t, *J* = 5.4 Hz, 1H), 4.10-4.05 (m, 1H), 4.00-3.98 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): 154.7, 138.7, 134.3, 133.8, 132.9, 128.9, 128.8, 127.6, 126.8, 125.2, 102.9, 74.3, 60.5; IR (film): ν 3059, 3024, 2920, 1601, 1588, 1490, 1446 cm⁻¹; HRMS (EI) Calcd for C₁₆H₁₃ClO₂ (M): 272.0604. Found: 272.0619.



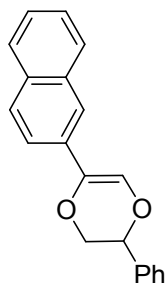
2-phenyl-5-*p*-tolyl-2,3-dihydro-1,4-dioxene (**4f**) white solid (90.6 mg), m.p. 107-108 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.42-7.34 (m, 5H), 7.20 (d, *J* = 8.5 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 5.79 (s, 1H), 5.14 (t, *J* = 6.3 Hz, 1H), 4.23-4.18 (m, 1H), 4.17-4.13 (m, 1H), 2.35 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): 154.9, 139.3, 138.0, 130.3, 129.4, 128.8, 128.6, 127.6, 126.3, 102.1, 74.3, 60.6, 21.2; IR (film): ν 3057, 3020, 2925, 1598, 1579, 1493, 1454 cm⁻¹; HRMS (EI) Calcd for C₁₇H₁₆O₂ (M): 252.1150. Found: 252.1171.



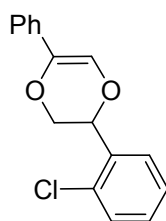
2-phenyl-5-*p*-phenylphenyl-2,3-dihydro-1,4-dioxene (**4g**), white solid (109.1 mg), m.p. 132-134 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.61-7.55 (m, 4H), 7.47-7.44 (m, 3H), 7.23-7.35 (m, 7H), 5.92 (s, 1H), 5.18 (t, *J* = 5.5 Hz, 1H), 4.29-4.26 (m, 1H), 4.23-4.19 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): 154.6, 140.1, 133.0, 128.8, 128.7, 128.5, 128.0, 127.7, 127.6, 127.3, 127.0, 126.7, 126.0, 103.0, 74.5, 60.6; IR (film): ν 3065, 3030, 2917, 1601, 1580, 1498, 1449 cm⁻¹; HRMS (EI) Calcd for C₂₂H₁₈O₂ (M): 304.1307. Found: 314.1321.



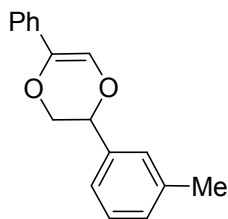
5-mesityl-2-phenyl-2,3-dihydro-1,4-dioxene (**4h**), white solid (62.5 mg), m.p. 99-100 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.40-7.30 (m, 5H), 6.87 (s, 2H), 5.18 (s, 1H), 5.02 (t, *J* = 6.5 Hz, 1H), 3.85-3.81 (m, 1H), 3.79-3.75 (m, 1H), 2.30(s, 3H), 2.21(s, 6H); ¹³C NMR (100 MHz, CDCl₃): 154.6, 138.0, 133.9, 131.7, 130.6, 129.9, 128.9, 128.4, 127.0, 101.6, 74.2, 60.3, 22.0, 20.6; IR (film): ν 3061, 3032, 2928, 1605, 1588, 1491, 1447 cm⁻¹; HRMS (EI) Calcd for C₁₉H₂₀O₂ (M): 280.1463. Found: 280.1450.



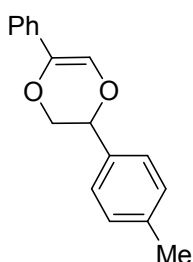
5-(naphthalen-2-yl)-2-phenyl-2,3-dihydro-1,4-dioxene (**4i**), white solid (96.7 mg), m.p. 138-140 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.74 (s, 1H), 7.52-7.50 (m, 2H), 7.49-7.36 (m, 9H), 6.00 (s, 1H), 5.19 (t, *J* = 6.8 Hz, 1H), 4.32-4.28 (m, 1H), 4.24-4.20 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): 154.9, 138.1, 133.5, 129.6, 128.9, 128.7, 128.6, 128.5, 128.4, 128.1, 126.8, 126.7, 126.1, 125.9, 123.5, 103.4, 74.5, 60.6; IR (film): ν 3059, 3030, 2921, 1600, 1582, 1490, 1450 cm⁻¹; HRMS (EI) Calcd for C₂₀H₁₆O₂ (M): 288.1150. Found: 288.1134.



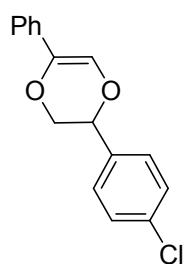
2-(2-chlorophenyl)-5-phenyl-2,3-dihydro-1,4-dioxene (**4j**), white solid (85.8 mg), m.p. 118-120 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.40-7.27 (m, 9H), 5.84 (s, 1H), 5.14 (t, *J* = 5.8 Hz, 1H), 4.24-4.20 (m, 1H), 4.17-4.14 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): 154.9, 139.8, 137.5, 135.3, 134.0, 130.5, 129.2, 128.4, 128.3, 127.9, 127.7, 103.0, 74.2, 60.5; IR (film): ν 3059, 3020, 2921, 1600, 1583, 1491, 1450 cm⁻¹; HRMS (EI) Calcd for C₁₆H₁₃ClO₂ (M): 272.0604. Found: 272.0622.



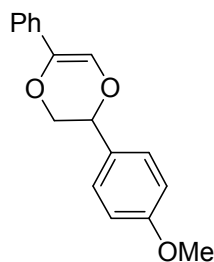
5-phenyl-2-*m*-tolyl-2,3-dihydro-1,4-dioxene(**4k**), white solid (81.5 mg), m.p. 104-106 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.50-7.30 (m, 5H), 7.24-7.21 (m, 3H), 7.08 (s, 1H), 5.79 (s, 1H), 5.13 (t, *J* = 5.8 Hz, 1H), 4.23-4.18 (m, 1H), 4.17-4.13 (m, 1H), 2.39 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): 154.8, 139.6, 133.3, 131.6, 130.2, 129.3, 128.3, 127.7, 126.5, 125.2, 124.6, 73.5, 60.6, 23.1; IR (film): ν 3061, 3028, 2923, 1600, 1580, 1495, 1451 cm⁻¹; HRMS (EI) Calcd for C₁₇H₁₆O₂ (M): 252.1150. Found: 252.1169.



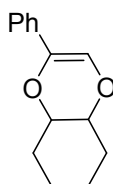
5-phenyl-2-*p*-tolyl-2,3-dihydro-1,4-dioxene(**4l**), white solid (86.7 mg), m.p. 107-108 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.32-7.26 (m, 5H), 7.09 (d, *J* = 6.5 Hz, 2H), 7.03 (d, *J* = 6.5 Hz, 2H), 5.84 (s, 1H), 5.14 (t, *J* = 5.8 Hz, 1H), 4.28-4.24 (m, 1H), 4.22-4.18 (m, 1H), 2.40 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): 154.8, 137.9, 137.4, 131.9, 130.1, 129.3, 128.8, 128.4, 127.5, 102.3, 74.4, 60.5, 21.3; IR (film): ν 3058, 3030, 2924, 1602, 1580, 1487, 1446 cm⁻¹; HRMS (EI) Calcd for C₁₇H₁₆O₂ (M): 252.1150. Found: 252.1137.



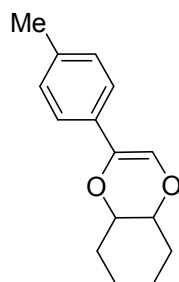
2-(4-chlorophenyl)-5-phenyl-2,3-dihydro-1,4-dioxene(**4m**), white solid (90.0 mg), m.p. 113-115 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.31-7.26 (m, 5H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 7.5 Hz, 2H), 5.84 (s, 1H), 5.19 (t, *J* = 5.5 Hz, 1H), 4.29-4.24 (m, 1H), 4.22-4.16 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): 155.2, 136.8, 133.7, 129.1, 128.7, 128.4, 128.1, 126.6, 103.0, 73.1, 60.5; IR (film): ν 3057, 3028, 2920, 1599, 1581, 1493, 1448 cm⁻¹; HRMS (EI) Calcd for C₁₆H₁₃ClO₂ (M): 272.0604. Found: 272.0623.



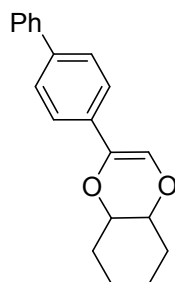
2-(4-methoxyphenyl)-5-phenyl-2,3-dihydro-1,4-dioxene (**4n**), white solid (91.0 mg), m.p. 109-111 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.29-7.24 (m, 5H), 7.20-7.18 (m, 2H), 6.91 (d, *J* = 7.5 Hz, 2H), 5.83 (s, 1H), 5.13 (t, *J* = 6.8 Hz, 1H), 4.22-4.16 (m, 1H), 4.15-4.12 (m, 1H), 3.83 (m, 3H); ¹³C NMR (100 MHz, CDCl₃): 159.2, 154.8, 134.3, 131.2, 129.7, 128.3, 127.9, 126.5, 113.5, 103.0, 73.9, 60.4, 55.2; IR (film): ν 3061, 3032, 2926, 1601, 1587, 1490, 1447 cm⁻¹; HRMS (EI) Calcd for C₁₇H₁₆O₃ (M): 268.1099. Found: 268.1085.



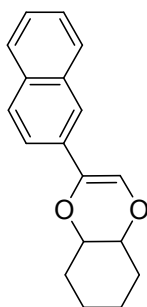
2-phenyl-4a, 5, 6,7, 8, 8a-hexahydrobenzo-1,4-dioxene (**4o**), white solid (63.9 mg), m.p. 93-94 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.48-7.46 (m, 2H), 7.40-7.37 (m, 3H), 5.79 (s, 1H), 4.20-4.08 (m, 1H), 3.88-3.84 (m, 1H), 2.40-2.30 (m, 1h), 2.02-1.98 (m, 1h), 1.80-1.55 (m, 4H), 1.43-1.35 (m, 1H), 1.26-1.20 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): 154.3, 130.0, 128.7, 127.0, 126.7, 103.0, 78.0, 61.1, 29.7, 29.4, 23.6, 22.5; IR (film): ν 3060, 3022, 2930, 1601, 1579, 1501, 1455 cm⁻¹; HRMS (EI) Calcd for C₁₄H₁₆O₂ (M): 216.1150. Found: 216.1171.



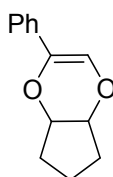
2-*p*-tolyl-4a,5,6,7,8,8a-hexahydrobenzo-1,4-dioxene (**4p**), white solid (74.3 mg), m.p. 97-99 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.34 (d, *J* = 6.5 Hz, 2H), 7.17 (d, *J* = 6.5 Hz, 2H), 5.72 (s, 1H), 4.10-4.06 (m, 1H), 3.86-3.83 (m, 1H), 2.36 (s, 3H), 2.32-2.29 (m, 1H), 2.00-1.98 (m, 1H), 1.74-1.60 (m, 3H), 1.40-1.30 (m, 1H), 1.25-1.18 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): 154.2, 139.2, 130.6, 129.4, 126.9, 102.2, 79.8, 61.7, 29.9, 29.8, 23.8, 22.4, 21.6; IR (film): ν 3058, 3026, 2919, 1598, 1579, 1502, 1460 cm⁻¹; HRMS (EI) Calcd for C₁₅H₁₈O₂ (M): 230.1307. Found: 230.1289.



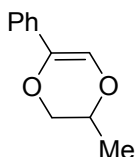
2-(4-phenylphenyl)-4a,5,6,7,8,8a-hexahydrobenzo-1,4-dioxene (**4q**), white solid (91.0 mg), m.p. 106-107 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.63-7.59 (m, 3H), 7.56-7.53 (m, 2H), 7.47-7.42 (m, 3H), 7.39-7.35 (m, 1H), 5.85 (s, 1H), 4.14-4.096 (m, 1H), 3.96-3.90 (m, 1H), 2.36-2.30 (m, 1H), 2.06-2.00 (m, 1H), 1.80-1.66 (m, 2H), 1.40-1.27 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3): 154.1, 139.4, 137.7, 131.3, 129.2, 128.7, 128.5, 127.0, 126.7, 103.0, 80.1, 30.7, 29.8, 23.7, 22.4; IR (film): ν 3061, 3020, 2924, 1602, 1586, 1497, 1451 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{20}\text{H}_{20}\text{O}_2$ (M): 292.1463. Found: 292.1450.



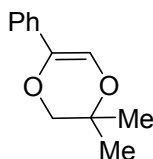
2-(naphthalen-2-yl)-4a,5,6,7,8,8a-hexahydrobenzo-1,4-dioxene (**4r**), white solid (77.2 mg), m.p. 116-118 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.96 (s, 1H), 7.87-7.40 (m, 3H), 7.58-7.50 (m, 3H), 5.92 (s, 1H), 4.18-4.11 (m, 1H), 3.92-3.89 (m, 1H), 2.37-2.33 (m, 1H), 2.06-2.01 (m, 1H), 1.80-1.67 (m, 3H), 1.40-1.33 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3): 154.8, 137.9, 133.2, 132.8, 131.3, 129.7, 128.2, 127.6, 127.1, 126.4, 125.7, 103.3, 79.9, 62.4, 30.2, 29.4, 23.3, 22.5; IR (film): ν 3058, 3020, 2925, 1600, 1593, 1501, 1452 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{18}\text{H}_{18}\text{O}_2$ (M): 266.1307. Found: 266.1288.



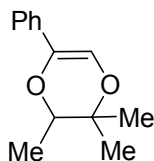
2-phenyl-5,6,7,7a-tetrahydro-4aH-cyclopenta-1,4-dioxene (**4s**), white solid (62.0 mg), m.p. 87-89 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.47-7.44 (m, 2H), 7.37-7.35 (m, 3H), 5.70 (s, 1H), 3.95-3.91 (m, 2H), 2.03-1.97 (m, 2H), 1.72-1.64 (m, 2H), 1.38-1.25 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): 154.5, 133.9, 129.0, 128.5, 127.0, 101.7, 79.4, 29.7, 28.5, 22.1; IR (film): ν 3065, 3030, 2928, 1599, 1571, 1502, 1450 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{13}\text{H}_{14}\text{O}_2$ (M): 201.0994. Found: 201.1014.



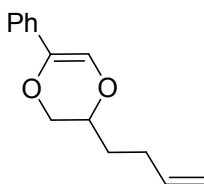
2-methyl-5-phenyl-2,3-dihydro-1,4-dioxene (**4t**), colourless oil (49.1 mg); ^1H NMR (500 MHz, CDCl_3) δ 7.45-7.43 (m, 2H), 7.39-7.37 (m, 3H), 5.89 (s, 1H), 4.27-4.20 (m, 1H), 3.95-3.93 (m, 1H), 3.86-3.82 (m, 1H), 1.63 (d, $J = 6.5$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): 154.3, 133.8, 129.0, 128.6, 126.5, 102.9, 78.9, 66.3, 18.3; IR (film): ν 3064, 3035, 2926, 1603, 1589, 1501, 1449 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{11}\text{H}_{12}\text{O}_2$ (M): 176.0838. Found: 176.0818.



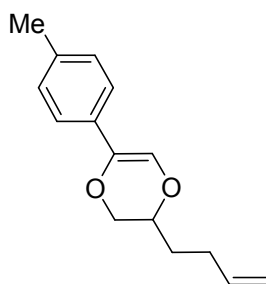
2,2-dimethyl-5-phenyl-2,3-dihydro-1,4-dioxene (**4u**), colourless oil (55.6 mg); ^1H NMR (500 MHz, CDCl_3) δ 7.45-7.41 (m, 2H), 7.28-7.35 (m, 3H), 5.89 (s, 1H), 4.20 (s, 2H), 1.71 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): 153.5, 129.2, 128.7, 127.0, 126.8, 102.9, 80.1, 63.3, 23.7; IR (film): ν 3055, 3030, 2930, 1599, 1576, 1490, 1461 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{12}\text{H}_{14}\text{O}_2$ (M): 190.0994. Found: 190.1021.



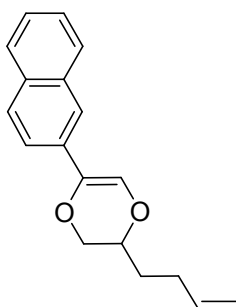
2,2,3-trimethyl-5-phenyl-2,3-dihydro-1,4-dioxene (**4v**), colourless oil (52.1 mg); ^1H NMR (500 MHz, CDCl_3) δ 7.45-7.35 (m, 5H), 5.85 (s, 1H), 3.80 (s, 1H), 1.84 (s, 3H), 1.71 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): 154.5, 133.9, 129.0, 128.5, 127.0, 101.7, 81.0, 71.9, 22.0, 14.4; IR (film): ν 3061, 3028, 2926, 1600, 1585, 1499, 1446 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{13}\text{H}_{16}\text{O}_2$ (M): 204.1150. Found: 204.1171.



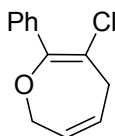
2-(but-3-enyl)-5-phenyl-2,3-dihydro-1,4-dioxene (**4w**), colourless oil (52.3 mg); ^1H NMR (500 MHz, CDCl_3) δ 7.44-7.41 (m, 2H), 7.38-7.35 (m, 3H), 5.89 (s, 1H), 5.83-5.77 (m, 1H), 5.11-5.04 (m, 1H), 5.04-5.00 (m, 1H), 4.14-4.11 (m, 1H), 3.98-3.92 (m, 1H), 3.92-3.88 (m, 1H), 2.28-2.20 (m, 2H), 1.90-1.83 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): 154.8, 138.0, 133.0, 129.2, 127.4, 126.3, 122.9, 102.8, 81.1, 74.3, 35.3, 29.7; IR (film): ν 3061, 3028, 2926, 1600, 1585, 1499, 1446 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{14}\text{H}_{16}\text{O}_2$ (M): 204.1150. Found: 204.1171.



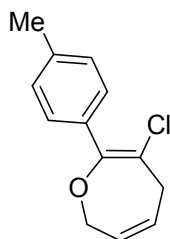
2-(but-3-enyl)-5-*p*-tolyl-2,3-dihydro-1,4-dioxene (**4x**), colourless oil (62.4 mg); ^1H NMR (500 MHz, CDCl_3) δ 7.32 (d, $J = 8.0$ Hz, 2H), 7.19 (d, $J = 8.0$ Hz, 2H), 5.83 (s, 1H), 5.80-5.77 (m, 1H), 5.11-5.07 (m, 1H), 5.04-5.01 (m, 1H), 4.12-4.08 (m, 1H), 4.00-3.94 (m, 1H), 3.91-3.87 (m, 1H), 2.37 (s, 3H), 2.28-2.21 (m, 2H), 1.89-1.83 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): 155.3, 137.6, 134.2, 129.0, 128.6, 126.4, 121.5, 102.3, 81.0, 70.8, 34.3, 27.8, 23.1; IR (film): ν 3059, 3025, 2923, 1605, 1579, 1495, 1453 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{15}\text{H}_{18}\text{O}_2$ (M): 230.1307. Found: 230.1320.



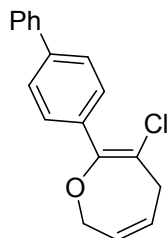
2-(but-3-enyl)-5-(naphthalen-2-yl)-2,3-dihydro-1,4-dioxene (**4y**), colourless oil (69.0 mg); ^1H NMR (500 MHz, CDCl_3) δ 7.93 (s, 1H), 7.86-7.82 (m, 3H), 7.52-7.48 (m, 3H), 6.02 (s, 1H), 5.83-5.76 (m, 1H), 5.11-5.01 (m, 2H), 4.20-4.15 (m, 1H), 4.03-4.00 (m, 1H), 4.00-3.95 (m, 1H), 2.36-2.32 (m, 2H), 2.28-2.21 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): 154.6, 138.0, 133.2, 132.9, 131.3, 129.8, 128.2, 128.0, 127.5, 127.1, 126.4, 126.3, 125.7, 102.7, 81.4, 66.5, 36.7, 29.7; IR (film): ν 3066, 3038, 2925, 1598, 1580, 1491, 1456 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{18}\text{H}_{18}\text{O}_2$ (M): 266.1307. Found: 266.1289.



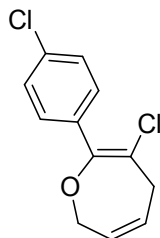
(*2E,5Z*)-3-chloro-2-phenyl-4,7-dihydrooxepine (**5a**), colourless oil (41.1 mg); ^1H NMR (500 MHz, CDCl_3) δ 7.38-7.34 (m, 4H), 7.33-7.26 (m, 1H), 5.93-5.89 (m, 1H), 5.81-5.77 (m, 1H), 4.66-4.63 (m, 2H), 2.98-2.95 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): 154.3, 132.7, 130.8, 129.5, 128.9, 126.2, 124.2, 104.1, 64.9, 29.7; IR (film): ν 3060, 3031, 2923, 1607, 1595, 1505, 1466 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{12}\text{H}_{11}\text{ClO}$ (M): 206.0498. Found: 206.0514.



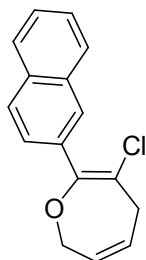
(2*E*,5*Z*)-3-chloro-2-*p*-tolyl-4,7-dihydrooxepine (**5b**), colourless oil (50.7 mg); ¹H NMR (500 MHz, CDCl₃) δ 7.30 (d, *J* = 7.5 Hz, 2H), 7.08 (d, *J* = 7.0 Hz, 2H), 5.92-5.89 (m, 1H), 5.83-5.75 (m, 1H), 4.65-4.63 (m, 2H), 3.02-3.00 (m, 2H), 2.35 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): 153.8, 137.9, 131.2, 129.0, 127.7, 126.9, 126.1, 100.5, 67.0, 29.2, 23.8; IR (film): ν 3055, 3028, 2920, 1601, 1585, 1496, 1462 cm⁻¹; HRMS (EI) Calcd for C₁₃H₁₃ClO (M): 220.0655. Found: 220.0641.



(2*Z*,5*Z*)-3-chloro-2-(4-phenylphenyl)-4,7-dihydrooxepine (**5c**), colourless oil (64.3 mg); ¹H NMR (500 MHz, CDCl₃) δ 7.58-7.55 (m, 4H), 7.45-7.42 (m, 4H), 7.36-7.33 (m, 1H), 5.94-5.90 (m, 1H), 5.84-5.80 (m, 1H), 4.66-4.64 (m, 2H), 3.03-3.01 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): 154.9, 140.4, 136.1, 130.8, 129.8, 128.8, 127.5, 127.0, 126.9, 124.7, 122.9, 104.1, 66.9, 28.8; IR (film): ν 3060, 3025, 2924, 1601, 1588, 1496, 1456 cm⁻¹; HRMS (EI) Calcd for C₁₈H₁₅ClO (M): 282.0811. Found: 282.0820.

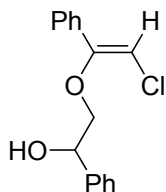


(2*E*,5*Z*)-3-chloro-2-(4-chlorophenyl)-4,7-dihydrooxepine (**5d**), colourless oil (59.4 mg); ¹H NMR (300 MHz, CDCl₃) δ 7.38 (d, *J* = 8.7 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 5.87-5.79 (m, 1H), 5.74-5.70 (m, 1H), 4.60-4.56 (m, 2H), 2.91-2.88 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): 154.6, 133.0, 131.6, 129.4, 128.6, 126.0, 123.6, 103.6, 66.1, 28.1; IR (film): ν 3062, 3030, 2926, 1600, 1580, 1501, 1465 cm⁻¹; HRMS (EI) Calcd for C₁₂H₁₀Cl₂O (M): 240.0109. Found: 240.0122.



(2*Z*,5*Z*)-3-chloro-2-(naphthalen-2-yl)-4,7-dihydrooxepine (**5e**), colourless oil (63.0

mg); ^1H NMR (500 MHz, CDCl_3) δ 7.82-7.74 (m, 4H), 7.49-7.40 (m, 3H), 5.79-5.73 (m, 1H), 5.66-5.62 (m, 1H), 4.48-4.45 (m, 2H), 3.46-3.42 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): 153.0, 135.9, 133.5, 132.9, 132.2, 129.5, 128.6, 128.2, 128.1, 127.8, 127.4, 126.8, 126.1, 99.6, 66.3, 29.6; IR (film): ν 3060, 3033, 2927, 1606, 1589, 1503, 1455 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{16}\text{H}_{13}\text{ClO}$ (M): 256.0655. Found: 256.0667.

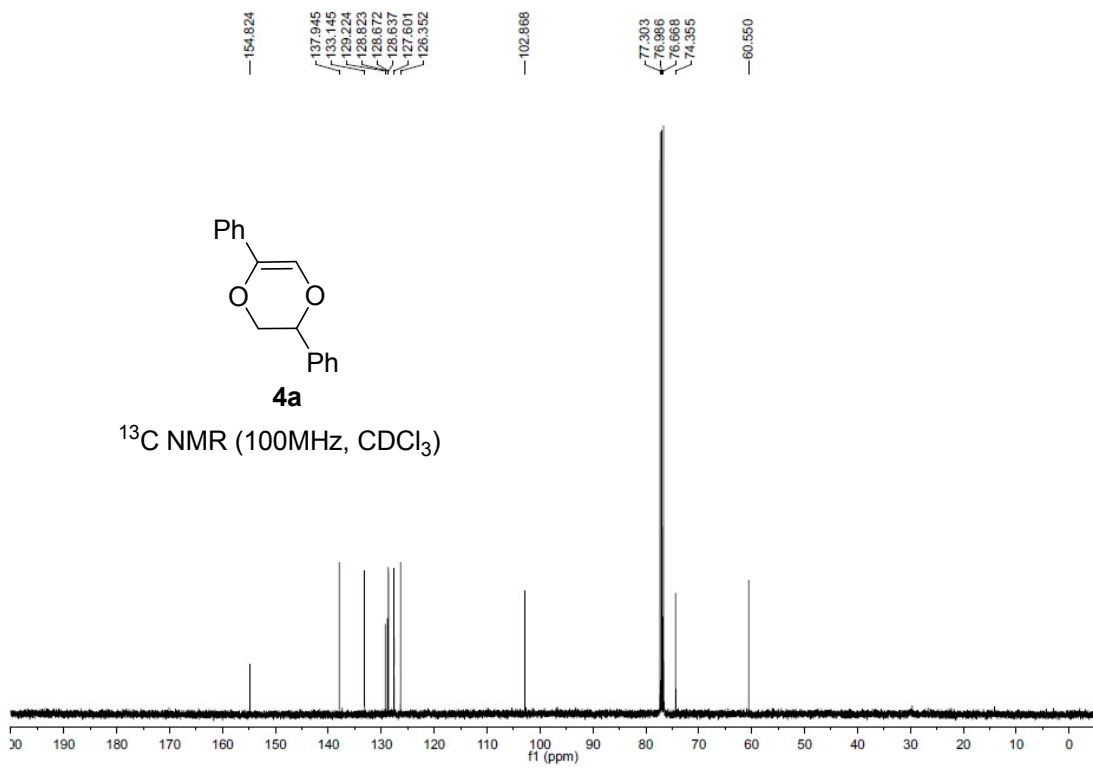
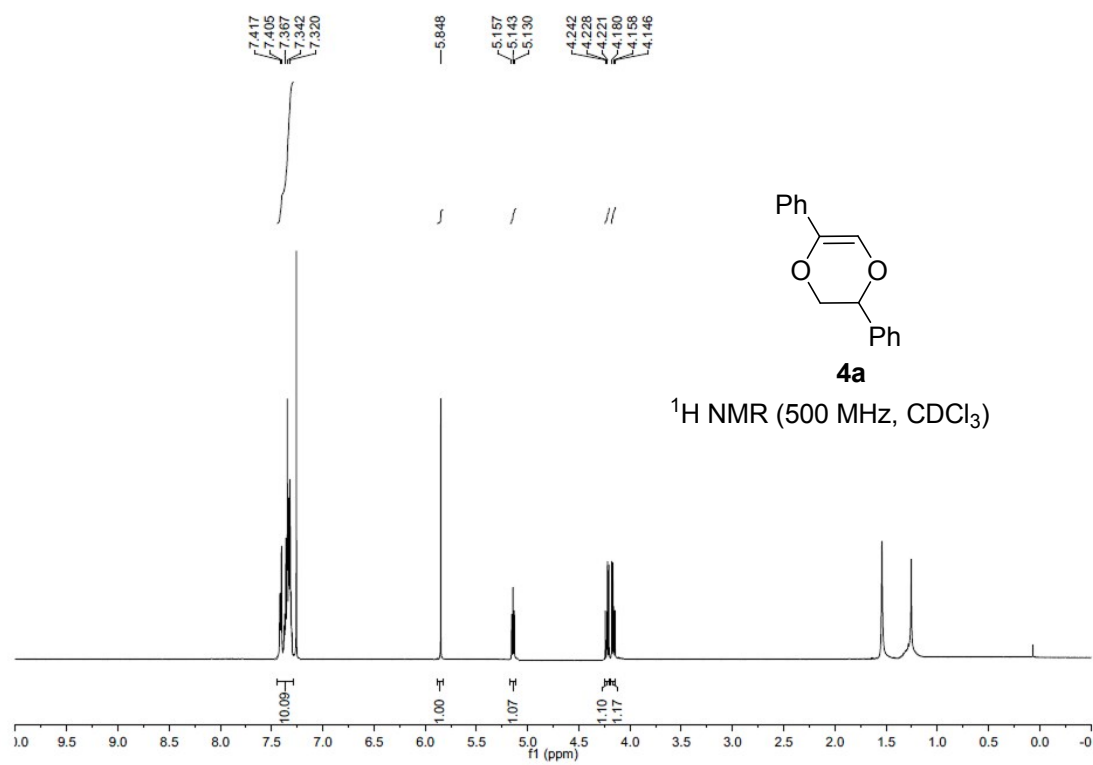


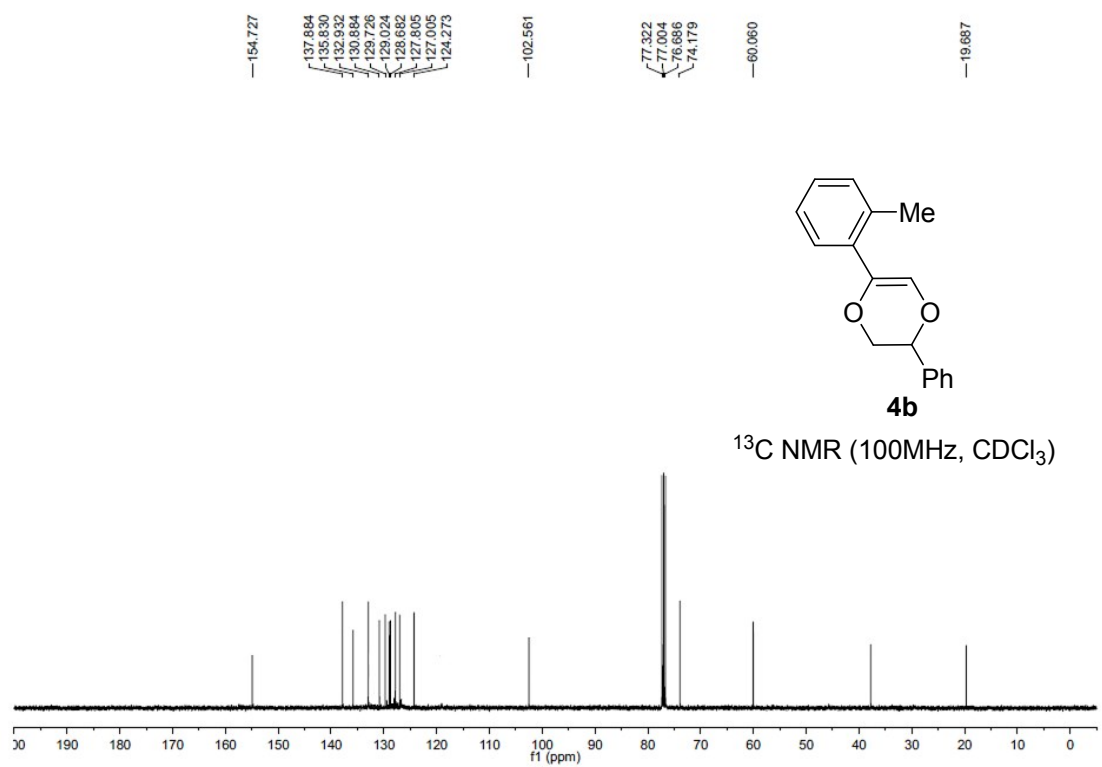
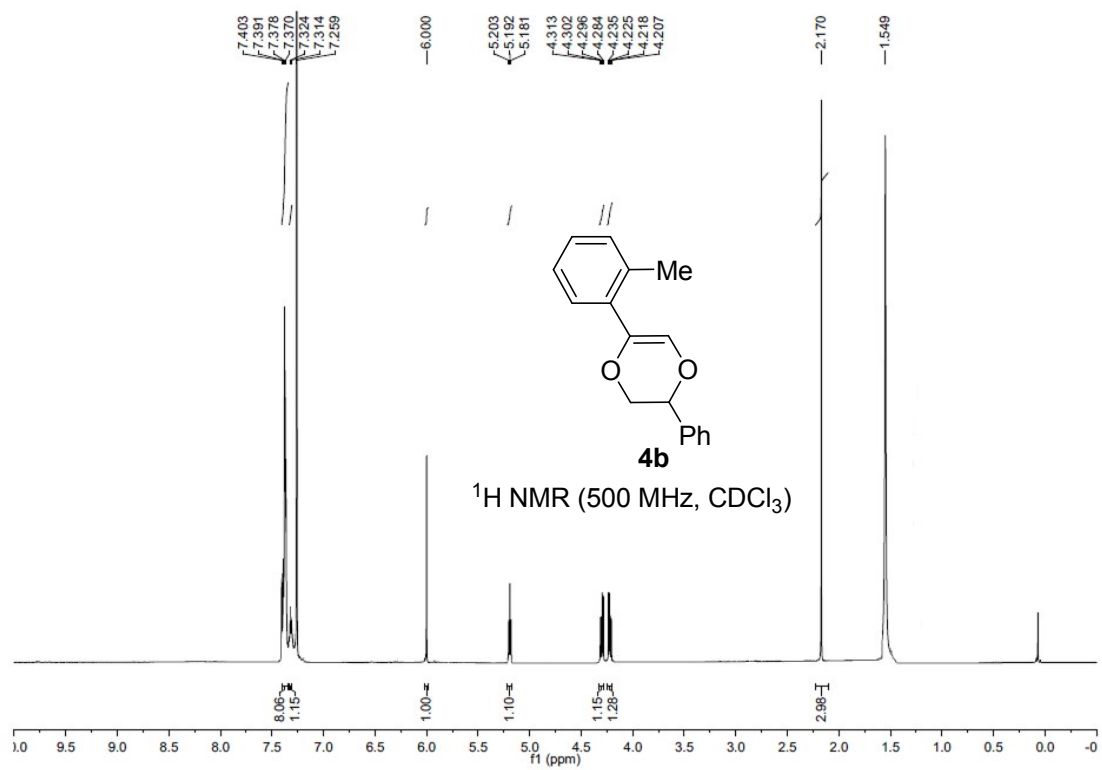
(*Z*)-2-(2-chloro-1-phenylvinyl)oxy-1-phenylethanol (**8**), white solid (83.5 mg), m.p. 151-153 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 7.42-7.37 (m, 2H), 7.34-7.29 (m, 8H), 5.62 (s, 1H), 4.92 (t, $J = 6.5$ Hz, 1H), 4.02-3.95 (m, 1H), 3.94-3.90 (m, 1H), 2.91 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3): 158.1, 138.7, 132.9, 129.2, 128.6, 127.4, 126.1, 125.2, 124.6, 91.5, 70.9, 57.5; IR (film): ν 3065, 3030, 2922, 1604, 1580, 1491, 1455 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{16}\text{H}_{15}\text{ClO}_2$ (M): 274.0761. Found: 274.0749.

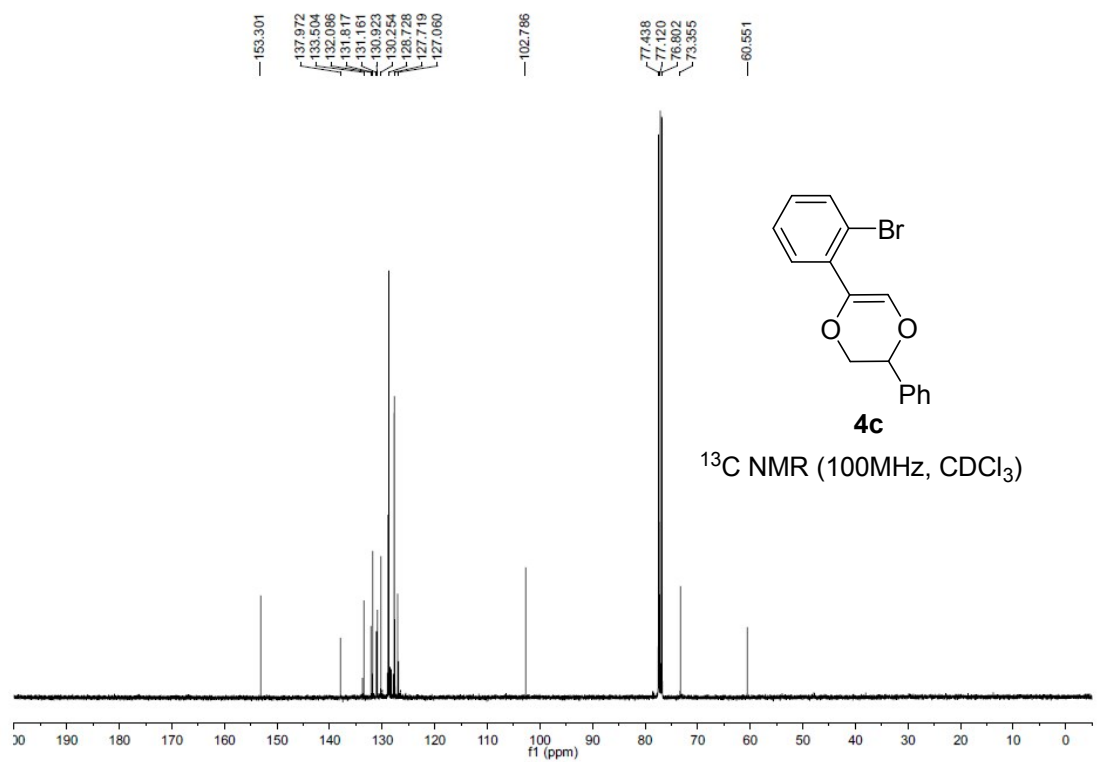
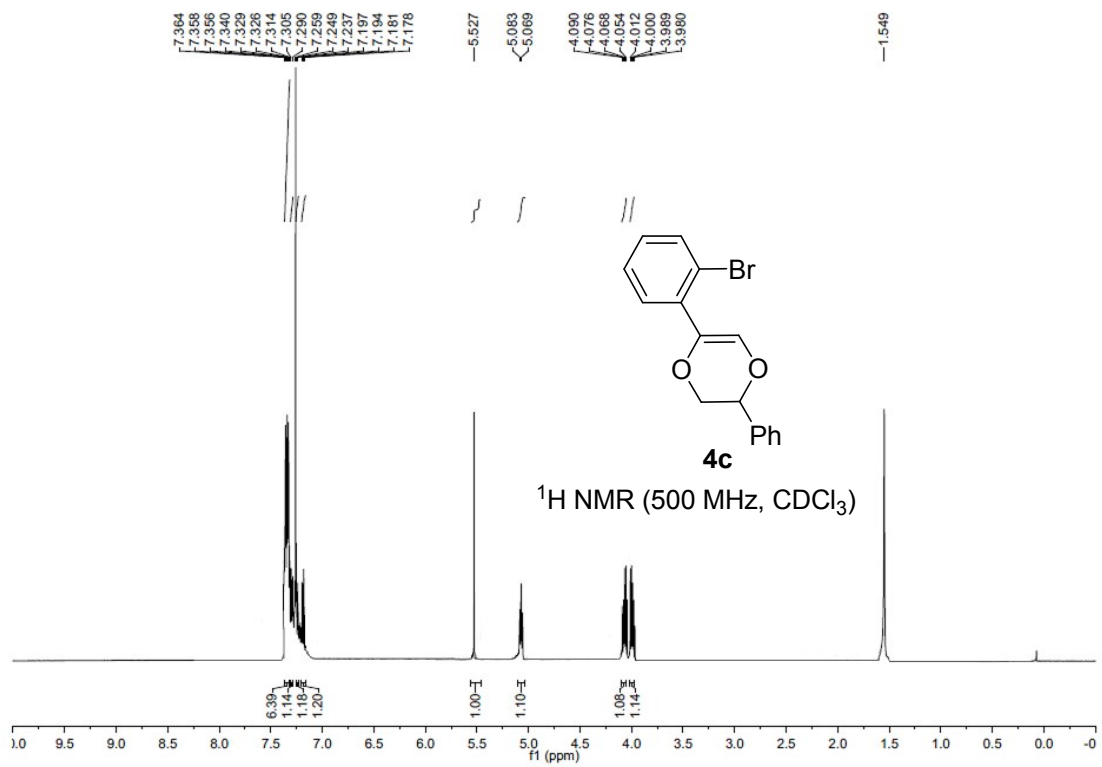
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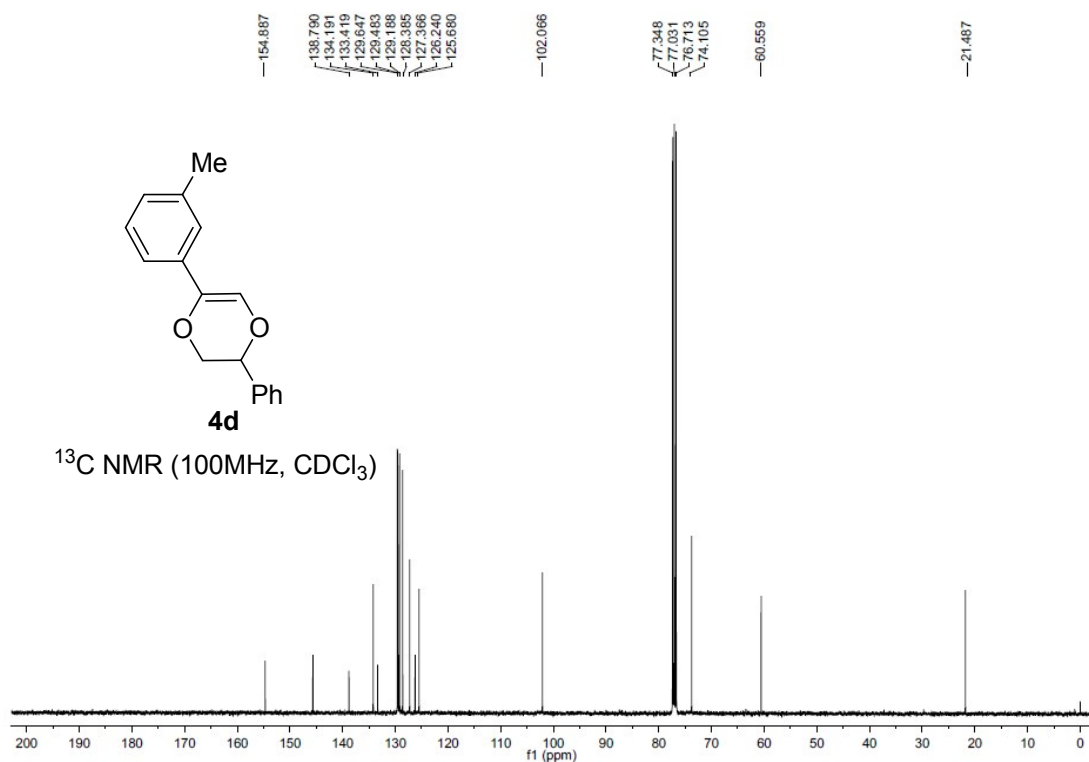
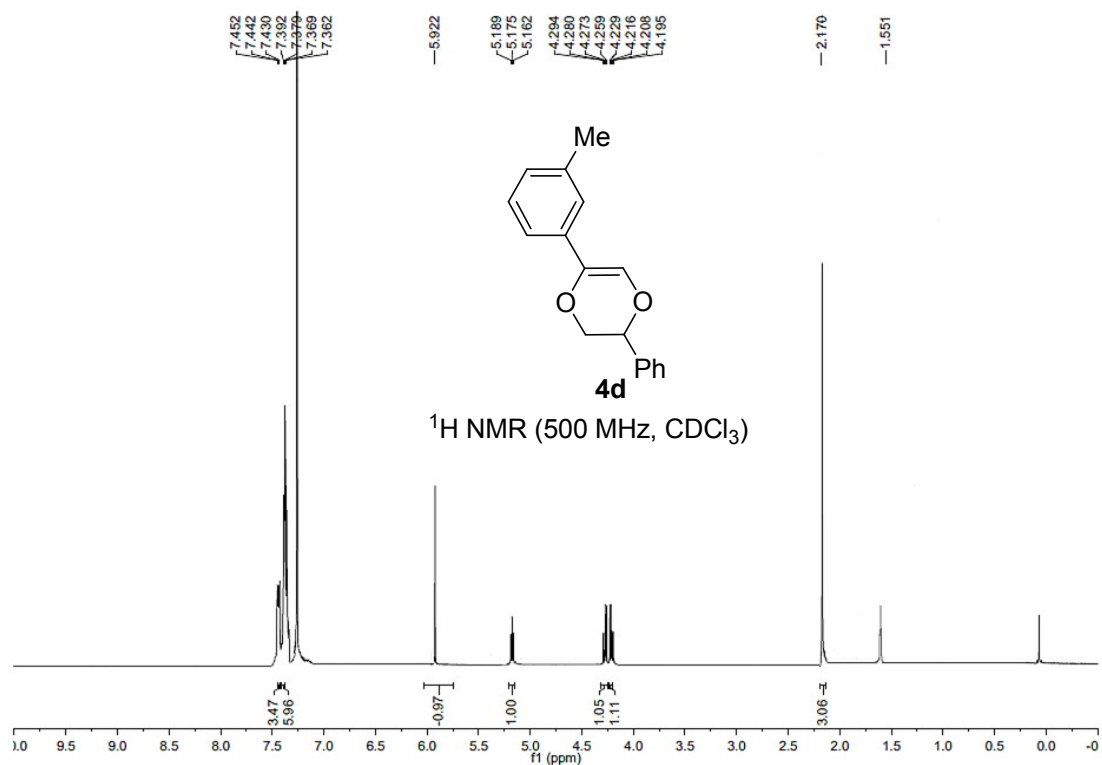
- [1] Z.-Y. Han, R. Guo, P.-S. Wang, D.-F. Chen, H. Xiao, L.-Z. Gong, *Tetrahedron Lett.* 2011, **52**, 5963; M. T. Johnson, J. Marthinus Janse van Rensburg, M. Axelsson, M. S. G. Ahlquist, O. F. Wendt, *Chem. Sci.* 2011, **2**, 2373.
[2] D. Sud, T. J. Wigglesworth, N. R. Branda, *Angew. Chem. Int. Ed.* 2007, **46**, 8017.

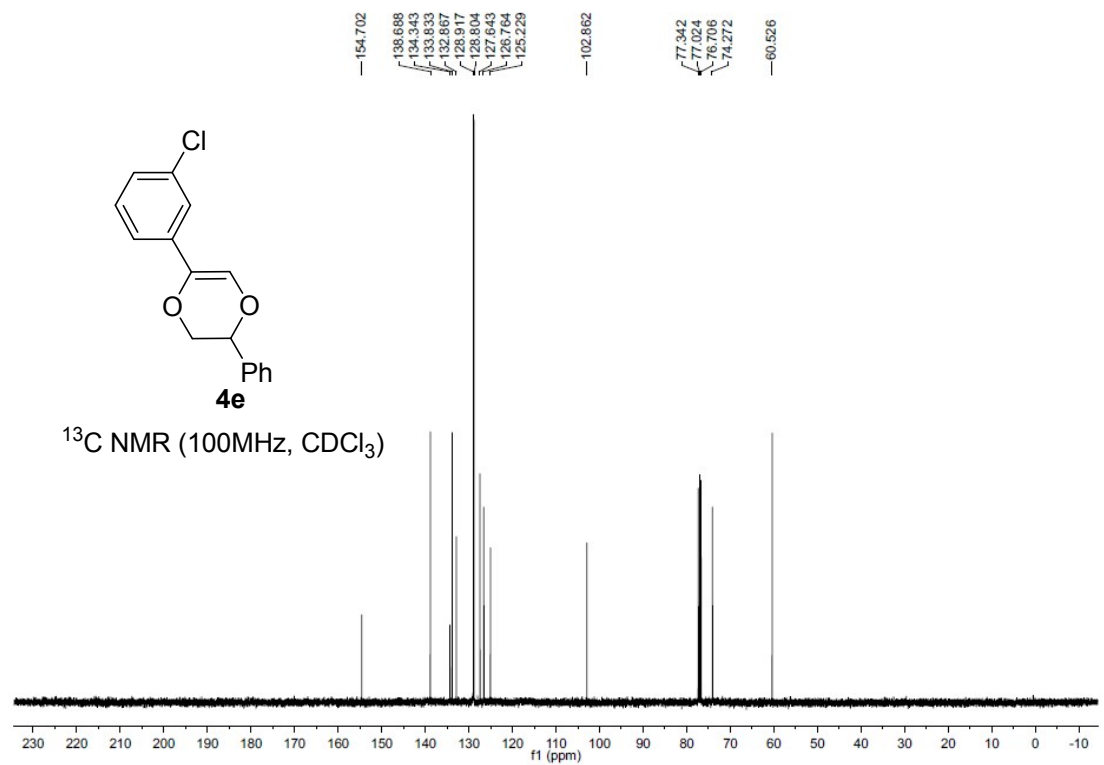
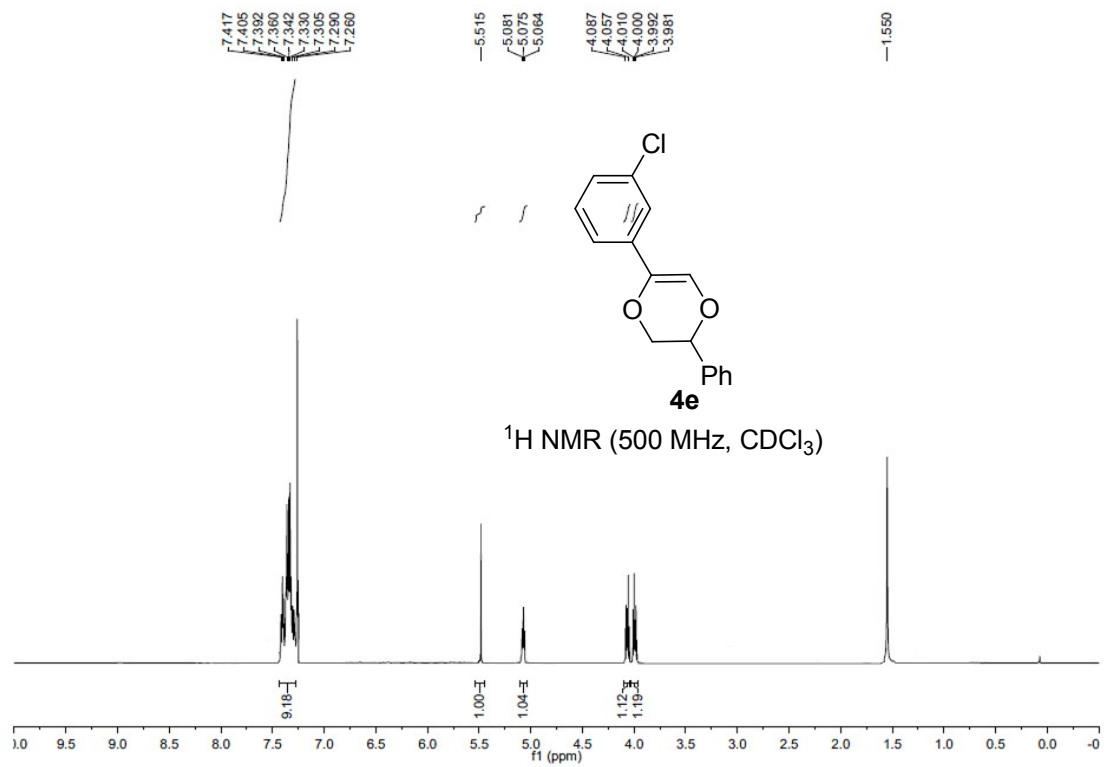
Copies of ^1H and ^{13}C NMR Spectra

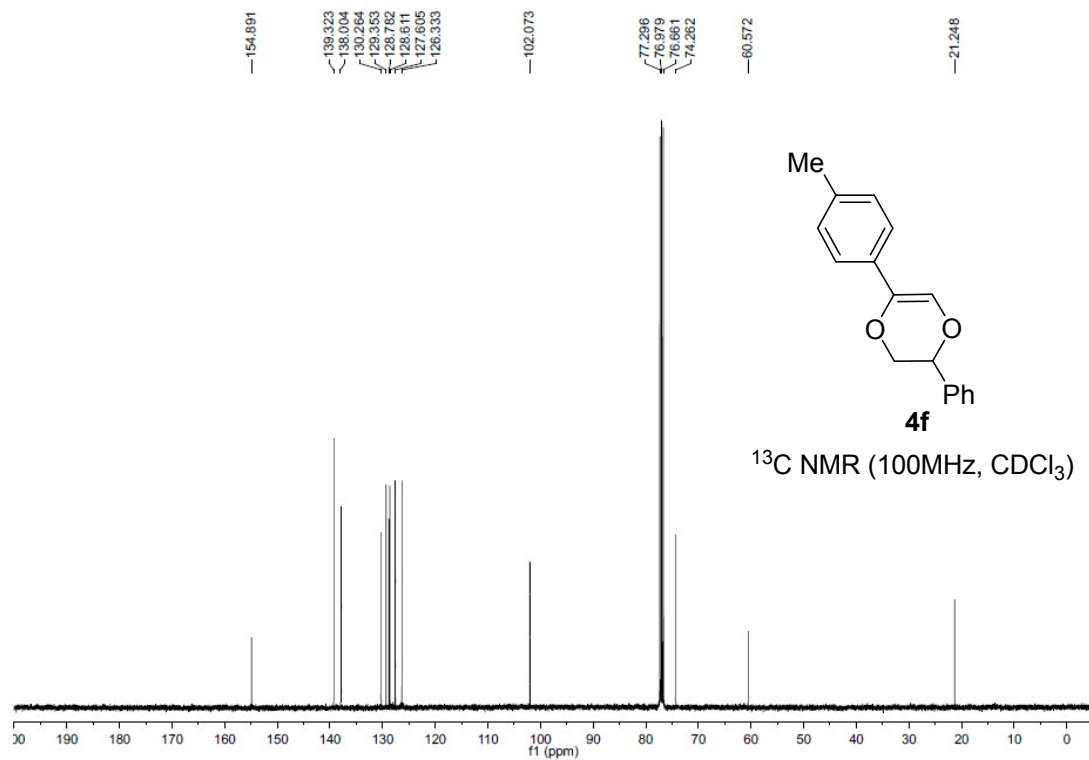
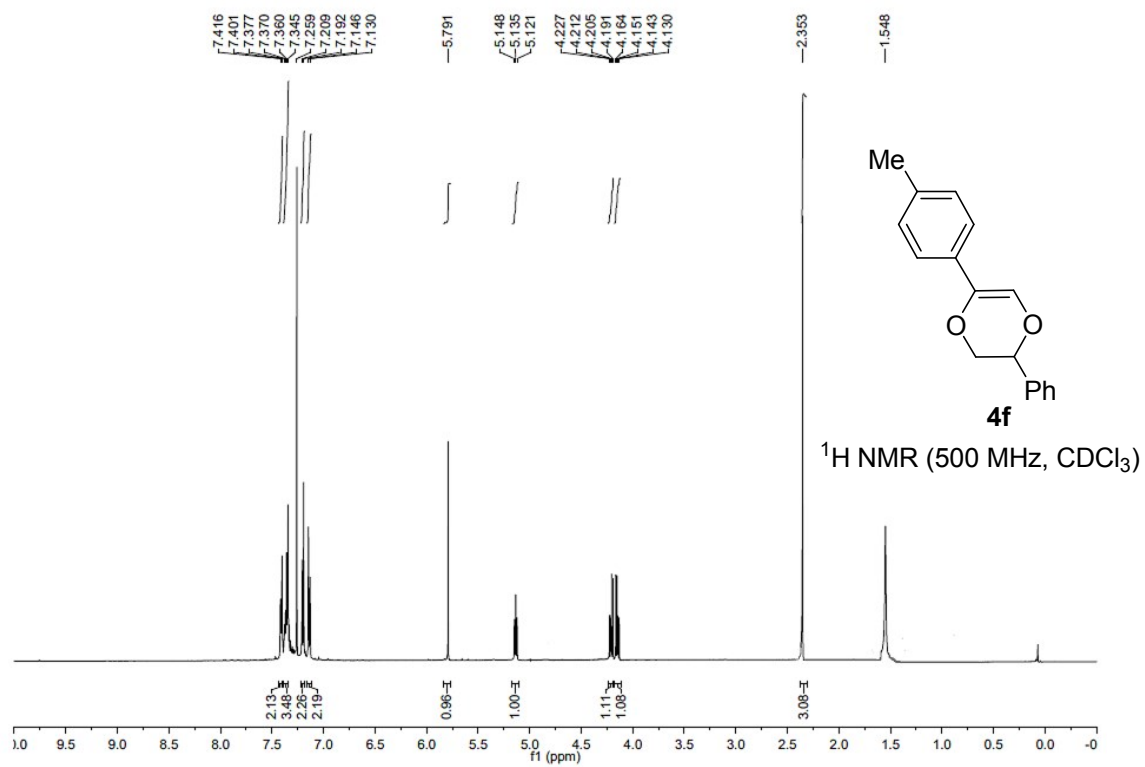


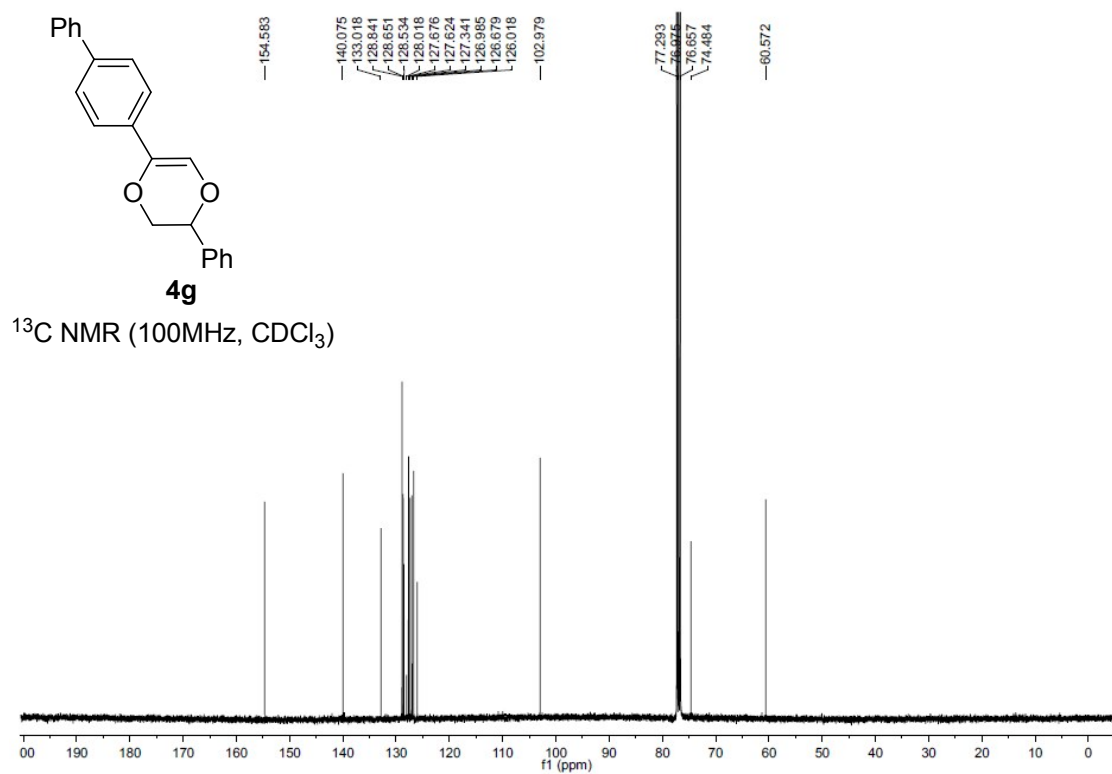
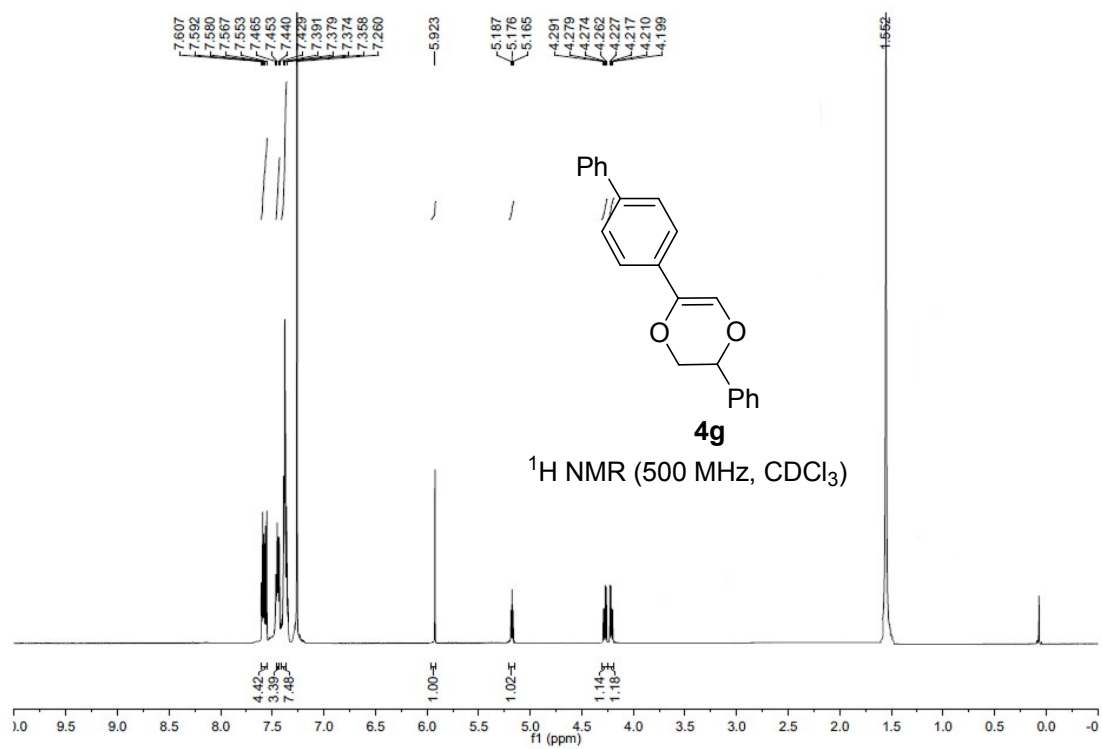


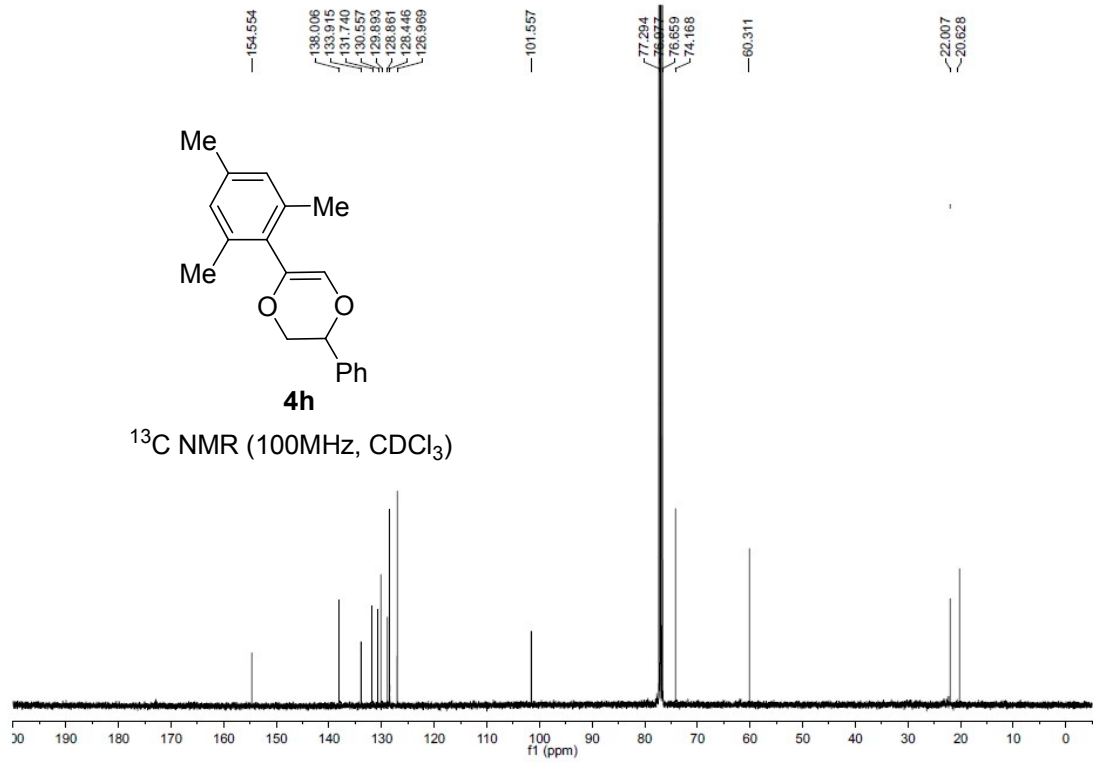
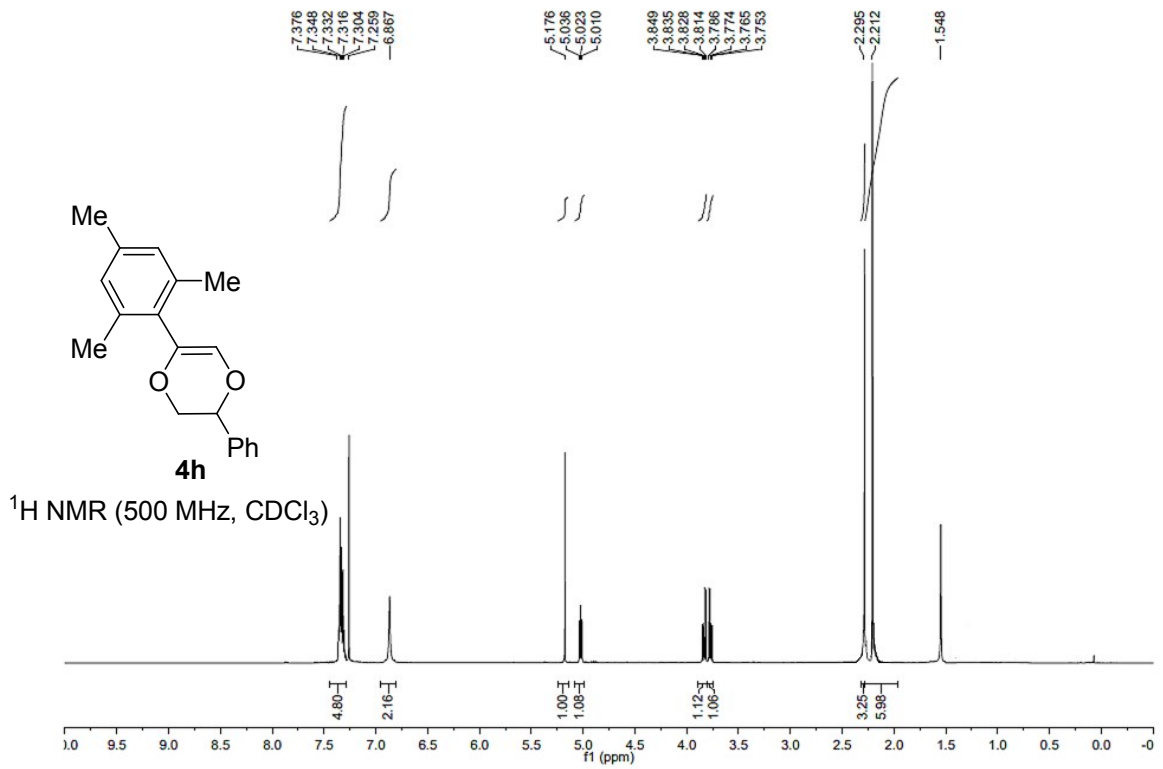


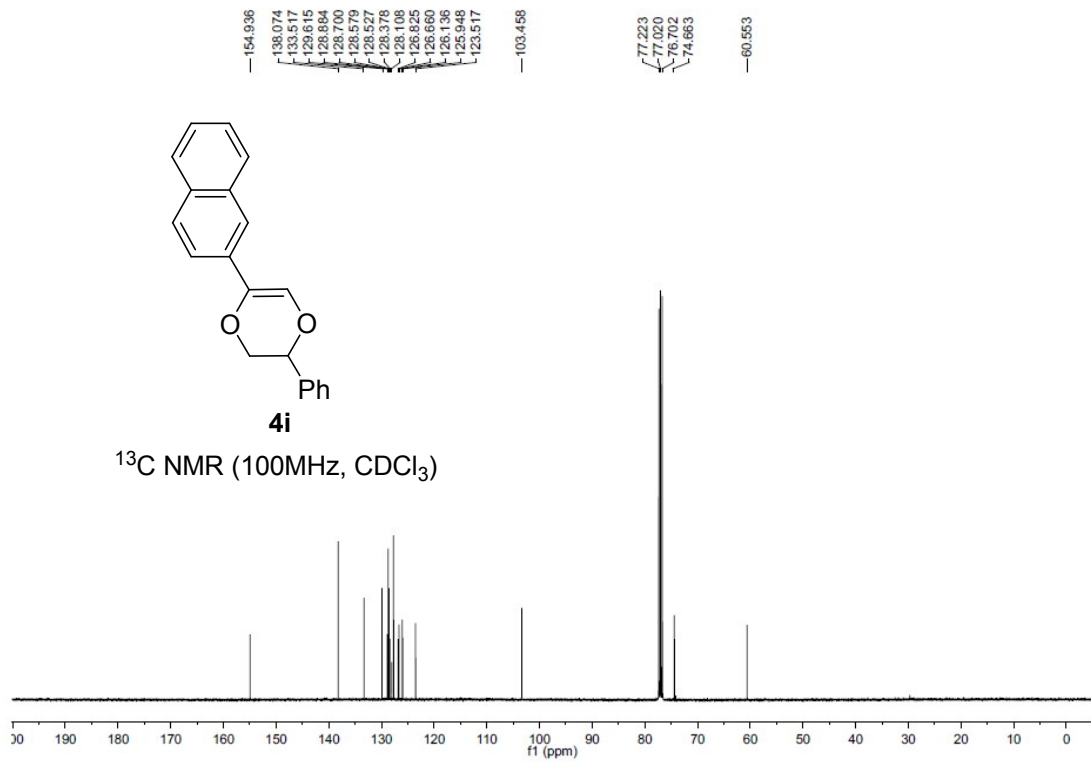
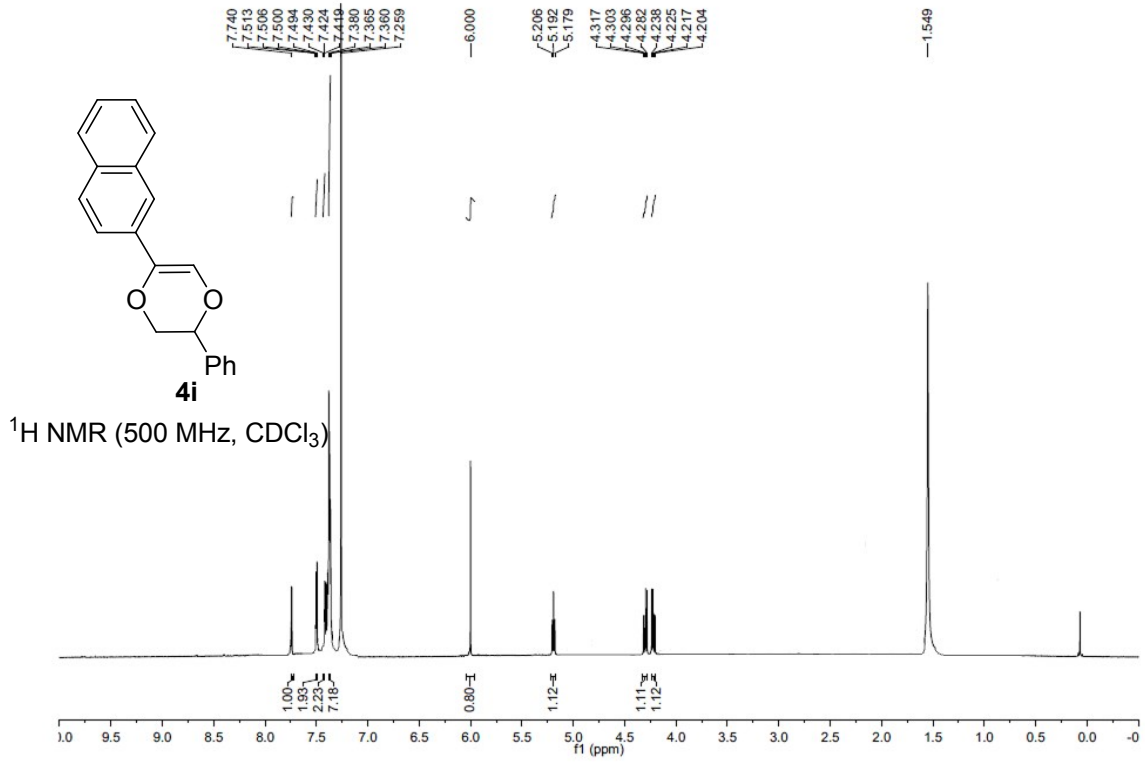


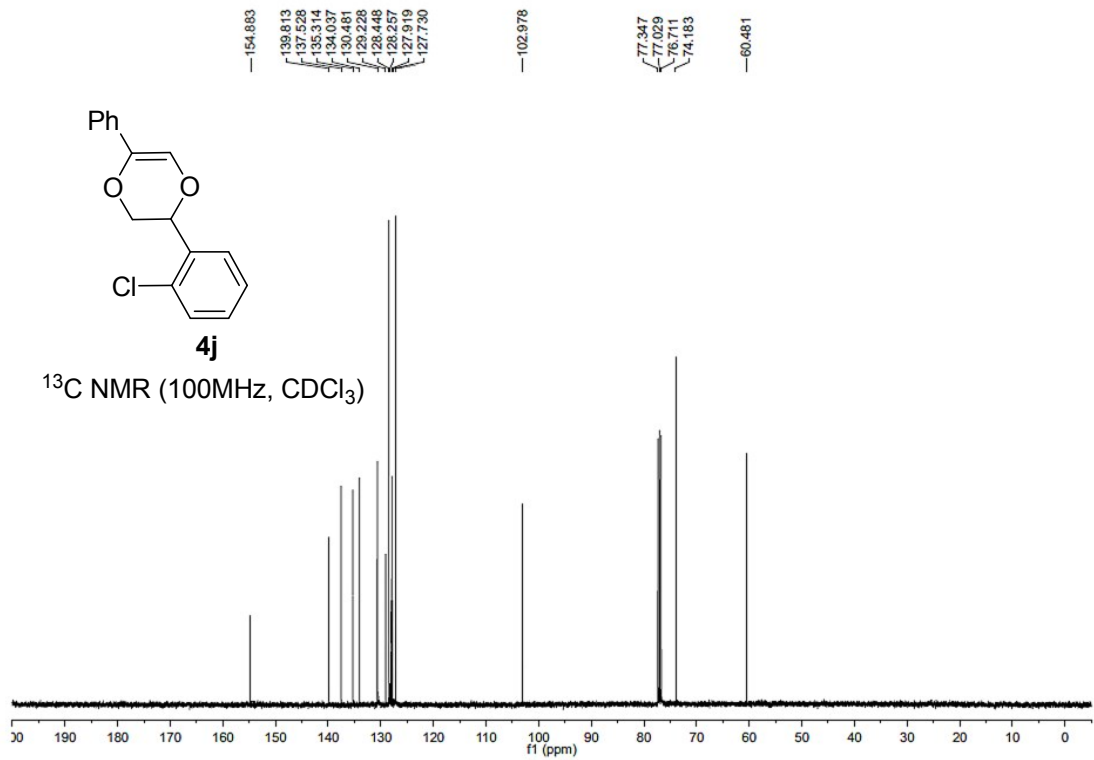
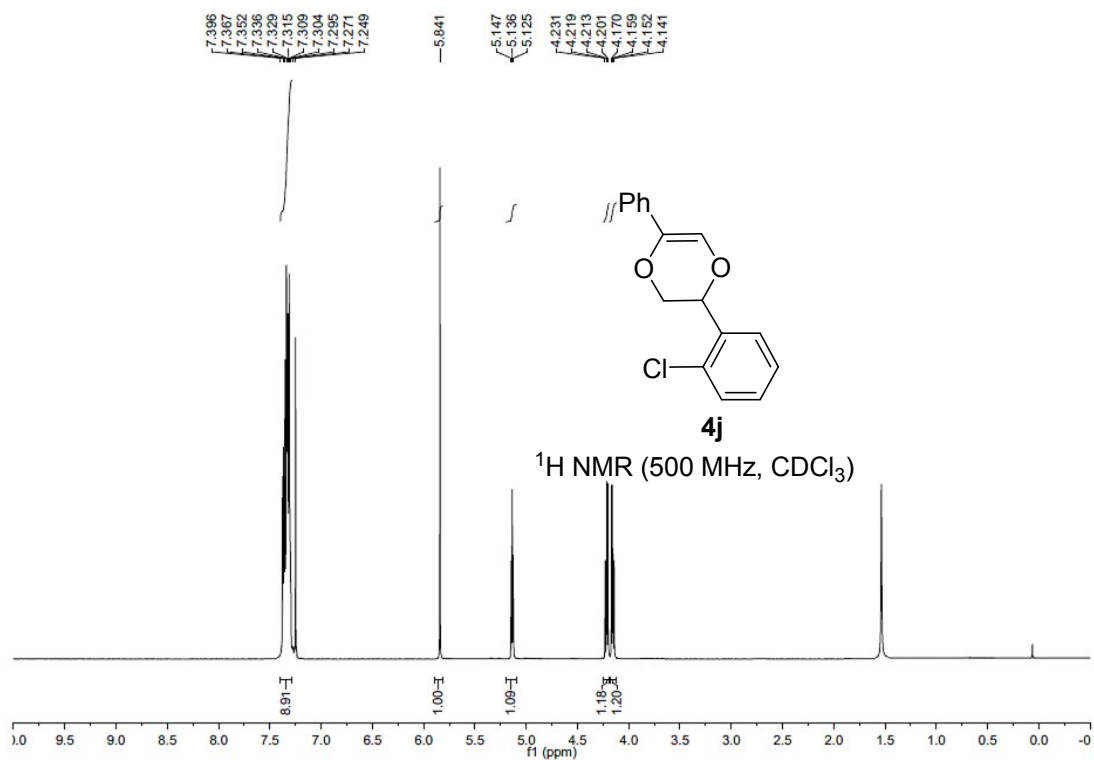


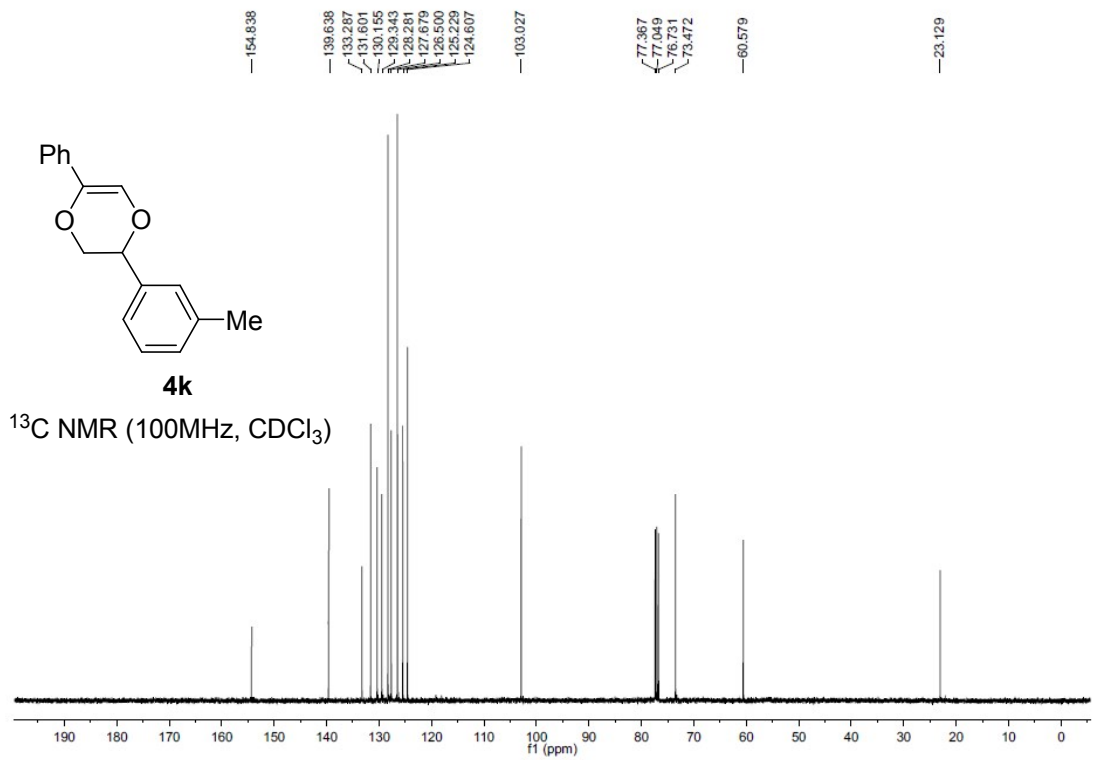
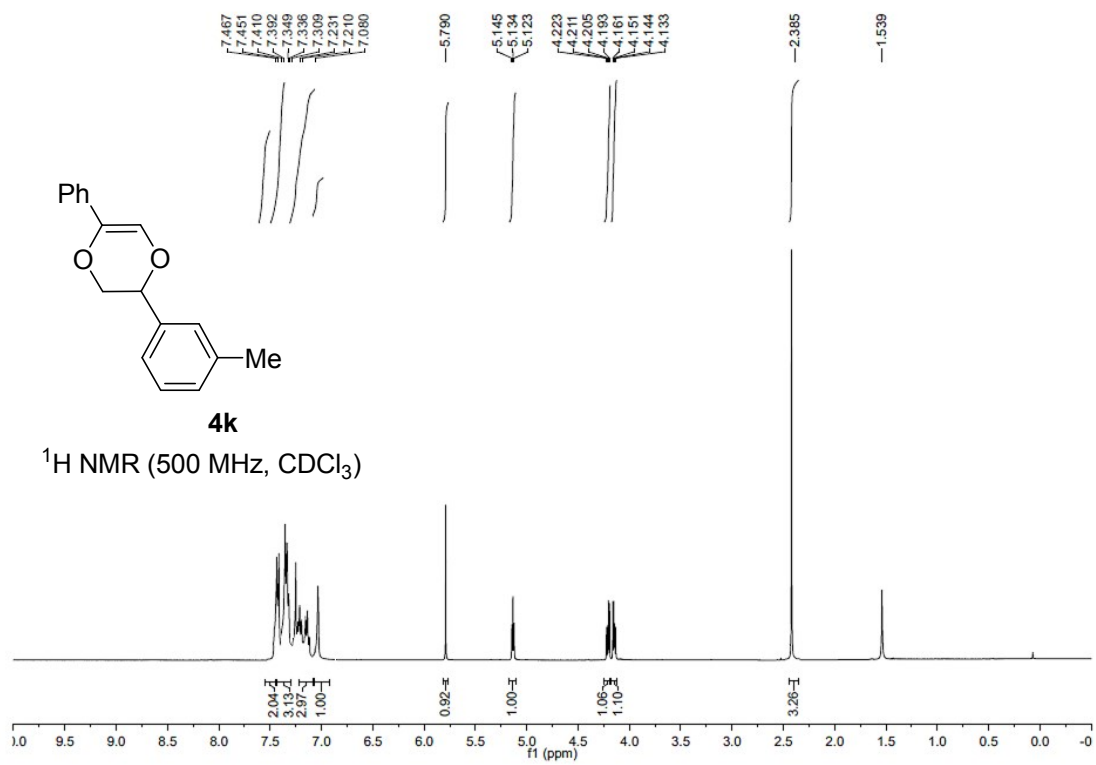


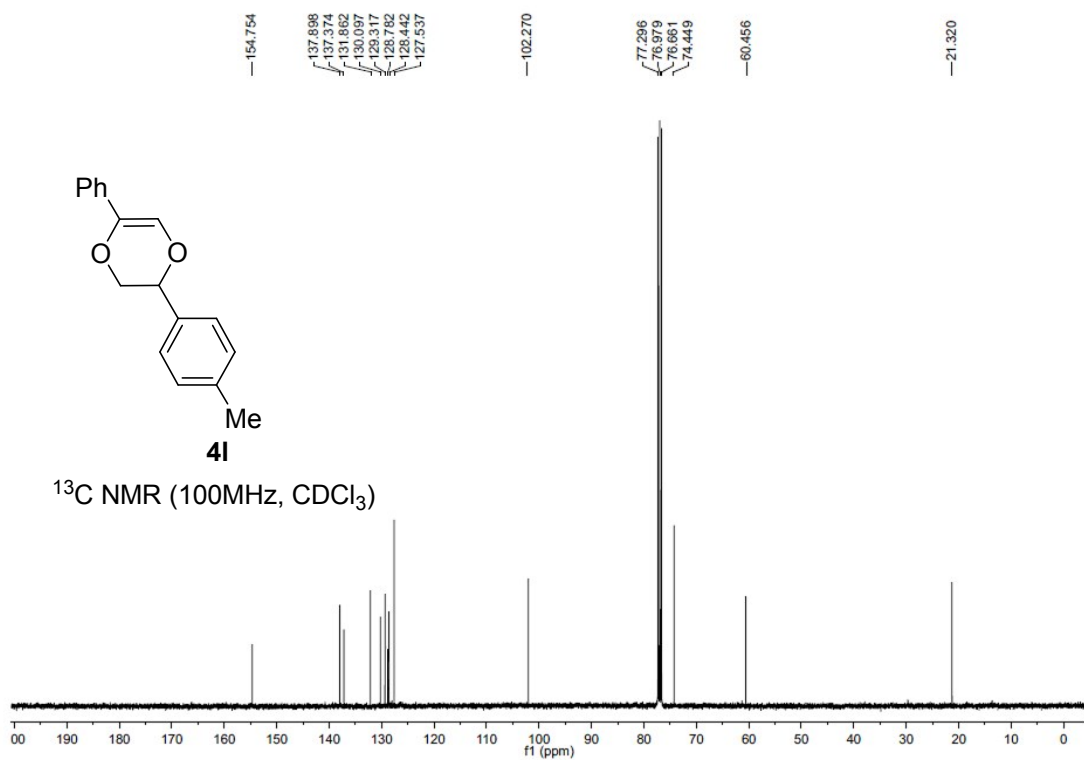
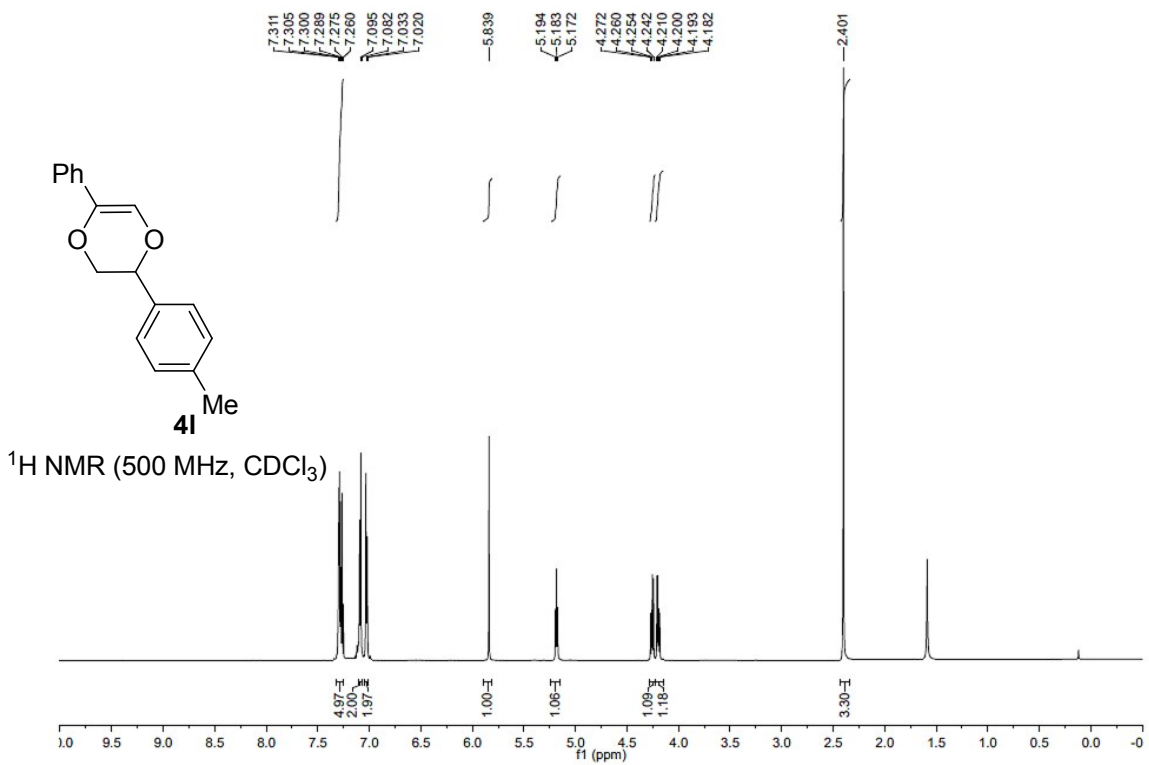


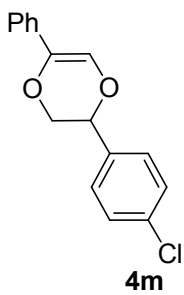




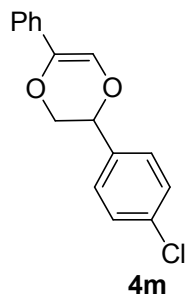
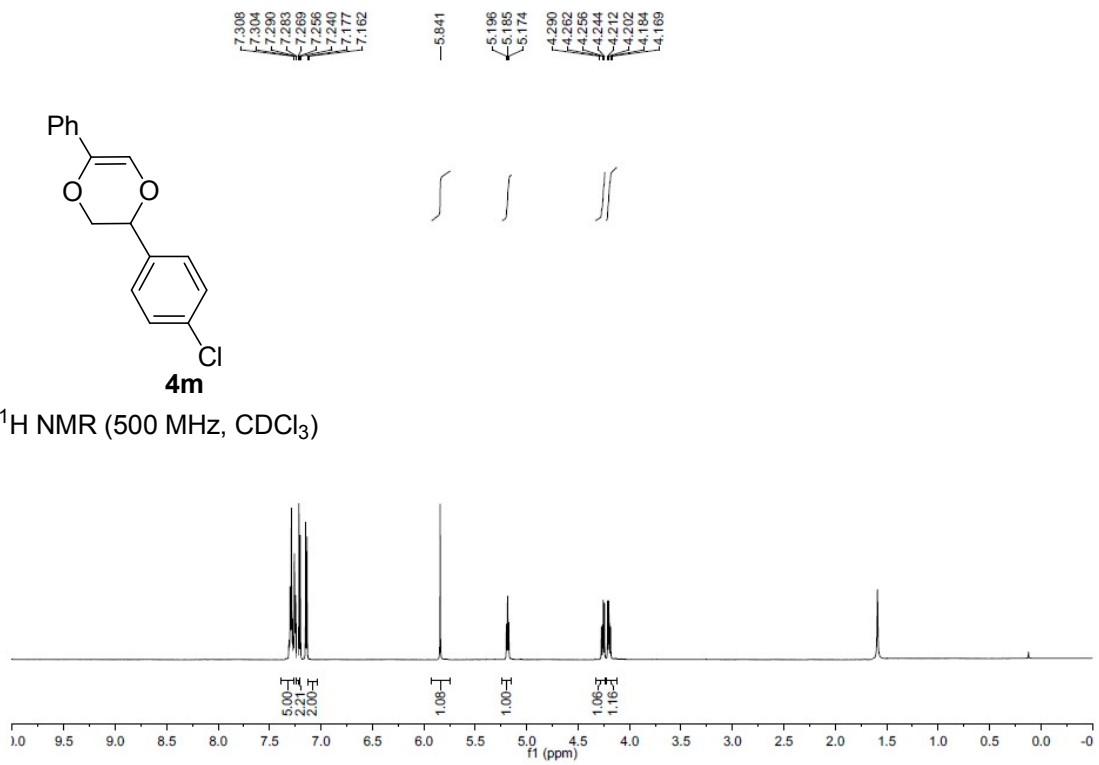








¹H NMR (500 MHz, CDCl₃)



¹³C NMR (100MHz, CDCl₃)

