

# Supporting Information

for

## Superoxide chemistry revisited: synthesis of tetrachloro-substituted methylenenortricyclenes

Basavaraj M. Budanur<sup>1</sup> and Faiz Ahmed Khan<sup>\*2</sup>

Address: <sup>1</sup>Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur-208016, India and <sup>2</sup>Department of Chemistry, Indian Institute of Technology Hyderabad, Ordnance Factory Estate, Yeddumailaram-502205, India

Email: Faiz Ahmed Khan\* - faiz@iith.ac.in

\*Corresponding author

### Experimental part and NMR spectra

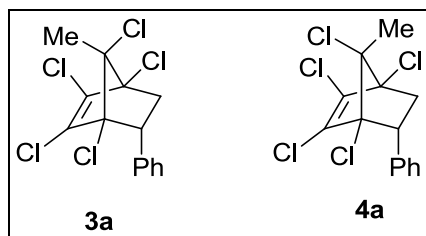
|                                                                                             |     |
|---------------------------------------------------------------------------------------------|-----|
| General methods                                                                             | S2  |
| General procedure for the preparation of Diels–Alder adducts 3/4                            | S2  |
| <sup>1</sup> H NMR, <sup>13</sup> C NMR NMR data of DA adducts 3/4                          | S2  |
| General procedure for the KO <sub>2</sub> Mediated reaction                                 | S12 |
| <sup>1</sup> H NMR, <sup>13</sup> C NMR NMR data of the nortricyclenes                      | S13 |
| General procedure for the acylation reaction of nortricyclenes                              | S21 |
| <sup>1</sup> H NMR, <sup>13</sup> C NMR NMR data of products of acylation reaction          | S21 |
| Copies of <sup>1</sup> H NMR, <sup>13</sup> C NMR spectra of DA adducts 3/4                 | S24 |
| Copies of <sup>1</sup> H NMR, <sup>13</sup> C NMR spectra of nortricyclenes 5               | S51 |
| Copies of <sup>1</sup> H NMR, <sup>13</sup> C NMR spectra of products of acylation reaction | S68 |
| Crystal data and structure refinement of compound 5a                                        | S71 |
| Crystal data and structure refinement of compound                                           | S72 |
| Reference                                                                                   | S72 |

**General methods:** Melting points are uncorrected. Unless otherwise specified, all reactions were carried out in oven-dried glassware, under argon atmosphere.  $^1\text{H}$  and proton decoupled  $^{13}\text{C}$  NMR spectra were recorded in 400 and 100 MHz, respectively, unless otherwise mentioned at field strength of 500 MHz ( $^1\text{H}$  NMR) and 125 MHz ( $^{13}\text{C}$  NMR). The NMR samples were prepared by dissolving in  $\text{CDCl}_3$ , chemical shifts are reported in parts per million downfield from TMS as an internal standard and the multiplicity are reported as follows s = singlet, d = doublet, dd = double doublet, t = triplet, dt = double triplet, td = triple doublet, q = quartet, dq = double quartet, m = multiplet and the coupling constants were in Hz. The powdered potassium superoxide was purchased from Alfa Aesar and used as such. 'Caution should be taken when using  $\text{KO}_2$ , since it is explosive'.

**General procedure for the preparation of Diels–Alder 3/4:** The mixture of 1,2,3,4,5-pentachloro-5-methylcyclopenta-1,3-diene **1** (1 g, 3.96 mmol), styrene **2a** (825 mg, 7.92 mmol), catalytic amount of hydroquinone (3 mg), epichlorohydrin (0.01 mL) in dry toluene (1.5 mL) was heated at 120 °C - 130 °C in a sealed tube. After being heated for 10 h (reaction monitored by TLC), the reaction mixture was concentrated and the resulting crude residue was purified over silica gel column chromatography using hexane as eluent to afford adducts **3a** and **4a** (1.15 g, 83%, in 4:1 ratio) as colourless solids. Spectral data matching with reported one<sup>1</sup>

**$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR data of Diels–Alder adducts 3/4:**

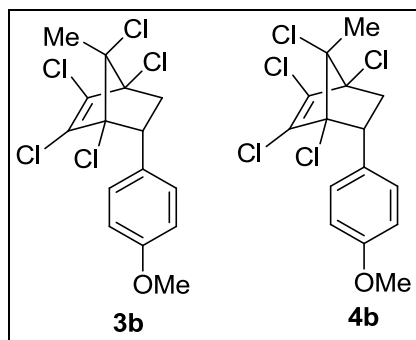
(1*R*\*,4*R*\*,5*R*\*,7*S*\*)-1,2,3,4,7-Pentachloro-7-methyl-5-phenylbicyclo[2.2.1]hept-2-ene (**3a**); and (1*R*\*,4*R*\*,5*R*\*,7*R*\*)-1,2,3,4,7-pentachloro-7-methyl-5-phenylbicyclo[2.2.1]hept-2-ene (**4a**)



Data is matching with reported compounds; Data for **3a**: mp: 52-54 °C,  $R_f$  = 0.8 (hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 - 7.30 (m, 3H), 7.16-7.05 (m, 2H), 4.09 (dd,  $J$  = 4.3, 9.3 Hz, 1H), 2.99 (dd,  $J$  = 9.3, 12.5 Hz, 1H), 2.43 (dd,  $J$  = 4.1, 12.6 Hz, 1H), 1.65 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  135.2, 130.7, 130.6, 129.0, 128.3, 128.1, 88.6, 82.5, 77.4, 52.3, 41.9, 19.8; IR (neat): 3032, 1601, 1496, 1455, 1381, 1268, 1211, 1187, 1151, 1093, 1011, 951  $\text{cm}^{-1}$ .

Data for **4a**: mp: 92-94 °C;  $R_f$  = 0.75 (hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 - 7.29 (m, 3H), 7.15 - 7.07 (m, 2H), 3.67 (dd,  $J$  = 4.5, 9.3 Hz, 1H), 2.65 (dd,  $J$  = 9.3, 13.1 Hz, 1H), 2.53 (dd,  $J$  = 4.6, 13.1 Hz, 1H), 1.83 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  135.2, 132.0, 128.9, 128.4, 128.3, 91.9, 83.1, 77.4, 51.5, 40.4, 20.9; IR (neat): 3032, 1602, 1492, 1453, 1382, 1267, 1211, 1182, 1151, 1097, 1011, 951  $\text{cm}^{-1}$ .

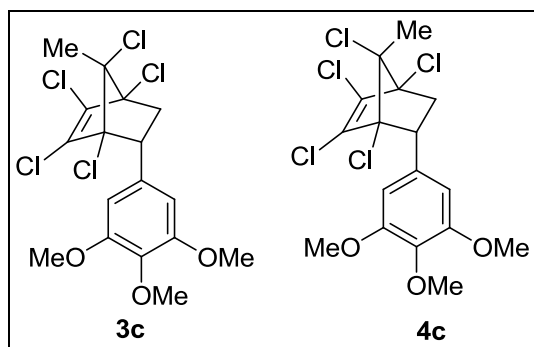
**(1*R*<sup>\*</sup>,4*R*<sup>\*</sup>,5*R*<sup>\*</sup>,7*S*<sup>\*</sup>)-1,2,3,4,7-Pentachloro-5-(4-methoxyphenyl)-7-methylbicyclo[2.2.1]hept-2-ene (3b)** and **(1*R*<sup>\*</sup>,4*R*<sup>\*</sup>,5*R*<sup>\*</sup>,7*R*<sup>\*</sup>)-1,2,3,4,7-pentachloro-5-(4-methoxyphenyl)-7-methylbicyclo[2.2.1]hept-2-ene (4b)**:



Following the same procedure as for **3a** starting from compound **1** (200 mg, 0.79 mmol) and 1-methoxy-4-vinylbenzene **2b** (211 mg, 1.58 mmol), compounds **3b** and **4b** (249 mg, 82%) were obtained in 3:1 ratio. Data for **3b**: colorless solid; mp: 90-92 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.02 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 4.02 (dd, *J* = 9.2, 4.1 Hz, 1 H), 3.80 (s, 3H), 2.96 (dd, *J* = 12.6, 9.2 Hz, 1H), 2.35 (dd, *J* = 12.6, 4.1 Hz, 1H), 1.62 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 159.5, 130.7, 130.6, 130.1 (2C), 127.2, 113.8 (2C), 88.6, 82.7, 76.8, 55.3, 52.3, 42.2, 20.0; IR (KBr): 3002, 2957, 2935, 2835, 1603, 1511, 1445, 1375, 1290, 1247, 1211, 1180, 1148, 1108, 1034, 1008, 947 cm<sup>-1</sup>; HRMS (ESI): *m/z* calcd for C<sub>15</sub>H<sub>17</sub>Cl<sub>5</sub>NO [M + NH<sub>4</sub>]<sup>+</sup> 403.9723; found: 403.9705.

Data for **4b**: colorless liquid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.01 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H), 3.60 (dd, *J* = 9.1, 4.5 Hz, 1H), 2.64 (dd, *J* = 13.1, 9.2 Hz, 1H), 2.45 (dd, *J* = 13.1, 4.4 Hz, 1H), 1.79 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 159.6, 132.1, 131.9, 130.0 (2C), 126.9, 113.9 (2C), 91.9, 83.2, 77.6, 55.3, 50.9, 40.7, 20.9; IR (neat): 3010, 2923, 2832, 1600, 1509, 1439, 1380, 1287, 1248, 1213, 1180, 1148, 1105, 1032, 998 cm<sup>-1</sup>. HRMS (MMI): *m/z* calcd for C<sub>15</sub>H<sub>17</sub>Cl<sub>5</sub>NO [M + NH<sub>4</sub>]<sup>+</sup> 403.9723; found: 403.9748.

**(1*R*<sup>\*</sup>,4*R*<sup>\*</sup>,5*R*<sup>\*</sup>,7*S*<sup>\*</sup>)-1,2,3,4,7-Pentachloro-7-methyl-5-(3,4,5-trimethoxyphenyl)bicyclo[2.2.1]hept-2-ene (3c)** and **(1*R*<sup>\*</sup>,4*R*<sup>\*</sup>,5*R*<sup>\*</sup>,7*R*<sup>\*</sup>)-1,2,3,4,7-pentachloro-7-methyl-5-(3,4,5-trimethoxyphenyl)bicyclo[2.2.1]hept-2-ene (4c)**:

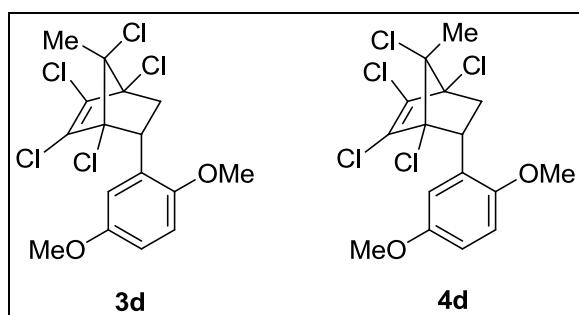


Following the same procedure as for **3a** starting from compound **1** (300 mg, 1.19 mmol) and 1,2,3-trimethoxy-5-vinylbenzene **2c** (256 mg, 1.3 mmol), compounds **3c** and **4c** (433 mg,

82%) were obtained in 4:1 ratio. Data for **3c**: colorless solid; mp: 110 - 112 °C;  $R_f$  = 0.5 (5% EtOAc in hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.32 (s, 2H), 4.00 (dd,  $J$  = 9.3, 3.9 Hz, 1H), 3.85 (s, 6H), 3.84 (s, 3H), 3.00 (dd,  $J$  = 12.7, 9.3 Hz, 1H), 2.35 (dd,  $J$  = 12.7, 4.4 Hz, 1H), 1.64 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  152.9 (2C), 137.8, 131.1, 130.7, 130.4, 106.1 (2C), 88.6, 82.6, 77.2, 60.9, 56.1 (2C), 53.3, 42.3, 19.7; IR (neat): 2989, 2935, 2833, 1603, 1587, 1510, 1460, 1453, 1420, 1382, 1346, 1328, 1268, 1238, 1152, 1127, 1092, 1005, 955  $\text{cm}^{-1}$ ; HRMS (APCI):  $m/z$  calcd for  $\text{C}_{17}\text{H}_{18}\text{Cl}_5\text{O}_3[\text{M} + \text{H}]^+$  446.9669; found: 446.9649.

Data for **4c**: colorless solid; mp: 80-82 °C,  $R_f$  = 0.45 (5% EtOAc in hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.31 (s, 2H), 3.86 (s, 6H), 3.85 (s, 3H), 3.59 (dd,  $J$  = 9.3, 4.4 Hz, 1H), 2.68 (dd,  $J$  = 13.4, 9.3 Hz, 1H), 2.46 (dd,  $J$  = 13.7, 4.4 Hz, 1H), 1.80 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  152.9 (2C), 138.0, 132.5, 131.6, 130.5, 106.1 (2C), 91.6, 83.1, 77.4, 60.9, 56.1 (2C), 52.0, 40.8, 20.8; IR (neat): 2990, 2932, 2833, 1600, 1582, 1513, 1460, 1451, 1422, 1382, 1342, 1325, 1273, 1242, 1152, 1128, 1092, 1013, 958  $\text{cm}^{-1}$ ; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{17}\text{H}_{21}\text{Cl}_5\text{NO}_3[\text{M} + \text{NH}_4]^+$  463.9935; found: 463.9906.

**(1*R*\*,4*R*\*,5*R*\*,7*S*\*)-1,2,3,4,7-Pentachloro-5-(2,5-dimethoxyphenyl)-7-methylbicyclo[2.2.1]hept-2-ene (3d)** and **(1*R*\*,4*R*\*,5*R*\*,7*R*\*)-1,2,3,4,7-pentachloro-5-(2,5-dimethoxyphenyl)-7-methylbicyclo[2.2.1]hept-2-ene (4d)**:

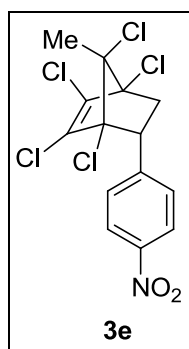


Following the same procedure as for **3a** starting from compound **1** (500 mg, 1.98 mmol) and 1,4-dimethoxy-2-vinylbenzene **2d** (325 mg, 1.98 mmol), compounds **3d** and **4d** (712 mg, 87%) were obtained in 3:1 ratio. Data for **3d**: colorless liquid;  $R_f$  = 0.6 (5% EtOAc in hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.84 - 6.77 (m, 2H), 6.43 (d,  $J$  = 2.9 Hz, 1H), 4.77 (dd,  $J$  = 4.4, 9.8 Hz, 1H), 3.82 (s, 3H), 3.77 (s, 3H), 2.95 (dd,  $J$  = 9.5, 12.5 Hz, 1H), 2.36 (dd,  $J$  = 4.4, 12.2 Hz, 1H), 1.64 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  153.3, 152.7, 131.1, 130.7, 124.9, 115.0, 114.0, 112.0, 88.7, 82.2, 77.1, 56.3, 55.8, 45.2, 42.5, 19.7; IR (neat): 2991, 2932, 2830, 1602, 1539, 1500, 1462, 1452, 1449, 1420, 1386, 1350, 1296, 1260, 1181, 1118, 1097, 1046, 976  $\text{cm}^{-1}$ ; HRMS (APCI):  $m/z$  calcd for  $\text{C}_{16}\text{H}_{15}\text{Cl}_5\text{O}_2[\text{M}]^+$  415.9485; found: 415.9466.

Data for **4d**: colorless solid; mp: 100-102 °C;  $R_f$  = 0.55 (5% EtOAc in hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.87-6.76 (m, 2H), 6.40 (d,  $J$  = 2.4 Hz, 1H), 4.41 (dd,  $J$  = 4.6, 9.5 Hz, 1H), 3.82 (s, 3H), 3.77 (s, 3H), 2.65 (dd,  $J$  = 9.5, 13.0 Hz, 1H), 2.40 (dd,  $J$  = 4.6, 13.0 Hz, 1H), 1.84 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  153.5, 152.5, 132.5, 132.0, 124.7, 114.6, 114.4,

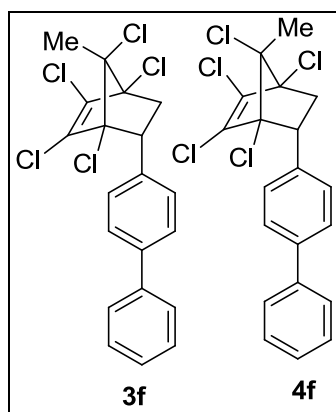
112.0, 92.4, 82.7, 77.6, 56.3, 55.8, 43.1, 41.4, 21.0; IR (neat): 2994, 2935, 2833, 1600, 1547, 1501, 1463, 1453, 1443, 1421, 1387, 1351, 1297, 1264, 1261, 1180, 1154, 1116, 1096, 1046, 1034, 968  $\text{cm}^{-1}$ ; HRMS(APCI):  $m/z$  calcd for  $\text{C}_{16}\text{H}_{15}\text{Cl}_5\text{O}_2$   $[\text{M}]^+$  415.9485; found: 415.9466.

**(1*R*<sup>\*</sup>,4*R*<sup>\*</sup>,5*R*<sup>\*</sup>,7*S*<sup>\*</sup>)-1,2,3,4,7-Pentachloro-7-methyl-5-(4-nitrophenyl)bicyclo[2.2.1]hept-2-ene (3e):**



Following the same procedure as for **3a** starting from compound **1** (100 mg, 0.39 mmol) and 1-nitro-4-vinylbenzene, **2e** (69 mg, 0.46 mmol), compound **3e** (118 mg, 75%) was obtained. colorless solid; mp: 130-132 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.2 (d,  $J$  = 8.8 Hz, 2H), 7.30 (d,  $J$  = 8.5 Hz, 2H), 4.19 (dd,  $J$  = 9.2, 4.1 Hz, 1H), 3.04 (dd,  $J$  = 12.7, 9.2 Hz, 1H), 2.42 (dd,  $J$  = 12.9, 4.1 Hz, 1H), 1.64 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  147.9, 142.9, 131.5, 130.1, 130.0 (2C), 123.5 (2C), 88.5, 82.4, 77.4, 52.8, 41.8, 19.7; IR (KBr): 3077, 1596, 1516, 1447, 1382, 1345, 1317, 1287, 1262, 1211, 1182, 1148, 1107, 1084, 1034, 1009  $\text{cm}^{-1}$ ; EI-HRMS: ( $m/z$ )  $\text{M}^+$  calculated for  $\text{C}_{14}\text{H}_{16}\text{Cl}_4$ : 398.9154; found : 398.9156.

**(1*R*<sup>\*</sup>,4*R*<sup>\*</sup>,5*R*<sup>\*</sup>,7*S*<sup>\*</sup>)-5-(Biphenyl-4-yl)-1,2,3,4,7-pentachloro-7-methylbicyclo[2.2.1]hept-2-ene (3f) and (1*R*<sup>\*</sup>,4*R*<sup>\*</sup>,5*R*<sup>\*</sup>,7*R*<sup>\*</sup>)-5-(biphenyl-4-yl)-1,2,3,4,7-pentachloro-7-methylbicyclo[2.2.1]hept-2-ene (4f):**

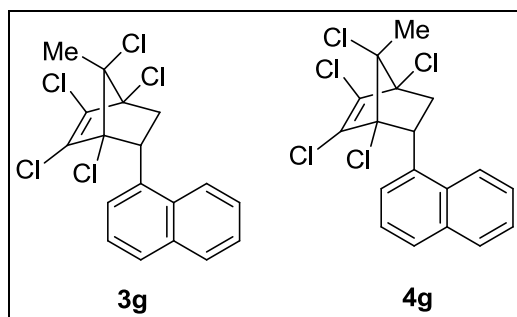


Following the same procedure as for **3a** starting from compound **1** (200 mg, 0.79 mmol) and 4-vinylbiphenyl **2f** (157 mg, 0.87 mmol), compounds **3f** and **4f** (323 mg, 94%) were obtained in 74:26 ratio. Data for **3f**: colorless solid; mp: 96-98 °C,  $R_f$  = 0.55 (hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60-7.53 (m, 4H), 7.43 (t,  $J$  = 7.5 Hz, 2H), 7.36-7.32 (m, 1H), 7.17 (d,  $J$  =

8.3 Hz, 2H), 4.11 (dd,  $J = 9.2, 4.1$  Hz, 1H), 3.00 (dd,  $J = 12.7, 9.1$  Hz, 1H), 2.43 (dd,  $J = 12.8, 4.1$  Hz, 1H), 1.65 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  140.8, 140.3, 134.2, 130.7, 130.6, 129.4 (2C), 128.8 (2C), 127.4, 127.0 (2C), 126.9 (2C), 88.6, 82.5, 77.3, 52.6, 42.0, 19.7; IR (neat): 3040, 2923, 1600, 1518, 1485, 1442, 1380, 1261, 1190, 1157, 1092, 1028, 1005, 972, 963  $\text{cm}^{-1}$ ; HRMS (APCI):  $m/z$  calcd for  $\text{C}_{20}\text{H}_{16}\text{Cl}_5\text{K}[\text{M} + \text{H}]^+$  432.9665; found: 432.9644.

Data for **4f**: colourless solid; mp: 110-112  $^\circ\text{C}$ ,  $R_f = 0.45$  (hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57 (t,  $J = 8.3$  Hz, 4H), 7.43 (t,  $J = 7.5$  Hz, 2H), 7.37-7.33 (m, 1H), 7.16 (d,  $J = 8.3$  Hz, 2H), 3.70 (dd,  $J = 9.0, 4.3$  Hz, 1H), 2.69 (dd,  $J = 13.3, 9.1$  Hz, 1H), 2.54 (dd,  $J = 13.1, 4.6$  Hz, 1H), 1.82 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  141.1, 140.2, 134.0, 132.0, 131.9, 129.3 (2C), 128.8 (2C), 127.5, 127.03 (2C), 127.02 (2C), 91.8, 83.1, 77.5, 51.2, 40.5, 20.8; IR (neat): 3030, 2926, 1601, 1520, 1487, 1440, 1383, 1263, 1186, 1154, 1097, 1027, 1007, 979, 969  $\text{cm}^{-1}$ ; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{20}\text{H}_{15}\text{Cl}_5\text{K} [\text{M} + \text{K}]^+$  470.9224; found: 470.9230.

**1-((1*R*<sup>\*</sup>,4*R*<sup>\*</sup>,5*R*<sup>\*</sup>,7*S*<sup>\*</sup>)-1,4,5,6,7-Pentachloro-7-methylbicyclo[2.2.1]hept-5-en-2-yl)naphthalene (3g)** and **1-((1*R*<sup>\*</sup>,4*R*<sup>\*</sup>,5*R*<sup>\*</sup>,7*R*<sup>\*</sup>)-1,4,5,6,7-pentachloro-7-methylbicyclo[2.2.1]hept-5-en-2-yl)naphthalene (4g):**

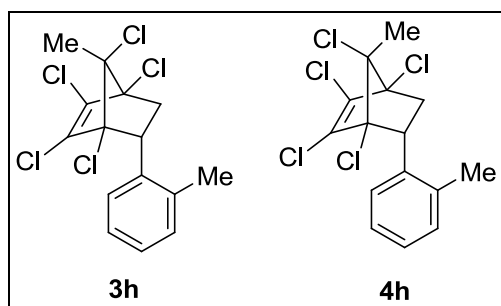


Following the same procedure as for **3a** starting from compound **1** (200 mg, 0.79 mmol) and 1-vinylnaphthalene, **2g** (146 mg, 0.95 mmol), compounds **3g** and **4g** (297 mg, 92%) were obtained in 4:1 ratio. Data for **3g**: colorless solid; mp: 128 - 130  $^\circ\text{C}$ ,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.35 (d,  $J = 8.5$  Hz, 1H), 7.86 (d,  $J = 8.0$  Hz, 1H), 7.81 (d,  $J = 8.2$  Hz, 1H), 7.59-7.55 (m, 1H), 7.51-7.419 (m, 1H), 7.43 (t,  $J = 7.8$  Hz, 1H), 7.01 (d,  $J = 7.3$  Hz, 1H), 5.26 (dd,  $J = 9.2, 4.2$  Hz, 1H), 3.13 (dd,  $J = 12.7, 9.2$  Hz, 1H), 2.51 (dd,  $J = 12.8, 4.2$  Hz, 1H), 1.68 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  134.0, 133.3, 132.1, 131.1, 131.0, 128.9, 128.7, 126.2, 125.9, 125.8, 125.2, 124.2, 89.4, 83.3, 77.4 (merged with  $\text{CDCl}_3$  peak), 45.9, 44.2, 19.9; IR (KBr): 3078, 1599, 1509, 1438, 1378, 1264, 1206, 1147, 1100, 1005, 945  $\text{cm}^{-1}$ ; EI-HRMS: ( $m/z$ )  $\text{M}^+$  calculated for  $\text{C}_{14}\text{H}_{16}\text{Cl}_4$ : 403.9460; found: 403.9462.

Data for **4g**: colorless solid; mp: 118-120  $^\circ\text{C}$ ,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.30 (d,  $J = 8.5$  Hz, 1H), 7.88 (d,  $J = 8.0$  Hz, 1H), 7.82 (d,  $J = 8.2$  Hz, 1H), 7.59-7.56 (m, 1H), 7.53-7.51 (m, 1H), 7.43 (t,  $J = 7.8$  Hz, 1H), 7.02 (d,  $J = 7.3$  Hz, 1H), 4.79 (dd,  $J = 9.3, 4.4$  Hz, 1H), 2.81 (dd,  $J = 13.1, 9.2$  Hz, 1H), 2.51 (dd,  $J = 12.7, 4.1$  Hz, 1H), 1.98 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  133.8, 132.9, 132.3, 132.1, 131.7, 129.0, 128.9, 126.2, 126.0, 125.8, 125.2, 123.7,

92.3, 83.8, 77.5, 44.4, 42.7, 21.0; IR (KBr): 3077, 1598, 1509, 1438, 1393, 1261, 1148, 1095; EI-HRMS: ( $m/z$ )  $M^+$  calculated for  $C_{14}H_{16}Cl_4$ : 403.9460; found: 403.9467.

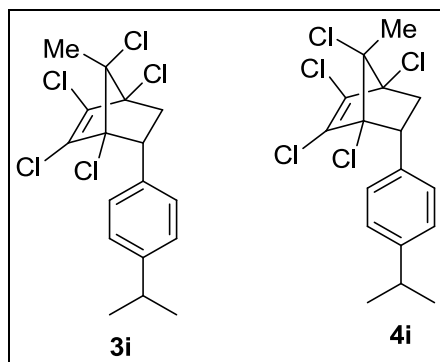
**(1*R*\*,4*R*\*,5*R*\*,7*S*\*)-1,2,3,4,7-Pentachloro-7-methyl-5-*o*-tolylbicyclo[2.2.1]hept-2-ene (3h)**  
and **(1*R*\*,4*R*\*,5*R*\*,7*R*\*)-1,2,3,4,7-pentachloro-7-methyl-5-*o*-tolylbicyclo[2.2.1]hept-2-ene (4h):**



Following the same procedure as for **3a** starting from compound **1** (200 mg, 0.79 mmol) and 1-methyl-2-vinylbenzene, **2h** (112 mg, 0.95 mmol), compounds **3h** and **4h** (251 mg, 86%) were obtained in 4:1 ratio. Data for **3h**: colorless solid; mp: 60-62 °C,  $R_f$  = 0.8 (hexane);  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.23 - 7.10 (m, 3H), 6.79 (d,  $J$  = 6.8 Hz, 1H), 4.62 (dd,  $J$  = 4.4, 9.3 Hz, 1H), 3.00 (dd,  $J$  = 9.3, 12.7 Hz, 1H), 2.53 (s, 3H), 2.33 (dd,  $J$  = 4.4, 12.7 Hz, 1H), 1.65 (s, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  138.4, 134.0, 130.7, 127.7, 127.5, 126.3, 89.1, 83.4, 77.2, 47.1, 43.8, 20.7, 19.7; IR (neat): 3024, 2961, 1601, 1491, 1453, 1381, 1269, 1208, 1188, 1153, 1090, 1009, 954  $cm^{-1}$ ; HRMS (ESI):  $m/z$  calcd for  $C_{15}H_{13}Cl_5Na$  [ $M + Na$ ] $^+$  392.9328; found: 392.9316.

Data for **4h**: colorless solid; mp: 102-104 °C;  $R_f$  = 0.7 (hexane);  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.23 - 7.16 (m, 3H), 6.82 - 6.75 (m, 1H), 4.14 (dd,  $J$  = 4.4, 9.3 Hz, 1H), 2.70 (dd,  $J$  = 9.3, 13.2 Hz, 1H), 2.51 (s, 3H), 2.43 (dd,  $J$  = 4.4, 13.2 Hz, 1H), 1.87 (s, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  138.0, 133.8, 132.1, 130.7, 127.9, 127.6, 126.5, 92.4, 83.7, 77.5, 45.6, 42.5, 20.9, 20.7; IR (neat): 2986, 2921, 1603, 1490, 1462, 1380, 1286, 1264, 1253, 1217, 1183, 1152, 1113, 1086, 1009, 974, 959  $cm^{-1}$ ; HRMS (ESI):  $m/z$  calcd for  $C_{15}H_{13}Cl_5Na$  [ $M + Na$ ] $^+$  392.9328; found: 392.9311.

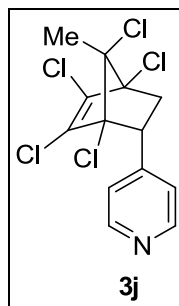
**(1*R*<sup>\*</sup>,4*R*<sup>\*</sup>,5*R*<sup>\*</sup>,7*S*<sup>\*</sup>)-1,2,3,4,7-Pentachloro-5-(4-isopropylphenyl)-7-methylbicyclo[2.2.1]hept-2-ene (3i) and (1*R*<sup>\*</sup>,4*R*<sup>\*</sup>,5*R*<sup>\*</sup>,7*R*<sup>\*</sup>)-1,2,3,4,7-pentachloro-5-(4-isopropylphenyl)-7-methylbicyclo[2.2.1]hept-2-ene (4i):**



Following the same procedure as for **3a** starting from compound **1** (400 mg, 1.58 mmol) and 1-isopropyl-4-vinylbenzene, **2i** (238 mg, 1.63 mmol), compounds **3i** and **4i** (556 mg, 89%) were obtained in 93:7 ratio. Data for **3i**: colorless solid; mp: 56-58 °C;  $R_f$  = 0.8 (hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.20 (d,  $J$  = 7.8 Hz, 2H), 7.05 (d,  $J$  = 8.3 Hz, 2H), 4.07 (dd,  $J$  = 4.4, 9.3 Hz, 1H), 2.98 (dd,  $J$  = 9.3, 12.7 Hz, 1H), 2.94 - 2.89 (m, 1H), 2.41 (dd,  $J$  = 4.2, 12.5 Hz, 1H), 1.65 (s, 3H), 1.26 (d,  $J$  = 7.3 Hz, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  148.7, 132.5, 130.7, 130.5, 128.9 (2C), 126.4 (2C), 88.6, 82.6, 77.3, 52.6, 42.1, 33.7, 23.95, 23.9, 19.8; IR (neat): 2956, 2928, 2872, 1601, 1550, 1513, 1450, 1419, 1381, 1362, 1269, 1256, 1184, 1151, 1105, 1089, 1058, 1009, 952  $\text{cm}^{-1}$ ; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{17}\text{H}_{17}\text{Cl}_5\text{Na}$   $[\text{M} + \text{Na}]^+$  420.9641; found: 420.9634.

Data for **4i**: colorless liquid;  $R_f$  = 0.6 (hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.21 (d,  $J$  = 8.3 Hz, 2H), 7.03 (d,  $J$  = 8.3 Hz, 2H), 3.65 (dd,  $J$  = 4.6, 9.0 Hz, 1H), 2.92 (td,  $J$  = 6.8, 13.4 Hz, 1H), 2.65 (dd,  $J$  = 9.1, 13.1 Hz, 1H), 2.50 (dd,  $J$  = 4.5, 13.1 Hz, 1H), 1.82 (s, 3H), 1.26 (d,  $J$  = 6.8 Hz, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  149.0, 132.3, 132.1, 131.8, 128.8 (2C), 126.5 (2C), 91.9, 83.1, 77.5, 51.2, 40.6, 33.7, 23.92, 23.88, 20.8; IR (neat): 2960, 2928, 2870, 1602, 1513, 1463, 1442, 1420, 1383, 1363, 1263, 1223, 1187, 1154, 1096, 1057, 1018, 980, 969  $\text{cm}^{-1}$ ; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{17}\text{H}_{18}\text{Cl}_5$   $[\text{M} + \text{H}]^+$  396.9851; found: 396.9902.

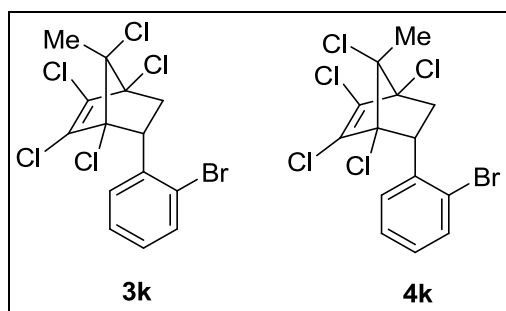
**4-((1*R*<sup>\*</sup>,4*R*<sup>\*</sup>,5*R*<sup>\*</sup>,7*S*<sup>\*</sup>)-1,4,5,6,7-Pentachloro-7-methylbicyclo[2.2.1]hept-5-en-2-yl)pyridine (3j):**





Following the same procedure as for **3a** starting from compound **1** (200 mg, 0.79 mmol) and 4-vinylpyridine, **2j** (174 mg, 0.95 mmol), compound **3j** (263 mg, 77%) was obtained as pale yellow solid; mp: 94-96 °C;  $R_f$  = 0.6 (25% EtOAc in hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.57 (d,  $J$  = 5.4 Hz, 2H), 7.05 (d,  $J$  = 5.9 Hz, 2H), 4.05 (dd,  $J$  = 4.2, 9.0 Hz, 1H), 2.99 (dd,  $J$  = 9.3, 12.7 Hz, 1H), 2.39 (dd,  $J$  = 4.4, 12.7 Hz, 1H), 1.64 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  149.8 (2C), 144.5, 131.2, 130.1, 124.1 (2C), 88.4, 82.1, 77.4, 52.3, 41.1, 19.6; IR (neat) 2925, 2853, 1599, 1557, 1494, 1453, 1415, 1381, 1272, 1258, 1203, 1151, 1107, 1088, 1029, 1012, 950  $\text{cm}^{-1}$ ; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{13}\text{H}_{11}\text{Cl}_5\text{N}$   $[\text{M} + \text{H}]^+$  357.9305; found: 357.9300.

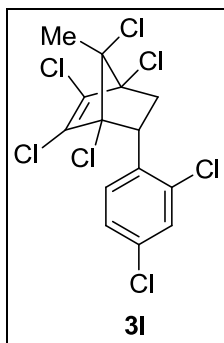
**(1*R*\*,4*R*\*,5*R*\*,7*S*\*)-5-(2-Bromophenyl)-1,2,3,4,7-pentachloro-7-methylbicyclo[2.2.1]hept-2-ene (3k)** and **(1*R*\*,4*R*\*,5*R*\*,7*R*\*)-5-(2-bromophenyl)-1,2,3,4,7-pentachloro-7-methylbicyclo [2.2.1] hept-2-ene (4k):**



Following the same procedure as for **3a** starting from compound **1** (200mg, 0.79 mmol) and 1-bromo-2-vinylbenzene, **2k** (174 mg, 0.95 mmol), compounds **3k** and **4k** (263 mg, 77%) were obtained in 4:1 ratio. Data for **3k**: colorless solid; mp: 78-80 °C,  $R_f$  = 0.8 (hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.61 (dd,  $J$  = 1.0, 8.0 Hz, 1H), 7.27 - 7.24 (m, 1H), 7.18 - 7.12 (m, 1H), 6.83 (dd,  $J$  = 1.0, 7.8 Hz, 1H), 4.99 (dd,  $J$  = 4.4, 9.3 Hz, 1H), 3.04 (dd,  $J$  = 9.3, 12.7 Hz, 1H), 2.23 (dd,  $J$  = 4.6, 12.5 Hz, 1H), 1.63 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  135.2, 133.4, 131.2, 130.6, 129.4, 129.2, 129.1, 127.6, 82.6, 77.4, 71.1, 50.0, 43.8, 19.5; IR (neat) 3030, 2921, 1602, 1473, 1435, 1384, 1259, 1184, 1155, 1097, 1033, 1009, 970  $\text{cm}^{-1}$ ; HRMS (APCI): calcd for  $\text{C}_{14}\text{H}_{10}\text{BrCl}_5$   $[\text{M}]^+$  431.8409; found: 431.8483.

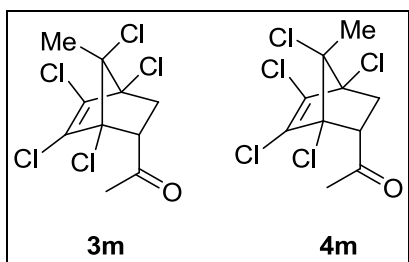
Data for **4k**: colorless solid; mp: 96-98 °C,  $R_f$  = 0.75 (hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.61 (d,  $J$  = 7.8 Hz, 1H), 7.32 - 7.27 (m, 1H), 7.19 - 7.11 (m, 1H), 6.84 (d,  $J$  = 7.8 Hz, 1H), 4.54 (dd,  $J$  = 4.9, 9.3 Hz, 1H), 2.75 (dd,  $J$  = 9.3, 13.2 Hz, 1H), 2.33 (dd,  $J$  = 4.9, 13.2 Hz, 1H), 1.87 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  134.9, 133.4, 132.5, 131.9, 129.7, 129.2, 127.8, 126.8, 92.3, 83.2, 77.1, 48.4, 42.5, 20.8; IR (neat) 2986, 2921, 1600, 1470, 1433, 1382, 1260, 1180, 1153, 1095, 1031, 1010, 968  $\text{cm}^{-1}$ ; HRMS (ESI): calcd for  $\text{C}_{14}\text{H}_{10}\text{BrCl}_5\text{Na}$   $[\text{M} + \text{Na}]^+$  454.8306; found: 454.8338.

**(1*R*<sup>\*</sup>,4*R*<sup>\*</sup>,5*R*<sup>\*</sup>,7*S*<sup>\*</sup>)-1,2,3,4,7-Pentachloro-5-(2,4-dichlorophenyl)-7-methylbicyclo[2.2.1]hept-2-ene (3l):**



Following the same procedure as for **3a** starting from compound **1** (300 mg, 1.2 mmol) and 2,4-dichloro-1-vinylbenzene, **2l** (216 mg, 1.25 mmol), compound **3l** (354 mg, 70%) was obtained as colorless solid; mp: 138-140 °C;  $R_f$  = 0.8 (hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 (d,  $J$  = 2.0 Hz, 1H), 7.22 (dd,  $J$  = 2.2, 8.6 Hz, 1H), 6.77 (d,  $J$  = 8.3 Hz, 1H), 4.92 (dd,  $J$  = 4.4, 9.3 Hz, 1H), 3.05 (dd,  $J$  = 9.3, 12.7 Hz, 1H), 2.20 (dd,  $J$  = 4.4, 12.7 Hz, 1H), 1.64 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  136.8, 134.4, 132.3, 131.4, 129.85, 129.83, 127.3, 88.7, 82.4, 77.1, 47.2, 43.2, 43.5, 19.5; IR (neat): 2954, 2923, 2853, 1601, 1587, 1555, 1470, 1453, 1379, 1270, 1154, 1154, 1145, 1103, 1088, 1049, 1011, 953  $\text{cm}^{-1}$ ; HRMS (APCI):  $m/z$  calcd for  $\text{C}_{14}\text{H}_{13}\text{Cl}_7\text{N} [\text{M} + \text{NH}_4]^+$  439.8868; found: 439.8897.

**1-((1*R*<sup>\*</sup>,4*R*<sup>\*</sup>,5*R*<sup>\*</sup>,7*S*<sup>\*</sup>)-1,4,5,6,7-Pentachloro-7-methylbicyclo[2.2.1]hept-5-en-2-yl)ethanone (3m) and 1-((1*R*<sup>\*</sup>,4*R*<sup>\*</sup>,5*R*<sup>\*</sup>,7*R*<sup>\*</sup>)-1,4,5,6,7-pentachloro-7-methylbicyclo[2.2.1]hept-5-en-2-yl)ethanone (4m):**

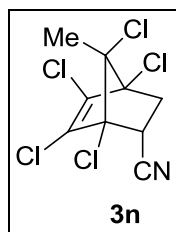


Following the same procedure as for **3a** starting from compound **1** (500 mg, 1.98 mmol) and methylvinyl ketone, **2m** (413 mg, 5.9 mmol), compounds **3m** and **4m** (610 mg, 95%) were obtained in 4:1 ratio. Data for **3m**: colorless solid; mp: 72-74 °C;  $R_f$  = 0.55 (5% EtOAc in hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.85 (dd,  $J$  = 4.4, 8.3 Hz, 1H), 2.62 - 2.47 (m, 2H), 2.39 (s, 3H), 1.60 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  203.5, 132.0, 128.0, 89.0, 79.6, 77.1, 58.8, 37.7, 31.7, 19.2; IR (neat): 2933, 2841, 1718, 1603, 1444, 1381, 1360, 1273, 1244, 1175, 1151, 1105, 983  $\text{cm}^{-1}$ ; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{10}\text{H}_9\text{Cl}_5\text{ONa} [\text{M} + \text{Na}]^+$  344.8964; found: 344.8955.

Data for **4m**: colourless solid; mp: 78-80 °C;  $R_f$  = 0.5 (5% EtOAc in hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.42 (dd,  $J$  = 4.3, 8.5 Hz, 1H), 2.62 (dd,  $J$  = 3.9, 12.6 Hz, 1H), 2.40 (s, 3H),

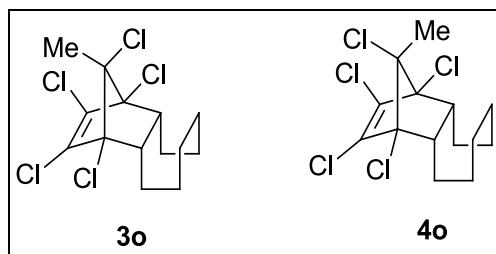
2.17 (dd,  $J = 8.7, 12.5$  Hz, 1H), 1.71 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  202.1, 133.3, 129.0, 91.5, 80.0, 77.1, 56.9, 35.8, 31.5, 20.7; IR (neat): 2930, 2840, 1716, 1604, 1439, 1384, 1359, 1270, 1241, 1175, 1153, 1101, 982  $\text{cm}^{-1}$ ; HRMS (APCI):  $m/z$  calcd for  $\text{C}_{10}\text{H}_9\text{Cl}_5\text{ONa}$   $[\text{M} + \text{Na}]^+$  344.8964; found: 344.8957.

**(1*R*\*,4*R*\*,5*R*\*,7*S*\*)-1,4,5,6,7-Pentachloro-7-methylbicyclo[2.2.1]hept-5-ene-2-carbonitrile (3n):**



Following the same procedure as for **3a** starting from compound **1** (200 mg, 0.79 mmol) and acrylonitrile, **2n** (167 mg, 3.16 mmol), compound **3n** (222 mg, 92%) was obtained as colorless solid; mp: 138-140 °C;  $R_f = 0.8$  (hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.78 (dd,  $J = 4.0, 9.4$  Hz, 1H), 2.96 (m, 1 H), 2.29 (m, 1H), 1.60 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  132.2, 129.9, 116.8, 86.3, 77.4, 76.3, 41.5, 39.2, 19.1; IR (neat): 3023, 2250, 1602, 1448, 1383, 1275, 1234, 1156, 1110, 1095, 1046, 1015, 953  $\text{cm}^{-1}$ ; HRMS (ESI):  $m/z$  calcd for  $\text{C}_9\text{H}_6\text{Cl}_5\text{NNa}$   $[\text{M} + \text{Na}]^+$  327.8811; found: 327.8806.

**Compound 3o, 4o:**

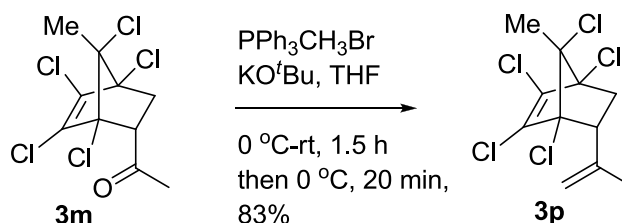


Following the same procedure as for **3a** starting from compound **1** (500 mg, 1.98 mmol) and cyclooctene, **2o** (468 mg, 4.26 mmol), compounds **3o** and **4o** (582 mg, 81%) were obtained in 4:1 ratio. Data for **3o**: colorless solid; mp: 42-44 °C;  $R_f = 0.85$  (hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.74 (dd,  $J = 2.1, 8.0$  Hz, 2H), 1.90 (dt,  $J = 14.0, 3.7$  Hz, 2H), 1.69-1.62 (m, 2H), 1.57 (s, 3H), 1.40-1.38 (m, 4H), 1.28-1.13 (m, 4H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  130.1 (2C), 87.6, 81.9, 51.7 (2C), 30.3 (2C), 25.9 (2C), 22.6 (2C), 20.1 (2C); IR (neat): 2922, 2852, 1602, 1465, 1445, 1380, 1283, 1249, 1162, 1108, 1091, 992, 947  $\text{cm}^{-1}$ ; HRMS (ESI): ( $m/z$ )  $\text{M}^+$  calcd for  $\text{C}_{14}\text{H}_{18}\text{Cl}_5$   $[\text{M} + \text{H}]^+$  360.9851, found: 360.9902

Data for **4o**: colorless solid; mp: 112-114 °C;  $R_f = 0.8$  (hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.35 (dd,  $J = 1.9, 7.3$  Hz, 2H), 1.96-1.91 (m, 2H), 1.74-1.68 (m, 2H), 1.71 (s, 3H), 1.40-1.38 (m, 4H), 1.25-1.20 (m, 4H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  131.5 (2C), 92.0, 82.4, 50.7 (2C), 30.3 (2C), 25.9 (2C), 23.3 (2C), 21.1 (2C); IR (neat): 3030, 1600, 1486, 1448, 1380,

1266, 1152, 1089, 1008, 954  $\text{cm}^{-1}$ ; HRMS (ESI): ( $m/z$ )  $M^+$  calcd for  $\text{C}_{14}\text{H}_{18}\text{Cl}_5[\text{M} + \text{H}]^+$  360.9851, found: 360.9890

**(1*R*\*,4*R*\*,5*R*\*,7*S*\*)-1,2,3,4,7-Pentachloro-7-methyl-5-(prop-1-en-2-yl)bicyclo[2.2.1]hept-2-ene (3p):**

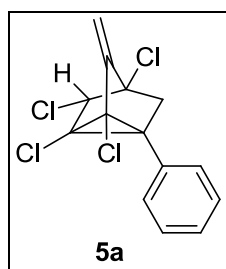


To the stirred suspension of methyltriphenylphosphonium bromide (443 mg, 1.24 mmol) in THF (3 mL) was added KOtBu (135 mg, 1.209 mmol) at 0 °C and the resulting ylide was stirred for 10 min. then allowed to warm to rt and stirred for 1.5 h. Then reaction mixture was cooled to -5 °C (ice salt mixture) and to this was added a solution of ketone **3m** (200 mg, 0.62 mmol) in THF (2 mL). Completion of starting material was monitored by tlc, after 20 min, 3 mL of water was added and diluted with EtOAc (30 mL), organic phase was separated, aqueous phase was extracted with EtOAc (25 mL x 3) combined organic phases was washed with water (25 mL), brine (20 mL), dried over  $\text{Na}_2\text{SO}_4$ , and concentrated in *vacuo*. The resulting crude was purified by silica gel column chromatography using hexane as eluent furnished diene **3p** (165 mg, 83%) as colorless liquid,  $R_f$  = 0.9 (hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.03 (s, 1H), 4.74 (s, 1H), 3.52 (dd,  $J$  = 4.2, 9.0 Hz, 1H), 2.72 (dd,  $J$  = 9.0, 12.5 Hz, 1H), 2.11 (dd,  $J$  = 4.2, 12.5 Hz, 1H), 1.87 (s, 3H), 1.60 (s, 3H),  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  140.4, 130.5, 130.2, 115.6, 88.8, 81.6, 76.9, 53.1, 40.6, 23.9, 19.6; IR (neat): 3084, 2994, 2972, 2942, 1644, 1601, 1446, 1379, 1269, 1212, 1152, 1107, 1091, 1046, 1010, 949  $\text{cm}^{-1}$ ; HRMS (ESI): ( $m/z$ )  $M^+$  calcd for  $\text{C}_{11}\text{H}_{11}\text{Cl}_5\text{Na} [\text{M} + \text{Na}]^+$  340.9201, found: 340.9256.

### General procedure for the $\text{KO}_2$ -mediated synthesis of tetrachloro-substituted 3-methylenenorbornenes 5:

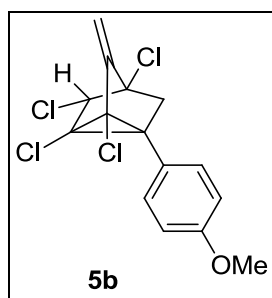
To a stirred solution of **3a** & **4a** (1.1 g, 3.09 mmol) in DMSO (31 mL) was added  $\text{KO}_2$  (660 mg, 9.26 mmol) in portions at ~15 °C (ice-water bath) under argon atmosphere and then allowed to warm to room temperature and then heated at 60 °C, reaction mixture turned deep wine-red color. After completion of reaction 6 h (monitored by TLC) 25 mL of water was added drop wise to destroy the extra  $\text{KO}_2$ . The mixture was then diluted with EtOAc (70 mL), organic phase was separated and aqueous phase was extracted with EtOAc (60 mL x 3). The combined organic phases were washed with water (50 mL), brine (50 mL), dried over  $\text{Na}_2\text{SO}_4$ , filtered and concentrated afforded the crude product. Column chromatography (hexane) provided compound **5a** as a colourless solid (837 mg, 85%)

## <sup>1</sup>H NMR, <sup>13</sup>C NMR data of the nortricyclenes **5**



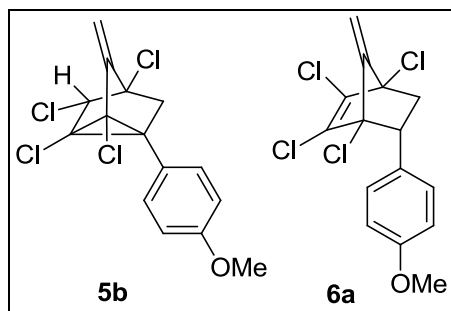
$R_f$  = 0.75 (Hexane), mp: 80-82 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.44-7.26 (m, 5H) 5.42 (s, 1H) 5.33 (s, 1H) 4.26 (s, 1H) 2.94 (d,  $J$  = 10.7 Hz, 1H) 2.31 (d,  $J$  = 10.7 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 147.2, 130.8, 130.1 (2C), 128.7 (2C), 128.5, 104.2, 71.4, 65.9, 57.7, 54.0, 48.0, 43.02; IR (KBr): 3044, 2977, 2942, 1691, 1603, 1500, 1446, 1368, 1279, 1233, 1177, 1119, 1092, 1047, 1023 cm<sup>-1</sup>; EI-HRMS: (m/z)  $M^+$  calculated for C<sub>14</sub>H<sub>10</sub>Cl<sub>4</sub>: 317.9537; found: 317.9538.

### Compound **5b**:



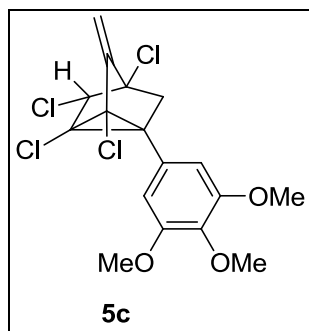
Following the same procedure as for **5a** starting from compound **3b** (30 mg, 0.077mmol), compound **5b** (23.8 mg, 88%) was obtained as colorless solid. mp: 42-44 °C;  $R_f$  = 0.5 (5% CH<sub>2</sub>Cl<sub>2</sub> in hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.30 (d,  $J$  = 8.8 Hz, 2H), 6.93 (d,  $J$  = 8.8 Hz, 2H), 5.40 (s, 1H), 5.31 (s, 1H), 4.24 (s, 1H), 3.82 (s, 3H), 2.90 (d,  $J$  = 10.7 Hz, 1H), 2.26 (d,  $J$  = 10.5 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 159.7, 147.3, 131.3 (2C), 122.7, 114.3 (2C), 104.0, 71.5, 66.0, 56.0, 55.4, 54.2, 48.1, 42.6; IR (neat): 2960, 2836, 1691, 1610, 1461, 1371, 1298, 1275, 1248, 1175, 1122, 1110, 1091, 1044, 1028, 999, 954 cm<sup>-1</sup>; EI-HRMS: (m/z)  $M^+$  calculated for C<sub>15</sub>H<sub>12</sub>Cl<sub>4</sub>O: 347.9642; Found: 347.9652.

### Compounds **5b** and **6a**:



Following the same procedure as for **5a** starting from compound **4b** (22 mg, 0.056 mmol), compounds **5b** and **6a** (17 mg, 86%) were obtained as inseparable mixture in 2:1 (**5b**:**6a**). NMR data for **5b**:  $R_f$  = 0.5 (5%  $\text{CH}_2\text{Cl}_2$  in hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30 (d,  $J$  = 8.8 Hz, 2H), 6.93 (d,  $J$  = 8.8 Hz, 2H), 5.40 (s, 1H), 5.31 (s, 1H), 4.24 (s, 1H), 3.82 (s, 3H), 2.90 (d,  $J$  = 10.7 Hz, 1H), 2.27 (d,  $J$  = 10.7 Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  159.7, 147.3, 131.3 (2C), 122.7, 114.3 (2C), 104.0, 71.5, 66.0, 56.0, 55.4, 54.2, 48.1, 42.6; NMR data for **6a**:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.03 (d,  $J$  = 8.8 Hz, 2H), 6.86 (d,  $J$  = 8.8 Hz, 2H), 4.94 (d,  $J$  = 1.48 Hz, 1H), 4.91 (d,  $J$  = 1.48 Hz, 1H), 3.60 (dd,  $J$  = 9.6, 4.9 Hz, 1H), 2.63 (dd,  $J$  = 12.3, 9.6 Hz, 1H), 2.45 (dd,  $J$  = 12.3, 4.9 Hz, 1H),  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  159.5, 157.7, 131.8, 131.7, 129.8 (2C), 127.8, 113.8 (2C), 93.8, 70.8, 58.0, 55.3, 55.0, 44.7, IR (neat): 3001, 2955, 2836, 1692, 1611, 1585, 1516, 1461, 1297, 1268, 1250, 1178, 1031, 1000, 959  $\text{cm}^{-1}$ ; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{15}\text{H}_{13}\text{Cl}_4\text{O}$   $[\text{M} + \text{H}]^+$  350.9691, found: 350.9674.

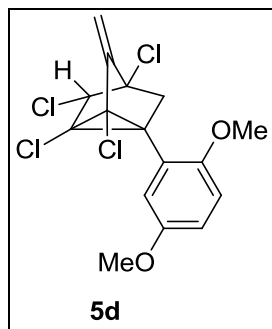
### Compound **5c**:



Following the same procedure as for **5a** starting from compounds **3c** and **4c** (30 mg, 0.067 mmol), compound **5c** (23 mg, 84%) was obtained at rt as colorless solid (in a separate experiment 5 mol% of BHT was used for the same scale yield of nortricyclene 94%).  $R_f$  = 0.5 (5% EtOAc in hexane); mp : 92-94  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.55 (s, 2H), 5.43 (d,  $J$  = 0.7 Hz, 1H), 5.34 (s, 1H), 4.26 (s, 1H), 3.88 (s, 3H), 3.88(s, 3H), 3.87 (s, 3H), 2.93 (d,  $J$  = 10.7 Hz, 1H), 2.30 (d,  $J$  = 10.7 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  153.4, 147.0 (2C), 138.2, 126.0, 107.0 (2C), 104.2, 71.3, 65.8, 60.9, 57.8, 56.2 (2C), 54.1, 47.9, 43.2; IR (neat): 2984, 2936, 2828, 1696, 1585, 1508, 1456, 1412, 1386, 1328, 1263, 1239, 1121,

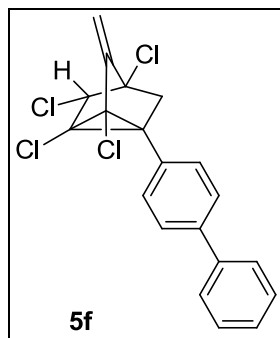
1005, 951  $\text{cm}^{-1}$ ; HRMS(ESI):  $m/z$  calcd for  $\text{C}_{17}\text{H}_{20}\text{Cl}_4\text{NO}_3$   $[\text{M} + \text{NH}_4]^+$  428.0168, found: 428.0145.

#### Compound 5d:



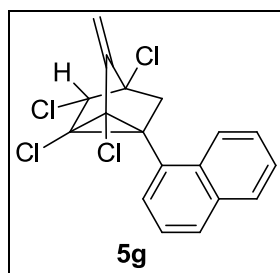
Following the same procedure as for **5a** starting from compounds **3d** and **4d** (38 mg, 0.091 mmol), compound **5d** (27 mg, 78%) was obtained as colorless liquid.  $R_f$  = 0.45(2% EtOAc in hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.91 (d,  $J$  = 2.3 Hz, 1H), 6.81-6.71 (m, 2H), 5.31 (s, 1H), 5.22 (s, 1H), 4.14 (s, 1H), 3.70 (s, 6H), 2.81 (d,  $J$  = 10.4 Hz, 1H), 2.30 (d,  $J$  = 10.4 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  153.3, 153.2, 147.4, 120.0, 117.3, 114.5, 111.8, 103.5, 71.4, 66.1, 57.3, 55.9, 55.8, 54.0, 45.3, 41.0; IR (neat): 2951, 2833, 1692, 1611, 1588, 1503, 1462, 1462, 1427, 1268, 1219, 1168, 1046, 1025, 998, 964  $\text{cm}^{-1}$ ; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{16}\text{H}_{18}\text{Cl}_4\text{NO}_2$   $[\text{M} + \text{NH}_4]^+$  398.0062; found: 398.0098.

#### Compound 5f:



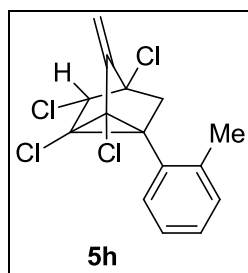
Following the same procedure as for **5a** starting from compounds **3f** and **4f** (60 mg, 0.138 mmol), compound **5f** (47 mg, 86%) was obtained at rt as colorless solid (in a separate experiment 5 mol% of BHT was used for the same scale yield of nortricyclene 91%).  $R_f$  = 0.5 (hexane); mp :106-108  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62 (d,  $J$  = 8.2 Hz, 2H), 7.58 (d,  $J$  = 7.8 Hz, 2H), 7.47- 7.42 (m, 4H), 7.37-7.34 (m, 1H), 5.43 (s, 1H), 5.35 (s, 1H), 4.28 (s, 1H), 2.97 (d,  $J$  = 10.6, 1H), 2.33(d,  $J$  = 10.7 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  147.1, 141.3, 140.5, 130.3 (2C), 129.7, 128.8 (2C), 127.6, 127.4 (2C), 127.2 (2C), 104.2, 71.4, 66.0, 57.8, 54.1, 47.8, 42.8; IR (neat): 3030, 1691, 1600, 1528, 1447, 1398, 1234, 1193, 1122, 998  $\text{cm}^{-1}$ ; HRMS (APCI):  $m/z$  calcd for  $\text{C}_{20}\text{H}_{14}\text{Cl}_4\text{K}$   $[\text{M} + \text{K}]^+$  434.9457, found: 434.9448.

### Compound 5g:



Following the same procedure as for **5a** starting from compounds **3g** and **4g** (40 mg, 0.098 mmol), compound **5g** (30.5mg, 83%) was obtained as colorless solid.  $R_f$  = 0.45 (hexane); mp : 82-84 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.89-7.85 (m, 2H), 7.62 (d,  $J$  = 7.0 Hz, 1H), 7.55-7.48 (m, 4H), 5.55 (s, 1H), 5.48 (s, 1H), 4.37 (s, 1H), 3.01 (d,  $J$  = 7.6 Hz, 1H), 2.54 (d,  $J$  = 7.6 Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  147.2, 134.1, 132.1, 129.9, 129.5, 129.0, 127.2, 126.5, 126.1, 125.4, 124.8, 104.8, 71.7, 66.1, 57.3, 54.1, 47.5, 42.8; IR (KBr): 3041, 1690, 1593, 1549, 1508, 1447, 1400, 1353, 1247, 1235, 1209, 1123, 997  $\text{cm}^{-1}$ ; HRMS (APCI):  $m/z$  calcd for  $\text{C}_{18}\text{H}_{13}\text{Cl}_4$   $[\text{M} + \text{H}]^+$  370.9742, found: 370.9740.

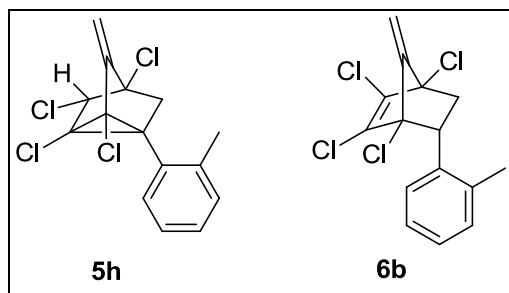
### Compound 5h:



Following the same procedure as for **5a** starting from compounds **3h** (25 mg, 0.067 mmol), compound **5h** (16.7 mg, 75%) was obtained as colorless liquid.  $R_f$  = 0.8 (hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 (d,  $J$  = 7.7 Hz, 1H), 7.29-7.17 (m, 3H), 5.44 (s, 1H), 5.35 (s, 1H), 4.26 (s, 1H), 2.89 (d,  $J$  = 10.8 Hz, 1H), 2.38 (s, 3H), 2.34 (d,  $J$  = 10.8, 1H),  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  147.1, 138.9, 131.4, 131.0, 129.0, 128.8, 125.9, 104.3, 71.5, 65.8, 57.0, 54.0, 46.2, 43.3, 19.7; IR (neat): 2950, 2926, 2855, 1692, 1511, 1495, 1452, 1381, 1273, 1236, 1122, 998, 946  $\text{cm}^{-1}$ ; HRMS (APCI):  $m/z$  calcd for  $\text{C}_{15}\text{H}_{13}\text{Cl}_4$   $[\text{M} + \text{H}]^+$  334.9742, found: 334.9744

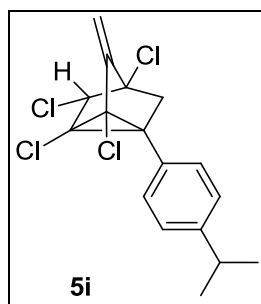


### Compound **5h** and **6b**:



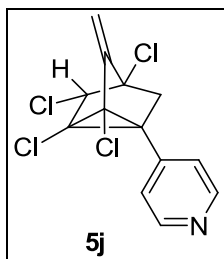
Following the same procedure as for **5a** starting from compounds **4h** (20 mg, 0.054 mmol), compound **5h** and **6b** (11.3 mg, 63% combined yield) were obtained inseparable mixture in 2:3 (**5h**:**6b**) ratio as colorless liquid.  $R_f = 0.5$  (hexane); NMR data of **5h**:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 (d,  $J = 7.7$  Hz, 1H), 7.29-7.17 (m, 3H), 5.44 (s, 1H), 5.35 (s, 1H), 4.26 (s, 1H), 2.89 (d,  $J = 10.8$  Hz, 1H), 2.38 (s, 3H), 2.34 (d,  $J = 10.8$  Hz, 1H),  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  147.1, 138.9, 131.4, 131.0, 129.0, 128.8, 125.9, 104.3, 71.5, 65.8, 57.0, 54.0, 46.2, 43.3, 19.7; NMR data of **6b**: 7.20-7.15 (m, 3H), 6.83-6.80 (m, 1H), 4.96 (d,  $J = 1.5$  Hz, 1H), 4.92 (d,  $J = 1.5$  Hz, 1H), 4.09 (dd,  $J = 9.6, 5$  Hz, 1H), 2.68 (dd,  $J = 12.2, 9.7$  Hz, 1H), 2.48 (s, 3H), 2.43-2.40 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158, 138.1, 134.7, 133.1, 132.5, 130.7, 127.7, 127.16, 126.3, 93.4, 70.7, 60.6, 49.8, 46.4, 20.7; IR (neat): 3023, 2955, 1692, 1587, 1492, 1454, 1380, 1268, 1235, 1189, 1141, 1030, 1000, 958  $\text{cm}^{-1}$ ; HRMS (APCI):  $m/z$  calcd for  $\text{C}_{15}\text{H}_{16}\text{NCl}_4$   $[\text{M} + \text{NH}_4]^+$  350.0037, found: 350.0011

### Compound **5i**:



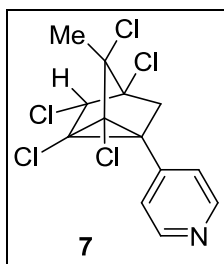
Following the same procedure as for **5a** starting from compound **3i** and **4i** (50mg, 0.125 mmol), compound **5i** (37.2 mg, 85%) was obtained as colorless liquid (in a separate experiment 5 mol% of BHT was used for the same scale yield of nortricyclene 89%).  $R_f = 0.6$  (hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28 (m, 4H), 5.40 (s, 1H), 5.32 (s, 1H), 4.25 (s, 1H), 2.96 - 2.87 (m, 2H), 2.28 (d,  $J = 10.8$  Hz, 1H), 1.26 (d,  $J = 6.8$  Hz, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  149.1, 147.3, 129.8, 128.0, 126.7, 103.9, 71.4, 65.9, 57.8, 54.1, 47.9, 42.8, 33.9, 23.91, 23.88; IR (neat): 2961, 2927, 2869, 1690, 1512, 1459, 1448, 1406, 1365, 1278, 1267, 1235, 1120, 1061, 1018, 998  $\text{cm}^{-1}$ ; HRMS (APCI):  $m/z$  calcd for  $\text{C}_{17}\text{H}_{17}\text{Cl}_4$   $[\text{M} + \text{H}]^+$  363.0055, found: 363.0042.

### Compound 5j :



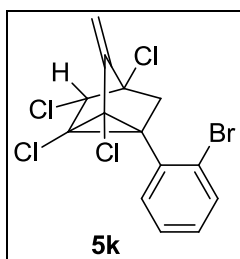
Following the same procedure as for **5a** starting from compound **3j** (24 mg, 0.067 mmol), compound **5j** (12.7 mg, 60%) and **7** (3.8 mg, 16%) were obtained at rt as colorless liquids.  $R_f$  = 0.45 (20% EtOAc in hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.66 (dd,  $J$  = 4.5, 1.6 Hz, 2H), 7.33 (dd,  $J$  = 4.5, 1.7 Hz, 2H), 5.46 (d,  $J$  = 1 Hz, 1H), 5.37 (s, 1H), 4.27 (s, 1H), 2.98 (d,  $J$  = 10.6 Hz, 1H), 2.34 (d,  $J$  = 10.6 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  150.1, 146.3, 139.6, 124.4, 105.0, 77.2, 71.0, 65.6, 57.6, 54.0, 46.4, 41.7; IR (neat): 3030, 2925, 2854, 1692, 1598, 1550, 1500, 1448, 1410, 1281, 1237, 1123, 1071, 999  $\text{cm}^{-1}$ ; HRMS (APCI):  $m/z$  calcd for  $\text{C}_{13}\text{H}_{10}\text{Cl}_4\text{ON}[\text{M} + \text{H}]^+$  321.9538, found: 321.9523.

### Compound 7:



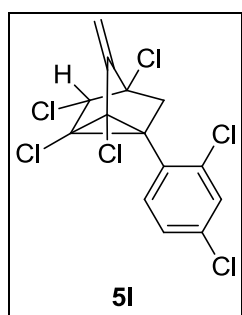
NMR data for **7**:  $R_f$  = 0.5 (20% EtOAc in hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.67 (d,  $J$  = 6.0 Hz, 2H), 7.31 (dd,  $J$  = 4.5, 1.5 Hz, 2H), 4.51 (s, 1H), 3.01 (d,  $J$  = 11.3 Hz, 1H), 2.96 (d,  $J$  = 11.6 Hz, 1H), 1.77 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  150.2 (2C), 139.0, 124.8 (2C), 78.8, 77.2, 71.0, 68.6, 60.4, 54.9, 45.4, 39.9, 29.7, 21.0; IR (neat) 3031, 2924, 2853, 1690, 1599, 1552, 1451, 1411, 1385, 1271, 1226, 1180, 1073, 1046, 1008  $\text{cm}^{-1}$ ; HRMS (APCI):  $m/z$  calcd for  $\text{C}_{13}\text{H}_{10}\text{Cl}_4\text{ON}[\text{M} + \text{H}]^+$  321.9538, found: 321.9534.

### Compound 5k:



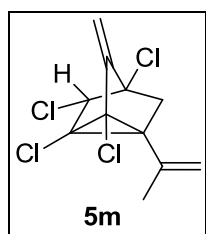
Following the same procedure as for **5a** starting from compounds **3k** and **4k** (25 mg, 0.057 mmol), compound **5k** (64%) was obtained as colorless solid.  $R_f = 0.5$  (hexane); mp: 78-80 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62 (dd,  $J = 7.9, 1.2$  Hz, 1H), 7.53 (dd,  $J = 7.7, 1.7$  Hz, 1H), 7.35 (td,  $J = 7.6, 1.3$  Hz, 1H), 7.23 (td,  $J = 7.6, 1.7$  Hz, 1H), 5.45 (s, 1H), 5.36 (s, 1H), 4.25 (s, 1H), 2.82 (d,  $J = 10.6$  Hz, 1H), 2.78 (d,  $J = 10.6$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  146.4, 133.7, 132.8, 131.0, 130.2, 127.4, 125.6, 104.7, 71.5, 65.6, 56.6, 54.4, 44.7, 43.9; IR (neat): 3023, 2955, 1694, 1582, 1477, 1442, 1428, 1400, 1277, 1233, 1178, 1119, 1065, 1022, 997  $\text{cm}^{-1}$ ; HRMS (APCI):  $m/z$  calcd for  $\text{C}_{14}\text{H}_{10}\text{BrCl}_4$   $[\text{M} + \text{H}]^+$  396.8720, found: 396.8773.

#### Compound 5l:



Following the same procedure as for **5a** starting from compound **3l** (50 mg, 0.117 mmol), compound **5l** (40.2 mg, 78%) was obtained as colorless liquid.  $R_f = 0.6$  (hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47-7.44 (m, 2H), 7.31-7.26 (m, 1H), 5.45 (d,  $J = 0.7$  Hz, 1H), 5.36 (s, 1H), 4.24 (s, 1H), 2.83 (d,  $J = 10.6$  Hz, 1H), 2.58 (d,  $J = 10.6$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  146.2, 136.9, 135.5, 133.2, 130.2, 127.8, 127.3, 104.8, 71.2, 65.6, 56.8, 54.1, 44.6, 42.1; IR (neat): 3022, 2950, 1693, 1589, 1554, 1482, 1448, 1385, 1281, 1234, 1124, 1106, 1072, 1001, 950  $\text{cm}^{-1}$ ; HRMS(ESI):  $m/z$  calcd for  $\text{C}_{14}\text{H}_9\text{Cl}_6$   $[\text{M} + \text{H}]^+$  388.8806, found: 388.8798.

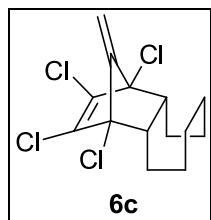
#### Compound 5m:



Following the same procedure as for **5a** starting from compound **2p** (40 mg, 0.125 mmol), compound **5m** (28.1 mg, 80%) was obtained as colorless liquid.  $R_f = 0.85$  (hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.35 (s, 1H), 5.28-5.21 (m, 3H), 4.14 (s, 1H), 2.81 (d,  $J = 10.8$  Hz, 1H), 2.15 (d,  $J = 10.8$  Hz, 1H), 1.89 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  147.3, 134.7, 119.0,

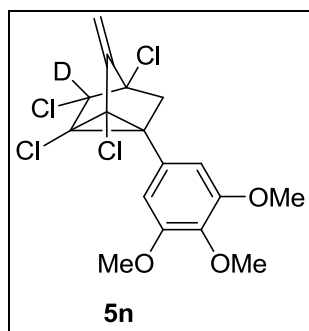
103.8, 71.4, 65.7, 57.1, 53.2, 45.2, 43.8, 20.8; IR (neat): 2947, 2923, 2855, 1692, 1648, 1527, 1501, 1451, 1381, 1271, 1234, 999, 904  $\text{cm}^{-1}$ ; HRMS (APCI): ( $m/z$ )  $M^+$  calcd for  $\text{C}_{11}\text{H}_{14}\text{Cl}_4\text{N}[\text{M} + \text{NH}_4]^+$  299.9880, found: 299.9885.

### Compound 6c:



Following the same procedure as for **5a** starting from compounds **3o** and **4o** (40 mg, 0.124 mmol), compound **6c** (34.6 mg, 89%) was obtained at 100 °C.  $R_f$  = 0.95 (hexane); mp: 116-118 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.83 (s, 2H), 2.34 (dd,  $J$  = 7.3, 2.6 Hz, 2H), 1.95 (dd,  $J$  = 10.7, 4.4 Hz, 2H), 1.71 - 1.67 (m, 2H), 1.38-1.37 (m, 4H), 1.25-1.23 (m, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.8 (2C), 131.9 (2C), 92.9, 75.6, 55.0 (2C), 30.2 (2C), 25.9 (2C), 22.9 (2C); IR (KBr): 2953, 2923, 2850, 1702, 1586, 1463, 1442, 1383, 1297, 1279, 1244, 1202, 1156, 1035, 999  $\text{cm}^{-1}$ ; EI-HRMS: ( $m/z$ )  $M^+$  calcd for  $\text{C}_{14}\text{H}_{16}\text{Cl}_4$ : 324.0006; found : 324.0007.

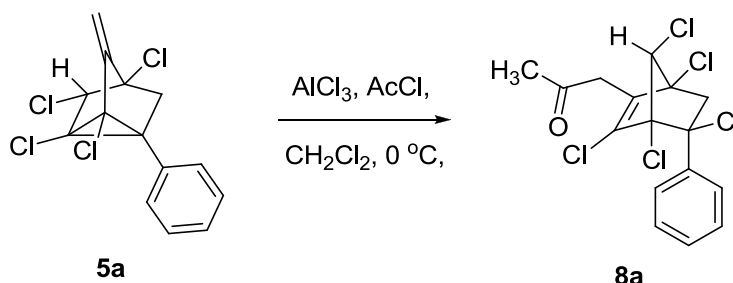
### Compound 5n:



Following the same procedure as for **5a** starting from compounds **3c** and **4c** (24 mg, 0.053 mmol), compound **5n** (16.7 mg, 77%) was obtained instead of DMSO, DMSO- $d_6$  was used as solvent and at room temperature.  $R_f$  = 0.5 (5% EtOAc in hexane); mp : 92-94 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.56 (s, 2H), 5.44 (s, 1H), 5.35 (s, 1H), 3.88 (s, 6H), 3.87 (s, 3H), 2.94 (d,  $J$  = 10.8 Hz, 1H), 2.31 (d,  $J$  = 10.8 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  153.4, 147.1, 138.3, 126.0, 107.1, 104.2, 70.9 (triplet,  $\text{C}_5$  attached to D), 65.7, 60.9, 57.7, 56.2, 54.1, 47.9, 43.2; IR(neat) 2937, 2830, 1693, 1585, 1509, 1453, 1413, 1388, 1300, 1263, 1237, 1125, 1008, 947  $\text{cm}^{-1}$ ; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{17}\text{H}_{19}\text{DCl}_4\text{NO}_3$   $[\text{M} + \text{NH}_4]^+$  429.0231, found: 429.0210.

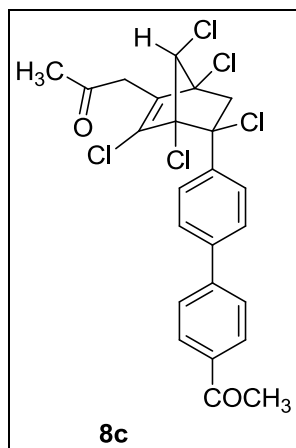
**General procedure for the acylation reaction of nortricyclenes and  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR data of products of acylation reaction of nortricyclens:**

**1-((1*R*<sup>\*</sup>,4*R*<sup>\*</sup>,5*R*<sup>\*</sup>,7*S*<sup>\*</sup>)-1,3,4,5,7-Pentachloro-5-phenylbicyclo[2.2.1]hept-2-en-2-yl)propan-2-one (8a):**



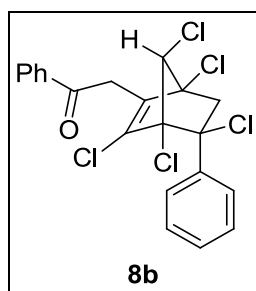
To a stirred suspension of  $\text{AlCl}_3$  (83 mg, 0.62 mmol) in  $\text{CH}_2\text{Cl}_2$  (3 mL) was added acetyl chloride (73 mg, 0.93 mmol) at  $0\text{ }^\circ\text{C}$  and the resulting mixture was stirred for 10 min. Then a solution of **5a** (100 mg, 0.31 mmol) in  $\text{CH}_2\text{Cl}_2$  (2 mL) was added. After being stirred for 5 min. 1 mL of dil. HCl was added drop wise and diluted with  $\text{CH}_2\text{Cl}_2$  (25 mL). The organic phase was separated and aqueous phase was extracted with  $\text{CH}_2\text{Cl}_2$  (30 mL x 3). The combined organic phases were washed with water (20 mL), brine (20 mL), dried over  $\text{Na}_2\text{SO}_4$  and concentrated *in vacuo*. The resulting crude was purified over silica gel column chromatography with 5% EtOAc in Hexane, which afforded product **8a** (93 mg, 76%);  $R_f$  = 0.5 (5% EtOAc in Hexane); mp:  $134\text{--}136\text{ }^\circ\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.67 (dd,  $J$  = 2.0, 7.3 Hz, 2H), 7.35 - 7.26 (m, 3H), 4.32 (d,  $J$  = 2.0 Hz, 1H), 3.97 (dd,  $J$  = 1.5, 13.7 Hz, 1H), 3.52 (d,  $J$  = 4.9 Hz, 2H), 3.37 (d,  $J$  = 13.7 Hz, 1H), 2.26 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  202.7, 139.2, 138.9, 134.9, 128.4, 128.2, 127.9, 80.9, 78.2, 75.1, 71.1, 48.5, 41.8, 30.2; IR (Neat) 2980, 1719, 1692, 1679, 1659, 1630, 1549, 1512, 1499, 1452, 1390, 1354, 1323, 1288, 1264, 1164, 1142, 1104, 1063, 1025, 995  $\text{cm}^{-1}$ ; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{16}\text{H}_{13}\text{Cl}_5\text{OK}$   $[\text{M} + \text{K}]^+$  436.9017; Found: 436.9003.

**1-((1*R*<sup>\*</sup>,4*R*<sup>\*</sup>,5*R*<sup>\*</sup>,7*S*<sup>\*</sup>)-5-(4'-Acetylbiphenyl-4-yl)-1,3,4,5,7-pentachlorobicyclo[2.2.1]hept-2-en-2-yl)propan-2-one, **8c**:**



Following the same procedure as for **8a** starting from compound **5f** (20 mg, 0.05 mmol), compound **8c** (17 mg, 68%) was obtained as pale yellow liquid.  $R_f = 0.5$  (30% EtOAc in Hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03 (d,  $J = 8.3$  Hz, 2H), 7.82 (d,  $J = 8.8$  Hz, 2H), 7.69 (d,  $J = 8.3$  Hz, 2H), 7.59 (d,  $J = 8.8$  Hz, 2H), 4.34 (d,  $J = 1.5$  Hz, 1H), 4.05 (dd,  $J = 1.5, 13.7$  Hz, 1H), 3.57 (s, 2H), 3.41 (d,  $J = 13.7$  Hz, 1H), 2.65 (s, 3H), 2.29 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  202.9, 197.7, 144.5, 139.6, 139.3, 139.2, 136.1, 134.7, 128.9, 128.8, 127.1, 126.6, 80.9, 78.2, 74.9, 71.1, 48.6, 41.9, 30.2, 26.7; IR (neat) 2923, 2852, 1721, 1680, 1604, 1417, 1397, 1358, 1323, 1266, 1185, 1165, 1146, 1109, 1024, 1002, 957  $\text{cm}^{-1}$ ; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{24}\text{H}_{19}\text{Cl}_5\text{O}_2\text{Na}$   $[\text{M} + \text{Na}]^+$  538.9696; Found: 538.9662.

**2-((1*R*<sup>\*</sup>,4*R*<sup>\*</sup>,5*R*<sup>\*</sup>,7*S*<sup>\*</sup>)-1,3,4,5,7-Pentachloro-5-phenylbicyclo[2.2.1]hept-2-en-2-yl)-1-phenylethanone (**8b**):**

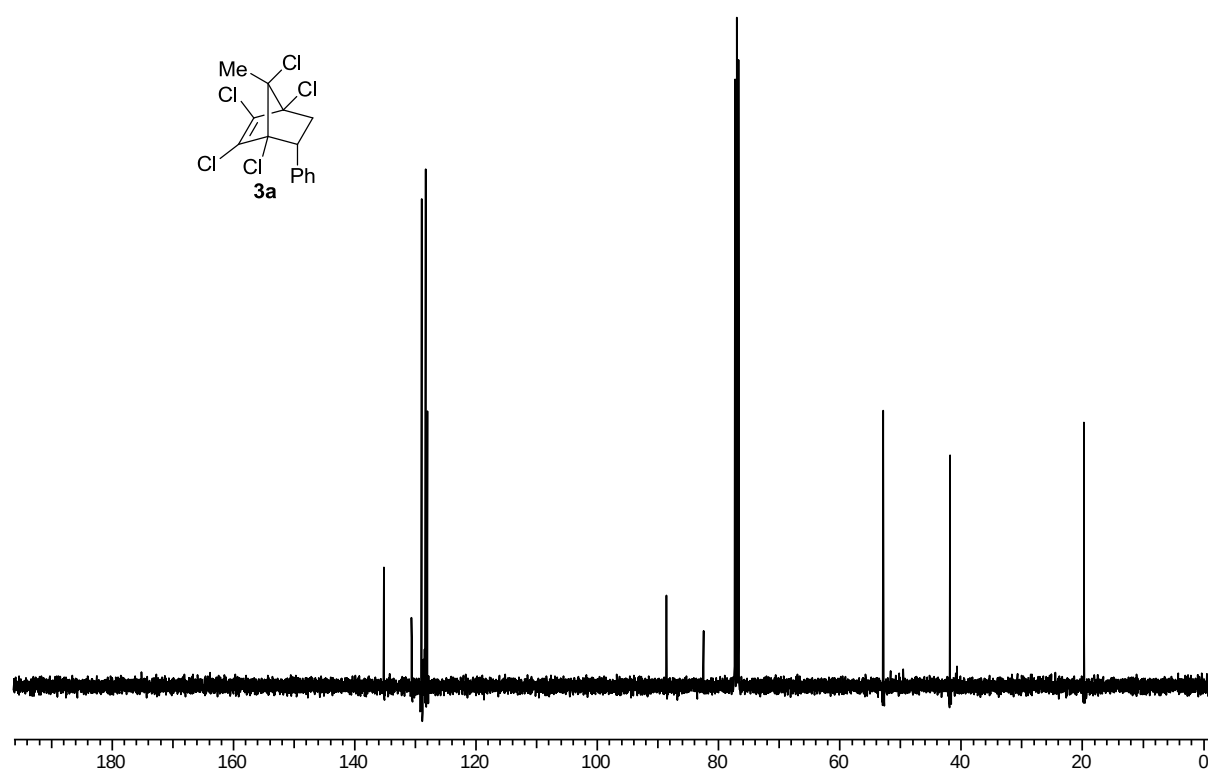
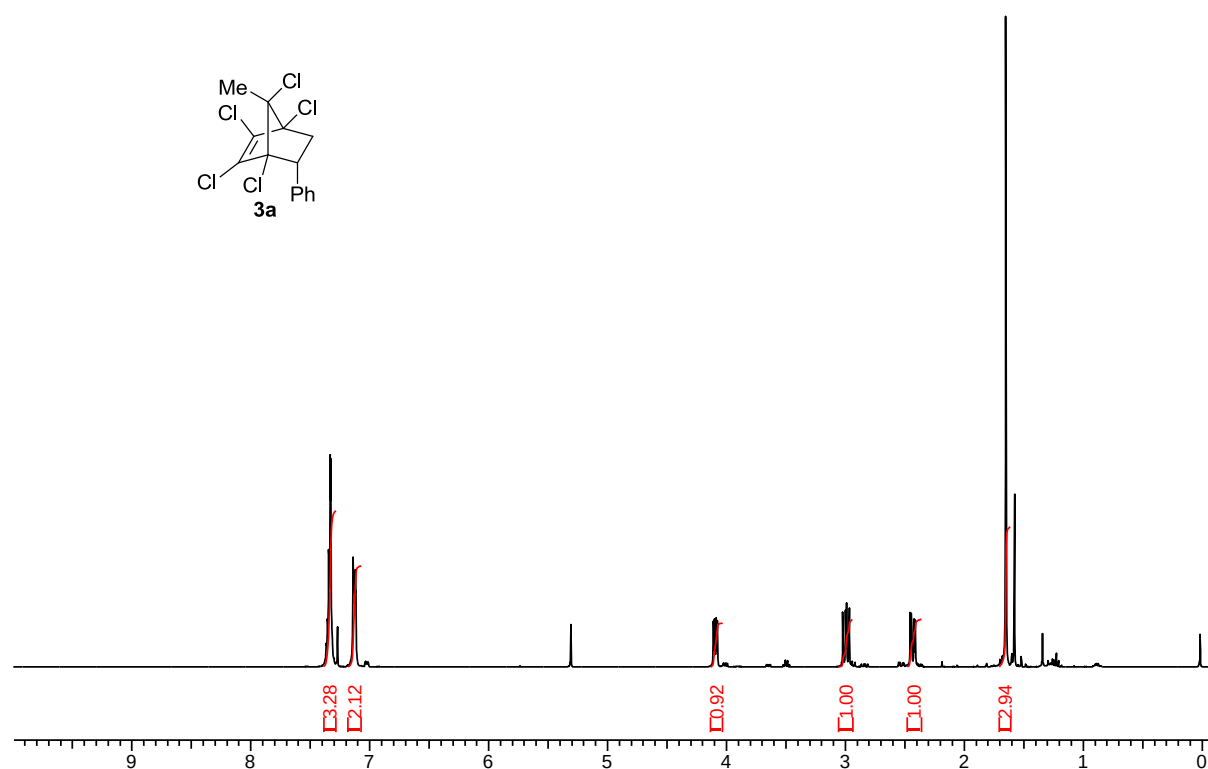


Following the same procedure as for **8a** starting from compound **5a** (45 mg, 0.14 mmol), compound **8b** (36 mg, 61%) instead of acetyl chloride, benzoyl chloride was used, obtained as colorless liquid;  $R_f = 0.5$  (5% EtOAc in Hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 - 7.96 (m, 2H), 7.79 - 7.72 (m, 2H), 7.68 - 7.59 (m, 1H), 7.56 - 7.48 (m, 2H), 7.32 - 7.24 (m, 3H), 4.40 (d,  $J = 1.5$  Hz, 1H), 4.18 (dd,  $J = 1.5, 13.7$  Hz, 1H), 4.10 (d,  $J = 6.4$  Hz, 2H), 3.43 (d,  $J = 13.7$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  194.5, 139.5, 139.3, 135.9, 135.1, 133.9, 128.9, 128.4, 128.3, 127.9, 81.1, 78.3, 75.2, 71.3, 48.7, 37.6; IR (neat) 2972, 2820, 1759,

1684, 1631, 1596, 1549, 1512, 1499, 1446, 1330, 1281, 1257, 1217, 1180, 1105, 1029, 989  $\text{cm}^{-1}$ ; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{21}\text{H}_{15}\text{Cl}_5\text{OK}$   $[\text{M} + \text{K}]^+$  498.9173; Found: 498.9146.

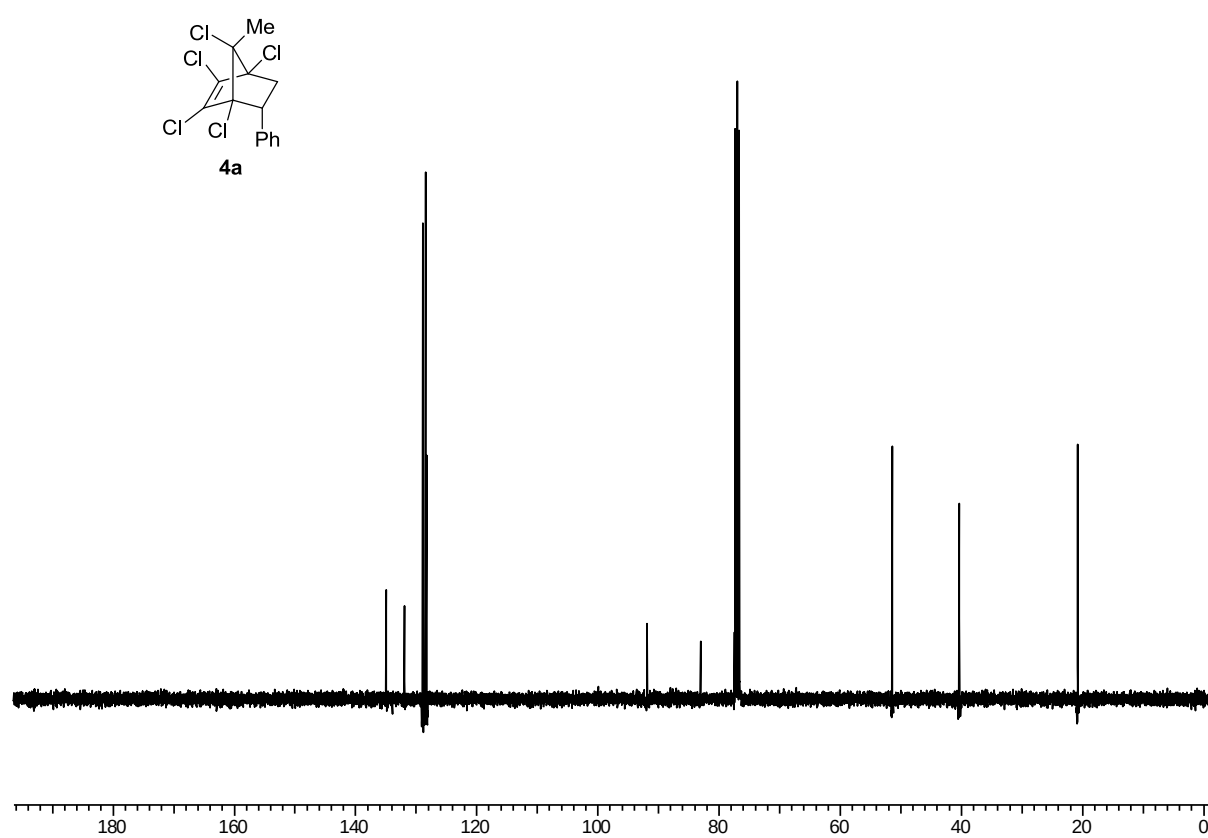
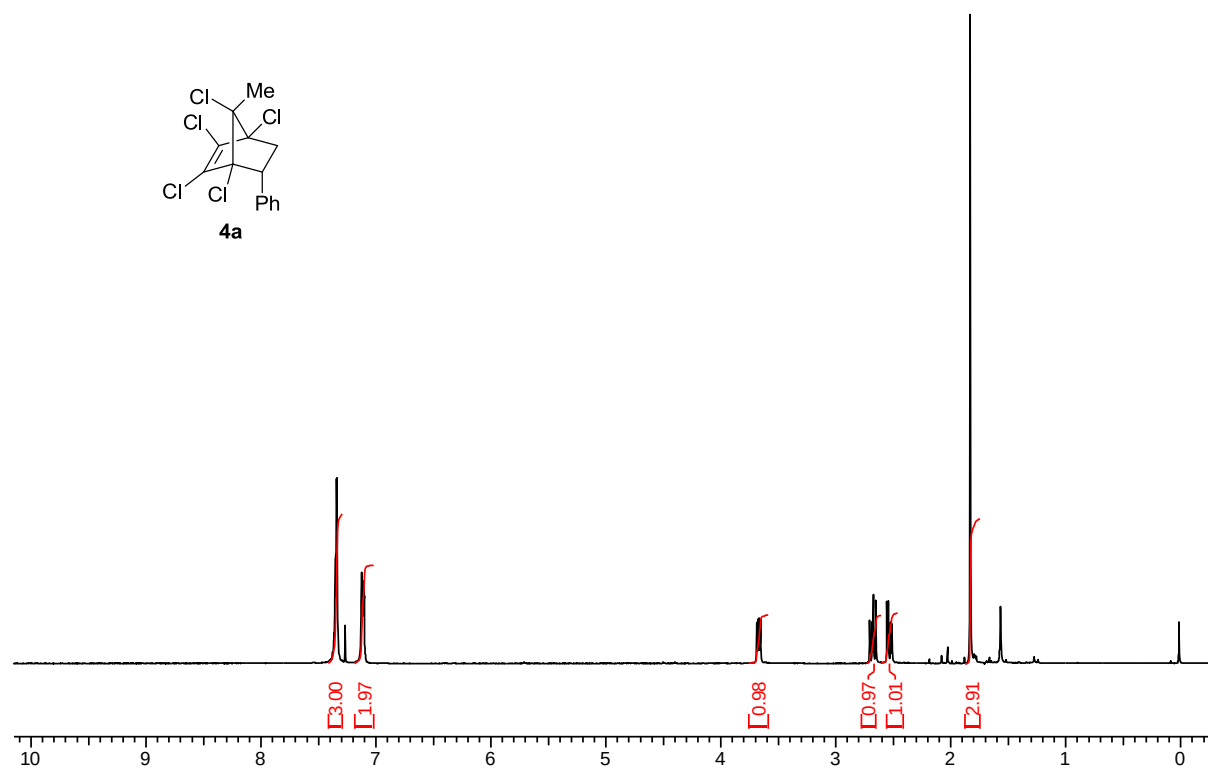
Copies of  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR spectra of DA adducts 3/4 :

$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) of 3a in  $\text{CDCl}_3$ :

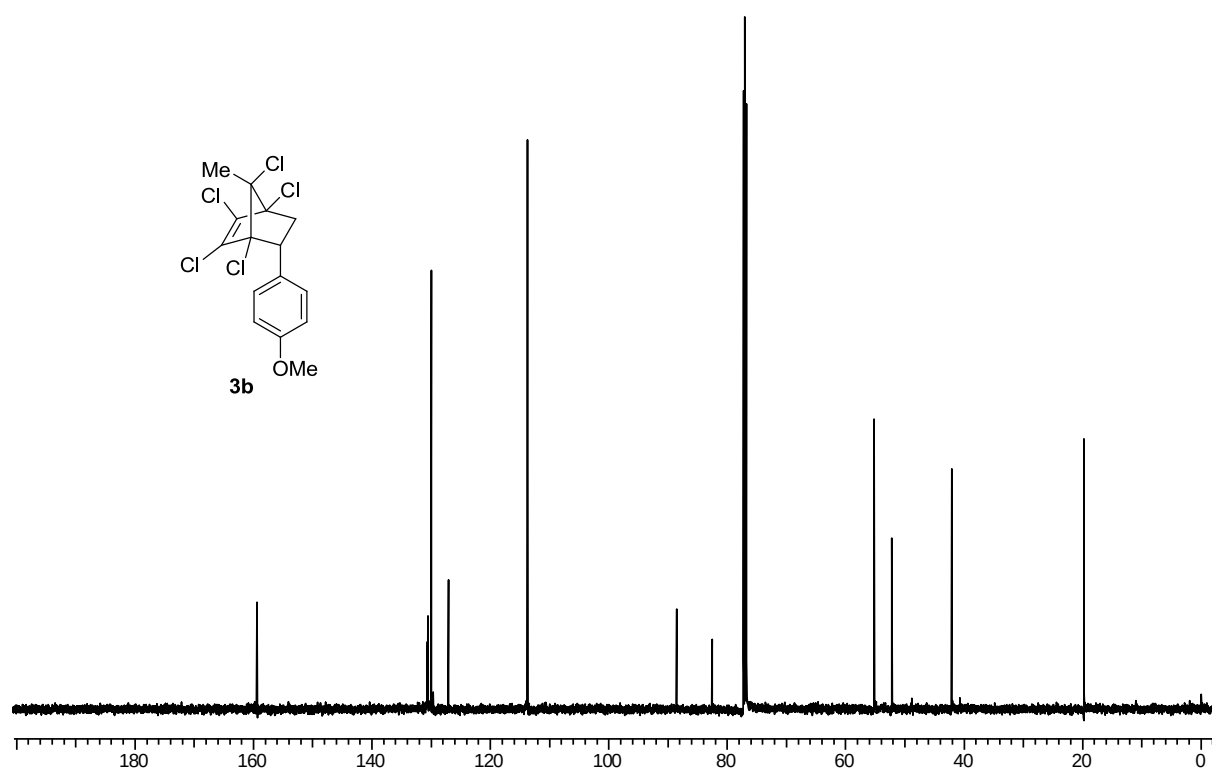
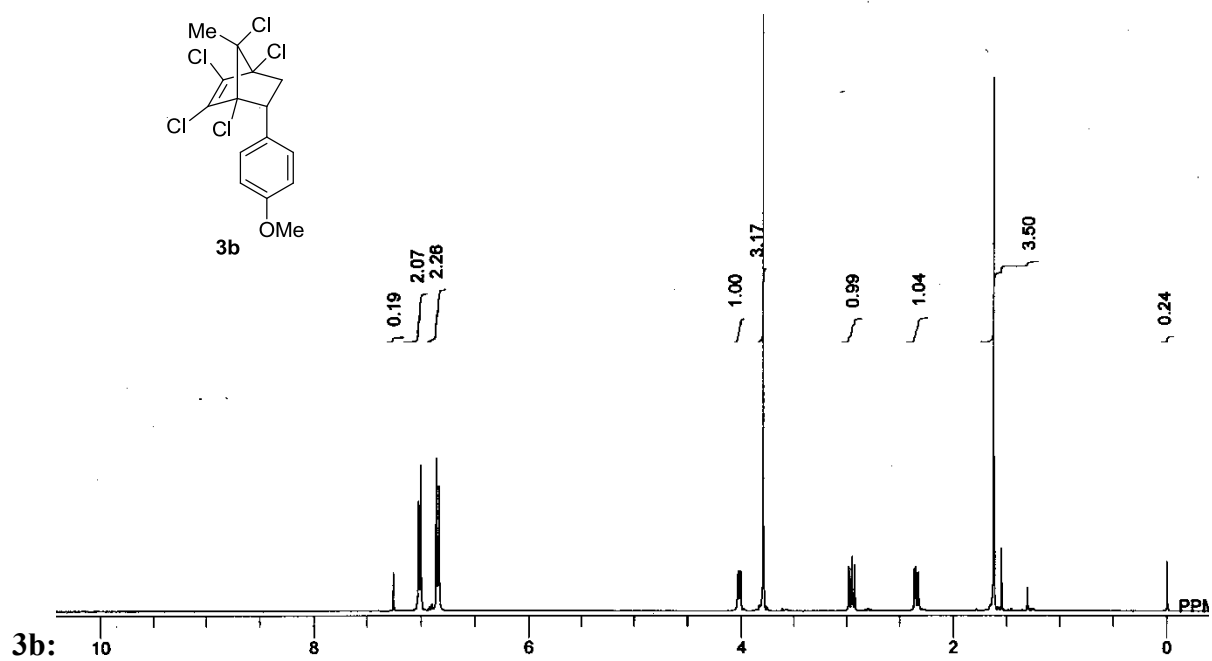




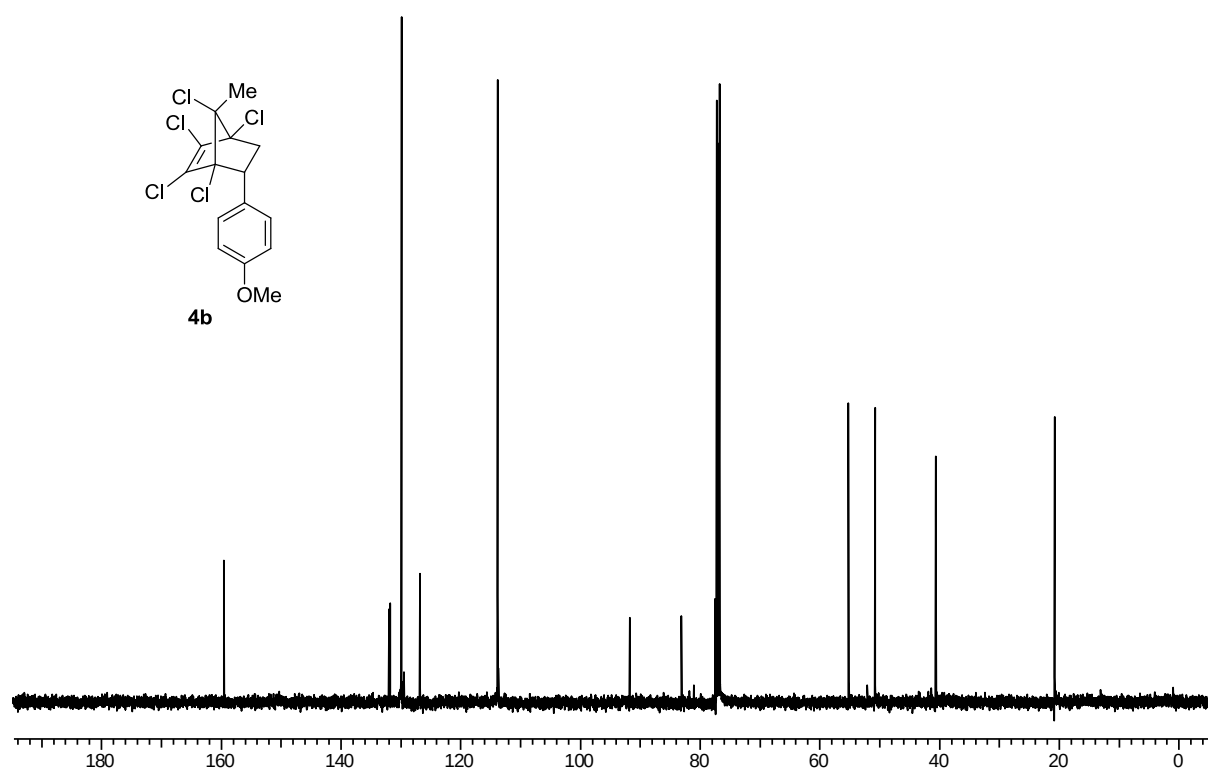
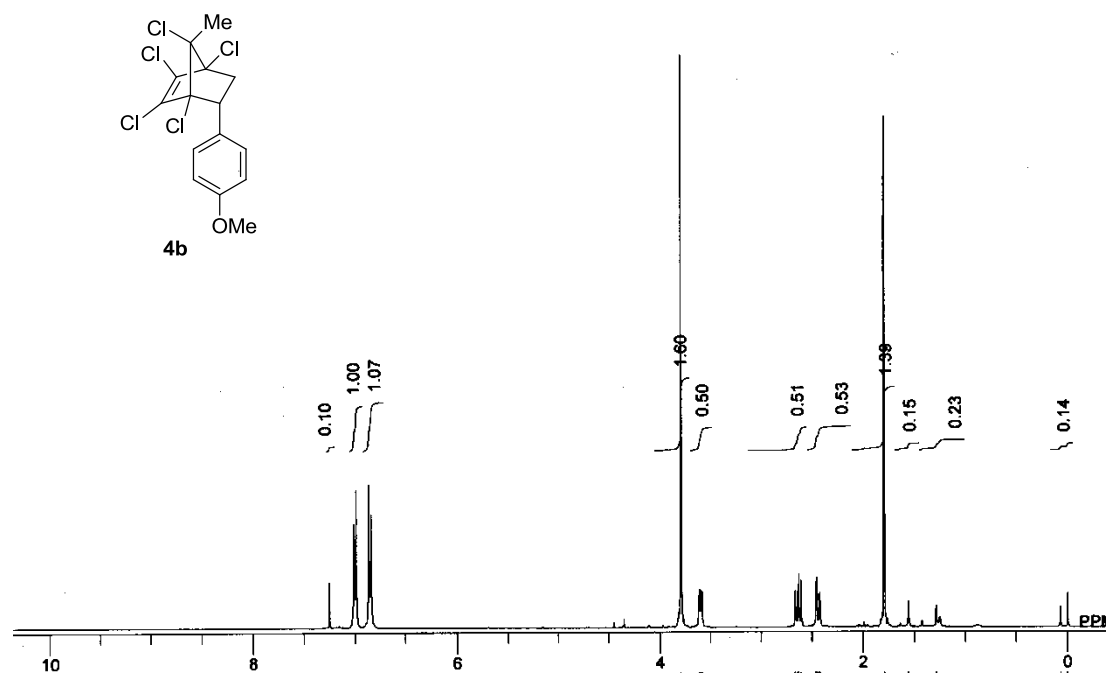
**$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) of 4a in  $\text{CDCl}_3$ :**



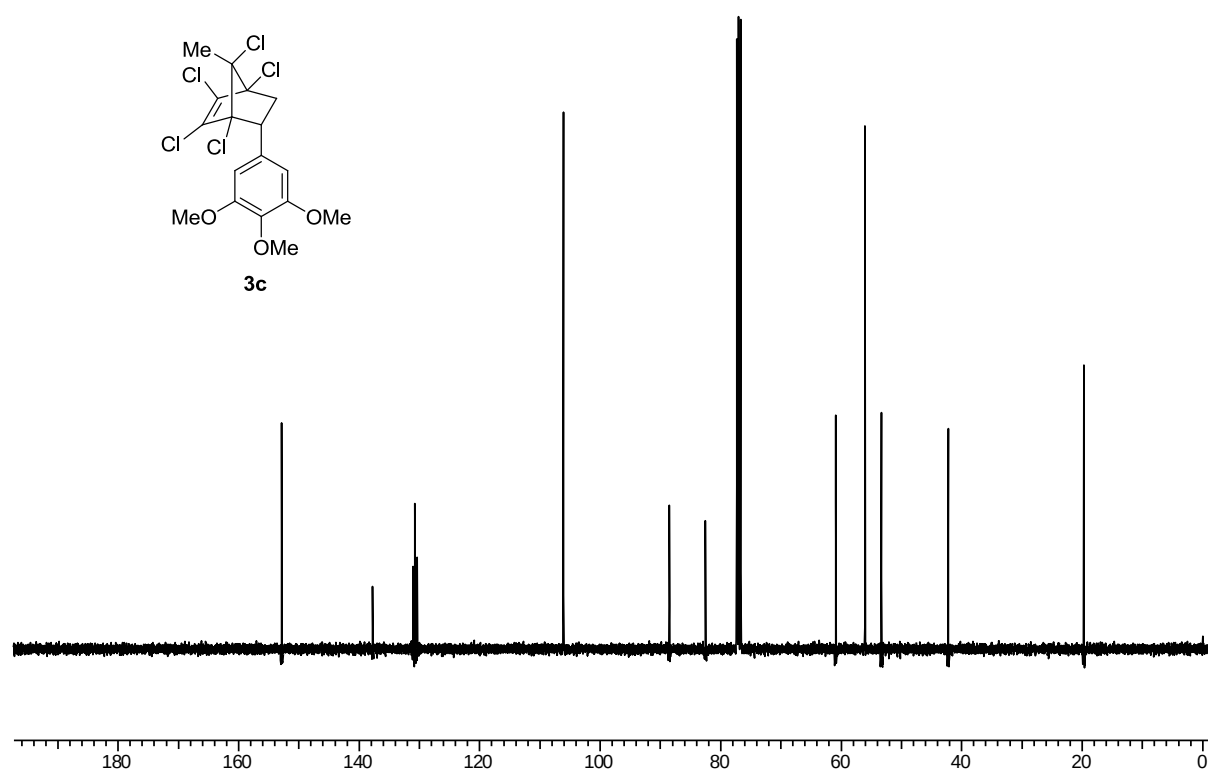
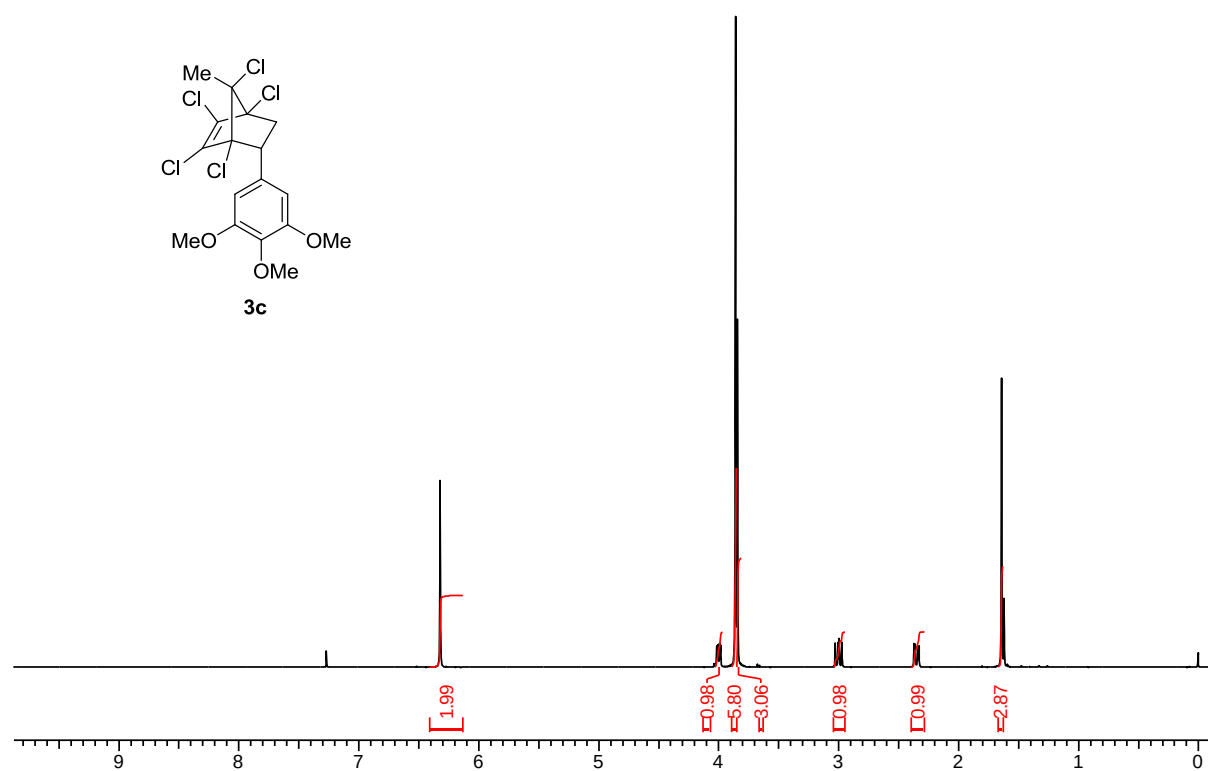
**$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (125 MHz) of 3b in  $\text{CDCl}_3$ :**



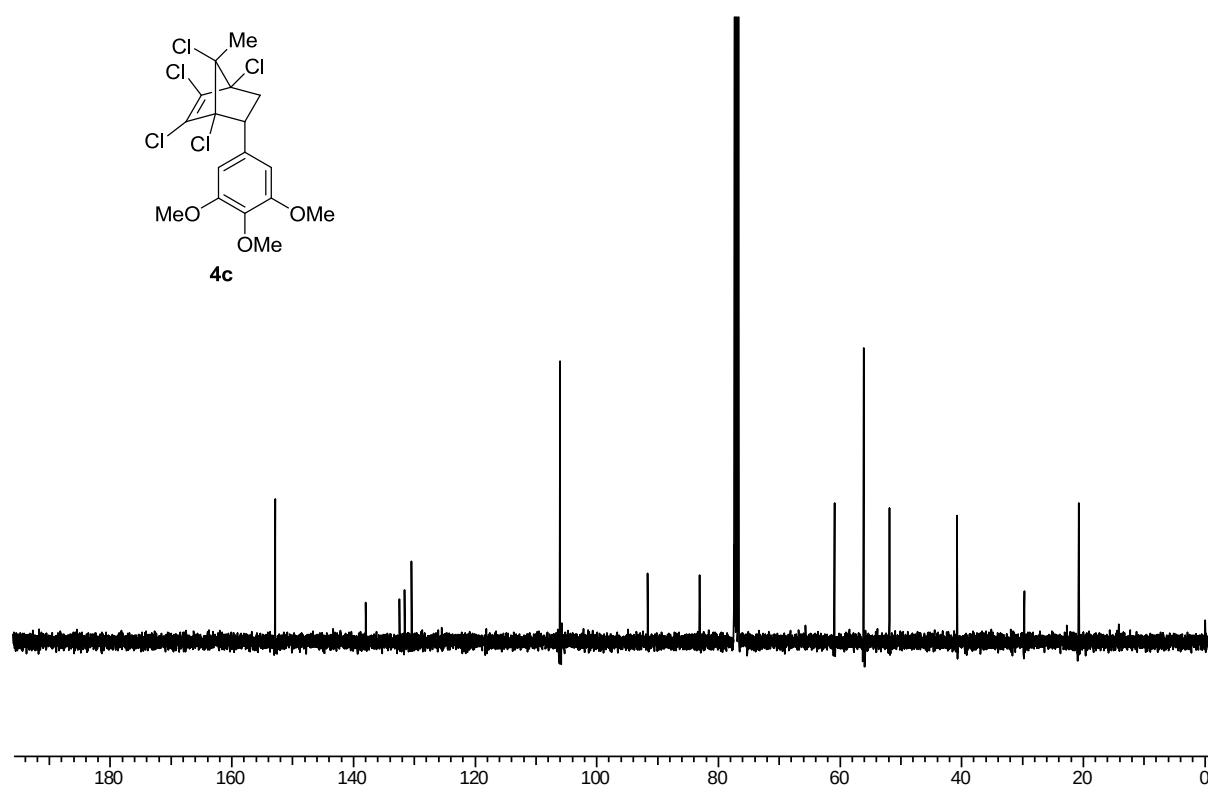
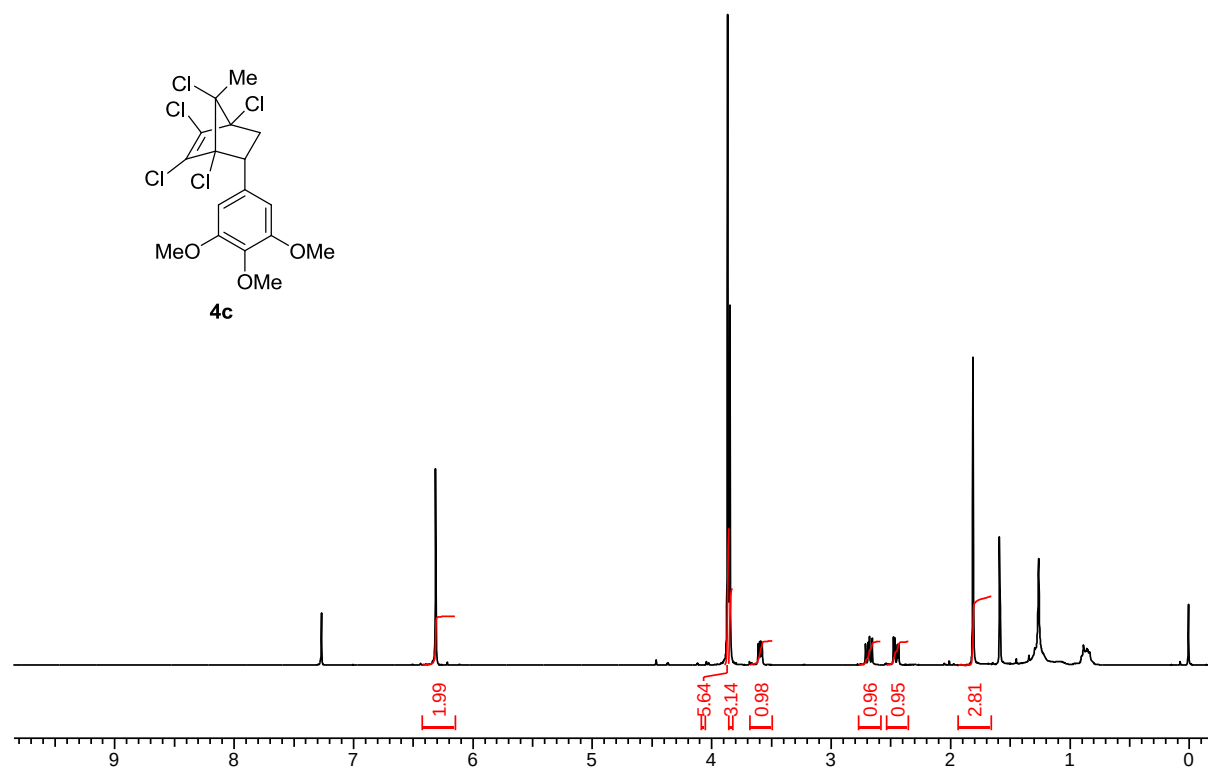
**$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (125 MHz) of 4b in  $\text{CDCl}_3$ :**



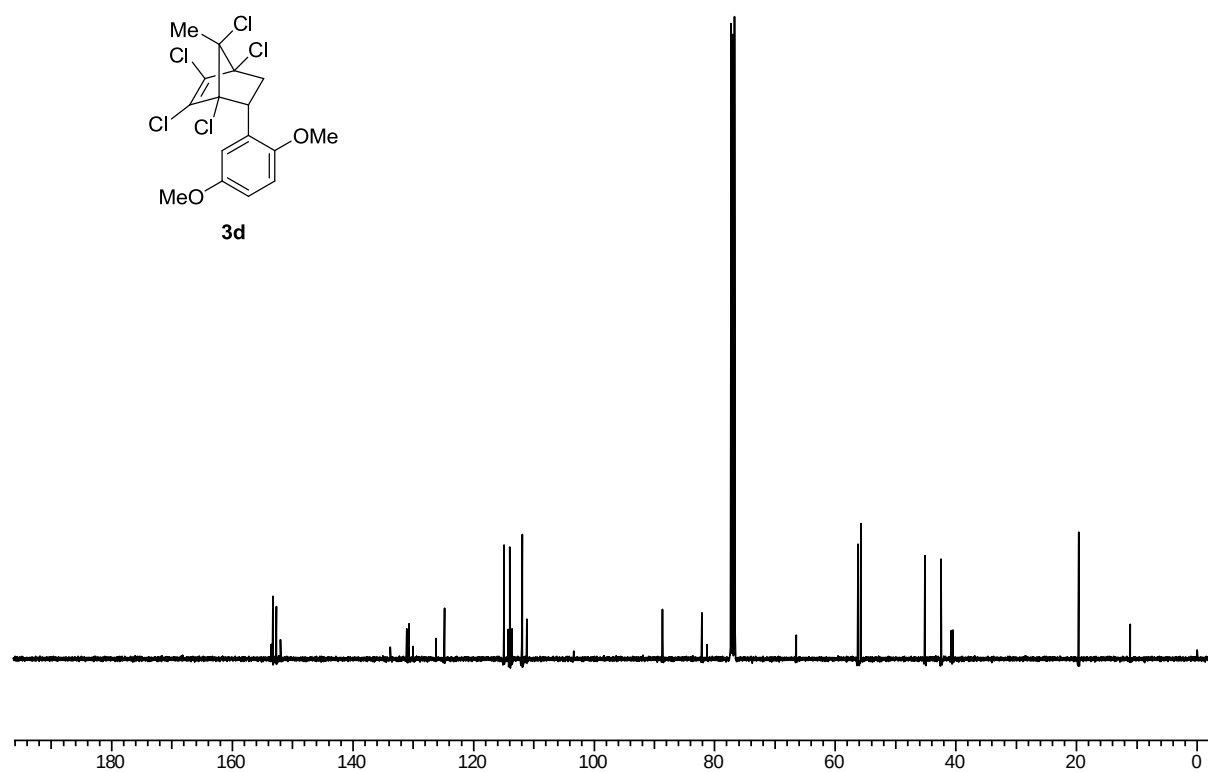
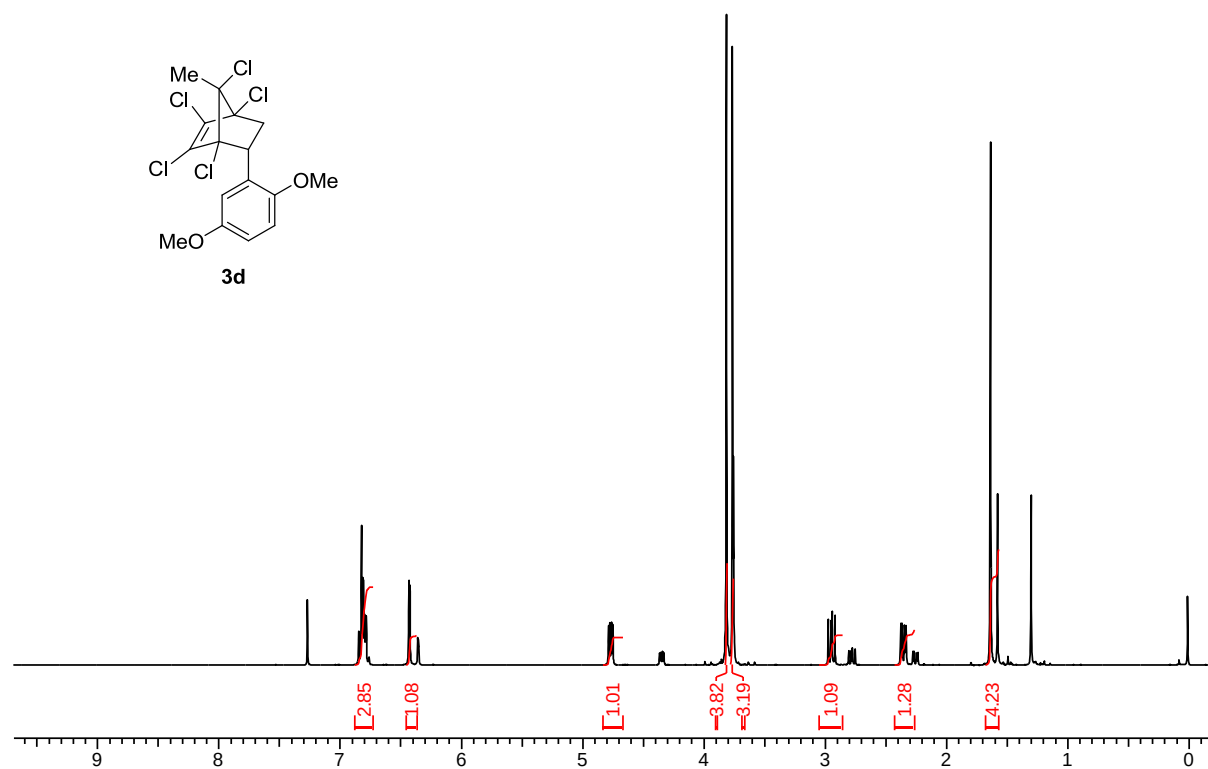
**$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) of **3c** in  $\text{CDCl}_3$ :**



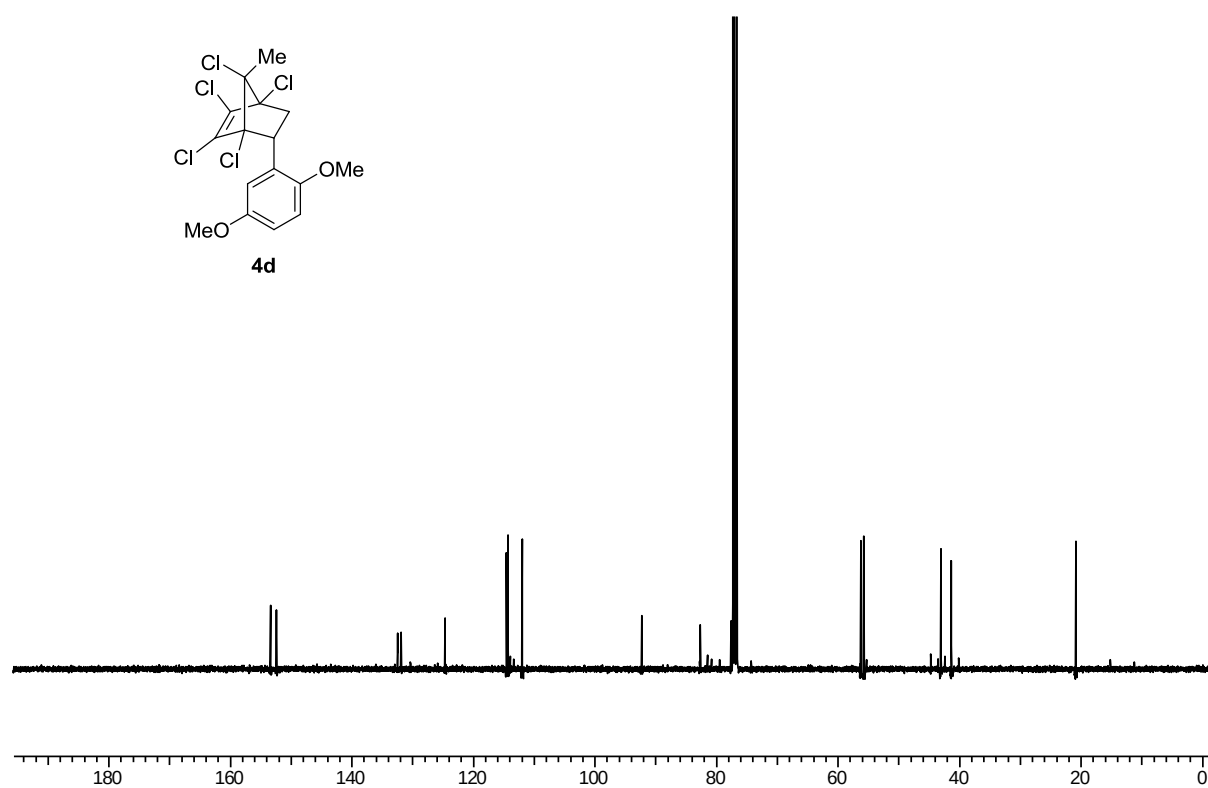
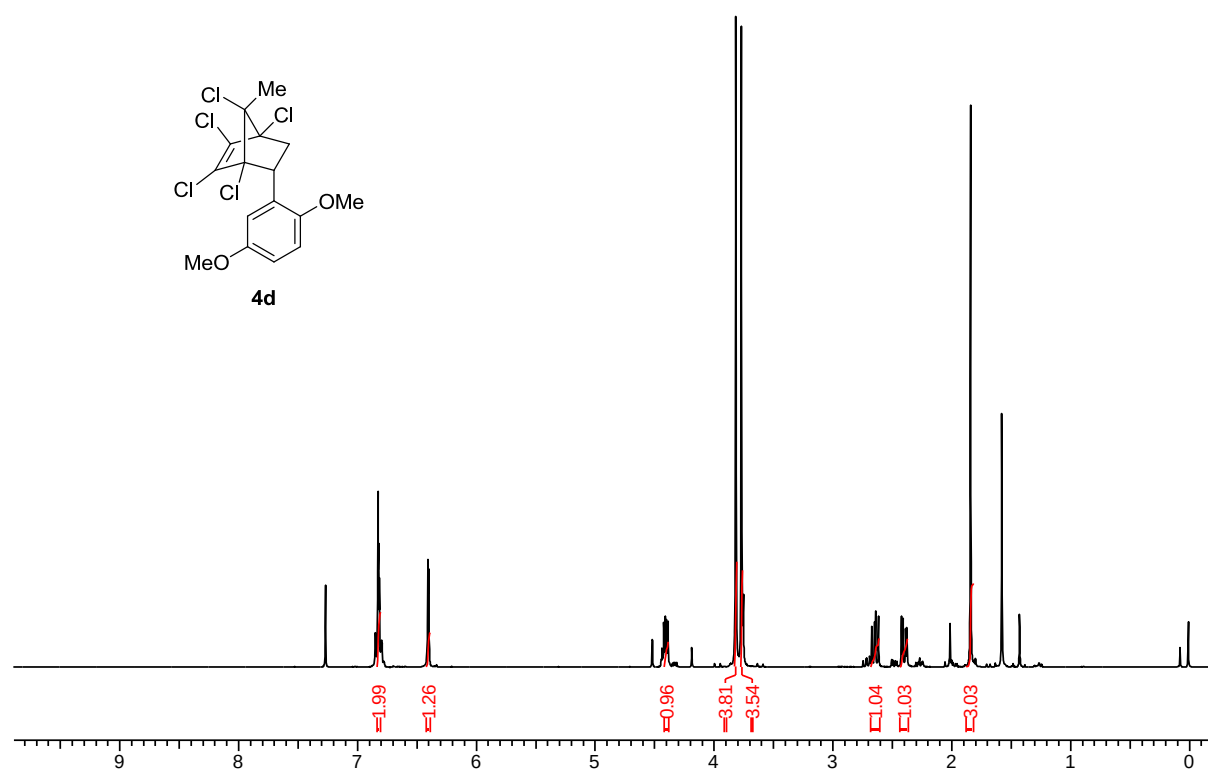
**$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) of 4c in  $\text{CDCl}_3$ :**



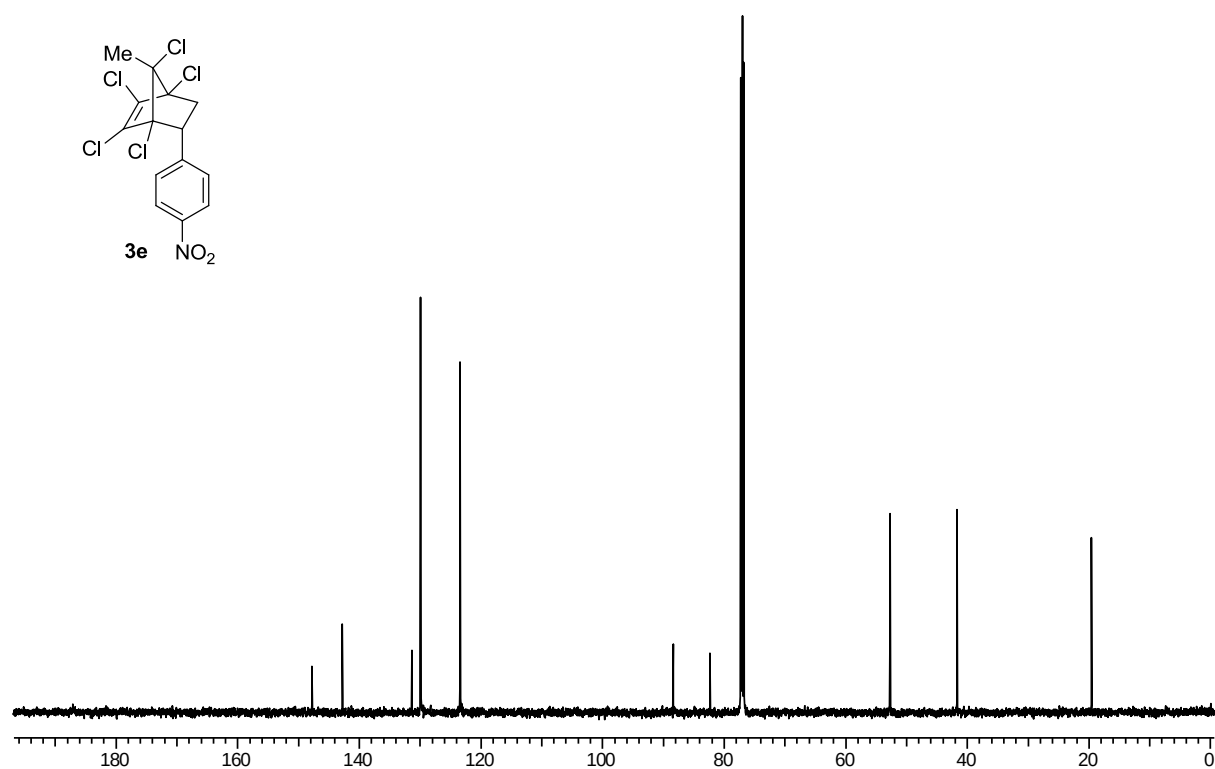
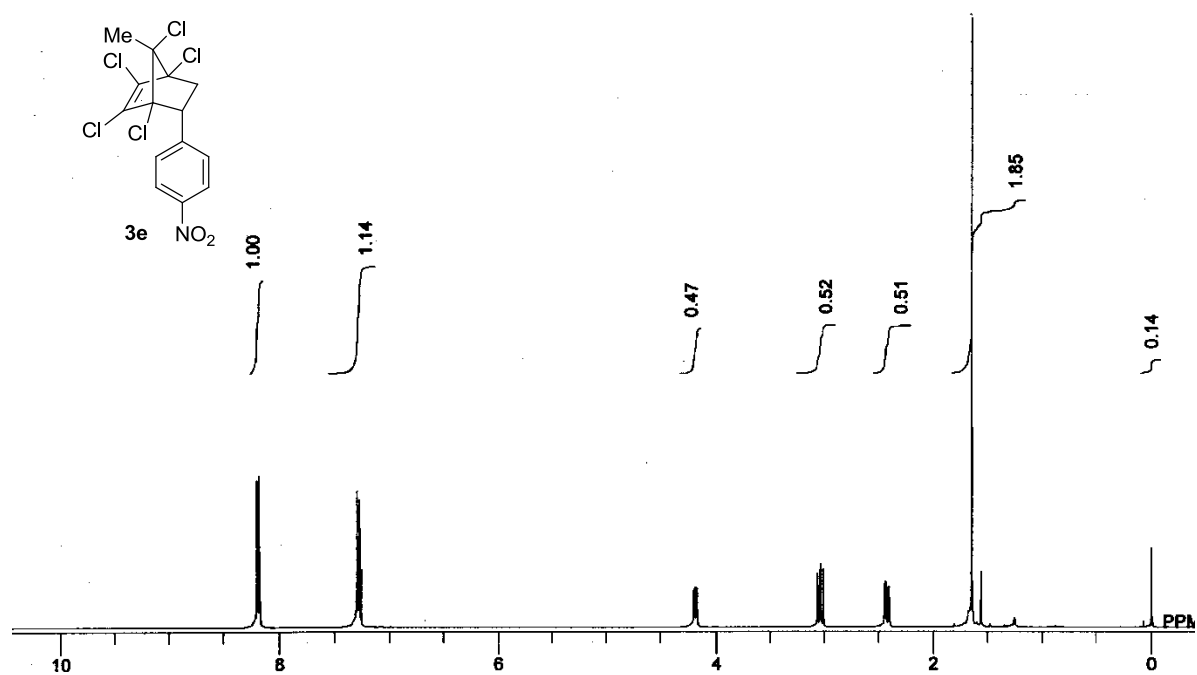
**$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) of **3d** in  $\text{CDCl}_3$ :**



**$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) of 4d in  $\text{CDCl}_3$ :**

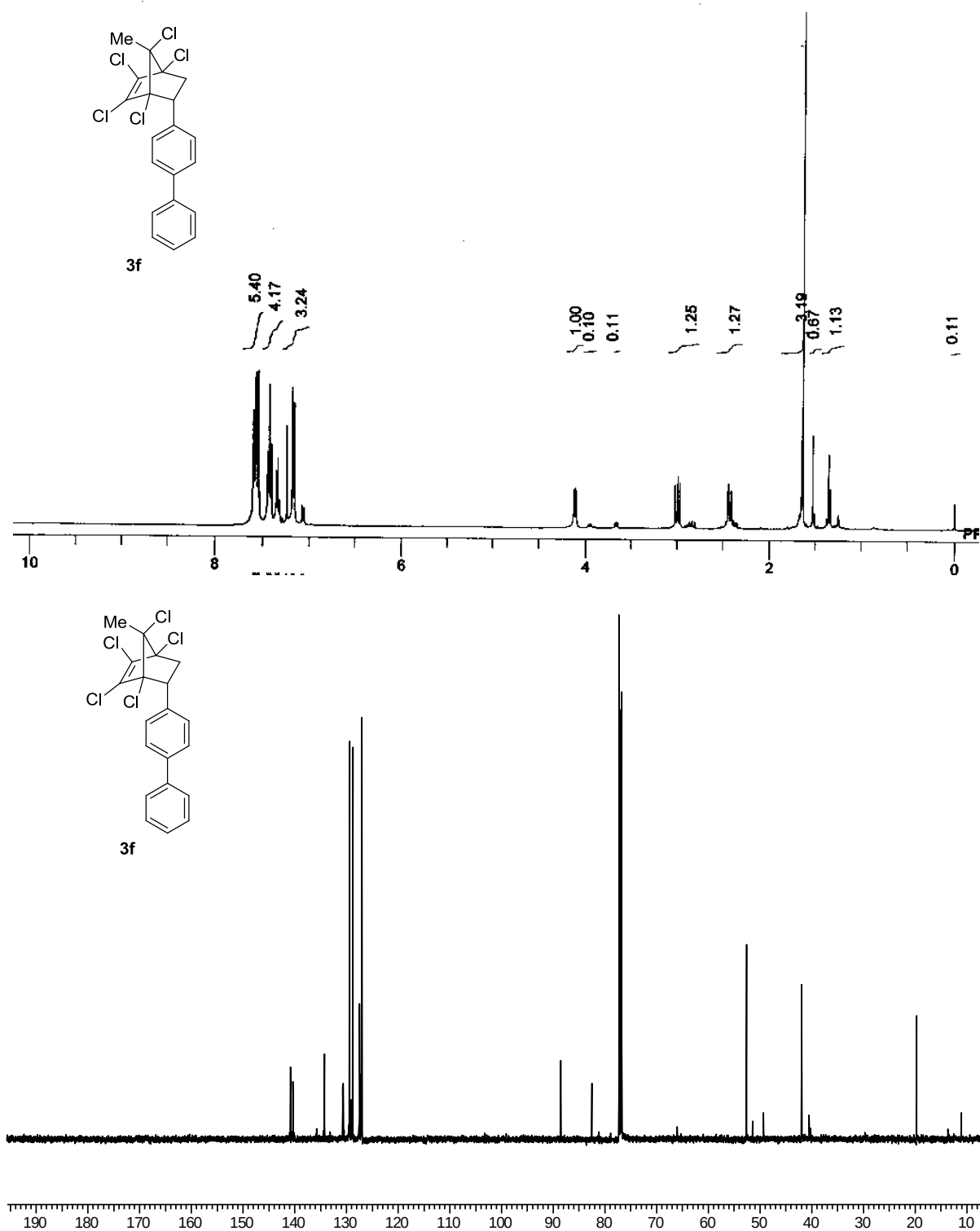


$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (125 MHz) of 3e in  $\text{CDCl}_3$ :

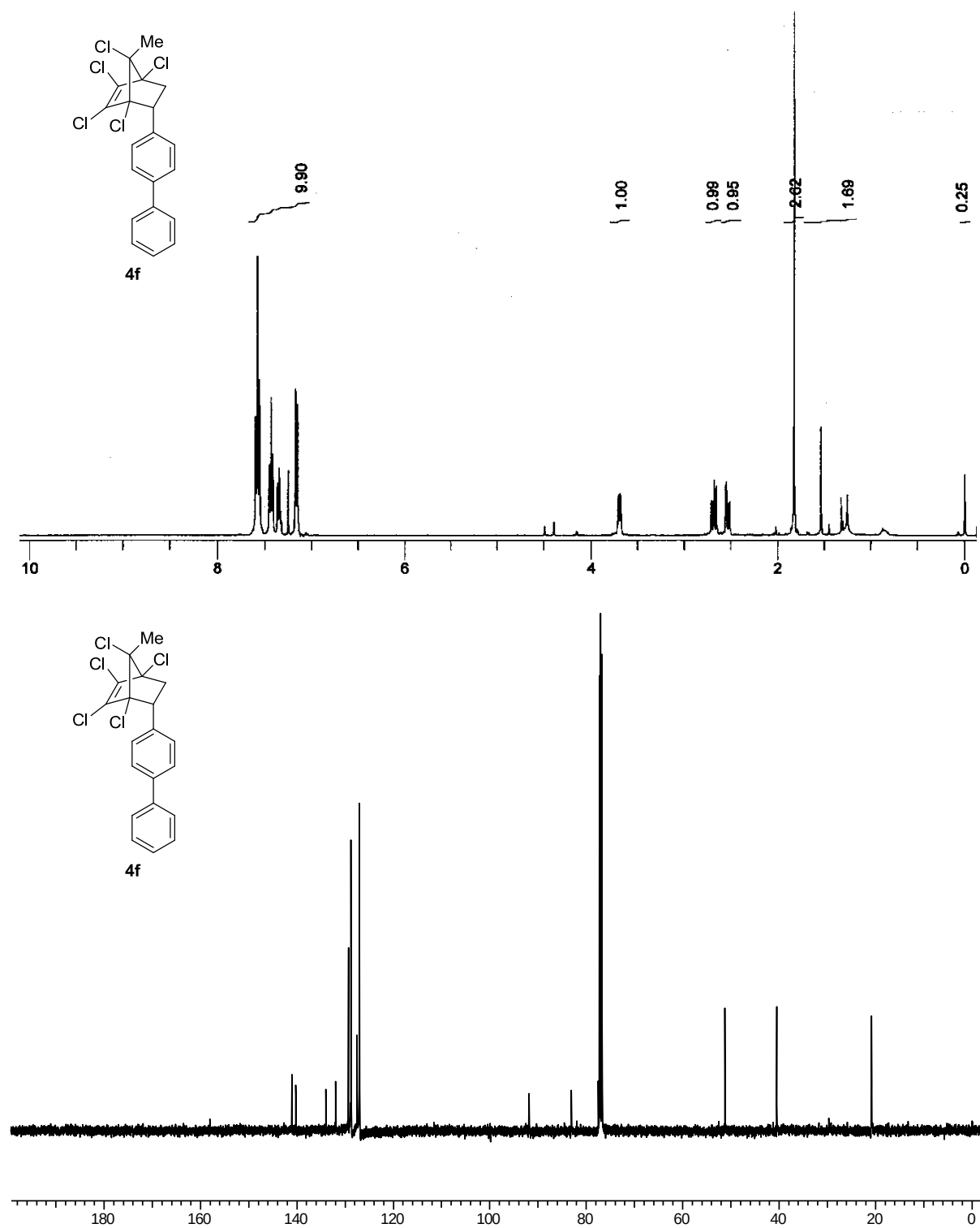




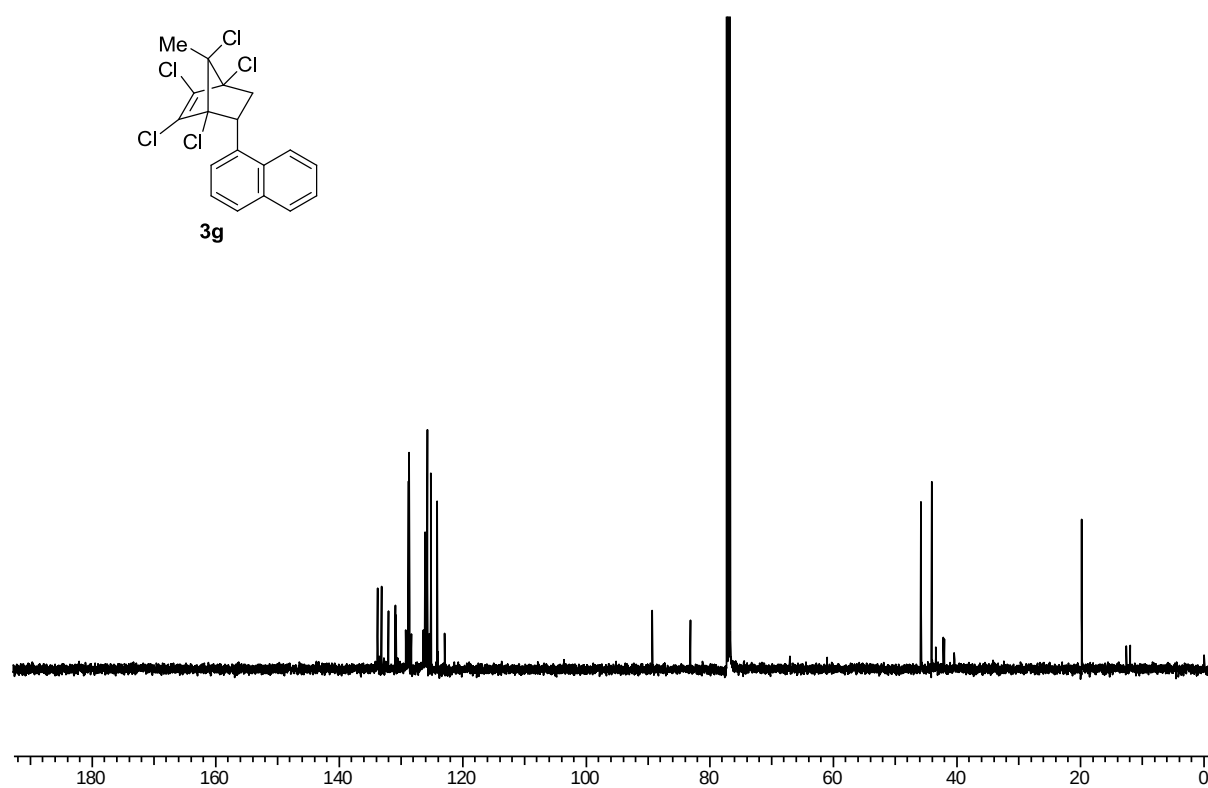
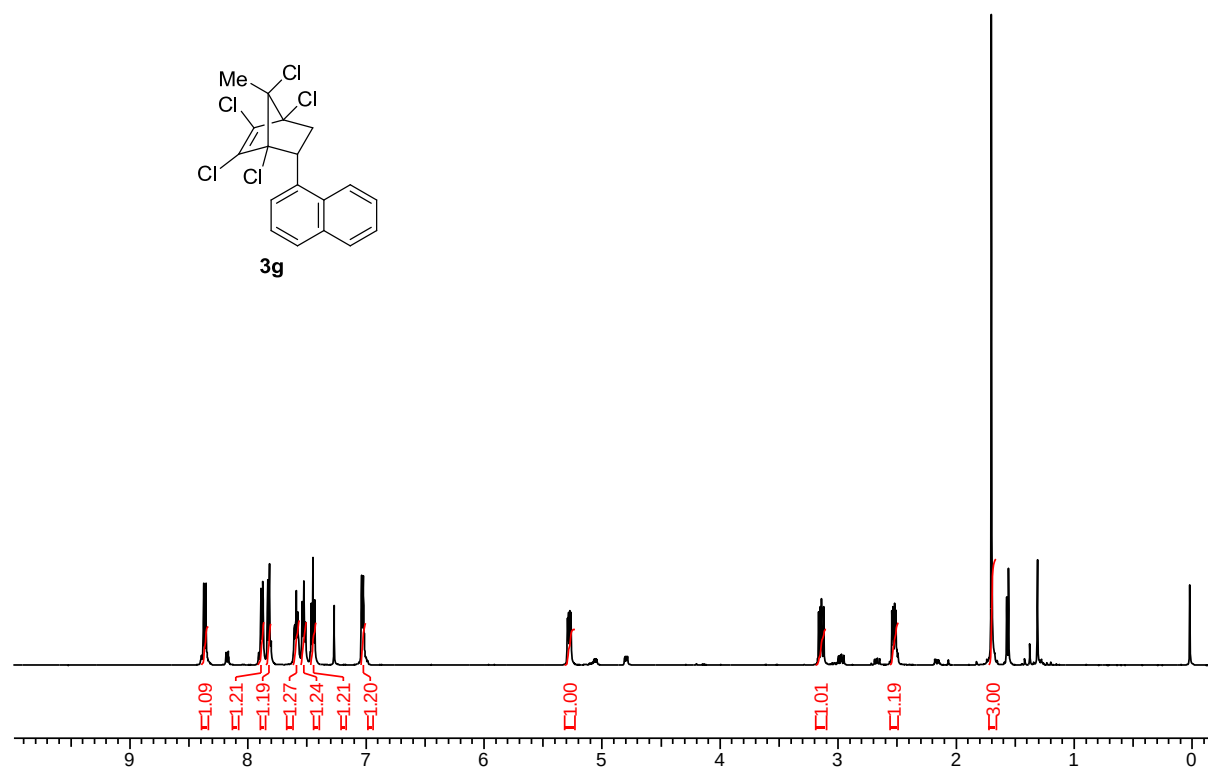
$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (125 MHz) of 3f in  $\text{CDCl}_3$ :



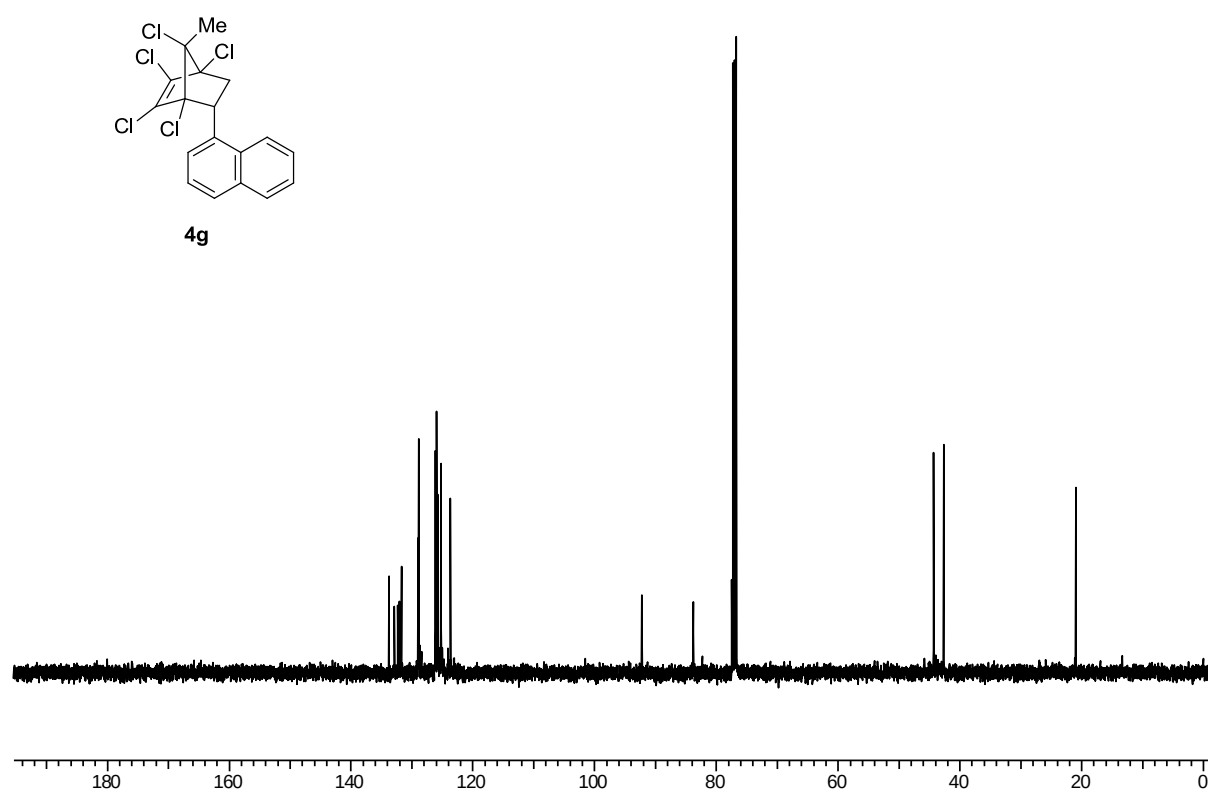
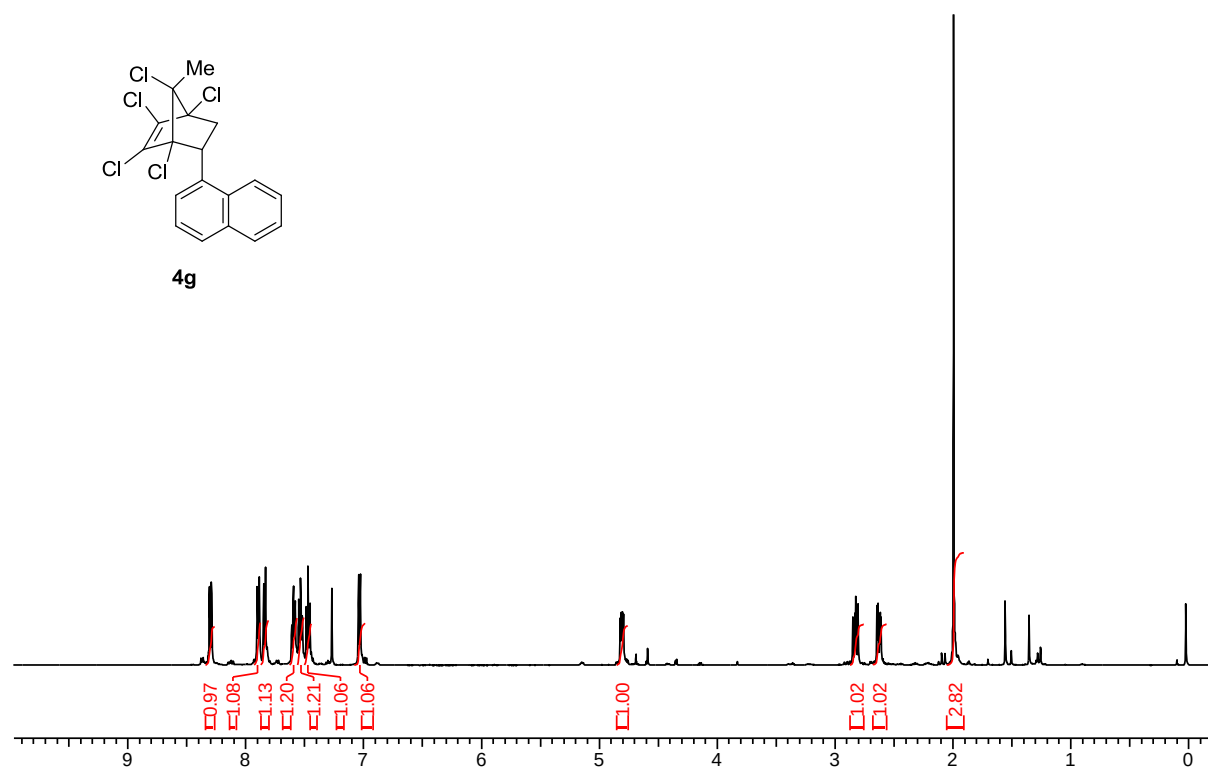
$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (125 MHz) of 4f in  $\text{CDCl}_3$ :



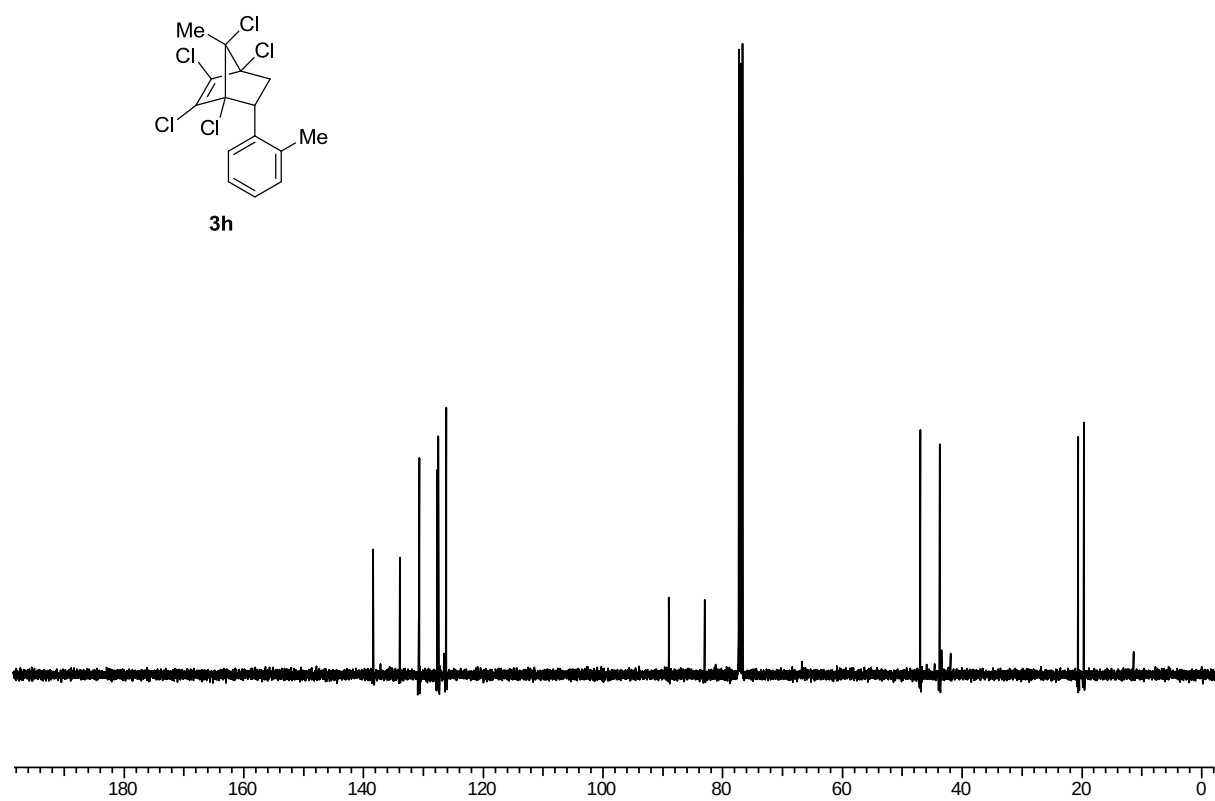
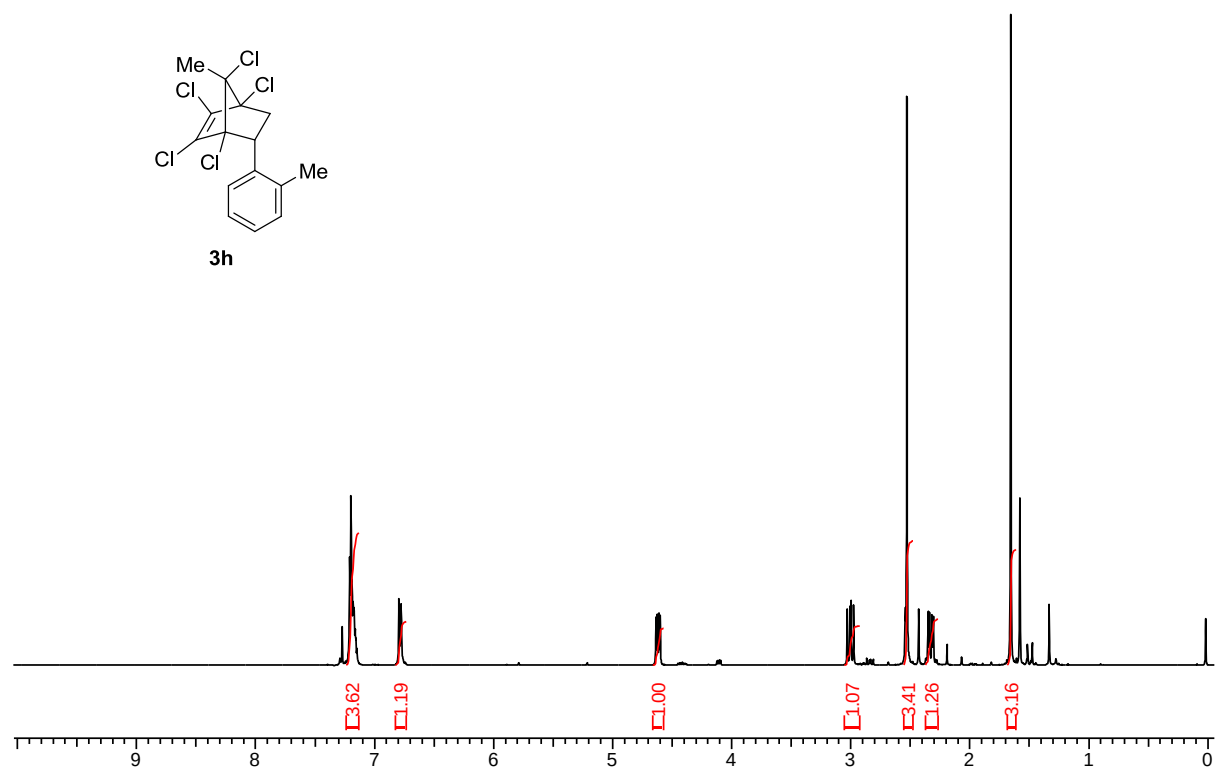
**$^1\text{H}$  NMR (500 MHz) and  $^{13}\text{C}$  NMR (125 MHz) of 3g in  $\text{CDCl}_3$ :**



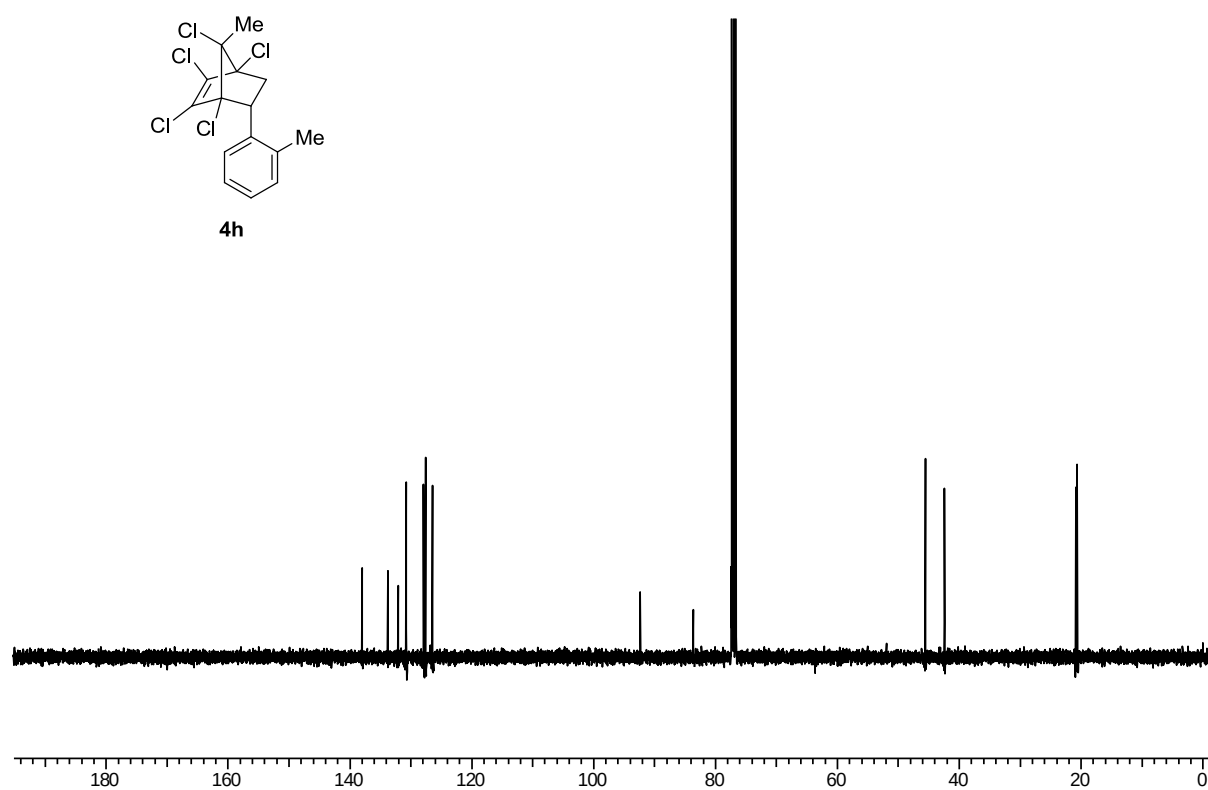
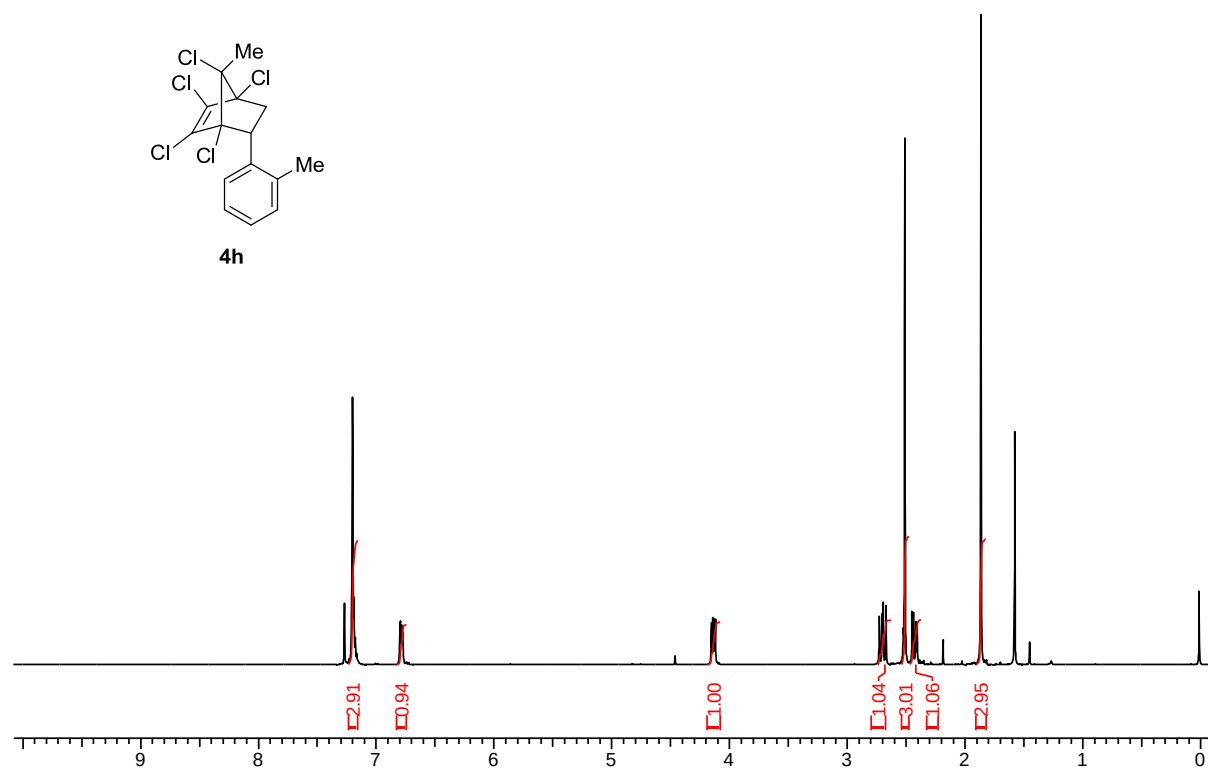
**$^1\text{H}$  NMR (500 MHz) and  $^{13}\text{C}$  NMR (125 MHz) of 4g in  $\text{CDCl}_3$ :**



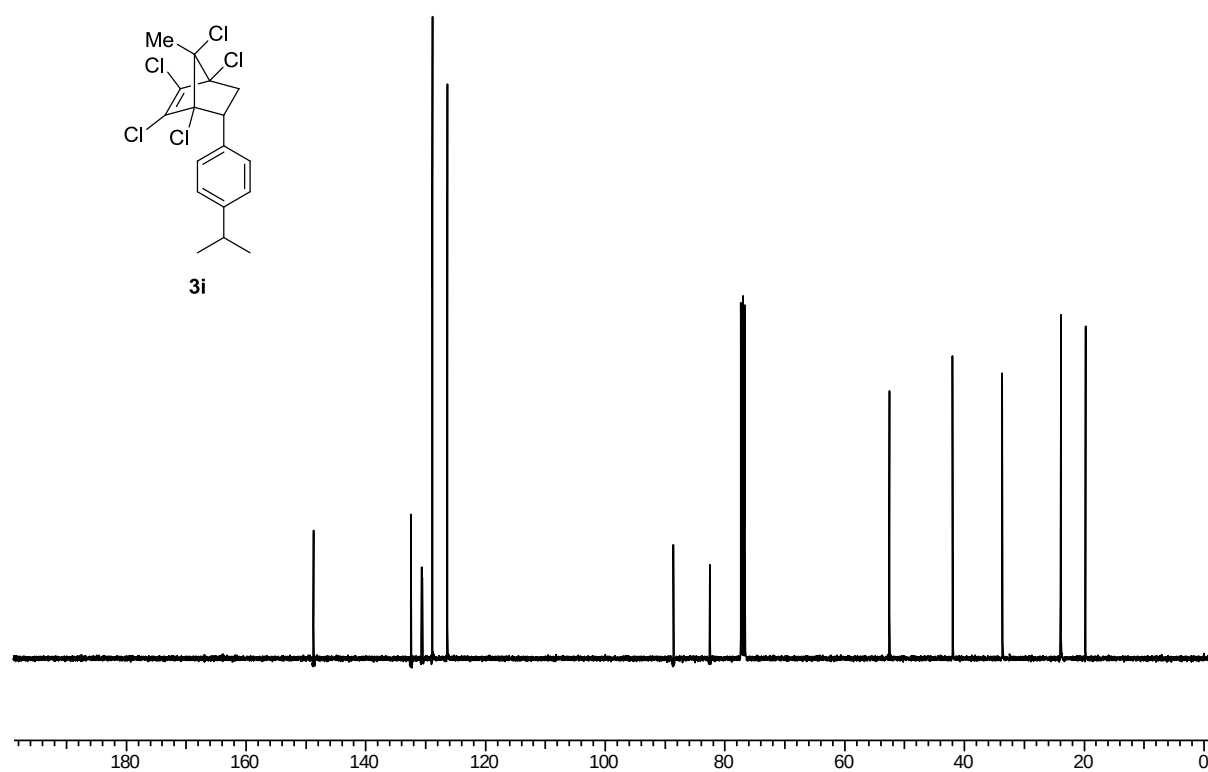
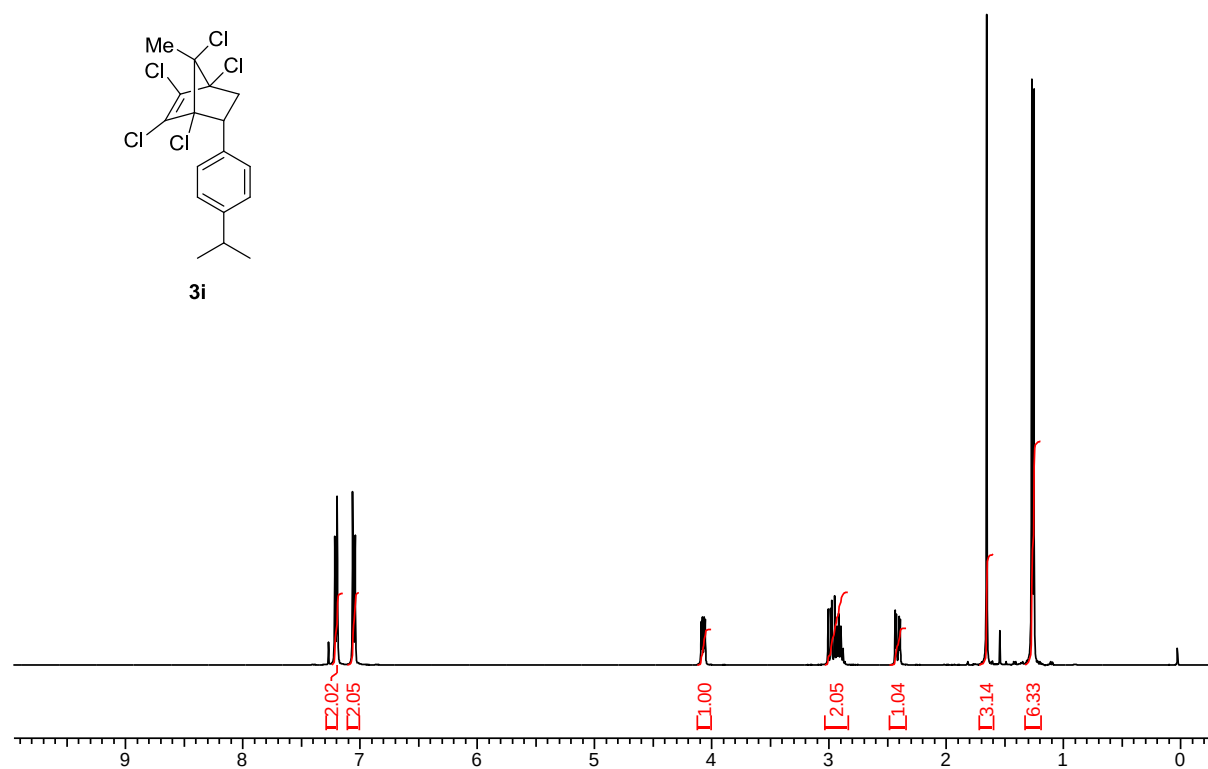
**$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) of 3h in  $\text{CDCl}_3$ :**



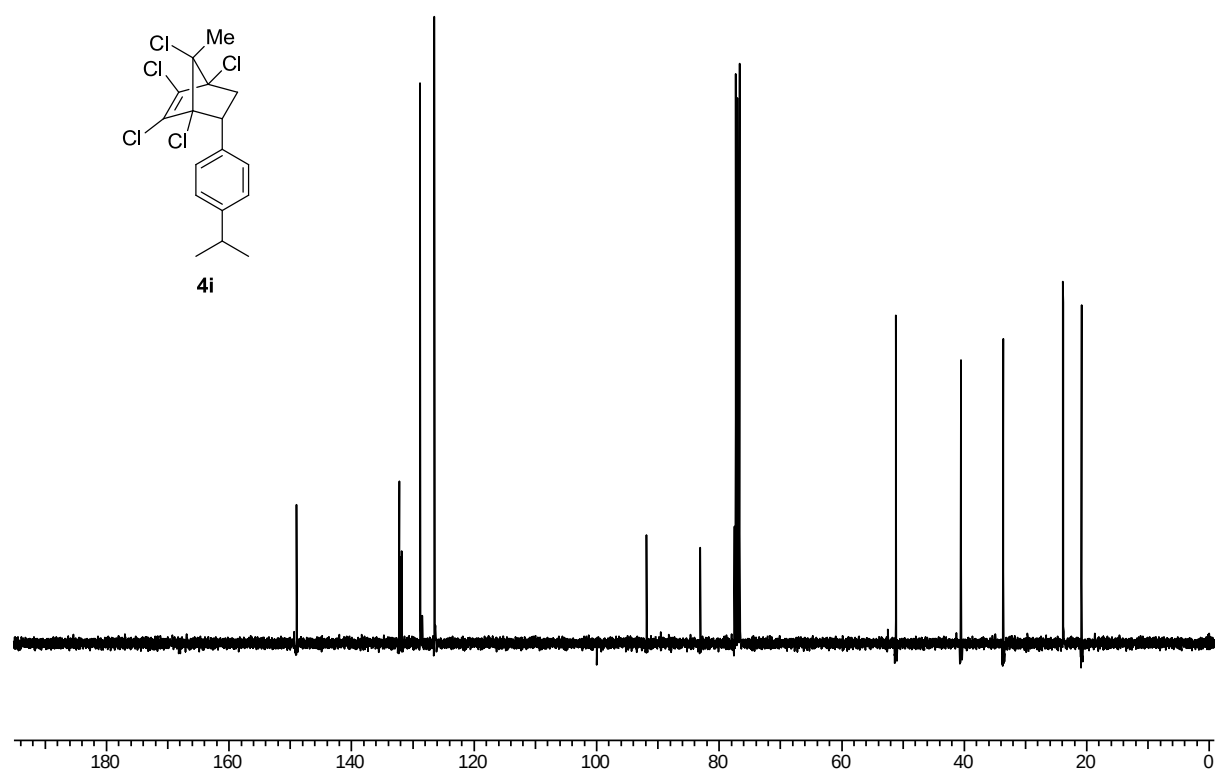
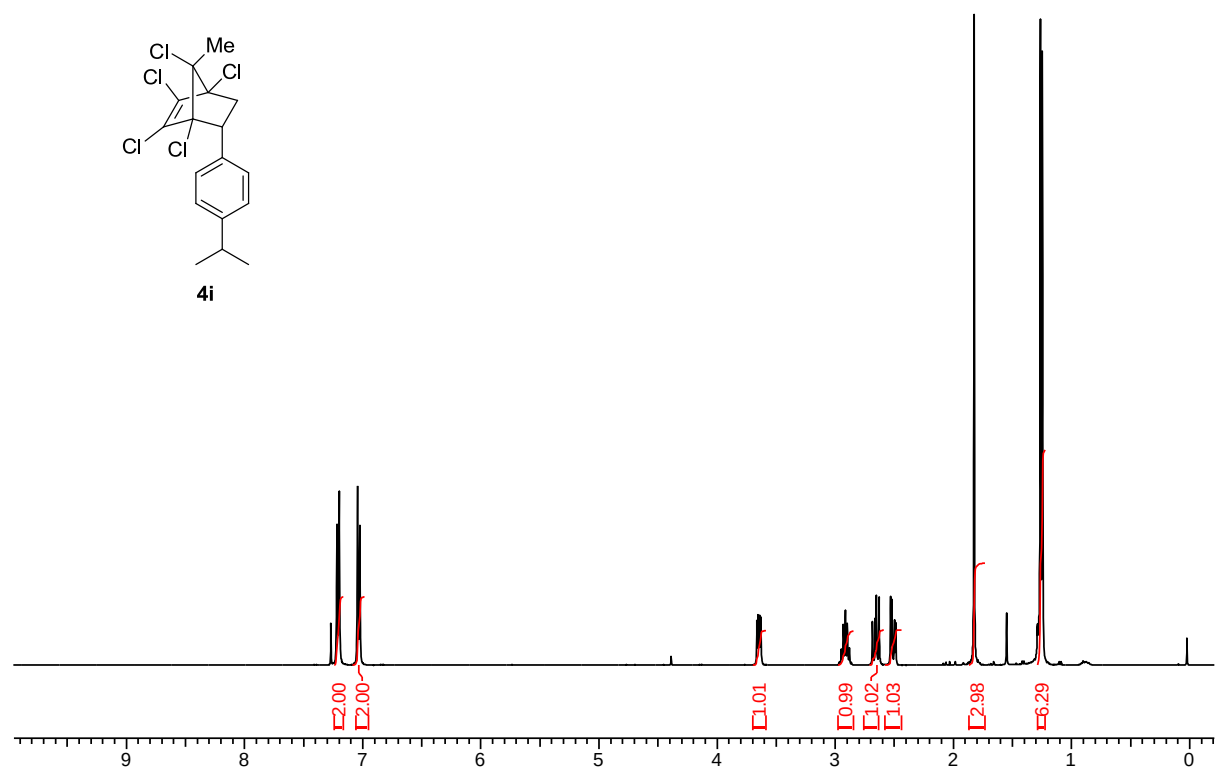
**$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) of 4h in  $\text{CDCl}_3$ :**



**$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) of 3i in  $\text{CDCl}_3$ :**

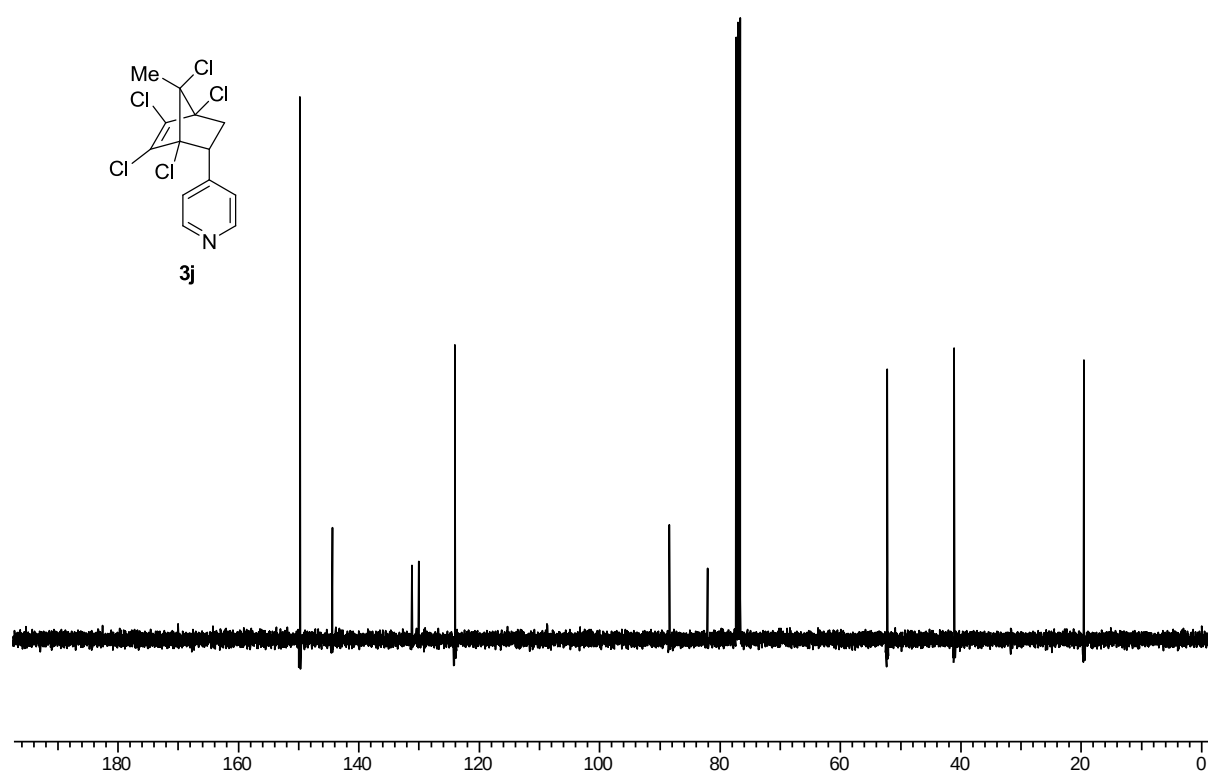
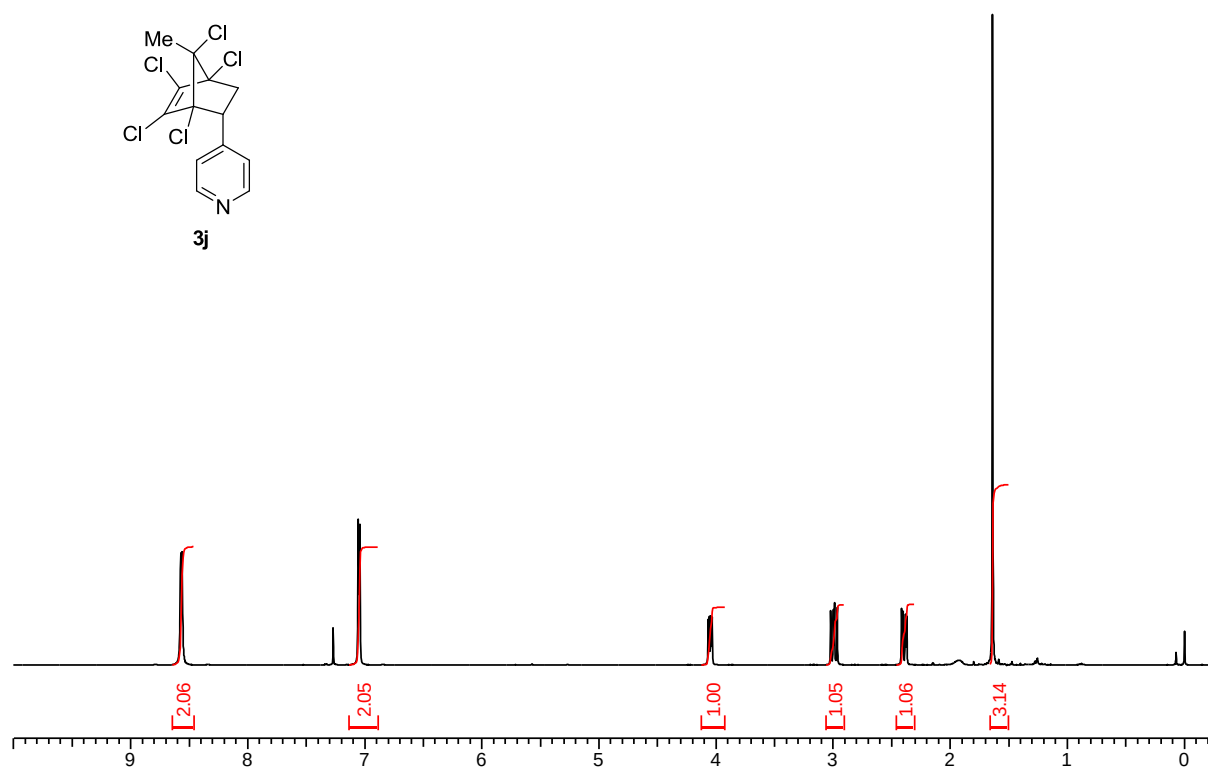


**$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) of 4i in  $\text{CDCl}_3$ :**

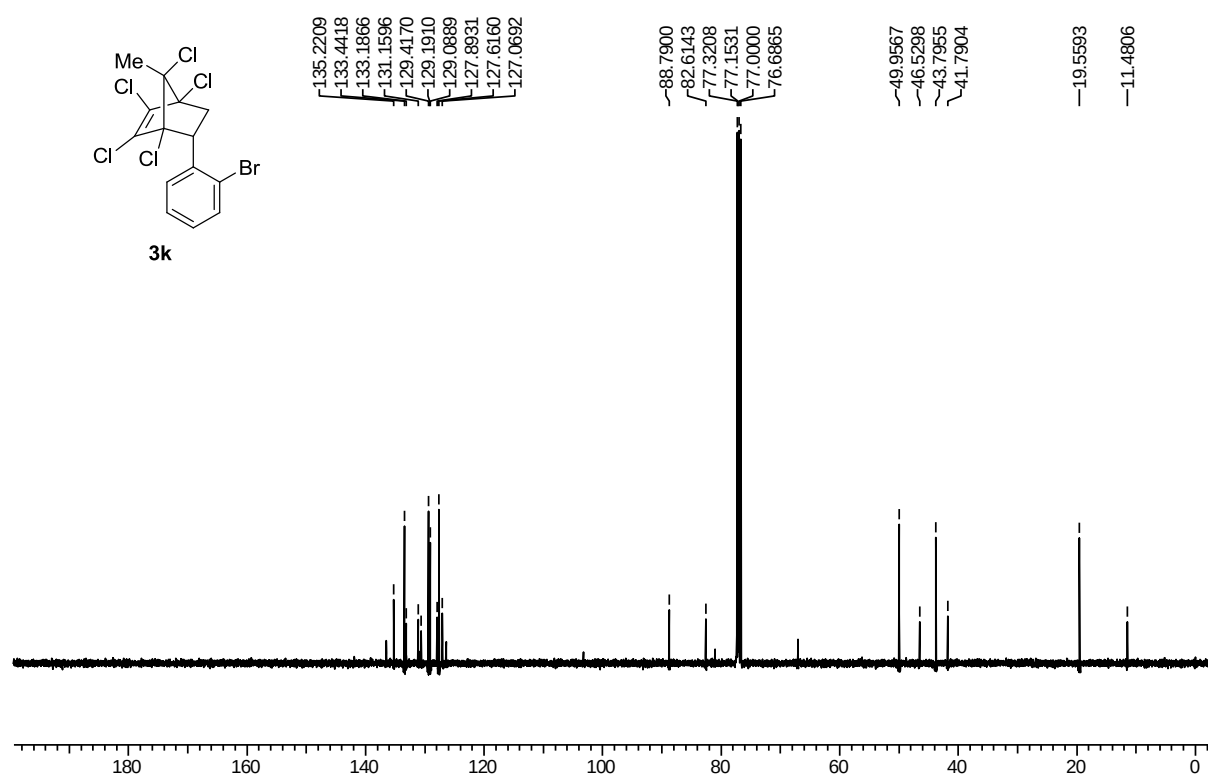
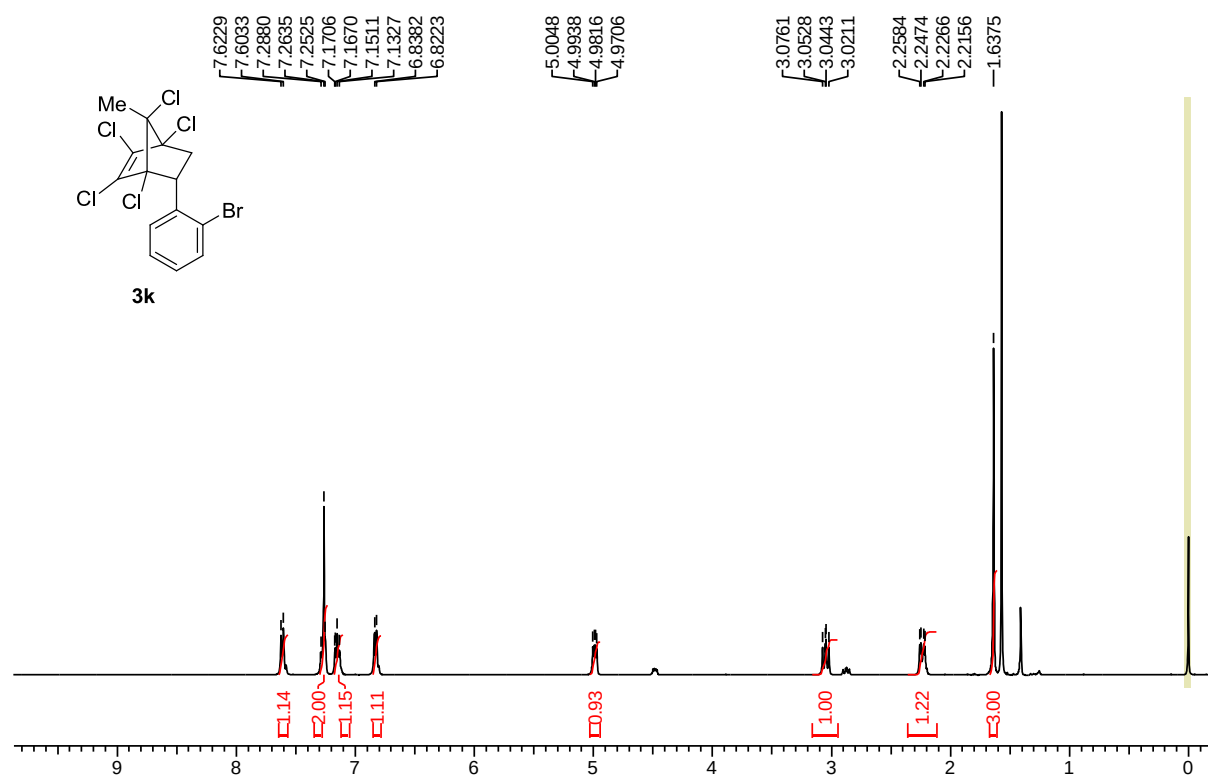




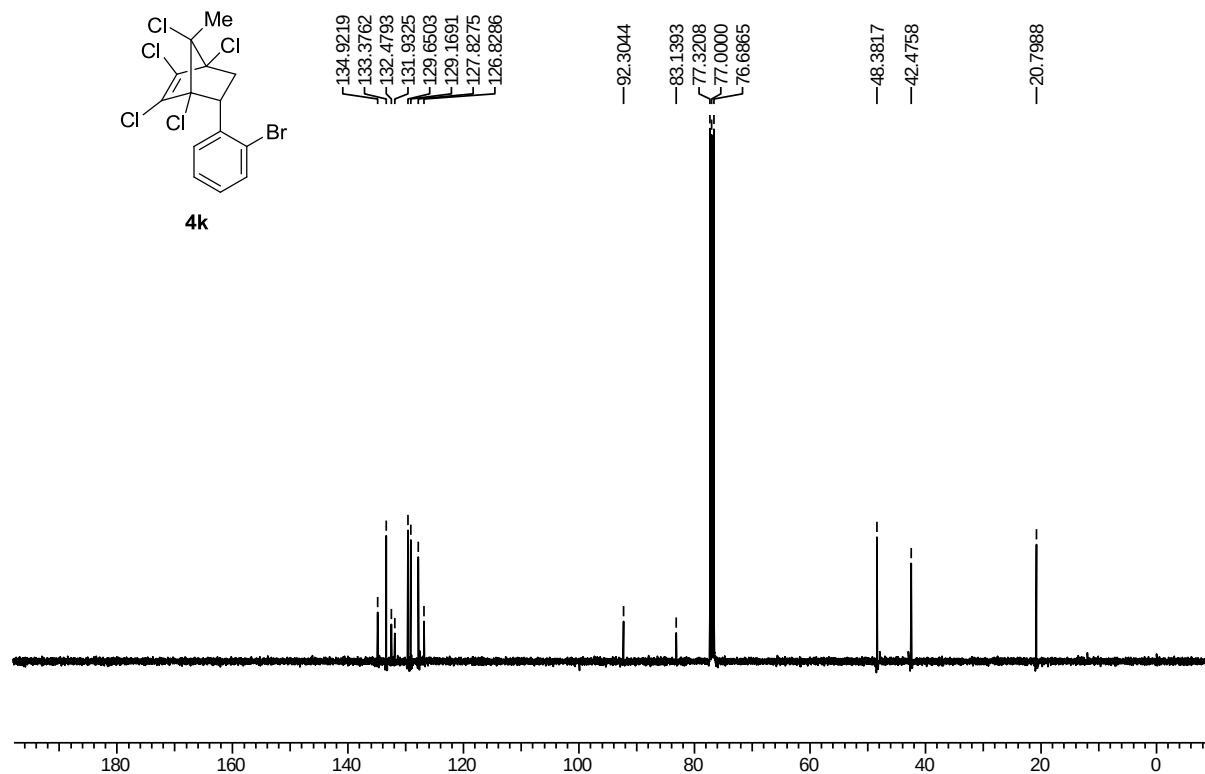
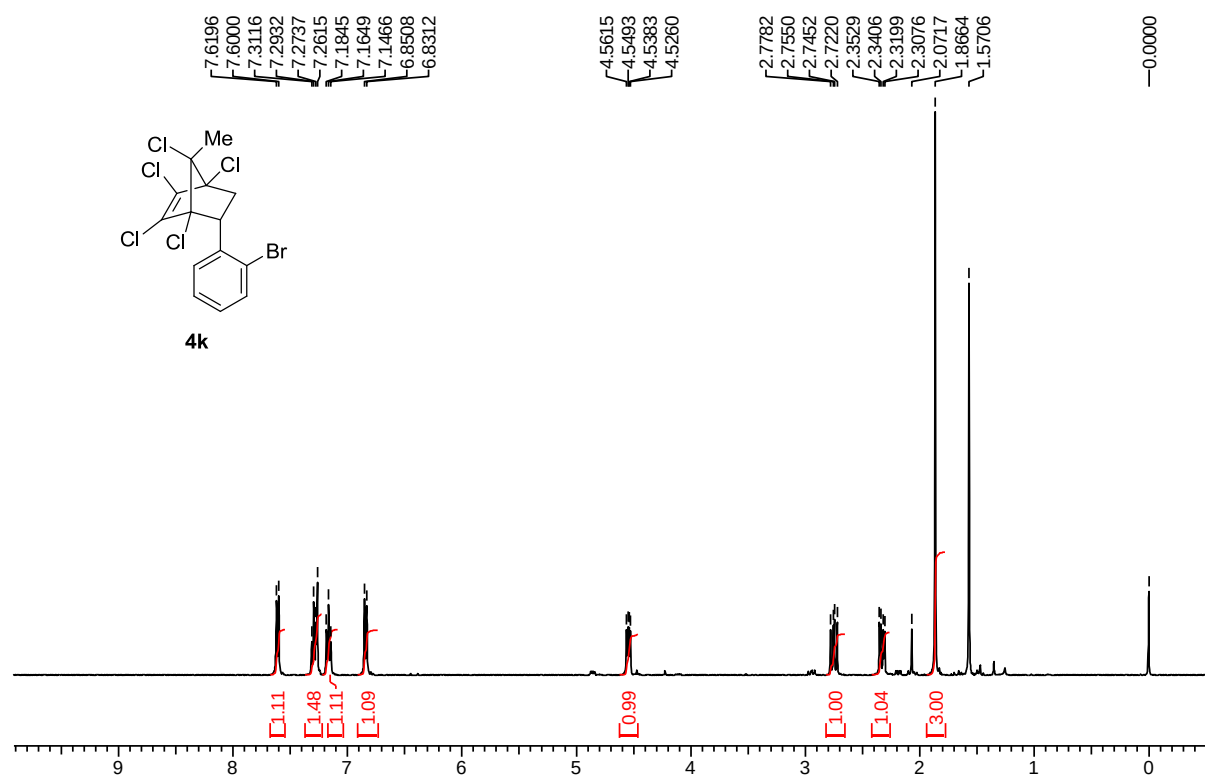
**$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) of 3j in  $\text{CDCl}_3$ :**



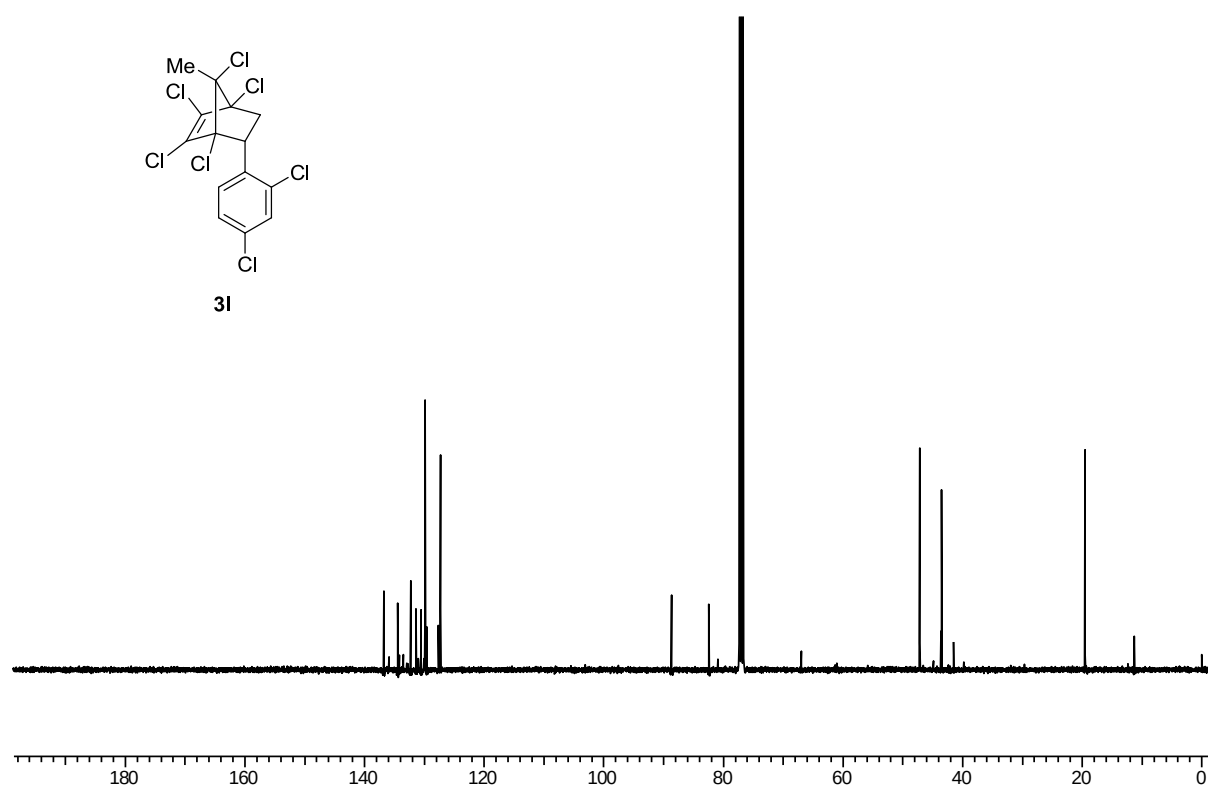
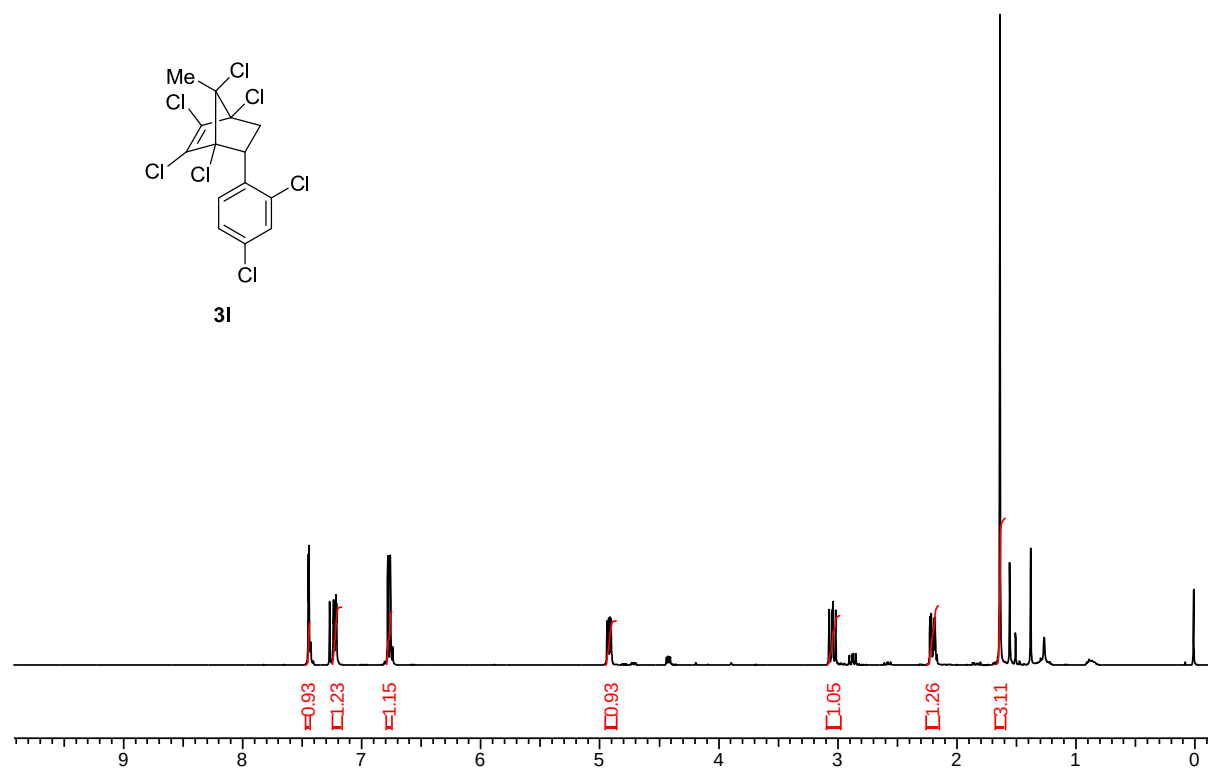
**$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) of 3k in  $\text{CDCl}_3$ :**



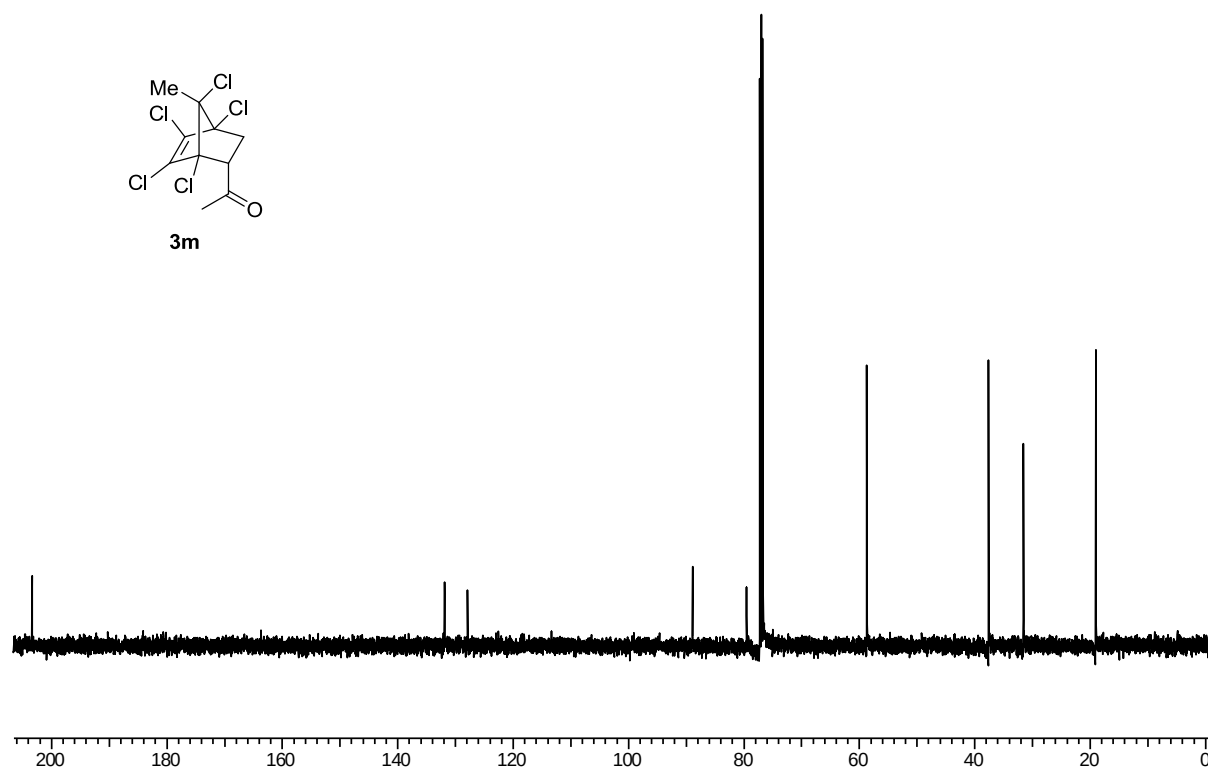
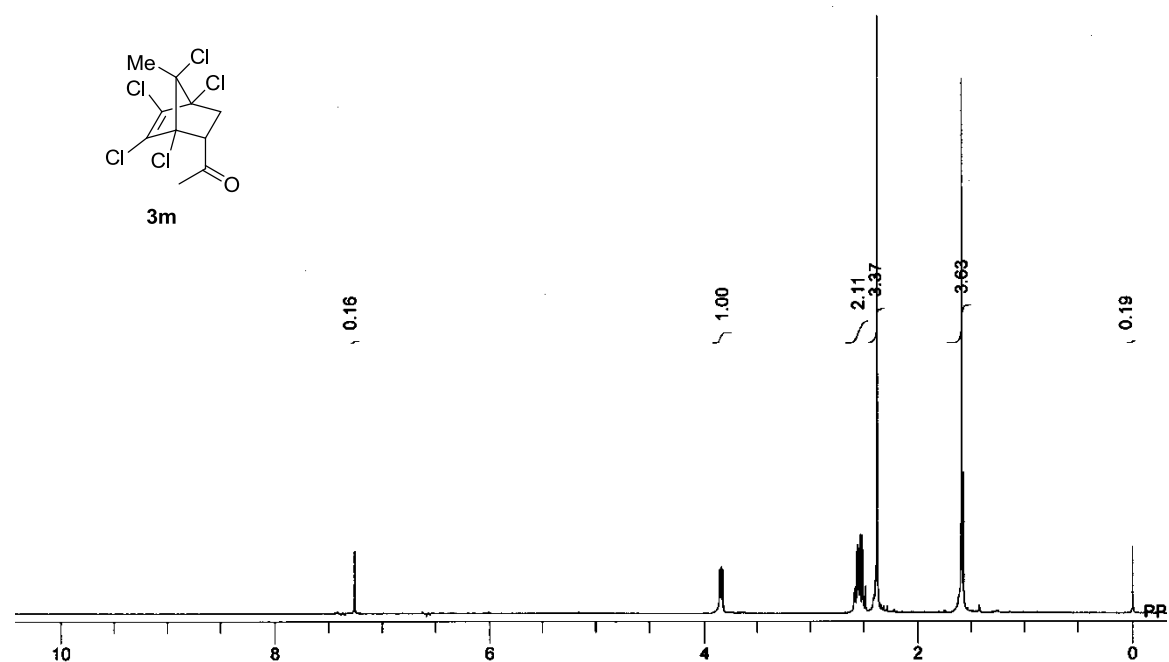
**$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) of 4k in  $\text{CDCl}_3$ :**



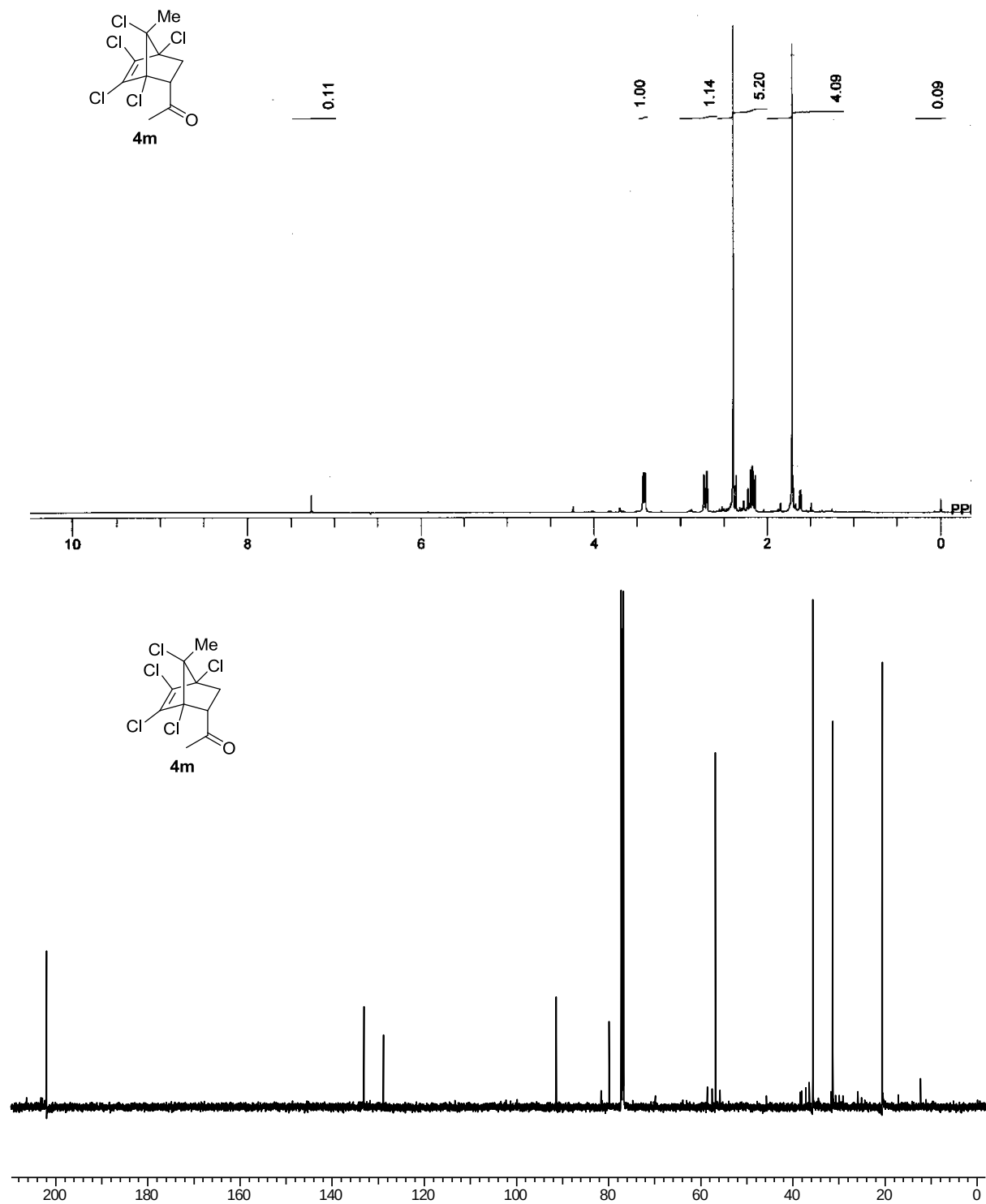
**$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) of 3I in  $\text{CDCl}_3$ :**



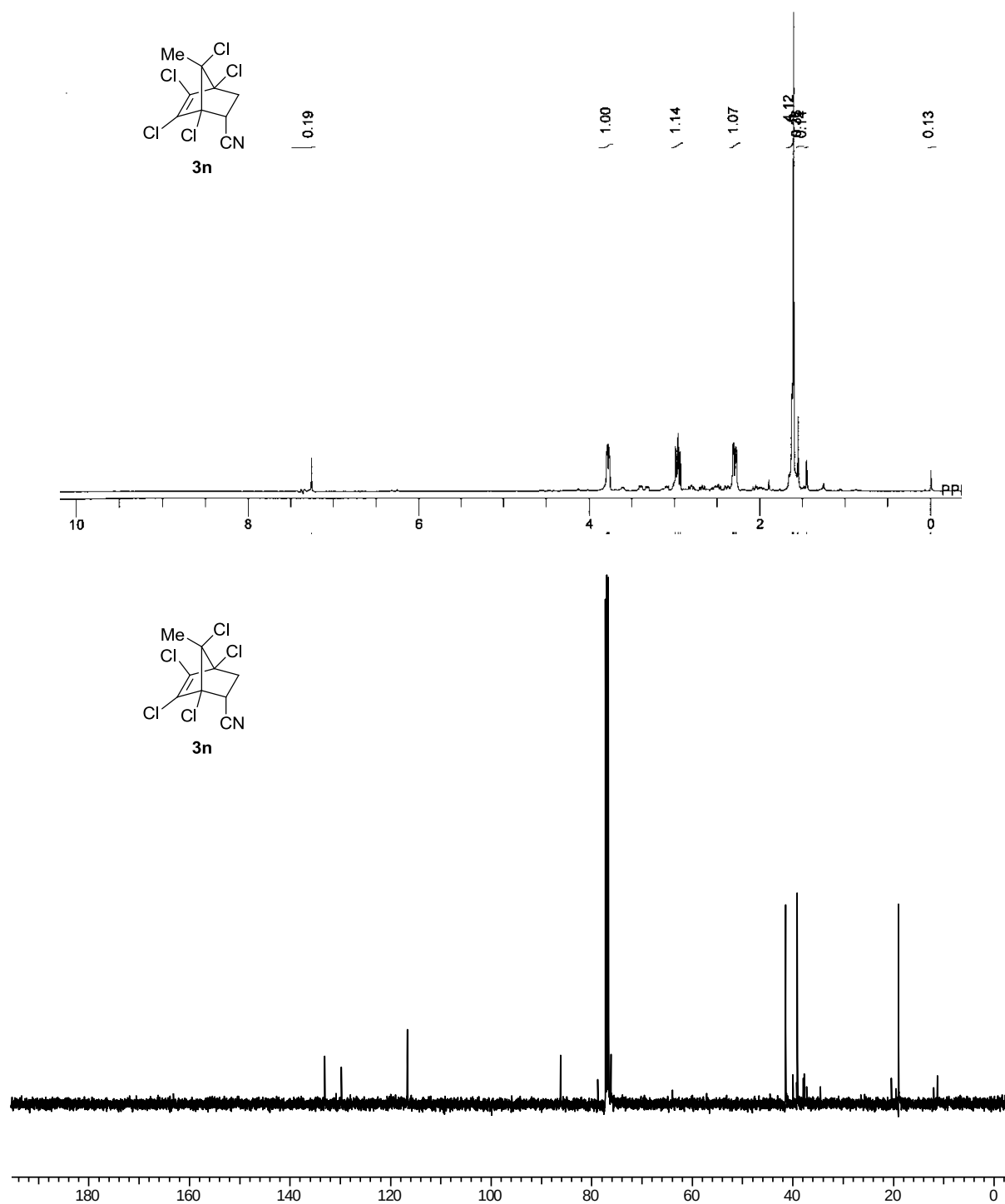
**$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (125 MHz) of 3m in  $\text{CDCl}_3$ :**



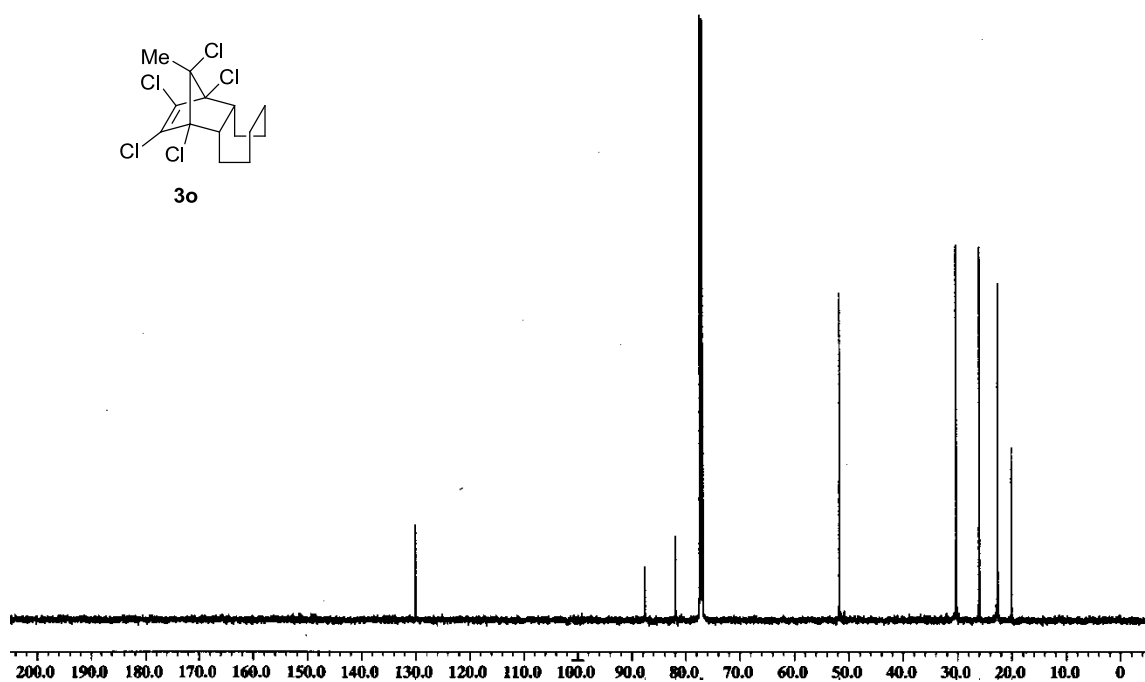
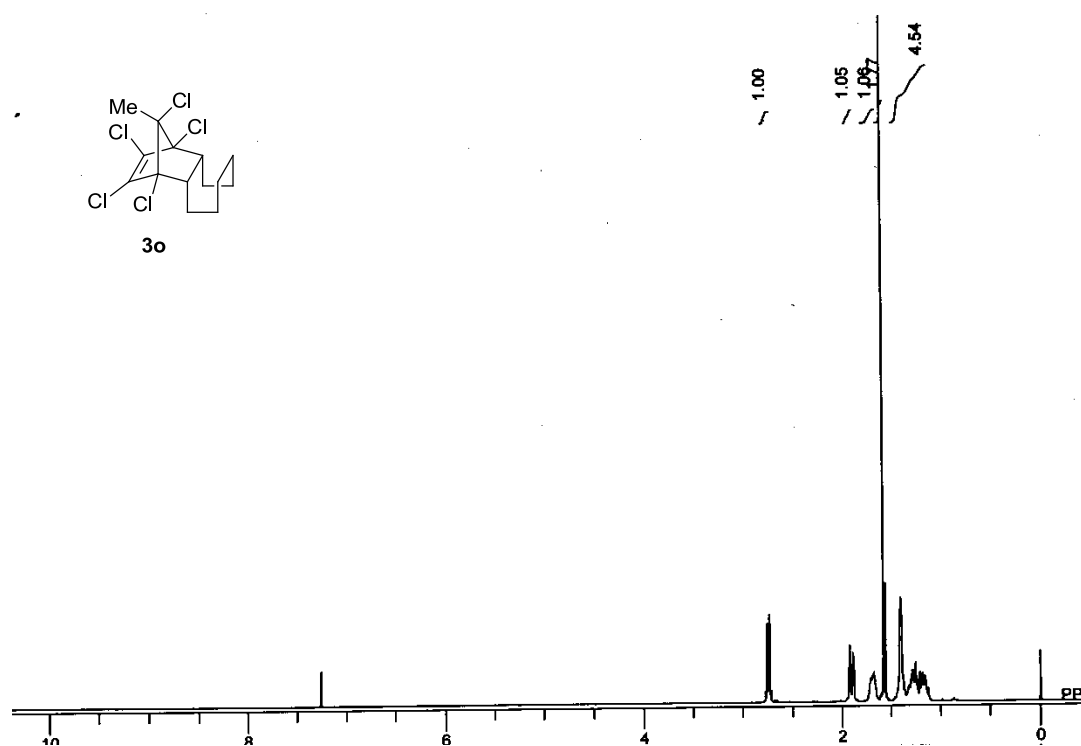
**$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (125 MHz) of 4m in  $\text{CDCl}_3$ :**



**$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (125 MHz) of 3n in  $\text{CDCl}_3$ :**

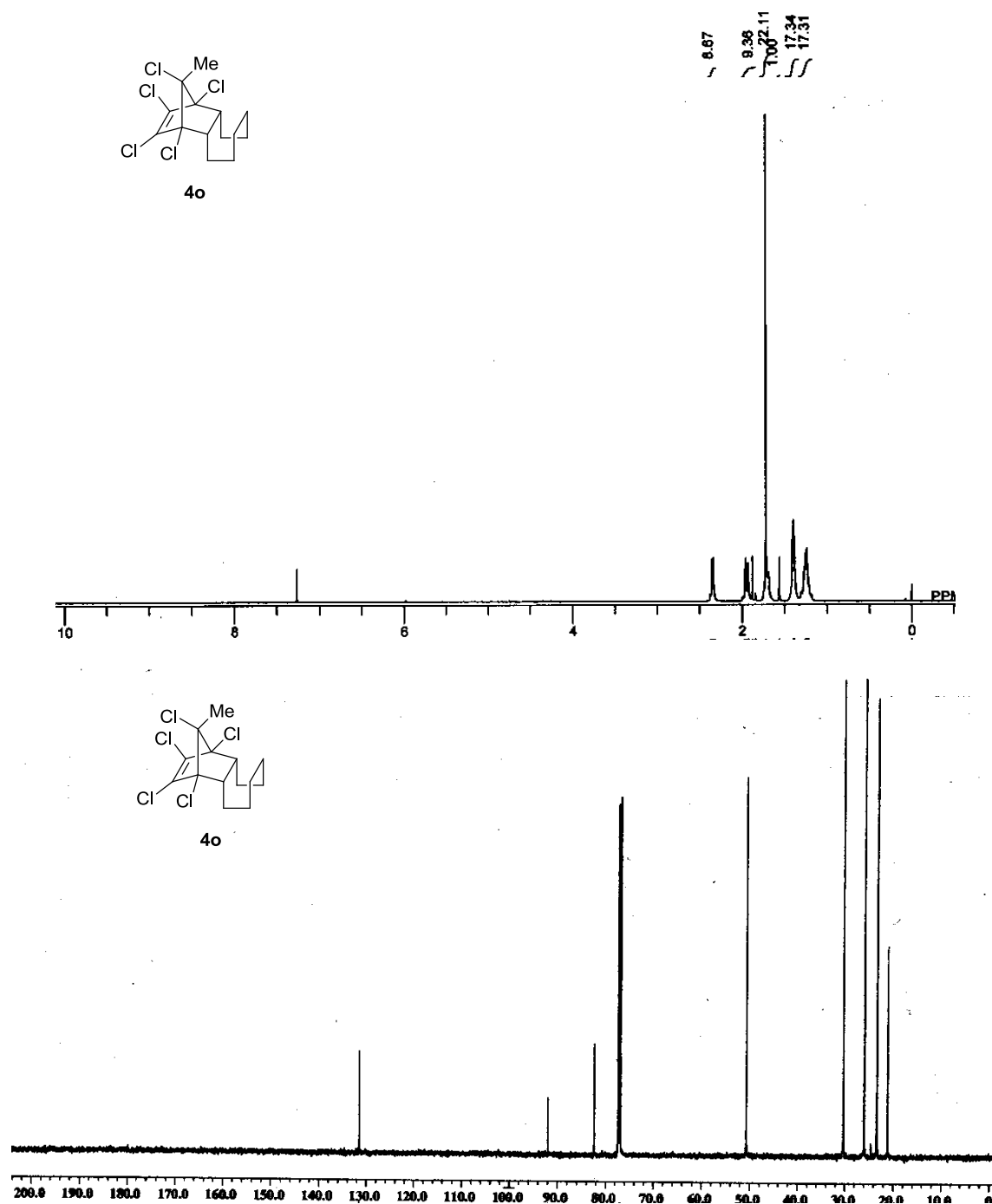


$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (125 MHz) of **3o** in  $\text{CDCl}_3$ :

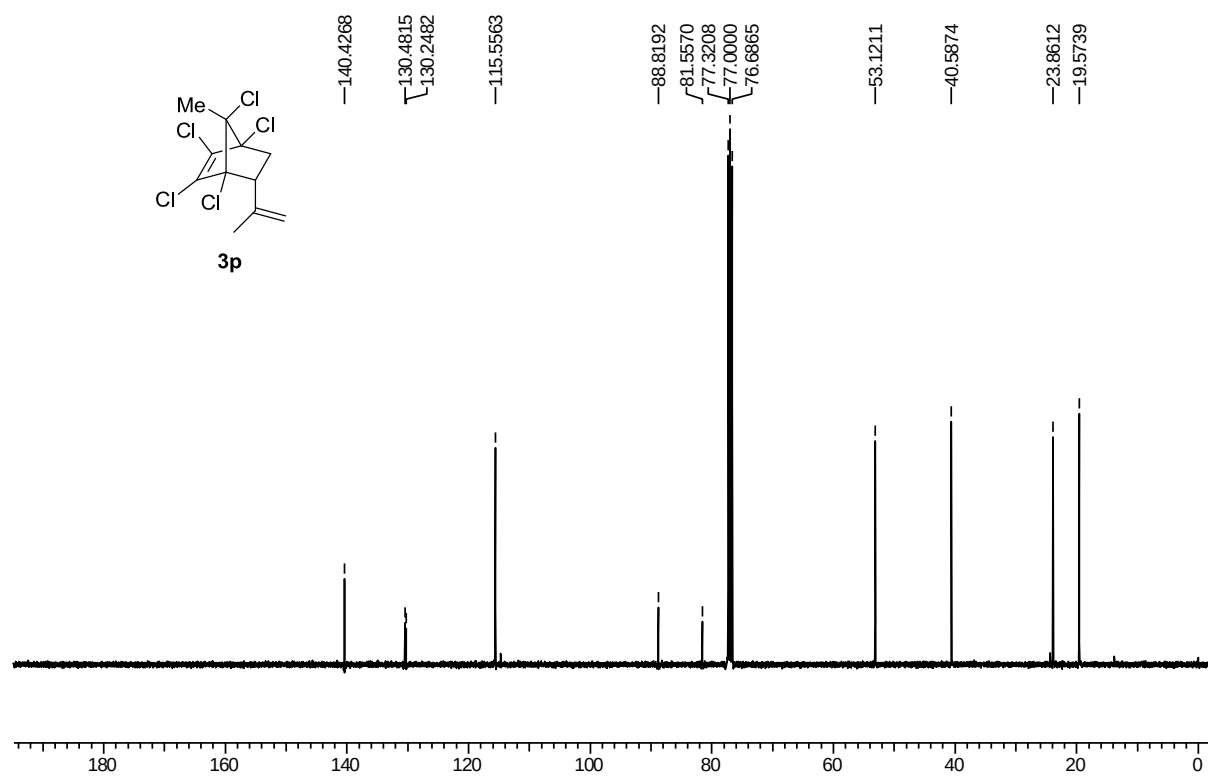
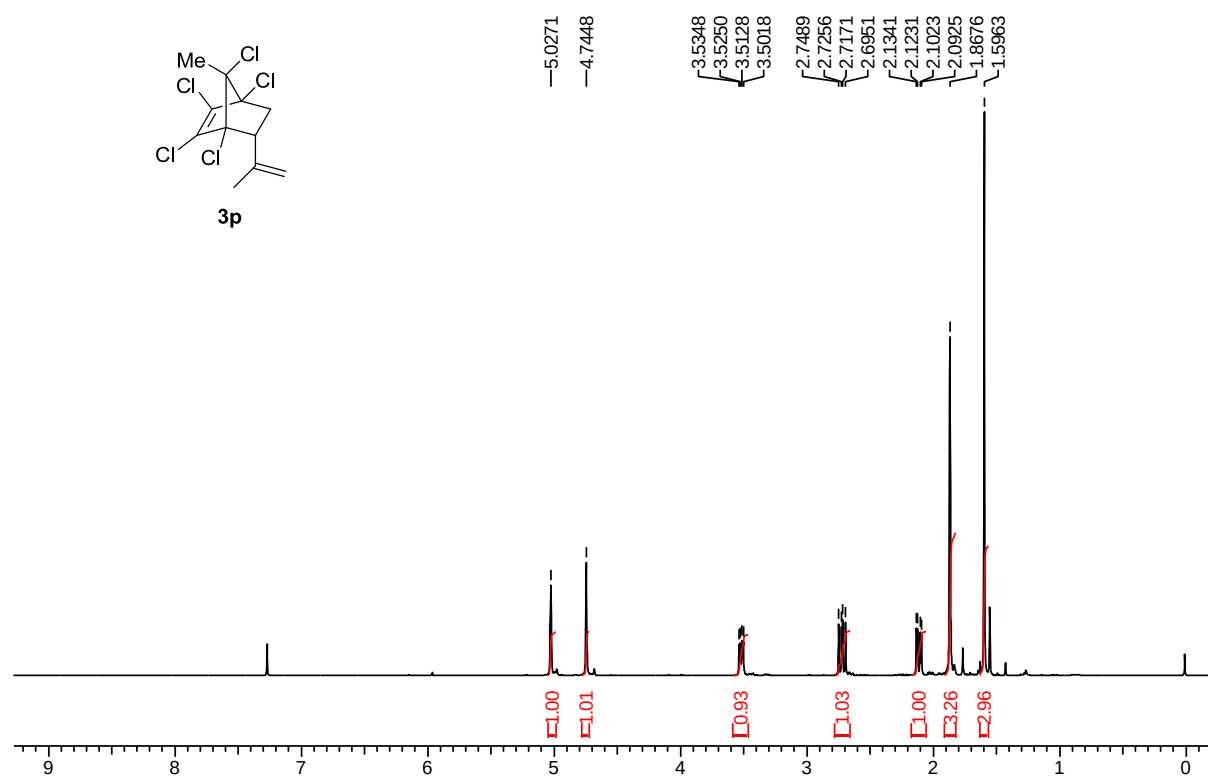




$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (125 MHz) of **4o** in  $\text{CDCl}_3$ :

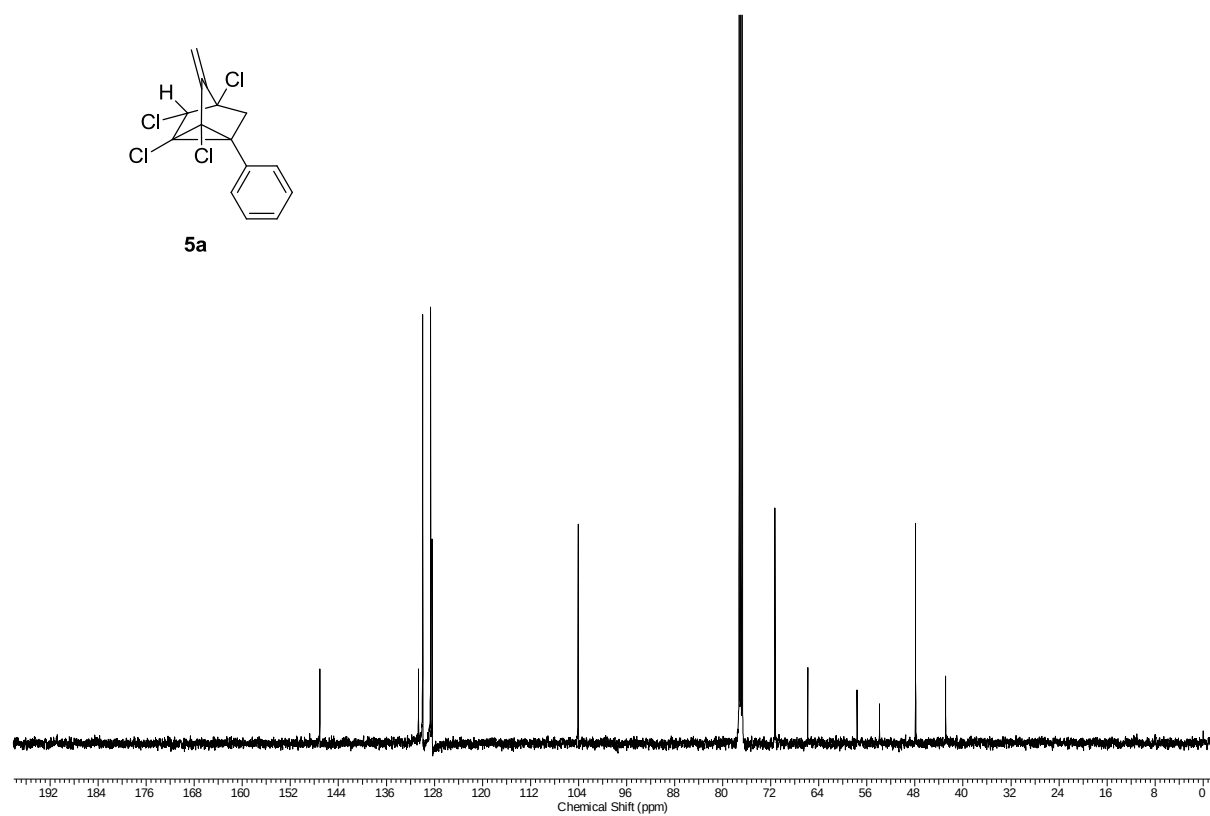
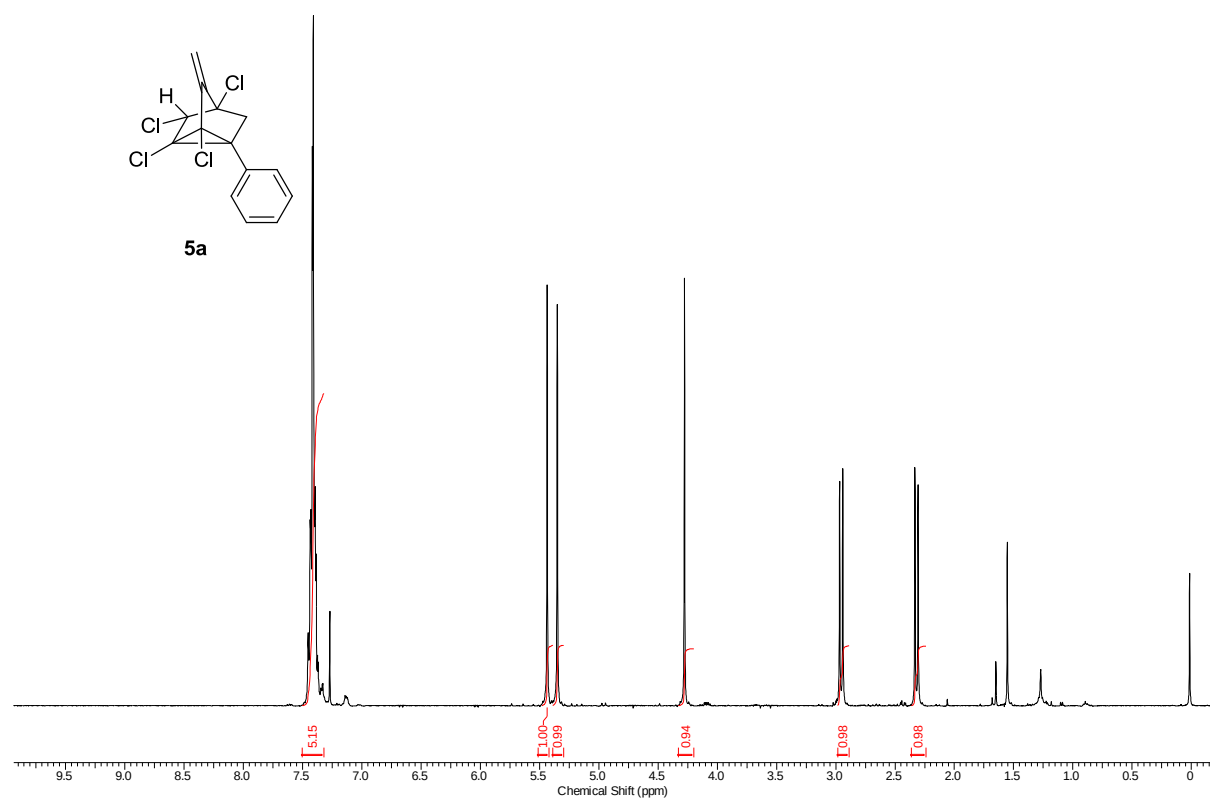


**$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) of 3p in  $\text{CDCl}_3$ :**

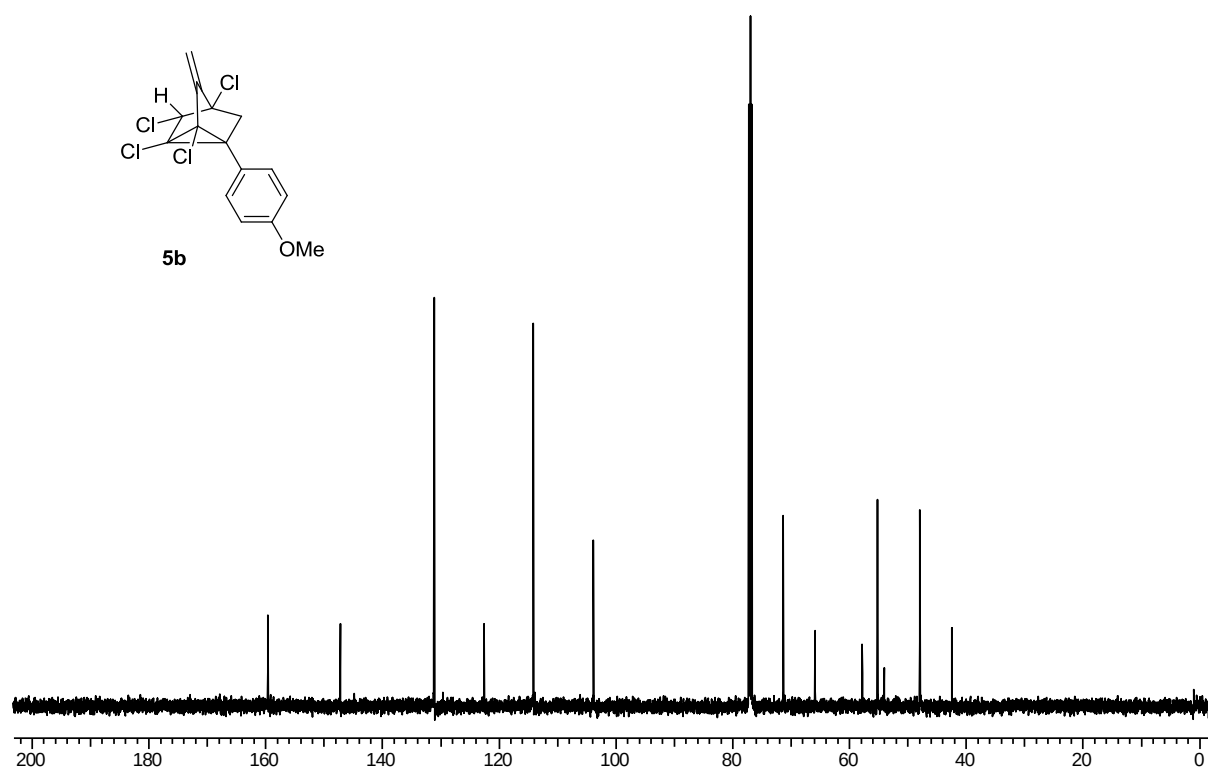
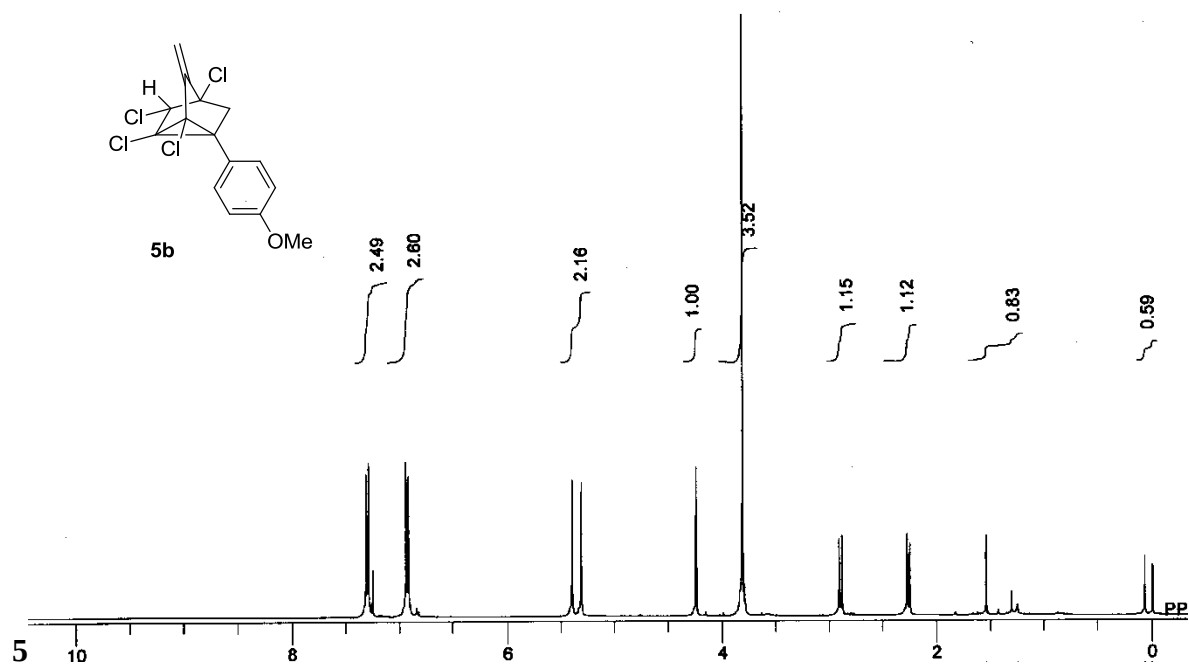


## Copies of $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of nortricyclenes **5**:

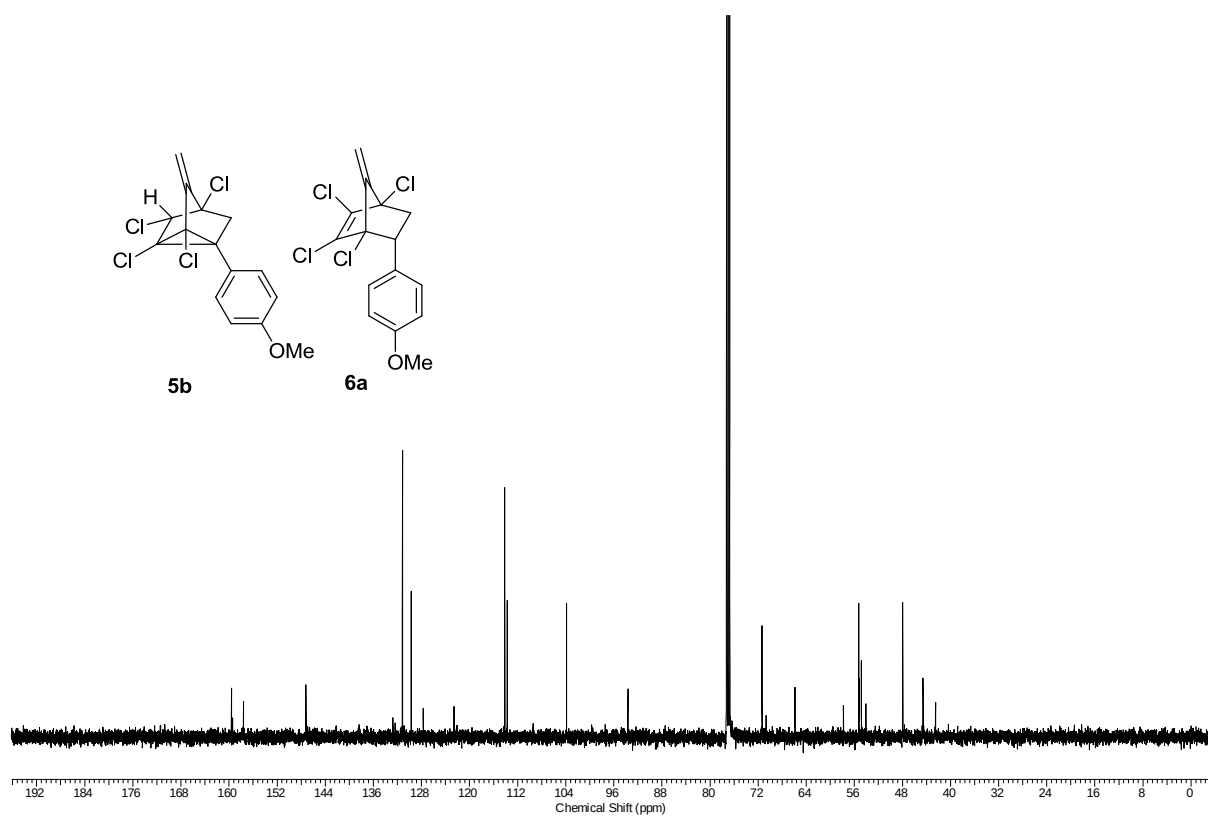
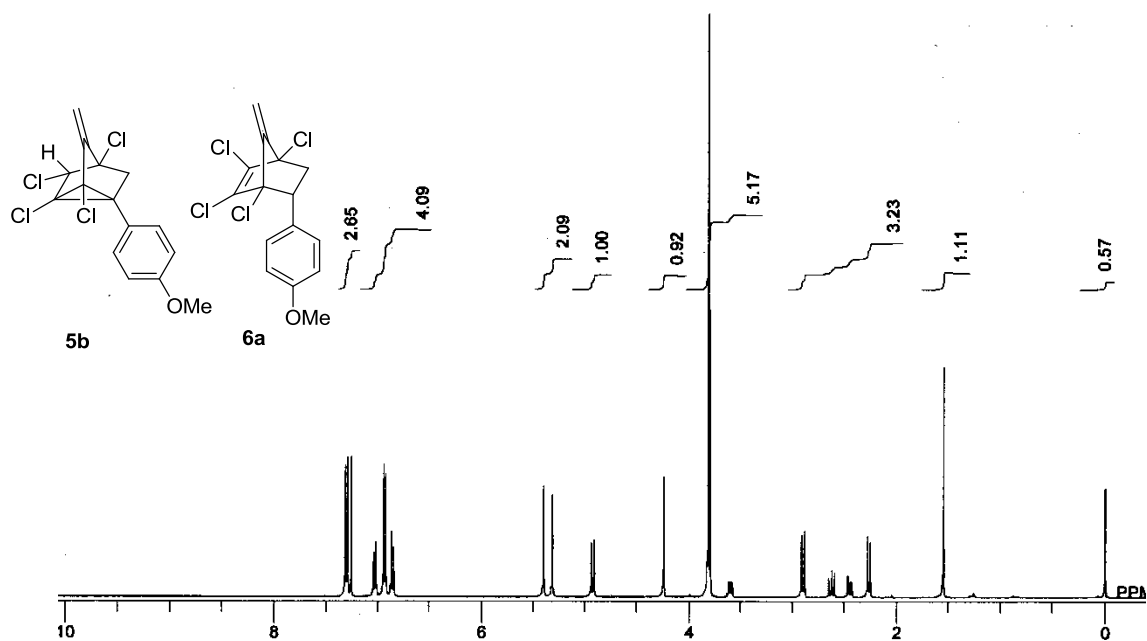
$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (125 MHz) of **5a** in  $\text{CDCl}_3$ :



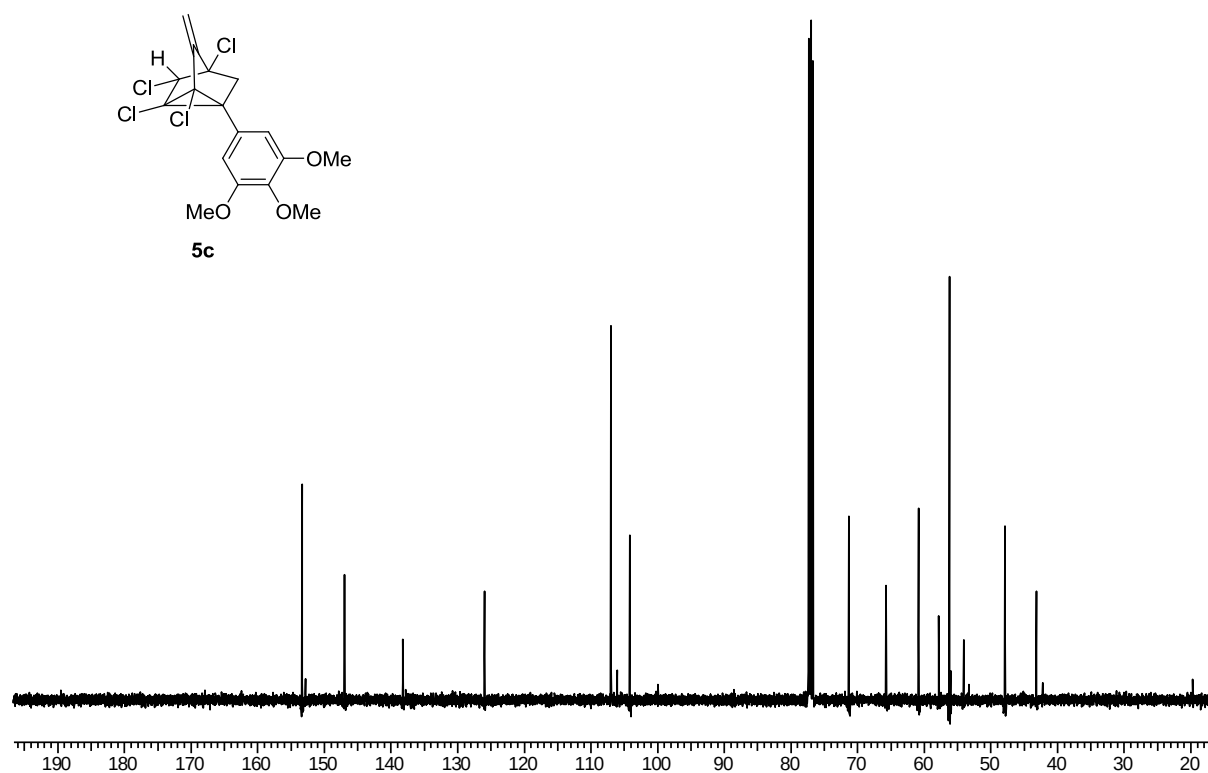
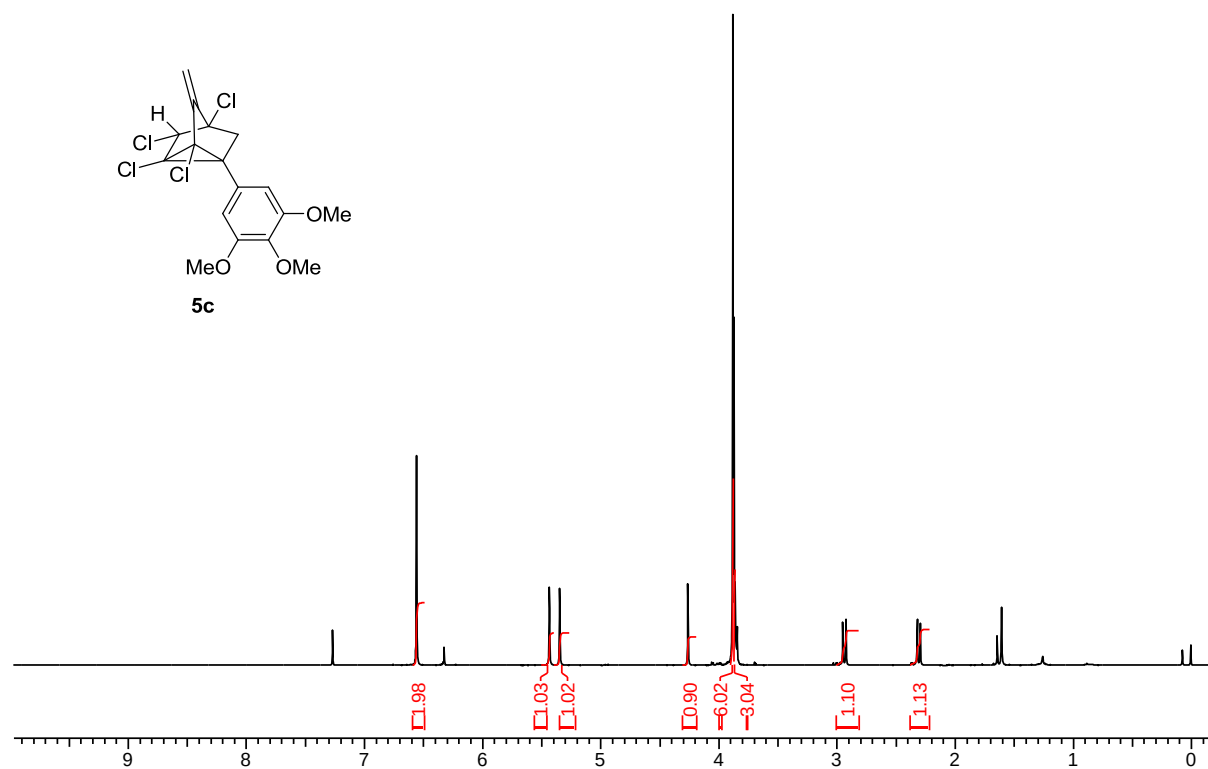
$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (125 MHz) of 5b in  $\text{CDCl}_3$ :



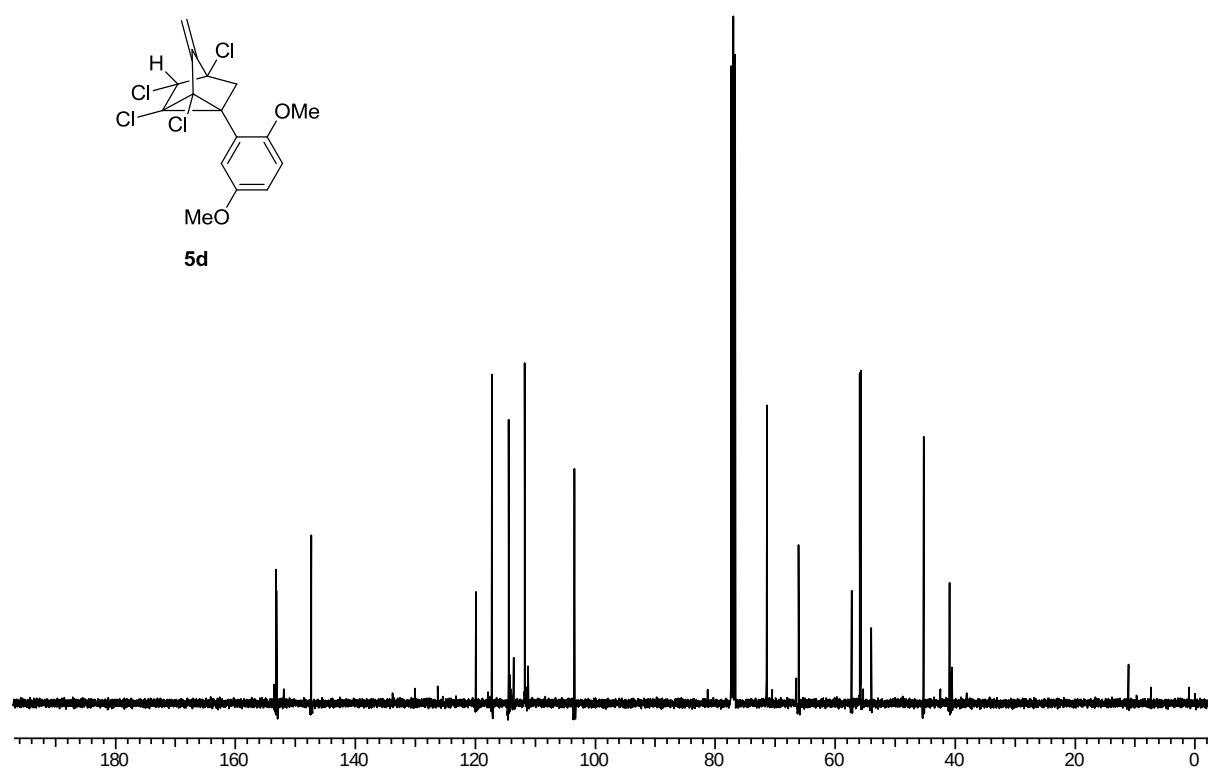
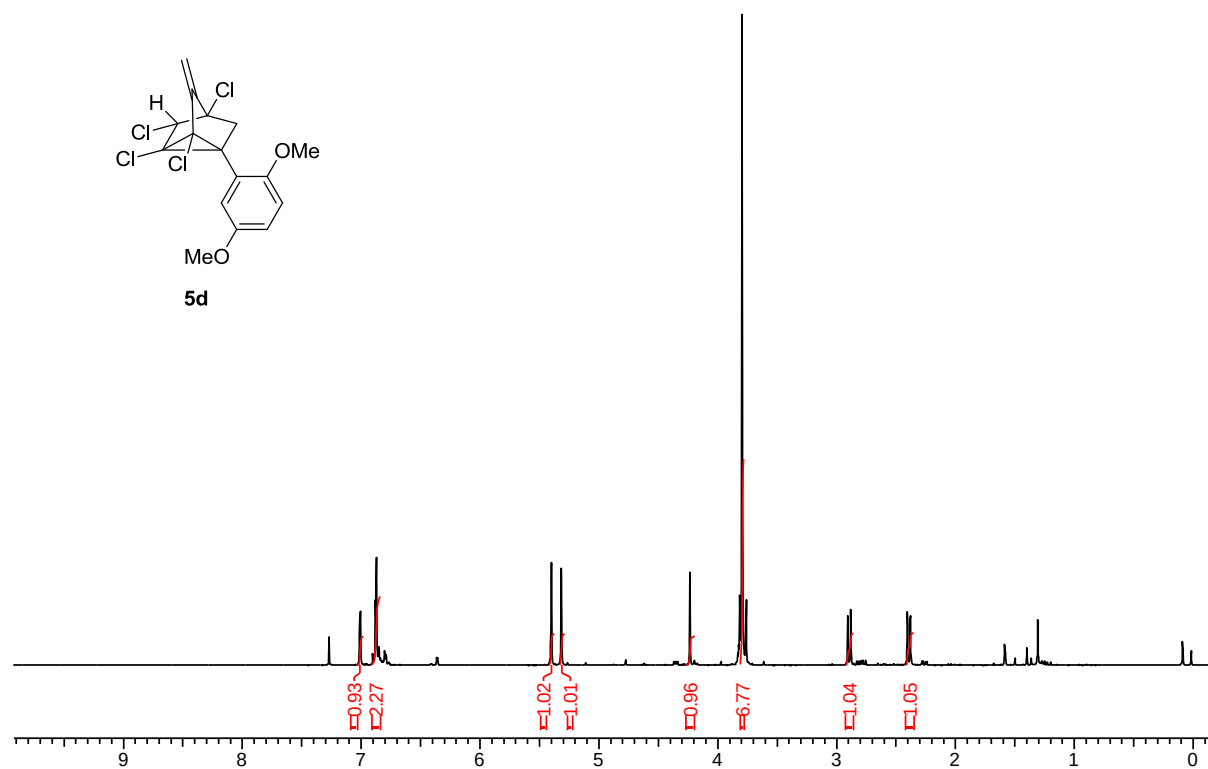
$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (125 MHz) of 5b and 6a in  $\text{CDCl}_3$ :



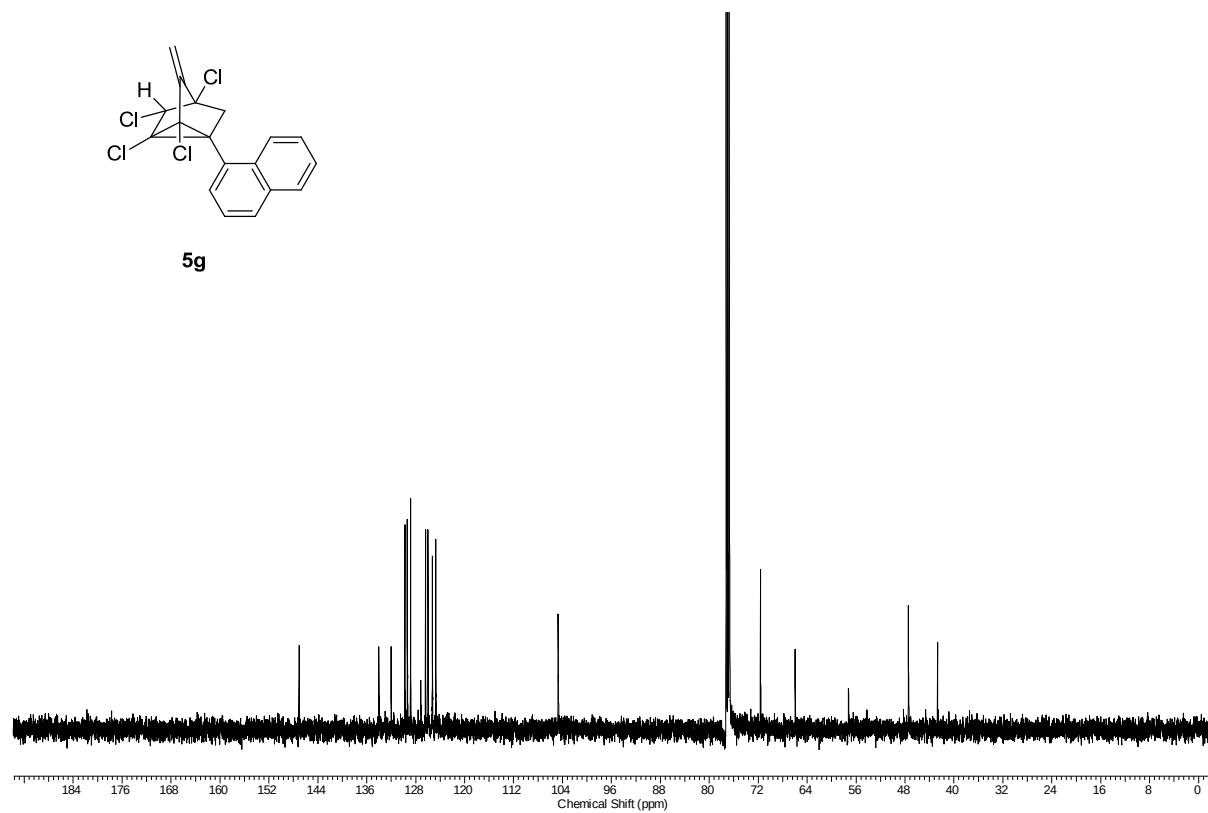
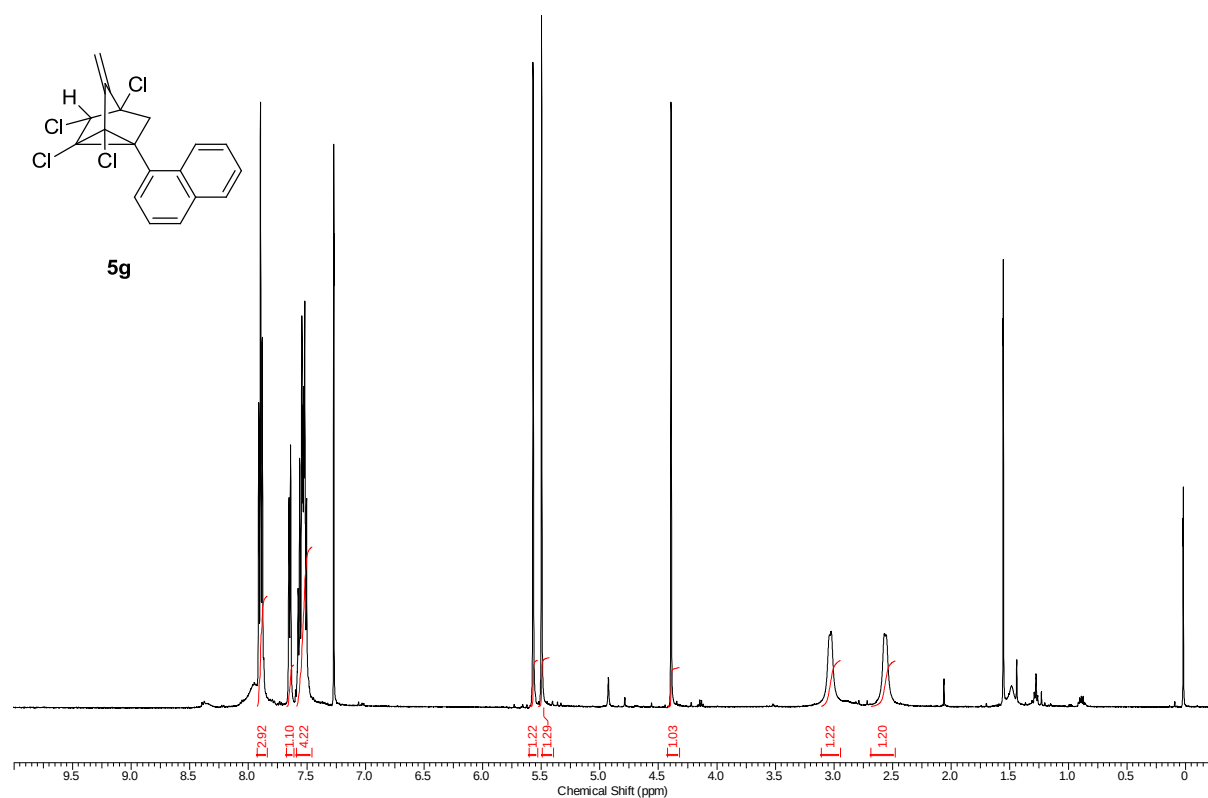
**$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) of 5c in  $\text{CDCl}_3$ :**



**$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) of 5d in  $\text{CDCl}_3$ :**

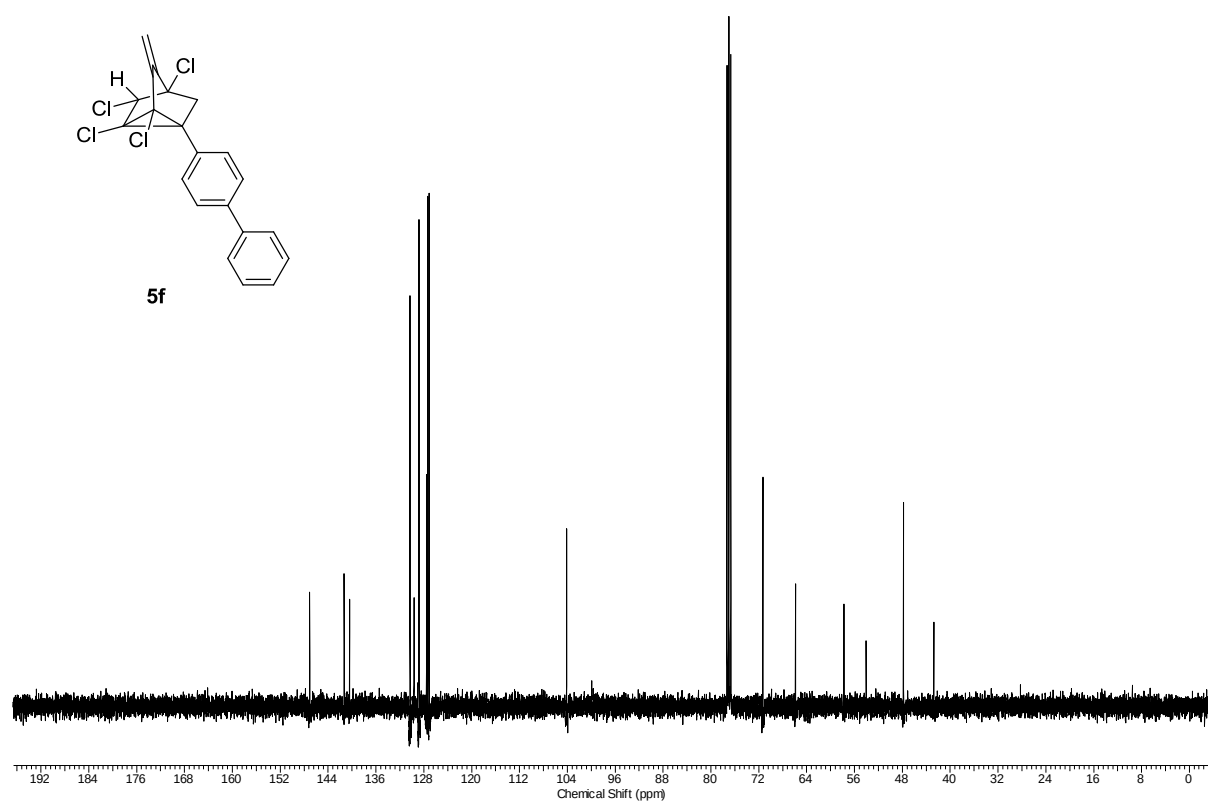
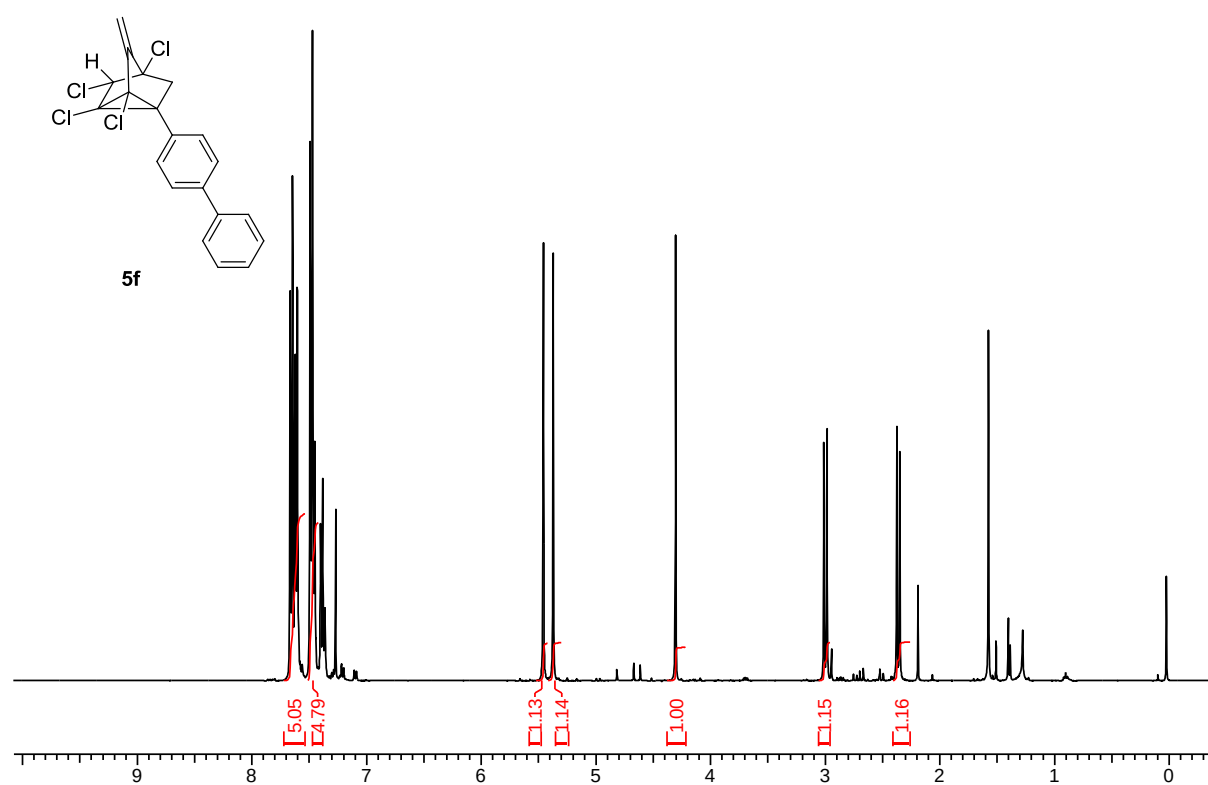


**$^1\text{H}$  NMR (500 MHz) and  $^{13}\text{C}$  NMR (125 MHz) of 5g in  $\text{CDCl}_3$ :**

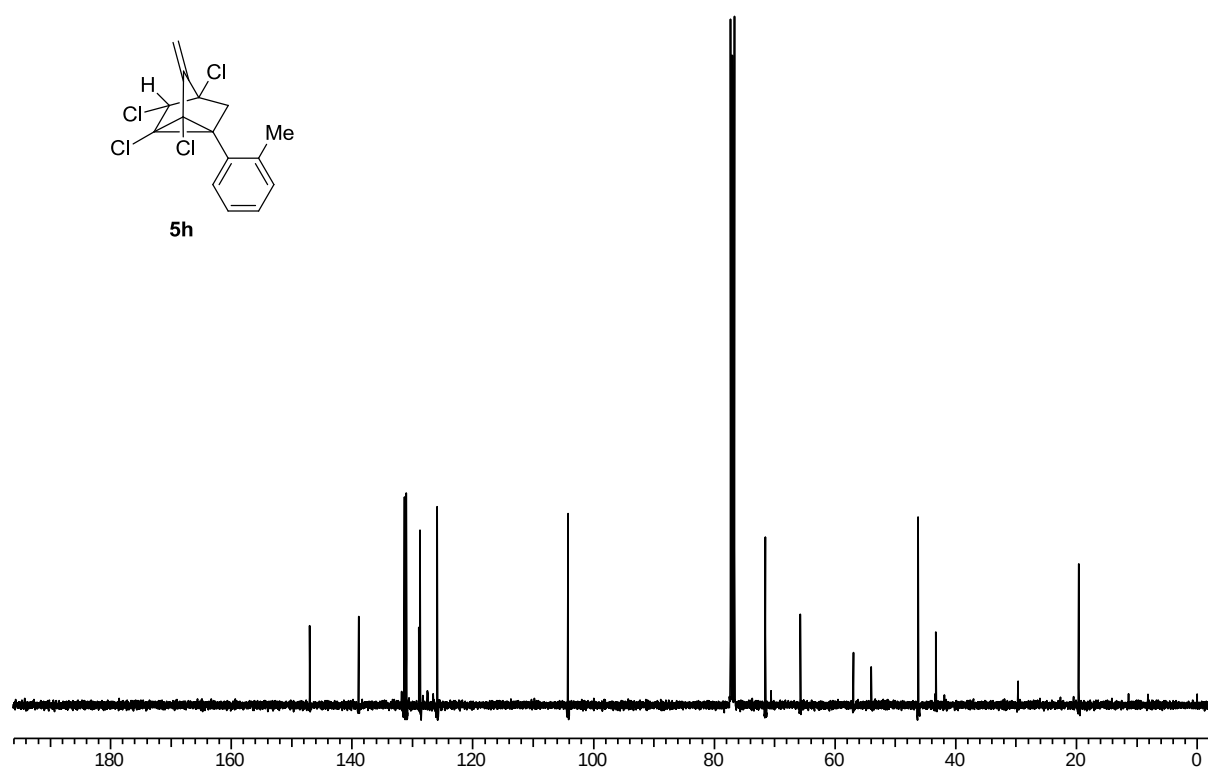
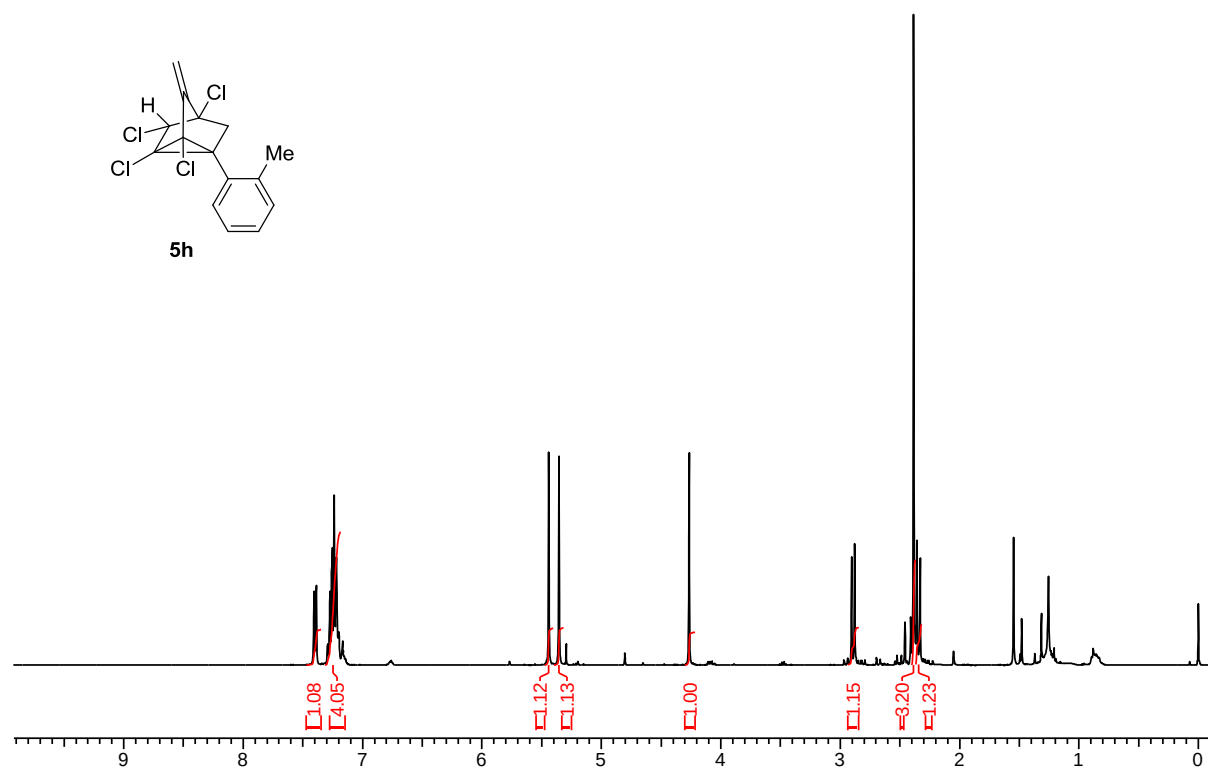




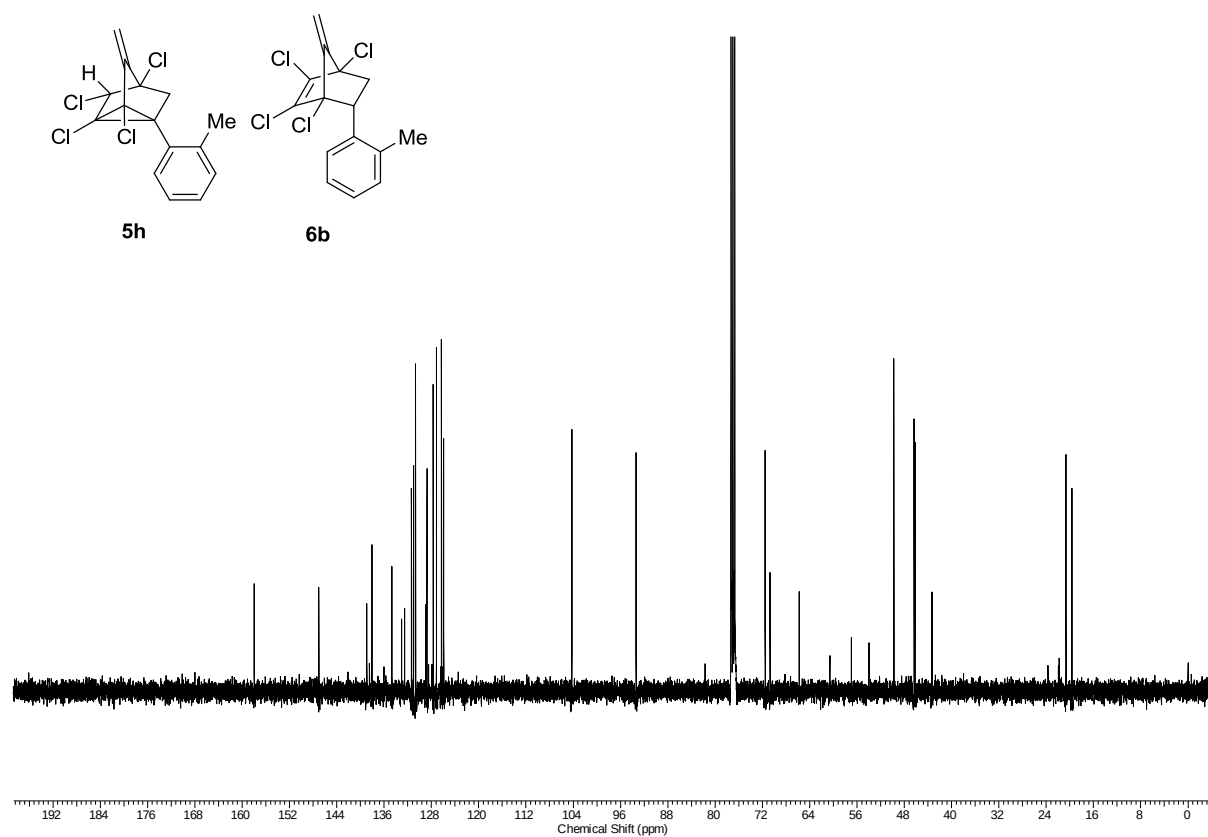
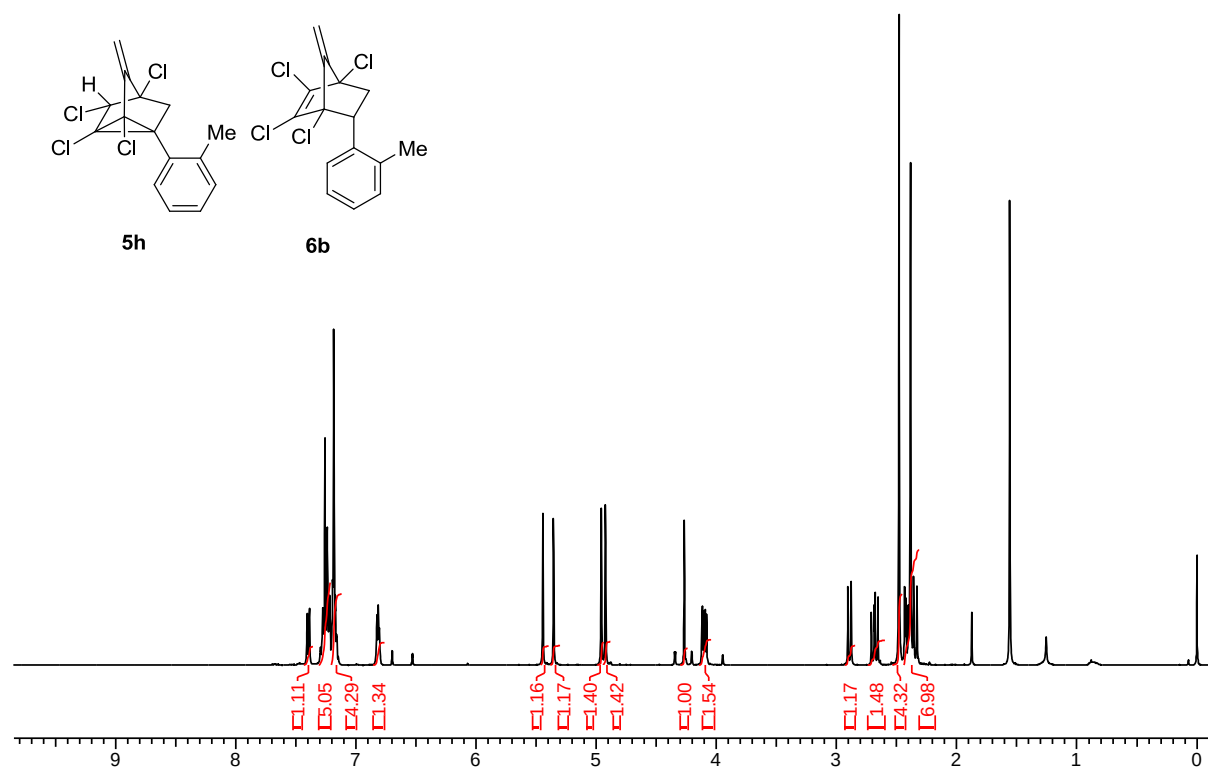
**$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) of 5f in  $\text{CDCl}_3$ :**



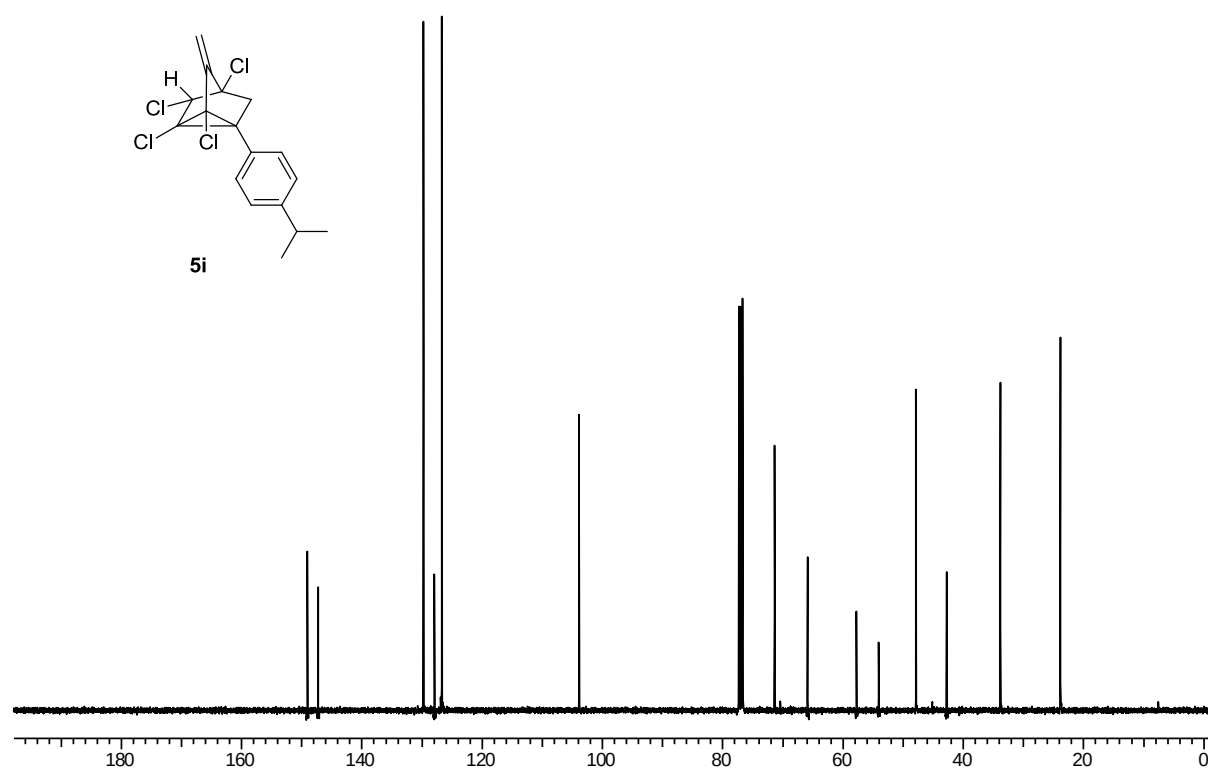
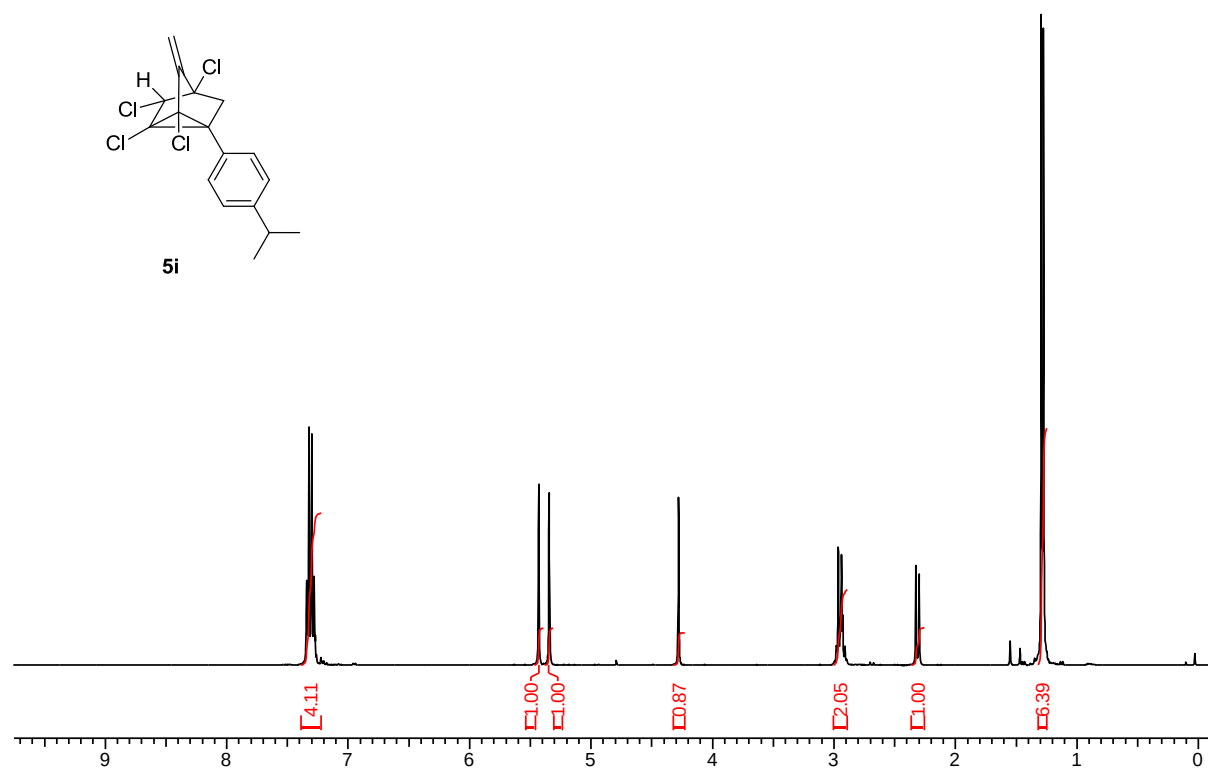
**$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) of 5h in  $\text{CDCl}_3$ :**



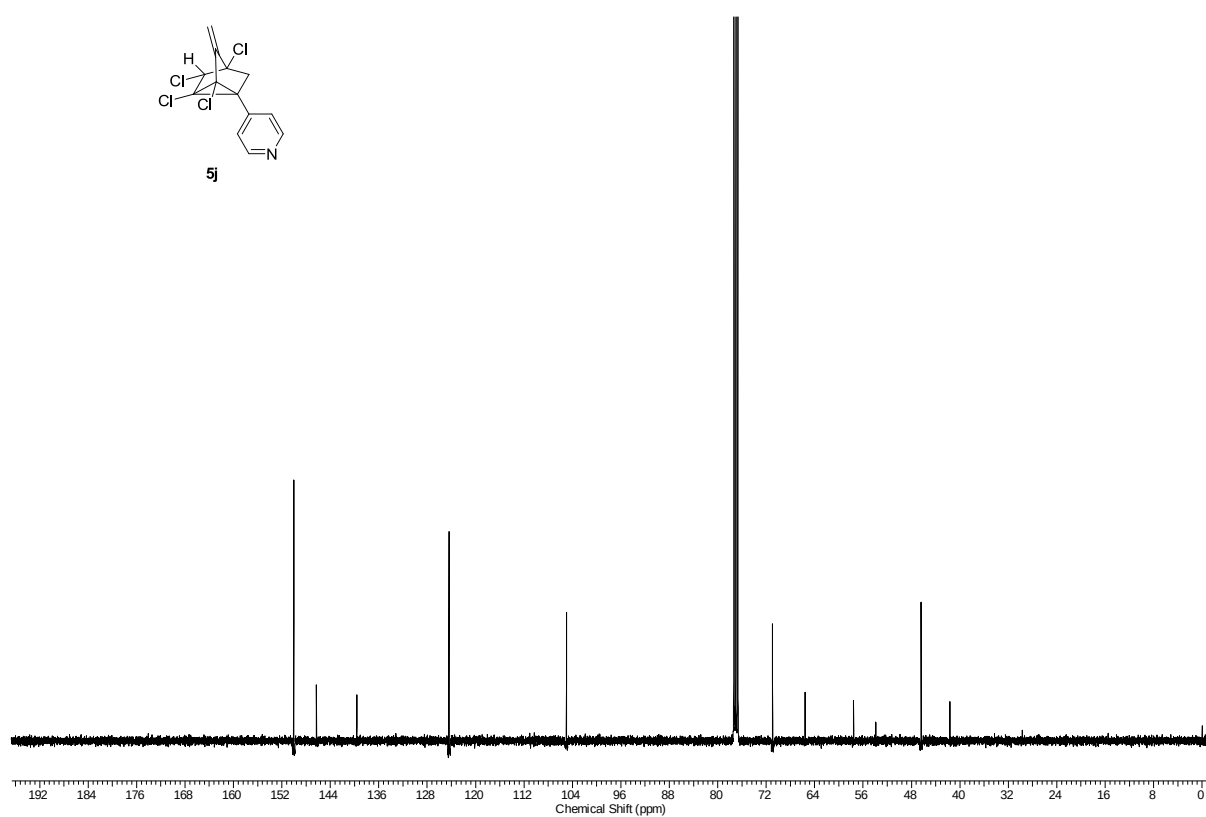
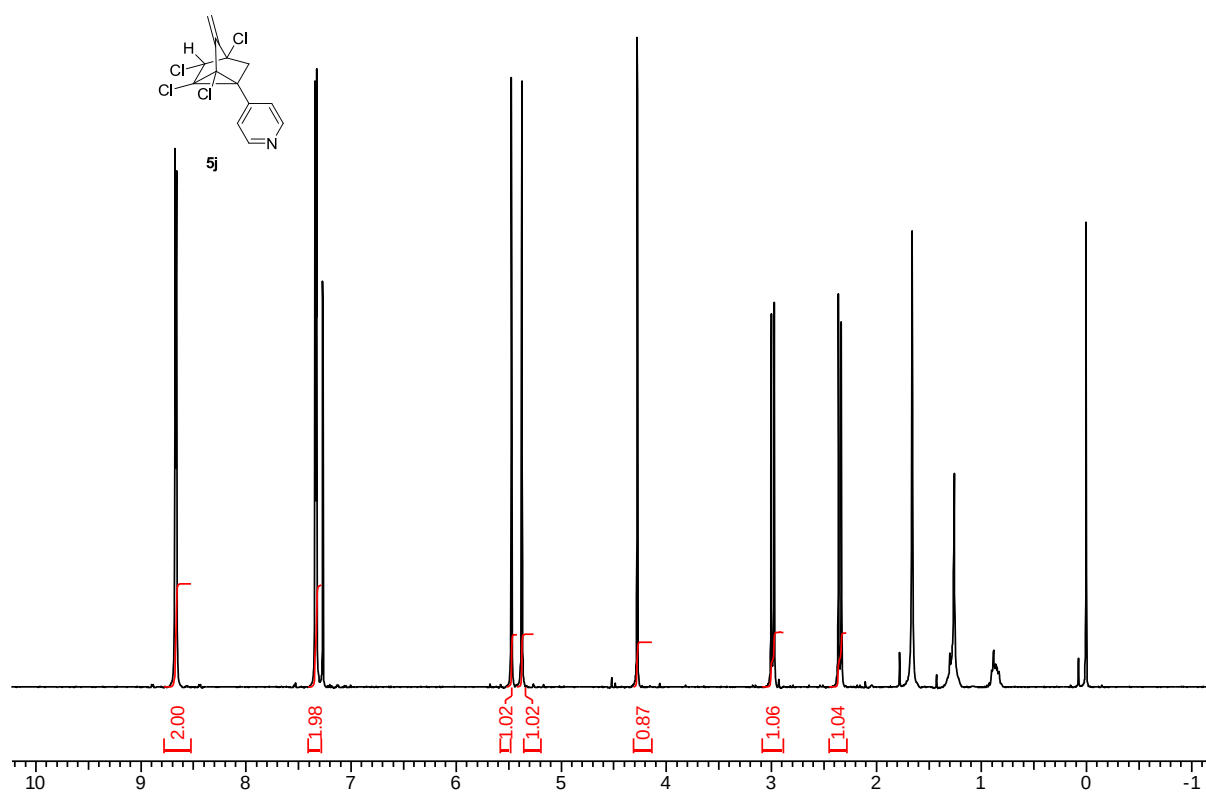
**$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) of 5h and 6b in  $\text{CDCl}_3$ :**



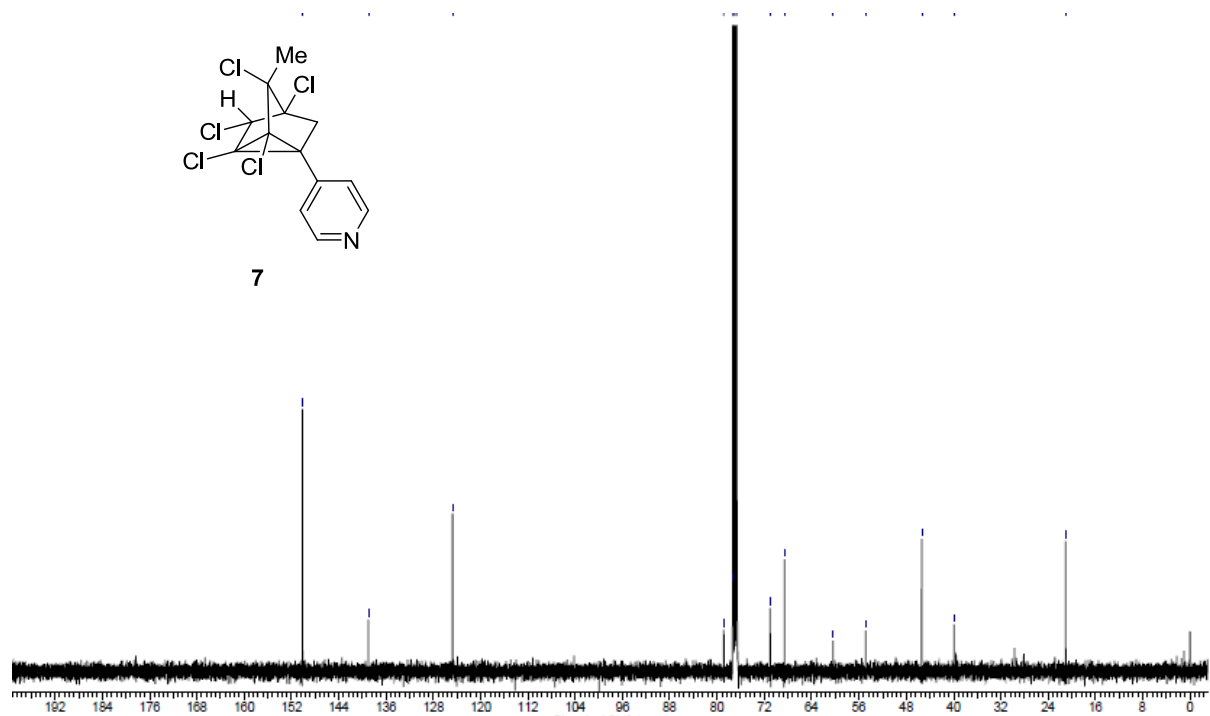
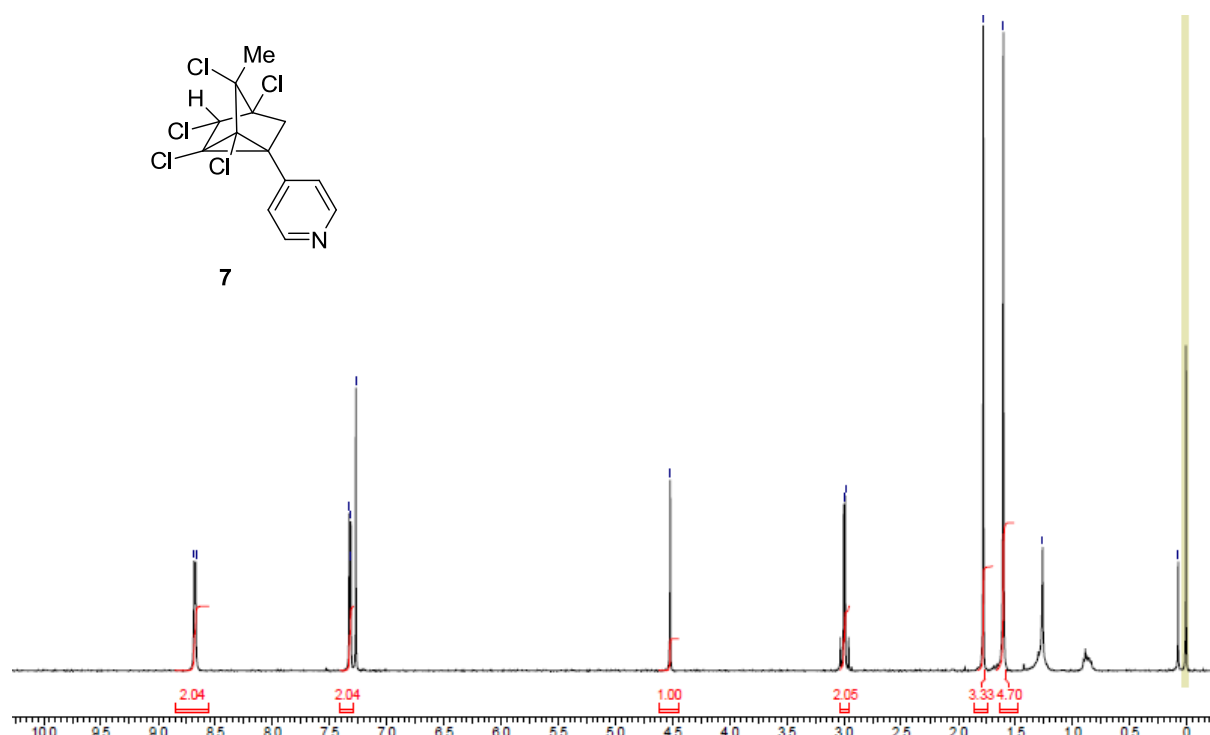
**$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) of 5i in  $\text{CDCl}_3$ :**



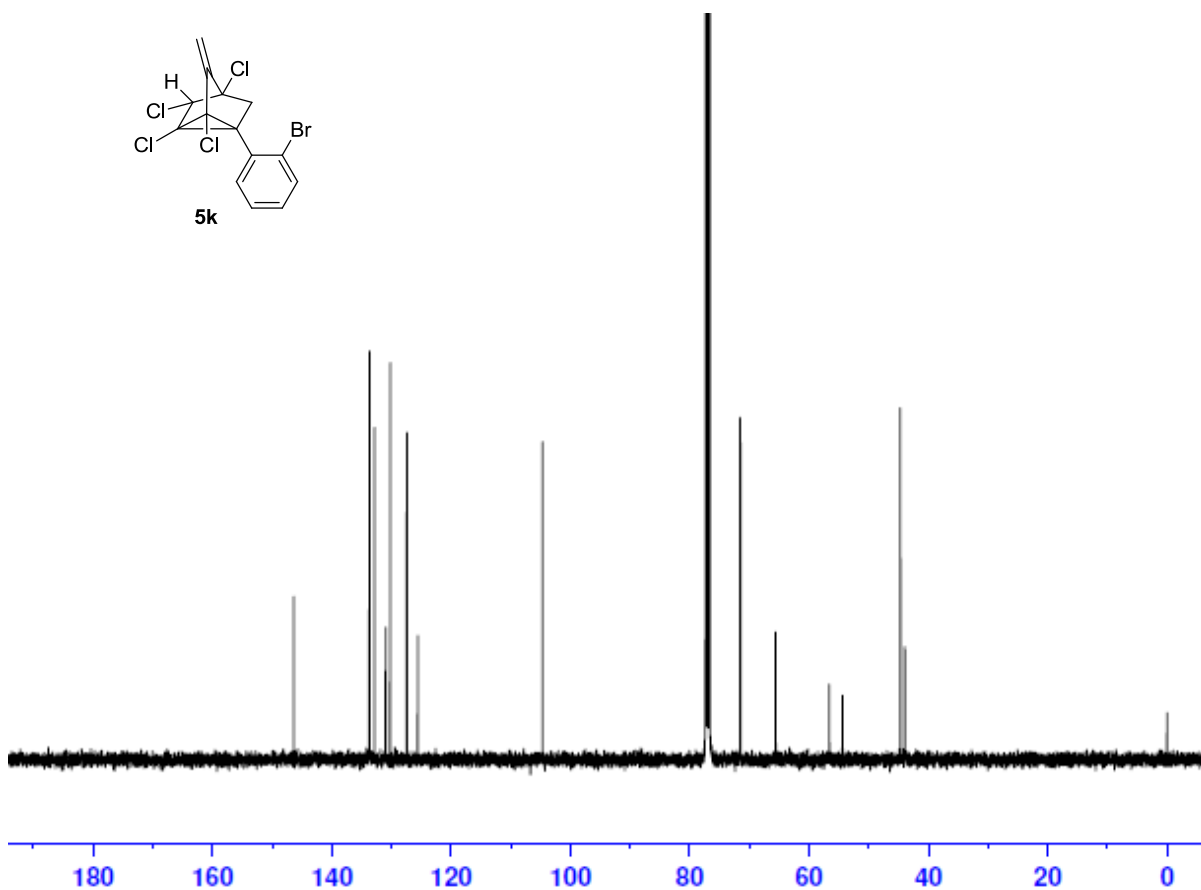
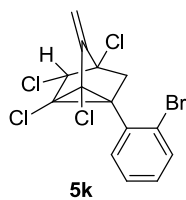
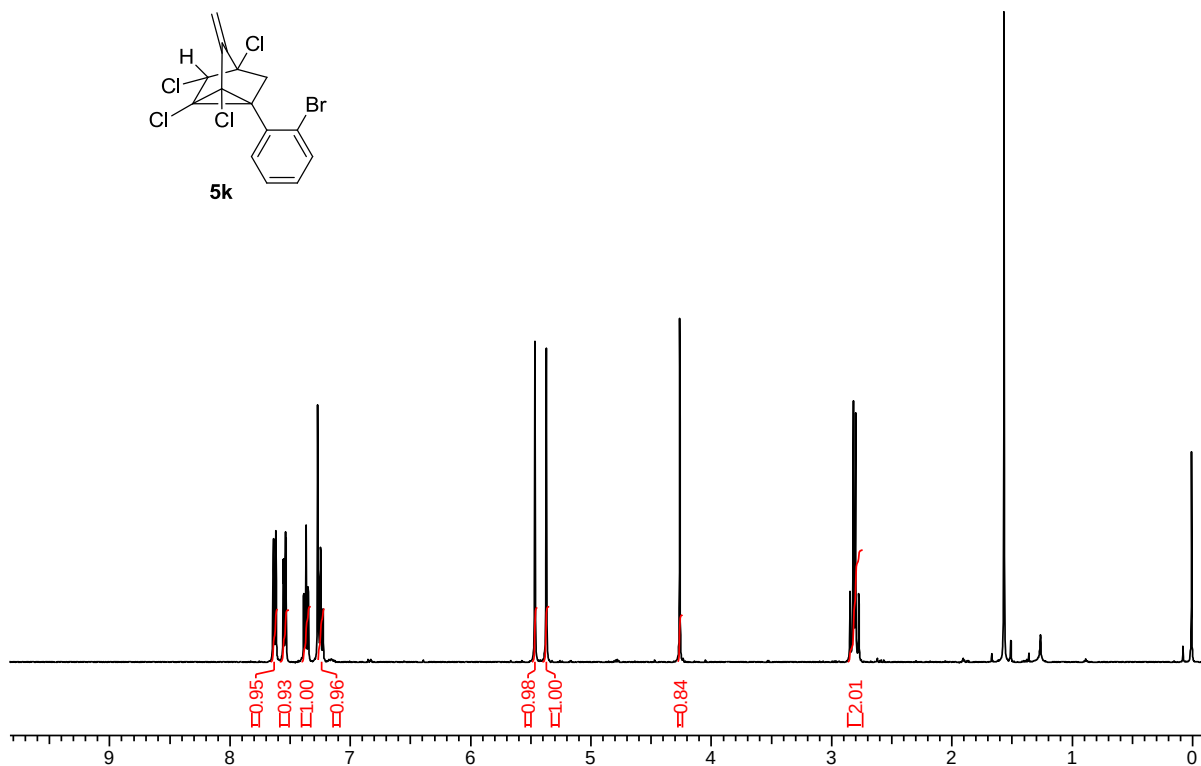
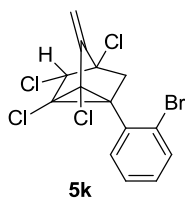
**$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) of 5j in  $\text{CDCl}_3$ :**



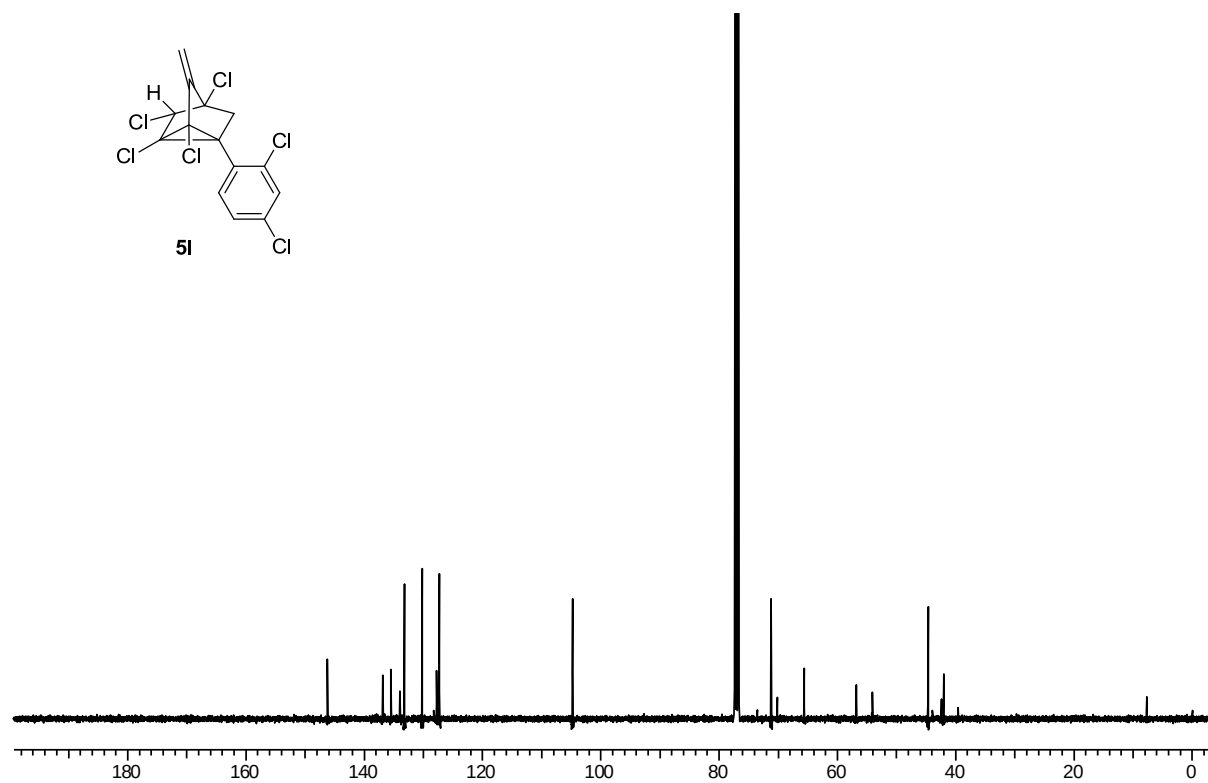
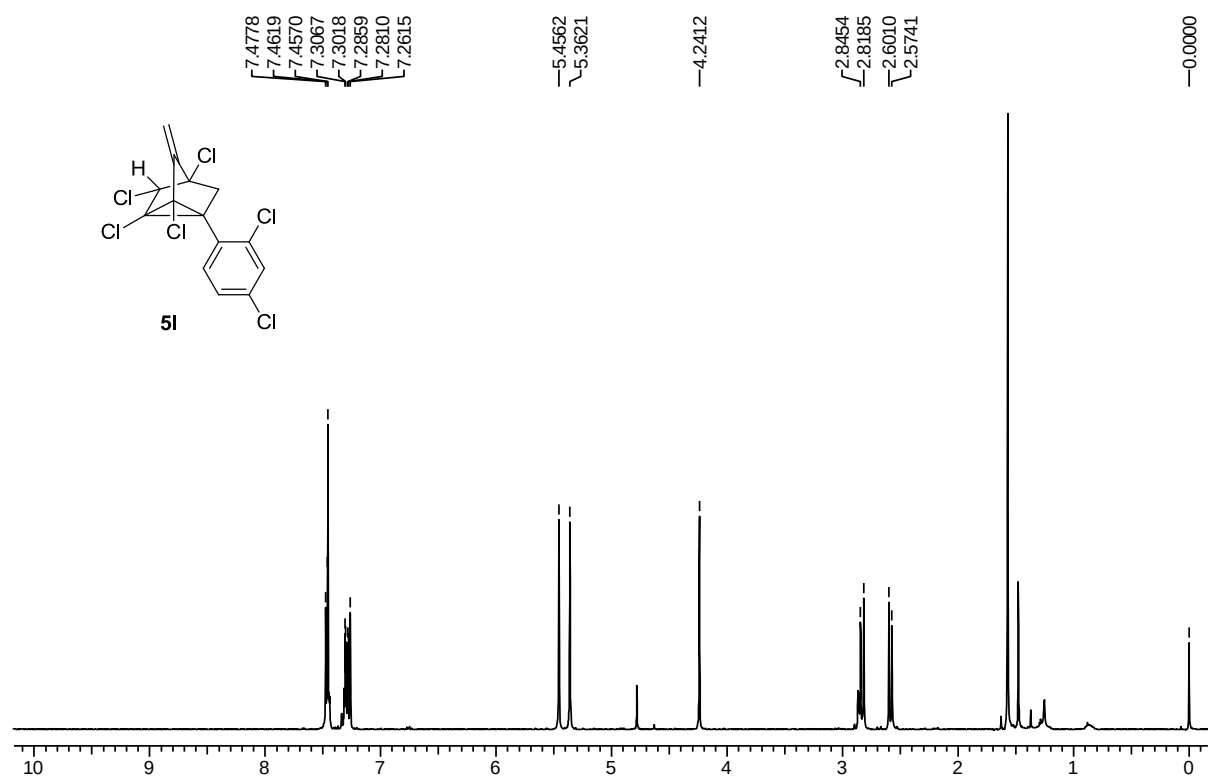
**$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) of 7 in  $\text{CDCl}_3$ :**



**$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) of 5k in  $\text{CDCl}_3$ :**

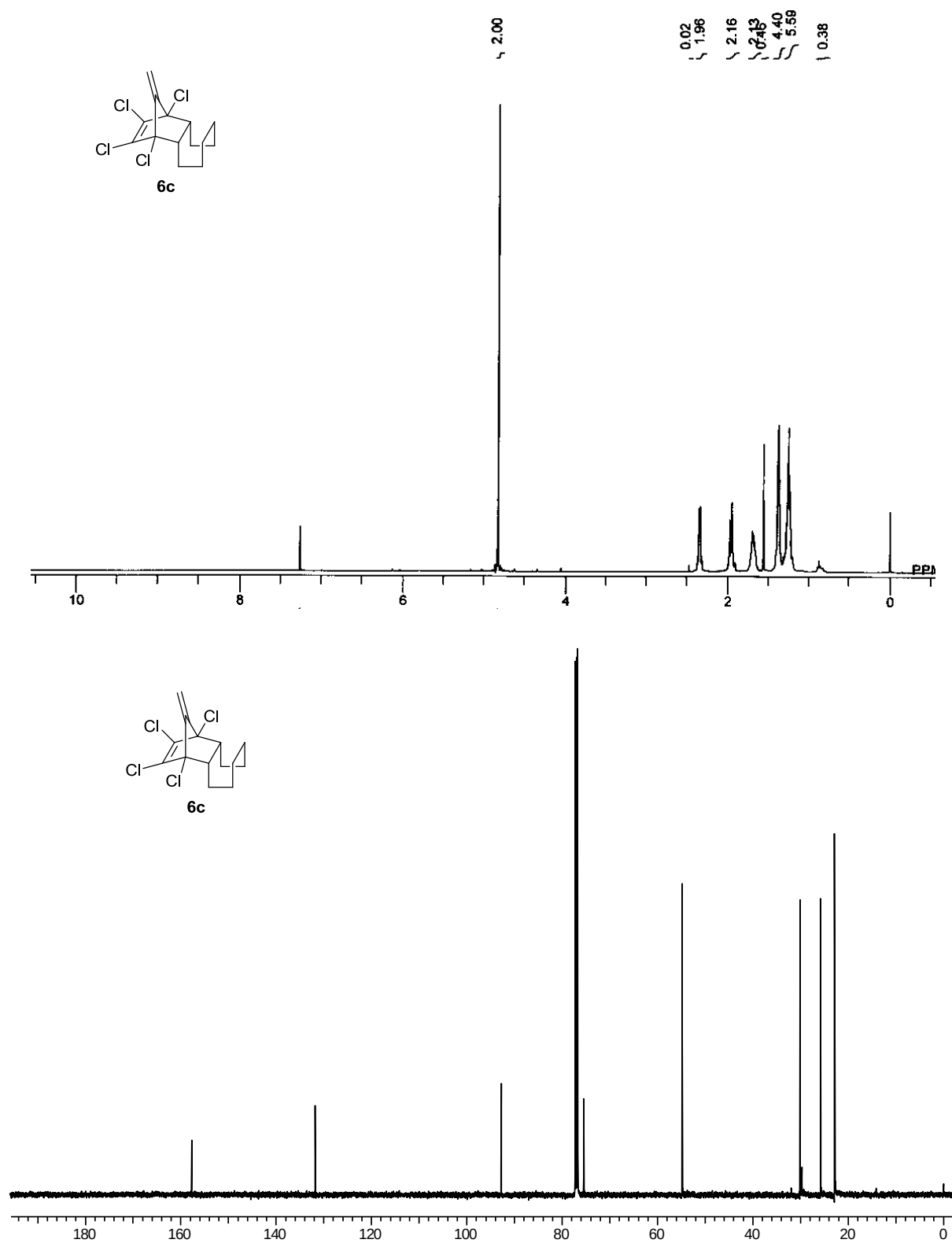


**$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) of 5I in  $\text{CDCl}_3$ :**

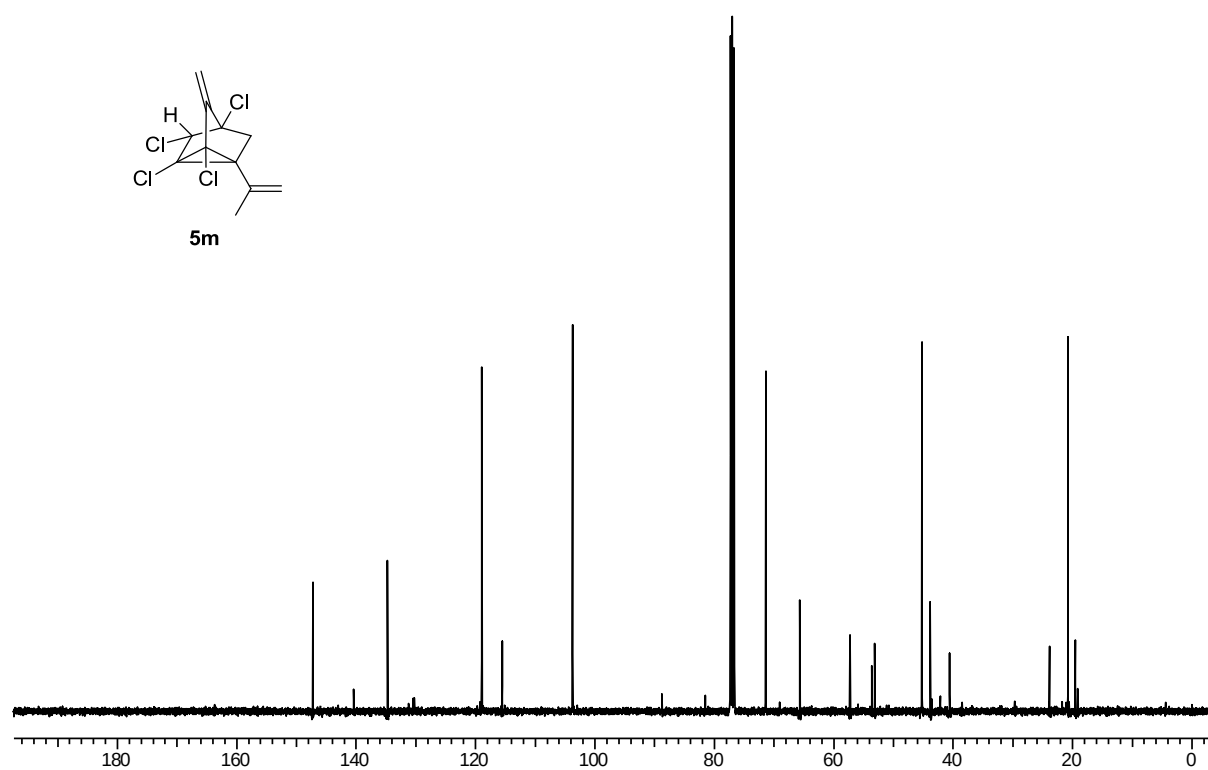
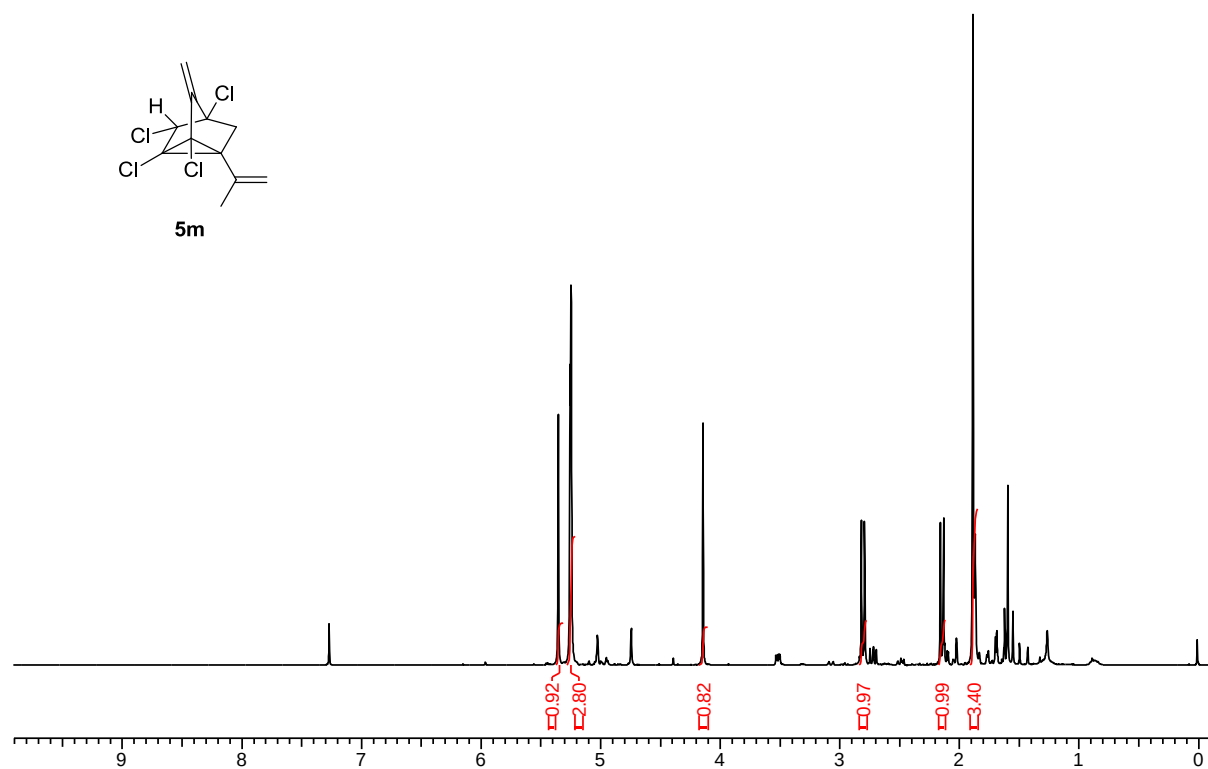




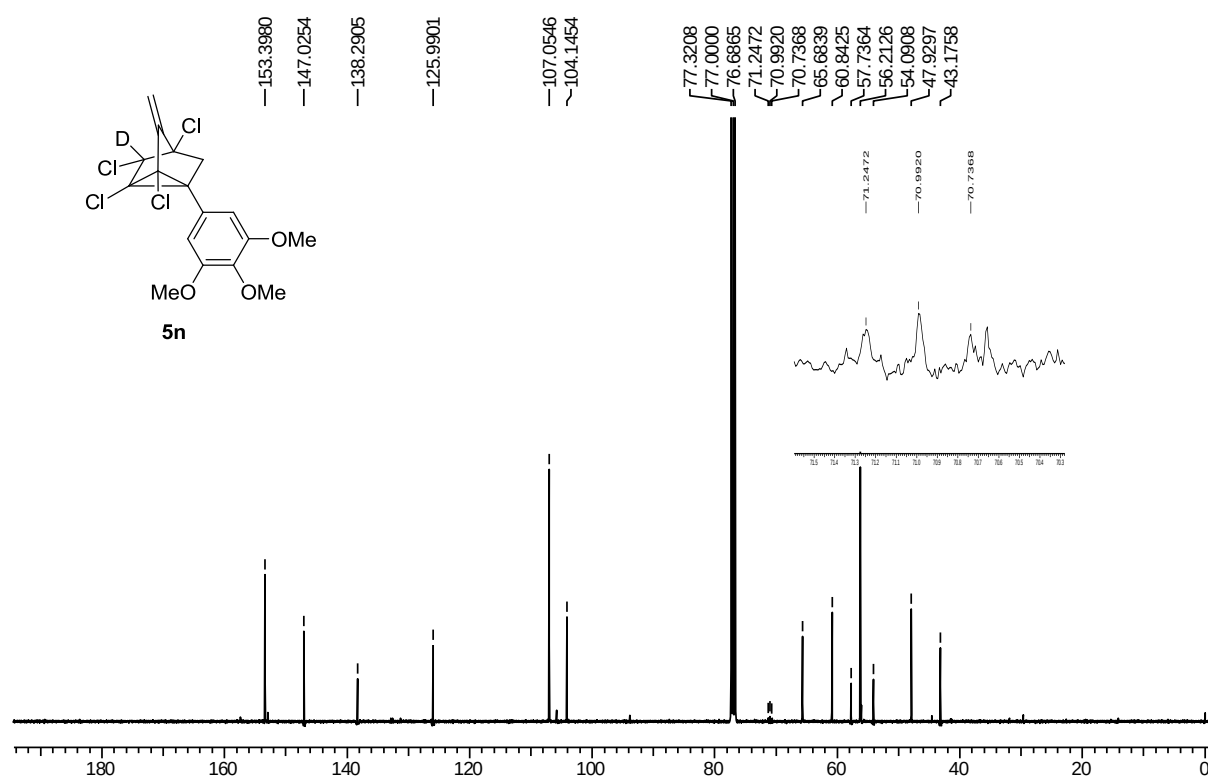
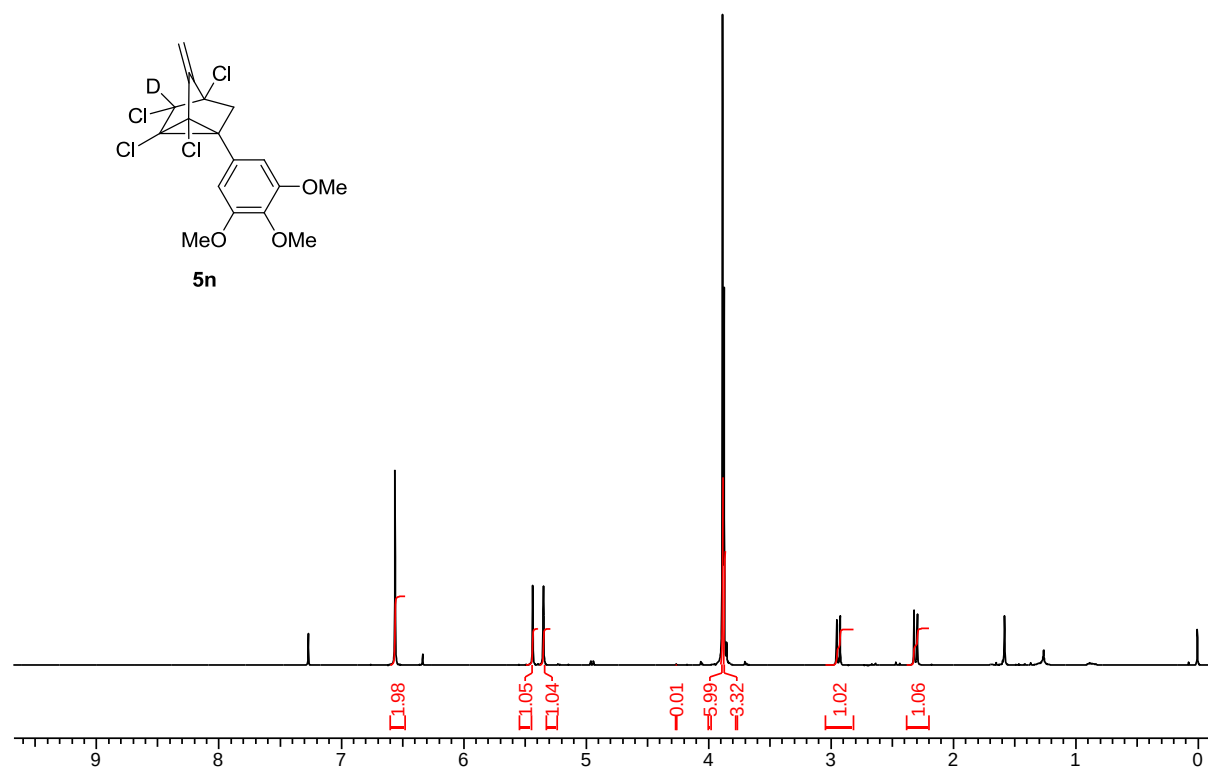
$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) of **6c** in  $\text{CDCl}_3$ :



**$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) of 5m in  $\text{CDCl}_3$ :**

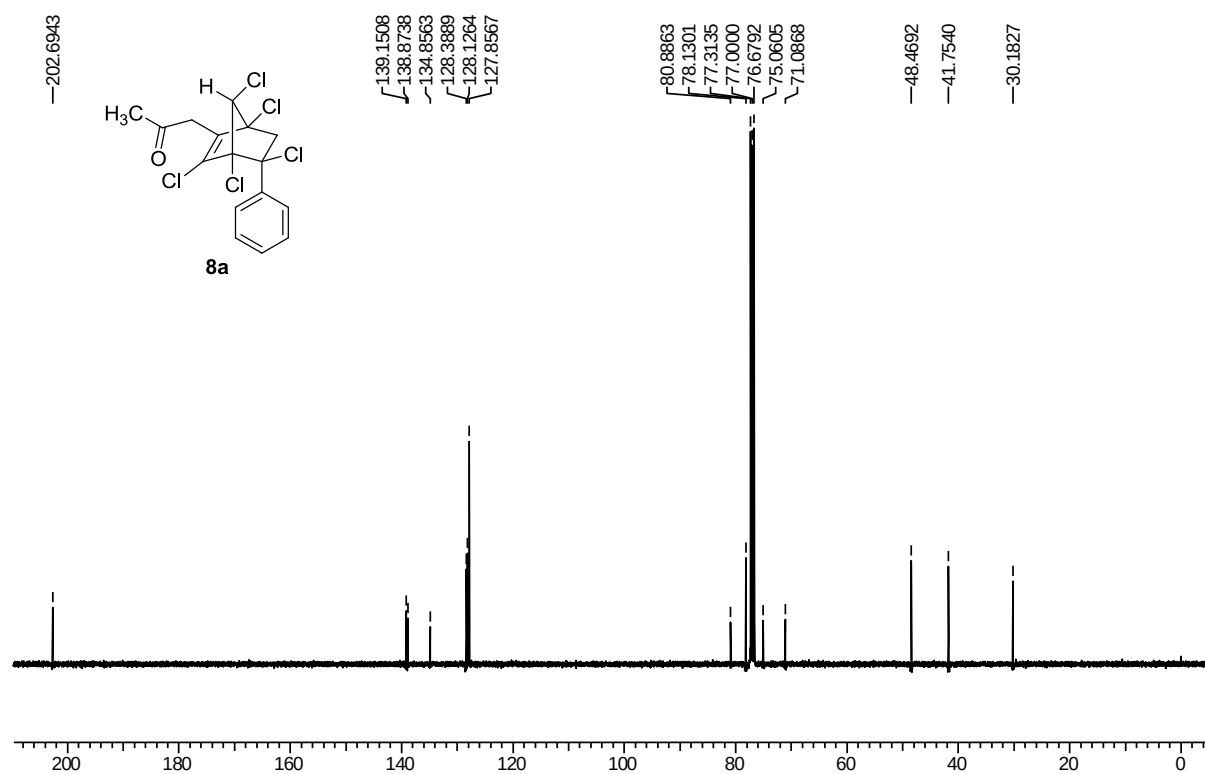
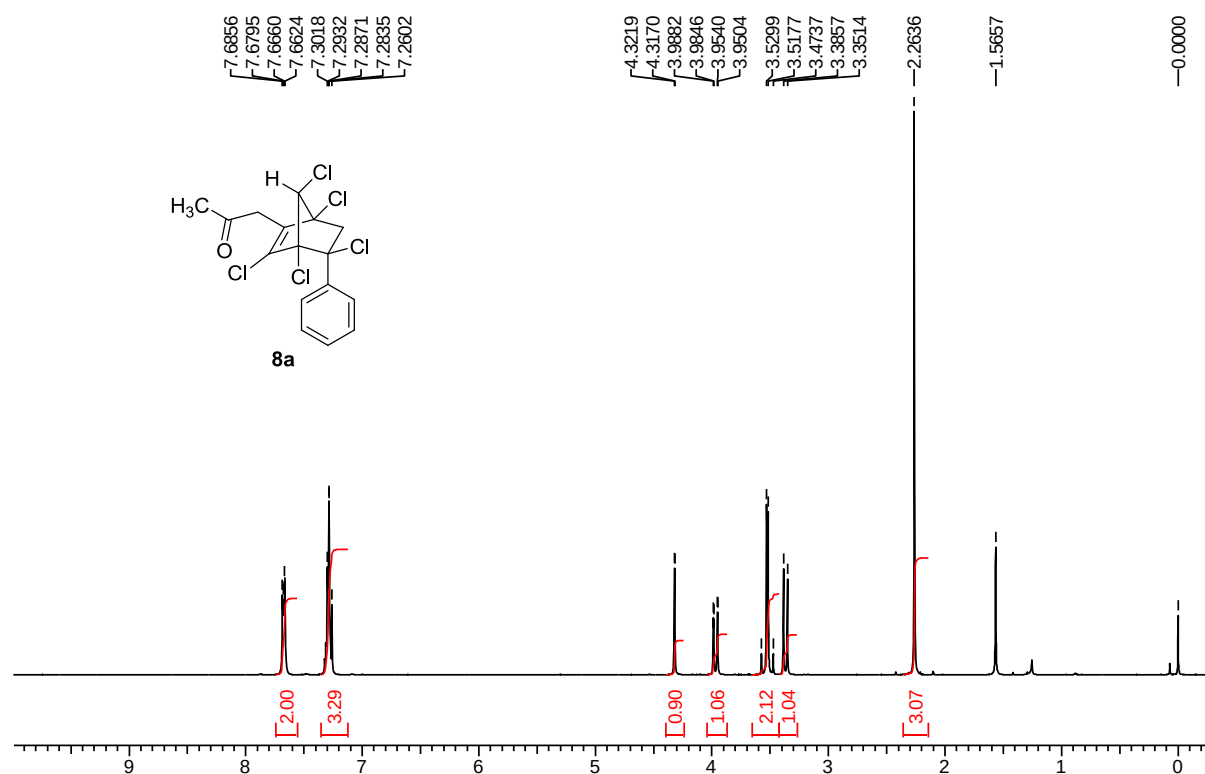


**$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) of 5n in  $\text{CDCl}_3$ :**

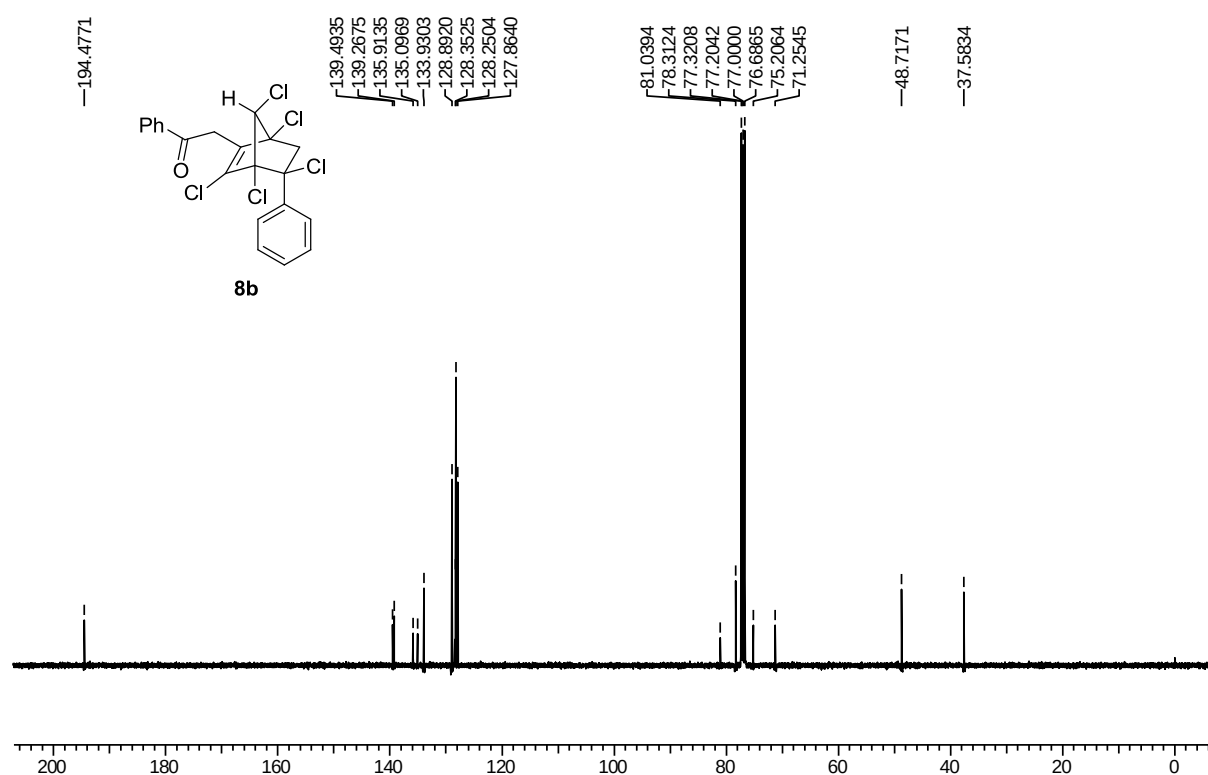
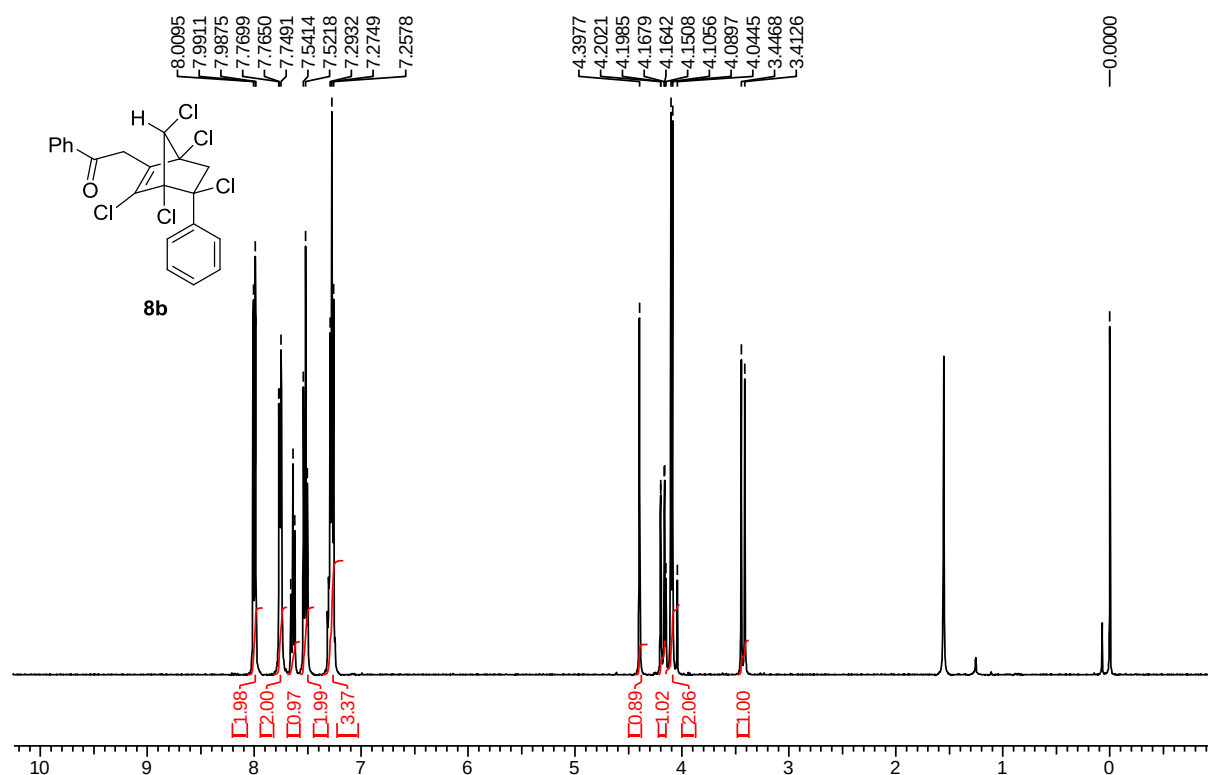


Copies of  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR spectra of products of acylation reaction of nortricyclens:

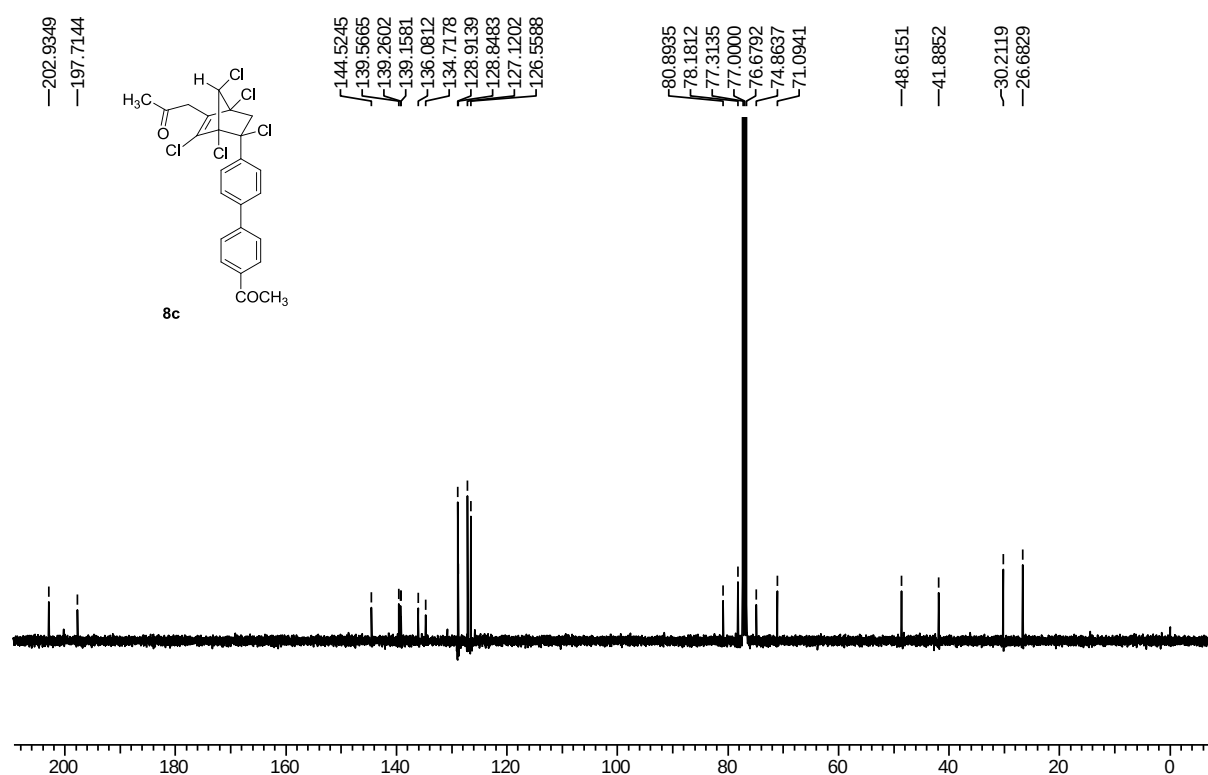
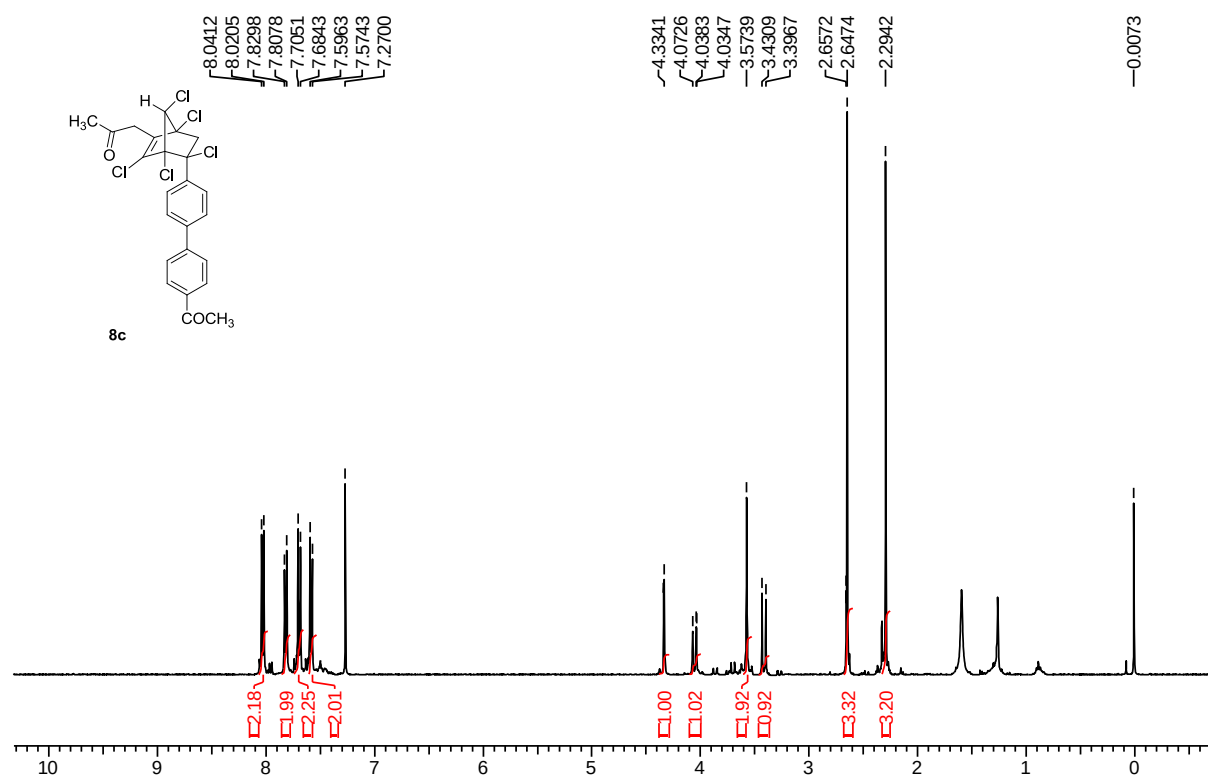
$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) of 8a in  $\text{CDCl}_3$ :



**$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) of 8b in  $\text{CDCl}_3$ :**



**$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) of 8c in  $\text{CDCl}_3$ :**



### Crystal data and structure refinement of compound 5a.

|                                             |                                                   |
|---------------------------------------------|---------------------------------------------------|
| Empirical formula                           | C <sub>14</sub> H <sub>10</sub> Cl <sub>4</sub>   |
| Formula weight                              | 320.02                                            |
| Temperature/K                               | 566(2)                                            |
| Crystal system                              | orthorhombic                                      |
| Space group                                 | Pbca                                              |
| a/Å                                         | 10.7170(4)                                        |
| b/Å                                         | 7.9683(2)                                         |
| c/Å                                         | 32.4915(10)                                       |
| $\alpha$ /°                                 | 90                                                |
| $\beta$ /°                                  | 90                                                |
| $\gamma$ /°                                 | 90                                                |
| Volume/Å <sup>3</sup>                       | 2774.65(15)                                       |
| Z                                           | 8                                                 |
| $\rho_{\text{calc}}$ /mg/mm <sup>3</sup>    | 1.532                                             |
| m/mm <sup>-1</sup>                          | 7.561                                             |
| F(000)                                      | 1296.0                                            |
| Crystal size/mm <sup>3</sup>                | 0.20 × 0.18 × 0.16                                |
| 2 $\theta$ range for data collection        | 9.888 to 141.98°                                  |
| Index ranges                                | -7 ≤ h ≤ 12, -5 ≤ k ≤ 9, -39 ≤ l ≤ 30             |
| Reflections collected                       | 5788                                              |
| Independent reflections                     | 2638[R(int) = 0.0340]                             |
| Data/restraints/parameters                  | 2638/0/172                                        |
| Goodness-of-fit on F <sup>2</sup>           | 1.064                                             |
| Final R indexes [I ≥ 2σ (I)]                | R <sub>1</sub> = 0.0490, wR <sub>2</sub> = 0.1347 |
| Final R indexes [all data]                  | R <sub>1</sub> = 0.0538, wR <sub>2</sub> = 0.1414 |
| Largest diff. peak/hole / e Å <sup>-3</sup> | 0.38/-0.58                                        |
| CCDC No.                                    | 1021351                                           |

## Crystal data and structure refinement of compound 8a

|                                             |                                                   |
|---------------------------------------------|---------------------------------------------------|
| Empirical formula                           | C <sub>16</sub> H <sub>13</sub> Cl <sub>5</sub> O |
| Formula weight                              | 398.51                                            |
| Temperature/K                               | 566(2)                                            |
| Crystal system                              | triclinic                                         |
| Space group                                 | P-1                                               |
| a/Å                                         | 7.9750(9)                                         |
| b/Å                                         | 8.5685(11)                                        |
| c/Å                                         | 13.0543(18)                                       |
| $\alpha$ /°                                 | 94.129(11)                                        |
| $\beta$ /°                                  | 102.281(11)                                       |
| $\gamma$ /°                                 | 99.211(10)                                        |
| Volume/Å <sup>3</sup>                       | 855.18(19)                                        |
| Z                                           | 2                                                 |
| $\rho_{\text{calc}}$ /mg/mm <sup>3</sup>    | 1.548                                             |
| m/mm <sup>-1</sup>                          | 7.706                                             |
| F(000)                                      | 404.0                                             |
| Crystal size/mm <sup>3</sup>                | 0.17 × 0.15 × 0.14                                |
| 2 $\theta$ range for data collection        | 6.972 to 141.328°                                 |
| Index ranges                                | -6 ≤ h ≤ 9, -10 ≤ k ≤ 9, -15 ≤ l ≤ 15             |
| Reflections collected                       | 5731                                              |
| Independent reflections                     | 3215[R(int) = 0.0319]                             |
| Data/restraints/parameters                  | 3215/0/200                                        |
| Goodness-of-fit on F <sup>2</sup>           | 1.033                                             |
| Final R indexes [ $I \geq 2\sigma(I)$ ]     | R <sub>1</sub> = 0.0423, wR <sub>2</sub> = 0.1155 |
| Final R indexes [all data]                  | R <sub>1</sub> = 0.0456, wR <sub>2</sub> = 0.1199 |
| Largest diff. peak/hole / e Å <sup>-3</sup> | 0.33/-0.45                                        |
| CCDC No.                                    | 1021303                                           |

## Reference

1. Wellman, M. A.; Burry, L. C.; Letourneau, J. E.; Bridson, J. N.; Miller, D. O.; Burnell, D. J. *J. Org. Chem.* **1997**, 62, 939-946.